Supporting Information for

Selective Hydrofunctionalization of Alkenyl Fluorides Enabled by Nickel-Catalyzed Hydrogen Atom and Group Transfer: Reaction Development and Mechanistic Study

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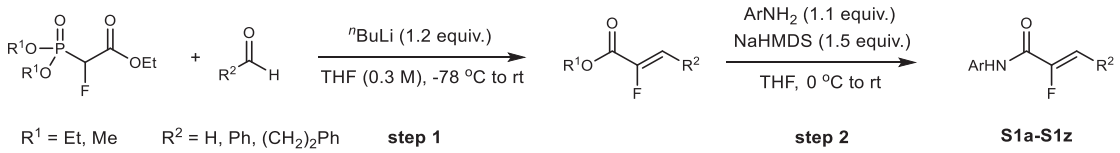
Contents

1. General Information.

Commercial reagents were purchased from Adamas-beta, TCI, Energy Chemical, Bide, Leyan.com, and J&K chemical, and were used as received. All reactions were carried out in oven-dried glassware under an atmosphere of nitrogen. Column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (300-400 mesh). Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.2 mm commercial silica gel plates. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Bruker 400 MHz spectrometer at 295 K in $CDCl_3$ unless otherwise noted. Data for ^{1}H NMR were reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. Data for ^{13}C NMR were reported as follows: chemical shift (δ ppm), multiplicity, and coupling constant (Hz). Data for ^{19}F NMR (^{19}F exp. no decoupling) were reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz). Chemical shifts were reported using the residual solvent $CHCl_3$ as the internal reference for ^{1}H NMR (δ = 7.26 ppm) and $CDCl_3$ peak as the internal reference for ^{13}C NMR (δ = 77.16 ppm). High resolution mass spectra (HRMS) were obtained at Shanghai Institute of Organic Chemistry mass spectrometry facilities. Optical rotations were measured on an automatic polarimeter. $[\alpha]_D^T$ values reported in 10^{-1}deg cm^2 g^{-1}; concentrations (c) are quoted in g/100 mL. D refers to the D-line of sodium (589 nm); temperatures (T) are given in degrees Celsius (^{o}C). High-performance liquid chromatography (HPLC) analysis was carried out on chiral stationary phase was performed on an Agilent 1260-series instrument. Chiralpak IA-H, IB-H, IC-H or AD-H columns with hexane: ^{i}PrOH as the eluents were used. Known chiral ligands,[1-2] olefins,[3] and alkyl halides[4-5] were synthesized following literature procedure.

2. The Preparation of Substrates and Ligands

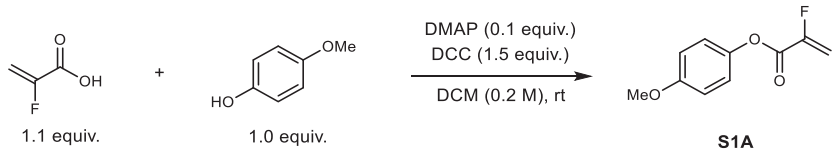
2.1 Preparation of fluoroalkenes



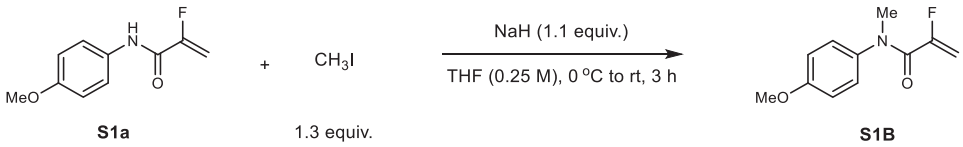
R^1 = Et, Me R^2 = H, Ph, $(CH_2)_2Ph$ **step 1** **step 2** **S1a-S1z**

step 1. To a solution of triethyl 2-fluoro-2-phosphonoacetate (12 mmol, 1.2 equiv.) in THF (40 mL) was added *n*-BuLi (1.6 M in *n*-hexane, 12 mmol, 1.2 equiv.) at -78 °C. After stirring of the reaction mixture for 30 min at that temperature, corresponding aldehyde (10 mmol, 1.0 equiv.) was added to the reaction mixture, and the resulting mixture was stirred at room temperature for 2 h. The reaction was quenched with diluted HCl aq., and the solution was extracted with EtOAc (2*30 mL). The combined organic layers were washed with brine (30 mL) and dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica.

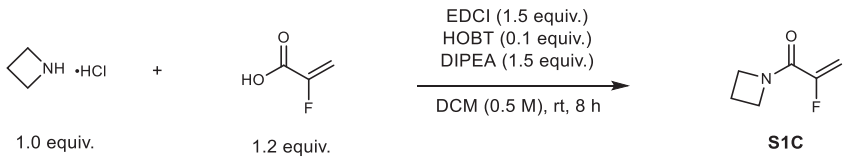
step 2. The solution of 2.0 M NaHMDS in THF (15.0 mmol, 1.5 equiv.) was added to the solution of $ArNH_2$ (11 mmol, 1.1 equiv.) in THF (25 mL, 0.4 M) at 0 °C under N_2 atmosphere. The reaction solution was then stirred for 30 min at 0 °C, after that, the alkenyl fluoride obtained in the first step or purchased methyl-2-fluoroacrylate (10 mmol, 1.0 equiv.) was added dropwise at 0 °C. The resulting solution was then warmed to room temperature and stirred for overnight. After quenched with saturated NH_4Cl aqueous solution, the mixture was extracted with EtOAc (2*30 mL), and the combined organic layers were washed with brine (30 mL) and dried over $MgSO_4$. After filtration and concentration, the residue was purified by flash column chromatography on silica and concentrate. Then, recrystallization using dichloromethane and petroleum ether to obtain a white solid or crystal unless otherwise noted. According to the reported literature,[3, 6] the fluoroalkenes (**S1a-S1w**) were conveniently synthesized in gram scale.



The 2-fluoroacrylic acid (11 mmol, 1.1 equiv.) was added to a solution of *N*,*N*′-dicyclohexylcarbodiimide (DCC, 1.2 mmol, 1.2 equiv.) and DMAP (1.0 mmol, 0.1 equiv.) in CH_2Cl_2 (50 mL) at 0 °C. The 4-methoxyphenol (10 mmol, 1.0 equiv.) was then added. The reaction mixture was stirred overnight. The resulting mixture was filtrated with celite and washed with 20 mL DCM to get a clear solution. After removal of the solvent, the resulting crude mixture was purified by flash column chromatography on silica.

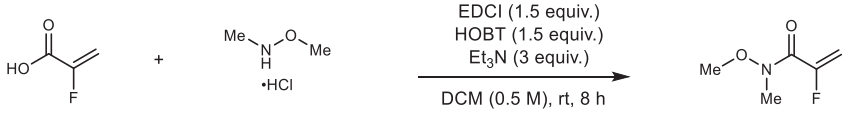


Add amide derivative (5 mmol, 1.0 equiv.) dissolved in 10 ml of THF dropwise to a stirred suspension of NaH (5.5 mmol, 1.1 equiv.) in 5 ml of dry THF at 0 °C, within 10 minutes. Stir the reaction mixture until the solution becomes clear (30 minutes, hydrogen gas evolved). Add the solution of MeI (6.5 mmol, 1.3 equiv.) in 5 ml of THF dropwise to the mixture within 10 minutes. The reaction mixture was stirred at room temperature for 3 hours. Quench the reaction mixture with water (30 ml). Extract the resulting solution with ethyl acetate (3 × 20 ml). Wash the combined organic layers with brine. Dry the combined organic layers over $MgSO_4$. After removal of the solvent, the resulting crude mixture was purified by flash column chromatography on silica to obtain the product.

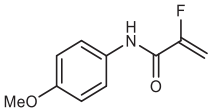


The 2-fluoroacrylic acid (10 mmol, 1.0 equiv.) was added to a solution of azetidine hydrochloride (12 mmol, 1.2 equiv.), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide

(EDCI, 15 mmol, 1.5 equiv.), hydroxybenzotriazole (HOBt, 1.0 mmol, 0.1 equiv.), and triethylamine (15 mmol, 1.5 equiv.) in anhydrous CH_2Cl_2 (25 mL). The reaction mixture was stirred overnight. Then wash the reaction mixture with water, saturated aqueous $NaHCO_3$, and brine. Dry the organic layer over anhydrous $MgSO_4$ and concentrate. Purify the residue by flash column chromatography on silica gel to obtain the product.



The 2-fluoroacrylic acid (10 mmol, 1.0 equiv.) was added to a solution of *N,O*-dimethylhydroxylamine (12 mmol, 1.2 equiv.), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDCI, 15 mmol, 1.5 equiv.), hydroxybenzotriazole (HOBt, 15 mmol, 1.5 equiv.), and triethylamine (30 mmol, 3.0 equiv.) in anhydrous CH_2Cl_2 (25 mL). The reaction mixture was stirred overnight. Then, wash the reaction mixture with water, saturated aqueous $NaHCO_3$, and brine. Dry the organic layer over anhydrous $MgSO_4$ and concentrate. Purify the residue by flash column chromatography on silica gel to obtain the product. (Note: be careful when evaporating the solvent, as the product is volatile).



2-Fluoro-*N*-(4-methoxyphenyl) acrylamide (S1a)

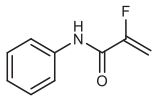
The title compound was obtained as a white solid, 88% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.56 – 7.43 (m, 2H), 6.96 – 6.82 (m, 2H), 5.79 (dd, *J* = 48.0, 3.3 Hz, 1H), 5.21 (dd, *J* = 15.4, 3.3 Hz, 1H), 3.79 (s, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -120.70 – -120.88 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.16 (d, *J* = 29.3 Hz), 157.02, 156.34 (d, *J* = 271.5 Hz), 129.61, 121.98, 114.28, 99.61 (d, *J* = 14.9 Hz), 55.48.

HRMS (ESI): $C_{10}H_{11}FNO_2^+$ ($M+H^+$): 196.0768, found: 196.0765.



2-Fluoro-*N*-phenylacrylamide (S1b)

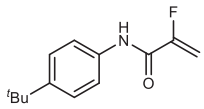
The title compound was obtained as a white solid, 82% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.63 – 7.55 (m, 2H), 7.41 – 7.30 (m, 2H), 7.19 – 7.12 (m, 1H), 5.82 (dd, *J* = 47.8, 3.4 Hz, 1H), 5.24 (dd, *J* = 15.3, 3.4 Hz, 1H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -120.48 – -120.66 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.26 (d, *J* = 29.4 Hz), 156.13 (d, *J* = 271.4 Hz), 136.49, 129.08, 125.16, 120.21, 99.86 (d, *J* = 14.9 Hz).

HRMS (ESI): $C_9H_9FNO^+$ ($M+H^+$): 166.0663, found: 166.0666.



***N*-(4-(*tert*-butyl) phenyl)-2-fluoroacrylamide (S1c)**

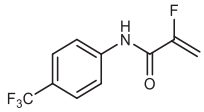
The title compound was obtained as a white solid, 77% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.59 – 7.45 (m, 2H), 7.42 – 7.31 (m, 2H), 5.81 (dd, *J* = 47.9, 3.3 Hz, 1H), 5.23 (dd, *J* = 15.4, 3.3 Hz, 1H), 1.32 (s, 9H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -120.59 – -120.78 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.21 (d, *J* = 29.2 Hz), 156.31 (d, *J* = 271.5 Hz), 148.29, 133.93, 126.00, 120.02, 99.74 (d, *J* = 15.1 Hz), 34.48, 31.34.

HRMS (ESI): $C_{13}H_{17}FNO^+$ ($M+H^+$): 222.1289, found: 222.1290.



2-Fluoro-*N*-(4-(trifluoromethyl)phenyl) acrylamide (S1d)

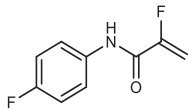
The title compound was obtained as a white solid, 66% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 5.85 (dd, *J* = 47.7, 3.5 Hz, 1H), 5.29 (dd, *J* = 15.2, 3.5 Hz, 1H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.29 (s), -120.86 – -121.04 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.48 (d, *J* = 29.9 Hz), 155.68 (d, *J* = 271.3 Hz), 139.57, 127.00 (q, *J* = 32.9 Hz), 126.39 (q, *J* = 3.8 Hz), 123.82 (q, *J* = 271 Hz), 119.90, 100.67 (d, *J* = 14.8 Hz).

HRMS (ESI): $C_{10}H_8F_4NO^+$ ($M+H^+$): 234.0537, found: 234.0539.



2-Fluoro-*N*-(4-fluorophenyl) acrylamide (S1e)

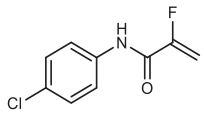
The title compound was obtained as a white solid, 74% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.69 – 7.43 (m, 2H), 7.17 – 6.95 (m, 2H), 5.81 (dd, *J* = 47.8, 3.4 Hz, 1H), 5.24 (dd, *J* = 15.3, 3.4 Hz, 1H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -116.54 – -116.61 (m), -120.83 – -121.02 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.88 (d, *J* = 244.8 Hz), 157.34 (d, *J* = 29.7 Hz), 156.05 (d, *J* = 271.1 Hz), 132.55 (d, *J* = 2.8 Hz), 122.12 (d, *J* = 8.0 Hz), 115.88 (d, *J* = 22.6 Hz), 100.08 (d, *J* = 15.0 Hz).

HRMS (ESI): $C_9H_8F_2NO^+$ ($M+H^+$): 184.0568, found: 184.0566.



***N*-(4-chlorophenyl)-2-fluoroacrylamide (S1f)**

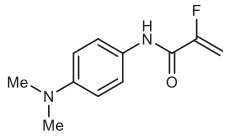
The title compound was obtained as a white solid, 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.61 – 7.47 (m, 2H), 7.37 – 7.28 (m, 2H), 5.82 (dd, *J* = 47.8, 3.4 Hz, 1H), 5.26 (dd, *J* = 15.3, 3.4 Hz, 1H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -120.88 – -121.06 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.30 (d, *J* = 29.8 Hz), 155.92 (d, *J* = 271.1 Hz), 135.13, 130.33, 129.22, 121.47, 100.29 (d, *J* = 14.8 Hz).

HRMS (ESI): $C_9H_8ClFNO^+$ ($M+H^+$): 200.0273, found: 200.0277.



***N*-(4-(dimethylamino) phenyl)-2-fluoroacrylamide (S1g)**

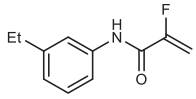
The title compound was obtained as a yellow crystal, 54% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 20.6 Hz, 1H), 7.55 – 7.32 (m, 2H), 6.70 (dd, *J* = 9.1, 3.4 Hz, 2H), 5.77 (dt, *J* = 48.0, 2.9 Hz, 1H), 5.18 (dt, *J* = 15.4, 2.8 Hz, 1H), 2.93 (d, *J* = 2.5 Hz, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -120.27 – -120.61 (m)

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.05 (d, *J* = 29.9 Hz), 156.69 (d, *J* = 272.4 Hz), 148.48, 126.31, 121.97, 112.88, 99.21 (d, *J* = 14.2 Hz), 40.83.

HRMS (ESI): $C_{11}H_{14}FN_2O^+$ ($M+H^+$): 209.1085, found: 209.1089.



***N*-(3-ethylphenyl)-2-fluoroacrylamide (S1h)**

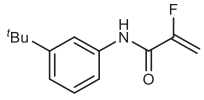
The title compound was obtained as a white solid, 82% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.51 – 7.36 (m, 2H), 7.26 (t, *J* = 7.8 Hz, 1H), 7.01 (dd, *J* = 7.6, 0.4 Hz, 1H), 5.82 (dd, *J* = 47.9, 3.3 Hz, 1H), 5.23 (dd, *J* = 15.3, 3.3 Hz, 1H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.24 (t, *J* = 7.6 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -120.70 – -120.87 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.26 (d, *J* = 29.2 Hz), 156.28 (d, *J* = 271.7 Hz), 145.52, 136.55, 129.06, 124.86, 119.73, 117.59, 99.81 (d, *J* = 14.9 Hz), 28.85, 15.46.

HRMS (ESI): $C_{11}H_{13}FNO^+$ ($M+H^+$): 194.0976, found: 194.0975.



***N*-(3-(*tert*-butyl)phenyl)-2-fluoroacrylamide (S1i)**

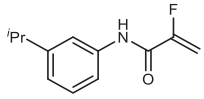
The title compound was obtained as a dark red oil, 91% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 42.3 Hz, 1H), 7.59 (t, *J* = 1.9 Hz, 1H), 7.52 – 7.43 (m, 1H), 7.30 (t, *J* = 7.9 Hz, 1H), 7.24 – 7.17 (m, 1H), 5.82 (dd, *J* = 47.9, 3.3 Hz, 1H), 5.24 (dd, *J* = 15.3, 3.3 Hz, 1H), 1.33 (s, 9H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -120.56 – -120.74 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.27 (d, *J* = 29.2 Hz), 156.31 (d, *J* = 271.7 Hz), 152.48, 136.32, 128.83, 122.36, 117.51, 117.44, 99.79 (d, *J* = 15.1 Hz), 34.82, 31.26.

HRMS (ESI): $C_{13}H_{17}FNO^+$ ($M+H^+$): 222.1289, found: 222.1287.



2-Fluoro-*N*-(3-isopropylphenyl) acrylamide (S1j)

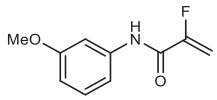
The title compound was obtained as a white solid, 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.50 – 7.39 (m, 2H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 7.7 Hz, 1H), 5.82 (dd, *J* = 47.9, 3.3 Hz, 1H), 5.24 (dd, *J* = 15.3, 3.3 Hz, 1H), 3.01 – 2.73 (m, 1H), 1.25 (d, *J* = 6.9 Hz, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -120.65 – -120.83 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.25 (d, *J* = 29.2 Hz), 156.29 (d, *J* = 271.7 Hz), 150.19, 136.54, 129.07, 123.45, 118.37, 117.76, 99.80 (d, *J* = 15.1 Hz), 34.14, 23.89.

HRMS (ESI): $C_{12}H_{15}FNO^+$ ($M+H^+$): 208.1132, found: 208.1135.



2-Fluoro-*N*-(3-methoxyphenyl) acrylamide (S1k)

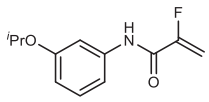
The title compound was obtained as a white solid, 79% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.39 (t, *J* = 2.2 Hz, 1H), 7.31 – 7.20 (m, 1H), 7.12 – 6.98 (m, 1H), 6.77 – 6.69 (m, 1H), 5.84 (dd, *J* = 47.8, 3.4 Hz, 1H), 5.27 (dd, *J* = 15.3, 3.4 Hz, 1H), 3.83 (s, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -120.70 – -120.88 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.22, 157.29 (d, *J* = 29.3 Hz), 156.15 (d, *J* = 271.7 Hz), 137.76, 129.84, 112.35, 111.19, 105.87, 99.97 (d, *J* = 15.0 Hz), 55.34.

HRMS (ESI): $C_{10}H_{11}FNO_2^+$ ($M+H^+$): 196.0768, found: 196.0769.



2-Fluoro-*N*-(3-isopropoxyphenyl)acrylamide (S1l)

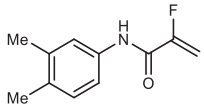
The title compound was obtained as a dark red oil, 93% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.35 (t, *J* = 2.2 Hz, 1H), 7.22 (t, *J* = 8.2 Hz, 1H), 7.02 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.70 (dd, *J* = 8.1, 2.1 Hz, 1H), 5.81 (dd, *J* = 47.9, 3.4 Hz, 1H), 5.24 (dd, *J* = 15.3, 3.4 Hz, 1H), 4.61 – 4.49 (m, 1H), 1.33 (d, *J* = 6.1 Hz, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -120.66 – -120.84 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.56, 157.24 (d, *J* = 29.5 Hz), 156.18 (d, *J* = 271.6 Hz), 137.71, 129.84, 113.07, 112.13, 107.71, 99.92 (d, *J* = 15.1 Hz), 70.09, 22.01.

HRMS (ESI): $C_{12}H_{15}FNO_2^+$ ($M+H^+$): 224.1081, found: 224.1085.



***N*-(3,4-dimethylphenyl)-2-fluoroacrylamide (S1m)**

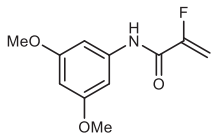
The title compound was obtained as a white solid, 79% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.38 (d, *J* = 2.0 Hz, 1H), 7.32 (dd, *J* = 8.1, 2.3 Hz, 1H), 7.10 (d, *J* = 8.1 Hz, 1H), 5.80 (dd, *J* = 47.9, 3.3 Hz, 1H), 5.22 (dd, *J* = 15.4, 3.3 Hz, 1H), 2.25 (s, 3H), 2.23 (s, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -120.62 – -120.80 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.15 (d, *J* = 29.2 Hz), 156.37 (d, *J* = 271.7 Hz), 137.46, 134.25, 133.69, 130.12, 121.52, 117.73, 99.62 (d, *J* = 15.1 Hz), 19.89, 19.26.

HRMS (ESI): $C_{11}H_{13}FNO^+$ ($M+H^+$): 194.0976, found:194.0977.



***N*-(3,5-dimethoxyphenyl)-2-fluoroacrylamide (S1n)**

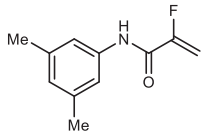
The title compound was obtained as a white solid, 88% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 6.83 (d, *J* = 2.2 Hz, 2H), 6.28 (t, *J* = 2.2 Hz, 1H), 5.80 (dd, *J* = 47.8, 3.4 Hz, 1H), 5.23 (dd, *J* = 15.3, 3.4 Hz, 1H), 3.77 (s, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -120.74 – -120.93 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.11, 157.29 (d, *J* = 29.5 Hz), 156.11 (d, *J* = 271.6 Hz), 138.27, 99.99 (d, *J* = 15.1 Hz), 98.46, 97.67, 55.42.

HRMS (ESI): $C_{11}H_{13}FNO_3^+$ ($M+H^+$): 226.0874, found: 226.0875.



***N*-(3,5-dimethylphenyl)-2-fluoroacrylamide (S1o)**

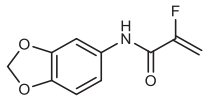
The title compound was obtained as a white solid, 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.23 (s, 2H), 6.81 (s, 1H), 5.81 (dd, *J* = 47.9, 3.3 Hz, 1H), 5.22 (dd, *J* = 15.3, 3.3 Hz, 1H), 2.31 (s, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -120.67 – -120.86 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.20 (d, *J* = 29.2 Hz), 156.32 (d, *J* = 271.7 Hz), 138.91, 136.38, 126.97, 117.99, 99.72 (d, *J* = 15.1 Hz), 21.35.

HRMS (ESI): $C_{11}H_{13}FNO^+$ ($M+H^+$): 194.0976, found: 194.0975.



***N*-(benzo[*d*][1,3]dioxol-5-yl)-2-fluoroacrylamide (S1p)**

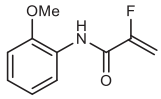
The title compound was obtained as a white solid, 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.29 (d, *J* = 2.1 Hz, 1H), 6.88 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.75 (d, *J* = 8.3 Hz, 1H), 5.96 (s, 2H), 5.79 (dd, *J* = 47.9, 3.4 Hz, 1H), 5.22 (dd, *J* = 15.4, 3.4 Hz, 1H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -120.86 – -121.05 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.17 (d, *J* = 29.5 Hz), 156.18 (d, *J* = 271.2 Hz), 147.94, 144.96, 130.73, 113.59, 108.18, 102.88, 101.45, 99.79 (d, *J* = 14.9 Hz).

HRMS (ESI): $C_{10}H_9FNO_3^+$ ($M+H^+$): 210.0561, found: 210.0565.



2-Fluoro-*N*-(2-methoxyphenyl)acrylamide (S1q)

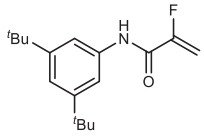
The title compound was obtained as a white solid, 42% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.42 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.14 – 7.06 (m, 1H), 7.03 – 6.96 (m, 1H), 6.90 (dd, *J* = 8.1, 1.3 Hz, 1H), 5.80 (dd, *J* = 47.6, 3.3 Hz, 1H), 5.23 (dd, *J* = 15.2, 3.3 Hz, 1H), 3.90 (s, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -120.42 – -120.60 (m)

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.06 (d, *J* = 29.4 Hz), 156.48 (d, *J* = 271.8 Hz), 148.26, 126.46, 124.74, 121.12, 120.06, 110.04, 99.51 (d, *J* = 15.2 Hz), 55.80.

HRMS (ESI): $C_{10}H_{11}FNO_2^+$ ($M+H^+$): 196.0768, found: 196.0769.



***N*-(3,5-di-*tert*-butylphenyl)-2-fluoroacrylamide (S1r)**

The title compound was obtained as a white solid, 86% yield.

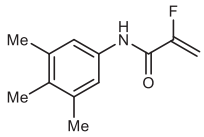
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.48 (d, *J* = 1.8 Hz, 2H), 7.35 – 7.06 (m, 1H), 5.83 (dd, *J* = 47.8, 3.3 Hz, 1H), 5.24 (dd, *J* = 15.4, 3.4 Hz, 1H), 1.35 (s, 18H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -120.41 – -120.59 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.35 (d, *J* = 29.1 Hz), 156.53 (d, *J* = 272.0 Hz),

152.01, 136.09, 119.54, 114.95, 99.72 (d, *J* = 15.1 Hz), 35.10, 31.49.

HRMS (ESI): $C_{17}H_{25}FNO^+$ ($M+H^+$): 278.1915, found: 278.1916.



2-Fluoro-*N*-(3,4,5-trimethylphenyl)acrylamide (S1s)

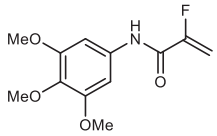
The title compound was obtained as a white solid, 65% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.25 (s, 2H), 5.80 (dd, *J* = 47.9, 3.3 Hz, 1H), 5.21 (dd, *J* = 15.4, 3.3 Hz, 1H), 2.27 (s, 6H), 2.14 (s, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -120.62 – -120.80 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.12 (d, *J* = 29.1 Hz), 156.42 (d, *J* = 271.7 Hz), 137.29, 133.53, 132.26, 119.45, 99.52 (d, *J* = 15.1 Hz), 20.68, 15.02.

HRMS (ESI): $C_{12}H_{15}FNO^+$ ($M+H^+$): 208.1132, found: 208.1136.



2-Fluoro-*N*-(3,4,5-trimethoxyphenyl)acrylamide (S1t)

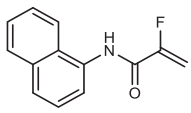
The title compound was obtained as a white solid, 72% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 6.93 (s, 2H), 5.82 (dd, *J* = 47.7, 3.4 Hz, 1H), 5.26 (dd, *J* = 15.3, 3.4 Hz, 1H), 3.85 (s, 6H), 3.83 (s, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -120.85 – -121.03 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.26 (d, *J* = 29.5 Hz), 156.12 (d, *J* = 271.6 Hz), 153.39, 135.32, 132.64, 99.91 (d, *J* = 15.1 Hz), 97.89, 60.97, 56.10.

HRMS (ESI): $C_{12}H_{15}FNO_4^+$ ($M+H^+$): 256.0980, found: 256.0981.



2-Fluoro-*N*-(naphthalen-1-yl)acrylamide (S1u)

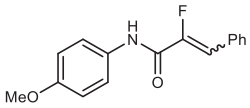
The title compound was obtained as a light red crystal, 56% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.03 (d, *J* = 7.5 Hz, 1H), 7.93 – 7.86 (m, 1H), 7.85 – 7.80 (m, 1H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.58 – 7.42 (m, 3H), 5.89 (dd, *J* = 48.0, 3.4 Hz, 1H), 5.32 (dd, *J* = 15.4, 3.4 Hz, 1H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -120.55 – -120.73 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.79, 156.59 (d, *J* = 300.5 Hz), 134.08, 130.88, 128.90, 126.84, 126.67, 126.51, 126.23, 125.71, 120.80, 120.24, 100.19 (d, *J* = 14.8 Hz).

HRMS (ESI): $C_{13}H_{11}FNO^+$ ($M+H^+$): 216.0819, found: 216.0821.



2-Fluoro-*N*-(4-methoxyphenyl)-3-phenylacrylamide *Z*/*E* = 5:1 (S1v)

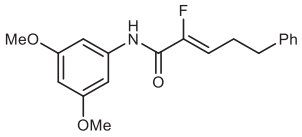
The title compound was obtained as a white solid, 44% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.79 (m, 1H), 7.66 (td, *J* = 8.2, 1.7 Hz, 2H), 7.59 – 7.27 (m, 5H), 7.14 – 6.66 (m, 3H), 3.79 (s, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -116.94 (dd, *J* = 26.8, 5.3 Hz), -129.32 (dd, *J* = 39.7, 5.2 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.58 (d, *J* = 30.8 Hz), 157.06, 149.02 (d, *J* = 258.5 Hz), 130.80 (d, *J* = 10.9 Hz), 130.39, 130.36, 129.84, 129.04, 128.93, 128.33, 122.16, 122.09, 119.86 (d, *J* = 27.0 Hz), 114.42, 114.35, 55.59.

HRMS (ESI): $C_{16}H_{15}FNO_2^+$ ($M+H^+$): 272.1081, found: 272.1084.



(*Z*)-*N*-(3,5-dimethoxyphenyl)-2-fluoro-5-phenylpent-2-enamide (S1w)

The title compound was obtained as a white solid, *Z*, 38% yield and *E*, 39% yield.

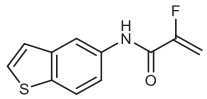
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 6.3 Hz, 1H), 7.36 – 7.19 (m, 5H), 6.83 (d,

J = 2.2 Hz, 2H), 6.31 (t, *J* = 2.2 Hz, 1H), 5.88 (dt, *J* = 24.7, 8.0 Hz, 1H), 3.82 (s, 6H), 3.11 – 3.01 (m, 2H), 2.83 (t, *J* = 7.6 Hz, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) -122.67 (dd, *J* = 24.8, 6.4 Hz)

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.23, 158.53 (d, *J* = 30.2 Hz), 148.82 (d, *J* = 257.6 Hz), 140.95, 138.61, 128.66, 128.56, 126.26, 121.02 (d, *J* = 18.0 Hz), 98.47, 97.58, 55.58, 35.44 (d, *J* = 1.9 Hz), 26.82 (d, *J* = 5.7 Hz).

HRMS (ESI): $C_{19}H_{21}FNO_3^+$ ($M+H^+$): 330.1500, found: 330.1501.



***N*-(benzo[b]thiophen-5-yl)-2-fluoroacrylamide (S1x)**

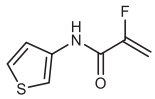
The title compound was obtained as a gray solid, 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 2.2 Hz, 1H), 8.09 (s, 1H), 7.82 (d, *J* = 8.6 Hz, 1H), 7.47 (d, *J* = 5.4 Hz, 1H), 7.40 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.29 (d, *J* = 5.4 Hz, 1H), 5.85 (dd, *J* = 47.9, 3.4 Hz, 1H), 5.27 (dd, *J* = 15.3, 3.4 Hz, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -120.60 – -120.80 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.48 (d, *J* = 29.5 Hz), 156.31 (d, *J* = 271.4 Hz), 140.27, 136.48, 133.41, 128.00, 124.06, 123.01, 117.70, 115.10, 100.06 (d, *J* = 15.0 Hz).

HRMS (ESI): $C_{11}H_9FNOS^+$ ($M+H^+$): 222.0383, found: 222.0384.



2-fluoro-*N*-(thiophen-3-yl)acrylamide (S1y)

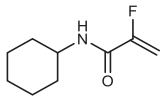
The title compound was obtained as a white solid, 34% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.53 (d, *J* = 3.2 Hz, 1H), 7.11 (dd, *J* = 5.1, 3.1 Hz, 1H), 6.92 (dd, *J* = 5.2, 1.4 Hz, 1H), 5.66 (dd, *J* = 47.9, 3.4 Hz, 1H), 5.08 (dd, *J* = 15.4, 3.5 Hz, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -121.06 – -121.30 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.83 (d, *J* = 30.2 Hz), 156.09 (d, *J* = 270.6 Hz), 134.23, 125.08, 121.17, 111.83, 100.07 (d, *J* = 14.8 Hz).

HRMS (ESI): $C_7H_7FNOS^+$ ($M+H^+$): 172.0227, found: 172.0227.



***N*-cyclohexyl-2-fluoroacrylamide (S1z)**

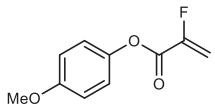
The title compound was obtained as a white solid, 41% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.04 (s, 1H), 5.55 (dd, *J* = 48.0, 3.1 Hz, 1H), 4.97 (dd, *J* = 15.4, 3.1 Hz, 1H), 3.78 – 3.64 (m, 1H), 1.87 – 1.79 (m, 2H), 1.65 – 1.58 (m, 2H), 1.55 – 1.47 (m, 1H), 1.33 – 1.20 (m, 2H), 1.14 – 0.97 (m, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -120.83 – -121.02 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.65 (d, *J* = 30.2 Hz), 156.72 (d, *J* = 270.6 Hz), 98.63 (d, *J* = 15.2 Hz), 48.39, 32.97, 25.52, 24.87.

HRMS (ESI): $C_9H_{15}FNO^+$ ($M+H^+$): 172.1132, found: 172.1135.



4-methoxyphenyl 2-fluoroacrylate (S1aa)

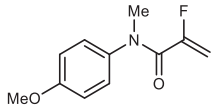
The title compound was obtained as a white solid, 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.03 (m, 2H), 6.98 – 6.83 (m, 2H), 5.89 (dd, *J* = 43.1, 3.4 Hz, 1H), 5.49 (dd, *J* = 13.0, 3.4 Hz, 1H), 3.80 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.78 (dd, *J* = 43.1, 13.0 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.26 (d, *J* = 37.1 Hz), 157.75, 153.01 (d, *J* = 261.9 Hz), 143.53, 122.12, 114.67, 104.25 (d, *J* = 14.9 Hz), 55.66.

HRMS (ESI): $C_{10}H_{10}FO_3^+$ ($M+H^+$): 197.0608, found: 197.0605.



2-Fluoro-*N*-(4-methoxyphenyl)-*N*-methylacrylamide (S1ab)

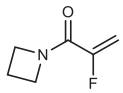
The title compound was obtained as a white solid, 88% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 – 7.04 (m, 1H), 6.91 – 6.83 (m, 1H), 5.34 – 5.09 (m, 1H), 5.01 – 4.83 (m, 1H), 3.79 (d, *J* = 7.2 Hz, 1H), 3.29 (d, *J* = 6.3 Hz, 1H).

^{19}F NMR (377 MHz, $CDCl_3$) -105.01 (dd, *J* = 45.9, 15.9 Hz)

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.85 (d, *J* = 28.9 Hz), 158.88, 157.42 (d, *J* = 272.5 Hz), 136.32, 127.23, 114.63, 100.55 (d, *J* = 16.1 Hz), 55.52, 38.80.

HRMS (ESI): $C_{11}H_{13}FNO_2^+$ ($M+H^+$): 210.0925, found: 210.0921.



1-(Azetidin-1-yl)-2-fluoroprop-2-en-1-one (S1ac)

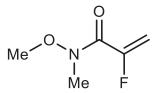
The title compound was obtained as a colorless oil, 71% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.55 (dd, *J* = 46.7, 3.1 Hz, 1H), 5.03 (dd, *J* = 15.8, 3.1 Hz, 1H), 4.46 – 4.31 (m, 2H), 4.10 (t, *J* = 7.9 Hz, 2H), 2.32 (m, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -115.47 – -115.75 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.91 (d, *J* = 32.2 Hz), 157.73 (d, *J* = 271.2 Hz), 99.66 (d, *J* = 14.5 Hz), 52.60 (d, *J* = 9.8 Hz), 48.79, 16.48 (d, *J* = 4.0 Hz).

HRMS (ESI): $C_6H_9FNO^+$ ($M+H^+$): 130.0663, found: 130.0665.



2-Fluoro-*N*-methoxy-*N*-methylacrylamide (S1ad)

The title compound was obtained as a colorless oil, 53% yield.

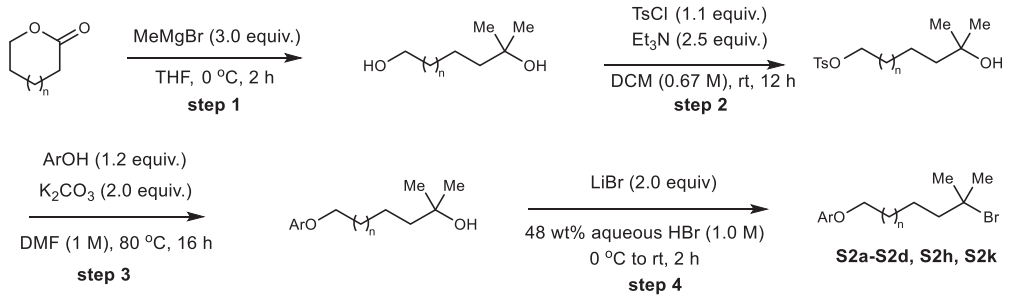
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.50 – 5.28 (m, 1H), 5.18 – 5.04 (m, 1H), 3.70 (d, *J* = 13.3 Hz, 3H), 3.21 (d, *J* = 13.5 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -110.29 (dd, *J* = 46.6, 16.6 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.06 (d, *J* = 30.0 Hz), 156.59 (d, *J* = 270.0 Hz), 100.61 (d, *J* = 15.9 Hz), 61.93 (d, *J* = 2.5 Hz), 33.66.

HRMS (ESI): $C_5H_9FNO_2^+$ ($M+H^+$): 134.0612, found: 134.0610.

2.2 Preparation of alkyl halides



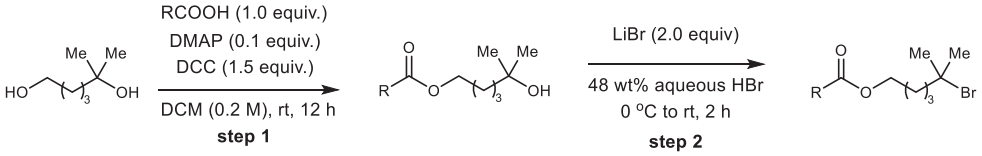
step 1. Tetrahydro-2H-pyran-2-one (10 mmol, 1.0 equiv.) in THF (20 mL) was slowly added to 3.0 M solution of MeMgBr in THF (30 mmol, 3.0 equiv.) at 0 °C. Stir the reaction mixture at 0 °C for 30 min and then at room temperature for 2 hours. Quench the reaction mixture with water (10 mL). Add ethyl acetate (20 mL) and saturated NH_4Cl aq. (10 mL) to the resulted mixture. Extract the mixture with ethyl acetate (20 mL x 2). Wash the collected organic layer with brine. Dry the organic layer over $MgSO_4$. The solvent was removed in vacuo and directly used for the next step without further purification.

step 2. Added 4-methylbenzenesulfonyl chloride (11 mmol, 1.1 equiv.) in 25 mL of DCM dropwise to a solution of 3-methylbutane-1,3-diol (10 mmol, 1.0 equiv.) and triethylamine (25 mmol, 2.5 equiv.) at 0 °C. Stir the resulting mixture at rt for 4 hours. Add water (20 mL) to the reaction mixture. Stir the reaction mixture for 45 minutes. Wash the organic phase with water, 1 M HCl, brine. Dry the solution over $MgSO_4$ and filter. Concentrate the solution to obtain a yellow oil. Purify the residue by flash column chromatography to obtain 3-hydroxy-3-methylbutyl 4-methylbenzenesulfonate.

step 3. In an oven-dried Schlenk tube equipped with a PTFE coated stirring bar, 3-hydroxy-3-methylbutyl 4-methylbenzenesulfonate (1.2 equiv.), the corresponding phenol (1.0 equiv.), K_2CO_3 (2.0 equiv.) and dry DMF (1 M) were charged under argon, then the reaction was stirred at 80 °C overnight. The reaction was cooled to room temperature, then the residue was taken-up with water and extracted twice with CH_2Cl_2, then the combined organic extracts were washed twice with water, dried over $MgSO_4$ and the solvent was removed in vacuo. The product used for the next step without

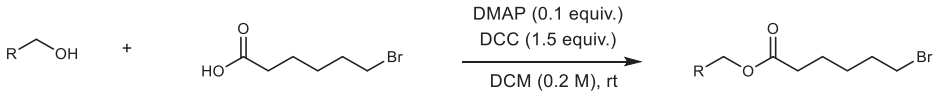
further purification.

step 4: The corresponding tertiary alcohol precursor (10 mmol, 1.0 equiv., neat or dissolved in a minimal amount of CH_2Cl_2) was added LiBr (1.80 g, 20 mmol, 2.0 equiv.) in 48 wt% aqueous HBr (0.2 M, 20 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for overnight. The reaction mixture was diluted with ethyl acetate, washed with water and saturated $NaHCO_3$. The organic layer was collected, washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography to afford the desired tertiary bromide. According to the reported literature,[4, 7] alkyl bromides (**S2a-S2d, S2h, S2k**) was conveniently synthesized in gram scale.



step 1. To a solution of acid (10 mmol, 1.0 equiv.) and 6-methyl-1,6-heptanediol (12 mmol, 1.2 equiv.) in CH_2Cl_2 (40 mL, 0.25 M) were added DCC (15 mmol, 1.5 equiv.) and DMAP (1 mmol, 0.1 equiv.) under N_2 flow. The reaction mixture was stirred for 12 h at room temperature. The resulting mixture was filtrated with celite and wash with 20 mL DCM to get a clear solution. After removal of the solvent, the resulting crude mixture was purified by flash column chromatography on silica.

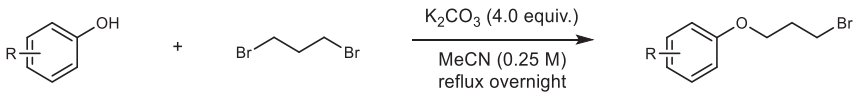
step 2. According to literature procedure,[4] the final tertiary bromides products (**S2e-S2g, S2i-S2j**) were obtained according to the above method.



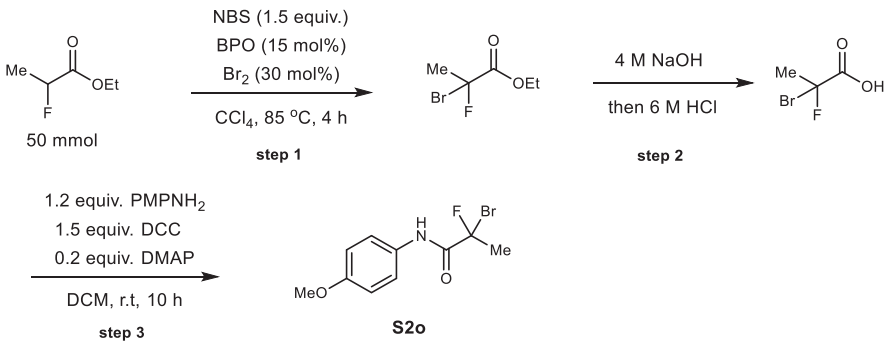
The alkyl bromide **S2l** was prepared according to literature procedure.[8] The carboxylic acid (4 mmol, 1.0 equiv.) was added to a solution of *N*,*N*′-dicyclohexylcarbodiimide (DCC, 6.0 mmol, 1.2 equiv.) and DMAP (0.4 mmol, 0.1 equiv.) in CH_2Cl_2 (20 mL) at 0 °C. The alcohol (4.8 mmol, 1.2 equiv.) was then added.

The reaction mixture was allowed to be warmed to room temperature slowly and stirred overnight. The resulting mixture was filtrated with celite and wash with 20 mL DCM to get a clear solution. After removal of the solvent, the resulting crude mixture was purified by flash column chromatography on silica.

The alkyl bromide **S2m** was prepared according to literature procedure.[9] The carboxylic acid (4 mmol, 1.0 equiv.) was added to a solution of *N*,*N*′-dicyclohexylcarbodiimide (DCC, 6.0 mmol, 1.2 equiv.) and DMAP (0.4 mmol, 0.1 equiv.) in CH_2Cl_2 (20 mL) at 0 °C. The alcohol (4.8 mmol, 1.2 equiv.) was then added. The reaction mixture was allowed to be warmed to room temperature slowly and stirred overnight. The resulting mixture was filtrated with celite and wash with 20 mL DCM to get a clear solution. After removal of the solvent, the resulting crude mixture was purified by flash column chromatography on silica.



The alkyl bromide **S2n** was prepared according to literature procedure.[10] A solution of phenol derivatives (10 mmol) and 1,3-dibromopropane (80 mmol, 8 equiv.) in MeCN (30 mL) was adding anhydrous potassium carbonate (40 mmol, 4 equiv.). The reaction mixture was stirred at reflux for 6-12 h, and then potassium carbonate was removed by suction filtration and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica to afford bromide product.

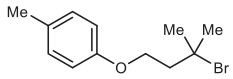


step 1. To a solution of 2-fluoro ethyl propionate (50 mmol, 1.0 equiv.) in carbon tetrachloride (25 mL) was added *N*-bromosuccinimide (NBS) (55 mmol, 1.2 equiv.), benzoyl peroxide (BPO, 2.5 mmol, 0.05 equiv.) and bromine (Br_2, 5 mmol, 0.1 equiv.) and stir for 1 hour under reflux. After that, additional BPO (2.5 mmol, 0.05 equiv.) and bromine (Br_2, 5 mmol, 0.1 equiv.) were added and stirred under reflux for 1 hour. Then, BPO (2.5 mmol, 0.05 equiv.), bromine (Br_2, 5 mmol, 0.1 equiv.) and NBS (55 mmol, 0.3 equiv.) were added again. According to ^{19}F NMR, the conversion of the raw materials was about 50%.

step 2. Place the reaction solution in an ice water bath and stop stirring. Remove the insoluble components by filtration, and wash the solid with a small amount of CCl_4. The obtained solution does not require further purification. The solution was treated with 4 M sodium hydroxide aqueous solution (attention for exothermic), adjust PH > 13 and continue stirred for 1 hour., After removing all solvents using rotary evaporation, a mixture of sodium carboxylate salts was obtained. The solid obtained by treating with 100 mL dichloromethane, and acidification with 6 M hydrochloric acid until all the solids were dissolved. The organic phase was separated and the aqueous phase was extracted with a minimum amount of dichloromethane. All organic phases were combined, dry with magnesium sulfate, and filter to obtain a solution of a-bromofluoropropionic acid (mixed with a-fluoropropionic acid). No further purification was required and the concentration was determined to be about 0.3 M by ^{19}F NMR.

step 3. Add *N*,*N*'-Dicyclohexylcarbodiimide (DCC, 45 mmol, 1.5 equiv. calculated according to the concentration of the reaction solution in the previous step), 4-dimethylaminopyridine (DMAP, 6 mmol, 0.2 equiv.) and 4-methoxyaniline (36 mmol,

1.2 equiv.) to the solution obtained in the previous step, the reaction mixture was stirred overnight. The resulting mixture was filtrated with celite and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica to afford the product **S2o** as a white solid, 2.9 g, 21%, total three steps.



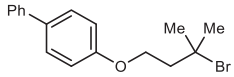
1-(3-Bromo-3-methylbutoxy)-4-methylbenzene (S2a)

The title compound was obtained as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.3 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 4.25 (t, *J* = 6.6 Hz, 2H), 2.37 – 2.24 (m, 5H), 1.89 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.56, 130.06, 130.03, 114.46, 66.11, 65.53, 46.03, 34.94, 20.58.

HRMS (ESI): $C_{12}H_{18}BrO^+$ ($M+H^+$): 257.0536, found: 257.5733.



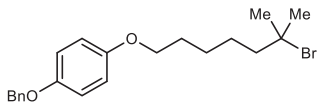
4-(3-Bromo-3-methylbutoxy)-1,1'-biphenyl (S2b)

The title compound was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.50 (m, 4H), 7.47 – 7.39 (m, 2H), 7.38 – 7.27 (m, 1H), 7.04 – 6.96 (m, 2H), 4.30 (t, *J* = 6.6 Hz, 2H), 2.35 (t, *J* = 6.6 Hz, 2H), 1.88 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.29, 140.92, 134.07, 128.86, 128.33, 126.88, 126.83, 114.94, 66.26, 65.46, 46.05, 35.01.

HRMS (ESI): $C_{17}H_{20}BrO^+$ ($M+H^+$): 319.0692, found: 319.0693.



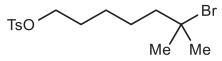
1-(Benzyloxy)-4-((6-bromo-6-methylheptyl)oxy)benzene (S2c)

The title compound was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.37 (m, 4H), 7.36 – 7.30 (m, 1H), 6.96 – 6.89 (m, 2H), 6.88 – 6.80 (m, 2H), 5.03 (s, 2H), 3.93 (t, *J* = 6.5 Hz, 2H), 1.88 – 1.79 (m, 3H), 1.77 (s, 6H), 1.69 – 1.41 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.48, 152.93, 137.36, 128.57, 127.90, 127.51, 115.86, 115.43, 70.73, 68.44, 68.43, 47.49, 34.30, 29.31, 26.15, 26.12.

HRMS (ESI): $C_{21}H_{28}BrO_2^+$ ($M+H^+$): 391.1267, found: 391.1268.



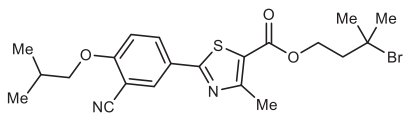
6-Bromo-6-methylheptyl 4-methylbenzenesulfonate (S2d)

The title compound was obtained as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.03 (t, *J* = 6.4 Hz, 2H), 2.44 (s, 3H), 1.77 – 1.57 (m, 10H), 1.55 – 1.41 (m, 2H), 1.41 – 1.28 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.84, 133.28, 129.97, 128.00, 70.54, 68.16, 47.30, 34.33, 28.80, 25.75, 25.41, 21.77.

HRMS (ESI): $C_{15}H_{24}BrO_3S^+$ ($M+H^+$): 363.0624, found: 363.0628.



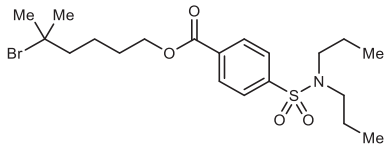
3-Bromo-3-methylbutyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (S2e)

The title compound was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 2.2 Hz, 1H), 8.12 – 8.05 (m, 1H), 7.01 (d, *J* = 8.9 Hz, 1H), 4.56 (t, *J* = 6.7 Hz, 2H), 3.90 (d, *J* = 6.5 Hz, 2H), 2.76 (s, 3H), 2.32 – 2.21 (m, 2H), 2.18 (m, 1H), 1.85 (s, 6H), 1.09 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.49, 162.67, 161.97, 161.70, 132.70, 132.26, 126.06, 121.48, 115.50, 112.76, 103.12, 75.84, 64.05, 63.58, 45.47, 34.88, 28.29, 19.18, 17.64.

HRMS (ESI): $C_{21}H_{26}BrN_2O_3S^+$ ($M+H^+$): 465.0842, found: 465.0844.



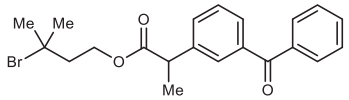
5-Bromo-5-methylhexyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (S2f)

The title compound was obtained as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.11 (m, 2H), 7.86 (d, *J* = 8.2 Hz, 2H), 4.37 (t, *J* = 6.5 Hz, 2H), 3.13 – 3.05 (m, 4H), 1.89 – 1.76 (m, 4H), 1.76 (s, 3H), 1.75 – 1.63 (m, 3H), 1.62 – 1.46 (m, 6H), 0.85 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.29, 144.23, 133.66, 130.19, 127.02, 67.76, 65.34, 49.94, 46.97, 34.25, 28.56, 22.89, 21.94, 11.16.

HRMS (ESI): $C_{20}H_{33}BrNO_4S^+$ ($M+H^+$): 462.1308, found: 462.1310.



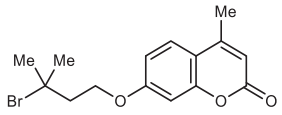
3-Bromo-3-methylbutyl 2-(3-benzoylphenyl)propanoate (S2g)

The title compound was obtained as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.72 (m, 3H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.63 – 7.56 (m, 1H), 7.54 – 7.42 (m, 4H), 4.33 (t, *J* = 6.8 Hz, 2H), 3.79 (q, *J* = 7.2 Hz, 1H), 2.09 (t, *J* = 6.8 Hz, 2H), 1.71 (d, *J* = 3.4 Hz, 6H), 1.53 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.46, 173.90, 140.71, 137.95, 137.49, 132.56, 131.52, 130.06, 129.22, 129.07, 128.59, 128.35, 64.19, 63.17, 45.43, 45.18, 34.61, 34.58, 18.37.

HRMS (ESI): $C_{21}H_{24}BrO_3^+$ ($M+H^+$): 403.0903, found: 403.0935.



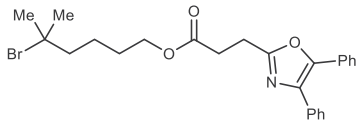
7-(3-Bromo-3-methylbutoxy)-4-methyl-2*H*-chromen-2-one (S2h)

The title compound was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.6 Hz, 1H), 6.90 – 6.79 (m, 2H), 6.13 (d, *J* = 1.1 Hz, 1H), 4.31 (t, *J* = 6.6 Hz, 2H), 2.39 (d, *J* = 1.2 Hz, 3H), 2.33 (t, *J* = 6.6 Hz, 2H), 1.86 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.62, 161.26, 155.28, 152.50, 125.62, 113.74, 112.41, 112.09, 101.68, 66.73, 64.60, 45.53, 34.86, 18.69.

HRMS (ESI): $C_{15}H_{18}BrO_3^+$ ($M+H^+$): 325.0434, found: 325.0439.



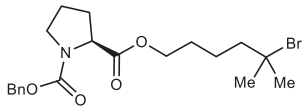
5-Bromo-5-methylhexyl 3-(4,5-diphenyloxazol-2-yl)propanoate (S2i)

The title compound was obtained as a pale yellow oil. Note: Do not perform column chromatography purification after the solvent was evaporated, then used directly, otherwise it will be completely decomposed.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 2H), 7.60 – 7.52 (m, 2H), 7.38 – 7.30 (m, 6H), 4.15 (t, *J* = 6.5 Hz, 2H), 3.20 (t, *J* = 7.5 Hz, 2H), 2.93 (t, *J* = 7.5 Hz, 2H), 1.81 – 1.73 (m, 2H), 1.72 (s, 6H), 1.70 – 1.64 (m, 2H), 1.63 – 1.53 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.02, 161.90, 145.48, 134.95, 132.24, 128.88, 128.68, 128.60, 128.16, 127.93, 126.50, 67.83, 64.58, 46.99, 34.21, 31.18, 28.55, 23.57, 22.79.

HRMS (ESI): $C_{25}H_{29}BrNO_3^+$ ($M+H^+$): 470.1325, found: 470.1329.



1-Benzyl 2-(5-bromo-5-methylhexyl) (*S*)-pyrrolidine-1,2-dicarboxylate (S2j)

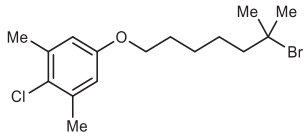
The title compound was obtained as a pale yellow oil. Note: after the solvent is evaporated, then used directly.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.24 (m, 5H), 5.21 – 5.01 (m, 2H), 4.36 (m, 1H), 4.16 (t, *J* = 6.3 Hz, 1H), 3.99 (m, 1H), 3.68 – 3.57 (m, 1H), 3.60 – 3.42 (m, 1H), 2.22

m, 1H), 2.06 – 1.76 (m, 5H), 1.73 (d, *J* = 8.1 Hz, 6H), 1.69 – 1.62 (m, 1H), 1.62 – 1.54 (m, 1H), 1.54 – 1.43 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.89, 172.74, 154.92, 154.37, 136.80, 136.67, 129.09, 128.85, 128.51, 128.47, 128.01, 127.90, 127.84, 68.03, 67.83, 67.03, 67.00, 64.81, 59.39, 59.05, 47.01, 46.96, 46.50, 34.26, 33.64, 31.05, 30.05, 28.57, 28.44, 24.38, 23.60, 22.74, 22.71.

HRMS (ESI): $C_{20}H_{29}BrNO_4^+$ ($M+H^+$): 426.1274, found: 426.1277.



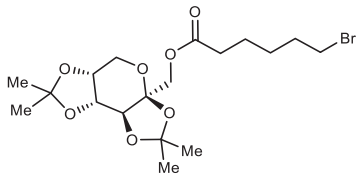
5-((6-Bromo-6-methylheptyl)oxy)-2-chloro-1,3-dimethylbenzene (S2k)

The title compound was obtained as a pale white solid. Note: Do not perform column chromatography purification after the solvent was evaporated, then used directly.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.64 (s, 2H), 3.92 (t, *J* = 6.4 Hz, 2H), 2.34 (s, 6H), 1.81 (m, 4H), 1.76 (s, 6H), 1.66 – 1.54 (m, 2H), 1.49 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.01, 137.16, 126.18, 114.64, 68.47, 68.05, 47.58, 34.40, 29.31, 26.22, 26.17, 21.08.

HRMS (ESI): $C_{16}H_{25}BrClO^+$ ($M+H^+$): 347.0772, found: 347.0771.



((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methyl 6-bromohexanoate (S2l)

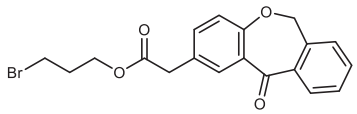
The title compound was obtained as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.58 (m, 1H), 4.38 (dd, *J* = 11.8, 1.1 Hz, 1H), 4.28 (dd, *J* = 2.6, 1.0 Hz, 1H), 4.25 – 4.19 (m, 1H), 4.02 (dd, *J* = 11.6, 1.2 Hz, 1H), 3.88 (dt, *J* = 12.9, 1.6 Hz, 1H), 3.74 (dt, *J* = 13.0, 1.1 Hz, 1H), 3.39 (t, *J* = 6.8 Hz, 2H), 2.36 (t, *J* =

7.5 Hz, 2H), 1.91 – 1.80 (m, 2H), 1.66 (m, 2H)1.52 (s, 3H), 1.51 – 1.40 (m, 5H), 1.38 (s, 3H), 1.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.66, 109.13, 108.71, 101.54, 70.77, 70.56, 70.06, 65.27, 61.24, 33.84, 33.43, 32.37, 27.63, 26.48, 25.90, 25.24, 24.07, 23.90.

HRMS (ESI): $C_{18}H_{30}BrO_7^+$ ($M+H^+$): 437.1169, found: 437.1165.



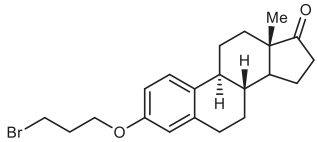
3-Bromopropyl 2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)acetate (S2m)

The title compound was obtained as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 2.4 Hz, 1H), 7.88 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.55 (td, *J* = 7.4, 1.4 Hz, 1H), 7.50 – 7.32 (m, 3H), 7.02 (d, *J* = 8.4 Hz, 1H), 5.17 (s, 2H), 3.65 (s, 2H), 4.23 (t, *J* = 6.1 Hz, 2H), 3.41 (t, *J* = 6.5 Hz, 2H), 2.24 – 2.08 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.94, 171.34, 160.62, 140.53, 136.38, 135.64, 132.92, 132.53, 129.60, 129.40, 127.94, 127.74, 125.26, 121.23, 73.75, 62.79, 40.27, 31.66, 29.43.

HRMS (ESI): $C_{19}H_{18}BrO^4+$ ($M+H^+$): 389.0383, found: 389.0383.



(8*R*,9*S*,13*S*)-3-(3-bromopropoxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (S2n)

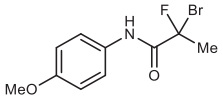
The title compound was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.6 Hz, 1H), 6.72 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.66 (d, *J* = 2.6 Hz, 1H), 4.08 (t, *J* = 5.8 Hz, 2H), 3.60 (t, *J* = 6.4 Hz, 2H), 2.94 – 2.83 (m, 2H), 2.51 (dd, *J* = 18.8, 8.5 Hz, 1H), 2.44 – 2.36 (m, 1H), 2.35 – 2.21 (m, 3H), 2.20 – 1.90 (m, 4H), 1.71 – 1.51 (m, 4H), 1.50 – 1.36 (m, 2H), 0.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.72, 137.85, 132.35, 126.41, 114.59, 112.18, 65.23,

50.43, 48.03, 44.00, 38.38, 35.90, 32.46, 31.61, 30.15, 29.68, 26.56, 25.95, 21.61, 13.88.

HRMS (ESI): $C_{21}H_{28}BrO_2^+$ ($M+H^+$): 391.1267, found: 391.1266.



2-Bromo-2-fluoro-*N*-(4-methoxyphenyl)propenamide (S2o)

The title compound was obtained as a white solid, 2.9 g, 21%, total three steps.

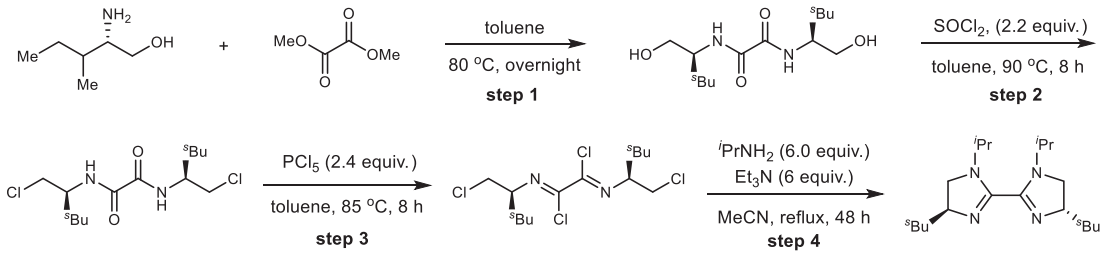
^{1}H NMR (400 MHz, $CDCl_3$) 7.89 (s, 1H), 7.66 – 7.41 (m, 2H), 6.99 – 6.74 (m, 2H), 3.81 (s, 3H), 2.33 (d, J = 20.7 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -106.99 – -107.40 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.42 (d, J = 21.4 Hz), 157.30, 129.39, 122.07, 114.43, 99.36 (d, J = 265.1 Hz), 55.60, 29.31 (d, J = 21.8 Hz).

HRMS (ESI): $C_{10}H_{12}BrFNO_2^+$ ($M+H^+$): 276.0030, found: 276.0032.

2.3 Preparation of chiral ligands



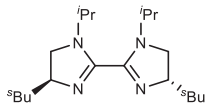
step 1: (2*S*)-2-Amino-3-methylpentan-1-ol (50 mmol, 5.85 g, 2.0 equiv.) and dimethyloxalate (25 mmol, 2.95 g, 1.0 equiv.) were dissolved in toluene (200 mL) and heated to 80 °C. The reaction was allowed to stir overnight and then cooled to room temperature then filtered and washed with petroleum ether to get the diamide precipitating out of solution as a white solid (7.0 g, 97%), which was used without further purification.

step 2: The crude diol (24.2 mmol, 7.0 g) was dissolved in toluene (100 mL) and heated to 70 °C where upon thionyl chloride (53.24 mmol, 4.4 mL, 2.2 equiv.) was added. The reaction was stirred at 70 °C for 30 minutes then heated to 90 °C for 8 h. The reaction was cooled to room temperature and concentrated under reduced pressure to afford the dichloro-intermediate which was used without further purification.

step 3: To an oven dried three-necked flask was added crude dichloro-intermediate (21.05 mmol, 6.82 g) and phosphorus pentachloride (50.5 mmol, 10.4 g, 2.4 equiv.) in 160 mL of toluene under N_2 atmosphere. The reaction was allowed to stir at 85 °C for 8 h before it was cooled to room temperature. Toluene was evaporated under reduced pressure to get the bisimine intermediate. And used directly without further purification

step 4: In a 150 mL thick-walled pressure bottle, equipped with a teflon stir bar, was charged the crude bisimine intermediate (5.0 mmol, 1.8 g) with MeCN (75 mL, 0.067 M). Then Et_3N (56 mmol, 11.2 equiv.) and isopropylamine (30 mmol, 6.0 equiv.) was added at N_2. Next, the reaction mixture heated to reflux under N_2 for 48 h. After been cooled to ambient temperature, the volatiles were removed by rotary evaporation. the residue was diluted with CH_2Cl_2 washed with saturated NH_4Cl solution (100 mL×3) and water. The organic layer was dried with $MgSO_4$, filtered and concentrated under

reduced pressure. The residue was purified by flash column chromatography (PE/EtOAc = 2:1 to DCM/MeOH = 10:1) to give corresponding ligand as a slight yellow oil. According to literature procedure,[11-12] ligands (**L12 and L25**) were synthesized.



(4*S*,4'*S*)-4-((*R*)-sec-butyl)-4'-((*S*)-sec-butyl)-1,1'-diisopropyl-4,4',5,5'-tetrahydro-1H,1'H-2,2'-biimidazole (L12)

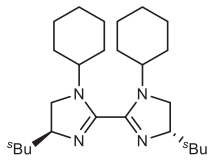
The title compound was obtained as a yellow oil, 840 mg, 50%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.09 – 3.90 (m, 4H), 3.30 (dd, *J* = 11.3, 9.2 Hz, 2H), 3.02 (t, *J* = 9.4 Hz, 2H), 1.77 – 1.59 (m, 2H), 1.59 – 1.36 (m, 2H), 1.22 – 1.15 (m, 2H), 1.13 (d, *J* = 6.7 Hz, 6H), 1.05 (d, *J* = 6.7 Hz, 6H), 0.88 (t, *J* = 7.4 Hz, 6H), 0.82 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.42, 68.81, 46.20, 44.09, 39.50, 26.07, 20.84, 20.18, 14.54, 11.75.

HRMS (ESI): $C_{20}H_{39}N_4^+$ ($M+H^+$): 335.3169, found: 335.3171.

$[\alpha]_D^{25}$ = -126.90 (c = 1.15, $CHCl_3$).



(4*S*,4'*S*)-4-((*R*)-sec-butyl)-4'-((*S*)-sec-butyl)-1,1'-dicyclohexyl-4,4',5,5'-tetrahydro-1H,1'H-2,2'-biimidazole (L25)

The title compound was obtained as a yellow oil, 910 mg, 44%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (m, 2H), 3.56 (m, 2H), 3.41 – 3.26 (m, 2H), 3.06 (t, *J* = 9.0 Hz, 2H), 1.94 – 1.51 (m, 11H), 1.51 – 1.24 (m, 7H), 1.23 – 0.95 (m, 8H), 0.90 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.44, 70.24, 54.25, 45.96, 33.21, 31.26, 25.84, 25.72,

25.51, 18.64, 18.39.

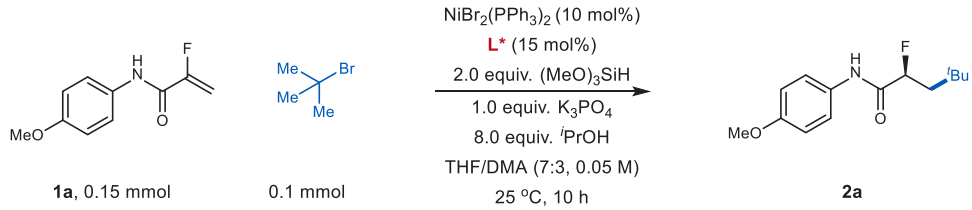
HRMS (ESI): $C_{26}H_{47}N_4^+$ ($M+H^+$): 415.3795, found: 415.3798.

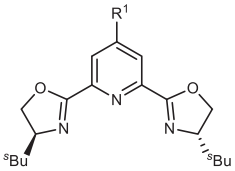
$[\alpha]_D^{25}$ = -195.62 (c = 1.07, $CHCl_3$).

3. Optimization of Reaction Conditions

3.1 Reaction optimizations for asymmetric group transfer

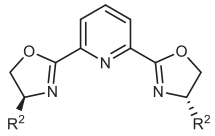
Table S1. Chiral ligand effect.





(*S*,*S*)-**L1** R = H 62%, 91% ee

(*S*,*S*)-**L2** R = OMe 43%, 85% ee



(*S*,*S*)-**L3** R = ^{t}Bu 51%, 54% ee

(*S*,*S*)-**L4** R = ^{i}Pr 64%, 86% ee

(*R*,*R*)-**L5** R = Cy 57%, -54% ee

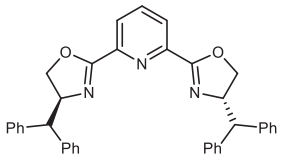
(*R*,*R*)-**L6** R = CH_2Cy 52%, -30% ee

(*S*,*S*)-**L7** R = Ph 14%, 7% ee

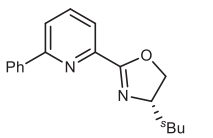
(*S*,*S*)-**L14** R = ^{i}Bu 60%, 32% ee

(*S*,*S*)-**L15** R = Bn 66%, 48% ee

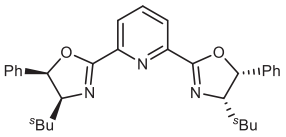
(*S*,*S*)-**L16** R = CO_2Me 5%, 5% ee



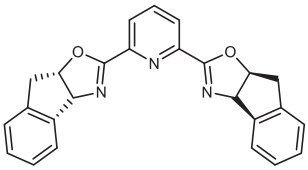
(*S*,*S*)-**L19** 45%, 78% ee



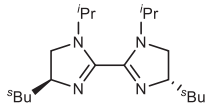
(*S*,*S*)-**L22** 29%, 0% ee



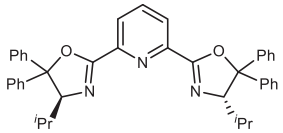
(*S*,*S*)-**L8** 51%, 82% ee



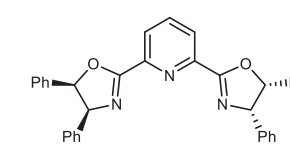
(*R*,*R*)-**L9** 41%, -12% ee



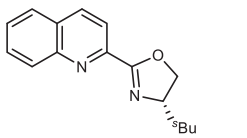
(*S*,*S*)-**L12** 47%, 34% ee



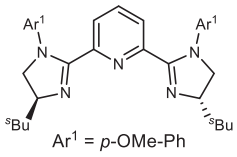
(*S*,*S*)-**L17** 4%, 9% ee



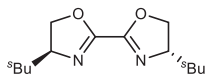
(*R*,*R*)-**L20** 49%, -67% ee



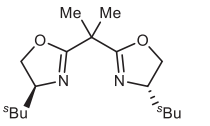
(*S*)-**L23** 8%, 12% ee



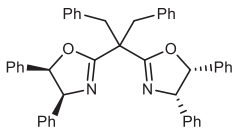
(*S*,*S*)-**L10** 36%, 17% ee



(*S*,*S*)-**L11** 13%, 4% ee

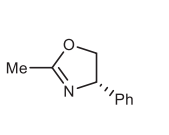


(*S*,*S*)-**L13** 13%, 0% ee



(*S*,*S*)-**L18** 37%, 2% ee

(*S*,*S*)-**L21** 5%, 19% ee



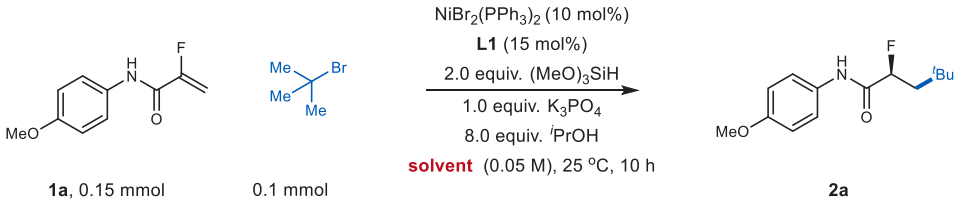
(*S*)-**L24** 3%, 4% ee

Reaction conditions: α-Fluoro alkenyl amide **1a** (0.15 mmol), *tert*-butyl bromide (0.1

mmol), $NiBr_2 \cdot (PPh_3)_2$ (10 mol%), ligand (15 mol%), K_3PO_4 (1.0 equiv.), $(MeO)_3SiH$ (2.0 equiv.), ^{i}PrOH (8.0 equiv.), THF/DMA (7:3, 0.05 M), 25 °C, 10 h.

Comment: The chiral tridentate Pybox ligand **L1** was selected as the optimal ligand.

Table S2. Solvent effect.

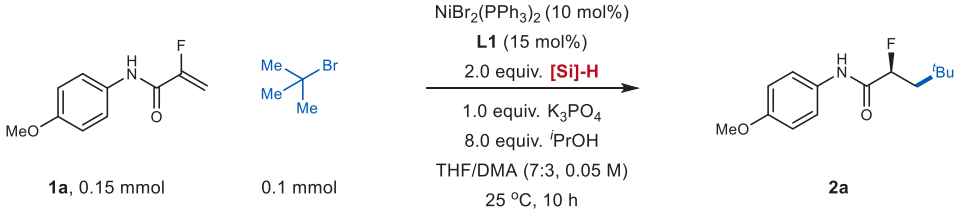


Entry	solvents	yield of 2a (%)	ee of 2a (%)
1	THF	35	84
2	DME	48	87
3	Dioxane	24	86
4	DMA	69	73
5	DMF	2	25
6	NMP	8	65
7	THF/NMP 4:1	49	87
8	**THF/DMA 7:3**	**62**	**91**

Reaction conditions: α-Fluoro alkenyl amide **1a** (0.15 mmol), *tert*-butyl bromide (0.1 mmol), $NiBr_2 \cdot (PPh_3)_2$ (10 mol%), (*S*,*S*)-**L1** (15 mol%), K_3PO_4 (1.0 equiv.), $(MeO)_3SiH$ (2.0 equiv.), ^{i}PrOH (8.0 equiv.), solvent (0.05 M), 25 °C, 10 h.

Comment: The mixed solvent THF/DMA = 7:3 (0.05M) was selected as the optimal solvent.

Table S3. Silane or reductant effect.

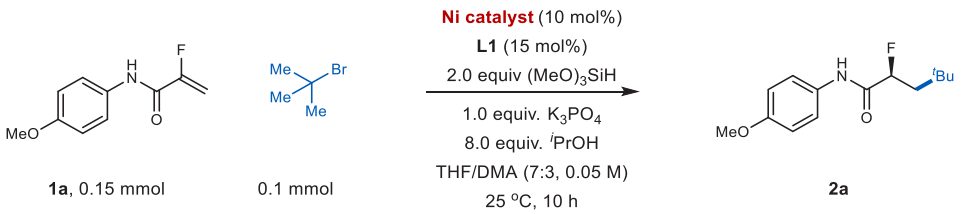


Entry	reductants	yield of 2a (%)	ee of 2a (%)
1	**$(MeO)_3SiH$**	**62**	**91**
2	$(EtO)_3SiH$	42	87
3	$(EtO)_2MeSiH$	43	87
4	Ph_2SiH_2	52	82
5	$(MeO)_2MeSiH$	55	86
6	$(Me_2SiH)_2O$	45	84
7	Zn	34	78
8	Mn	31	82

Reaction conditions: α-Fluoro alkenyl amide **1a** (0.15 mmol), *tert*-butyl bromide (0.1 mmol), $NiBr_2·(PPh_3)_2$ (10 mol%), (*S*,*S*)-**L1** (15 mol%), K_3PO_4 (1.0 equiv.), [Si]-H (2.0 equiv.), ^{i}PrOH (8.0 equiv.), THF/DMA (7:3, 0.05 M), 25 °C, 10 h.

Comment: The $(MeO)_3SiH$ was selected as the optimal reductant.

Table S4. Catalyst effect.



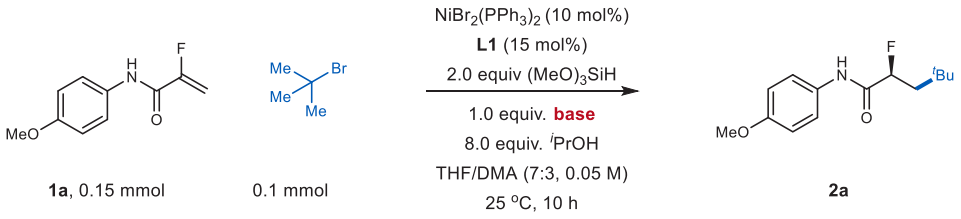
Entry	conditions	yield of 2a (%)	ee of 2a (%)
1	**$NiBr_2·(PPh_3)_2$**	**62**	**91**
2	$NiCl_2·(PPh_3)_2$	47	89
3	$NiBr_2·DME$	18	90
4	$NiBr_2·3H_2O$	16	88
5	NiI_2	12	88
6	$Ni(acac)_2$	38	64
7	$Ni(OAc)_2·4H_2O$	27	81
8	$Ni(COD)_2$	45	80
9	$CoBr_2·DME$	0	-

10	$CoBr_2$	0	-
11	$Co(acac)_2$	0	-
12	$Fe(acac)_3$	0	-
13	$Fe(OTf)_2$	0	-

Reaction conditions: α-Fluoro alkenyl amide **1a** (0.15 mmol), *tert*-butyl bromide (0.1 mmol), Ni catalyst (10 mol%), (*S*,*S*)-**L1** (15 mol%), K_3PO_4 (1.0 equiv.), $(MeO)_3SiH$ (2.0 equiv.), ^{i}PrOH (8.0 equiv.), THF/DMA (7:3, 0.05 M), 25 °C, 10 h.

Comment: The $NiBr_2{\cdot}(PPh_3)_2$ was selected as the optimal catalyst and Co-catalysts or Fe-catalysts were inefficient in the reaction.

Table S5. Base effect.



1a, 0.15 mmol 0.1 mmol **2a**

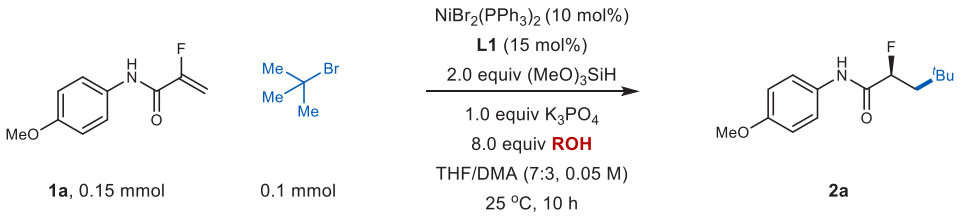
Entry	conditions	yield of 2a (%)	ee of 2a (%)
1	**K_3PO_4**	**62**	**91**
2	K_2HPO_4	7	87
3	KH_2PO_4	0	-
4	KF	32	89
5	Na_3PO_4	37	88
6	Na_2CO_3	45	84
7	Cs_2CO_3	35	72
8	K_2CO_3	31	80
9	Et_3N	15	87

Reaction conditions: α-Fluoro alkenyl amide **1a** (0.15 mmol), *tert*-butyl bromide (0.1 mmol), $NiBr_2{\cdot}(PPh_3)_2$ (10 mol%), (*S*,*S*)-**L1** (15 mol%), base (1.0 equiv.), $(MeO)_3SiH$ (2.0 equiv.), ^{i}PrOH (8.0 equiv.), THF/DMA (7:3, 0.05 M), 25 °C, 10 h.

Comment: The K_3PO_4 was selected as the optimal base, organic base Et_3N can also

promote the reaction in lower efficiency.

Table S6. Alcohol effect.



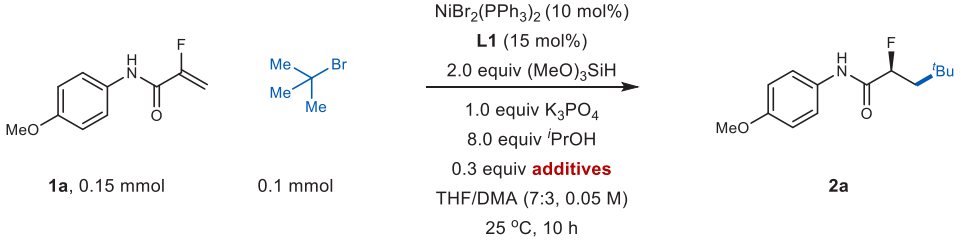
1a, 0.15 mmol 0.1 mmol **2a**

Entry	conditions	yield of 2a (%)	ee of 2a (%)
1	MeOH	60	79
2	EtOH	62	84
3	^{t}BuOH	47	82
4	CyOH	20	67
5	BnOH	76	86
6	**^{i}PrOH**	**62**	**91**
7	2.0 equiv ^{i}PrOH	60	89
8	HFIP	26	17
9	2.0 equiv. H_2O	28	71

Reaction conditions: α-Fluoro alkenyl amide **1a** (0.15 mmol), *tert*-butyl bromide (0.1 mmol), $NiBr_2 \cdot (PPh_3)_2$ (10 mol%), (*S*,*S*)-**L1** (15 mol%), K_3PO_4 (1.0 equiv.), $(MeO)_3SiH$ (2.0 equiv.), ROH (8.0 equiv.), THF/DMA (7:3, 0.05 M), 25 °C, 10 h.

Comment: The ^{i}PrOH was selected as the optimal base in 8.0 equiv., decreasing the equivalence of ^{i}PrOH to 2.0 equiv. with reduced enantioselectivity.

Table S7. Additives effect.



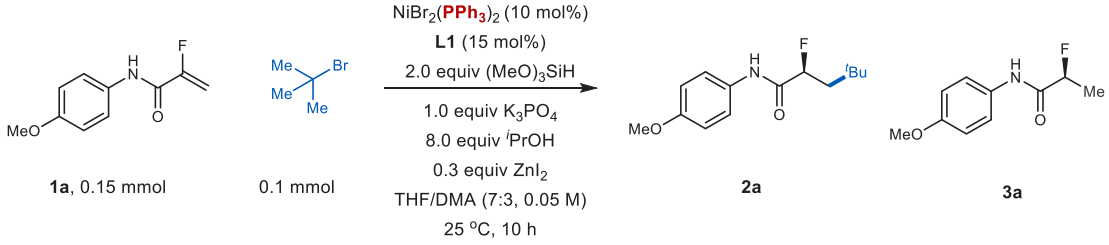
1a, 0.15 mmol 0.1 mmol **2a**

Entry	conditions	yield of 2a (%)	ee of 2a (%)
1	LiI	67	90
2	NaI	69	89
3	KI	61	88
4	CuI	43	91
5	**ZnI_2**	**76**	**91**
6	$ZnCl_2$	72	87
7	$ZnBr_2$	68	86
8	$Zn(OTf)_2$	12	70
9	$MgCl_2$	23	82

Reaction conditions: α-Fluoro alkenyl amide **1a** (0.15 mmol), *tert*-butyl bromide (0.1 mmol), $NiBr_2 \cdot (PPh_3)_2$ (10 mol%), (*S*,*S*)-**L1** (15 mol%), K_3PO_4 (1.0 equiv.), $(MeO)_3SiH$ (2.0 equiv.), ^{i}PrOH (8.0 equiv.), additives (0.3 equiv.), THF/DMA (7:3, 0.05 M), 25 °C, 10 h.

Comment: The addition of Lewis acid additive ZnI_2 can improve the yield of the reaction and without diminished the enantioselectivity.

Table S8. Phosphine ligand effect.



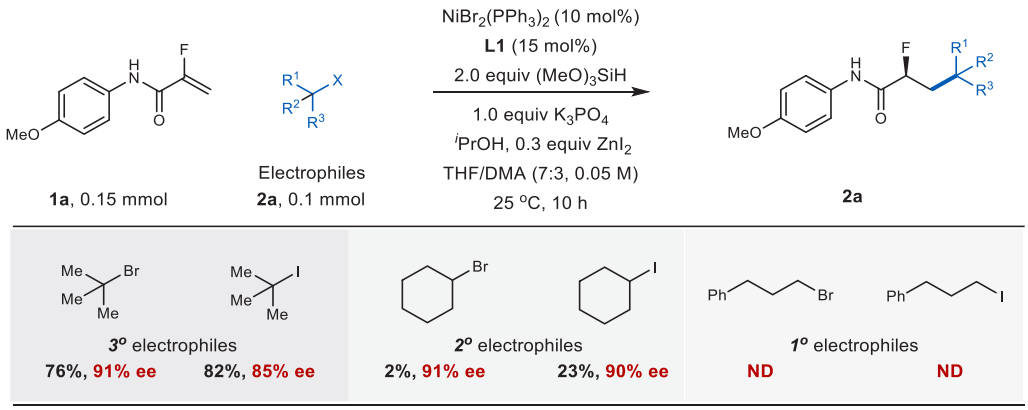
Entry	Ni catalyst	yield (ee) of 2a	yield (ee) of 3a	1a
1	$NiBr_2(PPh_3)_2$	78% (91% ee)	26% (51% ee)	11%
2	$NiCl_2(PPh_3)_2$	71% (89% ee)	31% (58% ee)	13%
3	$NiCl_2 \cdot DME$	4%	92% (87% ee)	0%
4	$NiCl_2 \cdot DME + PPh_3$	67% (89% ee)	39% (67% ee)	22%
5	$NiBr_2 \cdot DME$	10%	91% (87% ee)	0%

6	$NiBr_2$·DME + PPh_3	75% (89% ee)	33% (54% ee)	16%

Reaction conditions: α-Fluoro alkenyl amide **1a** (0.15 mmol), *tert*-butyl bromide (0.1 mmol), [Ni] (10 mol%), (*S*,*S*)-**L1** (15 mol%), K_3PO_4 (1.0 equiv.), $(MeO)_3SiH$ (2.0 equiv.), ^{i}PrOH (8.0 equiv.), ZnI_2 (0.3 equiv.) additional PPh_3 (20 mol%), THF/DMA (7:3, 0.05 M), 25 °C, 10 h.

Comment: Adding co-ligand PPh_3 leads to a significant increase of alkyl transfer product yet a significant decrease of HAT product, no matter whether using $NiCl_2$·DME or $NiBr_2$·DME. These results indicate that the HAT and hydroalkylation processes are competitive and could be modulated by using phosphine co-ligands

Table S9. Evaluation of alkyl halides.

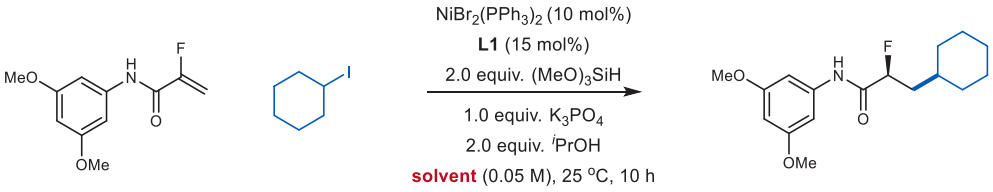


Reaction conditions: α-Fluoro alkenyl amide **1a** (0.15 mmol), alkyl halide (0.1 mmol), $NiBr_2$·$(PPh_3)_2$ (10 mol%), (*S*,*S*)-**L1** (15 mol%), K_3PO_4 (1.0 equiv.), $(MeO)_3SiH$ (2.0 equiv.), ^{i}PrOH (8.0 equiv.), ZnI_2 (0.3 equiv.), THF/DMA (7:3, 0.05 M), 25 °C, 10 h.

Comment: Both tertiary alkyl bromides and iodides work well, whilst bromides provide slightly higher enantiomeric excess than iodides. For secondary alkyl halides, both iodides and bromides work with comparable ees, while higher efficiency is observed in the cases of secondary alkyl iodides. While neither primary alkyl bromides nor alkyl iodines can participate in the asymmetric alkyl transfer reaction.

3.2 Reaction optimizations for asymmetric group transfer with secondary alkyl iodides

Table S10. Solvent effect.



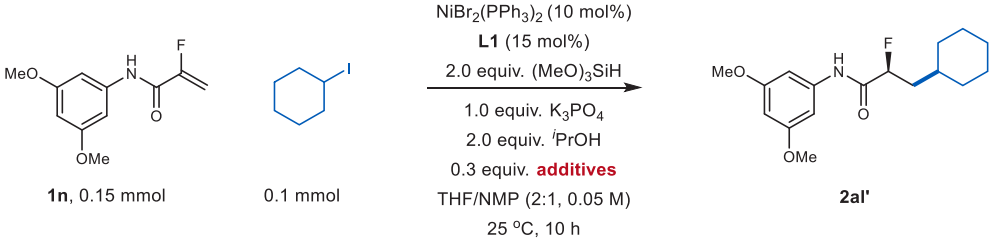
1n, 0.15 mmol 0.1 mmol **2al'**

Entry	solvents	Yield of 2ai (%)	ee of 2al' (%)
1	THF	11	93
2	2-Me-THF	10	89
3	DME	13	89
4	EtOAc	8	92
5	DMA	24	51
6	DMF	33	23
7	NMP	18	46
8	THF/DMA = 4:1	32	91
9	**THF/NMP = 2:1**	**31**	**93**

Reaction conditions: α-Fluoro alkenyl amide **1n** (0.15 mmol), iodocyclohexane (0.1 mmol), $NiBr_2 \cdot (PPh_3)_2$ (10 mol%), (*S*,*S*)-**L1** (15 mol%), K_3PO_4 (1.0 equiv.), $(MeO)_3SiH$ (2.0 equiv.), ^iPrOH (2.0 equiv.), solvent (0.04 M), 25 °C, 10 h.

Comment: The mixed solvent EtOAc/DMA (v/v = 4:1, 0.05M) was selected as the optimal solvent.

Table S11. Additives effect.



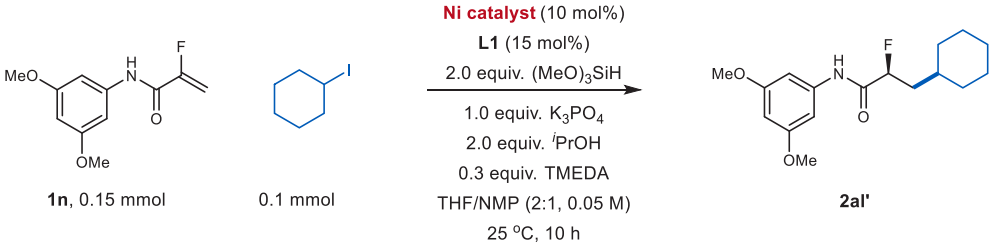
1n, 0.15 mmol 0.1 mmol **2al'**

Entry	additives	Yield of 2ai (%)	ee of 2al' (%)
1	$ZnCl_2$	31	87
2	$ZnBr_2$	25	89
3	ZnI_2	23	92
4	$MgCl_2$	33	89
5	Na_2CO_3	22	92
6	DABCO	35	88
7	**TMEDA**	**42**	**88**

Reaction conditions: α-Fluoro alkenyl amide **1n** (0.15 mmol), iodocyclohexane (0.1 mmol), $NiBr_2·(PPh_3)_2$ (10 mol%), (*S*,*S*)-**L1** (15 mol%), K_3PO_4 (1.0 equiv.), $(MeO)_3SiH$ (2.0 equiv.), ^{i}PrOH (2.0 equiv.), additives (0.3 equiv.), THF/NMP (v/v =2:1, 0.05M), 25 °C, 10 h.

Comment: The addition of TMEDA can improve the yield of the reaction but with diminished the enantioselectivity to 88%.

Table S12. Nickel catalyst effect.



Entry	conditions	Yield of 2ai (%)	ee of 2al' (%)
1	$NiBr_2·(PPh_3)_2$	42	88
2	$NiCl_2·(PPh_3)_2$	44	85
3	$NiCl_2·6H_2O$	36	43
4	$Ni(acac)_2$	0	--
5	$Ni(ClO_4)_2·6H_2O$	24	33
6	$NiCl_2·DPPF$	35	38
7	$NiCl_2·DME$	41	73

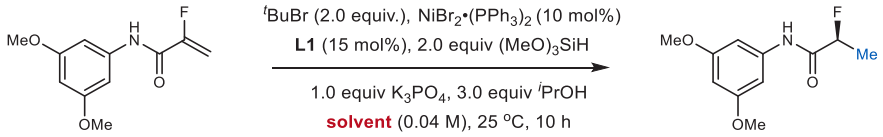
8	NiI_2	28	50
9	$NiBr_2$·DME	57	88
10	**$NiBr_2$·DME[a]**	**52**	**93**
11	$Ni(COD)_2$	38	90

Reaction conditions: α-Fluoro alkenyl amide **1n** (0.15 mmol), iodocyclohexane (0.1 mmol), $NiBr_2·(PPh_3)_2$ (10 mol%), (*S*,*S*)-**L1** (15 mol%), K_3PO_4 (1.0 equiv.), $(MeO)_3SiH$ (2.0 equiv.), ^{i}PrOH (2.0 equiv.), TMEDA (0.3 equiv.), THF/NMP (v/v = 2:1, 0.05M), 25 ^{o}C, 10 h. [a] EtOAc/DMA (v/v = 4:1, 0.05 M) as solvent.

Comment: The $NiBr_2$·DME was selected as the optimal catalyst.

3.3 Reaction optimizations for asymmetric hydrogenation

Table S13. Solvent effect.



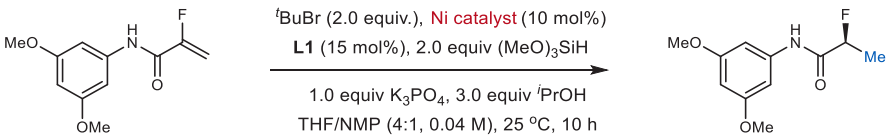
1n, 0.1 mmol — **3o**

Entry	conditions	Yield of 3o (%)	ee of 3o (%)
1	THF	73	91
2	DME	56	88
3	EtOAc	86	73
4	MeCN	19	57
5	NMP	55	81
6	DMA	52	76
7	THF/DMA = 4:1	82	93
8	**THF/NMP = 4:1**	**90**	**94**
9	THF/EtOAc = 4:1	83	90
10	**THF/NMP = 4:1**[a]	95	84

Reaction conditions for asymmetric hydrogenation: α-Fluoro alkenyl amide **1n** (0.1 mmol), *tert*-butyl bromide (0.2 mmol), $NiBr_2 \cdot (PPh_3)_2$ (10 mol%), (*S*,*S*)-**L1** (15 mol%), K_3PO_4 (1.0 equiv.), $(MeO)_3SiH$ (2.0 equiv.), ^{i}PrOH (3.0 equiv.), solvent (0.04 M), 25 ^{o}C, 10 h. [a] w/o ^{t}BuBr.

Comment: The mixed solvent THF/NMP (v/v = 4:1, 0.04M) was selected as the optimal solvent.

Table S14. Catalysts effect.



1n, 0.1 mmol — **3o**

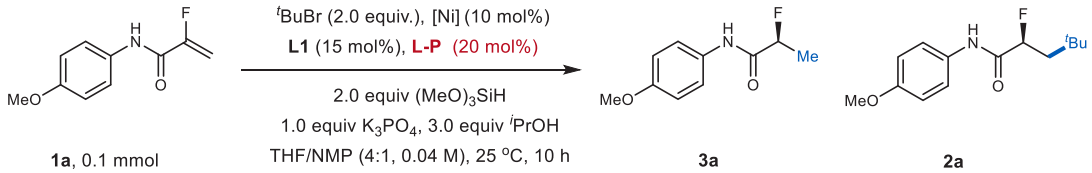
Entry	conditions	Yield of 3o (%)	ee of 3o (%)

1	$NiBr_2·(PPh_3)_2$	54	94
2	$NiCl_2·6H_2O$	86	91
3	$NiBr_2·3H_2O$	86	92
4	$Ni(COD)_2$	75	94
5	**$NiCl_2·DME$**	**90**	**94**
6[a]	**$NiCl_2·DME$**	**89**	**96**
7	$NiBr_2·DME$	90	93
8	$NiCl_2$	33	56
9	$NiBr_2$	79	93
10	NiI_2	87	93

Reaction conditions for asymmetric hydrogenation: α-Fluoro alkenyl amide **1n** (0.1 mmol), *tert*-butyl bromide (0.2 mmol), Ni catalyst (10 mol%), (*S*,*S*)-**L1** (15 mol%), K_3PO_4 (1.0 equiv.), $(MeO)_3SiH$ (2.0 equiv.), ^{i}PrOH (3.0 equiv.), THF/NMP = 4:1 (0.04 M), 25 °C, 10 h. [a]the reaction was carried out at 0 °C.

Comment: $NiCl_2·DME$ turned out to be the optimal catalyst.

Table S15. Phosphine ligand effect.



1a, 0.1 mmol — **3a** — **2a**

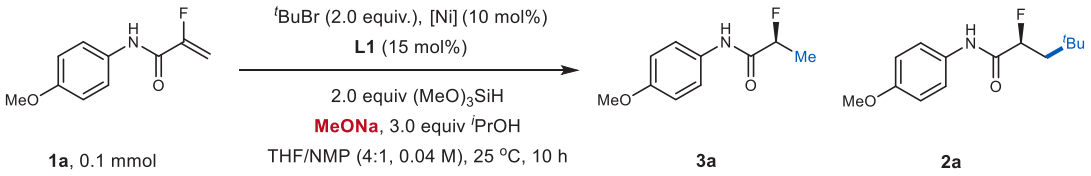
Entry	Ni	Phosphine ligand (x %)	3a (%) Yield (ee)	2a (%) Yield (ee)
1	$NiCl_2·DME$	0%	95 (91)	4 (91)
2	$NiBr_2·DME$	0%	90 (91)	8 (91)
3	$NiCl_2·DME$	PPh_3 (20%)	56 (92)	38 (90)
4	$NiBr_2·DME$	PPh_3 (20%)	40 (91)	40 (90)
5	$NiCl_2·(PPh_3)_2$	0%	52 (91)	42 (90)
6	$NiBr_2·(PPh_3)_2$	0%	48 (91)	44 (90)

7	$NiCl_2$·DME	$(4\text{-F-Ph})_3P$ (20%)	37 (91)	36 (90)
8	$NiCl_2$·DME	$(4\text{-OMe-Ph})_3P$ (20%)	40 (88)	35 (88)
9	$NiCl_2$·DME	Cy_3P (20%)	50 (74)	4 (62)
10	$NiCl_2$·DME	BINAP (10%)	64 (86)	20 (88)

Reaction conditions for asymmetric hydrogenation: α-Fluoro alkenyl amide **1a** (0.1 mmol), *tert*-butyl bromide (0.2 mmol), Ni catalyst (10 mol%), (*S*,*S*)-**L1** (15 mol%), additional P-ligand (20 mol%), K_3PO_4 (1.0 equiv.), $(MeO)_3SiH$ (2.0 equiv.), ^{i}PrOH (3.0 equiv.), THF/NMP = 4:1 (0.04 M), 25 °C, 10 h.

Comment: Adding co-ligand PPh_3 leads to a significant increase of alkyl transfer product yet a significant decrease of HAT product.

Table S16. The MeO^- effect.



Entry	Ni catalyst	MeONa	yield (ee) of 3a	yield of 2a	1a
1	$NiCl_2$·DME	20%	60% (83% ee)	trace	40%
2	$NiCl_2$·DME	50%	74% (64% ee)	10%	16%
3	$NiCl_2$·DME	100%	6%	trace	90%
4	$NiCl_2$·$6H_2O$	20%	61% (79% ee)	trace	33%
5	$NiCl_2$·$6H_2O$	w/ K_3PO_4	89% (87% ee)	7%	0%
6	$[Ni(OMe)_2]_n$	w/ K_3PO_4	0%	0%	100%

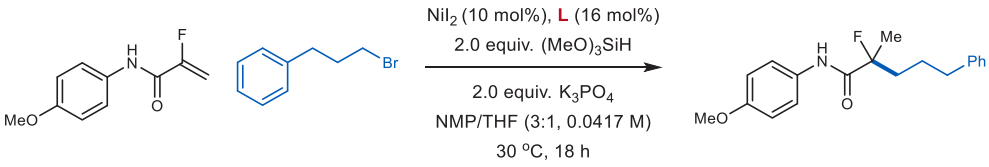
Reaction conditions for asymmetric hydrogenation: α-Fluoro alkenyl amide **1a** (0.1 mmol), *tert*-butyl bromide (0.2 mmol), [Ni] (10 mol%), (*S*,*S*)-**L1** (15 mol%), $(MeO)_3SiH$ (2.0 equiv.), ^{i}PrOH (3.0 equiv.), MeONa, THF/NMP = 4:1 (0.04 M), 25 °C, 10 h.

Comment: The addition of catalytic NaOMe significantly decreases the yield and ee of product **3a**, and adding 1 equivalent of NaOMe shuts down the HAT reaction (entries 1-3). The use of $[Ni(OMe)_2]n$, prepared according to the reported reference[13] , as the

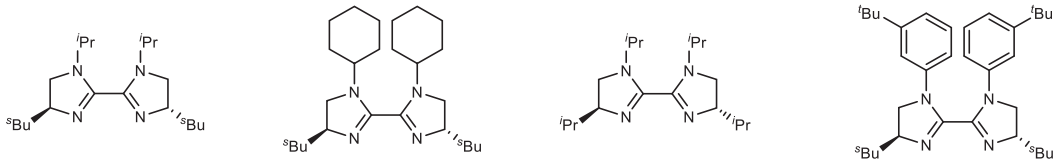
pre-catalyst leads to no reaction at all. Therefore, the metal-alkoxide species could be less likely to be involved in this reaction.

3.4 Reaction optimizations for HAT/alkyl coupling

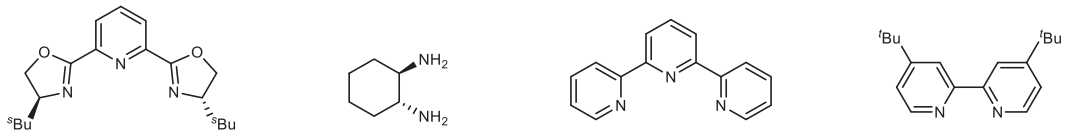
Table S17. Chiral ligand effect.



1a, 0.1 mmol 0.12 mmol **4a**



L12, 80%, 40% ee **L25**, 73%, 34% ee **L26**, 64%, 31% ee **L27**, 5%, 55% ee

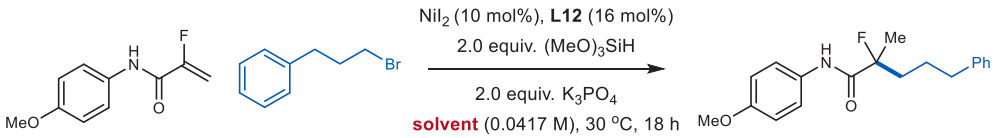


L1, ND **L28**, ND **L29**, ND **L30**, ND

Reaction conditions: α-Fluoro alkenyl amide (0.1 mmol), primary alkyl bromide (0.12 mmol), NiI_2 (10 mol%), ligand (16 mol%), K_3PO_4 (2.0 equiv.), $(MeO)_3SiH$ (2.0 equiv.), NMP/THF (3:1, 0.0417 M), 30 °C, 18 h.

Comment: The more electron-rich ligand bisimidazole (*S*,*S*)-**L12** was selected as the optimal ligand.

Table S18. Solvent effect.



1a, 0.1 mmol 0.12 mmol **4a**

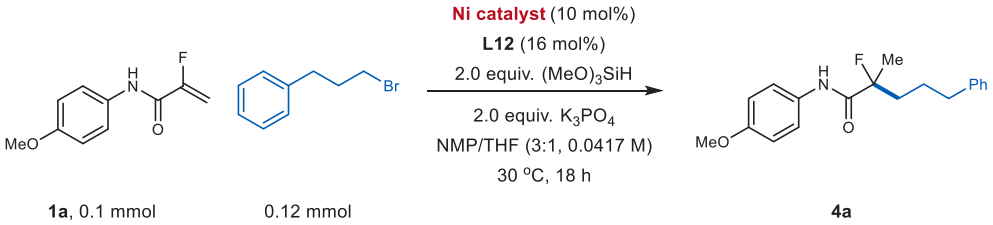
Entry	conditions	yield of 4a (%)
1	DMA	64
2	DMF	35
3	NMP	68
4	DMI	0
5	DMPU	0

6	THF	trace
7	DME	trace
8	**NMP/THF 3:1**	**80**

Reaction conditions: α-Fluoro alkenyl amide (0.1 mmol), primary alkyl bromide (0.12 mmol), NiI_2 (10 mol%), **L12** (16 mol%), K_3PO_4 (2.0 equiv.), $(MeO)_3SiH$ (2.0 equiv.), solvent [0.0417 M], 30 °C, 18 h.

Comment: The mixed solvent NMP/THF (v/v = 3:1, 0.0417M) was selected as the optimal solvent.

Table S19. Catalyst effect.



1a, 0.1 mmol 0.12 mmol **4a**

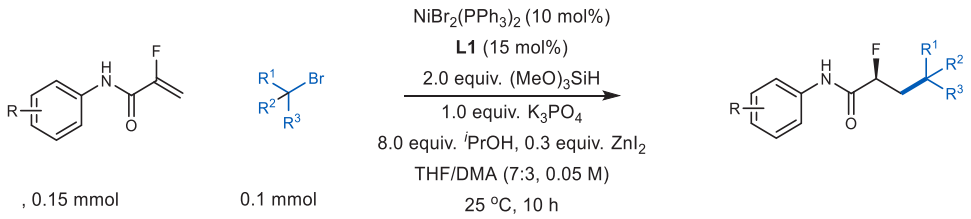
Entry	conditions	Yield of 4a (%)
1	$NiBr_2·(PPh_3)_2$	0
2	$NiCl_2$	55
3	$NiBr_2$	36
4	NiF_2	0
5	$NiBr_2·DME$	60
6	$NiCl_2·DPPF$	0
7	$NiCl_2·DME$	57
8	**NiI_2**	**80**
9	$Ni(COD)_2$	49

Reaction conditions: α-Fluoro alkenyl amide (0.1 mmol), primary alkyl bromide (0.12 mmol), NiI_2 (10 mol%), ligand (16 mol%), K_3PO_4 (2.0 equiv.), $(MeO)_3SiH$ (2.0 equiv.), NMP/THF (v/v = 3:1, 0.0417M) [0.0417 M], 30 °C, 18 h.

Comment: NiI_2 was selected as the optimal catalyst.

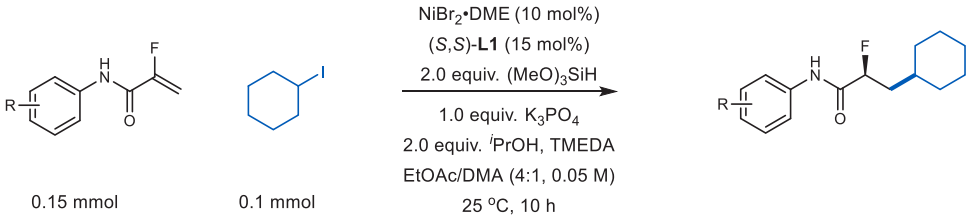
4. General Procedure for Hydroalkylation and Hydrogenation

4.1 General Procedure A for asymmetric group transfer with tertiary alkyl bromides



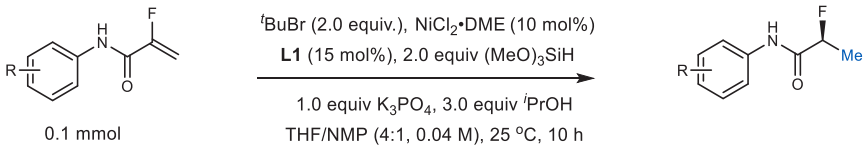
General Procedure A: In air, an 8 mL screw-cap reaction vial equipped with a magnetic stirrer was charged with (*S*,*S*)-**L1** (0.015 mmol, 15 mol%), [Note: 2,2′:6′,2″-terpyridine or (±)-2,6-bis(4-isopropyl-4,5-dihydrooxazol-2-yl)pyridine ((±)-**L4**) was used for the corresponding racemic reactions], $NiBr_2 \cdot (PPh_3)_2$ (0.01 mmol, 10 mol%), fluoroalkenes (0.15 mmol, 1.5 equiv.), K_3PO_4 (0.1 mmol, 1.0 equiv.) and ZnI_2 (0.03 mmol, 0.3 equiv.) (if the alkyl halides were solid, they were also added at this time). The test tube was evacuated and backfilled with nitrogen three times. Then, THF (1.4 mL) and DMA (0.6 mL) was added, followed by the isopropyl alcohol (0.8 mmol, 8.0 equiv.) and tertiary alkyl bromide (0.1 mmol, 1.0 equiv.). Then, $(MeO)_3SiH$ (0.2 mmol, 2.0 equiv.) was added dropwise via a syringe, and the solution was stirred for 10 h at 25 °C. The reaction mixture was diluted with saturated NaCl solution followed by extraction with EtOAc, dried with anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to obtain the target product.

4.2 General Procedure B for asymmetric group transfer with secondary alkyl iodides



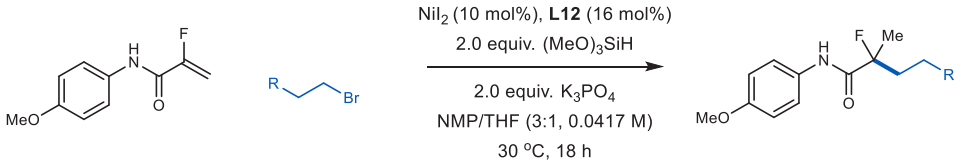
General Procedure B: In air, an 8 mL screw-cap reaction vial equipped with a magnetic stirrer was charged with (*S*, *S*)-**L1** (0.015 mmol, 15 mol%), [Note: 2,2′:6′,2″-terpyridine or (±)-2,6-bis(4-isopropyl-4,5-dihydrooxazol-2-yl)pyridine ((±)-**L4**) was used for the corresponding racemic reactions], $NiBr_2$·DME (0.01 mmol, 10 mol%), fluoroalkenes (0.15 mmol, 1.5 equiv.) and K_3PO_4 (0.1 mmol, 1.0 equiv.) (if the alkyl halides were solid, they were also added at this time). The test tube was evacuated and backfilled with nitrogen three times. Then, EtOAc (1.6 mL) and DMA (0.4 mL) was added, followed by the isopropyl alcohol (0.2 mmol, 2.0 equiv.) TMEDA (0.03 mmol, 0.3 equiv.) and alkyl iodide (0.1 mmol, 1.0 equiv.). Then, $(MeO)_3SiH$ (0.2 mmol, 2.0 equiv.) was added dropwise via a syringe, and the solution was stirred for 10 h at 25 °C. The reaction mixture was diluted with saturated NaCl solution followed by extraction with EtOAc, dried with anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to obtain the target product.

4.3 General Procedure C for asymmetric hydrogenation



General Procedure C: In air, an 8 mL screw-cap reaction vial equipped with a magnetic stirrer was charged with (*S*, *S*)-**L1** (0.015 mmol, 15 mol%), [Note: 2,2′:6′,2″-terpyridine was used for the corresponding racemic reactions], $NiCl_2$·DME (0.01 mmol, 10 mol%), fluoroalkenes (0.1 mmol, 1.0 equiv.) and K_3PO_4 (0.1 mmol, 1.0 equiv.). The test tube was evacuated and backfilled with nitrogen three times. Then, THF (2.0 mL) and NMP (0.5 mL) was added, followed by the isopropyl alcohol (0.3 mmol, 3.0 equiv.) *tert*-butyl bromide (0.2 mmol, 2.0 equiv.). Then, $(MeO)_3SiH$ (0.2 mmol, 2.0 equiv.) was added dropwise via a syringe, and the solution was stirred for 10 h at 25 °C. The reaction mixture was diluted with saturated NaCl solution followed by extraction with EtOAc, dried with anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to obtain the target product.

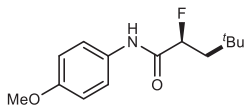
4.4 General Procedure D for HAT/alkyl coupling



1a, 0.1 mmol 0.12 mmol **4a**

General Procedure D: In air, an 8 mL screw-cap reaction vial equipped with a magnetic stirrer was charged with (*S*, *S*)-**L12** (0.016 mmol, 16 mol%), NiI_2 (0.01 mmol, 10 mol%), fluoroalkenes (0.1 mmol, 1.0 equiv.) and K_3PO_4 (0.2 mmol, 2.0 equiv.) (if the alkyl halides were solid, they were also added at this time). The test tube was evacuated and backfilled with nitrogen three times. Then, NMP (1.8 mL) and THF (0.6 mL) was added, followed by the primary alkyl bromides (0.12 mmol, 1.2 equiv.). Then, $(MeO)_3SiH$ (0.2 mmol, 2.0 equiv.) was added dropwise via a syringe, and the solution was stirred for 18 h at 30 °C. The reaction mixture was diluted with saturated NaCl solution followed by extraction with EtOAc, dried with anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to obtain the target product.

5. Characterization of Products



(*S*)-2-fluoro-*N*-(4-methoxyphenyl)-4,4-dimethylpentanamide (2a)

According to **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a colourless oil (19.7 mg, 78%, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 5.4 Hz, 1H), 7.50 – 7.41 (m, 2H), 6.92 – 6.81 (m, 2H), 5.17 – 4.99 (m, 1H), 3.79 (s, 3H), 2.14 – 1.92 (m, 1H), 1.83 – 1.68 (m, 1H), 1.03 (s, 9H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -182.07 – -182.40 (m).

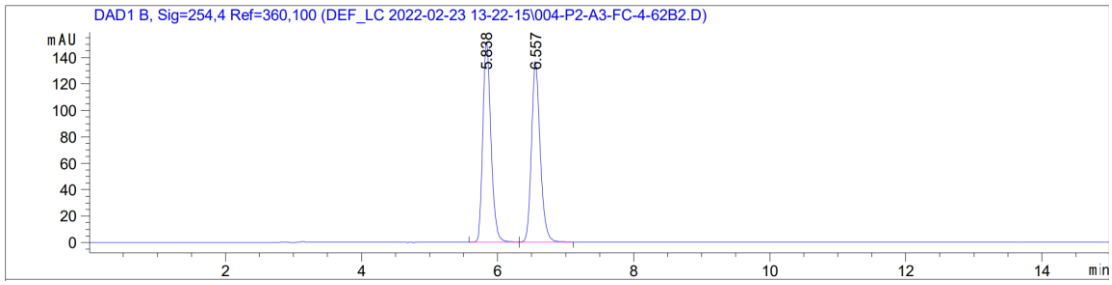
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.62 (d, *J* = 18.2 Hz), 156.76, 129.94, 121.69, 114.23, 90.97 (d, *J* = 187.2 Hz), 55.49, 45.84 (d, *J* = 18.6 Hz), 30.20, 29.69 (d, *J* = 1.0 Hz).

HRMS (ESI): $C_{14}H_{20}FNNaO_2^+$ ($M+Na^+$): 276.1370, found: 276.1370.

$[\alpha]_D^{25}$ = -23.48 (c = 1.08, $CHCl_3$).

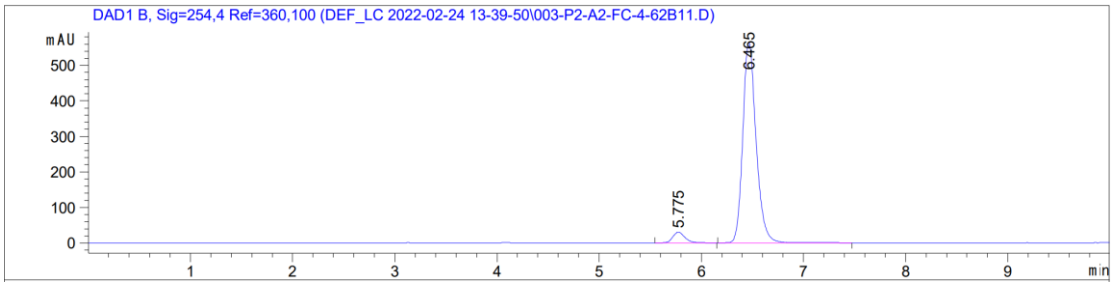
HPLC: The ee was determined to be 91% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 6.5 min, t_R (minor) = 5.8 min.

2a racemic

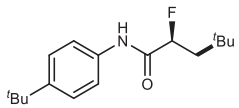


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.838	BB	0.1255	1241.97754	151.76488	49.9706
2	6.557	BB	0.1401	1243.43872	136.77461	50.0294

2a enantioenriched, 91% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.775	BB	0.1244	246.13800	30.40918	4.6004
2	6.465	BB	0.1372	5104.24463	566.04504	95.3996



(*S*)-*N*-(4-(*tert*-butyl)phenyl)-2-fluoro-4,4-dimethylpentanamide (2b)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 15:1) as a colourless oil (22.4 mg, 80%, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 5.8 Hz, 1H), 7.52 – 7.42 (m, 2H), 7.40 – 7.31 (m, 2H), 5.18 – 4.99 (m, 1H), 2.15 – 1.91 (m, 1H), 1.83 – 1.68 (m, 1H), 1.31 (s, 9H), 1.04 (d, *J* = 0.6 Hz, 9H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.91 – -182.24 (m).

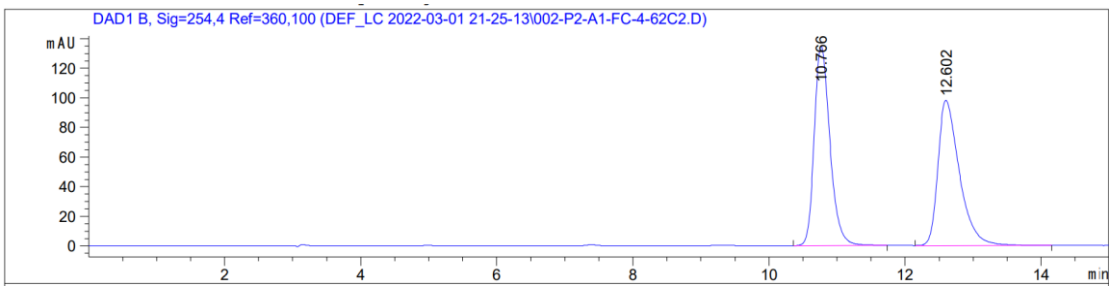
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.72 (d, *J* = 18.1 Hz), 147.90, 134.21, 125.95, 119.71, 90.98 (d, *J* = 187.4 Hz), 45.82 (d, *J* = 18.6 Hz), 34.45, 31.36, 30.20, 29.71.

HRMS (ESI): $C_{17}H_{26}FNNaO^+$ ($M+Na^+$): 302.1891, found: 302.1890.

$[\alpha]_D^{25}$ = -19.62 (c = 1.57, $CHCl_3$).

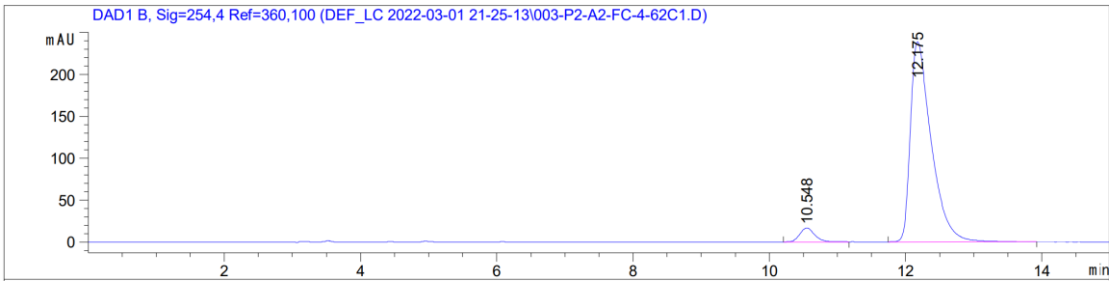
HPLC: The ee was determined to be 91% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 12.2 min, t_R (minor) = 10.5 min.

2b racemic

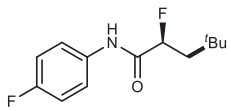


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.766	BB	0.2438	2149.70972	134.96364	50.0320
2	12.602	BB	0.3296	2146.96094	98.01121	49.9680

2b enantioenriched, 91% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.548	BB	0.2360	252.51219	16.55235	4.7471
2	12.175	BB	0.3155	5066.80078	238.82217	95.2529



(*S*)-2-fluoro-*N*-(4-fluorophenyl)-4,4-dimethylpentanamide (2c)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 15:1) as a colourless oil (15.9 mg, 66%, 89% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 2.7 Hz, 1H), 7.56 – 7.44 (m, 2H), 7.09 – 6.96 (m, 2H), 5.18 – 5.00 (m, 1H), 2.12 – 1.91 (m, 1H), 1.83 – 1.69 (m, 1H), 1.03 (s, 9H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -117.16 – -117.23 (m), -182.16 – -182.49 (m).

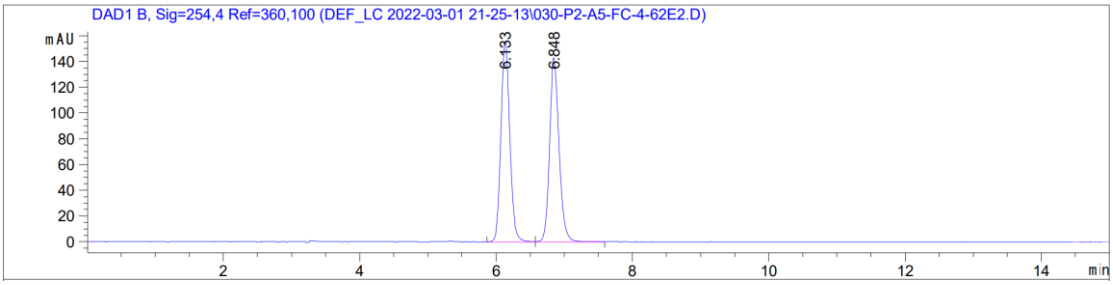
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.82 (d, *J* = 18.3 Hz), 159.68 (d, *J* = 244.2 Hz), 132.84 (d, *J* = 2.8 Hz), 121.74 (d, *J* = 8.0 Hz), 115.81 (d, *J* = 22.6 Hz), 90.93 (d, *J* = 187.1 Hz), 45.81 (d, *J* = 18.7 Hz), 30.20, 29.67 (d, *J* = 1.1 Hz).

HRMS (ESI): $C_{13}H_{17}F_2NNaO^+$ ($M+Na^+$): 264.1170, found: 264.1172.

$[\alpha]_D^{25}$ = -22.80 (c = 1.61, $CHCl_3$).

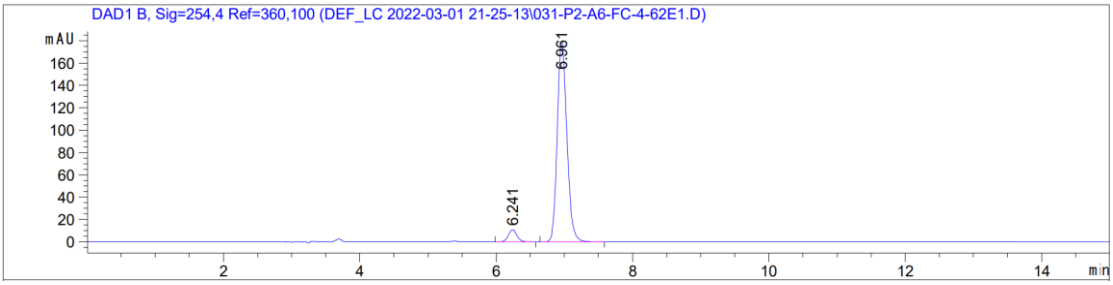
HPLC: The ee was determined to be 89% on a CHIRALPAK IB column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 80:20 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 7.0 min, t_R (minor) = 6.2 min.

2c racemic

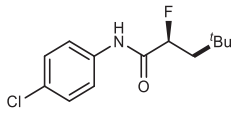


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.133	BV	0.1382	1390.62817	155.68161	49.9328
2	6.848	VB	0.1497	1394.37158	143.02487	50.0672

2c enantioenriched, 89% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.241	BB	0.1419	99.79527	10.98998	5.4203
2	6.961	BB	0.1490	1741.35754	179.79904	94.5797



(*S*)-*N*-(4-chlorophenyl)-2-fluoro-4,4-dimethylpentanamide (2d)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 15:1) as a colourless oil (17.0 mg, 66%, 88% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 5.1 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.34 – 7.26 (m, 2H), 5.17 – 4.99 (m, 1H), 2.11 – 1.91 (m, 1H), 1.85 – 1.68 (m, 1H), 1.03 (s, 9H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -182.08 – -182.41 (m).

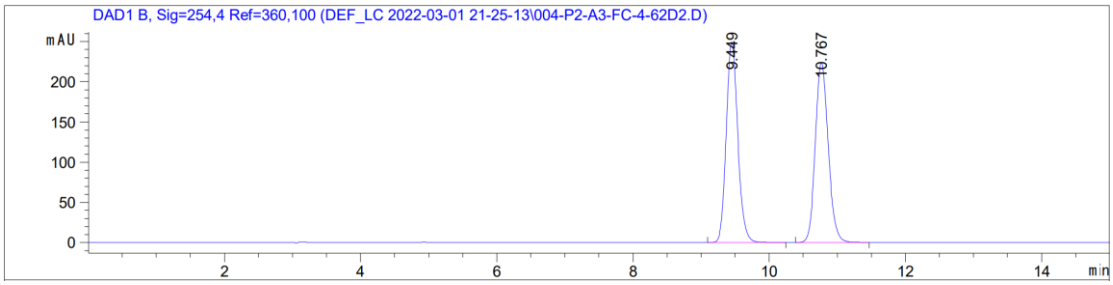
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.89 (d, *J* = 18.3 Hz), 135.41, 129.91, 129.15, 121.16, 90.92 (d, *J* = 187.4 Hz), 45.79 (d, *J* = 18.6 Hz), 30.20, 29.67 (d, *J* = 1.0 Hz).

HRMS (ESI): $C_{13}H_{18}ClFNO^+$ ($M+H^+$): 258.1055, found: 258.1059.

$[\alpha]_D^{25}$ = -27.21 (c = 1.66, $CHCl_3$).

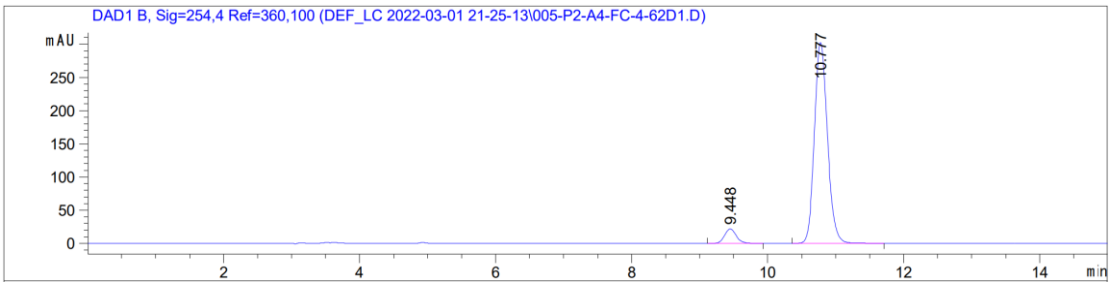
HPLC: The ee was determined to be 88% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 10.8 min, t_R (minor) = 9.4 min.

2d racemic

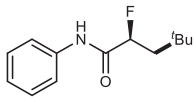


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.449	BB	0.1813	2935.15918	249.48006	50.0127
2	10.767	BB	0.2008	2933.66797	223.95911	49.9873

2d enantioenriched, 88% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.448	BB	0.1824	257.82181	21.73750	6.0516
2	10.777	BB	0.2045	4002.60205	302.21432	93.9484



(*S*)-2-fluoro-4,4-dimethyl-N-phenylpentanamide (2e)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 15:1) as a colourless oil (16.7 mg, 75%, 88% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 2.0 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.41 – 7.30 (m, 2H), 7.18 – 7.11 (m, 1H), 5.18 – 5.00 (m, 1H), 2.12 – 1.94 (m, 1H), 1.84 – 1.70 (m, 1H), 1.04 (d, *J* = 0.7 Hz, 9H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.89 – -182.23 (m).

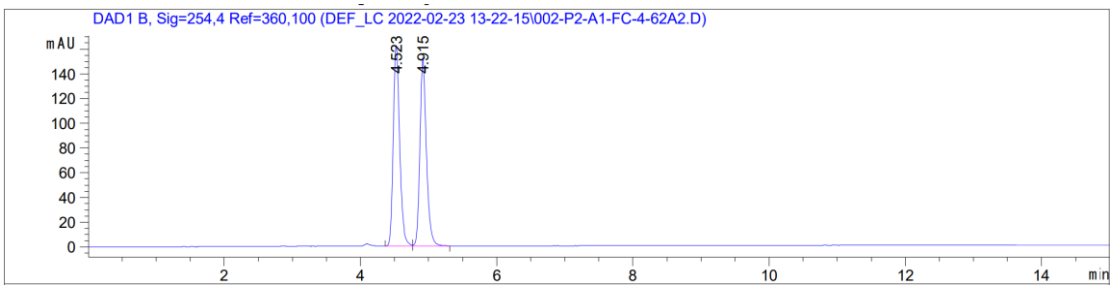
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.82 (d, *J* = 18.1 Hz), 136.83, 129.14, 124.89, 119.89, 90.97 (d, *J* = 187.3 Hz), 45.83 (d, *J* = 18.6 Hz), 30.20, 29.68.

HRMS (ESI): $C_{13}H_{19}FNO^+$ ($M+H^+$): 224.1445, found: 224.1443.

$[\alpha]_D^{25}$ = -18.59 (c = 0.820, $CHCl_3$).

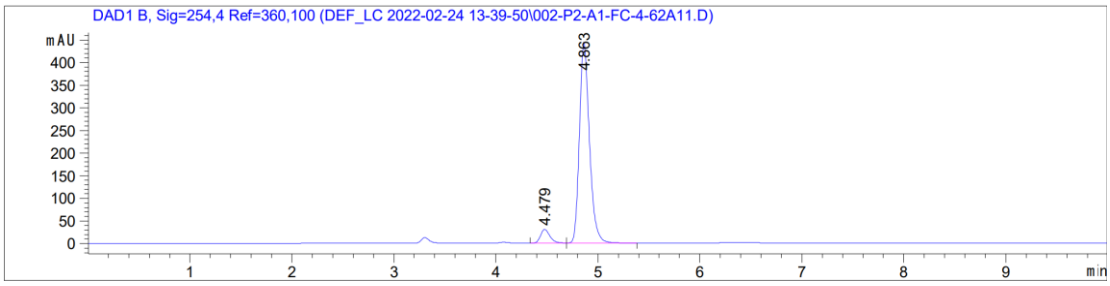
HPLC: The ee was determined to be 88% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 4.9 min, t_R (minor) = 4.5 min.

2e racemic

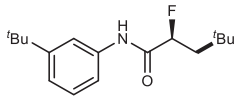


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.522	BB	0.0982	58.64601	9.21753	49.6037
2	4.914	BB	0.1031	59.58319	8.78769	50.3963

2e enantioenriched, 88% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.479	BV	0.0979	191.92580	30.30489	5.9878
2	4.863	VB	0.1053	3013.35278	443.15115	94.0122



(*S*)-*N*-(3-(*tert*-butyl)phenyl)-2-fluoro-4,4-dimethylpentanamide (2f)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 15:1) as a colourless oil (20.4 mg, 73%, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 5.8 Hz, 1H), 7.53 (t, *J* = 1.9 Hz, 1H), 7.41 – 7.34 (m, 1H), 7.23 (d, *J* = 9.0 Hz, 1H), 7.17 – 7.11 (m, 1H), 5.14 – 4.96 (m, 1H), 2.12 – 1.90 (m, 1H), 1.82 – 1.66 (m, 1H), 1.28 (s, 9H), 1.00 (s, 9H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.67 – -182.00 (m).

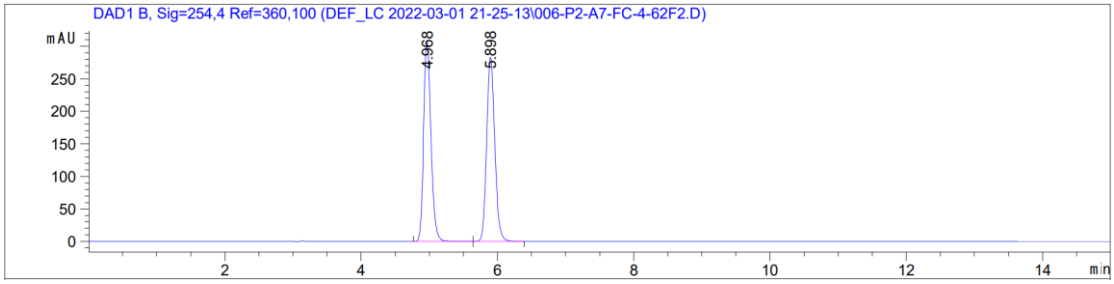
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.81 (d, J = 18.1 Hz), 152.41, 136.60, 128.78, 121.99, 117.16, 117.11, 90.96 (d, J = 187.4 Hz), 45.88 (d, J = 18.8 Hz), 34.81, 31.29, 30.20, 29.68.

HRMS (ESI): $C_{17}H_{26}FNNaO^+$ ($M+Na^+$): 302.1891, found: 302.1890.

$[\alpha]_D^{25}$ = -28.59 (c = 1.60, $CHCl_3$).

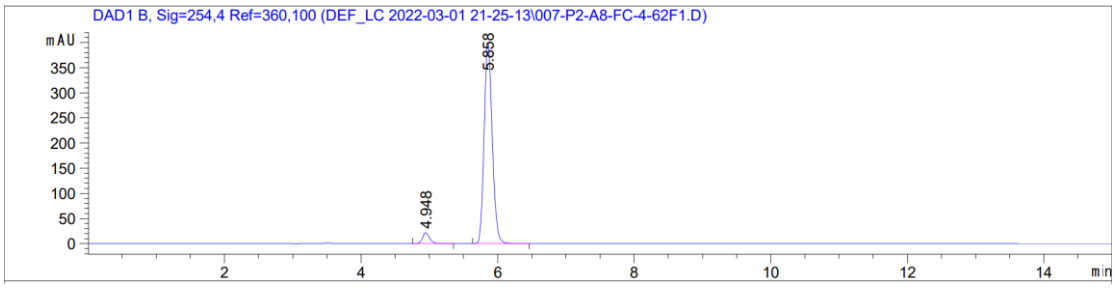
HPLC: The ee was determined to be 91% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 5.9 min, t_R (minor) = 4.9 min.

2f racemic

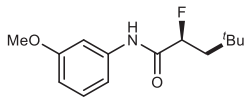


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.968	BB	0.1152	2305.55835	308.58679	50.0119
2	5.898	BB	0.1252	2304.46045	282.37784	49.9881

2f enantioenriched, 91% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.948	BB	0.1162	162.18726	21.45110	4.7754
2	5.858	BB	0.1243	3234.14404	400.14456	95.2246



(*S*)-2-fluoro-*N*-(3-methoxyphenyl)-4,4-dimethylpentanamide (2g)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a colourless oil (19.0 mg, 75%, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 5.4 Hz, 1H), 7.35 (t, *J* = 2.2 Hz, 1H), 7.23 (t, *J* = 8.2 Hz, 1H), 7.02 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.70 (dd, *J* = 8.2, 2.0 Hz, 1H), 5.17 – 4.99 (m, 1H), 3.80 (s, 3H), 2.13 – 1.92 (m, 1H), 1.85 – 1.69 (m, 1H), 1.03 (s, 9H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.85 – -182.19 (m).

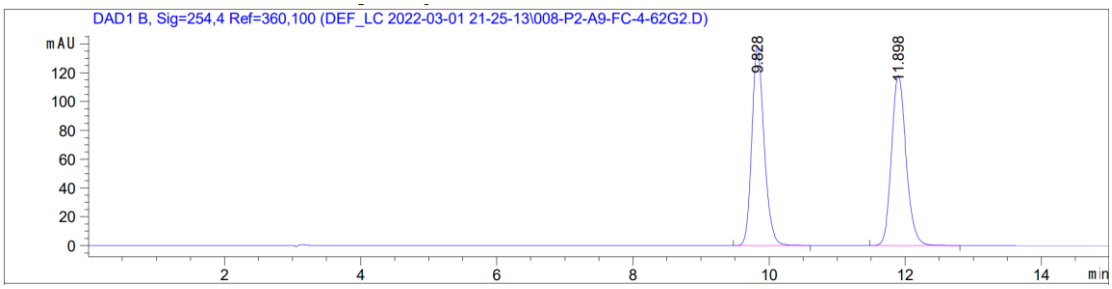
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.87 (d, *J* = 18.1 Hz), 160.21, 138.05, 129.80, 111.99, 110.86, 105.48, 90.92 (d, *J* = 187.5 Hz), 55.33, 45.83 (d, *J* = 18.8 Hz), 30.20, 29.67 (d, *J* = 1.0 Hz).

HRMS (ESI): $C_{14}H_{21}FNO_2^+$ ($M+H^+$): 254.1551, found: 254.1557.

$[\alpha]_D^{25}$ = -19.61 (c = 1.21, $CHCl_3$).

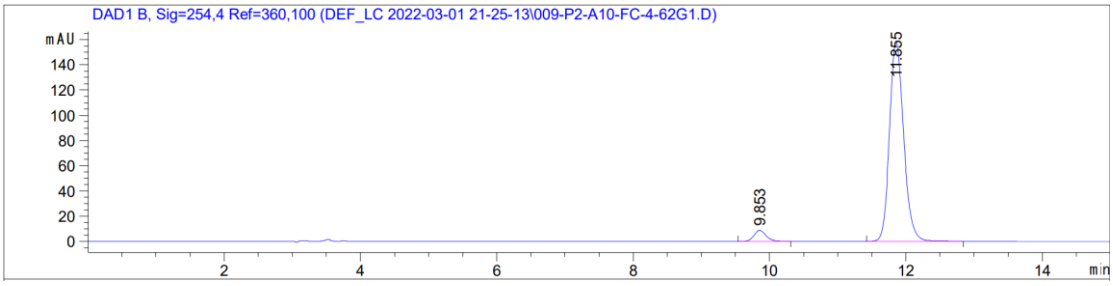
HPLC: The ee was determined to be 91% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 11.9 min, t_R (minor) = 9.9 min.

2g racemic

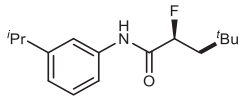


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.828	BB	0.1933	1753.18640	138.89223	49.9723
2	11.898	BB	0.2270	1755.13086	118.37514	50.0277

2g enantioenriched, 91% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.853	BB	0.1910	109.21813	8.78942	4.5742
2	11.855	BB	0.2217	2278.48560	158.51169	95.4258



(*S*)-2-fluoro-*N*-(3-isopropylphenyl)-4,4-dimethylpentanamide (2h)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 15:1) as a colourless oil (17.8 mg, 67%, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 5.5 Hz, 1H), 7.44 (t, *J* = 1.8 Hz, 1H), 7.41 – 7.35 (m, 1H), 7.30 – 7.21 (m, 1H), 7.02 (d, *J* = 7.7 Hz, 1H), 5.17 – 4.99 (m, 1H), 2.96 – 2.84 (m, 1H), 2.12 – 1.94 (m, 1H), 1.83 – 1.69 (m, 1H), 1.25 (d, *J* = 6.9 Hz, 6H), 1.03 (d, *J* = 0.7 Hz, 9H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.73 – -182.06 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.79 (d, *J* = 18.1 Hz), 150.14, 136.82, 129.03, 123.09, 118.03, 117.41, 90.95 (d, *J* = 187.4 Hz), 45.88 (d, *J* = 18.6 Hz), 34.15, 30.20, 29.68, 23.92.

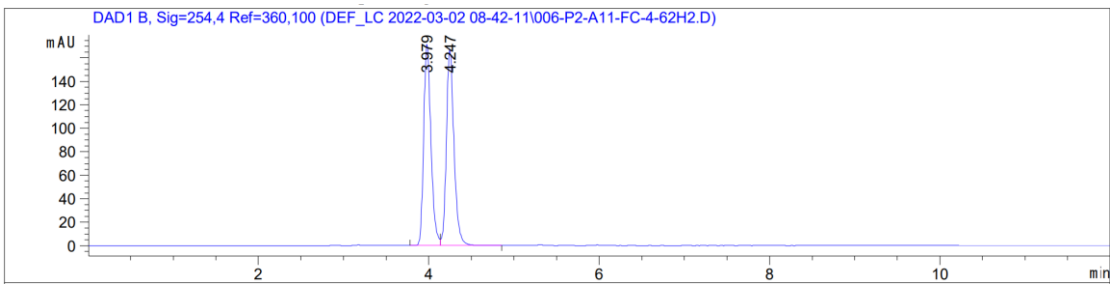
HRMS (ESI): $C_{16}H_{24}FNNaO^+$ ($M+Na^+$): 288.1734, found: 288.1733.

$[\alpha]_D^{25}$ = -38.81 (c = 1.52, $CHCl_3$).

HPLC: The ee was determined to be 91% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major)

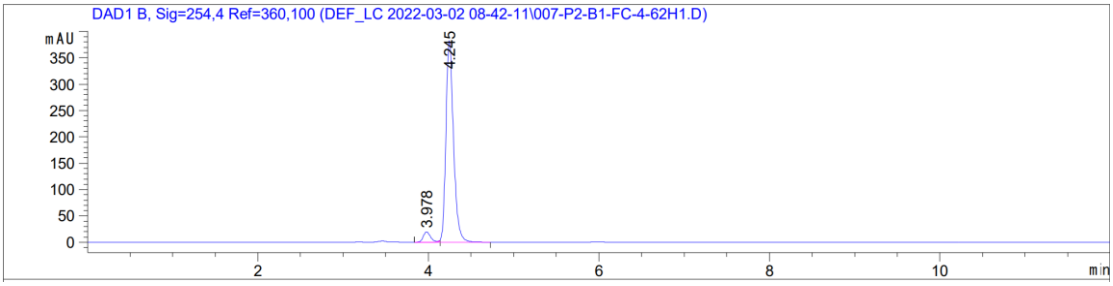
= 4.2 min, t_R (minor) = 4.0 min.

2h racemic

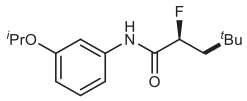


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.979	BV	0.0910	1012.67261	171.13211	49.4210
2	4.247	VB	0.0943	1036.40015	167.23772	50.5790

2h enantioenriched, 91% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.978	BV E	0.0909	115.86999	19.62226	4.6736
2	4.245	VB R	0.0920	2363.38477	383.18161	95.3264



(*S*)-2-fluoro-*N*-(3-isopropoxyphenyl)-4,4-dimethylpentanamide (2i)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a colourless oil (16.1 mg, 57%, 90% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 6.2 Hz, 1H), 7.33 (t, *J* = 2.2 Hz, 1H), 7.21 (t, *J* = 8.1 Hz, 1H), 7.02 – 6.95 (m, 1H), 6.71 – 6.60 (m, 1H), 5.17 – 4.99 (m, 1H), 4.62

– 4.51 (m, 1H), 2.13 – 1.92 (m, 1H), 1.86 – 1.68 (m, 1H), 1.33 (d, J = 6.1 Hz, 6H), 1.03 (d, J = 0.6 Hz, 9H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.85 – -182.19 (m).

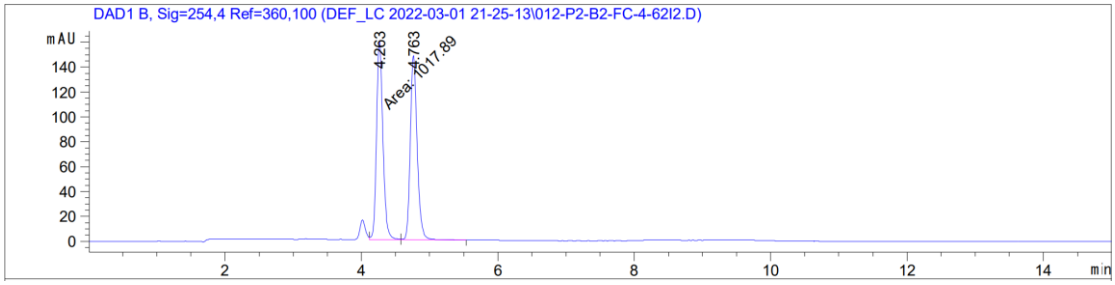
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.80 (d, J = 18.0 Hz), 158.54, 137.99, 129.81, 112.72, 111.79, 107.34, 90.93 (d, J = 187.5 Hz), 70.03, 45.82 (d, J = 18.6 Hz), 30.20, 29.68, 22.03 (d, J = 3.0 Hz).

HRMS (ESI): $C_{16}H_{24}FNNaO_2^+$ ($M+Na^+$): 304.1683, found: 304.1683.

$[\alpha]_D^{25}$ = -21.58 (c = 1.62, $CHCl_3$).

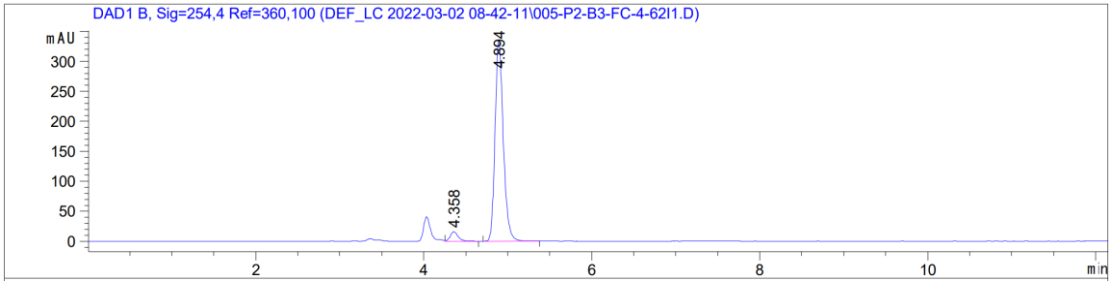
HPLC: The ee was determined to be 91% on a CHIRALPAK IA column at 254 nm, 25 ^oC, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 4.9 min, t_R (minor) = 4.4 min.

2i racemic

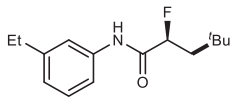


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.263	FM	0.1060	1017.88867	160.03940	50.0692
2	4.763	VB	0.1041	1015.07697	147.86958	49.9308

2i enantioenriched, 91% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.358	VB	0.0992	102.29800	15.87484	4.2818
2	4.894	BB	0.1057	2286.85718	334.61462	95.7182



(*S*)-*N*-(3-ethylphenyl)-2-fluoro-4,4-dimethylpentanamide (2j)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 15:1) as a colourless oil (17.6 mg, 70%, 90% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 5.1 Hz, 1H), 7.47 – 7.40 (m, 1H), 7.40 – 7.33 (m, 1H), 7.26 (t, *J* = 7.8 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 5.17 – 5.00 (m, 1H), 2.65 (q, *J* = 7.6 Hz, 2H), 2.15 – 1.89 (m, 1H), 1.88 – 1.67 (m, 1H), 1.24 (t, *J* = 7.6 Hz, 3H), 1.04 (d, *J* = 0.7 Hz, 9H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.77 – -182.11 (m).

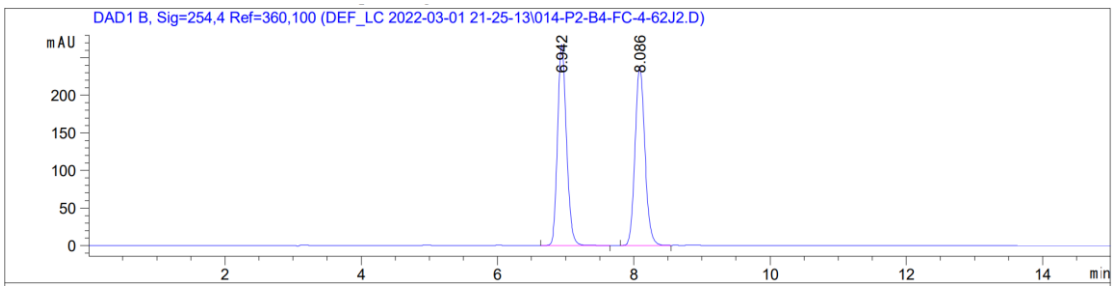
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.80 (d, *J* = 18.1 Hz), 145.47, 136.83, 129.03, 124.51, 119.41, 117.25, 90.95 (d, *J* = 187.4 Hz), 45.87 (d, *J* = 18.7 Hz), 30.20, 29.69 (d, *J* = 1.0 Hz), 28.87, 15.51.

HRMS (ESI): $C_{15}H_{23}FNO^+$ ($M+H^+$): 252.1758, found: 252.1760.

$[\alpha]_D^{25}$ = -29.83 (c = 1.81, $CHCl_3$).

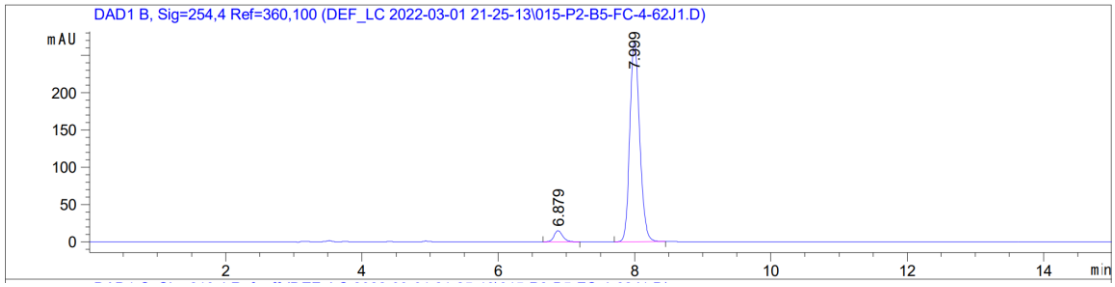
HPLC: The ee was determined to be 90% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 6.9 min, t_R (minor) = 8.0 min.

2j racemic

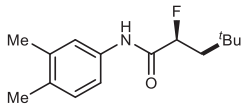


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.942	BB	0.1388	2399.29321	267.20526	50.1861
2	8.086	BB	0.1529	2381.50269	237.69310	49.8139

2j enantioenriched, 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.879	BB	0.1357	132.13387	14.86162	4.7012
2	7.999	BB	0.1542	2678.48022	268.96948	95.2988



(*S*)-*N*-(3,4-dimethylphenyl)-2-fluoro-4,4-dimethylpentanamide (2k)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 15:1) as a colourless oil (21.4 mg, 85%, 92% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 5.1 Hz, 1H), 7.35 (d, *J* = 1.8 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.09 (d, *J* = 8.1 Hz, 1H), 5.16 – 4.99 (m, 1H), 2.25 (s, 3H), 2.23 (s, 3H), 2.13 – 1.93 (m, 1H), 1.84 – 1.69 (m, 1H), 1.04 (s, 9H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.85 – -182.18 (m).

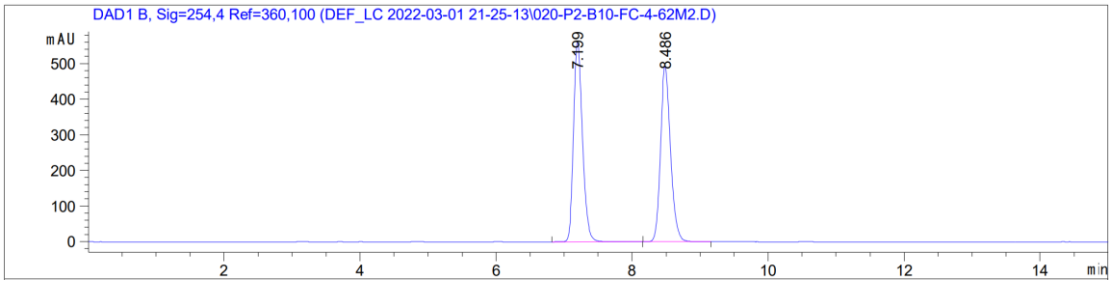
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.67 (d, *J* = 18.0 Hz), 137.40, 134.54, 133.27, 130.07, 121.27, 117.43, 90.96 (d, *J* = 187.3 Hz), 45.85 (d, *J* = 18.7 Hz), 30.20, 29.70 (d, *J* = 1.0 Hz), 19.92, 19.26.

HRMS (ESI): $C_{15}H_{22}FNNaO^+$ ($M+H^+$): 274.1578, found: 274.1576.

$[\alpha]_D^{25}$ = -22.95 (c = 1.55, $CHCl_3$).

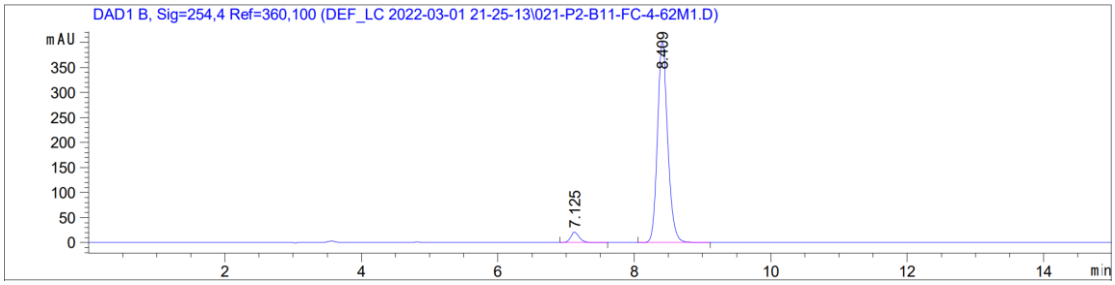
HPLC: The ee was determined to be 92% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 8.4 min, t_R (minor) = 7.1 min.

2k racemic

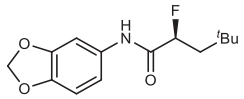


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.199	BB	0.1393	5081.06738	563.01373	50.0507
2	8.486	BB	0.1580	5070.76611	492.87799	49.9493

2k enantioenriched, 92% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.125	BB	0.1374	186.92131	20.69671	4.2498
2	8.409	BB	0.1602	4211.43018	401.96490	95.7502



(*S*)-*N*-(benzo[*d*][1,3]dioxol-5-yl)-2-fluoro-4,4-dimethylpentanamide (2l)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 5:1) as a colourless oil (15.8 mg, 59%, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 5.6 Hz, 1H), 7.27 (d, *J* = 2.2 Hz, 1H), 6.87 – 6.81 (m, 1H), 6.75 (d, *J* = 8.3 Hz, 1H), 5.95 (s, 2H), 5.15 – 4.98 (m, 1H), 2.10 – 1.90 (m, 1H), 1.83 – 1.68 (m, 1H), 1.02 (s, 9H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -182.22 – -182.54 (m).

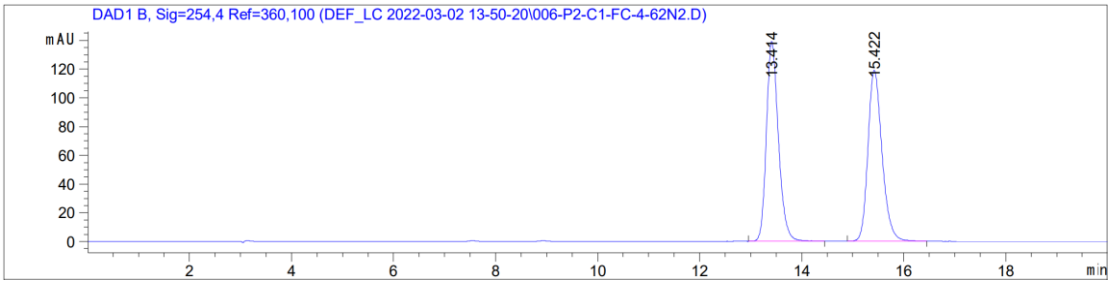
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.66 (d, *J* = 18.2 Hz), 147.92, 144.69, 131.08, 113.21, 108.17, 102.71, 101.41, 90.97 (d, *J* = 187.1 Hz), 45.82 (d, *J* = 18.7 Hz), 30.23, 29.71.

HRMS (ESI): $C_{14}H_{18}FNNaO_3^+$ ($M+H^+$): 290.1163, found: 290.1162.

$[\alpha]_D^{25}$ = -27.55 (c = 1.43, $CHCl_3$).

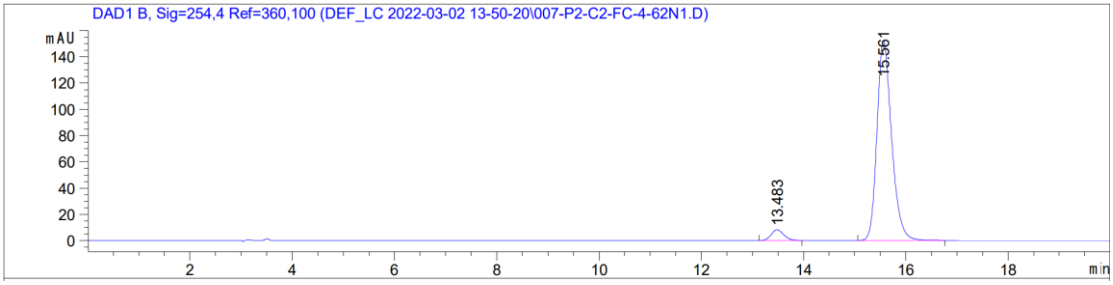
HPLC: The ee was determined to be 91% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 65:35 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 15.6 min, t_R (minor) = 13.5 min.

2l racemic

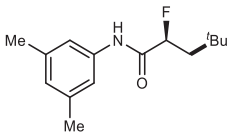


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.414	BB	0.2509	2275.95801	139.08006	49.9830
2	15.422	BB	0.2931	2277.50952	119.09074	50.0170

2l enantioenriched, 91% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.483	BB	0.2560	140.09309	8.09240	4.4274
2	15.561	BB	0.3016	3024.15552	152.32730	95.5726



(*S*)-*N*-(3,5-dimethylphenyl)-2-fluoro-4,4-dimethylpentanamide (2m)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 15:1) as a colourless oil (17.9 mg, 71%, 92% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 5.4 Hz, 1H), 7.20 (s, 2H), 6.79 (s, 1H), 5.16 – 4.96 (m, 1H), 2.31 (s, 6H), 2.13 – 1.92 (m, 1H), 1.84 – 1.68 (m, 1H), 1.04 (d, *J* = 0.7 Hz, 9H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.76 – -182.10 (m).

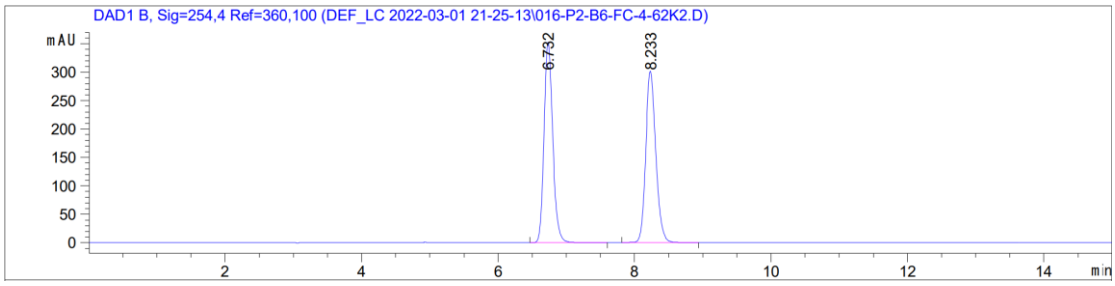
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.76 (d, *J* = 18.0 Hz), 138.86, 136.66, 126.61, 117.67, 90.94 (d, *J* = 187.4 Hz), 45.88 (d, *J* = 18.7 Hz), 30.20, 29.68, 21.38.

HRMS (ESI): $C_{15}H_{22}FNNaO^+$ ($M+Na^+$): 274.1578, found: 274.1577.

$[\alpha]_D^{25}$ = -23.12 (c = 2.03, $CHCl_3$).

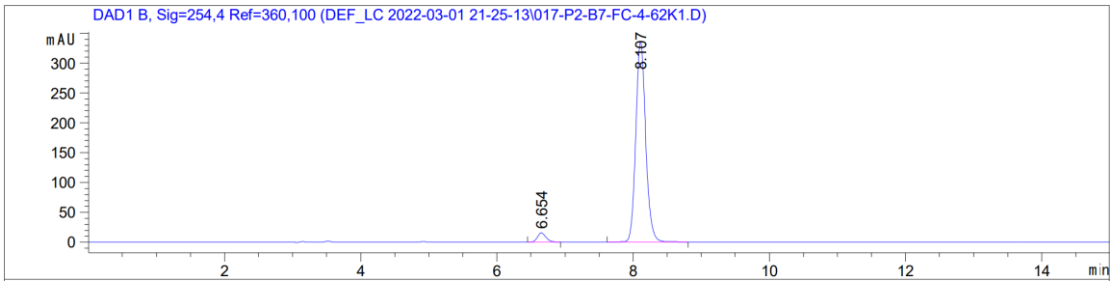
HPLC: The ee was determined to be 92% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 8.1 min, t_R (minor) = 6.7 min.

2m racemic

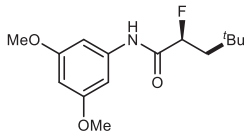


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.732	BB	0.1350	3110.73340	352.49948	50.0482
2	8.233	BB	0.1580	3104.74707	301.81305	49.9518

2m enantioenriched, 92% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.654	BB	0.1322	132.43141	15.42657	3.7557
2	8.107	BB	0.1559	3393.75635	335.92529	96.2443



(*S*)-*N*-(3,5-dimethoxyphenyl)-2-fluoro-4,4-dimethylpentanamide (2n)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a colourless oil (22.4 mg, 79%, 93% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 6.6 Hz, 1H), 6.81 (d, *J* = 2.2 Hz, 2H), 6.27 (t, *J* = 2.2 Hz, 1H), 5.15 – 4.98 (m, 1H), 3.77 (s, 6H), 2.13 – 1.92 (m, 1H), 1.83 – 1.69

(m, 1H), 1.03 (s, 9H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.80 – -182.13 (m).

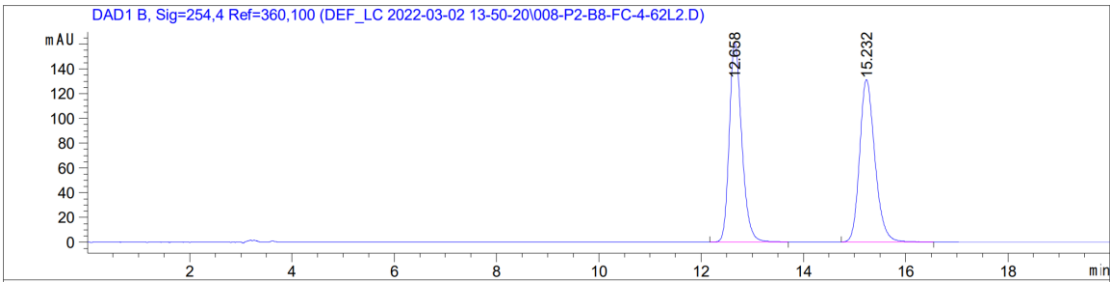
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.90 (d, J = 18.1 Hz), 161.10, 138.57, 98.06, 97.33, 90.88 (d, J = 187.7 Hz), 55.42, 45.82 (d, J = 18.6 Hz), 30.19, 29.65 (d, J = 0.9 Hz).

HRMS (ESI): $C_{15}H_{22}FNNaO_3^+$ ($M+Na^+$): 306.1476, found: 306.1473.

$[\alpha]_D^{25}$ = -21.30 (c = 1.28, $CHCl_3$).

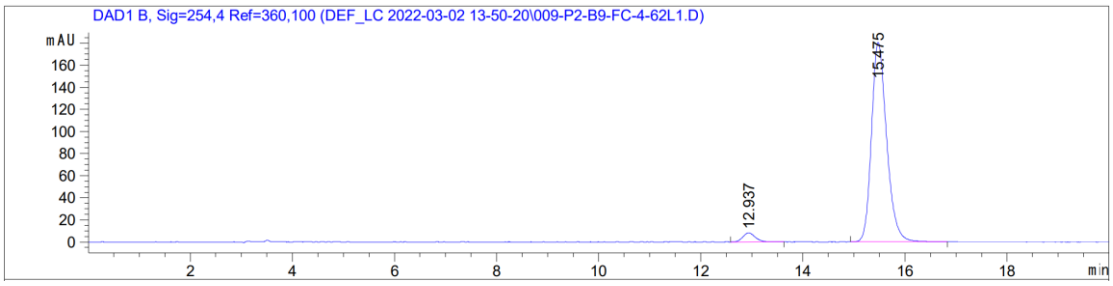
HPLC: The ee was determined to be 93% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 15.5 min, t_R (minor) = 12.9 min.

2n racemic

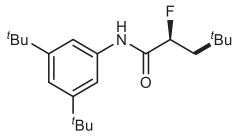


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.658	BB	0.2567	2728.83667	161.87294	50.0512
2	15.232	BB	0.3203	2723.24854	131.13100	49.9488

2n enantioenriched, 93% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.937	BB	0.2615	140.30666	8.20440	3.6319
2	15.475	BB	0.3146	3722.81787	180.52377	96.3681



(*S*)-*N*-(3,5-di-*tert*-butylphenyl)-2-fluoro-4,4-dimethylpentanamide (2o)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 20:1) as a colourless oil (26.5 mg, 79%, 94% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 6.2 Hz, 1H), 7.44 (d, *J* = 1.1 Hz, 2H), 7.22 (s, 1H), 5.10 (dd, *J* = 51.3, 9.8 Hz, 1H), 2.05 (dd, *J* = 45.5, 15.4 Hz, 1H), 1.77 (m, 1H), 1.33 (s, 18H), 1.04 (s, 9H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.45 – -181.78 (m).

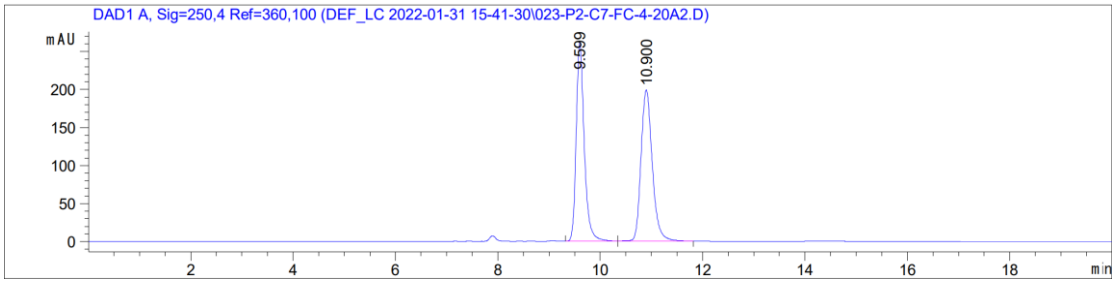
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.78 (d, *J* = 18.0 Hz), 151.84, 136.24, 119.06, 114.48, 90.94 (d, *J* = 187.5 Hz), 45.93 (d, *J* = 18.6 Hz), 35.00, 31.41, 30.20, 29.68.

HRMS (ESI): $C_{21}H_{34}FNNaO^+$ ($M+Na^+$): 358.2517, found: 358.2516.

$[\alpha]_D^{25}$ = -25.69 (c = 1.02, $CHCl_3$).

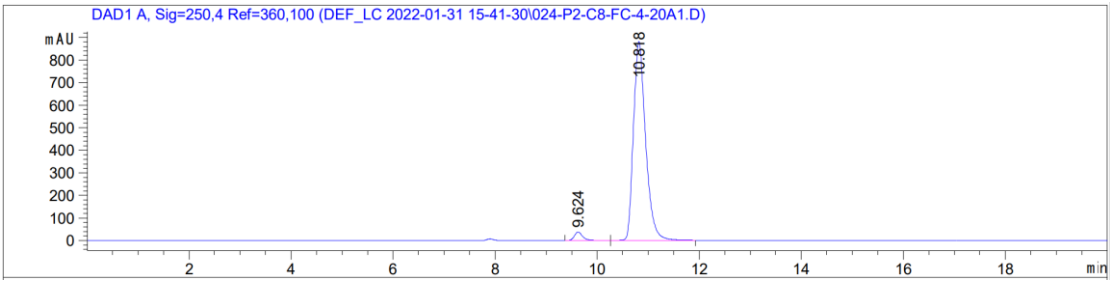
HPLC: The ee was determined to be 94% on a CHIRALPAK IB column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 200:1 at a flow rate 0.5 mL/min. Retention times: t_R (major) = 9.6 min, t_R (minor) = 10.8 min.

2o racemic

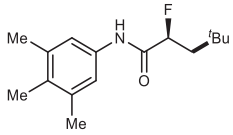


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.599	BB	0.1653	2868.59766	262.82272	48.5953
2	10.900	BB	0.2361	3034.43701	198.76158	51.4047

2o enantioenriched, 94% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.624	BB	0.1685	427.39523	38.21778	2.8504
2	10.818	BB	0.2547	1.45666e4	882.07922	97.1496



(*S*)-2-fluoro-4,4-dimethyl-*N*-(3,4,5-trimethylphenyl)pentanamide (2p)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 15:1) as a colourless oil (22.3 mg, 84%, 92% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 5.6 Hz, 1H), 7.22 (s, 2H), 5.15 – 4.98 (m, 1H), 2.27 (s, 6H), 2.14 (s, 3H), 2.11 – 1.94 (m, 1H), 1.82 – 1.69 (m, 1H), 1.04 (s, 9H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.78 – -182.11 (m).

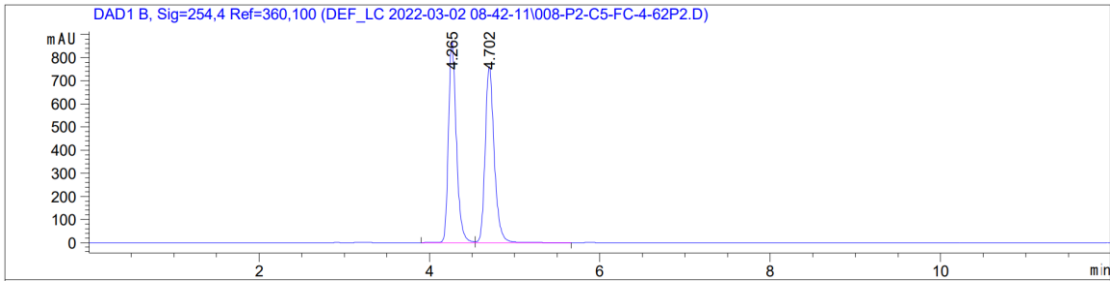
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.66 (d, *J* = 18.1 Hz), 137.23, 133.83, 131.83, 119.19, 90.95 (d, *J* = 187.4 Hz), 45.87 (d, *J* = 18.6 Hz), 30.20, 29.70 (d, *J* = 1.0 Hz), 20.71, 15.01.

HRMS (ESI): $C_{16}H_{24}FNNaO^+$ ($M+Na^+$): 288.1734, found: 288.1737.

$[\alpha]_D^{25}$ = -29.45 (c = 1.63, $CHCl_3$).

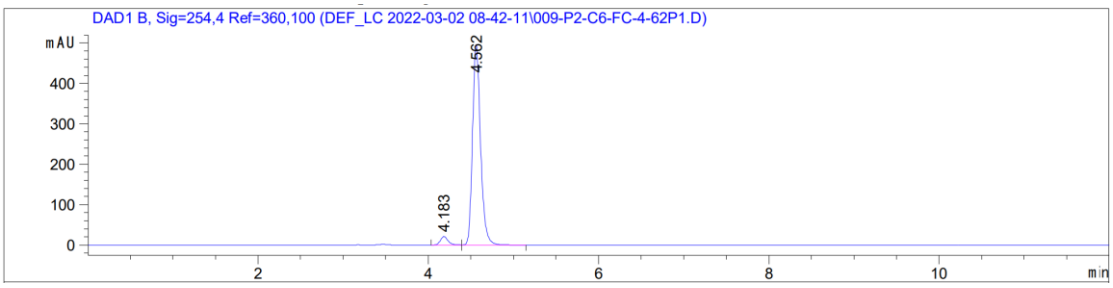
HPLC: The ee was determined to be 92% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 4.6 min, t_R (minor) = 4.2 min.

2p racemic

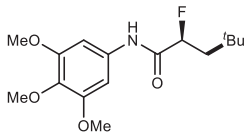


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.265	VV R	0.0969	5582.70361	870.08868	49.8003
2	4.702	VB	0.1121	5627.47559	762.09857	50.1997

2p enantioenriched, 92% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.183	BV	0.0960	133.32756	21.01962	3.9519
2	4.562	VB	0.0983	3240.45874	495.23480	96.0481



(*S*)-2-fluoro-4,4-dimethyl-*N*-(3,4,5-trimethoxyphenyl)pentanamide (2q)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 3:1) as a colourless oil (23.2 mg, 74%, 93% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 6.9 Hz, 1H), 6.88 (s, 2H), 5.15 – 4.98 (m, 1H), 3.84 (s, 6H), 3.81 (s, 3H), 2.13 – 1.90 (m, 1H), 1.85 – 1.67 (m, 1H), 1.03 (s, 9H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.80 – -182.14 (m).

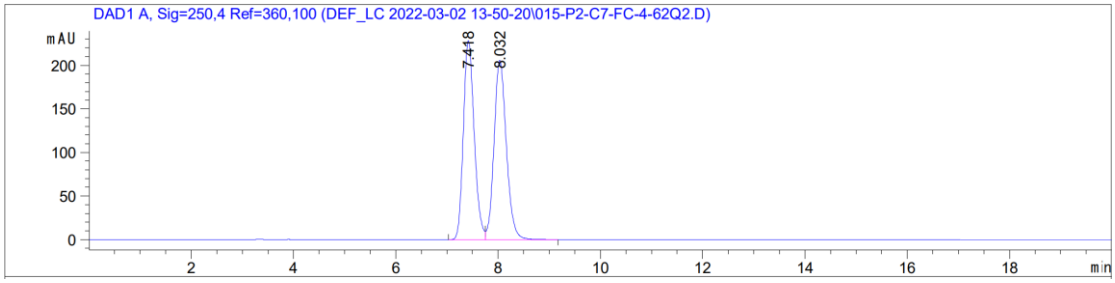
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.84 (d, *J* = 18.1 Hz), 153.39, 135.00, 132.95, 97.44, 90.87 (d, *J* = 187.5 Hz), 61.00, 56.11, 45.90 (d, *J* = 18.6 Hz), 30.19, 29.64 (d, *J* = 0.8 Hz).

HRMS (ESI): $C_{16}H_{24}FNNaO_4^+$ ($M+Na^+$): 336.1582, found: 336.1579.

$[\alpha]_D^{25}$ = -30.49 (c = 1.90, $CHCl_3$).

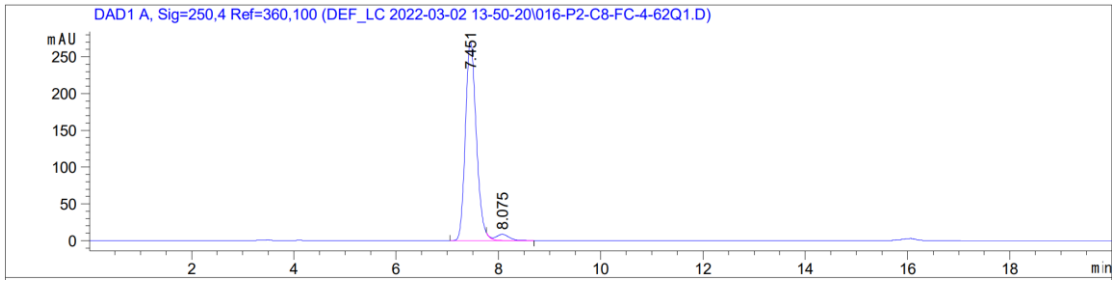
HPLC: The ee was determined to be 93% on a CHIRALPAK IC column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 50:50 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 7.5 min, t_R (minor) = 8.1 min.

2q racemic

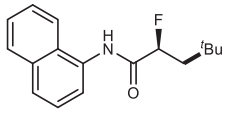


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.418	BV	0.2283	3372.23853	228.38441	49.4249
2	8.032	VB	0.2575	3450.71240	205.87502	50.5751

2q enantioenriched, 92% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.451	BV R	0.2280	4041.11450	271.02176	96.4879
2	8.075	VB E	0.2632	147.09367	8.36274	3.5121



(*S*)-2-fluoro-4,4-dimethyl-*N*-(naphthalen-1-yl)pentanamide (2r)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 15:1) as a colourless oil (14.5 mg, 53%, 87% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 5.6 Hz, 1H), 8.03 (d, *J* = 7.5 Hz, 1H), 7.93 – 7.79 (m, 2H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.60 – 7.46 (m, 3H), 5.34 – 5.16 (m, 1H), 2.24 – 2.02 (m, 1H), 1.98 – 1.81 (m, 1H), 1.09 (d, *J* = 0.4 Hz, 9H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.78 – -182.11 (m).

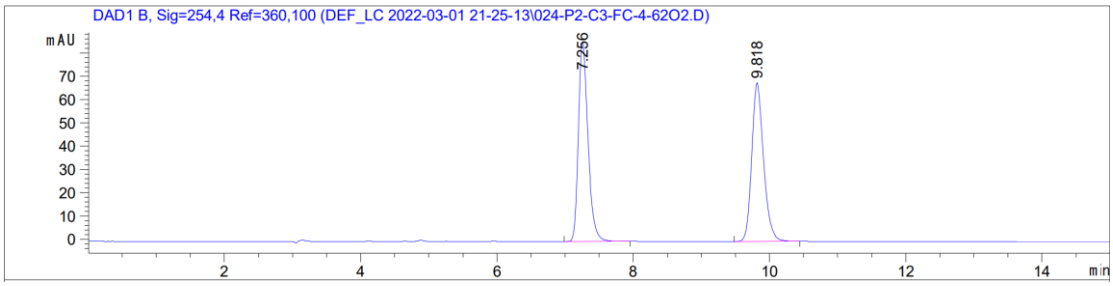
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.36 (d, *J* = 18.2 Hz), 134.09, 131.13, 128.89, 126.77, 126.56, 126.14 (d, *J* = 5.6 Hz), 125.77, 120.25 (d, *J* = 13.3 Hz), 91.47 (d, *J* = 187.1 Hz), 45.97 (d, *J* = 18.7 Hz), 30.31, 29.76.

HRMS (ESI): $C_{17}H_{20}FNNaO^+$ ($M+Na^+$): 296.1421, found: 296.1422.

$[\alpha]_D^{25}$ = -34.55 (c = 1.89, $CHCl_3$).

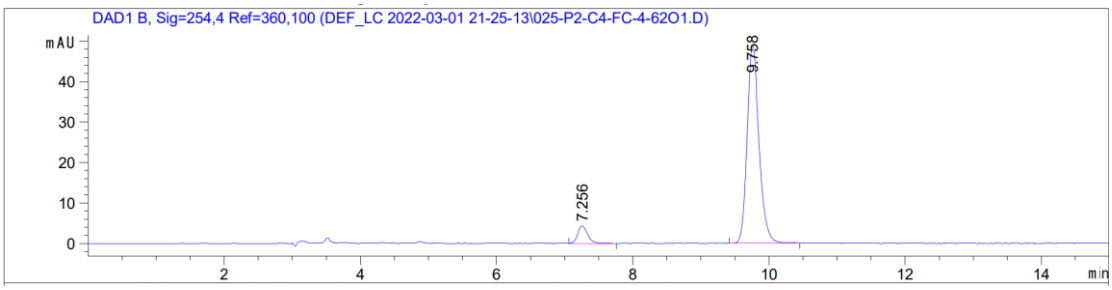
HPLC: The ee was determined to be 87% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 9.8 min, t_R (minor) = 7.3 min.

2r racemic

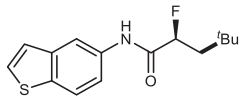


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.256	BB	0.1469	829.30225	85.67036	49.9864
2	9.818	BB	0.1860	829.75378	68.16933	50.0136

2r enantioenriched, 87% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.256	BB	0.1528	43.33706	4.32693	6.8251
2	9.758	BB	0.1848	591.62769	49.02603	93.1749



(*S*)-*N*-(benzo[*b*]thiophen-5-yl)-2-fluoro-4,4-dimethylpentanamide (2s)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (15.4 mg, 55%, 90% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 2.1 Hz, 1H), 8.16 (d, *J* = 7.3 Hz, 1H), 7.81 (d, *J* = 8.6 Hz, 1H), 7.47 (d, *J* = 5.4 Hz, 1H), 7.39 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.29 (d, *J* = 5.4 Hz, 1H), 5.24 – 5.03 (m, 1H), 2.17 – 1.96 (m, 1H), 1.89 – 1.74 (m, 1H), 1.05 (s, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -181.92 – -182.25 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.01 (d, *J* = 18.1 Hz), 140.27, 136.14, 133.73, 127.87, 124.04, 122.94, 117.57, 114.75, 91.11 (d, *J* = 187.4 Hz), 45.95 (d, *J* = 18.7 Hz), 30.31, 29.79.

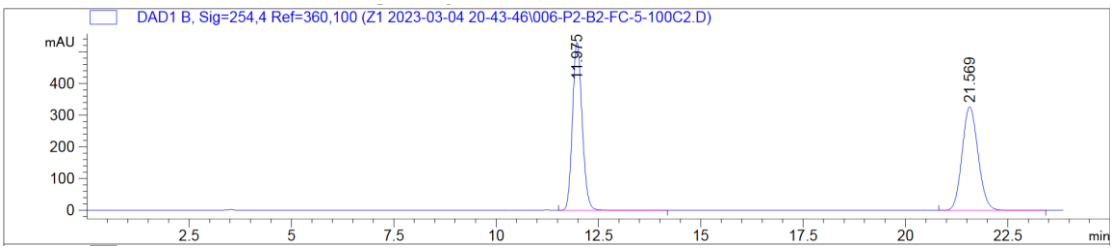
HRMS (ESI): $C_{15}H_{19}FNOS^+$ ($M+H^+$): 280.1166, found: 280.1168.

$[\alpha]_D^{25}$ = -27.50 (c = 1.50, $CHCl_3$).

HPLC: The ee was determined to be 90% on a CHIRALPAK AD-H column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major)

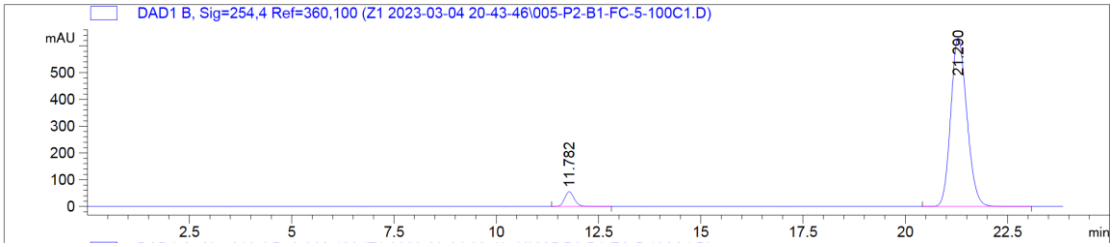
= 21.3 min, t_R (minor) = 11.8 min.

2s racemic

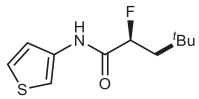


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.975	BB	0.2542	8733.69824	530.22003	49.6297
2	21.569	BB	0.4229	8864.04395	326.33221	50.3703

2s enantioenriched, 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.782	BB	0.2561	920.76288	55.33070	5.0563
2	21.290	BB	0.4266	1.72896e4	629.24103	94.9437



(*S*)-2-fluoro-4,4-dimethyl-*N*-(thiophen-3-yl)pentanamide (2t)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (14.2 mg, 62%, 89% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 2.1 Hz, 1H), 7.62 (dd, *J* = 3.3, 1.4 Hz, 1H), 7.25 (dd, *J* = 5.1, 3.2 Hz, 1H), 7.06 (dd, *J* = 5.1, 1.4 Hz, 1H), 5.27 – 4.95 (m, 1H), 2.15 – 1.91 (m, 1H), 1.87 – 1.68 (m, 1H), 1.03 (d, *J* = 1.0 Hz, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -182.75 – -183.09 (m).

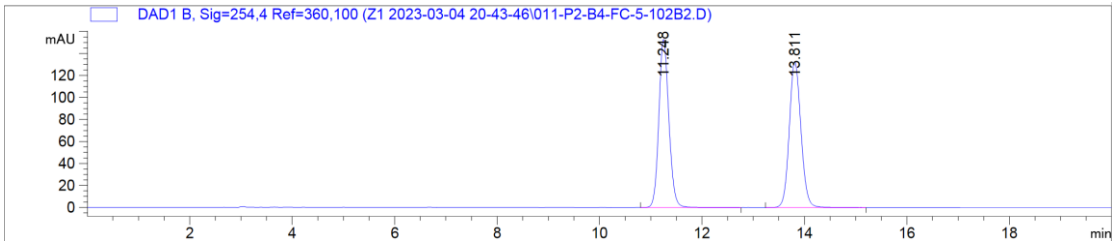
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.33 (d, J = 18.7 Hz), 134.55, 124.92, 121.13, 111.02, 90.99 (d, J = 186.8 Hz), 45.98 (d, J = 18.7 Hz), 30.28, 29.76.

HRMS (ESI): $C_{11}H_{17}FNOS^+$ ($M+H^+$): 230.1009, found: 230.1010.

$[\alpha]_D^{25}$ = -21.71 (c = 1.50, $CHCl_3$).

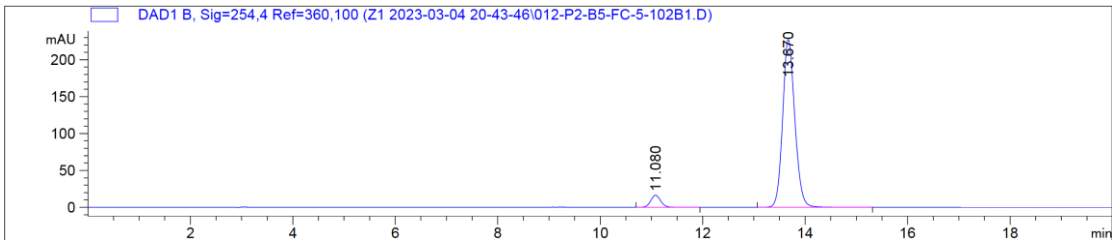
HPLC: The ee was determined to be 89% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 13.7 min, t_R (minor) = 11.1 min.

2t racemic

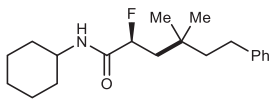


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.248	BB	0.2091	2086.98438	153.06685	49.8444
2	13.811	BB	0.2443	2100.01172	132.93527	50.1556

2t enantioenriched, 89% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.080	BB	0.2098	223.97699	16.35496	5.6161
2	13.670	BB	0.2550	3764.14844	227.48138	94.3839



(*S*)-*N*-cyclohexyl-2-fluoro-4,4-dimethyl-7-phenylheptanamide (2u)

According to the **General Procedure A**, the title compound was isolated by flash

chromatography (Petroleum ether: EtOAc = 15:1) as a white solid (23.7 mg, 71%, 67% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.15 (m, 2H), 7.13 – 7.04 (m, 3H), 6.15 (s, 1H), 5.13 – 4.73 (m, 1H), 3.77 – 3.66 (m, 1H), 2.56 – 2.47 (m, 2H), 2.11 – 1.79 (m, 3H), 1.75 – 1.59 (m, 3H), 1.59 – 1.43 (m, 3H), 1.33 – 1.20 (m, 2H), 1.20 – 1.03 (m, 3H), 0.97 (s, 6H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -183.40 – -183.73 (m).

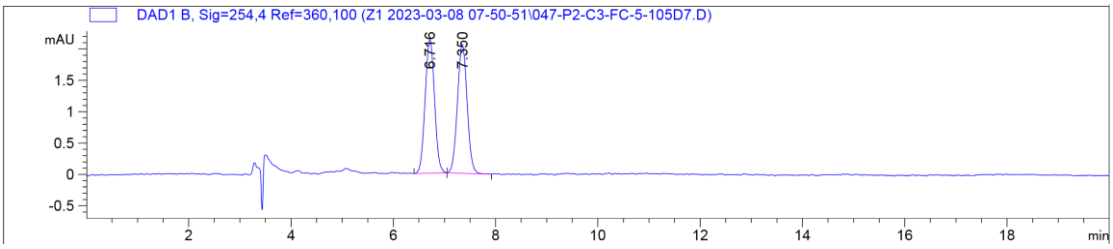
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.83 (d, J = 18.9 Hz), 143.13, 128.43, 128.42, 125.72, 90.67 (d, J = 185.7 Hz), 47.98, 44.82, 43.80 (d, J = 18.7 Hz), 33.12, 33.06, 32.84, 30.67, 27.53 (d, J = 1.7 Hz), 27.33, 25.54, 24.89.

HRMS (ESI): $C_{21}H_{32}FNNaO^+$ ($M+Na^+$): 342.2204, found: 342.2201.

$[\alpha]_D^{25}$ = -9.80 (c = 1.50, $CHCl_3$).

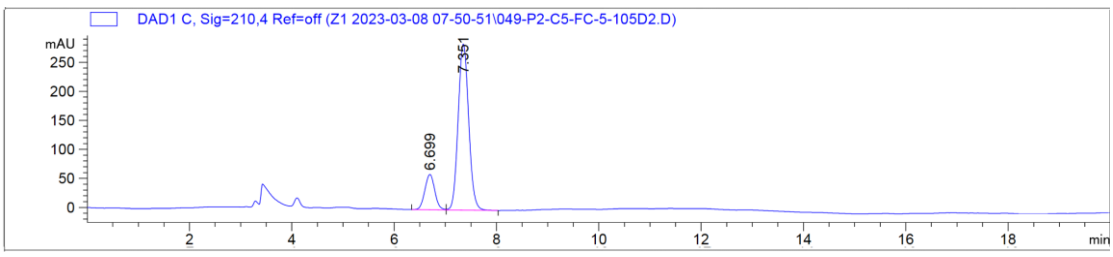
HPLC: The ee was determined to be 67% on a CHIRALPAK IB column at 210 nm, 25 °C, with hexane: ^{i}PrOH = 85:15 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 7.4 min, t_R (minor) = 6.7 min.

2u racemic

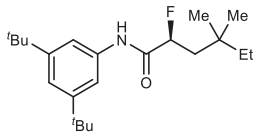


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.716	BB	0.2028	27.14653	2.12887	49.9772
2	7.350	BB	0.2062	27.17133	2.05619	50.0228

2u enantioenriched, 67% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.702	BB	0.2049	14.89067	1.12126	16.6699
2	7.352	BB	0.2242	74.43616	5.22654	83.3301



(*S*)-*N*-(3,5-di-*tert*-butylphenyl)-2-fluoro-4,4-dimethylhexanamide (2v)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 20:1) as a colourless oil (20.6 mg, 59%, 93% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 6.7 Hz, 1H), 7.43 (d, *J* = 1.6 Hz, 2H), 7.22 (t, *J* = 1.6 Hz, 1H), 5.09 (m, 1H), 2.04 (m, 1H), 1.76 (m, 1H), 1.41 – 1.34 (q, *J* = 15.2, 7.7 Hz, 2H), 1.32 (s, 18H), 0.99 (s, 6H), 0.88 (t, *J* = 7.5 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.25 – -181.59 (m).

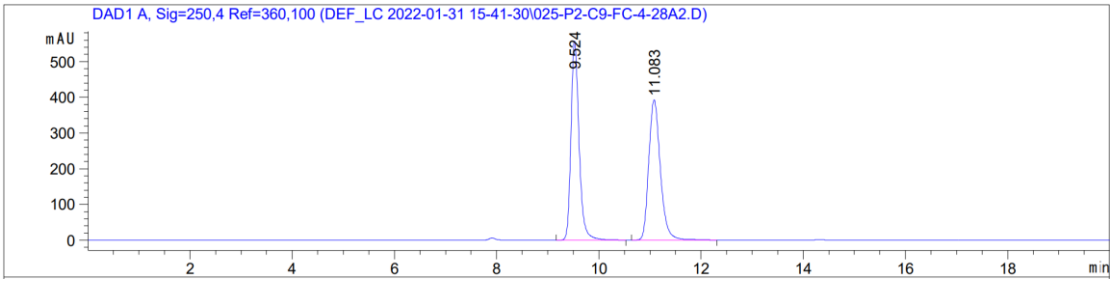
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.86 (d, *J* = 18.0 Hz), 151.85, 136.26, 119.03, 114.44, 90.78 (d, *J* = 187.3 Hz), 43.61 (d, *J* = 18.8 Hz), 34.99, 34.71, 32.66, 31.40, 26.89, 26.68, 8.36.

HRMS (ESI): $C_{22}H_{36}FNNaO^+$ ($M+Na^+$): 372.2673, found: 372.2671.

$[\alpha]_D^{25}$ = -26.36 (c = 1.96, $CHCl_3$).

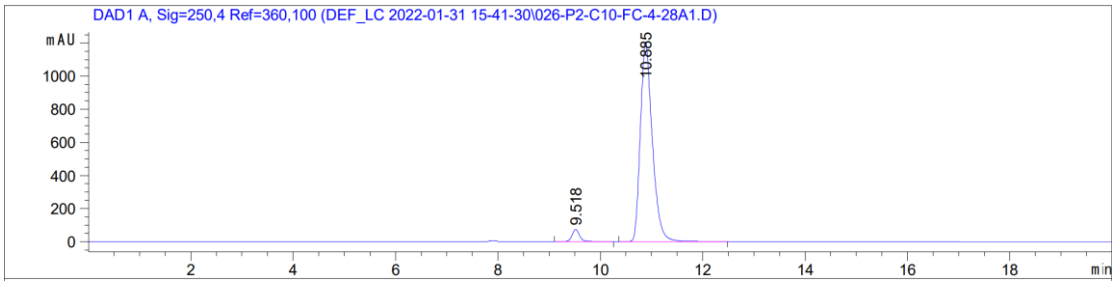
HPLC: The ee was determined to be 93% on a CHIRALPAK IB column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 200:1 at a flow rate 0.5 mL/min. Retention times: t_R (major) = 10.9 min, t_R (minor) = 9.5 min.

2v racemic

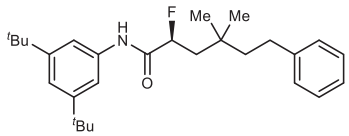


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.524	BB	0.1683	6129.35156	557.36078	49.8100
2	11.083	BB	0.2438	6176.10840	391.96869	50.1900

2v enantioenriched, 93% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.518	BB	0.1555	756.40527	73.82416	3.7229
2	10.885	BB	0.2471	1.95613e4	1206.86938	96.2771



(*S*)-*N*-(3,5-di-tert-butylphenyl)-2-fluoro-4,4-dimethyl-6-phenylhexanamide (2w)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 15:1) as a white solid (34.1 mg, 80%, 93% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 6.8 Hz, 1H), 7.40 (d, *J* = 1.3 Hz, 2H), 7.26 – 7.20 (m, 2H), 7.15 (m, *J* = 11.0, 7.6 Hz, 4H), 5.09 (dd, *J* = 51.3, 9.8 Hz, 1H), 2.67 – 2.48 (m, 2H), 2.10 (dd, *J* = 45.3, 15.4 Hz, 1H), 1.85 (m, 1H), 1.60 (m, 2H), 1.29 (s, 18H), 1.05 (s, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.33 – -181.66 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.67 (d, *J* = 18.0 Hz), 151.88, 142.98, 136.22, 128.40, 128.36, 125.70, 119.10, 114.48, 90.70 (d, *J* = 187.7 Hz), 44.73, 43.79 (d, *J* = 18.7 Hz),

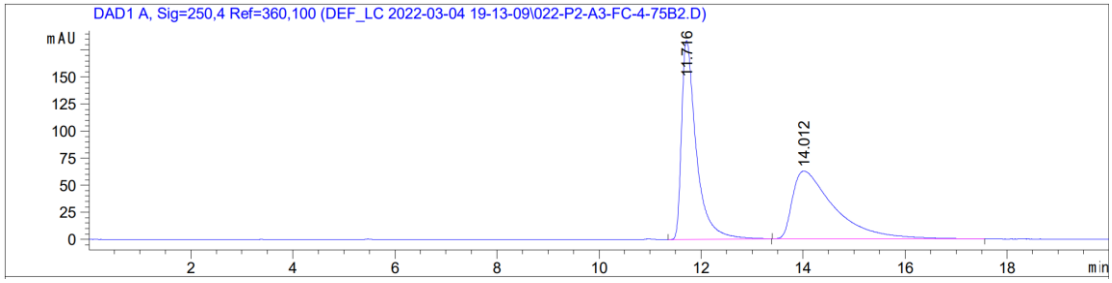
35.00, 32.85, 31.41, 30.62, 27.46, 27.28.

HRMS (ESI): $C_{28}H_{40}FNNaO^+$ ($M+Na^+$): 448.2986, found: 448.2984.

$[\alpha]_D^{25}$ = -18.31 (c = 1.02, $CHCl_3$).

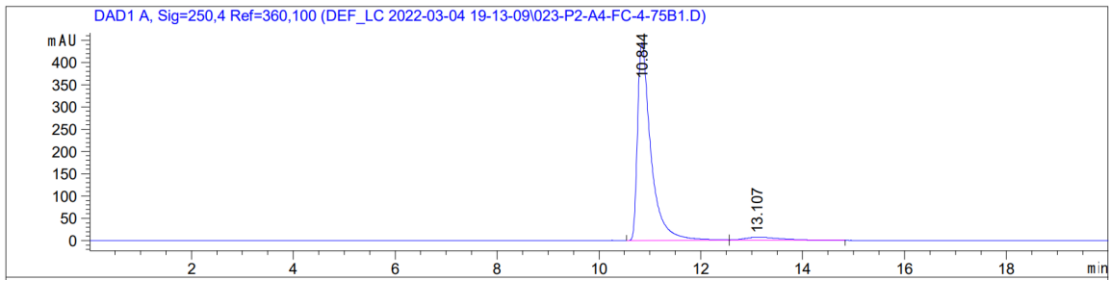
HPLC: The ee was determined to be 93% on a CHIRALPAK IC column at 254 nm, 25 ^oC, with hexane: ^iPrOH = 200:1 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 10.8 min, t_R (minor) = 13.1 min.

2w racemic

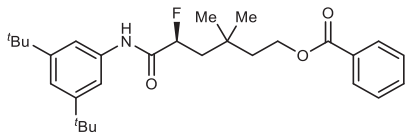


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.716	BB	0.2961	3690.56177	183.93446	50.7760
2	14.012	BB	0.7956	3577.75854	62.71560	49.2240

2w enantioenriched, 93% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.844	BB	0.2660	8076.20703	444.37494	96.4040
2	13.107	BB	0.5756	301.25064	6.28051	3.5960



(*S*)-6-((3,5-di-*tert*-butylphenyl)amino)-5-fluoro-3,3-dimethyl-6-oxohexyl benzoate (2x)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 15:1) as a white solid (32.9 mg, 70%, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.02 (m, 2H), 8.00 (d, *J* = 6.8 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.47 – 7.38 (m, 4H), 7.23 (t, *J* = 1.6 Hz, 1H), 5.25 – 5.06 (m, 1H), 4.44 (t, *J* = 7.2 Hz, 2H), 2.24 – 2.06 (m, 1H), 1.99 – 1.79 (m, 3H), 1.33 (s, 18H), 1.13 (s, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.53 – -181.86 (m).

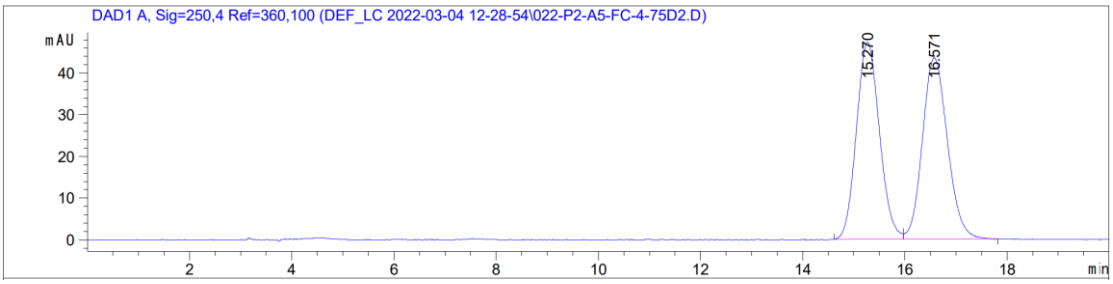
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.37 (d, *J* = 18.0 Hz), 166.68, 151.87, 136.17, 132.91, 130.36, 129.57, 128.38, 119.12, 114.51, 90.45 (d, *J* = 187.6 Hz), 62.00, 44.40 (d, *J* = 18.8 Hz), 40.21, 34.99, 32.16, 31.40, 27.51 (d, *J* = 8.8 Hz).

HRMS (ESI): $C_{29}H_{40}FNNaO_3^+$ ($M+Na^+$): 492.2884, found: 492.2881.

$[\alpha]_D^{25}$ = -18.22 (c = 1.23, $CHCl_3$).

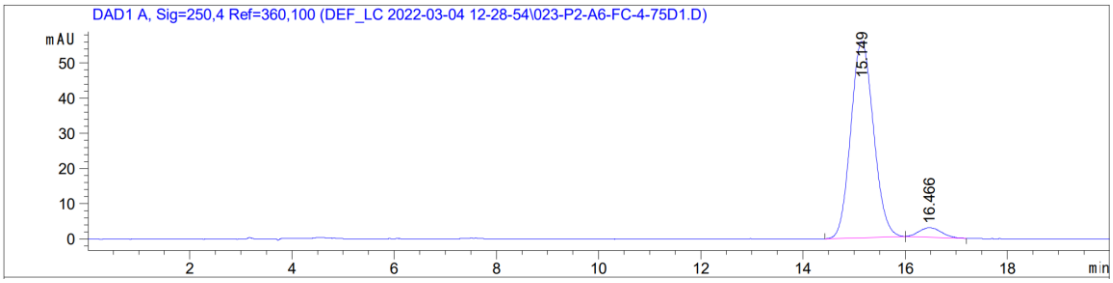
HPLC: The ee was determined to be 91% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 98:2 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 15.1 min, t_R (minor) = 16.5 min.

2x racemic

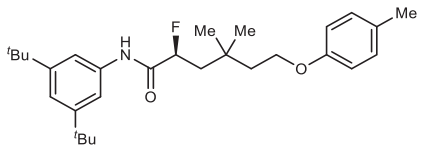


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.270	BV	0.4911	1479.19019	47.26491	49.9703
2	16.571	VB	0.5252	1480.94739	43.49369	50.0297

2x enantioenriched, 91% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.149	BB	0.4827	1725.72913	55.81806	95.4226
2	16.466	BB	0.3724	82.78275	2.74040	4.5774



(*S*)-*N*-(3,5-di-*tert*-butylphenyl)-2-fluoro-4,4-dimethyl-6-(p-tolyloxy)hexanamide (2y)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 15:1) as a white solid (37.4 mg, 82%, 90% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 6.9 Hz, 1H), 7.43 (d, *J* = 1.5 Hz, 2H), 7.23 (s, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 5.16 (dd, *J* = 51.3, 9.4 Hz, 1H), 4.04 (t, *J* = 7.1 Hz, 2H), 2.29 (s, 3H), 2.15 (dd, *J* = 44.6, 15.4 Hz, 1H), 1.96 – 1.82 (m, 3H), 1.33 (s, 18H), 1.12 (s, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.45 – -181.78 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.51 (d, *J* = 17.8 Hz), 156.73, 151.87, 136.17, 129.87 (d, *J* = 8.1 Hz), 119.13, 114.43 (d, *J* = 16.7 Hz), 90.54 (d, *J* = 187.7 Hz), 64.62, 44.41 (d, *J* = 18.7 Hz), 40.85, 35.00, 32.18, 31.41, 27.65, 20.52.

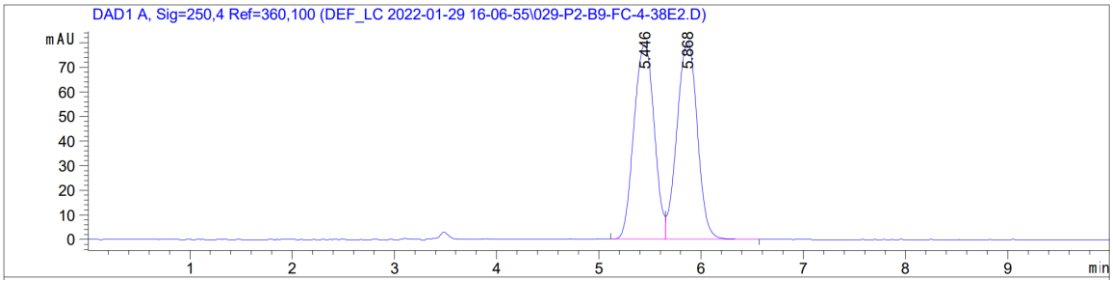
HRMS (ESI): $C_{29}H_{43}FNO_2^+$ ($M+H^+$): 456.3272, found: 456.3275.

$[\alpha]_D^{25}$ = -28.27 (c = 1.25, $CHCl_3$).

HPLC: The ee was determined to be 90% on a CHIRALPAK IA column at 254 nm, 25

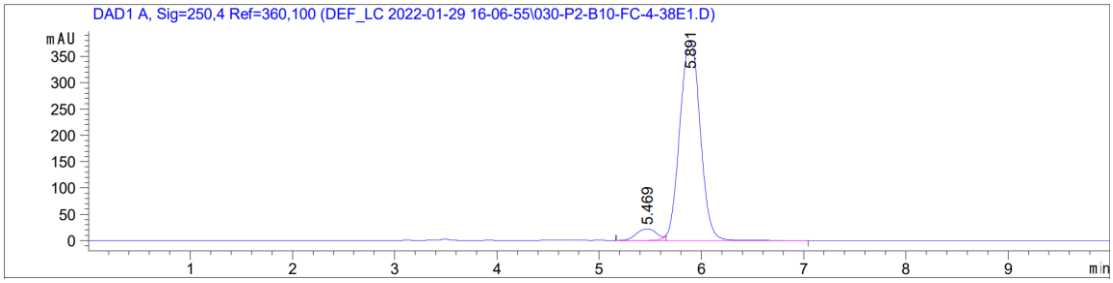
°C, with hexane: ^{i}PrOH = 98:2 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 5.9 min, t_R (minor) = 5.5 min.

2y racemic

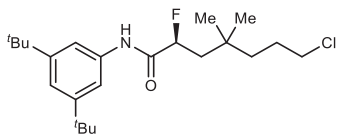


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.446	BV	0.2230	1088.15918	78.84562	49.4408
2	5.868	VB	0.2193	1112.77612	80.47268	50.5592

2y enantioenriched, 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.469	BV E	0.2177	290.52686	21.76337	5.2192
2	5.891	VB R	0.2202	5275.96973	379.45422	94.7808



(*S*)-7-chloro-*N*-(3,5-di-*tert*-butylphenyl)-2-fluoro-4,4-dimethylheptanamide (2z)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 20:1) as a white solid (29.5 mg, 74%, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 6.8 Hz, 1H), 7.36 (d, *J* = 1.7 Hz, 2H), 7.15 (t, *J* = 1.7 Hz, 1H), 5.02 (dd, *J* = 51.2, 11.4 Hz, 1H), 3.46 (t, *J* = 6.6 Hz, 2H), 1.99 (m, 1H), 1.81 – 1.63 (m, 3H), 1.44 – 1.30 (m, 2H), 1.25 (s, 18H), 0.95 (s, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.50 – -181.83 (m).

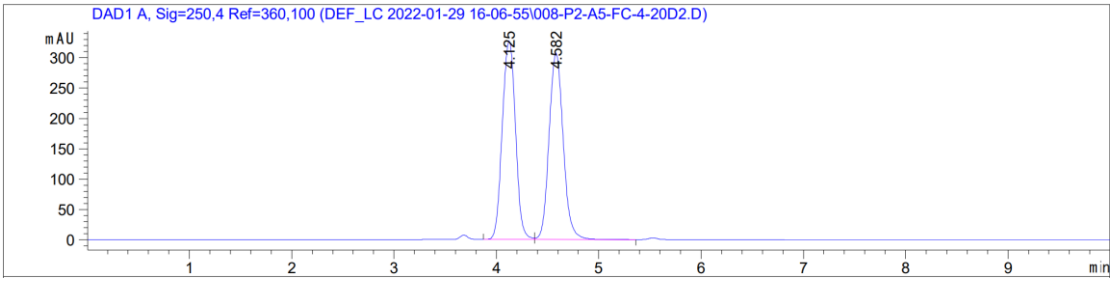
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.55 (d, *J* = 18.1 Hz), 151.87, 136.17, 119.12, 114.47, 90.55 (d, *J* = 187.6 Hz), 45.77, 43.81 (d, *J* = 18.6 Hz), 39.47, 35.00, 32.44, 31.40, 27.50, 27.32 (d, *J* = 12.5 Hz).

HRMS (ESI): $C_{23}H_{37}ClFNNaO^+$ ($M+Na^+$): 420.2440, found: 420.2438.

$[\alpha]_D^{25}$ = -20.08 (c = 1.74, $CHCl_3$).

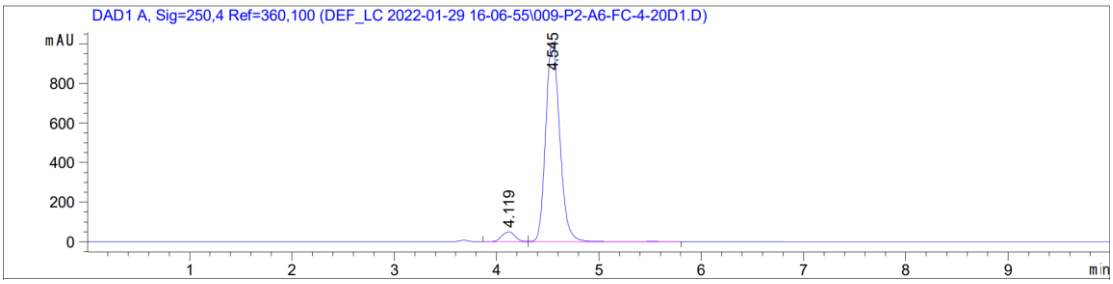
HPLC: The ee was determined to be 91% on a CHIRALPAK IB column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 97:3 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 4.5 min, t_R (minor) = 4.1 min.

2z racemic

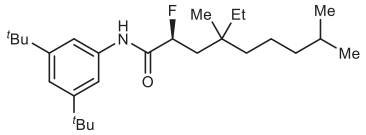


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.125	VV	0.1447	2942.14844	327.75574	49.8615
2	4.582	VB	0.1501	2958.49487	307.99139	50.1385

2z enantioenriched, 91% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.119	BV	0.1441	443.59326	49.72232	4.3841
2	4.545	VV R	0.1497	9674.69531	1008.25024	95.6159



(2*S*)-*N*-(3,5-di-*tert*-butylphenyl)-4-ethyl-2-fluoro-4,8-dimethylnonanamide (2aa)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 20:1) as a white solid (24.3 mg, 58%, 92% ee, d.r. = 1:1, d.r. was determined by deriving another similar substrate (**2aa'**)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.0 Hz, 1H), 7.43 (d, *J* = 1.6 Hz, 2H), 7.21 (t, *J* = 1.6 Hz, 1H), 5.07 (dd, *J* = 51.3, 10.0 Hz, 1H), 2.04 (dd, *J* = 46.3, 15.6 Hz, 1H), 1.86 – 1.71 (m, 1H), 1.62 – 1.47 (m, 2H), 1.37 (dd, *J* = 15.0, 7.5 Hz, 2H), 1.32 (s, 18H), 1.25 – 1.09 (m, 5H), 0.95 (s, 3H), 0.90 – 0.81 (m, 9H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.43 – -181.79 (m).

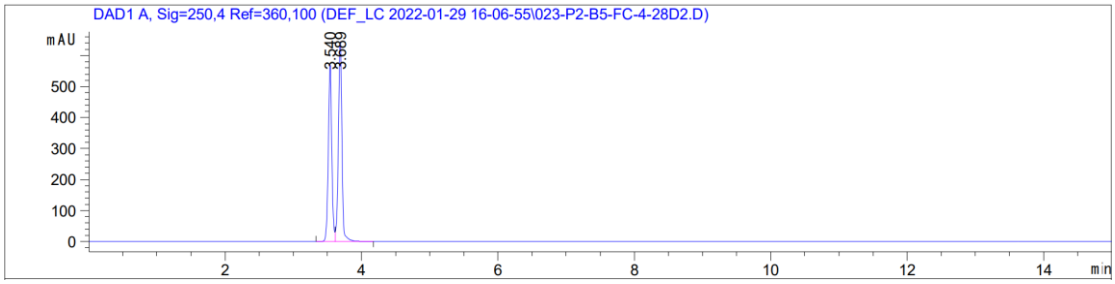
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.92 (d, *J* = 18.2 Hz), 151.84, 136.28, 119.01, 114.41, 90.65 (d, *J* = 187.4 Hz), 41.55 (d, *J* = 18.8 Hz), 39.90, 39.44, 39.25, 34.99, 31.91, 31.60, 31.40, 27.92, 24.67 (d, *J* = 8.1 Hz), 22.71, 21.12, 7.96.

HRMS (ESI): $C_{27}H_{46}FNNaO^+$ ($M+Na^+$): 442.3456, found: 442.3454.

$[\alpha]_D^{25}$ = -21.96 (c = 1.07, $CHCl_3$).

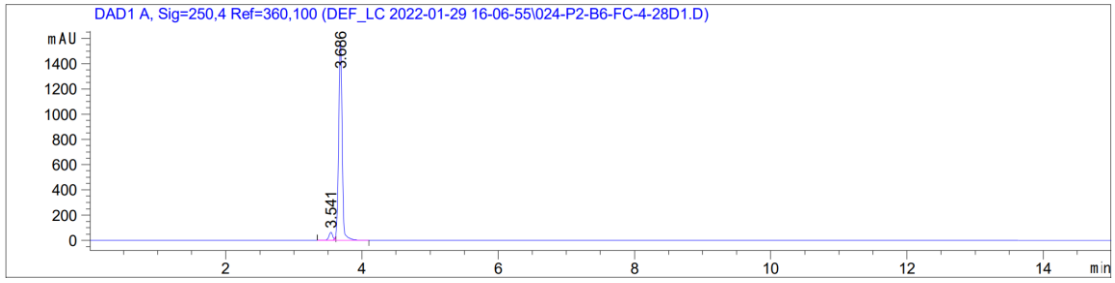
HPLC: The ee was determined to be 92% on a CHIRALPAK IB column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 100:1 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 3.7 min, t_R (minor) = 3.5 min.

2aa racemic

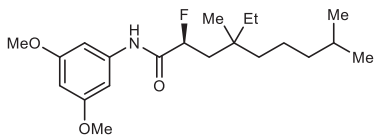


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.540	BV	0.0596	7.81131	2.08781	50.6095
2	3.688	VB	0.0522	7.62315	2.32579	49.3905

2aa enantioenriched, 92% ee



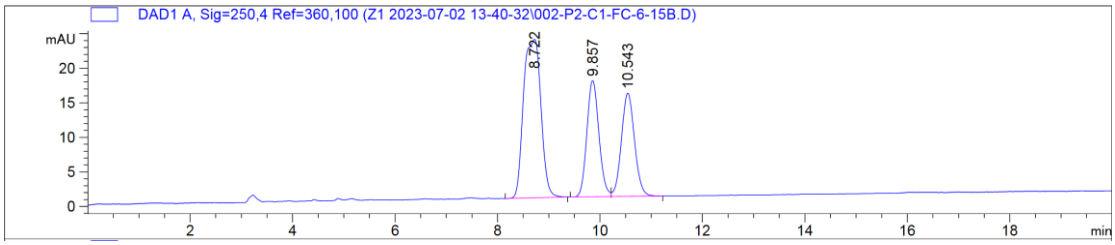
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.541	BV E	0.0566	231.87711	63.44945	3.9972
2	3.686	VB R	0.0551	5569.09473	1581.00720	96.0028



(2*S*)-*N*-(3,5-dimethoxyphenyl)-4-ethyl-2-fluoro-4,8-dimethylnonanamide (2aa')

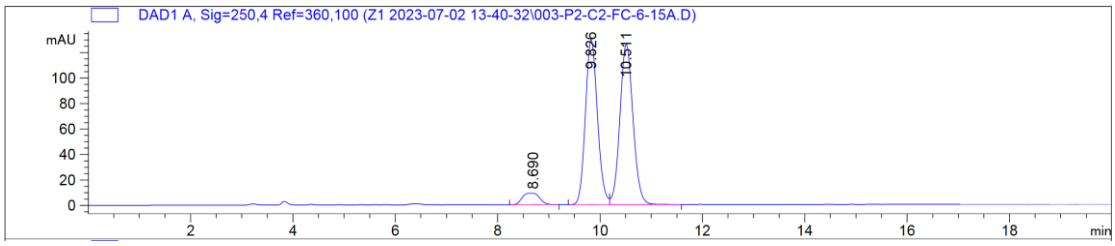
HPLC: The ee was determined to be 91% on a CHIRALPAK IC column at 250 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 9.8 min, 10.5 min, t_R (minor) = 8.7 min.

2aa' racemic, d.r. = 1:1

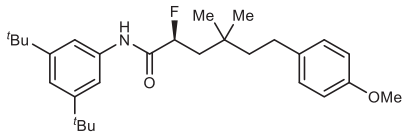


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.722	BB	0.3233	541.38043	22.94330	50.0312
2	9.857	BV	0.2547	274.73712	16.81211	25.3896
3	10.543	VB	0.2757	265.96756	14.93792	24.5792

2aa' enantioenriched, 91% ee, d.r. = 1:1



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.690	BB	0.3193	210.32333	8.91426	4.6033
2	9.826	BV	0.2528	2117.38867	129.48198	46.3427
3	10.511	VB	0.2759	2241.26465	125.76973	49.0540



(*S*)-*N*-(3,5-di-*tert*-butylphenyl)-2-fluoro-6-(4-methoxyphenyl)-4,4-dimethyl-hexanamide (2ab)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 15:1) as a white solid (35.5 mg, 78%, 92% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.0 Hz, 1H), 7.45 (d, *J* = 1.6 Hz, 2H), 7.23 (t, *J* = 1.6 Hz, 1H), 7.12 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 5.14 (dd, *J* = 51.3, 9.2 Hz, 1H), 3.79 (s, 3H), 2.57 (m, 2H), 2.14 (dd, *J* = 45.5, 15.5 Hz, 1H), 1.89 (m, 1H),

1.72 – 1.53 (m, 2H), 1.34 (s, 18H), 1.09 (s, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.32 – -181.65 (m).

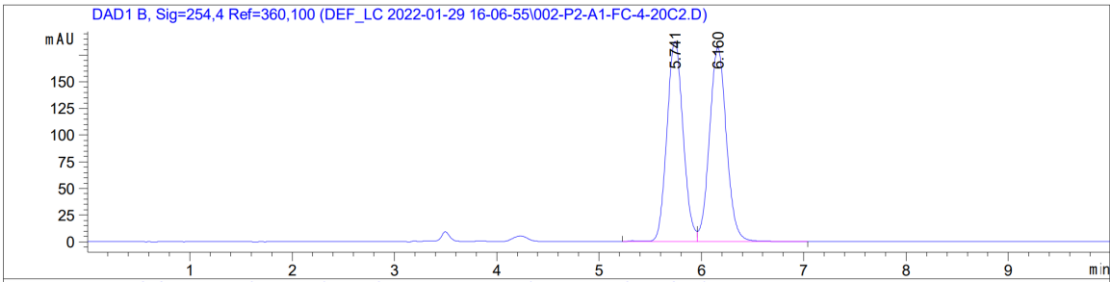
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.71 (d, J = 18.1 Hz), 157.67, 151.87, 136.23, 135.03, 129.21, 119.10, 114.48, 113.81, 90.71 (d, J = 187.6 Hz), 55.30, 44.98, 43.78 (d, J = 18.7 Hz), 35.01, 32.82, 31.42, 29.65, 27.39 (d, J = 19.0 Hz).

HRMS (ESI): $C_{29}H_{41}FNNaO_2^+$ ($M+Na^+$): 478.3092, found: 478.3088.

$[\alpha]_D^{25}$ = -26.70 (c = 1.29, $CHCl_3$).

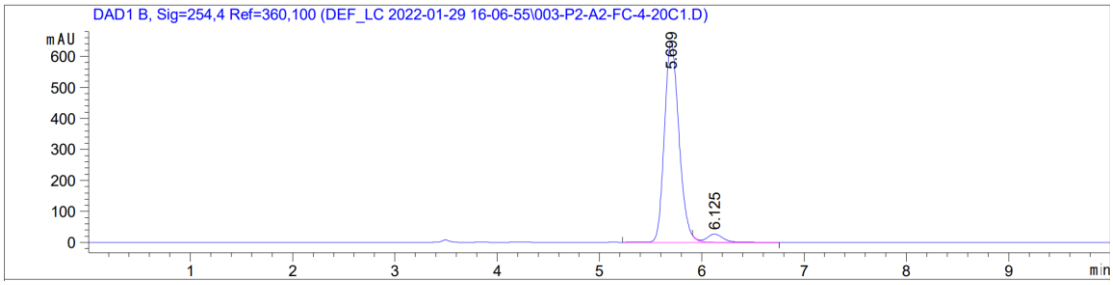
HPLC: The ee was determined to be 92% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 95:5 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 5.7 min, t_R (minor) = 6.1 min.

2ab racemic

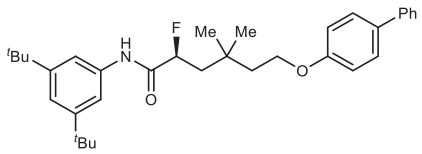


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.741	VV R	0.1728	2071.58350	187.69476	49.6125
2	6.160	VB	0.1790	2103.94116	181.80424	50.3875

2ab enantioenriched, 92% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.699	VV R	0.1515	6415.39795	648.18091	95.7923
2	6.125	VB E	0.1629	281.80093	26.32611	4.2077



(*S*)-6-([1,1'-biphenyl]-4-yloxy)-*N*-(3,5-di-*tert*-butylphenyl)-2-fluoro-4,4-dimethyl-hexanamide (2ac)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 15:1) as a white solid (38.8 mg, 75%, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 6.8 Hz, 1H), 7.61 – 7.46 (m, 4H), 7.47 – 7.37 (m, 4H), 7.34 – 7.27 (m, 1H), 7.23 (s, 1H), 6.99 (d, *J* = 8.5 Hz, 2H), 5.18 (dd, *J* = 51.3, 10.1 Hz, 1H), 4.12 (t, *J* = 7.0 Hz, 2H), 2.18 (dd, *J* = 45.1, 15.5 Hz, 1H), 1.98 – 1.83 (m, 3H), 1.33 (s, 18H), 1.15 (s, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.42 – -181.75 (m).

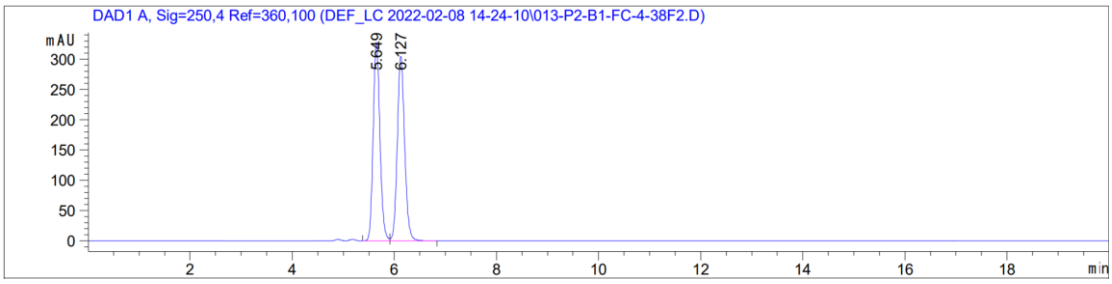
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.48 (d, *J* = 17.9 Hz), 158.44, 151.89, 140.87, 136.16, 133.71, 128.74, 128.18, 126.76, 126.66, 119.15, 114.79, 114.52, 90.54 (d, *J* = 187.8 Hz), 64.70, 44.40 (d, *J* = 18.6 Hz), 40.80, 35.01, 32.22, 31.41, 27.69.

HRMS (ESI): $C_{34}H_{44}FNNaO_2^+$ ($M+Na^+$): 540.3248, found: 540.3244.

$[\alpha]_D^{25}$ = -19.81 (c = 1.92, $CHCl_3$).

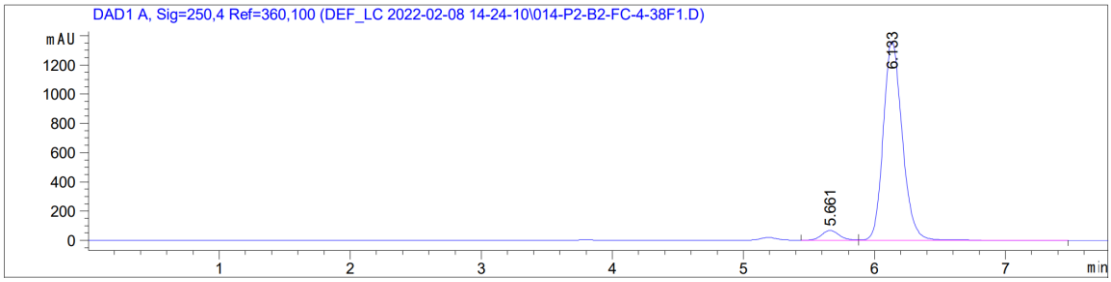
HPLC: The ee was determined to be 91% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 98:2 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 5.7 min, t_R (minor) = 6.1 min.

2ac racemic

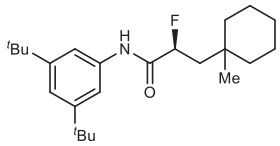


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.649	BV	0.1433	3017.90015	328.04245	49.6971
2	6.127	VB	0.1550	3054.68481	304.68488	50.3029

2ac enantioenriched, 91% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.661	VV	0.1413	624.45221	67.90471	4.3700
2	6.133	VB	0.1550	1.36650e4	1362.28894	95.6300



(*S*)-*N*-(3,5-di-*tert*-butylphenyl)-2-fluoro-3-(1-methylcyclohexyl)propenamide (2ad)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 25:1) as a white solid (23.6 mg, 63%, 94% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 6.8 Hz, 1H), 7.43 (d, *J* = 1.6 Hz, 2H), 7.22 (t, *J* = 1.6 Hz, 1H), 5.56 – 4.75 (m, 1H), 2.08 (dd, *J* = 45.3, 15.5 Hz, 1H), 1.81 (m, 1H), 1.55 – 1.41 (m, 5H), 1.37 (m, 5H), 1.32 (s, 18H), 1.03 (s, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -180.40 – -180.71 (m).

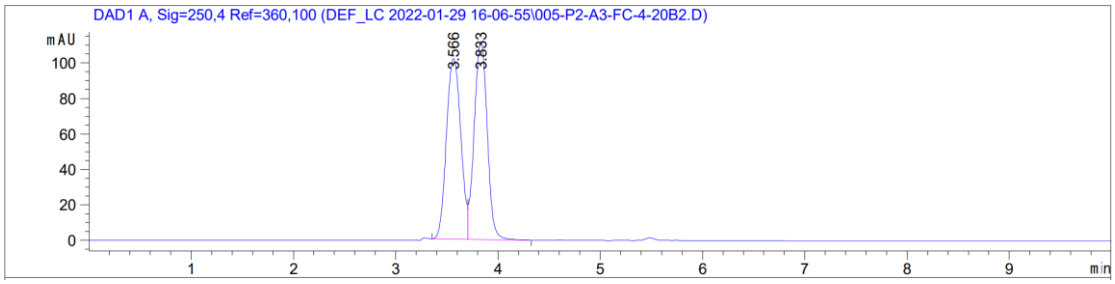
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.97 (d, *J* = 18.0 Hz), 151.84, 136.26, 119.03, 114.43, 90.48 (d, *J* = 187.5 Hz), 38.18, 37.68, 35.00, 32.52, 31.41, 26.24, 21.88.

HRMS (ESI): $C_{24}H_{39}FNO^+$ ($M+H^+$): 376.3010, found: 376.3013.

$[\alpha]_D^{25}$ = + 19.7256 (c = 0.4800, $CHCl_3$).

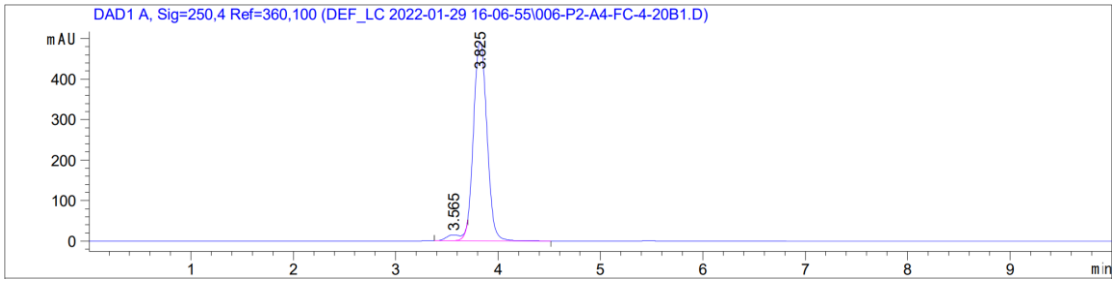
HPLC: The ee was determined to be 94% on a CHIRALPAK IB column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 97:3 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 3.8 min, t_R (minor) = 3.6 min.

2ad racemic

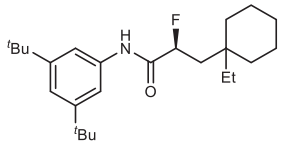


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.566	BV	0.1557	989.94745	101.61483	50.0585
2	3.833	VB	0.1395	987.63177	111.37479	49.9415

2ad enantioenriched, 94% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.565	BV E	0.1434	136.33357	14.53525	2.9163
2	3.825	VB R	0.1455	4538.50391	492.73743	97.0837



(*S*)-*N*-(3,5-di-*tert*-butylphenyl)-3-(1-ethylcyclohexyl)-2-fluoropropanamide (2ae)

According to the **General Procedure A**, the title compound was isolated by flash

chromatography (Petroleum ether: EtOAc = 25:1) as a white solid (24.9 mg, 64%, 92% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.0 Hz, 1H), 7.44 (d, *J* = 1.6 Hz, 2H), 7.22 (t, *J* = 1.6 Hz, 1H), 5.07 (dd, *J* = 51.3, 9.2 Hz, 1H), 2.10 (dd, *J* = 45.8, 15.8 Hz, 1H), 1.85 (m, 1H), 1.55 – 1.43 (m, 6H), 1.40 (m, 6H), 1.32 (s, 18H), 0.86 (t, *J* = 7.5 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.43 – -181.75 (m).

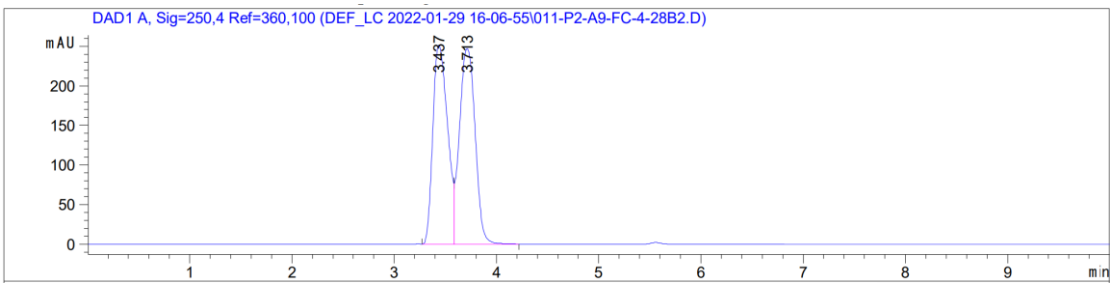
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.02 (d, *J* = 18.2 Hz), 151.85, 136.30, 118.99, 114.39, 90.42 (d, *J* = 187.3 Hz), 35.81, 35.27, 34.99, 34.75, 31.41, 26.32, 21.54, 21.50, 7.31.

HRMS (ESI): $C_{25}H_{40}FNNaO^+$ ($M+Na^+$): 412.2986, found: 412.2983.

$[\alpha]_D^{25}$ = -26.36 (c = 1.96, $CHCl_3$).

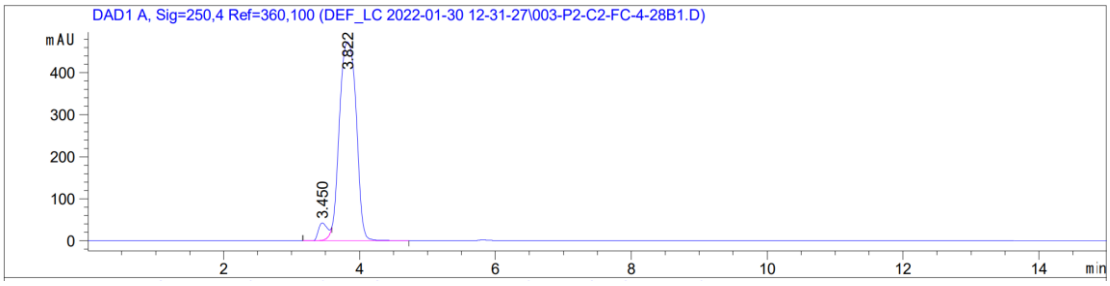
HPLC: The ee was determined to be 92% on a CHIRALPAK IB column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 98:2 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 3.5 min, t_R (minor) = 3.8 min.

2ae racemic

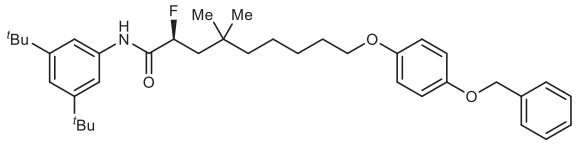


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.437	BV	0.1602	2506.65356	251.61015	48.7072
2	3.713	VB	0.1707	2639.72021	246.98276	51.2928

2ae enantioenriched, 92% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.450	BV E	0.1363	352.74707	41.02591	4.1349
2	3.822	VB R	0.2855	8178.32520	473.41901	95.8651



(*S*)-9-(4-(benzyloxy)phenoxy)-*N*-(3,5-di-*tert*-butylphenyl)-2-fluoro-4,4-dimethyl-nonanamide (2af)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 20:1) as a white solid (34.2 mg, 58%, 93% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.0 Hz, 1H), 7.44 – 7.29 (m, 7H), 7.22 (s, 1H), 6.93 – 6.79 (m, 4H), 5.18 – 4.98 (m, 3H), 3.91 (t, *J* = 6.5 Hz, 2H), 2.05 (dd, *J* = 45.5, 15.4 Hz, 1H), 1.85 – 1.71 (m, 3H), 1.47 – 1.40 (m, 2H), 1.38 – 1.34 (m, 4H), 1.32 (s, 18H), 1.00 (s, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.29 – -181.62 (m).

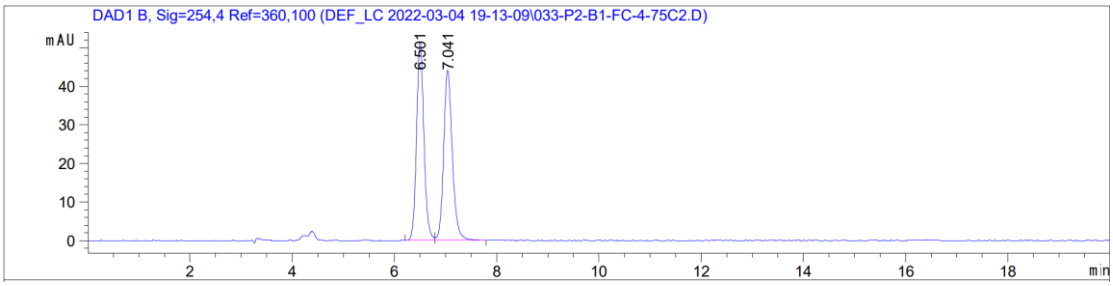
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.78 (d, *J* = 18.1 Hz), 153.50, 152.87, 151.86, 137.35, 136.24, 128.55, 127.88, 127.50, 119.05, 115.82, 115.42, 114.45, 90.75 (d, *J* = 187.2 Hz), 70.71, 68.60, 43.99 (d, *J* = 18.6 Hz), 42.45, 34.99, 32.59, 31.40, 29.42, 27.47, 27.19, 26.94, 23.78.

HRMS (ESI): $C_{38}H_{52}FNNaO_3^+$ ($M+Na^+$): 612.3823, found: 612.3818.

$[\alpha]_D^{25}$ = -14.94 (c = 1.16, $CHCl_3$).

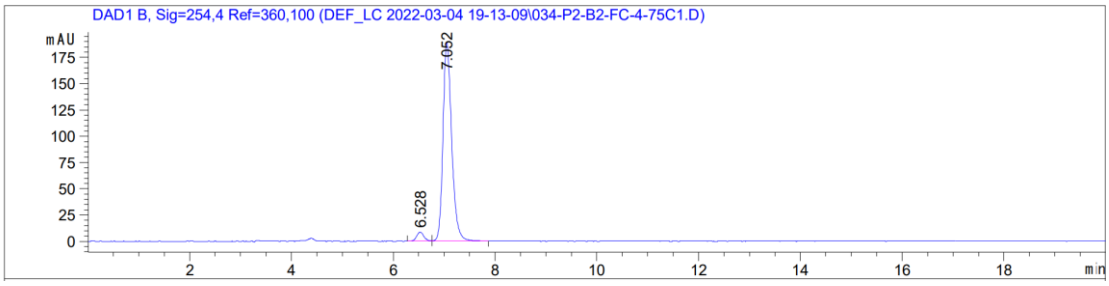
HPLC: The ee was determined to be 93% on a CHIRALPAK IB column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 88:20 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 7.1 min, t_R (minor) = 6.5 min.

2af racemic

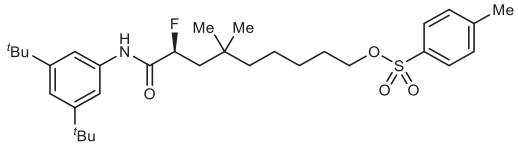


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.501	BV	0.1530	515.77118	51.41568	49.7474
2	7.041	VB	0.1797	521.00891	44.14527	50.2526

2af enantioenriched, 93% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.528	BV	0.1574	87.22022	8.66550	3.7353
2	7.052	VB	0.1783	2247.83618	189.63815	96.2647



(*S*)-9-((3,5-di-*tert*-butylphenyl)amino)-8-fluoro-6,6-dimethyl-9-oxononyl 4methyl-benzenesulfonate (2ag)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (34.3 mg, 61%, 92% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 6.9 Hz, 1H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 1.7 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.21 (t, *J* = 1.6 Hz, 1H), 5.05 (dd, *J* = 51.3,

9.2 Hz, 1H), 4.08 – 3.97 (m, 2H), 2.44 (s, 3H), 2.01 (dd, J = 44.8, 15.4 Hz, 1H), 1.83 – 1.71 (m, 1H), 1.70 – 1.63 (m, 2H), 1.32 (s, 18H), 1.28 – 1.23 (m, 6H), 0.96 (d, J = 2.5 Hz, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.52 – -181.85 (m).

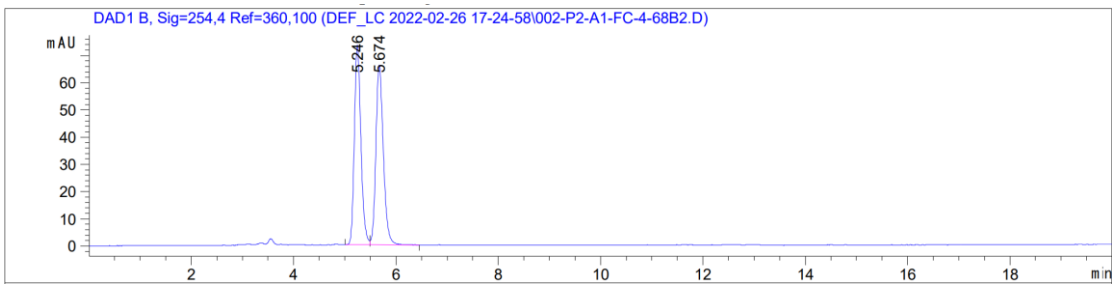
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.73 (d, J = 18.1 Hz), 151.84, 144.68, 136.25, 133.20, 129.85, 127.91, 119.05, 114.46, 90.67 (d, J = 187.5 Hz), 70.59, 43.76 (d, J = 18.5 Hz), 42.10, 34.98, 32.53, 31.39, 28.72, 27.47, 27.23, 26.09, 23.24, 21.66.

HRMS (ESI): $C_{32}H_{48}FNNaO_4S^+$ ($M+Na^+$): 584.3180, found: 584.3180.

$[\alpha]_D^{25}$ = -17.28 (c = 1.09, $CHCl_3$).

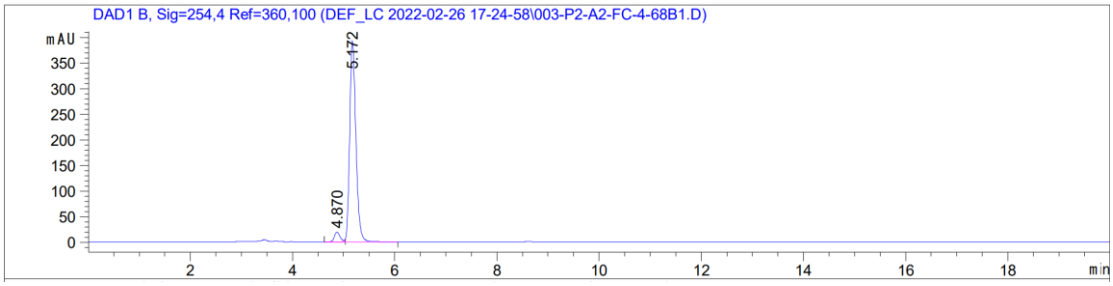
HPLC: The ee was determined to be 92% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 5.2 min, t_R (minor) = 4.9 min.

2ag racemic

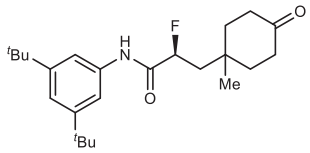


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.246	BV	0.1358	653.34290	73.45097	49.4856
2	5.674	VB	0.1557	666.92505	66.09911	50.5144

2ag enantioenriched, 92% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.870	BV E	0.1168	144.95938	19.05441	4.2001
2	5.172	VB R	0.1284	3306.35596	391.97327	95.7999



(*S*)-*N*-(3,5-di-*tert*-butylphenyl)-2-fluoro-3-(1-methyl-4-oxocyclohexyl) propenamide (2ah)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 15:1) as a white solid (23.4 mg, 60%, 90% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 6.6 Hz, 1H), 7.43 (d, *J* = 1.5 Hz, 2H), 7.23 (t, *J* = 1.5 Hz, 1H), 5.17 (dd, *J* = 51.2, 9.0 Hz, 1H), 2.46 – 2.35 (m, 4H), 2.26 (dd, *J* = 43.4, 15.6 Hz, 1H), 2.07 – 1.93 (m, 1H), 1.88 – 1.73 (m, 4H), 1.32 (s, 18H), 1.24 (s, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.27 – -181.60 (m).

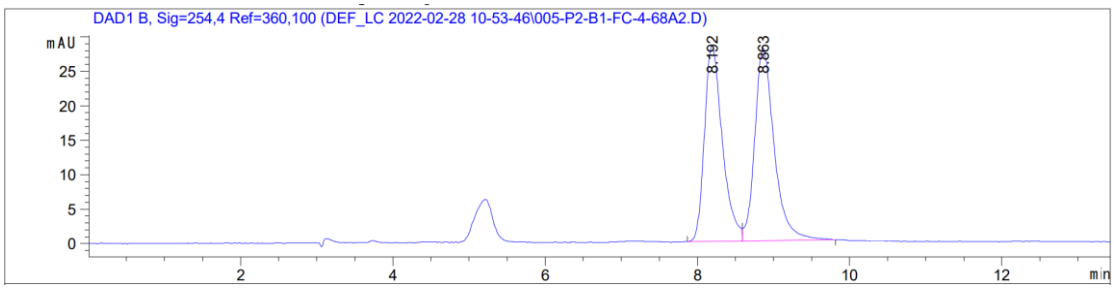
^{13}C NMR (101 MHz, $CDCl_3$) δ 211.54, 168.16 (d, *J* = 18.0 Hz), 151.94, 136.03, 119.27, 114.53, 90.20 (d, *J* = 188.2 Hz), 42.73 (d, *J* = 18.8 Hz), 37.61, 37.49, 37.43, 37.30 (d, *J* = 1.9 Hz), 35.00, 32.11, 31.39, 24.10.

HRMS (ESI): $C_{24}H_{36}FNNaO_2^+$ ($M+Na^+$): 412.2622, found: 412.2624.

$[\alpha]_D^{25}$ = -19.08 (c = 1.13, $CHCl_3$).

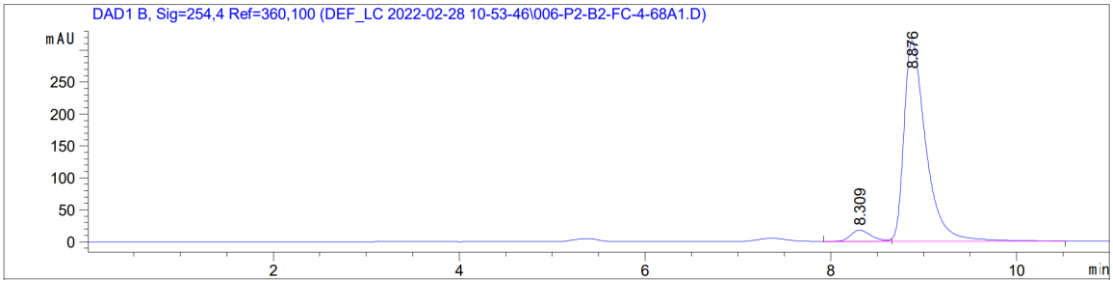
HPLC: The ee was determined to be 90% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 8.9 min, t_R (minor) = 8.3 min.

2ah racemic

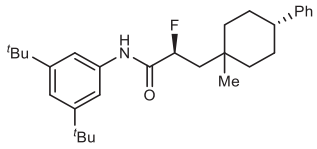


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.192	BV	0.2480	463.63232	28.47473	48.2164
2	8.863	VB	0.2698	497.93372	27.95252	51.7836

2ah enantioenriched, 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.309	BV E	0.2329	265.50064	17.71222	4.9199
2	8.876	VB R	0.2447	5130.95410	313.91855	95.0801



(2*S*)-*N*-(3,5-di-*tert*-butylphenyl)-2-fluoro-3-(1-methyl-4-phenylcyclohexyl)-propanamide (2ai)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 20:1) as a white solid (29.8 mg, 66%, 88% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.0 Hz, 1H), 7.45 (d, *J* = 1.7 Hz, 2H), 7.33 – 7.26 (m, 2H), 7.26 – 7.22 (m, 3H), 7.21 – 7.15 (m, 1H), 5.21 – 5.04 (m, 1H), 2.54 –

2.43 (m, 1H), 2.22 (dd, J = 45.6, 15.3 Hz, 1H), 2.13 – 2.00 (m, 1H), 1.83 – 1.64 (m, 6H), 1.48 – 1.37 (m, 2H), 1.33 (s, 18H), 1.10 (s, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.62 – -181.95 (m).

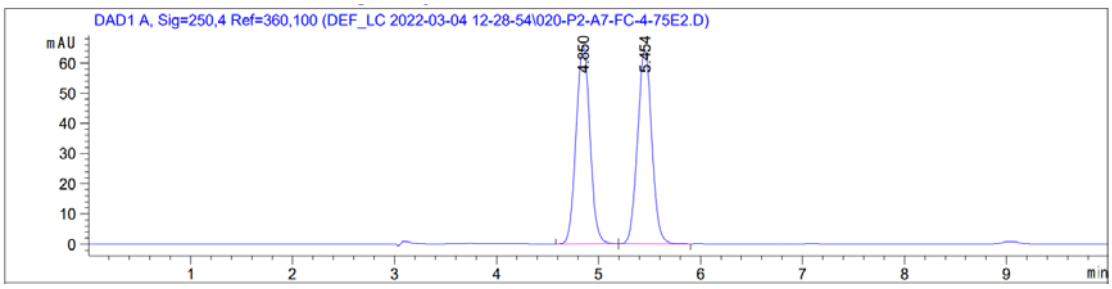
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.80 (d, J = 17.9 Hz), 151.89, 147.18, 136.23, 128.34, 126.92, 125.97, 119.10, 114.47, 90.78 (d, J = 187.8 Hz), 44.19, 38.66, 38.47, 38.42, 38.33, 35.01, 31.90, 31.42, 29.73 (d, J = 5.4 Hz), 29.24.

HRMS (ESI): $C_{30}H_{42}FNNaO^+$ ($M+Na^+$): 474.3143, found: 474.3142.

$[\alpha]_D^{25}$ = -18.31 (c = 1.16, $CHCl_3$).

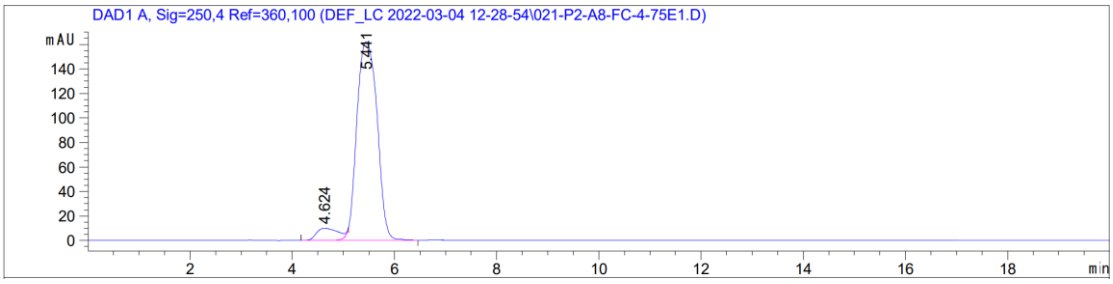
HPLC: The ee was determined to be 88% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 98:2 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 5.4 min, t_R (minor) = 4.6 min.

2ai racemic

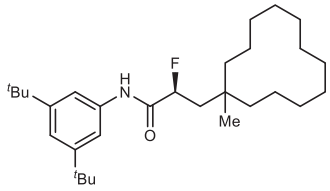


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.850	BB	0.1478	163.70116	17.38821	49.6209
2	5.454	BB	0.1535	166.20236	17.07898	50.3791

2ai enantioenriched, 88% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.624	BV E	0.4345	285.86191	9.85235	6.0163
2	5.441	VB R	0.4576	4465.57178	161.98570	93.9837



(*S*)-*N*-(3,5-di-*tert*-butylphenyl)-2-fluoro-3-(1-methylcyclododecyl)propenamide (2aj)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 20:1) as a white solid (24.8 mg, 54%, 93% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.1 Hz, 1H), 7.43 (d, *J* = 1.6 Hz, 2H), 7.21 (t, *J* = 1.6 Hz, 1H), 5.12 (dd, *J* = 51.3, 9.7 Hz, 1H), 2.03 (dd, *J* = 45.8, 15.5 Hz, 1H), 1.77 – 1.65 (m, 1H), 1.41 – 1.28 (m, 40H), 0.97 (d, *J* = 1.3 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -180.24 – -180.56 (m).

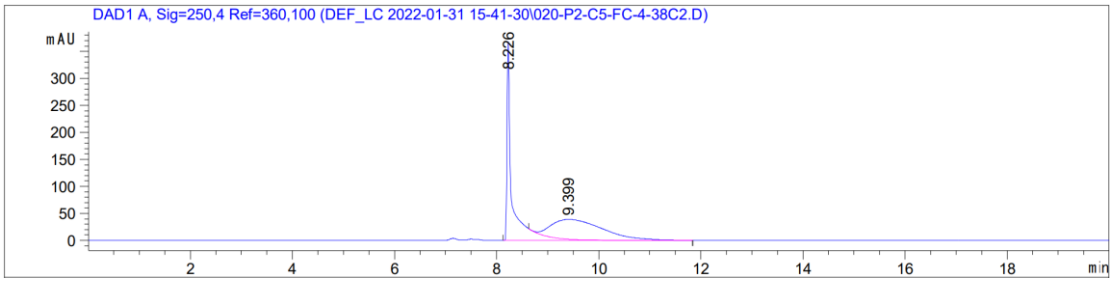
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.02 (d, *J* = 18.0 Hz), 151.90, 136.33, 119.06, 114.44, 90.65 (d, *J* = 187.3 Hz), 43.45 (d, *J* = 18.4 Hz), 35.28, 35.21, 35.04, 33.82, 31.45, 29.79, 26.85, 26.81, 26.21, 25.37, 22.74, 22.70, 22.15, 19.19, 19.03.

HRMS (ESI): $C_{30}H_{50}FNNaO^+$ ($M+Na^+$): 482.3769, found: 482.3758.

$[\alpha]_D^{25}$ = -18.36 (c = 10.2, $CHCl_3$).

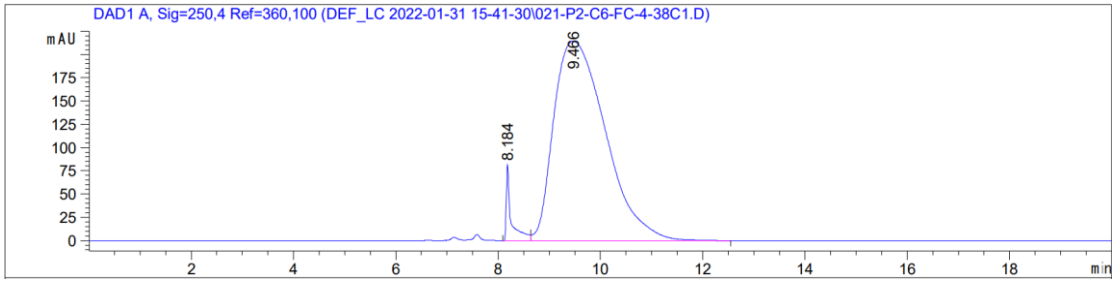
HPLC: The ee was determined to be 93% on a CHIRALPAK IC column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 100:1 at a flow rate 0.5 mL/min. Retention times: t_R (major) = 9.5 min, t_R (minor) = 8.2 min.

2aj racemic

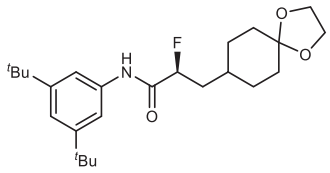


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.226	BV R	0.0919	2540.90674	370.96240	49.3927
2	9.399	VB E	0.9727	2603.39014	36.47482	50.6073

2aj enantioenriched, 93% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.184	BV	0.0916	540.20013	81.19943	3.4629
2	9.466	VB	1.1351	1.50593e4	214.48940	96.5371



***N*-(3,5-di-tert-butylphenyl)-2-fluoro-3-(1,4-dioxaspiro[4.5]decan-8-yl)propan-amide (2ak)**

According to the **General Procedure B**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 5:1) as a white solid (28.1 mg, 67%, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 6.9 Hz, 1H), 7.42 (d, *J* = 1.8 Hz, 2H), 7.22

(t, J = 1.7 Hz, 1H), 5.21 – 4.86 (m, 1H), 3.96 – 3.92 (m, 4H), 2.12 – 1.93 (m, 1H), 1.93 – 1.71 (m, 5H), 1.71 – 1.63 (m, 1H), 1.61 – 1.51 (m, 2H), 1.44 – 1.35 (m, 2H), 1.32 (s, 18H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -185.45 – -185.75 (m).

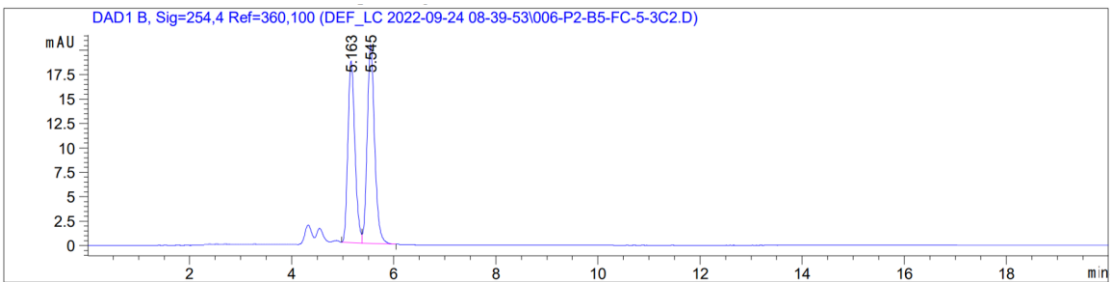
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.29 (d, J = 17.8 Hz), 151.98, 136.25, 119.24, 114.70, 108.81, 91.15 (d, J = 187.3 Hz), 64.39, 64.37, 38.96 (d, J = 19.6 Hz), 35.09, 34.55, 34.38, 32.93 (d, J = 1.6 Hz), 31.50, 30.77, 29.50.

HRMS (ESI): $C_{25}H_{38}FNNaO_3^+$ ($M+Na^+$): 442.2728, found: 442.2726.

$[\alpha]_D^{25}$ = -27.66 (c = 1.09, $CHCl_3$).

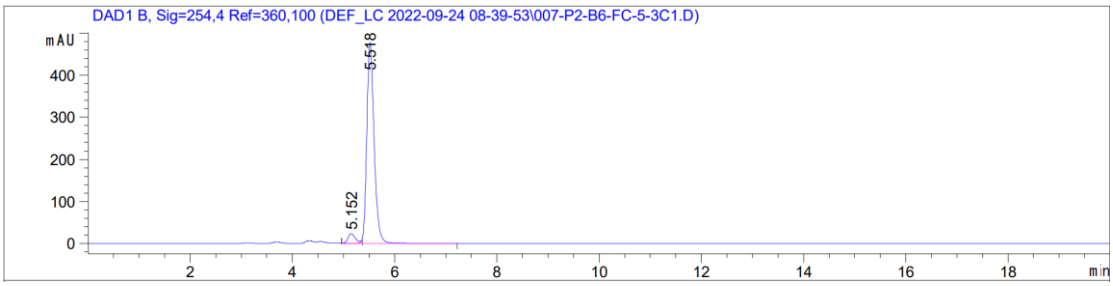
HPLC: The ee was determined to be 91% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 5.5 min, t_R (minor) = 5.2 min.

2ak racemic

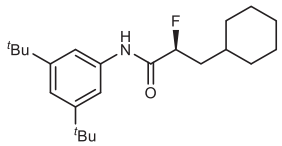


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.163	BV	0.1477	178.34412	18.63316	46.3199
2	5.545	VB	0.1565	206.68282	20.35409	53.6801

2ak enantioenriched, 91% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.152	BV E	0.1496	225.58128	23.16136	4.5338
2	5.518	VB R	0.1520	4749.95947	477.83179	95.4662



(*S*)-3-cyclohexyl-*N*-(3,5-di-*tert*-butylphenyl)-2-fluoropropanamide (2al)

According to the **General Procedure B**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 20:1) as a white solid (18.8 mg, 52%, 94% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 6.4 Hz, 1H), 7.43 (d, *J* = 1.7 Hz, 2H), 7.23 (t, *J* = 1.7 Hz, 1H), 5.16 – 4.97 (m, 1H), 2.03 – 1.69 (m, 6H), 1.65 – 1.55 (m, 1H), 1.40 – 1.14 (m, 22H), 1.10 – 0.92 (m, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -185.49 – -185.80 (m).

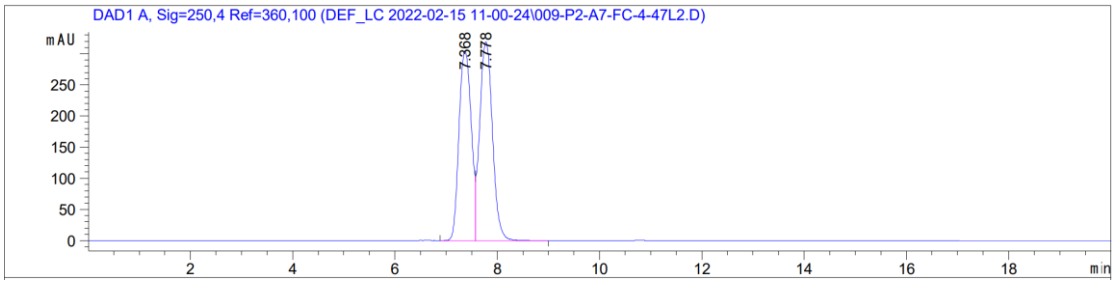
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.54 (d, *J* = 17.8 Hz), 151.83, 136.21, 119.07, 114.59, 90.82 (d, *J* = 186.9 Hz), 40.04 (d, *J* = 19.6 Hz), 34.99, 33.91, 33.82, 32.28, 31.41, 26.36, 26.21, 26.01.

HRMS (ESI): $C_{23}H_{36}FNNaO^+$ ($M+Na^+$): 384.2673, found: 384.2673.

$[\alpha]_D^{25}$ = -28.02 (c =1.65, $CHCl_3$).

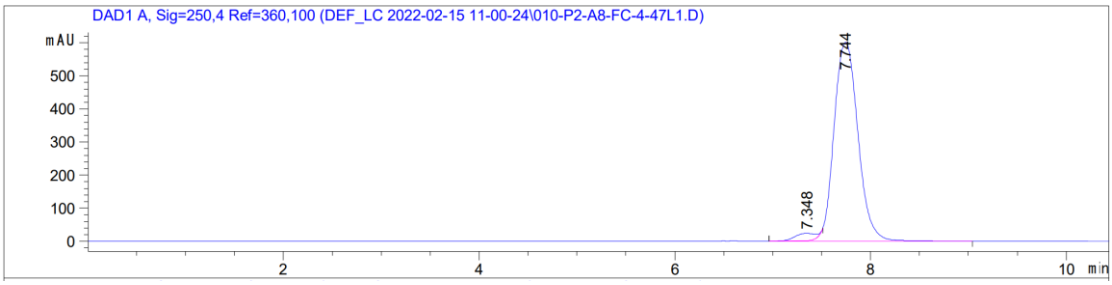
HPLC: The ee was determined to be 94% on a CHIRALPAK IC column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 100:1 at a flow rate 0.5 mL/min. Retention times: t_R (major) = 7.7 min, t_R (minor) = 7.3 min.

2al racemic

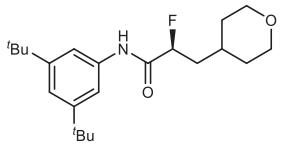


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.368	BV	0.2684	5062.52393	303.81210	47.7373
2	7.778	VB	0.2726	5542.44580	319.20441	52.2627

2al enantioenriched, 94% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.348	BV E	0.2207	313.60352	22.21111	2.9834
2	7.744	VB R	0.2699	1.01982e4	601.25464	97.0166



(*S*)-*N*-(3,5-di-*tert*-butylphenyl)-2-fluoro-3-(tetrahydro-2H-pyran-4-yl) propenamide (2am)

According to the **General Procedure B**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 15:1) as a white solid (19.3 mg, 53%, 87% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 6.3 Hz, 1H), 7.42 (d, *J* = 1.6 Hz, 2H), 7.23 (t, *J* = 1.6 Hz, 1H), 5.17 – 4.99 (m, 1H), 4.04 – 3.90 (m, 2H), 3.42 (t, *J* = 11.3 Hz, 2H), 2.12 – 1.81 (m, 3H), 1.77 – 1.64 (m, 2H), 1.49 – 1.36 (m, 2H), 1.34 – 1.30 (m, 18H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -185.72 – -186.03 (m).

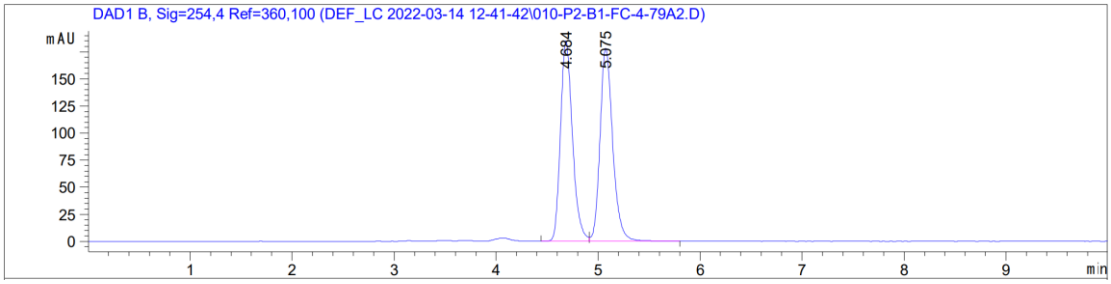
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.01 (d, *J* = 17.8 Hz), 151.91, 136.06, 119.22, 114.59, 90.45 (d, *J* = 187.6 Hz), 67.85, 67.76, 39.42 (d, *J* = 19.5 Hz), 34.99, 33.34, 32.32, 31.55, 31.39.

HRMS (ESI): $C_{22}H_{34}FNNaO_2^+$ ($M+Na^+$): 386.2466, found: 386.2463.

$[\alpha]_D^{25}$ = -23.91 (c = 0.95, $CHCl_3$).

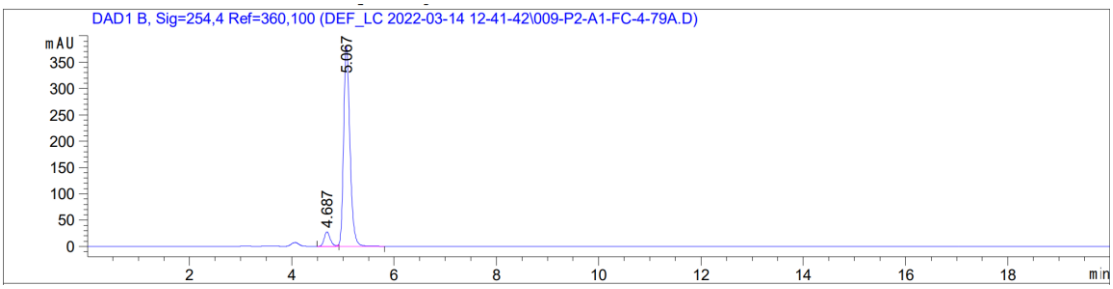
HPLC: The ee was determined to be 87% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 5.1 min, t_R (minor) = 4.7 min.

2am racemic

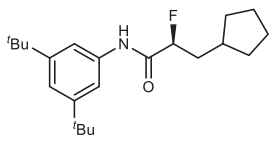


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.684	BV	0.1251	1509.29224	185.16435	49.5232
2	5.075	VB	0.1309	1538.35632	177.93130	50.4768

2am enantioenriched, 87% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.687	BV E	0.1255	225.71878	27.58191	6.4767
2	5.067	VB R	0.1315	3259.35059	381.98383	93.5233



(*S*)-3-cyclopentyl-*N*-(3,5-di-*tert*-butylphenyl)-2-fluoropropanamide (2an)

According to the **General Procedure B**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 20:1) as a white solid (19.5 mg, 52%, 92% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 6.3 Hz, 1H), 7.43 (d, *J* = 1.7 Hz, 2H), 7.23 (t, *J* = 1.7 Hz, 1H), 5.10 – 4.92 (m, 1H), 2.14 – 1.95 (m, 3H), 1.92 – 1.80 (m, 2H), 1.71 – 1.60 (m, 2H), 1.60 – 1.49 (m, 2H), 1.33 (s, 18H), 1.27 – 1.12 (m, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -186.62 – -186.93 (m).

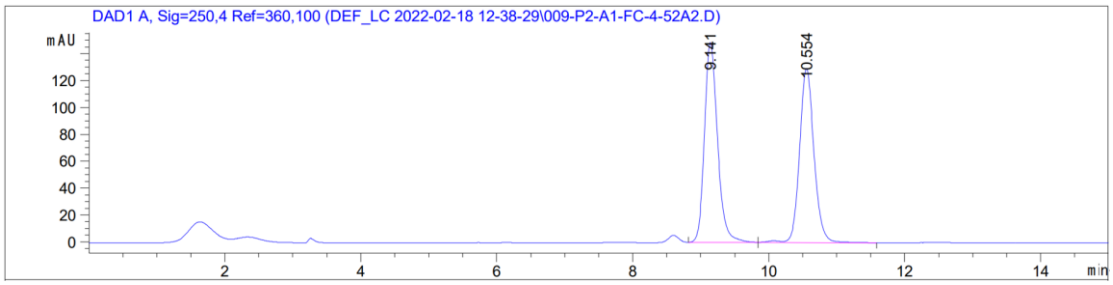
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.28 (d, *J* = 17.9 Hz), 151.85, 136.20, 119.08, 114.53, 92.21 (d, *J* = 187.2 Hz), 38.47 (d, *J* = 19.4 Hz), 36.23, 34.99, 33.09, 32.19, 31.40, 25.06, 24.92.

HRMS (ESI): $C_{22}H_{34}FNNaO^+$ ($M+Na^+$): 370.2517, found: 370.2514.

$[\alpha]_D^{25}$ = -16.23 (c = 0.96, $CHCl_3$).

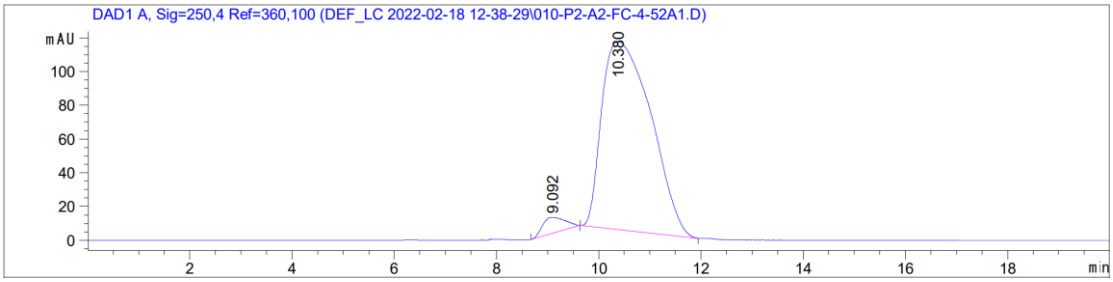
HPLC: The ee was determined to be 92% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 200:1 at a flow rate 0.5 mL/min. Retention times: t_R (major) = 10.4 min, t_R (minor) = 9.1 min.

2an racemic

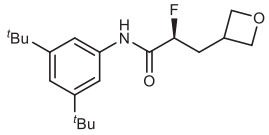


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.141	VB	0.2011	1977.98621	148.76534	50.9839
2	10.554	VB R	0.2241	1901.64404	129.36311	49.0161

2an enantioenriched, 92% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.092	BB	0.4472	291.94254	9.58969	3.7566
2	10.380	BB	0.9672	7479.60449	111.70806	96.2434



(*S*)-*N*-(3,5-di-*tert*-butylphenyl)-2-fluoro-3-(oxetan-3-yl)propenamide (2ao)

According to the **General Procedure B**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 5:1) as a white solid (12.1 mg, 36%, 93% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 6.5 Hz, 1H), 7.33 (d, *J* = 1.7 Hz, 2H), 7.17 (t, *J* = 1.8 Hz, 1H), 5.09 – 4.81 (m, 1H), 4.81 – 4.71 (m, 2H), 4.44 (q, *J* = 6.0 Hz, 2H), 3.33 – 3.17 (m, 1H), 2.52 – 2.20 (m, 2H), 1.26 (s, 18H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -188.66 – -188.95 (m).

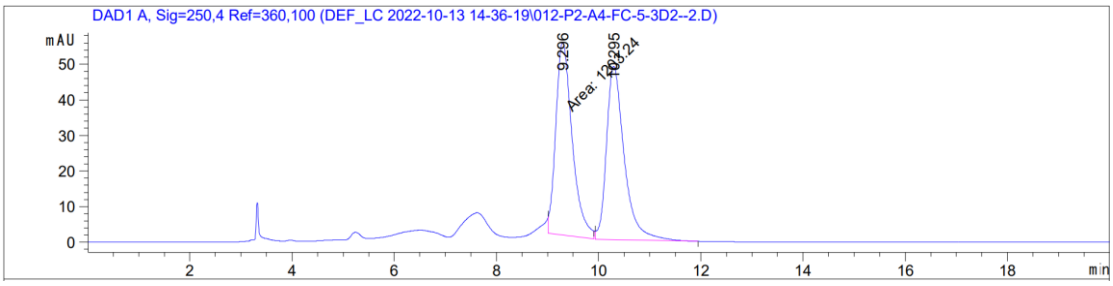
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.19 (d, *J* = 17.8 Hz), 152.10, 135.99, 119.51, 114.73, 91.29 (d, *J* = 187.9 Hz), 77.37, 77.24, 36.02 (d, *J* = 19.3 Hz), 35.12, 31.89 (d, *J* = 2.6 Hz), 31.51.

HRMS (ESI): $C_{20}H_{30}FNNaO_2^+$ ($M+Na^+$): 358.2153, found: 358.2152.

$[\alpha]_D^{25}$ = -25.42 (c = 1.29, $CHCl_3$).

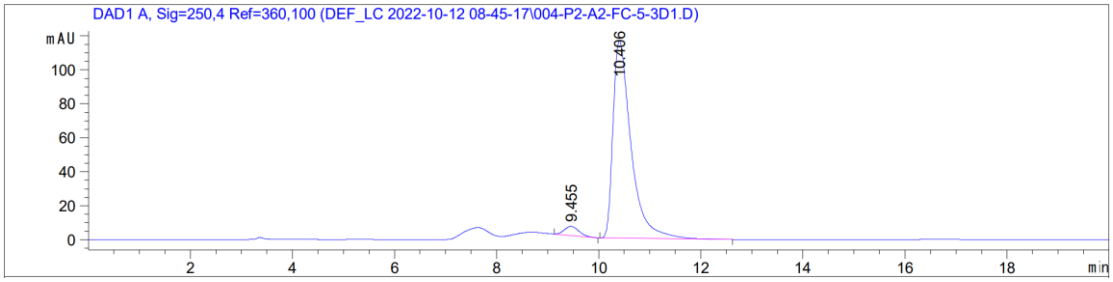
HPLC: The ee was determined to be 93% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 97:3 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 10.4 min, t_R (minor) = 9.5 min.

2ao racemic

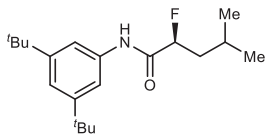


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.296	FM	0.3710	1203.24377	54.04847	50.4614
2	10.295	VB	0.3671	1181.24097	48.68566	49.5386

2ao enantioenriched, 93% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.455	BB	0.3076	106.16226	5.34818	3.5738
2	10.406	BB	0.3693	2864.38184	116.32984	96.4262



(*S*)-*N*-(3,5-di-*tert*-butylphenyl)-2-fluoro-4-methylpentanamide (2ap)

According to the **General Procedure B**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 20:1) as a white solid (21.2 mg, 66%, 87% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 6.0 Hz, 1H), 7.43 (d, *J* = 1.7 Hz, 2H), 7.22 (t, *J* = 1.7 Hz, 1H), 5.12 – 4.95 (m, 1H), 2.03 – 1.74 (m, 3H), 1.33 (s, 18H), 1.07 – 0.94 (m, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -186.09 – -186.40 (m).

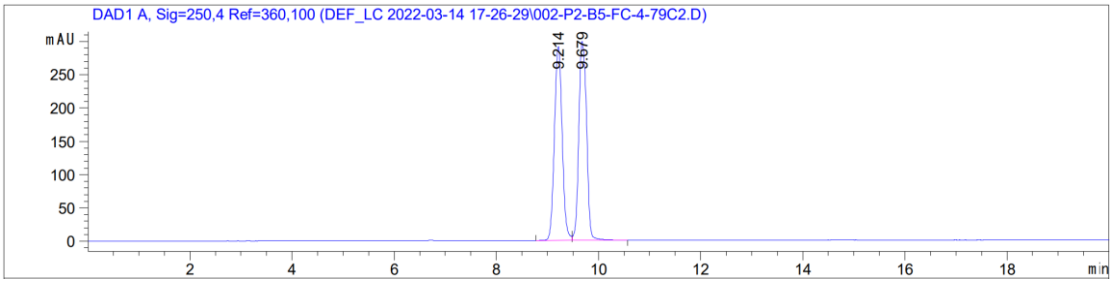
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.41 (d, J = 17.9 Hz), 151.85, 136.19, 119.09, 114.55, 91.26 (d, J = 186.9 Hz), 41.28 (d, J = 19.5 Hz), 34.99, 31.40, 24.71 (d, J = 1.5 Hz), 23.17, 21.67.

HRMS (ESI): $C_{20}H_{32}FNNaO^+$ ($M+Na^+$): 344.2360, found: 344.2364.

$[\alpha]_D^{25}$ = -1974 (c = 1.25, $CHCl_3$).

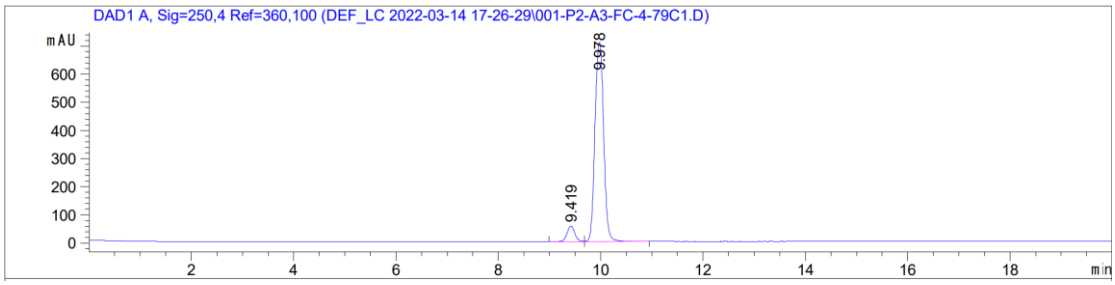
HPLC: The ee was determined to be 87% on a CHIRALPAK IB column at 250 nm, 25 °C, with hexane: ^{i}PrOH = 100:1 at a flow rate 0.5 mL/min. Retention times: t_R (major) = 10.0 min, t_R (minor) = 9.4 min.

2ap racemic

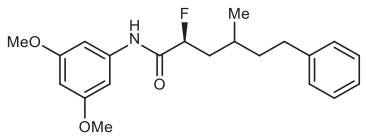


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.214	BV	0.1643	3052.15991	291.19312	49.1286
2	9.679	VB	0.1714	3160.43433	298.82938	50.8714

2ap enantioenriched, 87% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.419	BV	0.1629	578.18561	54.88225	6.5203
2	9.978	VB	0.1866	8289.23535	708.21497	93.4797



(2*S*)-*N*-(3,5-dimethoxyphenyl)-2-fluoro-4-methyl-6-phenylhexanamide (2aq)

According to the **General Procedure B**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (12.2 mg, 34%, 90% ee, 86% ee, d.r. 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (t, *J* = 6.9 Hz, 1H), 7.32 – 7.25 (m, 2H), 7.22 – 7.14 (m, 3H), 6.82 (dd, *J* = 4.4, 2.2 Hz, 2H), 6.29 (dd, *J* = 3.7, 2.1 Hz, 1H), 5.15 – 4.94 (m, 1H), 3.79 (s, 6H), 2.77 – 2.54 (m, 2H), 2.11 – 1.94 (m, 1H), 1.90 – 1.74 (m, 2H), 1.68 (m, 1H), 1.63 – 1.47 (m, 1H), 1.08 (d, *J* = 6.2 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -184.96 – -185.27 (m), -186.75 – -187.06 (m).

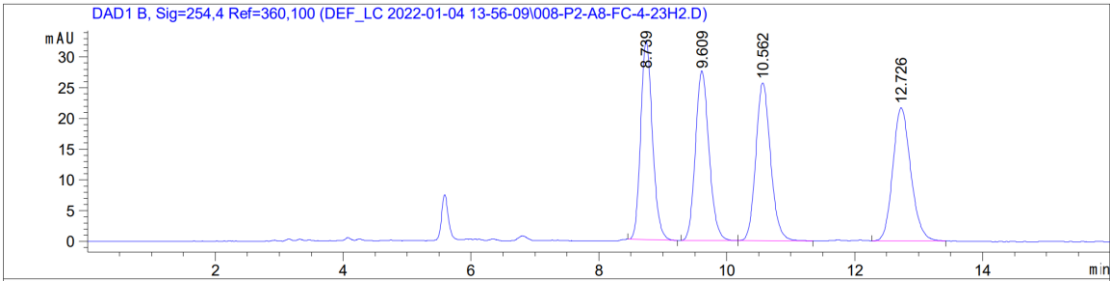
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.56 (d, *J* = 9.1 Hz), 168.38 (d, *J* = 9.1 Hz), 161.15, 142.40, 138.50, 128.39, 128.38, 128.34, 125.78 (d, *J* = 1.9 Hz), 98.22, 97.37, 91.97 (d, *J* = 47.5 Hz), 90.11 (d, *J* = 47.4 Hz), 55.44, 39.51 (d, *J* = 8.6 Hz), 39.32 (d, *J* = 9.1 Hz), 39.20, 38.06, 33.20, 33.13, 29.56 (d, *J* = 1.1 Hz), 28.86, 19.98, 18.86.

HRMS (ESI): $C_{21}H_{27}FNO_3^+$ ($M+H^+$): 360.1969, found: 360.1975.

$[\alpha]_D^{25}$ = -8.93 (c = 1.00, $CHCl_3$).

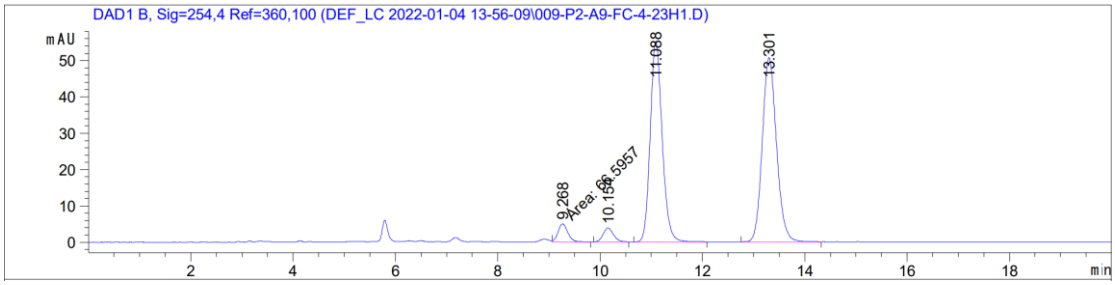
HPLC: The ee was determined to be 90% and 86% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 11.1 min and 13.3 min, t_R (minor) = 9.3 min and 10.2 min. dr = 1:1

2aq racemic

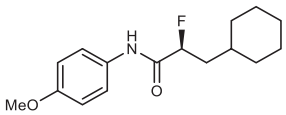


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.739	BB	0.1967	413.14038	32.41692	24.8999
2	9.609	BB	0.2267	408.70285	27.61556	24.6324
3	10.562	BB	0.2478	413.23358	25.67393	24.9055
4	12.726	BB	0.3022	424.12854	21.68081	25.5621

2aq enantioenriched, 90% and 86% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.268	FM	0.2228	66.59570	4.98266	3.3421
2	10.154	BB	0.2154	53.66077	3.83070	2.6930
3	11.088	BB	0.2492	894.49445	55.16242	44.8900
4	13.301	BB	0.2990	977.88617	50.70010	49.0750



(*S*)-3-cyclohexyl-2-fluoro-*N*-(4-methoxyphenyl)propenamide (2ar)

According to the **General Procedure B**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (16.5 mg, 59%, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 6.7 Hz, 1H), 7.50 – 7.42 (m, 2H), 6.92 – 6.82 (m, 2H), 5.05 (m, 1H), 3.79 (s, 3H), 2.11 – 1.73 (m, 3H), 1.77 – 1.51 (m, 5H), 1.34 – 1.22 (m, 1H), 1.25 – 1.08 (m, 2H), 1.08 – 0.97 (m, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -185.88 – -186.19 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.53 (d, *J* = 17.9 Hz), 156.90, 129.99, 121.89, 114.35,

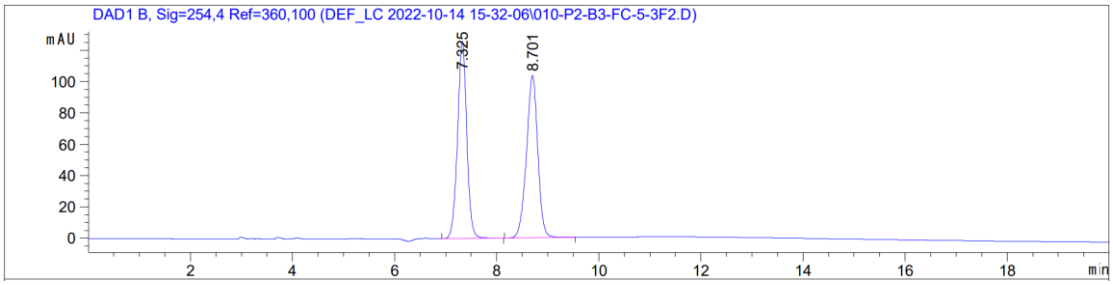
90.93 (d, J = 186.7 Hz), 55.59, 40.10 (d, J = 19.6 Hz), 34.04 (d, J = 1.6 Hz), 33.89, 32.42, 26.45, 26.32, 26.13.

HRMS (ESI): $C_{16}H_{22}FNNaO_2^+$ ($M+Na^+$): 302.1527, found: 302.1525.

$[\alpha]_D^{25}$ = -23.89 (c = 1.62, $CHCl_3$).

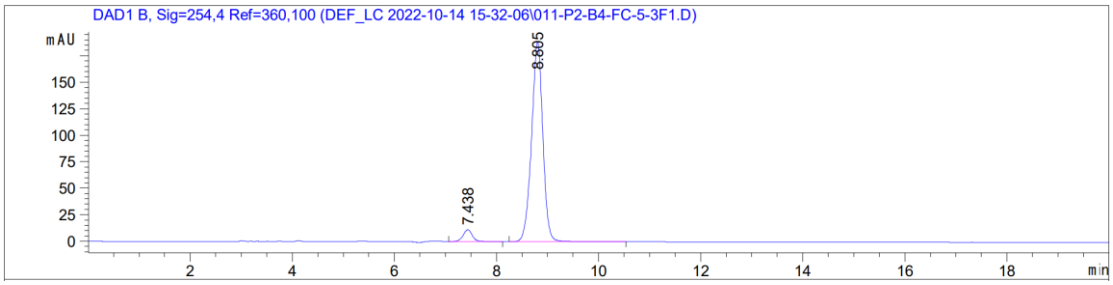
HPLC: The ee was determined to be 91% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 80:20 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 8.8 min, t_R (minor) = 7.4 min.

2ar racemic

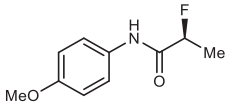


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.325	BB	0.1909	1582.79126	125.74104	49.7470
2	8.701	BB	0.2343	1598.89111	103.43224	50.2530

2ar enantioenriched, 91% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.438	BB	0.1904	140.10649	11.16628	4.6146
2	8.805	BB	0.2332	2896.05347	188.54523	95.3854



(*S*)-2-fluoro-*N*-(4-methoxyphenyl)propenamide (3a)

According to the **General Procedure C**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 5:1) as a white solid (18.7 mg, 95%, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.54 – 7.33 (m, 2H), 7.04 – 6.73 (m, 2H), 5.29 – 4.83 (m, 1H), 3.78 (s, 3H), 1.65 (dd, *J* = 24.9, 6.8 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -180.00 – -180.35 (m).

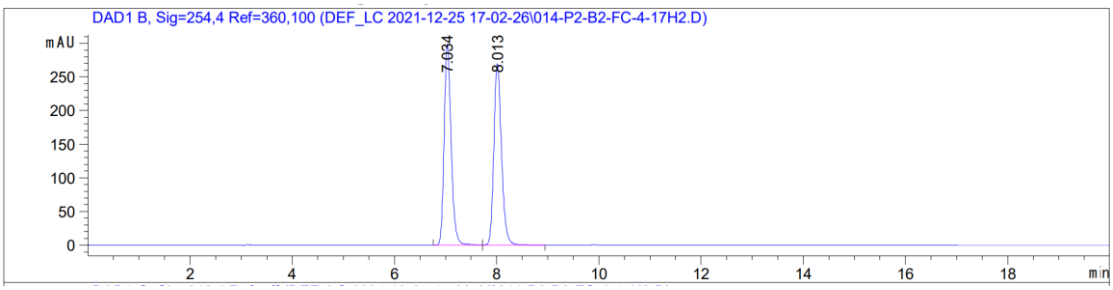
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.55 (d, *J* = 18.0 Hz), 156.90, 129.88, 121.90, 114.30, 89.01 (d, *J* = 184.3 Hz), 55.55, 18.54 (d, *J* = 21.4 Hz).

HRMS (ESI): $C_{10}H_{12}FNNaO_2^+$ ($M+Na^+$): 220.0744, found: 220.0745.

$[\alpha]_D^{25}$ = -21.35 (c = 1.55, $CHCl_3$).

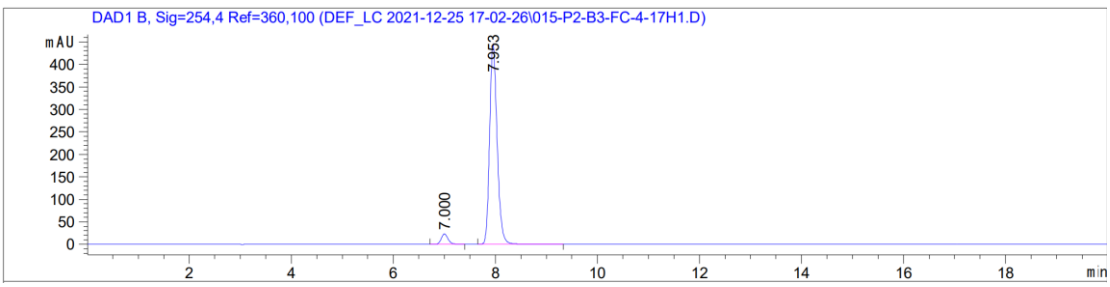
HPLC: The ee was determined to be 91% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 8.0 min, t_R (minor) = 7.0 min.

3a racemic

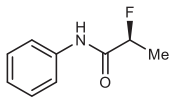


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.034	BB	0.1444	2819.13867	297.87738	50.0407
2	8.013	BB	0.1599	2814.55835	269.32309	49.9593

3a enantioenriched, 91% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.000	BB	0.1428	214.28000	22.98329	4.4897
2	7.953	BB	0.1576	4558.43164	444.79605	95.5103



(*S*)-2-fluoro-*N*-phenylpropanamide (3b)

According to the **General Procedure C**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (15.0 mg, 90%, 90% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.60 – 7.54 (m, 2H), 7.39 – 7.31 (m, 2H), 7.20 – 7.11 (m, 1H), 5.12 (m, 1H), 1.67 (dd, *J* = 24.9, 6.8 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -179.85 – -180.20 (m).

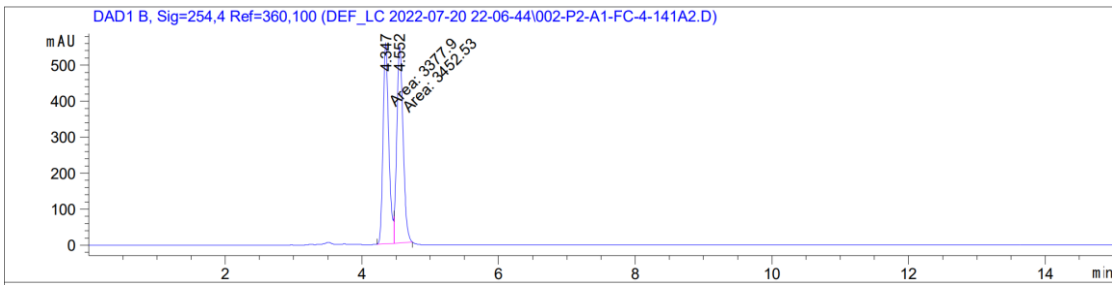
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.75 (d, *J* = 17.7 Hz), 136.82, 129.23, 125.06, 120.10, 89.03 (d, *J* = 184.1 Hz), 18.54 (d, *J* = 21.8 Hz).

HRMS (ESI): $C_9H_{10}FNNaO^+$ ($M+Na^+$): 190.0639, found: 190.0638.

$[\alpha]_D^{25}$ = -18.80 (c = 1.58, $CHCl_3$).

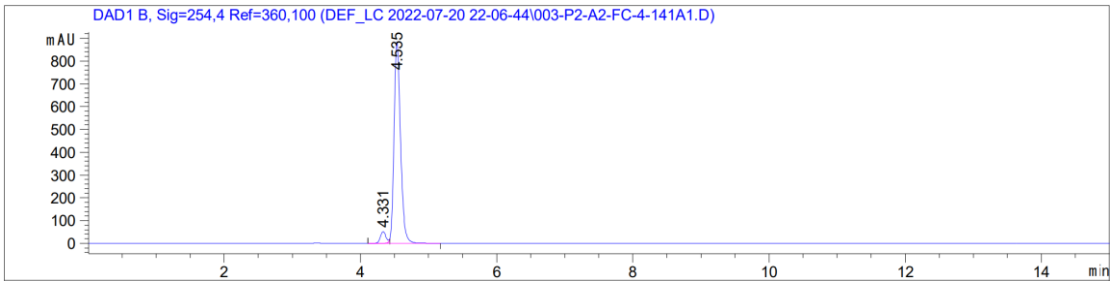
HPLC: The ee was determined to be 90% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 4.5 min, t_R (minor) = 4.3 min.

3b racemic

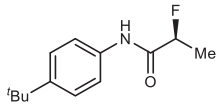


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.347	MF	0.1012	3377.89941	556.54901	49.4537
2	4.552	FM	0.1055	3452.52686	545.62634	50.5463

3b enantioenriched, 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.331	BV E	0.0889	294.55347	51.34468	4.8751
2	4.535	VB R	0.0998	5747.49170	884.46246	95.1249



(*S*)-*N*-(4-(*tert*-butyl)phenyl)-2-fluoropropanamide (3c)

According to the **General Procedure C**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (20.0 mg, 90%, 91% ee).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.53 – 7.45 (m, 2H), 7.41 – 7.33 (m, 2H), 5.28 – 4.86 (m, 1H), 1.67 (dd, *J* = 24.9, 6.8 Hz, 3H), 1.31 (s, 9H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -179.84 – -180.19 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.66 (d, *J* = 17.7 Hz), 148.09, 134.18, 126.04, 119.92, 89.04 (d, *J* = 184.4 Hz), 34.53, 31.45, 18.58 (d, *J* = 21.6 Hz).

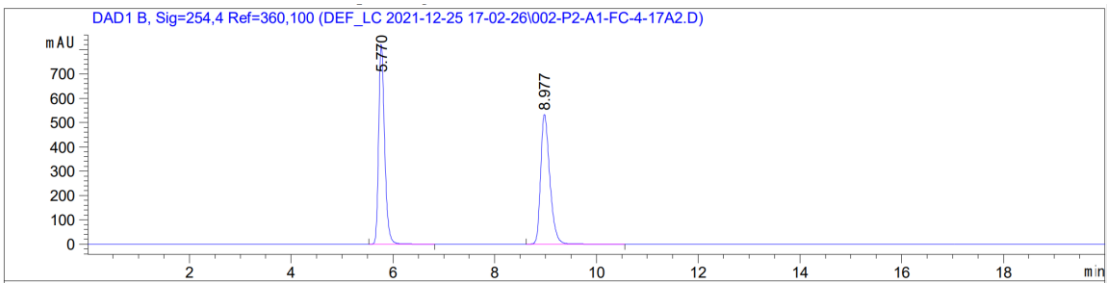
HRMS (ESI): $C_{13}H_{18}FNNaO^+$ ($M+Na^+$): 246.1265, found: 246.1266.

$[\alpha]_D^{25}$ = -31.41 (c = 1.80, $CHCl_3$).

HPLC: The ee was determined to be 91% on a CHIRALPAK IA column at 254 nm, 25

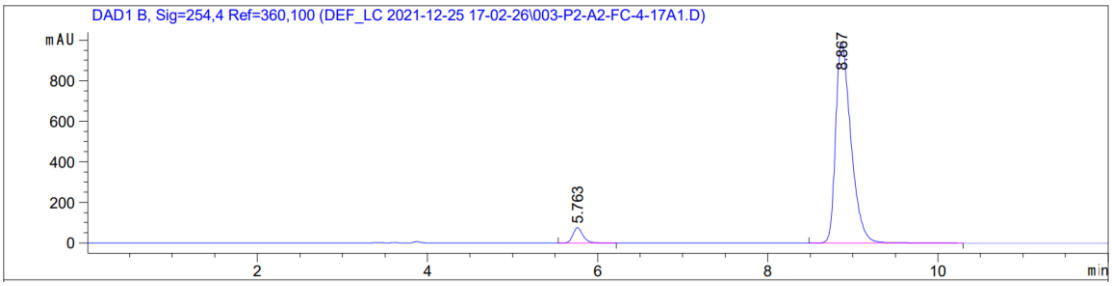
°C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 8.9 min, t_R (minor) = 5.8 min.

3c racemic

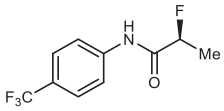


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.770	BB	0.1222	6629.34961	820.90961	49.8734
2	8.977	BB	0.1896	6663.00928	533.74323	50.1266

3c enantioenriched, 91% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.763	BB	0.1227	608.45740	74.95676	4.6943
2	8.867	BB	0.1874	1.23531e4	991.04382	95.3057



(*S*)-2-fluoro-*N*-(4-(trifluoromethyl)phenyl)propenamide (3d)

According to the **General Procedure C**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (20.9 mg, 89%, 88% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 – 8.06 (m, 1H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.59 (d,

J = 8.5 Hz, 2H), 5.37 – 4.84 (m, 1H), 1.67 (dd, J = 24.9, 6.9 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.25 (s), -180.17 – -180.52 (m).

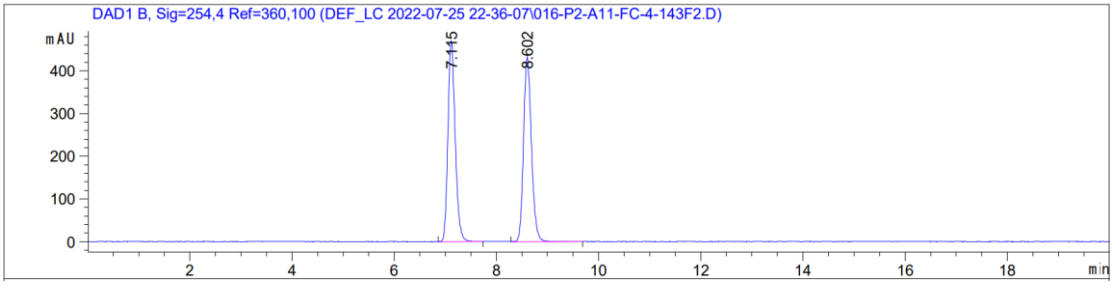
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.13 (d, J = 18.2 Hz), 139.90, 126.88 (q, J = 32.8 Hz), 126.49 (q, J = 3.8 Hz), 124.10 (q, J = 271.6 Hz), 119.80, 88.98 (d, J = 184.7 Hz), 18.42 (d, J = 21.3 Hz).

HRMS (ESI): $C_{10}H_9F_4NNaO^+$ ($M+Na^+$): 258.0512, found: 258.0516.

$[\alpha]_D^{25}$ = -19.57 (c = 1.88, $CHCl_3$).

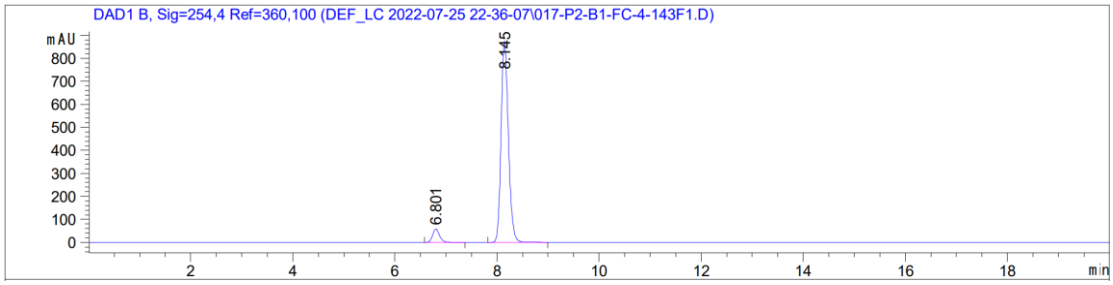
HPLC: The ee was determined to be 88% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 8.1 min, t_R (minor) = 6.8 min.

3d racemic

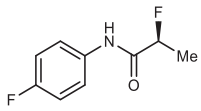


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.115	BB	0.1513	4646.30127	470.27045	49.9392
2	8.602	BB	0.1659	4657.60938	431.58954	50.0608

3c enantioenriched, 88% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.801	BB	0.1445	548.19794	57.86303	5.9182
2	8.145	BB	0.1545	8714.75000	873.00458	94.0818



(*S*)-2-fluoro-*N*-(4-fluorophenyl)propenamide (3e)

According to the **General Procedure C**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (17.0 mg, 92%, 90% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.58 – 7.48 (m, 2H), 7.09 – 6.98 (m, 2H), 5.38 – 4.80 (m, 1H), 1.66 (dd, *J* = 24.9, 6.8 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -117.08 – -117.15 (m), -180.13 – -180.48 (m).

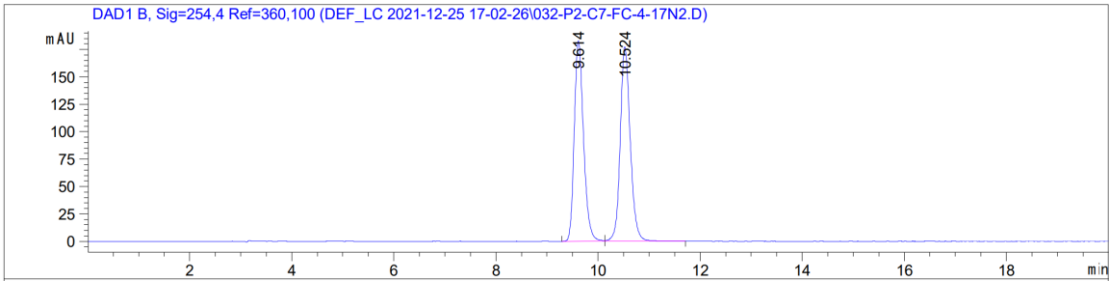
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.76 (d, *J* = 18.0 Hz), 159.84 (d, *J* = 244.5 Hz), 132.83 (d, *J* = 2.7 Hz), 121.96 (d, *J* = 7.9 Hz), 115.92 (d, *J* = 22.6 Hz), 89.02 (d, *J* = 184.4 Hz), 18.52 (d, *J* = 21.4 Hz).

HRMS (ESI): $C_9H_9F_2NNaO^+$ ($M+Na^+$): 208.0544, found: 208.0546.

$[\alpha]_D^{25}$ = -8.44 (c = 1.63, $CHCl_3$).

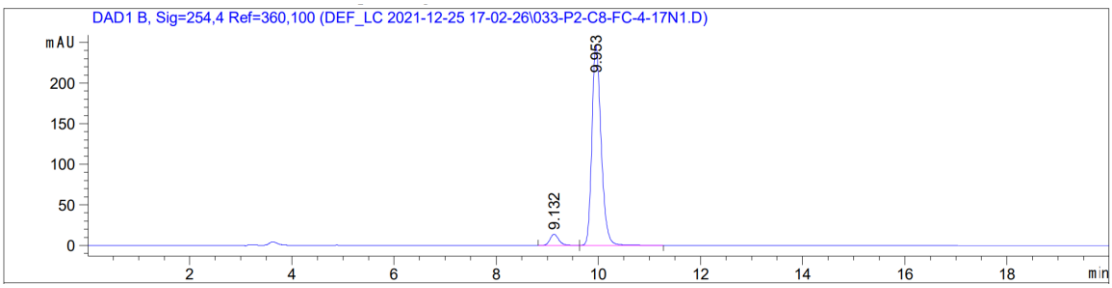
HPLC: The ee was determined to be 90% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 80:20 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 10.0 min, t_R (minor) = 9.1 min.

3e racemic

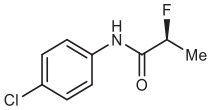


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.614	BV	0.1932	2305.41992	182.68390	48.7713
2	10.524	VB	0.2095	2421.58154	177.15184	51.2287

3e enantioenriched, 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.132	BB	0.1830	161.66304	13.76433	4.9571
2	9.953	BB	0.1924	3099.60889	247.06770	95.0429



(*S*)-*N*-(4-chlorophenyl)-2-fluoropropanamide (3f)

According to the **General Procedure C**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (28.1 mg, 94%, 90% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.56 – 7.48 (m, 2H), 7.34 – 7.26 (m, 2H), 5.27 – 4.86 (m, 1H), 1.66 (dd, *J* = 24.9, 6.8 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -180.07 – -180.41 (m).

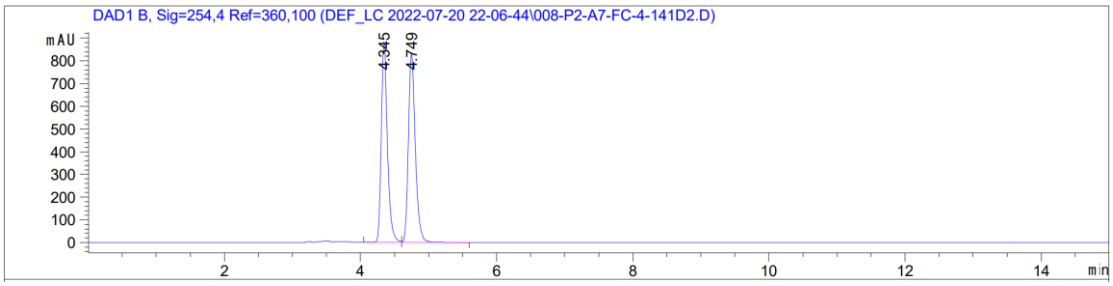
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.81 (d, *J* = 18.1 Hz), 135.40, 130.06, 129.20, 121.37, 88.94 (d, *J* = 184.6 Hz), 18.44 (d, *J* = 21.4 Hz).

HRMS (ESI): $C_9H_9ClFNNaO^+$ ($M+Na^+$): 224.0249, found: 224.0250.

$[\alpha]_D^{25}$ = -13.22 (c = 1.17, $CHCl_3$).

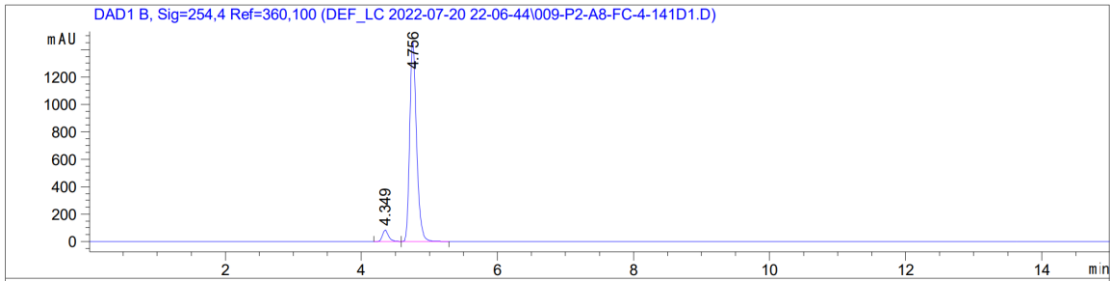
HPLC: The ee was determined to be 90% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 4.8 min, t_R (minor) = 4.3 min.

3f racemic

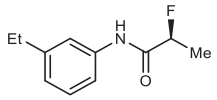


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.345	VV R	0.0971	5675.93652	881.84424	49.7521
2	4.749	VB	0.1067	5732.50635	828.57947	50.2479

3f enantioenriched, 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.349	BV	0.0994	536.77728	83.02771	5.1031
2	4.756	VB	0.1037	9981.88965	1460.27942	94.8969



(*S*)-*N*-(3-ethylphenyl)-2-fluoropropanamide (3g)

According to the **General Procedure C**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (16.6 mg, 85%, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.46 – 7.34 (m, 2H), 7.24 (t, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 5.27 – 4.98 (m, 1H), 2.63 (q, *J* = 7.6 Hz, 2H), 1.65 (dd, *J* = 24.9, 6.9 Hz, 3H), 1.22 (t, *J* = 7.6 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -179.77 – -180.12 (m).

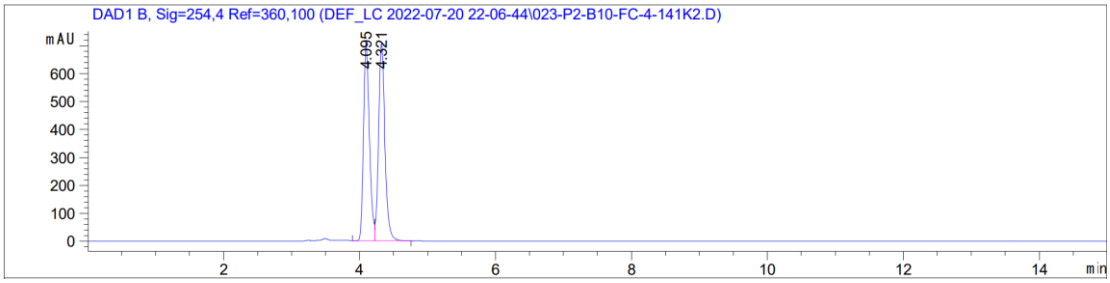
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.70 (d, J = 17.6 Hz), 145.56, 136.80, 129.10, 124.65, 119.59, 117.45, 89.02 (d, J = 184.6 Hz), 28.94, 18.53 (d, J = 21.5 Hz), 15.58.

HRMS (ESI): $C_{11}H_{14}FNNaO^+$ ($M+Na^+$): 218.0952, found: 218.0952.

$[\alpha]_D^{25}$ = -10.14 (c = 1.43, $CHCl_3$).

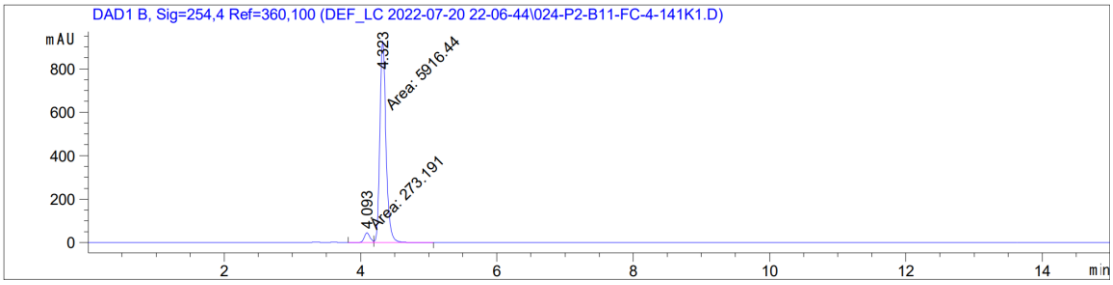
HPLC: The ee was determined to be 91% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 4.3 min, t_R (minor) = 4.1 min.

3g racemic

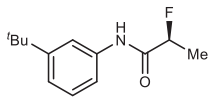


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.095	BV	0.0966	4456.48877	715.90588	48.9706
2	4.321	VB	0.1006	4643.84961	707.55475	51.0294

3g enantioenriched, 91% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.093	MF	0.0998	273.19086	45.62682	4.4137
2	4.323	FM	0.1064	5916.44336	926.97046	95.5863



(*S*)-*N*-(3-(*tert*-butyl)phenyl)-2-fluoropropanamide (3h)

According to the **General Procedure C**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (18.1 mg, 88%, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.99 (m, 1H), 7.55 (t, *J* = 2.0 Hz, 1H), 7.51 – 7.42 (m, 1H), 7.29 (t, *J* = 7.9 Hz, 1H), 7.23 – 7.16 (m, 1H), 5.27 – 4.99 (m, 1H), 1.68 (dd, *J* = 24.9, 6.8 Hz, 3H), 1.33 (s, 9H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -179.72 – -180.06 (m).

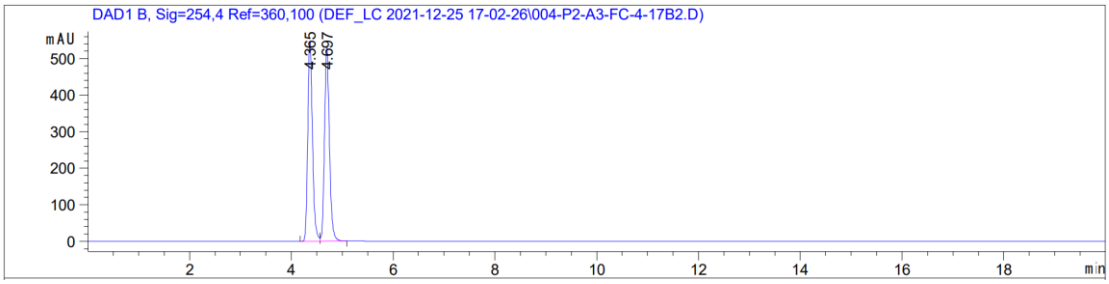
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.69 (d, *J* = 17.8 Hz), 152.48, 136.57, 128.85, 122.12, 117.38, 117.27, 89.02 (d, *J* = 184.6 Hz), 34.86, 31.35, 18.52 (d, *J* = 21.5 Hz).

HRMS (ESI): $C_{13}H_{18}FNNaO^+$ ($M+Na^+$): 246.1265, found: 246.1265.

$[\alpha]_D^{25}$ = -10.14 (c = 1.39, $CHCl_3$).

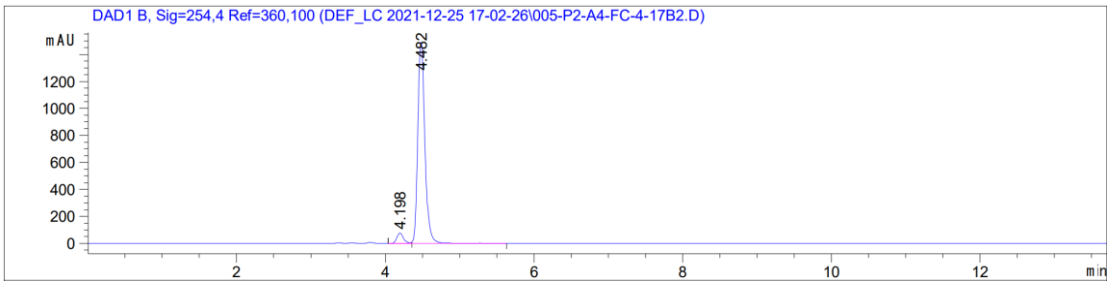
HPLC: The ee was determined to be 91% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 4.2 min, t_R (minor) = 4.5 min.

3h racemic

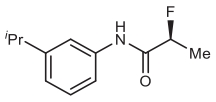


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.365	BV	0.0990	3522.20190	547.76666	49.7528
2	4.697	VB	0.1042	3557.20825	530.60370	50.2472

3h enantioenriched, 91% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.198	BV E	0.0961	471.18118	76.26644	4.5773
2	4.482	VV R	0.1029	9822.78906	1488.45056	95.4227



(*S*)-2-fluoro-*N*-(3-isopropylphenyl)propenamide (3i)

According to the **General Procedure C**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (18.6 mg, 89%, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.46 – 7.38 (m, 2H), 7.27 (t, *J* = 7.8 Hz, 1H), 7.03 (dt, *J* = 7.6, 1.4 Hz, 1H), 5.30 – 4.86 (m, 1H), 2.98 – 2.83 (m, 1H), 1.67 (dd, *J* = 24.9, 6.9 Hz, 3H), 1.25 (d, *J* = 6.9 Hz, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -179.75 – -180.10 (m).

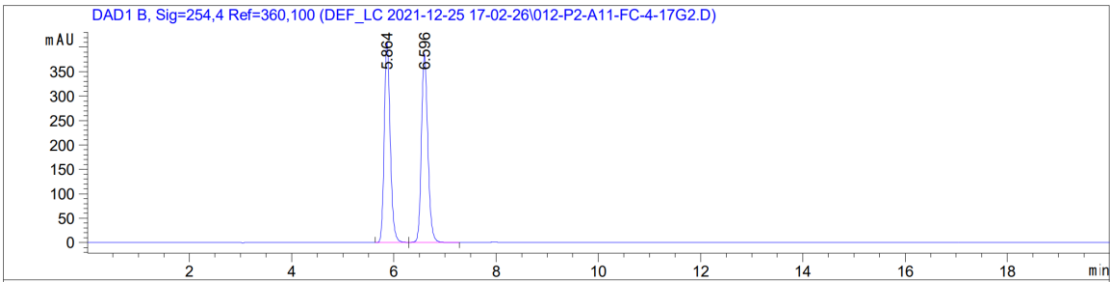
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.69 (d, *J* = 17.9 Hz), 150.25, 136.80, 129.14, 123.22, 118.23, 117.62, 89.04 (d, *J* = 184.6 Hz), 34.24, 24.00, 18.55 (d, *J* = 21.6 Hz).

HRMS (ESI): $C_{12}H_{16}FNNaO^+$ ($M+Na^+$): 232.1108, found: 232.1108.

$[\alpha]_D^{25}$ = -16.48 (c = 1.37, $CHCl_3$).

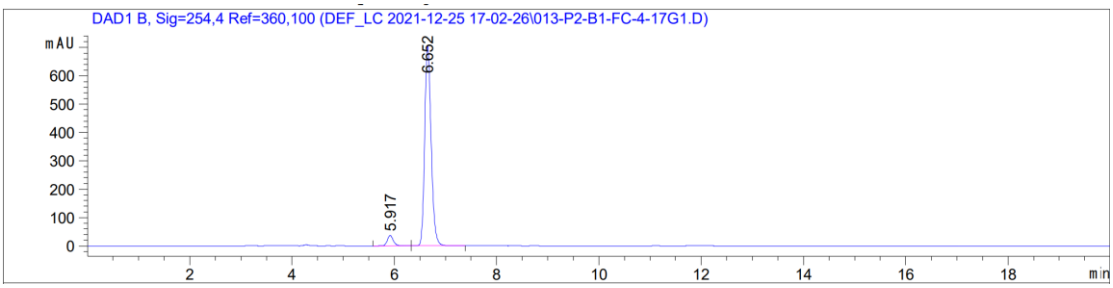
HPLC: The ee was determined to be 91% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 5.9 min, t_R (minor) = 6.7 min.

3i racemic

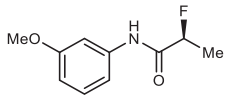


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.864	BB	0.1249	3340.26025	410.67603	49.8249
2	6.596	BB	0.1337	3363.73438	385.73779	50.1751

3i enantioenriched, 91% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.917	BB	0.1254	297.20801	36.35794	4.6041
2	6.652	BB	0.1335	6158.07617	707.64355	95.3959



(*S*)-2-fluoro-*N*-(3-methoxyphenyl)propenamide (3j)

According to the **General Procedure C**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (18.3 mg, 90%, 93% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.33 (t, *J* = 2.3 Hz, 1H), 7.23 (t, *J* = 8.2 Hz, 1H), 7.07 – 7.01 (m, 1H), 6.74 – 6.67 (m, 1H), 5.21 – 4.87 (m, 1H), 3.80 (s, 3H), 1.66 (dd, *J* = 24.9, 6.8 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -179.88 – -180.22 (m).

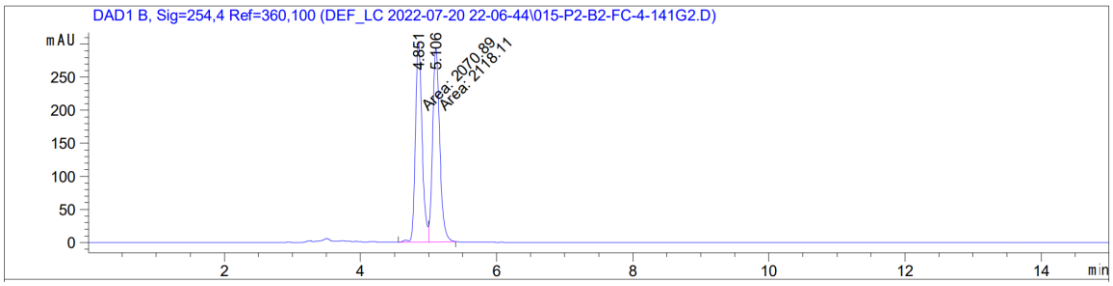
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.75 (d, J = 17.9 Hz), 160.29, 138.01, 129.88, 112.21, 110.91, 105.76, 88.97 (d, J = 184.6 Hz), 55.40, 18.48 (d, J = 21.3 Hz).

HRMS (ESI): $C_{10}H_{13}FNO_2^+$ ($M+H^+$): 198.0925, found: 198.0925.

$[\alpha]_D^{25}$ = -21.56 (c = 1.21, $CHCl_3$).

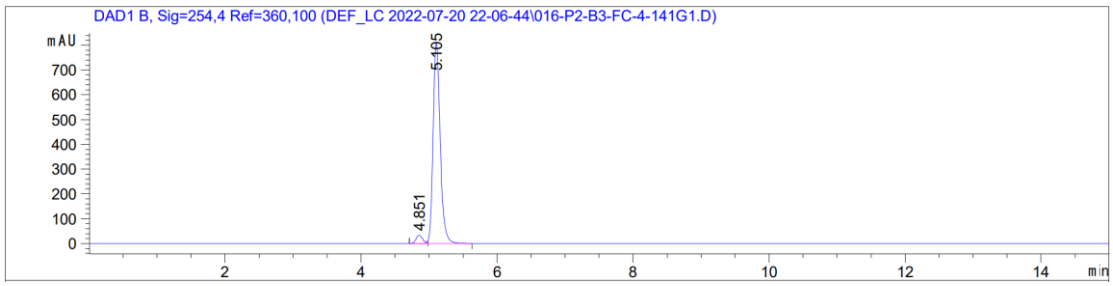
HPLC: The ee was determined to be 93% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 5.1 min, t_R (minor) = 4.9 min.

3j racemic

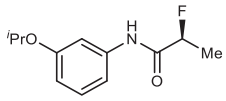


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.851	MF	0.1141	2070.89209	302.61859	49.4365
2	5.106	FM	0.1201	2118.10522	293.94827	50.5635

3j enantioenriched, 93% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.851	BV E	0.1004	221.12381	33.75185	3.6583
2	5.105	VB R	0.1100	5823.37939	808.87463	96.3417



(*S*)-2-fluoro-*N*-(3-isopropoxyphenyl)propenamide (3k)

According to the **General Procedure C**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (21.4 mg, 95%, 92% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.31 (t, *J* = 2.3 Hz, 1H), 7.21 (t, *J* = 8.1 Hz, 1H), 7.04 – 6.97 (m, 1H), 6.72 – 6.65 (m, 1H), 5.23 – 4.95 (m, 1H), 4.82 – 4.24 (m, 1H), 1.66 (dd, *J* = 24.9, 6.8 Hz, 3H), 1.33 (d, *J* = 6.1 Hz, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -179.87 – -180.22 (m).

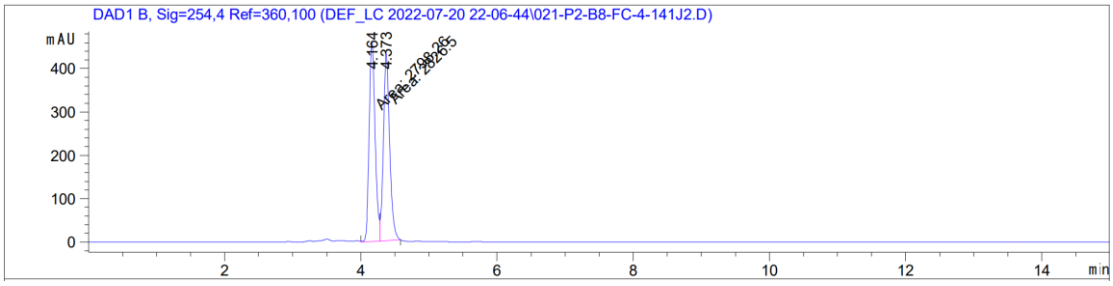
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.70 (d, *J* = 17.9 Hz), 158.66, 137.99, 129.91, 112.78, 112.03, 107.69, 89.01 (d, *J* = 184.6 Hz), 70.16, 22.12 (d, *J* = 2.1 Hz), 18.52 (d, *J* = 21.5 Hz).

HRMS (ESI): $C_{12}H_{16}FNNaO_2^+$ ($M+Na^+$): 248.1057, found: 248.1058.

$[\alpha]_D^{25}$ = -19.03 (c = 1.50, $CHCl_3$).

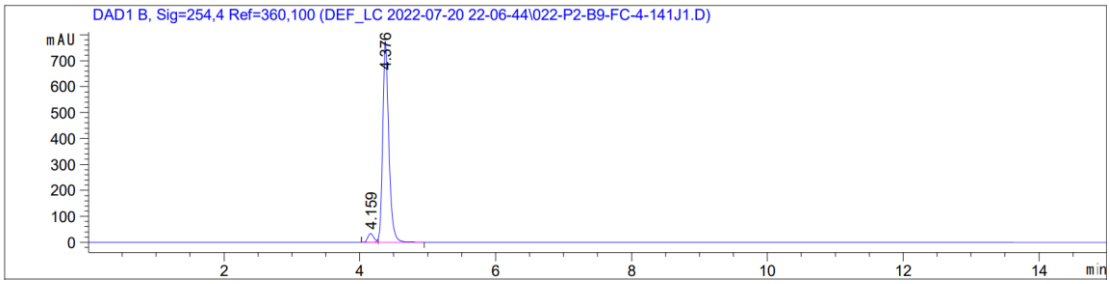
HPLC: The ee was determined to be 92% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 4.2 min, t_R (minor) = 4.4 min.

3k racemic

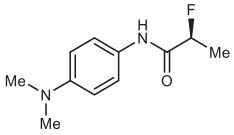


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.164	MF	0.1007	2798.26440	463.33395	49.7490
2	4.373	FM	0.1086	2826.50220	433.90231	50.2510

3k enantioenriched, 92% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.159	BV E	0.0908	197.48529	33.48838	3.7948
2	4.376	VB R	0.0996	5006.57275	772.52771	96.2052



(*S*)-*N*-(4-(dimethylamino)phenyl)-2-fluoropropanamide (3l)

According to the **General Procedure C**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 5:1) as a white solid (18.1 mg, 86%, 90% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.45 – 7.36 (m, 2H), 6.75 – 6.66 (m, 2H), 5.23 – 4.97 (m, 1H), 2.92 (s, 6H), 1.66 (dd, *J* = 24.9, 6.8 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -179.86 – -180.21 (m).

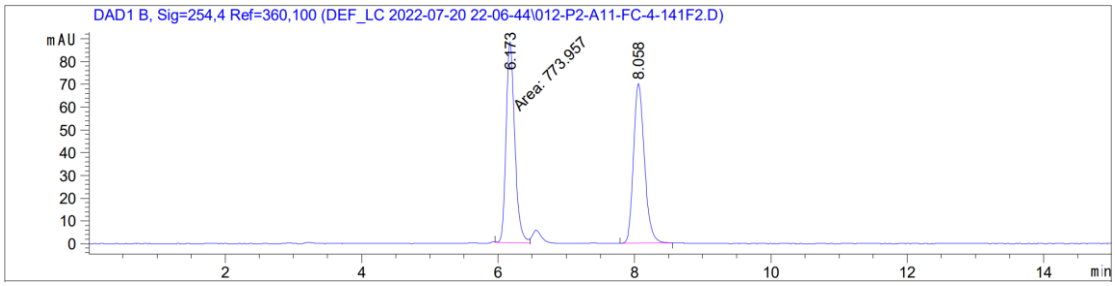
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.36 (d, *J* = 17.8 Hz), 148.40, 126.51, 121.85, 113.05, 89.06 (d, *J* = 184.2 Hz), 40.93, 18.61 (d, *J* = 21.4 Hz).

HRMS (ESI): $C_{11}H_{15}FN_2NaO^+$ ($M+Na^+$): 233.1061, found: 233.1059.

$[\alpha]_D^{25}$ = -13.84 (c = 0.57, $CHCl_3$).

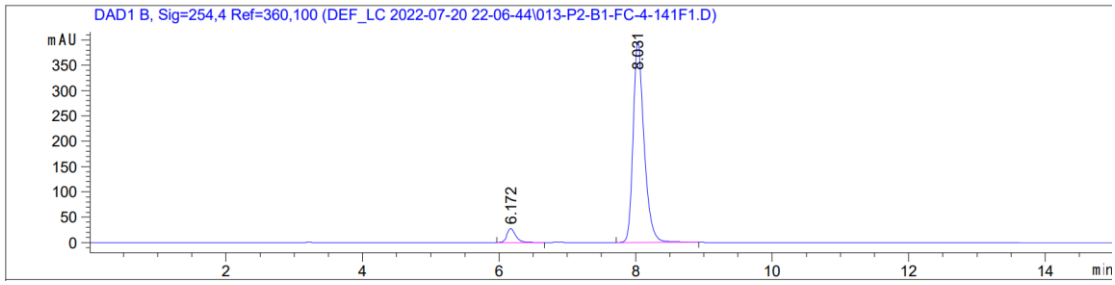
HPLC: The ee was determined to be 90% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 8.0 min, t_R (minor) = 6.2 min.

3l racemic

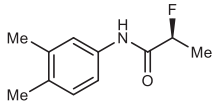


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.173	MM	0.1462	773.95709	88.22675	50.0040
2	8.058	BB	0.1689	773.83221	70.04630	49.9960

3l enantioenriched, 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.172	BB	0.1354	241.90637	27.30165	5.1503
2	8.031	BB	0.1712	4454.98926	396.26514	94.8497



(*S*)-*N*-(3,4-dimethylphenyl)-2-fluoropropanamide (3m)

According to the **General Procedure C**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (15.8 mg, 81%, 92% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.36 (d, *J* = 2.4 Hz, 1H), 7.28 (dd, *J* = 8.1, 2.4 Hz, 1H), 7.09 (d, *J* = 8.1 Hz, 1H), 5.26 – 4.94 (m, 1H), 2.25 (s, 1H), 2.23 (s, 1H), 1.66 (dd, *J* = 24.9, 6.8 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -179.80 – -180.15 (m).

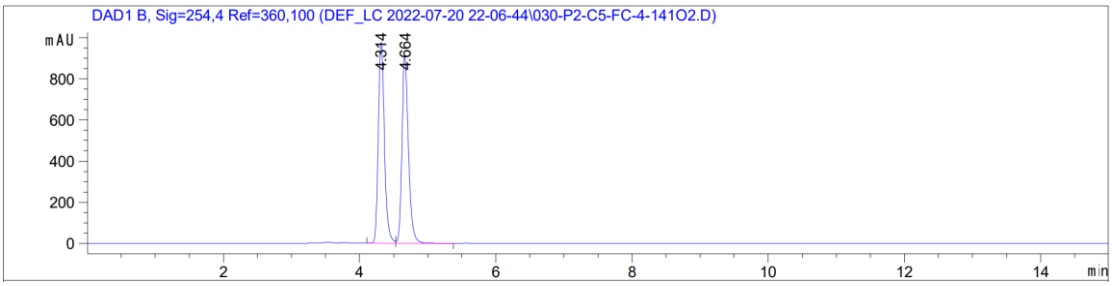
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.58 (d, J = 17.8 Hz), 137.44, 134.49, 133.38, 130.11, 121.44, 117.63, 88.99 (d, J = 184.5 Hz), 19.92, 19.27, 18.52 (d, J = 21.6 Hz).

HRMS (ESI): $C_{11}H_{14}FNNaO^+$ ($M+Na^+$): 218.0952, found: 218.0952.

$[\alpha]_D^{25}$ = -10.09 (c = 1.18, $CHCl_3$).

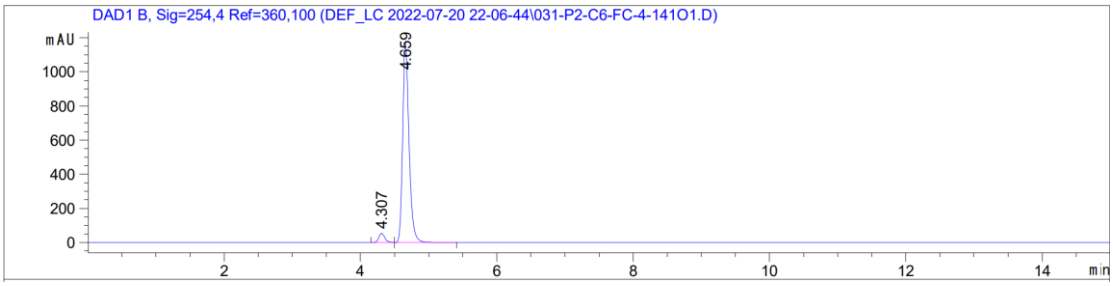
HPLC: The ee was determined to be 92% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 4.7 min, t_R (minor) = 4.3 min.

3m racemic

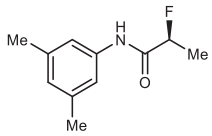


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.314	BV	0.0974	6149.84912	977.54846	49.8726
2	4.664	VB	0.1051	6181.27783	912.19928	50.1274

3m enantioenriched, 92% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.307	BV	0.0971	332.29358	53.02055	4.0706
2	4.659	VB	0.1015	7831.00146	1178.59924	95.9294



(*S*)-*N*-(3,5-dimethylphenyl)-2-fluoropropanamide (3n)

According to the **General Procedure C**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (17.4 mg, 89%, 93% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.21 (d, *J* = 1.5 Hz, 2H), 6.80 (s, 1H), 5.20 – 4.96 (m, 1H), 2.31 (s, 6H), 1.66 (dd, *J* = 24.9, 6.8 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -179.75 – -180.09 (m).

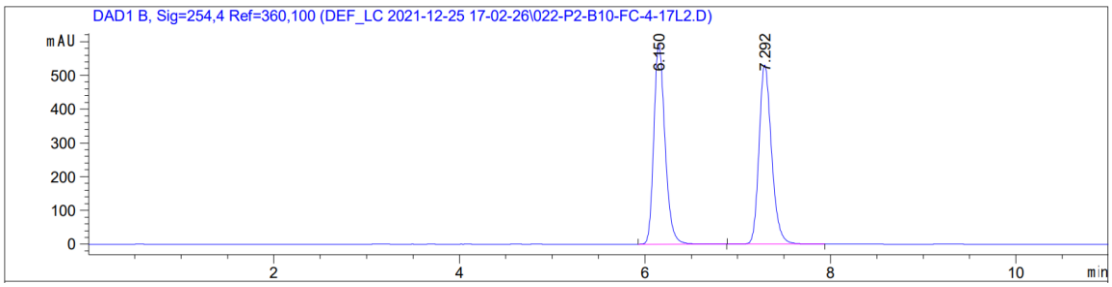
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.65 (d, *J* = 17.7 Hz), 138.90, 136.63, 126.72, 117.84, 88.97 (d, *J* = 184.6 Hz), 21.39, 18.51 (d, *J* = 21.4 Hz).

HRMS (ESI): $C_{11}H_{14}FNNaO^+$ ($M+Na^+$): 218.0952, found: 218.0951.

$[\alpha]_D^{25}$ = -14.92 (c = 1.89, $CHCl_3$).

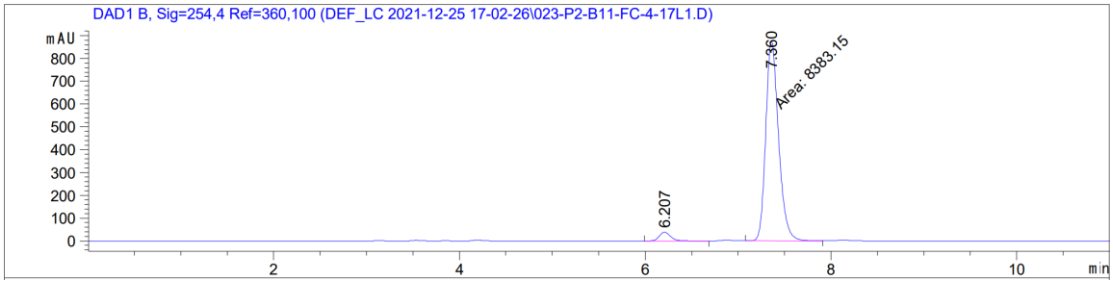
HPLC: The ee was determined to be 93% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 7.4 min, t_R (minor) = 6.2 min.

3n racemic

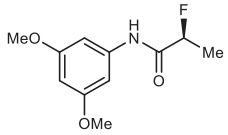


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.150	BB	0.1272	4961.40430	595.69128	49.9716
2	7.292	BB	0.1432	4967.04785	530.47327	50.0284

3n enantioenriched, 93% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.207	BB	0.1282	322.04971	38.25327	3.6995
2	7.360	MF	0.1591	8383.15430	878.03900	96.3005



(*S*)-*N*-(3,5-dimethoxyphenyl)-2-fluoropropanamide (3o)

According to the **General Procedure C**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (20.2 mg, 89%, 96% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 1H), 6.80 (d, *J* = 2.3 Hz, 2H), 6.26 (t, *J* = 2.3 Hz, 1H), 5.29 – 4.79 (m, 1H), 3.77 (s, 6H), 1.65 (dd, *J* = 24.9, 6.8 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -179.88 – -180.23 (m).

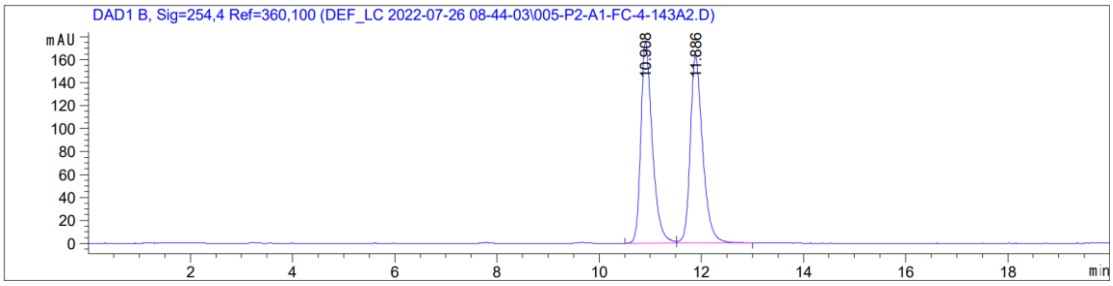
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.76 (d, *J* = 18.0 Hz), 161.21, 138.54, 98.31, 97.44, 88.97 (d, *J* = 184.8 Hz), 55.50, 18.46 (d, *J* = 21.3 Hz).

HRMS (ESI): $C_{11}H_{14}FNNaO_3^+$ ($M+Na^+$): 250.0850, found: 250.0849.

$[\alpha]_D^{25}$ = -18.77 (c = 1.45, $CHCl_3$).

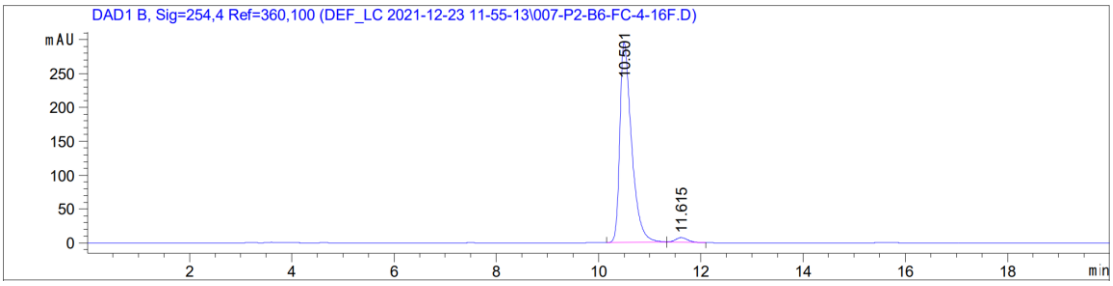
HPLC: The ee was determined to be 96% on a CHIRALPAK IB column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 80:20 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 11.6 min, t_R (minor) = 10.5 min.

3o racemic

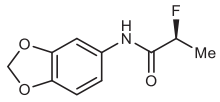


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.908	BV	0.2342	2737.43848	175.31502	49.7636
2	11.886	VB	0.2556	2763.44458	163.15346	50.2364

3o enantioenriched, 96% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.501	BB	0.2376	4710.08594	296.00656	97.7455
2	11.615	BB	0.2486	108.63972	6.79123	2.2545



(*S*)-*N*-(benzo[*d*][1,3]dioxol-5-yl)-2-fluoropropanamide (3p)

According to the **General Procedure C**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (17.1 mg, 81%, 92% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.25 (d, *J* = 2.2 Hz, 1H), 6.85 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.74 (d, *J* = 8.3 Hz, 1H), 5.94 (s, 2H), 5.24 – 4.88 (m, 1H), 1.64 (dd, *J* = 24.9, 6.8 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -180.14 – -180.48 (m).

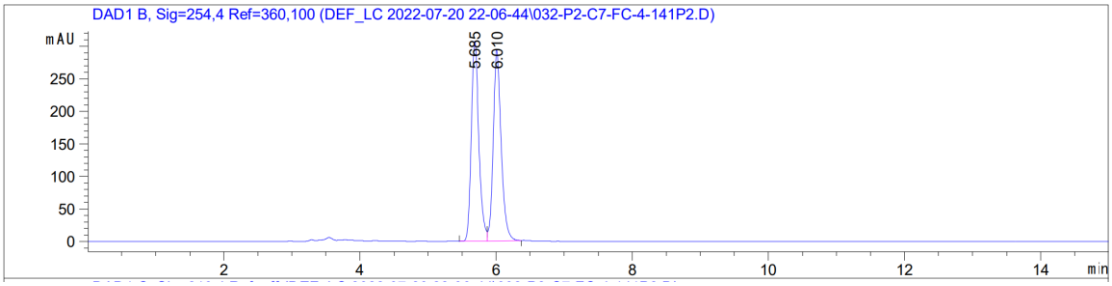
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.57 (d, J = 18.0 Hz), 147.95, 144.79, 130.98, 113.42, 108.18, 102.86, 101.44, 88.96 (d, J = 184.4 Hz), 18.49 (d, J = 21.3 Hz).

HRMS (ESI): $C_{10}H_{10}FNNaO_3^+$ ($M+Na^+$): 234.0537, found: 234.0538.

$[\alpha]_D^{25}$ = -13.17 (c = 2.28, $CHCl_3$).

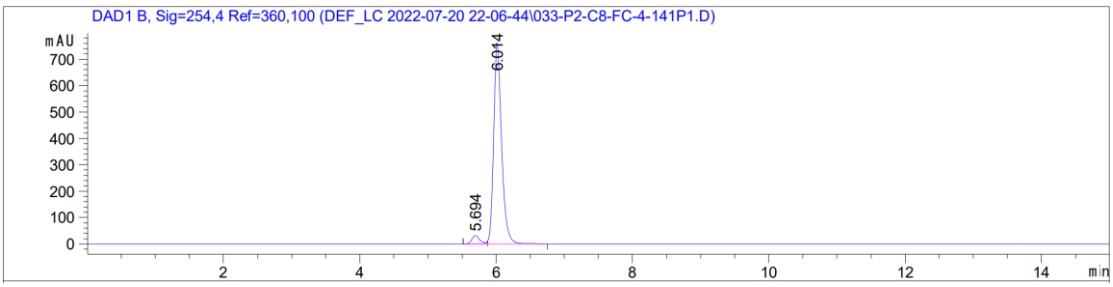
HPLC: The ee was determined to be 92% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 6.0 min, t_R (minor) = 5.7 min.

3p racemic

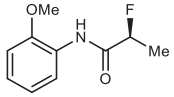


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.685	BV	0.1185	2389.62427	307.91745	49.5799
2	6.010	VB	0.1263	2430.11768	294.50510	50.4201

3p enantioenriched, 92% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.694	BV E	0.1202	251.07945	31.78723	3.8433
2	6.014	VB R	0.1241	6281.78076	762.58630	96.1567



(*S*)-2-fluoro-*N*-(2-methoxyphenyl)propenamide (3q)

According to the **General Procedure C**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (15.6 mg, 79%, 89% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.38 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.13 – 7.04 (m, 1H), 7.01 – 6.95 (m, 1H), 6.90 (dd, *J* = 8.1, 1.4 Hz, 1H), 5.21 – 4.97 (m, 1H), 3.89 (s, 3H), 1.67 (dd, *J* = 24.7, 6.8 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -180.02 – -180.36 (m).

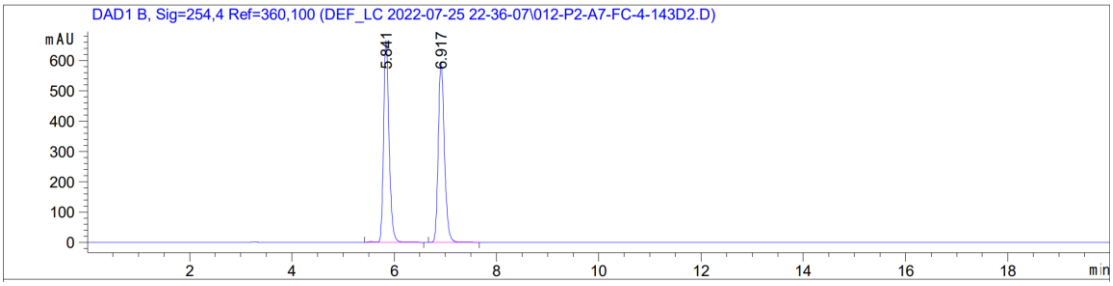
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.63 (d, *J* = 18.0 Hz), 148.37, 126.66, 124.53, 121.12, 119.90, 110.15, 89.02 (d, *J* = 184.9 Hz), 55.83, 18.61 (d, *J* = 21.4 Hz).

HRMS (ESI): $C_{10}H_{12}FNO_2^+$ ($M+Na^+$): 220.0744, found: 220.0744.

$[\alpha]_D^{25}$ = -18.90 (c = 1.03, $CHCl_3$).

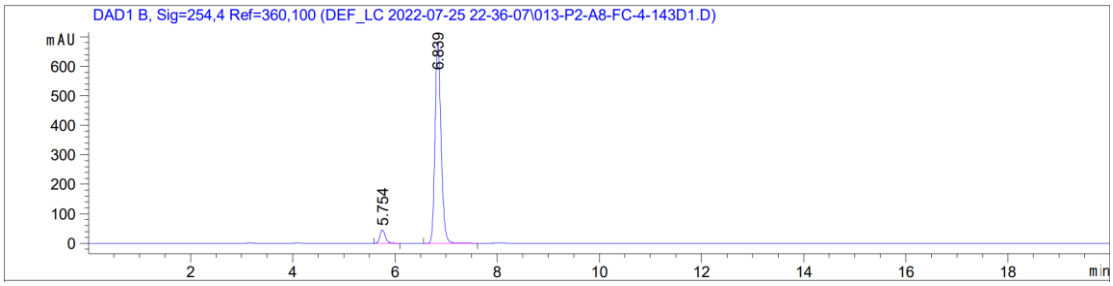
HPLC: The ee was determined to be 89% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 6.8 min, t_R (minor) = 5.8 min.

3q racemic

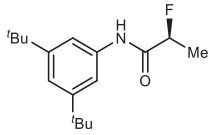


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.841	VB R	0.1150	4968.49463	664.37714	50.0428
2	6.917	BB	0.1272	4960.00049	595.44897	49.9572

3q enantioenriched, 89% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.754	BB	0.1128	326.96695	44.96394	5.4948
2	6.839	BB	0.1280	5623.47754	683.32709	94.5052



(*S*)-*N*-(3,5-di-*tert*-butylphenyl)-2-fluoropropanamide (3r)

According to the **General Procedure C**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (22.9 mg, 82%, 94% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 6.8 Hz, 1H), 7.44 (d, *J* = 1.7 Hz, 2H), 7.24 (t, *J* = 1.8 Hz, 1H), 5.24 – 4.94 (m, 1H), 1.68 (dd, *J* = 24.9, 6.8 Hz, 3H), 1.34 (s, 18H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -179.62 – -179.93 (m).

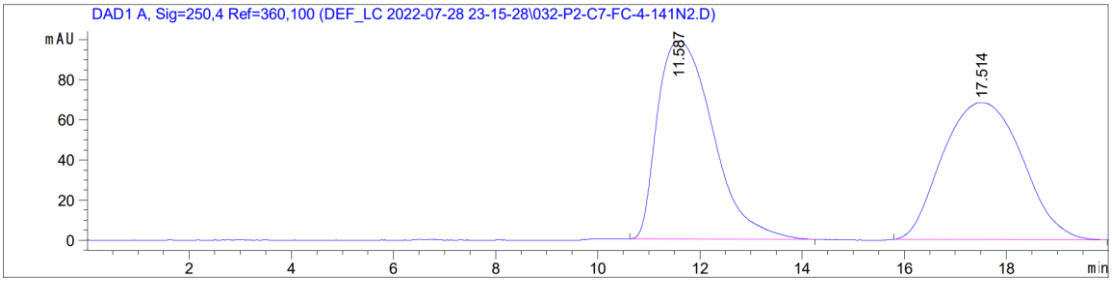
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.62 (d, *J* = 17.9 Hz), 151.95, 136.25, 119.20, 114.69, 89.07 (d, *J* = 184.6 Hz), 35.07, 31.49, 18.54 (d, *J* = 21.4 Hz).

HRMS (ESI): $C_{17}H_{26}FNNaO^+$ ($M+Na^+$): 302.1891, found: 302.1893.

$[\alpha]_D^{25}$ = -23.78 (c = 1.38, $CHCl_3$).

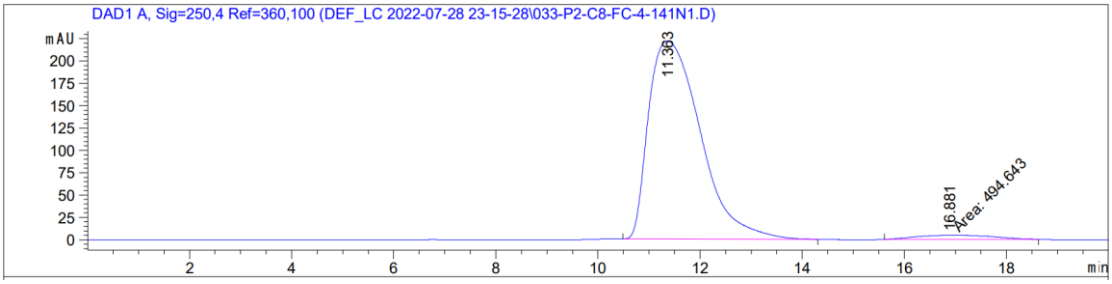
HPLC: The ee was determined to be 94% on a CHIRALPAK IC column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 100:1 at a flow rate 0.5 mL/min. Retention times: t_R (major) = 16.9 min, t_R (minor) = 11.4 min.

3r racemic

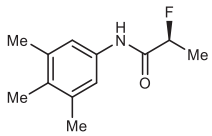


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.587	BB	1.0544	7461.57080	98.88103	50.1197
2	17.514	BB	1.2847	7425.92773	68.50481	49.8803

3r enantioenriched, 94% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.363	BB	1.0182	1.56295e4	221.77621	96.9323
2	16.881	MM	1.7386	494.64252	4.74182	3.0677



(*S*)-2-fluoro-*N*-(3,4,5-trimethylphenyl)propenamide (3s)

According to the **General Procedure C**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (18.8 mg, 90%, 93% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 6.7 Hz, 1H), 7.22 (s, 2H), 5.28 – 4.87 (m, 1H), 2.27 (s, 6H), 2.14 (s, 3H), 1.66 (dd, *J* = 24.9, 6.8 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -179.73 – -180.08 (m).

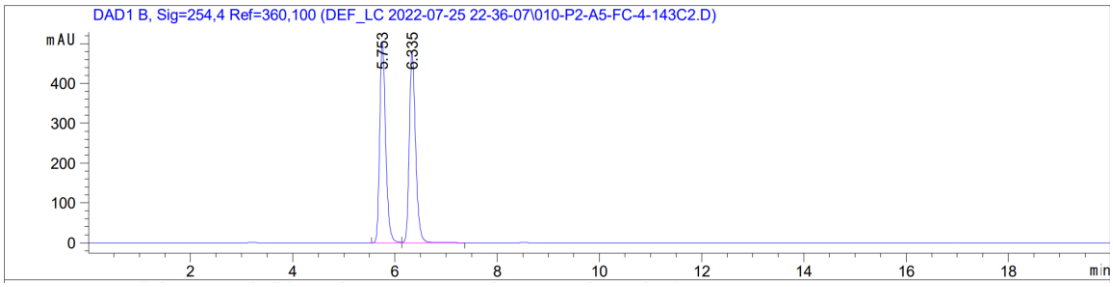
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.56 (d, J = 17.8 Hz), 137.28, 133.78, 131.95, 119.35, 89.00 (d, J = 184.5 Hz), 20.72, 18.54 (d, J = 21.3 Hz), 15.03.

HRMS (ESI): $C_{12}H_{16}FNNaO^+$ ($M+Na^+$): 232.1108, found: 232.1107.

$[\alpha]_D^{25}$ = -27.34 (c = 1.54, $CHCl_3$).

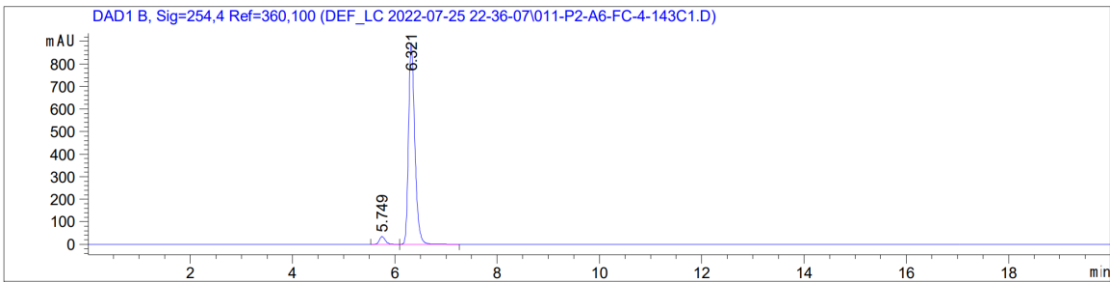
HPLC: The ee was determined to be 93% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 6.3 min, t_R (minor) = 5.7 min.

3s racemic

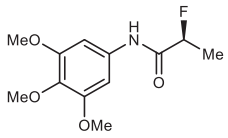


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.753	BV	0.1243	4074.11597	504.20477	49.7569
2	6.335	VB	0.1324	4113.93164	478.25671	50.2431

3s enantioenriched, 93% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.749	BB	0.1247	279.49219	34.42815	3.5246
2	6.321	BB	0.1301	7650.17920	892.06451	96.4754



(*S*)-2-fluoro-*N*-(3,4,5-trimethoxyphenyl)propenamide (3t)

According to the **General Procedure C**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 4:1) as a white solid (22.4 mg, 87%, 93% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 6.7 Hz, 1H), 6.86 (s, 2H), 5.27 – 4.89 (m, 1H), 3.81 (s, 6H), 3.79 (s, 3H), 1.63 (dd, *J* = 24.8, 6.8 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -180.01 – -180.27 (m).

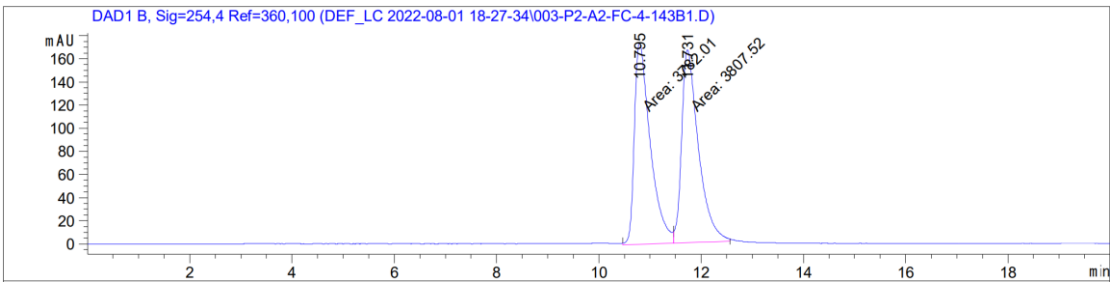
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.67 (d, *J* = 18.0 Hz), 153.42, 135.13, 132.91, 97.72, 88.89 (d, *J* = 184.6 Hz), 60.99, 56.14, 18.43 (d, *J* = 21.5 Hz).

HRMS (ESI): $C_{12}H_{16}FNNaO_4^+$ ($M+Na^+$): 280.0956, found: 280.0955.

$[\alpha]_D^{25}$ = -23.14 (c = 2.10, $CHCl_3$).

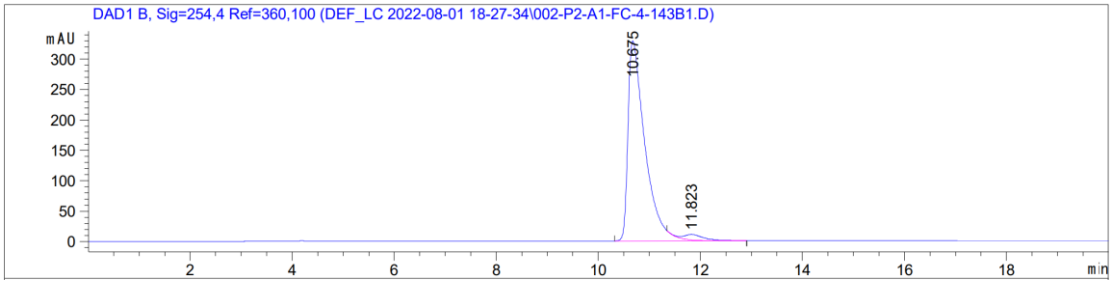
HPLC: The ee was determined to be 93% on a CHIRALPAK IB column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 80:20 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 11.8 min, t_R (minor) = 10.7 min.

3t racemic

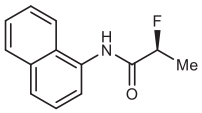


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.795	MF	0.3617	3782.01440	174.25743	49.8320
2	11.731	FM	0.3805	3807.52222	166.79094	50.1680

3t enantioenriched, 93% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.675	BV R	0.3362	7562.75195	328.96301	96.7452
2	11.823	VB E	0.3777	254.42987	9.11268	3.2548



(*S*)-2-fluoro-*N*-(naphthalen-1-yl)propenamide (3u)

According to the **General Procedure C**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (19.7 mg, 91%, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.02 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.94 – 7.81 (m, 2H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.60 – 7.45 (m, 3H), 5.39 – 5.05 (m, 1H), 1.77 (dd, *J* = 24.9, 6.8 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -179.78 – -180.13 (m).

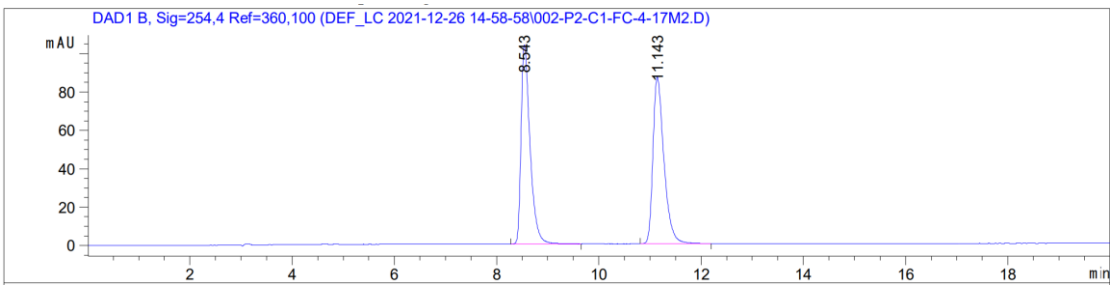
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.32 (d, *J* = 17.9 Hz), 134.23, 131.09, 129.02, 126.93, 126.72, 126.32, 126.30, 125.86, 120.55, 120.26, 89.56 (d, *J* = 184.2 Hz), 18.78 (d, *J* = 21.4 Hz).

HRMS (ESI): $C_{13}H_{12}FNNaO^+$ ($M+Na^+$): 240.0795, found: 240.0795.

$[\alpha]_D^{25}$ = -19.33 (c = 1.78, $CHCl_3$).

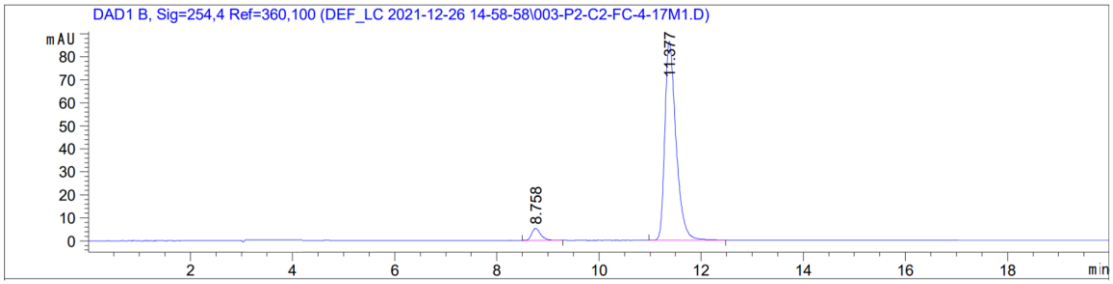
HPLC: The ee was determined to be 91% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 11.4 min, t_R (minor) = 8.8 min.

3u racemic

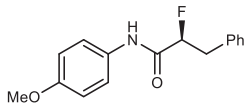


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.543	BB	0.1821	1265.10962	103.83508	49.3604
2	11.143	BB	0.2263	1297.89319	86.88491	50.6396

3u enantioenriched, 91% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.758	BB	0.1852	63.56799	5.17923	4.6119
2	11.377	BB	0.2294	1314.77332	86.48820	95.3881



(*S*)-2-fluoro-*N*-(4-methoxyphenyl)-3-phenylpropanamide (3v)

According to the **General Procedure C**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (11.8 mg, 43%, 79% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.44 – 7.22 (m, 7H), 6.90 – 6.82 (m, 2H), 5.36 – 5.02 (m, 1H), 3.79 (s, 3H), 3.51 – 3.32 (m, 1H), 3.22 (m, 1H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -187.28 – -187.59 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.16 (d, J = 18.2 Hz), 157.10, 135.39, 129.76, 129.55,

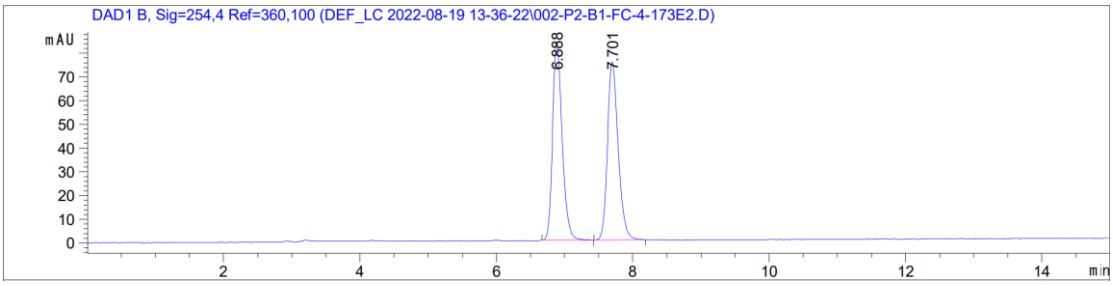
128.66, 127.29, 122.28, 114.35, 92.16 (d, J = 190.4 Hz), 55.61, 38.65 (d, J = 19.7 Hz).

HRMS (ESI): $C_{16}H_{16}FNNaO_2^+$ ($M+Na^+$): 296.1057, found: 296.1055.

$[\alpha]_D^{25}$ = -11.68 (c = 1.00, $CHCl_3$).

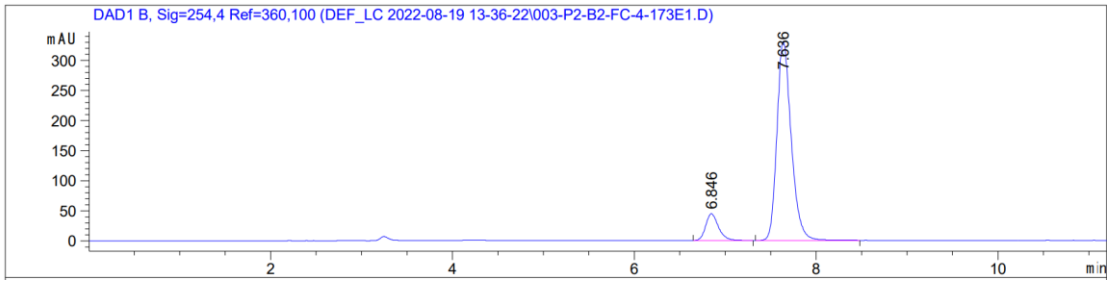
HPLC: The ee was determined to be 79% on a CHIRALPAK IA column at 254 nm, 25 ^oC, with hexane: ^iPrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 7.6 min, t_R (minor) = 6.8 min.

3v racemic

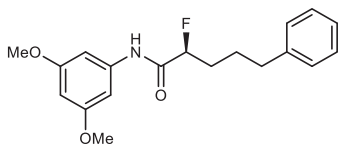


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.888	BB	0.1498	816.62848	83.69112	49.9302
2	7.701	BB	0.1653	818.91077	75.04420	50.0698

3v enantioenriched, 79% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.846	BB	0.1474	431.20410	44.36859	10.6865
2	7.636	BB	0.1652	3603.82813	330.66324	89.3135



(*S*)-*N*-(3,5-dimethoxyphenyl)-2-fluoro-5-phenylpentanamide (3w)

According to the **General Procedure C**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 5:1) as a white solid (20.2 mg, 61%, 77% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.0 Hz, 1H), 7.35 – 7.25 (m, 2H), 7.20 (d, *J* = 7.5 Hz, 3H), 6.82 (d, *J* = 2.3 Hz, 2H), 6.30 (t, *J* = 2.4 Hz, 1H), 5.16 – 4.90 (m, 1H), 3.80 (s, 6H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.17 – 1.94 (m, 2H), 1.97 – 1.81 (m, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -187.67 – -187.97 (m).

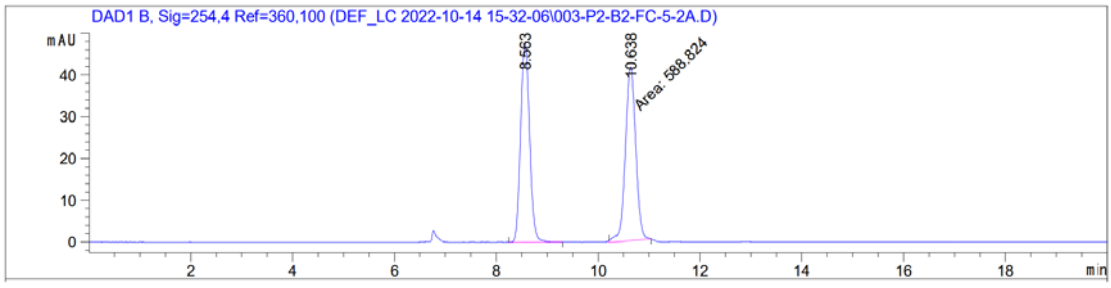
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.06 (d, *J* = 17.9 Hz), 161.23, 141.57, 138.48, 128.53, 128.51, 126.11, 98.29, 97.46, 92.09 (d, *J* = 187.6 Hz), 55.52, 35.47, 32.06 (d, *J* = 20.0 Hz), 26.29 (d, *J* = 2.5 Hz).

HRMS (ESI): $C_{19}H_{22}FNNaO_3^+$ ($M+Na^+$): 354.1476, found: 354.1475.

$[\alpha]_D^{25}$ = -16.25 (c = 1.32, $CHCl_3$).

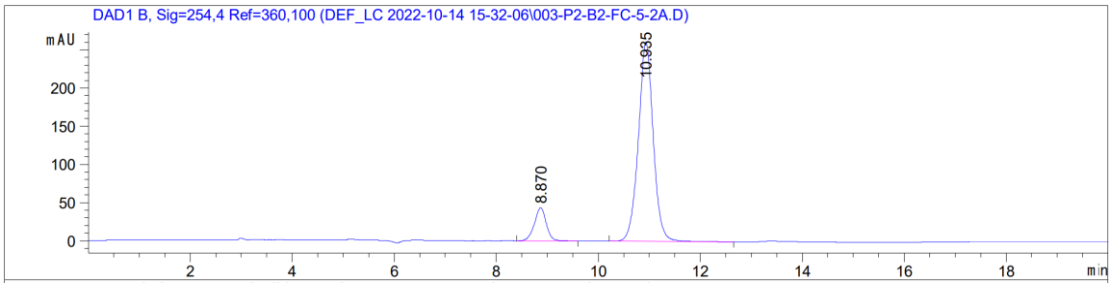
HPLC: The ee was determined to be 77% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 80:20 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 10.9 min, t_R (minor) = 8.9 min.

3w racemic

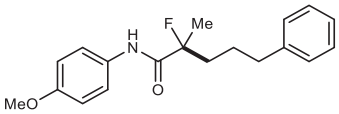


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.563	BB	0.1913	586.65857	47.76589	49.9079
2	10.638	MM	0.2364	588.82397	41.51134	50.0921

3w enantioenriched, 77% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.870	BB	0.2434	696.38367	43.35598	11.6112
2	10.935	BB	0.3048	5301.13721	261.12497	88.3888



2-Fluoro-*N*-(4-methoxyphenyl)-2-methyl-5-phenylpentanamide (4a)

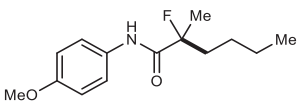
According to the **General Procedure D**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (25.2 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.1 Hz, 1H), 7.52 – 7.43 (m, 2H), 7.30 – 7.24 (m, 2H), 7.21 – 7.10 (m, 3H), 6.93 – 6.77 (m, 2H), 3.80 (s, 3H), 2.71 – 2.54 (m, 2H), 2.19 – 2.00 (m, 1H), 1.95 – 1.77 (m, 2H), 1.74 – 1.65 (m, 1H), 1.62 (d, *J* = 22.5 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -154.63 – -154.96 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.30 (d, *J* = 19.7 Hz), 156.72, 141.69, 130.02, 128.42, 128.41, 125.94, 121.61, 114.22, 98.73 (d, *J* = 185.4 Hz), 55.52, 37.74 (d, *J* = 22.0 Hz), 35.67, 25.09 (d, *J* = 2.8 Hz), 23.96 (d, *J* = 23.9 Hz).

HRMS (ESI): $C_{19}H_{22}FNNaO_2^+$ ($M+Na^+$): 338.1527, found: 338.1524.



2-Fluoro-*N*-(4-methoxyphenyl)-2-methylhexanamide (4b)

According to the **General Procedure D**, the title compound was isolated by flash

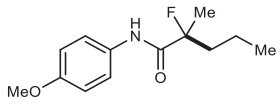
chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (16.2 mg, 64%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.2 Hz, 1H), 7.48 (d, *J* = 9.0 Hz, 2H), 6.88 (d, *J* = 9.0 Hz, 2H), 3.80 (s, 3H), 2.13 – 1.93 (m, 1H), 1.90 – 1.72 (m, 1H), 1.62 (d, *J* = 22.5 Hz, 3H), 1.51 – 1.41 (m, 1H), 1.39 – 1.24 (m, 3H), 0.89 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -154.69 – -155.02 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.64 (d, *J* = 19.8 Hz), 156.82, 130.23, 121.74, 114.34, 99.01 (d, *J* = 185.1 Hz), 55.63, 38.05 (d, *J* = 22.0 Hz), 25.45 (d, *J* = 2.8 Hz), 24.03 (d, *J* = 23.9 Hz), 22.75, 14.01.

HRMS (ESI): $C_{14}H_{20}FNNaO_2^+$ ($M+Na^+$): 276.1370, found: 276.1369.



2-Fluoro-*N*-(4-methoxyphenyl)-2-methylpentanamide (4c)

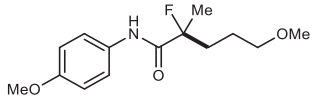
According to the **General Procedure D**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (13.6 mg, 57%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.2 Hz, 1H), 7.52 – 7.39 (m, 2H), 6.92 – 6.83 (m, 2H), 3.79 (s, 3H), 2.12 – 1.92 (m, 1H), 1.88 – 1.72 (m, 1H), 1.61 (d, *J* = 22.6 Hz, 3H), 1.56 – 1.47 (m, 1H), 1.42 – 1.31 (m, 1H), 0.93 (t, *J* = 7.4 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -154.68 – -154.93 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.62 (d, *J* = 19.8 Hz), 156.83, 130.22, 121.75, 114.34, 99.01 (d, *J* = 185.1 Hz), 55.63, 40.41 (d, *J* = 21.9 Hz), 24.01 (d, *J* = 23.9 Hz), 16.80 (d, *J* = 3.1 Hz), 14.13.

HRMS (ESI): $C_{13}H_{19}FNO_2^+$ ($M+H^+$): 240.1394, found: 240.1395.



2-Fluoro-5-methoxy-*N*-(4-methoxyphenyl)-2-methylpentanamide (4d)

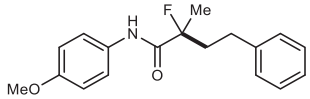
According to the **General Procedure D**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (15.6 mg, 58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 7.93 (m, 1H), 7.53 – 7.42 (m, 2H), 6.93 – 6.83 (m, 2H), 3.79 (s, 3H), 3.38 (td, *J* = 6.4, 2.7 Hz, 2H), 3.31 (s, 3H), 2.19 – 2.00 (m, 1H), 2.00 – 1.85 (m, 1H), 1.84 – 1.69 (m, 1H), 1.69 – 1.54 (m, 4H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -154.89 – -155.22 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.24 (d, *J* = 19.8 Hz), 156.73, 130.03, 121.65, 114.21, 98.60 (d, *J* = 185.6 Hz), 72.10, 58.52, 55.50, 34.78 (d, *J* = 22.1 Hz), 23.85 (d, *J* = 23.9 Hz), 23.57 (d, *J* = 3.0 Hz).

HRMS (ESI): $C_{14}H_{21}FNO_3^+$ ($M+H^+$): 270.1500, found: 270.1501.



2-Fluoro-*N*-(4-methoxyphenyl)-2-methyl-4-phenylbutanamide (4e)

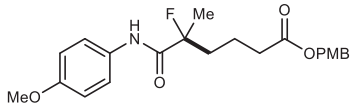
According to the **General Procedure D**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (19.9 mg, 66%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.9 Hz, 1H), 7.53 – 7.44 (m, 2H), 7.31 – 7.24 (m, 2H), 7.22 – 7.14 (m, 3H), 6.92 – 6.82 (m, 2H), 3.80 (s, 3H), 2.87 – 2.73 (m, 1H), 2.71 – 2.60 (m, 1H), 2.48 – 2.29 (m, 1H), 2.21 – 2.04 (m, 1H), 1.67 (d, *J* = 22.5 Hz, 4H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -155.08 – -155.29 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.09 (d, *J* = 19.7 Hz), 156.81, 140.93, 130.00, 128.49, 128.38, 126.11, 121.75, 114.26, 98.53 (d, *J* = 186.2 Hz), 55.53, 40.02 (d, *J* = 21.8 Hz), 29.70 (d, *J* = 3.4 Hz), 24.04 (d, *J* = 23.7 Hz).

HRMS (ESI): $C_{18}H_{20}FNNaO_2^+$ ($M+Na^+$): 324.1370, found: 324.1369.



4-Methoxybenzyl 5-fluoro-6-((4-methoxyphenyl)amino)-5-methyl-6-oxohexanoate (4f)

According to the **General Procedure D**, the title compound was isolated by flash

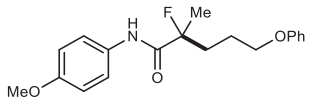
chromatography (Petroleum ether: EtOAc = 5:1) as a white solid (20.6 mg, 51%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.41 (m, 2H), 7.36 – 7.17 (m, 2H), 6.91 – 6.81 (m, 4H), 5.04 (s, 2H), 3.80 (s, 6H), 2.50 – 2.20 (m, 2H), 2.20 – 1.98 (m, 1H), 1.96 – 1.80 (m, 2H), 1.75 – 1.66 (m, 1H), 1.62 (d, *J* = 22.5 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -155.11 – -155.44 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.93, 170.08 (d, *J* = 19.7 Hz), 159.64, 156.77, 130.12, 129.98, 128.07, 121.72, 114.22, 113.96, 98.47 (d, *J* = 185.9 Hz), 66.11, 55.51, 55.29, 37.29 (d, *J* = 22.0 Hz), 33.91, 23.83 (d, *J* = 23.9 Hz), 18.86 (d, *J* = 3.4 Hz).

HRMS (ESI): $C_{22}H_{26}FNNaO_5^+$ ($M+Na^+$): 426.1687, found: 426.1683.



2-Fluoro-*N*-(4-methoxyphenyl)-2-methyl-5-phenoxypentanamide (4g)

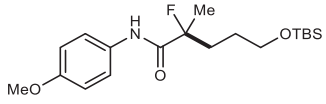
According to the **General Procedure D**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (19.9 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.34 – 7.21 (m, 2H), 6.93 (t, *J* = 7.3 Hz, 1H), 6.88 (m, 4H), 4.06 – 3.87 (m, 2H), 3.80 (s, 3H), 2.25 (m, 1H), 2.13 – 1.95 (m, 2H), 1.91 – 1.79 (m, 1H), 1.67 (d, *J* = 22.5 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -154.83 – -155.04 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.15 (d, *J* = 19.6 Hz), 158.86, 156.80, 129.99, 129.46, 121.69, 120.72, 114.49, 114.25, 98.60 (d, *J* = 185.6 Hz), 67.21, 55.52, 34.80 (d, *J* = 22.2 Hz), 23.94 (d, *J* = 23.9 Hz), 23.49 (d, *J* = 2.9 Hz).

HRMS (ESI): $C_{19}H_{23}FNO_3^+$ ($M+H^+$): 322.1656, found: 322.1657.



5-((*Tert*-butyldimethylsilyl)oxy)-2-fluoro-*N*-(4-methoxyphenyl)-2-methylpentanamide (4h)

According to the **General Procedure D**, the title compound was isolated by flash

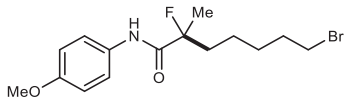
chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (17.0 mg, 46%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.5 Hz, 1H), 7.60 – 7.33 (m, 2H), 7.00 – 6.79 (m, 2H), 3.79 (s, 3H), 3.67 – 3.56 (m, 2H), 2.23 – 1.79 (m, 2H), 1.74 – 1.67 (m, 1H), 1.63 (d, *J* = 22.4 Hz, 3H), 1.59 – 1.51 (m, 1H), 0.88 (s, 9H), 0.03 (s, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -154.43 – -154.76 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.45 (d, *J* = 19.7 Hz), 156.82, 130.19, 121.76, 114.32, 98.80 (d, *J* = 185.4 Hz), 62.83, 55.60, 34.75 (d, *J* = 22.0 Hz), 26.80 (d, *J* = 2.9 Hz), 26.06, 23.96 (d, *J* = 23.9 Hz), 18.45, -5.20.

HRMS (ESI): $C_{19}H_{32}FNNaO_3Si^+$ ($M+Na^+$): 392.2028, found: 392.2030.



7-Bromo-2-fluoro-*N*-(4-methoxyphenyl)-2-methylheptanamide (4i)

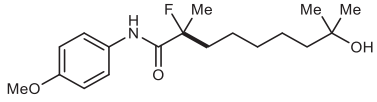
According to the **General Procedure D**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (17.7 mg, 51%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 1H), 7.56 – 7.42 (m, 2H), 7.01 – 6.72 (m, 2H), 3.79 (s, 3H), 3.38 (t, *J* = 6.7 Hz, 2H), 2.16 – 1.94 (m, 1H), 1.90 – 1.77 (m, 3H), 1.62 (d, *J* = 22.5 Hz, 3H), 1.56 – 1.50 (m, 1H), 1.45 (dt, *J* = 10.4, 6.8 Hz, 2H), 1.41 – 1.30 (m, 1H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -154.79 – -155.12 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.29 (d, *J* = 19.7 Hz), 156.76, 130.02, 121.64, 114.24, 98.71 (d, *J* = 185.6 Hz), 55.52, 37.91 (d, *J* = 22.1 Hz), 33.62, 32.47, 27.99, 23.98 (d, *J* = 23.9 Hz), 22.47 (d, *J* = 2.9 Hz).

HRMS (ESI): $C_{15}H_{21}BrFNNaO_2^+$ ($M+Na^+$): 368.0632, found: 368.0629.



2-Fluoro-8-hydroxy-*N*-(4-methoxyphenyl)-2,8-dimethylnonanamide (4j)

According to the **General Procedure D**, the title compound was isolated by flash

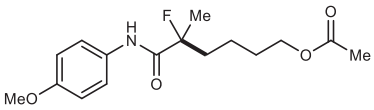
chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (19.8 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.5 Hz, 1H), 7.52 – 7.42 (m, 2H), 6.87 (dd, *J* = 9.6, 2.8 Hz, 2H), 3.79 (s, 3H), 3.78 (s, 1H), 2.15 – 1.94 (m, 1H), 1.81 (m, 1H), 1.61 (d, *J* = 22.5 Hz, 3H), 1.56 – 1.46 (m, 1H), 1.48 – 1.38 (m, 2H), 1.39 – 1.30 (m, 3H), 1.23 (dd, *J* = 13.1, 5.6 Hz, 2H), 1.19 (s, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -154.73 – -155.06 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.60 (d, *J* = 19.7 Hz), 156.85, 130.19, 121.76, 114.36, 98.98 (d, *J* = 185.2 Hz), 71.11, 55.64, 43.90, 38.20 (d, *J* = 21.9 Hz), 30.11, 29.34 (d, *J* = 8.6 Hz), 24.21, 24.06 (d, *J* = 23.9 Hz), 23.31 (d, *J* = 3.2 Hz).

HRMS (ESI): $C_{18}H_{29}FNO_3^+$ ($M+H^+$): 326.2126, found: 326.2129.



5-Fluoro-6-((4-methoxyphenyl)amino)-5-methyl-6-oxohexyl acetate (4k)

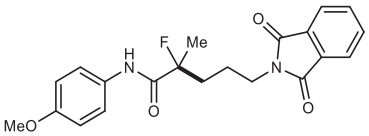
According to the **General Procedure D**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 5:1) as a white solid (22.4 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.1 Hz, 1H), 7.51 – 7.43 (m, 2H), 6.92 – 6.84 (m, 2H), 4.04 (t, *J* = 6.6 Hz, 2H), 3.79 (s, 3H), 2.17 – 1.96 (m, 4H), 1.93 – 1.73 (m, 1H), 1.70 – 1.51 (m, 6H), 1.44 – 1.36 (m, 1H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -155.00 – -155.21 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.18, 170.22 (d, *J* = 19.7 Hz), 156.78, 129.98, 121.68, 114.24, 98.64 (d, *J* = 185.7 Hz), 64.11, 55.51, 37.70 (d, *J* = 22.0 Hz), 28.47, 23.94 (d, *J* = 23.9 Hz), 20.97, 19.91 (d, *J* = 3.1 Hz).

HRMS (ESI): $C_{16}H_{22}FNNaO_4^+$ ($M+Na^+$): 334.1425, found: 334.1422.



5-(1,3-Dioxoisoindolin-2-yl)-2-fluoro-*N*-(4-methoxyphenyl)-2-methylpentanamide

(4l)

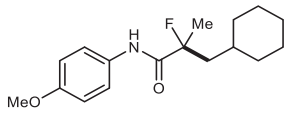
According to the **General Procedure D**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 5:1) as a white solid (17.7 mg, 46%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.3 Hz, 1H), 7.83 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.70 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.54 – 7.32 (m, 2H), 6.90 – 6.81 (m, 2H), 3.79 (s, 3H), 3.72 (t, *J* = 6.9 Hz, 2H), 2.22 – 2.03 (m, 1H), 1.98 – 1.83 (m, 2H), 1.81 – 1.71 (m, 1H), 1.62 (d, *J* = 22.5 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -154.55 – -154.88 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.99 (d, *J* = 19.7 Hz), 168.47, 156.88, 134.09, 132.20, 130.03, 123.40, 121.84, 114.33, 98.50 (d, *J* = 186.3 Hz), 55.63, 37.71, 35.48 (d, *J* = 22.1 Hz), 23.98 (d, *J* = 23.9 Hz), 22.92 (d, *J* = 2.8 Hz).

HRMS (ESI): $C_{21}H_{21}FN_2NaO_4^+$ ($M+Na^+$): 407.1378, found: 407.1376.



3-cyclohexyl-2-fluoro-*N*-(4-methoxyphenyl)-2-methylpropanamide (4m)

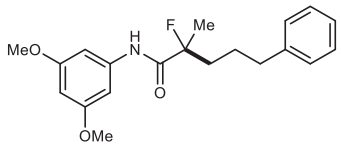
According to the **General Procedure D**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 5:1) as a white solid (13.8 mg, 47%, r.r = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.5 Hz, 1H), 7.53 – 7.37 (m, 2H), 7.13 – 6.75 (m, 2H), 3.80 (s, 3H), 2.07 – 1.89 (m, 1H), 1.83 – 1.67 (m, 4H), 1.67 – 1.56 (m, 5H), 1.53 (m, 1H), 1.28 – 1.08 (m, 3H), 1.04 – 0.89 (m, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -152.25 – -152.89 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.86 (d, *J* = 19.7 Hz), 156.85, 130.25, 121.86, 114.37, 99.34 (d, *J* = 186.1 Hz), 55.63, 45.20 (d, *J* = 20.7 Hz), 34.55 (d, *J* = 1.7 Hz), 33.91, 33.68, 26.38, 26.28, 25.04, 24.80.

HRMS (ESI): $C_{17}H_{24}FNNaO_2^+$ ($M+Na^+$): 316.1683, found: 316.1685.



***N*-(3,5-dimethoxyphenyl)-2-fluoro-2-methyl-5-phenylpentanamide (4n)**

According to the **General Procedure D**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 5:1) as a white solid (24.6 mg, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.9 Hz, 1H), 7.30 – 7.24 (m, 2H), 7.21 – 7.12 (m, 3H), 6.81 (d, *J* = 2.3 Hz, 2H), 6.26 (t, *J* = 2.3 Hz, 1H), 3.77 (s, 6H), 2.71 – 2.54 (m, 2H), 2.20 – 1.98 (m, 1H), 1.94 – 1.75 (m, 2H), 1.74 – 1.65 (m, 1H), 1.60 (d, *J* = 22.5 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -154.55 – -154.88 (m).

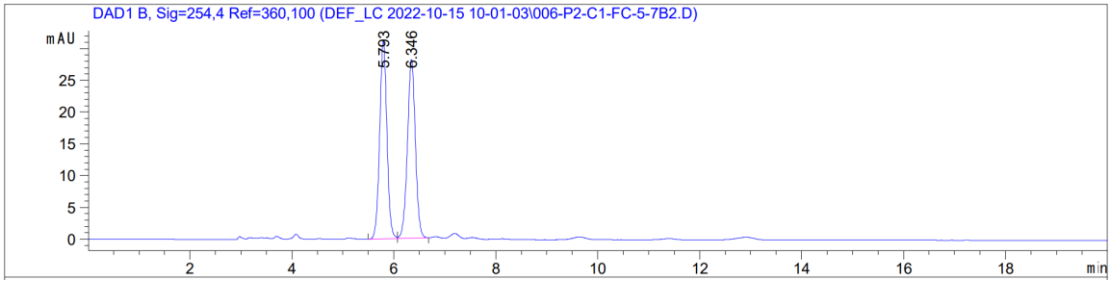
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.71 (d, *J* = 19.6 Hz), 161.22, 141.70, 138.74, 128.49, 126.05, 98.77 (d, *J* = 185.9 Hz), 98.10, 97.45, 55.50, 37.80 (d, *J* = 22.0 Hz), 35.73, 25.11 (d, *J* = 2.9 Hz), 23.98 (d, *J* = 23.9 Hz).

HRMS (ESI): $C_{20}H_{24}FNNaO_3^+$ ($M+Na^+$): 368.1632, found: 368.1630.

$[\alpha]_D^{25}$ = 10.20 (c = 1.00, $CHCl_3$).

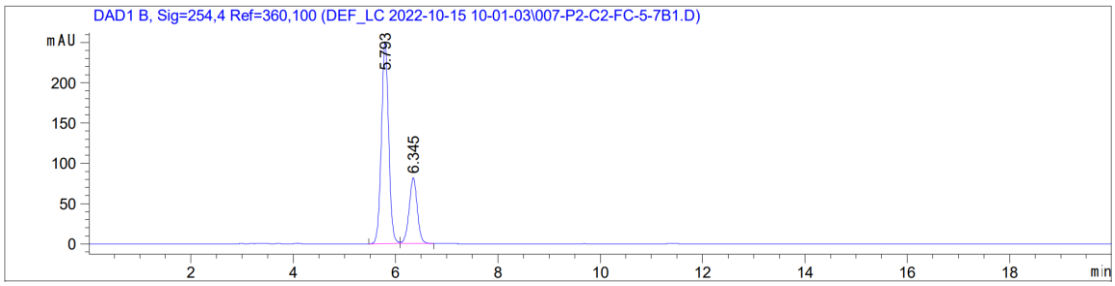
HPLC: The ee was determined to be 46% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 80:20 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 5.8 min, t_R (minor) = 6.3 min.

4n racemic



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.793	BV	0.1509	307.79538	31.25742	50.1036
2	6.346	VB	0.1649	306.52304	28.17248	49.8964

4n enantioenriched, 46% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.793	BV	0.1515	2471.11597	249.69031	73.2211
2	6.345	VB	0.1671	903.75104	81.66937	26.7789

6. Crystallographic Data

The absolute configuration of (*S*)-**2ar** (prepared according to **General Procedure B** using (*S*,*S*)-**L1**) was unambiguously determined by single-crystal X-ray crystallography. The absolute configurations of all other products were assigned by analogy. The data of crystal structures were collected at Shanghai Institute of Organic Chemistry (SIOC). And the X-ray data have been deposited at the Cambridge Crystallographic Data Centre (**2ar**: CCDC **2210184**).

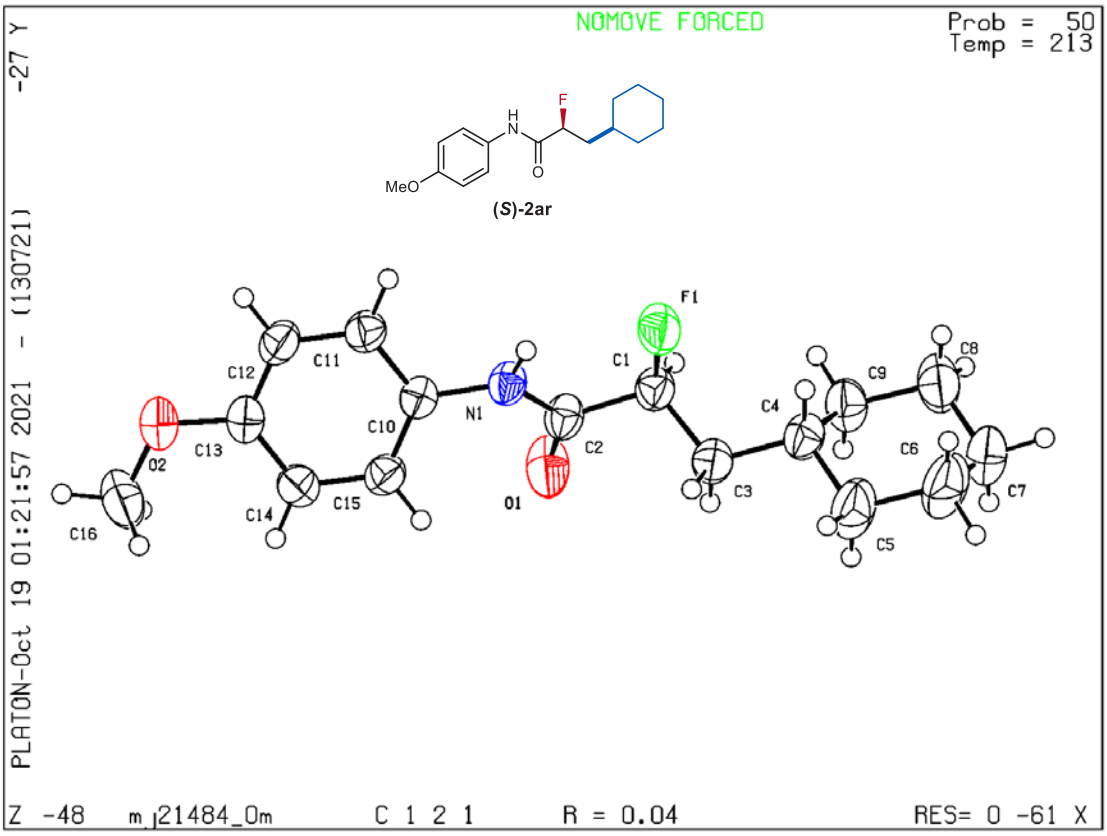


Table S20. Crystal data and structure refinement for mj21484_0m.

Identification code	mj21484_0m	
Empirical formula	C16 H22 F N O2	
Formula weight	279.34	
Temperature	212.99 K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	C 1 2 1	
Unit cell dimensions	a = 20.7274(5) Å	a= 90°.
	b = 5.15920(10) Å	b= 103.8940(10)°.
	c = 14.5091(3) Å	g = 90°.

Volume	1506.16(6) $Å^3$
Z	4
Density (calculated)	1.232 Mg/m^3
Absorption coefficient	0.462 mm^{-1}
F(000)	600
Crystal size	0.07 x 0.06 x 0.05 mm^3
Theta range for data collection	3.823 to 54.849°.
Index ranges	-24<=h<=24, -6<=k<=6, -17<=l<=17
Reflections collected	8973
Independent reflections	2811 [R(int) = 0.0380]
Completeness to theta = 53.594°	98.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7508 and 0.5485
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2811 / 1 / 182
Goodness-of-fit on F^2	1.067
Final R indices [I>2sigma(I)]	R1 = 0.0351, wR2 = 0.0878
R indices (all data)	R1 = 0.0382, wR2 = 0.0906
Absolute structure parameter	0.02(7)
Extinction coefficient	n/a
Largest diff. peak and hole	0.112 and -0.148 $e.Å^{-3}$

Table S21. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for mj21484_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	5130(1)	7485(3)	6493(1)	68(1)
O(1)	4226(1)	1977(3)	5526(1)	73(1)
O(2)	1767(1)	6170(4)	2308(1)	68(1)
N(1)	4037(1)	6279(3)	5285(1)	44(1)
C(1)	5025(1)	4818(4)	6437(1)	47(1)
C(2)	4385(1)	4235(4)	5703(1)	46(1)
C(3)	5015(1)	3782(5)	7405(1)	52(1)
C(4)	5643(1)	4361(5)	8173(1)	51(1)
C(5)	5537(1)	3744(9)	9146(2)	88(1)
C(6)	6153(2)	4337(9)	9938(2)	92(1)
C(7)	6748(1)	2887(7)	9777(2)	81(1)
C(8)	6860(1)	3504(8)	8813(2)	83(1)
C(9)	6247(1)	2942(6)	8020(2)	62(1)
C(10)	3447(1)	6147(4)	4540(1)	40(1)
C(11)	3347(1)	8021(4)	3837(1)	48(1)
C(12)	2780(1)	7969(4)	3107(1)	53(1)
C(13)	2310(1)	6056(5)	3068(1)	47(1)
C(14)	2403(1)	4199(5)	3773(1)	50(1)
C(15)	2972(1)	4258(4)	4511(1)	46(1)
C(16)	1308(1)	4094(7)	2201(2)	77(1)

Table S22. Bond lengths [Å] and angles [°] mj21484_0m.

F(1)-C(1)	1.393(2)
O(1)-C(2)	1.221(3)
O(2)-C(13)	1.375(2)
O(2)-C(16)	1.417(4)
N(1)-H(1)	0.8700
N(1)-C(2)	1.337(3)
N(1)-C(10)	1.427(2)
C(1)-H(1A)	0.9900
C(1)-C(2)	1.519(3)
C(1)-C(3)	1.507(3)
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-C(4)	1.527(3)
C(4)-H(4)	0.9900
C(4)-C(5)	1.514(3)
C(4)-C(9)	1.511(3)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-C(6)	1.529(4)
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-C(7)	1.509(4)
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-C(8)	1.505(4)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-C(9)	1.523(3)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(10)-C(11)	1.384(3)
C(10)-C(15)	1.378(3)
C(11)-H(11)	0.9400
C(11)-C(12)	1.380(3)
C(12)-H(12)	0.9400
C(12)-C(13)	1.380(3)
C(13)-C(14)	1.380(3)
C(14)-H(14)	0.9400
C(14)-C(15)	1.391(3)
C(15)-H(15)	0.9400
C(16)-H(16A)	0.9700
C(16)-H(16B)	0.9700

C(16)-H(16C)	0.9700

C(13)-O(2)-C(16)	117.00(19)
C(2)-N(1)-H(1)	117.4
C(2)-N(1)-C(10)	125.19(17)
C(10)-N(1)-H(1)	117.4
F(1)-C(1)-H(1A)	108.5
F(1)-C(1)-C(2)	109.58(16)
F(1)-C(1)-C(3)	109.47(18)
C(2)-C(1)-H(1A)	108.5
C(3)-C(1)-H(1A)	108.5
C(3)-C(1)-C(2)	112.24(17)
O(1)-C(2)-N(1)	124.65(19)
O(1)-C(2)-C(1)	118.83(18)
N(1)-C(2)-C(1)	116.51(18)
C(1)-C(3)-H(3A)	108.7
C(1)-C(3)-H(3B)	108.7
C(1)-C(3)-C(4)	114.26(17)
H(3A)-C(3)-H(3B)	107.6
C(4)-C(3)-H(3A)	108.7
C(4)-C(3)-H(3B)	108.7
C(3)-C(4)-H(4)	107.7
C(5)-C(4)-C(3)	110.51(18)
C(5)-C(4)-H(4)	107.7
C(9)-C(4)-C(3)	112.89(18)
C(9)-C(4)-H(4)	107.7
C(9)-C(4)-C(5)	110.2(2)
C(4)-C(5)-H(5A)	109.2
C(4)-C(5)-H(5B)	109.2
C(4)-C(5)-C(6)	112.1(2)
H(5A)-C(5)-H(5B)	107.9
C(6)-C(5)-H(5A)	109.2
C(6)-C(5)-H(5B)	109.2
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	108.1
C(7)-C(6)-C(5)	110.5(3)
C(7)-C(6)-H(6A)	109.5
C(7)-C(6)-H(6B)	109.5
C(6)-C(7)-H(7A)	109.5
C(6)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	108.1
C(8)-C(7)-C(6)	110.7(2)
C(8)-C(7)-H(7A)	109.5

C(8)-C(7)-H(7B)	109.5
C(7)-C(8)-H(8A)	109.2
C(7)-C(8)-H(8B)	109.2
C(7)-C(8)-C(9)	112.0(2)
H(8A)-C(8)-H(8B)	107.9
C(9)-C(8)-H(8A)	109.2
C(9)-C(8)-H(8B)	109.2
C(4)-C(9)-C(8)	111.5(2)
C(4)-C(9)-H(9A)	109.3
C(4)-C(9)-H(9B)	109.3
C(8)-C(9)-H(9A)	109.3
C(8)-C(9)-H(9B)	109.3
H(9A)-C(9)-H(9B)	108.0
C(11)-C(10)-N(1)	118.31(17)
C(15)-C(10)-N(1)	122.16(17)
C(15)-C(10)-C(11)	119.52(17)
C(10)-C(11)-H(11)	120.0
C(12)-C(11)-C(10)	120.09(19)
C(12)-C(11)-H(11)	120.0
C(11)-C(12)-H(12)	119.7
C(11)-C(12)-C(13)	120.51(19)
C(13)-C(12)-H(12)	119.7
O(2)-C(13)-C(12)	115.83(18)
O(2)-C(13)-C(14)	124.5(2)
C(14)-C(13)-C(12)	119.64(18)
C(13)-C(14)-H(14)	120.1
C(13)-C(14)-C(15)	119.9(2)
C(15)-C(14)-H(14)	120.1
C(10)-C(15)-C(14)	120.37(19)
C(10)-C(15)-H(15)	119.8
C(14)-C(15)-H(15)	119.8
O(2)-C(16)-H(16A)	109.5
O(2)-C(16)-H(16B)	109.5
O(2)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5

Table S23. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for mj21484_0m.

The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11}$ + ... + 2 h k a* b* $U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	69(1)	48(1)	73(1)	9(1)	-13(1)	-10(1)
O(1)	79(1)	36(1)	82(1)	-3(1)	-22(1)	4(1)
O(2)	56(1)	85(1)	54(1)	7(1)	-8(1)	-5(1)
N(1)	51(1)	36(1)	41(1)	0(1)	1(1)	1(1)
C(1)	49(1)	42(1)	46(1)	3(1)	4(1)	2(1)
C(2)	52(1)	39(1)	43(1)	0(1)	3(1)	5(1)
C(3)	47(1)	61(1)	46(1)	4(1)	8(1)	2(1)
C(4)	58(1)	53(1)	40(1)	-1(1)	6(1)	1(1)
C(5)	69(1)	150(3)	45(1)	12(2)	12(1)	15(2)
C(6)	104(2)	125(3)	41(1)	-1(2)	3(1)	8(2)
C(7)	72(2)	99(2)	59(1)	9(2)	-12(1)	1(2)
C(8)	55(1)	122(3)	64(2)	5(2)	-3(1)	0(2)
C(9)	54(1)	76(2)	50(1)	-5(1)	4(1)	3(1)
C(10)	45(1)	37(1)	37(1)	-2(1)	7(1)	4(1)
C(11)	51(1)	40(1)	49(1)	4(1)	6(1)	-2(1)
C(12)	59(1)	52(1)	43(1)	10(1)	4(1)	2(1)
C(13)	44(1)	54(1)	40(1)	-3(1)	4(1)	6(1)
C(14)	45(1)	50(1)	52(1)	1(1)	9(1)	-3(1)
C(15)	51(1)	44(1)	43(1)	6(1)	9(1)	0(1)
C(16)	55(1)	84(2)	80(2)	-7(2)	-8(1)	-7(1)

Table S24. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for mj21484_0m.

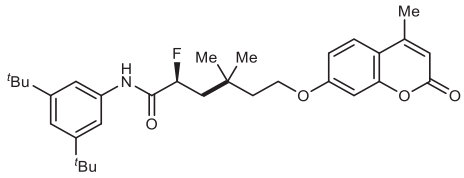
	x	y	z	U(eq)
H(1)	4182	7811	5484	53
H(1A)	5398	3997	6231	56
H(3A)	4951	1900	7360	63
H(3B)	4633	4526	7598	63
H(4)	5733	6242	8153	62
H(5A)	5424	1905	9172	106
H(5B)	5161	4761	9250	106
H(6A)	6242	6204	9955	111
H(6B)	6071	3833	10551	111
H(7A)	7143	3367	10268	98
H(7B)	6677	1019	9825	98
H(8A)	7234	2474	8711	100
H(8B)	6977	5339	8792	100
H(9A)	6331	3471	7411	74
H(9B)	6159	1073	7993	74
H(11)	3665	9332	3858	57
H(12)	2715	9247	2631	63
H(14)	2083	2898	3754	59
H(15)	3034	3001	4994	56
H(16A)	958	4356	1630	116
H(16B)	1116	4031	2748	116
H(16C)	1535	2476	2151	116

Table S25. Torsion angles [°] for mj21484_0m.

F(1)-C(1)-C(2)-O(1)	176.8(2)
F(1)-C(1)-C(2)-N(1)	-2.5(3)
F(1)-C(1)-C(3)-C(4)	-57.1(2)
O(2)-C(13)-C(14)-C(15)	179.80(19)
N(1)-C(10)-C(11)-C(12)	-179.67(18)
N(1)-C(10)-C(15)-C(14)	179.88(17)
C(1)-C(3)-C(4)-C(5)	168.5(2)
C(1)-C(3)-C(4)-C(9)	-67.5(3)
C(2)-N(1)-C(10)-C(11)	-143.8(2)
C(2)-N(1)-C(10)-C(15)	37.6(3)
C(2)-C(1)-C(3)-C(4)	-178.97(19)
C(3)-C(1)-C(2)-O(1)	-61.3(3)
C(3)-C(1)-C(2)-N(1)	119.4(2)
C(3)-C(4)-C(5)-C(6)	-179.1(3)
C(3)-C(4)-C(9)-C(8)	-178.4(2)
C(4)-C(5)-C(6)-C(7)	-56.4(4)
C(5)-C(4)-C(9)-C(8)	-54.3(3)
C(5)-C(6)-C(7)-C(8)	55.8(4)
C(6)-C(7)-C(8)-C(9)	-56.0(4)
C(7)-C(8)-C(9)-C(4)	55.5(4)
C(9)-C(4)-C(5)-C(6)	55.4(4)
C(10)-N(1)-C(2)-O(1)	-3.2(3)
C(10)-N(1)-C(2)-C(1)	176.02(16)
C(10)-C(11)-C(12)-C(13)	0.0(3)
C(11)-C(10)-C(15)-C(14)	1.3(3)
C(11)-C(12)-C(13)-O(2)	-179.51(19)
C(11)-C(12)-C(13)-C(14)	0.8(3)
C(12)-C(13)-C(14)-C(15)	-0.5(3)
C(13)-C(14)-C(15)-C(10)	-0.5(3)
C(15)-C(10)-C(11)-C(12)	-1.0(3)
C(16)-O(2)-C(13)-C(12)	174.1(2)
C(16)-O(2)-C(13)-C(14)	-6.1(3)

7. Synthetic Transformations

7.1 Hydroalkylation with complex alkyl halides



(*S*)-*N*-(3,5-di-*tert*-butylphenyl)-2-fluoro-4,4-dimethyl-6-((4-methyl-2-oxo-2H-chromen-7-yl)oxy)hexanamide (2as)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (36.1 mg, 69%, 92% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 6.7 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.43 (d, *J* = 1.6 Hz, 2H), 7.22 (t, *J* = 1.6 Hz, 1H), 6.86 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.81 (d, *J* = 2.4 Hz, 1H), 6.11 (d, *J* = 1.1 Hz, 1H), 5.25 – 5.05 (m, 1H), 4.13 (t, *J* = 7.0 Hz, 2H), 2.38 (d, *J* = 1.1 Hz, 3H), 2.27 – 2.06 (m, 1H), 1.93 – 1.82 (m, 3H), 1.32 (s, 18H), 1.13 (s, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.61 (s).

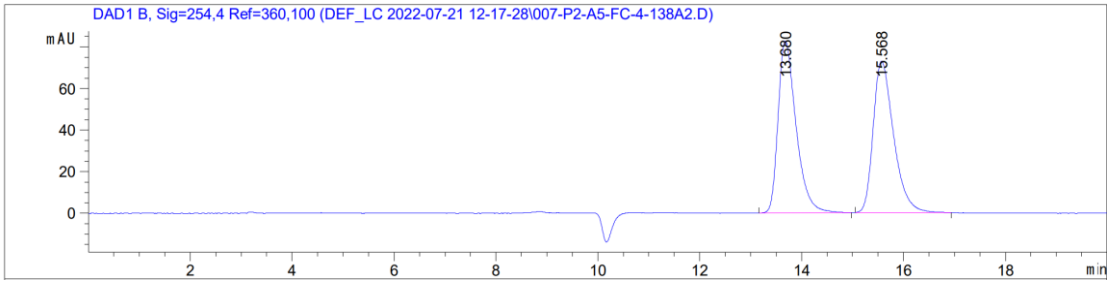
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.36 (d, *J* = 18.0 Hz), 161.93, 161.34, 155.29, 152.60, 151.86, 136.18, 125.55, 119.14, 114.56, 113.54, 112.71, 111.90, 101.40, 90.45 (d, *J* = 187.7 Hz), 65.33, 44.36 (d, *J* = 18.7 Hz), 40.39, 34.98, 31.40, 27.68, 27.62, 18.68.

HRMS (ESI): $C_{32}H_{43}FNO_4^+$ ($M+H^+$): 524.3171, found: 524.3177.

$[\alpha]_D^{25}$ = -10.96 (c = 1.42, $CHCl_3$).

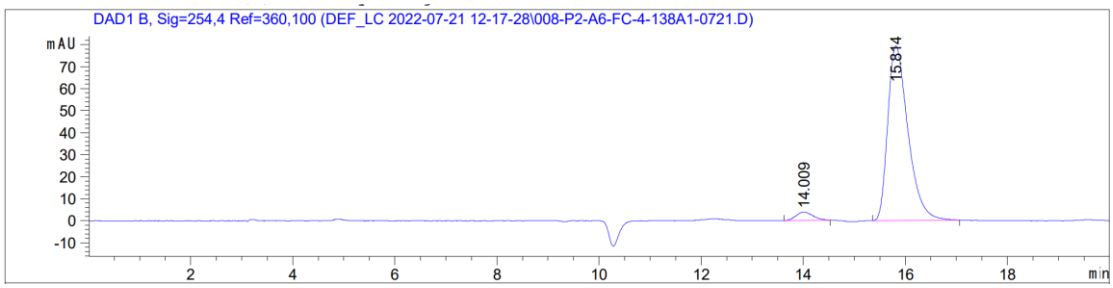
HPLC: The ee was determined to be 92% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 15.8 min, t_R (minor) = 14.0 min.

2as racemic

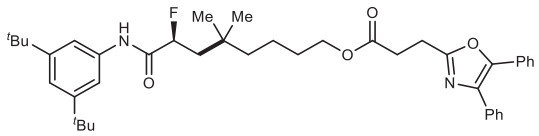


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.680	BB	0.3726	2032.55981	82.73204	50.0686
2	15.568	BB	0.4249	2026.98816	72.79497	49.9314

2as enantioenriched, 92% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.009	BB	0.2854	87.89754	3.75064	3.8725
2	15.814	BB	0.4229	2181.87183	79.31537	96.1275



(*S*)-8-((3,5-di-*tert*-butylphenyl)amino)-7-fluoro-5,5-dimethyl-8-oxooctyl 3-(4,5-di-phen-yloxazol-2-yl)propanoate (2at)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 5:1) as a white solid (54.2 mg, 81%, 90% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 6.9 Hz, 1H), 7.68 – 7.62 (m, 2H), 7.58 (dt, *J* = 8.4, 2.1 Hz, 2H), 7.45 (d, *J* = 1.7 Hz, 2H), 7.39 – 7.29 (m, 6H), 7.23 (t, *J* = 1.6 Hz,

1H), 5.08 (dd, J = 51.3, 9.1 Hz, 1H), 4.16 (t, J = 6.7 Hz, 2H), 3.20 (t, J = 7.5 Hz, 2H), 2.93 (t, J = 7.5 Hz, 2H), 2.06 (dd, J = 28.3, 16.2 Hz, 1H), 1.85 – 1.71 (m, 1H), 1.69 – 1.58 (m, 2H), 1.33 (s, 20H), 1.28 – 1.21 (m, 2H), 0.99 (s, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.31 – -181.64 (m).

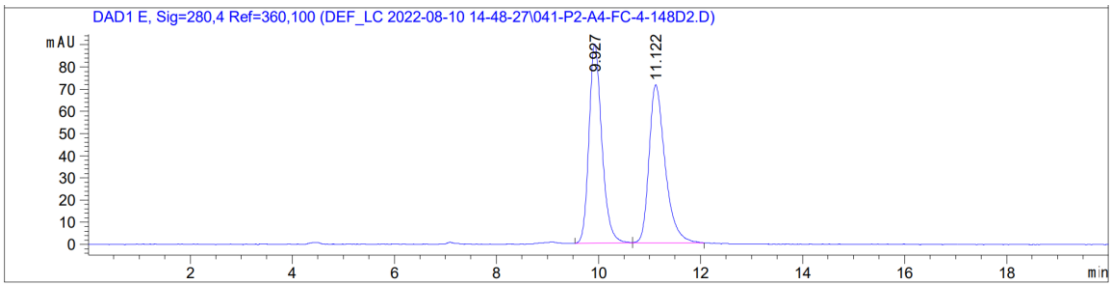
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.14, 168.76 (d, J = 18.0 Hz), 161.88, 151.86, 145.47, 136.33, 135.19, 132.51, 129.04, 128.69, 128.60, 128.51, 128.11, 127.97, 126.53, 119.08, 114.56, 90.69 (d, J = 187.5 Hz), 64.83, 43.94 (d, J = 18.7 Hz), 42.02, 35.02, 32.62, 31.45, 31.25, 29.43, 27.40, 27.19, 23.64, 20.40.

HRMS (ESI): $C_{42}H_{53}FN_2NaO_4^+$ ($M+Na^+$): 691.3882, found: 691.3876.

$[\alpha]_D^{25}$ = -15.69 (c = 1.93, $CHCl_3$).

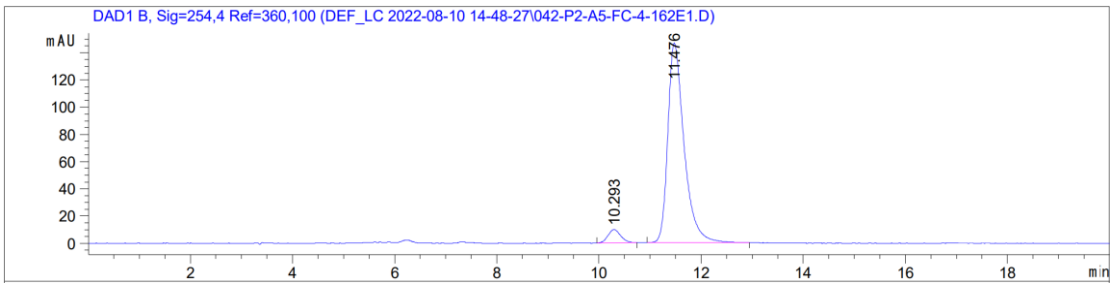
HPLC: The ee was determined to be 90% on a CHIRALPAK IB column at 254 nm, 25 ^oC, with hexane: ^{i}PrOH = 95:5 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 11.5 min, t_R (minor) = 10.3 min.

2at racemic

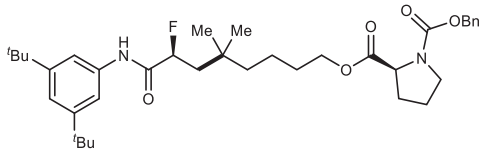


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.927	BV	0.2715	1581.94373	89.79356	50.2198
2	11.122	VB	0.3302	1568.09387	71.41300	49.7802

2at enantioenriched, 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.293	BB	0.2608	168.89319	9.81321	4.9441
2	11.476	BB	0.3322	3247.17188	146.71504	95.0559



1-Benzyl 2-((*S*)-8-((3,5-di-*tert*-butylphenyl)amino)-7-fluoro-5,5-dimethyl-8-oxooctyl) (*S*)-pyrrolidine-1,2-dicarboxylate (2au)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 5:1) as a white solid (55.0 mg, 88%, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 58.4, 6.5 Hz, 1H), 7.50 (d, *J* = 1.4 Hz, 1H), 7.44 (d, *J* = 1.4 Hz, 1H), 7.37 – 7.26 (m, 5H), 7.22 (s, 1H), 5.23 – 4.90 (m, 3H), 4.46 – 4.30 (m, 1H), 4.16 (t, *J* = 6.6 Hz, 1H), 4.04 – 3.97 (m, 1H), 3.72 – 3.57 (m, 1H), 3.56 – 3.40 (m, 1H), 2.31 – 2.12 (m, 1H), 2.11 – 1.83 (m, 5H), 1.82 – 1.72 (m, 1H), 1.70 – 1.34 (m, 5H), 1.32 (d, *J* = 1.5 Hz, 18H), 0.99 (d, *J* = 7.1 Hz, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.52 – -182.04 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.84 (d, *J* = 13.1 Hz), 168.80 (d, *J* = 18.1 Hz), 154.66 (d, *J* = 53.0 Hz), 151.83 (d, *J* = 1.7 Hz), 136.75 (d, *J* = 10.0 Hz), 136.46 (d, *J* = 10.9 Hz), 128.48 (d, *J* = 4.4 Hz), 127.98, 127.87 (d, *J* = 5.3 Hz), 119.02 (d, *J* = 3.1 Hz), 114.58 (d, *J* = 2.1 Hz), 90.66 (dd, *J* = 187.6, 7.9 Hz), 67.02 (d, *J* = 3.0 Hz), 65.01 (d, *J* = 5.8 Hz), 59.40, 46.75 (d, *J* = 50.1 Hz), 43.76 (dd, *J* = 18.7, 14.4 Hz), 41.87 (d, *J* = 8.8 Hz), 35.03, 32.63 (d, *J* = 3.2 Hz), 31.46, 31.07, 30.06, 29.38 (d, *J* = 6.2 Hz), 27.44 (dd, *J* = 17.6, 6.3 Hz), 24.37, 23.58, 20.32.

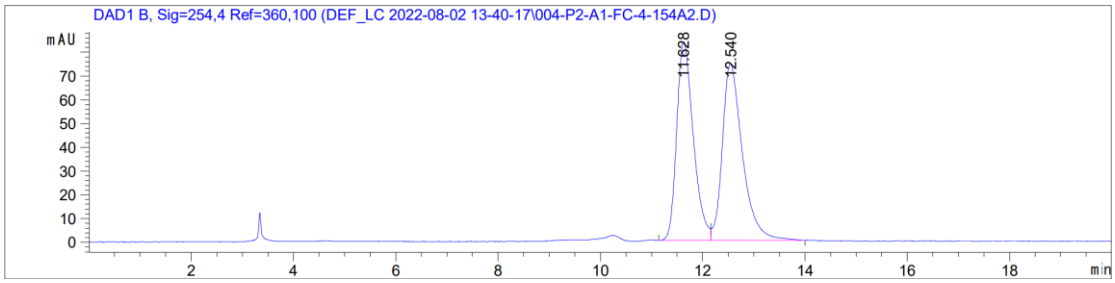
HRMS (ESI): $C_{37}H_{53}FN_2NaO_5^+$ ($M+Na^+$): 647.3831, found: 647.3827.

$[\alpha]_D^{25}$ = -25.63 (c = 1.34, $CHCl_3$).

HPLC: The ee was determined to be 91% on a CHIRALPAK IB column at 254 nm, 25

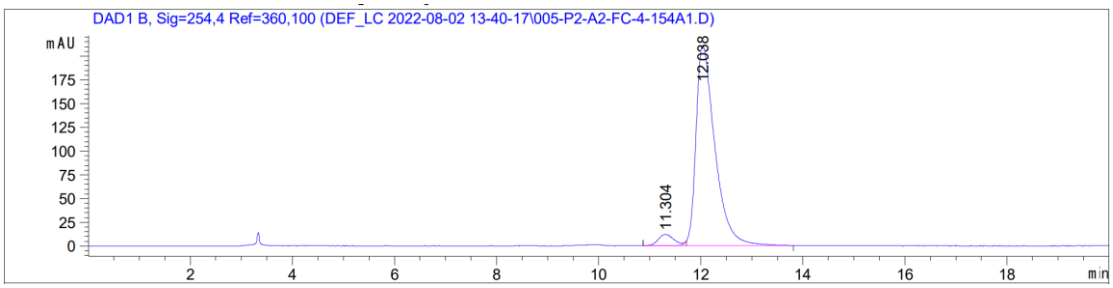
°C, with hexane: ^{i}PrOH = 95:5 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 12.0 min, t_R (minor) = 11.3 min.

2au racemic

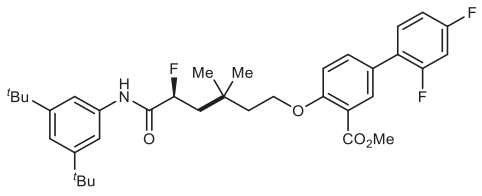


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.628	BV	0.3477	1889.27893	83.58991	48.2280
2	12.540	VB	0.4069	2028.11169	74.20543	51.7720

2au enantioenriched, 91% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.304	BV E	0.3084	250.99539	11.98266	4.4106
2	12.038	VB R	0.3851	5439.73535	210.80301	95.5894



Methyl (*S*)-4-((6-((3,5-di-*tert*-butylphenyl)amino)-5-fluoro-3,3-dimethyl-6-oxohex-yl)oxy)-2',4'-difluoro-[1,1'-biphenyl]-3-carboxylate (2av)

According to the **General Procedure A**, the title compound was isolated by flash

chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (47.1 mg, 77%, 89% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 6.6 Hz, 1H), 7.91 (dd, *J* = 2.3, 1.0 Hz, 1H), 7.64 – 7.57 (m, 1H), 7.45 (d, *J* = 1.7 Hz, 2H), 7.40 – 7.34 (m, 1H), 7.23 (t, *J* = 1.7 Hz, 1H), 7.06 (d, *J* = 8.7 Hz, 1H), 6.98 – 6.86 (m, 2H), 5.35 – 5.05 (m, 1H), 4.20 (t, *J* = 6.9 Hz, 2H), 3.87 (s, 3H), 2.23 – 2.06 (m, 1H), 2.00 – 1.87 (m, 3H), 1.32 (s, 18H), 1.15 (s, 5H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -111.37 – -111.45 (m), -113.59 – -113.66 (m), -181.42 – -181.75 (m).

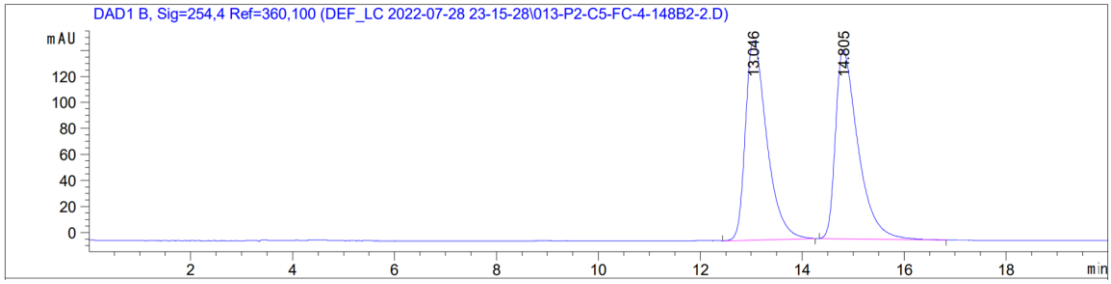
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.58 (d, *J* = 18.1 Hz), 166.69, 162.26 (dd, *J* = 250.0, 11.7 Hz), 159.77 (dd, *J* = 250.6, 11.8 Hz), 158.02, 151.91, 136.36, 133.81 (d, *J* = 3.3 Hz), 132.03 (d, *J* = 2.1 Hz), 131.22 (dd, *J* = 9.4, 4.9 Hz), 127.00, 124.12 (dd, *J* = 13.5, 3.9 Hz), 120.74, 119.14, 114.61, 113.25, 111.70 (dd, *J* = 21.1, 3.7 Hz), 104.47 (dd, *J* = 26.0, 25.6 Hz), 90.60 (d, *J* = 187.5 Hz), 65.93, 52.15, 44.31 (d, *J* = 18.8 Hz), 40.70, 35.06, 32.25, 31.47, 27.74.

HRMS (ESI): $C_{36}H_{44}F_3NNaO_4^+$ ($M+Na^+$): 634.3115, found: 634.3111.

$[\alpha]_D^{25}$ = -13.34 (c = 1.77, $CHCl_3$).

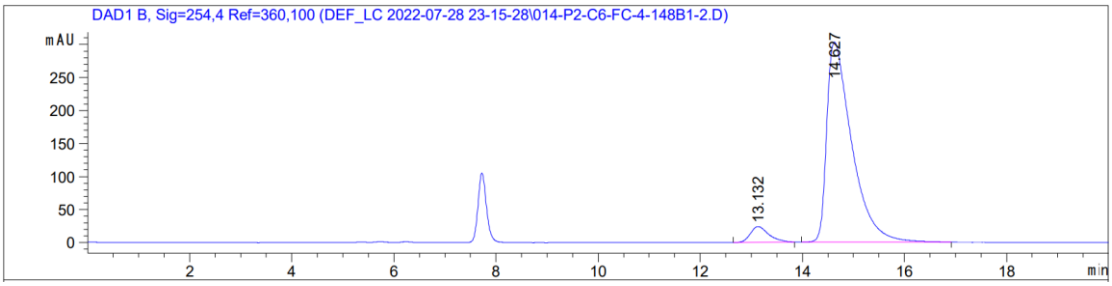
HPLC: The ee was determined to be 89% on a CHIRALPAK IB column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 95:5 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 14.6 min, t_R (minor) = 13.1 min.

2av racemic

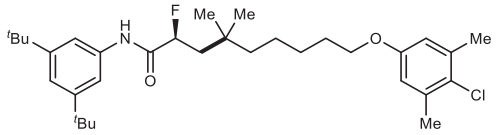


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.046	BB	0.4446	4470.89990	153.12442	50.1279
2	14.805	BB	0.4618	4448.08447	145.05415	49.8721

2av enantioenriched, 89% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.132	BB	0.3766	601.22058	23.97357	5.5132
2	14.627	BB	0.5008	1.03040e4	302.99075	94.4868



(*S*)-9-(4-chloro-3,5-dimethylphenoxy)-*N*-(3,5-di-*tert*-butylphenyl)-2-fluoro-4,4-dimethylnonanamide (2aw)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 20:1) as a white solid (42.6 mg, 78%, 95% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.0 Hz, 1H), 7.46 (d, *J* = 1.6 Hz, 2H), 7.24 (t, *J* = 1.5 Hz, 1H), 6.65 (s, 2H), 5.10 (dd, *J* = 51.3, 9.4 Hz, 1H), 3.92 (t, *J* = 6.5 Hz, 2H), 2.35 (s, 6H), 2.08 (dd, *J* = 45.3, 15.3 Hz, 1H), 1.86 – 1.69 (m, 3H), 1.51 – 1.35 (m, 6H), 1.34 (s, 18H), 1.03 (s, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.23 – -181.57 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.80 (d, *J* = 18.1 Hz), 156.96, 151.86, 137.02, 136.30, 126.02, 119.06, 114.56, 114.49, 90.76 (d, *J* = 187.5 Hz), 68.10, 44.00 (d, *J* = 18.6 Hz),

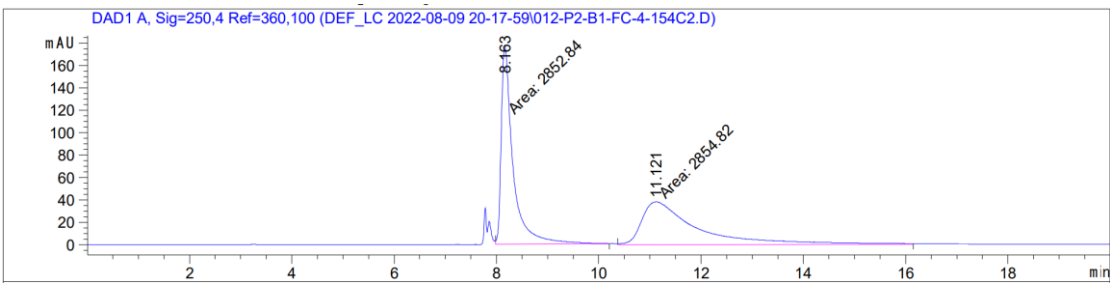
42.48, 35.00, 32.60, 31.42, 29.33, 27.51, 27.21, 26.92, 23.77, 20.98.

HRMS (ESI): $C_{33}H_{49}ClFNNaO_2^+$ ($M+Na^+$): 568.3328, found: 568.3324.

$[\alpha]_D^{25}$ = -13.04 (c =1.70, $CHCl_3$).

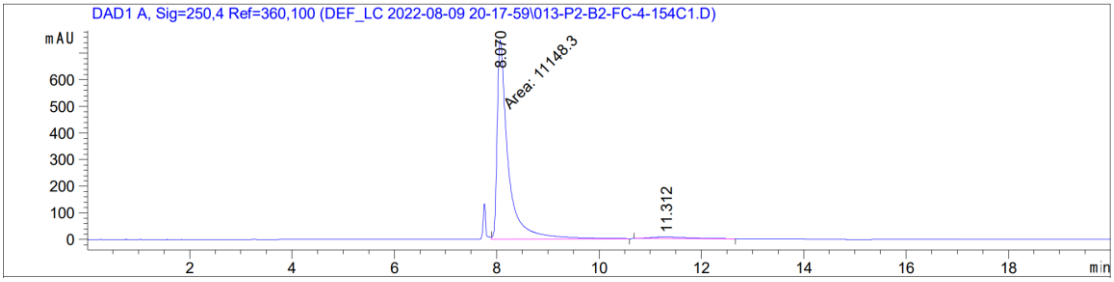
HPLC: The ee was determined to be 95% on a CHIRALPAK IA column at 254 nm, 25 ^oC, with hexane: ^iPrOH = 200:1 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 8.1 min, t_R (minor) = 11.3 min.

2aw racemic

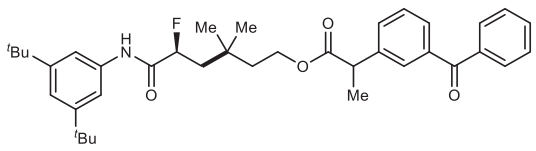


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.163	MM	0.2504	2634.78833	175.35371	50.1159
2	11.121	MM	1.1635	2622.60327	37.56819	49.8841

2aw enantioenriched, 95% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.070	FM	0.2489	1.11574e4	747.18579	97.2695
2	11.312	BB	0.6324	313.20923	5.89019	2.7305



(*S*)-6-((3,5-di-*tert*-butylphenyl)amino)-5-fluoro-3,3-dimethyl-6-oxohexyl 2-(3-benzoylphenyl)propanoate (2ax)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 10:1) as a white solid (46.3 mg, 77%, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 2.7 Hz, 1H), 7.83 – 7.73 (m, 3H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.62 – 7.51 (m, 2H), 7.51 – 7.40 (m, 5H), 7.22 (t, *J* = 1.7 Hz, 1H), 5.27 – 4.89 (m, 1H), 4.36 – 4.06 (m, 2H), 3.86 – 3.58 (m, 1H), 2.05 (dd, *J* = 44.7, 15.5 Hz, 1H), 1.88 – 1.75 (m, 1H), 1.65 (t, *J* = 7.3 Hz, 2H), 1.54 (d, *J* = 7.2 Hz, 3H), 1.32 (s, 18H), 1.00 (s, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.48 – -181.94 (m).

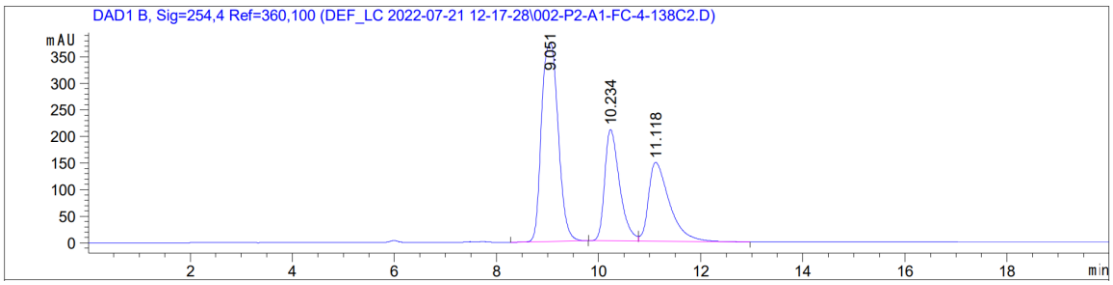
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.56, 174.13, 168.35 (d, *J* = 18.1 Hz), 151.84, 140.89, 140.86, 137.92, 137.53, 136.21, 132.53, 131.60, 131.58, 130.09, 129.21 (d, *J* = 3.3 Hz), 129.03, 128.56, 128.33, 119.10, 114.54, 90.35 (d, *J* = 187.7 Hz), 62.02, 45.47, 44.34 (d, *J* = 5.8 Hz), 44.16 (d, *J* = 5.8 Hz), 39.94 (d, *J* = 6.5 Hz), 34.98, 32.04, 31.40, 27.45 (d, *J* = 7.1 Hz), 27.34 (d, *J* = 4.3 Hz), 18.43 (d, *J* = 3.2 Hz).

HRMS (ESI): $C_{38}H_{48}FNNaO_4^+$ ($M+Na^+$): 624.3460, found: 624.3458.

$[\alpha]_D^{25}$ = -23.17 (c = 1.45, $CHCl_3$).

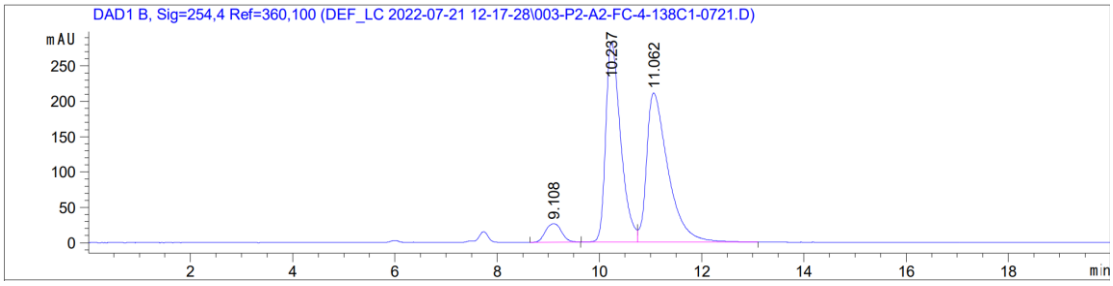
HPLC: The ee was determined to be 91% on a CHIRALPAK IB column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 95:5 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 10.2 min and11.1 min, t_R (minor) = 9.1 min. dr = 1:1.

2ax racemic

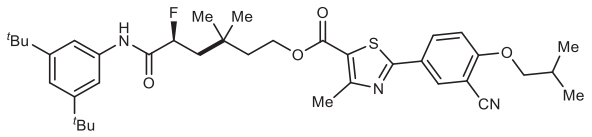


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.051	BB	0.3645	8494.31055	374.66260	50.0133
2	10.234	BV	0.3061	4248.10400	209.93515	25.0122
3	11.118	VB	0.4273	4241.68555	148.49315	24.9744

2ax enantioenriched, 91% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.108	BB	0.3534	574.33783	26.23243	4.6155
2	10.237	BV	0.3082	5745.37842	283.74979	46.1708
3	11.062	VB	0.4287	6124.02393	210.95370	49.2137



(*S*)-6-((3,5-di-*tert*-butylphenyl)amino)-5-fluoro-3,3-dimethyl-6-oxohexyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (2ay)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 3:1) as a white solid (43.2 mg, 65%, 87% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 2.3 Hz, 1H), 8.10 – 7.98 (m, 2H), 7.43 (d, *J* = 1.6 Hz, 2H), 7.22 (t, *J* = 1.6 Hz, 1H), 6.96 (d, *J* = 8.9 Hz, 1H), 5.14 (dd, *J* = 51.2, 9.3 Hz, 1H), 4.40 (t, *J* = 7.2 Hz, 2H), 3.88 (d, *J* = 6.5 Hz, 2H), 2.75 (s, 3H), 2.29 – 2.02 (m, 2H), 2.00 – 1.70 (m, 3H), 1.31 (s, 18H), 1.12 (s, 6H), 1.08 (d, *J* = 6.7 Hz, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.46 – -181.79 (m).

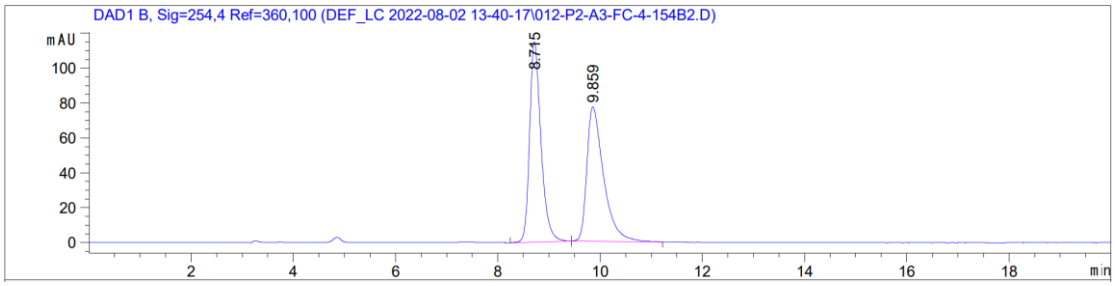
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.38 (d, J = 17.9 Hz), 167.27, 162.53, 162.06, 161.37, 151.91, 136.24, 132.63, 132.10, 126.01, 121.71, 119.16, 115.45, 114.59, 112.67, 103.01, 90.43 (d, J = 187.7 Hz), 75.75, 62.41, 44.39 (d, J = 18.8 Hz), 40.21, 35.02, 32.20, 31.44, 28.22, 27.55 (d, J = 4.0 Hz), 19.12, 17.55.

HRMS (ESI): $C_{38}H_{50}FN_3NaO_4S^+$ ($M+Na^+$): 686.3398, found: 686.3398.

$[\alpha]_D^{25}$ = -24.93 (c = 2.75, $CHCl_3$).

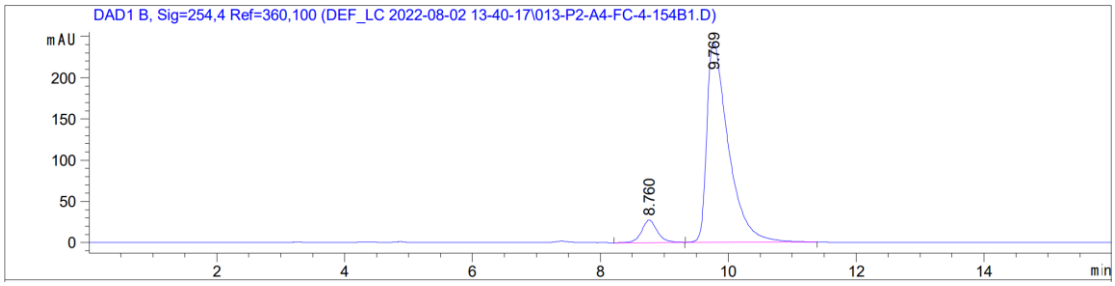
HPLC: The ee was determined to be 87% on a CHIRALPAK IB column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 9.8 min, t_R (minor) = 8.8 min.

2ay racemic

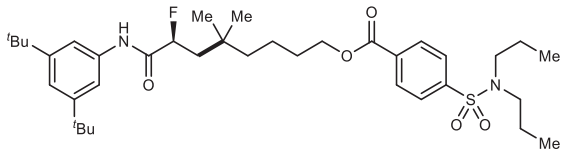


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.715	BB	0.2362	1772.31042	114.73432	50.3385
2	9.859	BB	0.3409	1748.47571	77.01064	49.6615

2ay enantioenriched, 87% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.904	BB	0.2467	231.91063	14.04369	6.3595
2	9.958	BB	0.3430	3414.77026	145.95363	93.6405



(*S*)-8-((3,5-di-*tert*-butylphenyl)amino) -7-fluoro-5,5-dimethyl-8-oxooctyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (2az)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 2:1) as a white solid (49.6 mg, 75%, 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.10 (m, 2H), 8.04 (d, *J* = 6.9 Hz, 1H), 7.93 – 7.83 (m, 2H), 7.43 (d, *J* = 1.7 Hz, 2H), 7.22 (t, *J* = 1.6 Hz, 1H), 5.08 (dd, *J* = 51.3, 9.1 Hz, 1H), 4.36 (t, *J* = 6.7 Hz, 2H), 3.14 – 2.96 (m, 4H), 2.06 (dd, *J* = 44.3, 15.4 Hz, 1H), 1.83 – 1.72 (m, 3H), 1.60 – 1.48 (m, 4H), 1.47 – 1.36 (m, 4H), 1.31 (s, 18H), 1.01 (s, 6H), 0.85 (t, *J* = 7.4 Hz, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -181.27 – -181.60 (m).

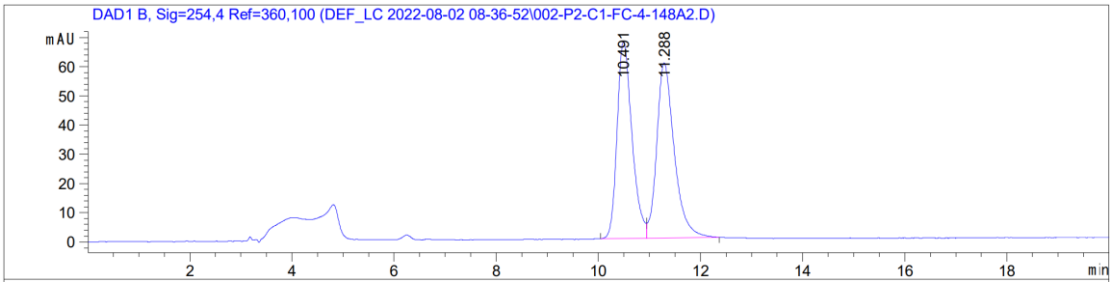
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.74 (d, *J* = 18.0 Hz), 165.39, 151.90, 144.24, 136.31, 133.81, 130.26, 127.08, 119.13, 114.54, 90.69 (d, *J* = 187.6 Hz), 65.69, 50.01, 43.99 (d, *J* = 18.7 Hz), 42.17, 35.04, 32.68, 31.46, 29.50, 27.44, 27.15, 22.01, 20.53, 11.23.

HRMS (ESI): $C_{37}H_{57}FN_2NaO_5S^+$ ($M+Na^+$): 683.3864, found: 683.3860.

$[\alpha]_D^{25}$ = -36.23 (c = 2.30, $CHCl_3$).

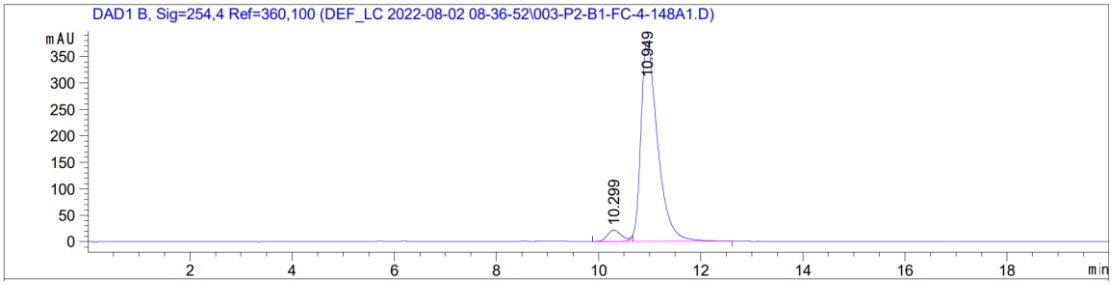
HPLC: The ee was determined to be 91% on a CHIRALPAK IB column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 95:05 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 10.9 min, t_R (minor) = 10.3 min.

2az racemic

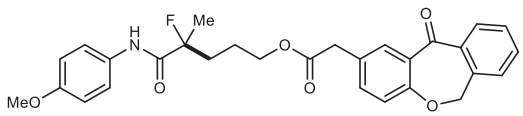


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.491	BV	0.3085	1366.78931	67.43402	48.7757
2	11.288	VB	0.3554	1435.40112	59.93681	51.2243

2az enantioenriched, 91% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.299	BV E	0.2870	402.05899	21.42236	4.4632
2	10.949	VB R	0.3413	8606.17578	378.41473	95.5368



4-Fluoro-5-((4-methoxyphenyl)amino)-4-methyl-5-oxopentyl 2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)acetate (4o)

According to the **General Procedure D**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 3:1) as a white solid (23.3 mg, 46%).

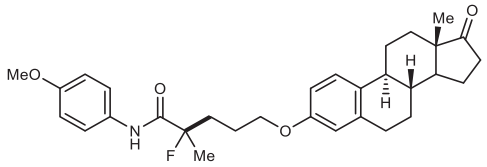
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.09 (m, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.88 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.59 – 7.52 (m, 1H), 7.49 – 7.44 (m, 3H), 7.43 – 7.39 (m, 1H), 7.37 – 7.33 (m, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.92 – 6.82 (m, 2H), 5.17 (s, 2H), 4.12 (t, *J* = 6.4 Hz, 2H), 3.79 (s, 3H), 3.63 (s, 2H), 2.21 – 2.04 (m, 1H), 1.98 – 1.78 (m, 2H), 1.77 – 1.68 (m, 1H), 1.62 (d, *J* = 22.5 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -154.80 – -155.12 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.87, 171.38, 169.98 (d, *J* = 19.7 Hz), 160.50, 156.78, 140.46, 136.38, 135.59, 132.78, 132.45, 129.95, 129.51, 129.27, 127.82, 125.16,

121.72, 121.08, 114.23, 98.34 (d, J = 186.0 Hz), 73.63, 64.36, 55.51, 40.22, 34.51 (d, J = 22.2 Hz), 23.81 (d, J = 23.9 Hz), 22.81 (d, J = 3.0 Hz).

HRMS (ESI): $C_{29}H_{28}FNNaO_6$+ ($M+Na^+$): 528.1793, found: 528.1793.



2-Fluoro-*N*-(4-methoxyphenyl)-2-methyl-5-(((8*R*,9*S*,13*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)oxy) pentanamide (4p)

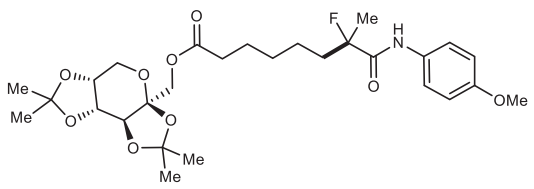
According to the **General Procedure D**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 5:1) as a white solid (28.9 mg, 57%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.2 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.17 (d, J = 8.6 Hz, 1H), 6.92 – 6.85 (m, 2H), 6.69 (dd, J = 8.6, 2.7 Hz, 1H), 6.62 (d, J = 2.6 Hz, 1H), 3.98 – 3.88 (m, 2H), 3.80 (s, 3H), 2.90 – 2.81 (m, 2H), 2.50 (dd, J = 18.8, 8.5 Hz, 1H), 2.42 – 2.33 (m, 1H), 2.23 (m, 2H), 2.16 – 2.08 (m, 1H), 2.08 – 1.92 (m, 5H), 1.89 – 1.80 (m, 1H), 1.66 (d, J = 22.5 Hz, 3H), 1.62 – 1.40 (m, 6H), 0.90 (s, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -154.73 – -155.06 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.19 (d, J = 19.7 Hz), 156.91, 156.77, 137.75, 132.10, 130.06, 126.34, 121.74, 114.59, 114.23, 112.20, 112.11, 98.55 (d, J = 185.8 Hz), 67.29, 55.51, 50.41, 48.03, 43.98, 38.38, 35.90, 34.80 (d, J = 22.1 Hz), 31.61, 29.66, 26.57, 25.94, 23.95 (d, J = 23.8 Hz), 23.54 (d, J = 2.8 Hz), 21.61, 13.88.

HRMS (ESI): $C_{31}H_{38}FNNaO_4^+$ ($M+Na^+$): 530.2677, found: 530.2676.



((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',

5'-d]pyran-3a-yl)methyl 7-fluoro-8-((4-methoxyphenyl)amino)-7-methyl-8-oxooctanoate (4q)

According to the **General Procedure D**, except for using **L25**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 3:1) as a white solid (29.3 mg, 53%).

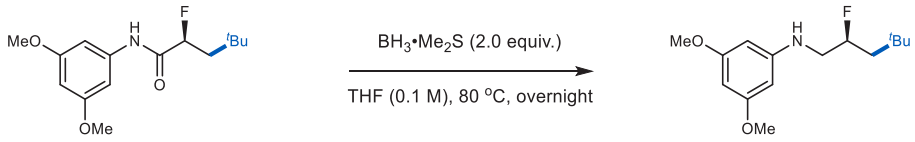
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 1H), 7.52 – 7.38 (m, 2H), 6.95 – 6.75 (m, 2H), 4.59 (dd, *J* = 7.9, 2.5 Hz, 1H), 4.37 (d, *J* = 11.7 Hz, 1H), 4.28 (d, *J* = 2.5 Hz, 1H), 4.22 (d, *J* = 7.9 Hz, 1H), 4.01 (dd, *J* = 11.7, 2.1 Hz, 1H), 3.89 (dd, *J* = 13.0, 1.7 Hz, 1H), 3.78 (s, 3H), 3.74 (d, *J* = 13.0 Hz, 1H), 2.33 (t, *J* = 7.5 Hz, 2H), 2.12 – 1.95 (m, 1H), 1.87 – 1.71 (m, 2H), 1.66 – 1.59 (m, 3H), 1.54 (d, *J* = 20.2 Hz, 5H), 1.46 (s, 3H), 1.37 (s, 3H), 1.34 – 1.28 (m, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -154.79 – -155.12 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 170.44 (d, *J* = 19.7 Hz), 156.82, 130.13, 121.77, 114.31, 109.23, 108.80, 101.66, 98.81 (d, *J* = 185.5 Hz), 70.87, 70.62, 70.15, 65.26, 61.32, 55.59, 37.99 (d, *J* = 22.0 Hz), 34.00, 29.00, 26.57, 25.98, 25.32, 24.60, 24.16, 24.02 (d, *J* = 24.6 Hz), 23.01 (d, *J* = 2.7 Hz).

HRMS (ESI): $C_{28}H_{40}FNNaO_9^+$ ($M+Na^+$): 576.2579, found: 576.2579.

7.2 Derivatizations of α-F amide products



2n **5**, 88%, 91% ee

Following literature procedure[14], Borane-SMe_2 (0.2 mL, 2.0 M in THF, 2.0 equiv.) was added dropwise to a solution of (*S*)-*N*-(3,5-dimethoxyphenyl)-2-fluoro-4,4-dimethylpentanamide **2n** (0.20 mmol, 1.0 equiv.) in THF (2.0 mL) at 0 ºC in a 10-mL Schlenk tube. The reaction mixture was allowed to warm to room temperature, and heated to reflux for overnight. Then the reaction was quenched with NaOH aqueous solution (1 M, 1.0 mL). The resulting mixture was extracted with EtOAc (3*20 mL). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated under

reduced pressure. The residue was purified by flash chromatography on silica gel (1:20 EtOAc/hexanes) to afford **5** as colorless oil. 47.3mg, 88% yield, 91% ee.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 (t, *J* = 2.1 Hz, 1H), 5.81 (d, *J* = 2.1 Hz, 2H), 4.97 – 4.70 (m, 1H), 3.75 (s, 6H), 3.33 – 3.09 (m, 2H), 1.81 – 1.61 (m, 1H), 1.51 – 1.29 (m, 1H), 0.99 (s, 9H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -182.12 – -182.54 (m).

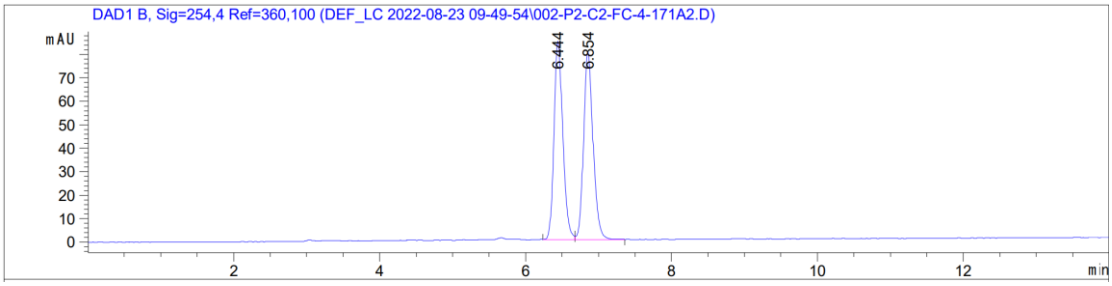
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.90, 149.85, 92.07, 90.81 (d, *J* = 168.8 Hz), 90.30, 55.28, 49.41 (d, *J* = 21.8 Hz), 46.44 (d, *J* = 19.2 Hz), 30.07, 29.94.

HRMS (ESI): $C_{15}H_{25}FNO_2^+$ ($M+H^+$): 270.1864, found: 270.1866.

$[\alpha]_D^{25}$ = -13.00 (c = 1.70, $CHCl_3$).

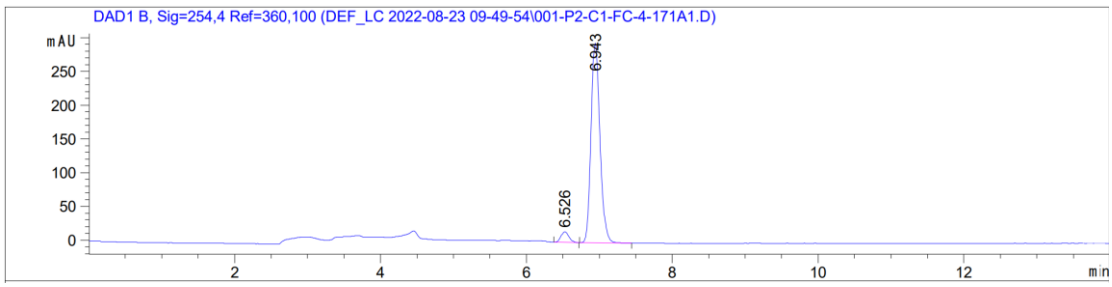
HPLC: The ee was determined to be 91% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 80:20 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 6.9 min, t_R (minor) = 6.5 min.

5 racemic

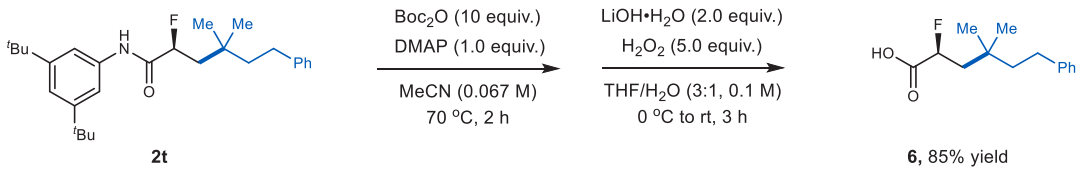


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.444	BV	0.1282	710.50549	84.40158	49.6131
2	6.854	VB	0.1374	721.58832	79.89265	50.3869

5 enantioenriched, 91% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.526	BB	0.1170	121.48647	15.92179	4.5970
2	6.943	BB	0.1295	2521.25977	295.69760	95.4030



Following literature procedure[15-16], to a solution (6 mL) of **2t** (0.4 mmol, 1.0 equiv.) in dry MeCN was added $(Boc)_2O$ (4.0 mmol, 10 equiv.) and DMAP (0.4, 1.0 equiv.), the resulting reaction mixture was stirred at 70 °C for 2 h. The resulting solution was concentrated under reduce pressure. The crude product was purified on flash column to afford *tert*-butyl (*S*)-(3,5-di-*tert*-butylphenyl)(2-fluoro-4,4-dimethyl-6-phenylhexanoyl) carbamate. A round-bottom flask equipped with a magnetic stirring bar was charged with *tert*-butyl (*S*)-(3,5-di-*tert*-butylphenyl)(2-fluoro-4,4-dimethyl-6-phenylhexanoyl) carbamate (0.20 mmol, 1.0 equiv.) in THF:H_2O (3:1, 2 mL). The solution was cooled to 0 °C followed by adding 30% (by wt.) aqueous solution of H_2O_2 (1.0 mmol, 5.0 equiv.) and $LiOH{\cdot}H_2O$ (0.40 mmol, 2.0 equiv.). The mixture was warmed slowly to room temperature and stirred for 3 h until completion as judged by TLC analysis. The reaction was cooled to 0 °C and treated with 1.5 N aqueous solution of Na_2SO_3 (1.1 equiv.). The mixture was stirred for 5 min at room temperature, and was diluted with H_2O. Then acidified with 1N HCl to pH = 4. The mixture was extracted with CH_2Cl_2 and dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (20:1 CH_2Cl_2/MeOH) to afford **6** as colorless oil. 40.5 mg, 85% yield, 90% ee (determined by reducing to corresponding alcohol).

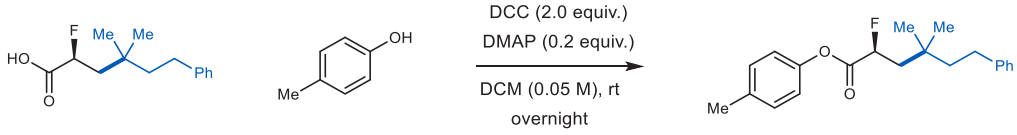
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 (s, 1H), 7.32 – 7.21 (m, 2H), 7.21 – 7.12 (m, 3H), 5.18 – 4.99 (m, 1H), 2.59 (m, 2H), 2.04 – 1.76 (m, 2H), 1.69 – 1.51 (m, 2H), 1.07 (s, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -186.45 – -186.75 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.80, 176.56, 142.88, 128.53, 128.44, 125.87, 86.92 (d, *J* = 185.5 Hz), 44.68, 43.53 (d, *J* = 19.7 Hz), 33.10, 30.68, 27.45 (d, *J* = 1.0 Hz), 27.28.

HRMS (ESI): $C_{14}H_{20}FO_2^+$ ($M+H^+$): 239.1442, found: 239.1445.

$[\alpha]_D^{25}$ = -50.42 (c = 1.90, $CHCl_3$).



6 2.0 equiv. **7**, 55%, 90% ee total three steps

Following the literature procedure[17], the (*S*)-2-fluoro-4,4-dimethyl-6-phenylhexanoic acid **6** (0.2 mmol, 1.0 equiv.) was added to a solution of *N*,*N*′-dicyclohexylcarbodiimide (DCC, 0.4 mmol, 2.0 equiv.) and DMAP (0.04 mmol, 0.2 equiv.) in CH_2Cl_2 (4 mL) at 0 °C. The *p*-cresol (0.4 mmol) was then added. The reaction mixture was allowed to be warmed to room temperature slowly and stirred overnight. The solution was diluted with CH_2Cl_2 and washed with 1N HCl (2 ×10 mL) and brine (20 mL) sequentially. The organic layer was dried over anhydrous $MgSO_4$. After the removal of solvent under reduced pressure, the residue was purified by flash chromatography on silica gel (1:20 EtOAc/hexanes) to afford *p*-tolyl (*S*)-2-fluoro-4,4-dimethyl-6-phenylhexanoate **7** as a write solid. 36 mg, 55% yield, 90% ee (total three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.22 (m, 2H), 7.21 – 7.11 (m, 5H), 7.04 – 6.93 (m, 2H), 5.36 – 5.09 (m, 1H), 2.75 – 2.53 (m, 2H), 2.34 (s, 3H), 2.17 – 1.86 (m, 2H), 1.78 – 1.56 (m, 2H), 1.11 (s, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -186.51 – -186.81 (m).

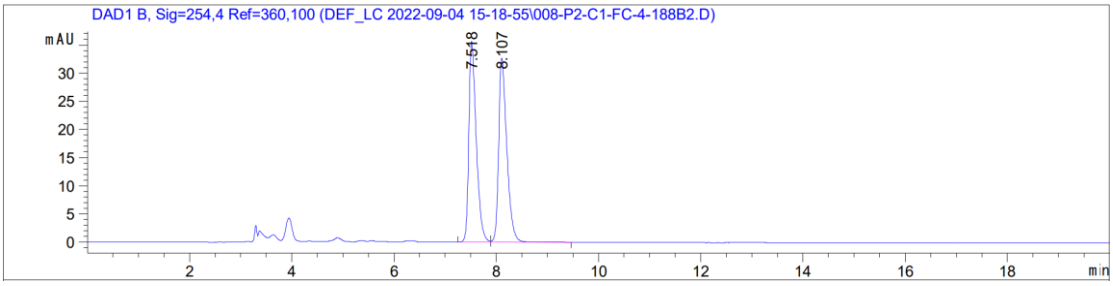
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.43 (d, *J* = 24.7 Hz), 147.94, 142.92, 136.15, 130.20, 128.52, 128.46, 125.85, 120.97, 87.40 (d, *J* = 185.8 Hz), 44.74, 43.67 (d, *J* = 20.1 Hz), 33.15, 30.73, 27.53 (d, *J* = 1.1 Hz), 27.37, 20.99.

HRMS (ESI): $C_{21}H_{26}FO_2^+$ ($M+H^+$): 329.1911, found: 329.1914.

$[\alpha]_D^{25}$ = -19.75 (c = 0.95, $CHCl_3$).

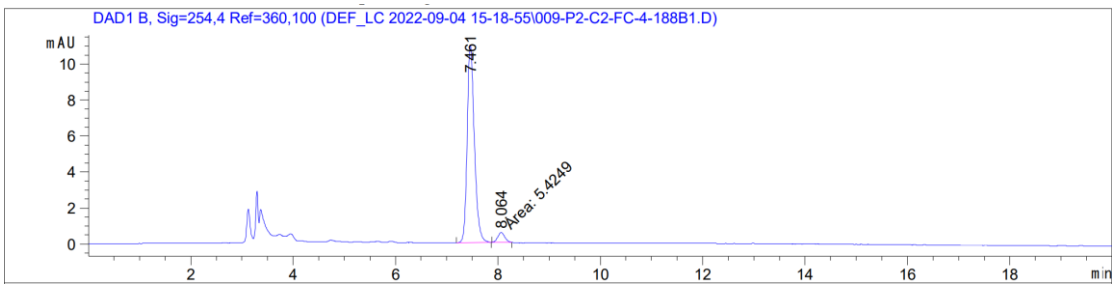
HPLC: The ee was determined to be 90% on a CHIRALPAK IB column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 95:05 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 7.5 min, t_R (minor) = 8.1 min.

7 racemic

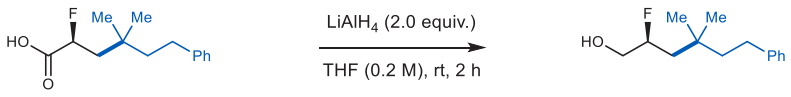


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.518	BV	0.1515	358.94537	35.63852	49.7985
2	8.107	VB	0.1651	361.85074	32.71136	50.2015

7 enantioenriched, 90% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.461	BB	0.1471	106.51274	10.98755	95.1536
2	8.064	MM	0.1617	5.42490	5.59055e-1	4.8464



6

8, 76%, 90% ee
total three steps

Following literature procedure[18], the acid intermediate (*S*)-2-fluoro-4,4-dimethyl-6-phenylhexanoic acid **6** (0.2 mmol, 1.0 equiv.), dissolved in THF (1.0 mL) was added to a solution of $LiAlH_4$(0.4 mmol, 1 M in Et_2O) at 0°C. After 2 h, the reaction was treated water, and the mixture was extracted with diethyl ether (2*20 mL), washed with brine and dried over $MgSO_4$. Then the solvent was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (1:5 EtOAc/hexanes) to afford (*S*)-2-fluoro-4,4-dimethyl-6-phenylhexan-1-ol **8** as colorless oil. 36 mg, 76% yield, 90% ee (total three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.14 (m, 2H), 7.13 – 7.01 (m, 3H), 4.92 – 4.44 (m, 1H), 3.77 – 3.35 (m, 2H), 2.61 – 2.32 (m, 2H), 1.99 (s, 1H), 1.72 – 1.60 (m, 1H), 1.57 – 1.40 (m, 2H), 1.39 – 1.22 (m, 1H), 0.95 (d, *J* = 1.7 Hz, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -185.47 – -185.89 (m).

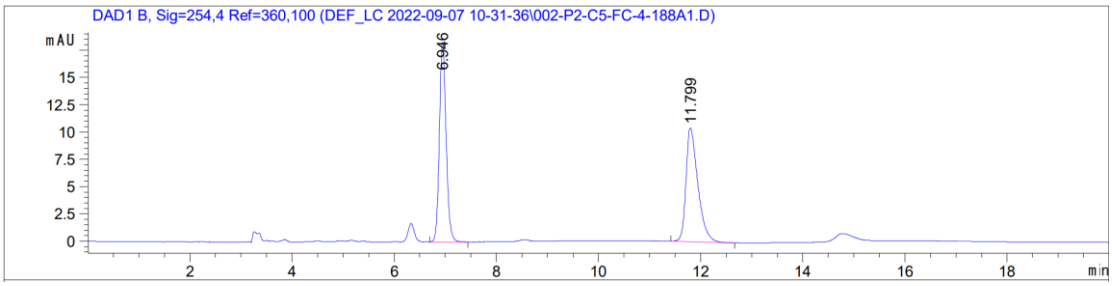
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.20, 128.48, 128.44, 125.77, 92.46 (d, *J* = 167.7 Hz), 66.33 (d, *J* = 22.5 Hz), 44.88, 42.35 (d, *J* = 19.3 Hz), 32.58, 30.79, 27.61 (d, *J* = 1.0 Hz), 27.53.

HRMS (ESI): $C_{14}H_{22}FO^+$ ($M+H^+$): 225.1649, found: 225.4651.

$[\alpha]_D^{25}$ = -23.62 (c = 1.86, $CHCl_3$).

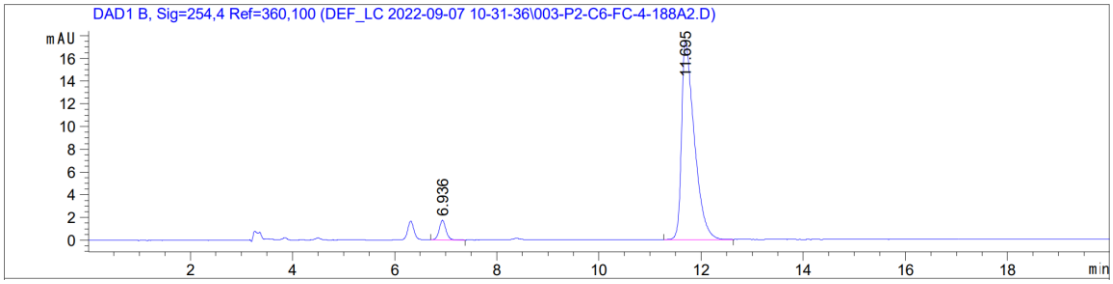
HPLC: The ee was determined to be 90% on a CHIRALPAK IB column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 90:10 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 11.7 min, t_R (minor) = 6.9 min.

8 racemic



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.946	BB	0.1384	167.02708	18.30588	49.9531
2	11.799	BB	0.2413	167.34047	10.42123	50.0469

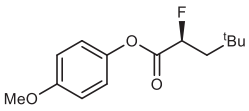
8 enantioenriched, 90% ee



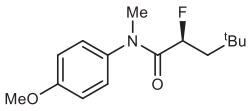
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.936	BB	0.1392	15.83109	1.72273	4.9598
2	11.695	BB	0.2563	303.35864	17.49808	95.0402

8. Additional Examples

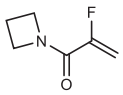
a) Asymmetric group transfer



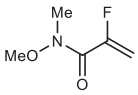
2ba 21%, 29% ee



2bb 50%, 11% ee

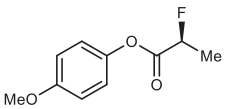


S1ac not detected

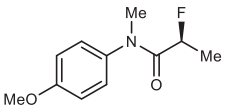


S1ad not detected

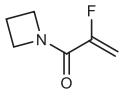
b) Asymmetric hydrogenation



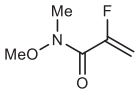
3x 59%, 32% ee



3y 15%, 28% ee

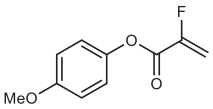


S1ac not detected

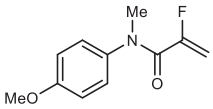


S1ad not detected

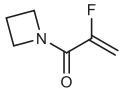
c) HAT/alkyl coupling



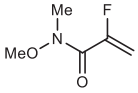
S1aa not detected



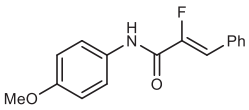
S1ab not detected



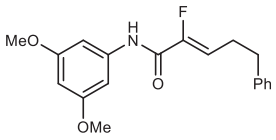
S1ac not detected



S1ad not detected

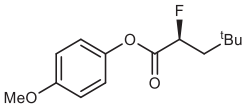


S1V not detected



S1W not detected

Figure S1. Additional examples



4-Methoxyphenyl (*S*)-2-fluoro-4,4-dimethylpentanoate (S2ba)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 20:1) as a colorless oil (5.3 mg, 21%, 29% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 – 6.97 (m, 2H), 6.93 – 6.84 (m, 2H), 5.36 – 4.86 (m, 1H), 3.80 (s, 3H), 2.04 – 1.78 (m, 2H), 1.07 (s, 9H).

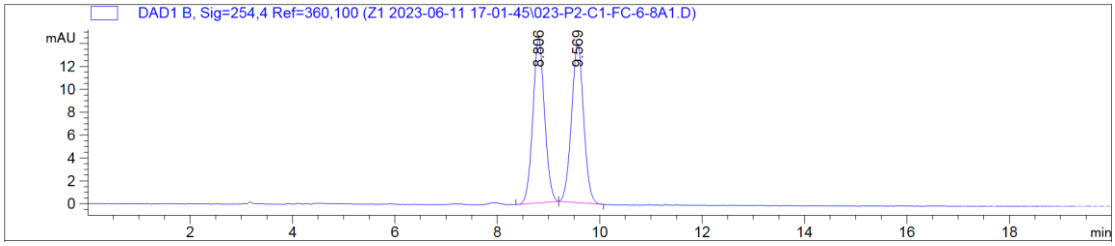
^{19}F NMR (377 MHz, $CDCl_3$) δ -186.48 – -187.44 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.64 (d, J = 24.4 Hz), 157.70, 143.66, 122.11, 114.70, 87.71 (d, J = 185.6 Hz), 55.73, 45.72 (d, J = 19.9 Hz), 30.48, 29.80.

HRMS (ESI): $C_{14}H_{20}FO_3^+$ ($M+H^+$): 255.1391, found: 255.1387.

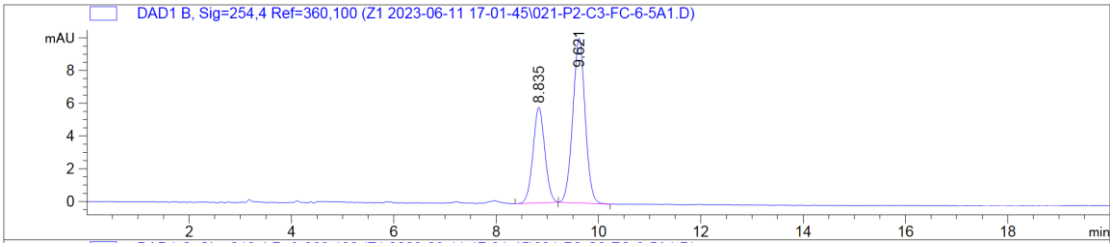
HPLC: The ee was determined to be 29% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 95:5 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 9.6 min, t_R (minor) = 8.8 min.

S2ba racemic

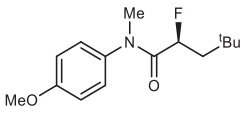


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.806	BB	0.2450	228.55067	14.41178	50.0504
2	9.569	BB	0.2521	228.09019	13.85178	49.9496

S2ba enantioenriched, 29% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.835	BB	0.2492	93.71243	5.84149	35.7080
2	9.621	BB	0.2535	168.72873	10.06793	64.2920



(*S*)-2-fluoro-*N*-(4-methoxyphenyl)-*N*,4,4-trimethylpentanamide (S2bb)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 5:1) as a colorless oil (13.4 mg, 50%, 11% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.03 (m, 2H), 6.95 – 6.79 (m, 2H), 4.96 (m, 1H),

3.79 (s, 3H), 3.21 (s, 3H), 1.78 (m, 1H), 1.47 (m, 1H), 0.70 (s, 9H).

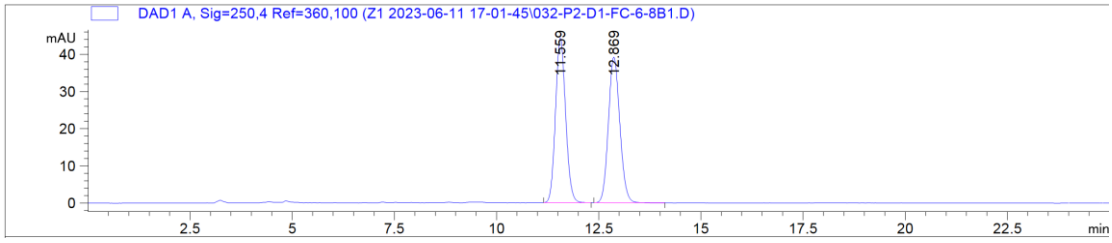
^{19}F NMR (377 MHz, $CDCl_3$) δ -183.61 – -183.98 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.02 (d, J = 22.2 Hz), 159.36, 135.10, 128.62, 115.12, 85.93 (d, J = 174.7 Hz), 55.60, 45.30 (d, J = 21.0 Hz), 37.96, 29.87, 29.48.

HRMS (ESI): $C_{15}H_{23}FNO_2^+$ ($M+H^+$): 268.1707, found: 268.1709.

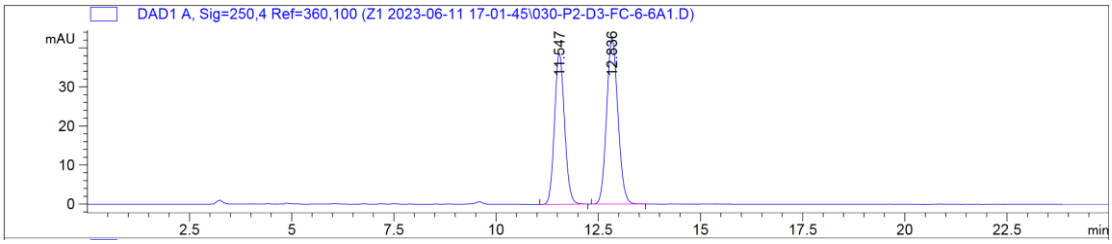
HPLC: The ee was determined to be 11% on a CHIRALPAK IC column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 80:20 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 12.8 min, t_R (minor) = 11.5 min.

S2bb racemic

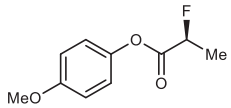


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.559	BB	0.2669	761.83569	44.23671	49.9423
2	12.869	BB	0.3016	763.59595	39.14431	50.0577

S2bb enantioenriched, 11% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.547	BB	0.2646	659.49182	38.73891	44.6821
2	12.836	BB	0.3012	816.47308	42.29833	55.3179



4-Methoxyphenyl (*S*)-2-fluoropropanoate (S3x)

According to the **General Procedure C**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 20:1) as a white solid (11.7 mg, 59%, 32% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 – 6.98 (m, 2H), 6.97 – 6.85 (m, 2H), 5.33 – 5.10 (m, 1H), 3.80 (s, 3H), 1.73 (dd, *J* = 23.5, 6.9 Hz, 3H).

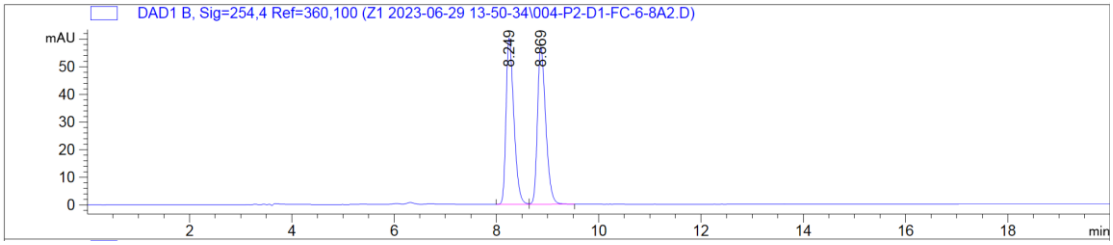
^{19}F NMR (376 MHz, $CDCl_3$) δ -184.07 – -184.47 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.34 (d, *J* = 24.0 Hz), 157.70, 143.55, 122.06, 114.66, 85.64 (d, *J* = 182.6 Hz), 55.68, 18.42 (d, *J* = 22.3 Hz).

HRMS (ESI): $C_{10}H_{12}FO_3^+$ ($M+H^+$): 199.0765, found: 199.0763.

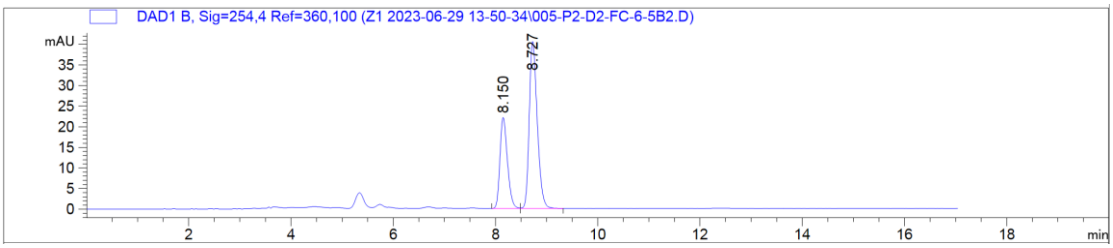
HPLC: The ee was determined to be 32% on a CHIRALPAK IB column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 80:20 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 8.7 min, t_R (minor) = 8.2 min.

S3x racemic

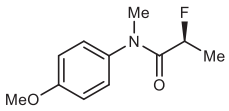


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.249	BV	0.1613	635.93115	60.19481	49.9208
2	8.869	VB	0.1709	637.94830	56.85778	50.0792

S3x enantioenriched, 32% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.150	BV	0.1566	224.72618	22.11063	33.7188
2	8.727	VB	0.1670	441.74435	40.57434	66.2812



(*S*)-2-Fluoro-*N*-(4-methoxyphenyl)-*N*-methylpropanamide (S3y)

According to the **General Procedure C**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 5:1) as a white solid (3.2 mg, 15%, 28% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.06 (m, 2H), 6.94 – 6.88 (m, 2H), 5.01 – 4.80 (m, 1H), 3.80 (s, 3H), 3.22 (s, 3H), 1.36 (dd, *J* = 24.5, 6.5 Hz, 3H).

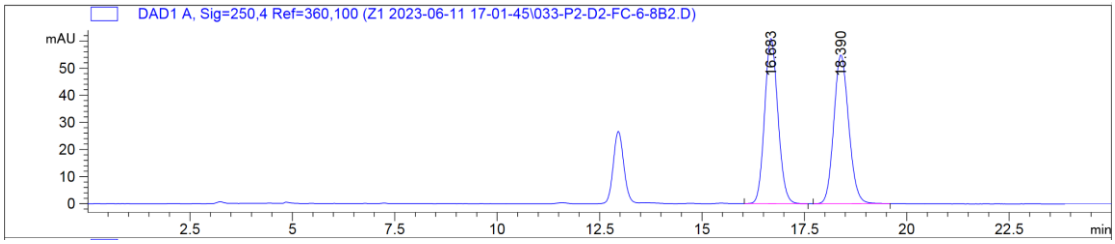
^{19}F NMR (376 MHz, $CDCl_3$) δ -178.85 – -179.27 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.72 (d, *J* = 21.2 Hz), 159.36, 135.11, 128.49, 115.10, 84.29 (d, *J* = 172.6 Hz), 55.57, 38.03, 18.16 (d, *J* = 23.8 Hz).

HRMS (ESI): $C_{11}H_{15}FNO_2^+$ ($M+H^+$): 212.1081, found: 212.1080.

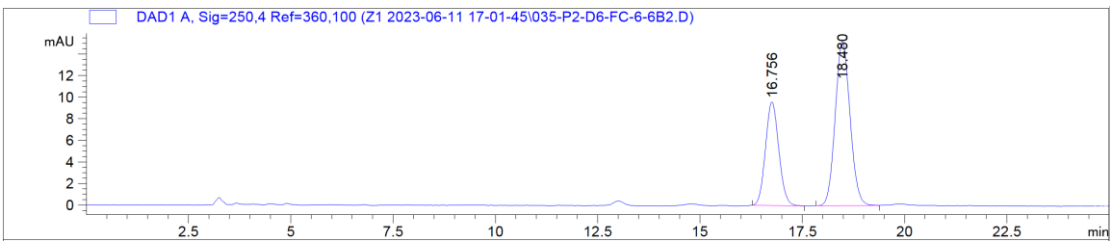
HPLC: The ee was determined to be 28% on a CHIRALPAK IC column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 80:20 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 18.5 min, t_R (minor) = 16.8 min.

S3y racemic



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.683	BB	0.3523	1379.43555	60.89082	49.8527
2	18.390	BB	0.3912	1387.58643	54.84244	50.1473

S3y enantioenriched, 28% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.756	BB	0.3519	216.99333	9.59255	36.1000
2	18.480	BB	0.3885	384.09549	15.21468	63.9000

9. Mechanistic Studies

9.1 Mechanism studies for asymmetric hydrogenation reaction

1) Deuterium-labeling experiments for hydrogenation reaction

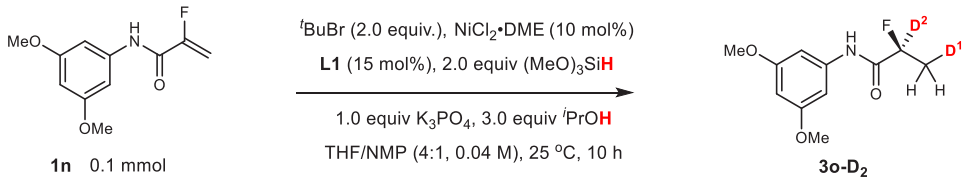


Table S26. Deuterium-Labeling experiments for asymmetric hydrogenation

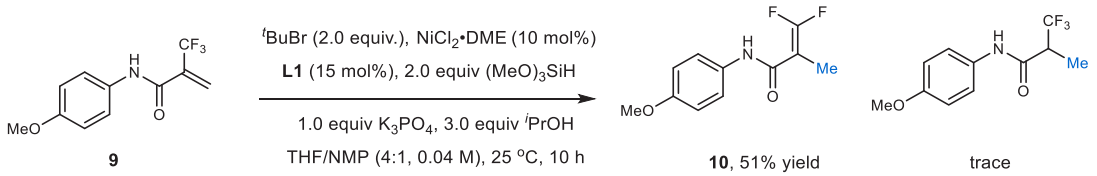
Entry	H/D sources	3o-D2		
		Yield, ee	D1	D2
1	2.0 equiv. **Ph_2SiD_2**	90%, 92% ee	98%	0%
2	2.0 equiv. **D_2O**	95%, 82% ee	0%	20%
3	3.0 equiv. **MeOD**	94%, 86% ee	0%	48%
4	2.0 equiv. **Ph_2SiD_2** 3.0 equiv. **MeOD**	89%, 83% ee	98%	50%
5	2.0 equiv. **Ph_2SiD_2** 3.0 equiv. **MeOD** 2.0 equiv. **D_2O**	81%, 79% ee	98%	62%

According to **General Procedure C**, *N*-(3,5-dimethoxyphenyl)-2-fluoroacryl amide **1n** (0.1 mmol, 1.0 equiv.), *tert*-butyl bromide (0.2 mmol, 2.0 equiv.), $NiCl_2$·DME (0.01 mmol, 10 mol%), (*S*,*S*)-**L1** (0.015 mmol, 15 mol%), K_3PO_4 (0.1 mmol, 1.0 equiv.), in THF/NMP (v/v = 4:1, 0.04 M) were used. Then, different hydrogen sources (Ph_2SiD_2 instead of $(MeO)_3SiH$, additional D_2O, MeOD instead of ^{i}PrOH) were added. The reaction mixture was allowed to stir for 10 h at 25 °C. After then, the products **3o-D2** were isolated for each reaction by flash chromatography (Petroleum ether: EtOAc = 3:1). Yields were analyzed by GC using *n*-dodecane as an internal standard and the incorporation of deuterium was determined by ^{1}H NMR.

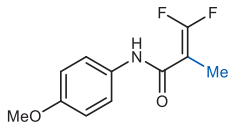
According to **General Procedure C, 3o-D_2** was obtained, Entry 1, the reaction of

1n with Ph_2SiD_2 gave the β-deuterated product **3o-D₂** (98% D) in 90% yield and 92% ee; Entry 2, the reaction of **1n** with D_2O gave the α-deuterated product **3o-D₂** (20% D) in 95% yield and 82% ee; Entry 3, the reaction of **1n** with CH_3OD gave the α-deuterated product **3o-D₂** (48% D) in 94% yield and 86% ee; Entry 4, the reaction of **1n** with CH_3OD and Ph_2SiD_2 gave the α–β-deuterated product **3o-D₂** (50% α-D, 98% β-D) in 89% yield and 83% ee; Entry 5, the reaction of **1n** with CH_3OD, Ph_2SiD_2 and D_2O gave the α–β-deuterated product **3o-D₂** (62% α-D, 98% β-D) in 81% yield and 79% ee. Accordingly, clearly indicated the β-hydrogen of alkane product **3o** came from silane (98% D) while the α-hydrogen of **3o** came from alcohol or water (48% ~ 62% D).

2) Reactions with CF_3-alkenes for hydrogenation reaction



According to General Procedure A, *N*-(4-methoxyphenyl)-2-(trifluoromethyl) acrylamide **9** (0.1 mmol, 1.0 equiv.), *tert*-butyl bromide (0.2 mmol, 2.0 equiv.), $NiCl_2$·DME (0.01 mmol, 10 mol%), (*S*,*S*)-**L1** (0.015 mmol, 15 mol%), $(MeO)_3SiH$ (0.2 mmol, 2.0 equiv.), K_3PO_4 (0.1 mmol, 1.0 equiv.) and ^{i}PrOH (0.3 mmol, 3.0 equiv.) in THF/NMP (v/v = 4:1, 0.04 M) were used.. The reaction mixture was allowed to stir for 10 h at 25 °C. After then, the *gem*-difluoroalkene product **10** were isolated by flash chromatography (Petroleum ether: EtOAc = 8:1) as a white solid (11.6 mg, 51% yield).



3,3-difluoro-*N*-(4-methoxyphenyl)-2-methylacrylamide (10)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 6.1 Hz, 1H), 7.44 – 7.33 (m, 2H), 6.90 – 6.83 (m, 2H), 3.79 (s, 3H), 1.88 (t, *J* = 3.4 Hz, 3H).

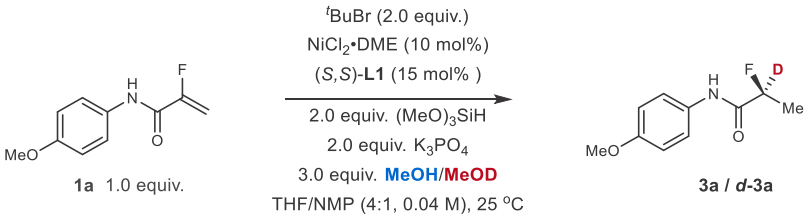
^{19}F NMR (376 MHz, $CDCl_3$) δ -76.75 – -77.14 (m), -80.56 – -81.05 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.08 (m), 156.90, 156.84 (t, J = 291.7 Hz), 130.48, 122.34, 114.31, 87.37 (m), 55.60, 10.06.

HRMS (ESI): $C_{11}H_{12}F_2NO_2^+$ ($M+H^+$): 228.0831, found: 228.0835.

3) Kinetic isotopic effect experiments for hydrogenation reaction

i) KIEs with MeOD/MeOH based on initial rates



According to **General Procedure C**, 2-fluoro-*N*-(4-metho-xyphenyl) acrylamide **1a** (0.1 mmol, 1.0 equiv.), *tert*-butyl bromide (0.2 mmol, 2.0 equiv.), $NiCl_2$·DME (0.01 mmol, 10 mol%), (*S*,*S*)-**L1** (0.015 mmol, 15 mol%), K_3PO_4 (0.1 mmol, 1.0 equiv.) and $(MeO)_3SiH$ (0.2 mmol, 2.0 equiv.) in THF/NMP (v/v = 4:1, 0.04 M) were used. Using MeOD or MeOH instead of ^{i}PrOH. The benzotrifluoride was added as an internal standard. Aliquots of the reaction mixture were taken via syringe at 1, 2, 3, 4, 5, 6, 7, 8 and 9 min, immediately placed to H_2O & $CDCl_3$ (0.1 mL & 0.6 mL). After filtration, the concentration of product is detected by ^{19}F NMR (^{19}F exp. comp. pulse decoupling).

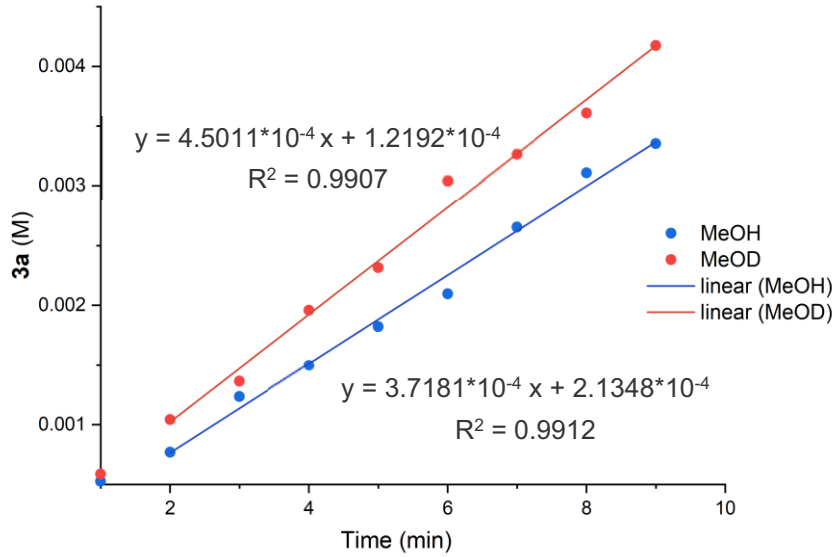
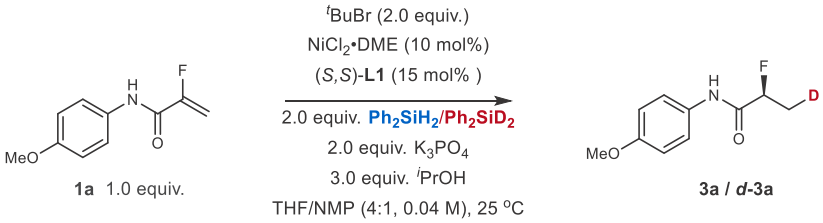


Figure S2. Determination of the kinetic isotope effect of MeOH.

Comment: A linear trendline was drawn between 2-9 min to obtain the initial rates of

the reaction. Dividing the slope of the trendline for the reaction using MeOH by the slope of the trendline for the reaction using MeOD gave k_H/k_D =3.7181/4.5011 = 0.83. Therefore, we believe that the protonation step is not the rate-determining step in asymmetric hydrogenation.

ii) KIEs with Ph_2SiD_2/Ph_2SiH_2 based on initial rates



1a 1.0 equiv. **3a** / ***d*-3a**

According to **General Procedure C**, 2-fluoro-*N*-(4-metho-xyphenyl) acrylamide **1a** (0.1 mmol, 1.0 equiv.), *tert*-butyl bromide (0.2 mmol, 2.0 equiv.), $NiCl_2$·DME (0.01 mmol, 10 mol%), (*S*,*S*)-**L1** (0.015 mmol, 15 mol%), K_3PO_4 (0.1 mmol, 1.0 equiv.) and ^{i}PrOH (0.3 mmol, 3.0 equiv.) in THF/NMP (v/v = 4:1, 0.04 M) were used. Using Ph_2SiH_2 or Ph_2SiD_2 instead of $(MeO)_3SiH$. The benzotrifluoride was added as an internal standard. Aliquots of the reaction mixture were taken via syringe at 1, 2, 3, 4, 5, 6, 7, 8 and 9 min, immediately placed to H_2O & $CDCl_3$ (0.1 mL & 0.6 mL). After filtration, the concentration of product is detected by ^{19}F NMR (^{19}F exp. comp. pulse decoupling).

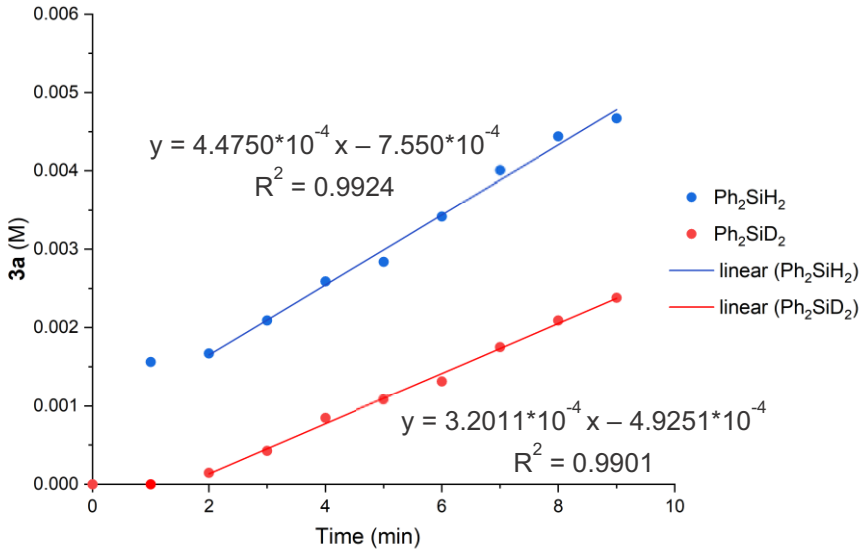


Figure S3. Determination of the kinetic isotope effect of [Si]-H.

Comment: A linear trendline was drawn between 2-9 min of each reaction progress curve to obtain the initial rates of the reaction. Dividing the slope of the trendline for the reaction using Ph_2SiH_2 by the slope of the trendline for the reaction using Ph_2SiD_2 gave k_H/k_D = 4.4750/3.2011 = 1.40.

iii) KIEs with Ph_2SiD_2/Ph_2SiH_2 in parallel and competitive reactions

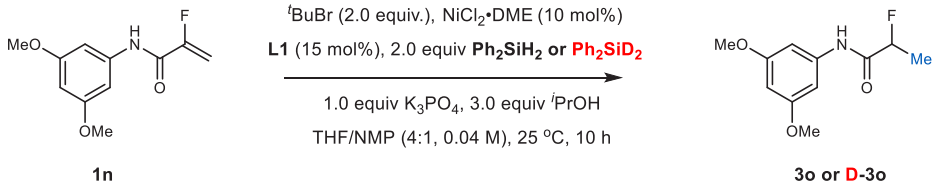


Table S27. KIEs for parallel reactions in asymmetric hydrogenation

Entry	Time	3o		D-3o		KIE =
		yield	D	yield	D	k_H/k_D
1	0.5 h	32%	0%	27%	98%	1.19
2	1 h	54%	0%	49%	98%	1.10
3	2 h	62%	0%	55%	98%	1.13

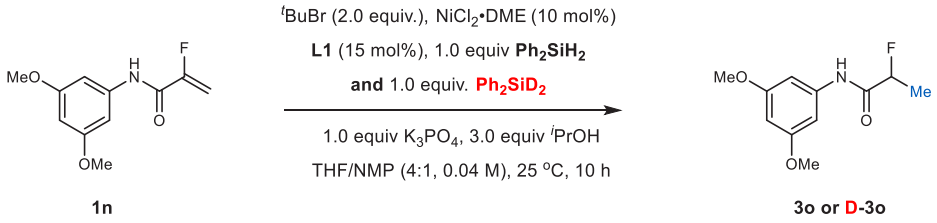


Table S28. KIEs for competitive reactions in asymmetric hydrogenation

Entry	Time	Yield of D-3o'	D	KIE = k_H/k_D
1	0.5 h	29%	44%	1.27
2	1 h	48%	44%	1.27
3	2 h	62%	42%	1.38

According to **General Procedure C**, *N*-(3,5-dimethoxyphenyl)-2-fluoroacryl-amide **1n** (0.1 mmol, 1.0 equiv.), *tert*-butyl bromide (0.2 mmol, 2.0 equiv.), $NiCl_2$·DME (0.01

mmol, 10 mol%), (*S*,*S*)-**L1** (0.015 mmol, 15 mol%) and K_3PO_4 (0.1 mmol, 1.0 equiv.) in THF/NMP (v/v = 4:1, 0.04 M) were used. Ph_2SiH_2 & Ph_2SiD_2 were used instead of $(MeO)_3SiH$. The reaction mixture was allowed to stir at 25 °C. After then, the product **3o**, **D-3o** and **D-3o'** were isolated by flash chromatography (Petroleum ether: EtOAc = 4:1) at 0.5 h, 1 h and 2 h respectively. Yields were analyzed by GC using *n*-dodecane as an internal standard and the incorporation of deuterium was determined by ^1H NMR. The KIEs value were found to be 1.1209, 1.1124, 1.1150 and 1.273, 1.373, 1.380 respectively. Thus, revealing a primary kinetic deuterium isotope effect under this system.

4) Kinetic studies of asymmetric hydrogenation

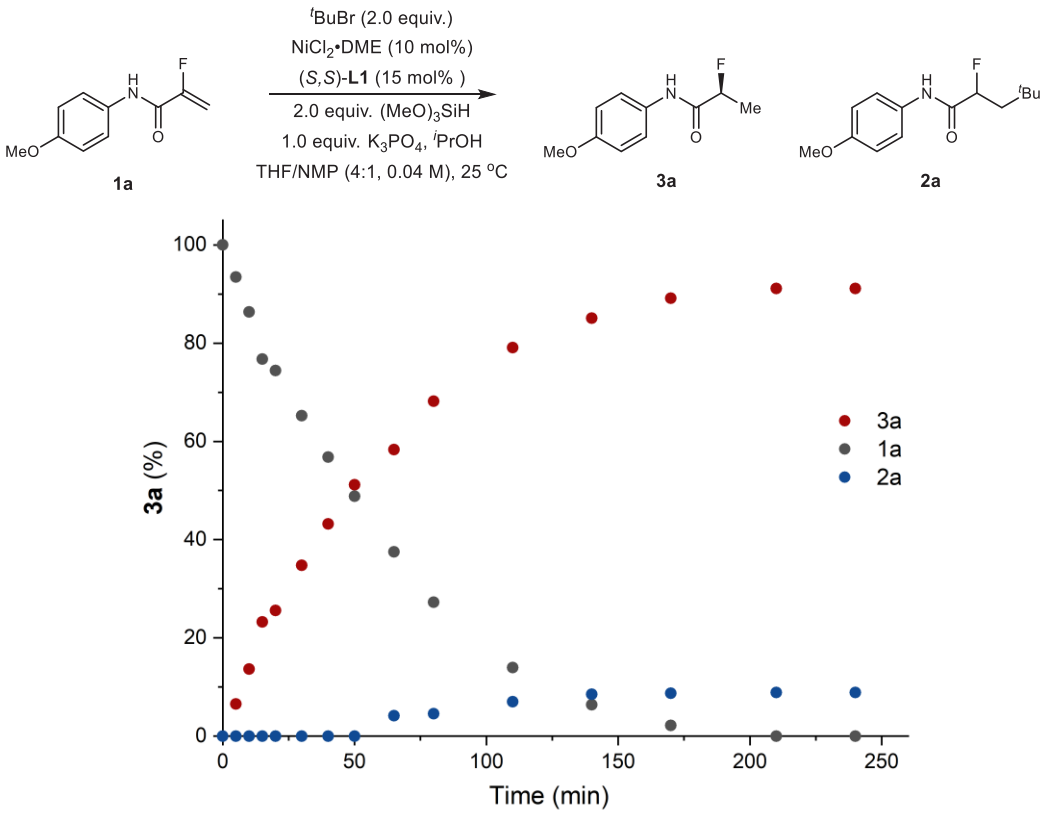


Figure S4. Time-course for asymmetric hydrogenation

Determination of the initial rate of asymmetric hydrogenation, according to the **General Procedure C**, using **1a**, ^{t}BuBr, $(MeO)_3SiH$, $NiCl_2$·DME & (*S*,*S*)-**L1**, and ^{i}PrOH in several different equivalents. The benzotrifluoride was added as an internal

standard and stir at 1500 rpm. After addition of silane, the stopwatch was started. The aliquots of the reaction mixture (60 μL) were taken out by syringe every 1 minute (2-8 min), and immediately placed to H_2O & $CDCl_3$ (0.1 mL & 0.6 mL). Then the clear solution is obtained after filtration, and the concentration of product was detected by ^{19}F NMR (^{19}F exp. comp. pulse decoupling).

Impact of stir rates

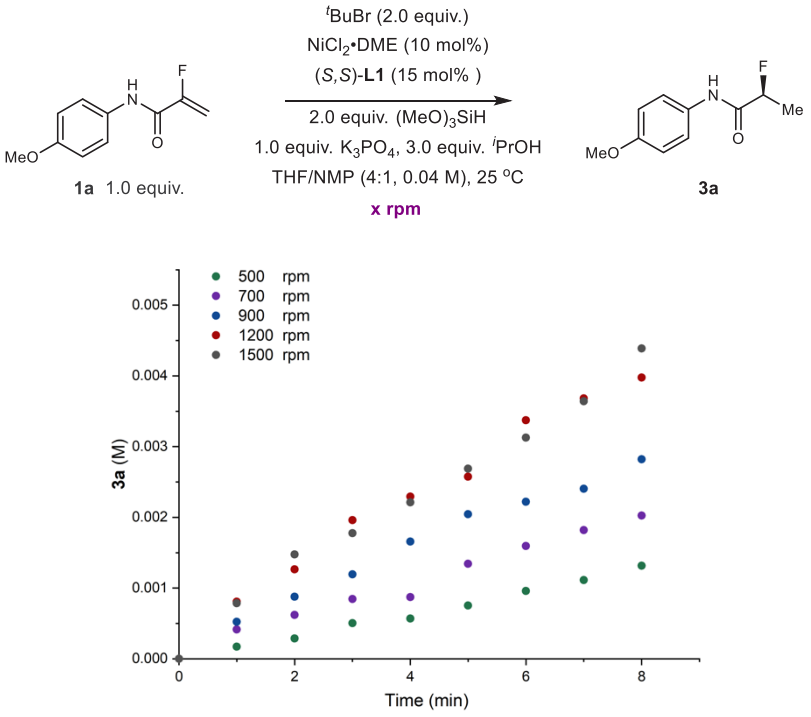
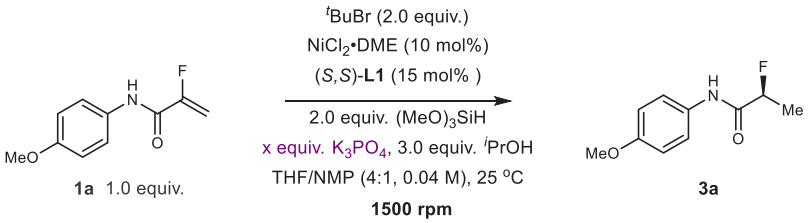


Figure S5. Rate of 3a formation at different stir rates

Comment: There is a positive-order rate dependence on the stirring rate from 500 rpm to 1500 rpm. The dependence is smaller at higher stirring rate and kinetic data measured at 1500 rpm are reproducible.

Excess K_3PO_4 profile



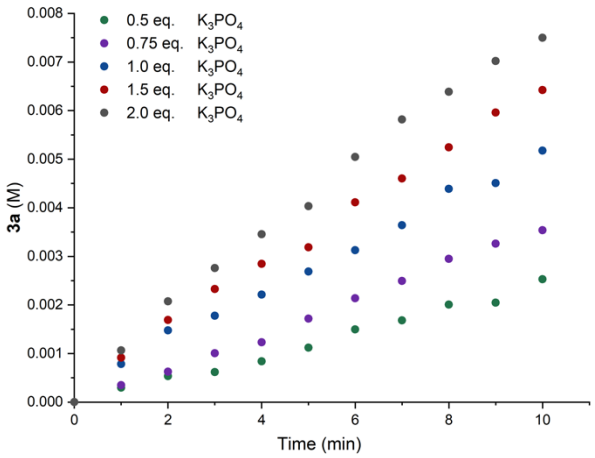
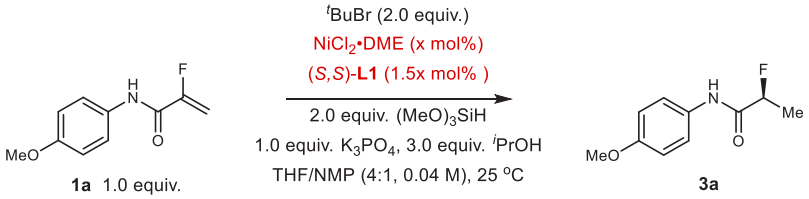


Figure S6: Rate of 3a formation with 0.5 equiv., 0.75 equiv., 1.0 equiv., 1.5 equiv. and 2.0 equiv. of K_3PO_4 stirring at 1500 rpm.

Comment: There is a positive-order rate dependence on the equivalent of K_3PO_4 in asymmetric hydrogenation. Although the mass transfer effect involved, we can obtain reproducible kinetic data at 1500 rpm.

The rate on the concentration of NiI_2 & (*S*,*S*)-L1



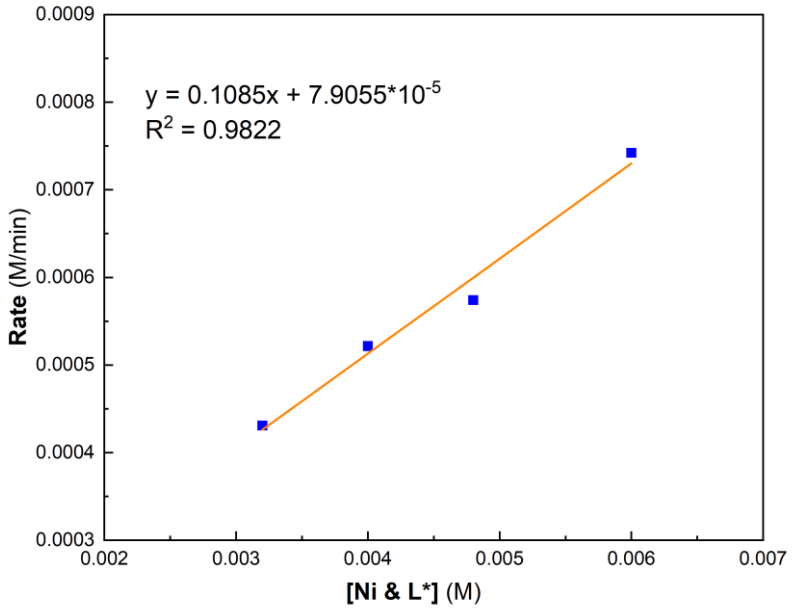


Figure S7. Rate on the concentration of $NiCl_2$·DME & (*S,S*)-L1 at 1500 rpm from the reaction of **1a** (0.04 M), ^{t}BuBr (0.08 M), K_3PO_4 (0.04 M), $(MeO)_3SiH$ (0.08 M), ^{i}PrOH (0.12 M) with 0.0032 M, 0.004 M, 0.0048 M, 0.006 M of $NiCl_2$·DME & (*S,S*)-L1.

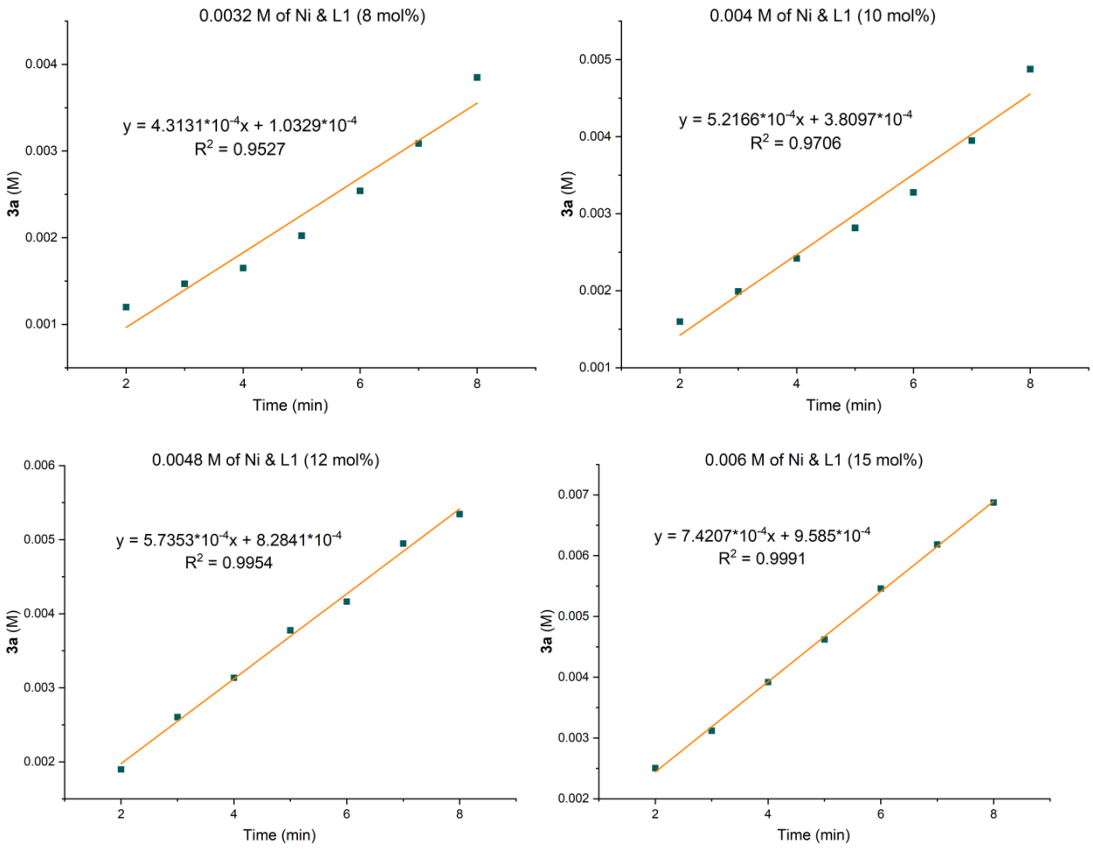
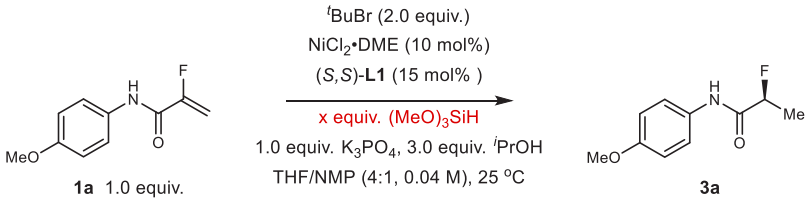


Figure S8. Plot of the rise of product from the reaction of **1a** (0.04 M), ^{t}BuBr (0.08 M), K_3PO_4 (0.04 M), $(MeO)_3SiH$ (0.08 M), ^{i}PrOH (0.12 M) with 0.0032 M, 0.004 M, 0.0048 M, 0.006 M of $NiCl_2$·DME & (*S,S*)-L1 at 1500 rpm.

The rate on the concentration of $(MeO)_3SiH$



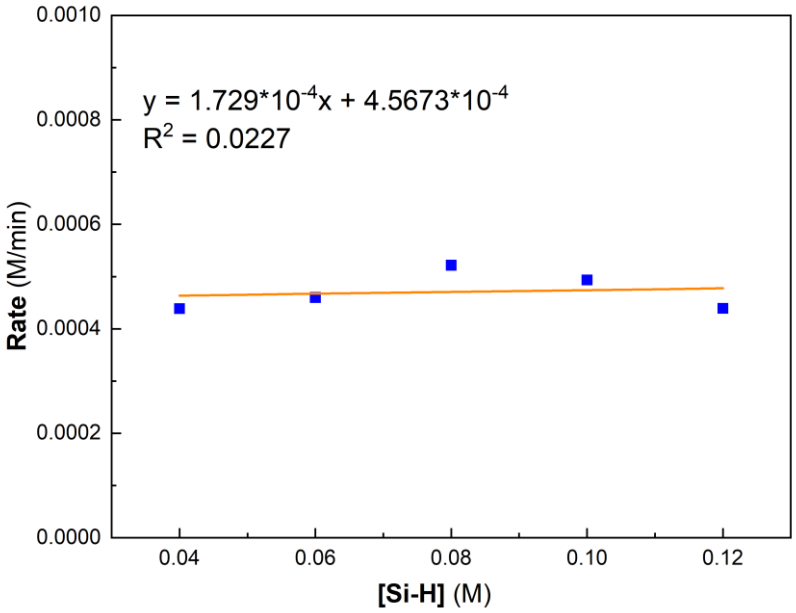
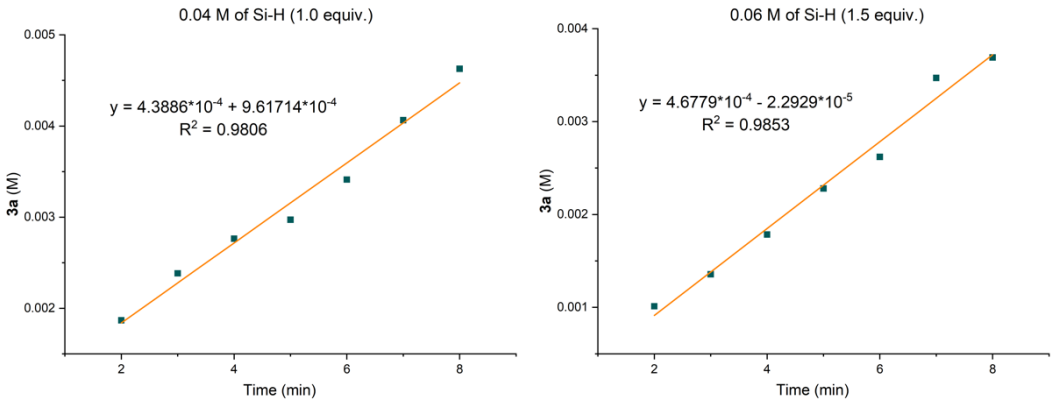


Figure S9. Rate on the concentration of $(MeO)_3SiH$ at 1500 rpm from the reaction of **1a** (0.04 M), ^{t}BuBr (0.08 M), $NiCl_2$·DME (0.004 M), (*S,S*)-L1 (0.006 M), K_3PO_4 (0.04 M), ^{i}PrOH (0.12 M) with 0.04 M, 0.06 M, 0.08 M, 0.1 M, 0.12 M, of $(MeO)_3SiH$.



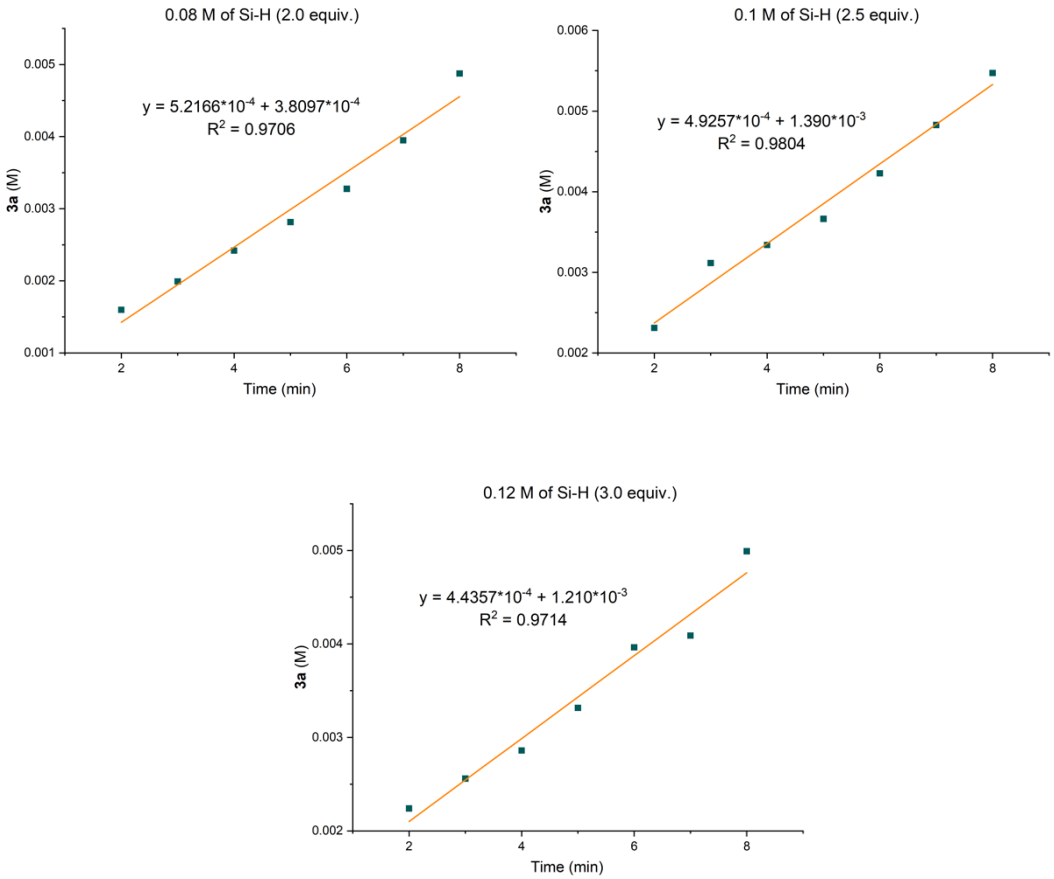
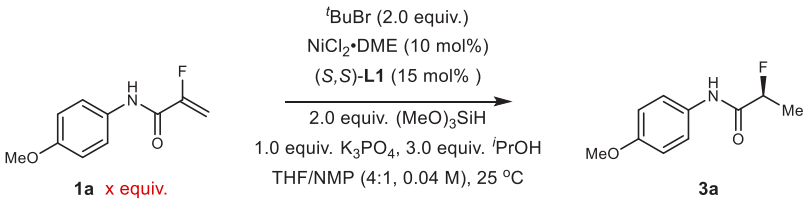


Figure S10. Plot of the rise of product from the reaction of **1a** (0.04 M), ^{t}BuBr (0.08 M), $NiCl_2$·DME (0.004 M), (*S,S*)-L1 (0.006 M), K_3PO_4 (0.04 M), ^{i}PrOH (0.12 M) with 0.04 M, 0.06 M, 0.08 M, 0.1 M, 0.12 M, of $(MeO)_3SiH$ at 1500 rpm.

The rate on the concentration of 1a



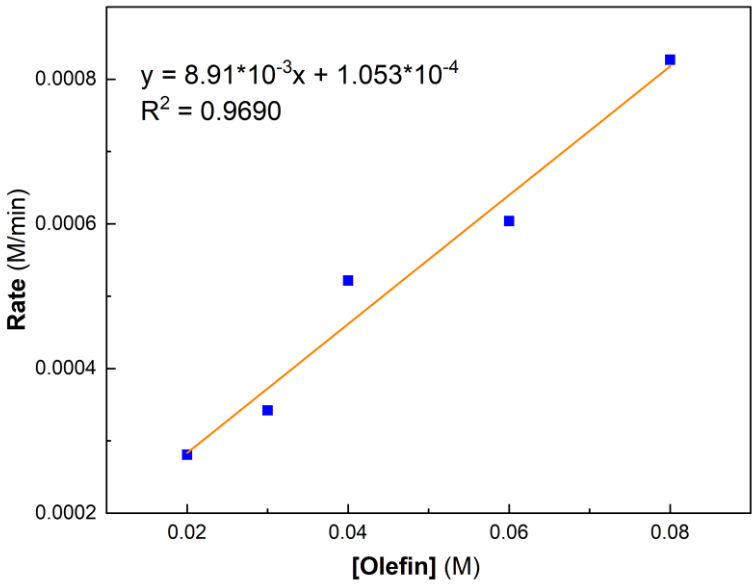
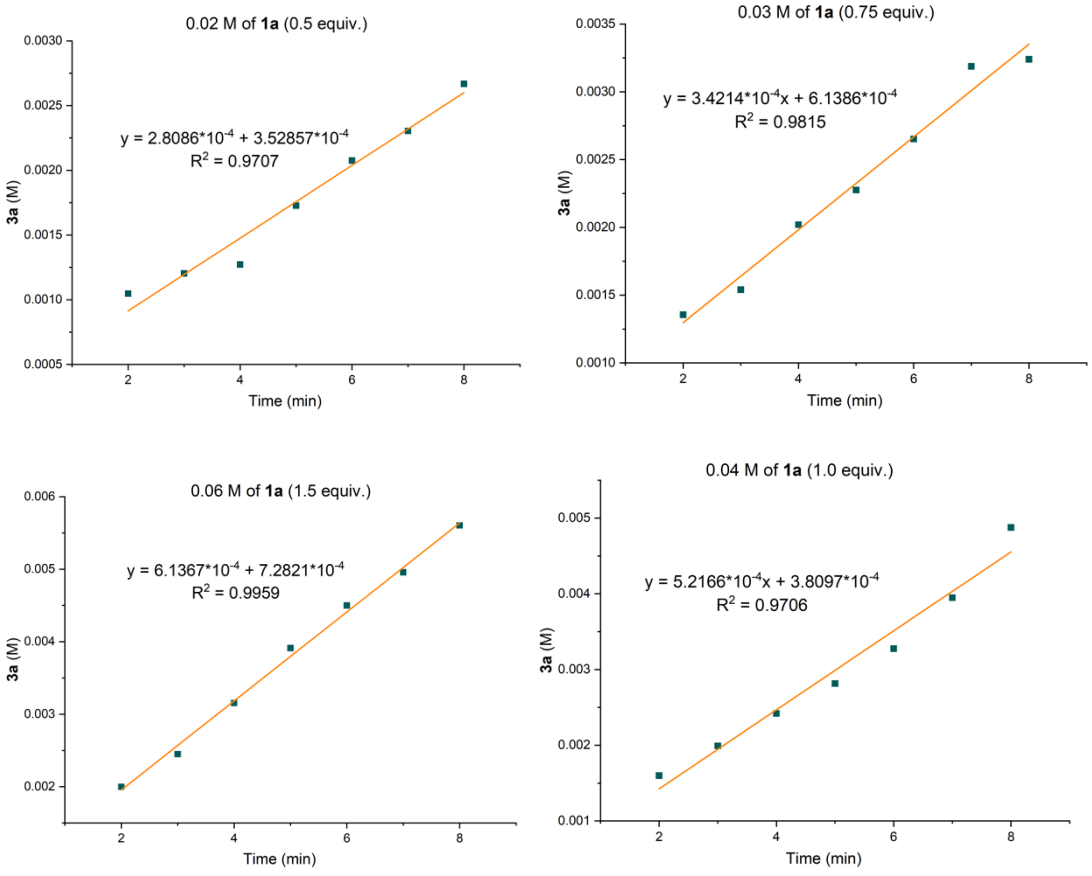


Figure S11. Rate on the concentration of **1a** at 1500 rpm from the reaction of ^{t}BuBr (0.08 M), $NiCl_2$·DME (0.004 M), (*S,S*)-L1 (0.006 M), K_3PO_4 (0.04 M), ^{i}PrOH (0.12 M), $(MeO)_3SiH$ (0.08 M) with 0.02 M, 0.03 M, 0.04 M, 0.06 M, 0.08 M of **1a**.



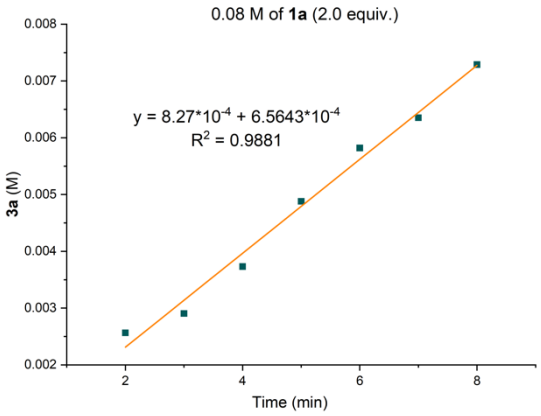


Figure S12. Plot of the rise of product from the reaction of ^{t}BuBr (0.08 M), $NiCl_2$·DME (0.004 M), (*S,S*)-L1 (0.006 M), K_3PO_4 (0.04 M), ^{i}PrOH (0.12 M), $(MeO)_3SiH$ (0.08 M) with 0.02 M, 0.03 M, 0.04 M, 0.06 M, 0.08 M of **1a** at 1500 rpm.

The rate on the concentration of ^{i}PrOH

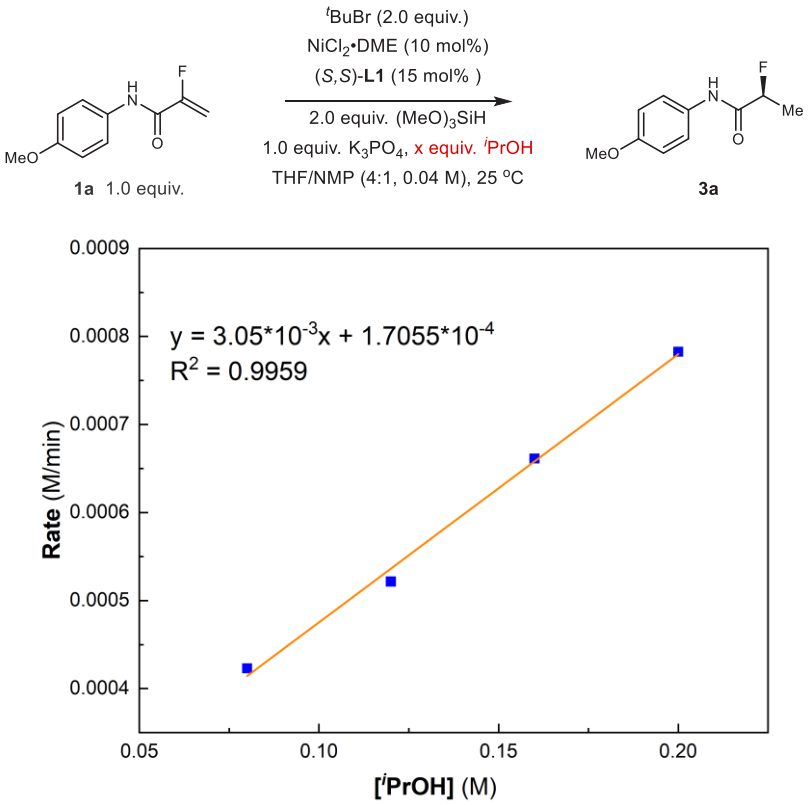


Figure S13. Rate on the concentration of ^{i}PrOH at 1500 rpm from the reaction of **1a**

(0.04 M) ^{t}BuBr (0.08 M), $NiCl_2$·DME (0.004 M), (*S,S*)-L1 (0.006 M), K_3PO_4 (0.04 M), $(MeO)_3SiH$ (0.08 M) with 0.08 M, 0.12 M, 0.16 M, 0.300 M, 0.2 M of ^{i}PrOH.

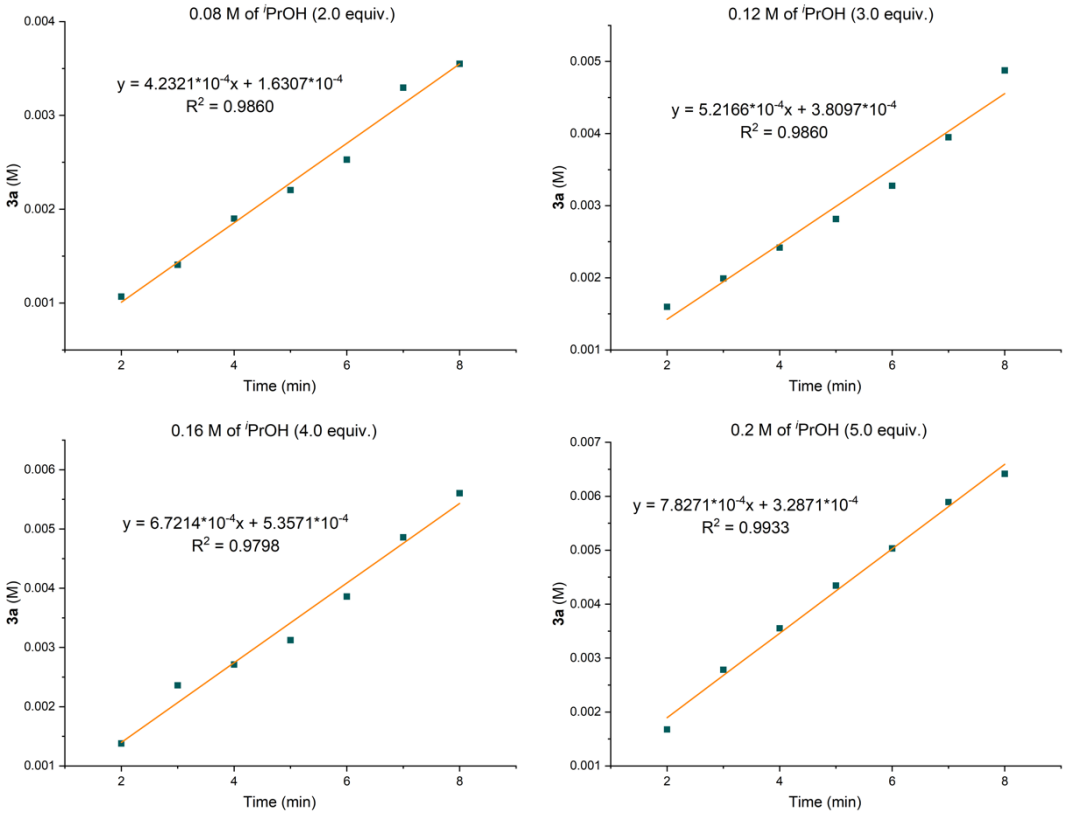
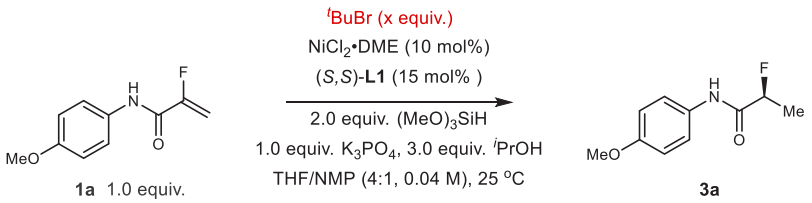


Figure S14. Plot of the rise of product from the reaction of **1a** (0.04 M) ^{t}BuBr (0.08 M), $NiCl_2$·DME (0.004 M), (*S,S*)-L1 (0.006 M), K_3PO_4 (0.04 M), $(MeO)_3SiH$ (0.08 M) with 0.08 M, 0.12 M, 0.16 M, 0.300 M, 0.2 M of ^{i}PrOH at 1500 rpm.

The rate on the concentration of ^{t}BuBr



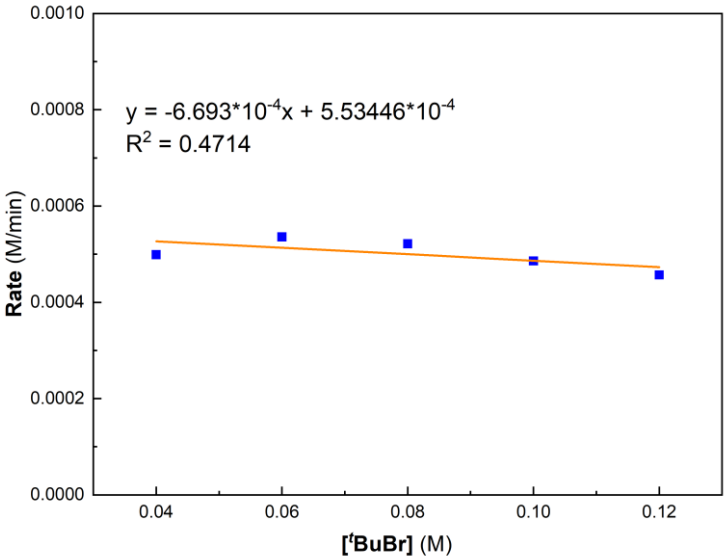
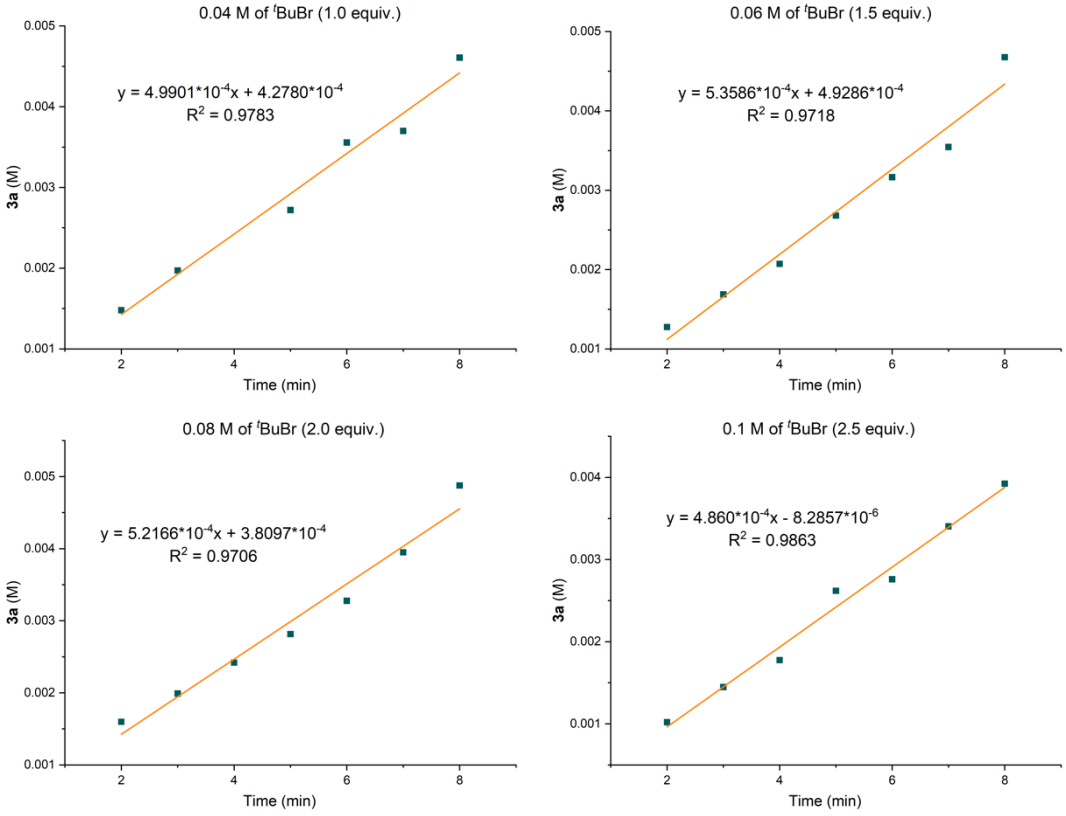


Figure S15. Rate on the concentration of ^{t}**BuBr** at 1500 rpm from the reaction of **1a** (0.04 M) ^{t}BuBr (0.08 M), $NiCl_2$·DME (0.004 M), (*S,S*)-L1 (0.006 M), K_3PO_4 (0.04 M), $(MeO)_3SiH$ (0.08 M) with 0.04 M, 0.06 M, 0.8 M, 0.1 M, 0.12 M of ^{t}**BuBr**.



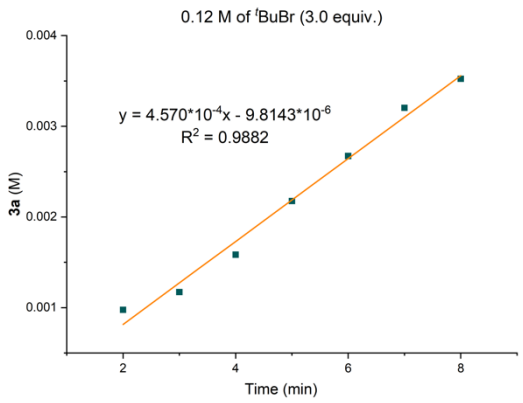


Figure S16. Plot of the rise of product from the reaction of **1a** (0.04 M) ^{t}BuBr (0.08 M), $NiCl_2$·DME (0.004 M), (*S,S*)-L1 (0.006 M), K_3PO_4 (0.04 M), $(MeO)_3SiH$ (0.08 M) with 0.04 M, 0.06 M, 0.8 M, 0.1 M, 0.12 M of **^{t}BuBr** at 1500 rpm.

Comment: For this asymmetric hydrogenation reaction, we conducted a series of kinetic analyses, and evaluated the dependence of the average rate after the initiation period on the nickel catalyst, alkene, alkyl bromide, silane, and ^{i}PrOH concentrations in each case. As shown above, this model reaction exhibited a first-order dependence on the concentration of the nickel catalyst, alkene, and ^{i}PrOH as well as a zeroth-order dependence on the concentration of silane and alkyl bromide.

Note: Although this system shows a mass-transfer effect, the kinetic data obtained at 1500 rpm are reproducible.

5) Determination of activation energy parameters at 298K

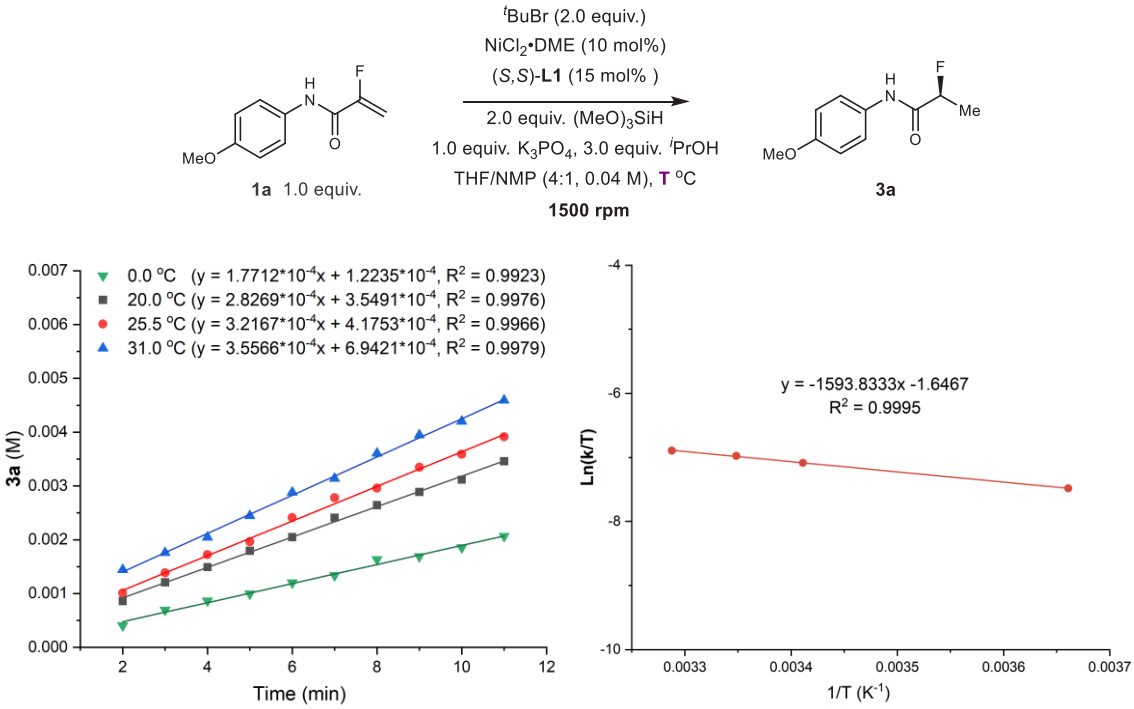


Figure S17: Rate of 3a formation under 0 °C, 20 °C, 25.5 °C, 31 °C at 1500 rpm (left) and Eyring analysis of Ln(k/T) vs 1/T (right).

Comment: There is a smaller rate dependence on the reaction temperature in asymmetric hydrogenation. As the reaction temperature increases, the initial rate gradually increases. The activation energy at 298 K calculated based on the Eyring equation is 18.2 kcal·mol^{-1}. The details of calculation of Eyring equation are as follows:

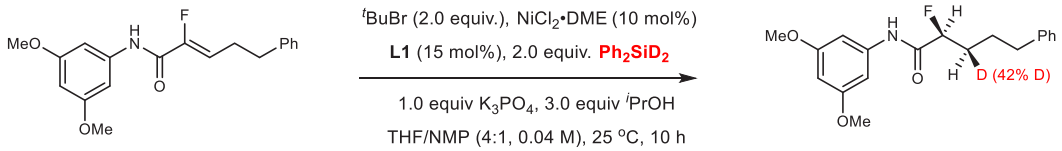
$$\ln\left(\frac{k}{T}\right) = \frac{-\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R} + \ln\left(\frac{k_{\mathrm{B}}}{h}\right)$$

$\Delta H = -(-15933.88333*8.314)$ J·mol^{-1} = 13.251 kJ·mol^{-1}

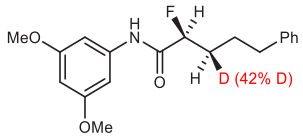
$\Delta S = ((-\mathrm{Ln}(k_B/h) - 1.6467)*8.314)$ (J·mol^{-1}·K^{-1}) = -0.211 kJ·mol^{-1}·K^{-1}

Thus, $G_{(298\ K)} = H - T*S$ = (13.251 + 298*0.211) kJ·mol^{-1} = 76.129 kJ·mol^{-1} = 18.2 kcal·mol^{-1}

6) Hydrogenation reactions of internal alkenes (Z)-14 (*Z*/*E* > 20:1)



According to **General Procedure C**, (*Z*)-*N*-(3,5-dimethoxyphenyl)-2-fluoro-5-phenylpent-2-enamide **14** (0.1 mmol, 1.0 equiv.), *tert*-butyl bromide (0.2 mmol, 2.0 equiv.), $NiCl_2$·DME (0.01 mmol, 10 mol%), (*S*,*S*)-**L1** (0.015 mmol, 15 mol%), K_3PO_4 (0.1 mmol, 1.0 equiv.) and Ph_2SiD_2 in THF/NMP (v/v = 4:1, 0.04 M) were used. The reaction mixture was allowed to stir for 10 h at 25 °C. After then, the product **15** was isolated by flash chromatography (Petroleum ether: EtOAc = 3:1) as a white solid (14.8 mg, 43% yield, 70% ee, 2.6:1 dr). The ratio of d.r. was determined by ^{19}F NMR and the incorporation of deuterium was determined by ^{1}H NMR.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.0 Hz, 1H), 7.35 – 7.25 (m, 2H), 7.20 (d, *J* = 7.5 Hz, 3H), 6.82 (d, *J* = 2.3 Hz, 2H), 6.30 (t, *J* = 2.4 Hz, 1H), 5.16 – 4.90 (m, 1H), 3.80 (s, 6H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.17 – 1.94 (m, **1.58H**), 1.97 – 1.81 (m, 2H).

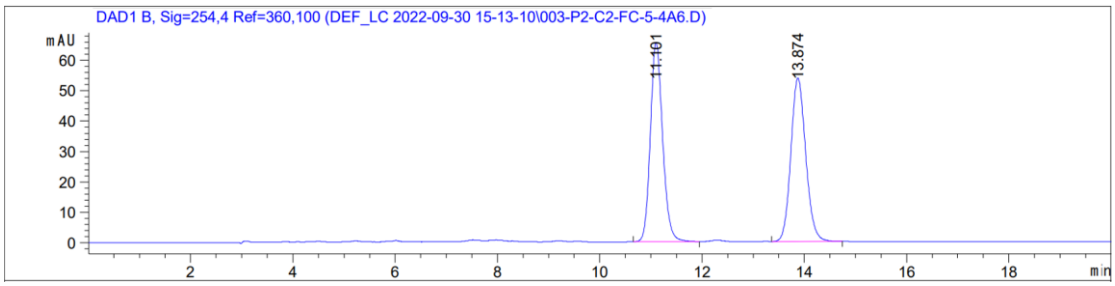
^{19}F NMR (377 MHz, $CDCl_3$) δ -187.71 – -187.94 (m), -187.99 – -188.20 (m).

HRMS (ESI): $C_{19}H_{22}DFNO_3^+$ ($M+H^+$): 333.1719, found: 333.1715.

$[\alpha]_D^{25}$ = -10.35 (c = 1.05, $CHCl_3$).

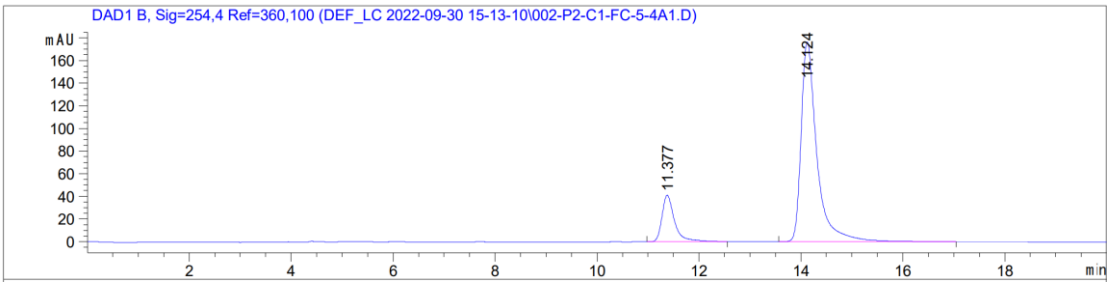
HPLC: The ee was determined to be 91% on a CHIRALPAK IA column at 250 nm, 25 °C, with hexane: ^{i}PrOH = 80:20 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 14.1 min, t_R (minor) = 11.4 min.

15 racemic



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.101	BB	0.2586	1530.08752	91.74881	50.0543
2	13.874	BB	0.3121	1526.77026	75.45714	49.9457

15 enantioenriched, 70% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.377	BB	0.2573	700.79260	41.01363	15.6207
2	14.124	BB	0.3185	3785.51489	176.31720	84.3793

7) Control reactions with 2-bromo-2-fluoro-*N*-(4-methoxyphenyl)propenamide in hydrogenation reaction

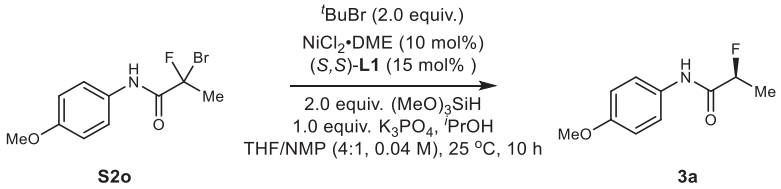


Table S29. Control reactions with S2o in asymmetric hydrogenation

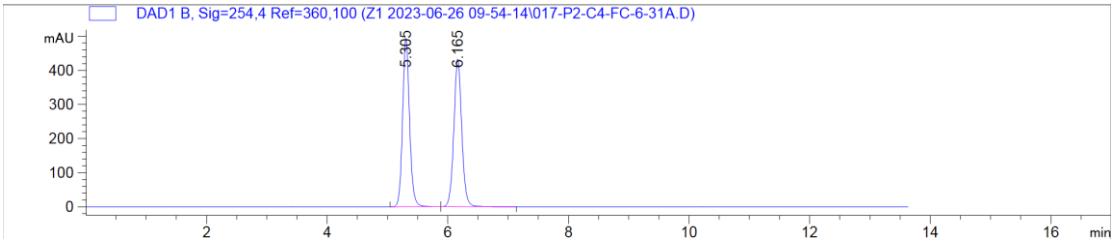
Entry	condition	Yield of 3a (%)	ee of 3a (%)
1	standard condition	59	17
2	w/o ^{t}BuBr	57	16

3	w/o ^{i}PrOH	22	16
4	w/o L*	23	--
5	terpyridine instead of L*	22	--
6	w/o Si-H & K_3PO_4	0	--
7	w/o Si-H & K_3PO_4 & ^{i}PrOH	0	--

According to **General Procedure C**, 2-bromo-2-fluoro-*N*-(4-methoxyphenyl) propanamide **S2o** (0.1 mmol, 1.0 equiv.), *tert*-butyl bromide (0.2 mmol, 2.0 equiv.), $NiCl_2$·DME (0.01 mmol, 10 mol%), (*S*,*S*)-**L1** (0.015 mmol, 15 mol%), K_3PO_4 (0.1 mmol, 1.0 equiv.), $(MeO)_3SiH$ (0.2 mmol, 2.0 equiv.), ^{i}PrOH (0.3 mmol, 3.0 equiv.) in THF/NMP (v/v = 4:1, 0.04 M) were used. The reaction mixture was allowed to stir for 10 h at 25 °C. After then, the yield of products **3a** were determined by flash chromatography (Petroleum ether: EtOAc = 5:1).

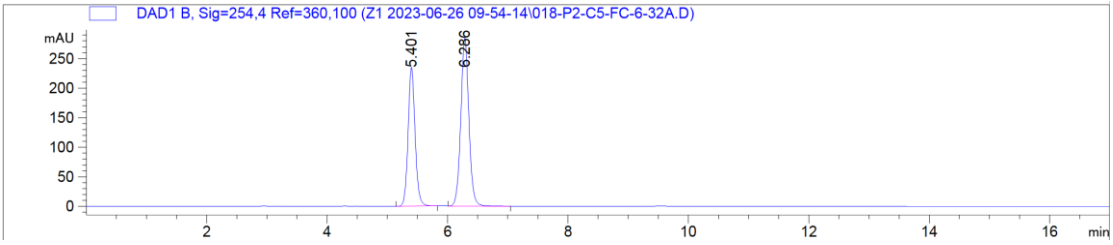
HPLC of 3a: The ee was determined to be 17% on a CHIRALPAK IA column at 254 nm, 25 °C, with hexane: ^{i}PrOH = 70:30 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 6.3 min, t_R (minor) = 5.4 min.

3a racemic



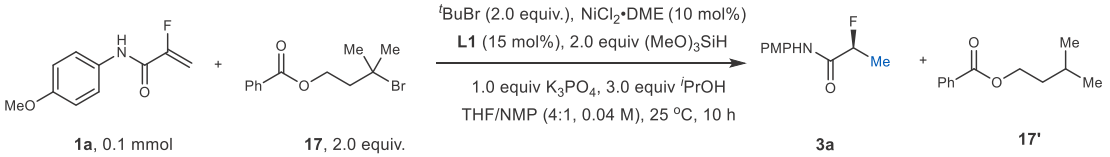
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.305	BB	0.1213	3948.92236	493.92688	49.9686
2	6.165	BB	0.1387	3953.88086	432.38980	50.0314

3a enantioenriched, 17% ee

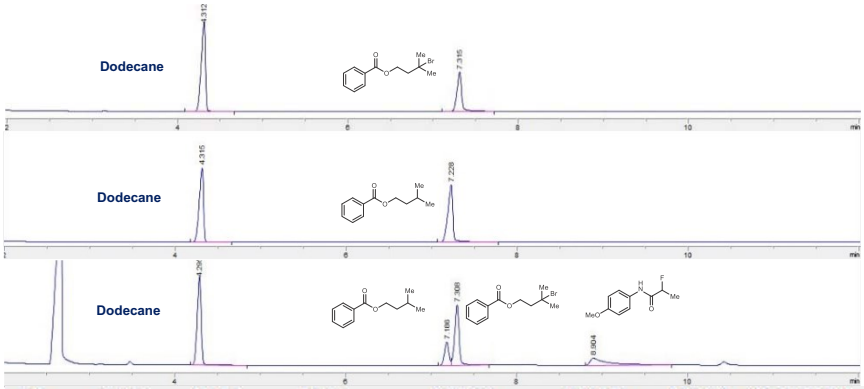


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.401	BB	0.1222	1901.64551	235.44193	41.6705
2	6.286	BB	0.1412	2661.88916	284.33322	58.3295

8) Tracing the fate of tertiary alkyl bromide in asymmetric hydrogenation



According to **General Procedure C,** 2-fluoro-*N*-(4-methoxyphenyl)acrylamide **1a** (0.1 mmol, 1.0 equiv.), 3-bromo-3-methylbutyl benzoate (0.2 mmol, 2.0 equiv.), $NiCl_2$·DME (0.01 mmol, 10 mol%), (*S*,*S*)-**L1** (0.015 mmol, 15 mol%), K_3PO_4 (0.1 mmol, 1.0 equiv.), ^{i}PrOH (0.3 mmol, 3.0 equiv.) and $(MeO)_3SiH$ (0.2 mmol, 2.0 equiv.) in THF/NMP (v/v = 4:1, 0.04 M) were used. The reaction mixture was allowed to stir for 10 h at 25 °C. Yields were analyzed by GC using *n*-dodecane as an internal standard. The tracking of the reaction system is as below.



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.295	BB	4999.4	1559.9	0.0504	40.269	1.302
2	7.186	BV	1468.6	410.9	0.0547	11.830	1.054
3	7.308	VB	3870.8	1067.3	0.0543	31.178	1.143
4	8.904	BV R	2076.1	125.4	0.2081	16.723	0.182

Figure S18. GC analysis of the reaction mixture with 17

Comment: Regarding the fate of *tert*-alkyl radical in the asymmetric hydrogenation, GC analysis of the reaction mixture with 3-bromo-3-methylbutyl benzoate **17** detected the formation of isopentyl benzoate and the ratio of **17**:**17'** is about 3:1, suggesting that tertiary alkyl bromide might undergo HAT directly.

9.2 Mechanism studies of alkyl transfer reaction

1) Deuterium-labeling experiments for alkyl transfer reaction

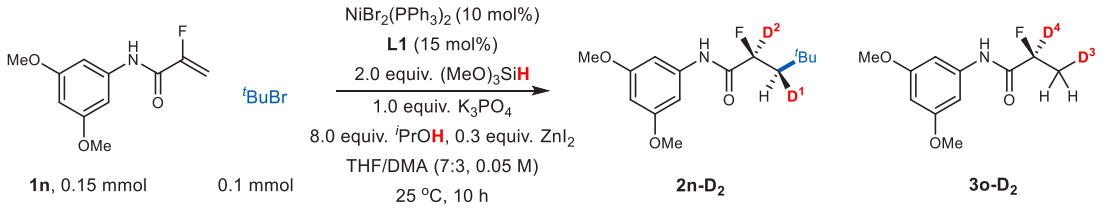


Table S30. Deuterium-Labeling experiments for asymmetric alkyl transfer

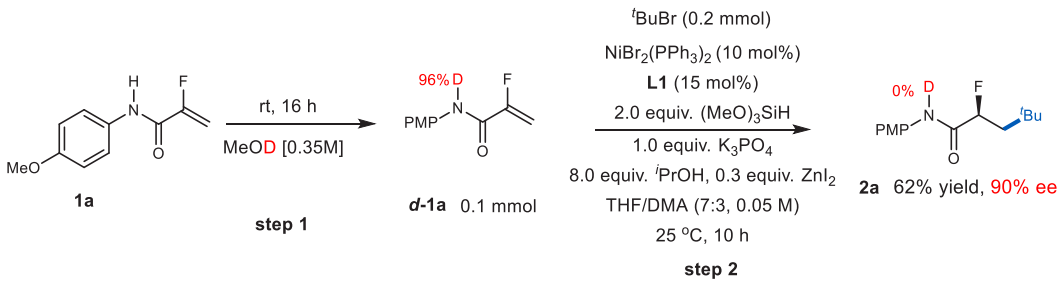
Entry	H/D sources	2n-D2			3o-D2		
		Yield, ee	D1	D2	Yield, ee	D3	D4
1	2.0 equiv. **Ph_2SiD_2**	81% 90% ee	0%	0%	33% 48% ee	98%	0%
2	2.0 equiv. **D_2O**	68% 79% ee	0%	40%	50% 47% ee	0%	42%
3	8.0 equiv. **MeOD**	69% 84% ee	0%	70%	48% 34% ee	0%	64%

According to **General Procedure A**, *N*-(3,5-dimethoxyphenyl)-2-fluoroacryl amide **1n** (0.15 mmol, 1.5 equiv.), *tert*-butyl bromide (0.1 mmol, 1.0 equiv.), $NiBr_2{\cdot}(PPh_3)_2$ (0.01 mmol, 10 mol%), (*S*,*S*)-**L1** (0.015 mmol, 15 mol%), K_3PO_4 (0.1 mmol, 1.0 equiv.) and ZnI_2 (0.03 mmol, 0.3 equiv.) in THF/DMA (v/v = 7:3, 0.05 M) were used. Then, different hydrogen sources (Ph_2SiD_2 instead of $(MeO)_3SiH$, D_2O or MeOD instead of ^{i}PrOH) were added. The reaction mixture was allowed to stir for 10 h at 25 °C. After then, the product **2n-D2** and by-product **3o-D2** were isolated for each reaction by flash chromatography (Petroleum ether: EtOAc = 5:1 to 3:1). Yields were

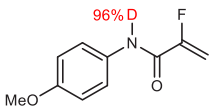
analyzed by GC using *n*-dodecane as an internal standard and the incorporation of deuterium was determined by ^{1}H NMR.

According to the **General Procedure A, 2n-D$_2$** and **3o-D$_2$** were obtained, Entry 1 the reaction of **1n** and ^{t}BuBr with Ph_2SiD_2 gave the non-deuterated product **2n-D$_2$** in 81% yield and 90% ee, together with 33% yield of β-deuterated hydrogenation product **3o-D$_2$** (98% D); Entry 2, the parallel reaction of **1n** and ^{t}BuBr with Ph_2SiH_2 and added D_2O produced the α-deuterated product **2n-D$_2$** in 68% yield (79% ee, 40% D), together with 50% yield of α–deuterated hydrogenation product **3o-D$_2$** (42% D); Entry 3, similar results were obtained with the addition of MeOD (**2n-D$_2$:** 69% yield, 84% ee, 70% D; **3o-D$_2$:** 48% yield, 62% D).

Deuterium-Labeling experiments with D-1a



Step 1: 2-Fluoro-*N*-(4-methoxyphenyl)acrylamide-*N*-*d* was prepared following the literature procedure[19]. A solution of 2-fluoro-*N*-(4-methoxyphenyl)acrylamide (135.5 mg, 0.7 mmol) in MeOD (2.0 mL) was stirred at rt for 16 h. Then, the reaction was taken to dryness under vacuum giving the corresponding product as a white solid (137 mg, 100% yield, 96% D).



2-Fluoro-*N*-(4-methoxyphenyl)acrylamide-*N*-*d* (S*d*-1a)

The title compound was obtained from **S1a** as a white solid, 100% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.46 (m, 2H), 6.94 – 6.85 (m, 2H), 5.81 (dd, *J* = 48.0, 3.3 Hz, 1H), 5.23 (dd, *J* = 15.4, 3.4 Hz, 1H), 3.81 (s, 3H).

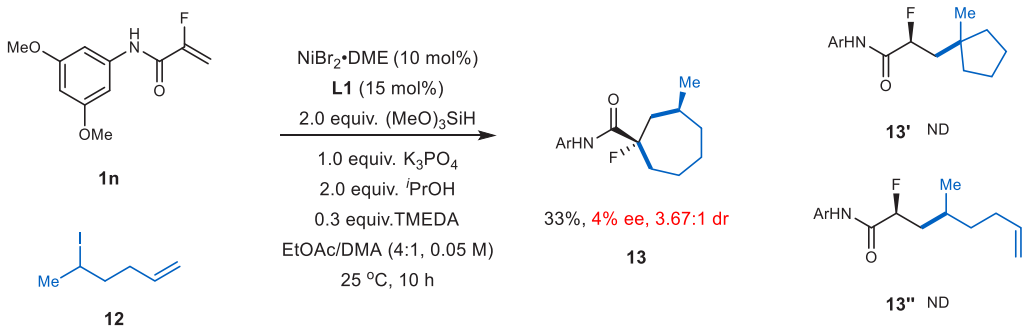
^{19}F NMR (377 MHz, $CDCl_3$) δ -120.84 – -121.01 (m)..

HRMS (ESI): $C_{10}H_{10}DFNO_2^+$ ($M+H^+$): 197.0831, found: 197.0835.

Step 2: According to **General Procedure A,** 2-fluoro-*N*-(4-methoxyphenyl)acrylamide-*N*-*d* (**S*d*-1a**) (0.1 mmol, 1.0 equiv.), *tert*-butyl bromide (0.2 mmol, 2.0 equiv.), $NiBr_2·(PPh_3)_2$ (0.01 mmol, 10 mol%), (*S*,*S*)-**L1** (0.015 mmol, 15 mol%), $(MeO)_3SiH$ (0.2 mmol, 2.0 equiv.), K_3PO_4 (0.1 mmol, 1.0 equiv.), ^{i}PrOH (0.8 mmol, 8.0 equiv.) and ZnI_2 (0.03 mmol, 0.3 equiv.) in THF/DMA (v/v = 7:3, 0.05 M) were used. The reaction mixture was allowed to stir for 10 h at 25 °C. After then, the product **2a** (0% D) were isolated by flash chromatography (Petroleum ether: EtOAc = 8:1) as a white solid (17.3 mg, 61% yield).

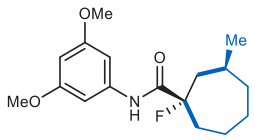
Comment: The *N*-H of acrylamides could undergo a quick hydrogen atom exchange with alcohols or water in this reaction.

2) Radical probe reactions for alkyl transfer reaction



According to General Procedure B, *N*-(3,5-dimethoxyphenyl)-2-fluoroacrylamide **1n** (0.15 mmol, 1.5 equiv.), 5-iodohex-1-ene **12** (0.1 mmol, 1.0 equiv.), $NiBr_2·DME$ (0.01 mmol, 10 mol%), (*S*, *S*)-**L1** (0.015 mmol, 15 mol%), $(MeO)_3SiH$ (0.2 mmol, 2.0 equiv.), K_3PO_4 (0.1 mmol, 1.0 equiv.), ^{i}PrOH (0.2 mmol, 2.0 equiv.), TMEDA (0.03 mmol, 0.3 equiv.) in EtOAc/DMA (v/v = 4:1, 0.05 M) were used. The reaction mixture was allowed to stir for 10 h at 25 °C. After then, the 7-membered cyclization product **13** was isolated by flash chromatography (Petroleum ether: EtOAc = 5:1) as a white solid (7.0 mg, 33% yield, 4% ee, d.r. = 3.67:1), which was probably

generated via radical addition to alkenyl fluoride followed by an intramolecular 7-*endo*-trig radical cyclization; no linear product **13"** was observed in this case. The ratio of d.r. was determined by ^{1}H NMR.



(1*S*,3*S*)-*N*-(3,5-dimethoxyphenyl)-1-fluoro-3-methylcycloheptane-1-carboxamide (13)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 – 7.80 (m, 1H), 6.93 – 6.66 (m, 2H), 6.33 – 6.03 (m, 1H), 3.79 (s, 6H), 2.20 – 2.00 (m, 1H), 1.98 – 1.90 (m, 1H),1.84 – 1.66 (m, 2H), 1.68 – 1.55 (m, 2H), 1.53 – 1.31 (m, 1H), 1.15 – 1.03 (m, 1H), 1.01 – 0.88 (m, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -151.34 – -151.50 (m), -177.09 – -177.34 (m)

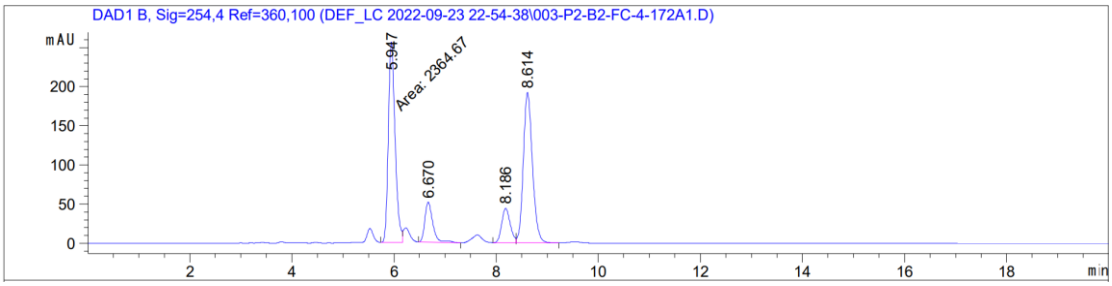
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.77 (d, J = 19.3 Hz), 161.12, 139.05, 138.76, 100.43 (d, J = 191.0 Hz), 98.00, 97.93, 97.27, 97.13, 55.42, 41.53 (d, J = 22.2 Hz), 35.82 (d, J = 21.2 Hz), 35.25 (d, J = 21.2 Hz), 34.85 (d, J = 22.6 Hz), 33.79, 29.72, 29.44, 28.33, 27.49 (d, J = 9.8 Hz), 27.25, 22.18, 21.82, 15.29, 15.15 (d, J = 3.5 Hz).

HRMS (ESI): $C_{17}H_{25}FNO_3^+$ ($M+H^+$): 310.1813, found: 310.1815.

HPLC: The ee was determined to be 4% on a CHIRALPAK IA column at 254 nm, 25 ^{o}C, with hexane: ^{i}PrOH = 80:20 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 6.0 min, 8.6 min, t_R (minor) = 6.7 min, 8.2 min.

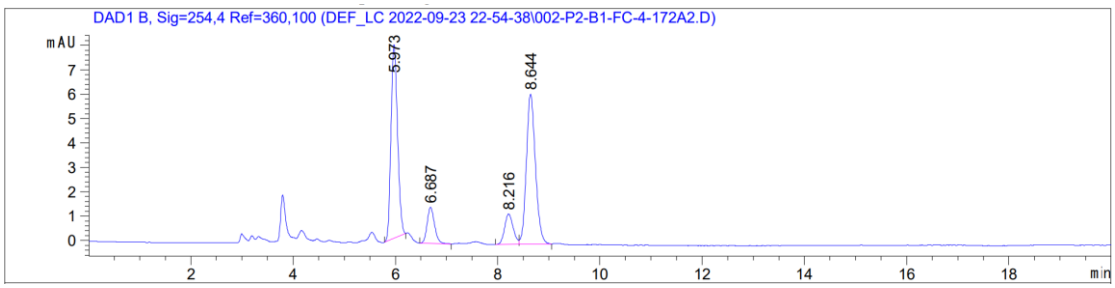
$[\alpha]_D^{25}$ = -6.19 (c = 1.00, $CHCl_3$)

13 racemic



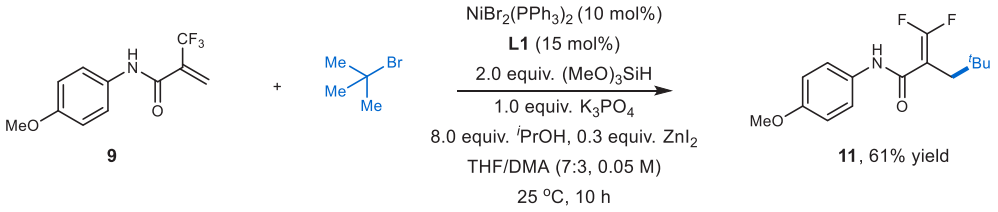
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.947	MF	0.1538	2364.67261	256.31537	40.6599
2	6.670	BV R	0.1602	563.94885	51.30858	9.6969
3	8.186	BV	0.1793	508.39969	43.84854	8.7418
4	8.614	VB	0.1886	2378.71973	191.90572	40.9014

13 enantioenriched, 4% ee



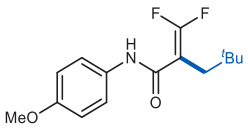
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.973	BB	0.1374	70.42020	7.94553	40.1059
2	6.687	BB	0.1525	14.77890	1.48061	8.4169
3	8.216	BV	0.1755	14.46702	1.24578	8.2393
4	8.644	VB	0.1901	75.91951	6.14546	43.2379

3) Reactions with CF_3-alkenes for alkyl transfer reaction



According to General Procedure A, *N*-(4-methoxyphenyl)-2-(trifluoromethyl) acrylamide **15** (0.15 mmol, 1.5 equiv.), *tert*-butyl bromide (0.1 mmol, 1.0 equiv.), $NiBr_2 \cdot (PPh_3)_2$ (0.01 mmol, 10 mol%), (*S*,*S*)-**L1** (0.015 mmol, 15 mol%), $(MeO)_3SiH$ (0.2 mmol, 2.0 equiv.), K_3PO_4 (0.1 mmol, 1.0 equiv.), ^{i}PrOH (0.8 mmol, 8.0 equiv.) and ZnI_2 (0.03 mmol, 0.3 equiv.) in THF/DMA (v/v = 7:3, 0.05 M) were used. The reaction mixture was allowed to stir for 10 h at 25 °C. After then, the *gem*-difluoroalkene product **17** were isolated by flash chromatography (Petroleum ether: EtOAc = 8:1) as a white

solid (17.3 mg, 61% yield).



2-(Difluoromethylene)-*N*-(4-methoxyphenyl)-4,4-dimethylpentanamide (11)

According to the **General Procedure A**, the title compound was isolated by flash chromatography (Petroleum ether: EtOAc = 8:1) as a white solid (17.3 mg, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.44 – 7.37 (m, 2H), 6.90 – 6.81 (m, 2H), 3.79 (s, 3H), 2.36 – 2.20 (m, 2H), 0.93 (s, 9H).

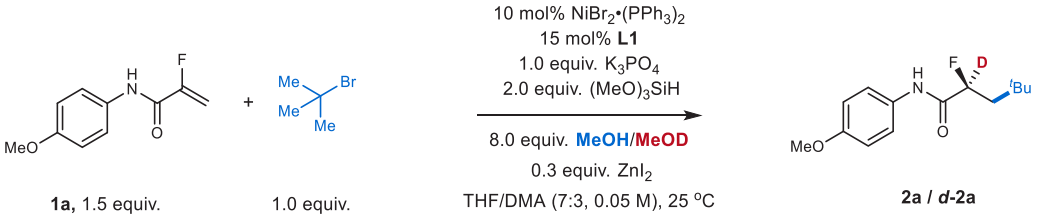
^{19}F NMR (377 MHz, $CDCl_3$) δ -77.57 – -77.92 (m), -80.77 (d, J = 32.6 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.41 (dd, J = 9.9, 5.0 Hz), 157.10 (dd, J = 296.2, 293.8 Hz), 156.83, 130.45, 122.27, 114.21, 90.31 (dd, J = 18.1, 10.8 Hz), 55.50, 37.70, 32.30 (d, J = 2.3 Hz), 29.08.

HRMS (ESI): $C_{15}H_{29}F_2NNaO_2^+$ ($M+Na^+$): 306.1276, found: 306.1274.

4) Kinetic isotopic effect of alkyl transfer

i) KIEs with MeOD/MeOH based on initial rates



According to **General Procedure A**, 2-fluoro-*N*-(4-metho-xyphenyl) acrylamide **1a** (0.15 mmol, 1.5 equiv.), *tert*-butyl bromide (0.1 mmol, 1.0 equiv.), $NiBr_2·(PPh_3)_2$ (0.01 mmol, 10 mol%), (*S*,*S*)-L1 (0.015 mmol, 15 mol%), $(MeO)_3SiH$ (0.2 mmol, 2.0 equiv.), K_3PO_4 (0.1 mmol, 1.0 equiv.), and ZnI_2 (0.03 mmol, 0.3 equiv.) in THF/DMA (v/v = 7:3, 0.05 M) were used. Using MeOD or MeOH instead of ^{i}PrOH. The *n*-dodecane was added as an internal standard. Aliquots of the reaction mixture were taken via syringe at 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 min, immediately placed to H_2O & EtOAc

(0.1 mL & 1.2 mL). Then the clear solution is obtained after filtration, and the concentration of product is detected by GC.

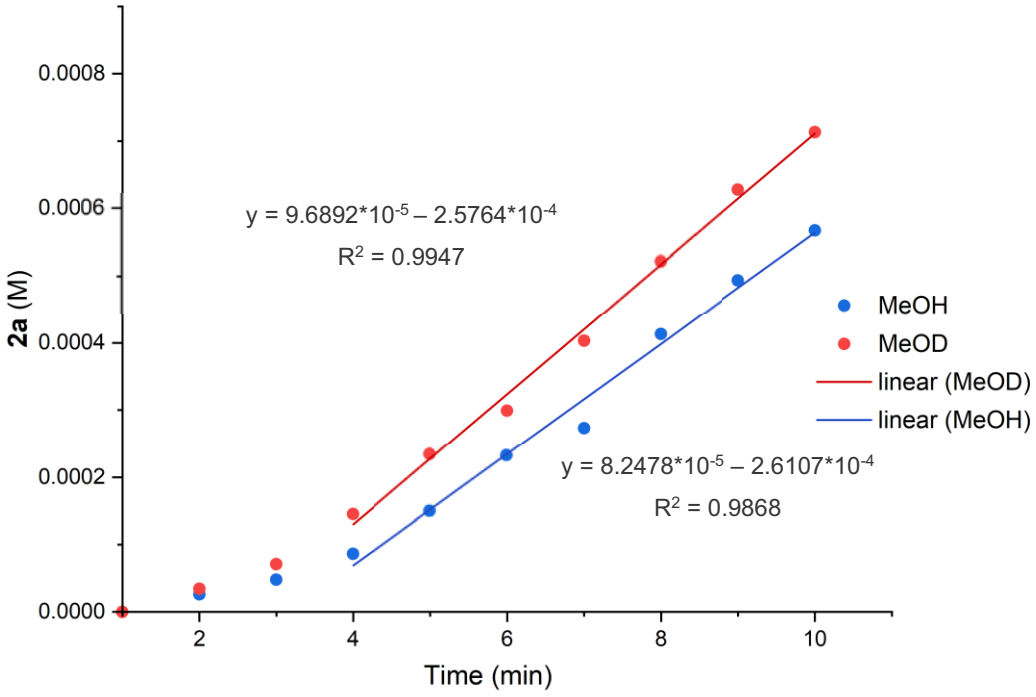
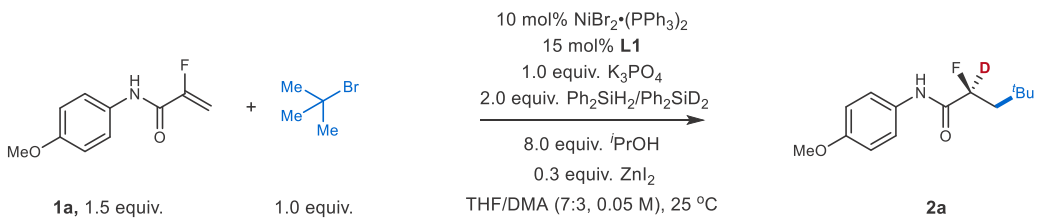


Figure S19. Determination of the kinetic isotope effect of MeOH.

Comment: A linear trendline was drawn between 4–10 min of each reaction progress curve to obtain the initial rates of the reaction. Dividing the slope of the trendline for the reaction using MeOH by the slope of the trendline for the reaction using MeOD gave k_H/k_D= 8.2478/9.6892 = 0.85. Therefore, we believe that the protonation step is not the rate-determining step in alkyl transfer reaction.

ii) KIEs with Ph_2SiD_2/Ph_2SiH_2 based on initial rates



1a, 1.5 equiv. 1.0 equiv. **2a**

According to **General Procedure A**, 2-fluoro-*N*-(4-metho-xyphenyl) acrylamide **1a** (0.15 mmol, 1.5 equiv.), *tert*-butyl bromide (0.1 mmol, 1.0 equiv.), $NiBr_2{\cdot}(PPh_3)_2$ (0.01 mmol, 10 mol%), (*S*,*S*)-L1 (0.015 mmol, 15 mol%), K_3PO_4 (0.1 mmol, 1.0 equiv.),

^{i}PrOH (0.8 mmol, 8.0 equiv.) and ZnI_2 (0.03 mmol, 0.3 equiv.) in THF/DMA (v/v = 7:3, 0.05 M) were used. Using Ph_2SiH_2 or Ph_2SiD_2 instead of $(MeO)_3SiH$. The *n*-dodecane was added as an internal standard. Aliquots of the reaction mixture were taken via syringe at 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 min, immediately placed to H_2O & EtOAc (0.1 mL & 1.2 mL). Then the clear solution is obtained after filtration, and the concentration of product is detected by GC.

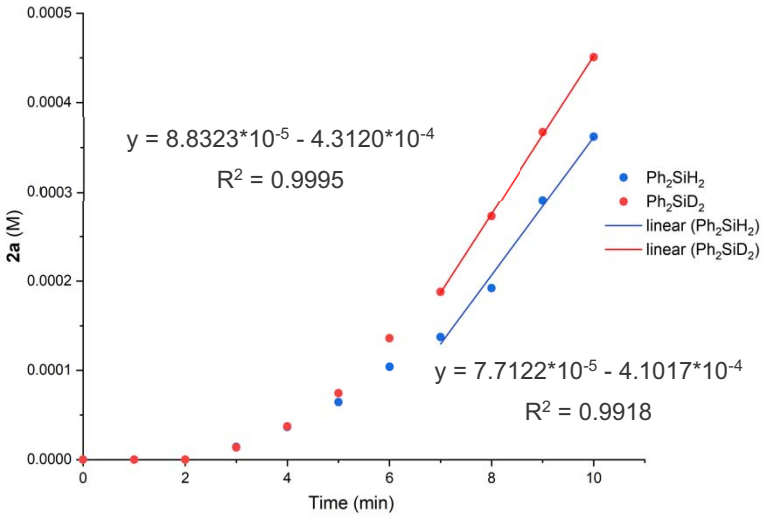
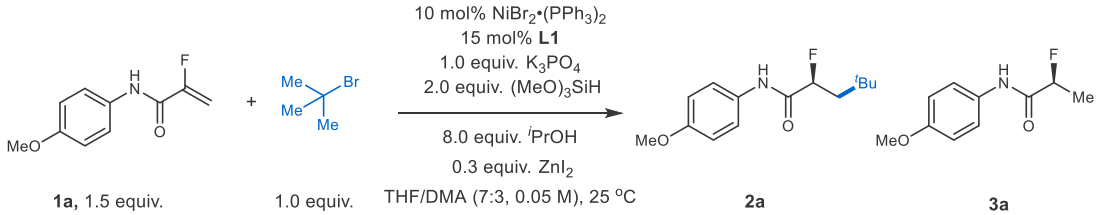


Figure S20. Determination of the kinetic isotope effect of [Si]-H.

Comment: A linear trendline was drawn between 7–10 min of each reaction progress curve to obtain the initial rates of the reaction. Dividing the slope of the trendline for the reaction using Ph_2SiH_2 by the slope of the trendline for the reaction using Ph_2SiD_2 gave k_H/k_D = 7.7122/8.8323 = 0.87. Since the silane only serves as a reductant, we believe that the reduction step is not the rate-determining step in alkyl transfer reaction.

5) Kinetic studies of alkyl transfer reaction



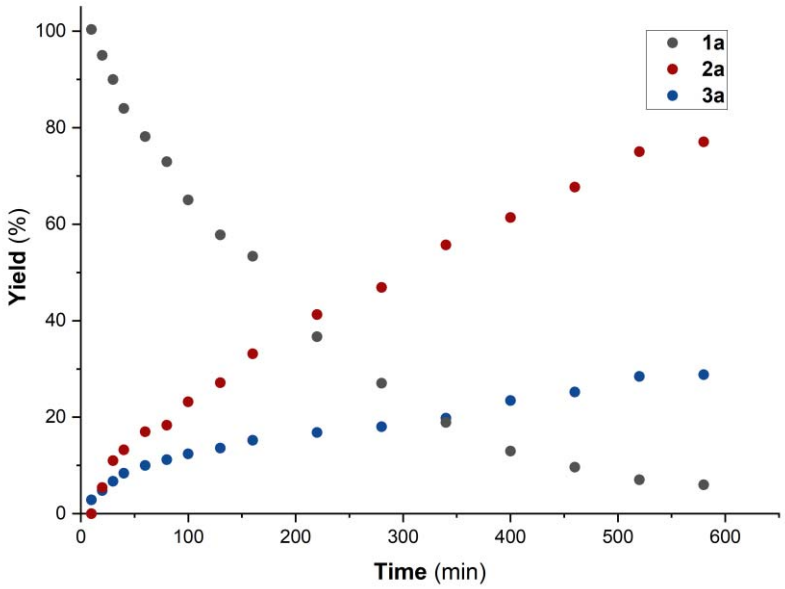
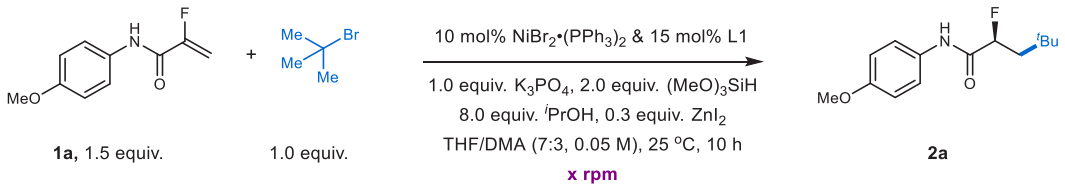


Figure S21. Time-course for asymmetric group transfer

Determination of the initial rate of asymmetric group transfer, according to the **General Procedure A**, using **1a**, ^{t}BuBr, $(MeO)_3SiH$, $NiBr_2{\cdot}(PPh_3)_2$ & (*S*,*S*)-**L1**, and ^{i}PrOH in several different equivalents. The *n*-dodecane was added as an internal standard and stir at 1500 rpm. After addition of silane, the stopwatch was started. The aliquots of the reaction mixture (30 μL) were taken out by syringe every 5 minutes (0 min - 60 min), and immediately placed to H_2O & EtOAc (0.1 mL & 1.2 mL). Then the clear solution is obtained after filtration, and the concentration of product was detected by GC.

Impact of stir rates



1a, 1.5 equiv. 1.0 equiv. **2a**

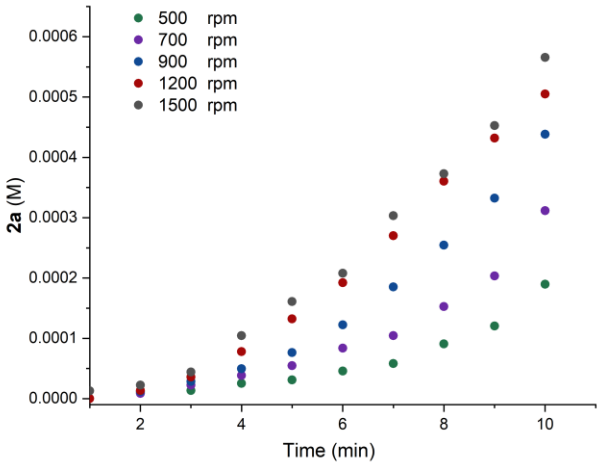
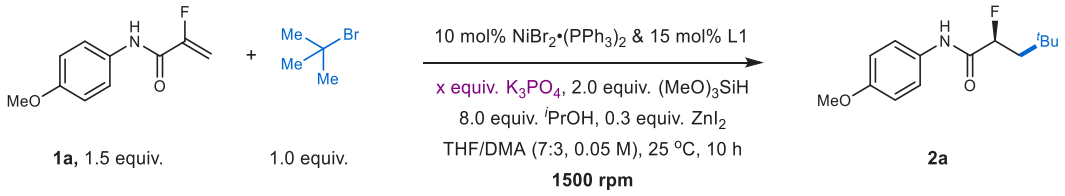


Figure S22. Rate of 2a formation at different stir rates

Comment: There is a significant rate dependence on stirring from 500 rpm to 1200 rpm and a smaller difference between 1200 rpm and 1500 rpm. The stir rate dependence is smaller at high stir rates and kinetic runs measured runs at 1500 rpm maybe reproducible.

Excess K_3PO_4 profile



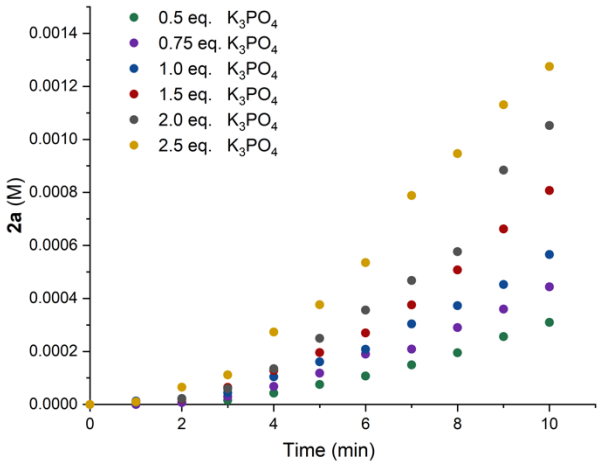
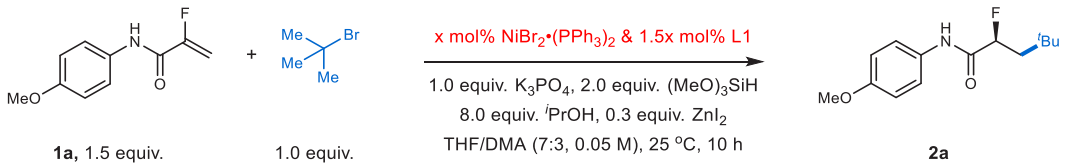


Figure S23: Rate of 2a formation with 0.5 equiv., 0.75 equiv., 1.0 equiv., 1.5 equiv., 2.0 equiv. and 2.5 equiv. of K_3PO_4 stirring at 1500 rpm.

Comment: There is a significant rate dependence on the equivalent of K_3PO_4 in

asymmetric alkyl transfer reaction.

The rate on the concentration of $NiBr_2(PPh_3)_2$ & (*S*,*S*)-L1



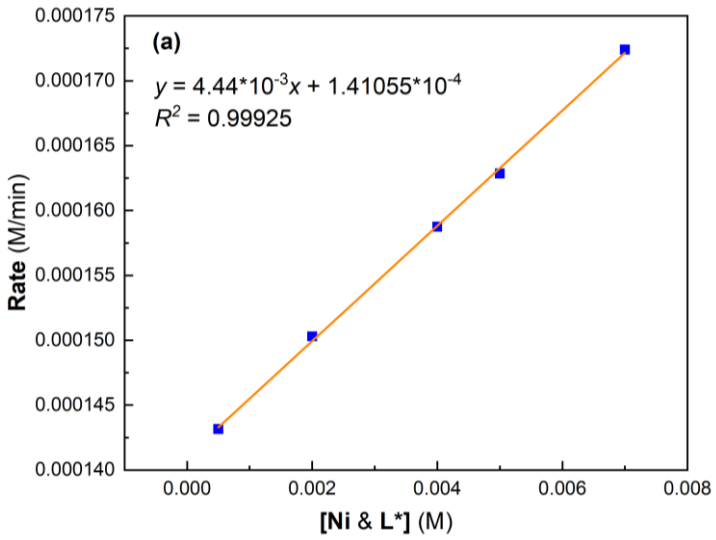
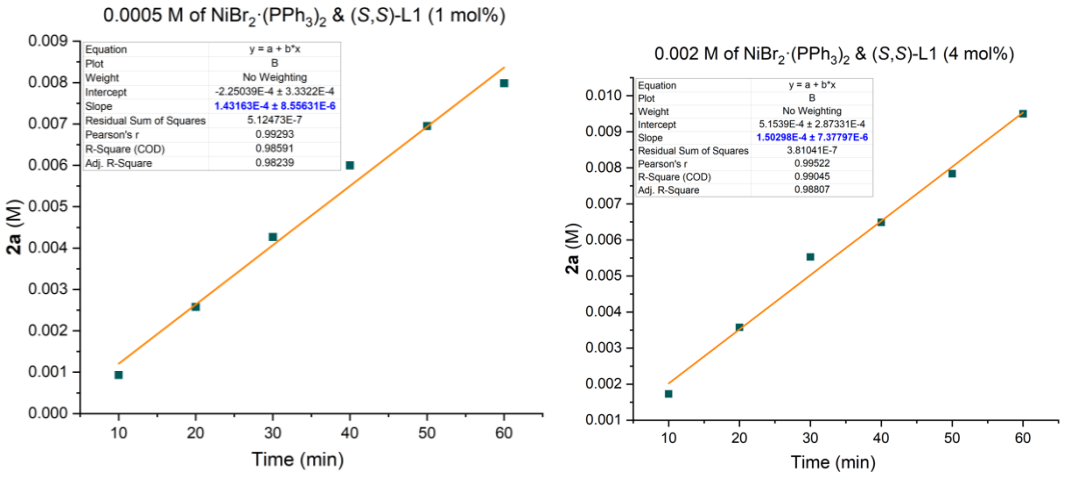


Figure S24. Rate on the concentration of $NiBr_2{\cdot}(PPh_3)_2$ & (*S*,*S*)-**L1** at 1500 rpm from the reaction of **1a** (0.075 M), ^{t}BuBr (0.05 M), K_3PO_4 (0.05 M), $(MeO)_3SiH$ (0.10 M), ZnI_2 (0.0015 M), ^{i}PrOH (0.4 M) with 0.0005 M, 0.002 M, 0.004 M, 0.005 M, 0.007 M of $NiBr_2{\cdot}(PPh_3)_2$ & (*S*,*S*)-L1.



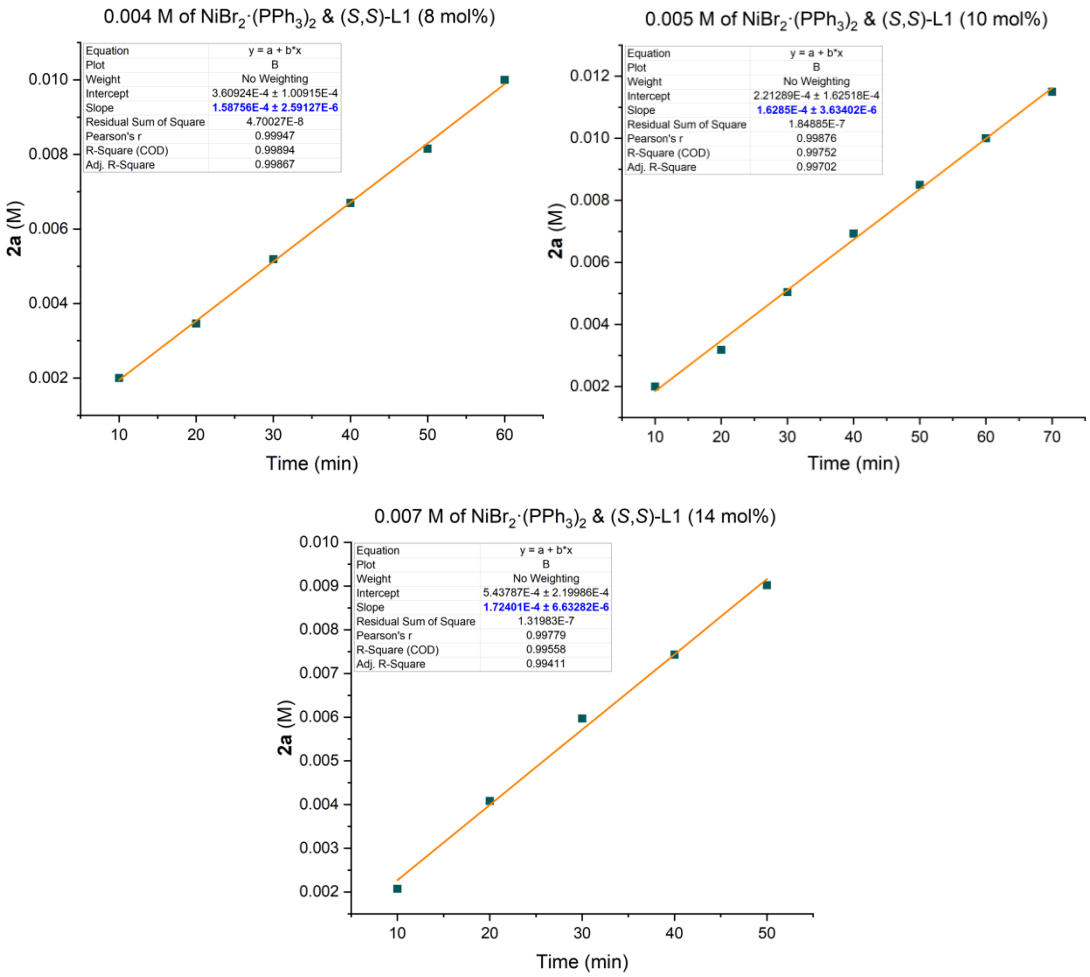
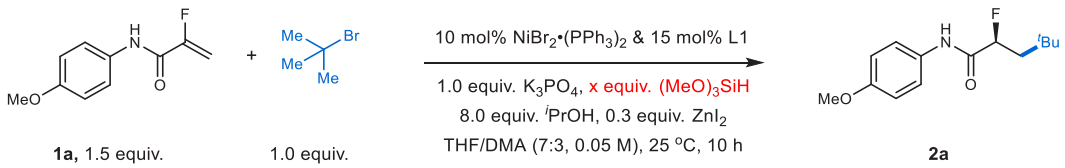


Figure S25. Plot of the rise of product from the reaction of **1a** (0.075 M), ^{t}BuBr (0.05 M), K_3PO_4 (0.05 M), $(MeO)_3SiH$ (0.10 M) ZnI_2 (0.0015 M), ^{i}PrOH (0.4 M) with 0.0005 M, 0.002 M, 0.004 M, 0.005 M, 0.007 M of $NiBr_2·(PPh_3)_2$ & (*S,S*)-L1 at 1500 rpm.

The rate on the concentration of $(MeO)_3SiH$



1a, 1.5 equiv. 1.0 equiv. **2a**

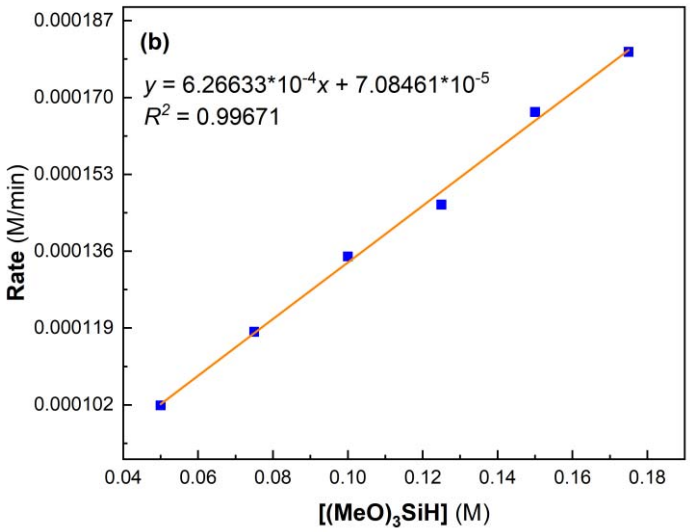
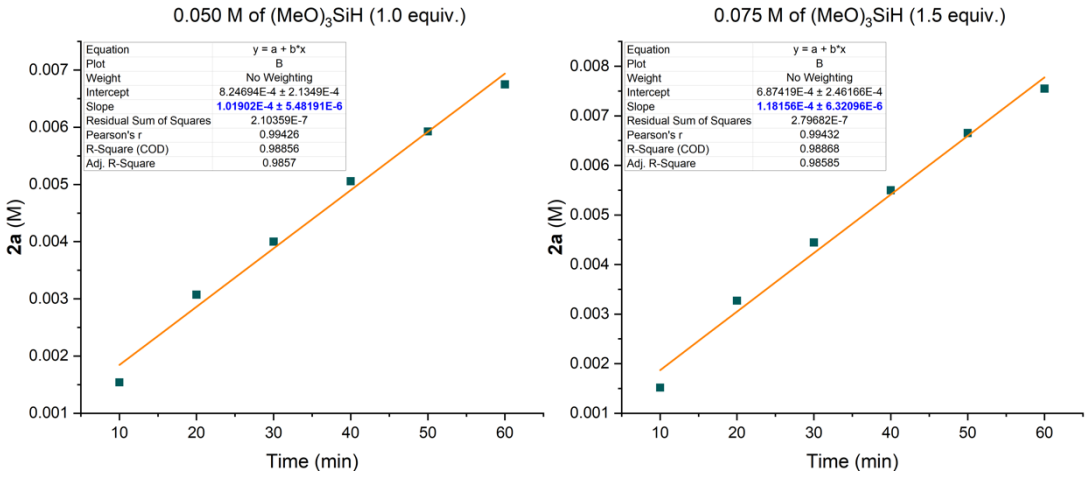


Figure S26. Rate on the concentration of $(MeO)_3SiH$ at 1500 rpm from the reaction of **1a** (0.075 M), ^{t}BuBr (0.05 M), $NiBr_2 \cdot (PPh_3)_2$ (0.005 M), (*S,S*)-L1 (0.0075 M), K_3PO_4 (0.05 M), ZnI_2 (0.0015 M), ^{i}PrOH (0.4 M) with 0.050 M, 0.075 M, 0.100 M, 0.125 M, 0.150 M, 0.175 M of $(MeO)_3SiH$.



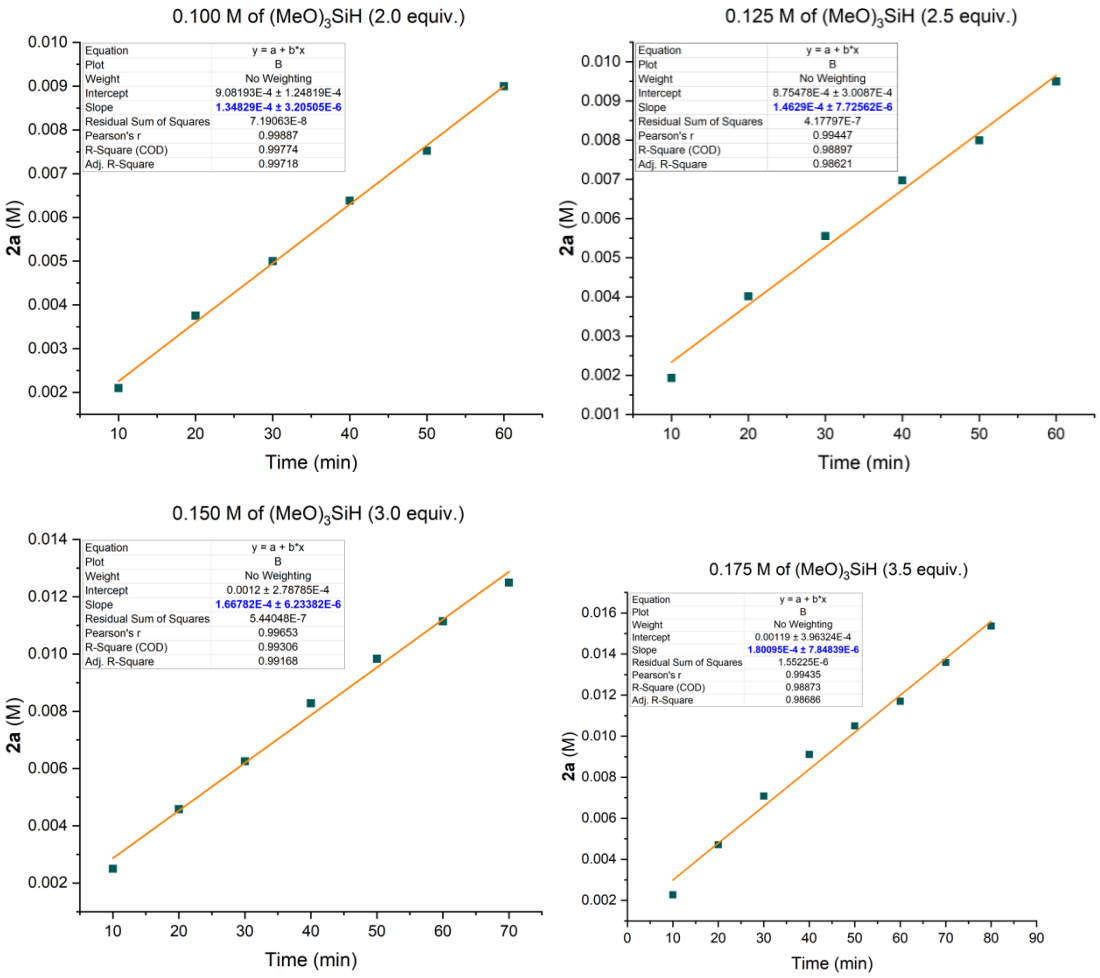
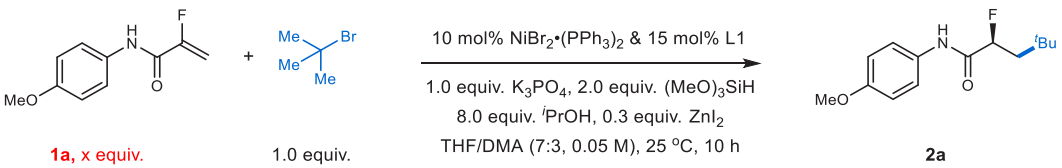


Figure S27. Plot of the rise of product from the reaction of **1a** (0.075 M), ^{t}BuBr (0.05 M), $NiBr_2 \cdot (PPh_3)_2$ (0.005 M), (*S,S*)-L1 (0.0075 M), K_3PO_4 (0.05 M), ZnI_2 (0.0015 M), ^{i}PrOH (0.4 M) with 0.050 M, 0.075 M, 0.100 M, 0.125 M, 0.150 M, 0.175 M of $(MeO)_3SiH$ at 1500 rpm.

The rate on the concentration of 1a



1a, x equiv. 1.0 equiv. **2a**

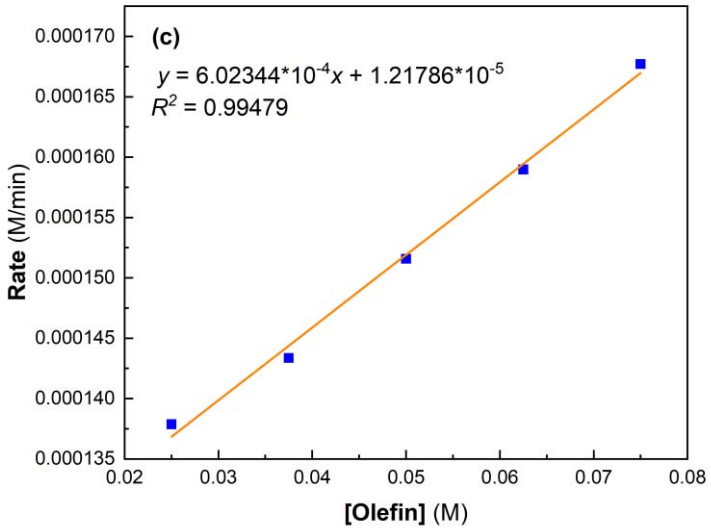
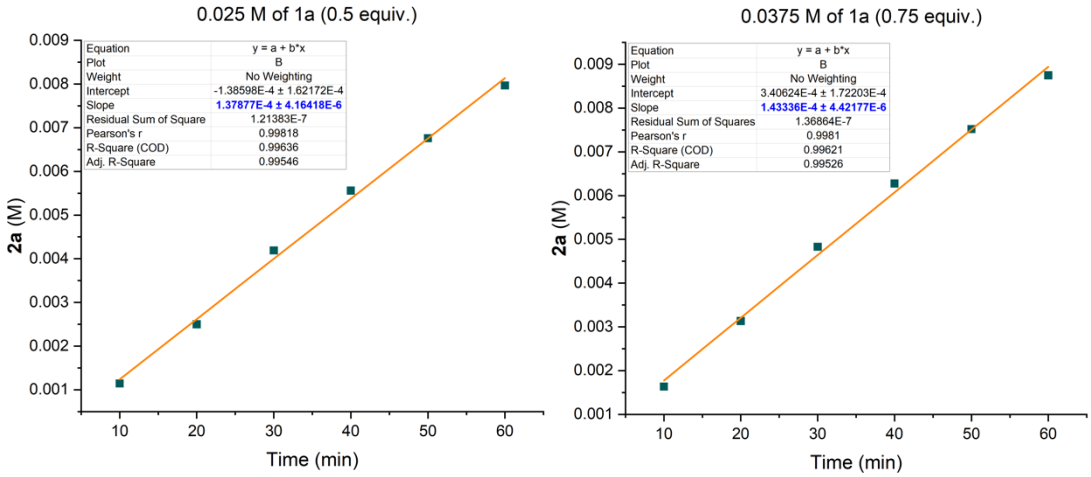


Figure S28. Rate on the concentration of **1a** at 1500 rpm from the reaction of ^{t}BuBr (0.05 M), $NiBr_2 \cdot (PPh_3)_2$ (0.005 M), (*S,S*)-L1 (0.0075 M), K_3PO_4 (0.05 M), $(MeO)_3SiH$ (0.10 M), ZnI_2 (0.0015 M), ^{i}PrOH (0.4 M) with 0.025 M, 0.0375 M, 0.050 M, 0.0625 M, 0.075 M of **1a**.



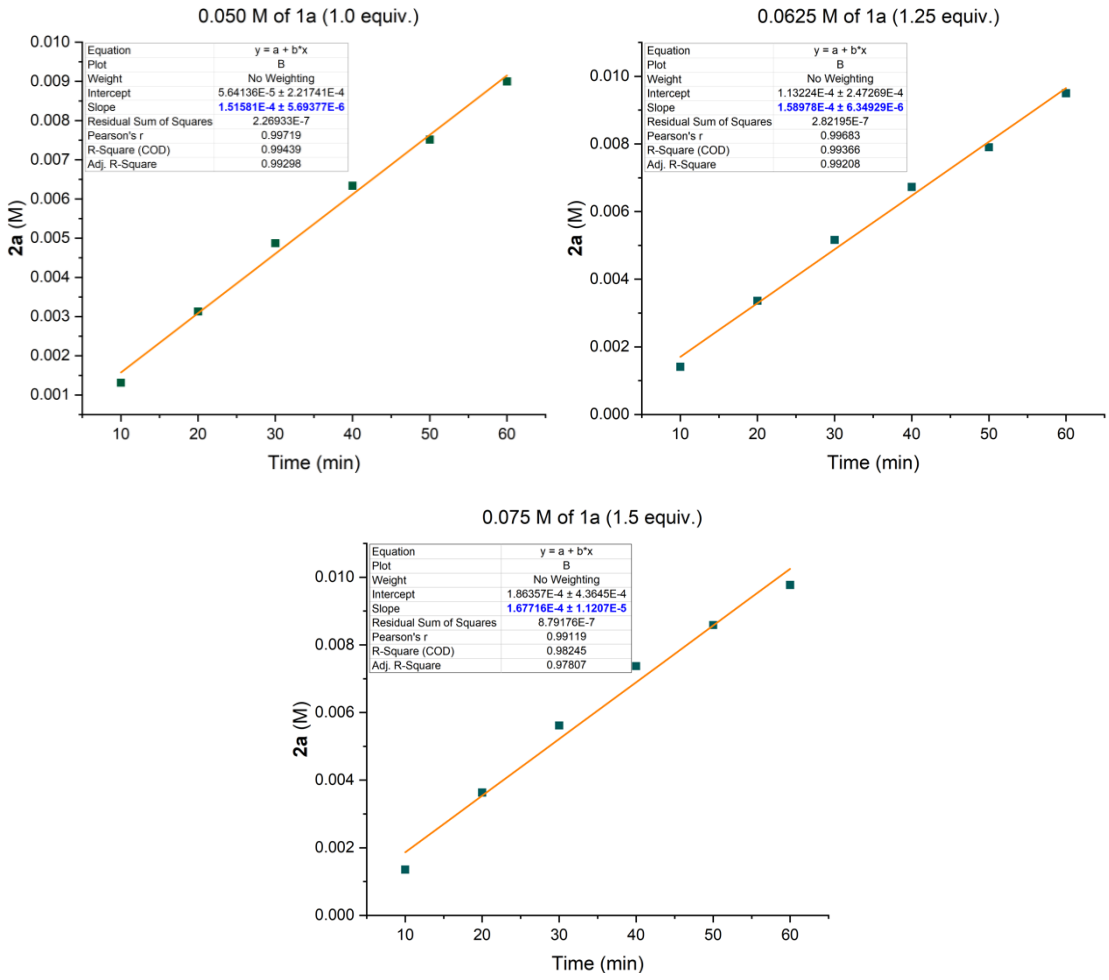
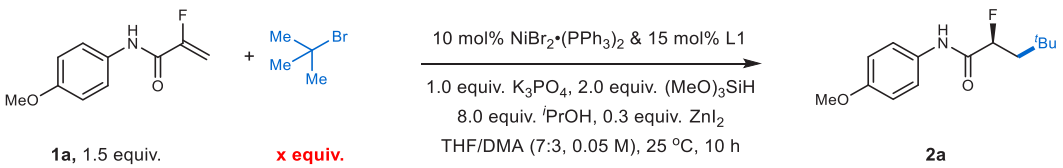


Figure S29. Plot of the rise of product from the reaction of ^{t}BuBr (0.05 M), $NiBr_2{\cdot}(PPh_3)_2$ (0.005 M), (*S,S*)-L1 (0.0075 M), K_3PO_4 (0.05 M), $(MeO)_3SiH$ (0.10 M), ZnI_2 (0.0015 M), ^{i}PrOH (0.4 M) with 0.050 M, 0.075 M, 0.100 M, 0.125 M, 0.150 M, 0.175 M of **1a** at 1500 rpm.

The rate on the concentration of ^{t}BuBr



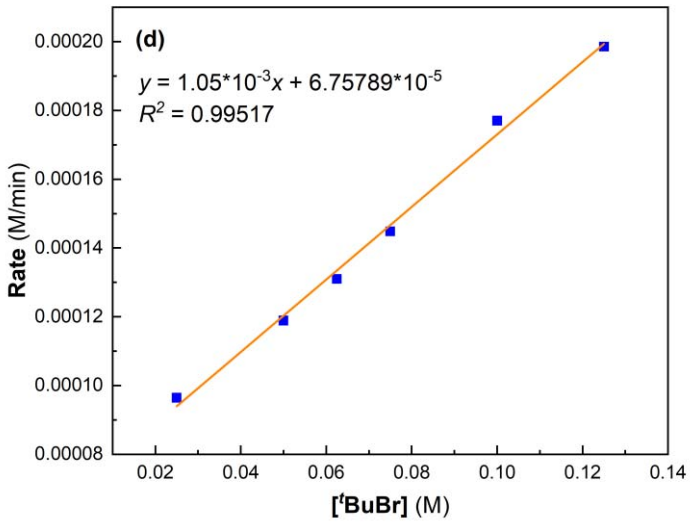
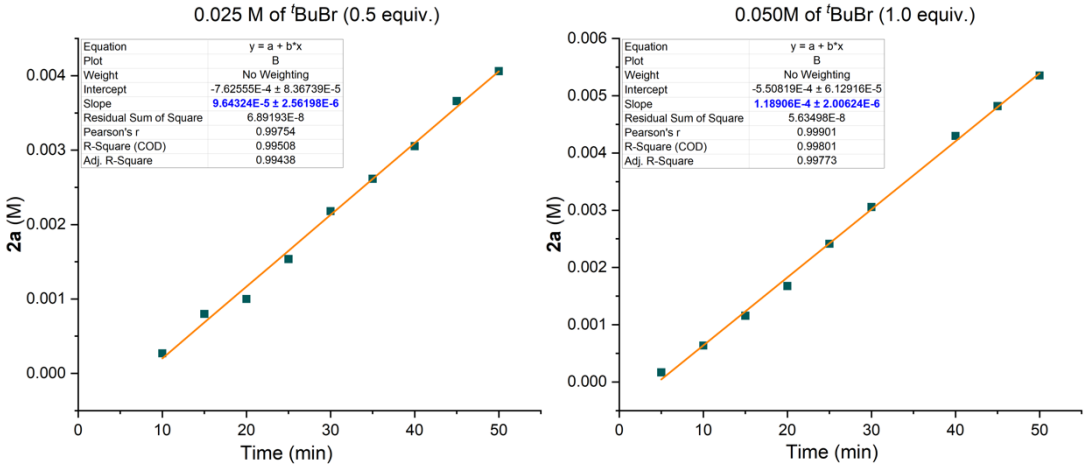


Figure S30. Rate on the concentration of ^{t}**BuBr** at 1500 rpm from the reaction of **1a** (0.075 M), $NiBr_2 \cdot (PPh_3)_2$ (0.005 M), (*S,S*)-L1 (0.0075 M), K_3PO_4 (0.05 M), $(MeO)_3SiH$ (0.10 M), ZnI_2 (0.0015 M), ^{i}PrOH (0.4 M) with 0.025 M, 0.050 M, 0.0625 M, 0.075 M, 0.100 M, 0.125 M of ^{t}**BuBr**.



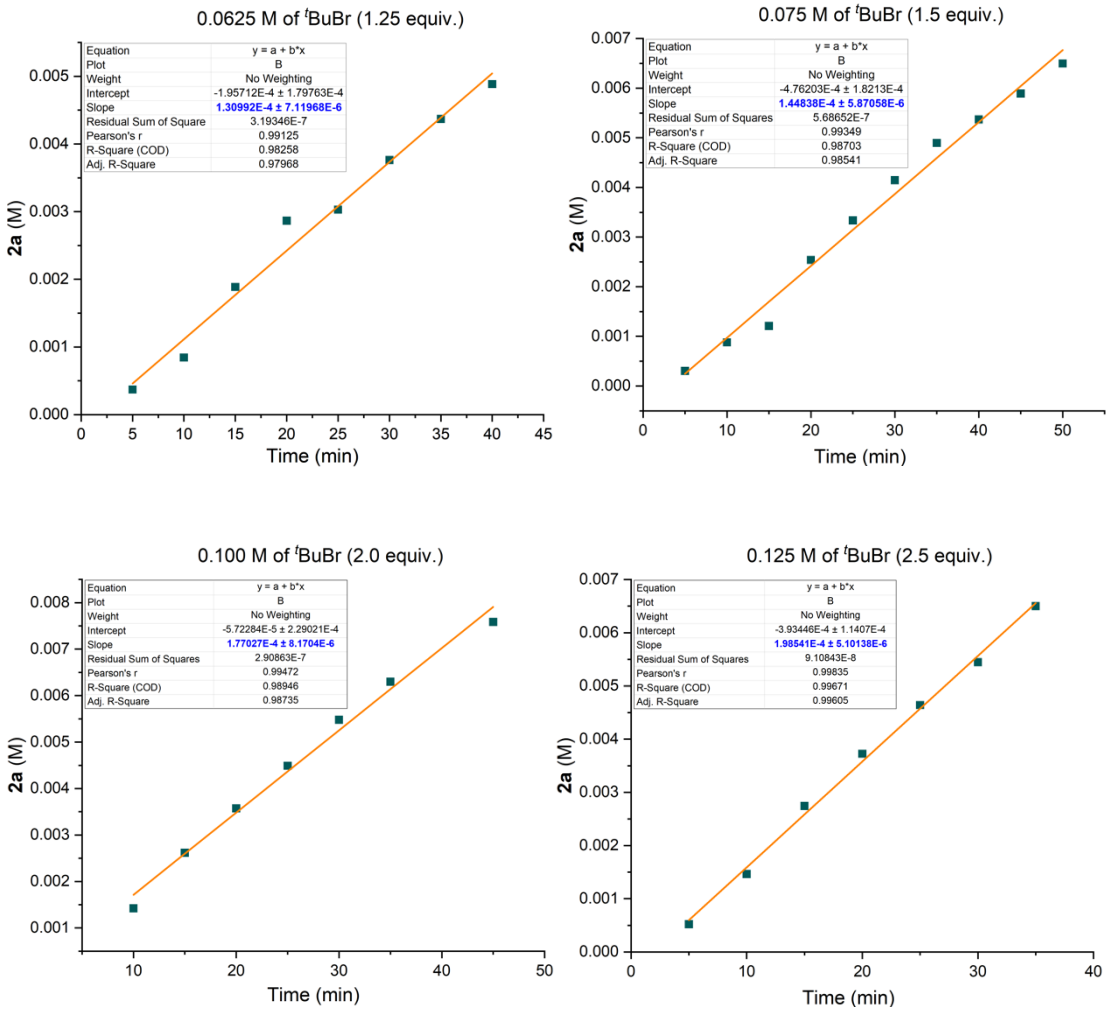
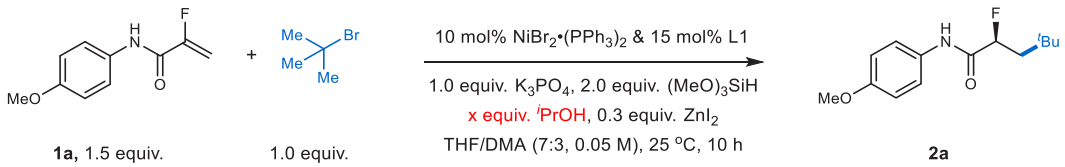


Figure S31. Plot of the rise of product from the reaction of **1a** (0.075 M), $NiBr_2{\cdot}(PPh_3)_2$ (0.005 M), (*S,S*)-L1 (0.0075 M), K_3PO_4 (0.05 M), $(MeO)_3SiH$ (0.10 M), ZnI_2 (0.0015 M), ^{i}PrOH (0.4 M) with 0.025 M, 0.0375 M, 0.050 M, 0.0625 M, 0.075 M of **^{t}BuBr** at 1500 rpm.

The rate on the concentration of ^{i}PrOH



1a, 1.5 equiv. 1.0 equiv. **2a**

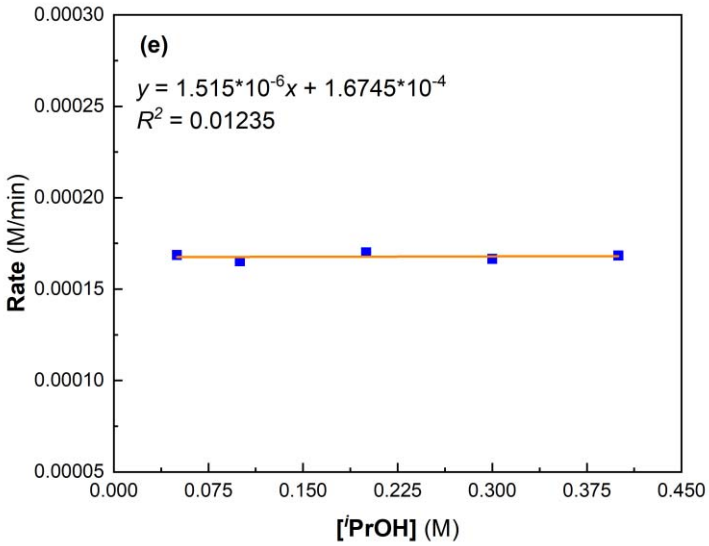
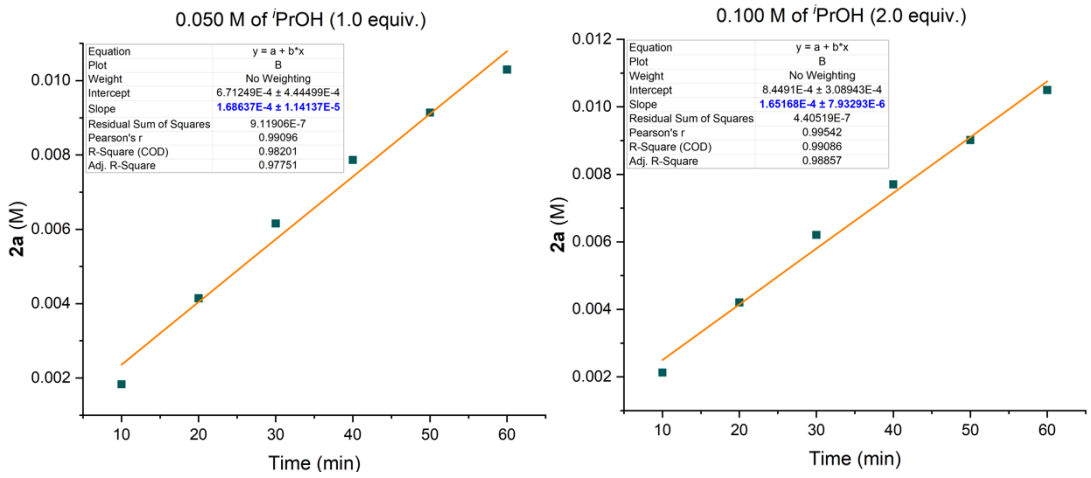


Figure S32. Rate on the concentration of ^{i}PrOH at 1500 rpm from the reaction of **1a** (0.075 M), ^{t}BuBr (0.05 M), $NiBr_2 \cdot (PPh_3)_2$ (0.005 M), (*S,S*)-L1 (0.0075 M), K_3PO_4 (0.05 M), $(MeO)_3SiH$ (0.10 M), ZnI_2 (0.0015 M) with 0.050 M, 0.100 M, 0.200 M, 0.300 M, 0.400 M of ^{i}PrOH.



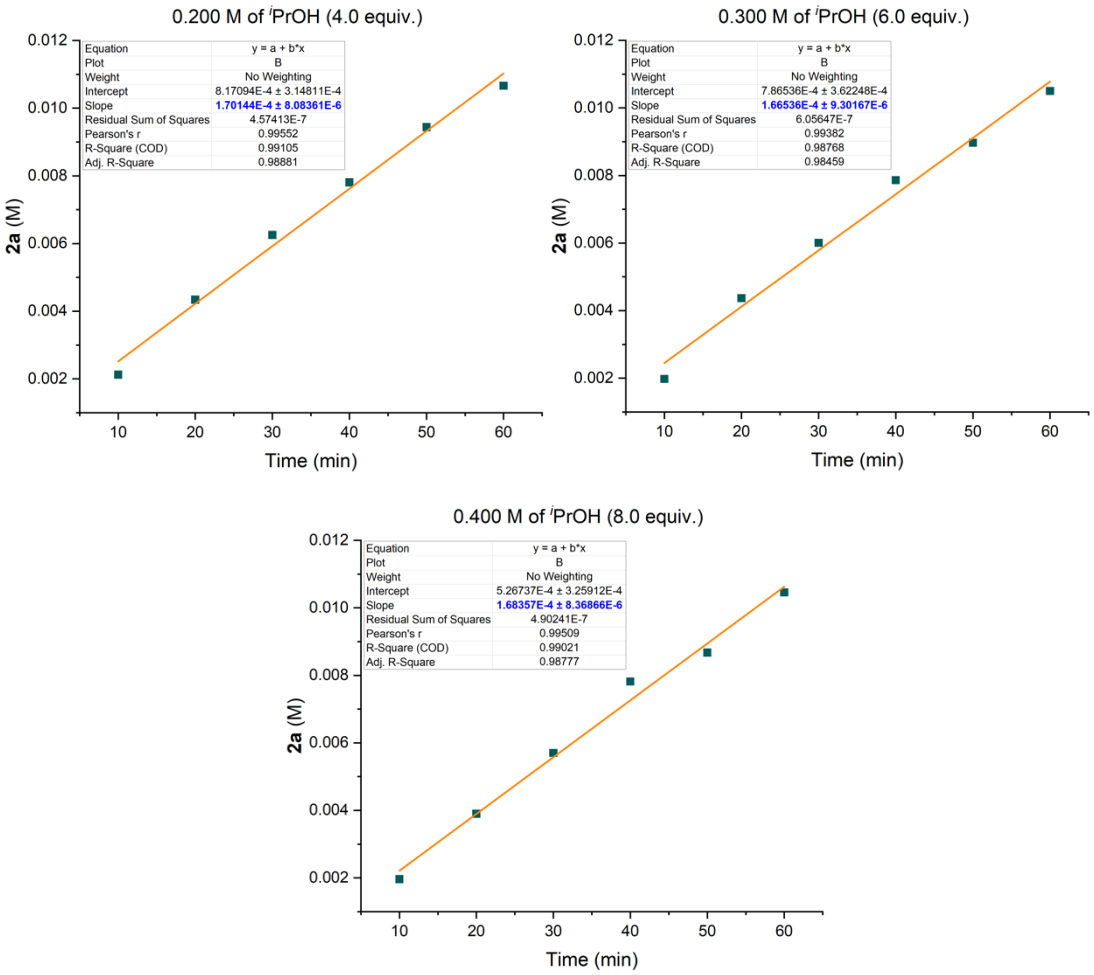
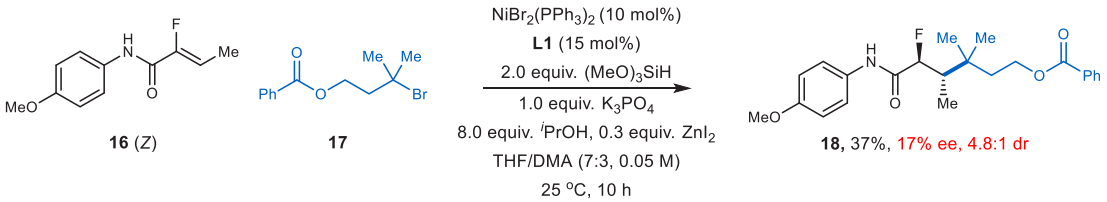


Figure S33. Plot of the rise of product from the reaction of **1a** (0.075 M), ^{t}BuBr (0.05 M), $NiBr_2 \cdot (PPh_3)_2$ (0.005 M), (*S,S*)-L1 (0.0075 M), K_3PO_4 (0.05 M), $(MeO)_3SiH$ (0.10 M), ZnI_2 (0.0015 M) with 0.050 M, 0.100 M, 0.200 M, 0.300 M, 0.400 M of ^{i}PrOH at 1500 rpm.

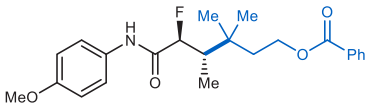
Comment: For this asymmetric alkyl transfer reaction, we conducted a series of reaction process kinetic analyses, and evaluated the dependence of the average rate after the initiation period on the nickel catalyst, alkene, alkyl bromide, silane and ^{i}PrOH concentrations in each case. As shown above, this model reaction exhibited a first-order dependence on the concentration of the nickel catalyst, alkyl bromide, silane, and monofluoroalkene, as well as a zeroth-order dependence on the concentration of iPrOH. The observed anomalous kinetic data could be related to the mass transfer effect. Also, DFT calculations indicate that this reaction does not have a single rate-determining

step.

6) Alkyl transfer reactions with internal alkenes (*Z*)-16 (*Z*/*E* > 20:1)



According to General Procedure A, (*Z*)-2-fluoro-*N*-(4-methoxyphenyl)but-2-enamide **16** (0.15 mmol, 1.5 equiv.), 3-bromo-3-methylbutyl benzoate **17** (0.1 mmol, 1.0 equiv.), $NiBr_2{\cdot}(PPh_3)_2$ (0.01 mmol, 10 mol%), (*S*,*S*)-**L1** (0.015 mmol, 15 mol%), $(MeO)_3SiH$ (0.2 mmol, 2.0 equiv.), K_3PO_4 (0.1 mmol, 1.0 equiv.), ^{i}PrOH (0.8 mmol, 8.0 equiv.) and ZnI_2 (0.03 mmol, 0.3 equiv.) in THF/DMA (v/v = 7:3, 0.05 M) were used. The reaction mixture was allowed to stir for 10 h at 25 °C. After then, the product **18** was isolated by flash chromatography (Petroleum ether: EtOAc = 3:1) as a white solid (14.8 mg, 37% yield, 17% ee, 4.8:1 dr). The ratio of dr was determined by ^{1}H NMR.



(5*S*)-5-fluoro-6-((4-methoxyphenyl)amino)-3,3,4-trimethyl-6-oxohexyl benzoate (18)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.84 (m, 3H), 7.53 – 7.26 (m, 5H), 6.86 – 6.60 (m, 2H), 5.34 – 4.76 (m, 1H), 4.41 – 4.26 (m, 2H), 3.71 (d, *J* = 3.4 Hz,3H), 2.25 – 2.05 (m, 1H), 1.84 – 1.76 (m, 3H), 1.08 – 0.97 (m, 9H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -183.89 – -184.11 (m), -197.66 – -197.91 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.25 (d, *J* = 18.2 Hz), 167.78 (d, *J* = 19.5 Hz), 166.78, 166.77, 156.93, 133.00, 132.98, 130.45, 129.98, 129.94, 129.66, 129.64, 128.47, 128.45, 122.03, 121.83, 114.35, 95.50 (d, *J* = 189.7 Hz), 92.82 (d, *J* = 191.8 Hz), 62.18, 62.14, 55.58, 43.95 (d, *J* = 18.5 Hz), 43.83 (d, *J* = 18.2 Hz), 38.96 (d, *J* = 1.9 Hz), 38.40,

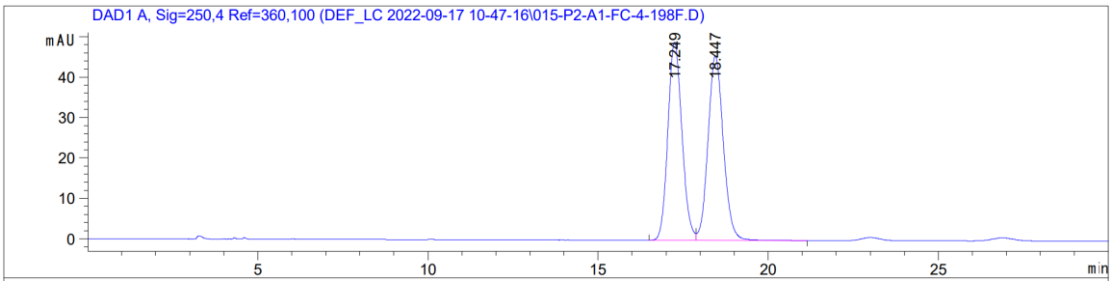
35.40 (d, J = 1.6 Hz), 34.82, 29.81, 25.71 (d, J = 1.7 Hz), 25.55 (d, J = 1.8 Hz), 25.50, 12.54 (d, J = 4.2 Hz), 8.02 (d, J = 7.2 Hz).

HRMS (ESI): $C_{23}H_{29}FNO_4^+$ ($M+H^+$): 402.2075, found: 402.2079.

$[\alpha]_D^{25}$ = -3.35 (c = 1.55, $CHCl_3$).

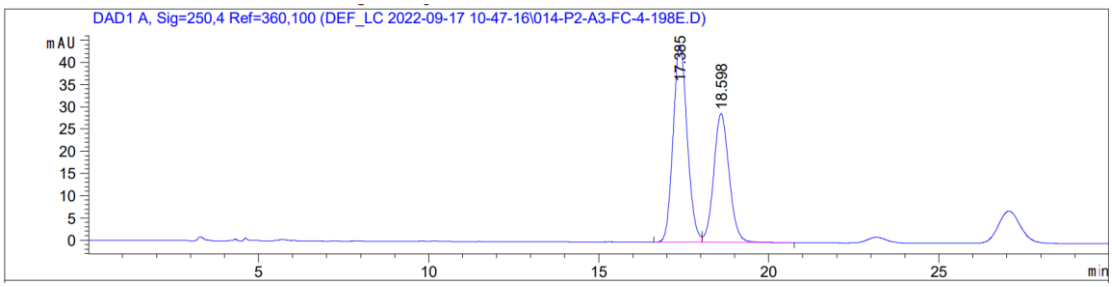
HPLC: The ee was determined to be 17% on a CHIRALPAK IC column at 250 nm, 25 ^oC, with hexane: ^{i}PrOH = 80:20 at a flow rate 1.0 mL/min. Retention times: t_R (major) = 17.4 min, t_R (minor) = 18.6 min.

18 racemic



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.249	BV	0.4475	1408.48071	48.98559	49.5922
2	18.447	VB	0.4843	1431.64453	45.59877	50.4078

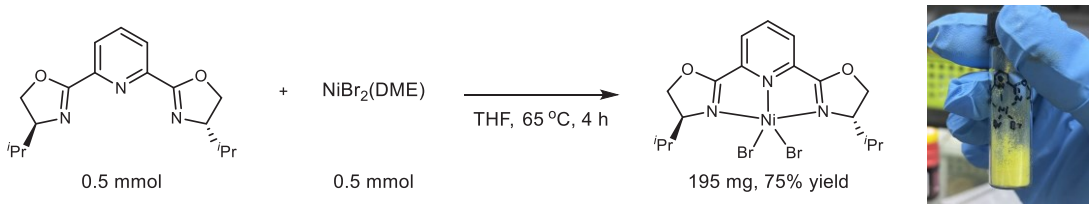
18 enantioenriched, 17% ee



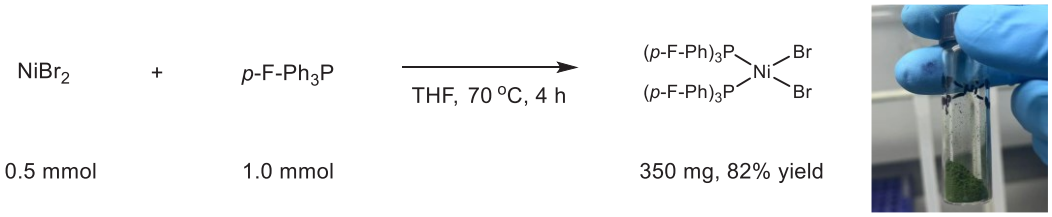
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.385	BV	0.4469	1280.84302	44.35602	58.3227
2	18.598	VB	0.4866	915.28943	28.97264	41.6773

7) Investigation of ligand exchange between Pybox and PPh_3

a. Preparation of $NiBr_2$(Pybox) and $NiBr_2$(p-F-$Ph_3P)_2$



The $NiBr_2$(Pybox) was prepared according to the reported literature.[20] (*S*)-^{i}Pr-Pybox (0.5 mmol) and $NiBr_2 \cdot DME$ (0.5 mmol) were charged to a 10 mL Schlenk flask under nitrogen. Dry THF (7.5 mL) was then added, and the mixture was heated to 65 °C for 4 h. Next, the heating bath was removed, and filter the hot mixture under N_2. Upon cooling, a solid formed. The flask was maintained at 0 °C in an ice bath for 2 h, and then the cold supernatant was removed using a filter paper. The resulting solid was washed with Et_2O (8 mL) and then dried under vacuum. The $NiBr_2$(Pybox) was obtained as a yellow solid (390 mg, 75%).



The $NiBr_2$(*p*-F-$Ph_3P)_2$ was prepared according to the reported literature.[21] $NiBr_2$ (0.5 mmol) and *p*-F-Ph_3P (1.0 mmol) were charged to a 10 mL Schlenk flask under nitrogen. Dry THF (5 mL) was then added, and the mixture was heated to 70 °C for 4 h. Next, remove the solvent under vacuum and 15 ml PE was added to the flask. The resulting solid was washed with Et_2O (4*2 mL) and then dried under vacuum. The $NiBr_2$(*p*-F-$Ph_3P)_2$ was obtained as a dark green solid (350 mg, 82%).

b. Product distributions with different nickel catalysts.

We have performed more detailed studies with several pre-catalysts **Ni-I**, **Ni-II**, **Ni-III**, and related ligands under otherwise same conditions. Using **1a**, ^{t}BuBr, $(MeO)_3SiH$, K_3PO_4 and ^{i}PrOH in THF/DMA with combination of different nickel catalysts and ligands. The Benzotrifluoride was added as an internal standard and stir at 1500 rpm and 25 °C. Aliquots of the reaction mixture (60 μL) were taken out via syringe, and

immediately placed to H_2O & $CDCl_3$ (0.1 mL & 0.6 mL). After filtration, the yields of products were detected by ^{19}F NMR (^{19}F exp. comp. pulse decoupling).

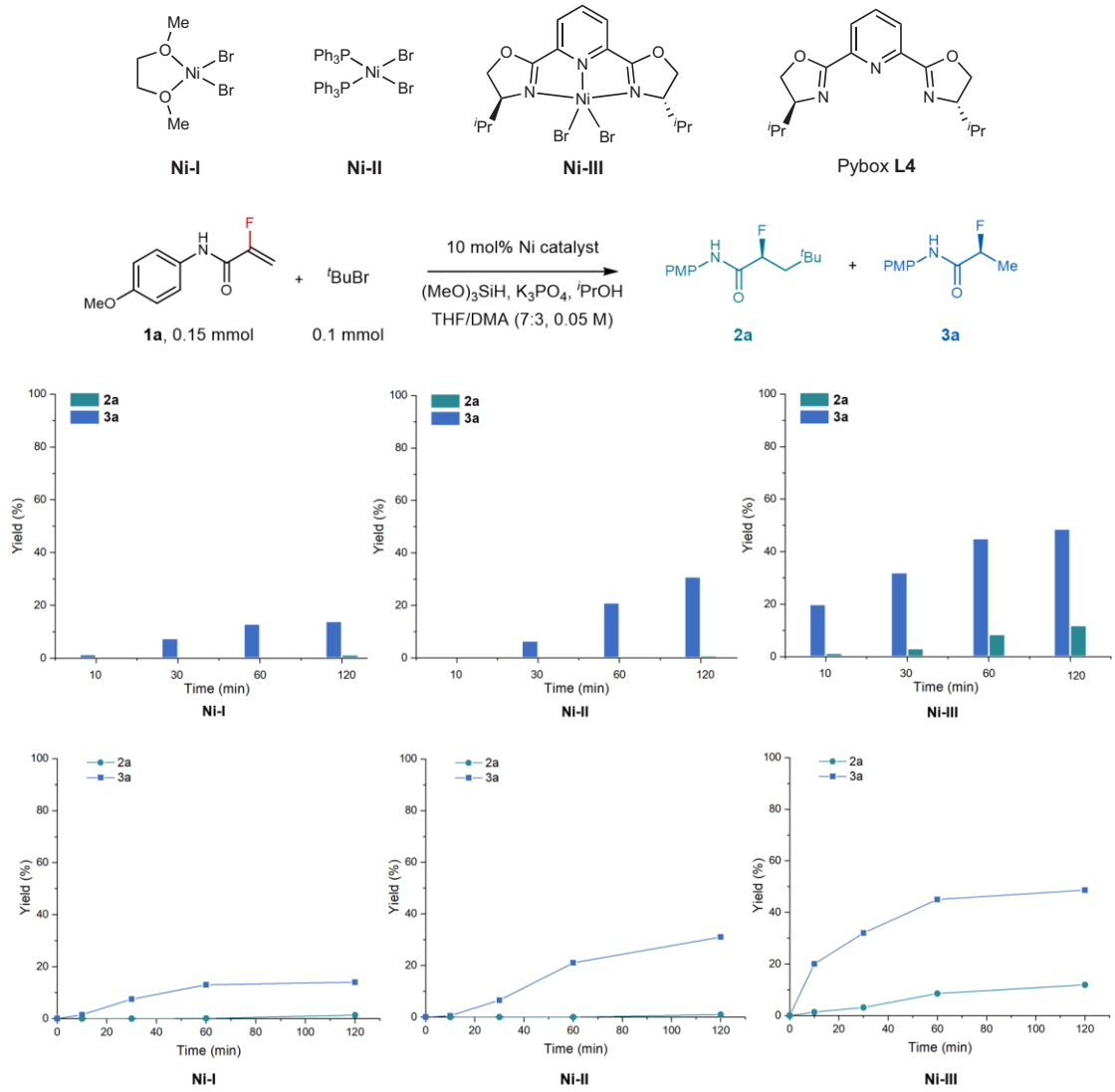


Figure S34. Products distribution of different nickel catalysts within 120 min.

Comment: For the reaction of alkene **1a** and *t*-BuBr in the presence of silane and alcohol, all **Ni-I**, **Ni-II**, and **Ni-III** afford the HAT product **3a**, with **Ni-III** being the highest and **Ni-I** lowest (trace). A small amount of alkylated product **2a** is observed in the case of **Ni-III**. These results are consisted with our previous finding, that is, both Pybox and PPh_3 can promote the generation of **3a** (PPh_3 may via Ni-H HAT or Ni-H insertion).

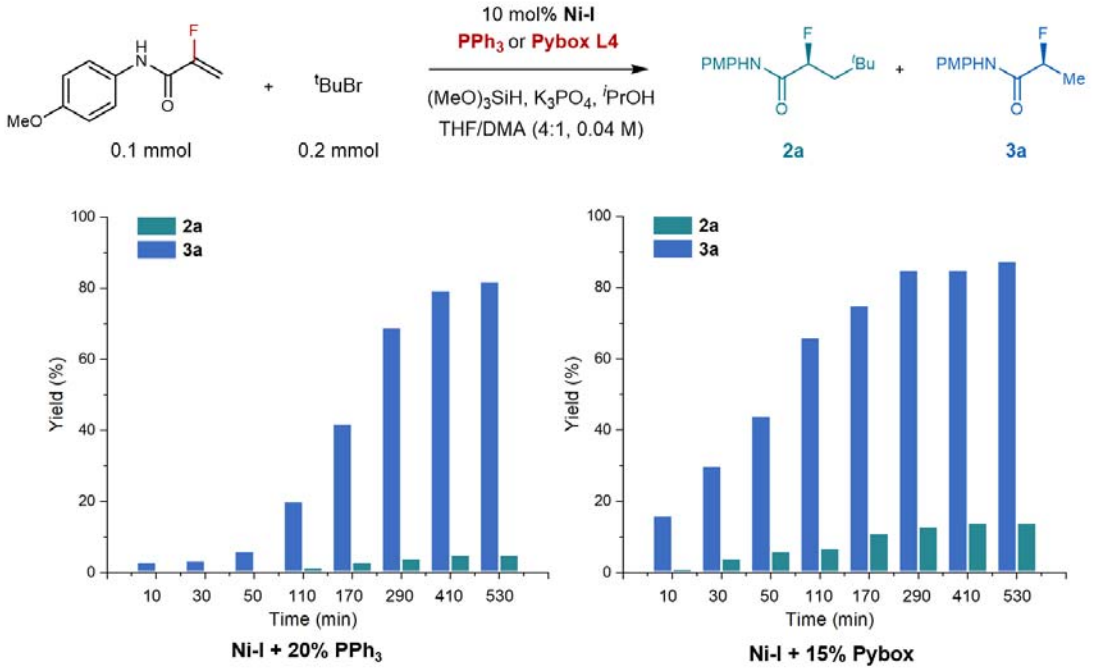


Figure S35. Products distribution of **Ni-I** + PPh_3 and **Ni-I** + Pybox.

Comment: The use of Pybox leads to more efficient HAT process, especially at the early stage of the reaction.

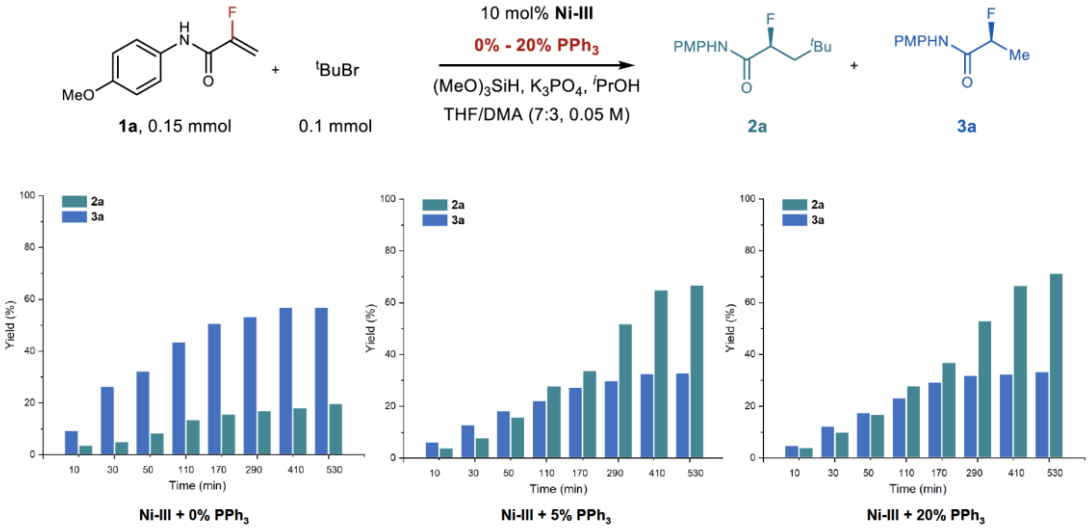


Figure S36. Products distribution of **Ni-III** + PPh_3.

Comment: With catalyst **Ni-III**, we further evaluate the effect of exogenous PPh_3. The addition of catalytic PPh_3 (5 mol% & 20 mol%) significantly increased the yields of **2a** and decreased the yields of **3a**, consistent with our previous results shown in the Table

S8. Also, the use of 5 mol% or 20 mol% PPh_3 gives similar results.

c. ^{19}F NMR monitoring of ligand exchange

we prepared precatalyst $NiBr_2$(Pybox) and $NiBr_2$(p-F-$Ph_3P)_2$ to pinpoint the potential ligand exchanges via ^{19}F NMR analysis. The reaction of $NiBr_2$(Pybox) with *p*-F-Ph_3P in THF/DMA at room temperature gives a new ^{19}F NMR signal at -106.1 ppm, which matches the one of prepared $NiBr_2$(*p*-F-$Ph_3P)_2$. On the other hand, the reaction of $NiBr_2$(*p*-F-$Ph_3P)_2$ with Pybox also forms the signal of *p*-F-Ph_3P. (note: making the sample and running the NMR take around 10 mins, suggesting the ligand exchange could be very fast and dynamic). These results support the involvement of ligand exchange.

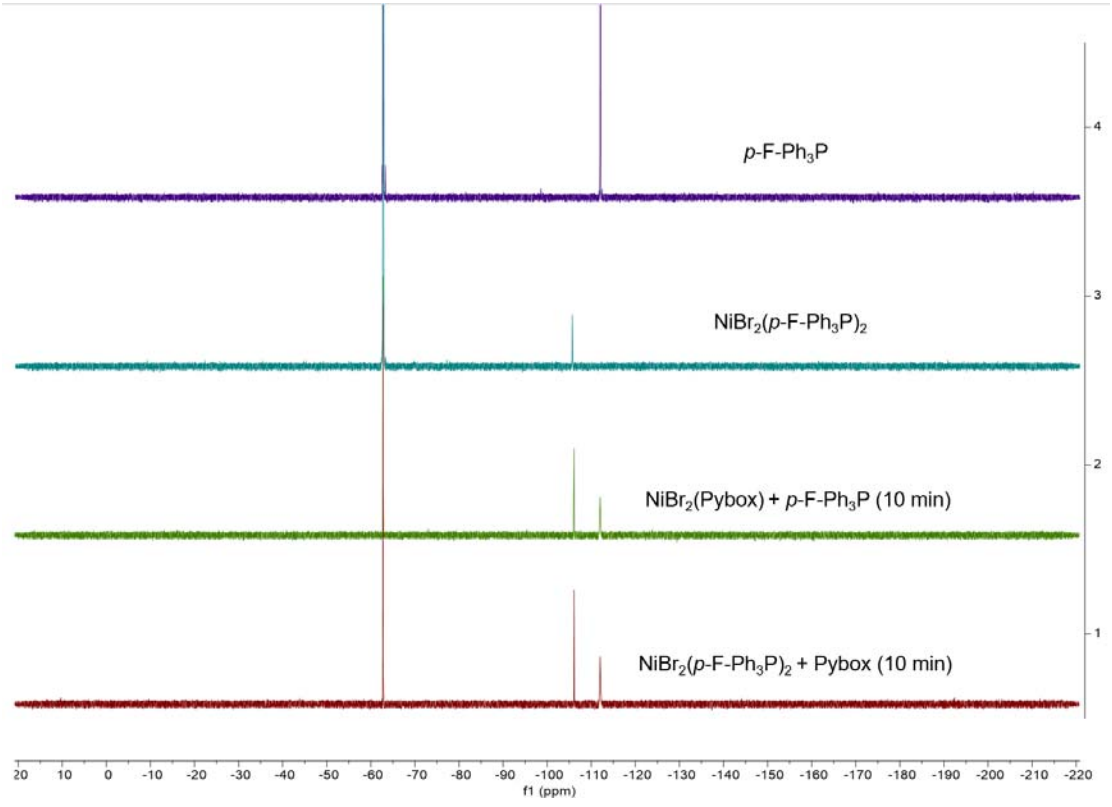


Figure S37. ^{19}F NMR tracking of ligand exchange process.

9.3 Mechanism studies of HAT/alkyl coupling reaction

1) Deuterium-Labeling experiments

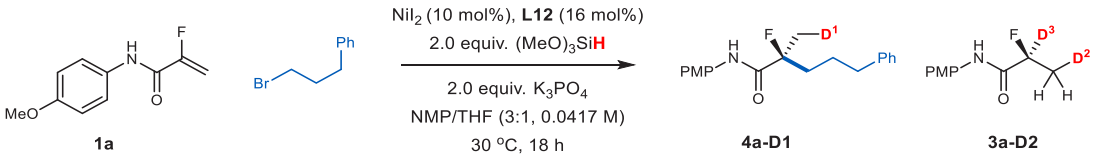


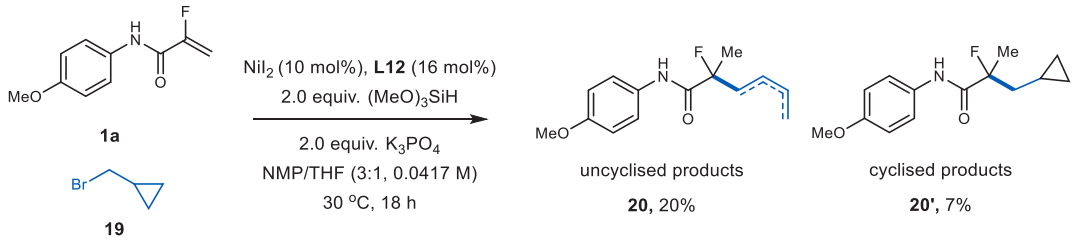
Table S31. Deuterium-Labeling experiments for HAT/alkyl coupling

Entry	H/D sources	4a-D1		3o-D2		
		Yield, ee	D1	Yield, ee	D2	D3
1	2.0 equiv. **Ph_2SiD_2**	33% 34% ee	99%	13% 13% ee	14%	0%
2	2.0 equiv. **D_2O**	trace	--	45% 13% ee	0%	42%

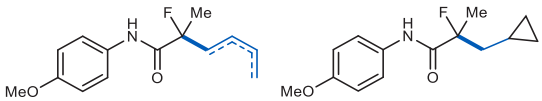
According to **General Procedure D**, 2-fluoro-*N*-(4-methoxyphenyl)acrylamide **1a** (0.1 mmol, 1.0 equiv.), (3-bromopropyl)benzene (0.12 mmol, 1.2 equiv.), NiI_2 (0.01 mmol, 10 mol%), (*S*,*S*)-**L12** (0.016 mmol, 16 mol%), K_3PO_4 (0.2 mmol, 2.0 equiv.), in NMP/THF (v/v = 3:1, 0.0417 M) were used. Then, different hydrogen sources (Ph_2SiD_2 instead of $(MeO)_3SiH$, additional D_2O) were added. The reaction mixture was allowed to stir for 18 h at 30 °C. After then, the products **4a-D1** and **3o-D2** were isolated for each reaction by flash chromatography (Petroleum ether: EtOAc = 5:1). Yields were analyzed by GC using *n*-dodecane as an internal standard and the incorporation of deuterium was determined by ^1H NMR.

According to **General Procedure D, 4a-D1** and **3o-D2** was obtained. Entry 1, the reaction of **1a** and phenylpropyl bromide with Ph_2SiD_2 gave 33% yield of β-deuterated product **4a-D** (99% D). Entry 2, the reaction of **1a** and phenylpropyl bromide with D_2O gave trace amount of **4a-D**, together with 45% yield of α-deuterated hydrogenation product **3o-D** (42% D).

2) Radical probe reactions.



According to General Procedure D, 2-fluoro-*N*-(4-methoxyphenyl)acrylamide **1a** (0.1 mmol, 1.0 equiv.), (bromomethyl)cyclopropane **11** (0.12 mmol, 1.2 equiv.), NiI_2 (0.01 mmol, 10 mol%), **L12** (0.016 mmol, 16 mol%), $(MeO)_3SiH$ (0.2 mmol, 2.0 equiv.), K_3PO_4 (0.2 mmol, 2.0 equiv.) in NMP/THF (v/v = 3:1, 0.0417 M) were used. The reaction mixture was allowed to stir for 18 h at 30 °C. After then, the mixture of ring-opening coupling product **20** and coupling product **20'** were isolated by flash chromatography (Petroleum ether: EtOAc = 5:1) as a white solid (6.8 mg, 27% yield). The ratio of **20:20'** was determined by ^{1}H NMR.

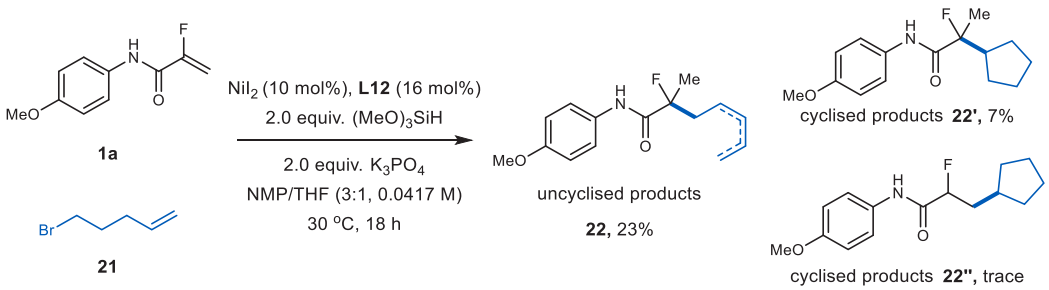


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.83 (m, 1H), 7.54 – 7.41 (m, 2H), 7.01 – 6.75 (m, 2H), 5.89 – 5.34 (m, **1.22H**), 5.12 – 4.80 (m, **1.05H**), 3.80 (s, 3H), 2.86 – 2.43 (m, 0.89H), 2.34 – 2.04 (m, 1.76H), 2.04 – 1.80 (m, 0.87H), 1.73 – 1.59 (m, 4.18H), 1.02 (dd, *J* = 6.9, 1.3 Hz, 0.3H).

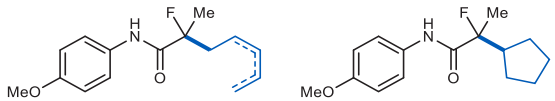
^{19}F NMR (377 MHz, Chloroform-*d*) δ -154.38 – -154.87 (m), -154.92 – -155.43 (m), -168.01 – -168.53 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.30 (dd, *J* = 19.6, 3.7 Hz), 156.89, 156.86, 137.35, 130.78, 130.21, 130.16, 130.12, 128.89, 123.29, 123.25, 122.37, 121.89, 121.79, 121.73, 115.34, 114.36, 114.34, 99.75 – 97.52 (m), 55.63, 43.22, 41.44, 41.22, 37.55, 37.33, 36.97, 35.69, 35.47, 32.20, 29.84, 27.80, 27.76, 24.24, 24.00, 23.56, 23.49, 23.33, 23.25, 22.70, 18.19, 13.14, 12.10.

HRMS (ESI): $C_{14}H_{19}FNO_2^+$ ($M+H^+$): 252.1394, found: 252.1397.



According to General Procedure D, 2-fluoro-*N*-(4-methoxyphenyl)acrylamide **1a** (0.1 mmol, 1.0 equiv.), 5-bromopent-1-ene **21** (0.12 mmol, 1.2 equiv.), NiI_2 (0.01 mmol, 10 mol%), **L12** (0.016 mmol, 16 mol%), $(MeO)_3SiH$ (0.2 mmol, 2.0 equiv.), K_3PO_4 (0.2 mmol, 2.0 equiv.) in NMP/THF (v/v = 3:1, 0.0417 M) were used. The reaction mixture was allowed to stir for 18 h at 30 °C. After then, the mixture of normal coupling product **22** and ring-closed coupling product **22'** were isolated by flash chromatography (Petroleum ether: EtOAc = 5:1) as a colorless oil (7.9 mg, 30% yield). The ratio of **22:22'** was determined by ^{1}H NMR.



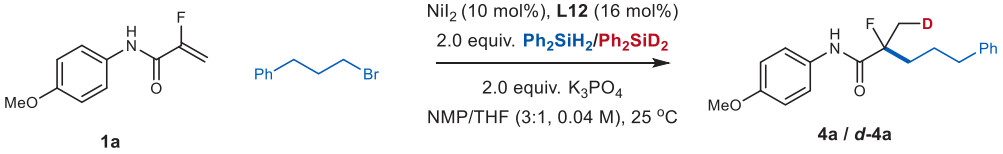
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.1 Hz, 1H), 7.60 – 7.35 (m, 2H), 7.02 – 6.70 (m, 2H), 5.77 (m, **0.7H**), 5.55 – 5.24 (m, **0.19H**), 5.16 – 4.82 (m, **1.43H**), 3.79 (s, 3H), 2.12 – 1.95 (m, 2.78H), 1.83 (m, 1.07H), 1.70 – 1.54 (m, 4.60H), 1.50 – 1.34 (m, 1.26H), 0.99 – 0.83 (m, 0.67H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -154.68 – -155.07 (m), -155.09 – -155.37 (m), -179.34 – -179.80 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.37 (d, *J* = 19.6 Hz), 156.74, 138.00, 130.06, 121.66 (d, *J* = 4.4 Hz), 115.12, 114.23, 98.78 (d, *J* = 185.3 Hz), 55.51, 37.57 (d, *J* = 21.9 Hz), 36.06 (d, *J* = 21.6 Hz), 33.46, 33.39 (d, *J* = 22.4 Hz), 29.57 (d, *J* = 29.4 Hz), 25.02, 23.91 (d, *J* = 23.9 Hz), 22.51 (d, *J* = 2.9 Hz), 20.71, 15.52 (d, *J* = 3.5 Hz).

HRMS (ESI): $C_{15}H_{21}FNO_2^+$ ($M+H^+$): 266.1551, found: 266.1553.

3) Kinetic isotopic effect of HAT/alkyl coupling (Ph_2SiH_2)



According to **General Procedure D**, 2-fluoro-*N*-(4-metho-xyphenyl) acrylamide **1a** (0.1 mmol, 1.0 equiv.), (3-bromopropyl)benzene (0.12 mmol, 1.2 equiv.), NiI_2 (0.01 mmol, 10 mol%), (*S*,*S*)-**L12** (0.015 mmol, 15 mol%) and K_3PO_4 (0.2 mmol, 2.0 equiv.) in NMP/THF (v/v = 3:1, 0.04 M) were used. Ph_2SiH_2 & Ph_2SiD_2 were used instead of $(MeO)_3SiH$. The *n*-dodecane was added as an internal standard. Aliquots of the reaction mixture were taken via syringe at 58, 59, 60, 61, 62, 63, 64, 65, 66 and 67 min, immediately placed to H_2O & EtOAc (0.1 mL & 1.2 mL). Then the clear solution is obtained after filtration, and the concentration of product is detected by GC.

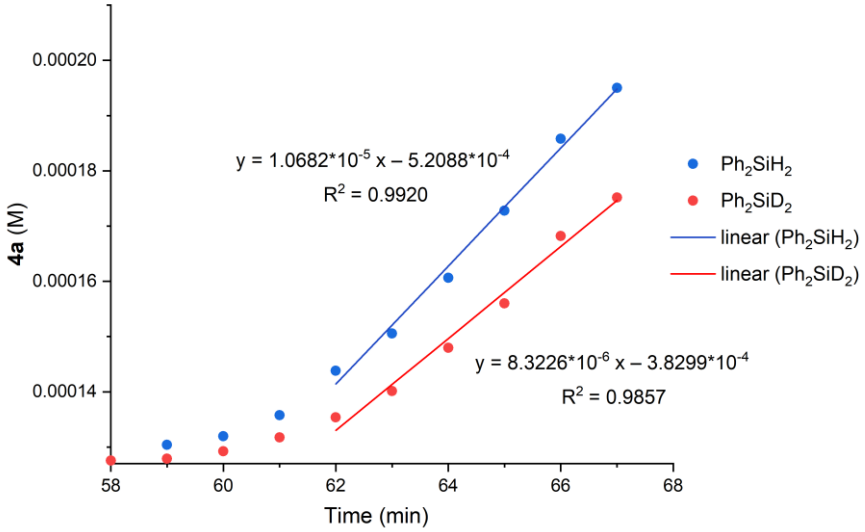


Figure S38. Determination of the kinetic isotope effect of HAT/alkyl coupling.

Comment: A linear trendline was drawn between 62-67 min to obtain the initial rates of the reaction. Minutes 0-62 were not included to account for the reaction's induction period. Dividing the slope of the trendline for the reaction using Ph_2SiH_2 by the slope of the trendline for the reaction using Ph_2SiD_2 gave k_H/k_D=1.0682/0.8323=1.29.

KIEs with Ph_2SiD_2/Ph_2SiH_2 in parallel and competitive reactions

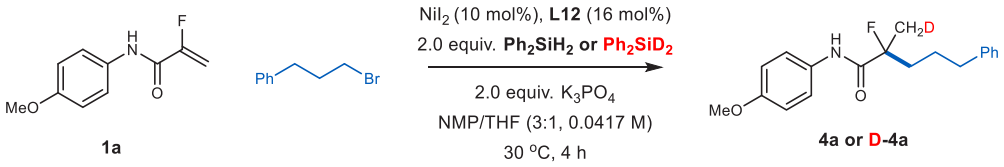


Table S32. KIEs for parallel reactions in HAT/alkyl transfer

Entry	Time	4a		D-4a		KIE =
		yield	D	yield	D	k_H/k_D
1	2 h	7%	0%	6%	98%	1.17
2	3 h	13.9%	0%	12.4%	98%	1.12
3	4 h	17.5%	0%	14.9%	98%	1.17

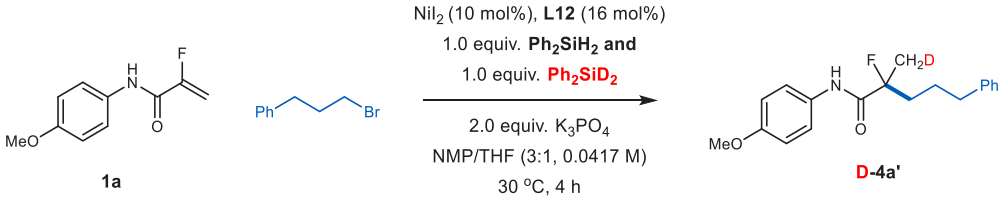


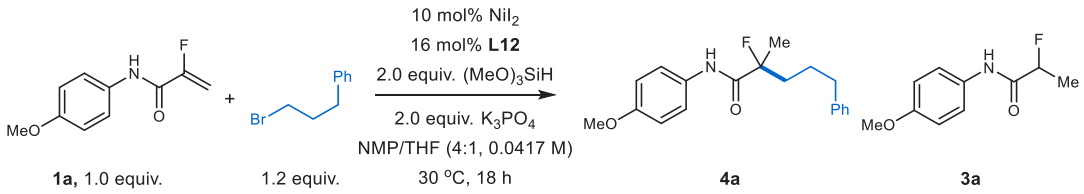
Table S33. KIEs for competitive reactions in HAT/alkyl transfer

Entry	Time	Yield of D-4a'	D	KIE = k_H/k_D
1	2 h	8.5%	42%	1.38
2	3 h	11.3%	44%	1.27
3	4 h	15.4%	42%	1.38

According to **General Procedure D**, 2-fluoro-*N*-(4-metho-xyphenyl) acrylamide **1a** (0.1 mmol, 1.0 equiv.), (3-bromopropyl)benzene (0.12 mmol, 1.2 equiv.), NiI_2 (0.01 mmol, 10 mol%), (*S*,*S*)-**L12** (0.015 mmol, 15 mol%) and K_3PO_4 (0.2 mmol, 2.0 equiv.) in NMP/THF (v/v = 3:1, 0.0417 M) were used. Ph_2SiH_2 & Ph_2SiD_2 were used instead of $(MeO)_3SiH$. The reaction mixture was allowed to stir at 25 °C. After then, the product **4a**, **D-4a** and **D-4a'** were isolated by flash chromatography (Petroleum ether: EtOAc = 5:1) at 2 h, 3 h and 4 h respectively. Yields were analyzed by GC using *n*-dodecane as an internal standard and the incorporation of deuterium was determined by ^1H NMR.

The KIEs value were found to be 1.17, 1.12, 1.17 and 1.38, 1.27, 1.38 respectively, revealing a primary kinetic deuterium isotope effect under this system.

4) Kinetic studies of alkyl transfer



1a, 1.0 equiv. 1.2 equiv. **4a** **3a**

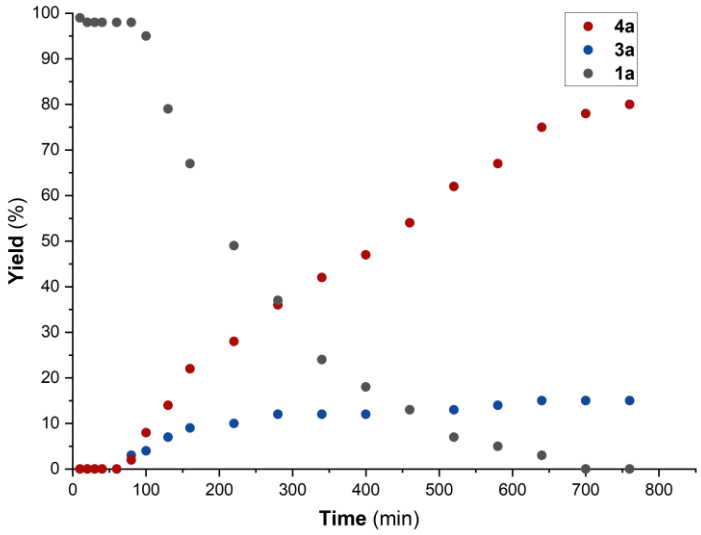
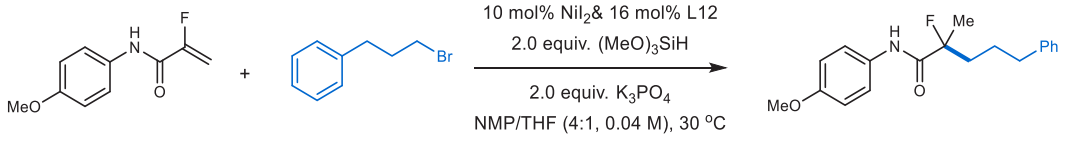


Figure S39. Time-course for HAT/alkyl coupling

Note: This reaction shows an obvious induction period (around 60 minutes at room temperature), which increased some challenges for kinetic studies. While, we managed to conduct a series of reaction process kinetic analyses using the reaction of alkene **1a** and (3-bromopropyl)benzene at room temperature.

Impact of stir rates



1a, 1.0 equiv. 1.2 equiv. **x rpm** **4a**

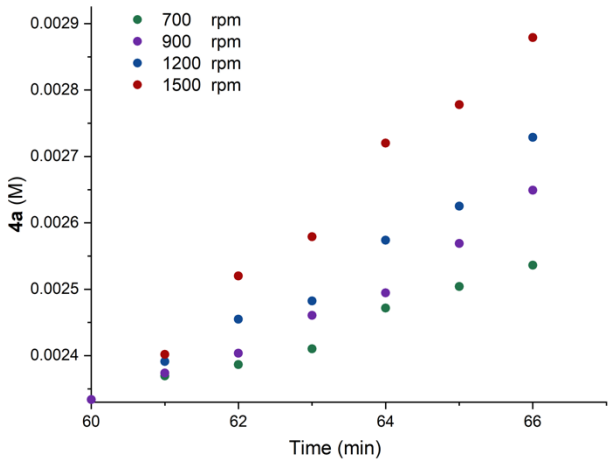
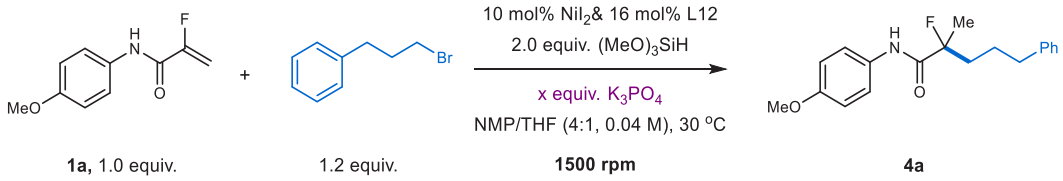


Figure S40. Rate of 4a formation at different stir rates

Comment: There is a positive-order rate dependence on stirring from 700 rpm to 1500 rpm in HAT/alkyl coupling reaction.

Excess K_3PO_4 profile



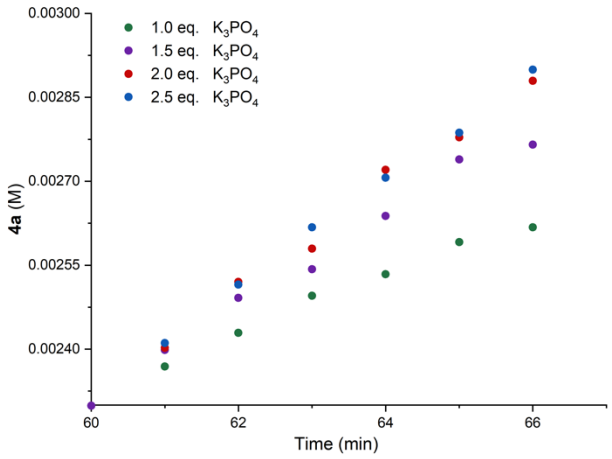
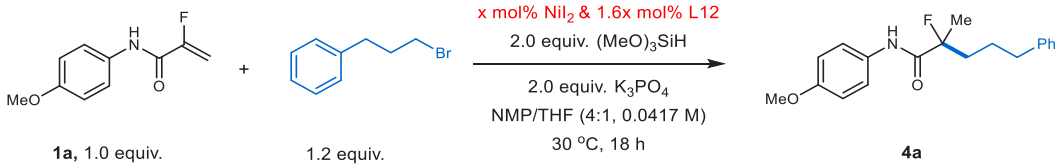


Figure S41: Rate of 2a formation with 1.0 equiv., 1.5 equiv., 2.0 equiv. and 2.5 equiv. of K_3PO_4 stirring at 1500 rpm.

Comment: There is a positive-order rate dependence on the equivalent of K_3PO_4 in HAT/alkyl coupling reaction.

According to the **General Procedure D**, using **1a**, phenylpropyl bromide, $(MeO)_3SiH$, and NiI_2 & (*S*,*S*)-**L12** in several different equivalents. Using *n*-dodecane as internal standard stir at 1500 rpm, and detected by gas chromatography. After addition of $(MeO)_3SiH$, the stopwatch was started. The aliquots of the reaction mixture (30 μL) were taken out by syringe after initiation period (60 min - 160 min) at about every 10 minutes, immediately placed to H_2O & EtOAc (0.1 mL & 1.2 mL). Then the clear solution is obtained after filtration, and the concentration of product is detected by GC.

The rate on the concentration of NiI_2 & (*S*,*S*)-L12



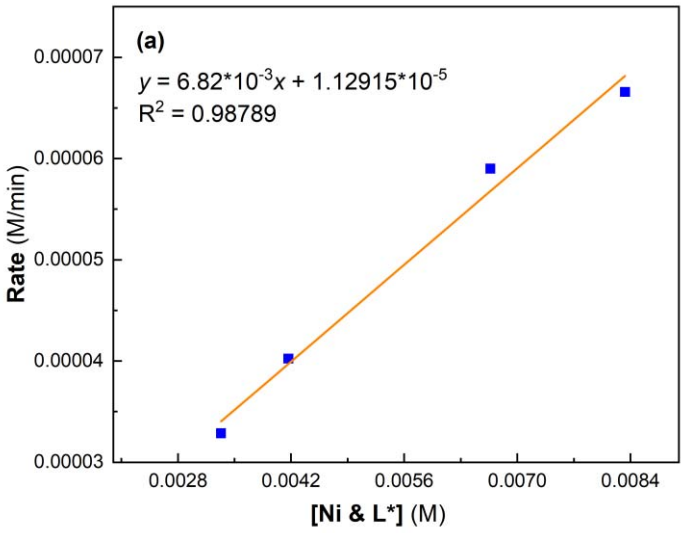


Figure S42. Rate on the concentration of NiI_2 & (*S,S*)-**L12** at 1500 rpm from the reaction of **1a** (0.0417 M), phenylpropyl bromide (0.050 M), K_3PO_4 (0.0833 M), $(MeO)_3SiH$ (0.0833 M) with 0.00333 M, 0.00417 M, 0.00667 M, 0.00833 M of NiI_2 & (*S,S*)-L12.

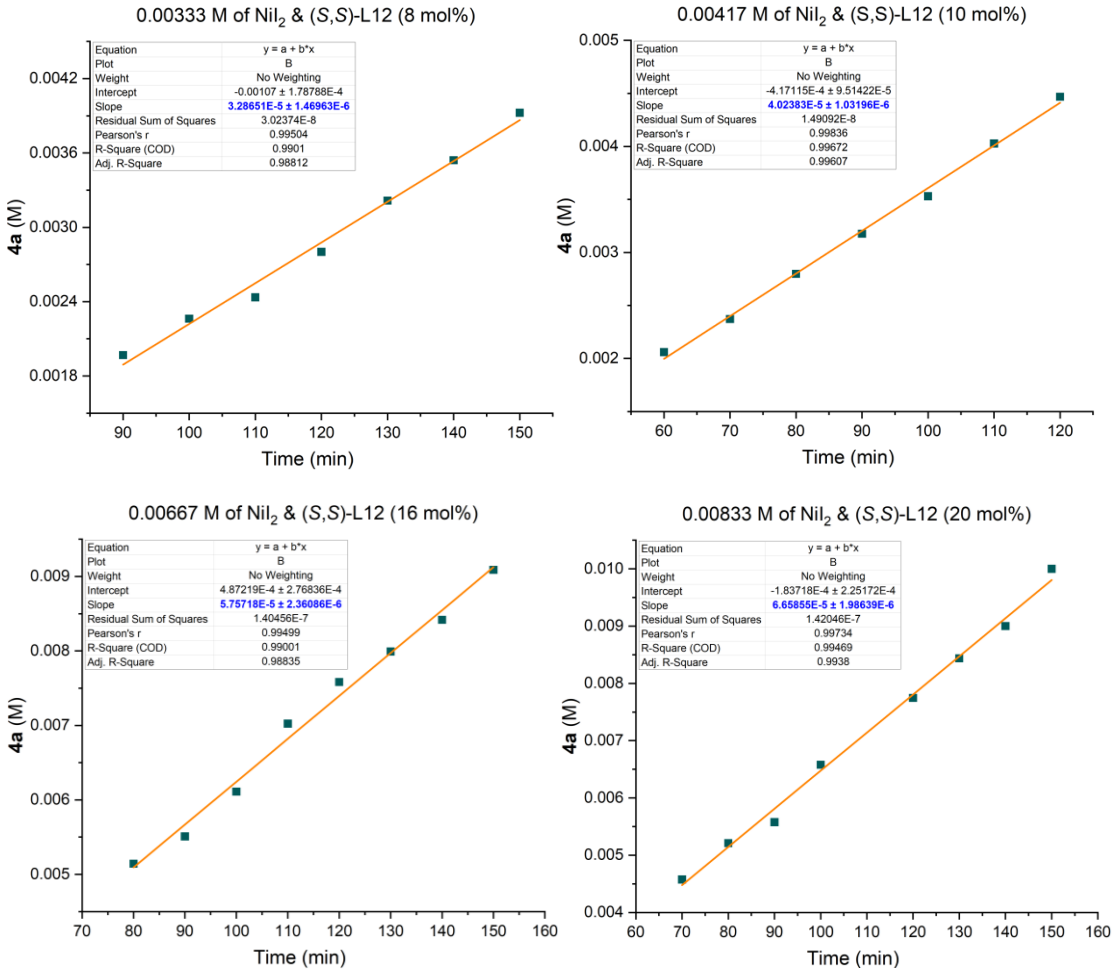
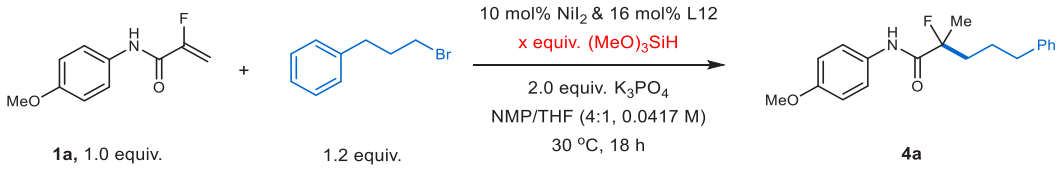


Figure S43. Plot of the rise of product from the reaction of **1a** (0.0417 M), phenylpropyl bromide (0.050 M), K_3PO_4 (0.0833 M), $(MeO)_3SiH$ (0.0833 M) with 0.00333 M, 0.00417 M, 0.00667 M, 0.00833 M of NiI_2 & (*S,S*)-L12 at 1500 rpm.

The rate on the concentration of $(MeO)_3SiH$



1a, 1.0 equiv. 1.2 equiv. **4a**

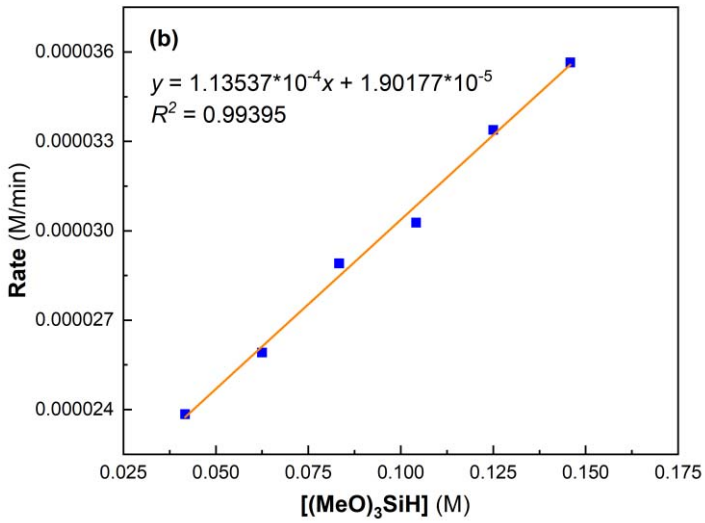
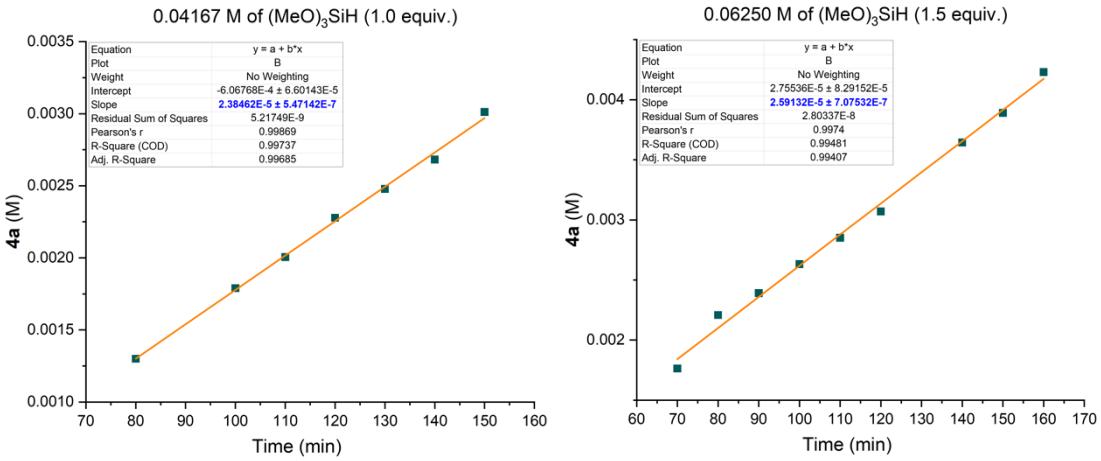


Figure S44. Rate on the concentration of $(MeO)_3SiH$ at 1500 rpm from the reaction of **1a** (0.0417 M), phenylpropyl bromide (0.050 M), NiI_2 (0.00417 M), (*S,S*)-L12 (0.00667 M), K_3PO_4 (0.0833 M) with 0.04167 M, 0.06250 M, 0.08333 M, 0.10417 M, 0.12500 M, 0.14583 M of $(MeO)_3SiH$.



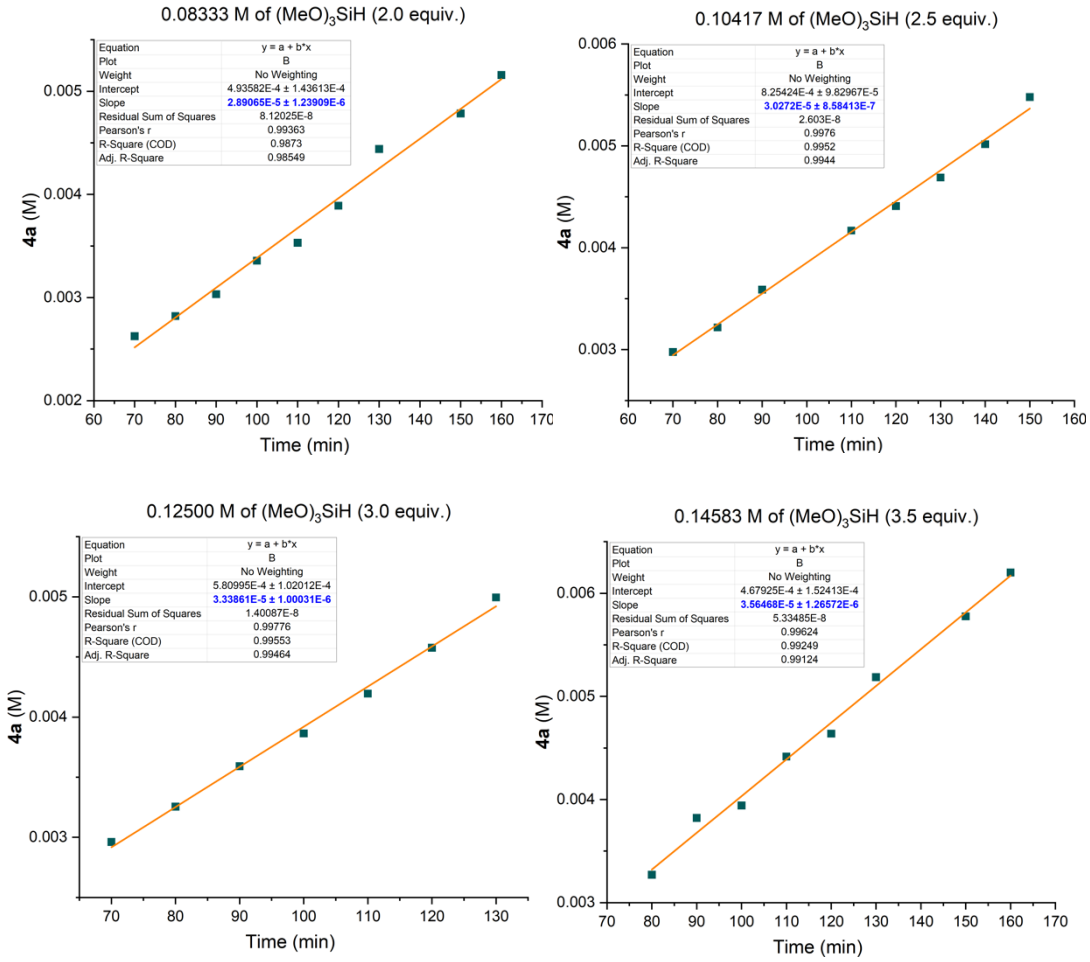
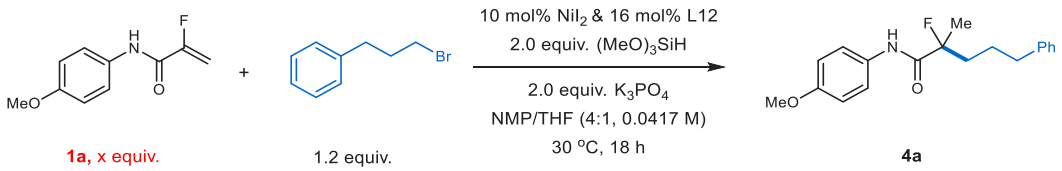


Figure S45. Plot of the rise of product from the reaction of **1a** (0.0417 M), phenylpropyl bromide (0.050 M), NiI_2 (0.00417 M), (*S,S*)-L12 (0.00667 M), K_3PO_4 (0.0833 M) with 0.04167 M, 0.06250 M, 0.08333 M, 0.10417 M, 0.12500 M, 0.14583 M of $(MeO)_3SiH$ at 1500 rpm.

The rate on the concentration of 1a



1a, x equiv. 1.2 equiv. **4a**

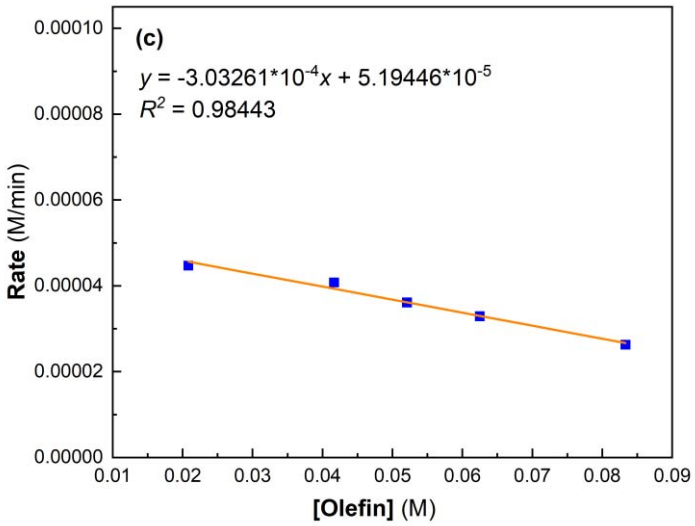
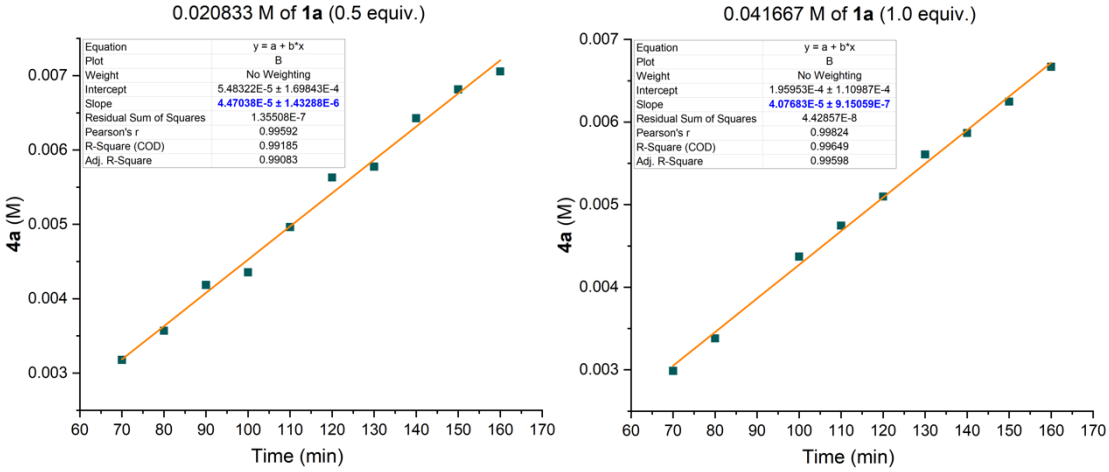


Figure S46. Rate on the concentration of **1a** at 1500 rpm from the reaction of phenylpropyl bromide (0.050 M), NiI_2 (0.00417 M), (*S,S*)-L12 (0.00667 M), K_3PO_4 (0.0833 M), $(MeO)_3SiH$ (0.0833 M) with 0.020833 M, 0.041667 M, 0.052083 M, 0.06250 M, 0.08333 M of **1a**.



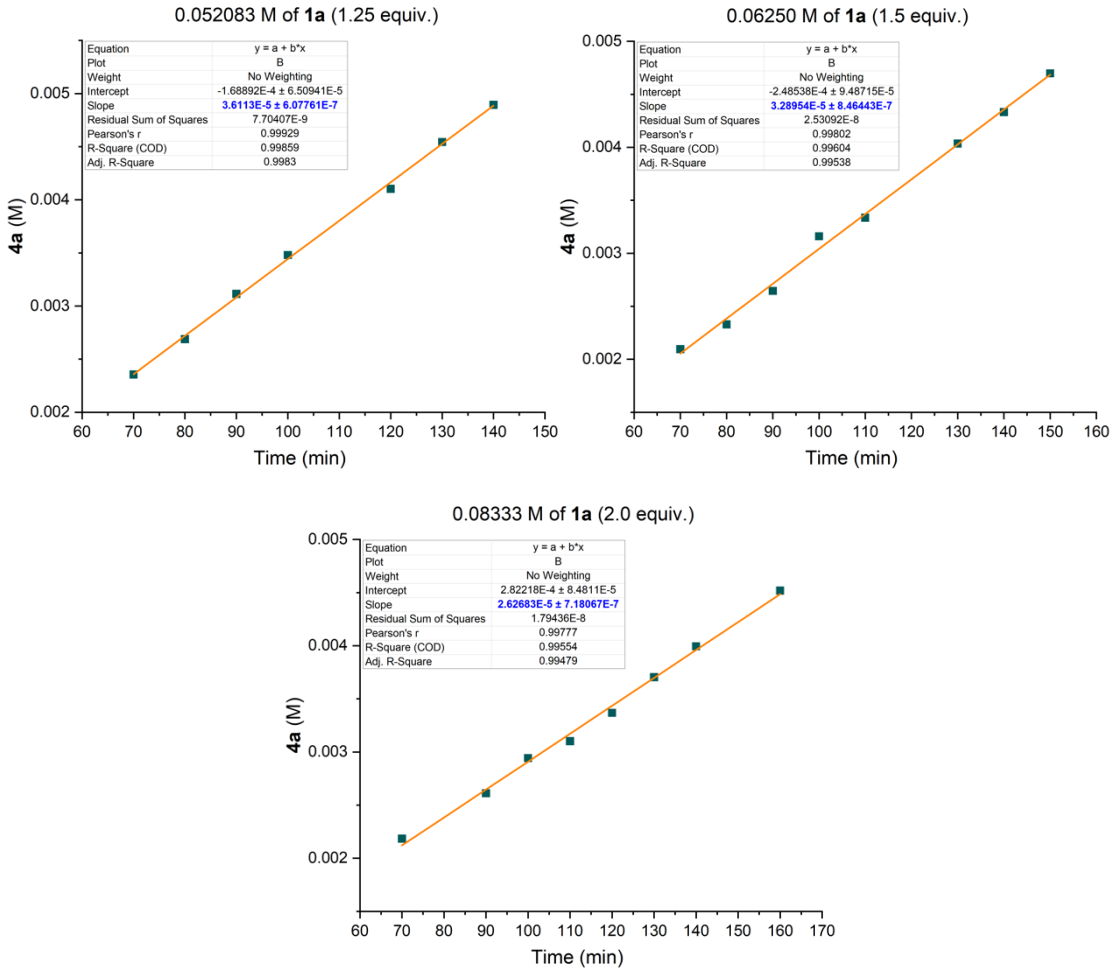
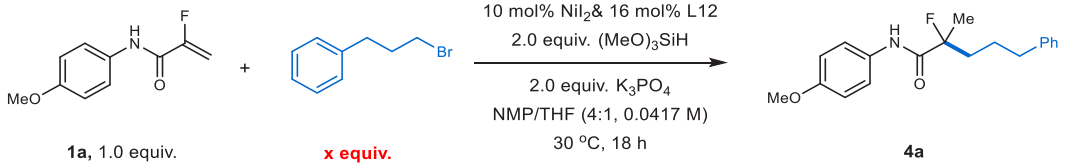


Figure S47. Plot of the rise of product from the reaction of phenylpropyl bromide (0.050 M), NiI_2 (0.00417 M), (*S,S*)-L12 (0.00667 M), K_3PO_4 (0.0833 M), $(MeO)_3SiH$ (0.0833 M) with 0.020833 M, 0.041667 M, 0.052083 M, 0.06250 M, 0.08333 M of **1a** at 1500 rpm.

The rate on the concentration of $Ph(CH_2)_3Br$



1a, 1.0 equiv. **x equiv.** **4a**

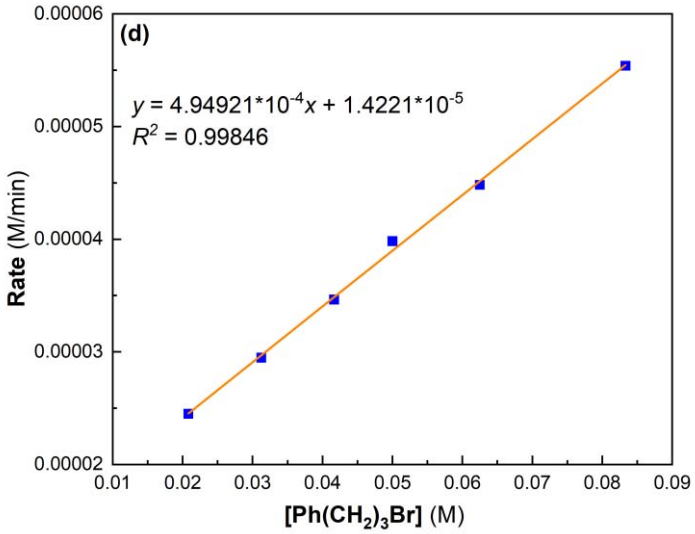
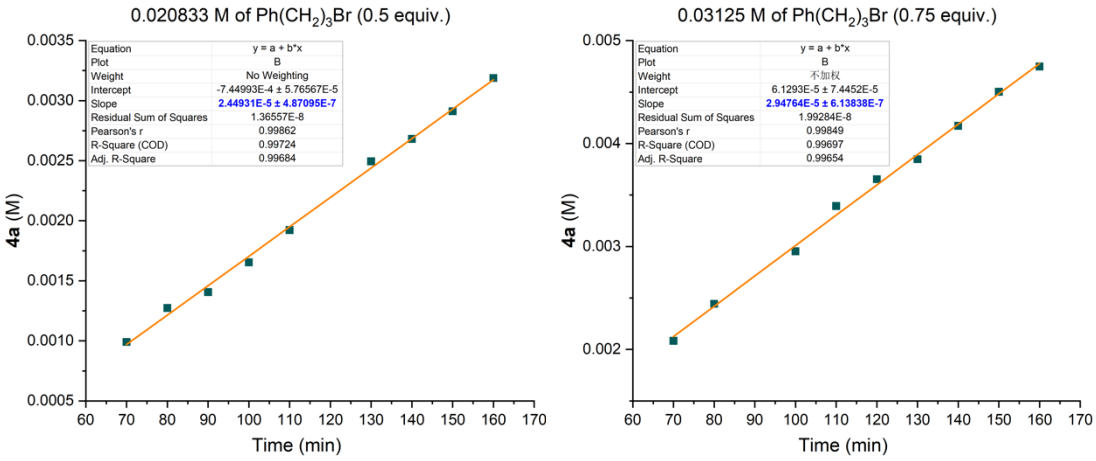


Figure S48. Rate on the concentration of **Ph(CH₂)₃Br** at 1500 rpm from the reaction of **1a** (0.0417 M), NiI_2 (0.00417 M), (*S,S*)-L12 (0.00667 M), K_3PO_4 (0.0833 M), $(MeO)_3SiH$ (0.0833 M) with 0.020833 M, 0.03125 M, 0.041667 M, 0.05000 M, 0.06250 M, 0.08333 M of **Ph(CH₂)₃Br**.



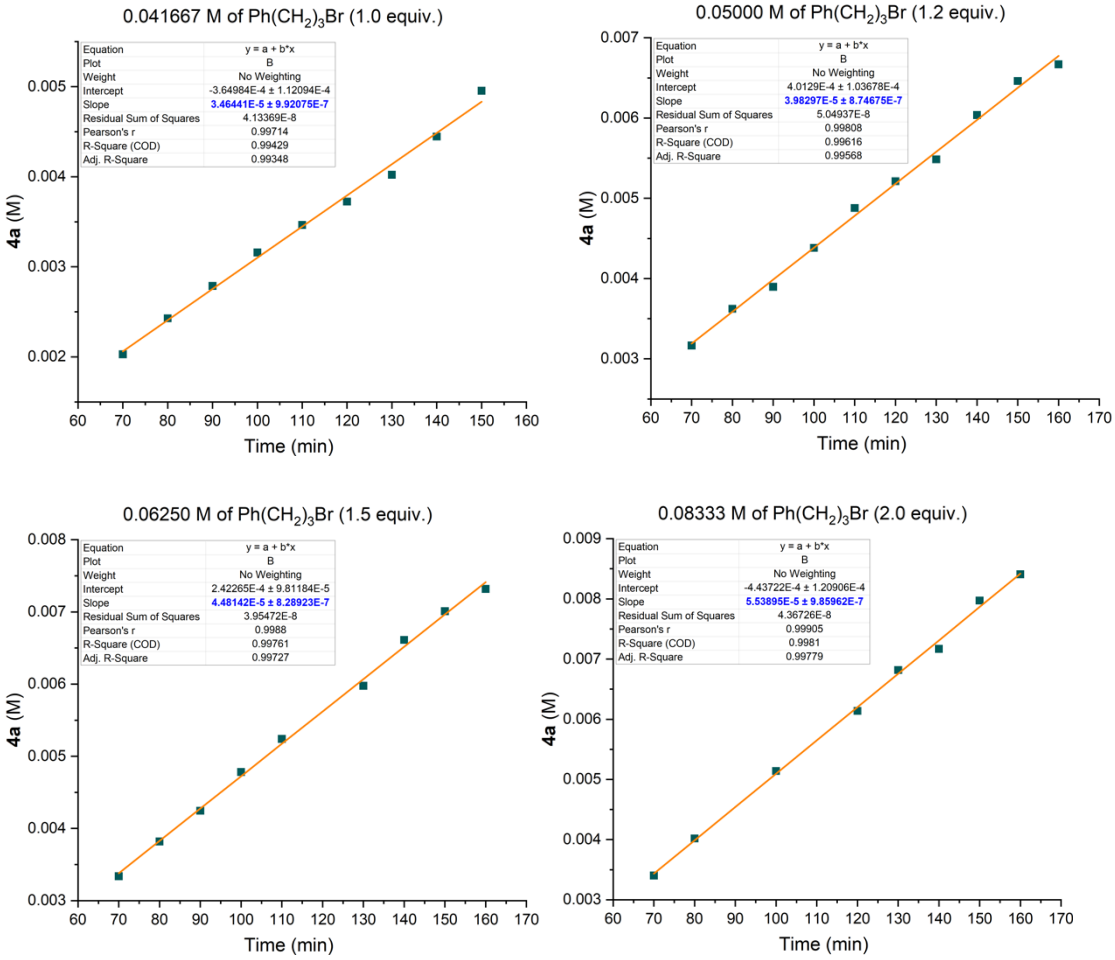


Figure S49. Plot of the rise of product from the reaction of **1a** (0.0417 M), NiI_2 (0.00417 M), (*S,S*)-L12 (0.00667 M), K_3PO_4 (0.0833 M), $(MeO)_3SiH$ (0.0833 M) with 0.020833 M, 0.03125 M, 0.041667 M, 0.05000 M, 0.06250 M, 0.08333 M of **$Ph(CH_2)_3Br$** at 1500 rpm.

Comment: This HAT/alkyl coupling reaction has a particularly evident initiation period (about 60 min), which increased the difficulty for kinetic studies. Despite all this, we conducted a series of reaction process kinetic analyses and evaluated the dependence of the average rate after the initiation period on the nickel catalyst, alkene, alkyl bromide, and silane concentrations in each case. As shown above, this model reaction exhibited a first-order dependence on the concentration of the nickel catalyst, alkyl bromide, and silane, as well as a zeroth-order dependence on the concentration of alkene. The observed anomalous kinetic data could be related to the mass transfer effect.

5) Proposed reaction pathway for HAT/alkyl coupling

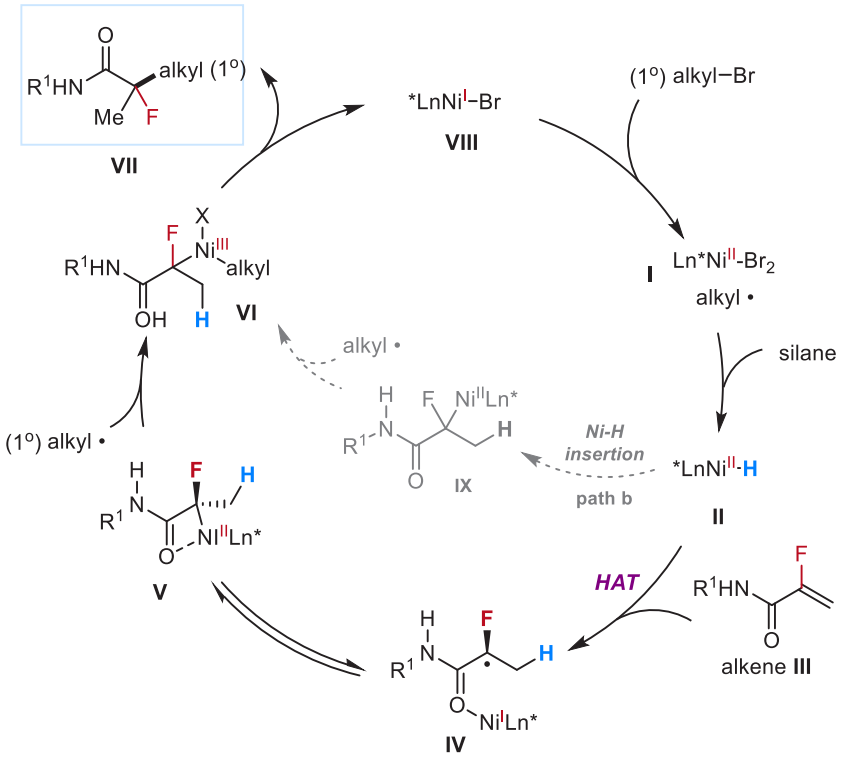


Figure S50. Proposed reaction pathway for HAT/alkyl coupling

Based on these mechanistic studies, we proposed a potential pathway for Markovnikov hydroalkylation. Oxidative addition of *LnNi^{I}-Br **VIII** with alkyl bromide gives *LnNi^{II}-Br$_2$ **I** and alkyl radical (or radical/nickel cage pair), which then reacts with silane to generate *LnNi^{II}-H **II**. Then, *LnNi^{II}-H undergoes HAT with alkenyl fluoride **III** to generate the α-F alkyl radical species **IV**, which subsequently undergoes a reversible radical capture/escape with Ni(I) assisted by the amide moiety to form Ni^{II} intermediate **V**. Then, the primary alkyl radical would directly add to Ni^{II} intermediate **V** to give the Ni^{III} species **VI**, followed by reductive elimination, to afford the product **VII** and regenerated *LnNi^{I}-Br **VIII** to close the catalytic cycle. Although the nickel hydrogen insertion pathway (path b) cannot be completely ruled out, we prefer the HAT pathway based on DFT calculations and experimental results.

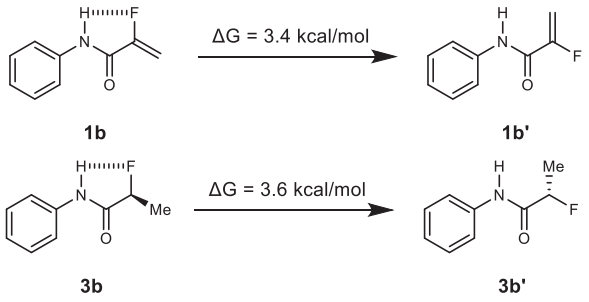
10. DFT Caculations

10.1 Computational methods

Geometry optimization at SMD (THF or DMA)/(U or R) PBE0-D3(BJ)/def2-SVP[22-26] level was carried out with *Gaussian* 09 E.01 program package,[27] with the FINE grid, unless otherwise mentioned. THF solvent was used for the asymmetric hydrogenation reaction and DMA was used for the asymmetric alkyl transfer reaction. Single point energies at SMD (THF or DMA)/(U or R) ωB97M-V/def2-TZVPP[23, 26, 28] level were calculated with ORCA 5.0.4 program package[29-30] and the default RIJCOSX approximation[31] along with the def2/J auxiliary basis set. [32]Both PBE0 and ωB97M-V functionals were appropriate to describe reactions involving open-shell transition metals.[33] T1 diagnostic values[34] of two typical transition states, **TS1** and **TS5**, were calculated at SMD (THF or DMA)/DLPNO-CCSD/def2-SVP level with ORCA 5.0.4 program package to test whether the static correlation of the system is strong or not. T1 diagnostic values of **TS1** and **TS5** were 0.01354 and 0.01064, respectively, verifying a modest static correlation. Spin density analysis was obtained with Multiwfn 3.8(dev),[35] and visualized with VMD 1.9.3.[36] Natural bond orbital analysis was performed with the NBO 3.1 built in Gaussian.[37] Other 3D structures were generated with CYLview 20.[38]

10.2 DFT studies of asymmetric hydrogenation reaction

To simplify calculations, (*S*,*S*)-**L4** (with ^{i}Pr side chain) was used as the ligand instead of the optimal ligand, (*S*,*S*)-**L1** (with ^{s}Bu side chain) in experiments, throughout the calculations. **1b** (Ar = Ph) was used as the model substrate. The amide hydrogen forms a hydrogen bonding with the adjacent fluorine atom and the Δ*G* values between corresponding conformers (with or without hydrogen bond) are 3-4 kcal/mol (see below).



1b **1b'**

3b **3b'**

10.2.1 Discussion of the coordination environment of Ni center

All Pybox-Ni(II)-Ln species involved are at their triplet states which are lower in energies than their singlet states. For those intermediates and transition states in asymmetric alkyl transfer reaction (in SI 10.3), in which PPh_3 ligand is present as well, their spin multiplicities are given in superscript.

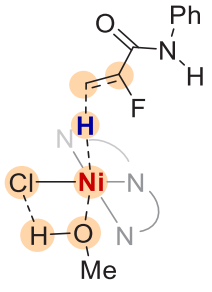
Coordination of a MeOH molecule to the penta-coordinated Ni center has been tested for all intermediates. **TS1-M** is higher in free energy than **TS1** under standard conditions (298 K, 1 M), but slightly lower when concentration correction of MeOH with c = 0.12 M is considered. By using the van't Hoff equation $\Delta G_{corr} = -RT\ln(c/c_0)$, where c_0 = 0.04 M (concentration of ideal gas under 1 atm), the free energy correction was determined to be +0.64 kcal/mol. Since excess alcohol was used experimentally, the ΔG_{corr} does not change greatly during the reaction. It is important to mention that MeOH coordination to all other species are endergonic (except **TS1-M**). Coordination of a NMP solvent molecule has been evaluated for intermediates and transition states as well, but all of them are disfavored, with slightly higher Gibbs free energies (these are not changed even when concentration correction is considered).

10.2.2 Discussion of basis sets used in the calculations

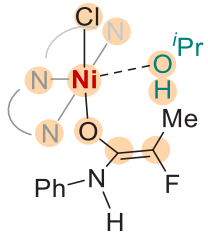
We initially calculated the reaction mechanism at (U)ωB97M-V/def2-TZVPP/SMD(THF)//(U)PBE0-D3(BJ)/def2-SVP/SMD(THF) level. However, during the investigation, we found the size of basis sets affects the geometries of studied species, especially the Ni-alcohol coordinate bond. To reduce possible basis set superposition error (BSSE) introduced by double-zeta basis set of def2-SVP, and to obtain a more accurate activation free energy for the HAT process and its competitive pathways, the free energies of **Int1**, **Int1-M**, **SI-Int1**, **TS1**, **TS1-M**, **SI-TS1'**, **SI-TS1'-M, TS-MI** and **TS-CA** were optimized at (U)PBE0-D3(BJ)/def2-SVP(def2-TZVPP)/SMD(THF), where def2-TZVPP were used for Ni, Cl, H (the transferring hydrogen and the proton of MeOH), O (of MeOH) and C (of C-C double bond in **1b**) atoms while def2-SVP was used for others. Single point energies were still calculated at (U)ωB97M-V/def2-TZVPP/SMD(THF) level (Figure S51). We were pleased to find that, the values of activation free energy using bigger basis set in optimization are close to the experimentally measured one.

For the same reason, the stereo-determining transition states **TS4** and **TS4'** were also refined with bigger mixed basis sets and a more realistic model (using ^{i}PrOH instead of MeOH) as **TS4-^{i}PrOH** and **TS4' -^{i}PrOH**. This resulted in slightly shorter Ni-O (of *i*-PrOH) distance and better accordance with experimental e.e. values.

Therefore, using such mixed basis sets of def2-TZVPP and def2-SVP achieving a better tradeoff of computational time and calculation accuracy is recommended in the two crucial steps. Other structures in this paper were all optimized at def2-SVP basis sets unless otherwise mentioned.



TS1-M



TS4-^{i}PrOH

Figure S51. TS1-M and **TS4-^{i}PrOH** are used as examples to illustrate the mix basis set used: def2-TZVPP basis sets are used for the orange atoms; def2-SVP basis sets are used for other atoms in this structure.

10.2.3 More information for reaction pathway of asymmetric hydrogenation

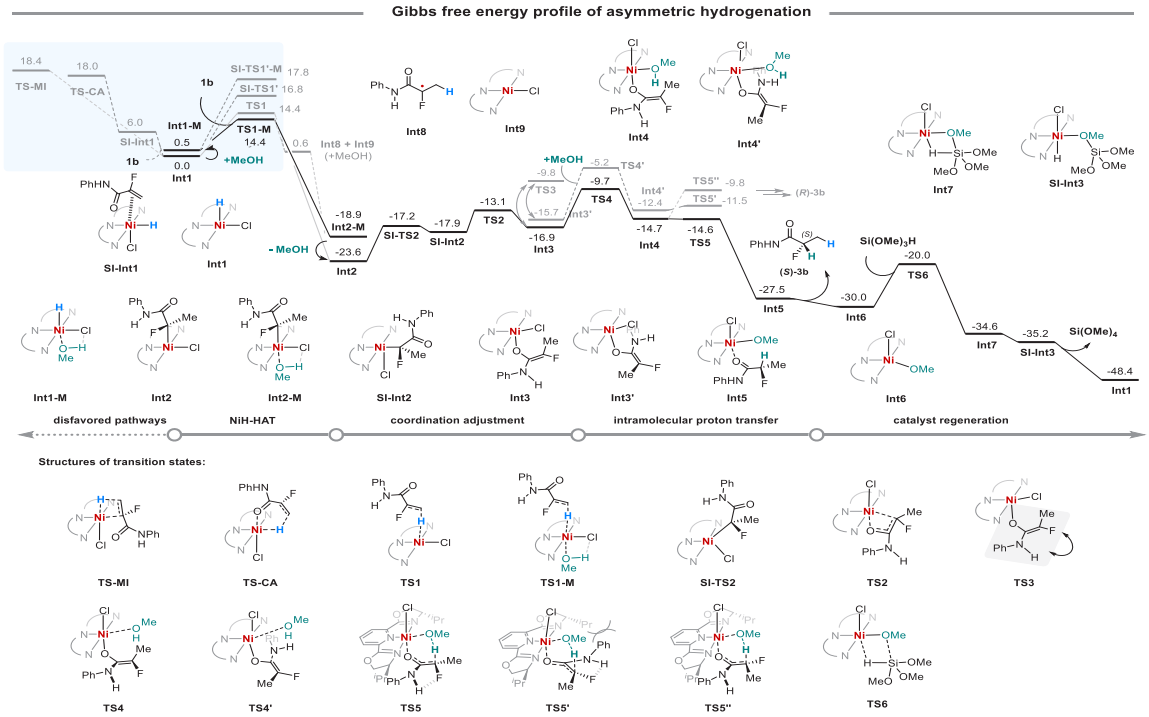


Figure S52. Gibbs free energy profile of asymmetric hydrogenation computed at (U)ωB97M-V/def2-TZVPP/SMD(THF)//(U)PBE0-D3(BJ)/def2-SVP/SMD(THF) except for the blue part. For the blue part, mixed basis sets def2-SVP/def2-TZVPP are used, as described above. Concentration correction of methanol is considered for **Int1-M** and **TS1-M** and **SI-TS1'-M**.

a. Hydrogen atom transfer and recombination

The catalytic cycle starts from **Int1** or its MeOH complex **Int1-M** (the latter is higher in free energy by 1.1 kcal/mol under standard conditions than the former). When concentration correction is considered, this value (ΔG_{rel}) is 0.5 kcal/mol. Both transition states of HAT process and hydrometallation processes (including migrative insertion and 1,4-conjugate addition of Ni-H) were located (we had searched for all possible

conformations related in these processes), and then computed at (U)ωB97M-V/def2-TZVPP/SMD(THF)//(U)PBE0-D3(BJ)/def2-SVP(def2-TZVPP)/SMD(THF) level. Their activation energies with respect to **Int1** were listed below. The activation free energy of **TS1** at (U)ωB97M-V/def2-TZVPP/SMD(THF)//(U)PBE0-D3(BJ)/def2-SVP/SMD(THF) level is 13.3 kcal/mol.

Structures of **TS1-M** and **SI-TS1'-M**, both of which have MeOH coordination, greatly resembles their analogues, **TS1** and **SI-TS1'**. Transition states **SI-TS1'** and **SI-TS1'-M** generating the opposite *C*-chirality at the α-carbon are higher in terms of activation free energies than **TS1** and **TS1-M**, respectively.

Table S34. Computed activation energies of HAT and hydrometallation transition states.

Transition state	activation energy $\Delta G^{\ddagger}$ (kcal/mol)	note
TS1	14.45	/
TS1-M	14.36	after concentration correction
SI-TS1'	16.76	/
SI-TS1'-M	17.78	after concentration correction
TS-CA	17.99	1,4- conjugate addition TS
TS-MI	18.35	migratory insertion TS

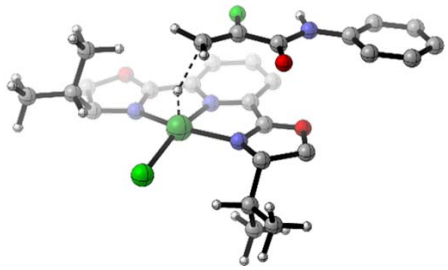
The structures of the above-mentioned transition states are shown below. The NPA spin and charge population of the transferring H and α-carbon are also given. Spin density isosurfaces of **TS1**, **TS1-M**, **TS-CA** and **TS-MI** are shown by isosurfaces (isovalue = 0.0055). NPA spins of the α-carbon of **TS1**, **TS1-M** and **SI-TS1'** are much larger than that in **Int2**. The transferring H shows relatively larger NPA spin. The above results strongly supported that these processes involving **TS1**, **TS1-M** and **SI-TS1'** are HAT processes.

Predicted KIE values of **TS1** (k_H/k_D = 1.49) and **TS1-M** (k_H/k_D = 1.53) for Ni-H were obtained by the following procedure. **TS1**, **TS1-M** and **Int1** were optimized at the

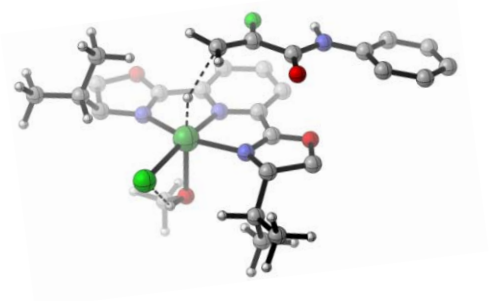
described level but with “int=ultrafine” keyword to upgrade the quality of DFT calculations, followed by frequency analyses. Then the transferring hydrogen was set as D by using “ISO=2” keyword, followed by second frequency analyses. The difference between the TCGs (thermal free energy correction) was converted to KIE value with Eyring’s equation as below.

$$\mathrm{KIE} = {}^{k_H}\!/_{k_D} = \exp\left\{\frac{[\mathrm{TCG(Int1\text{-}H)\text{-}TCG(TS1\text{-}H)}]\text{-}[\mathrm{TCG(Int1\text{-}D)\text{-}TCG(TS1\text{-}D)}]\times 627.51\times 4184}{\mathrm{RT}}\right\}$$

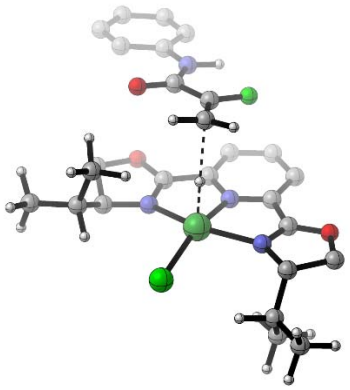
Similarly, the predicted KIE of **TS1-M** (k_H/k_D = 0.90) for methanol was obtained by comparing TCGs of **TS1-M** and methanol-NMP complex (we assumed the solvated methanol forms a hydrogen bond with NMP). We reason this inverse KIE may originate from different hydrogen bonding mode between solvated methanol and the methanol ligated to Ni center in **TS1-M**.



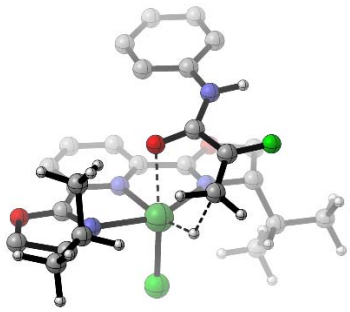
TS1
NPA charge of H: -0.156
NPA spin of H: 0.091
NPA charge of C: 0.135
NPA spin of C: 0.106



TS1-M
NPA charge of H: -0.200
NPA spin of H: 0.073
NPA charge of C: 0.128
NPA spin of C: 0.090



SI-TS1’



TS-CA
NPA charge of H: -0.252

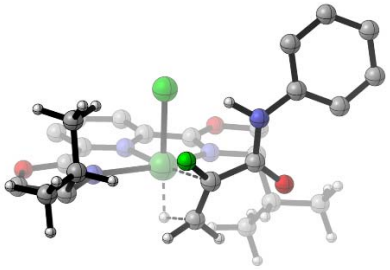
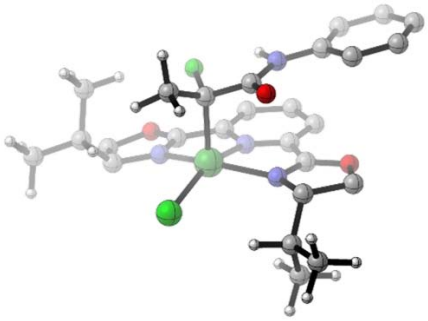
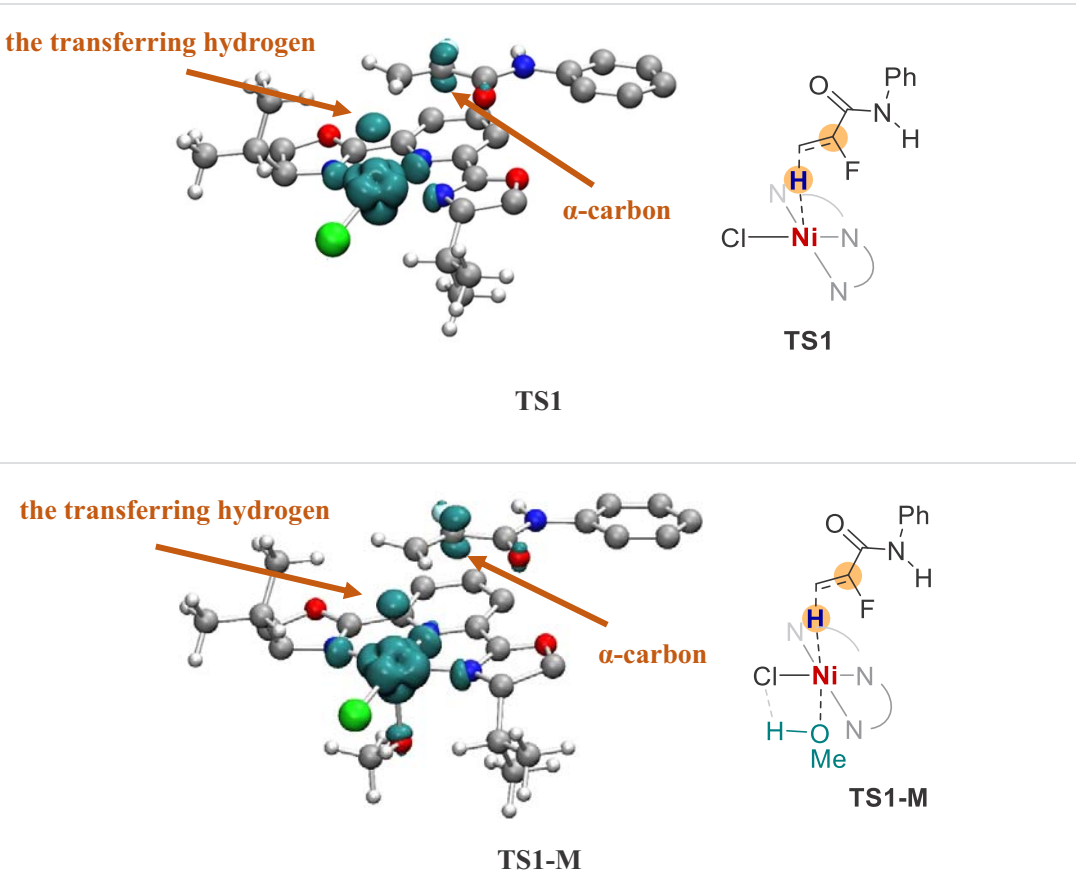
NPA charge of H: -0.148 NPA spin of H: 0.086 NPA charge of C: 0.133 NPA spin of C: 0.108	NPA spin of H: 0.038 NPA charge of C: 0.095 NPA spin of C: 0.080
 **TS-MI** NPA charge of H: -0.118 NPA spin of H: 0.100 NPA charge of C: 0.136 NPA spin of C: 0.211	 **Int2** NPA charge of C: 0.001 NPA spin of C: 0.099

Figure S53. 3D structures, NPA spins and NPA charges of above-mentioned transition states and **Int2**.



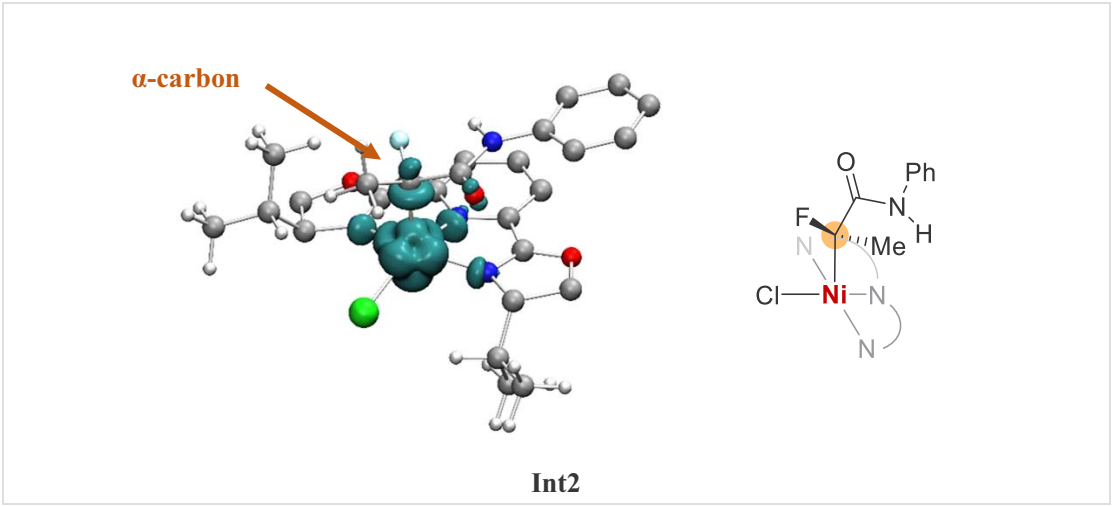


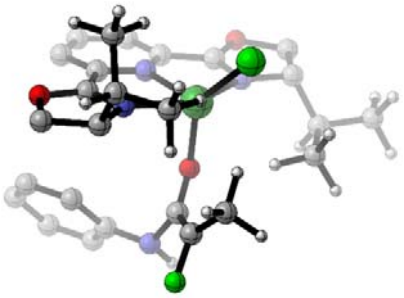
Figure S54. spin density isosurfaces of **TS1**, **TS1-M** and **Int2**.

After HAT processes, the Ni(I) species **Int9** and radical **Int8** can either dissociate from the solvent cage or enter the solvent cage. Distinct from previous DFT studies in MH-HAT, the recombination here is highly exergonic (downhill by 19.4 kcal/mol from **Int1-M** to **Int2-M**) as an irreversible step.

b. Coordination adjustment

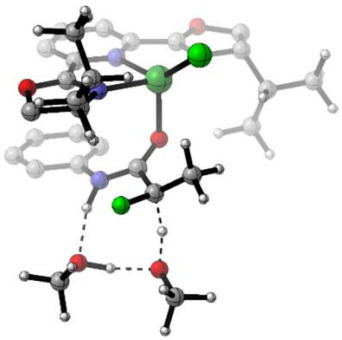
To undergo protonation of the α-carbon, alkylnickel complex **Int2** has to isomerize to nickel enolate **Int3**, with a computed activation free energy of 10.5 kcal/mol. The coordination mode first shifts from **Int2** to **SI-Int2** via a trigonal bipyramid transition state **SI-TS2**. The alkylnickel complex **SI-Int2** can then isomerize to nickel enolate **Int3** via a η^3-enolate transition state **TS2**. It is possible that **Int2** first undergoes Ni-C homolysis, followed by radical combination. But we found that the Ni-C homolysis requiring an activation free energy of 26.6 kcal/mol, which is disfavored compared to the isomerization of **Int2** to **Int3**.

Int3 can further isomerize to a less stable isomer **Int3'** via **TS3**. So far, the C(sp^3)-chirality at the α-carbon generated by the asymmetric NiH-HAT is lost.



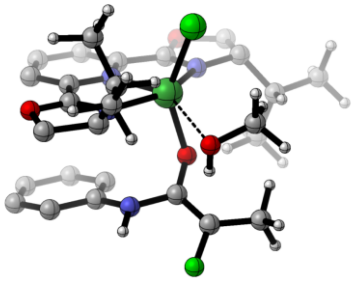
TS3

isomerization transition state between **Int3** and **Int3'**



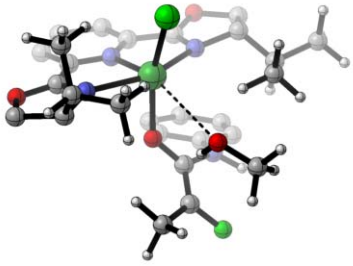
TS5-O

outer-sphere proton transfer transition state with two MeOH molecules



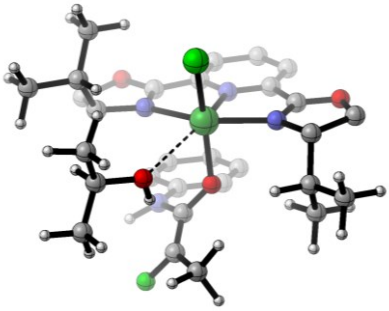
TS4

Ni-O (of MeOH) distance: 3.25 Å



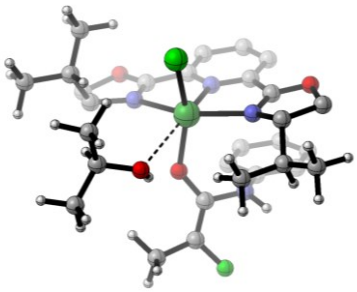
TS4'

Ni-O (of MeOH) distance: 3.63 Å



TS4-^{i}PrOH

Ni-O (of ^{i}PrOH) distance: 3.10 Å



TS4' -^{i}PrOH

Ni-O (of ^{i}PrOH) distance: 2.97 Å

Figure S55. 3D structure of **TS3**, **TS5-O**, **TS4, TS4', TS4-^{i}PrOH** and **TS4' -^{i}PrOH**.

c. Alcohol coordination (the stereo-determining step) and intramolecular proton transfer

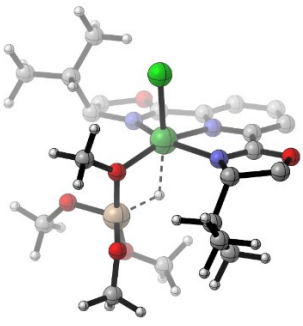
Both intermolecular and intramolecular proton transfer processes have been evaluated. The intermolecular pathway requires an outer-sphere MeOH molecule to deliver its proton to the α-carbon. To compute this process, another MeOH molecule is

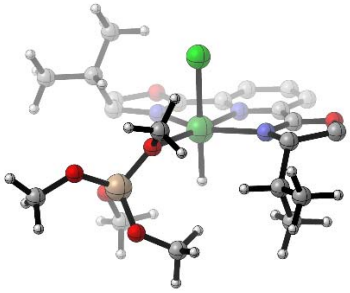
needed to stabilized the newly generated MeO^- anion. Otherwise the transition state cannot be located. This transition state **TS5-O** requires a much higher activation energy (19.1 kcal/mol with respect to **Int3**) compared to the intramolecular pathway with an activation free energy of 7.2 kcal/mol (see discussion below).

The intramolecular pathway first involves a MeOH coordination towards Ni. This step is found to be the stereoselectivity-determining step for the reaction. Starting from **Int3**, methanol coordination transition state **TS4** requires an activation energy of 7.2 kcal/mol. The less favored transition state **TS4'** (starting from **Int3'**) is higher in free energy than **TS4'** by 4.5 kcal/mol. Refinement with bigger mixed basis sets and a more realistic model (^{i}PrOH instead of MeOH) derived **TS4-^{i}PrOH** and **TS4'-^{i}PrOH**. The change in basis sets and model resulted in different conformations and shorter Ni-O distances. The $\Delta\Delta G^{\ddagger}$ between **TS4-^{i}PrOH** and **TS4'-^{i}PrOH** is 1.0 kcal/mol. We propose that the steric repulsion between the enol moiety and the ^{i}Pr side chain of Pybox ligand controls the stereoselectivity.

d. Formal σ-bond metathesis of Int6 with silane

Similar to the reported DFT studies in literature[39], the formal σ-bond metathesis of **Int6** with silane is feasible with a barrier of 10.0 kcal/mol. Intrinsic reaction coordinate (IRC) calculation of **TS6** showed that this transition state is directly connected to **Int7**, in which a weak Si-H bond still exists. The follow-up cleavage of the Si-H bond is found barrierless and nearly neutral in terms of thermodynamics (ΔG = -0.6 kcal/mol), resulting in **SI-Int3**. Exergonic dissociation of $Si(OMe)_4$ affords in **Int1** for the next catalytic cycle.





Int7	**SI-Int3**
d(Ni-H) = 1.864 Å	*d*(Ni-H) = 1.694 Å
d(Si-H) = 1.573 Å	*d*(Si-H) = 3.182 Å

Figure S56. 3D structure of **Int7** and **SI-Int3**.

10.2.4 Discussion of possible chloride/methoxy exchange on Ni center

We have also studied the anionic ligand effect of the Ni center. In our above-mentioned calculations, chloride from the precatalyst is kept during the catalytic cycle. However, one may speculate that methoxy anion from excess methanol can also acts as the ligand instead of the chloride anion (unfortunately, it is difficult to use experiments to support/disprove this hypothesis).

We computed the corresponding HAT processes in this speculative case to test whether such a case is possible or not. The barrier in this case is almost the same as that using chloride anion, but the predicted KIE for Ni-H/Ni-D was found to be 0.84, inconsistent with our experimental KIE for silane (1.40). These computational findings do not support the existence of methoxy-Nickel catalytic cycle. We hypothesized that the MeO^- anion, once generated, would be captured by excess $Si(OMe)_3H$ forming $[Si(OMe)_4H]^-$,[40] thus chloride/methoxy exchange on Ni center may be kinetically slow.

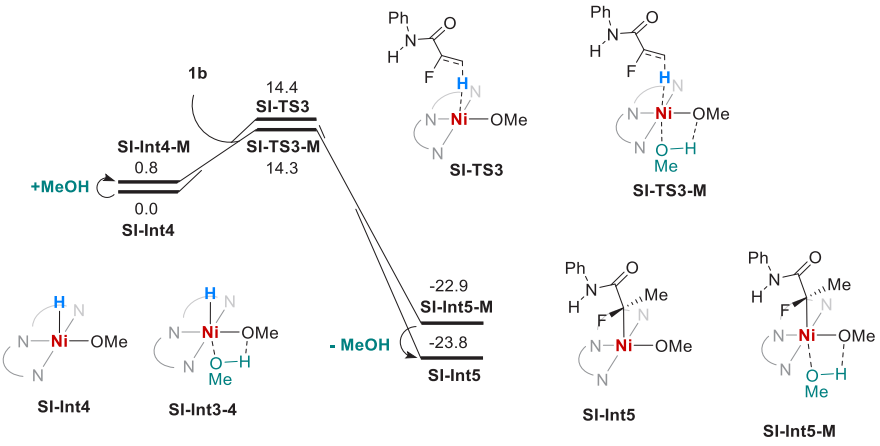


Figure S57. Gibbs free energy profile of asymmetric hydrogenation where methoxy is the anionic ligand instead of Cl. Free energies are computed at (U)ωB97M-V/def2-TZVPP/SMD(THF)//(U)PBE0-D3(BJ)/def2-SVP(def2-TZVPP)/SMD(THF) level. **L4** and **MeOH** are used in computations for simplification. Concentration correction of

methanol is considered for **SI-Int4-M** and **SI-TS3-M.**

10.3 DFT studies of asymmetric alkyl transfer reaction.

We proposed two catalytic cycles for the asymmetric alkyl transfer reaction, namely the Ni(1/2/3) cycle and Ni(0/1/2) cycles. In this section, we discuss why the latter one is favored. Experimentally, DMA/THF was used as a mixed solvent for this reaction. Due to existence of the ionic intermediates and transition states of the Ni(1/2/3) cycle, we chose DMA, which is more polar than THF, as the solvent for calculations. The stereo-determining transition states **TS7** and **TS7'** were also refined to be **TS7-^{i}PrOH** and **TS7'-^{i}PrOH** with bigger mixed basis sets and a more realistic model (^{i}PrOH instead of MeOH), which was the same treatment as **TS4-^{i}PrOH** and **TS4'-^{i}PrOH**.

10.3.1 Asymmetric alkyl transfer reaction via Ni(1/2/3) catalytic cycle

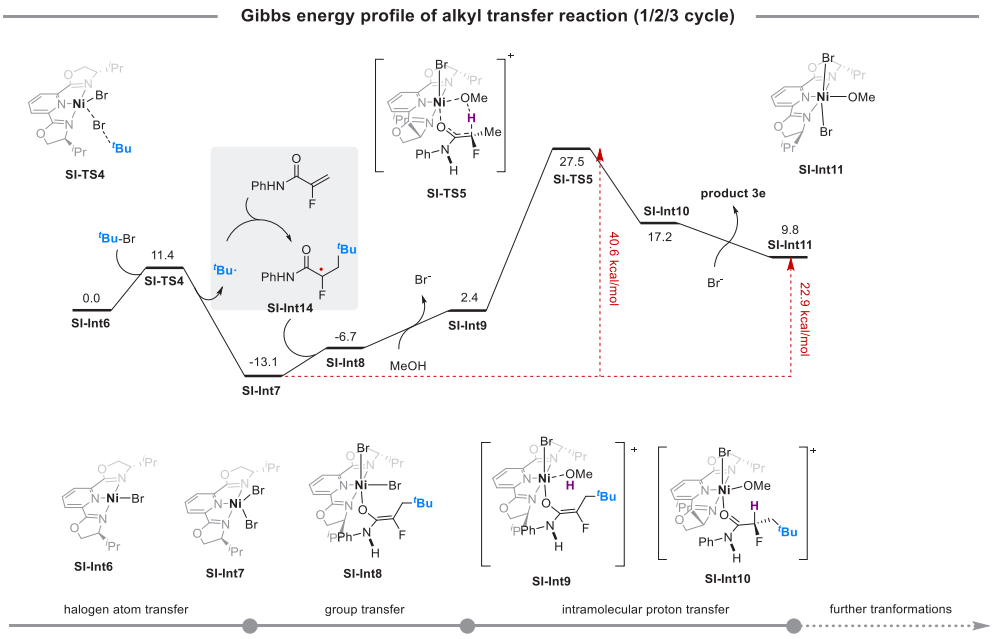


Figure S58. Gibbs free energy profile of asymmetric alkyl transfer reaction via Ni(1/2/3) catalytic cycle.

As shown above, the reaction starts with Pybox-Ni(I)-Br species **SI-Int6**, which can undergo a Br atom abstraction with ^{t}BuBr to afford Ni(II) species **SI-Int7**. The radical capture of **SI-Int7** with α-carbonyl radical **SI-Int14** is endergonic by 6.4

kcal/mol, forming **SI-Int8**. The six-coordinated Ni center has to undergo a ligand exchange, from a Br anion to a neutral MeOH, forming a cationic Ni(III) intermediate **SI-Int9**. The activation free energy of the subsequent intramolecular proton transfer, however, is exceptionally high (25.1 kcal/mol). For comparison, **Int4→TS5** is almost barrierless. This may be caused by the difference in electronic structure (triplet Ni(II) in **Int4** vs doublet Ni(III) in **SI-Int9**) as well as the charge separation. The overall barrier is 40.6 kcal/mol, which is too high to take place for a room temperature reaction. We therefore can conclude such a cycle is impossible.

The effect of the zinc salt additive (in certain experimental conditions) on the Ni(1/2/3) pathway is further investigated. Although the overall activation free energy barrier is reduced to 27.2 kcal/mol (from 40.6 kcal/mol), by the coordination of $ZnBr_2$ to the dissociated Br anion, such barrier is still too high for a reaction that take place at room temperature. Moreover, the zinc salt was not a required reagent for this reaction, suggesting that the zinc-assisted pathway can be excluded for consideration.

$$ZnBr_2(DMA)_2 + Br^- \rightarrow ZnBr_3(DMA)^- + DMA$$

In addition, the net free energy change (ΔG) of the Ni(III)-centered protonation, from **SI-Int7** to **Int11,** is endergonic by 22.9 kcal/mol, which is unfavored thermodynamically. In contrast, ΔG from **SI-Int16** to **SI-Int17** in Ni(0/1/2) catalytic cycle (discussed below) is exergonic by 7.7 kcal/mol (it is also exergonic by 7.7 kcal/mol in the asymmetric hydrogenation reaction, from **Int3** to **Int5**, involving Ni(II) as well). In conclusion, we suggest that such protonation of Ni(II)-enolates is feasible, but it is difficult for Ni(III)-enolates.

Based on these, we proposed that the following Ni(0/1/2) catalytic cycle is the favored one.

10.3.2 Asymmetric alkyl transfer reaction via Ni(0/1/2) catalytic cycle

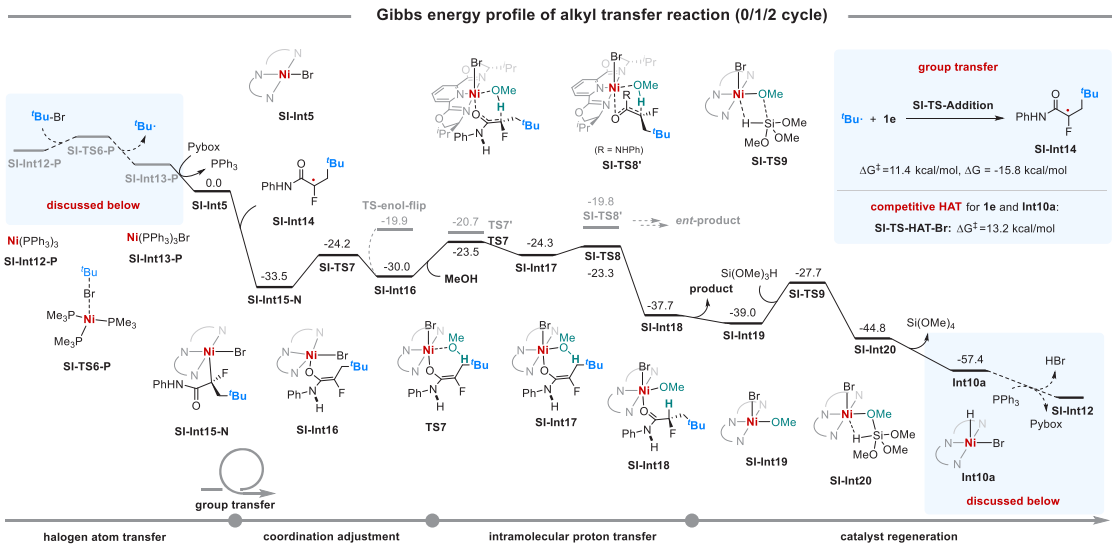


Figure S59. Gibbs free energy profile of asymmetric alkyl transfer reaction via Ni(0/1/2) catalytic cycle.

a) Ligand exchange and reaction initiation

According to our previous studies,[41] phosphine/pyridine-based ligand exchange on Ni center is feasible under room temperature. Our computational results showed that both **SI-Int12** and **SI-Int13** (namely Ni(0) and Ni(I) species) can be coordinated either by PPh_3 (forming **SI-Int12-P** and **SI-Int13-P**, respectively), or by Pybox ligated (forming **SI-Int12-N** and **SI-Int13-N**, respectively). The PPh_3 ligand is more favored than Pybox thermodynamically. In contrast, **SI-Int15-21** (namely all Ni(II) species) have the opposite trend, favoring coordination of Pybox **L4** rather than PPh_3.

The asymmetric alkyl transfer reaction starts with the Br abstraction of ^{t}BuBr with Ni(0) species $Ni(PPh_3)_3$ **SI-Int12-P**.[42] This step is supposed to be easy (unfortunately, we could not locate the transition state because the model, which includes three PPh_3 ligands, exceeded the our computing power). A similar transition state has been reported previously,[43] demonstrating its activation energy is very low (detailed experimental results are also included in the article).

After a reverting phosphine-to-Pybox ligand exchange (**SI-Int13P→SI-Int13N**) and recombination of **SI-Int13N** with α-carbonyl radical **SI-Int14**, intermediate **SI-Int15** is formed, which is the most stable conformer located by us.

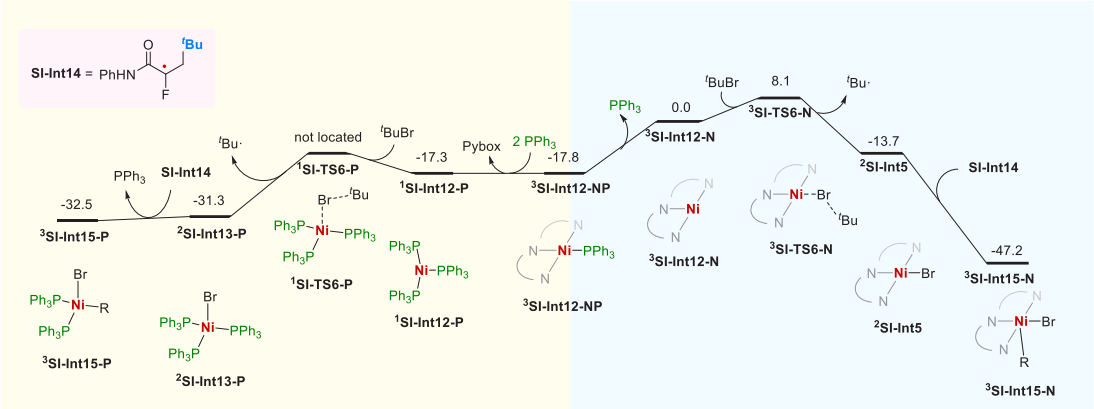


Figure S60. Relative Gibbs free energy profile of ligand exchange and reaction initiation computed at (U)ωB97M-V/def2-TZVPP/SMD(DMA)//(U)PBE0-D3(BJ)/def2-SVP/SMD(DMA) level.

b) Similar reaction processes to the asymmetric hydrogenation

The present reaction of asymmetric alkyl transfer reaction also includes coordination shift (from alkyl-nickel(II) complex to nickel(II)-enolate), alcohol coordination, intramolecular proton transfer and formal σ-bond metathesis. All these steps are easy, similar to the HAT-mediated hydrogenation reaction.

In fact, the divergence between the two reactions lies in the follow-up pathways of Pybox-Ni(II)XH species (X=Cl or Br), depending on whether PPh_3 is added to the reaction. It should be noted that Pybox-Ni(II)BrH (**SI-Int10a**) does have the potential for NiH HAT process with alkenes, generating hydrogenation product **3b** as a minor byproduct observed in experiments. In fact, the activation energy of 13.2 kcal/mol via NiH HAT transition state **SI-TS-HAT-Br** is very close to that of 13.3 kcal/mol via **TS1**. However, PPh_3 was found experimentally to suppress the production of hydrogenation product (see the experimental part), suggesting that the HBr elimination process, assisted by PPh_3, should be even easier to occur energetically than NiH HAT. Details are discussed below.

c) HBr elimination and regeneration of Ni(0)

Mechanism of HBr elimination forming Ni(0) species was studied. Direct reductive elimination of **SI-Int21** requires a high activation free energy (> 30 kcal/mol). Taking phosphine/PyBox ligand exchange into account, the reductive elimination of $NiH(PPh_3)_2Br$ with an assisting substrate (functioning as a π-acid) requires an activation free energy of 26.8 kcal/mol. The high barrier is mainly caused by steric repulsion of PPh_3 ligands in the *cis*-configuration (**SI-Int22**). Thus, reductive elimination pathways can be excluded.

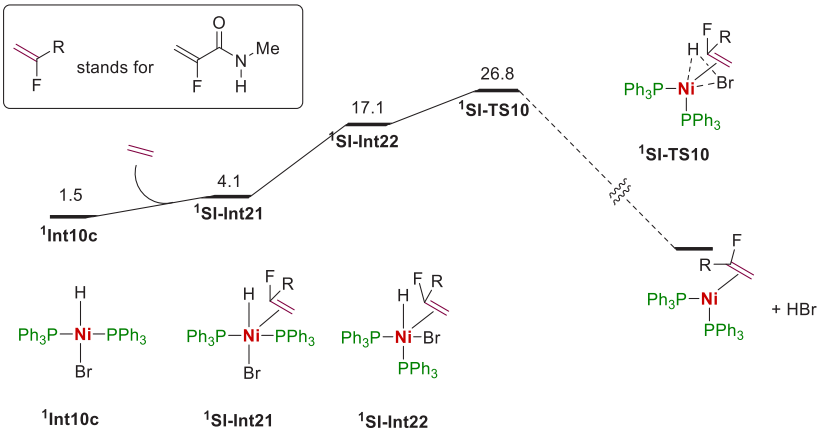


Figure S61. Gibbs free energy profile of reductive elimination of **Int10c** computed at (R)ωB97M-V/def2-TZVPP/SMD(DMA)//(R)PBE0-D3(BJ)/def2-SVP/SMD(DMA) level.

Deprotonation of M-H species has been previously reported and confirmed with calculations as well.[44] Herein, we assume the OMe^-, generated from MeOH, functions as the base to deprotonate Ni-H species. **Int10a**, **Int10b** and **Int10c** (which are in equilibrium by coordination/dissociation of PPh_3) were all found possible for deprotonation by MeO^-. Deprotonations of **Int10a** and **Int10b** require relatively high activation energies than **Int10c**. The overall activation energy for the elimination is 12.9 kcal/mol.

This is in line with the experimental observation that addition of PPh_3 switches the reaction pathway from HAT-mediated hydrogenation to alkyl transfer. When PPh_3 is present, the HBr elimination occurs readily via **Int10c** and **TS8b**, generating Ni(0) **SI-Int24** and then initiates the subsequent alkyl transfer process. In contrast, when PPh_3 is

absent, HBr elimination requires a much higher activation energy for **Int10a**, which would undergo HAT instead.

Since def2-SVP basis set was not sufficient to describe systems involving anion species in geometry optimization, the following free energies of deprotonation and regeneration were computed at PBE0-D3/6-311G**(6-311+G**,SDD)/SMD(DMA) level. 6-311+G** basis sets were used for O (of MeO^-) and Br atoms. SDD effective core potential and basis set were used for Ni.

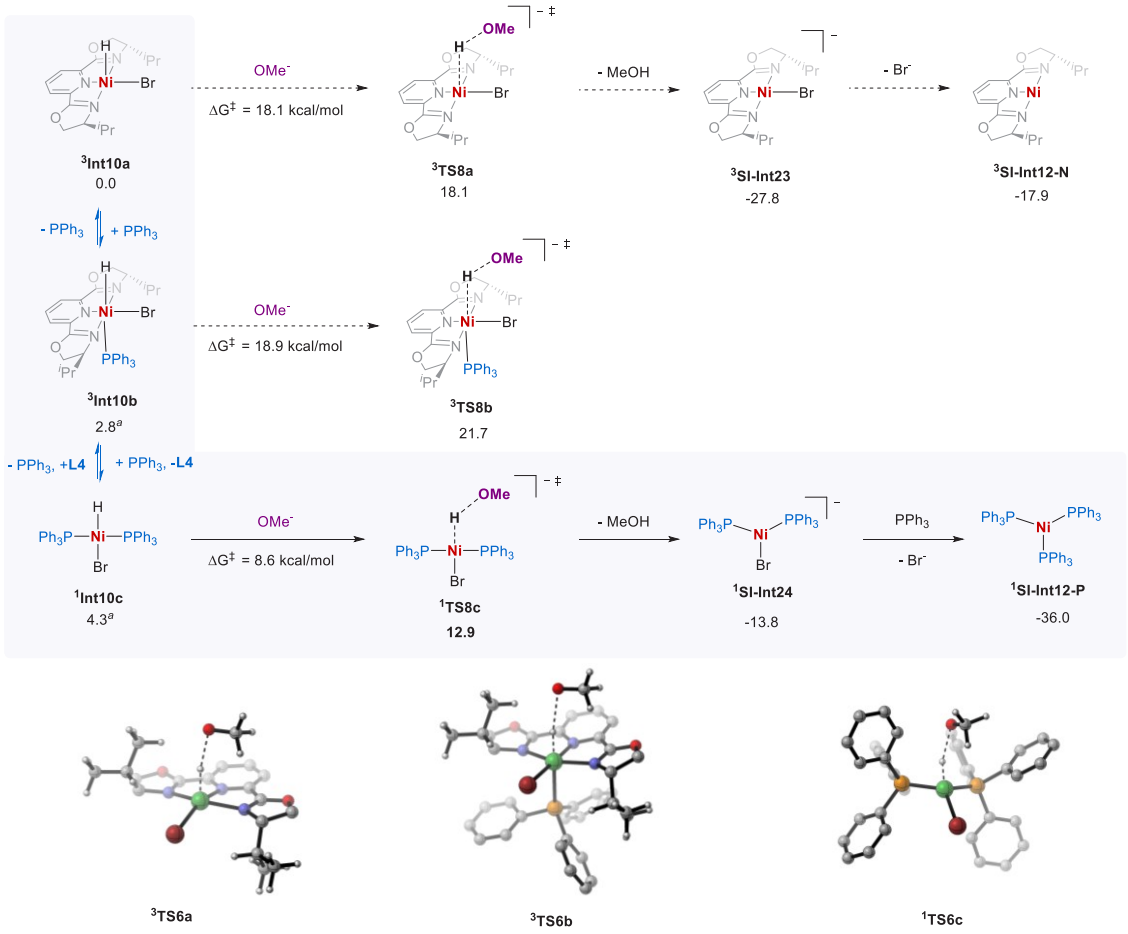


Figure S62. Different pathways of deprotonation-facilitated HBr-elimination. Relative free energies in kcal/mol are given by reference to **Int10a**.

Computing levels:

a: (U/R)ωB97M-V/def2-TZVPP/SMD(DMA)// (U/R)PBE0-D3(BJ)/def2-SVP/SMD(DMA);

others: (U/R)PBE0-D3/6-311G**(6-311+G**,SDD)/SMD(DMA)

10.4 DFT studies of HAT/alkyl coupling reaction.

The HAT process in the HAT/alkyl coupling reaction has also been studied

computationally. The main difference between this reaction and asymmetric hydrogenation lies in the ligand. A bidentate ligand **L12** is used here. Starting from the Ni-H species **SI-Int25**, two transition states have been located by us. The HAT activation free energy of **SI-Int25** is slightly higher than **Int1** with Pybox ligand. **SI-TS11**, which is more favored energetically, adopts a tetrahedral configuration, while **SI-TS12** adopts a pyramidal configuration. No hydrometallation transition state have been successfully located. With the DFT calculations above, we believe the HAT/alkyl coupling reaction also takes place via a HAT process.

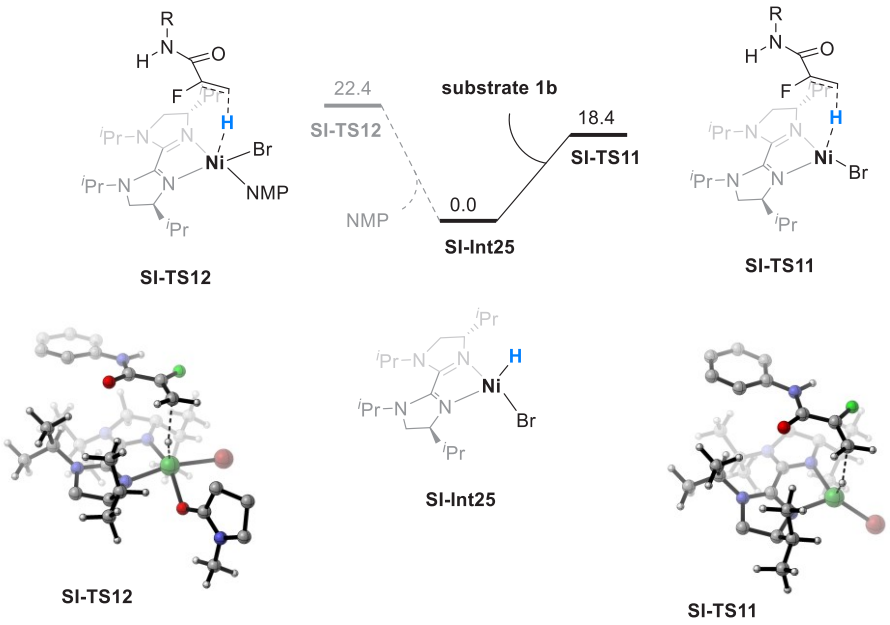


Figure S63. HAT process in the HAT/alkyl coupling reaction.

10.5 Summary of energies

Gibbs free energies computed at the optimizing level, thermal corrections to Gibbs free energy (TCG), single point energies at higher levels and final Gibbs free energies are given below.

Table S35. Summary of energies

Species	level	*G* (orig. level)	*TCG*	*SPE* (higher level)	Final *G*
1b	a	-576.52452	0.117501	-577.633180	-577.515679
MeOH	a	-115.57266	0.028309	-115.722285	-115.693976
Int1	a	-2943.14167	0.339366	-2945.526112	-2945.186746
Int1-M	a	-3058.71033	0.385459	-3061.264360	-3060.878901
TS1	a	-3519.65487	0.478395	-3523.157797	-3522.679402
TS1-M	a	-3635.22366	0.525954	-3638.898447	-3638.372493
SI-TS1'	a	-3519.65238	0.477725	-3523.153435	-3522.675710
SI-TS1'-M	a	-3635.21955	0.527543	-3638.894596	-3638.367053
SI-Int1	a	-3519.65998	0.480913	-3523.173818	-3522.692905
TS-CA	a	-3519.64682	0.481925	-3523.155677	-3522.673752
TS-MI	a	-3519.64545	0.478534	-3523.151712	-3522.673178
1b	b	-576.437781	0.117844	-577.632954	-577.515110
MeOH	b	-115.475441	0.028569	-115.721885	-115.693316
Int1	b	-2942.765462	0.338004	-2945.525100	-2945.187096
Int2	b	-3519.257452	0.485840	-3523.225636	-3522.739796
Int2-M	b	-3634.73306	0.534554	-3638.960185	-3638.425631
SI-TS2	b	-3519.243609	0.48515	-3523.214721	-3522.729568
SI-Int2	b	-3519.244683	0.48454	-3523.215246	-3522.730706
TS2	b	-3519.238182	0.48589	-3523.208967	-3522.723077
Int3	b	-3519.248465	0.485752	-3523.214909	-3522.729157
TS3	b	-3519.233235	0.484434	-3523.202303	-3522.717869
Int3'	b	-3519.2458	0.484901	-3523.212395	-3522.727494
TS4	b	-3634.715383	0.533702	-3638.944622	-3638.410920
TS4'	b	-3634.708013	0.533420	-3638.937249	-3638.403829
TS4-^{i}PrOH	a	-3634.724880	0.585667	-3717.570308	-3716.984641
TS4'-^{i}PrOH	a	-3634.725772	0.586840	-3717.569910	-3716.983070
Int4	b	-3634.727757	0.534038	-3638.953063	-3638.419025
Int4'	b	-3634.724983	0.535127	-3638.950438	-3638.415311
TS5	b	-3634.729593	0.530431	-3638.949286	-3638.418855
TS5'	b	-3634.72488	0.534159	-3638.947976	-3638.413817
TS5"	b	-3634.725772	0.531678	-3638.942880	-3638.411202
TS5-O	b	-3750.189120	0.575805	-3754.661102	-3754.085297
Int5	b	-3634.74565	0.534832	-3638.974157	-3638.439325
Int6	b	-3057.089594	0.369308	-3060.094115	-3059.724807

3b	b	-577.649031	0.140248	-578.858786	-578.718538
$Si(OMe_3)H$	b	-634.649724	0.097894	-635.618805	-635.520911
TS6	b	-3691.730375	0.495007	-3695.724845	-3695.229838
Int7	b	-3691.762063	0.497013	-3695.750043	-3695.253030
Int8	b	-577.009215	0.125443	-578.207845	-578.0824012
Int9	b	-2942.202838	0.330910	-2944.949834	-2944.618924
SI-Int3	b	-3691.746858	0.496207	-3695.750141	-3695.253934
$Si(OMe)_4$	b	-748.992528	0.128137	-750.216079	-750.087942
SI-Int4	a	-2597.98183	0.376321	-2600.400759	-2600.024438
SI-Int4-M	a	-2713.55257	0.424986	-2716.141960	-2715.716974
SI-TS2	a	-3174.49509	0.515432	-3178.032624	-3177.517192
SI-TS2-M	a	-3290.06928	0.564757	-3293.776046	-3293.211289
SI-Int4	b	-2597.67588	0.376216	-2600.399524	-2600.023308
SI-Int4-M	b	-2713.15894	0.426430	-2716.143748	-2715.717318
1b	c	-576.52452	0.117501	-577.633180	-577.515679
MeOH	c	-115.476115	0.028495	-115.722369	-115.693874
SI-Int5	c	-3174.16775	0.524200	-3178.100560	-3177.576360
SI-Int5-M	c	-3289.65218	0.572737	-3293.840956	-3293.268219
SI-Int6	c	-5055.83826	0.333072	-5058.763443	-5058.430371
^{t}BuBr	c	-2731.02175	0.091009	-2731.841859	-2731.750850
SI-TS3	c	-7786.84998	0.435835	-7790.598841	-7790.163006
SI-Int7	c	-7629.47262	0.327481	-7632.865352	-7632.537871
^{t}Bu·	c	-157.406946	0.086624	-157.750805	-157.664181
SI-Int8	c	-8363.34504	0.584907	-8368.317092	-8367.732185
SI-Int9	c	-5905.09457	0.639875	-5909.861314	-5909.221439
SI-TS4	c	-5905.06438	0.637364	-5909.818910	-5909.181546
SI-Int10	c	-5905.07419	0.644250	-5909.842095	-5909.197845
SI-Int11	c	-7744.29193	0.367465	-7747.928353	-7747.560888
SI-Int12-P	c	-4611.705966	0.742509	-4617.239194	-4616.496685
SI-Int12-N	c	-2482.201598	0.329338	-2484.659508	-2484.330170
SI-Int12-NP	c	-3516.81735	0.58405	-3521.003573	-3520.419523
SI-Int13-P	c	-7185.343475	0.740177	-7191.335602	-7190.595425
SI-Int15-P	c	-6884.635672	0.741348	-6890.47392	-6889.732572
SI-Int15-N	c	-5789.767647	0.591482	-5794.279583	-5793.688101
SI-TS7	c	-5789.750409	0.590265	-5794.264498	-5793.674233
SI-Int16	c	-5789.762186	0.588188	-5794.270724	-5793.682536
TS-enol-flip	c	-5789.745058	0.591045	-5794.257546	-5793.666501
TS7	c	-5905.233348	0.640235	-5910.006308	-5909.366073
TS7'	c	-5905.227193	0.639219	-5910.000926	-5909.361707
TS7-^{i}PrOH	d	-5984.629516	0.691537	-5988.631615	-5987.940078
TS7'-^{i}PrOH	d	-5984.310743	0.692848	-5988.630680	-5987.937832
SI-Int17	c	-5905.237248	0.639663	-5910.006987	-5909.367324

SI-TS8	c	-5905.237878	0.636973	-5910.002842	-5909.365869
SI-TS8'	c	-5905.231345	0.640342	-5910.000495	-5909.360153
SI-Int18	c	-5905.254381	0.636009	-5910.024814	-5909.388805
SI-Int19	c	-5170.737898	0.367266	-5173.91923	-5173.551964
SI-TS9	c	-5805.378573	0.493946	-5809.54878	-5809.054834
SI-Int20	c	-5805.410907	0.495673	-5809.577776	-5809.082103
Int10a	c	-5056.415669	0.337744	-5059.351839	-5059.014095
SI-Int14	c	-733.876647	0.231541	-735.4359541	-735.204413
SI-TS-Addition	c	-733.831541	0.224954	-735.3861135	-735.161160
SI-TS-HAT-Br	c	-5632.84136	0.475559	-5636.983771	-5636.508212
Int10b	c	-6090.999207	0.592421	-6095.662995	-6095.070574
Int10c	c	-6151.300773	0.488778	-6155.573866	-6155.085088
SI-Int21	c	-6536.392318	0.578290	-6541.473559	-6541.473559
SI-Int22	c	-6536.383723	0.586706	-6541.461150	-6541.461150
SI-TS10	c	-6536.370374	0.585255	-6541.444285	-6541.444285
Int10a	e	-3720.612877	0.337173		
Int10b	e	-4755.946169	0.591573		
Int10c	e	-4816.071822	0.484126		
TS8a	e	-3835.675425	0.369605		
TS8b	e	-4871.007398	0.622196		
TS8c	e	-4931.149492	0.520746		
PPh_3	c	-1035.335976	0.229323	-1036.290306	-1036.060983
PPh_3	e	-1035.335976	0.228280		
PyBox L4	c	-974.267186	0.332165	-976.376209	-976.044044
PyBox L4	e	-975.200526	0.331018		
MeOH	e	-115.604358	0.028469		
MeO-	e	-115.091426	0.013925		
Br^-	e	-2574.005701	-0.016176		
SI-Int23	e	-3720.144269	0.322979		
SI-Int24	e	-4815.58774	0.477147		
SI-Int12-N	e	-1146.122841	0.328187		
SI-Int12-P	e	-3276.953427	0.738517		
SI-Int25	c	-5005.410272	0.457011	-5008.305421	-5007.848410
SI-TS11	c	-5581.837285	0.598521	-5585.937334	-5585.338813
SI-TS12	c	-5907.084129	0.729799	-5911.900470	-5911.170671

Computing levels:

a. ωB97M-V/def2-TZVPP/SMD(THF)//PBE0-D3(BJ)/def2-SVP(def2-TZVPP)/SMD (THF)

b. ωB97M-V/def2-TZVPP/SMD(THF)//PBE0-D3(BJ)/def2-SVP/SMD(THF)

c. ωB97M-V/def2-TZVPP/SMD(DMA)//PBE0-D3(BJ)/def2-SVP/SMD(DMA)

d. ωB97M-V/def2-TZVPP/SMD(DMA)//PBE0-D3(BJ)/def2-SVP(def2-TZVPP)/SMD(DMA)

e. PBE0-D3(BJ)/6-311G**(6-311+G**,SDD)/SMD(DMA)

10.6 Summary of Cartesian Coordinate

1b

O	1.349865	-1.667264	-0.000008
C	1.461471	-0.454498	0.000004
C	2.814301	0.182396	0.000000
N	0.441584	0.442384	0.000016
C	-0.935730	0.200689	0.000008
C	-1.783976	1.319378	0.000001
C	-3.164317	1.155760	-0.000006
C	-3.722962	-0.123372	-0.000007
C	-2.879678	-1.233169	-0.000001
C	-1.493474	-1.086545	0.000006
F	2.807784	1.522553	-0.000008
H	0.710827	1.421847	0.000031
H	-1.348413	2.322687	0.000003
H	-3.808832	2.038523	-0.000010
H	-4.807791	-0.252633	-0.000014
H	-3.303366	-2.240930	-0.000002
H	-0.837036	-1.954152	0.000008
C	3.943502	-0.497890	-0.000003
H	3.896785	-1.578901	0.000004
H	4.902943	0.005510	-0.000011

MeOH

C	0.659237	-0.019325	0.000000
H	1.094024	0.991204	0.000000
H	1.029189	-0.549839	-0.896224
H	1.029189	-0.549840	0.896224
O	-0.746908	0.122516	0.000000
H	-1.132560	-0.755705	0.000000

Int1

C	-1.111932	3.470733	-0.507120
C	-1.084624	2.078477	-0.456101
N	0.021880	1.411498	-0.136216
C	1.156065	2.056959	0.123644
C	1.228022	3.448569	0.102754
C	0.068427	4.155468	-0.216420
Ni	-0.039449	-0.649878	0.025761
C	-2.201951	1.166253	-0.736059
C	2.254355	1.124127	0.411034
O	-3.400780	1.634284	-1.047793
C	-4.211252	0.470392	-1.341616
C	-3.333453	-0.726544	-0.910394
N	-2.036293	-0.100345	-0.672348
N	2.064277	-0.139225	0.357403
C	3.334749	-0.791810	0.659622
C	4.255968	0.399281	1.017543
O	3.457725	1.573073	0.732711
C	-3.818195	-1.486806	0.334901
C	3.808659	-1.667722	-0.509335
H	-2.029834	3.998595	-0.769445
H	2.165723	3.959353	0.325657
H	0.086170	5.246857	-0.244602
H	-5.153626	0.563899	-0.785776
H	-4.427164	0.478421	-2.419588
H	-3.231116	-1.452034	-1.731903
H	3.189827	-1.445789	1.533812
H	4.528411	0.430790	2.081531
H	5.170324	0.457926	0.411238
H	-3.023278	-2.220051	0.552972
H	3.001444	-2.404303	-0.659198
Cl	0.164768	-2.683060	-1.011068
C	3.967090	-0.882911	-1.803573
H	4.751662	-0.110805	-1.728977
H	4.251845	-1.556200	-2.626815
H	3.026413	-0.389583	-2.093203
C	5.082349	-2.411448	-0.131157
H	5.376839	-3.108282	-0.930923
H	5.927905	-1.720768	0.028199
H	4.948164	-2.997959	0.791744
C	-3.972893	-0.586810	1.552422
H	-4.262761	-1.181936	2.432083
H	-3.029445	-0.076575	1.799647
H	-4.754886	0.177191	1.405865
C	-5.099579	-2.248373	0.022510
H	-4.968018	-2.926673	-0.835460
H	-5.410388	-2.855599	0.886502
H	-5.932213	-1.563900	-0.212757
H	-0.399486	-0.746472	1.588484

Int1-M

C	-1.079409	3.550980	-0.382873
C	-1.055233	2.157465	-0.371680
N	0.048988	1.483174	-0.066341
C	1.183756	2.112571	0.220212
C	1.259332	3.504520	0.240564
C	0.102619	4.222384	-0.066262
Ni	-0.005026	-0.565248	-0.011908
C	-2.165704	1.245190	-0.679044
C	2.266758	1.158346	0.496348
O	-3.369538	1.711245	-0.976720
C	-4.169848	0.550053	-1.304313
C	-3.280938	-0.651505	-0.910790
N	-1.988865	-0.022060	-0.654899
N	2.066051	-0.099895	0.387255
C	3.315911	-0.777775	0.717874
C	4.227836	0.386204	1.172266
O	3.462143	1.580028	0.883539
C	-3.757939	-1.456574	0.308556
C	3.839648	-1.604194	-0.466161
H	-1.993783	4.090645	-0.633321
H	2.195587	4.008185	0.485005
H	0.123405	5.314125	-0.062769
H	-5.111952	0.617787	-0.744321
H	-4.388343	0.588994	-2.381205
H	-3.173730	-1.349810	-1.755503

H	3.122945	-1.469593	1.552795
H	4.435700	0.375604	2.251351
H	5.178052	0.452337	0.625083
C	4.100214	-0.757981	-1.704350
H	4.907320	-0.023670	-1.541817
H	4.412055	-1.398012	-2.544620
H	3.194017	-0.218666	-2.018494
C	5.067067	-2.403871	-0.050480
H	5.398835	-3.060449	-0.869565
H	5.915130	-1.745774	0.204654
H	4.858259	-3.038986	0.825166
C	-3.927733	-0.597095	1.552725
H	-4.209874	-1.223828	2.412748
H	-2.991151	-0.082833	1.816783
H	-4.720465	0.159906	1.429097
C	-5.027633	-2.225342	-0.032088
H	-4.883594	-2.875043	-0.910048
H	-5.333075	-2.863375	0.811353
H	-5.869074	-1.545615	-0.249556
H	-0.377054	-0.714016	1.552647
C	-0.284477	-0.122176	-3.364737
H	-0.499697	0.956398	-3.330773
H	-1.230652	-0.669618	-3.221125
H	0.108957	-0.361293	-4.368953
O	0.660398	-0.417320	-2.357455
H	0.657243	-1.378170	-2.199115

TS1

C	0.531837	-2.712129	-2.173209
C	1.282580	-1.697372	-1.588558
N	0.717605	-0.569063	-1.158426
C	-0.594719	-0.371044	-1.273808
C	-1.428940	-1.329276	-1.849866
C	-0.845748	-2.512158	-2.300946
Ni	1.811143	0.750240	-0.084668
C	2.725658	-1.688046	-1.321942
C	-0.980912	0.920661	-0.700328
O	3.504821	-2.697356	-1.677112
C	4.852097	-2.291343	-1.332338
C	4.661215	-1.014140	-0.485151
N	3.253249	-0.695998	-0.705188
N	-0.090209	1.680443	-0.176085
C	-0.768113	2.874481	0.321829
C	-2.259708	2.560747	0.055123
O	-2.241775	1.315904	-0.683590
C	4.960281	-1.164537	1.014797
C	-0.226954	4.147156	-0.345582
H	1.009815	-3.629804	-2.518431
H	-2.501046	-1.148099	-1.938644
H	-1.466285	-3.286156	-2.757126
H	5.331931	-3.121988	-0.798361
H	5.393651	-2.105738	-2.271055
H	5.278609	-0.190290	-0.874078
H	-0.580163	2.950279	1.404071
H	-2.828142	2.384434	0.975641
H	-2.773529	3.309144	-0.563722
H	4.632010	-0.213613	1.467548
H	-2.952014	-2.183668	0.505338
H	3.025723	-2.310958	-0.701235
Cl	0.120754	-2.845353	-0.715544
H	0.848933	4.162472	-0.102458
Cl	3.188966	2.486754	0.444022
C	-0.365585	4.117421	-1.861081
H	-1.421278	4.091335	-2.180100
H	0.085685	5.017639	-2.306338
H	0.143715	3.243451	-2.296195
C	-0.876012	5.382362	0.264156
H	-0.432243	6.300671	-0.150471
H	-1.958810	5.419257	0.056507
H	-0.742347	5.408802	1.357399
C	4.171707	-2.294991	1.661358
H	4.317264	-2.287757	2.752537
H	3.091919	-2.196174	1.473413
H	4.494895	-3.284674	1.297844
C	6.458088	-1.314823	1.243498
H	7.018042	-0.467359	0.817377
H	6.684939	-1.360545	2.319745
H	6.846993	-2.240834	0.786921
H	1.370925	-0.013125	1.235938
O	-2.291798	0.311177	2.290466
C	-2.125884	-0.774533	1.744801
C	-0.832804	-1.458468	1.781868
N	-3.094827	-1.460285	1.061769
C	-4.405802	-1.081755	0.784529
C	-5.142913	-1.900189	-0.088128
C	-6.456735	-1.582753	-0.414507
C	-7.061528	-0.444042	0.119964
C	-6.331220	0.366084	0.988891
C	-5.014607	0.060799	1.327765
F	-0.769830	-2.631630	1.101004
H	-2.799325	-2.340376	0.652925
H	-4.670954	-2.793790	-0.507533
H	-7.012518	-2.233592	-1.094579
H	-8.093328	-0.193024	-0.136817
H	-6.793359	1.258559	1.419547
H	-4.446468	0.690336	2.009125
C	0.268488	-0.975999	2.375643
H	0.170219	-0.085255	2.980245
H	1.142246	-1.600387	2.503519

TS1-M

C	0.394508	-2.767984	-2.126987
C	1.176008	-1.731504	-1.625430
N	0.639765	-0.572284	-1.246982
C	-0.672639	-0.364059	-1.323967
C	-1.537585	-1.343061	-1.814581
C	-0.983917	-2.556020	-2.221159
Ni	1.796193	0.819649	-0.330025
C	2.624494	-1.740332	-1.388584
C	-1.033641	0.952513	-0.789945
O	3.364226	-2.801438	-1.678742
C	4.728642	-2.415382	-1.386313
C	4.587570	-1.093657	-0.602873
N	3.195737	-0.727455	-0.850294

N	-0.128299	1.735846	-0.332912
C	-0.796977	2.923615	0.190438
C	-2.295080	2.609631	-0.038574
O	-2.298933	1.335230	-0.722171
C	4.861950	-1.187196	0.906969
C	-0.279903	4.208785	-0.469943
H	0.849901	-3.711253	-2.431433
H	-2.610431	-1.154221	-1.872498
H	-1.629303	-3.345492	-2.611811
H	5.201058	-3.229636	-0.821602
H	5.252555	-2.290201	-2.345359
H	5.246303	-0.317690	-1.022052
H	-0.580619	2.984946	1.268763
H	-2.851436	2.480861	0.896784
H	-2.809936	3.336265	-0.682651
H	4.548911	-0.211295	1.315017
H	0.801922	4.227365	-0.253304
Cl	3.246981	2.568898	0.371618
C	-0.457814	4.202623	-1.981390
H	-1.522058	4.182321	-2.271471
H	-0.019727	5.111409	-2.423192
H	0.043783	3.335779	-2.437202
C	-0.919622	5.429254	0.178648
H	-0.493035	6.358007	-0.230840
H	-2.007591	5.461376	-0.001400
H	-0.758918	5.437533	1.268586
C	4.037572	-2.272013	1.586456
H	4.161634	-2.219048	2.678991
H	2.963996	-2.161242	1.372400
H	4.348429	-3.282463	1.272834
C	6.351955	-1.363507	1.165242
H	6.938815	-0.546752	0.715916
H	6.561235	-1.372503	2.245988
H	6.725230	-2.315705	0.751232
H	1.442636	0.164570	1.091856
O	-2.270486	0.455092	2.264965
C	-2.070875	-0.654697	1.782428
C	-0.755741	-1.292418	1.846050
N	-3.022669	-1.413188	1.152462
C	-4.347917	-1.096996	0.866888
C	-5.066509	-1.993198	0.057033
C	-6.392666	-1.738671	-0.275106
C	-7.029058	-0.587305	0.190977
C	-6.317231	0.300094	0.997679
C	-4.988730	0.058789	1.341179
F	-0.665149	-2.508552	1.246348
H	-2.698808	-2.303535	0.789892
H	-4.570958	-2.896942	-0.310192
H	-6.933058	-2.449373	-0.905916
H	-8.070476	-0.385876	-0.070645
H	-6.803566	1.204152	1.374146
H	-4.433434	0.749211	1.972263
C	0.337712	-0.734459	2.380864
H	0.226408	0.205458	2.902773
H	1.238776	-1.312495	2.529038
C	3.121091	1.349491	-3.280338
H	2.636807	0.482009	-3.751207
H	4.063756	1.016182	-2.816779
H	3.356218	2.084545	-4.069582
O	2.224710	1.891723	-2.329421
H	2.713323	2.502529	-1.750919

SI-TS1'

C	0.154008	-0.752017	2.264394
C	0.818018	-0.284254	1.129918
N	0.485464	-0.698431	-0.091921
C	-0.520707	-1.554283	-0.275258
C	-1.243876	-2.071671	0.794317
C	-0.885931	-1.661469	2.081572
Ni	1.329621	0.203900	-1.682515
C	1.922551	0.676610	1.077630
C	-0.738537	-1.801590	-1.704479
O	2.392274	1.238263	2.180443
C	3.318576	2.254624	1.725437
C	3.591514	1.869937	0.260360
N	2.458989	0.988765	-0.046140
N	-0.026289	-1.188344	-2.575650
C	-0.448851	-1.648110	-3.895971
C	-1.666000	-2.546175	-3.571130
O	-1.677110	-2.633299	-2.126028
C	3.790635	3.032538	-0.714233
C	0.700379	-2.338354	-4.645267
H	0.446737	-0.409727	3.257828
H	-2.062353	-2.772653	0.625293
H	-1.427317	-2.050610	2.946278
H	2.807556	3.223441	1.823834
H	4.203297	2.225182	2.372120
H	4.500891	1.243172	0.205939
H	-0.758754	-0.772946	-4.488006
H	-2.623260	-2.108380	-3.886865
H	-1.590020	-3.566986	-3.970106
H	4.075664	2.566757	-1.672060
H	1.491331	-1.573246	-4.719280
Cl	2.700346	0.643628	-3.447545
C	1.268813	-3.526802	-3.882708
H	0.529555	-4.336681	-3.760716
H	2.128214	-3.952439	-4.423390
H	1.622823	-3.233389	-2.882100
C	0.260008	-2.718843	-6.052221
H	-0.539943	-3.478313	-6.038227
H	-0.115439	-1.844599	-6.607584
H	1.101710	-3.141589	-6.622073
C	2.525941	3.840000	-0.959583
H	2.739710	4.680277	-1.638696
H	1.756746	3.212424	-1.432036
H	2.095796	4.246386	-0.032020
C	4.948233	3.904200	-0.240252
H	5.858876	3.310481	-0.058144
H	5.192357	4.667032	-0.995348
H	4.699914	4.437422	0.692995
H	0.223704	1.339393	-1.485104
O	0.322061	3.600428	1.588481
C	-0.521407	2.728017	1.765825
C	-1.226352	2.100675	0.648434

N	-0.898569	2.253792	2.994355
C	-0.394435	2.578485	4.251215
C	0.591494	3.555329	4.464614
C	1.045837	3.803514	5.758337
C	0.539107	3.101076	6.851141
C	-0.443816	2.133333	6.637816
C	-0.9072	1.872771	5.353090
F	-2.106315	1.124493	0.992711
H	-1.620468	1.541466	2.984153
H	0.984116	4.105511	3.612512
H	1.813782	4.566980	5.909890
H	0.904365	3.306035	7.860170
H	-0.857039	1.573074	7.480617
H	-1.678908	1.114817	5.188746
C	-1.025362	2.382652	-0.649722
H	-1.702514	1.993811	-1.398999
H	-0.414055	3.240250	-0.891245

SI-TS1'-M

C	0.171266	-0.729377	2.334233
C	0.860426	-0.284299	1.205181
N	0.553422	-0.720923	-0.014632
C	-0.460240	-1.564852	-0.206531
C	-1.207447	-2.061117	0.857190
C	-0.868173	-1.638173	2.145308
Ni	1.461129	0.122087	-1.613080
C	1.955330	0.688449	1.163112
C	-0.681335	-1.805531	-1.637200
O	2.373518	1.284025	2.271302
C	3.288683	2.314511	1.828714
C	3.621824	1.907431	0.382847
N	2.525738	0.989856	0.053467
N	0.045438	-1.214685	-2.510031
C	-0.419427	-1.631374	-3.829520
C	-1.683438	-2.458936	-3.499294
O	-1.664092	-2.589298	-2.058258
C	3.825710	3.051512	-0.611789
C	0.676567	-2.377883	-4.604258
H	0.443934	-0.369096	3.326984
H	-2.032126	-2.753342	0.682470
H	-1.427826	-2.012009	3.005210
H	2.751148	3.272019	1.890141
H	4.151011	2.320686	2.505791
H	4.549485	1.304725	0.374893
H	-0.683159	-0.730343	-4.404852
H	-2.616773	-1.948156	-3.775696
H	-1.686359	-3.468582	-3.931530
H	4.146256	2.570946	-1.551225
H	1.525141	-1.673805	-4.643140
Cl	2.670363	0.822664	-3.536693
C	1.141331	-3.642544	-3.895833
H	0.343060	-4.401682	-3.838986
H	1.981447	-4.099286	-4.442079
H	1.491758	-3.424446	-2.875996
C	0.219172	-2.655725	-6.029864
H	-0.646025	-3.339854	-6.054027
H	-0.071037	-1.728193	-6.548584
H	1.025164	-3.128012	-6.612470
C	2.553288	3.828086	-0.910337
H	2.767497	4.647413	-1.614481
H	1.804875	3.170261	-1.374519
H	2.099519	4.260486	-0.005962
C	4.952773	3.956463	-0.126916
H	5.870519	3.386279	0.091572
H	5.200639	4.709135	-0.890926
H	4.668317	4.502629	0.788317
H	0.361334	1.300743	-1.484701
O	0.277508	3.654011	1.593067
C	-0.541089	2.755305	1.756711
C	-1.202083	2.097980	0.630295
N	-0.929756	2.276276	2.980626
C	-0.466828	2.626454	4.245741
C	0.447037	3.667144	4.478331
C	0.862918	3.940452	5.779924
C	0.388138	3.200789	6.862496
C	-0.524472	2.170480	6.630513
C	-0.948939	1.884336	5.337759
F	-2.069166	1.105906	0.967461
H	-1.616484	1.530279	2.956672
H	0.815960	4.245604	3.634269
H	1.574596	4.753820	5.945938
H	0.722811	3.425818	7.877836
H	-0.912715	1.580620	7.464987
H	-1.666568	1.077911	5.159666
C	-0.973656	2.363128	-0.665024
H	-1.610877	1.935984	-1.427660
H	-0.367687	3.223068	-0.910211
C	4.120988	-1.606375	-0.938502
H	3.771295	-1.851729	0.074216
H	4.656215	-0.644104	-0.902676
H	4.826462	-2.390959	-1.262214
O	2.993671	-1.554118	-1.793993
H	3.245840	-1.096567	-2.614011

SI-Int1

C	-1.648390	1.357360	2.301051
C	-0.486012	1.283506	1.535671
N	-0.072562	0.137503	1.010099
C	-0.761045	-0.984233	1.178122
C	-1.936067	-1.016556	1.927016
C	-2.371778	0.180526	2.496681
Ni	1.829112	0.060147	0.112838
C	0.442655	2.379052	1.214069
C	-0.125241	-2.106382	0.468716
O	0.231819	3.605005	1.665174
C	1.397565	4.374499	1.281888
C	2.212909	3.416350	0.381796
N	1.489635	2.156721	0.515407
N	0.998879	-1.949708	-0.120929
C	1.377824	-3.235295	-0.700443
C	0.109014	-4.090169	-0.481747
O	-0.716791	-3.289649	0.399549
C	2.346503	3.837210	-1.088808
C	2.661658	-3.781859	-0.058803

H	-1.975863	2.305833	2.728215
H	-2.488036	-1.946656	2.061760
H	-3.287583	0.196880	3.090414
H	1.050833	5.285074	0.774823
H	1.927554	4.655402	2.202653
H	3.227176	3.274051	0.786475
H	1.567839	-3.092997	-1.775177
H	-0.459877	-4.258135	-1.407265
H	0.291162	-5.055590	0.008268
H	2.829582	2.978625	-1.586988
H	3.421147	-2.997567	-0.219476
Cl	2.853970	-0.291309	2.209280
C	2.521656	-3.997886	1.441065
H	1.767258	-4.766575	1.679608
H	3.477589	-4.339965	1.867190
H	2.252720	-3.061557	1.953353
C	3.115677	-5.043846	-0.780738
H	4.080530	-5.393377	-0.382290
H	2.392772	-5.867557	-0.653336
H	3.241719	-4.869910	-1.861391
C	1.000698	4.080836	-1.758148
H	1.138296	4.261457	-2.835945
H	0.318784	3.223770	-1.649048
H	0.496378	4.971869	-1.347742
C	3.269299	5.042002	-1.213918
H	4.257543	4.842422	-0.770256
H	3.422503	5.308162	-2.271157
H	2.846813	5.928721	-0.711375
H	3.080868	0.068047	-0.897637
O	-1.334329	1.484424	-1.724812
C	-1.347954	0.293143	-1.984805
C	-0.203504	-0.348839	-2.688154
N	-2.343057	-0.573387	-1.658574
C	-3.496565	-0.325353	-0.907711
C	-4.248712	-1.438337	-0.502471
C	-5.386877	-1.270779	0.278147
C	-5.791927	0.007041	0.667146
C	-5.047526	1.111883	0.255932
C	-3.905909	0.960541	-0.528876
F	-0.363675	-1.659681	-2.942062
H	-2.210211	-1.536368	-1.951734
H	-3.921730	-2.440121	-0.794689
H	-5.959365	-2.148741	0.587773
H	-6.684503	0.139594	1.283000
H	-5.356348	2.118426	0.550008
H	-3.319503	1.822993	-0.837368
C	0.912196	0.276571	-3.011673
H	1.000444	1.332088	-2.795064
H	1.728034	-0.244877	-3.495509

TS-CA

C	1.279429	-3.131151	-1.726671
C	1.469608	-1.833376	-1.253414
N	0.461746	-0.976706	-1.154816
C	-0.775759	-1.328637	-1.473752
C	-1.070420	-2.601829	-1.959612
C	-0.015117	-3.504438	-2.090740
Ni	0.847669	0.952250	-0.450654
C	2.734011	-1.233378	-0.796195
C	-1.738624	-0.248952	-1.200987
O	3.866790	-1.917520	-0.860755
C	4.891887	-1.044142	-0.330353
C	4.150981	0.277455	-0.015169
N	2.766338	-0.040321	-0.340785
N	-1.358251	0.876229	-0.726684
C	-2.542077	1.724177	-0.603018
C	-3.694615	0.750553	-0.939226
O	-3.030112	-0.436450	-1.428018
C	4.301304	0.802378	1.418202
C	-2.443107	2.968740	-1.496450
H	2.117094	-3.825521	-1.803734
H	-2.094680	-2.878094	-2.212263
H	-0.204380	-4.511764	-2.467391
H	5.322350	-1.532467	0.556057
H	5.672661	-0.936468	-1.094410
H	4.481115	1.075976	-0.700396
H	-2.619175	2.070533	0.438398
H	-4.286139	0.460438	-0.059324
H	-4.374072	1.108027	-1.724553
H	3.711349	1.735075	1.443712
H	-1.509770	3.470911	-1.189792
Cl	1.339501	1.778214	-2.619375
C	-2.327116	2.626550	-2.974314
H	-3.228558	2.115538	-3.352441
H	-2.202012	3.544518	-3.569487
H	-1.449007	1.991770	-3.165943
C	-3.607495	3.908704	-1.213026
H	-3.506096	4.839945	-1.791323
H	-4.573237	3.454257	-1.492463
H	-3.658455	4.179404	-0.146110
C	3.719754	-0.147822	2.455404
H	3.798805	0.291080	3.462468
H	2.656081	-0.350159	2.257431
H	4.259060	-1.110059	2.480640
C	5.754832	1.155128	1.705241
H	6.156177	1.858984	0.958623
H	5.853016	1.624839	2.696059
H	6.398200	0.258915	1.704267
H	1.001287	2.400912	0.375838
O	0.319493	-0.117358	1.608070
C	-0.632277	0.475870	2.148730
C	-0.513157	1.874221	2.460078
N	-1.846217	-0.098913	2.388613
C	-2.296528	-1.363771	2.012449
C	-3.682418	-1.593451	2.034836
C	-4.199193	-2.828601	1.661640
C	-3.346766	-3.859163	1.260779
C	-1.971077	-3.634929	1.249764
C	-1.437251	-2.402340	1.621100
F	-1.680271	2.545997	2.657599
H	-2.546926	0.517567	2.788048
H	-4.352271	-0.787360	2.347189
H	-5.280604	-2.986021	1.682795
H	-3.753004	-4.829493	0.965929

H	-1.290027	-4.434247	0.946021
H	-0.363699	-2.227988	1.607023
C	0.633164	2.538965	2.196798
H	1.560627	1.992471	2.254962
H	0.674150	3.619329	2.277881

TS-MI

C	-1.594885	-3.408056	-2.385692
C	-1.041349	-2.544591	-1.442138
N	-1.756966	-1.580101	-0.871887
C	-3.034144	-1.400183	-1.189174
C	-3.679424	-2.215877	-2.117686
C	-2.937576	-3.231756	-2.719798
Ni	-0.818023	-0.301167	0.397287
C	0.340147	-2.557717	-0.948755
C	-3.635164	-0.283090	-0.450319
O	1.204556	-3.452687	-1.404169
C	2.476349	-3.095056	-0.815414
C	2.109178	-2.082161	0.286391
N	0.733334	-1.721196	-0.062763
N	-2.940748	0.458333	0.325784
C	-3.865535	1.398052	0.965053
C	-5.214870	1.087940	0.275635
O	-4.939158	-0.060269	-0.554354
C	2.191248	-2.622316	1.723429
C	-3.412365	2.859300	0.869630
H	-0.989255	-4.191279	-2.843178
H	-4.729668	-2.052110	-2.361999
H	-3.407335	-3.887500	-3.455663
H	2.953493	-4.013362	-0.449511
H	3.098802	-2.654475	-1.608117
H	2.744557	-1.187453	0.227535
H	-3.916549	1.134628	2.035892
H	-6.016898	0.819169	0.975141
H	-5.567239	1.898152	-0.379689
H	1.829700	-1.797456	2.356394
H	-2.464476	2.912348	1.426155
Cl	-0.191620	1.050531	-1.509371
C	-3.131984	3.294255	-0.560547
H	-4.039643	3.263768	-1.186720
H	-2.761651	4.331276	-0.577789
H	-2.366199	2.654305	-1.026201
C	-4.419062	3.766670	1.566338
H	-4.051447	4.804009	1.592592
H	-5.389947	3.779138	1.042849
H	-4.601515	3.449919	2.606106
C	1.310099	-3.841961	1.952300
H	1.366332	-4.162762	3.004276
H	0.252886	-3.626823	1.731598
H	1.621789	-4.701503	1.335329
C	3.643006	-2.883415	2.100612
H	4.256610	-1.980209	1.960683
H	3.721536	-3.183595	3.157036
H	4.086120	-3.693548	1.497171
H	-1.177170	-0.974136	1.787183
O	2.524087	0.483303	2.170197
C	1.811111	1.209808	1.483873
C	0.374912	1.341585	1.750015
N	2.244711	1.965947	0.432556
C	3.535672	2.078976	-0.073732
C	3.690998	2.714479	-1.318048
C	4.953752	2.875167	-1.876438
C	6.088097	2.408184	-1.209492
C	5.935326	1.778909	0.025237
C	4.676337	1.608242	0.598657
F	-0.202944	2.475697	1.291107
H	1.496399	2.281580	-0.187009
H	2.804080	3.079489	-1.843155
H	5.050766	3.371481	-2.845642
H	7.080468	2.534578	-1.648817
H	6.813723	1.408794	0.561209
H	4.559797	1.111037	1.559427
C	-0.347514	0.462866	2.515122
H	0.228797	-0.259434	3.076539
H	-1.291336	0.778576	2.941767

Int2

C	0.352273	-2.635878	-1.989253
C	1.124762	-1.675577	-1.339449
N	0.603645	-0.518077	-0.943642
C	-0.671099	-0.217947	-1.178652
C	-1.523502	-1.110687	-1.825119
C	-0.992247	-2.338766	-2.222992
Ni	1.705511	0.704575	0.274520
C	2.565751	-1.726454	-1.049761
C	-0.994034	1.120569	-0.666648
O	3.320666	-2.706608	-1.519261
C	4.685676	-2.353349	-1.186613
C	4.561243	-1.040430	-0.376393
N	3.124990	-0.776731	-0.400830
N	-0.094922	1.804559	-0.064851
C	-0.698443	3.061572	0.360144
C	-2.161381	2.921293	-0.126110
O	-2.203971	1.635553	-0.793213
C	5.129865	-1.080268	1.046755
C	0.075322	4.272021	-0.177165
H	0.792007	-3.581779	-2.308495
H	-2.567202	-0.851858	-2.006317
H	-1.629532	-3.068103	-2.727277
H	5.122421	-3.187714	-0.620721
H	5.237146	-2.232655	-2.128846
H	5.057766	-0.210305	-0.904460
H	-0.659935	3.080134	1.460222
H	-2.892139	2.894210	0.692658
H	-2.465269	3.685691	-0.855039
H	4.818508	-0.120049	1.492495
H	1.087452	4.167640	0.249397
Cl	3.191252	2.387217	0.704495
C	0.209381	4.255045	-1.692987
H	-0.768730	4.311503	-2.200698
H	0.803949	5.115764	-2.036763
H	0.720629	3.342193	-2.035947
C	-0.542570	5.566503	0.332568
H	0.066490	6.433621	0.033505

H	-1.556263	5.723845	-0.073924
H	-0.616369	5.571615	1.431837
C	4.560018	-2.215819	1.885244
H	4.883058	-2.115027	2.933144
H	3.460975	-2.220643	1.874983
H	4.913661	-3.199770	1.534634
C	6.651650	-1.118199	1.002489
H	7.061744	-0.259250	0.447947
H	7.072694	-1.094171	2.019394
H	7.018487	-2.039010	0.517149
H	3.085057	0.008113	2.894441
O	-0.660900	1.083584	2.816181
C	-0.299785	0.047747	2.264076
C	1.124474	-0.270931	2.009781
N	-1.179991	-0.884538	1.761760
C	-2.566743	-0.843021	1.685165
C	-3.217244	-1.937668	1.088512
C	-4.600351	-1.948838	0.945686
C	-5.366623	-0.871553	1.394076
C	-4.723489	0.210886	1.993630
C	-3.338455	0.236899	2.145479
F	1.238187	-1.673880	1.769917
H	-0.739346	-1.728860	1.412925
H	-2.620021	-2.783562	0.736239
H	-5.083698	-2.811102	0.478493
H	-6.453290	-0.879101	1.281260
H	-5.309773	1.059720	2.356666
H	-2.832865	1.076778	2.617341
C	2.023012	0.102279	3.154860
H	1.835962	1.152530	3.413466
H	1.821687	-0.519263	4.047842

Int2-M

C	0.324135	-2.760169	-1.954583
C	1.101730	-1.782277	-1.336397
N	0.591145	-0.600921	-1.005287
C	-0.673307	-0.291699	-1.274180
C	-1.530166	-1.201928	-1.891440
C	-1.011768	-2.454226	-2.224081
Ni	1.738457	0.708313	0.074451
C	2.539192	-1.848207	-1.026339
C	-0.999234	1.068739	-0.823765
O	3.279780	-2.848677	-1.486924
C	4.643250	-2.539145	-1.112803
C	4.546686	-1.173171	-0.392119
N	3.113971	-0.902670	-0.390506
N	-0.115112	1.794525	-0.248278
C	-0.794285	2.992633	0.245262
C	-2.187211	2.888661	-0.411554
O	-2.228554	1.545427	-0.949834
C	5.163394	-1.114302	1.009067
C	-0.022126	4.290967	0.006111
H	0.753411	-3.726931	-2.221250
H	-2.567154	-0.936688	-2.099715
H	-1.652347	-3.196835	-2.704375
H	5.009157	-3.352235	-0.469669
H	5.245688	-2.510731	-2.030358
H	5.021201	-0.381109	-0.995684
H	-0.879833	2.851216	1.335378
H	-3.019358	2.993661	0.295430
H	-2.333049	3.588009	-1.249835
H	4.885657	-0.116522	1.389767
H	0.919465	4.168670	0.567241
Cl	3.180878	2.488973	0.678699
C	0.350927	4.507387	-1.450809
H	-0.531640	4.586689	-2.107867
H	0.932445	5.435010	-1.567998
H	0.971775	3.676569	-1.810683
C	-0.791603	5.469296	0.588288
H	-0.198593	6.394579	0.521771
H	-1.737148	5.647504	0.047863
H	-1.037487	5.304533	1.649575
C	4.596851	-2.166805	1.951824
H	4.943965	-1.984801	2.980862
H	3.497826	-2.153522	1.960792
H	4.928012	-3.181957	1.675901
C	6.681740	-1.190893	0.920840
H	7.091280	-0.393261	0.280759
H	7.137272	-1.088737	1.917908
H	7.012733	-2.158912	0.506917
H	3.148762	0.169593	2.774119
O	-0.607698	1.190949	2.742982
C	-0.240735	0.150983	2.198104
C	1.176997	-0.161661	1.928906
N	-1.126103	-0.796874	1.726662
C	-2.512513	-0.763612	1.670158
C	-3.167818	-1.875299	1.109996
C	-4.552569	-1.896193	0.985982
C	-5.318680	-0.812182	1.418168
C	-4.672003	0.286687	1.983466
C	-3.285277	0.322807	2.115727
F	1.285204	-1.580742	1.750449
H	-0.684930	-1.647017	1.393542
H	-2.572093	-2.727264	0.769962
H	-5.037420	-2.772106	0.546366
H	-6.406724	-0.827372	1.320200
H	-5.257265	1.140951	2.335456
H	-2.779254	1.175224	2.563983
C	2.089223	0.245102	3.051059
H	1.886285	1.294902	3.297958
H	1.914504	-0.366934	3.956683
C	1.900750	1.550900	-3.191755
H	1.703908	0.545300	-3.592246
H	2.554248	2.076340	-3.909568
H	0.939503	2.091971	-3.140999
O	2.518014	1.405204	-1.941082
H	2.836233	2.244030	-1.560455

SI-TS2

C	0.894026	-2.279114	-3.799084
C	1.213216	-1.592344	-2.628748
N	0.366007	-0.739786	-2.068333
C	-0.825845	-0.504660	-2.602077
C	-1.246989	-1.148918	-3.764314

C	-0.362439	-2.048535	-4.360972
Ni	0.954729	0.322172	-0.277054
C	2.475050	-1.673340	-1.874464
C	-1.565870	0.512515	-1.837626
O	3.499713	-2.352608	-2.366219
C	4.607652	-2.088967	-1.473325
C	3.961700	-1.366105	-0.270184
N	2.613124	-1.073352	-0.754349
N	-1.053820	1.050119	-0.796098
C	-1.956708	2.121049	-0.374990
C	-3.205951	1.866864	-1.241474
O	-2.755710	0.922920	-2.245337
C	3.934347	-2.179864	1.032823
C	-1.283523	3.490551	-0.543452
H	1.605560	-2.969541	-4.253735
H	-2.230349	-0.946100	-4.190354
H	-0.652580	-2.570390	-5.275331
H	5.080228	-3.048519	-1.225176
H	5.329655	-1.461817	-2.015564
H	4.469192	-0.409597	-0.071110
H	-2.186164	1.996783	0.691020
H	-4.022586	1.389405	-0.679770
H	-3.592797	2.753961	-1.760133
H	3.372209	-1.567397	1.752860
H	-0.358513	3.423736	0.052458
Cl	2.203013	2.192036	-0.733366
C	-0.877898	3.776245	-1.981614
H	-1.744729	3.801178	-2.664038
H	-0.381418	4.756884	-2.049590
H	-0.156516	3.027104	-2.339865
C	-2.168339	4.583761	0.038666
H	-1.658963	5.559031	-0.001504
H	-3.114472	4.685357	-0.519861
H	-2.419600	4.379558	1.091488
C	3.189821	-3.498629	0.881417
H	3.139860	-4.023236	1.848065
H	2.155472	-3.334784	0.544057
H	3.685210	-4.178429	0.167687
C	5.347220	-2.372658	1.566227
H	5.860060	-1.407540	1.705555
H	5.327332	-2.885169	2.540396
H	5.962991	-2.985914	0.886987
H	2.990599	0.616850	2.040693
O	-0.714528	1.730734	2.509172
C	-0.452772	0.574220	2.191248
C	0.896965	0.142458	1.762501
N	-1.404601	-0.419576	2.114026
C	-2.785022	-0.325530	2.222178
C	-3.550180	-1.431022	1.808286
C	-4.938669	-1.399284	1.874275
C	-5.599572	-0.265000	2.349595
C	-4.843461	0.830099	2.767437
C	-3.450809	0.811710	2.714012
F	1.002123	-1.273040	1.973664
H	-1.039008	-1.327686	1.849396
H	-3.036275	-2.319059	1.429030
H	-5.510242	-2.271862	1.546625
H	-6.690688	-0.238331	2.398461
H	-5.344083	1.723235	3.151685
H	-2.861356	1.663838	3.046925
C	2.011953	0.827592	2.494531
H	1.849371	1.911388	2.434927
H	2.044650	0.534349	3.560735

SI-Int2

C	0.655282	-2.437510	-2.347757
C	1.339375	-1.541663	-1.527567
N	0.727143	-0.515244	-0.950875
C	-0.571913	-0.308051	-1.127806
C	-1.348739	-1.152850	-1.918948
C	-0.711653	-2.230208	-2.535087
Ni	1.863566	0.878056	0.177154
C	2.772671	-1.577158	-1.197226
C	-1.031237	0.899705	-0.425100
O	3.569309	-2.442113	-1.805049
C	4.907923	-2.134913	-1.351373
C	4.706933	-1.048233	-0.269032
N	3.275042	-0.765795	-0.347776
N	-0.217743	1.621530	0.248635
C	-0.951967	2.819428	0.660521
C	-2.411501	2.440656	0.344996
O	-2.295181	1.282016	-0.516731
C	5.136964	-1.454785	1.147549
C	-0.415772	4.062442	-0.065841
H	1.178026	-3.269448	-2.821348
H	-2.415388	-0.966839	-2.051104
H	-1.283757	-2.911653	-3.168099
H	5.359047	-3.063448	-0.975504
H	5.482122	-1.782202	-2.219200
H	5.247854	-0.127852	-0.541041
H	-0.816368	2.977673	1.738113
H	-2.975095	2.134957	1.239128
H	-2.978568	3.210694	-0.194047
H	4.871113	-0.603249	1.791429
H	0.657685	4.084908	0.179893
Cl	2.633197	2.189163	-1.557828
C	-0.555412	3.971926	-1.578337
H	-1.607819	3.883968	-1.897960
H	-0.148100	4.880053	-2.050185
H	0.019711	3.122037	-1.974697
C	-1.068289	5.315564	0.501102
H	-0.628706	6.219339	0.051403
H	-2.152249	5.342436	0.296334
H	-0.929592	5.381065	1.591581
C	4.375228	-2.667755	1.662073
H	4.670401	-2.895399	2.698091
H	3.289415	-2.486537	1.660518
H	4.574086	-3.571866	1.061853
C	6.645570	-1.651188	1.205185
H	7.180903	-0.751263	0.862257
H	6.971004	-1.862154	2.235511
H	6.974877	-2.497215	0.578499
H	4.728114	1.657233	1.009465
O	1.646926	3.625950	2.410609

C	1.778099	2.423488	2.619063
C	2.753625	1.583861	1.886346
N	0.982951	1.720145	3.498143
C	-0.113096	2.148189	4.233997
C	-0.855208	1.176008	4.929555
C	-1.974677	1.533969	5.672184
C	-2.384921	2.867000	5.738867
C	-1.647422	3.833709	5.056143
C	-0.519684	3.492517	4.311214
F	2.985794	0.393816	2.662313
H	1.231576	0.741395	3.593872
H	-0.541449	0.129441	4.876610
H	-2.534306	0.759162	6.203216
H	-3.266316	3.147721	6.320271
H	-1.949093	4.883843	5.103626
H	0.061947	4.246482	3.784178
C	4.071949	2.261503	1.652187
H	3.887929	3.210300	1.132276
H	4.603010	2.472712	2.599550

TS2

C	1.621907	4.058637	-0.808249
C	0.927316	2.866416	-0.606283
N	1.539681	1.766309	-0.185434
C	2.847234	1.760973	0.057491
C	3.626825	2.904675	-0.102351
C	2.991262	4.066042	-0.543295
Ni	0.492610	0.006062	0.048477
C	-0.511212	2.643016	-0.810626
C	3.310348	0.429549	0.474055
O	-1.278569	3.622583	-1.272481
C	-2.582631	3.029576	-1.467232
C	-2.484639	1.665561	-0.751187
N	-1.046997	1.516093	-0.540745
N	2.483605	-0.542154	0.557013
C	3.251820	-1.745917	0.860800
C	4.639629	-1.171225	1.210421
O	4.584058	0.200811	0.744544
C	-3.249661	1.581338	0.581658
C	3.200709	-2.736403	-0.311915
O	-0.226161	0.147508	1.965016
C	-0.004641	-1.110303	2.132054
C	-0.458031	-2.060394	1.224361
N	0.821137	-1.542842	3.160973
C	1.859474	-0.866450	3.782956
C	2.099542	0.511760	3.629417
C	3.199973	1.099910	4.247934
C	4.073950	0.354438	5.040466
C	3.826103	-1.009025	5.211171
C	2.737611	-1.613579	4.591113
F	0.066539	-3.330671	1.382465
H	1.103071	4.951271	-1.160116
H	4.696914	2.881959	0.107650
H	3.568135	4.982240	-0.684990
H	-3.333899	3.710272	-1.045916
H	-2.748957	2.933705	-2.550236
H	-2.834557	0.852252	-1.405420
H	2.808606	-2.239254	1.736068
H	4.826949	-1.143575	2.293772
H	5.479271	-1.667608	0.706438
H	-2.988520	0.601576	1.011775
H	2.125859	-2.880881	-0.511605
H	0.827168	-2.548135	3.293342
H	1.413167	1.093573	3.017672
H	3.372193	2.170961	4.107107
H	4.931037	0.829059	5.523827
H	4.491417	-1.615626	5.831773
H	2.558403	-2.685318	4.719126
Cl	0.482039	-0.895921	-2.075825
C	3.828518	-2.180128	-1.580728
H	4.907308	-1.982804	-1.461374
H	3.718342	-2.900589	-2.406239
H	3.320088	-1.256021	-1.892628
C	3.808601	-4.068870	0.102421
H	3.300529	-4.483254	0.987979
H	3.721471	-4.806791	-0.709965
H	4.881062	-3.971468	0.343395
C	-2.804078	2.637602	1.582561
H	-2.992305	3.662630	1.221403
H	-3.354789	2.521266	2.528882
H	-1.733515	2.532451	1.811384
C	-4.751356	1.612727	0.333365
H	-5.062179	0.816169	-0.361513
H	-5.303529	1.471737	1.275236
H	-5.075404	2.576479	-0.094102
C	-1.712662	-2.061469	0.433623
H	-2.177150	-1.068235	0.470575
H	-1.529334	-2.301952	-0.626308
H	-2.434267	-2.794626	0.842091

Int3

C	0.029048	3.549258	-0.129272
C	-0.528212	2.293013	-0.367733
N	0.221129	1.258425	-0.721700
C	1.540280	1.360444	-0.834114
C	2.193932	2.568997	-0.606842
C	1.411917	3.672119	-0.256268
Ni	-0.642030	-0.606080	-0.835979
C	-1.942856	1.899055	-0.258691
C	2.134789	0.062498	-1.185973
O	-2.875412	2.775595	0.070036
C	-4.119121	2.031868	0.130247
C	-3.744853	0.611601	-0.355266
N	-2.294579	0.690718	-0.490773
N	1.383826	-0.956640	-1.381495
C	2.239569	-2.069816	-1.775816
C	3.650280	-1.513552	-1.492108
O	3.443035	-0.090644	-1.302039
C	-4.193230	-0.546083	0.544169
C	1.948958	-2.499144	-3.221485
H	-0.596662	4.393434	0.161462
H	3.278070	2.643661	-0.696655
H	1.889862	4.635178	-0.066230
H	-4.473043	2.062588	1.171162

H	-4.847881	2.541252	-0.512670
H	-4.162375	0.428312	-1.359998
H	2.028901	-2.926692	-1.121412
H	4.073950	-1.911079	-0.558289
H	4.372003	-1.646665	-2.308438
H	-3.835036	-1.454673	0.030349
H	0.873962	-2.749446	-3.220740
Cl	-1.685693	-2.340204	-1.901807
C	2.175796	-1.379377	-4.227110
H	3.232528	-1.065027	-4.264496
H	1.899766	-1.710278	-5.240340
H	1.563152	-0.494691	-3.993470
C	2.740435	-3.751175	-3.572049
H	2.469649	-4.115791	-4.574931
H	3.826798	-3.558971	-3.575375
H	2.544944	-4.564691	-2.855275
C	-3.547780	-0.510664	1.921967
H	-3.926610	-1.341547	2.537720
H	-2.455431	-0.623483	1.844488
H	-3.773982	0.422629	2.466010
C	-5.714020	-0.592512	0.613682
H	-6.166780	-0.636884	-0.390094
H	-6.050202	-1.479827	1.171672
H	-6.123825	0.292368	1.129820
H	1.358189	-4.347779	0.429910
O	-0.368885	-0.979833	1.078970
C	0.831630	-1.256636	1.490865
C	1.340990	-2.517361	1.539859
N	1.683717	-0.194342	1.856317
C	1.335036	1.022275	2.403204
C	2.365728	1.937258	2.707618
C	2.077586	3.187469	3.242506
C	0.756869	3.573065	3.483888
C	-0.266202	2.668630	3.193903
C	0.004578	1.410500	2.664410
F	2.632658	-2.669817	1.995622
H	2.653752	-0.459311	1.983964
H	3.403232	1.647459	2.514824
H	2.899782	3.871998	3.469515
H	0.530989	4.557597	3.900174
H	-1.308020	2.945846	3.380417
H	-0.799731	0.716372	2.429653
C	0.688280	-3.761206	1.085039
H	-0.212928	-3.505785	0.509544
H	0.395689	-4.427985	1.917564

TS3

C	-0.330477	-2.797972	-2.833358
C	0.375953	-1.844711	-2.103779
N	-0.199891	-0.722054	-1.682302
C	-1.480628	-0.476930	-1.928974
C	-2.272158	-1.371124	-2.648061
C	-1.675510	-2.545540	-3.103568
Ni	0.846831	0.544031	-0.450723
C	1.787852	-1.924314	-1.698269
C	-1.928422	0.796773	-1.346415
O	2.567262	-2.891692	-2.155771
C	3.870635	-2.660952	-1.568630
C	3.701969	-1.365577	-0.737348
N	2.290998	-1.046265	-0.921307
N	-1.136348	1.561990	-0.694135
C	-1.916836	2.728975	-0.265199
C	-3.350277	2.371071	-0.720251
O	-3.198036	1.149835	-1.475182
C	4.101177	-1.522271	0.734025
C	-1.416151	4.058174	-0.857173
H	0.159758	-3.711391	-3.172435
H	-3.323000	-1.151967	-2.839151
H	-2.263299	-3.271971	-3.668232
H	4.115969	-3.537274	-0.950116
H	4.599425	-2.577872	-2.385562
H	4.288300	-0.533152	-1.164262
H	-1.863566	2.790616	0.833180
H	-4.034957	2.168187	0.115155
H	-3.800510	3.125884	-1.380113
H	3.570436	-2.415883	1.112496
H	-2.258470	4.758586	-0.708625
Cl	2.325373	2.185950	-1.044966
C	-0.214002	4.609509	-0.105992
H	0.654875	3.940182	-0.202680
H	0.074072	5.592760	-0.511042
H	-0.438826	4.742402	0.963846
C	-1.142795	3.943146	-2.351433
H	-0.929268	4.933146	-2.782735
H	-0.266666	3.301587	-2.533705
H	-1.998527	3.522509	-2.905135
C	5.601749	-1.767508	0.833722
H	5.926258	-2.644292	0.250306
H	6.163828	-0.892781	0.465821
H	5.899107	-1.939921	1.879424
C	3.670498	-0.324053	1.567214
H	2.574431	-0.237961	1.584816
H	4.025367	-0.431039	2.604566
H	4.082353	0.614213	1.161700
O	0.341779	-0.423489	1.162906
C	-0.265111	-0.081596	2.263039
C	-0.120989	1.083572	2.941844
N	-1.097200	-1.083802	2.856956
C	-2.123411	-1.663461	2.144934
C	-2.469131	-3.015346	2.330236
C	-3.534854	-3.578144	1.633877
C	-4.280501	-2.819827	0.728638
C	-3.946692	-1.475983	0.544943
C	-2.888912	-0.901763	1.241635
F	-0.834458	1.265301	4.093725
H	-0.596687	-1.722243	3.467835
H	-1.883546	-3.622630	3.026846
H	-3.780459	-4.631543	1.796775
H	-5.112111	-3.267588	0.179547
H	-4.522252	-0.858091	-0.149590
H	-2.648338	0.156015	1.126581
C	0.792759	2.212855	2.655508
H	1.334001	2.071706	1.710416
H	0.244947	3.168197	2.588774

H	1.543488	2.330864	3.458416\

Int3'

C	-1.746759	3.000955	1.7586
C	-1.310388	2.071729	0.816838
N	-0.042749	1.670997	0.769708
C	0.853408	2.131245	1.636268
C	0.516826	3.077166	2.602513
C	-0.806238	3.513631	2.6516
Ni	0.515364	0.258271	-0.613047
C	-2.129986	1.443783	-0.228550
C	2.160027	1.472416	1.483314
O	-3.401109	1.793133	-0.382990
C	-3.911783	0.904474	-1.403029
C	-2.645109	0.360750	-2.079204
N	-1.628059	0.603693	-1.052262
N	2.355484	0.600451	0.571130
C	3.697489	0.056046	0.756172
C	4.234193	0.862033	1.961514
O	3.136849	1.724963	2.342473
C	-2.723670	-1.080348	-2.572298
C	4.563794	0.134289	-0.507296
H	-2.791909	3.309970	1.787629
H	1.268497	3.446991	3.300751
H	-1.110508	4.247702	3.400238
H	-4.489590	0.112481	-0.898005
H	-4.571680	1.479158	-2.063046
H	-2.373631	0.997038	-2.943720
H	3.585318	-1.007664	1.023668
H	4.486455	0.234924	2.827003
H	5.096582	1.497699	1.714431
H	-2.830060	-1.725546	-1.684005
H	5.576094	-0.165625	-0.178279
Cl	1.167169	1.299551	-2.557249
C	4.085849	-0.863085	-1.555376
H	3.087384	-0.585563	-1.928382
H	4.768825	-0.876682	-2.419297
H	4.036081	-1.885427	-1.147862
C	4.626929	1.545177	-1.077904
H	5.343611	1.589943	-1.912756
H	3.639488	1.841358	-1.466706
H	4.948984	2.289790	-0.331973
C	-3.944640	-1.271214	-3.464814
H	-4.890329	-1.080120	-2.933577
H	-3.904849	-0.598720	-4.338334
H	-3.985845	-2.303993	-3.843522
C	-1.449158	-1.469074	-3.308566
H	-0.551513	-1.318588	-2.693897
H	-1.482968	-2.5274	-3.608129
H	-1.326208	-0.861474	-4.220428
O	0.428151	-1.531718	0.175021
C	-0.607190	-2.322746	0.120066
C	-0.628479	-3.484042	-0.585668
N	-1.778756	-1.955974	0.803278
C	-1.903156	-1.127318	1.891768
C	-0.808279	-0.715164	2.680170
C	-1.010907	0.108063	3.782614
C	-2.288577	0.544894	4.141197
C	-3.375925	0.138747	3.365412
C	-3.189808	-0.677261	2.254880
F	-1.784115	-4.232972	-0.537604
H	-2.618972	-2.441520	0.514177
H	0.192770	-1.039047	2.397297
H	-0.145642	0.410639	4.379621
H	-2.433720	1.189607	5.011096
H	-4.387234	0.465885	3.622999
H	-4.047263	-0.987391	1.650430
C	0.419697	-4.017064	-1.477183
H	0.062130	-4.140317	-2.516267
H	1.266657	-3.317663	-1.485758
H	0.793450	-5.003789	-1.146498

TS4

C	0.468136	3.961463	0.078144
C	0.842709	2.627319	0.232317
N	-0.050737	1.681490	0.499673
C	-1.343649	1.972010	0.622057
C	-1.815361	3.274817	0.481413
C	-0.883844	4.276336	0.207338
Ni	0.541333	-0.298559	0.669050
C	2.208613	2.087079	0.141156
C	-2.144765	0.775376	0.914736
O	3.244815	2.901027	-0.012276
C	4.411085	2.045481	-0.081943
C	3.868044	0.629921	0.224106
N	2.426448	0.834655	0.246176
N	-1.589982	-0.373517	0.997404
C	-2.612752	-1.331902	1.399997
C	-3.909173	-0.502316	1.277597
O	-3.449442	0.861658	1.125745
C	4.294311	-0.474822	-0.749272
C	-2.314713	-1.893876	2.797492
H	1.215515	4.725727	-0.137912
H	-2.878888	3.493020	0.581048
H	-1.215659	5.309799	0.088781
H	4.837106	2.143021	-1.091750
H	5.141844	2.406917	0.652430
H	4.165153	0.313975	1.239124
H	-2.606437	-2.171481	0.690412
H	-4.500690	-0.755479	0.385830
H	-4.558204	-0.544833	2.162229
H	3.842222	-1.399124	-0.349678
H	-1.297060	-2.304032	2.711061
Cl	1.245590	-0.707307	2.812200
C	-2.298064	-0.819606	3.874517
H	-3.282358	-0.338574	4.005793
H	-2.021066	-1.260495	4.845017
H	-1.548368	-0.046980	3.648872
C	-3.277818	-3.025993	3.123539
H	-3.037517	-3.473462	4.100528
H	-4.323022	-2.674910	3.173181
H	-3.224492	-3.824779	2.366927
C	3.746403	-0.264533	-2.153127
H	4.065579	-1.086214	-2.813714

H	2.646116	-0.255367	-2.134492
H	4.110931	0.674119	-2.603902
C	5.808364	-0.639349	-0.728216
H	6.184657	-0.804000	0.294369
H	6.115323	-1.500485	-1.341460
H	6.318665	0.249738	-1.135799
O	0.639249	-0.994609	-1.182862
C	-0.267397	-1.684634	-1.802213
C	-0.055336	-2.945450	-2.281887
N	-1.547574	-1.129482	-1.967485
C	-1.829407	0.188993	-2.255735
C	-3.174612	0.607146	-2.263642
C	-3.513293	1.921533	-2.566545
C	-2.524839	2.861500	-2.863722
C	-1.189547	2.453041	-2.857319
C	-0.835152	1.141425	-2.558211
F	-1.069291	-3.526594	-3.007136
H	-2.289711	-1.791437	-2.159997
H	-3.956001	-0.122635	-2.032952
H	-4.567050	2.213828	-2.566145
H	-2.790917	3.894514	-3.099372
H	-0.399325	3.171512	-3.092903
H	0.210956	0.838698	-2.544055
C	0.963005	-3.899969	1.215611
H	1.265800	-4.854606	0.743348
H	0.886040	-4.076667	2.299650
H	1.778881	-3.167842	1.075612
O	-0.276364	-3.439471	0.760565
H	-0.233184	-3.279929	-0.199611
C	1.207502	-3.717020	-2.269862
H	1.626349	-3.824680	-3.287831
H	1.951359	-3.192886	-1.655295
H	1.075393	-4.737617	-1.868867

TS4'

C	-1.254737	3.152887	2.265225
C	-0.982603	2.286986	1.207569
N	0.238058	1.806314	0.998549
C	1.251237	2.126190	1.797939
C	1.076929	2.979504	2.885523
C	-0.200084	3.495820	3.109956
Ni	0.535426	0.504938	-0.556294
C	-1.937753	1.818918	0.192911
C	2.504642	1.470559	1.390700
O	-3.157761	2.333277	0.142748
C	-3.830465	1.603563	-0.909788
C	-2.683518	0.936670	-1.685044
N	-1.591468	0.979137	-0.707776
N	2.563508	0.758098	0.333789
C	3.901921	0.179401	0.267080
C	4.619459	0.824885	1.473450
O	3.588024	1.582806	2.147254
C	-3.004324	-0.446425	-2.240309
C	4.590791	0.397562	-1.085252
H	-2.263711	3.536265	2.421027
H	1.917871	3.233240	3.532048
H	-0.373554	4.169760	3.951374
H	-4.493092	0.865532	-0.429587
H	-4.425285	2.314579	-1.494756
H	-2.362780	1.576289	-2.529588
H	3.794491	-0.907750	0.422447
H	5.023389	0.093443	2.185337
H	5.418129	1.522985	1.182245
H	-3.201515	-1.100811	-1.375196
H	5.639164	0.081385	-0.929277
Cl	0.903990	1.673272	-2.492809
C	3.972853	-0.492944	-2.154853
H	2.924403	-0.216304	-2.342436
H	4.517583	-0.391849	-3.106939
H	3.994472	-1.554674	-1.865150
C	4.573881	1.860695	-1.508868
H	5.181908	2.005007	-2.415493
H	3.543521	2.174646	-1.740558
H	4.978611	2.531884	-0.733811
C	-4.257339	-0.383678	-3.106748
H	-5.145770	-0.058146	-2.542841
H	-4.117682	0.312767	-3.950733
H	-4.483692	-1.374558	-3.529738
C	-1.831643	-1.014865	-3.023607
H	-0.909146	-1.078544	-2.432171
H	-2.066572	-2.027812	-3.385717
H	-1.604205	-0.390130	-3.902978
O	0.580514	-1.183197	0.491637
C	-0.136628	-2.265723	0.432787
C	0.406878	-3.513855	0.380428
N	-1.545356	-2.161638	0.413151
C	-2.281687	-1.475524	1.360151
C	-1.687611	-0.673030	2.352055
C	-2.482153	0.010015	3.269784
C	-3.873972	-0.079871	3.233783
C	-4.466569	-0.886322	2.258940
C	-3.686991	-1.575841	1.336594
F	-0.451835	-4.586545	0.369587
H	-2.019235	-2.964851	0.016061
H	-0.601590	-0.583421	2.374668
H	-1.996000	0.626063	4.031678
H	-4.487598	0.462144	3.956990
H	-5.554977	-0.984946	2.216236
H	-4.162065	-2.211244	0.583564
C	0.592691	-3.663418	-2.994690
H	-0.431884	-3.833841	-2.615654
H	1.181658	-4.575879	-2.772696
H	0.531406	-3.571947	-4.091010
O	1.178623	-2.501645	-2.484848
H	1.019044	-2.498973	-1.529678
C	1.840025	-3.880955	0.404290
H	2.146651	-4.473941	-0.476215
H	2.446924	-2.966141	0.437893
H	2.083755	-4.483408	1.298233

TS4-*i*PrOH

C	0.597504	3.970571	-0.107770
C	0.984023	2.664581	0.186266
N	0.100508	1.747172	0.553206

C	-1.192201	2.033276	0.644481
C	-1.678742	3.308023	0.368784
C	-0.757554	4.284701	-0.009328
Ni	0.716421	-0.147681	0.917664
C	2.347372	2.114553	0.144665
C	-1.973831	0.857413	1.044634
O	3.379765	2.890503	-0.154425
C	4.551985	2.051447	-0.029861
C	3.993834	0.643070	0.281036
N	2.558434	0.886827	0.406845
N	-1.403141	-0.266935	1.241720
C	-2.433520	-1.201421	1.701385
C	-3.732658	-0.409478	1.452766
O	-3.285021	0.942934	1.216201
C	4.296656	-0.439360	-0.763578
C	-2.190750	-1.619288	3.158189
H	1.337389	4.714256	-0.405709
H	-2.744880	3.522430	0.443842
H	-1.099341	5.296717	-0.235331
H	5.112449	2.112083	-0.973034
H	5.170925	2.459246	0.781069
H	4.364393	0.286557	1.254909
H	-2.396966	-2.099279	1.067103
H	-4.275171	-0.743378	0.556510
H	-4.423780	-0.396405	2.305653
H	3.759338	-1.336969	-0.413421
H	-1.158157	-2.002564	3.180710
Cl	1.297888	-0.112884	3.148593
C	-2.268105	-0.449176	4.128425
H	-3.283975	-0.023918	4.185387
H	-1.997405	-0.780242	5.142908
H	-1.563592	0.348317	3.850872
C	-3.139406	-2.743809	3.552108
H	-2.913012	-3.105607	4.566926
H	-4.189949	-2.407125	3.550746
H	-3.062703	-3.601625	2.865163
C	3.762857	-0.091750	-2.145232
H	3.966517	-0.912957	-2.850135
H	2.673233	0.053774	-2.113024
H	4.239091	0.813736	-2.558059
C	5.787645	-0.750479	-0.781942
H	6.155780	-1.029468	0.218268
H	6.001678	-1.586942	-1.464942
H	6.378295	0.114068	-1.128984
O	0.819291	-0.908023	-0.885944
C	-0.017465	-1.672895	-1.520838
C	0.338626	-2.864084	-2.055714
N	-1.353167	-1.249900	-1.648098
C	-1.723916	0.010389	-2.073466
C	-3.090418	0.347188	-2.101350
C	-3.507483	1.605287	-2.523173
C	-2.577997	2.566392	-2.924853
C	-1.221377	2.237134	-2.902661
C	-0.789931	0.982606	-2.483359
F	-0.607009	-3.552699	-2.774092
H	-2.033035	-1.984024	-1.804001
H	-3.825030	-0.399633	-1.787514
H	-4.576238	1.836406	-2.534983
H	-2.906299	3.554873	-3.254441
H	-0.477163	2.972109	-3.221943
H	0.272233	0.740993	-2.460349
C	-0.105905	-4.280796	1.586800
H	-1.152795	-3.923204	1.642823
O	0.714714	-3.241979	1.071196
H	0.470371	-3.097668	0.146024
C	1.671021	-3.497657	-2.061818
H	2.106612	-3.519549	-3.077296
H	2.348469	-2.924709	-1.416180
H	1.643811	-4.538199	-1.696172
C	-0.077325	-5.505875	0.689268
H	-0.722215	-6.302771	1.092485
H	-0.441131	-5.262940	-0.322222
H	0.947650	-5.901159	0.603507
C	0.370571	-4.577511	2.992316
H	0.376219	-3.661988	3.602382
H	-0.282853	-5.316910	3.480227
H	1.396769	-4.978746	2.974875

TS4'-^{i}PrOH

C	-1.569429	2.991772	1.927177
C	-1.239778	2.102156	0.907315
N	-0.016949	1.598913	0.790587
C	0.939577	1.926383	1.649479
C	0.709174	2.807156	2.702619
C	-0.571039	3.342177	2.833759
Ni	0.380649	0.307644	-0.728925
C	-2.135239	1.637414	-0.158829
C	2.211033	1.259491	1.342086
O	-3.338692	2.182592	-0.287278
C	-3.961863	1.490315	-1.387758
C	-2.825397	0.662188	-2.018453
N	-1.762360	0.764873	-1.010855
N	2.331338	0.505049	0.322050
C	3.737430	0.099204	0.250733
C	4.277797	0.541362	1.623638
O	3.265595	1.443343	2.125899
C	-3.236104	-0.764589	-2.376213
C	4.425970	0.735381	-0.966408
H	-2.580418	3.391686	2.003892
H	1.511117	3.061156	3.396268
H	-0.793349	4.033286	3.649055
H	-4.761616	0.854705	-0.974217
H	-4.403602	2.237481	-2.058620
H	-2.439172	1.147806	-2.932890
H	3.787201	-0.994932	0.147453
H	4.363024	-0.293090	2.335445
H	5.232361	1.081857	1.586201
H	-3.620369	-1.229575	-1.450754
H	3.803060	0.459017	-1.831919
Cl	0.930190	1.780140	-2.409252
C	4.463473	2.255408	-0.899472
H	5.098895	2.620660	-0.075715
H	4.876691	2.665357	-1.833893
H	3.454275	2.676792	-0.780187

C	5.811840	0.135970	-1.161409
H	6.285752	0.539439	-2.069428
H	6.477363	0.367547	-0.312808
H	5.767890	-0.960281	-1.263716
C	-4.363724	-0.734005	-3.402462
H	-5.253809	-0.196812	-3.038369
H	-4.031756	-0.244093	-4.333018
H	-4.679628	-1.756669	-3.659273
C	-2.057282	-1.578044	-2.881899
H	-1.249537	-1.640441	-2.143110
H	-2.368733	-2.606069	-3.123740
H	-1.631593	-1.131982	-3.795294
O	0.304600	-1.514498	0.076935
C	-0.733717	-2.267872	0.373613
C	-0.730697	-3.608913	0.280805
N	-1.925266	-1.642945	0.791375
C	-2.052796	-0.907261	1.945000
C	-0.967338	-0.677295	2.812514
C	-1.142494	0.073984	3.969855
C	-2.386769	0.617764	4.298141
C	-3.464305	0.395317	3.439052
C	-3.303466	-0.348829	2.274931
F	-1.864651	-4.277886	0.652668
H	-2.779803	-2.053753	0.437068
H	0.009349	-1.094893	2.562501
H	-0.286261	0.235356	4.630808
H	-2.514126	1.204728	5.210575
H	-4.448290	0.810150	3.674990
H	-4.152689	-0.518434	1.606870
C	2.614093	-2.119656	-2.705520
H	3.191523	-1.731809	-1.846392
O	1.227611	-1.970763	-2.437058
H	1.052131	-2.066109	-1.484301
C	0.338150	-4.501593	-0.202493
H	0.112000	-4.951161	-1.185707
H	1.279858	-3.946574	-0.288818
H	0.502407	-5.329448	0.508034
C	2.938953	-1.276597	-3.922207
H	2.628410	-0.234413	-3.755717
H	4.017128	-1.298457	-4.145112
H	2.398016	-1.656000	-4.804773
C	2.983921	-3.580846	-2.906889
H	4.057045	-3.688006	-3.133709
H	2.768188	-4.177353	-2.007671
H	2.410523	-4.008773	-3.745184

Int4

C	1.006119	3.982097	0.282981
C	1.215300	2.604402	0.321049
N	0.211529	1.756963	0.504400
C	-1.031790	2.184023	0.680174
C	-1.343673	3.542430	0.665027
C	-0.299643	4.443964	0.456694
Ni	0.599361	-0.251109	0.668990
C	2.503176	1.899736	0.226089
C	-1.963444	1.063421	0.881187
O	3.634508	2.587179	0.144148
C	4.695755	1.606340	0.120362
C	3.969720	0.247955	0.268447
N	2.562265	0.625390	0.282069
N	-1.539847	-0.142558	0.901747
C	-2.692906	-1.013381	1.107433
C	-3.872364	-0.014582	1.188533
O	-3.256947	1.286074	1.046114
C	4.284709	-0.785560	-0.818863
C	-2.516852	-1.936229	2.320206
H	1.839334	4.668981	0.129347
H	-2.370915	3.879045	0.809054
H	-0.503807	5.516454	0.434888
H	5.234070	1.716308	-0.832455
H	5.382805	1.828992	0.947151
H	4.197129	-0.206271	1.247842
H	-2.792652	-1.649800	0.213050
H	-4.598885	-0.131224	0.374342
H	-4.401685	-0.031595	2.151925
H	3.700908	-1.680175	-0.542893
H	-1.597482	-2.506287	2.106496
Cl	1.111577	0.018483	2.971624
C	-2.293958	-1.171396	3.616335
H	-3.149617	-0.522146	3.868654
H	-2.165159	-1.874499	4.454705
H	-1.380733	-0.558516	3.555039
C	-3.686719	-2.906802	2.412323
H	-3.528096	-3.633630	3.223989
H	-4.633776	-2.382300	2.625535
H	-3.819897	-3.472839	1.476063
C	3.822479	-0.335475	-2.197184
H	4.046579	-1.108362	-2.949005
H	2.735521	-0.160938	-2.202463
H	4.333515	0.587218	-2.520281
C	5.759944	-1.161169	-0.787373
H	6.070987	-1.497742	0.214814
H	5.968579	-1.977472	-1.495973
H	6.402291	-0.310609	-1.071148
O	0.450095	-0.597122	-1.382339
C	-0.300972	-1.544439	-1.802579
C	0.104004	-2.873428	-1.870901
N	-1.630447	-1.289952	-2.134325
C	-2.283893	-0.083478	-2.285403
C	-3.685882	-0.107790	-2.430605
C	-4.407206	1.067915	-2.605387
C	-3.757243	2.303296	-2.638139
C	-2.368812	2.331328	-2.504028
C	-1.630637	1.162957	-2.333184
F	-0.833080	-3.755919	-2.398237
H	-2.167288	-2.114720	-2.376315
H	-4.204221	-1.071177	-2.405539
H	-5.494071	1.015696	-2.714939
H	-4.324050	3.227674	-2.771294
H	-1.837951	3.287133	-2.536415
H	-0.548545	1.189272	-2.222597
C	1.677821	-3.034548	1.494289
H	1.366275	-4.077053	1.676339
H	1.869285	-2.540834	2.456988

H	2.613988	-3.043750	0.908648
O	0.656632	-2.308512	0.856281
H	0.386162	-2.703123	-0.022534
C	1.504009	-3.335716	-2.056216
H	1.730433	-3.527033	-3.123388
H	2.189359	-2.554389	-1.705908
H	1.729356	-4.265263	-1.505372

Int4'

C	-0.799499	3.326621	1.846351
C	-0.633191	2.314822	0.900329
N	0.515651	1.663726	0.768137
C	1.554359	1.955841	1.543627
C	1.484348	2.943914	2.524658
C	0.282087	3.634767	2.669040
Ni	0.701432	0.147991	-0.645478
C	-1.669804	1.864435	-0.039409
C	2.745614	1.150548	1.233819
O	-2.788193	2.576192	-0.122700
C	-3.631871	1.871505	-1.053770
C	-2.715846	0.781497	-1.650153
N	-1.526351	0.846178	-0.795080
N	2.763493	0.307720	0.274856
C	4.123890	-0.227638	0.197433
C	4.783701	0.331679	1.474790
O	3.844722	1.315649	1.960168
C	-3.387912	-0.590582	-1.699889
C	4.832828	0.172305	-1.105822
H	-1.751888	3.851185	1.930177
H	2.350245	3.164927	3.149687
H	0.189201	4.418097	3.424154
H	-4.470838	1.444330	-0.481868
H	-4.016040	2.592415	-1.786321
H	-2.390199	1.048420	-2.672847
H	4.078892	-1.326371	0.236712
H	4.908902	-0.428057	2.260325
H	5.746425	0.830048	1.296897
H	-3.681183	-0.835650	-0.664991
H	5.874320	-0.176136	-0.976038
Cl	1.144758	1.617840	-2.429044
C	4.224208	-0.544289	-2.302760
H	3.196699	-0.190683	-2.472086
H	4.808732	-0.342501	-3.214341
H	4.199009	-1.635090	-2.150728
C	4.840722	1.681253	-1.316895
H	5.458061	1.944358	-2.189914
H	3.818141	2.043179	-1.509717
H	5.250154	2.227020	-0.451404
C	-4.646479	-0.526325	-2.557324
H	-5.382694	0.198059	-2.175090
H	-4.402382	-0.243944	-3.595444
H	-5.141528	-1.509242	-2.587612
C	-2.440773	-1.663788	-2.205536
H	-1.518529	-1.699512	-1.613998
H	-2.914526	-2.656919	-2.158877
H	-2.161561	-1.473313	-3.254882
O	0.238654	-1.186338	0.942073
C	-0.234576	-2.359442	0.777775
C	0.499725	-3.406240	0.210541
N	-1.558153	-2.636085	1.089267
C	-2.550029	-1.806406	1.576388
C	-2.310134	-0.524560	2.104700
C	-3.373463	0.257036	2.548508
C	-4.688773	-0.208681	2.499967
C	-4.926417	-1.493490	2.006836
C	-3.875711	-2.282821	1.552768
F	-0.164943	-4.630800	0.157847
H	-1.839853	-3.589257	0.889584
H	-1.285519	-0.161583	2.138249
H	-3.164418	1.254390	2.946287
H	-5.514524	0.414572	2.851014
H	-5.945726	-1.887399	1.967475
H	-4.071802	-3.282055	1.152829
C	0.918613	-1.770660	-3.185692
H	0.067630	-2.401476	-3.491421
H	1.850418	-2.258579	-3.521334
H	0.836197	-0.791118	-3.677567
O	0.928476	-1.555143	-1.798302
H	0.671223	-2.370212	-1.256455
C	1.971693	-3.547831	0.379082
H	2.488053	-3.920013	-0.522855
H	2.385218	-2.560841	0.624653
H	2.216412	-4.238603	1.209217

TS5

C	1.031903	-3.896383	0.150267
C	1.244751	-2.537563	-0.074710
N	0.243430	-1.718147	-0.369431
C	-1.003374	-2.156979	-0.462586
C	-1.321284	-3.498455	-0.253264
C	-0.277732	-4.370626	0.056379
Ni	0.656764	0.254788	-0.764357
C	2.530622	-1.823777	-0.050425
C	-1.941456	-1.071833	-0.788200
O	3.664496	-2.485386	0.128770
C	4.721066	-1.507182	-0.007771
C	3.980737	-0.160481	-0.187461
N	2.580518	-0.561323	-0.237579
N	-1.529610	0.118992	-1.010473
C	-2.704881	0.915990	-1.373703
C	-3.873712	-0.040437	-1.055135
O	-3.239991	-1.323068	-0.854686
C	4.230390	0.879109	0.912940
C	-2.679209	1.374441	-2.841631
H	1.863797	-4.559506	0.390688
H	-2.353140	-3.843365	-0.327898
H	-0.485519	-5.429105	0.226381
H	5.346103	-1.556908	0.894511
H	5.327718	-1.787416	-0.879815
H	4.238037	0.297476	-1.156370
H	-2.738394	1.806445	-0.726844
H	-4.402084	0.216430	-0.126537
H	-4.599744	-0.138524	-1.873559
H	3.601805	1.742116	0.636605

H	-3.679241	1.817170	-3.008493
Cl	1.159454	-0.233219	-3.026428
C	-1.628400	2.447504	-3.082526
H	-0.620976	2.038955	-2.920677
H	-1.694109	2.824564	-4.115717
H	-1.759047	3.302249	-2.399887
C	-2.493643	0.203994	-3.800184
H	-1.481332	-0.217904	-3.688604
H	-3.231146	-0.598908	-3.637966
H	-2.604148	0.540926	-4.842837
C	3.777328	0.394063	2.282523
H	2.701719	0.161359	2.278322
H	4.331872	-0.503058	2.606169
H	3.950563	1.171374	3.042916
C	5.683701	1.331393	0.903088
H	5.841400	2.147814	1.624604
H	6.368229	0.512556	1.181601
H	5.985427	1.698464	-0.091089
O	0.293978	0.647257	1.364914
C	-0.419654	1.652300	1.614211
C	0.054019	2.991158	1.363276
N	-1.718558	1.536527	2.029089
C	-2.470021	0.400447	2.305949
C	-1.922626	-0.890807	2.384546
C	-2.746765	-1.975293	2.676387
C	-4.112253	-1.807109	2.901463
C	-4.653735	-0.521723	2.838906
C	-3.845132	0.570837	2.545053
F	-0.937844	3.950442	1.652880
H	-2.184081	2.426779	2.174788
H	-0.856486	-1.019961	2.211044
H	-2.303842	-2.973535	2.731320
H	-4.748085	-2.665753	3.129474
H	-5.720623	-0.365014	3.018884
H	-4.272870	1.576160	2.493378
C	1.896773	2.876800	-1.616304
H	2.814609	2.920373	-0.996095
H	1.625576	3.916834	-1.879502
H	2.145376	2.341418	-2.547741
O	0.842779	2.225912	-0.982445
H	0.430191	2.731720	-0.045581
C	1.357487	3.398512	1.986613
H	1.244989	3.615324	3.065876
H	2.081770	2.581142	1.880147
H	1.781628	4.293201	1.503219

TS5'

C	-0.779530	3.330476	1.817755
C	-0.608499	2.321461	0.869293
N	0.542500	1.675263	0.737476
C	1.576941	1.964971	1.519379
C	1.503094	2.950082	2.502843
C	0.299568	3.639842	2.643401
Ni	0.762828	0.180206	-0.697019
C	-1.644306	1.861997	-0.067037
C	2.762502	1.149789	1.214973
O	-2.772615	2.559792	-0.140572
C	-3.615269	1.845404	-1.065118
C	-2.693604	0.760526	-1.663067
N	-1.494363	0.844638	-0.822512
N	2.771390	0.309786	0.252941
C	4.123172	-0.246292	0.177515
C	4.781500	0.289598	1.465458
O	3.859459	1.292148	1.947676
C	-3.346593	-0.621891	-1.688514
C	4.847793	0.161394	-1.114792
H	-1.733748	3.851692	1.901763
H	2.365733	3.169359	3.133050
H	0.203026	4.421752	3.399530
H	-4.448825	1.415092	-0.487785
H	-4.008565	2.560713	-1.798432
H	-2.384689	1.021615	-2.692278
H	4.058712	-1.344459	0.203068
H	4.880699	-0.477263	2.247870
H	5.756909	0.767261	1.301218
H	-3.608844	-0.862550	-0.644254
H	5.882702	-0.205224	-0.982077
Cl	1.190043	1.705530	-2.433254
C	4.237775	-0.525913	-2.327763
H	3.217860	-0.153001	-2.501190
H	4.835611	-0.321300	-3.230076
H	4.189981	-1.617982	-2.192300
C	4.880944	1.673195	-1.303208
H	5.507089	1.938493	-2.169253
H	3.865303	2.054196	-1.496747
H	5.294551	2.200283	-0.428219
C	-4.628305	-0.586055	-2.512583
H	-5.370801	0.122360	-2.112993
H	-4.416743	-0.300701	-3.556979
H	-5.101693	-1.579959	-2.529100
C	-2.395155	-1.683273	-2.211750
H	-1.437018	-1.667881	-1.679313
H	-2.830603	-2.689099	-2.103665
H	-2.183431	-1.522228	-3.281574
O	0.204864	-1.139515	0.976923
C	-0.275604	-2.281537	0.760512
C	0.459421	-3.272715	0.022090
N	-1.557429	-2.605451	1.111563
C	-2.571089	-1.798511	1.615831
C	-2.352315	-0.509307	2.127530
C	-3.431100	0.252928	2.569755
C	-4.733431	-0.246724	2.532675
C	-4.946599	-1.541109	2.054493
C	-3.879988	-2.310520	1.602410
F	-0.268426	-4.467161	-0.126404
H	-1.821875	-3.555276	0.869747
H	-1.336860	-0.121319	2.151285
H	-3.244683	1.259551	2.954369
H	-5.571922	0.360765	2.881223
H	-5.957087	-1.957268	2.025539
H	-4.052328	-3.317887	1.212557
C	0.911073	-1.681894	-3.175272
H	0.179193	-2.465524	-3.445126
H	1.890045	-1.987244	-3.591518

H	0.618779	-0.740676	-3.668498
O	0.973225	-1.495944	-1.794672
H	0.674978	-2.391581	-1.164634
C	1.869644	-3.556704	0.447236
H	2.469344	-3.997298	-0.365838
H	2.344143	-2.610907	0.742118
H	1.906718	-4.245371	1.312496

TS5”

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C	2.673417	1.200570	-1.673950
N	1.473198	1.440514	-1.165318
C	0.707499	2.421409	-1.624359
C	1.121595	3.233668	-2.678609
C	2.377194	2.982243	-3.234202
Ni	0.846306	0.372715	0.480889
C	3.352567	0.113458	-0.950779
C	-0.566879	2.492833	-0.892565
O	4.598632	-0.219141	-1.257618
C	4.984896	-1.237196	-0.305893
C	3.719660	-1.462432	0.556338
N	2.775517	-0.493111	0.013653
N	-0.815970	1.674010	0.055885
C	-2.150872	1.969606	0.559728
C	-2.630508	3.101864	-0.379700
O	-1.484694	3.389282	-1.215656
C	3.151487	-2.886470	0.531553
C	-2.136182	2.293773	2.059234
H	4.167548	1.749956	-3.142431
H	0.482472	4.035949	-3.049305
H	2.737512	3.595879	-4.062486
H	5.299774	-2.125177	-0.872063
H	5.840809	-0.855249	0.266775
H	3.912573	-1.188350	1.606775
H	-2.772600	1.070008	0.418766
H	-3.453498	2.796161	-1.040014
H	-2.908576	4.027859	0.142740
H	2.236917	-2.846669	1.143465
H	-1.667230	1.410469	2.525358
Cl	1.991893	1.928486	1.861498
C	-1.275121	3.504069	2.389393
H	-1.646700	4.423756	1.906022
H	-1.279681	3.687333	3.475771
H	-0.229195	3.332525	2.089550
C	-3.559876	2.435161	2.579361
H	-3.564314	2.582498	3.670423
H	-4.071445	3.303682	2.130389
H	-4.163958	1.539981	2.358933
C	2.731003	-3.318195	-0.865288
H	2.283874	-4.323559	-0.834418
H	1.971679	-2.631749	-1.267442
H	3.584648	-3.360793	-1.563405
C	4.126693	-3.860091	1.178357
H	4.392882	-3.546410	2.200775
H	3.686041	-4.867129	1.240854
H	5.062320	-3.948440	0.600342
O	-0.058881	-1.055881	-0.910367
C	-1.117367	-1.603401	-0.518333
C	-1.144543	-2.464337	0.641135
N	-2.329547	-1.281590	-1.078219
C	-2.636905	-0.313614	-2.032938
C	-3.988895	0.036710	-2.189686
C	-4.370578	0.989043	-3.129146
C	-3.413249	1.617725	-3.926955
C	-2.072443	1.264499	-3.777937
C	-1.675816	0.304916	-2.849237
F	0.008105	-3.263127	0.695995
H	-3.130200	-1.790057	-0.721192
H	-4.741302	-0.447120	-1.559986
H	-5.428277	1.245250	-3.232899
H	-3.710889	2.370903	-4.660124
H	-1.310732	1.741623	-4.400785
H	-0.630788	0.026000	-2.733252
C	0.669763	-0.985458	3.135108
H	-0.012153	-1.353007	3.925888
H	1.234957	-0.127912	3.535485
H	1.393161	-1.796841	2.920502
O	-0.041610	-0.579632	2.007238
H	-0.700886	-1.424939	1.530693
C	-2.344440	-3.293807	0.986786
H	-3.235817	-2.665558	1.143589
H	-2.587711	-4.060886	0.226154
H	-2.167444	-3.816905	1.939185

TS5-O

C	0.565067	-2.358838	-2.730299
C	1.338860	-1.555167	-1.895954
N	0.796612	-0.569365	-1.191853
C	-0.504535	-0.310342	-1.239751
C	-1.362638	-1.058806	-2.041216
C	-0.803721	-2.093240	-2.793719
Ni	1.994006	0.526823	0.060487
C	2.790133	-1.630366	-1.652570
C	-0.845652	0.817531	-0.356920
O	3.555791	-2.504955	-2.275828
C	4.895634	-2.308108	-1.749349
C	4.775606	-1.059691	-0.844814
N	3.338687	-0.814533	-0.833552
N	0.073442	1.415787	0.305508
C	-0.552038	2.508930	1.047245
C	-2.056062	2.248990	0.812286
O	-2.089634	1.232970	-0.222822
H	1.017443	-3.167240	-3.305956
H	-2.430958	-0.842835	-2.070168
H	-1.444786	-2.705013	-3.431537
H	5.172252	-3.222468	-1.204181
H	5.574608	-2.175010	-2.600494
H	5.253414	-0.187966	-1.322993
H	-0.309916	2.392204	2.113645
H	-2.557592	1.832487	1.697191
H	-2.619841	3.119006	0.450604
Cl	3.362188	2.342350	0.022175
H	2.693088	1.947477	4.425753
O	1.681670	-0.659577	1.669077

C	0.861534	-0.298947	2.564148
C	1.245587	0.576629	3.656324
N	-0.394031	-0.797942	2.617741
C	-0.977240	-1.739780	1.766038
C	-2.377091	-1.731963	1.657060
C	-3.030754	-2.666864	0.860529
C	-2.301681	-3.623650	0.153458
C	-0.910760	-3.635007	0.261635
C	-0.244942	-2.706713	1.057848
F	0.161127	1.399765	4.045548
H	-0.938764	-0.586751	3.480700
H	-2.947527	-0.984140	2.213255
H	-4.121579	-2.645368	0.792508
H	-2.814206	-4.358292	-0.472338
H	-0.327845	-4.386600	-0.277344
H	0.839385	-2.724195	1.145509
C	2.486831	1.396997	3.494997
H	3.343384	0.732945	3.308687
H	2.446115	2.116437	2.659151
C	1.301808	-0.128203	6.878077
H	0.815475	-0.515576	7.798382
H	1.006962	0.943012	6.803523
H	2.394998	-0.132129	7.087225
O	0.965736	-0.880805	5.770330
H	1.271860	-0.253223	4.721385
C	-2.139734	0.201755	5.810943
H	-3.186705	0.282770	5.469980
H	-1.663177	1.187623	5.653393
H	-2.171878	0.017632	6.903389
O	-1.506529	-0.828416	5.117909
H	-0.547879	-0.904314	5.457131
C	-0.020755	3.870110	0.576488
H	1.071878	3.813331	0.716798
C	5.355026	-1.184389	0.567932
H	5.144342	-0.208990	1.039696
C	-0.571914	4.982298	1.457213
H	-0.128738	5.951986	1.183014
H	-1.665747	5.081268	1.353671
H	-0.349706	4.798678	2.520484
C	-0.277519	4.122404	-0.902135
H	-1.354347	4.170547	-1.136427
H	0.164903	5.082537	-1.209576
H	0.176740	3.338647	-1.528059
C	4.673494	-2.263615	1.396041
H	5.093422	-2.281588	2.413790
H	3.594250	-2.070627	1.486692
H	4.820877	-3.269217	0.967472
C	6.864903	-1.370676	0.502402
H	7.348083	-0.567679	-0.076949
H	7.301132	-1.364822	1.512928
H	7.134225	-2.333328	0.035554

Int5

C	-0.634103	3.727531	-1.234106
C	-1.008414	2.420430	-0.929661
N	-0.140150	1.413801	-0.969689
C	1.125021	1.621011	-1.303919
C	1.596347	2.891950	-1.636513
C	0.693854	3.953028	-1.598673
Ni	-0.913944	-0.526234	-0.671732
C	-2.354429	1.962767	-0.549414
C	1.947489	0.401708	-1.239936
O	-3.363088	2.811628	-0.419106
C	-4.518313	2.008375	-0.068161
C	-3.980340	0.557911	-0.007174
N	-2.577949	0.722880	-0.349228
N	1.467771	-0.733861	-0.909686
C	2.576101	-1.690223	-0.922556
C	3.791146	-0.824177	-1.325552
O	3.245955	0.497279	-1.511782
C	-4.137964	-0.183845	1.326647
C	2.308028	-2.894143	-1.835117
H	-1.361652	4.539272	-1.191593
H	2.642965	3.039572	-1.904349
H	1.026365	4.962356	-1.849866
H	-4.907877	2.381473	0.889728
H	-5.278663	2.157522	-0.846206
H	-4.447932	-0.059808	-0.791738
H	2.699856	-2.072510	0.104252
H	4.561790	-0.765678	-0.545140
H	4.259344	-1.138999	-2.269514
H	-3.588015	-1.128769	1.173627
H	3.260966	-3.455414	-1.864118
Cl	-1.293892	-0.653720	-2.995025
C	1.236470	-3.785853	-1.221811
H	0.302161	-3.224973	-1.054442
H	1.017448	-4.645350	-1.874674
H	1.558566	-4.179241	-0.243768
C	1.944318	-2.470424	-3.251427
H	1.847652	-3.353274	-3.902782
H	0.982337	-1.931024	-3.262136
H	2.709221	-1.816804	-3.702437
C	-3.476213	0.546668	2.486421
H	-3.563073	-0.047846	3.409535
H	-2.405278	0.703780	2.290944
H	-3.948255	1.523003	2.689010
C	-5.603214	-0.491818	1.596882
H	-6.057462	-1.055333	0.766236
H	-5.713954	-1.094896	2.511362
H	-6.191884	0.430696	1.739625
O	-0.191448	-0.051815	1.541212
C	0.622717	-0.853321	1.995411
C	0.214670	-2.286443	2.258028
N	1.901552	-0.559649	2.305686
C	2.602747	0.633518	2.094037
C	4.0036	0.570531	2.115429
C	4.761051	1.716883	1.901641
C	4.133762	2.941218	1.666177
C	2.741337	3.003023	1.656701
C	1.968735	1.862401	1.868734
F	1.358432	-3.066318	2.464024
H	2.452078	-1.351606	2.626487
H	4.492828	-0.390158	2.299454
H	5.851816	1.650951	1.917438

H	4.728098	3.841875	1.495590
H	2.237766	3.956785	1.479671
H	0.882152	1.910477	1.849588
C	-2.426428	-2.988243	-0.782609
H	-2.606820	-3.982294	-0.312255
H	-2.116461	-3.186112	-1.832907
H	-3.434260	-2.510431	-0.862671
O	-1.519976	-2.252184	-0.065686
H	-0.311174	-2.625204	1.340800
C	-0.690340	-2.399002	3.459468
H	-0.186393	-2.049271	4.374086
H	-1.591309	-1.792494	3.294766
H	-0.998159	-3.445838	3.595737

Int6

C	1.221194	3.507468	-0.091815
C	1.189298	2.117345	0.002932
N	0.067426	1.429603	-0.190075
C	-1.068866	2.048242	-0.492957
C	-1.139026	3.435732	-0.609998
C	0.030622	4.165973	-0.399663
Ni	0.073704	-0.637001	0.133954
C	2.327290	1.233222	0.299362
C	-2.177973	1.101907	-0.690996
O	3.550989	1.721958	0.446715
C	4.409219	0.577555	0.678287
C	3.451007	-0.639208	0.651948
N	2.157100	-0.026529	0.398784
N	-2.004322	-0.157720	-0.564315
C	-3.307275	-0.795366	-0.733384
C	-4.188799	0.366026	-1.240005
O	-3.387398	1.547359	-1.003232
C	3.759977	-1.723887	-0.389441
C	-3.771537	-1.455286	0.574967
H	2.151369	4.053699	0.070745
H	-2.081291	3.925202	-0.859745
H	0.015171	5.254761	-0.480522
H	5.167532	0.561649	-0.118144
H	4.908592	0.720078	1.645757
H	3.412631	-1.121676	1.642828
H	-3.221655	-1.581406	-1.499184
H	-4.390556	0.311021	-2.319792
H	-5.139103	0.482641	-0.702571
H	2.948800	-2.462070	-0.274621
H	-2.945889	-2.126354	0.868884
Cl	-0.425660	-0.447720	2.389606
C	-3.965538	-0.451935	1.703108
H	-4.757660	0.281089	1.475511
H	-4.263430	-0.974362	2.625735
H	-3.025275	0.075995	1.921933
C	-5.019956	-2.290737	0.326712
H	-5.323274	-2.819644	1.243292
H	-5.871159	-1.661834	0.014765
H	-4.854601	-3.045725	-0.458619
C	3.665813	-1.198609	-1.814270
H	3.903645	-1.998879	-2.532625
H	2.640308	-0.860985	-2.023874
H	4.366653	-0.368286	-2.007452
C	5.098892	-2.383017	-0.091793
H	5.137960	-2.772739	0.938279
H	5.278211	-3.226942	-0.775763
H	5.938923	-1.678296	-0.215946
C	-0.420794	-2.891848	-1.577456
H	0.052397	-3.779676	-2.056363
H	-1.270941	-3.299828	-0.979806
H	-0.890634	-2.321765	-2.414562
O	0.484292	-2.166485	-0.849255

3b

O	-1.272709	1.697405	-0.295854
C	-1.394261	0.487034	-0.240251
C	-2.785684	-0.135468	-0.312524
N	-0.390134	-0.415275	-0.119974
C	0.987951	-0.194013	-0.038426
C	1.563097	1.085338	-0.042942
C	2.948275	1.215265	0.044536
C	3.773780	0.095715	0.136418
C	3.197695	-1.175659	0.140212
C	1.817795	-1.322261	0.053366
F	-2.702621	-1.520311	-0.216214
H	-0.687007	-1.386575	-0.091519
H	0.918420	1.959102	-0.114998
H	3.385748	2.217201	0.040313
H	4.858037	0.211507	0.204458
H	3.828146	-2.065773	0.210841
H	1.367396	-2.318972	0.055475
C	-3.691547	0.394513	0.768128
H	-3.748683	1.488784	0.693050
H	-4.702217	-0.022871	0.656039
H	-3.299095	0.127969	1.761303
H	-3.187159	0.097328	-1.313484

Si(OMe)$_3$H

Si	0.003847	0.014540	0.283004
H	-0.015204	0.022245	1.773738
O	1.530394	-0.240131	-0.280243
O	-0.964860	-1.182124	-0.300779
O	-0.531541	1.455337	-0.307683
C	0.000235	2.707371	0.043078
H	-0.649738	3.496517	-0.365598
H	0.053965	2.847861	1.138442
H	1.013643	2.850283	-0.370707
C	-2.316194	-1.355767	0.041356
H	-2.954045	-0.575708	-0.409555
H	-2.655373	-2.333298	-0.335113
H	-2.477781	-1.340884	1.135071
C	2.317256	-1.360196	0.036102
H	1.904647	-2.285177	-0.402871
H	3.328971	-1.210018	-0.371488
H	2.411778	-1.510852	1.127356

TS6

C	-0.857572	-3.202059	2.400095
C	-0.907530	-2.153028	1.483944

N	0.155459	-1.813808	0.764309
C	1.313078	-2.449336	0.888735
C	1.463710	-3.515224	1.774367
C	0.352118	-3.886629	2.532816
Ni	-0.047084	-0.344152	-0.693588
C	-2.050368	-1.274575	1.176185
C	2.335984	-1.856237	0.010132
O	-3.213445	-1.396911	1.796499
C	-4.046089	-0.322447	1.286094
C	-3.202789	0.321599	0.160730
N	-1.924779	-0.359031	0.294760
N	2.050172	-0.847331	-0.721022
C	3.273364	-0.427473	-1.392306
C	4.247648	-1.579488	-1.065585
O	3.569859	-2.335313	-0.030098
C	-3.757208	0.183305	-1.263921
C	3.699193	0.967922	-0.909460
H	-1.734522	-3.472756	2.989869
H	2.418544	-4.033772	1.869908
H	0.430295	-4.716570	3.238231
H	-4.991605	-0.763925	0.943246
H	-4.252253	0.362096	2.120764
H	-3.034016	1.392320	0.348099
H	3.078530	-0.373868	-2.474406
H	4.411563	-2.256365	-1.916302
H	5.219204	-1.254431	-0.670678
H	-2.947988	0.571758	-1.905357
H	2.812188	1.606347	-1.058882
C	4.047215	1.004851	0.572324
H	4.953230	0.418486	0.800010
H	4.241190	2.040489	0.889904
H	3.226947	0.625944	1.199912
C	4.833094	1.505241	-1.770633
H	5.102201	2.528508	-1.466316
H	5.741209	0.885318	-1.678876
H	4.551526	1.533540	-2.835312
C	-4.015950	-1.261896	-1.662718
H	-4.374241	-1.308187	-2.703302
H	-3.087952	-1.851564	-1.614713
H	-4.788468	-1.736500	-1.033764
C	-4.991086	1.058731	-1.431954
H	-4.778847	2.110708	-1.181875
H	-5.354302	1.026731	-2.470820
H	-5.818683	0.719347	-0.785408
O	-0.212207	1.406504	-1.443268
C	0.313065	1.641978	-2.688240
H	1.418697	1.809391	-2.698838
H	0.126334	0.806190	-3.398627
H	-0.122037	2.550421	-3.164555
Si	0.528795	2.285098	1.111307
H	0.716945	0.837495	0.877353
O	1.321613	2.394585	2.576427
O	1.264122	3.397181	0.148721
O	-1.058457	2.722809	1.341475
C	-1.749720	2.400410	2.519091
H	-2.809356	2.675376	2.396774
H	-1.703781	1.322560	2.760297
H	-1.359784	2.951092	3.393563
C	0.635098	4.232154	-0.789939
H	0.423550	5.219072	-0.341500
H	1.310618	4.385182	-1.646324
H	-0.302653	3.794269	-1.160682
C	1.619338	3.625512	3.178189
H	0.811478	4.370426	3.055453
H	1.770496	3.472470	4.259658
H	2.543603	4.066612	2.764673
Cl	-0.524870	-1.873969	-2.374688

Int7

C	0.872891	-4.000005	1.361177
C	0.910437	-2.808981	0.638642
N	-0.161955	-2.033698	0.530162
C	-1.311822	-2.347168	1.115289
C	-1.448420	-3.514616	1.864479
C	-0.331895	-4.345115	1.976448
Ni	-0.047401	-0.320124	-0.602675
C	2.056741	-2.223525	-0.076848
C	-2.331198	-1.315757	0.858297
O	3.220799	-2.848264	-0.147920
C	4.064911	-2.016258	-0.984106
C	3.221808	-0.744906	-1.244241
N	1.938683	-1.086318	-0.646900
N	-2.047792	-0.302579	0.131818
C	-3.261226	0.492383	-0.016169
C	-4.212186	-0.165667	1.005497
O	-3.550886	-1.406997	1.363362
C	3.770314	0.562334	-0.655804
C	-3.737402	0.486269	-1.477286
H	1.757284	-4.633484	1.441182
H	-2.396147	-3.763822	2.343753
H	-0.400332	-5.270228	2.552463
H	5.001266	-1.831757	-0.440084
H	4.286649	-2.582420	-1.899221
H	3.066210	-0.595807	-2.324612
H	-3.026539	1.530594	0.260138
H	-4.324793	0.424760	1.926361
H	-5.206483	-0.412210	0.611206
H	2.987833	1.317908	-0.836720
H	-2.865151	0.826034	-2.060600
Cl	-0.544871	-1.225653	-2.681938
C	-4.097390	-0.905406	-1.976594
H	-4.947395	-1.341574	-1.424999
H	-4.387205	-0.863609	-3.038285
H	-3.231075	-1.579694	-1.907590
C	-4.873946	1.481185	-1.664362
H	-5.169032	1.541409	-2.723271
H	-5.769896	1.187114	-1.091319
H	-4.582344	2.492339	-1.337845
C	3.977172	0.482608	0.849900
H	4.284864	1.462180	1.245599
H	3.050631	0.195663	1.369178
H	4.763501	-0.240489	1.125783

C	5.037603	0.986636	-1.384435
H	4.869039	1.073177	-2.469805
H	5.384829	1.966269	-1.020926
H	5.860809	0.268599	-1.227413
C	-0.004721	2.310782	-2.274203
H	-0.015196	1.601065	-3.116453
H	-0.971785	2.842094	-2.242754
H	0.792018	3.057347	-2.442082
O	0.226833	1.600427	-1.095932
Si	0.284369	2.234891	0.567312
H	0.403450	0.699881	0.890314
O	-1.154914	3.081963	0.308749
O	0.249465	2.475761	2.287997
O	1.698489	3.090515	0.212920
C	2.333514	4.027057	1.025016
H	3.387641	3.741169	1.199573
H	2.342904	5.018721	0.534700
H	1.842953	4.141710	2.006198
C	1.002824	1.718334	3.164428
H	2.067316	2.029642	3.208564
H	0.597259	1.807266	4.189260
H	0.997254	0.636257	2.908069
C	-1.787444	3.934120	1.211638
H	-2.032937	3.435848	2.165272
H	-1.173769	4.821082	1.457962
H	-2.726405	4.298467	0.757966

Int8

O	1.302079	-1.641107	0.000675
C	1.415057	-0.417690	0.000219
C	2.727991	0.204938	0.000141
N	0.369952	0.471196	-0.000631
C	-0.997646	0.210211	-0.000181
C	-1.866005	1.315958	0.000434
C	-3.243582	1.132425	0.000607
C	-3.785697	-0.154161	0.000200
C	-2.925069	-1.250880	-0.000453
C	-1.541225	-1.084990	-0.000695
F	2.773565	1.541390	-0.000610
H	0.623466	1.454038	-0.000851
H	-1.445394	2.325772	0.000726
H	-3.900121	2.006484	0.001060
H	-4.868576	-0.298839	0.000344
H	-3.333797	-2.265004	-0.000848
H	-0.870829	-1.941865	-0.001230
C	4.011963	-0.501445	0.000372
H	3.832003	-1.583111	0.000437
H	4.610261	-0.232838	-0.888152
H	4.609884	-0.232862	0.889154

Int9

C	1.823470	-1.618804	-2.367811
C	1.206864	-0.492529	-1.844003
N	-0.011621	-0.552366	-1.241588
C	-0.643190	-1.753169	-1.140947
C	-0.086124	-2.920671	-1.641000
C	1.167402	-2.854988	-2.267221
Ni	-0.827669	1.039767	-0.530083
C	1.696705	0.874207	-1.824683
C	-1.913313	-1.583753	-0.458827
O	2.891009	1.222140	-2.288194
C	2.992274	2.652467	-2.107895
C	1.711604	3.043597	-1.333318
N	0.958137	1.799012	-1.310854
N	-2.244086	-0.413780	-0.025493
C	-3.592972	-0.500804	0.516635
C	-3.875007	-2.020187	0.476262
O	-2.775440	-2.576936	-0.277925
C	1.927393	3.584877	0.088711
C	-4.565373	0.380356	-0.284209
H	2.800494	-1.533754	-2.847303
H	-0.620551	-3.867383	-1.541617
H	1.629311	-3.757530	-2.670418
H	3.925371	2.859694	-1.565118
H	3.050298	3.115335	-3.103363
H	1.138631	3.800847	-1.892732
H	-3.590227	-0.135821	1.556150
H	-3.868446	-2.482723	1.474006
H	-4.809521	-2.291256	-0.034446
H	0.907607	3.741067	0.480748
H	-4.156105	1.400850	-0.188979
Cl	-1.800197	2.915036	0.254991
C	-4.589410	0.021888	-1.763324
H	-4.946902	-1.007708	-1.935525
H	-5.263352	0.696740	-2.313595
H	-3.588533	0.115381	-2.212679
C	-5.954786	0.352796	0.336491
H	-6.625875	1.058028	-0.177869
H	-6.415390	-0.647188	0.264520
H	-5.926562	0.634346	1.401427
C	2.626474	2.581376	0.994596
H	2.724259	2.985070	2.014374
H	2.055514	1.642385	1.063402
H	3.643133	2.338562	0.641440
C	2.647052	4.925357	0.049478
H	2.114504	5.650301	-0.587012
H	2.722150	5.358394	1.058984
H	3.674335	4.826594	-0.340882

SI-Int3

C	1.137539	-4.301390	0.914238
C	1.133147	-2.986204	0.449512
N	0.058945	-2.211488	0.558456
C	-1.063738	-2.672505	1.102612
C	-1.156881	-3.972304	1.598635
C	-0.030538	-4.789088	1.499964
Ni	0.110358	-0.250168	-0.131610
C	2.245791	-2.301157	-0.223446
C	-2.136287	-1.667916	1.084223
O	3.380746	-2.952379	-0.462103
C	4.221532	-2.031882	-1.191610
C	3.400655	-0.721194	-1.248181
N	2.145260	-1.088490	-0.608460
N	-1.938086	-0.506234	0.592550

C	-3.204850	0.213734	0.635035
C	-4.102263	-0.727093	1.467092
O	-3.342766	-1.955237	1.563207
C	4.042270	0.495144	-0.568062
C	-3.695497	0.540559	-0.784254
H	2.028740	-4.922328	0.813896
H	-2.086149	-4.331333	2.042828
H	-0.065518	-5.813786	1.875532
H	5.173586	-1.937930	-0.650077
H	4.415663	-2.464023	-2.183026
H	3.180692	-0.446932	-2.293241
H	-3.038560	1.168832	1.151146
H	-4.273025	-0.359883	2.489804
H	-5.070663	-0.958887	1.003730
H	3.288571	1.295843	-0.650021
H	-2.835707	1.033535	-1.269202
Cl	-0.523087	-0.997707	-2.334170
C	-4.027607	-0.699949	-1.600307
H	-4.862051	-1.274367	-1.163947
H	-4.330037	-0.413096	-2.619969
H	-3.143343	-1.347305	-1.697956
C	-4.857234	1.522067	-0.720366
H	-5.188094	1.805168	-1.731687
H	-5.727498	1.086168	-0.199980
H	-4.574432	2.444814	-0.188350
C	4.312657	0.265123	0.911616
H	4.698843	1.183697	1.380338
H	3.393115	-0.021657	1.444319
H	5.066775	-0.523185	1.074934
C	5.290303	0.933279	-1.321463
H	5.073043	1.130763	-2.383503
H	5.706822	1.855048	-0.886378
H	6.080401	0.164808	-1.277196
C	0.628124	2.134625	-2.135883
H	0.492533	1.239419	-2.757636
H	0.145999	2.997002	-2.620702
H	1.702863	2.347089	-2.010170
O	0.018214	1.863676	-0.877463
Si	-0.336714	3.130086	0.147942
H	0.665379	0.358555	1.348763
O	-1.129664	4.216453	-0.795746
O	-1.354912	2.680883	1.350869
O	1.023163	3.846228	0.726425
C	2.161463	3.209176	1.258827
H	2.025584	2.118676	1.341133
H	3.035384	3.413584	0.617923
H	2.376226	3.610613	2.263078
C	-1.042737	2.405368	2.694492
H	-0.385956	3.179102	3.127706
H	-1.979396	2.390692	3.273295
H	-0.544787	1.426073	2.786204
C	-1.708594	5.400300	-0.310046
H	-2.393307	5.205619	0.533965
H	-0.943185	6.122179	0.025277
H	-2.288620	5.868842	-1.120071

Si(OMe)$_4$

Si	0.000000	0.000000	0.000000
O	0.000000	1.378751	0.894522
O	1.378751	0.000000	-0.894522
O	-1.378751	0.000000	-0.894522
C	-1.798132	1.071666	-1.702284
H	-1.060142	1.307573	-2.489309
H	-2.743054	0.794664	-2.194767
H	-1.973004	1.986212	-1.109896
C	1.798132	-1.071666	-1.702284
H	1.060142	-1.307573	-2.489309
H	2.743054	-0.794664	-2.194767
H	1.973004	-1.986212	-1.109896
C	1.071666	1.798132	1.702284
H	1.986212	1.973004	1.109896
H	0.794664	2.743054	2.194767
H	1.307573	1.060142	2.489309
O	0.000000	-1.378751	0.894522
C	-1.071666	-1.798132	1.702284
H	-0.794664	-2.743054	2.194767
H	-1.307573	-1.060142	2.489309
H	-1.986212	-1.973004	1.109896

SI-Int4

C	-1.078021	3.535821	-0.404893
C	-1.033308	2.142602	-0.408005
N	0.073694	1.473139	-0.090686
C	1.194894	2.127696	0.212154
C	1.248127	3.519817	0.246151
C	0.085769	4.225551	-0.065162
Ni	0.050737	-0.588967	-0.024033
C	-2.138144	1.238783	-0.748168
C	2.303396	1.203288	0.476703
O	-3.338285	1.725410	-1.038953
C	-4.143998	0.583592	-1.409003
C	-3.276166	-0.634359	-1.022752
N	-1.972725	-0.029905	-0.754137
N	2.124944	-0.058384	0.384579
C	3.403806	-0.707591	0.644294
C	4.314514	0.476372	1.048836
O	3.507999	1.653181	0.804381
C	-3.774184	-1.439565	0.188825
C	3.862766	-1.521485	-0.574766
H	-1.998205	4.060330	-0.665872
H	2.176147	4.031887	0.504351
H	0.089089	5.317332	-0.050316
H	-5.098152	0.649784	-0.869617
H	-4.337887	0.645640	-2.489803
H	-3.179530	-1.327719	-1.871910
H	3.277862	-1.405045	1.487326
H	4.581930	0.469003	2.114837
H	5.231778	0.563359	0.450208
H	-2.977709	-2.175266	0.394528
H	3.036118	-2.226703	-0.766346
C	4.033942	-0.665122	-1.821384
H	4.842817	0.077003	-1.710959
H	4.290246	-1.296094	-2.686628
H	3.105932	-0.128073	-2.070749

C	5.124651	-2.306631	-0.244232
H	5.416132	-2.950871	-1.088182
H	5.977188	-1.638301	-0.033580
H	4.979209	-2.952592	0.636374
C	-3.952100	-0.584393	1.434943
H	-4.252893	-1.212023	2.288015
H	-3.014529	-0.080514	1.715065
H	-4.735234	0.181046	1.303349
C	-5.045642	-2.197325	-0.169676
H	-4.895682	-2.846347	-1.047248
H	-5.368425	-2.834067	0.668298
H	-5.877937	-1.509968	-0.397576
H	-0.382191	-0.702720	1.536354
O	0.444591	-2.119477	-1.039051
C	-0.511415	-2.840567	-1.719253
H	-0.076691	-3.751553	-2.190041
H	-1.344368	-3.205217	-1.075225
H	-0.993710	-2.275293	-2.550599

SI-Int4-M

C	-1.052755	3.606313	-0.358247
C	-1.039489	2.212676	-0.339484
N	0.056542	1.527052	-0.025037
C	1.192999	2.154341	0.263217
C	1.279286	3.545854	0.276682
C	0.131059	4.272331	-0.039085
Ni	-0.025775	-0.535260	0.088390
C	-2.165874	1.320636	-0.648121
C	2.280223	1.208002	0.547489
O	-3.356855	1.815620	-0.958948
C	-4.187222	0.673409	-1.273686
C	-3.320605	-0.549208	-0.890809
N	-2.020553	0.051177	-0.612963
N	2.092506	-0.053770	0.466563
C	3.367797	-0.703710	0.757991
C	4.254159	0.473717	1.222998
O	3.479830	1.651850	0.902574
C	-3.823893	-1.372307	0.305283
C	3.891920	-1.477370	-0.462487
H	-1.962802	4.149495	-0.616630
H	2.219170	4.041341	0.523666
H	0.159726	5.363883	-0.040467
H	-5.119858	0.762608	-0.700400
H	-4.420861	0.715632	-2.347180
H	-3.216790	-1.233367	-1.747760
H	3.215982	-1.423156	1.577552
H	4.431411	0.474380	2.308115
H	5.218377	0.547141	0.702507
H	-3.033304	-2.118911	0.491948
H	3.091834	-2.192503	-0.717390
C	4.119560	-0.582220	-1.672112
H	4.901190	0.173544	-1.486006
H	4.450029	-1.183014	-2.533872
H	3.191484	-0.070686	-1.966651
C	5.138777	-2.268420	-0.089661
H	5.476009	-2.885357	-0.936841
H	5.975707	-1.603933	0.184260
H	4.951014	-2.941039	0.762554
C	-3.987984	-0.538016	1.567013
H	-4.291052	-1.177194	2.410681
H	-3.043474	-0.048620	1.849284
H	-4.763801	0.237657	1.452398
C	-5.105098	-2.108312	-0.063595
H	-4.966922	-2.738548	-0.956654
H	-5.430215	-2.761019	0.761118
H	-5.931333	-1.407098	-0.270708
H	-0.388619	-0.636573	1.679756
C	-0.275029	-0.650475	-3.336040
H	-0.457624	0.411608	-3.572279
H	-1.239074	-1.100847	-3.041684
H	0.056681	-1.145849	-4.269615
O	0.689820	-0.743549	-2.321894
H	0.554274	-1.597881	-1.815318
O	0.009335	-2.389699	-0.559230
C	0.570258	-3.393496	0.201903
H	0.768034	-4.307437	-0.400973
H	1.541373	-3.119168	0.672737
H	-0.089123	-3.710508	1.040788

SI-TS2

C	0.505656	-2.775506	-2.142262
C	1.252274	-1.721522	-1.624339
N	0.683503	-0.583873	-1.218611
C	-0.640207	-0.426748	-1.303882
C	-1.469268	-1.426119	-1.813664
C	-0.878789	-2.615126	-2.235016
Ni	1.781775	0.830063	-0.240575
C	2.703293	-1.709939	-1.415970
C	-1.066915	0.873172	-0.783026
O	3.436517	-2.769435	-1.737038
C	4.806239	-2.388017	-1.478157
C	4.685138	-1.075141	-0.677152
N	3.286139	-0.702313	-0.881587
N	-0.206257	1.686496	-0.298218
C	-0.923015	2.871340	0.156183
C	-2.401790	2.515396	-0.131782
O	-2.344351	1.224729	-0.782776
C	5.004288	-1.189088	0.822754
C	-0.391904	4.139647	-0.525951
H	0.997563	-3.693917	-2.464979
H	-2.546707	-1.266563	-1.875025
H	-1.495637	-3.420334	-2.639063
H	5.294302	-3.208339	-0.935630
H	5.305700	-2.250804	-2.448656
H	5.334029	-0.296168	-1.105133
H	-0.760444	2.973343	1.240769
H	-2.997227	2.397436	0.780683
H	-2.904809	3.213187	-0.816191
H	4.722290	-0.213287	1.253086
H	0.680584	4.169965	-0.268878
C	-0.503624	4.077746	-2.042858
H	-1.552864	4.031788	-2.380567
H	-0.054979	4.974051	-2.498836
H	0.024071	3.200893	-2.448811

C	-1.072440	5.375197	0.047098
H	-0.642132	6.293888	-0.381027
H	-2.152803	5.384552	-0.176380
H	-0.956210	5.428014	1.141473
C	4.181680	-2.264231	1.519313
H	4.359229	-2.238261	2.605517
H	3.103121	-2.115541	1.359182
H	4.446359	-3.276446	1.171135
C	6.498818	-1.391121	1.032457
H	7.084434	-0.580775	0.569828
H	6.742714	-1.412104	2.105764
H	6.843438	-2.345438	0.599452
H	1.419027	0.045878	1.141322
O	-2.253837	0.420972	2.244459
C	-2.091609	-0.694674	1.760358
C	-0.797291	-1.371333	1.810209
N	-3.073609	-1.423981	1.140784
C	-4.391169	-1.065402	0.871637
C	-5.136099	-1.917038	0.038026
C	-6.457935	-1.620885	-0.276180
C	-7.063857	-0.470575	0.231404
C	-6.326251	0.372449	1.062210
C	-5.001881	0.088459	1.388815
F	-0.744857	-2.584230	1.198543
H	-2.779366	-2.319543	0.766265
H	-4.663585	-2.819251	-0.361846
H	-7.018915	-2.297450	-0.926282
H	-8.101703	-0.236007	-0.016458
H	-6.788928	1.274434	1.472079
H	-4.427327	0.744075	2.039628
C	0.314582	-0.855493	2.355066
H	0.226406	0.068570	2.908531
H	1.190682	-1.471949	2.502695
O	2.725424	2.438568	-0.111515
C	4.093539	2.518767	0.024285
H	4.448314	3.570469	-0.063072
H	4.461902	2.158273	1.012537
H	4.663666	1.944874	-0.742205

SI-TS2-M

C	0.334600	-2.816766	-2.105829
C	1.115100	-1.771918	-1.619586
N	0.578482	-0.618547	-1.221794
C	-0.739919	-0.427632	-1.283882
C	-1.603908	-1.417036	-1.753612
C	-1.047773	-2.625801	-2.166993
Ni	1.737135	0.806418	-0.318237
C	2.571880	-1.781819	-1.443783
C	-1.117401	0.899677	-0.789494
O	3.280837	-2.851274	-1.778990
C	4.663083	-2.482212	-1.567750
C	4.579577	-1.175928	-0.753027
N	3.182814	-0.779245	-0.930670
N	-0.218908	1.717146	-0.383969
C	-0.894922	2.933661	0.054482
C	-2.391008	2.561636	-0.075825
O	-2.385875	1.269903	-0.729515
C	4.918286	-1.312354	0.740955
C	-0.432593	4.150706	-0.759441
H	0.797451	-3.751110	-2.425781
H	-2.678932	-1.235490	-1.792720
H	-1.691884	-3.423743	-2.542105
H	5.164604	-3.311189	-1.051897
H	5.125634	-2.339048	-2.555645
H	5.234477	-0.404133	-1.184610
H	-0.634784	3.110744	1.109621
H	-2.880751	2.430953	0.896297
H	-2.975104	3.251702	-0.699590
H	4.662004	-0.336398	1.185813
H	0.663306	4.176095	-0.636226
C	-0.732281	4.013720	-2.245631
H	-1.816219	4.019799	-2.450501
H	-0.289759	4.852852	-2.803777
H	-0.307286	3.087845	-2.661558
C	-1.018867	5.430314	-0.178513
H	-0.639450	6.313029	-0.716198
H	-2.119188	5.445221	-0.258683
H	-0.758441	5.547145	0.885558
C	4.085733	-2.378786	1.439776
H	4.278218	-2.364042	2.523617
H	3.007322	-2.212374	1.296215
H	4.328074	-3.392963	1.081334
C	6.411685	-1.544504	0.925727
H	7.005131	-0.739051	0.464610
H	6.670772	-1.583663	1.994920
H	6.732112	-2.499134	0.475476
H	1.402213	0.150210	1.133276
O	-2.237883	0.444577	2.284097
C	-2.037499	-0.676144	1.825772
C	-0.719767	-1.302792	1.882411
N	-2.994900	-1.455906	1.229304
C	-4.326549	-1.155817	0.958046
C	-5.049918	-2.072493	0.175688
C	-6.382699	-1.834108	-0.141754
C	-7.021356	-0.679172	0.312201
C	-6.305078	0.228012	1.092584
C	-4.969983	0.003087	1.421172
F	-0.624611	-2.526292	1.296931
H	-2.669423	-2.350774	0.879518
H	-4.553043	-2.979480	-0.181618
H	-6.926546	-2.560475	-0.751420
H	-8.067896	-0.490401	0.061831
H	-6.793174	1.134946	1.459770
H	-4.411218	0.709002	2.031742
C	0.381803	-0.725656	2.388206
H	0.263440	0.208179	2.919753
H	1.280618	-1.305383	2.547923
O	2.774037	2.407371	-0.203622
C	4.102708	2.397667	0.192831
H	4.526146	3.424433	0.199354
H	4.238872	1.999815	1.220671
H	4.763042	1.796718	-0.470221
C	2.506104	2.003184	-3.391287
H	2.326157	2.228064	-4.456305

H	1.592377	1.504349	-3.007382
H	3.327121	1.258554	-3.344555
O	2.802805	3.187513	-2.714429
H	2.784712	2.970542	-1.743395

SI-Int5

C	0.401939	-2.707665	-1.939659
C	1.154825	-1.688553	-1.357527
N	0.608142	-0.527226	-1.007168
C	-0.686550	-0.292151	-1.229787
C	-1.519644	-1.247815	-1.807223
C	-0.956673	-2.475549	-2.156762
Ni	1.674558	0.824545	0.153594
C	2.603236	-1.722720	-1.108287
C	-1.074011	1.051606	-0.783753
O	3.311679	-2.758449	-1.543900
C	4.696187	-2.410764	-1.327990
C	4.636900	-1.105995	-0.501110
N	3.214745	-0.758741	-0.532043
N	-0.212848	1.801184	-0.211497
C	-0.867065	3.045367	0.156991
C	-2.318106	2.829020	-0.338644
O	-2.306912	1.509917	-0.940136
C	5.186855	-1.213378	0.928035
C	-0.112895	4.252494	-0.413269
H	0.871896	-3.651198	-2.219979
H	-2.576042	-1.032658	-1.971765
H	-1.577506	-3.252272	-2.607957
H	5.184392	-3.249708	-0.814354
H	5.164859	-2.274364	-2.313279
H	5.194073	-0.303286	-1.009908
H	-0.840471	3.108658	1.256398
H	-3.057630	2.817285	0.472658
H	-2.639348	3.545324	-1.108393
H	4.938353	-0.250748	1.406171
H	0.910716	4.136051	-0.016339
C	-0.023198	4.225394	-1.932445
H	-1.012493	4.318117	-2.412216
H	0.592884	5.062454	-2.296553
H	0.443622	3.293527	-2.287937
C	-0.717658	5.550719	0.101271
H	-0.132323	6.419394	-0.238490
H	-1.750416	5.689640	-0.262461
H	-0.744487	5.573834	1.202455
C	4.537302	-2.327466	1.736668
H	4.883475	-2.290003	2.781459
H	3.441956	-2.239027	1.746790
H	4.803303	-3.324017	1.346465
C	6.703828	-1.347229	0.896212
H	7.173595	-0.507430	0.359598
H	7.114989	-1.366919	1.917225
H	7.016552	-2.281359	0.399309
H	3.183809	0.133839	2.673892
O	-0.575688	1.210608	2.771991
C	-0.234395	0.160556	2.232291
C	1.172900	-0.168757	1.928772
N	-1.135993	-0.783595	1.785985
C	-2.523119	-0.739002	1.758722
C	-3.199394	-1.842435	1.207404
C	-4.586710	-1.851880	1.115944
C	-5.333899	-0.764780	1.572997
C	-4.665928	0.325482	2.129858
C	-3.275989	0.350471	2.229476
F	1.281639	-1.579540	1.735054
H	-0.709612	-1.635067	1.437367
H	-2.618176	-2.696694	0.848502
H	-5.088685	-2.721137	0.682445
H	-6.424032	-0.771198	1.500741
H	-5.236317	1.181676	2.501033
H	-2.751748	1.195671	2.670673
C	2.140262	0.257965	2.995197
H	1.975798	1.324027	3.201064
H	1.998726	-0.305058	3.937661
O	2.660989	2.406173	0.339053
C	3.994202	2.483362	0.623675
H	4.651347	1.865030	-0.035860
H	4.380248	3.524527	0.521902
H	4.254238	2.179555	1.667305

SI-Int5-M

C	0.359975	-2.800290	-1.974874
C	1.099509	-1.764661	-1.404120
N	0.532534	-0.616227	-1.052263
C	-0.764065	-0.400673	-1.263322
C	-1.587500	-1.375705	-1.823701
C	-1.005517	-2.594235	-2.174016
Ni	1.618533	0.815802	-0.023160
C	2.553051	-1.772027	-1.172592
C	-1.174414	0.942279	-0.829746
O	3.266383	-2.804736	-1.607557
C	4.649804	-2.438848	-1.418734
C	4.588491	-1.130943	-0.598089
N	3.162908	-0.794818	-0.617852
N	-0.328100	1.737023	-0.298828
C	-1.029887	2.957143	0.074902
C	-2.482295	2.671313	-0.377842
O	-2.430627	1.344729	-0.956340
C	5.158147	-1.227656	0.824001
C	-0.365115	4.204066	-0.519584
H	0.843891	-3.735713	-2.258398
H	-2.649485	-1.180922	-1.977160
H	-1.617311	-3.384623	-2.613756
H	5.157564	-3.268650	-0.909409
H	5.098660	-2.302197	-2.413276
H	5.135646	-0.327493	-1.116977
H	-0.975524	3.028361	1.172781
H	-3.199514	2.643186	0.452750
H	-2.853122	3.360156	-1.150628
H	4.917949	-0.261184	1.298346
H	0.671541	4.167381	-0.142372
C	-0.306148	4.175288	-2.040338
H	-1.311452	4.164211	-2.495196
H	0.206388	5.074688	-2.417924
H	0.258713	3.299794	-2.394662

C	-1.043609	5.460952	0.007924
H	-0.523576	6.365198	-0.344898
H	-2.090155	5.531115	-0.335521
H	-1.050453	5.485249	1.109505
C	4.520196	-2.334571	1.650810
H	4.889324	-2.295234	2.687652
H	3.426276	-2.236928	1.683490
H	4.771394	-3.334176	1.258575
C	6.674620	-1.361043	0.770353
H	7.135819	-0.526672	0.217943
H	7.100961	-1.369363	1.785256
H	6.981060	-2.300119	0.279085
H	3.263346	0.220294	2.545136
O	-0.482791	1.319125	2.748756
C	-0.163252	0.257259	2.219105
C	1.230244	-0.073122	1.855001
N	-1.081420	-0.703694	1.848781
C	-2.468220	-0.659182	1.872760
C	-3.164379	-1.763211	1.347408
C	-4.553961	-1.773239	1.307787
C	-5.284343	-0.686380	1.792158
C	-4.596655	0.403544	2.324849
C	-3.203856	0.428900	2.373094
F	1.321309	-1.493427	1.682454
H	-0.667244	-1.560197	1.498248
H	-2.596654	-2.616685	0.965623
H	-5.071399	-2.642471	0.892798
H	-6.376396	-0.693055	1.759883
H	-5.153142	1.259062	2.718067
H	-2.664427	1.274212	2.795462
C	2.229783	0.342982	2.895481
H	2.071707	1.405344	3.124265
H	2.112168	-0.232908	3.833483
O	2.648350	2.491596	0.185539
C	3.942295	2.560802	0.643406
H	4.636323	1.821074	0.179333
H	4.396206	3.558238	0.447568
H	4.027386	2.406432	1.741796
O	2.118618	1.895375	-2.185629
C	3.198078	1.512393	-2.978359
H	4.074588	1.189862	-2.387353
H	2.905574	0.664127	-3.621540
H	3.536092	2.327091	-3.650269
H	2.449348	2.380415	-1.358327

SI-Int6

C	-0.031515	1.219358	-3.714146
C	-0.025741	1.192446	-2.329549
N	0.000000	0.000000	-1.656033
C	0.000000	0.000000	-4.415764
Ni	0.000000	0.000000	0.180805
C	-0.027663	2.240985	-1.349574
O	-0.028651	3.540437	-1.594922
C	-0.157553	4.186660	-0.305822
C	0.151189	3.081185	0.721374
N	0.000000	1.878794	-0.091359
C	1.546207	3.155685	1.363027
H	-0.056128	2.173098	-4.245062
H	0.000000	0.000000	-5.506839
H	0.537514	5.035690	-0.280784
H	-1.188477	4.562194	-0.222181
H	-0.597032	3.076850	1.527802
H	1.620118	2.237866	1.970542
Br	0.000000	0.000000	2.512871
C	2.669403	3.138834	0.335868
H	3.649265	3.126486	0.838523
H	2.617884	2.243893	-0.304220
H	2.649900	4.028671	-0.315675
C	1.640586	4.355476	2.294981
H	0.844280	4.335978	3.056414
H	2.607897	4.365444	2.821150
H	1.556971	5.308374	1.745736
C	0.031515	-1.219358	-3.714146
C	0.025741	-1.192446	-2.329549
C	0.027663	-2.240985	-1.349574
O	0.028651	-3.540437	-1.594922
C	0.157553	-4.186660	-0.305822
C	-0.151189	-3.081185	0.721374
N	0.000000	-1.878794	-0.091359
C	-1.546207	-3.155685	1.363027
H	0.056128	-2.173098	-4.245062
H	-0.537514	-5.035690	-0.280784
H	1.188477	-4.562194	-0.222181
H	0.597032	-3.076850	1.527802
H	-1.620118	-2.237866	1.970542
C	-2.669403	-3.138834	0.335868
H	-3.649265	-3.126486	0.838523
H	-2.617884	-2.243893	-0.304220
H	-2.649900	-4.028671	-0.315675
C	-1.640586	-4.355476	2.294981
H	-0.844280	-4.335978	3.056414
H	-2.607897	-4.365444	2.821150
H	-1.556971	-5.308374	1.745736

^{t}BuBr

C	-0.842947	0.000069	0.000255
C	-1.282197	1.438940	-0.187406
H	-2.384880	1.474829	-0.191183
H	-0.922856	2.081889	0.629281
H	-0.924485	1.849669	-1.142823
C	-1.281868	-0.557635	1.339984
H	-2.384534	-0.571423	1.373345
H	-0.922901	-1.586753	1.486661
H	-0.923228	0.062878	2.174167
C	-1.281845	-0.881478	-1.152558
H	-0.922323	-0.495059	-2.117430
H	-0.924535	-1.914428	-1.031140
H	-2.384537	-0.902238	-1.181905
Br	1.168636	0.000571	0.001029

SI-TS3

C	1.452840	3.491358	-0.702619
C	1.382311	2.133572	-1.001839
N	0.221490	1.539450	-1.297931

C	-0.917237	2.241409	-1.323777
C	-0.941687	3.603927	-1.041554
C	0.267306	4.230014	-0.725471
Ni	0.180391	-0.422459	-1.664446
C	2.477051	1.162780	-1.022141
C	-2.045366	1.376997	-1.678200
O	3.717368	1.504412	-0.701501
C	4.492071	0.283377	-0.748798
C	3.492667	-0.795260	-1.231602
N	2.238226	-0.060422	-1.321905
N	-1.852266	0.119773	-1.831233
C	-3.127586	-0.490851	-2.177708
C	-4.062387	0.731788	-2.324269
O	-3.267945	1.854284	-1.868002
H	2.408905	3.957818	-0.459842
H	-1.879888	4.160418	-1.066383
H	0.285138	5.297290	-0.496547
H	5.337466	0.446038	-1.431847
H	4.881119	0.092271	0.260764
H	3.374248	-1.578943	-0.464832
H	-3.003745	-1.010089	-3.141118
H	-4.350944	0.929444	-3.366323
H	-4.968814	0.683059	-1.705789
Br	0.009251	-0.935555	0.818900
Br	0.190655	-1.997152	-3.496959
C	-0.275257	-2.124335	2.901724
C	1.133623	-2.253082	3.389119
H	1.152715	-2.789641	4.360310
H	1.758454	-2.824974	2.685971
H	1.602269	-1.269752	3.548383
C	-0.925606	-3.394521	2.451896
H	-1.120816	-4.051983	3.323968
H	-1.891494	-3.204357	1.959206
H	-0.285398	-3.954758	1.753355
C	-1.147705	-1.191166	3.681004
H	-0.668328	-0.211505	3.830908
H	-2.118360	-1.031040	3.187150
H	-1.354316	-1.614542	4.685730
C	-3.551852	-1.534929	-1.134727
H	-2.705765	-2.242184	-1.083919
C	3.849341	-1.482056	-2.556908
H	3.009054	-2.167684	-2.760260
C	-3.744001	-0.936932	0.251522
H	-2.819170	-0.455835	0.604045
H	-4.564396	-0.199914	0.271738
H	-4.003208	-1.726096	0.975099
C	-4.787170	-2.286233	-1.611748
H	-4.623135	-2.749546	-2.597951
H	-5.056249	-3.085894	-0.904136
H	-5.659647	-1.616360	-1.696797
C	3.917783	-0.502190	-3.718329
H	4.143529	-1.034301	-4.655870
H	2.953842	0.010931	-3.853851
H	4.704114	0.259131	-3.578151
C	5.128609	-2.293445	-2.407301
H	5.055168	-3.014708	-1.577181
H	5.340332	-2.861272	-3.326831
H	6.001916	-1.647639	-2.213769

^{t}Bu·

C	0.000269	0.000031	-0.165382
C	-0.622596	-1.340921	0.014467
H	-0.746571	-1.593308	1.090503
H	-1.629164	-1.392289	-0.433020
H	-0.007345	-2.144568	-0.423236
C	-0.850194	1.209443	0.014504
H	-1.012660	1.438972	1.090538
H	-0.389145	2.108412	-0.427470
H	-1.851596	1.080015	-0.428813
C	1.472820	0.131403	0.014695
H	2.020596	-0.715790	-0.430580
H	1.861155	1.064960	-0.425382
H	1.753360	0.153191	1.090693

SI-Int7

C	1.166754	3.709741	-0.220987
C	1.128378	2.325057	-0.072732
N	0.004374	1.638754	-0.255505
C	-1.130496	2.246210	-0.590436
C	-1.190990	3.626654	-0.767707
C	-0.017546	4.357254	-0.575328
Ni	0.007590	-0.374219	0.038785
C	2.238101	1.432287	0.291213
C	-2.222795	1.273305	-0.739266
O	3.432606	1.909413	0.598352
C	4.229442	0.762147	0.987129
C	3.309101	-0.455011	0.730292
N	2.052253	0.168740	0.337780
N	-2.016434	0.041280	-0.469249
C	-3.258777	-0.682809	-0.701612
C	-4.172936	0.402835	-1.314913
O	-3.419230	1.634227	-1.172499
C	3.801986	-1.446010	-0.332860
C	-3.775911	-1.335570	0.588173
H	2.094324	4.262665	-0.067025
H	-2.126612	4.114211	-1.044984
H	-0.026076	5.441501	-0.703841
H	5.145743	0.768070	0.381067
H	4.498128	0.886067	2.044999
H	3.133972	-1.011861	1.664761
H	-3.053808	-1.480481	-1.432750
H	-4.360454	0.251757	-2.387168
H	-5.132928	0.530565	-0.797166
H	2.990716	-2.187002	-0.434726
H	-2.948553	-1.976951	0.937867
C	-4.059983	-0.318833	1.684048
H	-4.871397	0.374480	1.405012
H	-4.374900	-0.831631	2.606499
H	-3.155742	0.259814	1.926285
C	-4.984489	-2.210762	0.286421
H	-5.319367	-2.739636	1.192255
H	-5.836254	-1.611569	-0.077577
H	-4.754554	-2.967295	-0.480938
C	3.987639	-0.791343	-1.693399

H	4.304228	-1.539446	-2.437034
H	3.041851	-0.355485	-2.049040
H	4.760215	-0.004024	-1.673912
C	5.061164	-2.153603	0.147943
H	4.901430	-2.644716	1.121396
H	5.373042	-2.926436	-0.571732
H	5.904847	-1.451708	0.260583
Br	-0.321721	-0.646569	2.435095
Br	0.280561	-1.879790	-1.846601

SI-Int8

C	-0.077864	-2.445423	-2.985153
C	0.676312	-1.490509	-2.306247
N	0.111665	-0.430148	-1.742349
C	-1.202723	-0.239349	-1.805370
C	-2.045023	-1.149372	-2.439411
C	-1.459398	-2.265470	-3.037982
Ni	1.309355	1.110618	-0.984100
C	2.136137	-1.495078	-2.132595
C	-1.592026	1.020955	-1.157042
O	2.871762	-2.354842	-2.820001
C	4.246176	-1.982879	-2.571058
C	4.156671	-0.927424	-1.445621
N	2.722244	-0.650605	-1.372889
N	-0.693834	1.804675	-0.690888
C	-1.360135	3.007585	-0.206300
C	-2.847730	2.599477	-0.259769
O	-2.856828	1.385116	-1.054318
C	4.737986	-1.428210	-0.115177
C	-0.967502	4.231440	-1.046492
H	0.402776	-3.311269	-3.441714
H	-3.122414	-0.982708	-2.471959
H	-2.084786	-3.001155	-3.547560
H	4.792996	-2.890518	-2.282516
H	4.661351	-1.590187	-3.510294
H	4.672530	0.004766	-1.728949
H	-1.040183	3.195828	0.829438
H	-3.258266	2.347326	0.728640
H	-3.504242	3.330553	-0.749007
H	4.301609	-2.429688	0.061307
H	0.134788	4.257722	-0.999361
C	-1.372850	4.100630	-2.507461
H	-2.467453	4.037331	-2.629351
H	-1.035525	4.982935	-3.074212
H	-0.902458	3.220568	-2.972614
C	-1.517204	5.500303	-0.409506
H	-1.187026	6.391010	-0.966425
H	-2.620426	5.505939	-0.405401
H	-1.177392	5.609628	0.633038
C	6.249706	-1.575171	-0.239519
H	6.675898	-2.002763	0.681277
H	6.545244	-2.229730	-1.074953
H	6.722266	-0.591729	-0.402053
C	4.365076	-0.529832	1.051681
H	3.278090	-0.484074	1.200268
H	4.825644	-0.904214	1.980739
H	4.714582	0.501849	0.889083
Br	1.731859	1.947638	-3.256332
Br	2.332157	2.535436	0.686233
O	1.151239	-1.531955	1.843764
C	-0.024490	-1.514486	1.486614
C	-0.891710	-0.406494	1.842408
N	-0.629499	-2.496893	0.744059
C	-0.048373	-3.617308	0.158406
C	-0.907486	-4.543902	-0.455902
C	-0.391289	-5.645421	-1.127796
C	0.989196	-5.847802	-1.199197
C	1.840777	-4.935668	-0.577011
C	1.338716	-3.828988	0.105776
F	-2.154507	-0.465230	1.389789
H	-1.627044	-2.390918	0.588463
H	-1.987179	-4.374744	-0.415483
H	-1.076174	-6.351105	-1.605273
H	1.394902	-6.710902	-1.732276
H	2.923624	-5.080217	-0.622770
H	2.004698	-3.116199	0.587316
C	-0.518431	0.766069	2.641663
H	0.559998	0.935227	2.502173
H	-1.039913	1.636204	2.212179
C	-0.851671	0.705476	4.156564
C	-0.388027	2.025142	4.770968
H	-0.597261	2.049172	5.852543
H	-0.902472	2.882682	4.307368
H	0.695618	2.168790	4.631615
C	-0.115675	-0.457858	4.818062
H	0.972042	-0.382584	4.666103
H	-0.444511	-1.427345	4.411261
H	-0.309762	-0.468019	5.902918
C	-2.358318	0.544267	4.355432
H	-2.722894	-0.408182	3.939088
H	-2.915873	1.361425	3.868948
H	-2.610965	0.556619	5.428075

SI-Int9

C	2.217319	2.308179	-2.801860
C	1.935383	1.443710	-1.745338
N	0.795117	1.530214	-1.075434
C	-0.126893	2.438101	-1.368838
C	0.061594	3.347777	-2.405927
C	1.257370	3.268804	-3.123525
Ni	0.557094	0.387756	0.588941
C	2.783964	0.372194	-1.197485
C	-1.289591	2.310856	-0.474171
O	3.976199	0.115945	-1.705455
C	4.558660	-0.909247	-0.861694
C	3.420647	-1.302073	0.108278
N	2.386924	-0.320898	-0.196717
N	-1.283982	1.449107	0.475139
C	-2.551323	1.565918	1.192247
C	-3.340144	2.564767	0.316537
O	-2.363379	3.061460	-0.632485
C	2.891025	-2.736622	-0.035702
C	-2.335648	1.981619	2.654245
H	3.155316	2.234511	-3.353663

H	-0.698143	4.092158	-2.646050
H	1.441337	3.963257	-3.945661
H	4.901340	-1.726428	-1.510344
H	5.425378	-0.466982	-0.351812
H	3.737639	-1.157108	1.153211
H	-3.048143	0.581988	1.189406
H	-4.145233	2.086799	-0.258430
H	-3.749029	3.423665	0.864616
H	2.030787	-2.798264	0.653190
H	-1.634978	1.232576	3.061105
C	-1.682126	3.349032	2.787763
H	-2.321321	4.153328	2.386581
H	-1.503091	3.579748	3.849937
H	-0.704604	3.372062	2.281422
C	-3.648139	1.893711	3.420627
H	-3.493406	2.119695	4.487024
H	-4.387948	2.615715	3.035509
H	-4.092440	0.887762	3.349208
C	2.385631	-3.035316	-1.439328
H	1.978551	-4.056858	-1.490047
H	1.581810	-2.341844	-1.727061
H	3.191612	-2.971784	-2.189135
C	3.942387	-3.737554	0.421854
H	4.276685	-3.529348	1.450865
H	3.540343	-4.762303	0.397785
H	4.830640	-3.717179	-0.231679
O	-0.404008	-1.285731	-0.415092
C	-1.639873	-1.450091	-0.476103
C	-2.302673	-2.323344	0.465531
N	-2.437824	-0.861463	-1.396912
C	-2.044002	-0.109899	-2.511936
C	-2.966185	0.799502	-3.045775
C	-2.644242	1.534551	-4.182665
C	-1.403572	1.370702	-4.798459
C	-0.488517	0.461246	-4.266589
C	-0.795713	-0.277947	-3.128291
F	-3.633252	-2.345082	0.420810
H	-3.439927	-0.988088	-1.279621
H	-3.938281	0.921937	-2.561282
H	-3.371163	2.243040	-4.587453
H	-1.149662	1.950126	-5.689246
H	0.484656	0.321835	-4.743583
H	-0.074785	-0.981764	-2.716073
C	1.175395	-1.121933	3.226797
H	0.748940	-1.334778	4.219487
H	1.908161	-0.309861	3.314866
H	1.667281	-2.029293	2.840101
O	0.163935	-0.658683	2.344429
H	-0.527763	-1.328658	2.271063
C	-1.628711	-3.291732	1.342437
H	-0.563941	-3.016213	1.372111
H	-2.044761	-3.217357	2.363085
C	-1.703841	-4.777847	0.879368
C	-3.130136	-5.310836	1.004365
H	-3.501520	-5.217665	2.037513
H	-3.828285	-4.777576	0.342181
H	-3.160467	-6.377557	0.730408
C	-1.225892	-4.889691	-0.567180
H	-1.889754	-4.343892	-1.257668
H	-0.208303	-4.485777	-0.686291
H	-1.210905	-5.943918	-0.885764
C	-0.775137	-5.573564	1.794873
H	-1.080047	-5.482801	2.849785
H	-0.792934	-6.642253	1.528457
H	0.265223	-5.219778	1.710220
Br	1.816369	2.110413	1.911856

SI-TS4

C	1.393522	3.547654	-0.780373
C	1.338619	2.181686	-1.042077
N	0.185685	1.568403	-1.333819
C	-0.959007	2.260117	-1.393279
C	-0.997678	3.629536	-1.149696
C	0.202048	4.275298	-0.837290
Ni	0.167004	-0.399070	-1.659081
C	2.441580	1.221304	-1.022214
C	-2.075118	1.376820	-1.735434
O	3.674160	1.579984	-0.687003
C	4.458068	0.365058	-0.693875
C	3.472305	-0.735658	-1.156675
N	2.217513	-0.010558	-1.295187
N	-1.870484	0.117028	-1.845625
C	-3.135749	-0.515137	-2.188021
C	-4.075968	0.695451	-2.392574
O	-3.299590	1.837595	-1.957764
H	2.343607	4.027502	-0.540378
H	-1.941060	4.175175	-1.200984
H	0.207983	5.348562	-0.637819
H	5.308117	0.515835	-1.374150
H	4.840424	0.205379	0.323755
H	3.340000	-1.491509	-0.364342
H	-2.993298	-1.068589	-3.129585
H	-4.345526	0.856923	-3.446078
H	-4.994354	0.659292	-1.790737
Br	-0.010964	-0.912305	0.816423
Br	0.224862	-1.905287	-3.538652
C	-0.218623	-2.197382	2.870032
C	1.203605	-2.567598	3.148778
H	1.264271	-3.171672	4.077737
H	1.634226	-3.172066	2.335892
H	1.836977	-1.678930	3.293550
C	-1.111592	-3.319524	2.444674
H	-1.292058	-4.007272	3.296555
H	-2.091708	-2.953257	2.103510
H	-0.662600	-3.911537	1.632726
C	-0.825574	-1.196645	3.801653
H	-0.182447	-0.312101	3.927042
H	-1.814501	-0.860449	3.454357
H	-0.964865	-1.648220	4.805873
C	-3.568221	-1.521598	-1.111548
H	-2.720249	-2.222697	-1.023094
C	3.856790	-1.468891	-2.448860
H	3.023281	-2.165210	-2.642893
C	-3.778584	-0.871611	0.248363

H	-2.857466	-0.380876	0.597118
H	-4.595863	-0.130931	0.230786
H	-4.050732	-1.631883	0.997416
C	-4.793819	-2.297713	-1.573929
H	-4.616756	-2.794791	-2.541089
H	-5.063517	-3.074213	-0.841458
H	-5.671476	-1.639164	-1.690117
C	3.943031	-0.532735	-3.644596
H	4.184827	-1.099339	-4.557283
H	2.979278	-0.030429	-3.815660
H	4.724982	0.236047	-3.520840
C	5.135161	-2.270280	-2.244531
H	5.047032	-2.962005	-1.391129
H	5.366433	-2.869953	-3.138507
H	6.003571	-1.615625	-2.057567

SI-Int10

C	2.182593	2.102245	-2.874498
C	1.964848	1.359370	-1.715465
N	0.845279	1.485155	-1.014716
C	-0.121434	2.314260	-1.390858
C	-0.000942	3.096714	-2.536140
C	1.176969	2.981611	-3.276694
Ni	0.631420	0.396585	0.693525
C	2.860226	0.362577	-1.105873
C	-1.267382	2.247490	-0.470125
O	4.031278	0.080461	-1.644156
C	4.666570	-0.861207	-0.742067
C	3.557103	-1.229031	0.267329
N	2.510669	-0.258868	-0.041836
N	-1.241476	1.460903	0.541804
C	-2.493291	1.650494	1.276681
C	-3.310539	2.542257	0.318401
O	-2.344726	2.981848	-0.669822
C	3.020611	-2.665766	0.172187
C	-2.238869	2.230580	2.675474
H	3.105915	1.993174	-3.444867
H	-0.803016	3.769092	-2.841624
H	1.308454	3.577782	-4.181851
H	5.036312	-1.705353	-1.338501
H	5.518701	-0.348636	-0.274666
H	3.905084	-1.058292	1.297827
H	-2.987257	0.674596	1.398060
H	-4.098317	1.990801	-0.213748
H	-3.747200	3.432740	0.787773
H	2.157042	-2.698501	0.858532
H	-1.482599	1.565432	3.125838
C	-1.659745	3.637191	2.633177
H	-2.381649	4.367957	2.232158
H	-1.392404	3.968541	3.648613
H	-0.740124	3.675900	2.030578
C	-3.513602	2.165337	3.505183
H	-3.334108	2.534279	4.526941
H	-4.311443	2.787830	3.065689
H	-3.894983	1.134299	3.579651
C	2.520632	-3.014031	-1.222191
H	2.083610	-4.024306	-1.228279
H	1.739638	-2.313657	-1.553105
H	3.335913	-3.011342	-1.964429
C	4.066003	-3.653793	0.669716
H	4.388158	-3.416929	1.696290
H	3.663322	-4.678544	0.669409
H	4.961945	-3.651970	0.026378
O	-0.261855	-1.242215	-0.301437
C	-1.484338	-1.416797	-0.210945
C	-2.041474	-2.030477	1.054767
N	-2.367319	-1.048889	-1.141282
C	-2.088861	-0.385458	-2.352035
C	-3.065991	0.473192	-2.866624
C	-2.837649	1.149786	-4.061715
C	-1.637280	0.974921	-4.750076
C	-0.670428	0.109302	-4.238117
C	-0.885899	-0.573736	-3.043938
F	-3.428080	-2.040083	1.007932
H	-3.348019	-1.189414	-0.906865
H	-4.004129	0.606684	-2.321714
H	-3.604976	1.821774	-4.453792
H	-1.456273	1.510523	-5.685035
H	0.269693	-0.040716	-4.774545
H	-0.128368	-1.249790	-2.651782
C	1.156033	-1.167672	3.244479
H	0.686614	-2.174665	3.260097
H	1.251305	-0.841931	4.295375
H	2.159956	-1.286400	2.803386
O	0.320768	-0.342971	2.521889
H	-1.747481	-1.323587	1.851297
C	-1.460581	-3.387903	1.402929
H	-0.370061	-3.232832	1.436034
H	-1.770434	-3.609372	2.437001
C	-1.762218	-4.614244	0.520724
C	-3.247684	-4.981081	0.559979
H	-3.598256	-5.117801	1.595970
H	-3.872727	-4.207374	0.092144
H	-3.420895	-5.926348	0.020402
C	-1.328460	-4.400213	-0.930989
H	-1.955686	-3.657517	-1.446547
H	-0.280852	-4.070100	-0.996471
H	-1.421241	-5.342387	-1.494585
C	-0.949949	-5.772284	1.108340
H	-1.219140	-5.955932	2.161237
H	-1.132978	-6.702014	0.546363
H	0.131216	-5.560283	1.069344
Br	1.674295	1.928952	2.364849

SI-Int11

C	1.593680	2.155267	2.937826
C	1.489849	1.269275	1.868494
N	0.315876	1.007495	1.295403
C	-0.802513	1.591050	1.718127
C	-0.793282	2.496877	2.776667
C	0.427990	2.773073	3.390162
Ni	0.256164	-0.253428	-0.247349
C	2.577516	0.515697	1.233784
C	-1.971392	1.155681	0.946584

O	3.815648	0.541210	1.701615
C	4.562301	-0.399142	0.885697
C	3.557411	-0.859581	-0.198252
N	2.324881	-0.210841	0.216639
N	-1.855089	0.263178	0.040109
C	-3.196804	-0.014312	-0.465458
C	-4.019898	1.145460	0.128542
O	-3.167818	1.681686	1.170417
C	3.914895	-0.504491	-1.648022
C	-3.659202	-1.421115	-0.050082
H	2.561798	2.355149	3.399037
H	-1.718966	2.968104	3.109488
H	0.472018	3.475109	4.225265
H	5.442709	0.123643	0.488072
H	4.894281	-1.215960	1.540883
H	3.401611	-1.948986	-0.143736
H	-3.185033	0.037638	-1.564447
H	-4.203952	1.951612	-0.596927
H	-4.971571	0.842653	0.583772
H	3.014787	-0.776305	-2.225651
H	-2.854589	-2.099488	-0.380446
C	-3.795590	-1.578684	1.457655
H	-4.587998	-0.933303	1.871778
H	-4.062095	-2.618141	1.705776
H	-2.846055	-1.358049	1.968257
C	-4.943246	-1.787419	-0.781126
H	-5.255148	-2.813707	-0.532393
H	-5.772377	-1.115220	-0.502322
H	-4.816721	-1.727892	-1.874087
C	4.162341	0.983961	-1.844065
H	4.343422	1.201842	-2.908631
H	3.285979	1.573348	-1.533826
H	5.048526	1.332932	-1.287579
C	5.089968	-1.347792	-2.122745
H	4.884537	-2.425181	-2.016639
H	5.311440	-1.149188	-3.182959
H	6.004653	-1.122415	-1.548171
Br	-0.013196	-2.130817	1.290122
Br	0.393060	1.672828	-1.746757
O	0.396284	-1.415831	-1.696045
C	-0.669730	-1.527806	-2.545321
H	-1.571723	-1.983604	-2.084915
H	-0.960327	-0.571783	-3.028469
H	-0.371619	-2.216543	-3.366722

SI-Int12-P

Ni	0.045703	0.025791	-0.057934
P	2.146252	-0.197701	-0.166404
C	2.984582	-1.498263	0.831595
C	2.564359	-2.824940	0.646396
C	3.924350	-1.222860	1.830048
C	3.085537	-3.851625	1.426689
H	1.810312	-3.049947	-0.113658
C	4.433029	-2.251513	2.627755
H	4.263310	-0.197192	1.995154
C	4.018826	-3.566535	2.427852
H	2.750518	-4.879590	1.265127
H	5.161403	-2.018853	3.409314
H	4.417132	-4.370314	3.052444
C	3.156889	1.286454	0.237129
C	4.308943	1.663152	-0.461448
C	2.691284	2.109013	1.272812
C	4.982732	2.839652	-0.129167
H	4.683748	1.039654	-1.277033
C	3.373105	3.273549	1.617423
H	1.771307	1.837010	1.799757
C	4.519101	3.644927	0.911041
H	5.876040	3.128969	-0.689280
H	2.997868	3.904734	2.427216
H	5.045881	4.567924	1.167146
C	2.670731	-0.626083	-1.874273
C	1.844940	-0.193882	-2.922594
C	3.814654	-1.375583	-2.175710
C	2.159566	-0.496044	-4.246061
H	0.938829	0.371433	-2.683621
C	4.127541	-1.680794	-3.500564
H	4.464196	-1.729410	-1.370989
C	3.302496	-1.242306	-4.537282
H	1.503545	-0.154978	-5.051271
H	5.022756	-2.267103	-3.724460
H	3.548840	-1.486559	-5.573945
P	-1.179632	-1.600407	0.521915
C	-2.927916	-1.300002	1.020500
C	-3.895754	-1.074636	0.028690
C	-3.302600	-1.170178	2.363577
C	-5.206877	-0.755714	0.372310
H	-3.623071	-1.158134	-1.026426
C	-4.615148	-0.842048	2.707124
H	-2.564801	-1.331794	3.153889
C	-5.573272	-0.639671	1.714937
H	-5.947964	-0.594315	-0.415279
H	-4.888378	-0.745383	3.761347
H	-6.601711	-0.386792	1.985290
C	-0.527463	-2.494409	1.992574
C	-0.720809	-3.855610	2.252519
C	0.260397	-1.740148	2.873219
C	-0.135857	-4.448804	3.371997
H	-1.322025	-4.466745	1.575514
C	0.827608	-2.326616	4.002230
H	0.442758	-0.684513	2.648933
C	0.635630	-3.686734	4.249904
H	-0.283262	-5.516045	3.558129
H	1.439148	-1.724786	4.679498
H	1.094898	-4.155350	5.124257
C	-1.386850	-2.897904	-0.763725
C	-0.490801	-2.870215	-1.840374
C	-2.385653	-3.881254	-0.737542
C	-0.575354	-3.813395	-2.863878
H	0.270900	-2.086466	-1.868822
C	-2.469507	-4.826223	-1.759265
H	-3.110653	-3.905776	0.080049
C	-1.564495	-4.795764	-2.822460
H	0.130453	-3.773105	-3.697900
H	-3.250122	-5.591001	-1.727301

H	-1.637038	-5.535897	-3.623793
P	-0.898923	1.889738	-0.363543
C	-1.915444	1.969497	-1.890221
C	-2.142741	0.768362	-2.573589
C	-2.439992	3.160782	-2.408703
C	-2.894840	0.751142	-3.747762
H	-1.715034	-0.154399	-2.169651
C	-3.194394	3.143585	-3.580920
H	-2.256784	4.108184	-1.894068
C	-3.424155	1.939569	-4.250786
H	-3.062599	-0.193313	-4.272214
H	-3.604202	4.076529	-3.977022
H	-4.013299	1.930737	-5.171656
C	0.053333	3.463632	-0.499981
C	-0.177837	4.598983	0.283501
C	1.118817	3.477188	-1.412951
C	0.642788	5.723043	0.159884
H	-1.001190	4.611065	1.001638
C	1.924223	4.603339	-1.550645
H	1.326733	2.584661	-2.010675
C	1.692710	5.729879	-0.756484
H	0.454698	6.600614	0.784465
H	2.749900	4.596515	-2.267078
H	2.335156	6.609318	-0.850130
C	-2.063967	2.262308	1.002991
C	-1.546611	2.201561	2.308199
C	-3.429491	2.512203	0.829993
C	-2.369892	2.416161	3.409930
H	-0.484207	1.986195	2.460478
C	-4.256597	2.713399	1.937162
H	-3.857457	2.549929	-0.174461
C	-3.730725	2.672818	3.227145
H	-1.949425	2.372801	4.418113
H	-5.322903	2.901216	1.785860
H	-4.381174	2.831058	4.091208

SI-Int12-N

C	-0.004291	1.225112	-3.294461
C	-0.002330	1.192234	-1.906533
N	0.000000	0.000000	-1.243195
C	0.000000	0.000000	-3.993930
Ni	0.000000	0.000000	0.656227
C	0.000345	2.246438	-0.922747
O	0.082074	3.544851	-1.219914
C	0.000000	4.257845	0.027426
C	0.107451	3.168400	1.113532
N	-0.039060	1.934187	0.352470
C	1.415437	3.156552	1.920725
H	-0.011196	2.175779	-3.832760
H	0.000000	0.000000	-5.085720
H	0.809064	5.001542	0.052795
H	-0.964888	4.786400	0.058483
H	-0.725147	3.264214	1.829588
H	1.338570	2.261261	2.564825
C	2.642664	2.984349	1.037018
H	3.555558	2.914680	1.649098
H	2.570318	2.063529	0.437500
H	2.775474	3.834980	0.347622
C	1.518035	4.384792	2.813494
H	0.637009	4.482649	3.468103
H	2.410736	4.330661	3.456027
H	1.598175	5.310213	2.218668
C	0.004291	-1.225112	-3.294461
C	0.002330	-1.192234	-1.906533
C	-0.000345	-2.246438	-0.922747
O	-0.082074	-3.544851	-1.219914
C	0.000000	-4.257845	0.027426
C	-0.107451	-3.168400	1.113532
N	0.039060	-1.934187	0.352470
C	-1.415437	-3.156552	1.920725
H	0.011196	-2.175779	-3.832760
H	-0.809064	-5.001542	0.052795
H	0.964888	-4.786400	0.058483
H	0.725147	-3.264214	1.829588
H	-1.338570	-2.261261	2.564825
C	-2.642664	-2.984349	1.037018
H	-3.555558	-2.914680	1.649098
H	-2.570318	-2.063529	0.437500
H	-2.775474	-3.834980	0.347622
C	-1.518035	-4.384792	2.813494
H	-0.637009	-4.482649	3.468103
H	-2.410736	-4.330661	3.456027
H	-1.598175	-5.310213	2.218668

SI-Int12-NP

C	1.828167	4.720712	0.720633
C	1.661226	3.348656	0.567667
N	0.437809	2.796722	0.268532
C	-0.607258	3.635869	0.016588
C	-0.507982	5.009969	0.138825
C	0.730145	5.570340	0.528044
Ni	0.287958	0.853424	0.012096
C	2.669937	2.328711	0.600465
C	-1.757848	2.886990	-0.439738
O	3.972426	2.607058	0.739846
C	4.658057	1.344082	0.708412
C	3.584049	0.330079	0.267482
N	2.344232	1.082416	0.407548
N	-1.712794	1.595679	-0.535774
C	-3.037004	1.159581	-0.983544
C	-3.704795	2.479268	-1.410621
O	-2.890716	3.497365	-0.802918
C	3.726837	-0.210074	-1.165389
C	-3.787647	0.386533	0.111867
H	2.812882	5.123174	0.970481
H	-1.371360	5.642034	-0.079612
H	0.837967	6.650502	0.641213
H	5.508759	1.430117	0.017372
H	5.044378	1.133702	1.717948
H	3.581010	-0.537076	0.945888
H	-2.926375	0.486813	-1.847849
H	-3.680558	2.628104	-2.501802
H	-4.738201	2.602873	-1.059416
H	2.835877	-0.844202	-1.311968

H	-3.112492	-0.434574	0.402277
C	-4.062775	1.227186	1.350488
H	-4.783502	2.035743	1.143950
H	-4.493151	0.605523	2.151227
H	-3.143022	1.684645	1.746041
C	-5.061953	-0.232769	-0.444601
H	-5.559057	-0.855854	0.315496
H	-5.783757	0.539601	-0.760030
H	-4.849953	-0.871156	-1.317006
C	3.683118	0.891761	-2.213973
H	3.723603	0.464540	-3.228486
H	2.750825	1.472399	-2.133316
H	4.533271	1.588384	-2.119037
C	4.962748	-1.087634	-1.300558
H	4.980575	-1.876535	-0.532282
H	4.990910	-1.578807	-2.285966
H	5.890517	-0.498978	-1.200934
P	-0.121228	-1.315291	0.119383
C	-1.208371	-1.873604	-1.249214
C	-0.955207	-1.304645	-2.506155
C	-2.266205	-2.778639	-1.113033
C	-1.727353	-1.655221	-3.612005
H	-0.149867	-0.570303	-2.609130
C	-3.049716	-3.116014	-2.217093
H	-2.493959	-3.218680	-0.140019
C	-2.779828	-2.560346	-3.467965
H	-1.515506	-1.208276	-4.586791
H	-3.879072	-3.817883	-2.096769
H	-3.395397	-2.827509	-4.330880
C	-0.988368	-1.789475	1.665670
C	-1.186691	-3.119073	2.064305
C	-1.437844	-0.753461	2.492485
C	-1.846985	-3.401639	3.258435
H	-0.815484	-3.939329	1.444298
C	-2.096807	-1.036680	3.688515
H	-1.265349	0.280739	2.179898
C	-2.305048	-2.361525	4.070414
H	-2.000793	-4.440825	3.560788
H	-2.444153	-0.218673	4.324945
H	-2.819261	-2.586955	5.008453
C	1.225190	-2.564978	0.089692
C	2.036819	-2.690298	1.227356
C	1.513147	-3.344389	-1.036407
C	3.103286	-3.585946	1.241466
H	1.828789	-2.085220	2.114838
C	2.588770	-4.233910	-1.023971
H	0.893777	-3.262195	-1.932743
C	3.383983	-4.360612	0.114033
H	3.722290	-3.676492	2.137962
H	2.800294	-4.836703	-1.911098
H	4.222958	-5.061095	0.123617

SI-Int13-P

Ni	0.006655	0.087336	-0.606372
P	-1.983400	0.963248	0.049658
C	-2.300481	1.257585	1.833112
C	-1.197820	1.523089	2.652319
C	-3.582494	1.256469	2.399285
C	-1.363777	1.787829	4.010265
H	-0.195496	1.489264	2.223894
C	-3.749290	1.512493	3.759724
H	-4.457924	1.054121	1.777950
C	-2.642369	1.780084	4.567381
H	-0.488316	1.987101	4.633654
H	-4.753408	1.505246	4.191656
H	-2.778086	1.978284	5.633772
C	-3.442755	-0.028009	-0.456085
C	-4.176763	0.266587	-1.609929
C	-3.772232	-1.174677	0.283094
C	-5.230188	-0.559032	-2.006537
H	-3.932636	1.149429	-2.205468
C	-4.834903	-1.985997	-0.103407
H	-3.195742	-1.436647	1.173416
C	-5.567889	-1.681400	-1.252027
H	-5.794963	-0.314790	-2.910149
H	-5.083469	-2.869484	0.490175
H	-6.397051	-2.323001	-1.561039
C	-2.321385	2.622239	-0.673275
C	-1.888904	2.877879	-1.982570
C	-2.952142	3.646920	0.044739
C	-2.101526	4.125510	-2.566570
H	-1.364753	2.096291	-2.541766
C	-3.153643	4.897342	-0.539674
H	-3.285453	3.478783	1.070878
C	-2.732146	5.140204	-1.846864
H	-1.756640	4.308212	-3.587805
H	-3.643190	5.687961	0.035121
H	-2.888898	6.122175	-2.300946
P	1.922716	1.084274	0.094840
C	3.537854	0.540160	-0.593713
C	3.561394	0.005062	-1.889758
C	4.731984	0.614754	0.134590
C	4.763395	-0.415855	-2.455572
H	2.626273	-0.084781	-2.451898
C	5.929835	0.174538	-0.428712
H	4.733708	1.013456	1.151261
C	5.950448	-0.335686	-1.726589
H	4.768061	-0.826816	-3.468613
H	6.853535	0.233394	0.153057
H	6.890624	-0.678323	-2.166735
C	2.313793	1.297111	1.873100
C	2.883232	2.462740	2.402221
C	2.037590	0.226101	2.731875
C	3.161498	2.552608	3.765684
H	3.111087	3.307934	1.748664
C	2.324156	0.311924	4.092814
H	1.568832	-0.675403	2.334944
C	2.884134	1.478851	4.613331
H	3.601309	3.468754	4.168376
H	2.095132	-0.532399	4.748082
H	3.101657	1.554373	5.681895
C	1.764157	2.812728	-0.506395
C	0.872442	3.676860	0.148723
C	2.413899	3.261236	-1.661299

C	0.657691	4.967311	-0.327123
H	0.340305	3.342552	1.042358
C	2.183134	4.549264	-2.146778
H	3.108005	2.604687	-2.190573
C	1.308800	5.406868	-1.481232
H	-0.033343	5.629107	0.200990
H	2.697213	4.883528	-3.051836
H	1.131465	6.416172	-1.861467
P	0.051203	-2.113064	0.047006
C	1.615629	-2.852960	-0.559660
C	2.796934	-2.673551	0.176009
C	1.678759	-3.511863	-1.792386
C	4.006696	-3.177270	-0.293662
H	2.775358	-2.139964	1.128938
C	2.896033	-3.998913	-2.270206
H	0.773035	-3.649979	-2.387149
C	4.060541	-3.841563	-1.520155
H	4.915494	-3.036878	0.296903
H	2.929750	-4.512008	-3.234892
H	5.011814	-4.229543	-1.893278
C	-1.237813	-3.161153	-0.739136
C	-1.688869	-4.356869	-0.166361
C	-1.788106	-2.734798	-1.955178
C	-2.665700	-5.118533	-0.807123
H	-1.282648	-4.699457	0.787881
C	-2.751421	-3.507552	-2.601186
H	-1.451714	-1.791535	-2.395890
C	-3.195164	-4.699149	-2.028113
H	-3.013757	-6.047400	-0.347658
H	-3.169128	-3.165669	-3.551779
H	-3.960007	-5.298857	-2.528571
C	-0.011571	-2.646496	1.799276
C	-0.791887	-1.885771	2.677248
C	0.663388	-3.771761	2.291847
C	-0.896987	-2.232874	4.022664
H	-1.302824	-0.996886	2.307145
C	0.563495	-4.116098	3.639272
H	1.274733	-4.383087	1.624341
C	-0.214303	-3.348249	4.507574
H	-1.504684	-1.619611	4.692982
H	1.098236	-4.993034	4.013277
H	-0.285350	-3.619462	5.564083
Br	0.142362	0.103805	-3.057449

SI-Int15-P

Ni	0.900922	1.416363	-0.442334
Br	0.466177	3.794974	-0.698389
O	-1.164536	-0.445533	0.815937
C	-0.030236	-0.386762	1.296805
C	0.635349	0.922794	1.521183
N	0.725790	-1.487712	1.594065
C	0.386790	-2.835050	1.505265
C	1.393766	-3.774367	1.785476
C	1.134217	-5.137610	1.698726
C	-0.134978	-5.595445	1.338734
C	-1.140745	-4.664173	1.080483
C	-0.895999	-3.294128	1.162043
F	1.858370	0.726933	2.199102
H	1.654520	-1.287011	1.952130
H	2.387593	-3.418737	2.068175
H	1.935420	-5.849215	1.915502
H	-0.338451	-6.666565	1.267302
H	-2.143020	-5.005282	0.806897
H	-1.681602	-2.569877	0.956528
C	-0.232168	1.938257	2.229108
H	-1.210460	1.866858	1.727326
H	0.126999	2.957123	2.014334
C	-0.444769	1.810857	3.756924
C	-1.607823	2.737329	4.121389
H	-1.782072	2.745065	5.209964
H	-1.403619	3.774380	3.807442
H	-2.541842	2.416793	3.631647
C	-0.799320	0.380661	4.163032
H	-1.673562	0.009472	3.605738
H	0.035710	-0.313137	3.981891
H	-1.039317	0.332948	5.237939
C	0.798568	2.270437	4.524222
H	1.666312	1.629060	4.318488
H	1.070439	3.303729	4.251822
H	0.610961	2.252402	5.610835
P	3.226810	1.453252	-0.468921
C	3.956174	-0.152684	0.011548
C	3.401272	-1.314614	-0.544275
C	4.999634	-0.270274	0.937502
C	3.917104	-2.567744	-0.220663
H	2.555531	-1.243213	-1.230581
C	5.499031	-1.528057	1.274569
H	5.426782	0.618175	1.405910
C	4.968845	-2.677280	0.688909
H	3.479915	-3.461720	-0.670522
H	6.312644	-1.606950	2.000174
H	5.366717	-3.660888	0.951253
C	4.034833	2.694742	0.590938
C	5.401569	2.979144	0.449848
C	3.288172	3.364434	1.564993
C	6.012021	3.909413	1.287091
H	5.992413	2.473566	-0.318334
C	3.903425	4.294272	2.402419
H	2.220623	3.168784	1.653655
C	5.264018	4.565528	2.266946
H	7.077635	4.123944	1.173367
H	3.311597	4.813916	3.160237
H	5.744714	5.296323	2.922585
C	3.904884	1.821413	-2.128064
C	4.028988	3.162849	-2.520445
C	4.208715	0.809673	-3.046239
C	4.471089	3.481457	-3.801754
H	3.775269	3.963916	-1.822008
C	4.636276	1.134514	-4.333617
H	4.120880	-0.240480	-2.761621
C	4.773063	2.468762	-4.713594
H	4.571554	4.530266	-4.092434
H	4.869553	0.334077	-5.040422
H	5.112283	2.720845	-5.721442

P	0.034716	0.580020	-2.556410
C	-1.789378	0.476424	-2.465219
C	-2.457312	1.509110	-1.794103
C	-2.526436	-0.561754	-3.047204
C	-3.848278	1.505286	-1.712862
H	-1.882165	2.319271	-1.333385
C	-3.917719	-0.564805	-2.955993
H	-2.016591	-1.376080	-3.567613
C	-4.580154	0.467156	-2.290236
H	-4.362420	2.314126	-1.187281
H	-4.487377	-1.380226	-3.409167
H	-5.670926	0.460265	-2.218887
C	0.596457	-1.130330	-2.842303
C	1.553333	-1.439689	-3.816374
C	0.166457	-2.129550	-1.955767
C	2.067960	-2.733595	-3.904209
H	1.907894	-0.669807	-4.504601
C	0.676752	-3.421374	-2.054053
H	-0.563149	-1.890723	-1.177323
C	1.630594	-3.725616	-3.027516
H	2.817346	-2.964460	-4.665577
H	0.335199	-4.189717	-1.355720
H	2.035975	-4.738054	-3.098850
C	0.328330	1.443015	-4.136911
C	1.036647	2.646918	-4.142190
C	-0.174284	0.924036	-5.339705
C	1.251498	3.324190	-5.343756
H	1.400931	3.060959	-3.199782
C	0.047331	1.600110	-6.535532
H	-0.736915	-0.013448	-5.341631
C	0.761653	2.801551	-6.538518
H	1.806077	4.265747	-5.341805
H	-0.341604	1.190315	-7.471151
H	0.932455	3.331949	-7.479036

SI-Int15-N

C	-0.636036	-2.463910	-2.591396
C	0.215059	-1.563758	-1.955211
N	-0.248156	-0.483591	-1.331291
C	-1.550206	-0.212975	-1.309793
C	-2.481468	-1.055435	-1.914322
C	-2.005771	-2.197449	-2.557129
Ni	1.051523	0.774468	-0.248772
C	1.684070	-1.628732	-1.904288
C	-1.824901	1.059324	-0.627474
O	2.347065	-2.533002	-2.609969
C	3.745995	-2.167157	-2.499388
C	3.769067	-1.075290	-1.406744
N	2.351285	-0.777637	-1.221835
N	-0.864207	1.794720	-0.208713
C	-1.446421	3.015443	0.337630
C	-2.962652	2.722560	0.281050
O	-3.064147	1.491637	-0.473455
C	4.439103	-1.475293	-0.084692
C	-0.969980	4.253029	-0.437471
H	-0.238818	-3.343885	-3.098271
H	-3.545962	-0.820429	-1.882848
H	-2.705436	-2.883469	-3.038387
H	4.316456	-3.071209	-2.250562
H	4.069212	-1.797452	-3.482968
H	4.262368	-0.162076	-1.773182
H	-1.119879	3.129031	1.382953
H	-3.399694	2.541658	1.273037
H	-3.554127	3.488499	-0.238367
H	4.136193	-0.694359	0.630819
H	0.130011	4.235523	-0.346742
C	-1.315864	4.187107	-1.918071
H	-2.405490	4.184045	-2.089766
H	-0.906555	5.061321	-2.448308
H	-0.892467	3.286589	-2.389670
C	-1.493899	5.523739	0.216856
H	-1.086201	6.416668	-0.282243
H	-2.593592	5.588606	0.157714
H	-1.211876	5.574546	1.280926
C	3.947536	-2.817161	0.440589
H	4.244443	-2.956326	1.491247
H	2.851971	-2.897979	0.394040
H	4.368399	-3.659469	-0.132443
C	5.954141	-1.454039	-0.228797
H	6.316899	-0.457540	-0.527210
H	6.441727	-1.720423	0.722025
H	6.295251	-2.178088	-0.988230
Br	2.662681	2.595053	-0.273809
O	-1.449990	-0.591163	1.641452
C	-0.274036	-0.956883	1.584908
C	0.859224	-0.023509	1.692733
N	0.090191	-2.256624	1.303124
C	-0.693140	-3.284395	0.792830
C	-0.033650	-4.391622	0.228304
C	-0.757270	-5.438110	-0.332661
C	-2.153359	-5.406399	-0.346625
C	-2.808998	-4.314708	0.222719
C	-2.097959	-3.260534	0.793584
F	2.053260	-0.740752	1.947604
H	1.091513	-2.416149	1.295695
H	1.059952	-4.410810	0.219261
H	-0.221559	-6.284146	-0.771593
H	-2.722296	-6.225654	-0.792776
H	-3.902060	-4.276295	0.224565
H	-2.607071	-2.401435	1.225160
C	0.686452	1.106859	2.672280
H	-0.351144	1.440933	2.519884
H	1.334143	1.951742	2.383476
C	0.893519	0.826896	4.180905
C	0.287588	2.006195	4.945819
H	0.453197	1.906043	6.031403
H	0.738641	2.960220	4.625619
H	-0.799367	2.076709	4.775231
C	0.194263	-0.463015	4.608150
H	-0.876876	-0.440345	4.355077
H	0.635633	-1.342164	4.113191
H	0.285681	-0.613741	5.696622
C	2.383840	0.741136	4.521449
H	2.866436	-0.100988	4.007094

H	2.910025	1.663057	4.222721
H	2.529660	0.610010	5.606847

SI-TS7

C	1.555555	4.066714	-0.646993
C	0.887941	2.850091	-0.508330
N	1.523058	1.745529	-0.135514
C	2.828083	1.761011	0.121952
C	3.581168	2.928731	0.023221
C	2.921826	4.094262	-0.369132
Ni	0.514658	-0.037792	0.035477
C	-0.542301	2.605076	-0.740739
C	3.319769	0.426063	0.489844
O	-1.311620	3.578487	-1.211662
C	-2.604027	2.974082	-1.443595
C	-2.495256	1.582949	-0.781436
N	-1.064986	1.463935	-0.506265
N	2.519631	-0.571560	0.516546
C	3.315732	-1.762746	0.802306
C	4.675274	-1.160338	1.209389
O	4.592793	0.223150	0.782297
C	-3.330145	1.413350	0.498829
C	3.332325	-2.717817	-0.400230
O	-0.138684	0.071844	1.976480
C	0.088291	-1.184703	2.136001
C	-0.385430	-2.134256	1.234124
N	0.931379	-1.617043	3.149075
C	1.973794	-0.937290	3.762799
C	2.200518	0.444335	3.621327
C	3.307121	1.034217	4.228019
C	4.198844	0.286125	4.997878
C	3.963276	-1.081203	5.158027
C	2.869328	-1.687152	4.549114
F	0.164645	-3.400668	1.380587
H	1.019266	4.963812	-0.959158
H	4.649415	2.923037	0.243527
H	3.477646	5.029575	-0.461104
H	-3.370061	3.625422	-1.002673
H	-2.759682	2.920769	-2.530783
H	-2.785420	0.790305	-1.488286
H	2.864572	-2.298490	1.648317
H	4.830102	-1.159895	2.298199
H	5.543253	-1.617888	0.717334
H	-3.103740	0.400291	0.866376
H	2.269393	-2.884771	-0.645570
H	0.951919	-2.623836	3.271462
H	1.502777	1.029346	3.025741
H	3.470548	2.107525	4.093633
H	5.061710	0.761162	5.470709
H	4.644093	-1.689835	5.759634
H	2.700514	-2.761871	4.665008
C	3.992155	-2.109497	-1.628139
H	5.061967	-1.897984	-1.462325
H	3.925538	-2.805057	-2.479421
H	3.478773	-1.184151	-1.929580
C	3.962701	-4.044739	-0.001326
H	3.433228	-4.500508	0.850914
H	3.932108	-4.759983	-0.838076
H	5.020436	-3.921182	0.287200
C	-2.935627	2.392583	1.594017
H	-3.090703	3.441777	1.290382
H	-3.545451	2.222794	2.495454
H	-1.881270	2.257872	1.876886
C	-4.816522	1.472481	0.174789
H	-5.085701	0.760043	-0.621451
H	-5.417204	1.226130	1.064107
H	-5.122108	2.478314	-0.158482
C	-1.676148	-2.126696	0.497540
H	-1.949498	-1.072745	0.347242
H	-1.523416	-2.535061	-0.517056
Br	0.492304	-0.879489	-2.268159
C	-2.879787	-2.848100	1.159339
C	-2.646789	-4.357923	1.235916
H	-1.803327	-4.605533	1.895822
H	-3.543421	-4.870019	1.623270
H	-2.427078	-4.776719	0.239801
C	-3.122754	-2.294590	2.562006
H	-2.257482	-2.473711	3.220292
H	-3.304048	-1.207512	2.537398
H	-4.001754	-2.771284	3.026282
C	-4.106888	-2.578985	0.286722
H	-3.949058	-2.939533	-0.743257
H	-4.999339	-3.087532	0.686981
H	-4.329409	-1.501084	0.233938

SI-Int16

C	-0.451684	-2.364739	-3.107877
C	0.300308	-1.525416	-2.289350
N	-0.244092	-0.474337	-1.686251
C	-1.533268	-0.187262	-1.828765
C	-2.369292	-0.965926	-2.625155
C	-1.805812	-2.068048	-3.269358
Ni	0.893651	0.630019	-0.392860
C	1.727131	-1.643853	-1.948815
C	-1.901365	0.995880	-1.036208
O	2.489769	-2.581318	-2.481848
C	3.807720	-2.400661	-1.901659
C	3.671814	-1.142389	-1.011455
N	2.256260	-0.816440	-1.129729
N	-1.017476	1.609353	-0.343266
C	-1.683354	2.702123	0.360558
C	-3.158214	2.547677	-0.079410
O	-3.147513	1.430876	-1.002573
C	4.107006	-1.307910	0.449270
C	-1.030419	4.056429	0.063302
H	0.004916	-3.226938	-3.595375
H	-3.426950	-0.722178	-2.730679
H	-2.430003	-2.706296	-3.897871
H	4.051787	-3.314972	-1.341650
H	4.523961	-2.281479	-2.724517
H	4.243559	-0.301183	-1.437091
H	-1.588660	2.510987	1.441196
H	-3.832592	2.290076	0.747826
H	-3.561048	3.419873	-0.612772

H	3.936441	-0.318883	0.908907
H	0.022165	3.938753	0.372675
C	-1.030983	4.396852	-1.419179
H	-2.051676	4.526231	-1.817396
H	-0.491657	5.340790	-1.594996
H	-0.525215	3.614934	-2.005730
C	-1.673414	5.146916	0.908491
H	-1.157562	6.108900	0.763436
H	-2.732748	5.299229	0.640171
H	-1.631218	4.900538	1.981846
C	3.258894	-2.323214	1.201630
H	3.620629	-2.430630	2.236469
H	2.209910	-1.992325	1.244078
H	3.305229	-3.323621	0.738419
C	5.595231	-1.620491	0.523738
H	6.195009	-0.870744	-0.017215
H	5.936926	-1.633145	1.570303
H	5.823568	-2.609794	0.092581
Br	2.441262	2.504211	-0.554542
O	0.543897	-0.364570	1.263727
C	-0.359821	0.088070	2.080114
C	-0.118628	1.053187	3.012889
N	-1.671115	-0.403997	1.984299
C	-2.152309	-1.444549	1.224819
C	-3.543236	-1.512493	0.992977
C	-4.098193	-2.555938	0.260605
C	-3.289611	-3.561003	-0.275197
C	-1.911933	-3.496761	-0.054333
C	-1.339924	-2.464300	0.683161
F	-1.193927	1.444480	3.793685
H	-2.369247	0.142356	2.475798
H	-4.184234	-0.724909	1.399986
H	-5.180168	-2.578384	0.101686
H	-3.725064	-4.378028	-0.855301
H	-1.259078	-4.272839	-0.464610
H	-0.263851	-2.419776	0.839623
C	1.099996	1.876273	3.175561
H	1.660684	1.845799	2.226955
H	0.783781	2.928486	3.313153
C	2.062958	1.508763	4.330111
C	3.183728	2.546925	4.359574
H	3.923268	2.316709	5.144169
H	2.787337	3.556720	4.557765
H	3.715907	2.581637	3.394437
C	2.657067	0.124053	4.079804
H	3.243013	0.109395	3.147425
H	1.863395	-0.633576	3.986449
H	3.324108	-0.176624	4.904863
C	1.319569	1.516655	5.665212
H	0.522727	0.756302	5.683621
H	0.852331	2.496772	5.857427
H	2.006654	1.302209	6.500597

TS-enol-flip

C	-1.188548	-1.940007	-3.505006
C	-0.405053	-1.329506	-2.527076
N	-0.789851	-0.209134	-1.923458
C	-1.957173	0.356796	-2.220554
C	-2.817786	-0.188922	-3.170068
C	-2.411781	-1.352476	-3.823004
Ni	0.417782	0.691013	-0.545624
C	0.883970	-1.824127	-2.026858
C	-2.197384	1.572344	-1.431185
O	1.478240	-2.831028	-2.651659
C	2.657522	-3.127647	-1.872394
C	2.766069	-1.949698	-0.882359
N	1.468438	-1.283890	-1.027513
N	-1.303353	2.039334	-0.640840
C	-1.832859	3.295697	-0.094550
C	-3.314040	3.238547	-0.514690
O	-3.357752	2.199279	-1.520775
C	3.094405	-2.383213	0.546602
C	-1.100707	4.535350	-0.641703
H	-0.852429	-2.856301	-3.991732
H	-3.773572	0.286644	-3.393391
H	-3.055723	-1.807145	-4.578442
H	2.484087	-4.088994	-1.363228
H	3.508686	-3.225110	-2.557276
H	3.533814	-1.224578	-1.210851
H	-1.737337	3.279272	1.001254
H	-3.981752	2.934539	0.304828
H	-3.686300	4.168764	-0.963411
H	2.264518	-3.035813	0.876737
H	-1.738873	5.383303	-0.332556
C	0.269030	4.725088	-0.008423
H	0.935122	3.880188	-0.245451
H	0.746236	5.639798	-0.395329
H	0.193231	4.825612	1.083912
C	-1.015275	4.526086	-2.163066
H	-0.616530	5.485130	-2.528888
H	-0.336511	3.728839	-2.506199
H	-1.998117	4.379486	-2.639529
C	4.388065	-3.189799	0.566266
H	4.331873	-4.101748	-0.048803
H	5.231693	-2.583735	0.194859
H	4.630333	-3.501879	1.593924
C	3.181605	-1.188844	1.483137
H	2.249015	-0.606338	1.478968
H	3.379837	-1.521651	2.514711
H	4.009227	-0.522124	1.185930
O	0.358407	0.374935	1.339407
C	-0.206022	0.332317	2.504008
C	-0.254233	1.385076	3.367300
N	-0.703607	-0.908229	2.946974
C	-1.128436	-1.937452	2.139301
C	-1.031311	-3.270712	2.583931
C	-1.471626	-4.320566	1.782797
C	-2.011806	-4.077555	0.517377
C	-2.125116	-2.756444	0.078079
C	-1.700159	-1.698139	0.874579
F	-0.831362	1.159773	4.598250
H	-0.605957	-1.105341	3.936047
H	-0.594806	-3.470734	3.566870
H	-1.381905	-5.346333	2.151779

H	-2.348549	-4.904491	-0.112338
H	-2.569008	-2.541311	-0.898277
H	-1.820739	-0.670285	0.535506
C	0.368448	2.715656	3.190781
H	0.493681	2.867298	2.109404
H	-0.335017	3.493884	3.542623
C	1.739380	2.959361	3.871634
C	2.776011	1.989845	3.307017
H	2.484946	0.946012	3.499165
H	2.883661	2.111671	2.217454
H	3.763552	2.156868	3.768008
C	1.628761	2.767267	5.384189
H	2.590463	2.983693	5.878216
H	0.869931	3.439558	5.818005
H	1.343137	1.734978	5.637197
C	2.170118	4.394696	3.570322
H	1.430177	5.121841	3.944352
H	3.137628	4.626391	4.045507
H	2.282365	4.557801	2.485950
Br	2.013949	1.870108	-1.947431

TS7

C	1.938812	2.714097	-2.955896
C	1.919387	1.801577	-1.902116
N	0.830190	1.619453	-1.165048
C	-0.299327	2.271573	-1.415402
C	-0.383243	3.196979	-2.452307
C	0.762553	3.415490	-3.220553
Ni	0.885310	0.277473	0.342214
C	3.024149	0.955349	-1.424812
C	-1.363378	1.858947	-0.487256
O	4.240827	1.069358	-1.931932
C	5.036718	0.059536	-1.260439
C	4.149614	-0.397595	-0.086761
N	2.841029	0.135398	-0.459176
N	-1.114030	1.035925	0.460803
C	-2.337817	0.873876	1.239229
C	-3.386457	1.576956	0.352879
O	-2.598499	2.314320	-0.615972
C	4.148596	-1.895803	0.219535
C	-2.168782	1.439730	2.656735
H	2.839866	2.861133	-3.551925
H	-1.313804	3.729053	-2.653398
H	0.733774	4.134498	-4.041902
H	5.239076	-0.740749	-1.988824
H	5.983078	0.520667	-0.953991
H	4.444464	0.127802	0.839268
H	-2.566318	-0.198998	1.321783
H	-4.011446	0.864584	-0.205159
H	-4.030551	2.290521	0.883036
H	3.495952	-2.011211	1.100109
H	-1.295913	0.909445	3.075358
C	-1.837282	2.924419	2.658581
H	-2.648828	3.530753	2.222085
H	-1.683716	3.280339	3.689457
H	-0.906552	3.120031	2.104967
C	-3.394245	1.119403	3.500849
H	-3.249780	1.450425	4.540995
H	-4.295281	1.627028	3.116995
H	-3.600547	0.037032	3.516714
C	3.528379	-2.733179	-0.888120
H	3.562701	-3.801163	-0.621330
H	2.472571	-2.459746	-1.025310
H	4.052532	-2.619064	-1.851879
C	5.556629	-2.354230	0.576818
H	5.988889	-1.742875	1.385657
H	5.550806	-3.401899	0.915681
H	6.237673	-2.294553	-0.289343
O	0.176226	-1.370745	-0.551113
C	-0.951182	-1.370254	-1.220205
C	-2.063201	-2.057450	-0.849513
N	-1.046443	-0.572987	-2.376054
C	-0.104872	-0.411636	-3.371154
C	-0.442003	0.375614	-4.491011
C	0.480521	0.600196	-5.506016
C	1.765899	0.055723	-5.436886
C	2.097994	-0.739177	-4.338798
C	1.181750	-0.980020	-3.318524
F	-3.150829	-1.978525	-1.693784
H	-1.998582	-0.369779	-2.659129
H	-1.442829	0.813662	-4.547506
H	0.192017	1.217491	-6.361533
H	2.492192	0.240706	-6.231835
H	3.094435	-1.185081	-4.268902
H	1.454403	-1.587995	-2.459640
C	0.467144	-2.250797	2.782241
H	-0.096840	-1.300667	2.751168
H	1.151959	-2.177728	3.642568
H	-0.249660	-3.067788	3.000042
O	1.217665	-2.482427	1.627804
H	0.693183	-2.257422	0.826903
C	-2.304371	-2.846085	0.378401
H	-1.591306	-2.511760	1.145609
H	-3.312264	-2.595184	0.759997
C	-2.203251	-4.387344	0.253838
C	-3.186964	-4.902678	-0.796754
H	-4.221529	-4.605548	-0.557843
H	-2.948603	-4.511777	-1.797999
H	-3.157816	-6.003542	-0.850367
C	-0.780977	-4.785231	-0.138475
H	-0.507886	-4.356528	-1.115874
H	-0.045569	-4.424531	0.597851
H	-0.686989	-5.881260	-0.211619
C	-2.549072	-4.993175	1.613526
H	-3.571822	-4.721128	1.923141
H	-2.488118	-6.093421	1.585889
H	-1.856988	-4.637875	2.394614
Br	1.706093	1.293182	2.396874

TS7'

C	-2.836636	2.701651	1.562164
C	-2.052161	1.957482	0.683932
N	-0.743186	1.816501	0.870057
C	-0.130308	2.392670	1.898280

C	-0.830323	3.153653	2.833282
C	-2.204827	3.301303	2.651730
Ni	0.367576	0.787532	-0.512417
C	-2.510331	1.277361	-0.535904
C	1.314082	2.115292	1.910911
O	-3.761824	1.406629	-0.952280
C	-3.806056	0.788317	-2.262827
C	-2.439730	0.082121	-2.396736
N	-1.700418	0.592903	-1.248042
N	1.874962	1.448160	0.975151
C	3.289151	1.3060	1.324587
C	3.373159	1.988390	2.708416
O	2.052885	2.533271	2.926930
C	-2.461535	-1.452708	-2.382949
C	4.236796	1.897827	0.272157
H	-3.909152	2.808241	1.394952
H	-0.311292	3.612764	3.675056
H	-2.788358	3.887734	3.364259
H	-4.671246	0.114104	-2.294469
H	-3.946179	1.589757	-3.001840
H	-1.923077	0.413016	-3.310839
H	3.508795	0.229705	1.414241
H	3.584745	1.283395	3.524262
H	4.096697	2.814330	2.750266
H	-1.421074	-1.739235	-2.159560
H	5.236736	1.860453	0.742742
C	4.265389	1.035188	-0.981143
H	3.274151	0.981066	-1.456056
H	4.973524	1.445003	-1.719287
H	4.580561	0.004975	-0.750235
C	3.904670	3.348337	-0.052245
H	4.683187	3.784554	-0.698065
H	2.944645	3.411338	-0.590466
H	3.842656	3.977078	0.851064
C	-3.347740	-2.024677	-1.284681
H	-3.187834	-1.513547	-0.324022
H	-4.417015	-1.938663	-1.537070
H	-3.134382	-3.093959	-1.132261
C	-2.829115	-2.006352	-3.750549
H	-2.130569	-1.654927	-4.526468
H	-2.805417	-3.107374	-3.746621
H	-3.845950	-1.697845	-4.047497
O	0.602254	-1.118749	0.036640
C	-0.194668	-1.890416	0.730545
C	-0.061015	-3.236310	0.821340
N	-1.228839	-1.270588	1.485104
C	-0.965393	-0.727480	2.729814
C	0.348863	-0.555294	3.201571
C	0.577716	0.017393	4.450795
C	-0.482268	0.434948	5.256194
C	-1.789248	0.259695	4.792360
C	-2.032761	-0.312364	3.548595
F	-0.935917	-3.892851	1.653111
H	-2.134222	-1.723151	1.419258
H	1.185998	-0.866792	2.574717
H	1.607412	0.139507	4.797871
H	-0.294838	0.886648	6.233120
H	-2.635692	0.575072	5.409133
H	-3.057776	-0.444152	3.190230
C	1.073300	-0.913899	-3.451921
H	0.627473	-1.875942	-3.769537
H	1.740489	-0.581643	-4.263929
H	0.268159	-0.161383	-3.380926
O	1.829218	-1.020200	-2.281838
H	1.283026	-1.319423	-1.521235
C	1.001046	-4.100418	0.252345
H	1.808407	-3.438570	-0.099620
H	1.422001	-4.698666	1.083261
C	0.626351	-5.070565	-0.892196
C	0.221282	-4.269179	-2.125407
H	-0.649958	-3.632495	-1.909325
H	1.042791	-3.613770	-2.452672
H	-0.044548	-4.932623	-2.964584
C	1.859574	-5.913790	-1.215847
H	2.175865	-6.509981	-0.343992
H	1.656083	-6.611606	-2.044507
H	2.709489	-5.277667	-1.513472
C	-0.521516	-5.989633	-0.474650
H	-0.743435	-6.718524	-1.271530
H	-0.271952	-6.555519	0.437937
H	-1.441812	-5.420201	-0.273915
Br	0.730633	2.595445	-2.121754

TS7-^{i}PrOH

C	-2.643150	2.928585	1.513076
C	-2.008693	2.132707	0.563300
N	-0.766495	1.696967	0.737754
C	-0.078339	2.010491	1.827445
C	-0.624341	2.802350	2.835283
C	-1.928282	3.263537	2.663412
Ni	0.152272	0.681967	-0.753475
C	-2.559473	1.675896	-0.719229
C	1.264249	1.414802	1.810742
O	-3.779945	2.024740	-1.099672
C	-3.910272	1.547139	-2.461329
C	-2.705239	0.606618	-2.647045
N	-1.863072	0.944195	-1.498135
N	1.688802	0.767050	0.794880
C	3.043005	0.292109	1.121916
C	3.183163	0.675236	2.608386
O	2.044715	1.521897	2.873908
C	-3.019921	-0.896704	-2.657057
C	4.130441	0.890153	0.219547
H	-3.664828	3.275824	1.355114
H	-0.044985	3.045199	3.726301
H	-2.392753	3.884347	3.431979
H	-4.888990	1.061436	-2.563457
H	-3.870664	2.423142	-3.124761
H	-2.158224	0.855083	-3.568209
H	3.057898	-0.800800	1.004831
H	3.117701	-0.191877	3.281348
H	4.096202	1.240757	2.837813
H	-2.045082	-1.392433	-2.519185
H	5.080412	0.573002	0.688098

C	4.073113	0.298798	-1.181067
H	3.120523	0.535106	-1.678467
H	4.889836	0.697214	-1.804130
H	4.175058	-0.797676	-1.155767
C	4.090934	2.412344	0.192125
H	4.956244	2.806907	-0.363599
H	3.177905	2.766504	-0.312854
H	4.126317	2.852541	1.201927
C	-3.925813	-1.324518	-1.510178
H	-3.572449	-0.950184	-0.537192
H	-4.959448	-0.968099	-1.649179
H	-3.966261	-2.422498	-1.442292
C	-3.592264	-1.311491	-4.004922
H	-2.907719	-1.057901	-4.829470
H	-3.773138	-2.397172	-4.036427
H	-4.554788	-0.809811	-4.201755
O	-0.120500	-1.255919	-0.503162
C	-0.219490	-1.819078	0.677819
C	0.598760	-2.798271	1.105225
N	-1.304368	-1.376667	1.453245
C	-1.292768	-0.882034	2.736907
C	-0.139794	-0.852017	3.544158
C	-0.188972	-0.296049	4.820321
C	-1.372367	0.235038	5.333392
C	-2.522852	0.198136	4.539411
C	-2.488901	-0.351452	3.263975
F	0.296395	-3.415901	2.288418
H	-2.100048	-1.098191	0.889661
H	0.796101	-1.255257	3.158360
H	0.724884	-0.274500	5.420607
H	-1.401260	0.667671	6.336129
H	-3.463360	0.608689	4.917730
H	-3.391968	-0.369424	2.647018
C	0.627639	-0.937245	-3.910955
H	-0.244327	-0.276652	-3.745598
O	1.332755	-1.093894	-2.689148
H	0.750650	-1.462186	-1.998792
C	1.839227	-3.281745	0.463111
H	2.143087	-2.523413	-0.274271
H	2.640877	-3.326927	1.224518
C	1.778735	-4.654284	-0.251429
C	0.763056	-4.601760	-1.390331
H	-0.240344	-4.341086	-1.018136
H	1.049928	-3.847346	-2.137832
H	0.692924	-5.575659	-1.901920
C	3.167537	-4.941948	-0.822113
H	3.926028	-4.986498	-0.023059
H	3.186440	-5.905651	-1.356823
H	3.475105	-4.156928	-1.532727
C	1.395445	-5.762873	0.729189
H	1.421538	-6.746492	0.232017
H	2.090666	-5.800704	1.584031
H	0.381063	-5.616223	1.129753
Br	0.903326	2.624721	-2.048494
C	1.561043	-0.237801	-4.876023
H	2.455470	-0.854443	-5.064315
H	1.062995	-0.050037	-5.839913
H	1.881427	0.726354	-4.454063
C	0.130159	-2.269618	-4.444903
H	-0.543711	-2.760683	-3.725434
H	-0.425307	-2.132980	-5.386489
H	0.975870	-2.948741	-4.641301

TS7'-^{i}PrOH

C	-2.634493	2.453033	1.621859
C	-1.879805	1.717562	0.711944
N	-0.564005	1.598877	0.833078
C	0.078947	2.157609	1.850168
C	-0.584550	2.921646	2.808819
C	-1.963611	3.067256	2.679453
Ni	0.455683	0.481725	-0.528061
C	-2.393650	1.018677	-0.472931
C	1.519805	1.879106	1.813730
O	-3.673859	1.143437	-0.797898
C	-3.863822	0.250663	-1.917707
C	-2.440162	-0.017580	-2.419100
N	-1.632456	0.337390	-1.239362
N	2.042093	1.199555	0.868859
C	3.495093	1.240475	1.071619
C	3.604531	1.757698	2.515187
O	2.310111	2.350520	2.768951
C	-2.208276	-1.425027	-2.956352
C	4.163569	2.123645	0.005356
H	-3.714779	2.541848	1.502435
H	-0.033347	3.378059	3.631017
H	-2.521895	3.653375	3.412082
H	-4.349889	-0.662722	-1.536462
H	-4.520059	0.741992	-2.645271
H	-2.167328	0.705106	-3.210500
H	3.900316	0.221801	0.990219
H	3.748078	0.946583	3.244667
H	4.372874	2.525444	2.670682
H	-2.310122	-2.116149	-2.100986
H	3.796209	1.743019	-0.962466
C	3.742335	3.583361	0.091982
H	4.076583	4.059252	1.028657
H	4.187142	4.153502	-0.738534
H	2.650553	3.689986	0.006654
C	5.675702	1.957651	0.061167
H	6.163337	2.544699	-0.732572
H	6.085788	2.302499	1.025475
H	5.969363	0.903657	-0.069463
C	-3.268092	-1.778003	-3.994972
H	-4.287604	-1.774643	-3.579109
H	-3.244072	-1.067885	-4.838777
H	-3.083762	-2.783893	-4.402880
C	-0.813112	-1.561647	-3.545903
H	-0.018577	-1.301448	-2.833591
H	-0.635088	-2.594433	-3.884676
H	-0.701356	-0.899750	-4.421078
O	0.450383	-1.283603	0.431362
C	-0.651812	-1.898362	0.788198
C	-1.052590	-3.088775	0.300273
N	-1.476497	-1.257584	1.730416

C	-1.058903	-0.745061	2.939760
C	0.296395	-0.686625	3.322415
C	0.656301	-0.121558	4.543510
C	-0.305190	0.392027	5.414973
C	-1.651787	0.315238	5.048670
C	-2.026848	-0.241307	3.831618
F	-2.200823	-3.626580	0.832180
H	-2.454916	-1.517364	1.689023
H	1.055079	-1.070735	2.641446
H	1.714946	-0.083006	4.815625
H	-0.012348	0.836229	6.369217
H	-2.424958	0.700558	5.719473
H	-3.082549	-0.290522	3.549777
C	3.344157	-1.239166	-1.662747
O	1.987515	-1.628083	-1.669396
H	1.620129	-1.717396	-0.769198
C	-0.456313	-3.888588	-0.785648
H	-1.255275	-4.193635	-1.476693
H	0.210384	-3.232909	-1.350169
C	0.335970	-5.153050	-0.376799
C	-0.579916	-6.167564	0.306439
H	-0.982234	-5.777167	1.253464
H	-1.435336	-6.429989	-0.337549
H	-0.032910	-7.097505	0.533368
C	0.908350	-5.762672	-1.655769
H	1.575512	-5.050930	-2.168700
H	1.488383	-6.675016	-1.440985
H	0.105042	-6.034303	-2.360431
C	1.474518	-4.771063	0.565225
H	2.067436	-5.656439	0.847491
H	2.153112	-4.045515	0.092685
H	1.088217	-4.313486	1.489314
Br	1.091544	1.971450	-2.334543
C	3.799611	-1.184625	-3.103593
H	3.162012	-0.499218	-3.668734
H	4.833043	-0.832355	-3.175717
H	3.741191	-2.175835	-3.566996
H	3.426976	-0.218519	-1.249843
C	4.194551	-2.173257	-0.821298
H	5.244878	-1.841780	-0.808043
H	3.837810	-2.201967	0.220695
H	4.162787	-3.198849	-1.223577

SI-Int17

C	2.676598	2.021700	-2.706775
C	2.247653	1.242446	-1.633502
N	1.071029	1.448533	-1.056585
C	0.257594	2.413468	-1.465134
C	0.597146	3.249759	-2.526772
C	1.826652	3.036133	-3.150697
Ni	0.550929	0.338602	0.583319
C	2.986639	0.160115	-0.965739
C	-0.977999	2.445334	-0.667811
O	4.227252	-0.128439	-1.331744
C	4.686854	-1.146429	-0.413185
C	3.460050	-1.443582	0.481808
N	2.469968	-0.483419	0.010023
N	-1.146111	1.633990	0.306591
C	-2.460429	1.901365	0.884078
C	-3.012329	3.030662	-0.018236
O	-1.938367	3.310789	-0.946732
C	2.934143	-2.883461	0.412269
C	-2.385581	2.224444	2.381863
H	3.644545	1.842961	-3.176855
H	-0.081452	4.037270	-2.856525
H	2.127158	3.667466	-3.989456
H	5.027695	-2.006786	-1.005523
H	5.539866	-0.736244	0.144284
H	3.684603	-1.209025	1.535124
H	-3.068047	0.989486	0.768428
H	-3.890679	2.729713	-0.603438
H	-3.240268	3.960312	0.521734
H	2.067073	-2.910193	1.094025
H	-1.868349	1.359128	2.828773
C	-1.558140	3.465660	2.680419
H	-2.002097	4.374778	2.240417
H	-1.502455	3.630345	3.768622
H	-0.526041	3.348971	2.313143
C	-3.789871	2.315334	2.963828
H	-3.752763	2.471410	4.053273
H	-4.352553	3.159929	2.530806
H	-4.367390	1.395969	2.774421
C	2.440958	-3.247083	-0.980289
H	2.099252	-4.293136	-1.006932
H	1.595065	-2.604486	-1.267682
H	3.237641	-3.149971	-1.737232
C	3.974980	-3.861109	0.939790
H	4.317409	-3.581376	1.949211
H	3.557440	-4.878429	0.996036
H	4.860845	-3.907565	0.284304
O	-0.341827	-1.192603	-0.549269
C	-1.546757	-1.509601	-0.268714
C	-1.890458	-2.357463	0.788136
N	-2.602513	-0.941075	-0.971558
C	-2.580828	-0.123942	-2.086492
C	-3.782662	0.509660	-2.460970
C	-3.838975	1.325211	-3.585579
C	-2.702890	1.534624	-4.370703
C	-1.513626	0.900900	-4.009150
C	-1.441069	0.078757	-2.887060
F	-3.266170	-2.561422	0.934173
H	-3.522773	-1.189737	-0.626665
H	-4.676653	0.350974	-1.850669
H	-4.785347	1.806013	-3.848862
H	-2.746061	2.178961	-5.252092
H	-0.613405	1.046040	-4.613227
H	-0.509397	-0.405579	-2.602896
C	0.505943	-1.162814	3.271173
H	-0.146137	-1.488539	4.099329
H	1.192514	-0.387693	3.640324
H	1.100003	-2.029140	2.931316
O	-0.251526	-0.593011	2.232422
H	-0.959117	-1.218811	1.881384

C	-1.053378	-3.507489	1.235482
H	-0.014515	-3.210220	1.025654
H	-1.119485	-3.656877	2.329727
C	-1.309904	-4.880526	0.557876
C	-2.614376	-5.503022	1.061089
H	-2.599759	-5.619114	2.157731
H	-3.484521	-4.884013	0.801551
H	-2.763242	-6.503968	0.622589
C	-1.368873	-4.720853	-0.959807
H	-2.223717	-4.095828	-1.262852
H	-0.454977	-4.244306	-1.347268
H	-1.476825	-5.700927	-1.453049
C	-0.148771	-5.802445	0.935159
H	-0.054806	-5.893858	2.030156
H	-0.295183	-6.815981	0.526872
H	0.808866	-5.417845	0.548748
Br	1.863133	1.940911	2.055066

SI-TS8

C	2.964932	1.978676	-2.818213
C	2.540326	1.240043	-1.714866
N	1.360075	1.457578	-1.150021
C	0.536137	2.393312	-1.602908
C	0.869412	3.186767	-2.698976
C	2.104716	2.962912	-3.307966
Ni	0.853497	0.410924	0.542091
C	3.284544	0.188034	-1.005246
C	-0.704848	2.441125	-0.813964
O	4.528912	-0.104654	-1.354109
C	4.993604	-1.078070	-0.390564
C	3.755714	-1.373036	0.488878
N	2.765361	-0.428136	-0.013073
N	-0.868106	1.661787	0.186520
C	-2.190251	1.926242	0.744803
C	-2.741371	3.038046	-0.179622
O	-1.675151	3.283256	-1.127949
C	3.239791	-2.817160	0.427660
C	-2.133068	2.264245	2.239583
H	3.936479	1.791380	-3.277472
H	0.182226	3.950131	-3.065706
H	2.401134	3.561768	-4.171651
H	5.368597	-1.949566	-0.944436
H	5.823495	-0.625950	0.169635
H	3.960678	-1.124329	1.542726
H	-2.789382	1.007270	0.636617
H	-3.630390	2.733738	-0.746215
H	-2.950983	3.983546	0.340435
H	2.353288	-2.835683	1.083970
H	-1.608611	1.406991	2.694266
C	-1.320502	3.516020	2.534090
H	-1.769763	4.417217	2.083242
H	-1.275193	3.690065	3.621361
H	-0.284236	3.406706	2.175965
C	-3.543422	2.346364	2.807473
H	-3.518764	2.513919	3.895585
H	-4.110440	3.180707	2.360173
H	-4.109881	1.419267	2.622126
C	2.791031	-3.209054	-0.972296
H	2.434214	-4.250298	-0.985517
H	1.966581	-2.563555	-1.310353
H	3.615445	-3.142041	-1.702271
C	4.268324	-3.780373	1.003371
H	4.574688	-3.483609	2.019449
H	3.855293	-4.799468	1.060674
H	5.176104	-3.830230	0.378863
O	-0.071618	-1.114911	-0.743400
C	-1.236626	-1.433986	-0.396559
C	-1.479579	-2.172759	0.818774
N	-2.340328	-0.992221	-1.073839
C	-2.426590	-0.146914	-2.175897
C	-3.682512	0.410465	-2.472202
C	-3.841974	1.254796	-3.565714
C	-2.755220	1.563047	-4.386252
C	-1.511038	1.003018	-4.098417
C	-1.336597	0.151130	-3.009551
F	-2.861028	-2.310732	1.071008
H	-3.223152	-1.282025	-0.665020
H	-4.534257	0.174369	-1.827624
H	-4.827505	1.679479	-3.774906
H	-2.878802	2.230380	-5.242568
H	-0.650426	1.229182	-4.733916
H	-0.363970	-0.279670	-2.781993
C	0.799278	-1.042256	3.169069
H	0.146408	-1.397235	3.989640
H	1.457454	-0.253902	3.572381
H	1.440858	-1.894120	2.866861
O	0.047664	-0.523281	2.117495
H	-0.747774	-1.253205	1.672965
C	-0.723002	-3.451797	1.059969
H	0.322880	-3.219246	0.805638
H	-0.726714	-3.684238	2.140277
C	-1.136850	-4.731737	0.294568
C	-2.488950	-5.257204	0.783051
H	-2.473360	-5.439463	1.870526
H	-3.299991	-4.546033	0.575297
H	-2.735063	-6.211958	0.289000
C	-1.203449	-4.466665	-1.208954
H	-2.007309	-3.756949	-1.459389
H	-0.257088	-4.047079	-1.584714
H	-1.403206	-5.399840	-1.760972
C	-0.071311	-5.794187	0.575353
H	0.027272	-5.982549	1.657303
H	-0.327313	-6.751230	0.091674
H	0.915785	-5.480117	0.199496
Br	2.151797	2.087404	1.932028

SI-TS8'

C	-0.858511	3.317904	1.814191
C	-0.684816	2.337740	0.836735
N	0.482421	1.733954	0.654178
C	1.530441	2.035536	1.414039
C	1.454486	2.993049	2.424029
C	0.234911	3.641649	2.615219
Ni	0.706681	0.274097	-0.809787

C	-1.734742	1.858394	-0.073431
C	2.728905	1.262737	1.054007
O	-2.878127	2.532729	-0.120462
C	-3.731946	1.791939	-1.014708
C	-2.796820	0.743247	-1.651915
N	-1.581429	0.846322	-0.836536
N	2.738836	0.466504	0.054300
C	4.100258	-0.057570	-0.067257
C	4.760712	0.417672	1.241732
O	3.834247	1.391738	1.775150
C	-3.412906	-0.655313	-1.688877
C	4.805534	0.442325	-1.338219
H	-1.825755	3.804902	1.943176
H	2.326317	3.224567	3.037106
H	0.136463	4.400840	3.393866
H	-4.527147	1.330410	-0.407548
H	-4.179093	2.494934	-1.728527
H	-2.519709	1.031974	-2.682915
H	4.058164	-1.156652	-0.102942
H	4.863824	-0.386849	1.984848
H	5.733448	0.906811	1.098613
H	-3.646113	-0.921942	-0.643958
H	5.852260	0.104223	-1.226457
C	4.218466	-0.201768	-2.585164
H	3.165513	0.093330	-2.710387
H	4.771235	0.117679	-3.483195
H	4.272167	-1.300169	-2.530618
C	4.791494	1.962230	-1.443267
H	5.411719	2.293288	-2.291111
H	3.765013	2.324279	-1.617901
H	5.189225	2.450908	-0.539058
C	-4.713356	-0.639101	-2.483251
H	-5.465245	0.039545	-2.050844
H	-4.533462	-0.324089	-3.525133
H	-5.158634	-1.645812	-2.511764
C	-2.445480	-1.681797	-2.251571
H	-1.475692	-1.646685	-1.741423
H	-2.849775	-2.701078	-2.147070
H	-2.265855	-1.500524	-3.324129
O	0.296147	-1.104117	0.864496
C	-0.210294	-2.234460	0.645727
C	0.496863	-3.244573	-0.100253
N	-1.486527	-2.538714	1.031919
C	-2.456920	-1.733032	1.618170
C	-2.187742	-0.471174	2.171938
C	-3.228134	0.290770	2.699301
C	-4.540127	-0.184475	2.707354
C	-4.802366	-1.453622	2.187075
C	-3.774898	-2.221183	1.649074
F	-0.294655	-4.412119	-0.225859
H	-1.779687	-3.479636	0.787185
H	-1.165308	-0.101141	2.162322
H	-3.002393	1.277020	3.114779
H	-5.348223	0.422732	3.122196
H	-5.821093	-1.850439	2.191636
H	-3.986077	-3.207775	1.226113
C	0.817915	-1.589842	-3.307170
H	0.137695	-2.427711	-3.543923
H	1.796942	-1.814480	-3.770318
H	0.427467	-0.674454	-3.780092
O	0.930665	-1.401430	-1.928397
H	0.710552	-2.301112	-1.319572
C	1.878665	-3.574385	0.406959
H	2.385440	-2.603131	0.523723
H	1.818891	-4.012066	1.425890
C	2.771277	-4.506594	-0.439119
C	2.782028	-4.086704	-1.906613
H	1.790966	-4.216480	-2.367886
H	3.061166	-3.028640	-2.017214
H	3.500533	-4.695683	-2.479656
C	4.192100	-4.415140	0.123042
H	4.212669	-4.666538	1.196632
H	4.872061	-5.110117	-0.396326
H	4.600368	-3.397212	0.010535
C	2.296414	-5.958417	-0.330350
H	2.967582	-6.630589	-0.890471
H	2.288060	-6.294506	0.720026
H	1.279284	-6.081587	-0.728092
Br	0.982273	1.961550	-2.648254

SI-Int18

C	2.110688	1.857303	-2.997339
C	1.939751	1.179958	-1.789796
N	0.858230	1.358157	-1.043748
C	-0.110052	2.186107	-1.414868
C	-0.029102	2.918407	-2.597432
C	1.105114	2.740749	-3.391509
Ni	0.753734	0.392739	0.793862
C	2.873871	0.236414	-1.153505
C	-1.219912	2.177047	-0.448248
O	4.049704	-0.039199	-1.701096
C	4.692818	-0.983790	-0.809781
C	3.725580	-1.099399	0.391259
N	2.585745	-0.301064	-0.031600
N	-1.181341	1.407290	0.570757
C	-2.427910	1.575263	1.306331
C	-3.195742	2.616136	0.456901
O	-2.289149	2.939893	-0.625415
C	3.311406	-2.517785	0.798501
C	-2.174699	1.933739	2.775286
H	3.002032	1.701010	-3.606569
H	-0.830592	3.596516	-2.892167
H	1.202817	3.291033	-4.329552
H	4.828369	-1.926229	-1.360694
H	5.677957	-0.580249	-0.543310
H	4.157355	-0.607452	1.279895
H	-2.961032	0.610670	1.294336
H	-4.118588	2.218553	0.013737
H	-3.428606	3.547446	0.991987
H	2.589926	-2.369951	1.620552
H	-1.483818	1.145500	3.122149
C	-1.478783	3.274995	2.947303
H	-2.104991	4.113401	2.597495
H	-1.265102	3.456516	4.013067

H	-0.514543	3.290833	2.414004
C	-3.473024	1.851198	3.565625
H	-3.294746	2.038995	4.636032
H	-4.203637	2.601633	3.217639
H	-3.942331	0.858385	3.470958
C	2.591211	-3.262808	-0.316284
H	2.259030	-4.250866	0.039519
H	1.703796	-2.703493	-0.647510
H	3.245566	-3.437268	-1.186869
C	4.508982	-3.289859	1.333460
H	5.000259	-2.752037	2.160378
H	4.200566	-4.277375	1.710656
H	5.264567	-3.460365	0.547675
O	-0.218256	-1.276778	-0.560673
C	-1.413301	-1.436039	-0.321211
C	-1.832624	-2.087064	0.973957
N	-2.411033	-1.031952	-1.133615
C	-2.279096	-0.352045	-2.353695
C	-3.311151	0.510473	-2.743446
C	-3.229900	1.196799	-3.951631
C	-2.121394	1.031856	-4.782723
C	-1.097825	0.166983	-4.394832
C	-1.166688	-0.526164	-3.188846
F	-3.214270	-1.952171	1.150806
H	-3.351699	-1.134753	-0.762366
H	-4.175917	0.640763	-2.087663
H	-4.040616	1.869673	-4.242442
H	-2.056118	1.574953	-5.728600
H	-0.226399	0.026568	-5.039398
H	-0.363159	-1.195030	-2.886895
C	1.057105	-0.645290	3.491405
H	0.603336	-1.286700	4.284956
H	1.171690	0.369584	3.937670
H	2.104035	-1.026643	3.375831
O	0.321061	-0.669237	2.341366
H	-1.306779	-1.499419	1.756816
C	-1.391559	-3.530031	1.130701
H	-0.290326	-3.498444	1.137846
H	-1.690856	-3.828684	2.149823
C	-1.861303	-4.614779	0.142172
C	-3.388142	-4.698519	0.080692
H	-3.824323	-4.826788	1.084552
H	-3.828254	-3.794292	-0.364406
H	-3.699138	-5.559713	-0.533316
C	-1.311156	-4.384246	-1.267906
H	-1.752875	-3.498130	-1.746817
H	-0.217515	-4.259253	-1.259693
H	-1.548268	-5.246967	-1.911520
C	-1.311588	-5.944886	0.666217
H	-1.693126	-6.163682	1.676832
H	-1.603952	-6.778301	0.007251
H	-0.210663	-5.927175	0.719322
Br	2.014884	2.350705	1.797429

SI-Int19

C	1.600428	2.222398	2.887091
C	1.467453	1.247785	1.900279
N	0.284845	0.952097	1.367584
C	-0.816906	1.591245	1.747080
C	-0.786508	2.583940	2.724945
C	0.447112	2.890650	3.300009
Ni	0.153351	-0.582089	0.009073
C	2.537624	0.441494	1.295462
C	-1.992520	1.119405	1.001230
O	3.805418	0.599627	1.645924
C	4.558561	-0.341608	0.840432
C	3.496897	-1.020500	-0.059460
N	2.254034	-0.419500	0.397174
N	-1.880375	0.189357	0.129139
C	-3.225263	-0.104272	-0.363872
C	-4.058989	1.052958	0.222558
O	-3.188086	1.646835	1.216184
C	3.671207	-0.830423	-1.573290
C	-3.668024	-1.515574	0.051745
H	2.576737	2.452627	3.315877
H	-1.699052	3.101575	3.023683
H	0.511320	3.660998	4.071309
H	5.319012	0.225104	0.284764
H	5.060794	-1.041076	1.522204
H	3.453151	-2.102826	0.145372
H	-3.219239	-0.058409	-1.462940
H	-4.292697	1.829297	-0.520432
H	-4.985323	0.739734	0.721206
H	2.788238	-1.318623	-2.018801
H	-2.853740	-2.182344	-0.281536
C	-3.799208	-1.672864	1.559730
H	-4.596297	-1.032540	1.973257
H	-4.057721	-2.713937	1.809619
H	-2.847390	-1.449863	2.065137
C	-4.949590	-1.898443	-0.675676
H	-5.245355	-2.930091	-0.429270
H	-5.786987	-1.239495	-0.389674
H	-4.829994	-1.832988	-1.769090
C	3.608240	0.634074	-1.980778
H	3.727685	0.733510	-3.071344
H	2.630318	1.061057	-1.713967
H	4.402630	1.238297	-1.510278
C	4.940186	-1.518248	-2.054779
H	4.957146	-2.582153	-1.767446
H	5.021252	-1.465649	-3.151814
H	5.844296	-1.043705	-1.636768
Br	-0.127475	-2.364905	1.692661
O	0.376575	-0.755203	-1.838506
C	-0.623530	-0.619936	-2.762308
H	-1.463048	-1.347406	-2.645786
H	-1.104118	0.387792	-2.769348
H	-0.250125	-0.772029	-3.801992

SI-TS9

C	-0.846841	-3.209943	2.382249
C	-0.901843	-2.162777	1.464387
N	0.157944	-1.822095	0.739850
C	1.318694	-2.452471	0.866876
C	1.474163	-3.516170	1.754019

C	0.364861	-3.890973	2.514007
Ni	-0.045136	-0.345015	-0.703373
C	-2.047131	-1.286812	1.161636
C	2.340146	-1.854216	-0.008381
O	-3.202642	-1.405668	1.795406
C	-4.031395	-0.316881	1.308409
C	-3.210536	0.308101	0.157185
N	-1.930259	-0.374160	0.274703
N	2.056609	-0.833795	-0.725008
C	3.279737	-0.414024	-1.397292
C	4.247265	-1.577267	-1.092980
O	3.569177	-2.343055	-0.064506
C	-3.798882	0.151775	-1.251922
C	3.721186	0.970098	-0.896466
H	-1.720648	-3.482428	2.975843
H	2.431257	-4.030152	1.852023
H	0.447033	-4.718970	3.221219
H	-4.996255	-0.739982	0.998316
H	-4.195005	0.374783	2.146513
H	-3.037683	1.380501	0.329191
H	3.081626	-0.343293	-2.477862
H	4.401358	-2.242646	-1.954494
H	5.223613	-1.265725	-0.699188
H	-2.999699	0.513056	-1.921530
H	2.841198	1.620544	-1.034969
C	4.072505	0.982681	0.584860
H	4.973564	0.384670	0.800723
H	4.277241	2.011881	0.917274
H	3.249534	0.601383	1.207784
C	4.859090	1.506635	-1.752767
H	5.141927	2.522142	-1.434369
H	5.759077	0.873610	-1.672815
H	4.574772	1.553267	-2.816239
C	-4.095717	-1.295466	-1.614636
H	-4.470047	-1.357458	-2.648970
H	-3.183215	-1.909268	-1.565478
H	-4.870867	-1.734245	-0.963624
C	-5.022527	1.044073	-1.408500
H	-4.787413	2.097416	-1.185752
H	-5.413603	0.995759	-2.436840
H	-5.837265	0.732468	-0.732687
Br	-0.504579	-1.961607	-2.521610
O	-0.215459	1.412384	-1.442871
C	0.363333	1.683816	-2.655620
H	1.461368	1.888053	-2.608359
H	0.239920	0.854565	-3.387828
H	-0.076403	2.586373	-3.140429
Si	0.528143	2.281450	1.087312
H	0.717011	0.832263	0.866239
O	1.312296	2.392350	2.558623
O	1.279011	3.387417	0.125008
O	-1.054732	2.737540	1.306503
C	-1.754355	2.418295	2.482479
H	-2.818177	2.666380	2.342458
H	-1.687396	1.346243	2.741738
H	-1.386931	2.993772	3.350726
C	0.642173	4.264159	-0.768332
H	0.419920	5.226066	-0.272672
H	1.315393	4.467584	-1.616147
H	-0.293109	3.838904	-1.160322
C	1.588889	3.627416	3.163097
H	0.789356	4.374032	3.002712
H	1.695948	3.483549	4.251176
H	2.531053	4.062291	2.784247

SI-Int20

C	-1.251324	-2.826932	2.599985
C	-1.144245	-1.805251	1.658595
N	0.018796	-1.508550	1.089131
C	1.127657	-2.177315	1.383200
C	1.121558	-3.220541	2.307590
C	-0.092315	-3.536390	2.919741
Ni	0.084565	-0.039511	-0.335343
C	-2.217689	-0.933260	1.154951
C	2.267552	-1.680898	0.596065
O	-3.448232	-1.012867	1.634463
C	-4.193168	0.051543	0.989989
C	-3.215705	0.624599	-0.062079
N	-1.970785	-0.069558	0.245250
N	2.130866	-0.663798	-0.165977
C	3.395377	-0.448740	-0.856165
C	4.251200	-1.648583	-0.386312
O	3.433746	-2.307064	0.613089
C	-3.625375	0.420913	-1.527308
C	3.976326	0.939784	-0.555849
H	-2.210052	-3.062056	3.064331
H	2.036472	-3.766842	2.541007
H	-0.136269	-4.345807	3.651483
H	-5.107115	-0.384525	0.564886
H	-4.469909	0.780128	1.764294
H	-3.051253	1.700866	0.104007
H	3.199193	-0.514041	-1.938493
H	4.449283	-2.376233	-1.185382
H	5.202288	-1.366802	0.085241
H	-2.753232	0.750993	-2.117032
H	3.185442	1.653967	-0.838928
C	4.260613	1.147798	0.923946
H	5.034304	0.456093	1.297731
H	4.626564	2.170515	1.101193
H	3.349766	1.019821	1.526247
C	5.204826	1.194838	-1.417532
H	5.583024	2.217759	-1.265106
H	6.025469	0.500719	-1.168818
H	4.978223	1.075567	-2.489250
C	-3.881789	-1.039350	-1.868497
H	-4.120575	-1.143431	-2.938822
H	-2.985289	-1.648546	-1.676011
H	-4.734928	-1.453190	-1.304839
C	-4.812435	1.311100	-1.867084
H	-4.597419	2.370472	-1.652992
H	-5.071374	1.227972	-2.934137
H	-5.707920	1.027101	-1.288582
Br	-0.144255	-1.570940	-2.288993
O	0.061369	1.744976	-1.303073

C -0.068347 2.096976 -2.657314
H 0.437104 3.052574 -2.861190
H 0.377264 1.299421 -3.270619
H -1.128056 2.194842 -2.948763
Si 0.154797 2.744361 0.124951
H 0.383657 1.296649 0.828738
O 1.694191 3.147562 0.669560
O -0.129378 4.203953 -0.726303
O -1.170360 2.971713 1.167052
C -1.379435 2.311713 2.371811
H -2.448850 2.064696 2.496117
H -0.804356 1.368816 2.447700
H -1.086352 2.946465 3.229517
C -1.388122 4.672889 -1.070120
H -1.289593 5.522312 -1.771353
H -2.021175 3.914967 -1.575497
H -1.960256 5.028094 -0.192105
C 2.406627 4.317872 0.403432
H 1.769973 5.217856 0.418967
H 3.197026 4.439080 1.164732
H 2.902322 4.285015 -0.585583

Int10a

C -1.078569 3.528733 -0.521742
C -1.065042 2.137614 -0.447447
N 0.037135 1.465595 -0.122165
C 1.178183 2.102339 0.124481
C 1.265202 3.492485 0.078273
C 0.110885 4.205117 -0.247532
Ni -0.061925 -0.594182 0.118524
C -2.183838 1.222586 -0.715969
C 2.264874 1.159025 0.423782
O -3.377604 1.672382 -1.064151
C -4.190392 0.494943 -1.305115
C -3.282389 -0.691269 -0.902901
N -2.011357 -0.040712 -0.615756
N 2.048419 -0.102157 0.425000
C 3.318943 -0.767979 0.698365
C 4.272645 0.415568 0.985994
O 3.485350 1.594770 0.689011
C -3.758788 -1.526604 0.293959
C 3.729449 -1.685540 -0.462797
H -1.990552 4.064612 -0.788835
H 2.208003 3.999758 0.287628
H 0.139768 5.295619 -0.294131
H -5.104117 0.586925 -0.702184
H -4.461558 0.489454 -2.369683
H -3.134898 -1.377269 -1.751682
H 3.201620 -1.393531 1.597532
H 4.580552 0.475878 2.038963
H 5.167368 0.438640 0.348908
H -2.937459 -2.242011 0.475782
H 2.910245 -2.419853 -0.549398
C 3.817331 -0.942971 -1.787922
H 4.588942 -0.154458 -1.774320
H 4.078637 -1.638863 -2.600549
H 2.853085 -0.480029 -2.048023
C 5.019295 -2.421679 -0.128040
H 5.266534 -3.149490 -0.916577
H 5.875007 -1.730837 -0.040981
H 4.934650 -2.972478 0.822674
C -3.951362 -0.695445 1.553953
H -4.222938 -1.343290 2.402029
H -3.027736 -0.162843 1.827822
H -4.759519 0.046477 1.440606
C -5.012751 -2.308584 -0.071075
H -4.852294 -2.935337 -0.962896
H -5.314760 -2.969560 0.756082
H -5.861582 -1.635747 -0.280548
H -0.432587 -0.570595 1.716035
Br 0.078342 -2.764915 -0.972788

SI-Int14

O 0.017912 -1.400433 -0.675271
C -0.012562 -0.180638 -0.522772
C -1.261923 0.550229 -0.651879
N 1.073587 0.602591 -0.227509
C 2.399963 0.221901 -0.046209
C 3.332585 1.239664 0.222796
C 4.674792 0.934661 0.416348
C 5.117560 -0.387927 0.345977
C 4.193515 -1.397275 0.079083
C 2.843610 -1.109242 -0.117237
F -1.208459 1.876415 -0.476027
H 0.892700 1.597163 -0.132132
H 2.988522 2.276680 0.276657
H 5.382228 1.741848 0.624053
H 6.172693 -0.627494 0.498004
H 4.524341 -2.437907 0.020708
H 2.124920 -1.898946 -0.326001
C -2.576552 -0.041095 -0.936537
H -2.395050 -1.026275 -1.390787
H -3.083551 0.592261 -1.685910
C -3.524190 -0.217380 0.282936
C -4.804525 -0.875614 -0.228056
H -5.521060 -1.026450 0.595276
H -5.295706 -0.252647 -0.993080
H -4.593971 -1.859448 -0.677618
C -2.865790 -1.113818 1.330495
H -2.595154 -2.094062 0.907936
H -1.948113 -0.656529 1.734730
H -3.551914 -1.285106 2.175557
C -3.856451 1.140415 0.901032
H -2.960897 1.631949 1.311481
H -4.305390 1.819797 0.158350
H -4.577066 1.019473 1.725901

SI-TS-Addition

O 0.029130 -1.241057 1.334309
C -0.006833 -0.032858 1.147999
C 1.232900 0.743515 0.913804
N -1.139475 0.727581 1.128167
C -2.463635 0.330674 1.311854
C -3.448685 1.331100 1.253208

C	-4.790456	1.010565	1.424477
C	-5.177429	-0.310573	1.658287
C	-4.199710	-1.302726	1.717939
C	-2.849765	-0.998447	1.547365
F	1.055761	2.072044	0.734333
H	-1.003984	1.719266	0.956219
H	-3.146089	2.366455	1.071825
H	-5.541108	1.803751	1.374618
H	-6.231997	-0.562631	1.793196
H	-4.487270	-2.341728	1.900845
H	-2.087782	-1.773765	1.593572
C	2.451302	0.198384	0.786066
H	2.564261	-0.866905	0.983197
H	3.335419	0.827635	0.680967
C	2.735706	-0.247976	-1.697110
C	3.752782	-1.332953	-1.615932
H	4.078648	-1.644884	-2.630999
H	3.358040	-2.233977	-1.120087
H	4.661308	-1.007941	-1.082855
C	1.330719	-0.620657	-2.019893
H	1.218719	-0.830806	-3.104140
H	0.626941	0.194798	-1.783785
H	1.007156	-1.523863	-1.480004
C	3.192413	1.112371	-2.100439
H	4.171981	1.367197	-1.665668
H	2.466967	1.888892	-1.808139
H	3.304063	1.179520	-3.203197

SI-TS-HAT-Br

C	0.583277	-2.827234	-2.189907
C	1.315826	-1.800918	-1.601848
N	0.732645	-0.677217	-1.182833
C	-0.580581	-0.496425	-1.312802
C	-1.396610	-1.464643	-1.898272
C	-0.794519	-2.642826	-2.336498
Ni	1.808565	0.668953	-0.107377
C	2.758998	-1.762068	-1.336484
C	-0.990076	0.789923	-0.744136
O	3.561320	-2.762448	-1.665762
C	4.894990	-2.342079	-1.283748
C	4.684224	-0.994019	-0.553876
N	3.263401	-0.741775	-0.750284
N	-0.120696	1.554201	-0.192889
C	-0.828652	2.717291	0.333643
C	-2.294066	2.454003	-0.087374
O	-2.255604	1.174085	-0.760326
C	5.042932	-0.974779	0.939059
C	-0.221483	4.035471	-0.161593
H	1.075049	-3.741213	-2.525755
H	-2.469379	-1.295234	-2.001621
H	-1.400228	-3.425542	-2.797673
H	5.329220	-3.130618	-0.653747
H	5.491375	-2.248134	-2.201890
H	5.251214	-0.187425	-1.044565
H	-0.741845	2.690288	1.431965
H	-2.978251	2.361147	0.763482
H	-2.689818	3.191676	-0.800657
H	4.736250	0.028669	1.281958
H	0.812966	4.037424	0.221792
Br	3.283059	2.570412	0.141000
C	-0.139155	4.104162	-1.678963
H	-1.133289	4.066233	-2.156231
H	0.338606	5.044501	-1.995367
H	0.466571	3.275582	-2.076349
C	-0.970293	5.220029	0.433713
H	-0.480228	6.167748	0.161642
H	-2.010229	5.273776	0.068919
H	-1.003571	5.164300	1.533811
C	4.261789	-2.006527	1.739065
H	4.480153	-1.906269	2.813501
H	3.178659	-1.865333	1.606163
H	4.518409	-3.039505	1.449600
C	6.546571	-1.115728	1.128040
H	7.097438	-0.337595	0.575754
H	6.815792	-1.025654	2.191751
H	6.910915	-2.097644	0.780542
H	1.409110	-0.106898	1.229796
O	-2.311253	0.281976	2.263921
C	-2.200314	-0.796546	1.692548
C	-0.933155	-1.543449	1.697638
N	-3.204964	-1.423967	1.007199
C	-4.506023	-0.989373	0.768450
C	-5.296396	-1.764078	-0.097056
C	-6.603967	-1.389653	-0.385650
C	-7.149740	-0.236806	0.181121
C	-6.367052	0.529101	1.044440
C	-5.055730	0.166363	1.345616
F	-0.933076	-2.698150	0.978028
H	-2.953877	-2.308979	0.579781
H	-4.870795	-2.668562	-0.541430
H	-7.201666	-2.006892	-1.061496
H	-8.176612	0.058906	-0.046126
H	-6.782786	1.431544	1.500866
H	-4.446469	0.760762	2.023208
C	0.189316	-1.140700	2.322484
H	0.136042	-0.264158	2.966208
H	1.040874	-1.815363	2.409241

Int10b

C	-1.350276	-3.454673	1.983270
C	-1.337558	-2.479162	0.988017
N	-0.269614	-2.283991	0.218577
C	0.820028	-3.034419	0.352405
C	0.897795	-4.045803	1.308157
C	-0.206755	-4.239904	2.138453
Ni	-0.351794	-0.863295	-1.275137
C	-2.438574	-1.587292	0.600032
C	1.854697	-2.639647	-0.612942
O	-3.623683	-1.659559	1.187577
C	-4.455655	-0.670762	0.529674
C	-3.554414	-0.081247	-0.580209
N	-2.279348	-0.748651	-0.353331
N	1.671211	-1.629585	-1.378107
C	2.848754	-1.502216	-2.231041

C 3.677314 -2.755169 -1.866145
O 2.975020 -3.336111 -0.739823
C -4.050378 -0.280657 -2.018628
C 3.546501 -0.152399 -2.019137
H -2.229476 -3.598134 2.612808
H 1.797465 -4.654896 1.405565
H -0.179114 -5.013653 2.908451
H -5.350507 -1.184261 0.151730
H -4.759053 0.068277 1.282169
H -3.407219 0.999279 -0.427730
H 2.518398 -1.548543 -3.280691
H 3.697984 -3.505586 -2.668651
H 4.706864 -2.538904 -1.550649
H -3.227074 0.100362 -2.647665
H 2.748282 0.595576 -2.160990
C 4.107378 0.009341 -0.614259
H 4.949299 -0.677747 -0.427033
H 4.482821 1.033325 -0.464998
H 3.340775 -0.170841 0.153065
C 4.615304 0.069644 -3.079606
H 5.077802 1.062322 -2.963496
H 5.420551 -0.680729 -3.002895
H 4.194854 0.009263 -4.096122
C -4.284227 -1.741985 -2.372364
H -4.560631 -1.839112 -3.434135
H -3.375139 -2.342480 -2.212816
H -5.103026 -2.187366 -1.782639
C -5.288693 0.571125 -2.261807
H -5.094022 1.634049 -2.045539
H -5.618189 0.494810 -3.309840
H -6.132619 0.249203 -1.628033
H -0.828768 -2.022272 -2.369235
Br -0.430017 1.125243 -2.797466
P 0.347607 0.978591 0.787907
C 1.695957 2.222617 0.582929
C 1.925047 2.768323 -0.688815
C 2.527623 2.608912 1.643682
C 2.955101 3.687160 -0.889642
H 1.291293 2.456960 -1.526792
C 3.562034 3.520748 1.436677
H 2.376544 2.193839 2.642207
C 3.779555 4.063969 0.170173
H 3.119157 4.102662 -1.887738
H 4.202506 3.808188 2.274845
H 4.592075 4.777732 0.010458
C 0.747834 0.324411 2.462225
C 0.277934 0.859800 3.669969
C 1.640929 -0.754336 2.515692
C 0.664569 0.306199 4.890023
H -0.387919 1.724593 3.667424
C 2.034460 -1.304939 3.733776
H 2.054173 -1.156466 1.590465
C 1.536660 -0.782108 4.926733
H 0.284530 0.735758 5.820677
H 2.730057 -2.147990 3.747074
H 1.834504 -1.215913 5.884793
C -1.126251 2.035563 1.078709
C -2.175942 1.590041 1.896769
C -1.282204 3.247627 0.393369
C -3.329608 2.355712 2.055645
H -2.097642 0.636874 2.424028
C -2.446449 4.001774 0.536249
H -0.490677 3.610915 -0.264408
C -3.472556 3.563577 1.372748
H -4.126570 1.998765 2.713316
H -2.547159 4.943781 -0.009293
H -4.380470 4.160237 1.492160

Int10c

P -2.107944 -0.037972 -0.076601
C -3.319579 1.227211 -0.584174
C -4.428007 1.561025 0.192031
C -3.119350 1.858787 -1.813667
C -5.330856 2.518183 -0.261038
H -4.589988 1.077061 1.149592
C -4.029732 2.802272 -2.269000
H -2.245835 1.613373 -2.409481
C -5.135515 3.135760 -1.491018
H -6.190401 2.777506 0.348712
H -3.871318 3.286893 -3.227055
H -5.842224 3.880291 -1.843349
C -2.485434 -0.358096 1.682392
C -3.265681 -1.433403 2.104979
C -1.937043 0.514564 2.627718
C -3.492210 -1.635402 3.462745
H -3.693553 -2.115795 1.378258
C -2.172104 0.312349 3.981198
H -1.325271 1.349291 2.295519
C -2.946840 -0.765711 4.400489
H -4.097530 -2.475829 3.786803
H -1.743972 0.992960 4.710006
H -3.123816 -0.928116 5.458815
C -2.698769 -1.542520 -0.941636
C -1.923121 -2.705026 -0.904341
C -3.922752 -1.564613 -1.612741
C -2.366031 -3.866922 -1.521919
H -0.969279 -2.704343 -0.386580
C -4.358433 -2.727273 -2.240114
H -4.541478 -0.675058 -1.649259
C -3.583434 -3.879732 -2.195954
H -1.754088 -4.762196 -1.481976
H -5.309262 -2.728797 -2.763097
H -3.925022 -4.785456 -2.686465
P 2.122172 -0.078513 -0.108886
C 3.374737 1.233721 0.104469
C 3.532482 2.171006 -0.920782
C 4.123410 1.362617 1.273319
C 4.448808 3.204138 -0.786925
H 2.939663 2.089184 -1.826131
C 5.032157 2.408183 1.409046
H 4.005281 0.647604 2.080357
C 5.200001 3.326076 0.379741
H 4.572672 3.921452 -1.591943
H 5.612885 2.498876 2.321385

H 5.913060 4.137516 0.484584
C 2.686878 -0.950210 -1.615160
C 1.747309 -1.622347 -2.401155
C 4.033987 -0.975052 -1.986956
C 2.151197 -2.321454 -3.532396
H 0.697552 -1.591132 -2.126453
C 4.433160 -1.674020 -3.119541
H 4.773091 -0.445074 -1.395457
C 3.494015 -2.349771 -3.892238
H 1.412402 -2.838635 -4.136062
H 5.481568 -1.689201 -3.399166
H 3.808570 -2.892544 -4.777802
C 2.468141 -1.233519 1.265796
C 3.592098 -2.060379 1.282540
C 1.576532 -1.260902 2.339554
C 3.817633 -2.905680 2.362126
H 4.290755 -2.051797 0.452401
C 1.809320 -2.100654 3.422407
H 0.693803 -0.627863 2.320306
C 2.929097 -2.925436 3.433193
H 4.689721 -3.551537 2.366385
H 1.110516 -2.114577 4.252751
H 3.108137 -3.587603 4.274163
Ni 0.014119 0.418837 -0.177874
H 0.043253 -1.019092 -0.162555
Br -0.004430 2.761881 -0.110067

SI-Int21

P -2.173983 0.217501 0.159740
C -3.490915 -0.578127 -0.826373
C -4.614284 0.098005 -1.314634
C -3.359550 -1.956025 -1.047583
C -5.594555 -0.597366 -2.024243
H -4.731605 1.170914 -1.145278
C -4.344902 -2.645826 -1.750454
H -2.485959 -2.485376 -0.653818
C -5.461127 -1.967901 -2.244642
H -6.468408 -0.062200 -2.405088
H -4.237488 -3.720816 -1.919509
H -6.229616 -2.509751 -2.802376
C -2.363820 2.013027 -0.119575
C -2.331890 2.921277 0.944727
C -2.378248 2.496847 -1.436477
C -2.336705 4.294004 0.696080
H -2.299814 2.557923 1.975003
C -2.397575 3.867947 -1.678965
H -2.355925 1.795334 -2.274786
C -2.376182 4.770251 -0.613646
H -2.310471 4.994628 1.534677
H -2.416446 4.234591 -2.708531
H -2.382352 5.846143 -0.806157
C -2.752025 -0.072018 1.869376
C -1.873255 -0.649081 2.790241
C -4.060730 0.239063 2.263268
C -2.289197 -0.904405 4.096725
H -0.861844 -0.896477 2.462556
C -4.472975 -0.011222 3.569810
H -4.760161 0.681773 1.548643
C -3.588154 -0.583015 4.487792
H -1.594257 -1.356257 4.809436
H -5.492252 0.239473 3.874788
H -3.916707 -0.780333 5.511619
P 1.977356 0.471495 0.001005
C 3.267387 -0.043659 -1.184638
C 3.130728 -1.286769 -1.811520
C 4.389253 0.749571 -1.456244
C 4.118380 -1.744603 -2.682165
H 2.236324 -1.882374 -1.625130
C 5.371021 0.293085 -2.334136
H 4.500140 1.726361 -0.977798
C 5.238664 -0.955779 -2.944219
H 4.006348 -2.717947 -3.167108
H 6.244701 0.915943 -2.542922
H 6.010184 -1.311951 -3.632026
C 2.737730 0.125192 1.632038
C 2.058915 0.520404 2.794959
C 3.954174 -0.554597 1.752757
C 2.591500 0.247677 4.051390
H 1.103898 1.047132 2.715684
C 4.478913 -0.840189 3.014474
H 4.497114 -0.873470 0.861017
C 3.801931 -0.440065 4.164723
H 2.053681 0.566529 4.947929
H 5.426188 -1.379592 3.094504
H 4.215502 -0.663949 5.151426
C 1.981991 2.299363 -0.131268
C 2.646626 3.138309 0.769089
C 1.265899 2.861021 -1.198856
C 2.589641 4.523436 0.607318
H 3.211007 2.714615 1.602822
C 1.221654 4.243231 -1.362157
H 0.742518 2.206756 -1.903579
C 1.878057 5.077849 -0.455651
H 3.107791 5.171877 1.318636
H 0.662155 4.671795 -2.197273
H 1.833422 6.163048 -0.578718
Ni -0.087954 -0.098452 -0.257728
H -0.057203 0.390920 1.104137
Br -0.247051 -0.547554 -2.563132
O -0.928391 -3.317211 0.693730
C 0.234348 -3.466106 0.334092
C 1.365398 -3.169676 1.267726
N 0.603918 -3.928286 -0.869930
F 2.586078 -3.264115 0.711495
H 1.593186 -4.008367 -1.074549
C 1.220524 -2.864173 2.551554
H 0.214409 -2.819642 2.967156
H 2.086732 -2.669923 3.186809
C -0.350798 -4.263636 -1.893310
H 0.129523 -4.921709 -2.629053
H -1.208683 -4.790255 -1.450511
H -0.716802 -3.358464 -2.405869

SI-Int22

P	1.928034	-0.083864	-0.041838
C	3.269781	-1.196962	-0.650722
C	4.542176	-0.657094	-0.897384
C	3.068236	-2.567758	-0.836603
C	5.589422	-1.473738	-1.312396
H	4.721739	0.412947	-0.768413
C	4.121695	-3.385662	-1.252808
H	2.082039	-3.018467	-0.679723
C	5.382181	-2.843735	-1.489369
H	6.574365	-1.037764	-1.498246
H	3.946183	-4.455030	-1.396105
H	6.205008	-3.485403	-1.815226
C	2.678480	0.502125	1.527982
C	3.618005	1.540838	1.591187
C	2.329302	-0.175686	2.702528
C	4.175674	1.909327	2.814052
H	3.920775	2.073580	0.687726
C	2.894801	0.192234	3.922718
H	1.587906	-0.979521	2.664298
C	3.813167	1.239680	3.983465
H	4.900777	2.726428	2.851134
H	2.607811	-0.341059	4.832891
H	4.249941	1.533730	4.941442
C	2.076523	1.324525	-1.199504
C	1.867448	2.646090	-0.783677
C	2.290871	1.065342	-2.562367
C	1.892927	3.688609	-1.709360
H	1.681612	2.870676	0.267264
C	2.308994	2.109266	-3.484688
H	2.446115	0.040755	-2.908674
C	2.113208	3.424764	-3.060639
H	1.731120	4.714002	-1.367661
H	2.476732	1.891986	-4.542519
H	2.129739	4.243312	-3.784611
P	-1.607031	0.727319	-0.002933
C	-3.197727	0.446696	0.870573
C	-3.723797	-0.843457	1.000049
C	-3.927692	1.535368	1.366458
C	-4.967823	-1.038240	1.598831
H	-3.151011	-1.698401	0.645925
C	-5.168618	1.337609	1.969463
H	-3.529630	2.549338	1.278719
C	-5.692777	0.049619	2.084325
H	-5.368165	-2.051104	1.693487
H	-5.728121	2.195719	2.350767
H	-6.666005	-0.106160	2.557389
C	-2.166288	1.342696	-1.633828
C	-1.215800	1.876403	-2.515454
C	-3.492288	1.211703	-2.063604
C	-1.587042	2.289243	-3.792876
H	-0.177435	1.974084	-2.198480
C	-3.859881	1.617733	-3.346530
H	-4.246529	0.788850	-1.396972
C	-2.911263	2.159223	-4.213182
H	-0.833113	2.710414	-4.462976
H	-4.898831	1.509557	-3.668580
H	-3.202954	2.478202	-5.217132
C	-0.968298	2.205590	0.863895
C	-1.104394	3.513376	0.387598
C	-0.304520	1.976575	2.077073
C	-0.559203	4.577848	1.106238
H	-1.624555	3.705844	-0.553291
C	0.238616	3.041381	2.791573
H	-0.211986	0.954310	2.454988
C	0.119820	4.343930	2.302151
H	-0.661146	5.596619	0.723530
H	0.765975	2.850913	3.730069
H	0.555115	5.179123	2.856862
Ni	-0.103629	-1.023873	-0.035537
H	0.824806	-2.068560	0.157676
Br	-0.733992	-1.899410	2.123045
O	0.136383	-4.215095	-1.010522
C	-0.955867	-3.657056	-0.996821
C	-1.101012	-2.213765	-1.359891
N	-2.112336	-4.263798	-0.670914
F	-2.405186	-1.835291	-1.540776
H	-2.964343	-3.716520	-0.706315
C	-0.112112	-1.471606	-1.997430
H	0.816959	-1.977170	-2.266702
H	-0.412759	-0.622696	-2.618033
C	-2.183567	-5.625824	-0.222232
H	-2.840936	-6.227797	-0.869858
H	-1.172824	-6.052133	-0.250235
H	-2.564264	-5.684942	0.810419

SI-TS10

P	-1.948785	-0.167594	-0.078768
P	1.564833	0.580261	-0.277201
Ni	0.089649	-0.366837	1.078131
O	2.507490	-1.431972	2.117744
C	2.028291	-2.375172	1.430067
C	0.601442	-2.261737	1.050726
N	2.723182	-3.428930	1.059384
F	0.262228	-3.118684	0.038465
H	2.229027	-4.145009	0.533824
C	-0.350893	-2.003643	2.065674
H	-1.347370	-2.434504	1.929039
H	-0.022428	-1.899297	3.103533
C	4.113056	-3.635844	1.381786
H	4.589502	-2.666081	1.572784
H	4.223018	-4.266806	2.278429
H	4.614347	-4.127694	0.538182
Br	-0.252935	1.228342	2.905298
H	1.501655	-0.585248	1.826638
C	-3.357541	-0.979223	0.788735
C	-4.418578	-1.603760	0.121909
C	-3.406167	-0.849658	2.183645
C	-5.501188	-2.108795	0.841521
H	-4.408867	-1.695269	-0.966753
C	-4.495571	-1.345902	2.898600
H	-2.583355	-0.347582	2.704506
C	-5.541848	-1.982628	2.230557
H	-6.321391	-2.599469	0.310782
H	-4.524225	-1.237273	3.986104

H	-6.392462	-2.377846	2.792106
C	-1.876980	-0.987850	-1.712568
C	-1.556400	-0.254580	-2.864327
C	-1.955037	-2.385612	-1.804744
C	-1.331310	-0.901016	-4.078649
H	-1.472156	0.832320	-2.817541
C	-1.729771	-3.029591	-3.019628
H	-2.181076	-2.981448	-0.918517
C	-1.416036	-2.290384	-4.161249
H	-1.080150	-0.310225	-4.963376
H	-1.795769	-4.119455	-3.072259
H	-1.236837	-2.797649	-5.112718
C	-2.809067	1.428708	-0.417303
C	-2.637302	2.474849	0.497367
C	-3.699193	1.597047	-1.486152
C	-3.321040	3.678558	0.328393
H	-1.960143	2.339374	1.347635
C	-4.371643	2.805725	-1.659397
H	-3.874476	0.782983	-2.193052
C	-4.181053	3.852179	-0.755670
H	-3.174501	4.488604	1.047976
H	-5.055044	2.927015	-2.504030
H	-4.709568	4.799139	-0.893653
C	2.881794	1.657372	0.416176
C	3.076326	1.751975	1.797057
C	3.716633	2.386574	-0.444760
C	4.099102	2.552290	2.309527
H	2.404704	1.223599	2.475935
C	4.737606	3.181614	0.068449
H	3.571739	2.329514	-1.526861
C	4.932004	3.264573	1.449171
H	4.239037	2.622266	3.391515
H	5.383806	3.741579	-0.612536
H	5.731492	3.891642	1.852715
C	2.514552	-0.698973	-1.184801
C	3.892555	-0.880282	-1.026447
C	1.797173	-1.588822	-1.997670
C	4.542449	-1.931018	-1.675836
H	4.466359	-0.207470	-0.386126
C	2.449391	-2.628801	-2.652969
H	0.717542	-1.471149	-2.108434
C	3.825086	-2.805756	-2.490179
H	5.618204	-2.066870	-1.537652
H	1.876361	-3.311256	-3.286049
H	4.336637	-3.628220	-2.996838
C	0.941776	1.673290	-1.612019
C	1.238348	1.518142	-2.970039
C	0.125726	2.736143	-1.204443
C	0.702525	2.401807	-3.907874
H	1.880929	0.701647	-3.305637
C	-0.410069	3.615700	-2.141336
H	-0.093288	2.866378	-0.141713
C	-0.129005	3.444097	-3.498356
H	0.933814	2.268824	-4.967988
H	-1.056428	4.432747	-1.810403
H	-0.554843	4.128165	-4.236930

TS8a

C	-1.637601	3.267392	-0.694952
C	-1.476212	1.892896	-0.634144
N	-0.259978	1.317363	-0.557296
C	0.838736	2.097472	-0.545660
C	0.760266	3.479929	-0.599883
C	-0.499097	4.072384	-0.679044
Ni	-0.110306	-0.654292	-0.147493
C	-2.535037	0.899411	-0.598279
C	2.050316	1.305270	-0.430620
O	-3.819819	1.257096	-0.613375
C	-4.566612	0.009885	-0.629269
C	-3.507799	-1.081143	-0.369785
N	-2.249718	-0.349300	-0.504294
N	1.983722	0.027865	-0.322226
C	3.353251	-0.483616	-0.282757
C	4.196568	0.802531	-0.172651
O	3.253178	1.881730	-0.416833
C	-3.596803	-1.777850	0.994678
C	3.639887	-1.359980	-1.509619
H	-2.630408	3.697197	-0.754456
H	1.663576	4.078013	-0.581328
H	-0.592819	5.150860	-0.725657
H	-5.340810	0.078067	0.134989
H	-5.032542	-0.080313	-1.612319
H	-3.554488	-1.851327	-1.144916
H	3.478759	-1.100045	0.611650
H	4.612271	0.950086	0.825529
H	4.991611	0.884327	-0.914260
H	-2.718018	-2.433014	1.038688
H	2.885645	-2.155120	-1.473291
C	3.468573	-0.605050	-2.820686
H	4.195293	0.209528	-2.920538
H	3.618912	-1.280127	-3.668812
H	2.464314	-0.179785	-2.909669
C	5.023335	-1.986989	-1.399498
H	5.204097	-2.673209	-2.232518
H	5.811945	-1.225873	-1.424229
H	5.131295	-2.552575	-0.468030
C	-3.519811	-0.801514	2.160768
H	-3.570552	-1.346972	3.108646
H	-2.580143	-0.240405	2.157760
H	-4.356304	-0.092932	2.151026
C	-4.850884	-2.639807	1.061735
H	-4.888959	-3.354676	0.232988
H	-4.879546	-3.206481	1.997244
H	-5.760022	-2.028703	1.020772
H	-0.229708	-0.333993	1.424588
Br	0.115622	-3.060044	-0.643442
C	1.197921	0.715150	3.293125
H	1.874162	0.037647	2.713297
H	1.647080	0.731589	4.318022
H	1.413014	1.735307	2.880236
O	-0.109354	0.356143	3.276091

TS8b

C	2.514898	2.191995	-0.251830

C	1.888585	0.958255	-0.224602
N	0.540692	0.843192	-0.215072
C	-0.223484	1.956653	-0.301952
C	0.334571	3.223188	-0.343569
C	1.724566	3.344406	-0.293250
Ni	-0.287252	-0.939407	-0.472296
C	2.513937	-0.343080	-0.324837
C	-1.621981	1.609261	-0.421565
O	3.840358	-0.483012	-0.414163
C	4.071548	-1.914545	-0.510963
C	2.671885	-2.524781	-0.714792
N	1.786509	-1.401197	-0.420402
N	-1.978246	0.370587	-0.436662
C	-3.422382	0.326067	-0.660517
C	-3.775449	1.801719	-0.933837
O	-2.565777	2.537756	-0.610238
H	3.597035	2.253437	-0.252251
H	-0.303606	4.096174	-0.415961
H	2.188297	4.323425	-0.312665
H	4.757294	-2.082610	-1.341538
H	4.541901	-2.237151	0.419601
H	2.490906	-3.318941	0.014637
H	-3.615573	-0.284620	-1.547174
H	-4.004138	1.992323	-1.983795
H	-4.580847	2.192206	-0.310733
H	-0.118242	-0.558612	-1.992179
Br	-1.313210	-3.218260	-0.834721
P	-0.250110	-1.419877	2.208334
C	-0.825709	1.261223	-3.914113
H	-0.660971	2.246573	-3.402477
H	-1.743554	0.851307	-3.419532
H	-1.183102	1.545458	-4.940002
O	0.241893	0.429984	-3.910929
C	2.401913	-3.097072	-2.112392
H	1.341569	-3.376578	-2.102492
C	-4.149525	-0.321541	0.522329
H	-3.662014	-1.293870	0.652988
C	2.616822	-2.080235	-3.225270
H	1.935616	-1.226004	-3.141459
H	3.650232	-1.712680	-3.246390
H	2.426735	-2.549331	-4.196885
C	3.239043	-4.352691	-2.323321
H	3.066156	-5.086558	-1.528503
H	2.991938	-4.826525	-3.278355
H	4.311305	-4.123570	-2.340074
C	-5.615057	-0.557838	0.184623
H	-6.120639	-1.078217	1.004164
H	-6.144063	0.388129	0.018749
H	-5.722704	-1.166697	-0.719097
C	-3.998401	0.465257	1.816056
H	-4.403621	-0.105466	2.657043
H	-2.950155	0.680382	2.038083
H	-4.540377	1.416973	1.775797
C	0.347670	-0.032989	3.253452
C	-0.111565	1.245046	2.928871
C	1.174434	-0.186147	4.369986
C	0.259090	2.350017	3.685684
H	-0.771752	1.373749	2.080794
C	1.550878	0.919262	5.124248
H	1.523840	-1.171073	4.658998
C	1.099991	2.190147	4.781305
H	-0.105747	3.335300	3.413324
H	2.195652	0.785136	5.987079
H	1.399317	3.051503	5.369861
C	0.949979	-2.755571	2.585622
C	0.534340	-4.074092	2.779126
C	2.321575	-2.480186	2.564059
C	1.466397	-5.091379	2.955349
H	-0.522752	-4.314771	2.796066
C	3.250495	-3.494932	2.755310
H	2.669831	-1.465309	2.404657
C	2.827095	-4.806362	2.947128
H	1.123588	-6.110478	3.104582
H	4.310035	-3.259271	2.746845
H	3.553340	-5.599943	3.090343
C	-1.743547	-1.947227	3.149092
C	-2.037229	-1.469166	4.428955
C	-2.638101	-2.829843	2.535040
C	-3.196929	-1.870464	5.082269
H	-1.364634	-0.774851	4.920167
C	-3.793173	-3.235110	3.194891
H	-2.427858	-3.186141	1.529575
C	-4.077936	-2.755113	4.468688
H	-3.412119	-1.487824	6.075102
H	-4.477929	-3.920479	2.704751
H	-4.983836	-3.065225	4.979870

TS8c

P	-1.458116	-1.103961	-0.763007
P	1.513554	0.736147	1.257066
Ni	0.509673	-0.765980	0.066124
H	0.292566	0.432216	-0.730583
Br	1.291337	-2.971615	0.578189
O	0.525490	1.319353	-2.442390
C	1.238420	0.406100	-3.158950
H	1.442353	-0.542999	-2.605723
H	0.743810	0.081936	-4.104259
H	2.249356	0.764920	-3.475909
C	2.929524	1.696563	0.601681
C	4.049743	1.992409	1.381542
C	2.863793	2.145899	-0.722251
C	5.099730	2.729481	0.843956
H	4.107848	1.650799	2.409262
C	3.915546	2.891887	-1.244473
H	1.978648	1.917582	-1.336692
C	5.034377	3.182400	-0.469041
H	5.968260	2.951943	1.455955
H	3.861605	3.245820	-2.269998
H	5.854003	3.758910	-0.886759
C	2.099270	0.257911	2.928547
C	1.832427	1.021354	4.067011
C	2.870159	-0.901025	3.045955
C	2.331033	0.629445	5.304775
H	1.236570	1.924627	3.990449

C	3.376507	-1.283239	4.282231
H	3.049061	-1.512969	2.167911
C	3.105388	-0.520702	5.414371
H	2.116084	1.227630	6.184668
H	3.976311	-2.184383	4.363303
H	3.494235	-0.824271	6.381216
C	0.254903	2.013468	1.644560
C	-0.968362	1.570258	2.159279
C	0.445266	3.373839	1.414624
C	-1.979536	2.475186	2.446098
H	-1.128564	0.508779	2.328069
C	-0.577910	4.278959	1.687515
H	1.388166	3.732238	1.015272
C	-1.787984	3.833866	2.204404
H	-2.924738	2.119320	2.842842
H	-0.423708	5.336079	1.495276
H	-2.584388	4.540848	2.413515
C	-2.405172	-2.394434	0.129918
C	-3.332387	-3.221621	-0.503513
C	-2.212314	-2.510269	1.508067
C	-4.059933	-4.150491	0.233816
H	-3.490487	-3.141982	-1.574240
C	-2.949375	-3.428304	2.245192
H	-1.472266	-1.885190	1.998019
C	-3.872924	-4.252322	1.608117
H	-4.776524	-4.793451	-0.267495
H	-2.794670	-3.508984	3.316539
H	-4.442640	-4.976217	2.182175
C	-1.555247	-1.669266	-2.498247
C	-2.451270	-1.142957	-3.426751
C	-0.682333	-2.690754	-2.884316
C	-2.471998	-1.631045	-4.730002
H	-3.131583	-0.349068	-3.137435
C	-0.714702	-3.183634	-4.182035
H	0.023324	-3.091657	-2.160548
C	-1.607538	-2.651756	-5.108890
H	-3.168839	-1.212521	-5.449335
H	-0.035183	-3.978155	-4.473880
H	-1.626370	-3.031088	-6.125582
C	-2.601651	0.330557	-0.677844
C	-3.834795	0.259119	-0.028056
C	-2.187589	1.541002	-1.248181
C	-4.646458	1.386908	0.058758
H	-4.166973	-0.670585	0.420294
C	-3.010745	2.657472	-1.164669
H	-1.217511	1.578781	-1.759449
C	-4.237445	2.587451	-0.508487
H	-5.600169	1.322550	0.573272
H	-2.686986	3.594925	-1.607477
H	-4.870038	3.466875	-0.437109

SI-Int23

C	-1.618884	3.302968	-0.677714
C	-1.475366	1.929835	-0.569278
N	-0.234669	1.334682	-0.462548
C	0.870823	2.143139	-0.470402
C	0.790491	3.513858	-0.572231
C	-0.481575	4.117386	-0.677710
Ni	-0.077027	-0.602206	-0.313539
C	-2.499879	0.932674	-0.558242
C	2.065529	1.342039	-0.361999
O	-3.811143	1.240454	-0.594660
C	-4.502946	-0.025156	-0.694117
C	-3.426098	-1.084961	-0.394704
N	-2.183082	-0.326583	-0.489908
N	1.975185	0.058917	-0.238158
C	3.332210	-0.479571	-0.260881
C	4.211123	0.784416	-0.188829
O	3.294032	1.882261	-0.413152
C	-3.546277	-1.778052	0.970256
C	3.547722	-1.362859	-1.498031
H	-2.611247	3.734219	-0.764138
H	1.695305	4.112338	-0.570335
H	-0.574389	5.193889	-0.760097
H	-5.332716	-0.011336	0.014429
H	-4.900227	-0.112637	-1.709072
H	-3.439382	-1.865595	-1.162486
H	3.490726	-1.104206	0.623960
H	4.665205	0.923759	0.795243
H	4.988052	0.836083	-0.953138
H	-2.641434	-2.393175	1.050842
H	2.774530	-2.137551	-1.425945
C	3.340402	-0.603341	-2.801212
H	4.083904	0.191659	-2.931648
H	3.435087	-1.280251	-3.656256
H	2.345094	-0.150599	-2.844116
C	4.917586	-2.026579	-1.449178
H	5.046412	-2.716613	-2.288981
H	5.724190	-1.286054	-1.506994
H	5.051653	-2.595946	-0.523110
C	-3.555371	-0.791143	2.129804
H	-3.561557	-1.324772	3.085656
H	-2.668988	-0.149696	2.113081
H	-4.443075	-0.148270	2.109861
C	-4.765606	-2.689990	1.004135
H	-4.742011	-3.416945	0.185090
H	-4.811016	-3.246736	1.945514
H	-5.696833	-2.117751	0.917127
Br	0.157228	-3.026622	-0.081688

SI-Int24

P	-1.280722	-1.175443	-0.656585
P	1.284509	0.572553	1.389802
Ni	0.618620	-1.059482	0.241438
Br	2.134453	-2.893911	-0.075850
C	2.617937	1.545584	0.569547
C	3.792320	1.955019	1.203756
C	2.448708	1.845601	-0.787894
C	4.771574	2.650353	0.499078
H	3.949166	1.731474	2.253889
C	3.418608	2.551849	-1.486583
H	1.547209	1.515069	-1.296815
C	4.587202	2.954776	-0.844490
H	5.681102	2.957518	1.006428

H	3.267232	2.780573	-2.537064
H	5.350813	3.498823	-1.391300
C	2.027415	0.269953	3.054057
C	1.964299	1.175155	4.116035
C	2.695038	-0.944699	3.234767
C	2.564431	0.873183	5.334313
H	1.446681	2.121287	3.991739
C	3.303837	-1.240557	4.449393
H	2.721816	-1.654525	2.409644
C	3.237816	-0.333000	5.502582
H	2.507649	1.582883	6.154151
H	3.822799	-2.185741	4.578007
H	3.705737	-0.566604	6.453871
C	0.082751	1.908733	1.815525
C	-1.144691	1.512342	2.356743
C	0.308648	3.267486	1.593143
C	-2.115687	2.448950	2.680686
H	-1.340767	0.454355	2.509974
C	-0.672343	4.207660	1.900502
H	1.253604	3.599439	1.175662
C	-1.883825	3.803182	2.447575
H	-3.062657	2.122318	3.099060
H	-0.484697	5.260600	1.712959
H	-2.648657	4.535968	2.684380
C	-2.398052	-2.409780	0.135770
C	-3.244416	-3.267333	-0.569305
C	-2.363777	-2.496435	1.532622
C	-4.042561	-4.185685	0.107226
H	-3.283940	-3.220212	-1.652712
C	-3.170202	-3.403075	2.208221
H	-1.691507	-1.846564	2.087270
C	-4.012000	-4.253410	1.495548
H	-4.693236	-4.848587	-0.455051
H	-3.135090	-3.453310	3.292168
H	-4.636743	-4.968870	2.020847
C	-1.419664	-1.646050	-2.438168
C	-2.421011	-1.184762	-3.295985
C	-0.448428	-2.519580	-2.935830
C	-2.453679	-1.595016	-4.625051
H	-3.180350	-0.502902	-2.926221
C	-0.489246	-2.938175	-4.261014
H	0.345115	-2.853602	-2.269273
C	-1.491007	-2.475048	-5.109446
H	-3.235238	-1.227876	-5.283387
H	0.268901	-3.619192	-4.636144
H	-1.518212	-2.794338	-6.146601
C	-2.359018	0.326066	-0.639144
C	-3.671998	0.341223	-0.167570
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C	-4.399218	1.529036	-0.133248
H	-4.134430	-0.576802	0.179935
C	-2.518514	2.708310	-1.058113
H	-0.763345	1.532500	-1.432398
C	-3.826863	2.714208	-0.578383
H	-5.417403	1.524449	0.243989
H	-2.060164	3.630534	-1.401599
H	-4.392265	3.640151	-0.547003

SI-Int25

C	-0.365882	-2.658513	-0.610294
C	-1.885881	-2.903044	-0.422186
C	-1.367551	-0.717569	-0.112018
H	-2.100856	-3.648733	0.357673
C	-1.368907	0.746881	0.135111
C	-0.366495	2.696539	0.598449
C	-1.887245	2.936724	0.412538
H	-2.105716	3.668398	-0.379548
N	-0.215123	-1.217717	-0.429520
N	-0.216208	1.252612	0.444682
N	-2.398222	-1.586038	-0.031867
N	-2.400229	1.613271	0.046125
C	-3.580694	-1.438129	0.816942
H	-3.686858	-0.360441	0.998710
C	-3.589086	1.450550	-0.790961
H	-3.691088	0.370639	-0.959977
C	-3.399434	-2.101881	2.177651
H	-2.498419	-1.728641	2.685925
H	-4.268548	-1.874437	2.813096
H	-3.328261	-3.197267	2.097261
C	-4.821199	-1.941126	0.096427
H	-5.717169	-1.749128	0.704961
H	-4.952178	-1.444541	-0.877171
H	-4.764555	-3.026963	-0.080278
C	-4.825944	1.954919	-0.065250
H	-4.774042	3.043016	0.098527
H	-5.726204	1.750647	-0.663401
H	-4.944723	1.468631	0.915037
C	-3.423840	2.099321	-2.160982
H	-3.354485	3.195760	-2.094653
H	-2.528028	1.721988	-2.675502
H	-4.299291	1.862476	-2.784161
C	0.564416	-3.448963	0.320863
H	1.570852	-3.031894	0.140336
C	0.557910	3.459037	-0.361713
H	1.570442	3.062953	-0.166718
C	0.241975	-3.254237	1.794880
H	0.997049	-3.756921	2.419126
H	0.251702	-2.188585	2.067322
H	-0.738091	-3.681942	2.060788
C	0.573770	-4.921969	-0.063825
H	0.860853	-5.064404	-1.117897
H	1.287037	-5.484474	0.558196
H	-0.419055	-5.381966	0.079264
C	0.549604	4.946852	-0.040469
H	0.827198	5.136551	1.008684
H	1.262091	5.489638	-0.680608
H	-0.446568	5.389944	-0.210010
C	0.241436	3.194204	-1.826249
H	-0.746074	3.591589	-2.111311
H	0.990255	3.679570	-2.470608
H	0.275608	2.119014	-2.056164
Ni	1.349069	0.019138	0.004604
Br	2.950908	0.454691	-1.716832
H	-2.367870	3.289031	1.337464

H -0.069735 2.964494 1.625199
H -0.075425 -2.900977 -1.645292
H -2.369900 -3.239634 -1.351228
H 1.859116 -0.489716 1.420782

SI-TS11

C 2.561472 2.304906 0.495626
C 1.448963 3.326440 0.840802
C 0.619256 1.217990 0.774404
H 1.350627 4.121867 0.088329
C -0.194379 -0.025705 0.862585
C -0.506873 -2.226402 0.566038
C -1.722199 -1.637142 1.322331
H -1.904064 -2.130788 2.288463
N 1.884845 1.013424 0.570416
N 0.323948 -1.061509 0.275740
N 0.235198 2.504732 0.887198
N -1.347062 -0.236718 1.524190
C -1.085775 3.063015 0.593353
H -1.780713 2.211376 0.592384
C -1.912158 0.565770 2.603939
H -1.408554 1.538124 2.550263
C -1.138632 3.683714 -0.797625
H -0.844921 2.952514 -1.562892
H -2.167784 4.011086 -1.008275
H -0.492996 4.572038 -0.873241
C -1.503426 4.053371 1.669498
H -2.531503 4.398725 1.485332
H -1.465258 3.609051 2.675657
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H -3.612286 1.197868 1.399860
C -1.595651 -0.019221 3.975762
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H 3.851189 1.569530 -0.999860
C 0.294544 -3.301374 1.314393
H 1.162882 -3.518105 0.667072
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H 0.069057 -5.376160 1.920226
H -1.410864 -4.413326 2.101720
C 0.835682 -2.815583 2.650802
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Ni 2.291756 -0.837508 -0.161279
Br 4.101477 -2.239794 0.450244
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H 3.341477 2.325678 1.273433
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C 1.227368 -0.955455 -3.214765
H 1.440549 0.072631 -3.503063
H 1.933478 -1.735138 -3.503563

SI-TS12

C 1.819016 2.602529 0.502113
C 0.690680 3.660883 0.549991
C -0.135721 1.573522 0.860731
H 0.675016 4.305142 -0.340821
C -0.971803 0.378987 1.151022
C -1.361092 -1.818215 1.308782
C -2.644289 -1.049079 1.706624
H -2.981969 -1.297574 2.723991
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N -0.413387 -0.769051 0.926746
N -0.526171 2.850112 0.632010
N -2.237072 0.351894 1.632545
C -1.798033 3.309399 0.074905
H -2.502172 2.475821 0.199590
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H -2.338113 2.302256 2.266445
C -1.706031 3.590007 -1.420550
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H -2.699225 3.881827 -1.794061
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C -2.311853 4.522609 0.837187
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H -2.369075 4.336226 1.920223
H -1.655149 5.392953 0.679263
C -4.331981 1.540928 2.060483
H -4.913681 0.630638 2.275145
H -4.788545 2.369263 2.622444

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C	-2.723207	1.082699	3.954841
H	-3.262124	0.173733	4.262875
H	-1.664623	0.972546	4.232905
H	-3.140092	1.922327	4.531498
C	2.577996	2.501572	-0.830813
H	3.151916	1.566280	-0.746827
C	-0.802874	-2.745335	2.395806
H	0.111578	-3.179110	1.959512
C	1.663402	2.376292	-2.039432
H	2.252151	2.122643	-2.935563
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H	1.137007	3.319254	-2.256820
C	3.550468	3.662956	-0.980067
H	4.265986	3.702744	-0.142802
H	4.128532	3.574438	-1.913444
H	3.021504	4.631051	-1.015105
C	-1.783674	-3.871765	2.690401
H	-2.051043	-4.422754	1.773790
H	-1.346781	-4.595136	3.396874
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C	-0.393670	-1.999490	3.656123
H	-1.254975	-1.543844	4.172561
H	0.089344	-2.685730	4.369547
H	0.331709	-1.203403	3.426101
Ni	1.658203	-0.635473	0.499336
Br	2.405625	-3.004253	0.835450
H	-3.484194	-1.238347	1.021921
H	-1.549897	-2.437337	0.419388
H	2.564089	2.806313	1.286689
H	0.769991	4.313027	1.434588
H	1.589169	-0.601641	-1.111930
C	6.097848	-1.765417	-1.007131
C	6.909353	-1.073808	0.089908
C	4.769737	-1.018480	-0.998937
H	6.609239	-1.751806	-1.978702
H	5.922857	-2.815237	-0.726363
H	7.530349	-0.246685	-0.301960
H	7.574186	-1.761113	0.635739
H	3.886870	-1.629190	-1.226593
H	4.766391	-0.144354	-1.674289
C	4.669670	-0.494878	0.408872
O	3.665184	-0.031422	0.960096
N	5.884983	-0.552847	0.975973
C	6.183606	-0.046876	2.284238
H	6.881147	0.805980	2.228436
H	5.247793	0.285748	2.751330
H	6.641213	-0.830168	2.909626
O	-1.469253	0.512507	-2.813799
C	-1.682343	-0.626152	-2.407653
C	-0.632744	-1.643900	-2.368362
N	-2.894626	-1.058844	-1.927469
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C	-6.324979	-0.328938	-0.828602
C	-6.476021	1.013675	-1.180232
C	-5.418406	1.669209	-1.809530
C	-4.219534	1.012775	-2.083845
F	-1.014398	-2.849315	-1.856728
H	-2.924574	-2.031221	-1.639892
H	-5.023481	-2.050688	-0.820333
H	-7.143264	-0.865756	-0.341527
H	-7.410121	1.539819	-0.970236
H	-5.523507	2.718036	-2.100944
H	-3.398323	1.523152	-2.580640
C	0.673577	-1.395598	-2.601414
H	0.937174	-0.473804	-3.116140
H	1.398515	-2.207725	-2.549477

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