Supporting Information

Rhodium-Catalyzed 1,5-Sigma Migratory Ring Expansion of *gem*-Difluorodienyl-Cyclopropanes and Cyclobutanes

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1. General Information

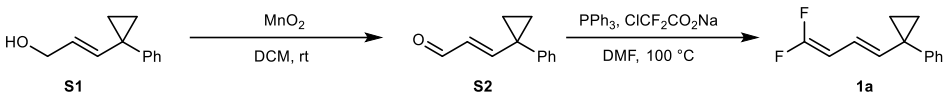
All chemicals were used as received without further purification. Deionized water was used for the 1,5-migratory ring-expansion reaction. Reaction tubes (25 mL) were purchased from Synthware. $[Rh(CO)_2Cl]_2$ was purchased from J&K. Ethyl acetate, petroleum ether, dichloromethane, diethyl ether, NaCl, Na_2SO_4, NH_4Cl were purchased from Bei Jing TongGuang Fine Chemicals Company. Difluoromethyl 2-pyridyl sulfone (no. 1112943) and $MgSO_4$ (no. 1087059) were purchased from Leyan, shanghai, China. HFIP was purchased from Adamas-beta and Macklin. Chloroform-d, DIBAL-H, cycloheptanone, and benzyl bromide were purchased from Energy Chemical. 1,2-Dibromoethane was purchased from Macklin. Reactions were stirred using Teflon-coated magnetic stir bar. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Analytical TLCs were performed with 0.25 mm silica gel HSGF254. The TLC plates were visualized by ultraviolet light and treatment with anisaldehyde-H_2SO_4 or phosphomolybdic acid stain followed by gentle heating. Purification of products was accomplished by flash chromatography on silica gel (200-300 mesh) purchased from Yantai Huayang New Material Technology Co. Ltd. and the purified compounds show a single spot by analytical TLC. Organic solutions were concentrated using a Büchi or Eyela rotary evaporator with a desktop vacuum pump. Nuclear magnetic resonance (NMR) spectra were measured on Bruker AVANCE III (^{1}H at 400 MHz, $^{13}C\{^1H\}$ at 101 MHz) or Bruker AVANCE III (^{1}H at 500 MHz, $^{13}C\{^1H\}$ at 126 MHz, ^{19}F at 471 MHz) nuclear magnetic resonance spectrometers. Data for ^{1}H NMR spectrum are reported as follows: chemical shift δ (ppm) referenced to tetramethylsilane (TMS, 0.00 ppm) or C_6D_5H (7.16 ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, ddd = doublet of doublet of doublets, dddq = doublet of doublet of doublet of quartets, dtdt = doublet of triplet of doublet of triplets, tq = triplet of quartets, qdd = quartet of doublet of doublets, m = multiplet), coupling constant *J* (Hz), and integration. Data for $^{13}C\{^1H\}$ NMR spectrum are reported as follows: chemical shift δ (ppm) referenced to $CDCl_3$ (77.16 ppm) or C_6D_6 (128.06 ppm). High-resolution mass spectra (HRMS) were recorded on a Bruker Solarix XR Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (ESI) and ThermoFisher Q Exactive GC Hybrid Quadrupole-Orbitrap GC-MS/MS System (EI).

Abbreviations

atm	atmosphere
Bn	benzyl group
Bu	butyl
d	density
DCM	dichloromethane
DCE	1,2-dichloroethane
DFT	density functional theory
DIAD	diisopropyl azodicarboxylate
DMA	N, N-dimethylacetamide
DMF	N, N-dimethylformamide
DMP	Dess-Martin periodinane
d.r.	diastereomeric ratio
EA	ethyl acetate
EI	electron impact ion source
ESI	electron spray ionization
Et	ethyl
HFIP	hexafluoroisopropanol
HRMS	high-resolution mass spectroscopy
INT	intermediate
Me	methyl
m.p.	melting point
PDC	pyridinium dichromate
PE	petroleum ether
Ph	phenyl
PPDP	4-piperidin-1-ylpyridine
Pr	propyl
PTLC	preparative thin-layer chromatography
rpm	revolutions per minute
rt	room temperature
TBAF	tetrabutylammonium fluoride
TFEA	2,2,2-trifluoroethanol
THF	tetrahydrofuran
TLC	thin layer chromatography
TS	transition state

2. Substrates Preparations

The synthesis of all substrates for the present study was not optimized. A syringe pump is recommended for the synthesis of *gem*-difluorides. *gem*-difluorodienylcyclopropanes are unstable and can be stored under an argon atmosphere at -10 °C for a few days (diluted with EA).



S1 **S2** **1a**

To a flask with **S1**[15a] (2.7 g, 15.5 mmol) in DCM (100 mL) was added MnO_2 (10.4 g, 119.6 mmol) at rt. The obtained mixture was stirred for 14 h at rt, filtered through silica gel, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 35:1 to 20:1 PE/EA) to afford **S2** (2.5048 g) as a light yellow oil.

S2 (2.5048 g, 14.5 mmol) and PPh_3 (7.633 g, 29.1 mmol) were dissolved in DMF (40 mL). The solution of $ClCF_2CO_2Na$ (5.092 g, 33.4 mmol) in DMF (50 mL) was then added by syringe pump in 1 h under an argon atmosphere at 100 °C. After that, the mixture was stirred at 100 °C for 3.5 h, cooled to rt, and then MeI (4.5 mL) was added and stirred at rt for 30 min to remove PPh_3. The reaction system was then quenched with water and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 PE/EA) to afford **1a** (2.3425 g, 73% over two steps) as a light yellow oil.

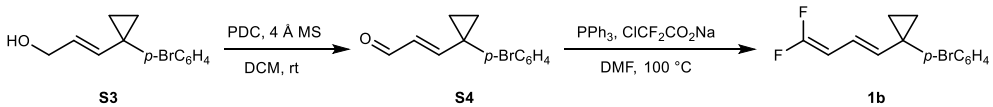
TLC (10:1 PE/EA, R_f): 0.8.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.34 – 7.27 (m, 4H), 7.25 – 7.19 (m, 1H), 5.57 – 5.43 (m, 2H), 4.88 (dddd, J = 24.6, 8.6, 1.8, 1.8 Hz, 1H), 1.15 – 1.09 (m, 2H), 1.02 – 0.96 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 155.8 (dd, J = 295.9, 289.9 Hz), 143.0, 140.16 (dd, J = 10.1, 3.0 Hz), 129.8, 128.5, 126.7, 117.0 (dd, J = 4.0, 2.0 Hz), 82.0 (dd, J = 27.3, 17.2 Hz), 28.5, 15.3.

^{19}F NMR (471 MHz, $CDCl_3$, δ): -87.46 (d, J = 33.9 Hz), -90.38 (d, J = 33.8 Hz). (page S180)

HRMS (EI) m/z: calcd. for $C_{13}H_{12}F_2$ ($[M\cdot]^+$): 206.0902, found: 206.0900.



S3 **S4** **1b**

To a flask with **S3**[15a] (569.7 mg, 2.25 mmol) in DCM (15 mL) was added PDC (752.4 mg, 2 mmol) and 4 Å molecular sieve (752.4 mg) at rt. The obtained mixture was stirred for 2 h at rt, filtered through silica gel, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 20:1 to 15:1 PE/EA) to afford **S4** (395.4 mg) as a light yellow oil.

S4 (395.4 mg, 1.57 mmol) and PPh_3 (742.3 mg, 2.83 mmol) were dissolved in DMF (5 mL). The solution of $ClCF_2CO_2Na$ (526 mg, 3.45 mmol) in DMF (7 mL) was then added by syringe pump in 1 h under an argon atmosphere at 100 °C. After that, the mixture was stirred at 100 °C for 1 h. Cooled to rt, and then MeI (0.5 mL) was added and stirred at rt for 30 min to remove PPh_3. The

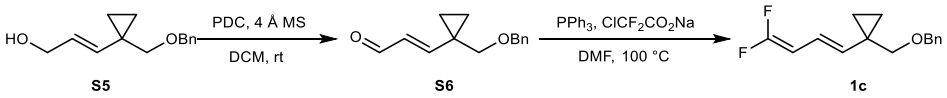
reaction system was then quenched with water and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 PE/EA) to afford **1b** (360.2 mg, 63% over two steps) as a light yellow oil.

TLC (10:1 PE/EA, R_f): 0.8.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.46 – 7.39 (m, 2H), 7.20 – 7.12 (m, 2H), 5.53 – 5.41 (m, 2H), 4.96 – 4.80 (m, 1H), 1.11 – 1.04 (m, 2H), 1.04 – 0.96 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 155.9 (dd, J = 296.9, 289.9 Hz), 142.0, 139.4 (dd, J = 11.1, 3.0 Hz), 131.6, 131.6, 120.6, 117.3 (dd, J = 4.0, 2.0 Hz), 81.9 (dd, J = 27.3, 18.2 Hz), 28.0, 15.3.

HRMS (EI) m/z: calcd. for $C_{13}H_{11}BrF_2$ ([M·]$^+$): 284.0007, found: 284.0002.



S5 S6 1c

To a flask with **S5**[15b] (502.1 mg, 2.3 mmol) in DCM (10 mL) was added PDC (1.29 g, 3.4 mmol) and 4 Å molecular sieve (915 mg) at rt. The obtained mixture was stirred for 2.5 h at rt, filtered through silica gel, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 100:1 to 50:1 to 25:1 to 10:1 to 5:1 PE/EA) to afford **S6** (283.3 mg).

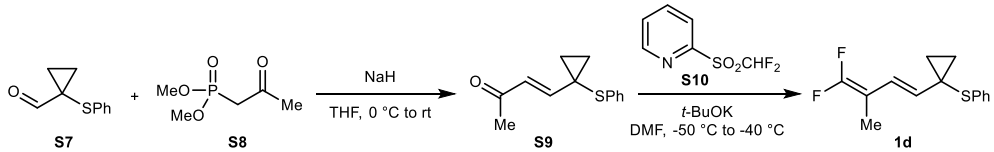
S6 (283.3 mg, 1.31 mmol) and PPh_3 (687 mg, 2.62 mmol) were dissolved in DMF (5 mL). The solution of $ClCF_2CO_2Na$ (602 mg, 3.95 mmol) in DMF (5 mL) was then added by syringe pump in 1 h under an argon atmosphere at 100 °C. After that, the mixture was stirred at 100 °C for 40 min. Cooled to rt, and then MeI (0.3 mL) was added and stirred at rt for 20 min to remove PPh_3. The reaction system was then quenched with water and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 to 100:1 PE/EA) to afford **1c** (248.6 mg, 43% over two steps) as a light yellow oil.

TLC (5:1 PE/EA, R_f): 0.8.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.37 – 7.32 (m, 4H), 7.32 – 7.26 (m, 1H), 5.97 (ddt, J = 15.7, 10.8, 1.2 Hz, 1H), 5.44 (d, J = 15.7 Hz, 1H), 4.90 (dddd, J = 24.6, 10.9, 1.8, 0.7 Hz, 1H), 4.54 (s, 2H), 3.41 (s, 2H), 0.77 – 0.72 (m, 2H), 0.71 – 0.66 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 155.9 (dd, J = 295.9, 289.9 Hz), 138.4, 136.3 (dd, J = 11.1, 3.0 Hz), 128.5, 128.0, 127.8, 116.3 (dd, J = 5.0, 2.0 Hz), 82.3 (dd, J = 27.3, 17.2 Hz), 75.2, 73.0, 22.5, 13.2.

HRMS (ESI) m/z: calcd. for $C_{15}H_{17}F_2O$ ([M+H]$^+$): 251.1242, found: 251.1234.



S7 S8 S9 1d

To a flask with NaH (297.2 mg, 60% dispersion in mineral oil, 7.4 mmol) in THF (14 mL) was added **S8** (1.23 g, 7.4 mmol) under an argon atmosphere at 0 °C, stirred for 20 min at 0 °C. Then

the solution of **S7** (881.5 mg, 4.95 mmol) in THF (7 mL) was added. The obtained mixture was stirred for 24 h at 0 °C to rt. The reaction system was then quenched with saturated aqueous NH_4Cl solution and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 20:1 to 10:1 PE/EA) to afford **S9** (961.1 mg).

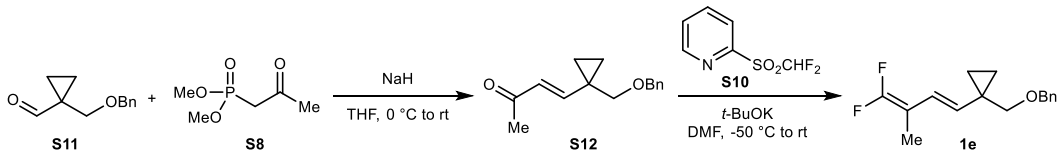
S9 (436.6 mg, 2.0 mmol) and **S10**[11] (328.4 mg, 1.7 mmol) were dissolved in DMF (7 mL). The solution of *t*-BuOK (347.8 mg, 3.1 mmol) in DMF (4 mL) was then added under an argon atmosphere at -50 °C. After that, the mixture was warmed to -40 °C within 1.5 h. The reaction system was then quenched with saturated aqueous NH_4Cl solution (3 mL) and 3 M HCl (3 mL), and then extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 PE/EA) to afford **1d** (355.7 mg, 74% over two steps) as a light yellow oil.

TLC (10:1 PE/EA, R_f): 0.8.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.32 – 7.21 (m, 4H), 7.15 – 7.09 (m, 1H), 6.39 (ddd, J = 15.4, 1.9, 1.9 Hz, 1H), 5.40 (d, J = 15.4 Hz, 1H), 1.64 (dd, J = 3.1 Hz, 3H), 1.31 – 1.24 (m, 2H), 1.23 – 1.16 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 153.9 (dd, J = 293.9, 289.9 Hz), 137.1, 132.2 (dd, J = 11.1, 3.0 Hz), 128.8, 127.6, 125.4, 122.2 (d, J = 2.0 Hz), 86.7 (dd, J = 22.2, 5.0 Hz), 26.8, 18.7, 9.4 (dd, J = 1.0, 1.0 Hz).

HRMS (EI) m/z: calcd. for $C_{14}H_{14}F_2S$ ($[M\cdot]^+$): 252.0779, found: 252.0780.



To a flask with NaH (108 mg, 60% dispersion in mineral oil, 2.7 mmol) in THF (8 mL) was added **S8** (475 mg, 2.86 mmol) under an argon atmosphere at 0 °C, stirred for 10 min at 0 °C. Then the solution of **S11** (414 mg, 2.18 mmol) in THF (2 mL) was added. The obtained mixture was stirred for 23 h at 0 °C to rt. The reaction system was then quenched with saturated aqueous NH_4Cl solution and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 50:1 to 25:1 to 10:1 PE/EA) to afford **S12** (407.7 mg).

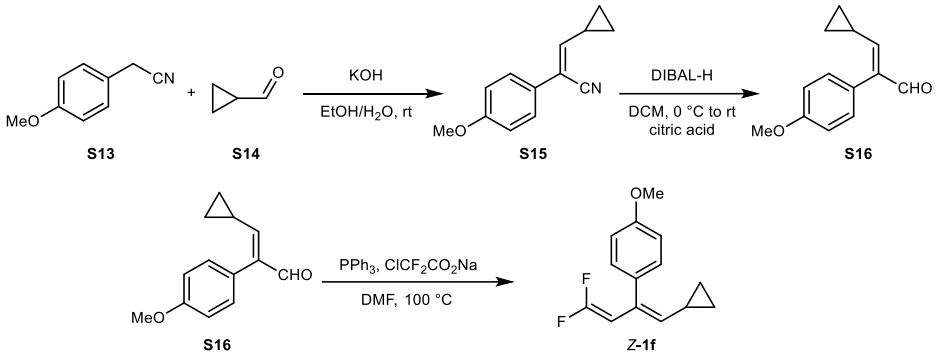
S12 (284 mg, 1.23 mmol) and **S10** (198.3 mg, 1.03 mmol) were dissolved in DMF (4 mL). The solution of *t*-BuOK (225 mg, 2 mmol) in DMF (2 mL) was then added under an argon atmosphere at -50 °C. After that, the mixture was stirred at -50 °C for 10 min. and at rt for 10 min. The reaction system was then quenched with saturated aqueous NH_4Cl solution (2 mL) and 3 M HCl (2 mL), and then extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 100:1 PE/EA) to afford **1e** (164.8 mg, 61% over two steps) as a colorless oil.

TLC (10:1 PE/EA, R_f): 0.7.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.42 – 7.32 (m, 4H), 7.32 – 7.25 (m, 1H), 6.20 (ddd, J = 15.9, 1.7, 1.7 Hz, 1H), 5.38 (d, J = 16.0 Hz, 1H), 4.54 (s, 2H), 3.42 (s, 2H), 1.68 – 1.63 (m, 3H), 0.77 – 0.73 (m, 2H), 0.73 – 0.67 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 153.8 (dd, J = 292.9, 287.8 Hz), 138.4, 133.0 (dd, J = 11.1, 4.0 Hz), 128.5, 128.0, 127.8, 119.6 (d, J = 3.0 Hz), 87.2 (dd, J =21.1, 14.1 Hz), 75.3, 73.0, 22.6, 13.3, 9.1 (dd, J = 2.0, 2.0 Hz).

HRMS (EI) m/z: calcd. for $C_{16}H_{18}F_2O$ ($[M\cdot]^+$): 264.1320, found: 264.1323.



To a flask with **S13** (3.8 g, 25.8 mmol) in EtOH (75 mL) and H_2O (25 mL) was added **S14** (1.97 g, 28.1 mmol) and KOH (214 mg, 3.8 mmol) at rt. The obtained mixture was stirred for 14 h at rt. The reaction system was then poured into H_2O (200 mL) and extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 100:1 to 50:1 to 25:1 PE/EA) to afford **S15** (1.74 g).

To a flask with **S15** (540 mg, 2.7 mmol) in DCM (8 mL) was added DIBAL-H (8.1 mL, 1 M in hexanes, 8.1 mmol) under an argon atmosphere at 0 °C. After that, the mixture was stirred for 10.5 h at 0 °C to rt. The reaction system was then quenched with saturated aqueous citric acid solution slowly and kept stirring until the upper organic phase was clear, and then extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered through silica gel (to avoid polymerization), and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 100:1:1 to 50:1:1 to 25:1:1 PE/EA/DCM) to afford **S16** (305.7 mg).

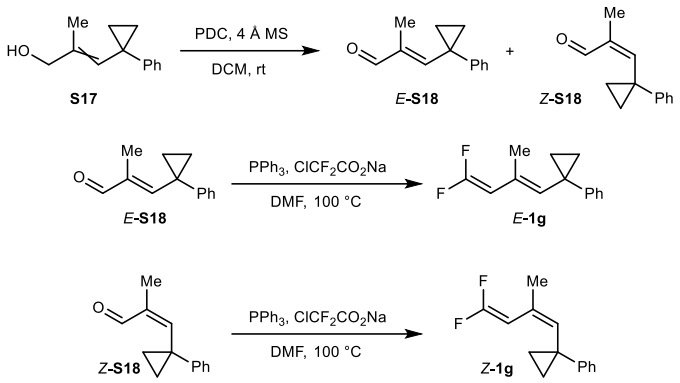
S16 (305.7 mg, 1.51 mmol) and PPh_3 (791 mg, 3 mmol) were dissolved in DMF (4 mL). The solution of $ClCF_2CO_2Na$ (702 mg, 4.6 mmol) in DMF (6 mL) was then added by syringe pump in 1 h under an argon atmosphere at 100 °C. Cooled to rt, and then MeI (0.3 mL) was added and stirred at rt for 20 min to remove PPh_3. The reaction system was then quenched with water and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 PE/EA) to afford *Z*-**1f** (195.9 mg, 10% over three steps) as a light yellow oil.

TLC (10:1 PE/EA, R_f): 0.7.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.28 – 7.22 (m, 2H), 6.92 – 6.86 (m, 2H), 5.04 (d, J = 10.0 Hz, 1H), 4.94 (ddd, J = 24.2, 4.5, 0.8 Hz, 1H), 3.81 (s, 3H), 1.43 (dddd, J = 12.9, 9.8, 8.1, 4.7 Hz, 1H), 0.75 – 0.68 (m, 2H), 0.47 – 0.41 (m, 2H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 158.7, 155.5 (dd, J =300.0, 287.8 Hz), 136.5 (dd, J =6.1, 6.1 Hz), 131.2, 130.3, 128.6 (dd, J =6.1, 6.1 Hz), 113.6, 84.7 (dd, J =28.3, 11.1 Hz), 55.3, 11.8, 8.0.

HRMS (EI) m/z: calcd. for $C_{14}H_{14}OF_2$ ($[M\cdot]^+$): 236.1007, found: 236.1008.



To a flask with **S17**[15c] (567 mg, 3 mmol, E/Z = 3.6:1) in DCM (10 mL) was added PDC (1.72 g, 4.6 mmol) and 4 Å molecular sieve (720 mg) at rt. The obtained mixture was stirred for 50 min at rt. The reaction system was then filtered through silica gel, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 100:1 to 50:1 PE/EA) to afford *E*-**S18** (344.6 mg) and *Z*-**S18** (79 mg).

E-**S18** (344.6 mg, 1.85 mmol) and PPh_3 (972 mg, 3.7 mmol) were dissolved in DMF (4 mL). The solution of $ClCF_2CO_2Na$ (857 mg, 5.6 mmol) in DMF (6 mL) was then added by syringe pump in 2.25 h under an argon atmosphere at 100 °C. Then the mixture was stirred at 100 °C for 30 min. Cooled to rt, and then MeI (0.3 mL) was added and stirred at rt for 10 min to remove PPh_3. The reaction system was then quenched with water and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 PE/EA) to afford *E*-**1g** (299.5 mg, 45% over two steps) as a colorless oil.

TLC (10:1 PE/EA, R_f): 0.9.

^1H NMR (400 MHz, $CDCl_3$, δ): 7.28 – 7.21 (m, 2H), 7.18 – 7.09 (m, 3H), 5.73 (s, 1H), 4.90 (ddd, J = 26.6, 5.1, 1.9 Hz, 1H), 1.89 – 1.81 (m, 3H), 1.20 – 1.13 (m, 2H), 1.04 – 0.98 (m, 2H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 155.5 (dd, J = 300.0, 287.9 Hz), 145.1, 133.3 (dd, J = 9.1, 6.1 Hz), 131.4 (dd, J = 7.1, 6.1 Hz), 128.4, 125.9, 125.5, 85.8 (dd, J = 28.3, 13.1 Hz), 23.1, 18.7, 16.3 (d, J = 6.1 Hz).

HRMS (EI) m/z: calcd. for $C_{14}H_{14}F_2$ ($[M\cdot]^+$): 220.1058, found: 220.1056.

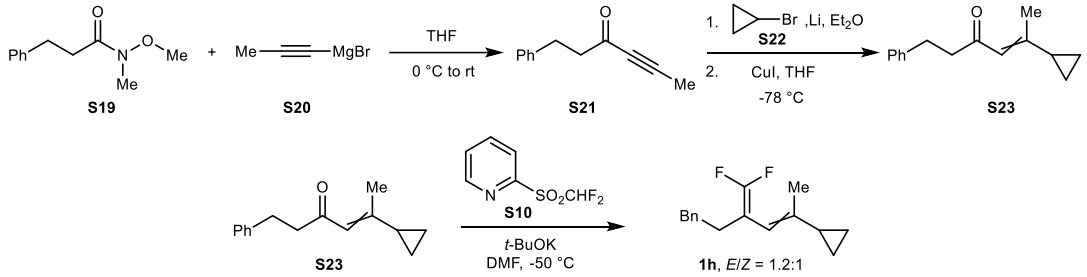
Z-**S18** (130.4 mg, 0.7 mmol) and PPh_3 (368 mg, 1.4 mmol) were dissolved in DMF (2 mL). The solution of $ClCF_2CO_2Na$ (362 mg, 2.4 mmol) in DMF (3 mL) was then added by syringe pump in 3 h under an argon atmosphere at 100 °C. Cooled to rt, and then MeI (0.2 mL) was added and stirred at rt for 20 min to remove PPh_3. The reaction system was then quenched with water and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 PE/EA) to afford *Z*-**1g** (67.6 mg, 6% over two steps) as a colorless oil.

TLC (10:1 PE/EA, R_f): 0.9.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.27 – 7.22 (m, 2H), 7.17 – 7.10 (m, 3H), 5.62 (s, 1H), 5.36 (dd, J = 28.0, 5.2 Hz, 1H), 1.95 (dd, J = 4.3, 1.5 Hz, 3H), 1.19 – 1.13 (m, 2H), 1.06 – 0.98 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 156.0 (dd, J = 302.0, 288.9 Hz), 145.1, 132.6 (dd, J = 9.1, 4.0 Hz), 129.7 (dd, J = 7.1, 5.0 Hz), 128.4, 126.0, 125.6, 81.0 (dd, J = 28.3, 11.1 Hz), 22.9, 21.7 (d, J = 6.1 Hz), 18.5.

HRMS (EI) m/z: calcd. for $C_{14}H_{14}F_2$ ([M·]$^+$): 220.1058, found: 220.1056.



To a flask with **S19** (969 mg, 5 mmol) in THF (20 mL) was added **S20** (0.5 M in THF, 12 mL, 6 mmol) under an argon atmosphere at 0 °C. The obtained mixture was stirred for 2 h at 0 °C to rt. The reaction system was then quenched with saturated aqueous NH_4Cl solution and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude **S21** (824.7 mg) was used for the next step without purification.

To flask A with Li (229 mg, 33 mmol) was added Et_2O (10 mL) under argon atmosphere. Then a solution of cyclopropyl bromide (1.514 g, 12.5 mmol) in Et_2O (5 mL) was prepared. Part of the cyclopropyl bromide solution, 1 mL was added to flask A in one portion. After the reaction was initiated, flask A was cooled at 0 °C. Then the rest of the cyclopropyl bromide solution was added to flask A. The reaction mixture was stirred at 0 °C for another 2 h, affording the cyclopropyl lithium **S22** solution. To flask B with CuI (1.292 g, 6.8 mmol) was added THF (20 mL) under argon atmosphere at −78 °C. Then all newly prepared solution of **S22** in flask A was transferred to flask B. Flask B was stirred at 0 °C for another 30 min, giving cyclopropyl copper lithium solution. Then flask B was cooled at −78 °C. A solution of crude **S21** (824.7 mg, 4.8 mmol) in THF (2 mL) was added to flask B. The reaction mixture was stirred at −78 °C for 3 h. The reaction system was then quenched with saturated aqueous NH_4Cl solution and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 100:1 PE/EA) to afford **S23** (710.1 mg).

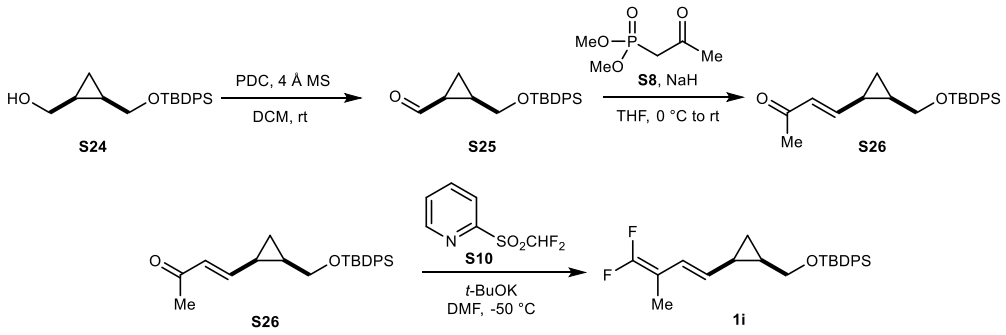
S23 (710.1 mg, 3.31 mmol) and **S10** (767 mg, 4 mmol) were dissolved in DMF (5 mL). The solution of *t*-BuOK (727 mg, 6.5 mmol) in DMF (10 mL) was then added by syringe pump in 1 h under an argon atmosphere at -50 °C. The reaction system was then quenched with saturated aqueous NH_4Cl solution (4 mL) and 3 M HCl (4 mL), and then extracted with ether. The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 PE/EA) to afford **1h** (355.2 mg, 29% over three steps, E/Z = 1.2:1) as a colorless oil.

TLC (10:1 PE/EA, R_f): 0.8.

^{1}H NMR for the major isomer (400 MHz, $CDCl_3$, δ): 7.31 – 7.23 (m, 2H), 7.21 – 7.13 (m, 3H), 5.38 (d, J = 6.3 Hz, 1H), 2.76 – 2.63 (m, 2H), 2.45 – 2.29 (m, 2H), 1.54 (dddd, J = 8.6, 5.7, 2.8, 2.8 Hz, 1H), 1.50 – 1.41 (m, 3H), 0.68 – 0.59 (m, 2H), 0.59 – 0.53 (m, 2H).

^{13}C{^{1}H} NMR for the major isomer (101 MHz, $CDCl_3$, δ): 155.6 (dd, J = 287.8, 287.8 Hz), 142.2 (dd, J = 2.0, 2.0 Hz), 141.6, 128.6, 128.4, 126.1, 116.2 (dd, J = 3.0, 3.0 Hz), 88.1 (dd, J = 21.2, 17.2 Hz), 34.2 (dd, J = 2.0, 2.0 Hz), 30.1 (d, J = 2.0 Hz), 18.7, 14.3 (d, J = 4.0 Hz), 5.1.

HRMS (EI) m/z: calcd. for $C_{16}H_{18}F_2$ ($[M\cdot]^+$): 248.1371, found: 248.1371.



To a flask with **S24**[15d] (1.17 g, 3.44 mmol) in DCM (10 mL) was added PDC (1.61 g, 4.3 mmol) and 4 Å molecular sieve (780 mg) at rt. The obtained mixture was stirred for 4 h at rt. The reaction system was then filtered through silica gel, and concentrated by rotary evaporation. The crude **S25** was used for the next step without purification.

To a flask with NaH (171 mg, 60% dispersion in mineral oil, 4.3 mmol) in THF (10 mL) was added **S8** (723 mg, 4.35 mmol) under an argon atmosphere at 0 °C, stirred for 10 min at 0 °C. Then the solution of crude **S25** in THF (10 mL) was added. The obtained mixture was stirred for 17 h at 0 °C to rt. The reaction system was then quenched with saturated aqueous NH_4Cl solution and extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 50:1 to 25:1 to 10:1 PE/EA) to afford **S26** (823.9 mg).

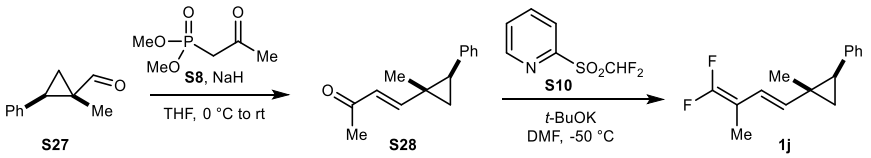
S26 (823.9 mg, 2.18 mmol) and **S10** (506 mg, 2.62 mmol) were dissolved in DMF (4 mL). The solution of *t*-BuOK (483 mg, 4.3 mmol) in DMF (6 mL) was then added by syringe pump in 1 h under an argon atmosphere at -50 °C. The reaction system was then quenched with saturated aqueous NH_4Cl solution (4 mL) and 3 M HCl (4 mL), and then extracted with ether. The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 to 250:1 PE/EA) to afford **1i** (395.1 mg, 28% over three steps) as a colorless oil.

TLC (10:1 PE/EA, R_f): 0.8.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.72 – 7.63 (m, 4H), 7.47 – 7.32 (m, 6H), 6.25 – 6.16 (m, 1H), 5.36 (dd, J = 15.6, 8.4 Hz, 1H), 3.78 (dd, J = 11.1, 5.8 Hz, 1H), 3.58 (dd, J = 11.1, 7.9 Hz, 1H), 1.69 – 1.62 (m, 1H), 1.59 (t, J = 3.1 Hz, 3H), 1.40 – 1.30 (m, 1H), 1.04 (s, 9H), 0.94 – 0.86 (m, 1H), 0.45 – 0.37 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 153.6 (dd, J = 292.9, 288.9 Hz), 135.7 (d, J = 2.0 Hz), 134.1 (d, J = 9.1 Hz), 129.7, 129.0 (dd, J = 11.1, 3.0 Hz), 127.7, 122.4 (d, J = 2.0 Hz), 87.3 (dd, J = 21.2, 14.1 Hz), 63.8, 27.0, 21.2, 19.6, 19.4, 10.9, 9.2.

HRMS (ESI) m/z: calcd. for $C_{25}H_{31}F_2OSi$ ($[M+H]^+$): 413.2107, found: 413.2089.



To a flask with NaH (280 mg, 60% dispersion in mineral oil, 7 mmol) in THF (20 mL) was added **S8** (1.161 g, 7 mmol) under an argon atmosphere at 0 °C, stirred for 10 min at 0 °C. Then the solution of **S27**[15e] (4.66 mmol) in THF (10 mL) was added. The obtained mixture was stirred for 24 h at 0 °C to rt. The reaction system was then quenched with saturated aqueous NH_4Cl solution and extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 30:1 PE/EA) to afford **S28** (494.7 mg).

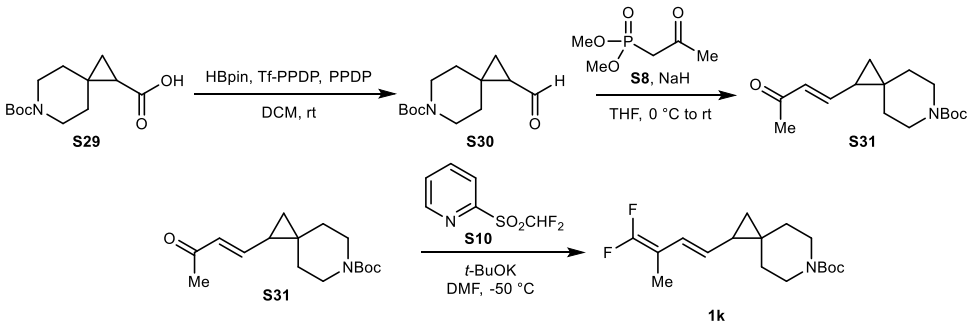
S28 (494.7 mg, 2.47 mmol) and **S10** (398 mg, 2.06 mmol) were dissolved in DMF (7 mL). The solution of *t*-BuOK (416.3 mg, 3.71 mmol) in DMF (4 mL) was then added under an argon atmosphere at -50 °C. After that, the mixture was stirred at -40 °C for 1 h. The reaction system was then quenched with saturated aqueous NH_4Cl solution (5 mL) and 3 M HCl (5 mL), and then extracted with ether. The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 PE/EA) to afford **1j** (327.1 mg, 36% over two steps) as a light yellow oil.

TLC (10:1 PE/EA, R_f): 0.9.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.32 – 7.24 (m, 2H), 7.22 – 7.14 (m, 3H), 6.16 – 6.07 (m, 1H), 5.35 (dd, J = 15.9, 3.1 Hz, 1H), 2.20 (dd, J = 8.8, 6.5 Hz, 1H), 1.70 (t, J = 3.1 Hz, 3H), 1.21 – 1.09 (m, 2H), 0.91 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 153.8 (dd, J = 291.9, 288.9 Hz), 138.6, 138.3 (dd, J = 11.1, 3.0 Hz), 129.2, 128.2, 126.2, 118.1 (d, J = 2.0 Hz), 87.1 (dd, J = 21.2, 14.1 Hz), 31.6, 25.1, 19.5, 16.8, 9.2 (dd, J = 2.0, 2.0 Hz).

HRMS (EI) m/z: calcd. for $C_{15}H_{16}F_2$ ($[M\cdot]^+$): 234.1215, found: 234.1213.



To a flask with **S29** (1 g, 3.9 mmol) and PPDP (1.047 g, 6.4 mmol) in DCM (24 mL) was added Tf-

PPDP[15f] (3.083 g, 6.9 mmol) and HBpin (673 mg, 5.3 mmol) at rt. The obtained mixture was stirred for 10 min at rt. *n*-Pentane was added. The reaction system was then filtered through silica gel, and concentrated by rotary evaporation. The crude **S30** was used for the next step without purification.

To a flask with NaH (241 mg, 60% dispersion in mineral oil, 6 mmol) in THF (15 mL) was added **S8** (990 mg, 6 mmol) under an argon atmosphere at 0 °C, stirred for 10 min at 0 °C. Then the solution of crude **S30** in THF (5 mL) was added. The obtained mixture was stirred for 15 h at 0 °C to rt. The reaction system was then quenched with saturated aqueous NH_4Cl solution and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 20:1 to 10:1 to 5:1 PE/EA) to afford **S31** (269.8 mg).

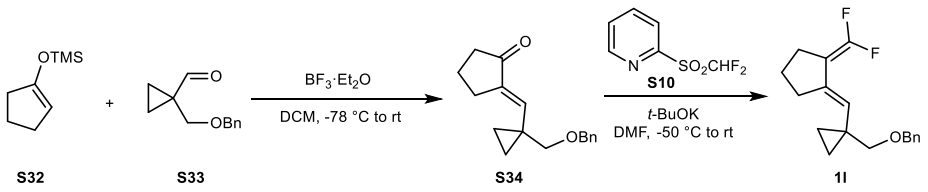
S31 (269.8 mg, 0.97 mmol) and **S10** (280 mg, 1.4 mmol) were dissolved in DMF (4 mL). The solution of *t*-BuOK (224 mg, 2 mmol) in DMF (4 mL) was then added by syringe pump in 1 h under an argon atmosphere at -50 °C. The reaction system was then quenched with saturated aqueous NH_4Cl solution (3 mL) and 3 M HCl (3 mL), and then extracted with ether. The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 50:1 PE/EA) to afford **1k** (206.5 mg, 17% over three steps) as a light yellow oil.

TLC (5:1 PE/EA, R_f): 0.5.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.28 – 6.16 (m, 1H), 5.32 (ddd, J = 15.6, 8.7, 2.0 Hz, 1H), 3.48 – 3.33 (m, 4H), 1.67 – 1.62 (m, 3H), 1.49 – 1.41 (m, 12H), 1.40 – 1.33 (m, 2H), 0.79 (ddd, J = 8.8, 4.8, 2.1 Hz, 1H), 0.55 – 0.49 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 155.1, 153.7 (dd, J = 291.9, 288.9 Hz), 128.8 (dd, J = 12.1, 4.0 Hz), 122.5, 87.1 (dd, J = 21.2, 14.1 Hz), 79.4 (2C), 43.6, 36.5, 30.6, 28.6, 27.0, 25.1, 19.6, 9.2.

HRMS (ESI) m/z: calcd. for $C_{17}H_{26}F_2NO_2$ ($[M+H]^+$): 314.1926, found: 314.1927.



To a flask with **S33** (571 mg, 3 mmol) in DCM (9 mL) was added $BF_3{\cdot}Et_2O$ (1.32 mL, d = 1.125 g/mL, 10.5 mmol) under an argon atmosphere at -78 °C. Then a solution of **S32** (641 mg, 4.1 mmol) in DCM (3 mL) was added by syringe pump in 50 min. The obtained mixture was stirred for 11 h at 0 °C to rt. The reaction system was then quenched with brine, and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 100:1 to 50:1 to 20:1 to 10:1 PE/EA) afforded compound **S34** (435.6 mg).

S34 (435.6 mg, 1.7 mmol) and **S10** (312 mg, 1.6 mmol) were dissolved in DMF (6 mL). The solution of *t*-BuOK (376 mg, 3.35 mmol) in DMF (3 mL) was then added under an argon atmosphere at -50 °C. After that, the mixture was stirred at -50 °C for 10 min and at rt for 10 min. The reaction system was then quenched with saturated aqueous NH_4Cl solution (3 mL) and 3 M HCl (3 mL), and

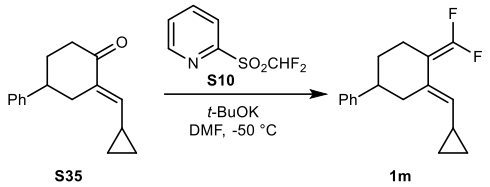
then extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 PE/EA) to afford **1l** (177.5 mg, 20% over two steps) as a colorless oil.

TLC (10:1 PE/EA, R_f): 0.6.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.35 – 7.28 (m, 4H), 7.28 – 7.23 (m, 1H), 5.86 (t, J = 2.4 Hz, 1H), 4.51 (s, 2H), 3.37 (s, 2H), 2.49 (td, J = 7.2, 2.4 Hz, 2H), 2.35 (tt, J = 7.0, 3.3 Hz, 2H), 1.74 – 1.63 (m, 2H), 0.72 – 0.65 (m, 2H), 0.64 – 0.60 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 152.3 (dd, J = 295.9, 287.8 Hz), 139.1 (dd, J = 8.1, 2.0 Hz), 138.8, 128.4, 127.6, 127.5, 125.4 (dd, J = 16.2, 6.1 Hz), 93.7 (dd, J = 22.2, 12.1 Hz), 76.6, 72.8, 31.8 (d, J = 3.0 Hz), 27.2 (dd, J = 3.0, 1.0 Hz), 24.8, 21.4, 12.2.

HRMS (EI) m/z: calcd. for $C_{18}H_{20}OF_2$ ([M·]$^+$): 290.1477, found: 290.1479.



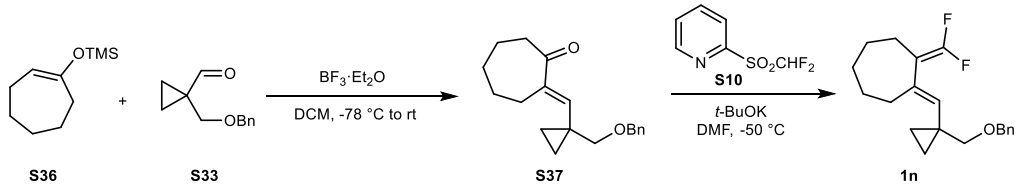
S35[4e] (433.2 mg, 1.91 mmol) and **S10** (450 mg, 2.3 mmol) were dissolved in DMF (4 mL). The solution of *t*-BuOK (422 mg, 3.8 mmol) in DMF (4 mL) was then added by syringe pump in 1 h under an argon atmosphere at -50 °C. The reaction system was then quenched with saturated aqueous NH_4Cl solution (3 mL) and 3 M HCl (3 mL), and then extracted with ether. The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 PE/EA) to afford **1m** (414.7 mg, 83%) as a colorless oil.

TLC (10:1 PE/EA, R_f): 0.9.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.35 – 7.28 (m, 2H), 7.26 – 7.18 (m, 3H), 4.87 (dt, J = 9.7, 2.4 Hz, 1H), 3.02 – 2.92 (m, 1H), 2.76 – 2.65 (m, 1H), 2.63 – 2.51 (m, 1H), 2.14 (ddd, J = 14.1, 12.1, 2.2 Hz, 1H), 2.08 – 1.94 (m, 2H), 1.75 – 1.61 (m, 1H), 1.59 – 1.46 (m, 1H), 0.80 – 0.69 (m, 2H), 0.44 – 0.32 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 152.2 (dd, J = 287.8, 284.8 Hz), 146.4, 132.9 (dd, J = 5.0, 2.0 Hz), 128.6, 127.6 (dd, J = 3.0, 3.0 Hz), 127.0, 126.5, 91.6 (dd, J = 22.2, 14.1 Hz), 43.9, 36.2 (d, J = 3.0 Hz), 33.3 (dd, J = 2.0, 2.0 Hz), 25.2, 10.1, 7.4, 7.2.

HRMS (EI) m/z: calcd. for $C_{17}H_{18}F_2$ ([M·]$^+$): 260.1371, found: 260.1371.



To a flask with **S33** (575 mg, 3 mmol) in DCM (9 mL) was added $BF_3{\cdot}Et_2O$ (1.32 mL, d = 1.125

g/mL, 10.5 mmol) under an argon atmosphere at -78 °C. Then a solution of **S36** (745 mg, 4.0 mmol) in DCM (3 mL) was added by syringe pump in 1 h. The obtained mixture was stirred for 23.5 h at 0 °C to rt. The reaction system was then quenched with saturated aqueous $NaHCO_3$ solution, and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 100:1 to 50:1 to 25:1 PE/EA) afforded compound **S37** (439.4 mg).

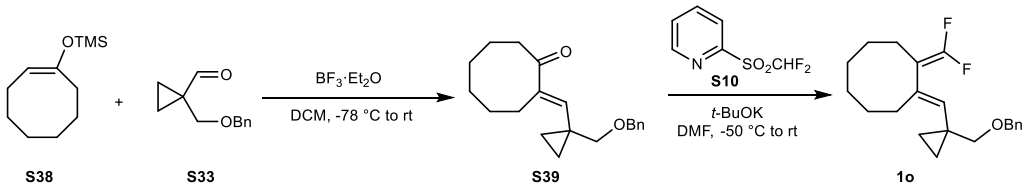
S37 (278.7 mg, 0.98 mmol) and **S10** (232 mg, 1.2 mmol) were dissolved in DMF (4 mL). The solution of *t*-BuOK (218 mg, 1.9 mmol) in DMF (4 mL) was then added by syringe pump in 1 h under an argon atmosphere at -50 °C. The reaction system was then quenched with saturated aqueous NH_4Cl solution (3 mL) and 3 M HCl (3 mL), and then extracted with ether. The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 to 100:1 PE/EA) to afford **1n** (212.3 mg, 22% over two steps) as a colorless oil.

TLC (10:1 PE/EA, R_f): 0.6.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.31 (d, J = 3.8 Hz, 4H), 7.28 – 7.22 (m, 1H), 5.65 (s, 1H), 4.51 (s, 2H), 3.36 (s, 2H), 2.53 – 2.44 (m, 2H), 2.19 – 2.10 (m, 2H), 1.60 – 1.47 (m, 6H), 0.72 – 0.66 (m, 2H), 0.61 – 0.55 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 153.6 (dd, J = 289.9, 286.8 Hz), 138.9, 138.2 (dd, J = 3.0, 3.0 Hz), 130.0 (dd, J = 6.1, 2.0 Hz), 128.4, 127.6, 127.5, 95.3 (dd, J = 20.2, 13.1 Hz), 76.9, 72.9, 30.9 (d, J = 2.0 Hz), 30.8, 28.6 (dd, J = 2.0, 1.0 Hz), 27.5, 26.9, 20.0, 12.2.

HRMS (ESI) m/z: calcd. for $C_{20}H_{28}F_2NO$ ($[M+NH_4]^+$): 336.2133, found: 336.2130.



To a flask with **S33** (568 mg, 3 mmol) in DCM (9 mL) was added $BF_3{\cdot}Et_2O$ (1.32 mL, d = 1.125 g/mL, 10.5 mmol) under an argon atmosphere at -78 °C. Then a solution of **S38** (1.074 g, 5.4 mmol) in DCM (3 mL) was added by syringe pump in 1 h. The obtained mixture was stirred for 20 h at 0 °C to rt. The reaction system was then quenched with saturated aqueous $NaHCO_3$ solution, and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 100:1 to 50:1 to 25:1 PE/EA) afforded compound **S39** (458.5 mg).

S39 (458.5 mg, 1.54 mmol) and **S10** (283 mg, 1.5 mmol) were dissolved in DMF (6 mL). The solution of *t*-BuOK (340 mg, 3 mmol) in DMF (3 mL) was then added under an argon atmosphere at -50 °C. After that, the mixture was stirred at -50 °C for 10 min and at rt for 10 min. The reaction system was then quenched with saturated aqueous NH_4Cl solution (3 mL), 3 M HCl (3 mL), and 12 M HCl (2 mL), and then extracted with ether. The combined organic layer was washed with

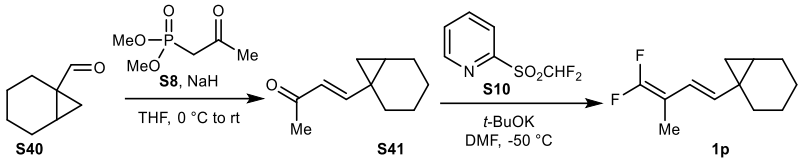
saturated aqueous $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 to 300:1 PE/EA) to afford **1o** (145.5 mg, 15% over two steps) as a colorless oil.

TLC (10:1 PE/EA, R_f): 0.7.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.34 – 7.29 (m, 4H), 7.28 – 7.24 (m, 1H), 5.57 (s, 1H), 4.51 (s, 2H), 3.37 (s, 2H), 2.50 – 2.42 (m, 2H), 2.22 – 2.14 (m, 2H), 1.60 – 1.52 (m, 4H), 1.50 – 1.44 (m, 4H), 0.73 – 0.68 (m, 2H), 0.63 – 0.58 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 151.8 (dd, J = 286.8, 286.8 Hz), 138.9 (dd, J = 4.0, 3.0 Hz), 138.8, 131.1 (dd, J = 3.0, 3.0 Hz), 128.4, 127.6, 127.5, 93.4 (dd, J = 19.2, 16.2 Hz), 77.2, 73.0, 29.5 (dd, J = 2.0, 2.0 Hz), 28.6 (d, J = 2.0 Hz), 27.6, 26.7, 25.9 (dd, J = 2.0, 2.0 Hz), 25.6, 19.9, 12.1.

HRMS (ESI) m/z: calcd. for $C_{21}H_{30}F_2NO$ ($[M+NH_4]^+$): 350.2290, found: 350.2290.



To a flask with NaH (182 mg, 60% dispersion in mineral oil, 4.5 mmol) in THF (18 mL) was added **S8** (754 mg, 4.5 mmol) under an argon atmosphere at 0 °C, stirred for 10 min at 0 °C. Then the solution of **S40** (390 mg, 3.1 mmol) in THF (2 mL) was added. The obtained mixture was stirred for 18 h at 0 °C to rt and 9.5 h at 50 °C. The reaction system was then quenched with saturated aqueous NH_4Cl solution and extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 100:1 to 50:1 to 25:1 PE/EA) to afford **S41** (232.4 mg).

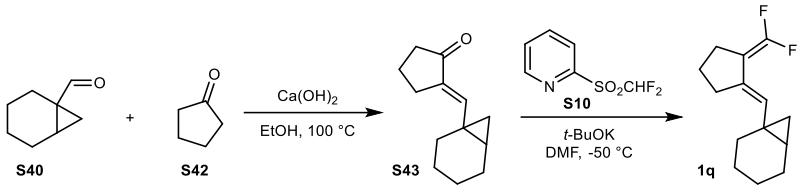
S41 (232.4 mg, 1.4 mmol) and **S10** (340 mg, 1.8 mmol) were dissolved in DMF (4 mL). The solution of *t*-BuOK (320 mg, 2.85 mmol) in DMF (4 mL) was then added by syringe pump in 1 h under an argon atmosphere at -50 °C. The reaction system was then quenched with saturated aqueous NH_4Cl solution (3 mL) and 3 M HCl (3 mL), and then extracted with ether. The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 PE/EA) to afford **1p** (201.7 mg, 32% over two steps) as a colorless oil.

TLC (10:1 PE/EA, R_f): 0.9.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.03 (ddd, J = 15.9, 2.0, 2.0 Hz, 1H), 5.24 (d, J = 15.9 Hz, 1H), 2.05 – 1.93 (m, 1H), 1.93 – 1.85 (m, 1H), 1.82 (ddd, J = 13.3, 4.9, 4.9 Hz, 1H), 1.64 (dd, J = 3.1, 3.1 Hz, 3H), 1.57 (dddd, J = 14.0, 9.4, 5.9, 1.8 Hz, 1H), 1.49 – 1.39 (m, 1H), 1.38 – 1.26 (m, 1H), 1.24 – 1.10 (m, 2H), 0.99 (dddd, J = 9.5, 7.7, 5.9, 1.8 Hz, 1H), 0.70 (dd, J = 9.3, 4.5 Hz, 1H), 0.57 (dd, J = 6.0, 4.5 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 153.6 (dd, J = 291.9, 287.8 Hz), 139.6 (dd, J = 11.1, 3.0 Hz), 117.1 (d, J = 2.0 Hz), 87.1 (dd, J = 21.2, 15.2 Hz), 27.0, 23.9, 21.8, 21.8, 21.1, 21.0, 19.6, 9.2 (dd, J = 1.0, 1.0 Hz).

HRMS (EI) m/z: calcd. for $C_{12}H_{16}F_2$ ($[M\cdot]^+$): 198.1215, found: 198.1212.



To a flask with **S40** (652.3 mg, 5.25 mmol) in EtOH (16 mL) was added **S42** (1.53 g, 18.2 mmol) and $Ca(OH)_2$ (151 mg, 2 mmol). The obtained mixture was then refluxed for 24 h at 100 °C. After that, the mixture was concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 100:1 PE/EA) to afford **S43** (258.5 mg).

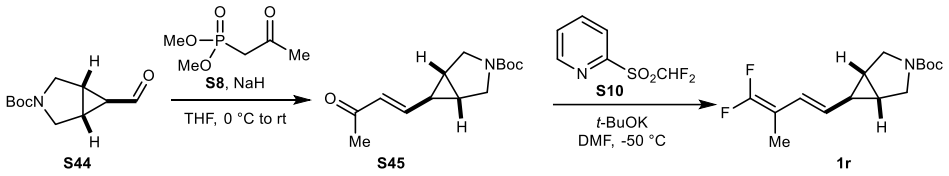
S43 (258.5 mg, 1.36 mmol) and **S10** (394 mg, 2.04 mmol) were dissolved in DMF (4 mL). The solution of *t*-BuOK (306 mg, 2.7 mmol) in DMF (4 mL) was then added by syringe pump in 1 h under an argon atmosphere at -50 °C. The reaction system was then quenched with saturated aqueous NH_4Cl solution (3 mL) and 3 M HCl (3 mL), and then extracted with ether. The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 PE/EA) to afford **1q** (210.1 mg, 18% over two steps) as a colorless oil.

TLC (10:1 PE/EA, R_f): 0.9.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.85 (dd, J = 2.5, 2.5 Hz, 1H), 2.47 (ddd, J = 7.3, 7.3, 2.5 Hz, 2H), 2.40 – 2.30 (m, 2H), 2.02 – 1.91 (m, 1H), 1.83 (ddd, J = 13.7, 6.6, 4.9 Hz, 1H), 1.77 – 1.65 (m, 3H), 1.60 (dddd, J = 13.9, 6.9, 6.9, 1.7 Hz, 1H), 1.41 – 1.29 (m, 1H), 1.29 – 1.20 (m, 2H), 1.20 – 1.09 (m, 1H), 0.93 (dddd, J = 9.1, 7.3, 5.6, 1.7 Hz, 1H), 0.63 (dd, J = 9.3, 4.2 Hz, 1H), 0.43 (dd, J = 5.7, 4.2 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 152.1 (dd, J = 294.9, 286.8 Hz), 136.6 (dd, J = 8.1, 1.0 Hz), 131.9 (dd, J = 15.2, 6.1 Hz), 93.7 (dd, J = 24.2, 13.1 Hz), 31.7 (d, J = 2.0 Hz), 29.6, 27.3 (dd, J = 1.0, 1.0 Hz), 24.8, 24.1, 21.8, 21.4, 20.3, 19.8, 19.0.

HRMS (EI) m/z: calcd. for $C_{14}H_{18}F_2$ ($[M\cdot]^+$): 224.1371, found: 224.1367.



To a flask with NaH (122 mg, 60% dispersion in mineral oil, 3 mmol) in THF (6 mL) was added **S8** (498 mg, 3 mmol) under argon atmosphere at 0 °C, stirred for 10 min at 0 °C. Then the solution of **S44** (422 mg, 2 mmol) in THF (4 mL) was added. The obtained mixture was stirred for 3.5 h at 0 °C to rt. The reaction system was then quenched with saturated aqueous NH_4Cl solution and extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 10:1 to 5:1 to 2:1 PE/EA) to afford **S45** (419.9 mg).

S45 (419.9 mg, 1.67 mmol) and **S10** (386 mg, 2 mmol) were dissolved in DMF (4 mL). The solution of *t*-BuOK (372 mg, 3.3 mmol) in DMF (6 mL) was then added by syringe pump in 1 h under an

argon atmosphere at -50 °C. The reaction system was then quenched with saturated aqueous NH_4Cl solution (3 mL) and 3 M HCl (3 mL), and then extracted with ether. The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 50:0 to 25:1 PE/EA) to afford **1r** (357.6 mg, 63% over two steps) as a white solid.

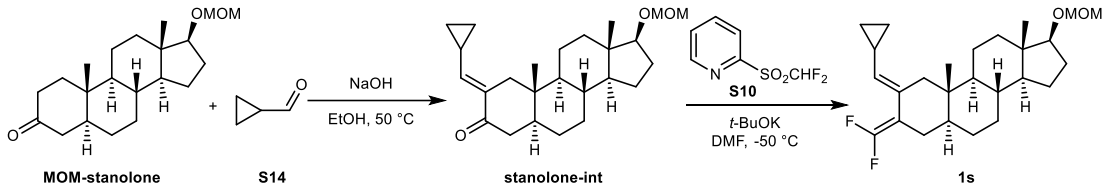
TLC (5:1 PE/EA, R_f): 0.4.

Melting Point: 72 – 74 °C.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.16 (ddd, J = 15.7, 1.9, 1.9 Hz, 1H), 5.15 (dd, J = 15.7, 8.8 Hz, 1H), 3.65 (d, J = 11.0 Hz, 1H), 3.57 (d, J = 10.9 Hz, 1H), 3.44 – 3.33 (m, 2H), 1.63 (dd, J = 3.1, 3.1 Hz, 3H), 1.58 – 1.53 (m, 2H), 1.44 (s, 9H), 1.31 (ddd, J = 9.1, 3.5, 3.5 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 155.0, 153.7 (dd, J = 292.9, 288.9 Hz), 150.8, 129.4 (dd, J = 11.1, 3.0 Hz), 120.8 (d, J = 2.0 Hz), 86.9 (dd, J = 21.2, 14.1 Hz), 79.5, 48.4, 48.1, 28.6, 26.3, 25.4, 24.7, 9.0 (dd, J = 1.0, 1.0 Hz).

HRMS (EI) m/z: calcd. for $C_{15}H_{21}O_2NF_2$ ($[M\cdot]^+$): 285.1535, found: 285.1536.



To a flask with **MOM-stanolone** (810.9 mg, 2.42 mmol) in EtOH (20 mL) was added **S14** (384 mg, 5.5 mmol) and NaOH (96.8 mg, 2.4 mmol). The obtained mixture was stirred for 2 h at 50 °C. After that, the mixture was concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 50:1 PE/EA) to afford **stanolone-int** (784.8 mg).

Stanolone-int (521.4 mg, 1.35 mmol) and **S10** (315 mg, 1.6 mmol) were dissolved in DMF (4 mL). The solution of *t*-BuOK (298.8 mg, 2.7 mmol) in DMF (4 mL) was then added by syringe pump in 1 h under an argon atmosphere at -50 °C. The reaction system was then quenched with saturated aqueous NH_4Cl solution (3 mL) and 3 M HCl (3 mL), and then extracted with ether. The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 100:0 PE/EA) to afford **1s** (455.7 mg, 67% over two steps) as a white solid.

TLC (5:1 PE/EA, R_f): 0.8.

Melting Point: 148 – 150 °C.

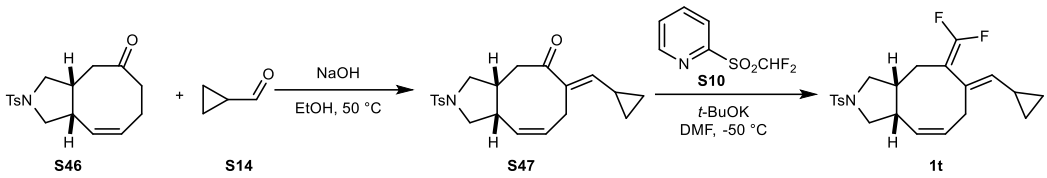
^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.86 (ddd, J = 9.5, 2.4, 2.4 Hz, 1H), 4.66 – 4.59 (m, 2H), 3.53 (dd, J = 8.4 Hz, 1H), 3.35 (s, 3H), 2.82 (dd, J = 13.4, 2.0 Hz, 1H), 2.10 (dddd, J = 14.4, 4.3, 2.2, 2.2 Hz, 1H), 2.06 – 1.96 (m, 1H), 1.91 – 1.83 (m, 1H), 1.82 – 1.73 (m, 1H), 1.73 – 1.65 (m, 1H), 1.65 – 1.57 (m, 2H), 1.52 (ddd, J = 13.8, 8.8, 3.2 Hz, 3H), 1.44 – 1.30 (m, 4H), 1.30 – 1.20 (m, 2H), 1.19 – 1.09 (m, 1H), 1.02 – 0.85 (m, 2H), 0.82 – 0.78 (m, 1H), 0.78 (s, 3H), 0.77 (s, 3H), 0.73 (dd, J = 8.2, 1.9 Hz, 2H), 0.41 – 0.28 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 152.0 (dd, J = 286.8, 284.8 Hz), 133.8 (dd, J = 5.0, 2.0 Hz), 126.9 (dd, J = 3.2, 3.2 Hz), 96.1, 92.0 (dd, J = 21.2, 13.1 Hz), 86.8, 55.2, 53.9, 51.1, 45.6, 42.8, 41.0

(d, J = 2.8 Hz), 37.6, 37.4, 35.5, 31.4, 28.5, 28.2, 28.1, 23.5, 20.8, 11.9, 11.6, 10.0, 7.2, 7.1.

^{19}F NMR (471 MHz, $CDCl_3$, δ): -95.08 (d, J = 51.2 Hz), -96.97 (d, J = 51.2 Hz). (page S181)

HRMS (EI) m/z: calcd. for $C_{26}H_{38}O_2F_2$ ($[M\cdot]^+$): 420.2834, found: 420.2841.



To a flask with **S46**[12] (401.4 mg, 1.26 mmol) in EtOH (13 mL) was added **S14** (184 mg, 2.6 mmol) and NaOH (104.3 mg, 2.6 mmol). The obtained mixture was stirred for 3.75 h at 50 °C. After that, the mixture was concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 25:1 to 20:1 to 10:1 to 5:1 PE/EA) to afford **S47** (216.6 mg).

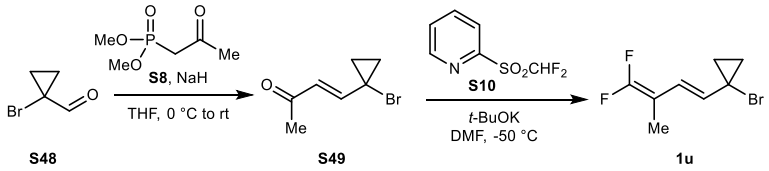
S47 (216.6 mg, 0.58 mmol) and **S10** (138 mg, 0.7 mmol) were dissolved in DMF (3 mL). The solution of *t*-BuOK (130 mg, 1.16 mmol) in DMF (3 mL) was then added by syringe pump in 1 h under an argon atmosphere at -50 °C. The reaction system was then quenched with saturated aqueous NH_4Cl solution (3 mL) and 3 M HCl (3 mL), and then extracted with ether. The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 50:0 to 25:1 PE/EA) to afford **1t** (215.2 mg, 42% over two steps) as a light yellow oil.

TLC (5:1 PE/EA, R_f): 0.5.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.72 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 5.67 (dddd, J = 10.9, 6.2, 6.2, 1.8 Hz, 1H), 4.99 (ddd, J = 11.1, 7.2, 1.6 Hz, 1H), 4.77 (dd, J = 9.6, 1.8 Hz, 1H), 3.44 – 3.34 (m, 2H), 3.34 – 3.22 (m, 2H), 3.04 (dd, J = 16.0, 6.4 Hz, 1H), 2.91 (dd, J = 16.0, 6.0 Hz, 1H), 2.80 – 2.72 (m, 1H), 2.44 (s, 3H), 2.36 (ddd, J = 15.0, 3.0, 3.0 Hz, 1H), 2.25 – 2.11 (m, 1H), 1.80 (dddd, J = 14.3, 11.8, 5.4, 2.7, 2.7 Hz, 1H), 1.49 (dddd, J = 12.8, 9.4, 8.0, 4.8 Hz, 1H), 0.81 – 0.70 (m, 2H), 0.40 – 0.29 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 153.3 (dd, J = 287.8, 287.8 Hz), 143.5, 136.1 (dd, J = 4.0, 3.0 Hz), 134.1, 130.2, 129.8, 128.8, 128.1 (dd, J = 4.0, 3.0 Hz), 127.5, 94.2 (dd, J = 20.2, 15.2 Hz), 54.3, 51.3, 44.4 (dd, J = 3.0, 2.0 Hz), 38.1, 31.5 (d, J = 3.0 Hz), 26.4, 21.6, 10.3, 7.0, 6.9.

HRMS (ESI) m/z: calcd. for $C_{22}H_{26}F_2NO_2S$ ($[M+H]^+$): 406.1647, found: 406.1646.



To a flask with NaH (240 mg, 60% dispersion in mineral oil, 6 mmol) in THF (20 mL) was added **S8** (996.6 mg, 6 mmol) under argon atmosphere at 0 °C, stirred for 10 min at 0 °C. Then the solution of **S48** (5 mmol) in THF (10 mL) was added. The obtained mixture was stirred for 47 h at 0 °C to rt. The reaction system was then quenched with saturated aqueous NH_4Cl solution and extracted

with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 20:1 to 15:1 PE/EA) to afford **S49** (435 mg).

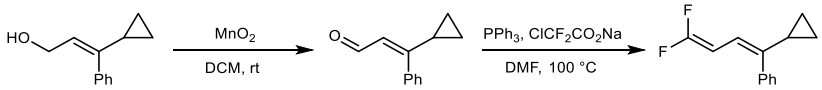
S49 (435 mg, 2.3 mmol) and **S10** (367 mg, 1.9 mmol) were dissolved in DMF (7 mL). The solution of *t*-BuOK (387 mg, 3.45 mmol) in DMF (4 mL) was then added by syringe pump in 1 h under an argon atmosphere at -50 °C. After that, the mixture was stirred at -50 °C for 50 min. The reaction system was then quenched with saturated aqueous NH_4Cl solution (5 mL) and 3 M HCl (5 mL), and then extracted with ether. The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 PE/EA) to afford **1u** (286.1 mg, 31% over two steps) as a colorless oil.

TLC (10:1 PE/EA, R_f): 0.7.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.38 (ddd, J = 15.2, 1.8, 1.8 Hz, 1H), 5.57 (d, J = 15.2 Hz, 1H), 1.67 (dd, J = 3.1, 3.1 Hz, 3H), 1.40 – 1.33 (m, 2H), 1.13 – 1.06 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 154.4 (dd, J = 294.9, 290.9 Hz), 131.6 (dd, J = 11.1, 3.0 Hz), 123.7 (d, J = 3.0 Hz), 86.6 (dd, J = 22.2, 14.1 Hz), 31.9, 18.0, 9.3 (dd, J = 2.0, 2.0 Hz).

HRMS (EI) m/z: calcd. for $C_8H_9BrF_2$ ($[M\cdot]^+$): 221.9850, found: 221.9849.



S50 **S51** **1v**

To a flask with **S50**[15c] (871.2 mg, 5 mmol) in DCM (30 mL) was added MnO_2 (3.48 g, 40 mmol) at rt. The obtained mixture was stirred for 21.5 h at rt, filtered through celite, and concentrated by rotary evaporation. The crude **S51** was used for the next step without purification.

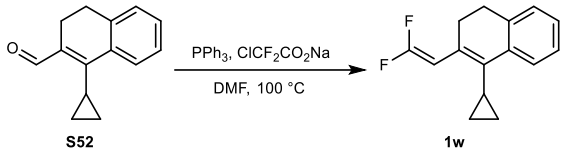
Crude **S51** (5 mmol) and PPh_3 (2.36 g, 9 mmol) were dissolved in DMF (7 mL). The solution of $ClCF_2CO_2Na$ (1.68 g, 11 mmol) in DMF (20 mL) was then added by syringe pump in 1 h under an argon atmosphere at 100 °C. Then the mixture was stirred at 100 °C for 20 min. Cooled to rt, and then MeI (0.5 mL) was added and stirred at rt for 30 min to remove PPh_3. The reaction system was then quenched with water and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 PE/EA) to afford **1v** (185.5 mg, 18% over two steps) as a colorless oil.

TLC (10:1 PE/EA, R_f): 0.9.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.39 – 7.31 (m, 2H), 7.31 – 7.25 (m, 1H), 7.20 – 7.13 (m, 2H), 5.95 (d, J = 11.2 Hz, 1H), 4.81 (ddd, J = 24.8, 11.3, 2.1 Hz, 1H), 1.65 (ddd, J = 13.6, 8.5, 5.3 Hz, 1H), 0.76 – 0.67 (m, 2H), 0.54 – 0.47 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 156.3 (dd, J = 296.9, 289.9 Hz), 144.3 (dd, J = 12.1, 4.0 Hz), 139.3, 129.0, 128.3, 127.4, 113.3 (dd, J = 4.0, 2.0 Hz), 80.1 (dd, J = 28.3, 15.2 Hz), 18.8, 6.1.

HRMS (EI) m/z: calcd. for $C_{13}H_{12}F_2$ ($[M\cdot]^+$): 206.0902, found: 206.0899.



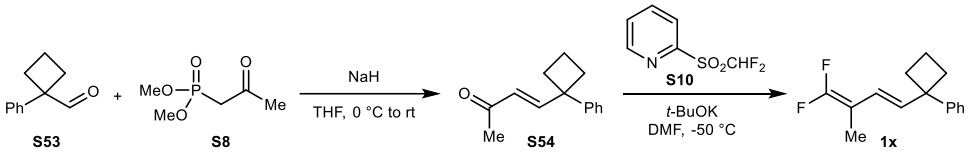
S52[15g] (350 mg, 1.76 mmol) and PPh_3 (925 mg, 3.5 mmol) were dissolved in DMF (5 mL). The solution of $ClCF_2CO_2Na$ (808 mg, 5.3 mmol) in DMF (10 mL) was then added by syringe pump in 2.5 h under an argon atmosphere at 100 °C. Cooled to rt, and then MeI (0.3 mL) was added and stirred at rt for 15 min to remove PPh_3. The reaction system was then quenched with water and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 PE/EA) to afford **1w** (297.7 mg, 73%) as a light yellow oil.

TLC (10:1 PE/EA, R_f): 0.8.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.65 – 7.57 (m, 1H), 7.24 – 7.16 (m, 1H), 7.15 – 7.04 (m, 2H), 5.91 – 5.79 (m, 1H), 2.74 – 2.61 (m, 2H), 2.53 – 2.41 (m, 2H), 1.61 – 1.47 (m, 1H), 1.06 – 0.94 (m, 2H), 0.46 – 0.34 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 155.9 (dd, J = 303.0, 288.9 Hz), 136.6, 135.6, 135.3 (dd, J = 10.1, 5.0 Hz), 129.2 (dd, J = 7.1, 5.0 Hz), 126.9, 126.5, 126.3, 124.7, 81.9 (dd, J = 29.3, 10.1 Hz), 28.2, 26.2 (d, J = 7.1 Hz), 10.3, 8.7.

HRMS (EI) m/z: calcd. for $C_{15}H_{14}F_2$ ($[M\cdot]^+$): 232.1058, found: 232.1055.



To a flask with NaH (303 mg, 60% dispersion in mineral oil, 7.5 mmol) in THF (20 mL) was added **S8** (1.24 g, 7.5 mmol) under an argon atmosphere at 0 °C, stirred for 10 min at 0 °C. Then the solution of **S53** (5 mmol) in THF (5 mL) was added. The obtained mixture was stirred for 12.5 h at 0 °C to rt. The reaction system was then quenched with saturated aqueous NH_4Cl solution and extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 100:1 to 25:1 PE/EA) to afford **S54** (759.3 mg).

S54 (759.3 mg, 3.79 mmol) and **S10** (875 mg, 4.5 mmol) were dissolved in DMF (5 mL). The solution of *t*-BuOK (830 mg, 7.4 mmol) in DMF (8 mL) was then added by syringe pump in 1 h under an argon atmosphere at -50 °C. The reaction system was then quenched with saturated aqueous NH_4Cl solution (5 mL) and 3 M HCl (5 mL), and then extracted with ether. The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 PE/EA) to afford **1x** (763 mg, 65% over two steps) as a colorless oil.

TLC (10:1 PE/EA, R_f): 0.9.

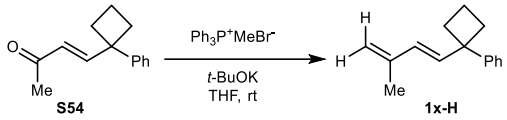
^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.35 – 7.27 (m, 2H), 7.21 – 7.14 (m, 3H), 6.04 (ddd, J = 15.8, 1.9, 1.9 Hz, 1H), 5.86 (d, J = 15.8 Hz, 1H), 2.56 – 2.44 (m, 2H), 2.40 – 2.31 (m, 2H), 2.12 – 1.99 (m,

1H), 1.91 – 1.80 (m, 1H), 1.66 (dd, J = 3.1, 3.1 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 154.0 (dd, J = 291.5, 288.3 Hz), 148.8, 137.7 (dd, J = 11.0, 3.1 Hz), 128.4, 126.0, 125.8, 118.9 (d, J = 2.4 Hz), 87.1 (dd, J = 20.8, 14.1 Hz), 49.3, 33.5, 16.4, 9.2 (dd, J = 1.8, 1.8 Hz).

^{19}F NMR (471 MHz, $CDCl_3$, δ): -92.42 (d, J = 38.7 Hz), -93.39 (d, J = 38.2 Hz). (page S181)

HRMS (EI) m/z: calcd. for $C_{15}H_{16}F_2$ ([M·]$^+$): 234.1215, found: 234.1212.



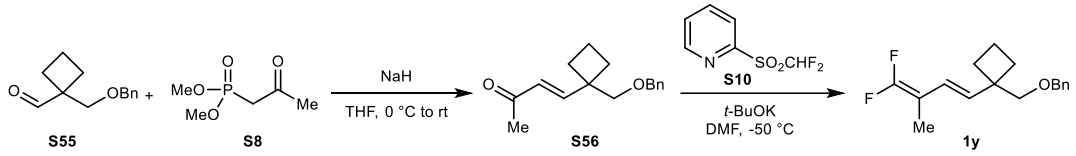
To a flask with $Ph_3P^+MeBr^-$ (714 mg, 2 mmol) and *t*-BuOK (226 mg, 2 mmol) was added THF (5 mL) under an argon atmosphere at rt. Stirred at rt for 5 min, **S54** (196.5 mg, 2 mmol) was added. The obtained mixture was stirred for 1 h at rt. The reaction system was then quenched with water, and extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 100:1 PE/EA) to afford **1x-H** (177.4 mg, 91%) as a colorless oil.

TLC (10:1 PE/EA, R_f): 0.9.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.31 (dd, J = 8.2, 7.0 Hz, 2H), 7.23 – 7.14 (m, 3H), 6.06 – 5.92 (m, 2H), 4.92 – 4.82 (m, 2H), 2.55 – 2.45 (m, 2H), 2.42 – 2.32 (m, 2H), 2.13 – 2.01 (m, 1H), 1.90 – 1.80 (m, 1H), 1.83 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 149.0, 142.2, 138.4, 129.2, 128.3, 126.1, 125.7, 115.3, 49.0, 33.6, 19.0, 16.4.

HRMS (EI) m/z: calcd. for $C_{15}H_{18}$ ([M·]$^+$): 198.1403, found: 198.1395.



To a flask with NaH (188 mg, 60% dispersion in mineral oil, 4.7 mmol) in THF (20 mL) was added **S8** (753 mg, 4.5 mmol) under an argon atmosphere at 0 °C, stirred for 10 min at 0 °C. Then the solution of **S55** (3 mmol) in THF (2 mL) was added. The obtained mixture was stirred for 14.5 h at 0 °C to rt. The reaction system was then quenched with saturated aqueous NH_4Cl solution and extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 50:1 to 25:1 PE/EA) to afford **S56** (432.3 mg).

S56 (432.3 mg, 1.77 mmol) and **S10** (411.4 mg, 2.1 mmol) were dissolved in DMF (4 mL). The solution of *t*-BuOK (359 mg, 3.2 mmol) in DMF (4 mL) was then added by syringe pump in 1 h under an argon atmosphere at -50 °C. The reaction system was then quenched with saturated aqueous NH_4Cl solution (3 mL) and 3 M HCl (3 mL), and then extracted with ether. The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column

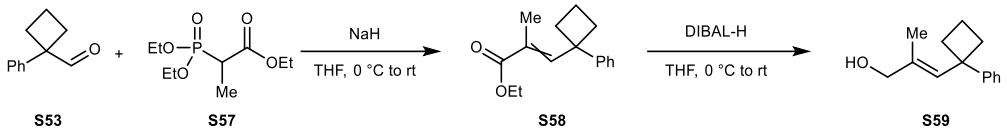
chromatography (silica gel, 1:0 to 50:1 PE/EA) to afford **1y** (361.8 mg, 43% over two steps) as a colorless oil.

TLC (10:1 PE/EA, R_f): 0.8.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.38 – 7.32 (m, 4H), 7.31 – 7.25 (m, 1H), 6.24 – 6.13 (m, 1H), 5.74 (d, J = 16.0 Hz, 1H), 4.56 (s, 2H), 3.44 (s, 2H), 2.05 – 1.96 (m, 4H), 1.95 – 1.79 (m, 2H), 1.72 – 1.67 (m, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 154.0 (dd, J = 291.6, 288.0 Hz), 138.8, 135.5 (dd, J = 11.0, 3.3 Hz), 128.5, 127.7, 127.6, 120.0 (d, J = 2.3 Hz), 87.2 (dd, J = 20.7, 14.2 Hz), 76.6, 73.4, 44.9, 29.4, 15.7, 9.2 (dd, J = 1.9, 1.9 Hz).

HRMS (EI) m/z: calcd. for $C_{17}H_{20}OF_2$ ([M·]$^+$): 278.1477, found: 278.1472.



S53 **S57** **S58** **S59**

To a flask with **S57** (2.85 g, 12 mmol) in THF (30 mL) was added NaH (600 mg, 60% dispersion in mineral oil, 15 mmol) slowly at 0 °C, stirred for 5 min at 0 °C. Then **S53** (10 mmol) was added. The obtained mixture was stirred for 30 min at 0 °C to rt. The reaction system was then quenched with saturated aqueous NH_4Cl solution, and then extracted with ether. The combined organic layer was washed with saturated aqueous $NaHSO_3$ solution and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude **S58** was used for the next step without purification.

To a flask with **S58** (10 mmol) in THF (30 mL) was added DIBAL-H (30 mL, 1 M in hexanes, 30 mmol) under an argon atmosphere at 0 °C. After that, the mixture was stirred for 4.5 h at 0 °C to rt. Cooled to 0 °C, diluted with Et_2O. The reaction system was then quenched with H_2O (1.2 mL), 15% NaOH (1.2 mL), and H_2O (3.6 mL), stirred for 15 min. $MgSO_4$ (7 g) was added and stirred for 5 min. Filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 50:1 PE/EA) to afford **S59** (803.5 mg, 40% over two steps) as a white solid.

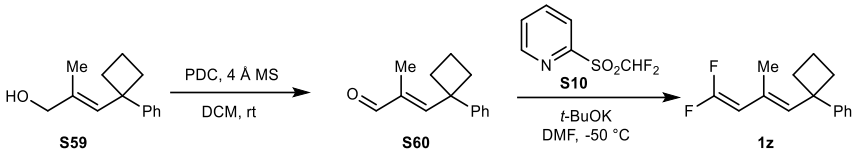
TLC (5:1 PE/EA, R_f): 0.3.

Melting Point: 56 – 58 °C.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.36 – 7.28 (m, 4H), 7.21 – 7.12 (m, 1H), 5.90 (s, 1H), 3.82 (s, 2H), 2.59 – 2.49 (m, 2H), 2.40 – 2.30 (m, 2H), 2.06 – 1.95 (m, 1H), 1.95 – 1.85 (m, 1H), 1.78 (d, J = 1.5 Hz, 3H), 1.01 (s, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 149.8, 138.9, 135.0, 128.6, 125.9, 125.6, 62.0, 47.2, 37.1, 21.5, 16.8.

HRMS (EI) m/z: calcd. for $C_{14}H_{18}O$ ([M·]$^+$): 202.1352, found: 202.1347.



To a flask with **S59** (788.9 mg, 4 mmol) in DCM (20 mL) was added PDC (1.84 g, 4.9 mmol) and 4 Å molecular sieve (1.04 g) at rt. The obtained mixture was stirred for 2 h at rt, filtered through silica gel, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 100:1 PE/EA) to afford **S60** (511.6 mg).

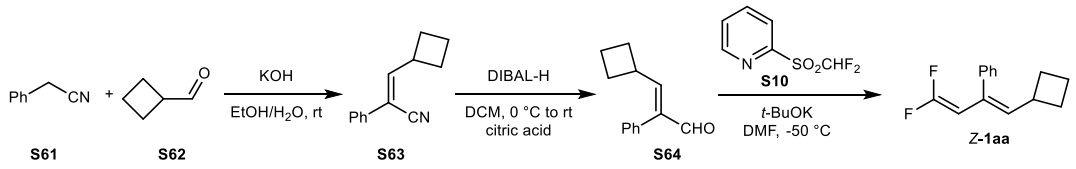
S60 (511.6 mg, 2.55 mmol) and **S10** (594 mg, 3.1 mmol) were dissolved in DMF (4 mL). The solution of *t*-BuOK (518 mg, 4.6 mmol) in DMF (4 mL) was then added by syringe pump in 1 h under an argon atmosphere at -50 °C. The reaction system was then quenched with saturated aqueous NH_4Cl solution (4 mL) and 3 M HCl (4 mL), and then extracted with ether. The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 PE/EA) to afford **1z** (95.9 mg, 10% over two steps) as a colorless oil.

TLC (10:1 PE/EA, R_f): 0.9.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.36 – 7.26 (m, 4H), 7.20 – 7.12 (m, 1H), 5.77 (s, 1H), 4.80 (dd, J = 27.6, 5.2 Hz, 1H), 2.57 – 2.46 (m, 2H), 2.43 – 2.33 (m, 2H), 2.04 – 1.87 (m, 2H), 1.90 (dd, J = 4.2, 1.5 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 155.5 (dd, J = 300.9, 287.1 Hz), 148.6, 140.0 (dd, J = 9.7, 4.4 Hz), 128.5, 126.0, 125.7, 125.1 (dd, J = 6.6, 5.3 Hz), 80.4 (dd, J = 28.4, 12.3 Hz), 47.2, 36.8, 22.4 (d, J = 6.3 Hz), 16.9.

HRMS (EI) m/z: calcd. for $C_{15}H_{16}F_2$ ([M·]$^+$): 234.1215, found: 234.1209.



To a flask with **S61** (1.21 g, 10.3 mmol) in EtOH (20 mL) and H_2O (10 mL) was added **S62** (0.77 mL, d = 1.085 g/mL, 10 mmol) and KOH (116 mg, 2.1 mmol) at rt. The obtained mixture was stirred for 3 h at rt, poured into H_2O, and then extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude **S63** was used for the next step without purification.

To a flask with **S63** (10 mmol) in DCM (25 mL) was added DIBAL-H (26 mL, 1 M in hexanes, 26 mmol) under an argon atmosphere at 0 °C. After that, the mixture was stirred for 50 min at 0 °C to rt. The reaction system was then quenched with saturated aqueous citric acid solution slowly, and kept stirring until the upper organic phase was clear, and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered through silica gel (to avoid polymerization), and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 100:1 PE/EA) to afford **S64** (736.4 mg).

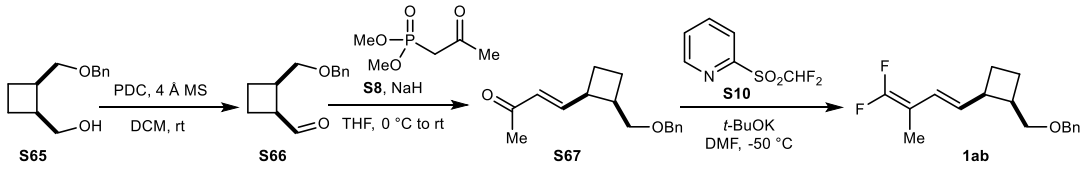
S64 (376 mg, 2 mmol) and **S10** (457 mg, 2.4 mmol) were dissolved in DMF (4 mL). The solution of *t*-BuOK (391 mg, 3.5 mmol) in DMF (4 mL) was then added by syringe pump in 1 h under an argon atmosphere at -50 °C. The reaction system was then quenched with saturated aqueous NH_4Cl solution (4 mL) and 3 M HCl (4 mL), and then extracted with ether. The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 PE/EA) to afford *Z*-**1aa** (122.1 mg, 10% over three steps) as a light yellow oil.

TLC (10:1 PE/EA, R_f): 0.9.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.37 – 7.25 (m, 3H), 7.16 – 7.07 (m, 2H), 5.81 (d, J = 9.5 Hz, 1H), 4.97 (dd, J = 24.3, 4.4 Hz, 1H), 3.00 – 2.85 (m, 1H), 2.08 – 1.96 (m, 2H), 1.94 – 1.82 (m, 2H), 1.82 – 1.71 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 155.8 (dd, J = 299.3, 286.9 Hz), 138.8, 137.8 (dd, J = 6.8, 6.0 Hz), 129.6 (dd, J = 5.4, 5.4 Hz), 128.8, 128.1, 127.2, 84.6 (dd, J = 28.1, 11.5 Hz), 35.4, 30.0, 18.8.

HRMS (EI) m/z: calcd. for $C_{14}H_{14}F_2$ ($[M\cdot]^+$): 220.1058, found: 220.1052.



To a flask with **S65** (1.02 g, 4.9 mmol) in DCM (20 mL) was added PDC (3.2 g, 8.5 mmol) and 4 Å molecular sieve (1.16 g) at rt. The obtained mixture was stirred for 12 h at rt, filtered through silica gel, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 100:1 to 50:1 to 25:1 PE/EA) to afford **S66** (496.9 mg).

To a flask with NaH (145 mg, 60% dispersion in mineral oil, 3.6 mmol) in THF (10 mL) was added **S8** (604 mg, 3.6 mmol) under an argon atmosphere at 0 °C, stirred for 10 min at 0 °C. Then the solution of **S66** (496.9 mg, 2.43 mmol) in THF (2 mL) was added. The obtained mixture was stirred for 22.5 h at 0 °C to rt. The reaction system was then quenched with saturated aqueous NH_4Cl solution, and then extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 50:1 to 25:1 PE/EA) to afford **S67** (450.1 mg).

S67 (450.1 mg, 1.84 mmol) and **S10** (532 mg, 2.75 mmol) were dissolved in DMF (4 mL). The solution of *t*-BuOK (383 mg, 3.4 mmol) in DMF (4 mL) was then added by syringe pump in 30 min under an argon atmosphere at -50 °C. The reaction system was then quenched with saturated aqueous NH_4Cl solution (4 mL) and 3 M HCl (4 mL), and then extracted with ether. The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 to 100:1 PE/EA) to afford **1ab** (347.8 mg, 25% over three steps) as a light yellow oil.

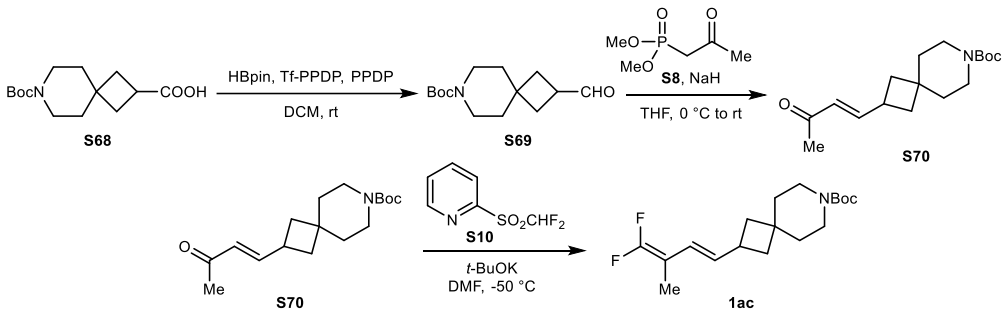
TLC (10:1 PE/EA, R_f): 0.8.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.36 – 7.29 (m, 4H), 7.29 – 7.24 (m, 1H), 6.09 (dd, J = 15.7, 1.7 Hz, 1H), 5.76 (dd, J = 15.8, 7.6 Hz, 1H), 4.46 (s, 2H), 3.53 (dd, J = 9.4, 7.8 Hz, 1H), 3.44 (dd, J =

9.4, 6.5 Hz, 1H), 3.26 – 3.14 (m, 1H), 2.82 – 2.69 (m, 1H), 2.18 – 2.01 (m, 2H), 2.01 – 1.90 (m, 1H), 1.72 – 1.66 (m, 1H), 1.64 (dd, *J* = 3.1, 3.1 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 154.0 (dd, *J* = 291.4, 288.0 Hz), 138.7, 130.6 (dd, *J* = 11.1, 3.2 Hz), 128.4, 127.7, 127.6, 121.9 (d, *J* = 2.2 Hz), 87.2 (dd, *J* = 20.6, 14.3 Hz), 73.3, 71.5, 39.8, 39.1, 24.8, 21.7, 9.2 (dd, *J* = 1.7, 1.7 Hz).

HRMS (ESI) m/z: calcd. for $C_{17}H_{20}F_2NaO$ ([M+Na]$^+$): 301.1374, found: 301.1371.



To a flask with **S68** (1 g, 3.7 mmol) and PPDP (941 mg, 5.8 mmol) in DCM (20 mL) was added Tf-PPDP (2.8 g, 6.3 mmol) and HBpin (579 mg, 4.5 mmol) at rt. The obtained mixture was stirred for 10 min at rt. The reaction system was then quenched with water and extracted with ether. *n*-Pentane was added, and dried over anhydrous Na_2SO_4. Filtered through silica gel, and concentrated by rotary evaporation. The crude **S69** was used for the next step without purification.

To a flask with NaH (226 mg, 60% dispersion in mineral oil, 5.6 mmol) in THF (20 mL) was added **S8** (958 mg, 5.8 mmol) under an argon atmosphere at 0 °C, stirred for 10 min at 0 °C. Then the solution of crude **S69** in THF (2 mL) was added. The obtained mixture was stirred for 16 h at 0 °C to rt. The reaction system was then quenched with saturated aqueous NH_4Cl solution and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 20:1 to 10:1 to 5:1 PE/EA) to afford **S70** (458.2 mg).

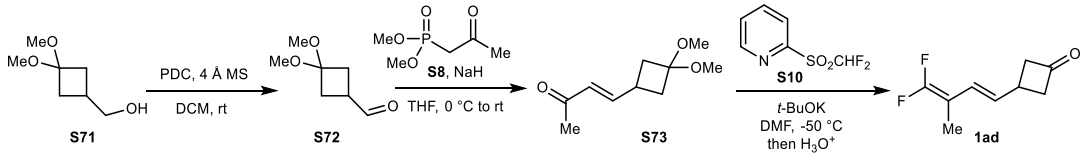
S70 (458.2 mg, 1.56 mmol) and **S10** (394 mg, 2 mmol) were dissolved in DMF (4 mL). The solution of *t*-BuOK (350 mg, 3.1 mmol) in DMF (4 mL) was then added by syringe pump in 1 h under an argon atmosphere at -50 °C. The reaction system was then quenched with saturated aqueous NH_4Cl solution (4 mL) and 3 M HCl (4 mL), and then extracted with ether. The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 50:1 PE/EA) to afford **1ac** (335.9 mg, 28% over three steps) as a light yellow oil.

TLC (5:1 PE/EA, R_f): 0.7.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.05 (dq, *J* = 15.6, 1.7 Hz, 1H), 5.65 (dd, *J* = 15.7, 7.1 Hz, 1H), 3.40 – 3.32 (m, 2H), 3.30 – 3.24 (m, 2H), 3.03 – 2.91 (m, 1H), 2.10 – 2.01 (m, 2H), 1.67 (dd, *J* = 3.1, 3.1 Hz, 3H), 1.65 – 1.57 (m, 4H), 1.49 – 1.43 (m, 2H), 1.45 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 155.1, 154.0 (dd, *J* = 291.5, 288.1 Hz), 134.7 (dd, *J* = 11.1, 3.2 Hz), 120.6 (d, *J* = 2.2 Hz), 87.0 (dd, *J* = 20.8, 14.4 Hz), 79.4, 40.8, 39.4, 38.3, 36.1, 34.2, 31.8, 28.6, 9.2 (dd, *J* = 1.8, 1.8 Hz).

HRMS (ESI) m/z: calcd. for $C_{18}H_{28}F_2NO_2$ ([M+H]$^+$): 328.2083, found: 328.2075.



To a flask with **S71** (1.47 g, 10 mmol) in DCM (30 mL) was added PDC (4.58 g, 12.2 mmol) and 4 Å molecular sieve (2.48 g) at rt. The obtained mixture was stirred for 2 h at rt, filtered through silica gel, and concentrated by rotary evaporation. The crude **S72** was used for the next step without purification.

To a flask with NaH (474 mg, 60% dispersion in mineral oil, 11.8 mmol) in THF (40 mL) was added **S8** (1.97 g, 11.9 mmol) under an argon atmosphere at 0 °C, stirred for 10 min at 0 °C. Then the solution of **S72** (1.12 g, 7.77 mmol) in THF (2 mL) was added. The obtained mixture was stirred for 22.5 h at 0 °C to rt. The reaction system was then quenched with saturated aqueous NH_4Cl solution, and then extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 50:1 to 25:1 to 10:1 PE/EA) to afford **S73** (565.6 mg).

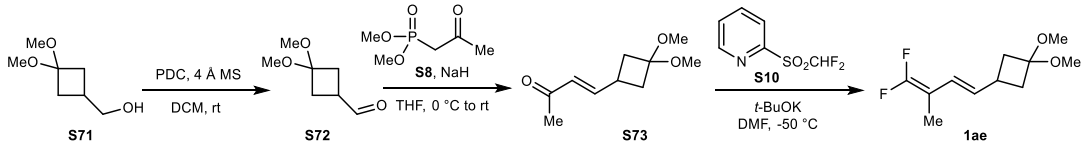
S73 (565.6 mg, 3.07 mmol) and **S10** (891 mg, 4.6 mmol) were dissolved in DMF (4 mL). The solution of *t*-BuOK (626 mg, 5.6 mmol) in DMF (4 mL) was then added by syringe pump in 1 h under an argon atmosphere at -50 °C. The reaction system was then quenched with saturated aqueous NH_4Cl solution (4 mL) and 3 M HCl (4 mL), stirred at rt for 14.5 h, and then extracted with ether. The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 50:1 PE/EA) to afford **1ad** (258.3 mg, 15% over three steps) as a yellow oil.

TLC (10:1 PE/EA, R_f): 0.4.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.26 (dq, J = 15.6, 1.7 Hz, 1H), 5.74 (dd, J = 15.6, 7.3 Hz, 1H), 3.33 – 3.23 (m, 2H), 3.23 – 3.11 (m, 1H), 3.01 – 2.91 (m, 2H), 1.71 (dd, J = 3.1, 3.1 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 206.6, 154.2(dd, J = 292.5, 289.2 Hz), 131.5 (dd, J = 11.3, 3.3 Hz), 122.9 (d, J = 2.5 Hz), 86.8 (dd, J = 21.5, 14.2 Hz), 53.6, 26.8, 9.1 (dd, J = 1.6, 1.6 Hz).

HRMS (ESI) m/z: calcd. for $C_9H_{11}F_2O$ ($[M+H]^+$): 173.0772, found: 173.0771.



To a flask with **S71** (1.46 g, 10 mmol) in DCM (40 mL) was added PDC (4.65 g, 12.4 mmol) and 4 Å molecular sieve (2.29 g) at rt. The obtained mixture was stirred for 12 h at rt, filtered through silica gel, and concentrated by rotary evaporation. The crude **S72** was used for the next step without purification.

To a flask with NaH (599 mg, 60% dispersion in mineral oil, 15 mmol) in THF (40 mL) was added **S8** (2.45 g, 14.7 mmol) under an argon atmosphere at 0 °C, stirred for 10 min at 0 °C. Then the solution of **S72** (10 mmol) in THF (2 mL) was added. The obtained mixture was stirred for 11 h at

0 °C to rt. The reaction system was then quenched with saturated aqueous NH_4Cl solution and extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 10:1 PE/EA) to afford **S73** (419.9 mg).

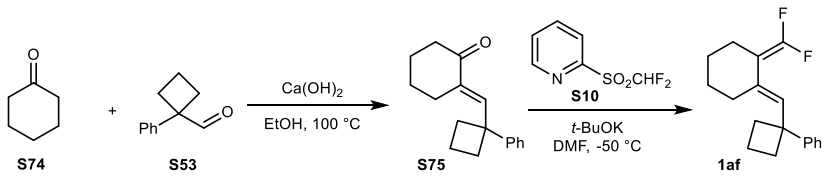
S73 (419.9 mg, 2.28 mmol) and **S10** (656 mg, 3.4 mmol) were dissolved in DMF (4 mL). The solution of *t*-BuOK (466 mg, 4.2 mmol) in DMF (4 mL) was then added by syringe pump in 1 h under an argon atmosphere at -50 °C. The reaction system was then quenched with saturated aqueous NH_4Cl solution (4 mL) and 3 M HCl (4 mL), and then extracted with ether. The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 100:1 PE/EA) to afford **1ae** (252.5 mg, 12% over three steps) as a yellow oil.

TLC (10:1 PE/EA, R_f): 0.5.

^{1}H NMR (400 MHz, C_6D_6, δ): 6.11 (dq, J = 15.6, 1.7 Hz, 1H), 5.47 (dd, J = 15.6, 7.7 Hz, 1H), 3.03 (s, 3H), 3.00 (s, 3H), 2.69 – 2.58 (m, 1H), 2.42 – 2.31 (m, 2H), 1.97 – 1.87 (m, 2H), 1.39 (dd, J = 3.1, 3.1 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, δ): 154.3 (dd, J = 291.4, 288.0 Hz), 134.2 (dd, J = 11.2, 3.3 Hz), 121.4 (d, J = 2.2 Hz), 100.4, 87.5 (dd, J = 20.7, 14.1 Hz), 48.4, 48.1, 38.5, 28.8, 8.9 (dd, J = 1.8, 1.8 Hz).

HRMS (EI) m/z: calcd. for $C_{11}H_{16}O_2F_2$ ([M·]$^+$): 218.1113, found: 218.1108.



To a flask with **S74** (1.48 g, 15.1 mmol) in EtOH (15 mL) was added **S53** (804 mg, 5 mmol) and $Ca(OH)_2$ (83.8 mg, 1.1 mmol). The obtained mixture was then refluxed for 35 h at 100 °C. After that, the mixture was concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 100:1 PE/EA) to afford **S75** (390.1 mg).

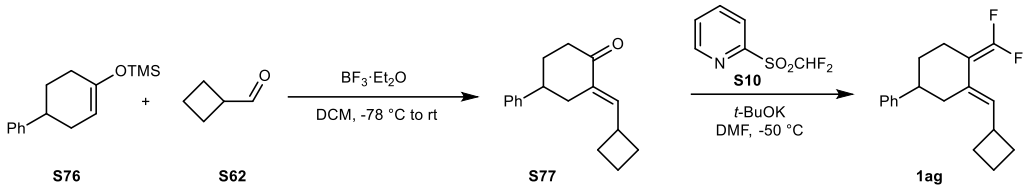
S75 (390.1 mg, 1.62 mmol) and **S10** (473 mg, 2.4 mmol) were dissolved in DMF (4 mL). The solution of *t*-BuOK (333 mg,3 mmol) in DMF (4 mL) was then added by syringe pump in 2.5 h under an argon atmosphere at -50 °C. The reaction system was then quenched with saturated aqueous NH_4Cl solution (4 mL) and 3 M HCl (4 mL), and then extracted with ether. The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 PE/EA) to afford **1af** (75 mg, 5% over two steps) as a colorless oil.

TLC (10:1 PE/EA, R_f): 0.8.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.37 (d, J = 7.3 Hz, 2H), 7.30 (dd, J = 7.7, 7.7 Hz, 2H), 7.15 (t, J = 7.3 Hz, 1H), 5.96 (s, 1H), 2.52 (ddd, J = 11.5, 8.9, 6.4 Hz, 2H), 2.37 (ddd, J = 11.3, 8.8, 6.5 Hz, 2H), 2.13 (tt, J = 6.5, 2.3 Hz, 2H), 2.07 – 1.98 (m, 1H), 1.95 (ddd, J = 11.2, 5.5, 2.3 Hz, 1H), 1.87 (t, J = 6.1 Hz, 2H), 1.58 – 1.47 (m, 2H), 1.43 – 1.33 (m, 2H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 152.1 (dd, J = 286.8, 284.8 Hz), 149.1, 137.9 (dd, J = 4.1, 1.7 Hz), 131.4 (dd, J = 4.0, 3.0 Hz), 128.3, 126.0, 125.4, 92.6 (dd, J = 21.0, 14.3 Hz), 47.1, 37.1, 29.5 (d, J = 2.7 Hz), 25.72, 25.68 (d, J = 1.7 Hz), 25.6 (d, J = 2.0 Hz), 16.8.

HRMS (EI) m/z: calcd. for $C_{18}H_{20}F_2$ ($[M\cdot]^+$): 274.1528, found: 274.1530.



To a flask with **S62** (0.47 mL, d = 1.085 g/mL, 6.1 mmol) in DCM (20 mL) was added $BF_3\cdot Et_2O$ (2.2 mL, d = 1.125 g/mL, 17.4 mmol) under an argon atmosphere at -78 °C. Then a solution of **S76** (1.23 g, 5 mmol) in DCM (4 mL) was added by syringe pump in 1 h. The obtained mixture was stirred for 9 h at 0 °C to rt. The reaction system was then quenched with saturated aqueous $NaHCO_3$ solution, and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 100:1 to 50:1 PE/EA) afforded compound **S77** (crude, 317.5 mg).

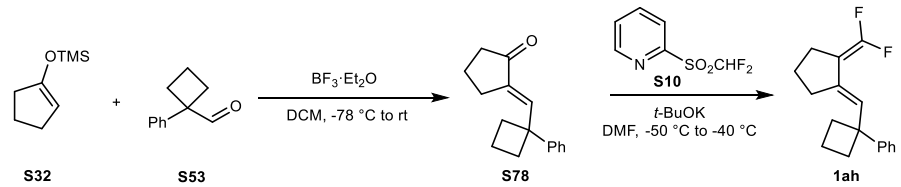
S77 (crude, 317.5 mg, 1.32 mmol) and **S10** (308 mg, 1.6 mmol) were dissolved in DMF (4 mL). The solution of *t*-BuOK (267 mg, 2.4 mmol) in DMF (4 mL) was then added by syringe pump in 1 h under an argon atmosphere at -50 °C. The reaction system was then quenched with saturated aqueous NH_4Cl solution (4 mL) and 3 M HCl (4 mL), and then extracted with ether. The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 PE/EA) to afford **1ag** (251.8 mg, 18% over two steps) as a colorless oil.

TLC (10:1 PE/EA, R_f): 0.9.

^1H NMR (400 MHz, $CDCl_3$, δ): 7.34 – 7.27 (m, 2H), 7.24 – 7.17 (m, 3H), 5.60 (dt, J = 8.5, 2.5 Hz, 1H), 3.27 – 3.13 (m, 1H), 2.79 – 2.68 (m, 1H), 2.65 – 2.52 (m, 2H), 2.21 – 2.07 (m, 2H), 2.03 – 1.93 (m, 3H), 1.91 – 1.77 (m, 4H), 1.72 – 1.57 (m, 1H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 152.1 (dd, J = 286.8, 284.2 Hz), 146.3, 134.4 (dd, J = 4.7, 1.7 Hz), 128.6, 127.8 (dd, J = 3.4, 3.4 Hz), 126.9, 126.5, 91.6 (dd, J = 21.4, 14.3 Hz), 44.0, 36.2 (d, J = 2.8 Hz), 34.0, 33.2 (dd, J = 1.7, 1.7 Hz), 30.0, 29.9, 25.2, 19.1.

HRMS (EI) m/z: calcd. for $C_{18}H_{20}F_2$ ($[M\cdot]^+$): 274.1528, found: 274.1527.



To a flask with **S33** (961.2 mg, 6 mmol) in DCM (20 mL) was added $BF_3\cdot Et_2O$ (1.73 mL, d = 1.125 g/mL, 13.7 mmol) under an argon atmosphere at -78 °C. Then a solution of **S32** (4 mmol) in DCM

(20 mL) was added by syringe pump in 1 h. The obtained mixture was stirred for 13 h at -78 °C to rt. The reaction system was then quenched with saturated aqueous NH_4Cl solution, and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 25:1 PE/EA) afforded compound **S78** (415.2 mg).

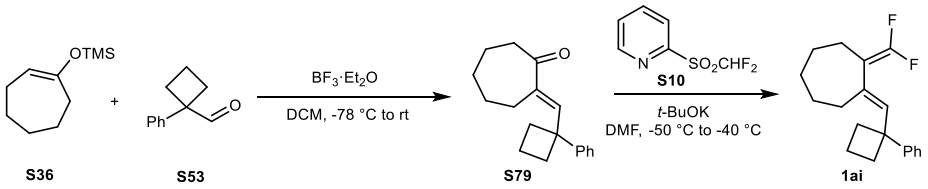
S78 (415.2 mg, 1.8 mmol) and **S10** (289.8 mg, 1.5 mmol) were dissolved in DMF (5 mL). The solution of *t*-BuOK (302.9 mg, 2.7 mmol) in DMF (5 mL) was added under an argon atmosphere at -50 °C. After that, the mixture was stirred at -50 °C to -40 °C for 1 h. The reaction system was then quenched with saturated aqueous NH_4Cl solution (4 mL) and 3 M HCl (4 mL), and then extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 PE/EA) to afford **1ah** (194.3 mg, 20% over two steps) as a colorless oil.

TLC (25:1 PE/EA, R_f): 0.9.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.35 – 7.26 (m, 4H), 7.19 – 7.13 (m, 1H), 6.23 (t, J = 2.5 Hz, 1H), 2.52 (ddd, J = 11.3, 8.8, 6.3 Hz, 2H), 2.41 (ddd, J = 11.3, 8.7, 6.5 Hz, 2H), 2.27 (tt, J = 7.1, 3.3 Hz, 2H), 2.06 – 1.96 (m, 3H), 1.95 – 1.84 (m, 1H), 1.61 – 1.51 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 151.9 (dd, J = 295.9, 287.8 Hz), 148.6, 135.41 (dd, J = 8.1, 1.7 Hz), 134.2 (dd, J = 15.3, 5.1 Hz), 128.3, 126.3, 125.5, 94.2 (dd, J = 24.0, 12.8 Hz), 48.2, 36.0, 31.1 (d, J = 2.0 Hz), 27.0 (dd, J = 2.0, 1.0 Hz), 24.7, 16.8.

HRMS (EI) m/z: calcd. for $C_{17}H_{18}F_2$ ($[M\cdot]^+$): 260.1371, found: 260.1370.



To a flask with **S53** (624.8 mg, 3.9 mmol) in DCM (15 mL) was added $BF_3\cdot Et_2O$ (1.3 mL, d = 1.125 g/mL, 10.3 mmol) under an argon atmosphere at -78 °C. Then a solution of **S36** (3 mmol) in DCM (15 mL) was added by syringe pump in 1 h. The obtained mixture was stirred for 11.5 h at -78 °C to rt. The reaction system was then quenched with saturated aqueous NH_4Cl solution, and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 25:1 PE/EA) afforded compound **S79** (333.3 mg).

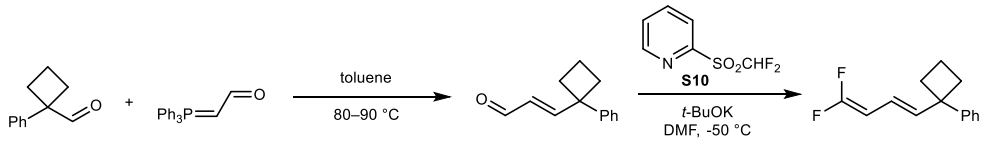
S79 (333.3 mg, 1.3 mmol) and **S10** (210.9 mg, 1.1 mmol) were dissolved in DMF (5 mL). The solution of *t*-BuOK (222.2 mg, 2 mmol) in DMF (3 mL) was then added by syringe pump in 30 min under an argon atmosphere at -50 °C. After that, the mixture was stirred at -50 °C to -40 °C for 1 h. The reaction system was then quenched with saturated aqueous NH_4Cl solution (3 mL) and 3 M HCl (3 mL), and then extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 PE/EA) to afford **1ai** (201.3 mg, 27% over two steps) as a colorless oil.

TLC (25:1 PE/EA, R_f): 0.9.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.36 (d, J = 7.7 Hz, 2H), 7.29 (dd, J = 7.6, 7.6 Hz, 2H), 7.18 – 7.12 (m, 1H), 6.02 (s, 1H), 2.56 – 2.45 (m, 2H), 2.42 – 2.32 (m, 2H), 2.17 – 2.08 (m, 2H), 2.04 – 1.86 (m, 4H), 1.54 – 1.46 (m, 2H), 1.46 – 1.38 (m, 2H), 1.28 – 1.17 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 153.6 (dd, J = 287.8, 286.8 Hz), 148.9, 139.3 (dd, J = 5.5, 2.3 Hz), 134.2 (dd, J = 3.1, 3.1 Hz), 128.3, 126.2, 125.4, 95.6 (dd, J = 19.4, 12.5 Hz), 47.3, 36.7, 30.6 (d, J = 2.9 Hz), 30.5, 28.3 ((dd, J = 2.0, 1.0 Hz)), 27.0, 26.6, 16.8.

HRMS (EI) m/z: calcd. for $C_{19}H_{22}F_2$ ([M·]$^+$): 288.1684, found: 288.1683.



S53 **S80** **S81** **1aj**

To a flask with **S80** (1.1 g, 3.6 mmol) in toluene (20 mL) was added **S53** (577.1 mg, 3.6 mmol) under an argon atmosphere at rt. The obtained mixture was stirred for 22.5 h at 80 °C and for 10 h at 90 °C, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 PE/EA) afforded compound **S81** (328.5 mg).

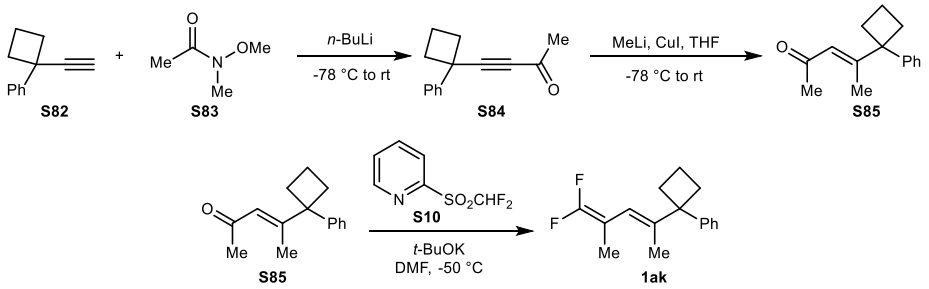
S81 (328.5 mg, 1.76 mmol) and **S10** (283.9 mg, 1.47 mmol) were dissolved in DMF (5 mL). The solution of *t*-BuOK (297.3 mg, 2.65 mmol) in DMF (5 mL) was then added by syringe pump in 1.5 h under an argon atmosphere at -50 °C. The reaction system was then quenched with saturated aqueous NH_4Cl solution (4 mL) and 3 M HCl (4 mL), and then extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 PE/EA) to afford **1aj** (292.8 mg, 44% over two steps) as a colorless oil.

TLC (50:1 PE/EA, R_f): 0.8.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.36 – 7.25 (m, 2H), 7.21 – 7.10 (m, 3H), 5.93 (d, J = 15.8 Hz, 1H), 5.84 – 5.73 (m, 1H), 4.91 (ddd, J = 24.6, 10.6, 1.9 Hz, 1H), 2.55 – 2.41 (m, 2H), 2.38 – 2.28 (m, 2H), 2.13 – 1.97 (m, 1H), 1.91 – 1.78 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 156.2 (dd, J = 295.0, 289.2 Hz), 148.5, 141.1 (dd, J = 10.9, 3.0 Hz), 128.4, 126.0, 125.9, 115.4 (dd, J = 4.4, 1.7 Hz), 82.2 (dd, J = 26.7, 16.9 Hz), 49.3, 33.4, 16.4.

HRMS (EI) m/z: calcd. for $C_{14}H_{14}F_2$ ([M·]$^+$): 220.1058, found: 220.1057.



S82 **S83** **S84** **S85** **S85** **1ak**

To a flask with **S82** (3 mmol) in THF (15 mL) was added *n*-BuLi (2.4 M in hexane, 1.25 mL, 3 mmol) under an argon atmosphere at -78 °C. The obtained mixture was stirred for 1 h at -78 °C. **S83** (361 mg, 3.5 mmol) was added. The obtained mixture was stirred for 2 h at rt. The reaction system was then quenched with saturated aqueous NH_4Cl solution and extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 100:1 PE/EA) to afford **S84** (361.9 mg).

To a flask with CuI (699 mg, 3.7 mmol) was added THF (10 mL) under argon atmosphere at −78 °C. Then MeLi (1.6 M, 4 mL, 6.4 mmol) was added. Stirred at 0 °C for another 30 min, giving methyl copper lithium solution. Then the flask was cooled at −78 °C. A solution of **S84** (361.9 mg, 1.8 mmol) in THF (2 mL) was added. The reaction mixture was stirred at −78 °C to rt for 10 h. The reaction system was then quenched with saturated aqueous NH_4Cl solution and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 to 100:1 PE/EA) to afford **S85** (179 mg).

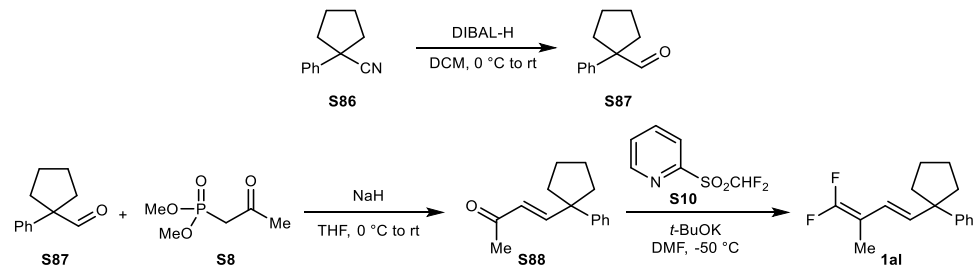
S85 (179 mg, 0.83 mmol) and **S10** (251 mg, 1.3 mmol) were dissolved in DMF (3 mL). The solution of *t*-BuOK (179 mg, 1.6 mmol) in DMF (3 mL) was then added by syringe pump in 1 h under an argon atmosphere at -50 °C. The reaction system was then quenched with saturated aqueous NH_4Cl solution (3 mL) and 3 M HCl (3 mL), and then extracted with ether. The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 PE/EA) to afford **1ak** (108.8 mg, 15% over three steps) as a colorless oil.

TLC (10:1 PE/EA, R_f): 0.8.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.34 – 7.25 (m, 4H), 7.20 – 7.14 (m, 1H), 5.72 – 5.66 (m, 1H), 2.48 – 2.33 (m, 4H), 1.89 – 1.76 (m, 2H), 1.68 (dd, J = 3.2, 3.2 Hz, 3H), 1.40 – 1.34 (m, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 152.4 (dd, J = 287.8, 287.8 Hz), 147.2, 145.7 (dd, J = 3.9, 2.2 Hz), 128.2, 126.4, 125.8, 115.4 (dd, J = 3.5, 1.7 Hz), 84.8 (dd, J = 21.9, 18.2 Hz), 54.0, 32.7, 16.0, 14.2 (d, J = 3.1 Hz), 13.5 (d, J = 2.0 Hz).

HRMS (EI) m/z: calcd. for $C_{16}H_{18}F_2$ ([M·]$^+$): 248.1371, found: 248.1368.



To a flask with **S86** (849 mg, 5 mmol) in DCM (10 mL) was added DIBAL-H (6.7 mL, 1.5 M in toluene, 10 mmol) under an argon atmosphere at 0 °C. After that, the mixture was stirred for 1 h at 0 °C to rt, diluted with ether. The reaction system was then quenched with saturated aqueous citric acid solution slowly, and kept stirring until the upper organic phase was clear, and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered

through silica gel, and concentrated by rotary evaporation. The crude **S87** (888.5 mg) was used for the next step without purification.

To a flask with NaH (307 mg, 60% dispersion in mineral oil, 7.5 mmol) in THF (25 mL) was added **S8** (1.28 g, 7.7 mmol) under an argon atmosphere at 0 °C, stirred for 10 min at 0 °C. Then the solution of **S87** (888.5 mg) in THF (2 mL) was added. The obtained mixture was stirred for 32 h at rt. The reaction system was then quenched with saturated aqueous NH_4Cl solution, and then extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 100:1 to 50:1 to 25:1 PE/EA) to afford **S88** (500.5 mg).

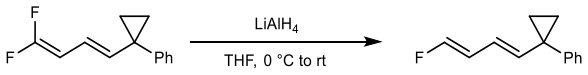
S88 (500.5 mg, 2.3 mmol) and **S10** (538 mg, 2.8 mmol) were dissolved in DMF (4 mL). The solution of *t*-BuOK (457 mg, 4 mmol) in DMF (4 mL) was then added by syringe pump in 1 h under an argon atmosphere at -50 °C. The reaction system was then quenched with saturated aqueous NH_4Cl solution (4 mL) and 3 M HCl (4 mL), and then extracted with ether. The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 PE/EA) to afford **1al** (524.3 mg, 43% over three steps) as a colorless oil.

TLC (10:1 PE/EA, R_f): 0.8.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.33 – 7.25 (m, 4H), 7.22 – 7.14 (m, 1H), 6.03 (dd, J = 16.2, 2.3 Hz, 1H), 5.66 (d, J = 15.8 Hz, 1H), 2.12 – 2.02 (m, 2H), 2.02 – 1.93 (m, 2H), 1.78 – 1.67 (m, 4H), 1.63 (dd, J = 2.9, 2.9 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 154.0 (dd, J = 291.5, 288.1 Hz), 147.6, 137.8 (dd, J = 11.0, 3.2 Hz), 128.3, 127.0, 126.0, 119.2 (d, J = 2.2 Hz), 87.2 (dd, J = 20.7, 14.1 Hz), 53.7, 37.7, 23.2, 9.2 (dd, J = 1.8, 1.8 Hz).

HRMS (EI) m/z: calcd. for $C_{16}H_{18}F_2$ ($[M\cdot]^+$): 248.1371, found: 248.1368.



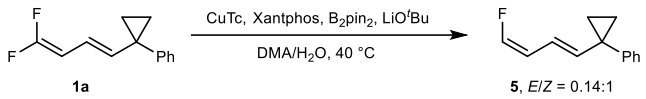
1a **5**, *E*/*Z* = 1:0.44

To a flask with $LiAlH_4$ (57 mg, 1.5 mmol) in THF (10 mL) was added the solution of **1a** (309.4 mg, 1.5 mmol) in THF (5 mL) by syringe pump in 1 h under an argon atmosphere at 0 °C. After that, the mixture was stirred at 0 °C to rt for 23.7 h. The reaction system was then quenched with 0.1 M NaOH (0.1 mL), filtered through silica gel, and washed with ether. The combined organic layer was concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 PE/EA) to afford **5** (138.3 mg, 49%, *E*/*Z* = 1:0.44) as a colorless oil.

TLC (10:1 PE/EA, R_f): 0.8.

^{1}H NMR for the major isomer (400 MHz, $CDCl_3$, δ): 7.34 – 7.28 (m, 4H), 7.24 – 7.20 (m, 1H), 6.61 (dd, J = 83.8, 11.0 Hz, 1H), 5.97 (ddd, J = 17.7, 11.0, 11.0 Hz, 1H), 5.53 (d, J = 15.2 Hz, 1H), 5.39 (ddd, J = 15.4, 10.9, 1.9 Hz, 1H), 1.17 – 1.10 (m, 2H), 1.00 – 0.95 (m, 2H).

^{13}C{^{1}H} NMR for the major isomer (101 MHz, $CDCl_3$, δ): 150.6 (d, J = 257.9 Hz), 143.1, 141.5 (d, J = 11.2 Hz), 130.1, 128.4, 126.7, 120.1 (d, J = 11.6 Hz), 113.8 (d, J = 14.9 Hz), 28.5, 15.2.



1a **5**, *E*/*Z* = 0.14:1

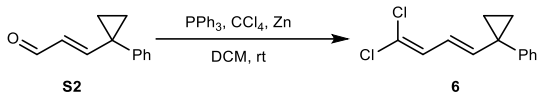
Following the reported procedure[15h]. In the glove box, to a flask with **1a** (133.9 mg, 0.65 mmol) in DMA (3.25 mL) was added CuTc (12.4 mg, 0.065 mmol), Xantphos (37.6 mg, 0.065 mg), B_2pin_2 (495.1 mg, 1.95 mmol), and Li^{t}OBu (156.2 mg, 1.95 mmol). After that, the mixture was removed from the glove box, and H_2O (35.1 mg, 1.95 mmol) was added and stirred at 40 °C for 20 h. The reaction system was then quenched with water and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 PE/EA) to afford **5** (100.6 mg, 82%, *E*/*Z* = 0.14:1) as a colorless oil.

TLC (10:1 PE/EA, R_f): 0.8.

^{1}H NMR for the major isomer (400 MHz, $CDCl_3$, δ): 7.33 – 7.28 (m, 4H), 7.25 – 7.20 (m, 1H), 6.29 (dd, *J* = 83.4, 4.7 Hz, 1H), 5.90 (ddd, *J* = 15.5, 10.8, 0.9 Hz, 1H), 5.63 (d, *J* = 15.4 Hz, 1H), 5.35 (ddd, *J* = 41.2, 10.9, 4.7 Hz, 1H), 1.17 – 1.11 (m, 2H), 1.04 – 1.00 (m, 2H).

^{13}C{^{1}H} NMR for the major isomer (101 MHz, $CDCl_3$, δ): 146.4 (d, *J* = 264.2 Hz), 143.0, 141.8 (d, *J* = 3.7 Hz), 129.9, 128.5, 126.7, 118.2 (d, *J* = 5.4 Hz), 111.3 (d, *J* = 2.9 Hz), 28.5, 15.5.

HRMS (EI) m/z: calcd. for $C_{13}H_{13}F_2$ ([M·]$^+$): 188.0996, found: 188.0995.



S2 **6**

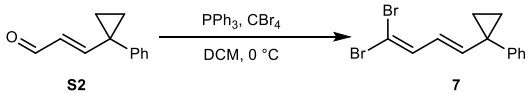
To a flask with PPh_3 (1.18 g, 4.5 mmol), and CCl_4 (692.1 mg, 4.5 mmol) in DCM (10 mL) was added Zn (294.3 mg, 4.5 mmol) under an argon atmosphere at rt, stirred 15 min at rt. The solution of **S2** (258.5 mg, 1.5 mmol) in DCM (5 mL) was added. Then the mixture was stirred at rt for 14 h, concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 PE/EA) to afford **6** (205 mg, 57%) as a light yellow oil.

TLC (10:1 PE/EA, R_f): 0.9.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.36 – 7.27 (m, 4H), 7.27 – 7.19 (m, 1H), 6.35 (dd, *J* = 6.3, 3.4 Hz, 1H), 5.73 (d, *J* = 2.9 Hz, 1H), 5.72 – 5.68 (m, 1H), 1.22 – 1.17 (m, 2H), 1.08 – 1.03 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 145.5, 142.4, 129.9, 128.8, 128.6, 126.9, 122.5, 118.8, 28.9, 15.9.

HRMS (EI) m/z: calcd. for $C_{13}H_{12}Cl_2$ ([M·]$^+$): 238.0311, found: 238.0314.



S2 **7**

To a flask with PPh_3 (1.57 g, 6 mmol), and in DCM (10 mL) was added CBr_4 (994.8 mg, 3 mmol) under an argon atmosphere at rt, stirred 10 min at 0 °C. The solution of **S2** (260.1 mg, 1.5 mmol) in DCM (5 mL) was added. Then the mixture was stirred at 0 °C for 35 min, filtered through silica gel, and washed with PE. The combined organic layer was concentrated by rotary evaporation. The

residue was purified by flash column chromatography (silica gel, 20:1 PE/EA) to afford **7** (204.8 mg, 41%) as a light yellow oil.

TLC (10:1 PE/EA, R_f): 0.9.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.35 – 7.27 (m, 4H), 7.27 – 7.21 (m, 1H), 6.87 (d, J = 10.0 Hz, 1H), 5.79 (d, J = 15.3 Hz, 1H), 5.65 (dd, J = 15.2, 10.0 Hz, 1H), 1.23 – 1.17 (m, 2H), 1.09 – 1.03 (m, 2H).

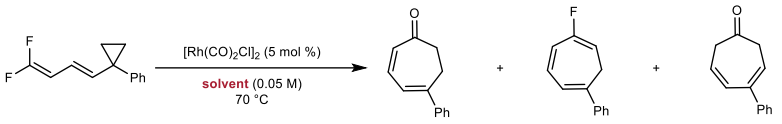
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 146.2, 142.3, 136.9, 129.9, 128.6, 127.0, 125.1, 88.3, 29.0, 15.9.

HRMS (EI) m/z: calcd. for $C_{13}H_{12}Br_2$ ($[M\cdot]^+$): 325.9300, found: 325.9295.

3. Reaction Optimization

Unless otherwise specified, all reactions were conducted on a 0.1 mmol scale. All yields are NMR yields, and 1,3,5-trimethoxybenzene was used as the internal standard.

Table S1. Screening of solvents.

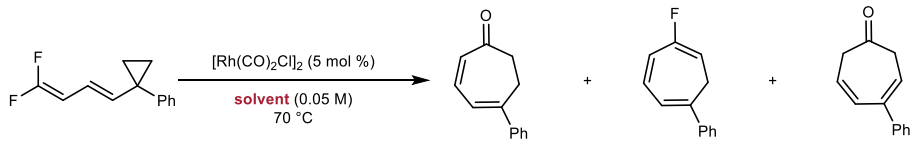


1a 2a 3a 4a

entry	solvent	t/h	yield (2a)	yield (3a)	yield (4a)
1	HFIP/H_2O = 19:1	1	94%	N. D.	1%
2	EtOH/H_2O = 19:1	1	84%	N. D.	1%
3	2,2,3,4,4,4-hexafluoro-1-butanol/H_2O = 19:1	1	54%	trace	N. D.
4	THF/H_2O = 19:1	1	21%	N. D.	6%
5	TFEA/H_2O = 19:1	1	16%	54%	2%
6	TFEA/H_2O = 19:1	4	80%	11%	3%
7	dioxane/H_2O = 19:1	1	14%	5%	N. D.
8	toluene/H_2O = 19:1	1	4%	N. D.	N. D.
9	EtOH/HFIP/H_2O = 2:1:1	1	85%	3%	2%
10	53% Chinese Baijiu	1	83%	4%	N. D.

In entry 10, KINMEN KAOLIANG LIQUOR was used.

Table S2. Screening of solvent/H_2O ratio.

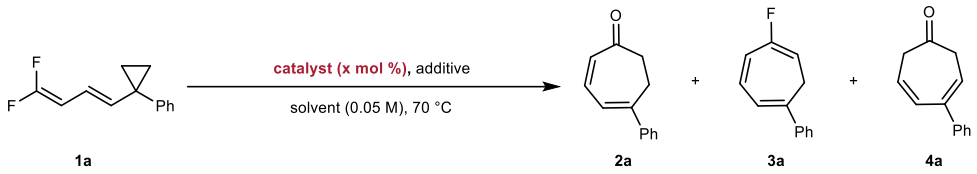


1a 2a 3a 4a

entry	solvent	t/h	yield (2a)	yield (3a)	yield (4a)
1	HFIP[a]	1	trace	42%	N. D.
2	HFIP/H_2O = 49:1	1	87%	N. D.	3%
3	HFIP/H_2O = 19:1	1	94%	N. D.	1%
4	HFIP/H_2O = 3:1	1	82%	13%	2%
5	HFIP/H_2O = 1:3	1	73%	7%	4%
6	TFEA/H_2O = 19:1	4	80%	11%	3%
7	TFEA/H_2O = 1:3	1	71%	3%	3%

[a]100 wt% 4Å MS was used as the additive.

Table S3. Screening of catalysts.

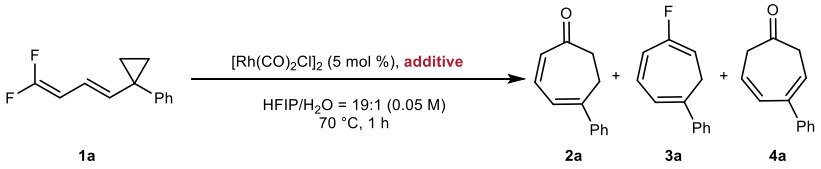


1a 2a 3a 4a

entry	catalyst	solvent	additive (equivalent)	t/h	yield (2a)
1	$[Rh(CO)_2Cl]_2$ (5 mol%)	HFIP/H_2O = 19:1	w/o	1	94%
2	$[Rh(COD)Cl]_2$ (5 mol%)	HFIP/H_2O = 19:1	w/o	1	N. D.
3	$Pd_2(dba)_3$ (5 mol%)	HFIP/H_2O = 19:1	w/o	1	N. D.
4	$Pd(PPh_3)_4$ (5 mol%)	HFIP/H_2O = 19:1	w/o	1	N. D.
5	$Pd(PPh_3)_4$ (5 mol%)	toluene/H_2O = 19:1	w/o	17	N. D.
6	$Ni(OAc)_2{\cdot}4H_2O$ (10 mol%)	HFIP/H_2O = 19:1	w/o	17	N. D.
7	$Ni(COD)_2$ (10 mol%)	HFIP	IPr (20 mol%)	17	N. D.
8	$Ni(COD)_2$ (10 mol%)	toluene	IPr (20 mol%)	17	N. D.

Entries 6-8 were conducted on a 0.2 mmol scale.

Table S4. Screening of additives.

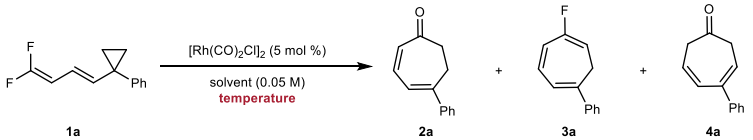


1a 2a 3a 4a

entry	additive	yield (2a)	yield (3a)	yield (4a)
1	w/o	94%	N. D.	1%
2	1 atm CO	81%	N. D.	3%
3	1 eq. NEt_3	N. D.	67%	N. D.
4	1 eq. $CaCO_3$	90%	N. D.	5%
5	PPh_3 (20 mol %)	N. D.	6%	N. D.

Entry 2 was conducted on a 0.2 mmol scale.

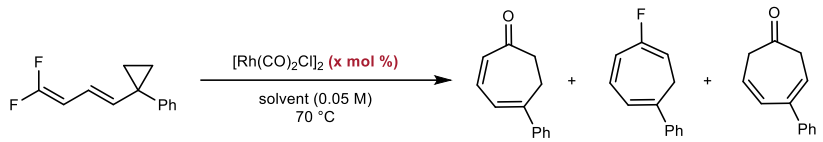
Table S5. Screening of temperature.



1a 2a 3a 4a

entry	solvent	temperature/°C	t/h	yield (2a)	yield (3a)	yield (4a)
1	HFIP/H_2O = 19:1	50	7	82%	N. D.	1%
2	HFIP/H_2O = 19:1	60	3	88%	N. D.	1%
3	HFIP/H_2O = 19:1	70	1	94%	N. D.	1%
4	HFIP/H_2O = 19:1	80	0.5	87%	N. D.	1%
5	TFEA/H_2O = 19:1	70	4	80%	11%	3%
6	TFEA/H_2O = 19:1	90	4	78%	N. D.	8%

Table S6. Trying to reduce catalyst loading.

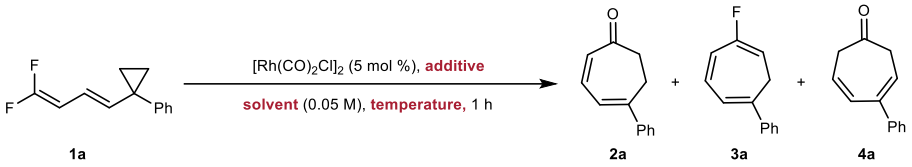


1a 2a 3a 4a

entry	catalyst	solvent	t/h	yield (2a)
1	$[Rh(CO)_2Cl]_2$ (5 mol %)	HFIP/H_2O = 19:1	1	94%
2	$[Rh(CO)_2Cl]_2$ (2 mol %)	HFIP/H_2O = 19:1	1	90%
3	$[Rh(CO)_2Cl]_2$ (1 mol %)	HFIP/H_2O = 19:1	1	43%
4	$[Rh(CO)_2Cl]_2$ (0.5 mol %)	HFIP/H_2O = 19:1	17	22%
5	$[Rh(CO)_2Cl]_2$ (0.5 mol %)	EtOH/HFIP/H_2O = 2:1:1	12	65%

Reactions in entries 1 and 2 were conducted on a 0.1 mmol scale and the reactions in entries 3–5 were conducted on a 0.5 mmol scale. Reaction in entry 5 was conducted under argon atmosphere.

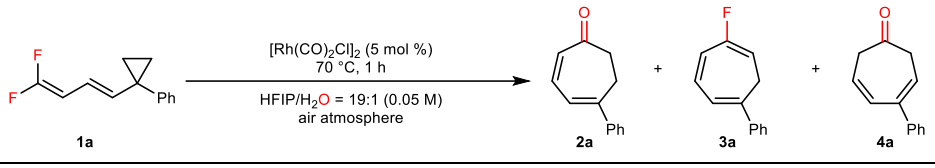
Table S7. Screening of bases and equivalent.



1a 2a 3a 4a

entry	solvent	additive (equivalent)	temperature/°C	yield (3a)
1	HFIP/H_2O = 19:1	pyridine (1.0)	60	N. D.
2	HFIP/H_2O = 19:1	pyrrolidine (1.0)	60	38%
3	HFIP/H_2O = 19:1	DBU (1.0)	60	78%
4	HFIP/H_2O = 19:1	DABCO (1.0)	60	67%
5	HFIP/H_2O = 19:1	K_2CO_3 (1.0)	60	76%
6	HFIP/H_2O = 19:1	NEt_3 (1.0)	60	80%
7	HFIP/H_2O = 19:1	NEt_3 (0.5)	60	70%
8	HFIP/H_2O = 19:1	NEt_3 (2.0)	60	59%
9	HFIP/H_2O = 19:1	NEt_3 (1.0)	70	67%
10	HFIP	NEt_3 (1.0)	60	<44%
11	TFEA/H_2O = 19:1	NEt_3 (1.0)	70	N. D.
12	EtOH/H_2O = 19:1	NEt_3 (1.0)	70	N. D.

Table S8. Summary of Table S1–S7[a]



1a 2a 3a 4a

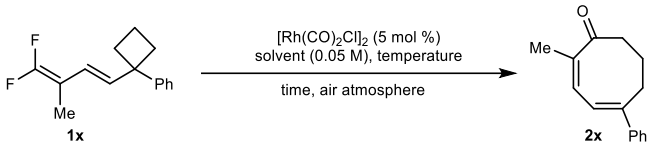
entry	variation from the optimal conditions	yield (**2a**)[b]	yield (**3a**)[b]	yield (**4a**)[b]
1	**None**	**94% (90%[c])**	**N. D.**	**1%**
2	THF instead of HFIP	21%	N. D.	6%
3	toluene instead of HFIP	4%	N. D.	N. D.
4	TFEA instead of HFIP	16%	54%	2%

5	dioxane instead of HFIP	14%	5%	N. D.
6	EtOH instead of HFIP	84%	N. D.	1%
7	**EtOH/HFIP/H_2O = 2:1:1**	**85%**	**3%**	**2%**
8	53% Chinese Baijiu as the solvent	83%	4%	N. D.
9	60 °C, 3 h	88%	N. D.	1%
10	80 °C, 0.5 h	87%	N. D.	1%
11	$[Rh(CO)_2Cl]_2$ (2 mol %)	90%	N. D.	3%
12	argon instead of air	88%	N. D.	3%
13	1.0 eq. NEt_3 added, 60 °C	N. D.	80% (73%[c])	N. D.
14	PPh_3 (20 mol %) added	N. D.	6%	N. D.
15	$[Rh(COD)Cl]_2$ instead of $[Rh(CO)_2Cl]_2$	N. D.	N. D.	N. D.

[a]All reactions were conducted on a 0.1 mmol scale, solvent (2 mL), 600 rpm. [b]NMR yield, 1,3,5-trimethoxybenzene as the internal standard. [c]Isolated yield. HFIP, hexafluoroisopropanol; TFEA, 2,2,2-trifluoroethanol; THF, tetrahydrofuran; Et, ethyl; Ph, phenyl; rpm, revolutions per minute; N. D., not detected; eq., equivalent; COD, 1,5-cyclooctadiene.

First, we optimized reaction conditions using **1a** as the standard substrate (Table S1–S8). After many attempts, **2a** can be obtained as the main product in 94% NMR yield (90% isolated yield, entry 1). Here adding water was critical for the success of the target reaction because this was the key to realizing atomic hybridization editing through the substitution of two fluorine atoms to form a carbonyl intermediate (see later mechanistic study). This reaction had two side products, **3a** and **4a**, which were generated after the catalytic circle. With this initial success, we further tested co-solvents of H_2O for the reaction, but inferior results were observed (entries 2–6). To our delight, using EtOH/HFIP/H_2O as the solvent, **2a** produced in 85% yield, with a slightly reduced chemoselectivity (entry 7). To our excitement, Chinese Baijiu was a compatible solvent for this reaction, and in this case, **2a** was obtained in 83% yield, demonstrating that this reaction had significant tolerance to many possible organic molecules present in the liquor (entry 8). Raising or lowering the reaction temperature decreased the yield of **2a** (entries 9, 10). The present reaction worked also very well when the catalyst loading was reduced to 2 mol % and product **2a** in this case can be obtained in 90% yield (entry 11). There is no significant difference between argon and air in this condition (entry 12). Interestingly, **3a** can be obtained as the major product in 80% NMR yield (73% isolated yield) when 1.0 eq. NEt_3 was added (entry 13). Two other ligands, PPh_3 and COD, were ineffective for the present reaction (entries 14, 15). We therefore used conditions in entries 1 and 7 for studying the reaction scope of the migratory ring expansion reaction.

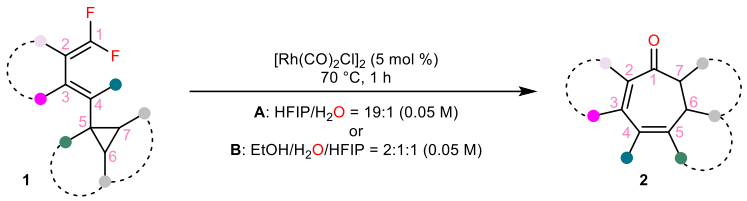
Table S9. Optimization of the reaction conditions (*gem*- difluorodienylcyclobutanes)[a]



entry	solvent	T (°C)	t (h)	yield (%)
1	EtOH/H_2O = 19:1	80	13	5
2	HFIP/H_2O = 19:1	80	13	77
3	PhMe/H_2O = 19:1	80	13	N. D.
4	dioxane/H_2O = 19:1	80	13	N. D.
5	DCE/H_2O = 19:1	80	13	N. D.
6	2-MeTHF/H_2O = 19:1	80	13	1
7	TFEA/H_2O = 19:1	80	10	12
8	HFIP/H_2O = 39:1	80	10	46
9	HFIP/H_2O = 9:1	80	10	65
10	HFIP/H_2O = 3:1	80	10	83
11	HFIP/H_2O = 1:1	80	10	53
12[b]	HFIP/H_2O = 3:1	80	10	92
13[b]	HFIP/H_2O = 3:1	80	5	79
14[b]	HFIP/H_2O = 3:1	90	5	93 (92[c])

[a]All reactions were conducted on a 0.1 mmol scale, solvent (2 mL), 600 rpm. [b]Argon atmosphere. [c]Isolated yield.

4. General Procedure for 1,5-Migratory Ring Expansion

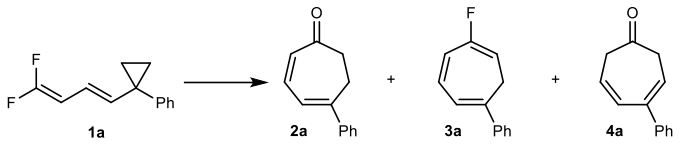


Procedure A: To a 25 mL reaction tube with **1** (0.2 mmol, 1 equiv.) and $[Rh(CO)_2Cl]_2$ (3.9 mg, 5 mol %) was added HFIP (3.8 mL), and H_2O (0.2 mL) sequentially under air atmosphere. The reaction mixture was charged with a flap plug and then stirred at 70 °C for 1 h, 600 revolutions per minute (rpm) for the magnetic stir bar. After cooling, quenched with aqueous $NaHCO_3$ solution, and extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel) to afford **2**.

Procedure B: To a 25 mL reaction tube with **1** (0.2 mmol, 1 equiv.) and $[Rh(CO)_2Cl]_2$ (3.9 mg, 5 mol %) was added EtOH (2 mL), H_2O (1 mL), and HFIP (1 mL) sequentially under air atmosphere. The reaction mixture was charged with a flap plug and then stirred at 70 °C for 1 h, 600 revolutions per minute (rpm) for the magnetic stir bar. After cooling, the solvent was evaporated and the residue was purified by flash column chromatography (silica gel) to afford **2**.

Procedure C: To a 25 mL reaction tube with **1** (0.2 mmol, 1 equiv.) and $[Rh(CO)_2Cl]_2$ (3.9 mg, 5 mol %) was added EtOH (2 mL), H_2O (1 mL), and HFIP (1 mL) sequentially under air atmosphere. The reaction mixture was charged with a flap plug and then stirred at 70 °C for 1 h, 600 revolutions per minute (rpm) for the magnetic stir bar. After cooling, the reaction system was then quenched with aqueous $NaHCO_3$ solution, and extracted with ether, the combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel) to afford **2**.

Note: this reaction runs faster in HFIP/H_2O (**Procedure A)** than EtOH/H_2O/HFIP (**Procedure B** and **C**), but **Procedure B** and **C** are milder for acid-sensitive substrates. For small-scale reactions, the work-up in **Procedure B** is convenient, but for large-scale and acid-sensitive substrates, quenched with aqueous $NaHCO_3$ solution is recommended.



For the synthesis of **2a**:

Run 1: Following general procedure A. Substrate: **1a** (41.3 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.8 mg, 0.01 mmol), flash column chromatography (silica gel, 25:1 PE/EA); product: **2a** (33.1 mg, 90%).

Run 2: Following general procedure A. Substrate: **1a** (41.2 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.8 mg, 0.01 mmol), flash column chromatography (silica gel, 25:1 PE/EA); product: **2a** (33.8 mg, 92%).

The average yield of two runs: 91%.

Physical Form: light yellow oil.

TLC (5:1 PE/EA, R_f): 0.5.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.45 (d, J = 7.2 Hz, 2H), 7.43 – 7.30 (m, 3H), 6.77 (dd, J = 12.3, 7.4 Hz, 1H), 6.35 (d, J = 7.4 Hz, 1H), 6.16 (d, J = 12.3 Hz, 1H), 2.93 – 2.83 (m, 2H), 2.81 – 2.73 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 201.3, 152.9, 141.9, 139.1, 130.1, 128.8, 128.7, 126.4, 123.4, 41.6, 26.3.

HRMS (EI) m/z: calcd. for $C_{13}H_{12}O$ ($[M\cdot]^+$): 184.0883, found: 184.0882.

For the synthesis of **3a**:

Run 1: Following general procedure A, 1 eq. NEt_3 (28 μL) was added, at 60 °C. Substrate: **1a** (41.7 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), flash column chromatography (silica gel, 1:0 PE/EA), then PTLC (30:1, PE/EA); product: **3a** (27.9 mg, 74%).

Run 2: Following general procedure A, 1 eq. NEt_3 (28 μL) was added, at 60 °C. Substrate: **1a** (42.1 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), flash column chromatography (silica gel, 1:0 PE/EA), then PTLC (30:1, PE/EA); product: **3a** (27.2 mg, 72%).

The average yield of two runs: 73%.

Physical Form: colorless oil.

TLC (10:1 PE/EA, R_f): 0.8.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.49 – 7.42 (m, 2H), 7.38 – 7.30 (m, 2H), 7.30 – 7.24 (m, 1H), 6.71 (ddd, J = 11.8, 6.1, 4.1 Hz, 1H), 6.43 (ddd, J = 11.7, 7.0, 1.9 Hz, 1H), 6.37 (dd, J = 6.0, 1.3 Hz, 1H), 5.09 (dddd, J = 12.6, 7.7, 7.7, 2.0 Hz, 1H), 2.74 (dd, J = 7.7, 1.5 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 159.5 (d, J = 238.6 Hz), 140.9, 137.6 (d, J = 5.1 Hz), 133.2 (d, J = 12.1 Hz), 128.7, 127.8, 127.4, 122.5, 122.0 (d, J = 33.0 Hz), 99.6 (d, J = 23.8 Hz), 26.5 (d, J = 8.8 Hz).

^{19}F NMR (471 MHz, $CDCl_3$, δ): -117.04. (page S182)

HRMS (EI) m/z: calcd. for $C_{13}H_{11}F$ ($[M\cdot]^+$): 186.0839, found: 186.0836.

Gram Scale Experiments:

Run 1: Following general procedure C, solvent (0.1 M), under argon atmosphere. Substrate: **1a** (1032.4 mg, 5 mmol), $[Rh(CO)_2Cl]_2$ (9.7 mg, 0.025 mmol, 0.5 mol %), EtOH (25.0 mL), HFIP (12.5 mL), H_2O (12.5 mL), 19.3 h, flash column chromatography (silica gel, 25:1 PE/EA); products: **2a** (664.2 mg, 72%), **4a** (56.7 mg, 6%).

Run 2: Following general procedure C, solvent (0.1 M), under argon atmosphere. Substrate: **1a** (1034.5 mg, 5 mmol), $[Rh(CO)_2Cl]_2$ (9.5 mg, 0.025 mmol, 0.5 mol %), EtOH (25.0 mL), HFIP (12.5 mL), H_2O (12.5 mL), 20 h, flash column chromatography (silica gel, 25:1 PE/EA); products: **2a** (681.7 mg, 74%), **4a** (51.8 mg, 6%).

The average yield of two runs: **2a** (73%) and **4a** (6%).

Characterization of **4a**:

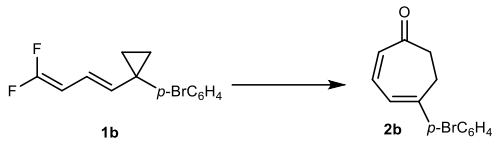
Physical Form: light yellow oil.

TLC (5:1 PE/EA, R_f): 0.6.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.42 – 7.34 (m, 4H), 7.34 – 7.29 (m, 1H), 6.56 (d, J = 10.4 Hz, 1H), 6.20 (t, J = 6.5 Hz, 1H), 6.14 (dt, J = 11.5, 6.1 Hz, 1H), 3.20 (d, J = 6.6 Hz, 2H), 3.13 (d, J = 6.2 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 212.8, 141.6, 139.8, 131.1, 128.6, 127.9, 127.0, 126.7, 120.8, 45.2, 45.2.

HRMS (EI) m/z: calcd. for $C_{13}H_{12}O$ ($[M\cdot]^+$): 184.0883, found: 184.0882.



Run 1: Following general procedure A. Substrate: **1b** (58.3 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), flash column chromatography (silica gel, 25:1 PE/EA); product: **2b** (50.6 mg, 94%).

Run 2: Following general procedure A. Substrate: **1b** (58.0 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), flash column chromatography (silica gel, 25:1 PE/EA); product: **2b** (49.9 mg, 93%).

The average yield of two runs: 94%.

Physical Form: light yellow solid.

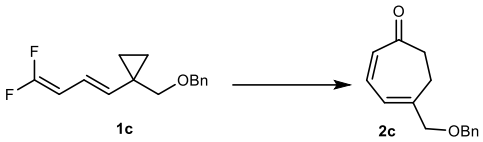
Melting Point: 95 – 97 °C.

TLC (10:1 PE/EA, R_f): 0.2.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.50 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 6.74 (dd, J = 12.3, 7.4 Hz, 1H), 6.33 (d, J = 7.4 Hz, 1H), 6.17 (d, J = 12.3 Hz, 1H), 2.88 – 2.79 (m, 2H), 2.78 – 2.69 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 200.9, 151.4, 140.7, 138.7, 131.9, 130.4, 127.9, 123.6, 122.7, 41.4, 26.1.

HRMS (EI) m/z: calcd. for $C_{13}H_{11}OBr$ ($[M\cdot]^+$): 261.9988, found: 261.9989.



Run 1: Following general procedure B. Substrate: **1c** (50.5 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), flash column chromatography (silica gel, 10:1 PE/EA); product: **2c** (43.4 mg, 94%).

Run 2: Following general procedure B. Substrate: **1c** (49.6 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.8 mg, 0.01 mmol), flash column chromatography (silica gel, 10:1 PE/EA); product: **2c** (41.8 mg, 92%).

The average yield of two runs: 93%.

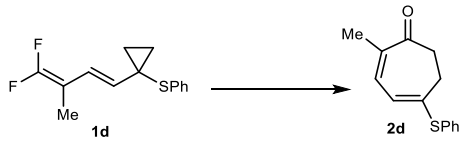
Physical Form: light yellow oil.

TLC (5:1 PE/EA, R_f): 0.2.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.40 – 7.33 (m, 4H), 7.33 – 7.28 (m, 1H), 6.60 (dd, J = 12.3, 7.2 Hz, 1H), 6.17 – 6.13 (m, 1H), 6.10 (d, J = 12.3 Hz, 1H), 4.55 (s, 2H), 4.10 (s, 2H), 2.65 – 2.57 (m, 2H), 2.39 – 2.32 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 201.2, 150.8, 138.2, 137.8, 130.7, 128.6, 127.9, 127.8, 121.7, 73.9, 72.6, 41.1, 23.6.

HRMS (EI) m/z: calcd. for $C_{15}H_{16}O_2$ ($[M\cdot]^+$): 228.1145, found: 228.1144.



Run 1: Following general procedure C, the reaction time is 2 h. Substrate: **1d** (50.4 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.8 mg, 0.01 mmol), flash column chromatography (silica gel, 20:1 PE/EA); product: **2d** (41.4 mg, 90%).

Run 2: Following general procedure C, the reaction time is 2 h. Substrate: **1d** (51.2 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), flash column chromatography (silica gel, 20:1 PE/EA); product: **2d** (42.1 mg, 90%).

The average yield of two runs: 90%.

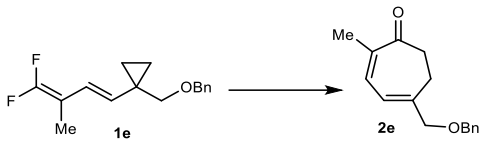
Physical Form: light yellow oil.

TLC (5:1 PE/EA, R_f): 0.6.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.51 – 7.44 (m, 2H), 7.43 – 7.36 (m, 3H), 6.44 (dd, J = 8.2, 1.6 Hz, 1H), 5.61 (d, J = 8.1 Hz, 1H), 2.74 – 2.66 (m, 2H), 2.52 – 2.45 (m, 2H), 1.91 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 199.9, 149.7, 135.4, 135.3, 134.3, 131.4, 129.7, 129.2, 120.2, 41.7, 28.0, 20.3.

HRMS (EI) m/z: calcd. for $C_{14}H_{14}OS$ ($[M\cdot]^+$): 230.0760, found: 230.0760.



Run 1: Following general procedure B, the reaction time is 1.5 h. Substrate: **1e** (53.0 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), flash column chromatography (silica gel, 10:1 PE/EA); product: **2e** (46.2 mg, 95%).

Run 2: Following general procedure B, the reaction time is 1.5 h. Substrate: **1e** (52.3 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), flash column chromatography (silica gel, 10:1 PE/EA); product: **2e** (45.2 mg, 94%).

The average yield of two runs: 94%.

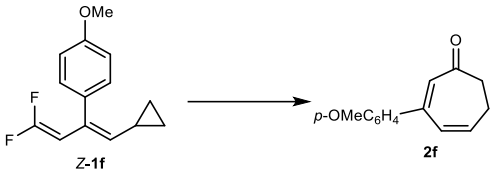
Physical Form: light yellow oil.

TLC (5:1 PE/EA, R_f): 0.4.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.40 – 7.32 (m, 4H), 7.32 – 7.26 (m, 1H), 6.59 (d, J = 7.5 Hz, 1H), 6.05 (d, J = 7.6 Hz, 1H), 4.53 (s, 2H), 4.08 (s, 2H), 2.69 – 2.63 (m, 2H), 2.35 – 2.28 (m, 2H), 1.95 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 200.9, 148.1, 138.0, 137.6, 135.5, 128.6, 127.9, 127.8, 122.5, 74.1, 72.4, 41.7, 23.6, 20.4.

HRMS (EI) m/z: calcd. for $C_{16}H_{18}O_2$ ($[M\cdot]^+$): 242.1301, found: 242.1299.



Run 1: Following general procedure B, the reaction time is 2 h. Substrate: *Z*-**1f** (47.3 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), flash column chromatography (silica gel, 20:1 to 10:1 PE/EA); product: **2f** (30.2 mg, 70%).

Run 2: Following general procedure B, the reaction time is 2 h. Substrate: *Z*-**1f** (47.1 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), flash column chromatography (silica gel, 20:1 to 10:1 PE/EA); product: **2f** (29.2 mg, 68%).

The average yield of two runs: 69%.

Physical Form: light yellow solid.

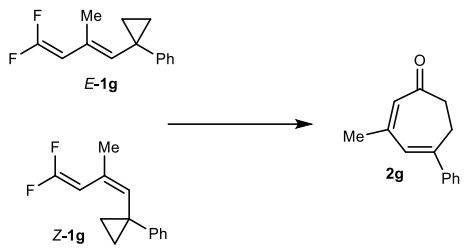
Melting Point: 53 – 55 °C.

TLC (5:1 PE/EA, R_f): 0.2.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.44 – 7.36 (m, 2H), 6.95 – 6.88 (m, 2H), 6.65 (dt, J = 11.3, 6.4 Hz, 1H), 6.41 (s, 1H), 6.38 – 6.32 (m, 1H), 3.84 (s, 3H), 2.74 – 2.67 (m, 2H), 2.52 – 2.44 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 201.8, 160.6, 149.0, 140.0, 134.3, 129.5, 128.7, 128.2, 114.1, 55.5, 42.6, 22.3.

HRMS (EI) m/z: calcd. for $C_{14}H_{14}O_2$ ($[M\cdot]^+$): 214.0988, found: 214.0988.



From *E*-**1g**:

Run 1: Following general procedure B. Substrate: *E*-**1g** (44.1 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), flash column chromatography (silica gel, 50:1 to 20:1 PE/EA); product: **2g** (35.4 mg, 89%).

Run 2: Following general procedure B. Substrate: *E*-**1g** (44.5 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), flash column chromatography (silica gel, 50:1 to 20:1 PE/EA); product: **2g** (36.7 mg, 92%).

The average yield of two runs: 90%.

From *Z*-**1g**:

Run 1: Following general procedure B, the reaction time is 17 h, solvent (2 mL). Substrate: *Z*-**1g** (22.4 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol), flash column chromatography (silica gel, 20:1 PE/EA); product: **2g** (7.2 mg, 36%).

Run 2: Following general procedure B, the reaction time is 17 h, solvent (2 mL). Substrate: *Z*-**1g** (22.5 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol), flash column chromatography (silica gel, 20:1 PE/EA); product: **2g** (7.4 mg, 37%).

The average yield of two runs: 36%.

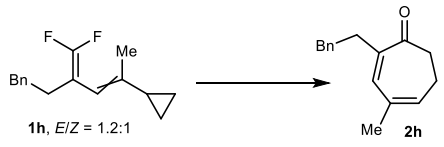
Physical Form: light yellow oil.

TLC (5:1 PE/EA, R_f): 0.4.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.47 – 7.42 (m, 2H), 7.42 – 7.31 (m, 3H), 6.20 (s, 1H), 6.11 (s, 1H), 2.89 – 2.81 (m, 2H), 2.74 – 2.67 (m, 2H), 2.10 (d, J = 1.3 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 200.9, 150.8, 149.8, 142.0, 128.7, 128.6, 128.5, 127.4, 126.4, 41.5, 27.4, 26.6.

The spectra of **2g** are consistent with the literature.[15i]



Run 1: Following general procedure B, the reaction time is 18 h. Substrate: **1h** (49.2 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.8 mg, 0.01 mmol), flash column chromatography (silica gel, 100:1 PE/EA); product: **2h** (22.2 mg, 50%).

Run 2: Following general procedure B, the reaction time is 18 h. Substrate: **1h** (49.8 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.8 mg, 0.01 mmol), flash column chromatography (silica gel, 100:1 PE/EA); product: **2h** (24.8 mg, 55%).

The average yield of two runs: 52%.

Physical Form: colorless oil.

TLC (10:1 PE/EA, R_f): 0.4.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.28 – 7.24 (m, 2H), 7.22 – 7.14 (m, 3H), 6.25 (s, 1H), 6.10 (t, J = 6.3 Hz, 1H), 2.79 – 2.71 (m, 2H), 2.68 – 2.57 (m, 4H), 2.25 – 2.15 (m, 2H), 1.81 (d, J = 1.5 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 201.9, 141.9, 140.1, 139.9, 134.3, 132.6, 128.8, 128.4, 126.0, 44.2, 36.4, 36.2, 24.4, 22.1.

HRMS (EI) m/z: calcd. for $C_{16}H_{18}O$ ($[M\cdot]^+$): 226.1352, found: 226.1354.

Run 1: Following general procedure B. Substrate: **1i** (82.0 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), flash column chromatography (silica gel, 100:1 PE/EA); product: **2i** (55.9 mg, 72%).

Run 2: Following general procedure B. Substrate: **1i** (82.5 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), flash column chromatography (silica gel, 100:1 PE/EA); product: **2i** (56.2 mg, 72%).

The average yield of two runs: 72%.

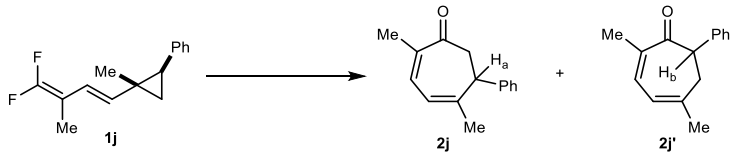
Physical Form: colorless oil.

TLC (10:1 PE/EA, R_f): 0.4.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.70 – 7.60 (m, 4H), 7.48 – 7.34 (m, 6H), 6.55 (d, J = 7.2 Hz, 1H), 6.28 (dd, J = 11.3, 3.6 Hz, 1H), 6.00 (ddd, J = 11.3, 7.4, 1.9 Hz, 1H), 3.72 – 3.60 (m, 2H), 2.73 – 2.62 (m, 3H), 1.94 (s, 3H), 1.05 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 200.5, 140.5, 138.1, 135.7, 135.3, 133.4, 133.4, 129.9, 127.9, 125.8, 66.1, 45.4, 36.5, 26.9, 20.4, 19.4.

HRMS (EI) m/z: calcd. for $C_{25}H_{30}O_2Si$ ($[M\cdot]^+$): 390.2010, found: 390.2012.



Run 1: Following general procedure C, the reaction time is 2.75 h. Substrate: **1j** (46.7 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.8 mg, 0.01 mmol), purified by PTLC (PE/EA = 10:1); products: **2j** (21.7 mg, 51%) and **2j'** (10.5 mg, 25%).

Run 2: Following general procedure C, the reaction time is 2.75 h. Substrate: **1j** (46.8 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), purified by PTLC (PE/EA = 10:1); products: **2j** (20.1 mg, 47%) and **2j'** (10.2 mg, 24%).

The average yield of two runs: **2j** (49%), **2j'** (24%).

Characterization of **2j**:

Physical Form: light yellow oil.

TLC (10:1 PE/EA, R_f): 0.5.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.25 (dd, J = 8.2, 6.4 Hz, 2H), 7.21 – 7.15 (m, 1H), 7.14 – 7.07 (m, 2H), 6.52 (d, J = 8.2 Hz, 1H), 6.01 (dd, J = 8.4, 1.7 Hz, 1H), 3.61 (dd, J = 7.1, 3.2 Hz, 1H, H_a), 3.17 (dd, J = 14.3, 3.2 Hz, 1H), 3.03 (dd, J = 14.3, 7.1 Hz, 1H), 1.90 (s, 3H), 1.84 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 199.2, 150.6, 138.6, 137.3, 135.3, 128.8, 127.6, 127.1, 123.0, 48.0, 45.1, 26.0, 19.8.

HRMS (EI) m/z: calcd. for $C_{15}H_{16}O$ ($[M\cdot]^+$): 212.1196, found: 212.1196.

Characterization of **2j'**:

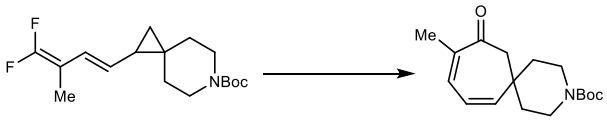
Physical Form: light yellow oil.

TLC (10:1 PE/EA, R_f): 0.5.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.30 (dd, J = 8.1, 6.5 Hz, 2H), 7.27 – 7.20 (m, 1H), 7.08 (dd, J = 7.2, 1.7 Hz, 2H), 6.55 (d, J = 7.6 Hz, 1H), 5.84 (d, J = 7.6 Hz, 1H), 3.85 (dd, J = 11.0, 2.1 Hz, 1H, H_b), 2.81 (dd, J = 16.2, 10.9 Hz, 1H), 2.55 (dd, J = 16.2, 2.1 Hz, 1H), 1.99 (s, 3H), 1.91 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 200.8, 147.8, 140.1, 136.1 (2C), 128.4, 128.2, 126.8, 122.4, 55.9, 35.6, 26.8, 20.9.

HRMS (EI) m/z: calcd. for $C_{15}H_{16}O$ ($[M\cdot]^+$): 212.1196, found: 212.1195.



1k **2k**

Run 1: Following general procedure B. Substrate: **1k** (63.4 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), flash column chromatography (silica gel, 10:1 PE/EA); product: **2k** (48.4 mg, 82%).

Run 2: Following general procedure B. Substrate: **1k** (62.2 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.8 mg, 0.01 mmol), flash column chromatography (silica gel, 10:1 PE/EA); product: **2k** (48.4 mg, 84%).

The average yield of two runs: 83%.

Physical Form: white solid.

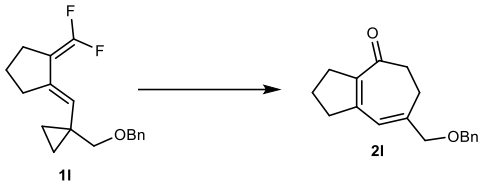
Melting Point: 87 – 89 °C.

TLC (5:1 PE/EA, R_f): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.55 (dd, J = 7.9, 1.5 Hz, 1H), 6.16 (d, J = 11.6 Hz, 1H), 5.94 (dd, J = 11.7, 8.0 Hz, 1H), 3.69 – 3.52 (m, 2H), 3.32 – 3.18 (m, 2H), 2.74 (s, 2H), 1.93 (s, 3H), 1.65 – 1.55 (m, 2H), 1.49 – 1.39 (m, 2H), 1.45 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 199.7, 154.9, 145.0, 138.3, 134.2, 124.0, 79.7, 51.6, 39.8, 33.8, 33.6, 28.5, 19.8.

HRMS (ESI) m/z: calcd. for $C_{17}H_{26}NO_3$ ($[M+H]^+$): 292.1907, found: 292.1900.



Run 1: Following general procedure B. Substrate: **1l** (58.3 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), flash column chromatography (silica gel, 10:1 PE/EA); product: **2l** (42.5 mg, 79%).

Run 2: Following general procedure B. Substrate: **1l** (57.7 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), flash column chromatography (silica gel, 10:1 PE/EA); product: **2l** (42.1 mg, 79%).

The average yield of two runs: 79%.

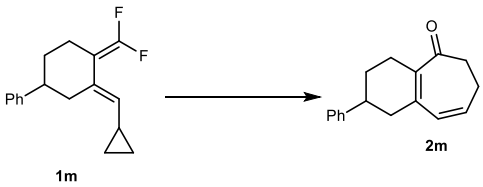
Physical Form: light yellow oil.

TLC (5:1 PE/EA, R_f): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.40 – 7.34 (m, 4H), 7.34 – 7.28 (m, 1H), 6.18 (s, 1H), 4.55 (s, 2H), 4.10 (s, 2H), 2.78 – 2.66 (m, 4H), 2.61 – 2.55 (m, 2H), 2.38 – 2.31 (m, 2H), 1.88 – 1.78 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 198.5, 151.7, 148.0, 139.0, 137.9, 128.6, 127.9, 127.8, 122.4, 74.0, 72.6, 40.5, 40.4, 33.5, 24.3, 21.3.

HRMS (EI) m/z: calcd. for $C_{18}H_{20}O_2$ ($[M\cdot]^+$): 268.1458, found: 268.1456.



Run 1: Following general procedure B, the reaction time is 1.5 h. Substrate: **1m** (51.8 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.8 mg, 0.01 mmol), flash column chromatography (silica gel, 20:1 PE/EA); product: **2m** (44.3 mg, 93%).

Run 2: Following general procedure B, the reaction time is 1.5 h. Substrate: **1m** (51.9 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.8 mg, 0.01 mmol), flash column chromatography (silica gel, 20:1 PE/EA); product: **2m** (41.8 mg, 88%).

The average yield of two runs: 90%.

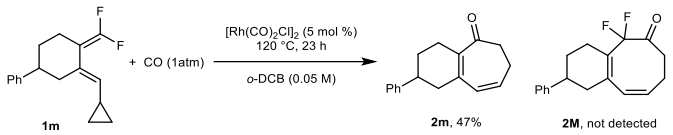
Physical Form: colorless oil.

TLC (10:1 PE/EA, R_f): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.32 (dd, J = 8.1, 6.9 Hz, 2H), 7.25 – 7.19 (m, 3H), 6.29 (ddd, J = 11.7, 6.0, 6.0 Hz, 1H), 5.83 (d, J = 11.3 Hz, 1H), 2.88 – 2.66 (m, 4H), 2.60 – 2.51 (m, 1H), 2.51 – 2.37 (m, 2H), 2.37 – 2.28 (m, 2H), 2.09 – 1.99 (m, 1H), 1.75 – 1.62 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 202.0, 146.0, 144.1, 136.0, 135.3, 131.8, 128.7, 126.9, 126.5, 43.9, 42.0, 40.2, 29.1, 26.7, 22.8.

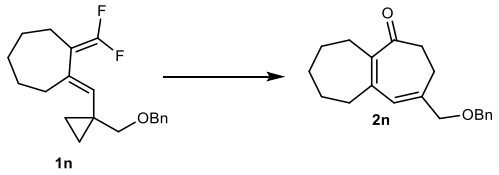
HRMS (ESI) m/z: calcd. for $C_{17}H_{19}O$ ($[M+H]^+$): 239.1430, found: 239.1430.



Run 1: To a reaction tube with **1m** (32.2 mg, 0.124 mmol) and $[Rh(CO)_2Cl]_2$ (2.5 mg, 0.0064 mmol) was added *o*-DCB (2.5 mL) under an argon atmosphere. The reaction mixture was charged with CO three times and bubbled with balloon-pressured (slightly higher than 1 atm) gas of CO at room temperature for 5 min and then stirred at 120 °C for 23 h under balloon-pressured gas of CO, 600 rpm for the magnetic stir bar. After cooling, purification of the crude product by flash column chromatography (silica gel, 100:1 to 20:1 to 5:1 PE/EA) afforded **2m** (13.9 mg, 47%). **2M**, not detected.

Run 2: Following the above procedure. Substrate: **1m** (30.4 mg, 0.117 mmol), $[Rh(CO)_2Cl]_2$ (2.3 mg, 0.0059 mmol), *o*-DCB (2.3 mL), flash column chromatography (silica gel, 20:1 PE/EA); product: **2m** (13.1 mg, 47%).

Note: the trace amounts of H_2O may come from the CO gas used.



Run 1: Following general procedure B, the reaction time is 2 h. Substrate: **1n** (63.0 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), flash column chromatography (silica gel, 50:1 to 20:1 PE/EA); product: **2n** (44.3 mg, 76%).

Run 2: Following general procedure B, the reaction time is 2 h. Substrate: **1n** (64.0 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), flash column chromatography (silica gel, 50:1 to 20:1 PE/EA); product: **2n** (44.4 mg, 75%).

The average yield of two runs: 76%.

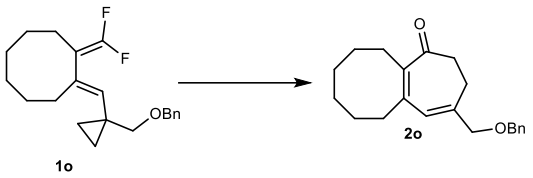
Physical Form: colorless oil.

TLC (5:1 PE/EA, R_f): 0.4.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.39 – 7.33 (m, 4H), 7.33 – 7.27 (m, 1H), 5.99 (s, 1H), 4.54 (s, 2H), 4.09 (s, 2H), 2.70 – 2.64 (m, 2H), 2.64 – 2.58 (m, 2H), 2.49 – 2.42 (m, 2H), 2.34 – 2.26 (m, 2H), 1.82 – 1.73 (m, 2H), 1.60 – 1.45 (m, 4H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 202.6, 150.8, 145.2, 141.8, 138.0, 129.3, 128.6, 127.9, 127.8, 74.1, 72.5, 44.5, 38.6, 32.1, 29.0, 26.7, 25.6, 24.0.

HRMS (EI) m/z: calcd. for $C_{20}H_{24}O_2$ ($[M\cdot]^+$): 296.1771, found: 296.1768.



Run 1: Following general procedure B, the reaction time is 4 h, solvent (3 mL). Substrate: **1o** (49.4 mg, 0.15 mmol), $[Rh(CO)_2Cl]_2$ (2.9 mg, 0.0074 mmol), flash column chromatography (silica gel, 20:1 PE/EA); product: **2o** (30.3 mg, 66%).

Run 2: Following general procedure B, the reaction time is 4 h, solvent (3 mL). Substrate: **1o** (50.2 mg, 0.15 mmol), $[Rh(CO)_2Cl]_2$ (3.0 mg, 0.0077 mmol), flash column chromatography (silica gel, 20:1 PE/EA); product: **2o** (31.5 mg, 67%).

The average yield of two runs: 66%.

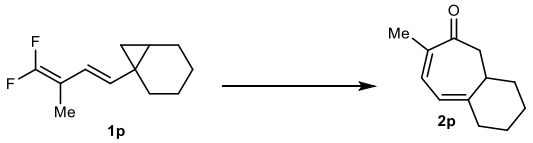
Physical Form: colorless oil.

TLC (10:1 PE/EA, R_f): 0.2.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.40 – 7.33 (m, 4H), 7.33 – 7.27 (m, 1H), 5.97 (s, 1H), 4.54 (s, 2H), 4.09 (s, 2H), 2.72 – 2.64 (m, 2H), 2.62 – 2.55 (m, 2H), 2.49 – 2.42 (m, 2H), 2.33 – 2.26 (m, 2H), 1.71 – 1.57 (m, 4H), 1.51 – 1.40 (m, 4H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 202.2, 147.7, 145.6, 138.8, 138.1, 128.6, 128.0, 127.9, 127.9, 74.3, 72.5, 44.4, 35.8, 30.7, 29.2, 28.4, 26.9, 26.4, 23.9.

HRMS (EI) m/z: calcd. for $C_{21}H_{26}O_2$ ($[M\cdot]^+$): 310.1927, found: 310.1927.



Run 1: Following general procedure B, the reaction time is 4 h. Substrate: **1p** (36.1 mg, 0.18 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), flash column chromatography (silica gel, 50:1 PE/EA); product: **2p** (15.1 mg, 47%).

Run 2: Following general procedure B, the reaction time is 4 h. Substrate: **1p** (35.4 mg, 0.18 mmol), $[Rh(CO)_2Cl]_2$ (3.8 mg, 0.01 mmol), flash column chromatography (silica gel, 50:1 PE/EA); product: **2p** (15.0 mg, 48%).

The average yield of two runs: 48%.

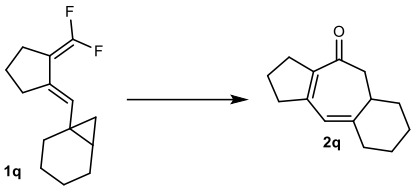
Physical Form: colorless oil.

TLC (10:1 PE/EA, R_f): 0.5.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.37 (d, J = 8.3 Hz, 1H), 5.70 (d, J = 8.4 Hz, 1H), 2.77 – 2.65 (m, 2H), 2.47 – 2.32 (m, 2H), 2.26 – 2.14 (m, 1H), 1.90 (s, 3H), 1.88 – 1.74 (m, 3H), 1.47 – 1.34 (m, 2H), 1.34 – 1.22 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 200.8, 154.5, 136.8, 134.7, 119.1, 48.7, 38.6, 37.0, 33.7, 26.8, 24.9, 19.7.

HRMS (EI) m/z: calcd. for $C_{12}H_{16}O$ ($[M\cdot]^+$): 176.1196, found: 176.1195.



Run 1: Following general procedure B, the reaction time is 4 h. Substrate: **1q** (44.7 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.8 mg, 0.01 mmol), flash column chromatography (silica gel, 100:1 to 50:1 PE/EA); product: **2q** (18.5 mg, 46%).

Run 2: Following general procedure B, the reaction time is 4 h. Substrate: **1q** (44.3 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.8 mg, 0.01 mmol), flash column chromatography (silica gel, 100:1 to 50:1 PE/EA); product: **2q** (18.5 mg, 46%).

The average yield of two runs: 46%.

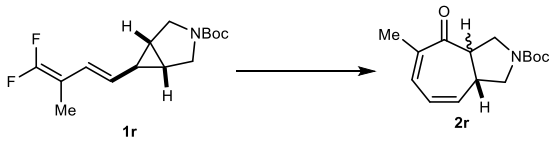
Physical Form: colorless oil.

TLC (10:1 PE/EA, R_f): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.86 (s, 1H), 2.76 – 2.62 (m, 5H), 2.61 – 2.53 (m, 1H), 2.53 – 2.39 (m, 2H), 2.30 – 2.19 (m, 1H), 1.88 – 1.71 (m, 5H), 1.58 – 1.30 (m, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 197.8, 155.7, 152.0, 137.7, 119.8, 48.2, 40.7, 37.7, 35.7, 33.4, 32.3, 25.4, 23.7, 21.5.

HRMS (EI) m/z: calcd. for $C_{14}H_{18}O$ ($[M\cdot]^+$): 202.1352, found: 202.1351.



Run 1: Following general procedure B, the reaction time is 6 h, 90 °C. Substrate: **1r** (56.1 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.8 mg, 0.01 mmol), flash column chromatography (silica gel, 10:1 PE/EA); product: **2r** (11.0 mg, 21%, d. r. = 3:2).

Run 2: Following general procedure B, the reaction time is 6 h, 90 °C. Substrate: **1r** (57.4 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), flash column chromatography (silica gel, 10:1 PE/EA); product: **2r** (9.1 mg, 17%, d. r. = 3:2).

The average yield of two runs: 19%.

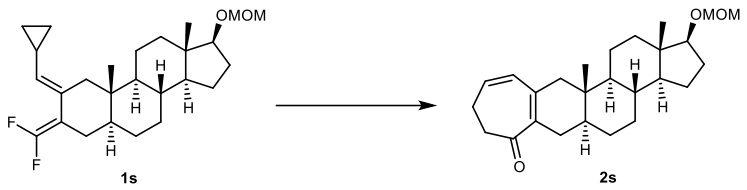
Physical Form: colorless oil.

TLC (5:1 PE/EA, R_f): 0.2.

^{1}H NMR for the major isomer (400 MHz, $CDCl_3$, δ): 6.29 (d, J = 6.7 Hz, 1H), 5.89 – 5.84 (m, 2H), 3.76 (dd, J = 10.4, 7.2 Hz, 1H), 3.58 – 3.47 (m, 2H), 3.39 – 3.18 (m, 3H), 1.95 (s, 3H), 1.47 (s, 9H).

^{13}C{^{1}H} NMR for the major isomer (101 MHz, $CDCl_3$, δ): 200.9, 154.7, 139.4, 135.1, 131.0, 125.8, 79.8, 56.3, 51.1, 47.2, 40.3, 28.6, 20.5.

HRMS (EI) m/z: calcd. for $C_{15}H_{21}O_3N$ ($[M\cdot]^+$): 263.1516, found: 263.1519.



Run 1: Following general procedure B. Substrate: **1s** (84.1 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), flash column chromatography (silica gel, 20:1 PE/EA); product: **2s** (71.4 mg, 90%).

Run 2: Following general procedure B. Substrate: **1s** (84.1 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), flash column chromatography (silica gel, 20:1 PE/EA); product: **2s** (69.8 mg, 88%).

The average yield of two runs: 89%.

Physical Form: white solid.

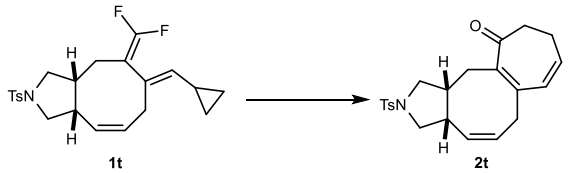
Melting Point: 141 – 143 °C.

TLC (5:1 PE/EA, R_f): 0.5.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.25 (ddd, J = 11.7, 6.0, 6.0 Hz, 1H), 5.80 (d, J = 11.3 Hz, 1H), 4.67 – 4.60 (m, 2H), 3.52 (dd, J = 8.4, 8.4 Hz, 1H), 3.35 (s, 3H), 2.75 – 2.61 (m, 2H), 2.51 – 2.40 (m, 1H), 2.35 – 2.23 (m, 2H), 2.19 (d, J = 17.4 Hz, 1H), 2.08 – 1.93 (m, 3H), 1.91 – 1.83 (m, 1H), 1.75 – 1.66 (m, 1H), 1.64 – 1.48 (m, 4H), 1.38 (ddd, J = 23.5, 12.0, 3.8 Hz, 2H), 1.32 – 1.19 (m, 3H), 1.13 (ddd, J = 12.6, 12.6, 4.3 Hz, 1H), 1.00 – 0.81 (m, 2H), 0.78 (s, 3H), 0.76 – 0.66 (m, 1H), 0.73 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 202.1, 143.6, 135.5, 134.4, 132.4, 96.1, 86.8, 55.2, 54.0, 51.0, 48.6, 44.1, 42.7, 40.9, 37.4, 35.4, 34.8, 31.3, 30.6, 28.1, 28.0, 23.4, 22.6, 20.9, 12.1, 11.9.

HRMS (EI) m/z: calcd. for $C_{26}H_{38}O_3$ ($[M\cdot]^+$): 398.2815, found: 398.2816.



Run 1: Following general procedure B, solvent (2 mL). Substrate: **1t** (40.3 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol), flash column chromatography (silica gel, 5:1 PE/EA); product: **2t** (26.2 mg, 69%).

Run 2: Following general procedure B, solvent (2 mL). Substrate: **1t** (40.1 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol), flash column chromatography (silica gel, 5:1 PE/EA); product: **2t** (26.5 mg, 70%).

The average yield of two runs: 70%.

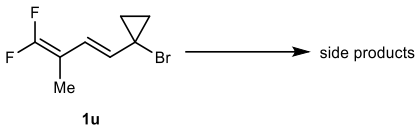
Physical Form: colorless oil.

TLC (3:1 PE/EA, R_f): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.71 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 7.9 Hz, 2H), 6.31 (ddd, J = 11.8, 6.1, 6.1 Hz, 1H), 5.94 (d, J = 11.3 Hz, 1H), 5.59 – 5.49 (m, 1H), 5.07 (dddd, J = 12.3, 4.9, 2.1, 2.1 Hz, 1H), 3.43 – 3.31 (m, 3H), 3.05 (dd, J = 9.3, 4.6 Hz, 1H), 2.94 (dd, J = 10.5, 9.3 Hz, 1H), 2.88 – 2.79 (m, 3H), 2.74 – 2.57 (m, 2H), 2.43 (s, 3H), 2.37 – 2.26 (m, 2H), 2.26 – 2.16 (m, 2H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 201.1, 145.9, 143.4, 139.2, 136.7, 134.5, 133.2, 130.2, 129.8, 129.6, 127.5, 54.9, 50.7, 45.5, 44.1, 41.3, 38.3, 29.4, 22.5, 21.6.

HRMS (ESI) m/z: calcd. for $C_{22}H_{26}NO_3S$ ($[M+H]^+$): 384.1628, found: 384.1628.

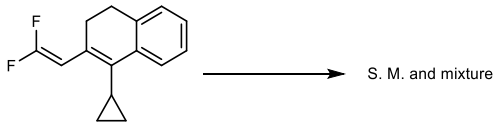


1u

Following general procedure C. Substrate: **1u** (44.6 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), gave side products.

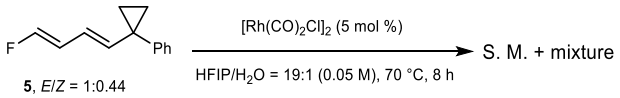
1v

Following general procedure C. Substrate: **1v** (41.2 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), from 70 °C to 100 °C, gave mixture.



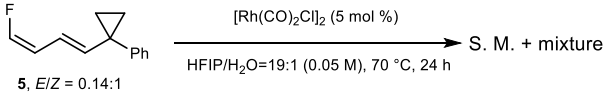
1w

Following general procedure B. Substrate: **1w** (46.0 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.8 mg, 0.01 mmol), from 70 °C to 90 °C, gave starting material and mixture.



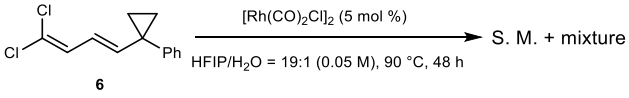
5, *E*/*Z* = 1:0.44

Following general procedure A. Substrate: **5** (18.8 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (1.8 mg, 0.005 mmol), gave starting material and mixture.



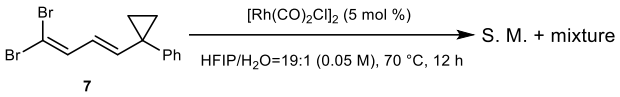
5, *E*/*Z* = 0.14:1

Following general procedure A. Substrate: **5** (37.8 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), gave starting material and mixture.

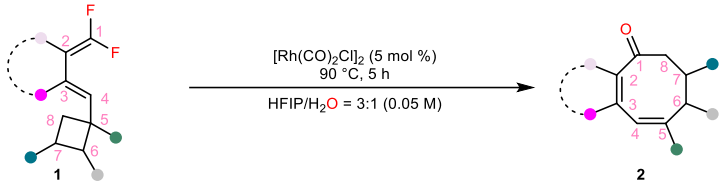


6

Following general procedure A. Substrate: **6** (23.5 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (1.8 mg, 0.005 mmol), gave starting material and mixture.

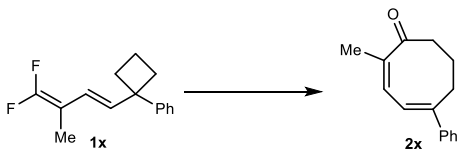


Following general procedure A. Substrate: **7** (32.3 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol), gave starting material and mixture.



Procedure A: To a 25 mL reaction tube with **1** (0.2 mmol, 1 equiv.) and $[Rh(CO)_2Cl]_2$ (3.9 mg, 5 mol %) was added HFIP (3.0 mL), and H_2O (1.0 mL) sequentially under argon atmosphere. The reaction mixture was charged with a flap plug and then stirred at 90 °C for 5 h, 600 revolutions per minute (rpm) for the magnetic stir bar. After cooling, the solvent was evaporated and the residue was purified by flash column chromatography (silica gel) to afford **2**.

Procedure B: To a 25 mL reaction tube with **1** (0.2 mmol, 1 equiv.) and $[Rh(CO)_2Cl]_2$ (3.9 mg, 5 mol %) was added HFIP (3.0 mL), and H_2O (1.0 mL) sequentially under argon atmosphere. The reaction mixture was charged with a flap plug and then stirred at 90 °C for 5 h, 600 revolutions per minute (rpm) for the magnetic stir bar. After cooling, the reaction system was then quenched with aqueous $NaHCO_3$ solution, and extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel) to afford **2**.



Run 1: Following general procedure A, solvent (4 mL). Substrate: **1x** (47.9 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), flash column chromatography (silica gel, 20:1 PE/EA); product: **2x** (40.0 mg, 92%).

Run 2: Following general procedure A, solvent (4 mL). Substrate: **1x** (46.7 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), flash column chromatography (silica gel, 20:1 PE/EA); product: **2x** (38.9 mg, 92%).

The average yield of two runs: 92%.

Physical Form: white solid.

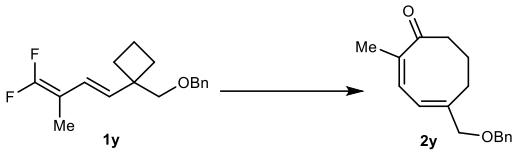
Melting Point: 68 – 70 °C.

TLC (10:1 PE/EA, R_f): 0.4.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.53 – 7.47 (m, 2H), 7.41 – 7.35 (m, 2H), 7.35 – 7.29 (m, 1H), 6.68 (d, J = 6.4 Hz, 1H), 6.57 (d, J = 6.3 Hz, 1H), 2.77 – 2.61 (m, 4H), 2.25 – 2.15 (m, 2H), 1.98 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 206.0, 147.0, 141.5, 137.6, 136.4, 128.8, 128.2, 126.3, 125.9, 38.7, 33.7, 30.0, 20.5.

HRMS (EI) m/z: calcd. for $C_{15}H_{16}O$ ($[M\cdot]^+$): 212.1196, found: 212.1192.



Run 1: Following general procedure A, solvent (4 mL), the reaction time is 2.5 h. Substrate: **1y** (55.3 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.8 mg, 0.01 mmol), flash column chromatography (silica gel, 50:1 to 20:1 PE/EA); product: **2y** (37.8 mg, 74%).

Run 2: Following general procedure A, solvent (4 mL), the reaction time is 2.5 h. Substrate: **1y** (55.1 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.8 mg, 0.01 mmol), flash column chromatography (silica gel, 50:1 to 20:1 PE/EA); product: **2y** (35.6 mg, 70%).

The average yield of two runs: 72%.

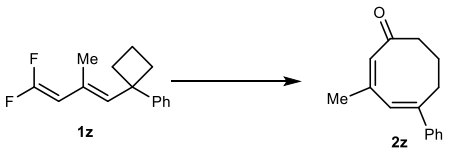
Physical Form: colorless oil.

TLC (10:1 PE/EA, R_f): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.40 – 7.32 (m, 4H), 7.32 – 7.27 (m, 1H), 6.50 (dq, J = 6.2, 1.5 Hz, 1H), 6.28 (dd, J = 6.2, 1.2 Hz, 1H), 4.55 (s, 2H), 4.10 (s, 2H), 2.64 (t, J = 6.5 Hz, 2H), 2.24 – 2.18 (m, 2H), 2.14 – 2.06 (m, 2H), 1.92 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 206.5, 145.5, 138.1, 137.6, 135.1, 128.6, 127.9, 127.7, 125.0, 73.8, 72.6, 38.8, 33.2, 28.0, 20.5.

HRMS (EI) m/z: calcd. for $C_{17}H_{20}O_2$ ($[M\cdot]^+$): 256.1458, found: 256.1456.



Run 1: Following general procedure A, solvent (2 mL), the reaction time is 2 h. Substrate: **1z** (24.7 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol), flash column chromatography (silica gel, 20:1 PE/EA); product: **2z** (17.8 mg, 79%).

Run 2: Following general procedure A, solvent (2 mL), the reaction time is 2 h. Substrate: **1z** (23.8 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (1.9 mg, 0.005 mmol), flash column chromatography (silica gel, 20:1 PE/EA); product: **2z** (17.5 mg, 81%).

The average yield of two runs: 80%.

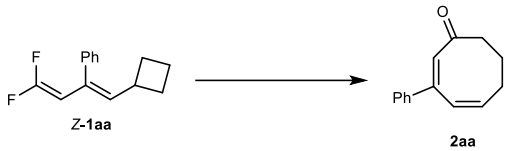
Physical Form: colorless oil.

TLC (10:1 PE/EA, R_f): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.55 – 7.48 (m, 2H), 7.43 – 7.31 (m, 3H), 6.48 (s, 1H), 6.00 (d, J = 1.2 Hz, 1H), 2.79 – 2.61 (m, 4H), 2.15 – 2.07 (m, 2H), 2.05 (d, J = 1.3 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 204.3, 149.5, 146.8, 141.1, 129.9, 128.8, 128.5, 128.3, 126.5, 38.4, 31.3, 30.3, 26.8.

HRMS (EI) m/z: calcd. for $C_{15}H_{16}O$ ($[M\cdot]^+$): 212.1196, found: 212.1190.



Run 1: Following general procedure A, solvent (4 mL), the reaction time is 1 h. Substrate: *Z*-**1aa** (43.6 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), flash column chromatography (silica gel, 20:1 PE/EA); product: **2aa** (28.7 mg, 73%).

Run 2: Following general procedure A, solvent (4 mL), the reaction time is 1 h. Substrate: *Z*-**1aa** (43.3 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.8 mg, 0.01 mmol), flash column chromatography (silica gel, 20:1 PE/EA); product: **2aa** (29.7 mg, 76%).

The average yield of two runs: 74%.

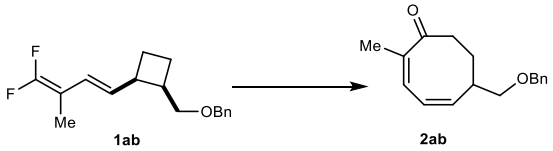
Physical Form: light yellow oil.

TLC (10:1 PE/EA, R_f): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.45 – 7.40 (m, 2H), 7.40 – 7.35 (m, 3H), 6.52 – 6.42 (m, 2H), 6.33 (s, 1H), 2.82 – 2.65 (m, 2H), 2.40 – 2.29 (m, 2H), 2.16 – 2.03 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 204.9, 148.4, 141.1, 139.0, 130.2, 129.5, 129.4, 128.6, 127.9, 38.6, 31.6, 26.9.

The spectrum of **2aa** is consistent with the literature.[10]



Run 1: Following general procedure A, solvent (4 mL), the reaction time is 25 h. Substrate: **1ab** (55.3 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.8 mg, 0.01 mmol), flash column chromatography (silica gel, 50:1 to 20:1 PE/EA); product: **2ab** (33.4 mg, 66%).

Run 2: Following general procedure A, solvent (4 mL), the reaction time is 25 h. Substrate: **1ab** (55.8 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), flash column chromatography (silica gel, 50:1 to 20:1 PE/EA); product: **2ab** (33.1 mg, 64%).

The average yield of two runs: 65%.

Physical Form: colorless oil.

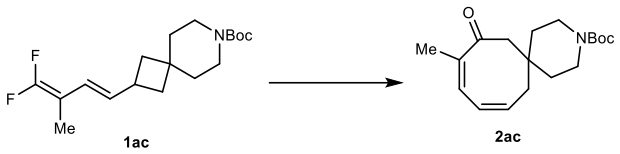
TLC (10:1 PE/EA, R_f): 0.2.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.37 – 7.27 (m, 5H), 6.48 (dd, J = 5.9, 1.6 Hz, 1H), 6.25 (dd, J = 11.5, 5.9 Hz, 1H), 6.01 (dd, J = 11.5, 8.3 Hz, 1H), 4.49 (s, 2H), 3.45 – 3.34 (m, 2H), 3.04 (ddd, J =

14.7, 11.2, 5.8 Hz, 1H), 2.74 – 2.62 (m, 1H), 2.29 – 2.16 (m, 2H), 1.91 (s, 3H), 1.76 – 1.62 (m, 1H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 206.3, 139.0, 138.3, 137.7, 135.2, 128.7, 128.5, 127.8, 127.7, 73.4, 73.3, 38.3 (2C), 36.4, 20.4.

HRMS (ESI) m/z: calcd. for $C_{17}H_{21}O_2$ ($[M+H]^+$): 257.1536, found: 257.1536.



Run 1: Following general procedure A, solvent (2 mL). Substrate: **1ac** (32.4 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (1.9 mg, 0.005 mmol), flash column chromatography (silica gel, 10:1 PE/EA); product: **2ac** (4.2 mg, 14%).

Run 2: Following general procedure A, solvent (2 mL). Substrate: **1ac** (32.8 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol), flash column chromatography (silica gel, 10:1 PE/EA); product: **2ac** (4.3 mg, 14%).

The average yield of two runs: 14%.

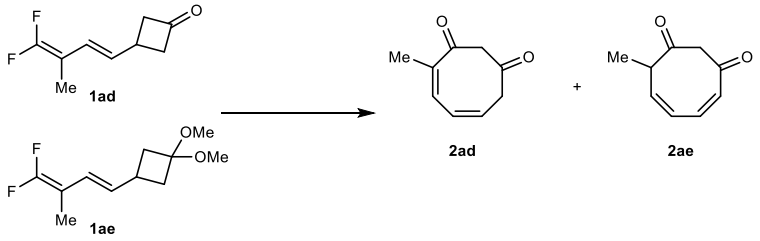
Physical Form: colorless oil.

TLC (5:1 PE/EA, R_f): 0.3.

^1H NMR (400 MHz, $CDCl_3$, δ): 6.51 (dd, J = 6.0, 1.6 Hz, 1H), 6.30 (ddd, J = 11.5, 6.0, 1.0 Hz, 1H), 6.22 (dt, J = 11.3, 8.1 Hz, 1H), 3.61 – 3.48 (m, 2H), 3.41 – 3.26 (m, 2H), 2.55 (s, 2H), 2.02 (d, J = 8.0 Hz, 2H), 1.93 (s, 3H), 1.64 – 1.52 (m, 2H), 1.51 – 1.40 (m, 2H), 1.46 (s, 9H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 203.5, 155.1, 138.8, 135.9, 134.4, 130.0, 79.6, 47.6, 46.8, 39.9, 37.8, 35.3, 28.6, 20.7.

HRMS (ESI) m/z: calcd. for $C_{18}H_{28}O_3$ ($[M+H]^+$): 306.2064, found: 306.2060.



From **1ad**:

Run 1: Following general procedure A, solvent (4 mL). Substrate: **1ad** (34.8 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), flash column chromatography (silica gel, 10:1 PE/EA); product: (18.8 mg, 62%, **2ad**:**2ae** = 8.5:1).

Run 2: Following general procedure A, solvent (4 mL). Substrate: **1ad** (34.7 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.8 mg, 0.01 mmol), flash column chromatography (silica gel, 10:1 PE/EA); product: (17.5 mg, 58%, **2ad**:**2ae** = 8.5:1).

The average yield of two runs: 60%.

From **1ae**:

Run 1: Following general procedure A, solvent (4 mL). Substrate: **1ae** (43.7 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.8 mg, 0.01 mmol), flash column chromatography (silica gel, 10:1 PE/EA); product: (16.6 mg, 55%, **2ad**:**2ae** = 8.1:1).

Run 2: Following general procedure A, solvent (4 mL). Substrate: **1ae** (44.2 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), flash column chromatography (silica gel, 10:1 PE/EA); product: (16.6 mg, 55%, **2ad**:**2ae** = 8.1:1).

The average yield of two runs: 55%.

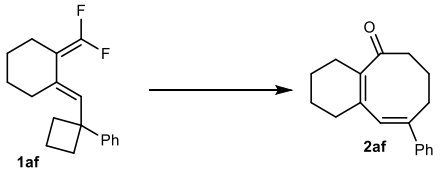
Physical Form: yellow oil.

TLC (5:1 PE/EA, R_f): 0.3.

^{1}H NMR for the major isomer (400 MHz, $CDCl_3$, δ): 6.85 (d, J = 6.0 Hz, 1H), 6.49 (dd, J = 11.4, 6.3 Hz, 1H), 6.20 (dt, J = 11.3, 7.9 Hz, 1H), 3.85 (s, 2H), 3.16 (d, J = 7.9 Hz, 2H), 2.06 (s, 3H).

^{13}C{^{1}H} NMR for the major isomer (101 MHz, $CDCl_3$, δ): 202.5, 193.7, 140.0, 135.1, 131.1, 130.1, 57.2, 46.2, 21.2.

HRMS (ESI) m/z: calcd. for $C_9H_{11}O_2$ ($[M+H]^+$): 151.0754, found: 151.0751.



Run 1: Following general procedure A, solvent (2 mL), the reaction time is 1 h. Substrate: **1af** (27.7 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (1.9 mg, 0.005 mmol), flash column chromatography (silica gel, 10:1 PE/EA); product: **2af** (20.7 mg, 81%).

Run 2: Following general procedure A, solvent (2 mL), the reaction time is 1 h. Substrate: **1af** (27.3 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (1.8 mg, 0.005 mmol), flash column chromatography (silica gel, 10:1 PE/EA); product: **2af** (21.0 mg, 84%).

The average yield of two runs: 82%.

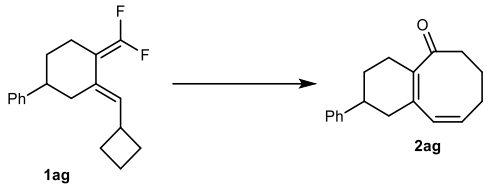
Physical Form: light yellow oil.

TLC (10:1 PE/EA, R_f): 0.5.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.52 – 7.46 (m, 2H), 7.37 (dd, J = 8.3, 6.5 Hz, 2H), 7.34 – 7.28 (m, 1H), 6.45 (s, 1H), 2.89 – 2.55 (m, 4H), 2.51 – 2.39 (m, 2H), 2.37 – 2.28 (m, 2H), 2.16 – 1.99 (m, 2H), 1.70 – 1.56 (m, 4H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 205.2, 146.6, 143.9, 141.8, 135.4, 130.7, 128.7, 128.0, 126.4, 38.6, 34.2, 31.9, 30.1, 25.7, 22.6, 22.4.

HRMS (ESI) m/z: calcd. for $C_{18}H_{21}O$ ($[M+H]^+$): 253.1587, found: 253.1587.



1ag 2ag

Run 1: Following general procedure A, solvent (4 mL), the reaction time is 1 h. Substrate: **1ag** (54.7 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), flash column chromatography (silica gel, 50:1 to 20:1 PE/EA); product: **2ag** (41.9 mg, 83%).

Run 2: Following general procedure A, solvent (4 mL), the reaction time is 1 h. Substrate: **1ag** (54.7 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), flash column chromatography (silica gel, 50:1 to 20:1 PE/EA); product: **2ag** (41.2 mg, 82%).

The average yield of two runs: 82%.

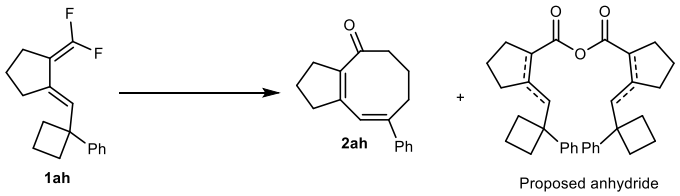
Physical Form: colorless oil.

TLC (10:1 PE/EA, R_f): 0.4.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.35 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 6.15 (d, J = 11.6 Hz, 1H), 6.04 (dt, J = 11.5, 8.2 Hz, 1H), 2.87 – 2.72 (m, 3H), 2.65 – 2.46 (m, 2H), 2.43 – 2.27 (m, 2H), 2.20 – 2.10 (m, 2H), 2.10 – 1.99 (m, 2H), 1.98 – 1.88 (m, 1H), 1.73 – 1.59 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 206.1, 145.9, 144.0, 135.1, 134.2, 133.3, 128.6, 126.9, 126.4, 41.6, 40.0, 38.3, 32.3, 29.4, 26.7, 26.4.

HRMS (EI) m/z: calcd. for $C_{18}H_{20}O$ ($[M\cdot]^+$): 252.1509, found: 252.1503.



1ah 2ah Proposed anhydride

Run 1: Following general procedure B, solvent (4 mL), the reaction time is 6 h. Substrate: **1ah** (52.8 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), flash column chromatography (silica gel, 50:1 PE/EA); product: **2ah** (14.4 mg, 30%). Proposed anhydride was detected by the crude ^{1}H NMR as the side product.

Run 2: Following general procedure B, solvent (4 mL), the reaction time is 6 h. Substrate: **1ah** (52.6 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), flash column chromatography (silica gel, 50:1 PE/EA); product: **2ah** (12.6 mg, 26%). Proposed anhydride was detected by the crude ^{1}H NMR as the side product.

The average yield of two runs: 28%.

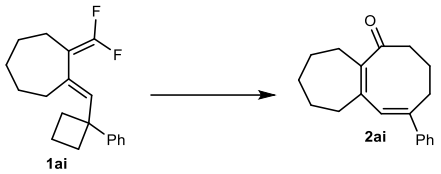
Physical Form: colorless oil.

TLC (10:1 PE/EA, R_f): 0.5.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.51 (d, J = 7.4 Hz, 2H), 7.41 – 7.29 (m, 3H), 6.60 (s, 1H), 2.80 – 2.74 (m, 2H), 2.74 – 2.63 (m, 6H), 2.17 (tt, J = 6.8, 6.8 Hz, 2H), 1.87 (tt, J = 7.7, 7.7 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 202.7, 151.8, 146.8, 141.3, 140.3, 128.8, 128.3, 126.4, 125.4, 40.7, 39.0, 33.7, 33.0, 30.5, 21.9.

HRMS (EI) m/z: calcd. for $C_{17}H_{18}O$ ([M·]$^+$): 238.1352, found: 238.1350.



Run 1: Following general procedure B, solvent (4 mL), the reaction time is 1 h. Substrate: **1ai** (57.4 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), flash column chromatography (silica gel, 100:1 PE/EA); product: **2ai** (29.8 mg, 56%).

Run 2: Following general procedure B, solvent (4 mL), the reaction time is 1 h. Substrate: **1ai** (56.6 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.8 mg, 0.01 mmol), flash column chromatography (silica gel, 100:1 PE/EA); product: **2ai** (27.9 mg, 53%).

The average yield of two runs: 54%.

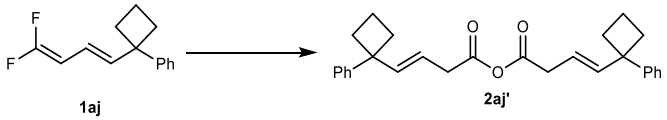
Physical Form: colorless oil.

TLC (10:1 PE/EA, R_f): 0.6.

^{1}H NMR (400 MHz, C_6D_6, δ): 7.26 – 7.20 (m, 2H), 7.16 – 7.08 (m, 3H), 6.31 (s, 1H), 3.05 – 2.52 (m, 4H), 2.44 (t, J = 6.7 Hz, 2H), 2.27 – 2.15 (m, 2H), 2.01 – 1.67 (m, 2H), 1.63 – 1.53 (m, 2H), 1.48 (tt, J = 5.7, 5.7 Hz, 2H), 1.39 – 1.27 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, δ): 202.5, 151.0, 143.8, 142.0, 141.9, 131.8, 128.8, 128.3, 126.7, 38.2, 38.2, 32.2, 31.9, 29.6, 27.9, 27.1, 25.6.

HRMS (ESI) m/z: calcd. for $C_{19}H_{23}O$ ([M+H]$^+$): 267.1743, found: 267.1743.



Following general procedure B, solvent (4 mL). Substrate: **1aj** (44.1 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), flash column chromatography (silica gel, 7:1 to 5:1 to 2:1 PE/EA); side product: **2aj'** (14.5 mg, 35%).

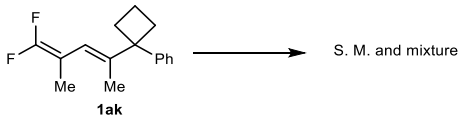
Physical Form: colorless oil.

TLC (10:1 PE/EA, R_f): 0.1.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.31 (dd, J = 7.6, 7.6 Hz, 4H), 7.21 – 7.13 (m, 6H), 5.91 (d, J = 15.4 Hz, 2H), 5.43 (dt, J = 15.4, 7.0 Hz, 2H), 3.09 (dd, J = 7.0, 1.4 Hz, 4H), 2.51 – 2.41 (m, 4H), 2.38 – 2.30 (m, 4H), 2.12 – 2.00 (m, 2H), 1.89 – 1.78 (m, 2H).

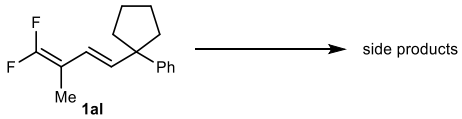
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 177.7, 148.7, 142.7, 128.4, 126.0, 125.8, 117.7, 49.0, 37.7, 33.2, 16.3.

HRMS (ESI) m/z: calcd. for $C_{28}H_{30}NaO_3$ ([M+Na]$^+$): 437.2087, found: 437.2093.



1ak

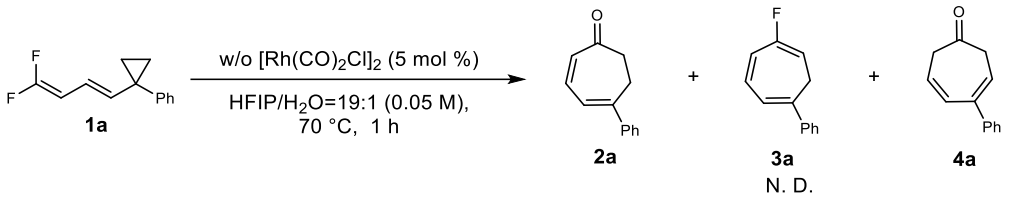
Following general procedure A, solvent (2 mL). Substrate: **1ak** (25.0 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (1.9 mg, 0.005 mmol), from 90 °C to 120 °C, gave starting material and mixture.



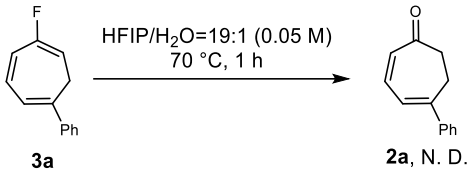
1al

Following general procedure A, solvent (4 mL). Substrate: **1al** (50.5 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), gave side products.

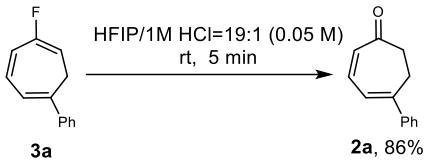
5. Control Experiments



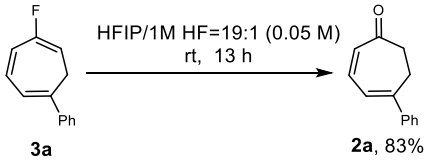
To a 25 mL reaction tube with **1a** (24.5 mg, 0.12 mmol), and $[Rh(CO)_2Cl]_2$ (0.0 mg, 0.00 mmol) was added HFIP (1.9 mL) and H_2O (0.1 mL) sequentially under air atmosphere. The reaction mixture was charged with a flap plug and then stirred at 70 °C for 1 h, 600 revolutions per minute (rpm) for the magnetic stir bar. After removing the solvent, 1,3,5-trimethoxybenzene (5.9 mg, 99.82% purity, internal standard) and $CDCl_3$ were added to measure ^1H NMR: **2a**, **3a**, **4a**, not detected.



To a 25 mL reaction tube with **3a** (18.3 mg, 0.1 mmol) was added HFIP (1.9 mL) and H_2O (0.1 mL) sequentially under air atmosphere. The reaction mixture was charged with a flap plug and then stirred at 70 °C for 1 h, 600 revolutions per minute (rpm) for the magnetic stir bar. Monitored by TLC: **2a**, not detected.

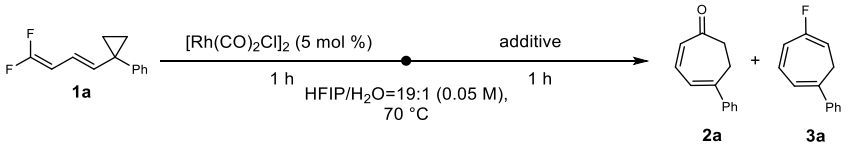


To a 25 mL reaction tube with **3a** (18.3 mg, 0.1 mmol) was added HFIP (1.9 mL) and 1 M HCl (0.1 mL) sequentially under air atmosphere. The reaction mixture was charged with a flap plug and then stirred at rt for 5 min. The reaction system was then quenched with aqueous $NaHCO_3$ solution, and extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 25:1 PE/EA) to afford **2a** (15.6 mg, 86%).



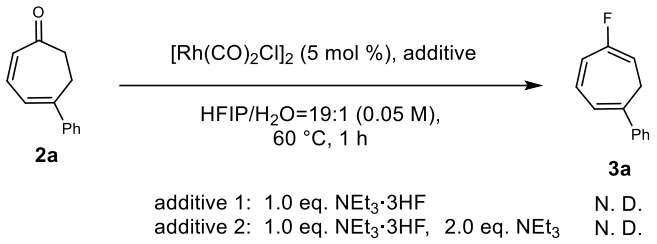
To a 25 mL reaction flask with **3a** (19.3 mg, 0.1 mmol) was added HFIP (1.9 mL) and 1 M HF (0.1

mL) sequentially under air atmosphere. The reaction mixture was charged with a flap plug and then stirred at rt for 13 h. The reaction system was concentrated by rotary evaporation. The yield was measured by ^{1}H NMR and 1,3,5-trimethoxybenzene was used as the internal standard.



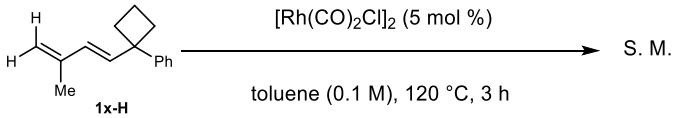
To a 25 mL reaction tube with **1a** (20.7 mg, 0.1 mmol), and $[Rh(CO)_2Cl]_2$ (1.8 mg, 0.005 mmol) was added HFIP (1.9 mL) and H_2O (0.1 mL) sequentially under air atmosphere. The reaction mixture was charged with a flap plug and then stirred at 70 °C for 1 h, then NEt_3 (14 μL) was added, and stirred at 70 °C for 1 h, 600 revolutions per minute (rpm) for the magnetic stir bar. After removing the solvent, 1,3,5-trimethoxybenzene (5.6 mg, 99.82% purity, internal standard) and $CDCl_3$ were added to measure ^{1}H NMR: **2a**, 92%, **3a**, not detected.

To a 25 mL reaction tube with **1a** (21.4 mg, 0.1 mmol), and $[Rh(CO)_2Cl]_2$ (1.9 mg, 0.005 mmol) was added HFIP (1.9 mL) and H_2O (0.1 mL) sequentially under air atmosphere. The reaction mixture was charged with a flap plug and then stirred at 70 °C for 1 h, then NEt_3 (42 μL) was added, and stirred at 70 °C for 1 h, 600 revolutions per minute (rpm) for the magnetic stir bar. After removing the solvent, 1,3,5-trimethoxybenzene (4.9 mg, 99.82% purity, internal standard) and $CDCl_3$ were added to measure ^{1}H NMR: **2a**, 86%, **3a**, not detected.



To a 25 mL reaction tube with **2a** (18.1 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (1.9 mg, 0.005 mmol) and NEt_3·3HF (16.3 μL) was added HFIP (1.9 mL) and H_2O (0.1 mL) sequentially under air atmosphere. The reaction mixture was charged with a flap plug and then stirred at 70 °C for 1 h, 600 revolutions per minute (rpm) for the magnetic stir bar. Monitored by TLC: **3a**, not detected.

To a 25 mL reaction tube with **2a** (18.8 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol), NEt_3·3HF (16.3 μL) and NEt_3 (28 μL) was added HFIP (1.9 mL) and H_2O (0.1 mL) sequentially under air atmosphere. The reaction mixture was charged with a flap plug and then stirred at 70 °C for 1 h, 600 revolutions per minute (rpm) for the magnetic stir bar. Monitored by TLC: **3a**, not detected.

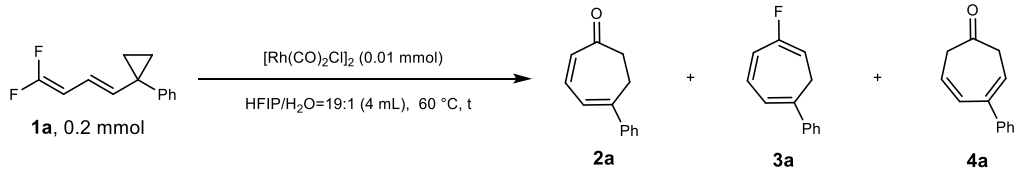


To a 25 mL reaction tube with **1x-H** (40.3 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.8 mg, 0.01 mmol) was

added toluene (2 mL) sequentially under argon atmosphere. The reaction mixture was stirred at 120 °C for 3 h, 600 revolutions per minute (rpm) for the magnetic stir bar, and rhodium black was formed. ^{1}H NMR crude spectrum: only starting material was observed.

6. Visual Kinetic Analysis

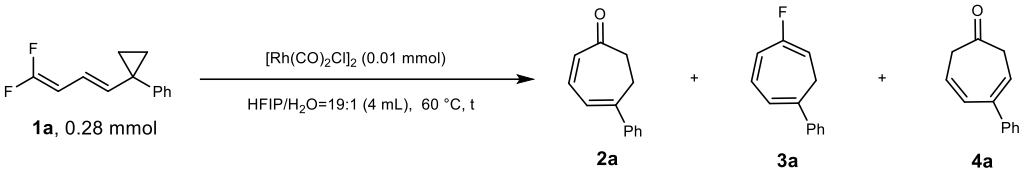
We used visual kinetic analysis[13] developed by Burés to understand the present reaction.



Concentration Profile Measurements. To a 25 mL reaction tube with **1a** (41.2 mg, 0.2 mmol), 1,3,5-trimethoxybenzene (11.0 mg, 99.82% purity, internal standard) and $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol) was added HFIP (3.8 mL) and H_2O (0.2 mL) sequentially under air atmosphere. The reaction mixture was charged with a flap plug and then stirred at 60 °C for 2 h, 600 revolutions per minute (rpm) for the magnetic stir bar. Every 20 min, 0.5–0.6 mL solution was taken out, filtered through silica gel, and washed with EA. After removing the solvent, 0.5 mL of $CDCl_3$ was added to measure ^1H NMR.

Table S10. Kinetic data for 1,5-migratory ring expansion of **1a** (n_0 = 0.2 mmol).

t/min	**1a** (mM)	**2a** (mM)	**3a** (mM)	**2a**+**3a** (mM)	$[n_{1a}]^0*dt$	sum($[n_{1a}]^0*dt$)
20	30.4	1.5	7.9	9.3	20	20
40	21.1	10.3	10.3	20.6	20	40
60	14.7	27.0	5.4	32.4	20	60
80	4.4	37.3	2.0	39.3	20	80
100	0.0	46.6	0.0	46.6	20	100
120	0.0	47.6	0.0	47.6	20	120

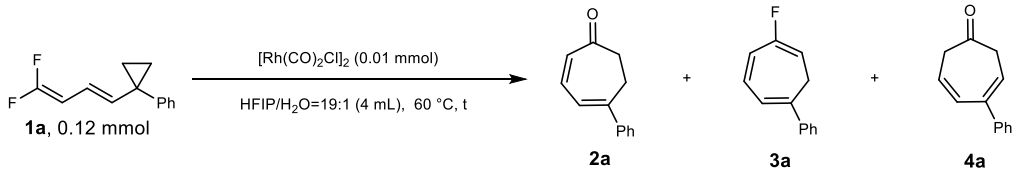


Concentration Profile Measurements. To a 25 mL reaction tube with **1a** (58.0 mg, 0.28 mmol), 1,3,5-trimethoxybenzene (11.4 mg, 99.82% purity, internal standard) and $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol) was added HFIP (3.8 mL) and H_2O (0.2 mL) sequentially under air atmosphere. The reaction mixture was charged with a flap plug and then stirred at 60 °C for 2 h, 600 revolutions per minute (rpm) for the magnetic stir bar. Every 20 min, 0.5–0.6 mL solution was taken out, filtered through silica gel, and washed with EA. After removing the solvent, 0.5 mL of $CDCl_3$ was added to measure ^1H NMR.

Table S11. Kinetic data for 1,5-migratory ring expansion of **1a** (n_0 = 0.28 mmol).

t/min	**1a** (mM)	**2a** (mM)	**3a** (mM)	**2a**+**3a** (mM)	$[n_{1a}]^0*dt$	sum($[n_{1a}]^0*dt$)
20	47.3	2.0	8.1	10.2	20	20

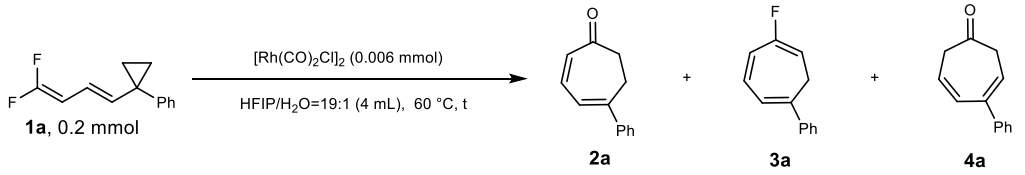
40	38.6	12.7	8.1	20.8	20	40
60	30.5	29.0	3.6	32.6	20	60
80	20.3	40.7	1.5	42.2	20	80
100	13.2	52.4	1.0	53.4	20	100
120	6.1	61.5	0.0	61.5	20	120



Concentration Profile Measurements. To a 25 mL reaction tube with **1a** (25.4 mg, 0.12 mmol), 1,3,5-trimethoxybenzene (10.9 mg, 99.82% purity, internal standard) and $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol) was added HFIP (3.8 mL) and H_2O (0.2 mL) sequentially under air atmosphere. The reaction mixture was charged with a flap plug and then stirred at 60 °C for 2 h, 600 revolutions per minute (rpm) for the magnetic stir bar. Every 20 min, 0.5–0.6 mL solution was taken out, filtered through silica gel, and washed with EA. After removing the solvent, 0.5 mL of $CDCl_3$ was added to measure ^1H NMR.

Table S12. Kinetic data for 1,5-migratory ring expansion of **1a** (n_0 = 0.12 mmol).

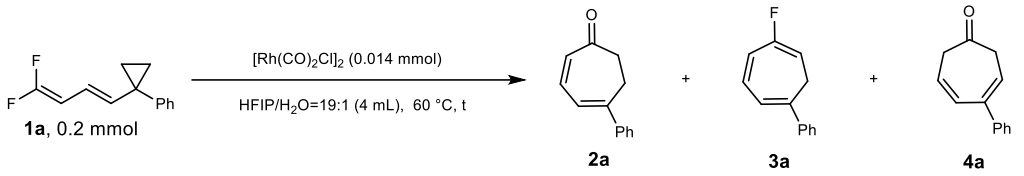
t/min	**1a** (mM)	**2a** (mM)	**3a** (mM)	**2a**+**3a** (mM)	$[n_{1a}]$^0*dt	sum($[n_{1a}]$^0*dt)
20	15.6	1.5	7.8	9.2	20	20
40	7.3	8.3	9.7	18.0	20	40
60	1.0	20.4	4.9	25.3	20	60
80	0.5	27.2	1.0	28.2	20	80
100	0.0	28.7	0.0	28.7	20	100
120	0.0	29.2	0.0	29.2	20	120



Concentration Profile Measurements. To a 25 mL reaction tube with **1a** (41.0 mg, 0.2 mmol), 1,3,5-trimethoxybenzene (11.0 mg, 99.82% purity, internal standard) and $[Rh(CO)_2Cl]_2$ (2.4 mg, 0.006 mmol) was added HFIP (3.8 mL) and H_2O (0.2 mL) sequentially under air atmosphere. The reaction mixture was charged with a flap plug and then stirred at 60 °C for 2 h, 600 revolutions per minute (rpm) for the magnetic stir bar. Every 20 min, 0.5–0.6 mL solution was taken out, filtered through silica gel, and washed with EA. After removing the solvent, 0.5 mL of $CDCl_3$ was added to measure ^1H NMR.

Table S13. Kinetic data for 1,5-migratory ring expansion of **1a** ([Rh] = 0.006 mmol).

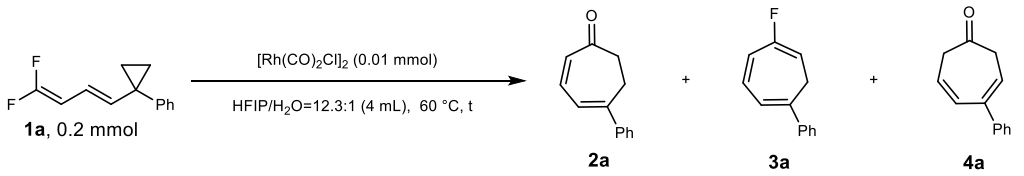
t/min	**1a** (mM)	**2a** (mM)	**3a** (mM)	**2a**+**3a** (mM)	t[Rh]^0.5
20	33.4	1.5	6.4	7.9	24.49489743
40	25.0	7.4	8.8	16.2	48.98979486
60	17.7	19.1	5.4	24.5	73.48469228
80	11.3	30.4	2.9	33.3	97.97958971
100	6.9	38.3	1.5	39.8	122.4744871
120	2.9	43.2	1.5	44.7	146.9693846



Concentration Profile Measurements. To a 25 mL reaction tube with **1a** (41.1 mg, 0.2 mmol), 1,3,5-trimethoxybenzene (11.0 mg, 99.82% purity, internal standard) and $[Rh(CO)_2Cl]_2$ (5.4 mg, 0.014 mmol) was added HFIP (3.8 mL) and H_2O (0.2 mL) sequentially under air atmosphere. The reaction mixture was charged with a flap plug and then stirred at 60 °C for 2 h, 600 revolutions per minute (rpm) for the magnetic stir bar. Every 20 min, 0.5–0.6 mL solution was taken out, filtered through silica gel, and washed with EA. After removing the solvent, 0.5 mL of $CDCl_3$ was added to measure ^1H NMR.

Table S14. Kinetic data for 1,5-migratory ring expansion of **1a** ([Rh] = 0.014 mmol).

t/min	**1a** (mM)	**2a** (mM)	**3a** (mM)	**2a**+**3a** (mM)	t[Rh]^0.5
20	27.5	3.9	10.3	14.2	37.41657387
40	14.2	18.6	7.8	26.4	74.83314774
60	5.9	34.8	2.9	37.7	112.2497216
80	0.5	43.2	1.0	44.2	149.6662955
100	0.0	48.1	0.0	48.1	187.0828693
120	0.0	49.5	0.0	49.5	224.4994432

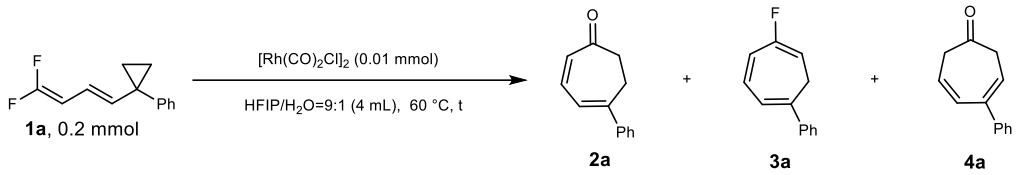


Concentration Profile Measurements. To a 25 mL reaction tube with **1a** (41.0 mg, 0.2 mmol), 1,3,5-trimethoxybenzene (11.1 mg, 99.82% purity, internal standard) and $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol) was added HFIP (3.7 mL) and H_2O (0.3 mL) sequentially under air atmosphere. The reaction mixture was charged with a flap plug and then stirred at 60 °C for 2 h, 600 revolutions per minute (rpm) for the magnetic stir bar. Every 20 min, 0.5–0.6 mL solution was taken out, filtered through silica gel, and washed with EA. After removing the solvent, 0.5 mL of $CDCl_3$ was added to

measure ^{1}H NMR.

Table S15. Kinetic data for 1,5-migratory ring expansion of **1a** (HFIP/H_2O = 12.3:1).

t/min	**1a** (mM)	**2a** (mM)	**3a** (mM)	**2a**+**3a** (mM)	t[H_2O]^0.5
20	26.7	3.0	9.9	12.9	40.84115571
40	16.3	10.4	13.9	24.3	81.68231143
60	7.9	23.3	10.9	34.2	122.5234671
80	1.5	36.1	6.4	42.5	163.3646229
100	0.0	45.0	2.0	47.0	204.2057786
120	0.0	48.0	0.0	48.0	245.0469343



Concentration Profile Measurements. To a 25 mL reaction tube with **1a** (42.0 mg, 0.2 mmol), 1,3,5-trimethoxybenzene (10.9 mg, 99.82% purity, internal standard) and $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol) was added HFIP (3.6 mL) and H_2O (0.4 mL) sequentially under air atmosphere. The reaction mixture was charged with a flap plug and then stirred at 60 °C for 2 h, 600 revolutions per minute (rpm) for the magnetic stir bar. Every 20 min, 0.5–0.6 mL solution was taken out, filtered through silica gel, and washed with EA. After removing the solvent, 0.5 mL of $CDCl_3$ was added to measure ^{1}H NMR.

Table S16. Kinetic data for 1,5-migratory ring expansion of **1a** (HFIP/H_2O = 9:1).

t/min	**1a** (mM)	**2a** (mM)	**3a** (mM)	**2a**+**3a** (mM)	t[H_2O]^0.5
20	26.7	2.9	8.7	11.6	47.11687596
40	17.0	9.7	13.6	23.3	94.23375192
60	8.7	19.9	13.1	33.0	141.3506279
80	1.9	30.6	10.7	41.3	188.4675038
100	0.0	38.9	6.8	45.7	235.5843798
120	0.0	43.7	2.9	46.6	282.7012557

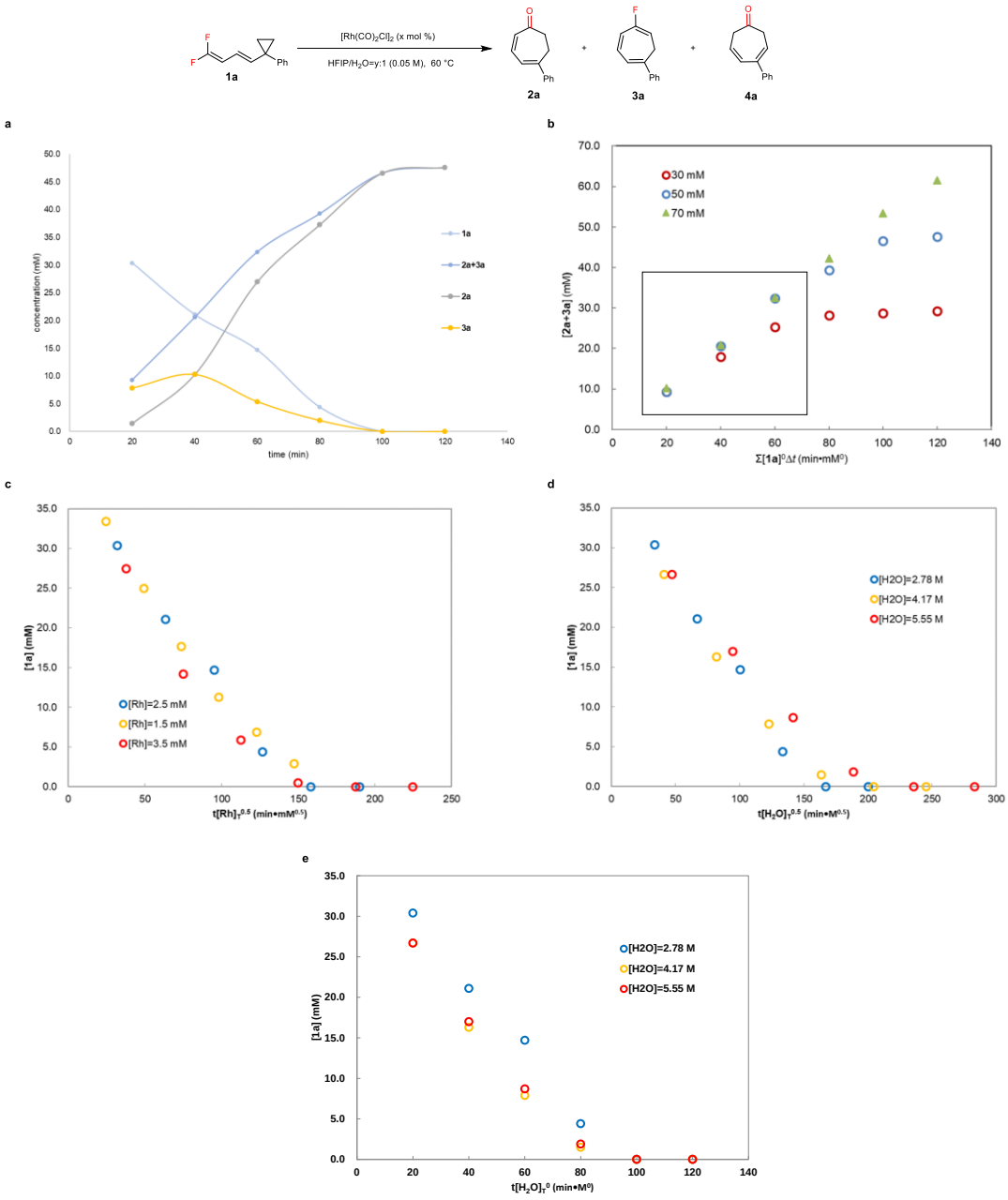


Fig. S1. Visual kinetic analysis. Reaction conditions: **a**, **1a** (50 mM), $[Rh(CO)_2Cl]_2$ (5 mol %), HFIP/H_2O = 19:1 (4 mL), 60°C; **b**, **1a** (30, 50, 70 mM), $[Rh(CO)_2Cl]_2$ (5 mol %), HFIP/H_2O = 19:1 (4 mL), 60°C; **c**, **1a** (50 mM), $[Rh(CO)_2Cl]_2$ (3, 5, 7 mol %), HFIP/H_2O = 19:1 (4 mL), 60°C; **d** and **e**, **1a** (50 mM), $[Rh(CO)_2Cl]_2$ (5 mol %), HFIP/H_2O = 19:1, 12.3:1, 9:1 (4 mL), 60°C; $[Rh]_T$ is the total concentration of catalyst added.

Order in substrate: To determine the order in substrate (a), we performed variable time normalization analysis via plotting the concentration of products **2a**+**3a** against $\Sigma[\mathbf{1a}]^{a}\Delta t$. *a* was adjusted until the concentration profiles overlaid and became straight lines. As shown in **Fig. S1b**, a equals 0. Note: This reaction is fast, therefor the overlap of three lines in **Fig. S1b** is good within 1 h. The lines branched off after 1 h because **1a** was consumed.

Order in catalyst: To determine the order in catalyst (n), we performed normalized time scale analysis via plotting the concentration of **1a** against $t[\mathrm{Cat}]_T^{n}$ ($[\mathrm{Cat}]_T$ is the total concentration of

catalyst added). *n* was adjusted until the concentration profiles overlaid. As shown in **Fig. S1c**, *n* equals 0.5.

Order in H_2O: For HFIP/H_2O = 19:1 and HFIP/H_2O = 12.3:1, the order of H_2O is approximately 0.5. Increasing the concentration of H_2O, the order of H_2O is approximately 0.

Discussion of water effect:

We will now utilize Figure 1 to delve into the kinetics of water for the reaction involving **1a** (model substrate **1** was used, devoid of a Ph group). The experimental results indicate that the presence of the Ph group in **1a**, or alternative groups such as H, Me, or SPh, does not exert a notable influence on either the reaction rate or yield. Consequently, we postulate that the R group does not significantly alter the reaction profile. Furthermore, we hypothesize that incorporating a single water molecule in our calculations does not appreciably impact the reaction profile, although water molecules in the reaction system have the potential to form clusters. Additionally, we assume that the hydrogen bonds of HFIP as a solvent to the water molecule do not substantially modify the energy profile depicted in Figure 1.

The concentration of rhodium catalyst is about 10^{-3} M, while the concentration of H_3O^+ is about 10^{-5} M (see below), the H_3O^+ from water hydrolysis is too small (10^{-7} M) and can be ignored.

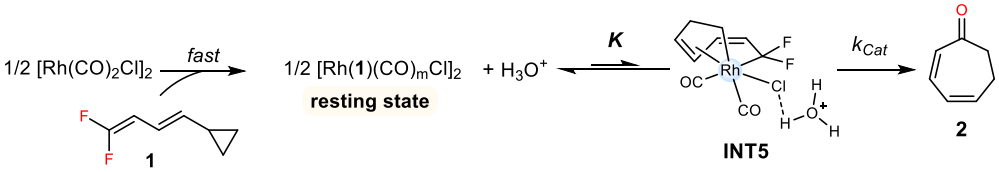
$$pK_a(HFIP) \approx 9.3,\ K_a \approx 10^{-9.3} \approx 5.01 \times 10^{-10}$$

$$For\ HFIP/H_2O = 19{:}1,\ \rho\ (HFIP) \approx 1.6 g/mL, M = 168\ g/mol$$

$$[HFIP] = \frac{19 \times 1.6}{168} \div 0.02 \approx 9.05\ M$$

$$[H_3O^+] \approx [\mathrm{H^+}] \approx \sqrt{K_a \times [\mathrm{HFIP}]} = \sqrt{5.01 \times 10^{-10} \times 9.05} \approx 6.73 \times 10^{-5}\ M$$

When the concentration of H_2O is low (in both cases of HFIP/H_2O = 19:1 and HFIP/H_2O = 12.3:1), the concentration of H_3O^+ is also low, **TS3** could be the rate-determining step. Therefore, we can have the rate equation shown below:



rate = k_{Cat}**INT5** = k_{Cat}***K*[resting state]**$^{1/2}[H_3O^+]_T = k_1[Cat]_T^{1/2}(k_2[H_2O][HFIP])^{1/2} = k[Cat]_T^{1/2}[H_2O]^{1/2}$

$$H_2O + HFIP \underset{}{\overset{k_2}{\rightleftharpoons}} H_3O^+ + HFIP^-$$

$$[H_3O^+] = [HFIP^-]$$

$$[H_3O^+] = (k_2[H_2O][HFIP])^{1/2}$$

[HFIP] ≈ a constant

Therefore, the order of the catalyst is 0.5, and the order of H_2O is 0.5.

1.0 M for other species:

$$\Delta G_{std} = -RTln\left(\frac{V_1}{V_2}\right) = -RTln\left(\frac{\frac{1}{24.46}}{1}\right) = 1.89\ kcal/mol$$

6.73×10^{-5} M for $[H_3O^+]$:

$$\Delta G_{H_3O^+} = -RTln\left(\frac{V_1}{V_2}\right) - RTln\left(\frac{c_1}{c_2}\right) = -RTln\left(\frac{\frac{1}{24.46}}{1}\right) - RTln\left(\frac{1}{6.73\times10^{-5}}\right)$$

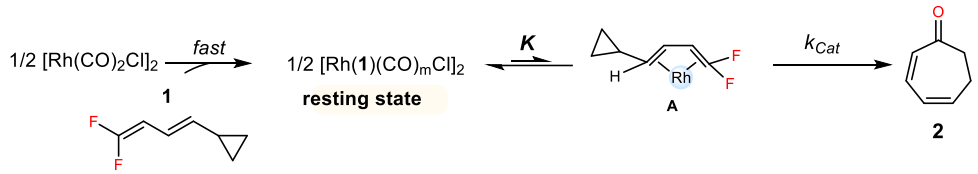
$$= -2.44\ kcal/mol$$

After concentration correction, $\Delta G^{\neq}_{TS3} = 19.4 + 1.89 + 2.44 = 23.73\ kcal/mol$

TS3 and **TS1** are close, therefore **TS3** may become the rate determining step.

Here we add another point to understand the above discussion: We can under the competition of **TS1** and **TS3** by analog that **TS1** is an intramolecular reaction transition state while **TS3** is an intermolecular reaction transition state, with the reasonable assumption that **IN1** and **IN5** have similar concentration. Then, the concentration of H_2O can affect the relative energy of **TS1** and **TS3**.

When increasing the concentration of H_2O (from HFIP/H_2O = 12.3:1 to HFIP/H_2O = 9:1), [H_3O^+] increases, and **TS1** becomes the rate-determining step. we can have the rate equation shown below:



rate = k_{Cat}**A** = k_{Cat}***K*****[resting state]**$^{1/2}$ = k$[Cat]_T^{1/2}$

Therefore, the order of the catalyst is 0.5, and the order of H_2O is 0.

In other words, the ring expansion reaction for **1** with higher H_3O^+ has **TS1** as the rate-determining step.

If we compare Figure 1 in the main text with **1** as the substrate and Figure S6 with **1-four** as the substrate, **1-four** is less reactive than **1**. The activation free energies are 24.3 kcal/mol (from $[Rh(CO)_2Cl]_2$ and substrate to **TS1**) and 29.0 kcal/mol (from $[Rh(CO)_2Cl]_2$ and substrate to **TS9**), with the assumption that the resting states are same for both substrates. This can explain why df-DECBs needed high reaction temperature and longer reaction time than df-DECPs.

An alternative explanation for the kinetics of H_2O is that various combinations of HFIP and H_2O exhibit distinct solvent effects due to potential changes in the properties of the co-solvents. These different solvent effects can also influence the reaction rate.

7. DFT Studies

DFT calculations were performed with Gaussian 16 C.02 program package.[16] Geometry optimizations of all of the minima and transition states were carried out with the PW6B95 functional[17] with D3 dispersion correction,[18] employing the IEFPCM model of ethanol.[19] The def2-TZVP basis set with corresponding effective core potential (ECP)[20] was used for Rh, and the 6-311G(d,p)[21] basis set was used for all other atoms. Pruned integration grids with 99 radial shells and 590 angular points per shell were used in DFT calculations (int = ultrafine). Enthalpy and Gibbs free energy corrections at 298 K were obtained through frequency analyses. Single-point energy calculations were performed with ORCA 5.0.4[22] based on the optimized structures. The ωB97M-V functional,[23] def2-QZVP basis set and corresponding ECP as well as SMD solvation model of ethanol[24] were utilized. The SCF convergence criterion was set via the 'TightSCF' keyword in ORCA. In this paper, all discussed energies are Gibbs free energies in the solution phase (ΔG_{EtOH} 298 K). Standard state concentrations of 1.0 M[25] were used for all species.

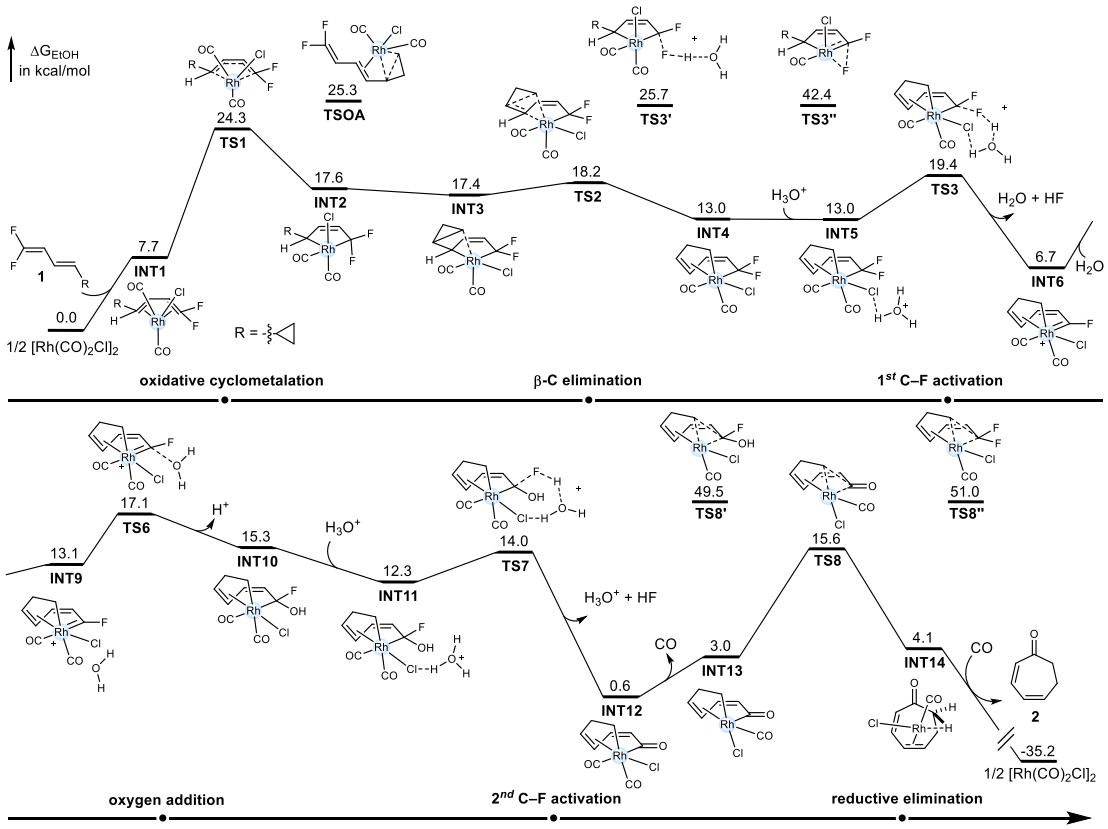


Fig. S2. Gibbs energy profile for 1,5-migratory ring expansion (alternative pathway). Computed at the SMD(EtOH)/ωB97M-V/def2-QZVP//IEFPCM(EtOH)/PW6B95D3/6-311G(d,p), (def2-TZVP for Rh) level.

HF was released during the reaction therefore the reaction condition is acidic. the promotor is likely to be H_3O^+ or H^+·ROH, we just selected H_3O^+ as the model.

For *gem*-difluorodienylcyclopropane **1**, oxidative cyclometallation (**TS1**, 24.3 kcal/mol) is significantly lower than oxidative addition (**TSOA**, 25.3 kcal/mol) because of the strong

electronegativity of F and the decrease of the electron density of diene. Then, β-C elimination occurred via **TS2** with an activation free energy of 0.8 kcal/mol to form **INT4**. The F migration is difficult to give Rh carbene (**TS3"**). Then 1st C–F activation occurred with a low activation free energy (**TS3**, 6.4 kcal/mol) to generate cationic **INT6**, followed by oxygen addition via **TS6** with an activation free energy of 4.0 kcal/mol. Next, **INT11** undergoes 2nd C–F activation via **TS7** with an activation free energy of 1.7 kcal/mol to produce **INT12**, followed by reductive elimination (**TS8**, 12.6 kcal/mol) to generate product **2**. The reductive elimination to form C(sp^3)–C(sp^3) bond is difficult (**TS8'** and **TS8"**, more than 40 kcal/mol). This pathway is disfavored by 2.7 kcal/mol (**TS4** and **TS6**) (**Fig. S2**).

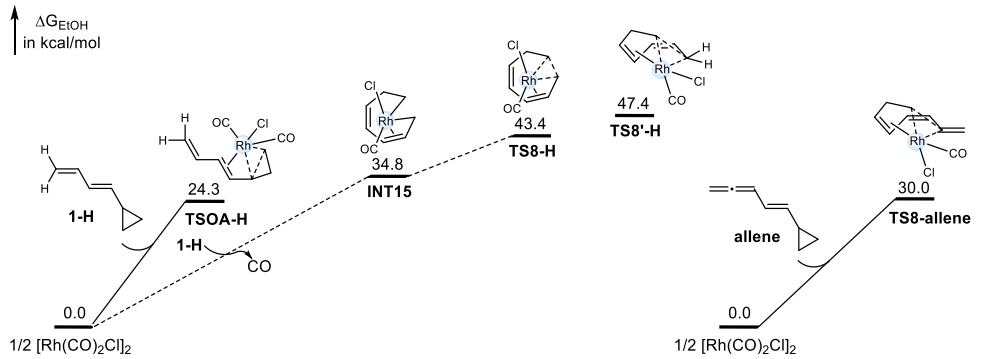


Fig. S3. Computed at the SMD(EtOH)/ωB97M-V/def2-QZVP//IEFPCM(EtOH)/PW6B95D3/6-311G(d,p), (def2-TZVP for Rh) level.

For common DECPs, it is easy to undergo the oxidative addition of cyclopropane to generate an eight-membered metallacycle. However, the reductive elimination to form seven-membered products is difficult. This process is easier for allene-VCP (**Fig. S3**).

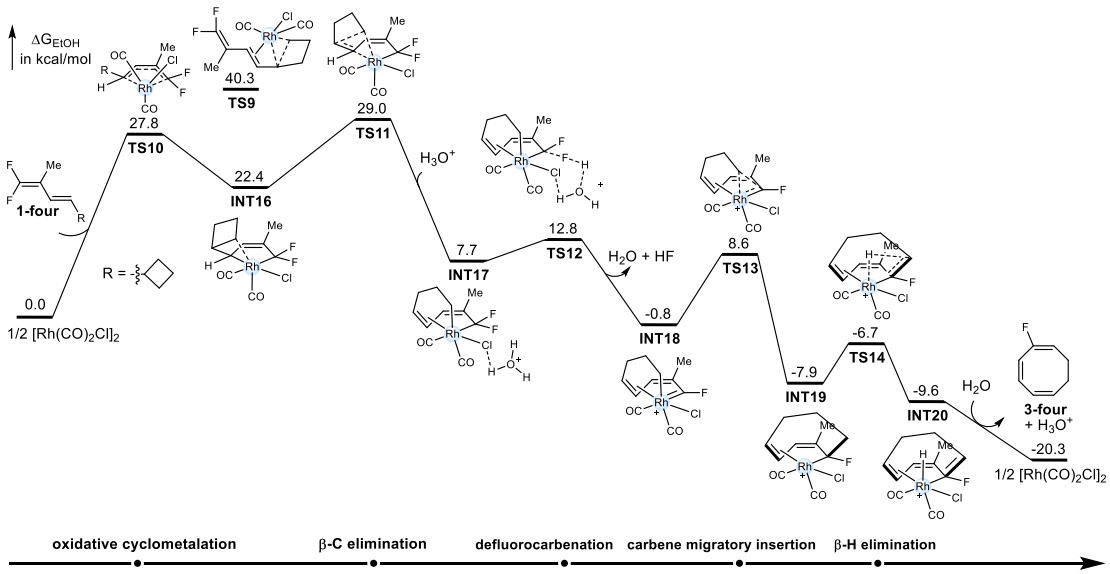


Fig. S4. Gibbs energy profile for 1,5-migratory ring expansion of df-DECB. Computed at the SMD(EtOH)/Ωb97M-V/def2-QZVP//IEFPCM(EtOH)/PW6B95D3/6-311G(d,p), (def2-TZVP for Rh) level.

As for df-DECB, the oxidative addition of **1-four** to open the four-membered ring is different (**TS9**,

40.3 kcal/mol). Therefore, an oxidative cyclometallation step is necessary (**TS10**, 27.8 kcal/mol). The success of df-DECB in experiments promotes us to locate the transition state **TS1** in the beginning. Then, β-C elimination occurred via **TS11** with an activation free energy of 6.6 kcal/mol to form **INT17**, which is the rate-determining step and the total activation free energy of this reaction is 29.0 kcal/mol. Therefore, the reaction temperature of df-DECB (90 °C) is higher than df-DECP (70 °C). **INT17** can undergo defluorocarbenation via **TS12** with an activation free energy of 5.1 kcal/mol to give rhodium carbene intermediate **INT18**, followed by carbene migratory insertion (**TS13**, 9.4 kcal/mol) to deliver intermediate **INT19**. Then, β-H elimination (**TS14**, 1.3 kcal/mol) and catalyst transfer to deliver product **3-four**.

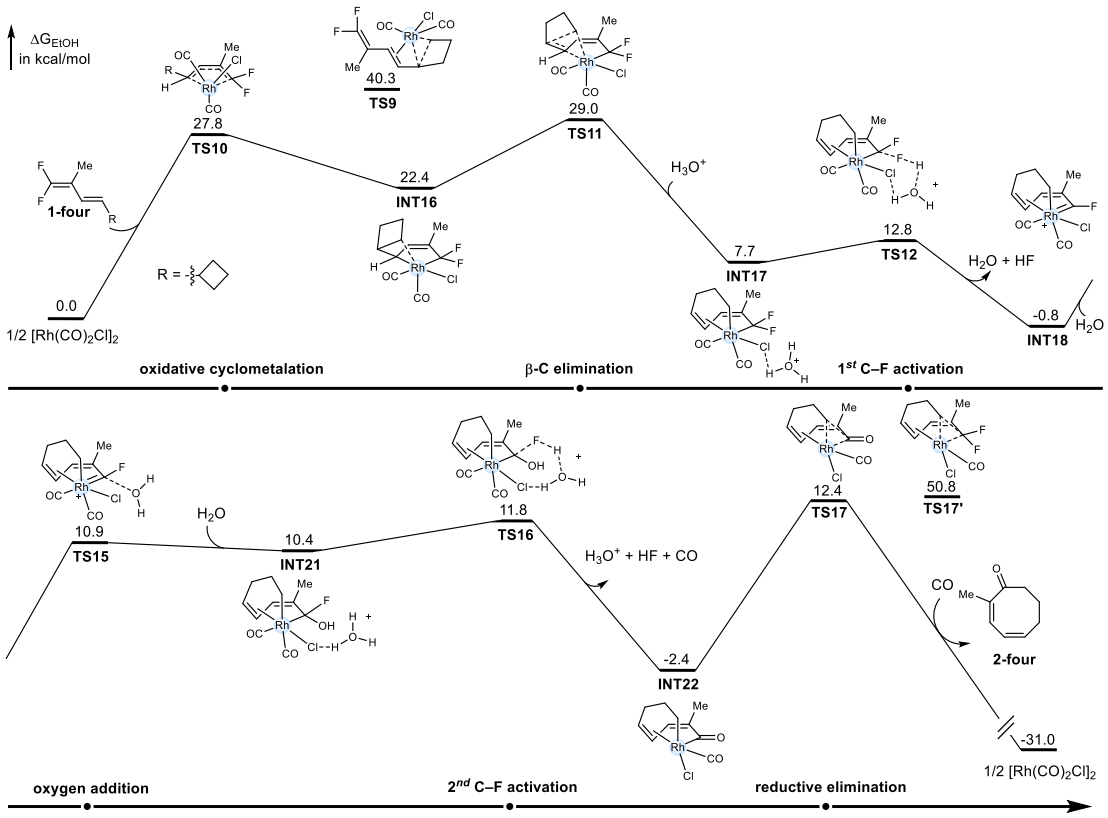


Fig. S5. Gibbs energy profile for 1,5-migratory ring expansion of df-DECB (alternative pathway). Computed at the SMD(EtOH)/Ωb97M-V/def2-QZVP//IEFPCM(EtOH)/PW6B95D3/6-311G(d,p), (def2-TZVP for Rh) level.

Started from **INT18**, the oxygen addition (**TS15**, 11.7 kcal/mol) is easy to give **INT21**, followed by 2^{nd} C–F activation (**TS16**, 1.4 kcal/mol) to generate **INT22**. Finally, reductive elimination (**TS17**, 14.8 kcal/mol) occurs to give the ketone product **2-four**. This pathway is disfavored than **TS13** by 3.8 kcal/mol (**TS13** and **TS17**) (**Fig. S5**).

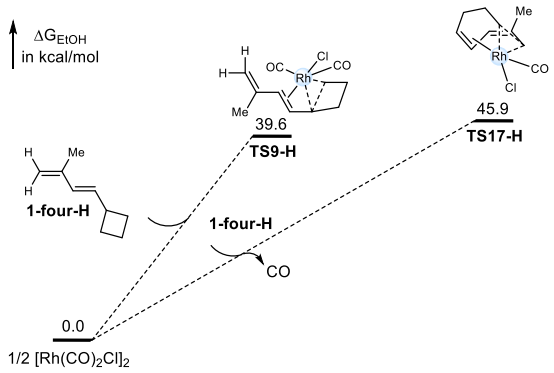


Fig. S6. Computed at the SMD(EtOH)/Ωb97M-V/def2-QZVP//IEFPCM(EtOH)/PW6B95D3/6-311G(d,p), (def2-TZVP for Rh) level.

For common DECBs, the oxidative addition and reductive elimination to form eight-membered products are difficult (**Fig. S6**).

Computed Energies for the Stationary Points:

Table S17. Thermal corrections to Gibbs energies (TCGs), single-point energies (SPEs) in solvent.

	Imaginary Frequencies (cm-1)	SPE[a] (a. u.)	TCG[a] (a. u.)	SPE[b] (a. u.)
CO	none	-113.478931	-0.01399	-113.3356869
H_2O	none	-76.532367	0.003936	-76.45097125
H_3O^+	none	-76.929652	0.017316	-76.86097355
HF	none	-100.575983	-0.006973	-100.4759453
$[Rh(CO)_2Cl]_2$	none	-1596.622724	-0.009937	-1595.079709
1	none	-471.870956	0.098648	-471.2275389
1-H	none	-273.128885	0.116815	-272.681453
TSOA	-261.64	-1270.153901	0.106056	-1268.737869
INT1	none	-1270.178229	0.106657	-1268.766545
TS1	-96.34	-1270.153551	0.107289	-1268.740719
INT2	none	-1270.165914	0.108097	-1268.752302
INT3	none	-1270.163345	0.10881	-1268.753357
TS2	-191.73	-1270.161908	0.108925	-1268.752184
INT4	none	-1270.170076	0.109547	-1268.76101
INT5	none	-1347.128428	0.142656	-1345.634742
TS3	-465.48	-1347.115258	0.139554	-1345.621531
TS3'	-482.66	-1347.106662	0.137471	-1345.609319
TS3"	-141.06	-1156.626894	0.10304	-1155.361031
INT6	none	-1169.978677	0.107503	-1168.685773
TS4	-326.32	-1169.966252	0.107657	-1168.673587

INT7	none	-1169.992209	0.108818	-1168.698968
TS5	-587.26	-1169.982804	0.106558	-1168.693318
INT8	none	-1169.99455	0.107613	-1168.70394
3	none	-371.310062	0.090068	-370.7785846
INT9	none	-1246.524347	0.128832	-1245.140955
TS6	-153.90	-1246.522861	0.132215	-1245.137869
INT10	none	-1246.124309	0.121746	-1244.733744
INT11	none	-1323.089182	0.154517	-1321.611903
TS7	-365.35	-1323.085911	0.153478	-1321.608108
INT12	none	-1145.549778	0.106856	-1144.262372
INT13	none	-1032.063064	0.102654	-1030.907619
TS8	-324.19	-1032.032373	0.102264	-1030.887113
INT14	none	-1032.051872	0.102729	-1030.906017
INT15	none	-957.90712	0.121253	-956.8270307
TS8'	-247.19	-1132.583484	0.11613	-1131.326906
TS8"	-279.76	-1156.621377	0.10378	-1155.348096
TSOA-H	-263.73	-1071.412048	0.123642	-1070.192824
TS8-H	-325.10	-957.893649	0.12218	-956.8142726
TS8'-H	-322.17	-957.885656	0.120494	-956.8062657
allene	none	-311.257375	0.119164	-310.7533507
TS8-allene	-430.62	-996.041172	0.124955	-994.9080255
2	none	-347.285471	0.102068	-346.7712474
TS1-H	-66.28	-1071.399687	0.12598	-1070.178286
1-Cl	none	-1193.059207	0.093887	-1191.906438
TS1-Cl	-113.37	-1991.338571	0.103706	-1989.412004
1-Br	none	-5422.42515	0.090479	-5419.623229
TS1-Br	-115.35	-6220.704575	0.100183	-6217.128671
1-four	none	-550.625742	0.153279	-549.8476376
TS9	-318.81	-1348.886542	0.161284	-1347.334701
TS10	-39.99	-1348.906483	0.162251	-1347.355563
INT16	none	-1348.909898	0.162459	-1347.364464
TS11	-263.65	-1348.90079	0.162869	-1347.354356
INT17	none	-1425.889842	0.195804	-1424.261926
TS12	-467.60	-1425.879828	0.193252	-1424.251125
INT18	none	-1248.744929	0.160751	-1247.316472
TS13	-265.79	-1248.730507	0.162469	-1247.30314

INT19	none	-1248.756311	0.163124	-1247.330182
TS14	-541.18	-1248.751096	0.160837	-1247.325955
INT20	none	-1248.757283	0.162087	-1247.331752
3-four	none	-450.055961	0.143391	-449.3902315
TS15	-220.65	-1325.287016	0.187235	-1323.768304
INT21	none	-1401.849279	0.210907	-1400.236793
TS16	-346.56	-1401.846217	0.208746	-1400.232457
INT22	none	-1110.825104	0.156548	-1109.53558
TS17	-411.59	-1110.79336	0.156143	-1109.511641
TS17'	-441.90	-1235.374034	0.15789	-1233.968015
2-four	none	-426.029097	0.155422	-425.3833867
1-four-H	none	-351.883601	0.171158	-351.3026555
TS9-H	-321.81	-1150.144731	0.178506	-1148.790234
TS17-H	-471.96	-1036.639276	0.174607	-1035.429568

[a]Computed at the IEFPCM(EtOH)/PW6B95D3/6-311G(d,p), (def2-TZVP for Rh) level

[b]Computed at the SMD(EtOH)/ωB97M-V/def2-QZVP//IEFPCM(EtOH)/PW6B95D3/6-311G(d,p), (def2-TZVP for Rh) level

Cartesian coordinates of the stationary points:

CO

C	0.00000000	0.00000000	-0.64153500
O	0.00000000	0.00000000	0.48115100

H_2O

O	0.00000000	0.00000000	0.11874800
H	0.00000000	0.75147400	-0.47499100
H	0.00000000	-0.75147400	-0.47499100

H_3O^+

O	0.00000000	0.00000000	0.08272900
H	0.00000000	0.92389400	-0.22061000
H	-0.80011500	-0.46194700	-0.22061000
H	0.80011500	-0.46194700	-0.22061000

HF

F	0.00000000	0.00000000	0.09178200
H	0.00000000	0.00000000	-0.82603700

$[Rh(CO)_2Cl]_2$

C	-2.61514000	1.31150600	-0.59635800
O	-3.26248600	2.13194500	-1.03511200
C	-2.61574500	-1.31108100	-0.59603900
O	-3.26356800	-2.13137600	-1.03435400
Rh	-1.53413100	0.00005300	0.12389200
Cl	0.00012400	1.62509100	1.06709500
Cl	-0.00001100	-1.62544600	1.06654700
Rh	1.53419300	-0.00008500	0.12390100
C	2.61537700	-1.31137600	-0.59641700
C	2.61546000	1.31135300	-0.59602800
O	3.26281400	2.13190500	-1.03455800
O	3.26268700	-2.13184100	-1.03517600

1

C	-3.57822200	-0.09983300	0.74512500
C	-3.57824900	-0.09990500	-0.74507600

C	-2.37805500	0.43555700	-0.00002300
H	-4.19976600	0.61626300	1.25982300
H	-3.46017400	-1.04563000	1.25226200
H	-4.19981500	0.61614000	-1.25981800
H	-3.46021900	-1.04575200	-1.25212500
H	-2.25940900	1.50989500	-0.00007800
C	-1.13168100	-0.33280700	-0.00000100
H	-1.23633300	-1.41366600	0.00004100
C	0.09349500	0.20086900	-0.00003700
H	0.20453700	1.27812300	-0.00008100
C	1.30598400	-0.58564400	-0.00003600
H	1.25004300	-1.66334200	-0.00000200
C	2.51807200	-0.05925600	-0.00004100
F	2.78431500	1.23486400	0.00000900
F	3.64380500	-0.74663200	0.00004800

1-H

C	2.58286200	-0.12614800	-0.74460500
C	2.58285800	-0.12628700	0.74457800
C	1.40774200	0.46417900	0.00003700
H	3.23608800	0.56169200	-1.25862500
H	2.42106700	-1.06460800	-1.25320500
H	3.23608600	0.56145400	1.25872800
H	2.42106200	-1.06484300	1.25300100
H	1.33688000	1.54267800	0.00013600
C	0.12982900	-0.24909500	-0.00003900
H	0.18991200	-1.33408700	-0.00014800
C	-1.07695400	0.32756500	0.00004600
H	-1.14828100	1.41056500	0.00017800
C	-2.32082700	-0.41229500	0.00000900
H	-2.23380700	-1.49391500	-0.00002000
C	-3.53357800	0.14242500	-0.00002000
H	-3.66005100	1.21706800	-0.00000900
H	-4.43055300	-0.45806900	-0.00006800

TSOA

Rh	-0.83485800	-0.20211500	0.12408500
Cl	0.10095500	-0.85595000	-2.23579400
O	0.34979800	-2.74127100	1.30290700
C	-0.10948800	-1.79894000	0.87738200
C	-1.59092000	1.70876500	-0.84425800
C	-1.21480000	2.95856700	-0.10114200
C	-1.19963200	1.96698500	0.98399000
C	-0.04787600	1.25609600	1.45106500
C	0.99623000	0.98671300	0.54829800
H	-2.64617200	1.58396500	-1.02006900
H	-0.93758700	1.43803400	-1.66372600
H	-1.98873800	3.70737600	-0.01854100
H	-0.25428300	3.37619100	-0.36965100
H	-2.08799300	1.90348200	1.59343000
H	-0.02155600	0.92597600	2.47762600
H	1.06478700	1.56949500	-0.36080000
C	2.20810900	0.29752700	0.94422700
H	2.29027600	-0.15291800	1.92081800
C	3.24640000	0.17830100	0.13535700
F	4.36582800	-0.43669200	0.43830400
F	3.30839900	0.66049200	-1.08583100
C	-2.61709400	-0.93109300	0.09114000
O	-3.68229700	-1.31585400	0.09421400

INT1

Rh	0.38609100	0.24843400	-0.04590400
C	0.23671800	0.41634200	1.88275000
O	0.14831000	0.43537000	3.00816700
C	-0.28824600	2.08612200	-0.51556500
O	-0.61242700	3.13613300	-0.75883600
Cl	2.64967600	1.22475600	-0.24109300
C	1.07903500	-1.68002100	-0.12609100
C	0.65187000	-1.36267900	-1.47430300
C	-0.65468700	-0.89268200	-1.61158600
C	-1.48171500	-0.78273200	-0.44919100
H	-1.48159900	-1.60134300	0.25481600
C	-2.73634500	-0.01493600	-0.50919200
C	-4.03352700	-0.71946000	-0.18220100

C	-3.47267000	0.28389100	0.76675300
H	-3.97223900	-1.76266100	0.08737900
H	-4.89732700	-0.44983200	-0.76913000
H	-3.95354700	1.24610300	0.84402900
H	-3.02987500	-0.07930500	1.68238100
H	1.36964600	-1.30360200	-2.27730700
H	-0.95372800	-0.44582300	-2.54938500
H	-2.78407000	0.73968900	-1.28189600
F	2.38396400	-1.92432300	0.02823900
F	0.41542200	-2.62219900	0.58181600

TS1

Rh	0.32548300	0.38306400	0.29017100
C	-0.16914000	-0.38548100	1.89458400
O	-0.44824200	-0.85751400	2.88573300
C	-1.00909600	1.96707300	0.37454100
O	-1.69753500	2.85257800	0.42954100
Cl	1.77085000	1.97768300	-0.91341500
C	1.62170700	-1.13822000	-0.07926100
C	1.26923000	-1.34884800	-1.51195200
C	-0.03439900	-1.24634100	-1.78969700
C	-0.97132800	-0.99295200	-0.67213300
H	-1.05957400	-1.84106900	0.00126500
C	-2.27421700	-0.39287300	-1.00309900
C	-3.49359400	-1.29823400	-1.01546300
C	-3.33222100	-0.28402300	0.06060400
H	-3.33614900	-2.33566200	-0.76465300
H	-4.21810900	-1.11866100	-1.79367500
H	-3.96074000	0.59237700	0.03979700
H	-3.07097400	-0.63475800	1.04874200
H	2.04085000	-1.49347300	-2.25384100
H	-0.41620100	-1.29583100	-2.80023100
H	-2.25339500	0.38298000	-1.75547300
F	2.93754000	-0.85905400	0.08982500
F	1.40109200	-2.29155800	0.65212000

INT2

Rh	-0.28049200	-0.63185300	-0.00472200
C	-0.56825600	-0.89355000	1.82355800
O	-0.72866800	-1.03723600	2.93265700
C	1.45307300	-1.78816500	-0.12081200
O	2.37424700	-2.41635900	-0.25149900
Cl	-0.01890300	-0.35148200	-2.36441200
C	-1.95713800	0.53214800	-0.06204600
C	-1.56912300	1.95995900	-0.16786100
C	-0.30199300	2.24234700	0.08485400
C	0.66515200	1.17654300	0.47205500
H	0.80333400	1.18012500	1.55416000
C	1.99653100	1.24965100	-0.18174100
C	3.04446300	2.11527800	0.48954500
C	3.18972600	0.63283900	0.49459500
H	2.77180300	2.59834400	1.41555500
H	3.67967200	2.69722200	-0.15950300
H	3.94151600	0.18315100	-0.13496400
H	3.01375500	0.12118300	1.43049900
H	-2.32303700	2.69871900	-0.40345300
H	0.07804500	3.25673500	0.05553100
H	1.99292500	1.25745700	-1.25983000
F	-2.76061700	0.15372200	-1.10593800
F	-2.78313400	0.36651100	1.04675300

INT3

Rh	-0.37546200	0.01729000	-0.13953800
C	-0.80217800	-1.36592000	-1.32467000
O	-1.06638800	-2.18104900	-2.06043900
Cl	-1.66421800	-0.77599100	1.85369400
C	1.28191300	-1.10220100	0.35341100
C	2.45917700	-0.68594900	-0.45377600
C	2.28686300	0.32762200	-1.28750000
C	0.97136100	1.01332300	-1.33929900
H	3.39591700	-1.20746000	-0.31019400
H	3.08943200	0.70195500	-1.91034600
H	0.60043800	1.20949400	-2.33759800
C	0.76504600	2.14405600	-0.42458500

C	1.66451300	2.61306500	0.63874100
C	0.51558500	1.82652700	1.19732900
H	0.02280000	2.86002100	-0.74214300
H	2.62946900	2.13495100	0.71533500
H	1.65635500	3.67462300	0.82775400
H	-0.31474500	2.37109500	1.61271200
H	0.80440600	0.93543900	1.73107700
C	-2.07817900	1.09247600	-0.57710800
O	-3.05193800	1.62378000	-0.75122900
F	1.05655700	-2.45385100	0.19255600
F	1.59515500	-0.98905700	1.69387900

TS2

Rh	-0.37537000	0.03981100	-0.13583100
C	-0.67237700	-1.42723300	-1.34741000
O	-0.84305600	-2.26930500	-2.07754500
Cl	-1.56174400	-1.01601200	1.77480300
C	1.39107000	-0.90549700	0.37293000
C	2.51110900	-0.48011000	-0.50885500
C	2.25672900	0.48137500	-1.38175900
C	0.91684500	1.11276800	-1.39984700
H	3.47674400	-0.95148700	-0.38401700
H	3.00722100	0.85122000	-2.06805300
H	0.47898400	1.26813500	-2.37720200
C	0.61768200	2.15677700	-0.46369100
C	1.33570900	2.53807600	0.75671900
C	0.19929800	1.71607500	1.30190600
H	-0.18662700	2.82262200	-0.74076900
H	2.30380800	2.07148300	0.88720200
H	1.32494100	3.59237200	0.99296500
H	-0.68834400	2.26343800	1.57482700
H	0.48265800	0.92622900	1.97732500
C	-2.16355600	0.91938100	-0.56081600
O	-3.18235200	1.36658900	-0.72041300
F	1.24256700	-2.27799900	0.29643500
F	1.76744800	-0.70102700	1.68657300

INT4

Rh	0.38312500	0.07100700	0.07842000
C	0.39759900	-1.29022100	1.61019900
O	0.40080600	-2.07746600	2.41244200
Cl	1.40442500	-1.49609600	-1.42500600
C	-1.47417100	-0.67417500	-0.45372700
C	-2.58948400	-0.11176400	0.35653000
C	-2.30944400	0.79755000	1.27510300
C	-0.95065500	1.33932700	1.43244700
H	-3.58840300	-0.48320000	0.16849700
H	-3.06887500	1.19516500	1.93539700
H	-0.54803500	1.36322900	2.43744800
C	-0.34807300	2.16740700	0.50558300
C	-0.77310600	2.38448000	-0.91776200
C	0.20922200	1.41446300	-1.53869200
H	0.51370300	2.73171000	0.83575700
H	-1.79808200	2.05735700	-1.07378700
H	-0.66961300	3.42174100	-1.22769400
H	1.17499700	1.86167300	-1.74482300
H	-0.15280700	0.83447000	-2.37472300
C	2.26511000	0.73402000	0.45149700
O	3.33163600	1.07088500	0.56606000
F	-1.46735500	-2.04857800	-0.26229800
F	-1.79933800	-0.53561100	-1.78380800

INT5

Rh	0.46863800	-0.28059100	0.05821600
C	0.07884700	-0.55267600	2.06826300
O	-0.16611800	-0.70503700	3.15260900
Cl	-1.16547400	-1.95053000	-0.60399800
C	-0.99533100	1.16890100	0.02748200
C	-0.54706300	2.50861500	0.47214700
C	0.71645000	2.63743600	0.84129800
C	1.67563200	1.53117200	0.69356100
H	-1.26978300	3.31255300	0.49729600
H	1.10460100	3.56331000	1.24411200
H	2.28074100	1.29100000	1.55882600

C	2.15320200	1.10727100	-0.53498000
C	1.55922500	1.40784300	-1.87841700
C	0.78007300	0.11674300	-1.99444600
H	3.05590000	0.51155000	-0.53355300
H	0.89868700	2.26976500	-1.83519000
H	2.31698200	1.56415600	-2.64101600
H	1.35741000	-0.69326600	-2.42361200
H	-0.20482700	0.18780000	-2.43248600
C	1.84951800	-1.77395200	0.00764100
O	2.57692700	-2.62515600	-0.06821500
F	-2.03152900	0.75870100	0.91005200
F	-1.67637900	1.27962900	-1.16336200
O	-3.69860100	-0.59235300	-0.66534800
H	-4.41628700	-1.13834500	-0.31225300
H	-3.53854900	0.16823200	-0.07555600
H	-2.81031600	-1.12388800	-0.68617300

TS3

Rh	-0.42728100	-0.29428000	-0.06321800
C	0.57387600	-0.63115000	-1.86514600
O	1.13010200	-0.83726100	-2.81585800
Cl	1.00493400	-1.78495600	1.15310500
C	0.72139700	1.29140000	0.39292800
C	0.38794600	2.58800000	-0.14945900
C	-0.67669900	2.59535400	-0.95017500
C	-1.50396400	1.39661700	-1.14120400
H	0.98352700	3.45455300	0.09315700
H	-0.99332500	3.49056200	-1.46874600
H	-1.73274300	1.12505500	-2.16381500
C	-2.34538100	0.90444300	-0.15756400
C	-2.31092500	1.25825000	1.30174600
C	-1.39686500	0.14097400	1.76160400
H	-3.12619700	0.22880900	-0.47840300
H	-1.86530500	2.23608200	1.46129900
H	-3.30309100	1.24020900	1.74204400
H	-1.92320800	-0.75144700	2.07561000
H	-0.63297200	0.41597400	2.47705100
C	-1.59748200	-1.92546600	-0.34791400
O	-2.21316800	-2.85707300	-0.44292100
F	2.24912800	1.02026500	-0.64633800
F	1.37825000	1.32592800	1.52806800
O	3.66188200	-0.43301600	0.48910100
H	4.31464600	-0.88493300	-0.05573900
H	3.00524300	0.32304300	-0.11496400
H	3.02886600	-1.09852700	0.82750700

TS3'

Rh	0.09983700	-0.66359600	-0.09076400
C	-0.41523500	-0.94526700	1.70956500
O	-0.69541100	-1.11043100	2.78723000
C	1.84152000	-1.74325500	0.06396800
O	2.79161800	-2.33727000	0.07365400
Cl	0.62071700	-0.37707500	-2.37615400
C	-1.50641700	0.47187700	-0.45782400
C	-1.27288900	1.89659500	-0.42373500
C	-0.05955000	2.21921000	0.01728700
C	0.90153900	1.18815400	0.49125000
H	-2.02340000	2.59863400	-0.75255900
H	0.27378100	3.24882800	0.06331500
F	-2.36453600	0.05206200	-1.36759900
F	-2.61491300	0.27118000	0.92006600
O	-4.88716200	0.15618000	0.43060000
H	-5.14590200	-0.66685100	0.00127200
H	-3.74835600	0.21424600	0.65751800
H	-5.20444500	0.88909500	-0.10871800
H	0.90496000	1.18217100	1.58219200
C	2.29021800	1.33929200	-0.00488300
C	3.20702800	2.24496300	0.79716400
C	3.43116800	0.77423000	0.79687400
H	2.40810200	1.37044700	-1.07569300
H	2.80519900	2.69344900	1.69277300
H	3.87204700	2.87488200	0.22817700
H	4.27006700	0.37741000	0.24739300
H	3.18145700	0.23795200	1.70125800

TS3”

Rh	0.29110800	-0.04367700	-0.11581800
Cl	1.71484900	1.75213700	0.53582100
C	-1.32906400	1.02174800	0.15935800
C	-2.60743500	0.51797100	-0.21208000
C	-2.55488200	-0.71701800	-0.73667800
C	-1.29782000	-1.45892000	-0.81757700
H	-3.50533900	1.10982100	-0.12087800
H	-3.43107200	-1.18155800	-1.16988000
H	-1.07489400	-1.87197500	-1.79310700
C	-0.63820000	-2.02419400	0.26213400
C	-0.82794700	-1.72700200	1.71885500
C	0.33921600	-0.76495400	1.84235300
H	0.08324800	-2.79516900	0.02848700
H	-1.77451300	-1.22483500	1.90326200
H	-0.76572500	-2.61981800	2.33652800
H	1.28285800	-1.25725200	2.04514200
H	0.18634100	0.08369300	2.49805300
C	1.96771100	-0.97597900	-0.67516000
O	2.94298600	-1.44656500	-0.98013200
F	-0.35347300	1.12014500	-1.81563200
F	-1.32503400	2.24416800	0.58997300.

INT6

Rh	0.25212800	0.05764800	0.04974900
C	0.71616900	-1.23345800	1.62796600
O	0.98450100	-1.99318500	2.40514300
Cl	1.71715400	-1.13316300	-1.37392000
C	-1.29352900	-1.00297800	-0.53931700
C	-2.55258500	-0.89677700	0.08847700
C	-2.56896900	0.00240800	1.09681600
C	-1.42735200	0.86980700	1.36609900
H	-3.39532300	-1.50351200	-0.20437400
H	-3.43157100	0.10996100	1.74161700
H	-1.14074700	0.96871900	2.40498900
C	-1.01242400	1.87346500	0.50274800
C	-1.41284600	2.05802200	-0.93311200
C	-0.28620000	1.28353200	-1.58928400
H	-0.37166600	2.63002000	0.93353000
H	-2.37977300	1.60811100	-1.13945700
H	-1.44673400	3.10944100	-1.20089400
H	0.57994400	1.88285900	-1.83667200
H	-0.57230100	0.65296200	-2.42178200
C	1.88567900	1.22187700	0.45328900
O	2.81024200	1.83487200	0.60209900
F	-1.22497900	-1.84198300	-1.51767500

TS4

Rh	0.27275100	0.05576600	0.05290500
C	1.01008900	-0.41171700	1.83160000
O	1.38866100	-0.78172700	2.82041600
Cl	1.70831100	-1.53855500	-0.93390000
C	-1.27016400	-1.05899500	-0.27387100
C	-2.52707900	-0.79640100	0.38518800
C	-2.52263900	0.28642100	1.16564500
C	-1.35433000	1.17539600	1.19368600
H	-3.36473900	-1.46408200	0.25790800
H	-3.36982600	0.56065600	1.77870500
H	-1.00291600	1.51119100	2.16060100
C	-0.99225600	1.90806300	0.07793700
C	-1.57950100	1.64545300	-1.28767500
C	-0.99155200	0.30964700	-1.72225400
H	-0.34857000	2.76295900	0.22101300
H	-2.66492000	1.61282400	-1.23765900
H	-1.29414900	2.42956900	-1.98131900
H	-0.13911500	0.33406600	-2.39391200
H	-1.72409900	-0.35378700	-2.17445200
C	1.88501200	1.38067700	-0.31475800
O	2.77352100	2.00720100	-0.58020800
F	-1.18330100	-2.24250200	-0.82111000

INT7

Rh	-0.38268400	-0.09573500	-0.09488600

C	-0.62202200	0.37968500	1.68829500
O	-0.76909800	0.71735200	2.74978600
Cl	-1.69686300	1.74300700	-0.64182700
C	1.41858800	0.86470400	-0.33117500
C	2.40007900	0.51721400	0.72648900
C	2.26192200	-0.64078100	1.35595100
C	1.15385400	-1.53794200	0.96973900
H	3.20224900	1.21545800	0.91484300
H	2.94185800	-0.97628400	2.12422500
H	0.62148700	-2.07982300	1.74053300
C	0.98081100	-1.91215700	-0.34342400
C	1.84627900	-1.34834300	-1.44476800
C	1.48412400	0.12495500	-1.64410100
H	0.30844600	-2.72677100	-0.56991500
H	2.89554400	-1.43749500	-1.16808400
H	1.68203500	-1.89490700	-2.36601900
H	0.49285200	0.22955500	-2.14052400
H	2.13803100	0.63824000	-2.35082600
C	-2.25287000	-1.30374100	-0.30563000
O	-3.23656900	-1.83407800	-0.31403700
F	1.31174400	2.19791300	-0.50194900

TS5

Rh	-0.38490900	-0.16413200	-0.08608600
C	-0.65790100	0.62568600	1.80117500
O	-0.83735600	1.13556700	2.78070300
Cl	-1.75159600	1.56170600	-0.89410100
C	1.46077000	0.92354600	-0.46508200
C	2.37187200	0.66338400	0.66713100
C	2.25438100	-0.45311500	1.37773100
C	1.20934300	-1.43989600	1.05159100
H	3.11922800	1.41650400	0.86739300
H	2.90609000	-0.66967900	2.21058000
H	0.72348700	-1.96538400	1.86224000
C	1.06948000	-1.93028400	-0.22922300
C	1.89009200	-1.36471500	-1.36874200
C	1.31302500	0.01962200	-1.55004100
H	0.46220600	-2.80484200	-0.40598800
H	2.94945400	-1.31889300	-1.11956400
H	1.75389500	-1.95396800	-2.26700400
H	-0.17357700	-0.47051000	-1.63740000
H	1.15269500	0.43983000	-2.53528400
C	-2.04717700	-1.30229300	-0.06169300
O	-2.97834400	-1.92217600	-0.10603100
F	1.28298200	2.22279400	-0.73731700

INT8

Rh	-0.47647700	-0.22779300	-0.14537300
C	-0.40524800	0.96532900	1.64680900
O	-0.47572000	1.63411400	2.53960000
Cl	-1.69921000	1.52327300	-1.11393400
C	1.73558200	0.86344400	-0.41889100
C	2.44773500	0.42651200	0.78180600
C	2.11533100	-0.70635500	1.40085500
C	1.01581700	-1.58488200	0.95934200
H	3.23012300	1.07545300	1.14490700
H	2.64116300	-1.01217000	2.29341300
H	0.49266200	-2.13795600	1.72614000
C	0.90083800	-2.00784800	-0.35372000
C	1.79174500	-1.41321800	-1.41544800
C	1.40328700	0.04646500	-1.46456800
H	0.28357500	-2.86247900	-0.58483000
H	2.84340800	-1.53769100	-1.15602700
H	1.60314100	-1.87614300	-2.37604800
H	-0.72781700	-0.93309600	-1.48269800
H	1.03958000	0.49599200	-2.37610700
C	-2.12877100	-1.07027800	0.31068200
O	-3.10425300	-1.57748900	0.52655100
F	1.58934000	2.17501600	-0.54672200

3

C	1.15381100	-0.07794600	0.00780000
C	0.60245500	1.19264300	0.38037700
C	-0.69192000	1.54880400	0.21126800

C	-1.71714200	0.74109700	-0.40035200
H	1.31365200	1.93624400	0.71331200
H	-0.95238300	2.57370900	0.44036600
H	-2.47245800	1.27462800	-0.96310900
C	-1.78024700	-0.59669900	-0.33837300
C	-0.85156800	-1.38294900	0.53969000
C	0.53395500	-1.26011000	-0.01165000
H	-2.52778200	-1.12554100	-0.91389100
H	-0.88321200	-0.97534100	1.55427700
H	-1.15021000	-2.42494300	0.58881500
H	1.05362000	-2.12166300	-0.40470300
F	2.45807900	-0.01401500	-0.37195900

INT9

Rh	0.37805700	-0.03802500	0.03033500
C	-0.26248500	-1.29944900	1.59415200
O	-0.53463400	-1.98482700	2.43648300
Cl	0.44176400	-1.85561500	-1.48845900
C	-1.42761800	0.44969800	-0.57653200
C	-2.24045300	1.33406000	0.17438900
C	-1.59560900	1.88857700	1.21863100
C	-0.17310100	1.65026800	1.45585700
H	-3.25972200	1.55264000	-0.10327000
H	-2.10287000	2.54685500	1.91154400
H	0.10614600	1.44311000	2.48104200
C	0.84031500	2.08743000	0.61473900
C	0.70966600	2.58617100	-0.79671100
C	0.96632500	1.27513900	-1.51453200
H	1.83141800	2.11360800	1.04558900
H	-0.29038600	2.96229600	-0.99649600
H	1.43248400	3.36783500	-1.00961700
H	2.01153700	1.09066700	-1.72650900
H	0.35178300	1.08046600	-2.38428900
C	2.32509500	-0.50424100	0.44350400
O	3.39915900	-0.78672200	0.58639600
F	-1.88819500	0.10809900	-1.73513400
O	-2.48704600	-1.79258200	0.13478800
H	-2.05491000	-2.27978300	-0.57306600
H	-3.42691500	-1.88685200	-0.03231000

TS6

Rh	0.39060400	0.05514800	0.03684800
C	0.26807700	-1.26413700	1.66744000
O	0.23244900	-1.97672400	2.53102100
Cl	0.98131900	-1.71711200	-1.43711600
C	-1.53143300	-0.18432500	-0.48188700
C	-2.55744700	0.42472400	0.32554400
C	-2.09320500	1.23473500	1.28062100
C	-0.66087600	1.51648000	1.43498600
H	-3.60457600	0.27328800	0.11056900
H	-2.76214400	1.74619000	1.95999500
H	-0.27178900	1.45870700	2.44349300
C	0.09018500	2.23858100	0.52240600
C	-0.27920400	2.57562600	-0.89476700
C	0.42730900	1.41778400	-1.57103600
H	1.03322000	2.62868600	0.88017400
H	-1.35498800	2.53172800	-1.04475600
H	0.08070900	3.55965200	-1.18066700
H	1.46007900	1.62889500	-1.81822900
H	-0.08961100	0.95989500	-2.40365000
C	2.37022700	0.33254900	0.35352400
O	3.47903600	0.46206100	0.45094100
F	-1.88249800	-0.40681900	-1.72432100
O	-1.75162900	-2.12829100	0.05136300
H	-1.08414900	-2.53594400	-0.52340500
H	-2.60451100	-2.48894200	-0.21941500

INT10

Rh	0.38722900	0.05849100	0.08055800
C	0.36083500	-1.30311100	1.60286700
O	0.34284000	-2.08051300	2.41555400
Cl	1.42753500	-1.49671900	-1.43158100
C	-1.49525000	-0.67587200	-0.45018100
C	-2.58886900	-0.04197700	0.34519400

C	-2.29227400	0.85038200	1.27496700
C	-0.92061200	1.35450400	1.43635700
H	-3.60488800	-0.36836100	0.15049000
H	-3.04411100	1.26474800	1.93382500
H	-0.51534400	1.36987400	2.44059700
C	-0.30066600	2.16867700	0.50816200
C	-0.72409400	2.39675800	-0.91353600
C	0.23890800	1.40839300	-1.53504000
H	0.57425200	2.71396900	0.83600200
H	-1.75400600	2.08578300	-1.06802900
H	-0.60222500	3.43265900	-1.22219800
H	1.21270100	1.83717400	-1.74383100
H	-0.13798300	0.83218200	-2.36652300
C	2.27038400	0.69453600	0.46282100
O	3.34238600	1.01285000	0.58655100
F	-1.83007200	-0.46214900	-1.80299700
O	-1.46959200	-2.04744500	-0.25948800
H	-2.36636600	-2.38943300	-0.35217600

INT11

Rh	0.50805000	-0.19602600	0.02832100
C	0.63411700	-0.32260400	2.08619900
O	0.65553200	-0.40599900	3.20508100
Cl	-0.76949700	-2.26344700	-0.06498600
C	-1.21247400	0.93879400	0.33390000
C	-0.92449200	2.36587000	0.62427700
C	0.33618200	2.76470500	0.64773000
C	1.43182000	1.86267900	0.26484900
H	-1.75772800	3.02765900	0.82853200
H	0.61397900	3.77048500	0.93303900
H	2.27948000	1.81526200	0.93688600
C	1.65271800	1.43527400	-1.03296900
C	0.68740600	1.48118300	-2.17824100
C	0.24149500	0.04066500	-2.05316000
H	2.63235500	1.03379300	-1.25574100
H	-0.13254000	2.16509300	-1.97753500
H	1.16822900	1.74291300	-3.11702700
H	0.88715000	-0.65281800	-2.57910400
H	-0.80226100	-0.15041000	-2.25317500
C	2.13007100	-1.36876700	-0.28175100
O	2.99073500	-2.05994700	-0.48664800
F	-2.10771000	0.99896900	-0.84586400
O	-3.38191100	-1.22540500	-0.69488100
H	-3.13040600	-0.27390200	-0.81922400
H	-3.72209200	-1.59348700	-1.52239800
H	-2.50592200	-1.69356200	-0.43414800
O	-1.96416400	0.31609400	1.29708400
H	-2.60425000	0.93325600	1.67288800

TS7

Rh	0.54709000	-0.08249100	0.00318900
C	1.05512400	-0.06928800	2.01174200
O	1.28901600	-0.10391500	3.10778100
Cl	-0.15809700	-2.38577400	0.15584700
C	-1.29457700	0.61361200	0.61951300
C	-1.40266400	2.06724500	0.78491900
C	-0.30622500	2.77779200	0.56118700
C	0.92044500	2.16506200	0.03147300
H	-2.33412200	2.49741400	1.12855200
H	-0.26672700	3.83977000	0.76315000
H	1.83734800	2.38505500	0.56383800
C	1.05250700	1.72509700	-1.27258900
C	-0.05182200	1.44098400	-2.24387500
C	-0.08014500	-0.05357200	-2.01496200
H	2.05945300	1.57602500	-1.63868700
H	-0.98557700	1.89775400	-1.92986100
H	0.19641400	1.75118600	-3.25527400
H	0.64013600	-0.59456100	-2.61674500
H	-1.05476000	-0.51324200	-2.04682500
C	2.32794700	-0.82678400	-0.56465900
O	3.29237300	-1.29593900	-0.89365000
F	-2.51360400	0.47101300	-0.63842000
O	-2.97971100	-1.83143000	-0.63691100
H	-2.84222300	-0.74654900	-0.68171700

H	-3.24721800	-2.20751800	-1.48366200
H	-2.09781200	-2.20779600	-0.37305200
O	-1.84819700	-0.14454700	1.55276300
H	-2.56525300	0.31933400	2.00681000

INT12

Rh	0.25320500	0.04668900	0.06916900
C	0.41707100	-1.37394700	1.50330400
O	0.49251800	-2.22221700	2.23965700
Cl	1.85076900	-1.13843900	-1.30835900
C	-1.31838200	-0.98544100	-0.76199100
C	-2.59269600	-0.83431100	-0.02544600
C	-2.62650700	0.03950700	0.97545500
C	-1.46125700	0.86786200	1.30696500
H	-3.44909800	-1.40916200	-0.35066800
H	-3.51571700	0.18628400	1.57430900
H	-1.18563200	0.91662100	2.35285200
C	-0.97816800	1.87656700	0.49194900
C	-1.30929100	2.10502600	-0.95599800
C	-0.11927800	1.36638200	-1.53674800
H	-0.31406600	2.59686600	0.94942000
H	-2.24689200	1.62339300	-1.22220100
H	-1.36874900	3.16294100	-1.19950900
H	0.74893900	1.99786100	-1.68507900
H	-0.31791600	0.75511700	-2.40828200
C	1.93444600	1.11205200	0.68197800
O	2.88518400	1.67256700	0.89637200
O	-1.23817800	-1.65280700	-1.75579700

INT13

Rh	0.28639900	0.09041200	0.40490300
C	1.99868400	0.83265900	0.06776100
O	3.00773300	1.29331500	-0.14335400
Cl	1.12566300	-2.23878400	0.47597400
C	-0.12578900	0.12270700	-1.51773500
C	-1.39709700	-0.55093600	-1.84479900
C	-2.15794100	-1.07143300	-0.88613000
C	-1.82426800	-0.92566500	0.53234700
H	-1.63682300	-0.62394900	-2.89613600
H	-3.04693600	-1.63697100	-1.13301600
H	-1.73421200	-1.83977500	1.10409000
C	-1.85057700	0.25658000	1.21243400
C	-1.99790300	1.63058600	0.62123600
C	-0.53223200	2.00648700	0.51077100
H	-1.70504000	0.20519400	2.28572100
H	-2.46820100	1.58100400	-0.35761200
H	-2.58732400	2.28476600	1.26094000
H	-0.14346200	2.45719700	1.42097400
H	-0.28285700	2.61690200	-0.35055400
O	0.60518800	0.59924700	-2.33438400

TS8

Rh	0.40217400	-0.07100800	0.14906000
C	1.73666100	1.29572700	0.16931700
O	2.54177800	2.08762400	0.18572800
Cl	2.04977600	-1.62915100	-0.45358300
C	-1.09035800	1.27362700	-0.53583800
C	-2.05742300	0.46962500	-1.32202000
C	-2.04032500	-0.86375300	-1.28770400
C	-1.16077200	-1.63330600	-0.40396100
H	-2.69825300	1.02024500	-1.99610300
H	-2.66689400	-1.43180400	-1.96296700
H	-0.67407100	-2.49869000	-0.83296300
C	-1.11689100	-1.46990400	0.95674700
C	-1.89310400	-0.37041800	1.63008500
C	-1.25807800	0.95683200	1.21296300
H	-0.59264800	-2.20429200	1.55084000
H	-2.93729200	-0.40605300	1.32137200
H	-1.85541200	-0.47603700	2.71009100
H	-0.49764100	1.34292700	1.88999800
H	-2.01073400	1.74011000	1.17442000
O	-0.75794400	2.39411700	-0.85685500

INT14

Rh	0.67390600	0.10453100	-0.11555400
C	1.80082900	1.63278300	-0.24429000
O	2.51717800	2.51003200	-0.21729900
Cl	2.56071500	-1.22999300	-0.23663000
C	-2.70070200	0.54705200	-0.37279300
C	-2.60087400	-0.80338400	-0.91333000
C	-1.65001900	-1.71880400	-0.64844700
C	-0.53834100	-1.70492000	0.28895500
H	-3.36973700	-1.04559600	-1.63245400
H	-1.71135700	-2.63668500	-1.21914300
H	0.11959100	-2.55783700	0.21246600
C	-0.40527900	-0.92974000	1.43413600
C	-1.35556400	0.17017300	1.76961500
C	-1.60648300	1.06210500	0.54176300
H	0.28537000	-1.25932400	2.19602300
H	-2.31271800	-0.22531600	2.12322400
H	-0.94307900	0.77462700	2.57148400
H	-0.72722900	1.32782000	-0.12187600
H	-1.89102700	2.06240600	0.85679700
O	-3.63832300	1.26925800	-0.64489600

INT15

C	0.52113600	-1.64428500	0.81548600
C	0.46625300	-0.56504700	1.72875900
H	-0.23868800	-0.62851600	2.54454500
H	1.33229200	0.04686500	1.90849800
Rh	-0.36702500	0.01119700	-0.11412200
Cl	-1.95352100	1.83261900	-0.03358100
O	-2.98337400	-1.75754200	-0.31394300
C	-2.01459100	-1.18193300	-0.26629400
C	1.06129500	1.48393800	-0.15245800
C	2.52498200	1.32400700	0.19749700
C	3.17112000	0.10616800	-0.35946800
C	2.57391700	-1.04875500	-0.64486100
C	1.20111400	-1.51332300	-0.41478300
H	0.63854300	2.33139600	0.38169000
H	0.96125200	1.68151900	-1.22923200
H	2.67242800	1.35516000	1.28134400
H	3.07010800	2.19944000	-0.16665900
H	3.17856300	-1.80908100	-1.12702300
H	-0.17302600	-2.46386600	0.93128100
H	0.89281500	-2.25374000	-1.14389700
H	4.22734300	0.17816400	-0.58591600

TS8'

Rh	0.54046800	-0.10327900	0.03210600
C	2.16957800	-0.81716300	-0.56255100
O	3.15478300	-1.25426400	-0.91322300
Cl	1.60052300	2.04061200	0.48217000
C	-1.53022200	0.81555600	-0.51578500
C	-2.41721700	-0.33314700	-0.81999200
C	-1.90817500	-1.55843000	-0.88261600
C	-0.53986400	-1.89013300	-0.45148400
H	-3.44053200	-0.09738800	-1.07691700
H	-2.51606600	-2.37286200	-1.25631800
H	-0.01278000	-2.58515400	-1.09215700
C	-0.16219300	-1.85804400	0.90694900
C	-1.06174700	-1.19413000	1.90795800
C	-1.05770300	0.28667400	1.54801800
H	0.62318200	-2.51621100	1.24758300
H	-2.06969000	-1.60544200	1.86606600
H	-0.68420100	-1.32283500	2.92036000
H	-0.33001300	0.90207000	2.06754200
H	-2.03292900	0.73687400	1.62045800
O	-0.85672600	1.31095000	-1.60150500
F	-2.19356200	1.89712100	-0.04435700
H	-0.66405500	0.58340600	-2.20424300

TS8"

Rh	0.53893800	-0.11290300	0.07324400
C	2.18661300	-0.80792400	-0.53138100
O	3.17052000	-1.22019400	-0.90706600
Cl	1.54957700	2.04276100	0.46013400
C	-1.47135200	0.80373300	-0.47205900
C	-2.35228300	-0.29925600	-0.91359600

C	-1.85560800	-1.52680900	-1.00332600
C	-0.52194300	-1.89432400	-0.50572600
H	-3.34841300	-0.03132100	-1.23588800
H	-2.44271100	-2.31463100	-1.45797100
H	0.03946500	-2.56533200	-1.14246900
C	-0.20786200	-1.89445700	0.86459800
C	-1.14769600	-1.24722700	1.83906800
C	-1.09799300	0.24333500	1.54012200
H	0.56742700	-2.55381500	1.22551000
H	-2.16021700	-1.63243200	1.72980800
H	-0.82650000	-1.41262700	2.86551600
H	-0.35591300	0.82448600	2.07978900
H	-2.05904800	0.72286700	1.61419900
F	-2.16080200	1.88692100	-0.04446700
F	-0.79081200	1.31481800	-1.56069300

TSOA-H

Rh	-0.38061700	-0.18183700	0.13569800
Cl	0.24339000	-1.02482800	-2.26159400
O	0.92270800	-2.63304000	1.37851900
C	0.42639900	-1.72065300	0.93000100
C	-1.24962200	1.65272800	-0.88392100
C	-0.80953900	2.95190200	-0.27241300
C	-0.67151400	2.04382300	0.87564500
C	0.52646500	1.36491300	1.26410700
C	1.47543000	1.02921100	0.27924500
H	-2.31648200	1.51400400	-0.93770500
H	-0.68452200	1.32778200	-1.74771800
H	-1.57740100	3.70373000	-0.16355200
H	0.11404400	3.35059200	-0.66895000
H	-1.49153800	2.02317200	1.57716900
H	0.66253200	1.10679200	2.30296000
H	1.45360500	1.55315800	-0.66871700
C	2.72506700	0.35563100	0.59763300
H	2.81187100	-0.05946700	1.59542500
C	3.73362200	0.23075300	-0.26104000
H	3.67007600	0.63113000	-1.26345700
H	4.64585400	-0.27585300	0.01378200
C	-2.15429500	-0.90187000	0.35209400
O	-3.21145500	-1.28057700	0.49815000

TS8-H

C	0.63297800	-1.20815800	1.29301800
C	0.95716900	0.11260400	1.72453700
H	0.39115800	0.52168200	2.54905400
H	1.98567000	0.42674200	1.70117700
Rh	-0.42797800	-0.04083400	-0.01918500
Cl	-2.00732500	1.80626600	-0.16915400
O	-2.73027800	-1.96812100	-0.46378000
C	-1.86692300	-1.24619600	-0.32418000
C	1.10337800	1.49681300	-0.02268600
C	2.56552800	1.27530900	-0.30383400
C	2.93495800	-0.07254900	-0.82157600
C	2.28628400	-1.23708200	-0.70626100
C	1.06450000	-1.61814000	0.00803200
H	0.89928600	2.35336300	0.60777600
H	0.57230500	1.63189000	-0.97607900
H	3.17970500	1.50641600	0.57060100
H	2.87085500	2.01729800	-1.04778800
H	2.73098200	-2.07304300	-1.23275400
H	-0.01839000	-1.83866400	1.87864800
H	0.68906900	-2.58526800	-0.29716200
H	3.85791200	-0.10003500	-1.38658000.

TS8'-H

Rh	-0.34152800	0.04284200	-0.07587800
C	-1.66763200	1.43585200	-0.23557700
O	-2.44804700	2.25218300	-0.29717200
Cl	-2.08245900	-1.63519900	0.01128900
C	1.05395600	-1.44885000	-0.75645900
C	2.36322900	-0.83806000	-1.05842800
C	2.46281400	0.48723000	-1.04612600
C	1.35785900	1.32075900	-0.53095000
H	3.20241100	-1.47070400	-1.31630900

H	3.36739200	0.99635800	-1.35393500
H	1.08743400	2.19019200	-1.11810500
C	1.05881500	1.34695400	0.83595800
C	1.64218000	0.31580700	1.76506600
C	0.89561200	-0.96041100	1.42275500
H	0.58147200	2.21936800	1.25799500
H	2.71296500	0.20473000	1.60963000
H	1.47378600	0.58094200	2.80711400
H	-0.00802000	-1.14543800	1.99537700
H	1.51265200	-1.84569300	1.40386700
H	1.05977000	-2.48653400	-0.45533200
H	0.36409200	-1.34586200	-1.60774800.

allene

C	-3.11414700	0.03232900	-0.74513600
C	-3.11418000	0.03225800	0.74512100
C	-1.90625700	-0.48546200	-0.00000900
H	-3.72529100	-0.69256500	-1.26000000
H	-3.00992200	0.97984500	-1.25211100
H	-3.72536800	-0.69267600	1.25987800
H	-3.00997600	0.97972500	1.25219300
H	-1.77267800	-1.55803600	-0.00005700
C	-0.67061600	0.30050300	0.00003000
H	-0.79031700	1.38009900	0.00010600
C	0.56336100	-0.21266200	0.00000200
H	0.69811300	-1.28751300	-0.00006800
C	1.76677000	0.60148500	0.00006400
H	1.63499000	1.67888500	-0.00003100
C	2.98730700	0.12795100	-0.00009600
C	4.19658000	-0.34442400	0.00002100
H	4.72382100	-0.54983900	-0.92336500
H	4.72371300	-0.54979200	0.92347700

TS8-allene

Rh	0.40489700	-0.03854100	0.06073600
C	1.69110800	1.34139100	0.15295000
O	2.49461600	2.13710000	0.21858700
Cl	2.14343700	-1.56089100	-0.47142500
C	-1.18387200	1.23545200	-0.43825600
C	-2.21353600	0.46848000	-1.14945900
C	-2.17175400	-0.86085500	-1.22115700
C	-1.13807300	-1.64370600	-0.52656800
H	-2.98913900	1.02741000	-1.65801300
H	-2.89838000	-1.40957900	-1.80553300
H	-0.62572700	-2.41069000	-1.09289800
C	-0.97234300	-1.61986600	0.83057100
C	-1.73917400	-0.65263500	1.69183800
C	-1.15243600	0.73152000	1.45070000
H	-0.32706100	-2.35241100	1.29382800
H	-2.79448100	-0.66866600	1.42473600
H	-1.64952100	-0.91297700	2.74377700
H	-0.32696100	0.99283400	2.10907400
H	-1.89705900	1.50642000	1.54915100
C	-0.99401700	2.53817200	-0.69404100
H	-0.28978200	3.14450600	-0.14573200
H	-1.57302300	3.02814600	-1.46547600

2

C	1.81848500	0.70530200	0.19971600
C	1.85743400	-0.61612100	-0.00414200
C	0.69249700	-1.44457800	-0.43320200
C	0.68553700	1.57866300	-0.03081100
C	-0.55779000	-1.21383400	0.41190100
C	-0.62785800	1.30627000	-0.14608600
C	-1.32682000	0.03226500	0.05189800
H	2.73370600	1.20441600	0.48689300
H	2.80330300	-1.12291200	0.13342600
H	0.46535100	-1.22984300	-1.48355000
H	0.95277600	2.62350300	-0.13486400
H	-1.25070400	-2.04601600	0.31883000
H	-1.30341100	2.12555300	-0.35137000
O	-2.54177200	-0.00091800	-0.04271800
H	-0.27639600	-1.13829000	1.46583300
H	0.96064500	-2.49686900	-0.38909000

TS1-H

Rh	-0.57086500	-0.01336100	0.00571600
C	-0.57831300	0.21742700	1.79414300
O	-0.59928500	0.36942700	2.91896900
C	0.02495300	-1.98819600	-0.02120100
O	0.24210100	-3.08821700	0.06608700
Cl	-2.68148100	-0.77964400	-1.04245900
C	-1.24159500	1.95301300	-0.05151900
C	-0.08802100	2.65625800	-0.67234900
C	1.12872600	2.12619000	-0.60730900
C	1.36385700	0.81889000	0.07287400
H	1.72876400	0.94369000	1.09161100
C	2.26882200	-0.09276400	-0.68040100
C	3.75823700	0.01998700	-0.43566300
C	3.00803500	-1.18269200	0.03679500
H	4.08079600	0.73637100	0.30473500
H	4.40977200	-0.07960100	-1.28957800
H	3.15889200	-2.11603100	-0.48310400
H	2.83057600	-1.27627300	1.09888100
H	-0.25623400	3.59493500	-1.18898200
H	1.98428200	2.60809200	-1.06731700
H	1.98073600	-0.28809500	-1.70544200
H	-2.12244800	1.91978700	-0.68943600
H	-1.53177200	2.39396900	0.90054500

1-Cl

C	-4.27347400	-0.19266800	0.74361400
C	-4.27348100	-0.19272300	-0.74356300
C	-3.08483300	0.37570400	-0.00000200
H	-4.90702200	0.51109400	1.26023900
H	-4.13009600	-1.13406100	1.25196500
H	-4.90703300	0.51100300	-1.26023400
H	-4.13010800	-1.13415300	-1.25184600
H	-2.99288900	1.45222100	-0.00004100
C	-1.82680200	-0.36426900	0.00001700
H	-1.90805600	-1.44692600	0.00005200
C	-0.60917700	0.19429300	0.00000000
H	-0.51334700	1.27174800	-0.00003500
C	0.59688100	-0.59143600	0.00003200
H	0.49354700	-1.66806500	0.00006200
C	1.84284200	-0.11809600	0.00001600
Cl	3.22660800	-1.15846200	0.00001900
Cl	2.23005500	1.56859800	-0.00006900

TS1-Cl

Rh	-0.01120300	0.50779900	0.32411700
C	-0.27678900	-0.51028900	1.85130600
O	-0.42872200	-1.11710800	2.79464600
C	-1.59456300	1.71300000	0.64713500
O	-2.45026300	2.41472700	0.84232900
Cl	0.88336600	2.58446400	-0.72248700
C	1.59965000	-0.63354500	-0.28760100
C	1.18619200	-0.59832600	-1.71350800
C	-0.13023000	-0.71261900	-1.96165100
C	-1.05083700	-0.94013000	-0.84001500
H	-0.88271600	-1.87346700	-0.31052700
C	-2.47080300	-0.62822400	-1.04359600
C	-3.44506000	-1.78962700	-1.15924400
C	-3.46234400	-0.92627000	0.04945900
H	-3.03495500	-2.78334800	-1.07021000
H	-4.23151500	-1.68023100	-1.88874000
H	-4.27419900	-0.22686600	0.17227300
H	-3.06969200	-1.33722100	0.96828400
H	1.90855800	-0.37856600	-2.48626600
H	-0.52786300	-0.56839000	-2.95658200
H	-2.67689300	0.22650900	-1.67184800
Cl	3.20076100	0.09722900	-0.02995200
Cl	1.69198900	-2.35546500	0.30001700

1-Br

C	5.13311000	-0.37624800	-0.74345900
C	5.13311600	-0.37630300	0.74341400
C	3.95940000	0.22323700	0.00000500

H	5.78441300	0.31106800	-1.26011800
H	4.96501900	-1.31344600	-1.25193700
H	5.78442400	0.31097500	1.26011700
H	4.96503000	-1.31353800	1.25182500
H	3.89561900	1.30174300	0.00004400
C	2.68343500	-0.48445500	-0.00001700
H	2.73752100	-1.56883700	-0.00005300
C	1.47957400	0.10401000	0.00000500
H	1.40871100	1.18341300	0.00004100
C	0.25643700	-0.65523700	-0.00001900
H	0.34810400	-1.73402000	-0.00005400
C	-0.98567300	-0.16743700	-0.00000200
Br	-1.38450300	1.67928400	0.00005600
Br	-2.49679000	-1.30164900	-0.00004000

TS1-Br

Rh	-0.55038300	0.63241400	0.34014400
C	-0.62836400	-0.48207200	1.82064800
O	-0.67103800	-1.13717400	2.74282400
C	-2.28514300	1.56084600	0.74127000
O	-3.24029000	2.10471900	0.97616100
Cl	-0.01056800	2.86591900	-0.62315400
C	1.19807800	-0.23359000	-0.35844000
C	0.75846000	-0.18455900	-1.77223900
C	-0.53825400	-0.45871600	-2.01147600
C	-1.39334300	-0.88262100	-0.89783500
H	-1.07139100	-1.80458500	-0.42135200
C	-2.84812600	-0.78409900	-1.06126100
C	-3.63007900	-2.07563200	-1.24155400
C	-3.75183600	-1.30690200	0.02356900
H	-3.06692400	-2.99556800	-1.22774200
H	-4.44213500	-2.04409500	-1.95025800
H	-4.66040000	-0.75530000	0.20681600
H	-3.27494400	-1.70950500	0.90554800
H	1.42755700	0.16151700	-2.54697400
H	-0.97002800	-0.31273700	-2.99192200
H	-3.20154300	0.06568800	-1.62737900
Br	2.81670800	0.79168300	-0.04649100
Br	1.58926300	-2.11856800	0.15313200

1-four

C	0.80863900	0.31353900	0.00000100
H	0.84949300	1.39827200	0.00002500
C	-0.37503800	-0.30449700	-0.00002000
H	-0.39797700	-1.38710900	-0.00004200
C	-1.66123500	0.37460800	-0.00001800
C	-2.77318000	-0.34748800	-0.00002300
F	-2.82408000	-1.66901600	-0.00000600
F	-4.00153600	0.13927800	0.00002200
C	2.11785000	-0.37846900	-0.00001300
C	3.17205000	0.00803400	-1.06828600
C	3.17203500	0.00796500	1.06829900
H	1.97519600	-1.45956100	-0.00004900
C	4.26382500	-0.17641300	0.00000800
H	3.06541900	1.05685800	-1.34427900
H	3.21579400	-0.59421400	-1.97270200
H	3.06540100	1.05677200	1.34435700
H	3.21576600	-0.59434000	1.97267700
H	5.10109900	0.51669300	0.00003700
H	4.64839900	-1.19478200	-0.00002200
C	-1.73690500	1.86945800	0.00001600
H	-1.23597500	2.27558700	0.87820000
H	-1.23600900	2.27561800	-0.87817300
H	-2.76431000	2.21743300	0.00004200

TS9

Rh	0.87337700	-0.47659800	-0.01662700
Cl	0.19836700	-0.12526900	2.49534400
O	-0.84427600	-2.93425700	0.00852400
C	-0.17944100	-2.01818500	-0.03550300
C	1.62877300	2.72463900	0.52240800
C	1.22379600	2.92849000	-0.92584100
C	1.29466000	1.46139700	-1.37188000
C	0.06933200	0.71293600	-1.58197100

C	-0.93414300	0.80077400	-0.61210100
H	2.28923700	3.47419100	0.95383000
H	0.76242500	2.61924300	1.17306000
H	1.95548600	3.50653100	-1.48483100
H	0.24226200	3.36710500	-1.08488100
H	2.05563900	1.22913600	-2.10228100
H	-0.05581400	0.14680900	-2.49200900
H	-0.85116200	1.56183200	0.15052400
C	-2.24377200	0.18411400	-0.76776600
C	-3.16810300	0.41236300	0.15634600
F	-4.39441700	-0.06356600	0.12757100
F	-3.00041900	1.15323400	1.23045600
C	2.27877100	1.37431900	0.32350000
H	2.36860200	0.76045800	1.21824300
H	3.23890200	1.41817800	-0.17566100
C	-2.56154000	-0.64567900	-1.97238200
H	-3.53315900	-1.11866600	-1.88148400
H	-2.56355100	-0.02688300	-2.86913500
H	-1.81849100	-1.42814700	-2.12046600
C	2.47428300	-1.50513200	-0.26770100
O	3.40593200	-2.10581200	-0.50632800

TS10

Rh	-0.39422500	-0.52421600	-0.08873900
C	-0.54093300	-0.78652100	1.69696400
O	-0.64138900	-0.96020100	2.80980400
C	0.81743100	-2.21497100	-0.43045500
O	1.30752000	-3.21564800	-0.56386200
Cl	-2.14465800	-2.09278700	-0.94715700
C	-1.63417700	1.08117300	0.09817400
C	-0.83261400	2.28532300	-0.27133200
C	0.48666700	2.14273300	-0.16995200
C	1.10355500	0.88576600	0.33064000
H	1.29011300	0.95440400	1.40253700
H	1.14883100	2.95647100	-0.44752000
F	-2.67590900	0.94478600	-0.77628700
F	-2.23872500	1.25074900	1.32499300
C	-1.56148400	3.51313900	-0.70348900
H	-2.25430500	3.83265800	0.07516400
H	-0.86816800	4.32419400	-0.90615500
H	-2.15150400	3.32032700	-1.59773100
C	2.38471100	0.52504200	-0.37467800
C	3.51800200	1.59068600	-0.31761200
C	3.36466800	-0.46962300	0.28232100
H	2.19448600	0.25865400	-1.41695600
C	4.52570400	0.44301800	-0.15211800
H	3.43594200	2.18515000	0.59201400
H	3.62360300	2.25583200	-1.17032200
H	3.23643500	-0.47364800	1.36460800
H	3.38134100	-1.49453000	-0.07635400
H	5.34183700	0.58843000	0.54998500
H	4.93418300	0.13155600	-1.11100900

INT16

Rh	-0.68276300	-0.01586200	-0.11018800
C	-1.11289600	-1.27164300	-1.38443200
O	-1.38068900	-2.04279900	-2.16431200
Cl	-2.13835300	-0.78382400	1.77502100
C	0.85397500	-1.25172900	0.40268600
C	2.06264800	-0.99898300	-0.44046900
C	1.96586900	0.03471700	-1.26775900
C	0.72826600	0.86110800	-1.32567000
H	2.79927900	0.31699700	-1.90089000
H	0.37311100	0.98985100	-2.34376600
C	-2.25025800	1.28949400	-0.57013900
O	-3.14942600	1.92616700	-0.77902300
F	0.51207600	-2.58176900	0.36483500
F	1.17068700	-1.02382600	1.72704200
C	3.25083500	-1.87699000	-0.23409800
H	2.99659700	-2.91679000	-0.43526000
H	4.07043100	-1.58315700	-0.88303700
H	3.58784500	-1.82313000	0.80086500
C	0.74712000	2.17562300	-0.56664700
C	0.45629000	1.98699000	0.97935800

C	2.11777000	2.77117300	-0.16897600
H	0.06125600	2.87270900	-1.03917600
C	1.95823700	2.17649500	1.24167300
H	0.04166100	1.06642600	1.45025000
H	-0.16729100	2.79361000	1.35046100
H	2.98034600	2.44951300	-0.74565100
H	2.07946000	3.85752700	-0.16910500
H	2.46242300	1.21918900	1.33520500
H	2.22010200	2.80192500	2.08985400

TS11

Rh	-0.58885100	-0.16848700	-0.16783300
C	-0.60380800	-1.90603100	-0.90972100
O	-0.60800600	-2.93517500	-1.37191100
Cl	-1.77741600	-0.90930600	1.91462700
C	1.25556800	-0.66153700	0.57521200
C	2.33236600	-0.47453600	-0.45174100
C	1.94608200	0.16265000	-1.55138900
C	0.56411900	0.69098700	-1.64357400
H	2.63350600	0.36186600	-2.36401600
H	0.09430500	0.61330000	-2.61593200
C	-2.45729100	0.30178900	-0.90870400
O	-3.50093000	0.51905300	-1.26090200
F	1.27688100	-1.96127800	1.03349800
F	1.57018700	0.08434600	1.69650300
C	3.70219300	-0.96645000	-0.12969700
H	3.68807500	-2.03859700	0.06147700
H	4.39319900	-0.76104800	-0.94189800
H	4.07466600	-0.48515900	0.77454600
C	0.24727000	1.90915900	-0.90297900
C	-0.60036500	1.99046100	0.85459800
C	1.26213700	2.76068100	-0.17547400
H	-0.52624400	2.50604500	-1.37273300
C	0.26517700	3.25112000	0.85532100
H	-0.33392300	1.32958600	1.67077200
H	-1.66980400	2.15245500	0.82078400
H	2.01748500	2.13456800	0.29012400
H	1.75182800	3.49803900	-0.80913500
H	0.66421200	3.50410400	1.83347900
H	-0.30575600	4.09658100	0.47774000

INT17

Rh	0.50142000	-0.33215300	0.15213300
C	-0.20862100	-1.12321200	1.95562100
O	-0.61871800	-1.60046100	2.88438000
Cl	-0.46562500	-2.25902100	-0.95015400
C	-1.26656300	0.68557400	-0.12583700
C	-1.28707600	2.11683100	0.28740800
C	-0.29814600	2.47403200	1.09483200
C	0.80657700	1.55631600	1.41277200
H	-0.27087000	3.44882700	1.56546200
H	0.88620600	1.22806100	2.44197100
C	1.93102500	1.42762000	0.62571600
C	2.20758300	2.15032200	-0.65193400
C	2.36542200	1.10658100	-1.74257600
H	2.78252800	0.93821700	1.08103700
H	1.38206300	2.81702600	-0.89515300
H	3.10818400	2.74970100	-0.51719600
H	3.22242700	0.46868200	-1.52083200
H	2.55535100	1.56853300	-2.71332500
C	2.23020000	-1.40088700	0.22401700
O	3.15773600	-2.03282600	0.19613900
F	-2.28148600	0.03477400	0.65825400
F	-1.78966000	0.54971000	-1.38764900
O	-3.30528100	-1.75589700	-0.98555400
H	-3.82259300	-2.50392200	-0.65311200
H	-3.36236400	-1.00423300	-0.36104300
H	-2.30493200	-1.99670400	-1.03067500
C	1.07735100	0.31348800	-1.76680000
H	0.26110900	0.92589300	-2.13375600
H	1.13582700	-0.58887400	-2.36897800
C	-2.43376200	2.96463500	-0.14555200
H	-2.37934900	3.95086300	0.30480400
H	-2.43738500	3.07414100	-1.22878800

H	-3.37800600	2.49933400	0.13507700

TS12

Rh	-0.51221500	0.33372900	0.13232100
C	0.42799900	1.16050400	1.82199800
O	0.94510100	1.67140000	2.67494300
Cl	0.32854800	2.20353300	-1.11113700
C	1.08887700	-0.78575400	-0.34616300
C	1.29678600	-2.09950700	0.24825600
C	0.41480700	-2.37729900	1.21048500
C	-0.70765200	-1.48410600	1.51658600
H	0.49377200	-3.27740800	1.80686600
H	-0.76277200	-1.11189400	2.53195300
C	-1.86284700	-1.43057900	0.76351200
C	-2.17428700	-2.20272200	-0.47474300
C	-2.53163100	-1.18834100	-1.54587500
H	-2.71222800	-0.95024200	1.23267900
H	-1.31893300	-2.79796500	-0.78878900
H	-3.00148100	-2.87834500	-0.25495000
H	-3.40861700	-0.62034800	-1.23189200
H	-2.78618100	-1.67509200	-2.48862300
C	-2.18897400	1.43754600	0.39391700
O	-3.10731900	2.07734200	0.46251600
F	2.47424500	0.04633500	0.53530000
F	1.63356100	-0.65283500	-1.53883700
O	3.32758700	1.71073500	-0.84961300
H	3.89988600	2.35572800	-0.41951800
H	2.97655500	0.88747500	-0.13901000
H	2.50181000	2.16015800	-1.12265400
C	-1.33359500	-0.28157400	-1.72072200
H	-0.53309800	-0.78639600	-2.25072600
H	-1.56299200	0.64012100	-2.24566200
C	2.43669800	-2.94516800	-0.20096800
H	3.36889700	-2.39459900	-0.09018000
H	2.48983900	-3.86028900	0.37950400
H	2.32960800	-3.20411900	-1.25276800

INT18

Rh	-0.46282500	-0.11661900	-0.07677100
C	-0.54519200	-1.77372200	-1.35761800
O	-0.60734300	-2.73004000	-1.93668100
Cl	-1.46336200	-1.54682500	1.52231400
C	1.33744700	-0.51144000	0.58582400
C	2.52767000	-0.27228200	-0.15435200
C	2.24861700	0.27504200	-1.36130100
C	0.89853800	0.68219000	-1.72648800
H	3.02285600	0.42447600	-2.10356000
H	0.54311100	0.33606800	-2.68920100
C	0.24685800	1.77320000	-1.17420300
C	0.73065000	2.70629200	-0.11733100
C	-0.34475100	2.73316500	0.95672700
H	-0.61843400	2.11814100	-1.72514900
H	1.68098800	2.38260400	0.30156200
H	0.87260800	3.68699300	-0.57189400
H	-1.27773700	3.09409500	0.52301400
H	-0.07778700	3.41705200	1.76325000
C	-2.36390500	0.47267000	-0.54895100
O	-3.42284100	0.79373300	-0.72008800
F	1.52640600	-1.03218700	1.75711600
C	3.87685200	-0.61926700	0.37510300
H	3.91628700	-1.66456200	0.67172900
H	4.63886700	-0.43321000	-0.37370000
H	4.10063900	-0.01793600	1.25425100
C	-0.51379500	1.32880100	1.48989900
H	0.27764100	1.05345800	2.17966900
H	-1.46489100	1.15893600	1.98163600

TS13

Rh	0.50328400	-0.06960300	0.09631200
C	1.19678900	-1.17085200	1.56581300
O	1.55613000	-1.88847400	2.35020600
Cl	1.64259300	-1.56538300	-1.33817200
C	-1.21926400	-0.71146500	-0.46243700
C	-2.43052200	-0.47112700	0.31867400

C	-2.19733600	0.20569200	1.44655900
C	-0.86715300	0.74744200	1.73475600
H	-2.97426200	0.37833600	2.17914900
H	-0.42693000	0.48425100	2.68856400
C	-0.34855400	1.84128900	1.06645800
C	-1.06300700	2.59547400	-0.01597700
C	-0.52398000	2.21999900	-1.39141700
H	0.52109200	2.30971900	1.50587000
H	-2.12997800	2.38762300	0.02946900
H	-0.92123200	3.65895600	0.15864400
H	0.51674500	2.52560900	-1.47177000
H	-1.08039400	2.75431700	-2.15997800
C	2.32454800	1.03512200	-0.00084100
O	3.30138000	1.56050000	-0.15096300
F	-1.34341400	-1.71306300	-1.30698800
C	-3.73559800	-1.02222500	-0.13984800
H	-3.66924200	-2.09757900	-0.28864100
H	-4.51247700	-0.81047300	0.58677700
H	-4.02197700	-0.57848100	-1.09309100
C	-0.63845900	0.72306400	-1.64830200
H	-1.65212000	0.49837500	-1.98523600
H	0.02477800	0.31985300	-2.40656000

INT19

Rh	0.59742500	0.04455100	0.04303000
C	0.57074000	-1.11950000	1.49253600
O	0.55252000	-1.86035700	2.33544100
Cl	1.55533400	-1.63255900	-1.26648400
C	-1.29785900	-0.52822900	-0.50622400
C	-2.34516600	-0.11282200	0.48454500
C	-2.01503500	0.73567400	1.45084700
C	-0.67169800	1.31336500	1.54583900
H	-2.72900400	1.04596000	2.20144900
H	-0.17894900	1.29918100	2.51093600
C	-0.12915700	2.13142200	0.57935100
C	-0.78351300	2.46798700	-0.73081600
C	-0.40359400	1.41657400	-1.78833900
H	0.77825000	2.66374100	0.82803000
H	-1.86598300	2.50144100	-0.62404600
H	-0.43766600	3.44628700	-1.04781500
H	0.68170600	1.12614200	-1.69753700
H	-0.35440700	1.87344400	-2.77406900
C	2.71165000	0.70936800	0.33773200
O	3.80163400	0.91558000	0.47141700
F	-1.38019700	-1.88624700	-0.67823400
C	-3.70163500	-0.70390000	0.29210700
H	-3.65873100	-1.78615900	0.39734800
H	-4.40356600	-0.30214000	1.01549800
H	-4.07619000	-0.49496700	-0.71004000
C	-1.30982100	0.18225900	-1.84667300
H	-2.32010000	0.47133200	-2.13649400
H	-0.92108700	-0.51430900	-2.58558600

TS14

Rh	0.65559900	0.07304100	0.00783100
C	0.69741700	-1.40332900	1.44583700
O	0.72786900	-2.26829300	2.15483500
Cl	1.74669500	-1.43678900	-1.43610800
C	-1.31015300	-0.59828900	-0.64919600
C	-2.29609900	-0.44745100	0.44854500
C	-2.00981000	0.41064700	1.42169800
C	-0.69402500	1.06553700	1.55249400
H	-2.71884500	0.61256600	2.21318200
H	-0.20913300	0.93142400	2.51256100
C	-0.18192300	2.07932200	0.76385700
C	-0.82554300	2.75012400	-0.41210100
C	-1.62556400	1.83149200	-1.32547400
H	0.65968300	2.61552000	1.18127100
H	-1.45608600	3.55214700	-0.02296700
H	-0.03788600	3.23329400	-0.98561100
H	-1.72255900	2.29709100	-2.30115700
H	-2.62667000	1.67722800	-0.93126200
C	2.48076800	0.79374000	0.37827600
O	3.51669100	1.19425500	0.52161300

F	-1.26087900	-1.83872000	-1.17014700
C	-3.56943300	-1.21017200	0.30898100
H	-4.07081400	-0.95760500	-0.62562700
H	-3.36714700	-2.27947000	0.28532700
H	-4.23580600	-0.99465800	1.13757600
C	-0.98262800	0.46902900	-1.51463600
H	-0.67931100	0.16552600	-2.50892300
H	0.56219700	0.98242100	-1.28287300

INT20

Rh	-0.72247700	0.13303500	0.01716300
C	-0.42619200	-1.57588500	-1.23057400
O	-0.34854500	-2.51831100	-1.82662100
Cl	-1.81287700	-1.29326600	1.54579000
C	1.42736600	-0.58189700	0.68658400
C	2.31316200	-0.39658300	-0.48055400
C	1.94195800	0.46327600	-1.42638100
C	0.61840300	1.11800300	-1.50736700
H	2.60067800	0.66293700	-2.26173400
H	0.12550300	1.00132200	-2.46530400
C	0.12038500	2.12655100	-0.69709300
C	0.77637300	2.77301800	0.48384300
C	1.60676400	1.82992000	1.34587200
H	-0.72200800	2.67337400	-1.09851400
H	1.39635500	3.58978000	0.10803400
H	-0.00378900	3.23419300	1.08449700
H	1.71080800	2.25949300	2.33790300
H	2.60542700	1.73186600	0.92815100
C	-2.46220500	0.55474100	-0.68903400
O	-3.48814700	0.82117600	-1.05139400
F	1.30144200	-1.84727200	1.10279200
C	3.60585400	-1.14106200	-0.45212600
H	4.17818200	-0.88421200	0.43912600
H	3.42295700	-2.21390100	-0.42091400
H	4.19746300	-0.90882800	-1.33126500
C	1.02925700	0.44097900	1.50863100
H	0.57397600	0.16049500	2.44792200
H	-1.08136000	1.22856900	1.02951600

3-four

C	0.88736800	-0.77514500	-0.24299300
C	1.15994700	0.59178800	0.17478800
C	0.24088500	1.56835500	0.10386600
C	-1.08447700	1.61172400	-0.51111000
H	0.57811800	2.54423900	0.43854400
H	-1.23529200	2.55059800	-1.03505500
C	-2.14489100	0.79554600	-0.53066000
C	-2.42882200	-0.49343700	0.16636500
C	-1.26778200	-1.08591400	0.95229300
H	-2.99228000	1.16632300	-1.09688200
H	-3.28089500	-0.32697800	0.83276600
H	-2.78192800	-1.22008200	-0.56875300
H	-1.62954800	-1.93669400	1.52814000
H	-0.90403000	-0.34439500	1.66320800
F	1.89767600	-1.31742800	-0.98358800
C	2.55405600	0.85768200	0.66291100
H	2.79735000	0.22558200	1.51761200
H	3.28106900	0.63052500	-0.11586000
H	2.67232700	1.89769000	0.95386500
C	-0.15099100	-1.53540900	0.06862000
H	-0.17573900	-2.54110000	-0.32977400

TS15

Rh	-0.54356500	-0.13977400	-0.08234300
C	-0.23102800	-1.67102400	-1.50213000
O	-0.12492400	-2.51810700	-2.22769700
Cl	-0.99900600	-1.85730200	1.50864700
C	1.39287200	-0.13225300	0.52118000
C	2.41876600	0.46273900	-0.33324200
C	1.92423800	1.00083100	-1.45109000
C	0.48751700	1.05495100	-1.73583200
H	2.57541900	1.44943600	-2.19071500
H	0.17329400	0.65266800	-2.69057000
C	-0.39269600	1.91007700	-1.10165300

C	-0.10875800	2.88792600	-0.01147000	H	0.03088200	-3.35423300	-2.03075200
C	-1.13453200	2.61553700	1.07425300	H	-1.91615500	-1.89096400	-2.48694300
H	-1.34938500	2.04386300	-1.59131300	H	-0.61894200	-1.38623600	-3.55626900
H	0.90225500	2.77006500	0.37390800	C	-2.62028900	-0.35331700	0.40810700
H	-0.20376700	3.89417200	-0.42165600	O	-3.73478400	-0.48359900	0.45235800
H	-2.13521800	2.77341800	0.66969600	F	1.86954100	0.50275300	-1.37524400
H	-1.01744100	3.29782800	1.91712300	O	1.13579300	2.95693000	-1.65810700
C	-2.50924100	-0.03060400	-0.49452500	H	1.59736300	2.07771300	-1.68061300
O	-3.61859500	0.03381400	-0.64464500	H	0.86948500	3.22479000	-2.54869600
F	1.69909000	-0.06965000	1.80680700	H	0.31344100	2.83053000	-1.05778000
O	1.79643000	-1.97548400	0.34274200	O	1.72438300	1.43692200	0.66894000
H	1.07058900	-2.36206600	0.87086400	H	2.67483400	1.50001500	0.82401900
H	2.62105100	-2.21871000	0.78406700	C	-0.93643600	-0.07423300	-1.86593000
C	-0.96033700	1.17973000	1.52302600	H	-0.11438800	0.53117500	-2.22185000
H	-0.12077300	1.06396800	2.19705600	H	-1.86371200	0.46354400	-2.04097900
H	-1.84243600	0.77307700	2.00766800	C	3.76574900	-0.74265500	0.38164900
C	3.84767600	0.48342900	0.09268600	H	4.13519900	0.07418200	1.00500000
H	4.44976100	1.03576800	-0.62079100	H	4.25896300	-1.65113000	0.71230700
H	3.94586800	0.95233900	1.06956900	H	4.06700200	-0.53240800	-0.64274800
H	4.25235600	-0.52482800	0.17187300				

INT21

Rh	-0.63227500	-0.06123600	0.23748900
C	-0.31205200	0.31861300	2.25406600
O	-0.14041700	0.59986900	3.32648400
Cl	-1.13443800	2.30432700	0.00907400
C	1.42500500	0.26267300	0.02467100
C	2.28082700	-0.88651000	0.46592000
C	1.64843800	-1.95601700	0.93016700
C	0.18869700	-2.08173600	0.87352500
H	2.18838000	-2.79389400	1.35240100
H	-0.31878700	-2.36214800	1.78806400
C	-0.51007600	-2.25761100	-0.30534500
C	0.02490600	-2.31451500	-1.69805800
C	-0.91901400	-1.44921000	-2.50966600
H	-1.52687700	-2.61791800	-0.20594300
H	1.04093100	-1.92961200	-1.74531500

TS16

Rh	-0.64697600	-0.03235100	0.24201300
C	-0.47844800	0.32498500	2.28826300
O	-0.40264900	0.60988500	3.36999800
Cl	-1.05176700	2.33035100	-0.00070500
C	1.40913800	0.25125200	0.20142400
C	2.26000700	-0.90736900	0.55851900
C	1.59469100	-1.99067300	0.94557700
C	0.13325100	-2.08553900	0.87663000
H	2.11226200	-2.85425000	1.34370600
H	-0.37981300	-2.35384800	1.79162800
C	-0.56201400	-2.25447100	-0.30203300
C	-0.01930100	-2.31178200	-1.68993900
C	-0.92740900	-1.40943000	-2.50231700
H	-1.58603000	-2.59409200	-0.20505200
H	1.00767700	-1.95398500	-1.72471500
H	-0.04301500	-3.34785400	-2.03225400

H	-1.94610200	-1.79831400	-2.46970800
H	-0.63105000	-1.36968800	-3.55131300
C	-2.63327500	-0.27615900	0.26514400
O	-3.75119700	-0.37082000	0.23371100
F	2.01657700	0.46980800	-1.43136400
O	1.33426200	2.70400500	-1.78867000
H	1.71305600	1.69241600	-1.70046400
H	1.08831600	2.92532300	-2.69477000
H	0.52564300	2.75076600	-1.21029500
O	1.76854900	1.41981300	0.71894800
H	2.71568200	1.44465300	0.91454800
C	-0.85895600	-0.03108400	-1.87664900
H	0.02957700	0.48844800	-2.19797000
H	-1.72847500	0.58265300	-2.09075300
C	3.74588600	-0.76408200	0.55230900
H	4.08606600	-0.03725600	1.29299100
H	4.22195500	-1.70976300	0.78975200
H	4.08588400	-0.43058600	-0.42512100

INT22

Rh	-0.55303900	0.35221800	-0.22448000
C	-2.11351800	0.33174600	0.86492000
O	-3.03297300	0.29969800	1.51724700
Cl	-1.67608300	-1.35288900	-1.67312800
C	0.32299700	-0.93274200	0.98205400
C	1.56385200	-1.55268300	0.44642800
C	1.96031500	-1.20552600	-0.77728500
C	1.24168700	-0.19723700	-1.55855900
H	2.81456700	-1.68478800	-1.23874700
H	0.77306900	-0.53845000	-2.47205200
C	1.31156700	1.14590400	-1.33043700
C	2.12441500	1.87066900	-0.31108100
C	1.15864900	2.75156700	0.46048300
H	0.81267000	1.78219900	-2.05651400
H	2.62447200	1.16926700	0.35544600
H	2.88854700	2.45856800	-0.82263100
H	0.69199700	3.45513800	-0.23067800
H	1.67446800	3.34436200	1.21915400
O	-0.13312900	-1.21524500	2.05177600
C	0.10630400	1.85931400	1.09250400
H	0.50106700	1.35564900	1.97340300
H	-0.75928400	2.43925300	1.41093600
C	2.23687500	-2.55262800	1.32684000
H	1.55662100	-3.36665700	1.57098900
H	3.11835800	-2.95971100	0.84046500
H	2.53356200	-2.09146100	2.26761900

TS17

Rh	0.70004600	-0.04762400	0.11428300
C	1.77583700	1.48127600	0.57141300
O	2.42507500	2.37012800	0.81955400
Cl	2.50938400	-0.87683500	-1.14097600
C	-1.01201300	1.15046600	-0.07026600
C	-2.02092800	0.49249600	-0.95480900
C	-1.79102000	-0.75215200	-1.36813200
C	-0.58747400	-1.50961600	-1.00203000
H	-2.45281300	-1.21956600	-2.08759000
H	0.02664100	-1.81686500	-1.84078600
C	-0.27281300	-2.07420600	0.20855800
C	-1.09358700	-2.09954500	1.46451400
C	-1.85174000	-0.81407900	1.75487100
H	0.57760900	-2.74446400	0.19773800
H	-1.77980000	-2.94777900	1.40450400
H	-0.41863700	-2.31245500	2.29271400
H	-2.19074700	-0.83058000	2.79081100
H	-2.74275700	-0.73412400	1.13953700
O	-0.84213900	2.35445800	-0.10531700
C	-0.95595300	0.39706900	1.57079200
H	-1.38622800	1.31158300	1.96192200
H	-0.03874900	0.27629200	2.16489000
C	-3.18622400	1.32961000	-1.36107500
H	-2.84141200	2.25302700	-1.82220900
H	-3.82769500	0.79728100	-2.05709800
H	-3.77498900	1.61233300	-0.48747800

TS17'

Rh	0.81773000	0.00548300	0.09755900
C	1.60488700	1.69700000	0.50093600
O	2.10685200	2.68286200	0.73242900
Cl	2.84314000	-0.57373700	-0.98295700
C	-1.34882600	0.87121200	-0.00255800
C	-1.93705300	0.01027900	-1.08542700
C	-1.36393200	-1.11519200	-1.50056800
C	-0.10744800	-1.67458800	-1.00979100
H	-1.80807800	-1.63401400	-2.34196700
H	0.61136600	-1.90501500	-1.78665800
C	0.18168600	-2.15895800	0.24137900
C	-0.74454500	-2.34626300	1.41478100
C	-1.55803400	-1.12026400	1.81558400
H	1.12662800	-2.68124700	0.31758100
H	-1.40540000	-3.18686500	1.19460700
H	-0.13071500	-2.64845300	2.26097600
H	-1.87153100	-1.22383500	2.85490800
H	-2.46884300	-1.02981200	1.23092300
C	-0.69375100	0.11624700	1.70115800
H	-1.05178200	1.00224200	2.20098600
H	0.30306800	-0.10323000	2.11987900
C	-3.20336300	0.54469800	-1.68371000
H	-3.08323200	1.59052800	-1.96250400
H	-3.47009700	-0.02538300	-2.56822900
H	-4.02361300	0.49207700	-0.97061400
F	-0.85760500	2.04053100	-0.53293200
F	-2.44145600	1.34301200	0.70627700

2-four

C	-0.54737100	1.86933900	-0.51169600
C	-1.68600100	1.22160800	-0.25321600
C	-1.89523900	0.16565500	0.79016500
C	0.74031400	1.57994800	0.11430000
C	-1.69185800	-1.27572500	0.29902600
C	1.27980300	0.36140800	0.17931800
C	0.62993100	-0.80467200	-0.51081500
H	-0.56701300	2.68341000	-1.22708900
H	-2.56414300	1.50330800	-0.82201800
H	-1.22367500	0.34268100	1.63281500
H	1.29779800	2.41404100	0.52755200
H	-2.25545600	-1.95635600	0.93469800
O	0.80905600	-0.99936300	-1.69225200
H	-2.08526700	-1.38459100	-0.71188700
H	-2.91299100	0.26111300	1.16585400
C	2.58017800	0.05212800	0.85226300
H	2.45223000	-0.70944500	1.62309700
H	3.30092200	-0.34074200	0.13431500
H	2.99791600	0.94228500	1.31519300
C	-0.22621600	-1.72135700	0.32299600
H	-0.14227000	-2.72757800	-0.08264000
H	0.12825700	-1.72321700	1.35408400

1-four-H

C	-0.01239400	0.13056300	0.00000200
H	-0.09156900	1.21351800	0.00002600
C	-1.12326400	-0.61088700	-0.00001400
H	-1.02667800	-1.69189800	-0.00003800
C	-2.48890400	-0.09640700	-0.00000300
C	-3.52155500	-0.94497700	-0.00002300
C	1.36654800	-0.40900500	-0.00000900
C	2.37000100	0.09546600	-1.06816400
C	2.36999900	0.09541600	1.06817100
H	1.34784100	-1.49930200	-0.00003400
C	3.47575700	0.03669300	0.00000300
H	2.14415500	1.12524500	-1.34408100
H	2.48219300	-0.49780000	-1.97260900
H	2.14415200	1.12518300	1.34413600
H	2.48218900	-0.49789200	1.97258900
H	4.22871500	0.82060500	0.00002200
H	3.97385100	-0.93125000	-0.00001900
C	-2.69523300	1.38865000	0.00002900
H	-2.23401300	1.84659400	0.87564200

H	-2.23401300	1.84663200	-0.87556300
H	-3.75333300	1.63505500	0.00003500
H	-4.54295100	-0.59270700	-0.00001600
H	-3.36626900	-2.01505300	-0.00004700

TS9-H

Rh	0.37070700	-0.53663700	-0.08303800
Cl	0.11633800	-0.34730700	2.52810000
O	-1.92681800	-2.46478800	-0.07423000
C	-1.05097600	-1.74760200	-0.11234400
C	2.02673500	2.25826000	0.67403400
C	1.50077700	2.77313000	-0.65286600
C	1.11253500	1.42069000	-1.26588400
C	-0.28642700	1.04412200	-1.34928100
C	-1.09321900	1.21822500	-0.22228700
H	2.91760600	2.74440400	1.06693000
H	1.25958500	2.27685900	1.44594000
H	2.27827100	3.22981000	-1.26033200
H	0.66103300	3.46028500	-0.59255300
H	1.68066900	1.11873400	-2.13349200
H	-0.67686800	0.66878300	-2.28281900
H	-0.70673500	1.79892000	0.60461800
C	-2.53425400	0.96156900	-0.19233600
C	-3.21444100	1.19652400	0.93181300
C	2.25430300	0.83348700	0.22314900
H	2.29302500	0.09129600	1.01875500
H	3.11447500	0.70861500	-0.42301600
C	-3.19660900	0.47282800	-1.44470500
H	-4.24746600	0.26309800	-1.26942300
H	-3.12143500	1.22030200	-2.23519900
H	-2.72818500	-0.43509900	-1.82594800
C	1.59253300	-1.88164100	-0.68555300
O	2.29475300	-2.65682900	-1.12413200
H	-4.27905400	1.02529900	0.99108200
H	-2.71369700	1.55696000	1.81892400.

TS17-H

Rh	0.68699000	0.12008900	-0.03367400
C	1.85371600	1.57305600	0.28266600
O	2.58175300	2.42302300	0.46170200
Cl	2.57880300	-1.13386700	-0.77640200
C	-1.13834900	1.32948200	-0.38601900
C	-2.24718100	0.50385500	-0.93035200
C	-2.01016200	-0.77870600	-1.19213200
C	-0.71964200	-1.42848700	-0.88906600
H	-2.77863900	-1.40829600	-1.62458000
H	-0.14904100	-1.80524100	-1.73147600
C	-0.34000500	-1.87148400	0.35101200
C	-1.10118700	-1.72251500	1.63738800
C	-1.77199300	-0.36913000	1.84515300
H	0.50757700	-2.54315700	0.38619500
H	-1.83940000	-2.52642100	1.69539600
H	-0.39922600	-1.89598000	2.45226100
H	-2.02056300	-0.26495400	2.90332700
H	-2.71067800	-0.30364100	1.30503100
C	-0.84112900	0.77029500	1.49765300
H	-1.20994800	1.73330400	1.81740600
H	0.10914300	0.62495800	2.02980300
C	-3.57206500	1.16458900	-1.12489500
H	-3.47897900	2.05320000	-1.74954000
H	-4.29059900	0.49025300	-1.58291400
H	-3.97160300	1.49504200	-0.16375000
H	-0.40598800	1.49711000	-1.19725600
H	-1.44231100	2.31566500	-0.06779300

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[3] 1,5-SMRE of allene-VCPs can be realized by using Rh catalyst, see: (a) X. Li, M. Zhang, D. Shu, P. J. Robichaux, S. Huang, W. Tang, *Angew. Chem., Int. Ed.* **2011**, *50*, 10421–10424. We found that the reductive elimination step here forming C(sp^2)–C(sp^3) bond is easier, with a computed activation energy of 13.4 kcal/mol (see Supporting Information). (b) I. Nakamura, M. Okamoto, Y. Sato, M. Terada, *Angew. Chem. Int. Ed.* **2012**, *51*, 10816–10819. SMREs for DECPs and DECBs with cis configuration of the middle alkene bond can be realized by photo reaction or heating, respectively (special substituents are also required for these reactions), see: (c) Z.-C. Zhang, D.-D. Zhao, Z.-C. Zhang, X.-Y. Tan, J.-X. Gong, J.-K. Fu, Z. Yang, *CCS Chem.* **2021**, *3*, 2074–2083. (d) T. Hamura, S. Tsuji, T. Matsumoto, K. Suzuki, *Chem. Lett.* **2002**, *31*, 280–281.

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9. NMR Spectra

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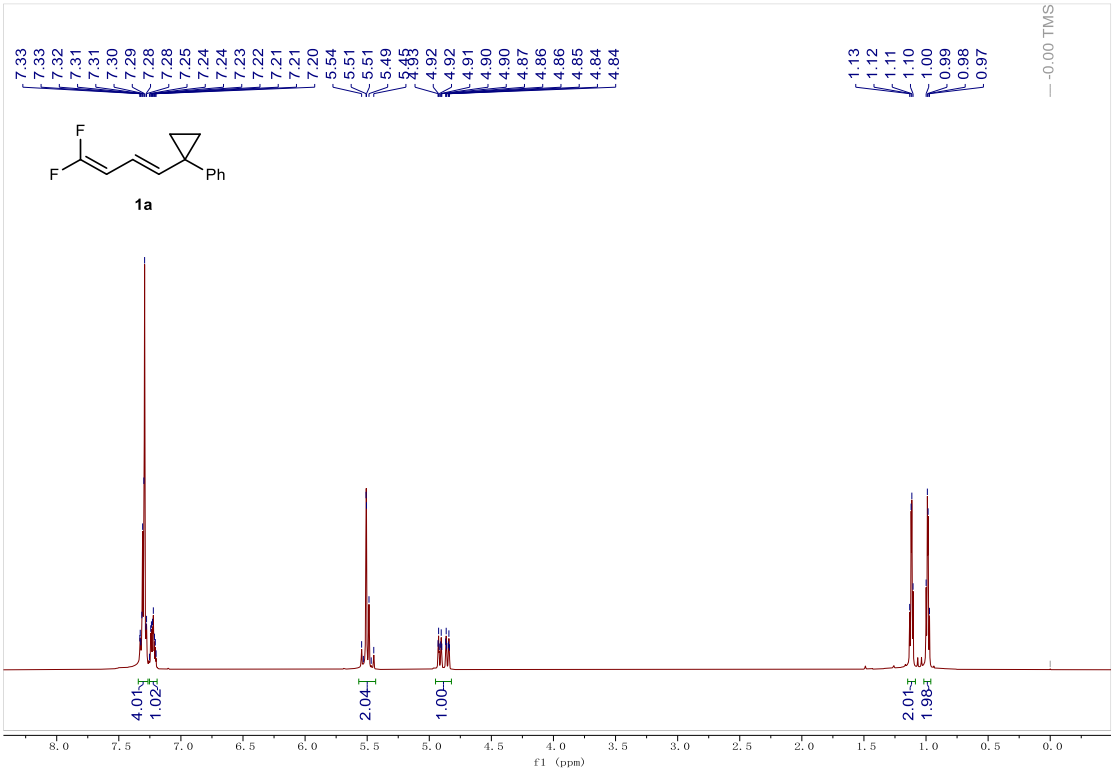

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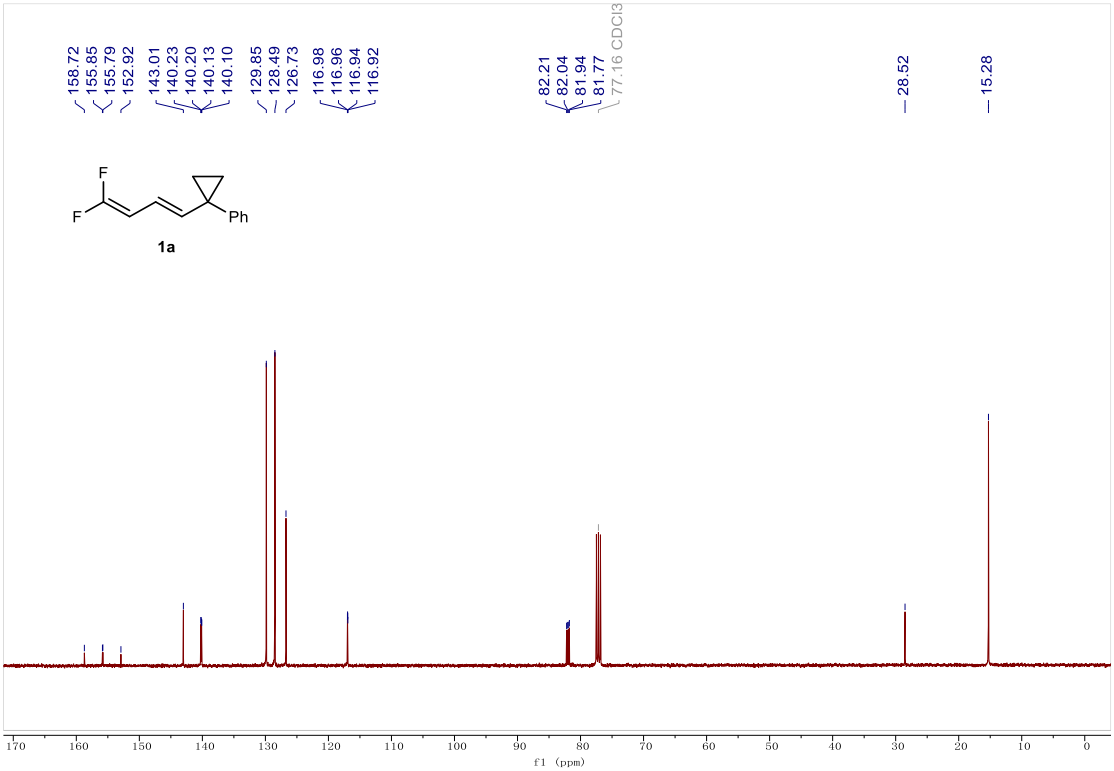

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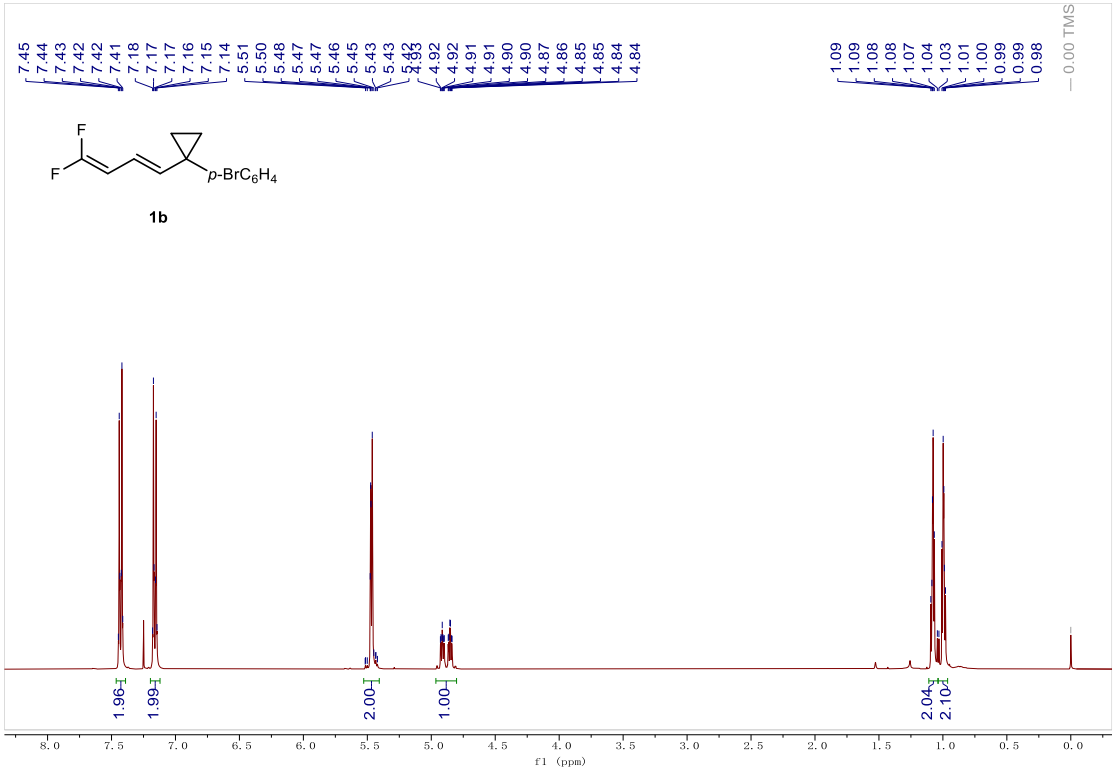

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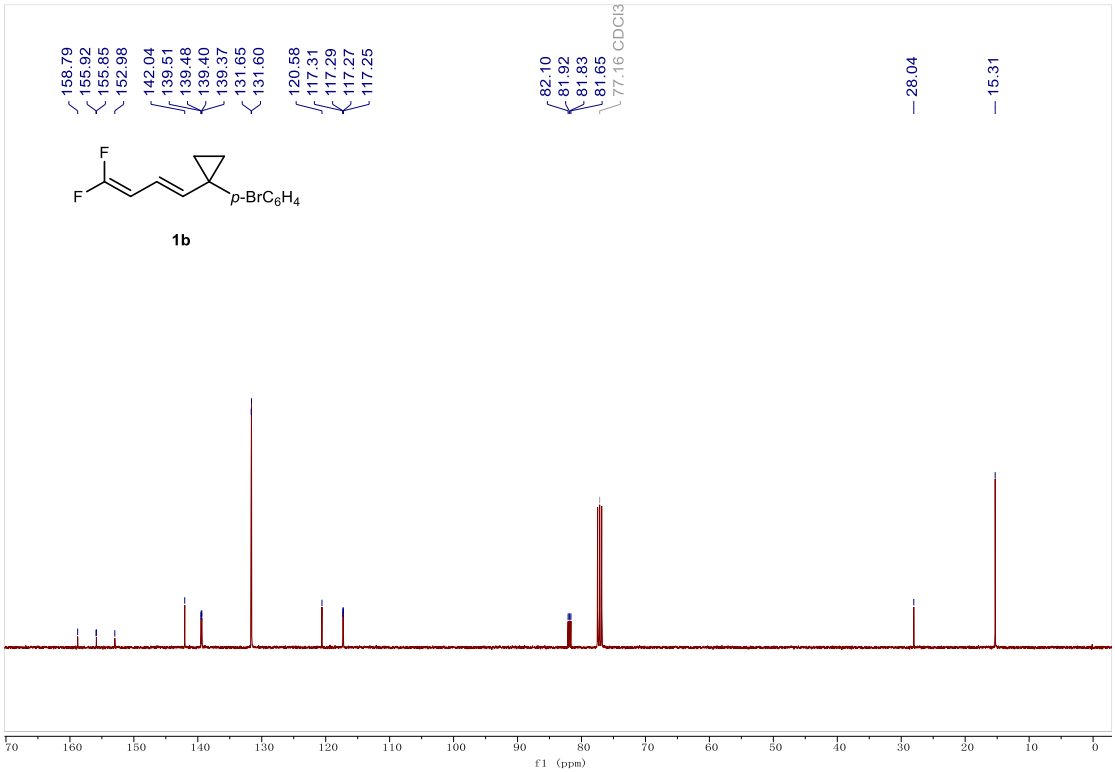

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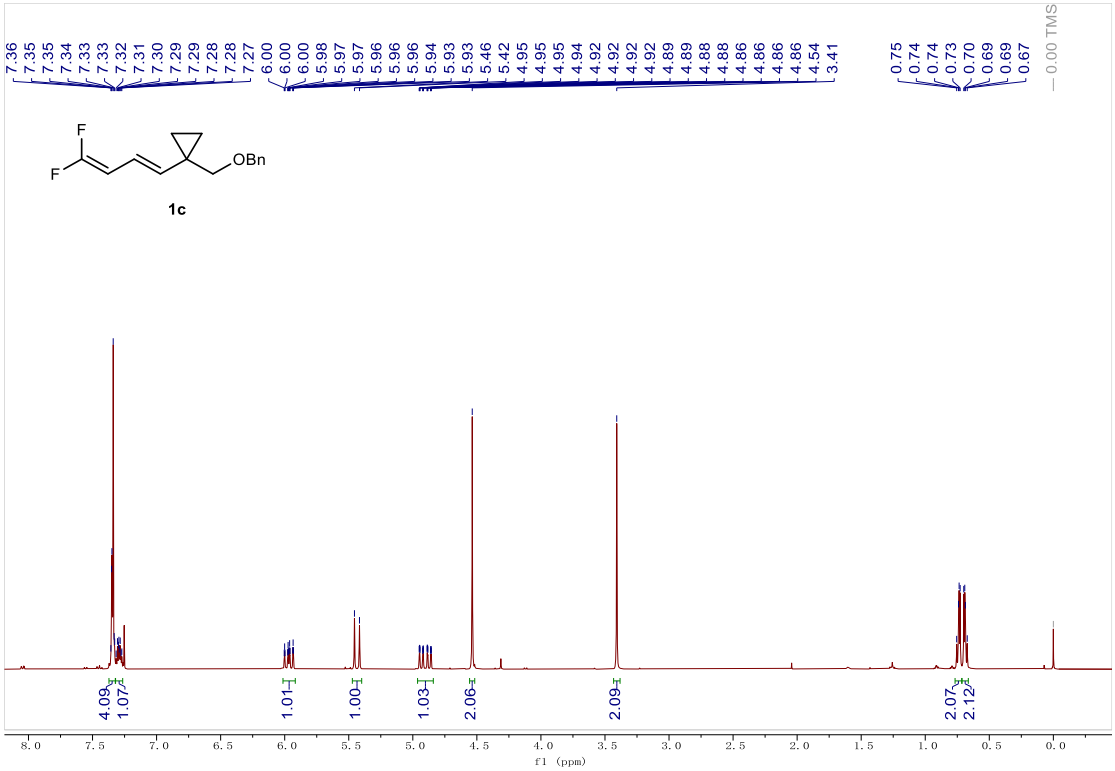

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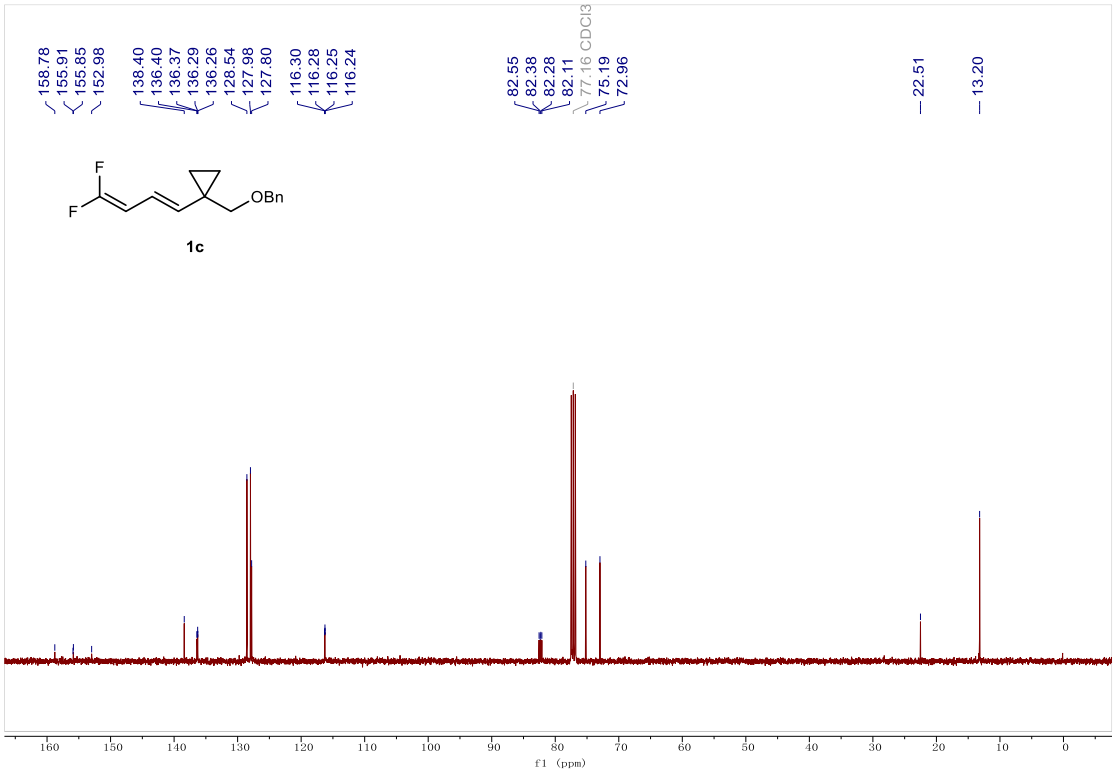

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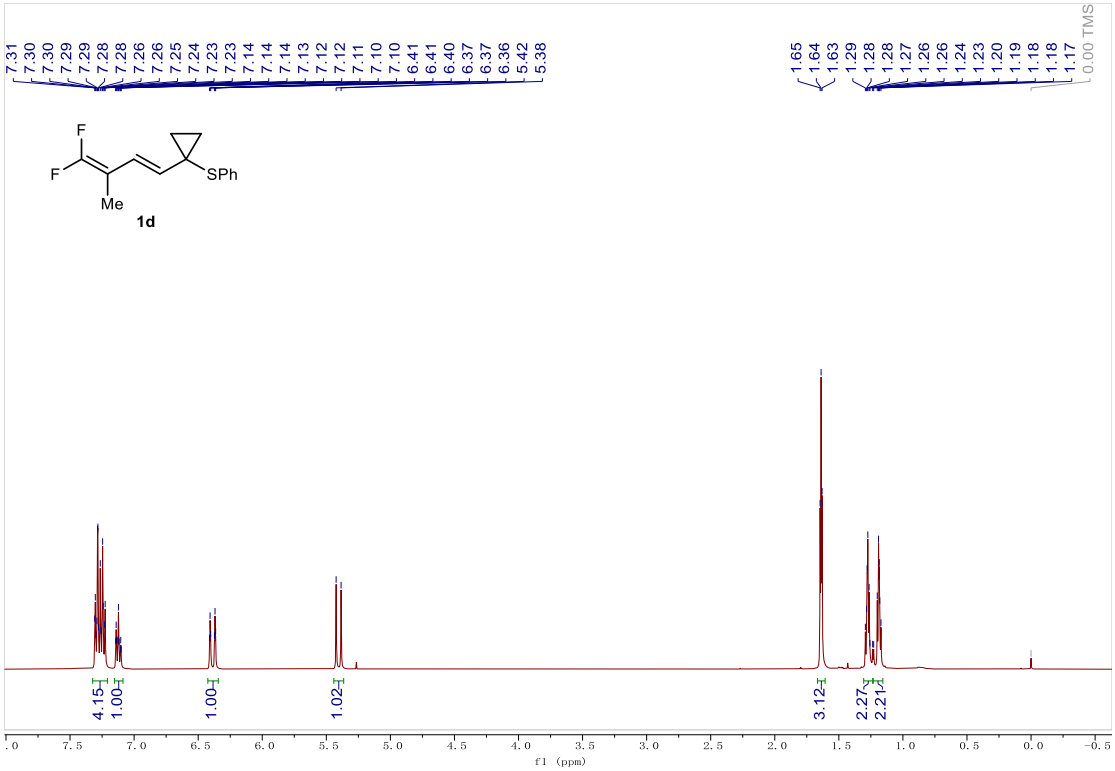

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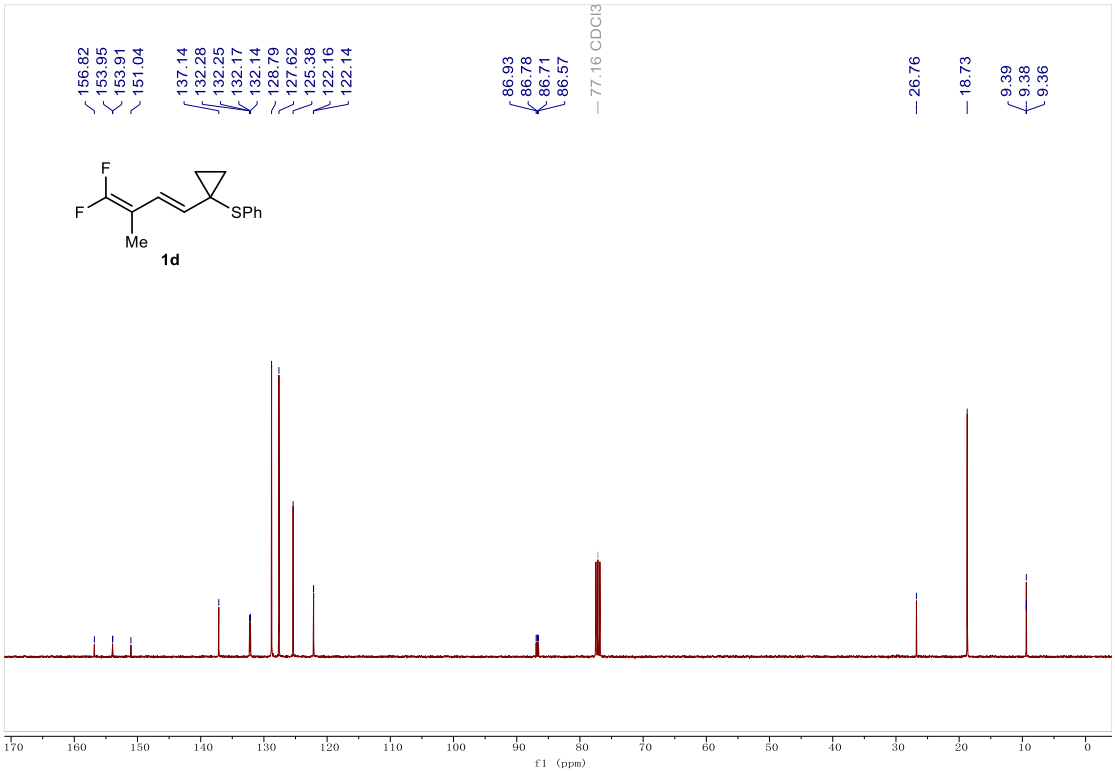

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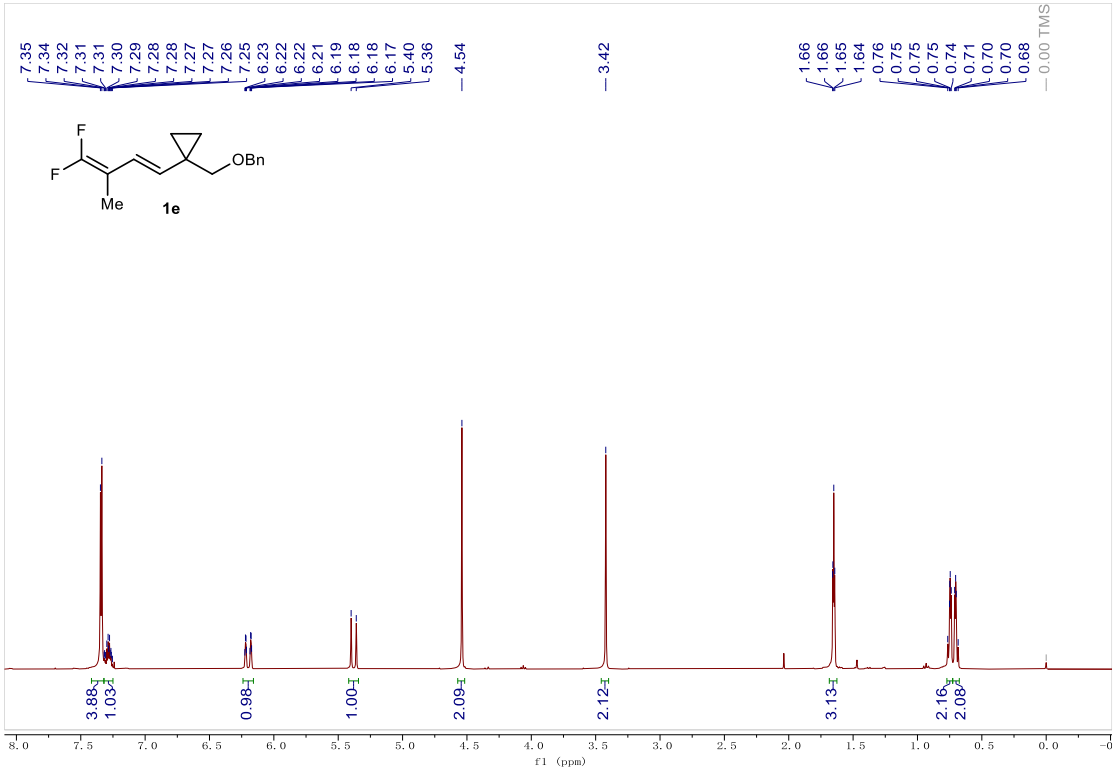

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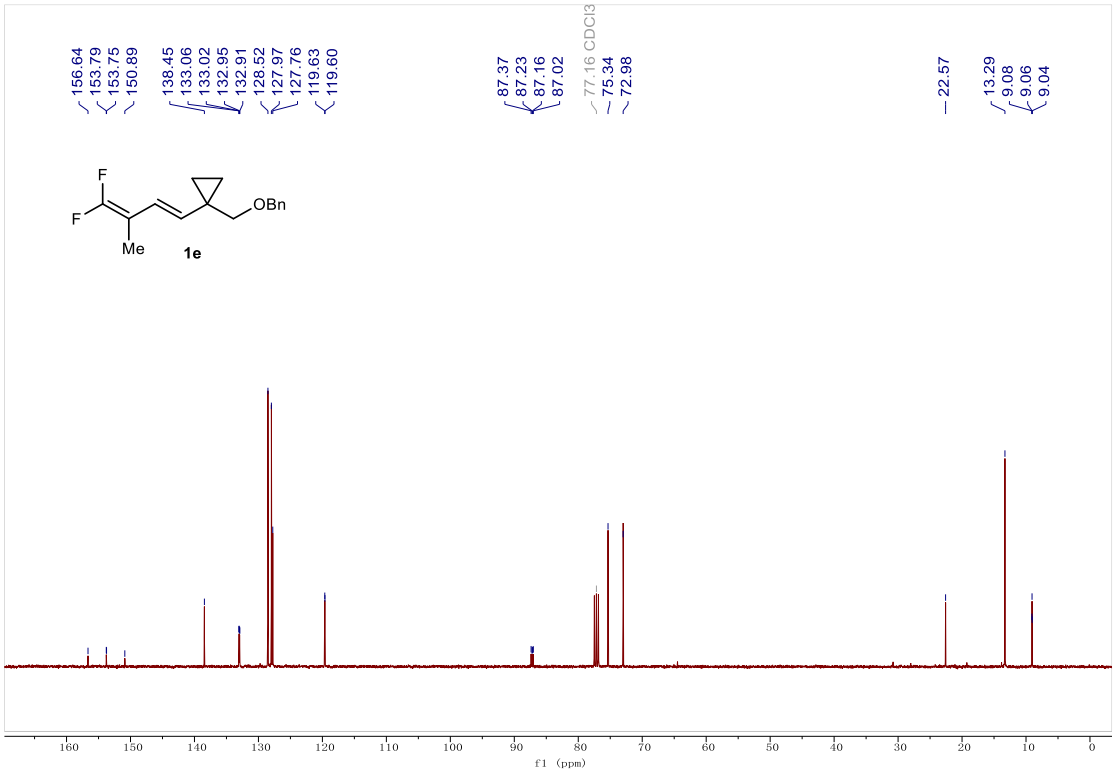

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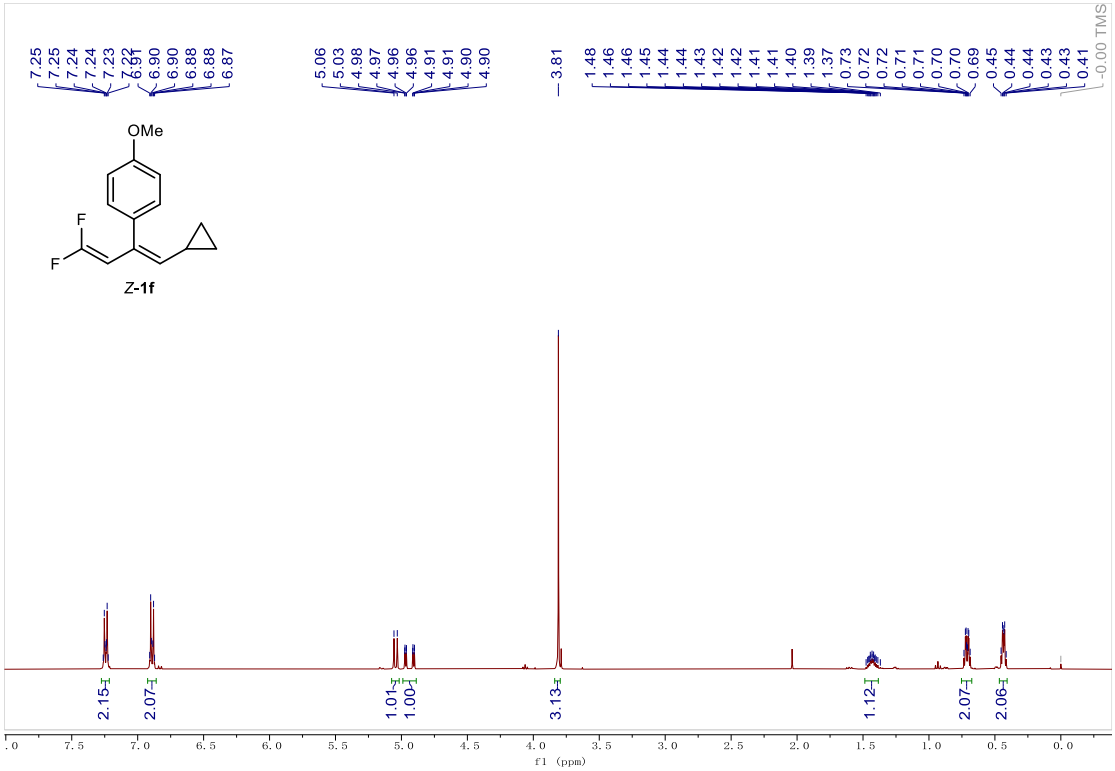

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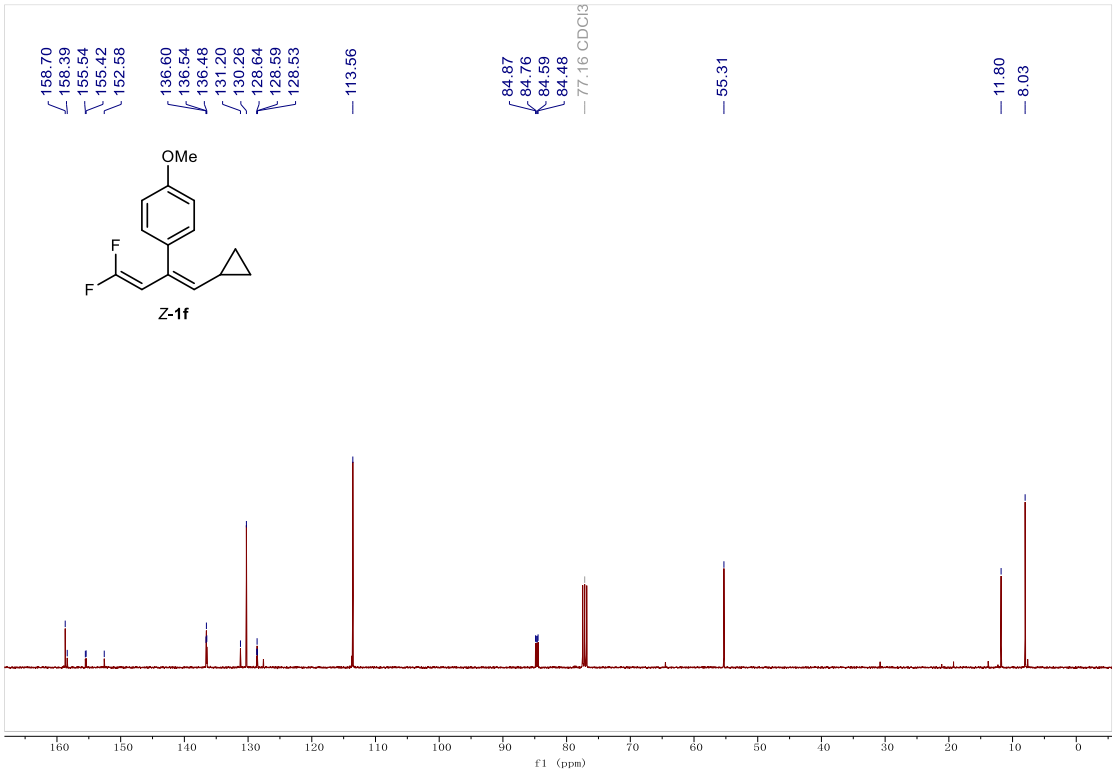

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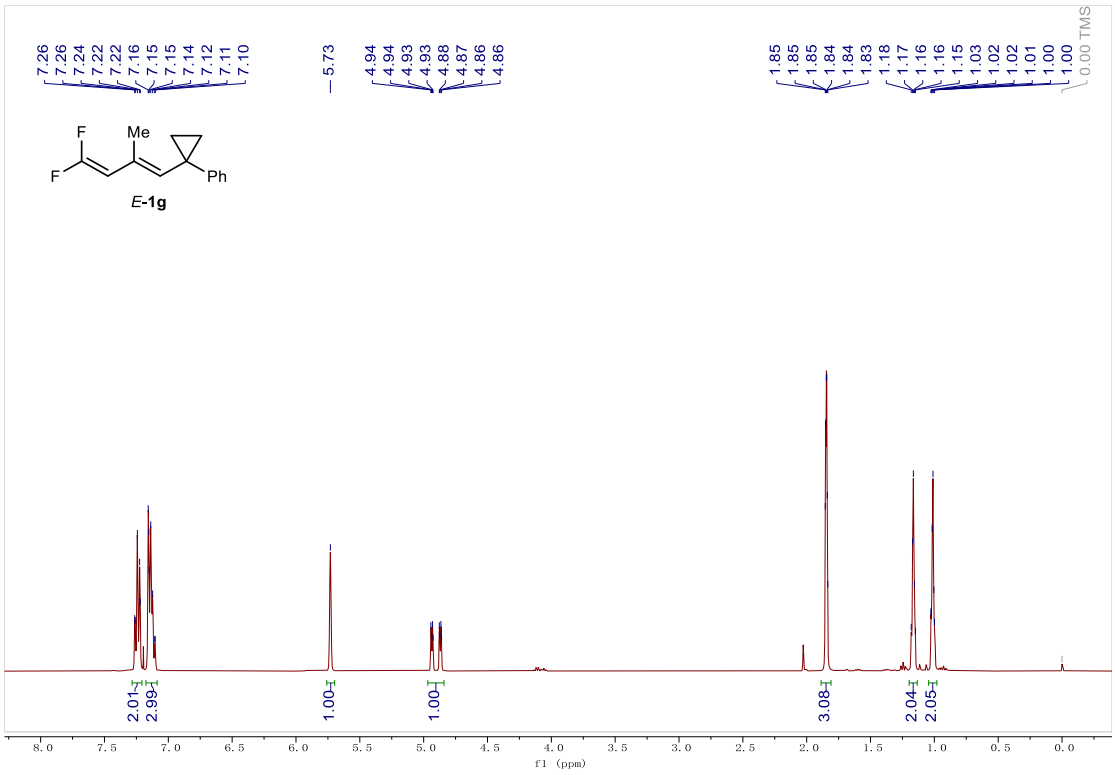

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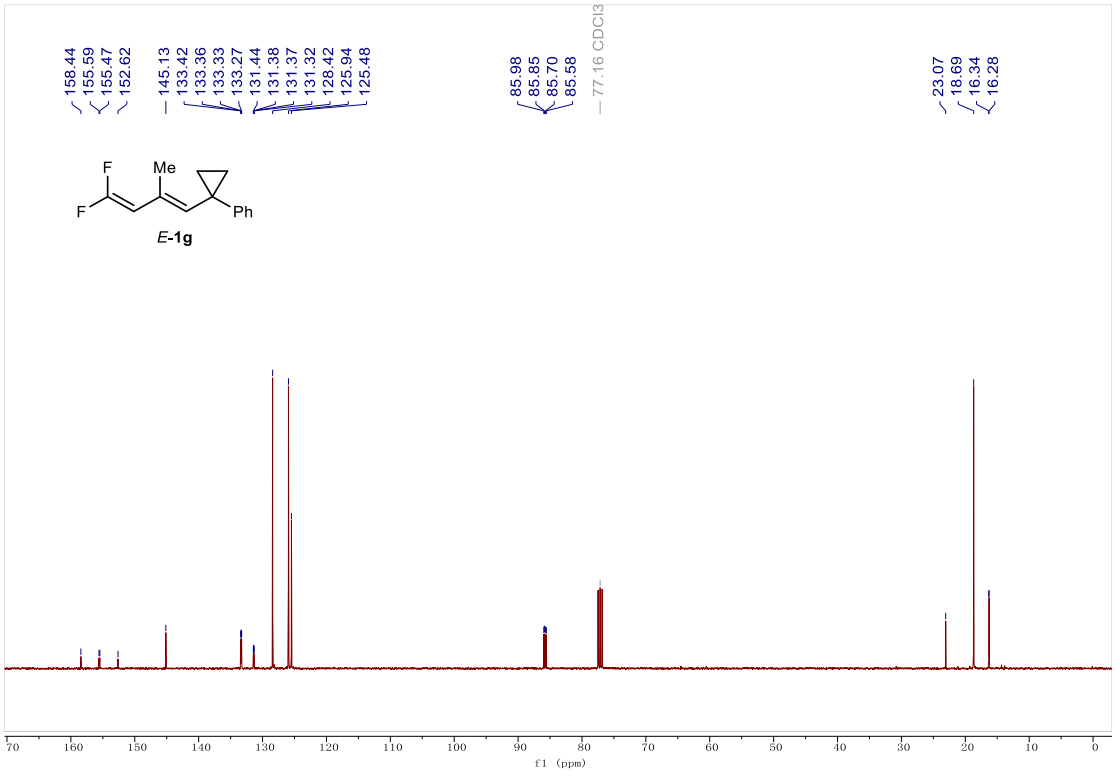

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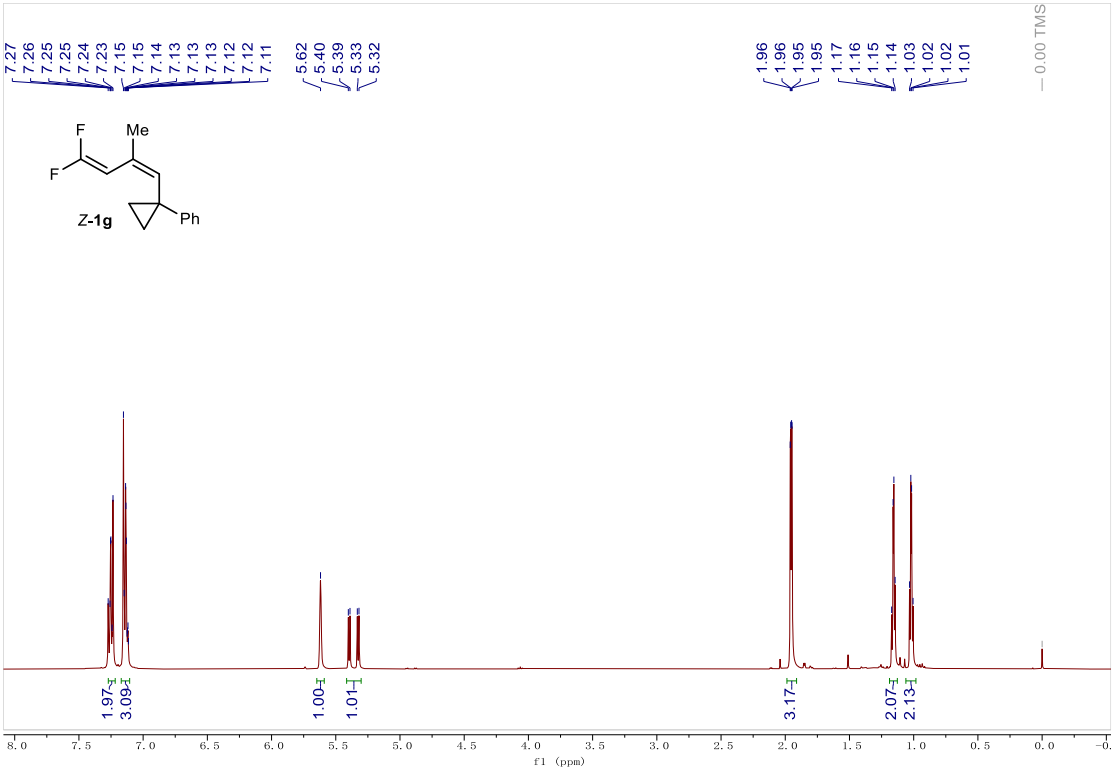

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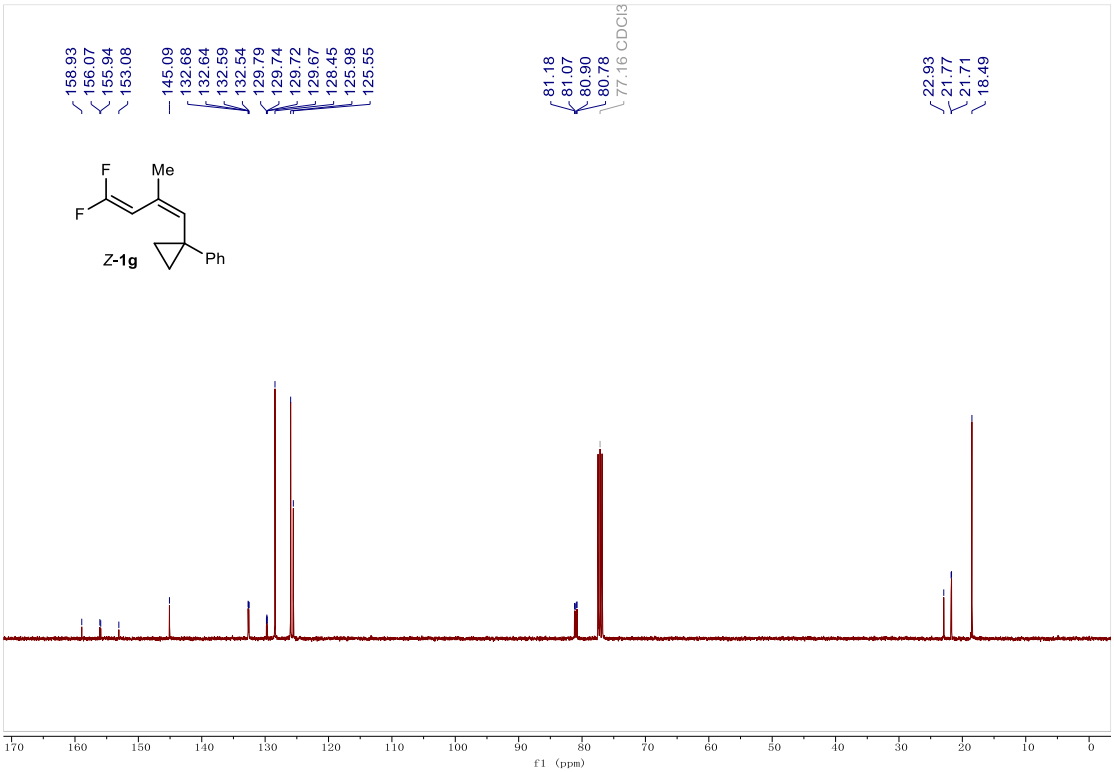

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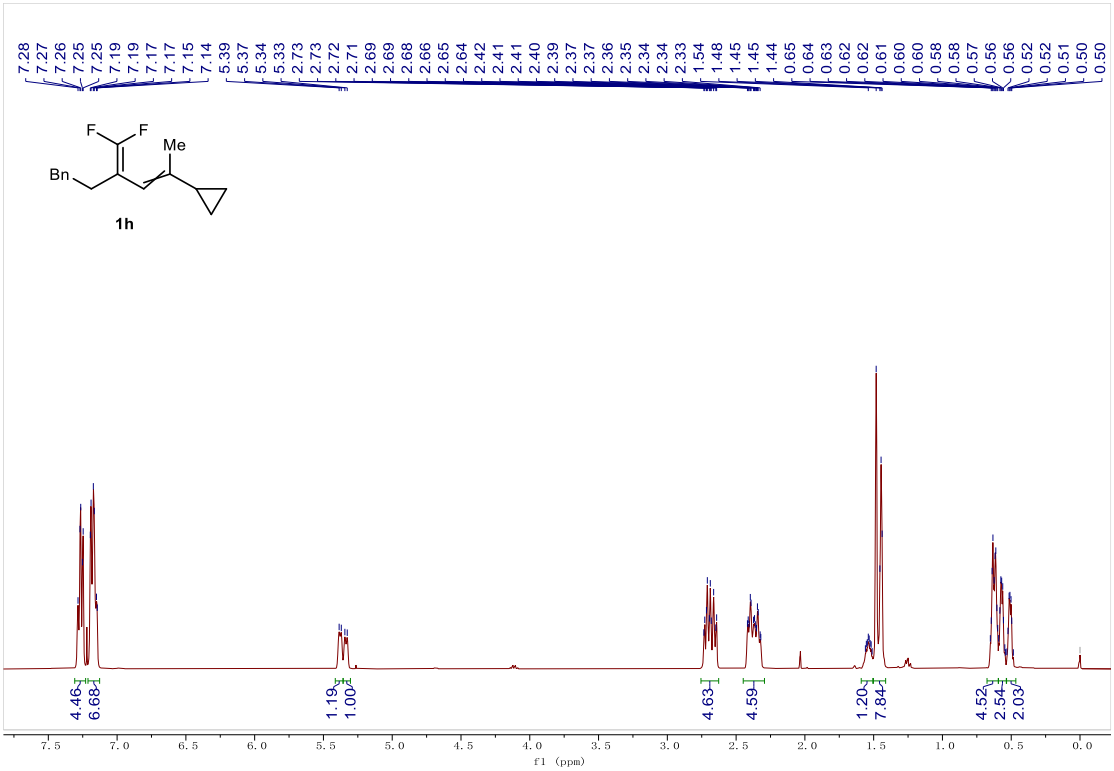

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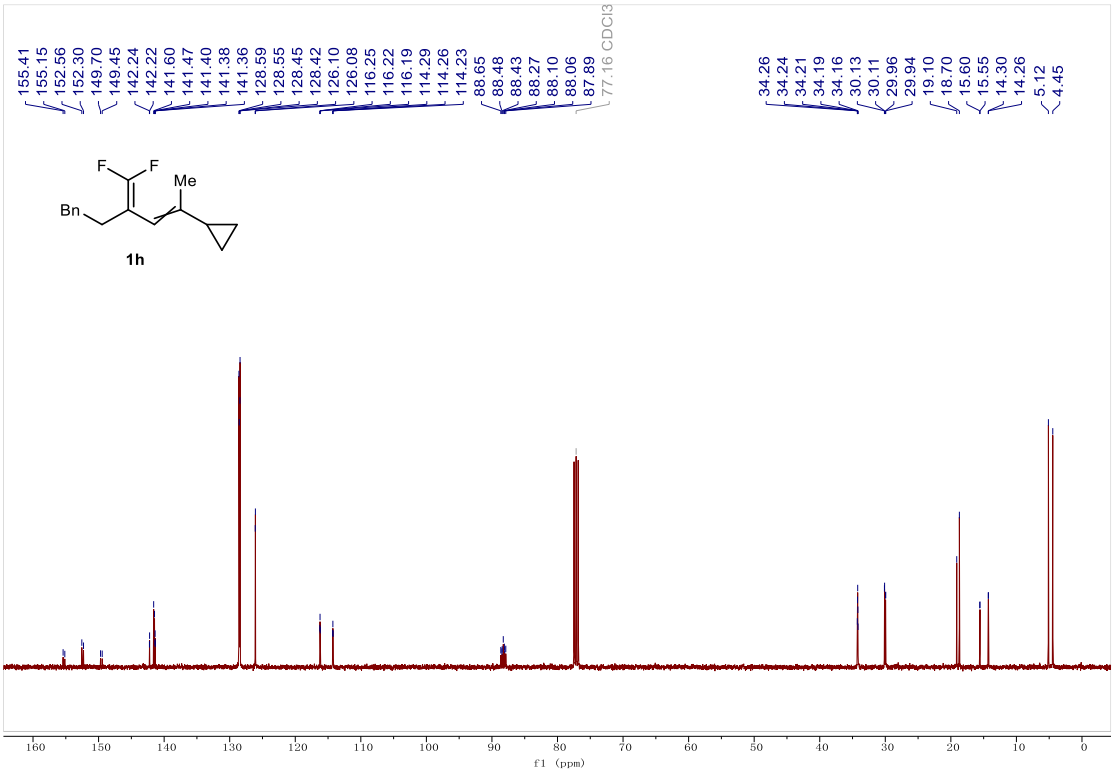

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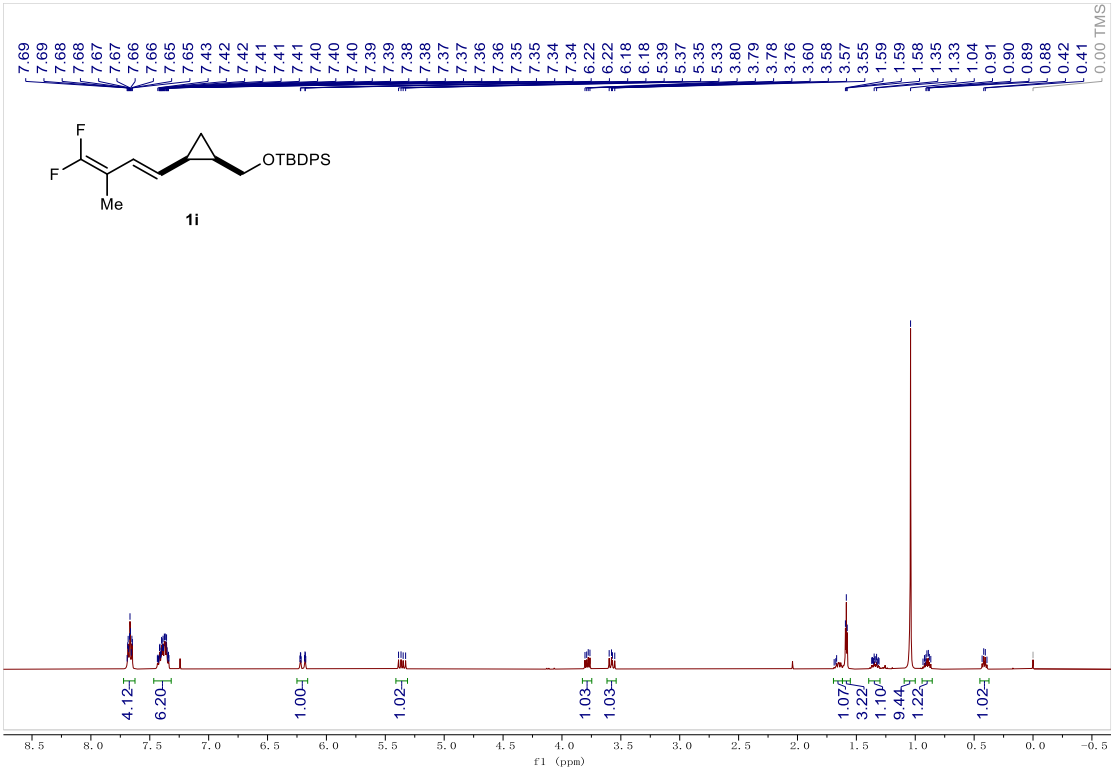

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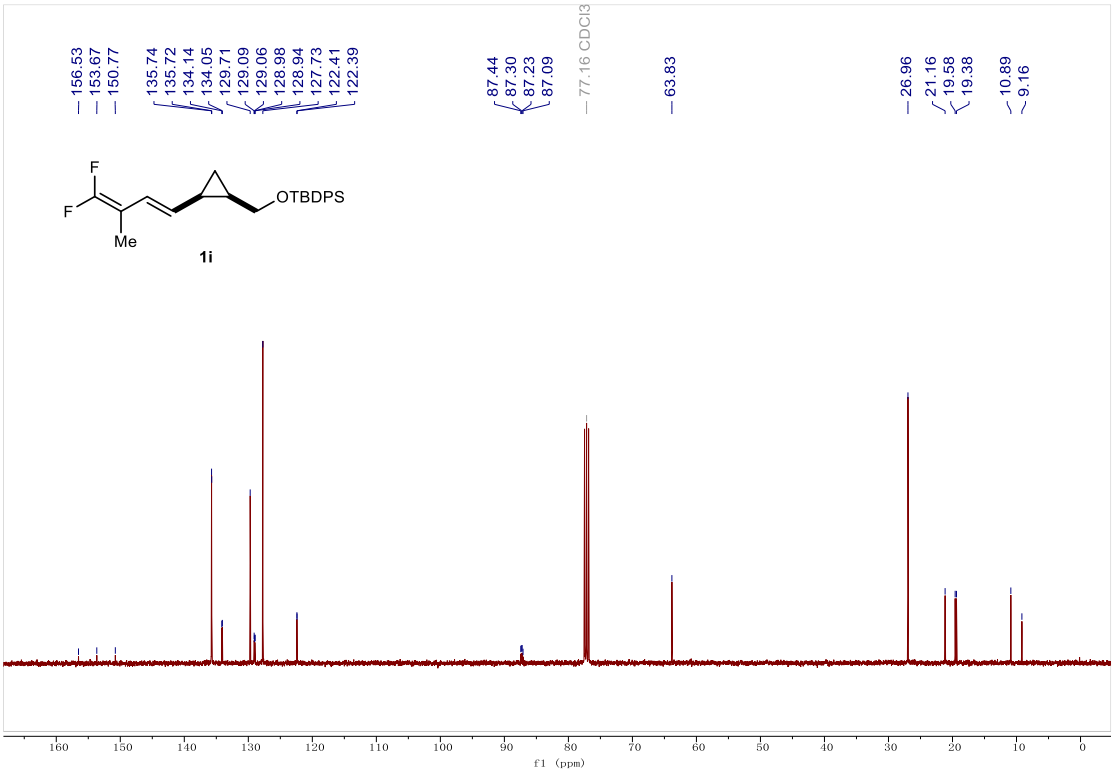

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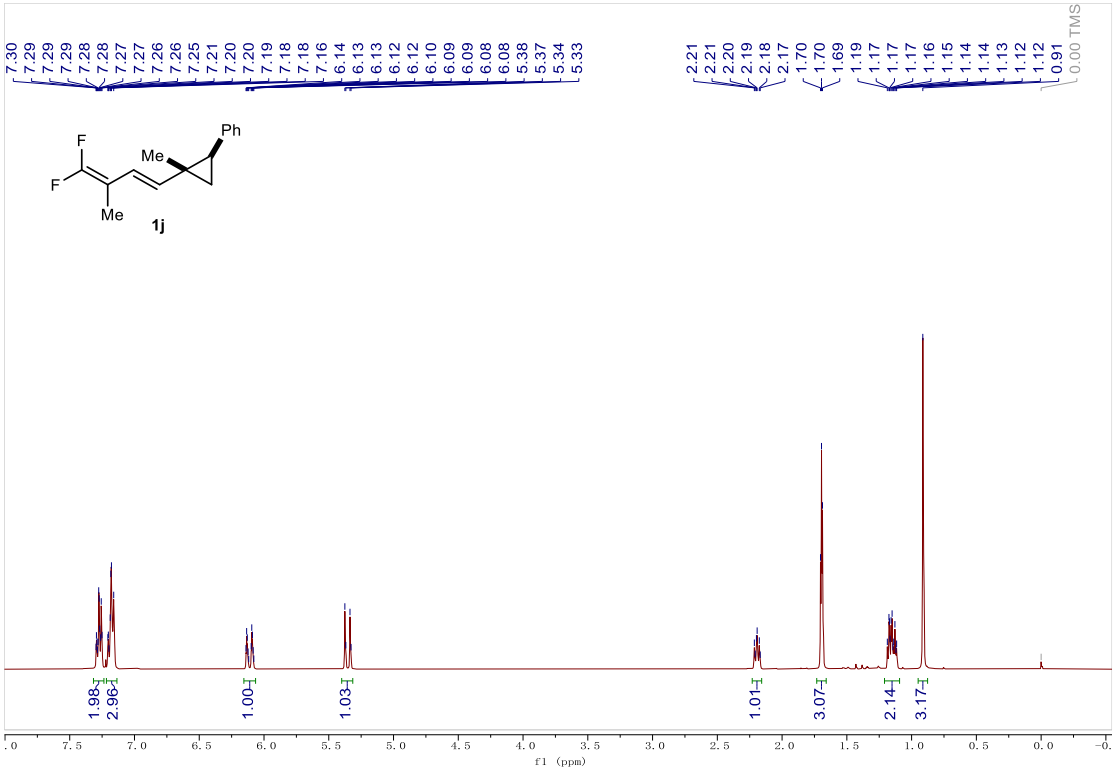

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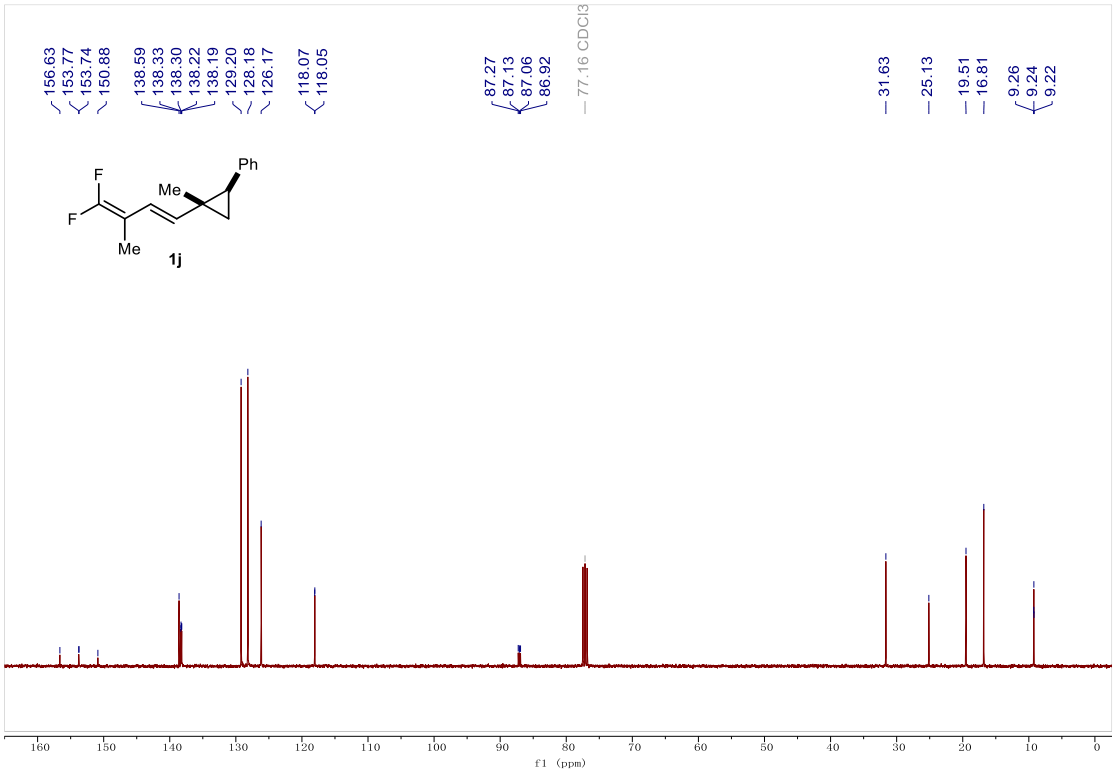

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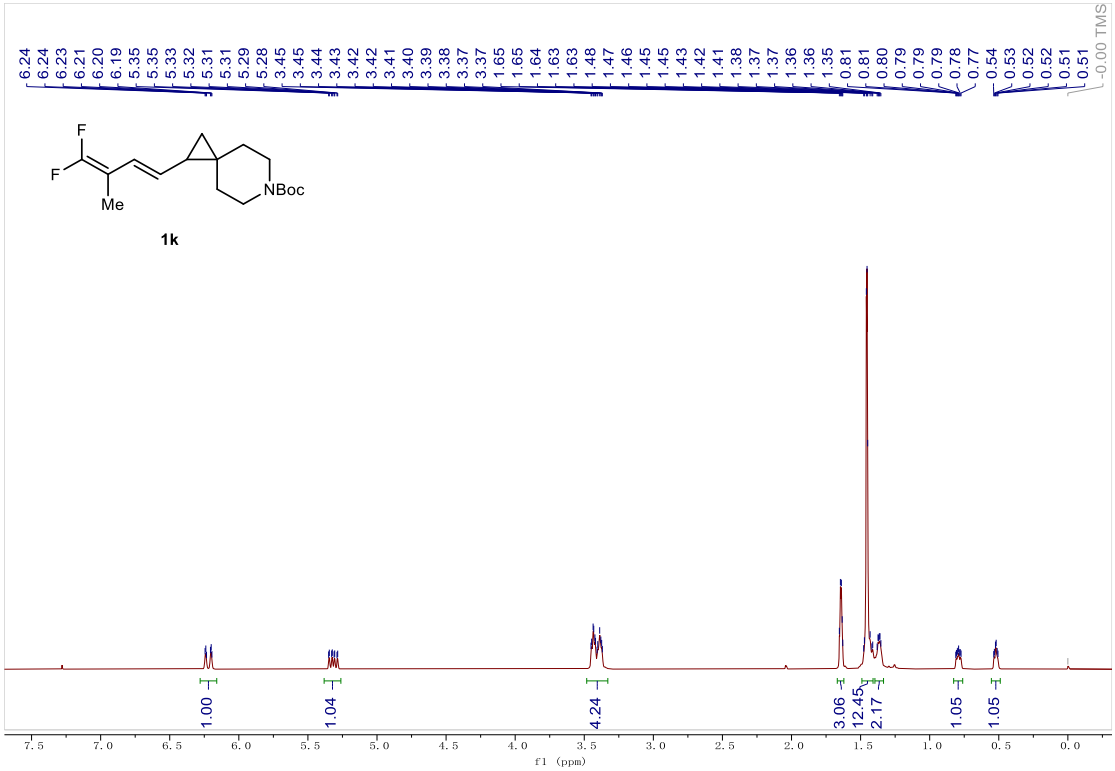
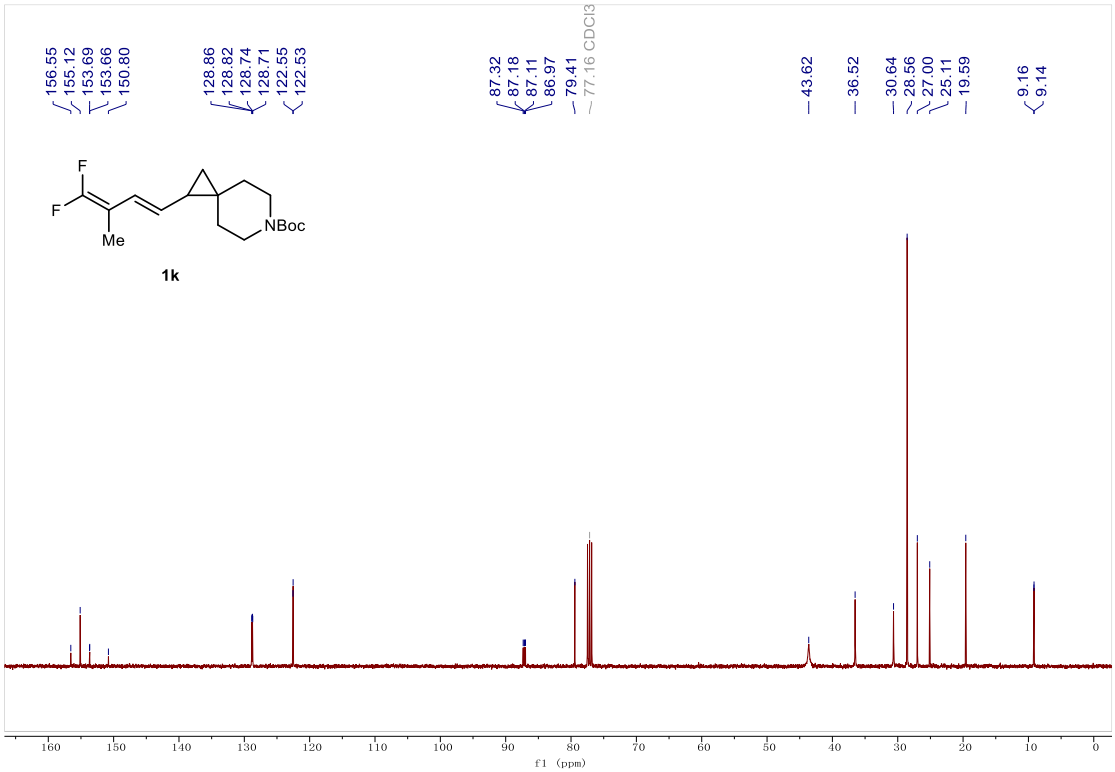
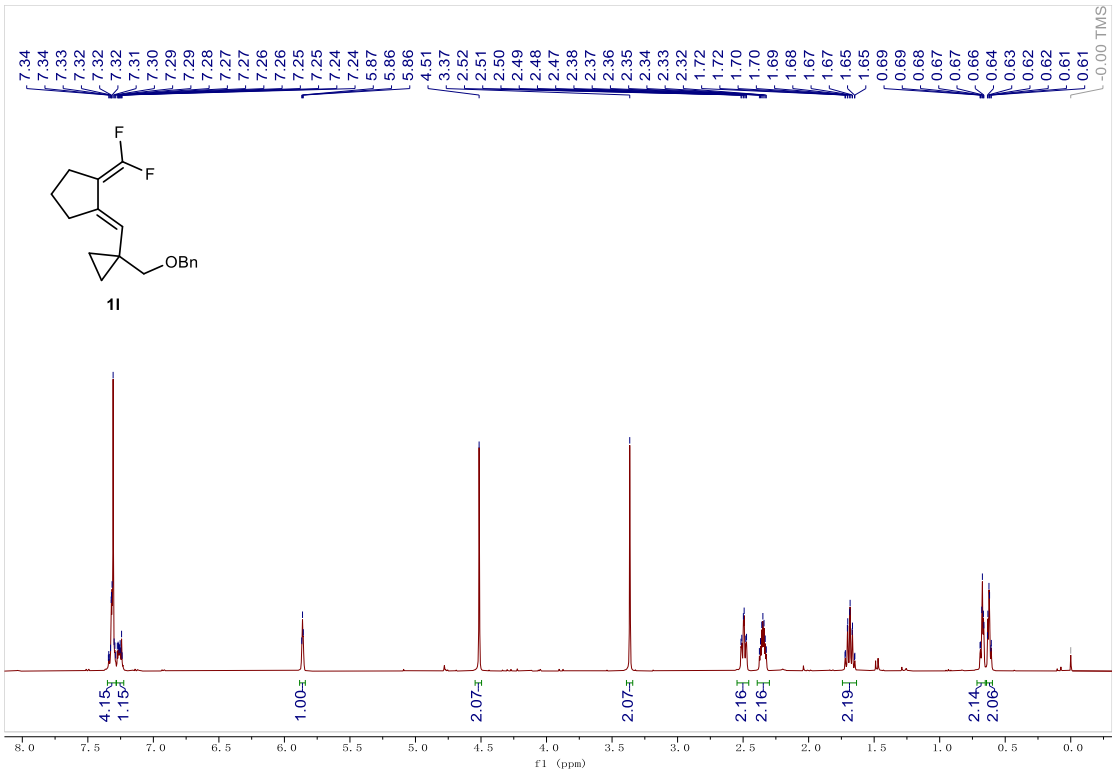


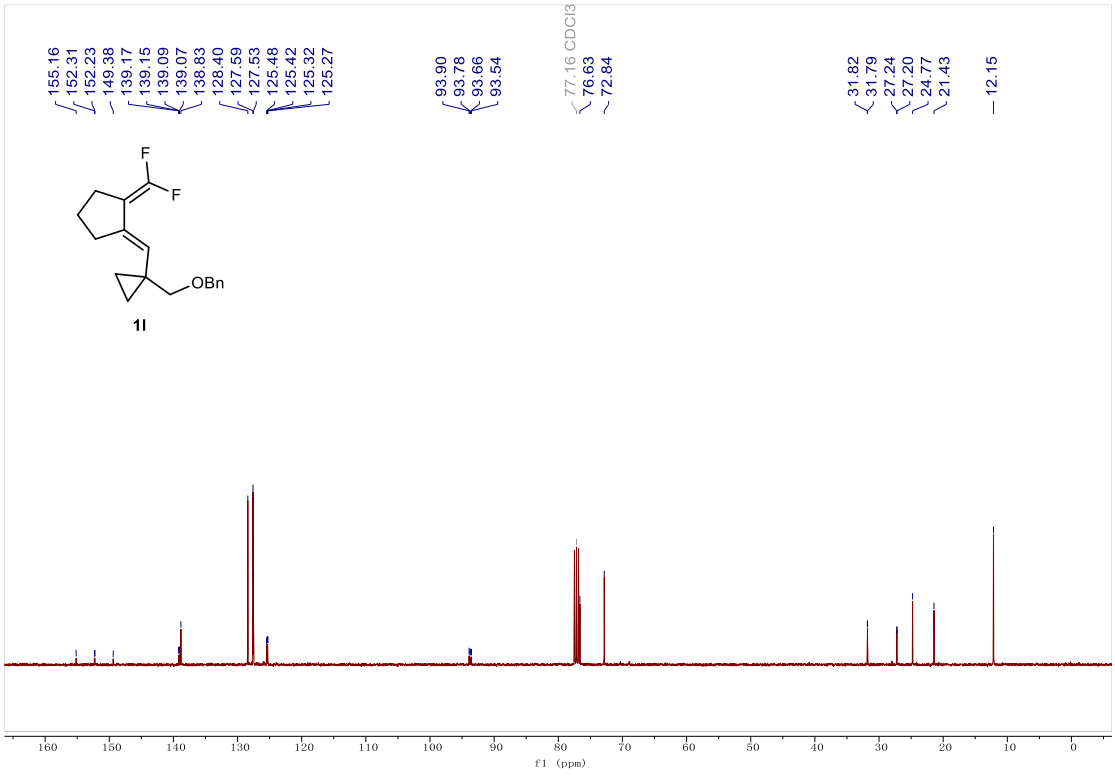
^{13}C NMR in $CDCl_3$, 101 MHz



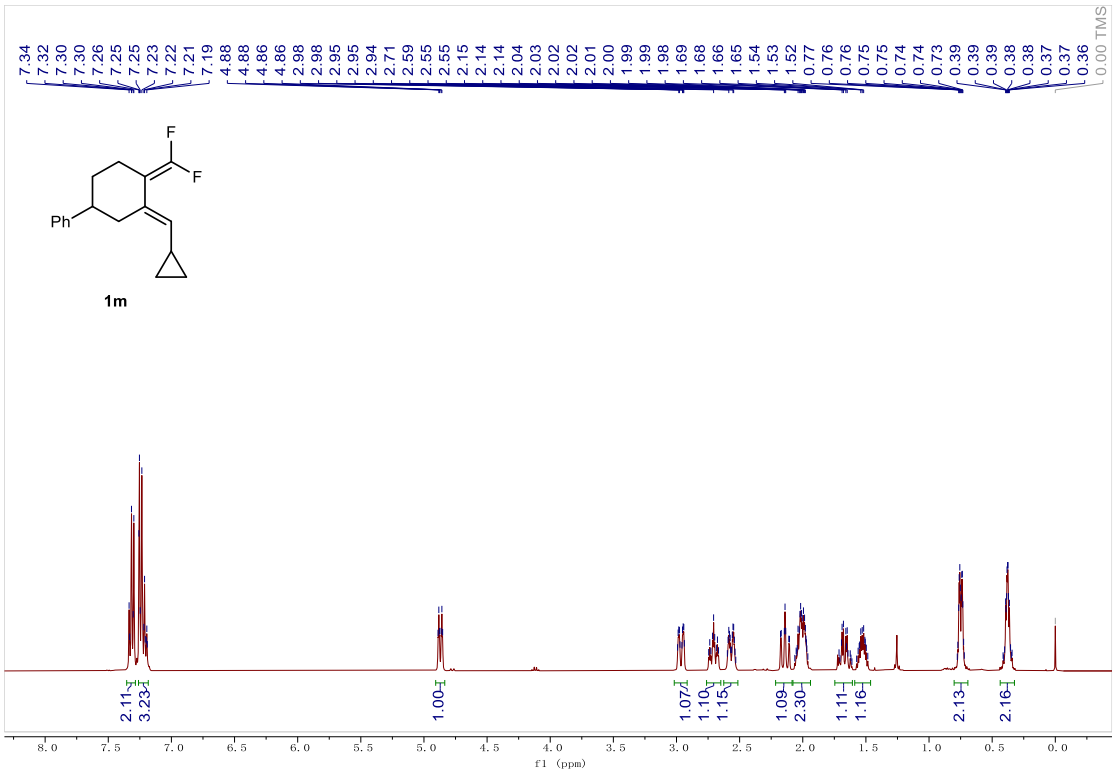
^{1}H NMR in $CDCl_3$, 400 MHz



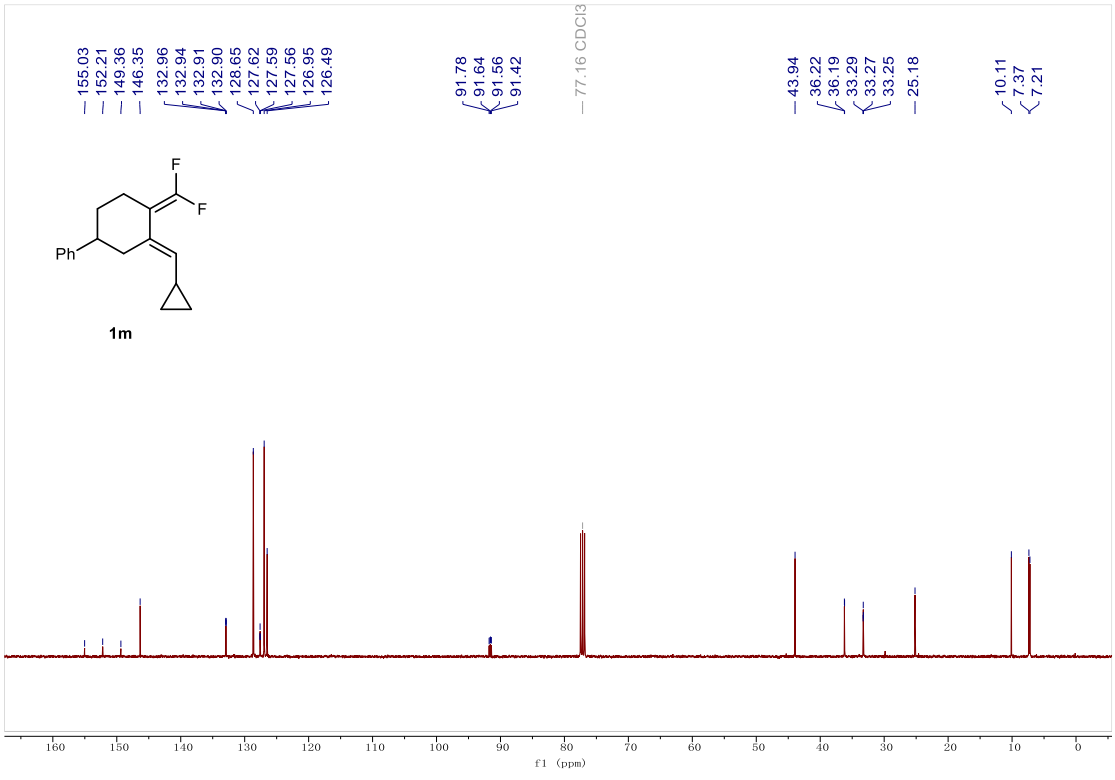
^{13}C NMR in $CDCl_3$, 101 MHz



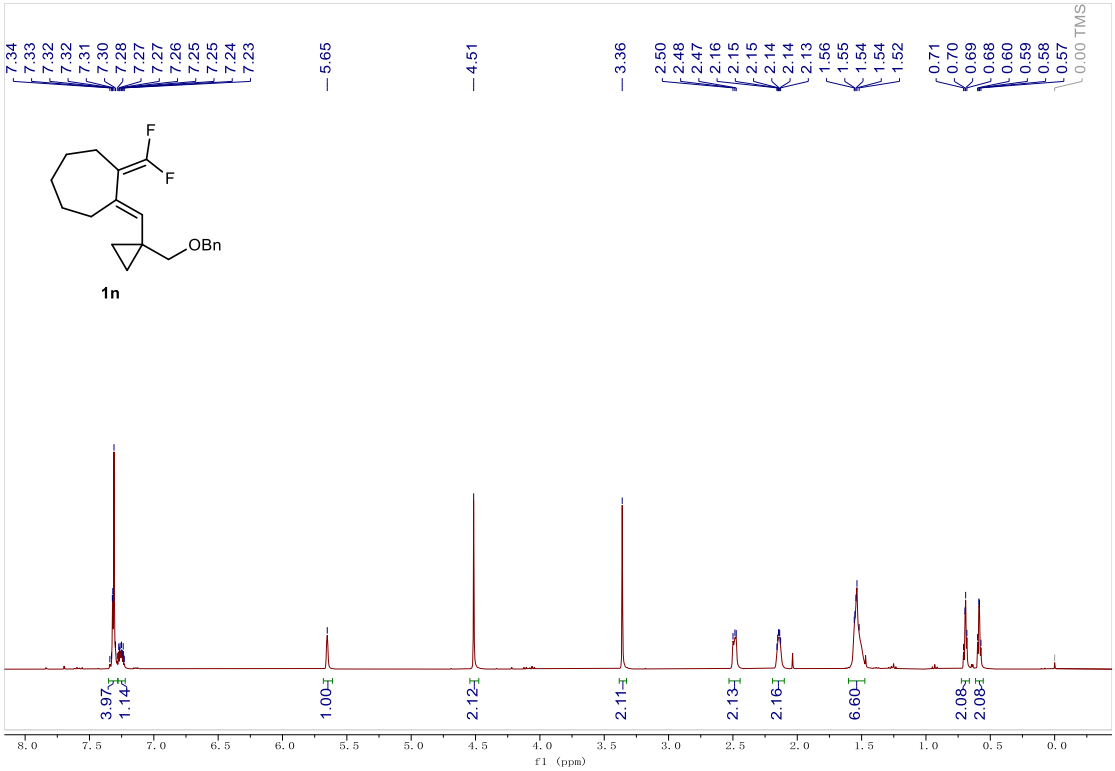
^{1}H NMR in $CDCl_3$, 400 MHz



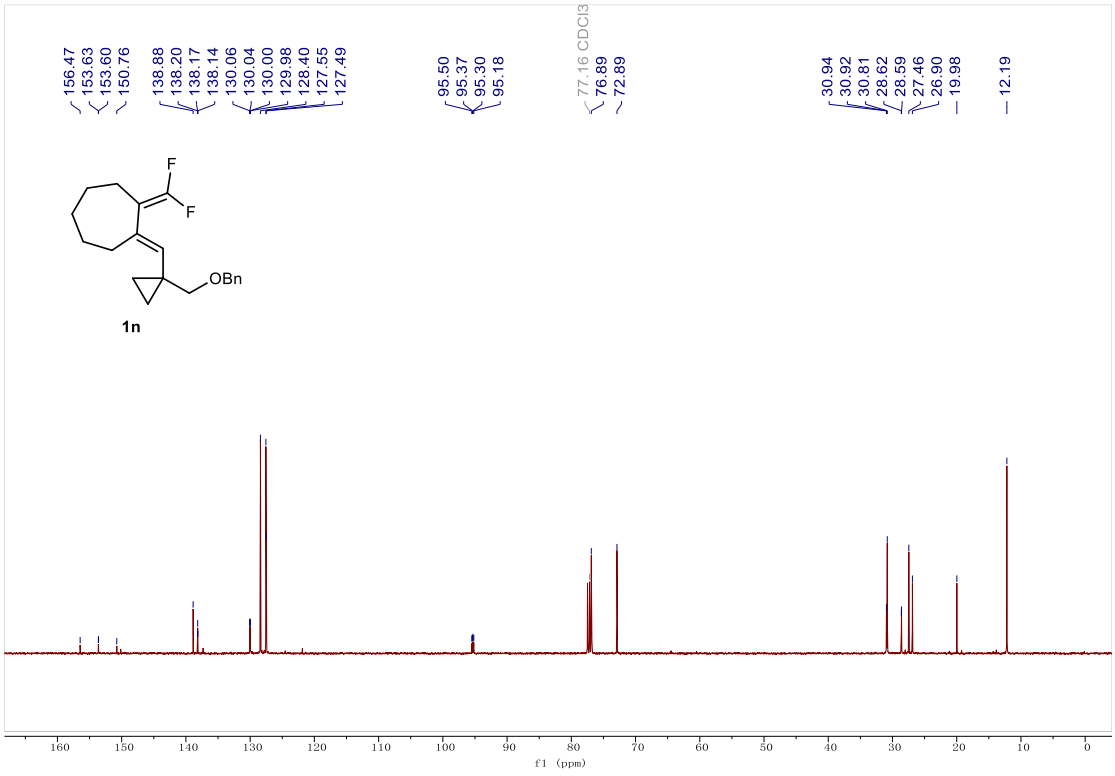
^{13}C NMR in $CDCl_3$, 101 MHz



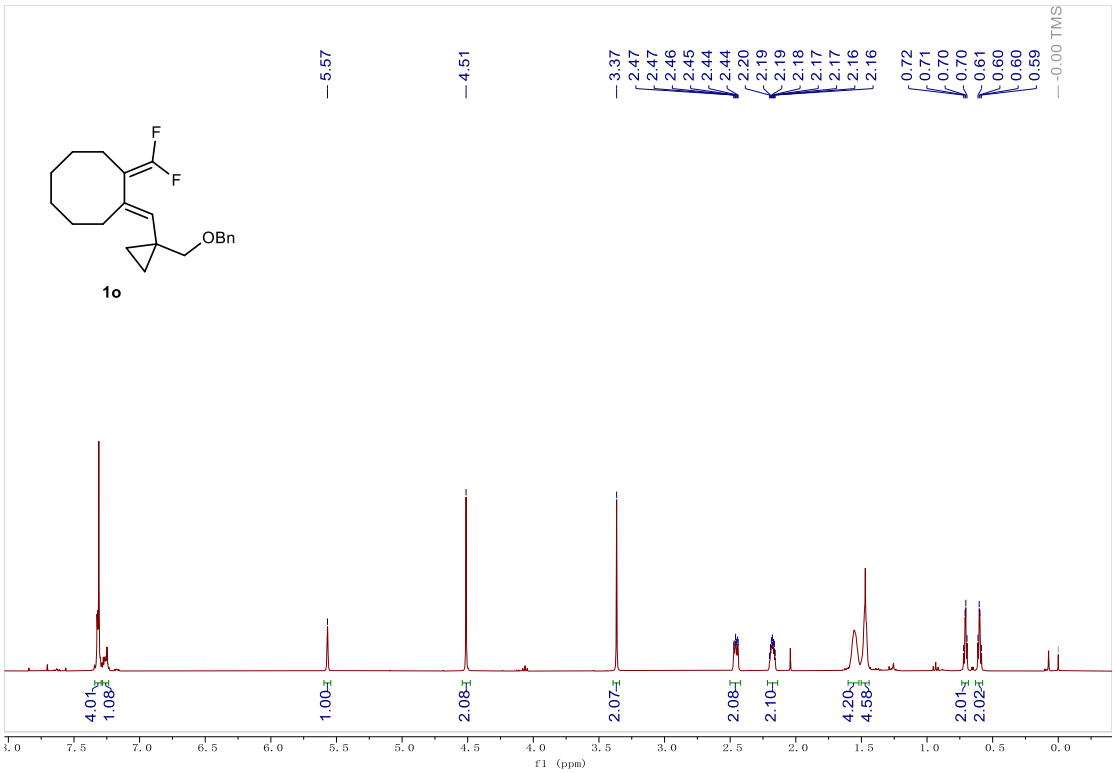
^{1}H NMR in $CDCl_3$, 400 MHz



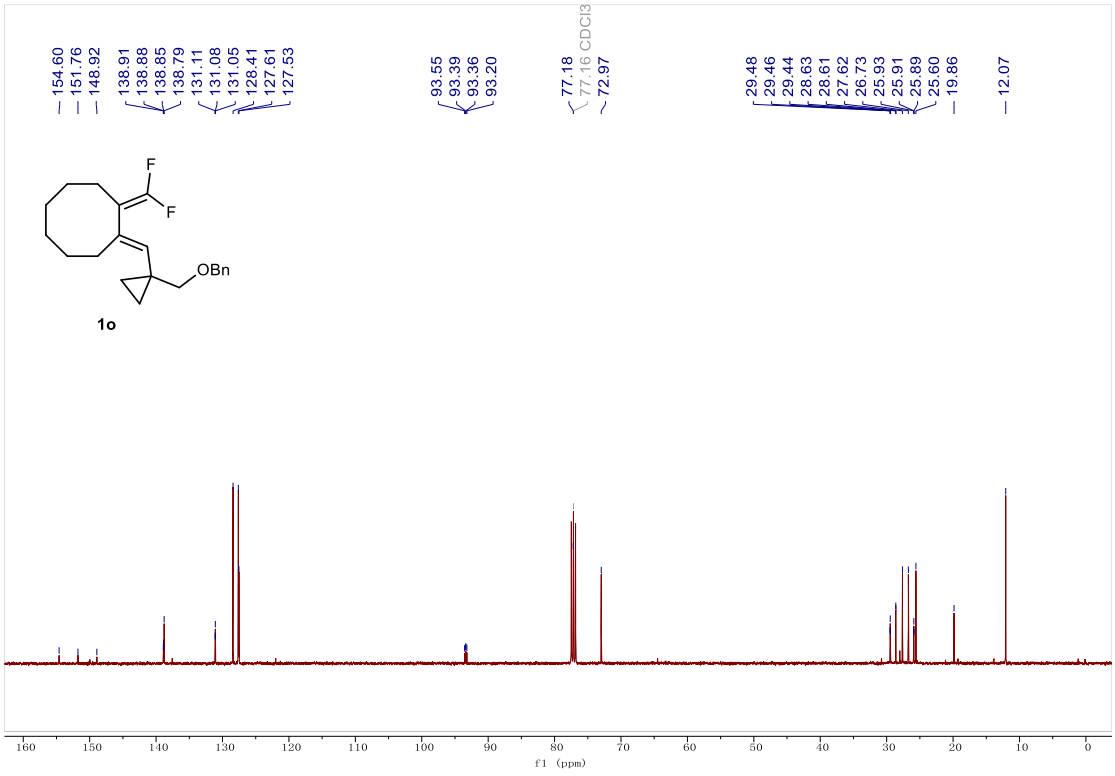
^{13}C NMR in $CDCl_3$, 101 MHz



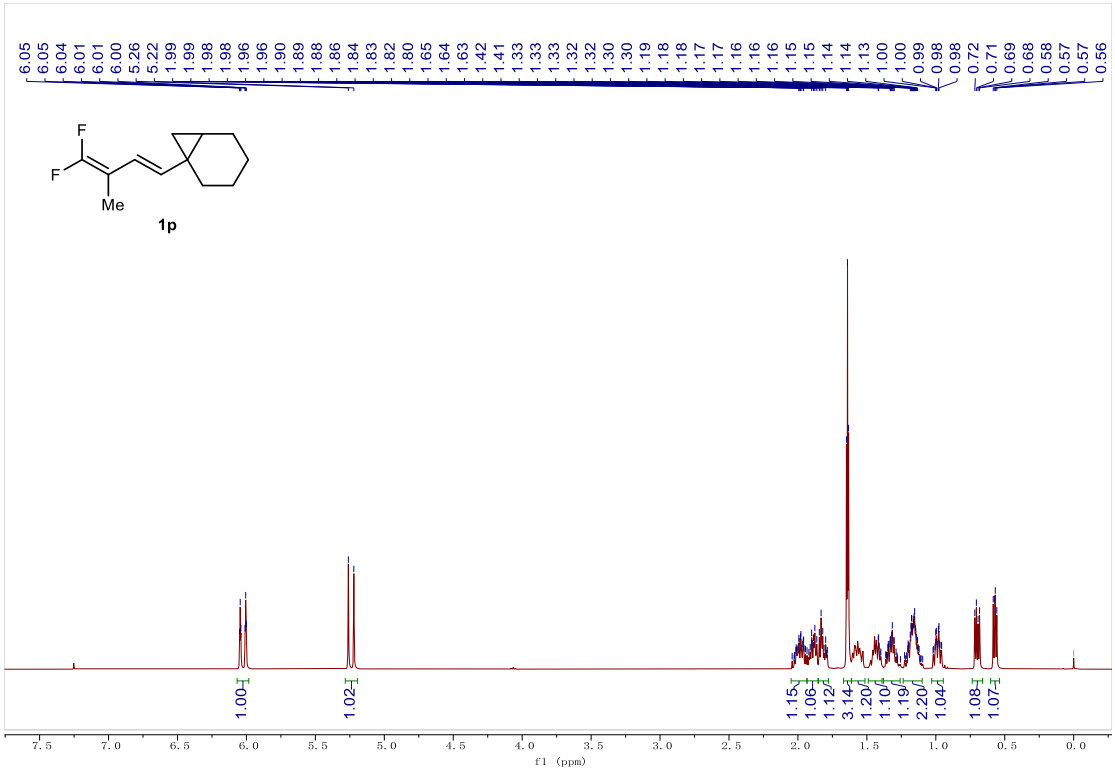
^{1}H NMR in $CDCl_3$, 400 MHz



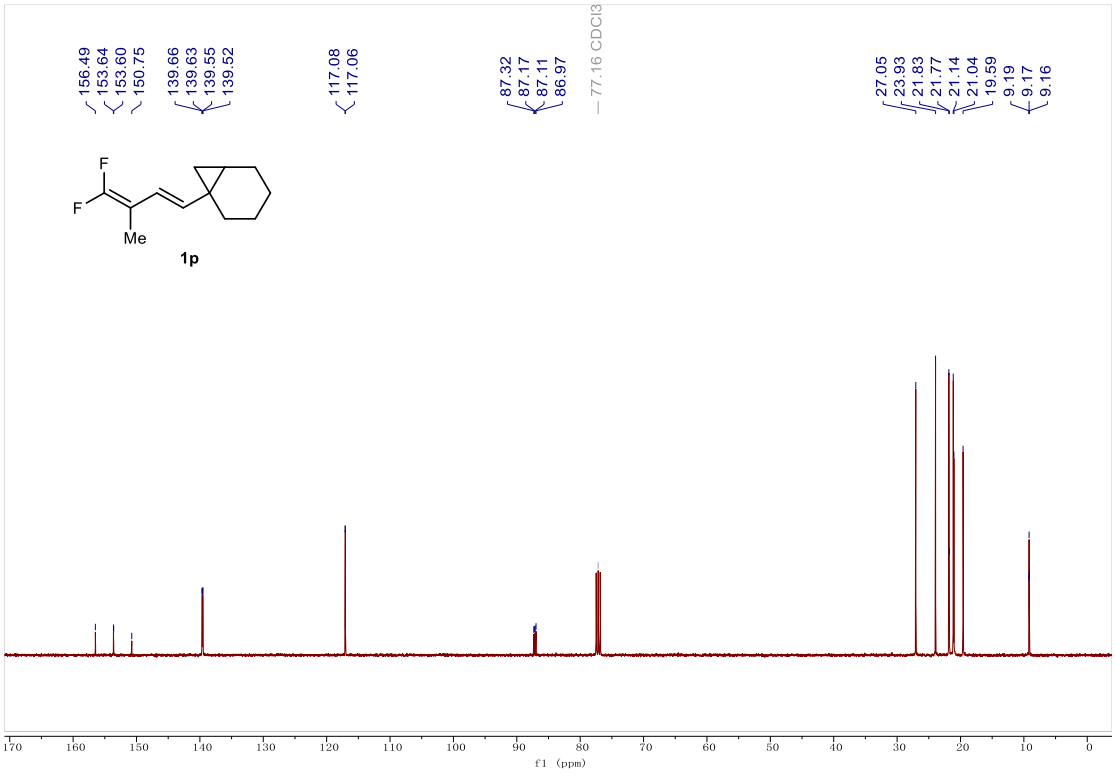
^{13}C NMR in $CDCl_3$, 101 MHz



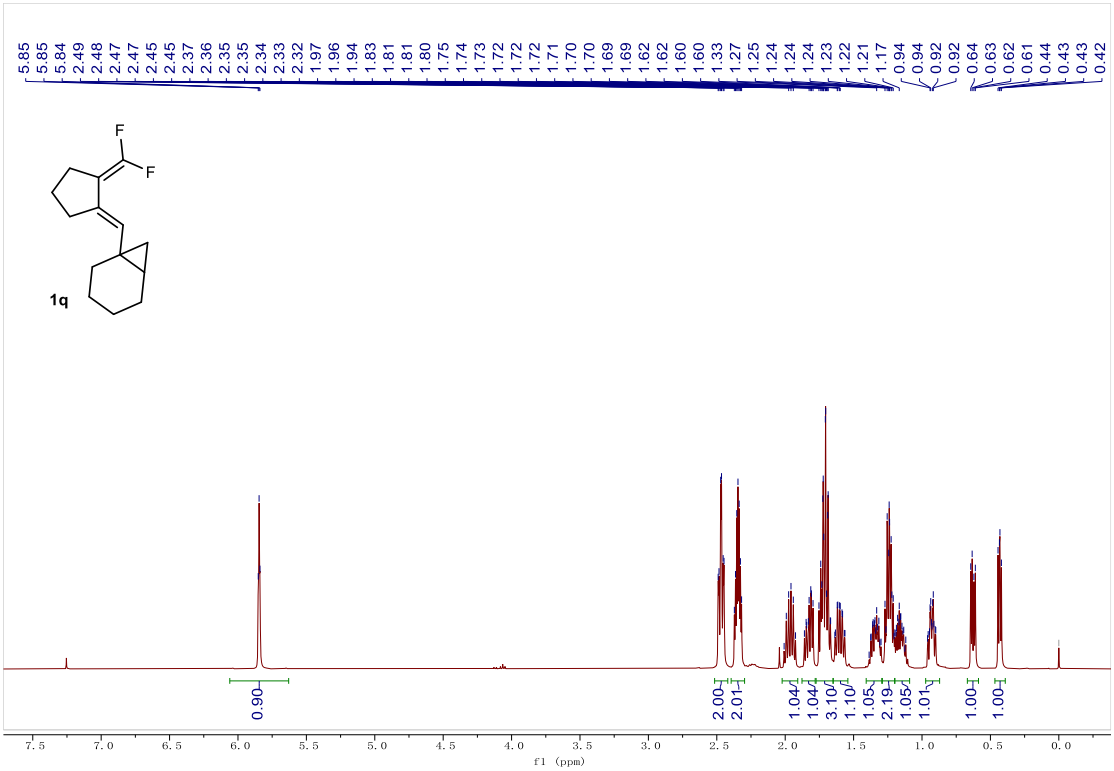
^{1}H NMR in $CDCl_3$, 400 MHz



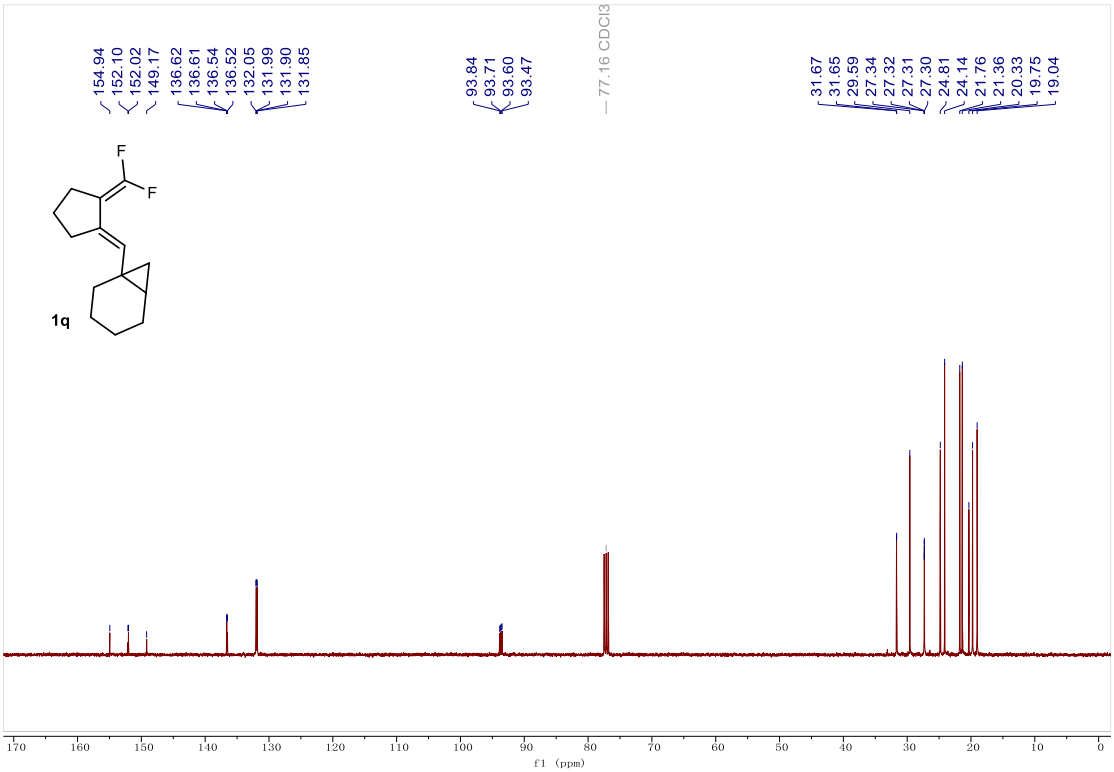
^{13}C NMR in $CDCl_3$, 101 MHz



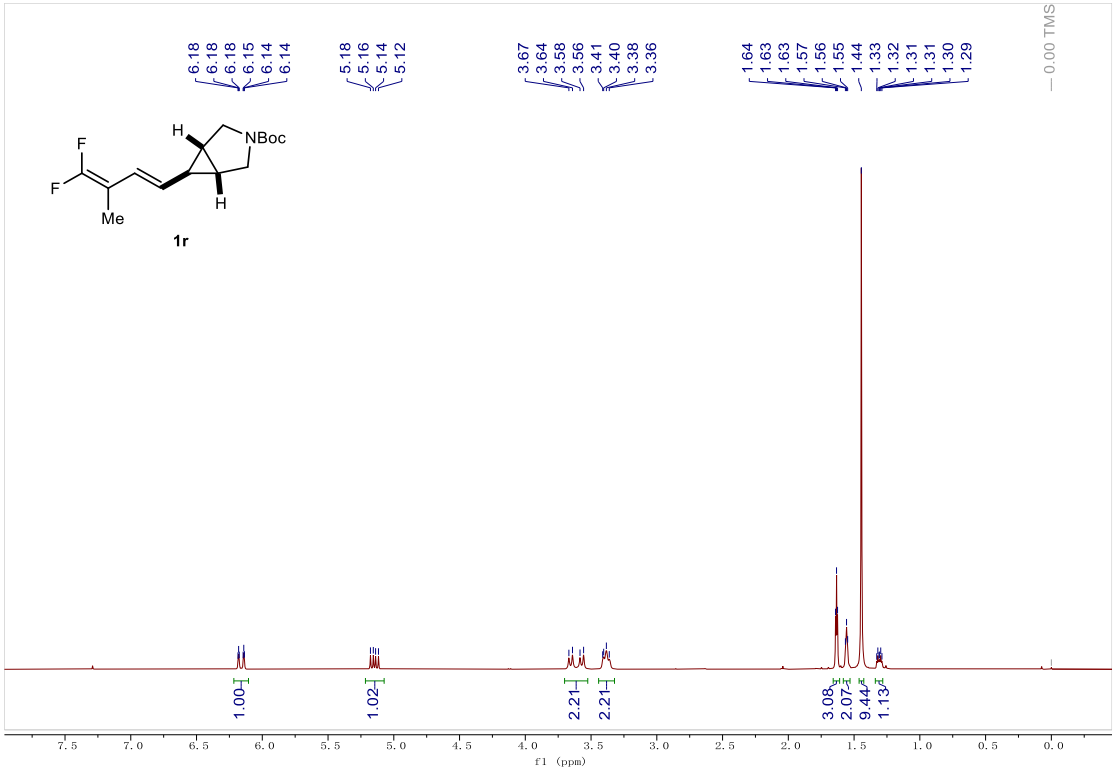
^{1}H NMR in $CDCl_3$, 400 MHz



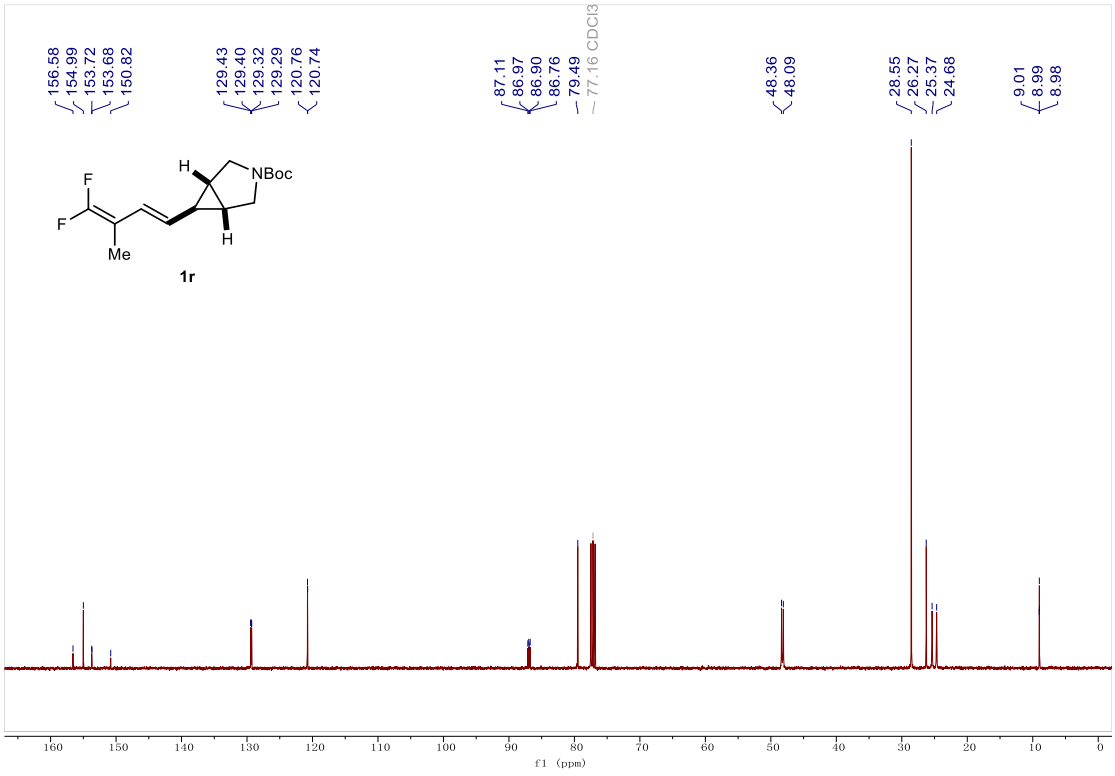
^{13}C NMR in $CDCl_3$, 101 MHz



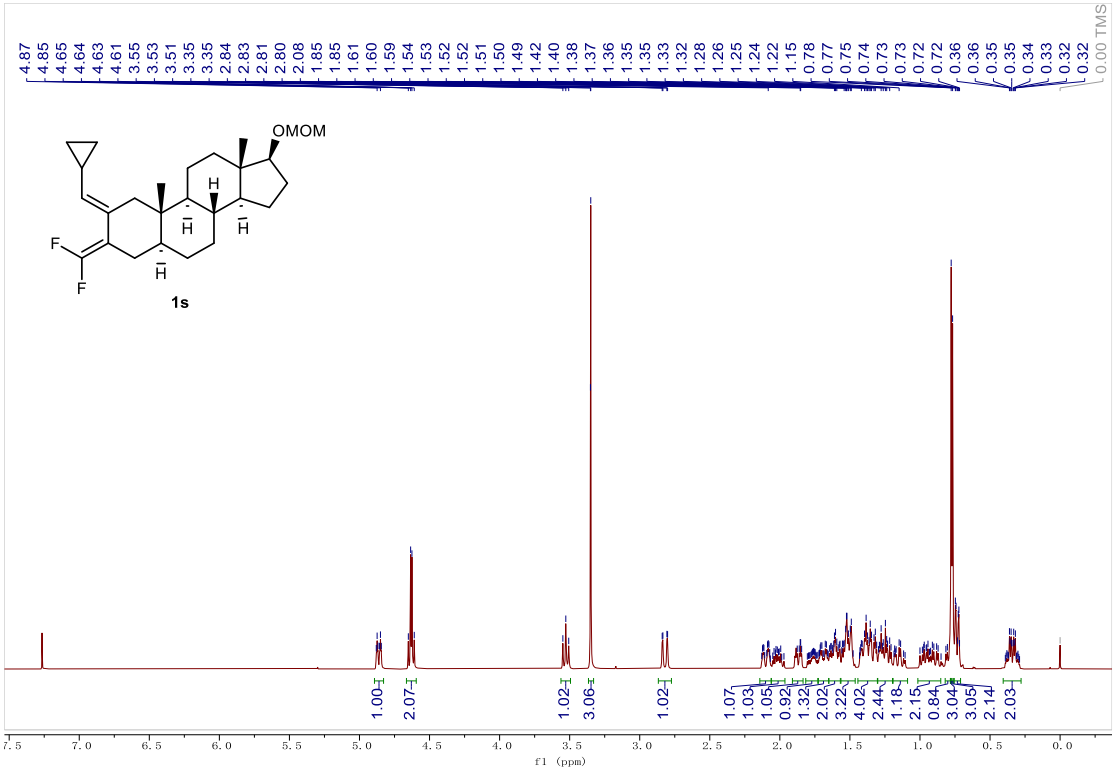
^{1}H NMR in $CDCl_3$, 400 MHz



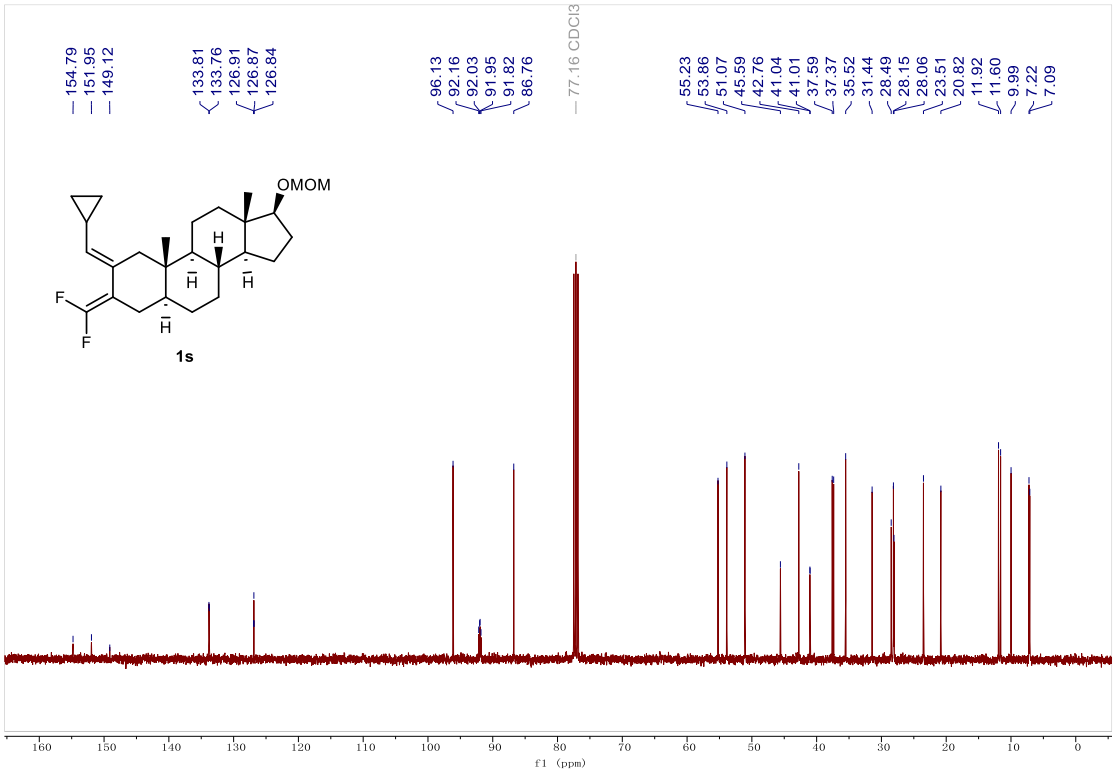
^{13}C NMR in $CDCl_3$, 101 MHz



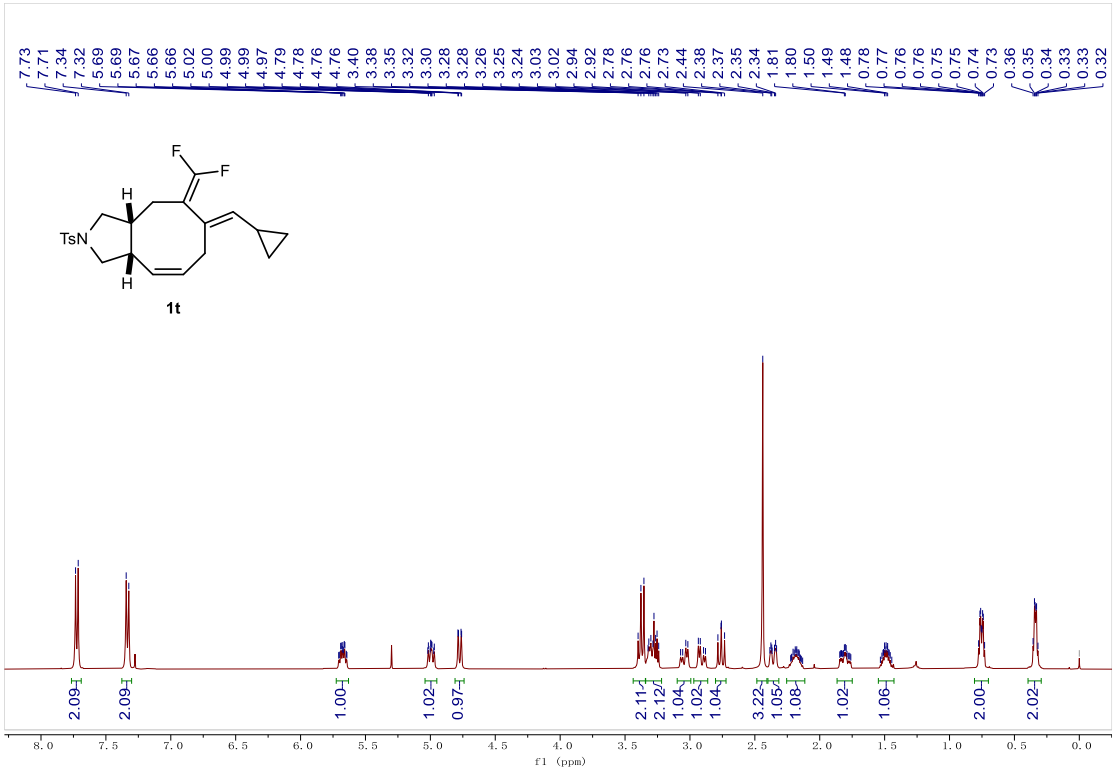
^{1}H NMR in $CDCl_3$, 400 MHz



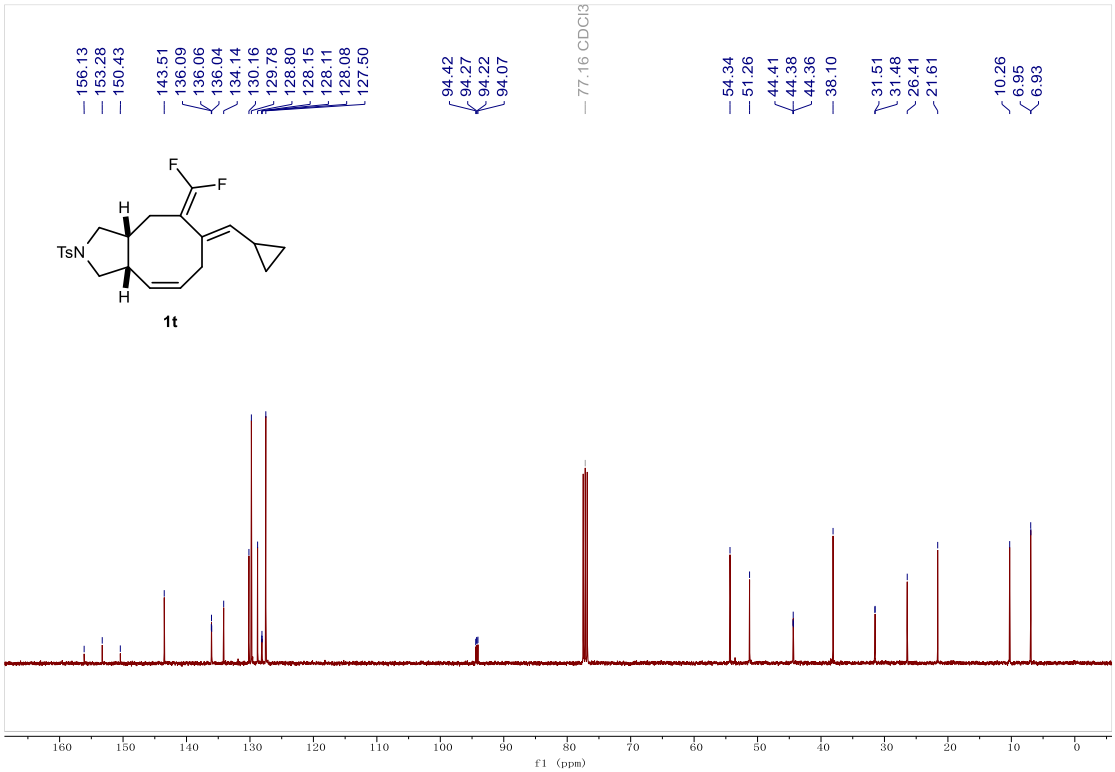
^{13}C NMR in $CDCl_3$, 101 MHz



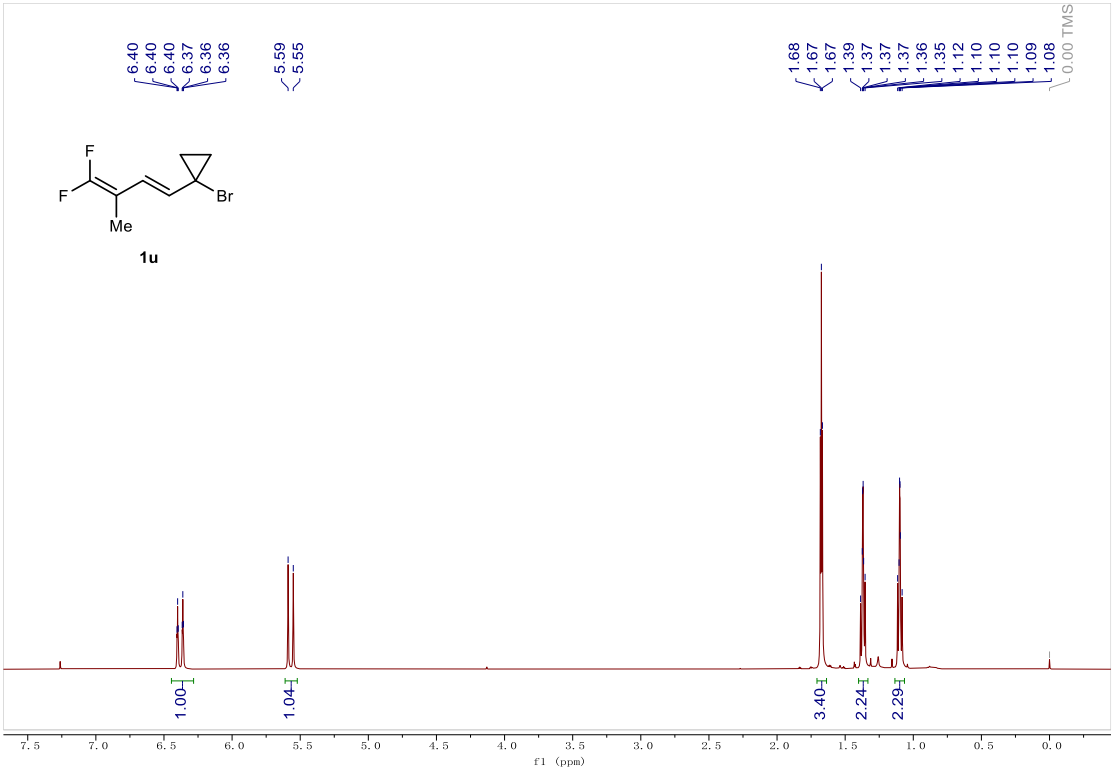
^{1}H NMR in $CDCl_3$, 400 MHz



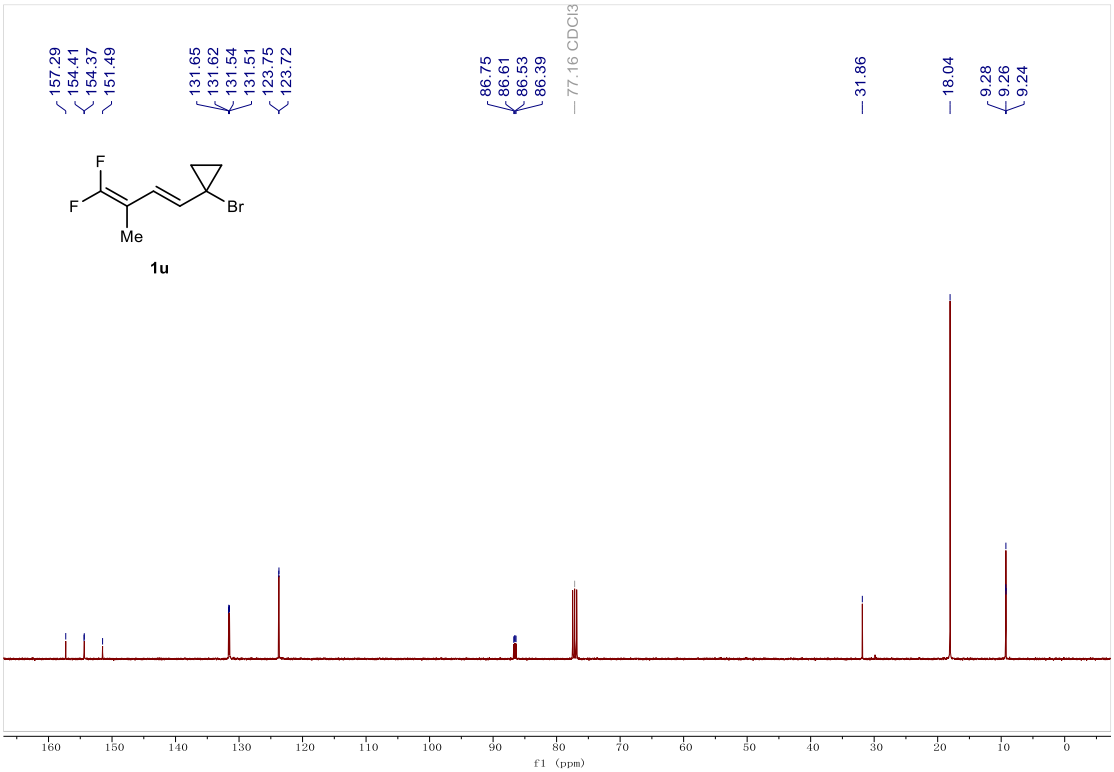
^{13}C NMR in $CDCl_3$, 101 MHz



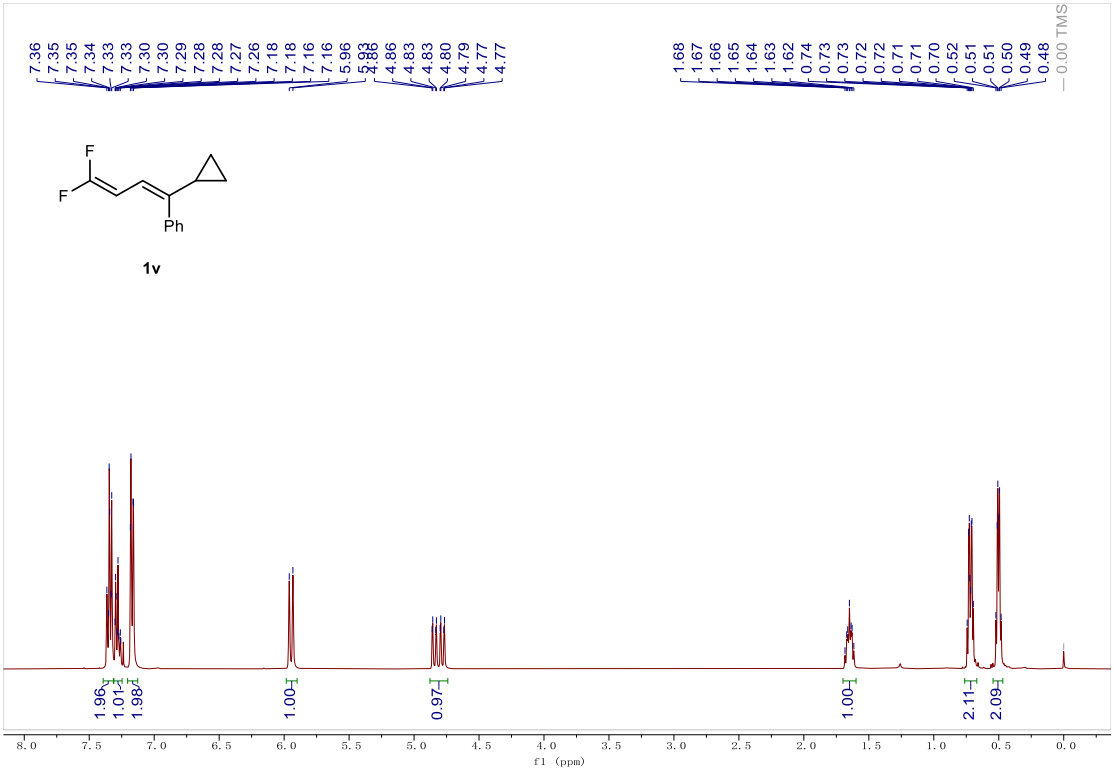
^{1}H NMR in $CDCl_3$, 400 MHz



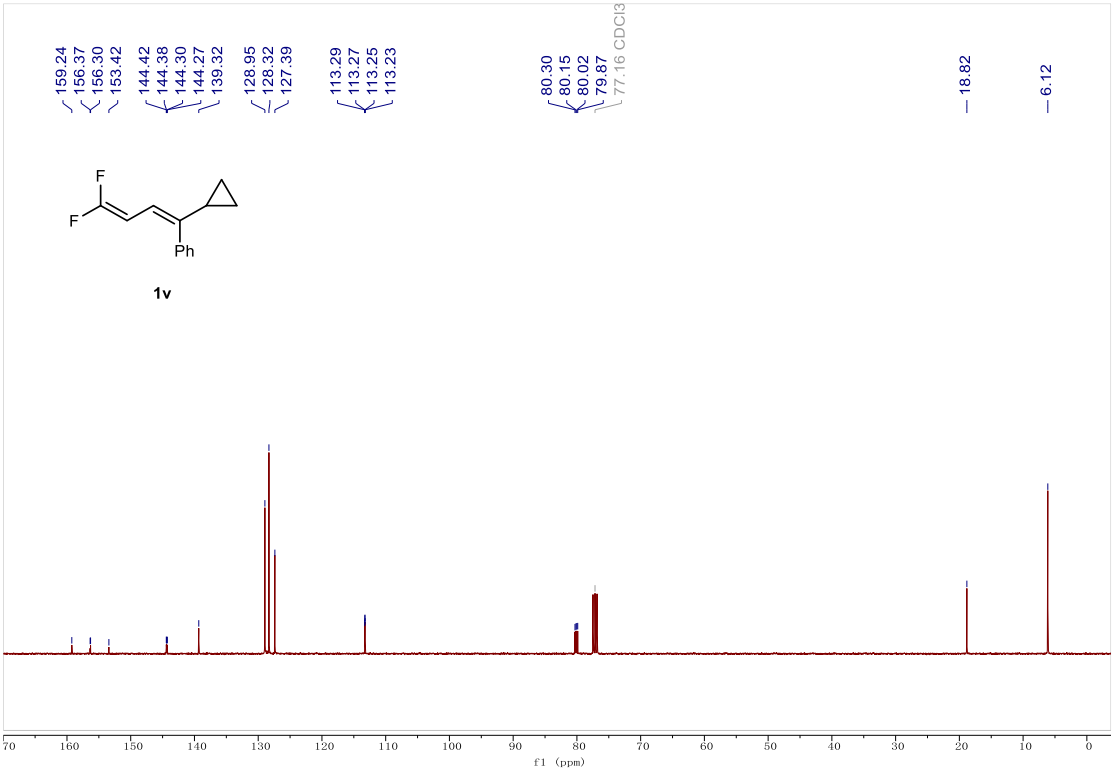
^{13}C NMR in $CDCl_3$, 101 MHz



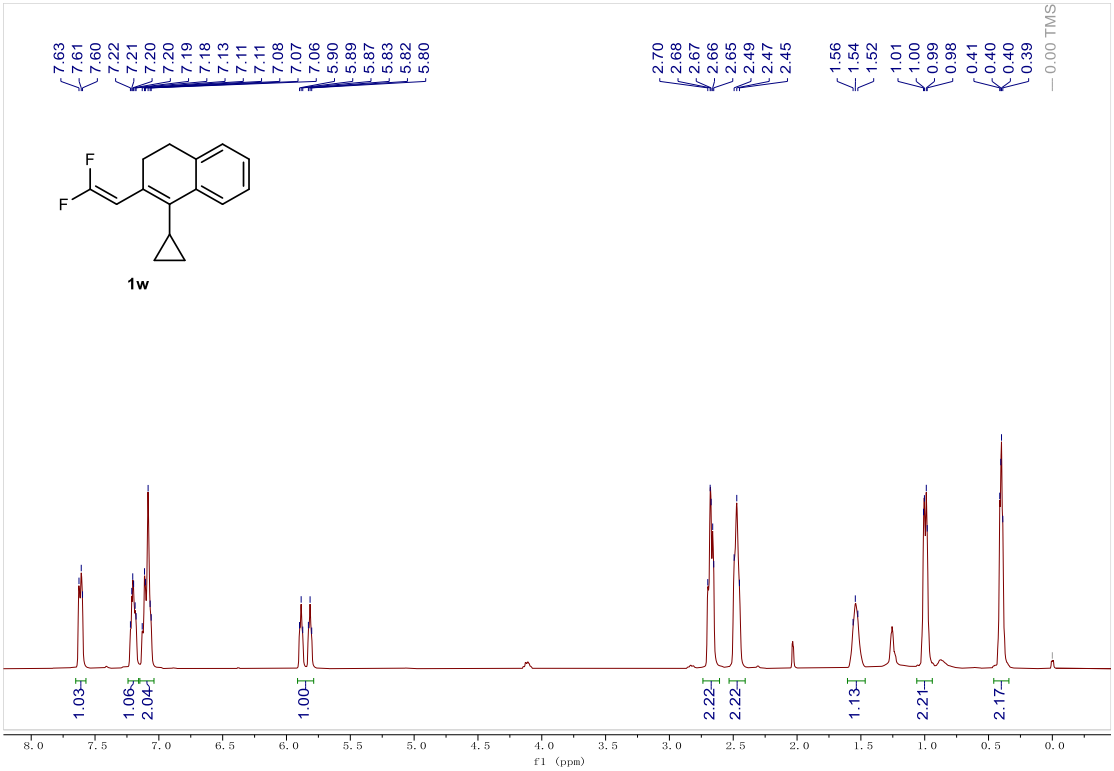
^{1}H NMR in $CDCl_3$, 400 MHz



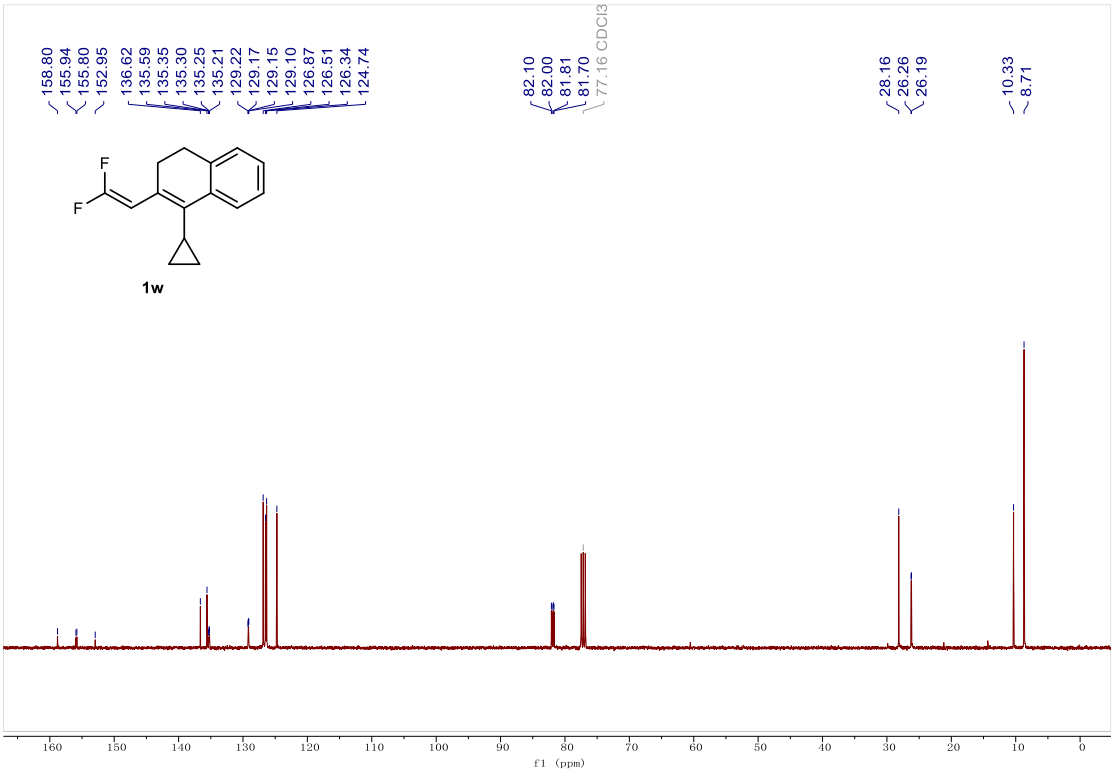
^{13}C NMR in $CDCl_3$, 101 MHz



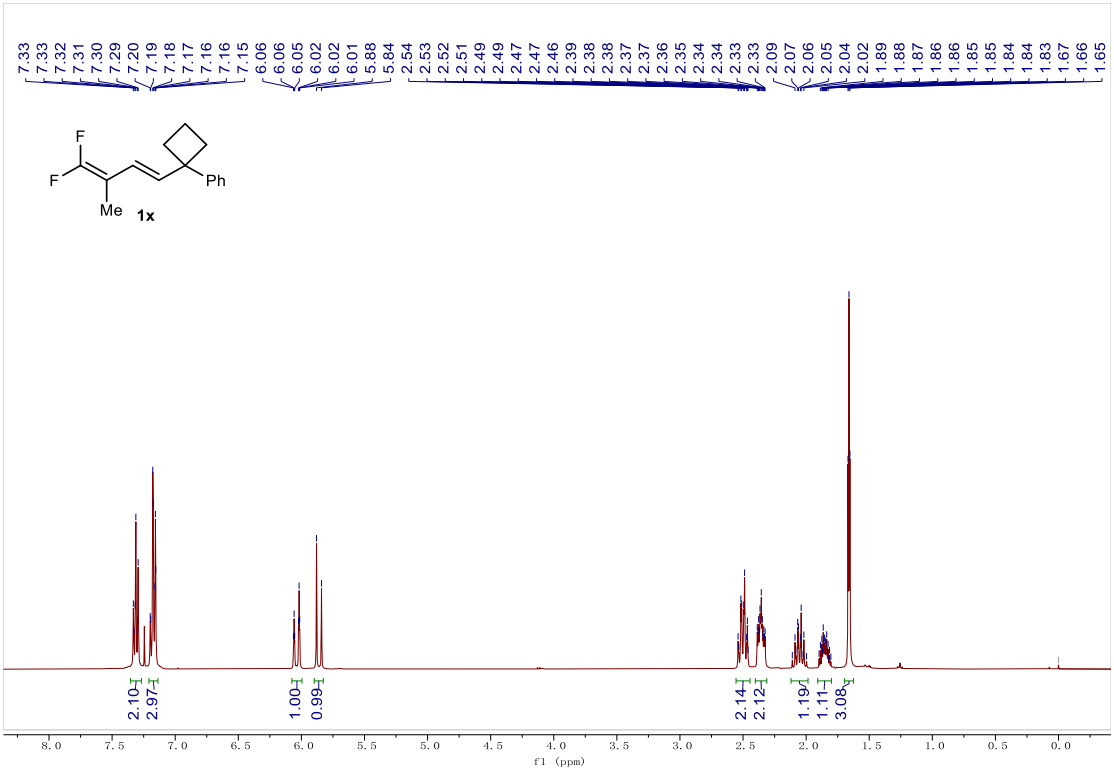
^{1}H NMR in $CDCl_3$, 400 MHz



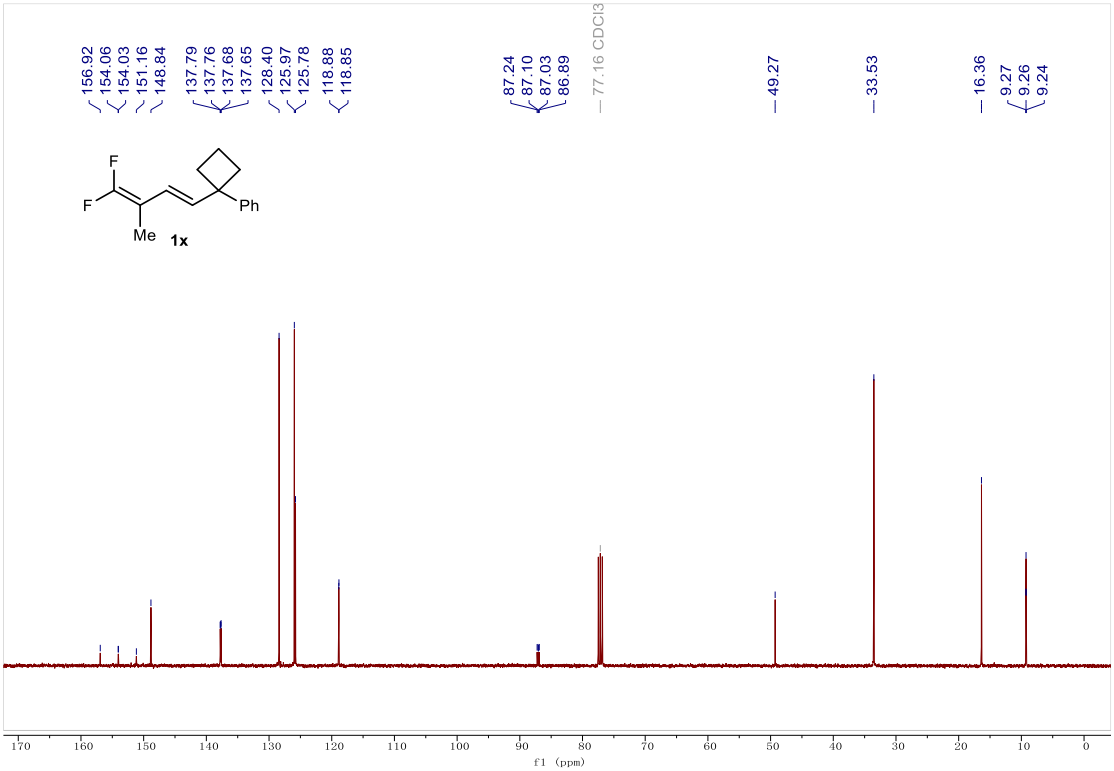
^{13}C NMR in $CDCl_3$, 101 MHz



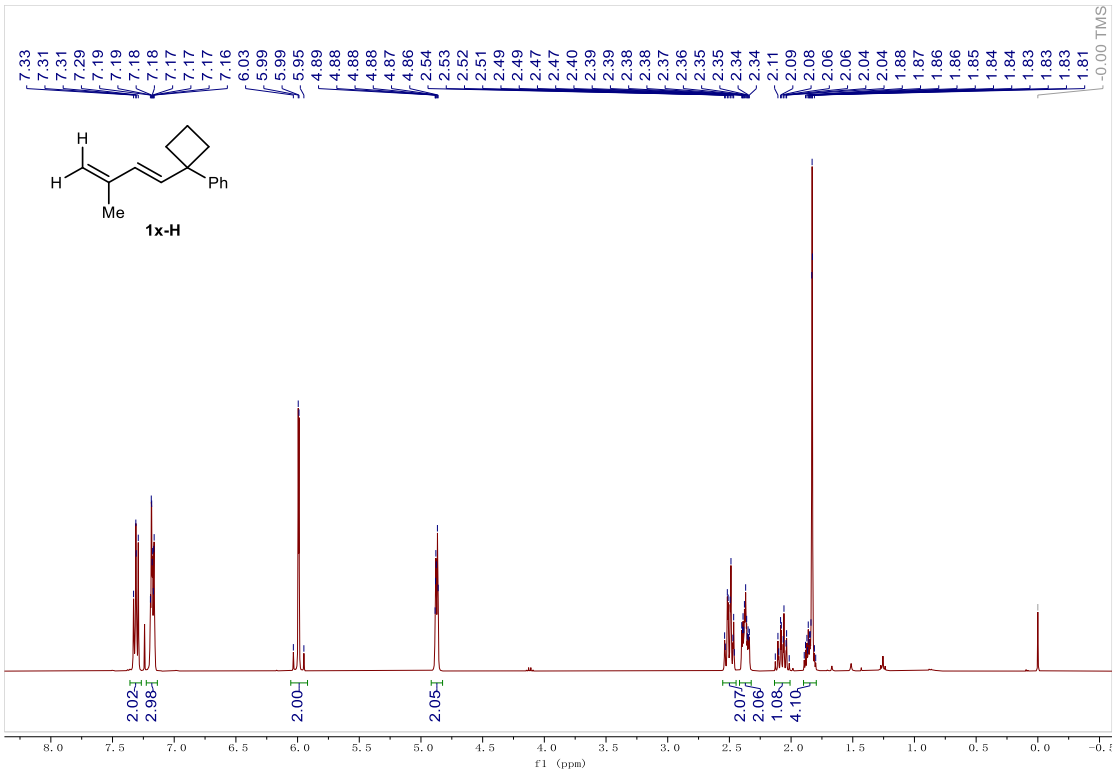
^{1}H NMR in $CDCl_3$, 400 MHz



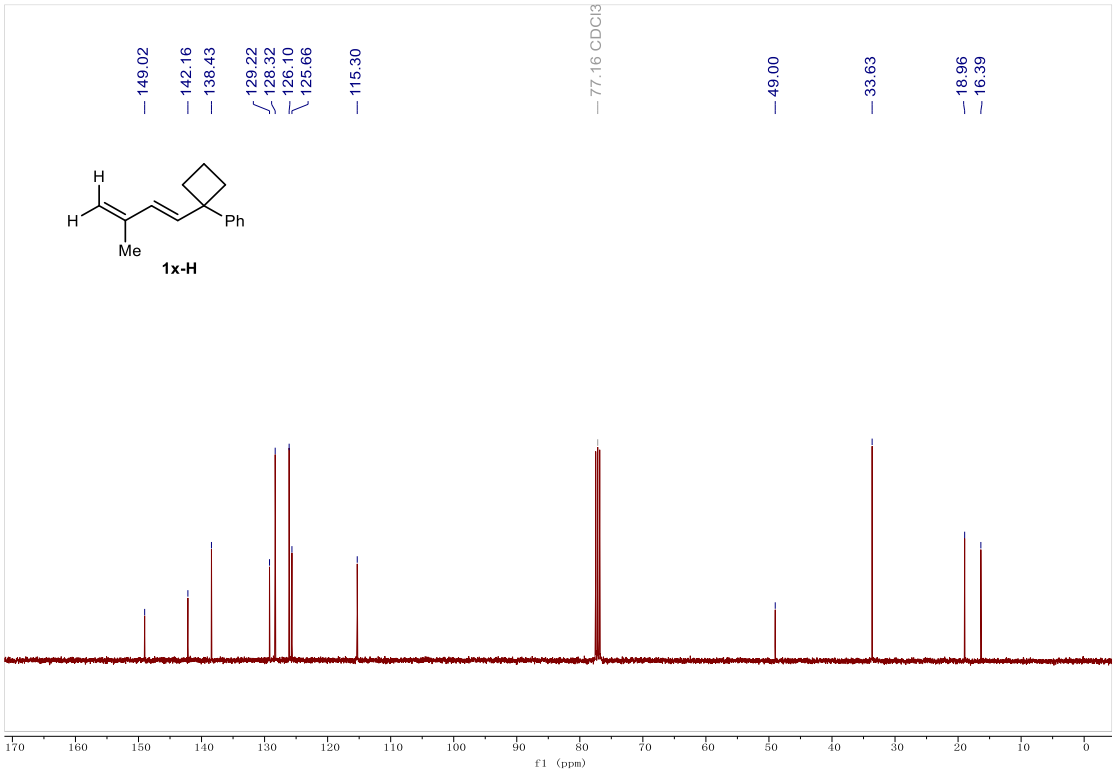
^{13}C NMR in $CDCl_3$, 101 MHz



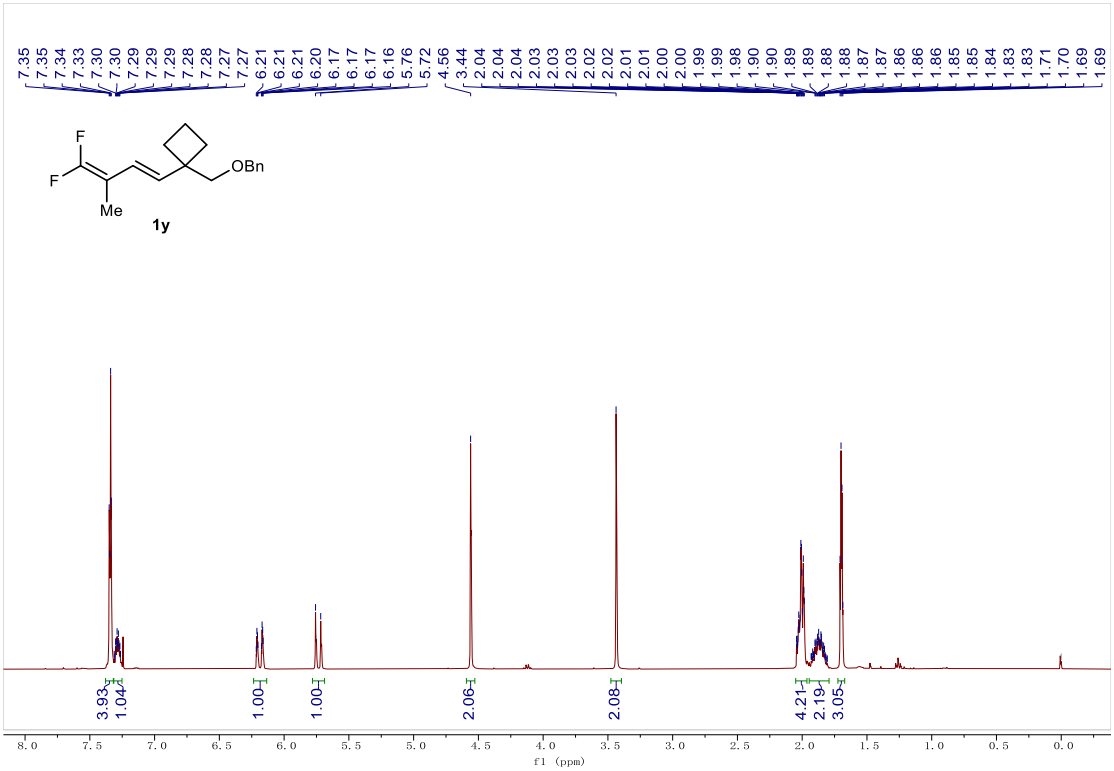
^{1}H NMR in $CDCl_3$, 400 MHz



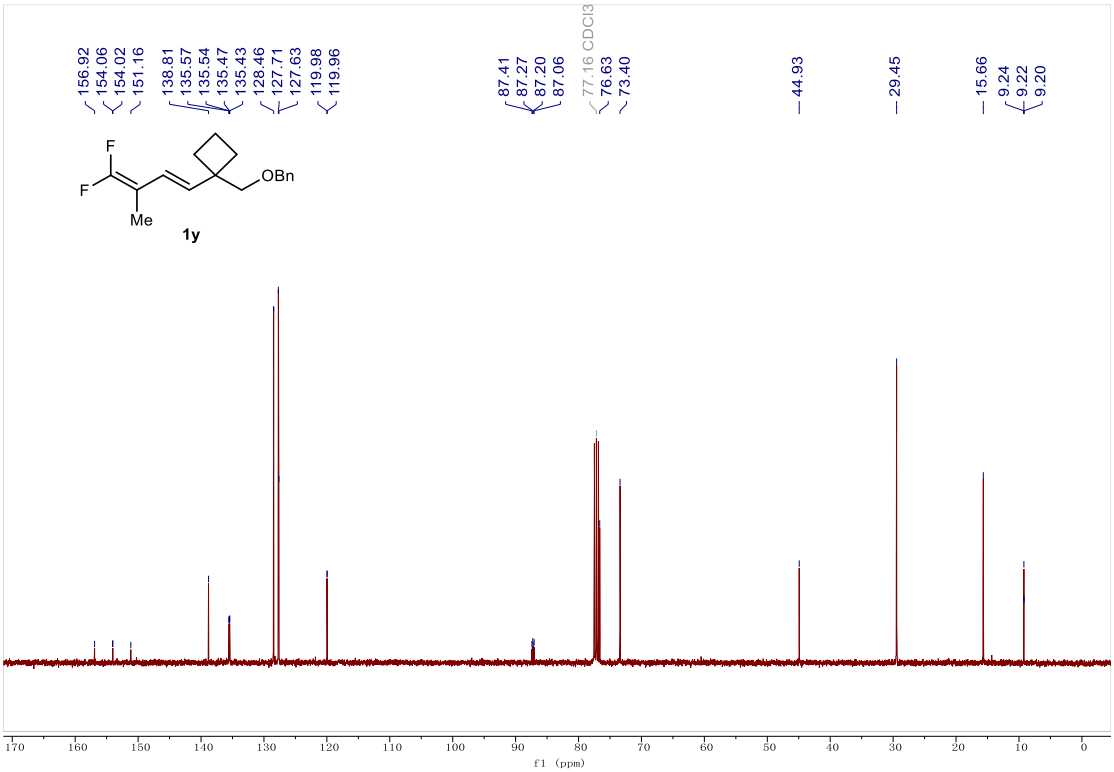
^{13}C NMR in $CDCl_3$, 101 MHz



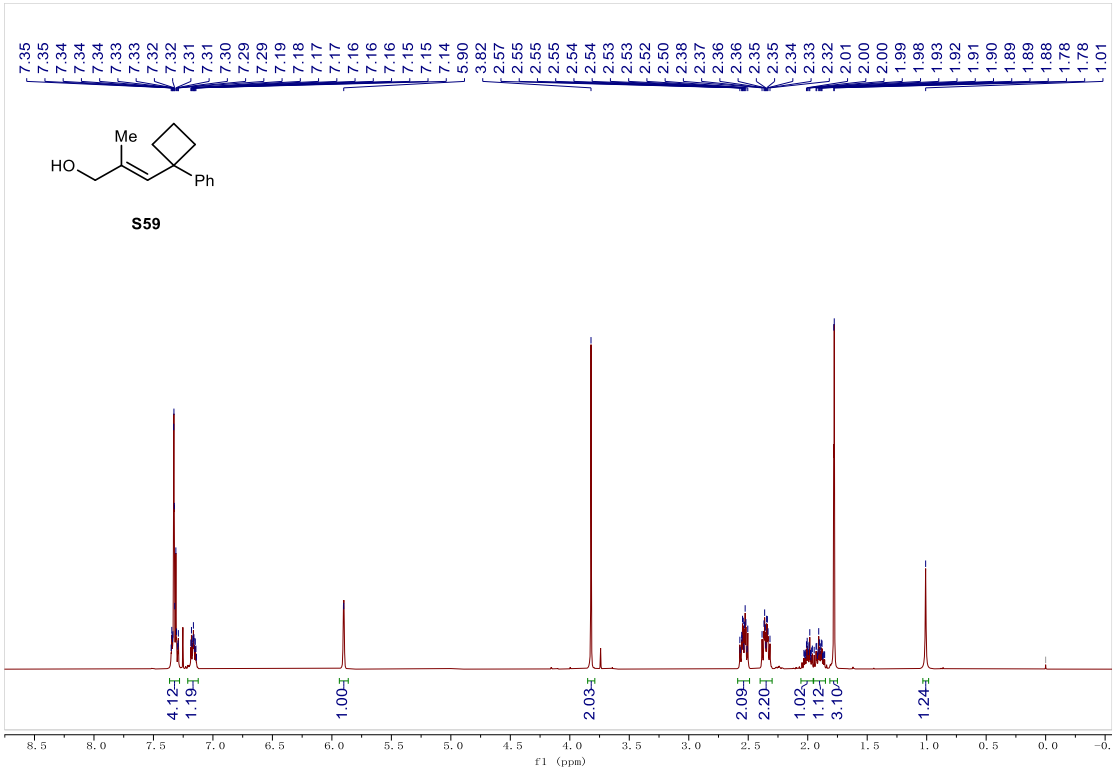
^{1}H NMR in $CDCl_3$, 400 MHz



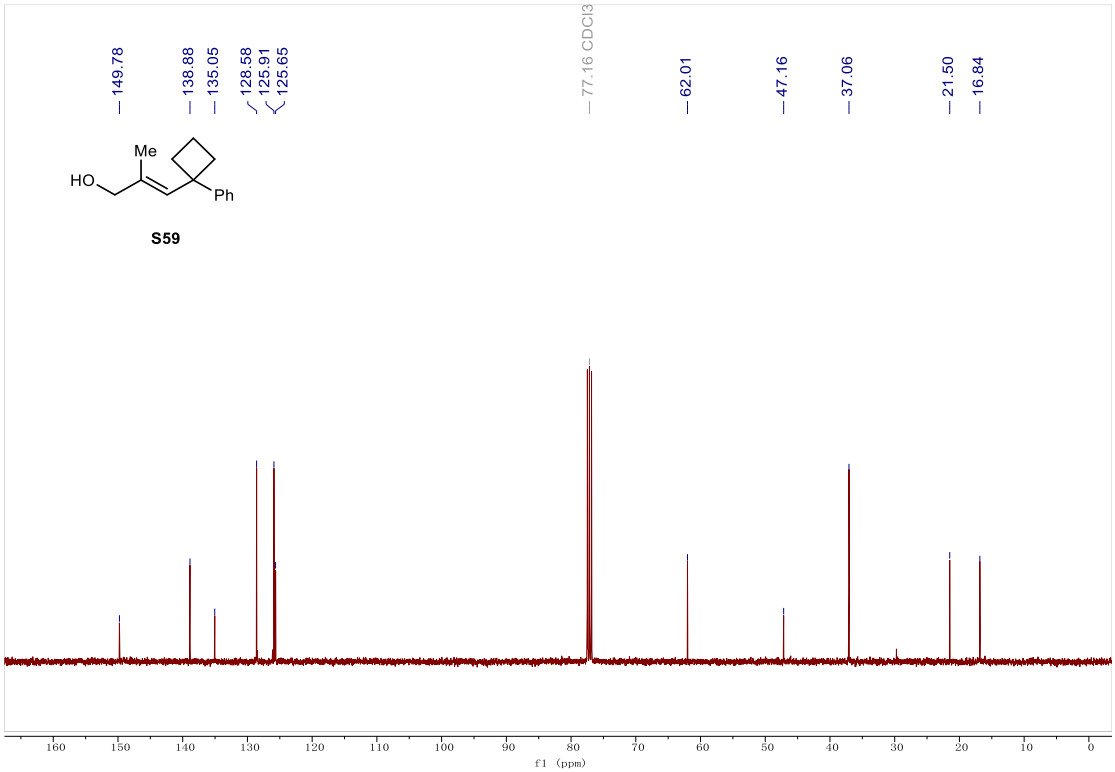
^{13}C NMR in $CDCl_3$, 101 MHz



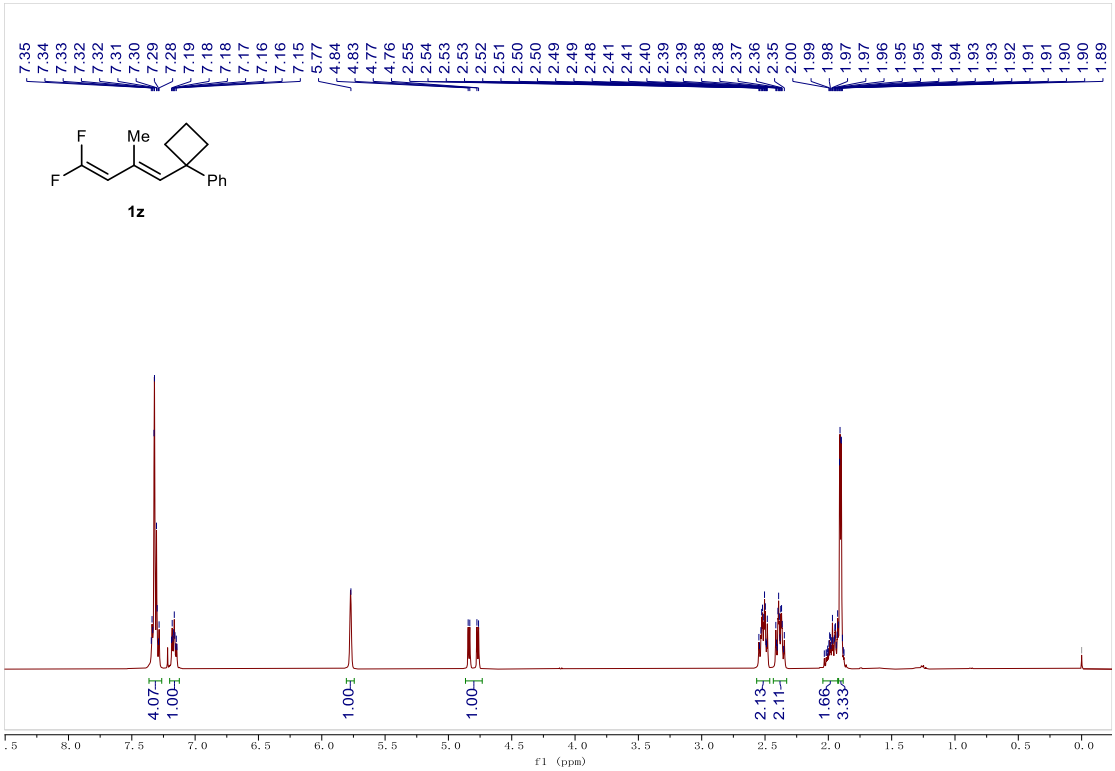
^{1}H NMR in $CDCl_3$, 400 MHz



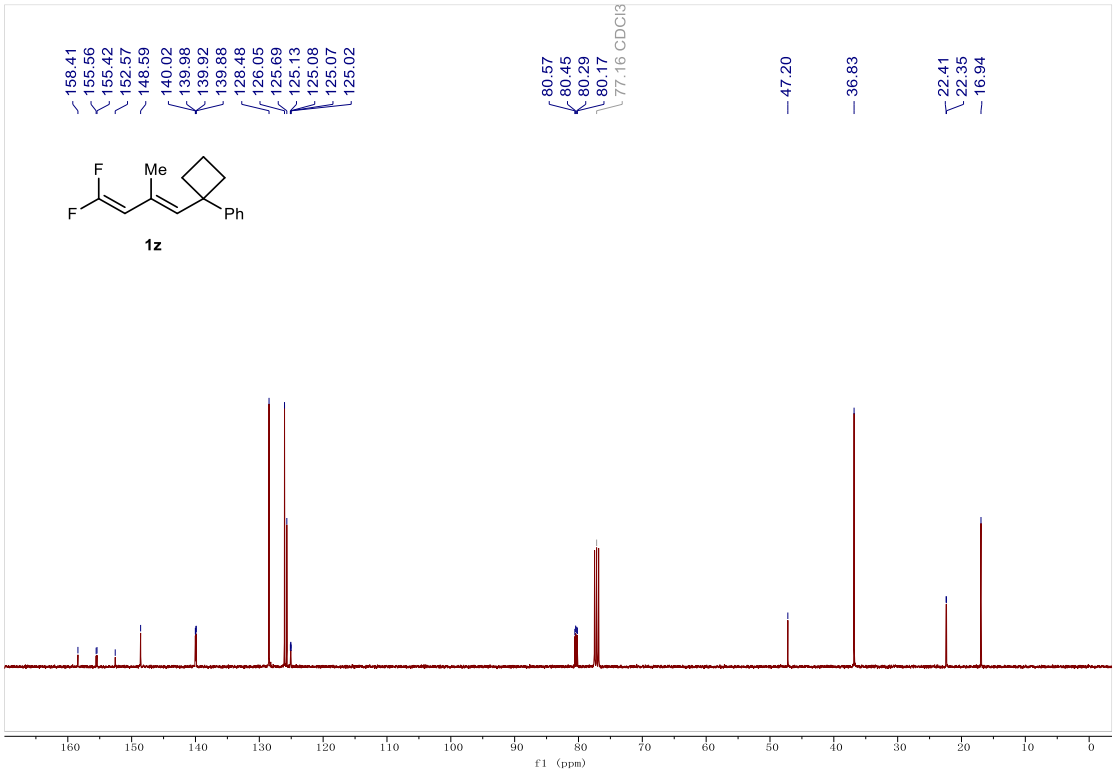
^{13}C NMR in $CDCl_3$, 101 MHz



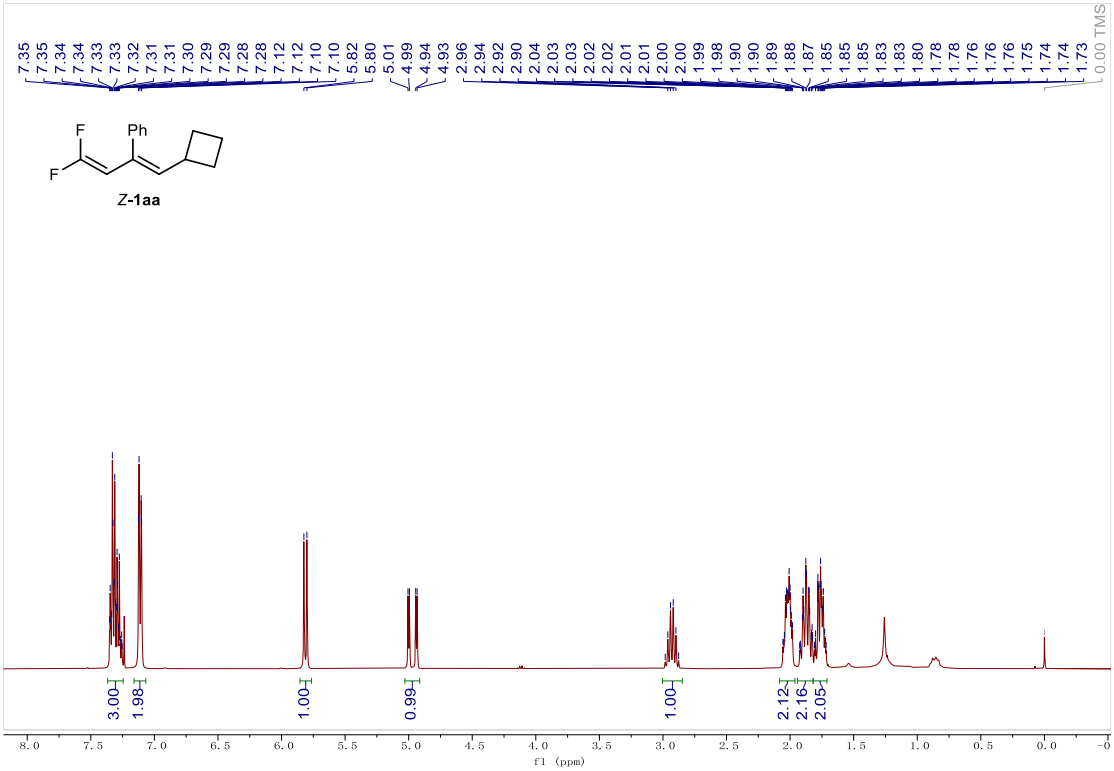
^{1}H NMR in $CDCl_3$, 400 MHz



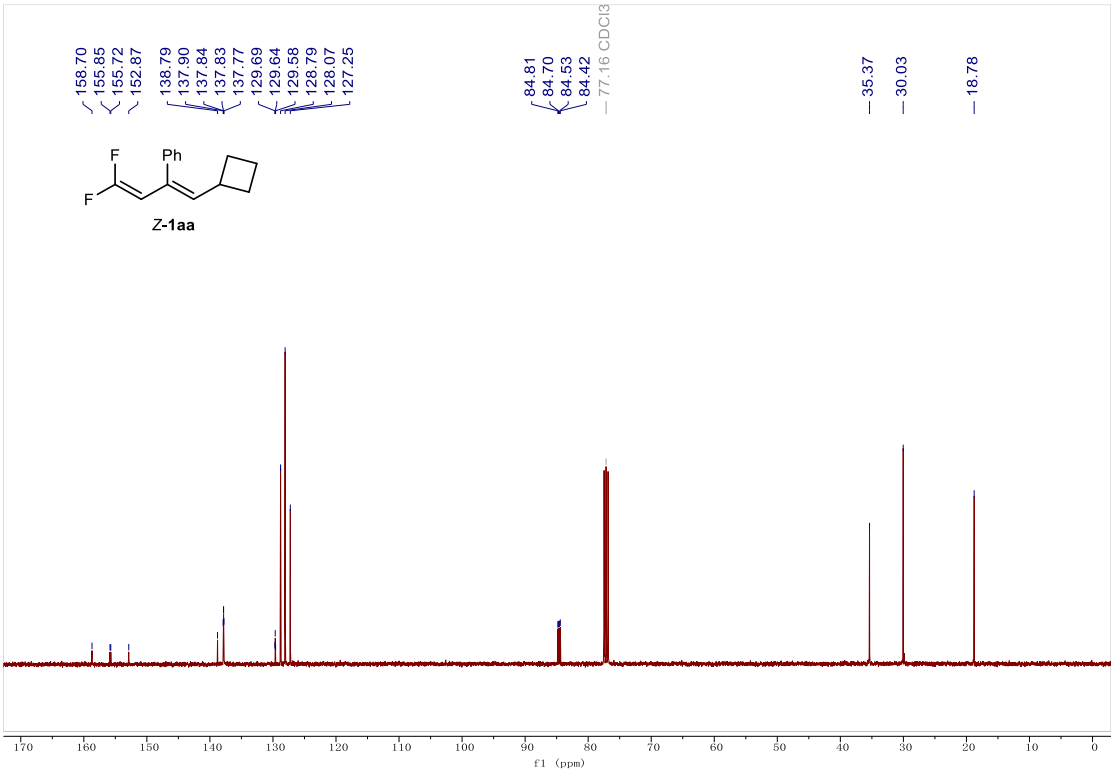
^{13}C NMR in $CDCl_3$, 101 MHz



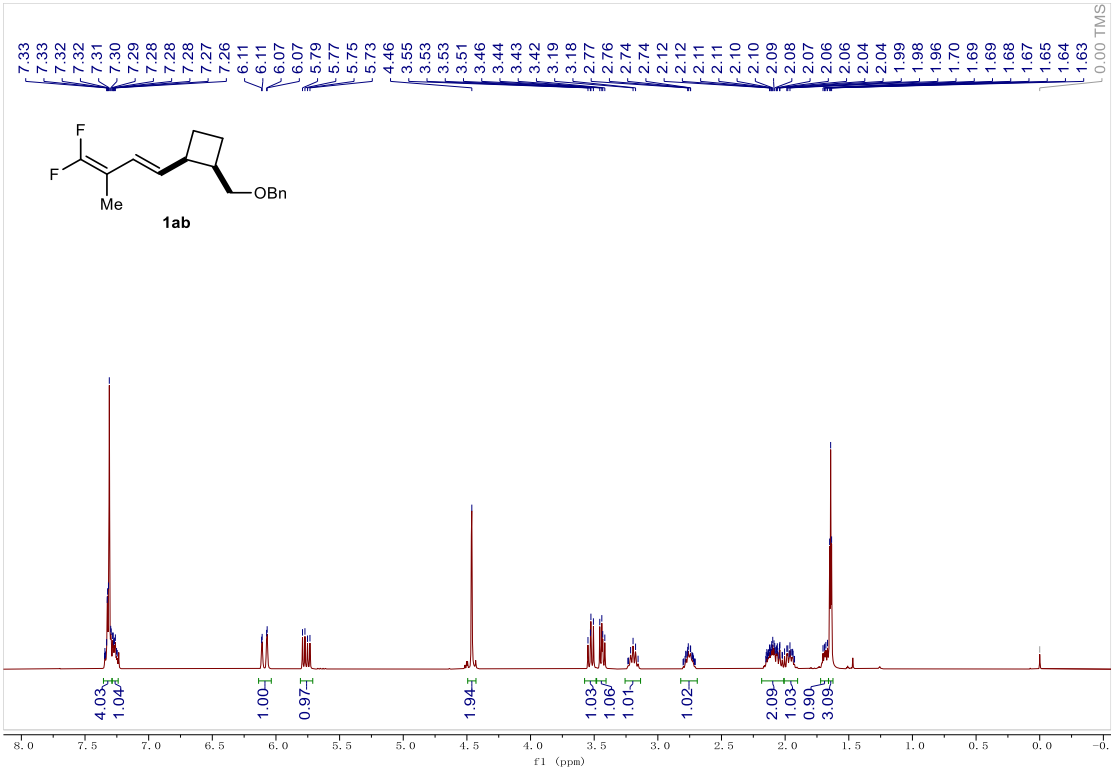
^{1}H NMR in $CDCl_3$, 400 MHz



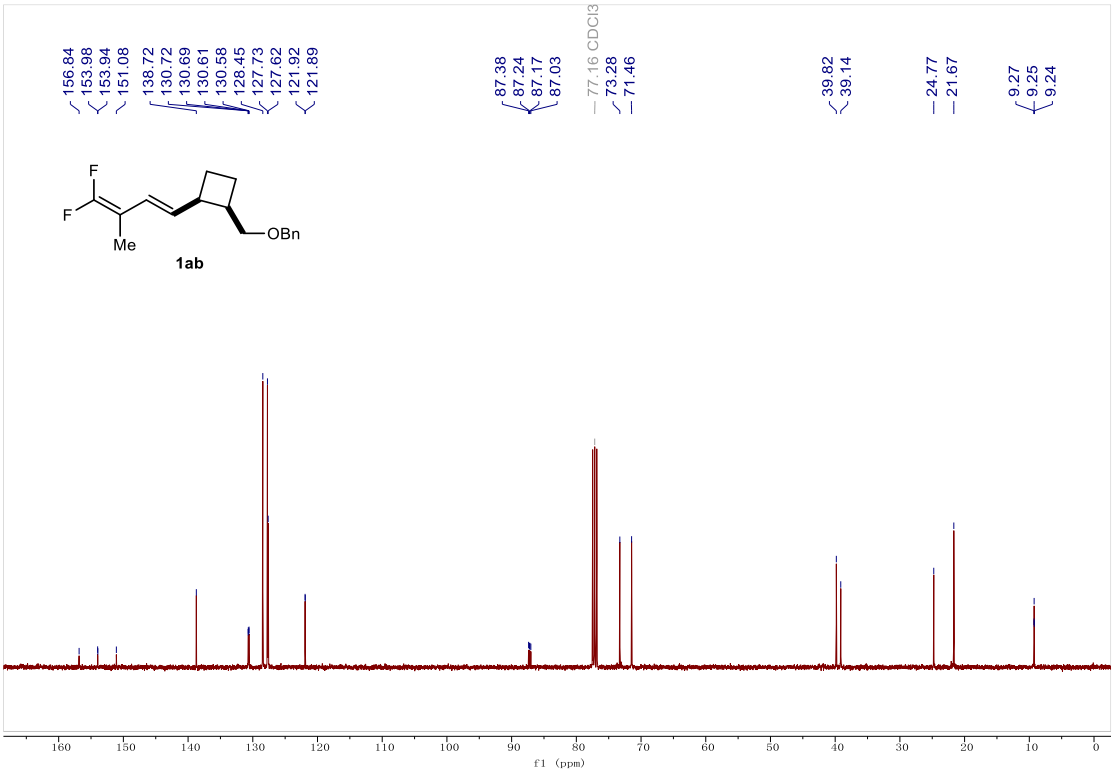
^{13}C NMR in $CDCl_3$, 101 MHz



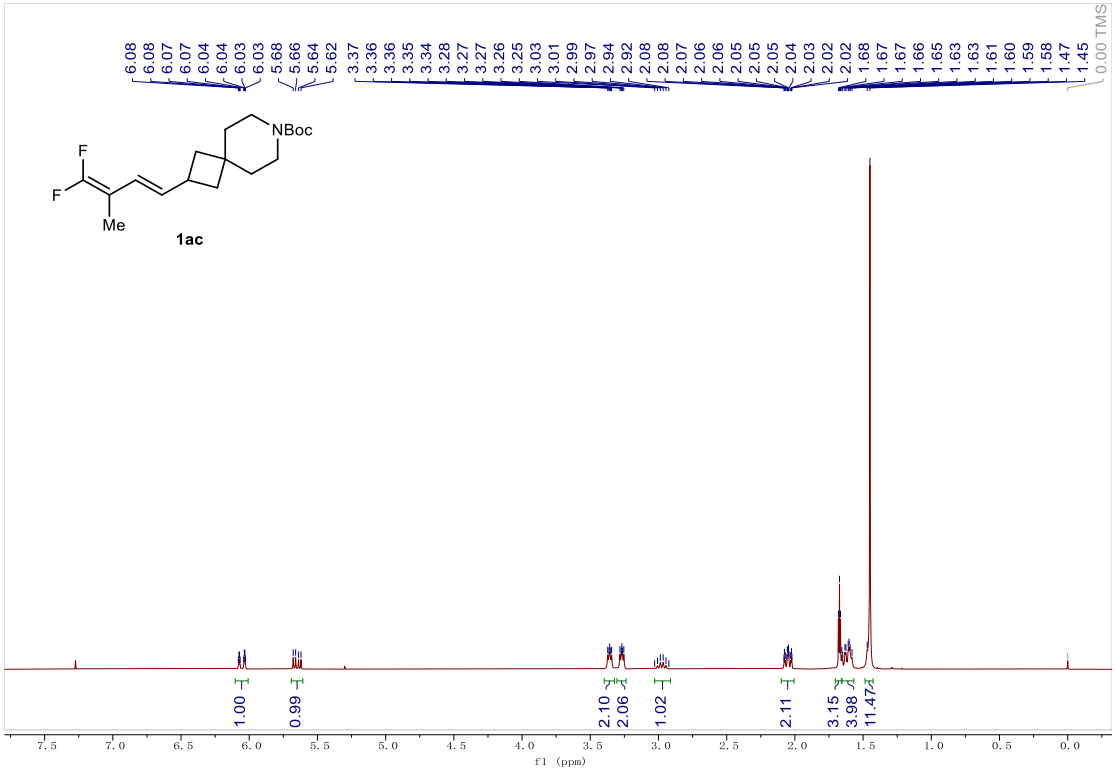
^{1}H NMR in $CDCl_3$, 400 MHz



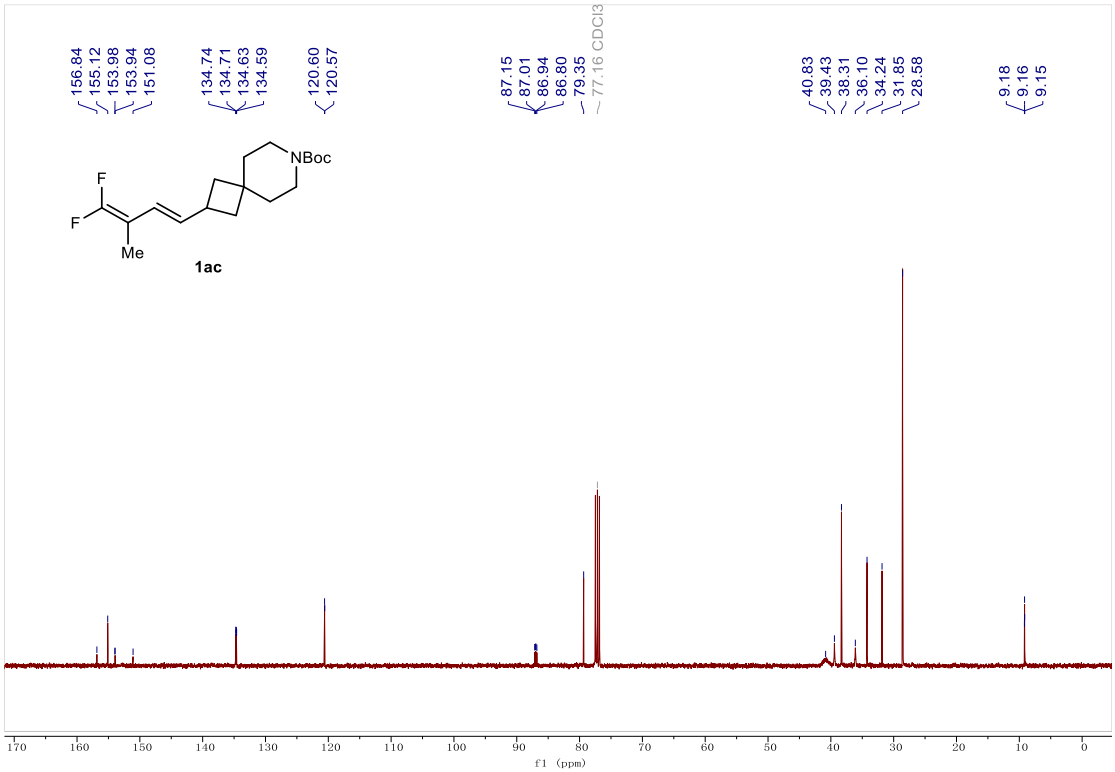
^{13}C NMR in $CDCl_3$, 101 MHz



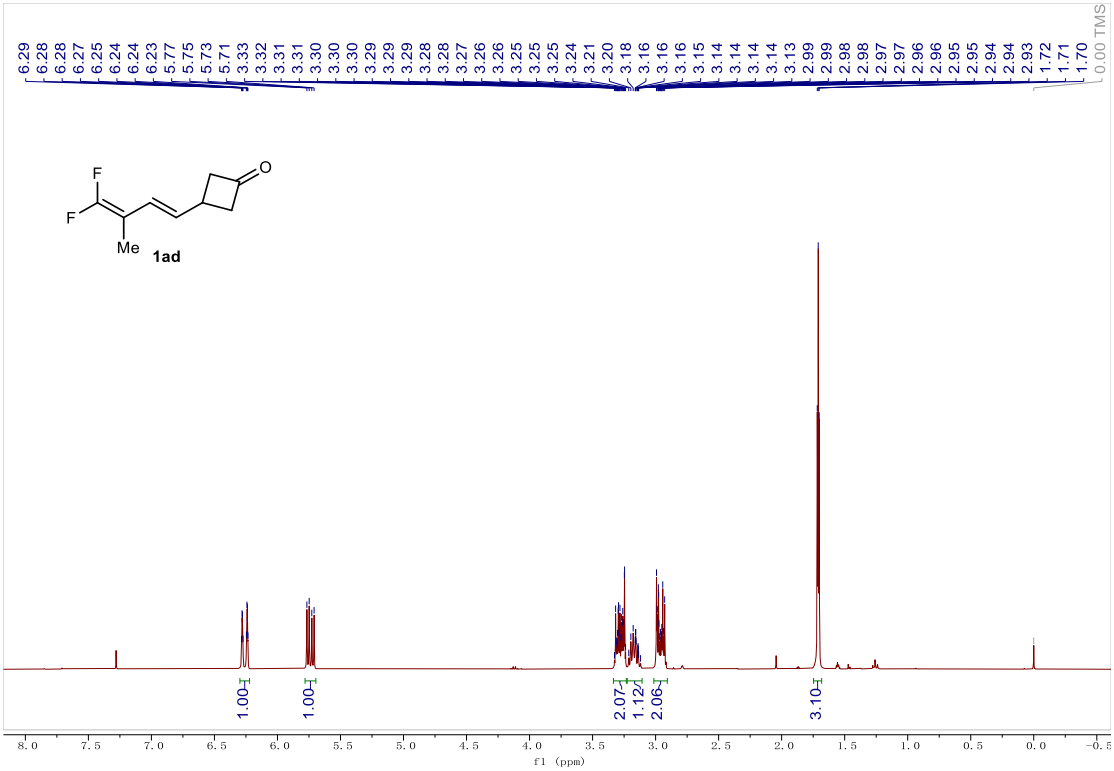
^{1}H NMR in $CDCl_3$, 400 MHz



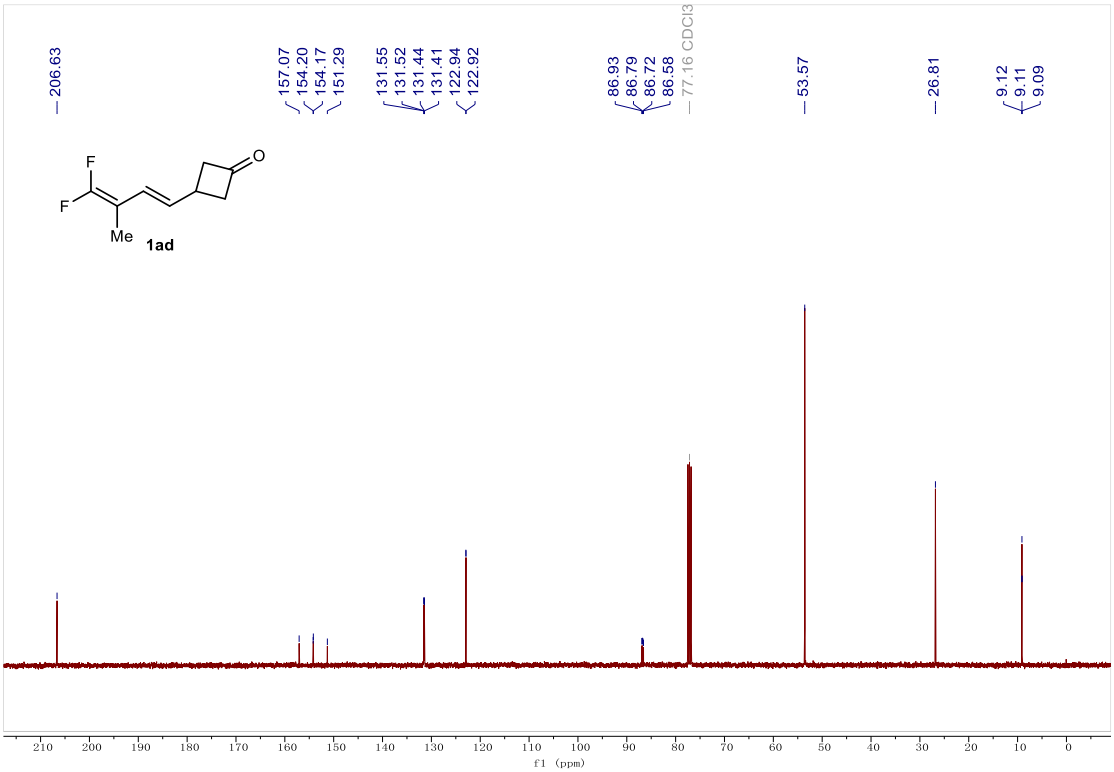
^{13}C NMR in $CDCl_3$, 101 MHz



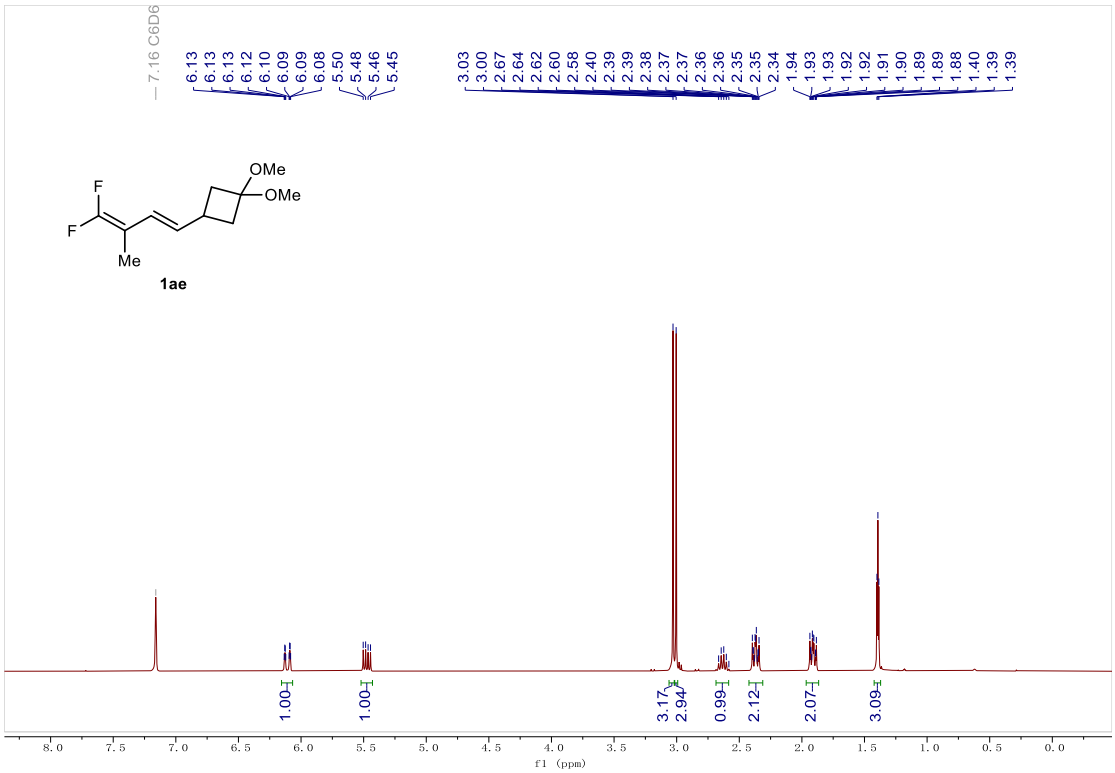
^{1}H NMR in $CDCl_3$, 400 MHz



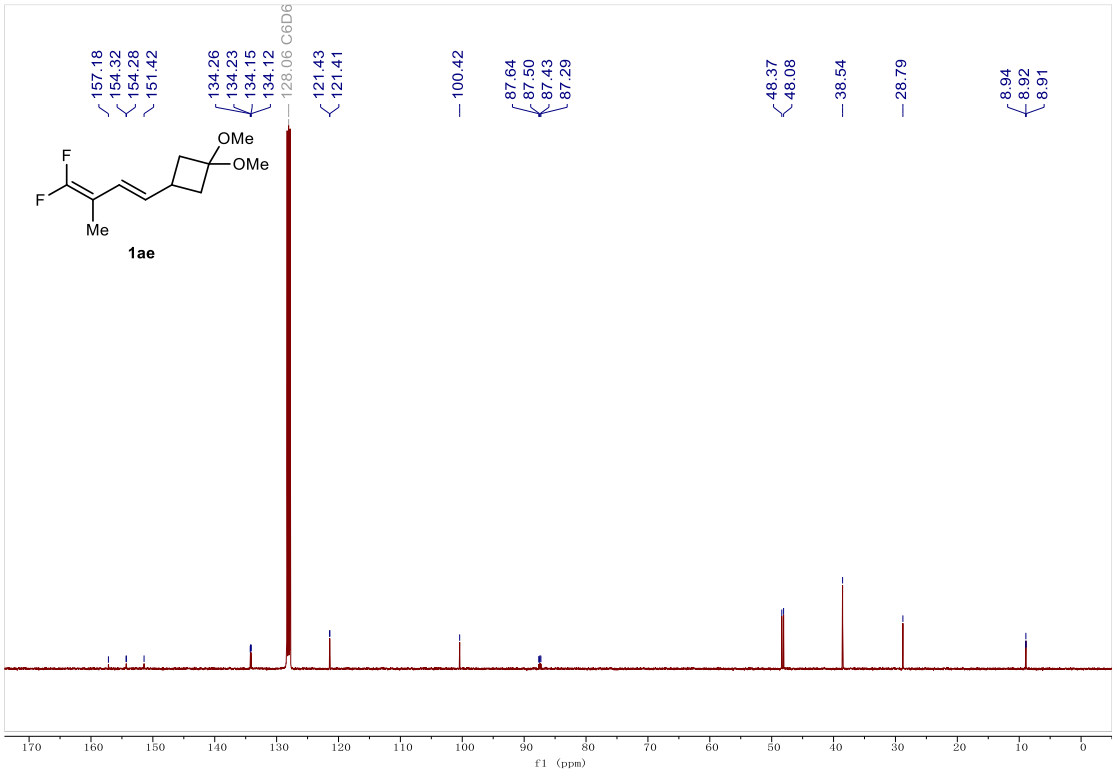
^{13}C NMR in $CDCl_3$, 101 MHz



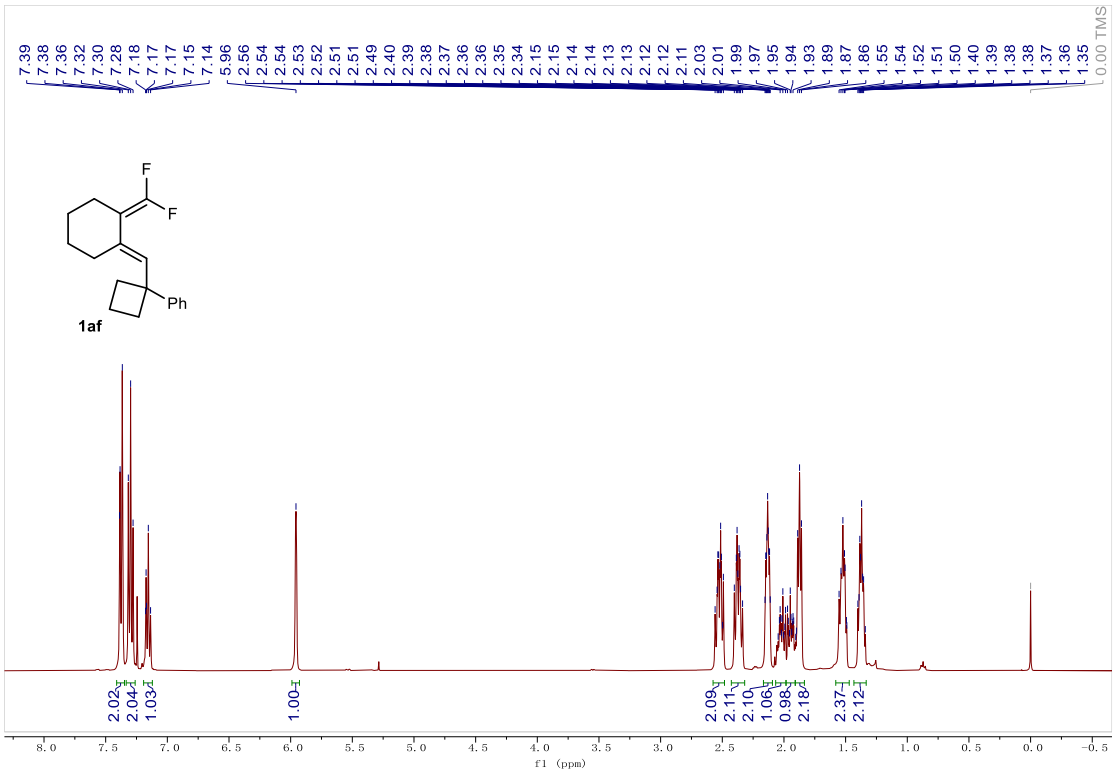
^{1}H NMR in C_6D_6, 400 MHz



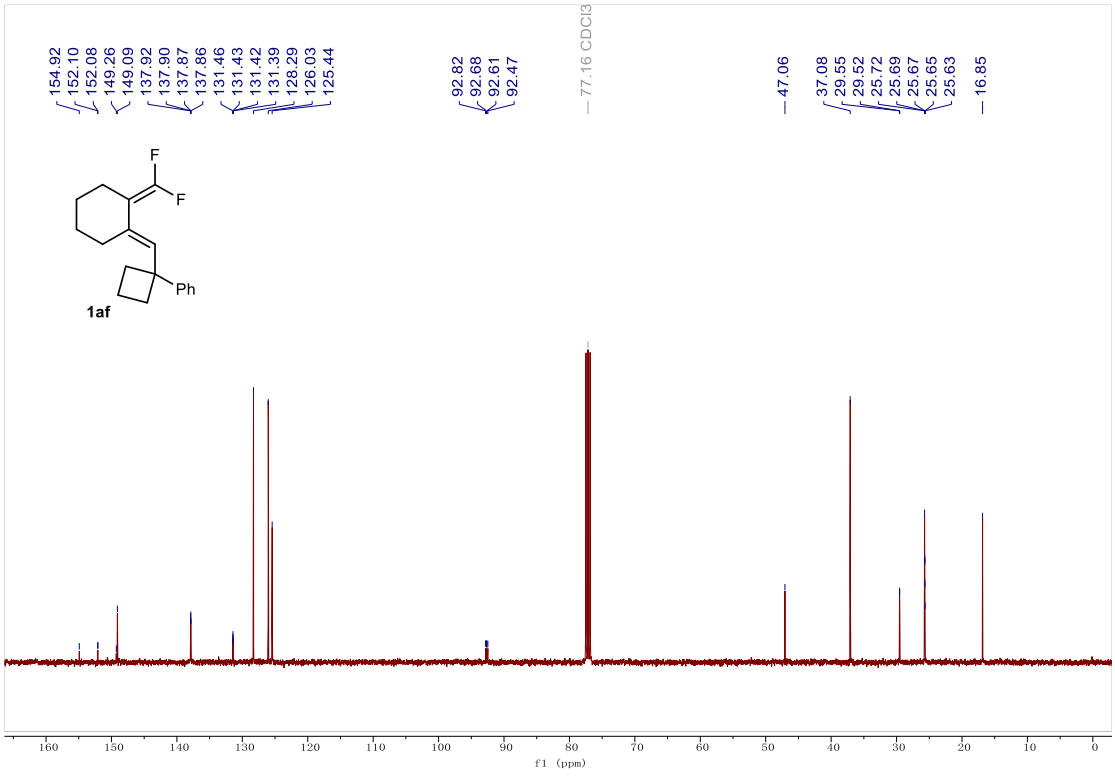
^{13}C NMR in C_6D_6, 101 MHz



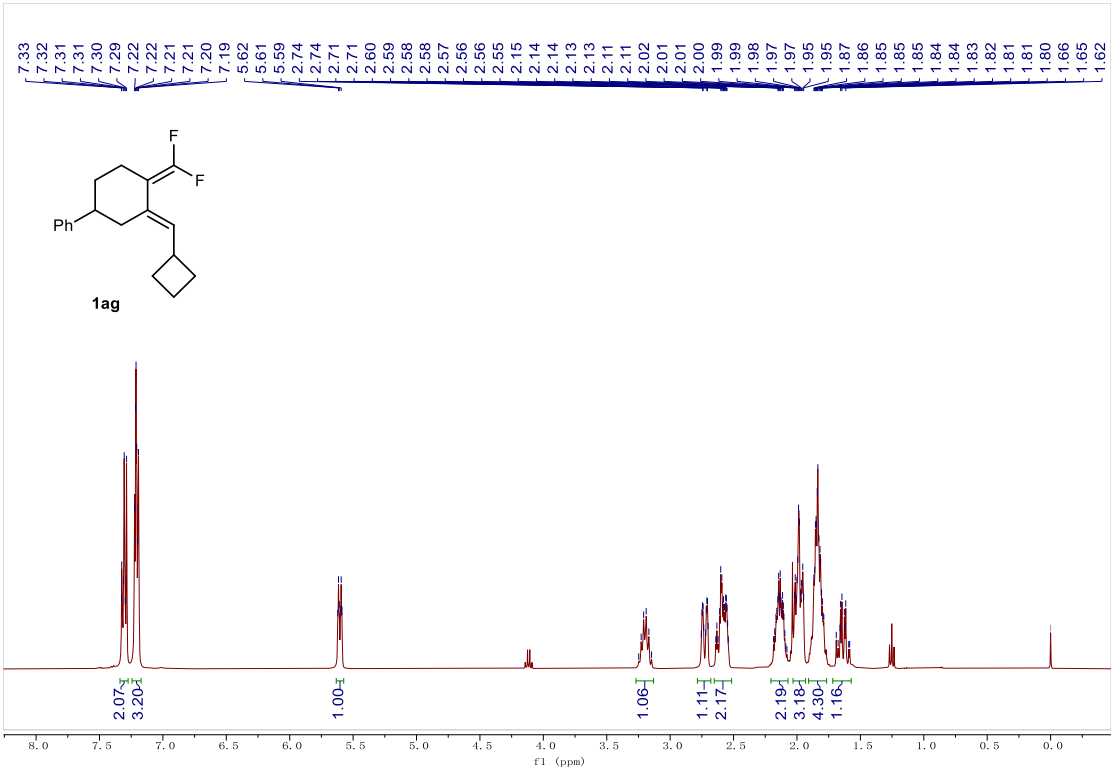
^{1}H NMR in $CDCl_3$, 400 MHz



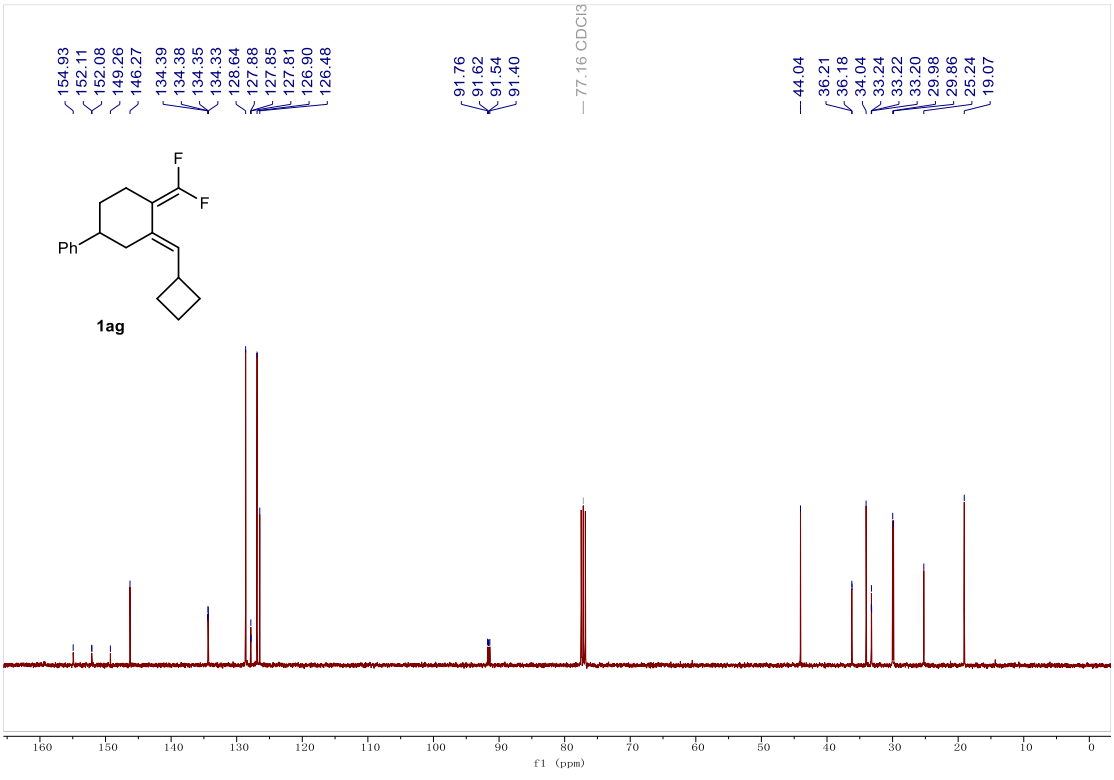
^{13}C NMR in $CDCl_3$, 101 MHz



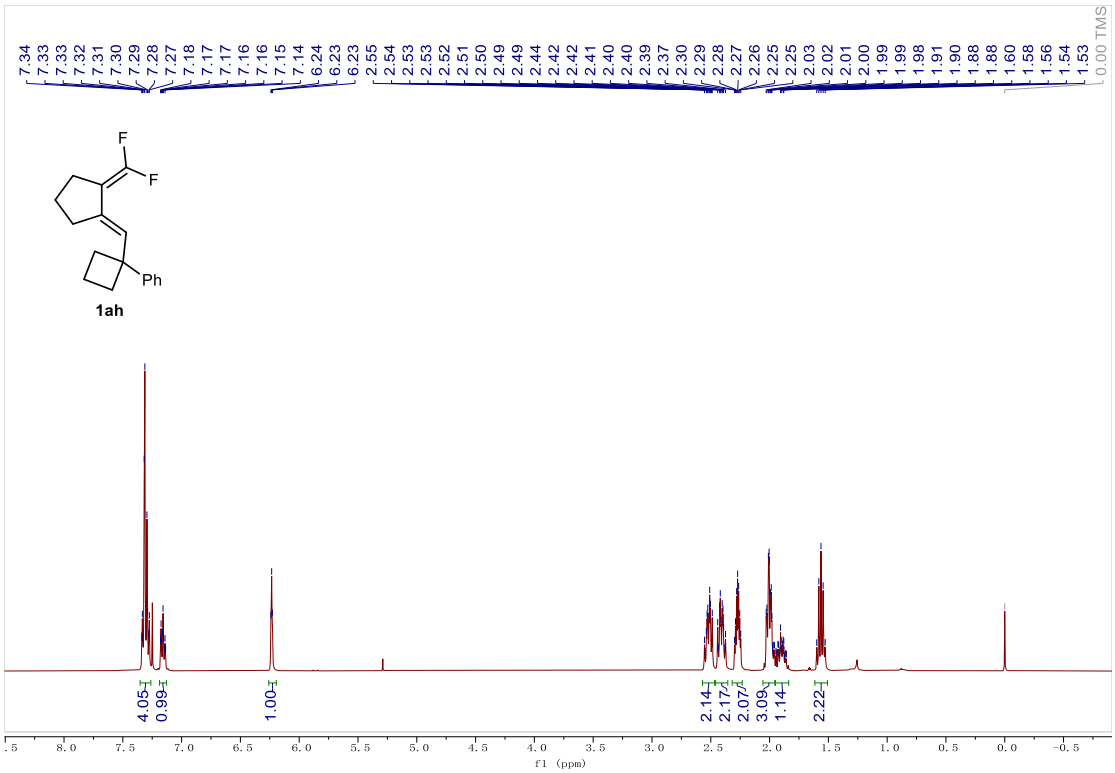
^{1}H NMR in $CDCl_3$, 400 MHz



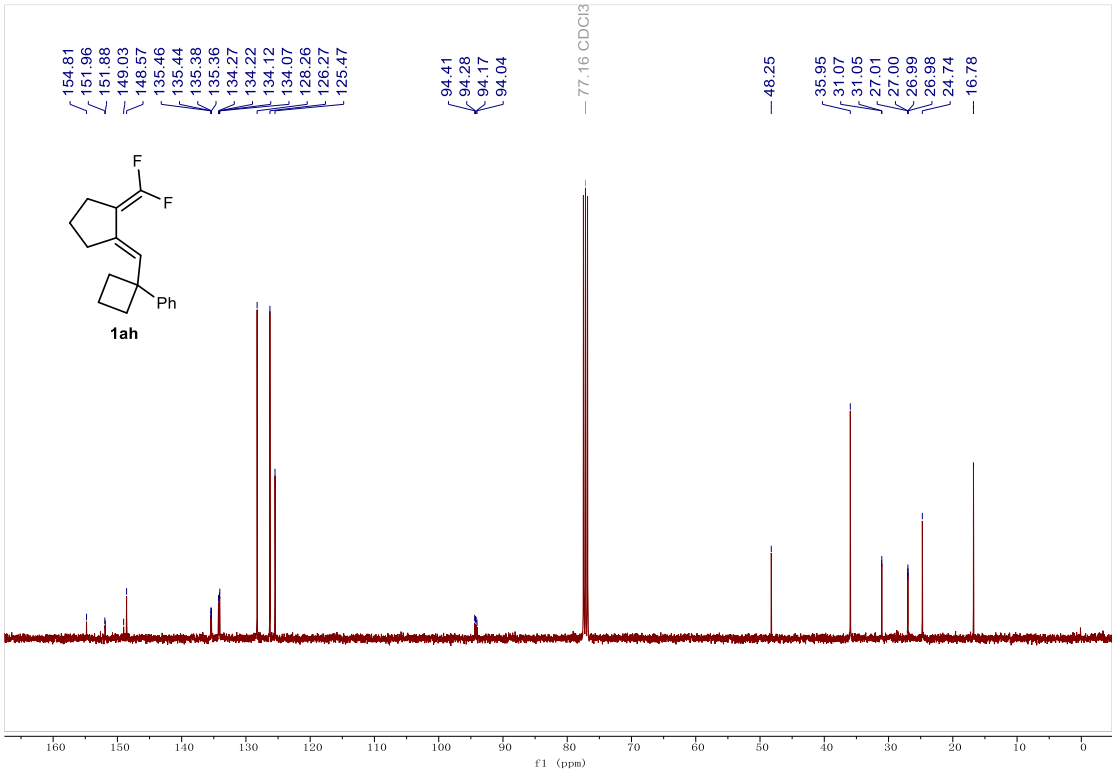
^{13}C NMR in $CDCl_3$, 101 MHz



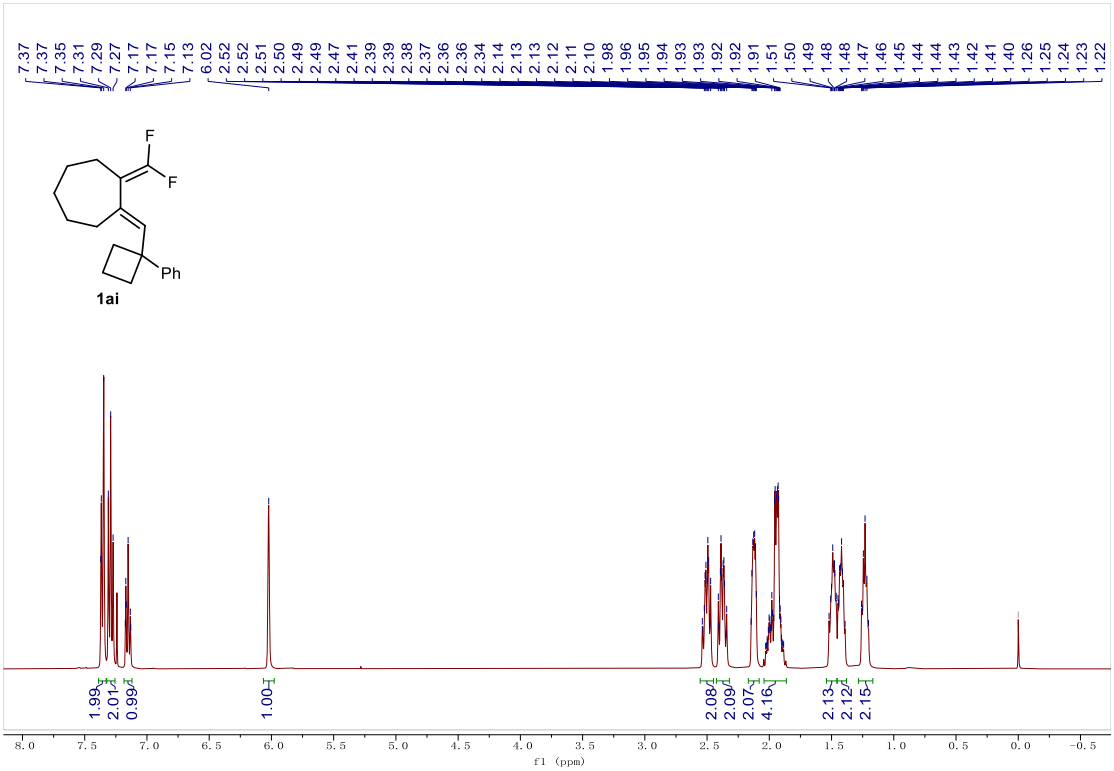
^{1}H NMR in $CDCl_3$, 400 MHz



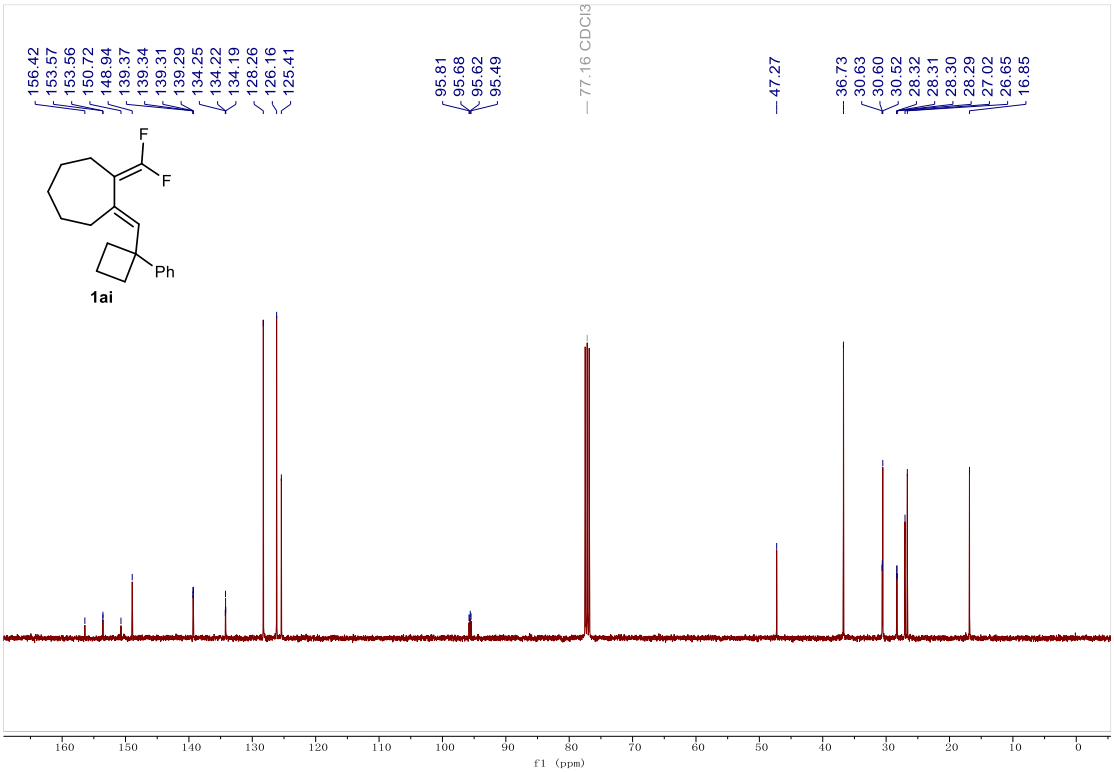
^{13}C NMR in $CDCl_3$, 101 MHz



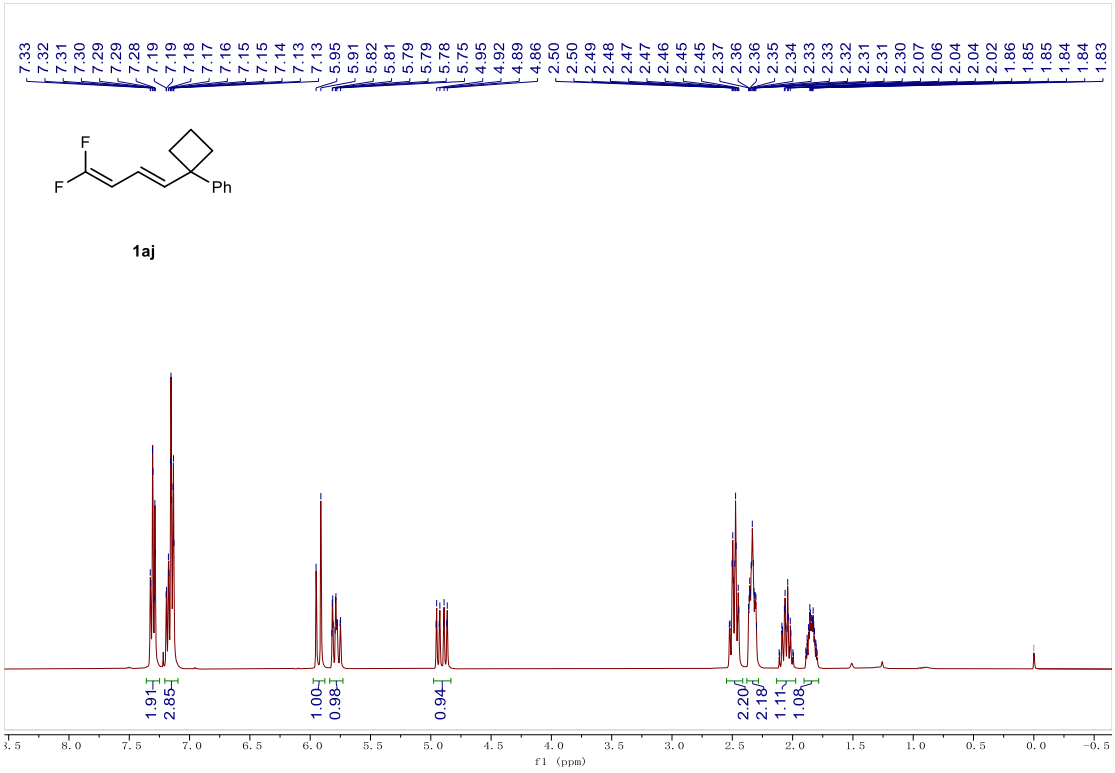
^{1}H NMR in $CDCl_3$, 400 MHz



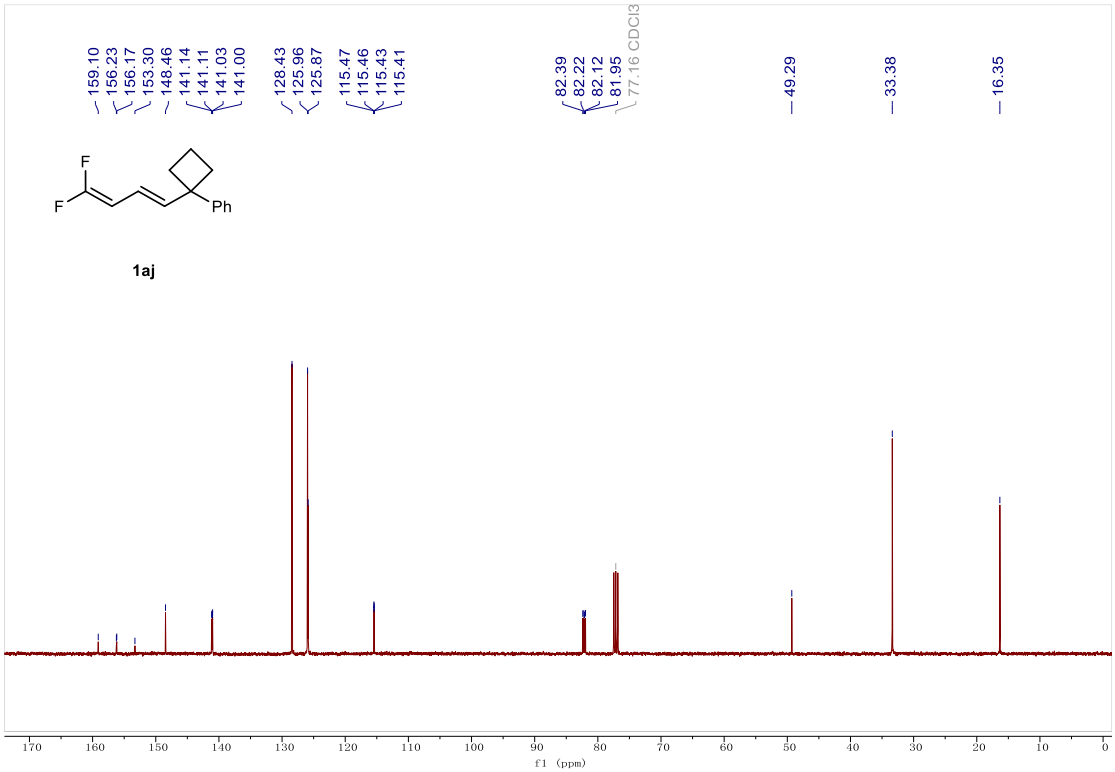
^{13}C NMR in $CDCl_3$, 101 MHz



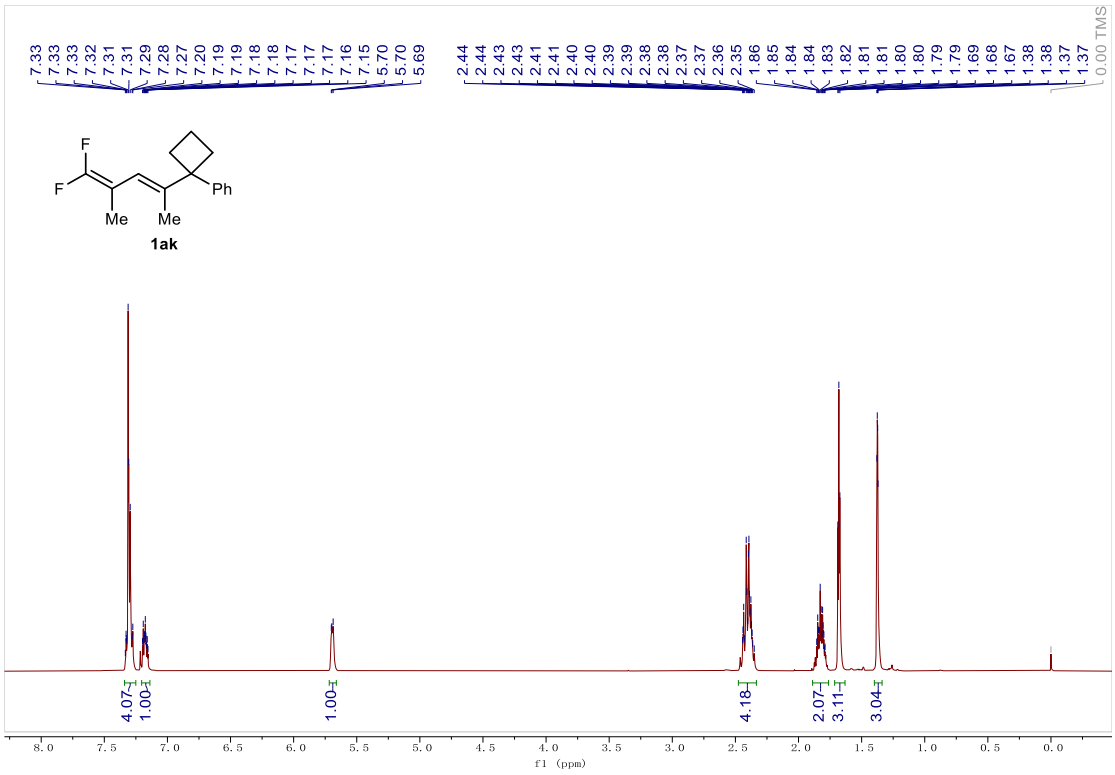
^{1}H NMR in $CDCl_3$, 400 MHz



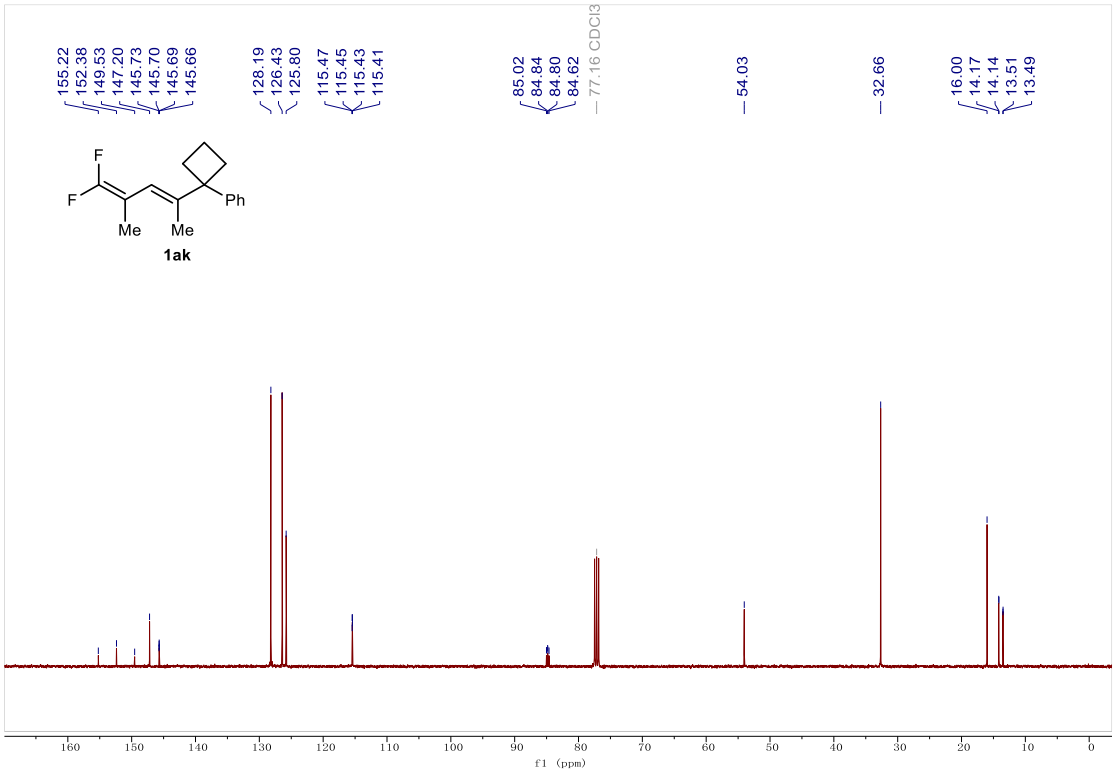
^{13}C NMR in $CDCl_3$, 101 MHz



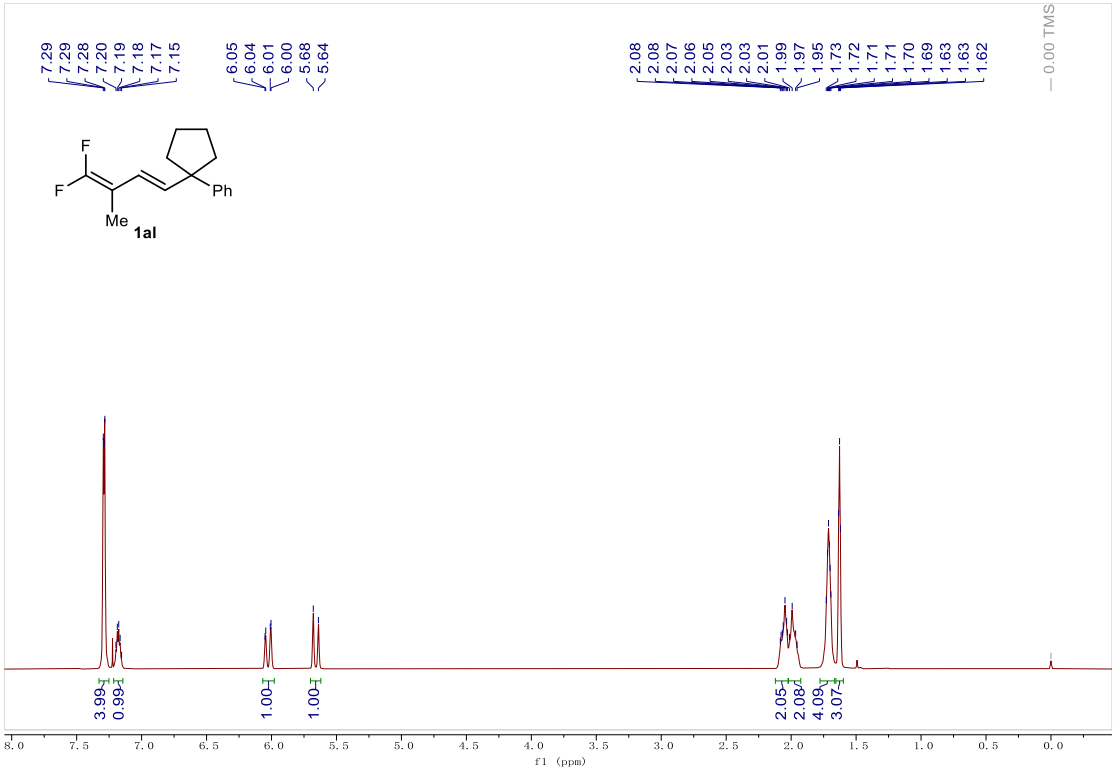
^{1}H NMR in $CDCl_3$, 400 MHz



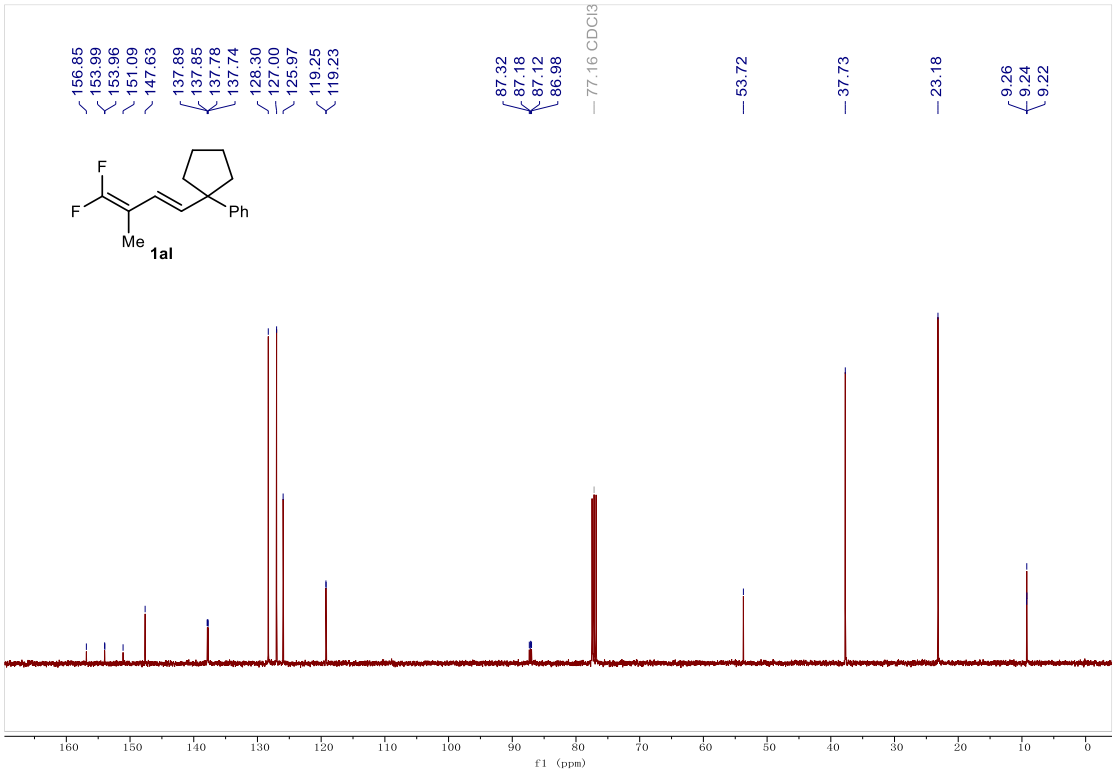
^{13}C NMR in $CDCl_3$, 101 MHz



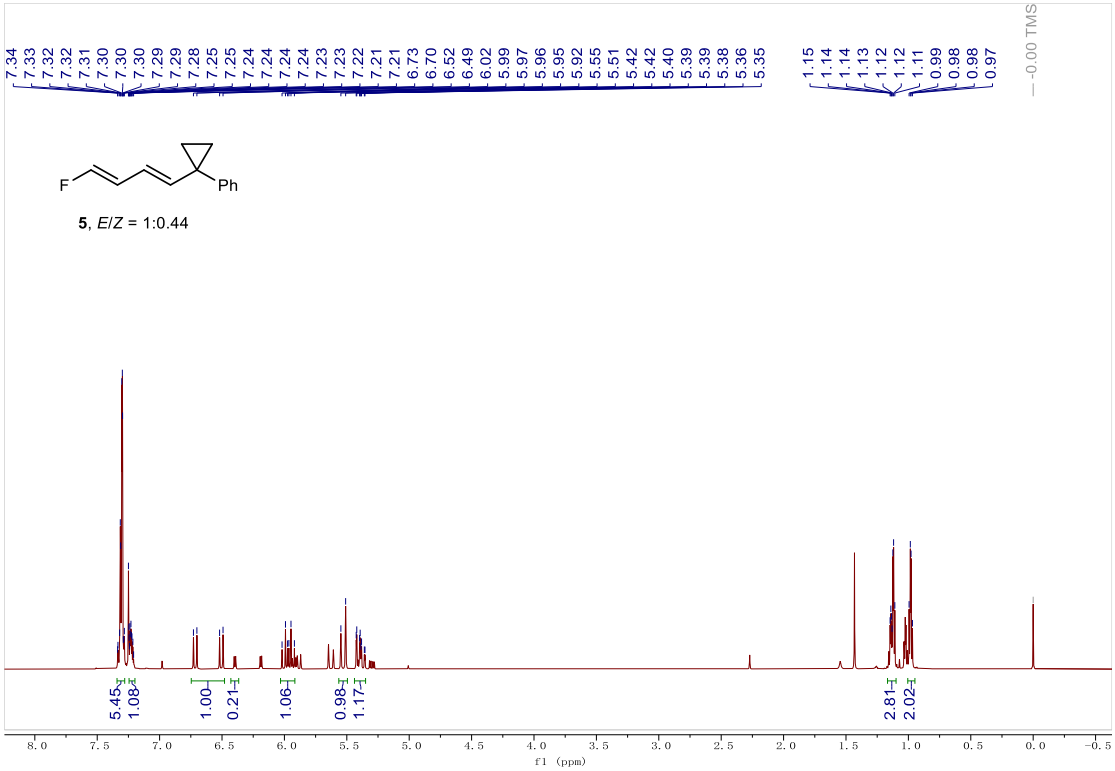
^{1}H NMR in $CDCl_3$, 400 MHz



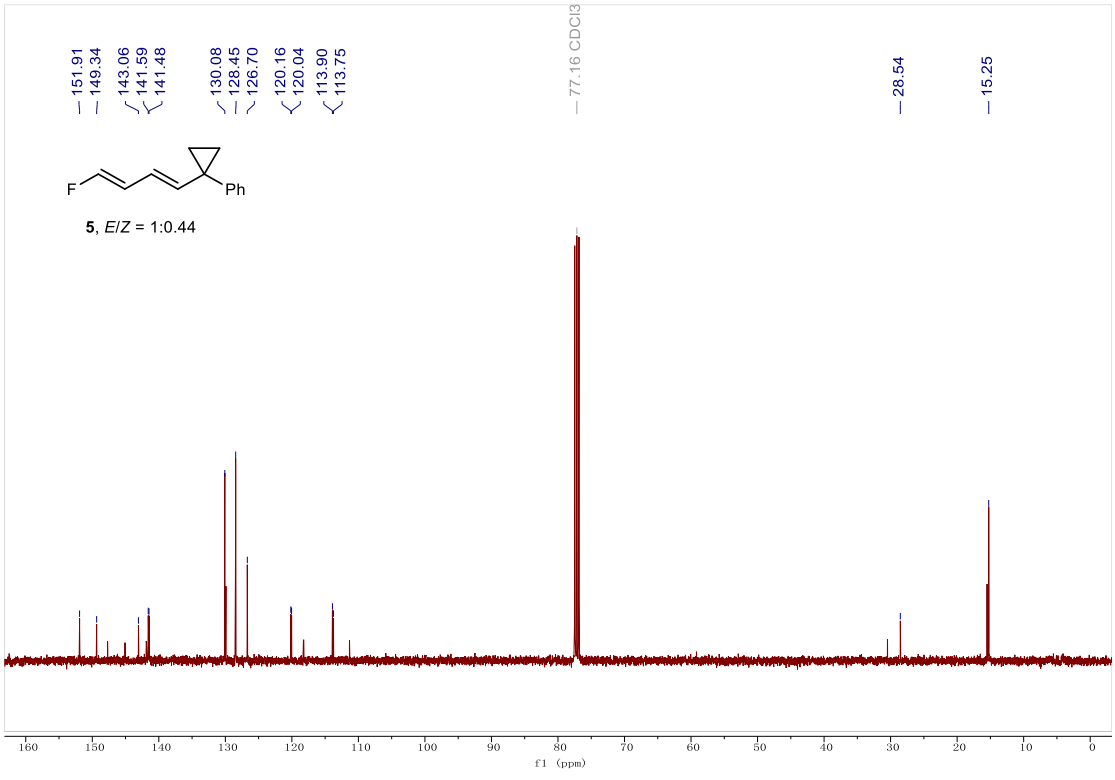
^{13}C NMR in $CDCl_3$, 101 MHz



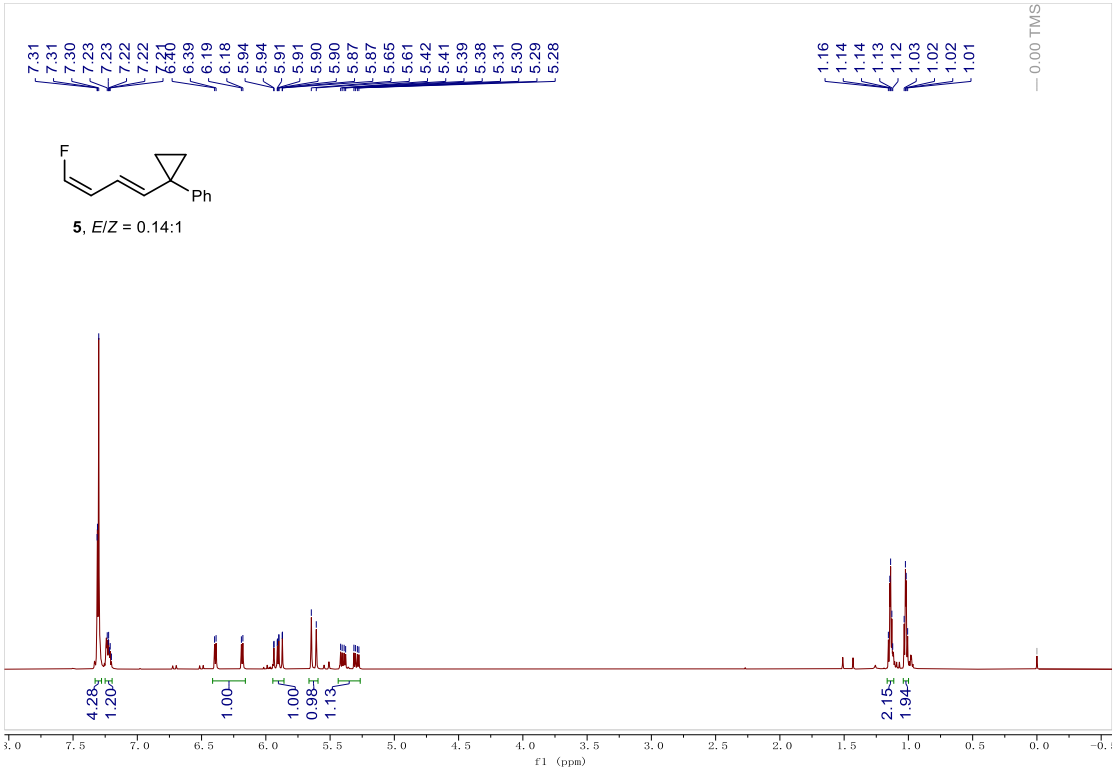
^{1}H NMR in $CDCl_3$, 400 MHz



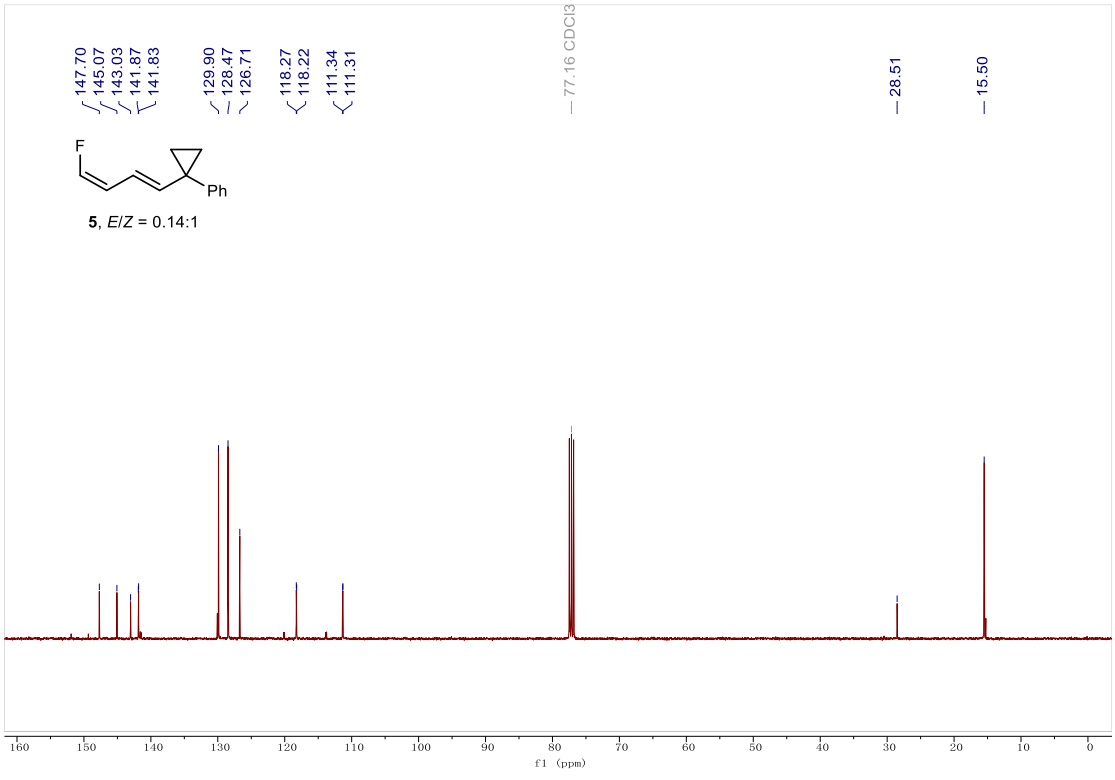
^{13}C NMR in $CDCl_3$, 101 MHz



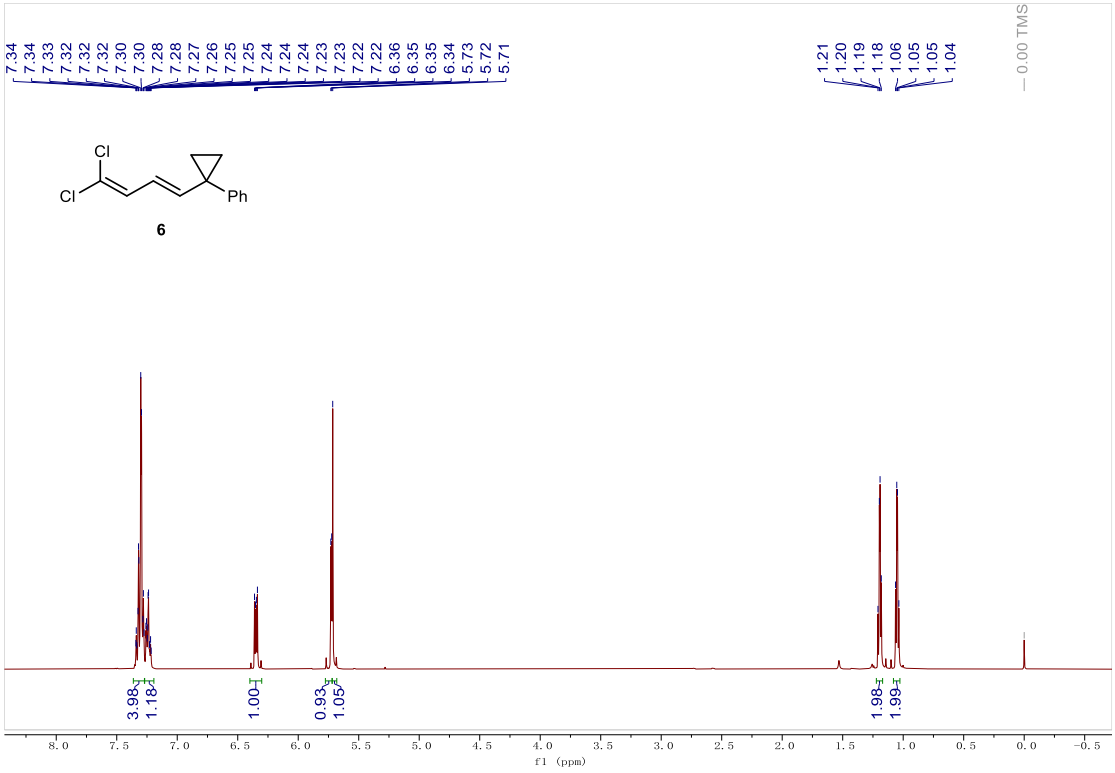
^{1}H NMR in $CDCl_3$, 400 MHz



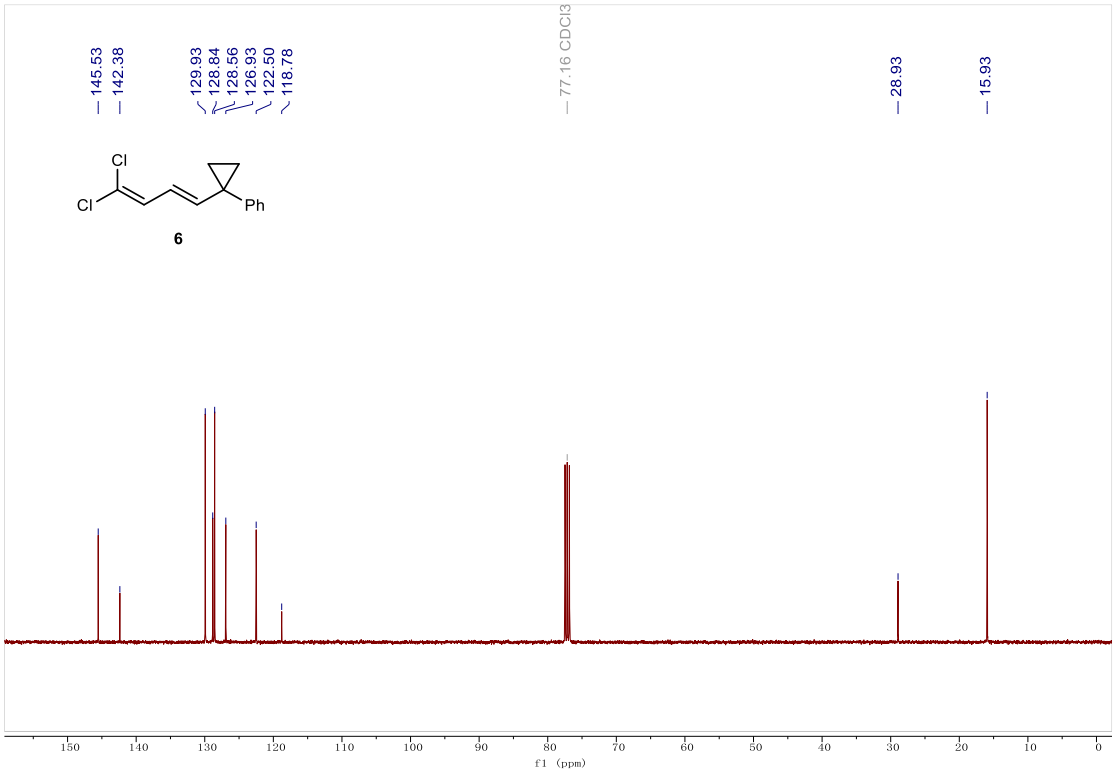
^{13}C NMR in $CDCl_3$, 101 MHz



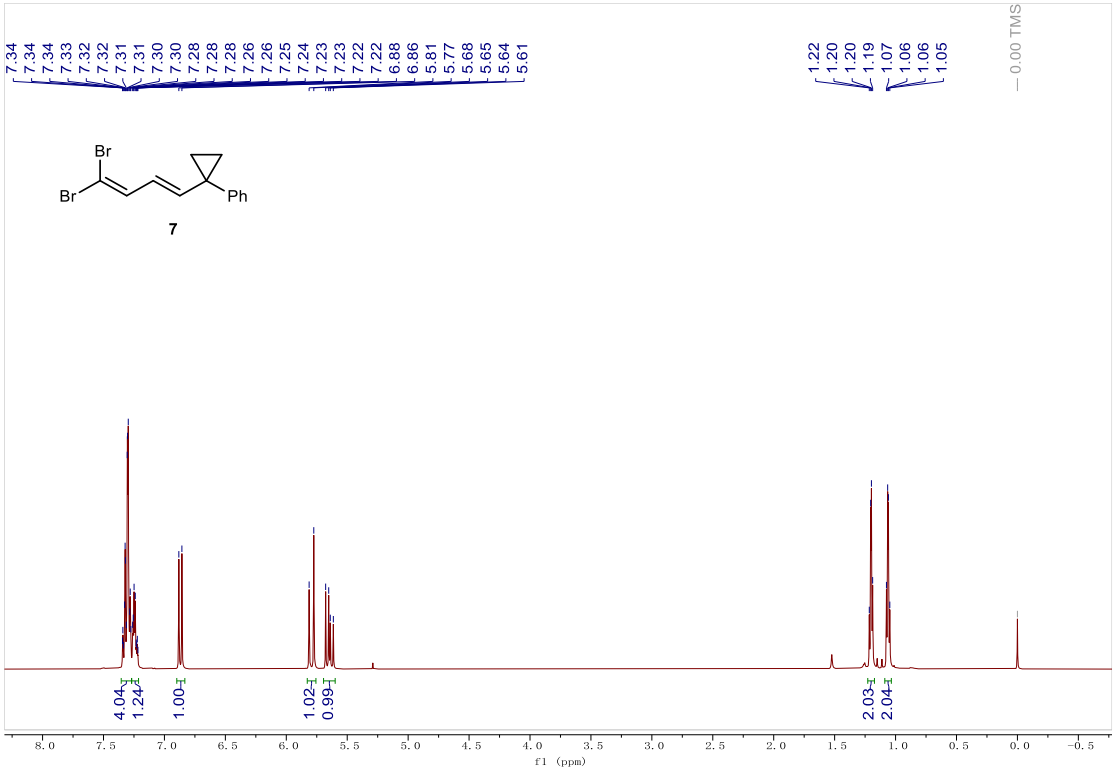
^{1}H NMR in $CDCl_3$, 400 MHz



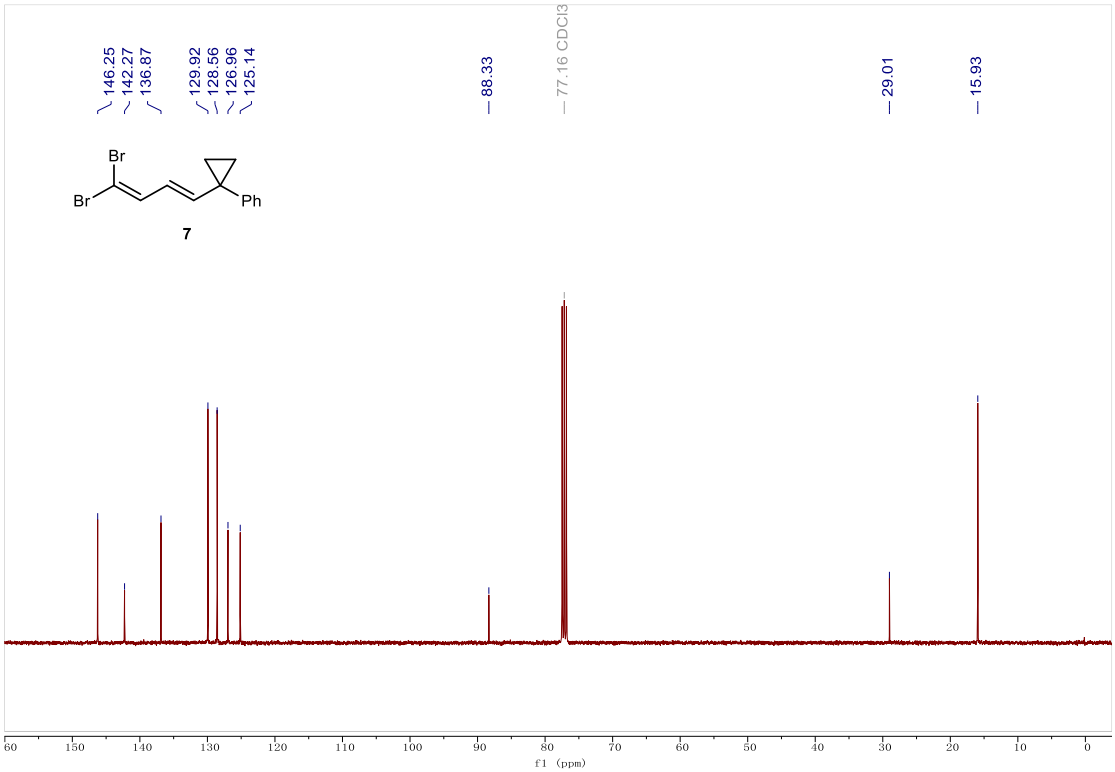
^{13}C NMR in $CDCl_3$, 101 MHz



^{1}H NMR in $CDCl_3$, 400 MHz



^{13}C NMR in $CDCl_3$, 101 MHz



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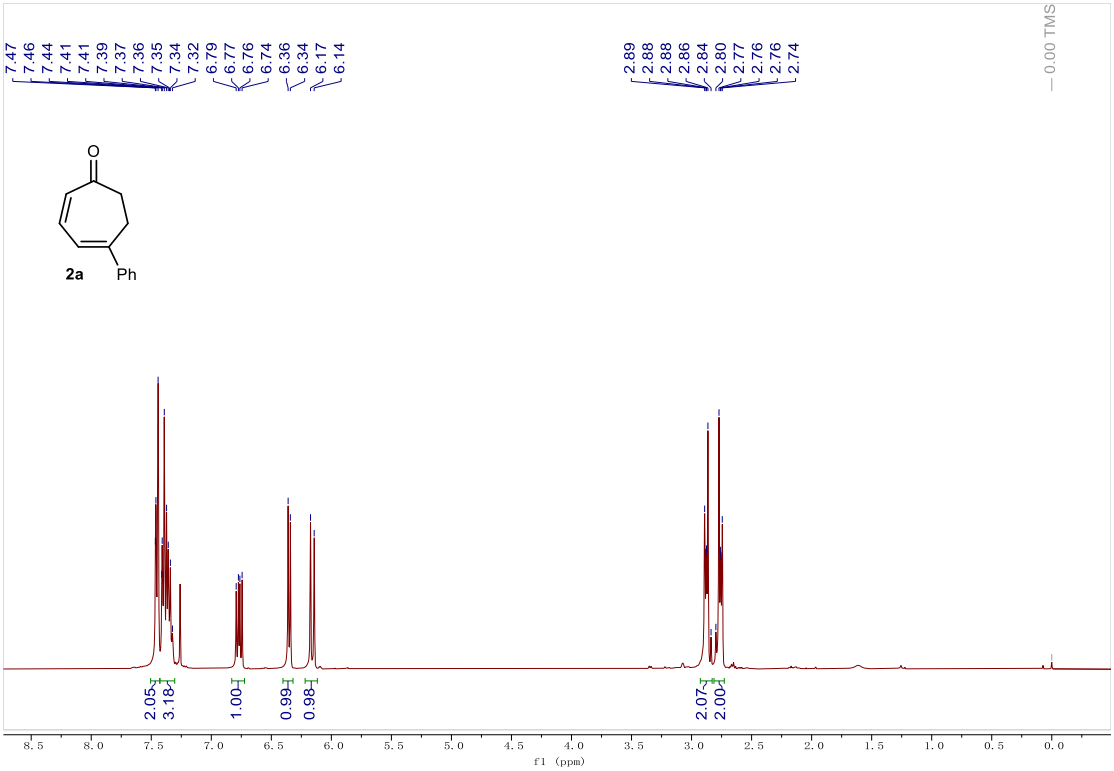
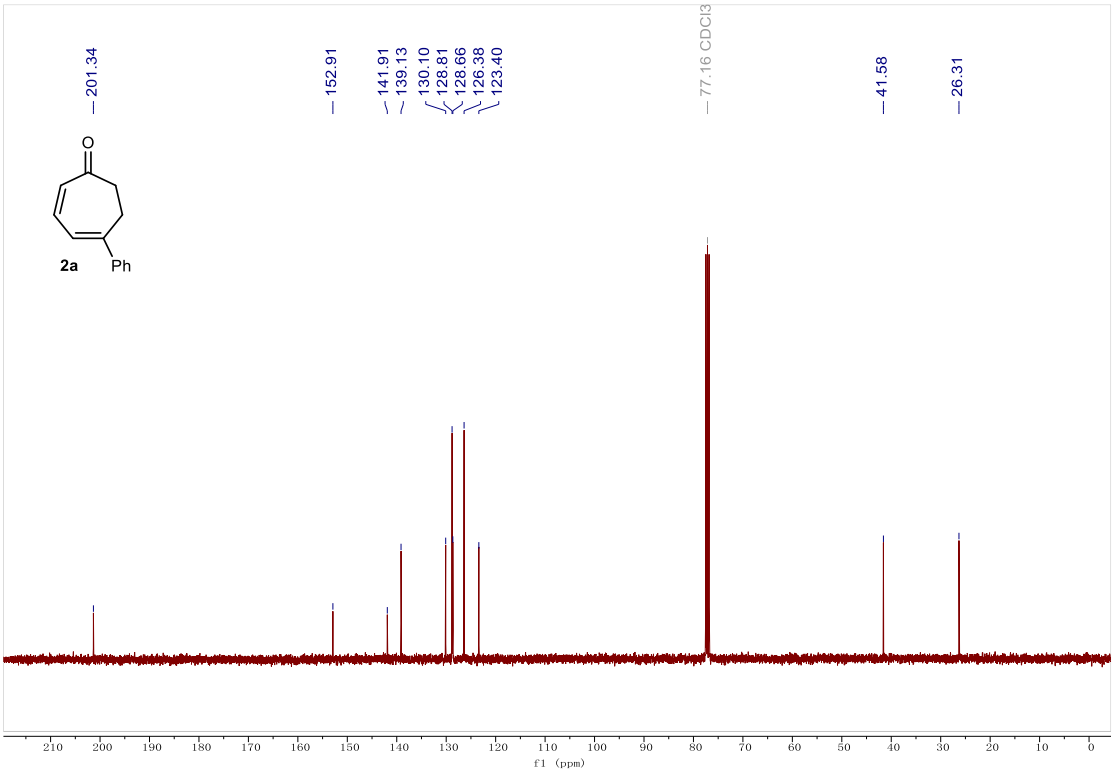
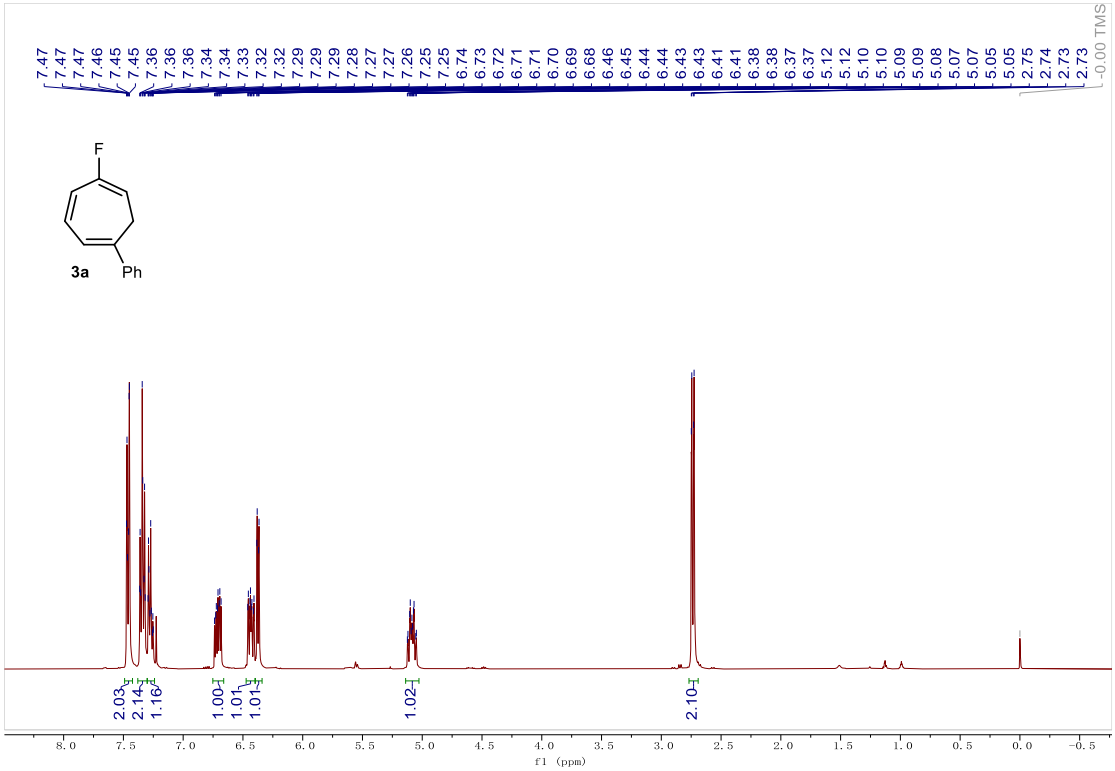


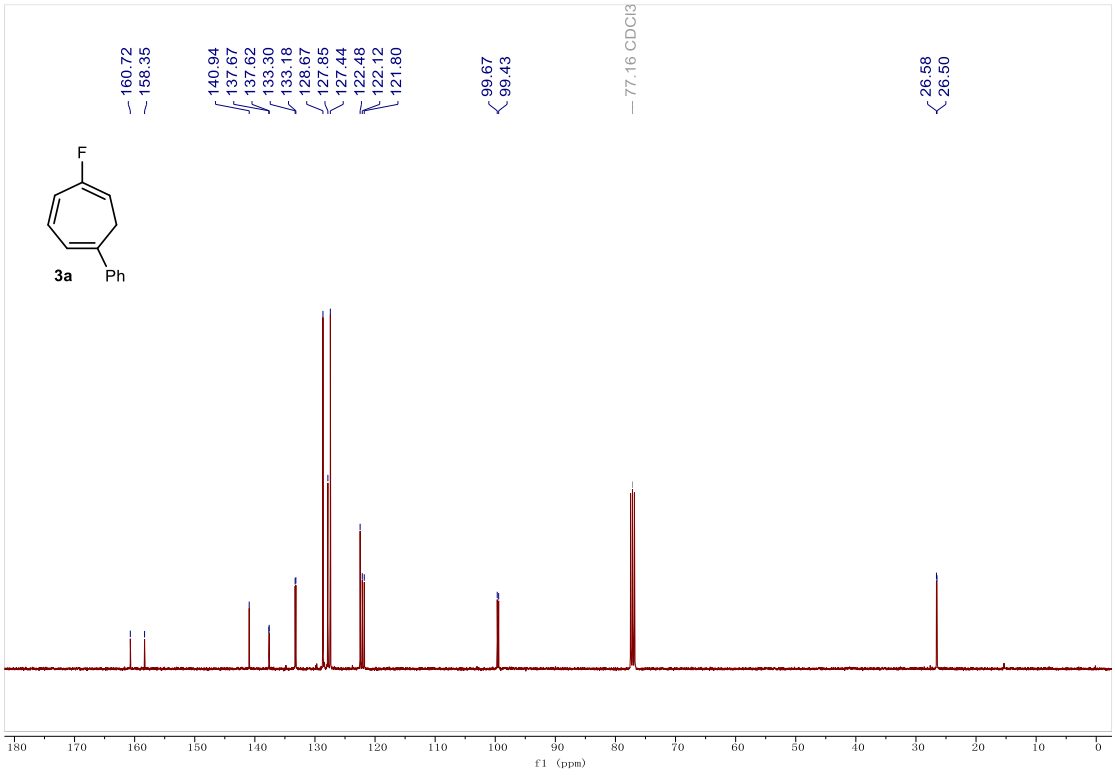
^{13}C NMR in $CDCl_3$, 101 MHz



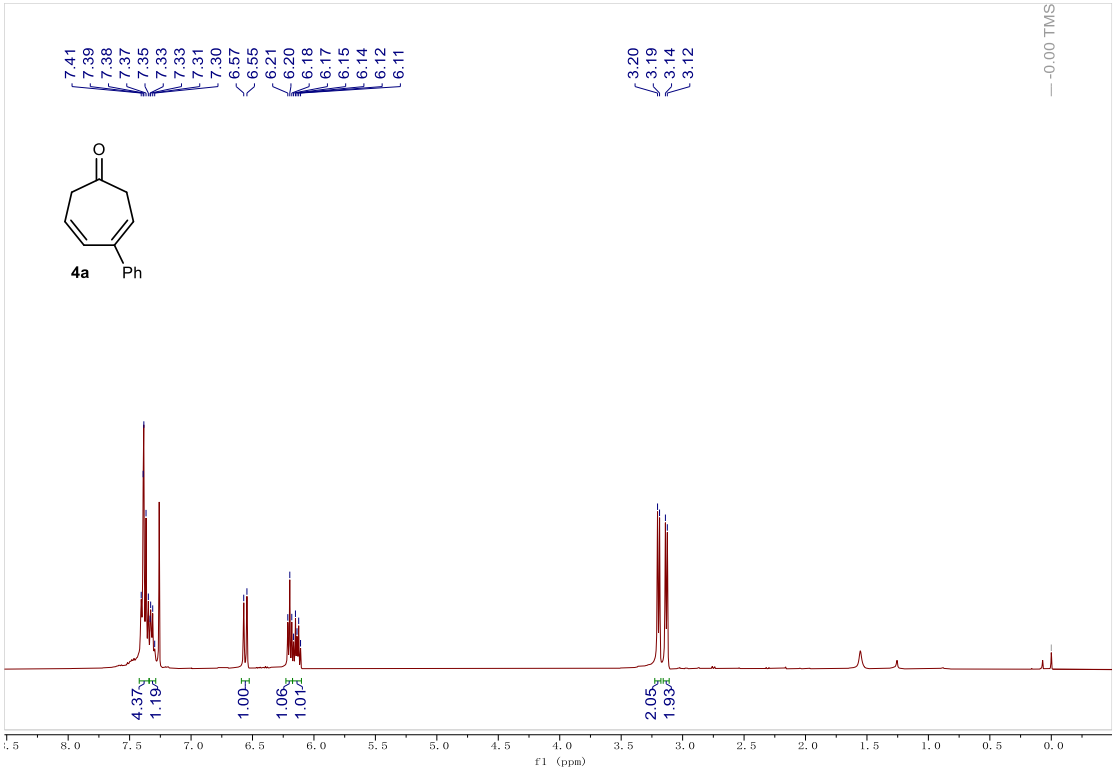
^{1}H NMR in $CDCl_3$, 400 MHz



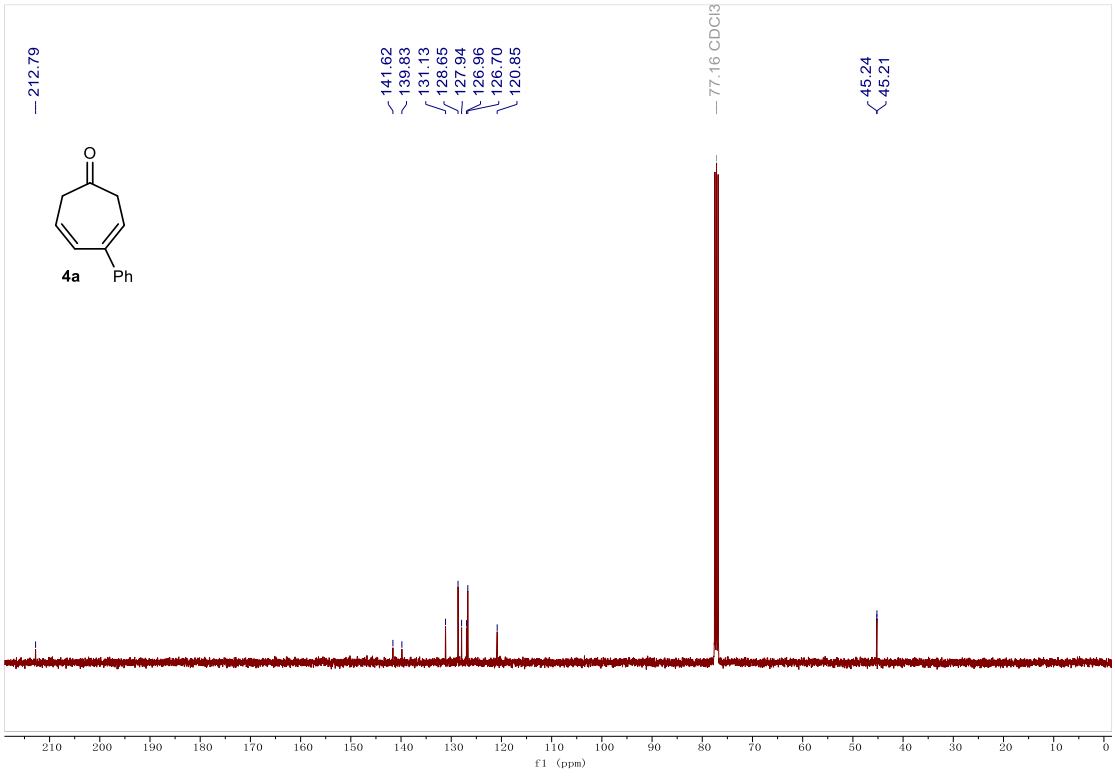
^{13}C NMR in $CDCl_3$, 101 MHz



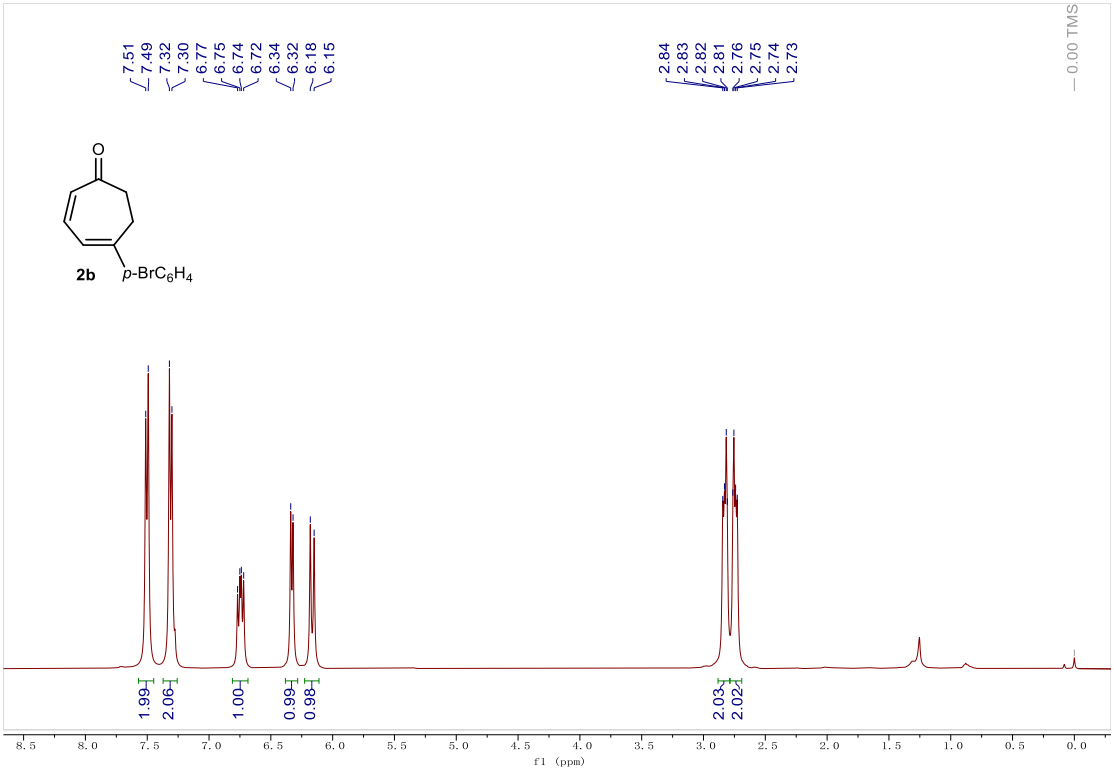
^{1}H NMR in $CDCl_3$, 400 MHz



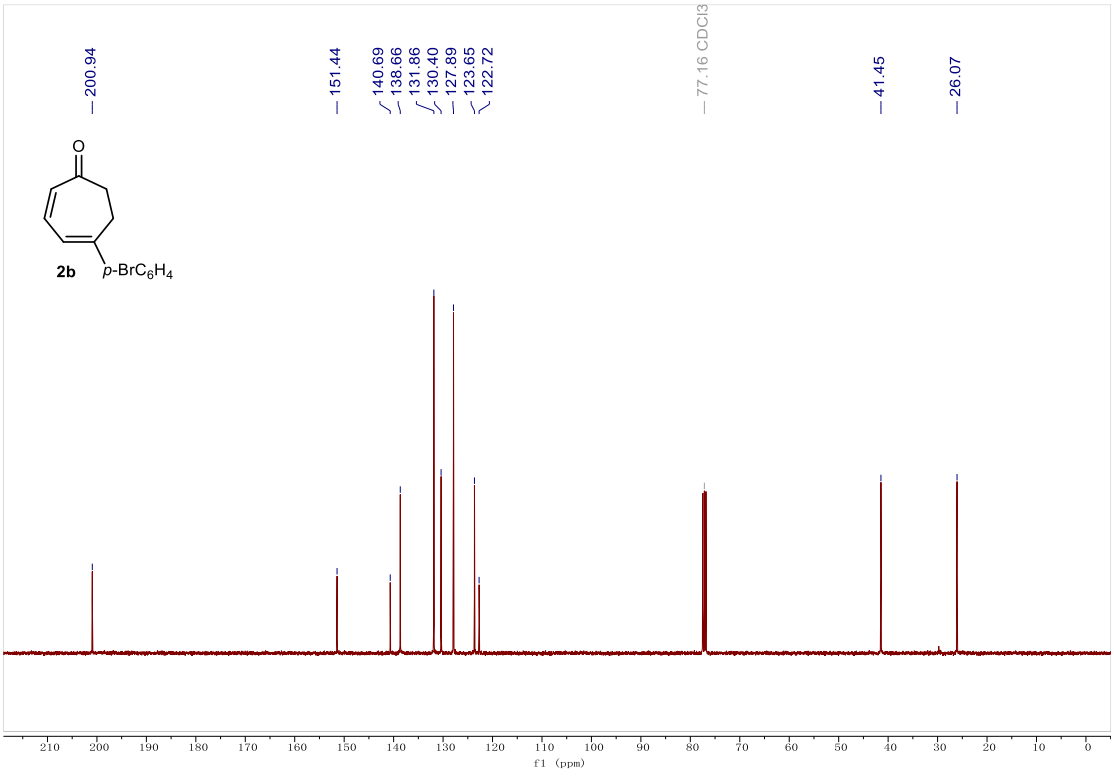
^{13}C NMR in $CDCl_3$, 101 MHz



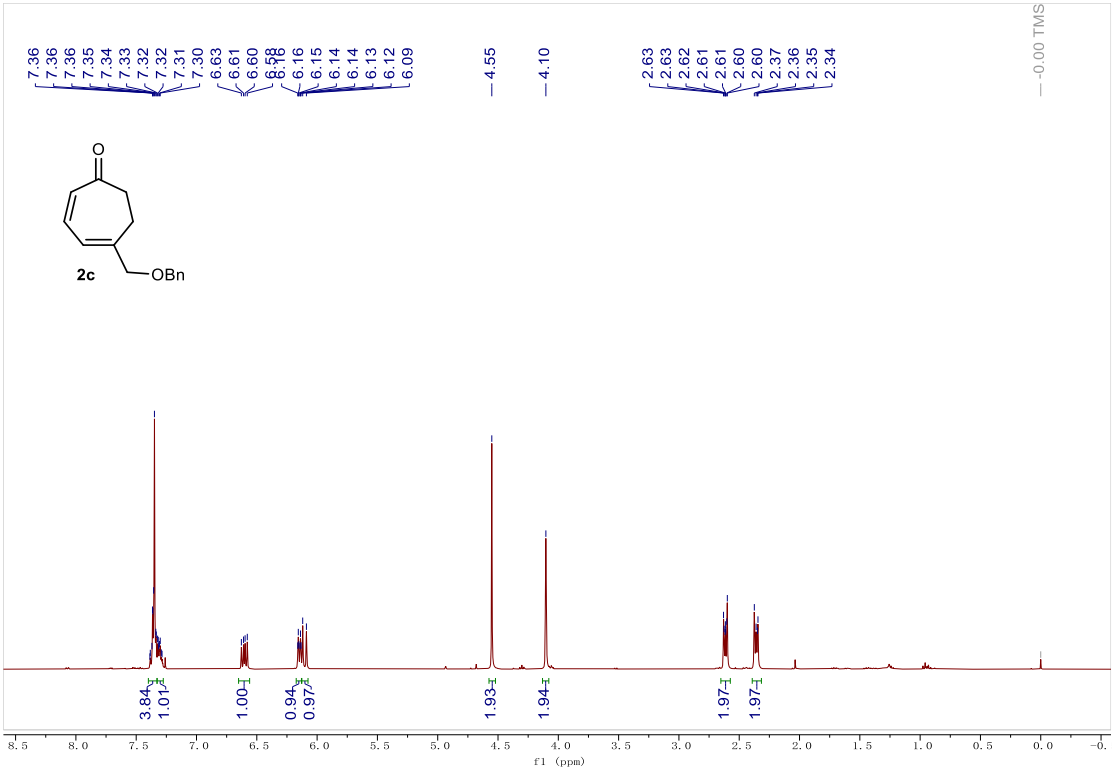
^{1}H NMR in $CDCl_3$, 400 MHz



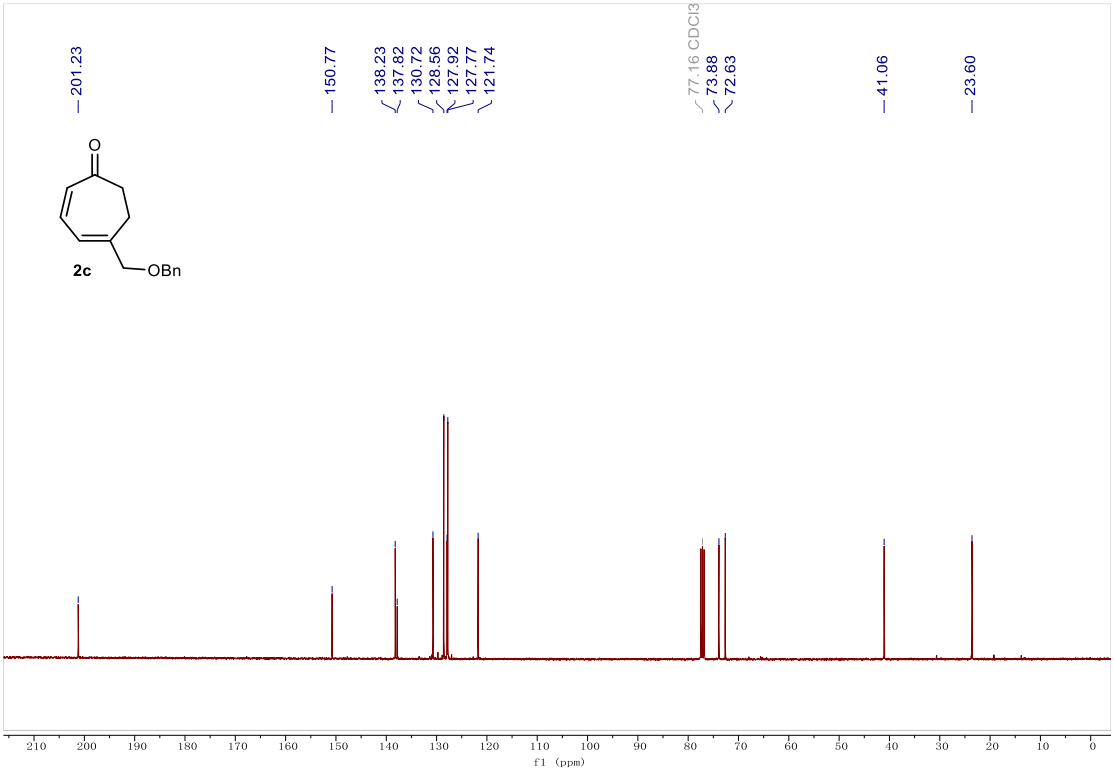
^{13}C NMR in $CDCl_3$, 101 MHz



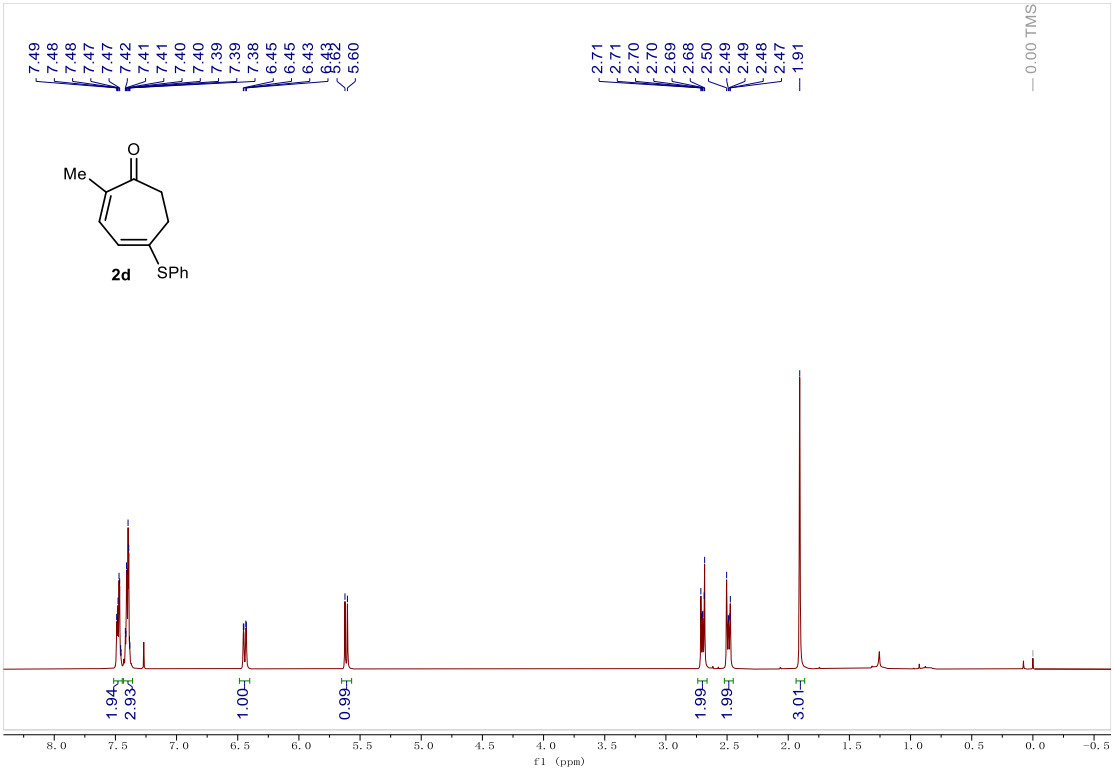
^{1}H NMR in $CDCl_3$, 400 MHz



^{13}C NMR in $CDCl_3$, 101 MHz



^{1}H NMR in $CDCl_3$, 400 MHz



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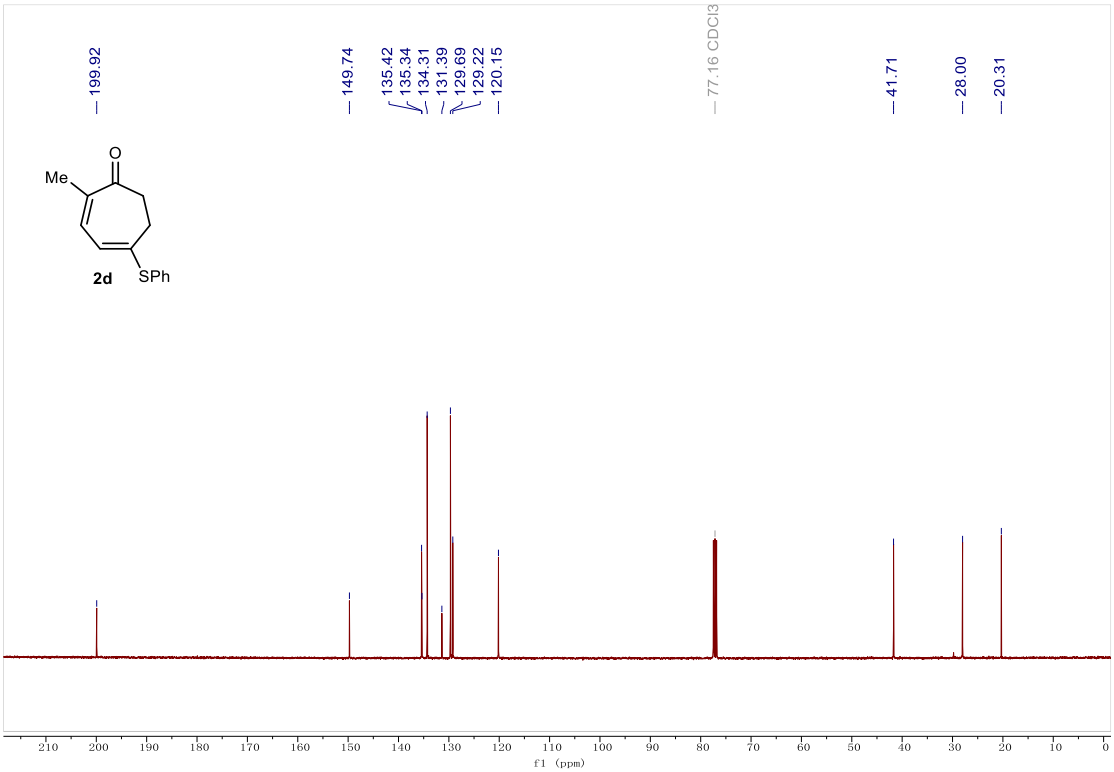
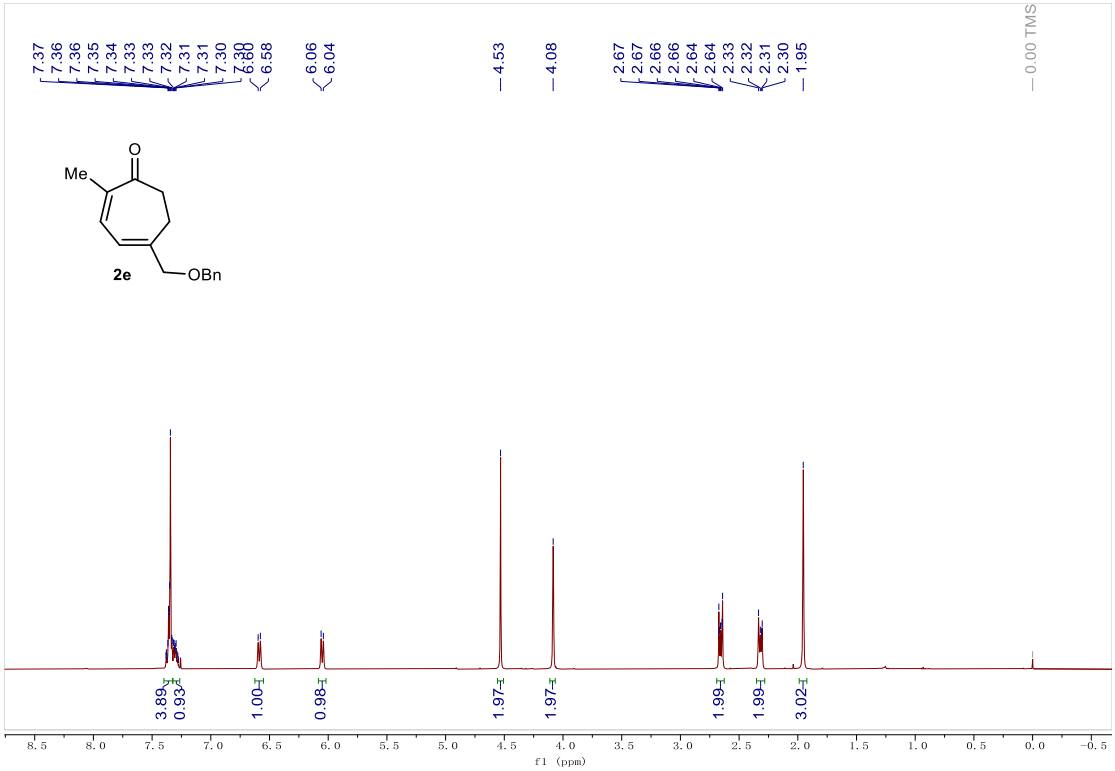
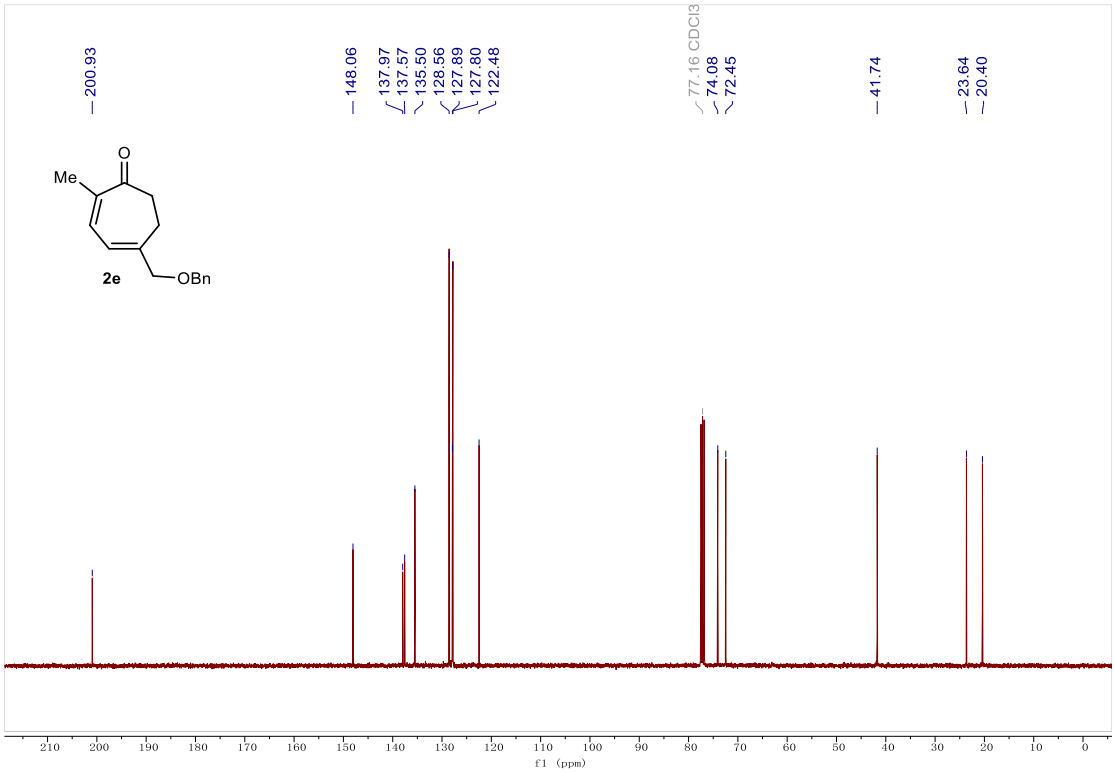


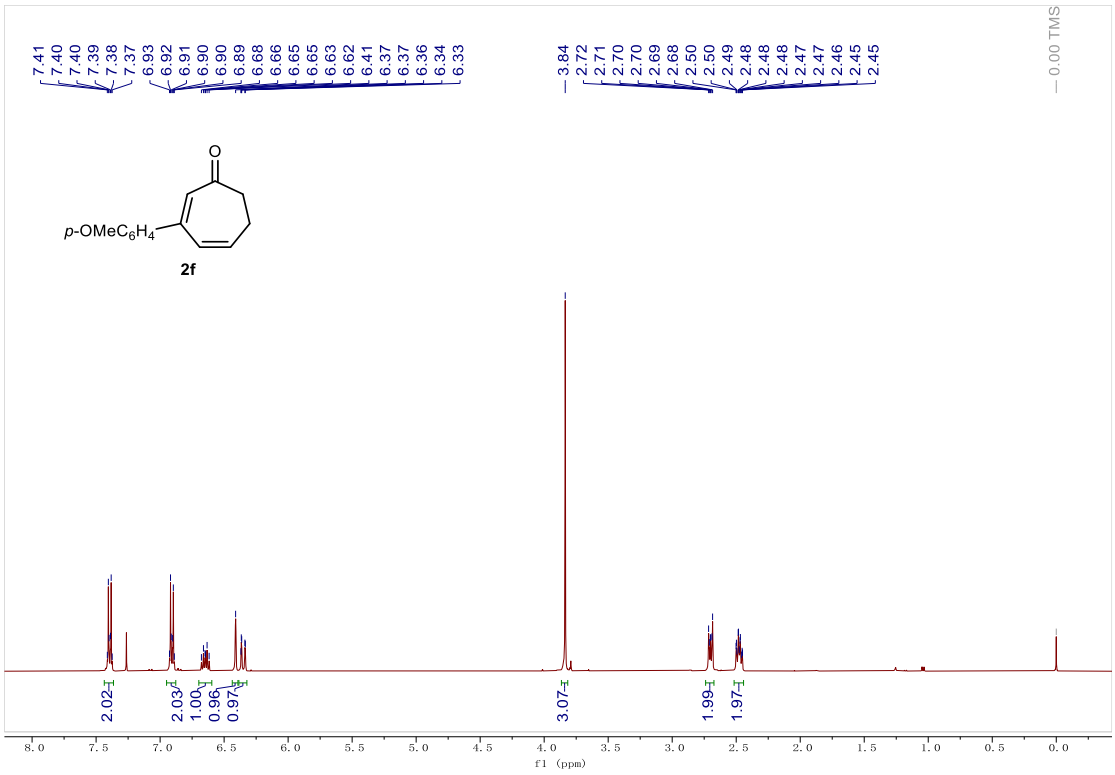
^{1}H NMR in $CDCl_3$, 400 MHz



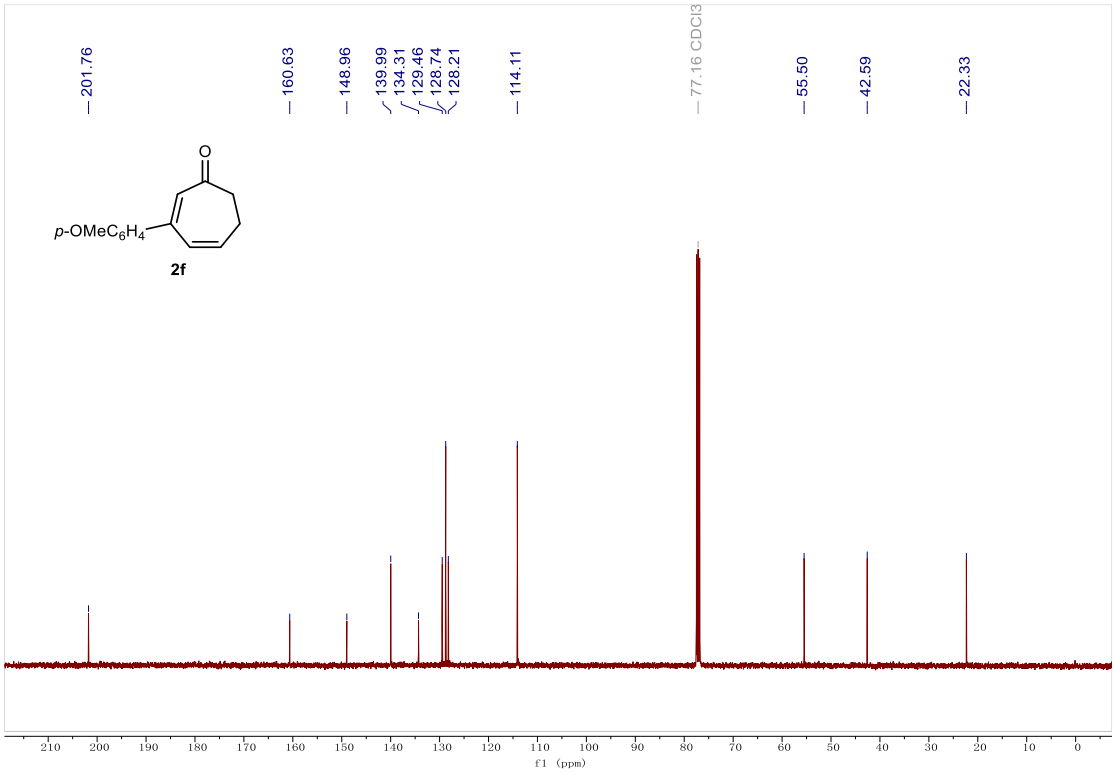
^{13}C NMR in $CDCl_3$, 101 MHz



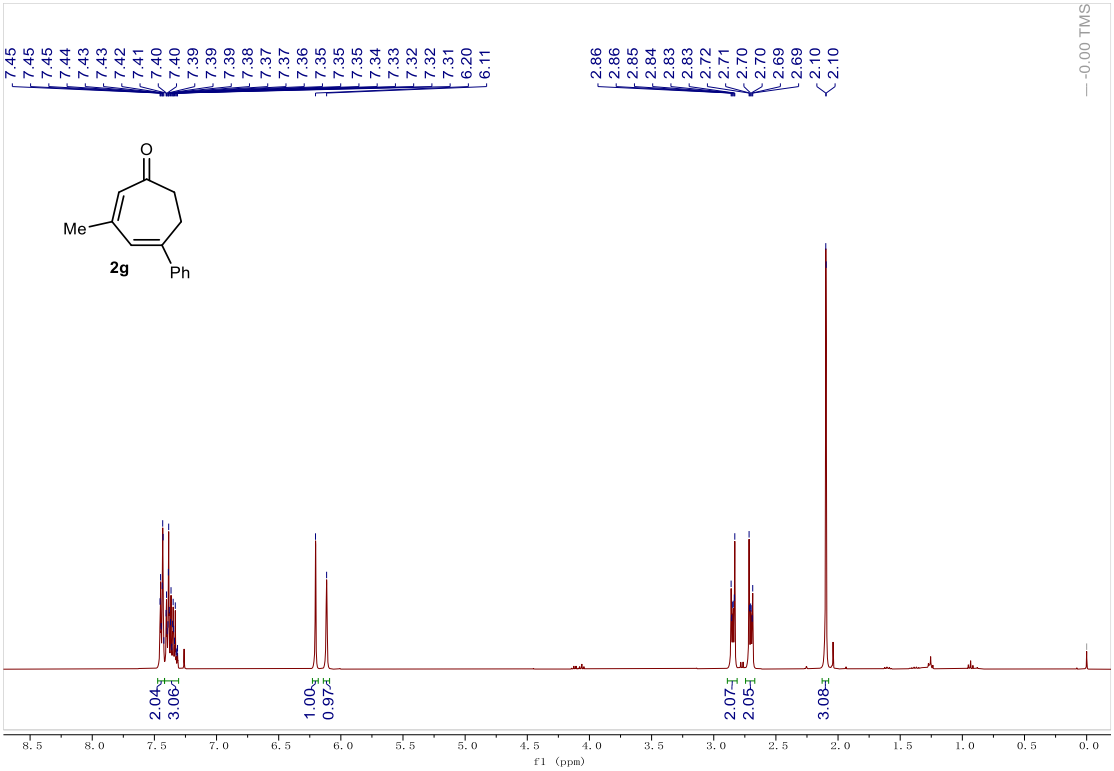
^{1}H NMR in $CDCl_3$, 400 MHz



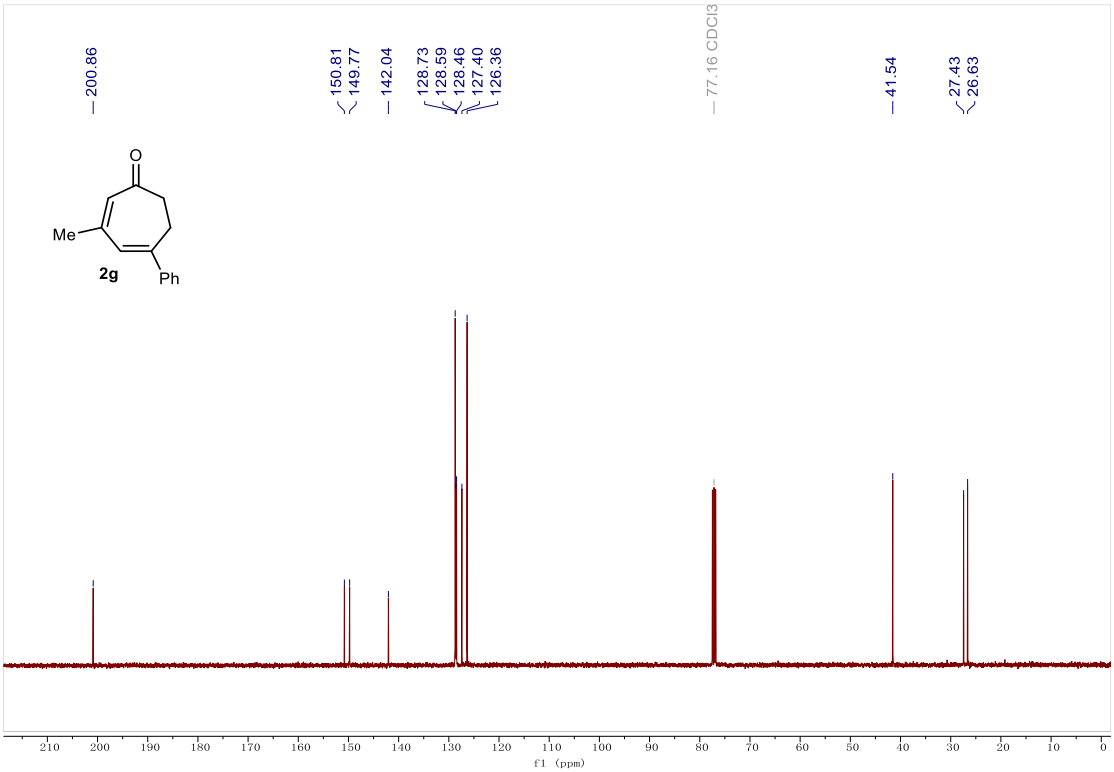
^{13}C NMR in $CDCl_3$, 101 MHz



^{1}H NMR in $CDCl_3$, 400 MHz



^{13}C NMR in $CDCl_3$, 101 MHz



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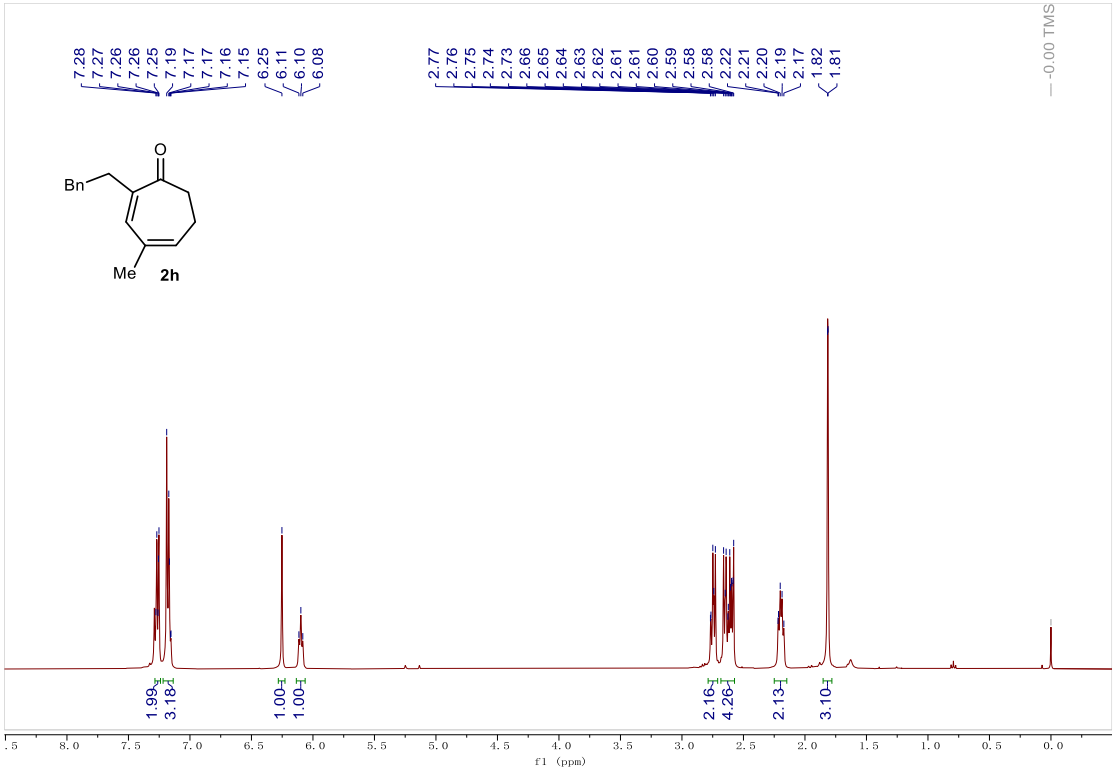
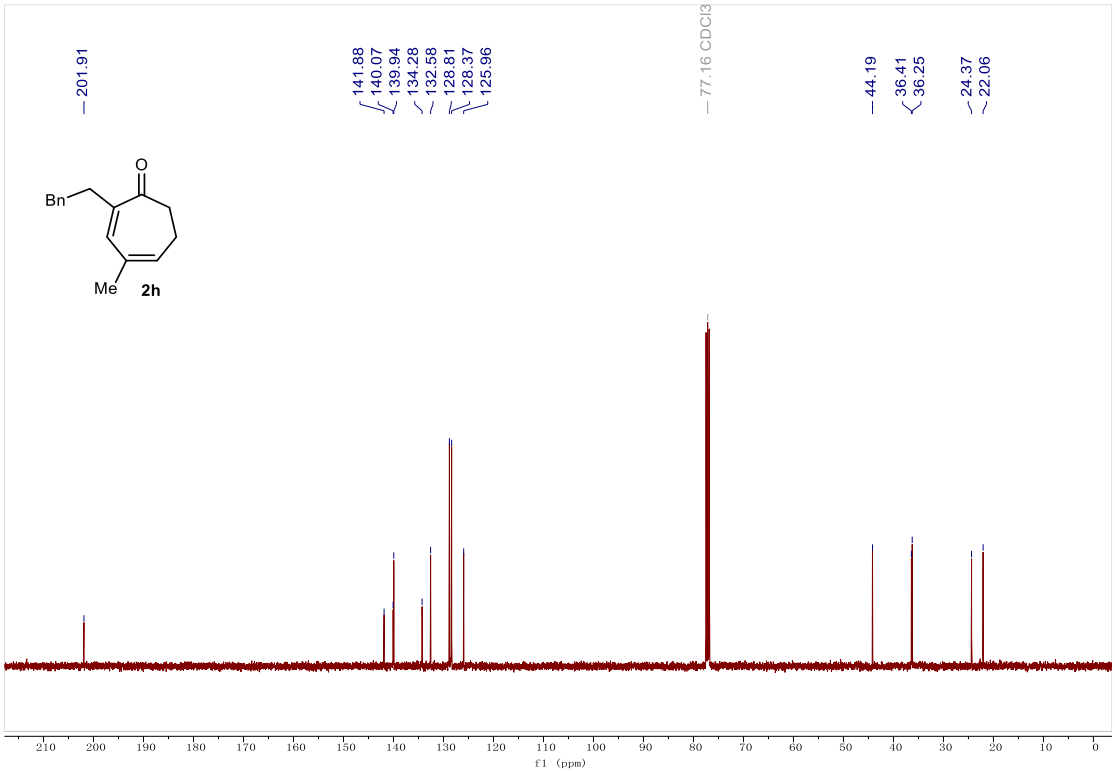
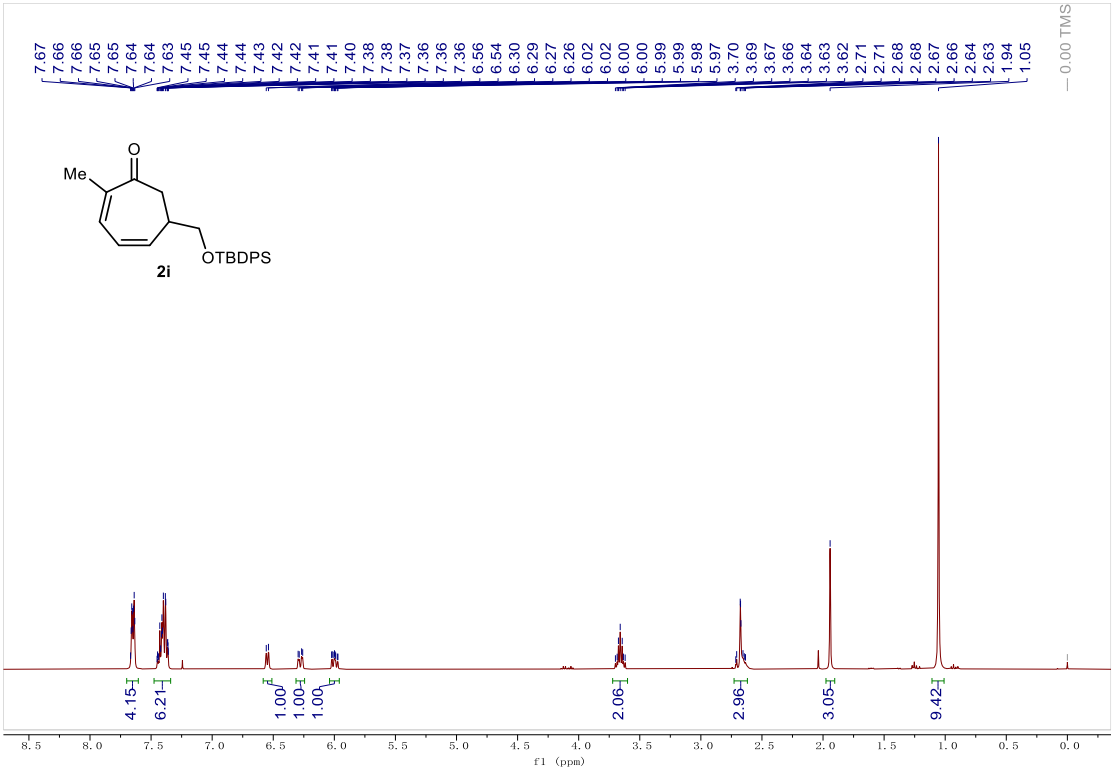


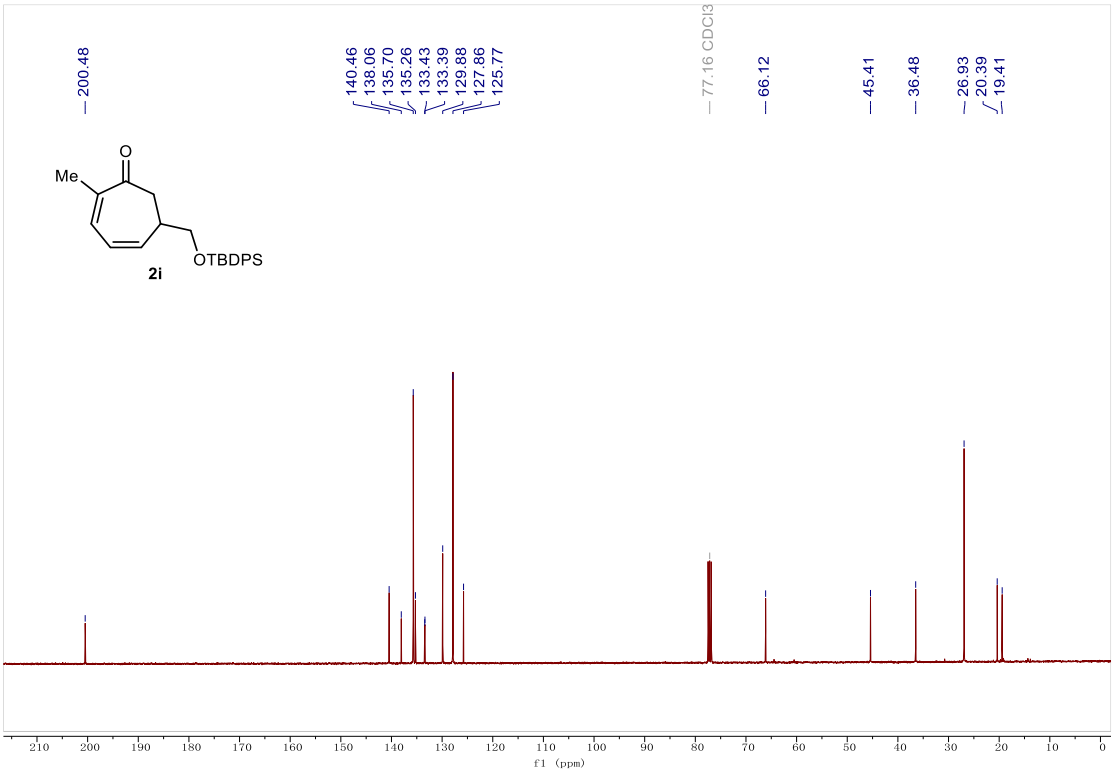
^{13}C NMR in $CDCl_3$, 101 MHz



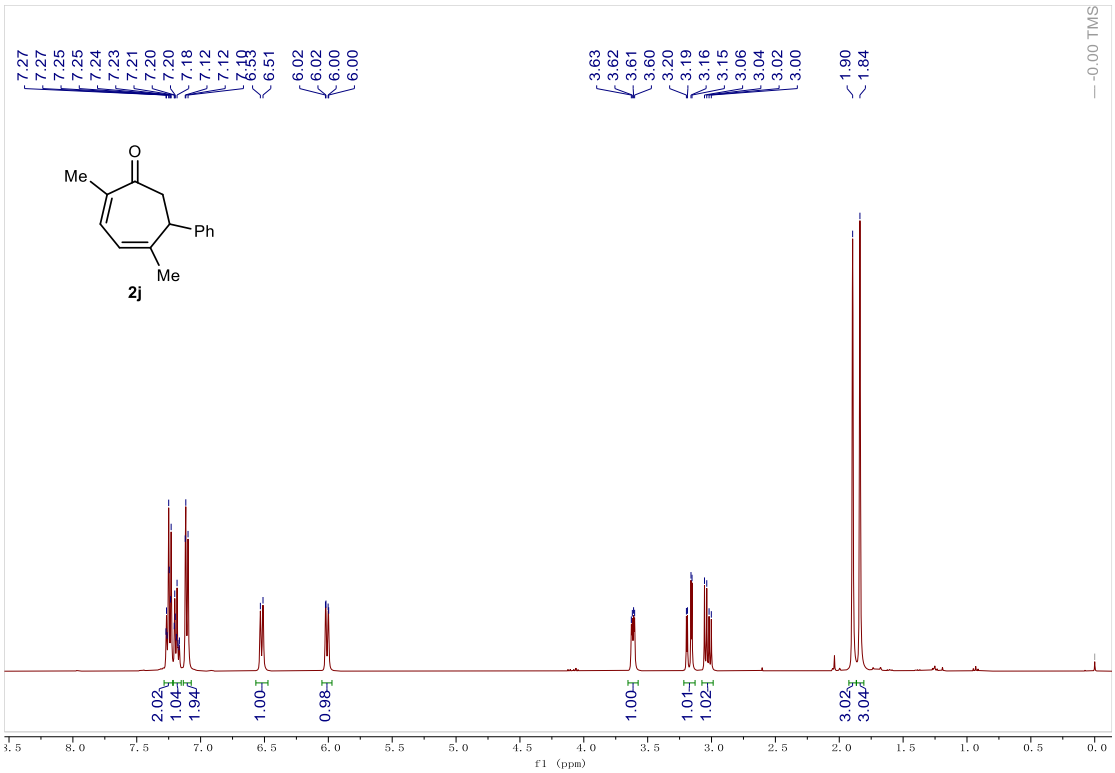
^{1}H NMR in $CDCl_3$, 400 MHz



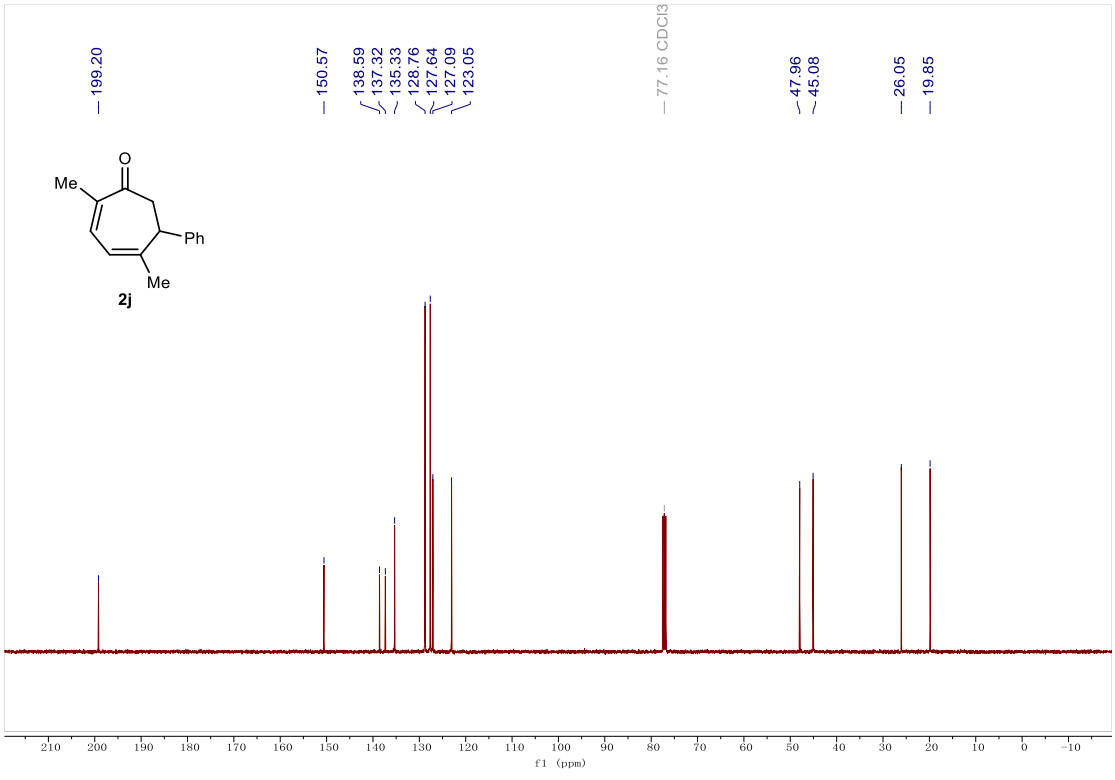
^{13}C NMR in $CDCl_3$, 101 MHz



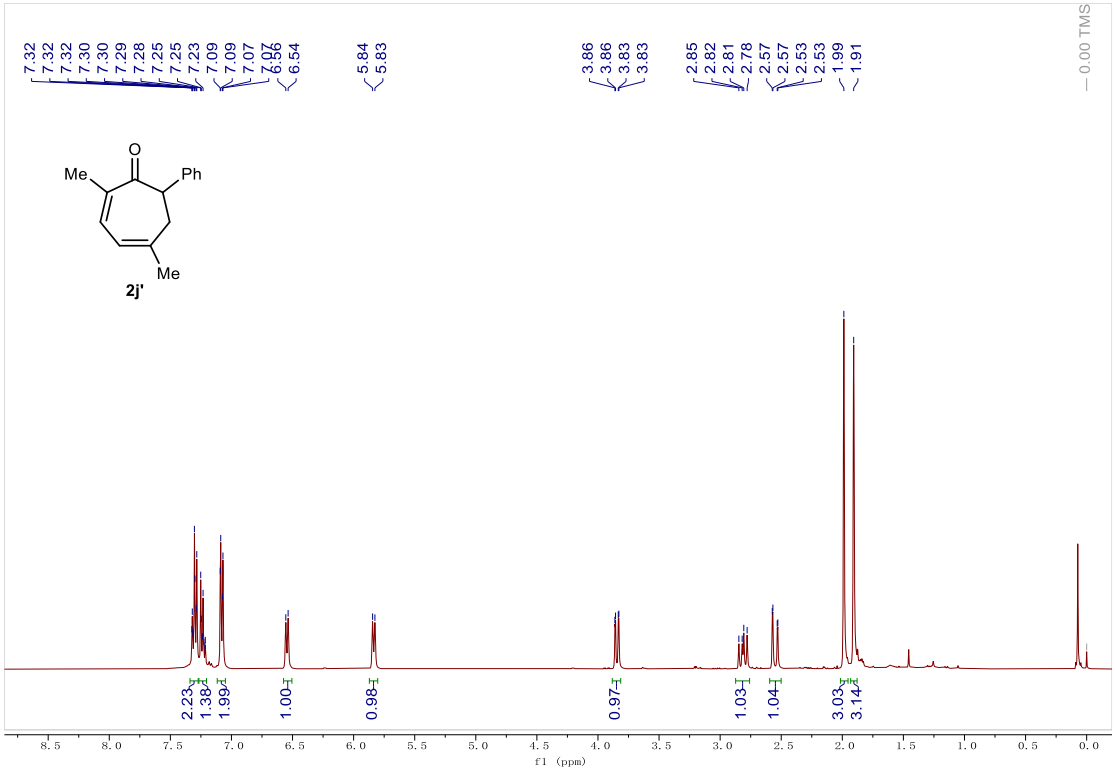
^{1}H NMR in $CDCl_3$, 400 MHz



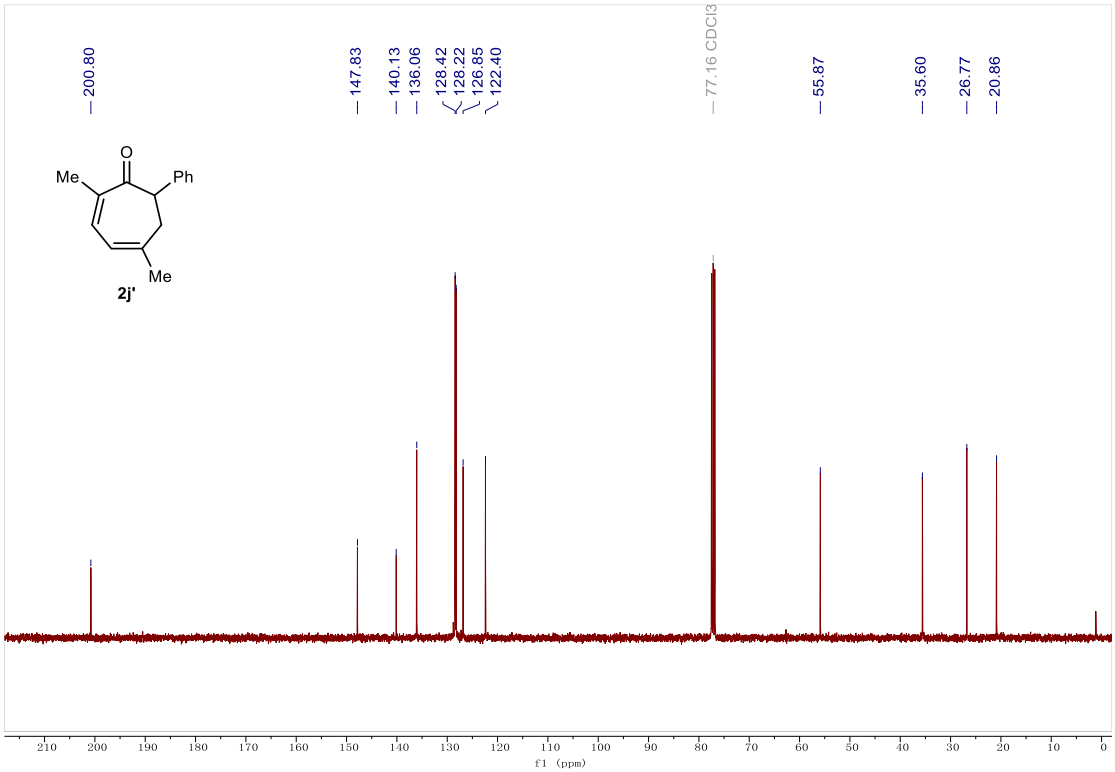
^{13}C NMR in $CDCl_3$, 101 MHz



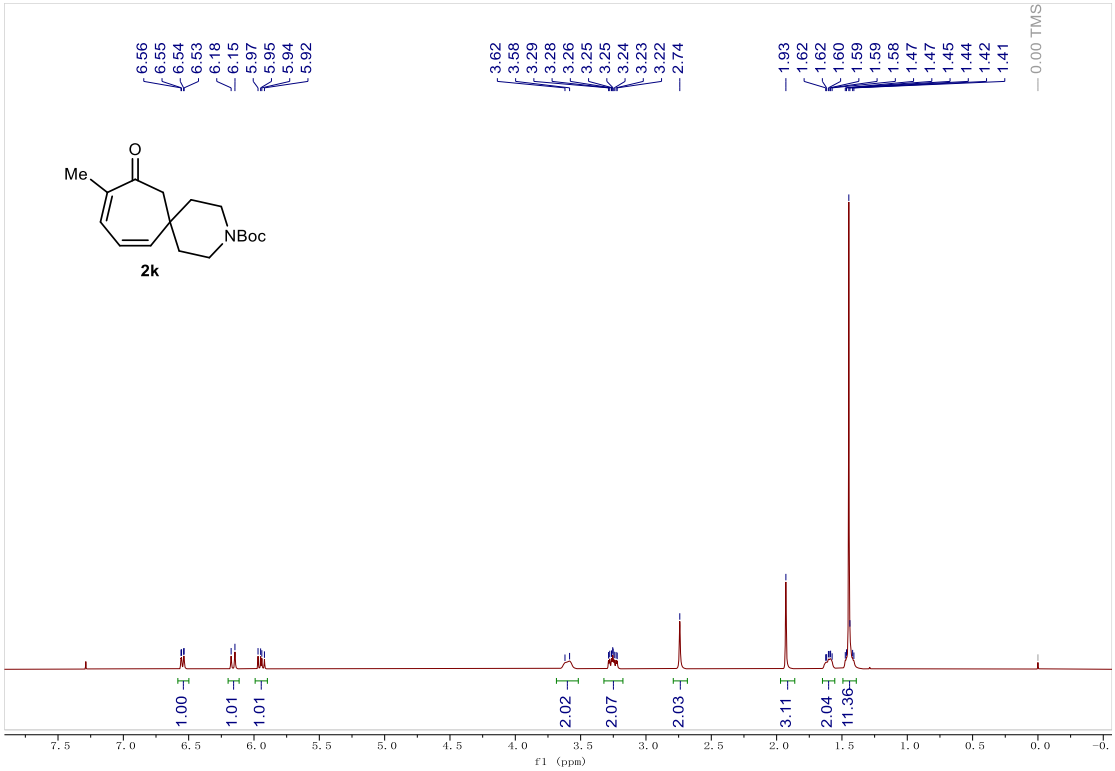
^{1}H NMR in $CDCl_3$, 400 MHz



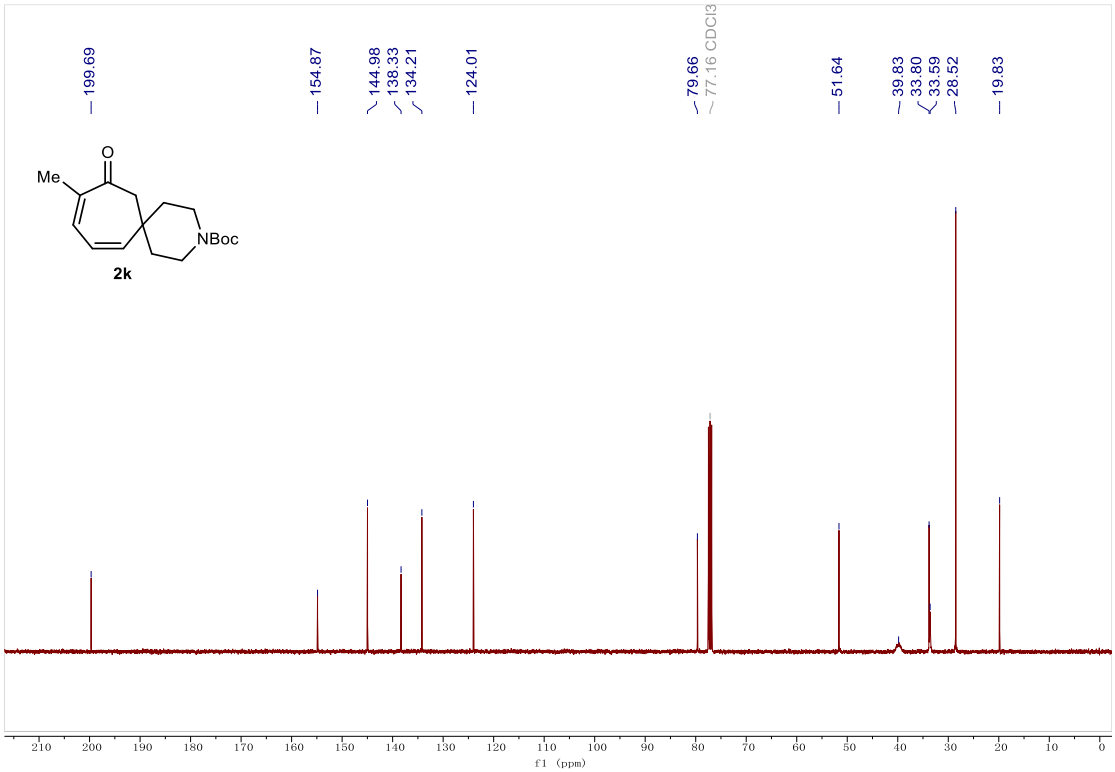
^{13}C NMR in $CDCl_3$, 101 MHz



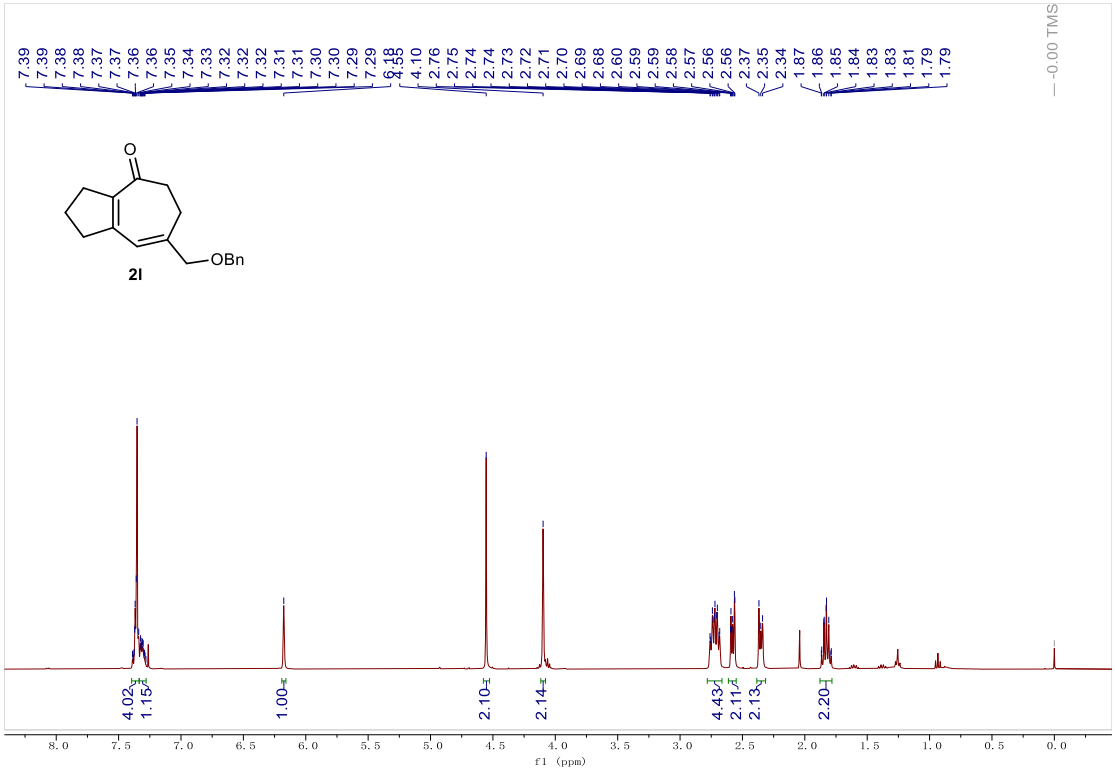
^{1}H NMR in $CDCl_3$, 400 MHz



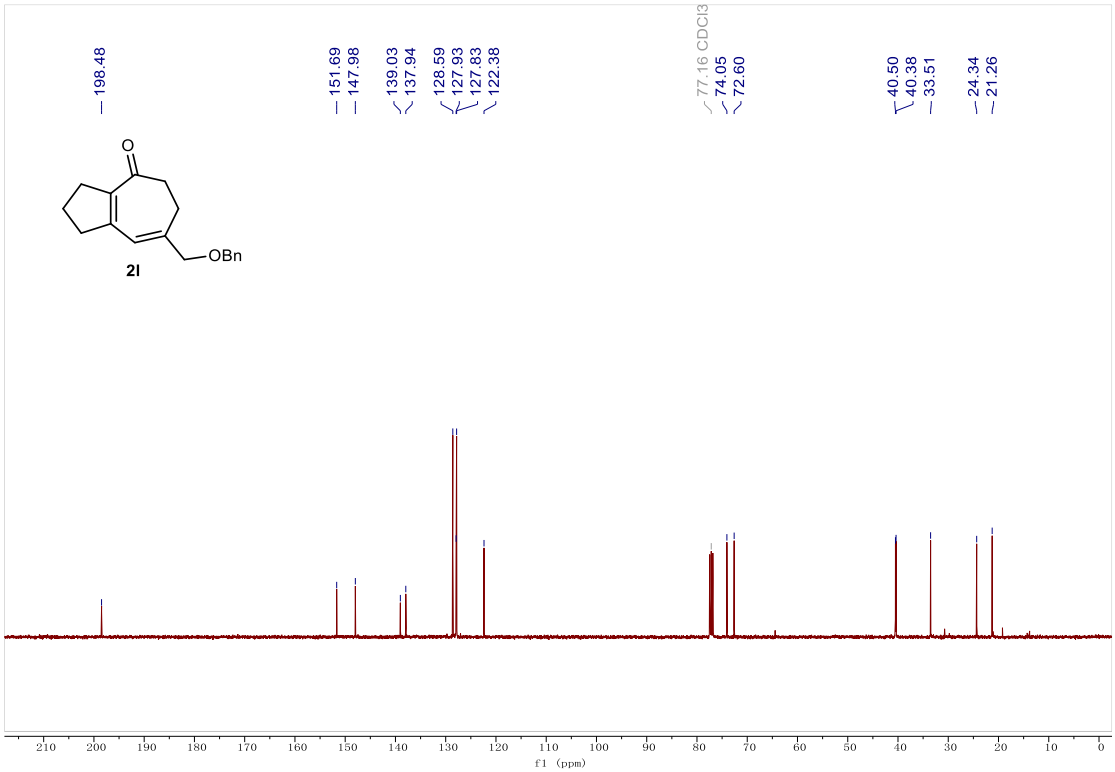
^{13}C NMR in $CDCl_3$, 101 MHz



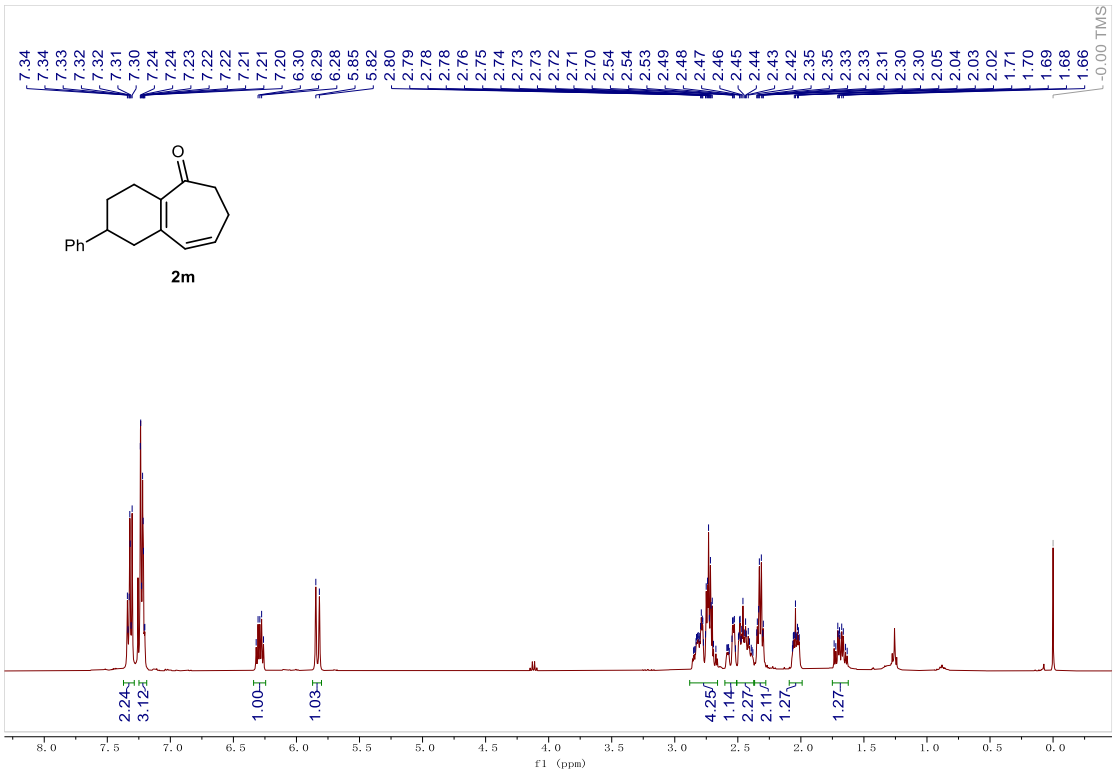
^{1}H NMR in $CDCl_3$, 400 MHz



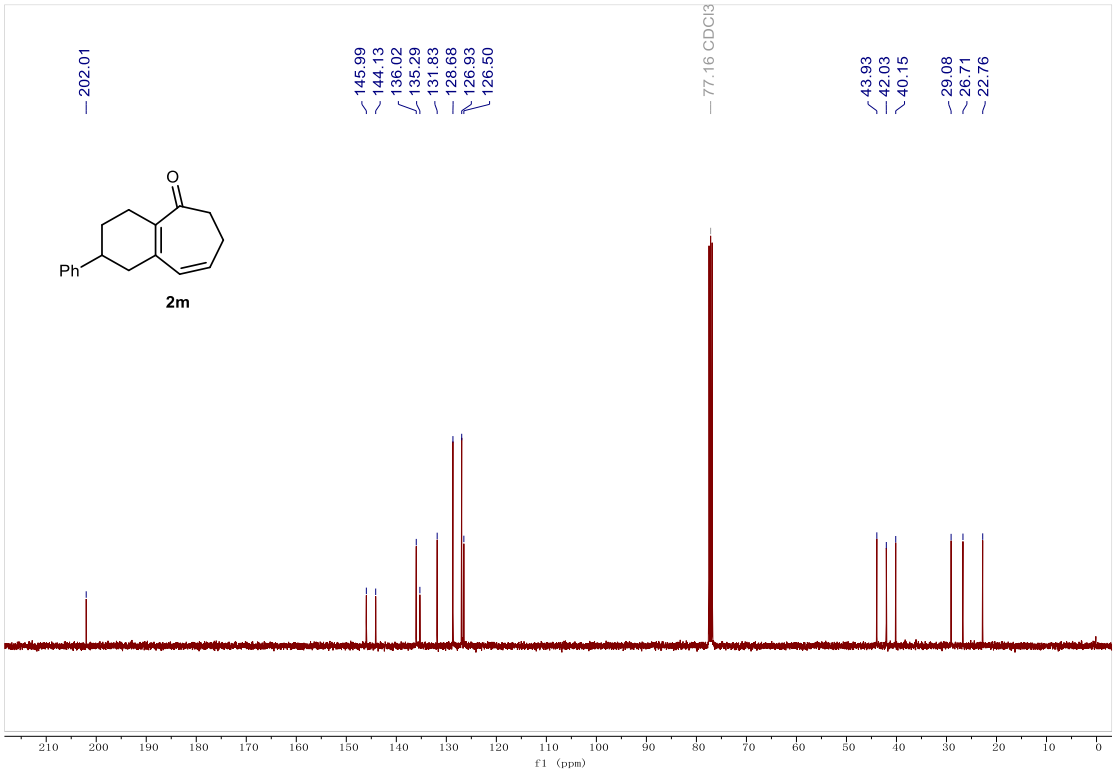
^{13}C NMR in $CDCl_3$, 101 MHz



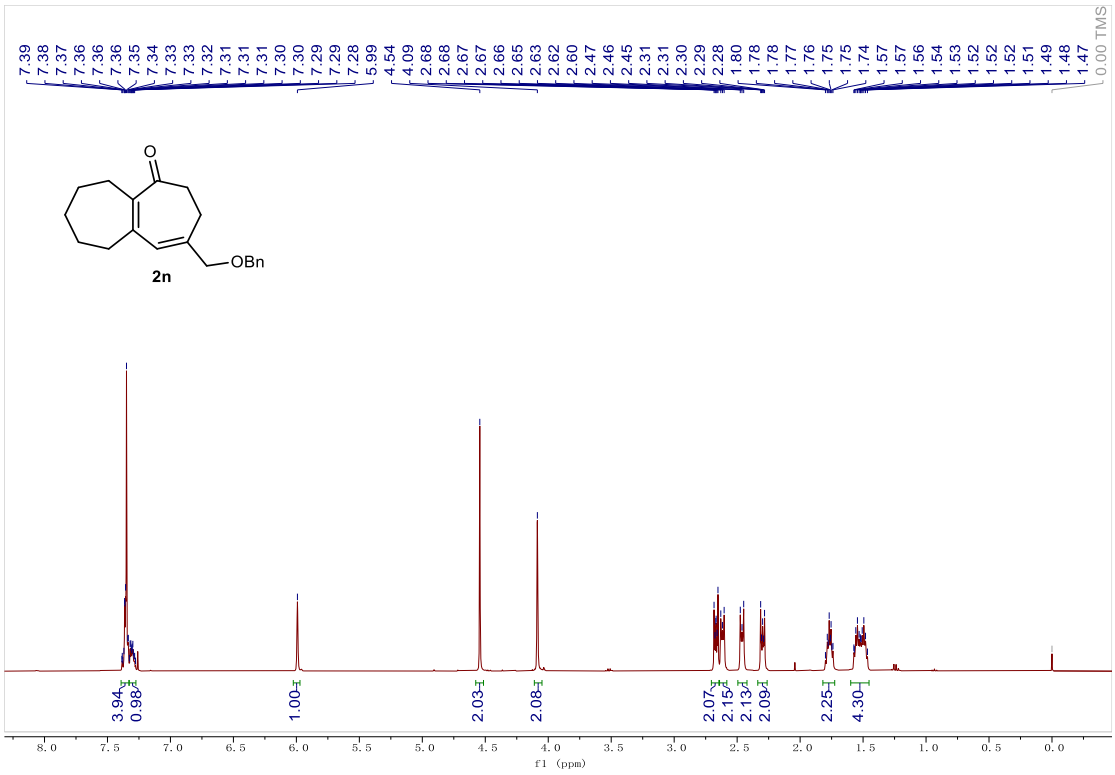
^{1}H NMR in $CDCl_3$, 400 MHz



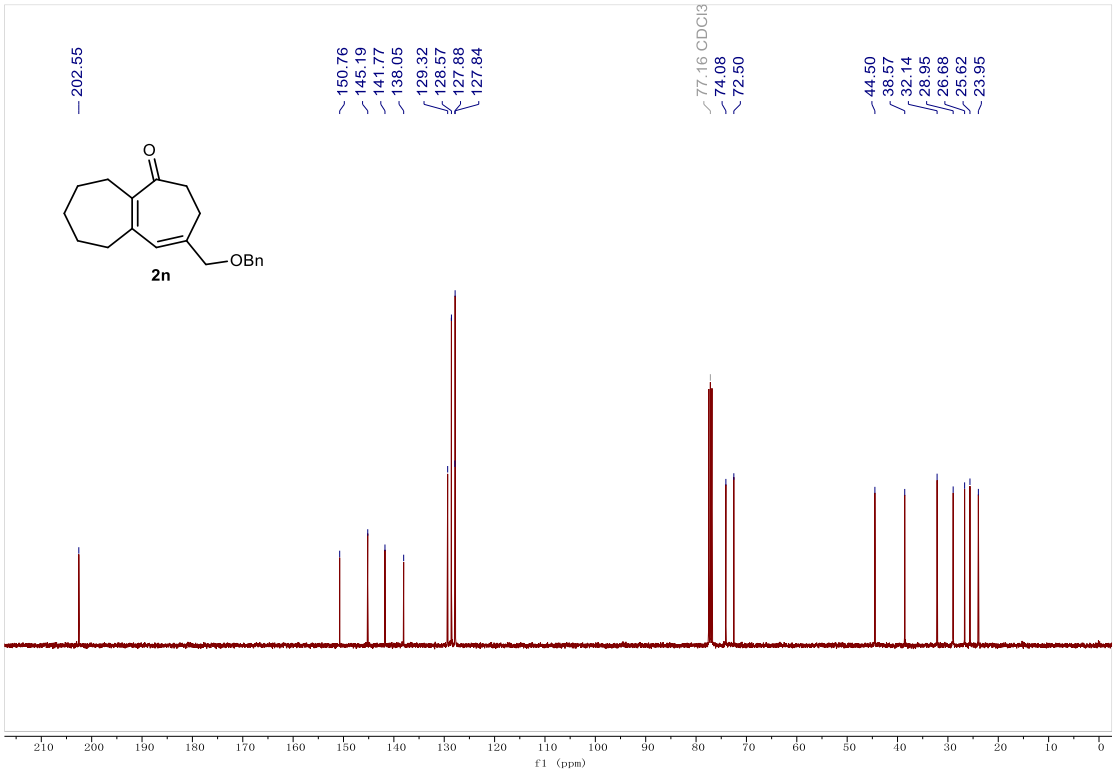
^{13}C NMR in $CDCl_3$, 101 MHz



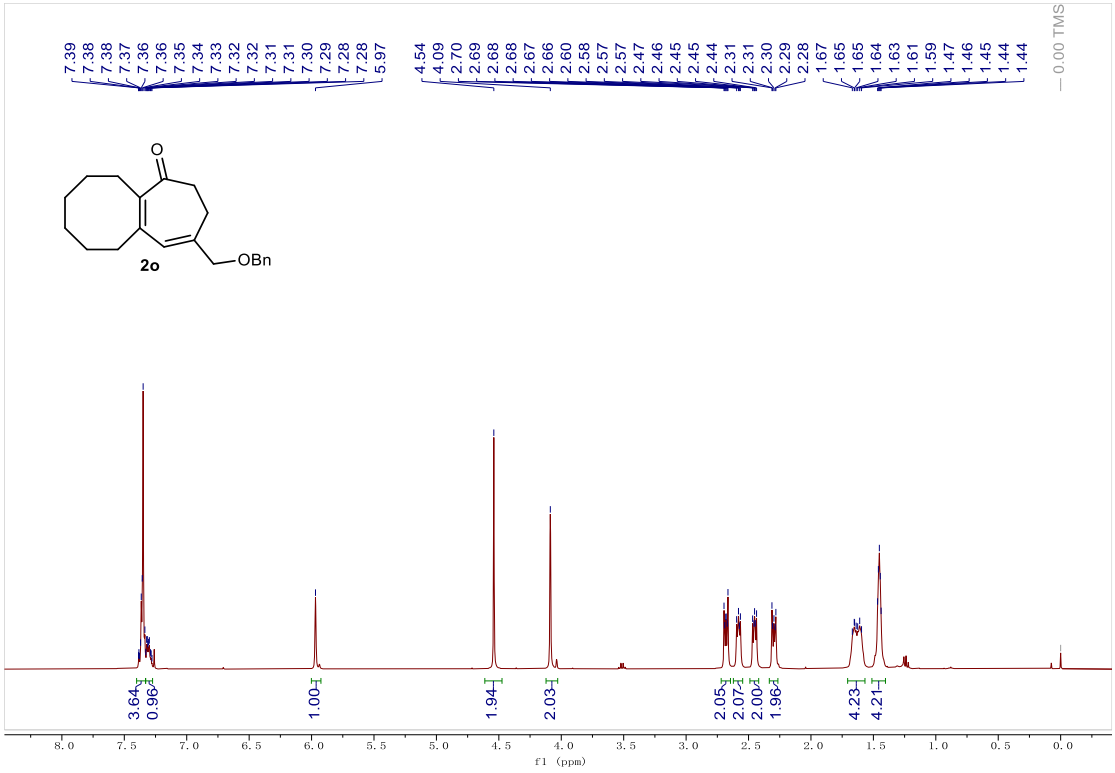
^{1}H NMR in $CDCl_3$, 400 MHz



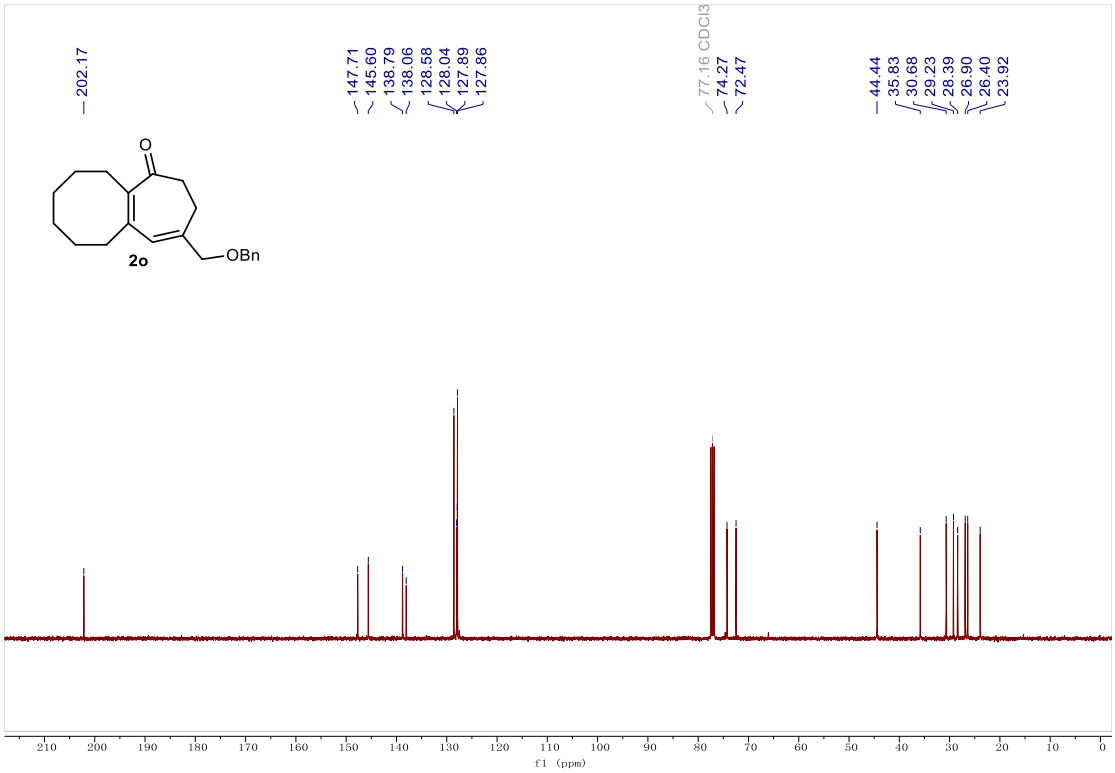
^{13}C NMR in $CDCl_3$, 101 MHz



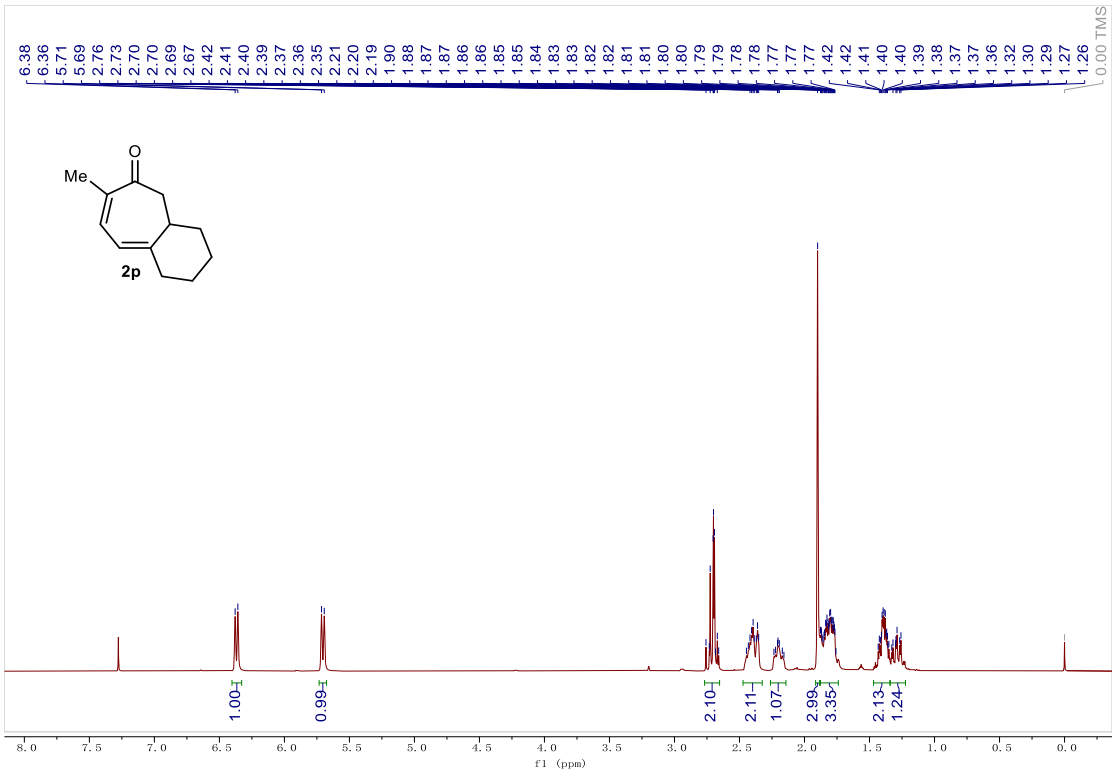
^{1}H NMR in $CDCl_3$, 400 MHz



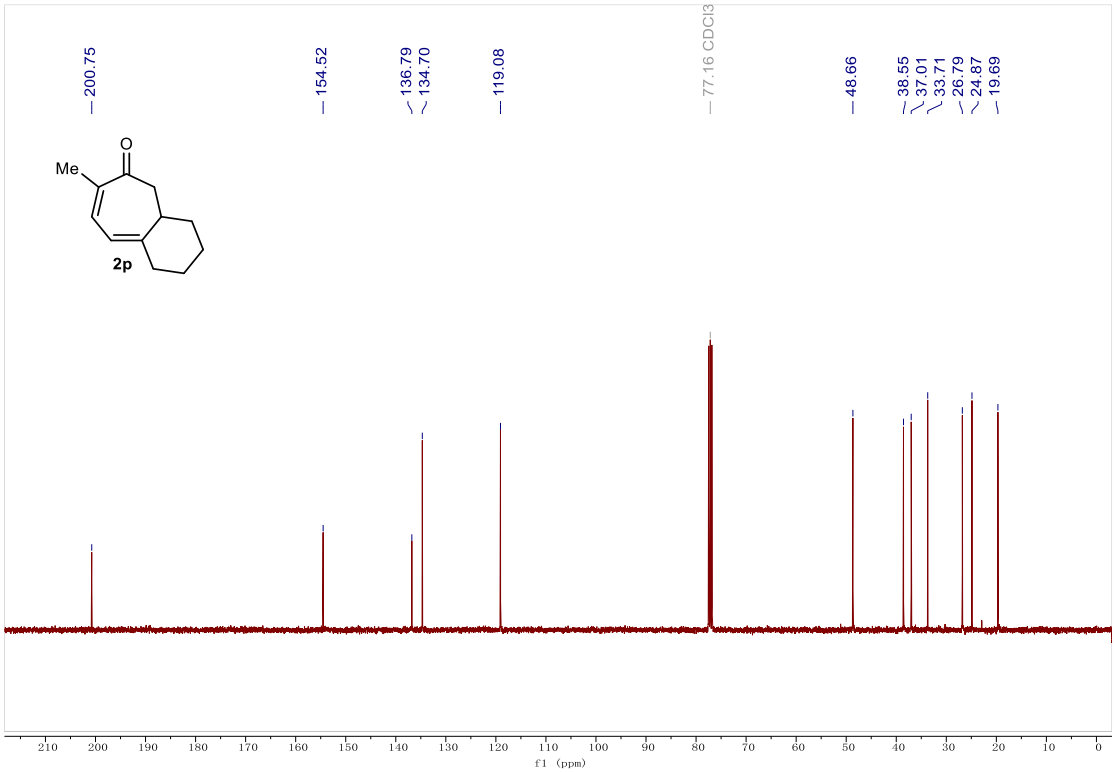
^{13}C NMR in $CDCl_3$, 101 MHz



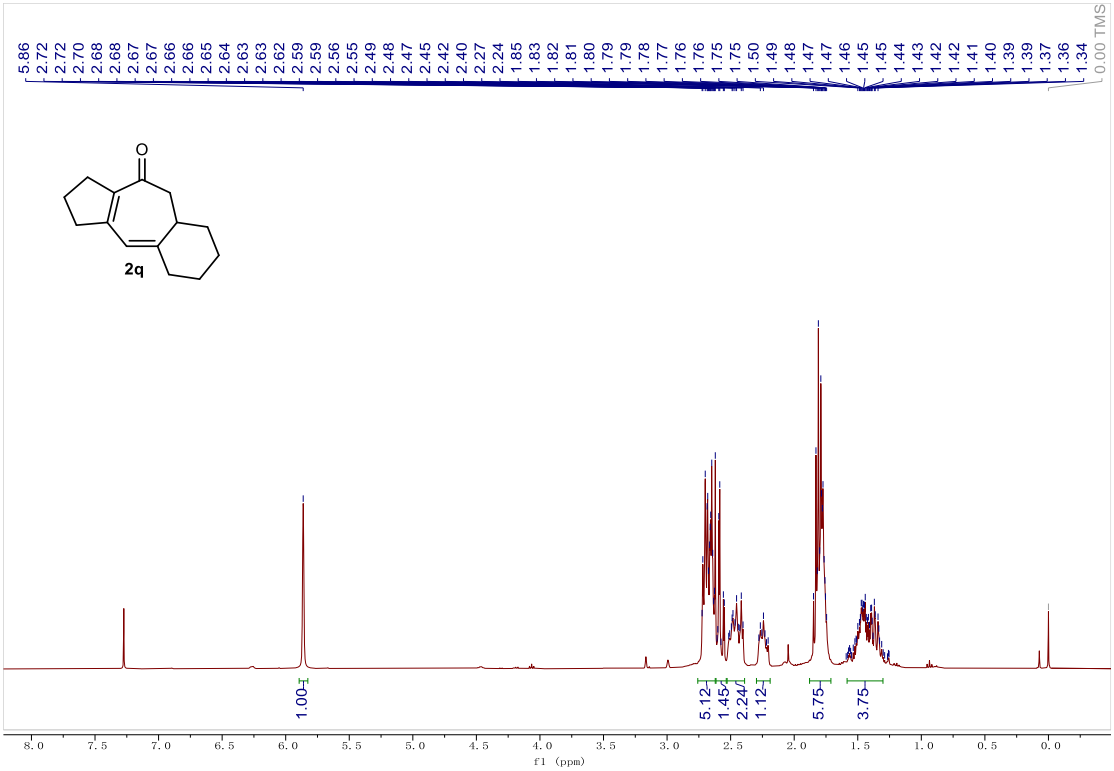
^{1}H NMR in $CDCl_3$, 400 MHz



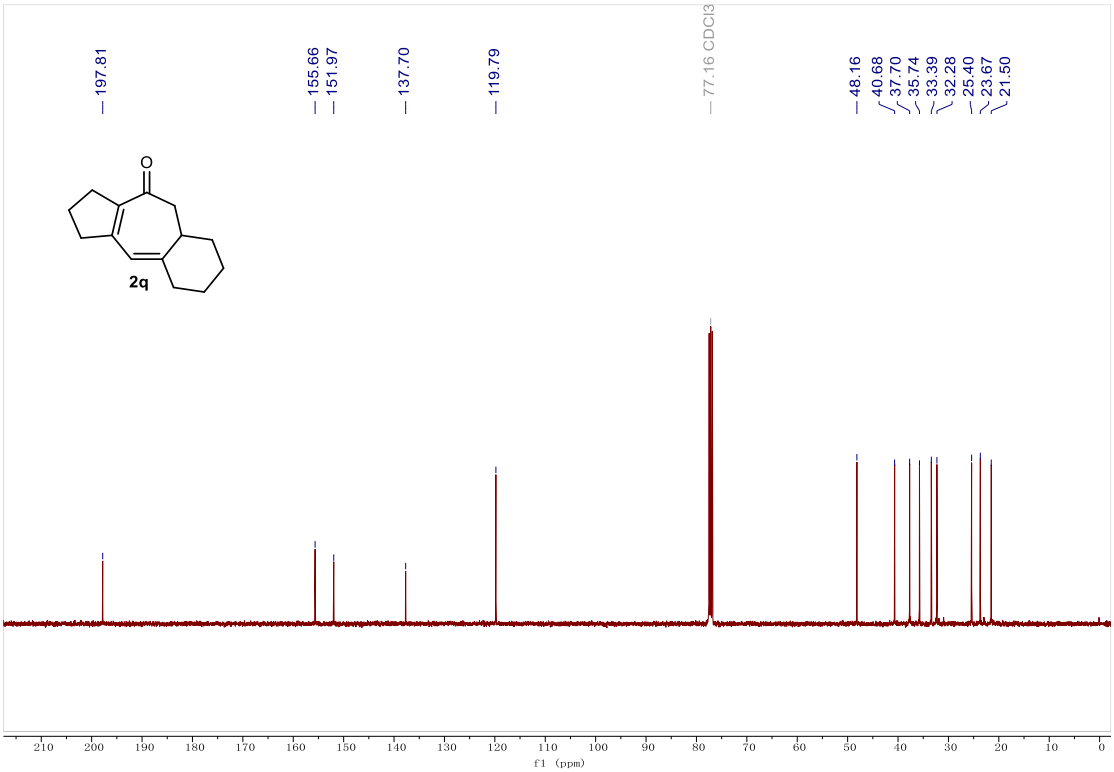
^{13}C NMR in $CDCl_3$, 101 MHz



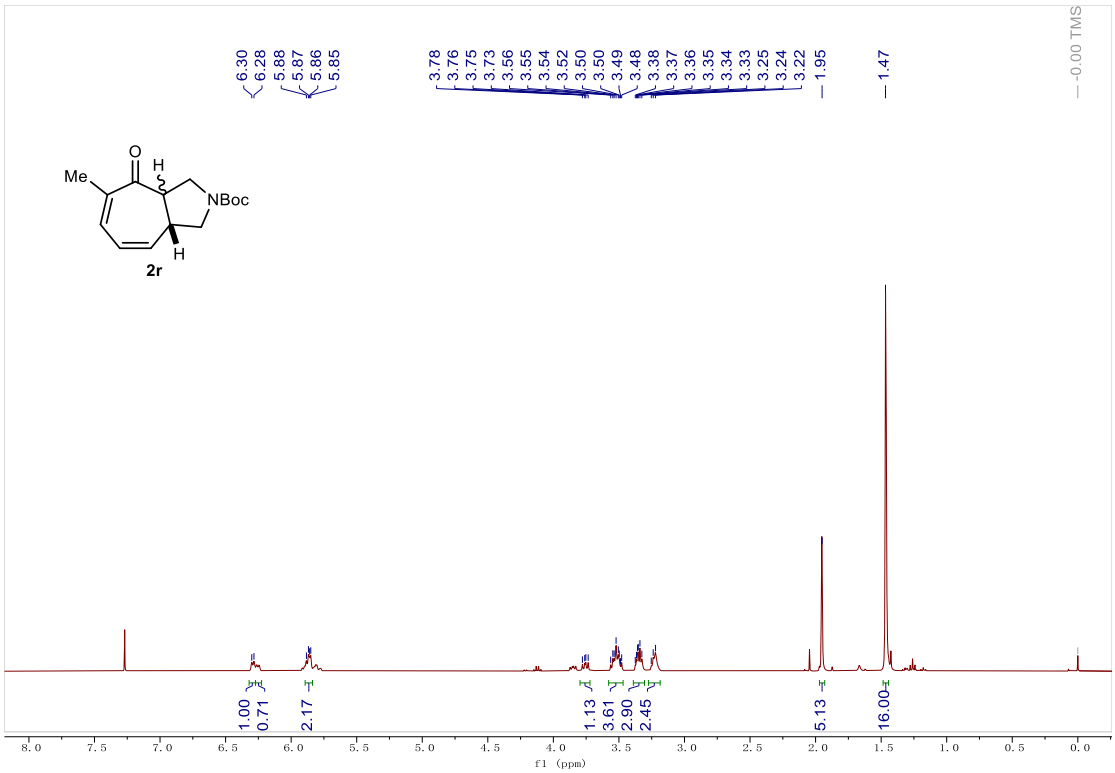
^{1}H NMR in $CDCl_3$, 400 MHz



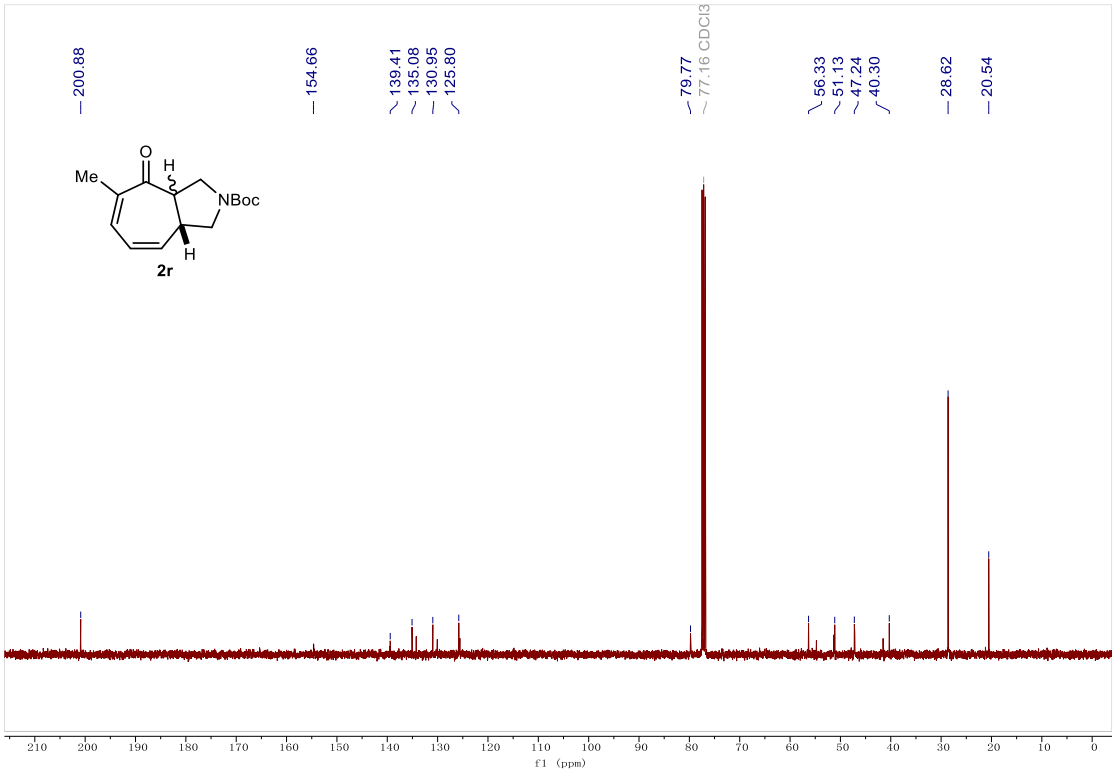
^{13}C NMR in $CDCl_3$, 101 MHz



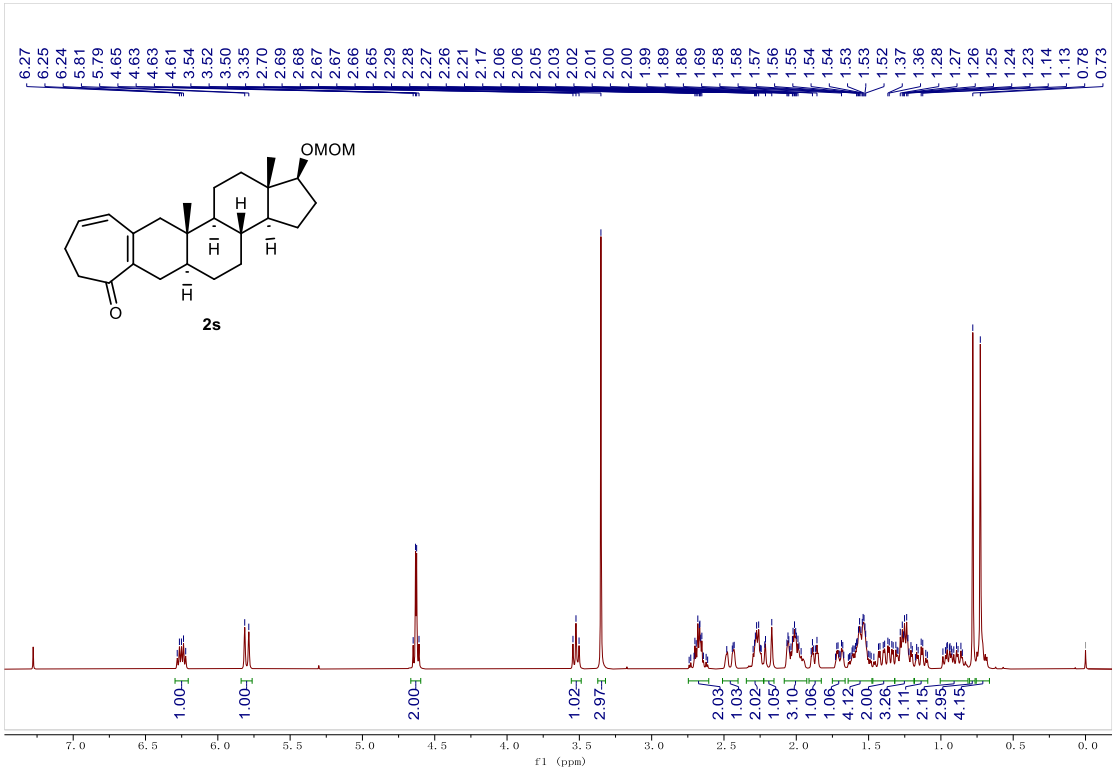
^{1}H NMR in $CDCl_3$, 400 MHz



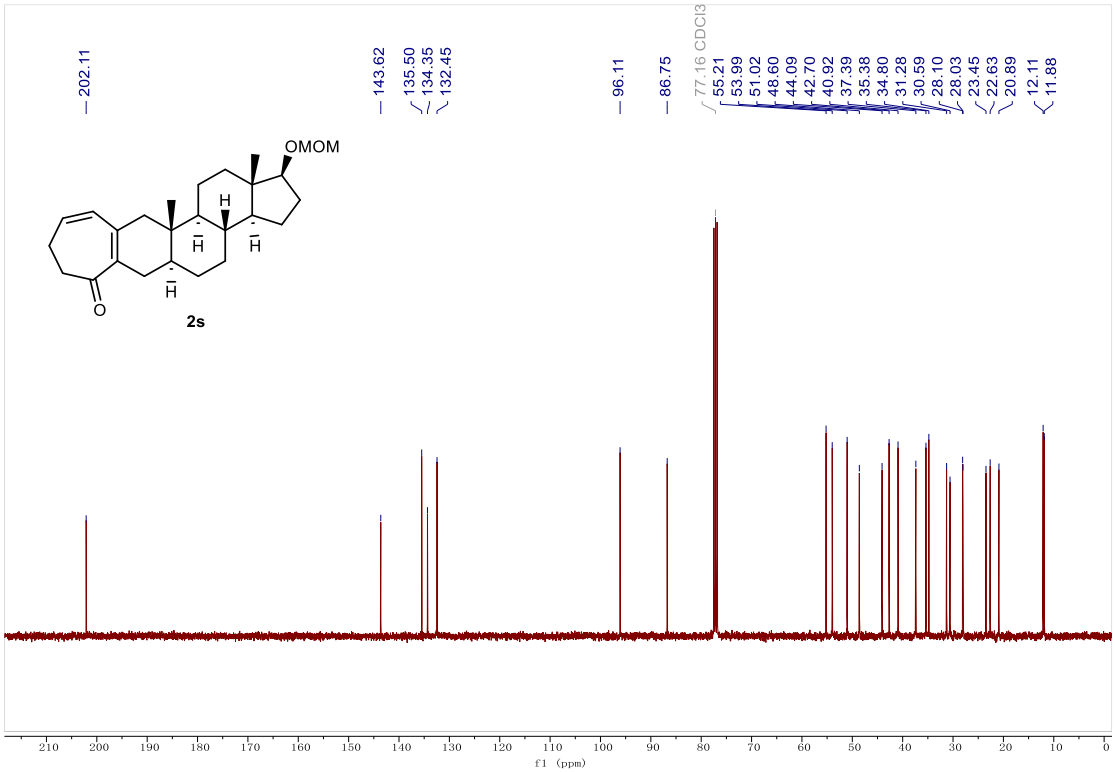
^{13}C NMR in $CDCl_3$, 101 MHz



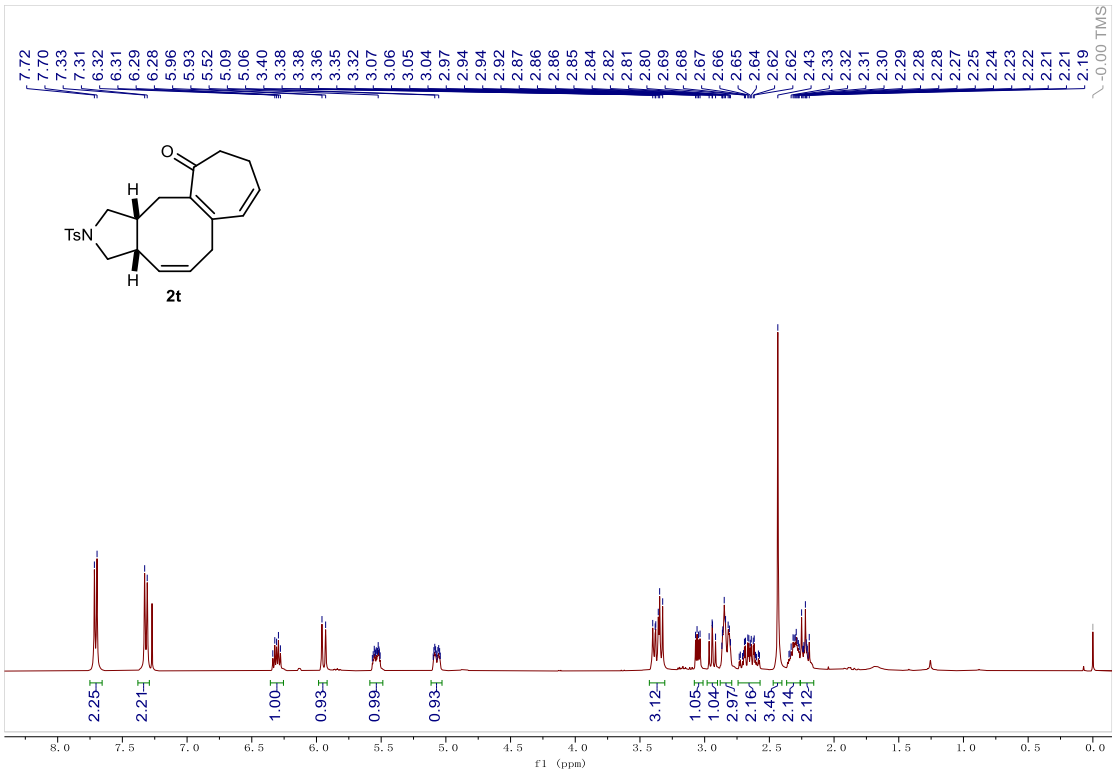
^{1}H NMR in $CDCl_3$, 400 MHz



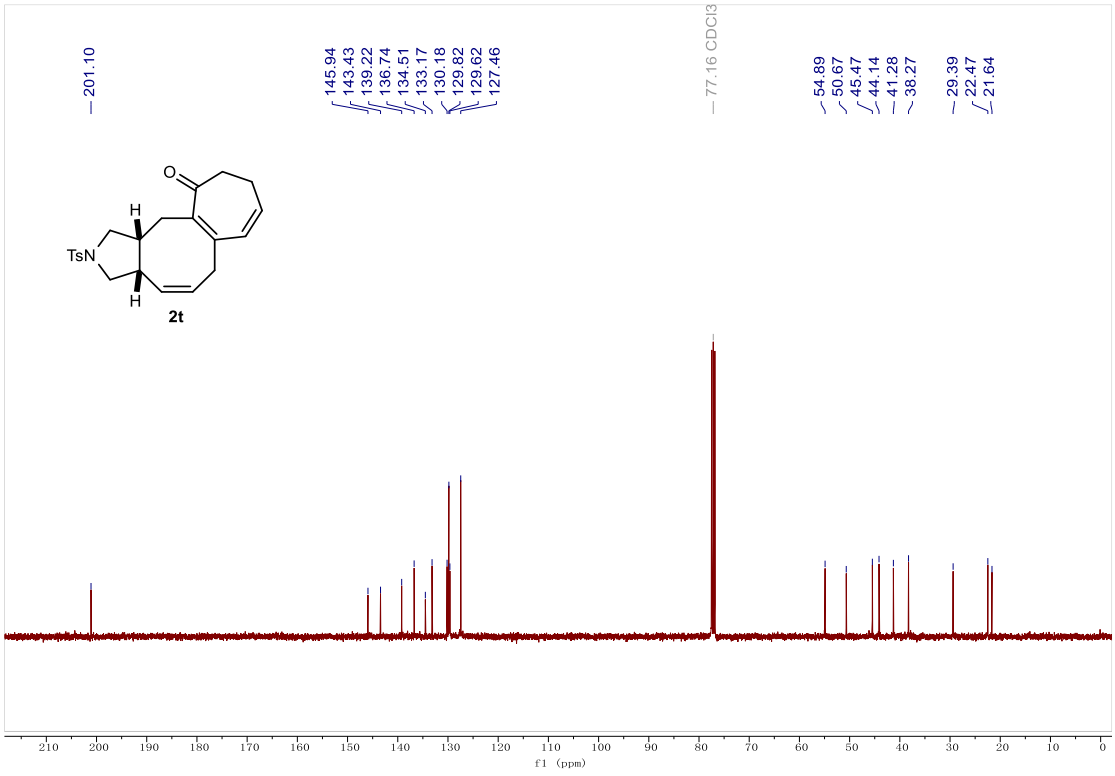
^{13}C NMR in $CDCl_3$, 101 MHz



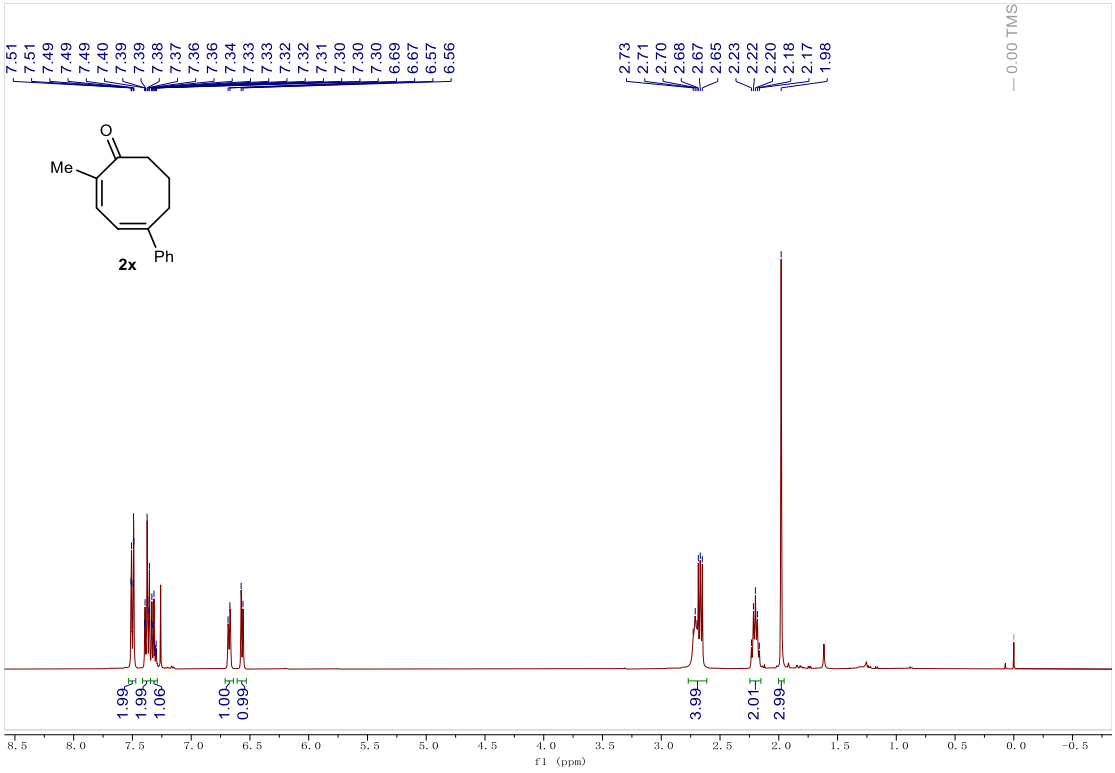
^{1}H NMR in $CDCl_3$, 400 MHz



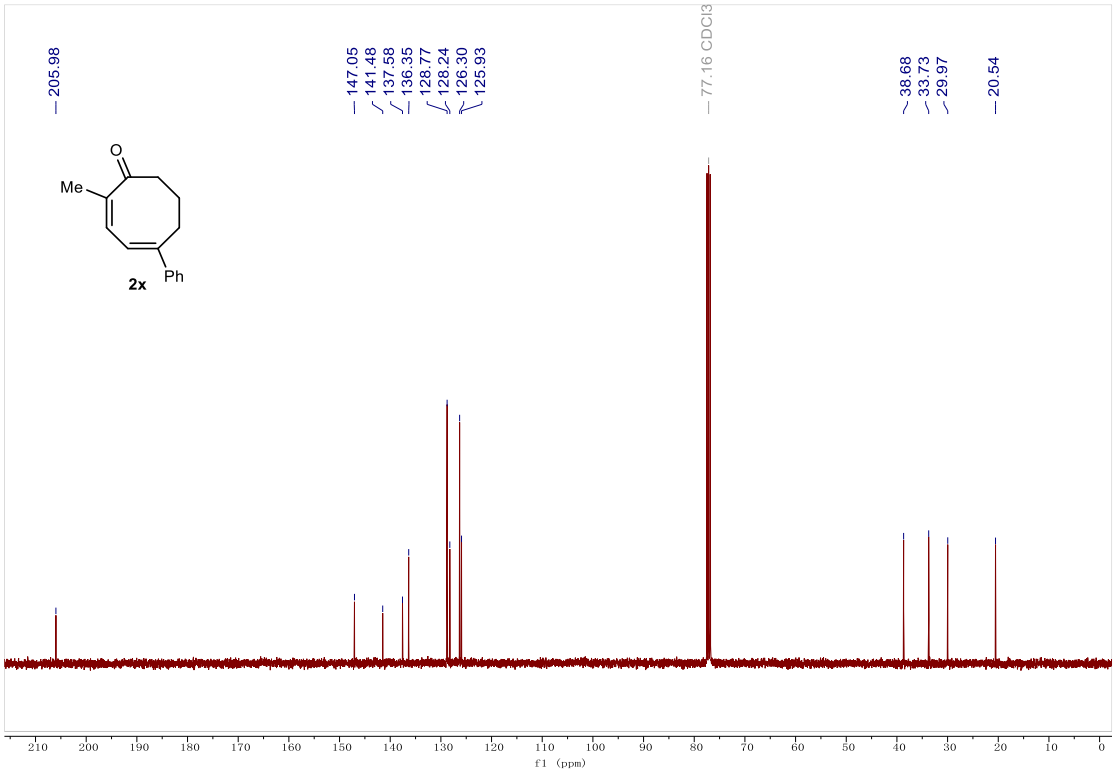
^{13}C NMR in $CDCl_3$, 101 MHz



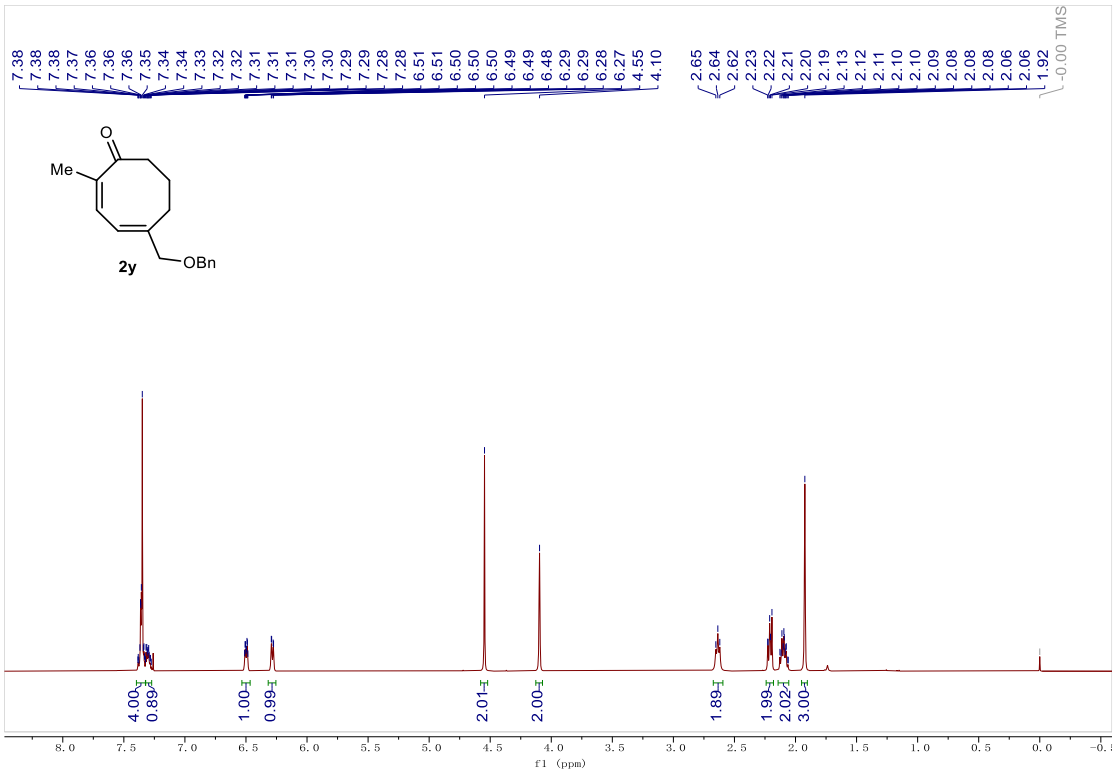
^{1}H NMR in $CDCl_3$, 400 MHz



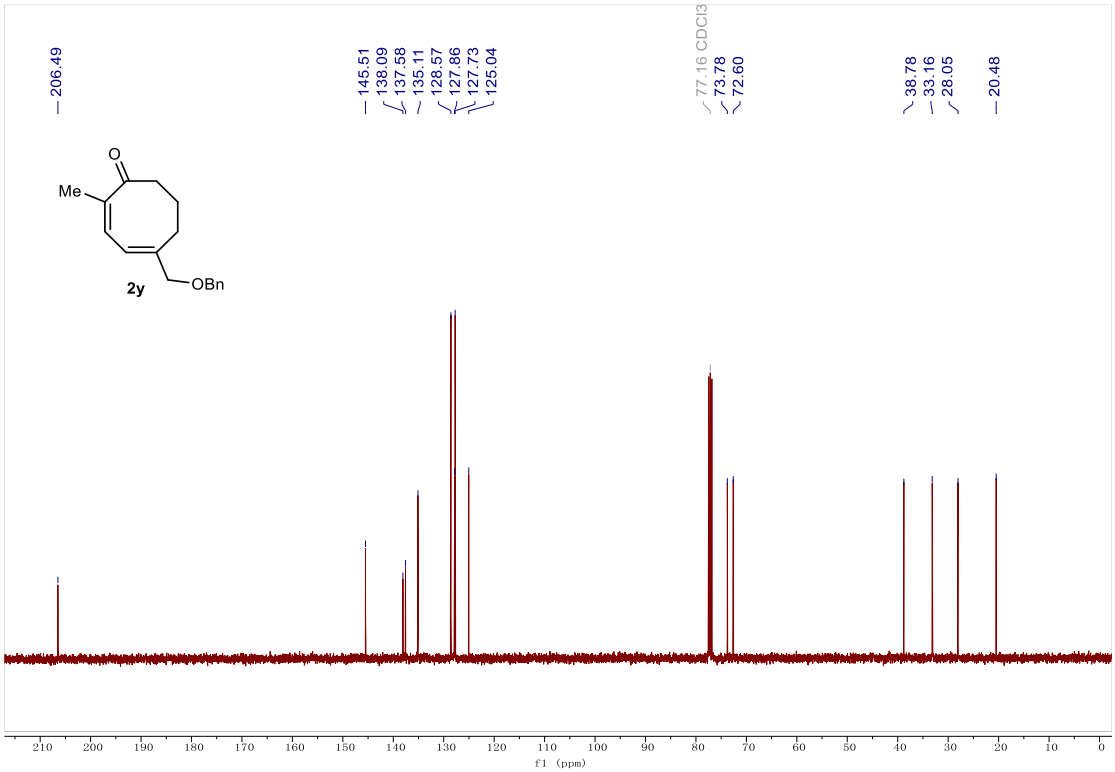
^{13}C NMR in $CDCl_3$, 101 MHz



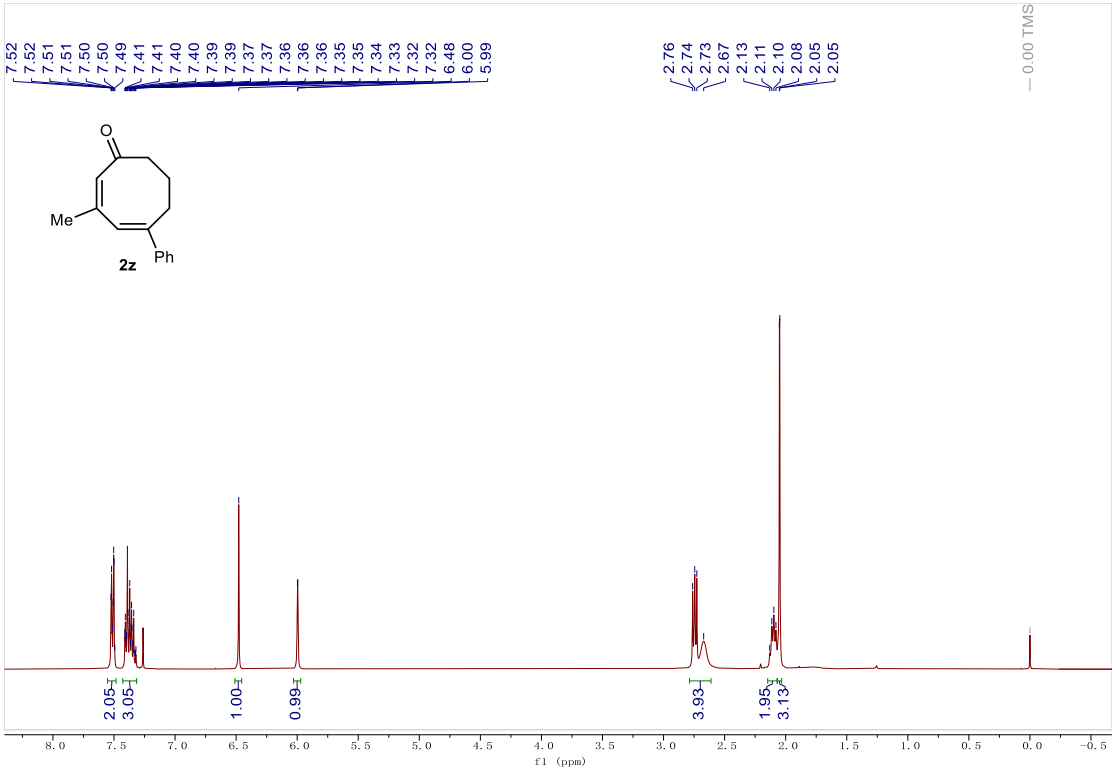
^{1}H NMR in $CDCl_3$, 400 MHz



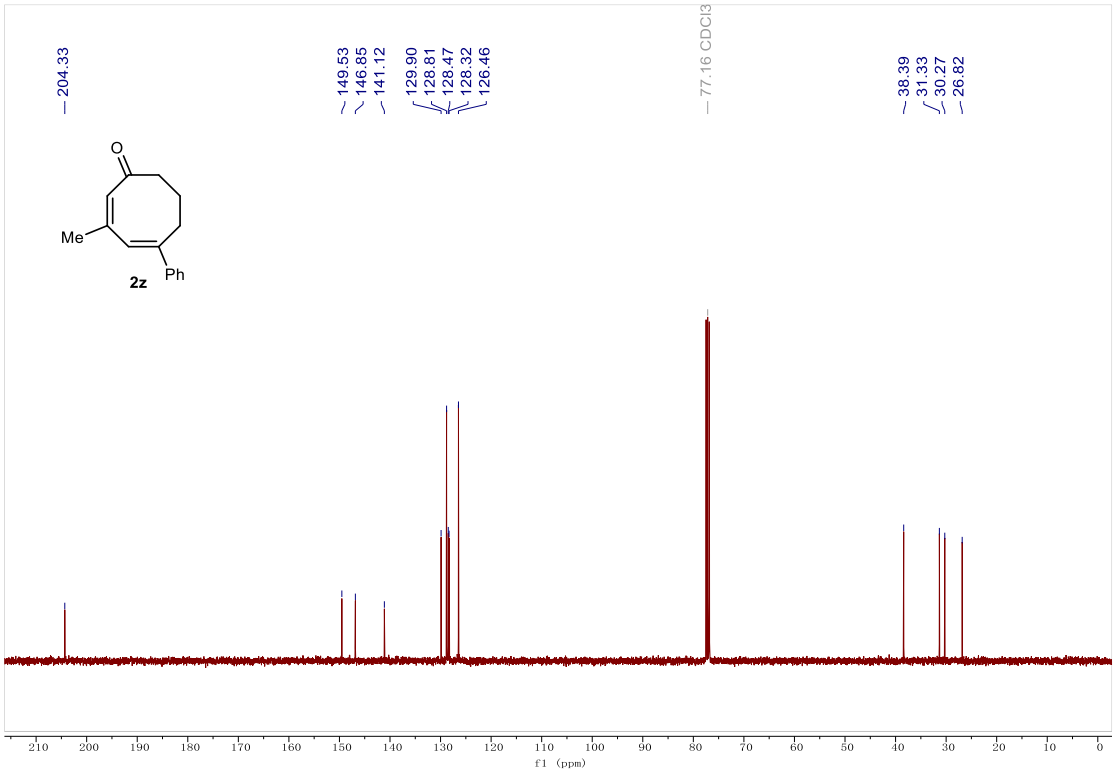
^{13}C NMR in $CDCl_3$, 101 MHz



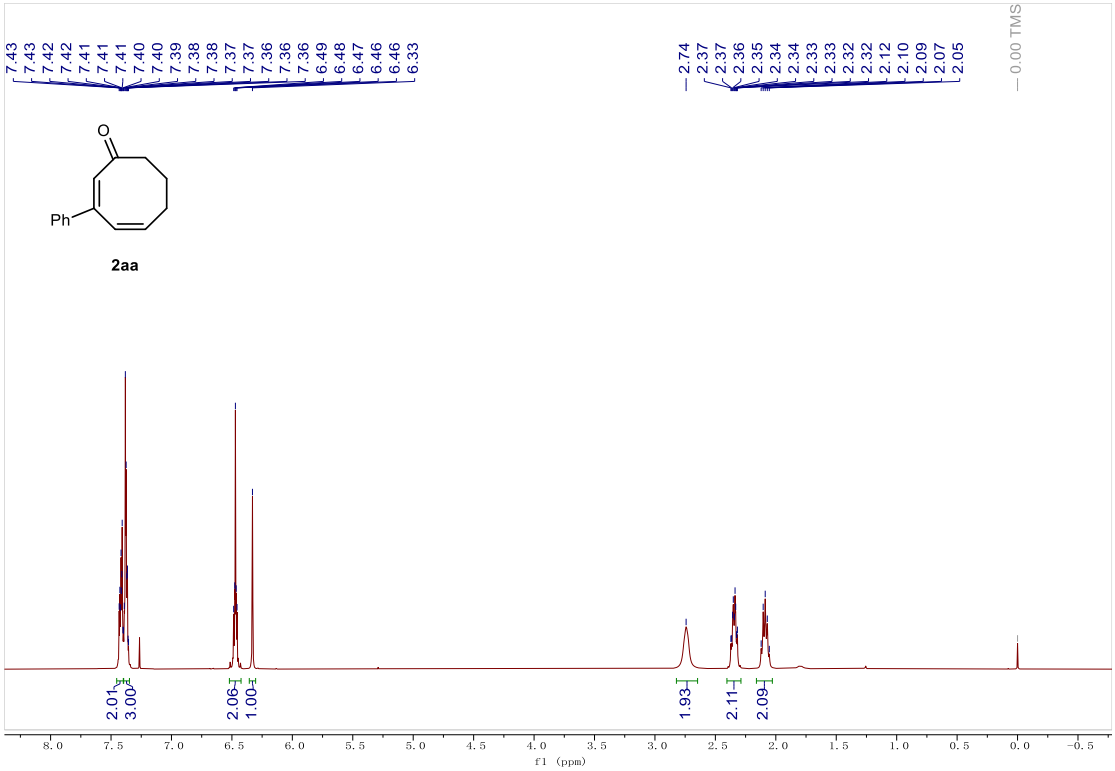
^{1}H NMR in $CDCl_3$, 400 MHz



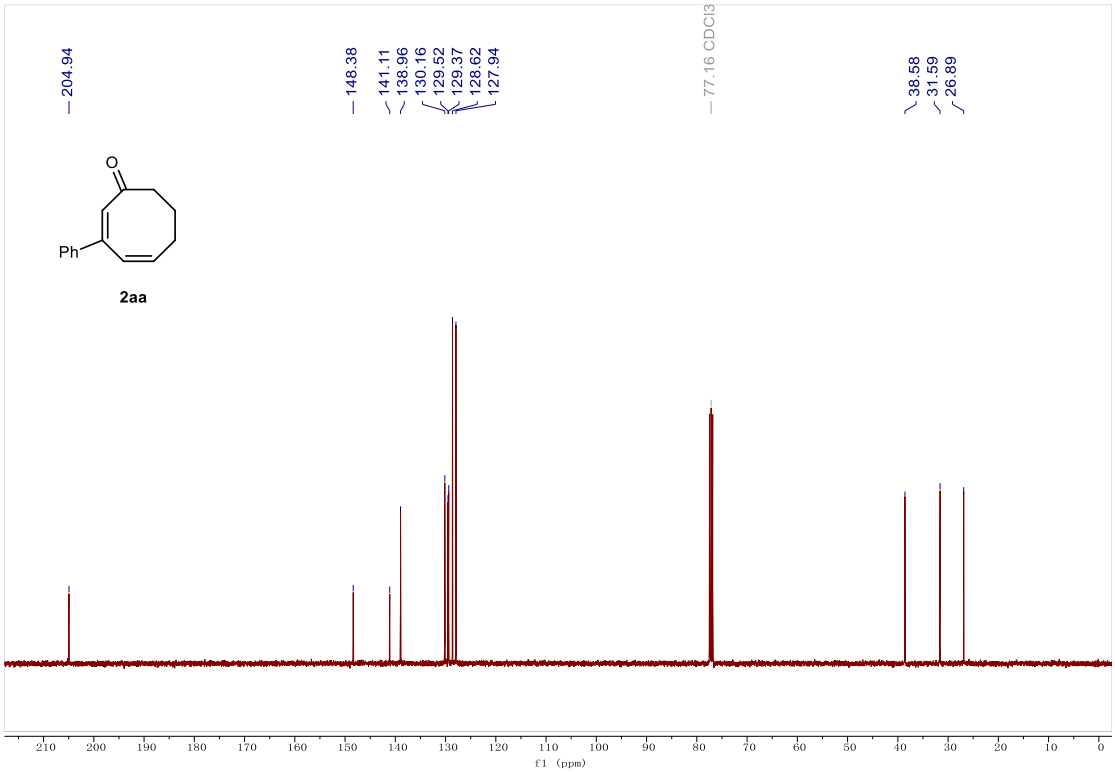
^{13}C NMR in $CDCl_3$, 101 MHz



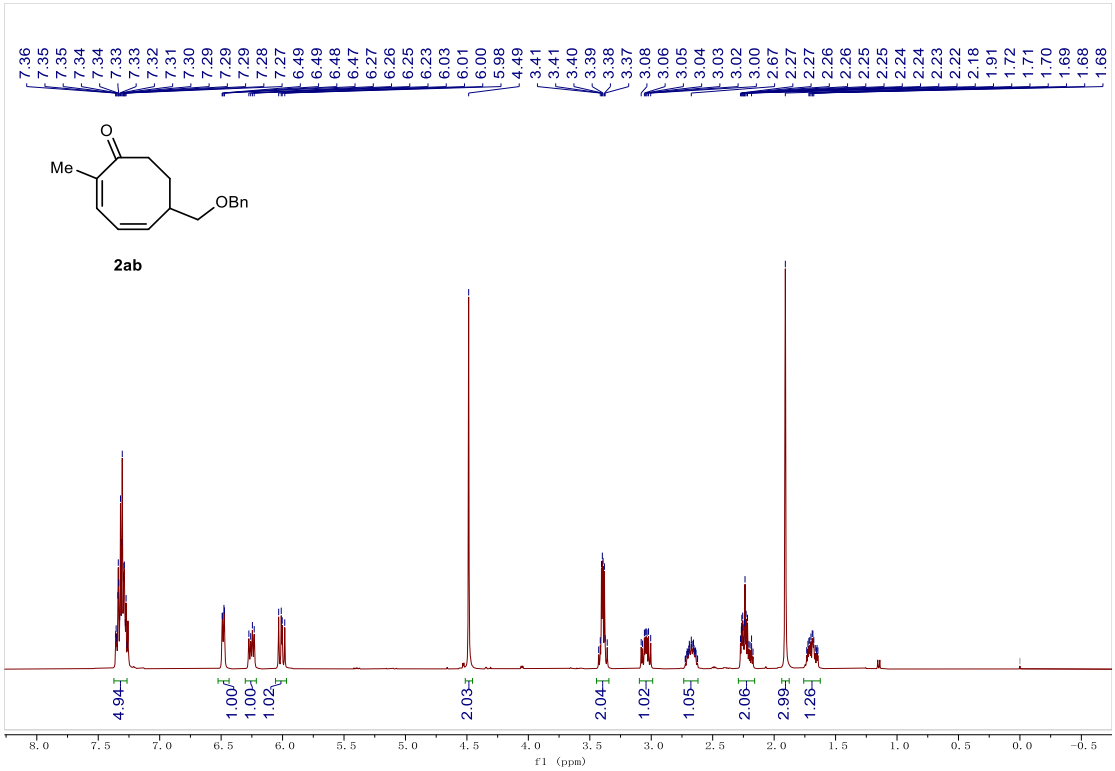
^{1}H NMR in $CDCl_3$, 400 MHz



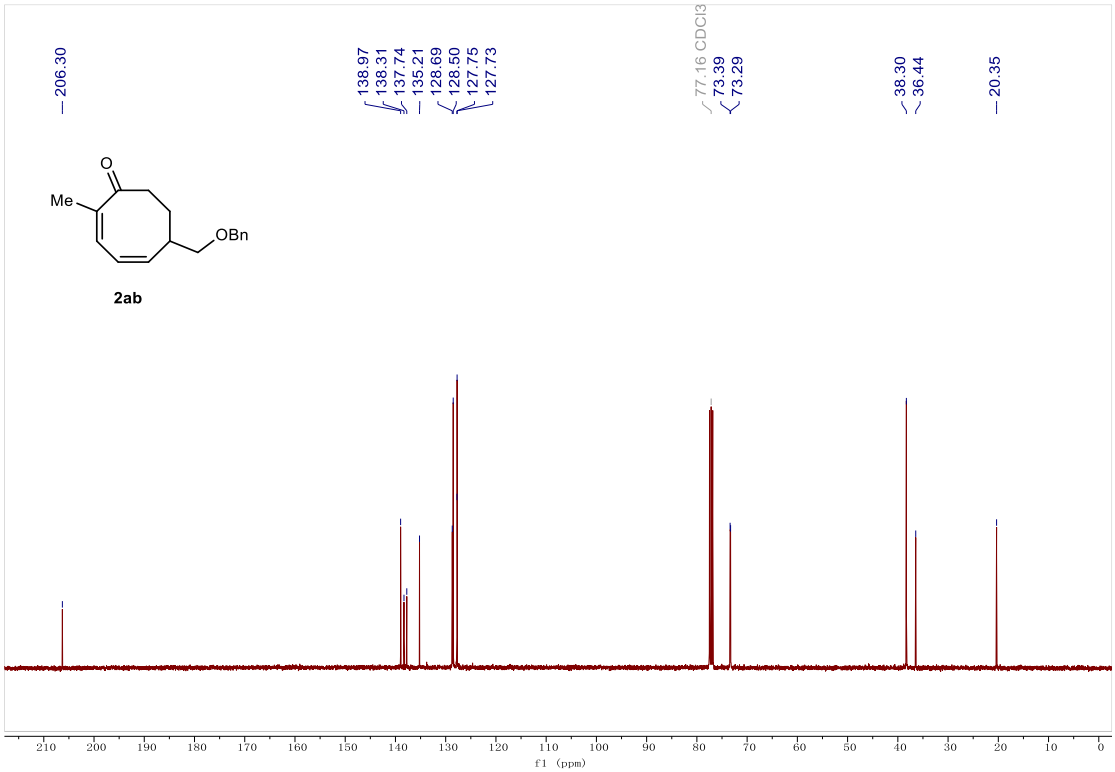
^{13}C NMR in $CDCl_3$, 101 MHz



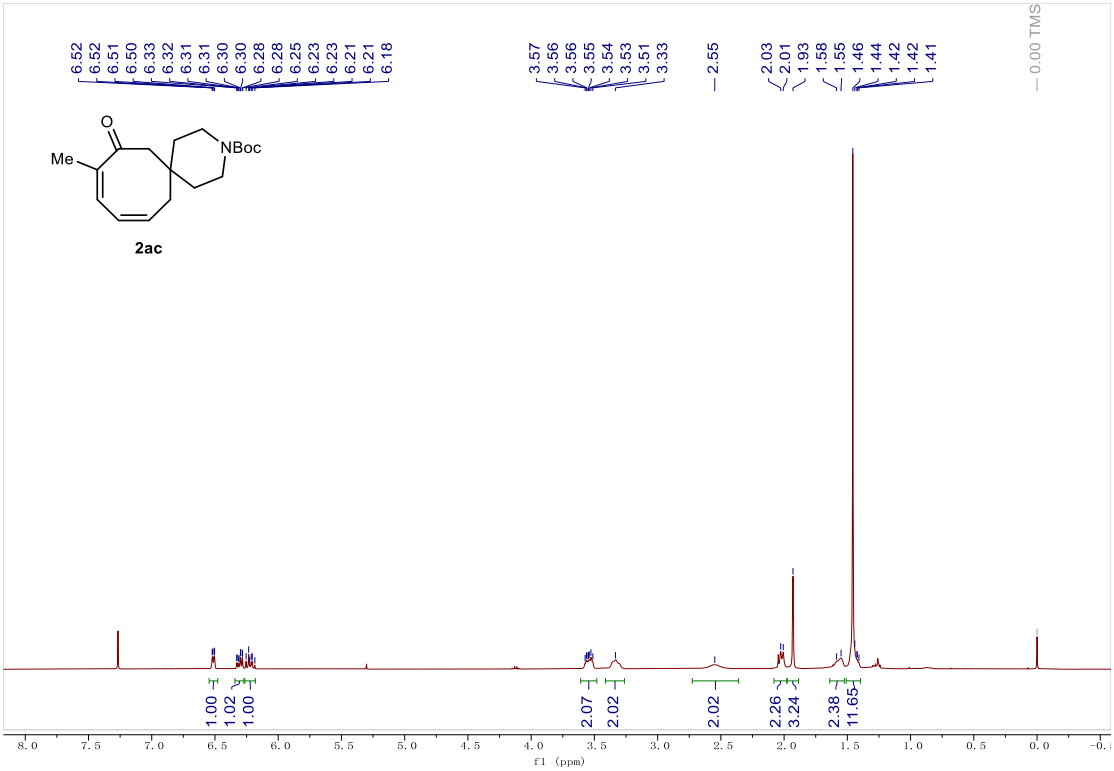
^{1}H NMR in $CDCl_3$, 400 MHz



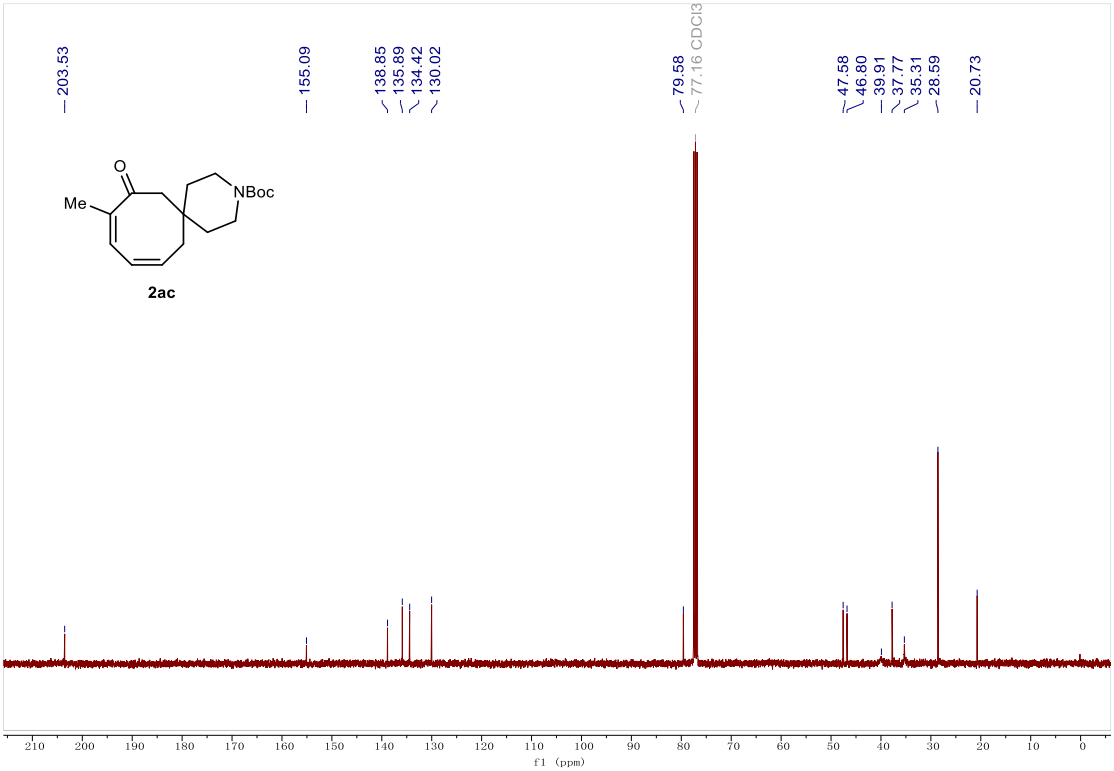
^{13}C NMR in $CDCl_3$, 101 MHz



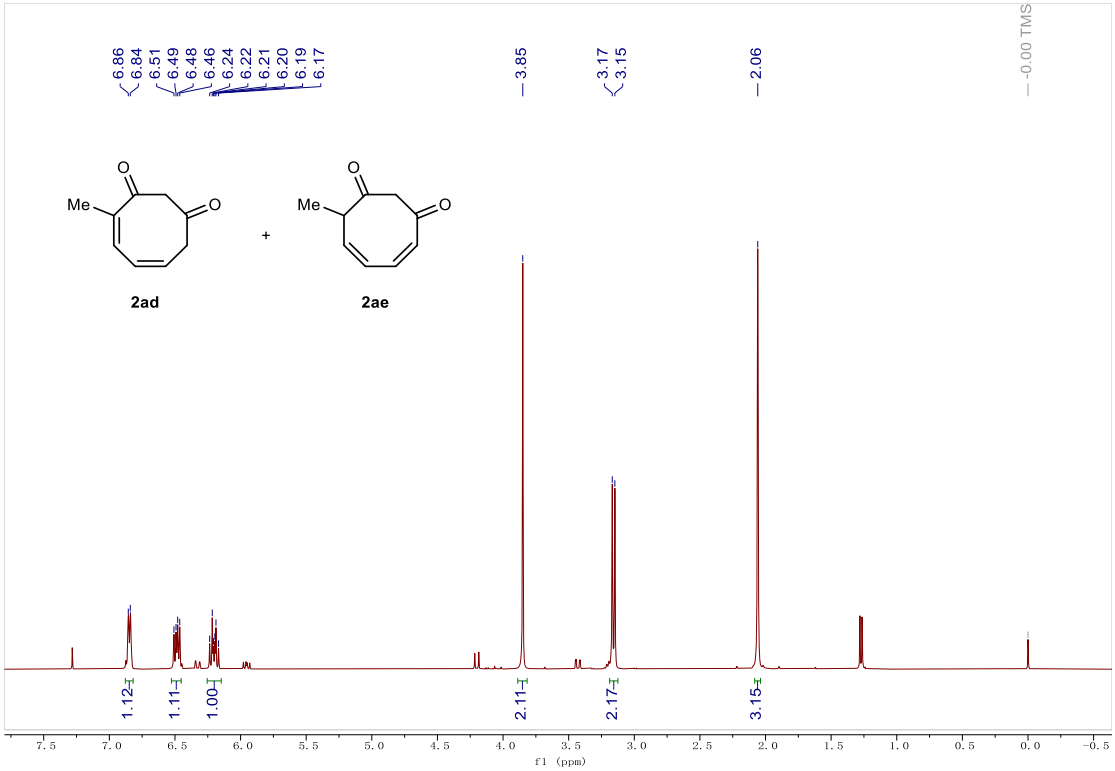
^{1}H NMR in $CDCl_3$, 400 MHz



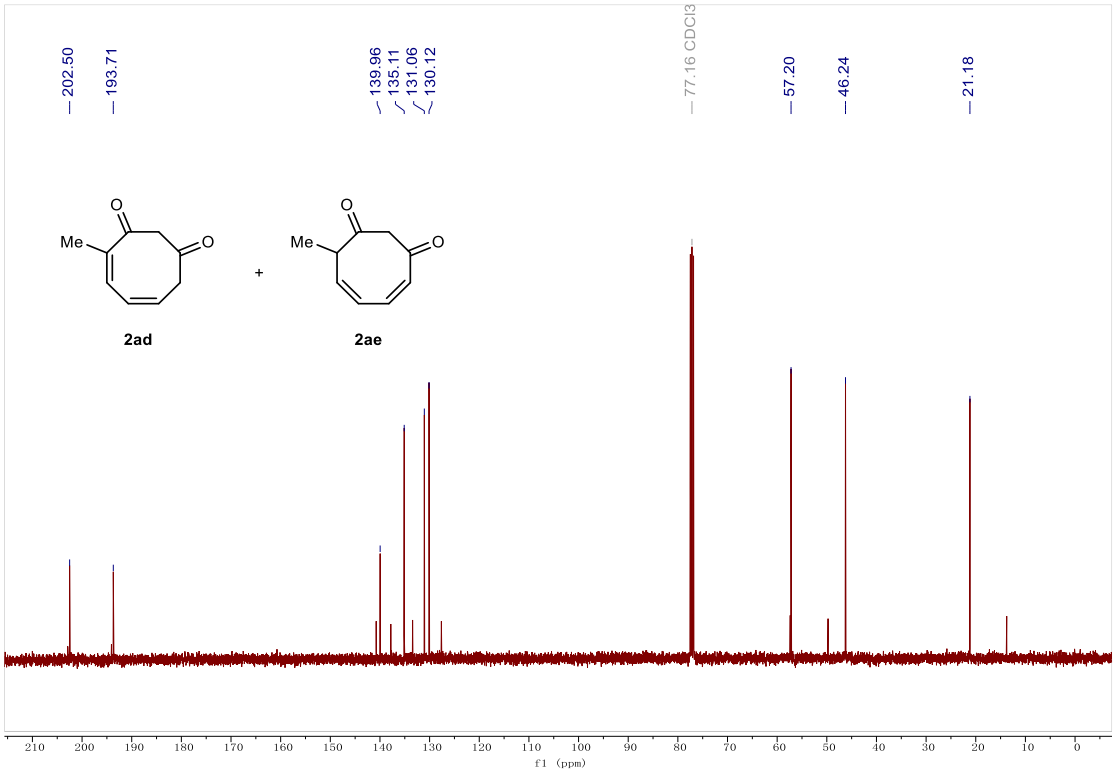
^{13}C NMR in $CDCl_3$, 101 MHz



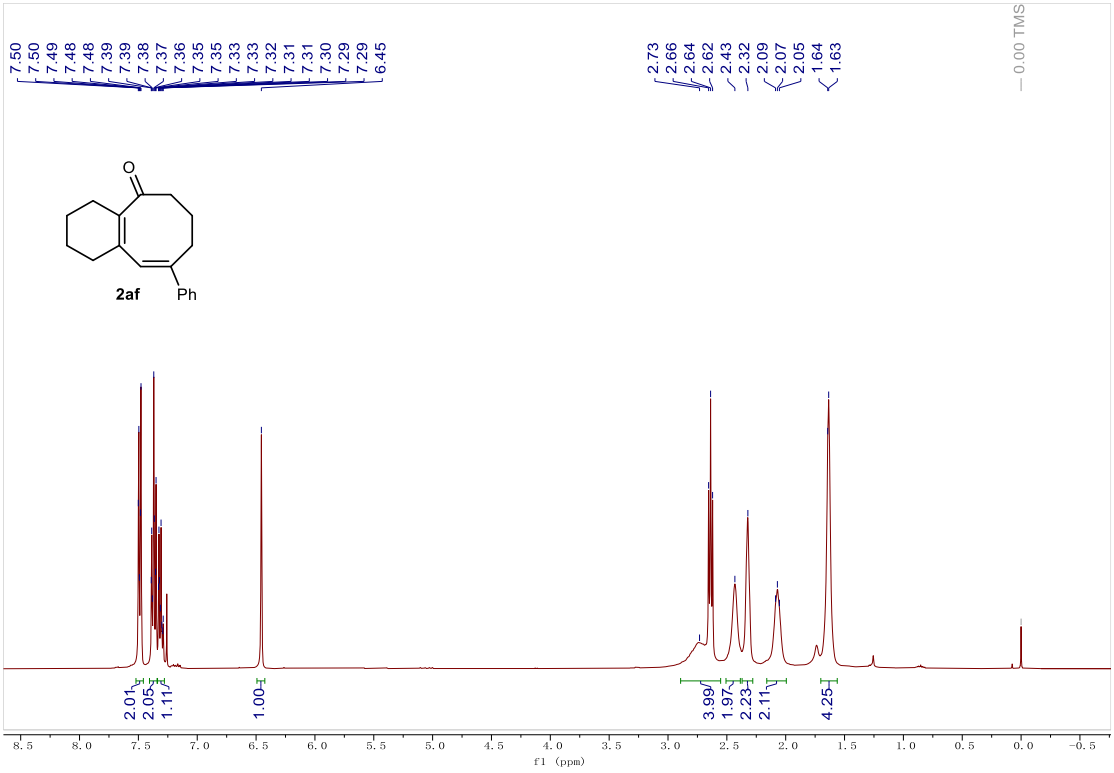
^{1}H NMR in $CDCl_3$, 400 MHz



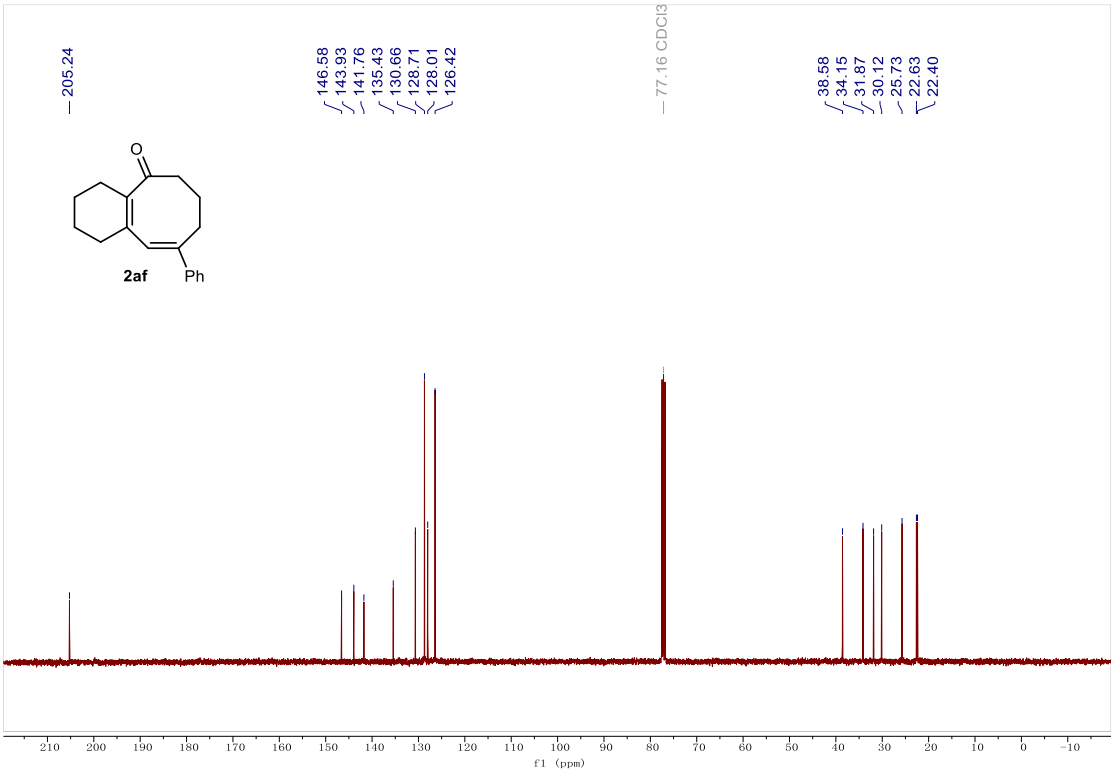
^{13}C NMR in $CDCl_3$, 101 MHz



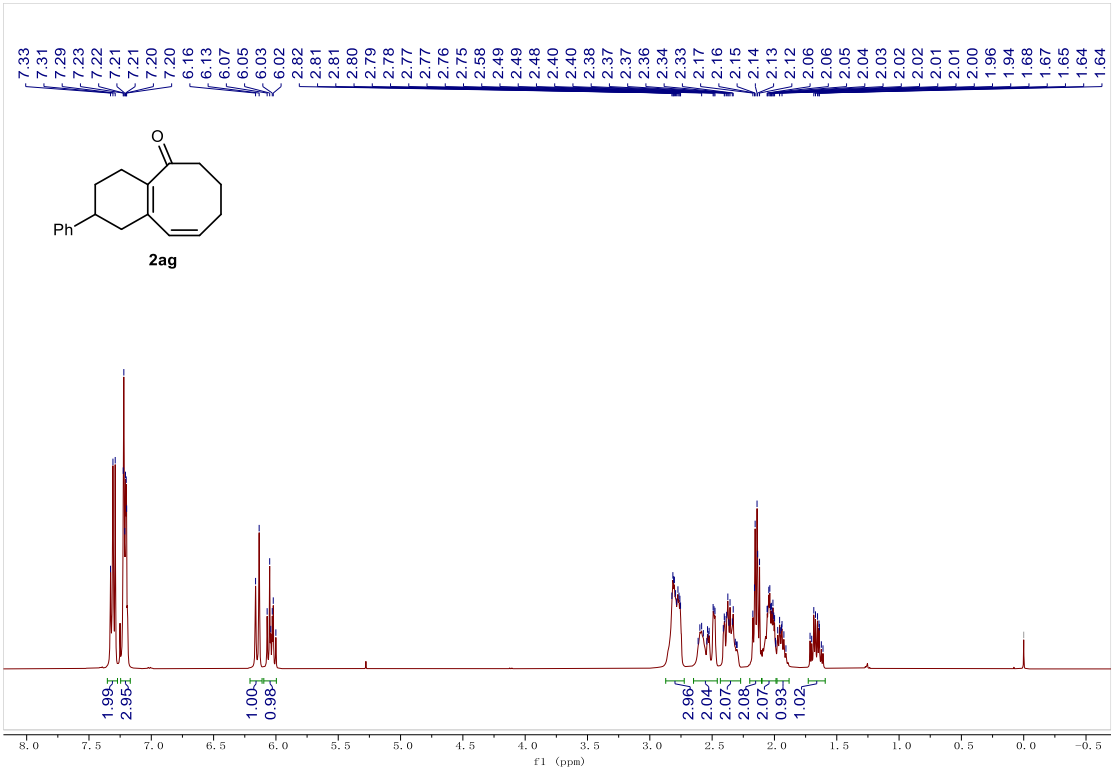
^{1}H NMR in $CDCl_3$, 400 MHz



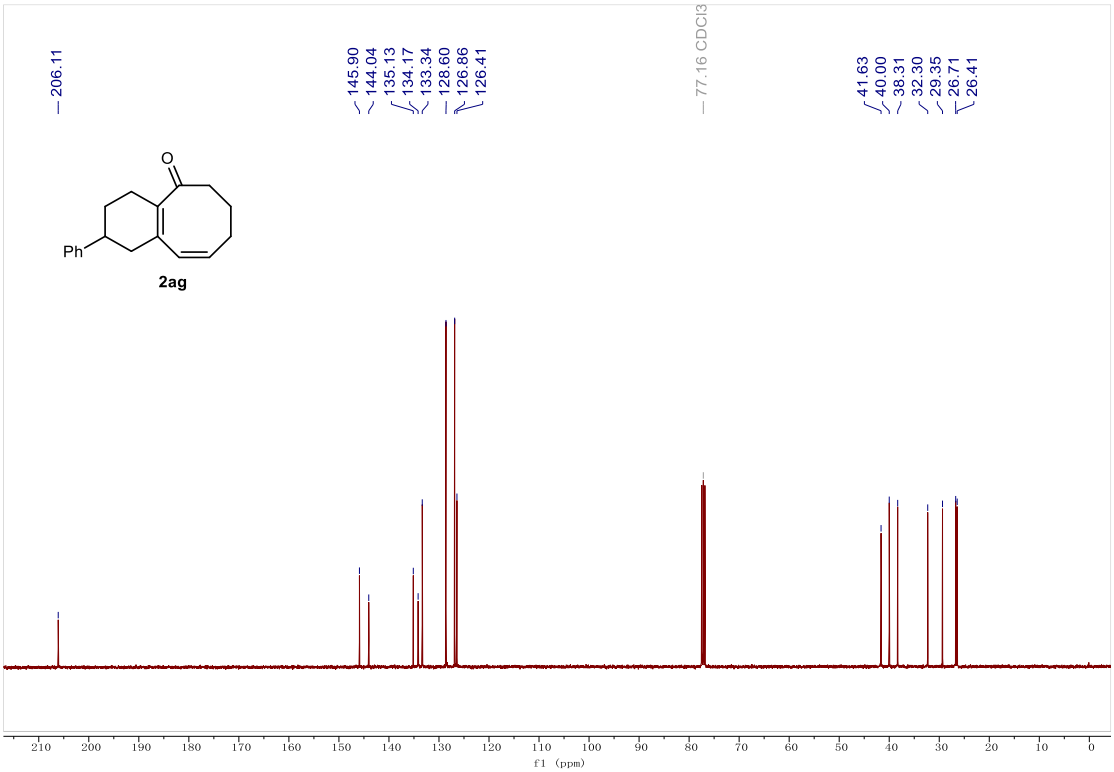
^{13}C NMR in $CDCl_3$, 101 MHz



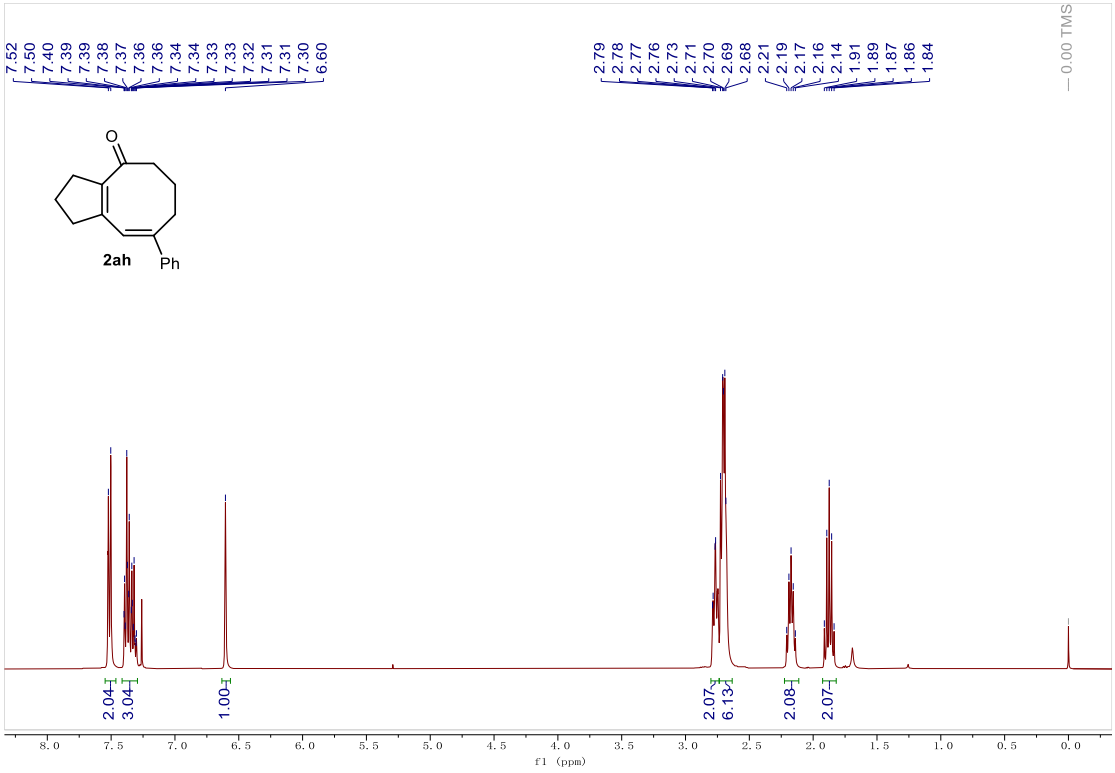
^{1}H NMR in $CDCl_3$, 400 MHz



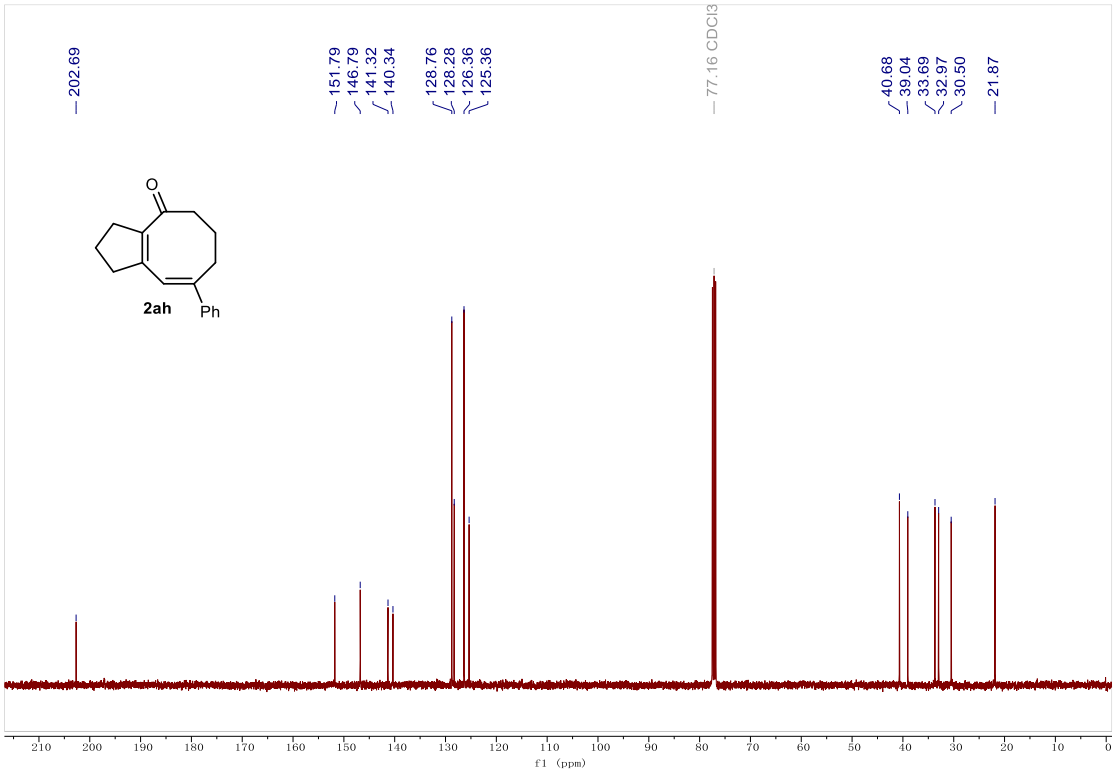
^{13}C NMR in $CDCl_3$, 101 MHz



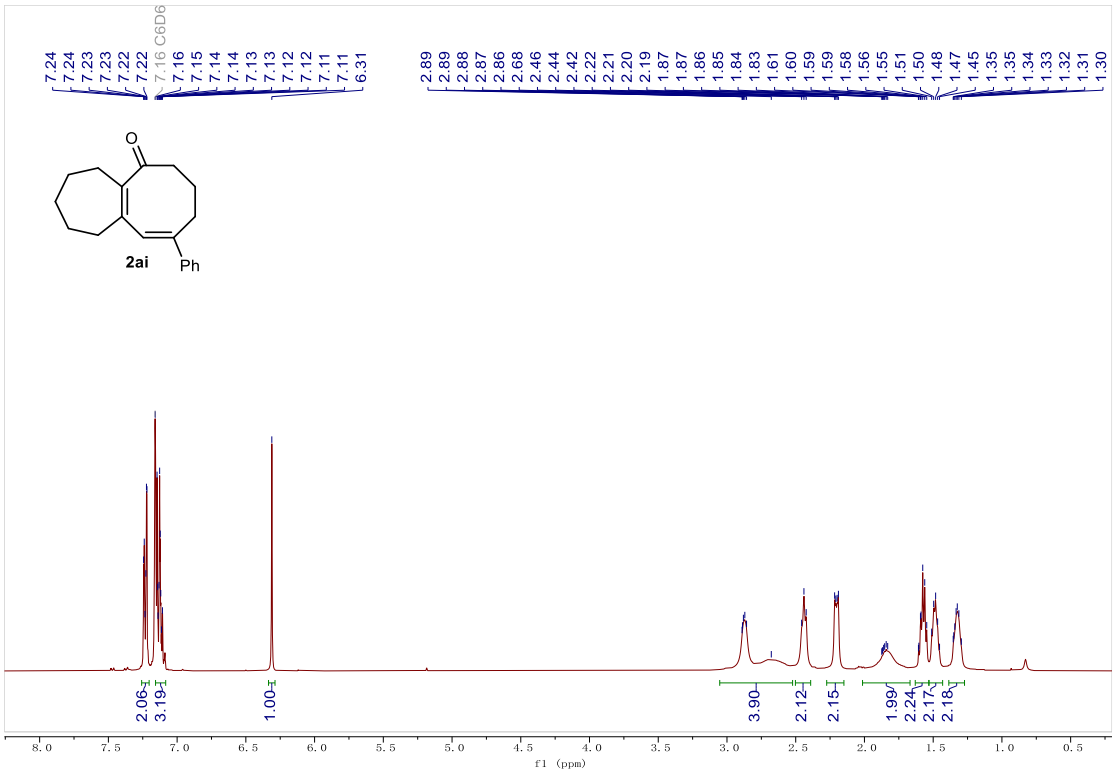
^{1}H NMR in $CDCl_3$, 400 MHz



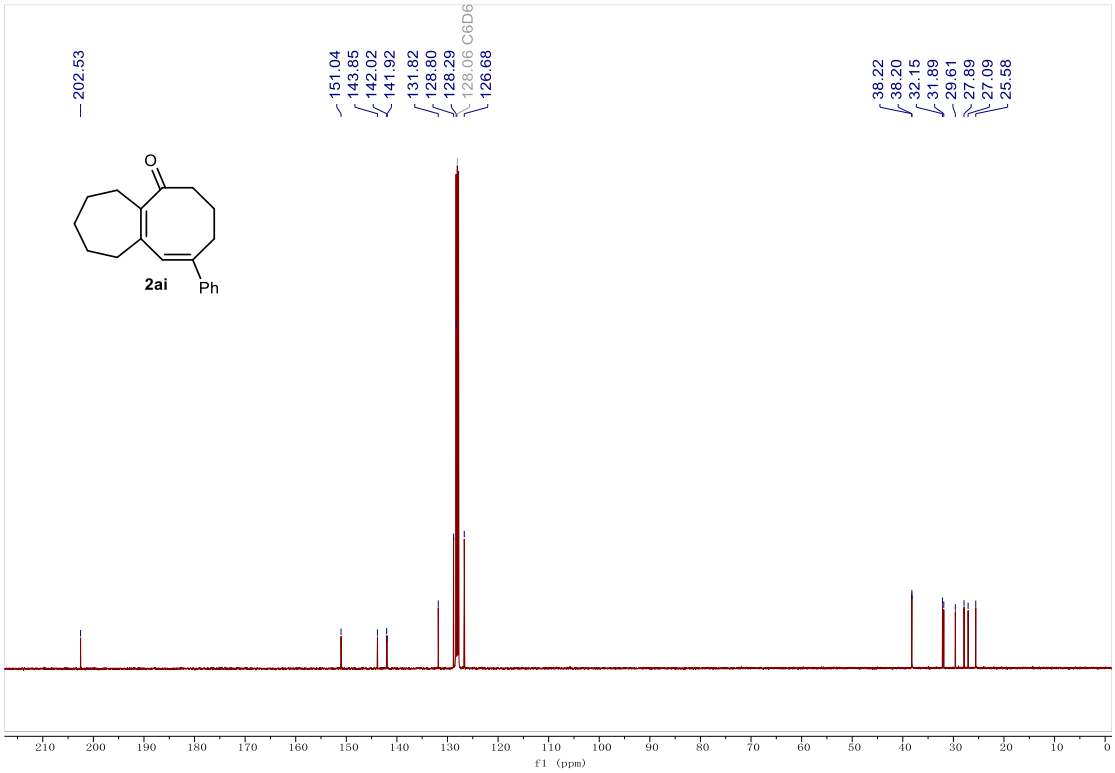
^{13}C NMR in $CDCl_3$, 101 MHz



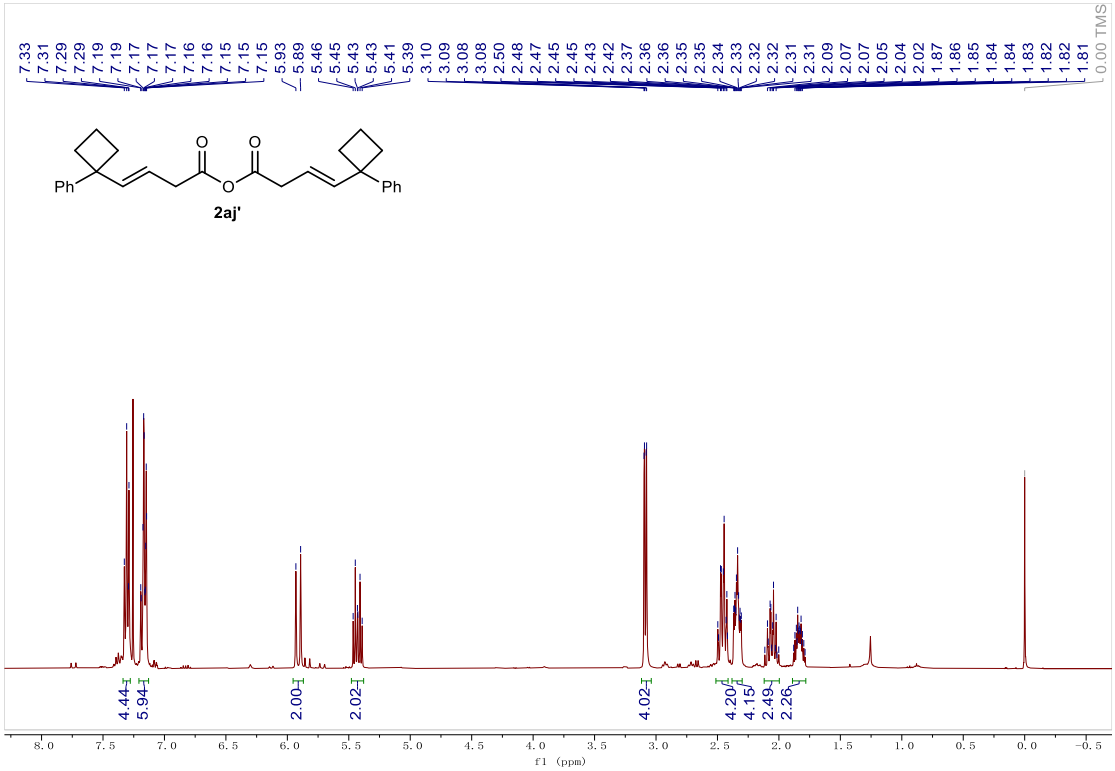
^{1}H NMR in C_6D_6, 400 MHz



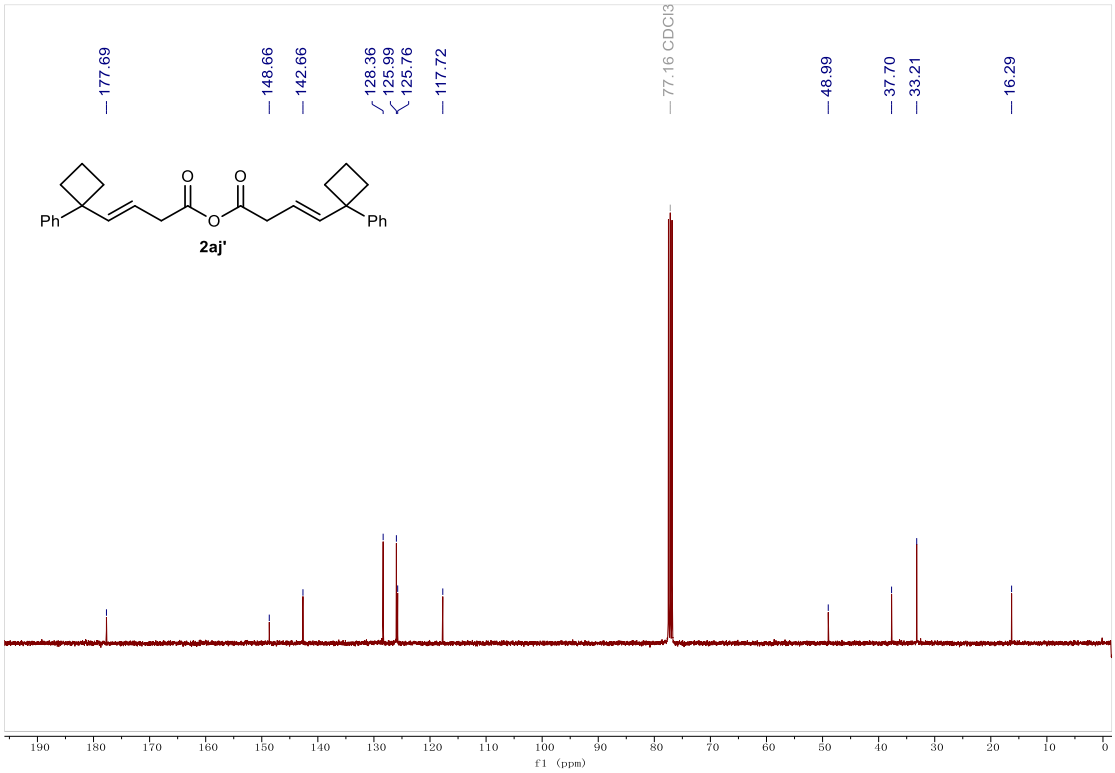
^{13}C NMR in C_6D_6, 101 MHz



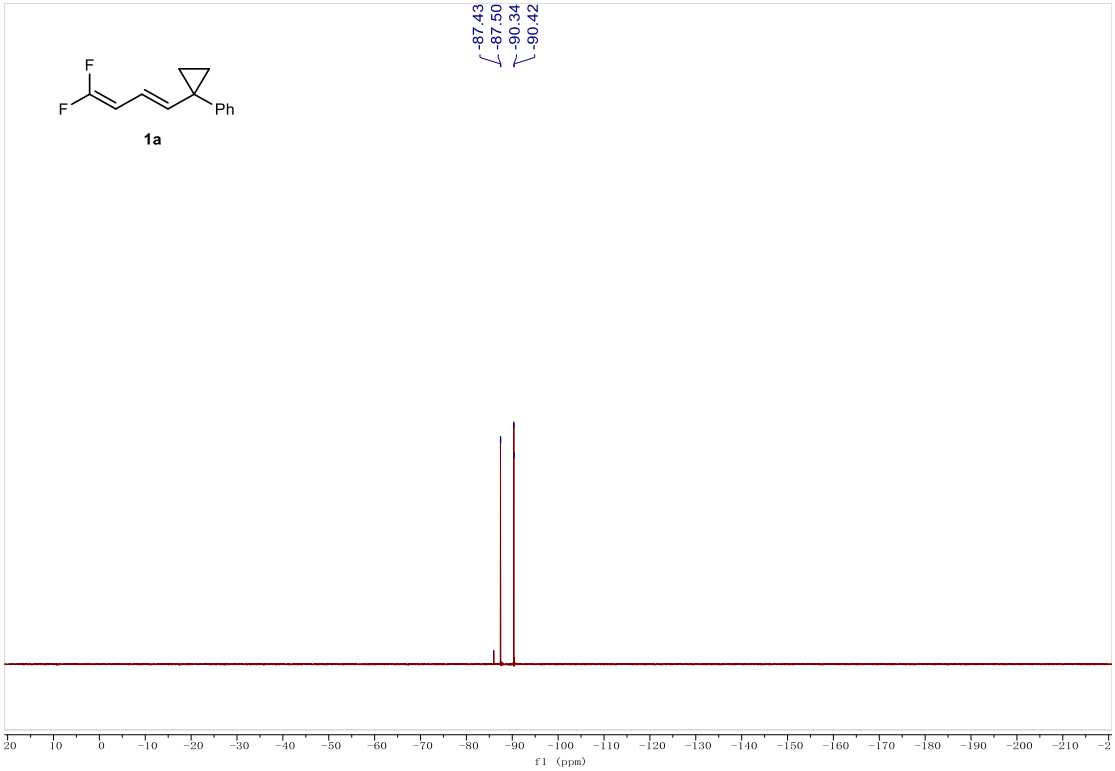
^{1}H NMR in $CDCl_3$, 400 MHz



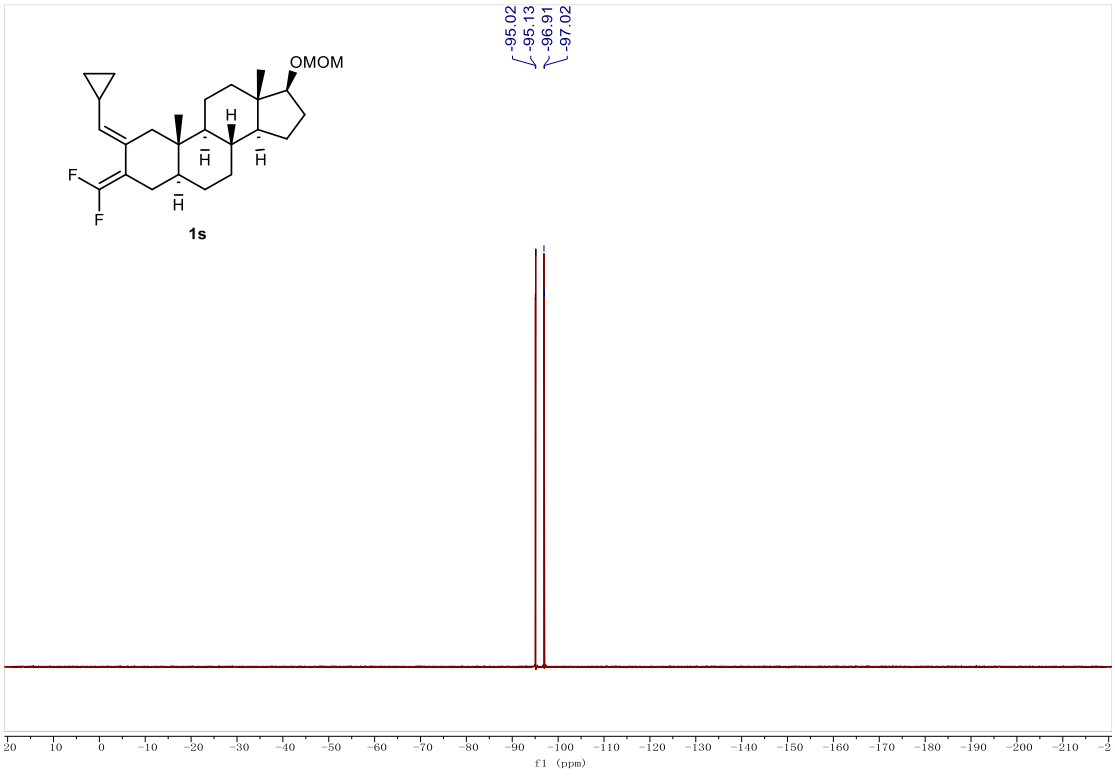
^{13}C NMR in $CDCl_3$, 101 MHz



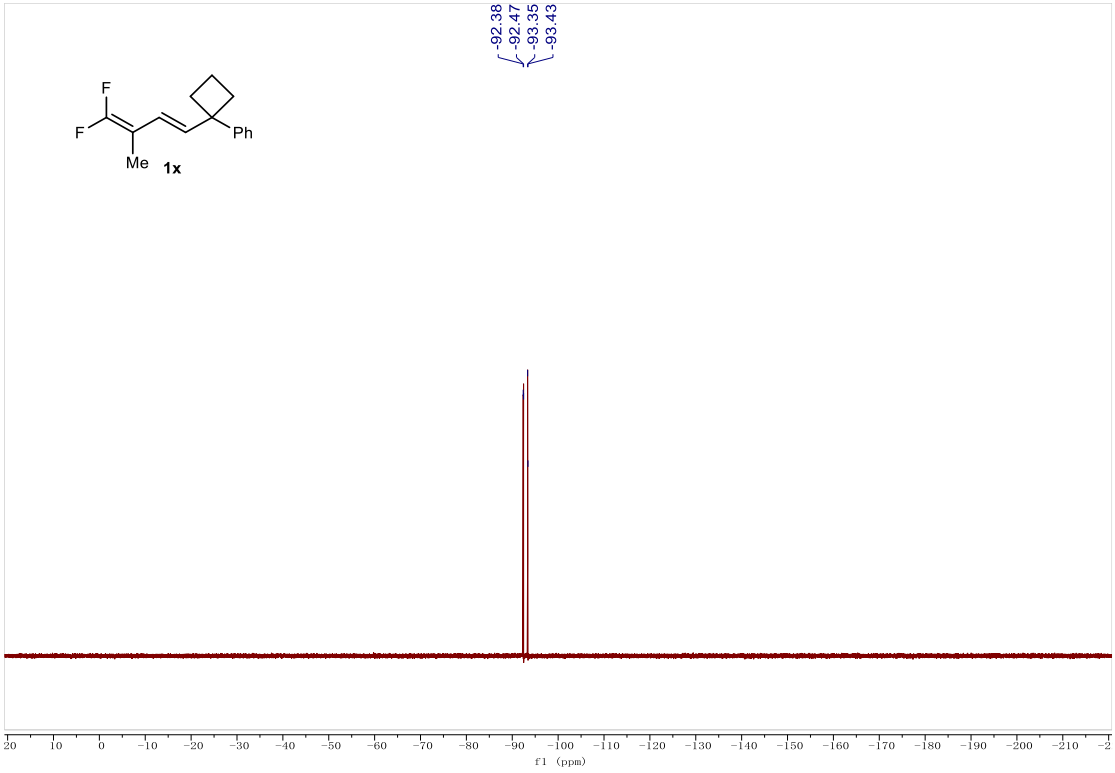
^{19}F NMR in $CDCl_3$, 471 MHz



^{19}F NMR in $CDCl_3$, 471 MHz



^{19}F NMR in $CDCl_3$, 471 MHz



^{19}F NMR in $CDCl_3$, 471 MHz