Supporting Information

Rhodium-Catalyzed [3+1+2] Cycloaddition of Type II Diene-Vinylcyclopropanes and Carbon Monoxide for the Synthesis of 5/6 Skeletons with Two Adjacent Bridgehead Quaternary Centers

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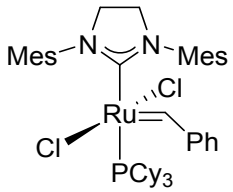
1. General Information

Unless otherwise stated, air and moisture sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry nitrogen or argon. Similarly, sensitive liquids and solutions were transferred via syringe. Reactions were stirred using Teflon-coated magnetic stirring bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a Büchi rotary evaporator with a desktop vacuum pump. Synthetic reagents were purchased from Bidepharm, J&K, Energy, Heowns or other similar suppliers, and were used without further purification. Super-dried DCE, 1,4-dioxane, THF, *i*-PrOH, MeCN and DMF was purchased from J&K. $[Rh(CO)_2Cl]_2$ catalyst was purchased from J&K, and was used without further purification. Analytical TLC was performed with 0.25 mm silica gel G plates with a 254 nm fluorescent indicator. The TLC plates were visualized by ultraviolet light and treatment with $KMnO_4$ stain or anisaldehyde stain followed by gentle heating. Purification of products was accomplished by flash chromatography on silica gel (200-300 mesh). Single crystal compounds were obtained through vapor diffusion method in $CDCl_3$/PE at 4 °C.

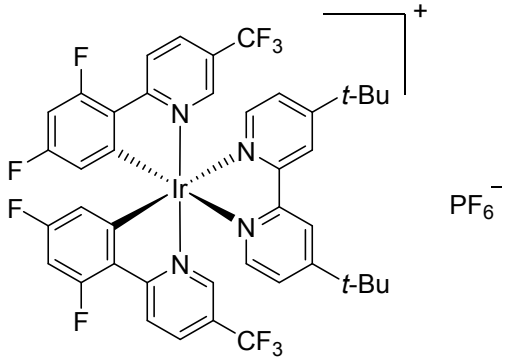
NMR spectra were measured on Bruker AVANCE III 400 (^{1}H at 400 MHz, ^{13}C at 101 MHz) and Bruker AVANCE III 500 (^{1}H at 500 MHz, ^{13}C at 126 MHz, ^{19}F at 471 MHz) nuclear magnetic resonance spectrometers. Data for ^{1}H NMR spectra were reported as follows: chemical shift δ (ppm) relative to residual solvent peak ($CDCl_3$ = δ 7.26 ppm, CD_2Cl_2 = δ 5.32 ppm; s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets, m = multiplet), coupling constant *J* (Hz), and integration. Data for ^{13}C NMR were reported in terms of chemical shift δ (ppm) relative to residual solvent peak ($CDCl_3$ = δ 77.16 ppm, CD_2Cl_2 = δ 53.84 ppm). High-resolution mass spectra (HRMS) were recorded on a Bruker Solarix XR Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (electrospray ionization, ESI), or a ThermoFisher Q Exactive GC Hybrid Quadrupole-Orbitrap GC-MS/MS System (electron ionization, EI). X-ray crystallographic data were measured on a Rigaku XtaLAB PRO 007HF(Mo) Single Crystal X-ray Diffractometer.

Abbreviations

Ac = acetyl
acac = acetylacetonyl
Bn = benzyl
Boc = *tert*-butoxycarbonyl
Bpin = boronic acid pinacol ester
Cy = cyclohexyl
DCM = dichloromethane
DCE = 1,2-dichloroethane
DIAD = diisopropyl azodicarboxylate
DMF = N,N-dimethylformamide
EA = ethyl acetate
LED = light-emitting diode
Mes = mesityl
m.p. = melting point
Ms = methanesulfonyl
PDC = pyridinium dichromate
PE = petroleum ether
TBAF = tetra-*n*-butylammonium fluoride
TBS = *tert*-butyldimethylsilyl
Tf = trifluoromethanesulfonyl
THF = tetrahydrofuran
TLC = thin layer chromatography
Ts = *p*-toluenesulfonyl

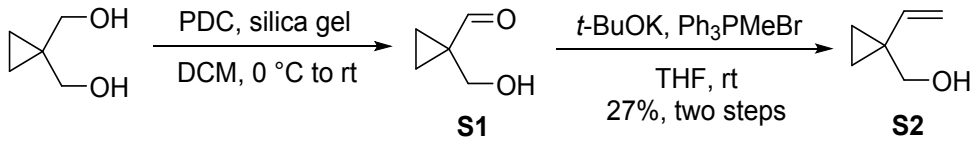


Grubbs-II catalyst



$[Ir(dFCF_3PPy)_2(dtbbpy)]PF_6$

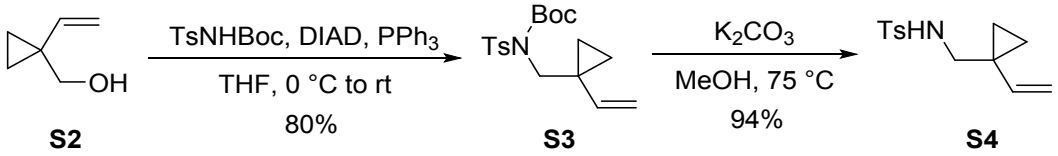
2. Syntheses of substrates



To a solution of 1,1-bis(hydroxymethyl)cyclopropane (8.17 g, 80 mmol) in DCM (160 mL) was added silica gel (31.60 g). The mixture was cooled to 0 °C and PDC (31.60 g, 84 mmol) was added. Then the reaction mixture was warmed to room temperature and stirred for 3.5 h. After completion, the reaction mixture was filtered through a pad of silica gel and washed with Et_2O. The combined filtrate was concentrated *in vacuo* and the crude product **S1** was directly used in the next step without further purification.

To a stirred mixture of Ph_3PMeBr (28.58 g, 80 mmol) and *t*-BuOK (17.95 g, 160 mmol) was added THF (400 mL). The resulted mixture was stirred for 10 min at room temperature before a solution of the above crude product **S1** in THF (100 mL) was added. Then the reaction mixture was stirred at room temperature for 1 h. After quenched by saturated NH_4Cl solution, the mixture was extracted with Et_2O. The combined organic layer was washed with 0.2 M HCl two times to remove the residual pyridine. Then the organic phase was washed successively with water and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* below 15 °C. The residue was distilled to afford **S2** (2.11 g, 27% for two steps) as a yellow liquid.

S2: yellow liquid. TLC R_f (PE/EA 5:1) = 0.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.64 (dd, *J* = 17.4, 10.7 Hz, 1H), 5.12 (dd, *J* = 17.5, 1.2 Hz, 1H), 5.02 (dd, *J* = 10.7, 1.2 Hz, 1H), 3.59 (s, 2H), 1.57 (s, 1H), 0.73 – 0.69 (m, 2H), 0.68 – 0.64 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 112.3, 68.0, 25.3, 12.4. HRMS (EI): calcd for $C_6H_{10}O^+$ ($[M]^{\bullet+}$) 98.0726, found 98.0727.

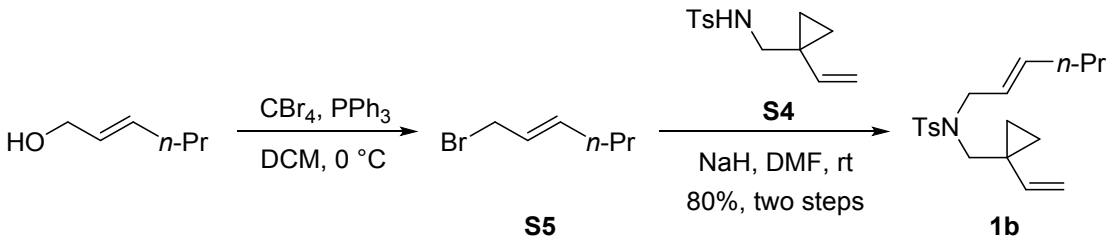


To a stirred mixture of *tert*-butyl tosylcarbamate (4.48 g, 16.5 mmol) and PPh_3 (5.90 g, 22.5 mmol) was added a solution of **S2** (1.47 g, 15.0 mmol) in super-dried THF (60 mL) under N_2 atmosphere. The mixture was cooled to 0 °C and DIAD (4.55 g, 4.42 mL, 22.5 mmol) was added dropwise. Then the reaction was warmed to room temperature and stirred for 23 h. After completion, the mixture was concentrated *in vacuo*. Purification of the residue through column chromatography on silica gel (PE/EA 50:1 to 20:1) afforded **S3** (4.19 g, 80%).

To a mixture of **S3** (4.16 g, 11.8 mmol) and K_2CO_3 (4.89 g, 22.5 mmol) was added MeOH (48 mL). The reaction mixture was heated to reflux at 75 °C and stirred for 24 h. After completion, the mixture was filtered through Celite and washed with EA. The combined filtrate was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel (PE/EA 10:1 to 5:1) to afford **S4** (2.80 g, 94%) as a white solid.

S4: white solid, m.p. = 62.2-63.7 °C. TLC R_f (PE/EA 5:1) = 0.24. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.43 (dd, *J* = 17.4, 10.8 Hz, 1H), 4.93 (dd, *J* = 10.8, 0.8 Hz, 1H), 4.85 (dd, *J* = 17.4, 0.8 Hz, 1H), 4.65 – 4.54 (m, 1H), 2.96 (d, *J* = 5.6 Hz, 2H), 2.43 (s, 3H), 0.66 – 0.56 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 140.7, 136.9, 129.8, 127.3,

112.7, 48.9, 22.4, 21.7, 13.2. HRMS (ESI): calcd for $C_{13}H_{18}NO_2S^+$ ([M + H]$^+$) 252.1053, found 252.1050.

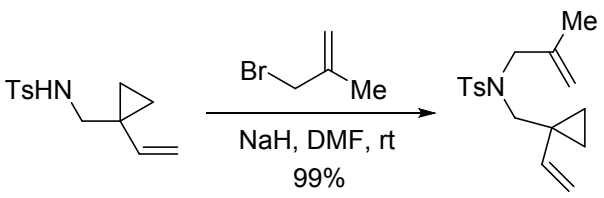


S5 **1b**

To a stirred solution of *E*-2-hexen-1-ol (200.3 mg, 2.0 mmol) and PPh_3 (577.0 mg, 2.2 mmol) in DCM (10 mL) was added CBr_4 (729.6 mg, 2.2 mmol) at 0 °C. The resulted mixture was stirred at 0 °C for 3 h. After quenched by saturated $NaHCO_3$ solution, the mixture was extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* at 0 °C. *n*-Pentane was added to the residue and white precipitation generated. The mixture was filtered through a pad of silica gel and washed with *n*-pentane/Et_2O 50:1. The combined filtrate was concentrated *in vacuo* at 0 °C and the crude product **S5** was directly used in the next step without further purification.

To NaH (60.0 mg, 60% weight in mineral oil, 1.5 mmol) was added a solution of **S4** (251.3 mg, 1.0 mmol) in super-dried DMF (10 mL) under N_2 atmosphere. The mixture was stirred for 10 min at room temperature before a solution of the above crude product **S5** in super-dried DMF (5 mL) was added. Then the reaction mixture was stirred at room temperature for 17 h. After quenched by saturated NH_4Cl solution, the mixture was extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (PE/EA 50:1) to afford **1b** (268.3 mg, 80% for two steps) as a yellow oil.

1b: yellow oil. TLC R_f (PE/EA 5:1) = 0.54. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 5.91 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.57 – 5.45 (m, 1H), 5.17 – 5.05 (m, 1H), 4.93 (dd, *J* = 17.2, 1.2 Hz, 1H), 4.89 (dd, *J* = 10.5, 1.2 Hz, 1H), 3.87 (d, *J* = 6.5 Hz, 2H), 3.23 (s, 2H), 2.41 (s, 3H), 1.94 – 1.84 (m, 2H), 1.37 – 1.23 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H), 0.71 – 0.64 (m, 2H), 0.64 – 0.58 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 140.6, 138.0, 135.3, 129.6, 127.4, 124.3, 112.2, 52.6, 49.0, 34.3, 22.2, 21.6, 21.1, 13.8, 13.2. HRMS (ESI): calcd for $C_{19}H_{27}NNaO_2S^+$ ([M + Na]$^+$) 356.1655, found 356.1651.

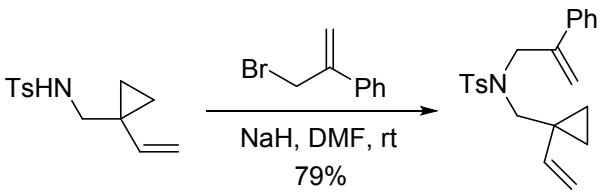


S4 **1c**

To a mixture of **S4** (251.3 mg, 1.0 mmol) and NaH (60.0 mg, 60% weight in mineral oil, 1.5 mmol) was added super-dried DMF (3 mL) under N_2 atmosphere. The mixture was stirred for 10 min at room temperature before a solution of 2-methyl-3-bromo-1-propene (175.5 mg, 1.3 mmol) in super-dried DMF (2 mL) was added. Then the reaction mixture was stirred at room temperature for 17 h. After quenched by saturated NH_4Cl solution, the mixture was extracted with Et_2O. The combined

organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (PE/EA 50:1) to afford **1c** (302.4 mg, 99%) as a yellow oil.

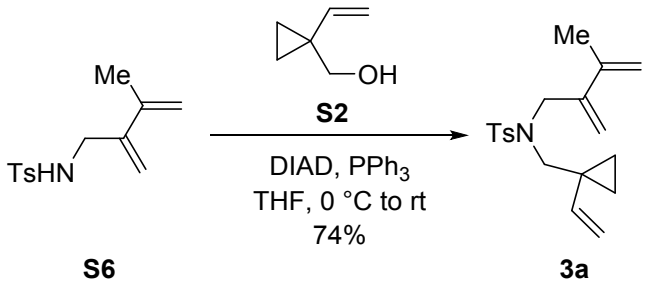
1c: yellow oil. TLC R_f (PE/EA 10:1) = 0.50. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 5.78 (dd, *J* = 17.2, 10.6 Hz, 1H), 4.88 – 4.85 (m, 1H), 4.83 (dd, *J* = 17.2, 1.3 Hz, 1H), 4.80 (dd, *J* = 10.5, 1.3 Hz, 1H), 4.79 – 4.75 (m, 1H), 3.83 (s, 2H), 3.23 (s, 2H), 2.42 (s, 3H), 1.64 (s, 3H), 0.66 – 0.59 (m, 2H), 0.59 – 0.54 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 140.5, 140.4, 137.9, 129.6, 127.4, 113.1, 112.3, 53.9, 53.2, 21.6, 21.2, 20.4, 13.4. HRMS (ESI): calcd for $C_{17}H_{24}NO_2S^+$ ($[M + H]^+$) 306.1522, found 306.1517.



S4 **1d**

To a mixture of **S4** (344.3 mg, 1.37 mmol) and NaH (82.4 mg, 60% weight in mineral oil, 2.06 mmol) was added super-dried DMF (4 mL) under N_2 atmosphere. The mixture was stirred for 10 min at room temperature before a solution of (3-bromoprop-1-en-2-yl)benzene[1] (537.2 mg, 2.73 mmol) in super-dried DMF (3 mL) was added. Then the reaction mixture was stirred at room temperature for 24 h. After quenched by saturated NH_4Cl solution, the mixture was extracted with EA. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (PE/EA 100:1 to 50:1) to afford **1d** (397.7 mg, 79%) as a yellow oil.

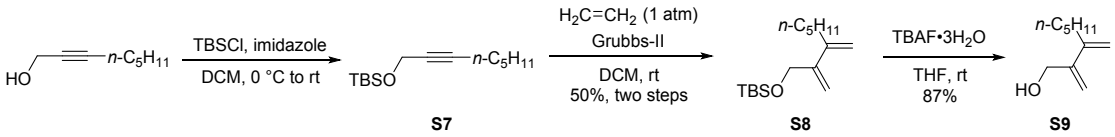
1d: yellow oil. TLC R_f (PE/EA 5:1) = 0.53. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.38 – 7.28 (m, 7H), 5.73 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.40 (q, *J* = 1.3 Hz, 1H), 5.15 (q, *J* = 1.5 Hz, 1H), 4.81 (dd, *J* = 17.3, 1.2 Hz, 1H), 4.77 (dd, *J* = 10.6, 1.2 Hz, 1H), 4.31 (t, *J* = 1.6 Hz, 2H), 3.29 (s, 2H), 2.43 (s, 3H), 0.62 – 0.57 (m, 2H), 0.57 – 0.52 (m, 2H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 143.7, 143.1, 140.8, 139.8, 137.9, 129.9, 128.7, 128.2, 127.6, 126.6, 114.6, 112.3, 54.3, 51.2, 21.6, 21.2, 13.4. HRMS (ESI): calcd for $C_{22}H_{26}NO_2S^+$ ($[M + H]^+$) 368.1679, found 368.1675.



S6 **3a**

To a stirred mixture of **S6**[2] (3.42 g, 13.60 mmol) and PPh_3 (4.86 g, 18.54 mmol) was added a solution of **S2** (1.2132 g, 12.36 mmol) in super-dried THF (50 mL) under N_2 atmosphere. The mixture was cooled to 0 °C and DIAD (3.75 g, 3.64 mL, 18.54 mmol) was added dropwise. Then the reaction was warmed to room temperature and stirred for 29 h. After completion, the mixture was concentrated *in vacuo*. Purification of the residue through column chromatography on silica gel (PE/EA 50:1 to 20:1) afforded **3a** (3.0259 g, 74%) as a white solid.

3a: white solid, m.p. = 49.5-50.7 °C. TLC R_f (PE/EA 10:1) = 0.41. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.69 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.23 (s, 1H), 5.10 (s, 1H), 4.98 (s, 2H), 4.82 (dd, *J* = 17.4, 1.0 Hz, 1H), 4.78 (dd, *J* = 10.7, 1.0 Hz, 1H), 4.13 (s, 2H), 3.27 (s, 2H), 2.42 (s, 3H), 1.91 (s, 3H), 0.62 – 0.55 (m, 2H), 0.55 – 0.48 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 141.5, 141.1, 140.4, 137.7, 129.6, 127.4, 113.8, 112.6, 112.2, 54.1, 49.4, 21.6, 21.6, 21.0, 13.1. HRMS (ESI): calcd for $C_{19}H_{26}NO_2S^+$ ([M + H]$^+$) 332.1679, found 332.1677.

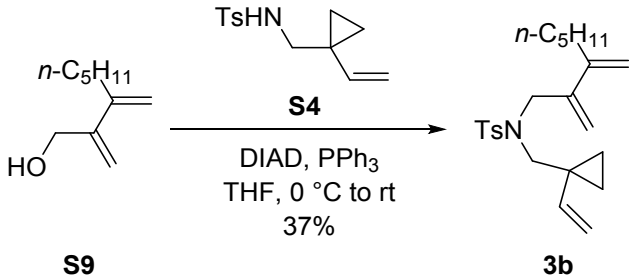


To a stirred solution of 2-octyn-1-ol (1.89 g, 15.0 mmol) and imidazole (1.23 g, 18.0 mmol) in DCM (30 mL) was added a solution of TBSCl (2.49 g, 16.5 mmol) in DCM (10 mL) dropwise at 0 °C. Then the reaction was warmed to room temperature and stirred for 14 h. After quenched by saturated $NaHCO_3$ solution, the mixture was extracted with DCM. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product **S7** was directly used in the next step without further purification.

A solution of the above crude product **S7** and Grubbs-II catalyst (382.0 mg, 0.45 mmol) in DCM (75 mL) was bubbled with C_2H_4 (1 atm) for 10 min. Then the reaction mixture was stirred at room temperature under balloon pressure gas of C_2H_4 (1 atm) for 60 h. After completion, the mixture was concentrated *in vacuo*. Purification of the residue through column chromatography on silica gel (PE) afforded **S8** (2.00 g, 50% for two steps) as a colorless liquid.

To a solution of **S8** (2.00 g, 7.45 mmol) in THF (15 mL) was added TBAF•3H_2O (16.39 mmol, 5.17 g). The resulted mixture was stirred at room temperature for 12 h. After quenched by saturated NH_4Cl solution, the mixture was extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. Purification of the residue through column chromatography on silica gel (PE/EA 20:1 to 10:1) afforded a mixture of **S9** and TBSOH. Toluene was added to the mixture and TBSOH can then be removed together with toluene through rotary evaporation at 45 °C to afford pure **S9** (1.00 g, 87%) as a yellow liquid.

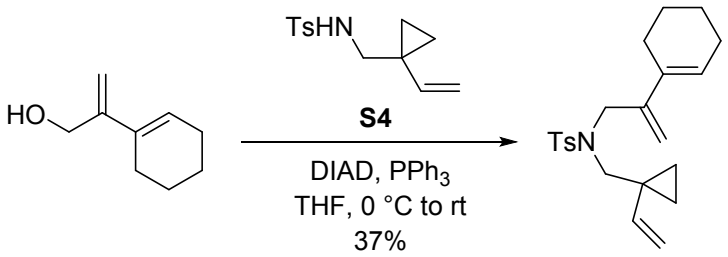
S9: yellow liquid. TLC R_f (PE/EA 5:1) = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.25 (s, 1H), 5.23 (s, 1H), 5.09 (s, 1H), 5.00 (s, 1H), 4.32 (s, 2H), 2.25 (t, *J* = 7.7 Hz, 2H), 1.58 (s, 1H), 1.52 – 1.40 (m, 2H), 1.39 – 1.22 (m, 4H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 145.9, 112.3, 112.0, 64.6, 34.3, 31.9, 28.3, 22.7, 14.2. HRMS (ESI): calcd for $C_{10}H_{19}O^+$ ([M + H]$^+$) 155.1430, found 155.1430.



A mixture of **S9** (308.5 mg, 2.0 mmol), **S4** (552.9 mg, 2.2 mmol) and PPh_3 (786.9 mg, 3.0 mmol)

was dissolved in super-dried THF (8 mL) under N_2 atmosphere. The mixture was cooled to 0 °C and DIAD (606.6 mg, 0.59 mL, 3.0 mmol) was added dropwise. Then the reaction was warmed to room temperature and stirred for 24 h. After completion, the mixture was concentrated *in vacuo*. Purification of the residue through column chromatography on silica gel (PE/EA 100:1 to 50:1) afforded **3b** (285.3 mg, 37%) as a colorless oil.

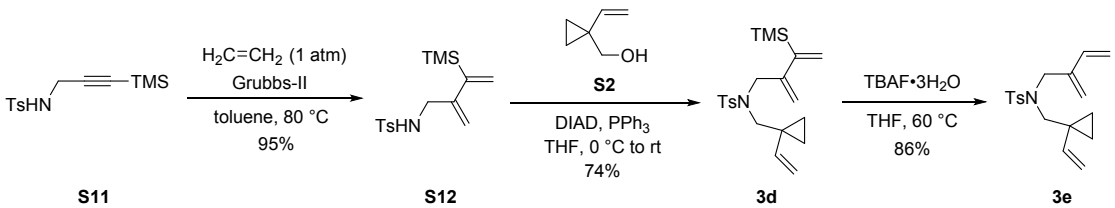
3b: colorless oil. TLC R_f (PE/EA 10:1) = 0.39. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 5.69 (dd, *J* = 17.2, 10.6 Hz, 1H), 5.21 (s, 1H), 5.04 (s, 1H), 4.96 (s, 1H), 4.93 (s, 1H), 4.82 (dd, *J* = 17.3, 1.1 Hz, 1H), 4.78 (dd, *J* = 10.7, 1.1 Hz, 1H), 4.10 (s, 2H), 3.28 (s, 2H), 2.42 (s, 3H), 2.22 (t, *J* = 7.6 Hz, 2H), 1.49 – 1.38 (m, 2H), 1.36 – 1.22 (m, 4H), 0.89 (t, *J* = 6.9 Hz, 3H), 0.62 – 0.55 (m, 2H), 0.55 – 0.48 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 143.1, 140.6, 140.4, 137.8, 129.6, 127.4, 113.1, 112.3, 111.6, 54.0, 49.7, 34.6, 31.9, 28.4, 22.7, 21.6, 21.0, 14.2, 13.1. HRMS (ESI): calcd for $C_{23}H_{34}NO_2S^+$ ([M + H]$^+$) 388.2305, found 388.2305.



S10 **3c**

A mixture of **S10**[3] (359.0 mg, 2.60 mmol), **S4** (593.2 mg, 2.36 mmol) and PPh_3 (928.5 mg, 3.54 mmol) was dissolved in super-dried THF (10 mL) under N_2 atmosphere. The mixture was cooled to 0 °C and DIAD (715.8 mg, 0.69 mL, 3.54 mmol) was added dropwise. Then the reaction was warmed to room temperature and stirred for 60 h. After completion, the mixture was concentrated *in vacuo*. Purification of the residue through column chromatography on silica gel (PE/EA 50:1) afforded **3c** (321.7 mg, 37%) as a yellow oil.

3c: yellow oil. TLC R_f (PE/EA 5:1) = 0.50. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.80 (dd, *J* = 4.1, 4.1 Hz, 1H), 5.74 (dd, *J* = 17.2, 10.6 Hz, 1H), 5.08 (s, 1H), 4.88 (s, 1H), 4.80 (d, *J* = 17.3 Hz, 1H), 4.78 (d, *J* = 10.6 Hz, 1H), 4.09 (s, 2H), 3.26 (s, 2H), 2.42 (s, 3H), 2.19 – 2.07 (m, 4H), 1.70 – 1.61 (m, 2H), 1.60 – 1.52 (m, 2H), 0.62 – 0.56 (m, 2H), 0.56 – 0.50 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 141.8, 140.6, 137.7, 134.8, 129.6, 127.5, 124.9, 112.0, 110.8, 54.0, 50.0, 26.3, 25.9, 22.9, 22.2, 21.6, 21.1, 13.2. HRMS (ESI): calcd for $C_{22}H_{30}NO_2S^+$ ([M + H]$^+$) 372.1992, found 372.1991.



S11 **S12** **3d** **3e**

A mixture of **S11**[4] (844.4 mg, 3.0 mmol) and Grubbs-II catalyst (127.3 mg, 0.15 mmol) was dissolved in toluene (15 mL). The resulted solution was bubbled with C_2H_4 (1 atm) for 10 min. Then the reaction mixture was stirred at 80 °C under balloon pressure gas of C_2H_4 (1 atm) for 13 h. After completion, the mixture was concentrated *in vacuo*. Purification of the residue through column

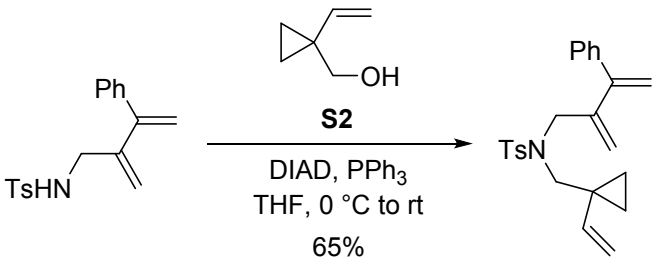
chromatography on silica gel (PE/EA 20:1 to 10:1) afforded **S12** (875.0 mg, 95%).

To a stirred mixture of **S12** (847.8 mg, 2.74 mmol) and PPh_3 (1.08 g, 4.11 mmol) was added a solution of **S2** (322.9 mg, 3.29 mmol) in super-dried THF (10 mL) under N_2 atmosphere. The mixture was cooled to 0 °C and DIAD (831.1 mg, 0.81 mL, 4.11 mmol) was added dropwise. Then the reaction was warmed to room temperature and stirred for 44 h. After completion, the mixture was concentrated *in vacuo*. Purification of the residue through column chromatography on silica gel (PE/EA 50:1) afforded **3d** (788.9 mg, 74%) as a colorless oil.

3d: colorless oil. TLC R_f (PE/EA 10:1) = 0.43. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 7.7 Hz, 2H), 5.71 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.65 (d, *J* = 2.3 Hz, 1H), 5.45 (d, *J* = 2.4 Hz, 1H), 4.94 (s, 1H), 4.92 (s, 1H), 4.83 (dd, *J* = 17.3, 1.1 Hz, 1H), 4.79 (d, *J* = 10.6, 1.1 Hz, 1H), 4.03 (s, 2H), 3.31 (s, 2H), 2.42 (s, 3H), 0.63 – 0.57 (m, 2H), 0.57 – 0.51 (m, 2H), 0.15 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.1, 143.9, 143.1, 140.4, 138.0, 129.6, 127.4, 125.9, 113.0, 112.4, 53.9, 50.7, 21.6, 21.0, 13.1, -0.6. HRMS (ESI): calcd for $C_{21}H_{32}NO_2SSi^+$ ($[M + H]^+$) 390.1918, found 390.1917.

To a solution of **3d** (410.5 mg, 1.05 mmol) in THF (5 mL) was added TBAF•$3H_2O$ (993.9 mg, 3.15 mmol). The resulted mixture was stirred at 60 °C for 18 h. After quenched by saturated NH_4Cl solution, the mixture was extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. Purification of the residue through column chromatography on silica gel (PE/EA 100:1 to 50:1) afforded **3e** (285.2 mg, 86%) as a yellow oil.

3e: yellow oil. TLC R_f (PE/EA 10:1) = 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.36 (dd, *J* = 17.9, 11.0 Hz, 1H), 5.71 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.18 (d, *J* = 17.9 Hz, 1H), 5.14 (s, 1H), 5.09 – 5.02 (m, 2H), 4.84 (dd, *J* = 17.5, 1.1 Hz, 1H), 4.80 (dd, *J* = 10.9, 1.1 Hz, 1H), 4.10 (s, 2H), 3.28 (s, 2H), 2.43 (s, 3H), 0.63 – 0.56 (m, 2H), 0.56 – 0.49 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 140.4, 139.9, 137.7, 137.3, 129.7, 127.4, 117.2, 113.9, 112.3, 54.0, 48.0, 21.6, 21.0, 13.1. HRMS (ESI): calcd for $C_{18}H_{24}NO_2S^+$ ($[M + H]^+$) 318.1522, found 318.1520.

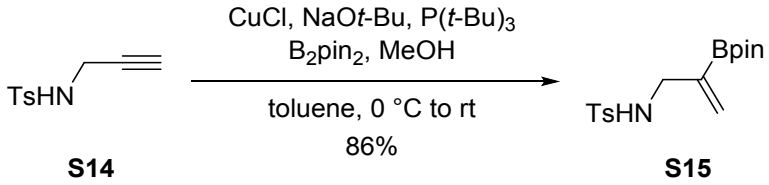


S13 **3f**

To a stirred mixture of **S13**[3] (455.4 mg, 1.45 mmol) and PPh_3 (571.8 mg, 2.18 mmol) was added a solution of **S2** (170.8 mg, 1.74 mmol) in super-dried THF (6 mL) under N_2 atmosphere. The mixture was cooled to 0 °C and DIAD (440.8 mg, 0.43 mL, 2.18 mmol) was added dropwise. Then the reaction was warmed to room temperature and stirred for 48 h. After completion, the mixture was concentrated *in vacuo*. Purification of the residue through column chromatography on silica gel (PE/EA 100:1 to 50:1) afforded **3f** (373.6 mg, 65%) as a white solid.

3f: white solid. m.p. = 75.2-77.4 °C. TLC R_f (PE/EA 5:1) = 0.49. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.38 – 7.24 (m, 7H), 5.72 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.23 (s, 1H), 5.19

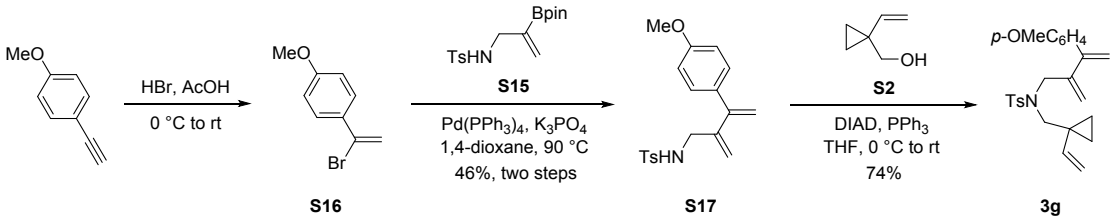
(s, 1H), 5.17 (s, 1H), 5.07 (s, 1H), 4.84 (dd, J = 17.3, 1.2 Hz, 1H), 4.79 (dd, J = 10.7, 1.2 Hz, 1H), 4.07 (s, 2H), 3.29 (s, 2H), 2.41 (s, 3H), 0.64 – 0.57 (m, 2H), 0.57 – 0.50 (m, 2H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 149.3, 143.7, 142.9, 141.0, 140.8, 138.0, 129.9, 128.5, 128.5, 128.0, 127.6, 117.5, 114.3, 112.3, 54.7, 50.5, 21.6, 21.3, 13.2. HRMS (ESI): calcd for $C_{24}H_{28}NO_2S^+$ ([M + H]$^+$) 394.1835, found 394.1834.



S14 **S15**

Following a procedure reported by Carretero et al.[5], **S14**[6] (2.09 g, 10 mmol), bis(pinacolato)diboron (2.79 g, 11 mmol), NaO*t*-Bu (43.2 mg, 0.45 mmol), and CuCl (29.7 mg, 0.3 mmol) were placed in a round-bottom flask. The flask was purged and backfilled with argon. In another flask, P(*t*-Bu)$_3$ (0.36 mL, 1 M in toluene, 0.36 mmol) was diluted with toluene (25 mL) and then transferred to the first flask. The resulted mixture was stirred at 0 °C and MeOH (640.8 mg, 0.81 mL, 20 mmol) was added dropwise. Then the reaction was warmed to room temperature and stirred for 4.5 h. After completion, the reaction was quenched with MeOH (40 mL) and then concentrated *in vacuo*. Purification of the residue through column chromatography on silica gel (PE/EA 10:1 to 5:1) afforded **S15** (2.89 g, 86%) as a white solid.

S15: white solid. m.p. = 70.9-73.1 °C. TLC R_f (PE/EA 3:1) = 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 7.8 Hz, 2H), 5.82 – 5.76 (m, 1H), 5.75 – 5.69 (m, 1H), 4.94 (t, J = 6.2 Hz, 1H), 3.69 (dt, J = 6.3, 1.4 Hz, 2H), 2.41 (s, 3H), 1.21 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 137.5, 131.6, 129.7, 127.4, 84.0, 47.8, 24.8, 21.6. HRMS (ESI): calcd for $C_{16}H_{25}BNO_4S^+$ ([M + H]$^+$) 338.1592, found 338.1591.



S16 **S17** **3g**

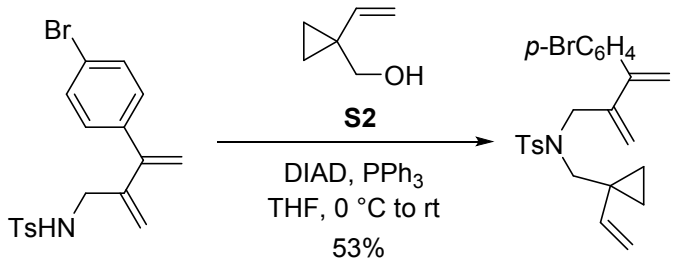
Following a procedure reported by Zuo et al.[7], to 4-ethynylanisole (1.32 g, 10 mmol) was added HBr (2.94 g, 33% in acetic acid, 12 mmol) dropwise at 0 °C. The reaction mixture was then stirred at room temperature for 1 h. After quenched by saturated $NaHCO_3$ solution, the mixture was extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product **S16** was directly used in the next step without further purification.

To a mixture of **S15** (1.69 g, 5 mmol), K_3PO_4 (4.25 g, 20 mmol) and $Pd(PPh_3)_4$ (288.9 mg, 0.25 mmol) was added a solution of the above crude product **S16** in 1,4-dioxane (25 mL) under N_2 atmosphere. The resulted mixture was stirred at 90 °C for 40 h. After quenched by saturated NH_4Cl solution, the mixture was extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. Purification of the residue through column chromatography on silica gel (PE/EA 20:1 to 10:1 to 5:1) afforded **S17** (792.5 mg,

46% for two steps) as a yellow solid.

To a stirred mixture of **S17** (780.9 mg, 2.27 mmol) and PPh_3 (894.4 mg, 3.41 mmol) was added a solution of **S2** (266.9 mg, 2.72 mmol) in super-dried THF (9 mL) under N_2 atmosphere. The mixture was cooled to 0 °C and DIAD (689.5 mg, 0.67 mL, 3.41 mmol) was added dropwise. Then the reaction was warmed to room temperature and stirred for 48 h. After completion, the mixture was concentrated *in vacuo*. Purification of the residue through column chromatography on silica gel (PE/EA 100:1 to 50:1) afforded **3g** (708.1 mg, 74%) as a white solid.

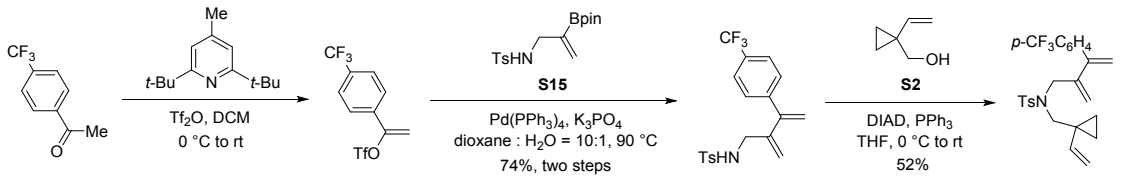
3g: white solid. m.p. = 68.1-69.3 °C. TLC R_f (PE/EA 5:1) = 0.52. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.72 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.21 (s, 1H), 5.14 (s, 1H), 5.09 (s, 1H), 5.08 (s, 1H), 4.83 (dd, *J* = 17.3, 1.2 Hz, 1H), 4.79 (dd, *J* = 10.6, 1.2 Hz, 1H), 4.05 (s, 2H), 3.80 (s, 3H), 3.29 (s, 2H), 2.41 (s, 3H), 0.64 – 0.57 (m, 2H), 0.57 – 0.50 (m, 2H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 159.8, 148.8, 143.7, 143.4, 140.8, 138.0, 133.2, 129.9, 129.5, 127.6, 117.1, 113.9, 113.1, 112.3, 55.6, 54.7, 50.6, 21.6, 21.3, 13.2. HRMS (ESI): calcd for $C_{25}H_{30}NO_3S^+$ ([M + H]$^+$) 424.1941, found 424.1943.



S18 **3h**

To a stirred mixture of **S18**[3] (750.9 mg, 1.91 mmol) and PPh_3 (752.8 mg, 2.87 mmol) was added a solution of **S2** (224.7 mg, 2.29 mmol) in super-dried THF (8 mL) under N_2 atmosphere. The mixture was cooled to 0 °C and DIAD (580.3 mg, 0.56 mL, 2.87 mmol) was added dropwise. Then the reaction was warmed to room temperature and stirred for 46 h. After completion, the mixture was concentrated *in vacuo*. Purification of the residue through column chromatography on silica gel (PE/EA 50:1) afforded **3h** (474.5 mg, 53%) as a white solid.

3h: white solid. m.p. = 76.0-77.6 °C. TLC R_f (PE/EA 5:1) = 0.51. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 5.69 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.29 (s, 1H), 5.20 (s, 1H), 5.18 (s, 1H), 5.08 (s, 1H), 4.83 (d, *J* = 17.1 Hz, 1H), 4.79 (d, *J* = 10.4 Hz, 1H), 4.08 (s, 2H), 3.30 (s, 2H), 2.42 (s, 3H), 0.66 – 0.59 (m, 2H), 0.59 – 0.51 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 143.3, 142.0, 140.3, 139.7, 137.5, 131.4, 129.9, 129.6, 127.4, 121.8, 117.8, 114.6, 112.4, 54.4, 50.1, 21.6, 21.1, 13.2. HRMS (ESI): calcd for $C_{24}H_{27}BrNO_2S^+$ ([M + H]$^+$) 472.0940, found 472.0940.



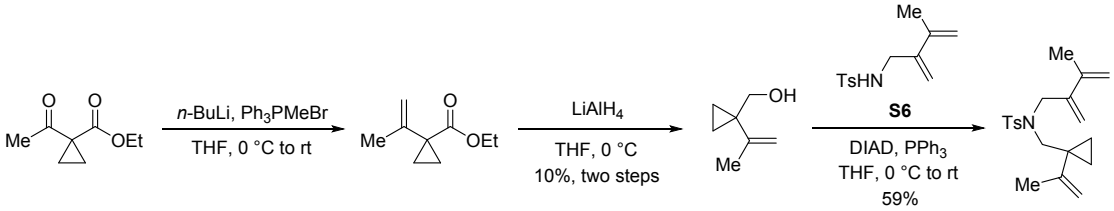
Following a procedure reported by Li et al.[8], a stirred solution of 4-(trifluoromethyl)acetophenone (1.88 g, 10 mmol) in DCM (15 mL) was cooled to 0 °C. 2,6-di-tert-butyl-4-methylpyridine (2.26 g,

11 mmol) and trifluoromethanesulfonic anhydride (3.39 g, 12 mmol) were successively added to the solution. The reaction mixture was warmed to room temperature and stirred for 12 h. Then another batch of trifluoromethanesulfonic anhydride (2.26 g, 8 mmol) was added. After stirred for further 2 h, the reaction mixture was concentrated *in vacuo*. PE was added to the residue and the mixture was filtered through a pad of silica gel and washed with PE to PE/Et_2O 10:1. The combined filtrate was washed successively with water and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product **S19** was directly used in the next step without further purification.

To a mixture of **S15** (1.69 g, 5 mmol), K_3PO_4 (4.25 g, 20 mmol) and $Pd(PPh_3)_4$ (288.9 mg, 0.25 mmol) was added a solution of the above crude product **S19** in 1,4-dioxane (25 mL) and water (2.5 mL) under N_2 atmosphere. The resulted mixture was stirred at 90 °C for 20 h. After quenched by saturated NH_4Cl solution, the mixture was extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. Purification of the residue through column chromatography on silica gel (PE/EA 50:1 to 20:1 to 10:1 to 5:1) afforded **S20** (1.4163 g, 74% for two steps) as an orange solid.

To a stirred mixture of **S20** (1.0082 g, 2.64 mmol) and PPh_3 (1.04 g, 3.96 mmol) was added a solution of **S2** (311.1 mg, 3.17 mmol) in super-dried THF (10 mL) under N_2 atmosphere. The mixture was cooled to 0 °C and DIAD (800.8 mg, 0.78 mL, 3.96 mmol) was added dropwise. Then the reaction was warmed to room temperature and stirred for 45 h. After completion, the mixture was concentrated *in vacuo*. Purification of the residue through column chromatography on silica gel (PE/EA 100:1 to 50:1) afforded **3i** (633.0 mg, 74%) as a yellow solid.

3i: yellow solid. m.p. = 59.3-60.8 °C. TLC R_f (PE/EA 10:1) = 0.44. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 5.70 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.33 (s, 1H), 5.30 (s, 1H), 5.24 (s, 1H), 5.07 (s, 1H), 4.84 (dd, *J* = 17.3, 1.1 Hz, 1H), 4.80 (dd, *J* = 10.6, 1.1 Hz, 1H), 4.10 (s, 2H), 3.31 (s, 2H), 2.42 (s, 3H), 0.67 – 0.60 (m, 2H), 0.60 – 0.53 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.8, 144.5, 143.4, 141.9, 140.3, 137.5, 129.8 (q, *J* = 32.4 Hz), 129.7, 128.6, 127.5, 125.3 (q, *J* = 3.9 Hz), 124.3 (q, *J* = 272.1 Hz), 118.1, 115.5, 112.4, 54.5, 50.1, 21.6, 21.1, 13.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.5. HRMS (ESI): calcd for $C_{25}H_{27}F_3NO_2S^+$ ($[M + H]^+$) 462.1709, found 462.1706.



S21 **S22** **S23** **3j**

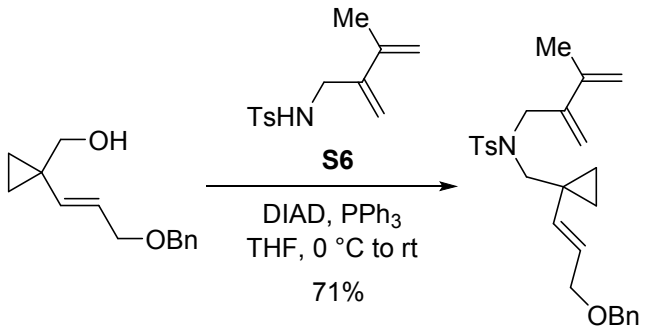
To a stirred solution of Ph_3PMeBr (9.17 g, 25.66 mmol) in super-dried THF (40 mL) was added *n*-BuLi (10.7 mL, 2.4 M in hexane, 25.66 mmol) under N_2 atmosphere at 0 °C. After stirred at 0 °C for 1 h, this mixture was added to a solution of **S21**[9] (3.34 g, 21.38 mmol) in THF (20 mL) under N_2 atmosphere. The resulted mixture was then stirred at room temperature for 11.5 h. After quenched by saturated NH_4Cl solution, the mixture was extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* at temperature below 15 °C. *n*-Pentane was added to the residue and white precipitation generated. The mixture was filtered through a pad of silica gel and washed with *n*-pentane/Et_2O 10:1. The

combined filtrate was concentrated *in vacuo* at temperature below 15 °C and the crude product **S22** was directly used in the next step without further purification.

To a suspension of $LiAlH_4$ (0.97 g, 25.66 mmol) in super-dried THF (15 mL) was added a solution of the above crude product **S22** in super-dried THF (15 mL) under N_2 atmosphere at 0 °C. The resulted mixture was then stirred at 0 °C for 2.5 h. After completion, the reaction was quenched with saturated NH_4Cl solution and saturated potassium sodium tartrate solution. The mixture was then extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. Purification of the residue through column chromatography on silica gel (PE/EA 5:1) afforded **S23** (244.5 mg, 10% for two steps) as a yellow liquid.

To a stirred mixture of **S6**[2] (586.1 mg, 2.33 mmol) and PPh_3 (834.1 mg, 3.18 mmol) was added a solution of **S23** (237.3 mg, 2.12 mmol) in super-dried THF (10 mL) under N_2 atmosphere. The mixture was cooled to 0 °C and DIAD (643.0 mg, 3.18 mmol) was added dropwise. Then the reaction was warmed to room temperature and stirred for 37 h. After completion, the mixture was concentrated *in vacuo*. Purification of the residue through column chromatography on silica gel (PE/EA 50:1) afforded **3j** (432.7 mg, 59%) as a white solid.

3j: white solid. m.p. = 58.0-59.7 °C. TLC R_f (PE/EA 5:1) = 0.56. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 5.22 (s, 1H), 5.03 (s, 1H), 4.97 (s, 1H), 4.96 (s, 1H), 4.73 – 4.68 (m, 1H), 4.67 (s, 1H), 4.21 (s, 2H), 3.29 (s, 2H), 2.42 (s, 3H), 1.91 (s, 3H), 1.60 (s, 3H), 0.57 – 0.48 (m, 2H), 0.48 – 0.40 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 143.1, 141.7, 140.7, 138.1, 129.5, 127.5, 113.4, 113.2, 112.4, 52.4, 48.5, 25.3, 21.7, 21.6, 20.5, 11.3. HRMS (ESI): calcd for $C_{20}H_{28}NO_2S^+$ ($[M + H]^+$) 346.1835, found 346.1835.

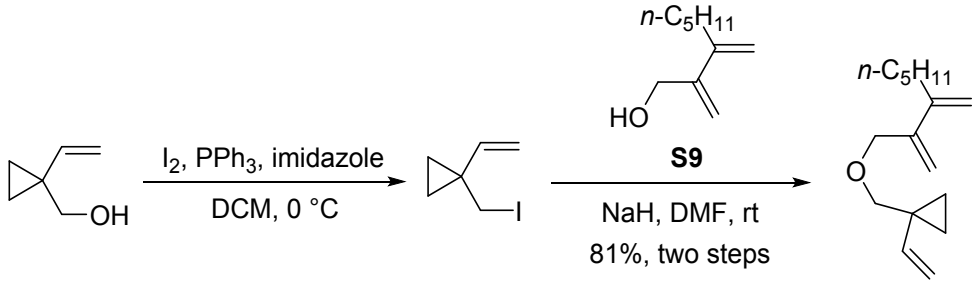


S24 **3k**

To a stirred mixture of **S24**[10] (543.6 mg, 2.49 mmol) and PPh_3 (981.0 mg, 3.74 mmol) was added a solution of **S6**[2] (688.3 mg, 2.74 mmol) in super-dried THF (10 mL) under N_2 atmosphere. The mixture was cooled to 0 °C and DIAD (756.3 mg, 0.73 mL, 3.74 mmol) was added dropwise. Then the reaction was warmed to room temperature and stirred for 41 h. After completion, the mixture was concentrated *in vacuo*. Purification of the residue through column chromatography on silica gel (PE/EA 50:1 to 20:1) afforded **3k** (795.1 mg, 71%) as a colorless oil.

3k: colorless oil. TLC R_f (PE/EA 5:1) = 0.41. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.38 – 7.27 (m, 5H), 7.27 – 7.26 (m, 1H), 7.25 – 7.23 (m, 1H), 5.55 (dt, *J* = 15.7, 1.3 Hz, 1H), 5.35 (dt, *J* = 15.6, 6.1 Hz, 1H), 5.24 (s, 1H), 5.11 (s, 1H), 4.98 (s, 2H), 4.43 (s, 2H) , 4.13 (s, 2H), 3.80 (dd, *J* = 6.1, 1.3 Hz, 2H), 3.26 (s, 2H), 2.38 (s, 3H), 1.90 (s, 3H), 0.64 – 0.56 (m, 2H), 0.56 – 0.48 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 141.5, 141.0, 138.5, 137.7, 136.0, 129.7, 128.5,

127.9, 127.7, 127.4, 124.4, 113.8, 112.7, 72.1, 70.8, 54.1, 49.3, 21.6, 21.6, 20.0, 13.3. HRMS (ESI): calcd for $C_{27}H_{34}NO_3S^+$ ([M + H]$^+$) 452.2254, found 452.2251.

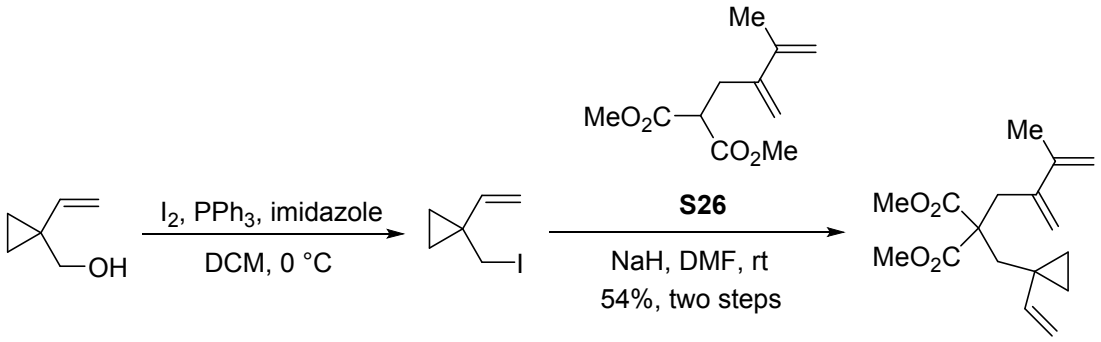


S2 **S25** **3l**

To a stirred solution of **S2** (196.3 mg, 2 mmol), PPh_3 (629.5 mg, 2.4 mmol) and imidazole (204.2 mg, 3 mmol) in DCM (5 mL) was added I_2 (761.4 mg, 3 mmol) at 0 °C. The resulted mixture was stirred at 0 °C for 15 min. After quenched by saturated $Na_2S_2O_3$ solution, the mixture was extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* at 0 °C. *n*-Pentane was added to the residue and white precipitation generated. The mixture was filtered through a pad of silica gel and washed with *n*-pentane/Et_2O 50:1. The combined filtrate was concentrated *in vacuo* at 0 °C and the crude product **S25** was directly used in the next step without further purification.

To NaH (60.0 mg, 60% weight in mineral oil, 1.5 mmol) was added a solution of **S9** (154.3 mg, 1.0 mmol) in super-dried DMF (3 mL) under N_2 atmosphere. The mixture was stirred for 10 min at room temperature before a solution of the above crude product **S25** in super-dried DMF (3 mL) was added. Then the reaction mixture was stirred at room temperature for 41 h. After quenched by saturated NH_4Cl solution, the mixture was extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (PE/EA 100:1) to afford **3l** (188.7 mg, 81% for two steps) as a yellow liquid.

3l: yellow liquid. TLC R_f (PE/EA 10:1) = 0.82. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.67 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.24 (s, 1H), 5.21 (s, 1H), 5.15 (s, 1H), 5.05 (dd, *J* = 17.4, 1.3 Hz, 1H), 4.97 (s, 1H), 4.95 (dd, *J* = 10.7, 1.3 Hz, 1H), 4.17 (s, 2H), 3.40 (s, 2H), 2.28 – 2.20 (m, 2H), 1.51 – 1.39 (m, 2H), 1.38 – 1.23 (m, 4H), 0.89 (t, *J* = 6.8 Hz, 3H), 0.74 – 0.69 (m, 2H), 0.69 – 0.63 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0, 143.9, 142.0, 113.8, 112.4, 111.4, 74.9, 72.5, 34.2, 31.9, 28.4, 22.7, 22.7, 14.2, 12.7. HRMS (ESI): calcd for $C_{16}H_{27}O^+$ ([M + H]$^+$) 235.2056, found 235.2055.

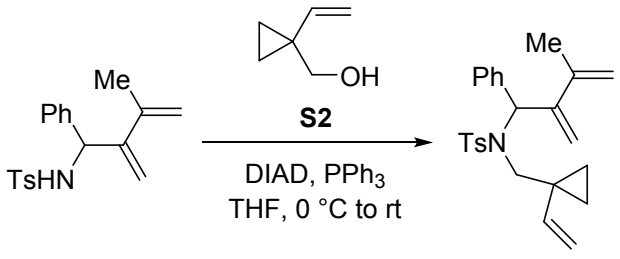


S2 **S25** **3m**

To a stirred solution of **S2** (912.7 mg, 9.30 mmol), PPh_3 (2.93 g, 11.16 mmol) and imidazole (0.95 g, 13.95 mmol) in DCM (20 mL) was added I_2 (3.54 g, 13.95 mmol) at 0 °C. The resulted mixture was stirred at 0 °C for 30 min. After quenched by saturated $Na_2S_2O_3$ solution, the mixture was extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* at 0 °C. *n*-Pentane was added to the residue and white precipitation generated. The mixture was filtered through a pad of silica gel and washed with *n*-pentane/Et_2O 50:1. The combined filtrate was concentrated *in vacuo* at 0 °C and the crude product **S25** was directly used in the next step without further purification.

To NaH (372.0 mg, 60% weight in mineral oil, 9.30 mmol) was added a solution of **S26**[2] (394.0 mg, 1.86 mmol) in super-dried DMF (6 mL) under N_2 atmosphere. The mixture was stirred for 10 min at room temperature before a solution of the above crude product **S25** in super-dried DMF (6 mL) was added. Then the reaction mixture was stirred at room temperature for 42 h. After quenched by saturated NH_4Cl solution, the mixture was extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (PE/EA 100:1 to 50:1) to afford **3m** (292.4 mg, 54% for two steps) as a yellow liquid.

3m: yellow liquid. TLC R_f (PE/EA 10:1) = 0.34. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 (dd, *J* = 17.0, 10.5 Hz, 1H), 5.18 (s, 1H), 5.00 (s, 1H), 4.97 (s, 1H), 4.92 (s, 1H), 4.81 (dd, *J* = 10.6, 1.4 Hz, 1H), 4.79 (dd, *J* = 17.0, 1.3 Hz, 1H), 3.64 (s, 6H), 3.01 (s, 2H), 2.17 (s, 2H), 1.86 (s, 3H), 0.62 – 0.55 (m, 2H), 0.55 – 0.48 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 144.0, 143.8, 141.9, 115.2, 112.8, 111.7, 57.2, 52.2, 41.1, 36.8, 21.7, 20.4, 13.7. HRMS (ESI): calcd for $C_{17}H_{25}O_4^+$ ($[M + H]^+$) 293.1747, found 293.1740.

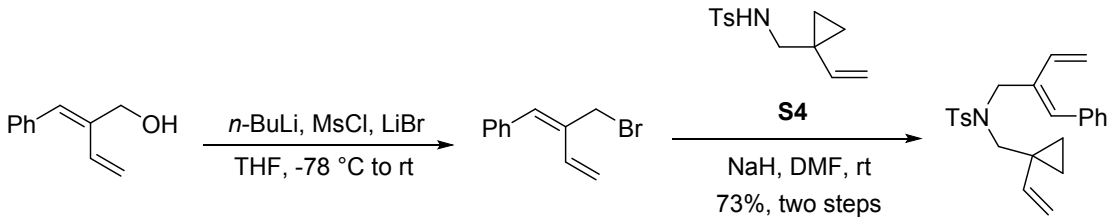


S27 **3n**

To a stirred mixture of **S27**[3] (392.3 mg, 1.20 mmol) and PPh_3 (472.1 mg, 1.80 mmol) was added a solution of **S2** (141.3 mg, 1.44 mmol) in super-dried THF (6 mL) under N_2 atmosphere. The mixture was cooled to 0 °C and DIAD (364.0 mg, 0.35 mL, 1.80 mmol) was added dropwise. Then the

reaction was warmed to room temperature and stirred for 48 h. After completion, the mixture was concentrated *in vacuo*. Purification of the residue through column chromatography on silica gel (PE/EA 100:1 to 50:1) afforded **3n** (281.6 mg, 58%) as a yellow solid.

3n: yellow solid. m.p. = 69.8-71.8 °C. TLC R_f (PE/EA 5:1) = 0.69. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.22 – 7.16 (m, 3H), 7.14 (d, *J* = 8.2 Hz, 2H), 7.10 – 7.04 (m, 2H), 5.92 (s, 1H), 5.69 (dd, *J* = 17.2, 10.6 Hz, 1H), 5.53 (s, 1H), 5.45 (s, 1H), 4.86 (s, 1H), 4.80 (s, 1H), 4.69 (dd, *J* = 10.6, 1.3 Hz, 1H), 4.60 (dd, *J* = 17.2, 1.3 Hz, 1H), 3.66 (d, *J* = 15.0 Hz, 1H), 3.15 (d, *J* = 14.9 Hz, 1H), 2.38 (s, 3H), 1.87 (s, 3H), 0.65 – 0.53 (m, 2H), 0.50 – 0.41 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 142.7, 141.5, 140.9, 138.7, 137.8, 130.4, 129.1, 128.2, 127.8, 127.6, 117.0, 114.5, 111.4, 64.5, 54.2, 22.3, 22.0, 21.6, 14.6, 13.9. HRMS (ESI): calcd for $C_{25}H_{29}KNO_2S^+$ ($[M + K]^+$) 446.1551, found 446.1553.

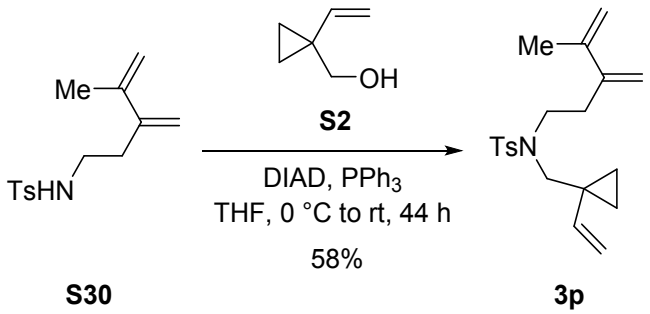


S28 **S29** **3o**

To a stirred solution of **S28**[11] (244.7 mg, 1.53 mmol) in super-dried THF (8 mL) was added *n*-BuLi (0.70 mL, 2.4 M in hexane, 1.68 mmol) dropwise under N_2 atmosphere at -78 °C. After stirred for 15 min, methanesulfonyl chloride (192.4 mg, 0.13 mL, 1.68 mmol) was added dropwise. After stirred for further 20 min at -78 °C, LiBr (398.6 mg, 4.59 mmol) was added. Then the reaction mixture was warmed to room temperature and stirred for 3 h. The solution of the corresponding product **S29** was directly used in the next step without further purification.

To NaH (94.4 mg, 60% weight in mineral oil, 2.36 mmol) was added a solution of **S4** (296.6 mg, 1.18 mmol) in super-dried DMF (6 mL) under N_2 atmosphere. After stirred for 5 min at room temperature, the solution of the above crude product **S29** was transferred to the reaction mixture. Then the reaction mixture was stirred at room temperature for 24 h. After quenched by saturated NH_4Cl solution, the mixture was extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (PE/EA 100:1 to 50:1) to afford **3o** (338.7 mg, 73% for two steps) as a yellow solid.

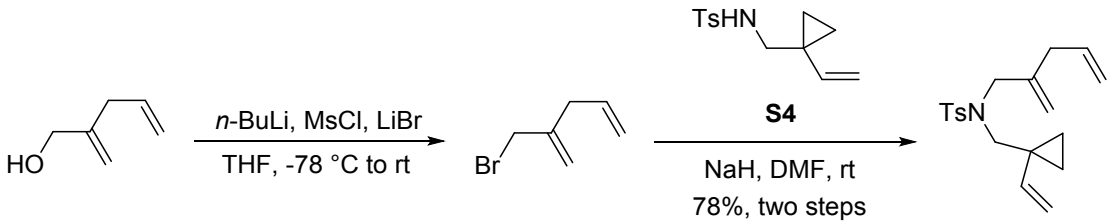
3o: yellow solid. m.p. = 64.5-66.3 °C. TLC R_f (PE/EA 5:1) = 0.44. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.27 (m, 4H), 7.25 – 7.19 (m, 1H), 7.17 – 7.11 (m, 2H), 6.73 (dd, *J* = 17.9, 11.4 Hz, 1H), 6.47 (s, 1H), 5.79 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.31 (d, *J* = 17.9 Hz, 1H), 5.17 (d, *J* = 11.1 Hz, 1H), 4.92 (dd, *J* = 17.3, 1.1 Hz, 1H), 4.86 (dd, *J* = 10.6, 1.1 Hz, 1H), 4.19 (s, 2H), 3.34 (s, 2H), 2.42 (s, 3H), 0.66 – 0.60 (m, 2H), 0.60 – 0.54 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 140.7, 137.5, 136.8, 133.4, 131.8, 130.1, 129.8, 129.6, 128.2, 127.4, 127.1, 115.4, 112.3, 54.8, 49.9, 21.6, 21.1, 13.4. HRMS (ESI): calcd for $C_{24}H_{28}NO_2S^+$ ($[M + H]^+$) 394.1835, found 394.1836.



S30 **3p**

To a stirred mixture of **S30**[2] (741.7 mg, 2.79 mmol) and PPh_3 (999.3 mg, 3.81 mmol) was added a solution of **S2** (249.3 mg, 2.54 mmol) in super-dried THF (10 mL) under N_2 atmosphere. The mixture was cooled to 0 °C and DIAD (770.4 mg, 0.75 mL, 3.81 mmol) was added dropwise. Then the reaction was warmed to room temperature and stirred for 44 h. After completion, the mixture was concentrated *in vacuo*. Purification of the residue through column chromatography on silica gel (PE/EA 50:1) afforded **3p** (512.1 mg, 58%) as a white solid.

3p: white solid. m.p. = 36.7-38.2 °C. TLC R_f (PE/EA 10:1) = 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 5.91 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.20 (s, 1H), 5.09 (s, 1H), 5.04 – 5.00 (m, 1H), 5.00 (dd, *J* = 17.3, 1.1 Hz, 1H), 4.93 (s, 1H), 4.93 (dd, *J* = 10.7, 1.1 Hz, 1H), 3.27 – 3.18 (m, 2H), 3.24 (s, 2H), 2.65 – 2.56 (m, 2H), 2.41 (s, 3H), 1.90 – 1.85 (m, 3H), 0.78 – 0.72 (m, 2H), 0.68 – 0.61 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 143.2, 142.0, 140.5, 137.1, 129.7, 127.3, 113.9, 113.6, 112.5, 55.3, 48.7, 33.7, 21.6, 21.3, 21.1, 13.5. HRMS (ESI): calcd for $C_{20}H_{28}NO_2S^+$ ($[M + H]^+$) 346.1835, found 346.1834.



S31 **S32** **3q**

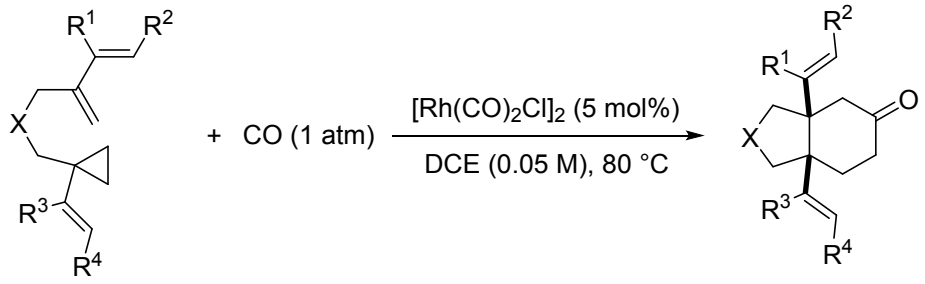
To a stirred solution of **S31**[12] (127.6 mg, 1.3 mmol) in super-dried THF (7 mL) was added *n*-BuLi (0.60 mL, 2.4 M in hexane, 1.43 mmol) dropwise under N_2 atmosphere at -78 °C. After stirred for 15 min, methanesulfonyl chloride (163.8 mg, 0.11 mL, 1.43 mmol) was added dropwise. After stirred for further 20 min at -78 °C, LiBr (338.7 mg, 3.9 mmol) was added. Then the reaction mixture was warmed to room temperature and stirred for 3 h. The solution of the corresponding product **S32** directly used in the next step without further purification.

To NaH (80.0 mg, 60% weight in mineral oil, 2.0 mmol) was added a solution of **S4** (251.3 mg, 1.0 mmol) in super-dried DMF (5 mL) under N_2 atmosphere. After stirred for 5 min at room temperature, the solution of the above crude product **S32** was transferred to the reaction mixture. Then the reaction mixture was stirred at room temperature for 24 h. After quenched by saturated NH_4Cl solution, the mixture was extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (PE/EA 100:1) to afford **3q** (258.1 mg, 78% for two steps) as a yellow oil.

3q: yellow oil. TLC R_f (PE/EA 5:1) = 0.48. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H),

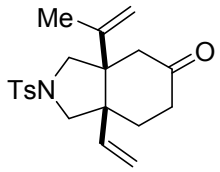
7.28 (d, J = 8.1 Hz, 2H), 5.84 – 5.72 (m, 2H), 5.07 (s, 1H), 5.06 – 5.01 (m, 1H), 4.92 – 4.89 (m, 1H), 4.87 (s, 1H), 4.83 (dd, J = 17.2, 1.2 Hz, 1H), 4.80 (dd, J = 10.6, 1.2 Hz, 1H), 3.85 (s, 2H), 3.24 (s, 2H), 2.71 (d, J = 6.9 Hz, 2H), 2.42 (s, 3H), 0.65 – 0.59 (m, 2H), 0.59 – 0.53 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 142.6, 140.4, 137.7, 135.5, 129.6, 127.4, 116.9, 112.9, 112.3, 54.2, 52.3, 38.2, 21.6, 21.2, 13.5. HRMS (ESI): calcd for $C_{19}H_{26}NO_2S^+$ ($[M + H]^+$) 332.1679, found 332.1677.

3. Rhodium-Catalyzed [3+1+2] Cycloaddition



3 **4**

General procedure: A solution of substrate (0.10 mmol) and $[Rh(CO)_2Cl]_2$ (1.9 mg, 5 μmol, 5 mol%) in super-dried DCE (2 mL, 0.05 M) was bubbled with CO (1 atm) for 5 min. The reaction mixture was stirred at 80 °C under balloon pressure gas of CO (1 atm) until TLC indicated complete consumption of the starting material. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. Purification of the residue through column chromatography on silica gel afforded the corresponding [3+1+2] product.



4a

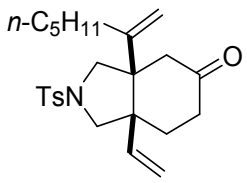
Reaction time: 24 h. Eluted with PE/EA 10:1 to 5:1.

Run 1: **3a** (32.9 mg) and $[Rh(CO)_2Cl]_2$ (1.9 mg) were used, **4a** (32.4 mg, 91%) was obtained.

Run 2: **3a** (33.1 mg) and $[Rh(CO)_2Cl]_2$ (2.0 mg) were used, **4a** (31.7 mg, 88%) was obtained.

Average yield of two runs: 90%.

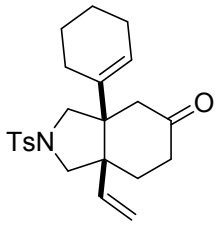
4a: white solid. m.p. = 84.7-86.5 °C. TLC R_f (PE/EA 3:1) = 0.24. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.62 (dd, *J* = 17.5, 11.0 Hz, 1H), 4.98 (d, *J* = 11.0 Hz, 1H), 4.88 (s, 1H), 4.85 (d, *J* = 17.8 Hz, 1H), 4.63 (s, 1H), 3.56 (d, *J* = 10.4 Hz, 1H), 3.51 (d, *J* = 9.9 Hz, 1H), 3.44 (d, *J* = 10.4 Hz, 1H), 3.20 (d, *J* = 9.8 Hz, 1H), 2.42 (s, 3H), 2.40 – 2.30 (m, 2H), 2.34 (d, *J* = 15.1 Hz, 1H), 2.26 (d, *J* = 15.1 Hz, 1H), 2.06 (ddd, *J* = 14.6, 9.3, 7.1 Hz, 1H), 1.77 (dt, *J* = 14.7, 5.8 Hz, 1H), 1.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.5, 145.0, 144.0, 139.8, 134.3, 130.0, 127.3, 114.6, 114.6, 56.6, 55.2, 54.3, 47.7, 47.2, 36.4, 30.1, 22.7, 21.7. HRMS (ESI): calcd for $C_{20}H_{26}NO_3S^+$ ($[M + H]^+$) 360.1628, found 360.1621.



4b

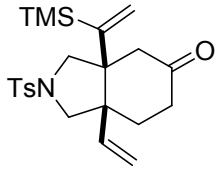
Reaction time: 48 h. Eluted with PE/EA 20:1 to 10:1 to 5:1.

Run 1: **3b** (38.8 mg) and $[Rh(CO)_2Cl]_2$ (2.0 mg) were used, **4b** (28.4 mg, 68%) was obtained.
Run 2: **3b** (38.8 mg) and $[Rh(CO)_2Cl]_2$ (1.9 mg) were used, **4b** (28.3 mg, 68%) was obtained.
Average yield of two runs: 68%.
4b: yellow oil. TLC R_f (PE/EA 3:1) = 0.27. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 5.59 (dd, *J* = 17.6, 11.0 Hz, 1H), 4.98 (d, *J* = 11.0 Hz, 1H), 4.92 (s, 1H), 4.85 (d, *J* = 17.5 Hz, 1H), 4.74 (s, 1H), 3.54 (d, *J* = 9.9 Hz, 1H), 3.53 (d, *J* = 10.3 Hz, 1H), 3.43 (d, *J* = 10.4 Hz, 1H), 3.21 (d, *J* = 9.9 Hz, 1H), 2.43 (s, 3H), 2.41 – 2.30 (m, 2H), 2.37 (d, *J* = 15.2 Hz, 1H), 2.22 (d, *J* = 15.6 Hz, 1H), 2.11 – 2.00 (m, 1H), 1.87 – 1.70 (m, 3H), 1.39 – 1.14 (m, 6H), 0.86 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.5, 149.3, 144.0, 139.9, 134.3, 130.0, 127.3, 114.5, 112.8, 56.4, 55.7, 54.2, 47.9, 47.3, 36.4, 34.1, 31.7, 30.0, 28.3, 22.6, 21.7, 14.1. HRMS (ESI): calcd for $C_{24}H_{34}NO_3S^+$ ($[M + H]^+$) 416.2254, found 416.2252.



4c

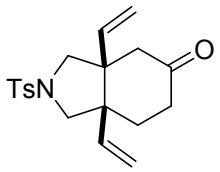
Reaction time: 72 h. Eluted with PE/EA 10:1 to 5:1.
Run 1: **3c** (37.2 mg) and $[Rh(CO)_2Cl]_2$ (1.9 mg) were used, **4c** (30.9 mg, 77%) was obtained.
Run 2: **3c** (37.3 mg) and $[Rh(CO)_2Cl]_2$ (2.0 mg) were used, **4c** (29.2 mg, 73%) was obtained.
Average yield of two runs: 75%.
4c: white foam. TLC R_f (PE/EA 3:1) = 0.29. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 5.62 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.35 (t, *J* = 4.0 Hz, 1H), 4.98 (d, *J* = 11.0 Hz, 1H), 4.85 (d, *J* = 17.6 Hz, 1H), 3.50 (d, *J* = 9.9 Hz, 1H), 3.49 (d, *J* = 10.4 Hz, 1H), 3.41 (d, *J* = 10.3 Hz, 1H), 3.16 (d, *J* = 9.9 Hz, 1H), 2.43 (s, 3H), 2.41 – 2.28 (m, 2H), 2.37 (d, *J* = 15.2 Hz, 1H), 2.22 (d, *J* = 15.2 Hz, 1H), 2.04 (ddd, *J* = 15.4, 9.7, 6.2 Hz, 1H), 1.99 – 1.88 (m, 2H), 1.83 – 1.66 (m, 3H), 1.58 – 1.38 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.1, 143.9, 139.9, 137.5, 134.3, 130.0, 127.4, 125.0, 114.3, 56.4, 55.4, 54.5, 48.0, 47.2, 36.5, 30.3, 27.6, 25.6, 22.9, 21.8, 21.7. HRMS (ESI): calcd for $C_{23}H_{30}NO_3S^+$ ($[M + H]^+$) 400.1941, found 400.1939.



4d

Reaction time: 23 h. Eluted with PE/EA 20:1 to 10:1 to 5:1.
Run 1: **3d** (38.9 mg) and $[Rh(CO)_2Cl]_2$ (1.8 mg) were used, **4d** (39.0 mg, 94%) was obtained.
Run 2: **3d** (39.1 mg) and $[Rh(CO)_2Cl]_2$ (1.9 mg) were used, **4d** (41.2 mg, 98%) was obtained.
Average yield of two runs: 96%.
4d: yellow oil. TLC R_f (PE/EA 5:1) = 0.12. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 5.59 (s, 1H), 5.55 (d, *J* = 17.6, 11.0 Hz, 1H), 5.51 (s, 1H), 4.93 (d, *J* = 11.0

Hz, 1H), 4.77 (d, *J* = 17.6 Hz, 1H), 3.55 (d, *J* = 10.5 Hz, 1H), 3.53 (d, *J* = 9.5 Hz, 1H), 3.44 (d, *J* = 10.4 Hz, 1H), 3.31 (d, *J* = 9.6 Hz, 1H), 2.43 (s, 3H), 2.39 (dd, *J* = 8.5, 5.7 Hz, 2H), 2.29 (d, *J* = 14.9 Hz, 1H), 2.23 (d, *J* = 14.9 Hz, 1H), 2.06 (dt, *J* = 14.8, 8.4 Hz, 1H), 1.76 (dt, *J* = 14.8, 5.7 Hz, 1H), 0.08 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.1, 152.9, 144.0, 140.5, 134.3, 130.0, 129.4, 127.3, 114.5, 57.5, 55.9, 53.3, 48.8, 48.6, 36.5, 29.8, 21.7, 1.3. HRMS (ESI): calcd for $C_{22}H_{32}NO_3SSi^+$ ([M + H]$^+$) 418.1867, found 418.1866.



4e

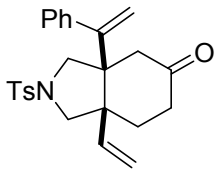
Reaction time: 24 h. Eluted with PE/EA 10:1 to 5:1.

Run 1: **3e** (31.7 mg) and $[Rh(CO)_2Cl]_2$ (1.9 mg) were used, **4e** (32.0 mg, 93%) was obtained.

Run 2: **3e** (31.6 mg) and $[Rh(CO)_2Cl]_2$ (1.9 mg) were used, **4e** (33.7 mg, 98%) was obtained.

Average yield of two runs: 96%.

4e: yellow solid. m.p. = 101.2-103.6 °C. TLC R_f (PE/EA 3:1) = 0.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.77 (dd, *J* = 17.6, 11.1 Hz, 1H), 5.58 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.15 (d, *J* = 11.1 Hz, 1H), 5.08 (d, *J* = 11.0 Hz, 1H), 5.00 (d, *J* = 17.6 Hz, 1H), 4.95 (d, *J* = 17.5 Hz, 1H), 3.51 – 3.40 (m, 2H), 3.36 (d, *J* = 10.1 Hz, 1H), 3.16 (d, *J* = 10.2 Hz, 1H), 2.43 (s, 3H), 2.40 – 2.30 (m, 1H), 2.36 (d, *J* = 15.0 Hz, 1H), 2.29 – 2.21 (m, 1H), 2.19 (d, *J* = 15.0 Hz, 1H), 1.88 (ddd, *J* = 13.8, 7.6, 5.8 Hz, 1H), 1.68 (ddd, *J* = 14.7, 9.2, 5.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.8, 143.9, 138.3, 137.8, 134.4, 130.0, 127.3, 116.3, 116.2, 55.6, 54.4, 53.0, 48.2, 44.4, 37.0, 30.5, 21.7. HRMS (ESI): calcd for $C_{19}H_{24}NO_3S^+$ ([M + H]$^+$) 346.1471, found 346.1471.



4f

Reaction time: 72 h. Eluted with PE/EA 10:1 to 5:1.

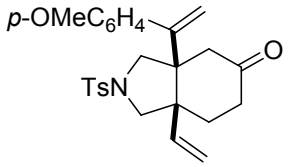
Run 1: **3f** (39.4 mg) and $[Rh(CO)_2Cl]_2$ (2.0 mg) were used, **4f** (35.6 mg, 84%) was obtained.

Run 2: **3f** (39.5 mg) and $[Rh(CO)_2Cl]_2$ (2.0 mg) were used, **4f** (36.0 mg, 85%) was obtained.

Average yield of two runs: 85%.

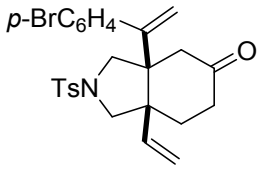
4f: white solid. m.p. = 100.3-101.4 °C. TLC R_f (PE/EA 3:1) = 0.20. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.30 – 7.21 (m, 3H), 7.08 – 6.99 (m, 2H), 5.79 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.07 (s, 1H), 5.02 (s, 1H), 5.01 (d, *J* = 11.0 Hz, 1H), 4.86 (d, *J* = 17.6 Hz, 1H), 3.67 (d, *J* = 10.4 Hz, 1H), 3.44 (d, *J* = 10.4 Hz, 1H), 3.37 (d, *J* = 10.0 Hz, 1H), 3.16 (d, *J* = 10.0 Hz, 1H), 2.48 (d, *J* = 15.1 Hz, 1H), 2.42 (s, 3H), 2.40 – 2.34 (m, 1H), 2.33 – 2.24 (m, 1H), 2.29 (d, *J* = 15.2 Hz, 1H), 2.03 (ddd, *J* = 14.5, 11.5, 5.7 Hz, 1H), 1.84 (ddd, *J* = 14.7, 7.0, 3.8 Hz, 1H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 208.5, 150.8, 144.4, 142.4, 141.1, 134.7, 130.2, 129.0, 128.2, 127.6, 127.5, 118.8, 114.8, 57.7, 54.9, 54.5, 48.7, 48.4, 36.6, 29.6, 21.7. HRMS (ESI): calcd for

$C_{25}H_{28}NO_3S^+$ ([M + H]$^+$) 422.1784, found 422.1783.



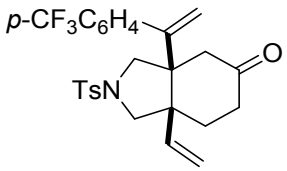
4g

Reaction time: 72 h. Eluted with PE/EA 10:1 to 5:1.
Run 1: **3g** (42.5 mg) and $[Rh(CO)_2Cl]_2$ (1.9 mg) were used, **4g** (39.2 mg, 87%) was obtained.
Run 2: **3g** (42.5 mg) and $[Rh(CO)_2Cl]_2$ (2.0 mg) were used, **4g** (41.2 mg, 91%) was obtained.
Average yield of two runs: 89%.
4g: yellow solid. m.p. = 123.3-125.2 °C. TLC R_f (PE/EA 3:1) = 0.17. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.76 (d, *J* = 8.7 Hz, 2H), 5.78 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.04 (s, 1H), 5.01 (d, *J* = 11.0 Hz, 1H), 5.00 (s, 1H), 4.84 (d, *J* = 17.5 Hz, 1H), 3.78 (s, 3H), 3.65 (d, *J* = 10.4 Hz, 1H), 3.45 (d, *J* = 10.3 Hz, 1H), 3.44 (d, *J* = 10.1 Hz, 1H), 3.19 (d, *J* = 10.1 Hz, 1H), 2.49 (d, *J* = 15.2 Hz, 1H), 2.42 (s, 3H), 2.39 – 2.24 (m, 2H), 2.29 (d, *J* = 15.1 Hz, 1H), 1.98 (ddd, *J* = 14.7, 11.0, 6.3 Hz, 1H), 1.81 (ddd, *J* = 14.7, 6.8, 4.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.7, 158.8, 149.9, 143.9, 140.7, 134.5, 134.1, 129.9, 129.9, 127.2, 118.7, 114.8, 113.3, 57.4, 55.3, 54.9, 54.2, 48.3, 48.0, 36.3, 29.4, 21.7. HRMS (ESI): calcd for $C_{26}H_{30}NO_4S^+$ ([M + H]$^+$) 452.1890, found 452.1890.



4h

Reaction time: 108 h. Eluted with PE/EA 20:1 to 10:1 to 5:1.
Run 1: **3h** (47.2 mg) and $[Rh(CO)_2Cl]_2$ (2.0 mg) were used, **4h** (39.6 mg, 79%) was obtained.
Run 2: **3h** (47.2 mg) and $[Rh(CO)_2Cl]_2$ (1.9 mg) were used, **4h** (39.0 mg, 78%) was obtained.
Average yield of two runs: 79%.
4h: white solid. m.p. = 80.8-82.6 °C. TLC R_f (PE/EA 3:1) = 0.20. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.66 (d, *J* = 7.9 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 5.75 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.10 (s, 1H), 5.03 (s, 1H), 5.02 (d, *J* = 9.9 Hz, 1H), 4.86 (d, *J* = 17.5 Hz, 1H), 3.66 (d, *J* = 10.3 Hz, 1H), 3.42 (d, *J* = 10.3 Hz, 1H), 3.36 (d, *J* = 10.0 Hz, 1H), 3.17 (d, *J* = 10.0 Hz, 1H), 2.51 – 2.36 (m, 2H), 2.43 (s, 3H), 2.36 – 2.25 (m, 2H), 2.00 (ddd, *J* = 16.8, 11.3, 5.9 Hz, 1H), 1.84 (ddd, *J* = 14.9, 7.0, 4.1 Hz, 1H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 208.4, 149.7, 144.5, 141.3, 140.9, 134.6, 131.3, 130.8, 130.3, 127.5, 121.7, 119.5, 115.1, 57.5, 54.9, 54.6, 48.7, 48.3, 36.6, 29.7, 21.7. HRMS (ESI): calcd for $C_{25}H_{27}BrNO_3S^+$ ([M + H]$^+$) 500.0890, found 500.0888.



4i

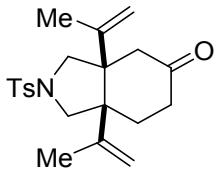
Reaction time: 144 h. Eluted with PE/EA 10:1 to 5:1.

Run 1: **3i** (46.3 mg) and $[Rh(CO)_2Cl]_2$ (1.9 mg) were used, **4i** (37.7 mg, 77%) was obtained.

Run 2: **3i** (46.2 mg) and $[Rh(CO)_2Cl]_2$ (1.9 mg) were used, **4i** (37.7 mg, 77%) was obtained.

Average yield of two runs: 77%.

4i: yellow solid. m.p. = 117.6-119.9 °C. TLC R_f (PE/EA 3:1) = 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.76 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.16 (s, 1H), 5.05 (s, 1H), 5.05 (d, *J* = 11.0 Hz, 1H), 4.88 (d, *J* = 17.5 Hz, 1H), 3.67 (d, *J* = 10.4 Hz, 1H), 3.45 (d, *J* = 10.4 Hz, 1H), 3.38 (d, *J* = 10.1 Hz, 1H), 3.19 (d, *J* = 10.0 Hz, 1H), 2.48 (d, *J* = 15.1 Hz, 1H), 2.42 (s, 3H), 2.41 – 2.30 (m, 2H), 2.33 (d, *J* = 15.0 Hz, 1H), 2.07 – 1.94 (m, 1H), 1.86 (ddd, *J* = 14.7, 6.5, 4.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.3, 149.3, 145.5, 144.1, 140.3, 134.4, 130.0, 129.7 (q, *J* = 32.7 Hz), 129.1, 127.2, 125.0 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 272.1 Hz), 119.9, 115.3, 57.2, 54.6, 54.2, 48.5, 48.0, 36.4, 29.5, 21.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.6. HRMS (ESI): calcd for $C_{26}H_{27}F_3NO_3S^+$ ($[M + H]^+$) 490.1658, found 490.1661.



4j

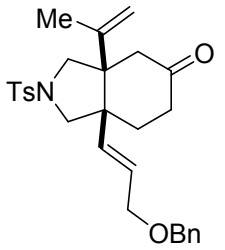
Reaction time: 24 h. Eluted with PE/EA 10:1 to 5:1.

Run 1: **3j** (34.6 mg) and $[Rh(CO)_2Cl]_2$ (1.9 mg) were used, **4j** (34.3 mg, 92%) was obtained.

Run 2: **3j** (34.5 mg) and $[Rh(CO)_2Cl]_2$ (1.9 mg) were used, **4j** (33.7 mg, 90%) was obtained.

Average yield of two runs: 91%.

4j: white solid. m.p. = 139.4-141.0 °C. TLC R_f (PE/EA 3:1) = 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.93 (s, 1H), 4.84 (s, 1H), 4.82 (s, 1H), 4.66 (s, 1H), 3.62 (d, *J* = 10.2 Hz, 1H), 3.61 (d, *J* = 10.1 Hz, 1H), 3.53 (d, *J* = 10.2 Hz, 1H), 3.15 (d, *J* = 10.1 Hz, 1H), 2.47 – 2.28 (m, 2H), 2.42 (s, 3H), 2.40 (d, *J* = 15.6 Hz, 1H), 2.22 – 2.10 (m, 1H), 2.18 (d, *J* = 15.3 Hz, 1H), 1.74 – 1.67 (m, 1H), 1.69 (s, 3H), 1.66 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.6, 146.2, 146.0, 144.0, 134.5, 130.0, 127.3, 114.7, 114.5, 57.1, 56.0, 54.8, 50.7, 48.6, 36.5, 30.4, 22.6, 22.1, 21.7. HRMS (ESI): calcd for $C_{21}H_{28}NO_3S^+$ ($[M + H]^+$) 374.1784, found 374.1784.



4k

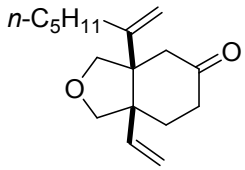
Reaction time: 48 h. Eluted with PE/EA 10:1 to 5:1 to 3:1.

Run 1: **3k** (45.1 mg) and $[Rh(CO)_2Cl]_2$ (1.9 mg) were used, **4k** (32.9 mg, 69%) was obtained.

Run 2: **3k** (45.3 mg) and $[Rh(CO)_2Cl]_2$ (1.9 mg) were used, **4k** (35.4 mg, 74%) was obtained.

Average yield of two runs: 72%.

4k: yellow oil. TLC R_f (PE/EA 3:1) = 0.10. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.2 Hz, 2H), 7.38 – 7.24 (m, 7H), 5.48 (d, J = 16.0 Hz, 1H), 5.36 (dt, J = 16.0, 5.5 Hz, 1H), 4.89 (s, 1H), 4.65 (s, 1H), 4.40 (s, 2H), 3.88 – 3.74 (m, 2H), 3.60 (d, J = 10.5 Hz, 1H), 3.52 (d, J = 9.9 Hz, 1H), 3.43 (d, J = 10.5 Hz, 1H), 3.23 (d, J = 9.9 Hz, 1H), 2.42 – 2.32 (m, 3H), 2.39 (s, 3H), 2.28 (d, J = 15.1 Hz, 1H), 2.07 (ddd, J = 14.7, 9.4, 7.2 Hz, 1H), 1.79 (dt, J = 14.7, 5.9 Hz, 1H), 1.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.4, 145.0, 144.0, 138.2, 134.5, 134.1, 130.0, 128.5, 127.8, 127.7, 127.3, 126.6, 114.8, 72.2, 70.4, 56.7, 55.3, 54.7, 47.2, 47.1, 36.5, 30.4, 22.7, 21.6. HRMS (ESI): calcd for $C_{28}H_{34}NO_4S^+$ ($[M + H]^+$) 480.2203, found 480.2199.



4l

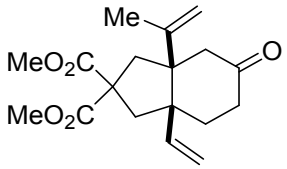
Reaction time: 40 h. Eluted with PE/EA 20:1 to 10:1.

Run 1: **3l** (23.4 mg) and $[Rh(CO)_2Cl]_2$ (1.9 mg) were used, **4l** (23.1 mg, 88%) was obtained.

Run 2: **3l** (23.4 mg) and $[Rh(CO)_2Cl]_2$ (1.9 mg) were used, **4l** (23.6 mg, 90%) was obtained.

Average yield of two runs: 89%.

4l: yellow oil. TLC R_f (PE/EA 5:1) = 0.24. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 (dd, J = 17.6, 11.0 Hz, 1H), 5.12 (d, J = 10.6 Hz, 1H), 5.09 (d, J = 17.7 Hz, 1H), 4.97 (s, 1H), 4.84 (s, 1H), 4.08 (d, J = 8.9 Hz, 1H), 3.94 (d, J = 9.1 Hz, 1H), 3.85 (d, J = 9.1 Hz, 1H), 3.69 (d, J = 8.9 Hz, 1H), 2.64 (d, J = 14.7 Hz, 1H), 2.56 – 2.44 (m, 2H), 2.41 (d, J = 14.8 Hz, 1H), 2.20 (ddd, J = 14.4, 10.2, 6.1 Hz, 1H), 2.03 (dt, J = 14.4, 5.7 Hz, 1H), 1.98 – 1.81 (m, 2H), 1.46 – 1.33 (m, 2H), 1.33 – 1.19 (m, 4H), 0.87 (t, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.2, 149.8, 141.0, 113.6, 111.6, 77.3, 76.9, 57.0, 48.4, 48.0, 36.0, 33.7, 31.8, 30.0, 28.3, 22.6, 14.1. HRMS (ESI): calcd for $C_{17}H_{27}O_2^+$ ($[M + H]^+$) 263.2006, found 263.2002.



4m

Reaction time: 110 h. Eluted with PE/EA 20:1 to 10:1.

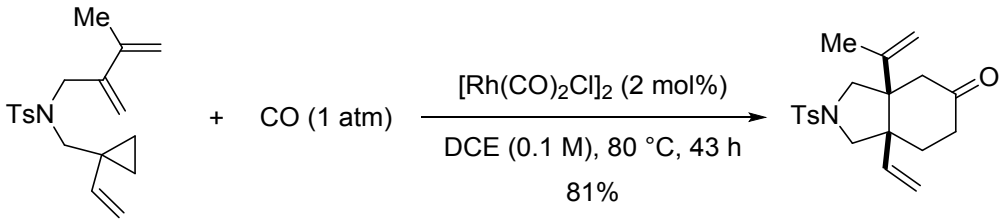
Run 1: **3m** (29.1 mg) and $[Rh(CO)_2Cl]_2$ (1.9 mg) were used, **4m** (12.8 mg, 40%) was obtained.

Run 2: **3m** (29.2 mg) and $[Rh(CO)_2Cl]_2$ (1.9 mg) were used, **4m** (11.8 mg, 37%) was obtained.

Average yield of two runs: 39%.

4m: white solid. m.p. = 78.0-79.9 °C. TLC R_f (PE/EA 3:1) = 0.38. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.96 (dd, *J* = 17.4, 11.1 Hz, 1H), 5.04 (d, *J* = 11.4 Hz, 1H), 5.03 (d, *J* = 17.5 Hz, 1H), 4.87 (s, 1H), 4.73 (s, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 3.18 (d, *J* = 14.7 Hz, 1H), 3.13 (d, *J* = 14.6 Hz, 1H), 2.66 – 2.52 (m, 1H), 2.56 (d, *J* = 14.7 Hz, 1H), 2.47 (d, *J* = 14.6 Hz, 1H), 2.40 (ddt, *J* = 15.4, 5.3, 2.6 Hz, 1H), 2.24 – 2.09 (m, 2H), 2.13 (d, *J* = 14.6 Hz, 1H), 2.04 (ddd, *J* = 14.6, 7.4, 3.0 Hz, 1H), 1.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.9, 173.7, 172.8, 147.7, 142.9, 114.0, 113.4, 57.0, 56.3, 53.5, 53.3, 49.2, 49.0, 44.5, 42.3, 36.8, 31.6, 22.6. HRMS (ESI): calcd for $C_{18}H_{25}O_5^+$ ($[M + H]^+$) 321.1697, found 321.1695.

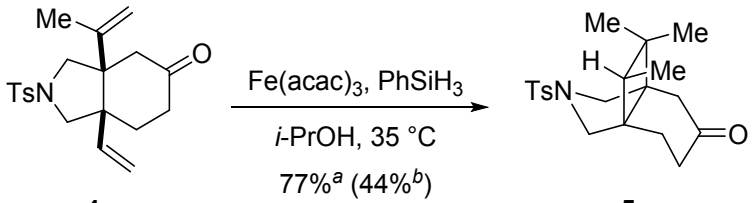
4. Gram-Scale Experiment



3a (4.0 mmol, 1.33 g) **4a** (1.17 g)

A solution of **3a** (1.33g, 4.0 mmol) and $[Rh(CO)_2Cl]_2$ (31.1 mg, 0.08 mmol, 2 mol%) in super-dried DCE (40 mL, 0.1 M) was bubbled with CO (1 atm) for 10 min. The reaction mixture was stirred at 80 °C under balloon pressure gas of CO (1 atm) for 43 h. Then reaction mixture was cooled to room temperature and concentrated *in vacuo*. Purification of the residue through column chromatography on silica gel (PE/EA 10:1 to 5:1) afforded **4a** (1.17 g, 81%) as a yellow solid.

5. Further Transformations of 1,5-Dienes

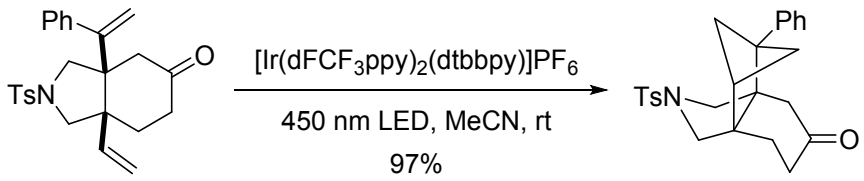


4a **5**

Following a modified procedure reported by Shenvi et al.[13], **4a** (18.0 mg, 0.05 mmol) was placed in 10 mL Schlenk tube. The Schlenk tube was then transferred to the glove box. $Fe(acac)_3$ (17.7 mg, 0.05 mmol), super-dried *i*-PrOH (2 mL) and phenylsilane (16.2 mg, 18.5 μL, 0.15 mmol) were added successively. Then the Schlenk tube was properly sealed and moved out of the glove box. After stirred at 35 °C for 14 h, the reaction mixture was cooled to room temperature and concentrated *in vacuo*. Purification of the residue through column chromatography on silica gel (PE/EA 5:1) afforded **5** (13.9 mg, 77%, with inseparable impurities) as a white solid. Recrystallization of the above crude product with PE/DCM gave pure **5** (8.0 mg, 44%) as a white solid.

Note: Conduct the reaction outside the glove box using a simple round-bottom flask sealed with rubber septa will lead to a significant decrease of reaction yield.

5: white solid. m.p. = 182 °C (decompose). TLC R_f(PE/EA 3:1) = 0.19. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 3.76 (d, *J* = 10.6 Hz, 1H), 3.24 (d, *J* = 9.4 Hz, 1H), 2.63 (d, *J* = 15.7 Hz, 1H), 2.44 (s, 3H), 2.41 (d, *J* = 9.1 Hz, 1H), 2.34 – 2.23 (m, 2H), 2.20 – 2.06 (m, 1H), 2.12 (d, *J* = 10.5 Hz, 1H), 1.99 – 1.85 (m, 1H), 1.93 (d, *J* = 15.5 Hz, 1H), 1.69 – 1.61 (m, 1H), 1.13 (s, 3H), 1.02 (s, 3H), 0.92 (d, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.5, 144.1, 131.9, 129.8, 127.9, 55.8, 55.5, 49.1, 44.1, 43.8, 41.9, 37.7, 35.3, 24.6, 22.2, 22.1, 21.7, 9.2. HRMS (ESI): calcd for $C_{20}H_{28}NO_3S^+$ ($[M + H]^+$) 362.1784, found 362.1778.



4f **6**

Following a modified procedure reported by Walker et al.[14], **4f** (21.1 mg, 0.05 mmol) was placed in 10 mL Schlenk tube. The Schlenk tube was then transferred to the glove box. $[Ir(dFCF_3PPy)_2(dtbbpy)]PF_6$ (5.6 mg, 5 μmol) and super-dried MeCN (1 mL) were added successively. Then the Schlenk tube was properly sealed and moved out of the glove box, placed near the 450 nm LED light source (see reaction details below) and stirred at room temperature for 48 h. After completion, the reaction mixture was concentrated *in vacuo*. Purification of the residue through column chromatography on silica gel (PE/EA 5:1 to 3:1) afforded **6** (20.5 mg, 97%) as a white solid.

6: white solid. m.p. = 152.5-154.4 °C. TLC R_f (PE/EA 3:1) = 0.12. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.32 – 7.26 (m, 2H), 7.26 – 7.21 (m, 1H), 7.05 – 6.96 (m, 2H), 3.52 (d, *J* = 11.0 Hz, 1H), 3.47 (d, *J* = 10.3 Hz, 1H), 3.24 (d, *J* = 10.3 Hz, 1H), 2.64 (d, *J* = 11.0 Hz, 1H), 2.45 (s, 3H), 2.42 – 2.40 (m, 1H), 2.41 (d, *J* = 15.8 Hz, 1H), 2.35 (dd, *J* = 10.6, 7.8 Hz, 1H), 2.31 – 2.22 (m, 1H), 2.18 (dd, *J* = 10.7, 8.0 Hz, 1H), 2.04 (d, *J* = 15.7 Hz, 1H), 1.99 – 1.88 (m, 2H), 1.88 – 1.71 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.7, 144.1, 139.7, 132.2, 129.9, 128.4, 127.8, 127.1, 126.4, 60.7, 57.0, 55.6, 54.6, 52.7, 45.6, 44.6, 42.6, 37.7, 34.4, 27.9, 21.7. HRMS (ESI): calcd for $C_{25}H_{28}NO_3S^+$ ($[M + H]^+$) 422.1784, found 422.1783.

The 40 W LED light source (JD-208, peak wavelength = 454.2 nm) was purchased from Xuzhou Ai Jia electronic technology Co. LTD. The light source was placed at a distance of approximately 5 cm from the Schlenk tube, which is made from regular borosilicate glass. One electric fan was placed close to the Schlenk tube to keep the reaction at room temperature.

6. Computational studies

6.1 Computational methods

All DFT calculations were performed with *Gaussian* 09, E.01 program package.[15] Pruned integration grids with 99 radial shells and 590 angular points per shell (int = ultrafine) were used in DFT calculations. Geometry optimizations were carried out at BMK[16]/def2-SVP[17] level in the gas phase. The functional was chosen according to our previous benchmark study in $[Rh(CO)_2Cl]_2$-catalyzed [5 + 2 + 1] cycloaddition.[18] Frequency analysis was carried out to check the nature of each intermediate or transition state. Thermal corrections to Gibbs free energy at 353.15K with Grimme's entropy interpolation[19] was performed with *Shermo* 2.6[20]. The frequency scale factors for BMK/6-31G(d,p)[21] (0.9750 for ZPE, 0.9682 for H(T)-H(0) and 0.9739 for S(T)) were utilized[22], since the frequency scale factors for BMK/def2-SVP have not been reported. Solvent effects were considered based on gas-phase-optimized structures using the same basis set and functional. Solvation energies in DCE were evaluated by a self-consistent reaction field employing the SMD model.[23] Base on the optimized structures, single-point energy refinements were performed with *ORCA* 5.0.4 program package[24] at the DLPNO-CCSD(T)[25]/def2-TZVPP[17] level (def2-TZVPP/C auxiliary basis set[26]) with TightSCF and TightPNO keywords. Standard state concentration of 5.5 mM for CO[27] and 1.0 M for all other species were used.[28] 3D structures were prepared by CYLview.[29]

6.2 Discussion of the alkene insertion step

We have also calculated other possible transition states for the alkene insertion step (Figure S1). **IN6-η^3** can be generated from **IN5** if only the internal double bond of diene moiety coordinates to the Rh center. Two different types of alkene insertion can occur from **IN6-η^3**. The first is *exo*-insertion via **TS3-*exo***, with an activation free energy of 45.0 kcal/mol. The second is *endo*-insertion via **TS3-η^3**, with an activation free energy of 34.0 kcal/mol. However, both of the energy barriers are too high and not suitable for a reaction occurs at 80 °C.

We then turned to the intermediate **IN6**, in which both of the double bonds of diene moiety coordinate to the Rh center, accompanied by dissociation of the vinyl moiety. **IN6** can undergo *exo*-insertion transition state **TS3**, with a more reasonable activation free energy of 29.5 kcal/mol. Unfortunately, we failed to locate an *exo*-insertion transition state from **IN6**.

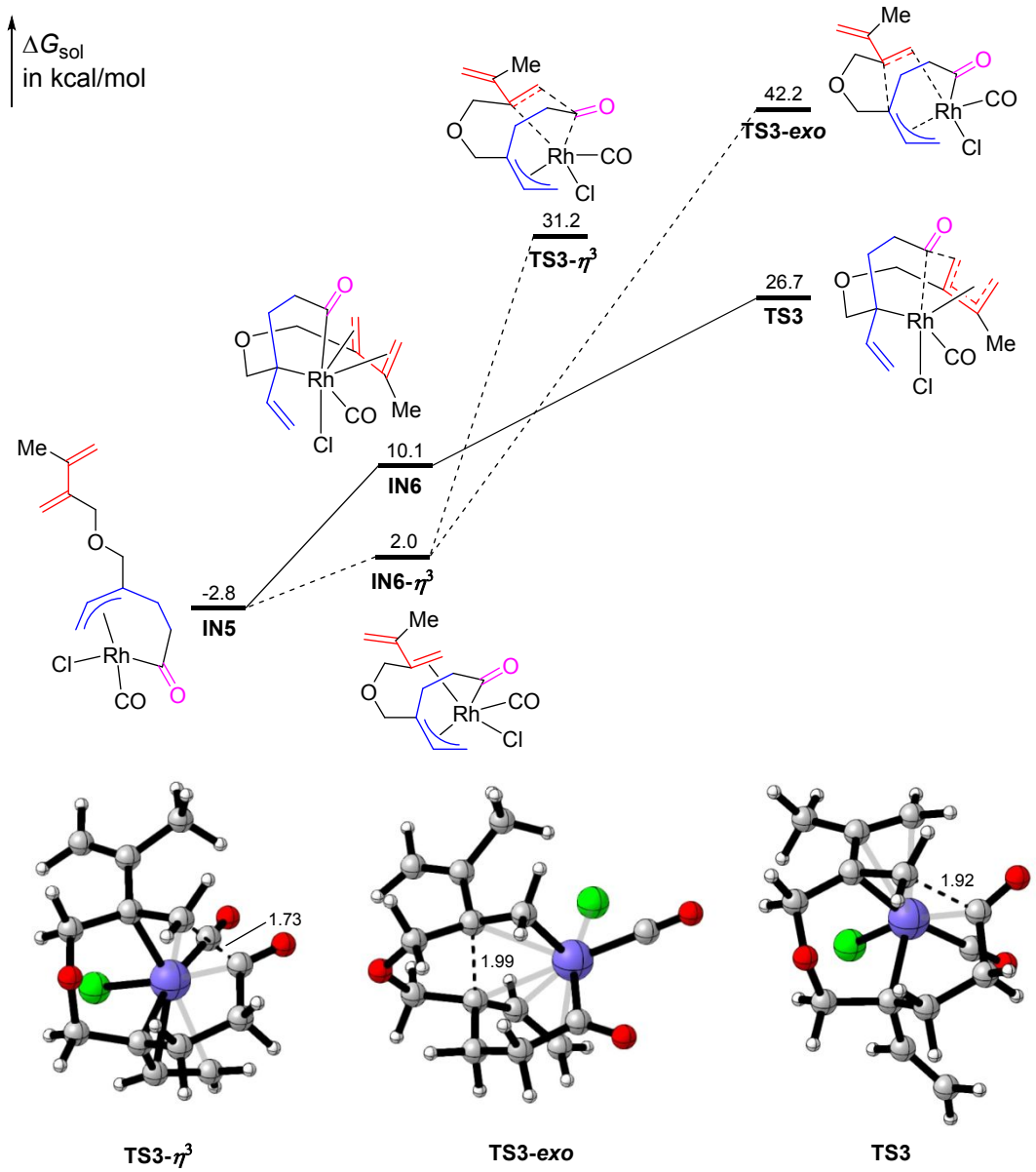


Figure S1. Gibbs free energy profile for the alkene insertion step

For comparison, we calculated similar *endo*-alkene insertion step of substrate bearing a normal alkene moiety (Figure S2). From **IN5-H** to **TS3-H**, the activation free energy is 32.7 kcal/mol, higher than the energy barrier of **IN5** to **TS3**. It's worth mentioning that the mechanism of [3+2+1] reaction of normal ene-VCPs and CO have already been reported in our previous work[30], which includes an *exo*-alkene insertion transition state with a relatively low activation free energy.

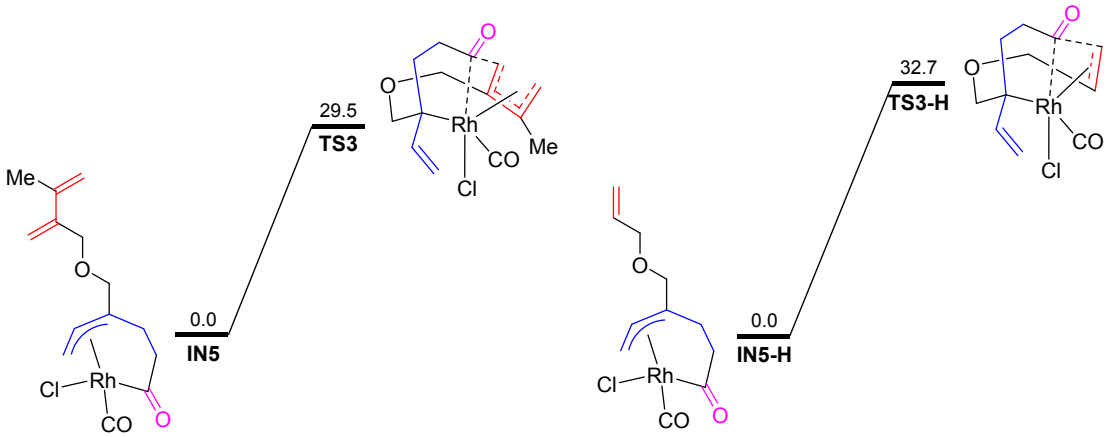


Figure S2. Comparison of the *endo*-alkene insertion step between normal alkene and type-II diene.

We have also calculated the *endo*-alkene insertion step using substrate **3a**, which has a NTs-tether rather than a O tether (Figure S3). To our surprise, the activation free energy from **IN5-NTs** to **TS3-NTs** is 25.5 kcal/mol, 4 kcal/mol lower than that from **IN5** to **TS3** (29.5 kcal/mol). We did not search for all possible conformations for **IN5-NTs** and **TS3-NTs** (for example, using NTs to coordinate to Rh center in the former). Based on the present computational results, alkene insertion step for the NTs-tethered substrates should be easier than that for O-tethered substrates. We hypothesized that N and O have different atomic radius, affecting the energies of alkene insertion transition states. However, these computational results could not explain why **3b** had a lower reaction yield compared to that of **3l**, if we assume that the overall activation free energies are the activation free energies of alkene insertion steps (25.5 and 29.5 kcal/mol, respectively). We hypothesized that unknown resting-states with energy lower than **IN5-NTs** could affect the overall activation free energy of **3b**. In addition, unidentified side reactions using **3b** as substrate could be the reason for its lower yield of [3+1+2] cycloadduct.

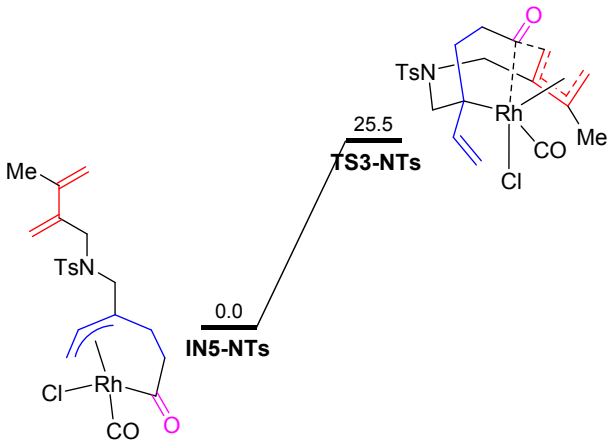


Figure S3. *Endo*-alkene insertion step of substrate **3a**.

6.3 Computed Energies of the Stationary Points

Table S1 Thermal Corrections to Gibbs Energies (TCGs) and Single-Point Energies (SPEs)

Stationary points	SPE[a] / Hartree	SPE[b] / Hartree	SPE[c] / Hartree	TCG[a] / Hartree
$[Rh(CO)_2Cl]_2$	-1592.916752	-1592.918391	-1593.122136	-0.016321
3r	-542.43277	-542.445355	-542.2696922	0.215385

CO	-113.172745	-113.16729	-113.1581717	-0.01818
IN1	-1225.674828	-1225.700226	-1225.635132	0.217464
TS1	-1225.66469	-1225.687097	-1225.626087	0.216504
IN2	-1225.671408	-1225.694879	-1225.633439	0.217104
IN3	-1338.883725	-1338.904292	-1338.831866	0.224545
TS2	-1338.852409	-1338.877615	-1338.791246	0.224694
IN3'	-1225.69844	-1225.715084	-1225.65969	0.226387
TS2'	-1225.648805	-1225.666929	-1225.611654	0.224369
IN4	-1338.892761	-1338.923529	-1338.829951	0.227702
IN5	-1338.905815	-1338.930498	-1338.842465	0.227695
IN6	-1338.884721	-1338.905802	-1338.826506	0.228692
TS3	-1338.870677	-1338.888466	-1338.805781	0.23099
IN6-η^3	-1338.904437	-1338.924658	-1338.84484	0.233144
TS3-η^3	-1338.867445	-1338.886171	-1338.800171	0.233538
TS3-*exo*	-1338.837071	-1338.86082	-1338.778334	0.234311
IN7	-1338.88958	-1338.905119	-1338.814358	0.233841
IN8	-1338.87984	-1338.903273	-1338.821218	0.238738
TS4	-1338.864908	-1338.894499	-1338.807175	0.238569
IN9	-1338.912168	-1338.936608	-1338.839606	0.237182
4r	-655.686168	-655.701304	-655.4935507	0.231438
IN5-H	-1222.36228	-1222.385241	-1222.340306	0.17144
TS3-H	-1222.318903	-1222.344544	-1222.289698	0.175613
IN5-NTs	-2137.189351	-2137.225102	-2136.833113	0.34441
TS3-NTs	-2137.162052	-2137.190587	-2136.801667	0.346336

[a] Computed at the BMK/def2-SVP level.

[b] Computed at the SMD(DCE)/BMK/def2-SVP//BMK/def2-SVP level.

[c] Computed at the DLPNO-CCSD(T)/def2-TZVPP//BMK/def2-SVP level.

We used 6.05 mM as the concentration of CO[27] and 1.0 M for other species.[28]

$$\Delta G_{std} = -RT\ln\frac{V_2}{V_1} = -RT\ln\frac{1}{28.98} = 2.36 \text{ kcal/mol}$$

$$\Delta G_{\mathrm{CO}} = -RT\ln\frac{V_2}{V_1} - RT\ln\frac{c_1}{c_2} = -RT\ln\frac{1}{28.98} - RT\ln\frac{1}{0.00605} = -1.22 \text{ kcal/mol}$$

6.4 Cartesian coordinates of the stationary points

$[Rh(CO)_2Cl]_2$

Rh	1.62711900	-0.00001500	0.09781400
Rh	-1.62701200	-0.00002400	0.09784400
Cl	0.00009000	-1.66182700	0.90043000
Cl	-0.00012200	1.66166400	0.90031700
O	3.46489100	2.19644100	-0.85489300
O	3.46551700	-2.19599800	-0.85522700
O	-3.46557300	-2.19595000	-0.85508600
O	-3.46536800	2.19596400	-0.85501300
C	2.78814200	1.35730700	-0.50223100
C	2.78853500	-1.35715500	-0.50242500
C	-2.78842600	-1.35717900	-0.50234800
C	-2.78825200	1.35717500	-0.50225700

3r

H	3.26641900	2.01306800	-0.23977500
C	2.28171600	1.52627300	-0.27530100
C	1.18609200	2.28801300	-0.38074300
C	2.32290300	0.03689000	-0.20851600
H	1.26927700	3.37754400	-0.43727300

H	0.17882500	1.85918200	-0.39427100
C	3.42420900	-0.59284700	0.66047900
C	3.54848900	-0.64582800	-0.85362200
C	1.00842400	-0.71111700	-0.29090600
H	3.16712700	-1.51210700	1.19682700
H	4.08133500	0.08474600	1.21525000
H	4.28514000	0.00139100	-1.34068800
H	3.38895100	-1.60508500	-1.35764200
H	0.42886700	-0.35691200	-1.16841700
H	1.21171300	-1.79231600	-0.44939700
C	-0.88749300	-1.29846000	0.97583600
H	-1.24298000	-1.19512600	2.01492700
H	-0.66031400	-2.37060600	0.80187000
O	0.28210000	-0.53700900	0.89220600
C	-2.00194600	-0.87999100	0.01960700
C	-2.44782600	-1.76209400	-0.89598100
H	-1.99947400	-2.75784000	-0.97792300
H	-3.26599500	-1.53473400	-1.58424500
C	-2.59659400	0.47820000	0.16670700
C	-2.11916800	1.36060100	1.06732600
H	-1.24658900	1.14387900	1.68796900
H	-2.58087100	2.34741400	1.17582500
C	-3.77046900	0.83601100	-0.72068600
H	-3.49020100	0.78936000	-1.78763600
H	-4.61110100	0.13583700	-0.57263100
H	-4.12695500	1.85447700	-0.50561400

CO

C	0.00000000	0.00000000	-0.64337400
O	0.00000000	0.00000000	0.48253000

IN1

H	-0.03200800	1.08458000	-1.17305900
C	0.52595000	0.14327400	-1.21020600
C	1.53265500	-0.09885000	-2.17560600
H	1.78128500	0.69714700	-2.88422800
H	1.74696400	-1.11012200	-2.54377900
C	1.12231300	-2.12278100	0.07844200
C	-0.10418200	-2.37734100	-0.77545300
C	-0.85847000	-0.49130600	0.81680600
H	1.12392400	-2.42753400	1.12854400
H	2.09566900	-2.24501500	-0.42511400
H	0.06070300	-2.58851600	-1.83679400
H	-0.91453800	-2.95823100	-0.32390600
H	-1.00776900	-1.32024900	1.54168000
H	-0.36717900	0.34081300	1.36370100
C	-2.96029700	0.45677700	1.20693900
H	-2.49210600	1.31593100	1.72726100
H	-3.19606100	-0.30657700	1.98011700
C	0.03174600	-0.95283200	-0.32518800
Rh	2.31871900	0.03888400	-0.19395700
Cl	3.49120000	-0.31189000	1.80775600
C	3.16691300	1.66379900	-0.47894000
O	3.67739700	2.66224700	-0.66359500
O	-2.06896600	-0.07965300	0.26493400
C	-4.23989000	0.91471100	0.53366700
C	-4.54619100	2.22617500	0.54169600
H	-3.87490800	2.95772800	1.00212600
H	-5.46551200	2.61487500	0.09671000
C	-5.13719000	-0.10637000	-0.07471400
C	-4.80692100	-1.41185400	-0.09605700
H	-3.85109800	-1.77328400	0.28804300
H	-5.48479500	-2.15259600	-0.53158600
C	-6.44665100	0.36887600	-0.66721900
H	-7.06659700	0.88071400	0.08921800
H	-6.27210400	1.08571400	-1.48855500
H	-7.02277300	-0.47746800	-1.06990600

TS1

H	0.34679000	-1.78821100	0.18584900
C	0.98598600	-1.29578900	0.92567900
C	1.93138300	-2.02491200	1.70723500
H	1.95118400	-3.11415200	1.60022300
H	2.24335700	-1.66420900	2.69393100
C	2.84606600	0.78500800	1.61329600
C	1.44189200	0.90216900	2.19030300
C	0.33090600	0.93871800	-0.12501600
H	3.19276000	1.66911700	1.06602500
H	3.61424700	0.37952000	2.29524700
H	1.27991900	0.36001100	3.13118300
H	1.01433400	1.91147000	2.25561100
H	1.05038800	1.68909700	-0.51834700
H	0.06079200	0.27166000	-0.97025000
C	-1.50230900	2.34514100	-0.49797300
H	-1.98980700	1.70106400	-1.25699100
H	-0.80586200	3.02041400	-1.03994700
C	0.99709100	0.14016600	0.97946600
Rh	2.89856300	-0.83678500	0.22661700

Cl	4.49590700	0.35664300	-1.03858100
C	3.09746600	-2.29414700	-1.09417100
O	3.19521600	-3.09209600	-1.89015600
O	-0.78874200	1.56176500	0.42067800
C	-2.55363400	3.16543300	0.22299000
C	-3.85541400	2.91542700	-0.01347600
H	-4.15754400	2.12080100	-0.70275300
H	-4.65816400	3.48436400	0.46194400
C	-2.10434000	4.24086500	1.15044200
C	-0.79842900	4.50392800	1.35141100
H	-0.00296400	3.93058400	0.86972700
H	-0.48851000	5.31050300	2.02308900
C	-3.16975200	5.04855900	1.86044200
H	-3.82279700	5.56960600	1.13878500
H	-3.81448900	4.39738700	2.47603700
H	-2.71467000	5.80320700	2.51894900

IN2

H	-0.68723400	1.76710100	1.49428800
C	-0.76864900	0.67347200	1.48948300
C	-1.87502000	0.02731900	2.14201100
H	-2.56862900	0.66086300	2.70636800
H	-1.76443000	-0.98386400	2.54778100
C	-1.36467600	-1.99295300	0.22252500
C	0.05992600	-1.58163800	0.63100900
C	0.89246400	0.66025400	-0.41867800
H	-1.41393100	-2.46360000	-0.77120900
H	-1.88618300	-2.63819100	0.94772700
H	0.34883100	-1.88733100	1.65032200
H	0.84154400	-1.95066500	-0.05170300
H	0.75866900	0.23476600	-1.43854900
H	0.63689900	1.74062300	-0.47755600
C	3.16238700	1.02972200	-0.83467100
H	2.99386300	2.12038000	-0.94134000
H	3.06755700	0.58225300	-1.84810500
C	-0.03566300	-0.05635400	0.53537400
Rh	-2.18865900	-0.12111500	0.08172900
Cl	-3.97043100	-0.92793500	-1.19595400
C	-3.03198000	1.76876500	-0.20813900
O	-3.58163800	2.72447200	-0.44666900
O	2.20097000	0.47481100	0.02266500
C	4.55996400	0.79062400	-0.29701700
C	5.29951700	1.84881900	0.08656500
H	4.89473900	2.86443700	0.03664900
H	6.32124600	1.74608800	0.46014700
C	5.08145300	-0.60342300	-0.25025900
C	4.32449300	-1.65340300	-0.62230000
H	3.28400600	-1.54014700	-0.93400200
H	4.72903400	-2.67002200	-0.59701500
C	6.50415300	-0.80771300	0.22521000
H	7.22098900	-0.25683300	-0.40832700
H	6.63142600	-0.44193200	1.25911700
H	6.77373400	-1.87408200	0.20417200

IN3

O	0.42244700	-2.26412800	-1.56224200
C	-0.16975600	-1.46662900	-1.03052600
O	-0.87773800	-0.99874000	2.79586600
C	-1.04163400	-0.68097600	1.72291400
Rh	-1.44758000	-0.12669900	-0.09760600
C	-0.71548600	1.43878300	-1.46651800
C	-1.94012300	0.92301700	-1.97010000
C	-0.61328100	1.91612100	-0.13503500
C	-1.85265900	2.49756700	0.55889300
C	-2.74879300	1.25908200	0.75482400
H	-1.55966000	2.95191900	1.52033300
H	-2.97505000	1.06769700	1.81377800
H	-2.31071100	3.29533800	-0.05236600
H	-3.69825300	1.27506000	0.20133500
Cl	-3.07460800	-1.92301600	-0.24077000
H	-2.89481400	1.40739900	-1.75034600
H	0.22566400	1.18139900	-1.96596300
H	-1.90968300	0.37210600	-2.91483500
C	0.75418900	2.24028000	0.42959400
H	0.72455800	2.12877200	1.53560400
H	0.99281000	3.31009800	0.22610200
O	1.71275800	1.40128200	-0.12700500
C	3.01319600	1.58610800	0.36016000
H	3.43243400	2.54552400	-0.00298400
H	2.99725500	1.63310200	1.47016700
C	3.89798900	0.43854900	-0.08702800
C	4.93969600	0.69165700	-0.90168300
H	5.62378700	-0.09071800	-1.23929700
H	5.14044000	1.70736300	-1.25657600
C	3.59621900	-0.93043900	0.41850900
C	2.56727700	-1.16626800	1.25698800
H	1.88883800	-0.37478800	1.58409000
H	2.37580600	-2.17492800	1.63669700

C	4.49625600	-2.06139900	-0.03097200
H	4.48861400	-2.15899200	-1.13043400
H	5.54172200	-1.88533000	0.27648800
H	4.16741300	-3.01831000	0.40046400

TS2

O	0.61629800	0.09550500	2.70687300
C	1.09570300	-0.12131700	1.67298700
Rh	1.67251900	0.18211900	-0.09762700
C	1.26824400	-1.04969700	-1.97020600
C	2.65348200	-1.02336800	-1.95842500
C	0.48923900	-1.43137500	-0.80972600
C	1.06985500	-2.43733900	0.20915500
C	1.92465500	-1.65524600	1.24560600
H	0.23152300	-2.92847700	0.72382500
H	1.81473500	-2.03878000	2.26767900
H	1.67482600	-3.21590900	-0.28597600
H	3.00969700	-1.62944800	1.04592000
H	3.24020300	-1.68749700	-1.31602600
H	0.74309200	-0.51156500	-2.77080900
H	3.19995700	-0.51587500	-2.75697500
C	-1.02086700	-1.39880100	-0.92533800
H	-1.37980300	-2.32476000	-1.43011000
H	-1.33125700	-0.53921000	-1.55377200
O	-1.57800300	-1.32115200	0.35326900
C	-2.97175600	-1.23224700	0.37974000
H	-3.40909700	-1.88597800	-0.40111700
H	-3.30273100	-1.62812400	1.35638800
C	-3.50373200	0.18925800	0.21182900
C	-2.66288600	1.23419200	0.31820400
H	-3.00348900	2.26766200	0.22469500
H	-1.60496800	1.06568600	0.53853100
C	-4.96476100	0.35922900	-0.01669100
C	-5.80864700	-0.69237900	-0.02924200
H	-5.47723300	-1.72273600	0.12226000
H	-6.88186500	-0.54480400	-0.18445000
C	-5.48931100	1.76612900	-0.21073500
H	-4.99536600	2.26071700	-1.06470600
H	-6.57375500	1.75711000	-0.39560700
H	-5.29756300	2.38560000	0.68242600
Cl	3.60079300	1.48582000	0.54300800
C	0.83782400	1.78014100	-0.72059100
O	0.38220800	2.75802500	-1.06257700

IN3'

C	-0.14170500	1.86136400	0.75431600
C	-1.57186200	-0.39903100	-0.94671400
C	-2.07691600	1.01475300	-1.23589800
C	-1.63075100	1.89269300	0.99658100
C	0.46521600	2.71651900	-0.36422700
C	1.21800900	1.69250100	-1.24042400
C	-0.55182600	-0.89067700	-1.73993800
Rh	0.89276900	-0.00337700	-0.07362300
H	-0.33316900	3.25096900	-0.90249700
H	1.12808700	3.48445800	0.07216800
H	2.28558800	1.93669400	-1.36054500
H	0.78419200	1.60854600	-2.24963600
H	-0.34331200	-1.96222100	-1.76865900
H	-0.16403100	-0.29214100	-2.56803000
H	-1.34717600	1.51184700	-1.89737500
H	-3.01239300	0.90013400	-1.81168900
H	-1.89850800	2.84691200	1.48618700
H	-1.90180800	1.06889400	1.68657100
C	0.70068500	1.24659700	1.69222900
C	2.08083000	0.99447600	1.36588300
H	2.68032000	1.77374700	0.88319000
H	2.62998300	0.34548100	2.05526400
H	0.24694700	0.68188800	2.51463500
Cl	0.63229900	-1.89906100	1.51664900
C	2.29841400	-1.05831900	-0.86663400
O	3.15952200	-1.66168500	-1.28475300
O	-2.41937500	1.85216100	-0.16343300
C	-2.41575400	-1.31659700	-0.12367400
C	-3.47789400	-0.84524900	0.56293900
H	-4.13307000	-1.54168900	1.09565200
H	-3.73144100	0.21583600	0.60379800
C	-2.14500800	-2.80362100	-0.19972100
H	-2.28295700	-3.17000500	-1.23278200
H	-1.11849800	-3.03006500	0.12794400
H	-2.84224000	-3.34955000	0.45299400

TS2'

C	1.12505400	-1.05241700	0.65682200
C	1.32866300	0.40861800	-0.76869300
C	2.46426400	-0.43673200	-1.36465400
C	2.62775800	-1.04075800	0.88246700
C	0.69229300	-2.36866000	-0.03482800
C	-0.63613000	-2.13394900	-0.76607600

C	0.09684800	0.49502600	-1.59689200
Rh	-1.04312800	-0.24140200	-0.06440400
H	1.49766400	-2.72822200	-0.69157800
H	0.60346100	-3.12652100	0.76480500
H	-1.41553400	-2.86078400	-0.47982600
H	-0.52190900	-2.18697200	-1.86045900
H	-0.24826500	1.50755500	-1.82810200
H	0.08699300	-0.16041400	-2.47727700
H	2.05019700	-1.23473900	-2.00611500
H	3.08773200	0.21659700	-1.99729700
H	2.90149000	-1.99223500	1.37291900
H	2.93186600	-0.21119200	1.54523100
C	0.29734800	-0.67120500	1.82430200
C	-0.83692800	-1.32444300	2.22583600
H	-1.11268900	-2.31381200	1.85218700
H	-1.43652500	-0.90405500	3.03772700
H	0.56735900	0.26819500	2.32410500
Cl	-1.81470700	1.80977900	1.11824300
C	-2.69152200	-0.12840900	-0.92229100
O	-3.68776100	-0.04867500	-1.45849700
O	3.27512500	-0.97746100	-0.35560700
C	1.83988900	1.73525300	-0.19537400
C	3.10701900	1.88300700	0.24693800
H	3.45064500	2.87396700	0.55895100
H	3.84442000	1.08038700	0.26686700
C	0.99170700	2.98725900	-0.33035500
H	0.92715700	3.28493000	-1.39262200
H	-0.02949500	2.86207600	0.05505700
H	1.46974500	3.81565900	0.21307200

IN4

O	-3.04894200	0.46916800	2.00459700
C	-2.46387500	0.88454900	1.05960600
Rh	-1.60109400	-0.38974600	-0.20152900
C	-1.21898900	0.85847700	-1.89927100
C	-2.60822900	0.60703800	-1.90491400
C	-0.48953100	1.41011200	-0.79414600
C	-0.96191300	2.60312700	0.04258000
C	-2.32024300	2.37024000	0.70767000
H	-0.20595100	2.74995400	0.83072600
H	-2.45381400	2.95252000	1.63354600
H	-0.97148900	3.51907700	-0.57597600
H	-3.16404200	2.62401900	0.04408000
H	-3.34102900	1.28385200	-1.46253000
H	-0.62483300	0.27658000	-2.61929100
H	-3.00032400	-0.04655400	-2.68885400
C	1.02568200	1.30375000	-0.87039300
H	1.45290300	2.28172200	-1.18511800
H	1.32413400	0.55456500	-1.62923800
O	1.52630500	0.96463900	0.39409200
C	2.91717800	1.00166700	0.51906600
H	3.31963600	1.89812000	0.00573400
H	3.13696700	1.11868800	1.59501400
C	3.63808700	-0.24087100	0.00195500
C	2.94064800	-1.32668800	-0.37830800
H	3.42811500	-2.23693100	-0.73378700
H	1.84870000	-1.33632200	-0.32884100
C	5.12726900	-0.20687800	-0.01746000
C	5.81901300	0.85938000	0.43277800
H	5.33947000	1.75643200	0.83230400
H	6.91329500	0.85903800	0.42067100
C	5.85610800	-1.42534300	-0.54340200
H	5.55964300	-1.64891800	-1.58265000
H	6.94469700	-1.26840500	-0.52104900
H	5.62486700	-2.31773900	0.06346100
Cl	-2.83772000	-2.40354700	-0.30538700
C	-0.51006300	-1.06881100	1.28850600
O	0.10422300	-1.48372100	2.13838300

IN5

O	-3.79509400	0.54787900	1.31699700
C	-2.62158400	0.62237800	1.14744700
Rh	-1.69100700	-0.13879800	-0.41608100
C	-0.48174100	1.49728500	-1.15553500
C	-1.86888900	1.74022300	-1.44834000
C	-0.00632400	1.32847900	0.15518400
C	-0.59278700	2.09313200	1.34195300
C	-1.61977000	1.25333700	2.11635900
H	0.22378400	2.39855000	2.01812100
H	-1.12449300	0.39755500	2.60975200
H	-1.06981800	3.02008400	0.98155800
H	-2.17658500	1.83494000	2.86933700
H	-2.45070500	2.43835400	-0.83346600
H	0.15298800	1.07995300	-1.94817400
H	-2.15978700	1.74060500	-2.50428500
C	1.35278400	0.69802200	0.39083800
H	1.26183800	0.01943700	1.26272000
H	2.08441700	1.49076100	0.66191800

O	1.77374800	0.00437800	-0.73904800
C	2.59880100	-1.10918800	-0.49203900
H	2.03499900	-1.85619900	0.09700500
H	2.81253300	-1.54117200	-1.48381100
C	3.90849500	-0.78592100	0.21834500
C	4.16794000	-1.38551300	1.39694900
H	5.10296000	-1.23252900	1.94230700
H	3.43875600	-2.06592700	1.84892400
C	4.87718800	0.14155900	-0.43073500
C	4.58700700	0.76226100	-1.59161700
H	3.61923400	0.64458000	-2.08381200
H	5.31638800	1.42875200	-2.06316100
C	6.21111800	0.36185900	0.25160100
H	6.76143400	-0.58821300	0.36660000
H	6.83759400	1.05578000	-0.32858800
H	6.07567400	0.78461300	1.26252300
Cl	-0.80214900	-1.95721300	0.83718300
C	-3.31408000	-1.07120700	-0.96918500
O	-4.25344200	-1.60370800	-1.29935800

IN6

Rh	-0.00257600	-0.44653900	0.00069200
C	2.24707500	1.04083200	1.17823300
C	3.57978300	0.87690600	1.17207200
C	1.32673600	1.17473300	-0.00874000
C	2.05941200	1.16575600	-1.36749700
C	2.31637200	-0.26765600	-1.85100000
H	1.45428500	1.70836900	-2.10967900
H	2.59506000	-0.34211700	-2.91595000
H	3.00655500	1.72703000	-1.29009400
H	3.13244500	-0.73366300	-1.26514100
H	4.17145000	0.82376300	0.25255800
H	1.73312100	1.08267600	2.14742400
C	1.08916200	-1.14284200	-1.57426800
O	0.85531900	-2.17002300	-2.14671500
H	4.12944000	0.78764000	2.11417600
C	1.12931400	-1.56888800	1.14968500
O	1.70643000	-2.26020600	1.82882400
O	-0.58417300	2.68636500	-0.66042300
C	0.50230300	2.47410600	0.20699800
H	1.18681200	3.32616800	0.03934100
H	0.15982700	2.50733200	1.25616100
C	-0.95433800	0.29485200	-1.94016100
H	-0.38358000	1.10361400	-2.39519100
C	-1.75520600	0.58204300	-0.84437700
H	-1.12520900	-0.59643800	-2.54594700
C	-1.77033200	2.02667100	-0.33484300
H	-2.59104400	2.57059200	-0.83673000
H	-1.95288400	2.03822400	0.75346300
C	-2.70231900	-0.46263500	-0.33232700
C	-2.47502100	-1.77391000	-0.59969900
H	-1.68477900	-2.12907200	-1.27155800
H	-3.11722300	-2.53977300	-0.15439700
C	-3.82724500	-0.00715900	0.56218400
H	-3.41260600	0.36699300	1.51348900
H	-4.40057800	0.80732000	0.08645300
H	-4.51418300	-0.83733000	0.78309600
Cl	-0.86216000	0.11476800	2.29214100

TS3

Rh	0.17474000	-0.46999100	-0.04760000
C	-2.13819100	0.81389700	-1.43801300
C	-3.44363000	0.49789600	-1.38370700
C	-1.22237300	1.13850800	-0.29176600
C	-1.97586600	1.37846200	1.03747200
C	-2.13485900	0.10468600	1.86219600
H	-1.42844300	2.13040300	1.62623800
H	-2.49077400	0.28945900	2.89223800
H	-2.96841800	1.81775400	0.83645100
H	-2.85611300	-0.59384700	1.39847000
H	-4.01183200	0.45440000	-0.44845500
H	-1.65560600	0.82123700	-2.42216300
C	-0.84078700	-0.69285200	1.95705300
O	-0.71233900	-1.70896800	2.56446200
H	-3.99451400	0.26119900	-2.29907500
C	-1.06665900	-1.91796400	-0.67697700
O	-1.72067600	-2.73910300	-1.09004900
O	0.51238600	2.80512700	0.34647300
C	-0.40760700	2.40580500	-0.64479500
H	-1.10624600	3.25706300	-0.74881700
H	0.10566700	2.25897200	-1.61339800
C	0.73765200	0.39411200	1.97490700
H	0.22970100	1.27526700	2.38117300
C	1.61298800	0.70814100	0.83108900
H	1.18051000	-0.26121900	2.73255600
C	1.74175500	2.14629900	0.35077100
H	2.40059100	2.72613400	1.02148700
H	2.19508100	2.15077900	-0.65832200

C	2.45716100	-0.40137300	0.37382400
C	2.09419600	-1.69590000	0.73864800
H	1.54252500	-1.94118200	1.65088600
H	2.58603600	-2.53403600	0.23624000
C	3.54001200	-0.15241500	-0.64756600
H	3.16077800	0.40894800	-1.51401300
H	4.35096700	0.42881200	-0.17387100
H	3.95814200	-1.10170600	-1.01197400
Cl	0.74005500	-0.34818400	-2.38644600

IN6-η^3

Rh	0.55375500	0.22057700	0.28693200
C	-0.19677200	0.65621300	2.26678500
C	1.22846300	0.83544800	2.22551800
C	-1.11004400	1.26110400	1.37192700
C	-1.09999500	2.72207100	0.91857900
C	0.26364000	3.23161700	0.44647300
H	-1.83313200	2.80904800	0.09903800
H	0.18306300	4.09012100	-0.24068100
H	-1.49291300	3.34274500	1.74518700
H	0.88367800	3.57173800	1.29461300
H	1.69359900	1.82149500	2.16391500
H	-0.52963100	-0.28171500	2.72304000
C	1.05947400	2.11262700	-0.25432800
O	1.93298200	2.37600300	-1.03832200
H	1.80806100	0.09988200	2.79318100
C	2.25693400	-0.46640400	-0.39906500
O	3.25962400	-0.87296700	-0.72013300
Cl	0.18104400	-2.14101500	1.05250700
O	-2.85375700	0.40952400	-0.10800300
C	-2.48111400	0.59952200	1.23348100
H	-3.25394000	1.25464900	1.67438100
H	-2.49254600	-0.36446700	1.77464400
C	-0.58794200	0.62882900	-1.76535500
H	-1.17221500	1.50499400	-1.47952000
C	-1.10350100	-0.62232400	-1.51472900
H	0.21674400	0.78422200	-2.48583800
C	-2.40470400	-0.76014500	-0.72382700
H	-3.18284700	-1.06272800	-1.44815700
H	-2.28403600	-1.57357500	0.01350000
C	-0.59253300	-1.82802500	-2.22440000
C	-1.09822800	-3.04894300	-1.97036700
H	-1.84781700	-3.23046300	-1.19829200
H	-0.74079100	-3.92350600	-2.52251300
C	0.47820300	-1.63557900	-3.27758300
H	0.13148900	-0.97087900	-4.08758600
H	1.39189000	-1.18361700	-2.85548900
H	0.75990100	-2.60198700	-3.72081700

TS3-η^3

Rh	0.60598900	-0.22938500	0.18553500
C	0.10688700	0.54222100	2.19037500
C	1.47092100	0.85307500	2.09880200
C	-0.86204300	0.96508500	1.21200900
C	-0.88202100	2.42069000	0.70171100
C	0.33232700	2.86944000	-0.12861300
H	-1.79467400	2.53657400	0.09695100
H	0.05017800	3.67473200	-0.83185200
H	-0.99824000	3.09406600	1.57000000
H	1.15025100	3.28204200	0.48167000
H	1.84383200	1.78703700	1.67542600
H	-0.16040000	-0.31202000	2.82157800
C	0.93707400	1.74053600	-0.96170500
O	2.03010000	1.81456200	-1.46032600
H	2.16644600	0.31141100	2.74655300
C	2.25789200	-1.17818700	-0.44727800
O	3.18715900	-1.75419500	-0.72584400
Cl	0.12119200	-2.36589500	1.21516300
O	-2.66382800	0.22131500	-0.17937500
C	-2.23858200	0.31837200	1.16043200
H	-2.99680300	0.93863000	1.67179800
H	-2.21310400	-0.67808900	1.63878900
C	-0.25591500	0.76852100	-1.74307100
H	-1.11264800	1.44284400	-1.61164500
C	-0.66599700	-0.64004900	-1.41100400
H	0.20462300	0.85785000	-2.73195000
C	-2.12337200	-0.82592300	-0.93148100
H	-2.77043300	-0.92259700	-1.82159100
H	-2.18099700	-1.77144000	-0.36431700
C	-0.18167000	-1.73332800	-2.32359700
C	-0.64739600	-2.99495300	-2.23411500
H	-1.37912200	-3.30375800	-1.48561800
H	-0.26414700	-3.77443600	-2.89984200
C	0.85442800	-1.38810100	-3.37950100
H	0.40101700	-0.80290400	-4.20047400
H	1.68301500	-0.78024900	-2.97690400
H	1.28268400	-2.30193100	-3.81746200

TS3-*exo*

Rh	-0.88249200	0.00302800	0.07178600
C	0.47829200	0.06285200	1.93152200
C	-0.44558200	-0.78972400	2.47000400
C	1.45004800	-0.26827500	0.84733500
C	1.66572500	-1.79283700	0.59816100
C	0.69667900	-2.54469300	-0.32023300
H	2.69376800	-1.93933200	0.23830400
H	1.04274300	-2.50411200	-1.36873800
H	1.64016800	-2.24833300	1.60326200
H	0.63218500	-3.61385000	-0.05844800
H	-0.46243600	-1.86344400	2.26445300
H	0.47436500	1.10755300	2.26363600
C	-0.72096600	-1.96160000	-0.33146600
O	-1.67019400	-2.66626500	-0.55635100
H	-1.14019700	-0.41329300	3.22646100
C	-2.60819600	0.02731500	-0.69898200
O	-3.63865000	0.06372600	-1.16138400
Cl	-1.68129700	2.18691700	1.01299100
O	3.57072100	0.29139200	-0.06098000
C	2.83263100	0.31865300	1.12822800
H	3.34188800	-0.31614500	1.87424200
H	2.75398600	1.33907400	1.53996200
C	0.19791600	0.27039800	-1.65816400
H	0.39431800	-0.64964700	-2.22159300
C	1.34614900	0.77315200	-0.84912500
H	-0.28498900	1.01796000	-2.29294600
C	2.74540600	0.23176200	-1.19434700
H	2.68125300	-0.80069900	-1.58287800
H	3.18607900	0.86514700	-1.98088600
C	1.38318400	2.30970600	-0.72133300
C	2.45015400	2.98363600	-0.24525900
H	2.44395100	4.07725400	-0.27765800
H	3.36126700	2.51398700	0.12205100
C	0.30399400	3.13176400	-1.41264500
H	0.44241600	3.07875500	-2.50816400
H	-0.71524500	2.81909900	-1.16047300
H	0.40318300	4.18605000	-1.11635500

IN7

Rh	-0.10678500	-0.56839100	-0.30987900
C	2.41931000	-0.24790100	1.17297500
C	3.67498000	-0.31867900	0.69692300
C	1.33140700	0.69665800	0.76104900
C	1.84419900	1.96145400	-0.00323800
C	1.62520000	1.96958100	-1.52712300
H	1.30252900	2.82606300	0.40779500
H	1.65161400	3.00454200	-1.91297600
H	2.91340400	2.12917200	0.21084400
H	2.36848600	1.36161400	-2.06560500
H	4.05443200	0.35586300	-0.07802700
H	2.11368500	-0.97423400	1.93841000
C	0.27981000	1.35288200	-1.77975200
O	0.22258100	0.26085400	-2.35873900
H	4.36863700	-1.07921400	1.06801800
C	1.11663100	-2.12573200	-0.76610900
O	1.79275000	-3.00047900	-0.98563600
O	-0.38528500	2.19354100	1.72027600
C	0.62280900	1.26004600	2.01979400
H	1.37255900	1.82459400	2.60546200
H	0.23213200	0.44650400	2.65361600
C	-1.02075100	1.95051100	-1.22877800
H	-0.84335100	2.95719300	-0.82129600
C	-1.49638600	0.99629200	-0.09943800
H	-1.75034500	2.00938300	-2.05529500
C	-1.59437100	1.65164900	1.27797000
H	-2.31063100	2.49485700	1.25423600
H	-1.96134200	0.91359500	2.01164100
C	-2.45182400	-0.08597700	-0.41712800
C	-2.32590500	-0.84121500	-1.56774600
H	-1.75595600	-0.51183700	-2.43719300
H	-2.96288200	-1.72230400	-1.69168100
C	-3.46518900	-0.51743300	0.62685600
H	-2.97307000	-0.90301500	1.53260900
H	-4.09983700	0.33969500	0.90950600
H	-4.11138000	-1.31156600	0.22522100
Cl	-0.54136800	-1.78984900	1.65791400

IN8

Rh	0.33839500	-0.71365000	-0.28425200
C	0.34094200	0.18870100	-2.24214800
C	-0.07406400	-1.18187000	-2.40309600
C	-0.27997600	1.20206600	-1.47906300
C	-1.77323100	1.54360200	-1.33885800
C	-2.75248000	0.71543100	-0.48784200
H	-1.79939600	2.57536400	-0.95382500
H	-3.69891100	1.28720700	-0.42527000
H	-2.19293200	1.58850200	-2.36088300

H	-3.03291600	-0.23330300	-0.96988000
H	-1.12705800	-1.41932100	-2.58764600
H	1.39136100	0.37095900	-2.48478400
C	-2.40799400	0.38551200	0.97126400
O	-3.06946000	-0.43276400	1.55958100
H	0.63832400	-1.84474900	-2.90354600
C	-1.21327000	-1.78910800	-0.27342100
O	-2.02907300	-2.58538200	-0.30568900
Cl	2.78376800	-0.56800100	-0.65101100
O	0.41487300	2.91587900	0.11624100
C	0.60406900	2.41404500	-1.17872300
H	0.33035600	3.23728400	-1.86295200
H	1.66621400	2.15345300	-1.34195400
C	-1.29594300	1.14243300	1.69611200
H	-1.44499900	2.21602200	1.49003500
C	0.17854700	0.83267600	1.36423500
H	-1.46532000	0.96487200	2.77118500
C	0.97942200	2.11317600	1.11679800
H	0.97993100	2.73028000	2.03415700
H	2.02010500	1.86725200	0.85079000
C	0.88075600	-0.32430000	1.83908100
C	0.27119100	-1.62259800	1.75217600
H	0.89517500	-2.48387100	2.01015100
H	-0.79052800	-1.73036500	2.00123500
C	2.30548700	-0.26853700	2.34843300
H	2.82381700	-1.21885100	2.16415700
H	2.91522100	0.53057600	1.91564800
H	2.22825300	-0.11029900	3.44115900

TS4

Rh	-0.90461100	0.09011000	-0.11773600
C	-0.12301300	-0.60454600	-1.93587700
C	-0.99308600	0.46702200	-2.25717600
C	1.18019500	-0.41001500	-1.30646700
C	2.02065100	0.86161300	-1.52302900
C	1.66817800	2.14216400	-0.75387400
H	3.05986500	0.59156400	-1.27634300
H	2.49408100	2.86843900	-0.87986200
H	2.00866500	1.08100600	-2.60659000
H	0.77016900	2.64625100	-1.13919700
H	-0.59759300	1.46216200	-2.47632200
H	-0.46230400	-1.62907200	-2.12092200
C	1.49816700	1.97062800	0.75413300
O	1.09094100	2.86863300	1.44439100
H	-1.95805100	0.21549500	-2.70641200
C	-1.59781600	1.90733000	0.03459000
O	-2.16493500	2.89221800	0.11132000
Cl	-2.63833300	-1.63396900	-0.37597900
O	2.92689600	-1.73236400	-0.30565500
C	2.06400000	-1.65708900	-1.39253900
H	2.67671100	-1.58879300	-2.30823700
H	1.43317100	-2.56561600	-1.45912100
C	1.96037400	0.64598400	1.35705300
H	3.01234900	0.50368700	1.05177600
C	1.17823300	-0.61499800	0.94618900
H	1.93440200	0.75329800	2.45392800
C	2.12172700	-1.82021100	0.82527100
H	2.77998200	-1.82854600	1.71185100
H	1.55319000	-2.76375000	0.80473300
C	-0.12003100	-0.91760200	1.58882500
C	-0.91429400	0.16847800	2.05438600
H	-1.86473000	-0.07694500	2.53767300
H	-0.46145700	1.12182800	2.34103400
C	-0.54945000	-2.33965300	1.90361300
H	-1.59970700	-2.34280400	2.22199900
H	-0.48036400	-3.01544900	1.04089200
H	0.07453000	-2.73276000	2.72786700

IN9

Rh	1.20809200	0.03903200	0.16762700
C	-0.25492700	-1.08912100	1.22378900
C	0.74011200	-0.69329700	2.15615900
C	-1.58623500	-0.36652200	0.94592300
C	-1.62844800	1.00409600	1.65074200
C	-0.73567700	2.02825500	0.94639600
H	-2.66118600	1.39127700	1.64543100
H	-0.63903100	2.98144200	1.49294200
H	-1.34768000	0.88940900	2.70865600
H	0.34982300	1.70925800	0.88288300
H	0.59797600	0.13856800	2.85261700
H	-0.22865900	-2.13605600	0.90476200
C	-1.25424800	2.32774500	-0.46010600
O	-0.98405100	3.34454700	-1.04105700
H	1.47741000	-1.43706900	2.47024900
C	2.86684300	1.10760500	0.09060000
O	3.87160500	1.63304100	0.05764800
Cl	2.56756800	-1.80958700	-0.21504200
O	-3.75112300	-1.00092200	0.27469900

C	-2.83967000	-1.21099300	1.31633200
H	-3.30674000	-0.90774900	2.26637300
H	-2.56732600	-2.28456100	1.38495500
C	-2.15462300	1.24315400	-1.02580600
H	-3.16367400	1.42754800	-0.61173900
C	-1.74970200	-0.20189800	-0.64040700
H	-2.21669600	1.37012100	-2.11763700
C	-2.99419000	-1.10365400	-0.89812500
H	-3.60645400	-0.76349200	-1.74803000
H	-2.70609500	-2.15616400	-1.07030600
C	-0.44364400	-0.64841700	-1.36534700
C	0.43263800	0.25109100	-1.97425100
H	1.20701200	-0.14487200	-2.63816700
H	0.22603300	1.31743500	-2.08978200
C	-0.33105300	-2.10791700	-1.77525500
H	0.69393800	-2.33903200	-2.09409900
H	-0.60200700	-2.81307400	-0.97575300
H	-1.01393400	-2.29053100	-2.62504500

4r

C	1.07592400	0.28276600	-1.84809200
C	0.19887000	0.48542500	-0.59209800
C	-1.28892900	0.43377700	-1.07437600
C	-2.29462900	-0.12000500	-0.07862100
C	-1.90158000	-1.47006500	0.49758800
C	-0.50581500	-1.38401500	1.14004800
C	0.59472500	-0.82483600	0.21285900
C	0.91350500	-1.81239300	-0.96982600
C	0.45014300	1.79955200	0.14507600
C	-0.26587200	2.01189800	1.46203600
C	1.22677800	2.76499700	-0.37278100
C	1.88675700	-0.58287700	0.98003300
C	2.15157800	-0.91110400	2.24960700
H	0.73563300	0.88289600	-2.70770800
H	2.13333200	0.54143500	-1.64252700
H	-1.61975800	1.43189700	-1.40131200
H	-1.32843600	-0.25009000	-1.94314800
H	-1.90272600	-2.20425000	-0.32911500
H	-2.66075000	-1.77992100	1.23162400
H	-0.57876800	-0.75065200	2.03866100
H	-0.19917100	-2.38505600	1.49161000
H	1.88842800	-2.30760000	-0.80008300
H	0.15075000	-2.60444100	-1.06368800
H	-1.35505900	1.86393000	1.36337500
H	-0.09665600	3.03337800	1.83564000
H	0.10306000	1.30863000	2.22780100
H	1.75049100	2.66179400	-1.32654200
H	1.35807100	3.71555500	0.15429800
H	2.68680300	-0.11103800	0.39553800
H	1.41693100	-1.38778600	2.90527700
H	3.13648700	-0.70762600	2.68051400
O	0.93325400	-1.07160900	-2.16328100
O	-3.31667700	0.44788700	0.21091400

IN5-H

O	-3.04680500	0.73365300	1.31232100
C	-1.89943500	0.84020400	1.02315500
Rh	-1.00616700	-0.28147700	-0.33251800
C	-0.02978700	1.14230700	-1.63073500
C	-1.44657300	1.20102400	-1.84738500
C	0.54962700	1.38139200	-0.36985600
C	-0.00492800	2.43077100	0.59520200
C	-0.90095900	1.80033400	1.67164900
H	0.83266500	2.96672000	1.07331000
H	-0.30118000	1.16762400	2.35065800
H	-0.58016200	3.18302100	0.02955600
H	-1.45856300	2.54344700	2.26512400
H	-2.04774300	1.99859600	-1.39361600
H	0.57897600	0.55882600	-2.33374100
H	-1.81589500	0.87098700	-2.82403100
C	1.97652300	0.93952100	-0.10398300
H	2.02620900	0.56915200	0.93988200
H	2.65287300	1.81992700	-0.17262800
O	2.35314400	-0.05324200	-1.00380100
C	3.31168000	-0.96432100	-0.52543800
H	2.94161500	-1.45377800	0.39689600
H	3.39787000	-1.73671700	-1.30869900
C	4.66113900	-0.32647700	-0.29034100
C	5.34407600	-0.41925900	0.85520300
H	6.33270700	0.03569300	0.97352200
H	4.93872200	-0.96684400	1.71465200
Cl	0.11835500	-1.58026500	1.31177500
C	-2.56593600	-1.45986400	-0.43565400
O	-3.46715200	-2.13646900	-0.50331400
H	5.08133100	0.22900800	-1.14028600

TS3-H

Rh	0.10806600	-0.24787800	-0.68595000

C	0.96849000	-0.70869400	2.02880600
C	2.00372900	-0.19995600	2.71719700
C	-0.14750100	0.04934900	1.36790800
C	-0.18067200	1.56354200	1.67031500
C	0.62019900	2.40496500	0.67743500
H	-1.23232700	1.88754200	1.65341800
H	0.41440200	3.48550700	0.78850700
H	0.17905000	1.74748300	2.69697400
H	1.71045100	2.27753600	0.80020700
H	2.14142000	0.87453900	2.87689700
H	0.90692800	-1.79818600	1.90908700
C	0.33570700	2.01995500	-0.77319200
O	0.94489000	2.46906800	-1.70129800
H	2.76157900	-0.86093700	3.14889700
C	2.18634100	-0.40473700	-0.59494400
O	3.29383000	-0.59305600	-0.69068100
O	-2.61163000	0.03782900	1.22141300
C	-1.49522700	-0.58243600	1.78686300
H	-1.59614200	-0.45225200	2.88092500
H	-1.48642100	-1.66641600	1.56648400
C	-1.30983900	1.47937300	-1.13504800
H	-1.78149400	2.11890900	-0.37263700
C	-1.82800100	0.06630200	-1.09473000
H	-1.33199900	1.91841700	-2.13913500
C	-2.89342400	-0.34657000	-0.09173200
H	-3.86816800	0.10960900	-0.34200100
H	-3.00772500	-1.44721900	-0.16153700
Cl	0.04676500	-2.59160800	-0.72529800
H	-2.04303100	-0.33998400	-2.09698800

IN5-NTs

O	-5.01120300	-1.27354800	-1.37589700
C	-3.84431100	-1.12664500	-1.21591100
Rh	-3.07124100	-0.02137400	0.22375500
C	-1.59787900	-1.32668700	1.16703000
C	-2.93550800	-1.74010600	1.49262600
C	-1.12986400	-1.25524400	-0.15289500
C	-1.59906200	-2.24898000	-1.22322200
C	-2.73672900	-1.70171700	-2.09694100
H	-0.74521000	-2.52188200	-1.86559400
H	-2.38355800	-0.85062100	-2.70634900
H	-1.92958800	-3.17879100	-0.73004800
H	-3.17682500	-2.46511500	-2.75946100
H	-3.38929200	-2.59659700	0.97804000
H	-1.03578200	-0.76097700	1.91933200
H	-3.23490600	-1.65536800	2.54272000
C	0.19412100	-0.56426400	-0.49516600
H	0.03789200	0.07086700	-1.38396500
H	0.90466600	-1.35077600	-0.81225300
C	0.59574100	1.70210200	0.56750000
H	-0.46758000	1.85739500	0.32316300
H	0.75094300	2.04443600	1.59730300
C	1.42008300	2.52325800	-0.42933800
C	0.96241600	2.63131200	-1.69497500
H	1.49849000	3.19198600	-2.46436200
H	0.00093300	2.19413400	-1.98170100
C	2.64582300	3.25443400	0.00958300
C	3.06863300	3.28176500	1.29026000
H	2.59362400	2.71587500	2.09353500
H	3.95118400	3.87080400	1.56108900
C	3.39919600	4.04188100	-1.04495900
H	2.76195100	4.82710800	-1.48709200
H	4.28632100	4.52577500	-0.61018100
H	3.73043500	3.38762700	-1.87005400
Cl	-2.58336400	1.73892100	-1.32083200
C	-4.83667100	0.65458800	0.70194400
O	-5.85559300	1.04244100	0.99469700
N	0.80708300	0.24316400	0.54390500
S	1.86445900	-0.51990100	1.55718100
C	3.31839300	-0.96138600	0.57840500
C	3.45652300	-2.27941200	0.13091100
C	4.29633500	0.00243700	0.30139200
C	4.58092900	-2.62734300	-0.62804700
H	2.69912200	-3.02090800	0.39780400
C	5.41167500	-0.36442000	-0.45423300
H	4.18379300	1.02202100	0.67836500
C	5.57154700	-1.67969900	-0.93371600
H	4.69263700	-3.65807600	-0.97931000
H	6.18028300	0.38476800	-0.67102000
C	6.79661400	-2.05525900	-1.73736300
H	7.70323000	-2.01364300	-1.10873000
H	6.71365400	-3.07407600	-2.14564600
H	6.94733500	-1.35721300	-2.57785600
O	2.25322200	0.44779300	2.56220000
O	1.25611700	-1.78368500	1.93498500

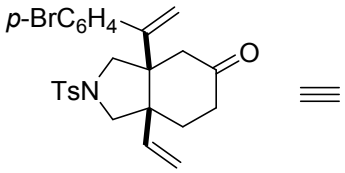
TS3-NTs

Rh	-2.16901300	0.50356700	0.07490800

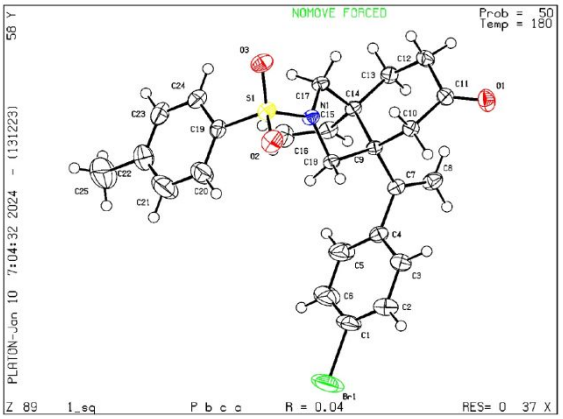
C	-1.85401700	-1.79101600	1.95521300
C	-2.61836400	-2.88737300	2.09734000
C	-1.17679700	-1.29218200	0.70743600
C	-1.20120300	-2.32466000	-0.44343000
C	-2.42657800	-2.18391500	-1.34037200
H	-0.29743500	-2.22501100	-1.05962000
H	-2.35600900	-2.78484100	-2.26524400
H	-1.14960700	-3.34859400	-0.03567700
H	-3.35402300	-2.49890600	-0.82686300
H	-2.82908900	-3.58245000	1.27799800
H	-1.70758800	-1.15461000	2.83587400
C	-2.68857300	-0.74109900	-1.74722000
O	-3.58052400	-0.38850400	-2.45367300
H	-3.07010600	-3.12409200	3.06551900
C	-3.97752300	-0.01812200	0.78613100
O	-4.98889500	-0.24512400	1.23114800
C	0.29023900	-0.93188500	1.07420600
H	0.81137200	-1.85235600	1.38327400
H	0.28855300	-0.22879200	1.92416900
C	-1.11742500	0.31853100	-1.93695600
H	-0.44300100	-0.51602400	-2.16348900
C	-0.55997100	1.26159600	-0.94679400
H	-1.54722200	0.79548200	-2.82443900
C	0.82981900	1.05624600	-0.36760200
H	1.60166600	1.37604500	-1.08741100
H	0.93811500	1.67550300	0.53853900
C	-1.32610800	2.50112000	-0.76496900
C	-2.65683600	2.51597200	-1.17102100
H	-3.05739500	1.89315700	-1.97576800
H	-3.28771800	3.35072200	-0.85149900
C	-0.74798400	3.63120000	0.05239100
H	-0.44235500	3.28597000	1.05190800
H	0.13280600	4.04345300	-0.47036100
H	-1.48631000	4.43585300	0.17970200
Cl	-1.86441500	1.45019500	2.27068500
N	1.06249000	-0.33647700	-0.01724200
S	2.21994300	-1.16662900	-0.83693700
O	2.08778500	-0.82446200	-2.24472600
O	2.14677000	-2.54441300	-0.39399200
C	3.80030500	-0.49453500	-0.28936600
C	4.49847900	0.39586100	-1.10855400
C	4.30827400	-0.88325000	0.95839300
C	5.71574300	0.92295700	-0.65709000
H	4.09693200	0.65367500	-2.09224500
C	5.52162100	-0.34765900	1.39130800
H	3.76387100	-1.60727700	1.57122800
C	6.24284900	0.56493900	0.59422400
H	6.26771900	1.61982100	-1.29570200
H	5.92439800	-0.64822100	2.36420200
C	7.56141000	1.12343300	1.08097500
H	7.44896000	1.59151500	2.07349600
H	8.31318800	0.32117400	1.17907700
H	7.95913700	1.87944800	0.38698700

7. X-ray crystallographic data of 4h and 5

X-ray data of 4h



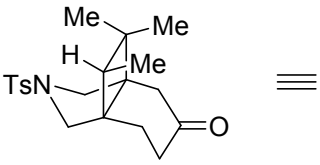
CCDC : 2443512



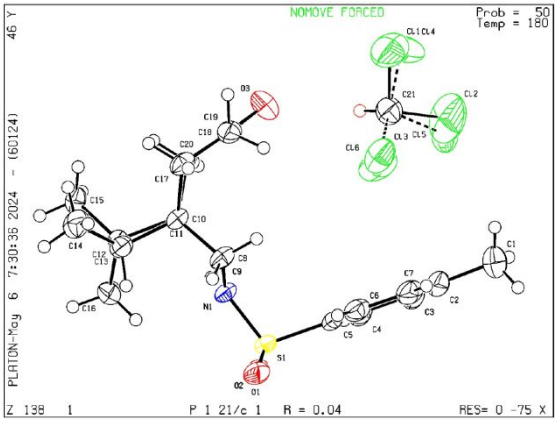
Ellipsoids are drawn at 50% probability

Crystal data	
Chemical formula	$C_{25}H_{26}BrNO_3S$
M_r	500.44
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	180
a, *b*, *c* (Å)	6.6067 (2), 21.1596 (5), 36.4896 (7)
V (Å^3)	5101.1 (2)
Z	8
Radiation type	Mo *K*α
μ (mm^{-1})	1.72
Crystal size (mm)	0.5 × 0.15 × 0.1
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.043, 0.104, 1.01
No. of reflections	6627
No. of parameters	281
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.35, −0.59

X-ray data of 5



CCDC : 2443513

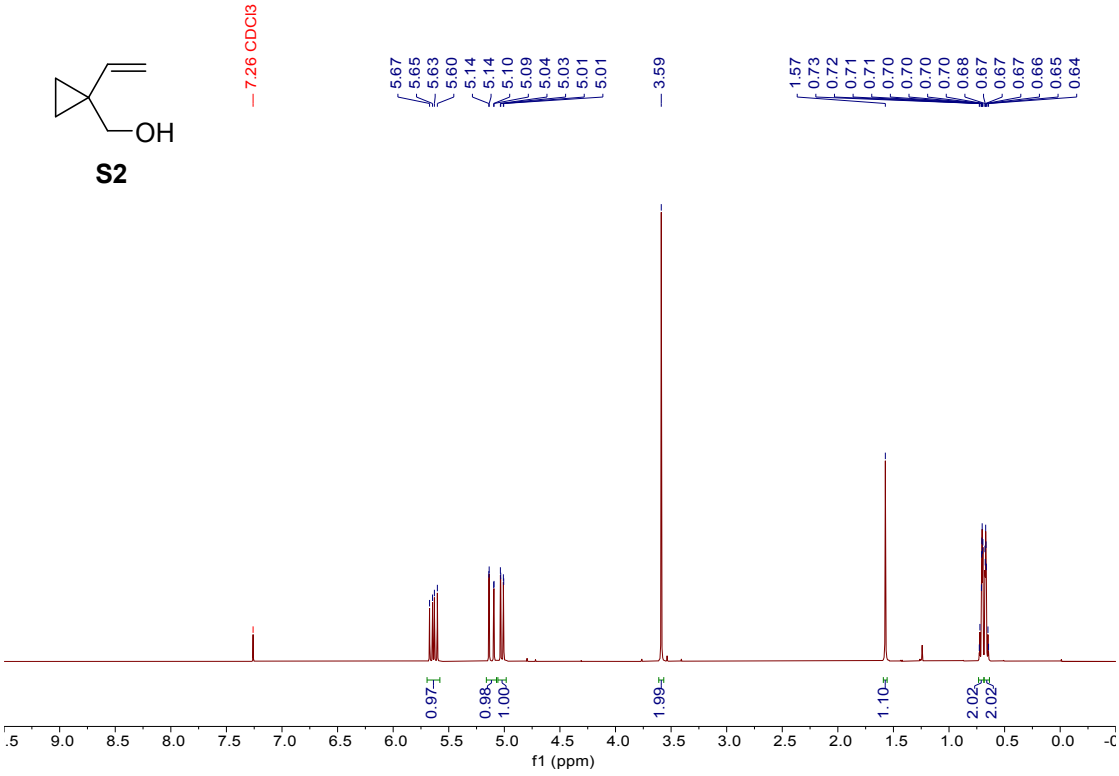


Ellipsoids are drawn at 50% probability

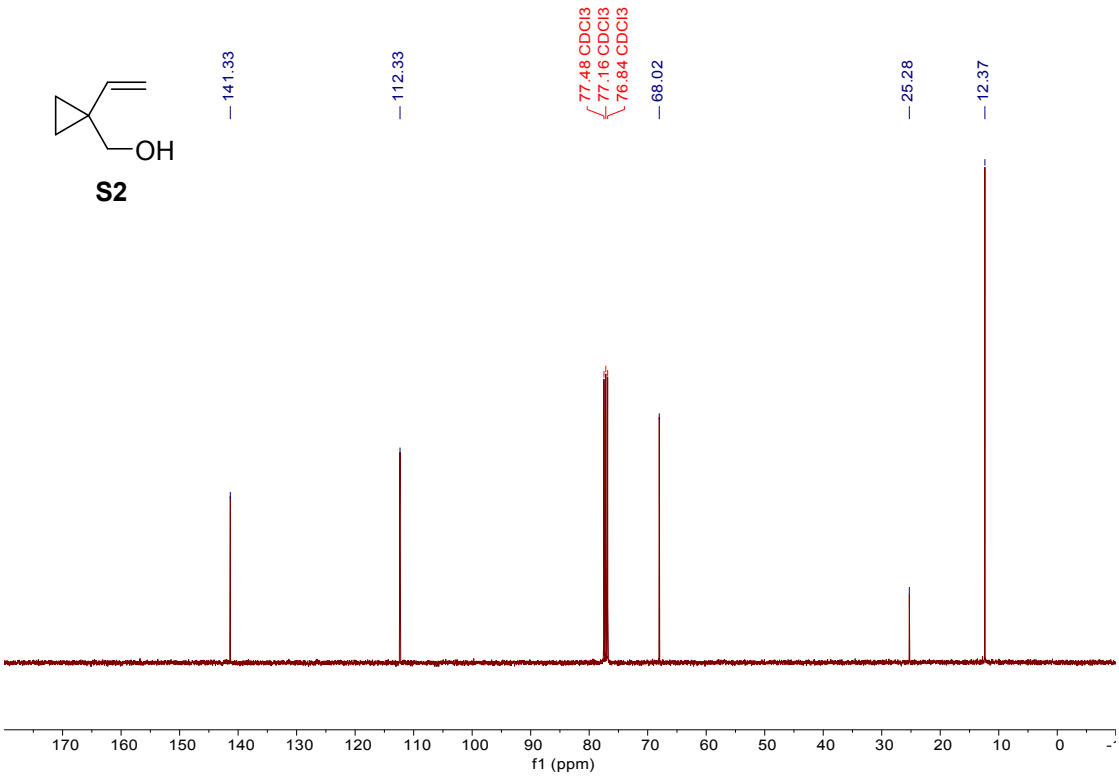
Crystal data	
Chemical formula	$C_{20}H_{27}NO_3S{\cdot}CDCl_3$
M_r	481.86
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	180
a, b, c (Å)	15.5499 (3), 8.1707 (2), 17.9434 (3)
β (°)	95.161 (2)
V (Å^3)	2270.53 (8)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.52
Crystal size (mm)	0.4 × 0.26 × 0.03
R_{int}	0.032
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.717
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.129, 1.05
No. of reflections	6416
No. of parameters	298
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.41, −0.37

8. Copies of NMR spectra

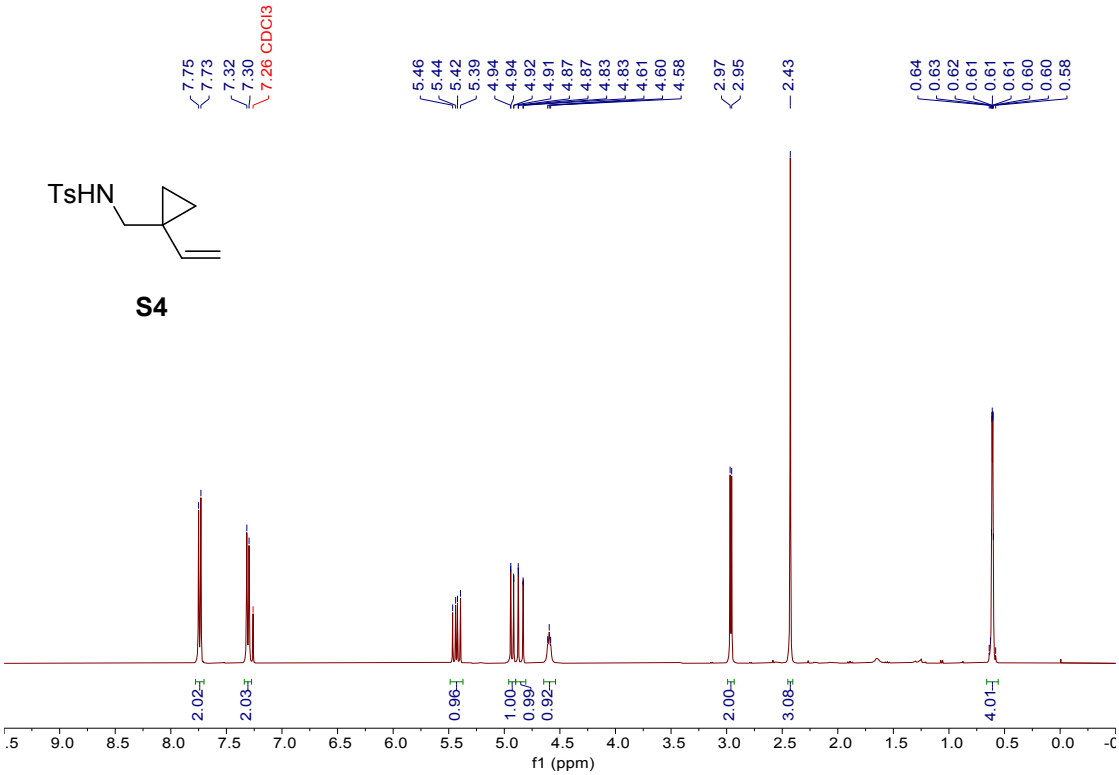
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



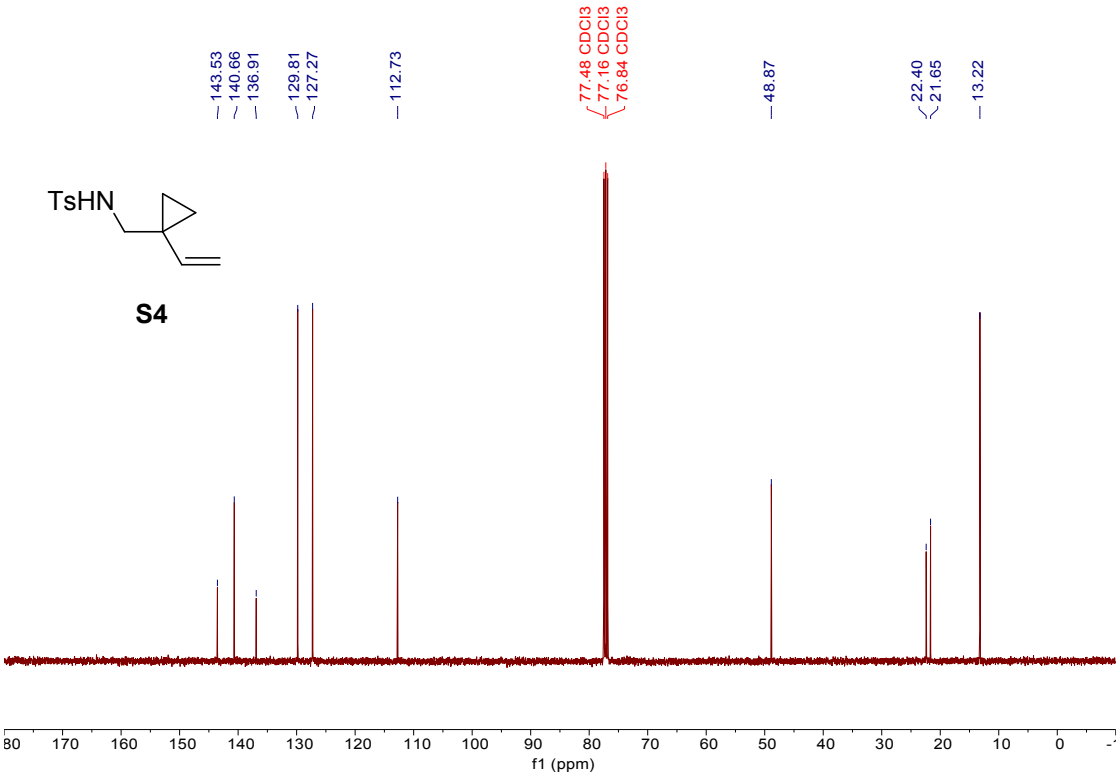
^{13}C NMR spectrum in $CDCl_3$, 101 MHz



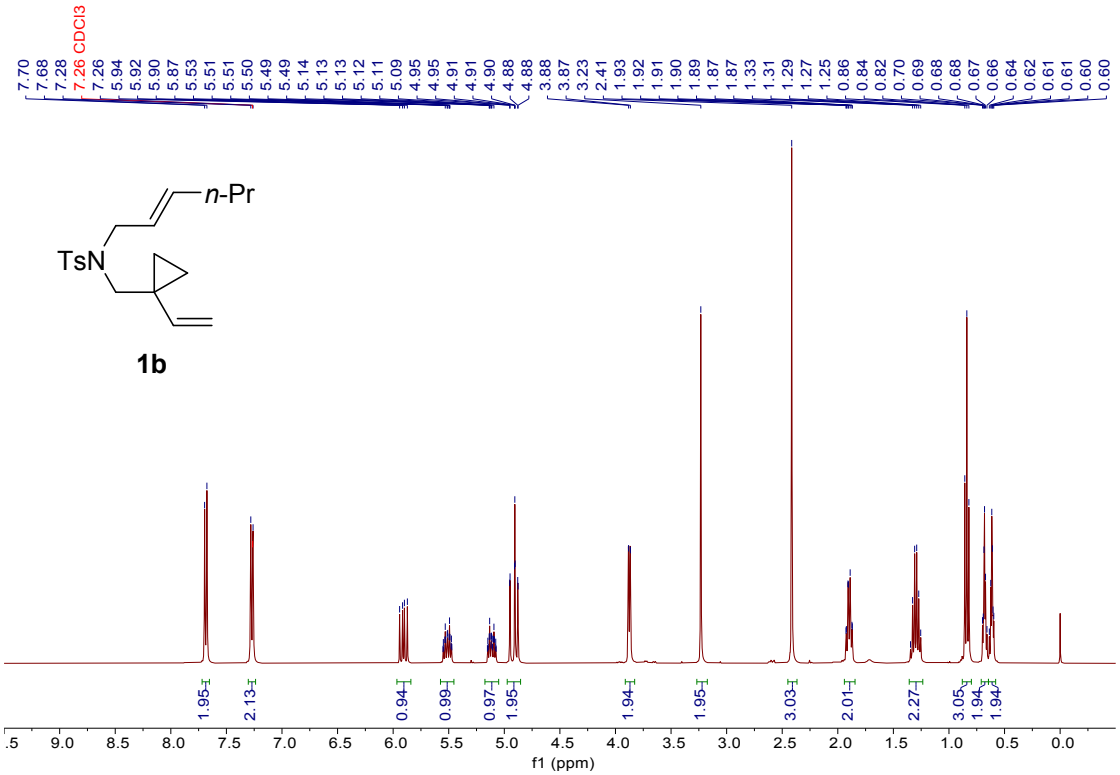
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



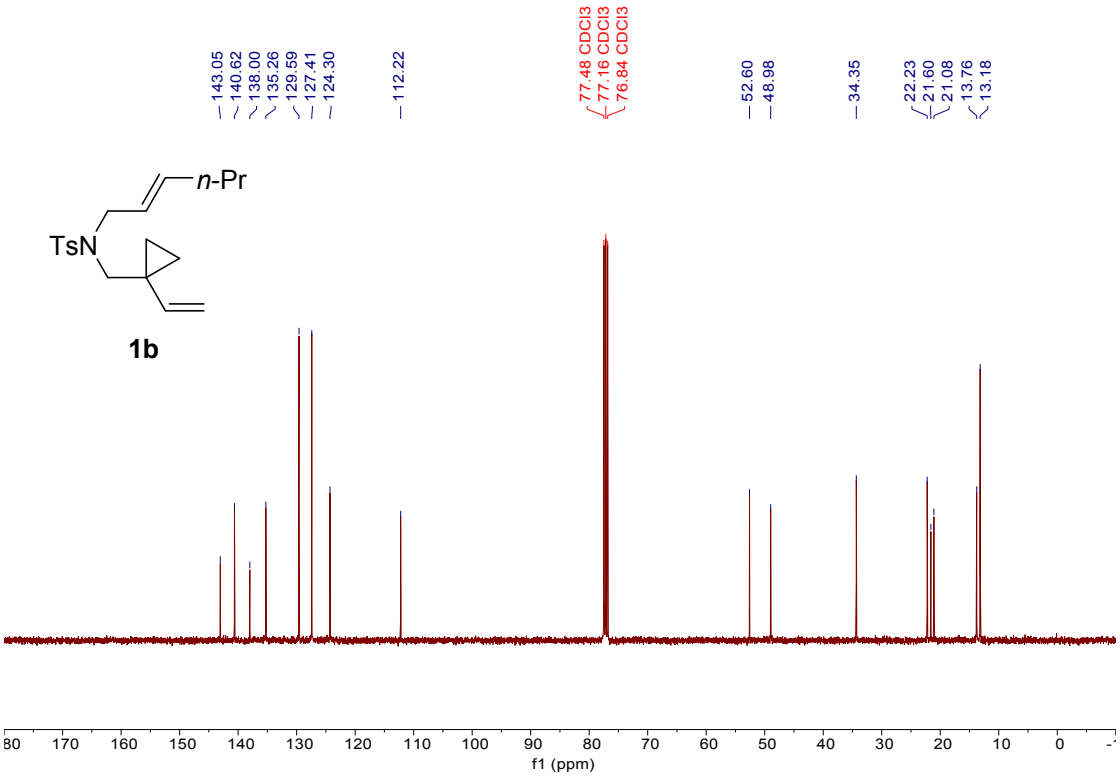
^{13}C NMR spectrum in $CDCl_3$, 101 MHz



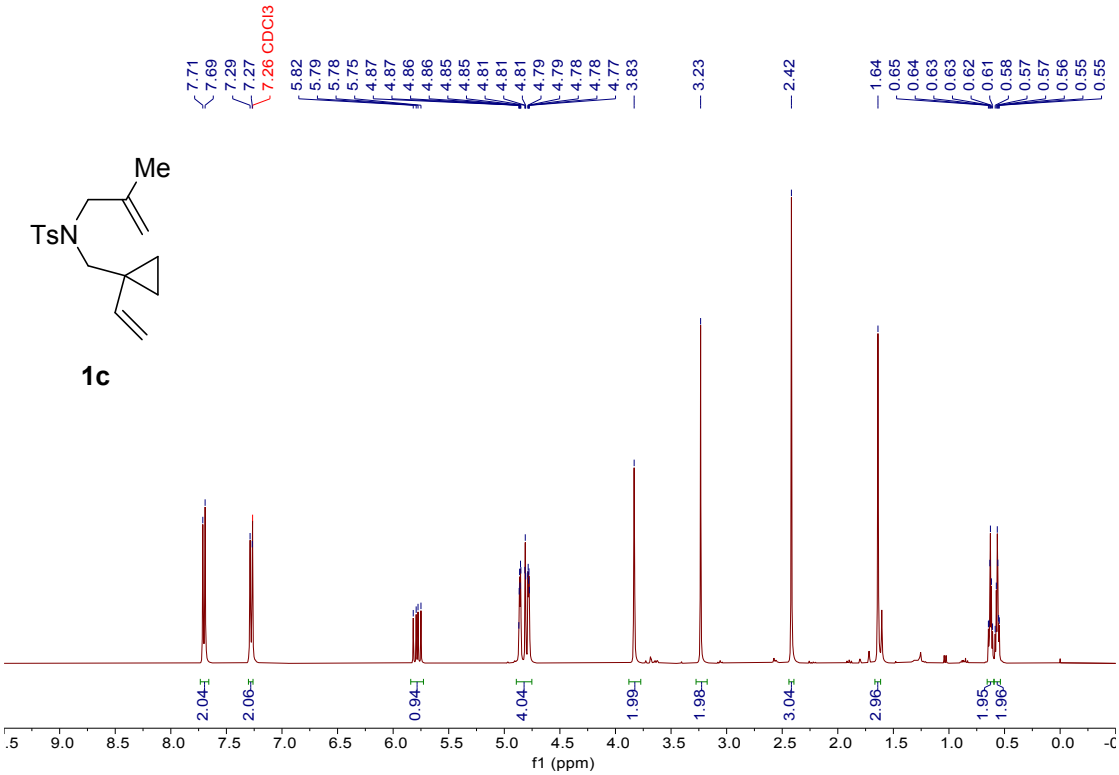
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



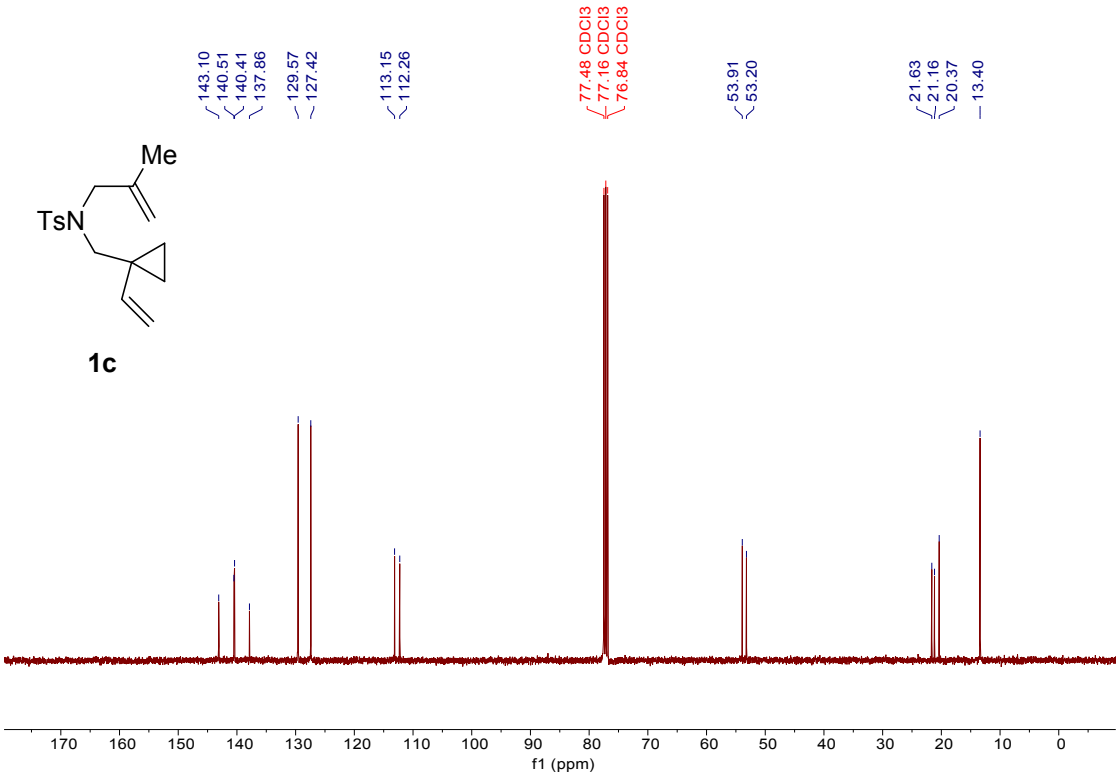
^{13}C NMR spectrum in $CDCl_3$, 101 MHz



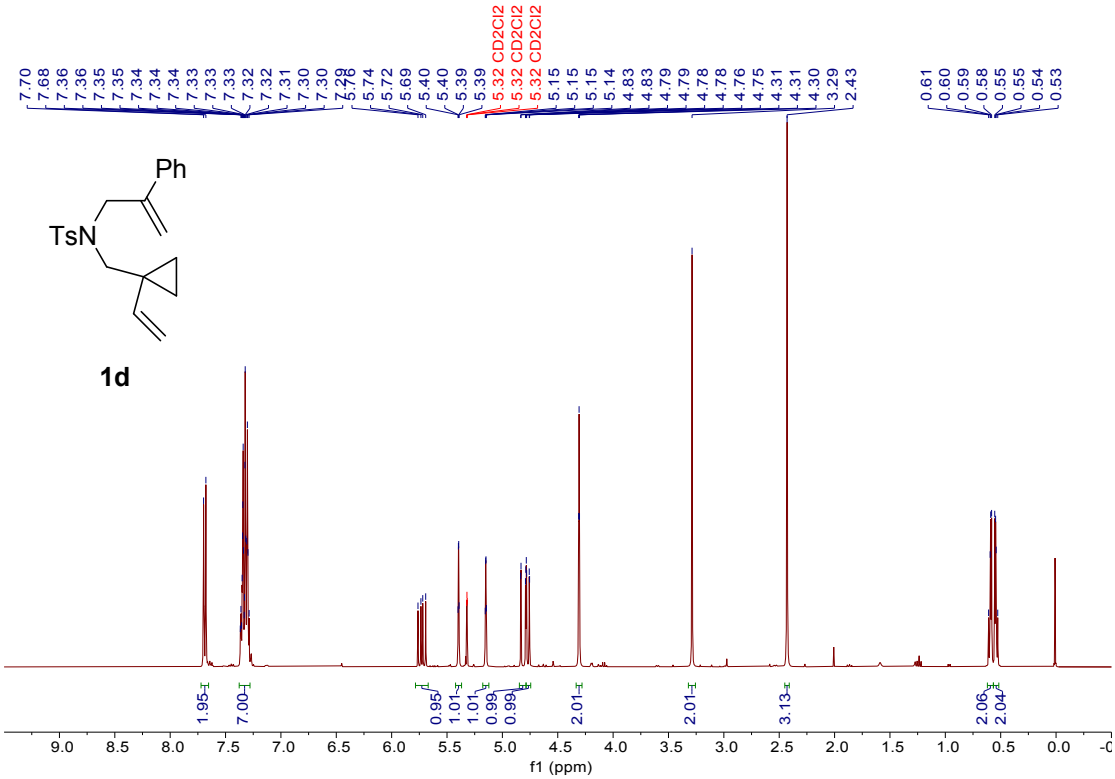
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



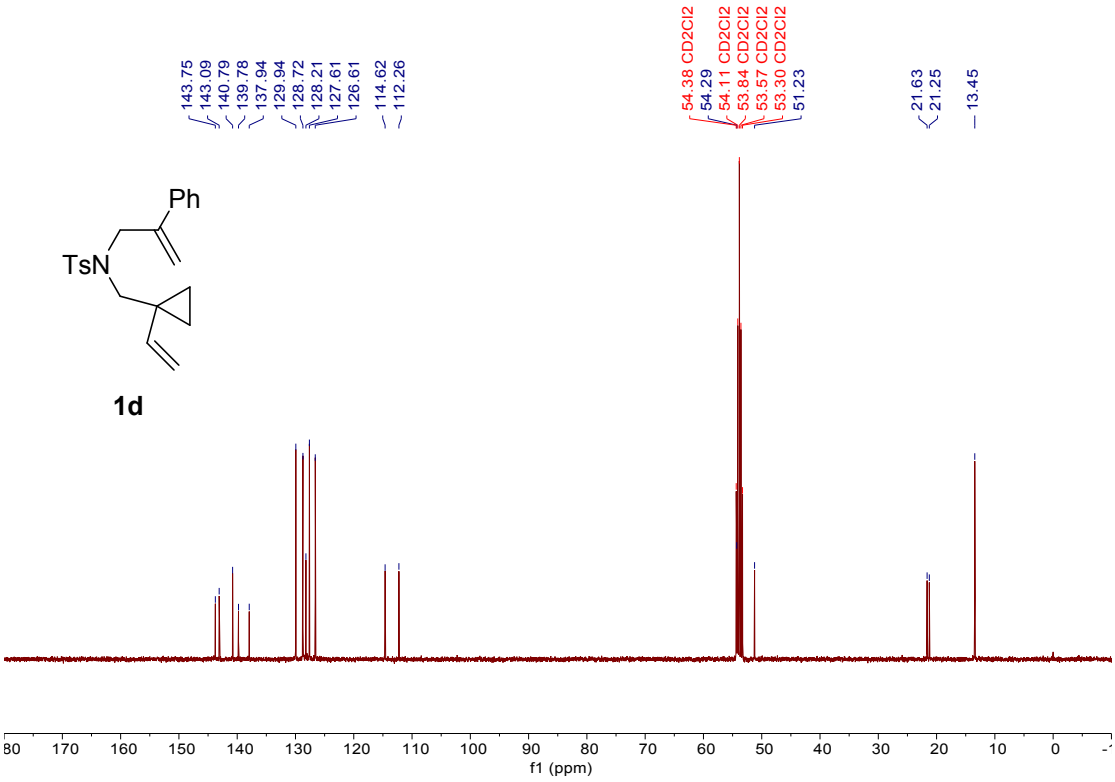
^{13}C NMR spectrum in $CDCl_3$, 101 MHz



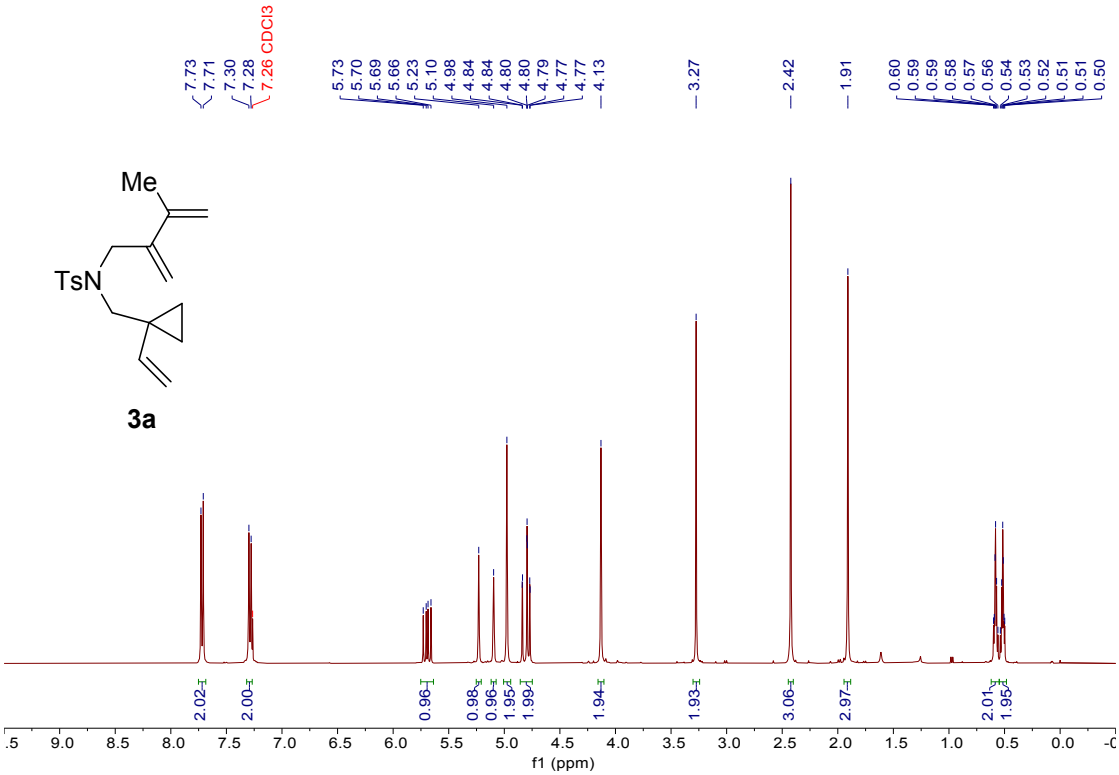
^{1}H NMR spectrum in CD_2Cl_2, 400 MHz



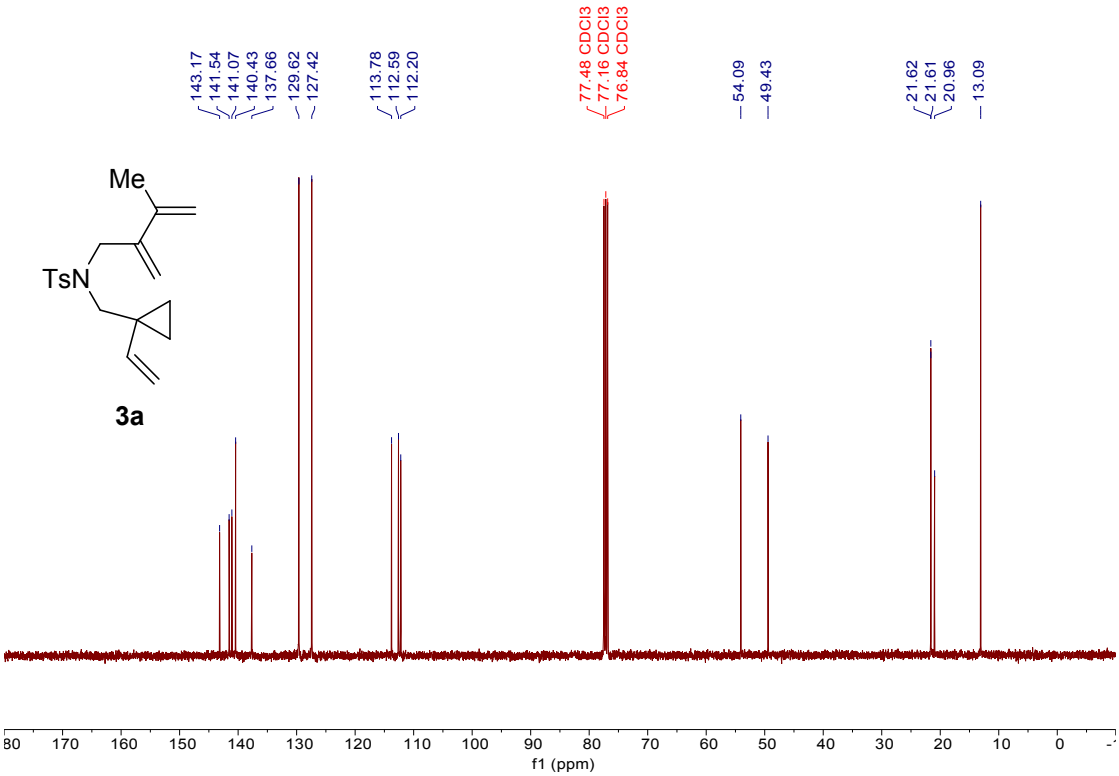
^{13}C NMR spectrum in CD_2Cl_2, 101 MHz



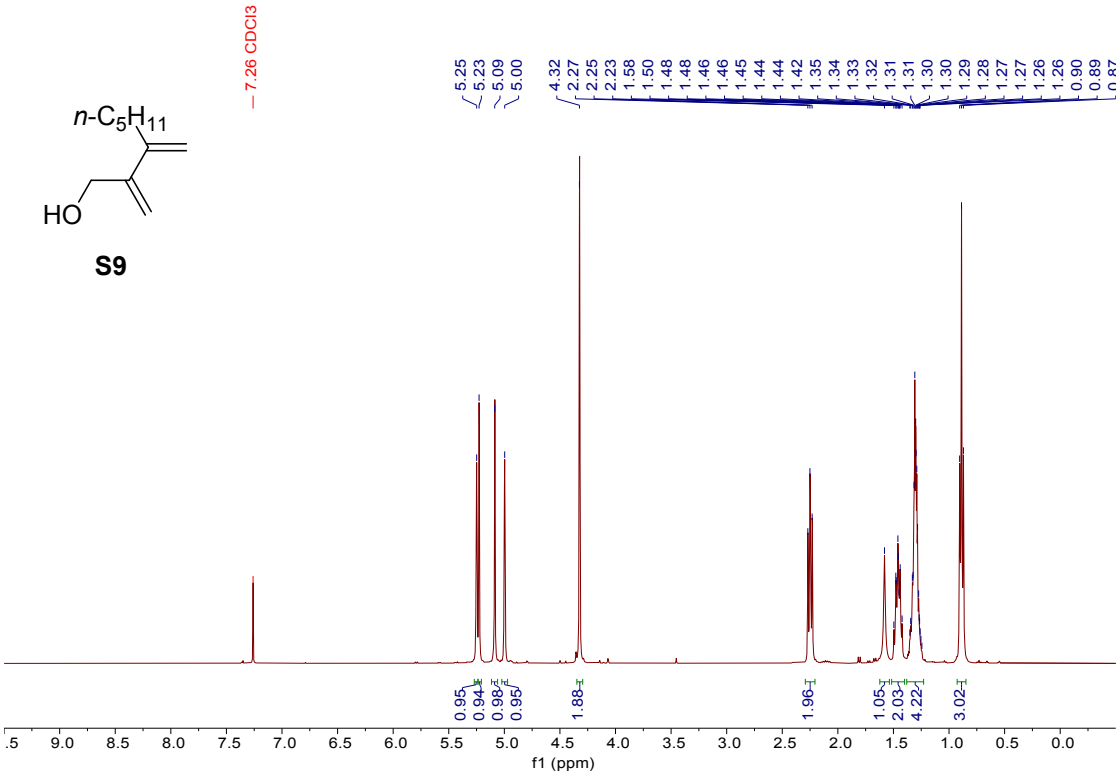
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



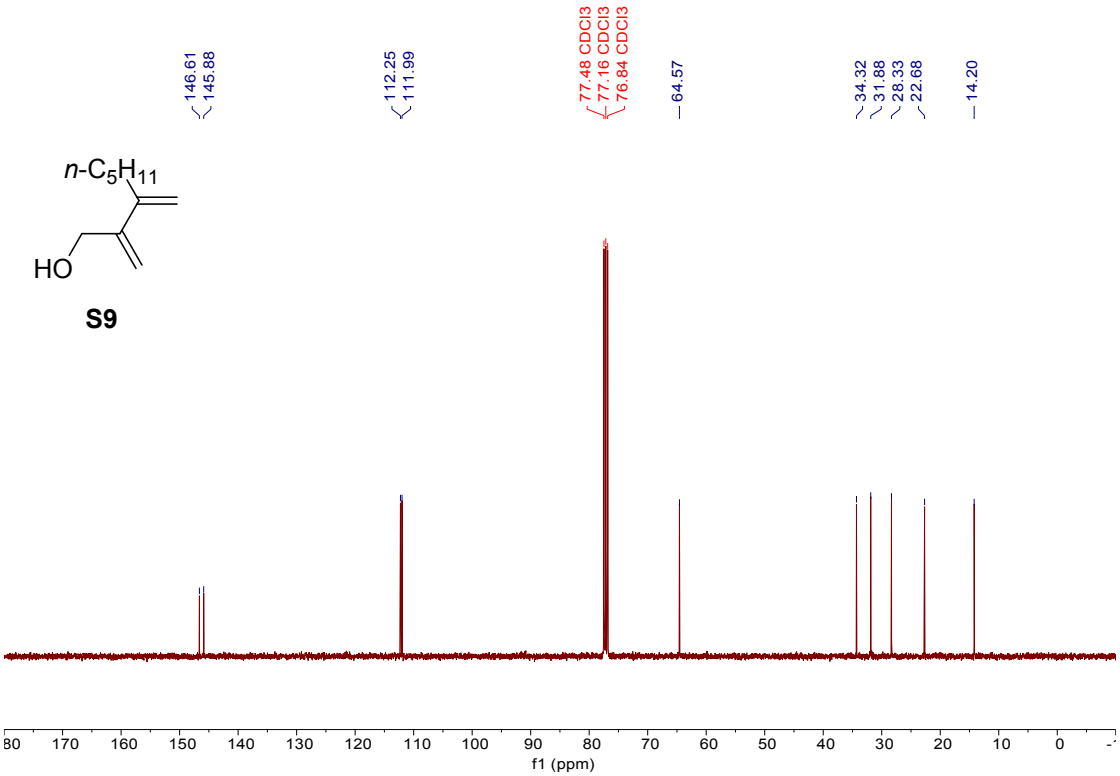
^{13}C NMR spectrum in $CDCl_3$, 101 MHz



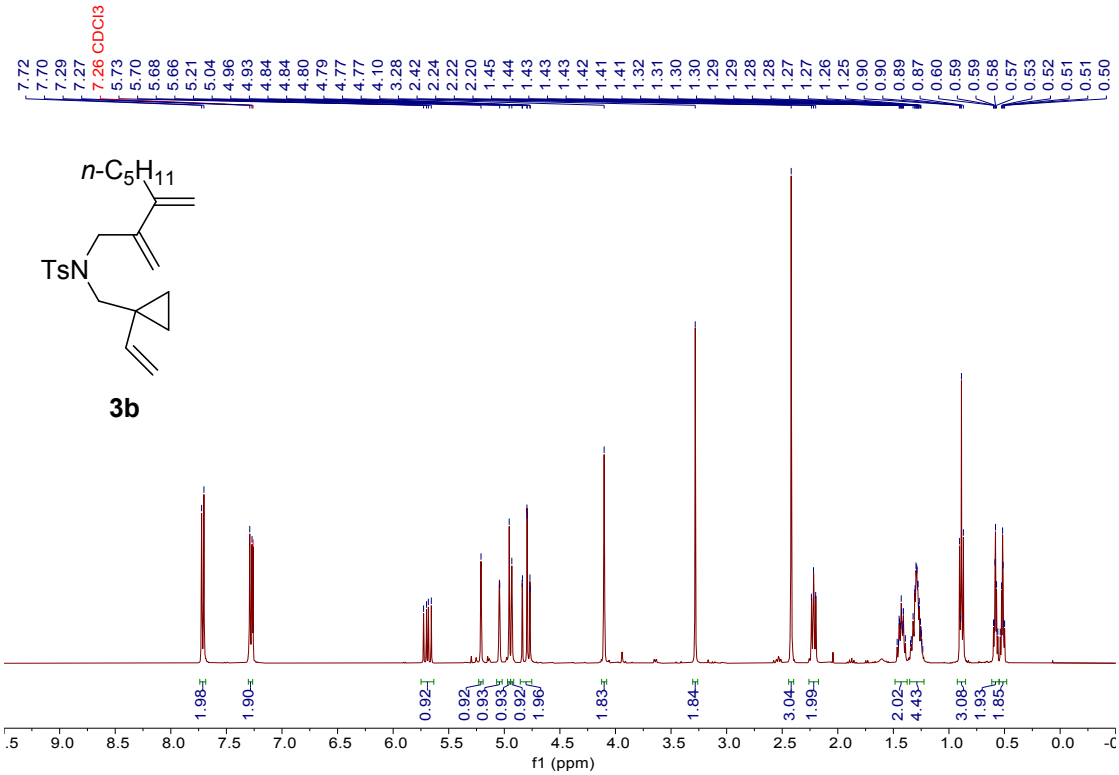
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



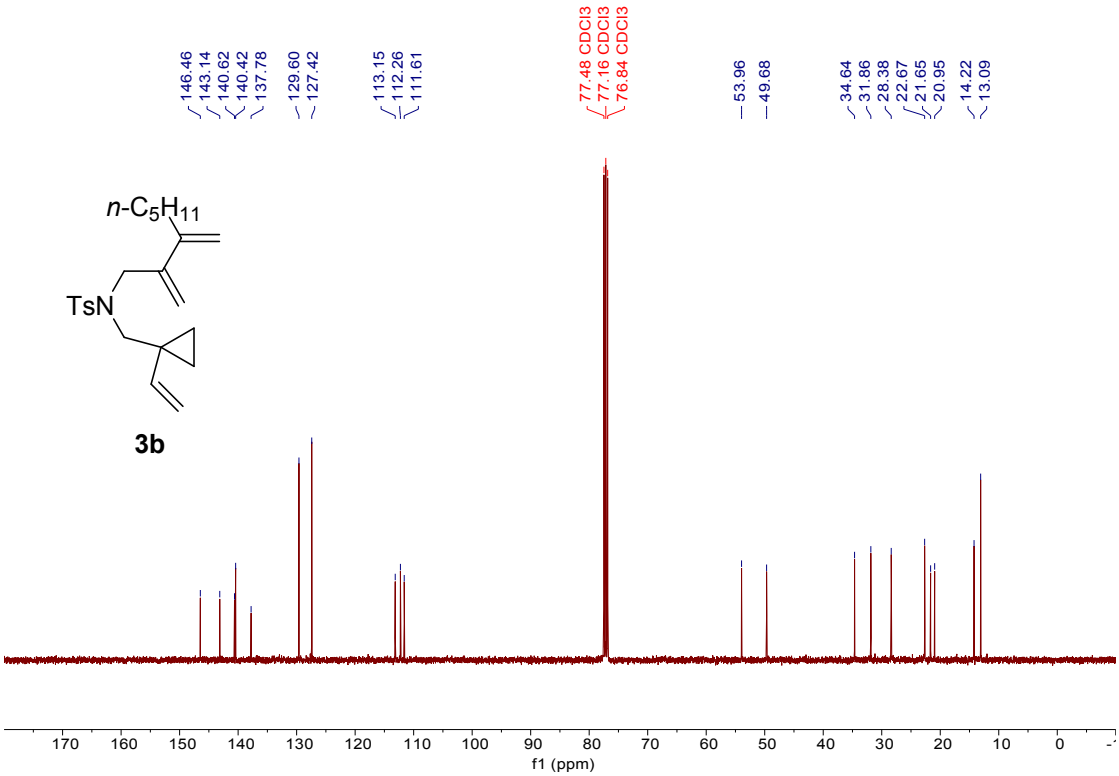
^{13}C NMR spectrum in $CDCl_3$, 101 MHz



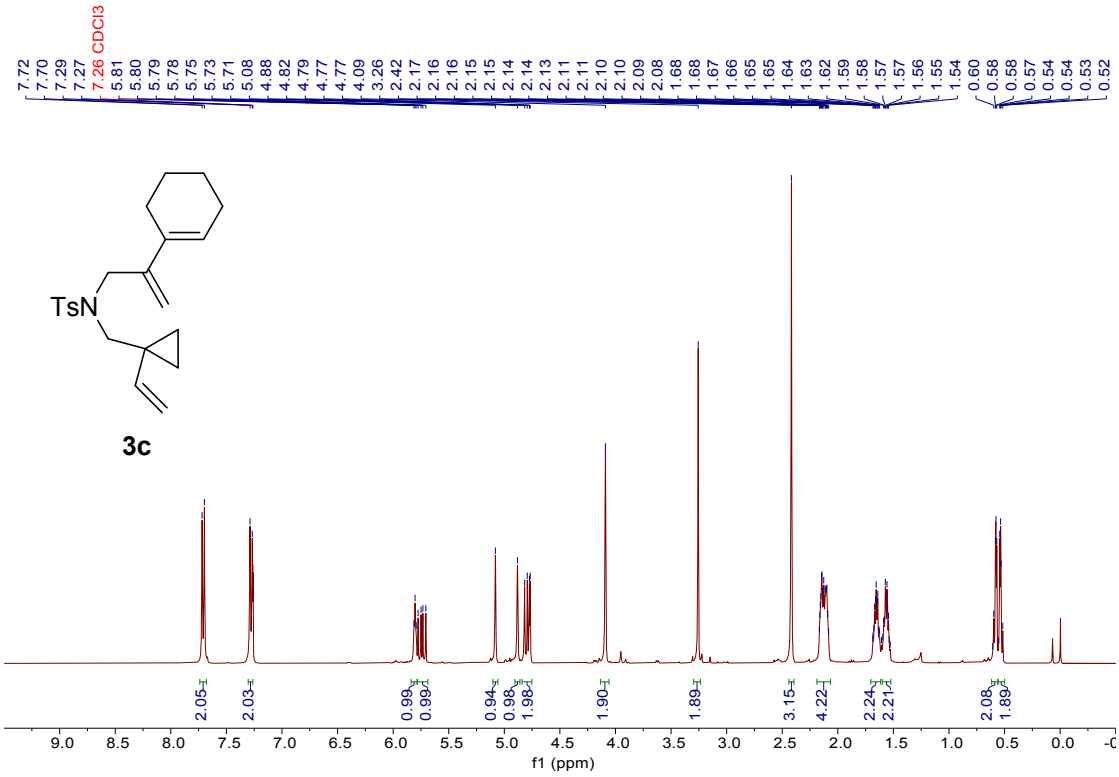
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



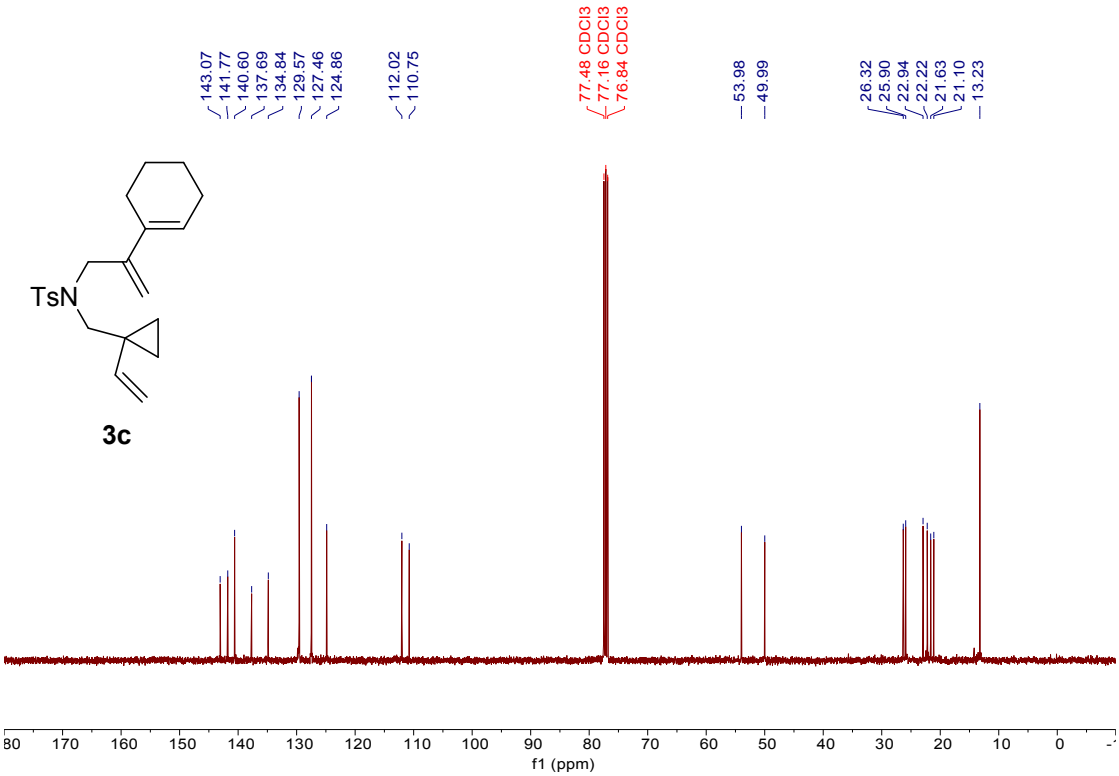
^{13}C NMR spectrum in $CDCl_3$, 101 MHz



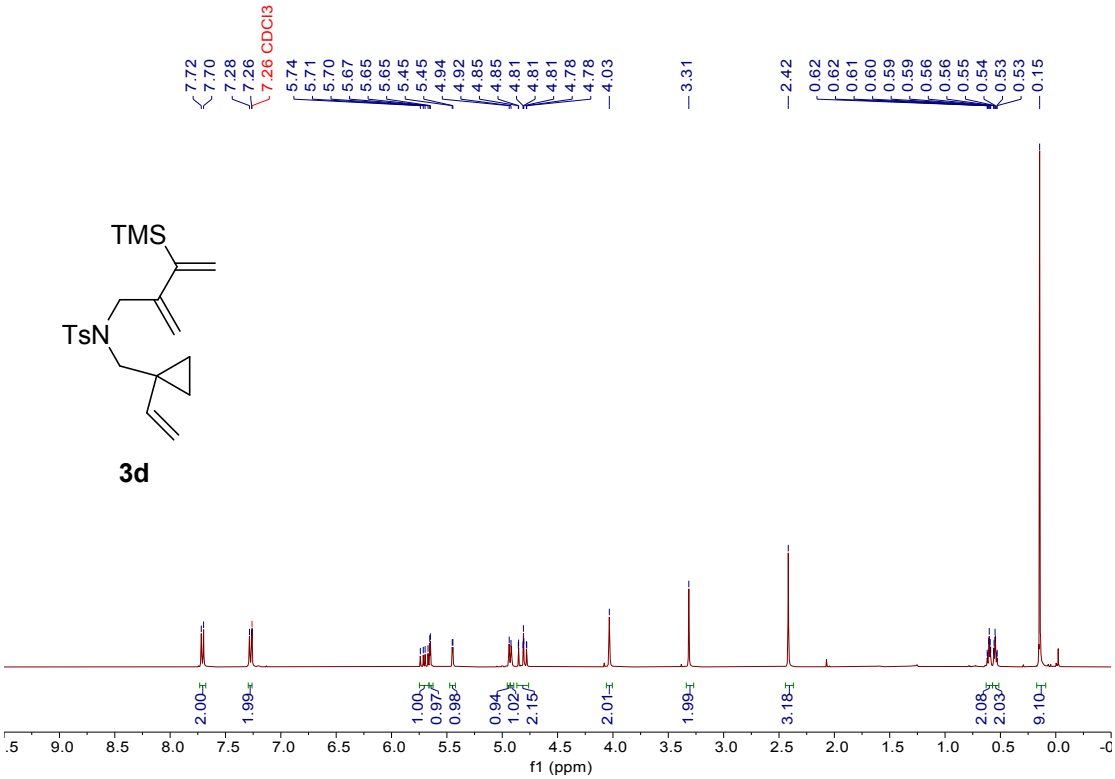
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



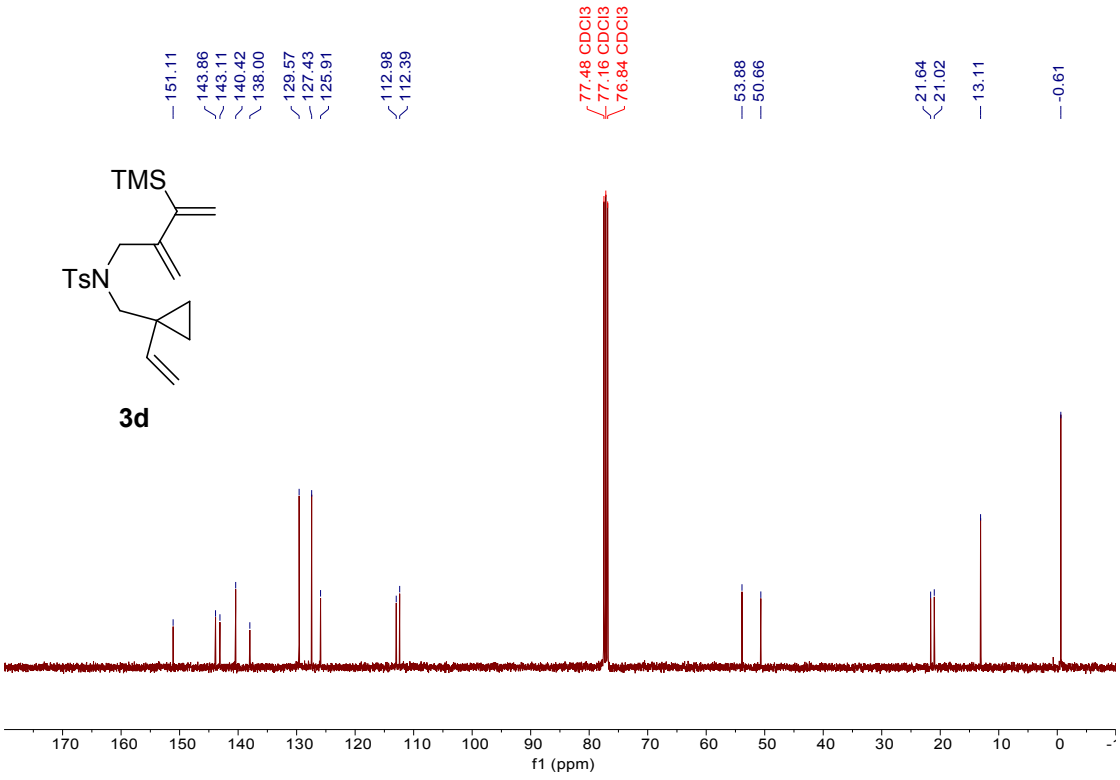
^{13}C NMR spectrum in $CDCl_3$, 101 MHz



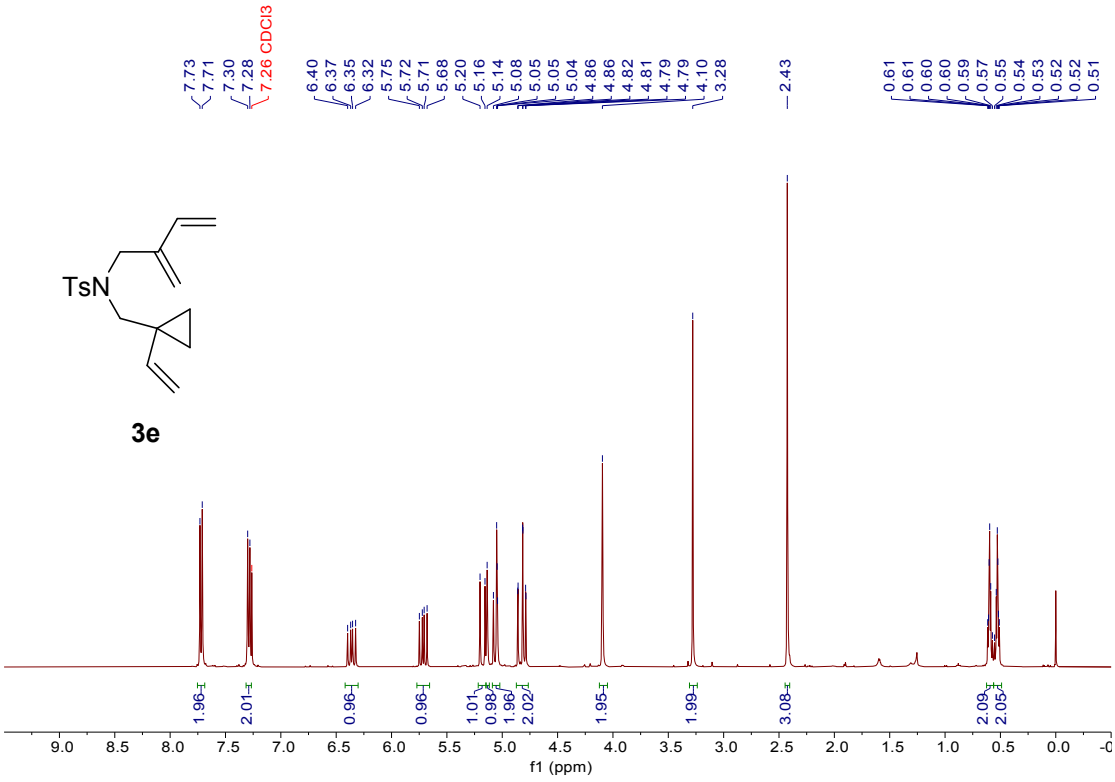
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



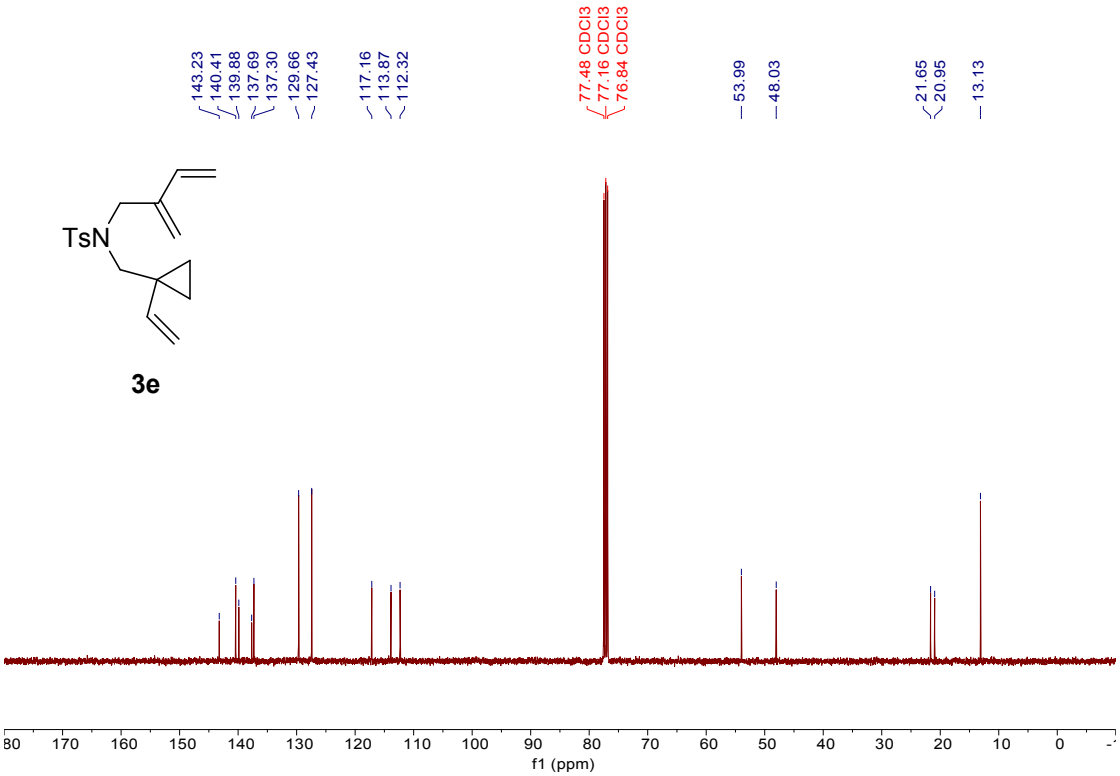
^{13}C NMR spectrum in $CDCl_3$, 101 MHz



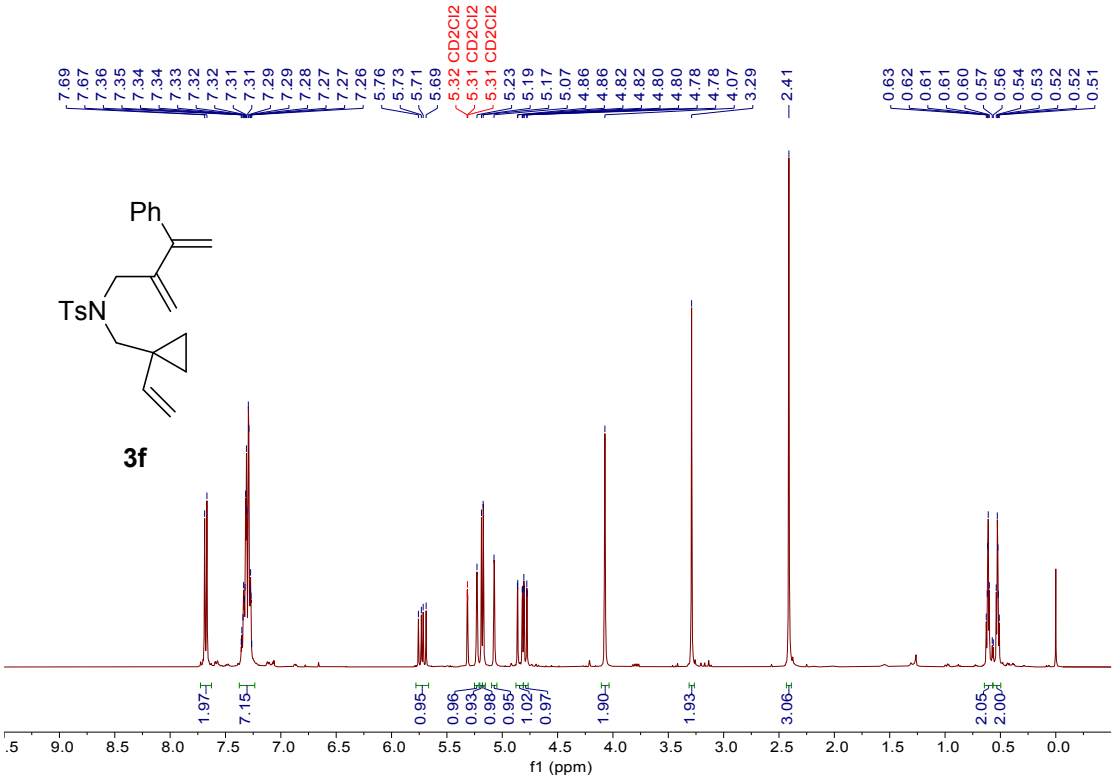
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



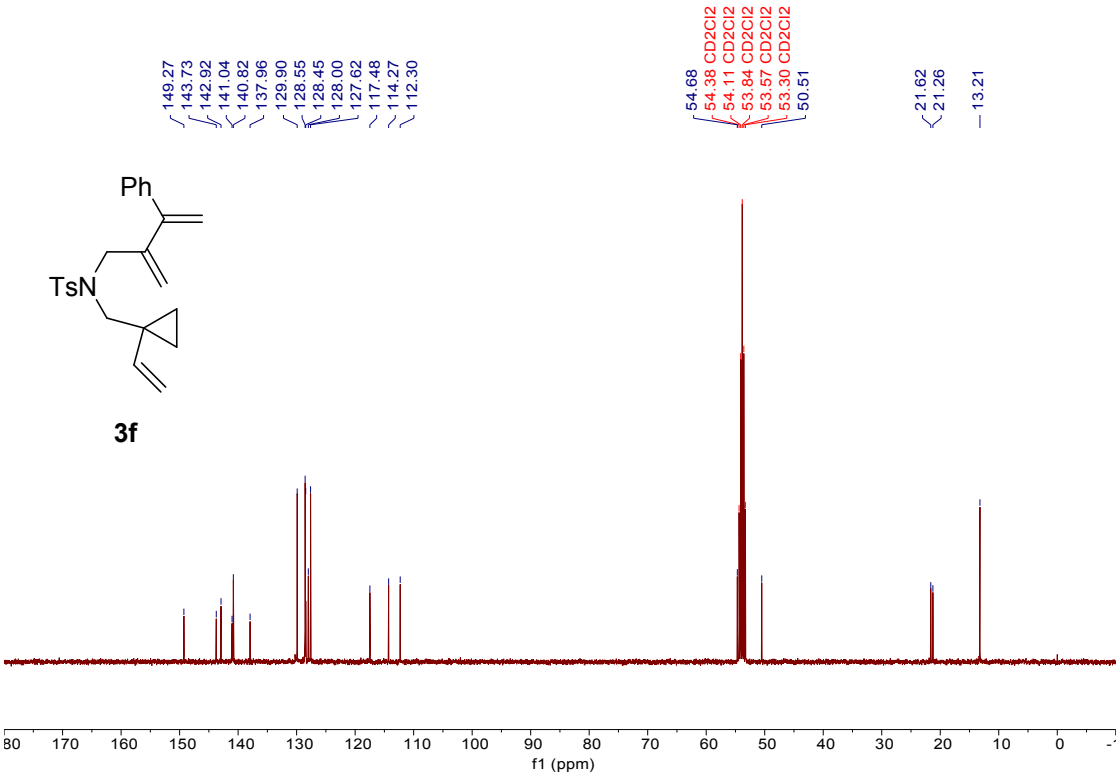
^{13}C NMR spectrum in $CDCl_3$, 101 MHz



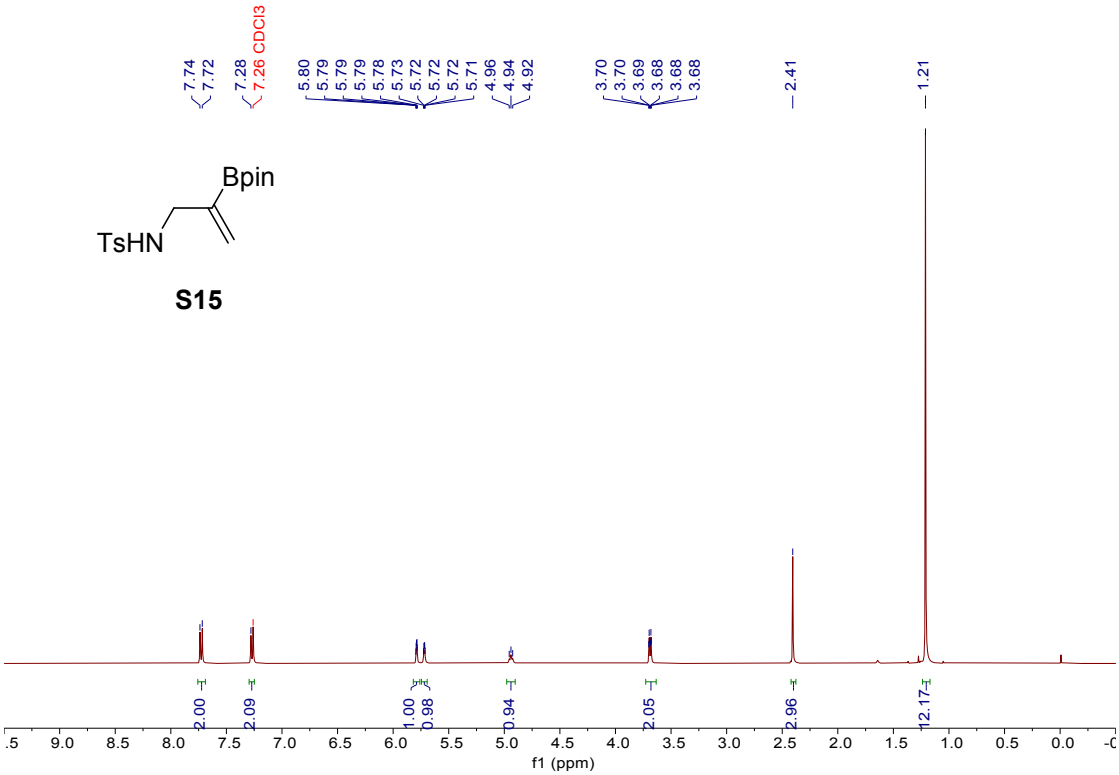
^{1}H NMR spectrum in CD_2Cl_2, 400 MHz



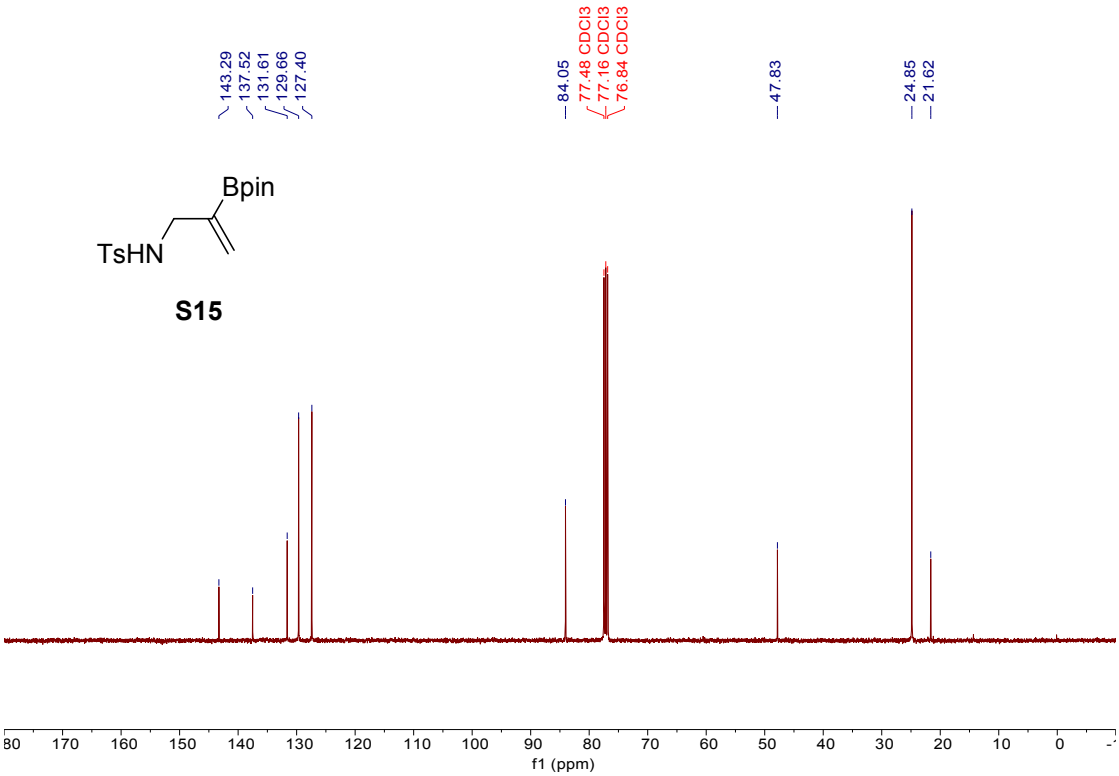
^{13}C NMR spectrum in CD_2Cl_2, 101 MHz



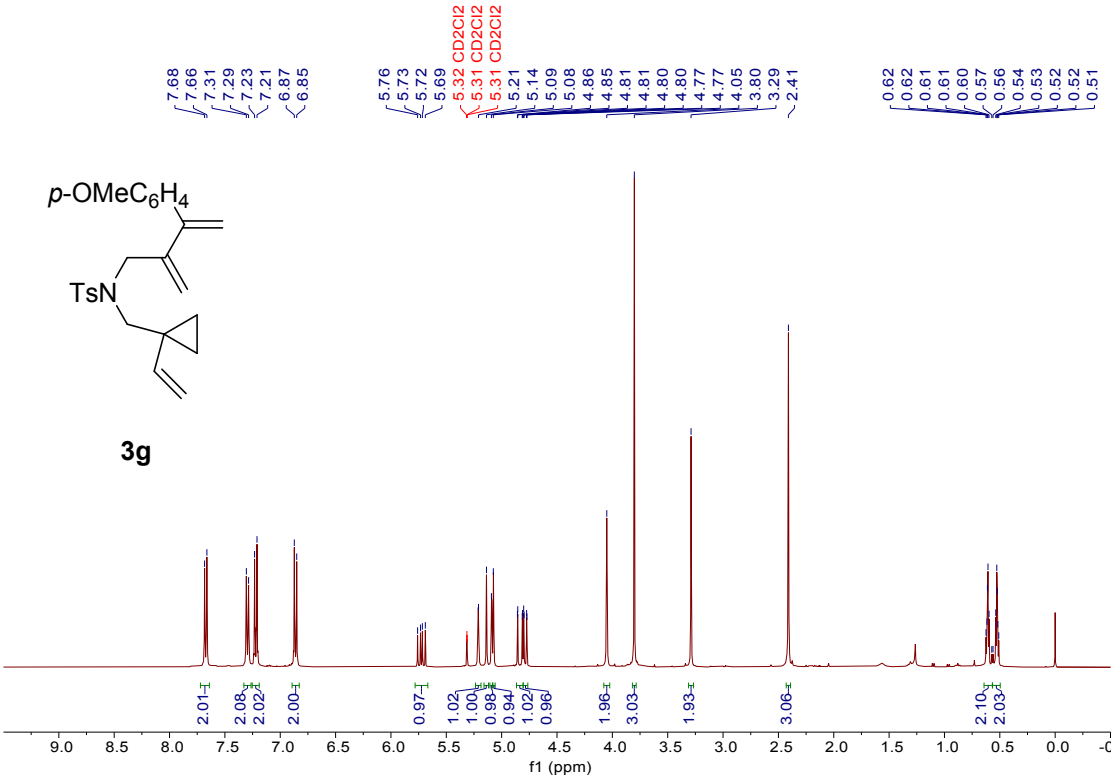
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



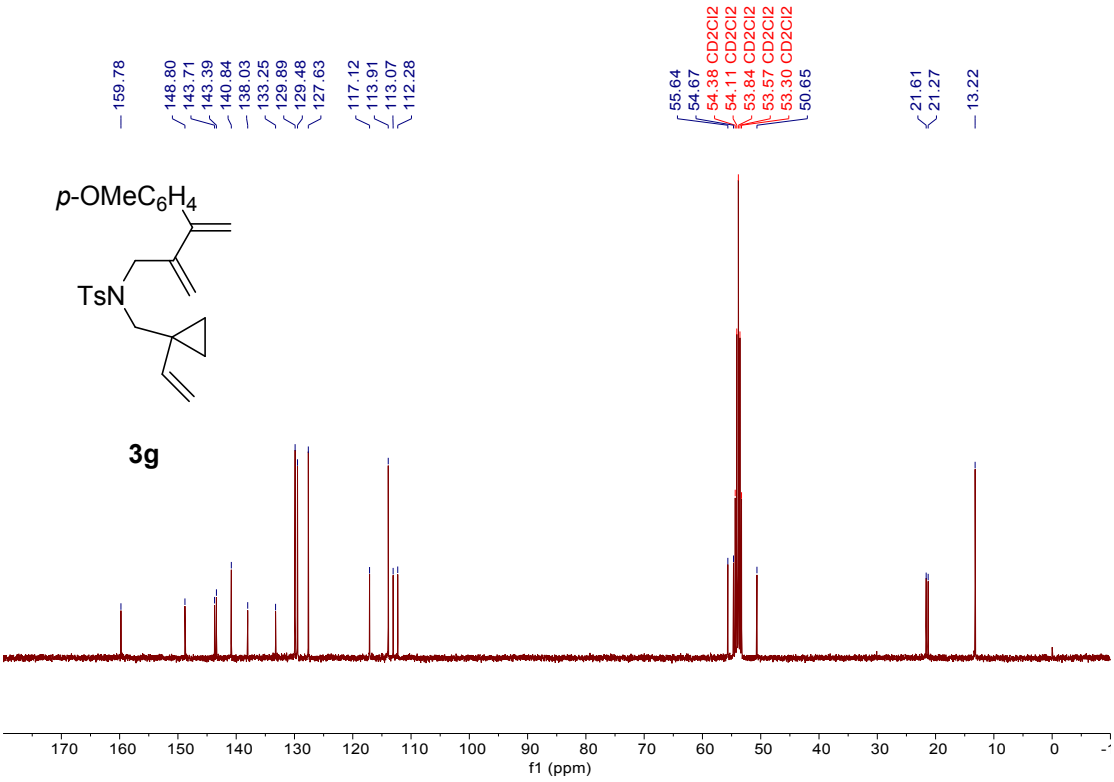
^{13}C NMR spectrum in $CDCl_3$, 101 MHz



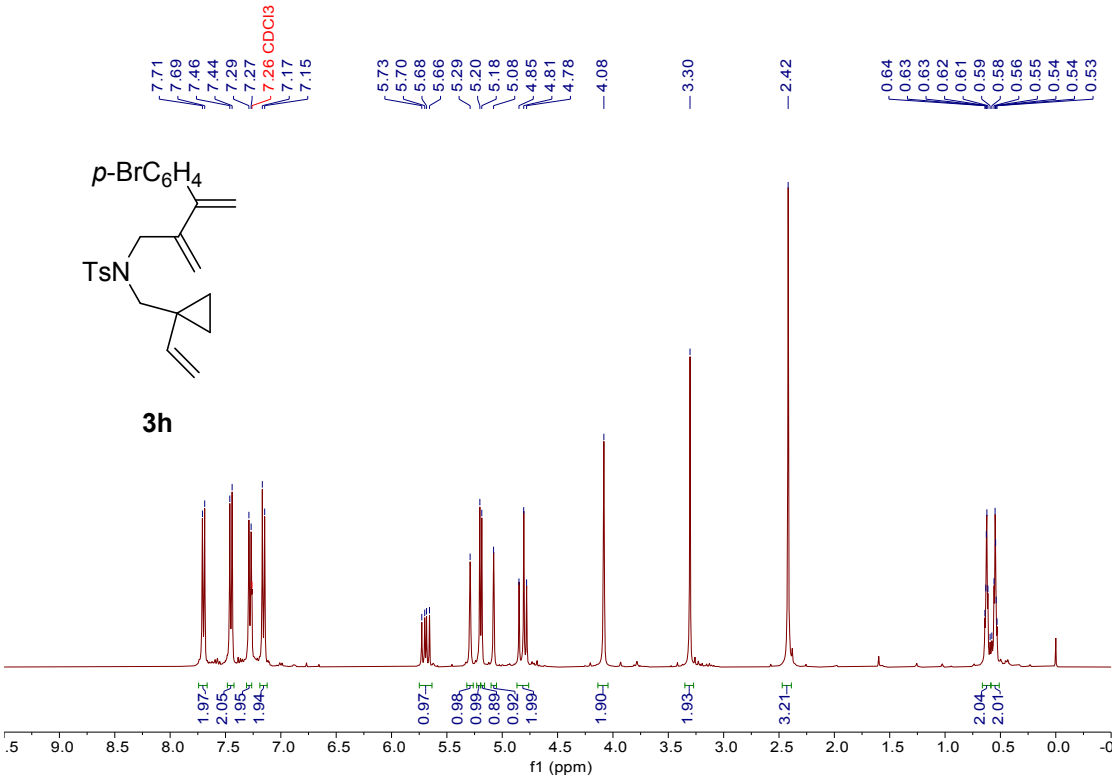
^{1}H NMR spectrum in CD_2Cl_2, 400 MHz



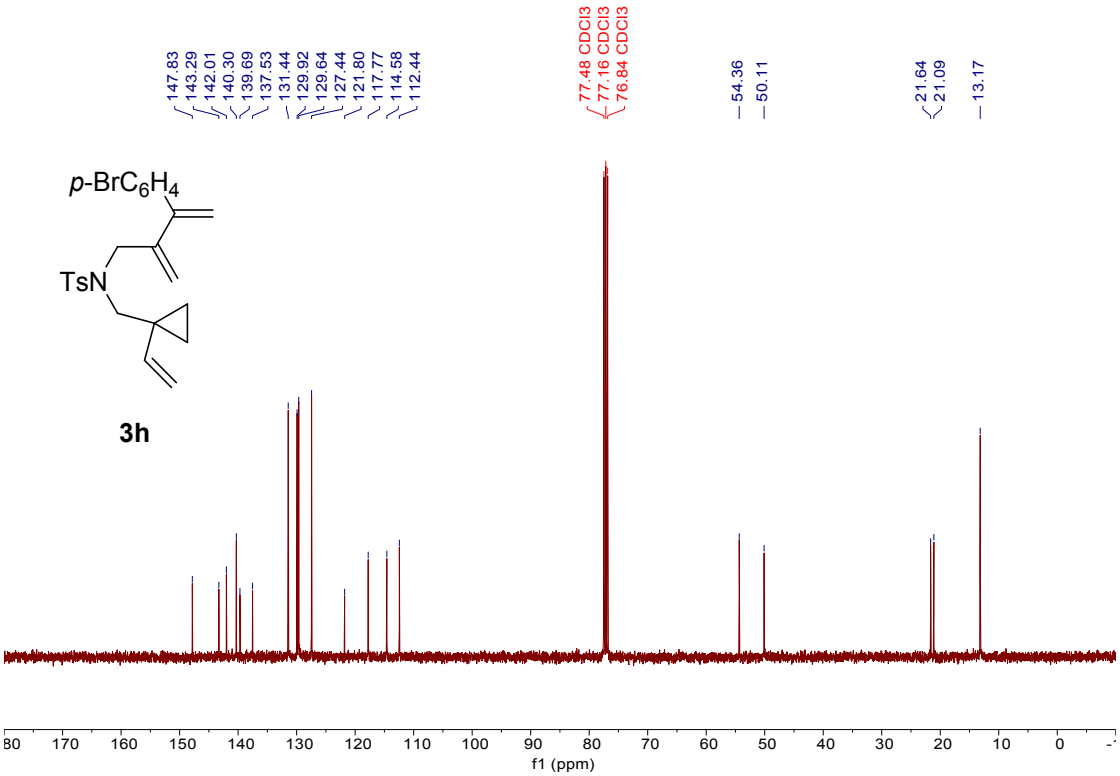
^{13}C NMR spectrum in CD_2Cl_2, 101 MHz



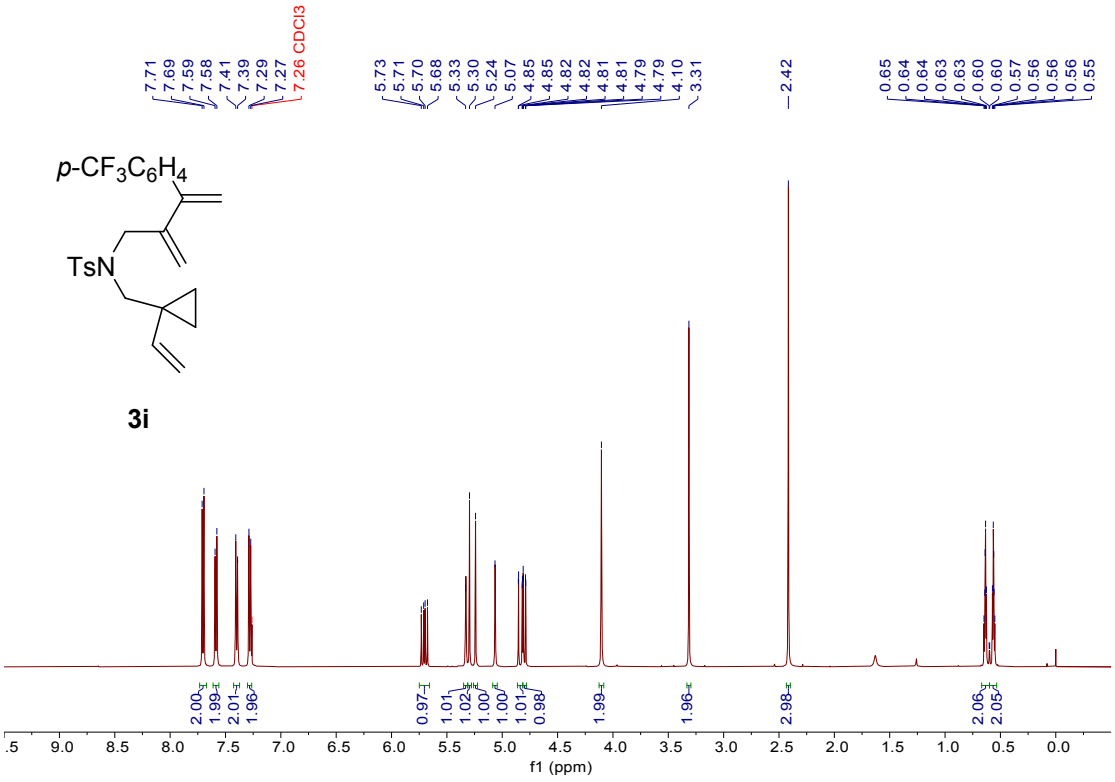
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



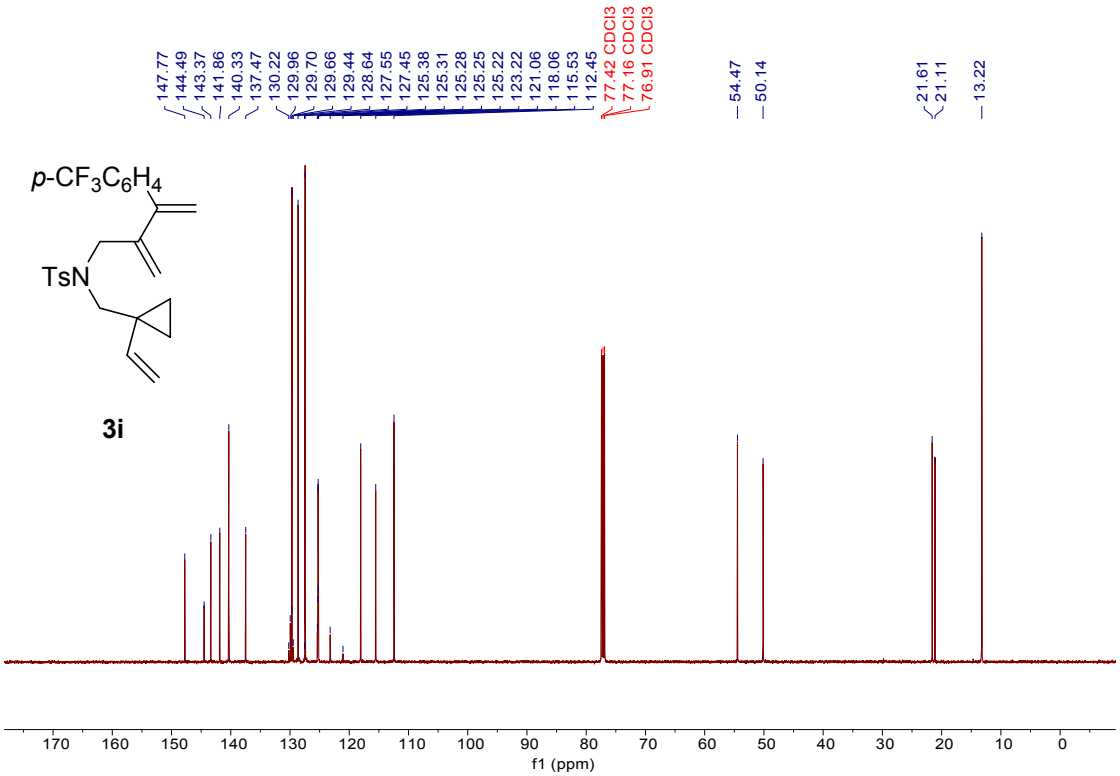
^{13}C NMR spectrum in $CDCl_3$, 101 MHz



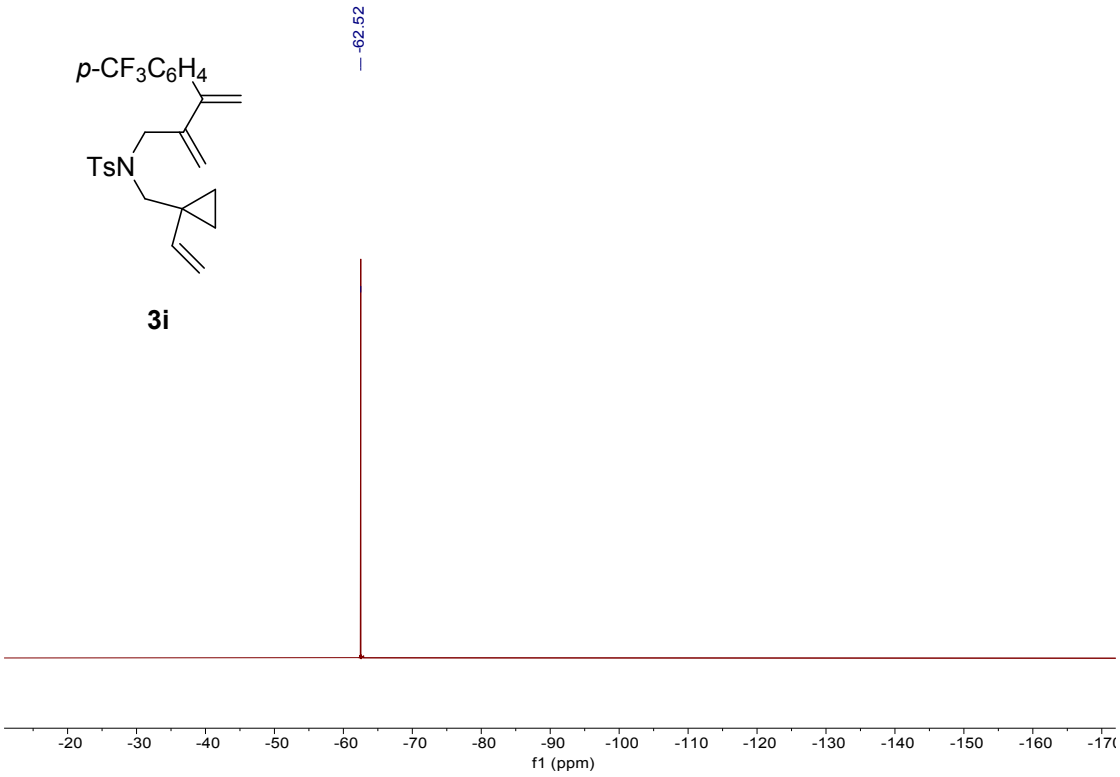
^{1}H NMR spectrum in $CDCl_3$, 500 MHz



^{13}C NMR spectrum in $CDCl_3$, 126 MHz

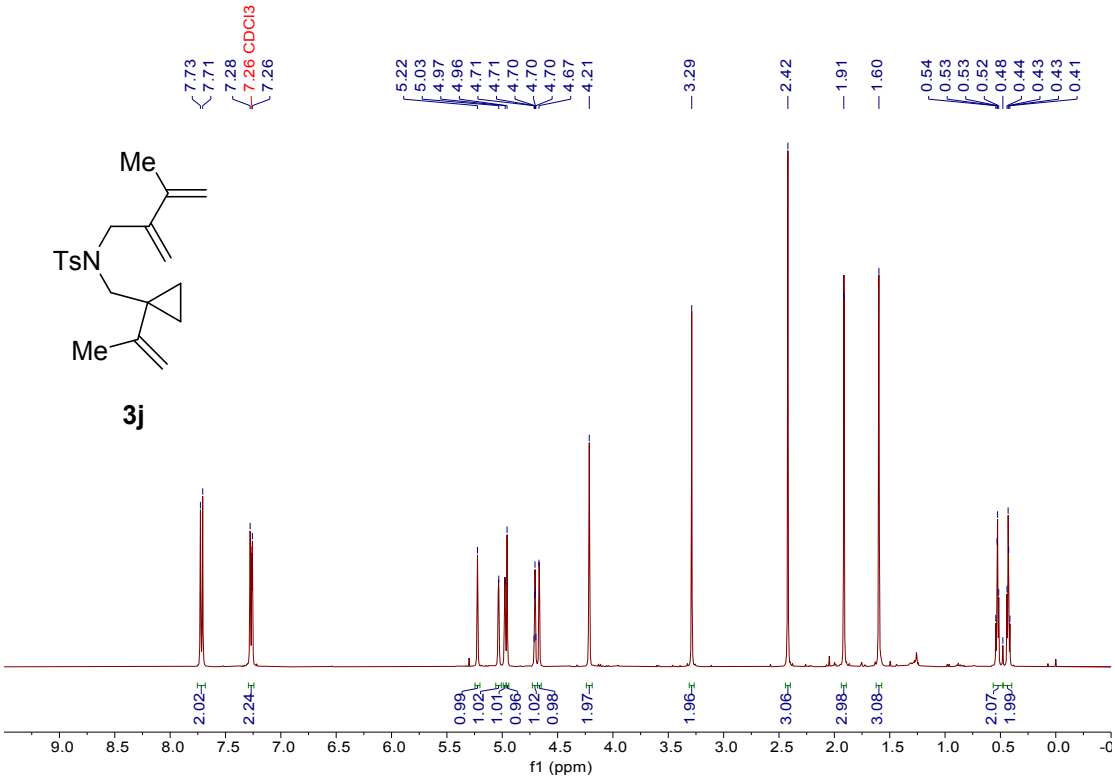


^{19}F NMR spectrum in $CDCl_3$, 471 MHz

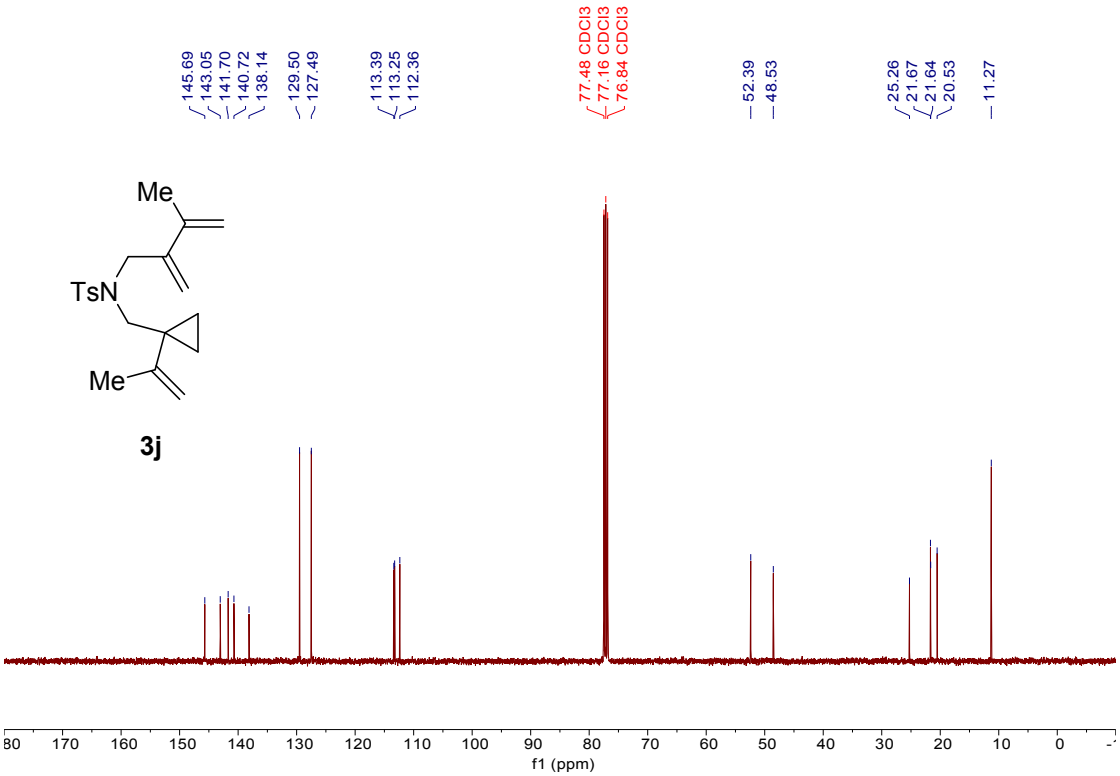


3i

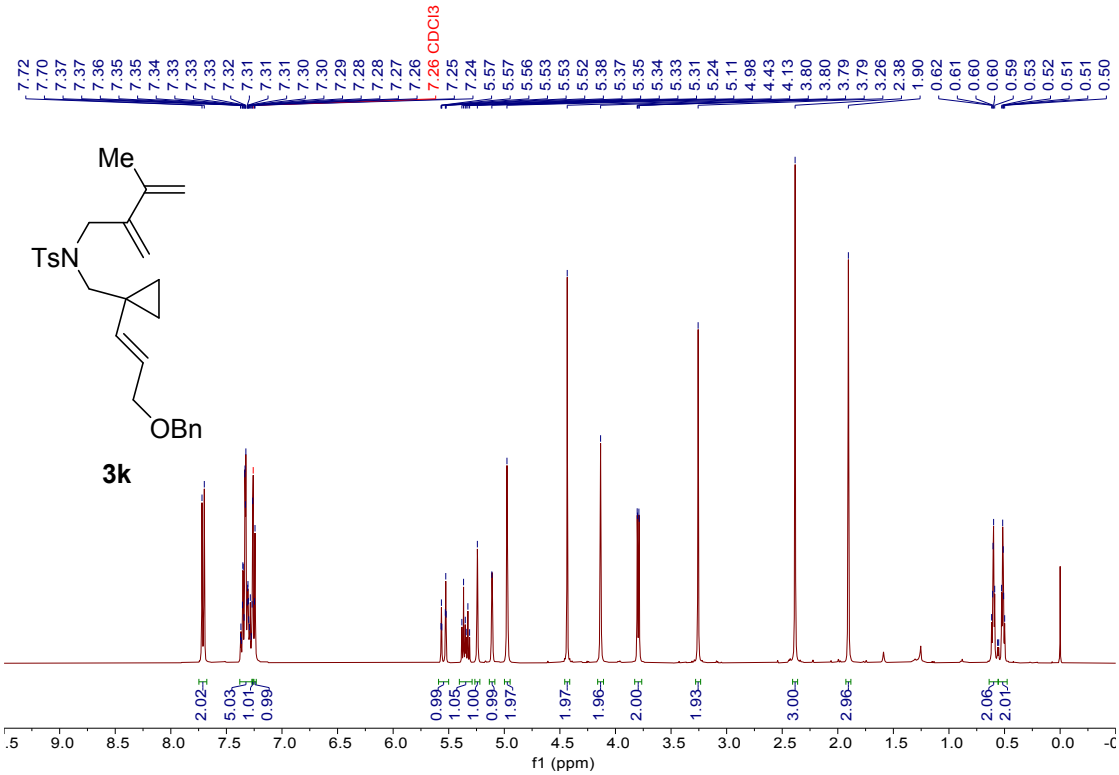
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



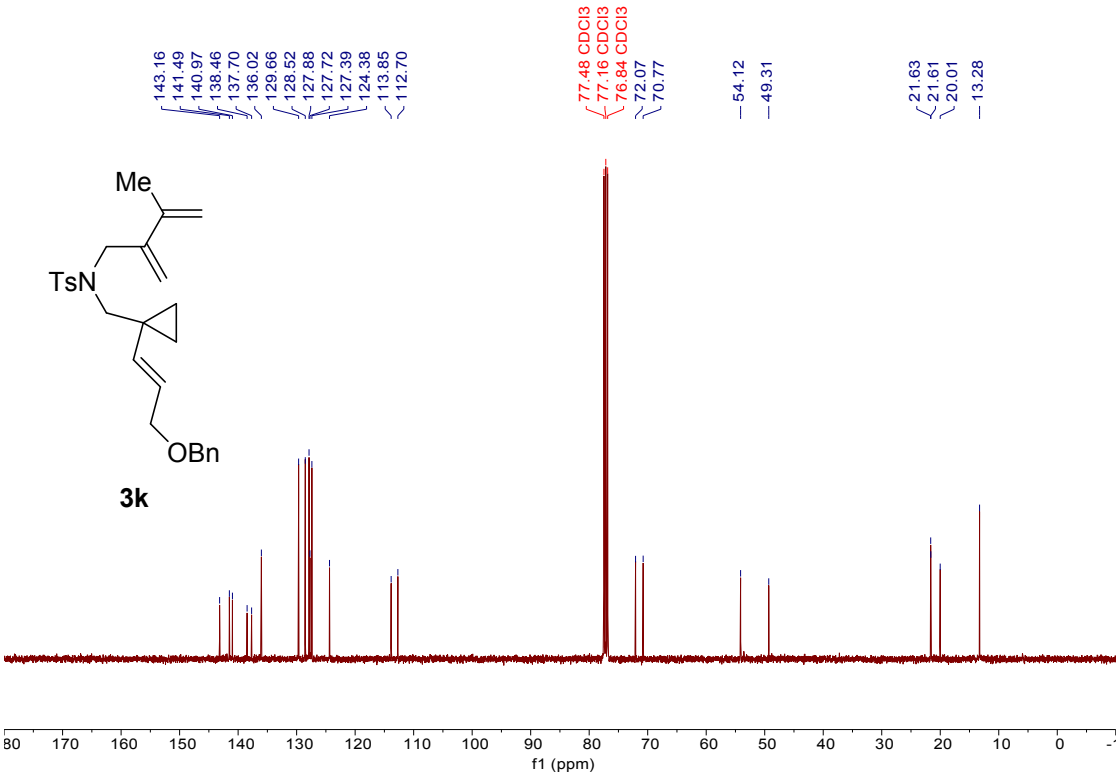
^{13}C NMR spectrum in $CDCl_3$, 101 MHz



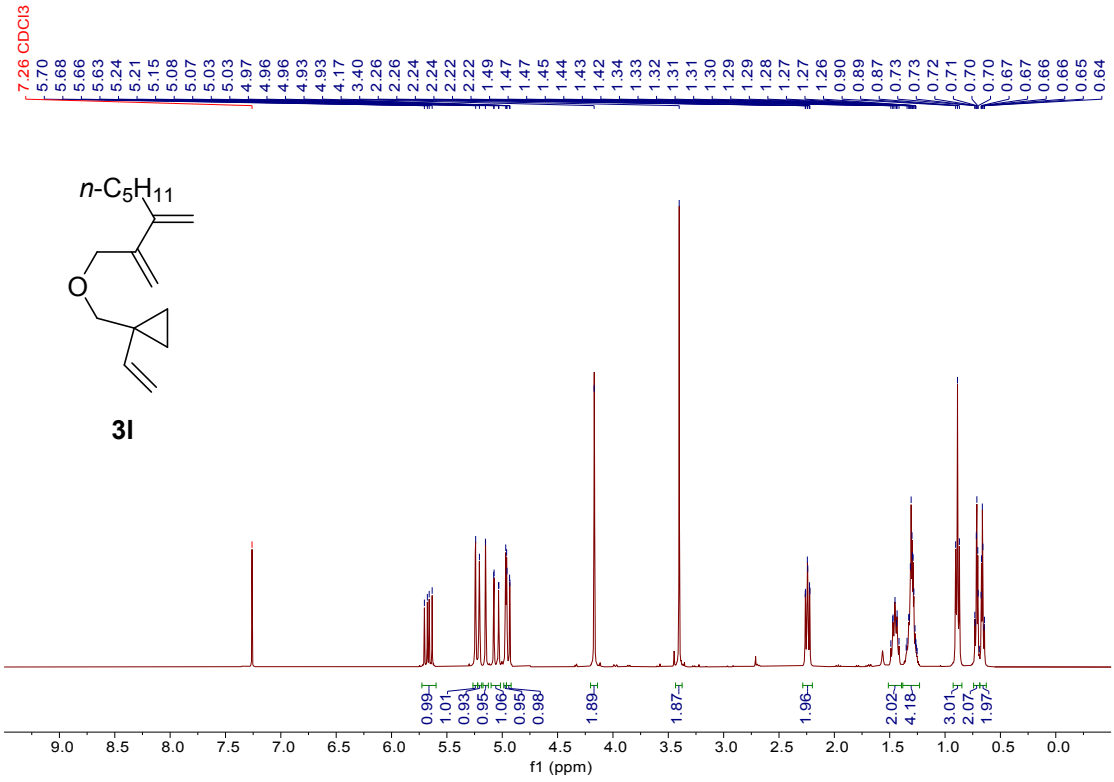
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



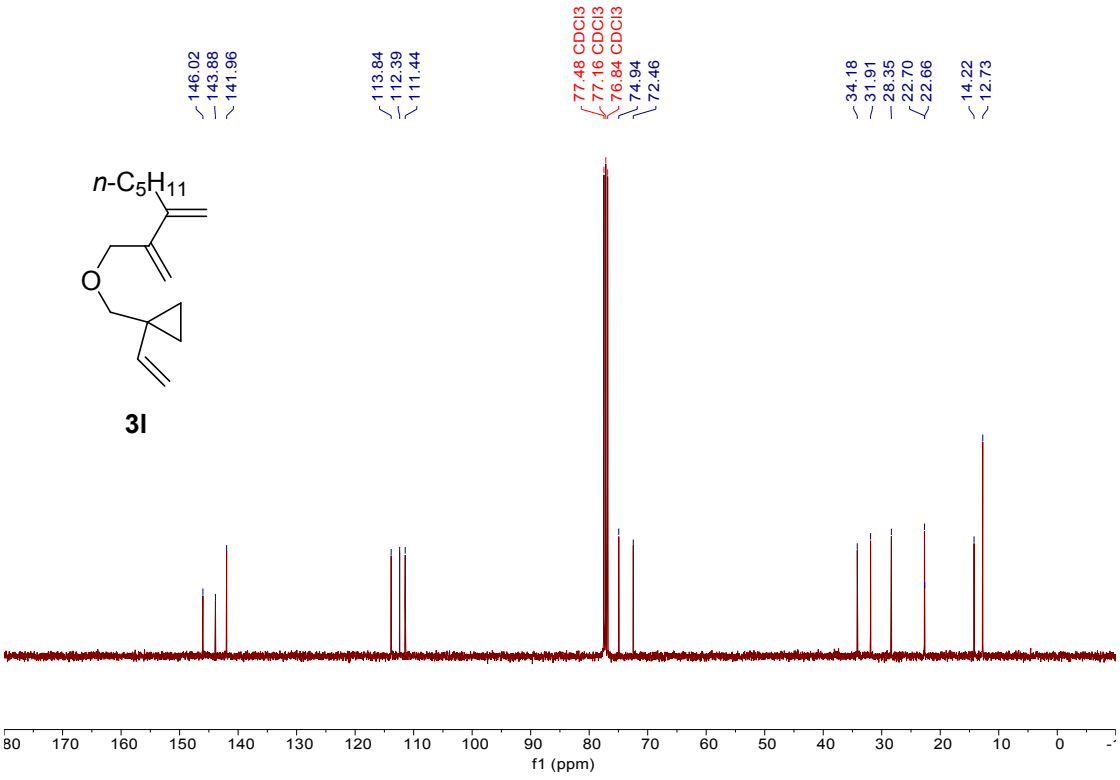
^{13}C NMR spectrum in $CDCl_3$, 101 MHz



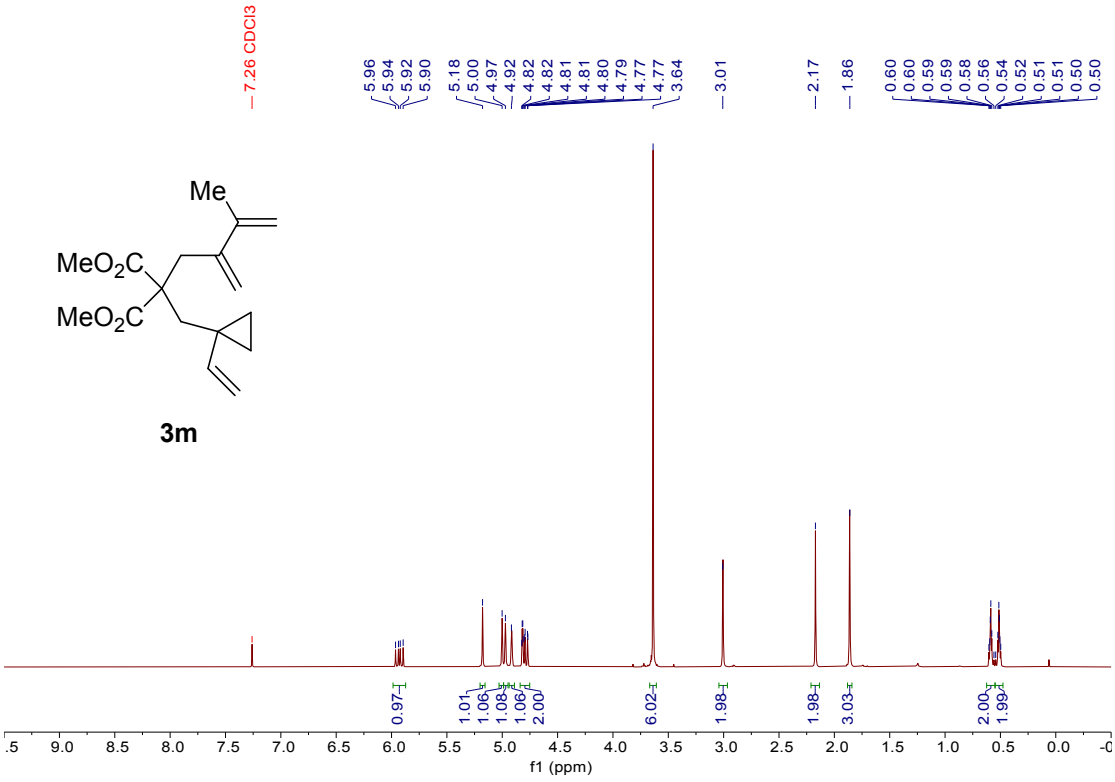
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



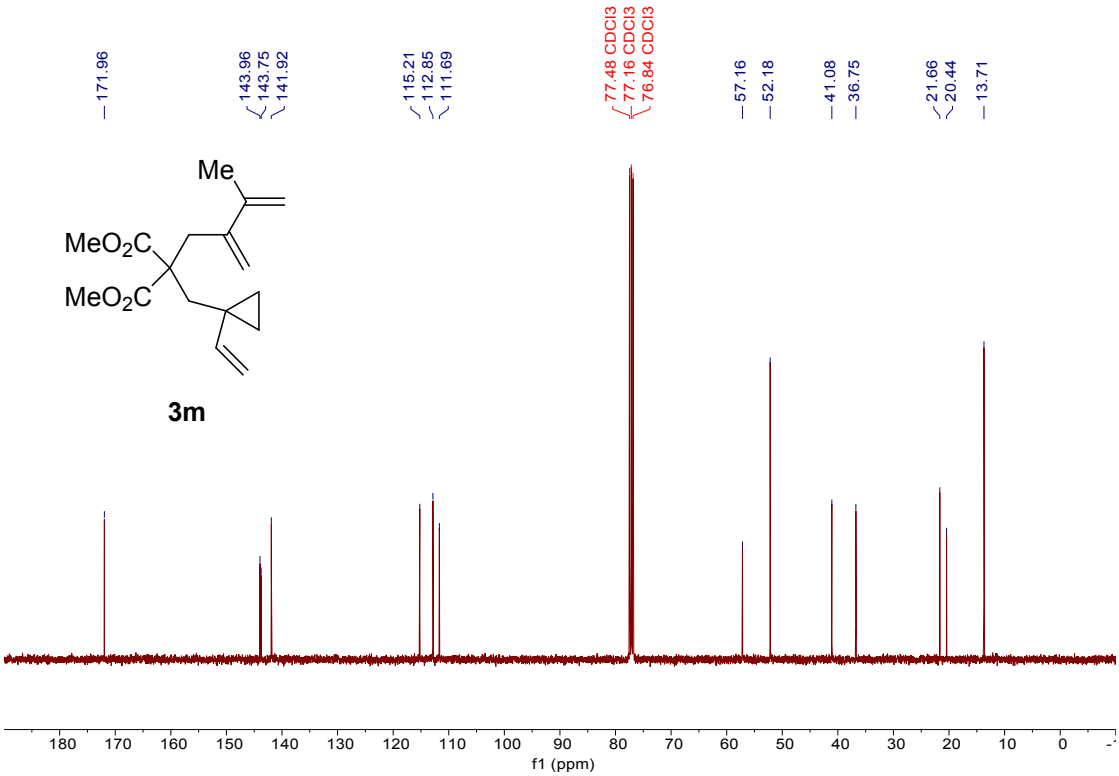
^{13}C NMR spectrum in $CDCl_3$, 101 MHz



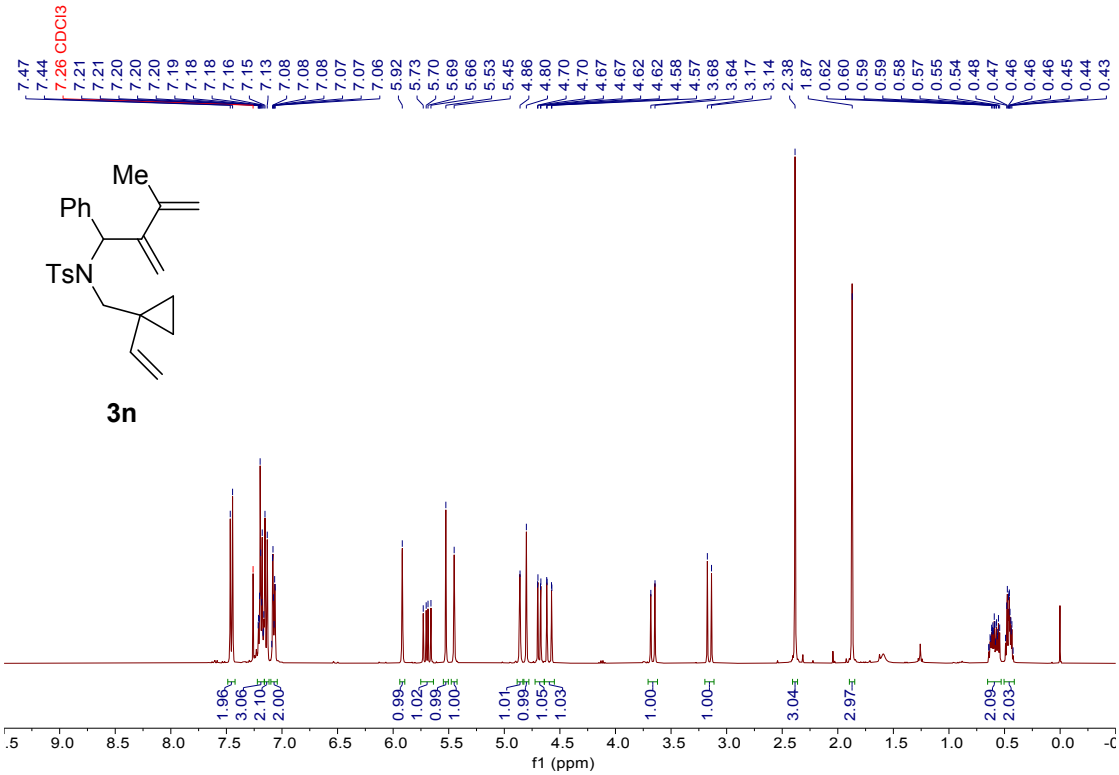
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



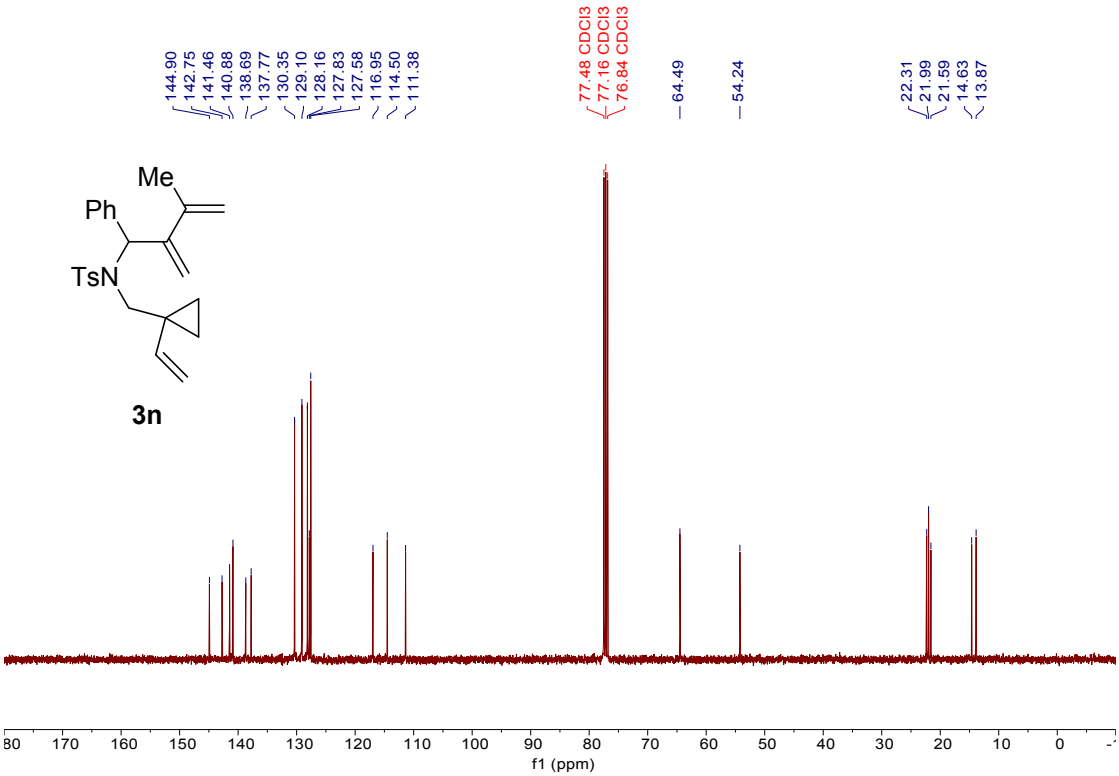
^{13}C NMR spectrum in $CDCl_3$, 101 MHz



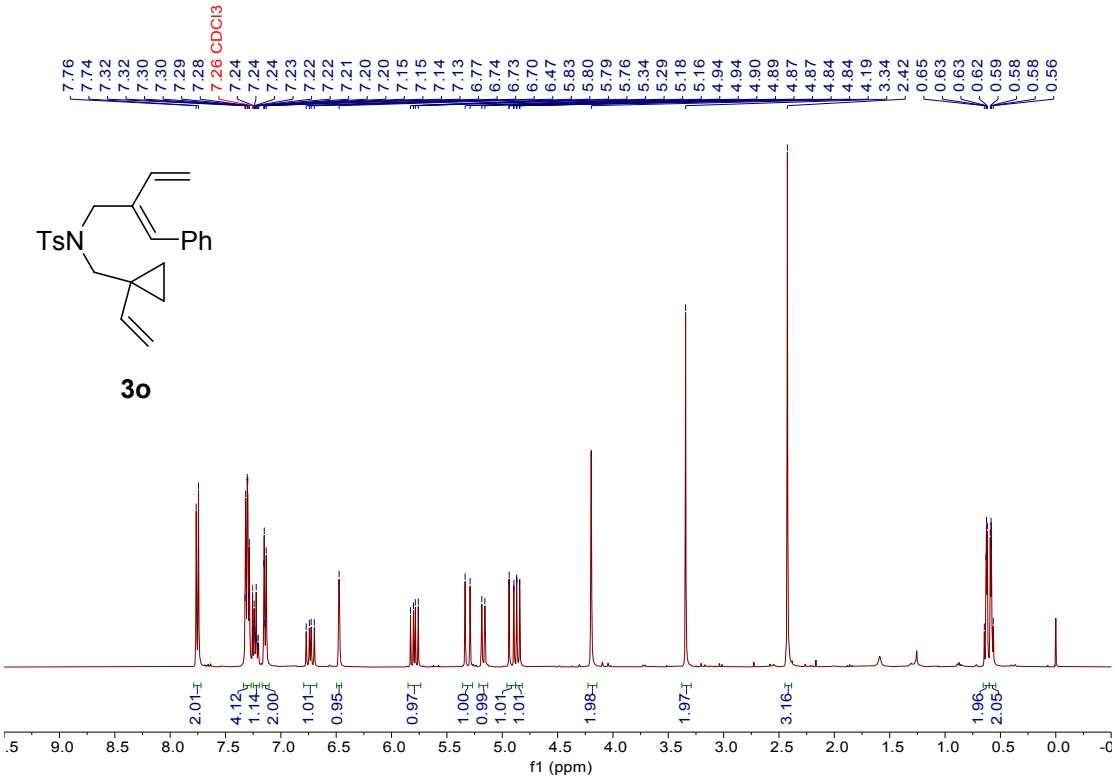
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



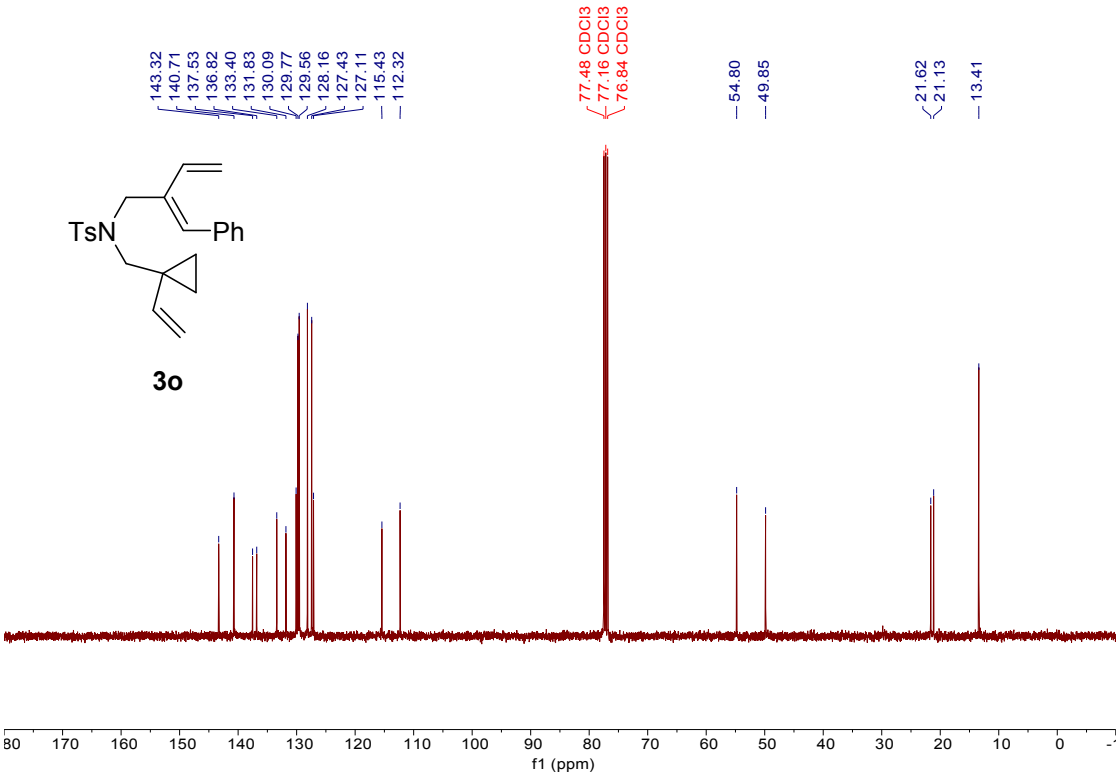
^{13}C NMR spectrum in $CDCl_3$, 101 MHz



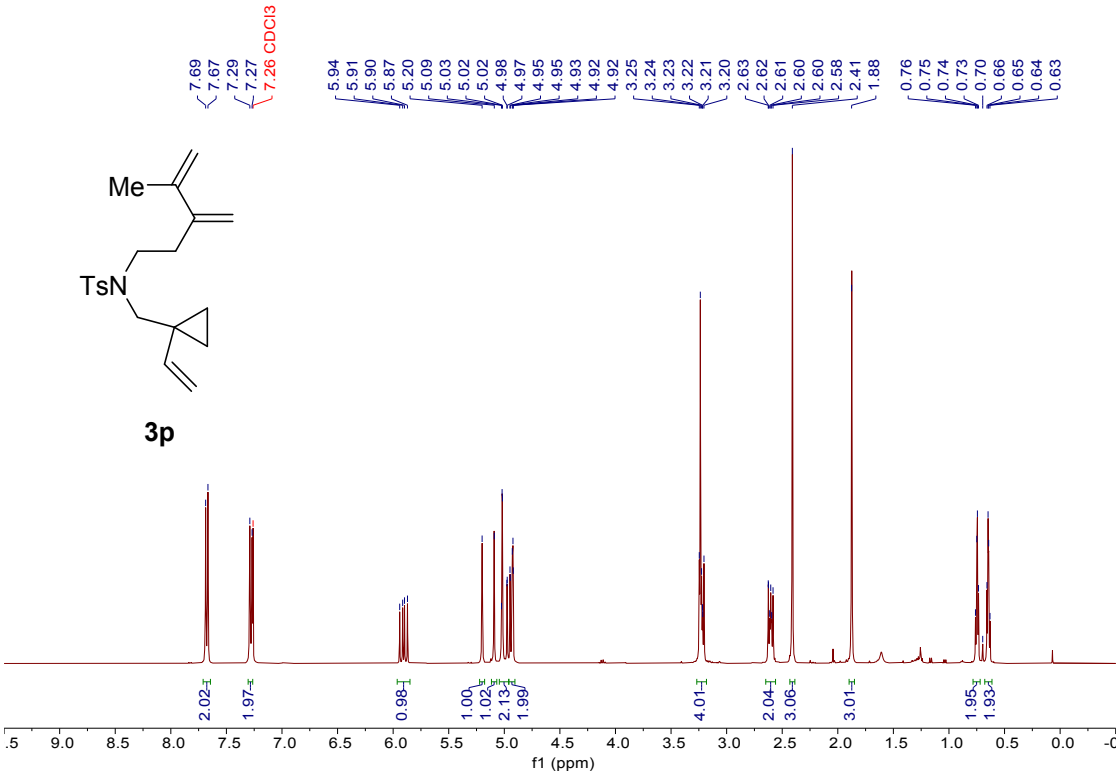
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



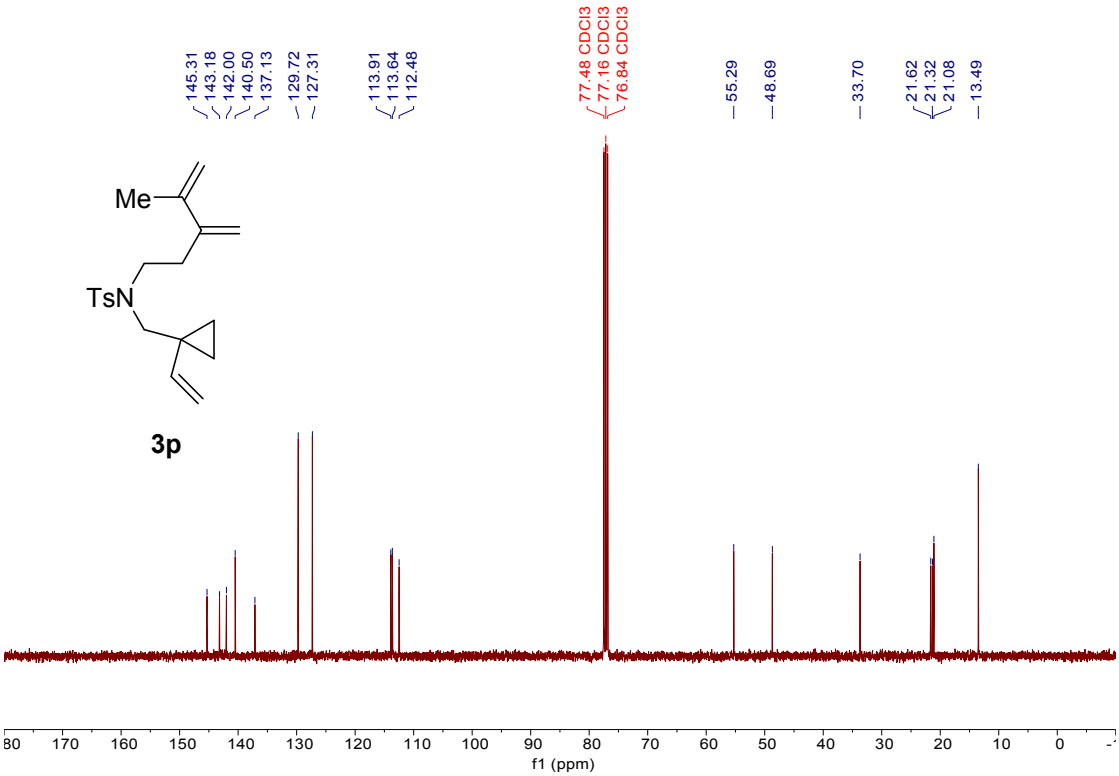
^{13}C NMR spectrum in $CDCl_3$, 101 MHz



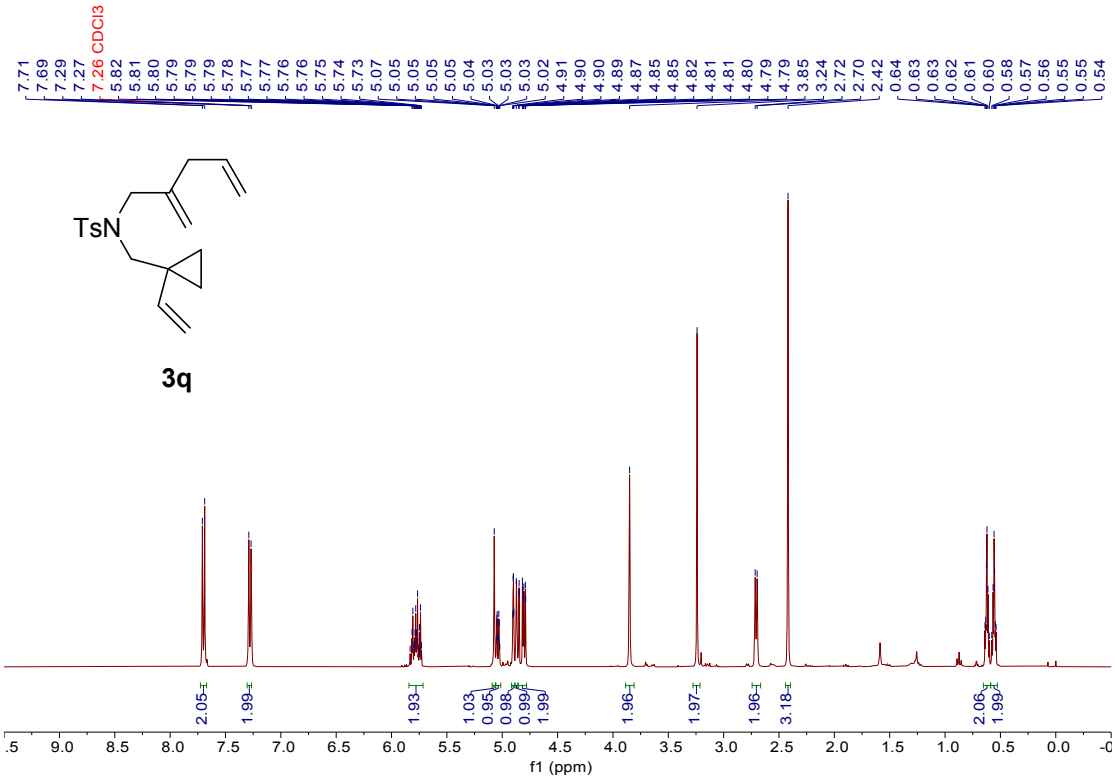
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



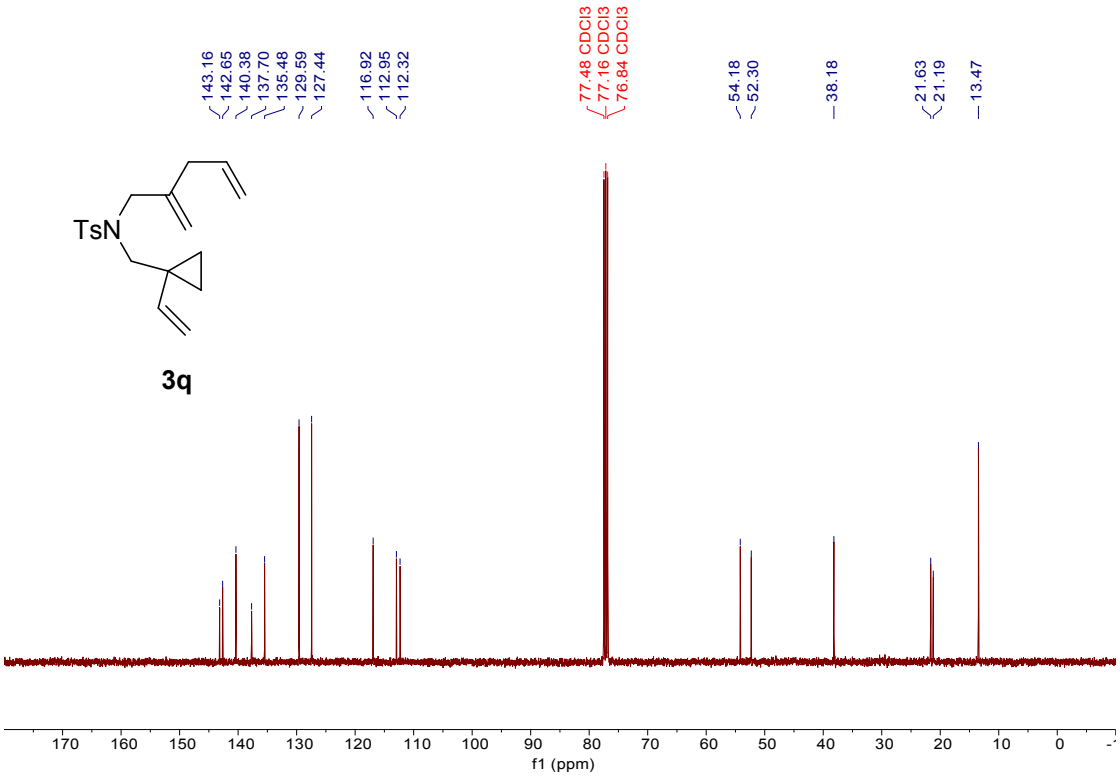
^{13}C NMR spectrum in $CDCl_3$, 101 MHz



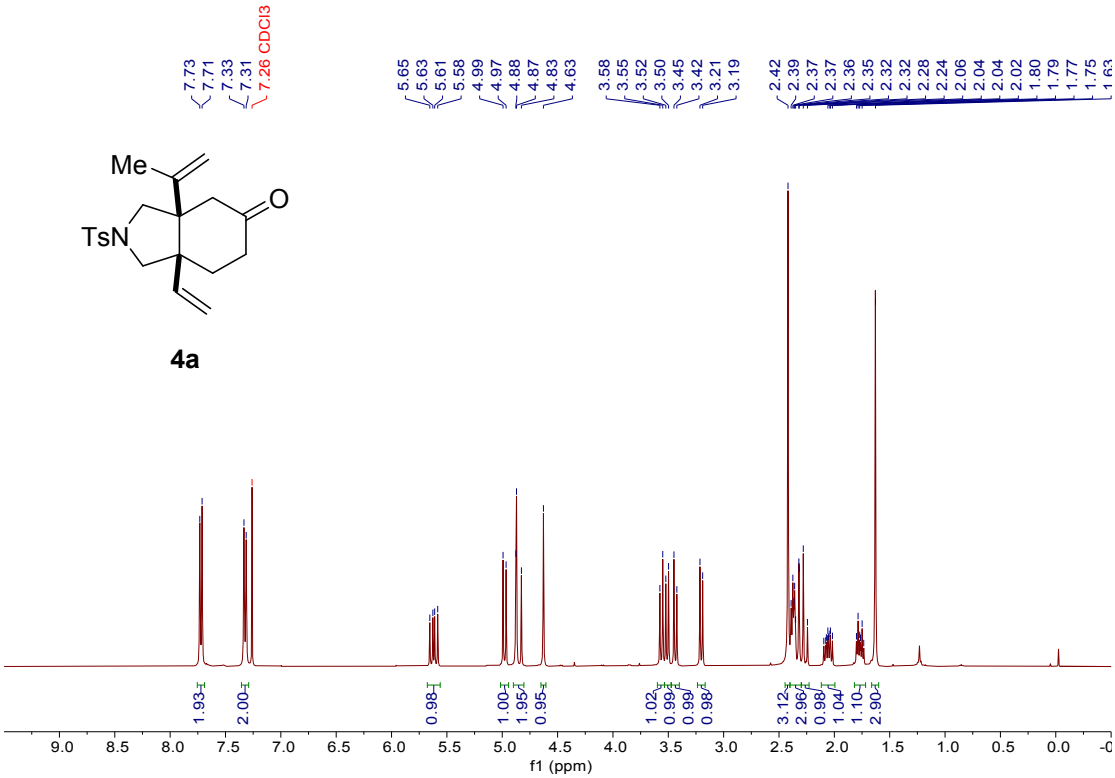
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



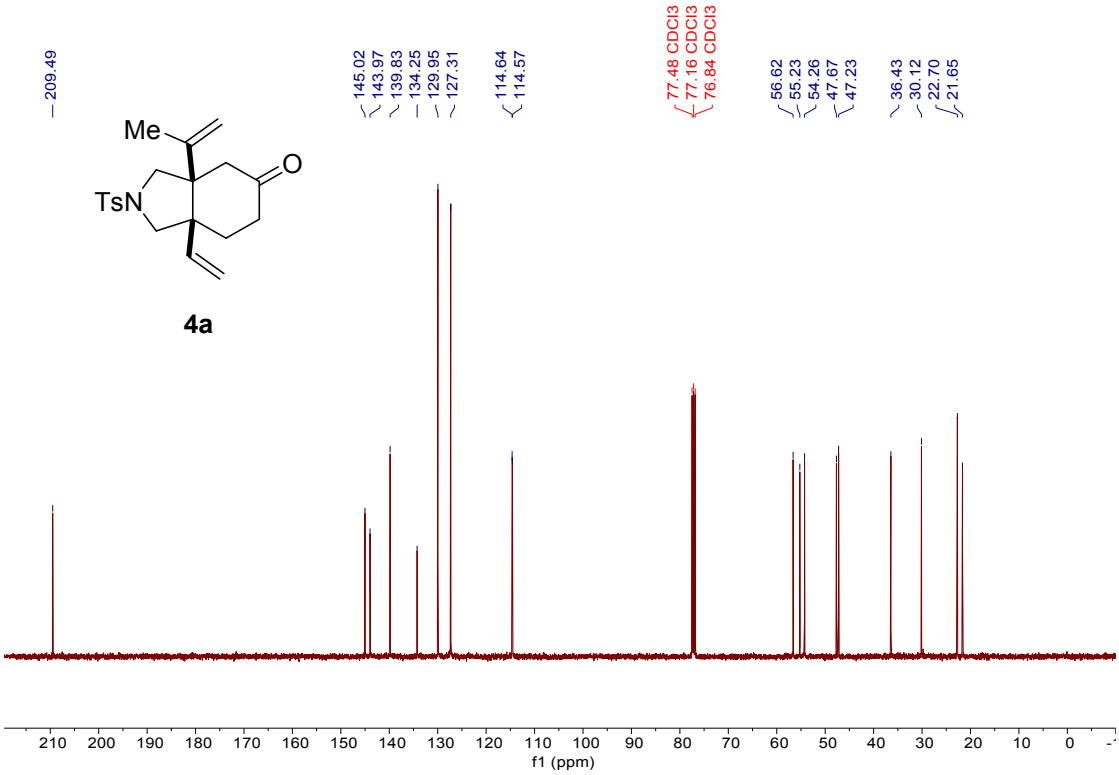
^{13}C NMR spectrum in $CDCl_3$, 101 MHz



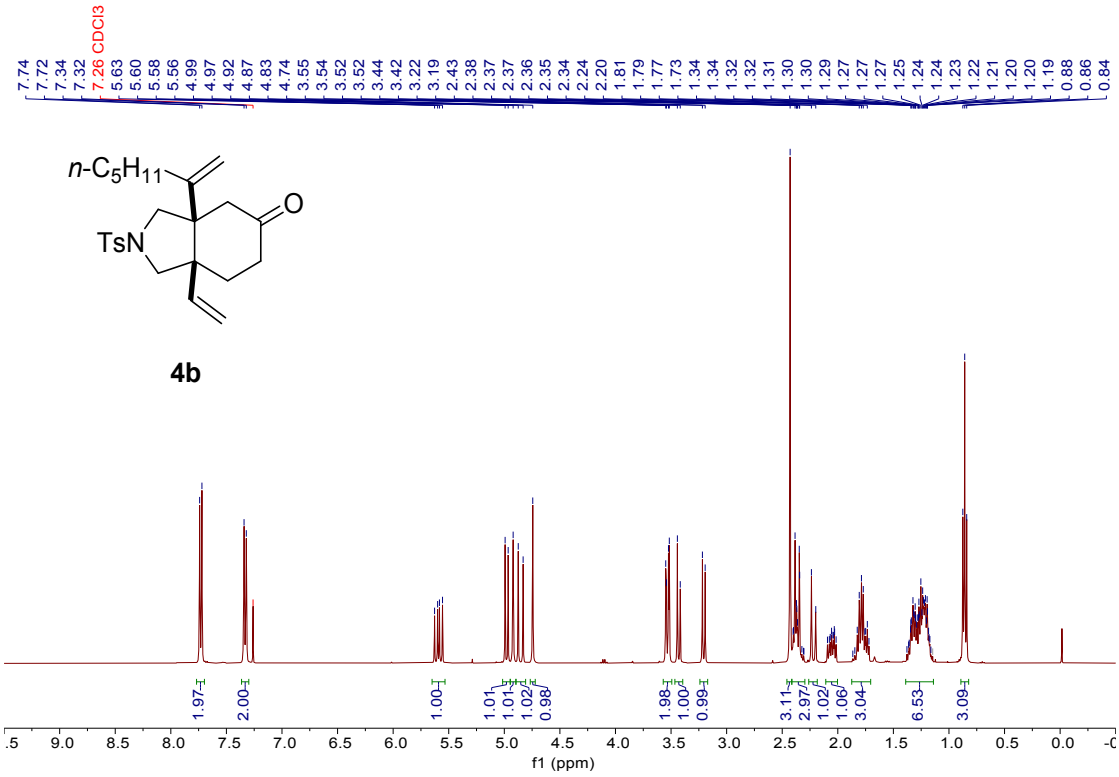
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



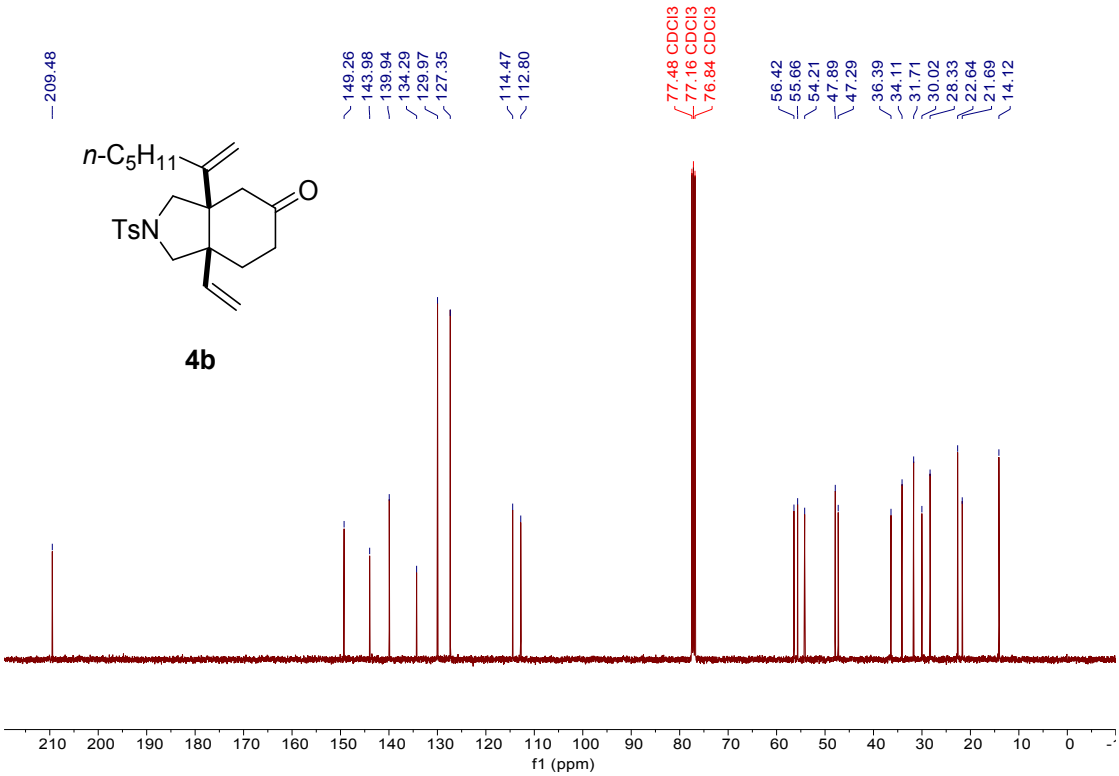
^{13}C NMR spectrum in $CDCl_3$, 101 MHz



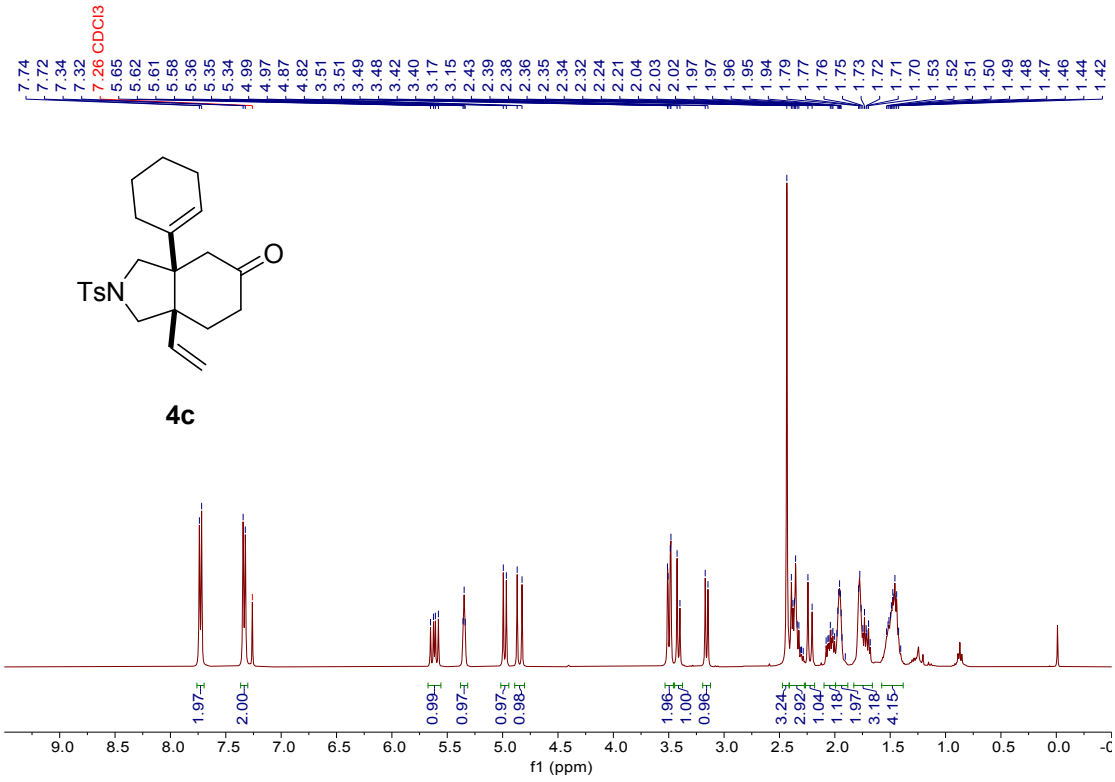
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



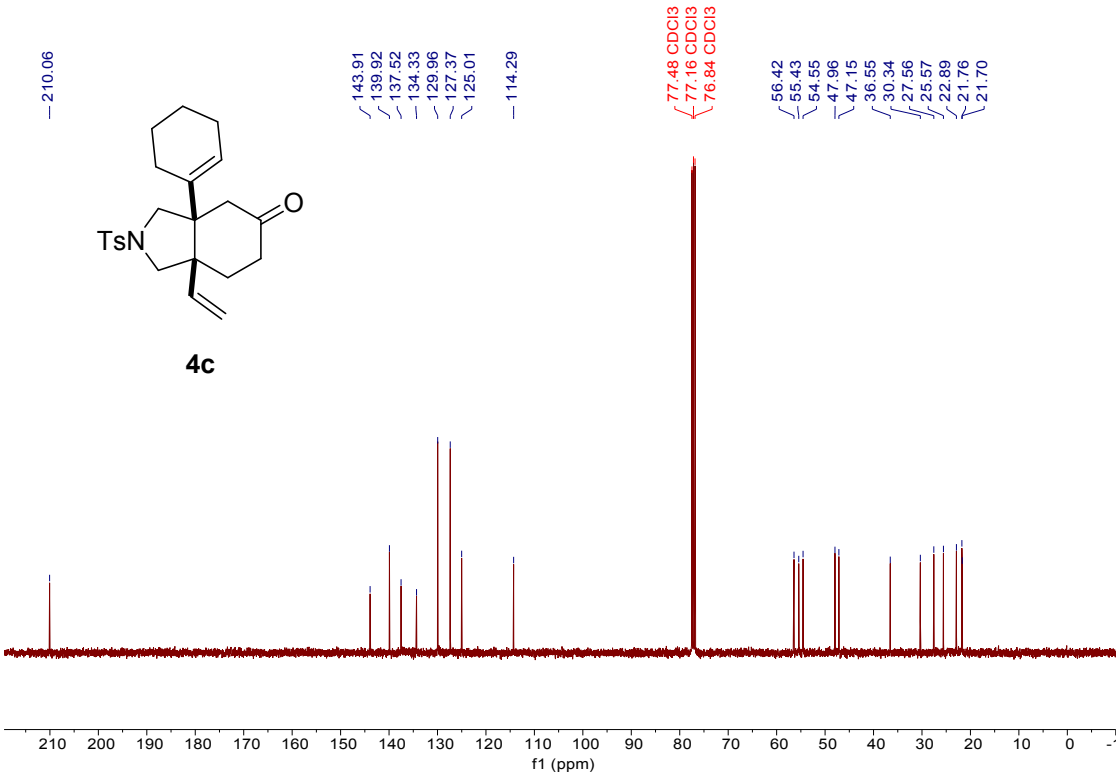
^{13}C NMR spectrum in $CDCl_3$, 101 MHz



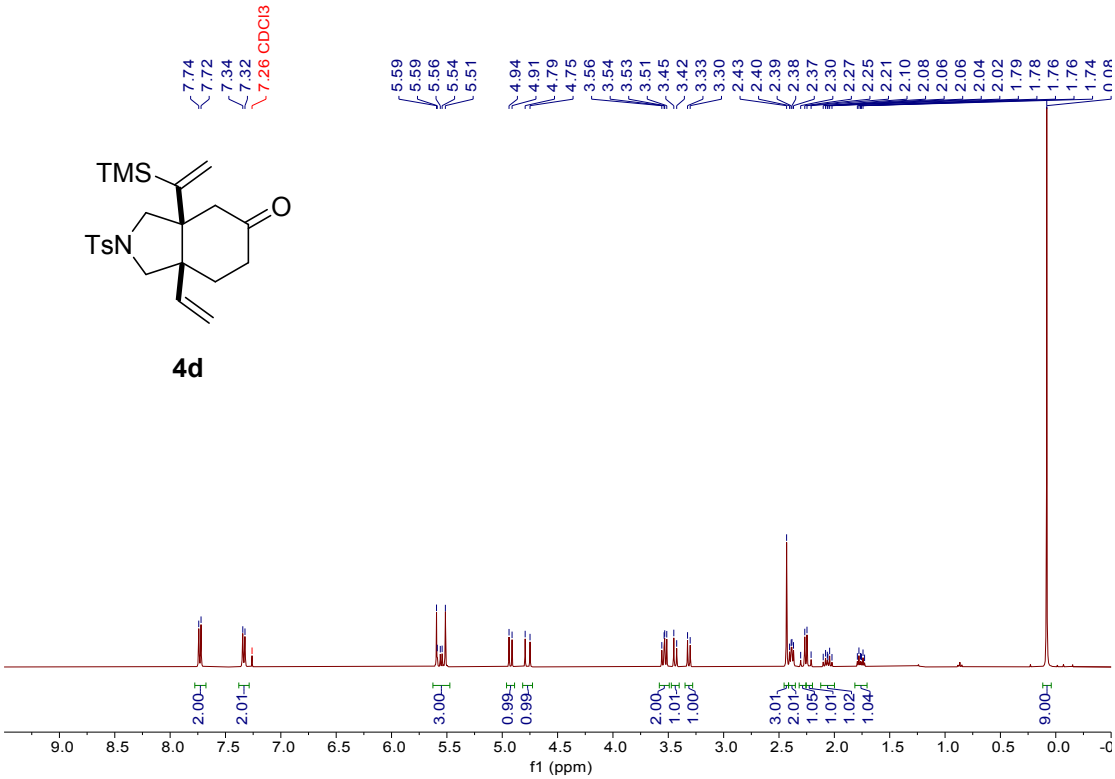
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



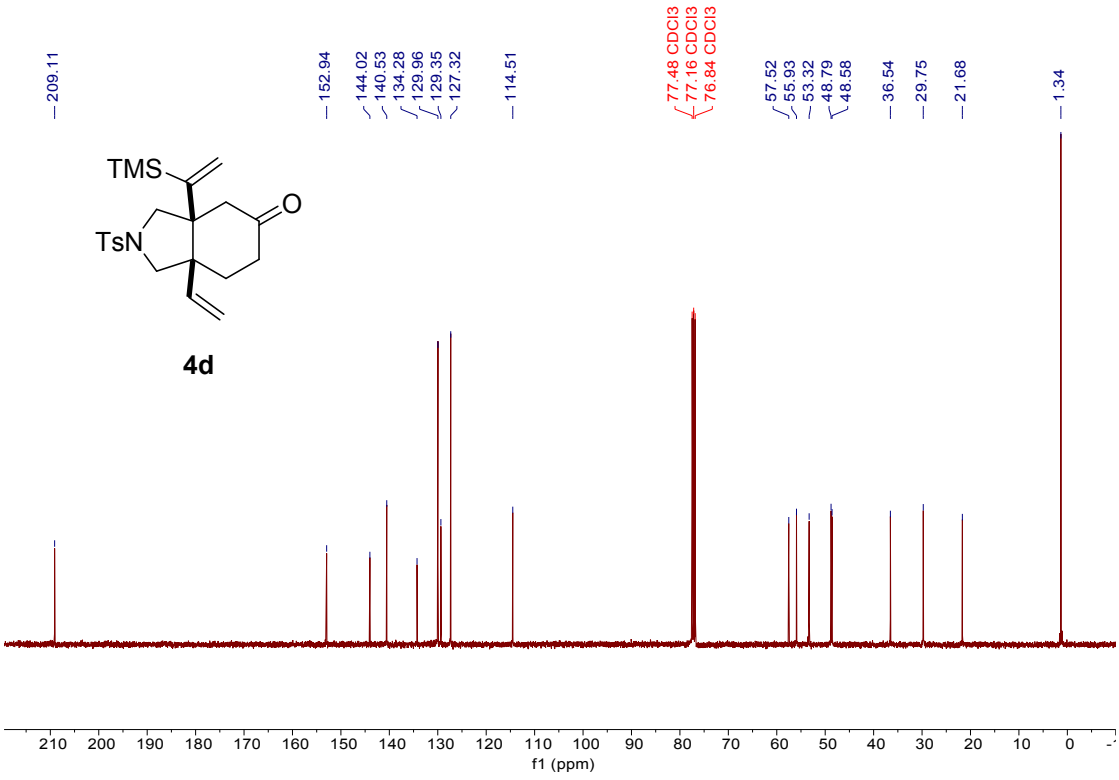
^{13}C NMR spectrum in $CDCl_3$, 101 MHz



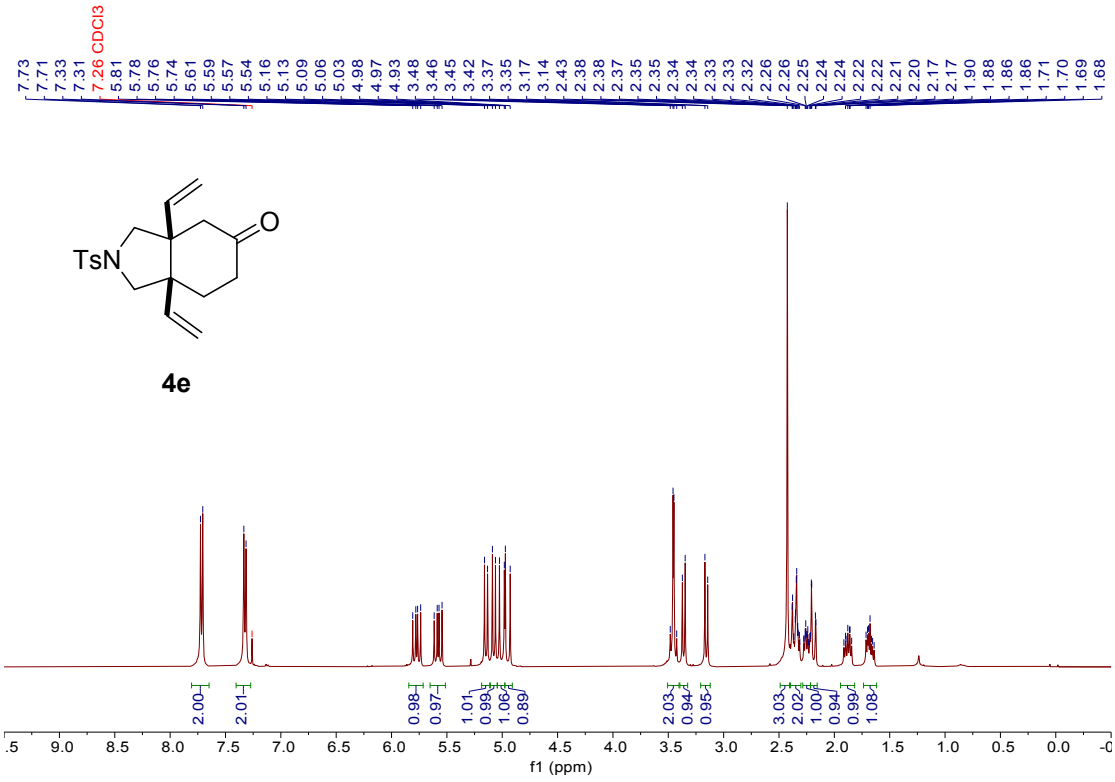
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



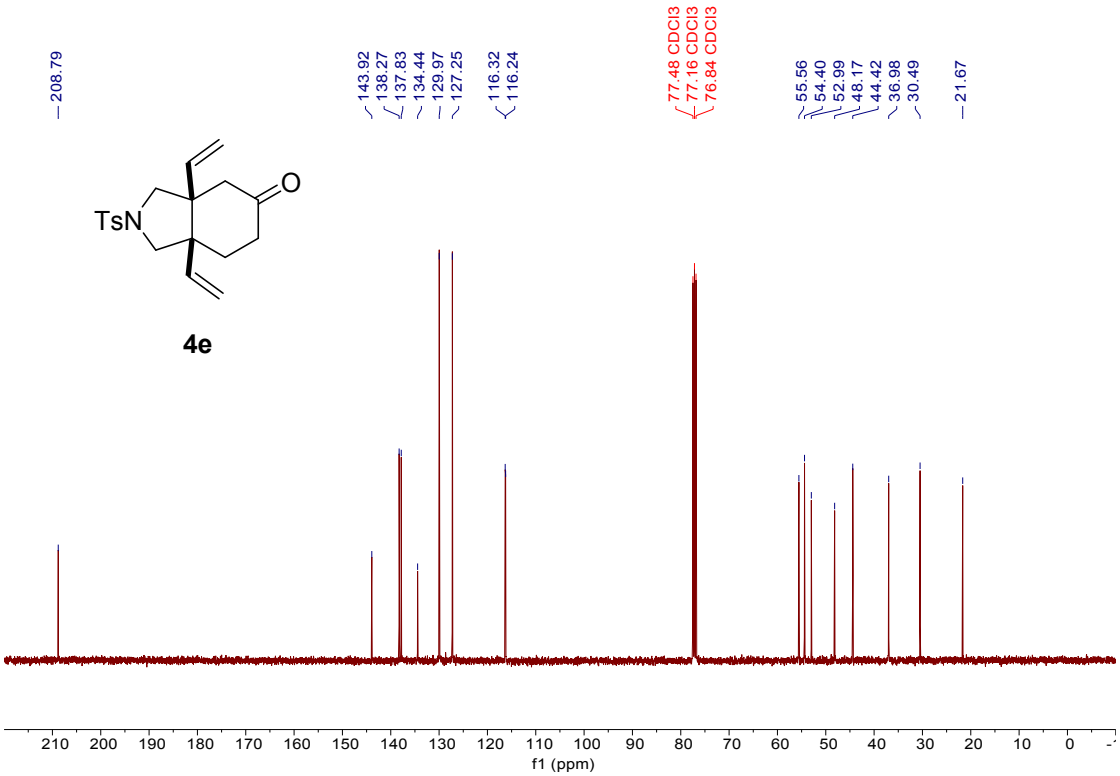
^{13}C NMR spectrum in $CDCl_3$, 101 MHz



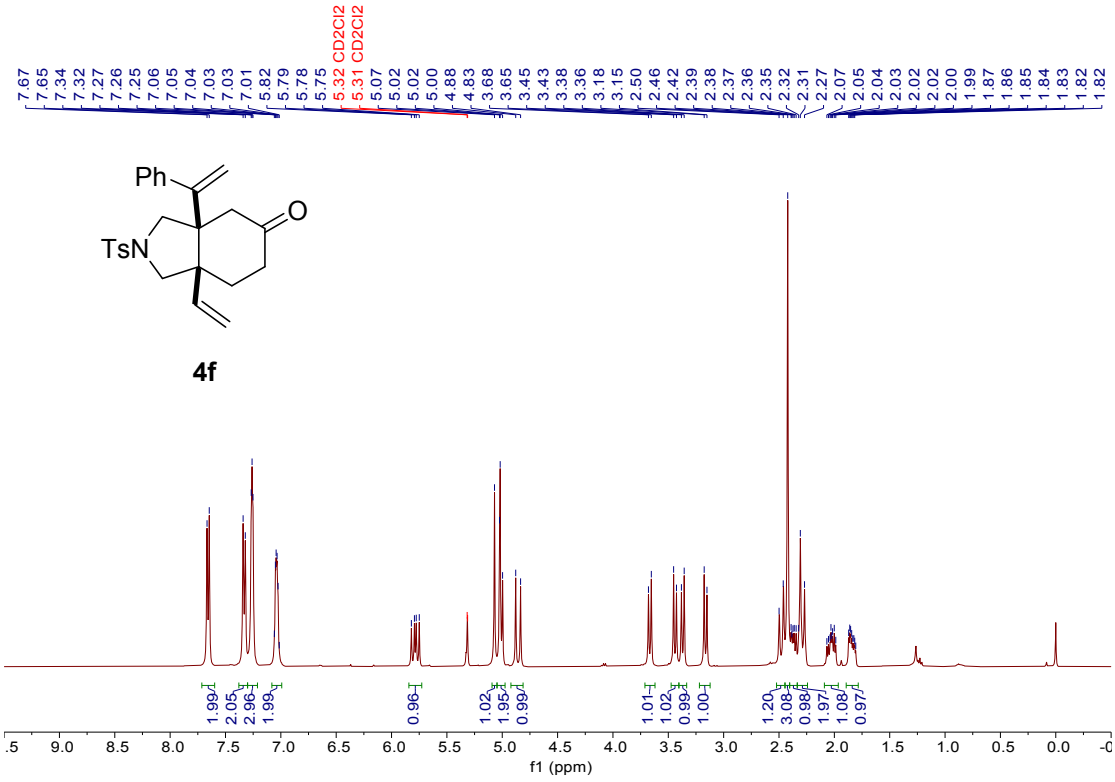
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



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

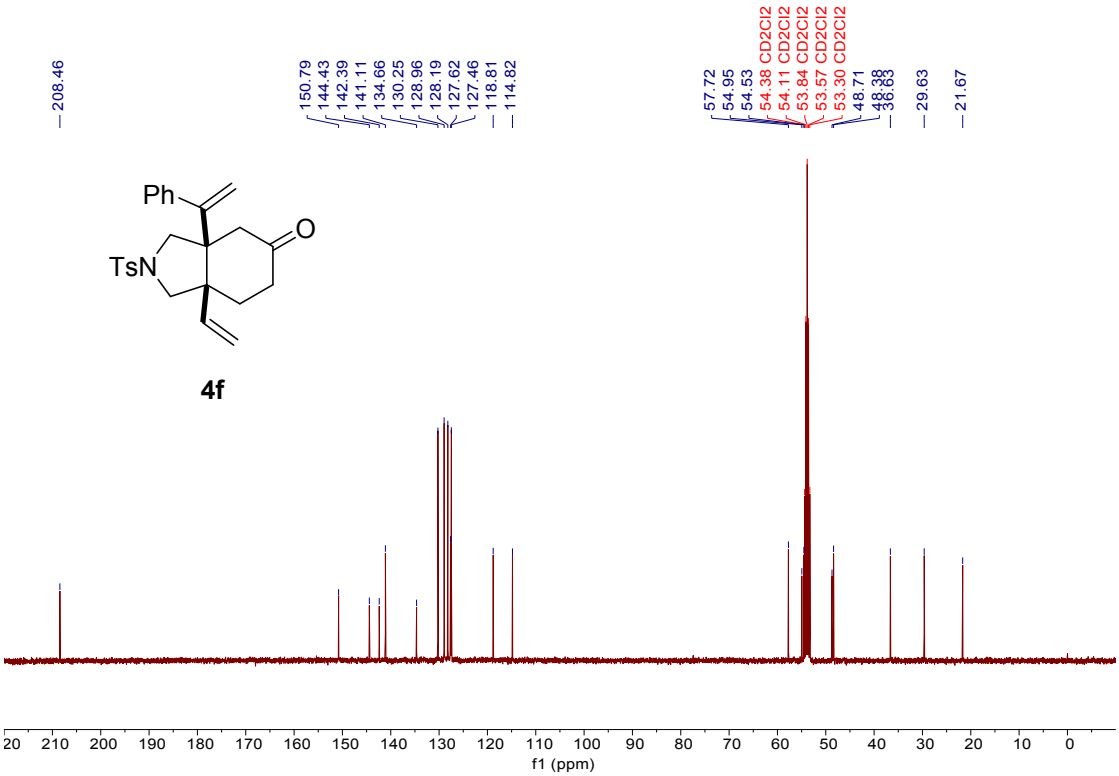


^{1}H NMR spectrum in CD_2Cl_2, 400 MHz



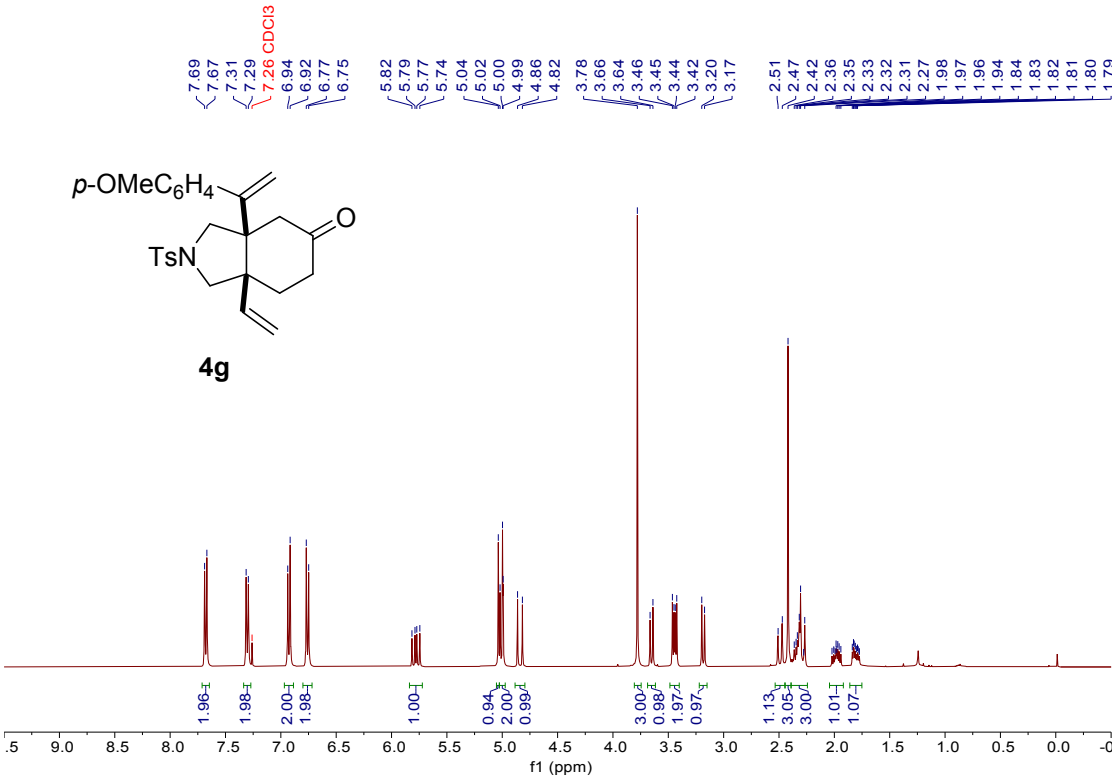
4f

^{13}C NMR spectrum in CD_2Cl_2, 101 MHz

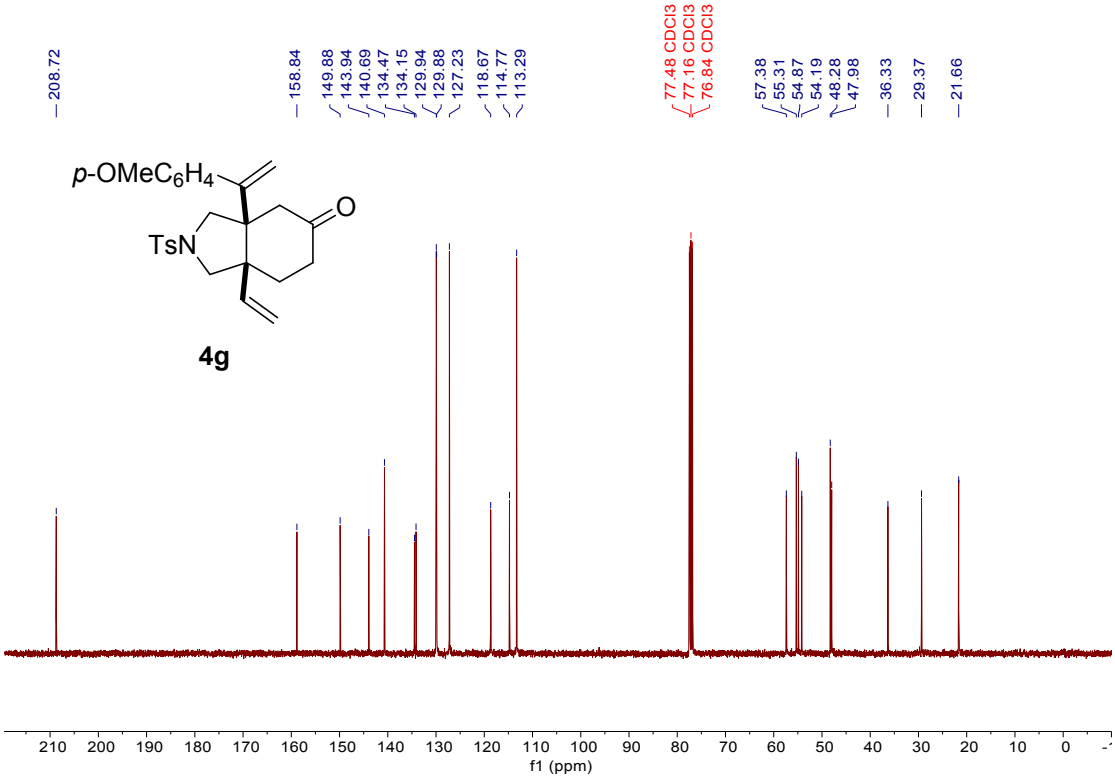


4f

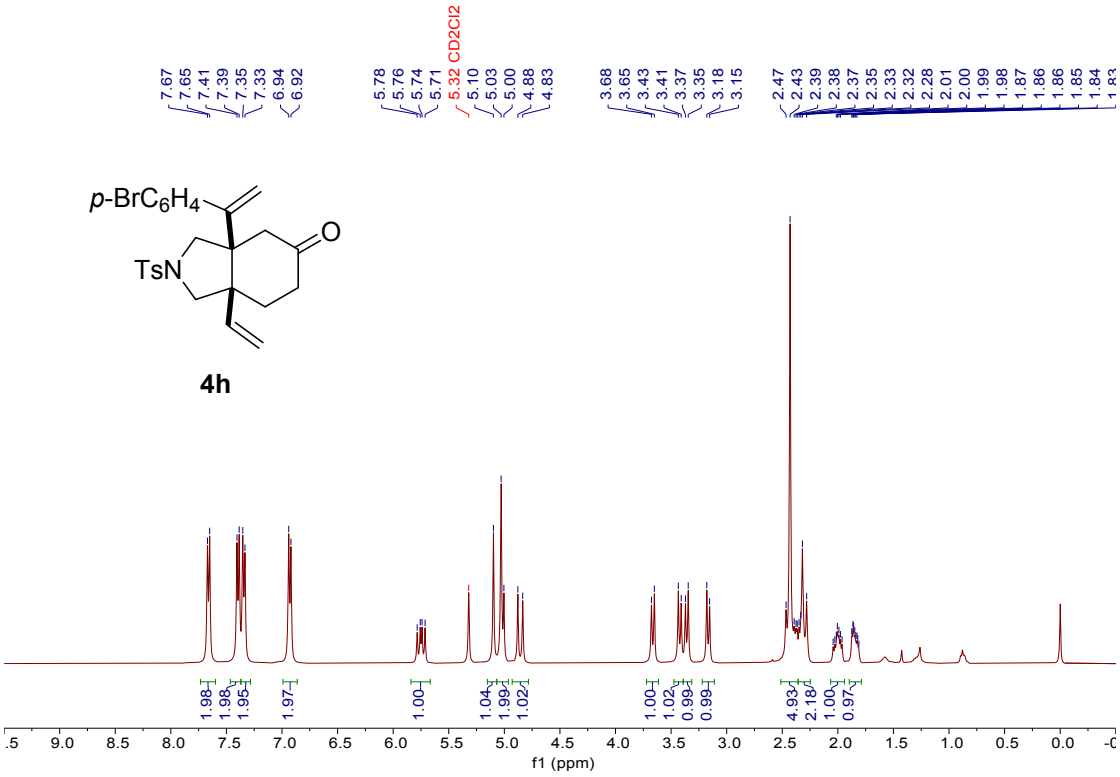
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



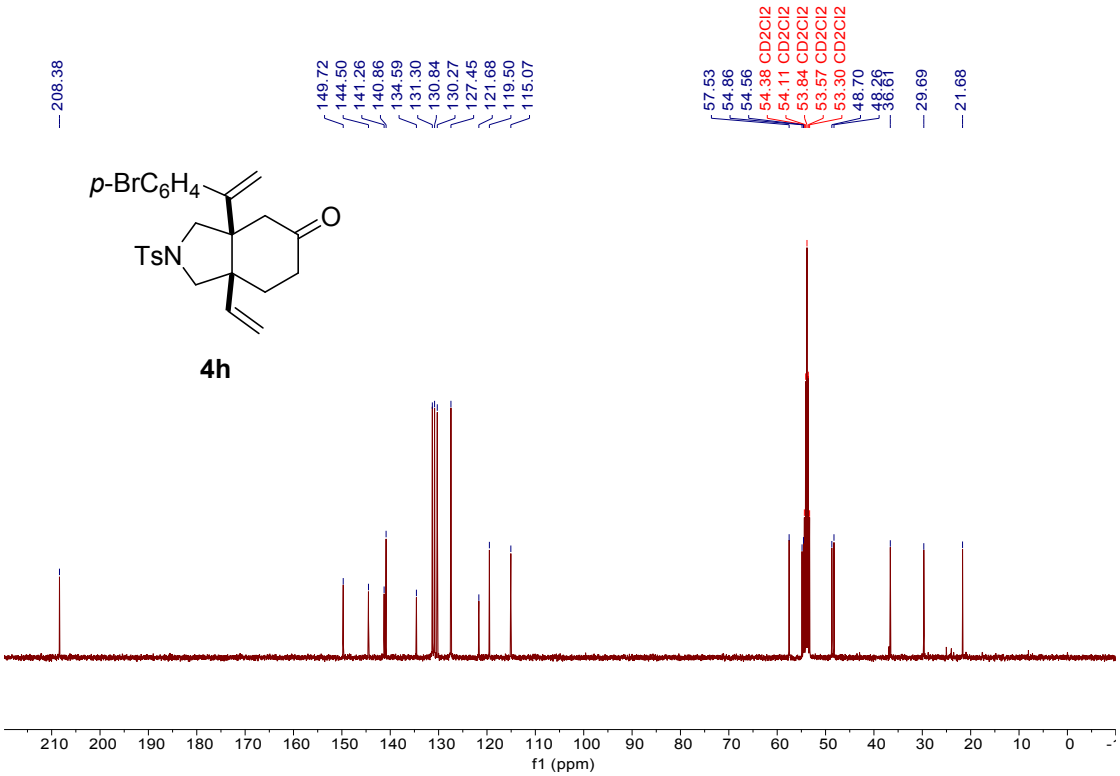
^{13}C NMR spectrum in $CDCl_3$, 101 MHz



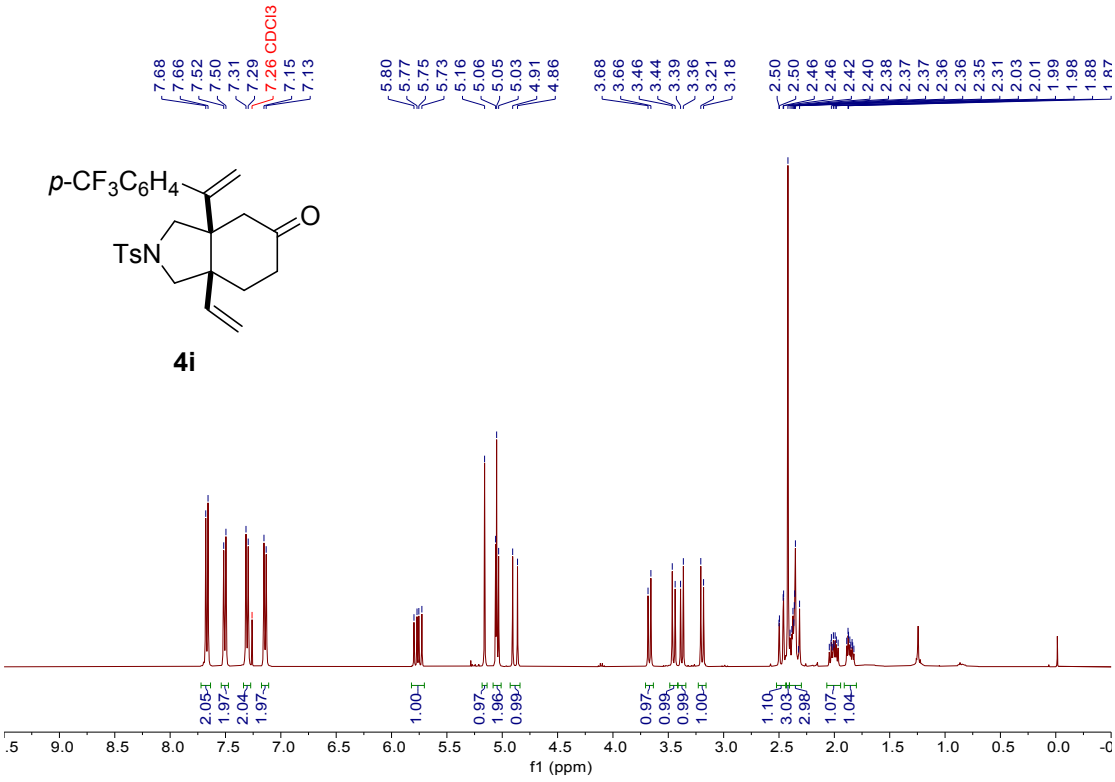
^{1}H NMR spectrum in CD_2Cl_2, 400 MHz



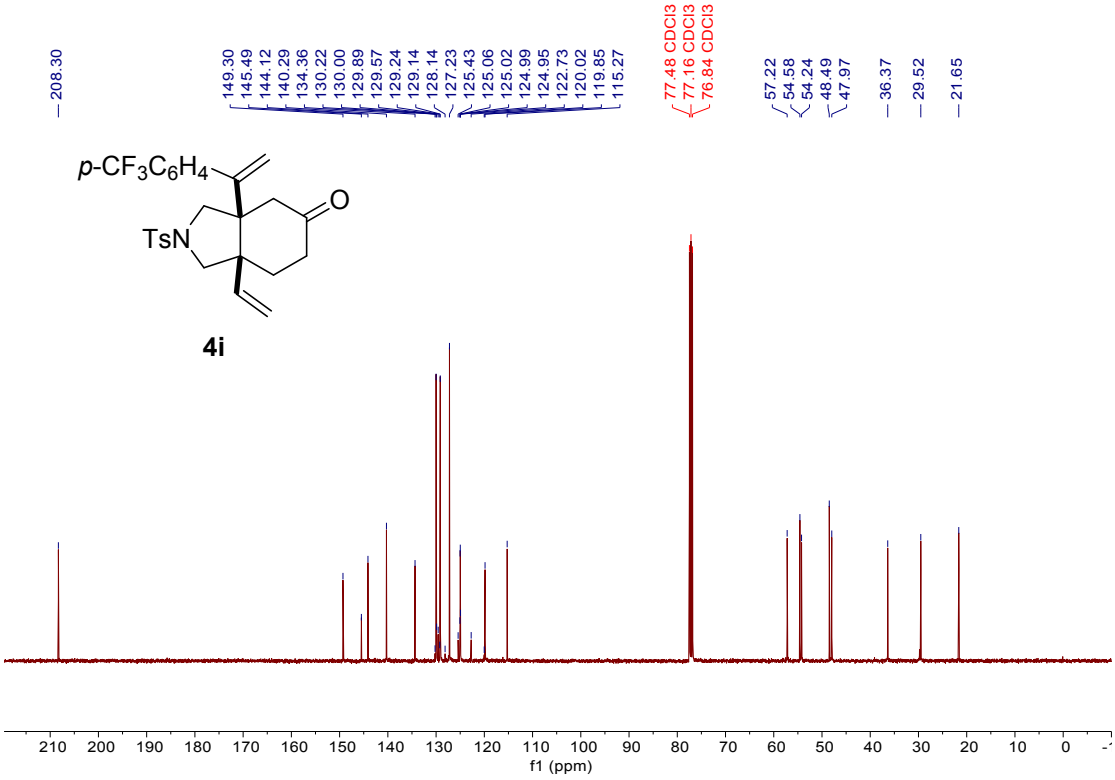
^{13}C NMR spectrum in CD_2Cl_2, 101 MHz



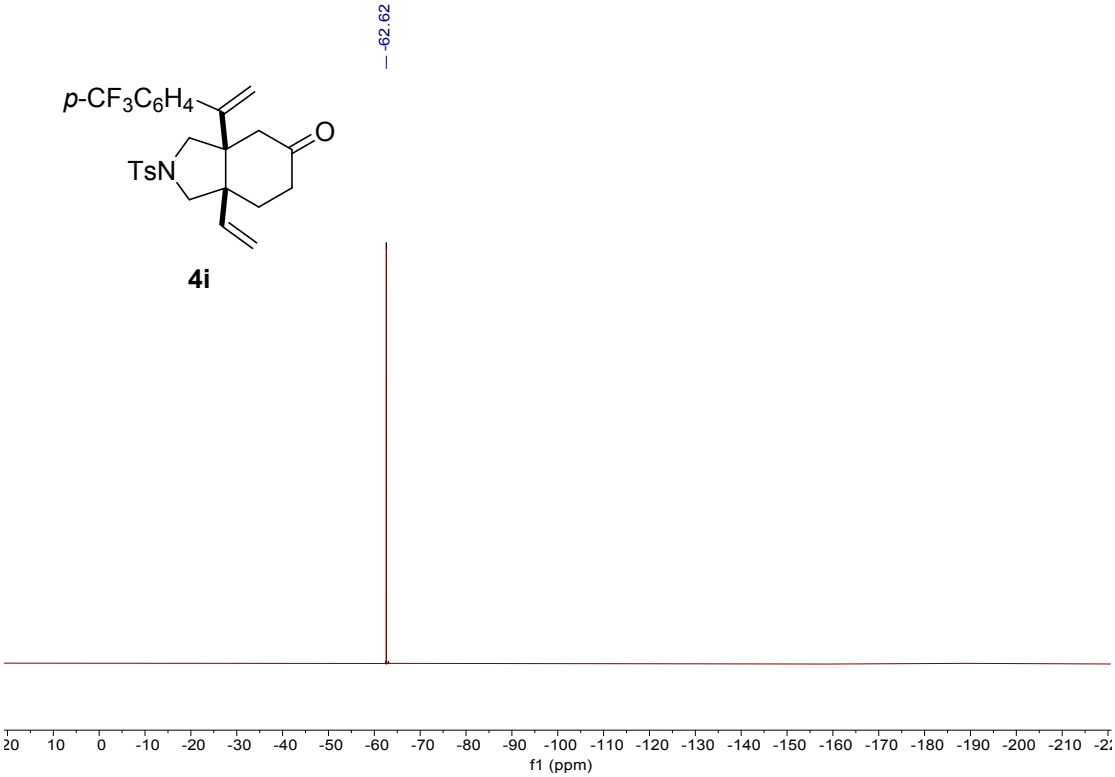
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



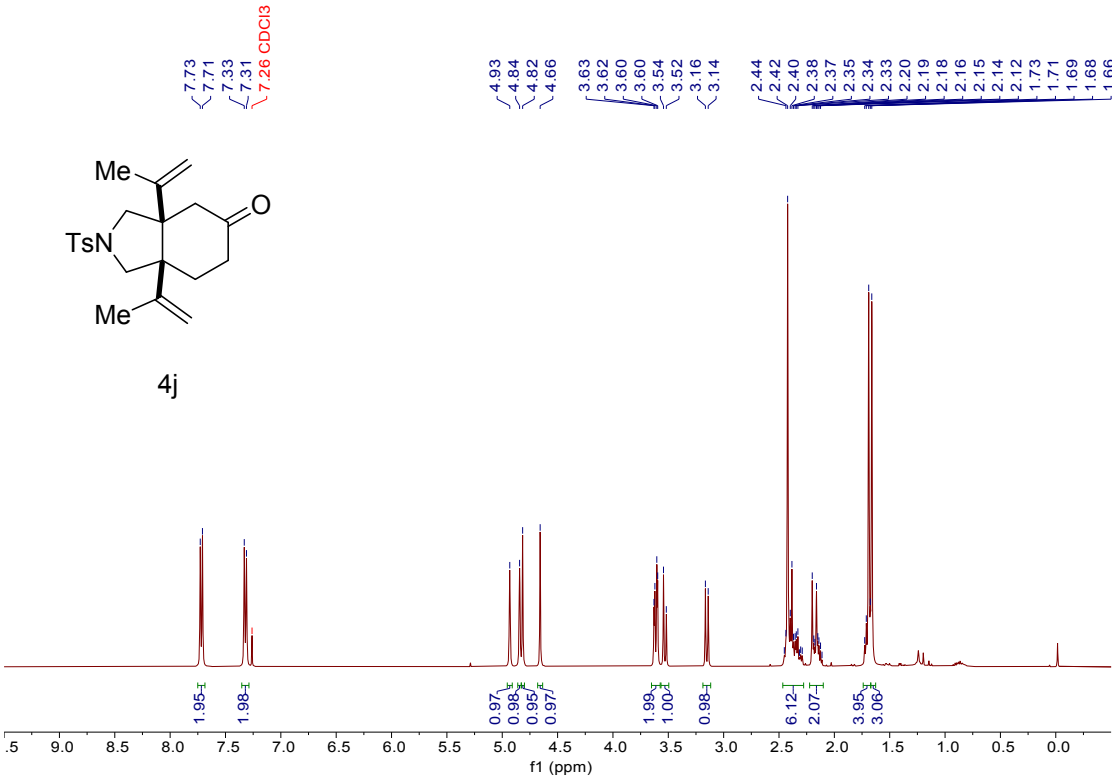
^{13}C NMR spectrum in $CDCl_3$, 101 MHz



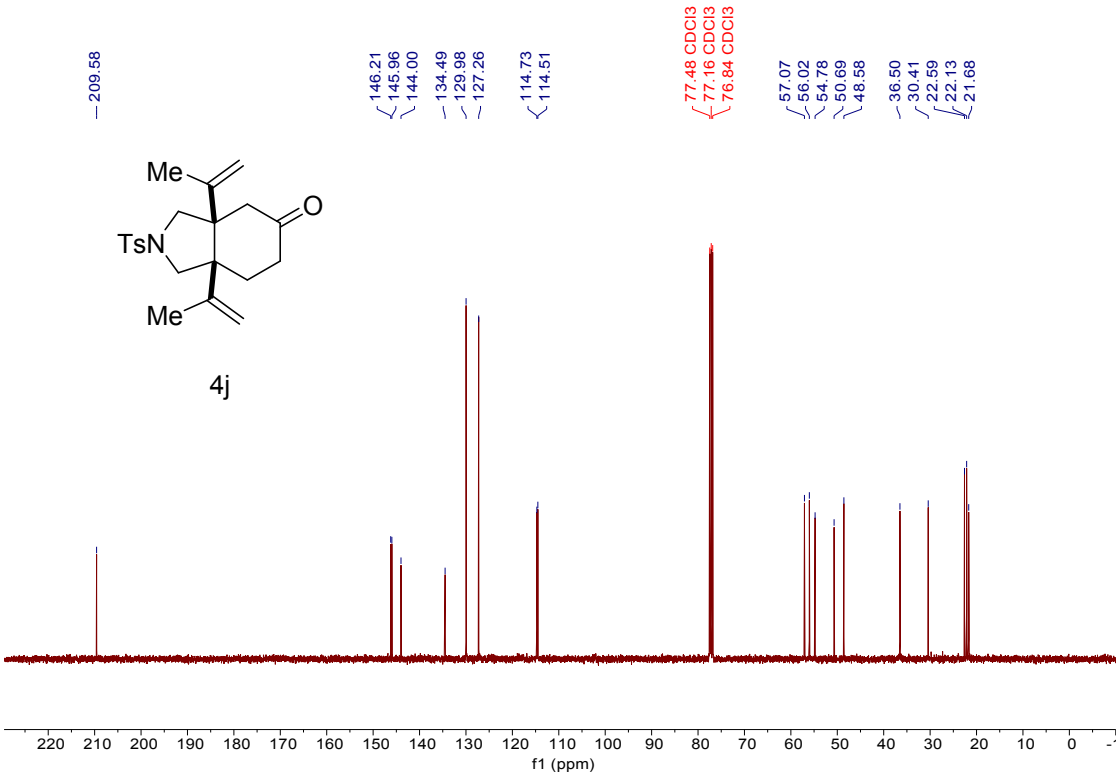
^{19}F NMR spectrum in $CDCl_3$, 471 MHz



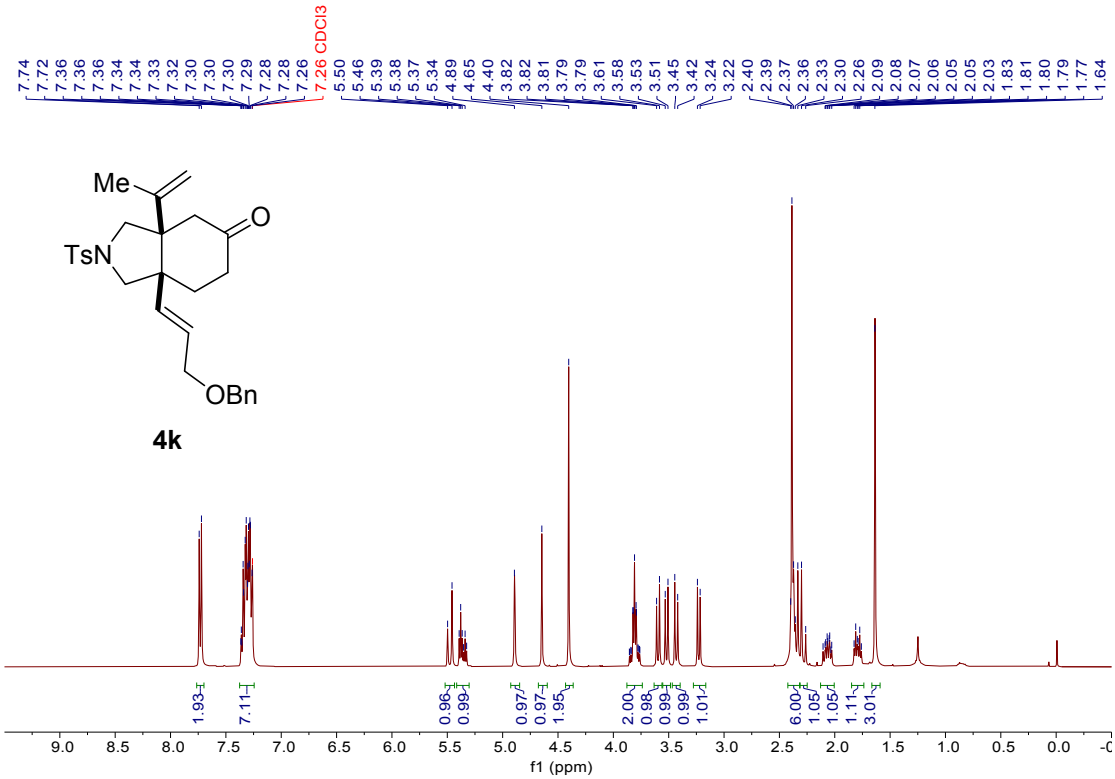
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



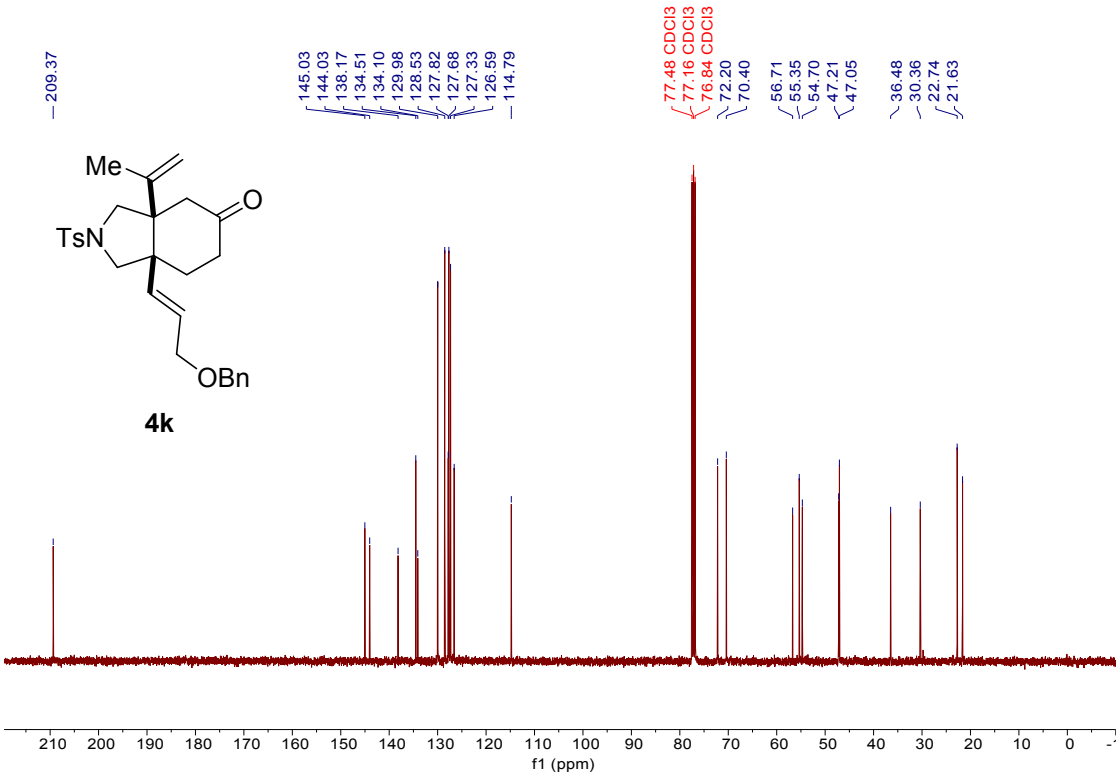
^{13}C NMR spectrum in $CDCl_3$, 101 MHz



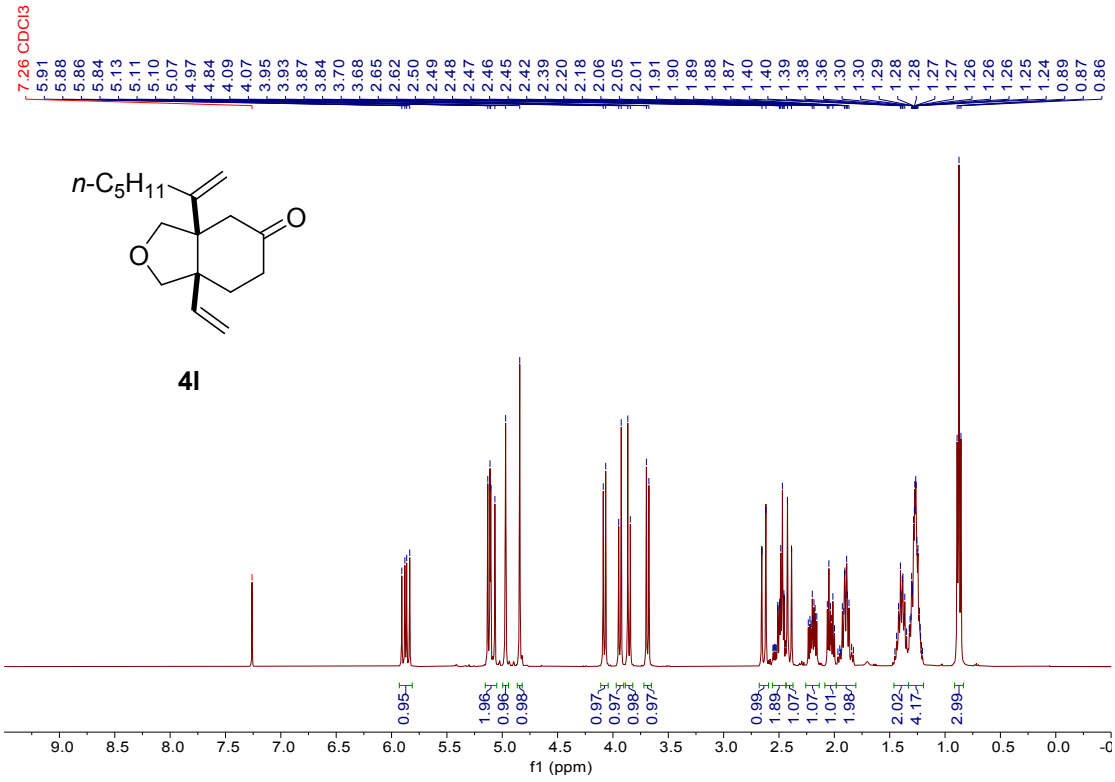
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



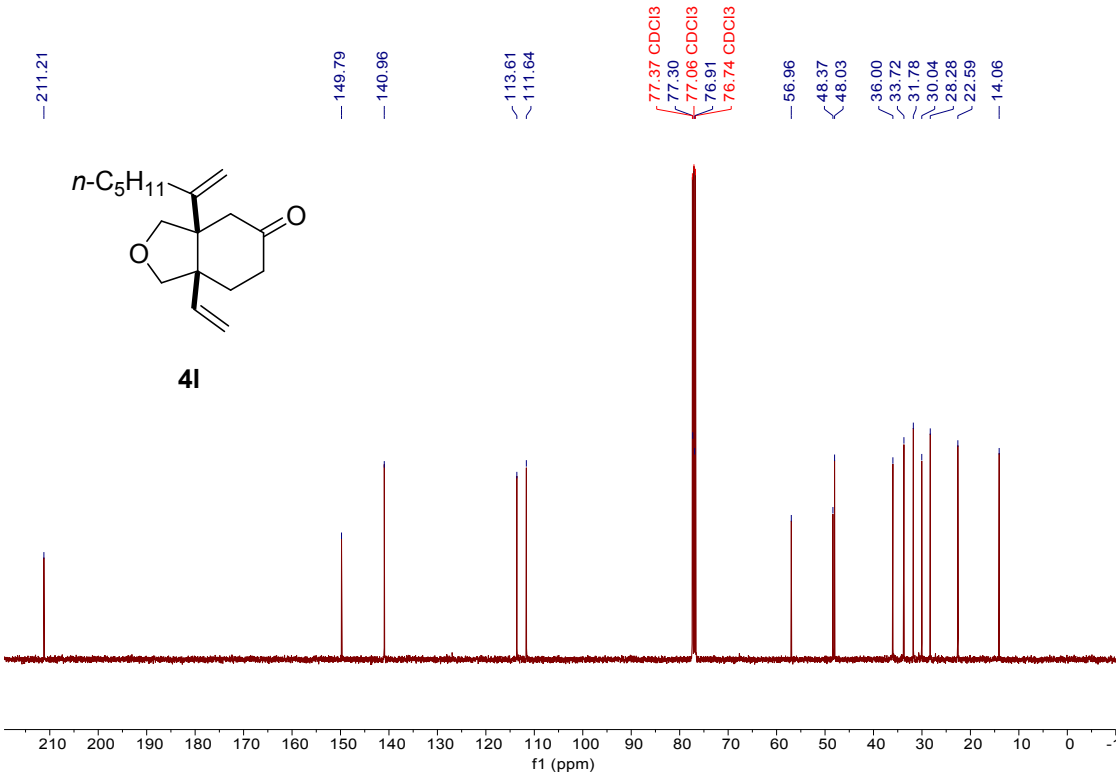
^{13}C NMR spectrum in $CDCl_3$, 101 MHz



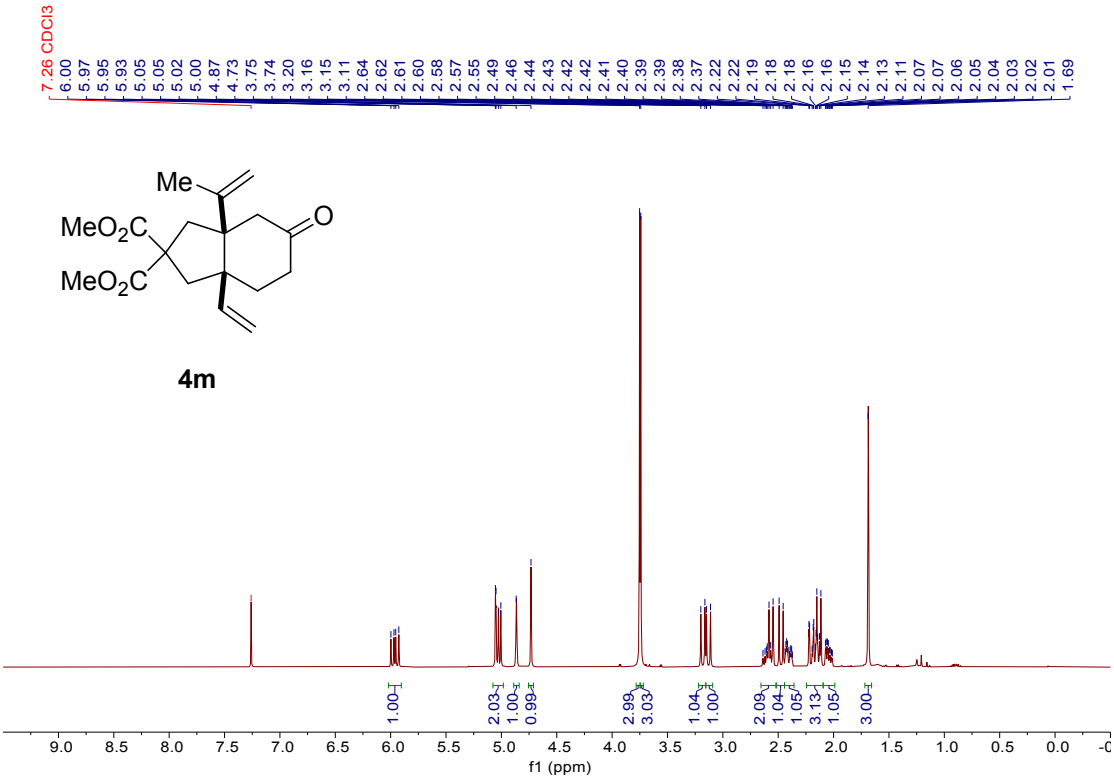
^{1}H NMR spectrum in $CDCl_3$, 400 MHz



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

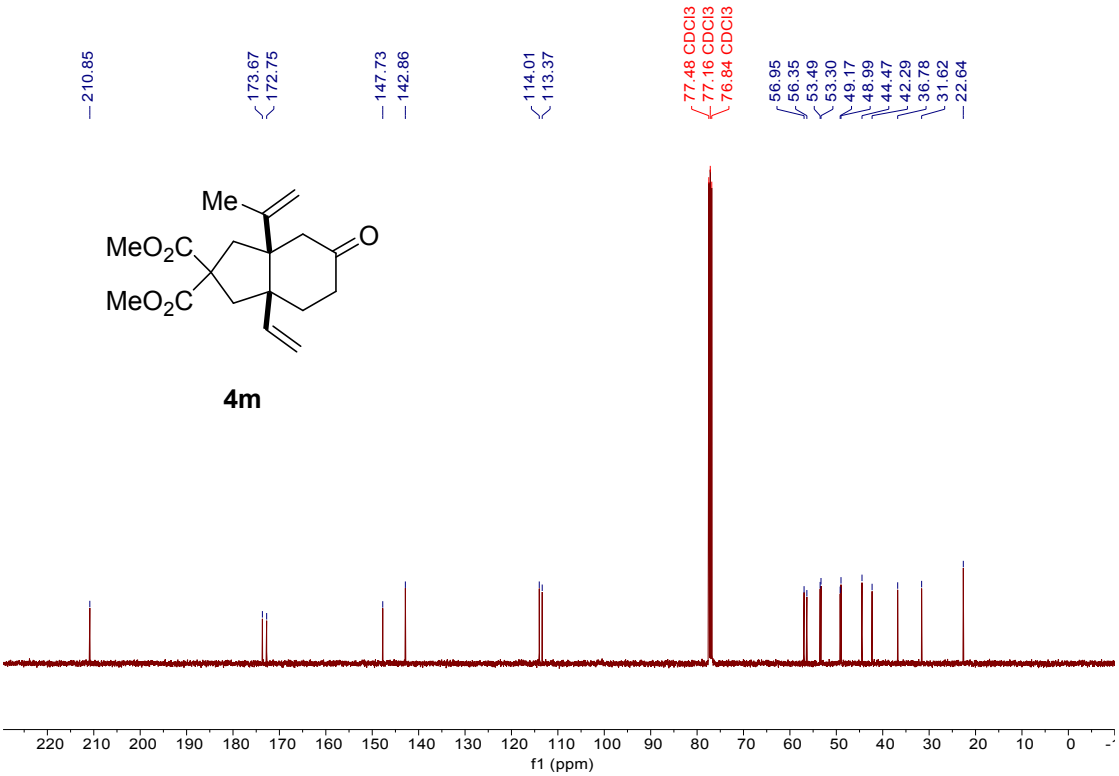


^{1}H NMR spectrum in $CDCl_3$, 400 MHz



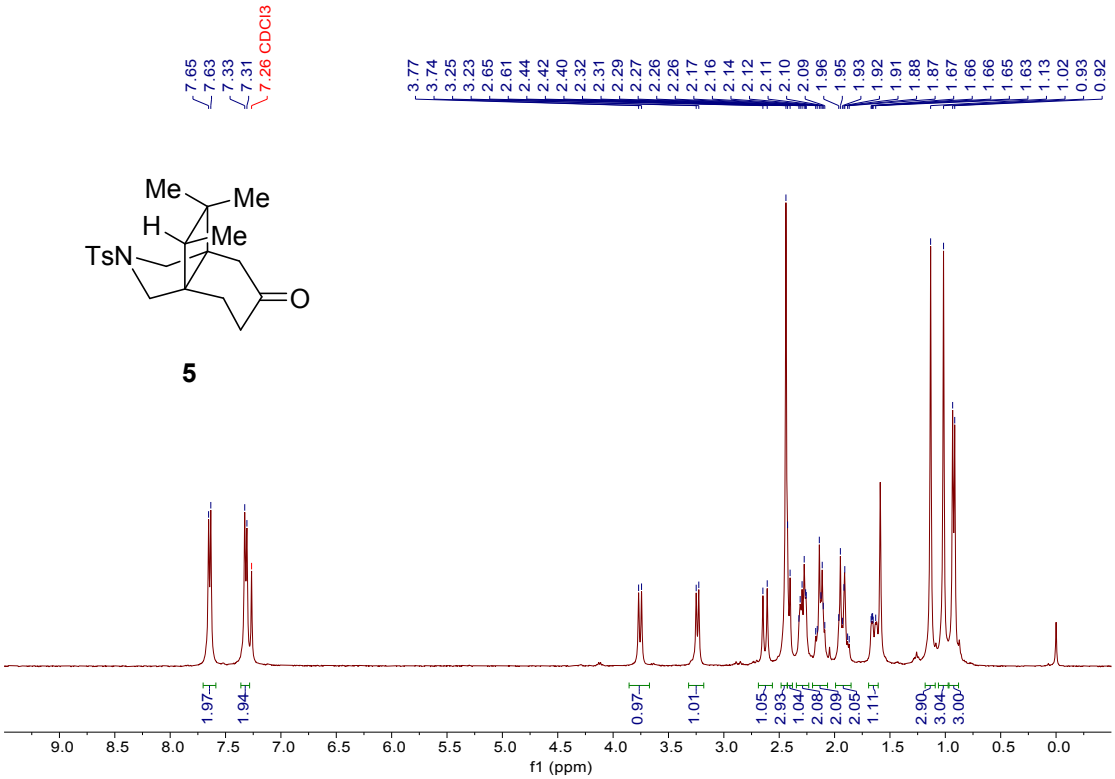
4m

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



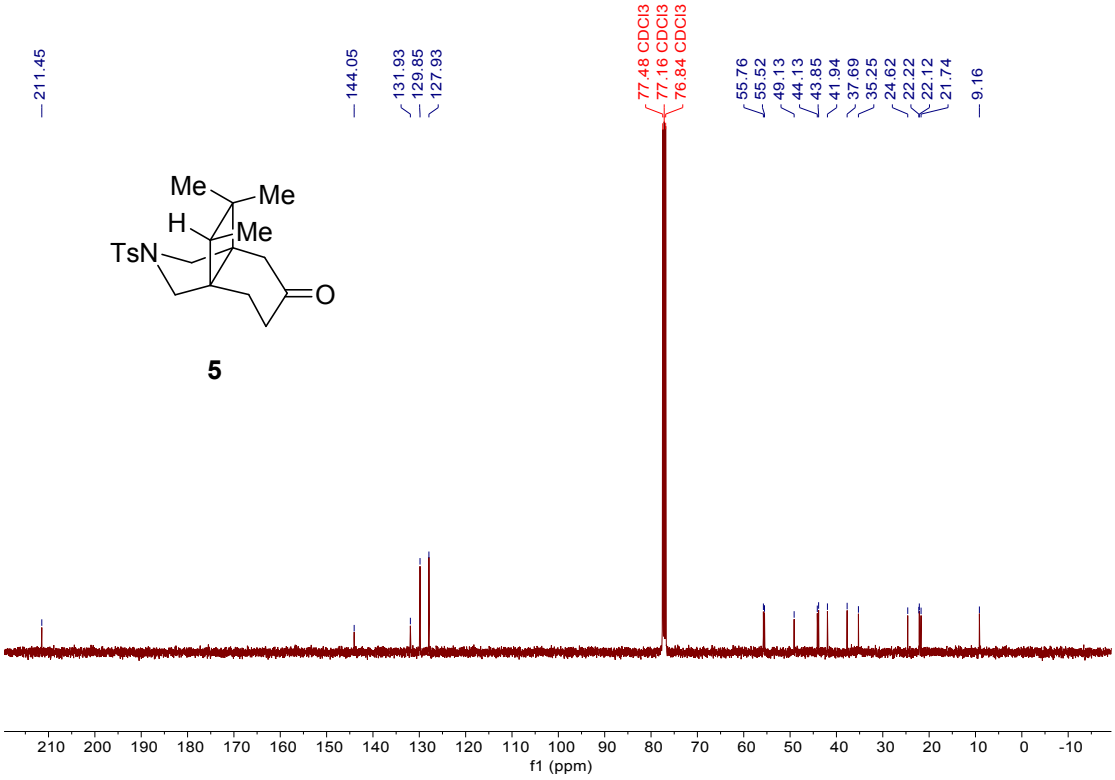
4m

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



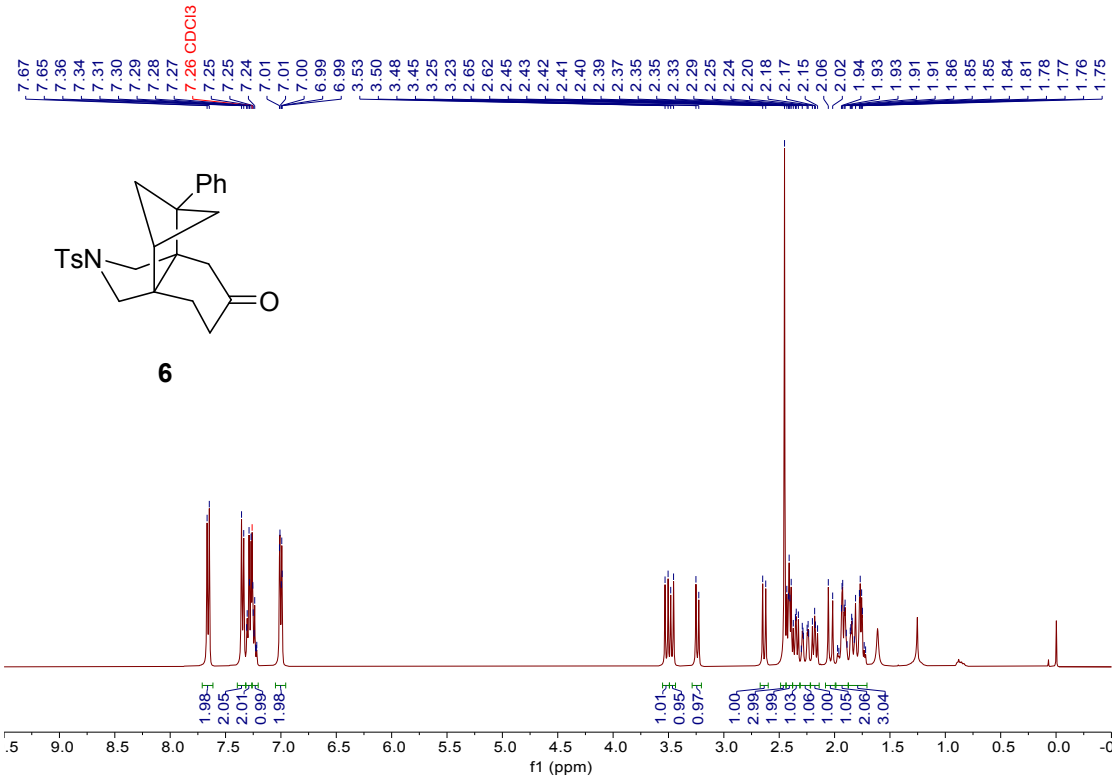
5

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

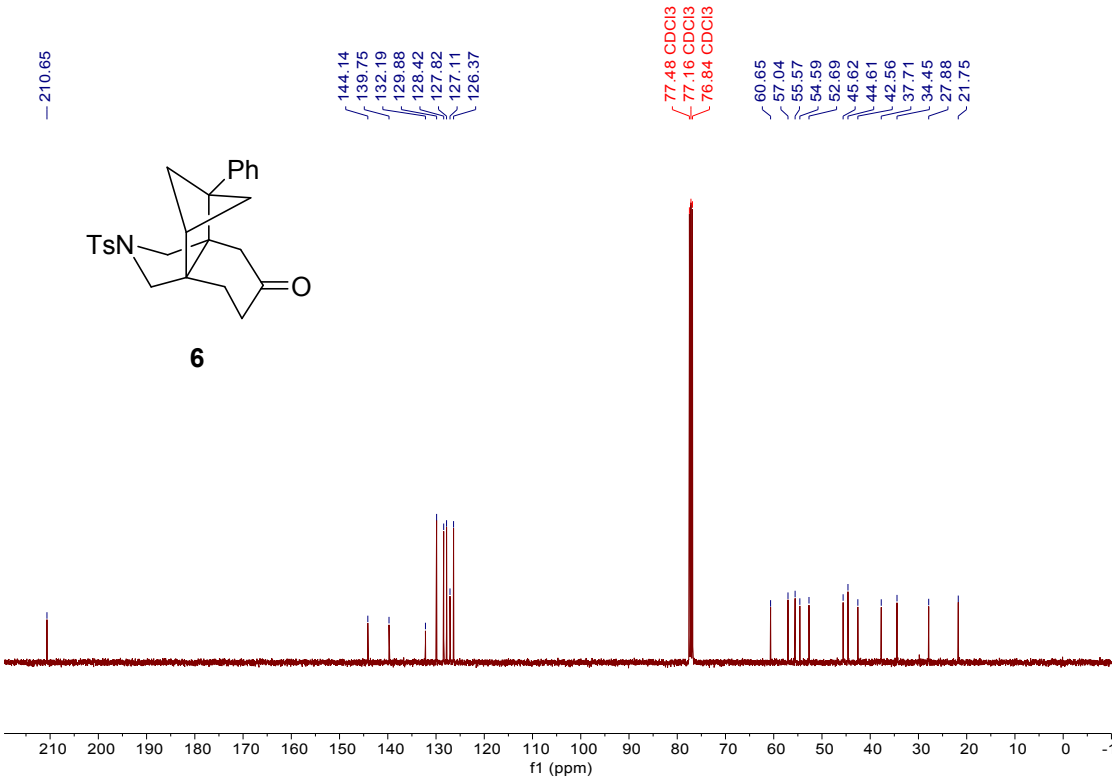


5

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



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



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