Supporting Information

Synthesizing Molecules with Linear Tricyclic 5/5/5 and 6/5/5 Skeletons via [5+2+1]/Ene Strategy

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1. General information

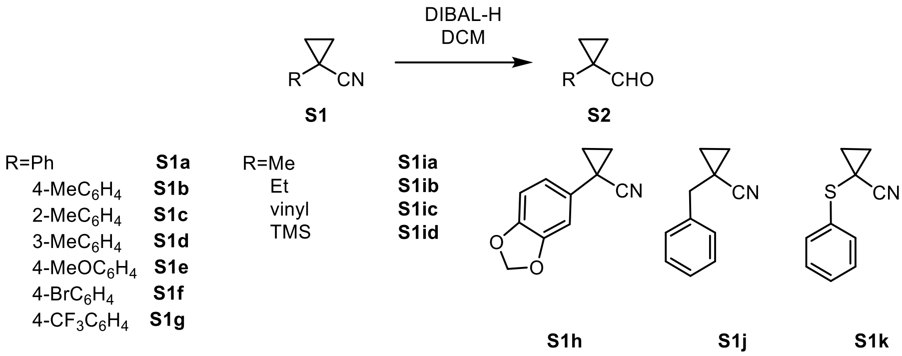
All chemicals were used as received without further purification. DCE (with molecular sieves, water ≤30 ppm) was purchased from J&K. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Analytical TLCs were performed with 0.25 mm silica gel HSGF254. The TLC plates were visualized by ultraviolet light and treatment with anisaldehyde-H_2SO_4 or phosphomolybdic acid stain followed by gentle heating. Purification of products was accomplished by flash chromatography on silica gel (200-300 mesh) and the purified compounds show a single spot by analytical TLC. Organic solutions were concentrated using a Büchi or Eyela rotary evaporator with a desktop vacuum pump. Nuclear magnetic resonance (NMR) spectra were measured on Bruker ARX 400 (^{1}H at 400 MHz; ^{13}C at 101 MHz), Bruker AVANCE III 500 (^{1}H at 500 MHz; ^{13}C at 126 MHz) and Bruker-600M Hz (^{1}H at 600 MHz; ^{13}C at 151 MHz) NMR spectrometers. Data for ^{1}H NMR spectra are reported as follows: chemical shift δ (ppm) referenced to either tetramethylsilane (TMS, 0.00 ppm) or $CHDCl_2$ (5.32 ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets), coupling constant J (Hz), and integration. Data for ^{13}C{1H} NMR spectra are reported in terms of chemical shift δ (ppm) referenced to either $CDCl_3$ (77.16 ppm) or CD_2Cl_2 (53.84 ppm). High-resolution mass spectrometry (HRMS) data were recorded on Bruker Apex IV and Bruker Solarix XR fourtier transform ion cyclotron resonance (FTICR) mass spectrometers (electrospray ionization, ESI). Single crystal X-ray diffractometer were measured on XtaLAB PRO 007HF(Mo). All crystal compounds were obtained by adding *n*-hexane to their dichloromethane solutions and then stilling for several days.

2. Substrates preparations

The synthesis of all substrates for the present study was not optimized.

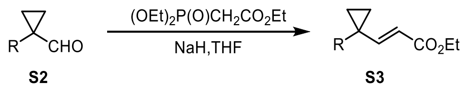
Synthesis of 1-Arylcyclopropanecarbonitrile and 1-Arylcyclopropane aldehyde:

The following synthetic intermediates are known compounds and were synthesized according to the reported literature: **S1c**[1-3], **S1d**[1-3], **S1f** [1-3], **S1e**[4], **S1k**[5,6], **S1b**[7], **S1h**[1], **S1g**[2]; **S2e**[8], **S2k**[9,10], **S2c**[1], **S2d**[1], **S2f**[11], **S2h**[12], **S2ia-b**[13], **S2ic**[14], **S2id**[15].

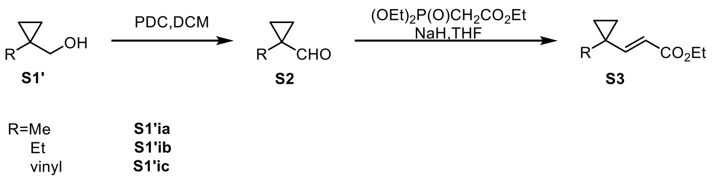


General Two-step Synthesis of Cyclopropyl Allyl Alcohols:

Step 1 (via either procedure A or procedure B)



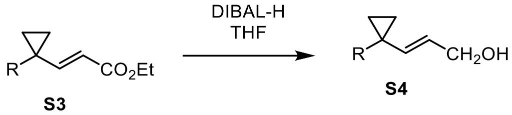
Procedure A: To a solution of NaH (1.5 equiv.) and THF was added ethyl 2-(diethoxyphosphoryl)acetate (1.5 equiv.) dropwise at 0 ˚C under an argon atmosphere. After stirred for 30 min, cyclopropyl aldehyde compound **S2** (1.0 equiv.) was added dropwise and stirred overnight at room temperature. The reaction was quenched by brine, and extracted with Et_2O. The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography afforded **S3**.



Procedure B: To a solution of **S1’** (1.0 equiv.) and DCM was added PDC (2.0 equiv.) and stirred until the reaction completed. Filtered with the DCM. The solution of product was used in the next step directly. (**S1’ia**[18], **S1’ib**[19] and **S1’ic**[20] are all known compounds).

To a solution of NaH (1.5 equiv.) and THF was added ethyl 2-(diethoxyphosphoryl)acetate (1.5 equiv.) dropwise at 0 ˚C under an argon atmosphere. After stirred for 30 min, cyclopropyl aldehyde compound **S1’** (1.0 equiv.) was added dropwise and stirred overnight at room temperature. The reaction was quenched by brine, and extracted with Et_2O. The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography afforded **S3**.

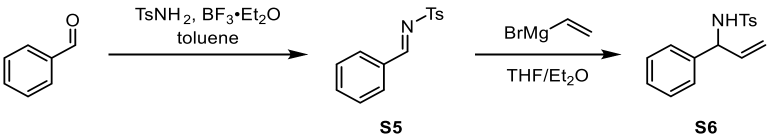
Step 2



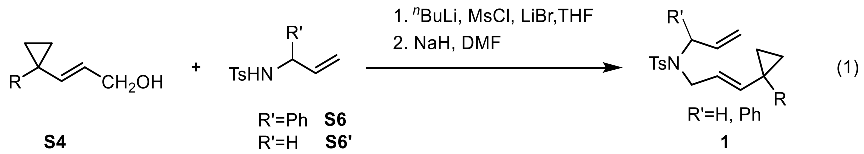
To a solution of ester **S3** (1.0 equiv.) in THF was added DIBAL-H (1.0 M in hexane, 2.5 equiv.) dropwise at −78 ˚C under an argon atmosphere. The reaction was warmed to room temperature slowly and stirred overnight. The reaction was quenched by saturated aqueous potassium tartrate tetrahydrate solution. The mixture was stirred until clear and extracted with Et_2O. The combined organic phase was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography afforded **S4**.

Synthesis of *N*-benzylidene-4-methylbenzenesulfonamide and 4-methyl-*N*-(1-phenylallyl)benzenesulfonamide

The following synthetic intermediates are known compounds and were synthesized according to the reported literature: **S5**[16], **S6**[17].



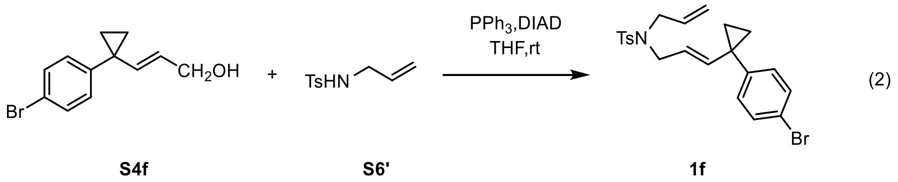
General Synthesis of Tosylamide-Tether Ene-VCP Substrates (reaction 1)



General Procedure: To a stirred solution of alcohol **S4** (1.0 equiv.) in anhydrous THF was added *n*-BuLi (1.6 M in hexane, 1.1 equiv.) at -78 ºC under N_2. The mixture was then stirred for 15 min at -78 ºC and MsCl (1.1 equiv.) was added. After 15 min, LiBr (5.0 equiv.) was added and the mixture was stirred for another 30 min at room temperature. The solution of bromide product was used in the nextstep directly.

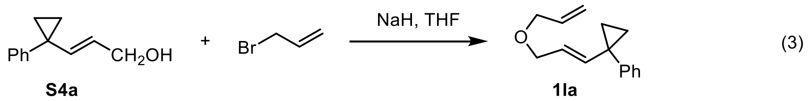
To a stirred solution of sulfonamide derivative (1.1 equiv.) in DMF was added NaH (60% purity in mineral oil, 2.1 equiv.) at 0 ºC under N_2. After 30 min, the above THF solution was added at 0 ºC and the reaction mixture was stirred overnight at room temperature. After the completion of this transformation, saturated aqueous NH_4Cl solution was added to quench the reaction, and the mixture was extracted with ether. The combined extract was washed with water and brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography on silica gel to afford **1**.

Synthesis of Tosylamide-Tether Ene-VCP Substrate 1f (reaction 2)



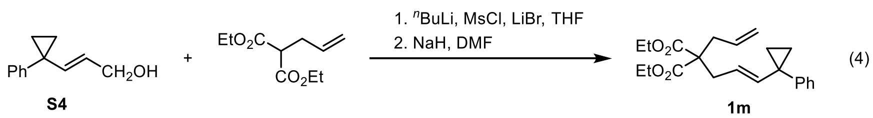
Procedure: To a solution of alcohol **S4f** (1.0 g, 1.0 equiv.), sulfonamide derivative (843 mg, 1.01 equiv.), and PPh_3 (2.1 g, 2.0 equiv.) in THF was added DIAD (1.6 g, 2.0 equiv.) dropwise at room temperature and the reaction mixture was stirred for 20 h. The resulting mixture was diluted with Et_2O, washed with water and brine, and the organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by flash column chromatography with silica gel to give product **1f** (1.0 g, 57%).

Synthesis of Ether-Tether Ene-VCP Substrate 1la (reaction 3)



To a solution of NaH (60% purity in mineral oil, 129.6 mg, 1.2 equiv.) in THF was added a solution of alcohol **S4a** (472.6 mg, 1.0 equiv.) in THF at 0 ºC and the mixture was refluxed for 2 h. The solution was warmed to room temperature, then allyl bromide (392.0 mg, 1.2 equiv.) was added and the mixture was refluxed overnight. After cooled to room temperature, the reaction was quenched by water and extracted with Et_2O. The combined organic phase was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography afforded **1la** (202.3 mg, 35%) as a colorless oil.

Synthesis of Diester-Tether Ene-VCP Substrate 1m (reaction 4)

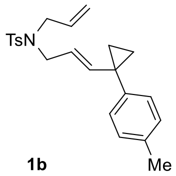


To a solution of alcohol **S4** (173.4 mg, 1.0 equiv.) and THF (2mL) was added *n*-BuLi (1.6 M in hexane,0.69 mL, 1.2 equiv.) at −78 ˚C under N_2. After stirred for 10 min, methane sulfonyl chloride (126.0 mg, 1.2 equiv.) was added. The reaction mixture was stirred for 20 min then warmed to room temperature and LiBr (400.1 mg, 4.5 equiv.) was added immediately. The reaction mixture was stirred for 5 min. The resulting solution of bromide product was used in the next step directly.

To a stirred solution of NaH (60% purity in mineral oil, 160.0 mg, 1.6 equiv.) in DMF (2 mL), diester derivative (220.0 mg, 1.6 equiv.) was added dropwise over 15 min at 0 ˚C and heated to 60 ˚C. After stirred for 20 min, the solution was cooled to -78 ˚C and the solution of the bromide product was transferred in. The reaction mixture was stirred overnight at room temperature, and then quenched by saturated aqueous NH_4Cl solution. After separation of the organic phase, the aqueous layer was extracted with Et_2O (20 mL) twice. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The crude product was purified by column chromatography on silica gel to afford ene-VCP substrate **1m** (108.9 mg, 30%) as a colorless oil.

Physical data for new Ene-VCP substrates

1a, **1la**, **1lb**, **1n** are known compounds.[21]



1b

Reaction 1: S4 (R=4-MePh) (212.2 mg, 1.13 mmol), **S6'** (238.7 mg, 1.13 mmol), **1b (**219.4mg, 51%), colorless oil, TLC: R_f (PE/EA = 5/1) = 0.57

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.62 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.09-7.03 (m, 4H), 5.58 (ddt, *J* = 17.0, 10.3, 6.2 Hz, 1H), 5.38 (d, *J* = 15.2 Hz, 1H), 5.11 (dd, *J* = 10.3, 1.5 Hz, 1H), 5.09 (dd, *J* = 17.0, 1.5 Hz, 1H), 4.78 (dt, *J* = 15.2, 6.9 Hz, 1H), 3.76-3.70 (m, 4H), 2.42 (s, 3H), 2.33 (s, 3H), 1.03 – 0.99 (m, 2H), 0.86 – 0.82 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 142.9, 139.8, 137.6, 136.0, 133.0, 129.6, 129.5, 128.9, 127.2, 121.6, 118.6, 49.1, 48.6, 27.3, 21.5, 21.1, 14.7.

HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{23}H_{28}NO_2S^+$: 382.1835; found: 382.1835

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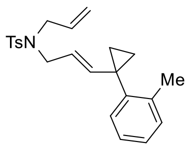
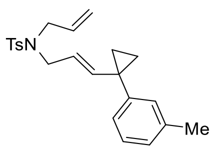


1c

Reaction 1: S4 (R=2-MePh) (600.0 mg, 3.19 mmol), **S6'** (674.0 mg, 3.19 mmol), **1c** (729.1mg, 60%), pale pink oil, TLC: R_f (PE/EA = 5/1) = 0.45

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.18 – 7.08 (m, 4H), 5.60 (ddt, *J* = 16.8, 9.8, 6.3 Hz, 1H), 5.18 (d, *J* = 15.3 Hz, 1H), 5.12 (dd, *J* = 9.8, 1.4 Hz, 1H), 5.10 (dd, *J* = 16.8, 1.4 Hz, 1H), 4.55 (dt, *J* = 15.3, 6.8 Hz, 1H), 3.77 – 3.69 (m, 4H), 2.43 (s, 3H), 2.21 (s, 3H), 1.05 – 1.00 (m, 2H), 0.95 – 0.90 (m, 2H). ^{13}C NMR (101 MHz, CDCl3) δ 143.0, 142.3, 140.2, 138.5, 137.5, 132.9, 130.6, 130.1, 129.6, 127.0, 126.8, 125.8, 120.9, 118.7, 48.9, 48.4, 26.8, 21.6, 19.4, 15.3.

HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{23}H_{28}NO_2S^+$: 382.1835; found: 382.1833

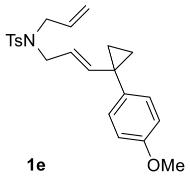


1d

Reaction 1: S4 (R=3-MePh) (1076.6 mg, 5.72 mmol), **S6'** (1210.0 mg, 5.72 mmol), **1d** (1264.2 mg, 68%), pale pink oil, TLC: R_f (PE/EA = 10/1) = 0.28

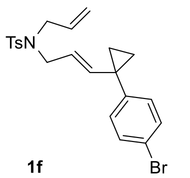
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.15 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.04 – 6.94 (m, 3H), 5.59 (ddt, *J* = 17.0, 10.6, 6.2 Hz, 1H), 5.41 (d, *J* = 15.3 Hz, 1H),

5.11 (dd, J = 10.3, 1.4Hz, 1H), 5.10 (dd, J = 17.0, 1.4 Hz, 1H), 4.77 (dt, J = 15.3, 6.8 Hz, 1H), 3.76-3.71 (m, 4H), 2.42 (s, 3H), 2.32 (s, 3H), 1.05 – 1.01 (m, 2H), 0.87 – 0.83 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 142.8, 142.7, 137.7, 137.5, 133.0, 130.3, 129.6, 128.1, 127.2, 127.1, 126.6, 121.7, 118.6, 49.1, 48.6, 27.6, 21.5, 21.4, 14.6.
HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{23}H_{28}NO_2S^+$: 382.1835; found: 382.1832



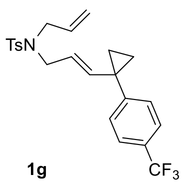
1e

Reaction 1: S4 (R=4-OMePh) (357.4 mg, 1.75 mmol), **S6'** (369.7 mg, 1.75 mmol), **1e** (446.2mg, 64%), colorless oil TLC: R_f (PE/EA = 5/1) = 0.47
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 8.7 Hz, 2H), 6.80 (d, J = 8.7 Hz, 2H), 5.58 (ddt, J = 17.1, 9.6, 6.2 Hz, 1H), 5.34 (d, J = 14.7 Hz, 1H), 5.11 (dd, J = 9.6, 1.4 Hz, 1H), 5.10 (dd, J = 17.1, 1.4 Hz, 1H), 4.73 (dt, J = 14.7, 6.9 Hz, 1H), 3.80 (s, 3H), 3.75-3.70 (m, 4H), 2.42 (s, 3H), 1.02 – 0.97 (m, 2H), 0.85 – 0.80 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 143.2, 143.0, 137.5, 134.8, 133.0, 130.8, 129.6, 127.1, 121.5, 118.6, 113.6, 55.3, 49.1, 48.5, 27.0, 21.5, 14.6.
HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{23}H_{28}NO_3S^+$: 398.1784; found: 398.1784



1f

Reaction 2, **1f** (446.2mg, 57%), colorless oil, TLC: R_f (PE/EA = 5/1) = 0.52
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.2 Hz, 2H), 7.40-7.35 (m, 2H), 7.23 (d, J = 8.2 Hz, 2H), 7.06-7.01 (m, 2H), 5.60 (ddt, J = 16.8, 10.3, 6.2 Hz, 1H), 5.35 (d, J = 15.3 Hz, 1H), 5.12 (dd, J = 10.3, 1.4 Hz, 1H), 5.10 (dd, J = 16.8, 1.4 Hz, 1H), 4.71 (dt, J = 15.3, 6.8 Hz, 1H), 3.76 – 3.70 (m, 4H), 2.44 (s, 3H), 1.02 – 0.98 (m, 2H), 0.90 – 0.86 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 142.0, 141.8, 137.5, 133.0, 131.5, 131.3, 129.6, 127.1, 122.2, 120.3, 118.6, 49.2, 48.4, 27.2, 21.6, 14.7.
HRMS (ESI−FTICR, m/z): $[M + NH_3]^+$ calculated for $C_{22}H_{28}BrN_2O_2S^+$: 463.1049; found: 463.1052.

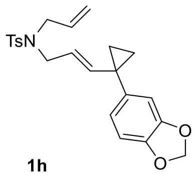


1g

Reaction 1: S4 (R=4-CF_3Ph) (1.0688 g, 4.41 mmol), **S6'** (932.2 mg, 4.41 mmol), **1g** (1.3534 g, 70%), pale yellow oil, TLC: R_f (PE/EA = 5/1) = 0.51

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 5.59 (ddt, *J* = 16.9, 10.4, 6.3 Hz, 1H), 5.43 (d, *J* = 15.4 Hz, 1H), 5.12 (dd, *J* = 10.4, 1.4 Hz, 1H), 5.10 (dd, *J* = 16.9, 1.4 Hz, 1H), 4.78 (dt, *J* = 15.4, 6.7 Hz, 1H), 3.76-3.71 (m, 4H), 2.41 (s, 3H), 1.09 – 1.03 (m, 2H), 0.97 – 0.91 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 143.2, 141.4, 137.5, 133.0, 129.9, 129.6, 128.7 (q, *J* = 32.4 Hz), 127.1, 125.2 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 271.9 Hz), 122.7, 118.7, 49.3, 48.5, 27.5, 21.5, 14.9.

HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{23}H_{25}F_3NO_2S^+$: 436.1553; found: 436.1552

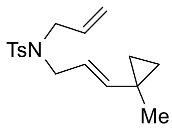


1h

Reaction 1: S4 (R=4-CF_3Ph) (164.1 mg, 0.75 mmol), **S6'** (143.7 mg, 0.68 mmol), **1g** (131.4 mg, 47%), colorless oil, TLC: R_f (PE/EA = 10/1) = 0.18

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 6.71 – 6.62 (m, 3H), 5.96-5.93 (m, 2H), 5.59 (ddt, *J* = 16.8, 10.6, 6.3 Hz, 1H), 5.31 (d, *J* = 15.2 Hz, 1H), 5.12 (dd, *J* = 10.6, 1.4 Hz, 1H), 5.10 (dd, *J* = 16.8, 1.4 Hz, 1H), 4.77 (dt, *J* = 15.2, 6.8 Hz, 1H), 3.76-3.70 (m, 4H), 2.42 (s, 3H), 1.01 – 0.93 (m, 2H), 0.88 – 0.80 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.3, 146.1, 143.1, 142.9, 137.5, 136.7, 133.0, 129.6, 127.1, 122.8, 121.7, 118.6, 110.4, 107.9, 100.9, 49.1, 48.5, 27.6, 21.5, 14.8.

HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{23}H_{26}NO_4S^+$: 412.1577; found: 412.1577

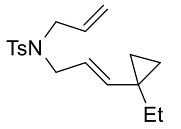


1ia

Reaction 1: S4 (R=Me) (372.5 mg, 3.32 mmol), **S6'** (771.2 mg, 3.65 mmol), **1ia** (510.4 mg, 50%), light yellow oil, TLC: R_f (PE/EA = 5/1) = 0.56

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 5.62 (ddt, *J* = 17.5, 9.7, 6.3 Hz, 1H), 5.17 – 5.06 (m, 4H), 3.80 (d, *J* = 6.2 Hz, 2H), 3.76 (d, *J* = 4.6 Hz, 2H), 2.42 (s, 3H), 1.04 (s, 3H), 0.56 – 0.51 (m, 2H), 0.51 – 0.44 (m, 2H) ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 143.1, 137.7, 133.0, 129.6, 127.2, 119.2, 118.7, 49.0, 48.7, 21.5, 21.1, 17.0, 15.0.

HRMS (ESI−FTICR, m/z): $[M + Na]^+$ calculated for $C_{17}H_{23}NNaO_2S^+$: 328.1342; found: 328.1344

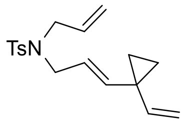


1ib

Reaction 1: S4 (R=Et) (804.0 mg, 6.37 mmol), **S6'** (1479.0 mg, 7.0 mmol), **1ib** (1047.9 mg, 52%), light pink oil, TLC: R_f (PE/EA = 5/1) = 0.62

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 5.61 (ddt, *J* = 17.6, 9.6, 6.2 Hz, 1H), 5.23 (d, *J* = 15.4 Hz, 1H), 5.16 – 5.10 (m, 2H), 5.04 (dt, *J* = 15.4, 6.7 Hz, 1H), 3.82 – 3.73 (m, 4H), 2.43 (s, 3H), 1.32 (q, *J* = 7.3 Hz, 2H), 0.81 (t, *J* = 7.3 Hz, 3H), 0.52 – 0.47 (m, 2H), 0.45 – 0.41 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 141.2, 137.6, 133.0, 129.6, 127.2, 120.0, 118.7, 48.9, 48.8, 28.7, 22.6, 21.5, 13.8, 11.1.

HRMS (ESI−FTICR, m/z): $[M + Na]^+$ calculated for $C_{18}H_{25}NNaO_2S^+$: 342.1498; found: 342.1500

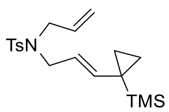


1ic

Reaction 1: S4 (R=vinyl) (621.3 mg, 5.0 mmol), **S6'** (1162.0 mg, 5.5 mmol), **1ic** (1075.8 mg, 68%), light pink oil, TLC: R_f (PE/EA = 5/1) = 0.6

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 5.73 – 5.48 (m, 3H), 5.20 – 5.09 (m, 3H), 4.95 – 4.85 (m, 2H), 3.82 – 3.75 (m, 4H), 2.43 (s, 3H), 0.84 – 0.77 (m, 2H), 0.76 – 0.70 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 141.6, 138.7, 137.7, 133.1, 129.8, 127.3, 122.3, 118.9, 112.5, 49.3, 48.7, 24.6, 21.6, 15.3.

HRMS (ESI−FTICR, m/z): $[M + Na]^+$ calculated for $C_{18}H_{23}NNaO_2S^+$: 340.1342; found: 340.1341

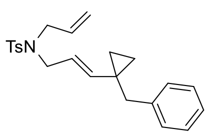


1id

Reaction 1: S4 (R=TMS) (417.1 mg, 2.5 mmol), **S6'** (581.0 mg, 2.75 mmol), **1id** (474.7 mg, 53%), colorless oil, TLC: R_f (PE/EA = 10/1) = 0.49

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.62-5.55 (m, 2H), 5.15–5.02 (m, 3H), 3.74 (dd, *J* = 11.2, 6.8 Hz, 4H), 2.42 (s, 3H), 0.55–0.47 (m, 2H), 0.41 (s, 2H), -0.10 (s, 9H). 13C NMR (101 MHz, CDCl3) δ 143.2, 140.7, 137.8, 133.1, 129.8, 127.3, 122.8, 118.7, 48.9, 21.6, 10.2, 10.0, -3.1.

HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{19}H_{30}NO_2SSi^+$: 364.1761; found: 364.1760

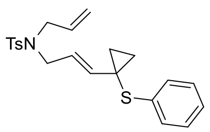


1j

Reaction 1: S4 (R=CH_2Ph) (505.3 mg, 2.68 mmol), **S6’** (515.5 mg, 2.44 mmol), **1j** (681.5 mg, 67%), colorless oil, TLC: R_f (PE/EA = 3/1) = 0.67

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.26 – 7.20 (m, 2H), 7.19 – 7.12 (m, 3H), 5.51 (ddt, *J* = 16.7, 10.2, 6.2 Hz, 1H), 5.32 (d, *J* = 15.4 Hz, 1H), 5.05 (dd, *J* = 10.2, 1.5 Hz, 1H), 4.99 (dd, *J* = 16.7, 1.5 Hz, 1H), 4.94 (dt, *J* = 15.4, 6.8 Hz, 1H), 3.66 (d, *J* = 6.8 Hz, 2H), 3.58 (d, *J* = 6.2 Hz, 2H), 2.70 (s, 2H), 2.42 (s, 3H), 0.69 – 0.63 (m, 2H), 0.62 – 0.56 (m, 2H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 143.3, 140.8, 139.7, 137.6, 133.0, 129.6, 129.0, 128.0, 127.0, 125.9, 120.9, 118.3, 48.7, 48.6, 41.2, 21.2, 21.2, 13.5.

HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{23}H_{28}NO_2S^+$: 382.1835; found: 382.1835

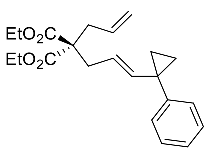


1k

Reaction 1: S4 (R=CH_2Ph) (1220.0 mg, 5.9 mmol), **S6’** (1250.0 mg, 5.9 mmol), **1k** (1703.8 mg, 72%), Pale pink oil, TLC: R_f (PE/EA = 10/1) = 0.23.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.24 (d, J = 8.2 Hz, 2H), 7.24 – 7.17 (m, 4H), 7.15 – 7.10 (m, 1H), 5.53 (ddt, J = 16.8, 10.2, 6.3 Hz, 1H), 5.40 – 5.27 (m, 2H), 5.07 (dd, *J* = 10.2, 1.54 Hz, 1H), 5.02 (dd, J = 16.8, 1.54 Hz, 1H), 3.74 (d, *J* = 5.4 Hz, 2H), 3.61 (d, *J* = 6.3 Hz, 2H), 2.40 (s, 3H), 1.21 – 1.16 (m, 2H), 1.10 – 1.05 (m, 2H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 143.3, 137.7, 137.4, 136.9, 132.9, 129.6, 128.6, 127.1, 126.9, 125.1, 123.8, 118.4, 48.9, 47.8, 25.3, 21.2, 17.6.

HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{22}H_{26}NO_2S_2^+$: 400.1399; found: 400.1390

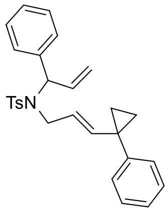


1m

Reaction 4: 1m (108.9 mg, 30%), yellow oil, TLC: R_f (PE/EA = 5/1) = 0.59

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.31 – 7.22 (m, 4H), 7.21 – 7.16 (m, 1H), 5.61 (ddt, *J* = 17.8, 10.5, 7.4 Hz, 1H), 5.49 (d, *J* = 15.2 Hz, 1H), 5.07 – 4.99 (m, 2H), 4.89 (dt, *J* = 15.2, 7.6 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 4H), 2.52 (t, *J* = 7.9 Hz, 4H), 1.17 (t, *J* = 7.1 Hz, 6H), 1.05 – 1.01 (m, 2H), 0.94 – 0.90 (m, 2H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 170.6, 143.6, 141.4, 132.7, 129.3, 128.1, 126.2, 121.9, 118.6, 61.1, 57.5, 36.6, 35.1, 27.6, 14.5, 13.9.

HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{22}H_{29}O_4^+$: 357.2060; found: 357.2052



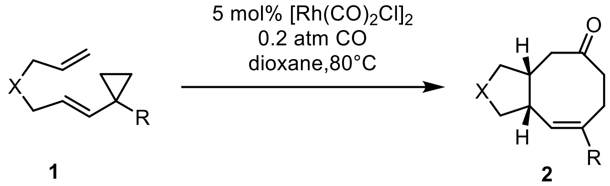
1o

Reaction 1: S4 (R=Ph) (202.1 mg, 1.16 mmol), **S6** (300.5 mg, 1.05 mmol), **1o** (200.3 mg, 43%), colorless oil, TLC: R_f (PE/EA = 5/1) = 0.54

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 1H), 7.25 – 7.15 (m, 9H), 7.06-7.01 (m, 2H), 5.98 (ddd, *J* = 17.2, 10.4, 6.9 Hz, 1H), 5.59 (d, *J* = 6.9 Hz, 1H), 5.25 (d, *J* = 10.4 Hz, 1H), 5.14 (dt, J = 15.3, 1.4 Hz, 1H), 5.12 (dt, J = 17.2, 1.4 Hz, 1H), 4.57 (dt, *J* = 15.3, 6.9 Hz, 1H), 3.72 (dd, J = 6.9, 1.4 Hz, 1H), 2.44 (s, 3H), 0.98 – 0.90 (m, 2H), 0.76-0.69 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 142.9, 140.6, 138.6, 138.4, 134.6, 129.5, 129.4, 128.3, 128.2, 128.1, 127.7, 127.5, 126.3, 124.3, 119.1, 63.1, 46.9, 27.4, 21.6, 14.4, 14.4.

HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{28}H_{30}NO_2S^+$: 444.1992; found: 444.1991

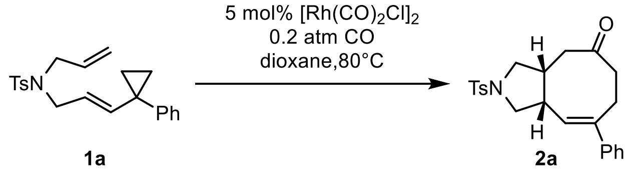
3. General procedure for [5+2+1] cycloaddition and product characterization



The catalyst $[Rh(CO)_2Cl]_2$ (5 mol% to ene-VCP) and substrates **1** (0.50-0.68 mmol scale) were added in glass flask and sealed, then displaced gas with 0.2 atm CO. The super-dried dioxane (0.05 M) was added and bubbled 0.2 atm CO for 5 min. The solution was heated to 80 ˚C in oil bath with stirring under a positive pressure of 0.2 atm CO. TLC indicated the absence of the starting material and the resulting solution was cooled to room temperature. Solvent was evaporated and the residue was purified by flash column chromatography on silica gel (eluted with petroleum ether/ethyl acetate) to afford cycloadduct **2**.

2a, **2la, 2lb**, **2n** are known compounds[21] and the syntheses in this paper are summarized:

(1)

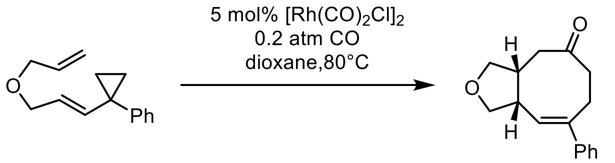


1a **2a**

Previous	0.30 mmol	10 h	92%
This work	0.68 mmol	20.5 h	63%

$[Rh(CO)_2Cl]_2$ (26.5 mg, 0.068 mmol), **1a** (256.6 mg, 0.68 mmol), dioxane (15 mL), **2a** (172.5 mg, 64%)
$[Rh(CO)_2Cl]_2$ (26.5 mg, 0.068 mmol), **1a** (256.6 mg, 0.68 mmol), dioxane (15 mL), **2a** (162.1 mg, 62%)
80 °C, 20.5 h, yellow solid, m.p. = 169-172 °C

(2)

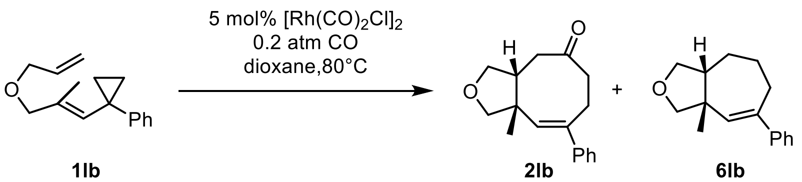


1la **2la**

Previous	0.40 mmol	16 h	73%
This work	0.50 mmol	36 h	55%

$[Rh(CO)_2Cl]_2$ (9.7 mg, 0.025 mmol), **1la** (107.2 mg, 0.50 mmol), dioxane (10 mL), **2la** (66.0 mg, 54%)
$[Rh(CO)_2Cl]_2$ (9.7 mg, 0.025 mmol), **1la** (107.2 mg, 0.50 mmol), dioxane (10 mL), **2la** (66.2 mg, 55%),
80 °C, 36 h, yellow oil

(3)

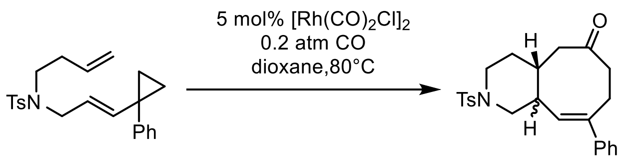


1lb **2lb** **6lb**

Previous	0.20 mmol	110 h	83%	11%
This work	0.60 mmol	110 h	58%	38%

$[Rh(CO)_2Cl]_2$ (11.7 mg, 0.03 mmol), **1lb** (137.0mg, 0.60 mmol), dioxane (12 mL), **2lb**(87.9 mg, 57%), **6lb** (53.5 mg, 39%),
$[Rh(CO)_2Cl]_2$ (11.7 mg, 0.03 mmol), **1lb** (137.0mg, 0.60 mmol), dioxane (12 mL), **2lb**(90.3 mg, 59%), **6lb** (49.4 mg, 36%);
80 °C, 110 h, **6lb**, yellow oil; **2lb**, pale yellow solid.m.p. = 91-93 °C TLC Rf (PE/EA = 3/1) = 0.19 for **2lb**, 0.82 for **6lb.**

(4)



1n **2n**

Previous	0.24 mmol	30 h	90% trans:cis=5:1
This work	0.63 mmol	20.5 h	66% trans:cis=7:1

$[Rh(CO)_2Cl]_2$ (12.2 mg, 0.03 mmol), **1n** (242.1 mg, 0.63 mmol), dioxane (13 mL), **2n** (166.2 mg, 64%),
$[Rh(CO)_2Cl]_2$ (12.2 mg, 0.03 mmol), **1n** (242.1 mg, 0.63 mmol), dioxane (13 mL), **2n** (173.7 mg, 67%),
80 °C, 20.5 h, white solid (trans : cis = 7:1), m.p.= 147-152 °C

Description about the used catalyst and reaction conditions:

1. We found that the quality of catalyst $[Rh(CO)_2Cl]_2$ varied, depending on the vendors (different batches for the same vendor could also be different) and this affected reaction yields. For example, for substrate **1a** in 0.30 mmol, the yields of its [5+2+1] reaction were 49%, 35% with ACROS and Bidepharm's catalysts; for substrate **1la** in 0.40 mmol, the yields of its [5+2+1] reaction were 59%, 52%, 43% with STREM, ACROS and ALDRICH's catalysts; for substrate **1n** in 0.24 mmol, the

NMR yields of its [5+2+1] reaction were 68% and 53% with ACROS and Bidepharm's catalysts. Besides, for substrate **1b-1e** in 0.6 mmol, different batches of ACROS's catalysts gave nearly 20% difference in yields. For example, we had some active catalysts of $[Rh(CO)_2Cl]_2$ bought a few year ago and the catalyzed [5+2+1] reaction yields: for substrate **1b** (85% yield), **1c** (90% yield), **1d** (91% yield), **1e** (73%), all in 0.6 mmol scale. Unfortunately, we did not have enough this active catalyst for all reactions. Therefore, to keep consistency and to compare the relative reactivity of all substrates, we used the same catalyst (with moderate activity) from a vendor to do all the [5+2+1] reaction (in this case, all reactions have been repeated two times).

2. We checked that whether keeping the catalyst in the glovebox or not was critical. We found that the reaction outcomes were the same (for substrate **1la** in 0.40 mmol, the yields of its [5+2+1] reaction were 55% and 52% for catalysts stored outside or in glovebox). Therefore, all reactions were carried out outside glovebox and the catalyst used was not stored in the glovebox.

3. We found that $[Rh(COD)Cl]_2$ and CO could replace $[Rh(CO)_2Cl]_2$ and CO in this [5+2+1] reaction and both gave similar yields (for example, $[Rh(COD)Cl]_2$ gave 53% yield of [5+2+1] reaction for substrate **1la** in 0.40 mmol, compared to 55% yield for the traditional catalyst of $[Rh(CO)_2Cl]_2$). Thus, if the quality of $[Rh(CO)_2Cl]_2$ is not satisfied, $[Rh (COD)Cl]_2$ could also be used in this reaction. For example, for substrate **1n** in 0.24 mmol, the NMR yields of its [5+2+1] reaction were 68% and 53% with present ACROS and Bidepharm's catalyst of $[Rh(CO)_2Cl]_2$, but this can be increased to 76% yield by using $[Rh(COD)Cl]_2$.

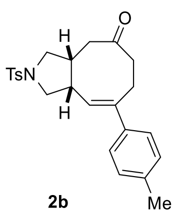
4. For substrate **1la**, the [5+2+1] reaction gave **2la**, which was sometimes accompanied by an unidentified byproduct (we speculated that this was an alkene isomerization of **2la**, as revealed by crude ^{1}H, ^{13}C NMR and HRMS with some impurities), depending on the used catalyst of $[Rh(CO)_2Cl]_2$. If using $[Rh(COD)Cl]_2$ and CO, the yield of the byproduct reduced a lot (<10%).

5. It should be noted that for [5+2+1] reaction, which is a multiphase reaction, adequately stirring and large liquid-gas surface (reactor) are preferred. Otherwise, the interphase mass transfer rate of CO from gas phase to solution will be inefficient, which inhibits [5+2+1] reaction but affords [5+2] product instead.

6. The pressure of CO gas was estimated as 0.2 atm in the balloon filled by mixed gas of CO and N_2 (ratio is 1/4). If the balloon is tight, the CO pressure could be a little bit higher than 0.2 atm. This difference of CO pressure is usually tolerated, but for some substrates, the reaction yields could be different.

7. A large scale of the [5+2+1] reaction of **1a** (in 1.8 mmol, see part 5 of the Supporting Information) gave 71% yield, higher than that of 63% from a 0.68 mmol scale by using the same catalyst (both of them used 5 mol % catalyst). We hypothesized that in large scale, the relative ratio of active catalyst over substrate could become higher because larger amount of $[Rh(CO)_2Cl]_2$ catalyst was used.

Physical data for new [5+2+1] products from Ene-VCP substrates



2b

average of the yields: 55%

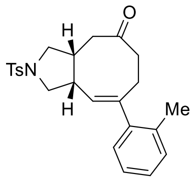
[Rh(CO)$_2$Cl]$_2$ (11.2 mg, 0.029 mmol), **1b** (219.4 mg, 0.575 mmol), dioxane (12 mL), **2b** (125.9 mg, 53%), 80˚C, 16 h;

[Rh(CO)$_2$Cl]$_2$ (11.2 mg, 0.029 mmol), **1b** (224.1 mg, 0.575 mmol), dioxane (12 mL), **2b** (137.9 mg, 57%), 80˚C, 16 h.

Pale yellow solid, m.p. = 194-197 ˚C. TLC: R_f (PE/EA = 3/1) = 0.36

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.16-7.13 (m, 4H), 5.31 (d, *J* = 9.1 Hz, 1H), 3.50 (dd, *J* = 9.9, 6.7 Hz, 2H), 3.39 (dd, *J* = 10.2, 5.2 Hz, 1H), 2.88-2.82 (m, 2H), 2.77 (ddd, *J* = 13.7, 5.7, 2.9 Hz, 1H), 2.67 – 2.55 (m, 2H), 2.51 (dd, *J* = 14, 1.9 Hz, 1H), 2.44 (s, 3H), 2.37 (s, 3H), 2.35 – 2.32 (m, 1H), 2.32-2.23 (m, 2H), . ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.5, 143.7, 141.3, 138.2, 137.6, 133.6, 129.9, 129.2, 127.5, 125.6, 125.3, 53.8, 51.4, 46.5, 41.5, 40.4, 39.3, 27.1, 21.6, 21.1.

HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{24}H_{28}NO_3S^+$: 410.1784; found: 410.1778



2c

average of the yields: 70%

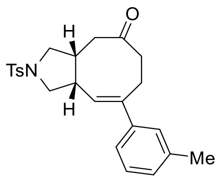
[Rh(CO)$_2$Cl]$_2$ (11.7 mg, 0.03 mmol), **1c** (228.9 mg, 0.6 mmol), dioxane (12 mL), **2c** (172.2 mg, 70%), 80˚C, 12.5 h;

[Rh(CO)$_2$Cl]$_2$ (11.7 mg, 0.03 mmol), **1c** (228.9 mg, 0.6 mmol), dioxane (12 mL), **2c** (170.8 mg, 70%), 80˚C, 12.5 h.

White foam, TLC R_f (PE/EA = 5/1) = 0.13

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.68 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.24-7.10 (m, 3H), 7.00 (d, *J* = 7.3 Hz, 1H), 4.73 (d, *J* = 8.8 Hz, 1H), 3.50 (dd, *J* = 9.8, 7.6 Hz, 1H), 3.42-3.32 (m, 2H), 2.90-2.79 (m, 2H), 2.60-2.46 (m, 3H), 2.44-2.29 (m, 4H), 2.27 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.5, 143.8, 143.3, 143.1, 134.6, 133.5, 130.4, 129.7, 128.7, 127.7, 127.5, 127.3, 125.7, 53.7, 51.4, 45.5, 41.6, 39.9, 39.2, 29.0, 21.4, 20.0.

HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{24}H_{28}NO_3S^+$: 410.1784; found: 410.1784

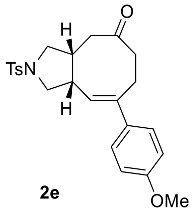


2d

average of the yields: 68%

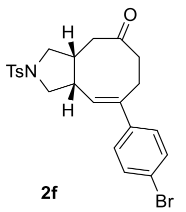
[Rh(CO)$_2$Cl]$_2$ (11.7 mg, 0.03 mmol), **1d** (228.9 mg, 0.6 mmol), dioxane (12 mL), **2d** (161.1 mg, 66%), 80˚C, 11 h;

$[Rh(CO)_2Cl]_2$ (11.7 mg, 0.03 mmol), **1d** (228.9 mg, 0.6 mmol), dioxane (12 mL), **2d** (171.1 mg, 70%), 80˚C, 11 h.
Yellow solid, m.p. = 153-158 ˚C. TLC R_f (PE/EA = 5/1) = 0.1
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.23 (dd, *J* = 8.0, 7.9 Hz, 1H), 7.15-7.09 (m, 2H), 7.04 (d, *J* = 7.9 Hz, 1H), 5.38 (d, *J* = 9.1 Hz, 1H), 3.52 (d, *J* = 9.9 Hz, 1H), 3.49 (dd, *J* = 9.9, 5.2 Hz, 1H), 3.37 (dd, *J* = 9.9, 5.2 Hz, 1H), 2.91 – 2.81 (m, 2H), 2.78 (ddd, *J* = 13.7, 5.8, 2.8 Hz, 1H), 2.69-2.57 (m, 2H), 2.57 – 2.46 (m, 1H), 2.42 (s, 3H), 2.38 (s, 3H), 2.35 – 2.23 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.5, 143.7, 141.7, 141.3, 138.2, 133.6, 129.8, 128.5, 128.5, 127.5, 126.6, 126.0, 122.9, 53.7, 51.3, 46.6, 41.5, 40.4, 39.2, 27.3, 21.6, 21.6.
HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{24}H_{28}NO_3S^+$: 410.1784; found: 410.1775



2e

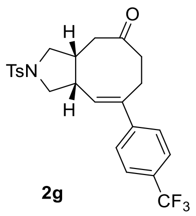
average of the yields: 52%
$[Rh(CO)_2Cl]_2$ (8.6 mg, 0.03 mmol), **1e** (174.6 mg, 0.44 mmol), dioxane (9 mL), **2e** (92.7 mg, 50%), 80˚C, 12 h;
$[Rh(CO)_2Cl]_2$ (8.5 mg, 0.03 mmol), **1e** (174.6 mg, 0.44 mmol), dioxane (9 mL), **2e** (99.7 mg, 53%); 80˚C, 12 h.
White solid, m.p. = 238-240 ˚C. TLC R_f (PE/EA = 1/1) = 0.55
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 5.25 (d, *J* = 8.9 Hz, 1H), 3.83 (s, 3H), 3.55-3.45 (m, 2H), 3.39 (dd, *J* = 10.0, 5.0 Hz, 1H), 2.90-2.80 (m, 2H), 2.80 – 2.70 (m, 1H), 2.66 – 2.48 (m, 3H), 2.45 (s, 3H), 2.37-2.23 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.5, 159.3, 143.7, 140.8, 133.6, 133.5, 129.9, 127.5, 126.9, 124.4, 113.9, 55.4, 53.8, 51.4, 46.4, 41.5, 40.4, 39.3, 27.1, 21.6.
HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{24}H_{28}NO_4S^+$: 426.1733; found: 426.1728



2f

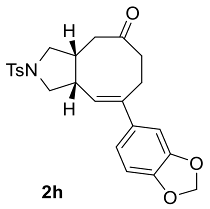
average of the yields: 71%
$[Rh(CO)_2Cl]_2$ (11.7 mg, 0.03 mmol), **1f** (267.8 mg, 0.6 mmol), dioxane (12 mL), **2f** (196.7 mg, 69%), 80˚C, 25 h;
$[Rh(CO)_2Cl]_2$ (11.7 mg, 0.03 mmol), **1f** (267.8 mg, 0.6 mmol), dioxane (12 mL), **2f** (206.2 mg, 72%), 80˚C, 25 h.
White solid, m.p. = 185-187 ˚C. TLC R_f (PE/EA = 3/1) = 0.23

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.1 Hz, 2H), 7.45 (dd, J = 8.8, 2.2 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 8.8, 2H), 5.33 (d, J = 9.1 Hz, 1H), 3.55-3.45 (m, 2H), 3.37 (dd, J = 10.2, 5.1 Hz, 1H), 2.90 – 2.77 (m, 2H), 2.75 – 2.67 (m, 1H), 2.62-2.55 (m, 2H), 2.55 – 2.47 (m, 1H), 2.44 (s, 3H), 2.37-2.25 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.0, 143.8, 140.6, 140.1, 133.6, 131.6, 129.9, 127.5, 127.4, 126.9, 121.7, 53.6, 51.3, 46.4, 41.5, 40.5, 39.2, 27.0, 21.6.
HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{23}H_{25}BrNO_3S^+$: 474.0733; found: 474.0720



2g

average of the yields: 77%
$[Rh(CO)_2Cl]_2$ (11.7 mg, 0.03 mmol), **1g** (261.3 mg, 0.6 mmol), dioxane (12 mL), **2g** (215.5 mg, 77%), 80˚C, 23.5 h;
$[Rh(CO)_2Cl]_2$ (11.7 mg, 0.03 mmol), **1g** (261.3 mg, 0.6 mmol), dioxane (12 mL), **2g** (212.5 mg, 76%), 80˚C, 23.5 h;
White solid, m.p. = 198-200 ˚C. TLC R_f (PE/EA = 5/1) = 0.1
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.2 Hz, 2H), 7.58 (d, J = 8.2 Hz, 2H), 7.39-7.31 (m, 4H), 5.38 (d, J = 9.0 Hz, 1H), 3.57 – 3.46 (m, 2H), 3.39 (dd, J = 10.3, 5.0 Hz, 1H), 2.91 – 2.81 (m, 2H), 2.80 – 2.71 (m, 1H), 2.66 – 2.50 (m, 3H), 2.42 (s, 3H), 2.38-2.29 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.8, 144.8, 143.8, 140.6, 133.5, 129.9, 129.6 (q, J = 32.5 Hz), 128.5, 127.5, 126.1, 125.5 (q, J = 3.7 Hz), 124.1 (q, J = 271.9 Hz), 53.6, 51.3, 46.4, 41.5, 40.5, 39.2, 27.1, 21.5.
HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{24}H_{25}F_3NO_3S^+$: 464.1502; found: 464.1512

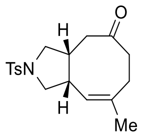


2h

average of the yields: 74%
$[Rh(CO)_2Cl]_2$ (11.3 mg, 0.03 mmol), **1h** (238.9 mg, 0.58 mmol), dioxane (12 mL), **2h** (188.8 mg, 74%), 80˚C, 24 h;
$[Rh(CO)_2Cl]_2$ (11.3 mg, 0.03 mmol), **1h** (238.9 mg, 0.58 mmol), dioxane (12 mL), **2h** (186.9 mg, 73%), 80˚C, 24 h.
Light yellow solid, m.p. = 167-170 ˚C. TLC R_f (PE/EA = 3/1) = 0.2
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 6.77 (d, J = 8.1 Hz, 1H), 6.73 (dd, J = 8.1, 1.6 Hz, 1H), 6.68 (d, J = 1.6 Hz, 1H), 5.99 (s, 2H), 5.15 (d, J = 9.1 Hz, 1H), 3.51 (dd, J = 9.9, 7.2 Hz, 1H), 3.48 (d, J = 10.3 Hz, 1H), 3.40 (dd, J = 10.3, 5.1 Hz, 1H), 2.88-

2.77 (m, 2H), 2.75 – 2.66 (m, 1H), 2.64 – 2.46 (m, 3H), 2.44 (s, 3H), 2.38 – 2.23 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.3, 147.9, 147.3, 143.8, 141.1, 135.4, 133.5, 129.9, 127.5, 125.0, 119.3, 108.1, 106.4, 101.3, 53.8, 51.4, 46.4, 41.5, 40.4, 39.3, 27.3, 21.5.

HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{24}H_{26}NO_5S^+$: 440.1526; found: 440.1526



2ia

average of the yields: 60%

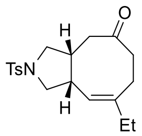
[Rh(CO)$_2$Cl]$_2$ (11.7 mg, 0.03 mmol), **1ia** (183.3 mg, 0.6 mmol), dioxane (12 mL), **2ia** (124.0 mg, 62%), 80˚C, 12 h;

[Rh(CO)$_2$Cl]$_2$ (11.7 mg, 0.03 mmol), **1ia** (183.3 mg, 0.6 mmol), dioxane (12 mL), **2ia** (116.0mg, 58%), 80˚C, 12 h.

Light yellow oil, TLC R_f (PE/EA = 3/1) = 0.29

^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 4.81 (d, *J* = 8.5 Hz, 1H), 3.39 (dd, J = 15.4, 9.4 Hz, 2H), 3.24 (dd, J = 9.8, 5.2 Hz, 1H), 2.78 (t, J = 10.3 Hz, 1H), 2.65 (d, J = 7.3 Hz, 1H), 2.55 – 2.37 (m, 4H), 2.27 (q, J = 16.0, 13.8 Hz, 2H), 2.21 – 2.09 (m, 2H), 2.03 (dd, J = 9.4, 4.4 Hz, 1H), 1.77 (s, 2H). ^{13}C NMR (101 MHz, CDCl3) δ 211.9, 143.7, 138.4, 133.8, 129.9, 127.6, 123.5, 53.8, 51.3, 45.4, 41.5, 39.7, 39.1, 28.9, 24.4, 21.7.

HRMS (ESI−FTICR, m/z): $[M + Na]^+$ calculated for $C_{18}H_{23}NNaO_3S^+$: 356.1291; found: 356.1293



2ib

average of the yields: 55%

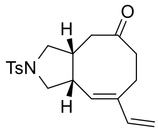
[Rh(CO)$_2$Cl]$_2$ (11.7 mg, 0.03 mmol), **1ib** (191.7 mg, 0.6 mmol), dioxane (12 mL), **2ib** (119.0 mg, 57%), 80˚C, 14 h;

[Rh(CO)$_2$Cl]$_2$ (11.7 mg, 0.03 mmol), **1ib** (191.7 mg, 0.6 mmol), dioxane (12 mL), **2ib** (109.2 mg, 52%), 80˚C, 14 h.

Light yellow oil, TLC R_f (PE/EA = 5/1) = 0.12

^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 7.7 Hz, 2H), 4.73 (d, *J* = 8.6 Hz, 1H), 3.41 (dd, *J* = 20.1, 9.8 Hz, 2H), 3.29 (dd, *J* = 9.8, 5.2 Hz, 1H), 2.78 (t, *J* = 9.9 Hz, 1H), 2.67 (d, *J* = 6.9 Hz, 1H), 2.54-2.40 (m, 2H) 2.45 (s, 3H), 2.32 – 2.15 (m, 4H), 2.15 – 1.98 (m, 3H), 0.95 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.0, 143.9, 143.8, 133.8, 129.9, 127.6, 121.6, 53.9, 51.4, 46.2, 41.5, 39.6, 39.0, 30.9, 27.9, 21.6, 12.6.

HRMS (ESI−FTICR, m/z): $[M + Na]^+$ calculated for $C_{19}H_{25}NNaO_3S^+$: 370.1447; found: 370.1449



2ic

average of the yields: 68%

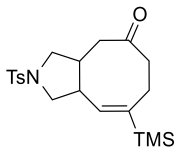
[Rh(CO)$_2$Cl]$_2$ (11.7 mg, 0.03 mmol), **1ic** (190.5 mg, 0.6 mmol), dioxane (12 mL), **2ic** (138.4 mg, 67%), 80 ˚C, 21 h;

[Rh(CO)$_2$Cl]$_2$ (11.7 mg, 0.03 mmol), **1ic** (190.5 mg, 0.6 mmol), dioxane (12 mL), **2ic** (141.0 mg, 68%), 80 ˚C, 21 h.

Light yellow oil, TLC R_f (PE/EA = 5/1) = 0.12

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 6.19 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.20 (d, *J* = 17.4 Hz, 1H), 5.13 (d, *J* = 9.1 Hz, 1H), 5.09 (d, *J* = 10.8 Hz, 1H), 3.49 – 3.39 (m, 2H), 3.29 (dd, *J* = 9.9, 5.0 Hz, 1H), 2.88 – 2.76 (m, 2H), 2.68 – 2.58 (m, 1H), 2.52 – 2.48 (m, 2H), 2.46 (s, 3H), 2.31 – 2.09 (m, 4H). ^{13}C NMR (101 MHz, CDCl3) δ 211.6, 143.9, 140.2, 138.3, 133.7, 130.3, 129.9, 127.6, 112.6, 53.6, 51.3, 45.9, 41.5, 40.0, 39.5, 22.3, 21.7.

HRMS (ESI−FTICR, m/z): $[M + Na]^+$ calculated for $C_{19}H_{23}NNaO_3S^+$: 368.1291; found: 368.1293



2id

average of the yields: 31%

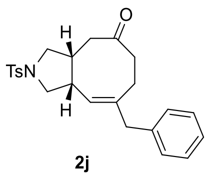
[Rh(CO)$_2$Cl]$_2$ (11.7 mg, 0.03 mmol), **1id** (218.2 mg, 0.6 mmol), dioxane (12 mL), **2id** (68.3 mg, 29%); 80 ˚C, 23 h;

[Rh(CO)$_2$Cl]$_2$ (11.7 mg, 0.03 mmol), **1id** (217.8 mg, 0.6 mmol), dioxane (12 mL), **2id** (78.3 mg, 33%); 80 ˚C, 23 h.

White solid, m.p. =168.2-169.8 ˚C. TLC R_f (PE/EA = 3/1) = 0.47

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 5.32 (dd, *J* = 8.6, 1.5 Hz, 1H), 3.50 – 3.32 (m, 3H), 2.87–2.63 (m, 3H), 2.46-2.44 (m, 1H), 2.45 (s, 3H), 2.40-2.33 (m, 2H), 2.23-2.18 (m, 3H), 0.04 (s, 9H). 13C NMR (101 MHz, CDCl3) δ 212.0, 144.7, 143.9, 137.8, 133.8, 130.0, 127.6, 53.5, 51.4, 46.8, 41.3, 39.8, 38.7, 25.5, 21.7, -1.6.

HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{20}H_{30}NO_3SSi^+$: 392.1710; found: 392.1708



2j

average of the yields: 84%

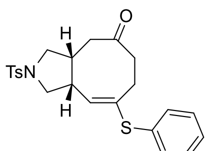
$[Rh(CO)_2Cl]_2$ (19.4 mg, 0.065 mmol), **1j** (190.8 mg, 0.5 mmol), dioxane (10 mL), **2j** (176.3 mg, 86%), 80 ˚C,48 h;

$[Rh(CO)_2Cl]_2$ (19.4 mg, 0.065 mmol), **1j** (190.8 mg, 0.5 mmol), dioxane (10 mL), **2j** (165.7 mg, 81%); 80 ˚C,48 h.

White solid, m.p. = 129-134 ˚C. TLC R_f (PE/EA = 3/1) = 0.24

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.30 (dd, J = 7.2, 7.0 Hz, 2H), 7.25 – 7.19 (m, 1H), 7.16 (d, *J* = 7.2 Hz, 2H), 4.87 (d, *J* = 8.7 Hz, 1H), 3.48 – 3.22 (m, 5H), 2.80 (t, *J* = 10.1 Hz, 1H), 2.66 (dt, *J* = 9.3, 5.4 Hz, 1H), 2.42 (s, 3H), 2.28 – 2.04 (m, 7H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 211.7, 144.4, 142.0, 139.8, 134.2, 130.3, 129.3, 129.0, 128.0, 127.0, 125.5, 54.3, 51.9, 46.3, 45.6, 41.6, 40.1, 39.6, 27.3, 21.8.

HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{24}H_{28}NO_3S^+$: 410.1784; found: 410.1774



2k

average of the yields: 41%

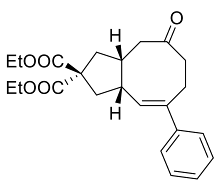
$[Rh(CO)_2Cl]_2$ (11.7 mg, 0.03 mmol), **1k** (239.7 mg, 0.6 mmol), dioxane(12 mL), **2k** (111.6 mg, 43%), 80 ˚C, 72 h;

$[Rh(CO)_2Cl]_2$ (11.7 mg, 0.03 mmol), **1k** (239.7 mg, 0.6 mmol), dioxane(12 mL), **2k** (98.5 mg, 38%), 80 ˚C, 72 h.

Orange solid, m.p. = 168-170 ˚C. TLC R_f (PE/EA = 5/1) = 0.1

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.28 (m, 7H), 5.36 (d, *J* = 9.0 Hz, 1H), 3.45 – 3.35 (m, 2H), 3.28 (dd, *J* = 10.1, 5.3 Hz, 1H), 2.81 (dt, *J* = 9.0, 5.6 Hz, 1H), 2.77 – 2.69 (m, 1H), 2.69-2.63 (m, 1H), 2.43 (s, 3H), 2.42 – 2.12 (m, 6H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 211.0, 144.5, 137.5, 134.2, 133.9, 132.2, 131.2, 130.4, 129.8, 128.2, 127.9, 53.7, 51.7, 46.3, 41.8, 41.3, 39.9, 29.0, 21.8.

HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{23}H_{26}NO_3S_2^+$: 428.1349; found: 428.1345



2m

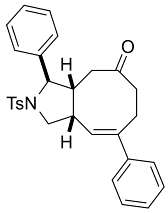
average of the yields: 70%

$[Rh(CO)_2Cl]_2$ (11.9 mg, 0.031 mmol), **1m** (218.6mg, 0.61 mmol), dioxane (13 mL), **2m** (164.1 mg, 70%), 80 ˚C, 17.5 h;

$[Rh(CO)_2Cl]_2$ (11.9 mg, 0.031 mmol), **1m** (218.6mg, 0.61 mmol), dioxane (13 mL), **2m** (163.2 mg, 69%), 80 ˚C, 17.5 h;

Yellow oil. TLC R_f (PE/EA = 3/1) = 0.48

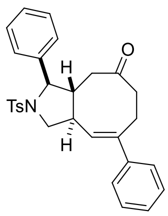
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H), 7.39-7.32 (m, 2H), 7.32 – 7.26 (m, 1H), 5.80 (d, J = 9.0 Hz, 1H), 4.21 (q, J = 7.1 Hz, 4H), 2.91 (dd, J = 7.6, 7.1Hz, 1H), 2.82 – 2.71 (m, 1H), 2.71 – 2.57 (m, 4H), 2.52 – 2.40 (m, 3H), 2.39 – 2.27 (m, 2H), 1.86 (dd, J = 12.8, 12.8 Hz, 1H), 1.26 (t, J = 7.1 Hz, 3H), 1.25 (t, J = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 212.5, 172.5, 172.3, 142.1, 140.4, 130.1, 128.5, 127.3, 125.9, 61.7, 59.2, 46.6, 43.6, 41.3, 41.0, 40.0, 39.9, 27.3, 14.1.
HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{23}H_{29}O_5^+$: 385.2010; found: 385.215



2oa

average of the yields: 40%

$[Rh(CO)_2Cl]_2$ (7.8 mg, 0.02 mmol), **1o** (191.5 mg, 0.43 mmol), dioxane (9 mL), **2oa** (82.9 mg, 41%), 80 ˚C, 24 h;
$[Rh(CO)_2Cl]_2$ (7.8 mg, 0.02 mmol), **1o** (191.5 mg, 0.43 mmol), dioxane (9 mL), **2oa** (77.7 mg, 38%), 80 ˚C, 24 h.
White solid, m.p. = 232-233 ˚C. TLC R_f (PE/EA = 3/1) = 0.31
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.64 (d, J = 8.2 Hz, 2H), 7.38 – 7.27 (m, 10H), 7.16-7.11 (m, 2H), 4.86 (d, J = 9.1 Hz, 1H), 3.96 (d, J = 9.6 Hz, 1H), 3.91 (dd, J = 11.4, 5.0 Hz, 1H), 3.74 (d, J = 11.4 Hz, 1H), 2.95-2.86 (m, 1H), 2.77 – 2.68(m, 1H), 2.63 – 2.46 (m, 3H), 2.38 (s, 3H), 2.39 – 2.29 (m, 2H), 2.03 – 1.97 (m, 1H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 210.9, 143.8, 141.7, 141.4, 141.2, 134.9, 129.8, 128.4, 128.4, 127.7, 127.5, 127.5, 126.8, 125.8, 125.8, 68.1, 54.6, 50.9, 46.6, 40.4, 40.2, 27.3, 21.4.
HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{29}H_{30}NO_3S^+$: 472.1941; found: 472.1939



2ob

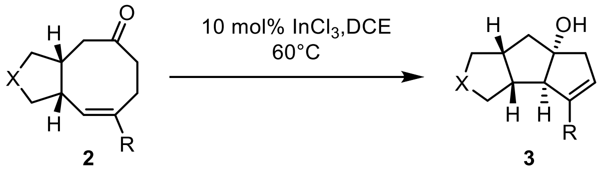
average of the yields: 32%

$[Rh(CO)_2Cl]_2$ (7.8 mg, 0.02 mmol), **1o** (191.5 mg, 0.43 mmol), dioxane (9 mL), **2ob** (60.7 mg, 30%), 80 ˚C, 14 h;
$[Rh(CO)_2Cl]_2$ (7.8 mg, 0.02 mmol), **1o** (191.5 mg, 0.43 mmol), dioxane (9 mL), **2ob** (69.0 mg, 34%), 80 ˚C, 14 h.
White solid, m.p. = 197-199 ˚C. TLC R_f (PE/EA = 3/1) = 0.25
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.57 (d, J = 8.2 Hz, 2H), 7.38 – 7.22 (m, 12H), 5.64 (d, J = 6.9 Hz, 1H), 4.12 (d, J = 9.7 Hz, 1H), 4.05 (dd, J = 11.2, 7.8 Hz, 1H), 3.51 (dd, J = 11.2, 11.2 Hz, 1H), 3.18-

3.07 (m, 1H), 2.78 – 2.62 (m, 4H), 2.44 (s, 3H), 2.41 – 2.29 (m, 1H), 2.12 (dd, J = 11.2, 2.9 Hz, 1H), 2.00-1.90 (m, 1H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 209.2, 143.7, 143.5, 140.5, 140.5, 135.3, 129.7, 128.5, 128.5, 127.9, 127.7, 127.4, 127.2, 125.9, 125.7, 69.8, 54.8, 53.0, 47.1, 44.2, 41.5, 26.0, 21.3.

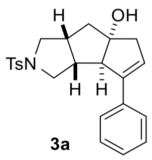
HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{29}H_{30}NO_3S^+$: 472.1941; found: 472.1940

4. General procedure for ene reaction and product characterization



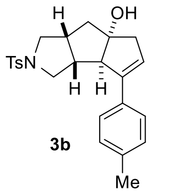
Substrate **2** (0.1 mmol) was added in the reaction flask (10 mL) which was then moved to glovebox, charged with $InCl_3$ (10 mol%, 0.01 mmol) and sealed with rubber stopper. After that, the flask was moved from the glovebox to the hood for the ene reaction. Super-dried DCE (2 mL) was added under argon to the flask in the hood and then the mixture was heated in the oil bath. Or the reaction flask was first charged with $InCl_3$ (10 mol%, 0.01 mmol) in glovebox and sealed. After removed from glovebox, the flask was added by substrate **2** (0.1 mmol) dissolved in the super-dried DCE (2 mL) under argon and the flask was then heated in oil bath. The reaction was monitored by TLC. The reaction mixture was finally cooled to room temperature and concentrated. The crude mixture was purified by flash column chromatography with silica gel to afford the pure product **3**. The yield reported for ene reaction is the average of two runs.

Physical data for new ene Reaction Product



average of the yields: 95%

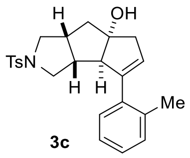
$InCl_3$ (2.1 mg, 0.01 mmol), **2a** (39.4 mg, 0.1 mmol), DCE (2 mL), **3a** (37.6 mg, 95%);
60˚C, 1.5 h;
$InCl_3$ (2.2 mg, 0.01 mmol), **2a** (39.5 mg, 0.1 mmol), DCE (2 mL), **3a** (37.5 mg, 95%);
60˚C, 1.5 h.
White solid, m.p. = 163-169 ˚C. TLC R_f (PE/EA = 3/1) = 0.1
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.27 (m, 4H), 7.26 – 7.20 (m, 1H), 5.97 (dd, *J* = 4.1, 2.5 Hz, 1H), 3.40 – 3.30 (m, 2H), 3.26 (dd, *J* = 9.8, 2.5 Hz, 1H), 3.14 (s, 1H), 3.07 (dd, *J* = 9.8, 7.3 Hz, 1H), 2.72 – 2.61 (m, 2H), 2.62-2.52 (m, 1H), 2.42 (s, 3H), 2.40 – 2.32 (m, 1H), 2.06 (dd, *J* = 13.3, 7.5 Hz, 1H), 1.72 (dd, *J* = 13.3, 7.9 Hz, 1H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 143.9, 143.6, 135.5, 132.5, 129.6, 128.5, 127.8, 127.2, 125.9, 123.7, 90.7, 64.0, 54.5, 53.3, 47.4, 47.4, 44.9, 42.8, 21.3.
HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{23}H_{26}NO_3S^+$: 396.1628; found: 396.1621



3b

average of the yields: 99%

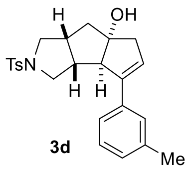
$InCl_3$ (2.2 mg, 0.01 mmol), **2b** (40.7 mg, 0.1 mmol), DCE (2 mL), **3b** (40.6 mg, 99%); 60˚C, 1 h;
$InCl_3$ (2.3 mg, 0.01 mmol), **2b** (40.9 mg, 0.1 mmol), DCE (2 mL), **3b** (40.9 mg, 100%); 60˚C, 1 h.
White solid, m.p. = 153-156 ˚C. TLC R_f (PE/EA = 3/1) = 0.13
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 8.1 Hz, 2H), 5.89 (dd, J = 4.2, 2.6 Hz, 1H), 3.36 (dd, J = 6.9, 3.4 Hz, 2H), 3.30 (dd, J = 9.7, 2.3 Hz, 1H), 3.14 (s, 1H), 3.08 (dd, J = 9.7, 7.4 Hz, 1H), 2.69-2.64 (m, 2H), 2.63 – 2.53 (m, 1H), 2.43 (s, 3H), 2.42 – 2.36 (m, 1H), 2.34 (s, 3H), 2.08 (dd, J = 13.3, 7.5 Hz, 1H), 1.78 (dd, J = 13.3, 7.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 143.6, 137.2, 132.6, 132.6, 129.7, 129.3, 127.9, 125.8, 122.6, 90.8, 64.3, 54.5, 53.4, 47.3, 47.3, 45.0, 42.7, 21.6, 21.2.
HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{24}H_{28}NO_3S^+$: 410.1784; found: 410.1775



3c

average of the yields: 90%

$InCl_3$ (2.2 mg, 0.01 mmol), **2c** (41.1mg, 0.1 mmol), DCE (2 mL), **3c** (36.5 mg, 89%); 60˚C, 4 h;
$InCl_3$ (2.2 mg, 0.01 mmol), **2c** (41.1mg, 0.1 mmol), DCE (2 mL), **3c** (37.1 mg, 90%); 60˚C, 4 h.
Colorless oil, TLC R_f (PE/EA = 3/1) = 0.13
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.19-7.08 (m, 3H), 7.05 – 6.97 (m, 1H), 5.52 (dd, J = 4.6, 2.3 Hz, 1H), 3.30 (dd, J = 9.7, 2.5 Hz, 1H), 3.27-3.18 (m, 2H), 3.05-2.96 (m, 2H), 2.80 – 2.65 (m, 3H), 2.65 – 2.46 (m, 1H), 2.41 (s, 3H), 2.31 – 2.23 (m, 1H), 2.27 (s, 3H), 2.17 (dd, J = 13.8, 8.2 Hz, 1H), 1.85 (dd, J = 13.8, 5.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 143.9, 136.6, 135.8, 132.1, 130.6, 129.7, 128.5, 128.1, 127.2, 126.9, 125.7, 90.6, 67.2, 54.8, 54.3, 46.6, 46.2, 46.2, 42.9, 21.6, 21.0.
HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{24}H_{28}NO_3S^+$: 410.1784; found: 410.1793



3d

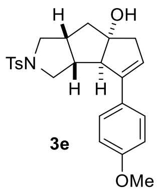
average of the yields: 83%

$InCl_3$ (2.2 mg, 0.01 mmol), **2d** (40.9mg, 0.1 mmol), DCE (2 mL), **3d** (34.2 mg, 84%), 60˚C, 2 h;
$InCl_3$ (2.2 mg, 0.01 mmol), **2d** (41.0mg, 0.1 mmol), DCE (2 mL), **3d** (33.6 mg, 82%), 60˚C, 2 h.

Colorless oil, TLC R_f (PE/EA = 3/1) = 0.07

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.23-7.15 (m, 1H), 7.10 (s, 1H), 7.08-6.99 (m, 2H), 5.92 (dd, *J* = 4.2, 2.5 Hz, 1H), 3.37 (d, *J* = 7.1 Hz, 2H), 3.29 (dd, *J* = 9.8, 2.2 Hz, 1H), 3.15 (s, 1H), 3.09 (dd, *J* = 9.8, 7.4 Hz, 1H), 2.68-2.64 (m, 2H), 2.59 – 2.51 (m, 1H), 2.47-2.37 (m, 1H), 2.42 (s, 3H), 2.34 (s, 3H), 2.07 (dd, *J* = 13.3, 7.5 Hz, 1H), 1.77 (dd, *J* = 13.3, 7.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 143.8, 138.2, 135.5, 132.6, 129.8, 128.5, 128.3, 128.0, 126.7, 123.6, 123.2, 90.8, 64.3, 54.6, 53.5, 47.4, 47.3, 45.1, 42.8, 21.7, 21.6.

HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{24}H_{28}NO_3S^+$: 410.1784; found: 410.1794



3e

average of the yields: 93%

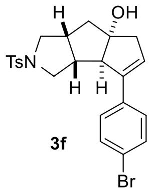
$InCl_3$ (2.3 mg, 0.01 mmol), **2e** (42.5mg, 0.1 mmol), DCE (2 mL), **3e** (39.1 mg, 92%), 60˚C, 1 h;

$InCl_3$ (2.2 mg, 0.01 mmol), **2e** (42.7mg, 0.1 mmol), DCE (2 mL), **3e** (38.0 mg, 93%), 60˚C, 1 h.

White solid, m.p. = 159-161 ˚C, TLC R_f (PE/EA = 3/1) = 0.1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.81 (dd, *J* = 4.2, 2.4 Hz, 1H), 3.81 (s, 3H), 3.37 (d, *J* = 7.0 Hz, 2H), 3.29 (dd, *J* = 9.8, 2.4 Hz, 1H), 3.14 – 3.06 (m, 2H), 2.73 – 2.62 (m, 2H), 2.63 – 2.52 (m, 1H), 2.43 (s, 3H), 2.46 – 2.36 (m, 1H), 2.08 (dd, *J* = 13.3, 7.5 Hz, 1H), 1.77 (dd, *J* = 13.3, 7.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 143.7, 143.1, 132.5, 129.7, 128.2, 127.9, 127.1, 121.4, 114.0, 90.8, 64.3, 55.3, 54.5, 53.3, 47.4, 47.3, 44.9, 42.7, 21.6.

HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{24}H_{28}NO_4S^+$: 426.1733; found: 426.1732



3f

average of the yields: 97%

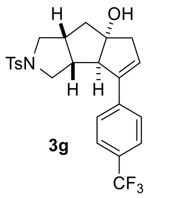
$InCl_3$ (2.2 mg, 0.01 mmol), **2f** (47.4mg, 0.1 mmol), DCE (2 mL), **3f** (45.0 mg, 95%), 60˚C, 2.5 h;

$InCl_3$ (2.2 mg, 0.01 mmol), **2f** (47.4mg, 0.1 mmol), DCE (2 mL), **3f** (47.2 mg, 99%), 60˚C, 2.5 h.

White solid, m.p. = 162-165 ˚C, TLC R_f (PE/EA = 3/1) = 0.1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 5.98-5.92 (m, 1H), 3.37 (dd, *J* = 9.5, 5.8 Hz, 1H), 3.34 – 3.24 (m, 2H), 3.13 (s, 1H), 3.06 (dd, *J* = 9.5, 7.6 Hz, 1H), 2.71-2.62 (m, 2H), 2.63-2.51 (m, 1H), 2.42 (s, 3H), 2.37 – 2.29 (m, 1H), 2.08 (dd, *J* = 13.3, 7.5 Hz, 1H), 1.80 (dd, *J* = 13.3, 7.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 142.8, 134.4, 132.4, 131.7, 129.7, 127.9, 127.5, 124.6, 121.2, 90.8, 64.1, 54.5, 53.4, 47.3, 47.1, 45.1, 42.8, 21.6.

HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{23}H_{25}BrNO_3S^+$: 474.0733; found: 474.0733



3g

average of the yields: 88%

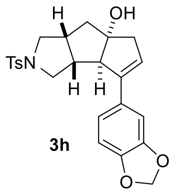
$InCl_3$ (2.2 mg, 0.01 mmol), **2g** (46.4mg, 0.1 mmol), DCE (2 mL), **3g** (40.7 mg, 88%); 60˚C, 13.5 h

$InCl_3$ (2.2 mg, 0.01 mmol), **2g** (46.4mg, 0.1 mmol), DCE (2 mL), **3g** (40.9 mg, 88%); 60˚C, 13.5 h

White foam, TLC R_f (PE/EA = 3/1) = 0.1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.5 Hz, 2H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 6.12-6.01 (m, 1H), 3.49 – 3.37 (m, 1H), 3.37-3.25 (m, 2H), 3.21 (s, 1H), 3.11-2.99 (m, 1H), 2.81-2.64 (s, 2H), 2.65 – 2.53 (m, 1H), 2.42 (s, 3H), 2.39 – 2.29 (m, 1H), 2.11 (dd, J = 13.0, 7.6 Hz, 1H), 1.84 (dd, *J* = 13.0, 7.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 142.3, 138.7, 132.1, 129.4, 128.7 (q, *J* = 32.2 Hz), 127.5, 126.4, 125.8, 125.2 (q, *J* = 3.5 Hz) 123.9 (q, *J* = 271.8 Hz), 90.4, 63.5, 54.0, 52.9, 47.2, 46.9, 44.7, 42.4, 21.2.

HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{24}H_{25}F_3NO_3S^+$: 464.1502; found: 464.1489



3h

average of the yields: 92%

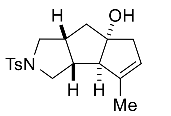
$InCl_3$ (2.2 mg, 0.01 mmol), **2h** (43.9mg, 0.1 mmol), DCE (2 mL), **3h** (40.6 mg, 92%); 60˚C, 1 h

$InCl_3$ (2.2 mg, 0.01 mmol), **2h** (43.4mg, 0.1 mmol), DCE (2 mL), **3h** (39.8 mg, 92%); 60˚C, 1 h

White solid, m.p. = 162-165 ˚C, TLC R_f (PE/EA = 3/1) = 0.08

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 6.81 (d, *J* = 1.7 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 5.96 (s, 2H), 5.81-5.77 (s, 1H), 3.35 (d, *J* = 6.9 Hz, 2H), 3.29 (dd, *J* = 9.8, 2.2 Hz, 1H), 3.14 – 3.05 (m, 2H), 2.72-2.62 (m, 2H), 2.62 – 2.53 (m, 1H), 2.44 (s, 3H), 2.42 – 2.37 (m, 1H), 2.08 (dd, *J* = 13.3, 7.5 Hz, 1H), 1.77 (dd, *J* = 13.3, 7.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 147.0, 143.8, 143.3, 132.5, 129.9, 129.7, 127.9, 122.2, 119.6, 108.2, 106.2, 101.1, 90.8, 64.5, 54.5, 53.4, 47.3, 47.2, 45.0, 42.7, 21.6.

HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{24}H_{26}NO_5S^+$: 440.1526; found: 440.1526

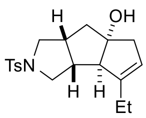


3ia

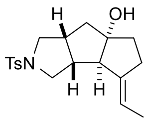
average of the yields: 72%

$InCl_3$ (2.2 mg, 0.01 mmol), **2ia** (33.3mg, 0.1 mmol), DCE (2 mL), **3ia** (24.1 mg,72%); 60˚C, 13 h

InCl3 (2.2 mg, 0.01 mmol), **2ia** (33.3mg, 0.1 mmol), DCE (2 mL), **3ia** (24.1 mg,72%); 60˚C, 13 h
Colorless oil, TLC R_f (PE/EA = 3/1) = 0.16
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 5.14 (s, 1H), 3.33 – 3.09 (m, 4H), 2.62 – 2.53 (m, 1H), 2.50 (s, 1H), 2.47 – 2.36 (m, 3H), 2.43 (s, 3H), 2.17 (s, 1H), 1.98 (dd, *J* = 13.4, 7.7 Hz, 1H), 1.68 (dd, *J* = 13.5, 6.6 Hz, 1H), 1.62 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 140.5, 132.7, 129.8, 128.0, 122.7, 91.2, 67.3, 54.5, 53.7, 47.1, 46.1, 45.6, 43.0, 21.7, 15.6.
HRMS (ESI−FTICR, m/z): [M + Na]$^+$ calculated for $C_{18}H_{23}NNaO_3S^+$: 356.1291; found: 356.1292



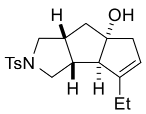
3ib (major product)



3ib' possible side product

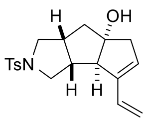
average of the yields: 79%

InCl3 (2.2 mg, 0.01 mmol), **2ib** (34.7mg, 0.1 mmol), DCE (2 mL), **3ib+3ib'** (26.8 mg, 77%); 60˚C, 12 h
InCl3 (2.2 mg, 0.01 mmol), **2ib** (34.7mg, 0.1 mmol), DCE (2 mL), **3ib+3ib'** (27.7 mg, 80%); 60˚C, 12 h
Yellow oil, TLC R_f (PE/EA = 3/1) = 0.21
The product from this reaction was **3ib**, but some impurities could not be separated from it and we speculated these sider products with about 1/3 of the total products could be alkene isomer and others. The following are the crude NMR data, read by comparing to those of **3ia**.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.7 Hz, 2H), 7.32 (d, *J* = 7.7 Hz, 2H), 5.15 (s, 1H), 3.35 – 3.06 (m, 4H), 2.58 – 2.53 (m, 2H), 2.48 – 2.39 (m, 2H), 2.42 (s, 3H), 2.28 – 2.19 (m, 1H), 2.04 – 1.86 (m, 3H), 1.73 – 1.61 (m, 1H), 1.00 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 146.6, 143.8, 132.6, 129.7, 128.0, 120.3, 91.1, 66.0, 54.5, 53.6, 46.8, 46.4, 45.4, 42.9, 22.9, 21.7, 12.0.
HRMS (ESI−FTICR, m/z): [M + Na]$^+$ calculated for $C_{19}H_{25}NNaO_3S^+$: 370.1447; found: 370.1448
The following NMR data was obtained by further plate TLC purification.



3ib (major product)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 5.18 – 5.15 (m, 1H), 3.33 – 3.11 (m, 4H), 2.63 – 2.36 (m, 5H), 2.43 (s, 3H), 2.08 – 1.80 (m, 4H), 1.69 (dd, *J* = 13.5, 6.6 Hz, 1H), 1.01 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 143.8, 132.8, 129.8, 128.1, 120.3, 91.2, 66.2, 54.6, 53.7, 46.8, 46.4, 45.5, 43.0, 22.9, 21.7, 12.1.
HRMS (ESI−FTICR, m/z): [M + H]$^+$ calculated for $C_{19}H_{26}NO_3S^+$: 348.1628; found: 348.1622



3ic

average of the yields: 17%

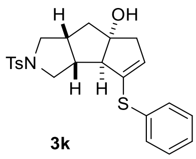
$InCl_3$ (4.4 mg, 0.02 mmol), **2ic** (34.5mg, 0.1 mmol), DCE (2 mL), **3ic** (6.0 mg, 17%); 80˚C, 6 h

$InCl_3$ (4.4 mg, 0.02 mmol), **2ic** (34.5mg, 0.1 mmol), DCE (2 mL), **3ic** (5.5 mg, 16%); 80˚C, 6 h

Light yellow oil, TLC R_f (PE/EA = 3/1) = 0.11

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 7.7 Hz, 2H), 7.34 (d, J = 7.7 Hz, 2H), 6.40 (dd, J = 17.5, 10.9 Hz, 1H), 5.54 (s, 1H), 5.07 (d, J = 10.7 Hz, 1H), 4.91 (d, J = 17.5 Hz, 1H), 3.40 (dd, J = 9.0, 9.0 Hz, 1H), 3.33 – 3.22 (m, 2H), 3.19 – 3.11 (m, 1H), 2.82 (s, 1H), 2.67 – 2.39 (m, 4H), 2.44 (s, 3H), 2.05 – 1.97 (m, 2H), 1.69 (dd, J = 12.7, 8.9 Hz, 1H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 144.5, 144.4, 133.3, 133.2, 130.2, 128.9, 128.3, 115.0, 91.4, 62.8, 54.9, 53.6, 48.0, 47.9, 45.1, 43.2, 21.8.

HRMS (ESI−FTICR, m/z): $[M + Na]^+$ calculated for $C_{19}H_{23}NNaO_3S^+$: 368.1291; found: 368.1289



3k

average of the yields: 44%

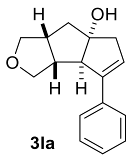
$InCl_3$ (2.2 mg, 0.01 mmol), **2k** (42.6mg, 0.1 mmol), DCE (2 mL), **3k** (17.3 mg, 41%); 60˚C, 2 h

$InCl_3$ (2.2 mg, 0.01 mmol), **2k** (41.2mg, 0.1 mmol), DCE (2 mL), **3k** (18.8 mg, 46%); 60˚C, 2 h

Yellow oil, TLC R_f (PE/EA = 3/1) = 0.13

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.43 – 7.25 (m, 7H), 5.53 (dd, *J* = 3.5, 1.9 Hz, 1H), 3.20 (dd, *J* = 9.8, 2.2 Hz, 1H), 2.99 (ddd, *J* = 19.1, 9.8, 7.4 Hz, 2H), 2.84 (dd, *J* = 9.8, 4.1 Hz, 1H), 2.66 (s, 1H), 2.63 – 2.55 (m, 2H), 2.56 – 2.52 (m, 2H), 2.43 (s, 3H), 2.02 (dd, *J* = 13.6, 7.7 Hz, 1H), 1.69 (dd, *J* = 13.6, 5.2 Hz, 1H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 143.9, 137.8, 132.8, 132.3, 131.9, 129.6, 129.1, 128.5, 127.9, 127.5, 90.7, 65.8, 54.3, 53.7, 46.8, 46.5, 45.6, 42.8, 21.3.

HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{23}H_{26}NO_3S_2^+$: 428.1349; found: 428.1342



3la

average of the yields: 90%

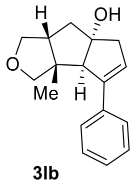
$InCl_3$ (4.4 mg, 0.02 mmol), **2la** (24.2mg, 0.1 mmol), DCE (2 mL), **3la** (21.5 mg, 88%); 80˚C, 13.5 h;

$InCl_3$ (4.4 mg, 0.02 mmol), **2la** (24.2mg, 0.1 mmol), DCE (2 mL), **3la** (22.3 mg, 92%); 80˚C, 13.5 h.

Colorless oil, TLC R_f (PE/EA = 3/1) = 0.05

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.39 – 7.28 (m, 4H), 7.28-7.18 (m, 1H), 5.97-5.89 (m, 1H), 3.97 (dd, *J* = 8.8, 3.0 Hz, 1H), 3.86 – 3.72 (m, 2H), 3.66-3.57 (m, 1H), 3.16 (s, 1H), 2.96 (s, 1H), 2.76-2.52 (m, 4H), 2.18 (dd, *J* = 13.6, 8.2 Hz, 1H), 1.88 (dd, *J* = 13.6, 4.5 Hz, 1H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 144.9, 136.0, 128.4, 127.1, 126.0, 124.0, 90.8, 76.1, 75.2, 65.7, 47.9, 46.0, 45.0, 44.5.

HRMS (ESI−FTICR, m/z): $[M + Na]^+$ calculated for $C_{16}H_{18}NaO_2^+$: 265.1199; found: 265.1200



3lb

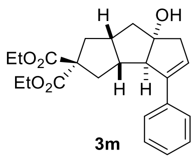
average of the yields: 93%

InCl3 (2.2 mg, 0.01 mmol), **2lb** (25.6mg, 0.1 mmol), DCE (2 mL), **3lb** (23.4 mg, 91%); 60˚C, 33 h;
InCl3 (2.2 mg, 0.01 mmol), **2lb** (25.6mg, 0.1 mmol), DCE (2 mL), **3lb** (24.2 mg, 95%); 60˚C, 33 h.

Yellow oil, TLC R_f (PE/EA = 3/1) = 0.09

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.34 (m, 2H), 7.33-7.30 (m, 2H), 7.25–7.20 (m, 1H), 6.13 (dd, *J* = 2.4 Hz, 2.4 Hz, 1H), 4.00 (d, *J* = 8.5 Hz, 1H), 3.96–3.89 (m, 1H), 3.81 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.61 (d, *J* = 8.5 Hz, 1H), 3.29 (s, 1H), 2.72 (dm, *J*=18.1 Hz, 1H), 2.61 (dd, *J* = 18.1, 3.0 Hz, 1H), 2.29–2.18 (m, 2H), 1.92–1.88 (m, 2H), 0.79 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 137.0, 128.5, 127.2, 125.9, 125.1, 92.3, 82.1, 73.6, 66.2, 53.1, 52.7, 47.3, 42.7, 22.2.

HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{17}H_{21}O_2{}^+$: 257.1536; found: 257.1534



3m

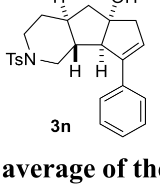
average of the yields: 92%

InCl3 (2.2 mg, 0.01 mmol), **2m** (40.0 mg, 0.1 mmol), DCE (2 mL), **3m** (36.6 mg, 92%); 60˚C, 1 h;
InCl3 (2.2 mg, 0.01 mmol), **2m** (39.4 mg, 0.1 mmol), DCE (2 mL), **3m** (36.6 mg, 92%); 60˚C, 1 h.

Yellow oil, TLC R_f (PE/EA = 3/1) = 0.22

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.1 Hz, 1H), 6.00-5.95 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.16 (s, 1H), 2.79 – 2.66 (m, 2H), 2.66-2.60 (m, 1H), 2.60 – 2.48 (m, 2H), 2.39-2.28 (m, 2H), 2.24-2.07 (m, 3H), 1.86 (dd, *J* = 13.0, 8.3 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 172.2, 144.5, 135.8, 128.6, 127.3, 126.0, 122.8, 92.3, 64.2, 62.5, 61.6, 61.5, 48.9, 48.1, 45.9, 43.3, 41.4, 39.6, 14.2, 14.1.

HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{23}H_{29}O_5{}^+$: 385.2010; found: 385.2009



3n

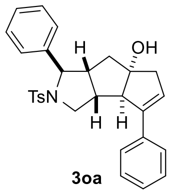
average of the yields: 93%

InCl3 (4.5 mg, 0.02 mmol), **2n** (41.0 mg, 0.1 mmol), DCE (2 mL), **3n** (38.1 mg, 93%); 80˚C, 4 h
InCl3 (4.5 mg, 0.02 mmol), **2n** (41.0 mg, 0.1 mmol), DCE (2 mL), **3n** (38.1 mg, 93%); 80˚C, 4 h

Pale yellow form, TLC R_f (PE/EA = 3/1) = 0.1

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.46 (d, *J* = 8.2Hz, 2H), 7.42-7.36 (m, 2H), 7.36-7.31 (m, 3H), 7.31-7.26 (m, 2H), 5.86 – 5.80 (m, 1H), 3.79 (ddd, *J* = 15.0, 10.7, 2.9 Hz, 2H), 2.95 (d, *J* = 9.8 Hz, 1H), 2.71 (ddd, J = 18.5, 2.4, 2.3 Hz, 1H), 2.61 (dd, J = 18.5, 2.4 Hz, 1H), 2.42 (s, 3H), 2.36 – 2.23 (m, 2H), 2.04 (dd, *J* = 12.6, 5.4 Hz, 1H), 1.84 – 1.68 (m, 2H), 1.63 – 1.46 (m, 1H), 1.36 (dd, *J* = 12.6, 12.6 Hz, 1H), 1.26 (qd, J = 12.3, 4.3 Hz, 1H), 1.09 (qd, *J* = 11.2, 4.0 Hz, 1H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 145.0, 144.7, 137.8, 135.7, 130.9, 129.7, 128.9, 128.6, 127.6, 124.9, 90.6, 64.5, 53.1, 51.9, 49.9, 48.2, 47.3, 44.9, 31.1, 22.5.

HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{24}H_{28}NO_3S^+$: 410.1784; found: 410.1783



3oa

average of the yields: 71%

$InCl_3$ (2.2 mg, 0.01 mmol), **2oa** (47.2mg, 0.1 mmol), DCE (2 mL), **3oa** (32.9 mg, 70%); 80˚C, 7 h

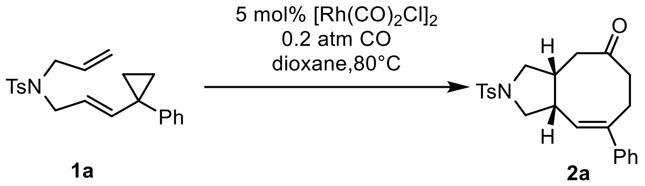
$InCl_3$ (2.2 mg, 0.01 mmol), **2oa** (47.2mg, 0.1 mmol), DCE (2 mL), **3oa** (34.2 mg, 72%); 80˚C, 7 h

White solid, m.p. = 198-200 ˚C, TLC R_f (PE/EA = 3/1) = 0.08

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.29 (m, 4H), 7.28-7.16 (m, 6H), 5.96 (dd, *J* = 3.8, 2.4 Hz, 1H), 4.68 – 4.61 (m, 1H), 4.07 (dd, *J* = 9.7, 8.7 Hz, 1H), 3.40 (dd, *J* = 9.5, 9.5 Hz, 1H), 3.10 (s, 1H), 2.66 – 2.53 (m, 3H), 2.45 (s, 3H), 2.40-2.31 (m, 1H), 2.04 (dd, *J* = 12.8, 6.8 Hz, 1H), 1.25 (dd, *J* = 12.1, 12.1 Hz, 1H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 143.9, 143.4, 142.2, 135.1, 134.2, 129.6, 128.5, 128.3, 127.6, 127.3, 127.0, 126.0, 125.8, 123.5, 89.5, 68.0, 62.1, 54.4, 52.9, 49.2, 45.7, 44.1, 21.3.

HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{29}H_{30}NO_3S^+$: 472.1941; found: 472.194

5. General procedure for [5+2+1] cycloaddition and ene reaction at 1-2 mmol scale.

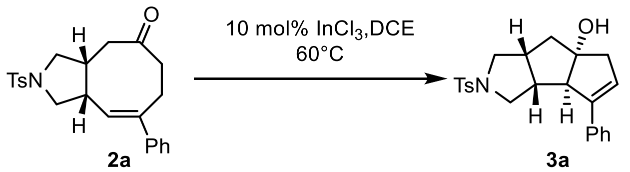


The catalyst $[Rh(CO)_2Cl]_2$ (5 mol% to ene-VCP) and substrates **1** (1.8 mmol scale) were added in glass flask(150 mL) and sealed, then displaced gas with 0.2 atm CO. The super-dried dioxane (0.05 M) was added and bubbled 0.2 atm CO for 5 min. The solution was heated to 80 ˚C in oil bath with stirring under a positive pressure of 0.2 atm CO. TLC indicated the absence of the starting material and the resulting solution was cooled to room temperature. Solvent was evaporated and the residue was purified by flash column chromatography on silica gel (eluted with petroleum ether/ethyl acetate) to afford cycloadduct **2**.

average of the yields: 71%

$[Rh(CO)_2Cl]_2$ (35.0mg, 0.09mmol), **1a** (661.5 mg, 1.8 mmol), dioxane (36 mL), **2a** (519.7 mg, 73%), 80 ˚C, 20.5 h.

$[Rh(CO)_2Cl]_2$ (35.0 mg, 0.029 mmol), **1a** (663.7 mg, 1.8 mmol), dioxane (36 mL), **2a** (490.6 mg, 69%), 80 ˚C, 20.5 h.



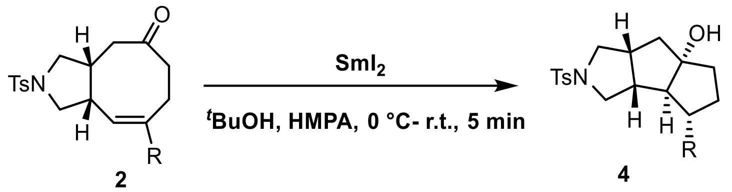
Substrate **2a** (1.0 mmol) was added in the reaction flask (100 mL) which was then moved to glovebox, charged with $InCl_3$ (10 mol%, 0.1 mmol) and sealed with rubber stopper. After that, the flask was moved from the glovebox to the hood for the ene reaction. Super-dried DCE (20 mL) was added under argon to the flask in the hood and then the mixture was heated in the oil bath. The reaction was monitored by TLC. The reaction mixture was finally cooled to room temperature and concentrated. The crude mixture was purified by flash column chromatography with silica gel to afford the pure product **3a**. The yield reported for ene reaction is the average of two runs.

average of the yields: 86%

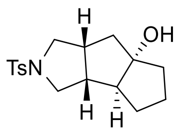
$InCl_3$ (22.1 mg, 0.1 mmol), **2a** (396.1 mg, 1.0 mmol), DCE (20 mL), **3a** (349.8 mg, 88%); 60˚C, 29 h;

$InCl_3$ (22.1 mg, 0.1 mmol), **2a** (397.6 mg, 1.0 mmol), DCE (20 mL), **3a** (330.5 mg, 83%); 60˚C, 29 h.

6. General procedure for SmI_2-mediated cyclization and product characterization



Substrate **2** (0.1 mmol) was added in 10 mL Schlenk tube and protected by Argon. HMPA (0.8 mL) and *t*-BuOH (0.2 mL) was added under Argon atmosphere. A solution of SmI_2 (0.1 M in THF, 2.5 equiv.) was added dropwise at 0 ˚C, and then the purple reaction mixture was stirred at room temperature. The reaction color faded and precipitation appeared after several minutes. Then the reaction system was quenched by water and turned to clear. After separation of the organic phase, the aqueous layer was extracted with Et_2O (5 mL) twice. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The crude product was purified by column chromatography on silica gel to afford pure product **4**.



4p

average of the yields: 48%

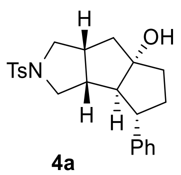
SmI_2 (0.1 M in THF, 2.5 mL), **2p**[21] (30.7 mg, 0.1 mmol), HMPA (0.8 mL) and *t*-BuOH (0.2 mL), **4p** (16.1 mg, 50%), 0˚C-r.t., 5 minutes;

SmI_2 (0.1 M in THF, 2.5 mL), **2p**[21] (30.9 mg, 0.1 mmol), HMPA (0.8 mL) and *t*-BuOH (0.2 mL), **4p** (14.3 mg, 46%), 0˚C-r.t., 5 minutes.

Colorless oil, TLC R_f (PE/EA = 1/1) = 0.50

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 3.30–3.10 (m, 4H), 2.67-2.57 (m, 1H), 2.44 (s, 3H), 2.27–2.17 (m, 1H), 2.06–1.95 (m, 3H), 1.77–1.67 (m, 4H), 1.64–1.57 (m, 2H), 1.31-1.25 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 132.9, 129.6, 127.9, 92.0, 57.4, 53.9, 53.6, 49.7, 44.9, 42.5, 40.7, 32.6, 24.9, 21.6.

HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{17}H_{24}NO_3S^+$: 322.1471; found: 322.1469



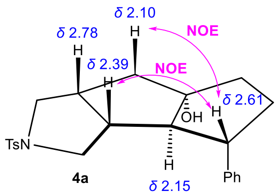
4a

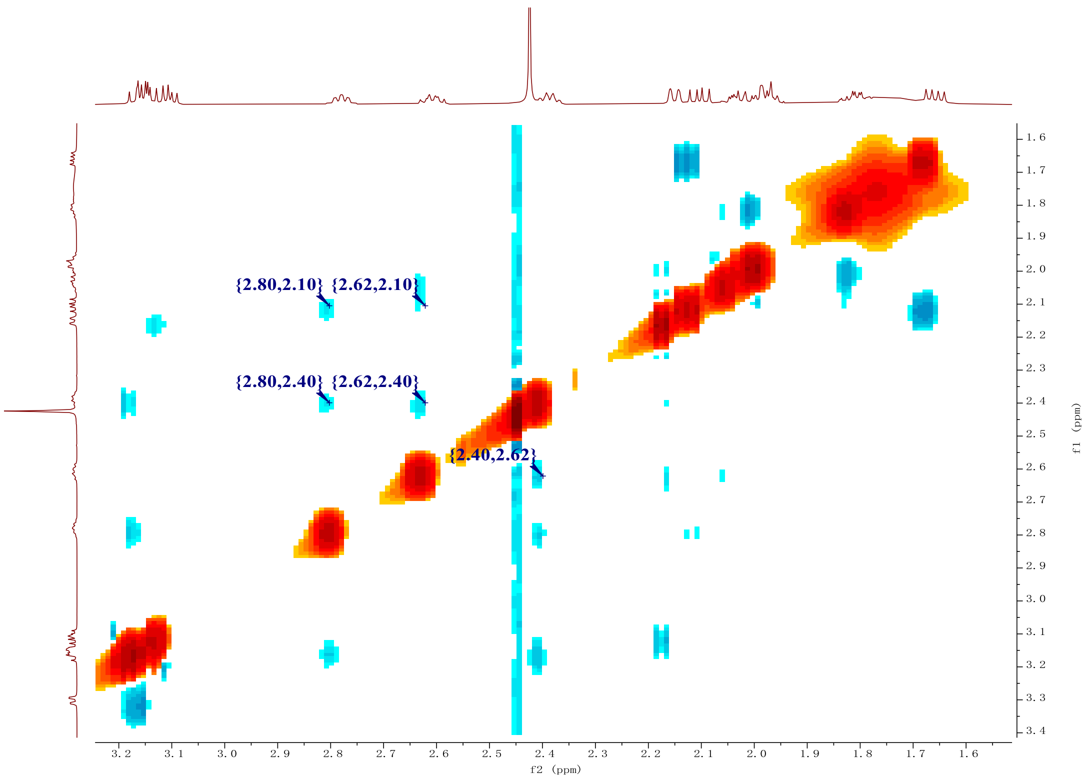
average of the yields: 53%

SmI$_2$ (0.1 M in THF, 2.5 mL), **2a** (39.6 mg, 0.1 mmol), **HMPA** (0.8 mL) and ***t*-BuOH** (0.2 mL), **4a** (19.9 mg, 50%), 0˚C-r.t., 5 minutes;
SmI$_2$ (0.1 M in THF, 2.5 mL), **2a** (39.6 mg, 0.1 mmol), **HMPA** (0.8 mL) and ***t*-BuOH** (0.2 mL), **4a** (21.9 mg, 55%), 0˚C-r.t., 5 minutes.
Colorless oil, TLC R_f (PE/EA = 1/1) = 0.49
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70–7.64 (m, 2H), 7.35–7.27 (m, 4H), 7.23–7.15 (m, 3H), 3.30 (dd, *J* = 9.8, 2.4 Hz, 1H), 3.19–3.15 (m, 1H), 3.15–3.12 (m, 1H), 3.10 (dd, *J* = 9.9, 5.8 Hz, 1H), 2.81-2.75 (m, 1H), 2.65–2.57 (m, 1H), 2.42 (s, 3H), 2.39 (dddd, *J* = 8.0, 8.0, 5.8, 2.0 Hz, 1H), 2.17 – 2.13 (m, 1H), 2.10 (dd, *J* = 13.8, 8.1 Hz, 1H), 2.05–2.01 (m, 1H), 2.01–1.98 (m, 1H), 1.98–1.95 (m, 1H), 1.83– 1.79 (m, 1H), 1.75 (s, 1H), 1.66 (dd, *J* = 13.8, 6.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.7, 143.7, 132.6, 129.6, 128.6, 127.9, 127.2, 126.5, 91.7, 65.9, 53.9, 53.8, 53.7, 47.8, 45.8, 43.1, 40.0, 34.5, 21.6.
HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{23}H_{28}NO_3S^+$: 398.1784; found: 398.1784

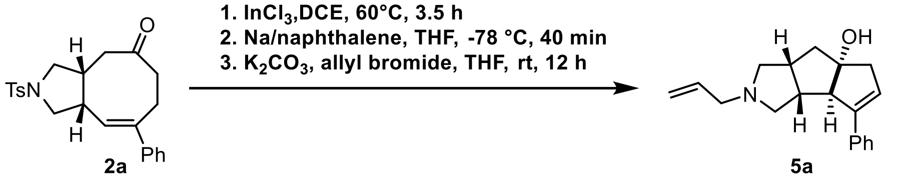
Stereochemical Determination of 4a

The stereochemistry of **4a** was determined by nOe experiments.
NOESY of **4a** in $CDCl_3$, 600 MHz



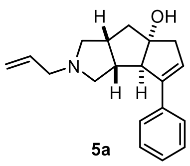


7. Experiments for removing Ts protecting group



2a 5a

Substrate **2a** (0.2 mmol, 1.0 equiv.) was added in the reaction flask (10 mL) which was then moved to glovebox, charged with $InCl_3$ (0.02 mmol, 0.1 equiv.) and sealed with rubber stopper. The flask was then moved from glovebox to the hood for the ene reaction. Super-dried DCE (4 mL) was added under argon to the flask and then the reaction mixture was heated in the oil bath. The reaction was monitored by TLC. The reaction mixture was finally cooled to room temperature, filtered and concentrated. The crude mixture was used without further purification.
Naphthalene (0.71mmol, 1.0 equiv.) in THF was added to Sodium (1.07 mmol, 1.5 equiv.) at RT and stirred vigorously. The resulting green suspension was stirred for 1.5 h at RT, then this was transferred to a solution of the previous product in THF at -78 ˚C. The dark-green solution was stirred at -78 ˚C for 40 min. After that, the reaction system was added by saturated aqueous $NaHCO_3$, extracted with EA, dried over Na_2SO_4, filtered, and concentrated. The crude amine was used without further purification.
To the generated amine dissolved in THF (4 mL) was added K_2CO_3 (0.8 mmol, 4.0 equiv.) and allyl bromide (0.8 mmol, 4.0 equiv.) at RT and stirred for 12 h. Upon completion, the resulting mixture was quenched by water and extracted with EA, dried with Na_2SO_4, filtered, and concentrated. The crude product was purified by flash column chromatography on silica gel to afford **5a**.

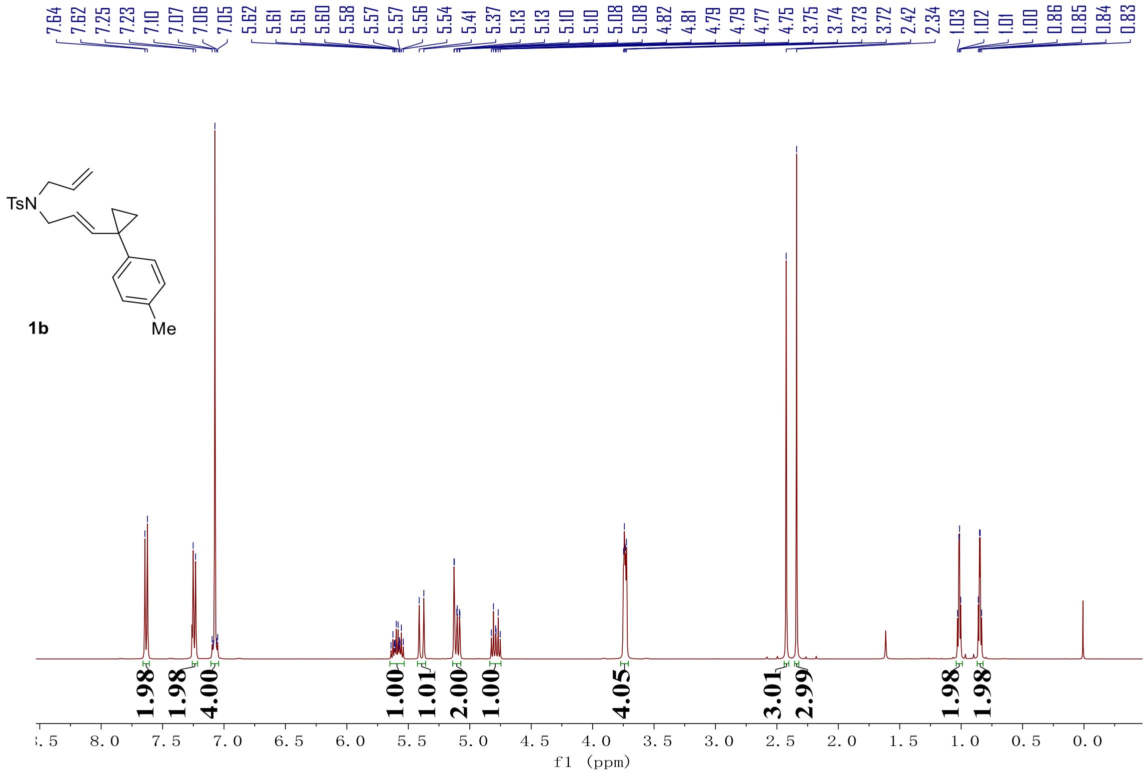


5a

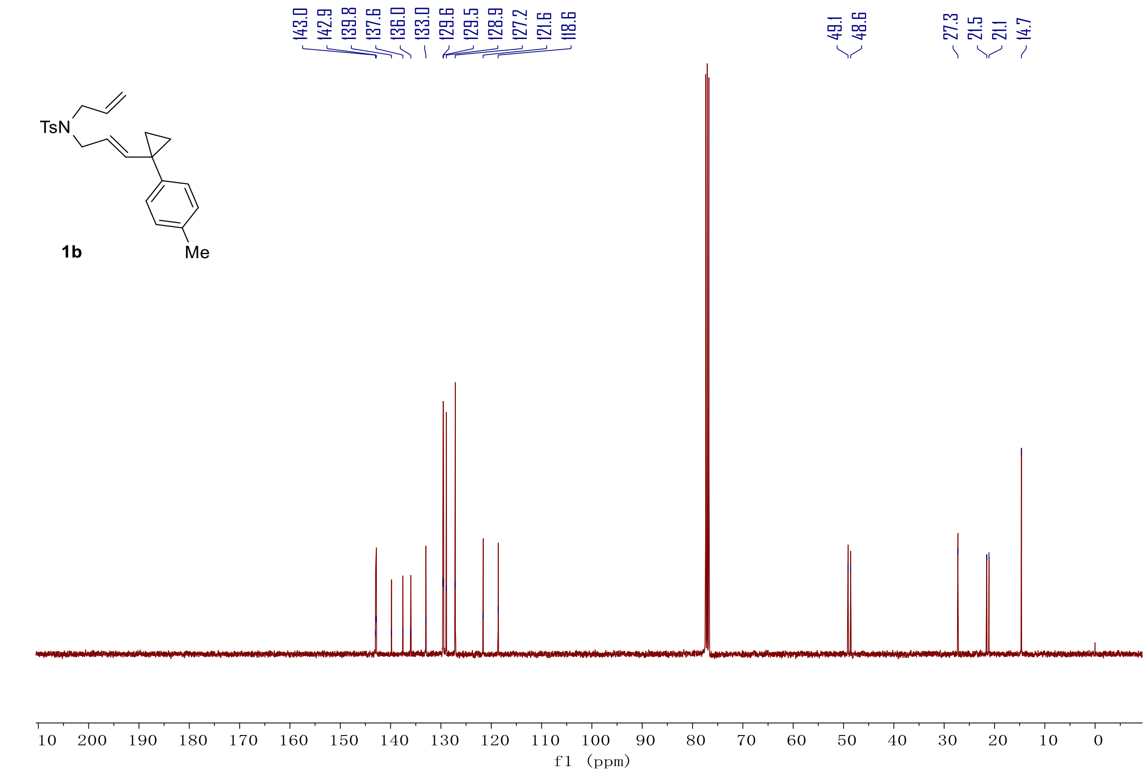
average of the yields: 73%
2a (79.5 mg, 0.20 mmol), **$InCl_3$** (4.4 mg, 0.020 mmol); **Naphthalene** (91.2 mg, 0.71mmol), **Na** (24.6 mg, 1.07 mmol); **K_2CO_3** (110.6 mg, 0.80 mmol), **allyl bromide** (96.8 mg, 0.80 mmol), **5a** (42.1 mg, 75%).
2a (79.5 mg, 0.20 mmol), **$InCl_3$** (4.4 mg, 0.020 mmol); **Naphthalene** (91.2 mg, 0.71mmol), **Na** (24.6 mg, 1.07 mmol); **K_2CO_3** (110.6 mg, 0.80 mmol), **allyl bromide** (96.8 mg, 0.80 mmol), **5a** (39.9 mg, 71%).
Colorless oil, TLC R_f (DCM/MeOH = 10/1) = 0.42
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.19 (m, 5H), 5.91 (ddt, *J* = 16.8, 10.1, 6.4 Hz, 1H), 5.84 – 5.81 (m, 1H), 5.21 (dd, *J* = 17.2, 1.7 Hz, 1H), 5.14 (dd, *J* = 10.1, 1.8 Hz, 1H), 3.17 – 3.09 (m, 3H), 3.04 (d, *J* = 9.1 Hz, 1H), 2.90 (d, *J* = 9.3 Hz, 1H), 2.72 – 2.64 (m, 2H), 2.62 – 2.49 (m, 2H), 2.25 – 2.06 (m, 3H), 1.83 (d, *J* = 13.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 136.6, 135.2, 128.5, 127.0, 126.2, 124.9, 117.6, 88.9, 67.8, 63.4, 62.6, 58.0, 48.2, 44.6, 42.6, 42.6.
HRMS (ESI−FTICR, m/z): $[M + H]^+$ calculated for $C_{19}H_{24}NO^+$: 282.1852; found: 282.1848

8. NMR spectra and crystal structures of new compounds

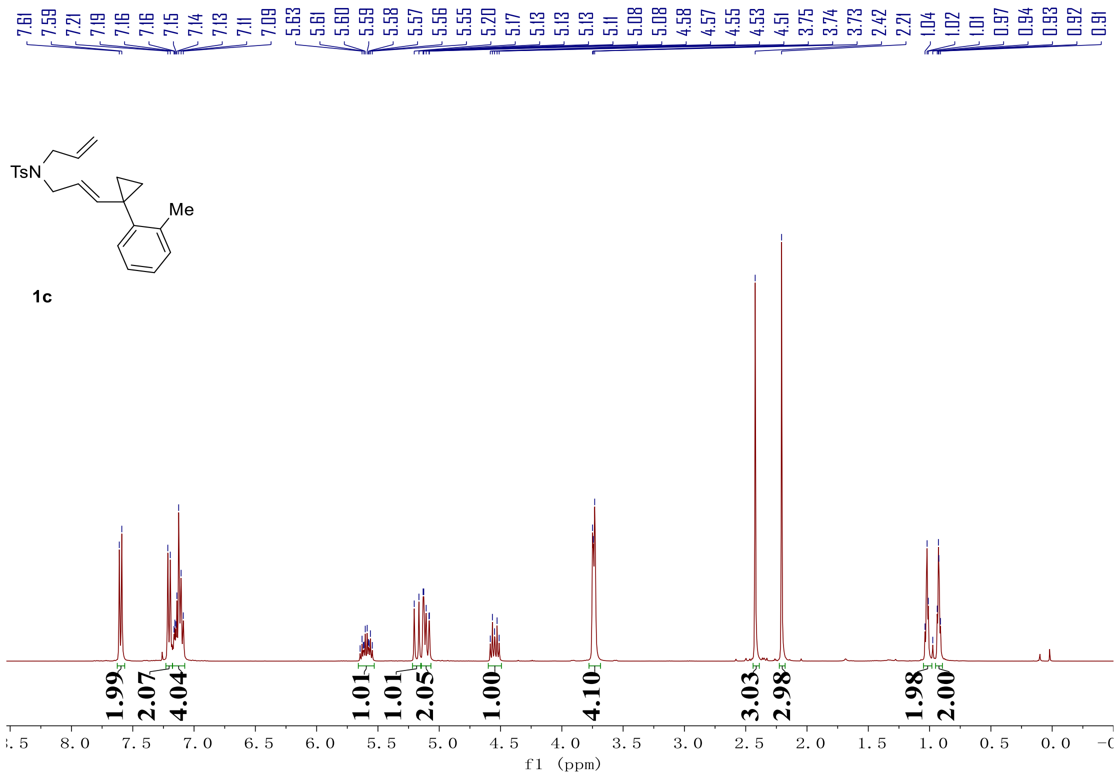
^{1}H NMR in $CDCl_3$, 400 MHz



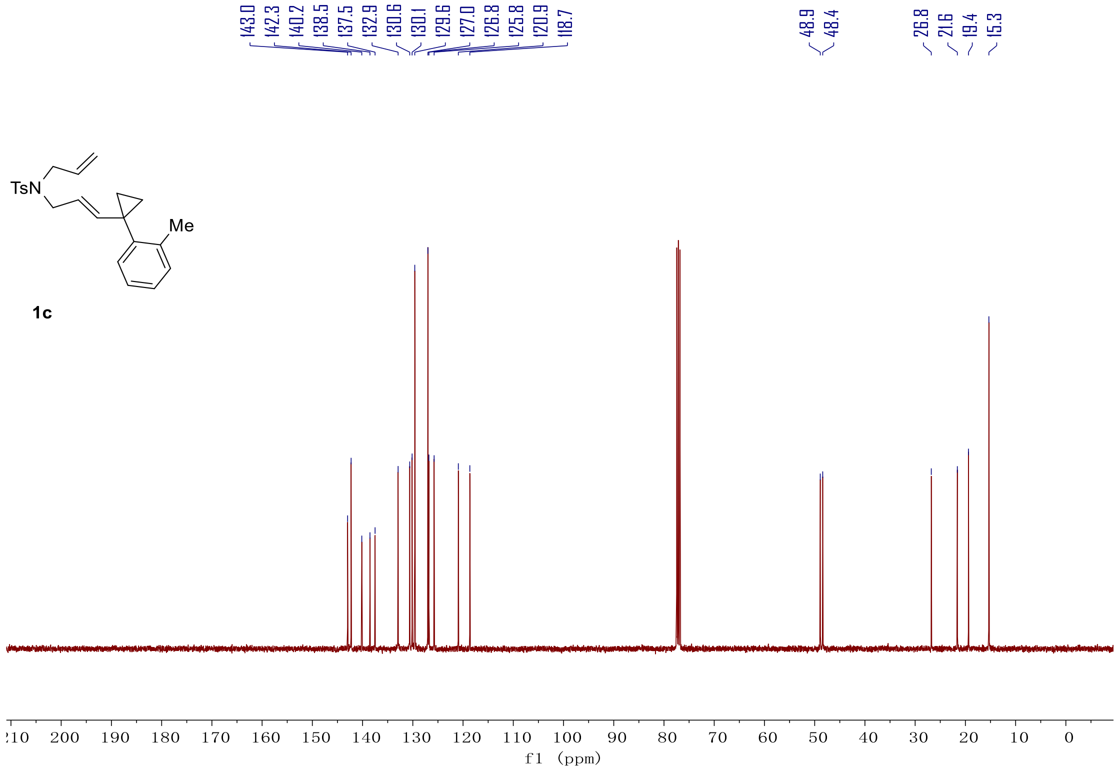
^{13}C NMR in $CDCl_3$, 101 MHz



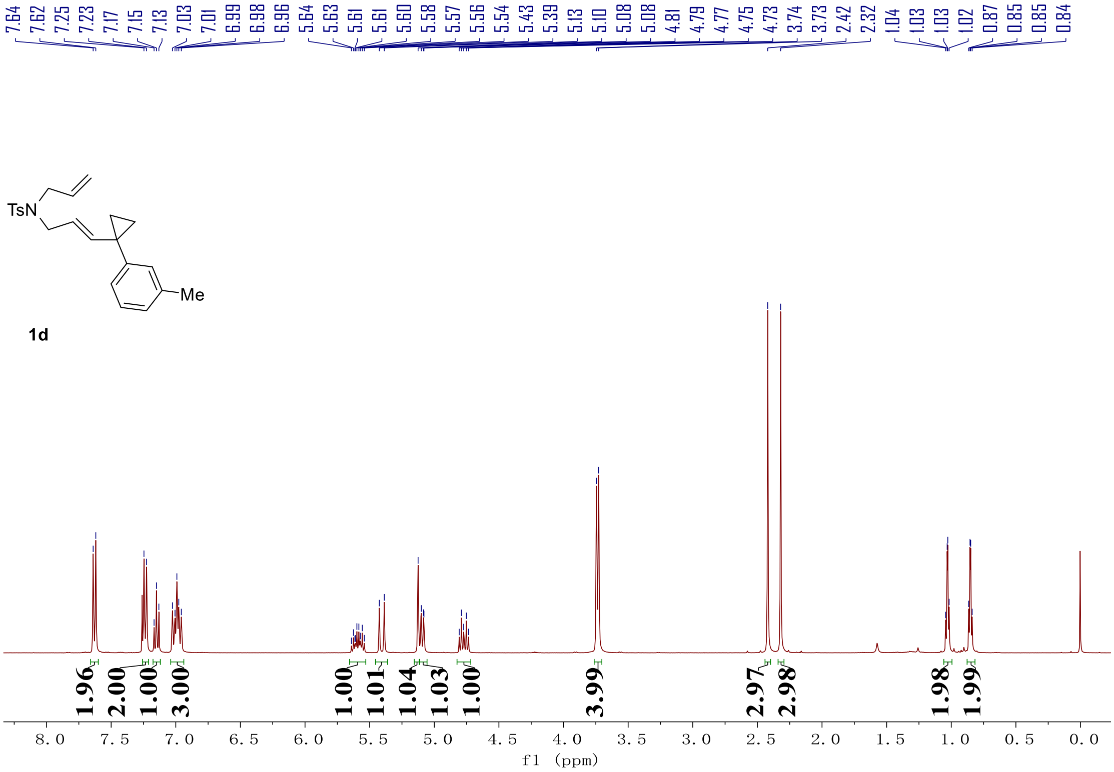
^{1}H NMR in $CDCl_3$, 400 MHz



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

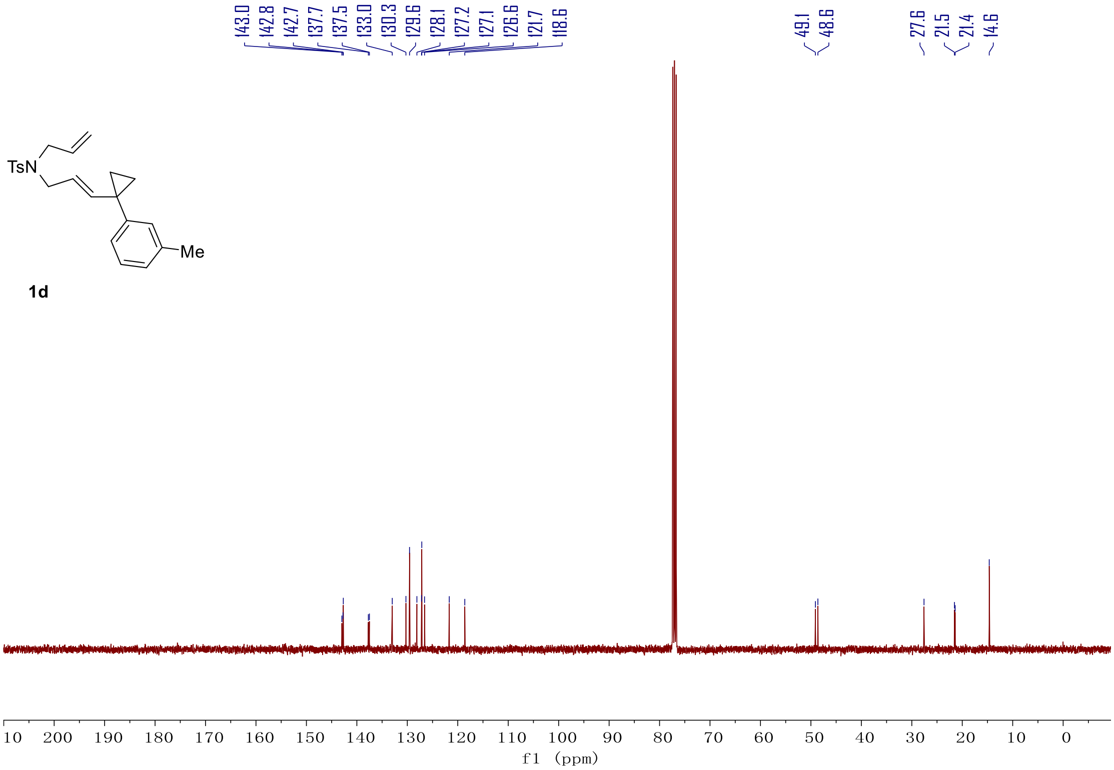


^{1}H NMR in $CDCl_3$, 400 MHz



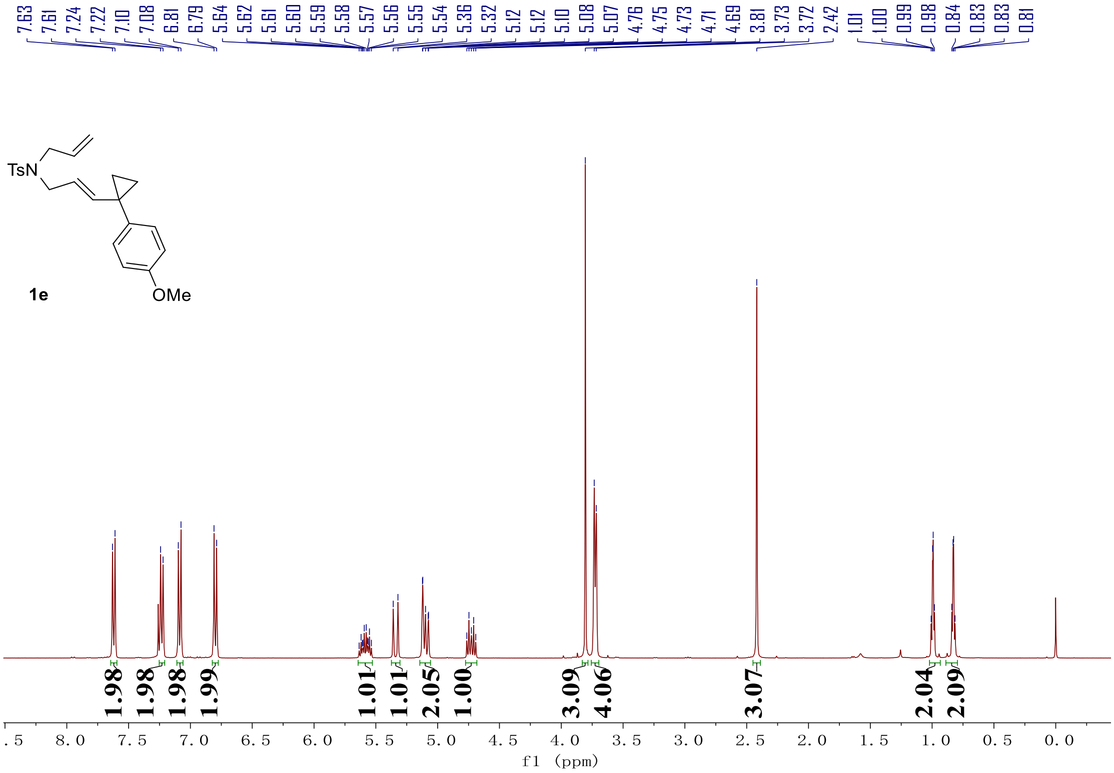
1d

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

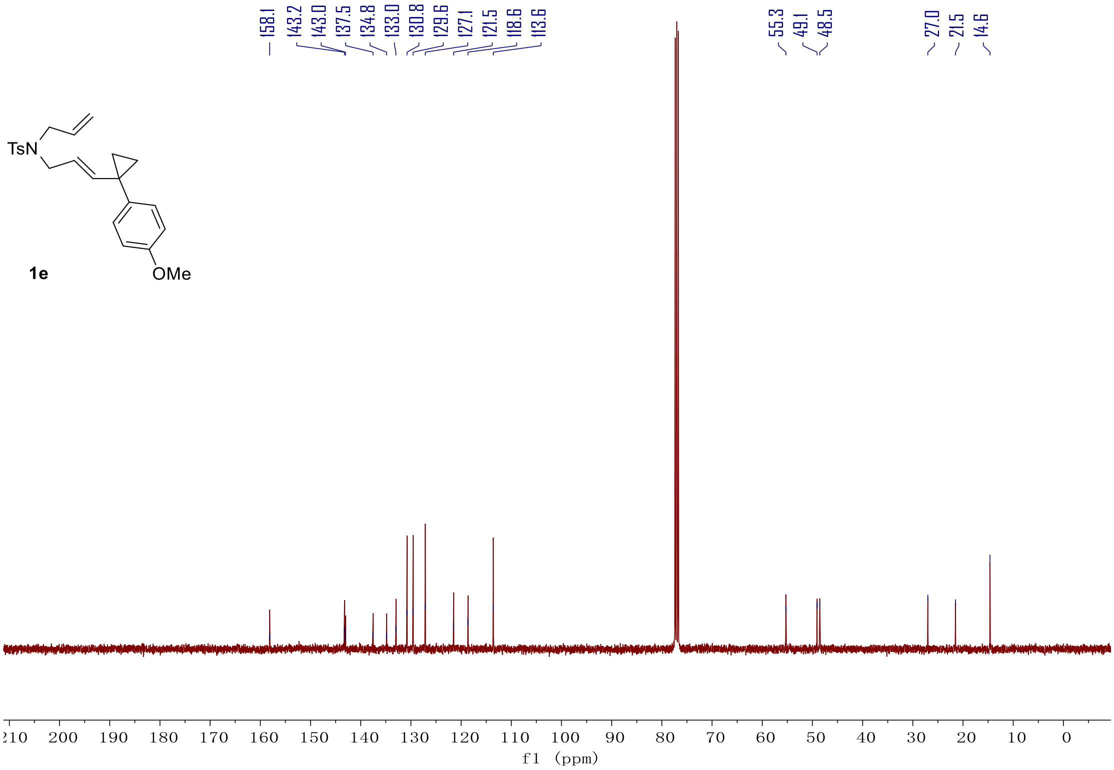


1d

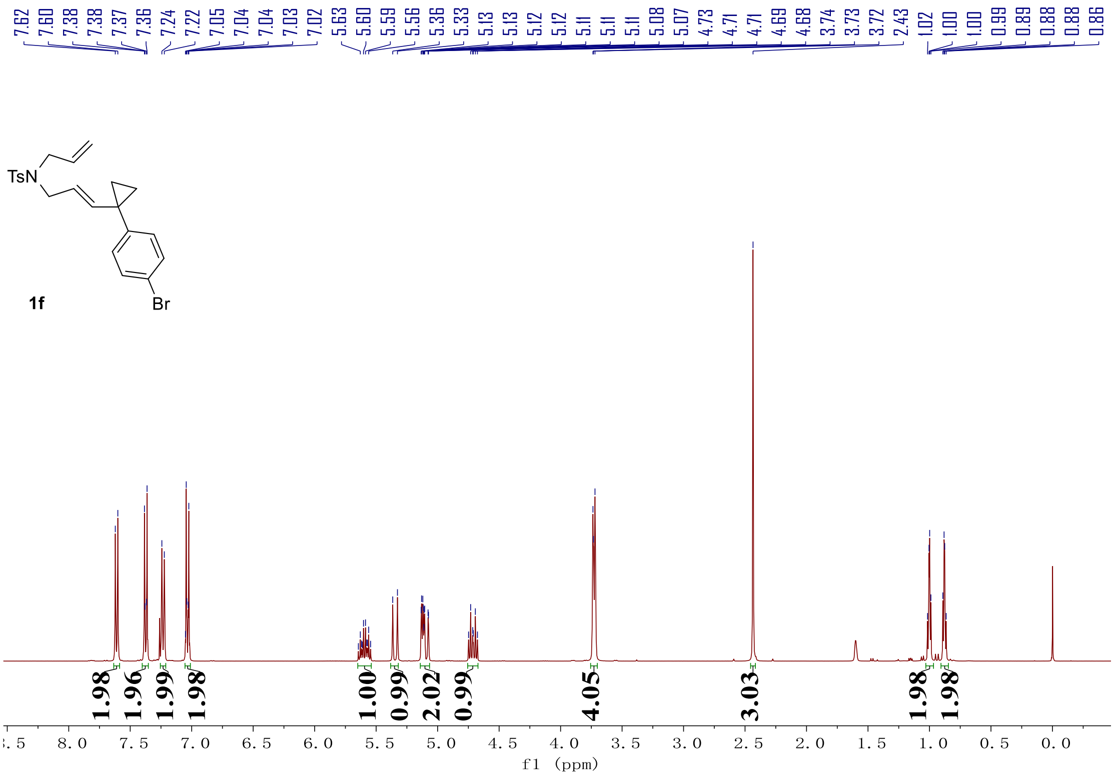
^{1}H NMR in $CDCl_3$, 400 MHz



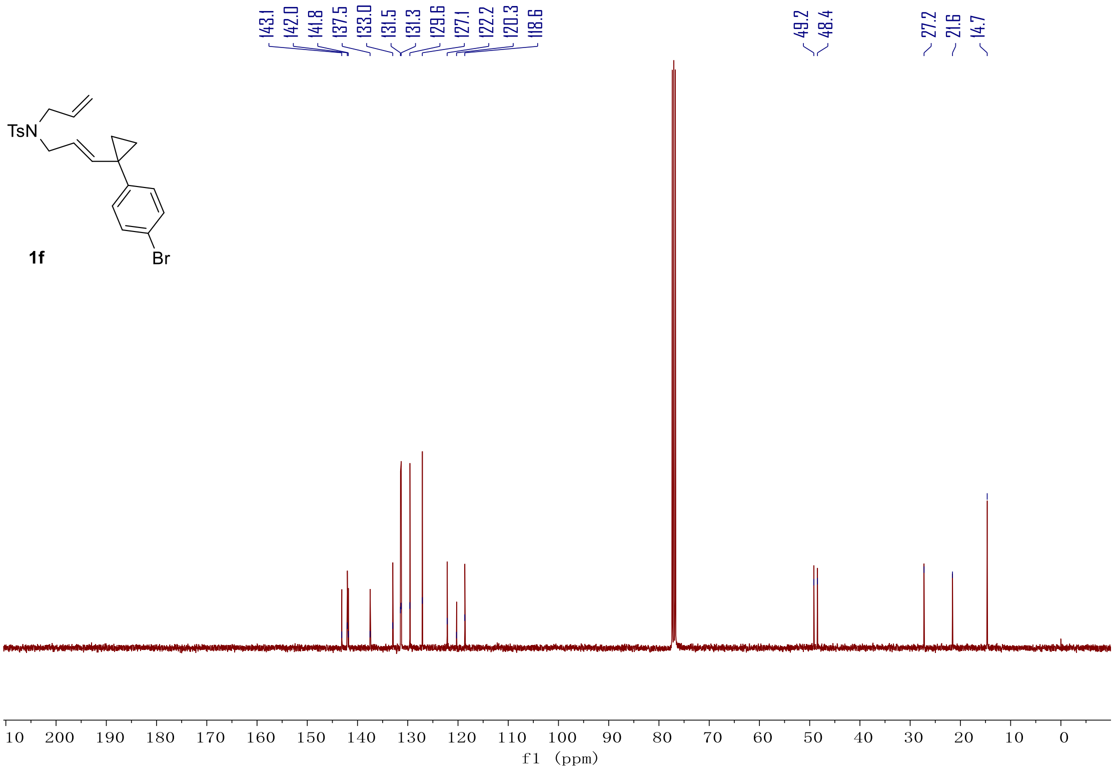
^{13}C NMR in $CDCl_3$, 101 MHz



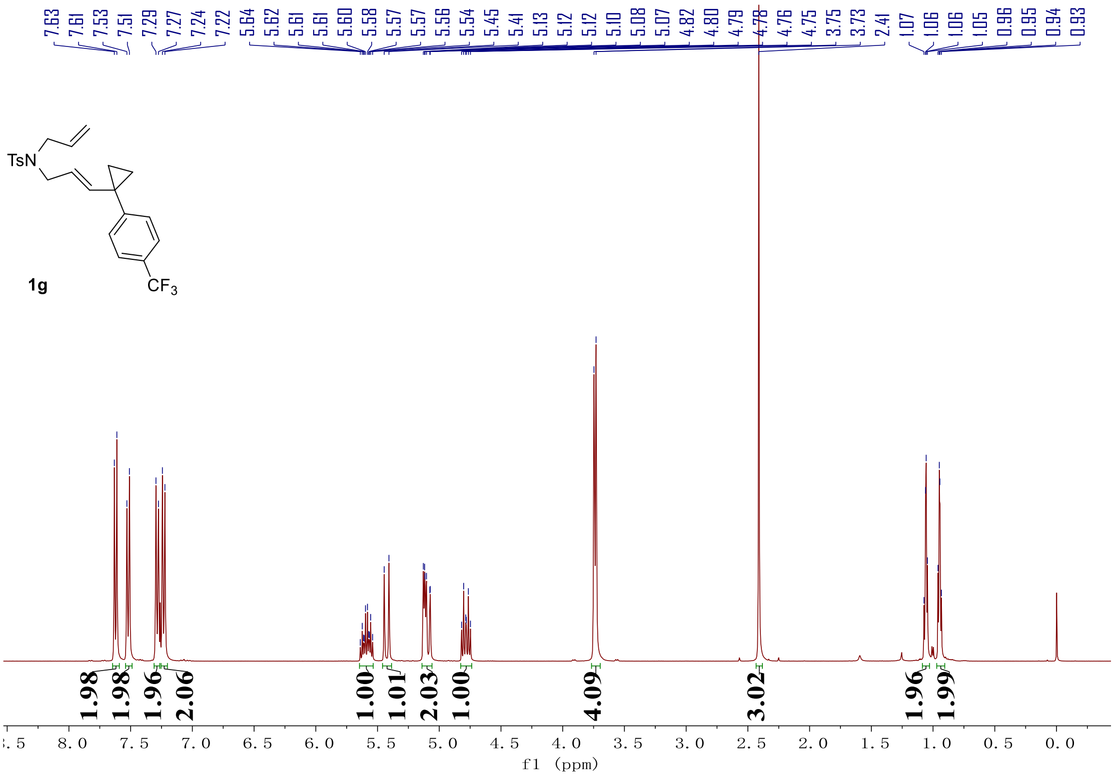
^{1}H NMR in $CDCl_3$, 400 MHz



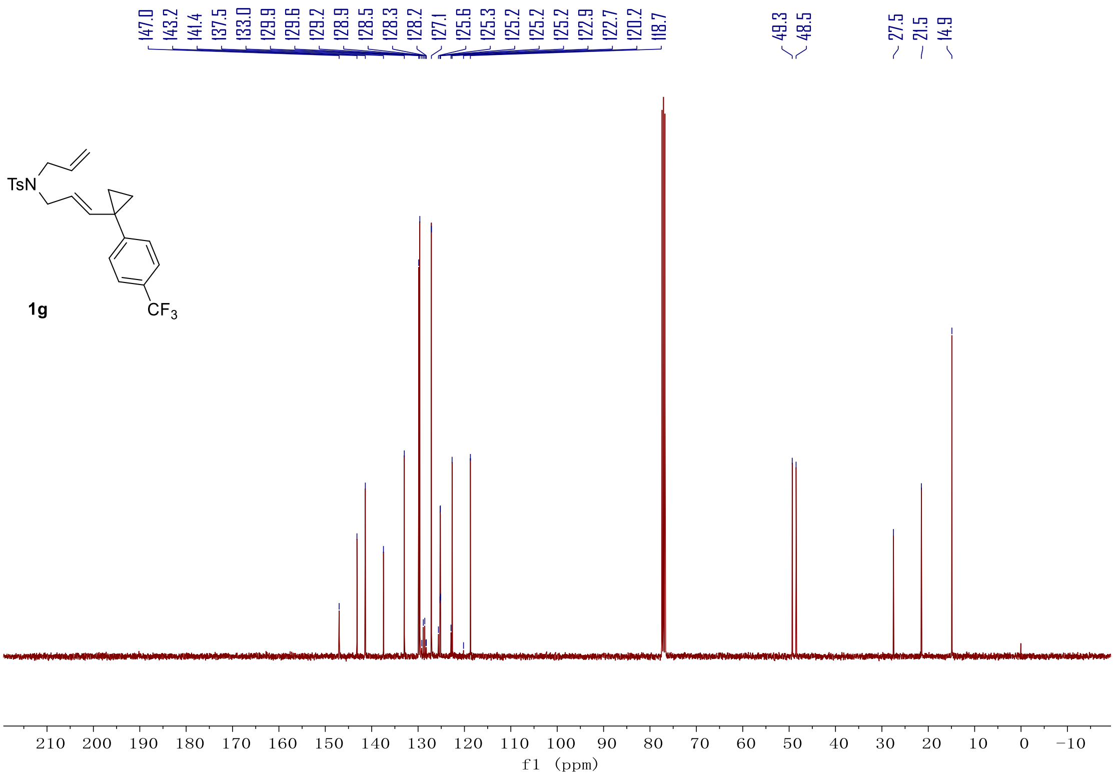
^{13}C NMR in $CDCl_3$, 101 MHz



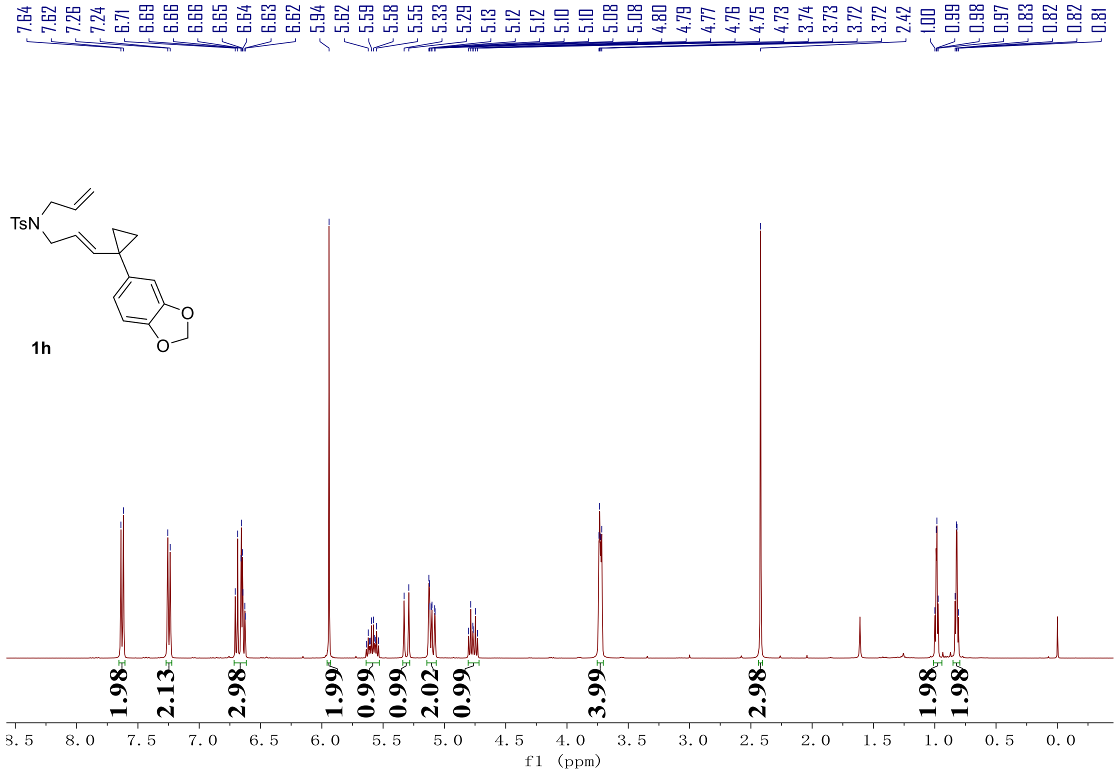
^{1}H NMR in $CDCl_3$, 400 MHz



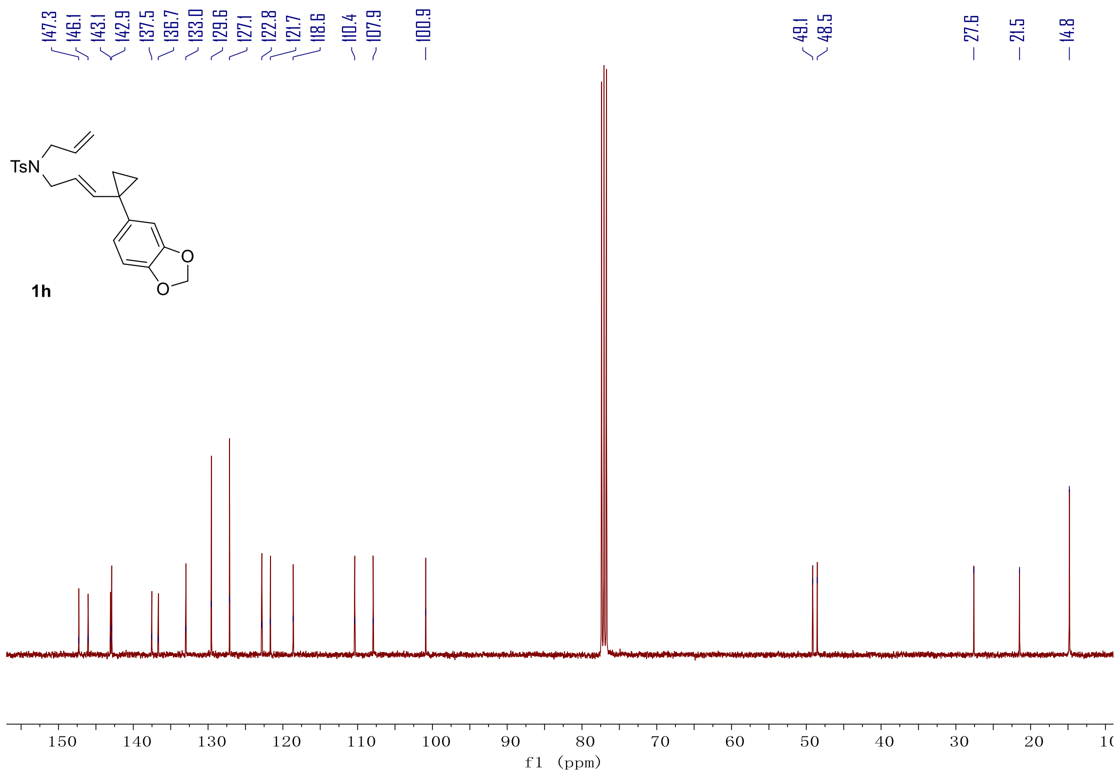
^{13}C NMR in $CDCl_3$, 101 MHz



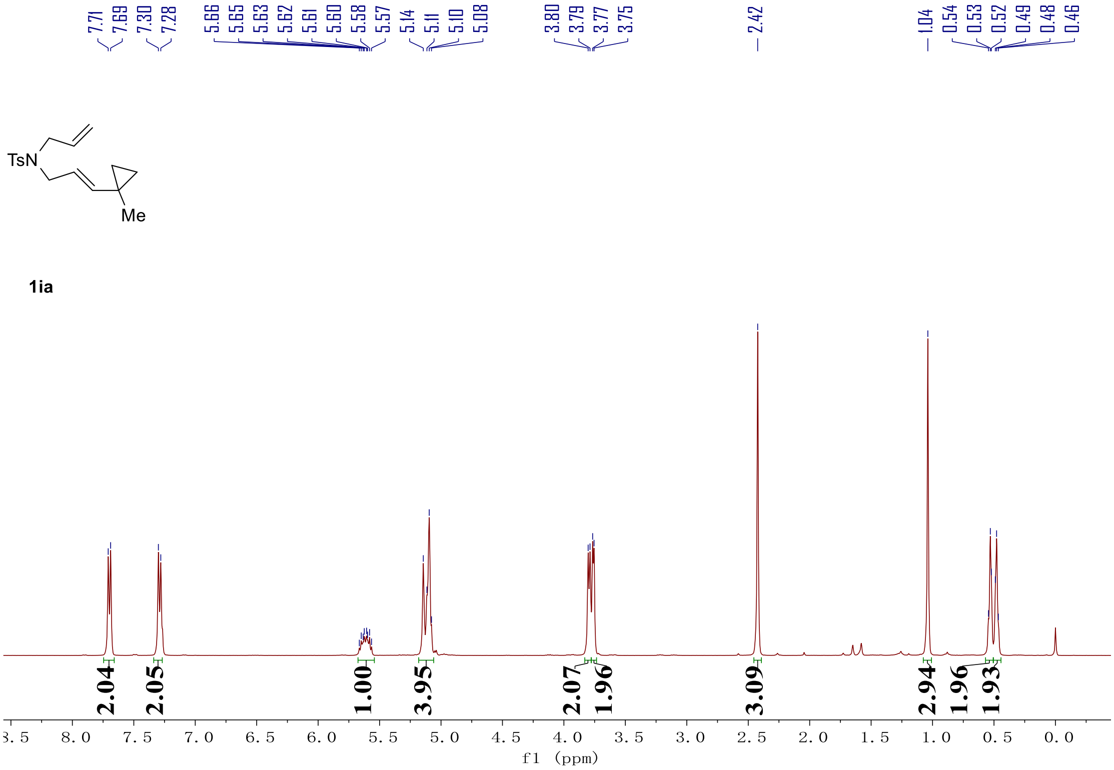
^{1}H NMR in $CDCl_3$, 400 MHz



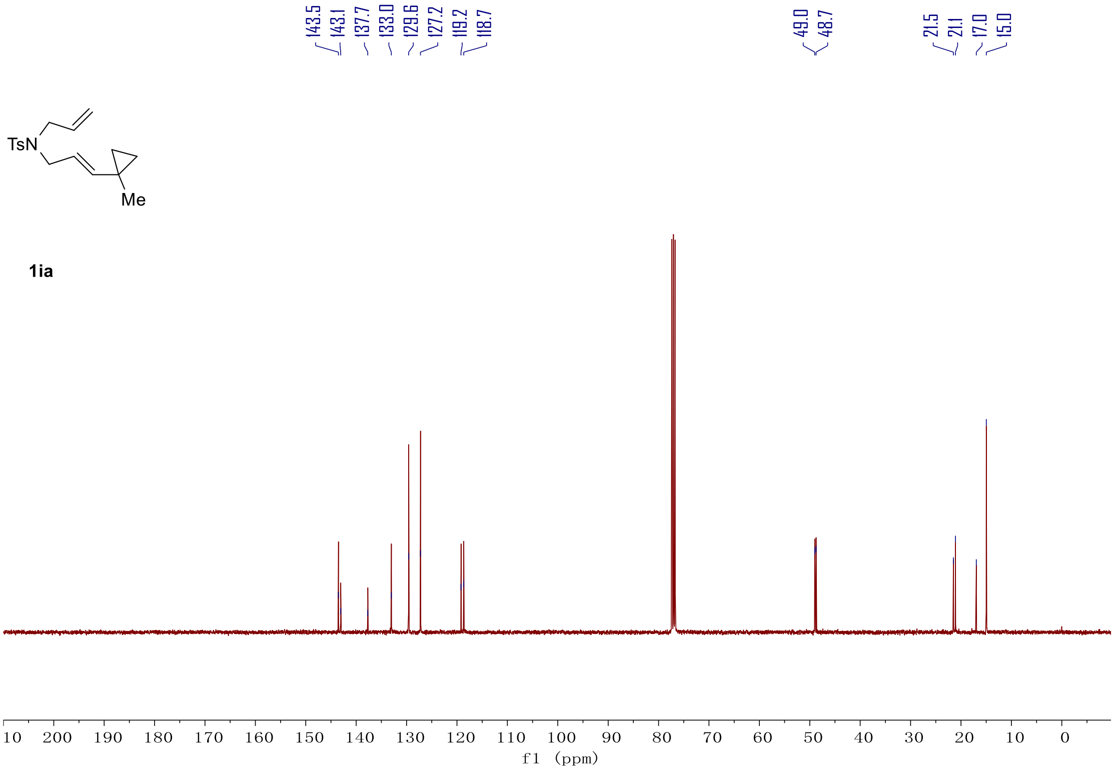
^{13}C NMR in $CDCl_3$, 101 MHz



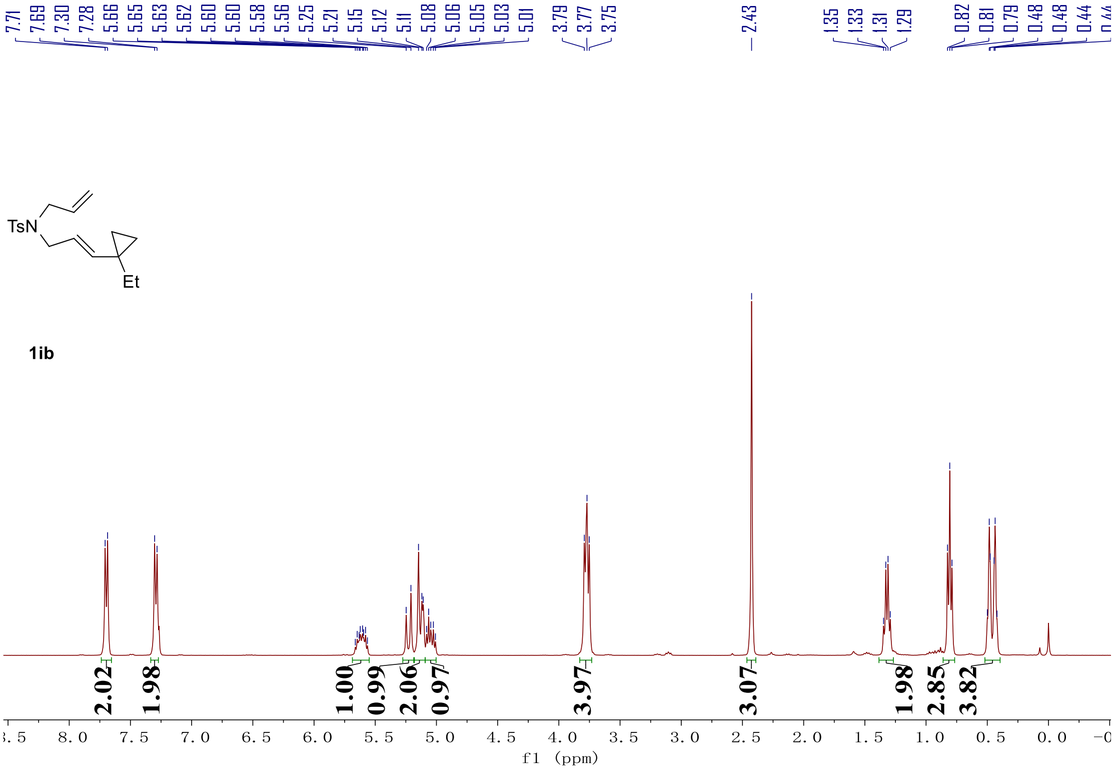
^{1}H NMR in $CDCl_3$, 400 MHz



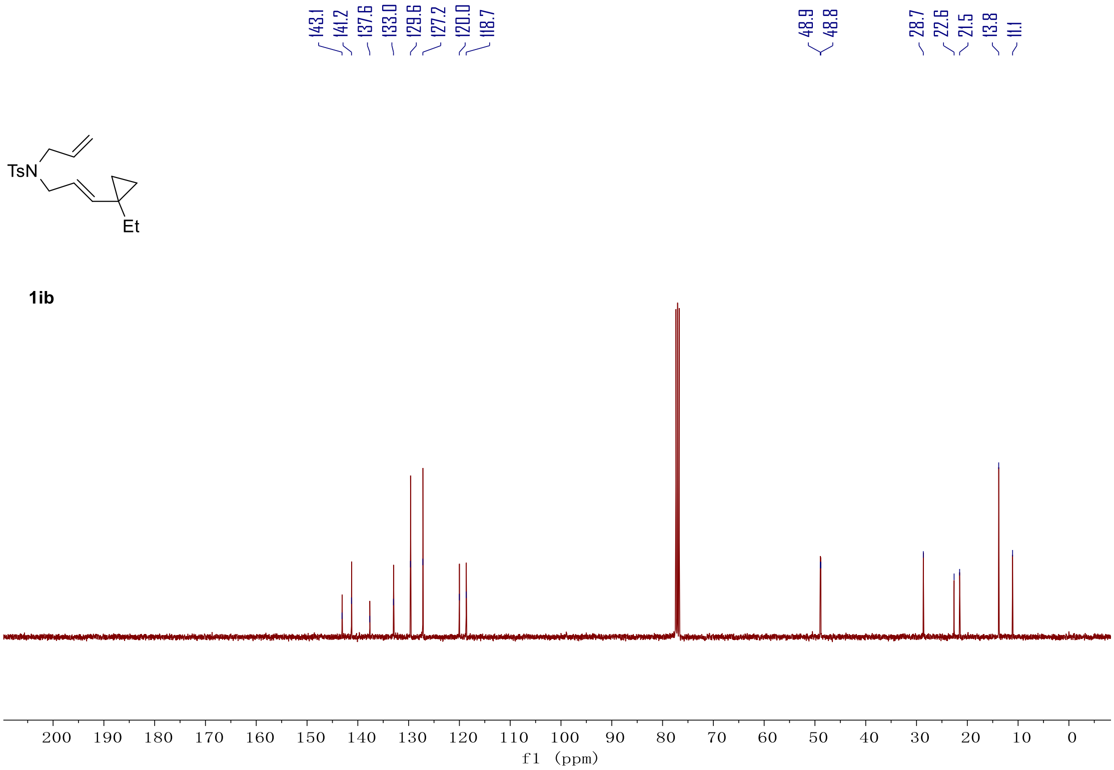
^{13}C NMR in $CDCl_3$, 101 MHz



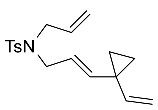
^1H NMR in $CDCl_3$, 400 MHz



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



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



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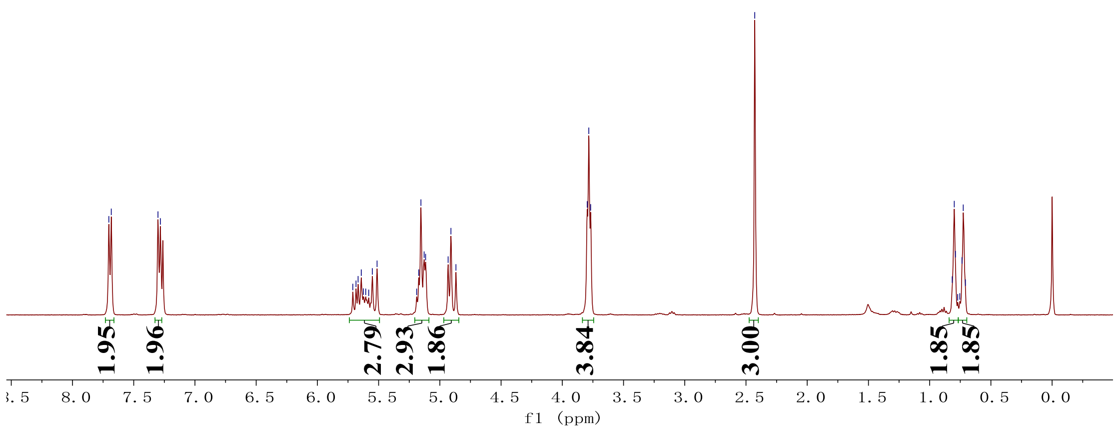
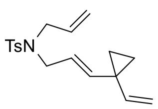


^{13}C NMR in $CDCl_3$, 101 MHz



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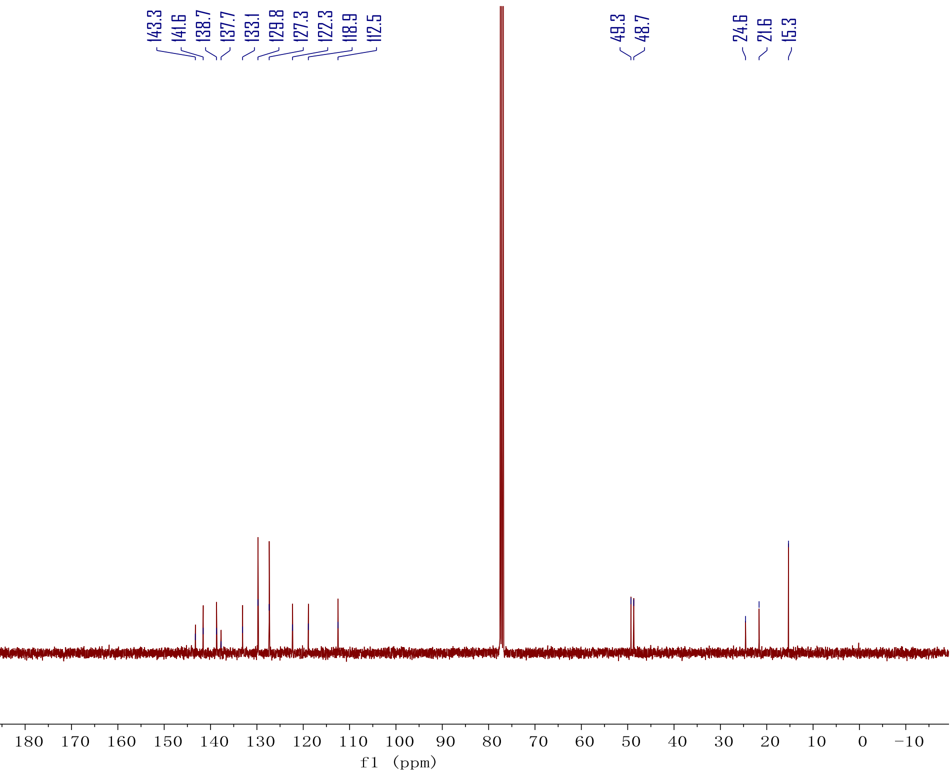
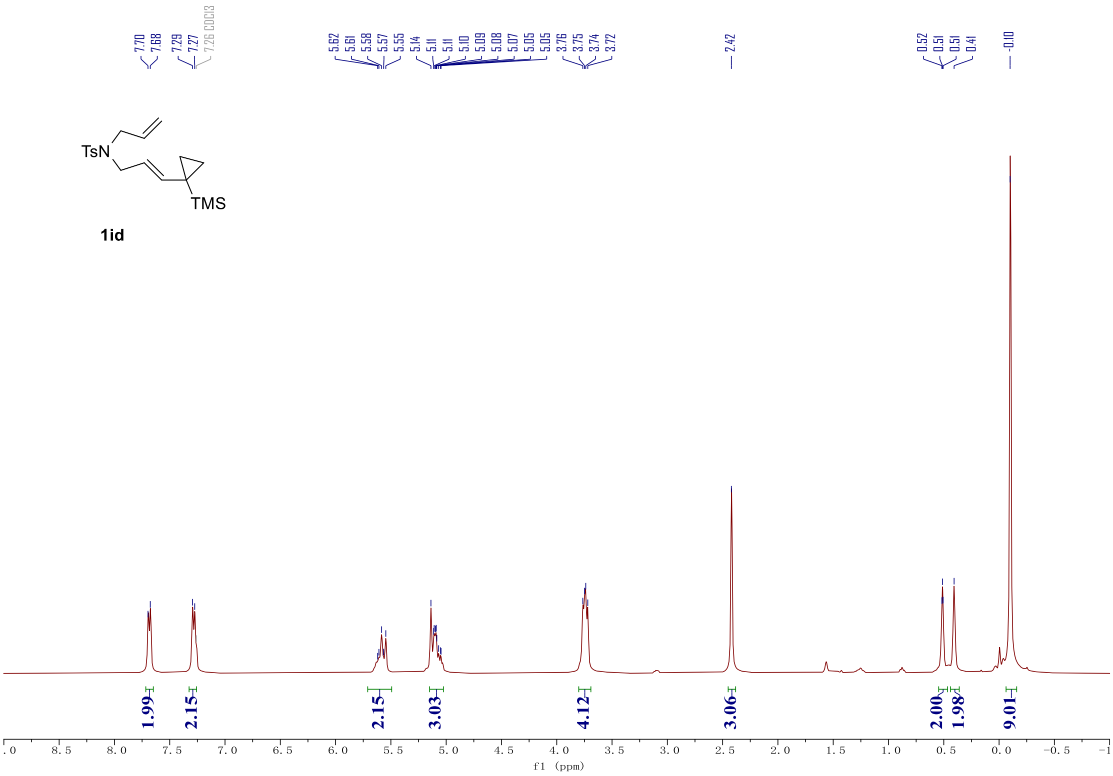
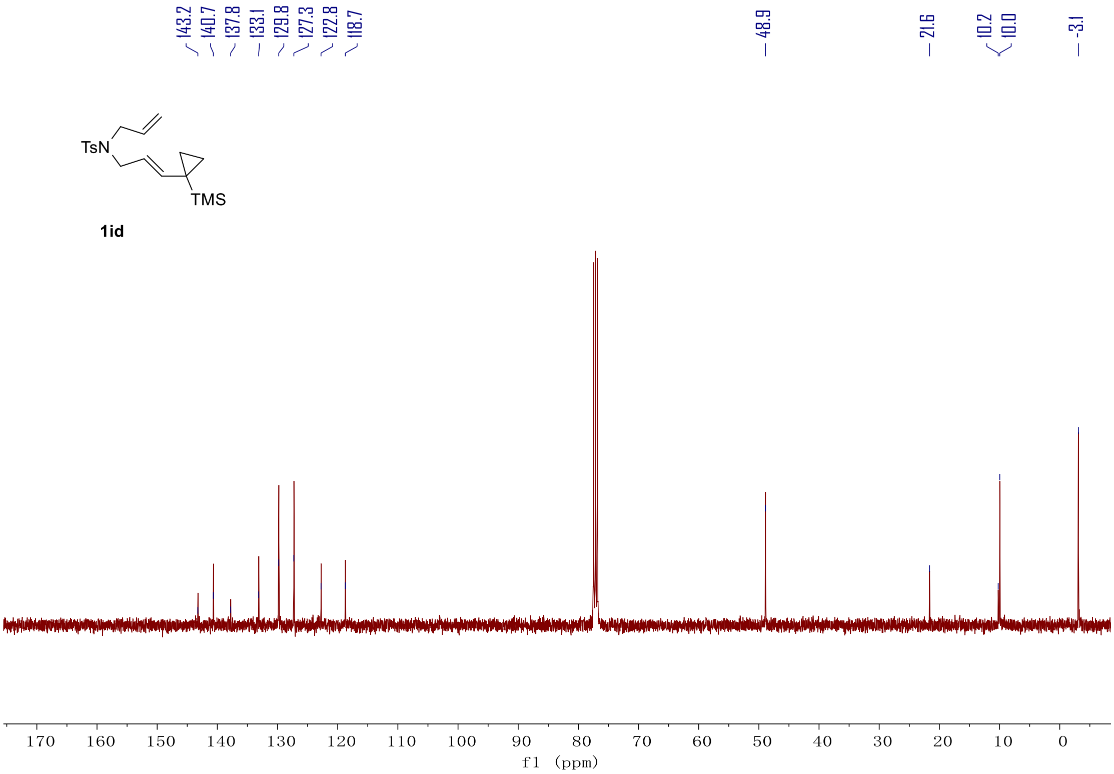


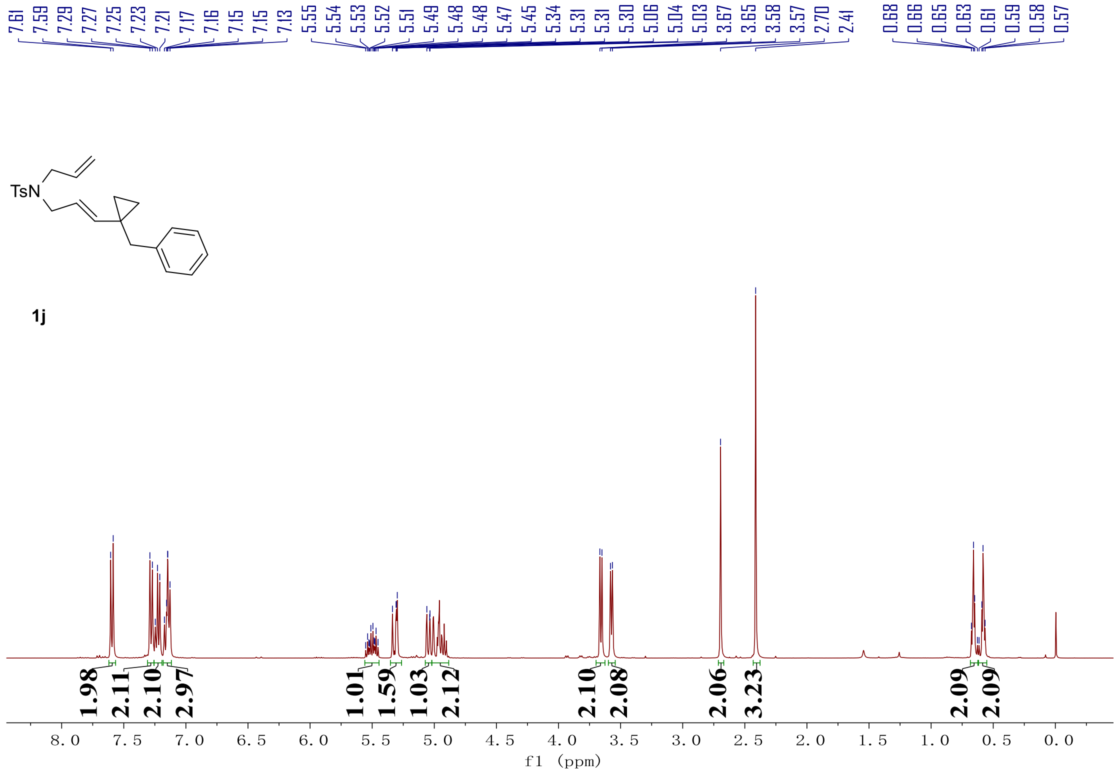
^1H NMR in $CDCl_3$, 400 MHz



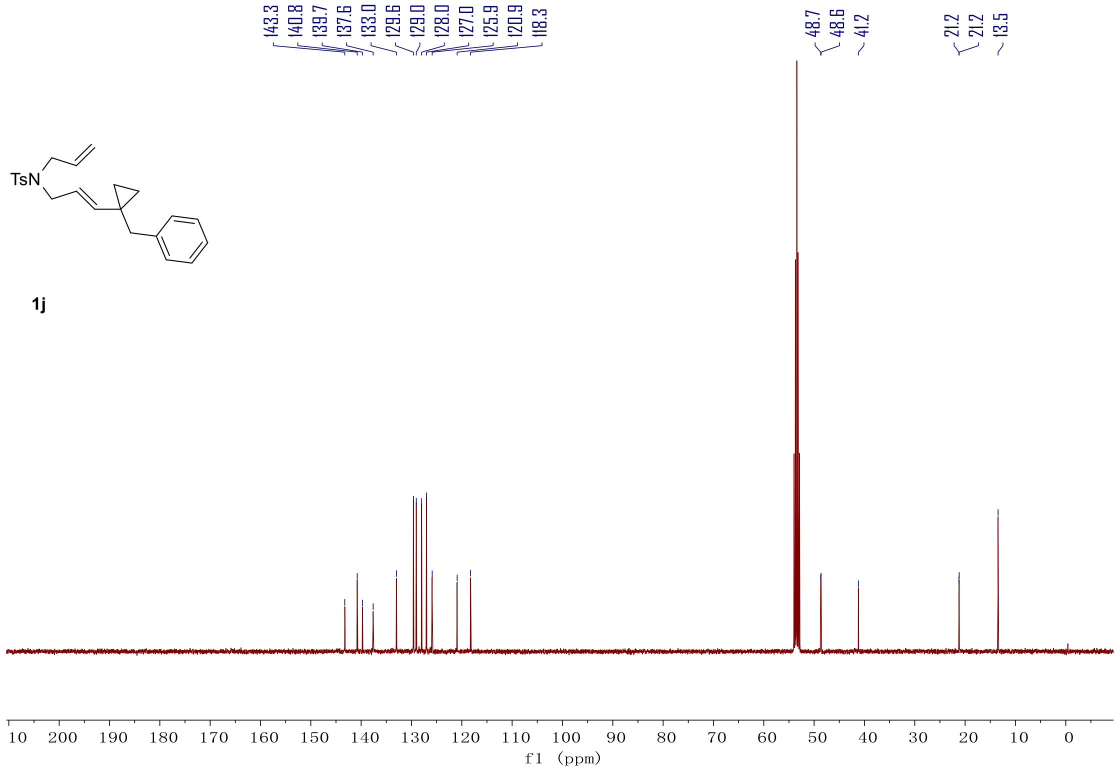
^{13}C NMR in $CDCl_3$, 101 MHz



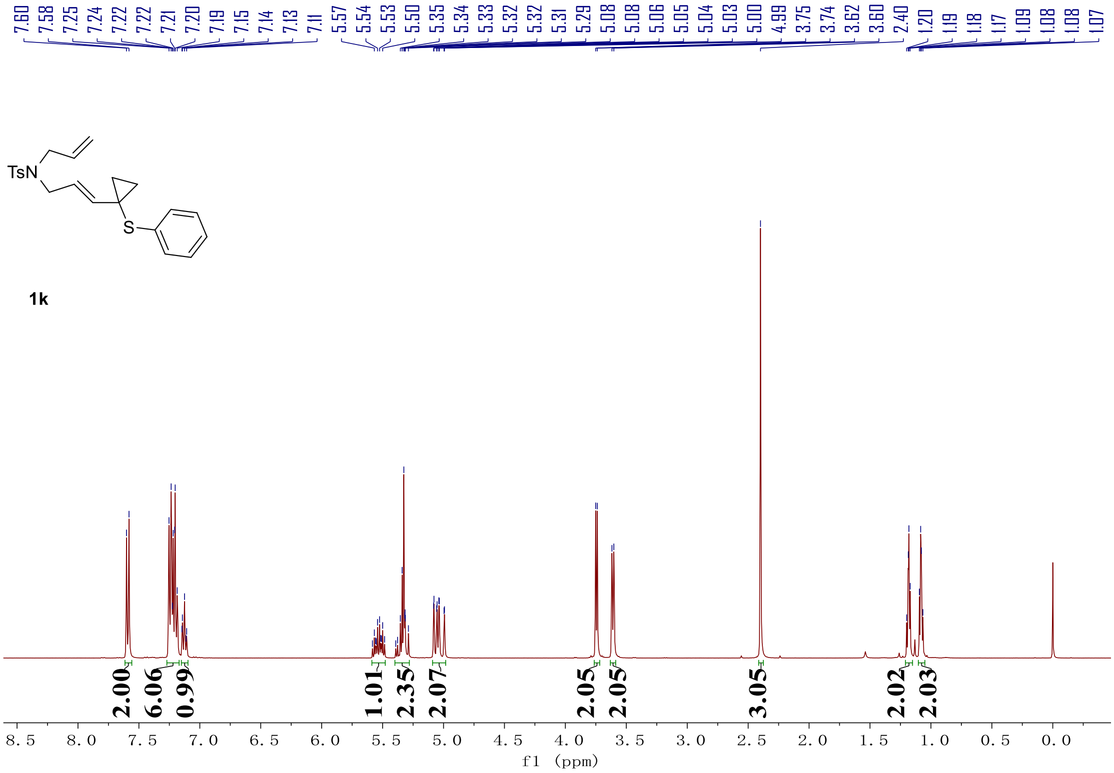
^{1}H NMR in CD_2Cl_2, 400 MHz



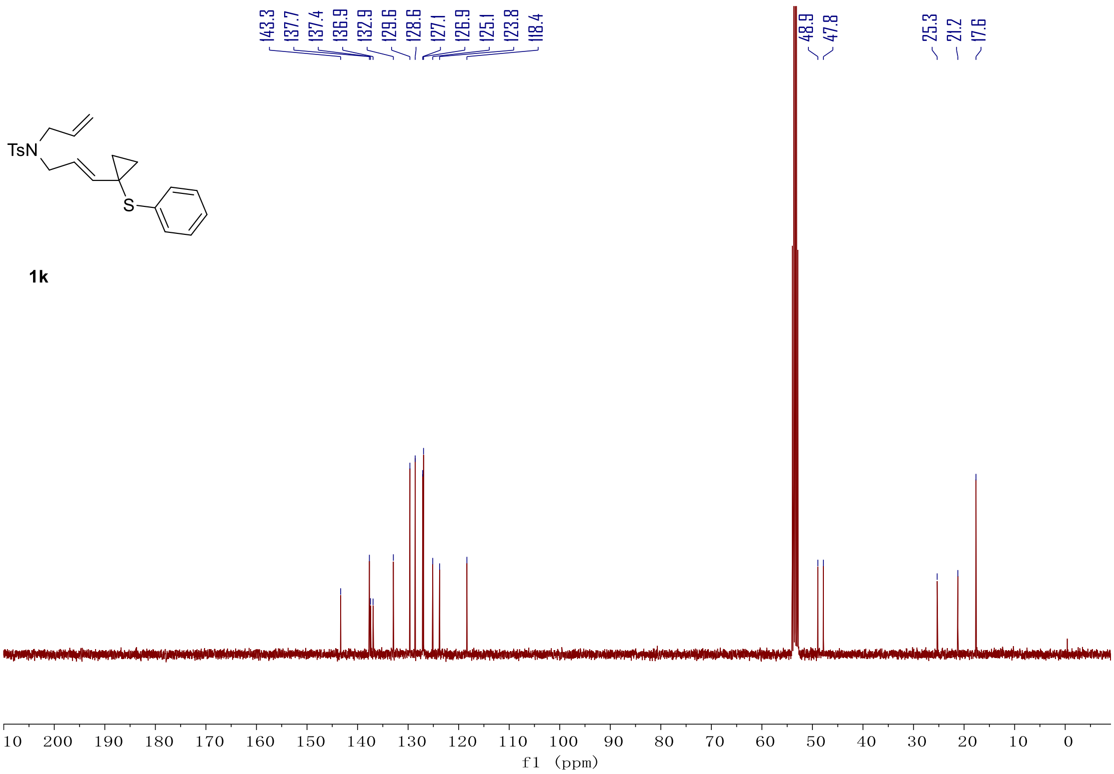
^{13}C NMR in CD_2Cl_2, 101 MHz



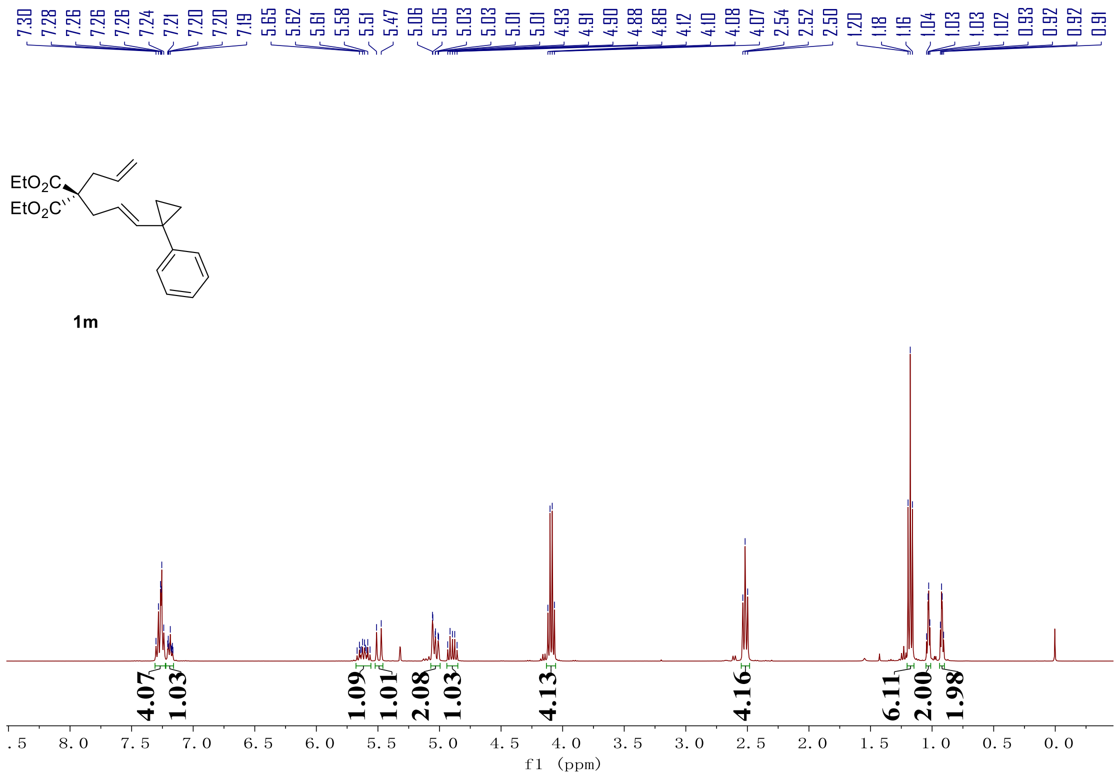
^{1}H NMR in CD_2Cl_2, 400 MHz



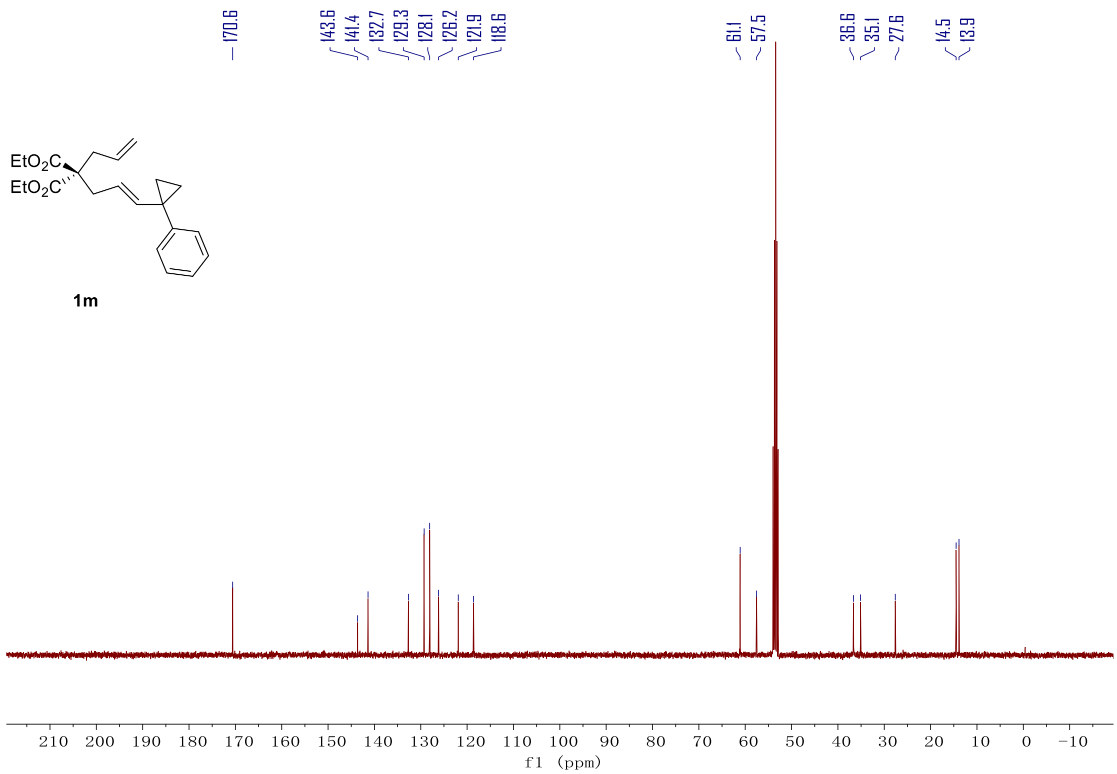
^{13}C NMR in CD_2Cl_2, 101 MHz



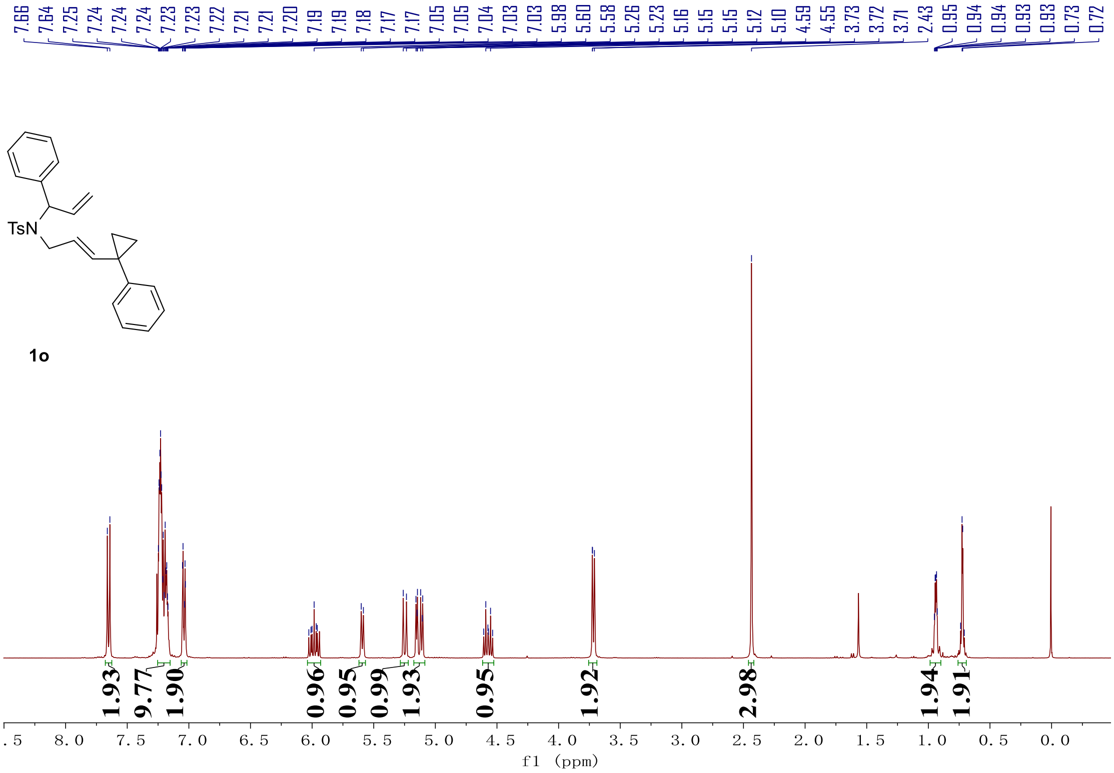
^{1}H NMR in CD_2Cl_2, 400 MHz



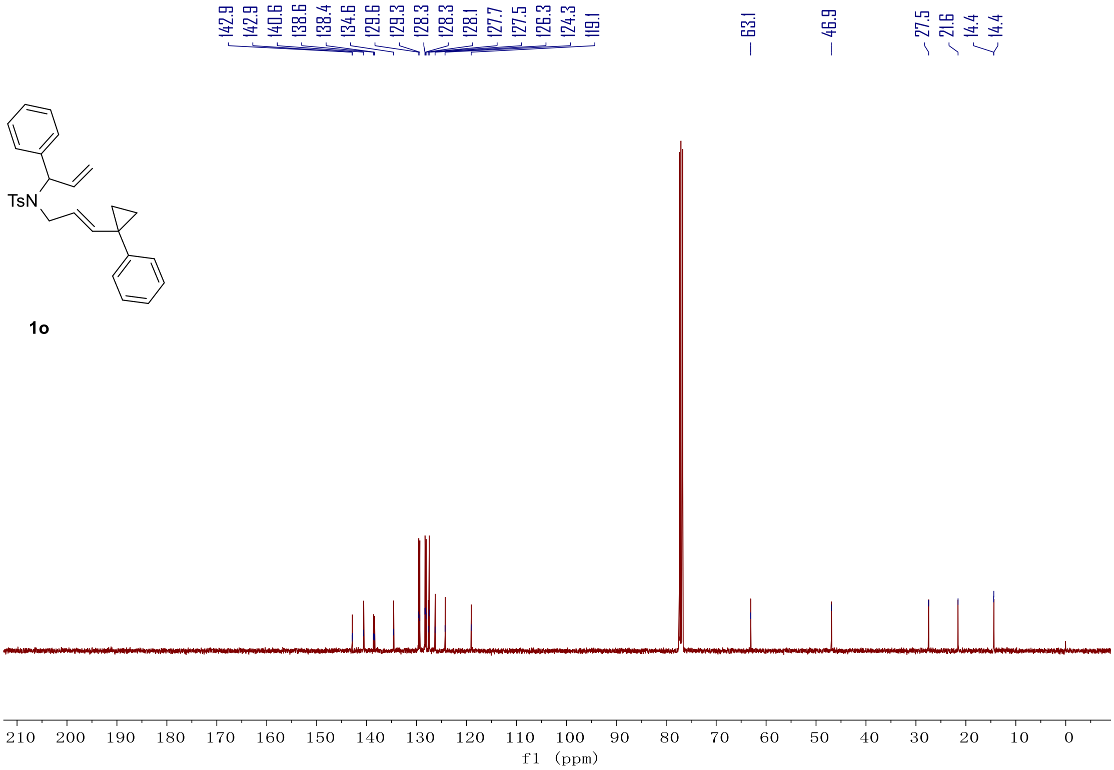
^{13}C NMR in CD_2Cl_2, 101 MHz



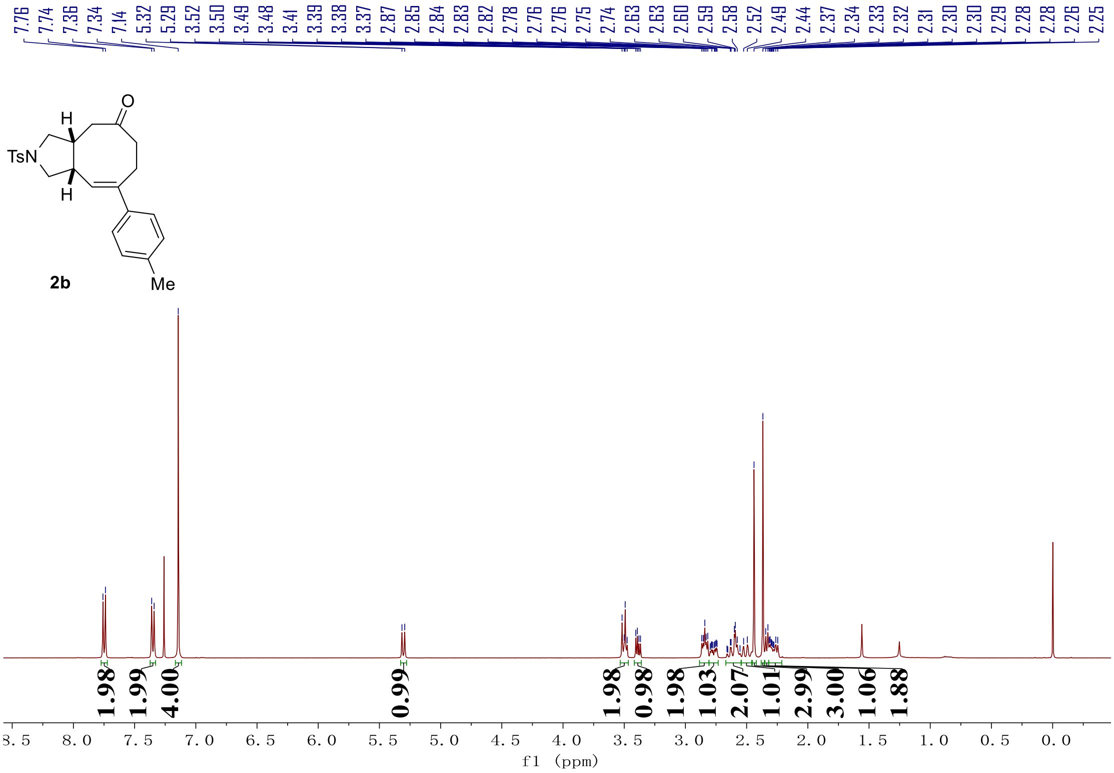
^{1}H NMR in $CDCl_3$, 400 MHz



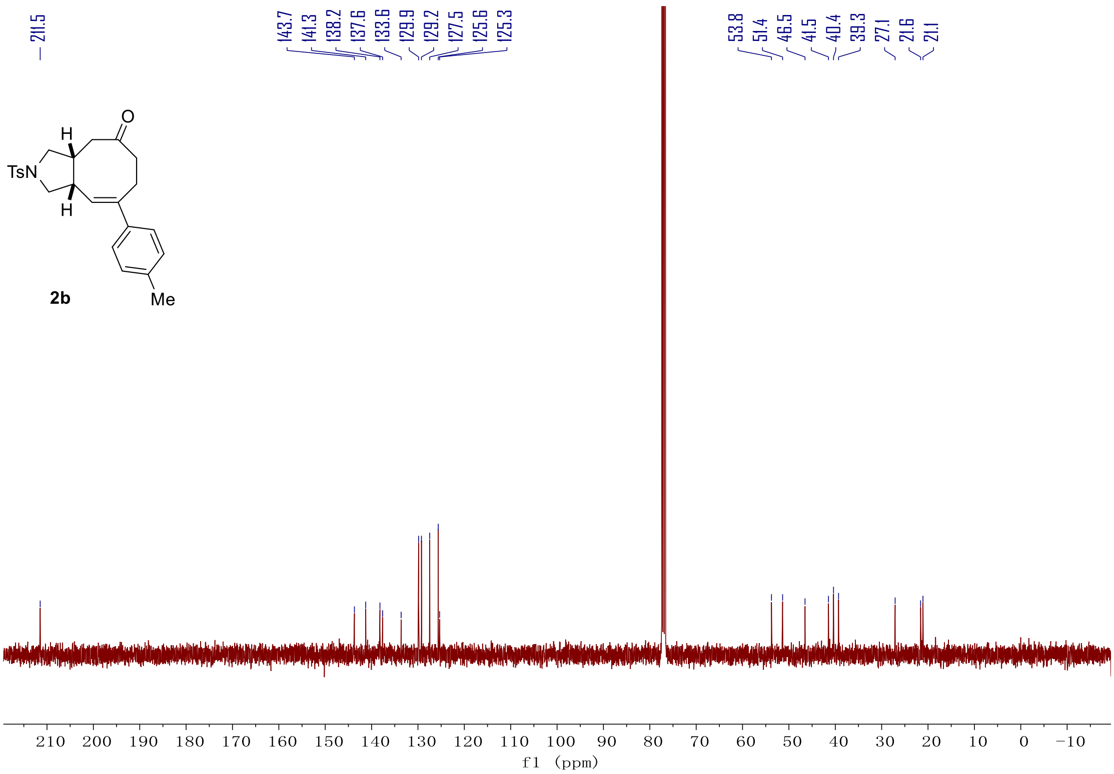
^{13}C NMR in $CDCl_3$, 101 MHz



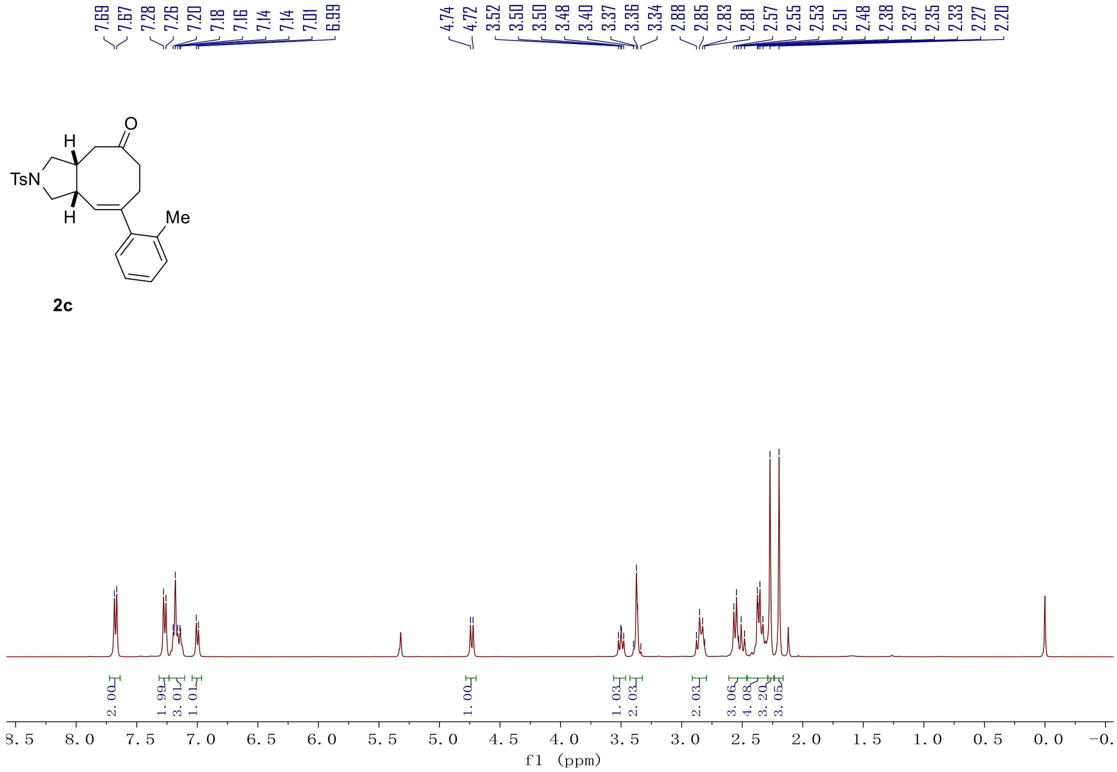
^{1}H NMR in $CDCl_3$, 400 MHz



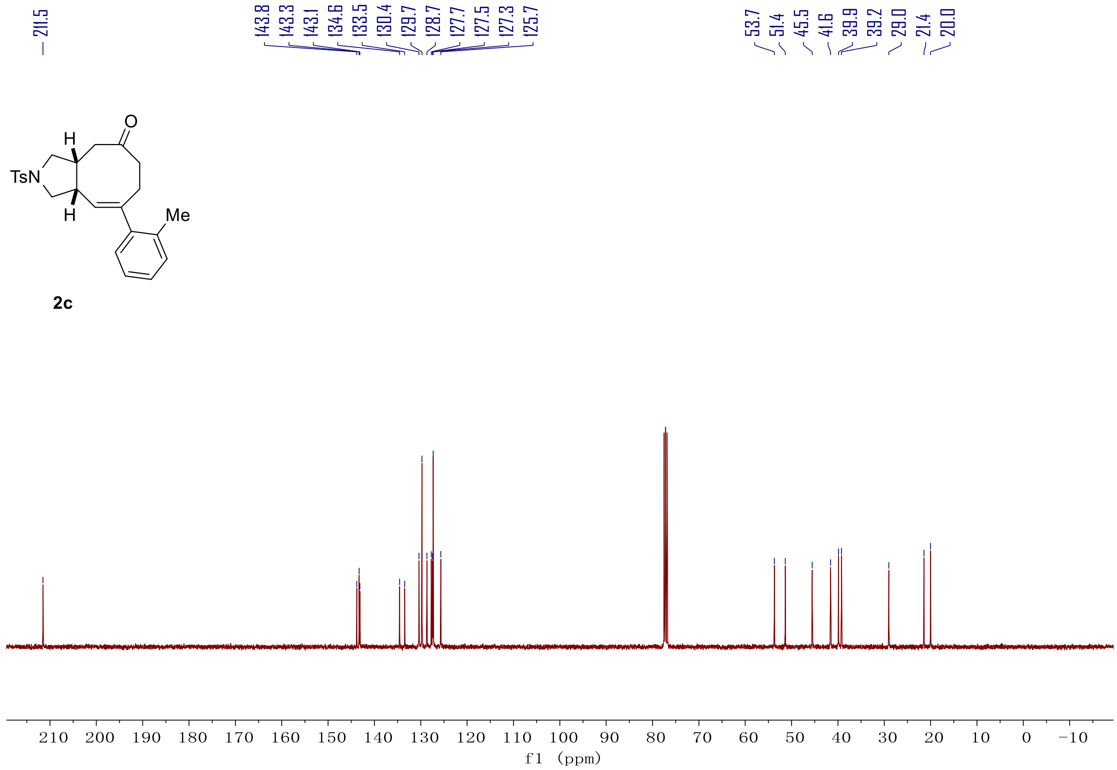
^{13}C NMR in $CDCl_3$, 101 MHz



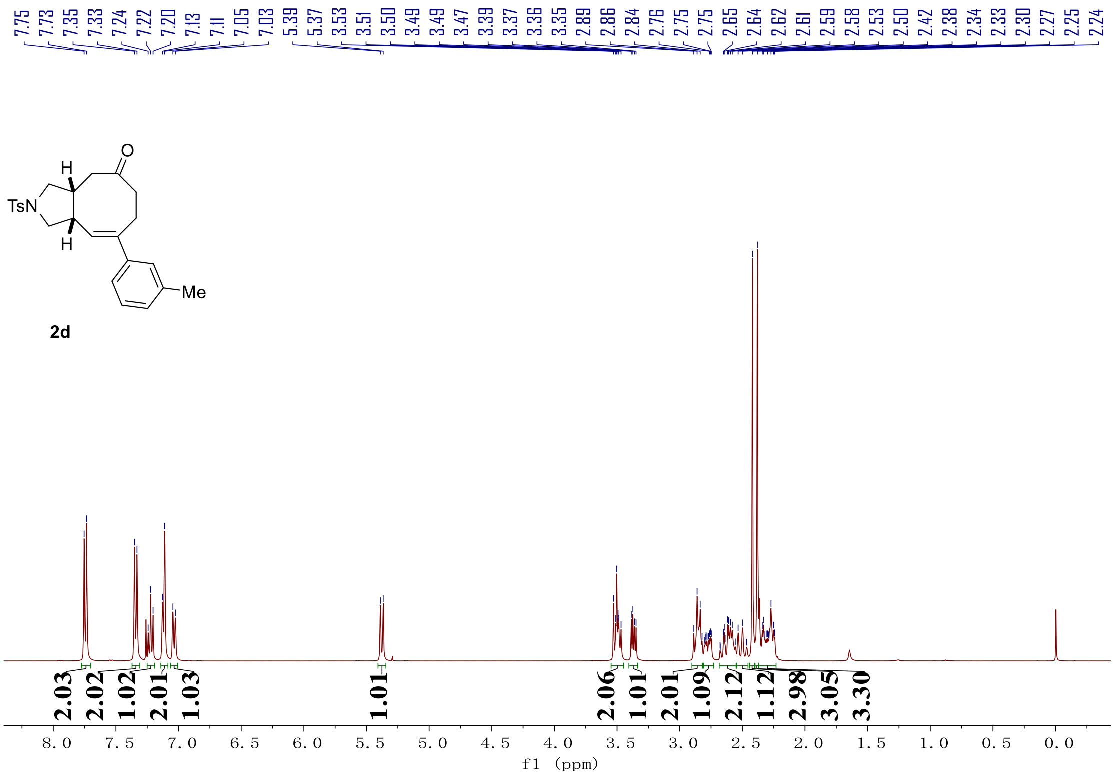
^{1}H NMR in $CDCl_3$, 400 MHz



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

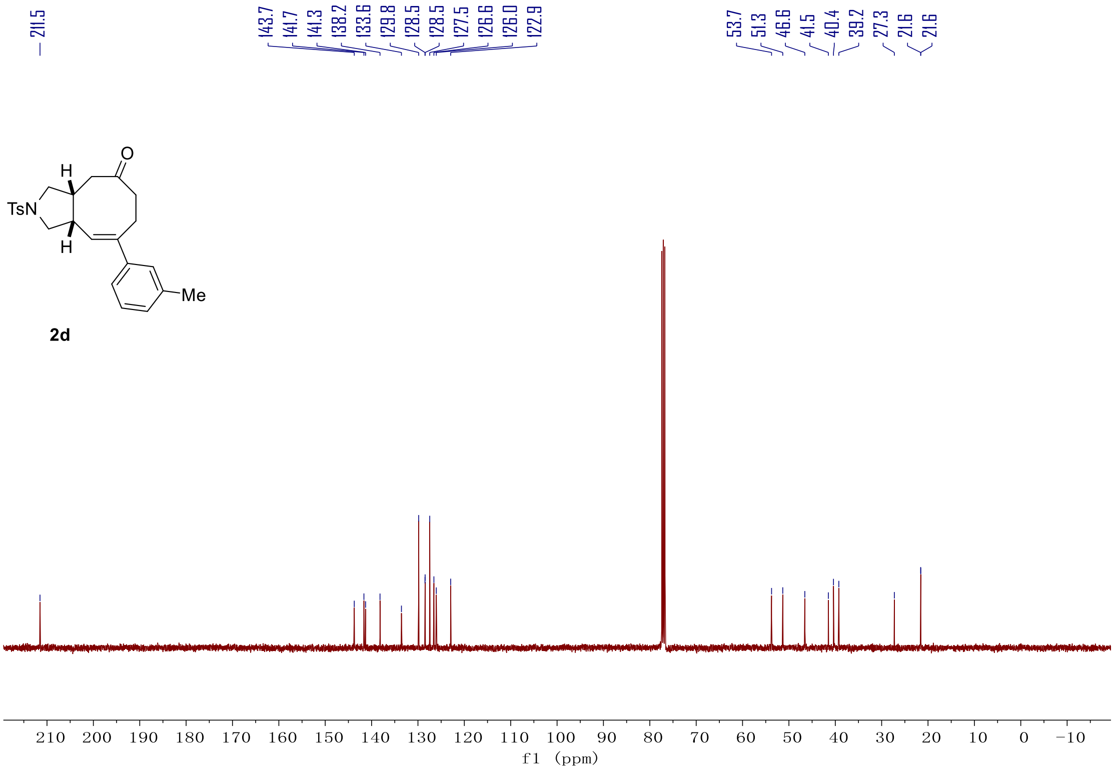


^{1}H NMR in $CDCl_3$, 400 MHz



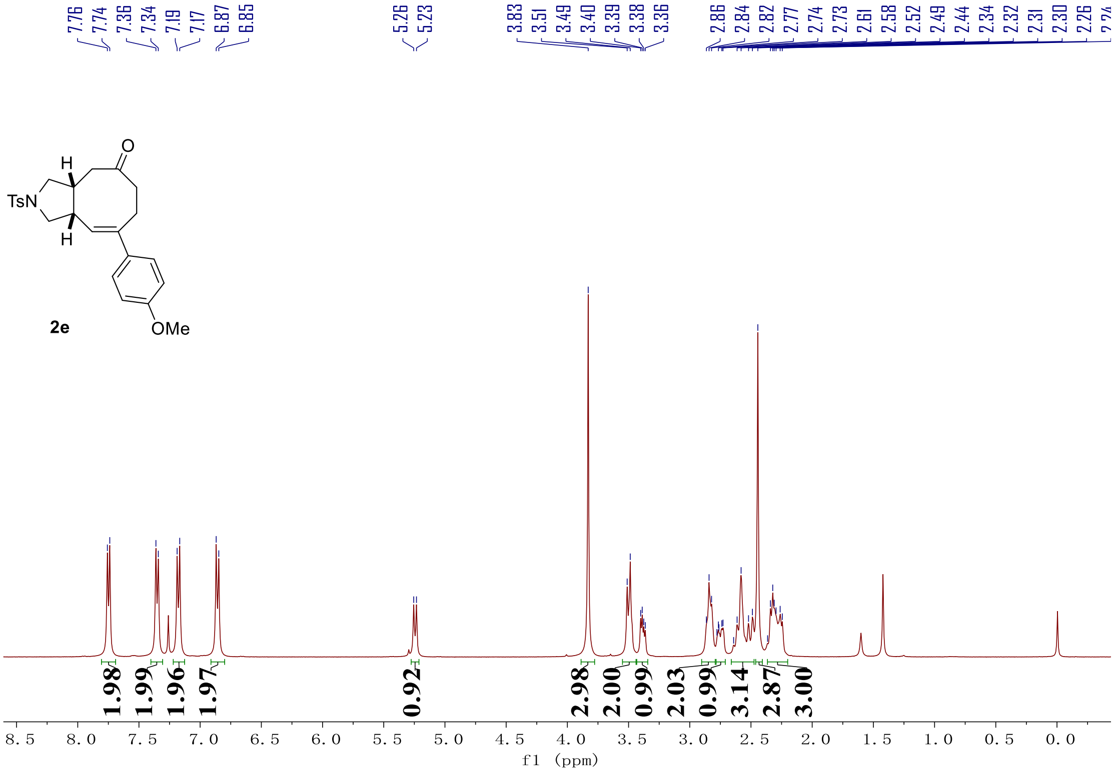
2d

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

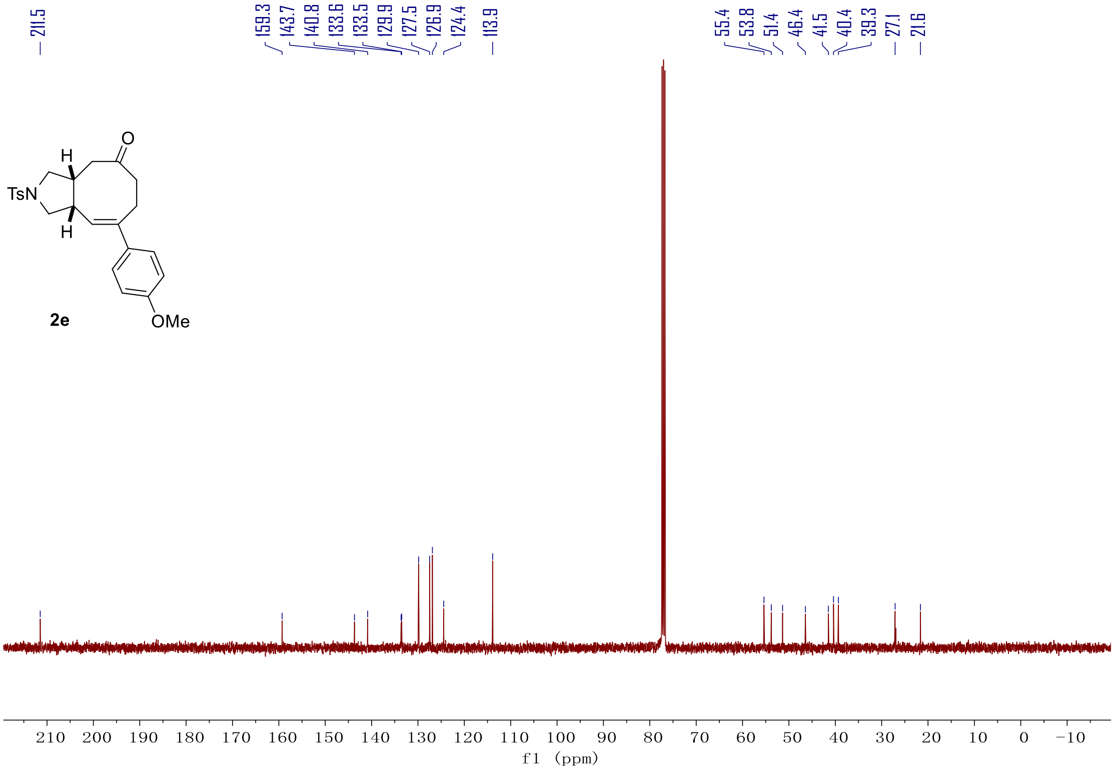


2d

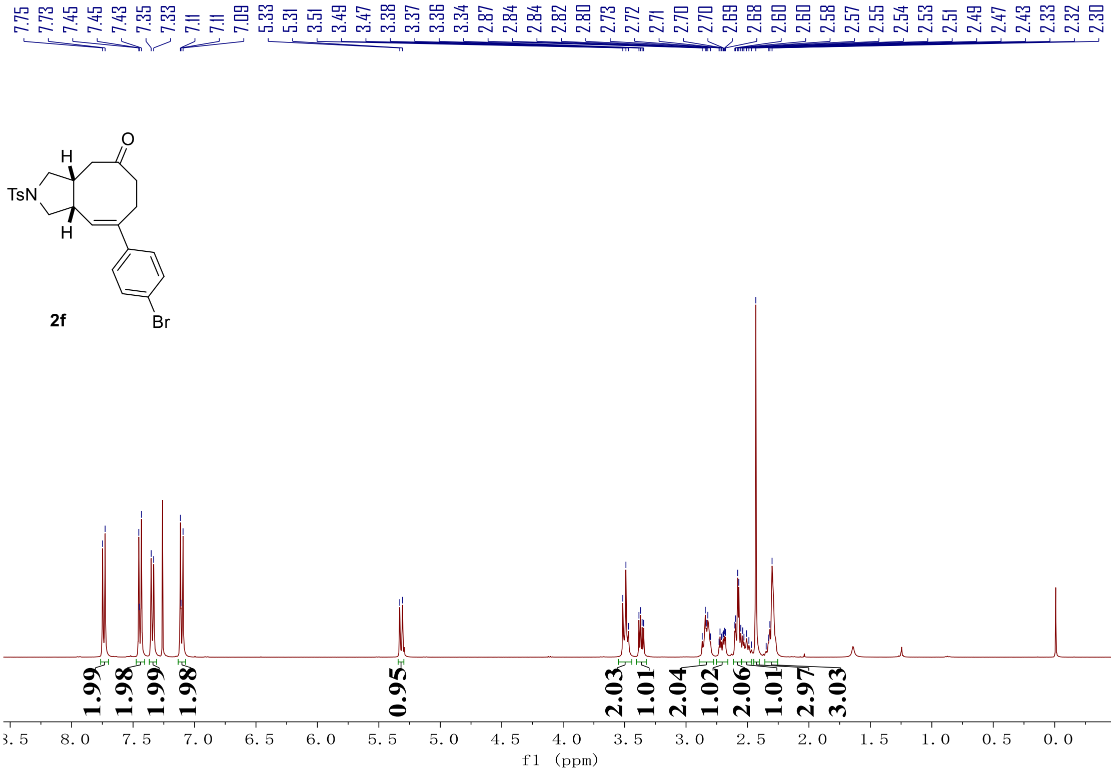
^{1}H NMR in $CDCl_3$, 400 MHz



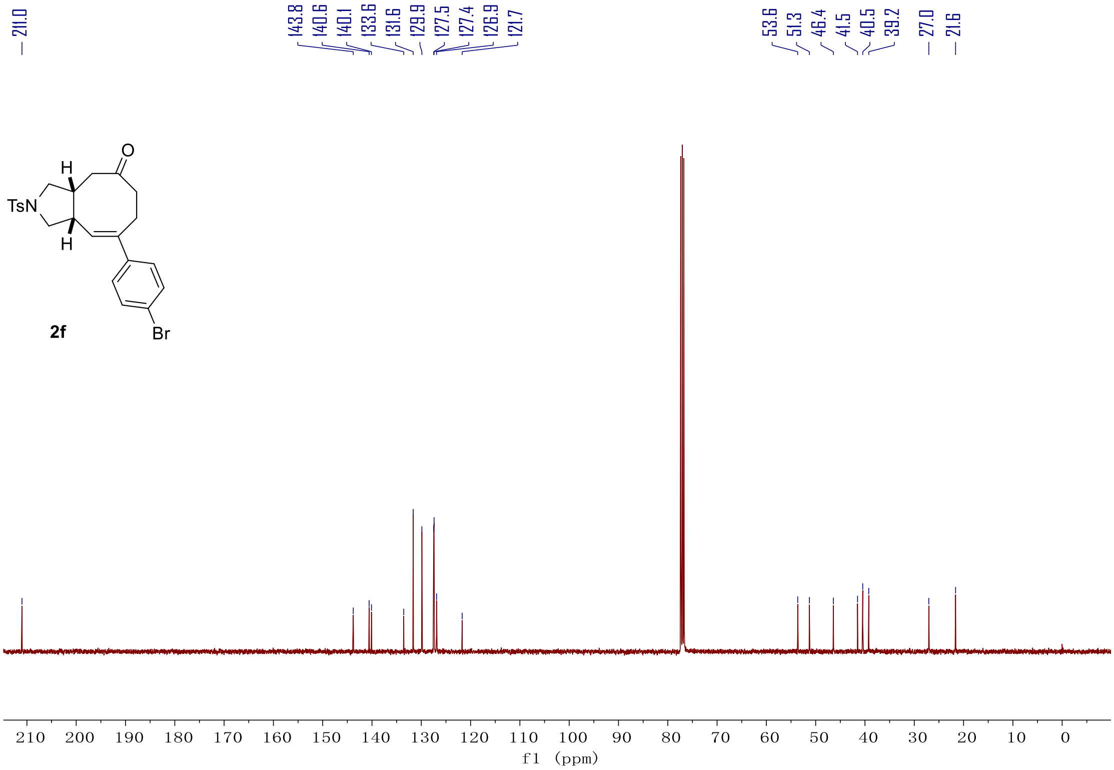
^{13}C NMR in $CDCl_3$, 101 MHz



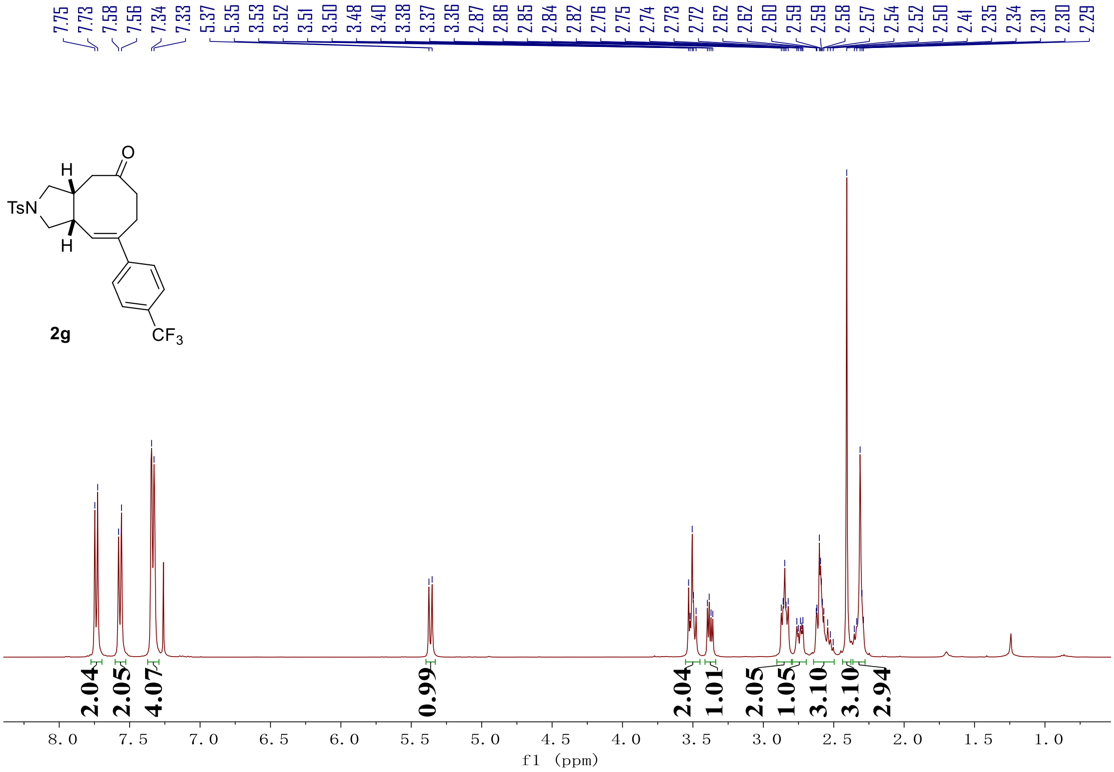
^{1}H NMR in CDCl3, 400 MHz



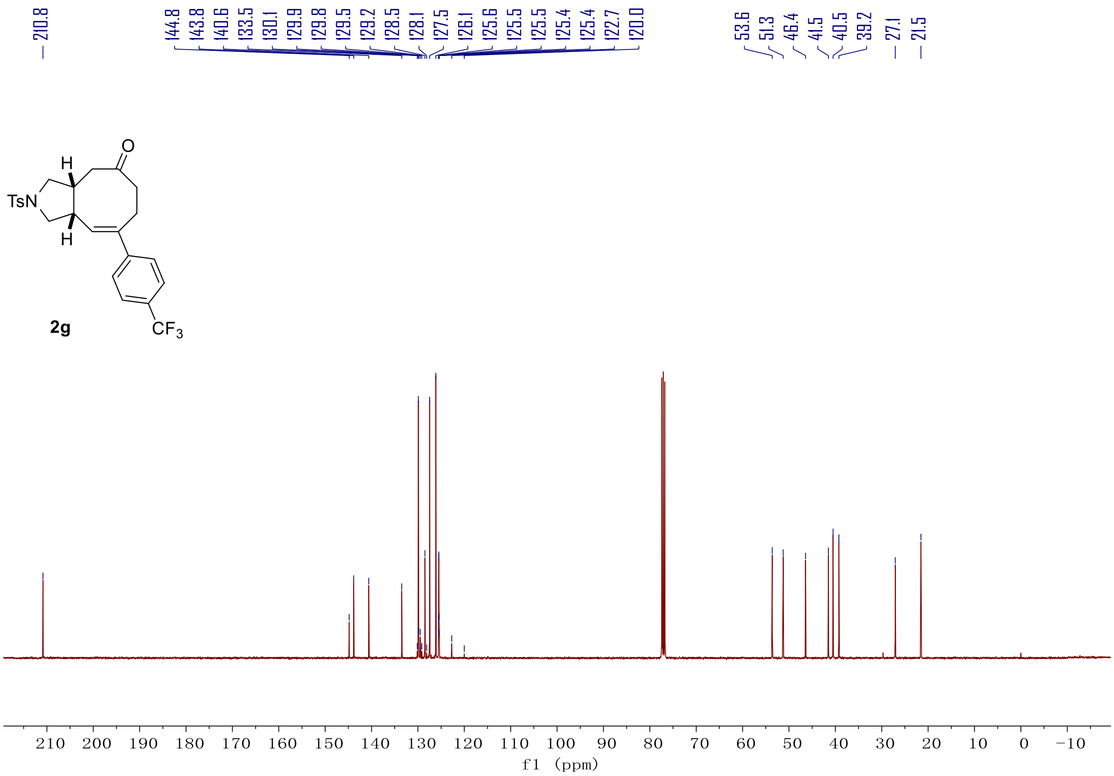
^{13}C NMR in $CDCl_3$, 101 MHz



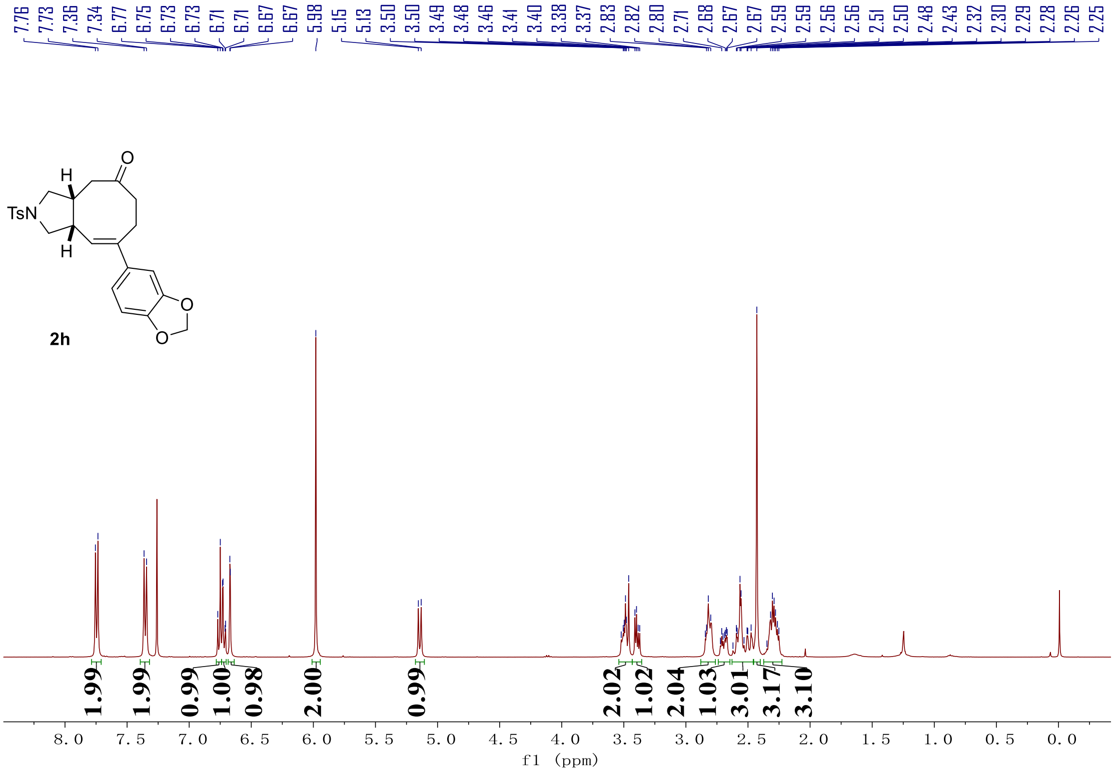
^{1}H NMR in CDCl$_3$, 400 MHz



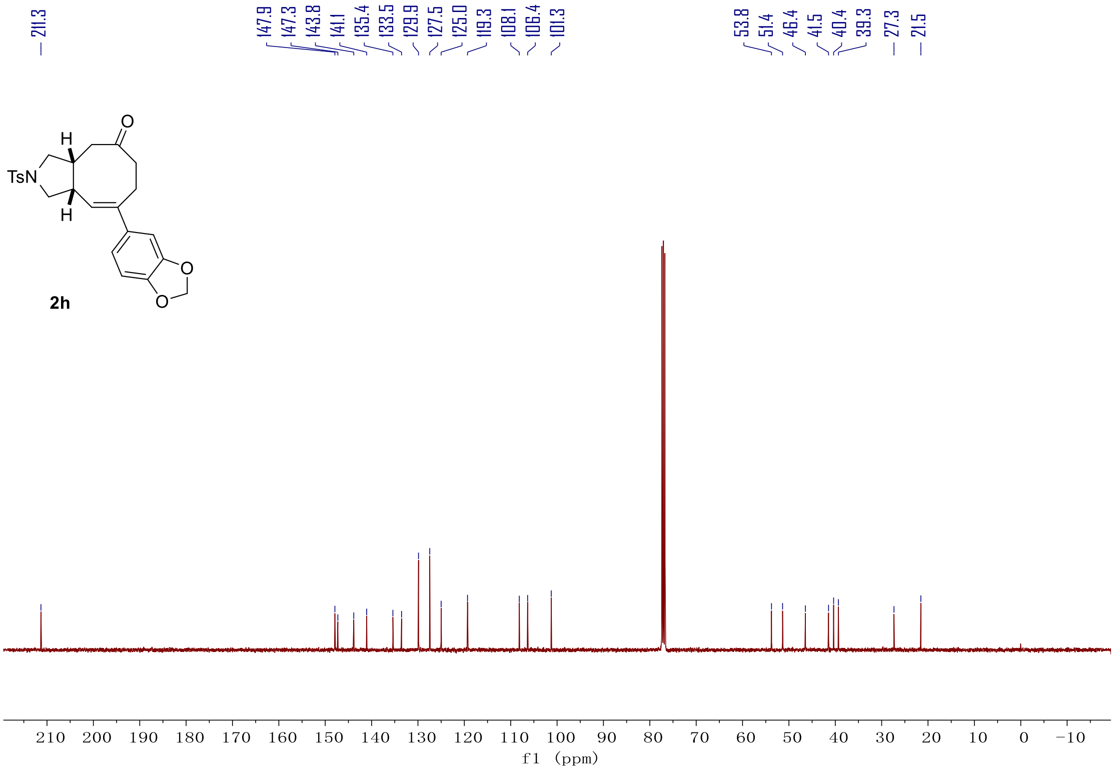
^{13}C NMR in CDCl$_3$, 101 MHz



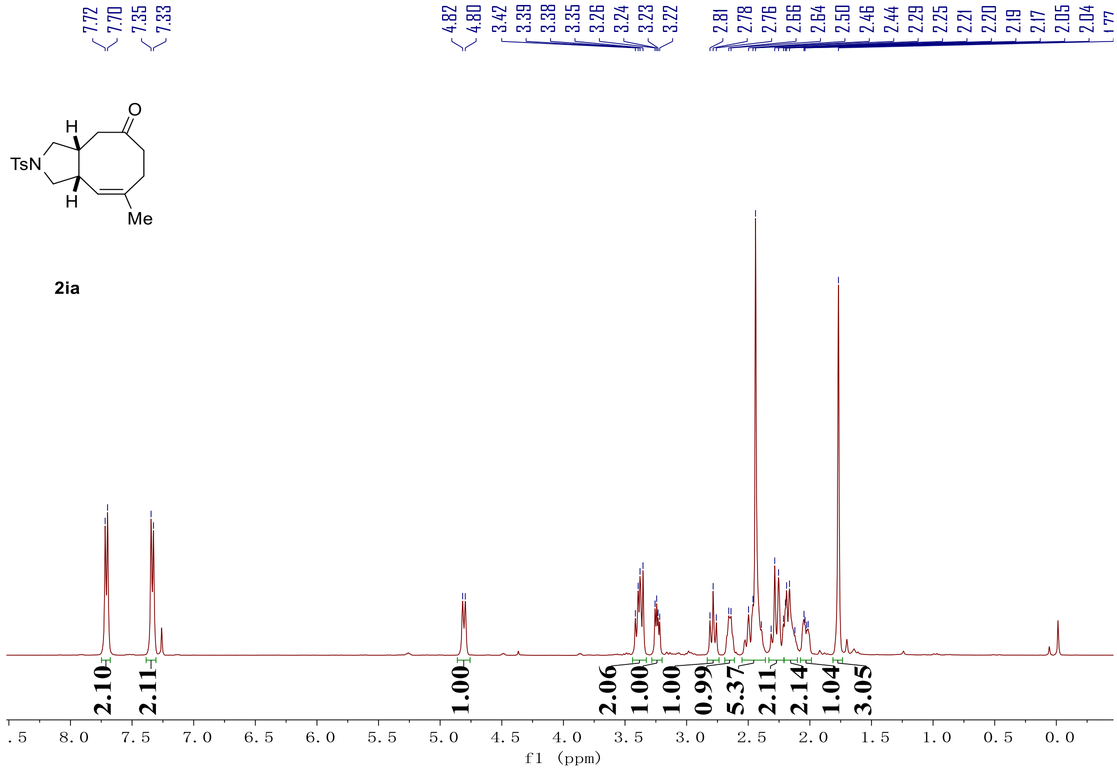
^{1}H NMR in $CDCl_3$, 400 MHz



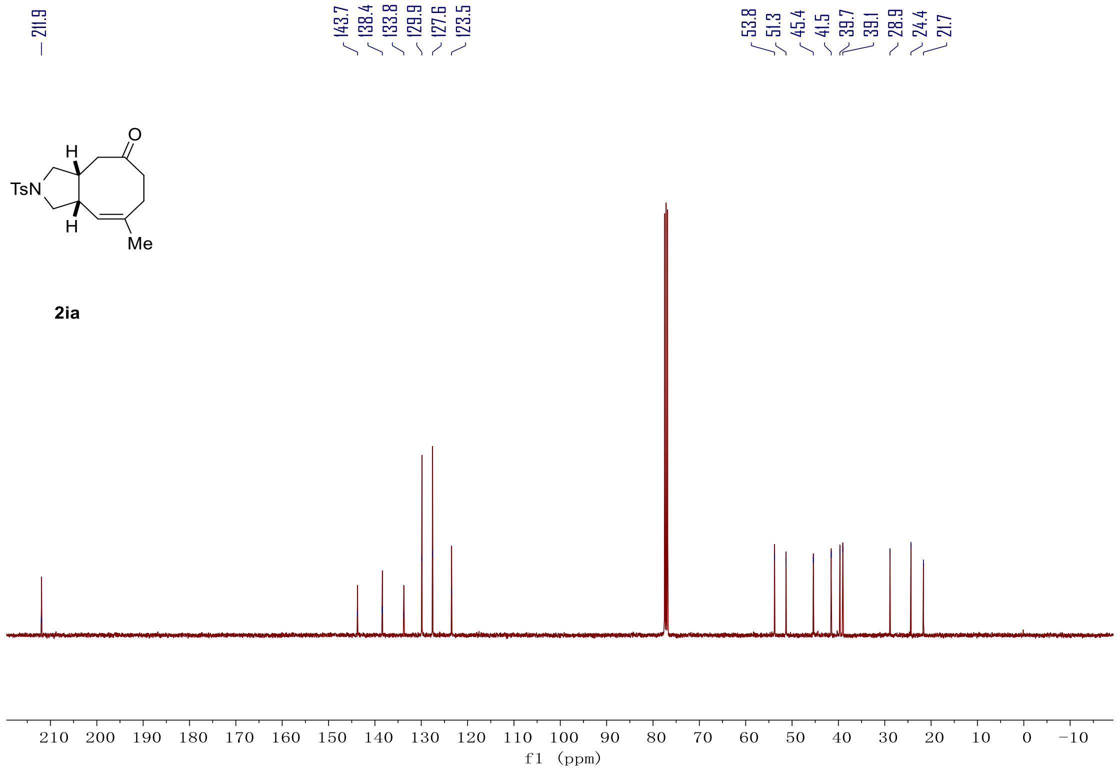
^{13}C NMR in $CDCl_3$, 101 MHz



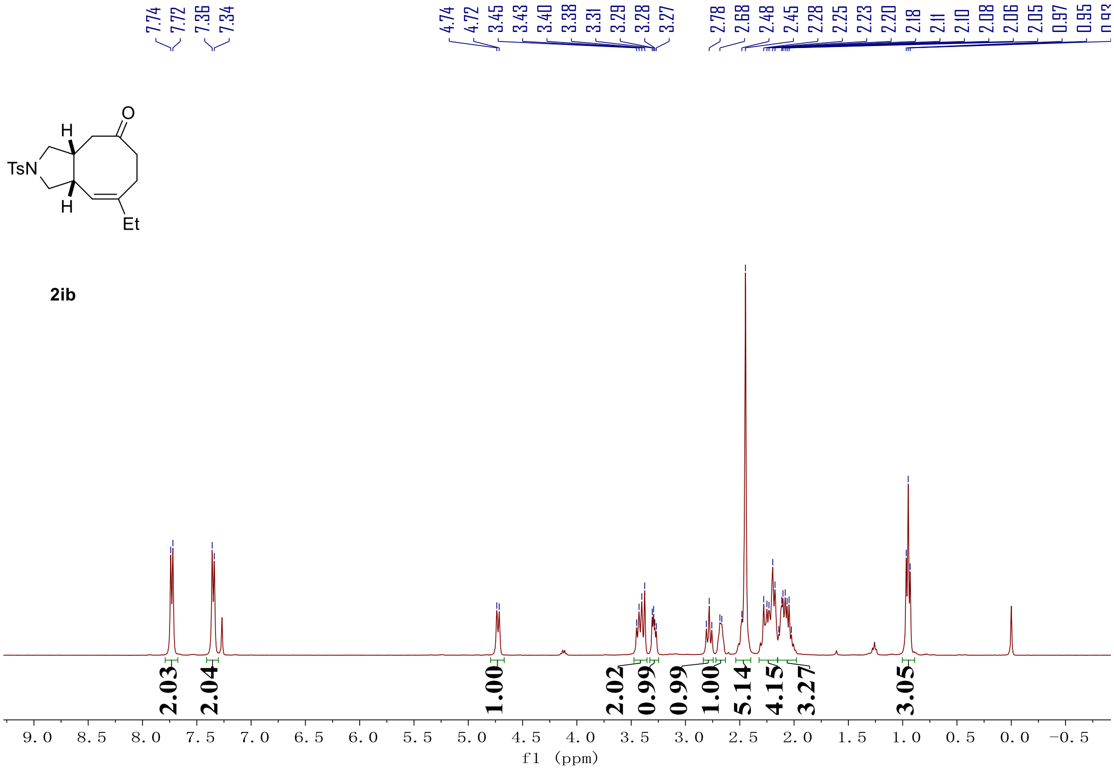
^{1}H NMR in $CDCl_3$, 400 MHz



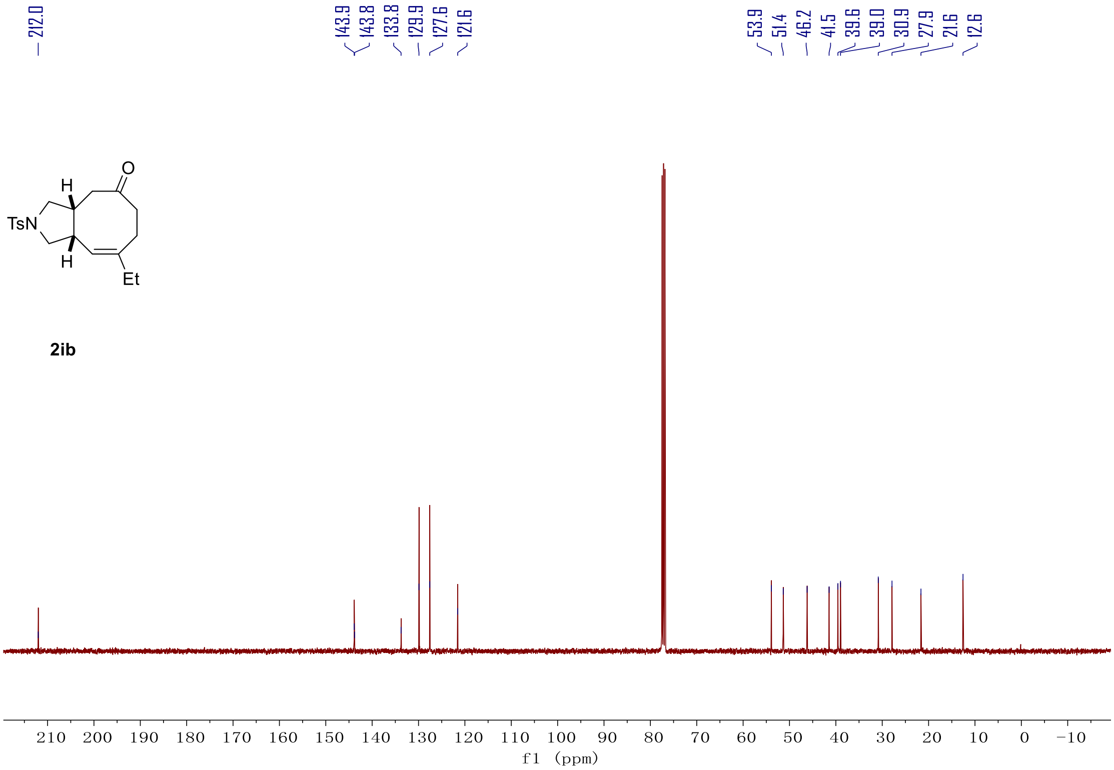
^{13}C NMR in $CDCl_3$, 101 MHz



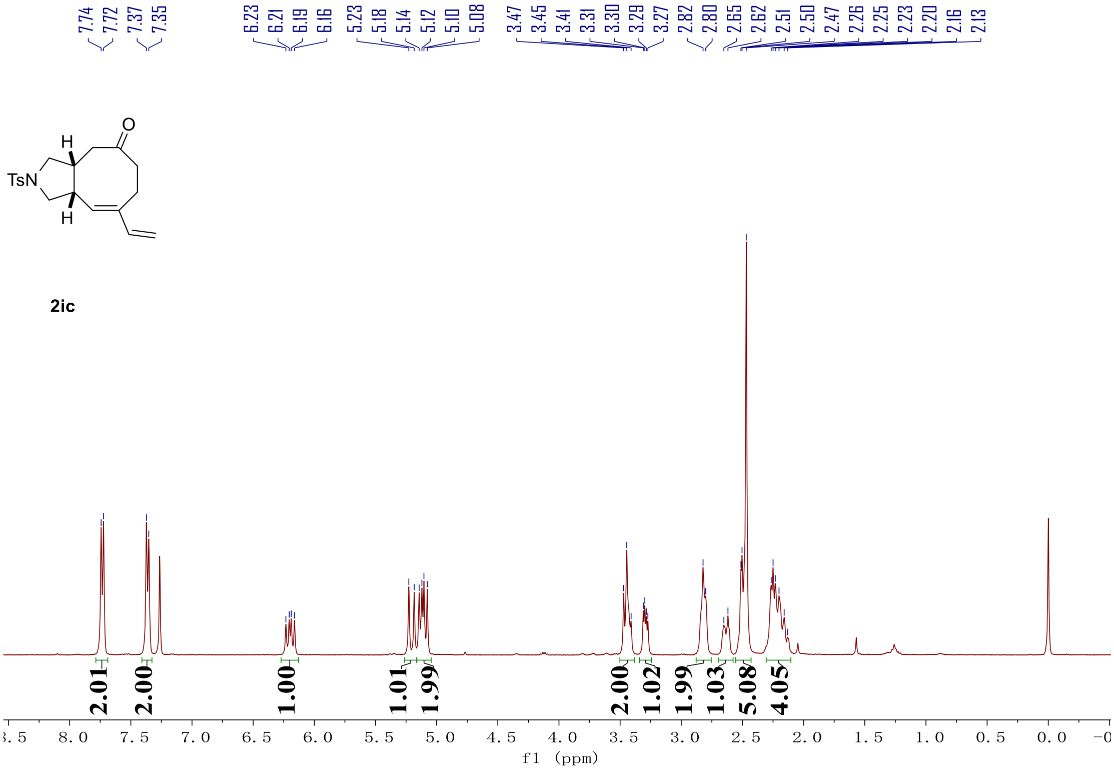
^{1}H NMR in $CDCl_3$, 400 MHz



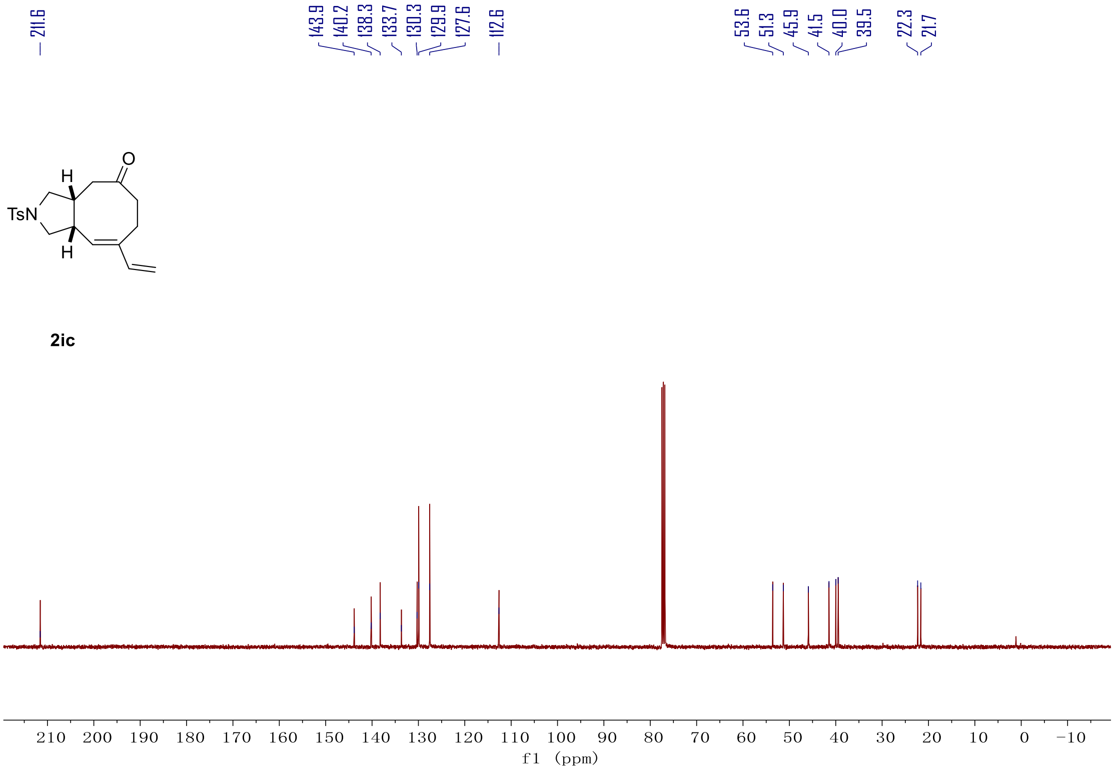
^{13}C NMR in $CDCl_3$, 101 MHz



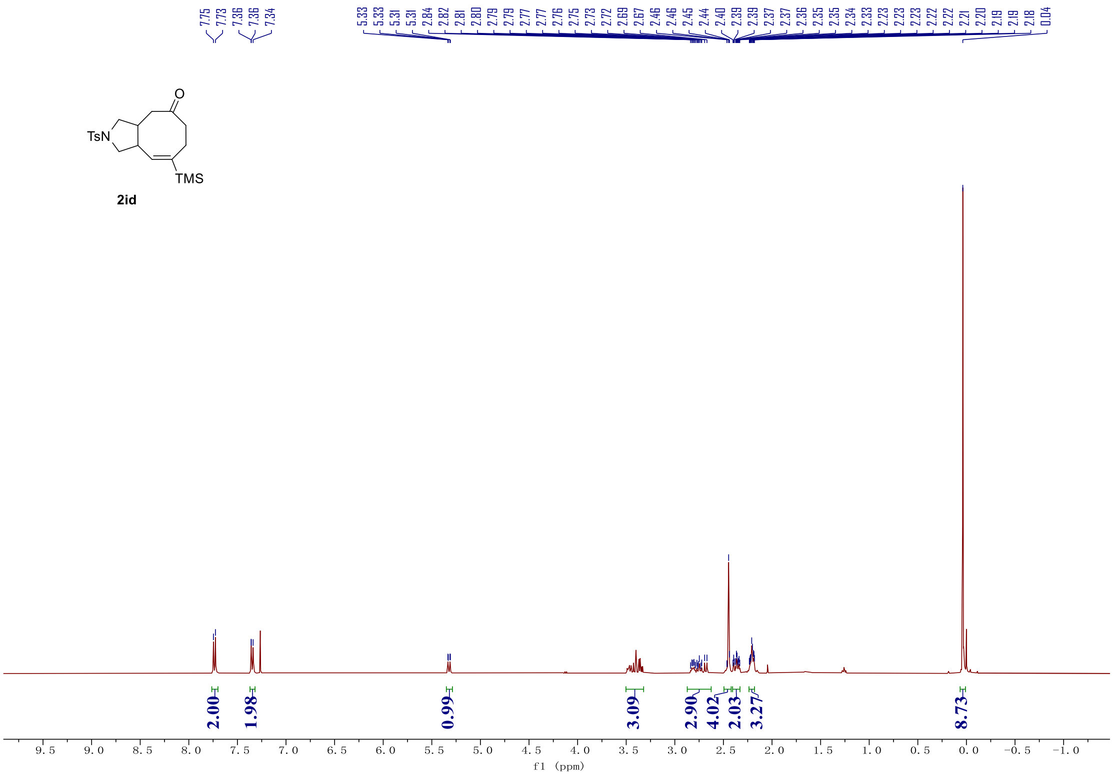
^{1}H NMR in $CDCl_3$, 400 MHz



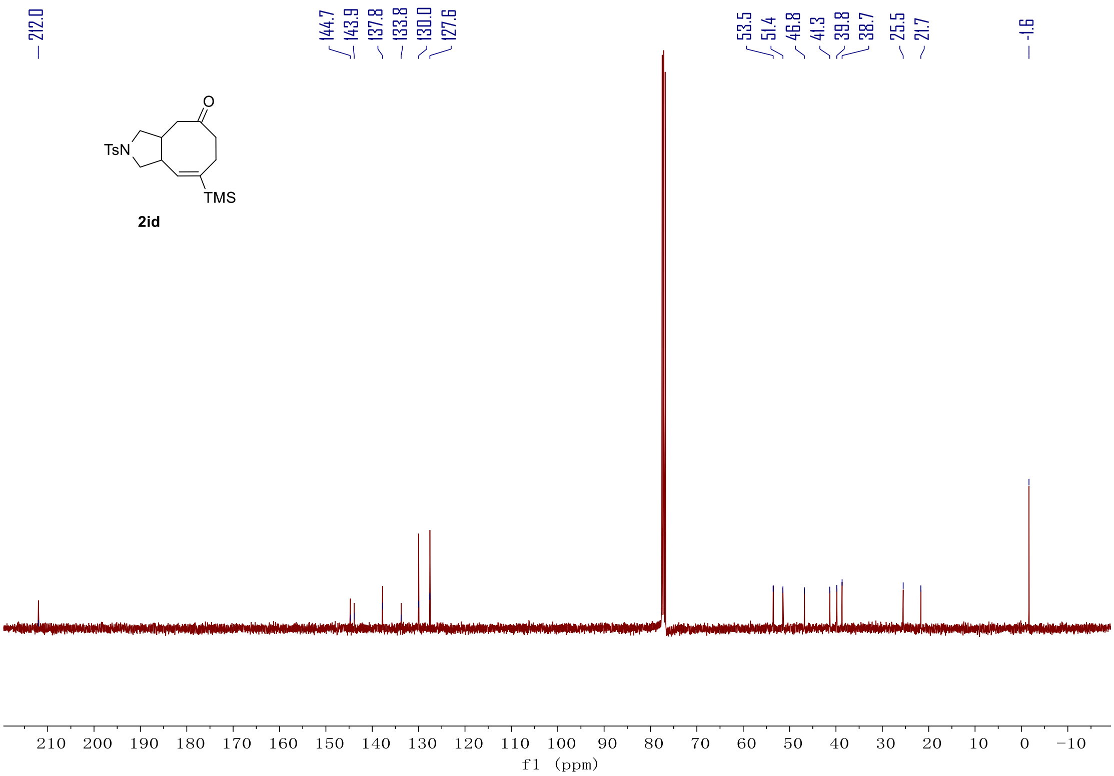
^{13}C NMR in $CDCl_3$, 101 MHz



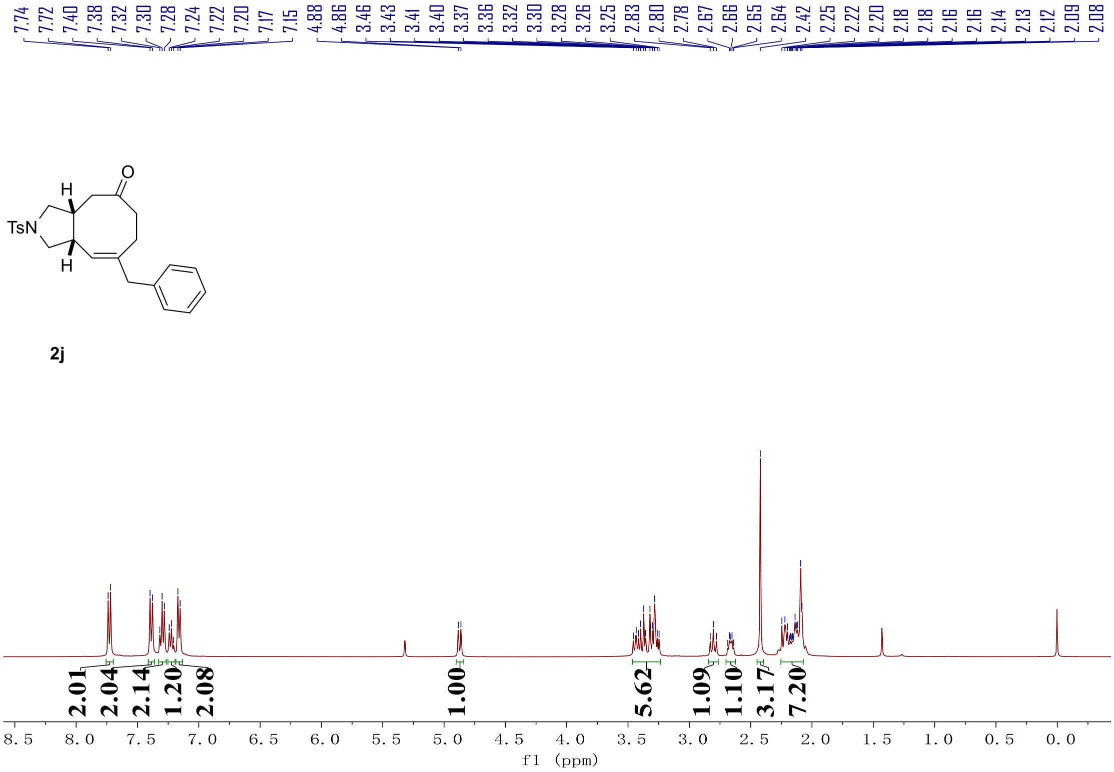
^{1}H NMR in $CDCl_3$, 400 MHz



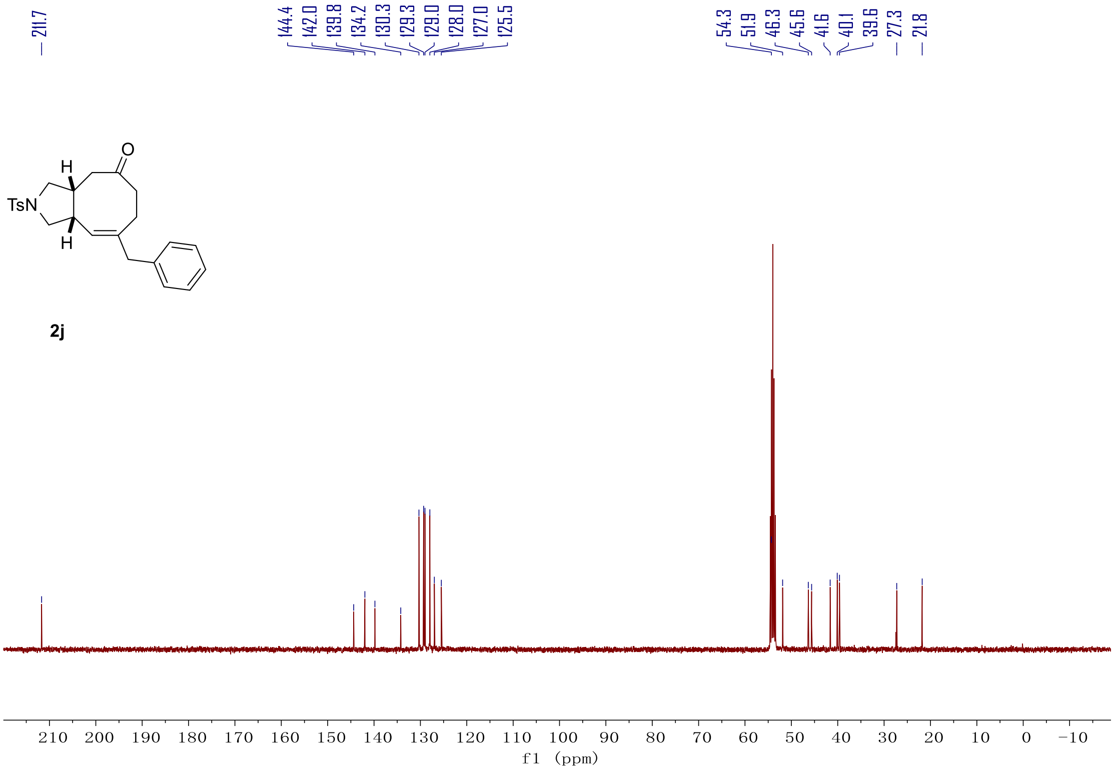
^{13}C NMR in $CDCl_3$, 101 MHz



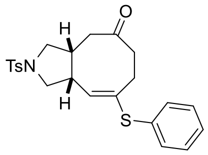
[1]H NMR in CD_2Cl_2, 400 MHz



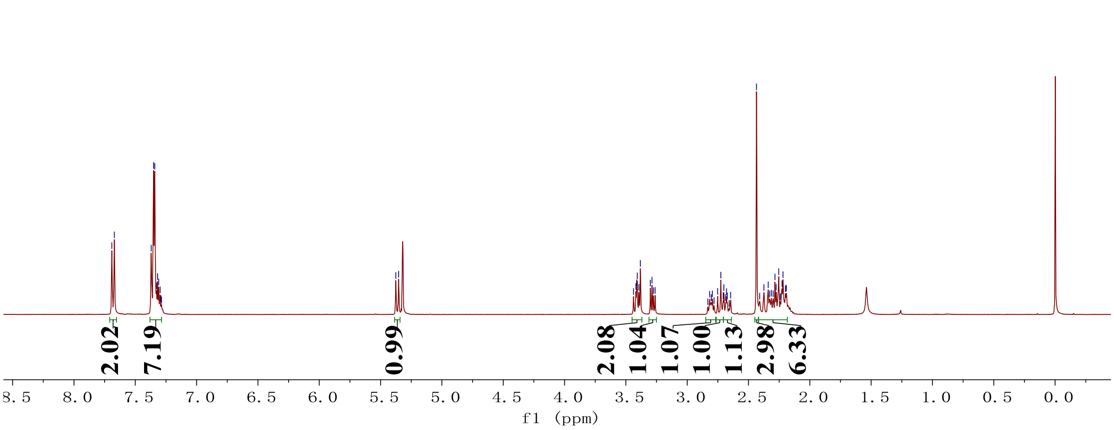
[13]C NMR in CD_2Cl_2, 101 MHz



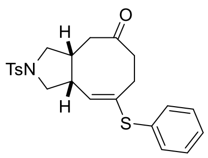
^{1}H NMR in CD_2Cl_2, 400 MHz



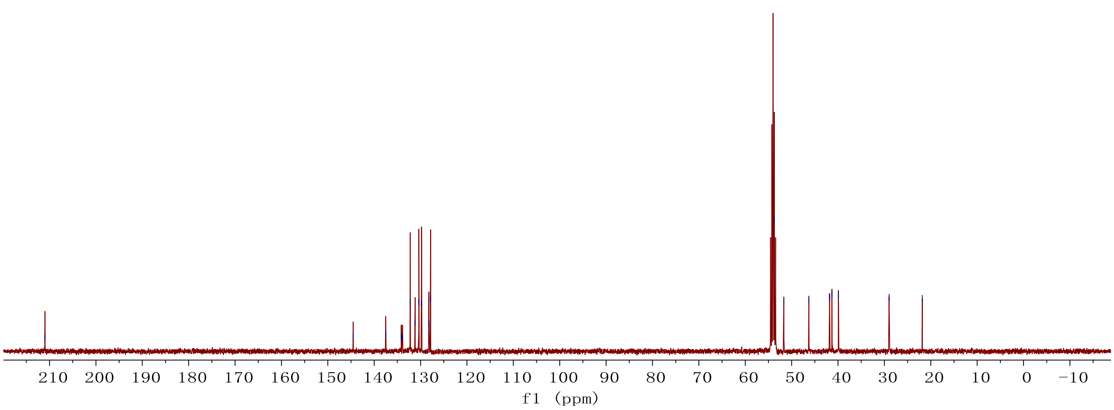
2k



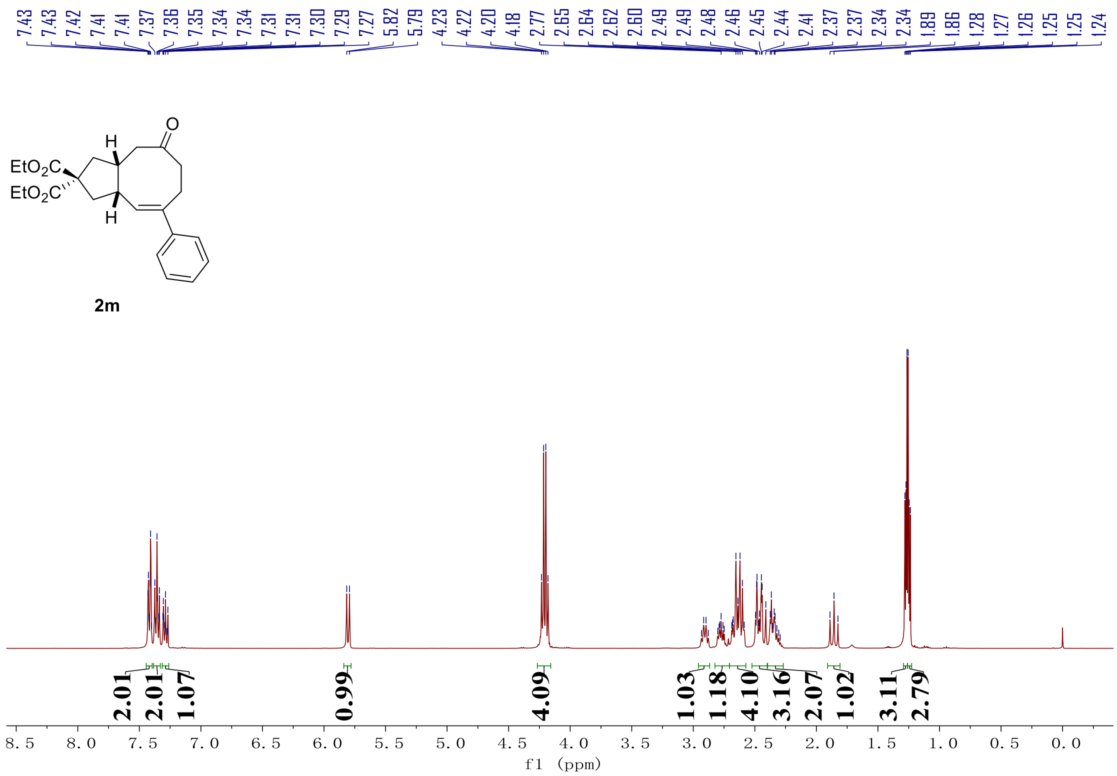
^{1}H NMR in CD_2Cl_2, 101 MHz



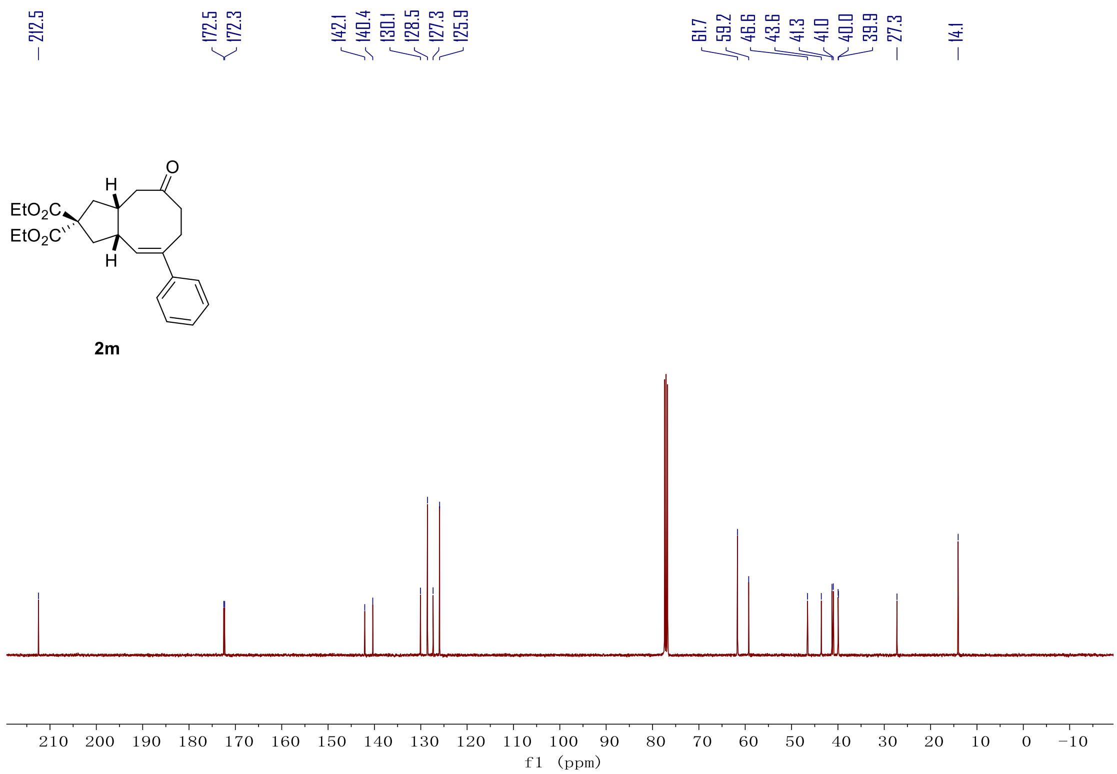
2k



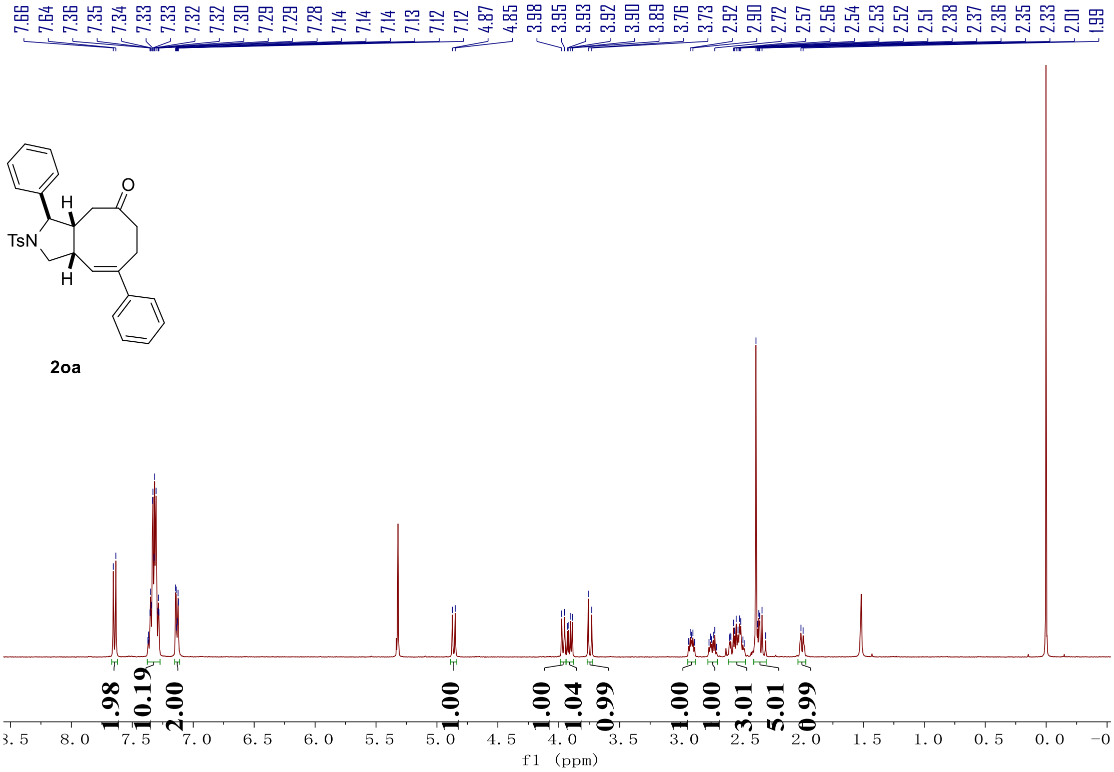
^1H NMR in $CDCl_3$, 400 MHz



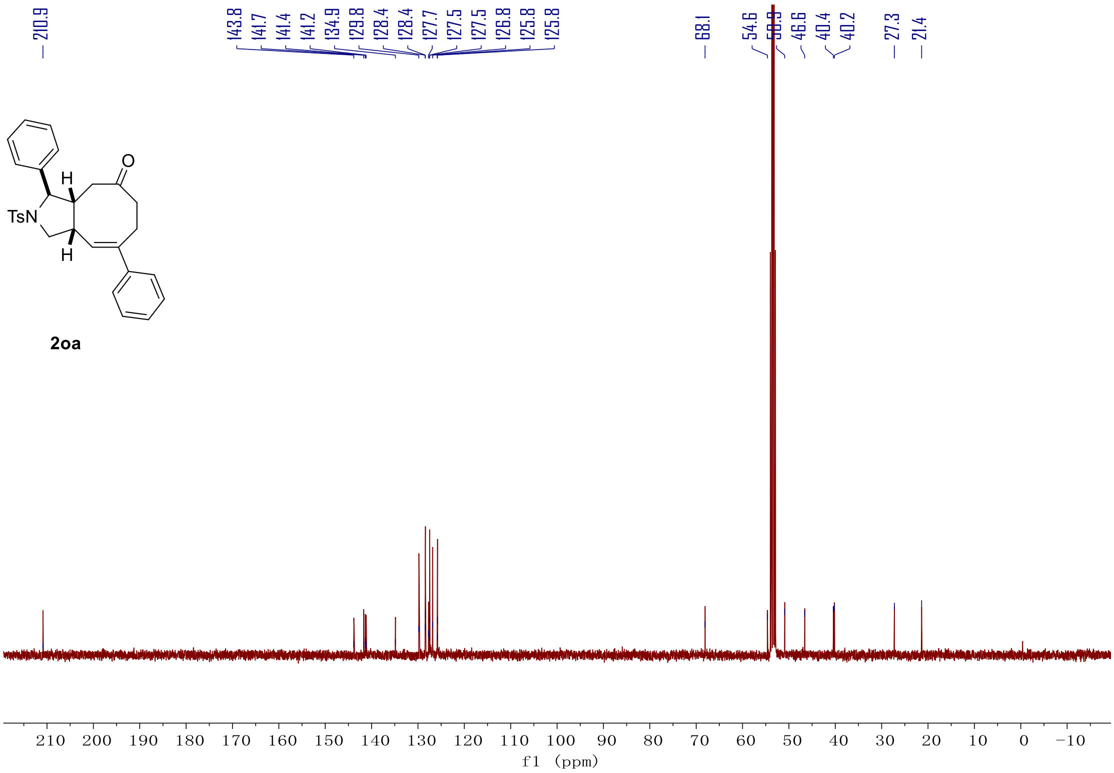
^{13}C NMR in $CDCl_3$, 101 MHz



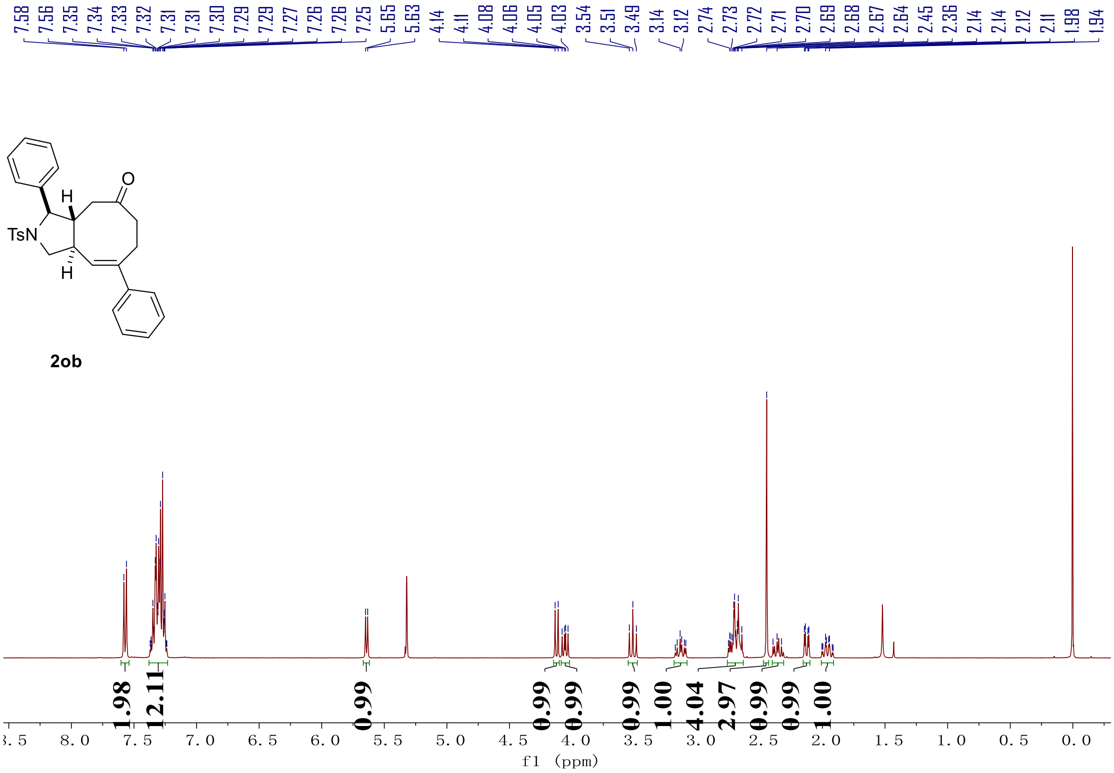
¹H NMR in CD_2Cl_2, 400 MHz



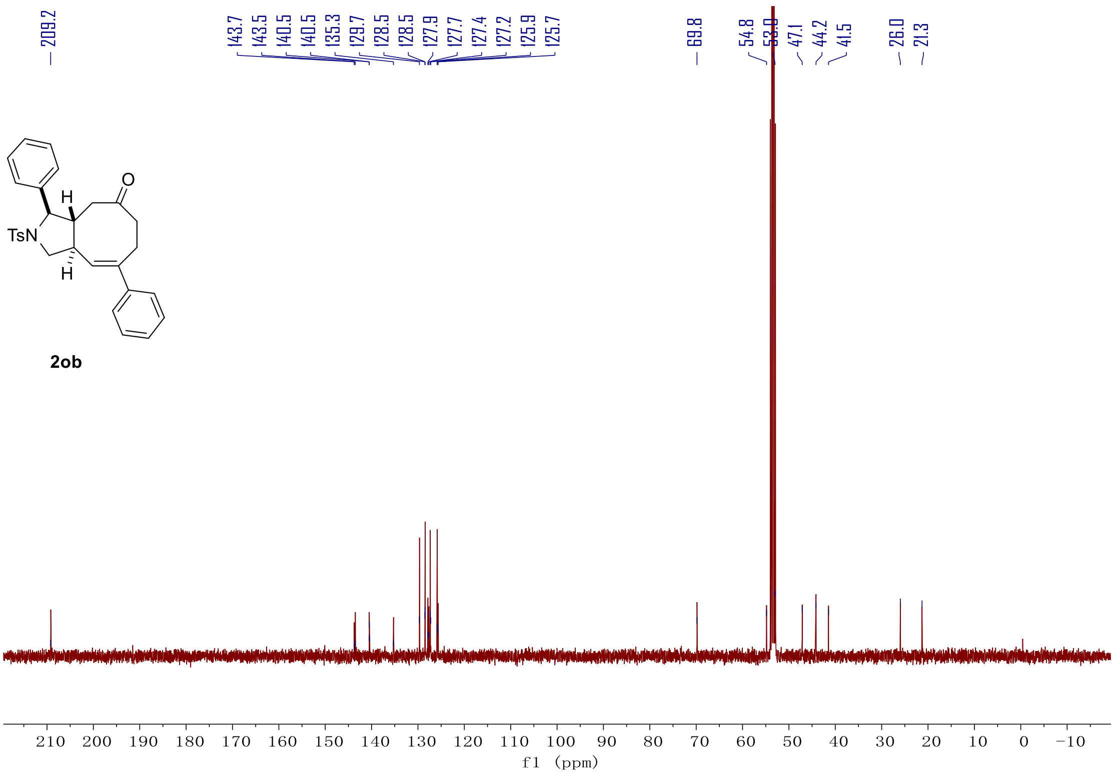
¹³C NMR in CD_2Cl_2, 101 MHz



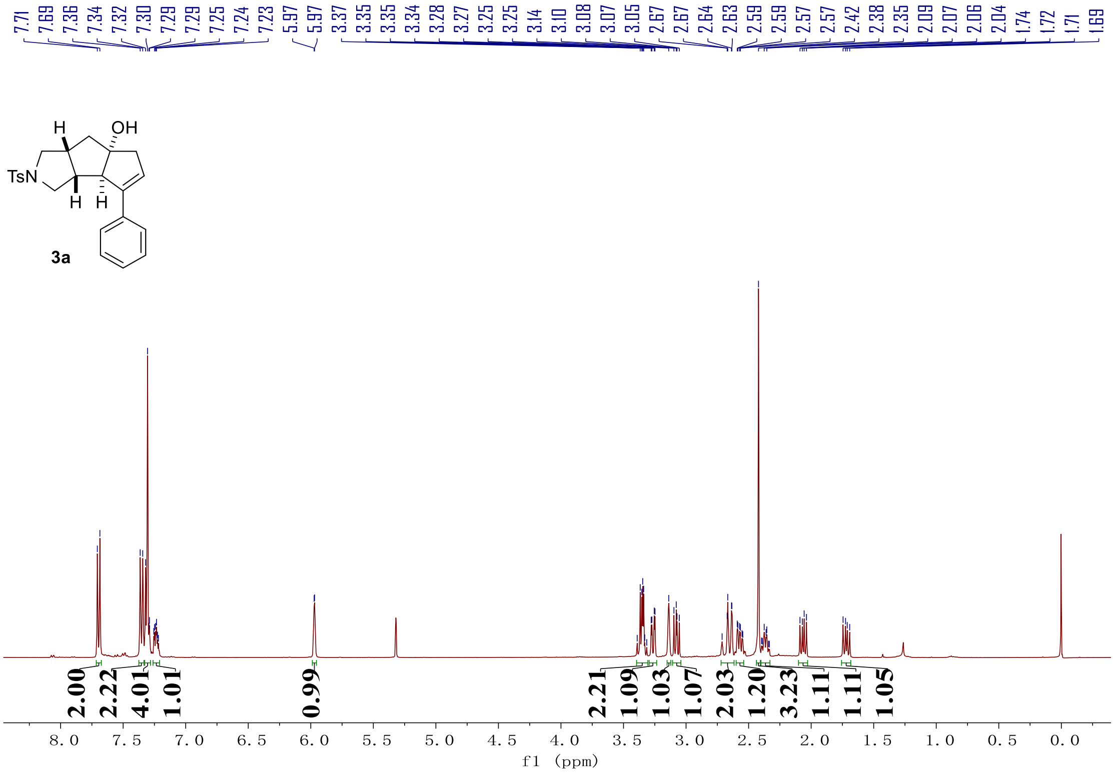
^{1}H NMR in CD_2Cl_2, 400 MHz



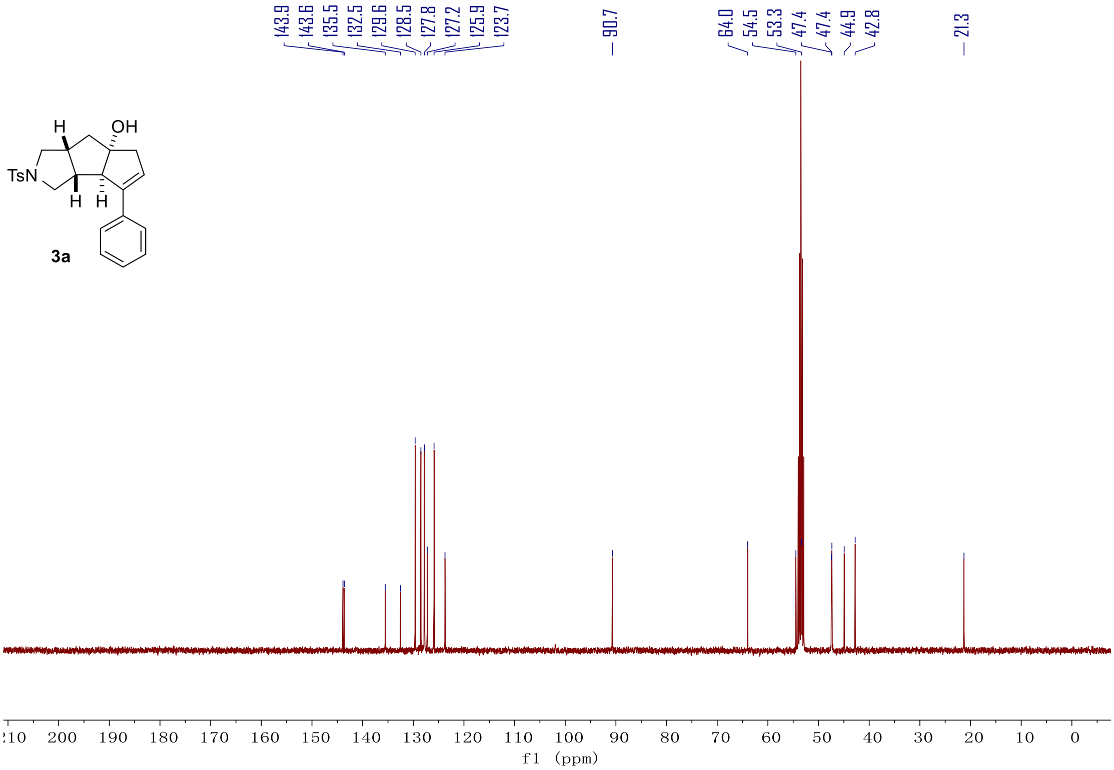
^{13}C NMR in CD_2Cl_2, 101 MHz



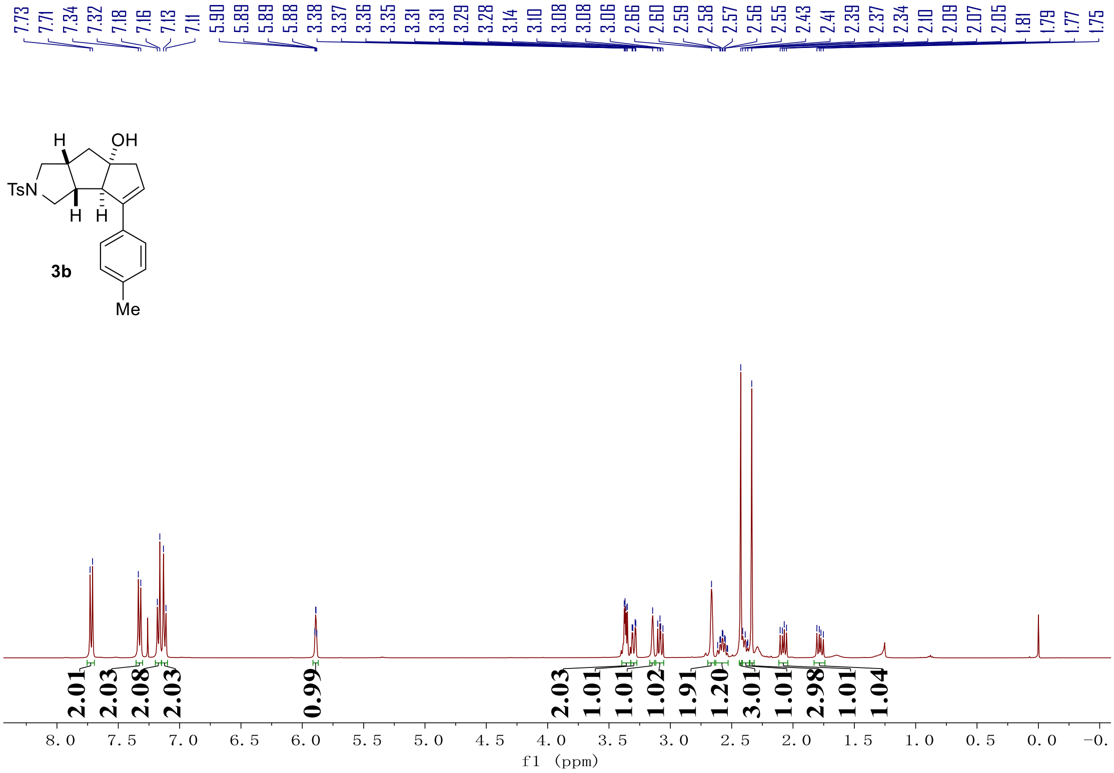
^{1}H NMR in CD_2Cl_2, 400 MHz



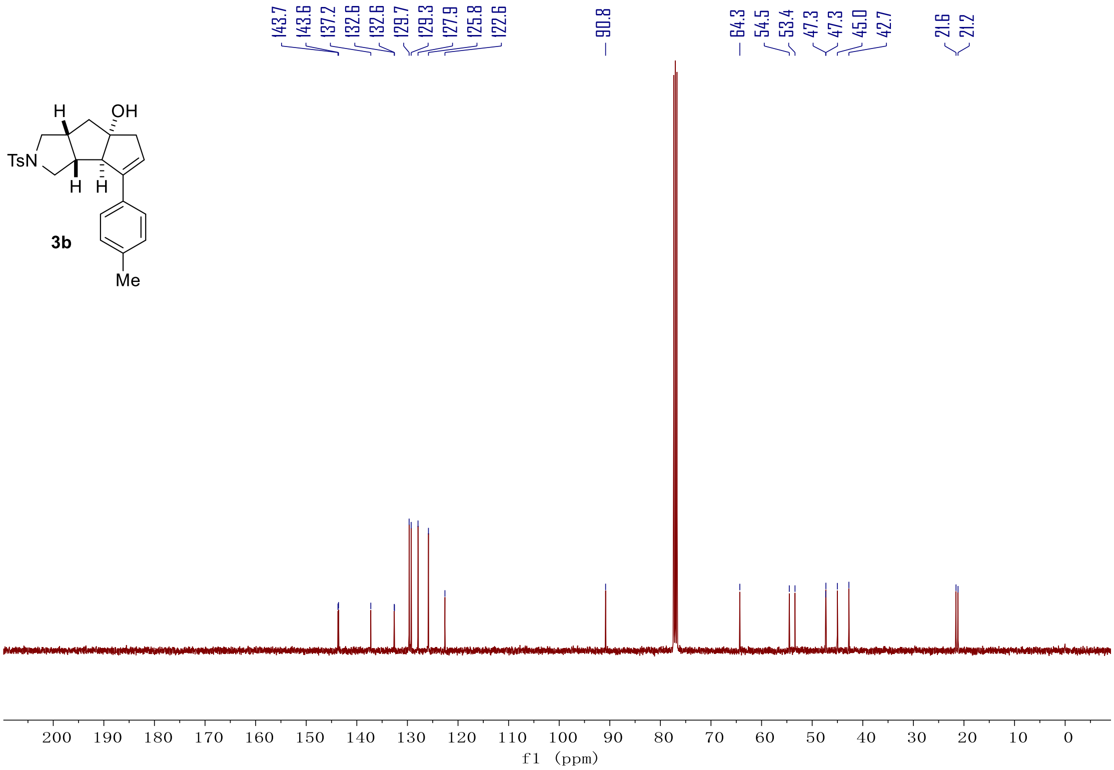
^{13}C NMR in CD_2Cl_2, 101 MHz



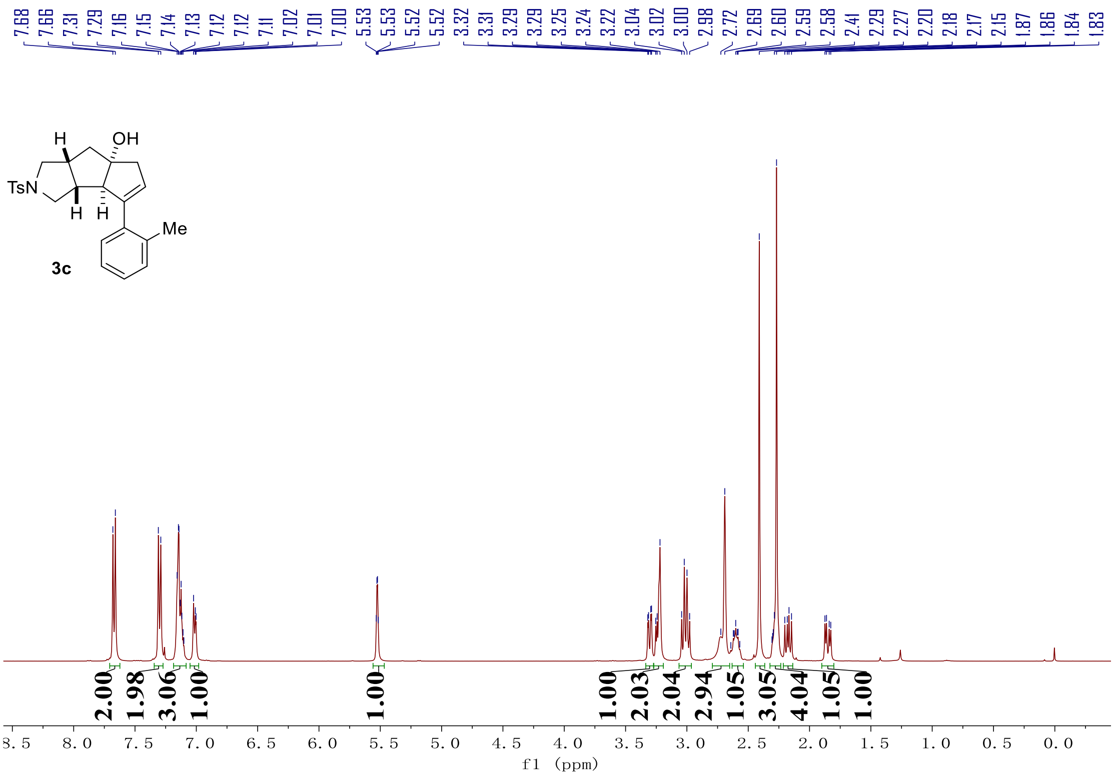
^1H NMR in $CDCl_3$, 400 MHz



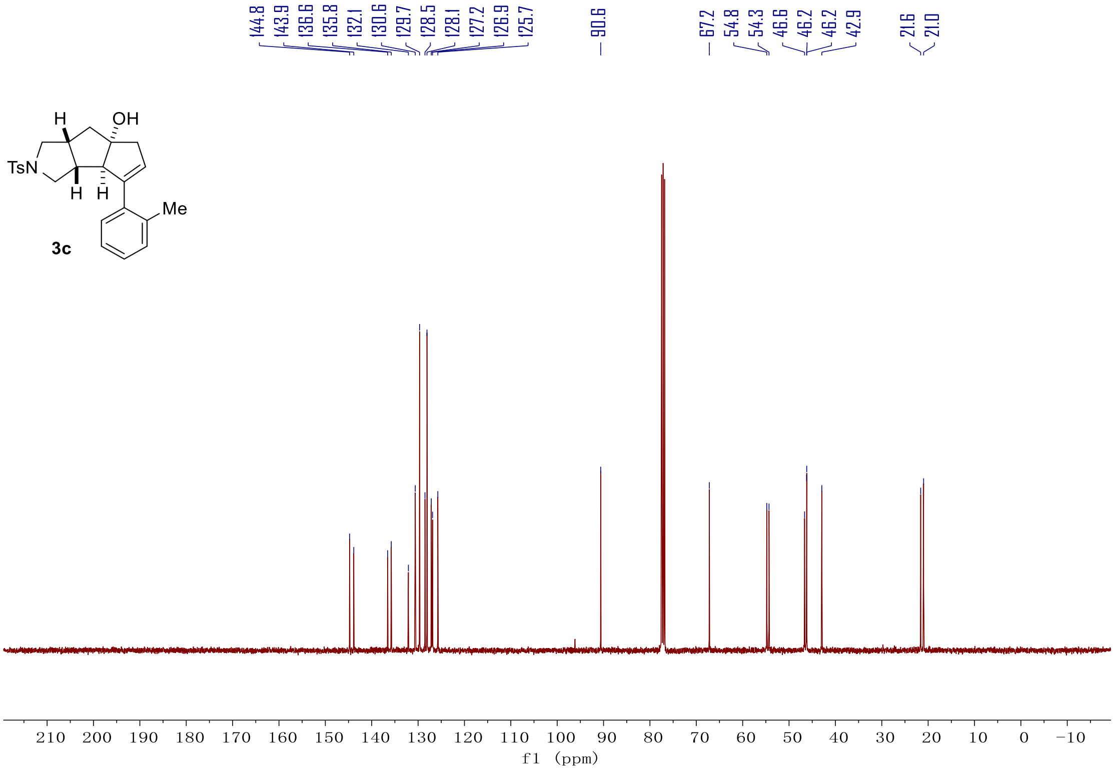
^{13}C NMR in $CDCl_3$, 101 MHz



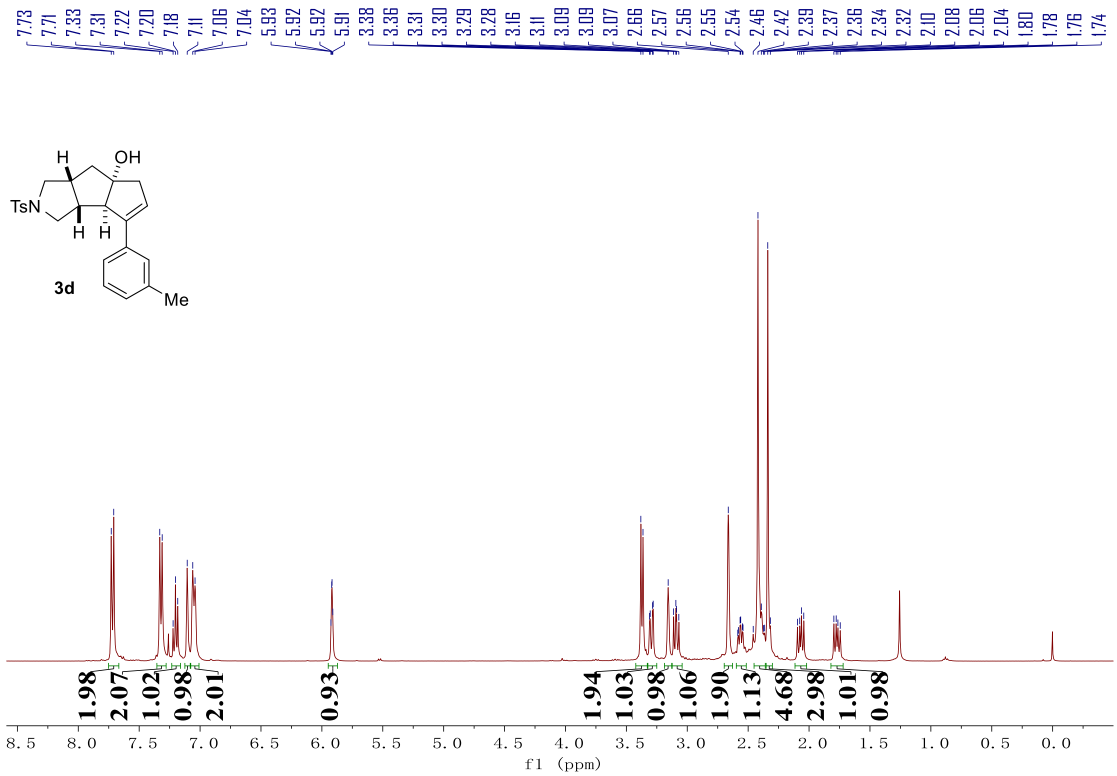
^{1}H NMR in $CDCl_3$, 400 MHz



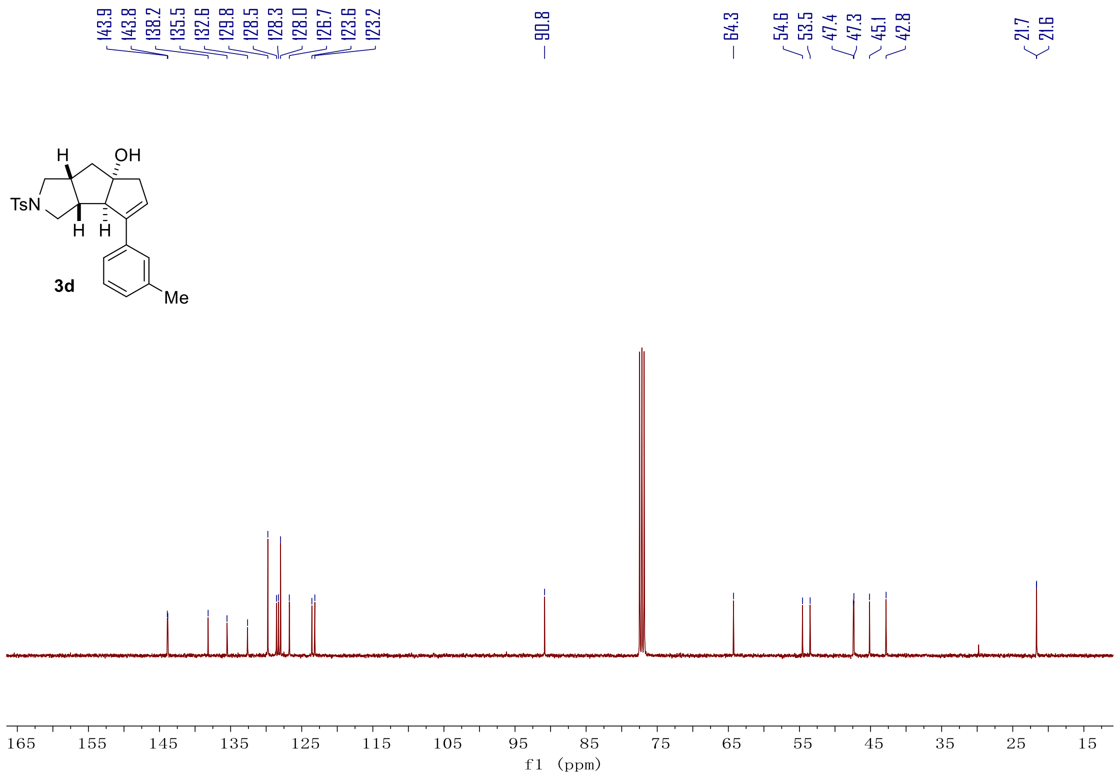
^{13}C NMR in $CDCl_3$, 101 MHz



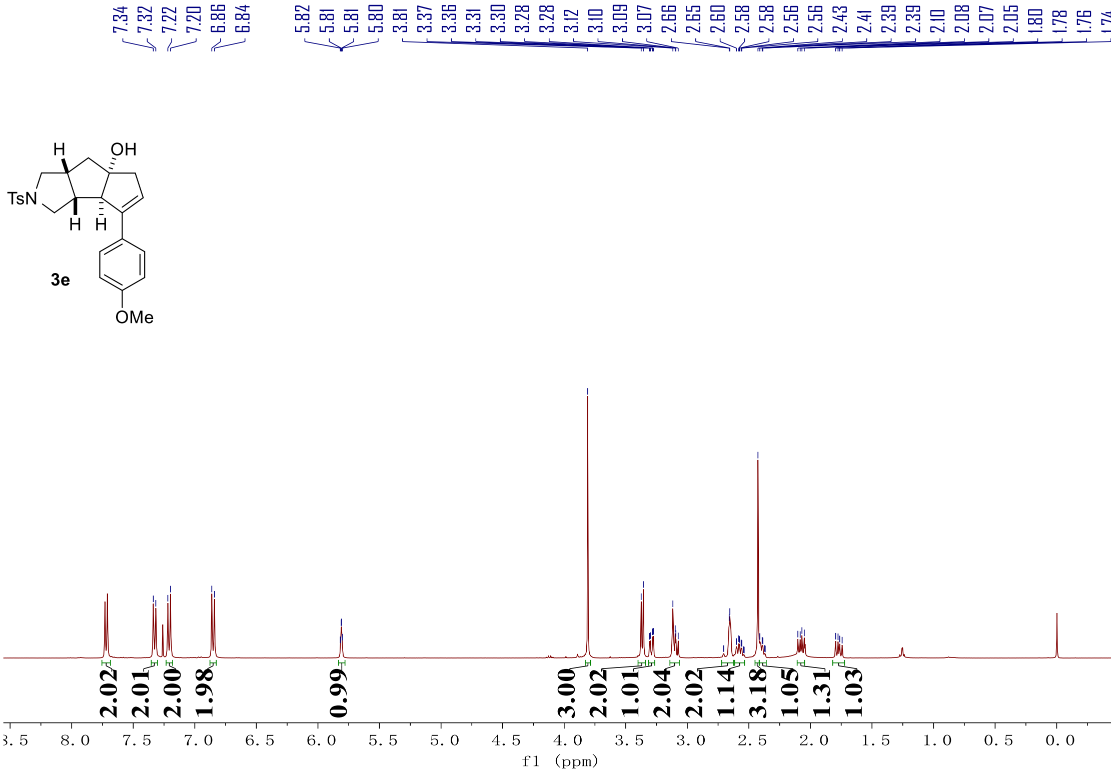
[1]H NMR in $CDCl_3$, 400 MHz



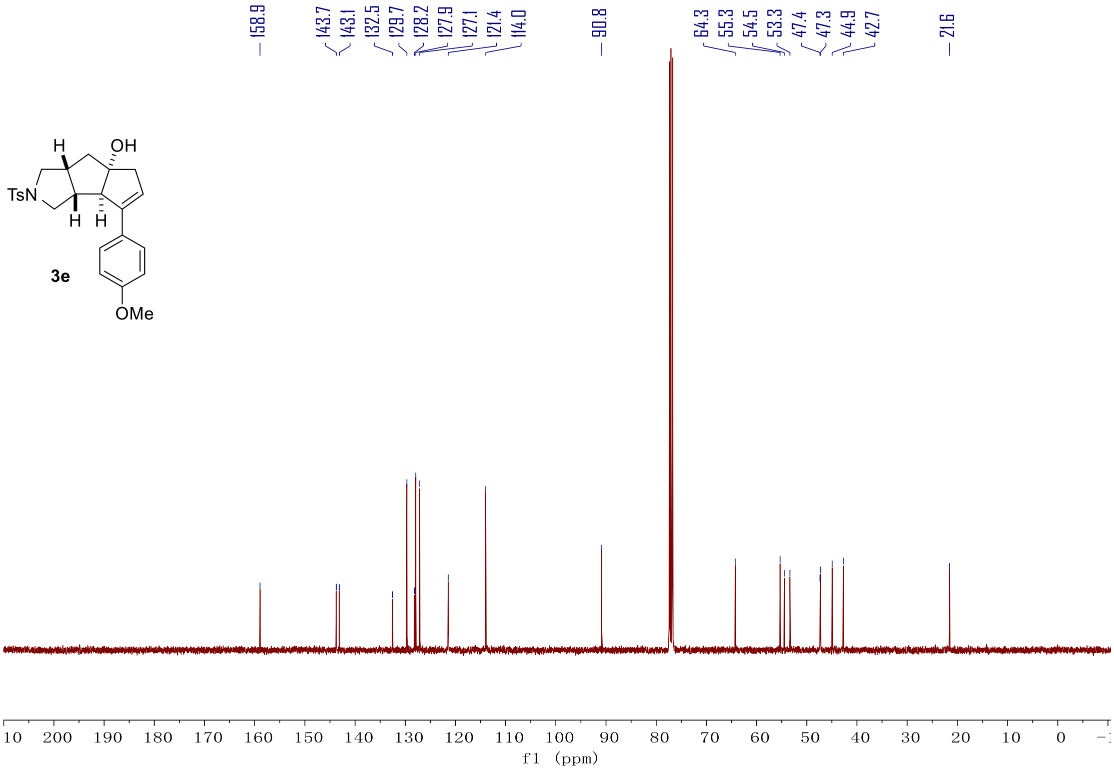
[13]C NMR in $CDCl_3$, 101MHz



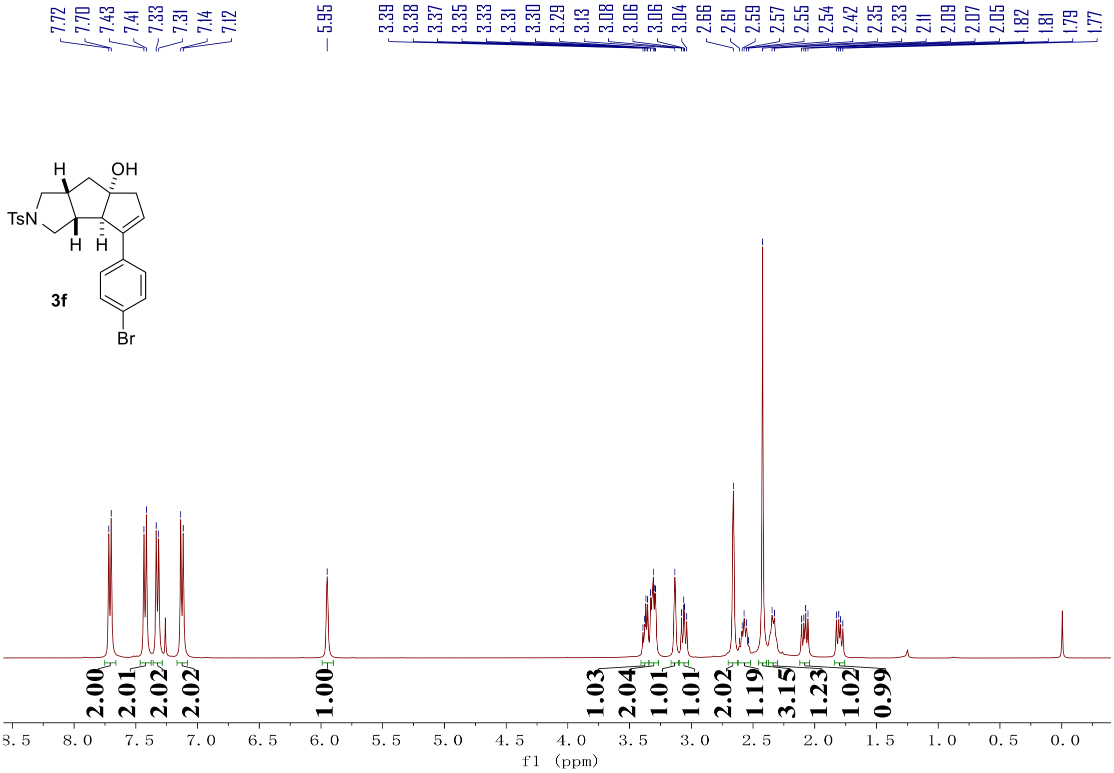
^{1}H NMR in $CDCl_3$, 400 MHz



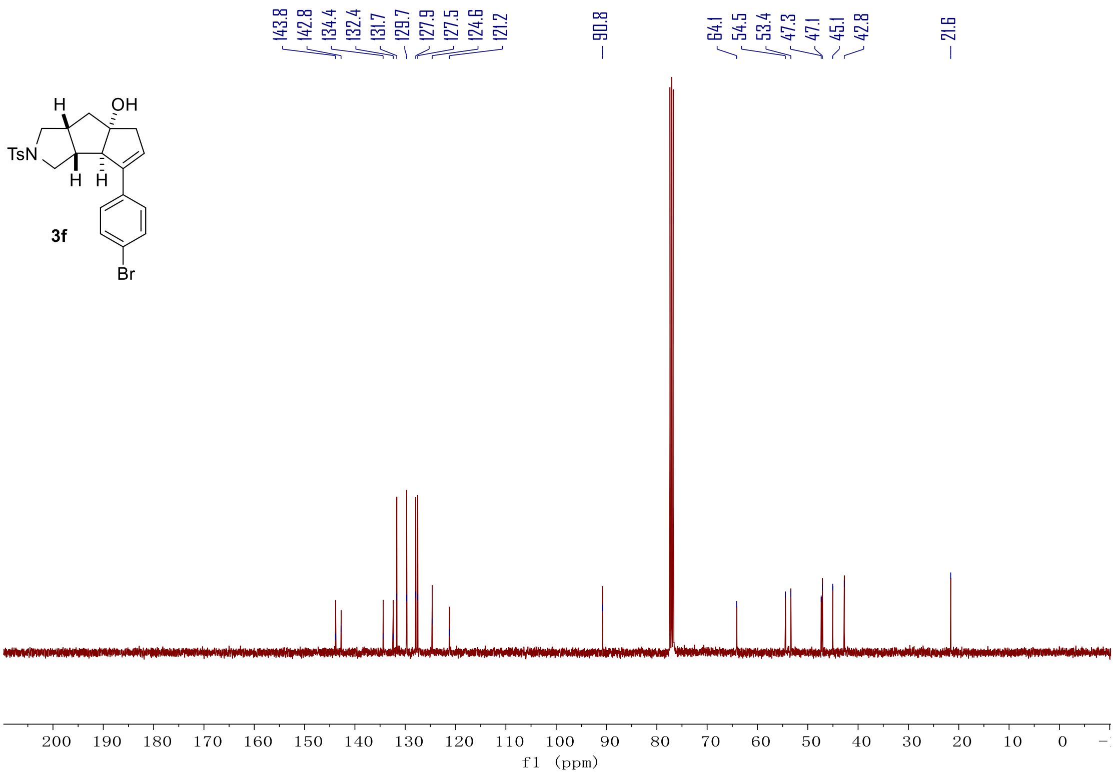
^{13}C NMR in $CDCl_3$, 101 MHz



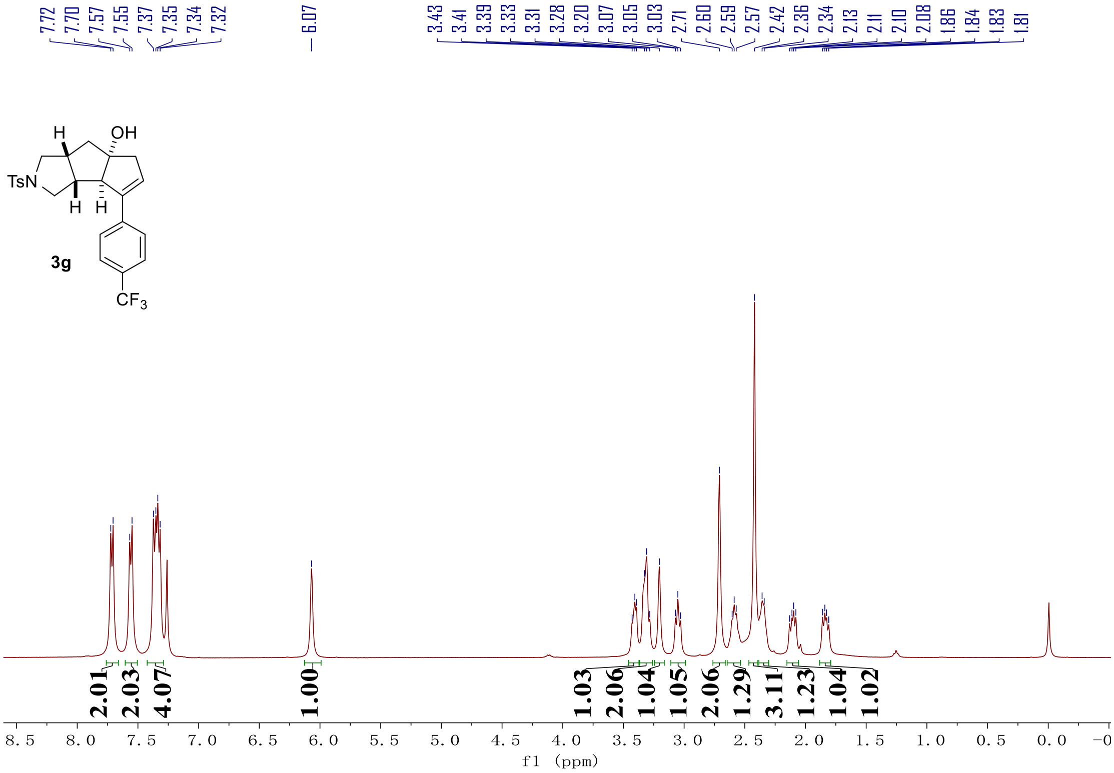
[1]H NMR in $CDCl_3$, 400 MHz



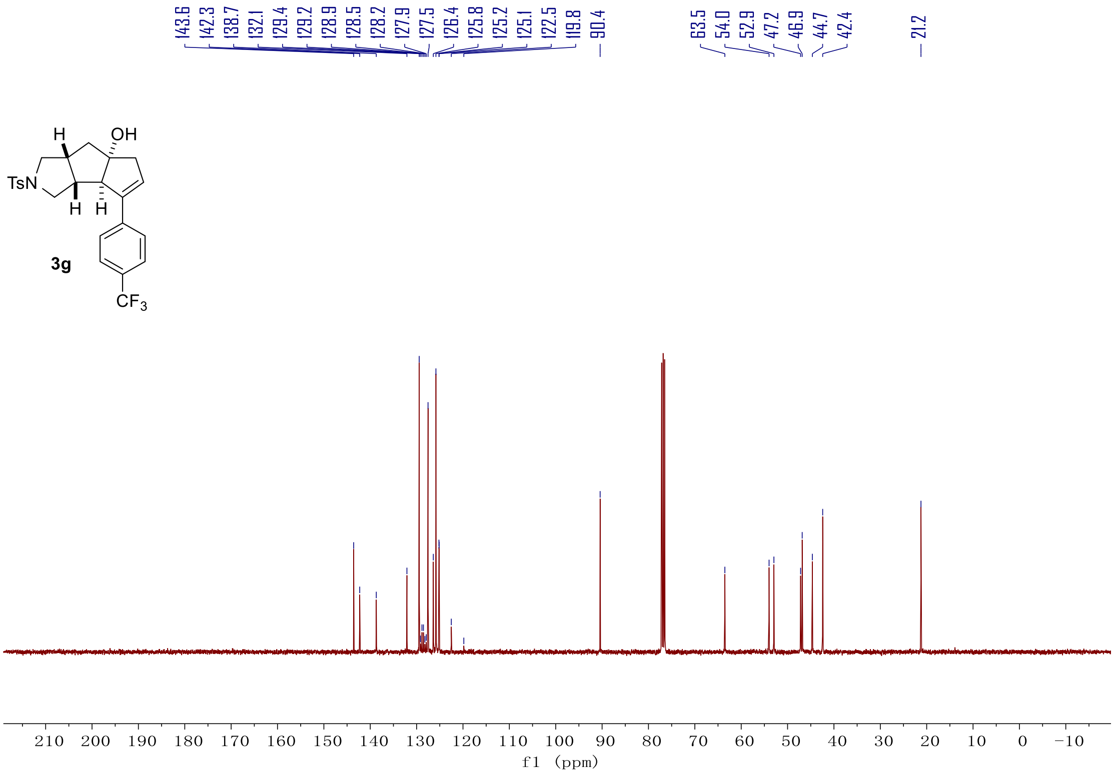
[13]C NMR in $CDCl_3$, 101 MHz



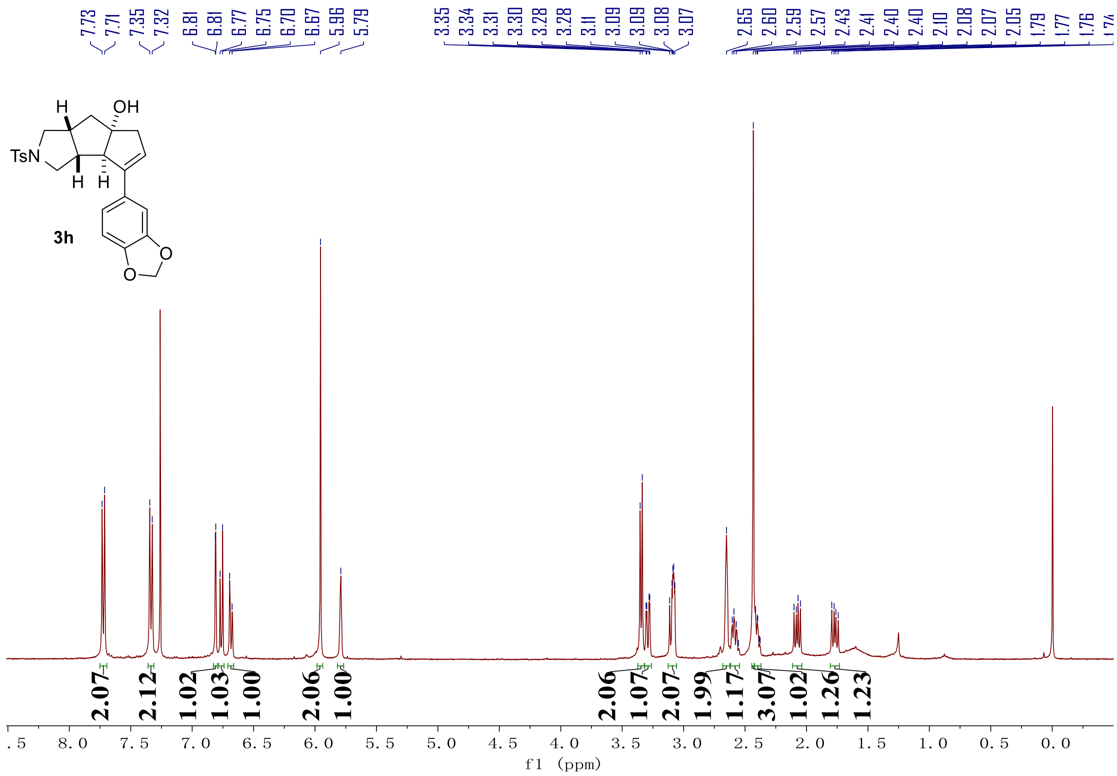
^{1}H NMR in $CDCl_3$, 400 MHz



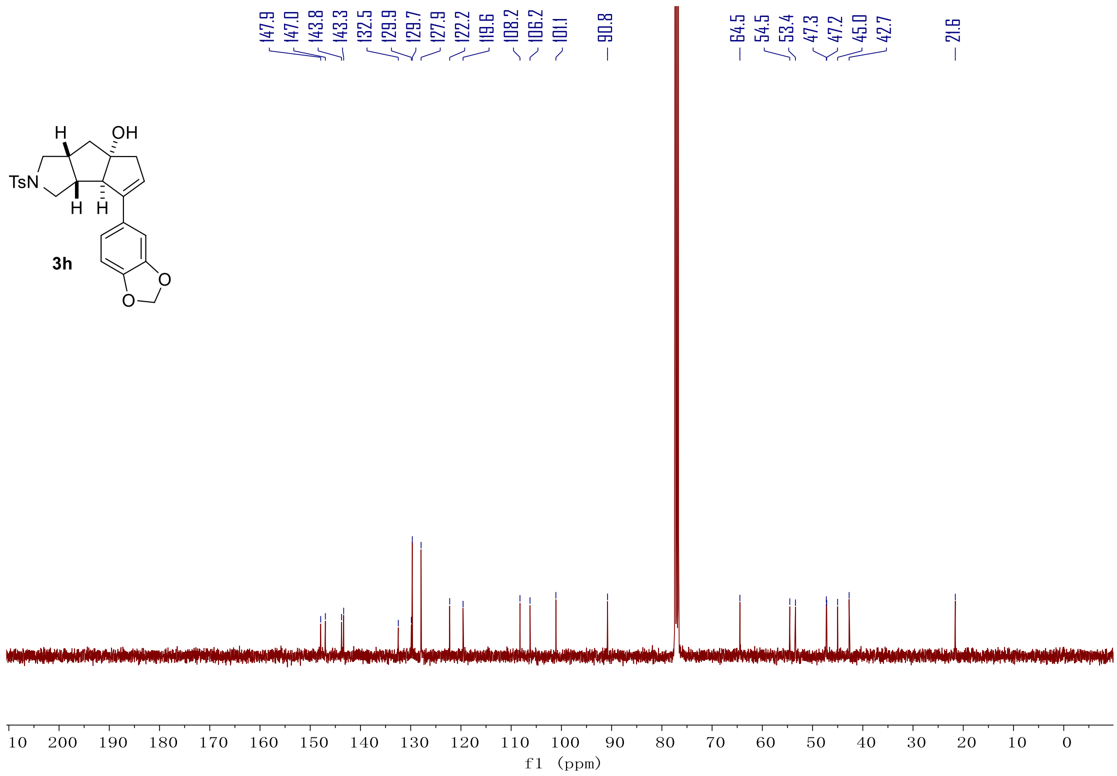
^{13}C NMR in $CDCl_3$, 101 MHz



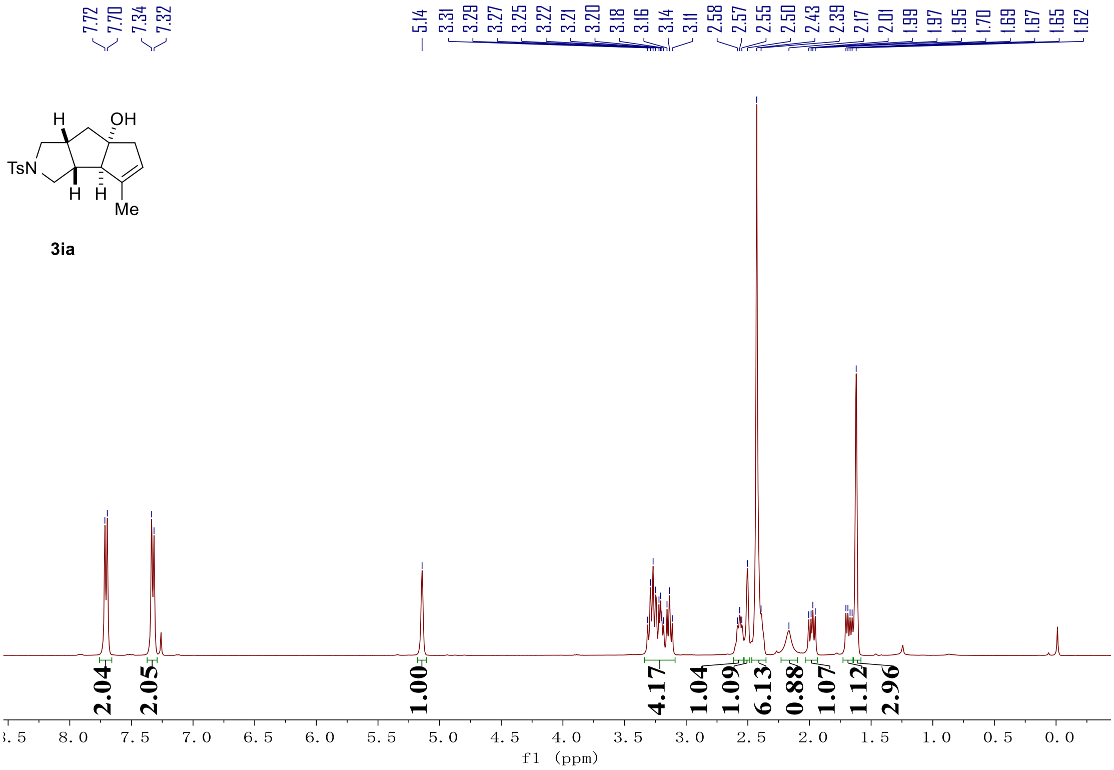
^{1}H NMR in $CDCl_3$, 400 MHz



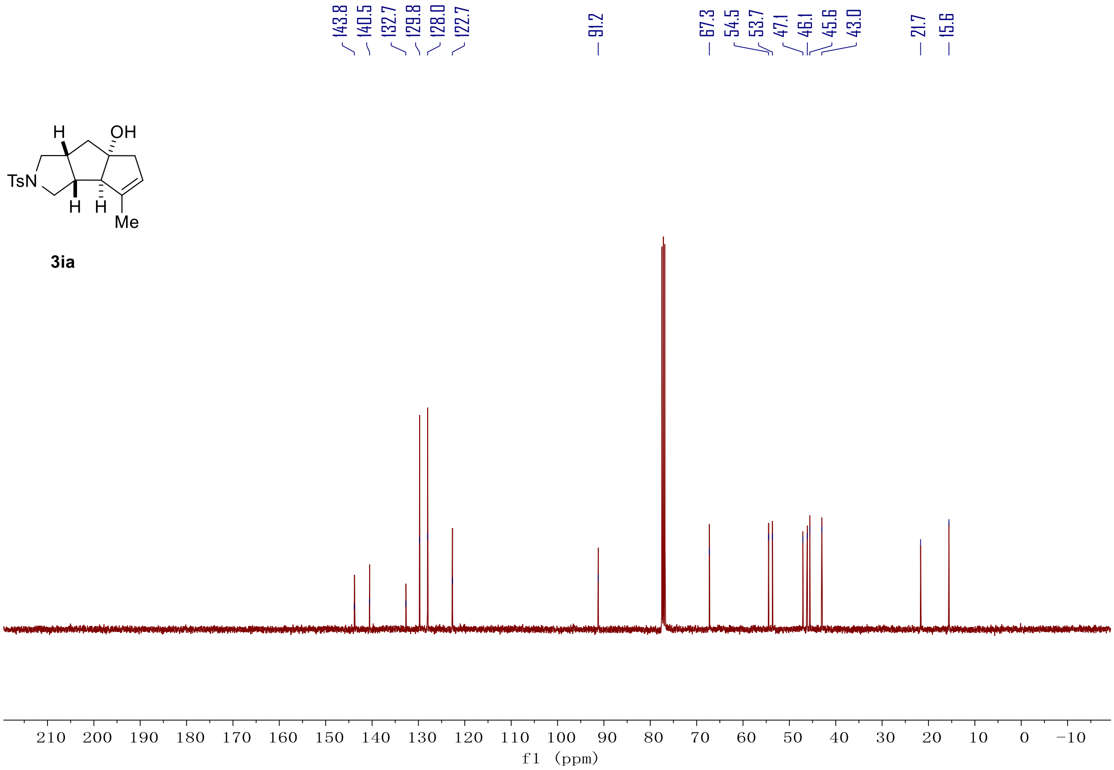
^{13}C NMR in $CDCl_3$, 101 MHz



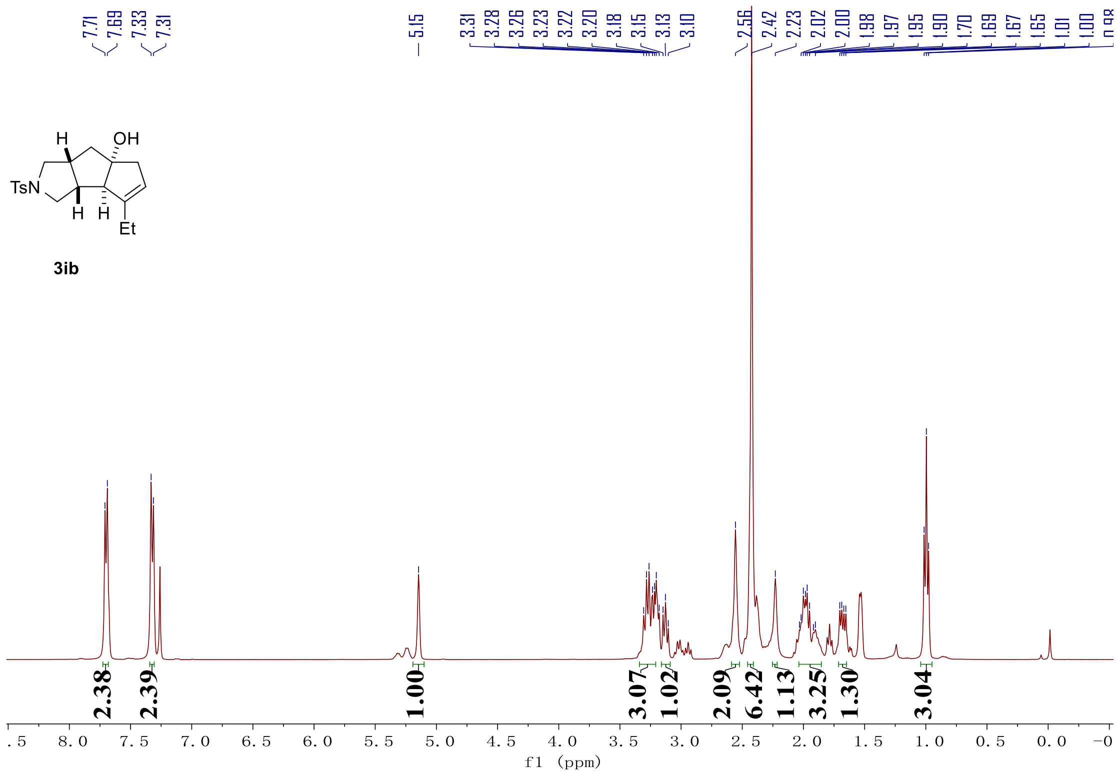
^{1}H NMR in $CDCl_3$, 400 MHz



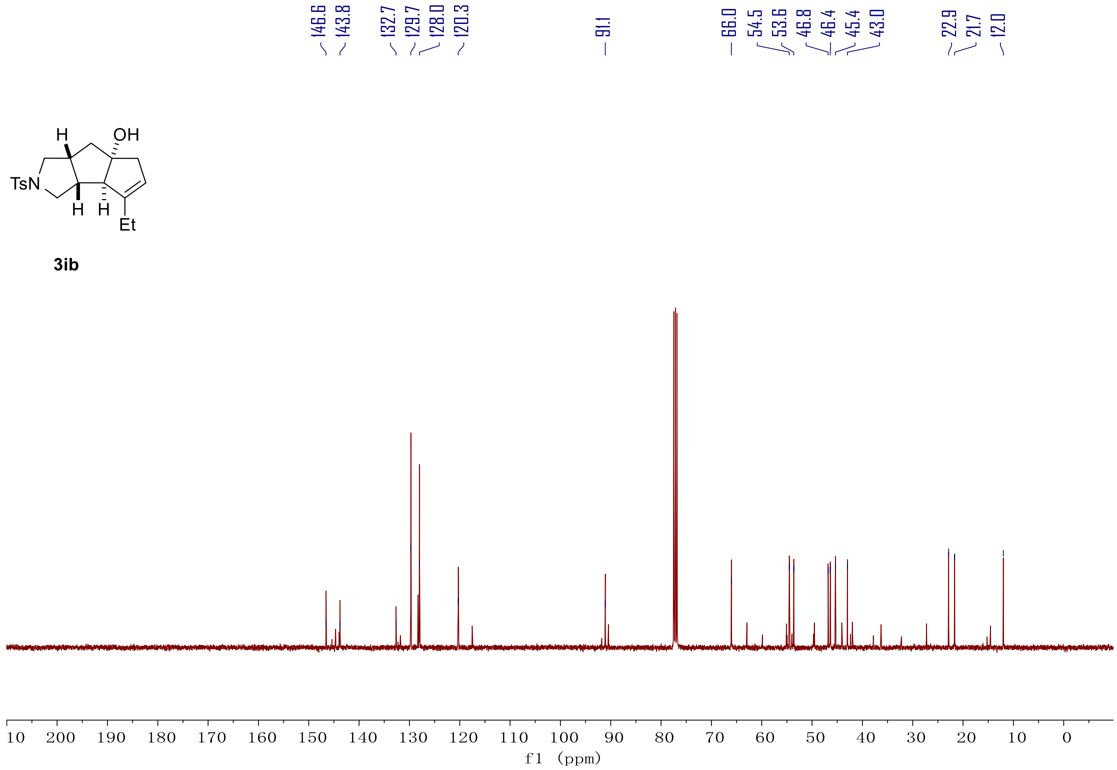
^{13}C NMR in $CDCl_3$, 101 MHz



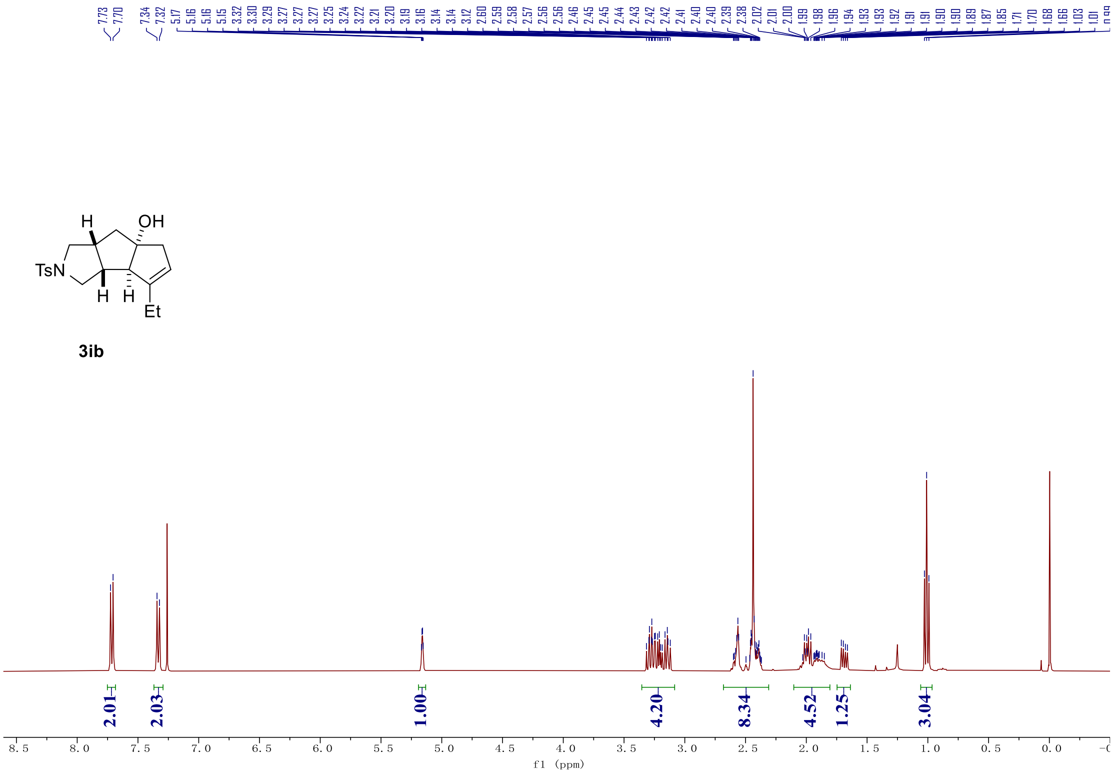
^{1}H NMR in $CDCl_3$, 400 MHz



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

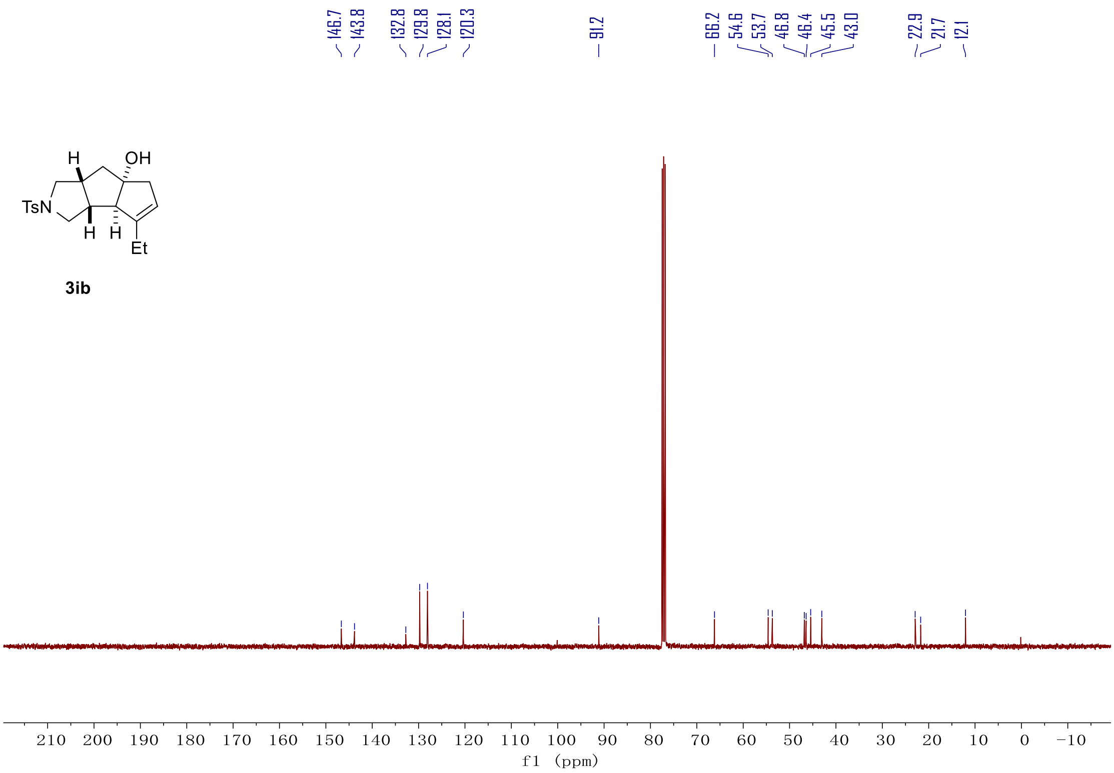


^{1}H NMR in $CDCl_3$, 400 MHz



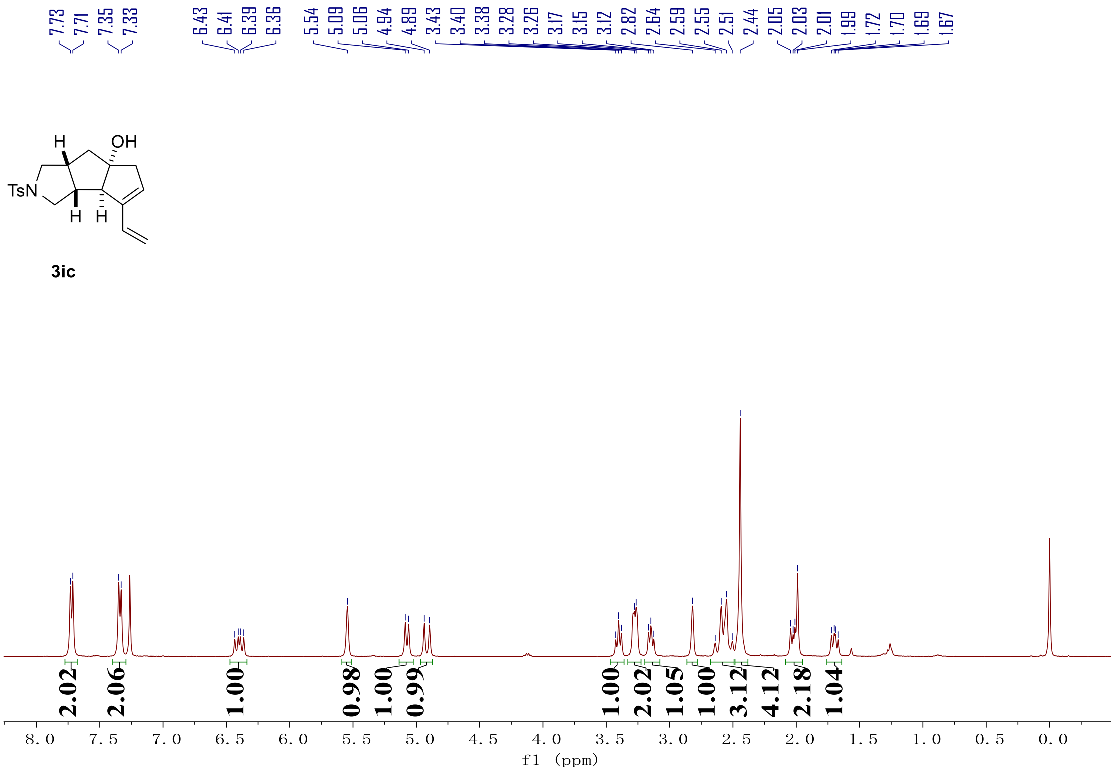
3ib

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

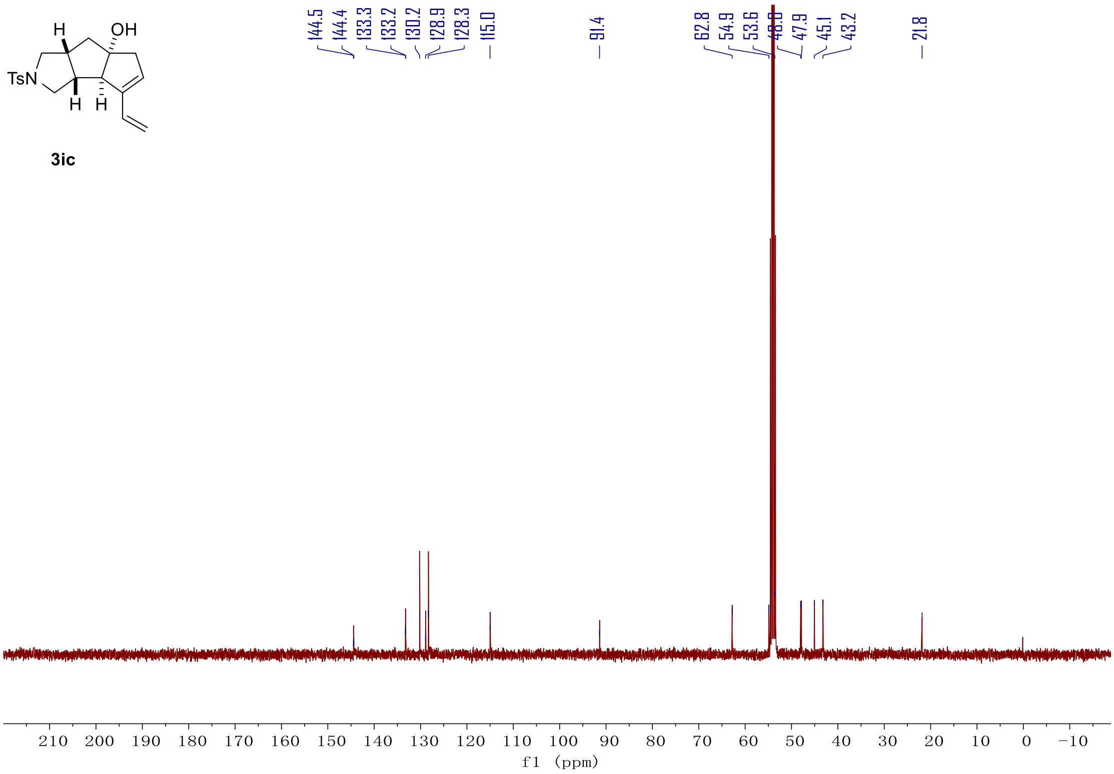


3ib

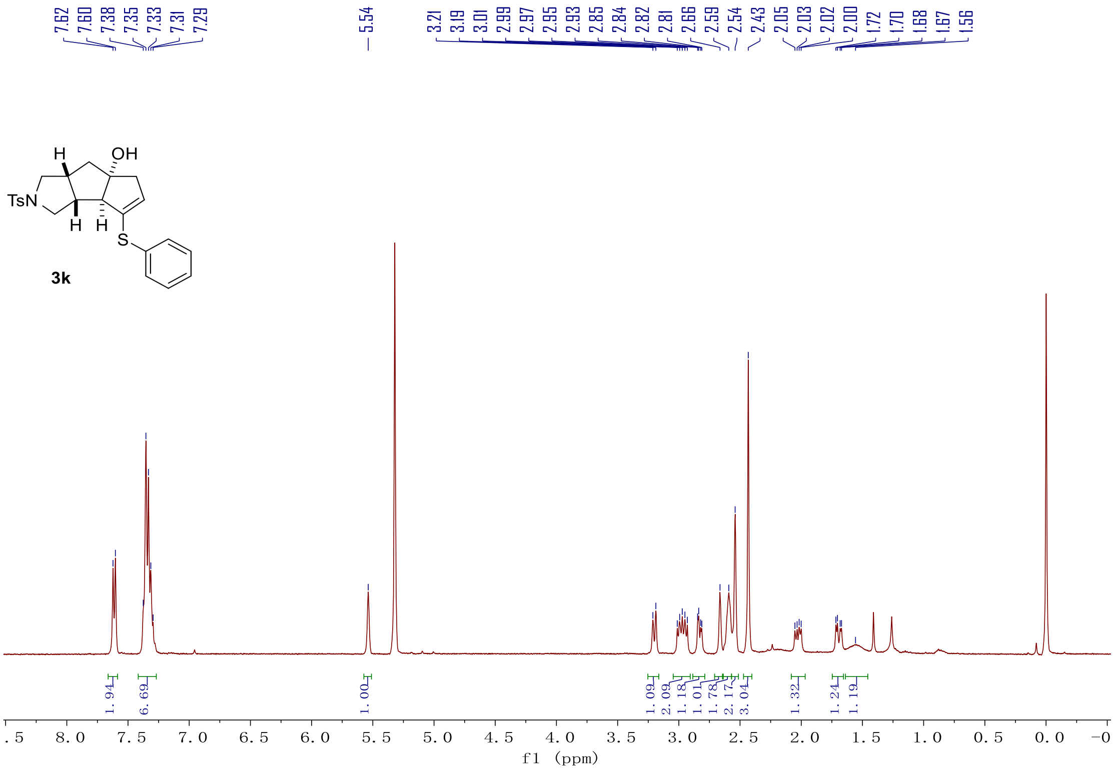
[1]H NMR in $CDCl_3$, 400 MHz



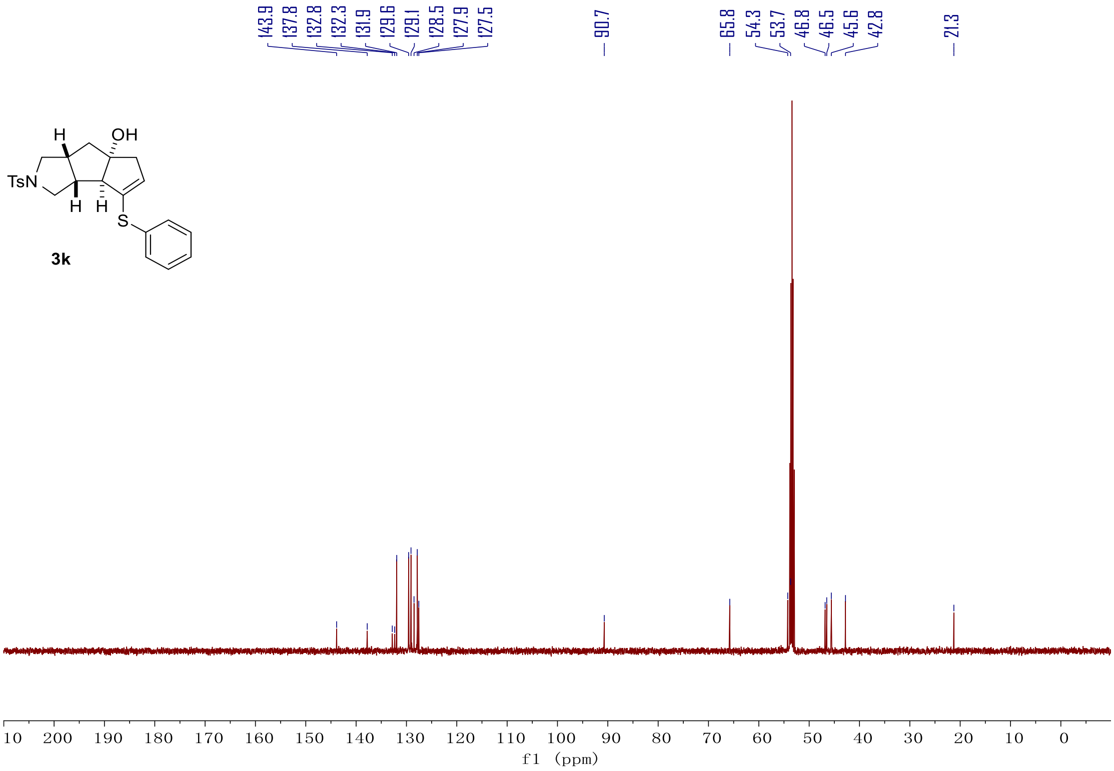
[13]C NMR in CD_2Cl_2, 101 MHz



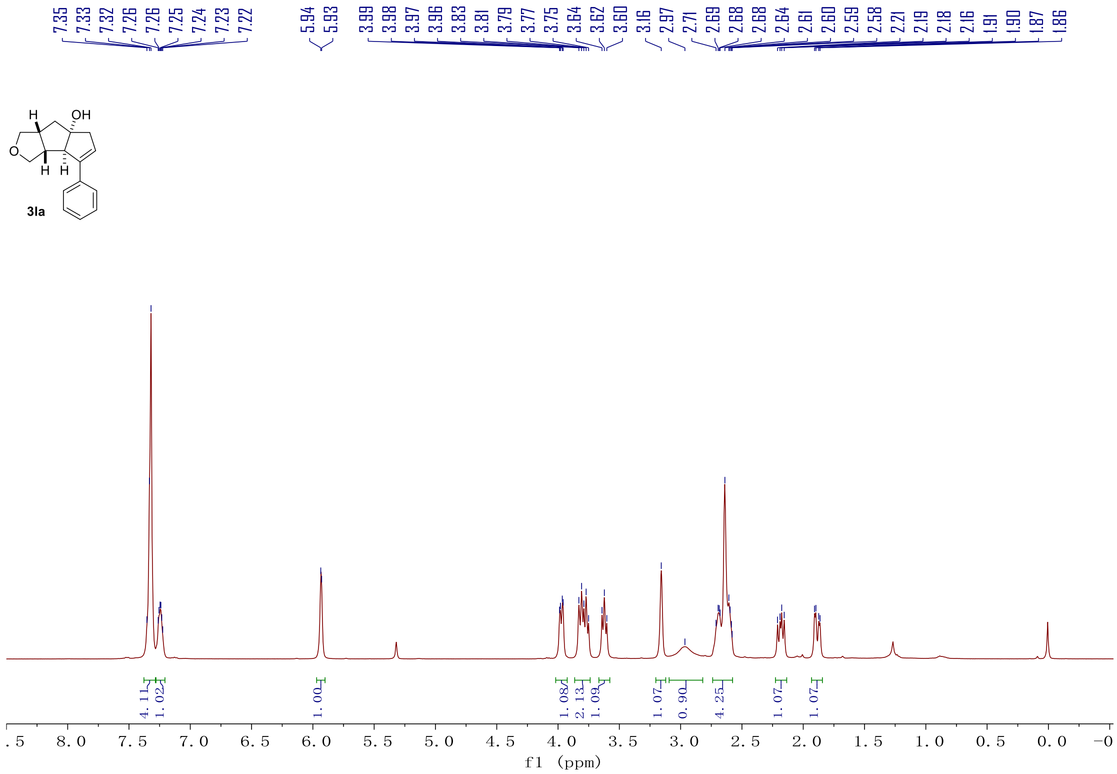
^{1}H NMR in CD_2Cl_2, 500 MHz



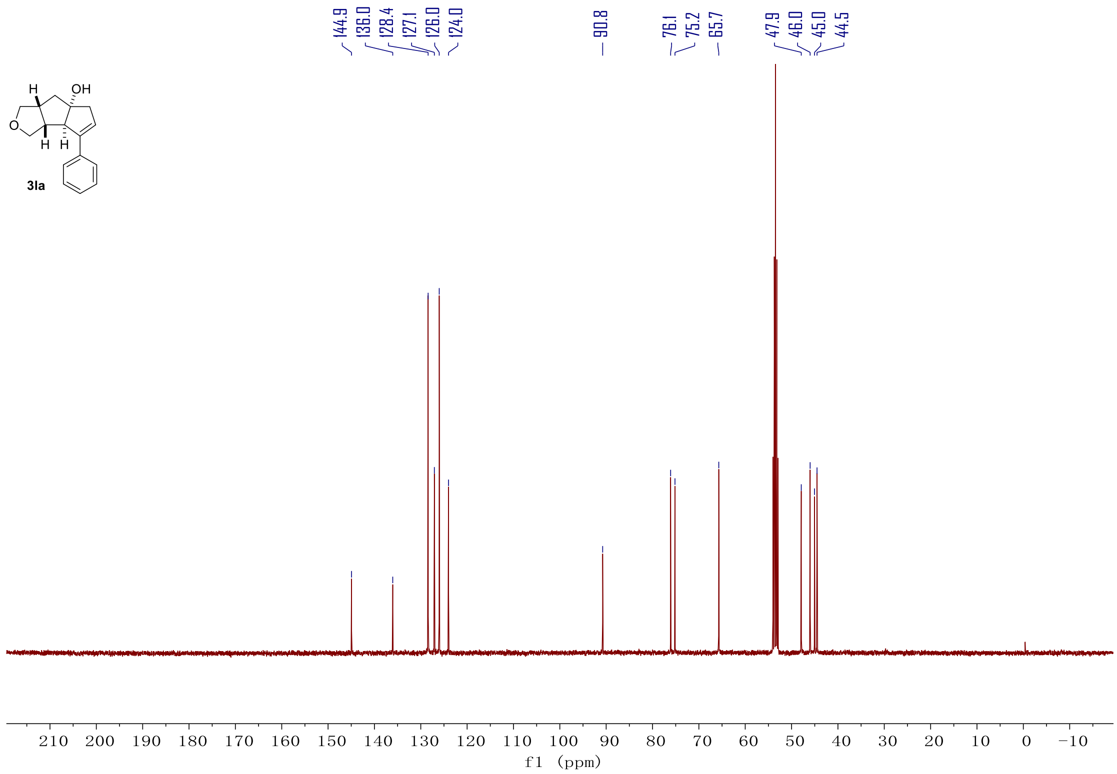
^{13}C NMR in CD_2Cl_2, 126 MHz



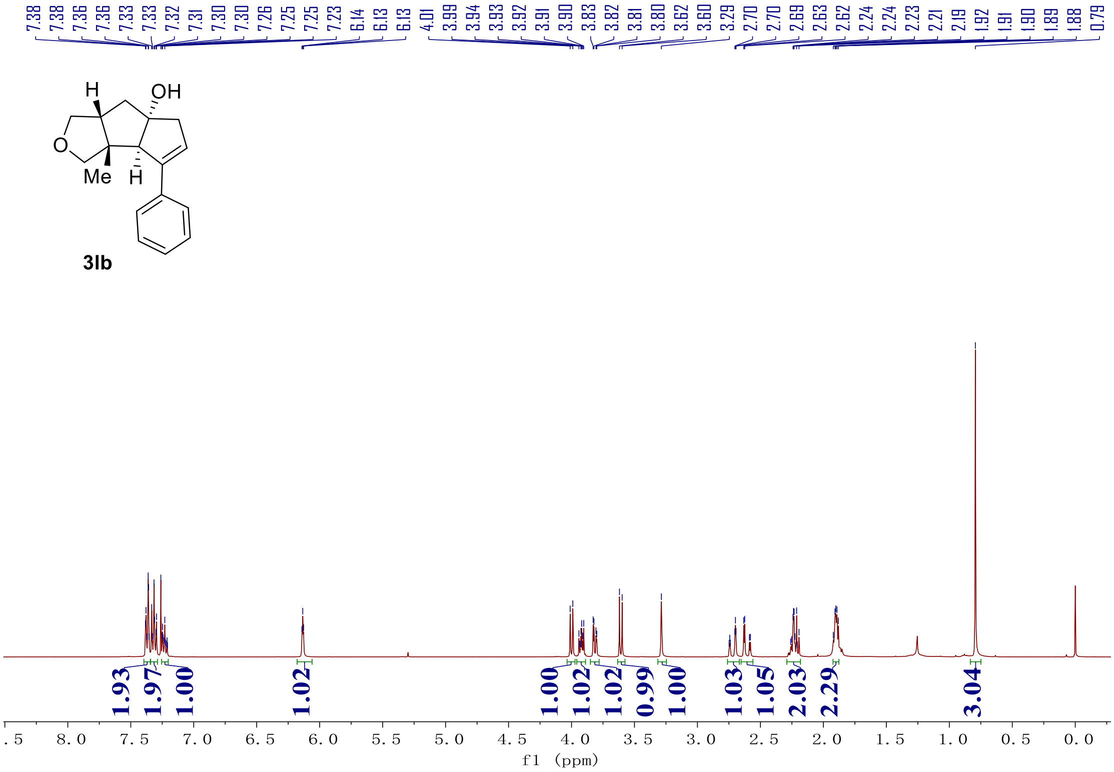
^{1}H NMR in CD_2Cl_2, 400 MHz



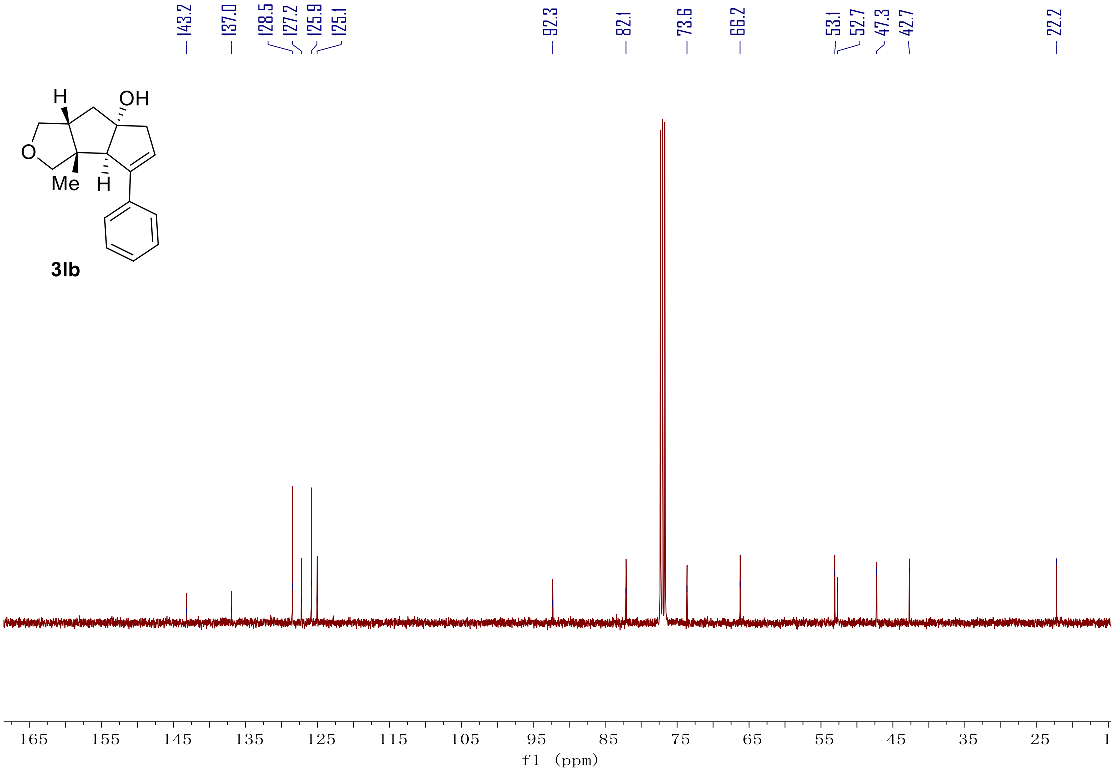
^{13}C NMR in CD_2Cl_2, 101 MHz



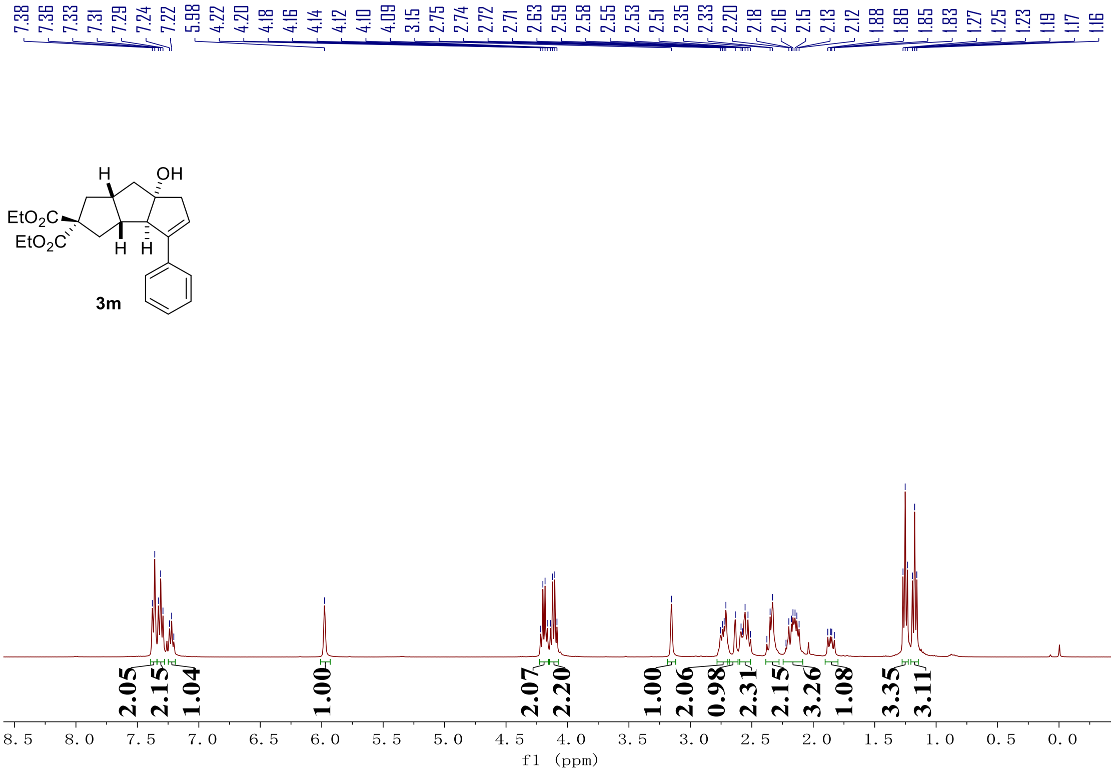
^{1}H NMR in $CDCl_3$, 400 MHz



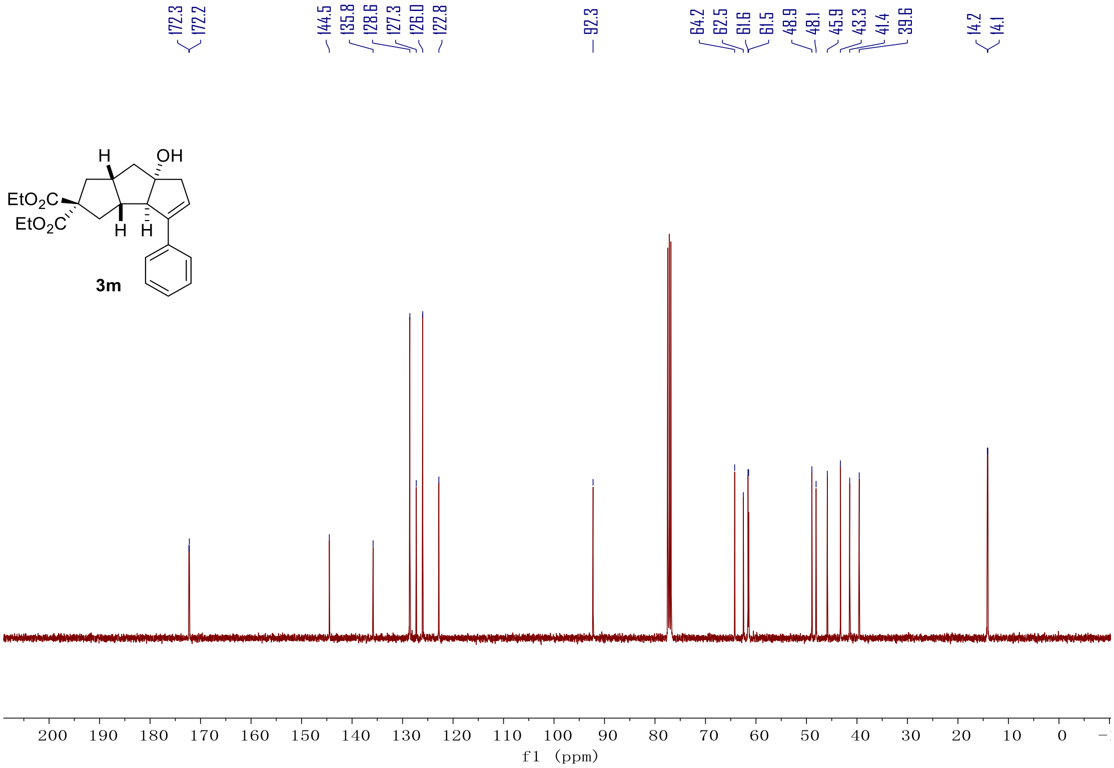
^{13}C NMR in $CDCl_3$, 101 MHz



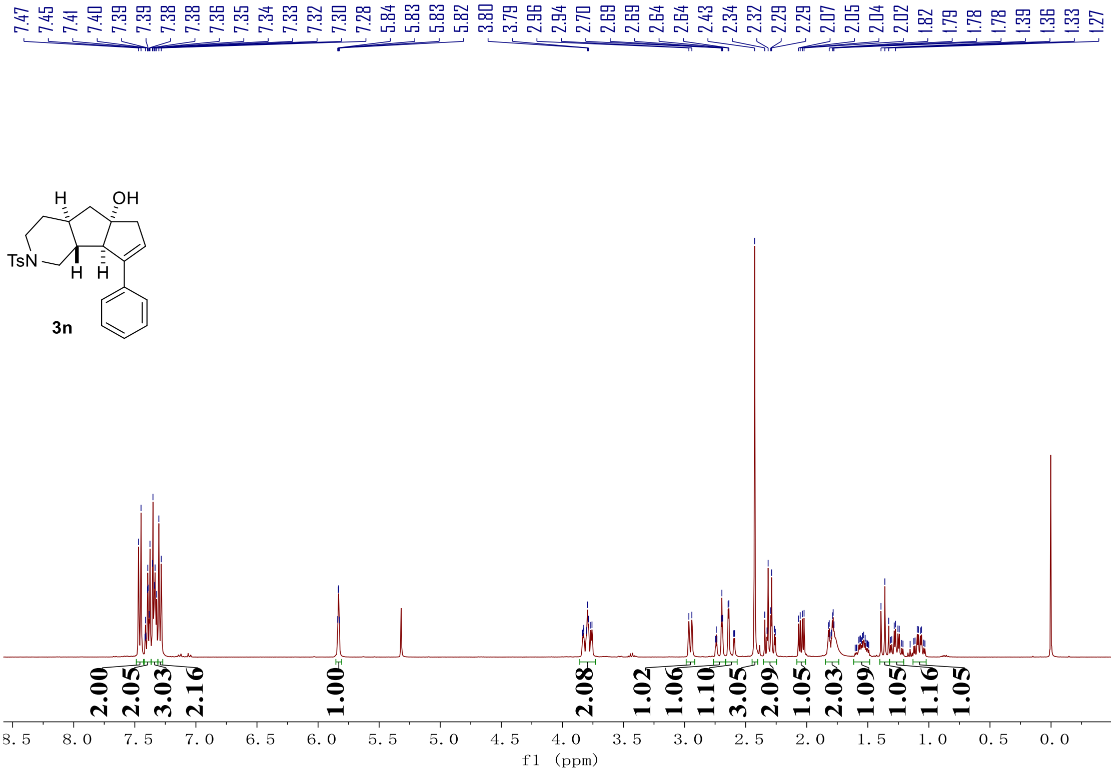
[1]H NMR in $CDCl_3$, 400 MHz



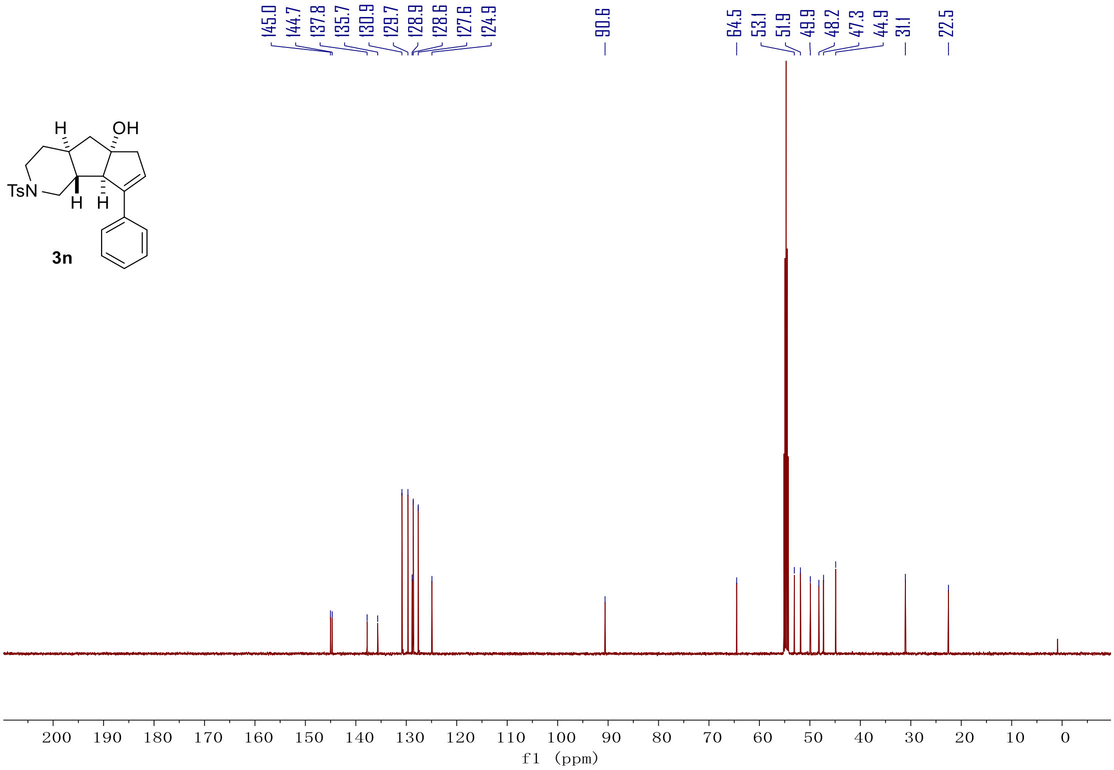
[13]C NMR in $CDCl_3$, 101 MHz



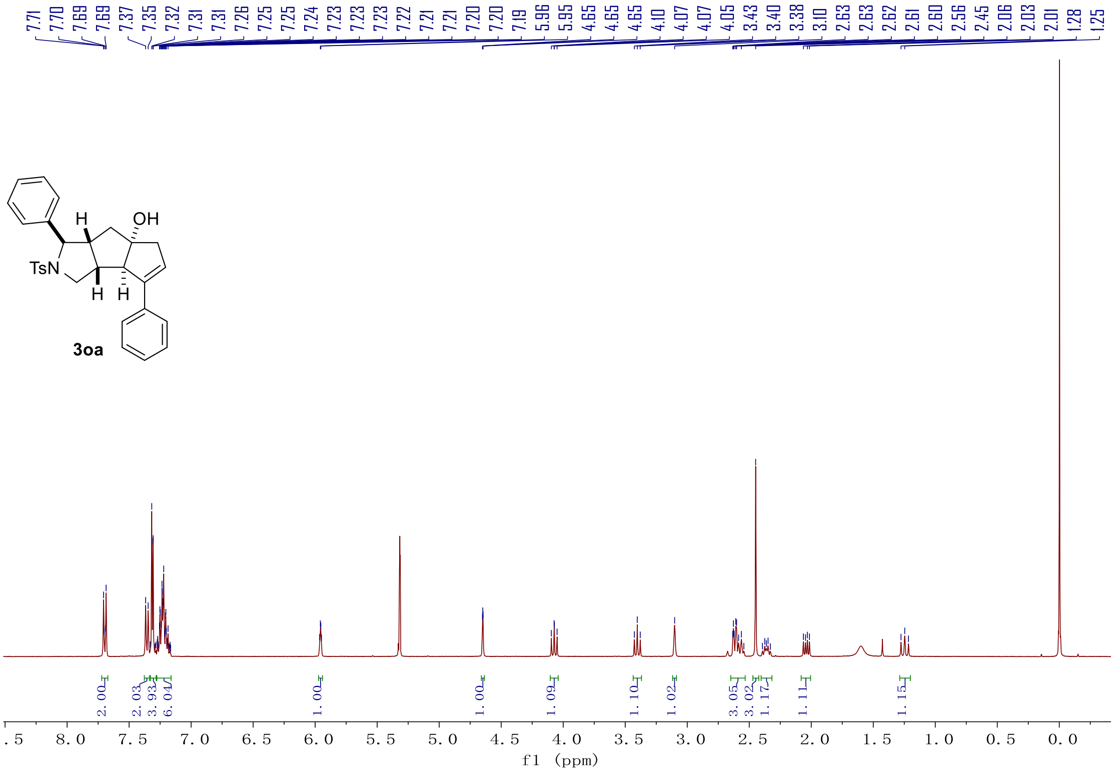
^{1}H NMR in CD_2Cl_2, 400 MHz



^{13}C NMR in CD_2Cl_2, 126 MHz

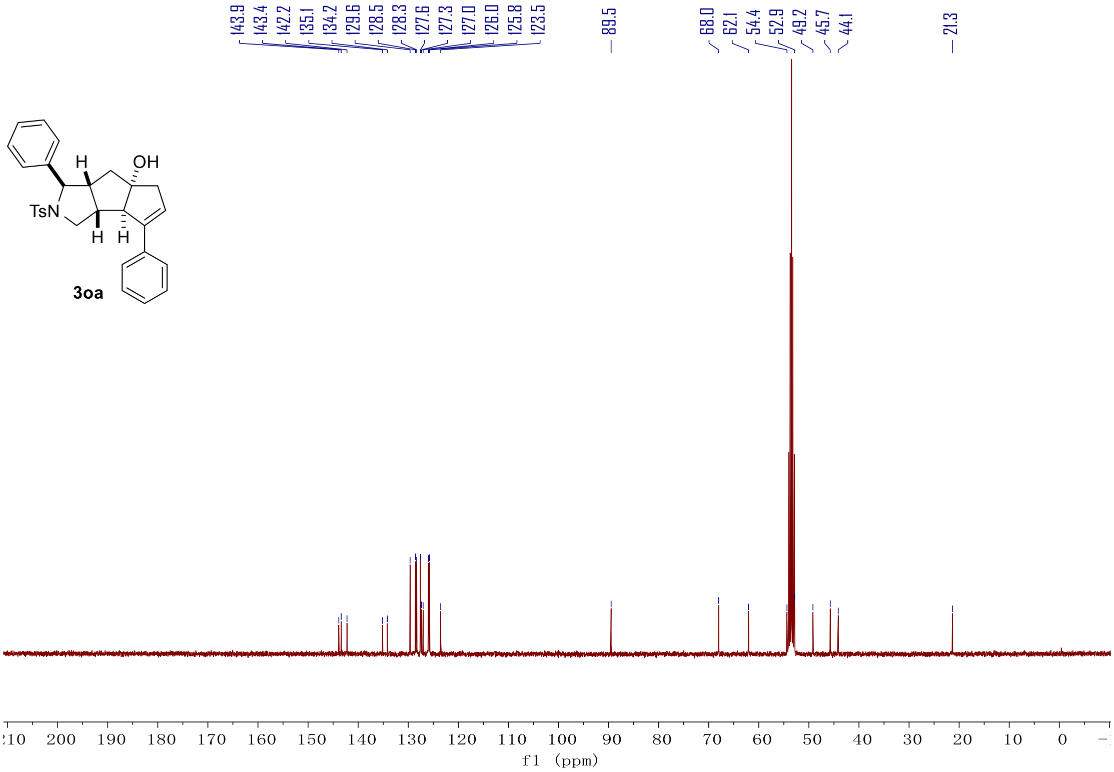


^{1}H NMR in CD_2Cl_2, 400 MHz



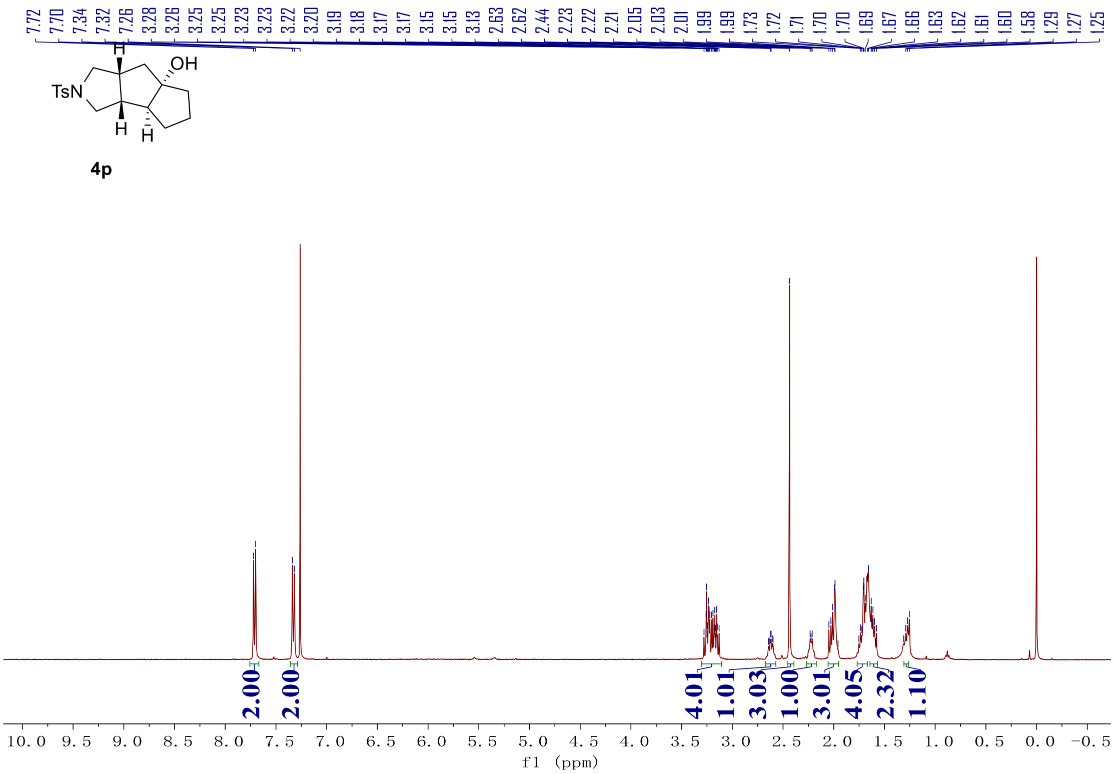
3oa

^{13}C NMR in CD_2Cl_2, 101 MHz

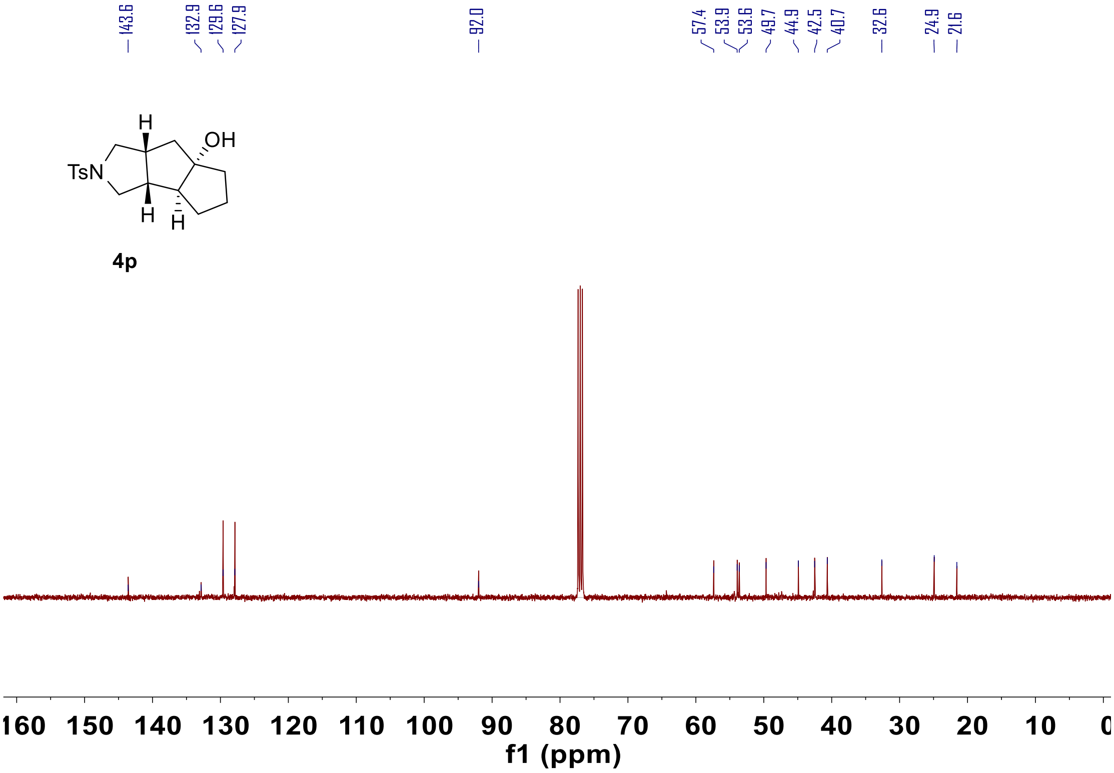


3oa

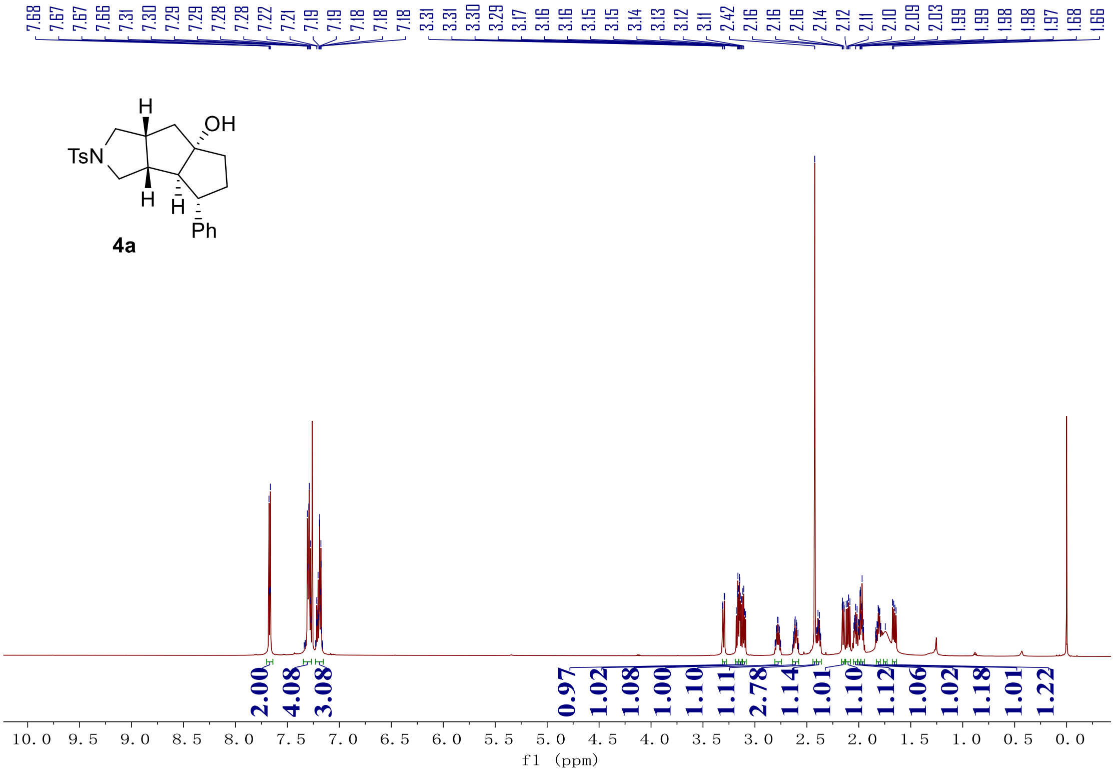
^{1}H NMR in $CDCl_3$, 400 MHz



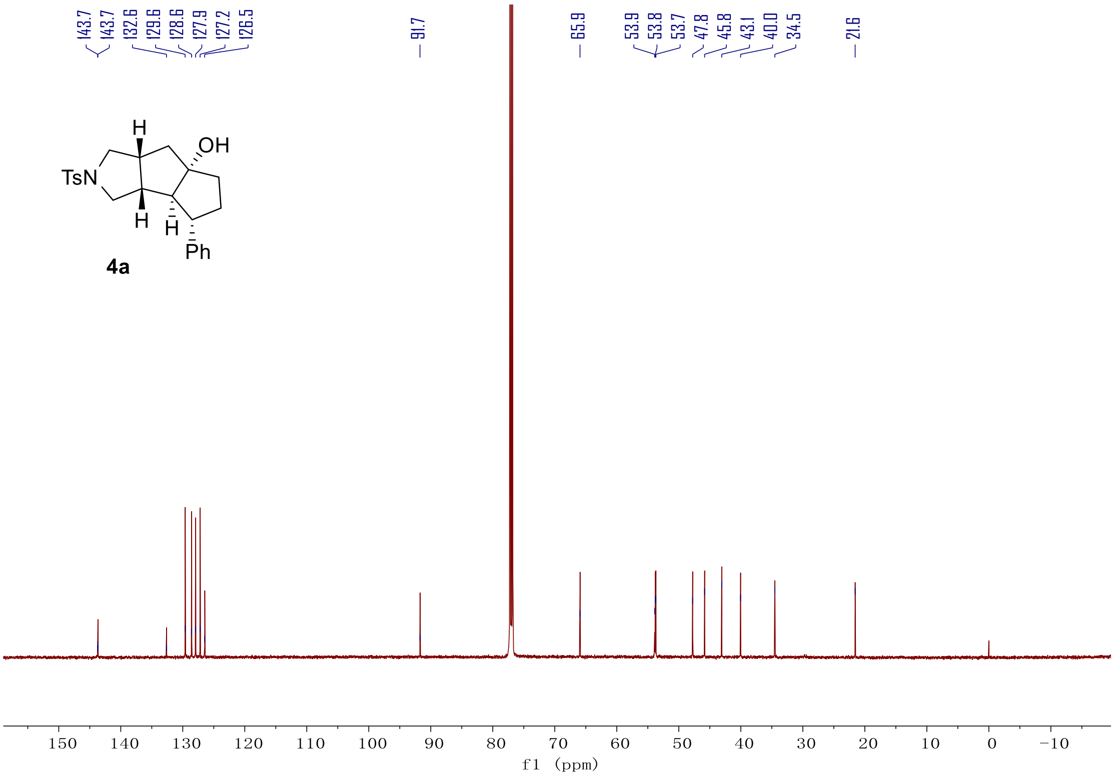
^{13}C NMR in $CDCl_3$, 101 MHz



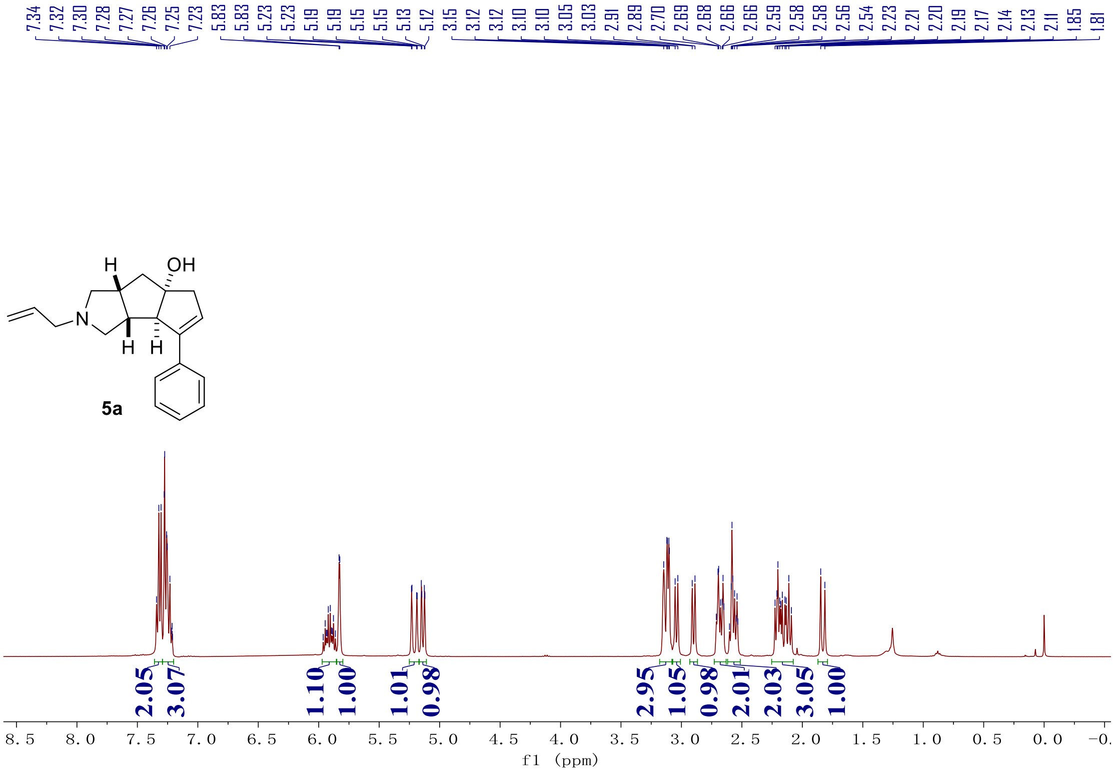
^{1}H NMR in $CDCl_3$, 600 MHz



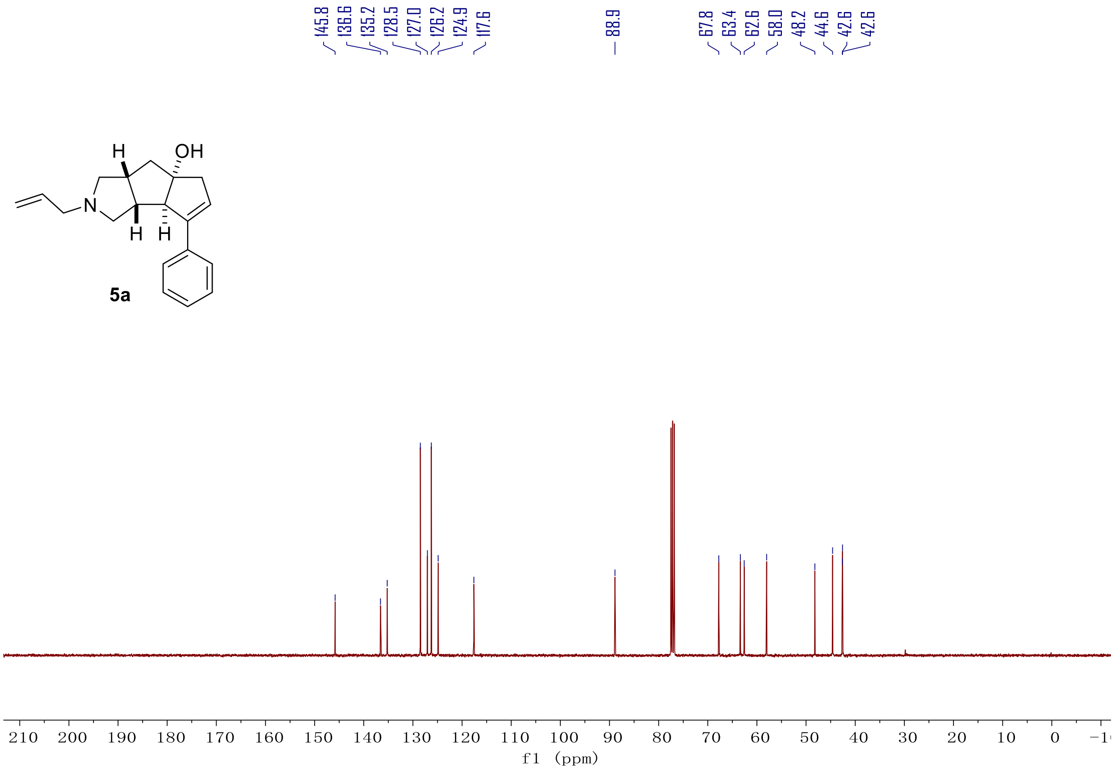
^{13}C NMR in $CDCl_3$, 151 MHz



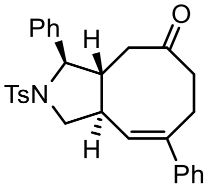
^{1}H NMR in $CDCl_3$, 400 MHz



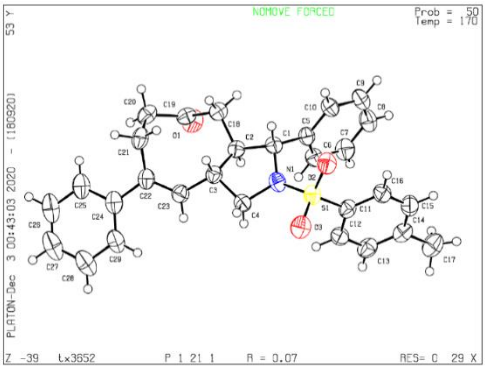
^{13}C NMR in $CDCl_3$, 101 MHz



X-ray data of 2ob (CCDC-2047673)



2ob

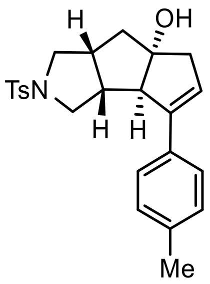


Ellipsoids are drawn at 50% probability

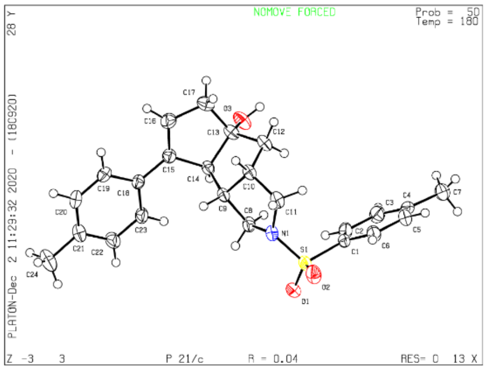
Table 1 Crystal data and structure refinement for TX3652.

Identification code	TX3652
Empirical formula	$C_{29}H_{29}NO_3S$
Formula weight	471.59
Temperature/K	169.99(12)
Crystal system	Monoclinic
Space group	$P2_1$
a/Å	6.0097(2)
b/Å	15.4823(5)
c/Å	13.2450(5)
α/°	90
β/°	101.648(4)
γ/°	90
Volume/Å^3	1206.99(7)
Z	2
ρ_{calc}g/cm^3	1.298
μ/mm^{-1}	1.438
F(000)	500.0
Crystal size/mm^3	0.15 × 0.04 × 0.03
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.894 to 150.784
Index ranges	$-7 \leq h \leq 7, -19 \leq k \leq 19, -16 \leq l \leq 15$
Reflections collected	14704
Independent reflections	4755 [R_{int} = 0.0550, R_{sigma} = 0.0402]
Data/restraints/parameters	4755/1/308
Goodness-of-fit on F^2	1.110
Final R indexes [I>=2σ (I)]	R_1 = 0.0668, wR_2 = 0.1825
Final R indexes [all data]	R_1 = 0.0687, wR_2 = 0.1844
Largest diff. peak/hole / e Å^{-3}	0.77/-0.24
Flack parameter	0.372(18)

X-ray data of 3b (CCDC-2047674)



3b

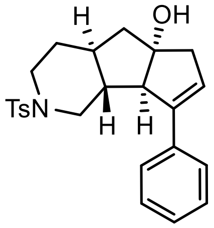


Ellipsoids are drawn at 50% probability

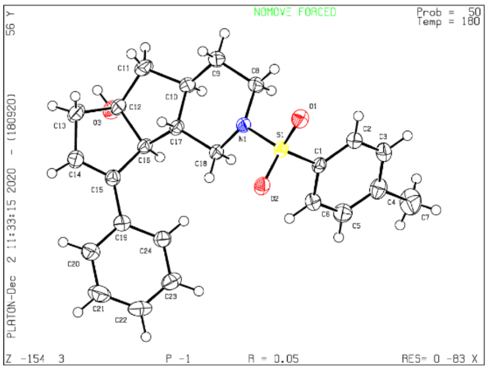
Table 1 Crystal data and structure refinement for 3b.

Identification code	3b
Empirical formula	$C_{24}H_{27}NO_3S$
Formula weight	409.52
Temperature/K	180.00(10)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	12.3661(4)
b/Å	7.9900(2)
c/Å	21.4501(7)
α/°	90
β/°	96.162(3)
γ/°	90
Volume/Å^3	2107.14(11)
Z	4
ρ_{calc}g/cm^3	1.291
μ/mm^{-1}	0.179
F(000)	872.0
Crystal size/mm^3	0.6 × 0.2 × 0.18
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.312 to 54.97
Index ranges	$-11 \leq h \leq 16, -10 \leq k \leq 10, -27 \leq l \leq 27$
Reflections collected	14095
Independent reflections	4789 [R_{int} = 0.0248, R_{sigma} = 0.0297]
Data/restraints/parameters	4789/0/265
Goodness-of-fit on F^2	1.068
Final R indexes [I>=2σ (I)]	R_1 = 0.0394, wR_2 = 0.1056
Final R indexes [all data]	R_1 = 0.0489, wR_2 = 0.1106
Largest diff. peak/hole / e Å^{-3}	0.28/-0.33

X-ray data of 3n (CCDC-2047675)



3n

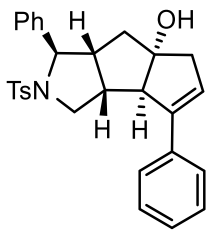


Ellipsoids are drawn at 50% probability

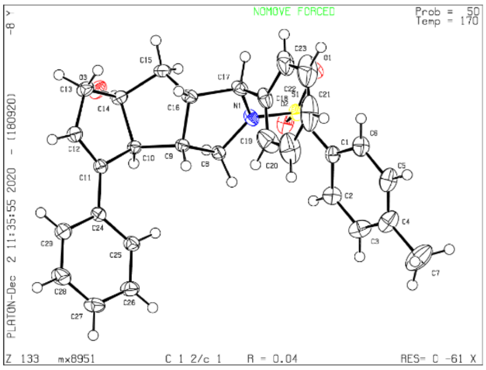
Table 1 Crystal data and structure refinement for 3n.

Identification code	3n
Empirical formula	$C_{24}H_{27}NO_3S$
Formula weight	409.52
Temperature/K	180.00(10)
Crystal system	Triclinic
Space group	P-1
a/Å	9.6104(4)
b/Å	9.9807(5)
c/Å	11.3344(10)
α/°	84.216(6)
β/°	80.159(5)
γ/°	86.824(4)
Volume/Å^3	1064.92(12)
Z	2
ρ_{calc}g/cm^3	1.277
μ/mm^{-1}	0.177
F(000)	436.0
Crystal size/mm^3	0.23 × 0.21 × 0.18
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.168 to 54.964
Index ranges	$-12 \leq h \leq 12, -12 \leq k \leq 9, -14 \leq l \leq 14$
Reflections collected	13918
Independent reflections	4887 [R_{int} = 0.0453, R_{sigma} = 0.0502]
Data/restraints/parameters	4887/0/264
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0475, wR_2 = 0.1179
Final R indexes [all data]	R_1 = 0.0590, wR_2 = 0.1258
Largest diff. peak/hole / e Å^{-3}	0.34/-0.45

X-ray data of 3oa (CCDC-2047676)



3oa



Ellipsoids are drawn at 50% probability

Table 1 Crystal data and structure refinement for MX8951.

Identification code	MX8951
Empirical formula	$C_{29}H_{29}NO_3S$
Formula weight	471.59
Temperature/K	170.00(10)
Crystal system	Monoclinic
Space group	C2/c
a/Å	17.5274(3)
b/Å	12.9373(2)
c/Å	21.4003(4)
α/°	90
β/°	101.990(2)
γ/°	90
Volume/Å^3	4746.81(15)
Z	8
ρ_{calc}g/cm^3	1.320
μ/mm^{-1}	0.169
F(000)	2000.0
Crystal size/mm^3	0.32 × 0.21 × 0.04
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.944 to 62.19
Index ranges	-24 ≤ h ≤ 23, -17 ≤ k ≤ 17, -29 ≤ l ≤ 30
Reflections collected	45360
Independent reflections	6670 [R_{int} = 0.0175, R_{sigma} = 0.0122]
Data/restraints/parameters	6670/0/309
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0383, wR_2 = 0.1067
Final R indexes [all data]	R_1 = 0.0421, wR_2 = 0.1089
Largest diff. peak/hole / e Å^{-3}	0.41/-0.38

9. DFT study on the mechanism of $InCl_3$-catalyzed ene reaction

DFT calculations were performed with Gaussian 09[22]. The functional B3LYP[23] with Becke-Johnson damped D3 dispersion corrections[24] and a mixed basis set (6-31+G(d,p) for C, H, O, Cl and LANL2DZ basis set[25] with ECP for In) were employed for optimizing the geometries of minima and transition states under the SMD[26] implicit solvation model to account for solvation effects of dichloroethane (DCE). Unscaled harmonic frequency calculations at the same level were performed to validate each structure as either a minimum or a transition state and to evaluate its zero-point energy and thermal corrections at 298 K. On the basis of the optimized structures, single-point energies were computed under the SMD(DCE) solvation model with the functional ωB97XD[27] using 6-311+G(d,p) for C, H, O, Cl and SDD[28] (Stuttgart/Dresden ECP) for In. Pruned integration grids with 99 radial shells and 590 angular points per shell were used. All discussed energy differences were based on the Gibbs energies in DCE at 298 K. Standard states for solutes in DCE solution are the hypothetical states at 1 mol/L. For all transition states and intermediates, we have manually searched for their conformations and the most stable ones are present here.

To elucidate reaction mechanism, we performed density functional theory (DFT) calculations (**Figure S1**). First, we chose ether tether substrate with phenyl substituted VCP and $InCl_3$ as the catalyst to investigate the reaction mechanism. The ene reaction of **2la** initiates from the coordination of $InCl_3$ to the oxygen atom of the carbonyl group, which activates the carbonyl carbon towards nucleophilic attack by the phenyl substituted alkene. Subsequently, the intramolecular transannulation occurs to give **INT2** via **TS1**. The Gibbs energy of activation involving **TS1** is 18.2 kcal/mol. After that, **INT2** undergoes the intramolecular proton transfer to form the **INT3**, requiring the Gibbs free energy of activation of 26.6 kcal/mol. Finally, **INT3** exchanges the coordinated catalyst with substrate **2la** to afford the product **3la** and closes the catalytic cycle. The computations suggest that the proton transfer is the rating-limiting step. The overall activation free energy for this stepwise ene reaction is 26.6 kcal/mol, which is a reasonable value considering that this reaction for substrate **2la** occurs at 80 ˚C (Other substrates reacted at 60 ˚C).

In the light of our previous work, proposing that $InCl_3$ could dissociate into its cationic species and an anion[29], $InCl_2^+$ was considered as the catalytic species for the ene reaction (**Figure S2**). Our computational results showed that the overall activation free energy for $InCl_2^+$ catalyzed ene reaction is 32.1 kcal/mol, which is too high for a reaction at 80 °C. Therefore, we proposed that $InCl_3$ is the catalytic species in the present ene reaction.

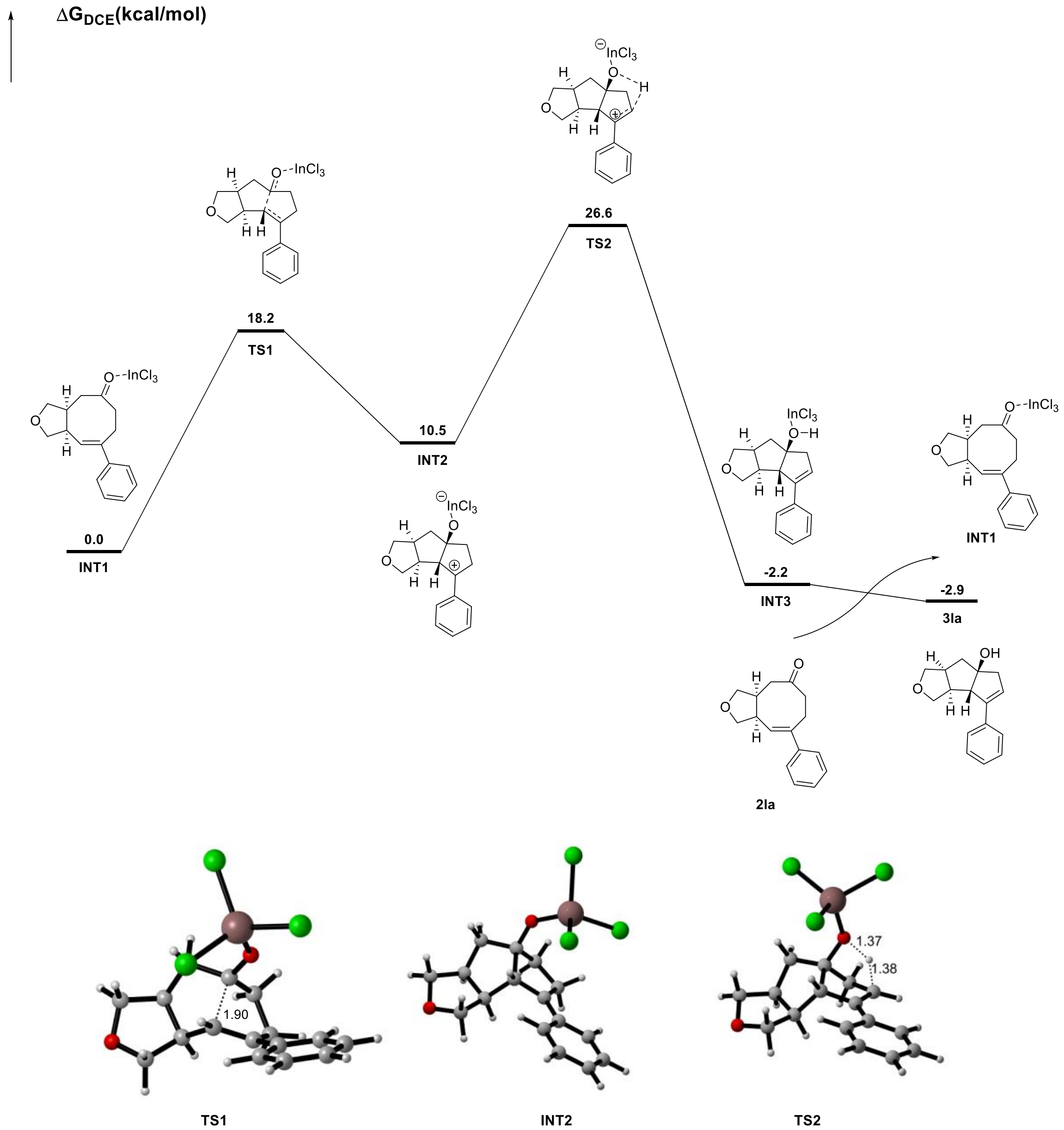


Figure S1. **Computed energy surface for the ene reaction of 2la catalyzed by $InCl_3$.**

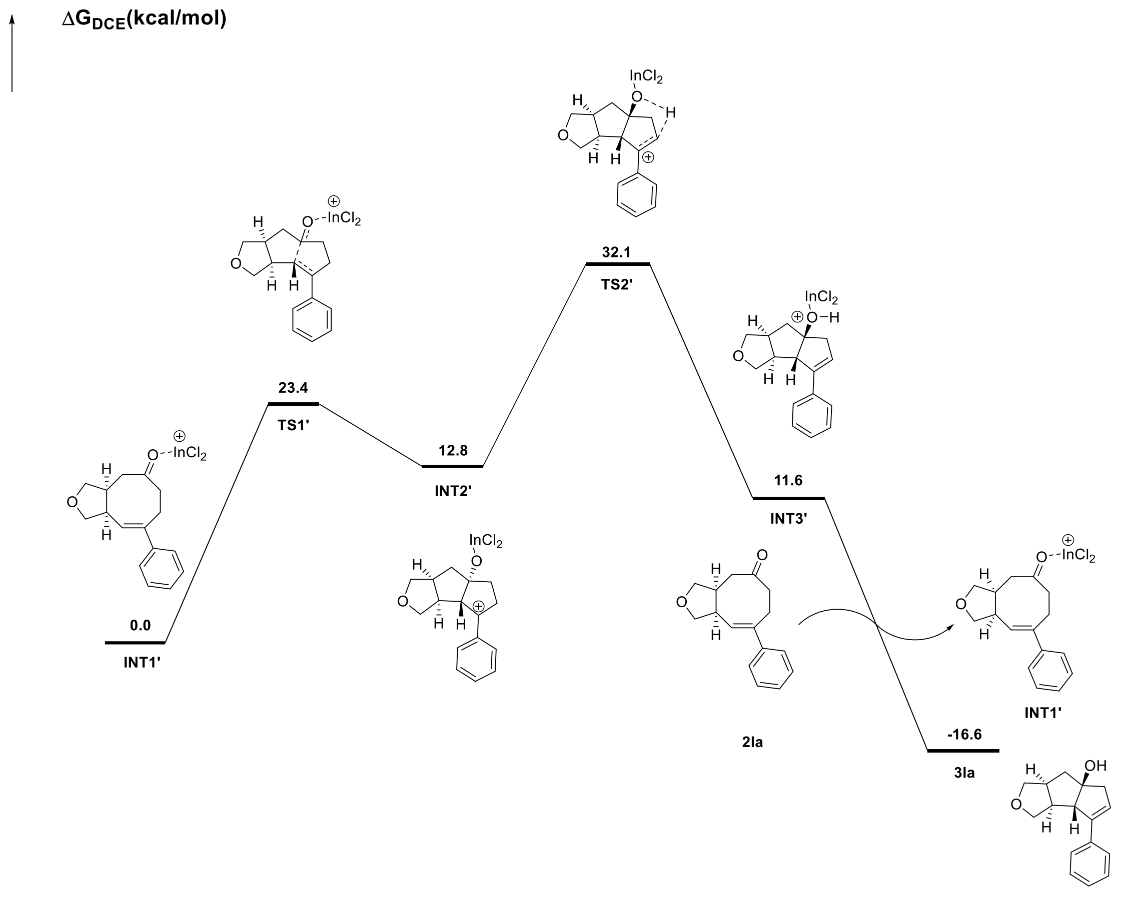
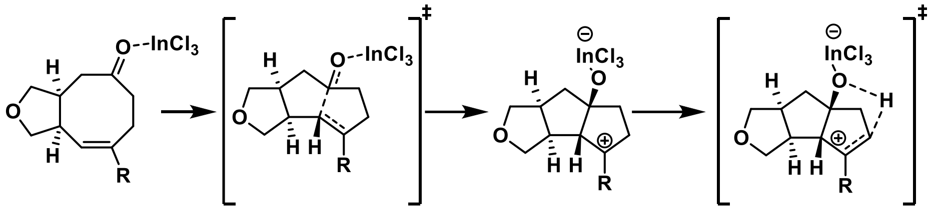


Figure S2. Computed energy surface for the ene reaction of 2la catalyzed by $InCl_2^+$.

To answer the question why some substrates (with methyl group and aryl group) undergo ene reaction smoothly while other substrates (with hydrogen atom and TMS group) cannot afford the desire product, we carried out DFT calculations to study the substituent effect. For comparison, the computed model substrates all have ether tether. The activation free energies of the $InCl_3$-catalyzed ene reaction for substrates with different substituents are shown in **Table S1**. For all substituents, the second step of the ene reaction is the rate-limiting step. The overall activation free energy for the substrate with methyl group (R=Me) is 24.6 kcal/mol, which is consistent with our experiment that **2ia** could afford the corresponding product at 60 °C. As for the substrate with hydrogen atom (R=H), the nucleophilic step via **TS1-H** and proton transfer via **TS2-H** require activation free energies of 28.2 kcal/mol and 30.1 kcal/mol, respectively. These activation free energies are too high for a reaction at 60 °C. That's why we failed to achieve the ene reaction for substrate with hydrogen atom (substrate **2p** was used experimentally) under standard reaction conditions. The starting material of **2p** recovered at elevated temperature (80 °C) after 4 h, and we did not try other conditions for this substrate. The TMS group, which has the well-known β-silicon effect, is not efficient to stabilize carbocation at α-position due to the long C-Si bond.[30] Here we found the activation free energy of nucleophilic step via **TS1-TMS** is 24.8 kcal/mol, which is much higher than **TS1-Me** by 7.1 kcal/mol in the first step, and the overall activation free energy of the ene reaction for TMS-substituted substrates is 27.6 kcal/mol, which is also higher by 1-3 kcal/mol compared to those successful ene reaction at 60-80 °C. We tried to carry out the ene reaction of substrate **2id** with TMS group for 18h at 60 °C and another 7h at 80 °C, finding that substrates decomposed without any desired product. Therefore, we suggest that this ene reaction requires the substituents to stabilize the carbocation at α-position efficiently. These computational results help us to understand the success and failure of our ene reaction for different substrates.

Table S1. The computed activation free energies of the $InCl_3$-catalyzed ene reaction for substrates with different substituents[a]



ΔG_{DCE}(kcal/mol)	INT1-R	TS1-R	INT2-R	TS2-R
R=Ph	0.0	18.2	10.5	26.6
R=Me	0.0	17.7	12.8	24.6
R=H	0.0	28.2	25.2	30.1
R=TMS	0.0	24.8	21.5	27.6

[a]**For R=Ph, the labelled species are INT1, TS1, INT2, TS2 shown in Figure S1.**

Table S2. Computed Energies for the Stationary Points

Thermal corrections to Gibbs energies (TCGs), single-point energies (SPEs) at high/low level.

	Imaginary Frequencies (cm^{-1})	TCGs (low level) (hartree)	SPEs (low level) (hartree)	SPEs (high level) (hartree)
2la	**None**	0.263516	-771.096191	-770.938515
3la	**None**	0.264852	-771.101446	-770.947935
INT1	**None**	0.255868	-2153.807352	-2153.693174
TS1	**-303.73**	0.257469	-2153.781893	-2153.665743
INT2	**None**	0.255886	-2153.792411	-2153.676514
TS2	**-1511.65**	0.254535	-2153.763579	-2153.649382
INT3	**None**	0.257175	-2153.807947	-2153.697969
INT1'	**None**	0.263404	-1693.376551	-1693.249133
TS1'	**-236.77**	0.263471	-1693.343215	-1693.211945
INT2'	**None**	0.262664	-1693.360370	-1693.227928
TS2'	**-1613.56**	0.255817	-1693.320657	-1693.190401
INT3'	**None**	0.263283	-1693.355575	-1693.230563
INT1-Me	**None**	0.20789	-1962.033216	-1961.971359
TS1-Me	**-207.93**	0.206871	-1962.003252	-1961.942071
INT2-Me	**None**	0.204172	-1962.008119	-1961.947288
TS2-Me	**-1335.01**	0.202795	-1961.986382	-1961.927106
INT1-H	**None**	0.180085	-1922.703159	-1922.650437
TS1-H	**-372.49**	0.179754	-1922.659034	-1922.605169
INT2-H	**None**	0.180431	-1922.663278	-1922.610658
TS2-H	**-1068.78**	0.175985	-1922.647965	-1922.598375
INT1-TMS	**None**	0.274339	-2331.424845	-2331.340611
TS1-TMS	**-294.84**	0.272561	-2331.385326	-2331.299347
INT2-TMS	**None**	0.273667	-2331.391158	-2331.305726
TS2-TMS	**-1155.57**	0.268757	-2331.373214	-2331.290976

Cartesian coordinates for the stationary points

2la

O	4.06571900	-1.56616300	-0.04067500
O	0.01179300	2.36726700	-1.49544700
C	1.86227500	-0.98562600	0.49666500
C	0.40545700	-1.04340100	0.12467500
C	-0.55248300	-0.25481300	0.65599500
C	-0.15412700	0.86052700	1.60634700
C	0.25005000	2.17688100	0.87069500
C	0.69011100	1.94474200	-0.56403700
C	2.01041900	1.25392900	-0.85969300
C	2.63164400	0.35154500	0.21029500
C	4.02834700	-0.14805000	-0.25078900
C	2.72559800	-2.02098800	-0.23034200
C	-1.98099200	-0.40269900	0.28313300
C	-2.50269400	-1.64229400	-0.13945800
C	-3.84134200	-1.77423400	-0.50746100
C	-4.70188500	-0.67167100	-0.45251400
C	-4.20586100	0.56034700	-0.01853200
C	-2.86442600	0.69154100	0.34958200
H	0.12825300	-1.78135000	-0.62544100
H	0.68372600	0.51790200	2.21768000
H	-0.97143200	1.08996500	2.29497500
H	-0.59391000	2.86869800	0.83136800
H	1.06552000	2.66314000	1.41963400
H	2.71336900	2.07694200	-1.06133700
H	1.89313200	0.71624100	-1.80664000
H	2.73256400	0.91551300	1.14104500
H	4.17694100	0.06608800	-1.31950900
H	4.85472100	0.29303300	0.31222700
H	2.64661200	-3.03047500	0.18105900
H	2.47766400	-2.05179700	-1.30407700
H	-1.85906000	-2.51593700	-0.15956300
H	-4.21710600	-2.74321700	-0.82448700
H	-5.74558800	-0.77525700	-0.73490400
H	-4.86174600	1.42500400	0.03269600
H	-2.50369800	1.66134300	0.67384300
H	1.95940100	-1.17907900	1.57304500

3la

O	-1.65032800	2.06666000	1.75070700
C	-1.53502700	-2.08095800	0.54911400
C	-1.09382700	-0.87055900	-0.27723800
C	-2.44923900	-0.39117700	-0.87547200
C	-3.34270700	-1.64807000	-0.84232000

C	-2.88428900	0.75376100	0.05519700
C	-1.57752700	1.44829100	0.45617800
C	-0.50681600	0.32204100	0.52099100
C	0.73097500	0.93542000	-0.10639300
C	0.42622800	2.09888900	-0.71530700
C	-1.03021600	2.45167900	-0.59481100
H	-2.23068500	2.84022300	1.68455900
H	-0.74904200	-2.82444200	0.70579700
H	-1.92402600	-1.76589400	1.53042900
H	-0.41046800	-1.20539900	-1.06256500
H	-2.31960900	-0.02498900	-1.89782300
H	-4.25556900	-1.47151100	-0.25632100
H	-3.63009200	-2.00189000	-1.83662700
H	-3.60501500	1.43758100	-0.40656800
H	-3.34499600	0.34159000	0.96067200
H	-0.33768100	0.03984500	1.56609500
H	1.12629900	2.72269500	-1.26248500
H	-1.54248800	2.33805200	-1.56080600
H	-1.19765800	3.48829800	-0.27461500
O	-2.56862100	-2.69903400	-0.22545100
C	2.04414000	0.26957200	-0.04906300
C	2.19680800	-0.94408200	0.64823500
C	3.18313400	0.81309400	-0.67963800
C	3.43531600	-1.58872700	0.71600400
H	1.34288600	-1.39188400	1.14427200
C	4.41806300	0.17175900	-0.61106300
H	3.10222400	1.74589900	-1.22864200
C	4.55305800	-1.03500900	0.08817000
H	3.52305500	-2.52416400	1.26165300
H	5.27951700	0.61327400	-1.10463900
H	5.51649900	-1.53382300	0.14005100

INT1

C	-4.16637000	-1.81573200	-0.06788400
O	-4.92178600	-1.10639400	-1.05468600
C	-4.06801700	-0.05860900	-1.51565800
C	-3.43112000	0.51157400	-0.24253400
C	-3.28627500	-0.76743200	0.66134600
H	-4.87186600	-2.32379500	0.59333500
H	-3.53431900	-2.57042100	-0.55934200
H	-3.29517500	-0.46104800	-2.19015300
H	-4.67893100	0.66233300	-2.06375000
H	-4.17185900	1.15679000	0.24485100
H	-3.69732200	-0.55950800	1.65133800

C	-1.33243900	0.56304300	2.58523400
C	-2.17677300	1.29852300	-0.49577300
C	-1.89925400	1.85920100	1.90681000
C	-1.47880200	1.96749000	0.44807800
H	-0.46690200	0.79826000	3.20628800
H	-1.55590900	2.72291800	2.47901100
H	-2.10188200	0.09192200	3.20288000
H	-1.80472600	1.29415900	-1.51718400
H	-2.98940400	1.84188900	1.96595400
C	-1.85167100	-1.28404200	0.81407500
C	-0.88584900	-0.38816600	1.51562500
O	0.34529800	-0.43671500	1.27374400
C	-0.24264300	2.71293000	0.11111700
C	-0.05622700	3.27344100	-1.16847300
C	0.79031200	2.86793500	1.05473000
C	1.12380300	3.93829300	-1.49745100
H	-0.84803200	3.19916000	-1.90677200
C	1.97253900	3.53492300	0.72554700
H	0.68996100	2.44959000	2.04966200
C	2.14770900	4.07027000	-0.55225800
H	1.24159000	4.36182800	-2.49085600
H	2.75956600	3.62648800	1.46847000
H	3.06717100	4.58835400	-0.80857200
H	-1.43781400	-1.58862300	-0.15101200
H	-1.87112100	-2.19163700	1.44138000
In	1.59603600	-1.25806700	-0.15484200
Cl	3.63770800	-0.24299400	0.37679900
Cl	1.57654100	-3.55949500	0.33350000
Cl	0.72807700	-0.71576600	-2.26770500

INT2

C	-3.65495600	-3.24918000	-0.57109100
O	-4.58020200	-2.21784300	-0.95563400
C	-3.81295000	-1.01337000	-1.00056900
C	-2.91284100	-1.08752600	0.24606800
C	-2.76707600	-2.62484100	0.51984200
H	-4.23966300	-4.10710600	-0.23273800
H	-3.05192400	-3.54498000	-1.44254900
H	-3.20611800	-0.98756000	-1.91803700
H	-4.50661500	-0.17019700	-1.00350900
H	-3.40669500	-0.59605100	1.08701000
H	-3.17610900	-2.85542200	1.50630400
C	-0.62866200	-1.17054100	2.23010300
C	-1.45269000	-0.53819500	0.04516600

C	-0.78295700	0.35898100	2.19152900
C	-1.28870200	0.69634400	0.82986100
H	0.26767600	-1.48691100	2.76714900
H	0.18643900	0.86693200	2.30663200
H	-1.49562400	-1.62138800	2.72150500
H	-1.23507700	-0.43075000	-1.01897700
H	-1.42127200	0.77637300	2.97846400
C	-1.26719400	-2.94140900	0.45626600
C	-0.55179300	-1.61254300	0.74354500
O	0.75952600	-1.64854400	0.26785100
C	-1.52558400	2.00994500	0.36002200
C	-1.97897300	2.23334200	-0.97077300
C	-1.29353500	3.13148900	1.20630700
C	-2.19338400	3.52258800	-1.42874600
H	-2.15329700	1.39355800	-1.63144500
C	-1.50343600	4.41635100	0.73637600
H	-0.94248800	2.97829100	2.22006600
C	-1.95145700	4.61222500	-0.57971500
H	-2.53569700	3.68947700	-2.44441100
H	-1.31684000	5.26980900	1.37932500
H	-2.10905800	5.62220900	-0.94636600
H	-0.97983400	-3.26350000	-0.55062800
H	-0.95781600	-3.72066800	1.15922000
In	2.11627200	-0.34795900	-0.19409900
Cl	4.02011400	-1.59168700	-0.87335200
Cl	2.78710000	1.10406800	1.58918800
Cl	1.46015200	1.05861900	-2.01048500

INT3

C	0.26751800	4.07271900	-0.20132400
O	1.28986200	3.98474900	-1.20638700
C	1.61068400	2.59497700	-1.32806100
C	1.65468800	2.07792100	0.11507800
C	0.57950100	2.96675700	0.82982000
H	0.30101200	5.08367300	0.21123700
H	-0.71803100	3.90909200	-0.66153300
H	0.83222200	2.07423500	-1.90614000
H	2.56232600	2.51837300	-1.85853800
H	2.64477900	2.26662300	0.53628600
H	0.99284800	3.39659100	1.74513900
C	0.75746900	0.41968800	2.72586100
C	1.23994400	0.59780200	0.33636600
C	2.00101400	-0.34768100	2.35165500
C	2.27859800	-0.26412300	1.03306800

H	0.08501200	-0.11007600	3.41016000
H	-0.46384700	-1.26518400	1.43548800
H	1.00781300	1.37137700	3.21256800
H	0.88246900	0.15984700	-0.60056100
H	2.60125600	-0.86446800	3.09243100
C	-0.59144100	2.02364500	1.16802800
C	0.08969600	0.68001900	1.36320900
O	-0.87731900	-0.42844200	1.14748100
C	3.41789200	-0.85351700	0.31150300
C	3.55654200	-0.66806300	-1.07692700
C	4.39708300	-1.61930400	0.97767600
C	4.63199100	-1.22568800	-1.77405800
H	2.82169600	-0.08824600	-1.62439100
C	5.46748000	-2.17646500	0.28226500
H	4.31952700	-1.78185700	2.04793200
C	5.59218700	-1.98259300	-1.09979700
H	4.71505300	-1.06744500	-2.84556300
H	6.20770600	-2.76415300	0.81794800
H	6.42731900	-2.41813100	-1.64051500
H	-1.27199300	1.97889300	0.30990600
H	-1.17157600	2.33234000	2.04137000
In	-2.40450100	-0.73898600	-0.28030100
Cl	-1.71887800	0.30534700	-2.25623000
Cl	-4.31534100	0.14215400	0.73591800
Cl	-2.19874900	-3.07974800	-0.22106400

TS1

C	4.15576100	-1.35958600	0.65797800
O	4.81361600	-0.28930700	1.34758600
C	3.87055000	0.78578900	1.37409300
C	3.18482400	0.76831900	-0.01054600
C	3.43822000	-0.69101100	-0.52517900
H	4.91668400	-2.08673600	0.36671400
H	3.43029400	-1.84629700	1.32790900
H	3.13416100	0.61835600	2.17434700
H	4.41689600	1.70848400	1.58110300
H	3.66862400	1.48727000	-0.67307700
H	4.10915000	-0.65820700	-1.38671000
C	1.55895800	0.72152400	-2.52055400
C	1.68609900	1.03296600	0.06812500
C	1.47069500	2.19784700	-2.05029200
C	1.02443900	2.06816400	-0.61590700
H	0.86879700	0.51319700	-3.34136000
H	0.79523600	2.79846400	-2.65499600

H	2.56722500	0.46399000	-2.85128200
H	1.23575300	0.69929200	0.99880500
H	2.44869000	2.69163800	-2.08466800
C	2.08478300	-1.28612500	-0.91508400
C	1.14096400	-0.15586000	-1.30835900
O	-0.16094400	-0.41360000	-1.29732200
C	-0.19353800	2.65187700	-0.11001000
C	-0.44763600	2.66396300	1.28589600
C	-1.17488700	3.19019900	-0.97872400
C	-1.63265000	3.18581800	1.78610200
H	0.29940200	2.28425400	1.97258500
C	-2.36266300	3.70332700	-0.47144600
H	-1.02518200	3.17310400	-2.05088500
C	-2.59498300	3.70134100	0.90871400
H	-1.81205100	3.19093700	2.85631200
H	-3.11463400	4.09345400	-1.14964800
H	-3.52588200	4.09957500	1.30102800
H	1.64498600	-1.84157500	-0.07965100
H	2.14830000	-1.97273500	-1.76872500
In	-1.31289200	-1.35160000	0.01444600
Cl	-3.42936400	-0.32331400	-0.20062300
Cl	-0.44640900	-1.12303900	2.21192600
Cl	-1.43891700	-3.64988800	-0.54639700

TS2

C	0.67463800	4.19486900	-0.57083000
O	1.98828200	4.11712500	-1.14020200
C	2.35472400	2.73493900	-1.06813700
C	1.85470600	2.25434100	0.30611400
C	0.70886200	3.27637100	0.66133600
H	0.47268600	5.24342000	-0.34144700
H	-0.06847300	3.83678300	-1.30008100
H	1.85993300	2.17772800	-1.87839300
H	3.43687400	2.66800200	-1.19756700
H	2.65855600	2.31166000	1.04268200
H	0.99454600	3.85107700	1.54542500
C	0.62874500	0.87076600	2.67070900
C	1.17543700	0.86293900	0.33559200
C	1.35656000	-0.43319700	2.28887900
C	1.89634200	-0.27935400	1.00667100
H	-0.11669300	0.73447400	3.45560100
H	0.15558000	-0.79455400	1.70925800
H	1.32703600	1.66210000	2.95703500
H	0.84106800	0.58988100	-0.66895900

H	1.73295900	-1.14218700	3.01786600
C	-0.57277300	2.45774300	0.94324400
C	-0.02346400	1.08999300	1.29552700
O	-0.90011300	-0.05195500	1.23545900
C	2.85948100	-1.13352300	0.34451700
C	3.18684400	-0.91926200	-1.01249200
C	3.50981700	-2.17502300	1.04539300
C	4.13123700	-1.72152700	-1.64723000
H	2.70305900	-0.12748100	-1.57178100
C	4.44797000	-2.97652200	0.40566700
H	3.27959600	-2.35050100	2.09048500
C	4.76133400	-2.75163900	-0.94169500
H	4.37379800	-1.54636600	-2.69057500
H	4.93971700	-3.77491300	0.95247000
H	5.49681600	-3.37784300	-1.43794700
H	-1.18475800	2.38557200	0.03727800
H	-1.19469300	2.87867400	1.73705600
In	-2.15113100	-0.66139000	-0.20059300
Cl	-0.98190600	-0.95019200	-2.24137900
Cl	-3.91775900	0.88458700	-0.46442200
Cl	-2.90682600	-2.72558800	0.66044700

INT1’

C	4.95092800	-1.10498400	0.57292900
O	5.56364600	0.16833000	0.80103000
C	4.49493400	1.10598700	0.90846200
C	3.54015800	0.72291900	-0.22773800
C	3.66212300	-0.84578400	-0.25459500
H	5.67447900	-1.73603700	0.05238100
H	4.70108500	-1.57221500	1.53655900
H	3.99424900	1.01405000	1.88580600
H	4.91111200	2.11133000	0.81330600
H	3.97435800	1.08314100	-1.16833600
H	3.80704900	-1.18009300	-1.28365600
C	1.05707200	-1.25872300	-1.80511100
C	2.16349900	1.30380400	-0.08255100
C	1.36714300	0.23376300	-2.17485100
C	1.16276200	1.15108100	-0.98110100
H	0.04844800	-1.53617300	-2.12130400
H	0.73876400	0.52121500	-3.01966700
H	1.77265700	-1.92277800	-2.29604200
H	1.97294700	1.86131000	0.83103800
H	2.40373900	0.30823500	-2.50420800
C	2.47379700	-1.60580800	0.35882000

C	1.16003300	-1.41416000	-0.31634200
O	0.13446600	-1.38249000	0.41057900
C	-0.17504600	1.72753500	-0.73582600
C	-0.36642200	2.84183600	0.10090300
C	-1.34895100	1.15690900	-1.33730100
C	-1.63221900	3.38905100	0.30308700
H	0.48664800	3.31447700	0.57273500
C	-2.62713400	1.76609000	-1.16481300
H	-1.24871800	0.44293200	-2.15519500
C	-2.76943000	2.86384200	-0.32751800
H	-1.73200600	4.25435300	0.95095900
H	-3.48017900	1.34838400	-1.69112100
H	-3.74231500	3.31850200	-0.17687300
H	2.34907000	-1.38030100	1.42116700
H	2.68158600	-2.68566500	0.27879900
In	-1.77824800	-0.61313600	0.23808800
Cl	-3.10179300	-2.29269100	-0.70723200
Cl	-2.21839600	-0.06071300	2.45404100

INT2'

C	0.38525300	4.01187700	-0.47571500
O	1.58276000	3.86314500	-1.25443200
C	1.86704400	2.46415400	-1.25871700
C	1.59378000	2.01416300	0.18889400
C	0.55064200	3.05889200	0.72157500
H	0.29954000	5.06418300	-0.19791100
H	-0.48640600	3.72728100	-1.08407200
H	1.19689500	1.94469800	-1.96076300
H	2.90118400	2.32970000	-1.58085800
H	2.51403500	2.06173500	0.77391400
H	0.98098300	3.59755300	1.56835100
C	0.59507200	0.66799700	2.71814700
C	0.90752500	0.60813500	0.32877900
C	1.64008200	-0.41280600	2.39860700
C	1.84498000	-0.36785700	0.92199600
H	-0.07113600	0.38505400	3.53445300
H	1.24879000	-1.41747700	2.62344700
H	1.09303500	1.60301900	2.98995200
H	0.51881200	0.30863400	-0.64719700
H	2.57794500	-0.32685900	2.95612100
C	-0.69585600	2.26941400	1.15119000
C	-0.19683800	0.84058200	1.40310500
O	-1.20596000	-0.15528700	1.38680800
C	2.77997100	-1.14956700	0.20574700

C	2.85308500	-1.08062800	-1.21620100
C	3.67052300	-2.01983600	0.89954200
C	3.78025000	-1.84310100	-1.90581300
H	2.18047500	-0.43255900	-1.76475600
C	4.59143400	-2.77956300	0.19965300
H	3.62804400	-2.08400300	1.98061000
C	4.64767400	-2.69082600	-1.20033800
H	3.83452600	-1.78788800	-2.98767100
H	5.26876300	-3.44113000	0.72891200
H	5.37263800	-3.28830200	-1.74502300
H	-1.43364000	2.26044700	0.33848400
H	-1.18712400	2.68165800	2.03692500
In	-2.33369100	-0.60372900	-0.08566900
Cl	-2.12141200	0.14103100	-2.29441000
Cl	-3.99556500	-2.18879900	0.24106700

INT3’

C	0.06012500	4.05947100	0.17535800
O	0.81904100	3.93193600	-1.03905800
C	1.02433500	2.53464900	-1.25436100
C	1.34922100	1.97485000	0.13587100
C	0.44555000	2.85417500	1.06158300
H	0.31329000	5.02557000	0.61776000
H	-1.01445600	4.04672500	-0.05671300
H	0.11139700	2.06996000	-1.65975500
H	1.83333200	2.42317900	-1.97961200
H	2.40612900	2.14028200	0.35491700
H	0.99950300	3.17644200	1.94616700
C	0.67595000	0.18210600	2.80551500
C	0.95838900	0.49327000	0.38938700
C	1.89076300	-0.54127700	2.28678200
C	2.05848800	-0.38503400	0.95811200
H	0.05992500	-0.40624900	3.49781600
H	-0.97684500	-1.27507100	1.87115600
H	0.95229600	1.09198000	3.35383300
H	0.52655800	0.06135900	-0.52063500
H	2.55555400	-1.08653500	2.94729900
C	-0.72402500	1.94213100	1.47766900
C	-0.08564500	0.56649000	1.52585000
O	-1.15643500	-0.48327500	1.32554200
C	3.13694800	-0.92386200	0.11365400
C	3.15580500	-0.66865200	-1.27039200
C	4.17297300	-1.71256800	0.65553900
C	4.17174900	-1.17832300	-2.08361600

H	2.37597100	-0.06731000	-1.72365000
C	5.18415700	-2.22193600	-0.15556300
H	4.18727300	-1.92981600	1.71893500
C	5.19038200	-1.95707200	-1.53142300
H	4.16425900	-0.96380400	-3.14844200
H	5.97152100	-2.82691200	0.28489800
H	5.98083100	-2.35384300	-2.16158600
H	-1.50103700	1.96951700	0.70486300
H	-1.18771100	2.22078300	2.42713800
In	-2.40711400	-0.76851100	-0.27252100
Cl	-2.62678500	0.80703800	-1.92064500
Cl	-3.43798300	-2.76933200	0.20578900

TS1'

C	-5.03303800	-0.83141400	-0.80363400
O	-5.47765600	0.53186400	-0.73234400
C	-4.29519200	1.32322300	-0.63306900
C	-3.40717200	0.56431600	0.37059500
C	-3.81524900	-0.92751100	0.13894000
H	-5.87084400	-1.46728900	-0.51110200
H	-4.74450200	-1.07219100	-1.83750300
H	-3.79858500	1.39481200	-1.61351500
H	-4.58174500	2.32367700	-0.30222000
H	-3.66442000	0.87539700	1.38438900
H	-4.10284600	-1.38491200	1.08831600
C	-1.17051300	-1.20653500	1.72397900
C	-1.91137300	0.73904000	0.10727100
C	-1.14409800	0.21485100	2.34896000
C	-0.97025800	1.05522600	1.11407100
H	-0.23594600	-1.74298600	1.90777000
H	-0.36459200	0.35258900	3.09459100
H	-1.97928100	-1.81691000	2.13086400
H	-1.68128000	1.09364100	-0.89464500
H	-2.09893000	0.45356100	2.82686900
C	-2.58715900	-1.62643300	-0.44209900
C	-1.34464800	-1.00621100	0.18501100
O	-0.24993400	-1.19664300	-0.57097900
C	0.26717800	1.73303800	0.80262700
C	0.32161900	2.68387100	-0.24875600
C	1.46464000	1.44658900	1.52413800
C	1.51104300	3.33795700	-0.54551500
H	-0.57847400	2.93215200	-0.79848100
C	2.65618800	2.09189400	1.19883300
H	1.45431800	0.74087800	2.34783400

C	2.67777000	3.04066800	0.16856700
H	1.53417000	4.07816700	-1.33832700
H	3.56217700	1.85527200	1.74631300
H	3.60468100	3.55022200	-0.07473500
H	-2.52610700	-1.48653200	-1.52551400
H	-2.56415100	-2.70367200	-0.23601300
In	1.64942400	-0.88404600	-0.38442000
Cl	2.97438800	-2.03058200	1.14224700
Cl	2.57366400	-0.03616900	-2.32996800

TS2'

C	0.49397900	4.12749000	-0.36610200
O	1.76573800	4.05808700	-1.02205700
C	2.11636600	2.67096700	-1.03770600
C	1.69145000	2.13005700	0.33964000
C	0.59787200	3.15706600	0.82212800
H	0.32231000	5.16716300	-0.07975300
H	-0.30043800	3.80959300	-1.05887900
H	1.56818700	2.15752000	-1.84270900
H	3.18793100	2.59753400	-1.23272000
H	2.54021900	2.12650900	1.02610400
H	0.96081100	3.68738300	1.70489500
C	0.56378900	0.63132000	2.70592100
C	0.98088800	0.75502300	0.34224700
C	1.26117200	-0.64656200	2.21440300
C	1.71428600	-0.44090900	0.91120100
H	-0.14696500	0.45987800	3.51561900
H	-0.02455200	-0.95485900	1.64357000
H	1.28237600	1.39973900	3.00469900
H	0.57113500	0.54542000	-0.65284100
H	1.65616500	-1.40344700	2.88158500
C	-0.68380600	2.35643100	1.16671000
C	-0.14105000	0.96051400	1.38387900
O	-1.04937200	-0.18737900	1.29272800
C	2.62824700	-1.26945800	0.15177900
C	2.86902500	-0.99947200	-1.21312000
C	3.32348600	-2.33441800	0.76928900
C	3.77859300	-1.76791600	-1.93545800
H	2.35063300	-0.18667900	-1.70775100
C	4.22607500	-3.10151500	0.04236800
H	3.16042200	-2.55272300	1.81906700
C	4.45720400	-2.81930000	-1.31079600
H	3.96007800	-1.54752200	-2.98258200
H	4.75642900	-3.91515800	0.52695400

H	5.16828700	-3.41629400	-1.87387400
H	-1.37817000	2.37268800	0.31894900
H	-1.21104000	2.73957100	2.04331100
In	-2.28317200	-0.62450800	-0.17375800
Cl	-2.65105300	0.64489800	-2.06783100
Cl	-3.32216900	-2.63942700	0.26647000

INT1-Me

C	3.53971600	-2.04077000	-0.64154900
O	4.31145900	-1.99896700	0.56510800
C	3.67701700	-1.03732900	1.40985700
C	3.33207400	0.12469500	0.47419700
C	2.94190600	-0.62319600	-0.84948300
H	4.20490400	-2.35046500	-1.45102400
H	2.73718700	-2.78593000	-0.54004400
H	2.76662000	-1.46186100	1.86201700
H	4.37682800	-0.76991300	2.20523000
H	4.26349800	0.66533700	0.26464600
H	3.41965000	-0.13625300	-1.70216200
C	1.36146000	1.72307400	-2.05480800
C	2.31362600	1.08317300	1.03265800
C	2.28494700	2.46962400	-1.03455200
C	1.85109700	2.17117600	0.39018200
H	0.57070500	2.38102700	-2.41795200
H	2.22254900	3.54121800	-1.24113300
H	1.94640500	1.35833200	-2.90487900
H	1.91745300	0.85961800	2.02211200
H	3.32076200	2.16235200	-1.19024700
C	1.43181300	-0.71409600	-1.10253000
C	0.70676800	0.56599900	-1.35788600
O	-0.50772500	0.69484600	-1.06298400
H	0.93473500	-1.26628600	-0.30008100
H	1.26740500	-1.29363200	-2.02706500
In	-1.91369800	-0.29101100	0.09296900
Cl	-3.48565800	1.42979600	0.34823100
Cl	-2.56490500	-2.08706400	-1.27081100
Cl	-0.86857100	-0.92495100	2.09942900
C	0.80060200	3.06937200	0.97973800
H	-0.09677400	3.08783200	0.34674600
H	0.50605200	2.74441200	1.98167400
H	1.16248600	4.10409200	1.03829300

TS1-Me

C	-3.38538800	-2.26394700	0.08475900

O	-4.42486600	-1.76480800	-0.76724800
C	-3.94386800	-0.51474700	-1.26863700
C	-3.22547700	0.15167300	-0.07482000
C	-2.90855300	-1.04299700	0.88586300
H	-3.80984400	-3.06310500	0.69588400
H	-2.56580500	-2.67272700	-0.52594500
H	-3.24398500	-0.68780000	-2.09948500
H	-4.80083500	0.05330500	-1.63660300
H	-3.88943000	0.86751100	0.41115500
H	-3.50719600	-0.94677400	1.79446500
C	-1.62547100	1.52010800	1.97111700
C	-1.90465400	0.83790500	-0.46668000
C	-1.99846000	2.72574800	1.07178900
C	-1.70264900	2.22291400	-0.30663700
H	-0.89903200	1.79195100	2.73970300
H	-1.41471200	3.62471300	1.28157500
H	-2.50203000	1.09839300	2.46572800
H	-1.43600000	0.40581700	-1.35080400
H	-3.05836200	3.00249300	1.15437700
C	-1.41491500	-0.97413400	1.20357600
C	-0.96786100	0.47807600	1.01622600
O	0.34821400	0.70847500	0.89210100
H	-0.84721000	-1.62261700	0.52697600
H	-1.17253700	-1.27366900	2.23002800
In	1.80885000	-0.23618900	-0.03602700
Cl	1.15480800	-0.88373200	-2.23011700
Cl	2.54624700	-2.10971000	1.21645500
Cl	3.51171300	1.40552400	-0.16384700
C	-0.86939100	3.00337900	-1.22440500
H	-0.92224200	2.66016400	-2.25886900
H	-1.05429400	4.07782700	-1.13323700
H	0.16615900	2.83916100	-0.86371200

IN2-Me

C	4.21189100	-2.12408500	0.15727900
O	5.27799400	-1.21233200	0.46728000
C	4.64058800	0.01206700	0.83605900
C	3.47501900	0.15398700	-0.16337900
C	3.20347000	-1.30775400	-0.66725100
H	4.64454700	-2.97075600	-0.37930300
H	3.75038500	-2.48356700	1.08941700
H	4.26717100	-0.05244400	1.86832200
H	5.38096500	0.81176600	0.77004700
H	3.77114500	0.79247800	-0.99853300

H	3.46073800	-1.36969900	-1.72726400
C	0.85631600	0.55342900	-1.58008200
C	2.10808700	0.63396500	0.47583500
C	1.03812500	2.01780800	-1.15830900
C	1.88932700	2.00116100	0.03141700
H	-0.10783800	0.36562200	-2.05744900
H	0.08673100	2.42306500	-0.74763900
H	1.63185900	0.27763000	-2.30101800
H	2.14034900	0.51237700	1.56085500
H	1.34307700	2.74808200	-1.91569500
C	1.71650500	-1.60886200	-0.43328900
C	1.03366400	-0.24263800	-0.25492500
O	-0.12124300	-0.31313100	0.51955300
H	1.57350700	-2.17197900	0.49500600
H	1.25864300	-2.17951900	-1.24642600
In	-2.01322600	-0.19906200	0.13498000
Cl	-2.71410000	-1.39456800	-1.80419100
Cl	-2.56613500	2.11614200	-0.17601200
Cl	-3.15530000	-1.00941800	2.04907500
C	2.44158200	3.19265500	0.66915800
H	2.50221300	3.08203300	1.75554500
H	3.48269200	3.26799800	0.30673600
H	1.92454300	4.10761000	0.37284700

TS2-Me

C	-3.66330800	-2.31253300	-0.10974700
O	-4.90353100	-1.65958800	-0.41046600
C	-4.55893300	-0.31008200	-0.74626900
C	-3.43639800	0.08197500	0.23184900
C	-2.86587000	-1.30063000	0.72702400
H	-3.89469400	-3.24268100	0.41399200
H	-3.12993500	-2.54882200	-1.04373500
H	-4.20373000	-0.26435900	-1.78679000
H	-5.46183000	0.29706200	-0.65192500
H	-3.84262300	0.64899100	1.07224500
H	-3.09940100	-1.43247400	1.78602200
C	-0.99254200	1.06417600	1.66843000
C	-2.21634700	0.80849700	-0.38639400
C	-1.13875600	2.41562600	0.94584100
C	-2.03729800	2.27141800	-0.10423000
H	-0.05229800	0.96283200	2.21203500
H	-0.22341100	1.95060400	0.04669400
H	-1.82740700	0.87770400	2.34985000
H	-2.15313900	0.60145700	-1.45977100

H	-0.88212200	3.37954900	1.37437200
C	-1.33411000	-1.28373300	0.50706200
C	-1.02207200	0.19706000	0.39271200
O	0.16866600	0.61268300	-0.29844500
H	-1.07278100	-1.77709500	-0.43599400
H	-0.78047500	-1.77079300	1.31289400
In	1.99210700	-0.17182200	-0.12264100
Cl	2.25222500	-1.82789700	-1.78735700
Cl	2.21554600	-1.10506300	2.04457800
Cl	3.44363400	1.66793300	-0.43823800
C	-2.60988300	3.34054500	-0.94560200
H	-3.70515300	3.27935700	-0.87763400
H	-2.28551100	4.33661200	-0.63857600
H	-2.36059900	3.16811200	-1.99977200

IN1-H

C	3.51442000	-1.72954300	-1.01835700
O	4.34821700	-1.98809500	0.11846200
C	3.82340900	-1.19916500	1.18691600
C	3.50339800	0.15001500	0.53922900
C	2.96810000	-0.28231700	-0.86905500
H	4.12261900	-1.86719400	-1.91549500
H	2.68753800	-2.45398600	-1.03968900
H	2.91211100	-1.66171300	1.59919200
H	4.58075400	-1.14347700	1.97244900
H	4.45502100	0.66906100	0.36791800
H	3.39133900	0.35904900	-1.64456800
C	1.36928000	2.29572700	-1.46788900
C	2.60530800	1.03765000	1.36195500
C	2.42966200	2.78301200	-0.42679900
C	2.14686400	2.22911300	0.95002200
H	0.57912400	3.03723500	-1.59454600
H	2.40562100	3.87541700	-0.41655800
H	1.84821400	2.11541400	-2.43741300
H	2.31882200	0.67524500	2.34807000
H	3.42708400	2.48130500	-0.75529200
C	1.44131800	-0.28703500	-0.99439100
C	0.72267300	1.02329400	-1.00875900
O	-0.49375400	1.08127600	-0.70144700
H	0.99290000	-0.93202800	-0.23172300
H	1.17263800	-0.73433700	-1.96652000
In	-1.93696800	-0.19247600	0.08211500
Cl	-3.73227700	1.29645700	0.30364400
Cl	-2.25741400	-1.88759700	-1.51320800

Cl	-1.03711500	-0.97725600	2.10582900
H	1.49102000	2.80410400	1.60068300

TS1-H

C	-3.45187900	-2.01651700	0.46273300
O	-4.47616400	-1.68677200	-0.48751300
C	-3.95947400	-0.59086600	-1.24342300
C	-3.25072900	0.30443700	-0.20147900
C	-2.94725100	-0.66330700	0.98635500
H	-3.90011300	-2.65273700	1.22825300
H	-2.64249100	-2.56878800	-0.03839500
H	-3.24669700	-0.95505500	-1.99709600
H	-4.79525700	-0.09942100	-1.74568600
H	-3.91603100	1.10767300	0.11430700
H	-3.53923700	-0.36397200	1.85434300
C	-1.64290900	2.05664200	1.47427700
C	-1.91504100	0.90594700	-0.75155000
C	-1.84934700	3.07771700	0.34291100
C	-1.83056300	2.29367400	-0.90797400
H	-0.97534400	2.43245500	2.25259400
H	-1.01661100	3.79252300	0.27592700
H	-2.58790800	1.77796600	1.94386900
H	-1.50531500	0.31283000	-1.56905600
H	-2.75046200	3.70478800	0.42495800
C	-1.45463600	-0.55183600	1.27551000
C	-0.99014100	0.82239400	0.79317700
O	0.32721500	0.99362400	0.63981900
H	-0.90350400	-1.32624800	0.73172100
H	-1.20183400	-0.64935000	2.33752300
In	1.77659700	-0.16089700	-0.04416000
Cl	1.13593900	-1.10946100	-2.12779800
Cl	2.35304000	-1.83615700	1.53290500
Cl	3.59430900	1.31745900	-0.37003800
H	-1.54495900	2.76546700	-1.84724900

IN2-H

C	4.47295500	-1.69693400	-0.08518800
O	5.45241900	-0.77361200	0.41799900
C	4.71093400	0.29935100	0.99982500
C	3.54691800	0.52680700	0.01587600
C	3.40392700	-0.82900600	-0.76845400
H	4.98251400	-2.38425000	-0.76331200
H	4.03670000	-2.26584400	0.74921800
H	4.33987400	0.00970800	1.99284900

H	5.37724300	1.15833400	1.09834900
H	3.79053600	1.33634200	-0.67523700
H	3.67817000	-0.65609500	-1.81163200
C	0.94387300	0.97775800	-1.37701100
C	2.12083300	0.73679300	0.71593200
C	1.05536500	2.34481100	-0.68394700
C	1.86001200	2.12800800	0.49855200
H	-0.00103900	0.83851900	-1.90526500
H	0.08237000	2.60947400	-0.19335100
H	1.74228600	0.88801000	-2.11979900
H	2.16904000	0.40446100	1.75392400
H	1.30429400	3.22984700	-1.27778700
C	1.94919100	-1.29688800	-0.64047300
C	1.14246200	-0.05369800	-0.22764200
O	-0.02019800	-0.37345400	0.46042400
H	1.84517000	-2.03693700	0.15977000
H	1.55598900	-1.73747400	-1.56098100
In	-1.91805300	-0.19781800	0.10410200
Cl	-2.56989600	-0.99622700	-2.04162200
Cl	-2.48825500	2.12965400	0.26416100
Cl	-3.04814600	-1.38503000	1.81186800
H	2.19192000	2.93076000	1.15512100

TS2-H

C	-3.97355000	1.86209900	-0.22425500
O	-5.12671400	1.20846200	0.32256500
C	-4.63377300	0.02403200	0.95855200
C	-3.54505400	-0.51986200	0.01598100
C	-3.12069300	0.73847000	-0.83371200
H	-4.32246700	2.60104500	-0.94869800
H	-3.42218400	2.37708700	0.57767400
H	-4.20639000	0.27761500	1.94033400
H	-5.47741700	-0.65459100	1.10104800
H	-3.95404300	-1.29714600	-0.63221100
H	-3.40503500	0.58211000	-1.87693900
C	-1.08565900	-1.61909400	-1.33821500
C	-2.23522500	-0.99398900	0.69645800
C	-1.12625900	-2.79198600	-0.35114700
C	-1.93028700	-2.45226700	0.72023300
H	-0.17329500	-1.58788300	-1.93528900
H	-0.26926700	-2.13490400	0.45536100
H	-1.95467700	-1.64524100	-2.00248100
H	-2.13326400	-0.54391600	1.68843800
H	-0.79699800	-3.80452500	-0.56047700

C	-1.58730000	0.89416900	-0.70763300
C	-1.13061800	-0.49080500	-0.28301900
O	0.10487400	-0.64427000	0.41226100
H	-1.33415400	1.60792600	0.08441100
H	-1.11155800	1.22798200	-1.63277400
In	1.87019400	0.19340300	0.08654500
Cl	2.10503800	1.99642300	1.60375200
Cl	2.09766300	0.97124800	-2.14069600
Cl	3.41320500	-1.54277800	0.54641400
H	-2.16393200	-3.12363000	1.54180300

IN1-TMS

C	2.20310700	-3.73979200	-0.20788100
O	3.10584300	-3.72765900	0.90448700
C	3.00756500	-2.42402100	1.48036900
C	2.98386500	-1.47695300	0.27746700
C	2.14611400	-2.29129200	-0.76684200
H	2.57810700	-4.46538400	-0.93349600
H	1.20702100	-4.06120800	0.12958700
H	2.08172400	-2.33056500	2.07040700
H	3.86601400	-2.27793900	2.14019500
H	4.00577300	-1.41866300	-0.11860300
H	2.62901000	-2.24965300	-1.74530300
C	1.34447200	0.15439900	-2.47045700
C	2.51298600	-0.08031200	0.60127700
C	2.64606300	0.65440800	-1.76388500
C	2.38967900	0.92727000	-0.28677900
H	0.80630100	0.98787200	-2.92319800
H	2.97172000	1.55785900	-2.28693500
H	1.59230300	-0.57795400	-3.24662200
H	2.27444800	0.10509600	1.64819200
H	3.43795400	-0.08908300	-1.88613000
C	0.68870700	-1.84122100	-0.90397500
C	0.42500100	-0.48692400	-1.47535400
O	-0.63387000	0.12656700	-1.19324600
H	0.15872300	-1.94260300	0.04847000
H	0.17879800	-2.51971000	-1.60917400
In	-2.21401900	-0.12843000	0.12725600
Cl	-3.22969900	1.97320700	-0.06388200
Cl	-3.39350900	-1.93710400	-0.80253600
Cl	-1.29044100	-0.54180100	2.24797400
Si	1.89017200	2.67284300	0.24086900
C	3.43261000	3.76082400	0.16091400
H	3.87305600	3.75929700	-0.84365100

H	3.18417000	4.79897600	0.41517900
H	4.19784900	3.41331200	0.86535100
C	0.60978900	3.36025900	-0.96244200
H	-0.31953900	2.78268200	-0.95356000
H	0.36332700	4.39403200	-0.68898900
H	0.99268000	3.37319600	-1.98982700
C	1.19998400	2.65729200	1.99212300
H	0.30461300	2.03083600	2.06955900
H	1.93486400	2.28871600	2.71743400
H	0.92221700	3.67613000	2.28979500

TS1-TMS

C	1.94374700	-3.76537500	0.50047100
O	3.22702400	-3.47006100	1.06985900
C	3.31154600	-2.04374000	1.10814100
C	2.67304300	-1.56735100	-0.21555900
C	1.79145100	-2.77666800	-0.66530400
H	1.94586000	-4.81495700	0.19996100
H	1.15560600	-3.60657900	1.25252700
H	2.75281200	-1.65667200	1.97267400
H	4.36356900	-1.76884800	1.21017200
H	3.44990200	-1.35895600	-0.95205300
H	2.21466800	-3.21556300	-1.57197800
C	1.36772900	-0.38290500	-2.51244100
C	1.78058900	-0.31245600	-0.01701100
C	2.21179200	0.84089900	-2.10027200
C	2.12582900	0.91245000	-0.60875200
H	0.69426000	-0.15806200	-3.34260900
H	1.83257500	1.77253700	-2.53407900
H	1.99406100	-1.22675100	-2.80631400
H	1.38630900	-0.25767400	0.99794900
H	3.26549100	0.78421500	-2.41555300
C	0.39030200	-2.23081000	-0.92203700
C	0.51947900	-0.74656400	-1.26408100
O	-0.59541400	-0.01384200	-1.20175100
H	-0.23126000	-2.34044800	-0.02620400
H	-0.13230000	-2.72838500	-1.74750800
In	-2.10783400	-0.00204200	0.06692400
Cl	-1.25240800	0.18732800	2.27844900
Cl	-3.39066100	-1.99260800	-0.11140800
Cl	-3.40144400	1.87558900	-0.54398900
Si	2.10315400	2.58486900	0.31762900
C	0.36495000	3.25656500	0.06133100
H	0.07927800	3.26962400	-0.99503500

H	-0.36993400	2.66581400	0.61433200
H	0.32300300	4.28506700	0.44134500
C	3.40582400	3.66101000	-0.50465200
H	4.40286400	3.21273500	-0.42770900
H	3.18255200	3.82926400	-1.56384400
H	3.43777600	4.63863500	-0.00836700
C	2.47268000	2.26316400	2.12694900
H	3.44622300	1.77679400	2.25771600
H	2.49187900	3.20955500	2.68087800
H	1.70461400	1.62719700	2.58016000

IN2-TMS

C	3.08612700	-3.61565500	0.41628700
O	4.35602800	-2.95237400	0.51928100
C	4.05503900	-1.56355400	0.66510000
C	2.89671900	-1.31929700	-0.32254100
C	2.23706500	-2.73560900	-0.51458900
H	3.26690600	-4.62144000	0.03171000
H	2.62415600	-3.68650900	1.41243400
H	3.74148900	-1.35230300	1.69722100
H	4.95933200	-0.99764200	0.43842500
H	3.28681400	-0.95152300	-1.27358000
H	2.37866000	-3.05013300	-1.55115400
C	0.38800300	-0.59360400	-1.75748700
C	1.72815500	-0.39432000	0.23278100
C	0.98693800	0.81693600	-1.67191800
C	1.83811500	0.86198400	-0.48318700
H	-0.62043900	-0.60780500	-2.17600900
H	0.19399000	1.55342800	-1.40018000
H	1.01361700	-1.21814700	-2.40198100
H	1.80437700	-0.32740300	1.32065300
H	1.43606100	1.24949800	-2.57317800
C	0.74832200	-2.60402400	-0.16906400
C	0.42901400	-1.10603800	-0.29282000
O	-0.65626000	-0.71654500	0.48218700
H	0.56008500	-2.90065200	0.86824100
H	0.09980500	-3.20381500	-0.81442000
In	-2.44341000	-0.05996200	0.14840700
Cl	-3.83173700	-1.58361200	-1.04607900
Cl	-2.35951500	2.00662800	-1.07536900
Cl	-3.38502900	0.37584400	2.28198800
Si	2.73404500	2.43465400	0.14496700
C	1.47046100	3.08550500	1.38099800
H	0.52598000	3.34656700	0.89268200

H	1.26442800	2.35698500	2.17209300
H	1.87636200	3.99196400	1.84766500
C	2.98364600	3.58707100	-1.30883500
H	3.62144400	3.13298600	-2.07571400
H	2.02843900	3.86143800	-1.77008600
H	3.47039500	4.51029300	-0.97218800
C	4.33636400	1.92111300	0.96783600
H	5.03238200	1.46844300	0.25412200
H	4.81973600	2.81082600	1.38969500
H	4.16126200	1.21563600	1.78578500

TS2-TMS

C	-2.13643800	3.83012400	0.48430800
O	-3.54663300	3.59052500	0.56842300
C	-3.70129200	2.16548600	0.55495700
C	-2.64902100	1.64546900	-0.44208900
C	-1.61955700	2.83350400	-0.56356700
H	-1.99181800	4.87877900	0.21506800
H	-1.66586600	3.64208500	1.46214100
H	-3.51692100	1.76185000	1.56192600
H	-4.73118700	1.94703700	0.26665200
H	-3.10941400	1.43615900	-1.40967400
H	-1.69113300	3.27579300	-1.56000500
C	-0.51614000	0.24031800	-1.99447500
C	-1.79417900	0.44735700	0.03447200
C	-1.20483800	-1.08377800	-1.63401900
C	-2.07003900	-0.90711100	-0.56085800
H	0.45647900	0.10866100	-2.47101100
H	-0.35686100	-1.21297300	-0.58461200
H	-1.15564300	0.84978600	-2.64012300
H	-1.77113000	0.41509800	1.12822500
H	-1.21373100	-1.96270200	-2.27137300
C	-0.20225900	2.25781700	-0.32158400
C	-0.39313800	0.76863700	-0.55042000
O	0.50193500	-0.16344800	0.06401300
H	0.11124500	2.42033100	0.71557500
H	0.55486900	2.69260400	-0.97889000
In	2.48223000	-0.17591400	0.13120200
Cl	3.17862900	0.90590100	2.11525400
Cl	3.42579700	0.88034300	-1.77205700
Cl	2.98465900	-2.48679300	0.21381300
Si	-3.23771900	-2.20120800	0.21236200
C	-3.22932200	-3.73800300	-0.86134000
H	-2.22906000	-4.18296200	-0.91477400

H	-3.90681200	-4.49115400	-0.44094600
H	-3.56428000	-3.51897500	-1.88170600
C	-2.56817500	-2.53513300	1.93615000
H	-2.56966900	-1.62601400	2.54743300
H	-3.19129900	-3.28329600	2.44109400
H	-1.54275600	-2.91982900	1.89638600
C	-4.92301200	-1.37094900	0.27143700
H	-5.66866300	-2.07954100	0.65250700
H	-4.91185100	-0.50321200	0.93912700
H	-5.24812100	-1.04054000	-0.72146500

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