Supporting Information

Cobalt Catalyzed Intramolecular [4+2] Cycloaddition of Cyclopropyl-Capped Dienes with Alkynes/Alkenes/Allene and Reaction Mechanism

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1. General Information

All chemicals were used as received without further purification. Dry DCE and THF (with molecular sieves) was purchased from J&K. Reaction tubes (25 mL) were purchased from Synthware. 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 stain followed by gentle heating. Purification of products was accomplished by flash chromatography on SiliaFlash P60 (Particle size: 40-63um, Pore size 60A) purchased from Innochem. Organic solutions were concentrated using a Büchi or Eyela rotary evaporator with a desktop vacuum pump. Nuclear magnetic resonance (NMR) spectra were measured on Bruker AVANCE III 400 (^{1}H at 400 MHz, ^{13}C{^{1}H} at 101 MHz). Data for ^{1}H NMR spectrum are reported as follows: chemical shift δ (ppm) referenced to tetramethylsilane (TMS, 0.00 ppm), $CHCl_3$ (7.26 ppm) or $CHDCl_2$ (5.32 ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, ddd = doublet of doublet of doublets, dddq = doublet of doublet of doublet of quartets, dtdt = doublet of triplet of doublet of triplets, tq = triplet of quartets, qdd = quartet of doublet of doublets, m = multiplet), coupling constant *J* (Hz), and integration. Data for ^{13}C{^{1}H} NMR spectrum are reported as follows: chemical shift δ (ppm) referenced to $CDCl_3$ (77.16 ppm) or CD_2Cl_2 (53.84 ppm). Structural assignments for some substrates were made with additional information from gCOSY, gHSQC, and gHMBC experiments. High-resolution mass spectrometry (HRMS) data were recorded on Bruker Solarix XR fourier transform ion cyclotron resonance (FTICR) mass spectrometers (ionization: ESI; mass analyzer: FT-ICR). Single crystal X-ray diffractometer was measured on XtaLAB PRO 007HF(Mo). Single Crystal was obtained by slowly evaporating DCM solution of the compounds. The enantiomeric excess (ee) of **2a** were determined by chiral HPLC analysis using UltiMate 3000 Pump (OD-H, hexanes:^{i}PrOH = 95:5, flow rate = 1.0 mL/min, l = 205 nm).

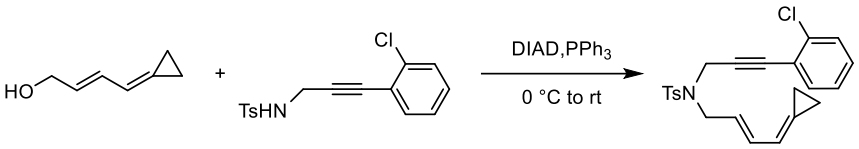
Abbreviations

d	Density
DCM	Dichloromethane
DCE	Dichloroethane
DFT	density functional theory
EA	ethyl acetate
ESI	electron spray ionization
Et	Ethyl
HRMS	high-resolution mass spectroscopy
Me	methyl
m. p.	melting point
Ms	Methanesulfonyl
PE	petroleum ether
Ph	phenyl
PTLC	preparative thin-layer chromatography
r. t.	room temperature
THF	Tetrahydrofuran
TLC	thin layer chromatography
TS	transition state
Ts	tosyl
TFA	trifluoroacetic acid

2. Substrates preparations

Note here: 1. We did not optimize all reactions in this part; 2. The substrates of all [4+2] reactions are recommended to store at -20 °C refrigerator under N_2 and use as soon as possible. Otherwise, the substrates gradually decompose.

Substrates **1a**-**1d, 1f**, **1h-1k, 1n** were synthesized according to the procedure we previously reported[1].



S1 **S2** **1e**

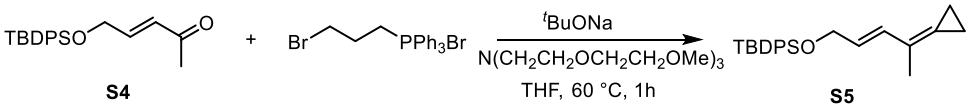
At 0 ºC, to a stirred solution of **S1**[1] (88.0 mg, 0.80 mmol), **S2**[2] (150.0 mg, 0.47 mmol) and PPh_3 (246.0 mg, 0.94 mmol) in dry THF (5 mL) was added DIAD (205.0 mg, 1.0 mmol) for 10 minutes. The reaction was gradually allowed to warm to room temperature and stirred overnight. Upon completion, the reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 50:1 to 20:1) to afford **1e** (129.0 mg, 67%) as a colorless oil.

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

^{1}H NMR (400 MHz, Methylene Chloride-d2) δ 7.76 – 7.73 (m, 2H), 7.35 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.24 (dd, *J* = 7.9, 1.5 Hz, 3H), 7.20 – 7.16 (m, 1H), 7.12 (dd, *J* = 7.7, 1.9 Hz, 1H), 6.51 – 6.44 (m, 1H), 6.44 – 6.40 (m, 1H), 5.61 (dd, *J* = 14.5, 7.0 Hz, 1H), 4.34 (s, 2H), 3.97 (d, *J* = 7.0 Hz, 2H), 2.26 (s, 3H), 1.17 – 1.08 (m, 4H).

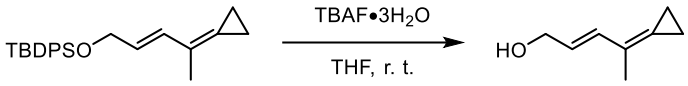
^{13}C NMR (101 MHz, Methylene Chloride-d_2) δ 144.2, 136.3, 136.0, 135.2, 133.8, 129.94, 129.93, 129.5, 129.0, 128.1, 126.8, 124.6, 122.6, 118.1, 87.7, 82.8, 49.1, 37.1, 21.5, 2.8, 2.5.

HRMS (ESI) m/z: calcd. for $C_{23}H_{23}ClNO_2S$ ($[M+H]^+$): 412.1133, found: 412.1131.



S4 **S5**

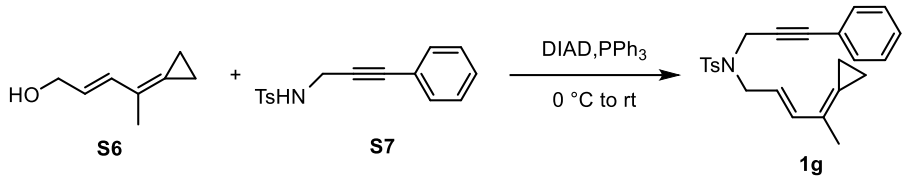
Under N_2 atmosphere, a solution of $Br(CH_2)_3PPh_3Br$ (2.40 g, 5.2 mmol), ^{t}BuONa (1.00 g, 10.4 mmol) in THF (8 mL) was heated in an oil bath at 65 °C for 3 h. Then a solution of **S4**[3] (1.30 g, 4.0 mmol) and tris[2-(2-methoxyethoxy)ethyl]amine[4] (129.0 mg, 0.4 mmol) in THF (3 mL) was added. The reaction mixture was further stirred in an oil bath at 65 °C for 1 h. The reaction mixture was concentrated *in vacuo* and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 50:1) to afford **S5** (859.0 mg, 59%).



S5 **S6**

To a stirred solution of **S5** (1.07 g, 3.0 mmol) in THF (20 mL) was added TBAF•3H_2O (3.00 g, 10.0 mmol, 3.3 equiv.). The reaction was stirred for 6.5 h at room temperature and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (eluted with PE/EA, 5:1) to afford **S6** (208.0 mg, 56%)

The product was immediately used for the next step to avoid potential decomposition.



S6 **S7** **1g**

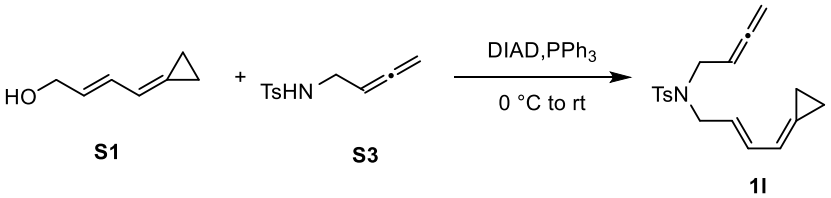
At 0 ºC, to a stirred solution of **S6** (208.0 mg, 1.7 mmol), **S7**[5] (570.0 mg, 2.0 mmol, 1.2 equiv.) and PPh_3 (668.9 mg, 2.55 mmol, 1.5 equiv.) in dry THF (20 mL) was carefully added DIAD (515.6 mg, 2.55 mmol, 1.5 equiv.) dropwise in 10 minutes. The reaction was gradually allowed to warm to room temperature and stirred for 24 h. Upon completion, the reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 20:1) to afford **1g** (633.4 mg, 96%) as a colorless oil.

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

^{1}H NMR (400 MHz, Methylene Chloride-d2) 7.80 – 7.74 (m, 2H), 7.34 – 7.24 (m, 5H), 7.16 – 7.08 (m, 2H), 6.54 (d, *J* = 15.6 Hz, 1H), 5.56 (dt, *J* = 15.5, 6.9 Hz, 1H), 4.30 (s, 2H), 3.97 (d, *J* = 6.9 Hz, 2H), 2.34 (s, 3H), 1.91 (dd, *J* = 1.6, 1.6 Hz, 3H), 1.12 (s, 4H).

^{13}C NMR (101 MHz, Methylene Chloride-d2) δ 144.1, 137.3, 136.6, 131.9, 130.0, 128.8, 128.6, 128.2, 126.3, 122.8, 122.7, 120.8, 85.9, 82.4, 49.5, 37.2, 21.6, 17.1, 3.1, 2.6.

HRMS (ESI): calcd. for $C_{24}H_{26}NO_2S$([M+H]$^+$): 392.1679, found 392.1678.



S1 **S3** **1l**

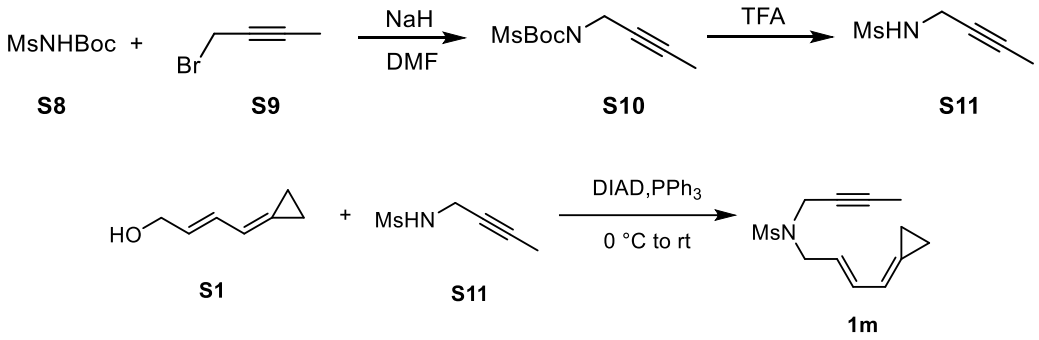
At 0 ºC, to a stirred solution of **S1**[1] (110.0 mg, 1.0 mmol), **S3**[6] (244.0 mg, 1.1 mmol) and PPh_3 (393.0 mg, 1.5 mmol) in dry THF (10 mL) was added DIAD (303.0 mg, 1.5 mmol) for 10 minutes. The reaction was gradually allowed to warm to room temperature and stirred for 24 h. Upon completion, the reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 20:1) to afford **1l** (196.0 mg, 62%) as a colorless oil.

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

^{1}H NMR (400 MHz, Methylene Chloride-d2) δ 7.70 – 7.64 (m, 2H), 7.34 – 7.27 (m, 2H), 6.33 (dt, *J* = 10.5, 1.9 Hz, 1H), 6.26 (ddt, *J* = 15.0, 10.5, 1.3 Hz, 1H), 5.48 – 5.40 (m, 1H), 4.91 – 4.87 (m, 1H), 4.69 (ddd, *J* = 6.6, 2.5, 2.5 Hz, 2H), 3.87 (d, *J* = 6.9 Hz, 2H), 3.82 (ddd, *J* = 7.1, 2.5, 2.5 Hz, 2H), 2.41 (s, 3H), 1.14 – 1.06 (m, 4H).

^{13}C NMR (101 MHz, Methylene Chloride-d2) δ 209.9, 143.9, 138.0, 134.3, 130.1, 128.5, 127.5, 125.3, 118.1, 86.1, 76.2, 49.1, 46.0, 21.6, 2.8, 2.4.

HRMS (ESI): calcd. for $C_{18}H_{22}NO_2S$([M+H]$^+$): 316.1366, found 316.1366.



At 0 °C, to a mixture of **S8**[7] (1.95 g, 10 mmol) and NaH (400.0 mg, 10 mmol, 60% in oil) was added DMF (20 mL) under Ar. The reaction was stirred at 0 °C for 10 minutes. Then **S9** (1.46 g, 11 mmol) was added. The reaction mixture was stirred at room temperature for 12 h. Upon completion, the reaction was quenched by H_2O, extracted with diethyl ether three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 20:1~10/1) to afford **S10** (2.25 g, 91%) as a white solid.

At 0 °C, to a stirred solution of **S10** (2.25 g, 9.1 mmol) in DCM (30 mL) was added TFA (9.1 mL) dropwise. Then the reaction was allowed to warm to room temperature and stirred for 6 h. Upon completion, the reaction was quenched by saturated $NaHCO_3$, extracted with diethyl ether three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 5/1) to afford **S11** (1.07 g, 80%) as a colorless oil.

At 0 °C, to a stirred solution of **S1**[1] (111.2 mg, 1.0 mmol), **S11** (148.4 mg, 1.0 mmol) and PPh_3 (393.4 mg, 1.5 mmol) in dry THF (3 mL) was added DIAD (303.3 mg, 1.5 mmol) in 10 minutes. The reaction was gradually allowed to warm to room temperature and stirred for 5 h. Upon completion, the reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 20:1~10/1) to afford **1m** (52.2 mg, 22%) as a white solid.

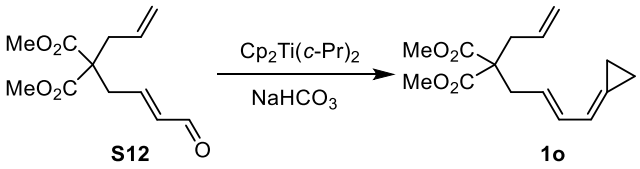
m.p. = 87.3-89.0 °C.

TLC (3:1 PE/EA, R_f): 0.5.

^{1}H NMR (400 MHz, Methylene Chloride-d2) δ 6.54 – 6.35 (m, 2H), 5.72 – 5.58 (m, 1H), 3.98 (q, *J* = 2.4 Hz, 2H), 3.90 (d, *J* = 6.8 Hz, 2H), 2.91 (s, 3H), 1.85 (t, *J* = 2.4 Hz, 3H), 1.18 – 1.14 (m, 4H).

^{13}C NMR (101 MHz, Methylene Chloride-d2) δ 134.5, 128.9, 125.0, 118.1, 82.5, 72.7, 48.8, 38.5, 36.6, 3.5, 2.8, 2.6.

HRMS (ESI): calcd. for $C_{12}H_{18}NO_2S$ ([M+H]$^+$): 240.1053, found 240.1050.



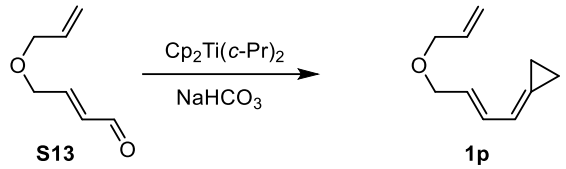
To a stirred solution of **S12**[8] (0.55 g, 2.3 mmol) and $NaHCO_3$ (0.46 g, 5.8 mmol) in toluene (10 mL) was added bis(cyclopentadienyl)dicyclopropyltitanium (1.50 g, 5.8 mmol) in toluene (15 mL) at 60 ºC. The reaction was monitored by TLC and stirred at the same temperature for 1 h. Upon completion, the reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 100:1~40/1) to afford **1o** (282.1 mg, 46%) as a light yellow oil.

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

^{1}H NMR (400 MHz, Methylene Chloride-d2) δ 6.36 (dt, *J* = 10.4, 2.0 Hz, 1H), 6.24 (dd, *J* = 15.2, 10.4 Hz, 1H), 5.73 – 5.60 (m, 1H), 5.55 – 5.44 (m, 1H), 5.15 – 5.11 (m, 1H), 5.09 (d, *J* = 1.2 Hz, 1H), 3.69 (s, 6H), 2.66 (d, *J* = 7.7 Hz, 2H), 2.61 (ddd, *J* = 7.5, 1.2, 1.2 Hz, 2H), 1.15 – 1.09 (m, 4H).

^{13}C NMR (101 MHz, Methylene Chloride-d2) δ 171.5, 134.2, 133.0, 126.7, 125.4, 119.3, 118.7, 58.4, 52.6, 37.3, 36.2, 2.7, 2.4.

HRMS (ESI): calcd. for $C_{15}H_{21}O_4$ ([M+H]$^+$): 265.1434, found 265.1431.



To a stirred solution of **S13**[9] (252.3 mg, 2.0 mmol) and $NaHCO_3$ (0.42 g, 5.0 mmol) in toluene (10 mL) was added bis(cyclopentadienyl)dicyclopropyltitanium[2] (1.30 g, 5.0 mmol) in toluene (15 mL) at 60 ºC. The reaction was monitored by TLC and stirred at the same temperature for 1 h. Upon completion, the reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 200:1) to afford **1p** (131.4 mg, 44%) as a yellow oil.

TLC (5:1 PE/EA, R_f): 0.9.

^{1}H NMR (400 MHz, Methylene Chloride-d2) δ 6.47 – 6.34 (m, 2H), 5.98 – 5.84 (m, 1H), 5.82 – 5.71 (m, 1H), 5.26 (dd, *J* = 17.2, 1.7 Hz, 1H), 5.16 (dd, *J* = 10.4, 1.7 Hz, 1H), 4.02 (d, *J* = 6.2 Hz, 2H), 3.97 (dd, *J* = 5.5, 1.6 Hz, 2H), 1.18 – 1.11 (m, 4H).

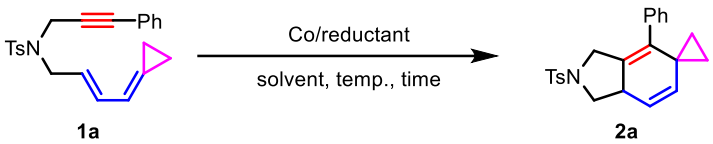
^{13}C NMR (101 MHz, Methylene Chloride-d2) δ 135.6, 132.3, 128.1, 127.8, 118.5, 116.6, 71.3, 70.9, 2.8, 2.5.

HRMS (ESI): calcd. for $C_{10}H_{15}O$ ([M+H]$^+$): 151.1117, found 151.1118.

3. Attempts of enantioselective [4+2] cycloaddition

We have tested cobalt-catalyzed enantioselective [4+2] cycloaddition using various chiral ligands, as shown in Table S1. Unfortunately, low yield and no ee value were observed. The enantiomeric excess (ee) of **2a** were determined by chiral HPLC analysis using UltiMate 3000 Pump (OD-H, hexanes:^{i}PrOH = 95:5, flow rate = 1.0 mL/min, l = 205 nm).

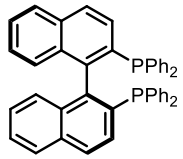
Table S1. Optimization of enantioselective [4+2] cycloaddition



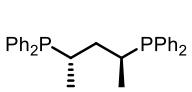
1a **2a**

entry	catalyst	L/reductant	solvent	temperature	time	yield[a]	ee
1	$CoCl_2$**L**$_1$ (5 mol%)	Zn (1.0 eq) ZnI_2 (0.5 eq)	DCE	60 °C	3 h	< 5%	
2	$CoCl_2$**L**$_2$ (5 mol%)	Zn (1.0 eq) ZnI_2 (0.5 eq)	DCE	60 °C	3 h	< 5%	
3	$CoCl_2$**L**$_3$ (5 mol%)	Zn (1.0 eq) ZnI_2 (0.5 eq)	DCE	60 °C	3 h	< 5%	
4	$CoBr_2$**L**$_1$ (5 mol%)	Zn (1.0 eq) ZnI_2 (0.5 eq)	DCE	60 °C	3 h	66%	0
5	$CoBr_2$**L**$_1$ (5 mol%)	$AlEt_3$ (1.0 eq)	DCE	60 °C	3 h	70%	0
6	$CoBr_2$**L**$_2$ (5 mol%)	Zn (1.0 eq) ZnI_2 (0.5 eq)	DCE	60 °C	3 h	< 5%	
7	$CoBr_2$**L**$_4$ (5 mol%)	Zn (1.0 eq) ZnI_2 (0.5 eq)	DCE	60 °C	3 h	< 5%	
8	$CoBr_2$**L**$_5$ (5 mol%)	Zn (1.0 eq) ZnI_2 (0.5 eq)	DCE	60 °C	3 h	< 5%	
9	$CoBr_2$**L**$_2$ (5 mol%)	$AlEt_3$ (1.0 eq)	DCE	60 °C	3h	24%	0
10	$CoBr_2$**L**$_5$ (5 mol%)	$AlEt_3$ (1.0 eq)	DCE	60 °C	3h	45%	0
11	$CoBr_2$**L**$_4$ (5 mol%)	$AlEt_3$ (1.0 eq)	DCE	60 °C	3h	29%	0

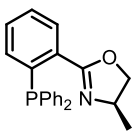
[a]Isolated yield at 0.05 mmol scale



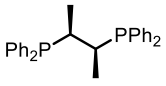
L$_1$



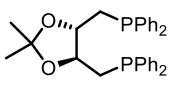
L$_2$



L$_3$



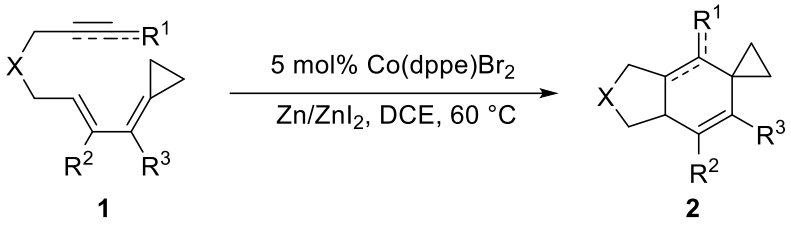
L$_4$



L$_5$

4. General Procedure for [4+2] cycloaddition

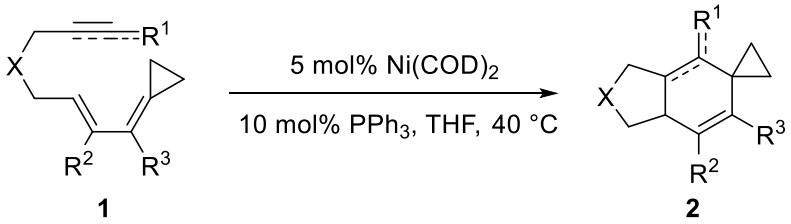
General Procedure A



1 **2**

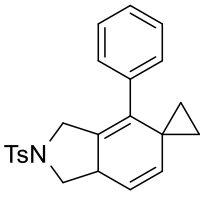
In glovebox, to a 10mL reaction tube with **1** (0.1-0.2 mmol), Zn (1.0 equiv.), ZnI_2 (0.5 equiv.) and $Co(dppe)Br_2$ (5 mol%) was added DCE (0.05 M of **1**). Then the tube was sealed and moved out of the glovebox. The reaction mixture was stirred at 60 °C for 3 h under 700 rpm. Upon completion, the reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (silica gel, PE/EA), affording [4+2] cycloadduct **2**.

General Procedure B



1 **2**

In glovebox, to a 10mL reaction tube with **1** (0.1 mmol), PPh_3 (10 mol%) and $Ni(COD)_2$ (5 mol%) was added THF (0.05 M of **1**). Then the tube was sealed and moved out of the glovebox. The reaction mixture was stirred at 40 °C under 700 rpm and was monitored by TLC. Upon completion, the reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (silica gel, PE/EA), affording [4+2] cycloadduct **2**.



2a

run 1: Following General Procedure A. Substrate: **1a** (38.3 mg, 0.10 mmol), Zn (6.5 mg, 0.10 mmol, 1.0 equiv.), ZnI_2 (16.0 mg, 0.05 mmol, 0.5 equiv.), $Co(dppe)Br_2$ (3.0 mg, 0.005 mmol, 5 mol%), DCE (2 mL, 0.05M), flash column chromatography (silica gel, 10:1 PE/EA); product: **2a** (34.3 mg, 90%).

run 2: Following General Procedure A. Substrate: **1a** (38.2 mg, 0.10 mmol), Zn (6.5 mg, 0.10 mmol, 1.0 equiv.), ZnI_2 (16.0 mg, 0.05 mmol, 0.5 equiv.), $Co(dppe)Br_2$ (3.0 mg, 0.005 mmol, 5 mol%), DCE (2 mL, 0.05M), flash column chromatography (silica gel, 10:1 PE/EA); product: **2a** (33.6 mg, 88%).

The average yield of two runs: 89%.

Gram scale experiments:

run 1: Following General Procedure A with 100 mL flask. Substrate: **1a** (1.06 g, 2.8 mmol), Zn (183.0 mg, 2.8 mmol, 1.0 equiv.), ZnI_2 (447.0 mg, 1.4 mmol, 0.5 equiv.), Co(dppe)Br_2 (86.4 mg, 0.14 mmol, 5 mol%), DCE (30 mL, 0.1M), flash column chromatography (silica gel, 10:1 PE/EA); product: **2a** (845.1 mg, 80%).

run 2: Following General Procedure A with 100 mL flask. Substrate: **1a** (1.06 g, 2.8 mmol), Zn (0.18 g, 2.8 mmol, 1.0 equiv.), ZnI_2 (0.45 g, 1.4 mmol, 0.5 equiv.), Co(dppe)Br_2 (86.4 mg, 0.14 mmol, 5 mol%), DCE (30 mL, 0.1M), flash column chromatography (silica gel, 10:1 PE/EA); product: **2a** (829.0 mg, 78%).

The average yield of two runs: 79%.

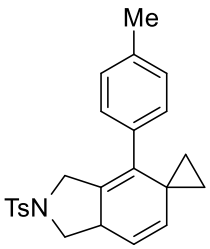
Physical Form: off-white foam

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

^{1}H NMR (400 MHz, Methylene Chloride-d2) δ 7.64 – 7.57 (m, 2H), 7.35 – 7.28 (m, 5H), 6.92 (brs, 1H), 6.80 (brs, 1H), 5.66 (dd, *J* = 9.7, 2.5 Hz, 1H), 5.20 (dd, *J* = 9.7, 2.6 Hz, 1H), 3.85 (dd, *J* = 8.8, 7.6 Hz, 1H), 3.72 (dd, *J* = 13.9, 1.8 Hz, 1H), 3.38 – 3.31 (m, 2H), 2.75 (dd, *J* = 11.4, 8.8 Hz, 1H), 2.44 (s, 3H), 0.74 – 0.68 (m, 1H), 0.68 – 0.58 (m, 3H).

^{13}C NMR (101 MHz, Methylene Chloride-d2) δ 144.1, 136.9, 136.1, 134.4, 134.0, 131.5, 130.1, 128.5, 127.9, 127.7, 121.3, 53.6, 50.4, 40.0, 23.5, 21.7, 13.7, 13.4.

HRMS (ESI) calcd. for $C_{23}H_{24}NO_2S([M+H]^+)$: 378.1522, found 378.1518.



2b

run 1: Following General Procedure A. Substrate: **1b** (78.3 mg, 0.20 mmol), Zn (13.7 mg, 0.20 mmol, 1.0 equiv.), ZnI_2 (31.9 mg, 0.1 mmol, 0.5 equiv.), Co(dppe)Br_2 (6.1 mg, 0.01 mmol, 5 mol%), DCE (4 mL, 0.05M), flash column chromatography (silica gel, 10:1 PE/EA); product: **2b** (58.8 mg, 75%).

run 2: Following General Procedure A. Substrate: **1b** (71.0 mg, 0.18 mmol), Zn (11.8 mg, 0.18 mmol, 1.0 equiv.), ZnI_2 (28.7 mg, 0.09 mmol, 0.5 equiv.), Co(dppe)Br_2 (5.5 mg, 0.0089 mmol, 5 mol%), DCE (4 mL, 0.05M), flash column chromatography (silica gel, 10:1 PE/EA); product: **2b** (56.1 mg, 79%).

The average yield of two runs: 77%.

Physical Form: white solid

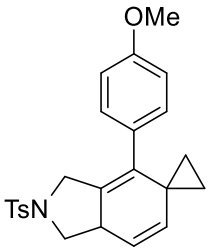
TLC (10:1 PE/EA, R_f): 0.4

m. p.: 185 °C.

^{1}H NMR (400 MHz, Methylene Chloride-d2) δ 7.61 – 7.54 (m, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 6.72 (brs, 2H), 5.63 (dd, *J* = 9.8, 2.5 Hz, 1H), 5.17 (dd, *J* = 9.7, 2.5 Hz, 1H), 3.81 (dd, *J* = 8.3, 8.3 Hz, 1H), 3.68 (dd, *J* = 13.9, 1.8 Hz, 1H), 3.35 – 3.29 (m, 2H), 2.71 (dd, *J* = 11.5, 8.8 Hz, 1H), 2.42 (s, 3H), 2.32 (s, 3H), 0.71 (ddd, *J* = 9.7, 5.6, 3.5 Hz, 1H), 0.63 – 0.53 (m, 3H).

^{13}C NMR (101 MHz, Methylene Chloride-d2) δ 144.0, 137.5, 136.2, 134.4, 134.1, 133.8, 131.5, 130.1, 129.2, 127.9, 121.3, 53.6, 50.5, 40.0, 23.5, 21.7, 21.3, 13.7, 13.4.

HRMS (ESI) calcd. for $C_{24}H_{26}NO_2S$([M+H]$^+$): 392.1679, found 392.1680.



2c

run 1: Following General Procedure A. Substrate: **1c** (40.7 mg, 0.10 mmol), Zn (6.5 mg, 0.10 mmol, 1.0 equiv.), ZnI_2 (16.0 mg, 0.05 mmol, 0.5 equiv.), Co(dppe)Br_2 (3.0 mg, 0.005 mmol, 5 mol%), DCE (2 mL, 0.05M), flash column chromatography (silica gel, 10:1 PE/EA); product: **2c** (25.3 mg, 62%).

run 2: Following General Procedure A. Substrate: **1c** (40.0 mg, 0.10 mmol), Zn (6.5 mg, 0.10 mmol, 1.0 equiv.), ZnI_2 (16.0 mg, 0.05 mmol, 0.5 equiv.), Co(dppe)Br_2 (3.0 mg, 0.005 mmol, 5 mol%), DCE (2 mL, 0.05M), flash column chromatography (silica gel, 10:1 PE/EA); product: **2c** (26.6 mg, 67%).

The average yield of two runs: 65 %.

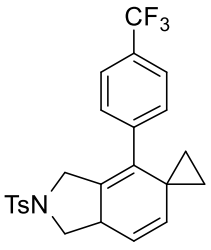
Physical Form: colorless oil

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

^{1}H NMR (400 MHz, Methylene Chloride-d2) δ 7.52 – 7.48 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.78 – 6.72 (m, 4H), 5.55 (dd, *J* = 9.8, 2.4 Hz, 1H), 5.10 (dd, *J* = 9.8, 2.5 Hz, 1H), 3.77 – 3.73 (m, 1H), 3.71 (s, 3H), 3.63 (dd, *J* = 13.9, 1.7 Hz, 1H), 3.28 – 3.22 (m, 2H), 2.63 (dd, *J* = 11.5, 8.8 Hz, 1H), 2.35 (s, 3H), 0.68 – 0.62 (m, 1H), 0.56 – 0.46 (m, 3H).

^{13}C NMR (101 MHz, Methylene Chloride-d2) δ 159.3, 144.0, 136.2, 134.09, 134.07, 131.8, 130.1, 128.9, 127.9, 121.3, 114.0, 55.6, 53.6, 50.5, 40.1, 23.6, 21.7, 13.7, 13.4.

HRMS (ESI) calcd. for $C_{24}H_{26}NO_3S$([M+H]$^+$): 408.1628, found 408.1627.



2d

run 1: Following General Procedure A. Substrate: **1d** (44.5 mg, 0.10 mmol), Zn (6.5 mg, 0.10 mmol,

1.0 equiv.), ZnI_2 (16.0 mg, 0.05 mmol, 0.5 equiv.), Co(dppe)Br_2 (3.0 mg, 0.005 mmol, 5 mol%), DCE (2 mL, 0.05M), flash column chromatography (silica gel, 10:1 PE/EA); product: **2d** (23.7 mg, 53%).

run 2: Following General Procedure A. Substrate: **1d** (44.5 mg, 0.10 mmol), Zn (6.5 mg, 0.10 mmol, 1.0 equiv.), ZnI_2 (16.0 mg, 0.05 mmol, 0.5 equiv.), Co(dppe)Br_2 (3.0 mg, 0.005 mmol, 5 mol%), DCE (2 mL, 0.05M), flash column chromatography (silica gel, 10:1 PE/EA); product: **2d** (25.2 mg, 57%).

The average yield of two runs: 55%.

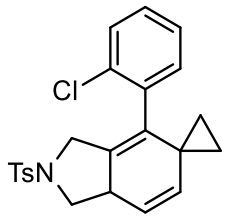
Physical Form: colorless oil

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

^{1}H NMR (400 MHz, Methylene Chloride-d2) δ 7.64 – 7.52 (m, 4H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.18 – 6.88 (m, 2H), 5.66 (dd, *J* = 9.7, 2.5 Hz, 1H), 5.20 (dd, *J* = 9.8, 2.7 Hz, 1H), 3.86 (dd, *J* = 8.8, 7.8 Hz, 1H), 3.73 (dd, *J* = 14.0, 1.8 Hz, 1H), 3.39 – 3.34 (m, 1H), 3.29 (dd, *J* = 13.9, 1.5 Hz, 1H), 2.75 (dd, *J* = 11.5, 8.8 Hz, 1H), 2.43 (s, 3H), 0.72 – 0.57 (m, 4H).

^{13}C NMR (101 MHz, Methylene Chloride-d2) δ 144.2, 141.0, 135.9, 134.0, 133.3, 132.6, 130.1, 129.9 (q, *J* = 32.3 Hz), 127.9, 125.6 (br), 124.7 (q, *J* = 272.7Hz), 120.6, 53.4, 50.3, 40.1, 23.5, 21.7, 13.7, 13.4.

HRMS (ESI) calcd. for $C_{24}H_{23}F_3NO_2S([M+H]^+)$: 446.1396, found 446.1393.



2e

run 1: Following General Procedure A. Substrate: **1e** (40.0 mg, 0.10 mmol), Zn (6.5 mg, 0.10 mmol, 1.0 equiv.), ZnI_2 (16.0 mg, 0.05 mmol, 0.5 equiv.), Co(dppe)Br_2 (3.0 mg, 0.005 mmol, 5 mol%), DCE (2 mL, 0.05 M), flash column chromatography (silica gel, 5:1 PE/EA); product: **2e** (16.2 mg, 41%).

run 2: Following General Procedure A. Substrate: **1e** (40.0 mg, 0.10 mmol), Zn (6.5 mg, 0.10 mmol, 1.0 equiv.), ZnI_2 (16.0 mg, 0.05 mmol, 0.5 equiv.), Co(dppe)Br_2 (3.0 mg, 0.005 mmol, 5 mol%), DCE (2 mL, 0.05 M), flash column chromatography (silica gel, 5:1 PE/EA); product: **2e** (17.4 mg, 44%).

The average yield of two runs: 43%.

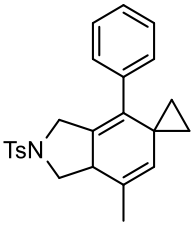
Physical Form: colorless oil

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

^{1}H NMR (400 MHz, Methylene Chloride-d2) δ 7.56 – 7.47 (m, 2H), 7.27 – 7.18 (m, 4H), 6.90 – 6.57 (m, 2H), 5.56 (dd, *J* = 9.7, 2.5 Hz, 1H), 5.10 (dd, *J* = 9.7, 2.6 Hz, 1H), 3.75 (dd, *J* = 8.8, 7.7 Hz, 1H), 3.63 (dd, *J* = 13.9, 1.8 Hz, 1H), 3.30 – 3.19 (m, 2H), 2.64 (dd, *J* = 11.4, 8.8 Hz, 1H), 2.35 (s, 3H), 0.62 – 0.48 (m, 4H).

^{13}C NMR (101 MHz, Methylene Chloride-d2) δ 144.1, 136.0, 135.4, 134.0, 133.7, 133.3, 132.4, 130.1, 128.8, 127.9, 121.4, 53.5, 50.4, 40.1, 23.5, 21.7, 13.7, 13.4.

HRMS (ESI) calcd. for $C_{23}H_{23}ClNO_2S([M+H]^+)$: 412.1133, found 412.1131.



2f

run 1: Following General Procedure A. Substrate: **1f** (40.0 mg, 0.10 mmol), Zn (6.5 mg, 0.10 mmol, 1.0 equiv.), ZnI_2 (16.0 mg, 0.05 mmol, 0.5 equiv.), $Co(dppe)Br_2$ (3.0 mg, 0.005 mmol, 5 mol%), DCE (2 mL, 0.05M), flash column chromatography (silica gel, 10:1 PE/EA); (31.5 mg, <79%) mixture was obtained, which consists of **2f** and some impurities from substrate & product decomposition. The following peaks selected from this mixture can be used to judge that [4+2] cycloadduct **2f** was generated.

run 2: Following General Procedure A. Substrate: **1f** (39.0 mg, 0.10 mmol), Zn (6.5 mg, 0.10 mmol, 1.0 equiv.), ZnI_2 (16.0 mg, 0.05 mmol, 0.5 equiv.), $Co(dppe)Br_2$ (3.0 mg, 0.005 mmol, 5 mol%), DCE (2 mL, 0.05M), flash column chromatography (silica gel, 10:1 PE/EA); mixture obtained (30.2 mg, <77%).

The average yield of two runs: <78%.

Physical Form: yellow oil

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

^{1}H NMR (400 MHz, Methylene Chloride-d2) δ 7.63 – 7.55 (m, 2H), 7.35 – 7.28 (m, 5H), 6.91 (brs, 1H), 6.75 (brs, 1H), 4.90 – 4.82 (m, 1H), 3.90 (dd, *J* = 8.1, 8.1 Hz, 1H), 3.73 (dd, *J* = 13.8, 1.7 Hz, 1H), 3.36 – 3.26 (m, 2H), 2.77 – 2.72 (m, 1H), 2.45 (s, 3H), 1.70 (dd, *J* = 1.3, 1.3 Hz, 3H), 0.68 (ddd, *J* = 9.7, 5.6, 3.5 Hz, 1H), 0.62 – 0.50 (m, 3H).

^{13}C NMR (101 MHz, Methylene Chloride-d2) δ 144.1, 137.0, 134.6, 134.0, 131.3, 130.2, 130.1, 129.37, 129.35, 128.6, 127.9, 127.7, 53.0, 50.6, 43.7, 24.1, 21.7, 20.7, 13.2, 13.1.

HRMS (ESI): calcd. for $C_{24}H_{26}NO_2S([M+H]^+)$: 392.1679, found 392.1676.

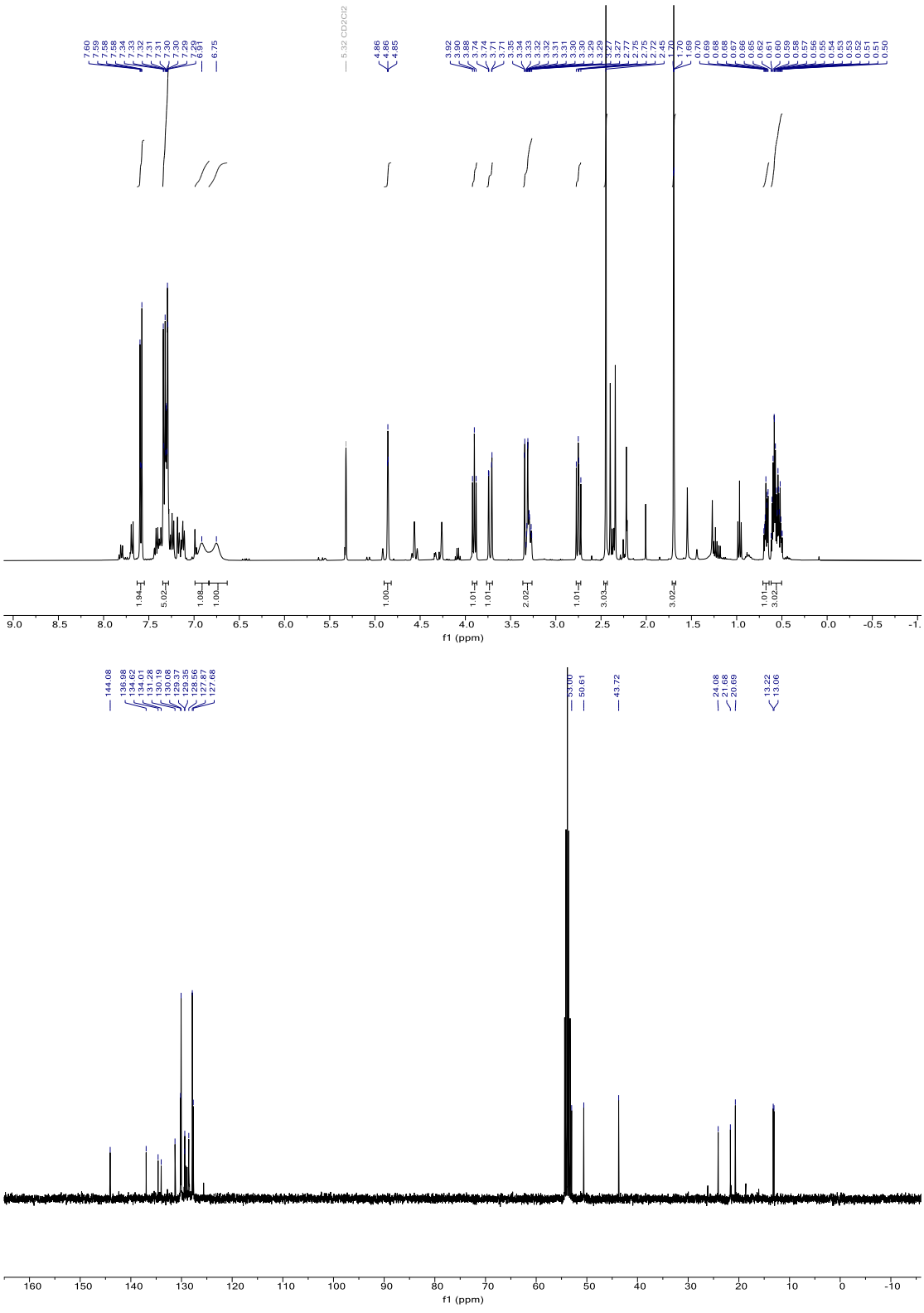
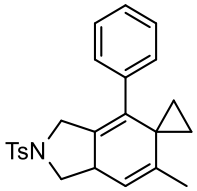


Figure S1. NMR spectra of **2f**.



2g

run 1: Following General Procedure A. Substrate: **1g** (31.0 mg, 0.08 mmol), Zn (6.5 mg, 0.10 mmol, 1.0 equiv.), ZnI_2 (16.0 mg, 0.05 mmol, 0.5 equiv.), Co(dppe)Br_2 (3.0 mg, 0.005 mmol, 5 mol%), DCE (2 mL, 0.05M), flash column chromatography (silica gel, DCM); product: **2g** (15.6 mg, 50%).

run 2: Following General Procedure A. Substrate: **1g** (30.0 mg, 0.08 mmol), Zn (6.5 mg, 0.10 mmol, 1.0 equiv.), ZnI_2 (16.0 mg, 0.05 mmol, 0.5 equiv.), Co(dppe)Br_2 (3.0 mg, 0.005 mmol, 5 mol%), DCE (2 mL, 0.05M), flash column chromatography (silica gel, DCM); product: **2g** (14.8 mg, 49%).

The average yield of two runs: 50%.

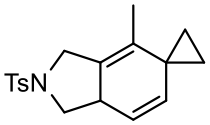
Physical Form: colorless oil

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

^{1}H NMR (400 MHz, Methylene Chloride-d2) δ 7.60 – 7.54 (m, 2H), 7.35 – 7.27 (m, 5H), 6.92 (brs, 1H), 6.81 (brs, 1H), 5.53 (dd, *J* = 1.9, 1.9 Hz, 1H), 3.81 (dd, *J* = 8.7, 7.7 Hz, 1H), 3.73 (dd, *J* = 13.9, 1.8 Hz, 1H), 3.33 – 3.24 (m, 2H), 2.67 (dd, *J* = 11.3, 8.7 Hz, 1H), 2.43 (s, 3H), 1.48 (dd, *J* = 1.7, 1.7 Hz, 3H), 0.97 – 0.91 (m, 1H), 0.84 – 0.78 (m, 1H), 0.57 – 0.47 (m, 2H).

^{13}C NMR (101 MHz, Methylene Chloride-d2) δ 143.6, 137.4, 137.1, 134.6, 133.6, 131.6, 129.6, 128.1, 127.5, 127.2, 119.2, 53.4, 50.3, 39.6, 25.0, 21.2, 18.3, 10.6, 9.5.

HRMS (ESI): calcd. for $C_{24}H_{26}NO_2S([M+H]^+)$: 392.1679, found 392.1678.



2h

run 1: Following General Procedure A. Substrate: **1h** (31.5 mg, 0.10 mmol), Zn (6.5 mg, 0.10 mmol, 1.0 equiv.), ZnI_2 (16.0 mg, 0.05 mmol, 0.5 equiv.), Co(dppe)Br_2 (3.0 mg, 0.005 mmol, 5 mol%), DCE (2 mL, 0.05M), flash column chromatography (silica gel, 10:1 PE/EA); product: **2h** (27.7 mg, 88%).

run 2: Following General Procedure A. Substrate: **1h** (31.5 mg, 0.10 mmol), Zn (6.5 mg, 0.10 mmol, 1.0 equiv.), ZnI_2 (16.0 mg, 0.05 mmol, 0.5 equiv.), Co(dppe)Br_2 (3.0 mg, 0.005 mmol, 5 mol%), DCE (2 mL, 0.05M), flash column chromatography (silica gel, 10:1 PE/EA); product: **2h** (28.5 mg, 90%).

The average yield of two runs: 89%.

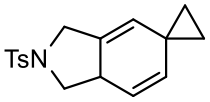
Physical Form: yellow oil

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

^{1}H NMR (400 MHz, Methylene Chloride-d2) δ 7.75 – 7.68 (m, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 5.57 (dd, *J* = 9.7, 2.4 Hz, 1H), 5.05 (dd, *J* = 9.7, 2.6 Hz, 1H), 3.95 (ddd, *J* = 13.5, 1.7, 1.7 Hz, 1H), 3.82 – 3.75 (m, 2H), 3.25 – 3.16 (m, 1H), 2.63 (dd, *J* = 11.5, 8.6 Hz, 1H), 2.43 (s, 3H), 1.27 (s, 3H), 1.12 (ddd, *J* = 9.6, 4.8, 1.8 Hz, 1H), 0.92 – 0.87 (m, 1H), 0.67 – 0.52 (m, 2H).

^{13}C NMR (101 MHz, Methylene Chloride-d2) δ 144.1, 136.1, 133.9, 130.1, 129.2, 127.9, 126.7, 121.4, 53.6, 50.1, 40.2, 23.7, 21.7, 13.5, 13.0, 12.9.

HRMS (ESI): calcd. for $C_{18}H_{22}NO_2S([M+H]^+)$: 316.1366, found 316.1364.



2i

run 1: Following General Procedure A. Substrate: **1i** (30.0 mg, 0.10 mmol), Zn (6.5 mg, 0.10 mmol, 1.0 equiv.), ZnI_2 (16.0 mg, 0.05 mmol, 0.5 equiv.), $Co(dppe)Br_2$ (3.0 mg, 0.005 mmol, 5 mol%), DCE (2 mL, 0.05M), flash column chromatography (silica gel, 10:1 PE/EA); product: **2i** (23.3 mg, 78%).

run 2: Following General Procedure A. Substrate: **1i** (29.0 mg, 0.10 mmol), Zn (6.5 mg, 0.10 mmol, 1.0 equiv.), ZnI_2 (16.0 mg, 0.05 mmol, 0.5 equiv.), $Co(dppe)Br_2$ (3.0 mg, 0.005 mmol, 5 mol%), DCE (2 mL, 0.05M), flash column chromatography (silica gel, 10:1 PE/EA); product: product: **2i** (22.3 mg, 77%).

The average yield of two runs: 77%.

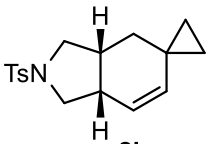
Physical Form: colorless oil

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

^{1}H NMR (400 MHz, Methylene Chloride-d2) δ 7.71 – 7.66 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.59 (dd, *J* = 9.8, 2.6 Hz, 1H), 5.08 (ddd, *J* = 9.9, 2.1, 2.1 Hz, 1H), 4.93 (dd, *J* = 2.3, 2.3 Hz, 1H), 3.95 (ddd, *J* = 13.0, 2.0, 2.0 Hz, 1H), 3.80 (dd, *J* = 8.3, 8.3 Hz, 1H), 3.72 (ddd, *J* = 13.2, 1.5, 1.5 Hz, 1H), 3.19 – 3.12 (m, 1H), 2.74 – 2.68 (m, 1H), 2.42 (s, 3H), 0.78 – 0.73 (m, 3H), 0.73 – 0.68 (m, 1H).

^{13}C NMR (101 MHz, Methylene Chloride-d2) δ 144.1, 134.9, 134.3, 134.0, 130.1, 127.9, 125.1, 121.6, 53.5, 51.0, 39.1, 30.1, 21.7, 17.2, 15.6.

HRMS (ESI): calcd. for $C_{17}H_{20}NO_2S([M+H]^+)$: 302.1209, found 302.1205.



2k

run 1: Following General Procedure A. Substrate: **1k** (30.0 mg, 0.10 mmol), Zn (6.5 mg, 0.10 mmol, 1.0 equiv.), ZnI_2 (16.0 mg, 0.05 mmol, 0.5 equiv.), $Co(dppe)Br_2$ (3.0 mg, 0.005 mmol, 5 mol%), DCE (2 mL, 0.05M), flash column chromatography (silica gel, DCM); product: **2k** (26.7 mg, 89%).

run 2: Following General Procedure A. Substrate: **1k** (30.0 mg, 0.10 mmol), Zn (6.5 mg, 0.10 mmol, 1.0 equiv.), ZnI_2 (16.0 mg, 0.05 mmol, 0.5 equiv.), $Co(dppe)Br_2$ (3.0 mg, 0.005 mmol, 5 mol%), DCE (2 mL, 0.05M), flash column chromatography (silica gel, DCM); product: **2k** (26.7 mg, 89%).

The average yield of two runs: 89%.

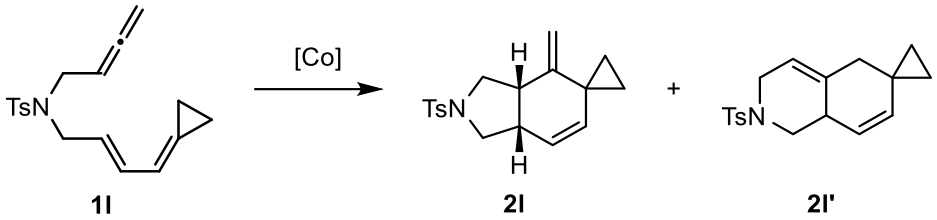
Physical Form: colorless oil

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

^{1}H NMR (400 MHz, Methylene Chloride-d2) δ 7.73 – 7.63 (m, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 5.30 (dd, *J* = 9.9, 3.5 Hz, 1H), 4.93 (dd, *J* = 9.8, 1.9 Hz, 1H), 3.49 (dd, *J* = 9.9, 7.3 Hz, 1H), 3.40 (dd, *J* = 9.8, 7.4 Hz, 1H), 3.19 (dd, *J* = 9.8, 6.0 Hz, 1H), 3.02 (dd, *J* = 9.9, 5.9 Hz, 1H), 2.64 – 2.57 (m, 1H), 2.42 (s, 3H), 2.38 (dd, *J* = 5.8, 1.9 Hz, 1H), 1.45 – 1.40 (m, 1H), 1.26 – 1.21 (m, 1H), 0.56 – 0.50 (m, 1H), 0.49 – 0.44 (m, 3H).

^{13}C NMR (101 MHz, Methylene Chloride-d2) δ 143.8, 136.3, 134.4, 129.9, 127.9, 124.9, 53.6, 51.9, 38.3, 37.0, 33.3, 21.6, 16.5, 15.2, 13.6.

HRMS (ESI): calcd. for $C_{17}H_{22}NO_2S([M+H]^+)$: 304.1366, found 304.1366.

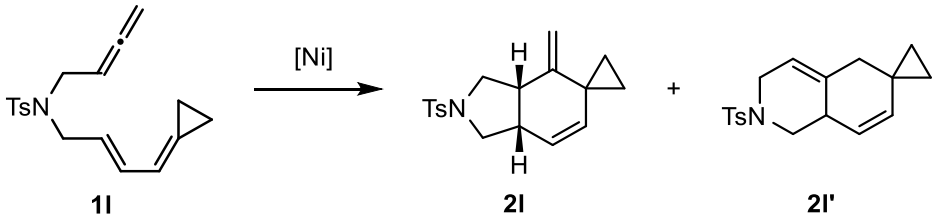


1l **2l** **2l'**

run 1: Following General Procedure A. Substrate: **1l** (40.0 mg, 0.13 mmol), Zn (8.5 mg, 0.13 mmol, 1.0 equiv.), ZnI_2 (22.0 mg, 0.07 mmol, 0.5 equiv.), Co(dppe)Br_2 (3.9 mg, 0.006 mmol, 5 mol%), DCE (2.5 mL, 0.05M), flash column chromatography (silica gel, 20:1 PE/EA); product: **2l** (9.2 mg, 23%), **2l'** (16.8 mg, 42%).

run 2: Following General Procedure A. Substrate: **1l** (32.0 mg, 0.10 mmol), Zn (6.5 mg, 0.10 mmol, 1.0 equiv.), ZnI_2 (16.0 mg, 0.05 mmol, 0.5 equiv.), Co(dppe)Br_2 (3.0 mg, 0.005 mmol, 5 mol%), DCE (2 mL, 0.05M), flash column chromatography (silica gel, 20:1 PE/EA); product: **2l** (7.8 mg, 24%), **2l'** (14.4 mg, 45%).

The average yield of two runs: **2l** 24%, **2l'** 44%, 68% combined.

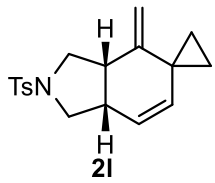


1l **2l** **2l'**

run 1: Following General Procedure B. Substrate: **1l** (30.0 mg, 0.10 mmol), PPh_3 (2.6 mg, 0.010 mmol, 0.1 equiv.), Ni(COD)$_2$ (1.4 mg, 0.005 mmol, 5 mol%), THF (2 mL, 0.05M), reaction time: 9h. Flash column chromatography (silica gel, 20:1 PE/EA); product: **2l** (13.8 mg, 46%), **2l'** (6.0 mg, 20%).

run 2: Following General Procedure B. Substrate: **1l** (30.0 mg, 0.10 mmol), PPh_3 (2.6 mg, 0.010 mmol, 0.1 equiv.), Ni(COD)$_2$ (1.4 mg, 0.005 mmol, 5 mol%), THF (2 mL, 0.05M), reaction time: 9h. Flash column chromatography (silica gel, 20:1 PE/EA); product: **2l** (13.5 mg, 45%), **2l'** (4.3 mg, 14%).

The average yield of two runs: **2l** 46%, **2l'** 17%, 63% combined.



2l

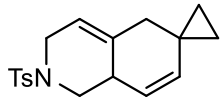
Physical Form: colorless oil

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

^{1}H NMR (400 MHz, Methylene Chloride-d2) δ 7.72 – 7.63 (m, 2H), 7.36 – 7.24 (m, 2H), 5.06 (ddd, *J* = 9.8, 2.3, 1.2 Hz, 1H), 4.72 (dd, *J* = 9.8, 2.4 Hz, 1H), 4.64 (d, *J* = 0.8 Hz, 1H), 4.49 (d, *J* = 0.9 Hz, 1H), 3.44 – 3.36 (m, 2H), 3.36 – 3.27 (m, 2H), 2.98 (dddd, *J* = 8.7, 8.7, 6.5, 3.1 Hz, 1H), 2.77 (dddd, *J* = 6.1, 4.0, 1.9, 1.9 Hz, 1H), 2.41 (s, 3H), 1.24 – 1.19 (m, 1H), 0.74 (ddd, *J* = 6.2, 6.2, 3.2 Hz, 1H), 0.70 – 0.65 (m, 1H), 0.58 (ddd, *J* = 9.6, 6.8, 4.7 Hz, 1H).

^{13}C NMR (101 MHz, Methylene Chloride-d2) δ 146.3, 143.9, 135.1, 129.9, 128.0, 125.4, 106.3, 54.5, 51.0, 46.8, 41.0, 21.7, 21.3, 20.5, 13.0.

HRMS (ESI): calcd. for $C_{18}H_{22}NO_2S([M+H]^+)$: 316.1366, found 316.1366.



2l'

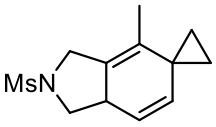
Physical Form: colorless oil

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

^{1}H NMR (400 MHz, Methylene Chloride-d2) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 5.30 (dddd, *J* = 8.9, 6.8, 3.3, 3.3 Hz, 2H), 5.10 (d, *J* = 9.7 Hz, 1H), 3.94 – 3.86 (m, 2H), 3.13 – 3.04 (m, 2H), 2.63 (d, *J* = 13.6 Hz, 1H), 2.37 (s, 3H), 2.00 (dd, *J* = 11.0, 11.0 Hz, 1H), 1.49 (d, *J* = 13.4 Hz, 1H), 0.60 – 0.49 (m, 2H), 0.38 (ddd, *J* = 13.7, 6.7, 6.7 Hz, 2H).

^{13}C NMR (101 MHz, Methylene Chloride-d2) δ 144.2, 136.8, 136.7, 130.1, 128.1, 124.5, 115.9, 48.8, 45.6, 40.5, 36.5, 21.6, 20.6, 15.4, 13.8.

HRMS (ESI): calcd. for $C_{18}H_{22}NO_2S([M+H]^+)$: 316.1366, found 316.1366.



2m

run 1: Following General Procedure A. Substrate: **1m** (23.9 mg, 0.10 mmol), Zn (6.5 mg, 0.10 mmol, 1.0 equiv.), ZnI_2 (16.0 mg, 0.05 mmol, 0.5 equiv.), $Co(dppe)Br_2$ (2.9 mg, 0.005 mmol, 5 mol%), DCE (2 mL, 0.05M), flash column chromatography (silica gel, 10:1 PE/EA); product: **2m** (17.9 mg, 75%).

run 2: Following General Procedure A. Substrate: **1m** (23.9 mg, 0.10 mmol), Zn (6.5 mg, 0.10 mmol, 1.0 equiv.), ZnI_2 (16.0 mg, 0.05 mmol, 0.5 equiv.), $Co(dppe)Br_2$ (2.9 mg, 0.005 mmol, 5 mol%), DCE (2 mL, 0.05M), flash column chromatography (silica gel, 10:1 PE/EA); product: **2m** (18.1 mg, 76%). The product **2m** was not stable enough under an air atmosphere, and it completely transformed into aromatic byproducts after 24 hours. Therefore, it's difficult to obtain a clean NMR spectroscopy of **2m**. The following peaks were selected from the mixture.

The average yield of two runs: 76%.

Physical Form: white solid, m.p. = 116.2-117.1 °C

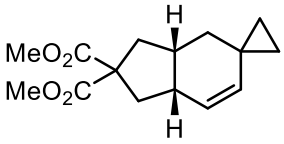
TLC (3:1 PE/EA, R_f): 0.4

^{1}H NMR (400 MHz, Methylene Chloride-d2) δ 5.66 (dd, *J* = 9.7, 2.5 Hz, 1H), 5.14 (dd, *J* = 9.7, 2.6 Hz, 1H), 4.68 – 4.62 (m, 1H), 3.96 (s, 2H), 3.76 (dd, *J* = 8.1, 8.1 Hz, 1H), 3.47 – 3.35 (m, 1H), 2.80 (s, 3H),

1.37 (s, 3H), 1.25 – 1.20 (m, 1H), 0.96 (ddd, *J* = 9.3, 6.6, 4.4 Hz, 1H), 0.71 (ddd, *J* = 10.3, 6.1, 4.4 Hz, 1H), 0.62 (ddd, *J* = 9.4, 6.5, 4.7 Hz, 1H).

^{13}C NMR (101 MHz, Methylene Chloride-d2) δ 136.3, 129.1, 127.1, 121.4, 53.3, 50.1, 40.5, 34.5, 23.8, 13.6, 13.1, 13.0.

HRMS (ESI): calcd. for $C_{12}H_{18}NO_2S$ ([M+H]$^+$): 240.1053, found 240.1050.



2o

run 1: Following General Procedure A. Substrate: **1o** (26.4 mg, 0.10 mmol), Zn (6.5 mg, 0.10 mmol, 1.0 equiv.), ZnI_2 (16.0 mg, 0.05 mmol, 0.5 equiv.), Co(dppe)Br_2 (2.9 mg, 0.005 mmol, 5 mol%), DCE (2 mL, 0.05M), flash column chromatography (silica gel, 10:1 PE/EA); product: **2o** (20.5 mg, 78%).

run 2: Following General Procedure A. Substrate: **1o** (26.4 mg, 0.10 mmol), Zn (6.5 mg, 0.10 mmol, 1.0 equiv.), ZnI_2 (16.0 mg, 0.05 mmol, 0.5 equiv.), Co(dppe)Br_2 (2.9 mg, 0.005 mmol, 5 mol%), DCE (2 mL, 0.05M), flash column chromatography (silica gel, 10:1 PE/EA); product: **2o** (19.8 mg, 75%).

The average yield of two runs: 77%.

Physical Form: light yellow oil

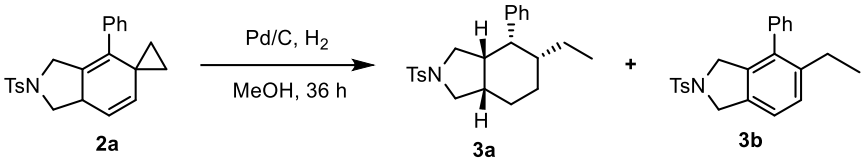
TLC (10:1 PE/EA, R_f): 0.5

^{1}H NMR (400 MHz, Methylene Chloride-d2) δ 5.54 (dd, *J* = 9.8, 3.6 Hz, 1H), 5.05 (dd, *J* = 9.8, 1.9 Hz, 1H), 3.69 (s, 3H), 3.67 (s, 3H), 2.63 – 2.54 (m, 1H), 2.49 (dd, *J* = 13.2, 7.4 Hz, 1H), 2.42 (dd, *J* = 13.3, 7.5 Hz, 1H), 2.37 – 2.28 (m, 1H), 2.18 (dd, *J* = 13.4, 6.5 Hz, 1H), 2.05 (dd, *J* = 13.2, 7.9 Hz, 1H), 1.46 (s, 1H), 1.45 (d, *J* = 1.1 Hz, 1H), 0.63 – 0.58 (m, 1H), 0.57 – 0.51 (m, 1H), 0.51 – 0.45 (m, 2H).

^{13}C NMR (101 MHz, Methylene Chloride-d2) δ 173.7, 173.2, 134.8, 128.0, 60.0, 53.0, 52.9, 40.4, 39.3, 38.6, 37.6, 35.6, 17.1, 14.8, 13.5.

HRMS (ESI): calcd. for $C_{15}H_{21}O_4$ ([M+H]$^+$): 265.1434, found 265.1432.

5. Transformation of [4+2] adducts



5-ethyl-4-phenyl-2-tosyloctahydro-1H-isoindole (**3b**): To a 10 mL reaction tube charged with 4 mL dry MeOH were added Pd/C (106 mg, 10% w/w dry basis, 0.1 mmol, 50 mol%), **2a** (75 mg, 0.2 mmol). The tube was bubbled with H_2 for 5 minutes and then stirred under 1 atm H_2 ballon for 36h. Upon completion, the reaction mixture was filtered through a pad of silica gel, washed with EA, concentrated *in vacuo* and purified by flash column chromatography to afford a mixture of **3a** and **3b**. The pure sample for analysis was obtained by preparative TLC.

run 1: Substrate: **2a** (76.0 mg, 0.20 mmol), Pd/C (106.0 mg, 10% w/w dry basis, 0.1 mmol, 50 mol%) and MeOH (4 mL, 0.05 M), flash column chromatography (silica gel, 20:1 PE/EA); product: **3a** and **3b** combined (58.8 mg).

run 2: Substrate: **2a** (75.0 mg, 0.20 mmol), Pd/C (106.0 mg, 10% w/w dry basis, 0.1 mmol, 50 mol%) and MeOH (4 mL, 0.05 M), flash column chromatography (silica gel, 20:1 PE/EA); product: **3a** and **3b** combined (57.1 mg).

The percentage of products:

The percentage of **3a** and **3b** was determined by crude NMR (**Fig. S2**) to be 1.00:0.77.

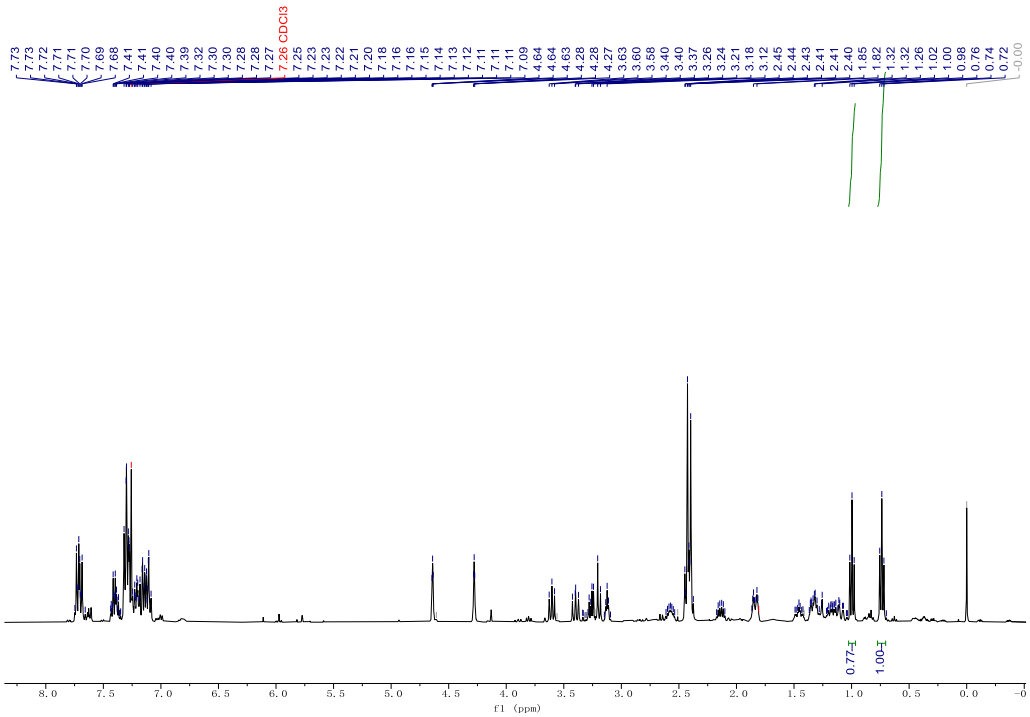
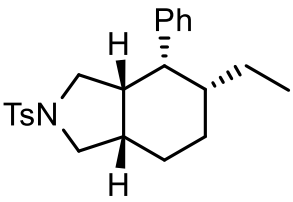


Figure S2. NMR of mixture of **3a** and **3b** and integral of Ethyl-C*H*$_3$ of **3a** (δ 1.00) and **3b** (δ 0.74).

The average yield of two runs: 77% combined, 44 % **3a**, 33% **3b**.



3a

Physical Form: colorless oil

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

^{1}H NMR (400 MHz, Chloroform-d) δ 7.74 – 7.70 (m, 2H), 7.32 – 7.28 (m, 4H), 7.24 – 7.21 (m, 1H), 7.15 (dd, *J* = 7.5, 1.7 Hz, 2H), 3.60 (dd, *J* = 9.9, 8.7 Hz, 1H), 3.40 (dd, *J* = 11.2, 9.8 Hz, 1H), 3.26 (dd, *J* = 9.7, 5.4 Hz, 1H), 3.19 (d, *J* = 9.6 Hz, 1H), 3.12 (dd, *J* = 4.7, 4.7 Hz, 1H), 2.57 (ddd, *J* = 9.0, 5.5, 5.5 Hz, 1H), 2.43 (s, 3H), 2.17 – 2.10 (m, 1H), 1.85 (dd, *J* = 3.2, 3.2 Hz, 1H), 1.82 (dd, *J* = 3.3, 3.3 Hz, 1H), 1.49 – 1.43 (m, 1H), 1.36 – 1.30 (m, 2H), 1.17 (ddd, *J* = 10.8, 5.4, 2.9 Hz, 1H), 1.13 – 1.06 (m, 1H), 0.74 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 143.4, 143.0, 134.3, 129.7, 128.5, 128.1, 127.6, 126.2, 53.5, 49.0, 46.7, 41.1, 40.5, 39.8, 27.3, 21.7, 21.6, 20.8, 14.1.

HRMS (ESI): calcd. for $C_{23}H_{30}NO_2S([M+H]^+)$: 384.1992, found 384.1990.

Determination of relative conformation:

^{1}H-^{1}H COSY, HSQC and NOESY spectra of **3a** was collected to determine the relative configuration.

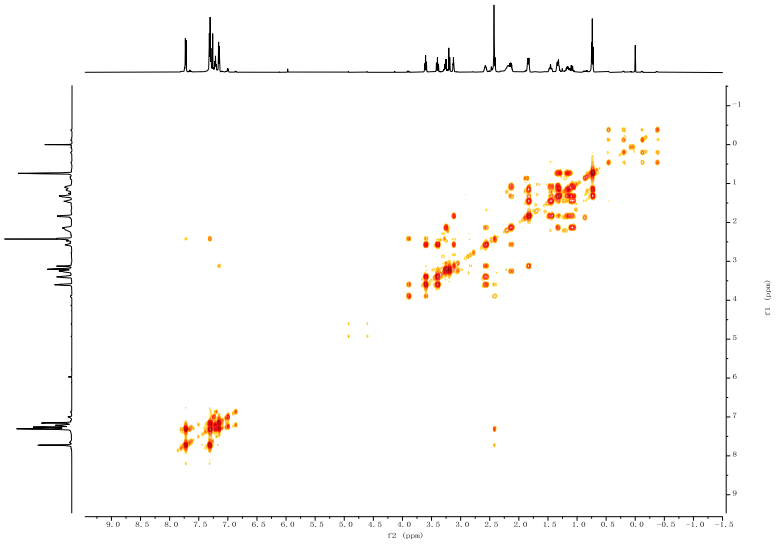


Figure S3. ^{1}H-^{1}H COSY of **3a**.

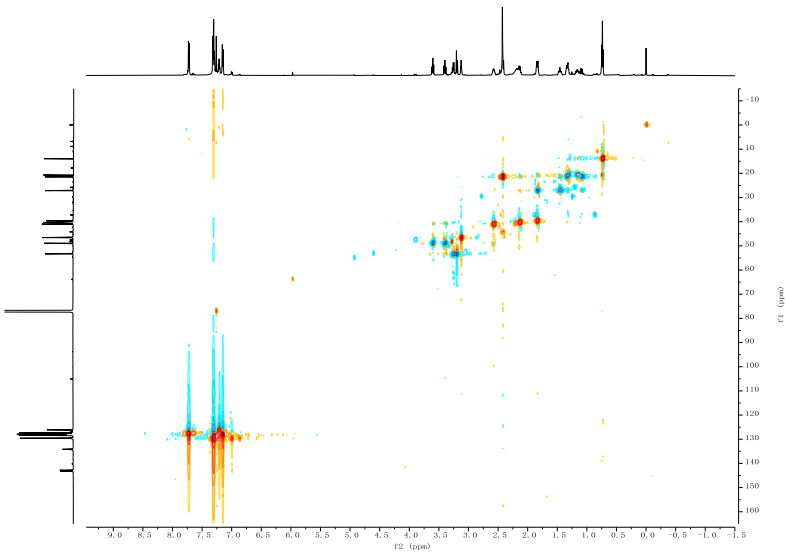


Figure S4. HSQC of **3a**.

Assignment of selected hydrogens in 3a:

δ 3.60 (dd, *J* = 9.9, 8.7 Hz, 1H, **13**), 3.40 (dd, *J* = 11.2, 9.8 Hz, 1H, **12**), 3.26 (dd, *J* = 9.7, 5.4 Hz, 1H, **15**), 3.19 (d, *J* = 9.6 Hz, 1H, **14**), 3.12 (dd, *J* = 4.7, 4.7 Hz, 1H, **5**), 2.57 (ddd, *J* = 9.0, 5.5, 5.5 Hz, 1H, **11**), 2.43 (s, 3H, C***H*₃**$C_6H_4SO_2N$-), 2.17 – 2.10 (m, 1H, **10**), 1.85 (dd, *J* = 3.2, 3.2 Hz, 1H, **7**), 1.82 (dd, *J* = 3.3, 3.3 Hz, 1H, **4**), 1.49 – 1.43 (m, 1H, **6**), 1.36 – 1.30 (m, 2H, **3** and **9**), 1.17 (ddd, *J* = 10.8, 5.4, 2.9 Hz, 1H, **2**), 1.13 – 1.06 (m, 1H, **8**), 0.74 (t, *J* = 7.3 Hz, 3H, **1**).

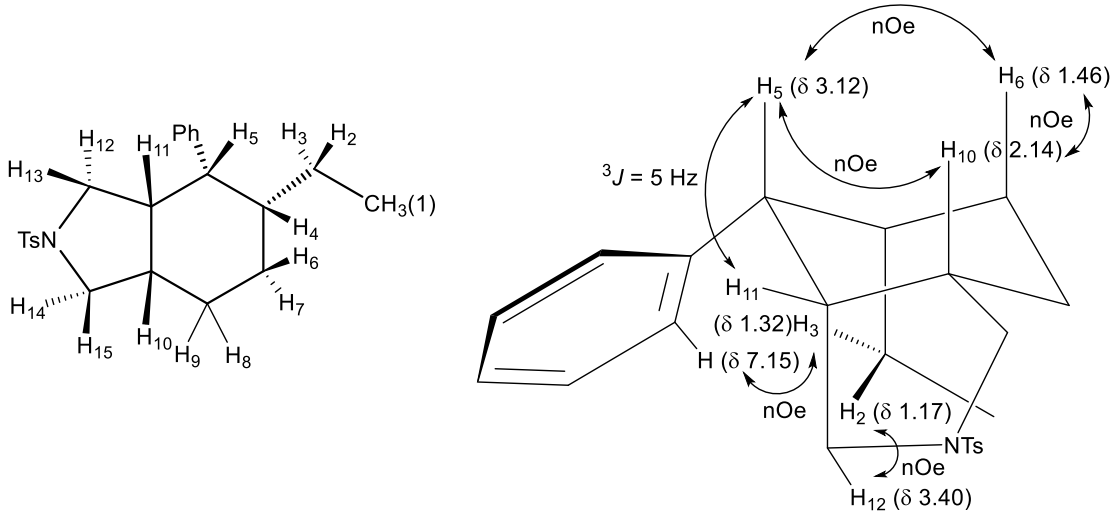
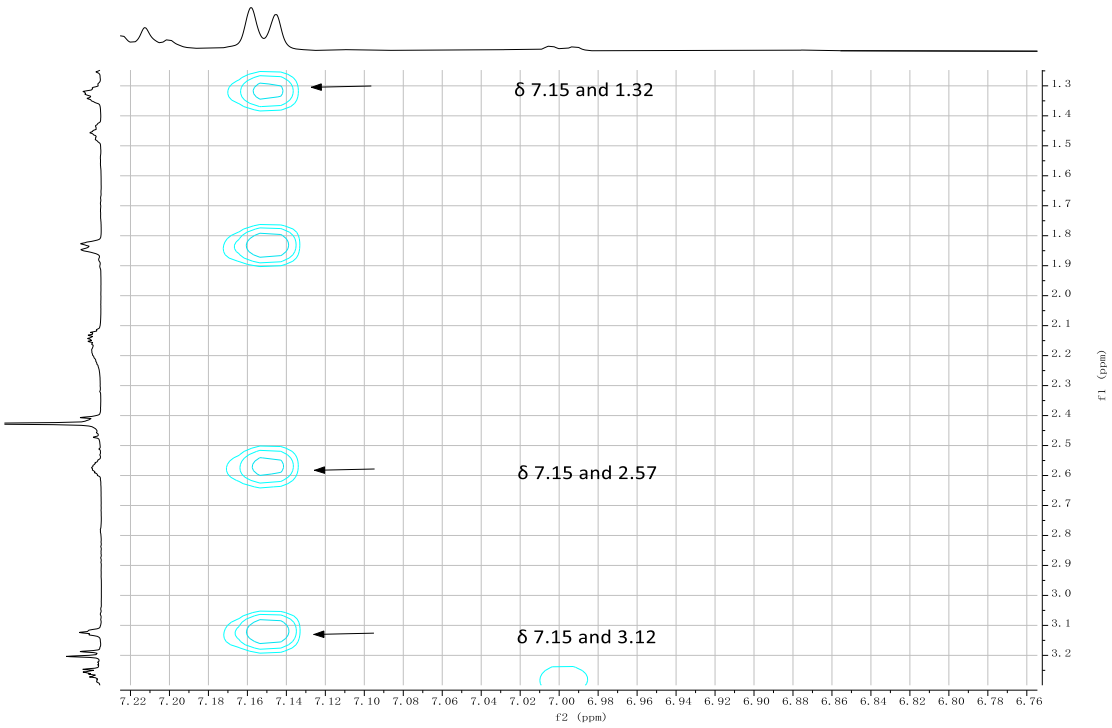


Figure S5. Labeling of **3a** hydrogens and relative configuration.



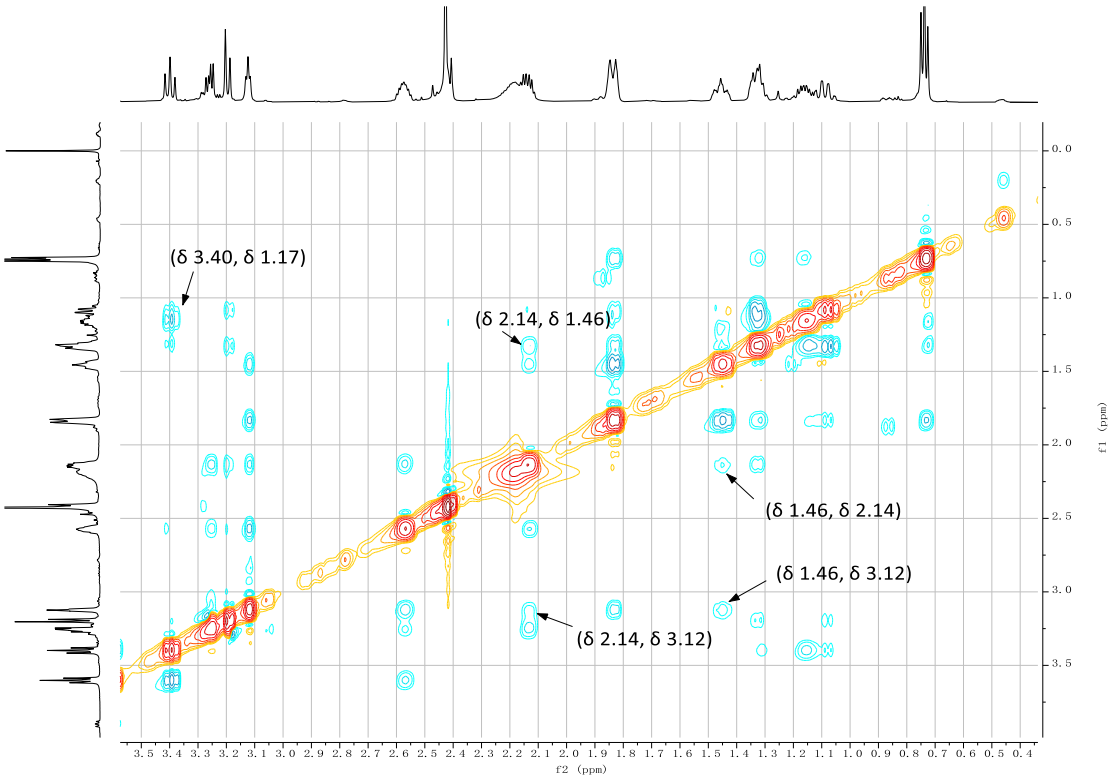
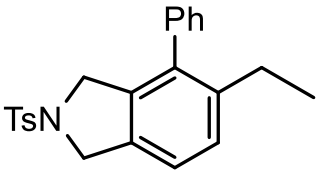


Figure S6. NOESY of **3a**.



3b

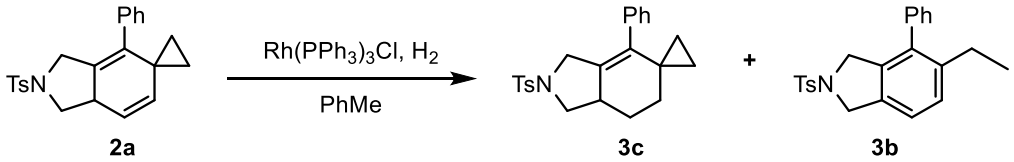
Physical Form: pale yellow oil

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

^{1}H NMR (400 MHz, Methylene Chloride-d2) δ 7.70 – 7.66 (m, 2H), 7.47 – 7.37 (m, 3H), 7.34 – 7.31 (m, 2H), 7.20 (d, *J* = 7.9 Hz, 1H), 7.16 – 7.09 (m, 3H), 4.62 (t, *J* = 2.1 Hz, 2H), 4.25 (t, *J* = 2.0 Hz, 2H), 2.40 (q, *J* = 6.1 Hz, 2H), 2.39 (s, 3H), 0.98 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, Methylene Chloride-d2) δ 144.2, 142.0, 139.0, 137.1, 135.8, 134.0, 133.7, 130.2, 129.0, 128.9, 128.7, 127.9, 127.8, 121.9, 54.5, 54.0, 26.2, 21.6, 16.0.

HRMS (ESI): calcd. for $C_{23}H_{24}NO_2S([M+H]^+)$: 378.1523, found 378.1522.



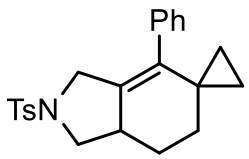
2a **3c** **3b**

4'-phenyl-2'-tosyl-1',2',3',6',7',7a'-hexahydrospiro[cyclopropane-1,5'-isoindole] (**3d**): To a 25 mL reaction tube was added **2a** (37.8 mg, 0.10 mmol). The tube was transferred to a glovebox and added $Rh(PPh_3)_3Cl$ (9.3 mg, 0.010 mmol, 10 mol%) and toluene (2 mL, 0.1 M). The tube was sealed, transferred out of the glovebox and bubbled with H_2 for 10 min. The reaction mixture was stirred under r. t. for 13.5 h, concentrated *in vacuo* and purified by flash column chromatography (PE/EA 20:1) to afford an inseparable mixture of **3c** and **3b**. The molar ratio of **3c** and **3b** was determined by ^{1}H-NMR integral.

run 1: product: 31.6 mg combined, **3c** 71%, **3b** 12%.

run 2: product: 31.7 mg combined, **3c** 71%, **3b** 12%.

The average yield of 3c: 71%.



3c

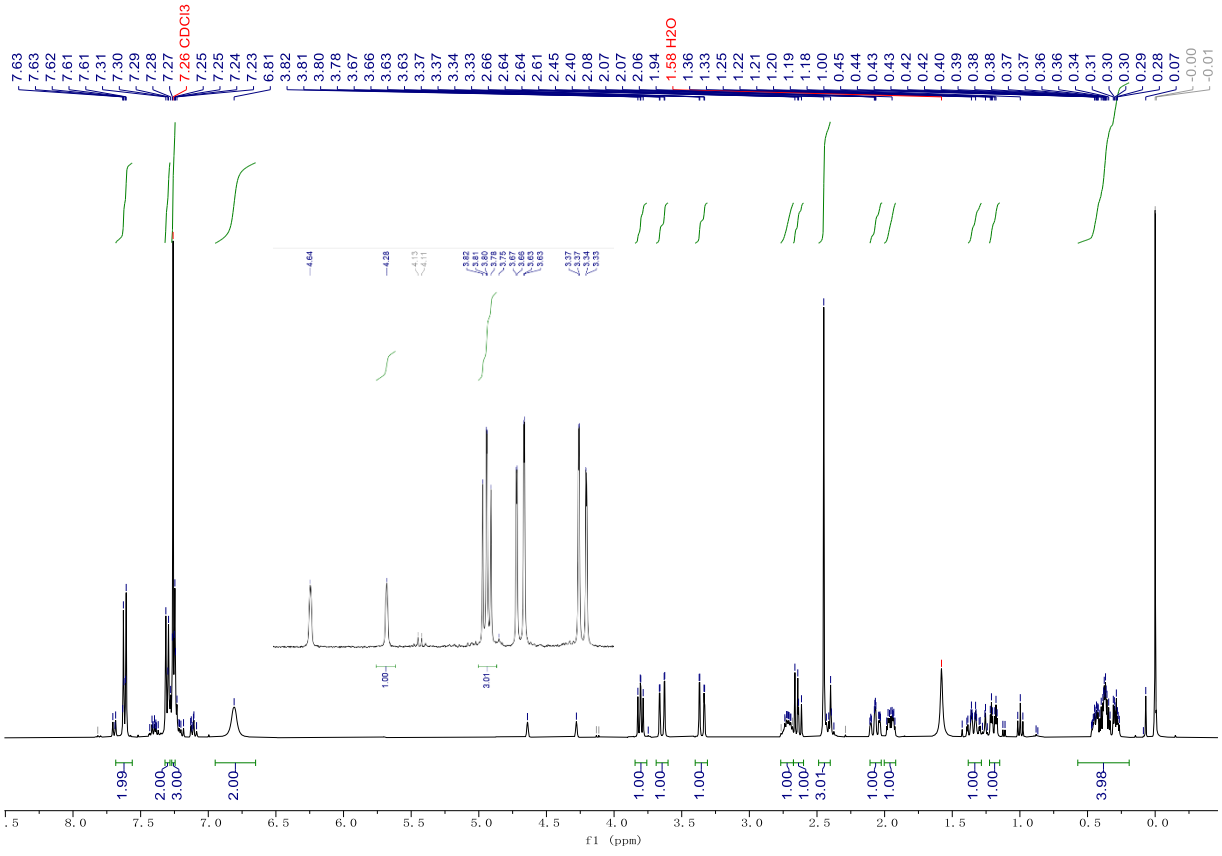
The following peaks selected from this mixture (**Fig. S3**) can be used to characterize **3c**.

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

^{1}H NMR (400 MHz, Chloroform-d) δ 7.68 – 7.56 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 7.4 Hz, 3H), 6.81 (brs, 2H), 3.80 (dd, *J* = 8.6, 7.1 Hz, 1H), 3.65 (dd, *J* = 14.2, 1.7 Hz, 1H), 3.35 (dd, *J* = 14.2, 1.8 Hz, 1H), 2.77 – 2.67 (m, 1H), 2.64 (dd, *J* = 10.9, 8.6 Hz, 1H), 2.45 (s, 3H), 2.11 – 2.02 (m, 1H), 2.00 – 1.92 (m, 1H), 1.38 – 1.28 (m, 1H), 1.19 (ddd, *J* = 13.4, 3.4, 3.4 Hz, 1H), 0.57 – 0.19 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-d) δ 143.4, 141.3, 137.5, 134.1, 133.1, 132.8, 129.7, 127.8, 127.2, 54.5, 50.6, 40.1, 34.6, 25.7, 21.7, 20.5, 13.1, 11.0.

HRMS (ESI): calcd. for $C_{23}H_{26}NO_2S$([M+H]$^+$): 380.1679, found 380.1680.



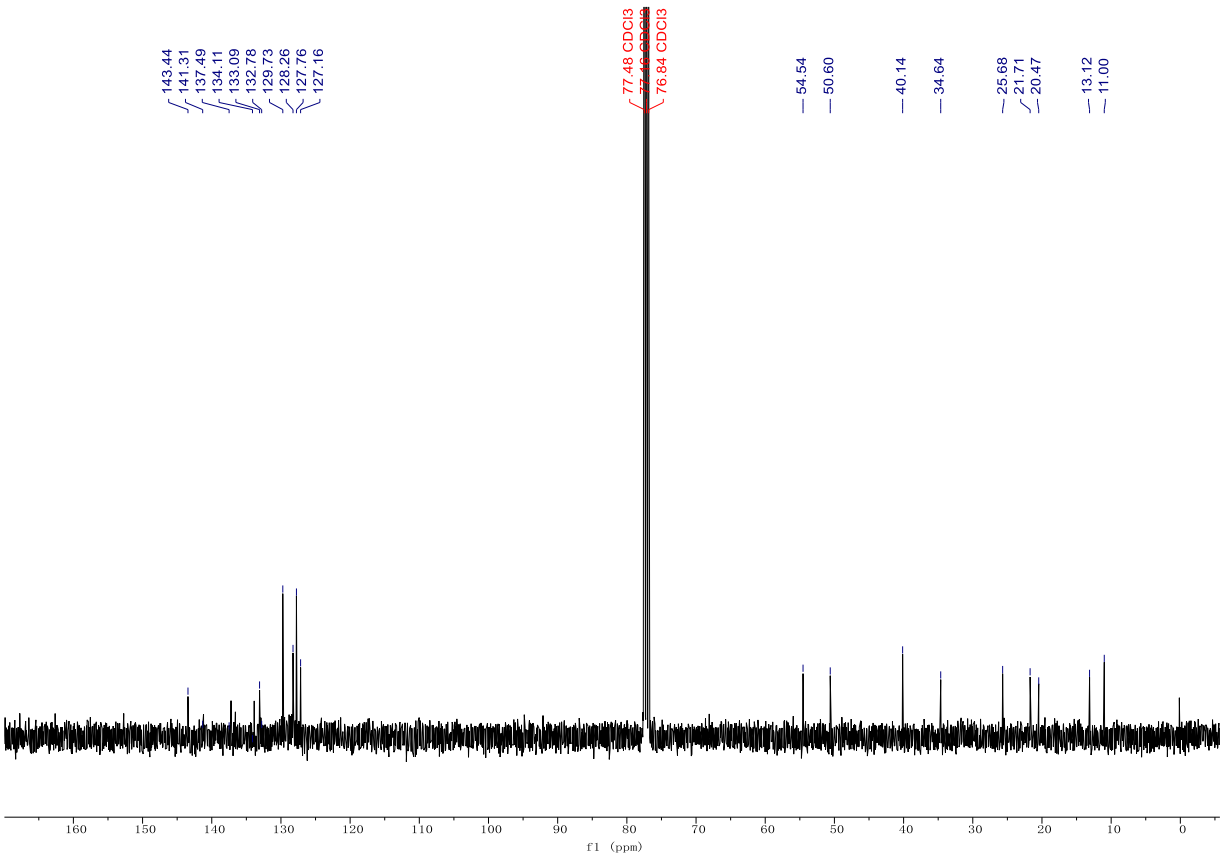
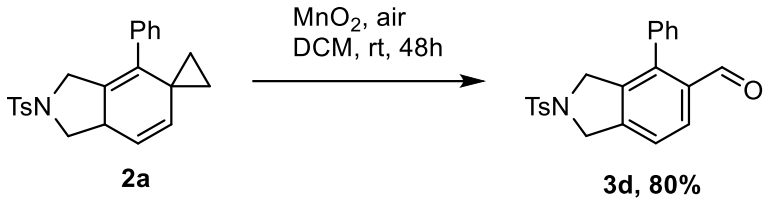


Figure S7. ^{1}H-NMR spectra of **3c.**



2a **3d, 80%**

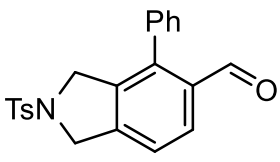
4-phenyl-2-tosylisoindoline-5-carbaldehyde (**3d**):

To a 10 mL reaction tube containing substrate **2a** (75.0 mg, 0.2 mmol) and MnO_2 (174.0 mg, 2 mmol, 10 equiv.) was added DCM (2 mL, 0.1M) and stirred at room temperature for 48 h. The reaction mixture was filtered through a pad of silica gel (c.a. 4 cm thick in a 15 mL funnel with a coarse silica frit), washed with 20 mL EA, concentrated *in vacuo* and purified by flash column chromatography (PE/EA 2:1).

run 1: Substrate: **2a** (75.0 mg, 0.20 mmol), product: **3d** (60.2 mg, 0.16 mmol, 80%).

run 2: Substrate: **2a** (75.0 mg, 0.20 mmol), product: **3d** (60.5 mg, 0.16 mmol, 80%).

The average yield of two runs: 80%.



3d

Physical Form: white solid

TLC (2:1 PE/EA, R_f): 0.3

m. p.: 204.5 °C (decompose).

^{1}H NMR (400 MHz, Chloroform-d) δ 9.75 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.75 – 7.69 (m, 2H), 7.48 – 7.46 (m, 3H), 7.32 – 7.28 (m, 3H), 7.25 – 7.19

(m, 2H), 4.71 (dd, *J* = 2.0, 2.0 Hz, 2H), 4.43 (dd, *J* = 2.1, 2.1 Hz, 2H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 191.2, 144.0, 142.3, 141.2, 136.6, 134.7, 133.7, 133.7, 130.0, 129.3, 128.9, 128.8, 127.8, 127.6, 122.3, 54.3, 53.0, 21.6.

HRMS (ESI) calcd. for $C_{22}H_{20}NO_3S([M+H]^+)$: 378.1158, found 378.1157.

Discussion

We observed **S14** as an intermediate that finally gave **3d**, which provides further evidence for the plausible mechanism proposed (**Fig. S8**). The substrate **2a** would probably undergo an allylic C-H oxidation by either MnO_2 or oxygen, follow by aromatization to give **S14**. The intermediate **S14**, as a phenethyl alcohol derivative, would be oxidized to **3d** as reported by Havare et al[16].

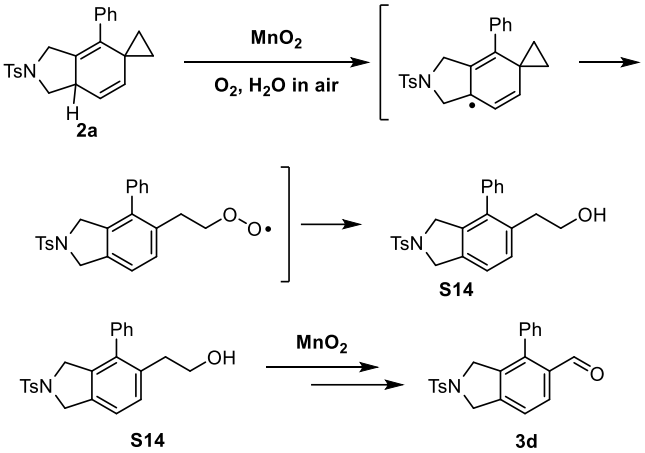
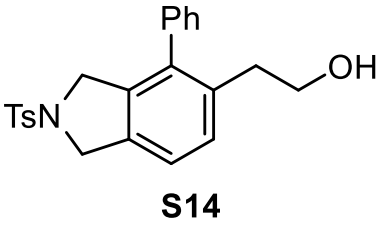


Figure S8. Plausible mechanism forming **3d**.



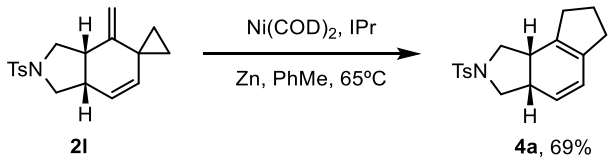
S14

TLC (3:1 PE/EA, R_f): 0.2

^{1}H NMR (400 MHz, Methylene Chloride-d2) δ 7.70 – 7.65 (m, 2H), 7.46 – 7.39 (m, 3H), 7.34 – 7.31 (m, 2H), 7.25 – 7.22 (m, 1H), 7.19 – 7.12 (m, 3H), 4.62 (s, 2H), 4.25 (s, 2H), 3.96 – 3.86 (m, 2H), 2.79 – 2.75 (m, 2H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, Methylene Chloride-d2) δ 144.3, 138.6, 137.8, 136.1, 134.7, 134.0, 130.2, 130.0, 129.2, 129.0, 128.1, 127.9, 122.0, 77.5, 54.5, 54.0, 31.3, 21.6.

HRMS (ESI): calcd. for $C_{23}H_{24}NO_3S([M+H]^+)$: 394.1471, found 394.1473.



2-tosyl-1,2,3,3a,6,7,8,8b-octahydrocyclopenta[e]isoindole (**4a**): In a glove box, to a 10 mL reaction tube was added $Ni(COD)_2$ (14.0 mg, 0.05 mmol), 1,3-bis(2,6-diisopropylphenyl)-1H-imidazol-3-ium-2-ide (IPr, 40.0 mg, 0.10 mmol), Zn (3.3 mg, 0.05 mmol) and 1 mL toluene. The mixture was stirred under room temperature for 4 h to form a $Ni(IPr)_2$ solution A.

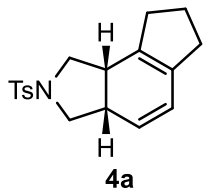
In a glove box, to a 10 mL Schlenk tube containing substrate **2l** (18.5 mg, 0.06 mmol) was added toluene (0.2 mL) and solution A above (0.2 mL, 17 mol%). The tube was sealed and transferred out of the glove box. The tube was heated to 65°C and stirred for 48 h. The product was purified by

flash column chromatography (PE/EA 20:1).

run 1: Substrate: **2l** (18.5 mg, 0.06 mmol), product: **4a** (12.8 mg, 0.04 mmol, 69%).

run 2: Substrate: **2l** (18.3 mg, 0.06 mmol), product: **4a** (12.8 mg, 0.04 mmol, 70%).

The average yield of two runs: 70%.



4a

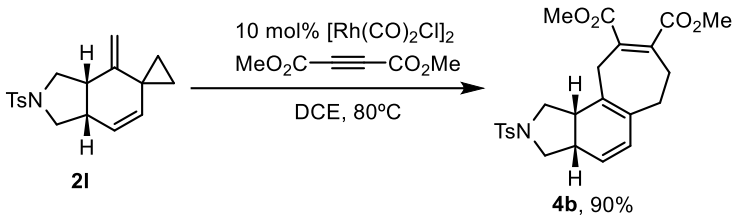
Physical Form: colorless oil

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

^{1}H NMR (400 MHz, Chloroform-d) δ 7.73 – 7.69 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.83 (d, *J* = 9.5 Hz, 1H), 5.47 (dd, *J* = 9.8, 3.2 Hz, 1H), 3.65 – 3.61 (m, 1H), 3.60 – 3.56 (m, 1H) 3.15 (dd, *J* = 9.8, 4.7 Hz, 1H), 3.00 – 2.93 (m, 1H), 2.88 – 2.84 (m, 2H), 2.43 (s, 3H), 2.31 – 2.26 (m, 2H), 2.20 – 2.10 (m, 2H), 1.86 – 1.67 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-d) δ 143.5, 134.9, 133.8, 132.8, 129.7, 127.8, 124.8, 123.8, 54.3, 52.6, 39.0, 38.5, 33.8, 33.5, 22.3, 21.7.

HRMS (ESI) calcd. for $C_{18}H_{22}NO_2S([M+H]^+)$: 316.1366, found 316.1365.



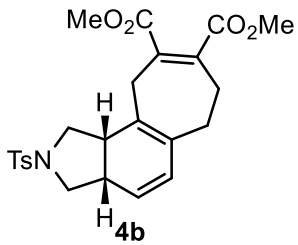
dimethyl 2-tosyl-1,2,3,3a,6,7,10,10b-octahydrocyclohepta[e]isoindole-8,9-dicarboxylate (**4b**):

To a 25 mL reaction tube was added substrate **2l** (6.6 mg, 0.02 mol), $[Rh(CO)_2Cl]_2$, (0.7 mg, 20 μmol, 10 mol%), dimethyl but-2-ynedioate (4.0 mg, 0.03 mmol, 1.3 equiv.). The tube was evacuated and backfilled with N_2 for three times, and then DCE (0.5 mL, 0.04 M) was charged. The reaction mixture was heated to 80°C and stirred for 9 h. The product was purified by flash column chromatography (PE/EA 1:1).

run 1: Substrate: **2l** (6.6 mg, 0.02 mmol), product: **4b** (8.9 mg, 0.019 mmol, 93%).

run 2: Substrate: **2l** (6.6 mg, 0.02 mmol), product: **4b** (8.5 mg, 0.019 mmol, 89%).

The average yield of two runs: 91%.



4b

Physical Form: yellow oil

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

^{1}H NMR (400 MHz, Chloroform-d) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 5.46 (dd, *J* = 9.6, 2.6 Hz, 1H), 5.19 (dd, *J* = 9.6, 2.8 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.67 – 3.61 (m, 2H), 3.27 – 3.18 (m, 2H), 3.07 – 3.00 (m, 2H), 2.93 (dd, *J* = 9.7, 9.7 Hz, 1H), 2.65 – 2.52 (m, 2H), 2.53 – 2.49 (m, 1H), 2.44 (s, 3H), 2.30 (t, *J* = 6.5 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-d) δ 169.1, 168.2, 143.6, 139.6, 135.6, 133.9, 129.8, 129.7, 128.3, 127.8, 127.2, 126.1, 54.8, 52.6, 52.5, 52.2, 44.1, 38.3, 32.6, 29.1, 27.5, 21.7.

HRMS (ESI): calcd. for $C_{24}H_{31}N_2O_6S([M+NH_4]^+)$: 475.1897, found 475.1898.

6. DFT Studies

All DFT calculations were performed by Gaussian 16.[10] Geometry optimizations of all the minima and transition states were carried out with the PBE0 functional[11] with SMD solvation model[12] of corresponding solvent (DCE for Co reaction and THF for Ni reaction), and the def2-SVP[13] basis set was used for all atoms. Grimme's D3 dispersion correction with Becke-Johnson damping[14] was applied. Vibrational analyses were carried at the same level to check whether each optimized structure was an energy minimum or a transition state. Thermal correction to Gibbs energy (TCG) was obtained through frequency analysis. The minimum energy crossing points (MECPs) between the singlet and triplet states were located with the sobMECP[15] program at PBE0-D3BJ/def2-SVP/SMD level. Based on the optimized structures, single-point energy refinements were performed at the PBE0-D3BJ/def2-TZVPP/SMD level. In this paper, all discussed energies are Gibbs free energies in the solution phase (ΔG_{sol} 298 K), unless otherwise specified. The standard state for all the species are 1.0 M[16]. The conformational search was performed for all stationary points and transition states with *crest* 2.12[17] and *xtb* 6.6.1[18], at GFN2-xTB level.[19] An energy window of 6 kcal/mol was utilized for conformation searching.

We also calculated other possible pathways in Co-catalyzed [4+2] reactions, finding out that they are energetically less favored than the main pathway (**Fig. S9**). We studied the possibility of beta-C elimination from **INT2-Co** to open the cyclopropane ring. DFT calculations showed that beta-C elimination required an activation free energy of 28.2 kcal/mol (**TS3-Co**) from **INT4-Co**, which was disfavored over the MECP process by about 32.0 kcal/mol and could be ruled out. We then studied the possibility of the reaction initiating at a 14e Cobalt complex, where the MCP alkene dissociated from the metal center. Our calculations showed that this Cobalt complex, **INT6-Co**, preferred a triplet spin state, and its cyclometallation reaction required an activation free energy of 16.5 kcal/mol. Therefore, this pathway is disfavored over the main pathway by 10.1 kcal/mol of activation free energy and could be also ruled out.

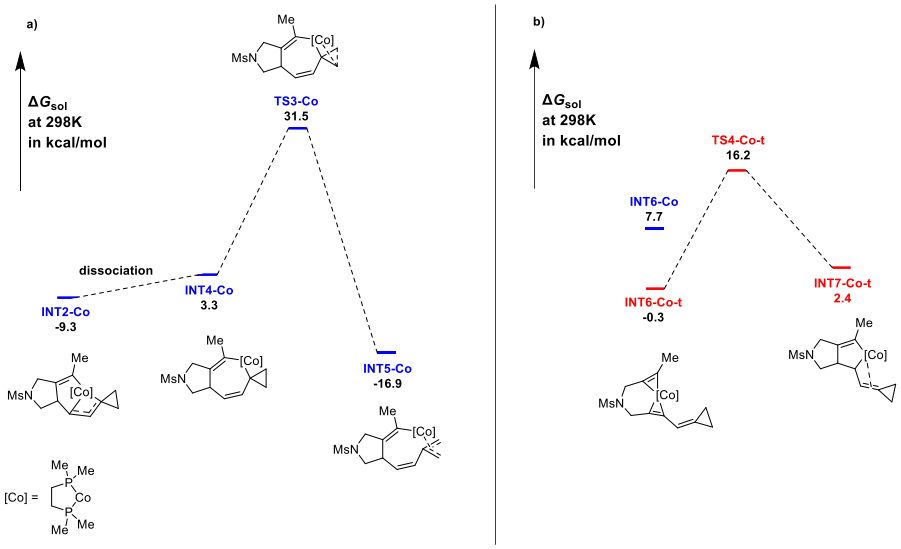


Figure S9. Gibbs energy profile for less possible pathways. **a)** β-C elimination reaction cleaving CP ring. **b)** Reaction initiation from a 14e Co complex. Computed at SMD(THF)/PBE0-D3BJ/def2-

TZVPP//SMD(THF)/PBE0-D3BJ/def2-SVP level, energy shown is the ΔG_{sol} compared with **INT1-Co**.

The Mechanism of Ni-catalyzed [4+2] reaction of CP-capped diene and alkyne was also studied (**Fig. S1**). The reaction starts from generating tricoordinated complex **INT0-Ni** from the active species $NiPMe_3$ and model substrate **1m**. Then, **INT0-Ni** generates tetracoordinated, 18e complex **INT1-Ni** through the coordination of methylenecyclopropane moiety. After that, **INT1-Ni** undergoes oxidative cyclometallation to give 16e intermediate **INT2-Ni** via transition state **TS1-Ni**. Notably, the activation free energy for this step is much higher compared to the cyclometallation step of Co. **INT2-Ni** then undergoes a direct reductive elimination (via **TS2-Ni**) to give [4+2] cycloadduct. The reaction is exergonic by 54.6 kcal/mol and the rate-determining step is cyclometallation step, with an overall Gibbs activation energy of 22.5 kcal/mol (from **INT0-Ni** to **TS1-Ni**).

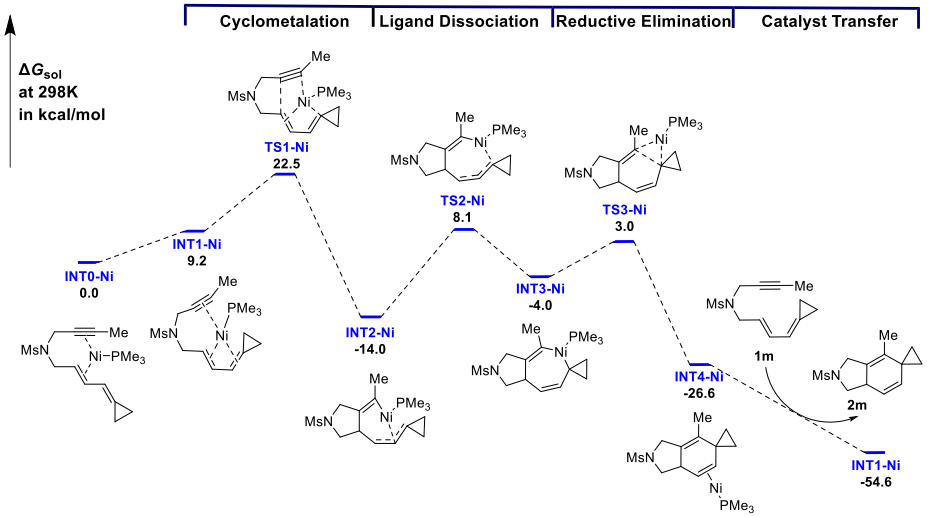


Figure S10. Gibbs energy profile for nickel catalyzed [4+2] cycloaddition of CP-capped diene and alkyne. Computed at SMD(THF)/PBE0-D3BJ/def2-TZVPP//SMD(THF)/PBE0-D3BJ/def2-SVP level.

Energy and Cartesian Coordinates of the Stationary Points:

Computed Energies for the Stationary Points

Thermal corrections to Gibbs energies (TCGs), single-point energies (SPEs) in gas phase and solvent ([a]Computed at the SMD(DCE or THF)/PBE0/def2-SVP level; [b]Computed at 298 K; [c]Computed at the SMD(DCE or THF)/PBE0/def2-TZVPP//PBE0/def2-SVP level.)

	Number of imaginary frequency	TCG[a,b] (a. u.)	SPE[a] (a. u.)	SPE[c] (a. u.)
1a	none	0.219981	-1069.214242	-1070.146268
2a	none	0.23231	-1069.321010	-1070.245617
INT0-Co	none	0.425149	-3371.661221	-3373.266733
INT1-Co	none	0.432814	-3371.663441	-3373.271086
INT1-Co-t	none	0.424401	-3371.653597	-3373.261556
MECP1	none	N/A	-3371.645365	N/A
TS1-Co	1	0.431233	-3371.656775	-3373.263146
TS1-Co-t	1	0.422416	-3371.630007	-3373.233891
INT2-Co	none	0.429974	-3371.676387	-3373.286303
INT2-Co-t	none	0.422291	-3371.662061	-3373.277993
MECP2	none	N/A	-3371.662365	N/A
TS2-Co-s	1	0.428729	-3371.652919	-3373.26229
TS2-Co-t	1	0.422844	-3371.661308	-3373.276251
INT3-Co-t	none	0.428806	-3371.741749	-3373.348326
INT4-Co	none	0.430854	-3371.658678	-3373.267232
INT5-Co	none	0.432813	-3371.693880	-3373.301309
TS3-Co	1	0.427081	-3371.606601	-3373.218456
INT6-Co	none	0.425920	-3371.645535	-3373.256288
INT6-Co-t	none	0.422067	-3371.654450	-3373.264154
TS4-Co-t	1	0.420055	-3371.627500	-3373.235828
INT7-Co-t	none	0.420668	-3371.647315	-3373.258400
INT0-Ni	none	0.331891	-3037.835215	-3039.225732
INT1-Ni	none	0.330129	-3037.826910	-3039.209328
TS1-Ni	1	0.333174	-3037.809919	-3039.191096
INT2-Ni	none	0.335182	-3037.860965	-3039.251378
TS2-Ni	1	0.331979	-3037.822035	-3039.212929
INT3-Ni	none	0.336140	-3037.851485	-3039.236344
TS3-Ni	1	0.332947	-3037.833017	-3039.221944
INT4-Ni	none	0.333549	-3037.873672	-3039.269773

Cartesian coordinates for the stationary points:

1a

C	4.21671400	-0.52715200	0.27745600
C	2.95905800	-0.54704900	0.72515600
C	1.84017100	-1.05266200	-0.04965400
C	0.56580600	-1.05089100	0.37671900
C	-0.58579300	-1.56096700	-0.43049400
C	5.61880700	-0.19266300	0.49928800
C	5.14756400	-0.82857700	-0.80748700
N	-1.60035400	-0.55690600	-0.73632000
C	-1.23346300	0.58848200	-1.55400400
C	-0.50512100	1.65417700	-0.85749100
C	0.08928000	2.54200900	-0.28087200
C	0.82290700	3.58167400	0.42066700
S	-2.98656500	-0.48263300	0.16552700
O	-3.93109500	0.34216400	-0.58362900
O	-3.33903900	-1.85347300	0.52542400
H	2.74244000	-0.15606200	1.72700200
H	2.06809800	-1.44482600	-1.04923800
H	0.33430700	-0.64742000	1.37046800
H	-0.22262800	-1.97281600	-1.38656500
H	-1.10212800	-2.37896300	0.09485400
H	5.91841400	0.86216300	0.47849100
H	6.20557500	-0.81197700	1.18853300
H	5.41636400	-1.87505600	-0.99536900
H	5.12808900	-0.20116900	-1.70676200
H	-0.62134900	0.20559000	-2.38738200
H	-2.15178800	0.99488400	-2.00254700
H	1.03212100	4.43450600	-0.24422300
H	0.25098600	3.96057100	1.28236600
H	1.78686000	3.19977800	0.79309600
C	-2.60418200	0.37862700	1.66776800
H	-1.85089200	-0.19176200	2.22632500
H	-2.23676000	1.38253400	1.41843400
H	-3.53960900	0.44093200	2.24164900

2a

C	0.71107200	0.35622600	-0.04605600
C	0.31010000	-1.08211200	0.13839400
C	1.43721000	-2.03412200	-0.07624900
C	2.70650400	-1.61258100	-0.08608100
C	3.09725200	-0.18834700	0.06117300
C	1.97836000	0.79784400	-0.08578900
C	-0.54325500	1.14786600	-0.32693400
N	-1.55979300	0.12199200	-0.62104500
C	-0.90239000	-1.17843200	-0.79169900
C	4.48937000	0.17764900	-0.41777700
C	4.22625500	0.09732100	1.04354700
C	2.31044200	2.23969800	-0.32302000
S	-2.96055000	0.13620600	0.28568600
O	-3.14149600	1.50220700	0.77515300
O	-2.97722900	-0.96771400	1.24962700
H	-0.09070200	-1.21342800	1.16559900
H	1.20745900	-3.09960700	-0.17919700
H	3.52420900	-2.33302100	-0.19569100
H	-0.42171300	1.81946500	-1.19206100
H	-0.86633600	1.76815100	0.52344800
H	-1.58612400	-1.99881900	-0.53728000
H	-0.58609900	-1.29306700	-1.84209400
H	5.06977600	-0.62150500	-0.88752100
H	4.63609700	1.16342600	-0.86468500
H	4.16596200	1.02905200	1.61361600
H	4.61935900	-0.75486200	1.60529300
H	3.05015600	2.61143700	0.40465500
H	2.74716300	2.39161300	-1.32446300
H	1.42424600	2.88271300	-0.24153900
C	-4.20421400	-0.19906900	-0.92528600
H	-5.16481700	-0.23193600	-0.39219500
H	-4.19394400	0.60911900	-1.66725400
H	-3.99777200	-1.16956600	-1.39587300

INT0-Co

C	3.34212700	0.22356800	1.29572700

C	1.93283400	1.42930200	-0.38779700
C	0.47372100	1.73254700	-0.61899200
C	-0.09335500	1.46776900	-1.90077500
C	-1.48884000	1.44405900	-2.03382900
C	-2.21196400	1.70993000	-0.81538200
H	3.34540200	-0.71326000	1.87142000
H	3.15271700	1.03483300	2.01733000
H	2.39150300	2.23014500	0.20704400
H	2.48950300	1.40276200	-1.34235100
H	0.06993800	2.56483300	-0.03564600
H	0.52425900	1.05088100	-2.70503600
H	-1.96439200	1.11169700	-2.96196500
P	-2.54980900	-1.22522700	-0.48693000
P	-1.04088100	0.19933900	1.69104500
C	4.63590700	0.42454000	0.64129500
C	5.70285900	0.59286200	0.08704100
C	-2.82678000	-0.04678500	2.06168400
H	-2.97353000	-0.26766700	3.13106500
C	-3.38950300	-1.15977300	1.17668400
H	-4.47436900	-1.04449700	1.02985500
Co	-0.93998700	0.27990300	-0.48295100
H	-3.32232800	0.91443400	1.85657000
H	-3.23683200	-2.14303200	1.64849800
C	-2.56341000	2.99740800	-0.15438200
H	-2.39078700	3.92955200	-0.70314400
H	-2.44992200	3.08918300	0.93052400
C	-3.64155800	2.05924800	-0.65298300
H	-4.20563900	2.34415400	-1.54831300
H	-4.24343800	1.54139000	0.10122400
C	-0.51154800	1.62213600	2.69086300
H	-0.92463100	2.55496800	2.28465100
H	-0.83511500	1.50377600	3.73638200
H	0.58649600	1.68256500	2.65920500
C	-0.26120600	-1.20653500	2.55288400
H	0.82989500	-1.16372500	2.44717800
H	-0.52668100	-1.17939900	3.62106900
H	-0.60869300	-2.15493400	2.11971400
C	-1.96663600	-2.94572300	-0.63019500
H	-1.16018600	-3.12856200	0.09293500
H	-2.79279400	-3.65168600	-0.45425700
H	-1.56286600	-3.10279000	-1.64127300
C	-3.88729700	-1.16049500	-1.72052500
H	-3.45557200	-1.31674400	-2.72043200
H	-4.62640400	-1.95171900	-1.52135900
H	-4.38634200	-0.18316500	-1.69782300
N	2.19604200	0.19861400	0.38554300
S	1.85721600	-1.24551700	-0.33583500
C	2.89921800	-1.47083700	-1.74276900
H	2.58351000	-2.41411500	-2.21027000
H	2.76396300	-0.63413800	-2.44042800
H	3.93772100	-1.53834900	-1.39377100
O	0.48062800	-1.12955700	-0.88221900
O	2.12868700	-2.31162000	0.61748900
C	6.98170000	0.78865400	-0.57303700
H	7.34162200	1.82154400	-0.44568100
H	7.74472700	0.10885700	-0.16250600
H	6.89938500	0.58930300	-1.65313200

INT1-Co

C	-1.87643000	-1.21607800	1.12781300
C	-1.99834900	-0.92454200	-1.33016800
C	-0.57347200	-1.37389200	-1.23892700
C	0.43930300	-0.91546600	-2.11672400
C	1.74526600	-1.34471400	-1.79495700
C	1.89236700	-2.06954900	-0.58234200
H	-2.05058800	-2.30653900	1.05046400
H	-2.36873900	-0.86396600	2.04601300
H	-2.60712500	-1.76979100	-1.70650500
H	-2.11690000	-0.08814800	-2.02900700
H	-0.45814300	-2.39697500	-0.87130900
H	0.25684100	-0.19850700	-2.92172500
H	2.59794300	-0.98558300	-2.37517300
P	2.82734100	0.78852100	0.05763000
P	-0.02872300	1.74533800	-0.18956300
C	-0.43089900	-0.94681700	1.22777600

C	0.67853000	-0.79497900	1.78417200
C	1.31620200	3.01057400	-0.14775100
H	1.64689500	3.19155900	-1.18349800
C	2.44855000	2.46437400	0.70284400
H	2.14448100	2.36609000	1.75794200
Co	0.92235200	-0.35896000	-0.21725600
H	0.91505900	3.95947800	0.24154500
H	3.35190200	3.09389300	0.66966000
C	1.57452700	-3.44230100	-0.12092400
H	1.37842800	-4.21384800	-0.87346600
H	1.01077300	-3.56091500	0.81123100
C	2.98133600	-2.88654300	-0.01691900
H	3.75155400	-3.27797600	-0.69163600
H	3.34209000	-2.65579800	0.99058700
N	-2.45553100	-0.50692200	-0.00366500
S	-4.00264800	0.06909600	0.13560500
O	-4.23830600	0.89267100	-1.04845200
O	-4.12052900	0.65475000	1.46955700
C	-5.09316600	-1.32216400	0.05246400
H	-4.88407000	-1.99345800	0.89628000
H	-6.11671000	-0.92789300	0.12359400
H	-4.94940300	-1.83274700	-0.90916100
C	-0.91786900	2.15312100	1.35168200
H	-1.14448600	3.23031900	1.35853100
H	-1.85906900	1.59343900	1.42125000
H	-0.29156500	1.90833700	2.22136300
C	-1.13199200	2.38168600	-1.49294900
H	-0.71817900	2.15394600	-2.48599300
H	-2.13331800	1.93833400	-1.39844200
H	-1.22318500	3.47384700	-1.38557600
C	3.68488300	1.18741400	-1.51010900
H	4.41009500	1.99666700	-1.33287000
H	4.23092000	0.30495100	-1.87277800
H	2.96854400	1.50368800	-2.28118800
C	4.22264700	0.20086200	1.06777700
H	5.03784700	0.93708400	0.99451000
H	3.93931200	0.08685100	2.12050500
H	4.58028900	-0.76375000	0.68361600
C	1.56762900	-0.79182500	2.94848700
H	1.96079200	0.21709600	3.14846100
H	1.01484900	-1.12392900	3.84111500
H	2.42747800	-1.46312800	2.80622900

INT1-Co-t

C	1.95777100	1.12497100	1.36964700
C	2.43979700	1.60554500	-1.03817800
C	0.99371700	1.92364900	-1.22148100
C	0.15866100	1.21229000	-2.01902700
C	-1.29191100	1.34543200	-1.97019400
C	-1.91544800	2.12473700	-1.04427100
H	2.15780700	2.19167200	1.58388000
H	2.40711200	0.53834500	2.18404000
H	3.01889500	2.53730400	-0.89901900
H	2.83831100	1.07082800	-1.91047600
H	0.59149300	2.75186300	-0.63279300
H	0.56946600	0.44405400	-2.67977700
H	-1.88552900	0.73863400	-2.65815600
P	-2.96188800	-0.75497500	0.25681500
P	-0.09427900	-1.81354000	-0.53224100
C	0.49318300	0.89767300	1.40179500
C	-0.62017600	0.83808400	1.99407800
C	-1.55323000	-2.92659200	-0.73068900
H	-1.93723400	-2.78892000	-1.75485100
C	-2.61574100	-2.57019300	0.30162000
H	-2.26942700	-2.81032000	1.32047800
Co	-0.84764700	0.34882000	0.05592900
H	-1.23850500	-3.97889600	-0.64186200
H	-3.54881200	-3.13266800	0.13639900
C	-1.84442900	3.37371200	-0.27158400
H	-1.47475300	4.26277700	-0.79535400
H	-1.59846000	3.34365700	0.79419500
C	-3.17815900	2.77702600	-0.69994600
H	-3.75075400	3.26014700	-1.49872500
H	-3.79112400	2.34660600	0.09901300
N	2.59586900	0.72611800	0.12641600

S	3.93854700	-0.24282200	0.18472100
O	4.10258200	-0.81385300	-1.14975700
O	3.77708200	-1.12186500	1.34156100
C	5.33799600	0.80170800	0.49185700
H	5.20641600	1.29888400	1.46108600
H	6.22011000	0.14827200	0.51131400
H	5.42358100	1.53135100	-0.32318200
C	0.73334300	-2.52413300	0.93361300
H	0.86146000	-3.61135200	0.81980400
H	1.71841900	-2.05445200	1.06586000
H	0.13124900	-2.31741000	1.82982500
C	1.00791200	-2.27489700	-1.90952500
H	0.56610600	-1.95900300	-2.86559400
H	1.98054700	-1.77774600	-1.77655000
H	1.16264500	-3.36438400	-1.92949800
C	-3.99796100	-0.62381000	-1.24967500
H	-4.88633300	-1.26606700	-1.15666100
H	-4.31798900	0.41528400	-1.40474800
H	-3.42053700	-0.94111700	-2.12891000
C	-4.20130600	-0.55278500	1.58840300
H	-5.06580100	-1.21003700	1.41078300
H	-3.75521400	-0.80424200	2.55956700
H	-4.54912300	0.48949200	1.62492500
C	-1.50954300	0.96046600	3.15585400
H	-1.79956600	-0.03244400	3.53074900
H	-0.99696500	1.49414900	3.97085800
H	-2.43053000	1.50611000	2.90601700

MECP1

C	1.94545750	0.87186560	1.35442670
C	2.28303690	1.27524630	-1.07730960
C	0.84959420	1.68757000	-1.12859540
C	-0.06802290	1.14908430	-2.01029360
C	-1.46953540	1.40406060	-1.85303930
C	-1.90617270	2.10512470	-0.72734010
H	2.24342450	1.91232230	1.59107730
H	2.33065740	0.22675400	2.15820800
H	2.91929050	2.18077800	-1.04040080
H	2.55539840	0.69505090	-1.96848580
H	0.57414220	2.58567380	-0.57137560
H	0.25452690	0.42868690	-2.76782590
H	-2.17383410	0.92442350	-2.53579390
P	-2.88687800	-0.77143840	0.15521870
P	0.00342020	-1.77199390	-0.50674580
C	0.47000080	0.80398960	1.35825220
C	-0.67815110	0.93227720	1.84852960
C	-1.42714050	-2.90821910	-0.76594720
H	-1.78128750	-2.76205660	-1.80011960
C	-2.52302060	-2.57664830	0.23458370
H	-2.19556360	-2.80323180	1.26316270
Co	-0.84720120	0.41890990	-0.11903930
H	-1.09282010	-3.95450650	-0.67573720
H	-3.44401420	-3.15284810	0.04875490
C	-1.75706490	3.43700520	-0.10187340
H	-1.46197330	4.27268440	-0.74649610
H	-1.39000090	3.51034890	0.92739890
C	-3.12607510	2.81367980	-0.31836130
H	-3.77564470	3.23016630	-1.09661260
H	-3.65849020	2.46961780	0.57542720
N	2.52711020	0.42531620	0.09808930
S	4.00895640	-0.32714950	0.16992570
O	4.27551180	-0.84328610	-1.17088020
O	3.96713030	-1.24369920	1.30815820
C	5.21543390	0.92013690	0.51829800
H	4.98406360	1.38490650	1.48644120
H	6.18886760	0.41178940	0.56190780
H	5.21029730	1.66097090	-0.29268370
C	0.77833840	-2.48142170	0.98625170
H	0.85517750	-3.57593870	0.89167890
H	1.78730070	-2.06525840	1.11735700
H	0.17561090	-2.23375430	1.87225530
C	1.14632870	-2.22919760	-1.84867550
H	0.73548190	-1.90452920	-2.81611980
H	2.12324560	-1.75068880	-1.68960510
H	1.28800710	-3.32123430	-1.86830720

C	-3.95839250	-0.65788090	-1.32140660
H	-4.84034990	-1.30518310	-1.19769540
H	-4.29212370	0.38027870	-1.46401130
H	-3.40295570	-0.97494160	-2.21565980
C	-4.09230790	-0.53520010	1.50540800
H	-4.96386230	-1.18610270	1.33436940
H	-3.64209260	-0.79254270	2.47336060
H	-4.42890670	0.51066380	1.53405000
C	-1.65197180	1.25364420	2.89509660
H	-2.02599000	0.33683250	3.37471250
H	-1.17357230	1.86822820	3.67345200
H	-2.51867470	1.80199420	2.49897550

INT2-Co

N	-3.43383500	-0.70567600	0.33371900
C	-2.38523600	-0.44363500	1.33377000
C	-1.13056900	-0.20759400	0.51349900
C	0.13939100	-0.19300400	0.93047200
C	-2.79008500	-1.01383500	-0.94528400
C	-1.54312500	-0.11593700	-0.93368800
C	-0.48452700	-0.41830300	-1.94402200
C	0.44855800	-1.44563600	-1.94376200
S	-4.70529000	0.38346800	0.25914100
O	-4.86925400	0.94307600	1.59950900
O	-4.55073400	1.30162200	-0.87354400
H	-2.67337200	0.40949700	1.96600500
H	-2.27766000	-1.31989300	1.99408200
H	-2.50238900	-2.07782000	-0.95904200
H	-3.46578700	-0.82038900	-1.78857200
H	-1.91125600	0.90937900	-1.12684500
H	1.04900300	-1.50777500	-2.86383700
P	1.59709000	2.03554300	-0.41100900
C	1.00741600	-2.12331200	-0.80976200
H	-0.55915700	0.14152900	-2.88186100
C	0.52304800	-3.18173300	0.10700100
C	1.72885100	-3.42033900	-0.77491300
P	3.26301200	-0.34899300	0.58868000
C	3.73941700	1.31624300	1.21104800
C	1.49189600	2.95509100	-1.97905400
H	0.45000700	2.94245900	-2.33229300
H	1.81669100	3.99874600	-1.84537200
C	0.50018800	2.95418900	0.70941600
H	-0.54331800	2.81175700	0.39266600
H	0.60703200	2.57973900	1.73683800
H	0.74960900	4.02583200	0.68000300
C	3.31162900	2.37166300	0.19825900
C	3.72984200	-1.51891400	1.89154500
H	3.44267700	-2.53988200	1.60288100
H	4.82016600	-1.47768000	2.03777800
H	3.23204400	-1.25729600	2.83462100
H	4.82343800	1.34654500	1.40671600
H	3.22914500	1.46051800	2.17689500
C	-6.07834100	-0.67225000	-0.09118200
H	-6.19122800	-1.38256500	0.73726100
H	-6.96047000	-0.02218200	-0.17601100
H	-5.90008300	-1.19558500	-1.04001700
Co	1.39983600	-0.19312300	-0.49054900
H	0.68742200	-3.06019100	1.18217000
H	-0.41129000	-3.69330100	-0.14837400
H	2.70964200	-3.46935500	-0.29020400
H	1.61903900	-4.09713800	-1.63011700
C	4.41451100	-0.68642200	-0.78315900
H	5.45293200	-0.48655500	-0.47646500
H	4.31748800	-1.74138600	-1.07896100
H	4.16853400	-0.05614500	-1.65163400
H	3.96698700	2.34501800	-0.68789100
H	3.37033200	3.38937300	0.61570700
H	2.12550400	2.46959400	-2.73612500
C	0.52143700	-0.30098900	2.36850200
H	1.00072800	-1.26898800	2.58825100
H	1.23212500	0.48516000	2.66993500
H	-0.35607200	-0.20999900	3.02944200

INT2-Co-t

N	-3.53202600	-0.62484200	0.35404200
C	-2.51291800	-0.28632700	1.36004200

C	-1.22760400	-0.14497700	0.56772200
C	0.03062200	-0.15469400	1.00517200
C	-2.85947000	-1.00935600	-0.88890900
C	-1.60872600	-0.11385400	-0.89874800
C	-0.55414300	-0.45849200	-1.89790900
C	0.36661000	-1.48592800	-1.87327700
S	-4.82892100	0.42221200	0.19032400
O	-4.99133400	1.11047100	1.46967100
O	-4.70483400	1.22264100	-1.03166800
H	-2.80242700	0.62838700	1.89903900
H	-2.43678200	-1.09504400	2.10538100
H	-2.57497800	-2.07286500	-0.83684600
H	-3.51536700	-0.85952900	-1.75586600
H	-1.97889200	0.90085400	-1.13845900
H	0.97009700	-1.60089000	-2.78437700
P	1.67527200	2.02348400	-0.38280000
C	0.84579200	-2.17384900	-0.70695800
H	-0.60842500	0.09707500	-2.83989700
C	0.28032400	-3.19335100	0.20028100
C	1.52766500	-3.48660500	-0.60668700
P	3.57396100	-0.36904000	0.41153700
C	3.94224600	1.31875100	1.05070700
C	1.42515200	2.87993000	-1.96924000
H	0.35537300	2.85464700	-2.22430700
H	1.75765200	3.92767400	-1.90207700
C	0.68328800	2.98293500	0.79670300
H	-0.38270700	2.86016300	0.55805300
H	0.85581700	2.62399500	1.82058200
H	0.95638300	4.04725600	0.72920800
C	3.43283300	2.36215700	0.06641600
C	3.93488400	-1.48199600	1.78850900
H	3.83671700	-2.52751800	1.46336700
H	4.94972800	-1.31332500	2.17989500
H	3.19679800	-1.28448900	2.57239600
H	5.02312100	1.42515200	1.23847500
H	3.42816300	1.40833400	2.02280900
C	-6.18524300	-0.68783500	-0.03264500
H	-6.27608100	-1.30950400	0.86672200
H	-7.08128100	-0.06738000	-0.17461500
H	-6.00394300	-1.30413500	-0.92314000
Co	1.40089200	-0.27566700	-0.42943000
H	0.39151100	-3.05343400	1.28000300
H	-0.65662300	-3.67706900	-0.09688100
H	2.47457700	-3.55774000	-0.06142800
H	1.44834400	-4.17189200	-1.45870200
C	4.87715700	-0.70441700	-0.81678100
H	5.87663000	-0.61827200	-0.36276200
H	4.74329700	-1.72326900	-1.21080500
H	4.79348300	0.00275300	-1.65504100
H	4.00963200	2.32604100	-0.87270500
H	3.52416200	3.38491900	0.46595800
H	1.99002800	2.36622600	-2.76085900
C	0.43954700	-0.21511200	2.43900600
H	0.80305800	-1.22528400	2.70015300
H	1.27563700	0.47275400	2.65341300
H	-0.37711000	0.03348900	3.13894300

MECP2

N	-3.42057360	-0.91327830	0.21710560
C	-2.33524140	-1.08229230	1.19715380
C	-1.06743950	-0.87721750	0.40073950
C	0.19441140	-1.13994900	0.76918170
C	-2.84637190	-1.07990120	-1.12329320
C	-1.46239880	-0.42242930	-0.98232770
C	-0.44574850	-0.63882760	-2.05481700
C	0.61944850	-1.49859490	-2.03704940
S	-4.36683220	0.46297100	0.42131160
O	-4.44017280	0.72010020	1.85673050
O	-3.92409590	1.54649880	-0.46360650
H	-2.47123100	-0.38079960	2.03265760
H	-2.37255280	-2.10179140	1.61931260
H	-2.75786720	-2.15601350	-1.34158410
H	-3.47847300	-0.61436090	-1.89086950
H	-1.68161870	0.66260680	-0.95616840
H	1.24406070	-1.53103220	-2.93805330

P	1.11175540	2.06273810	-0.45814160
C	1.12133380	-2.15137480	-0.83155040
H	-0.60402760	-0.07140270	-2.97823380
C	0.90936250	-3.57053870	-0.41433950
C	2.27198640	-3.11496030	-0.83763480
P	3.26967140	0.14426260	0.67242900
C	3.32420390	1.91183450	1.19803190
C	0.67428060	3.04236490	-1.92955860
H	-0.33332200	2.75946740	-2.26589830
H	0.69309910	4.11969400	-1.70751210
C	-0.10415470	2.56501250	0.80844730
H	-1.11360050	2.25046700	0.50553090
H	0.13535250	2.07006930	1.76001720
H	-0.09035420	3.65691020	0.94324180
C	2.70219920	2.79673350	0.12355990
C	3.95006280	-0.75893810	2.10094400
H	4.00926440	-1.83227820	1.87237240
H	4.95885470	-0.38799730	2.33473100
H	3.30142460	-0.61854680	2.97592810
H	4.36038360	2.20961330	1.42393680
H	2.75459220	1.97842030	2.13978950
C	-5.94841920	-0.08820560	-0.14529260
H	-6.27125800	-0.91881220	0.49234370
H	-6.62464190	0.77149770	-0.05119280
H	-5.87080650	-0.39715560	-1.19461000
Co	1.33988280	-0.21689840	-0.45811810
H	0.74580340	-3.80422770	0.64105680
H	0.32881610	-4.18797110	-1.10529670
H	3.02795130	-3.01563590	-0.05365340
H	2.66970010	-3.42944660	-1.80910030
C	4.58820770	0.01123250	-0.58715660
H	5.55128940	0.37268870	-0.19654260
H	4.68939530	-1.04229620	-0.88586950
H	4.31310600	0.59405900	-1.47803150
H	3.36018610	2.86393480	-0.75861010
H	2.54018090	3.82440910	0.48475490
H	1.38788480	2.81982890	-2.73551090
C	0.59818320	-1.62872710	2.11627360
H	1.48798070	-2.27306680	2.07903810
H	0.84290110	-0.77660590	2.77071330
H	-0.21024980	-2.19596040	2.60558250

INT3-Co-t

N	3.07161500	-0.23550800	-0.69276800
C	3.00272100	1.12857300	-0.14179700
C	1.58846500	1.58718900	-0.41147000
C	1.02290000	2.76952100	-0.12809100
C	2.05467700	-0.31316600	-1.74861800
C	0.88992200	0.47648100	-1.15189500
C	-0.24162800	0.94628900	-2.01122400
C	-0.90503300	2.09053100	-1.63181900
S	3.01684300	-1.48530200	0.43285000
O	3.64211800	-0.99493400	1.65857500
O	1.66487900	-2.05985400	0.53046100
H	3.28305100	1.12369000	0.92071800
H	3.73808900	1.75523300	-0.67308400
H	2.44982000	0.18188000	-2.64991200
H	1.80758700	-1.35224800	-1.99952100
H	0.48885300	-0.23979500	-0.37175900
H	-1.72495100	2.46811500	-2.25152200
P	-2.10033200	-1.69936500	-1.05742600
H	-0.47515300	0.42797100	-2.94480500
C	-0.91490500	4.43842400	-0.63588000
C	-1.39875900	3.53363700	0.43974100
P	-1.62221600	-0.29417700	1.80326200
C	-1.69948300	-2.13283900	1.66473000
C	-3.51714400	-2.01445100	-2.16666900
H	-3.27158700	-1.65773400	-3.17874100
H	-3.76247300	-3.08728500	-2.21335800
C	-0.80057000	-2.79698100	-1.72822700
H	-0.48206500	-2.42676200	-2.71474400
H	0.06751500	-2.78985800	-1.05187800
H	-1.17304900	-3.82776200	-1.83826300
C	-2.60033900	-2.55273200	0.50788300
C	-0.25083700	-0.00977500	2.97212500

H	-0.14468500	1.07026100	3.15574600
H	-0.42857500	-0.52398400	3.92980400
H	0.68380100	-0.38529400	2.52964400
H	-2.03478500	-2.56813600	2.62062100
H	-0.66130400	-2.46425500	1.49390200
C	4.05566500	-2.69893600	-0.31298800
H	5.06572000	-2.28070100	-0.40452600
H	4.04650900	-3.57074500	0.35611300
H	3.64622200	-2.96770700	-1.29563800
Co	-1.42597700	0.42104800	-0.38336700
H	-0.23588000	5.24954700	-0.36369900
H	-1.59140200	4.67119300	-1.46271100
H	-1.04319700	3.69638600	1.46133200
H	-2.41289100	3.12875300	0.36946800
C	-3.11274200	0.15507200	2.75645100
H	-3.15354100	-0.38709800	3.71407800
H	-3.10252600	1.23818900	2.95314100
H	-4.01257000	-0.07767300	2.16736200
H	-3.64622100	-2.26108000	0.70501000
H	-2.59077300	-3.64607300	0.36638200
H	-4.39613100	-1.45720700	-1.80883800
C	-0.38444900	3.02102700	-0.58015900
C	1.76224000	3.85414300	0.59182800
H	2.70538800	3.48805700	1.01901300
H	2.00232700	4.69022500	-0.08593400
H	1.16750000	4.27635800	1.41791300

INT4-Co

C	2.70088400	0.46501200	1.67734400
C	1.45069700	0.70904500	0.86080200
C	0.21558200	0.34159400	1.18676900
C	3.35163300	1.65169300	-0.22334800
C	1.85942800	1.35483700	-0.44601200
C	-1.40183200	1.92358500	-0.38722800
C	-2.74921200	2.43506200	-0.79366800
C	-2.33061200	2.53999200	0.64642700
Co	-1.50523500	0.30892700	0.55354100
P	-3.64995600	-0.63638200	0.39564700
P	-0.95786000	-1.00741300	-1.05012400
C	-2.34558100	-2.17615000	-1.41408000
C	0.45132200	-2.13130800	-0.82678600
C	-0.68855600	-0.18909600	-2.64866100
C	-5.26220700	0.19075700	0.58270800
C	-3.69240900	-1.49701500	-1.22507400
C	-3.76021200	-1.99952500	1.60877500
C	1.06414700	2.54524100	-0.87975600
C	-0.26204800	2.74641500	-0.84625300
H	2.74000400	-0.52518000	2.15058500
H	2.82090900	1.22137000	2.47267700
H	3.48913100	2.63745200	0.25058800
H	3.94418600	1.63271700	-1.14755400
H	1.81460200	0.58244900	-1.23747000
H	-2.21331900	-2.56801400	-2.43522600
H	-2.23492600	-3.02612300	-0.72108600
H	0.43790700	-2.88066500	-1.63368300
H	1.40960600	-1.59503000	-0.85277400
H	0.35589400	-2.64551800	0.14072700
H	-1.61435200	0.31837400	-2.95474700
H	0.10960500	0.56016500	-2.57191000
H	-0.41724400	-0.94603600	-3.40023700
H	-6.07582000	-0.54796900	0.51574400
H	-5.30481300	0.68086300	1.56707200
H	-5.40488500	0.95377400	-0.19527700
H	-3.86809400	-0.73362600	-2.00105300
H	-4.52638000	-2.21582700	-1.26564500
H	-4.64511900	-2.62527500	1.41379200
H	-2.85568900	-2.62330900	1.56264500
H	-3.83598200	-1.57457500	2.62111800
H	1.65745700	3.36232100	-1.30892400
H	-0.58766200	3.71673100	-1.24806500
H	-3.53947600	1.72108000	-1.03815100
H	-2.78129900	3.35719000	-1.38482900
H	-2.85651800	1.87343100	1.35775700
H	-2.04516100	3.49801500	1.09030600
C	-0.23277100	-0.40548100	2.39809000

H	-1.33614400	-0.64029700	2.35586100
H	0.25932700	-1.38518600	2.51238500
H	-0.11947800	0.17032400	3.33056600
N	3.80640900	0.63365900	0.72741400
S	4.37758100	-0.78550100	0.02458900
O	3.79858100	-0.99496000	-1.30922300
O	4.23558500	-1.84796900	1.01822600
C	6.09085400	-0.41892500	-0.19008500
H	6.53533500	-0.24695900	0.79806400
H	6.53893000	-1.29583700	-0.67785500
H	6.19392700	0.46649100	-0.83098600

INT5-Co

C	2.70298600	0.92395700	1.50978300
C	1.44440700	1.00449600	0.68598700
C	0.20693200	0.66407900	0.99742600
C	3.36769400	1.61690200	-0.61411100
C	1.82524300	1.59594900	-0.66520700
C	-1.29577500	2.32374000	-0.56789000
C	-1.55111000	1.29596100	-1.52753300
C	-2.23832600	2.42993900	0.47809800
Co	-1.50682900	0.48558900	0.29560900
P	-3.60345200	-0.36811400	0.16319100
P	-0.82936700	-1.49864600	-0.46685100
C	-2.30638400	-2.57017500	-0.78279000
C	0.19697900	-2.54165300	0.61553000
C	0.09285900	-1.53386400	-2.03330000
C	-5.03346200	0.63415400	-0.34783700
C	-3.52742500	-1.71782300	-1.08139300
C	-4.18348200	-1.18533800	1.68637600
C	1.18872600	2.94720000	-0.80322300
C	-0.11714400	3.21834800	-0.66777600
H	2.71323400	0.11479900	2.24941500
H	2.92028900	1.87349100	2.02990200
H	3.73756200	2.62696500	-0.37726200
H	3.83835700	1.29478000	-1.55143900
H	1.48544400	0.92999700	-1.47362200
H	-2.08028300	-3.27854500	-1.59498200
H	-2.46471600	-3.16288200	0.13291500
H	0.32185200	-3.52807900	0.14293700
H	1.18972500	-2.09189000	0.75884200
H	-0.29219600	-2.67495000	1.59080900
H	-0.47806500	-1.04649200	-2.83484400
H	1.06531900	-1.03866100	-1.90209800
H	0.27684900	-2.58370600	-2.30828400
H	-5.90156000	-0.02007500	-0.52020200
H	-5.28627700	1.35802200	0.44091700
H	-4.80954900	1.18198600	-1.27535100
H	-3.44468200	-1.23450900	-2.06910700
H	-4.45908600	-2.30584400	-1.07360100
H	-5.14397200	-1.69651000	1.51899900
H	-3.43625400	-1.91682200	2.02725800
H	-4.30935200	-0.42692000	2.47392100
H	1.86427900	3.80070600	-0.93565600
H	-0.41181400	4.27450600	-0.68160100
H	-2.56327900	1.17394600	-1.92829700
H	-0.76091600	1.09347800	-2.25619300
H	-1.97450700	3.04792800	1.34391600
H	-3.30724700	2.36790900	0.26823500
C	-0.48913600	0.26576500	2.22967100
H	-1.61545200	0.08773000	2.02237100
H	-0.17006600	-0.69348100	2.66376300
H	-0.50342700	1.05273100	2.99773500
N	3.75167400	0.73753800	0.49815200
S	4.00675800	-0.87084800	0.05212700
O	3.33281600	-1.18544600	-1.21287900
O	3.71537800	-1.70149900	1.22180100
C	5.74630800	-0.89009100	-0.24314800
H	6.25944800	-0.63635700	0.69280600
H	5.99844700	-1.90894100	-0.56901200
H	5.98381400	-0.16673100	-1.03418400

INT6-Co

C	-2.31151200	-0.29846800	-1.69656900
C	-1.63839800	1.77200800	-0.46325300
C	-0.26000100	1.46374100	-0.97624000

C	0.92910700	1.69620200	-0.26677100
C	2.14150400	2.12611100	-0.96366300
C	3.11553500	2.83274300	-0.39333400
H	-2.38716500	0.21677000	-2.67282200
H	-3.09494900	-1.06912100	-1.66518800
H	-2.02695300	2.63208000	-1.04212600
H	-1.60653400	2.07572100	0.58950600
H	-0.17062100	1.53632000	-2.06954100
H	0.87201700	1.97301600	0.79077700
H	2.21847400	1.88284900	-2.03089300
P	2.55751500	-1.22239200	-0.04669800
P	-0.09286100	-0.84178900	1.43208800
C	-0.98389900	-0.91887700	-1.53993600
C	-0.12996100	-1.87084500	-1.59151100
C	1.31422200	-1.63300400	2.32692600
H	1.87587300	-0.82416800	2.82179200
C	2.19640600	-2.38070300	1.33768000
H	1.67481000	-3.25923700	0.92627900
Co	0.55771100	-0.34947800	-0.59839900
H	0.92047100	-2.28635000	3.12093700
H	3.12794400	-2.73752300	1.80343000
C	3.64159800	3.47045700	0.81106100
H	4.03602300	2.84207900	1.61849600
H	3.18049000	4.40278500	1.15706800
C	4.40749800	3.49884400	-0.51115500
H	5.31188300	2.88298000	-0.58985900
H	4.46828500	4.45059500	-1.05130500
C	-1.40436600	-2.10524100	1.45446700
H	-1.61328500	-2.38854400	2.49680800
H	-2.31914500	-1.70000200	1.00029200
H	-1.08764600	-2.99217200	0.89023000
C	-0.70333500	0.41367200	2.59482800
H	-0.00884100	1.26176300	2.66032000
H	-1.69908400	0.76157500	2.28467000
H	-0.78694300	-0.05307800	3.58818900
C	3.88221000	-0.18419100	0.66187800
H	4.66991200	-0.82861200	1.07962900
H	4.30900400	0.45469100	-0.12164000
H	3.47680800	0.46443900	1.44951100
C	3.46270900	-2.19033800	-1.29736200
H	4.39119200	-2.59643500	-0.86986000
H	2.84203700	-3.01458000	-1.66879800
H	3.71390700	-1.53264700	-2.14218200
C	0.15859600	-3.25275800	-2.01655500
H	-0.75527100	-3.75808600	-2.36337600
H	0.88774300	-3.26447800	-2.84114000
H	0.59054700	-3.84849800	-1.19853700
N	-2.52904500	0.62029300	-0.58836700
S	-3.98142700	0.63215200	0.19249000
O	-3.77184600	1.35867600	1.44351500
O	-4.45982100	-0.74870400	0.22034500
C	-5.11174900	1.57762500	-0.79186800
H	-4.72566000	2.59996400	-0.88987400
H	-5.22000800	1.09525400	-1.77138200
H	-6.07079500	1.58113000	-0.25738300

INT6-Co-t

C	-2.37240300	-0.38377000	-1.74806400
C	-1.77748100	1.77822600	-0.64382700
C	-0.39227900	1.60835700	-1.20288200
C	0.72871000	1.92040100	-0.45932100
C	2.01283600	2.23513300	-1.07008900
C	2.99168200	2.87513700	-0.42732100
H	-2.48082900	0.11845300	-2.72718100
H	-3.14679700	-1.16214300	-1.68481700
H	-2.27894500	2.56482400	-1.24171600
H	-1.71683100	2.13306400	0.39233100
H	-0.30075200	1.61069300	-2.29538400
H	0.61130200	2.17139500	0.60018500
H	2.14695200	1.97560700	-2.12770200
P	2.61019000	-1.26148000	-0.09479100
P	-0.02086400	-0.68579800	1.60048400
C	-1.04265300	-1.00805400	-1.63171500
C	-0.18295400	-1.93332900	-1.65678300
C	1.46237100	-1.41775900	2.41857500

H	2.07923500	-0.58059200	2.78613400
C	2.24018200	-2.25731500	1.41191100
H	1.64855300	-3.12987200	1.08645100
Co	0.56736200	-0.31357100	-0.72562800
H	1.16236900	-2.01201300	3.29712000
H	3.18198200	-2.63915500	1.83901900
C	3.47072600	3.48349000	0.81018700
H	3.75004100	2.83263600	1.64767800
H	3.05364800	4.45129000	1.11317400
C	4.33389100	3.44144200	-0.44916600
H	5.18841300	2.75327400	-0.45897700
H	4.50600800	4.38061400	-0.98820400
C	-1.25667600	-2.02363800	1.73545000
H	-1.40453300	-2.31548400	2.78715600
H	-2.21607000	-1.68660200	1.31558900
H	-0.91848600	-2.89886400	1.16098000
C	-0.62476300	0.56213300	2.78306600
H	0.05370400	1.42846200	2.79316000
H	-1.62771100	0.89057500	2.46883700
H	-0.68782200	0.14220700	3.79947800
C	3.92678200	-0.14284500	0.49498200
H	4.72728800	-0.72619200	0.97606100
H	4.34555000	0.41727200	-0.35246600
H	3.51281900	0.57504300	1.21577400
C	3.54487900	-2.40717100	-1.16451200
H	4.46387500	-2.74138900	-0.65867000
H	2.93471400	-3.28472400	-1.41491000
H	3.81641300	-1.89044300	-2.09753000
C	0.24589300	-3.30816900	-1.94770000
H	-0.61132400	-3.92052700	-2.26913500
H	1.00129500	-3.32458800	-2.74825000
H	0.69862500	-3.78021500	-1.06242200
N	-2.56667800	0.55048300	-0.65329200
S	-3.95930100	0.49641500	0.22835400
O	-3.72624000	1.28835200	1.43492400
O	-4.34313500	-0.90986200	0.34309700
C	-5.20889500	1.32073600	-0.71579800
H	-4.89579400	2.35916100	-0.88888200
H	-5.35253200	0.78543700	-1.66406100
H	-6.13154500	1.29641800	-0.11898200

INT7-Co-t

C	2.64693000	-2.14885600	0.72871700
C	2.71417300	0.03811900	1.62828000
C	1.22454700	-0.27027300	1.32935600
C	0.48503100	0.75622000	0.46131200
C	0.16452000	2.01614700	1.14644400
C	0.47435800	3.22638900	0.67751100
H	2.74493800	-2.72662200	1.66490300
H	2.98742100	-2.77960300	-0.10104300
H	2.94836800	-0.10164200	2.69469800
H	2.99502700	1.06274000	1.34956400
H	0.68763800	-0.39859300	2.28639700
H	1.07176300	0.93442900	-0.45499600
H	-0.32870000	1.94649700	2.12618500
P	-2.90729800	-1.68371800	0.36561300
P	-2.71778700	1.26845700	-0.57981100
C	1.27805900	-1.55653100	0.55444400
C	0.30047900	-1.80848900	-0.33113000
C	-4.25376800	0.72450100	0.27929200
H	-4.12112400	0.96905100	1.34640200
C	-4.47668900	-0.76825200	0.08170300
H	-4.78850900	-0.98621400	-0.95300900
Co	-1.02369000	-0.37397800	-0.27888700
H	-5.10849300	1.31451100	-0.08934900
H	-5.26203900	-1.15731300	0.74985700
C	1.05024700	4.00584700	-0.41515600
H	0.50000200	4.07565100	-1.36215500
H	2.14059300	4.02744500	-0.53204900
C	0.44185900	4.67917200	0.81554200
H	-0.51597000	5.20095100	0.69251600
H	1.12503700	5.16176600	1.52489800
C	-3.10636400	1.09229100	-2.35470900
H	-4.03393200	1.62895600	-2.60847000
H	-2.27423900	1.50633500	-2.94418700

H	-3.21809300	0.02891200	-2.61469200
C	-2.66216000	3.06135500	-0.31059500
H	-3.60946100	3.50966500	-0.64838800
H	-2.51176500	3.27841700	0.75542700
H	-1.83086100	3.49246300	-0.88491800
C	-2.74688500	-1.80404400	2.17511200
H	-3.62869000	-2.29684800	2.61343100
H	-1.84385100	-2.38527100	2.41468700
H	-2.63765000	-0.79791700	2.60651600
C	-3.22133700	-3.37881900	-0.19934600
H	-4.17085000	-3.74561900	0.22057600
H	-3.27267100	-3.40241300	-1.29764000
H	-2.40217400	-4.03097800	0.13500700
C	0.25207300	-2.95951100	-1.28072400
H	-0.40298400	-3.76878500	-0.91686500
H	-0.14332000	-2.65889200	-2.26528900
H	1.25322200	-3.39647300	-1.44369800
N	3.49290800	-0.94772600	0.85903400
S	4.17205200	-0.38386400	-0.57020100
O	3.41809500	0.74485200	-1.12756100
O	4.41441300	-1.54913000	-1.41995000
C	5.72328300	0.24684400	-0.00486700
H	6.23152500	0.66707900	-0.88414800
H	5.54222800	1.03306600	0.74003500
H	6.30014400	-0.58095800	0.42569000

TS1-Co

C	-2.02217600	-1.47144100	1.10184000
C	-2.06060000	-1.04912600	-1.30117600
C	-0.62420000	-1.43174100	-1.04607800
C	0.36586200	-0.97200900	-2.00566000
C	1.68758900	-1.39778200	-1.81009900
C	1.94338000	-2.04710400	-0.56930400
H	-2.11413500	-2.57258100	1.11879200
H	-2.44030400	-1.07891200	2.03892800
H	-2.51830300	-1.84225500	-1.91943100
H	-2.13119000	-0.10830400	-1.85941800
H	-0.50345400	-2.48956700	-0.78440900
H	0.08808700	-0.31994000	-2.83757600
H	2.47985400	-1.06136900	-2.48456500
P	2.88979800	0.67278800	0.23391700
P	0.14306100	1.78385400	-0.40056700
C	-0.60305900	-1.05789200	0.98389700
C	0.42058900	-0.61869600	1.61040700
C	1.55393300	2.96656400	-0.38749300
H	1.96123700	3.00137100	-1.41165500
C	2.59019400	2.45143000	0.59386700
H	2.22155400	2.51620900	1.63109100
Co	0.99924800	-0.31661600	-0.22235500
H	1.19833300	3.97818700	-0.13521900
H	3.54044700	3.00641800	0.54420000
C	1.63430700	-3.40268600	-0.04631800
H	1.34505000	-4.18315200	-0.75840100
H	1.15957300	-3.48566500	0.93755600
C	3.05855300	-2.88943000	-0.09375000
H	3.74485700	-3.31770700	-0.83324800
H	3.52375000	-2.66213100	0.86998300
N	-2.74864500	-0.92398900	-0.02564200
S	-4.00453800	0.12268800	0.16845000
O	-3.98688000	1.04886700	-0.96424100
O	-3.95060300	0.64392800	1.53484000
C	-5.46689700	-0.85943200	0.02812200
H	-5.45825100	-1.61893900	0.82113000
H	-6.32517400	-0.18357700	0.15002500
H	-5.48230900	-1.32512600	-0.96606800
C	-0.84453400	2.30675900	1.03893500
H	-1.11518900	3.36916500	0.93939800
H	-1.76444800	1.71033800	1.11199800
H	-0.26797700	2.16292200	1.96333300
C	-0.86531600	2.34522900	-1.81152200
H	-0.42545300	2.00271400	-2.75925300
H	-1.88967000	1.95622700	-1.71397000
H	-0.91107700	3.44557200	-1.81216900
C	4.05283200	0.72040800	-1.16995000
H	4.92492200	1.33775600	-0.90553200

H	4.39409800	-0.29827200	-1.40371700
H	3.56057200	1.14376400	-2.05697800
C	3.96521400	0.14254800	1.60099700
H	4.82529700	0.82786500	1.64989500
H	3.43054000	0.17259400	2.55765300
H	4.33566800	-0.87559100	1.42573700
C	0.87322900	-0.35188900	2.98826500
H	1.26317000	0.67231500	3.09315100
H	0.04954600	-0.48414900	3.70793200
H	1.68738300	-1.03690500	3.27377900

TS1-Co-t

C	-2.20516200	-1.53520700	1.18041200
C	-2.31962700	-1.40001600	-1.22025400
C	-0.85062500	-1.66664300	-0.96796300
C	0.08310500	-1.10332800	-1.91701100
C	1.45231400	-1.48142900	-1.90062800
C	1.94141100	-2.15511500	-0.79170800
H	-2.29484200	-2.62962300	1.29704600
H	-2.56989700	-1.06099700	2.10064100
H	-2.76838200	-2.29392900	-1.68455900
H	-2.45293700	-0.55654400	-1.90932000
H	-0.62802700	-2.70795600	-0.70466500
H	-0.28196500	-0.41916000	-2.68648900
H	2.13761800	-1.02226800	-2.62016400
P	3.03954800	0.66846700	0.36639600
P	0.24858600	1.86068000	-0.54595300
C	-0.77827700	-1.16119200	0.94458700
C	0.24634300	-0.74810100	1.62689600
C	1.76589600	2.89723200	-0.65286200
H	2.19307800	2.73926600	-1.65757700
C	2.75688400	2.49174300	0.43138200
H	2.35410600	2.72442900	1.43122000
Co	0.86248500	-0.39299200	-0.14304900
H	1.49044400	3.96213000	-0.57797200
H	3.71144700	3.03404700	0.33093600
C	1.77098900	-3.41649500	-0.03721200
H	1.40970700	-4.28881500	-0.59383900
H	1.45573300	-3.38427300	1.00992000
C	3.14924400	-2.87432100	-0.37771000
H	3.74399400	-3.38362900	-1.14426900
H	3.73438800	-2.46616300	0.45393500
N	-2.99257100	-1.10749200	0.04272800
S	-3.92435100	0.26718700	0.17498800
O	-3.79346000	1.03770500	-1.06277000
O	-3.62937400	0.91065600	1.45697300
C	-5.57633500	-0.34975100	0.25101600
H	-5.66657500	-1.00067100	1.13035500
H	-6.24248200	0.51996600	0.34132300
H	-5.78438400	-0.90403000	-0.67357300
C	-0.62436300	2.54616300	0.90047500
H	-0.78136700	3.62978500	0.78131200
H	-1.59844600	2.04837900	1.01813500
H	-0.03391600	2.36240900	1.81009800
C	-0.76852500	2.39565700	-1.95711900
H	-0.31378200	2.05441000	-2.89890900
H	-1.77326000	1.95727100	-1.85546300
H	-0.85855300	3.49317400	-1.97599100
C	4.27886200	0.52598400	-0.97301000
H	5.17541200	1.12547700	-0.74896300
H	4.57291100	-0.52584400	-1.10194100
H	3.84027500	0.87935200	-1.91825700
C	4.02553500	0.34676200	1.87100100
H	4.93221000	0.97205600	1.89620900
H	3.41866300	0.55741400	2.76327200
H	4.32103200	-0.71298800	1.89664900
C	0.62598500	-0.47134500	3.02432300
H	0.93767500	0.57837200	3.13993200
H	-0.19920300	-0.66964200	3.72802200
H	1.48857200	-1.09087800	3.31842600

TS2-Co-s

N	-3.41213900	-0.90896500	0.22669800
C	-2.32125600	-1.07665700	1.20380100
C	-1.05930500	-0.88318900	0.39765100
C	0.20923800	-1.16679700	0.74468600

C	-2.84392200	-1.06714400	-1.11808500
C	-1.46016700	-0.41240500	-0.97707700
C	-0.44191000	-0.63013200	-2.04772800
C	0.62204200	-1.49233100	-2.01701400
S	-4.36715600	0.45993800	0.43432600
O	-4.44986400	0.70730900	1.87211100
O	-3.93028600	1.55597900	-0.43911400
H	-2.44813600	-0.36547600	2.03346500
H	-2.36429100	-2.09076000	1.63830900
H	-2.75565800	-2.14220800	-1.34295300
H	-3.48157300	-0.59800700	-1.87875700
H	-1.67200300	0.67379000	-0.94321100
H	1.25281900	-1.53765500	-2.91327600
P	1.13215600	2.06740900	-0.46404700
C	1.11038200	-2.13860700	-0.79987800
H	-0.59624600	-0.06973700	-2.97575600
C	0.92638000	-3.57443400	-0.41112400
C	2.28417900	-3.07842000	-0.79193600
P	3.23016100	0.15136600	0.67503100
C	3.32131500	1.91559300	1.20273200
C	0.68407300	3.03821300	-1.93679200
H	-0.33487400	2.76689300	-2.25110100
H	0.71991300	4.11824500	-1.72510600
C	-0.08222500	2.57898900	0.79872500
H	-1.09322400	2.26405400	0.50009000
H	0.15938800	2.09870600	1.75800400
H	-0.06755000	3.67304700	0.92244500
C	2.71815600	2.80412700	0.12154300
C	3.91048600	-0.77409300	2.08524900
H	3.95910200	-1.84509400	1.84041100
H	4.92493600	-0.41269300	2.31464000
H	3.27051600	-0.64040200	2.96833200
H	4.36387000	2.19101400	1.42988900
H	2.74768800	1.99413600	2.14142700
C	-5.94004100	-0.09578800	-0.14446200
H	-6.26828400	-0.92895900	0.48909600
H	-6.62243900	0.76105100	-0.05392100
H	-5.85668300	-0.40446100	-1.19478200
Co	1.34078000	-0.19467800	-0.45156500
H	0.73949700	-3.82812100	0.63614300
H	0.37612900	-4.18869700	-1.12985900
H	3.01640600	-2.96021400	0.01259300
H	2.71066900	-3.36662200	-1.75928300
C	4.52719500	0.00448300	-0.60275000
H	5.49390800	0.37744100	-0.22974900
H	4.63128500	-1.05336000	-0.88739500
H	4.23918400	0.57389800	-1.49918900
H	3.38469900	2.86154300	-0.75499200
H	2.55443200	3.83385300	0.47784500
H	1.37836600	2.80231500	-2.75690000
C	0.60993200	-1.66928600	2.08997000
H	1.49832600	-2.31472300	2.04915900
H	0.85975100	-0.82537300	2.75408700
H	-0.20236200	-2.23802300	2.57263600

TS2-Co-t

N	-3.57676800	-0.92773900	0.44674500
C	-2.46014300	-0.91986500	1.40008700
C	-1.21527800	-0.76813000	0.54684100
C	0.02920000	-0.52369200	0.95266200
C	-3.04219500	-1.50333600	-0.79090600
C	-1.63309500	-0.89144100	-0.90221700
C	-0.71394200	-1.53570000	-1.88437900
C	0.47354800	-2.17594200	-1.71473600
S	-4.37145100	0.54671700	0.25922200
O	-4.36505300	1.20504300	1.56400300
O	-3.86374300	1.29305800	-0.89930100
H	-2.59750400	-0.12879700	2.14930000
H	-2.46219900	-1.88626800	1.93297700
H	-2.99153700	-2.59662000	-0.66347000
H	-3.68688600	-1.28375800	-1.65226500
H	-1.81124200	0.13427700	-1.28354300
H	0.96487200	-2.50191500	-2.64183600
P	0.98546600	1.94257600	-0.53844400
C	1.27292900	-2.31774700	-0.49128000

H	-1.05336700	-1.43941500	-2.92293300
C	1.18671400	-3.39988800	0.52441100
C	2.39657400	-3.29941100	-0.36678600
P	3.55307200	0.28374300	0.37647100
C	3.35907700	2.03699100	0.91463000
C	0.54414300	2.56453900	-2.19355800
H	-0.45302500	2.18698500	-2.46510900
H	0.53015200	3.66568300	-2.20736100
C	-0.28982500	2.65055100	0.54609400
H	-1.26896700	2.21297300	0.30112500
H	-0.06002400	2.42846800	1.59751100
H	-0.33256000	3.74137600	0.40375500
C	2.55254300	2.82167000	-0.11307400
C	4.27720400	-0.56029800	1.81602700
H	4.52189700	-1.59847300	1.54649200
H	5.19338000	-0.04879100	2.14996800
H	3.54719100	-0.57625300	2.63800200
H	4.34924200	2.49078600	1.08432800
H	2.83917100	2.01119400	1.88708600
C	-6.01574800	0.02604700	-0.11685200
H	-6.40234500	-0.54523900	0.73595900
H	-6.60152400	0.94202000	-0.27678600
H	-6.00587800	-0.58177900	-1.03095700
Co	1.41469400	-0.37198600	-0.41780600
H	1.29887900	-3.13741600	1.58140900
H	0.47626600	-4.21231900	0.33718300
H	3.33849700	-2.97085300	0.08420500
H	2.51478800	-4.04250800	-1.16482000
C	4.90270400	0.32147100	-0.84899000
H	5.81608900	0.76138900	-0.41928500
H	5.11611300	-0.70643300	-1.17970000
H	4.59226400	0.90753600	-1.72668200
H	3.11716900	2.91883000	-1.05560800
H	2.32803600	3.84202400	0.23691700
H	1.27181200	2.19820500	-2.93263200
C	0.47838300	-0.34152300	2.36185500
H	1.10408500	-1.18711200	2.69550400
H	1.09508500	0.56623400	2.47525500
H	-0.36853000	-0.25905800	3.06500800

TS3-Co

C	2.71548100	0.64917000	1.61903500
C	1.44319800	0.80790900	0.81413500
C	0.21361500	0.45789600	1.18118600
C	3.31633300	1.63824400	-0.40780000
C	1.81894000	1.32209200	-0.55882600
C	-1.48206100	2.06284200	-0.55964900
C	-2.67395400	2.54306600	-1.06012300
C	-1.88895600	2.18742500	0.96412900
Co	-1.51019700	0.38532500	0.50522100
P	-3.66844600	-0.49189600	0.33400900
P	-0.95393100	-1.27402500	-0.87843500
C	-2.35604000	-2.47045800	-1.04141300
C	0.48090600	-2.34580600	-0.56252600
C	-0.72445600	-0.69687500	-2.59436500
C	-5.27016800	0.36966500	0.18523200
C	-3.68019600	-1.71915000	-1.04062300
C	-3.91605500	-1.52749700	1.82212000
C	1.03244200	2.45247000	-1.13375300
C	-0.27988000	2.73232100	-1.12526500
H	2.77258800	-0.28807600	2.18890900
H	2.86411000	1.48109400	2.32991900
H	3.46431800	2.66623800	-0.03809700
H	3.88400500	1.52670700	-1.34124200
H	1.75077600	0.47540100	-1.26984200
H	-2.22763000	-3.08171300	-1.94932000
H	-2.29516100	-3.15175800	-0.17617700
H	0.50131600	-3.17606300	-1.28542300
H	1.41893200	-1.77799900	-0.64489700
H	0.40913400	-2.75694900	0.45555500
H	-1.63277900	-0.17418600	-2.92826800
H	0.11588800	0.00891400	-2.64450100
H	-0.52683500	-1.54900800	-3.26306100
H	-6.09764800	-0.34829300	0.29590500
H	-5.35680700	1.13427000	0.97232100

H	-5.35868200	0.85580600	-0.79748200
H	-3.81295700	-1.15097400	-1.97667600
H	-4.54201500	-2.39895100	-0.94139100
H	-4.83061500	-2.13440200	1.73289300
H	-3.05166900	-2.19254100	1.96306500
H	-3.99864600	-0.87582700	2.70505100
H	1.63781100	3.16230400	-1.71271900
H	-0.54884900	3.62733600	-1.70184200
H	-3.63615200	2.13490200	-0.75092100
H	-2.70338300	3.37533200	-1.77792600
H	-2.92968200	2.41908900	1.23576400
H	-1.20092300	2.90523000	1.43395500
C	-0.16576000	-0.17396600	2.49155100
H	-1.23366300	-0.51788200	2.50336700
H	0.42887500	-1.07645300	2.71086900
H	-0.08611300	0.53020200	3.33484600
N	3.79671200	0.71936500	0.62663300
S	4.34867500	-0.76069400	0.04729200
O	3.74089500	-1.09201700	-1.24865000
O	4.23042100	-1.72657400	1.13783600
C	6.05708500	-0.42040900	-0.24127400
H	6.52544000	-0.15806900	0.71537400
H	6.49332800	-1.33971800	-0.65624300
H	6.14552100	0.40171700	-0.96356100

TS4-Co-t

C	-2.55101700	-0.09151400	-2.02083700
C	-2.06973900	1.88989600	-0.83395000
C	-0.69270900	1.41250000	-1.29965700
C	0.41378700	1.82519200	-0.44623000
C	1.66849400	2.27967300	-1.03152500
C	2.66012800	2.84299800	-0.32731700
H	-2.59030000	0.36886700	-3.02253100
H	-3.14314100	-1.01422100	-2.03379500
H	-2.32712500	2.79317200	-1.40871300
H	-2.04449800	2.15602200	0.22954300
H	-0.50727900	1.63938000	-2.35856400
H	0.16942900	2.20008400	0.55184100
H	1.79679400	2.15244400	-2.11453700
P	2.67325100	-1.31427700	-0.42621800
P	0.33958600	-0.63446700	1.67120100
C	-1.13628700	-0.36916200	-1.61655400
C	-0.43978800	-1.44730700	-1.41108700
C	1.92782300	-1.38767200	2.23698600
H	2.60920200	-0.55447600	2.47799400
C	2.52069700	-2.26643400	1.14070000
H	1.86273700	-3.12570600	0.92742100
Co	0.67142900	-0.13385500	-0.57906200
H	1.76739400	-1.95731800	3.16683700
H	3.50500600	-2.67151200	1.42694800
C	3.15386900	3.24484000	0.98591500
H	3.43431400	2.46111800	1.70189400
H	2.75433000	4.15358000	1.45290200
C	4.00394600	3.40296600	-0.27470800
H	4.86216100	2.73143700	-0.40400100
H	4.17224700	4.42007600	-0.64973700
C	-0.87923300	-1.95370300	1.99784800
H	-0.93316800	-2.17962800	3.07432200
H	-1.86864100	-1.63602400	1.64160200
H	-0.58830800	-2.86349200	1.45275500
C	-0.02640600	0.61743000	2.94198100
H	0.69492200	1.44486000	2.86834800
H	-1.04048800	1.00489900	2.76517100
H	0.02315100	0.18132300	3.95201400
C	4.18445400	-0.31863600	-0.20239800
H	5.04233500	-0.96826900	0.03208400
H	4.39122500	0.23805300	-1.12798300
H	4.03770500	0.40205900	0.61464700
C	3.13603600	-2.54659900	-1.68094200
H	4.05605000	-3.07599200	-1.38829900
H	2.32167200	-3.27440900	-1.80414600
H	3.30091800	-2.03840400	-2.64295600
C	-0.59016800	-2.90158000	-1.59851900
H	-1.64466800	-3.18353300	-1.75886700
H	-0.01467000	-3.23266600	-2.47816300

H	-0.20643600	-3.46609200	-0.73615600
N	-3.07679600	0.85841100	-1.05884300
S	-3.81658300	0.21036000	0.31185800
O	-4.02786500	-1.21770400	0.07769000
O	-3.09288200	0.63046500	1.51551300
C	-5.38218600	1.02293100	0.31601900
H	-5.21578700	2.10618300	0.38375000
H	-5.91217600	0.76127600	-0.60857000
H	-5.92739500	0.66049700	1.19906400

INT0-Ni

C	2.44792300	-0.17145000	-1.74197700
C	1.35040900	-2.04606900	-0.56339200
C	0.06573200	-1.44638900	-1.08339600
C	-1.11506000	-1.39600200	-0.30250700
C	-2.42914400	-1.51035100	-0.93864500
C	-3.53448900	-1.98398900	-0.36131000
H	2.30974800	-0.71512400	-2.69135500
H	3.40681500	0.36128900	-1.80112200
H	1.56470800	-2.98030800	-1.11180100
H	1.22481300	-2.30845200	0.49590600
H	-0.07183100	-1.55612300	-2.16813800
H	-1.06187800	-1.71480000	0.74688200
H	-2.48843800	-1.20174600	-1.99087800
P	-1.60731800	1.58227600	0.68656500
C	1.33145400	0.75530000	-1.48131000
C	0.76009700	1.87339300	-1.28106400
C	-2.54971100	2.98199100	-0.02132100
H	-3.26167200	2.59064700	-0.76436200
H	-3.10559700	3.52658500	0.75831800
C	-4.17033100	-2.54812000	0.82802700
H	-4.38351200	-1.89463300	1.68345800
H	-3.94625500	-3.58539300	1.10729900
C	-4.95484700	-2.31059800	-0.46242100
H	-5.68940400	-1.49499300	-0.46677600
H	-5.26364500	-3.18774900	-1.04488300
C	-0.58871200	2.36480300	1.99122700
H	-1.20787900	2.92436900	2.71028300
H	-0.03274300	1.57696800	2.52158400
H	0.14748000	3.04462700	1.53908500
C	-2.89779400	0.75993000	1.68795500
H	-3.66273300	0.33630200	1.02277000
H	-2.44667400	-0.05891400	2.26722000
H	-3.37188000	1.47383700	2.37984000
C	0.79561200	3.34299400	-1.39469600
H	1.75363900	3.69035200	-1.81469300
H	-0.01386500	3.71472600	-2.04329500
H	0.66331200	3.82715600	-0.41464700
N	2.53392500	-1.17832600	-0.68504300
S	3.18073600	-0.64190200	0.76726100
O	2.15936100	-0.53811200	1.81345800
O	4.01275500	0.52209000	0.46878800
C	4.24212900	-1.98898500	1.21028800
H	3.64559600	-2.90568900	1.30826700
H	5.00752900	-2.09988400	0.43209600
H	4.69774000	-1.72947500	2.17630300
H	-1.86920900	3.67700300	-0.53272100
Ni	-0.32000600	0.41226500	-0.60195400

INT1-Ni

C	1.25417100	1.37860100	1.50438900
C	1.34084100	1.96941400	-0.92941600
C	-0.14851400	1.78340500	-1.03105100
C	-0.73693200	0.86230900	-1.90862000
C	-2.12584000	0.50882200	-1.72520000
C	-2.83559400	1.05649400	-0.65018900
H	1.14472900	2.44982200	1.75305900
H	1.89479600	0.92887700	2.27595900
H	1.58357400	3.04344200	-0.84839700
H	1.83745200	1.57622600	-1.82684700
H	-0.76283600	2.58818100	-0.61644200
H	-0.13185900	0.29869200	-2.62589600
H	-2.55046700	-0.30105900	-2.32832800
P	-0.56283400	-2.03361300	-0.23488600
C	-0.07707700	0.73492500	1.51069400
C	-1.18700900	0.30394200	1.91884900

C	0.36749800	-2.72251100	1.18171200
H	-0.18550700	-2.52841900	2.11356500
H	0.52492900	-3.80796000	1.07601500
C	-3.31866800	2.36787500	-0.16534700
H	-3.47125100	3.17744400	-0.88989000
H	-3.01563900	2.71407300	0.83081400
C	-4.24826800	1.16621300	-0.25308000
H	-5.02465000	1.17469800	-1.02855900
H	-4.57127000	0.70791900	0.68953200
N	1.93151900	1.28003700	0.22355000
S	3.13073200	0.17412100	0.00186900
O	3.03642800	-0.37424100	-1.35234200
O	3.13049300	-0.73097400	1.15271700
C	4.63573300	1.10770900	0.06901100
H	4.71114800	1.58303200	1.05581100
H	5.46662300	0.40522300	-0.08644700
H	4.61960400	1.86252900	-0.72861200
C	0.42328400	-2.62496800	-1.66242400
H	0.60781300	-3.71097100	-1.61842800
H	-0.11278900	-2.39454700	-2.59655800
H	1.38359000	-2.08643900	-1.67433700
C	-2.01664200	-3.15430800	-0.30905900
H	-1.72619600	-4.21737100	-0.34414500
H	-2.65148200	-2.98261000	0.57400600
H	-2.61511300	-2.91687700	-1.20245100
C	-2.23776300	-0.03664000	2.88294000
H	-2.51719800	-1.10015800	2.80964000
H	-1.91540700	0.16286100	3.91833800
H	-3.15384600	0.54566300	2.69231600
H	1.34143800	-2.21361200	1.24933500
Ni	-1.06252500	0.15833500	-0.06059900

INT2-Ni

N	-2.97967600	0.07402800	0.32447300
C	-2.15968200	-1.14348400	0.32366000
C	-0.81071400	-0.61893000	-0.10623200
C	0.30731600	-1.23929400	-0.54592000
C	-2.34616800	1.17731900	-0.39432700
C	-0.85863700	0.89396800	-0.15979600
C	0.08405400	1.29960100	-1.27336300
C	1.25662600	2.06206300	-1.21621400
S	-4.61495400	-0.03769000	0.41323700
O	-4.91939000	-1.09903600	1.36862300
O	-5.13038400	1.31300700	0.61838900
H	-2.16517300	-1.59281800	1.33031600
H	-2.54131500	-1.90917100	-0.37901600
H	-2.56954400	1.14829400	-1.47956800
H	-2.68940300	2.13905400	0.00820300
H	-0.55817700	1.35140300	0.79984400
H	1.68957800	2.37869000	-2.17457500
C	2.11427900	2.03507300	-0.09315100
H	-0.32557800	1.12544600	-2.27552300
C	3.15348200	2.96098600	0.39442700
C	2.02871700	2.51830000	1.31133600
P	3.27943200	-0.92371400	0.26572900
C	4.85131400	-0.07498000	0.64997900
C	2.89265100	-1.72102000	1.86262300
H	2.66841600	-0.93790200	2.60287800
H	2.00369400	-2.35926800	1.76500700
H	3.74129500	-2.32406500	2.22171300
H	5.61012800	-0.80178800	0.98029700
H	4.69716500	0.66013000	1.45283300
C	-5.17657000	-0.58295700	-1.18343200
H	-4.90136700	0.16449400	-1.93944900
H	-4.72967000	-1.55983900	-1.41210800
H	-6.27005800	-0.67354600	-1.12197600
H	4.15855000	2.58574100	0.60753600
H	3.13216400	3.99275600	0.02539900
H	2.27816800	1.82820100	2.12508100
H	1.25158500	3.24730800	1.56606200
C	3.86261900	-2.28506000	-0.80296000
H	4.24714400	-1.85621500	-1.74096900
H	4.66708600	-2.85393400	-0.31080700
H	3.03428000	-2.96192100	-1.04905600
C	0.35334300	-2.72849400	-0.69757200

H	1.02836900	-3.20799900	0.03220100
H	-0.63518000	-3.20831800	-0.58009300
H	0.73930300	-3.01308500	-1.69182200
Ni	1.63593800	0.18211400	-0.58207100
H	5.22021900	0.44938400	-0.24388300

INT3-Ni

N	-2.73231800	-1.26070200	0.24958000
C	-1.84357000	-1.31082700	1.42338400
C	-0.47410600	-1.07334600	0.83974400
C	0.56218900	-0.38973700	1.34338600
C	-1.99293700	-1.95930000	-0.80969100
C	-0.50304700	-1.62795000	-0.58945000
C	0.40408100	-2.81127700	-0.77955600
C	1.73257300	-2.83613700	-0.55951500
S	-3.26600300	0.27856900	-0.17167800
O	-3.32551700	1.08429300	1.04890900
O	-2.53490300	0.80761100	-1.32914000
H	-2.15362700	-0.57727300	2.17731500
H	-1.96100100	-2.31987200	1.85899000
H	-2.17828700	-3.03788900	-0.67833600
H	-2.36193900	-1.67081400	-1.80229700
H	-0.20739200	-0.81623600	-1.27833700
H	2.24471000	-3.80176100	-0.68745900
C	2.55245300	-1.71017800	-0.10240100
H	-0.07481400	-3.74821100	-1.09176000
C	4.02126200	-1.87494400	0.10242300
C	3.53821400	-0.97853600	-1.00450300
P	1.26660400	2.09732600	-0.23502600
C	0.51332500	2.19484600	-1.89900500
C	-0.02399700	2.85781700	0.80750700
H	0.35516600	3.01440700	1.82765500
H	-0.33034800	3.82891000	0.38773500
H	-0.90050700	2.19457200	0.85229400
H	0.29579000	3.23930700	-2.17508600
H	-0.42766700	1.62292600	-1.88984200
C	-4.91861400	-0.05571800	-0.70411100
H	-5.47862600	-0.47380500	0.14148600
H	-5.34895100	0.90223800	-1.02780500
H	-4.88884000	-0.76277800	-1.54360600
H	4.51149500	-1.40089500	0.95959800
H	4.47245200	-2.83110800	-0.19457100
H	3.66192400	0.12563300	-0.83864700
H	3.64984400	-1.24815200	-2.05910500
C	2.56237200	3.38909600	-0.28918200
H	2.14480300	4.37025900	-0.56612100
H	3.04315300	3.46757000	0.69806000
H	3.33121900	3.10453000	-1.02395400
C	0.62817000	0.07080100	2.76738400
H	1.03871800	1.08921100	2.85778200
H	-0.35244500	0.05221800	3.27645800
H	1.30693800	-0.58085800	3.34573700
H	1.19628400	1.75644200	-2.64233200
Ni	1.93315400	0.03451600	0.16445300

INT4-Ni

N	-2.81474600	0.52267800	0.53751300
C	-2.29686200	1.62669200	-0.29349700
C	-0.80560400	1.62945600	-0.04061700
C	0.06875200	2.60579900	-0.33129900
C	-1.76923000	0.15950900	1.50348200
C	-0.47737100	0.37306000	0.71729300
C	0.81699700	0.42591300	1.48315500
C	1.73585600	1.48464600	1.23421300
S	-3.51360900	-0.76469400	-0.27258700
O	-4.11629500	-0.23223400	-1.49306600
O	-2.59280300	-1.90211300	-0.38277400
H	-2.57010200	1.46337700	-1.34709100
H	-2.76872800	2.57221500	0.02060700
H	-1.82854400	0.84208600	2.36828700
H	-1.90173900	-0.87030000	1.86193300
H	-0.45766000	-0.45564000	-0.01831200
H	2.39171800	1.83309800	2.04448600
P	2.13204700	-2.18456100	-0.29973600
H	0.79218400	-0.02274800	2.48732800
C	2.41370400	3.65989500	0.05833600

C	2.58960400	2.56383200	-0.93967700
C	3.59023000	-3.26145600	-0.00880100
H	3.82831000	-3.26797300	1.06605300
H	3.41220300	-4.29564700	-0.34550800
C	0.79433500	-3.14185100	0.51233500
H	0.92133600	-3.09109200	1.60442000
H	-0.18590700	-2.71017900	0.25516700
H	0.81157600	-4.19756500	0.19594600
C	1.78197400	-2.51337700	-2.07259700
C	-4.80429900	-1.23699500	0.84053400
H	-5.49759700	-0.39350900	0.94670100
H	-5.30581800	-2.10515700	0.39074300
H	-4.36656100	-1.51217700	1.80920200
H	2.02213300	4.61635700	-0.29710000
H	3.14950500	3.74952100	0.86310100
H	2.29554200	2.75220900	-1.97708700
H	3.44123800	1.88410000	-0.82244100
H	2.58351400	-2.08071000	-2.69115600
H	1.70456300	-3.59229800	-2.28386300
H	4.45956200	-2.85227300	-0.54671600
C	1.49216400	2.46860400	0.12209400
C	-0.33833800	3.83794000	-1.08145900
H	-1.35972700	3.76034300	-1.47822300
H	-0.29251600	4.73421300	-0.43999700
H	0.32867000	4.02998200	-1.93867200
H	0.83530800	-2.02460200	-2.35058100
Ni	2.22925400	-0.15843200	0.37512000

TS1-Ni

C	1.33684400	1.86845100	1.08357500
C	1.32418700	1.70567800	-1.30581600
C	-0.15231300	1.57396100	-0.99009000
C	-0.95593000	0.72041100	-1.84976600
C	-2.36259400	0.63659900	-1.63412300
C	-2.86706500	1.21112000	-0.45241600
H	1.21376600	2.96589600	1.09311300
H	1.87334800	1.57704100	1.99582500
H	1.53382000	2.70482200	-1.72237100
H	1.62909300	0.95574600	-2.04675300
H	-0.63443900	2.52565000	-0.73446400
H	-0.48351500	0.15943700	-2.66177100
H	-2.96617200	-0.03194900	-2.25868400
P	-0.72125100	-2.15130700	-0.12030800
C	0.02681000	1.16978000	0.98958000
C	-0.80674700	0.46167700	1.68655400
C	0.50270400	-2.70426000	1.12338500
H	0.08032600	-2.58229700	2.13190200
H	0.77565600	-3.76167600	0.97723900
C	-3.06843400	2.57619500	0.08878800
H	-3.12141000	3.41802200	-0.61229700
H	-2.63364500	2.83296300	1.06232200
C	-4.20475500	1.56798600	0.05173000
H	-5.01944400	1.73865300	-0.66345000
H	-4.53558800	1.14859300	1.00899600
N	2.13045800	1.53437700	-0.09145900
S	3.09239500	0.16554000	-0.00378900
O	2.68747400	-0.81886800	-1.01127300
O	3.17138900	-0.24360900	1.39870600
C	4.67639500	0.78416300	-0.48821400
H	4.98317100	1.55705800	0.22769100
H	5.37253200	-0.06630400	-0.47030100
H	4.60117100	1.19618800	-1.50326100
C	-0.00005500	-2.79435000	-1.67642200
H	0.19692900	-3.87733600	-1.62006300
H	-0.69125100	-2.59886800	-2.51082900
H	0.94409900	-2.26107600	-1.86254900
C	-2.10232800	-3.32467300	0.16608500
H	-1.76591100	-4.37440300	0.15406600
H	-2.56813000	-3.10303500	1.13856500
H	-2.86581400	-3.18008400	-0.61402200
C	-1.05337600	0.12605800	3.10446900
H	-1.11862000	-0.96424200	3.24765100
H	-0.27319900	0.52009300	3.77861000
H	-2.02409400	0.53376600	3.43394200
Ni	-1.28970300	-0.03730600	-0.07145800

H	1.40527000	-2.08072400	1.05378500

TS2-Ni

N	3.41139100	0.43050500	-0.70902200
C	2.47997400	1.53638100	-0.45546400
C	1.08833100	0.91913100	-0.46861300
C	-0.08986100	1.50091100	-0.17445800
C	2.66850200	-0.61538900	-1.41350200
C	1.26443900	-0.56803300	-0.81311100
C	0.20222200	-1.12749600	-1.69553900
C	-1.01128100	-1.58111800	-1.30244500
S	4.37028100	-0.08380800	0.56040000
O	4.56773100	1.05843500	1.45105600
O	3.88423500	-1.34716400	1.12290200
H	2.73636300	2.03147000	0.49200600
H	2.60098000	2.28785700	-1.25609000
H	2.64342200	-0.36004000	-2.48731300
H	3.16072100	-1.59086600	-1.30434600
H	1.29042200	-1.12404800	0.14023100
H	-1.70285100	-1.93234500	-2.07891200
C	-1.54584200	-1.48978900	0.05568100
H	0.41897100	-1.12507300	-2.77165200
C	-2.22231600	-2.59176700	0.78602400
C	-0.90954500	-2.03658100	1.29325300
P	-3.82978400	0.29254800	0.14393100
C	-4.82414400	-0.89323200	-0.81971700
C	-4.48094900	0.15979200	1.84267000
H	-4.23053900	-0.81837400	2.27764000
H	-4.01573500	0.94131700	2.46181000
H	-5.57469500	0.28861700	1.85266800
H	-5.90057700	-0.71175700	-0.67482800
H	-4.58608100	-1.92210700	-0.51471600
C	5.90243600	-0.42863100	-0.25657500
H	5.73883700	-1.19611300	-1.02474700
H	6.27600200	0.50112200	-0.70319600
H	6.59507200	-0.80226800	0.51062900
H	-3.11459400	-2.38651700	1.38467500
H	-2.21609900	-3.58574800	0.32451300
H	-0.94021100	-1.43193500	2.20536800
H	-0.01010000	-2.65233500	1.19028700
C	-4.46012100	1.91513400	-0.41151000
H	-4.21397200	2.05650400	-1.47477000
H	-5.55106900	1.99032500	-0.27682600
H	-3.96556500	2.71089200	0.16599100
C	-0.09900700	2.95238300	0.24207700
H	0.89804100	3.42120600	0.34696700
H	-0.67008300	3.56748100	-0.47736500
H	-0.62217500	3.08371600	1.20608000
Ni	-1.72199700	0.35278000	-0.10121900
H	-4.57879600	-0.77998700	-1.88647900

TS3-Ni

N	2.80880100	1.06869200	0.25733100
C	1.76086500	1.15660300	1.28401200
C	0.47481000	1.03110800	0.50541000
C	-0.75382400	0.70934000	0.95649700
C	2.25850400	1.74539000	-0.92011200
C	0.76198900	1.38417300	-0.93897400
C	-0.12098600	2.49779300	-1.42429300
C	-1.37195800	2.70321900	-0.98788400
S	3.47268000	-0.45269100	-0.00812300
O	3.04803400	-1.34842500	1.07006700
O	3.25890400	-0.86081000	-1.39836500
H	1.90289400	0.38151800	2.04837000
H	1.87068200	2.13965600	1.78017200
H	2.39478500	2.82933300	-0.77066200
H	2.79654300	1.45117200	-1.82894700
H	0.62391200	0.49303600	-1.58401300
H	-1.92187900	3.57567900	-1.36921700
C	-2.11530500	1.84140300	-0.04697700
H	0.29795600	3.18910400	-2.16542300
C	-3.22326900	2.43827900	0.75819600
C	-3.60842100	1.57394800	-0.40081900
P	-1.66353100	-2.10901500	-0.24500700
C	-0.00689100	-2.46053600	-0.94028800
C	-1.58004300	-2.97971800	1.36591300

H	-2.55479100	-2.91891000	1.87355700
H	-1.30404900	-4.03876800	1.23817100
H	-0.82739800	-2.48732100	1.99996500
H	0.20814500	-3.54141300	-0.93460000
H	0.76075400	-1.94093400	-0.34884500
C	5.20226600	-0.14464000	0.19718200
H	5.37289500	0.22010100	1.21799800
H	5.72253300	-1.09844500	0.03089900
H	5.51913200	0.60100500	-0.54346100
H	-3.40842000	2.04045200	1.76129700
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C	-1.01646300	0.59659300	2.43631600
H	-1.90401000	-0.01132800	2.67223400
H	-0.15736600	0.14120900	2.95902500
H	-1.17680400	1.59030400	2.88953700
H	0.04786300	-2.09188500	-1.97538900
Ni	-2.07869500	-0.01403500	-0.10333000

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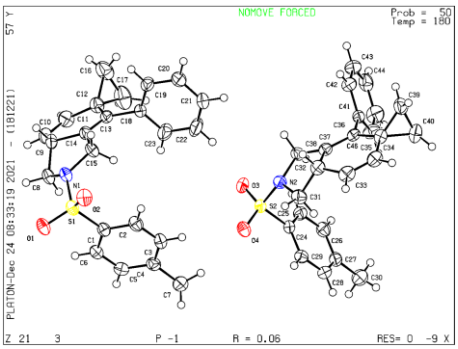
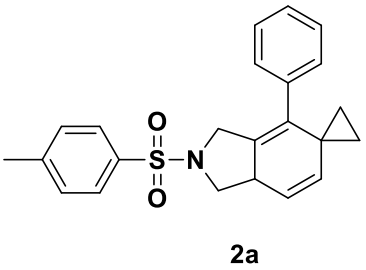
8. NMR Spectra and Crystal Structures of New Compounds

X-Ray Data of 2a





2a

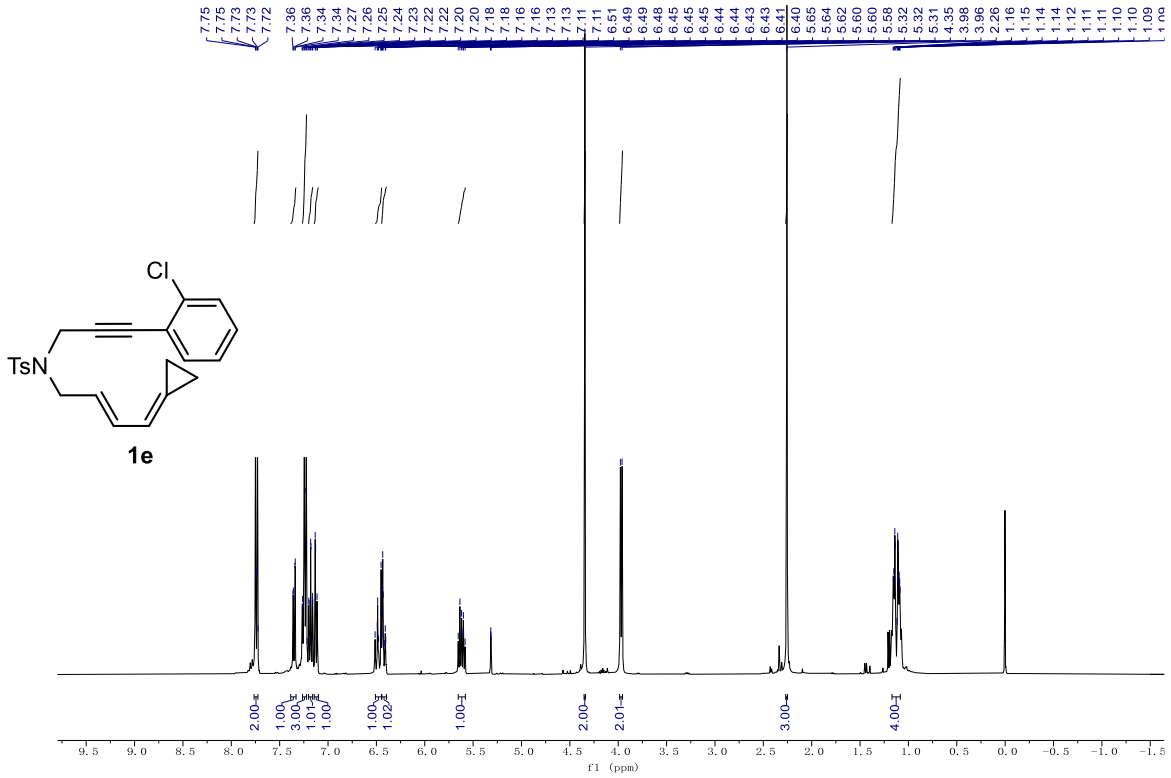
Ellipsoids are drawn at 50% probability

CCDC 2307636

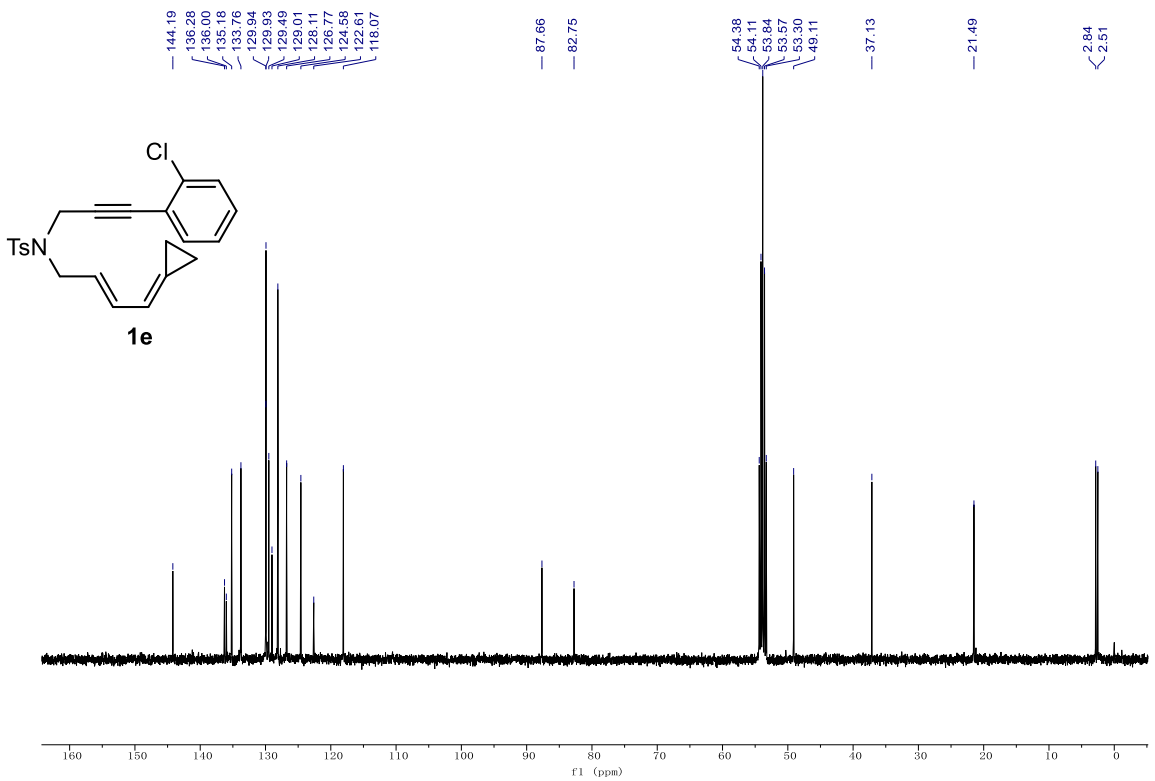
Chemical formula	$C_{23}H_{23}NO_2S$
***M*$_r$**	377.48
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	180
***a*, *b*, *c* (Å)**	8.4565 (3), 15.3620 (4), 15.8074 (4)
α, β, γ (°)	102.544 (2), 92.621 (2), 97.581 (2)
***V* (Å^3)**	1981.10 (10)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.18
Crystal size (mm)	0.11 × 0.05 × 0.03
Refinement	
R*[F^2 > 2σ(F^2)], *wR*(F^2), *S	0.055, 0.137, 1.02
No. of reflections	10429
No. of parameters	489
H-atom treatment	H-atom parameters constrained
Δρ$_{max}$, Δρ$_{min}$ (e Å^{-3})	0.35, −0.29

1e

^{1}H NMR (400 MHz, Methylene Chloride-d2)

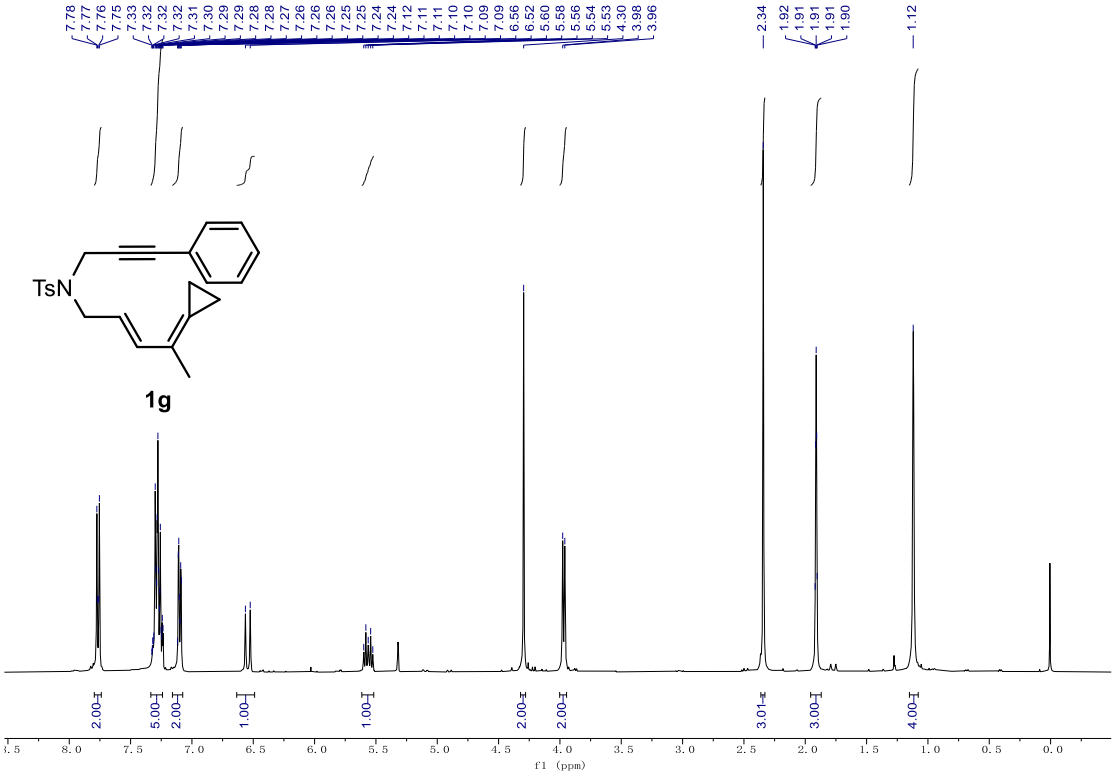


^{13}C NMR (101 MHz, Methylene Chloride-d2)

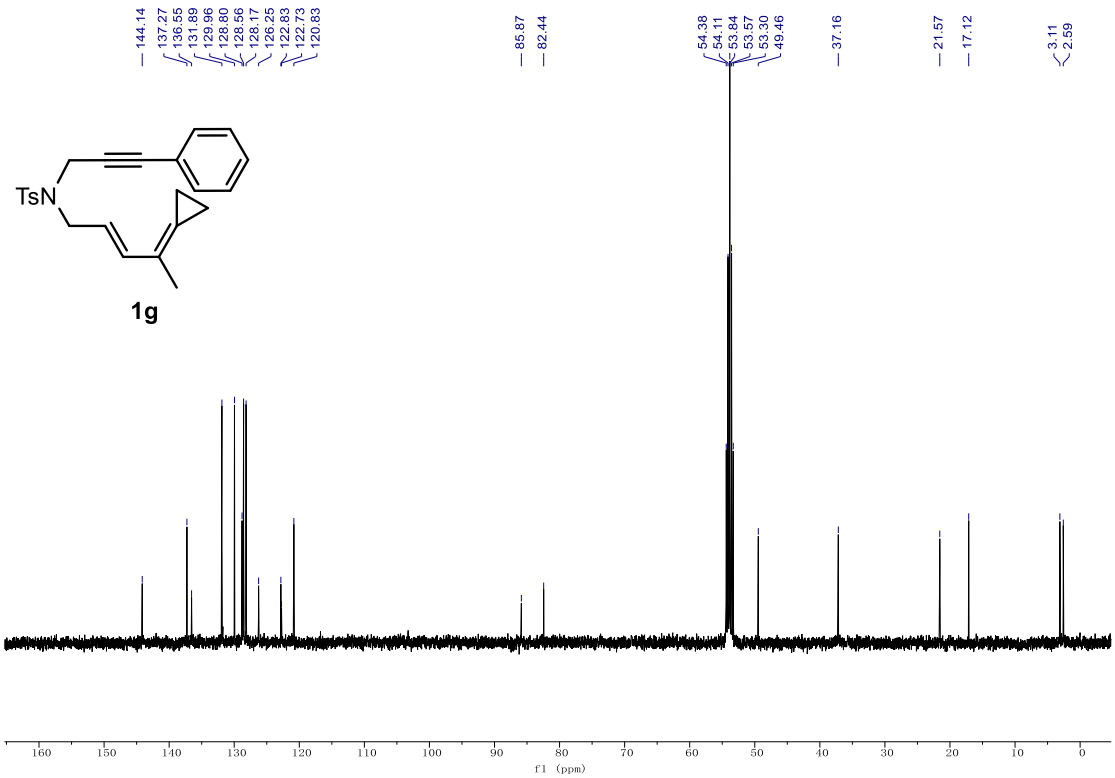


1g

^{1}H NMR (400 MHz, Methylene Chloride-d2)

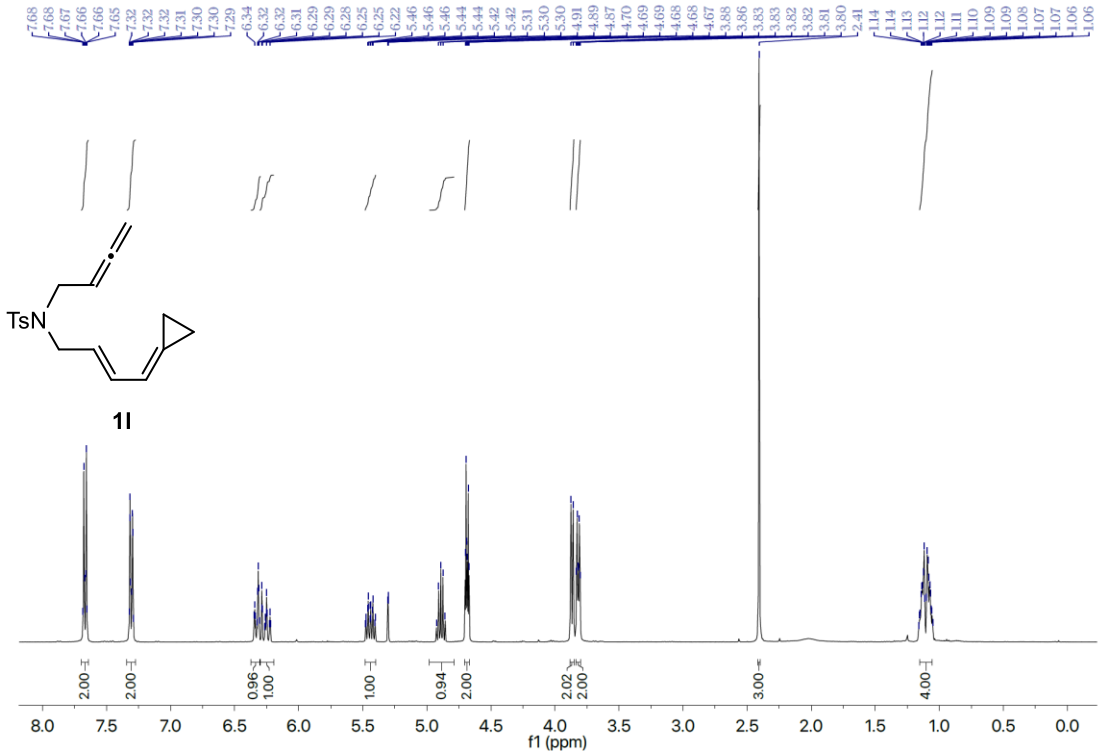


^{13}C NMR (101 MHz, Methylene Chloride-d2)

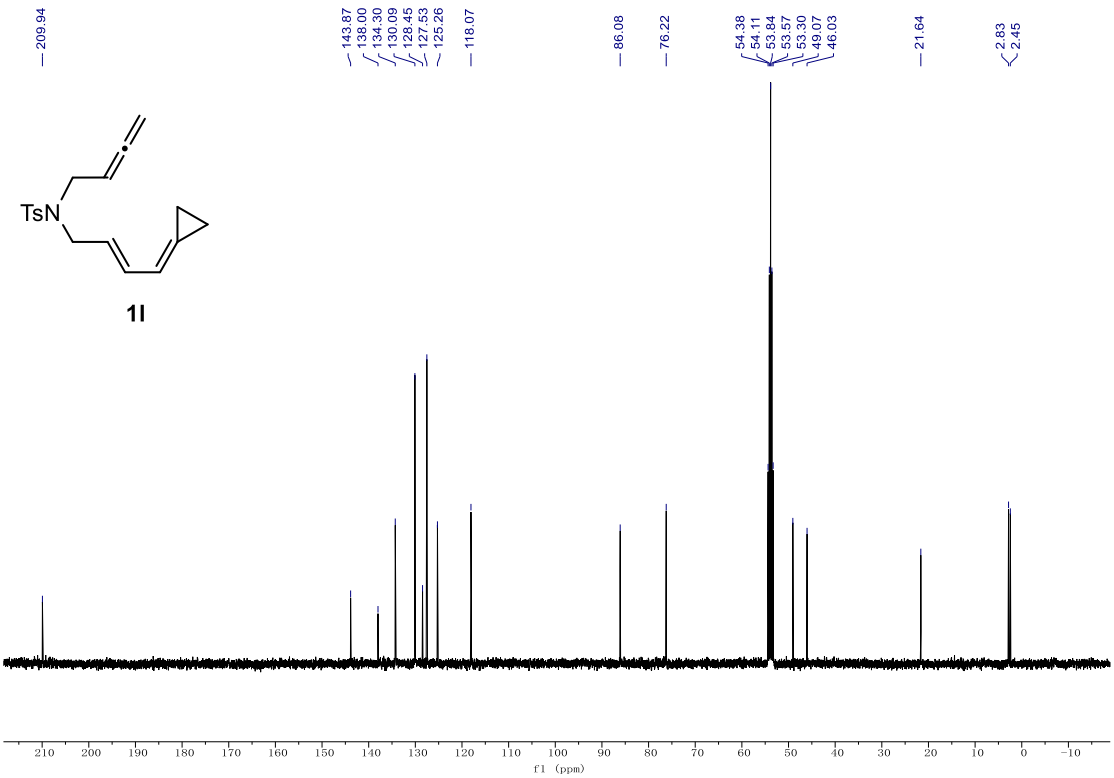


1l

^{1}H NMR (400 MHz, Methylene Chloride-d2)

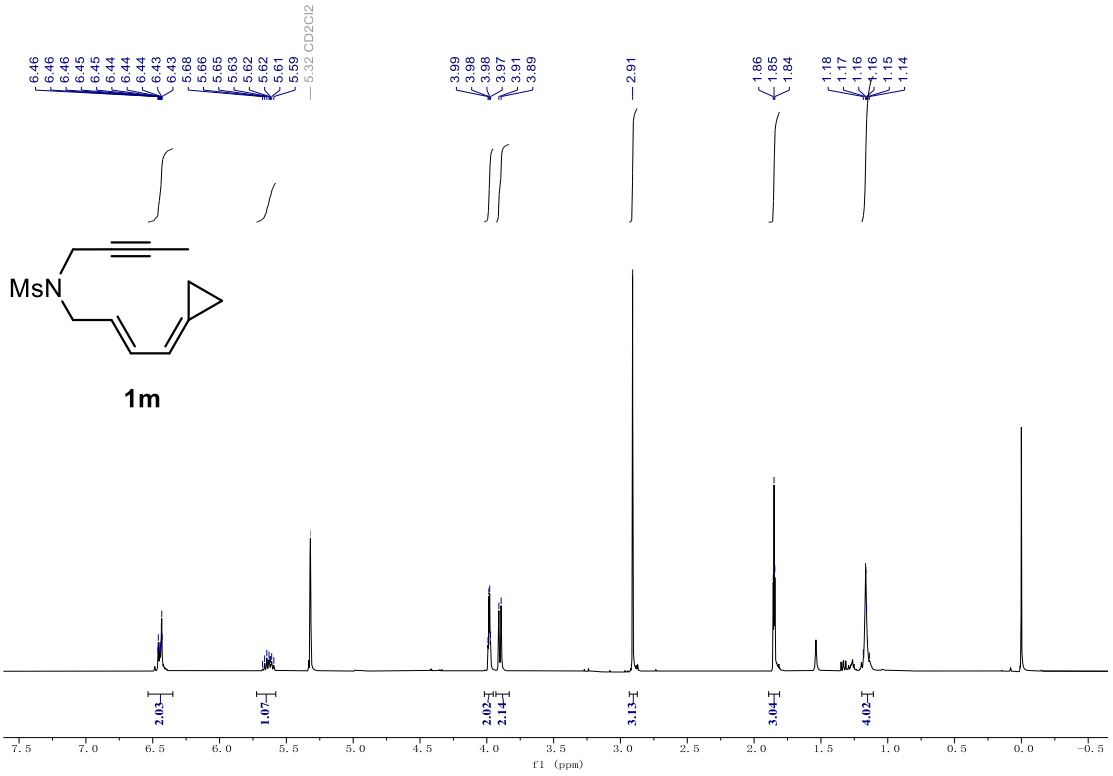


^{13}C NMR (101 MHz, Methylene Chloride-d2)

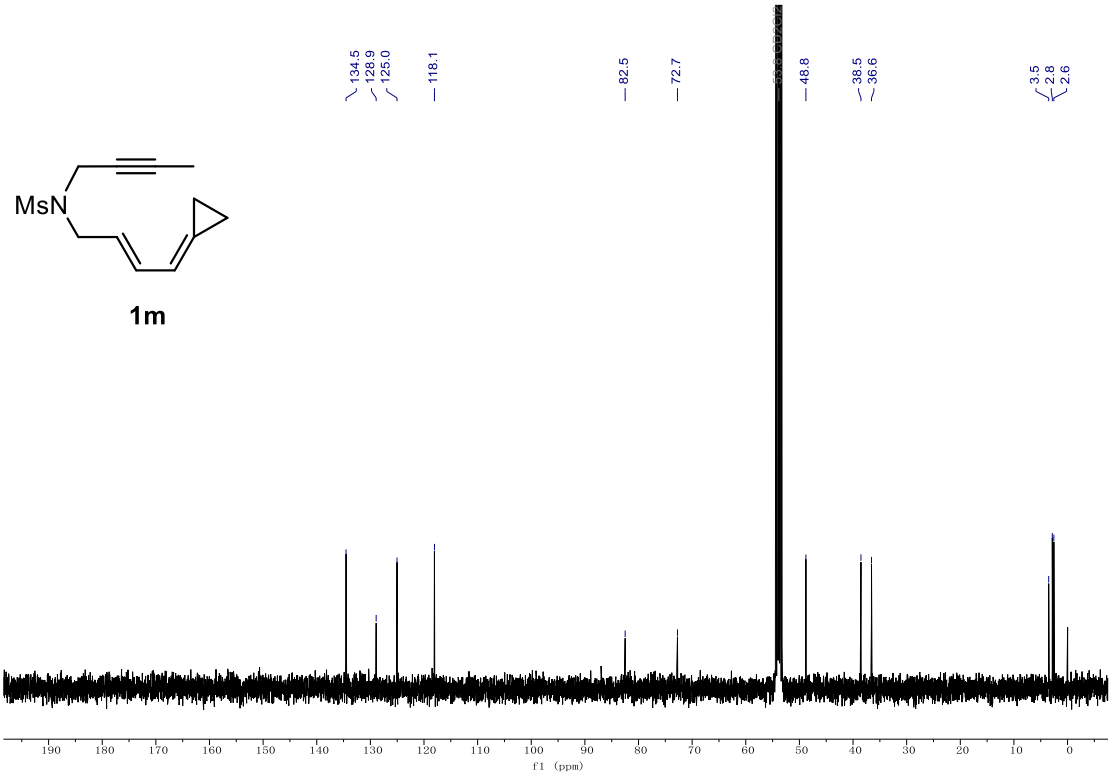


1m

^{1}H NMR (400 MHz, Methylene Chloride-d2)



^{13}C NMR (101 MHz, Methylene Chloride-d2)



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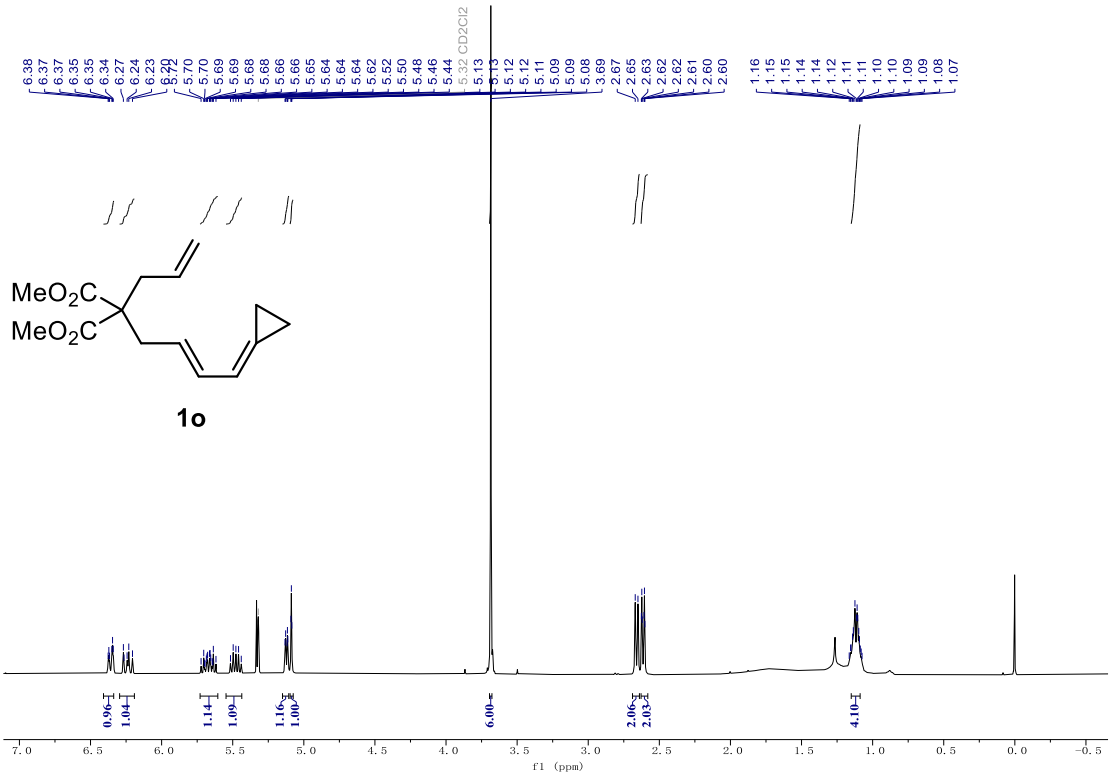
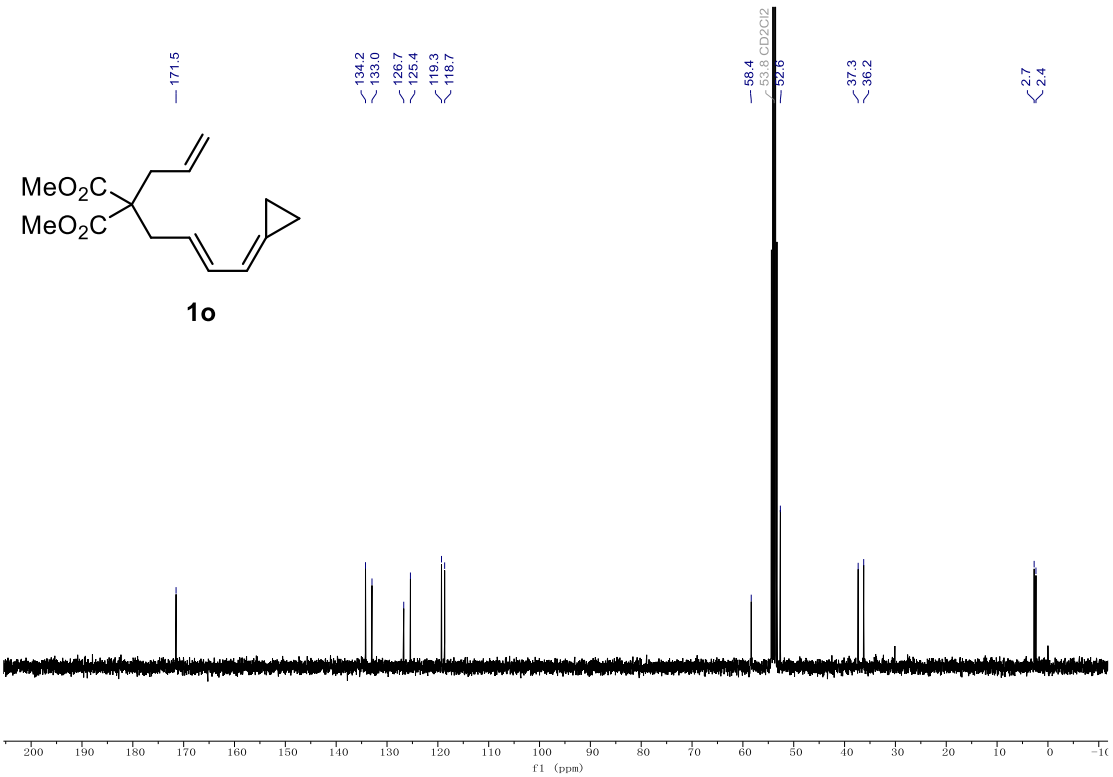
^{1}H NMR (400 MHz, Methylene Chloride-d2)



^{13}C NMR (101 MHz, Methylene Chloride-d2)



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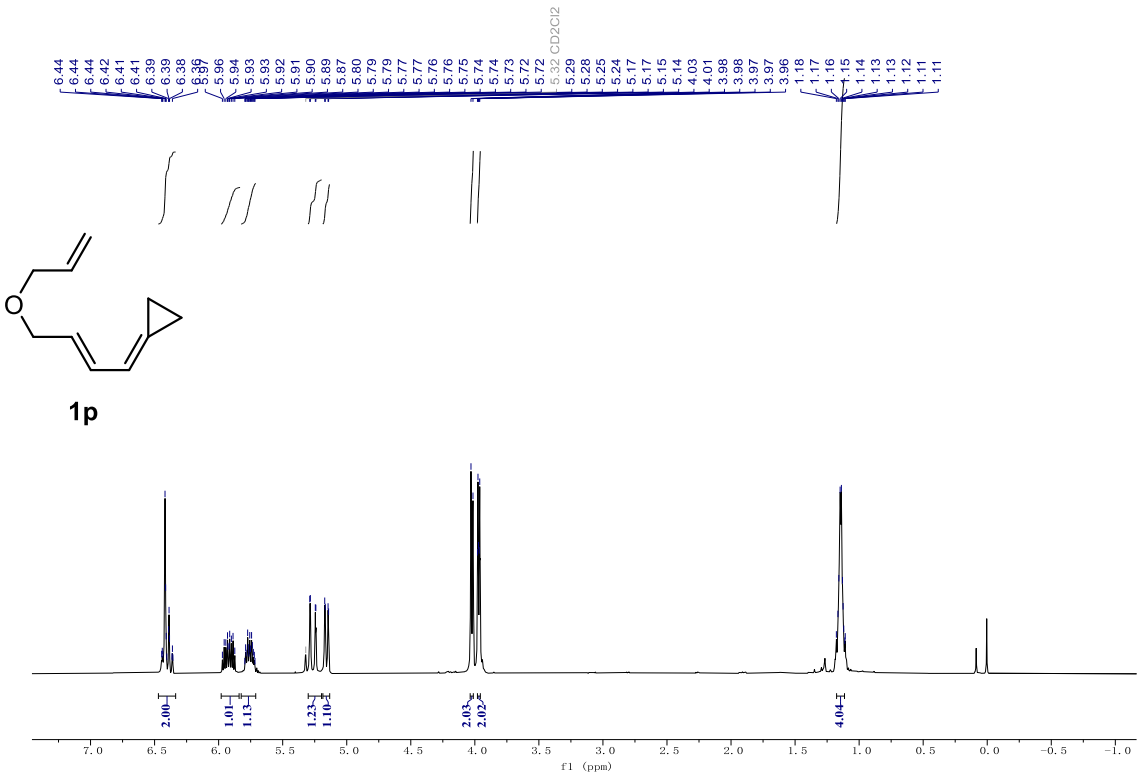
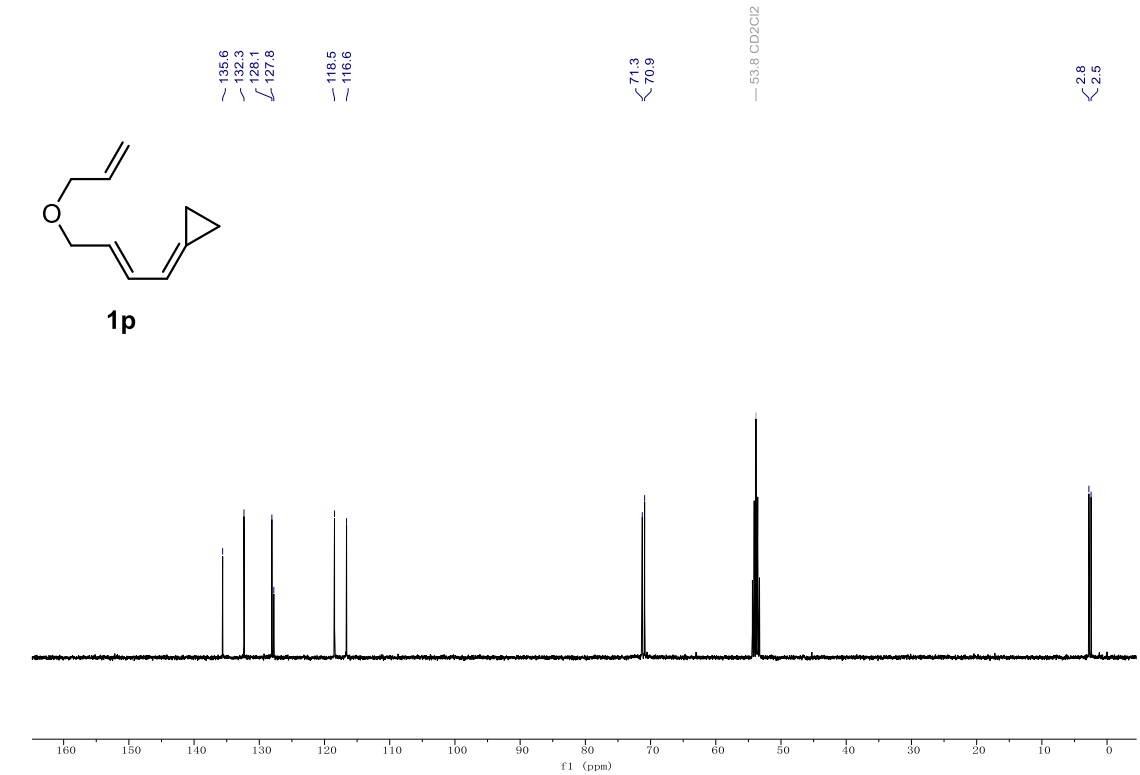
^{1}H NMR (400 MHz, Methylene Chloride-d2)

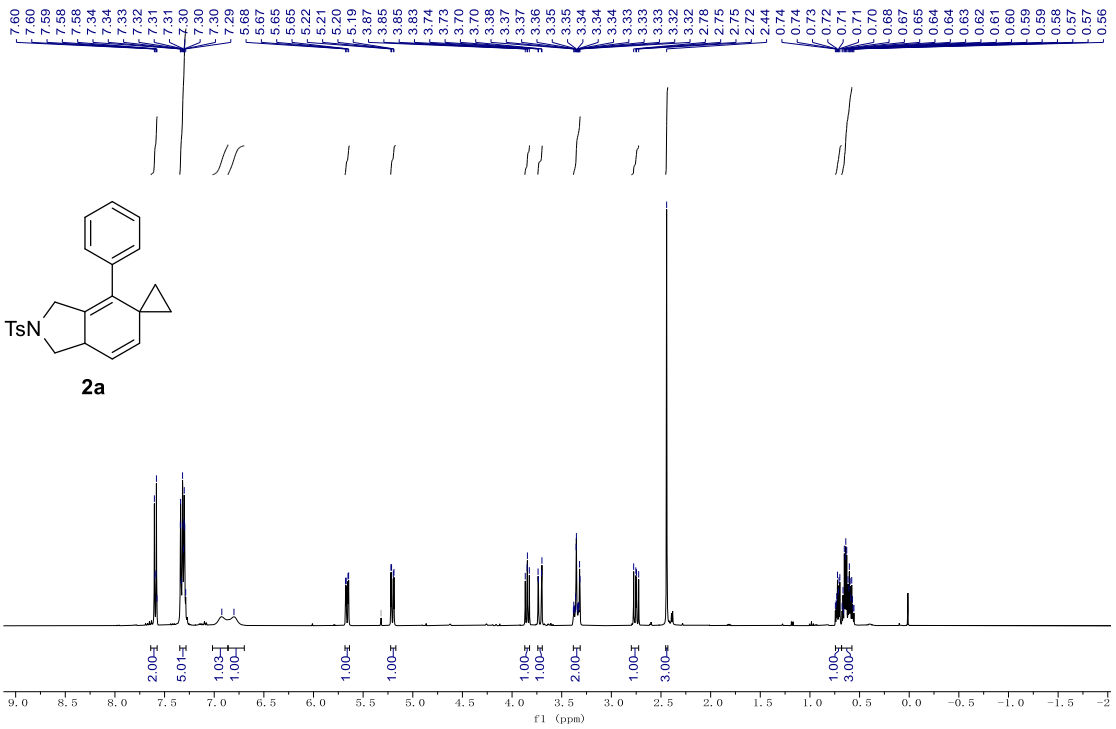


^{13}C NMR (101 MHz, Methylene Chloride-d2)

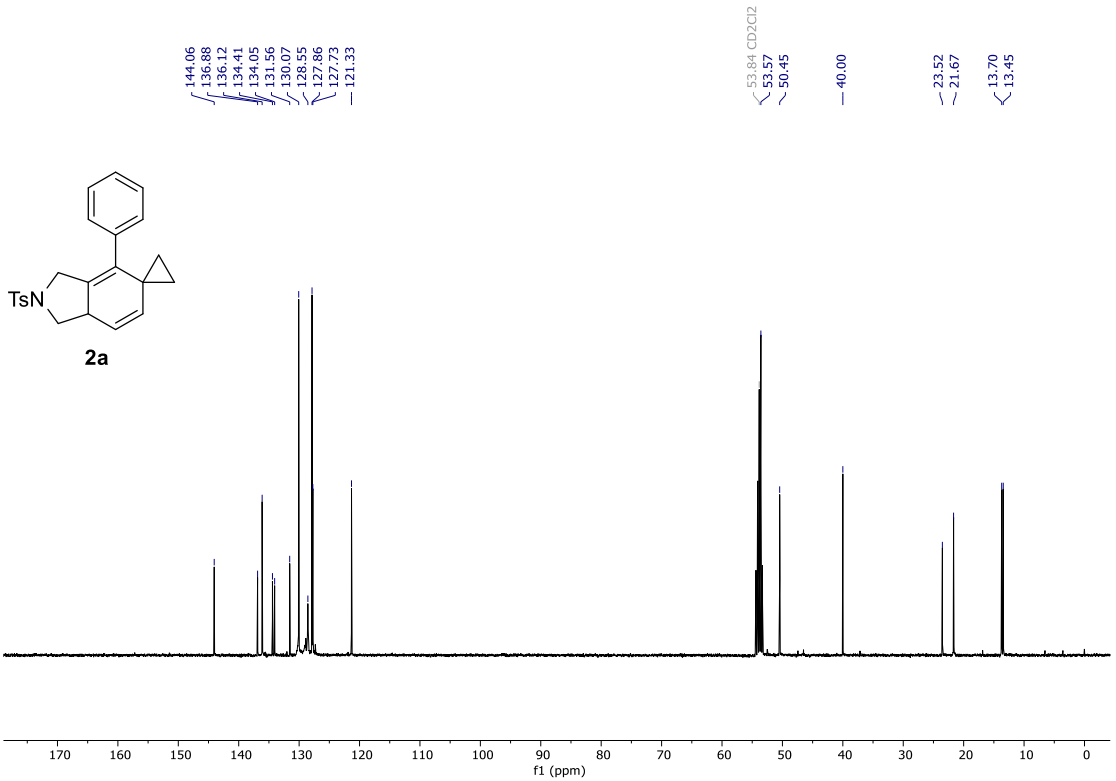


2a

^{1}H NMR (400 MHz, Methylene Chloride-d2)

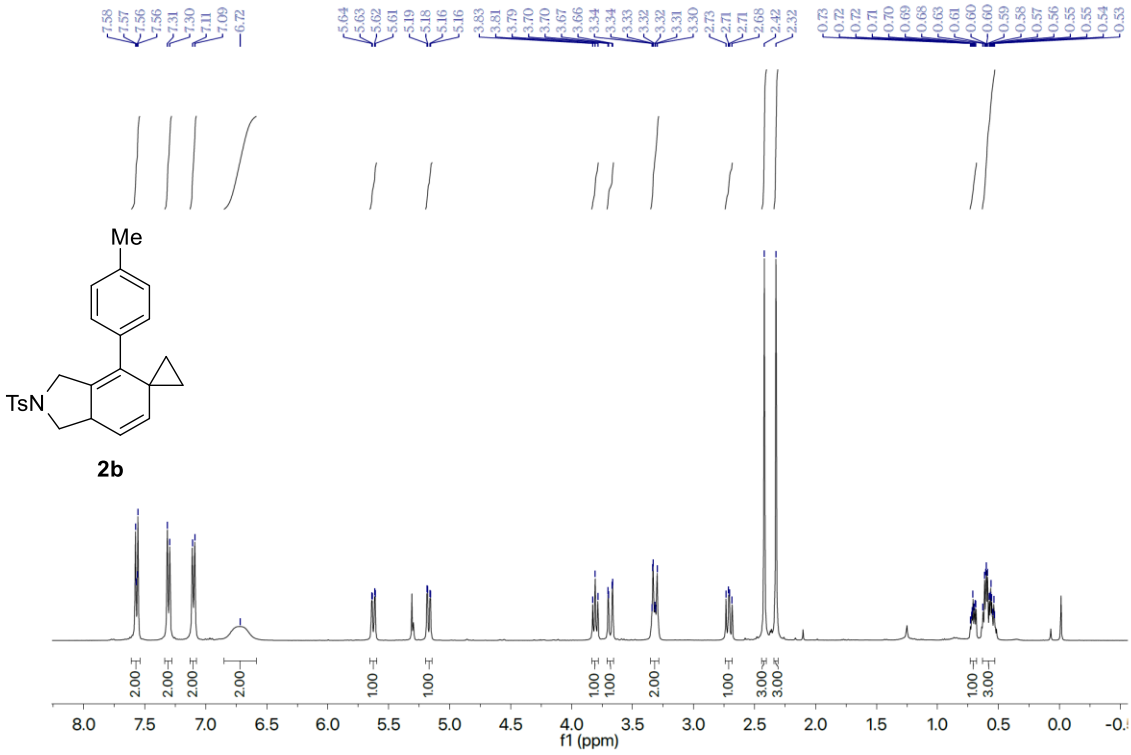


^{13}C NMR (101 MHz, Methylene Chloride-d2)

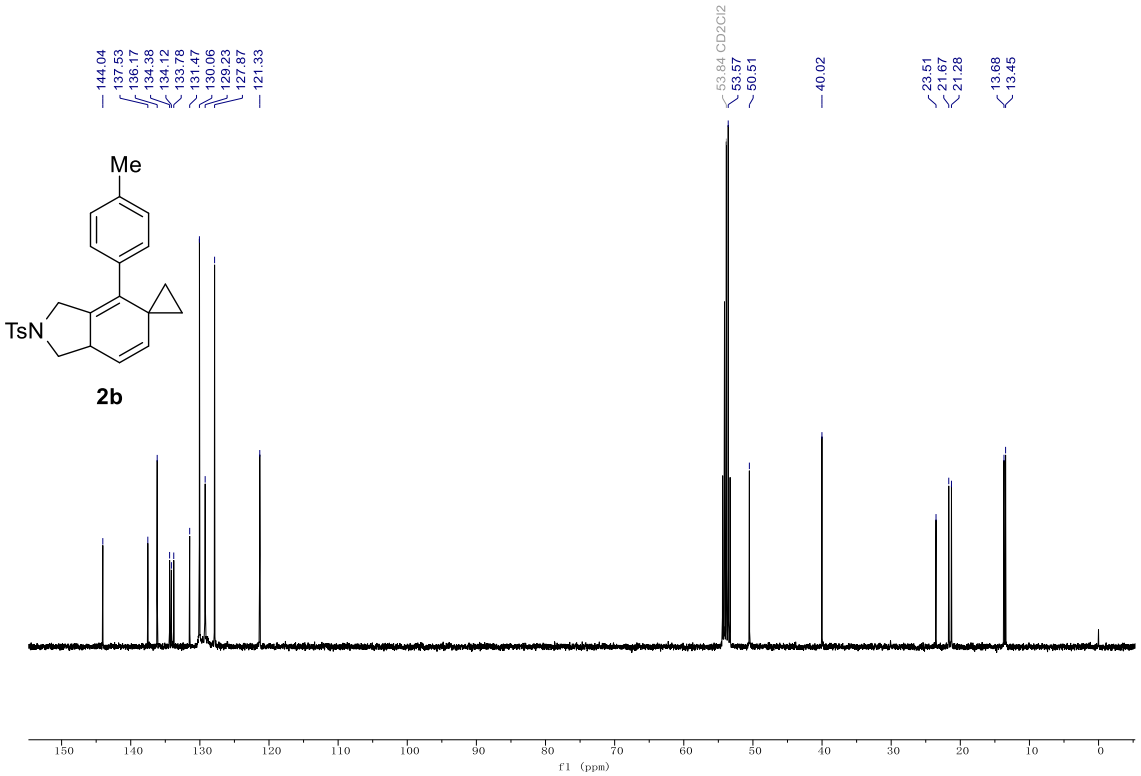


2b

^{1}H NMR (400 MHz, Methylene Chloride-d2)



^{13}C NMR (101 MHz, Methylene Chloride-d2)



2c

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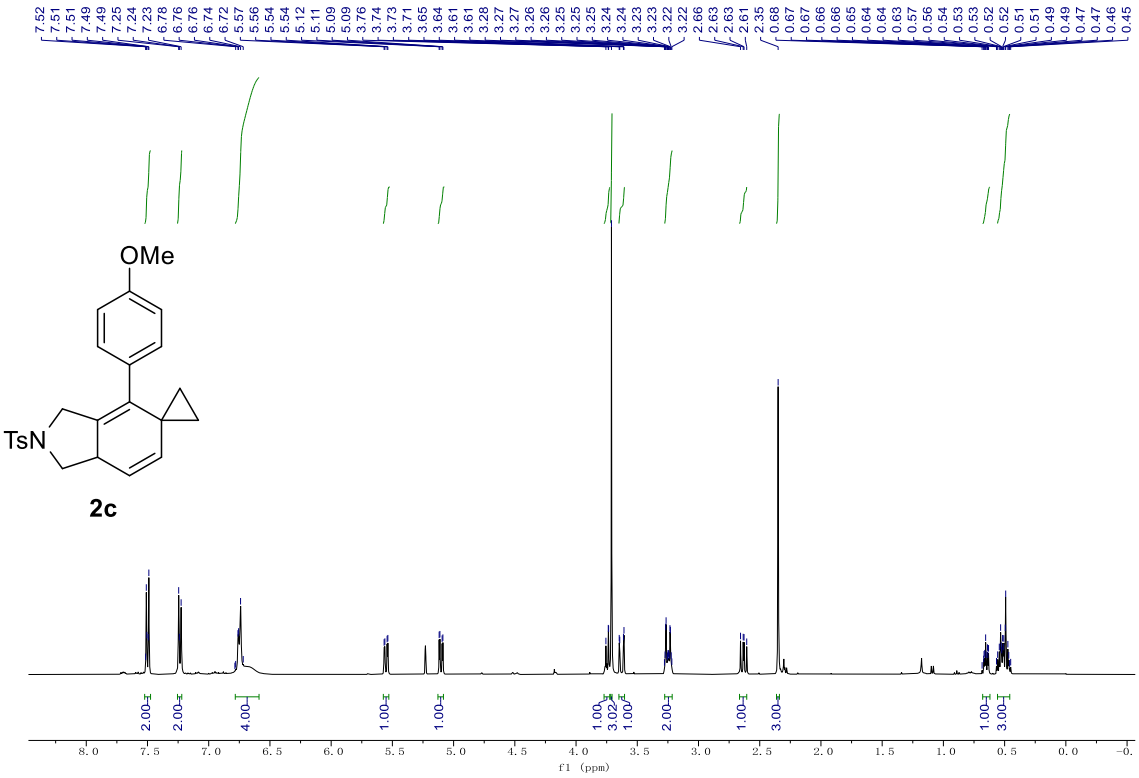

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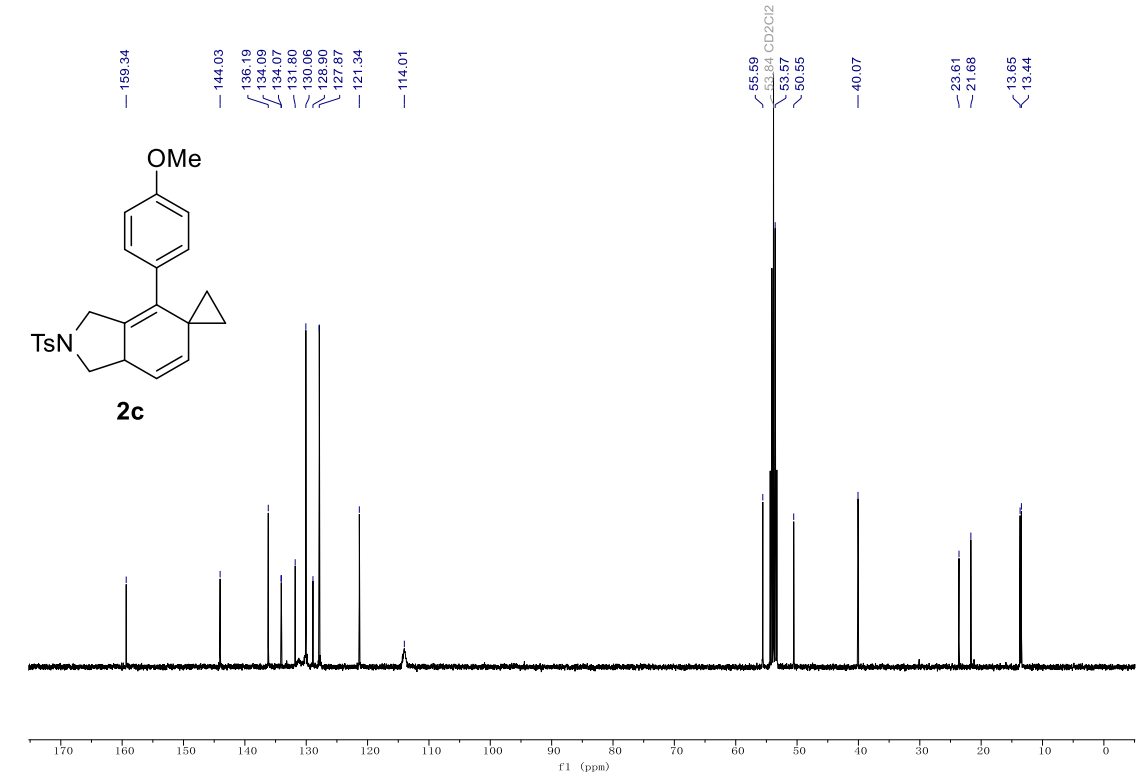
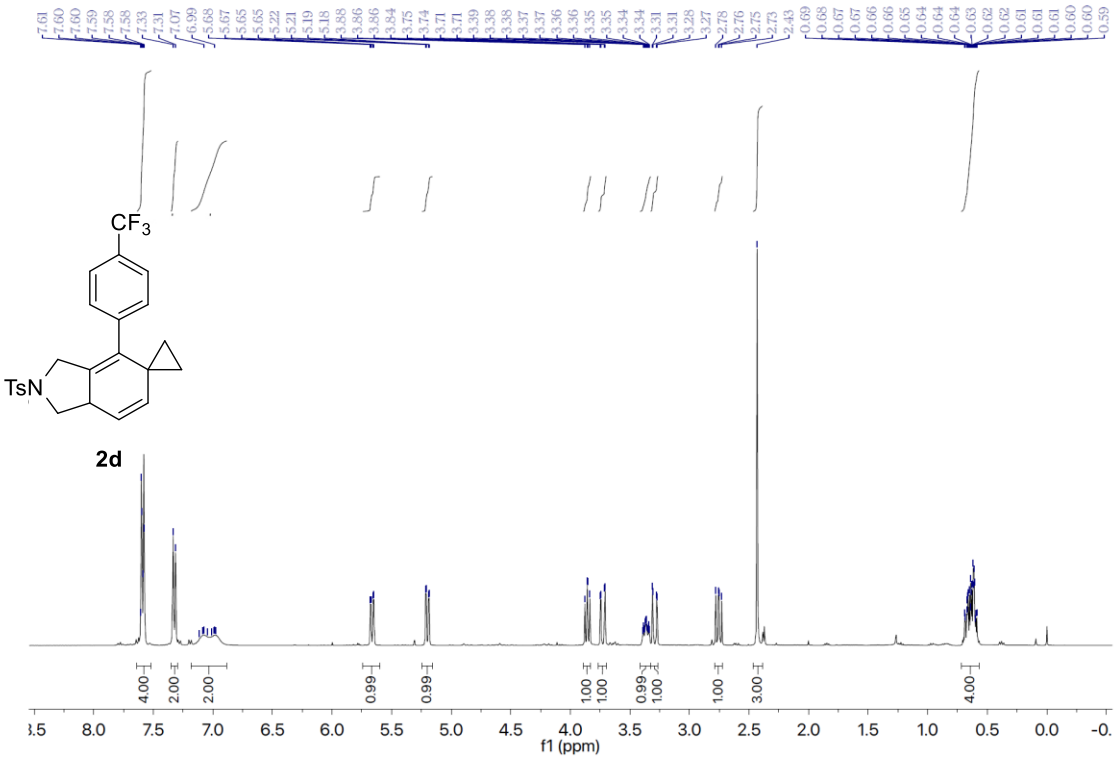


2d

^{1}H NMR (400 MHz, Methylene Chloride-d2)



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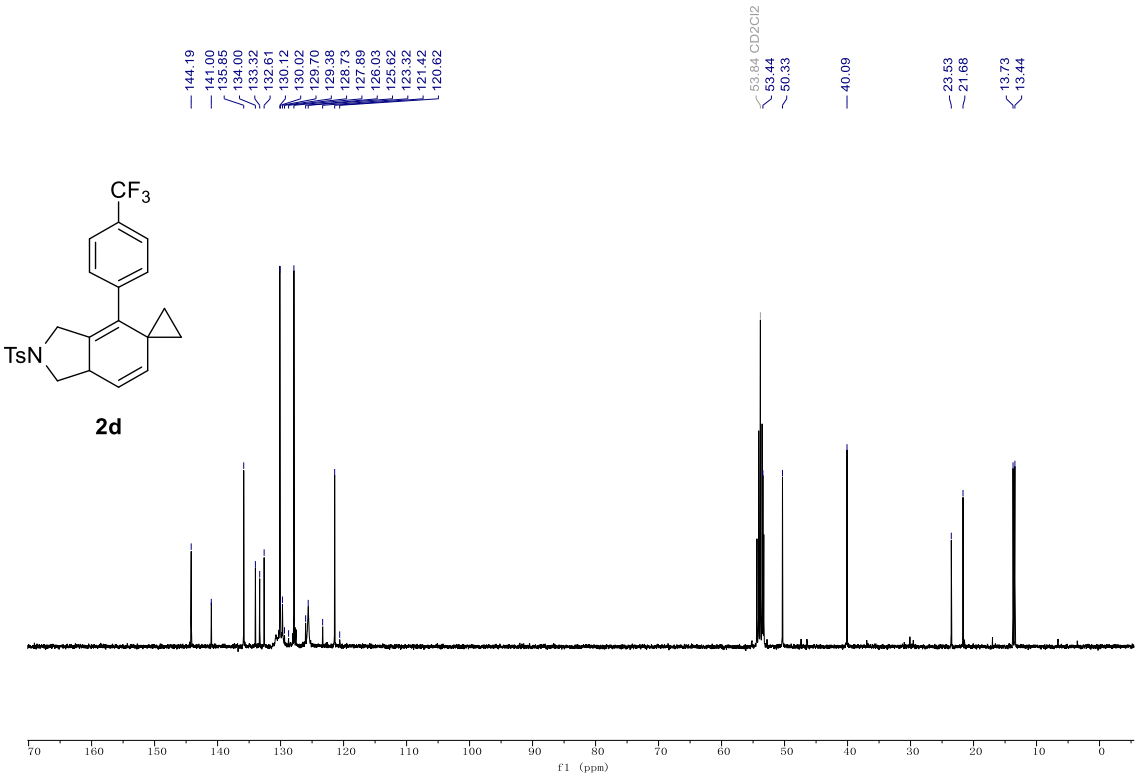

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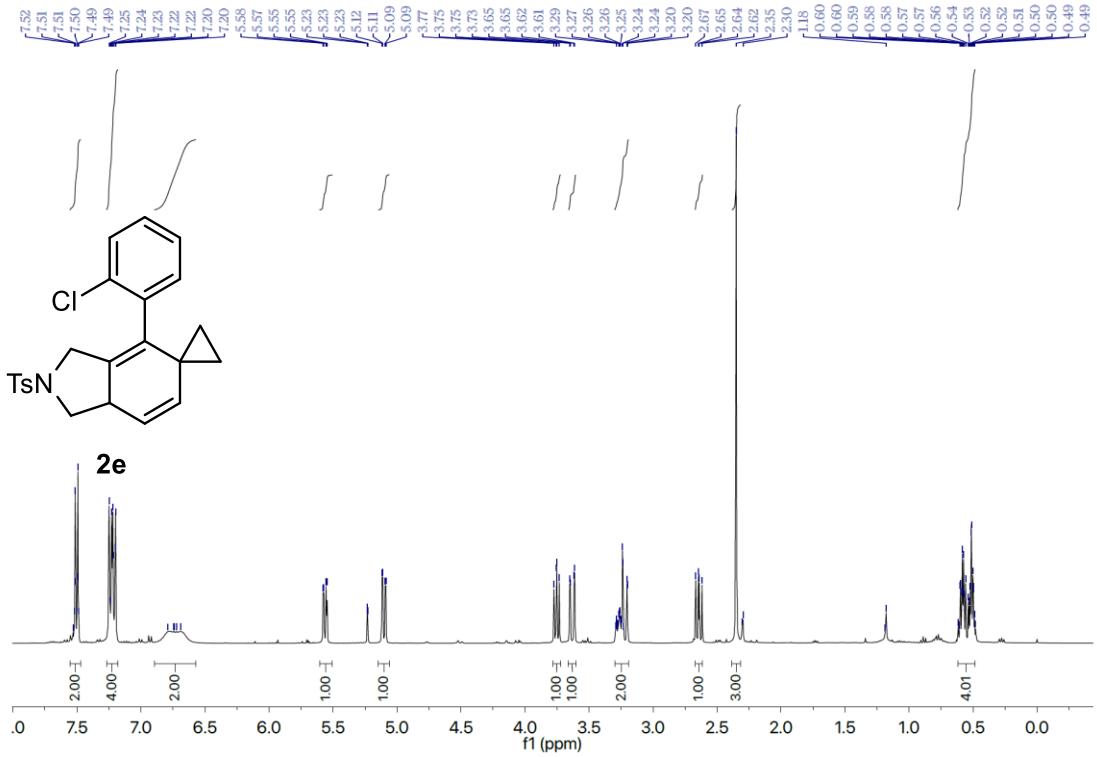
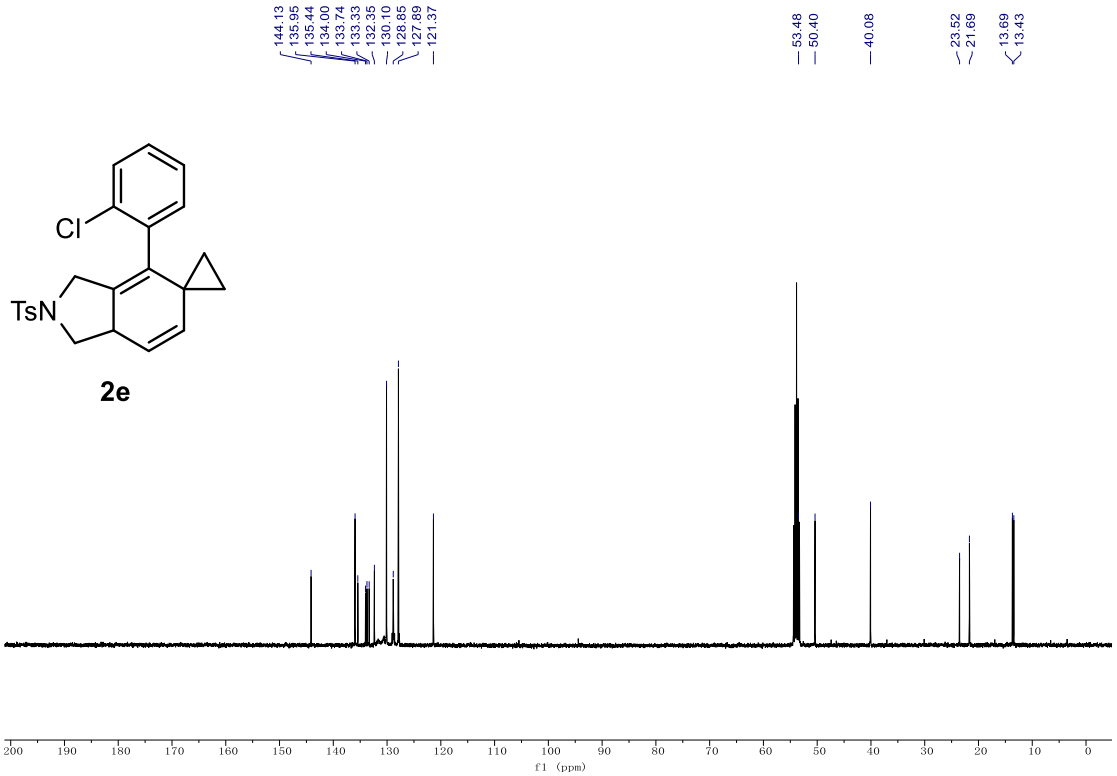
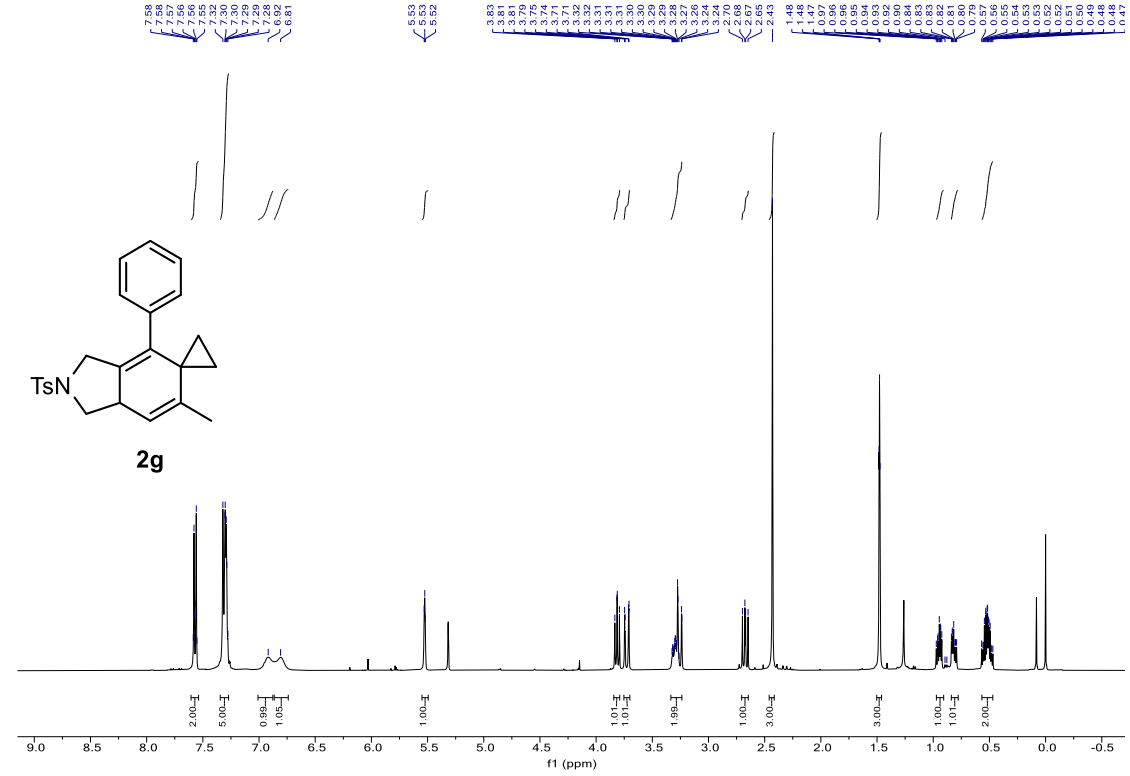


^{13}C NMR (101 MHz, Methylene Chloride-d2)

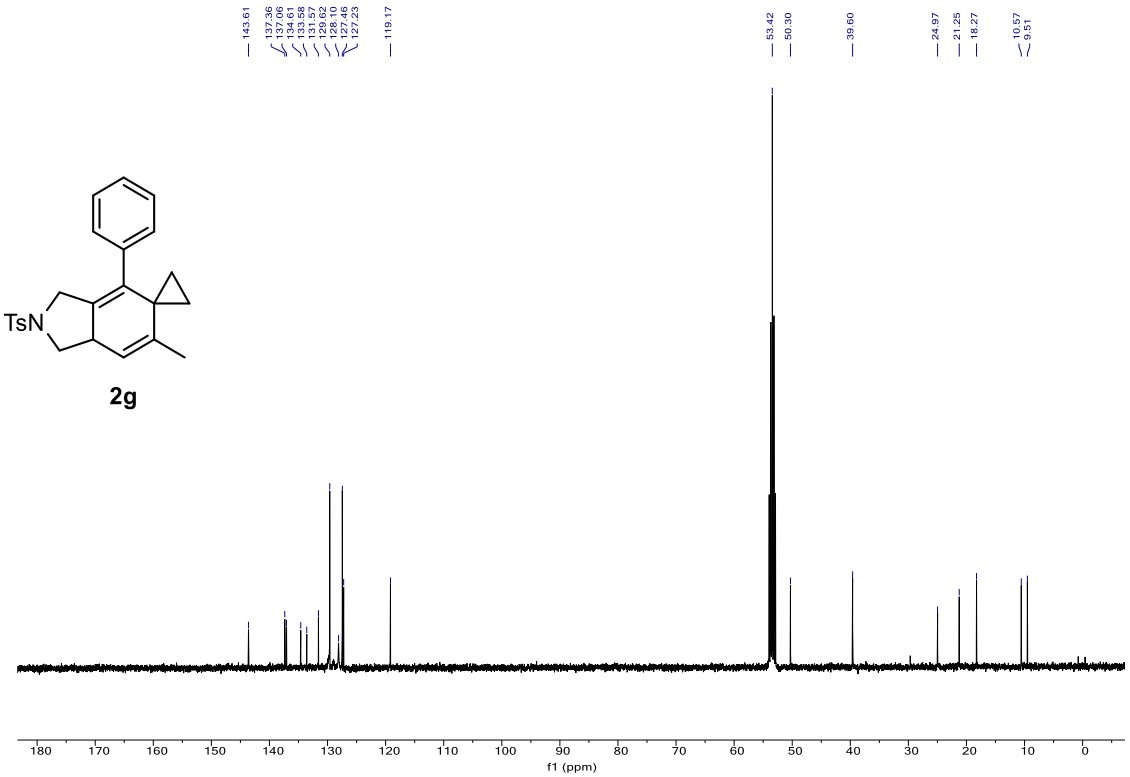


2g

^{1}H NMR (400 MHz, Methylene Chloride-d2)

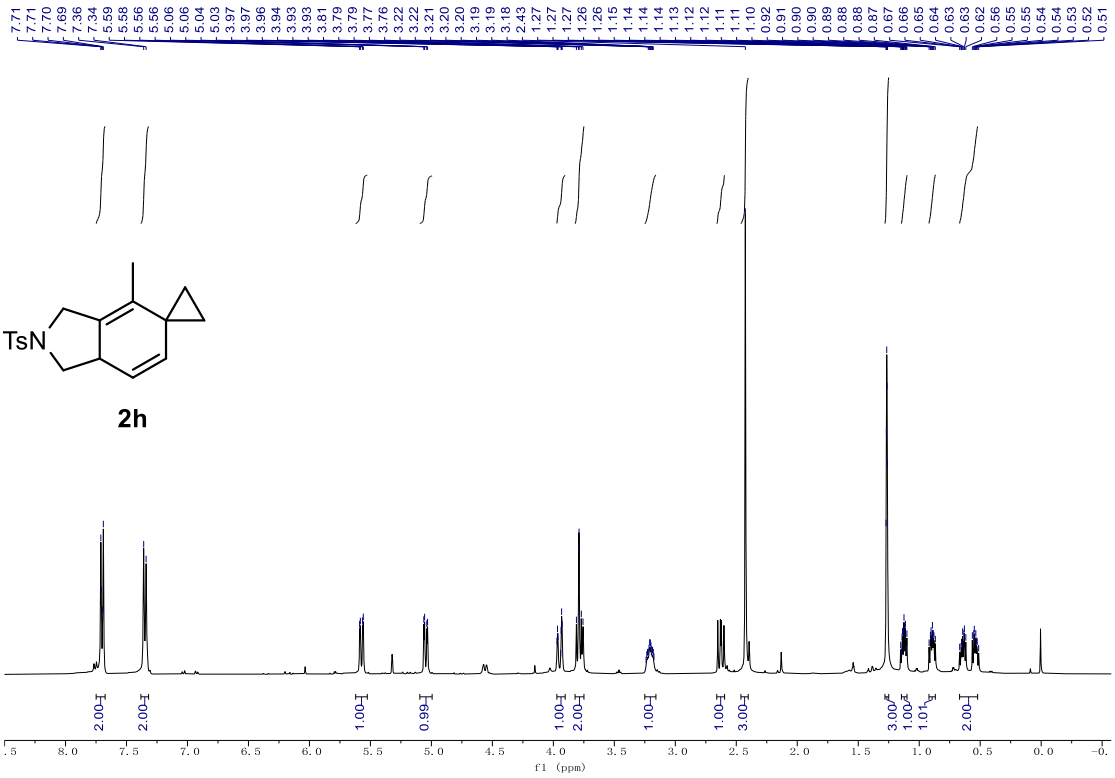


^{13}C NMR (101 MHz, Methylene Chloride-d2)

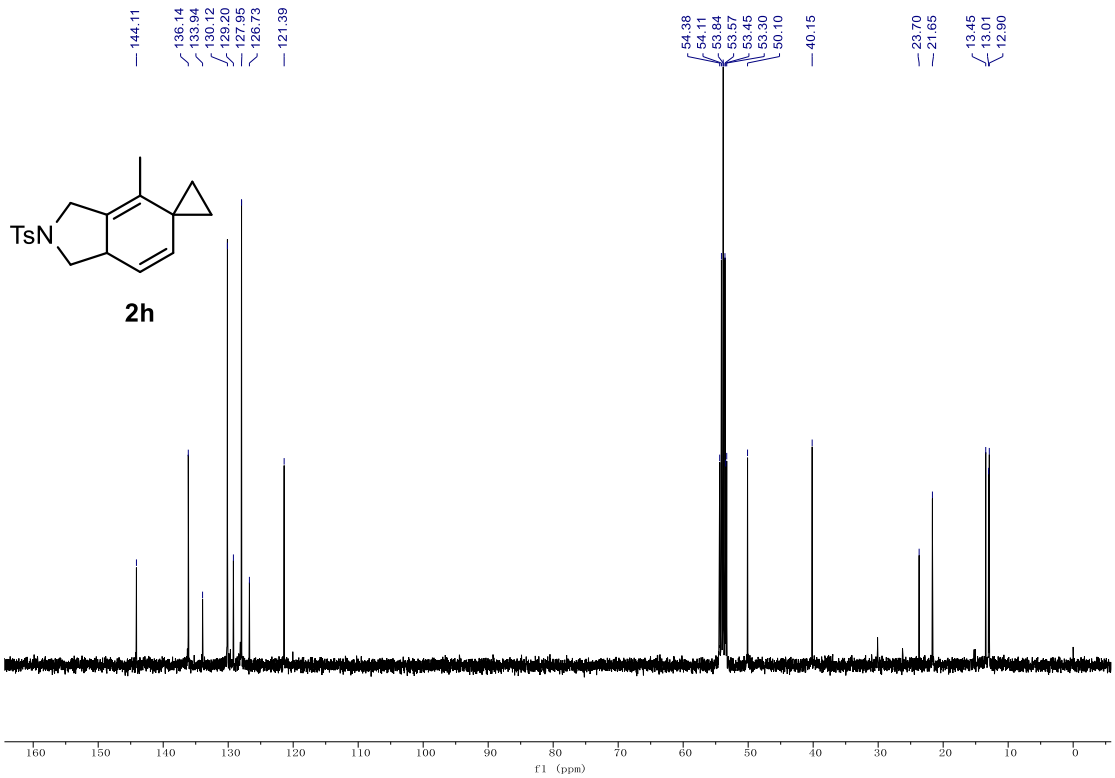


2h

^{1}H NMR (400 MHz, Methylene Chloride-d2)

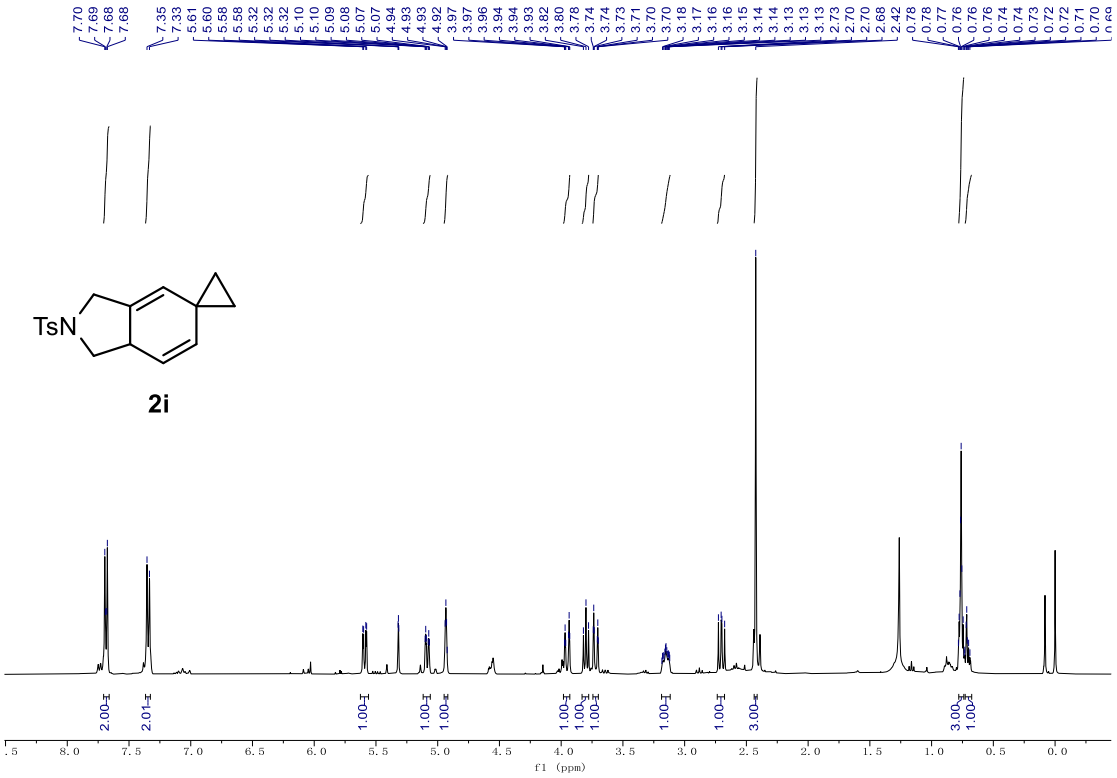


^{13}C NMR (101 MHz, Methylene Chloride-d2)

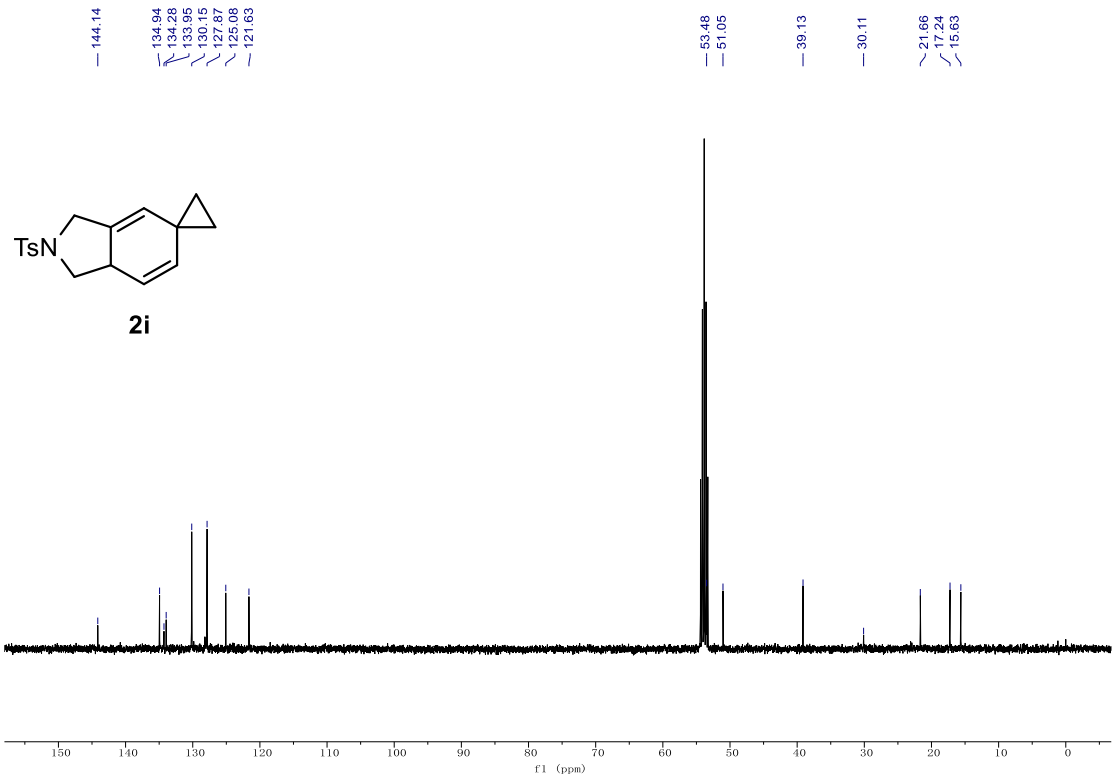


2i

^{1}H NMR (400 MHz, Methylene Chloride-d2)

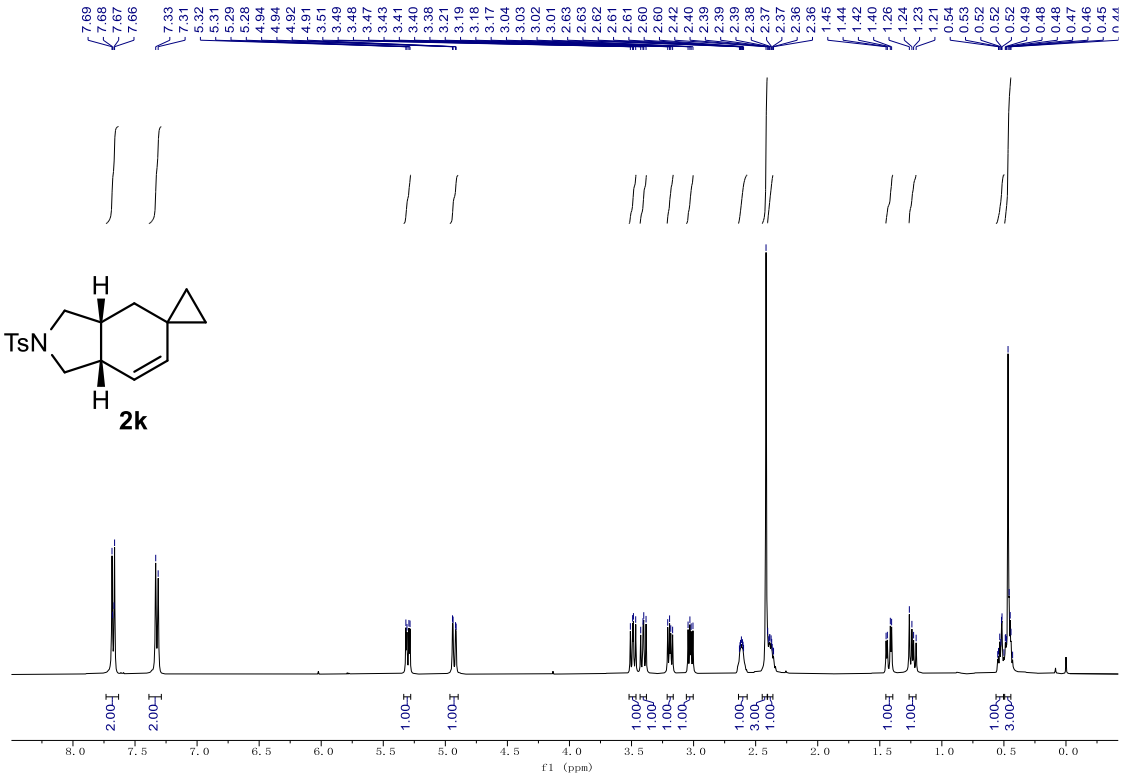


^{13}C NMR (101 MHz, Methylene Chloride-d2)

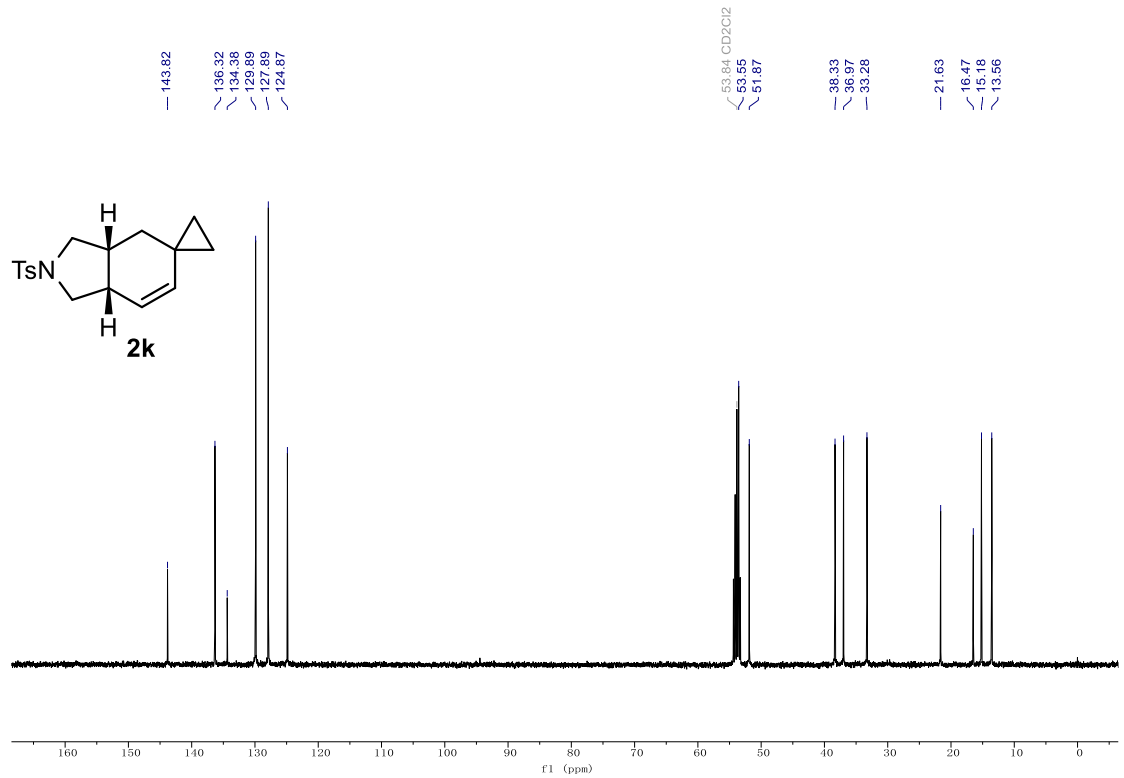


2k

^{1}H NMR (400 MHz, Methylene Chloride-d2)

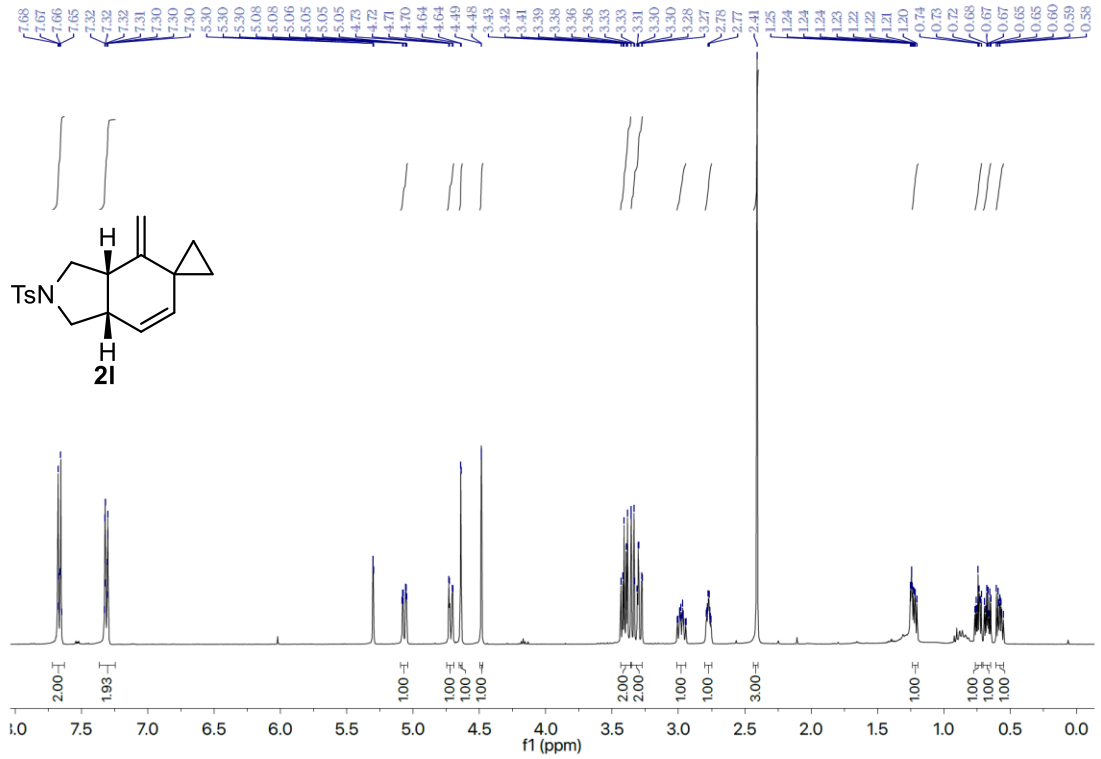


^{13}C NMR (101 MHz, Methylene Chloride-d2)

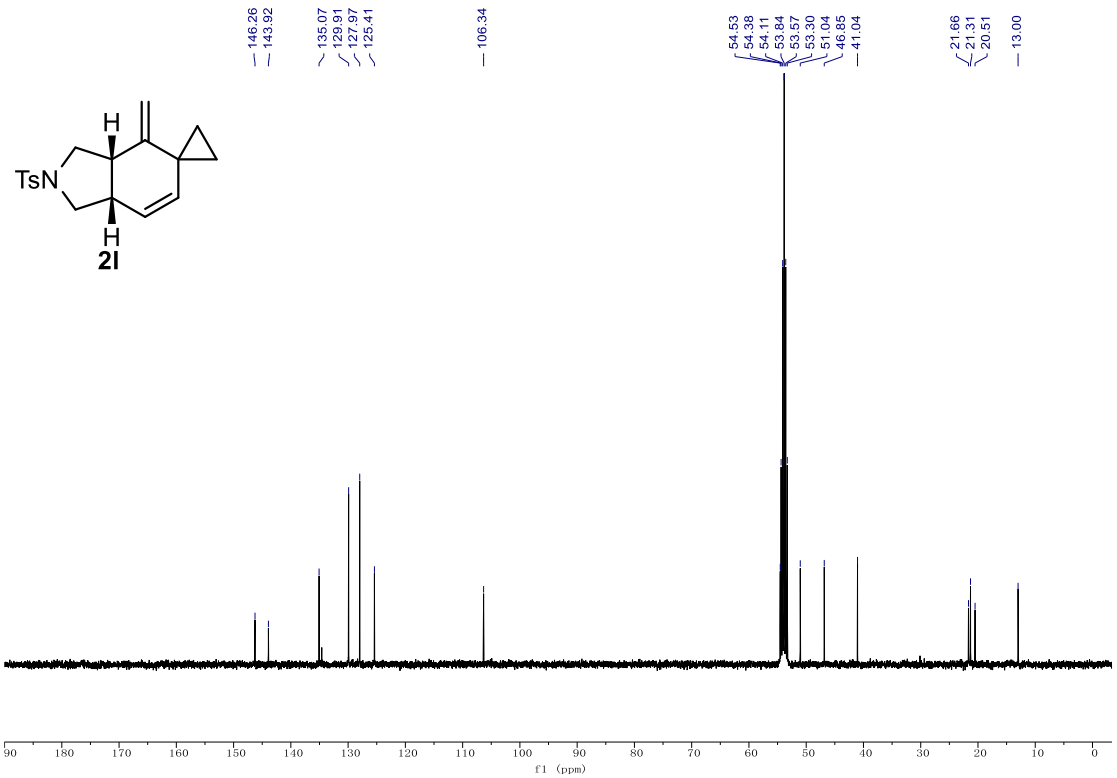


2l

^{1}H NMR (400 MHz, Methylene Chloride-d2)

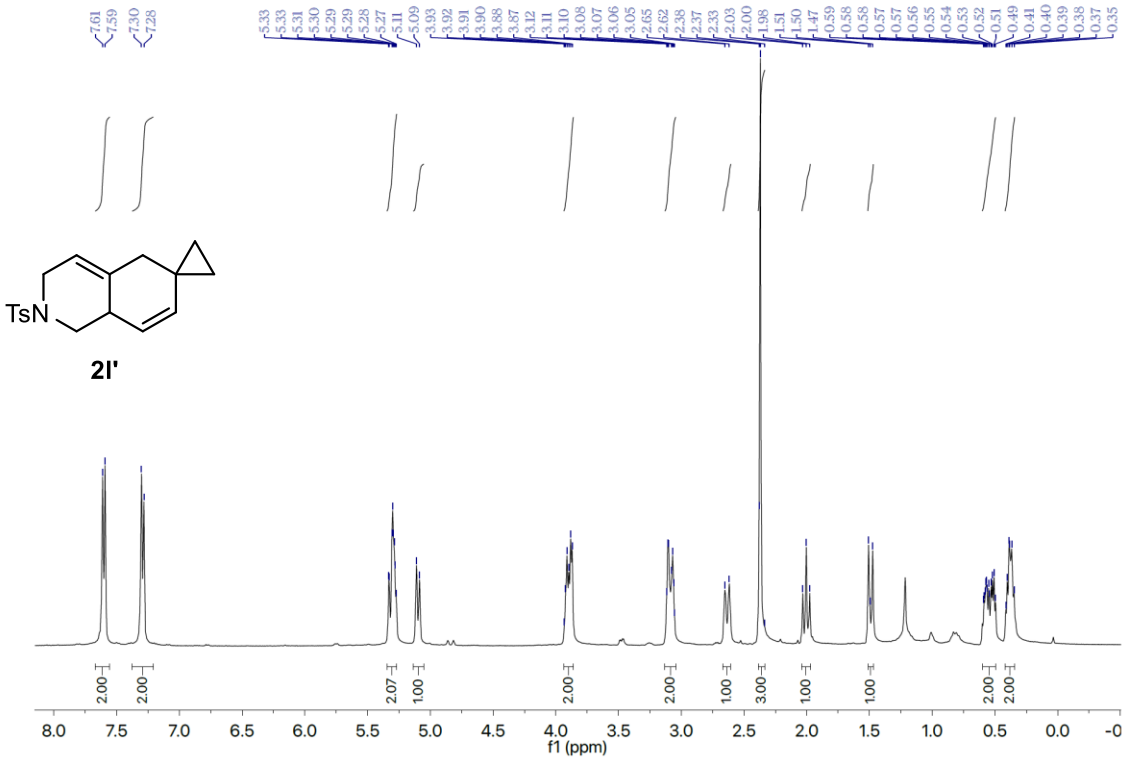


^{13}C NMR (101 MHz, Methylene Chloride-d2)

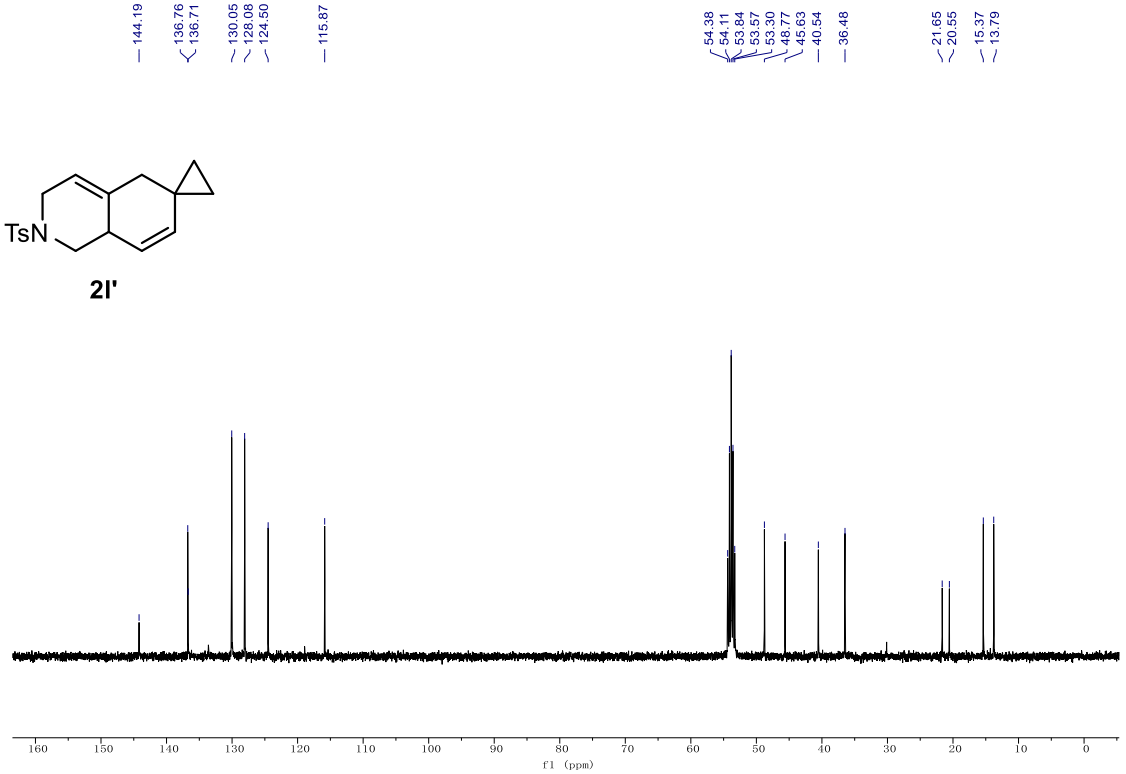


2l'

^{1}H NMR (400 MHz, Methylene Chloride-d2)

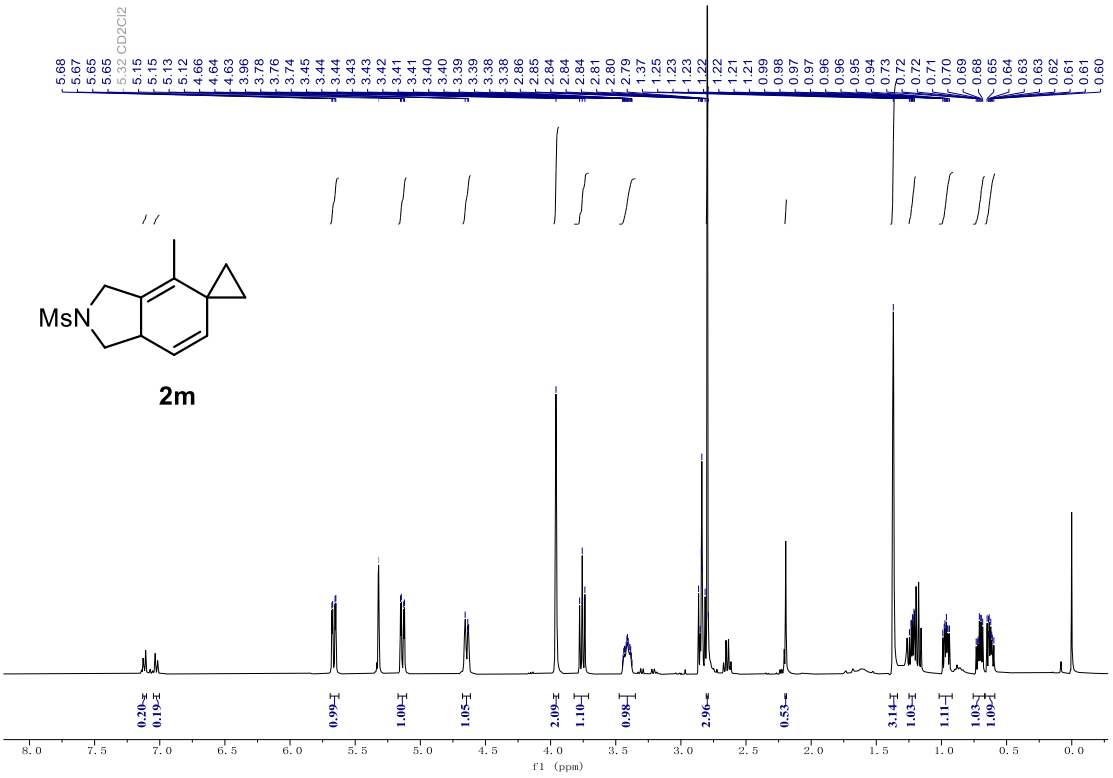


^{13}C NMR (101 MHz, Methylene Chloride-d2)

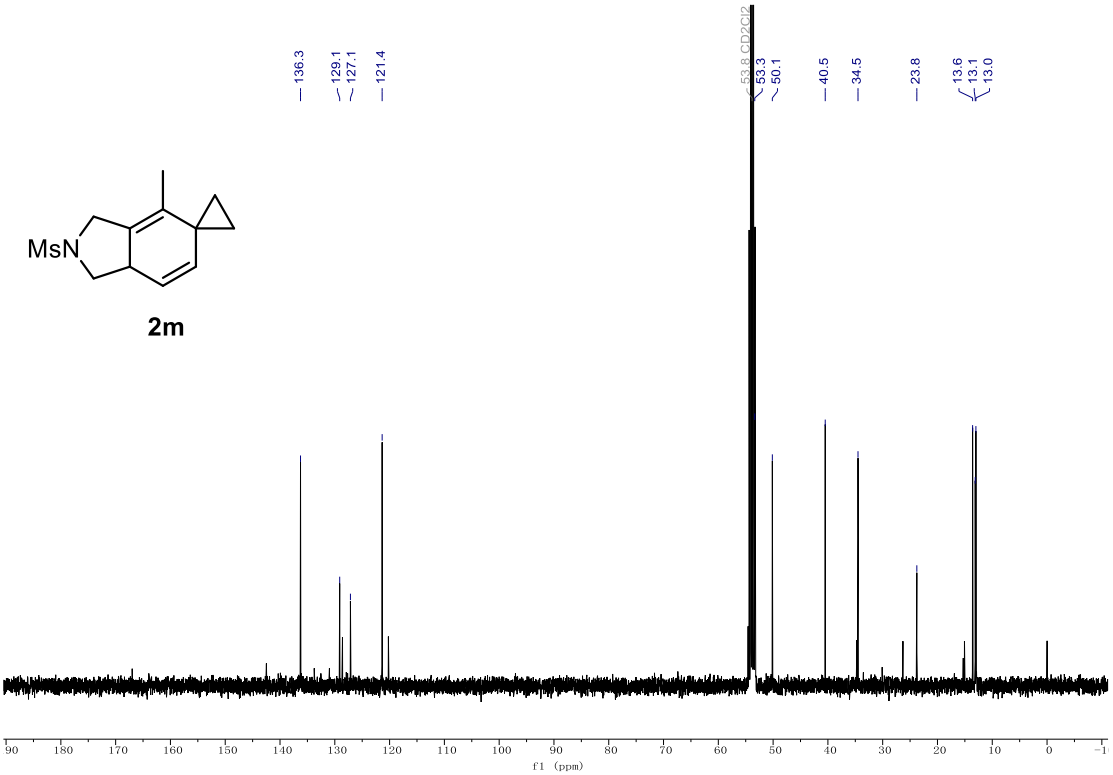


2m

^{1}H NMR (400 MHz, Methylene Chloride-d2)

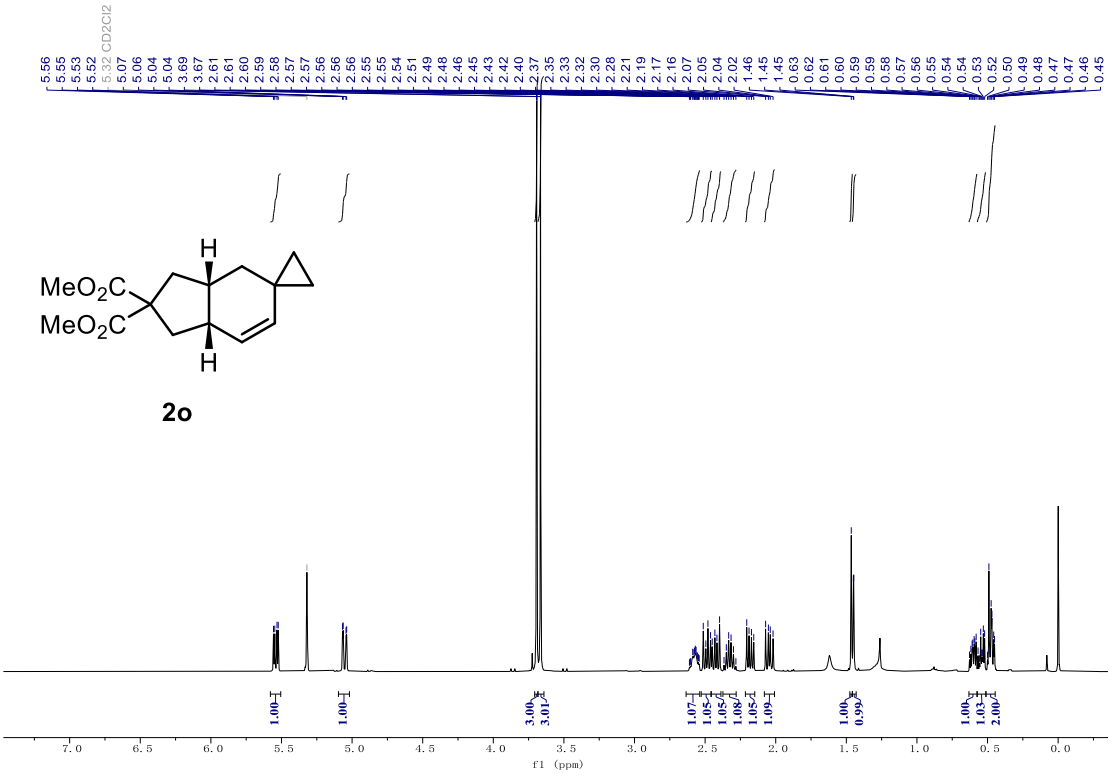


^{13}C NMR (101 MHz, Methylene Chloride-d2)

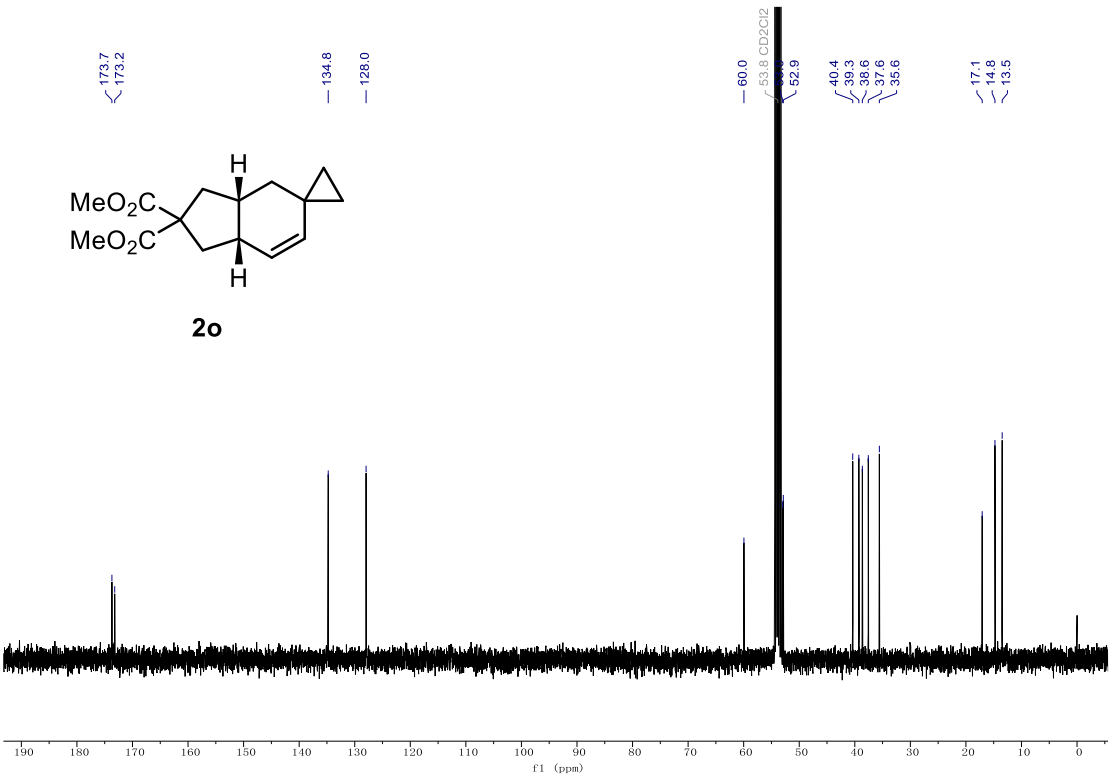


2o

^{1}H NMR (400 MHz, Methylene Chloride-d2)

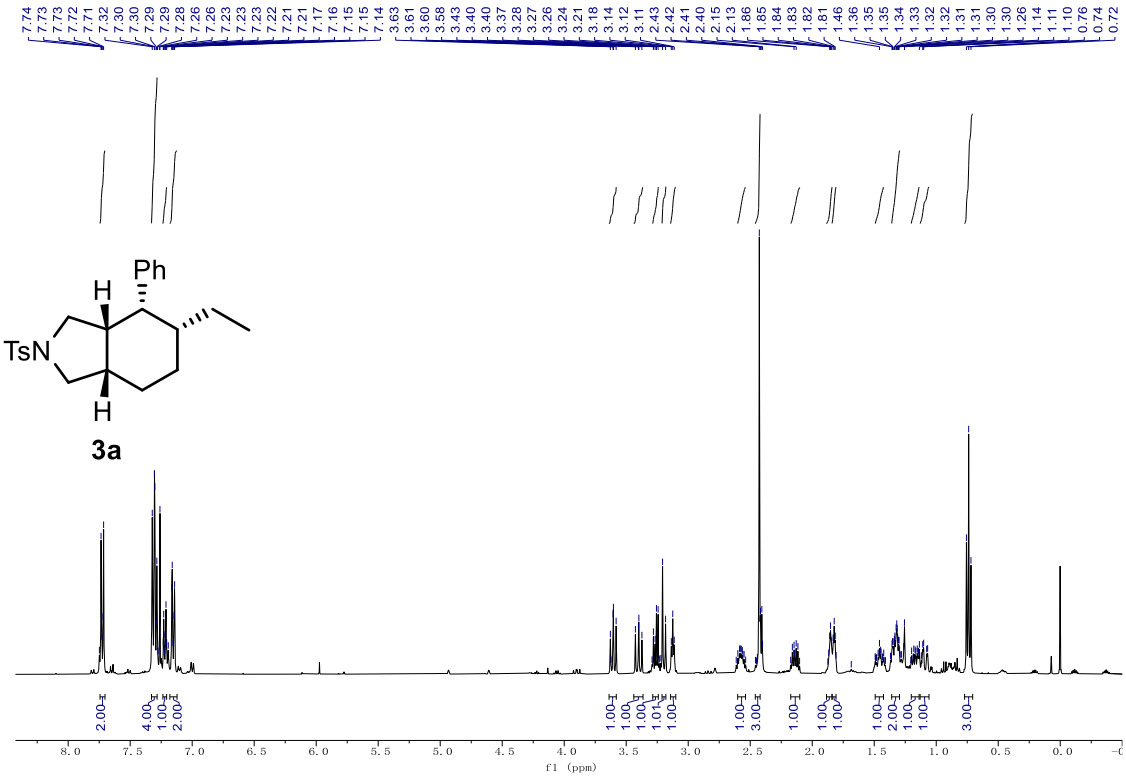


^{13}C NMR (101 MHz, Methylene Chloride-d2)



3a

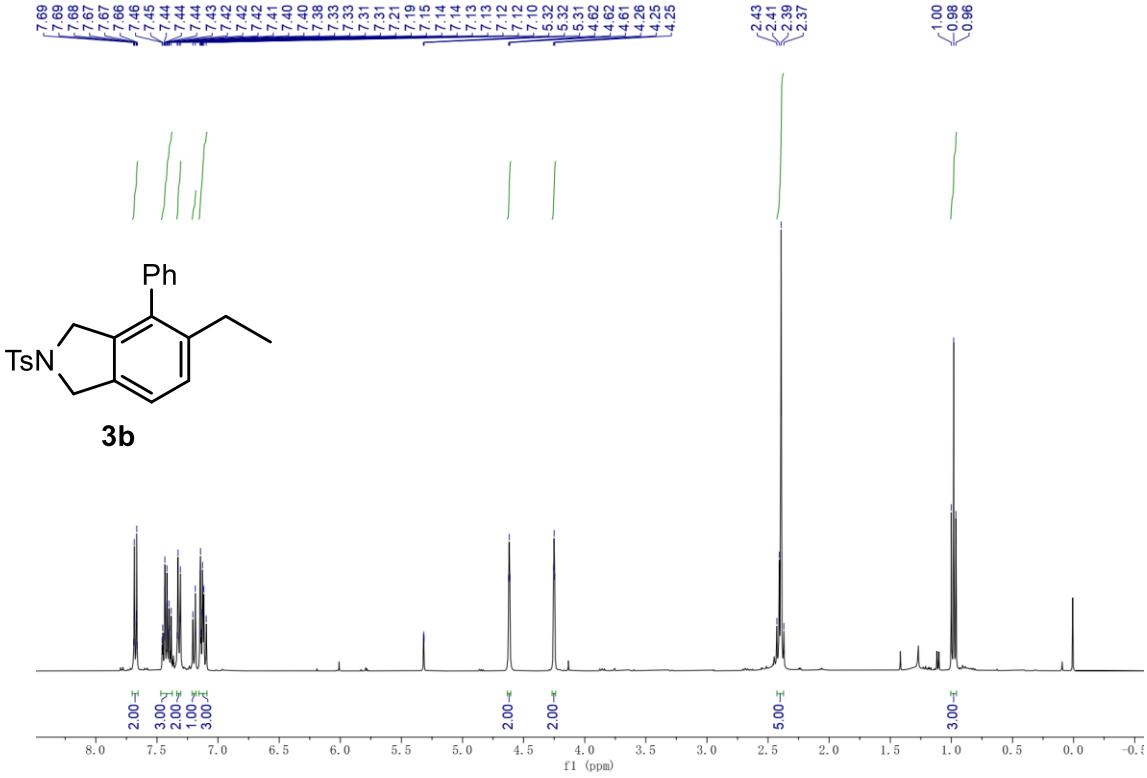
^{1}H NMR (400 MHz, Chloroform-*d*)



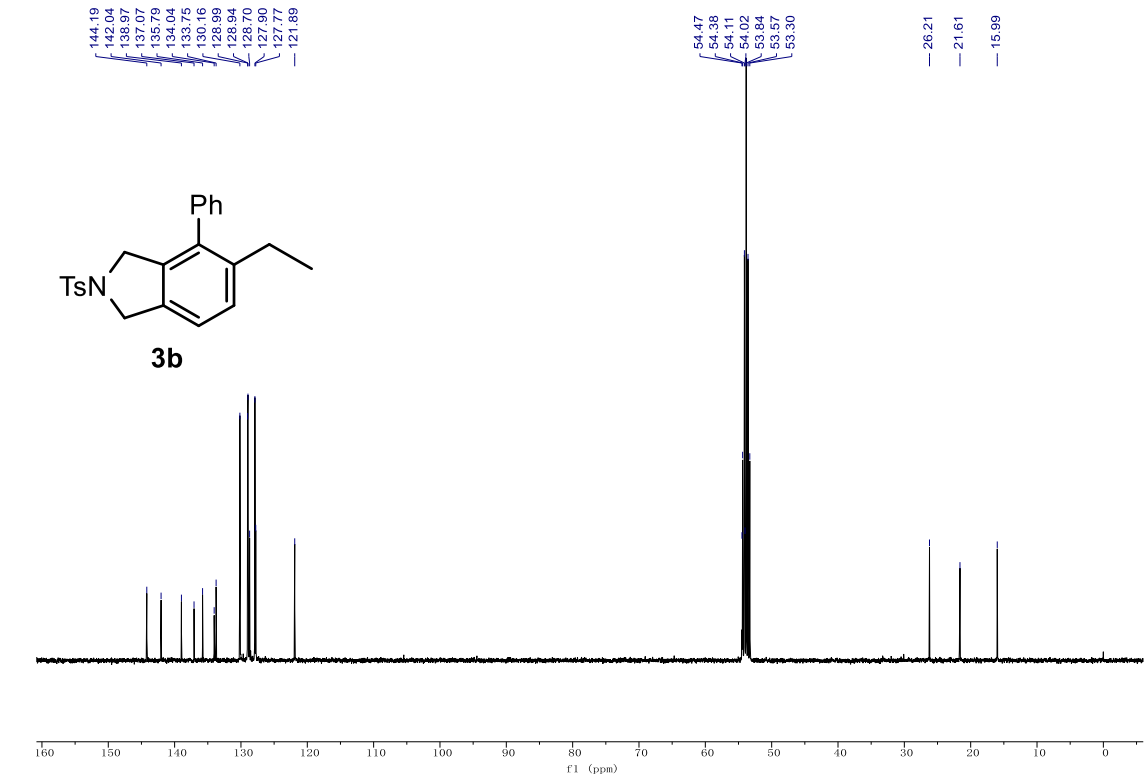
^{13}C NMR (101 MHz, Chloroform-*d*)

3b

^{1}H NMR (400 MHz, Chloroform-*d*)

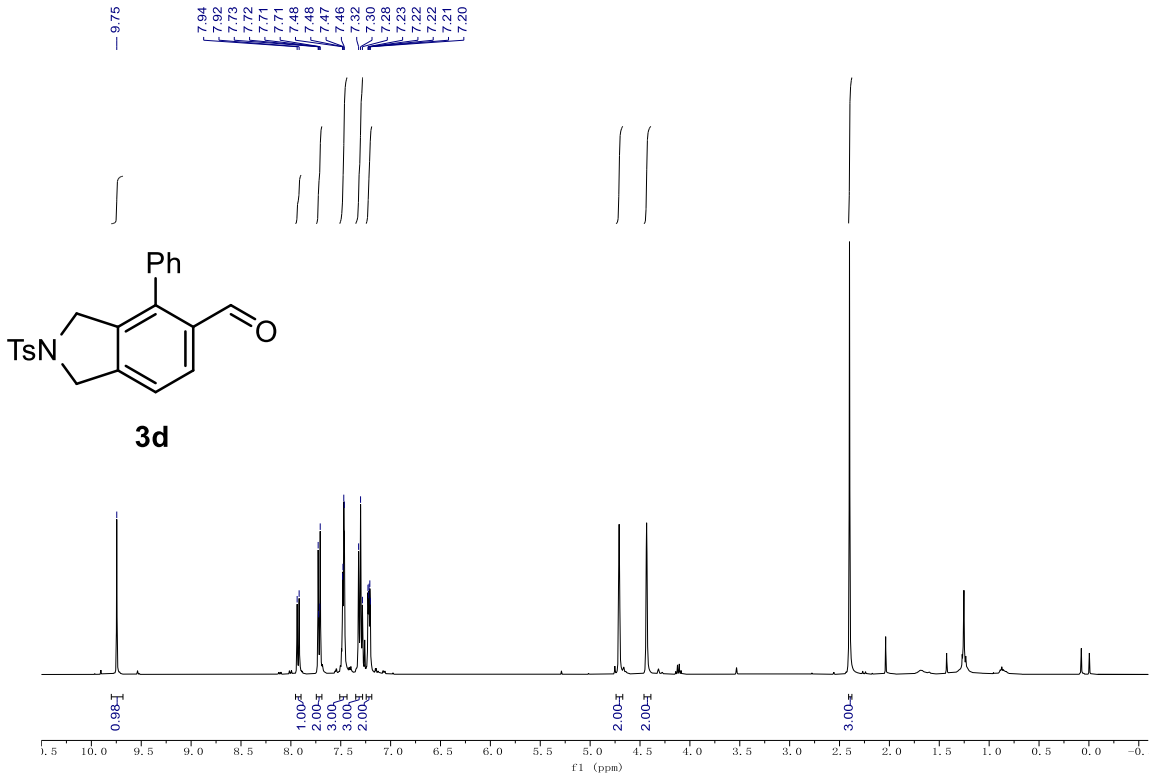


^{13}C NMR (101 MHz, Chloroform-*d*)

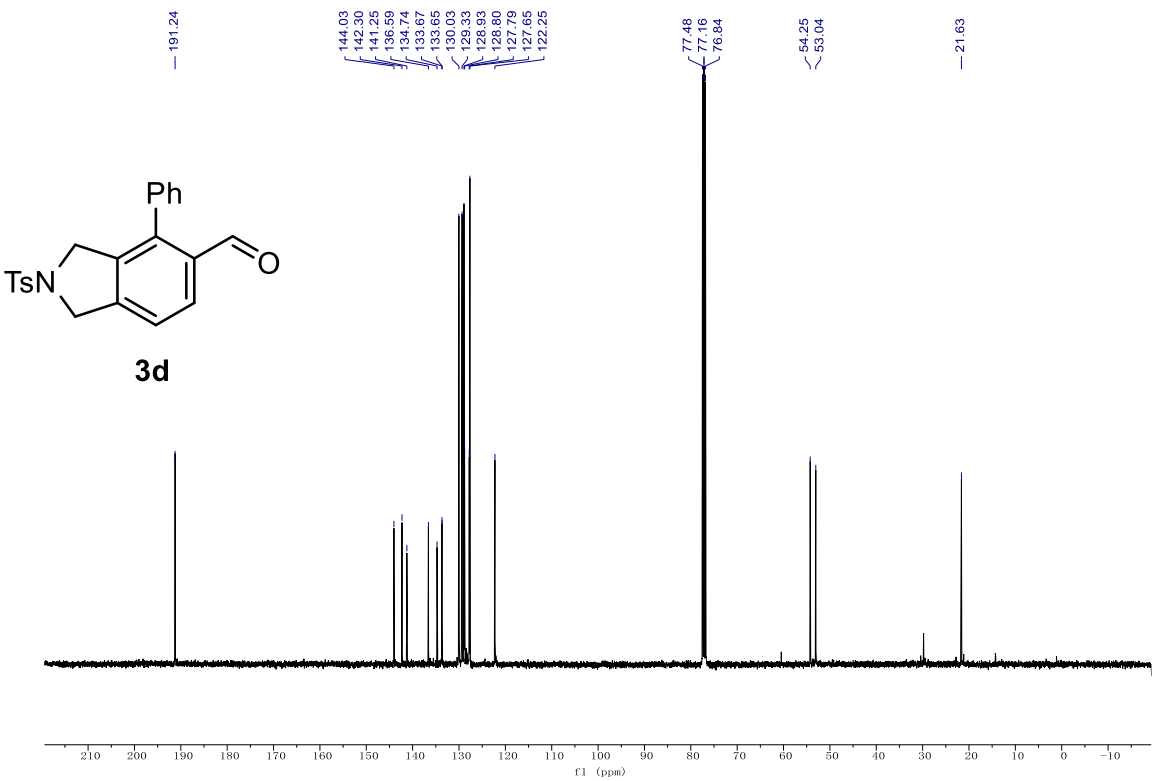


3d

^{1}H NMR (400 MHz, Chloroform-*d*)

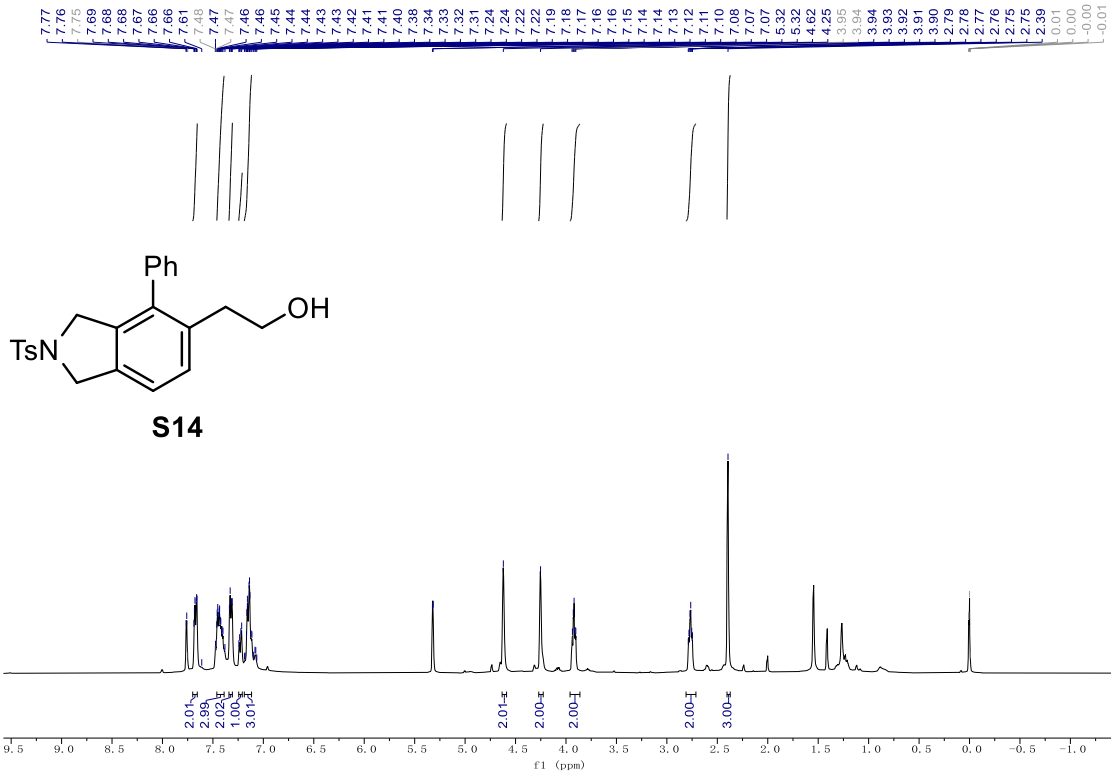


^{13}C NMR (101 MHz, Chloroform-*d*)

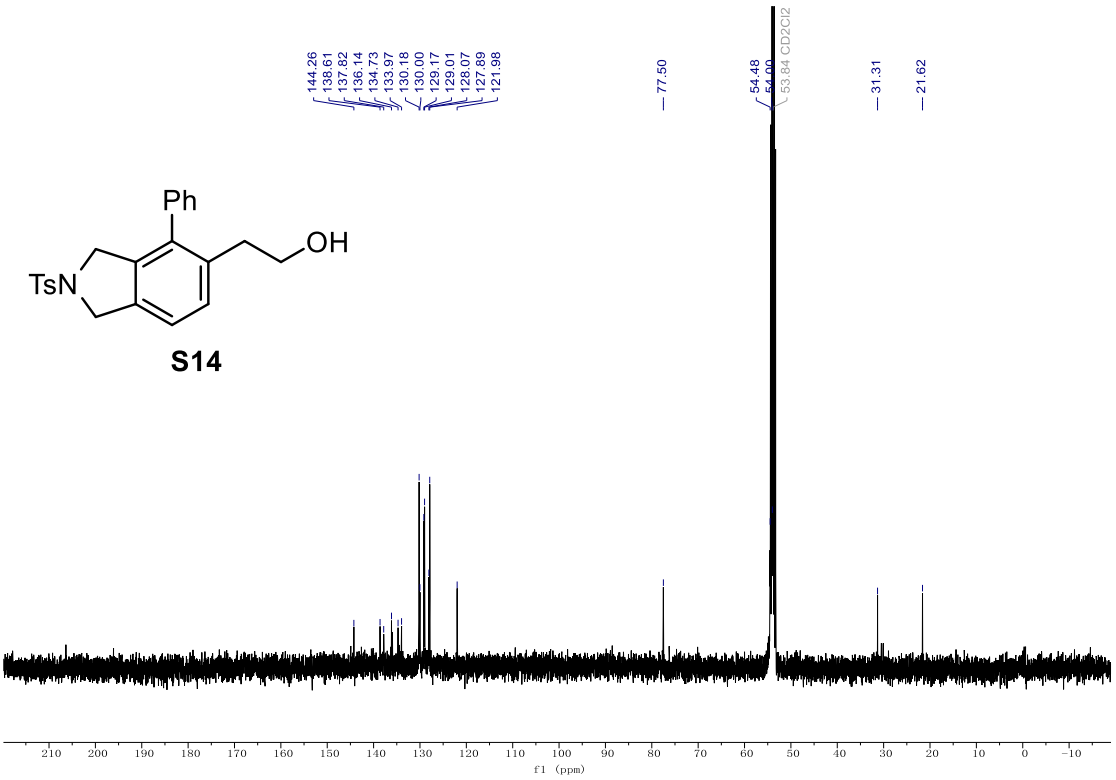


S14

^{1}H NMR (400 MHz, Methylene Chloride-d2)

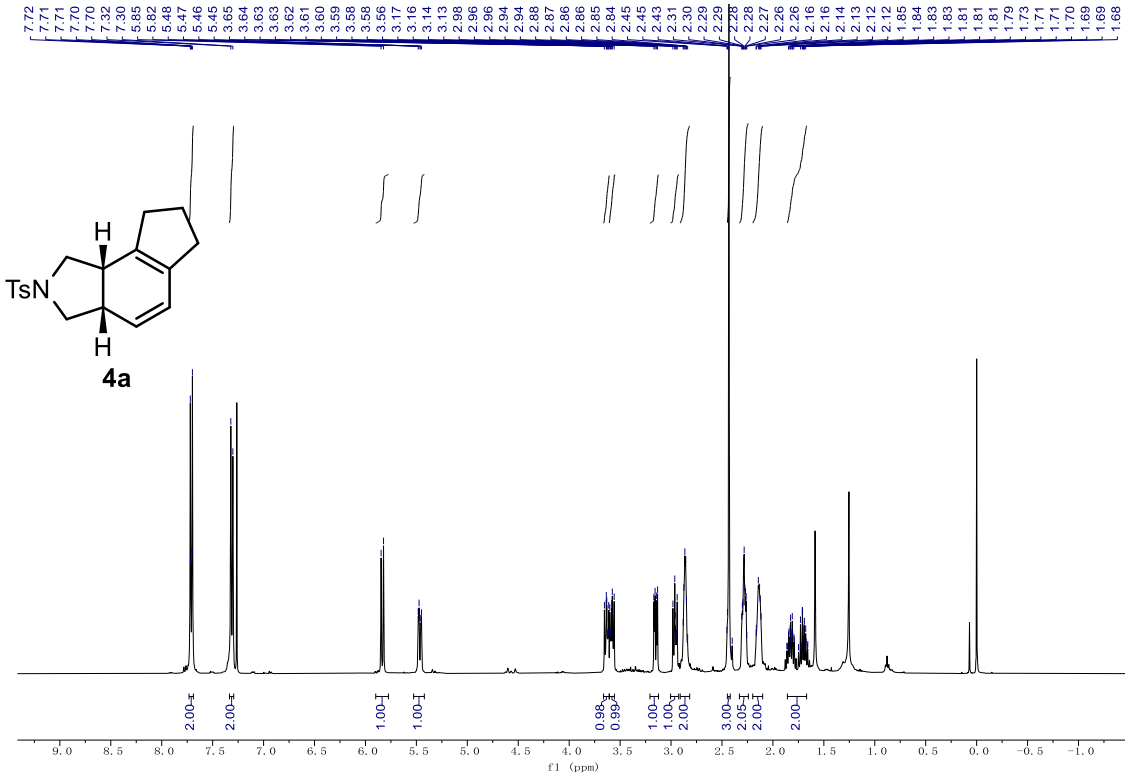


^{13}C NMR (101 MHz, Methylene Chloride-d2)

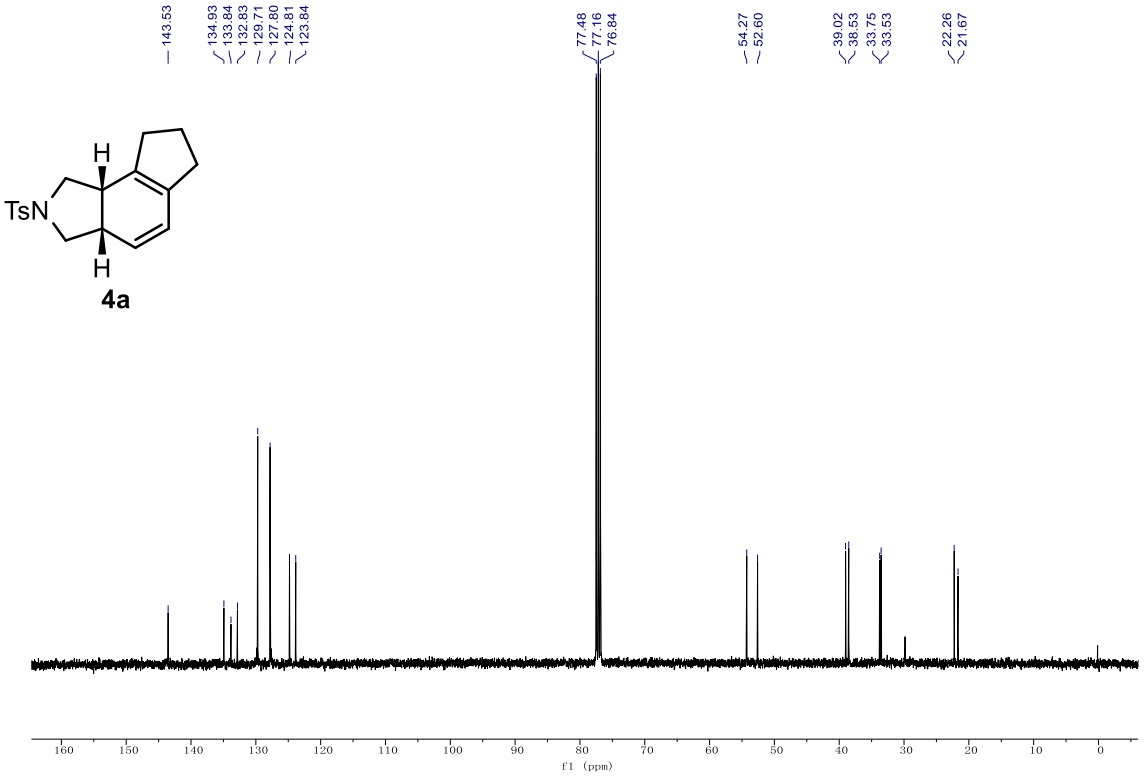


4a

^{1}H NMR (400 MHz, Chloroform-*d*)

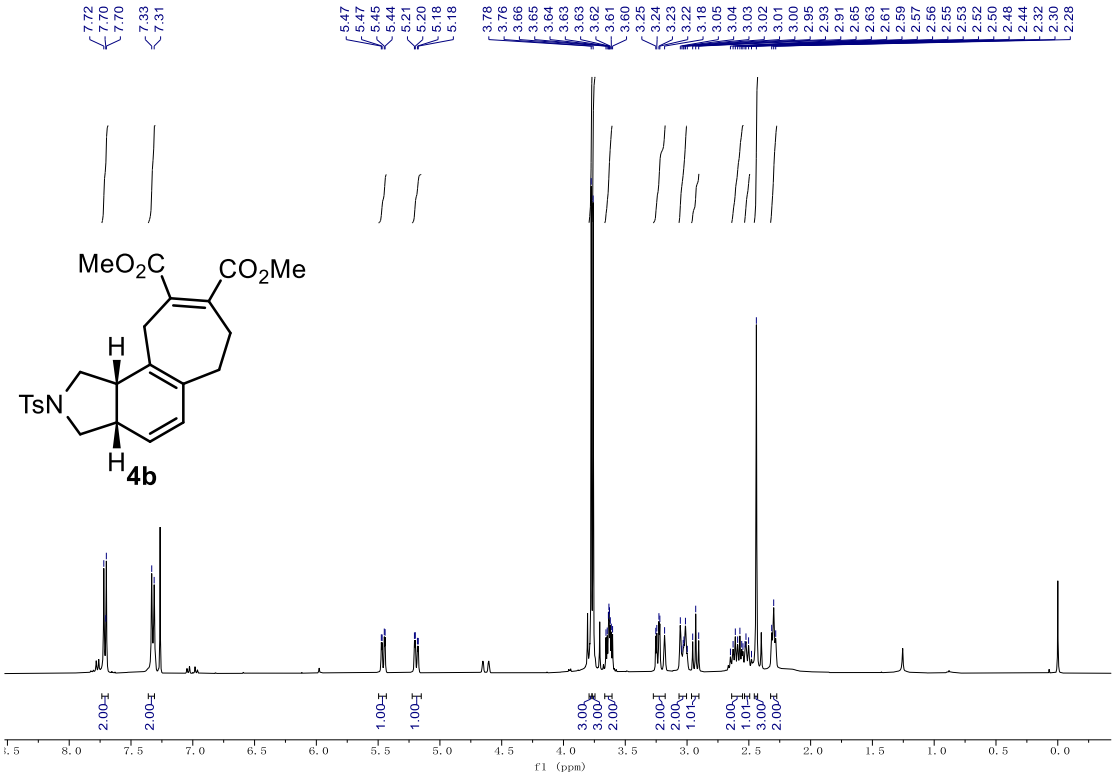


^{13}C NMR (101 MHz, Chloroform-*d*)



4b

^{1}H NMR (400 MHz, Chloroform-*d*)



^{13}C NMR (101 MHz, Chloroform-*d*)