# Rh-Catalyzed [8+1] Cycloaddition of Vinyl Biscyclopropanes with CO for the Synthesis of Nine-Membered Carbocycles

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# Content

# I. General Information

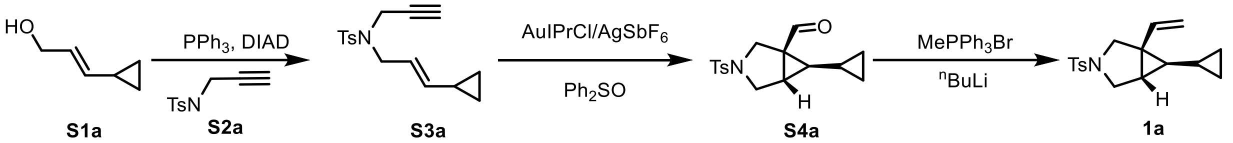
Air and moisture sensitive reactions were carried out in oven and flame-dried glassware sealed with rubber septa under a positive pressure of dry nitrogen or argon. Similarly, sensitive liquids and solutions were transferred via syringe. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a Büchi rotary evaporator with a desktop vacuum pump. DCE was superdry (water ≤ 30 ppm), which could be purchased from J&K. Synthetic reagents and catalysts were purchased from J&K, and used without further purification, unless otherwise indicated. Analytical TLC was performed with 0.25 mm silica gel G plates with a 254 nm fluorescent indicator. The TLC plates were visualized by ultraviolet light and treatment with phosphomolybdic acid stain or $KMnO_4$ stain followed by gentle heating. Purification of products was accomplished by flash chromatography on silica gel and the purified compounds show a single spot by analytical TLC. NMR spectra were measured on Bruker ARX 400 ($^1$H at 400 MHz, $^{13}$C at 101 MHz), Bruker AVANCE III ($^1$H at 600 MHz, $^{13}$C at 151 MHz). Data for $^1$H NMR spectra were reported as follows: chemical shift (ppm, referenced to residual solvent peak ($CDCl_3$ = δ 7.26 ppm; s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets, tt = triplet of triplets, tq = triplet of quartets, m = multiplet), coupling constant (Hz), and integration. Data for $^{13}$C NMR were reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$ = δ 77.16 ppm). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer (ESI, EI or MALDI) with an FT-ICR analyzer and Hybrid Quadrupole-Orbitrap GC-MS/MS System (Q Exactive GC).

Abbreviations

DCE = 1,2-dichloroethane
DCM = dichloromethane
DIAD = diisopropyl azodicarboxylate
DIBAL-H = diisobutylaluminum hydride
EA = ethyl acetate
IPr = 1,3-Bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene
m.p. = melting point
Ms = methylsulfonyl
$N_2$ = nitrogen
Ns = *p*-nitrobenzenesulfonyl
PE = petroleum ether
rt = room temperature
THF = tetrahydrofuran
TLC = thin layer chromatography
Ts = *p*-toluenesulfonyl
CuTc = Copper(I) thiophene-2-carboxylate hydrate

## II. Preparation of Substrates 1

Note: The cyclopropanation reactions used in this work, including gold-catalyzed cyclopropanation[1], Rh-catalyzed cyclopropanation[2], Corey-Chaykovsky reaction[3-5], were reported before and has not been optimized by us. **S1a-S1f**[6-7], **S2a-S2d**[8], **S3a-S3d**[7,9], **S9c**[10]were reported compounds, **S9a-S9b**, **S9d-S9l**, **S10a-S10c** were commercially available and purchased from Bidepharm, J&K, Konoscience.



A 100 mL reaction flask equipped with a magnetic stirrer was charged with substrate **S1a** (0.49 g, 5.0 mmol), **S2a** (1.05 g, 5.0 mmol), PPh$_3$ (1.97 g, 7.5 mmol), and THF (40 mL). DIAD (1.5 g, 7.5 mmol) was added dropwise at 0 °C. The reaction was gradually allowed to warm to room temperature. After 18 hours of reaction, the solvent was removed by rotary evaporation, and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 20:1) to afford 1.21 g of a white solid, which was a mixture of **S3a** and its $S_N2$’ isomer[11] in a ratio of 4:1 (total yield: 84%). This mixture was directly used in the next step.

Inside a glovebox, IPrAuCl (63.7 mg, 0.1 mmol) and AgSbF$_6$ (35.2 mg, 0.1 mmol) were weighed into a 10 mL reaction tube equipped with a magnetic stirrer. The tube was sealed and removed from the glovebox. Under an argon atmosphere, DCM (1 mL) was added, and the mixture was stirred for 10 minutes at room temperature. In a separate reaction flask equipped with a magnetic stirrer, the mixture of **S3a** (1.2 g, 4.1 mmol) prepared above was added, along with DCM (40 mL) and Ph$_2$SO (1.66 g, 8.2 mmol). The flask was evacuated and purged with argon, and then the gold catalyst solution was added. The reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 12 h. The reaction mixture was concentrated, and the residue was purified by column chromatography using PE/EA = 5/1 as the eluent to obtain a mixture of white solid **S4a** and unreacted Ph$_2$SO (1.26 g), which was directly used in the next step.

A reaction flask equipped with a magnetic stirrer was charged with MePPh$_3$Br (2.37 g, 6.3 mmol). The flask was evacuated and purged with argon, and then THF (20 mL) was added. After that, $^n$BuLi (2.6 mL, 2.4 M, 5.9 mmol) was added dropwise at 0 °C, and the mixture was stirred for 30 minutes at this temperature. Then, **S4a** (1.26 g) in 5 mL THF was added, and the reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 12 h. The reaction was quenched with saturated ammonium chloride solution, and the product was extracted with diethyl ether three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE/EA = 20/1 as the eluent yielded 740.9 mg **1a** as a white solid, with an overall yield of 49% over three steps.

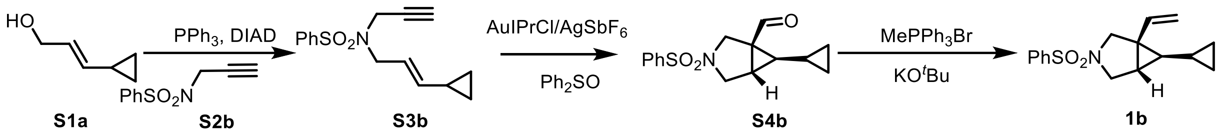
**TLC** (5:1 PE/EA, $R_f$): 0.6.

White solid, m.p. = 85.2-86.9 °C

**$^1$H NMR** (400 MHz, CDCl$_3$) δ 7.68 (d, $J$ = 8.0 Hz, 2H), 7.32 (d, $J$ = 8.0 Hz, 2H), 5.84 (dd, $J$ = 17.6, 10.9 Hz, 1H), 5.06 (dd, $J$ = 10.9, 1.1 Hz, 1H), 4.97 (dd, $J$ = 17.6, 1.1 Hz, 1H), 3.54 (d, $J$ = 9.0 Hz, 1H), 3.50 (d, $J$ = 9.2 Hz, 1H), 3.16 (d, $J$ = 9.0 Hz, 1H), 3.03 (dd, $J$ = 9.2, 3.9 Hz, 1H), 2.44 (s, 3H), 1.32 (dd, $J$ = 4.1, 4.1 Hz, 1H), 0.99 (dd, $J$ = 5.8, 4.3 Hz, 1H), 0.65 – 0.55 (m, 1H), 0.54 – 0.42 (m, 2H), 0.19 – 0.06 (m, 2H).

**$^{13}$C NMR** (101 MHz, CDCl$_3$) δ 143.7, 136.0, 133.4, 129.8, 127.7, 114.0, 51.5, 50.1, 34.5, 30.4, 28.6, 21.7, 8.4, 5.0, 4.8.

**HRMS** (ESI−FTICR, $m/z$): $[M + H]^+$ calculated for $C_{17}H_{22}NO_2S^+$: 304.1366, found: 304.1365



A 100 mL reaction flask equipped with a magnetic stirrer was charged with substrate **S1a** (589.0 mg, 6.0 mmol), **S2b** (984.0 mg, 5.0 mmol), $PPh_3$ (1.97 g, 7.5 mmol), and THF (20 mL). DIAD (1.52 g, 7.5 mmol) was added dropwise at 0 °C. The reaction was gradually allowed to warm to room temperature. After 7 hours of reaction, the reaction was quenched with $H_2O$, and the product was extracted with DCM three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE/EA = 20/1 as the eluent yielded 1.22 g of a yellow oil, which was a mixture of **S3b** and its $S_N2'$ isomer.[11] This mixture was directly used in the next step.

Inside a glovebox, IPrAuCl (31.1 mg, 0.05 mmol) and $AgSbF_6$ (17.2 mg, 0.05 mmol) were weighed into a 10 mL reaction tube equipped with a magnetic stirrer. The tube was sealed and removed from the glovebox. Under an argon atmosphere, DCM (2 mL) was added, and the mixture was stirred for 10 minutes at room temperature. In a separate reaction flask equipped with a magnetic stirrer, the mixture of **S3b** (523.0 mg, 2.0 mmol) prepared above was added, along with DCM (5 mL) and $Ph_2SO$ (859.0 mg, 4.0 mmol). The flask was evacuated and purged with argon, and then the gold catalyst solution was added. The reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 18 h. The reaction mixture was concentrated, and the residue was purified by column chromatography using PE/EA = 5/1 as the eluent to obtain a mixture of white solid **S4b** and unreacted $Ph_2SO$, which was directly used in the next step.

A reaction flask equipped with a magnetic stirrer was charged with $MePPh_3Br$ (857.0 mg, 2.4 mmol), ${}^tBuOK$ (269.0 mg, 2.4 mmol). The flask was evacuated and purged with argon, and then THF (10 mL) was added. After that, the mixture was stirred for 30 minutes at room temperature. Then, **S4b** in THF (2 mL) was added, and the reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 3 h. The reaction was quenched with saturated ammonium chloride solution, and the product was extracted with DCM three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE/EA = 15/1 as the eluent yielded 167.0 mg **1b** as a white solid, with an overall yield of 11% over three steps.

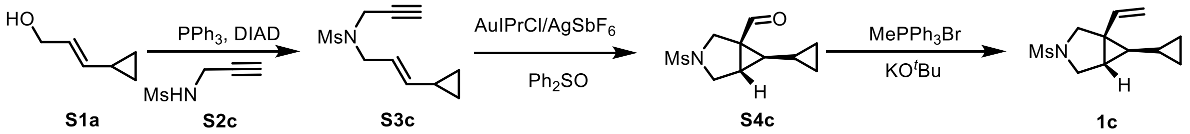
White solid, m.p. = 80.1-83.4 °C

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

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.75 (m, 2H), 7.63 – 7.57 (m, 1H), 7.56 – 7.50 (m, 2H), 5.84 (dd, $J$ = 17.6, 10.9 Hz, 1H), 5.06 (dd, $J$ = 10.9, 1.2 Hz, 1H), 4.97 (dd, $J$ = 17.5, 1.1 Hz, 1H), 3.56 (d, $J$ = 9.0 Hz, 1H), 3.52 (d, $J$ = 9.2 Hz, 1H), 3.18 (d, $J$ = 9.0 Hz, 1H), 3.06 (dd, $J$ = 9.2, 3.9 Hz, 1H), 1.33 (dd, $J$ = 4.0, 4.0 Hz, 1H), 0.96 (dd, $J$ = 5.8, 4.2 Hz, 1H), 0.66 – 0.55 (m, 1H), 0.57 – 0.39 (m, 2H), 0.19 – 0.07 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 136.5, 135.9, 132.9, 129.2, 127.6, 114.1, 51.5, 50.1, 34.4, 30.4, 28.6, 8.4, 5.0, 4.8.

**HRMS** (ESI−FTICR, $m/z$): $[M + H]^+$ calculated for $C_{16}H_{20}NO_2S^+$: 290.1209, found: 290.1206



A 100 mL reaction flask equipped with a magnetic stirrer was charged with substrate **S1a** (589.0 mg, 6.0 mmol), **S2c** (665.8 mg, 5.0 mmol), $PPh_3$ (1.57 g, 6.0 mmol), and THF (20 mL). DIAD (1.21 g, 6.0 mmol) was added dropwise at 0 °C. The reaction was gradually allowed to warm to room temperature. After 12 hours of reaction, the reaction was quenched with $H_2O$, and the product was extracted with DCM three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE/EA = 10/1 as the eluent yielded 853.2 mg of a white solid, which was a mixture of **S3c** and its $S_N2$’ isomer[11] (total yield: 80%). This mixture was directly used in the next step.

Inside a glovebox, IPrAuCl (49.7 mg, 0.080 mmol) and $AgSbF_6$ (27.5 mg, 0.080 mmol) were weighed into a 20 mL reaction tube equipped with a magnetic stirrer. The tube was sealed and removed from the glovebox. Under an argon atmosphere, DCM (2 mL) was added, and the mixture was stirred for 10 minutes at room temperature. In a separate reaction flask equipped with a magnetic stirrer, the mixture of **S3c** (566.0 mg, 2.6 mmol) prepared above was added, along with DCM (5 mL) and $Ph_2SO$ (1.05 g, 5.2 mmol). The flask was evacuated and purged with argon, and then the gold catalyst solution was added. The reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 24 h. The reaction mixture was concentrated, and the residue was purified by column chromatography using PE/EA = 2/1 to 1/1 as the eluent to obtain **S4c** (81.2 mg, 13%) as a white solid.

A reaction flask equipped with a magnetic stirrer was charged with $PPh_3MeBr$ (189.0 mg, 0.53 mmol), $^t$BuOK (59.5 mg, 0.53 mmol). The flask was evacuated and purged with argon, and then THF (2 mL) was added. After that, the mixture was stirred for 30 minutes at room temperature. Then, a THF solution of **S4c** in 2 mL of THF was added, and the reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 30 min. The reaction was quenched with saturated ammonium chloride solution, and the product was extracted with diethyl ether three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE/EA = 6/1 as the eluent yielded **1c** (54.4 mg, 68%) as a white solid.

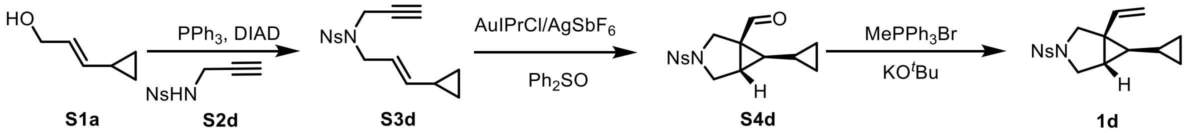
White solid, m.p. = 95.7-98.0 °C

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

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.93 (dd, $J$ = 17.6, 11.0 Hz, 1H), 5.14 (dd, $J$ = 11.0, 1.1 Hz, 1H), 5.06 (dd, $J$ = 17.5, 1.1 Hz, 1H), 3.56 (d, $J$ = 9.0 Hz, 1H), 3.51 (d, $J$ = 9.1 Hz, 1H), 3.45 (d, $J$ = 9.0 Hz, 1H), 3.33 (dd, $J$ = 9.1, 3.9 Hz, 1H), 2.83 (s, 3H), 1.45 (dd, $J$ = 4.1 Hz, 1H), 1.13 (dd, $J$ = 5.6, 4.2 Hz, 1H), 0.74 – 0.65 (m, 1H), 0.61 – 0.46 (m, 2H), 0.26 – 0.15 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 135.9, 114.3, 51.6, 50.1, 35.3, 34.7, 30.3, 28.6, 8.4, 5.0, 4.9.

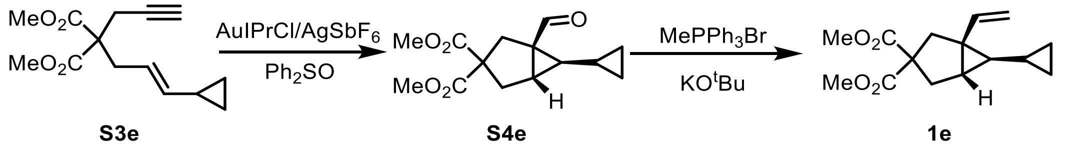
**HRMS** (ESI−FTICR, $m/z$): $[M + H]^+$ calculated for $C_{11}H_{18}NO_2S^+$: 228.1053, found: 228.1052.



A 100 mL reaction flask equipped with a magnetic stirrer was charged with substrate **S1a** (118.0 mg, 1.2 mmol), **S2d** (231.0 mg, 1.0 mmol), $PPh_3$ (393.0 mg, 1.5 mmol), and THF (5 mL). DIAD (303.0 mg, 1.5 mmol) was added dropwise at 0 °C. The reaction was gradually allowed to warm to room temperature. After 21 hours of reaction, the reaction was quenched with $H_2O$, and the product was extracted with DCM three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE/EA = 20/1 as the eluent yielded 240.0 mg of a yellow oil, which was a mixture of **S3c** and its $S_N2$’ isomer (total yield: 84%).[11] This mixture was directly used in the next step.

Inside a glovebox, IPrAuCl (14.9 mg, 0.024 mmol) and $AgSbF_6$ (8.2 mg, 0.024 mmol) were weighed into a 10 mL reaction tube equipped with a magnetic stirrer. The tube was sealed and removed from the glovebox. Under an argon atmosphere, DCM (1 mL) was added, and the mixture was stirred for 10 minutes at room temperature. In a separate reaction flask equipped with a magnetic stirrer, the mixture of **S3d** (240.0 mg, 0.8 mmol) prepared above was added, along with DCM (5 mL) and $Ph_2SO$ (318.0 mg, 1.6 mmol). The flask was evacuated and purged with argon, and then the gold catalyst solution was added. The reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 13.5 h. The reaction mixture was concentrated, and the residue was purified by column chromatography using PE/EA = 5/1 as the eluent to obtain a mixture of white solid **S4d** and unreacted $Ph_2SO$, which was directly used in the next step.

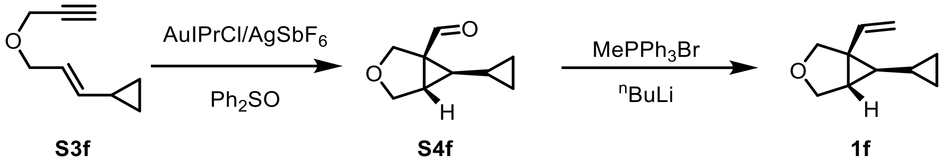
A reaction flask equipped with a magnetic stirrer was charged with $PPh_3MeBr$ (336.0 mg, 0.9 mmol), $^t$BuOK (105.0 mg, 0.9 mmol). The flask was evacuated and purged with argon, and then THF (5 mL) was added. After that, the mixture was stirred for 30 minutes at room temperature. Then, a THF solution of **S4d** in 5 mL of THF was added, and the reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 12 h. The reaction was quenched with saturated ammonium chloride solution, and the product was extracted with diethyl ether three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE/EA = 15/1 as the eluent yielded 69.5 mg **1d** as a white solid, with an overall yield of 21% over three steps.
White solid, m.p. = 124.7-127.1 °C
**TLC** (5:1 PE/EA, $R_f$): 0.8.
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.39 (d, $J$ = 8.8 Hz, 2H), 7.98 (d, $J$ = 8.8 Hz, 2H), 5.84 (dd, $J$ = 17.6, 10.9 Hz, 1H), 5.09 (dd, $J$ = 10.9, 1.0 Hz, 1H), 4.98 (dd, $J$ = 17.5, 1.0 Hz, 1H), 3.62 (d, $J$ = 9.0 Hz, 1H), 3.57 (d, $J$ = 9.2 Hz, 1H), 3.20 (d, $J$ = 9.0 Hz, 1H), 3.10 (dd, $J$ = 9.2, 3.9 Hz, 1H), 1.37 (t, $J$ = 4.1 Hz, 1H), 1.02 (dd, $J$ = 5.6, 4.2 Hz, 1H), 0.68 – 0.59 (m, 1H), 0.57 – 0.41 (m, 2H), 0.24 – 0.07 (m, 2H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 150.3, 142.5, 135.4, 128.7, 124.5, 114.6, 51.7, 50.4, 34.5, 30.5, 28.3, 8.3, 5.0, 4.9.
**HRMS** (ESI−FTICR, $m/z$): $[M + H]^+$ calculated for $C_{16}H_{19}N_2O_4S^+$: 335.1060, found: 335.1059



In a glovebox, IPrAuCl (80.7 mg, 0.13 mmol) and $AgSbF_6$ (44.7 mg, 0.13 mmol) were weighed into a 10 mL reaction tube equipped with a magnetic stirrer. The tube was sealed and removed from the glovebox. Under an argon atmosphere, DCM (5 mL) was added, and the mixture was stirred for 10 minutes at room temperature. In another reaction flask equipped with a magnetic stirrer, **S3e** (1.3 g, 5.2 mmol) was added, along with DCM (25 mL) and $Ph_2SO$ (2.1 g, 10.3 mmol). The flask was evacuated and purged with argon, and then the gold catalyst solution was added. The reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 16 h. The reaction mixture was concentrated, and the residue was purified by column chromatography using PE/EA = 10/1 as the eluent to obtain a mixture of colorless oil **S4e** and unreacted $Ph_2SO$ (968.6 mg, the ratio is 1:3.75, 18%), which was directly used in the next step.

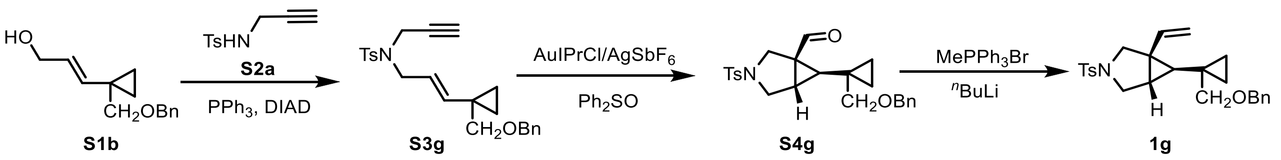
A reaction flask equipped with a magnetic stirrer was charged with $MePPh_3Br$ (1.2 g, 3.4 mmol), $^t$BuOK (336.6 mg, 3.0 mmol). The flask was evacuated and purged with argon, and THF (8 mL) was added. The mixture was stirred for 30 minutes at 0 °C. Then, a THF (2 mL) solution of **S4e** prepared above was added, and the reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 3 h. The reaction was quenched with saturated ammonium chloride solution, and the product was extracted with diethyl ether three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE/EA = 20/1 as the eluent yielded 44.8 mg **1e** as a light yellow oil, with an overall yield of 3% over two steps.
Light yellow oil
**TLC** (5:1 PE/EA, $R_f$): 0.6
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.94 (dd, $J$ = 17.4, 10.8 Hz, 1H), 5.09 (d, $J$ = 17.5 Hz, 1H), 5.04 (dd, $J$ = 10.8, 1.5 Hz, 1H), 3.71 (s, 3H), 3.69 (s, 3H), 2.69 – 2.55 (m, 2H), 2.55 – 2.46 (m, 2H), 1.26 (dd, $J$ = 4.5, 4.5 Hz, 1H), 0.69 – 0.60 (m, 2H), 0.52 – 0.40 (m, 2H), 0.13 (dd, $J$ = 6.7, 4.1 Hz, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 173.2, 172.5, 139.1, 112.5, 60.2, 53.1, 53.0, 38.5, 36.5, 36.5, 32.7, 30.8, 9.3, 5.0, 4.9.
**HRMS** (ESI−FTICR, *m*/*z*): $[M + H]^+$ calculated for $C_{15}H_{21}O_4^+$: 265.1434, found: 265.1432



In a glovebox, IPrAuCl (47.0 mg, 0.08 mmol) and $AgSbF_6$ (26.1 mg, 0.08 mmol) were weighed into a 10 mL reaction tube equipped with a magnetic stirrer. The tube was sealed and removed from the glovebox. Under an argon atmosphere, DCM (2 mL) was added, and the mixture was stirred for 10 minutes at room temperature. In another reaction flask equipped with a magnetic stirrer, **S3f** (515.4 mg, 3.8 mmol) was added, along with DCM (50 mL) and $Ph_2SO$ (1.53 g, 7.8 mmol). The flask was evacuated and purged with argon, and then the gold catalyst solution was added. The reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 16 h. The reaction mixture was concentrated, and the residue was purified by column chromatography using PE/EA = 100/1 ~ 75/1 ~ 30/1 as the eluent to obtain a mixture of white solid **S4f** and unreacted $Ph_2SO$ (285.0 mg), which was directly used in the next step.

A reaction flask equipped with a magnetic stirrer was charged with $PPh_3MeBr$ (1.12 g, 3 mmol). The flask was evacuated and purged with argon, and then THF (10 mL) was added. After that, *$^n$*BuLi (1.2 mL, 2.4 M, 2.8 mmol) was added dropwise at 0 °C, and the mixture was stirred for 30 minutes at this temperature. Then, a THF (2 mL) solution of **S4f** (285.0 mg) was added, and the reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 16 h. The reaction was quenched with saturated ammonium chloride solution, and the product was extracted with diethyl ether three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE/EA = 20/1 as the eluent yielded 142.9 mg **1f** as a light yellow oil, with an overall yield of 25% over two steps.
Light yellow oil
**TLC** (5:1 PE/EA, *R$_f$*): 0.8.
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 6.09 – 6.00 (m, 1H), 5.17 – 4.93 (m, 2H), 3.87 (d, *J* = 8.1 Hz, 1H), 3.81 – 3.76 (m, 2H), 3.72 (dd, *J* = 8.2, 2.9 Hz, 1H), 1.42 (dd, *J* = 4.4, 2.9 Hz, 1H), 0.97 (dd, *J* = 5.0, 5.0 Hz, 1H), 0.74 – 0.67 (m, 1H), 0.57 – 0.47 (m, 2H), 0.20 – 0.17 (m, 2H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 135.9, 113.8, 71.1, 70.0, 35.8, 30.1, 29.5, 8.4, 4.9, 4.8.
**HRMS** (ESI−FTICR, *m*/*z*): $[M + H]^+$ calculated for $C_{10}H_{15}O^+$: 151.1117, found: 151.1118.



A 100 mL reaction flask equipped with a magnetic stirrer was charged with substrate **S1b** (512.9 mg, 2.4 mmol), **S2a** (491.7 mg, 2.4 mmol), $PPh_3$ (924.4 mg, 3.5 mmol), and THF (15 mL). DIAD (712.7 mg, 3.5 mmol) was added dropwise at 0 °C. The reaction was gradually allowed to warm to room temperature. After 12 hours of reaction, the solvent was removed by rotary evaporation, and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 20:1) to afford 0.73 g of a light yellow oil, which was a mixture of **S3g** and its $S_N2'$ isomer.[11] This mixture was directly used in the next step.

Inside a glovebox, IPrAuCl (22.4 mg, 0.036 mmol) and $AgSbF_6$ (12.4 mg, 0.036 mmol) were weighed into a 10 mL reaction tube equipped with a magnetic stirrer. The tube was sealed and removed from the glovebox. Under an argon atmosphere, DCM (2 mL) was added, and the mixture was stirred for 10 minutes at room temperature. In a separate reaction flask equipped with a magnetic stirrer, **S3g** (730.0 mg, 1.8 mmol) prepared above was added, along with DCM (18 mL) and Ph$_2$SO (721.1 mg, 3.6 mmol). The flask was evacuated and purged with argon, and then the gold catalyst solution was added. The reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 24 h. The reaction mixture was concentrated, and the residue was purified by column chromatography using PE/EA = 6/1 as the eluent to obtain a mixture of white solid **S4g** and unreacted Ph$_2$SO (307.4 mg), which was directly used in the next step.

A reaction flask equipped with a magnetic stirrer was charged with PPh$_3$MeBr (412.9 mg, 1.2 mmol). The flask was evacuated and purged with argon, and then THF (5 mL) was added. After that, $^{n}$BuLi (0.45 mL, 2.4 M, 1.1 mmol) was added dropwise at 0 °C, and the mixture was stirred for 30 minutes at this temperature. Then, **S4g** (307.4 mg) in 2 mL THF was added, and the reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 14 h. The reaction was quenched with saturated ammonium chloride solution, and the product was extracted with diethyl ether three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE/EA = 10/1 as the eluent yielded 178.0 mg **1g** as a yellow oil, with an overall yield of 18% over three steps.

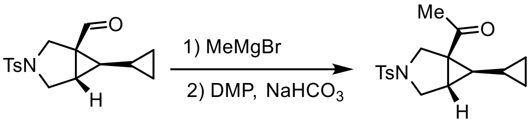
Yellow oil

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

**$^1$H NMR** (400 MHz, CDCl$_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.39 – 7.26 (m, 7H), 5.79 (dd, *J* = 17.6, 11.0 Hz, 1H), 4.97 (dd, *J* = 11.0, 1.1 Hz, 1H), 4.88 (dd, *J* = 17.6, 1.1 Hz, 1H), 4.52 (d, *J* = 12.3 Hz, 1H), 4.44 (d, *J* = 12.3 Hz, 1H), 3.57 (d, *J* = 9.6 Hz, 1H), 3.55 (d, *J* = 9.6 Hz, 1H), 3.44 (d, *J* = 9.1 Hz, 1H), 3.17 (d, *J* = 8.9 Hz, 1H), 3.02 (dd, *J* = 9.0, 4.0 Hz, 1H), 2.95 (d, *J* = 9.6 Hz, 1H), 2.42 (s, 3H), 1.80 (d, *J* = 4.4 Hz, 1H), 1.20 (dd, *J* = 4.2, 4.2 Hz, 1H), 0.68 – 0.57 (m, 1H), 0.46 – 0.34 (m, 2H), 0.32 – 0.23 (m, 1H).

**$^{13}$C NMR** (101 MHz, CDCl$_3$) δ 143.6, 138.7, 136.0, 133.6, 129.8, 128.5, 127.7, 127.7, 127.6, 113.6, 76.0, 72.9, 51.5, 50.0, 35.0, 29.5, 26.5, 21.7, 17.6, 9.9, 8.9.

**HRMS** (ESI−FTICR, *m/z*): $[M + H]^+$ calculated for C$_{25}$H$_{30}$NO$_3$S$^+$: 424.1941, found: 424.1938



**S4a** **S5a**

The 100 mL reaction flask was evacuated, protected by N$_2$, and **S4a** in THF (5 mL) was added, followed by the slow dropwise addition of MeMgBr (1.1 mL, 1.0 M in THF), brought to room temperature and stirred. After stirring for 17 h, the reaction was quenched by saturated ammonium chloride, extracted three times with ether, washed with brine, dried with anhydrous sodium sulfate, filtered, concentrated, and purified through column chromatography (by PE/EA = 2/1) to obtain the target product. To the above product was added NaHCO$_3$ (588.0 mg, 7.0 mmol), DCM (10 mL) followed by DMP (467.0 mg, 1.1 mmol), stirred at room temperature for 12 h, then DMP (933.0 mg, 2.2 mmol) was added and stirred at room temperature for 0.5 h. The reaction was quenched by the addition of H$_2$O, extracted with DCM, washed with saturated NaHCO$_3$ solution, washed with brine, dried with anhydrous sodium sulfate, filtered, concentrated, and separated by column chromatography using PE/EA = 4/1 to give **S5a** (157.0 mg) as a colorless oil, with a total yield of 70% in two steps.

Colorless oil

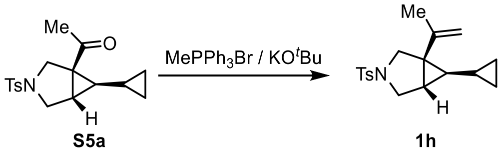
**TLC** (3:1 PE/EA, $R_f$): 0.3.

**$^1$H NMR** (400 MHz, CDCl$_3$) δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 3.77 (d, *J* = 9.2 Hz, 1H), 3.55 (d, *J* = 9.3 Hz, 1H), 3.23 (d, *J* = 9.2 Hz, 1H), 3.03 (dd, *J* = 9.3, 3.9 Hz, 1H), 2.43 (s, 3H), 2.17 (s, 3H), 2.09 (dd, *J* = 5.3, 3.9 Hz, 1H), 1.03 (dd, *J* = 7.8, 5.3 Hz, 1H), 0.74 – 0.63 (m, 1H), 0.61 – 0.52 (m, 1H), 0.46

(dddd, *J* = 9.4, 8.0, 5.5, 4.2 Hz, 1H), 0.27 – 0.21 (m, 1H), 0.12 – 0.04 (m, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 203.9, 144.0, 133.0, 129.9, 127.8, 127.7, 50.4, 49.7, 43.6, 36.6, 31.2, 29.7, 21.7, 7.6, 5.9, 5.0.

**HRMS** (ESI−FTICR, *m*/*z*): $[M + H]^+$ calculated for $C_{17}H_{22}NO_3S^+$: 320.1315, found: 320.1316



A reaction flask equipped with a magnetic stirrer was charged with $PPh_3MeBr$ (357.0 mg, 1.00 mmol) and $^t$BuOK (112.0 mg, 1.00 mmol). The flask was evacuated and purged with $N_2$, and THF (5 mL) was added at room temperature, and the mixture was stirred for 30 minutes at this temperature. Then, **S5a** (157.0 mg) in 5 mL THF was added, and the reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 4 h. The reaction was quenched with saturated ammonium chloride solution, and the product was extracted with DCM three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE/EA = 10/1 as the eluent yielded **1h** (108.0 mg, 69%) as a white solid.

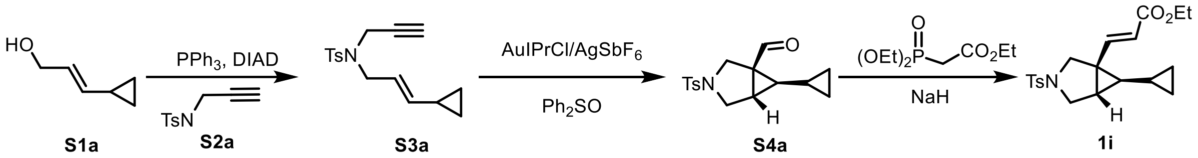
White solid, m.p. = 105.5-106.1 °C

**TLC** (3:1 PE/EA, $R_f$): 0.8.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.89 (d, *J* = 1.7 Hz, 1H), 4.70 (d, *J* = 1.9 Hz, 1H), 3.66 (d, *J* = 8.9 Hz, 1H), 3.54 (d, *J* = 9.1 Hz, 1H), 3.08 (dd, *J* = 9.1, 3.8 Hz, 1H), 2.89 (d, *J* = 8.9 Hz, 1H), 2.43 (s, 3H), 1.77 (d, *J* = 1.2 Hz, 3H), 1.39 (dd, *J* = 3.8, 3.8 Hz, 1H), 0.58 (dd, *J* = 7.4, 3.8 Hz, 1H), 0.48 – 0.41 (m, 1H), 0.41 – 0.31 (m, 2H), 0.15 – 0.07 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 143.6, 141.5, 133.7, 129.8, 127.7, 113.3, 54.0, 50.5, 38.2, 29.9, 25.8, 22.6, 21.7, 8.5, 4.8, 4.4.

**HRMS** (ESI−FTICR, *m*/*z*): $[M + H]^+$ calculated for $C_{18}H_{24}NO_2S^+$: 318.1522, found: 318.1521



A 100 mL reaction flask equipped with a magnetic stirrer was charged with substrate **S1a** (1.6 g, 16 mmol), **S2a** (4.0 g, 19.2 mmol), $PPh_3$ (6.3 g, 24.0 mmol), and THF (40 mL). DIAD (4.9 g, 24.0 mmol) was added dropwise at 0 °C. The reaction was gradually allowed to warm to room temperature. After 18 hours of reaction, the solvent was removed by rotary evaporation, and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 20:1) to afford 3.4 g white solid, which was a mixture of **S3a** and its $S_N2'$ isomer (total yield: 72%).[11] This mixture was directly used in the next step.

Inside a glovebox, IPrAuCl (82.2 mg, 0.13 mmol) and $AgSbF_6$ (45.5 mg, 0.13 mmol) were weighed into a 10 mL reaction tube equipped with a magnetic stirrer. The tube was sealed and removed from the glovebox. Under an argon atmosphere, DCM (6 mL) was added, and the mixture was stirred for 10 minutes at room temperature. In a separate reaction flask equipped with a magnetic stirrer, the mixture of **S3a** (3.4 g, 11.6 mmol) prepared above was added, along with DCM (60 mL) and $Ph_2SO$ (2.7 g, 13.2 mmol). The flask was evacuated and purged with argon, and then the gold catalyst solution was added. The reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 12 h. The reaction mixture was concentrated, and the residue was purified by column chromatography using PE/EA = 5/1 as the eluent to obtain a white solid **S4a** (2.0 g, 6.7 mmol).

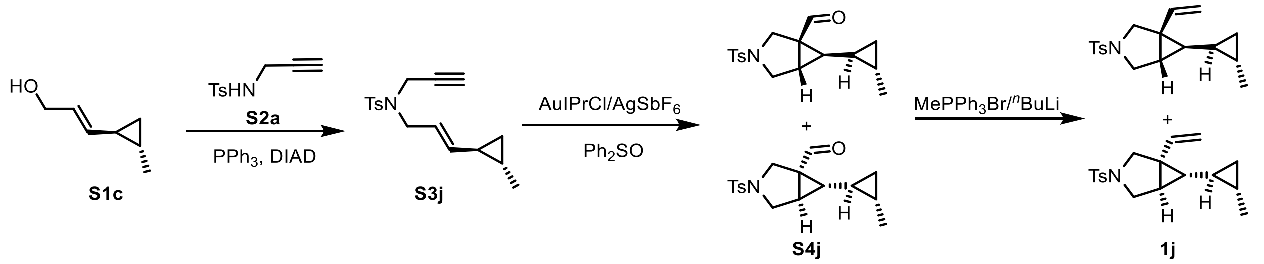
A reaction flask equipped with a magnetic stirrer was charged with NaH (0.26 g, 6.5 mmol, 60% weight in mineral oil). The flask was evacuated and purged with argon, and THF (30 mL) was added. $(EtO)_2POCH_2COOEt$ (2.37 g, 6.3 mmol) was added dropwise at 0 °C, and the mixture was stirred for 30 minutes at this temperature. Then, **S4a** (1.52 g) in 5 mL THF was added, and the reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 12 h. The reaction was quenched with saturated ammonium chloride solution, and the product was extracted with diethyl ether three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE/EA = 15/1 as the eluent yielded 1.60 g **1i** as a white solid, with an overall yield of 35% over three steps.

White solid, m.p. = 99.8-101.2 °C

$^1$**H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, $J$ = 8.2 Hz, 2H), 7.34 (d, $J$ = 8.3 Hz, 2H), 6.97 (d, $J$ = 15.9 Hz, 1H), 5.73 (d, $J$ = 15.9 Hz, 1H), 4.17 (qd, $J$ = 7.2, 1.2 Hz, 2H), 3.56 (dd, $J$ = 9.2, 2.3 Hz, 2H), 3.11 (d, $J$ = 9.0 Hz, 1H), 3.00 (dd, $J$ = 9.3, 3.9 Hz, 1H), 2.44 (s, 3H), 1.61 (t, $J$ = 4.2 Hz, 1H), 1.31 (t, $J$ = 5.3 Hz, 1H), 1.27 (t, $J$ = 7.2 Hz, 3H), 0.76 – 0.66 (m, 1H), 0.61 – 0.49 (m, 2H), 0.24 – 0.12 (m, 2H).

$^{13}$**C NMR** (101 MHz, $CDCl_3$) δ 166.3, 147.2, 143.9, 133.0, 129.9, 127.7, 119.6, 60.5, 50.6, 49.8, 34.6, 32.8, 31.5, 21.7, 14.4, 8.5, 5.3, 5.0.

**HRMS** (ESI−FTICR, *m/z*): $[M + H]^+$ calculated for $C_{20}H_{26}NO_4S^+$: 376.1577, found: 376.1571.



A 100 mL reaction flask equipped with a magnetic stirrer was charged with substrate **S1c** (199.2 mg, 1.8 mmol), **S2a** (371.6 mg, 1.8 mmol), $PPh_3$ (698.7 mg, 2.7 mmol), and THF (15 mL). DIAD (538.6 mg, 2.7 mmol) was added dropwise at 0 °C. The reaction was gradually allowed to warm to room temperature. After 21 hours of reaction, the solvent was removed by rotary evaporation, and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 20:1) to afford 462.8 mg of a light red oil, which was a mixture of **S3j** and its $S_N2'$ isomer.[11] This mixture was directly used in the next step.

Inside a glovebox, IPrAuCl (23.7 mg, 0.038 mmol) and $AgSbF_6$ (13.1 mg, 0.038 mmol) were weighed into a 10 mL reaction tube equipped with a magnetic stirrer. The tube was sealed and removed from the glovebox. Under an argon atmosphere, DCM (1 mL) was added, and the mixture was stirred for 10 minutes at room temperature. In a separate reaction flask equipped with a magnetic stirrer, the mixture of **S3j** (462.8 mg, 1.5 mmol) prepared above was added, along with DCM (15 mL) and $Ph_2SO$ (617.0 mg, 3.0 mmol). The flask was evacuated and purged with argon, and then the gold catalyst solution was added. The reaction was stirred at room temperature for 18 h and then moved into a 40 °C oil bath. The reaction was monitored by TLC and stirred for further 24 h. The reaction mixture was concentrated, and the residue was purified by column chromatography using PE/EA = 10/1~5/1 as the eluent to obtain a mixture of white solid **S4j** and unreacted $Ph_2SO$ (501.0 mg), which was directly used in the next step.

A reaction flask equipped with a magnetic stirrer was charged with $PPh_3MeBr$ (571.6 mg, 1.6 mmol). The flask was evacuated and purged with argon, and THF (5 mL) was added. $^n$BuLi (0.6 mL, 2.4 M, 1.5 mmol) was added dropwise at 0 °C, and the mixture was stirred for 30 minutes at this temperature. Then, a THF (1 mL) solution of **S4j** was added, and the reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 5 h. The reaction was quenched with saturated ammonium chloride solution, and the product was extracted with diethyl ether three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using

PE/EA = 15/1 as the eluent yielded 76.9 mg **1j** as a light yellow oil, with an overall yield of 14% over three steps. The obtained **1j** is an inseparable mixture of two diastereomers, *dr* = 1:2 according to the $^{13}$C NMR). The following peaks for the major isomer were selected from the $^{1}$H NMR and $^{13}$C NMR of the diastereomers:

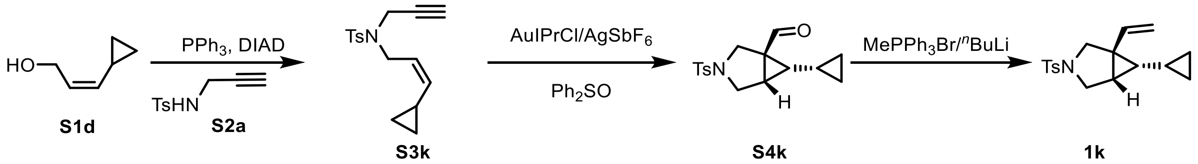
Light yellow oil

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

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, $J$ = 8.1 Hz, 2H), 7.32 (d, $J$ = 8.1 Hz, 2H), 5.80 (ddd, $J$ = 17.6, 10.9, 9.5 Hz, 1H), 5.06 (ddd, $J$ = 10.9, 4.1, 1.1 Hz, 1H), 4.96 (ddd, $J$ = 17.6, 1.5, 1.5 Hz, 1H), 3.53 (dd, $J$ = 8.9, 1.9 Hz, 1H), 3.49 (d, $J$ = 9.2 Hz, 1H), 3.16 (dd, $J$ = 9.0, 2.0 Hz, 1H), 3.02 (dd, $J$ = 9.1, 3.9 Hz, 1H), 2.43 (s, 3H), 1.29 (t, $J$ = 4.2 Hz, 1H), 1.06 – 1.00 (m, 1H), 0.98 (dd, $J$ = 9.0, 5.9 Hz, 3H), 0.56 – 0.45 (m, 1H), 0.32 – 0.20 (m, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 143.6, 136.0, 133.5, 129.8, 127.7, 114.0, 51.4, 50.1, 34.3, 30.1, 28.8, 21.7, 18.7, 17.1, 13.3, 12.9.

**HRMS** (ESI−FTICR, *m/z*): $[M + H]^+$ calculated for $C_{18}H_{24}NO_2S^+$: 318.1522, found: 318.1520



A 250 mL reaction flask equipped with a magnetic stirrer was charged with substrate **S1d** (980.0 mg, 10.0 mmol), **S2a** (2.09 g, 10.0 mmol), $PPh_3$ (3.93 g, 15.0 mmol), and THF (50 mL). DIAD (3.03 g, 15.0 mmol) was added dropwise at 0 °C. The reaction was gradually allowed to warm to room temperature. After 16 hours of reaction, the solvent was removed by rotary evaporation, and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 20:1~10:1) to afford 1.26 g of while solid, which was a mixture of **S3k** and its S$_N$2’ isomer.[11] This mixture was directly used in the next step.

Inside a glovebox, IPrAuCl (68.3 mg, 0.1 mmol) and $AgSbF_6$ (37.8 mg, 0.1 mmol) were weighed into a 10 mL reaction tube equipped with a magnetic stirrer. The tube was sealed and removed from the glovebox. Under an argon atmosphere, DCM (2 mL) was added, and the mixture was stirred for 10 minutes at room temperature. In a separate reaction flask equipped with a magnetic stirrer, the mixture of **S3k** (1.26 g, 4.4 mmol) prepared above was added, along with DCM (40 mL) and $Ph_2SO$ (1.78 g, 8.8 mmol). The flask was evacuated and purged with argon, and then the gold catalyst solution was added. The reaction was stirred at room temperature for 19 h. The reaction mixture was concentrated, and the residue was purified by column chromatography using PE/EA = 5/1 as the eluent to obtain a mixture of white solid **S4k** and unreacted $Ph_2SO$ (497.3 mg), which was directly used in the next step.

A reaction flask equipped with a magnetic stirrer was charged with $MePPh_3Br$ (685.3 mg, 1.6 mmol). The flask was evacuated and purged with argon, and THF (8 mL) was added. $^{n}$BuLi (0.75 mL, 2.4 M, 1.8 mmol) was added dropwise at 0 °C, and the mixture was stirred for 30 minutes at this temperature. Then, a THF (2 mL) solution of **S4k** (497.3 mg) was added, and the reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 5 h. The reaction was quenched with saturated ammonium chloride solution, and the product was extracted with diethyl ether three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE/EA = 20/1 as the eluent yielded 338.3 mg **1k** as a colorless oil, with an overall yield of 11% over three steps.

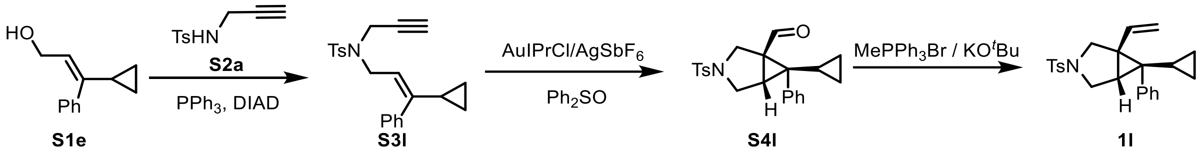
Colorless oil

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

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, $J$ = 8.2 Hz, 2H), 7.32 (d, $J$ = 8.2 Hz, 2H), 5.51 (dd, $J$ = 17.3, 10.7 Hz, 1H), 4.91 – 4.82 (m, 2H), 3.62 (dd, $J$ = 15.7, 9.3 Hz, 2H), 3.42 (d, $J$ = 9.2 Hz, 1H), 3.36 (dd, $J$ = 9.4, 4.9 Hz, 1H), 2.42 (s, 3H), 1.52 (dd, $J$ = 8.1, 4.8 Hz, 1H), 0.64 – 0.58 (m, 1H), 0.54 (dd, $J$ = 8.3, 8.3 Hz, 1H), 0.51 – 0.43 (m, 2H), 0.19 – 0.13 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 143.5, 139.6, 133.8, 129.7, 127.6, 112.2, 49.1, 47.6, 34.3, 33.6, 28.5, 21.6, 5.0, 4.9, 3.6.

**HRMS** (ESI−FTICR, *m*/*z*): $[M + H]^+$ calculated for $C_{17}H_{22}NO_2S^+$: 304.1366, found: 304.1368



A 100 mL reaction flask equipped with a magnetic stirrer was charged with substrate **S1e** (0.80 g, 4.6 mmol), **S2b** (1.20 g, 5.5 mmol), $PPh_3$ (1.80 g, 6.4 mmol), and THF (20 mL). DIAD ((1.40 g, 6.4 mmol) was added dropwise at 0 °C. The reaction was gradually allowed to warm to room temperature. After 4 hours of reaction, the reaction was quenched with $H_2O$, and the product was extracted with DCM three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE/EA = 20/1~10/1 as the eluent yielded 0.8 g of a pink oil, which was a mixture of **S3l** and its $S_N2'$ isomer.[11] This mixture was directly used in the next step.

Inside a glovebox, IPrAuCl (37.3 mg, 0.06 mmol) and $AgSbF_6$ (24.6 mg, 0.06 mmol) were weighed into a 10 mL reaction tube equipped with a magnetic stirrer. The tube was sealed and removed from the glovebox. Under an argon atmosphere, DCM (5 mL) was added, and the mixture was stirred for 10 minutes at room temperature. In a separate reaction flask equipped with a magnetic stirrer, the mixture of **S3l** prepared above was added, along with DCM (8 mL) and $Ph_2SO$ (0.6 g, 3 mmol). The flask was evacuated and purged with argon, and then the gold catalyst solution was added. The reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 19 h. The reaction mixture was concentrated, and the residue was purified by column chromatography using PE/EA = 6/1~4/1 as the eluent to obtain a mixture of white solid **S4l** and unreacted $Ph_2SO$ (<2 mmol), which was directly used in the next step.

A reaction flask equipped with a magnetic stirrer was charged with $MePPh_3Br$ (714.0 mg, 2.0 mmol), $^t$BuOK (224.0 mg, 2.0 mmol). The flask was evacuated and purged with argon, and then THF (10 mL) was added. The mixture was stirred for 30 minutes at room temperature. Then, **S4l** in THF (5 mL) was added, and the reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 12 h. The reaction was quenched with saturated ammonium chloride solution, and the product was extracted with DCM three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE/EA = 40/1 as the eluent yielded 167.0 mg **1l** as a yellow solid, with an overall yield of 12% over three steps.

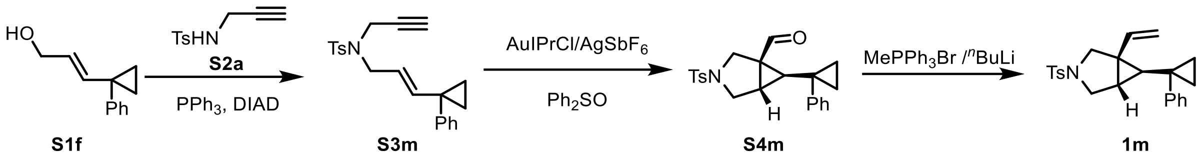
Yellow solid, m.p. = 116.5-117.7 °C.

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

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.27 (dd, $J$ = 6.1, 4.6 Hz, 3H), 7.18 (d, $J$ = 8.2 Hz, 2H), 7.13 (d, $J$ = 8.1 Hz, 2H), 7.06 – 7.01 (m, 2H), 6.19 (dd, $J$ = 17.5, 10.9 Hz, 1H), 5.23 – 5.10 (m, 2H), 3.47 (d, $J$ = 9.3 Hz, 1H), 3.45 – 3.36 (m, 2H), 3.33 (d, $J$ = 9.3 Hz, 1H), 2.38 (s, 3H), 1.74 (d, $J$ = 4.3 Hz, 1H), 0.91 (td, $J$ = 8.2, 4.1 Hz, 1H), 0.49 – 0.35 (m, 2H), 0.22 – 0.10 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 143.1, 137.4, 136.7, 134.5, 129.5, 128.5, 128.3, 127.5, 126.7, 115.2, 49.5, 47.4, 39.4, 38.4, 32.4, 21.6, 17.7, 5.1, 3.3.

**HRMS** (ESI−FTICR, *m*/*z*): $[M + H]^+$ calculated for $C_{23}H_{26}NO_2S^+$: 380.1679, found: 380.1680



A 100 mL reaction flask equipped with a magnetic stirrer was charged with substrate **S1f** (1.00 g, 5.7 mmol), **S2a** (1.20 g, 5.7 mmol), $PPh_3$ (2.00 g, 7.7 mmol), and THF (23 mL). DIAD (1.20 g, 6.0 mmol) was added dropwise at 0 °C. The reaction was gradually allowed to warm to room temperature. After 16 hours of reaction, the solvent was removed by rotary evaporation, and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 20:1~10:1) to afford 1.90 g of while solid, which was a mixture of **S3m** and its $S_N2'$ isomer.[11] This mixture was directly used in the next step.

Inside a glovebox, IPrAuCl (62.1 mg, 0.1 mmol) and $AgSbF_6$ (34.3 mg, 0.1 mmol) were weighed into a 10 mL reaction tube equipped with a magnetic stirrer. The tube was sealed and removed from the glovebox. Under an argon atmosphere, DCM (5 mL) was added, and the mixture was stirred for 10 minutes at room temperature. In a separate reaction flask equipped with a magnetic stirrer, the mixture of **S3m** (1.9 g, 5.2 mmol) prepared above was added, along with DCM (50 mL) and $Ph_2SO$ (2.1 g, 10.4 mmol). The flask was evacuated and purged with argon, and then the gold catalyst solution was added. The reaction was stirred at room temperature for 18 h. The reaction mixture was concentrated, and the residue was purified by column chromatography using PE/EA = 6/1~4/1 as the eluent to obtain a mixture of white solid **S4m** and unreacted $Ph_2SO$ (299.8 mg), which was directly used in the next step.

A reaction flask equipped with a magnetic stirrer was charged with $MePPh_3Br$ (407.0 mg, 1.1 mmol). The flask was evacuated and purged with argon, and then THF (4 mL) was added. After that, $^n$BuLi (0.5 mL, 2.4 M, 1.1 mmol) was added dropwise at 0 °C, and the mixture was stirred for 30 minutes at this temperature. Then, a THF (1 mL) solution of **S4m** (299.8 mg) was added, and the reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 12 h. The reaction was quenched with saturated ammonium chloride solution, and the product was extracted with diethyl ether three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE/EA = 15/1 as the eluent yielded 186.9 mg **1m** as a white solid, with an overall yield of 9% over three steps.

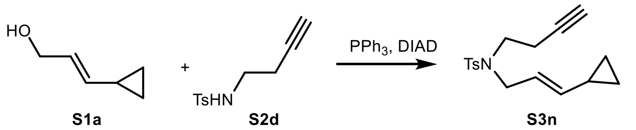
White solid, m.p.= 151.3-152.6 °C

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

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, $J$ = 8.2 Hz, 2H), 7.33 (d, $J$ = 8.0 Hz, 2H), 7.26 – 7.22 (m, 2H), 7.18 – 7.11 (m, 3H), 5.79 (dd, $J$ = 17.6, 11.0 Hz, 1H), 4.95 (dd, $J$ = 10.9, 1.0 Hz, 1H), 4.90 (dd, $J$ = 17.6, 1.1 Hz, 1H), 3.65 (d, $J$ = 9.1 Hz, 1H), 3.54 (d, $J$ = 9.2 Hz, 1H), 3.22 (d, $J$ = 9.1 Hz, 1H), 3.08 (dd, $J$ = 9.2, 4.0 Hz, 1H), 2.43 (s, 3H), 1.92 (d, $J$ = 4.3 Hz, 1H), 1.28 (dd, $J$ = 4.2, 4.2 Hz, 1H), 1.01 – 0.90 (m, 2H), 0.85 – 0.70 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 145.2, 143.8, 135.5, 133.4, 129.8, 128.2, 127.7, 126.6, 125.8, 114.1, 51.5, 50.3, 35.7, 32.4, 26.7, 21.7, 20.7, 15.4, 14.5.

**HRMS** (ESI–FTICR, $m/z$): $[M + H]^+$ calculated for $C_{23}H_{26}NO_2S^+$: 380.1679, found: 380.1680



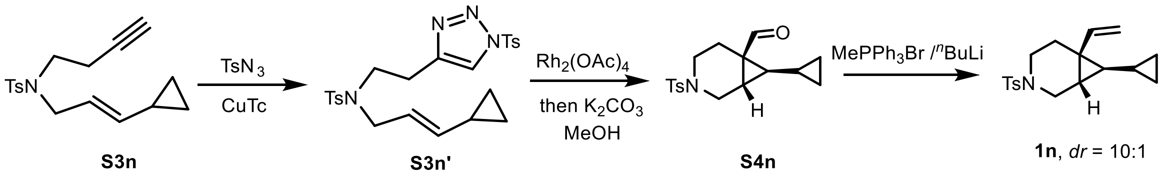
A 100 mL reaction flask equipped with a magnetic stirrer was charged with substrate **S1a** (294.4 mg, 3.0 mmol), **S2d** (669.9 mg, 3.0 mmol), $PPh_3$ (1180.3 mg, 4.5 mmol), and THF (30 mL). DIAD (909.9 mg, 4.5 mmol) was added dropwise at 0 °C. The reaction was gradually allowed to warm to room temperature. After 16 hours of reaction, the solvent was removed by rotary evaporation, and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA = 30:1) to afford **S3n** (599.2 mg, 66%). Light yellow oil.

**TLC** (5:1 PE/EA, *R<sub>f</sub>*): 0.4.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 5.30 (dt, *J* = 15.3, 6.7 Hz, 1H), 5.11 (ddt, *J* = 15.3, 8.7, 1.2 Hz, 1H), 3.77 (dd, *J* = 6.7, 1.2 Hz, 2H), 3.27 (dd, *J* = 8.2, 6.9 Hz, 2H), 2.48 – 2.42 (m, 2H), 2.42 (s, 3H), 1.96 (s, 1H), 1.39 – 1.25 (m, 1H), 0.75 – 0.63 (m, 2H), 0.38 – 0.24 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 143.4, 140.0, 137.2, 129.8, 127.3, 121.6, 81.3, 70.1, 50.6, 45.7, 21.6, 19.5, 13.4, 6.9.

**HRMS** (ESI−FTICR, *m/z*): $[M + H]^+$ calculated for $C_{17}H_{22}NO_2S^+$: 304.1366, found: 304.1362



The following procedure was based on the reported literature.[2]

To a solution of **S3n** (303.4 mg, 1.0 mmol) in $CHCl_3$ (5 mL) under Ar, CuTc (38.1 mg, 0.2 mmol) and $TsN_3$ (289.2 mg, 75% in EA, 1.1 mmol) were added in sequence, the reaction mixture was stirred at room temperature for 1 h. The reaction was quenched by saturated $NH_4Cl$, extracted with DCM, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE/EA = 4/1~3/1 as the eluent yielded **S3n'** (420.4 mg, 84%) as a white solid.

*N*-Allyl triazole **S3n'** (420.4 mg, 0.8 mmol) and $Rh_2(OAc)_4$ (7.4 mg, 0.02 mmol, 2 mol %) were added to a 50 mL round bottom flask equipped with a stirrer bar, then 8 mL of toluene was added to the flask. The reaction mixture was stirred at room temperature for 2 h and 80 °C for 3 h under $N_2$. Then, it was cooled to room temperature and concentrated under reduced pressure. The resulting residue was diluted with methanol (5 mL), then $K_2CO_3$ (232.1 mg, 1.7 mmol) was added to the mixture. The new reaction mixture was stirred at room temperature for 44 h. Then, the mixture was filtered and concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel using PE/EA = 5/1~4/1 as the eluent to give aldehyde **S4n** (104.9 mg, 39%) as a yellow foam.

A reaction flask equipped with a magnetic stirrer was charged with $PPh_3MeBr$ (187.7 mg, 0.5 mmol). The flask was evacuated and purged with argon, and then THF (2 mL) was added. After that, $^n$BuLi (0.2 mL, 2.4 M, 0.5 mmol) was added dropwise at 0 °C, and the mixture was stirred for 30 minutes at this temperature. Then, a THF (1 mL) solution of **S4n** (104.9 mg) was added, and the reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 12 h. The reaction was quenched with saturated ammonium chloride solution, and the product was extracted with diethyl ether three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE/EA = 20/1 as the eluent yielded **1n** (58.6 mg, *dr* = 10:1, 56%) as a light yellow oil. The following peaks for the major isomer were selected from the $^1$H NMR of the diastereomers:

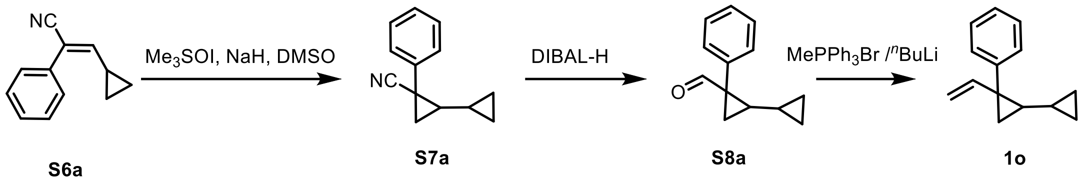
Light yellow oil

**TLC** (5:1 PE/EA, *R<sub>f</sub>*): 0.7.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 5.70 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.01 (dd, *J* = 10.8, 1.1 Hz, 1H), 4.97 (dd, *J* = 17.3, 1.1 Hz, 1H), 3.38 (d, *J* = 11.6 Hz, 1H), 3.19 – 3.03 (m, 2H), 2.65 – 2.55 (m, 1H), 2.42 (s, 3H), 2.22 – 2.10 (m, 1H), 1.82 (ddd, *J* = 14.2, 9.1, 5.3 Hz, 1H), 1.02 (td, *J* = 5.6, 1.8 Hz, 1H), 0.79 (dd, *J* = 5.6 Hz, 1H), 0.63 – 0.55 (m, 1H), 0.53 – 0.38 (m, 2H), 0.19 – 0.08 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 143.5, 141.5, 133.8, 129.8, 127.7, 112.3, 44.5, 42.7, 33.2, 27.1, 25.1, 24.2, 21.6, 9.2, 5.0, 4.8.

**HRMS** (ESI−FTICR, *m/z*): $[M + H]^+$ calculated for $C_{18}H_{24}NO_2S^+$: 318.1522, found: 318.1523



$Me_3SOI$ (6.08 g, 27.6 mmol) and NaH (1.31 g, 32.7 mmol, 60% weight in mineral oil) were added in 50 mL reaction tube. Then DMSO (30 mL) was added under Argon. The resulting mixture was stirred at rt for 30 min. Then a solution of substrate **S6a** (4.25, 25.1 mmol) in DMSO (10 mL) was added (2 mL THF was used to transfer the residual substrate from the container). The mixture was stirred at rt for 21 hours. The reaction system was quenched by water at 0 °C and extracted with $Et_2O$ three times. The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, PE/EA = 100/1~30/1) afforded **S7a** (4.37 g, 95%) as a colorless oil.

To a solution of **S7a** in DCM under Ar was added DIBAL-H (45.8 mmol, 1 M in toluene) at 0 °C, the reaction mixture was stirred at room temperature for 1h. Then the reaction system was quenched by citric acid (1 M, aq.) at 0°C. The reaction system was extracted with $Et_2O$ three times. The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, PE/EA = 50/1) afforded **S8a** (3.51 g, 82%) as a colorless oil.

A reaction flask equipped with a magnetic stirrer was charged with $PPh_3MeBr$ (1.71 g, 4.8 mmol). The flask was evacuated and purged with argon, and then THF (14 mL) was added. After that, $^n$BuLi (1.9 mL, 2.4 M, 4.5 mmol) was added dropwise at 0 °C, and the mixture was stirred for 30 minutes at this temperature. Then, a THF (4 mL) solution of **S8a** (0.56 mg, 3.0 mmol) was added, and the reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 14 h. The reaction was quenched with saturated ammonium chloride solution, and the product was extracted with diethyl ether three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE as the eluent afforded **1o** (0.33 g, 60%) as a colorless oil. The relative configuration of **1o** was uncertain.

Colorless oil

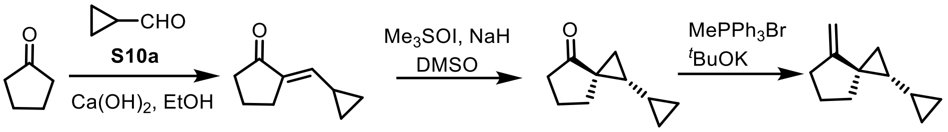
**TLC** (10:1 PE/EA, $R_f$): 0.9.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 4H), 7.21 – 7.15 (m, 1H), 6.01 (dd, $J$ = 17.2, 10.5 Hz, 1H), 5.03 (dd, $J$ = 10.5, 1.7 Hz, 1H), 4.65 (dd, $J$ = 17.1, 1.7 Hz, 1H), 1.16 – 1.15 (m, 1H), 0.91 – 0.88 (m, 1H), 0.88 – 0.74 (m, 2H), 0.62 – 0.51 (m, 2H), 0.30 – 0.22 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 144.5, 142.3, 129.8, 128.3, 126.3, 114.4, 34.2, 30.5, 19.2, 10.0, 5.3, 5.0.

**HRMS** (EI−GC-MS, $m/z$): $[M]^{+\cdot}$ calculated for $C_{14}H_{16}^{+\cdot}$: 184.1247, found: 184.1240

## III. Preparation of Substrates 4



**S9a** **S11a** **S12a** **4a**

To a flask with **S9a** (2.53 g, 30.0 mmol) in EtOH (30 mL) was added **S10a** (0.70 g, 10.0 mmol) and $Ca(OH)_2$ (0.15 g, 2.0 mmol). The obtained mixture was then refluxed for 12 h at 100 °C. The mixture was concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, PE/EA = 50/1~25/1) afforded compound **S11a** (848.1 mg) as white solid.

$Me_3SOI$ (1.51 g, 6.8 mmol) and NaH (274.0 mg, 6.8 mmol, 60% weight in mineral oil) were added in 50 mL reaction tube. Then DMSO (10 mL) was added under Argon. The resulting mixture was stirred at rt for 30 min. Then a solution of substrate **S11a** (848.1 mg, 6.2 mmol) in DMSO (5 mL) was added (1 mL THF was used to transfer the residual substrate from the container). The mixture was stirred at rt for 21 hours. The reaction system was quenched by water at 0 °C and extracted with $Et_2O$ three times. The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, PE/EA = 50/1~25/1) afforded **S12a** (332.9 mg) as a colorless oil.

A reaction flask equipped with a magnetic stirrer was charged with $MePPh_3Br$ (1.27 g, 3.6 mmol). The flask was evacuated and purged with argon, and then THF (10 mL) was added. After that, $^n$BuLi (1.4 mL, 2.4 M, 3.3 mmol) was added dropwise at 0 °C, and the mixture was stirred for 30 minutes at this temperature. Then, a THF (2 mL) solution of **S12a** (332.9 mg, 2.2 mmol) was added, and the reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 14 h. The reaction was quenched with saturated ammonium chloride solution, and the product was extracted with diethyl ether three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE as the eluent afforded 141.4 mg **4a** as a colorless oil, with an overall yield of 10% over three steps.

Colorless oil

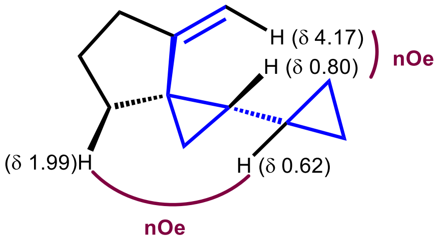
**TLC** (5:1 PE/EA, $R_f$): 0.9.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 4.51 (dd, $J$ = 2.1, 2.1 Hz, 1H), 4.17 (dd, $J$ = 2.3, 2.3 Hz, 1H), 2.45 (tt, $J$ = 7.2, 2.1 Hz, 2H), 1.99 (dt, $J$ = 12.2, 6.7 Hz, 1H), 1.82 – 1.70 (m, 2H), 1.63 (dt, $J$ = 12.9, 6.7 Hz, 1H), 0.83 – 0.69 (m, 2H), 0.62 (dtt, $J$ = 8.1, 5.1, 4.1 Hz, 1H), 0.56 – 0.45 (m, 2H), 0.41 (ddd, $J$ = 12.4, 8.0, 2.4 Hz, 1H), 0.22 – 0.11 (m, 2H).

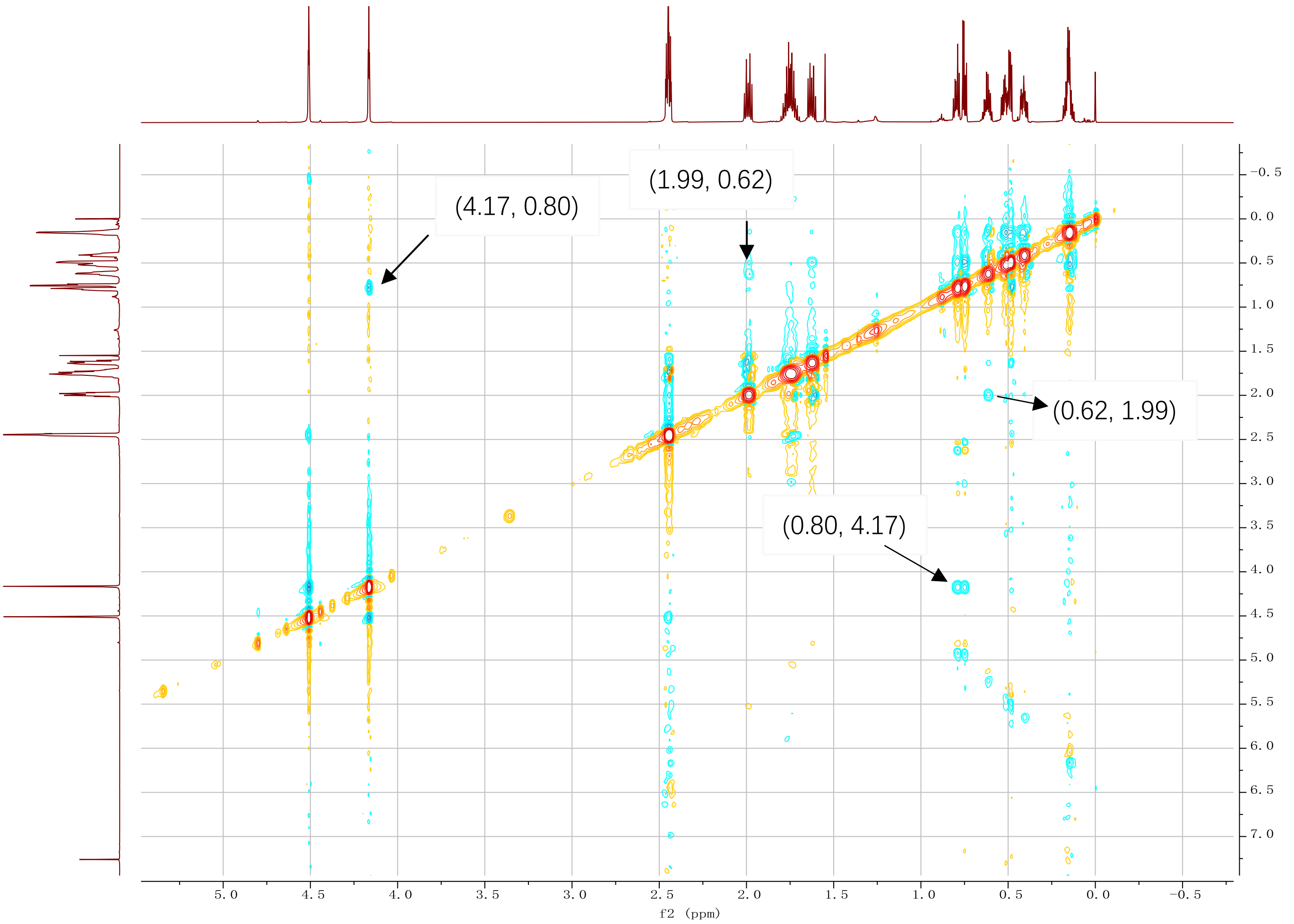
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 159.8, 96.3, 34.8, 32.5, 31.9, 30.1, 25.3, 21.5, 10.3, 4.3, 3.7.

**HRMS** (EI−GC-MS, $m/z$): $[M]^{+\cdot}$ calculated for $C_{11}H_{16}^{+\cdot}$: 148.1247, found: 148.1245

The relative configuration of **4a** was determined by 2D NMR:



### $^1$H-$^1$H NOESY


(4.17, 0.80)
(1.99, 0.62)
(0.62, 1.99)
(0.80, 4.17)
f2 (ppm)
f1 (ppm)
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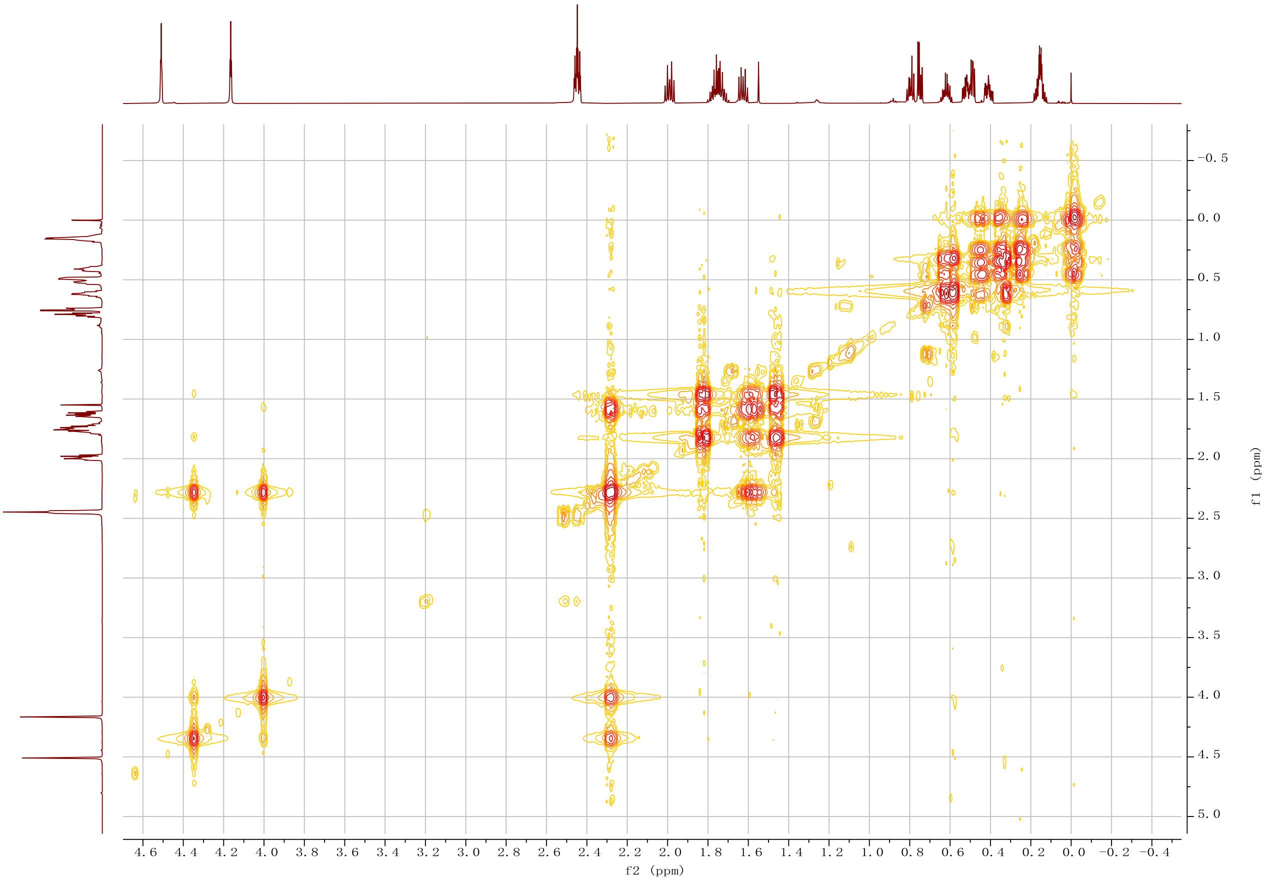
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
7.0
6.5
6.0
5.5

**$^1$H-$^1$H COSY:**


f2 (ppm)
f1 (ppm)
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4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
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1.5
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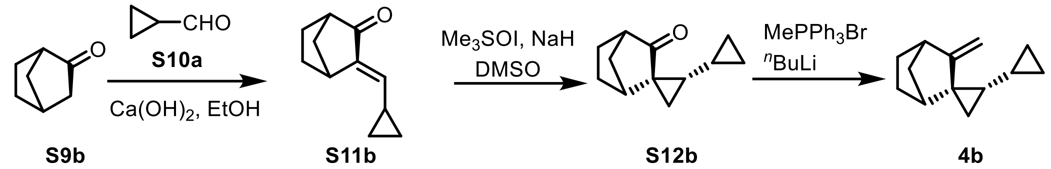
4.5
5.0



To a flask with **S9b** (1.10 g, 10.0 mmol) in EtOH (20 mL) was added **S10a** (1.40 g, 20.0 mmol) and NaOH (0.08 g, 2.0 mmol). The obtained mixture was then refluxed for 21 h at 70 °C. The mixture was concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, PE/EA = 40/1~20/1) afforded compound **S11b** (698.5 mg) as a white solid.

$Me_3SOI$ (1.04 g, 4.7 mmol) and NaH (189.4 mg, 4.7 mmol, 60% weight in mineral oil) were added in 50 mL reaction tube. Then DMSO (8 mL) was added under Argon. The resulting mixture was stirred at rt for 30 min. Then a solution of substrate **S11b** (698.5 mg, 4.3 mmol) in DMSO (2 mL) was added. The mixture was stirred at rt for 15 hours. The reaction system was quenched by water at 0 °C and extracted with $Et_2O$ three times. The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, PE/EA = 50/1) afforded **S12b** (97.9 mg) as a colorless oil.

A reaction flask equipped with a magnetic stirrer was charged with $MePPh_3Br$ (317.5 mg, 0.9 mmol). The flask was evacuated and purged with argon, and then THF (4 mL) was added. After that, $^n$BuLi (0.35 mL, 2.4 M, 0.8 mmol) was added dropwise at 0 °C, and the mixture was stirred for 30 minutes at this temperature. Then, a THF (1 mL) solution of **S12b** (97.9 mg, 0.6 mmol) was added, and the reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 12 h. The reaction was quenched with saturated ammonium chloride solution, and the product was extracted with diethyl ether three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE as the eluent afforded **4b** (71.3 mg, *dr* = 4:1) as a colorless oil, with an overall yield of 4% over three steps. The following peaks for the major isomer were selected from the $^1$H NMR of the diastereomers.

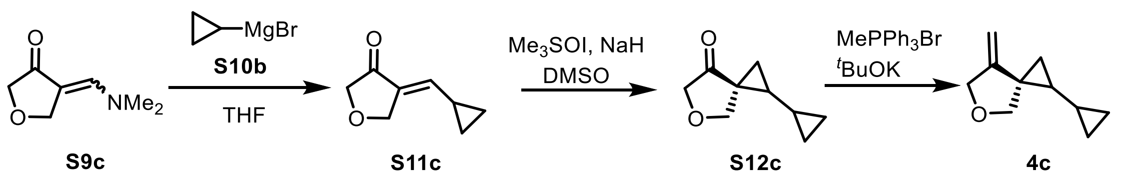
Colorless oil

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

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 4.44 (s, 1H), 3.94 (s, 1H), 2.80 (dd, $J$ = 3.8, 1.7 Hz, 1H), 2.12 (d, $J$ = 4.0 Hz, 1H), 1.72 – 1.58 (m, 3H), 1.55 – 1.44 (m, 1H), 1.40 – 1.33 (m, 2H), 0.89 – 0.65 (m, 3H), 0.57 – 0.48 (m, 1H), 0.47 – 0.37 (m, 2H), 0.21 – 0.11 (m, 2H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 163.9, 92.8, 46.5, 40.2, 39.8, 35.9, 33.8, 30.1, 27.1, 16.8, 10.1, 4.2, 4.0.

**HRMS** (EI−GC-MS, *m/z*): [M]$^{+\cdot}$ calculated for $C_{13}H_{18}^{+\cdot}$: 174.1399, found: 174.1403



A reaction flask equipped with a magnetic stirrer was charged with **S9c**[10] (2.82 g, 20.0 mmol). Then the flask was evacuated and purged with $N_2$. After adding THF (130 mL), **S10b** (60 mL, 0.5 M in THF, 30.0 mmol) was added dropwise under -50 °C in 1 h. After stirring under -50 °C for 4 h, the reaction was quenched with saturated ammonium chloride solution, and the product was extracted with DCM three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE/EA = 10/1 to 5/1 as the eluent afforded **S11c** (2.13 g) as a yellow oil, with a yield of 77%.

$Me_3SOI$ (858.0 mg, 3.9 mmol) and NaH (156.0 mg, 3.9 mmol, 60% weight in mineral oil) were added in 100 mL reaction flask. Then DMSO (10 mL) was added under Argon. The resulting mixture was stirred at rt for 30 min. Then a solution of substrate **S11c** (360.0 mg, 2.6 mmol) in DMSO (5 mL) was added. The mixture was stirred at rt for 4 hours. The reaction system was quenched by water and extracted with DCM three times. The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, PE/EA = 10/1) afforded **S12c** (138.0 mg) as a yellow oil, with a yield of 35%.

A reaction flask equipped with a magnetic stirrer was charged with $PPh_3MeBr$ (1.71 g, 4.8 mmol) and $^t$BuOK (539 mg, 4.8 mmol). The flask was evacuated and purged with $N_2$, and THF (20 mL) was added under 0 °C. The mixture was stirred for 30 minutes at this temperature. Then, a THF (5 mL) solution of **S12c** (250.4 mg, 1.6 mmol) was added, and the reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 12 h. The reaction was quenched with saturated ammonium chloride solution, and the product was extracted with diethyl ether three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE/EA = 50:1 as the eluent afforded **4c** (190.0 mg, *dr* = 1:1 according to the $^1$H NMR at δ 4.59 ppm and δ 4.57 ppm) as a light yellow oil, with a yield of 79%. The following NMR peaks are the mixture of the two diastereomers.

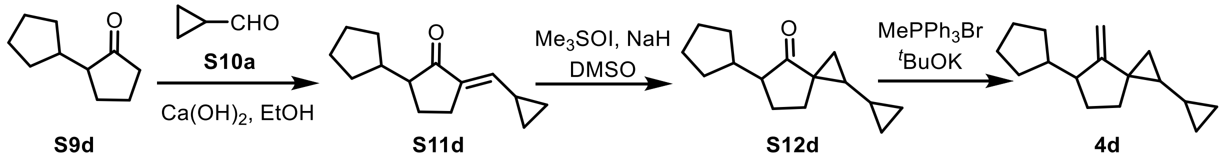
Light yellow oil

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

**$^1$H NMR** (400 MHz, $CD_2Cl_2$) δ 4.85 (dd, *J* = 2.0 Hz, 1H), 4.59 (dd, *J* = 2.4 Hz, 1H), 4.57 (dd, *J* = 2.0 Hz, 1H), 4.51 (dt, *J* = 12.8, 2.2 Hz, 1H), 4.44 – 4.39 (m, 3H), 4.30 (dd, *J* = 2.3 Hz, 1H), 4.07 (d, *J* = 8.5 Hz, 1H), 3.83 (d, *J* = 8.1 Hz, 1H), 3.79 (d, *J* = 8.5 Hz, 1H), 3.62 (d, *J* = 8.1 Hz, 1H), 1.06 (ddd, *J* = 8.9, 6.3, 5.1 Hz, 1H), 0.98 (dd, *J* = 8.7, 4.9 Hz, 1H), 0.89 – 0.80 (m, 2H), 0.73 (dd, *J* = 6.3, 4.9 Hz, 1H), 0.67 (dddd, *J* = 13.5, 8.5, 6.3, 4.2 Hz, 2H), 0.62 – 0.58 (m, 1H), 0.57 – 0.52 (m, 1H), 0.52 – 0.44 (m, 2H), 0.44 – 0.36 (m, 1H), 0.29 – 0.22 (m, 1H), 0.22 – 0.15 (m, 2H), 0.12 – 0.05 (m, 1H).

**$^{13}$C NMR** (101 MHz, $CD_2Cl_2$) δ 155.0, 149.4, 100.1, 95.3, 77.8, 73.7, 72.8, 72.4, 33.1, 31.8, 31.5, 30.4, 18.9, 16.2, 9.9, 9.2, 5.3, 5.0, 4.5, 3.2.

**HRMS** (EI−GC-MS, *m*/*z*): $[M]^{+\cdot}$ calculated for $C_{10}H_{14}O^{+\cdot}$: 150.1039, found: 150.1036



To a flask with **S9d** (1.52 g, 10.0 mmol) in EtOH (20 mL) was added **S10a** (1.05 g, 15.0 mmol) and $Ca(OH)_2$ (0.15 g, 2.0 mmol). The obtained mixture was then refluxed for 20 h at 100 °C. The mixture was concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, PE/EA = 100/1) afforded compound **S11d** (1.66 g) as a colorless oil.

$Me_3SOI$ (2.68 g, 12.2 mmol) and NaH (496.0 mg, 12.2 mmol, 60% weight in mineral oil) were added in 50 mL reaction tube. Then DMSO (20 mL) was added under Argon. The resulting mixture was stirred at rt for 30 min. Then a solution of substrate **S11d** (1.66 g, 8.1 mmol) in DMSO (5 mL) was added. The mixture was stirred at rt for 12 hours. The reaction system was quenched by water at 0 °C and extracted with $Et_2O$ three times. The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, PE/EA = 100/1) afforded **S12d** (1.71 g) as a colorless oil.

A reaction flask equipped with a magnetic stirrer was charged with $MePPh_3Br$ (4.20 g, 11.8 mmol), $^t$BuOK (1.32 g, 11.8 mmol). The flask was evacuated and purged with argon, and then THF (20 mL) was added. The mixture was stirred for 30 minutes at room temperature. Then, **S12d** in THF (2 mL) was added, and the reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 24 h. The reaction was quenched with saturated ammonium chloride solution, and the product was extracted with DCM three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE as the eluent yielded **4d (**708.6 mg) as a colorless oil, with an overall yield of 33% over three steps. The obtained **4d** is an inseparable mixture of three diastereomers (*dr* = 5:2:1). The following peaks for the major isomer were selected from the $^1$H NMR of the mixture.

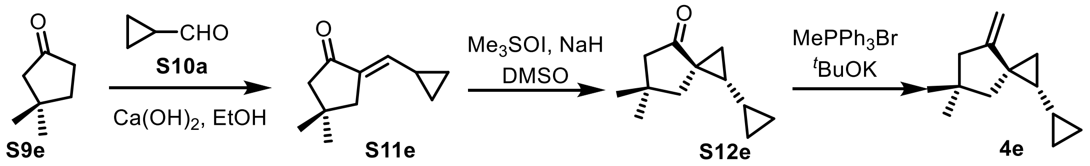
Colorless oil

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

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 4.49 (d, *J* = 1.9 Hz, 1H), 4.18 (d, *J* = 2.2 Hz, 1H), 2.54 – 2.45 (m, 1H), 2.02 – 1.96 (m, 1H), 1.87 – 1.81 (m, 1H), 1.70 (ddt, *J* = 13.4, 8.2, 3.2 Hz, 2H), 1.63 – 1.47 (m, 7H), 1.34 – 1.26 (m, 1H), 1.22 – 1.14 (m, 1H), 0.86 – 0.77 (m, 1H), 0.71 – 0.58 (m, 2H), 0.55 – 0.48 (m, 1H), 0.46 – 0.38 (m, 2H), 0.19 – 0.09 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 162.8, 96.6, 50.7, 42.8, 33.7, 31.7, 31.4, 30.0, 29.9, 29.1, 25.8, 25.5, 22.7, 10.4, 4.4, 3.7.

**HRMS** (EI–GC-MS, *m/z*): $[M]^{+\cdot}$ calculated for $C_{16}H_{24}^{+\cdot}$: 216.1873 found: 216.1867



To a flask with **S9e** (1.12 g, 10.0 mmol) in EtOH (15 mL) was added **S10a** (350.0 mg 5.0 mmol) and $Ca(OH)_2$ (37.0 mg, 0.5 mmol). The obtained mixture was then refluxed for 22.5 h at 100 °C. The mixture was concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, PE/EA = 20/1) afforded a mixture of **S11e** and **S9e** (585.0 mg) as a colorless oil.

$Me_3SOI$ (1.96 g, 8.9 mmol) and NaH (356.0 mg, 8.9 mmol, 60% weight in mineral oil) were added in 100 mL reaction flask. Then DMSO (20 mL) was added under $N_2$. The resulting mixture was stirred at rt for 30 min. Then a solution of compound **S11e** and **S9e** (585.0 mg) in DMSO (5 mL) was added. The mixture was stirred at rt for 1 hours. The reaction system was quenched by water at 0 °C and extracted with DCM three times. The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, PE/EA = 25/1) afforded **S12e** (442.0 mg) as a colorless oil.

A reaction flask equipped with a magnetic stirrer was charged with $PPh_3MeBr$ (1.79 g, 5.0 mmol), $^t$BuOK (561.0 mg, 5.0 mmol). The flask was evacuated and purged with $N_2$, and then THF (15 mL) was added. The mixture was stirred for 30 minutes at room temperature. Then, **S12e** in THF (5 mL) was added, and the reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 11 h. The reaction was quenched with $H_2O$, and the product was extracted with DCM three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE as the eluent yielded **4e** (310.0 mg) as a colorless oil, with an overall yield of 35% over three steps. The obtained **4e** is an inseparable mixture of two diastereomers (*dr* = 13:1). The following peaks for the major isomer were selected from the $^1$H NMR of the mixture.

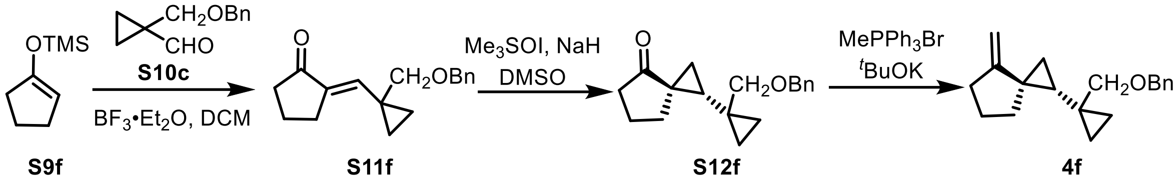
Colorless oil

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

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 4.48 (dd, *J* = 2.1, 2.1 Hz, 1H), 4.16 (dd, *J* = 2.2, 2.2 Hz, 1H), 2.26 (s, 2H), 1.83 (d, *J* = 12.4 Hz, 1H), 1.47 (d, *J* = 12.4 Hz, 1H), 1.08 (s, 3H), 1.07 (s, 3H), 0.85 – 0.78 (m, 1H), 0.75 (dd, *J* = 8.8, 3.9 Hz, 1H), 0.62 – 0.56 (m, 1H), 0.54 – 0.48 (m, 1H), 0.44 (dd, *J* = 5.8, 3.9 Hz, 1H), 0.43 – 0.36 (m, 1H), 0.19 – 0.09 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 160.2, 97.0, 49.6, 46.1, 37.8, 32.3, 29.5, 28.1, 28.0, 21.9, 10.6, 4.4, 3.5.

**HRMS** (EI−GC-MS, *m/z*): $[M]^{+\cdot}$ calculated for $C_{13}H_{20}^{+\cdot}$: 176.1560 found: 176.1555



A reaction flask equipped with a magnetic stirrer was evacuated and purged with $N_2$. **S10c** (1.03 g, 5.4 mmol) and DCM (45 mL) was added. After cooling to -78 °C, $BF_3\cdot Et_2O$ (2.5 mL, 19.0 mmol) was added. Then DCM (5 mL) solution of **S9f** (938 mg, 6.0 mmol) was added dropwise at same temperature in 0.5 h. The mixture was brought to room temperature slowly and stirred for 12.5 h. The reaction was quenched with saturated ammonium chloride solution, and the product was extracted with DCM three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE/EA = 10:1 to 5:1 as the eluent yielded **S11f (**1.00 g) as a yellow oil, with a yield of 72%.

$Me_3SOI$ (902.2 mg, 4.1 mmol) and NaH (164.0 mg, 4.1 mmol, 60% weight in mineral oil) were added in 50 mL reaction tube. Then DMSO (10 mL) was added under $N_2$. The resulting mixture was stirred at rt for 30 min. Then a solution of substrate **S11f** (704.0 mg, 2.7 mmol) in DMSO (5 mL) was added. The mixture was stirred at rt for 4 hours. The reaction system was quenched by water at 0 °C and extracted with DCM three times. The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, PE/EA = 10/1) afforded **S12f** (366.0 mg) as a colorless oil, with a yield of 50%.

A reaction flask equipped with a magnetic stirrer was charged with $PPh_3MeBr$ (1.25 g, 3.5 mmol), $^t$BuOK (393.0 mg, 3.5 mmol). The flask was evacuated and purged with $N_2$, and then THF (10 mL) was added. The mixture was stirred for 30 minutes at room temperature. Then, **S12f** (470.0 mg) in THF (5 mL) was added, and the reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 3 h. The reaction was quenched with saturated ammonium chloride solution, and the product was extracted with DCM three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE to PE/EA = 100:1 to 50:1 as the eluent yielded **4f** (317.0 mg) as a colorless oil, with a yield of 68%.

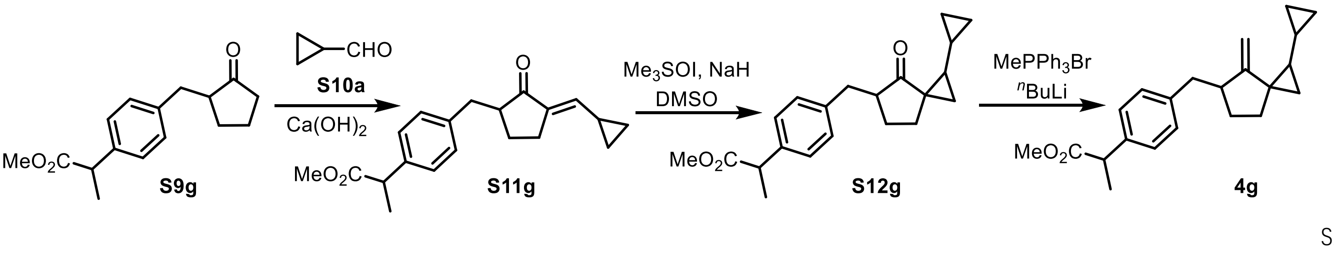
Colorless oil

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

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 4H), 7.28 – 7.25 (m, 1H), 4.63 – 4.55 (m, 2H), 4.48 (d, *J* = 12.5 Hz, 1H), 4.27 (dd, *J* = 2.2, 2.2 Hz, 1H), 3.55 (dd, *J* = 9.5, 1.0 Hz, 1H), 3.12 (d, *J* = 9.5 Hz, 1H), 2.45 – 2.37 (m, 2H), 1.97 – 1.86 (m, 1H), 1.74 – 1.65 (m, 1H), 1.64 – 1.56 (m, 3H), 0.66 (dd, *J* = 9.3, 4.5 Hz, 1H), 0.56 (ddd, *J* = 9.0, 5.6, 3.6 Hz, 1H), 0.44 – 0.33 (m, 2H), 0.33 – 0.24 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 159.7, 138.9, 128.4, 127.5, 127.5, 96.7, 77.2, 72.9, 34.8, 32.1, 31.6, 30.7, 25.4, 19.3, 19.1, 9.5, 7.3.

**HRMS** (ESI−FTICR, *m/z*): $[M + H]^+$ calculated for $C_{19}H_{25}O^+$: 269.1900, found: 269.1905



To a flask with **S9g** (0.93 g, 15.4 mmol) in MeOH (30 mL) was added **S10a** (0.74 g, 15.0 mmol) and $Ca(OH)_2$ (0.05 g, 3.1 mmol). The obtained mixture was then refluxed for 20 h. The mixture was concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, PE/EA = 40/1) afforded compound **S11g** (0.94 g, 84%) as a yellow oil.

$Me_3SOI$ (4.26 g, 19.4 mmol) and NaH (0.77 g, 19.4 mmol, 60% weight in mineral oil) were added in 50 mL reaction tube. Then DMSO (20 mL) was added under Argon. The resulting mixture was stirred at rt for 30 min. Then a solution of substrate **S11g** (4.04 g, 12.9 mmol) in DMSO (5 mL) was added. The mixture was stirred at rt for 12 hours. The reaction system was quenched by water at 0 °C and extracted with $Et_2O$ three times. The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, PE/EA = 25/1) afforded **S12g** (2.77 g, 66%) as a colorless oil.

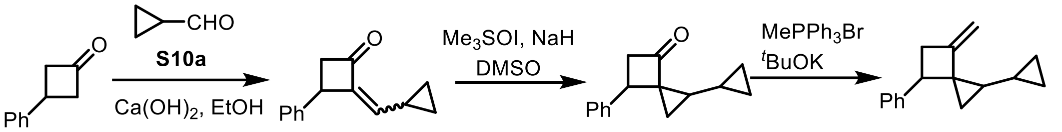
A reaction flask equipped with a magnetic stirrer was charged with $MePPh_3Br$ (2.00 g, 5.6 mmol). The flask was evacuated and purged with argon, and then THF (20 mL) was added. After that, $^n$BuLi (2.2 mL, 2.4 M, 0.8 mmol) was added dropwise at 0 °C, and the mixture was stirred for 30 minutes at this temperature. Then, **S12g** (1.25 g, 3.5 mmol) in THF (5 mL) was added, and the reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 24 h. The reaction was quenched with saturated ammonium chloride solution, and the product was extracted with $Et_2O$ three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE as the eluent yielded **4g** (0.37 g, 30%, *dr* = 1:1) as a colorless oil. The following peaks for one of the isomers were selected from the $^1$H NMR of the mixture.

Colorless oil

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.15 (m, 4H), 4.49 (dd, *J* = 4.2, 2.1 Hz, 1H), 4.24 (dd, *J* = 2.8, 2.8 Hz, 1H), 3.76 – 3.68 (m, 1H), 3.66 (d, *J* = 1.1 Hz, 3H), 2.97 (ddd, *J* = 23.7, 13.4, 5.0 Hz, 1H), 2.88 – 2.73 (m, 1H), 2.50 (ddd, *J* = 18.8, 13.4, 9.7 Hz, 1H), 2.00 – 1.87 (m, 1H), 1.87 – 1.69 (m, 1H), 1.60 – 1.52 (m, 1H), 1.49 (dd, *J* = 7.2, 1.3 Hz, 3H), 1.47 – 1.38 (m, 1H), 0.86 – 0.69 (m, 2H), 0.63 – 0.55 (m, 1H), 0.54 – 0.46 (m, 2H), 0.45 – 0.38 (m, 1H), 0.17 – 0.10 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 175.3, 162.6, 140.2, 138.0, 129.3, 127.3, 96.3, 52.1, 47.1, 45.2, 40.2, 32.0, 31.1, 30.3, 29.2, 20.5, 18.7, 10.2, 4.1, 3.6.

**HRMS** (ESI−FTICR, *m*/*z*): $[M + H]^+$ calculated for $C_{22}H_{29}O_2^+$: 325.2162, found: 325.2157



**S9h** **S11h** **S12h** **4h**

To a flask with **S9h** (2.92 g, 20.0 mmol) in EtOH (20 mL) was added **S10a** (700.9 mg, 10.0 mmol) and $Ca(OH)_2$ (0.15 g, 2.0 mmol). The obtained mixture was then refluxed for 21 h at 80 °C. The mixture was concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, PE/EA = 50/1~25/1) afforded compound **S11h** (579.3 mg) as a colorless oil.

$Me_3SOI$ (1.29 g, 5.8 mmol) and NaH (233.7 mg, 5.8 mmol, 60% weight in mineral oil) were added in 50 mL reaction tube. Then DMSO (10 mL) was added under Argon. The resulting mixture was stirred at rt for 30 min. Then a solution of substrate **S11h** (579.3 mg, 2.9 mmol) in DMSO (2 mL) was added. The mixture was stirred at rt for 17.5 hours. The reaction system was quenched by water at 0 °C and extracted with $Et_2O$ three times. The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, PE/EA = 50/1) afforded **S12h** (79.2 mg) as a colorless oil.

A reaction flask equipped with a magnetic stirrer was charged with $MePPh_3Br$ (199.9 mg, 0.6 mmol),

$^t$BuOK (62.8 mg, 0.6 mmol). The flask was evacuated and purged with argon, and then THF (2 mL) was added. The mixture was stirred for 30 minutes at room temperature. Then, **S12h** in THF (1 mL) was added, and the reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 11 h. The reaction was quenched with saturated ammonium chloride solution, and the product was extracted with DCM three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE as the eluent yielded **4h** (57.8 mg, *dr* = 14.3:1) as a colorless oil, with an overall yield of 3% over three steps. The following peaks for the major isomer were selected from the $^1$H NMR of the mixture.

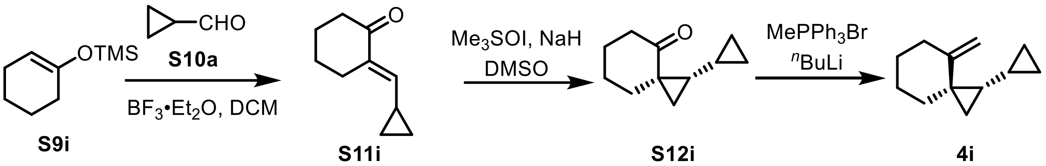
Colorless oil

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

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.14 (m, 5H), 4.81 (dd, $J$ = 2.2 Hz, 1H), 4.64 (dd, $J$ = 2.7 Hz, 1H), 3.50 (dd, $J$ = 8.7, 6.7 Hz, 1H), 3.19 (dddd, $J$ = 15.5, 8.7, 2.2, 2.2 Hz, 1H), 2.88 (dddd, $J$ = 15.5, 6.7, 2.6, 2.6 Hz, 1H), 0.87 (dd, $J$ = 9.0, 5.0 Hz, 1H), 0.72 (dd, $J$ = 6.7, 5.0 Hz, 1H), 0.68 (ddd, $J$ = 10.9, 5.4, 2.8 Hz, 1H), 0.56 – 0.48 (m, 1H), 0.48 – 0.36 (m, 2H), 0.15 – 0.07 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 152.7, 143.7, 128.3, 128.1, 126.4, 101.8, 44.1, 39.8, 38.1, 29.4, 20.4, 9.6, 4.9, 4.3.

**HRMS** (EI−GC-MS, *m/z*): $[M]^{+\cdot}$ calculated for $C_{16}H_{18}^{+\cdot}$: 210.1403 found: 210.1398



To a flask with **S10a** (2.10 g, 30.0 mmol) in DCM (100 mL) was added $BF_3 \cdot Et_2O$ (13.3 mL, 105.0 mmol) slowly at -78 °C under Ar. Then **S9i** (5.62 g, 33.0 mmol) in DCM (4 mL) was added. The obtained mixture was stirred for 30 min at -78 °C and warmed to room temperature for 8 h. The reaction system was quenched by water at 0 °C and extracted with DCM three times. The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, PE/EA = 15/1) afforded **S11i** (3.22 g) as a light yellow oil.

$Me_3SOI$ (5.19 g, 23.6 mmol) and NaH (0.94 g, 23.6 mmol, 60% weight in mineral oil) were added in 50 mL reaction tube. Then DMSO (25 mL) was added under Argon. The resulting mixture was stirred at rt for 30 min. Then a solution of substrate **S11i** (3.22 g, 21.4 mmol) in DMSO (5 mL) was added. The mixture was stirred at rt for 16 hours. The reaction system was quenched by water at 0 °C and extracted with $Et_2O$ three times. The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, PE/EA = 20/1) afforded **S12i** (1.23 g) as a colorless oil.

A reaction flask equipped with a magnetic stirrer was charged with $MePPh_3Br$ (4.28 g, 12.0 mmol). The flask was evacuated and purged with argon, and then THF (40 mL) was added. After that, $^n$BuLi (4.7 mL, 2.4 M, 11.2 mmol) was added dropwise at 0 °C, and the mixture was stirred for 30 minutes at this temperature. Then, a THF (5 mL) solution of **S12i** (1.23 g, 7.5 mmol) was added, and the reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 3 h. The reaction was quenched with saturated ammonium chloride solution, and the product was extracted with diethyl ether three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE as the eluent afforded **4i** (949.8 mg) as a colorless oil, with an overall yield of 20% over three steps.

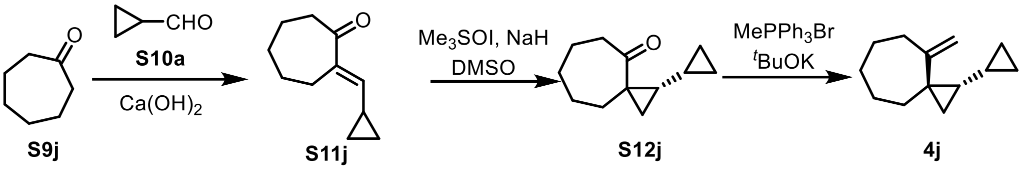
Colorless oil.

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

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 4.50 (d, $J$ = 1.1 Hz, 1H), 4.43 (d, $J$ = 2.1 Hz, 1H), 2.31 – 2.20 (m, 1H), 2.20 – 2.09 (m, 1H), 1.74 – 1.63 (m, 3H), 1.58 – 1.50 (m, 3H), 0.76 (dd, $J$ = 8.8, 4.5 Hz, 1H), 0.69 – 0.60 (m, 1H), 0.56 – 0.41 (m, 3H), 0.21 – 0.14 (m, 2H), 0.13 (dd, $J$ = 5.6, 4.5 Hz, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 154.0, 103.6, 35.5, 32.5, 29.0, 28.7, 28.2, 25.9, 16.1, 9.4, 4.89, 4.85.

**HRMS** (EI−GC-MS, $m/z$): $[M]^{+\cdot}$ calculated for $C_{12}H_{18}^{+\cdot}$: 162.1403 found: 162.1400



To a flask with **S9j** (3.37 g, 30 mmol) in EtOH (40 mL) was added **S10a** (0.70 g, 10 mmol) and $Ca(OH)_2$ (0.15 g, 2 mmol). The obtained mixture was then refluxed for 19 h at 100 °C. The mixture was concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, PE/EA = 40/1) afforded white solid (2.00 g, **S11j** + **S9j**), which was directly used in the next step.

$Me_3SOI$ (3.22 g, 14.6 mmol) and NaH (0.58 g, 14.6 mmol, 60% weight in mineral oil) were added in 50 mL reaction tube. Then DMSO (20 mL) was added under Argon. The resulting mixture was stirred at rt for 30 min. Then a solution of substrate **S11j** (2.00 g) in DMSO (5 mL) was added. The mixture was stirred at rt for 12 hours. The reaction system was quenched by water at 0 °C and extracted with $Et_2O$ three times. The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, PE/EA = 40/1) afforded **S12j** (147.3 mg) as a colorless oil.

A reaction flask equipped with a magnetic stirrer was charged with $PPh_3MeBr$ (428.7 mg, 1.2 mmol), $^t$BuOK (134.7 mg, 1.2 mmol). The flask was evacuated and purged with argon, and then THF (4 mL) was added. The mixture was stirred for 30 minutes at room temperature. Then, **S12j** (147.3 mg, 0.8 mmol) in THF (2 mL) was added, and the reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 24 h. The reaction was quenched with saturated ammonium chloride solution, and the product was extracted with DCM three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE as the eluent yielded **4j (**80.0 mg, *dr* > 20:1) as a colorless oil, with an overall yield of 5% over three steps.

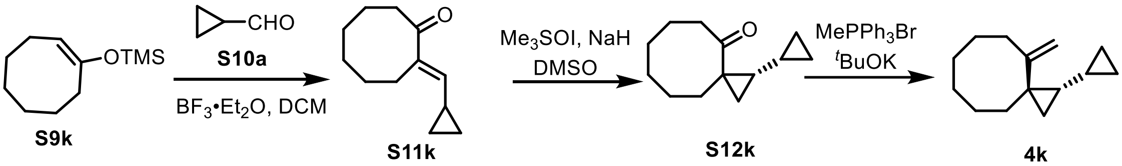
Colorless oil

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

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 4.57 (d, $J$ = 1.5 Hz, 1H), 4.43 (d, $J$ = 1.8 Hz, 1H), 2.39 – 2.23 (m, 2H), 1.80 – 1.64 (m, 3H), 1.68 – 1.51 (m, 5H), 0.79 (dd, $J$ = 8.5, 4.2 Hz, 1H), 0.72 – 0.61 (m, 2H), 0.59 – 0.47 (m, 1H), 0.49 – 0.39 (m, 1H), 0.29 (dd, $J$ = 5.4, 4.2 Hz, 1H), 0.25 – 0.12 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 157.9, 106.8, 36.7, 33.6, 32.3, 29.7, 29.7, 29.6, 27.9, 20.9, 10.1, 5.0, 4.9.

**HRMS** (EI−GC-MS, $m/z$): $[M]^{+\cdot}$ calculated for $C_{13}H_{20}^{+\cdot}$: 176.1560 found: 176.1553.



To a flask with **S10a** (1.05 g, 15.0 mmol) in DCM (50 mL) was added $BF_3{\cdot}Et_2O$ (4.4 mL, 35.0 mmol) slowly at -78 °C under Ar. Then **S9k** (1.98 g, 10.0 mmol) in DCM (10 mL) was added. The obtained mixture was stirred for 60 min at -78 °C and warmed to room temperature for 5 h. The reaction system was quenched by $NH_4Cl$ at 0 °C and extracted with DCM three times. The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, PE/EA = 15/1) afforded **S11k** (1.02 g, 57%) as a light yellow oil.

$Me_3SOI$ (1.89 g, 8.6 mmol) and NaH (0.34 g, 8.6 mmol, 60% weight in mineral oil) were added in 50 mL reaction tube. Then DMSO (20 mL) was added under Argon. The resulting mixture was stirred at rt for 30 min. Then a solution of substrate **S11k** (1.02 g, 5.7 mmol) in DMSO (5 mL) was added. The mixture was stirred at rt for 14 hours. The reaction system was quenched by water at 0 °C and extracted with $Et_2O$ three times. The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, PE/EA = 20/1) afforded **S12k** (0.97 g, 90%) as a light yellow oil.

A reaction flask equipped with a magnetic stirrer was charged with $PPh_3MeBr$ (3.64 g, 10.2 mmol), $^t$BuOK (1.14 g, 10.2 mmol). The flask was evacuated and purged with argon, and then THF (25 mL) was added. The mixture was stirred for 30 minutes at room temperature. Then, **S12k** (0.97 g, 5.1 mmol) in THF (5 mL) was added, and the reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 13 h. The reaction was quenched with saturated ammonium chloride solution, and the product was extracted with DCM three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE as the eluent yielded **4k (**0.70 g, *dr* = 14:1, 72%) as a colorless oil. The following peaks for the major isomer were selected from the $^1$H NMR of the mixture.

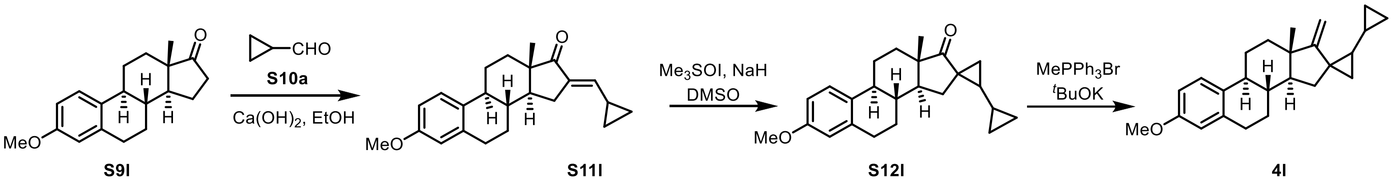
Colorless oil.

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

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 4.71 – 4.68 (m, 1H), 4.67 (d, *J* = 1.9 Hz, 1H), 2.25 – 2.19 (m, 2H), 1.96 – 1.85 (m, 1H), 1.82 – 1.72 (m, 1H), 1.63 – 1.49 (m, 8H), 0.75 (ddd, *J* = 8.8, 4.4, 1.1 Hz, 1H), 0.72 – 0.64 (m, 1H), 0.60 – 0.55 (m, 1H), 0.53 (ddd, *J* = 8.2, 5.4, 2.2 Hz, 1H), 0.44 (ddd, *J* = 12.2, 7.9, 2.5 Hz, 1H), 0.25 (dd, *J* = 5.8, 4.3 Hz, 1H), 0.22 – 0.12 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 157.5, 109.2, 34.6, 31.9, 30.9, 29.8, 29.0, 26.7, 26.5, 25.8, 18.4, 9.9, 5.1, 4.9.

**HRMS** (EI−GC-MS, *m*/*z*): $[M]^{+\cdot}$ calculated for $C_{14}H_{22}^{+\cdot}$: 190.1716 found: 190.1712.



To a flask with **S9l** (3.13 g, 11 mmol) in EtOH (125 mL) was added **S10a** (2.31 g, 33 mmol) and $Ca(OH)_2$ (0.14 g, 2.2 mmol). The obtained mixture was then refluxed for 48 h at 100 °C. The mixture was concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, PE/EA = 40/1) afforded compound **S11l** (2.95 g) as a white solid.

$Me_3SOI$ (4.22 g, 19.2 mmol) and NaH (0.77 g, 19.2 mmol, 60% weight in mineral oil) were added in 50 mL reaction tube. Then DMSO (20 mL) was added under Argon. The resulting mixture was stirred at rt for 30 min. Then a solution of substrate **S11l** (2.95 g, 9.6 mmol) in DMSO (5 mL) was added. The mixture was stirred at rt for 12 hours. The reaction system was quenched by water at 0 °C and extracted with $Et_2O$ three times. The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, PE/EA = 100/1) afforded **S12l** (2.0 g) as a white solid.

A reaction flask equipped with a magnetic stirrer was charged with $PPh_3MeBr$ (19.9 g, 5.6 mmol), $^t$BuOK (0.63 g, 5.6 mmol). The flask was evacuated and purged with argon, and THF (20 mL) was added. The mixture was stirred for 30 minutes at room temperature. Then, **S12l** in THF (5 mL) was added, and the reaction was stirred at room temperature. The reaction was monitored by TLC and stirred for 24 h. The reaction was quenched with saturated ammonium chloride solution, and the product was extracted with DCM three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. Purification by column chromatography using PE as the eluent yielded **4l (**370 mg) as a colorless oil, with an overall yield of 15% over three steps. The obtained **4l** is an inseparable mixture of two diastereomers (*dr* = 2:1). The following peaks for the major isomer were selected from the $^1$H NMR of the mixture.

Colorless oil

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

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.25 (d, $J$ = 7.6 Hz, 1H), 6.74 (dd, $J$ = 8.6, 2.8 Hz, 1H), 6.66 (d, $J$ = 2.8 Hz, 1H), 4.33 (s, 1H), 4.07 (s, 1H), 3.80 (s, 3H), 2.94 – 2.83 (m, 2H), 2.42 – 2.35 (m, 1H), 2.35 – 2.26 (m, 1H), 2.05 – 1.89 (m, 3H), 1.59 – 1.47 (m, 5H), 1.35 – 1.27 (m, 1H), 0.96 (s, 3H), 0.93 – 0.86 (m, 2H), 0.80 – 0.72 (m, 1H), 0.60 – 0.56 (m, 1H), 0.52 – 0.42 (m, 2H), 0.25 – 0.13 (m, 2H).

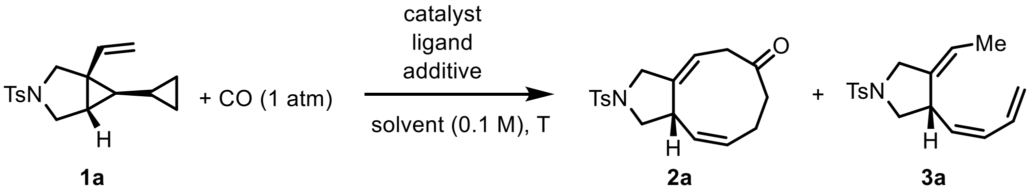
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 169.4, 157.6, 138.2, 133.0, 126.4, 114.0, 111.6, 92.4, 55.3, 52.3, 45.6, 44.2, 38.7, 35.9, 33.5, 31.8, 30.1, 28.4, 27.8, 26.7, 20.6, 19.2, 10.8, 4.2, 3.4.

**HRMS** (ESI−FTICR, *m/z*): $[M + H]^+$ calculated for $C_{25}H_{33}O^+$: 349.2526, found: 349.2527

## IV. Optimization of [8+1] Cycloaddition

We have tried about one hundred conditions with various solvents, ligands, and CO pressure, the selected conditions were shown here (Table S1). Among all the conditions, the *β*-H elimination pathway is difficult to avoid, due to the intrinsic strains in the cyclic transition states in [8+1] cycloaddition.

**Table S1. Optimization of [8+1] Cycloaddition of 1a and CO**[a]

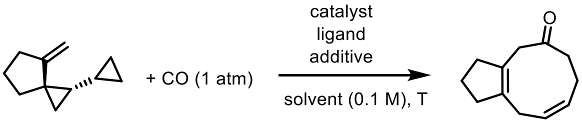


| entry | catalyst (10 mol%) | additive (20 mol%) | ligand (40 mol%) | solvent | T (°C) | **2a** (%) | **3a** (%) |
|---|---|---|---|---|---|---|---|
| 1 | $Co_2(CO)_8$ | none | none | THF | 60 | 0 | 0 |
| 2 | $[Ir(COD)Cl]_2$ | none | none | MeCN | 80 | 0 | 0 |
| 3 | $[Rh(COD)Cl]_2$ | none | none | DCE | 80 | 11 | – |
| 4 | $[Rh(COD)Cl]_2$ | none | none | dioxane | 80 | trace | – |
| 5 | $[Rh(COD)Cl]_2$ | none | none | toluene | 110 | 10 | – |
| 6 | $[Rh(COE)_2Cl]_2$ | none | none | MeCN | 80 | 25 | – |
| 7 | $[Rh(CO)_2Cl]_2$ | none | none | PhCN | 130 | 39 | 12 |
| 8 | $[Rh(CO)_2Cl]_2$ | $AgBF_4$ | none | MeCN | 80 | 8 | 8 |
| 9 | $[Rh(CO)_2Cl]_2$ | $AgPF_6$ | none | MeCN | 80 | 8 | 7 |
| 10 | $[Rh(CO)_2Cl]_2$ | AgOTf | none | MeCN | 80 | 0 | – |
| 11 | $[Rh(CO)_2Cl]_2$ | $NaBPh_4$ | none | MeCN | 80 | 0 | – |
| 12 | $[Rh(CO)_2Cl]_2$ | $NaBARF_4$ | none | MeCN | 80 | 15 | 8 |
| 13 | $[Rh(CO)_2Cl]_2$ | $NaBARF_4$ | none | mesitylene | 130 | 22 | – |
| 14 | $[Rh(CO)_2Cl]_2$ | $NaBARF_4$ | none | TFE | 80 | 7 | 31 |
| 15 | $[Rh(CO)_2Cl]_2$ | $NaBARF_4$ | none | $ClCH_2CN$ | 100 | 34 | 8 |
| 16 | $[Rh(CO)_2Cl]_2$ | $NaBARF_4$ | none | $Cl_2CHCN$ | 80 | 23 | 7 |
| 17 | $[Rh(CO)_2Cl]_2$ | $NaBARF_4$ | none | PhCN | 130 | 38 | 34 |
| 18 | $[Rh(CO)_2Cl]_2$ | $NaBARF_4$ | $P(3,5\text{-}(CF_3)_2C_6H_3)_3$ | PhCN | 130 | 23 | 27 |
| 19 | $[Rh(CO)_2Cl]_2$ | $NaBARF_4$ | $P(4\text{-}FC_6H_4)_3$ | PhCN | 130 | 39 | 35 |
| 20 | $[Rh(CO)_2Cl]_2$ | $NaBARF_4$ | $P(4\text{-}CF_3C_6H_4)_3$ | PhCN | 130 | 0 | – |
| 21 | $[Rh(CO)_2Cl]_2$ | $NaBARF_4$ | $P(C_6F_5)_2Ph$ | PhCN | 130 | 49 | 35 |
| 22 | $[Rh(CO)_2Cl]_2$ | $NaBARF_4$ | $P(C_6F_5)_3$ | PhCN | 130 | 51 | 41 |
| 23 | $[Rh(CO)_2Cl]_2$ | $NaBARF_4$ | $((C_6F_5)_2PCH_2)_2$ (20 mol%) | PhCN | 130 | 50 | 49 |
| 24 | $[Rh(CO)_2Cl]_2$ | $NaBARF_4$ | $P(C_6F_5)_2Ph$ (20 mol%) | PhCN | 130 | 46 | 34 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 25 | $[Rh(CO)_2Cl]_2$ | $NaBARF_4$ | $P(C_6F_5)_3$ (60 mol%) | PhCN | 130 | 50 | 48 |
| 26 | $[Rh(CO)_2Cl]_2$ | $NaBARF_4$ | $P(C_6F_5)_3$ + $(CHCO_2Me)_2$ (100 mol%) | DCB | 130 | 39 | 13 |
| 27 | $[Rh(CO)_2Cl]_2$ | $AgSbF_6$ | $P(C_6F_5)_2Ph$ (20 mol%) | PhCN | 130 | 27 | 44 |
| 28 | $[Rh(CO)_2Cl]_2$ | none | $P(C_6F_5)_3$ | PhCN | 130 | 47 | 30 |
| 29 | $[Rh(CO)_2Cl]_2$ | $NaBARF_4$ + 4Å MS (60 mg) | $P(C_6F_5)_3$ | PhCN | 130 | 38 | 16 |
| 30 | $[Rh(CO)_2Cl]_2$ | $NaBARF_4$ | $P(C_6F_5)_3$ | PhCN (0.2 M) | 130 | 51 | 45 |
| 31 | $[Rh(CO)_2Cl]_2$ | $NaBARF_4$ | $P(C_6F_5)_3$ | PhCN | 110 | 50 | 26 |
| **32** | **$[Rh(CO)_2Cl]_2$** | **$NaBARF_4$** | **$P(C_6F_5)_3$** | **PhCN** | **120** | **52(49[b])** | **36** |
| 33[c] | $[Rh(CO)_2Cl]_2$ | $NaBARF_4$ + $Mo(CO)_6$ (1.0 equiv) | $P(C_6F_5)_3$ | PhCN | 150 | 17 | 12 |
| 34[d] | $[Rh(COE)Cl]_2$ | none | none | MeCN | 80 | NR | NR |
| 35[e] | $[Rh(COD)Cl]_2$ | none | none | DCE | 80 | 10 | – |
| 36[e] | $[Rh(COE)Cl]_2$ | none | none | DCE | 80 | 18 | – |
| 37[e] | $[Rh(CO)_2Cl]_2$ | $AgSbF_6$ | dppp | DCE | 80 | NR | – |
| 38[e] | $Rh(COD)_2SbF_6$ | none | BINAP | DCE | 80 | NR | – |
| 39[e] | $[Rh(COD)Cl]_2$ | none | $PPh_3$ | MeCN | 80 | <5 | – |
| 40[e] | $[Rh(COE)Cl]_2$ | none | none | MeCN | 80 | 14[g] | – |
| 41[e,f] | $[Rh(COE)Cl]_2$ | $NaBARF_4$ | none | MeCN | 80 | 34[h] | – |

[a]Reaction conditions: 0.1 mmol substrate, 10 mol% catalyst, solvent (0.1 M), 24 h, NMR yields using 1,3,5-trimethoxybenzene as internal standard. [b]Isolated yield. [c]without CO. [d]3 atm CO. [e]0.2 atm. [f]20 h. [g]46% conversion. [h]75% conversion. "–" means "observed but not determined".

**Table S2. Optimization of [8+1] Cycloaddition of 4a with CO**



4a 5a

| entry | catalyst (10 mol%) | additive (20 mol%) | ligand (40 mol%) | solvent | T (°C) | **5a** (%) |
|---|---|---|---|---|---|---|
| 1 | $[Rh(CO)_2Cl]_2$ | – | – | MeCN | 80 | 41 |
| 2 | $[Rh(CO)_2Cl]_2$ | – | – | DCE | 80 | 18 |
| 3 | $[Rh(CO)_2Cl]_2$ | – | – | dioxane | 80 | <5 |
| 4 | $[Rh(CO)_2Cl]_2$ | – | – | toluene | 80 | <5 |
| 5 | $[Rh(CO)_2Cl]_2$ | – | – | TFE | 80 | 13 |
| 6 | $[Rh(CO)_2Cl]_2$ | $NaBARF_4$ | – | MeCN | 80 | 44 |

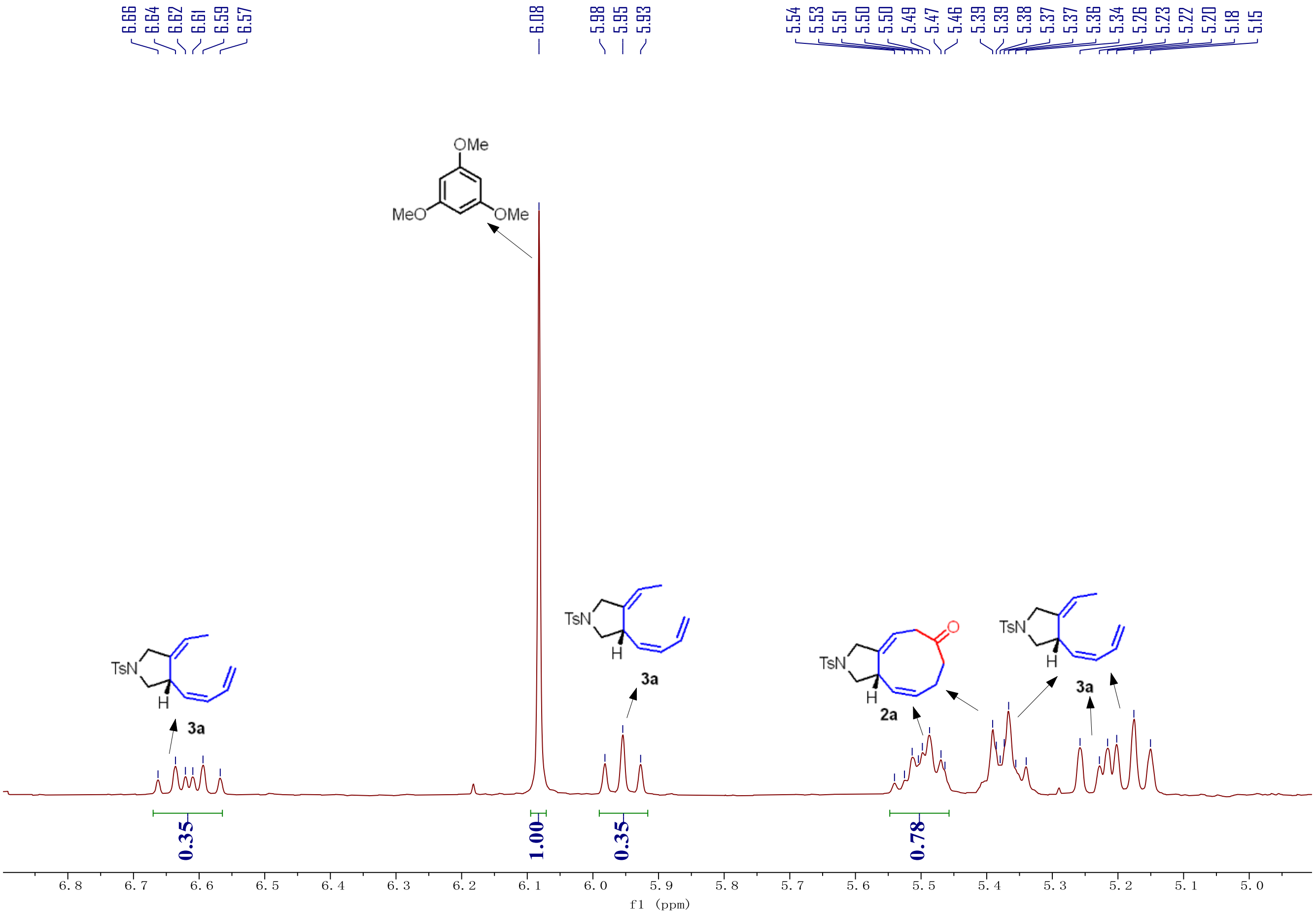
|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| 7 | [Rh(CO)$_2$Cl]$_2$ | – | P(C$_6$F$_5$)$_3$ | MeCN | 80 | 44 |
| 8 | [Rh(CO)$_2$Cl]$_2$ | NaBARF$_4$ | P(C$_6$F$_5$)$_3$ | MeCN | 80 | 46(53[b]) |

[a]Reaction conditions: 0.2 mmol substrate, 10 mol% catalyst, solvent (0.1 M), 24 h. [b]Isolated yield.

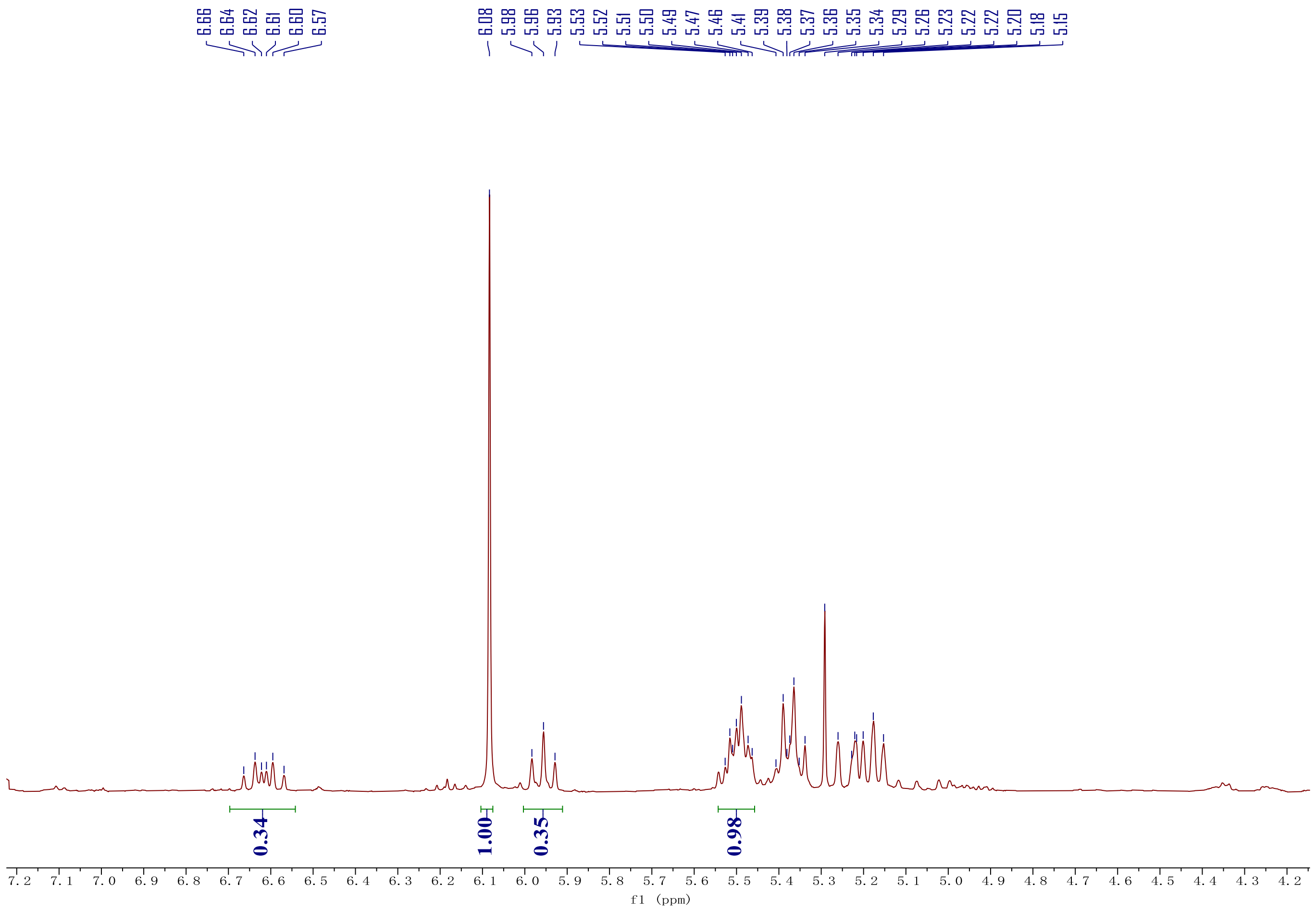
## The crude $^1$H NMR of the [8+1] cycloaddition

The yields and the **2a**/**3a** ratio were determined by the crude $^1$H NMR of the reaction mixture. The spectra reveal that the peak areas of the two products and the internal standard vary with different conditions (see spectra for entries 4 and 6 of table 2 below). This observation can be attributed to the differing abilities of ligands to compete with CO for coordination with rhodium, which affects both the oxidative addition and CO insertion steps. Strong ligands accelerate the oxidative addition step but inhibit the CO insertion step, leading to variations in the **2a**/**3a** ratio depending on the ligand used. The experimental error is unlikely to have a significant impact on the **2a**/**3a** ratio.

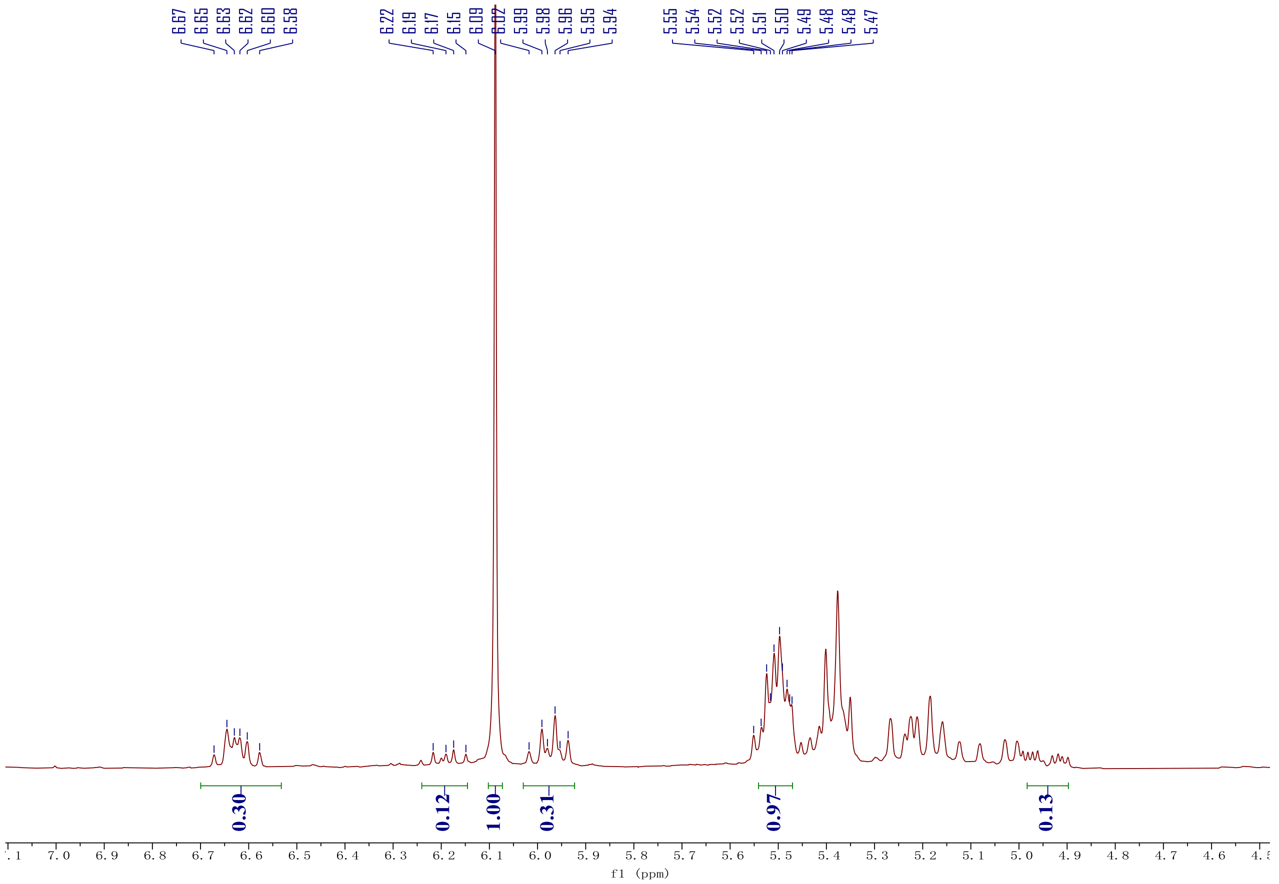
For Table 1, entry 4:



For Table 1, entry 6:

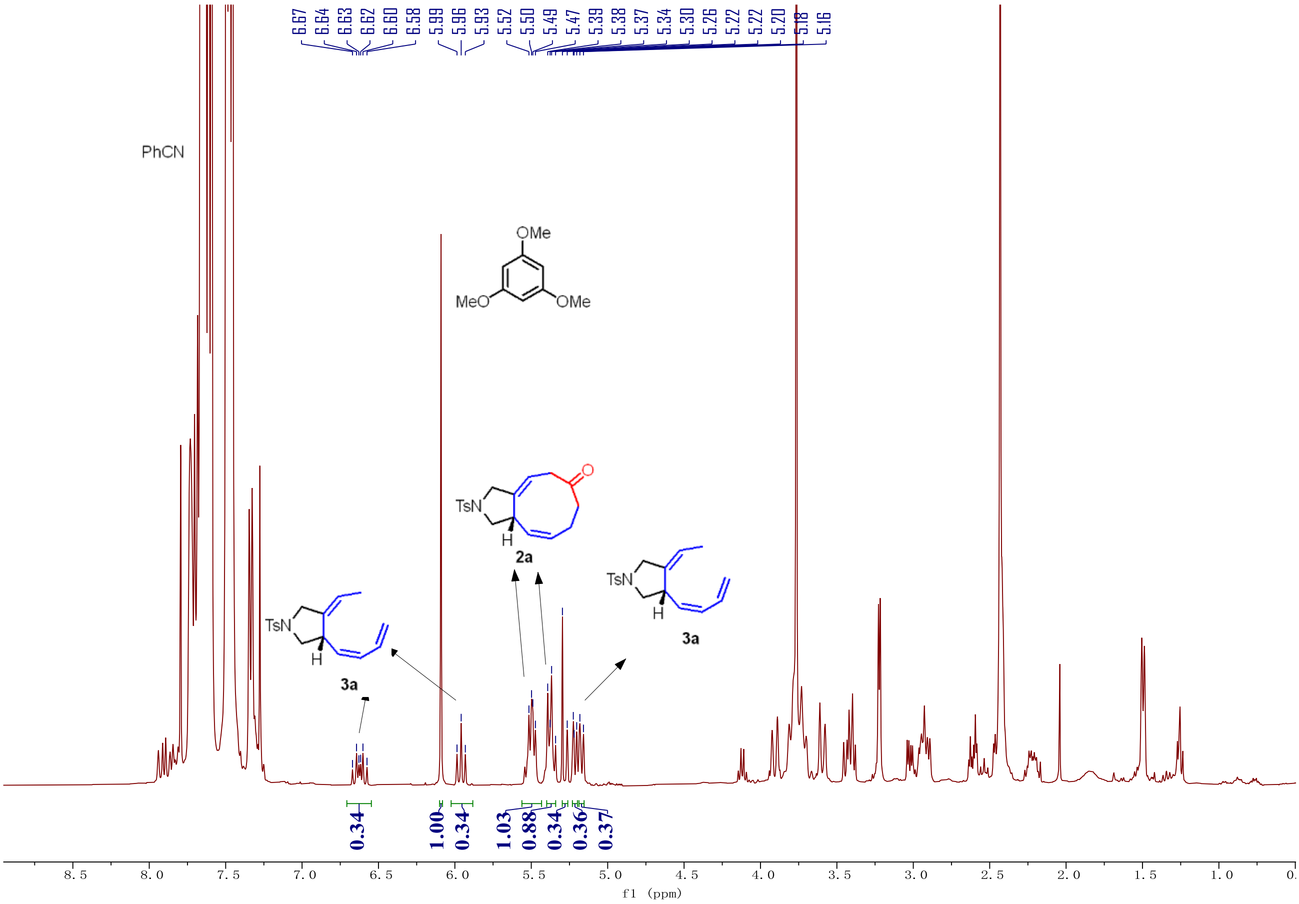


For Table 1, entry 12:

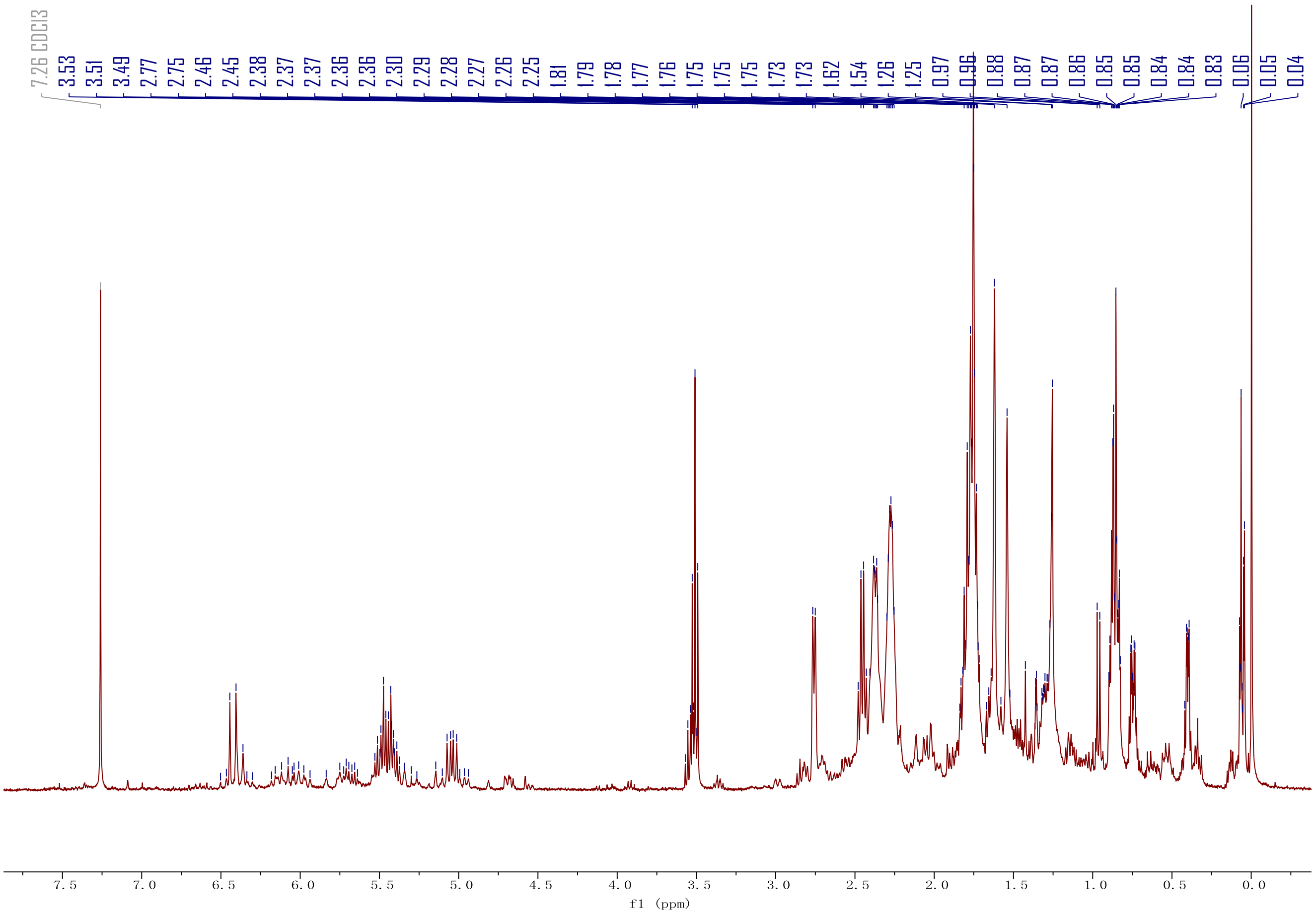


For substrate **1**, the reaction proceeds cleanly under the current conditions, with alkene **3** as the only side product, as confirmed by crude NMR analysis and TLC. In contrast, for the cis/trans-VBCP substrate **4**, the side products include the $\beta$-H elimination product and the VCP rearrangement product **6**. We proposed that the $\beta$-H elimination product may undergo polymerization and isomerization, forming a complex mixture characterized by multiple alkene peaks in the $^1$H NMR (see below).

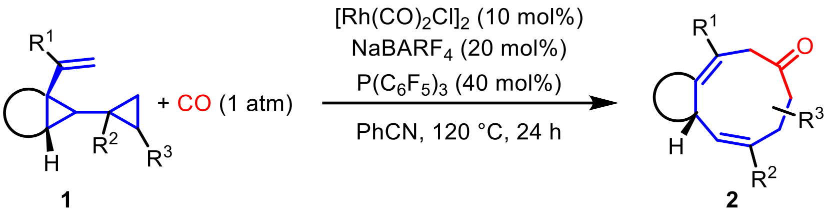
The crude $^1$H NMR of the [8+1] cycloaddition of **1a** under standard conditions:



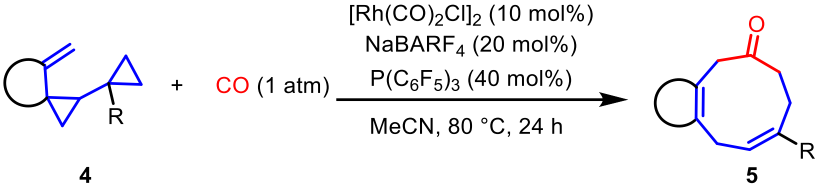
The crude $^1$H NMR of the isolated $\beta$-H elimination product in the [8+1] cycloaddition of **4a**:


7.26 CDCl3
3.53
3.51
3.49
2.77
2.75
2.46
2.45
2.38
2.37
2.37
2.36
2.36
2.30
2.29
2.28
2.27
2.26
2.25
1.81
1.79
1.78
1.77
1.76
1.75
1.75
1.75
1.73
1.73
1.62
1.54
1.26
1.25
0.97
0.96
0.88
0.87
0.87
0.86
0.85
0.85
0.84
0.84
0.83
0.06
0.05
0.04
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

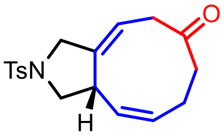
## V. General Procedure and Experimental Details of [8+1] Cycloaddition



General Procedure A: In glove box, the catalyst of $[Rh(CO)_2Cl]_2$ (10 mol%) and substrates **1** (0.1-0.2 mmol), $P(C_6F_5)_3$ (40 mol%), $NaBARF_4$ (20 mol%) were added in a reaction tube (25 mL) and sealed. Then the reaction tube was moved out, and purged with CO (1 atm) three times. The super-dried PhCN (0.1 M) was added and bubbled with balloon pressured of CO for 10 min. The solution was immersed into an oil bath at 120 ºC and reacted under the atmosphere pressure of CO. After stirring for 24 h, the resulting solution was cooled to room temperature. The mixture was purified by flash column chromatography on silica gel (eluted with PE/EA) to afford cycloadduct **2**.



General Procedure B: In glove box, the catalyst of $[Rh(CO)_2Cl]_2$ (10 mol%) and $P(C_6F_5)_3$ (40 mol%), $NaBARF_4$ (20 mol%) were added in a reaction tube (25 mL) and sealed. Then the reaction tube was moved out, and purged with CO (1 atm) three times. Substrates **4** (0.1-0.2 mmol) in the super-dried MeCN (0.1 M) was added and bubbled with balloon pressured of CO for 10 min. The solution was immersed into an oil bath at 80 ºC and reacted under the atmosphere pressure of CO. After stirring for 24 h, the resulting solution was cooled to room temperature. Solvent was evaporated and the residue was purified by flash column chromatography on silica gel (eluted with PE/EA) to afford cycloadduct **5**.



**2a**

Several substrates including **1a**, **1i**, and **1k** all gave the [8+1] products **2a**. Therefore, all these results were summarized here.

For substrate **1a**:

Run 1: Following general procedure A, **1a** (60.7 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (7.8 mg, 0.02 mmol), $P(C_6F_5)_3$ (42.6 mg, 0.08 mmol), $NaBARF_4$ (34.5 mg, 0.04 mmol), PhCN (2 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 20/1~1.5/1), 32.2 mg **2a** was obtained in 49% yield

Run 2: Following general procedure A, **1a** (60.7 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (7.8 mg, 0.02 mmol), $P(C_6F_5)_3$ (42.6 mg, 0.08 mmol), $NaBARF_4$ (34.5 mg, 0.04 mmol), PhCN (2 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 20/1~1.5/1), 31.8 mg **2a** was obtained in 48% yield. The average yield of two runs was 49%.

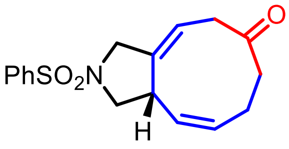
For substrate **1i**:

Run 1: Following general procedure A, **1i** (37.5 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), $P(C_6F_5)_3$

(21.3 mg, 0.04 mmol), NaBARF$_4$ (17.7 mg, 0.04 mmol), PhCN (1 mL), 140 °C was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 3/1), 4.2 mg **2a** was obtained in 13% yield.
Run 2: Following general procedure A, **1i** (37.5 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), $P(C_6F_5)_3$ (21.3 mg, 0.04 mmol), NaBARF$_4$ (17.7 mg, 0.04 mmol), PhCN (1 mL), 140 °C was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 3/1), 4.5 mg **2a** was obtained in 14% yield. The average yield of two runs was 14%.

For substrate **1k**:
Run 1: Following general procedure A, **1k** (30.3 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), $P(C_6F_5)_3$ (21.3 mg, 0.04 mmol), NaBARF$_4$ (17.7 mg, 0.04 mmol), PhCN (1 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 3/1), 10.8 mg **2a** was obtained in 33% yield.
Run 2: Following general procedure A, **1k** (30.3 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), $P(C_6F_5)_3$ (21.3 mg, 0.04 mmol), NaBARF$_4$ (17.7 mg, 0.04 mmol), PhCN (1 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 3/1), 12.0 mg **2a** was obtained in 36% yield. The average yield of two runs was 35%.

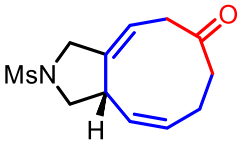
Yellow oil
**TLC** (3:1 PE/EA, *R$_f$*): 0.1
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.56 – 5.44 (m, 2H), 5.36 (t, *J* = 10.3 Hz, 1H), 3.94 – 3.86 (m, 1H), 3.77 – 3.67 (m, 1H), 3.58 (d, *J* = 13.7 Hz, 1H), 3.41 (dd, *J* = 14.8, 8.6 Hz, 1H), 3.22 (s, 1H), 3.21 (s, 1H), 2.99 – 2.85 (m, 2H), 2.59 (dt, *J* = 13.0, 4.2 Hz, 1H), 2.43 (s, 3H), 2.46 – 2.39 (m, 1H), 2.26 – 2.17 (m, 1H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 211.2, 144.0, 143.0, 132.2, 131.0, 129.8, 128.1, 127.0, 116.3, 53.6, 51.8, 46.1, 38.6, 38.5, 24.0, 21.7.
**HRMS** (ESI−FTICR, *m/z*): $[M + H]^+$ calculated for $C_{18}H_{22}NO_3S^+$: 332.1315, found: 332.1314



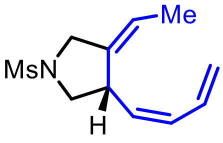
**2b**

Run 1: Following general procedure A, **1b** (33.4 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), $P(C_6F_5)_3$ (21.3 mg, 0.04 mmol), NaBARF$_4$ (17.7 mg, 0.04 mmol), PhCN (1 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 3/1), 13.2 mg **2b** was obtained in 42% yield.
Run 2: Following general procedure A, **1b** (33.4 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), $P(C_6F_5)_3$ (21.3 mg, 0.04 mmol), NaBARF$_4$ (17.7 mg, 0.04 mmol), PhCN (1 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 3/1), 14.4 mg **2b** was obtained in 45% yield. The average yield of two runs was 44%.
Yellow oil
**TLC** (3:1 PE/EA, *R$_f$*): 0.2
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.78 (m, 2H), 7.68 – 7.58 (m, 1H), 7.59 – 7.51 (m, 2H), 5.62 – 5.41 (m, 2H), 5.36 (t, *J* = 10.3 Hz, 1H), 3.94 (d, *J* = 13.7 Hz, 1H), 3.78 – 3.67 (m, 1H), 3.63 (d, *J* = 13.7 Hz, 1H), 3.41 (dd, *J* = 14.9, 8.6 Hz, 1H), 3.26 (s, 1H), 3.25 (s, 1H), 2.99 – 2.87 (m, 2H), 2.66 – 2.54 (m, 1H), 2.50 – 2.37 (m, 1H), 2.30 – 2.16 (m, 1H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 211.2, 142.9, 135.4, 133.2, 131.0, 129.2, 128.0, 127.1, 116.4, 53.6, 51.8, 46.1, 38.6, 38.5, 24.1.

**HRMS** (ESI−FTICR, *m*/*z*): $[M + H]^+$ calculated for $C_{17}H_{20}NO_3S^+$: 318.1158, found: 318.1155

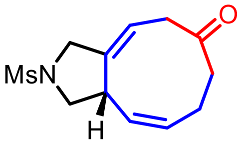

**2c**

+


**3c**

Run 1: Following general procedure A, **1c** (22.7 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), $P(C_6F_5)_3$ (21.3 mg, 0.04 mmol), $NaBARF_4$ (17.7 mg, 0.04 mmol), PhCN (1 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 5/1), 10.7 mg **2c** was obtained in 42% yield, and 9.0 mg **3c** was obtained in 40% yield.

Run 2: Following general procedure A, **1c** (22.7 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), $P(C_6F_5)_3$ (21.3 mg, 0.04 mmol), $NaBARF_4$ (17.7 mg, 0.04 mmol), PhCN (1 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 20/1~5/1), 10.5 mg **2c** was obtained in 41% yield, and 10.1 mg **3c** was obtained in 44% yield. The average yield of two runs was 42% **2c** and 42% **3c**.


**2c**

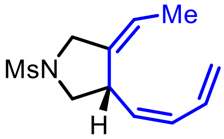
Yellow oil

**TLC** (1:1 PE/EA, $R_f$): 0.1

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.65 – 5.54 (m, 2H), 5.50 (dd, *J* = 10.2 Hz, 1H), 4.03 (dt, *J* = 14.0, 1.9 Hz, 1H), 3.85 (d, *J* = 14.1 Hz, 2H), 3.56 – 3.46 (m, 2H), 3.30 (dd, *J* = 10.0, 2.9 Hz, 1H), 3.06 – 2.94 (m, 2H), 2.85 (s, 3H), 2.64 (dt, *J* = 13.0, 4.3 Hz, 1H), 2.48 (td, *J* = 13.1, 4.2 Hz, 1H), 2.27 (ddt, *J* = 14.4, 6.3, 4.4 Hz, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 211.2, 143.0, 130.8, 127.4, 116.7, 53.5, 51.7, 46.0, 38.9, 38.6, 35.2, 24.1.

**HRMS** (ESI−FTICR, *m*/*z*): $[M + H]^+$ calculated for $C_{12}H_{18}NO_3S^+$: 256.1002, found: 256.0999


**3c**

The product **3c** was isolated with inseparable impurities (shown below, about 6:1), we proposed that the triene product **3** was not stable enough, which could easily undergo transformations such as isomerization, polymerization and oxidation under air conditions.

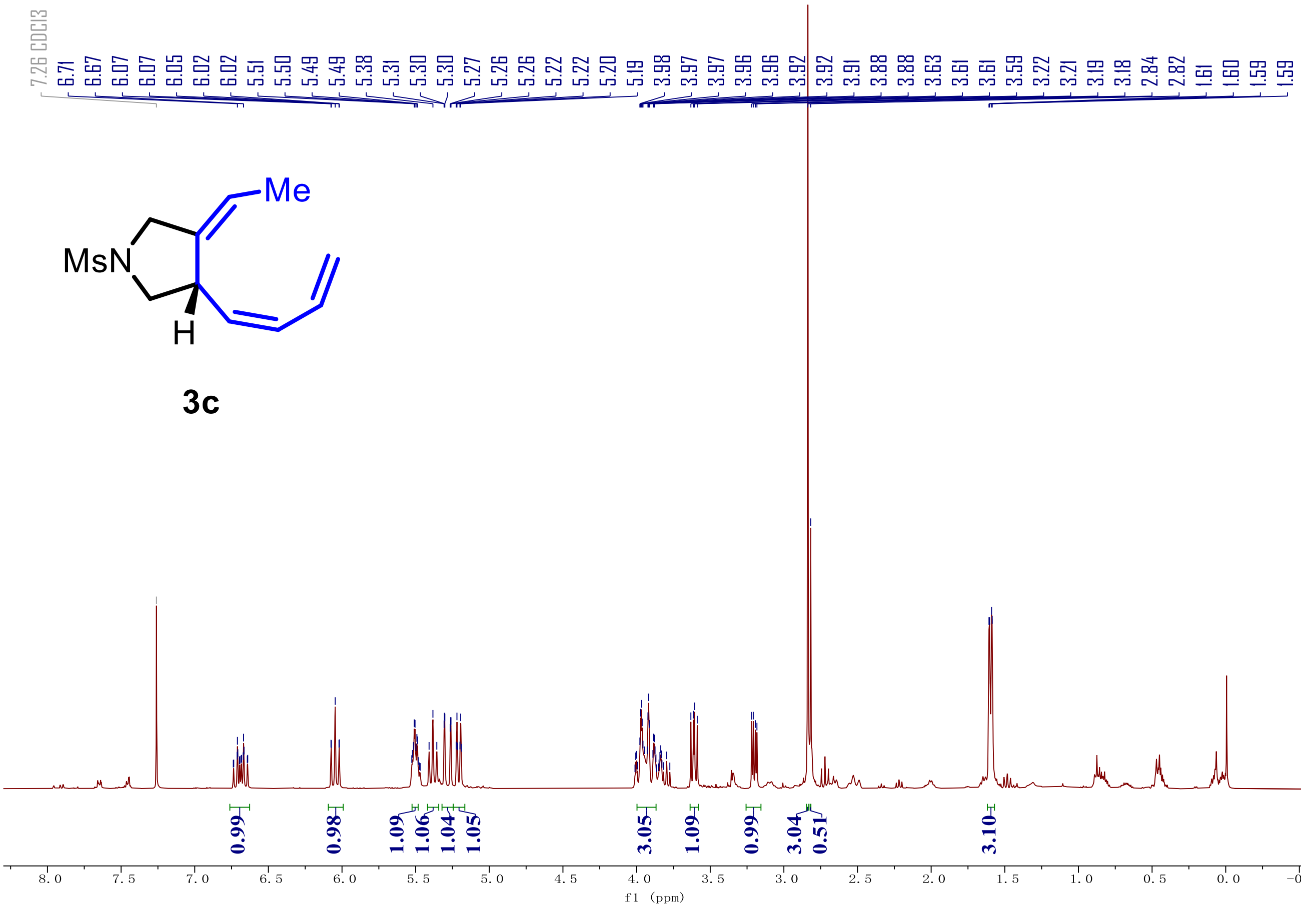
Yellow oil

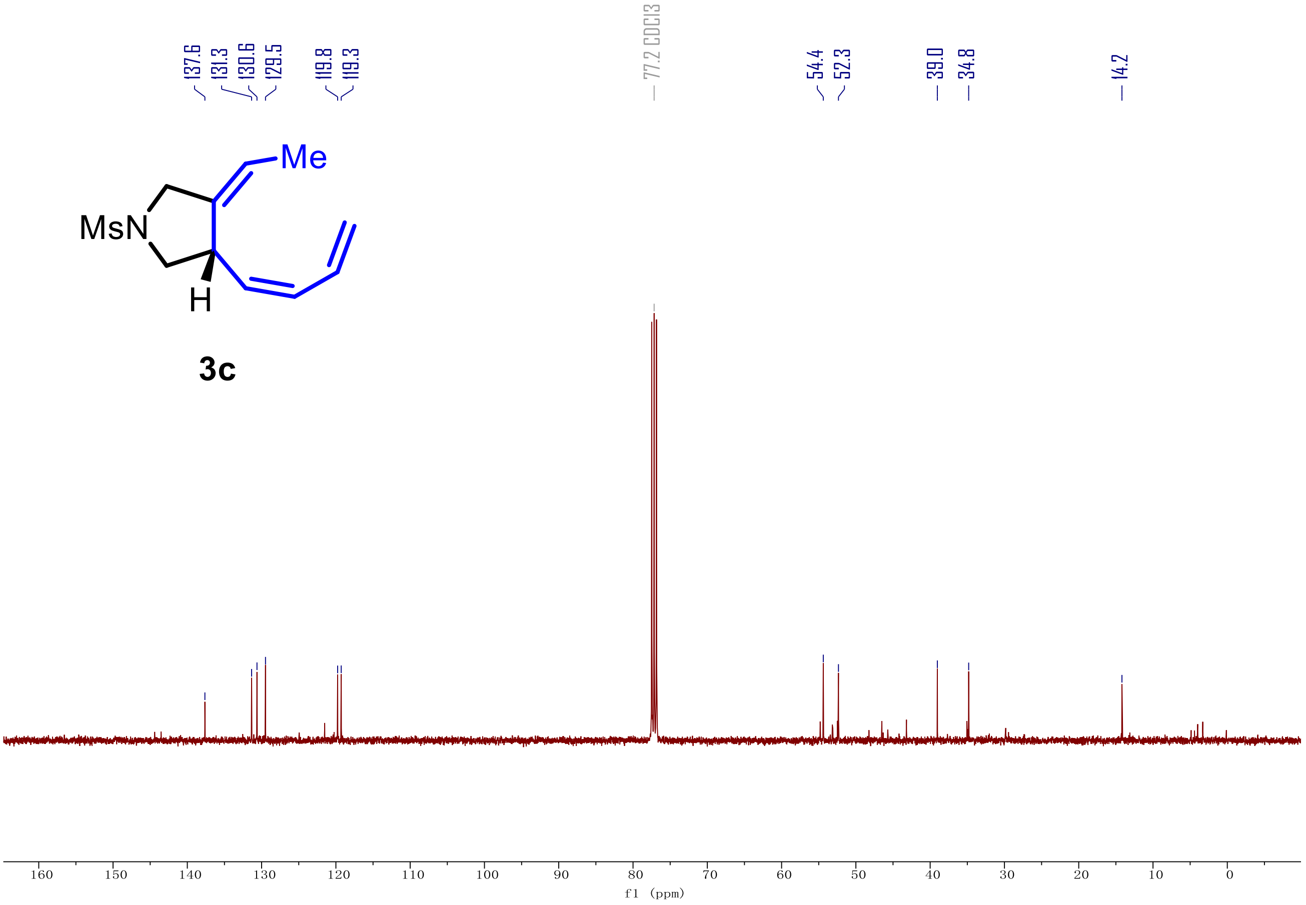
**TLC** (1:1 PE/EA, $R_f$): 0.8

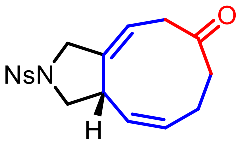
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 6.69 (dddd, *J* = 16.7, 11.3, 10.2, 1.1 Hz, 1H), 6.09 – 5.99 (m, 1H), 5.56 – 5.46 (m, 1H), 5.45 – 5.34 (m, 1H), 5.32 – 5.24 (m, 1H), 5.24 – 5.17 (m, 1H), 4.05 – 3.82 (m, 3H), 3.61 (dd, *J* = 10.0, 7.3 Hz, 1H), 3.20 (dd, *J* = 9.9, 4.3 Hz, 1H), 2.84 (s, 3H), 1.60 (dd, *J* = 7.0, 1.7 Hz, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 137.6, 131.3, 130.6, 129.5, 119.8, 119.3, 54.4, 52.3, 39.0, 34.8, 14.2.

**HRMS** (ESI−FTICR, *m*/*z*): $[M + H]^+$ calculated for $C_{11}H_{18}NO_2S^+$: 228.1053, found: 228.1054


7.26 CDCl3
6.71
6.67
6.07
6.07
6.05
6.02
6.02
5.51
5.50
5.49
5.49
5.38
5.31
5.30
5.30
5.27
5.26
5.26
5.22
5.22
5.20
5.19
3.98
3.97
3.97
3.96
3.96
3.92
3.92
3.91
3.88
3.88
3.63
3.61
3.61
3.59
3.22
3.21
3.19
3.18
2.84
2.82
1.61
1.60
1.59
1.59
Me
MsN
H
3c
0.99
0.98
1.09
1.06
1.04
1.05
3.05
1.09
0.99
3.04
0.51
3.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


137.6
131.3
130.6
129.5
119.8
119.3
77.2 CDCl3
54.4
52.3
39.0
34.8
14.2
Me
MsN
H
3c
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



**2d**

Run 1: Following general procedure A, **1d** (33.4 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), $P(C_6F_5)_3$ (21.3 mg, 0.04 mmol), $NaBARF_4$ (17.7 mg, 0.04 mmol), PhCN (1 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 5/1~3/1), 12.4 mg **2d** was obtained in 34% yield.

Run 2: Following general procedure A, **1d** (33.4 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), $P(C_6F_5)_3$ (21.3 mg, 0.04 mmol), $NaBARF_4$ (17.7 mg, 0.04 mmol), PhCN (1 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 5/1~3/1), 12.6 mg **2d** was obtained in 35% yield. The average yield of two runs was 35%.

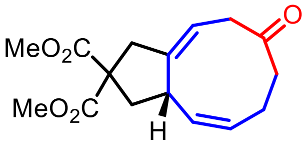
Yellow solid, m.p.= 198.5 -199.7 °C

**TLC** (3:1 PE/EA, *Rf*): 0.1

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.8 Hz, 2H), 8.00 (d, *J* = 8.8 Hz, 2H), 5.65 – 5.46 (m, 2H), 5.35 (t, *J* = 10.3 Hz, 1H), 4.00 (d, *J* = 13.8 Hz, 1H), 3.76 (s, 1H), 3.69 (d, *J* = 13.9 Hz, 1H), 3.42 (dd, *J* = 14.9, 8.6 Hz, 1H), 3.39 – 3.25 (m, 2H), 3.03 – 2.85 (m, 2H), 2.61 (dt, *J* = 13.1, 4.3 Hz, 1H), 2.45 (td, *J* = 13.1, 4.2 Hz, 1H), 2.31 – 2.18 (m, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 210.8, 150.4, 142.0, 141.7, 130.4, 129.0, 127.6, 124.5, 117.1, 53.7, 51.7, 46.0, 38.6, 38.5, 24.1.

**HRMS** (ESI−FTICR, *m/z*): $[M + H]^+$ calculated for $C_{17}H_{19}N_2O_5S^+$: 363.1009, found: 363.1013



**2e**

Run 1: Following general procedure A, **1e** (26.4 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), $P(C_6F_5)_3$ (21.3 mg, 0.04 mmol), $NaBARF_4$ (17.7 mg, 0.04 mmol), PhCN (1 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 5/1~3/1), 11.2 mg **2e** was obtained in 38% yield.

Run 2: Following general procedure A, **1e** (26.4 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), $P(C_6F_5)_3$ (21.3 mg, 0.04 mmol), $NaBARF_4$ (17.7 mg, 0.04 mmol), PhCN (1 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 5/1~3/1), 11.1 mg **2d** was obtained in 38% yield. The average yield of two runs was 38%.

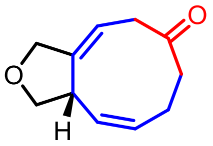
Yellow oil

**TLC** (3:1 PE/EA, *Rf*): 0.2

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.59 – 5.48 (m, 2H), 5.33 (t, *J* = 10.3 Hz, 1H), 3.73 (s, 6H), 3.64 (d, *J* = 8.9 Hz, 1H), 3.38 – 3.18 (m, 1H), 3.07 – 2.80 (m, 4H), 2.75 (dd, *J* = 13.6, 8.4 Hz, 1H), 2.58 – 2.50 (m, 1H), 2.48 – 2.39 (m, 1H), 2.31 – 2.22 (m, 1H), 1.94 (dd, *J* = 13.5, 7.2 Hz, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 212.8, 171.9, 171.8, 146.6, 133.5, 126.7, 116.9, 59.4, 53.0, 52.9, 45.1, 41.9, 40.9, 39.3, 38.2, 24.3.

**HRMS** (ESI−FTICR, *m/z*): $[M + H]^+$ calculated for $C_{16}H_{21}O_5^+$: 293.1384, found: 293.1387



**2f**

Run 1: Following general procedure A, **1f** (30.0 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (7.8 mg, 0.02 mmol), $P(C_6F_5)_3$ (42.6 mg, 0.08 mmol), $NaBARF_4$ (35.4 mg, 0.04 mmol), PhCN (2 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 20/1~3/1), 14.1 mg **2f** was obtained in 40% yield.

Run 2: Following general procedure A, **1f** (30.0 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (7.8 mg, 0.02 mmol), $P(C_6F_5)_3$ (42.6 mg, 0.08 mmol), $NaBARF_4$ (35.4 mg, 0.04 mmol), PhCN (2 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 20/1~3/1), 15.1 mg **2f** was obtained in 42% yield. The average yield of two runs was 41%.

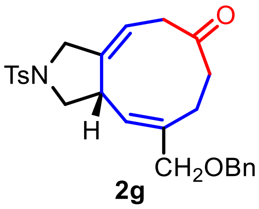
Yellow oil

**TLC** (3:1 PE/EA, *R<sub>f</sub>*): 0.2

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.59 – 5.45 (m, 3H), 4.34 (d, *J* = 12.9 Hz, 1H), 4.20 (d, *J* = 13.0 Hz, 1H), 3.96 (dd, *J* = 8.8, 6.2 Hz, 1H), 3.76 – 3.70 (m, 2H), 3.47 (dd, *J* = 15.0, 8.5 Hz, 1H), 3.14 – 2.96 (m, 2H), 2.62 (dt, *J* = 12.5, 4.1 Hz, 1H), 2.47 (td, *J* = 13.0, 4.2 Hz, 1H), 2.30 – 2.22 (m, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 212.3, 147.2, 131.5, 126.7, 113.2, 74.2, 71.2, 45.8, 40.4, 39.1, 24.2.

**HRMS** (ESI−FTICR, *m/z*): $[M + H]^+$ calculated for $C_{11}H_{15}O_2^+$: 179.1067, found: 179.1070



**2g**

Run 1: Following general procedure A, **1g** (42.4 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), $P(C_6F_5)_3$ (21.3 mg, 0.04 mmol), $NaBARF_4$ (17.7 mg, 0.04 mmol), PhCN (1 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 5/1~4/1), 5.6 mg **2g** was obtained in 12% yield.

Run 2: Following general procedure A, **1e** (42.4 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), $P(C_6F_5)_3$ (21.3 mg, 0.04 mmol), $NaBARF_4$ (17.7 mg, 0.04 mmol), PhCN (1 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 5/1~4/1), 6.0 mg **2g** was obtained in 13% yield. The average yield of two runs was 13%.

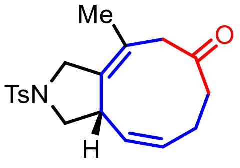
Brown oil

**TLC** (3:1 PE/EA, *R<sub>f</sub>*): 0.1

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.40 – 7.27 (m, 7H), 5.57 – 5.48 (m, 1H), 5.38 (d, *J* = 9.9 Hz, 1H), 4.47 (d, *J* = 11.9 Hz, 1H), 4.42 (d, *J* = 11.8 Hz, 1H), 4.02 (dd, *J* = 11.8, 1.3 Hz, 1H), 3.92 (d, *J* = 13.8 Hz, 1H), 3.78 (d, *J* = 11.8 Hz, 1H), 3.67 (t, *J* = 8.3 Hz, 1H), 3.60 (d, *J* = 13.8 Hz, 1H), 3.37 (dd, *J* = 15.1, 8.6 Hz, 1H), 3.31 – 3.18 (m, 2H), 2.99 – 2.88 (m, 2H), 2.65 – 2.53 (m, 2H), 2.47 – 2.37 (m, 4H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 211.5, 144.0, 142.9, 138.2, 135.3, 132.3, 129.9, 128.9, 128.6, 128.1, 127.9, 116.9, 73.5, 72.4, 53.7, 51.9, 44.7, 39.4, 39.0, 24.8, 21.7.

**HRMS** (ESI−FTICR, *m/z*): $[M + H]^+$ calculated for $C_{26}H_{30}NO_4S^+$: 452.1890, found: 452.1883



**2h**

Run 1: Following general procedure A, **1h** (31.7 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), $P(C_6F_5)_3$ (21.3 mg, 0.04 mmol), $NaBARF_4$ (17.7 mg, 0.04 mmol), PhCN (1 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 4/1), 4.1 mg **2h** was obtained in 12% yield.

Run 2: Following general procedure A, **1h** (31.7 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), $P(C_6F_5)_3$ (21.3 mg, 0.04 mmol), $NaBARF_4$ (17.7 mg, 0.04 mmol), PhCN (1 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 4/1), 5.2 mg **2h** was obtained in 15% yield. The average yield of two runs was 14%.

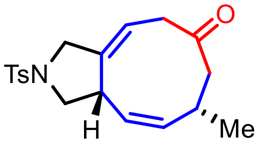
Yellow oil

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

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, $J$ = 8.0 Hz, 2H), 7.34 (d, $J$ = 8.0 Hz, 2H), 5.47 – 5.37 (m, 2H), 3.94 (d, $J$ = 13.9 Hz, 1H), 3.76 – 3.66 (m, 2H), 3.54 (d, $J$ = 13.8 Hz, 1H), 3.31 (dd, $J$ = 9.4, 1.5 Hz, 1H), 3.13 (dd, $J$ = 9.4, 6.2 Hz, 1H), 3.05 – 2.89 (m, 1H), 2.68 (dt, $J$ = 13.7, 4.2 Hz, 1H), 2.54 (d, $J$ = 14.5 Hz, 1H), 2.46 – 2.39 (m, 1H), 2.44 (s, 3H), 2.20 – 2.14 (m, 1H), 1.76 – 1.70 (m, 3H).

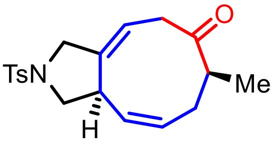
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 209.3, 143.7, 134.6, 132.5, 131.7, 129.7, 127.9, 126.0, 124.4, 53.3, 50.1, 47.5, 43.6, 39.2, 23.6, 23.0, 21.6.

**HRMS** (ESI−FTICR, $m/z$): $[M + H]^+$ calculated for $C_{19}H_{24}NO_3S^+$: 346.1471, found: 346.1469



**2j**

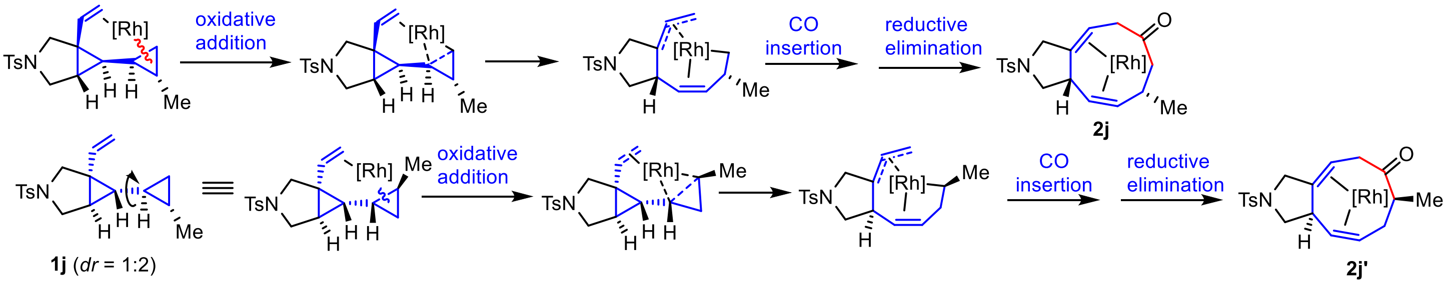
+



**2j'**

Run 1: Following general procedure A, **1j** (31.7 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), $P(C_6F_5)_3$ (21.3 mg, 0.04 mmol), $NaBARF_4$ (17.7 mg, 0.04 mmol), PhCN (1 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 4/1), 4.3 mg (**2j**+**2j'**) was obtained in 12% yield.

Run 2: Following general procedure A, **1j** (31.7 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), $P(C_6F_5)_3$ (21.3 mg, 0.04 mmol), $NaBARF_4$ (17.7 mg, 0.04 mmol), PhCN (1 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 4/1), 5.2 mg (**2j**+**2j'**) was obtained in 15% yield. The average yield of two runs was 14%, the ratio of **2j**:**2j'** is 1:2 according to the $^1$H NMR peaks of methyl group (δ 1.08: δ 1.10), the configuration of **2j** and **2j'** was proposed by the mechanism of [8+1] cycloaddition from both diastereomers of **1j**, see below:



The following peaks for **2j'** were selected from the crude NMR.

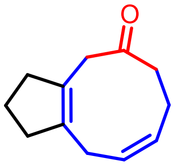
Yellow oil

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

**$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.69 (d, $J$ = 8.1 Hz, 2H), 7.34 (d, $J$ = 8.0 Hz, 2H), 5.56 – 5.50 (m, 1H), 5.44 – 5.32 (m, 1H), 5.25 – 5.19 (m, 1H), 3.89 (d, $J$ = 13.6 Hz, 1H), 3.66 (dd, $J$ = 4.0 Hz 1H), 3.62 (d, $J$ = 13.4 Hz, 1H), 3.34 (dd, $J$ = 15.2, 8.7 Hz, 1H), 3.31 – 3.18 (m, 2H), 2.97 (dd, $J$ = 15.2, 7.4 Hz, 1H), 2.56 (dd, $J$ = 12.3, 4.1 Hz, 1H), 2.44 (s, 3H), 2.25 (dd, $J$ = 12.4, 12.4 Hz, 1H), 2.04 – 1.97 (m, 1H), 1.10 (d, $J$ = 6.5 Hz, 3H).

**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 210.7, 144.0, 142.9, 133.7, 129.8, 128.8, 128.2, 128.1, 116.8, 54.3, 53.7, 52.0, 39.4, 39.2, 30.7, 21.7, 21.7.

**HRMS** (ESI−FTICR, $m/z$): $[M + H]^+$ calculated for $C_{19}H_{24}NO_3S^+$: 346.1471, found: 346.1475



**5a**

Run 1: Following general procedure B, **4a** (29.6 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (7.8 mg, 0.02 mmol), $P(C_6F_5)_3$ (42.6 mg, 0.08 mmol), $NaBARF_4$ (35.4 mg, 0.04 mmol), MeCN (2 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 1/0~50/1~25/1), 19.0 mg **5a** was obtained in 54% yield.

Run 2: Following general procedure B, **4a** (29.6 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (7.8 mg, 0.02 mmol), $P(C_6F_5)_3$ (42.6 mg, 0.08 mmol), $NaBARF_4$ (35.4 mg, 0.04 mmol), MeCN (2 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 1/0~50/1~25/1), 17.9 mg **5a** was obtained in 51% yield. The average yield of two runs was 53%.

Gram-scale:

Run 1: Following general procedure B, **4a** (1.04 g, 7 mmol), $[Rh(CO)_2Cl]_2$ (68.0 mg, 0.175 mmol), $P(C_6F_5)_3$ (375.5 mg, 0.7 mmol), $NaBARF_4$ (310.2 mg, 0.35 mmol), MeCN (70 mL) was used, bubbled with CO for 5 min, 80 °C, 48 h. After flash column chromatography on silica gel (eluted with PE/EA, 50/1~40/1), 0.62 g **5a** was obtained in 51% yield.

Run 2: Following general procedure B, **4a** (1.04 g, 7 mmol), $[Rh(CO)_2Cl]_2$ (68.0 mg, 0.175 mmol), $P(C_6F_5)_3$ (375.5 mg, 0.7 mmol), $NaBARF_4$ (310.2 mg, 0.35 mmol), MeCN (70 mL) was used, bubbled with CO for 5 min, 80 °C, 48 h. After flash column chromatography on silica gel (eluted with PE/EA, 50/1~40/1), 0.62 g **5a** was obtained in 50% yield. The average yield of two runs was 51%.

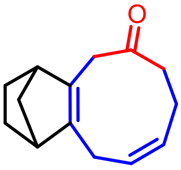
Yellow oil

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

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.67 (dt, $J$ = 10.6, 8.4 Hz, 1H), 5.51 (dt, $J$ = 10.5, 8.0 Hz, 1H), 3.22 (s, 2H), 2.80 (d, $J$ = 8.2 Hz, 2H), 2.64 – 2.48 (m, 4H), 2.40 (dt, $J$ = 20.3, 7.7 Hz, 4H), 1.77 (tt, $J$ = 7.6, 7.6 Hz, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 210.4, 137.3, 129.5, 128.9, 127.9, 46.7, 39.4, 39.2, 37.7, 27.0, 23.0, 21.7.

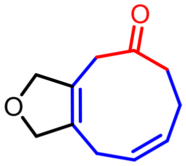
**HRMS** (ESI−FTICR, $m/z$): $[M + H]^+$ calculated for $C_{12}H_{17}O^+$: 177.1274, found: 177.1275



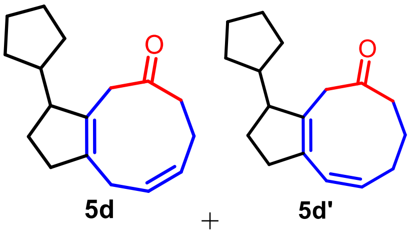
**5b**

Run 1: Following general procedure B, **4b** (31.3 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (7.0 mg, 0.02 mmol), $P(C_6F_5)_3$ (38.3 mg, 0.08 mmol), $NaBARF_4$ (31.9 mg, 0.04 mmol), MeCN (1.8 mL) was used, 24 h. After flash column

chromatography on silica gel (eluted with PE/EA, 1/0~50/1~25/1), 15.4 mg **5b** was obtained in 42% yield.
Run 2: Following general procedure B, **4b** (31.3 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (7.0 mg, 0.02 mmol), $P(C_6F_5)_3$ (38.3 mg, 0.08 mmol), $NaBARF_4$ (31.9 mg, 0.04 mmol), MeCN (1.8 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 1/0~50/1~25/1), 15.8 mg **5b** was obtained in 43% yield. The average yield of two runs was 43%.
Light yellow oil
**TLC** (10:1 PE/EA, *R<sub>f</sub>*): 0.5
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.69 (dt, *J* = 10.3, 8.0 Hz, 1H), 5.54 (dt, *J* = 10.8, 8.1 Hz, 1H), 3.52 (d, *J* = 13.5 Hz, 1H), 3.08 (d, *J* = 13.6 Hz, 1H), 2.96 (dd, *J* = 14.9, 8.8 Hz, 1H), 2.75 – 2.68 (m, 1H), 2.68 – 2.58 (m, 3H), 2.51 (ddd, *J* = 14.4, 8.5, 3.1 Hz, 1H), 2.45 – 2.38 (m, 1H), 2.37 – 2.29 (m, 1H), 1.64 – 1.56 (m, 2H), 1.36 (dp, *J* = 6.5, 2.1 Hz, 1H), 1.21 – 1.14 (m, 1H), 1.12 – 1.04 (m, 1H), 1.01 (d, *J* = 7.8 Hz, 1H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 210.9, 141.6, 133.0, 129.0, 128.6, 49.1, 48.6, 48.1, 45.0, 40.6, 26.9, 26.0, 24.9, 23.2.
**HRMS** (ESI−FTICR, *m*/*z*): $[M + H]^+$ calculated for $C_{14}H_{19}O^+$: 203.1430, found: 203.1431


**5c**

Run 1: Following general procedure B, **4c** (30.0 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (7.8 mg, 0.02 mmol), $P(C_6F_5)_3$ (42.6 mg, 0.08 mmol), $NaBARF_4$ (35.4 mg, 0.04 mmol), PhCN (2 mL) was used, 130 °C, 48 h. After flash column chromatography on silica gel (eluted with PE/EA, 10/1~5/1), 15.9 mg **5c** was obtained in 45% yield.
Run 2: Following general procedure B, **4c** (30.0 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (7.8 mg, 0.02 mmol), $P(C_6F_5)_3$ (42.6 mg, 0.08 mmol), $NaBARF_4$ (35.4 mg, 0.04 mmol), PhCN (2 mL) was used, 130 °C, 48 h. After flash column chromatography on silica gel (eluted with PE/EA, 10/1~5/1), 15.5 mg **5a** was obtained in 44% yield. The average yield of two runs was 45%.
Light yellow solid, m.p. = 66.2-67.3 °C
**TLC** (10:1 PE/EA, *R<sub>f</sub>*): 0.5
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.69 – 5.59 (m, 2H), 4.65 – 4.59 (m, 4H), 3.21 (s, 2H), 2.80 (d, *J* = 6.5 Hz, 2H), 2.65 – 2.59 (m, 2H), 2.59 – 2.54 (m, 2H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 209.0, 132.5, 129.4, 127.3, 125.6, 80.0, 78.9, 46.0, 35.8, 23.3, 22.9.
**HRMS** (ESI−FTICR, *m*/*z*): $[M + H]^+$ calculated for $C_{11}H_{15}O_2^+$: 179.1067, found: 179.1064



Run 1: Following general procedure B, **4d** (43.3 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (7.8 mg, 0.02 mmol), $P(C_6F_5)_3$ (42.6 mg, 0.08 mmol), $NaBARF_4$ (35.4 mg, 0.04 mmol), MeCN (2 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 40/1), 14.8 mg (**5d+5d'**) was obtained in 30% yield.
Run 2: Following general procedure B, **4d** (43.3 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (7.8 mg, 0.02 mmol), $P(C_6F_5)_3$ (42.6 mg, 0.08 mmol), $NaBARF_4$ (35.4 mg, 0.04 mmol), MeCN (2 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 10/1~5/1), 16.5 mg (**5d+5d'**) was obtained in 34% yield.

The average yield of two runs was 32%.

**5d** was obtained with the hypothesized **5d'** (not confirmed structure) in 3:1 ratio according to the crude $^1$H NMR, the following peaks for **5d** were selected from the crude NMR.

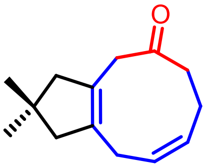
Yellow oil

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

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.69 – 5.61 (m, 1H), 5.59 – 5.48 (m, 1H), 3.54 (d, $J$ = 14.4 Hz, 1H), 3.07 (dd, $J$ = 13.7, 9.3 Hz, 1H), 2.89 – 2.79 (m, 2H), 2.60 (ddd, $J$ = 13.7, 7.2, 3.8 Hz, 1H), 2.54 – 2.44 (m, 1H), 2.41 (dq, $J$ = 9.6, 3.0, 2.3 Hz, 1H), 2.36 – 2.22 (m, 3H), 2.17 – 1.96 (m, 2H), 1.88 – 1.82 (m, 1H), 1.75 – 1.68 (m, 1H), 1.63 – 1.58 (m, 1H), 1.56 – 1.41 (m, 5H), 1.25 – 1.18 (m, 1H), 1.17 – 1.05 (m, 1H).

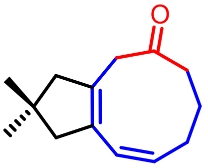
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 211.5, 137.8, 133.3, 128.9, 127.8, 52.8, 46.2, 42.0, 38.4, 36.2, 31.1, 27.7, 27.4, 26.2, 25.8, 24.7, 23.0.

**HRMS** (ESI−FTICR, $m/z$): $[M + H]^+$ calculated for $C_{17}H_{25}O^+$: 245.1990, found: 245.1899



**5e**

+



**5e'**

Run 1: Following general procedure B, **4e** (35.3 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (7.8 mg, 0.02 mmol), $P(C_6F_5)_3$ (42.6 mg, 0.08 mmol), $NaBARF_4$ (35.4 mg, 0.04 mmol), MeCN (2 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 20/1~10/1), 10.3 mg (**5e+5e'**) was obtained in 25% yield.

Run 2: Following general procedure B, **4e** (35.3 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (7.8 mg, 0.02 mmol), $P(C_6F_5)_3$ (42.6 mg, 0.08 mmol), $NaBARF_4$ (35.4 mg, 0.04 mmol), MeCN (2 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 20/1~10/1), 11.2 mg (**5e+5e'**) was obtained in 27% yield.

The average yield of two runs was 26%.

**5e** was obtained with the hypothesized **5e'** (not confirmed structure) in 8:1 ratio according to the crude $^1$H NMR, the following peaks for **5e** were selected from the crude NMR.

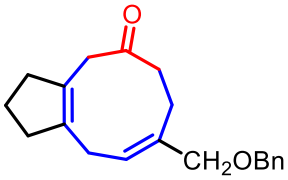
Yellow oil

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

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.73 – 5.62 (m, 1H), 5.57 – 5.48 (m, 1H), 3.18 (s, 2H), 2.76 (d, $J$ = 8.2 Hz, 2H), 2.57 (ddd, $J$ = 8.4, 5.7, 2.5 Hz, 2H), 2.54 – 2.48 (m, 2H), 2.28 – 2.21 (m, 2H), 2.20 – 2.15 (m, 2H), 1.03 (s, 6H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 210.2, 136.1, 128.9, 128.1, 127.9, 54.0, 52.7, 46.6, 39.5, 36.6, 29.8, 27.2, 22.9.

**HRMS** (ESI−FTICR, $m/z$): $[M + H]^+$ calculated for $C_{14}H_{21}O^+$: 205.1587, found: 205.1587



**5f**

Run 1: Following general procedure B, **4f** (53.7 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (7.8 mg, 0.02 mmol), $P(C_6F_5)_3$ (42.6 mg, 0.08 mmol), $NaBARF_4$ (35.4 mg, 0.04 mmol), MeCN (2 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 20/1~10/1), 13.2 mg **5f** was obtained in 22% yield.

Run 2: Following general procedure B, **4f** (53.7 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (7.8 mg, 0.02 mmol), $P(C_6F_5)_3$ (42.6 mg, 0.08 mmol), $NaBARF_4$ (35.4 mg, 0.04 mmol), MeCN (2 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 20/1~10/1), 15.1 mg **5f** was obtained in 26% yield. The average yield of two runs was 24%.

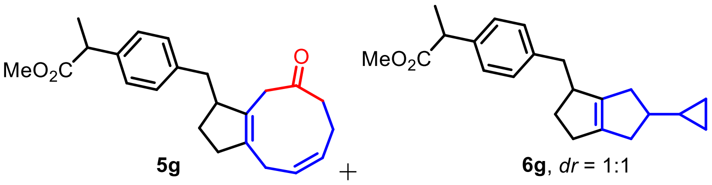
Brown oil

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

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 5H), 5.71 (t, *J* = 8.4 Hz, 1H), 4.44 (s, 2H), 3.93 (d, *J* = 1.1 Hz, 2H), 3.21 (s, 2H), 2.83 (d, *J* = 8.5 Hz, 2H), 2.72 – 2.66 (m, 2H), 2.61 – 2.56 (m, 2H), 2.44 – 2.36 (m, 4H), 1.80 – 1.75 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 210.8, 138.5, 137.3, 136.0, 130.1, 128.6, 128.5, 127.9, 127.9, 127.7, 127.3, 74.0, 72.0, 45.1, 40.0, 39.1, 37.7, 27.7, 23.5, 21.7.

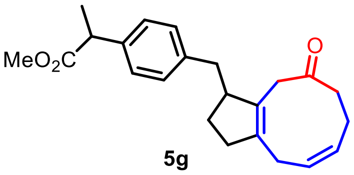
**HRMS** (ESI−FTICR, *m*/*z*): $[M + H]^+$ calculated for $C_{20}H_{25}O_2^+$: 297.1849, found: 297.1849



**5g** + **6g**, *dr* = 1:1

Run 1: Following general procedure B, **4g** (32.4 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), $P(C_6F_5)_3$ (21.3 mg, 0.04 mmol), $NaBARF_4$ (17.7 mg, 0.04 mmol), MeCN (1 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 4/1), 9.1 mg **5g** was obtained in 26% yield, and 8.8 mg **6g** was obtained in 27% yield.

Run 2: Following general procedure B, **4g** (32.4 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), $P(C_6F_5)_3$ (21.3 mg, 0.04 mmol), $NaBARF_4$ (17.7 mg, 0.04 mmol), MeCN (1 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 4/1), 10.2 mg **5g** was obtained in 29% yield, and 7.8 mg **6g** was obtained in 24% yield. The average yield of two runs was 28% **5g** + 26% **6g**.



**5g**

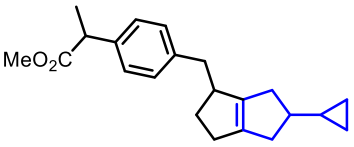
Yellow oil

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

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 5.70 – 5.60 (m, 1H), 5.60 – 5.51 (m, 1H), 3.71 – 3.65 (m, 1H), 3.65 (s, 3H), 3.50 (d, *J* = 14.3 Hz, 1H), 3.05 – 2.90 (m, 4H), 2.85 – 2.75 (m, 1H), 2.64 – 2.58 (m, 1H), 2.58 – 2.53 (m, 1H), 2.53 – 2.44 (m, 1H), 2.43 – 2.36 (m, 1H), 2.32 (dd, *J* = 13.2, 9.7 Hz, 1H), 2.28 – 2.23 (m, 2H), 1.85 – 1.78 (m, 1H), 1.50 – 1.45 (m, 1H), 1.48 (d, *J* = 7.2 Hz, 3H)

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 211.0, 175.4, 140.2, 138.4, 138.0, 133.1, 129.4, 128.6, 127.9, 127.4, 52.1, 51.1, 46.4, 45.2, 39.5, 38.0, 35.7, 28.3, 27.3, 23.1, 18.7.

**HRMS** (ESI−FTICR, *m*/*z*): $[M + H]^+$ calculated for $C_{23}H_{29}O_3^+$: 353.2111, found: 353.2115



**6g**, *dr* = 1:1

The *dr* value of 1:1 for **6g** was proposed based on the $^{13}$C NMR, which showed two distinct sets of peaks with similar peak heights, indicating two diastereomers in approximately equal proportions. The following peaks are the mixture of two diastereomers, and they could not be identified.

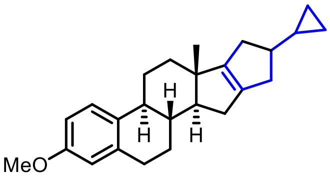
Yellow oil

**TLC** (10:1 PE/EA, *Rf*): 0.2

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 7.88 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 3.72 – 3.64 (m, 1H), 3.66 (s, 3H), 2.93 (dd, *J* = 13.1, 4.3 Hz, 1H), 2.78 (d, *J* = 8.7 Hz, 1H), 2.43 (dd, *J* = 12.5, 7.1 Hz, 1H), 2.36 – 2.27 (m, 2H), 2.22 – 2.17 (m, 1H), 2.07 – 1.99 (m, 1H), 1.85 – 1.76 (m, 1H), 1.71 – 1.61 (m, 4H), 1.55 – 1.45 (m, 1H), 1.49 (d, *J* = 7.3 Hz, 3H), 0.59 – 0.37 (m, 2H), 0.37 – 0.24 (m, 1H), 0.27 – 0.13 (m, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 175.4, 140.5, 140.3, 138.0, 137.7, 134.0, 133.03, 133.01, 132.94, 132.91, 132.8, 129.4, 129.37, 127.35, 127.3, 75.1, 74.9, 52.1, 51.4, 51.3, 45.2, 39.6, 39.5, 39.3, 37.0, 36.9, 34.7, 29.8, 28.4, 28.3, 18.8, 18.7, 17.7, 17.5, 12.8, 12.7, 2.9, 2.8, 2.6, 2.5.

**HRMS** (ESI–FTICR, *m/z*): $[M + H]^+$ calculated for $C_{22}H_{29}O_2^+$: 325.2162, found: 325.2160



**6l**, *dr* = 1:1

Following general procedure B, **4l** (69.7 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (7.8 mg, 0.02 mmol), $P(C_6F_5)_3$ (42.6 mg, 0.08 mmol), $NaBARF_4$ (35.4 mg, 0.04 mmol), MeCN (2 mL) was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA, 20/1~10/1), 18.8 mg **6l** was obtained in 27% yield.

The *dr* value of 1:1 for **6l** was proposed based on the $^{13}$C NMR, which showed two sets of peaks with similar peak heights, indicating two diastereomers in approximately equal proportions. The following peaks are the mixture of two diastereomers, and they could not be identified.

**TLC** (5:1 PE/EA, *Rf*): 0.5

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.6 Hz, 1H), 6.71 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.64 (d, *J* = 2.8 Hz, 1H), 3.78 (s, 3H), 3.04 – 2.96 (m, 1H), 2.93 – 2.80 (m, 2H), 2.49 – 2.38 (m, 1H), 2.38 – 2.23 (m, 3H), 2.07 (d, *J* = 7.7 Hz, 1H), 1.95 – 1.87 (m, 1H), 1.86 – 1.77 (m, 1H), 1.63 (d, *J* = 2.1 Hz, 3H), 1.61 – 1.40 (m, 6H), 0.90 (ddd, *J* = 8.0, 5.3, 2.6 Hz, 1H), 0.77 (d, *J* = 5.7 Hz, 2H), 0.59 – 0.44 (m, 2H), 0.39 – 0.29 (m, 1H), 0.26 – 0.15 (m, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 157.4, 146.1, 138.1, 133.1, 130.7, 130.6, 126.0, 126.0, 113.9, 111.4, 75.3, 74.9, 55.2, 55.1, 55.0, 47.9, 47.9, 44.5, 37.3, 36.9, 36.8, 35.2, 34.9, 34.7, 34.7, 29.8, 27.9, 26.5, 17.4, 17.4, 15.4, 14.9, 9.6, 2.7, 2.6, 2.5, 2.5.

**HRMS** (ESI–FTICR, *m/z*): $[M + H]^+$ calculated for $C_{25}H_{33}O^+$: 349.2526, found: 349.2528.

## VI. Computational Study of [8+1] Cycloaddition

According to the vinylcyclopropane chemistry, we hypothesized that there are three possible pathways for this [8+1] cycloaddition reaction (Figure S1), with the first and second pathways being through vinyl-directed activation of the inner cyclopropane to give the intermediate **B**. Subsequently, **B** can first undergo *β*-C elimination, CO insertion, and reductive elimination to obtain the [8+1] cycloaddition product, while **B** can also first undergo CO insertion, followed by *β*-C elimination and reductive elimination to give the [8+1] cycloaddition product. The third pathway, on the other hand, occurs first with activation of the outer cyclopropane, followed by *β*-C elimination, CO insertion, and reductive elimination. Pathway I was discussed in the main text (Figure 3 and Figure S2), and pathway II and III were discussed here (Figure S3).

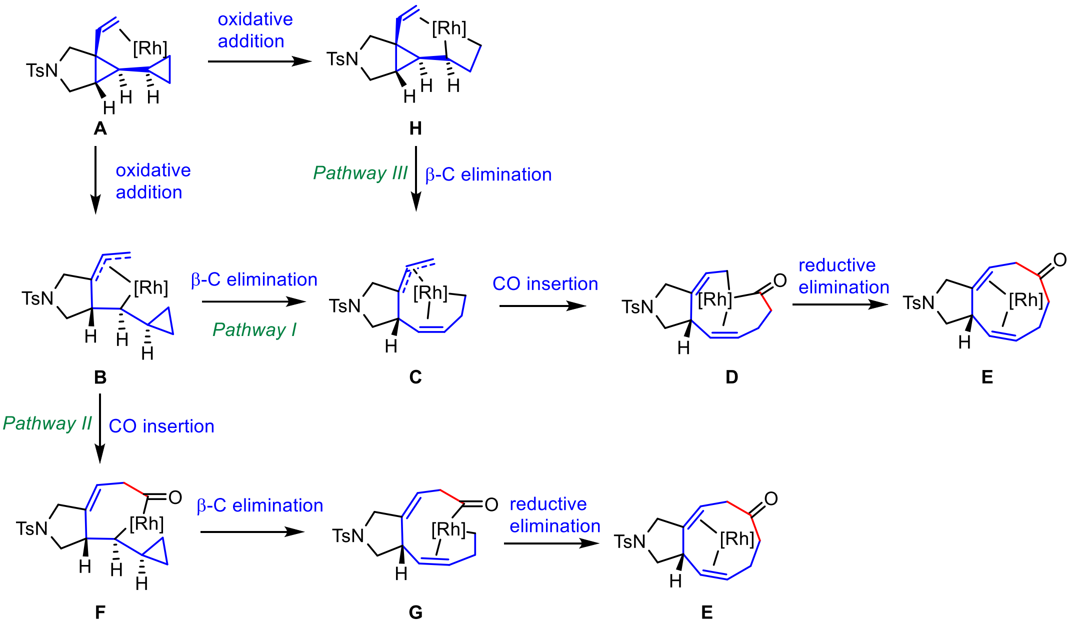


**Figure S1**. Possible pathway for [8+1] cycloaddition

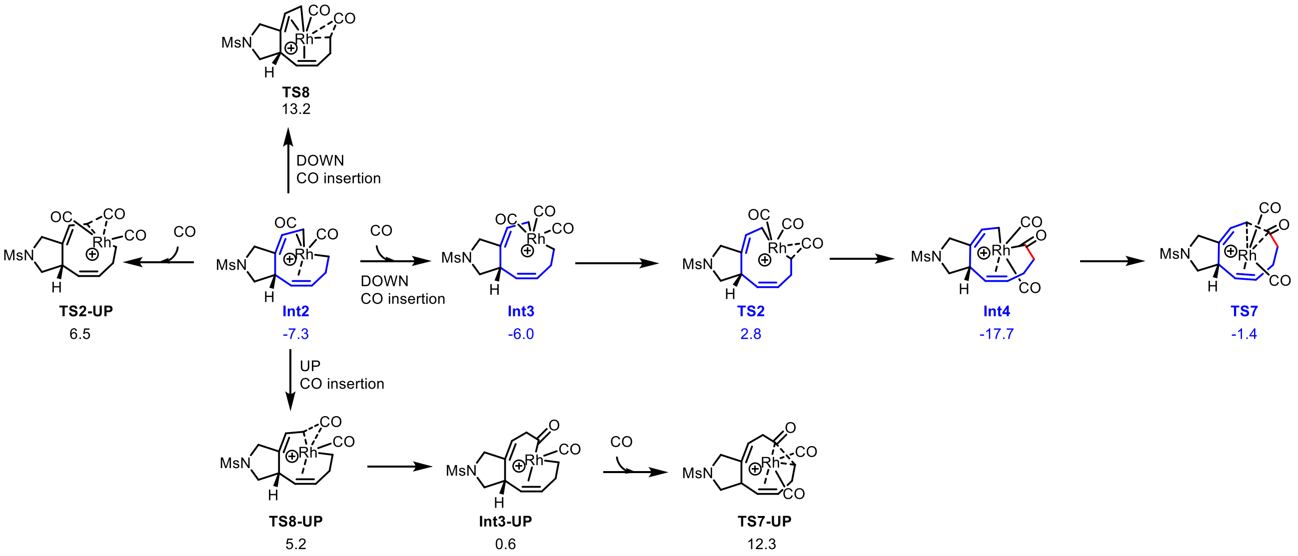


**Figure S2**. Gibbs free energy surface for other CO insertion pathways in pathway I.

We carried out a detailed computational study of the CO insertion step in pathway I (Figure S2). Our calculations showed that the activation free energy of the downward CO insertion into the rhodium-carbon bond from **Int2** via **TS2** is 10.1 kcal/mol, whereas the activation free energy for the direct downward CO insertion via **TS8** from **Int2** is 13.2 kcal/mol. Similarly, **Int2** could undergo an upward CO insertion via **TS8-**

**UP**, requiring an activation energy of 12.5 kcal/mol. The CO insertion via **TS2-UP** by introducing additional CO ligand requires an activation energy of 13.8 kcal/mol. In summary, since **TS2** is favored over **TS8-UP** by 2.4 kcal/mol, the intermediate **Int2** prefers downward CO insertion via **TS2** to obtain the [8+1] cycloaddition product. We attributed to the fact that the upward CO insertion into the C-Rh bond disrupts the coordination of the allyl group to the rhodium center, leading to a larger distortion energy and thus a higher activation energy.

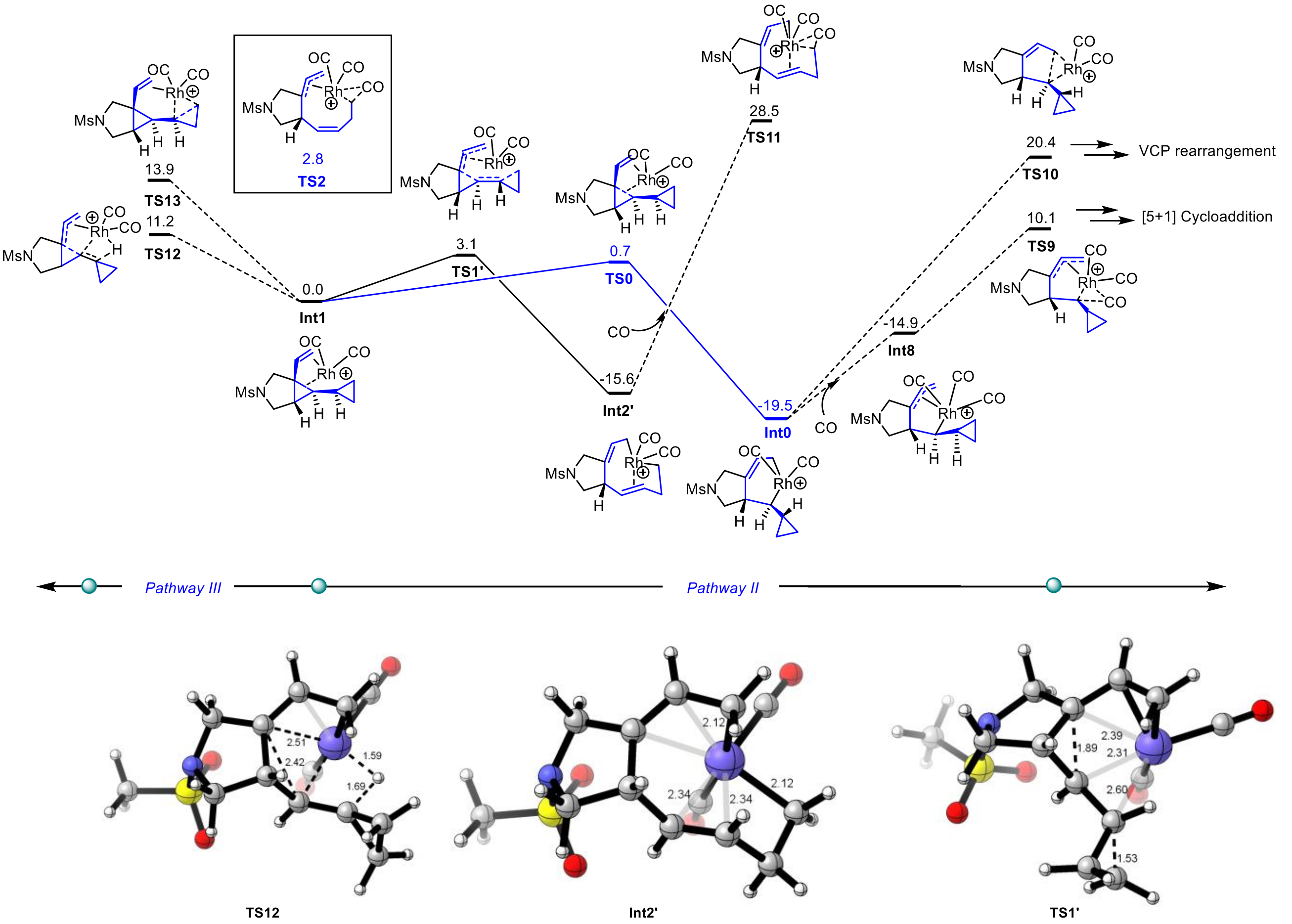


**Figure S3**. Gibbs free energy surface for other pathways and side reactions.

The Gibbs free energy surface of pathway II and III was shown in Figure S3. Our calculations found that **Int1** undergoes oxidative addition via **TS0** to give the inner cyclopropane ring-opened **Int0**. This intermediate **Int0** can undergo CO insertion for either path II or [5+1] cycloaddition reactions; however, the activation free energy for CO insertion via **TS9** is as high as 29.5 kcal/mol, which is disfavored over **TS2** by 7.3 kcal/mol, suggesting that the [5+1] cycloaddition reaction could not occur. On the other hand, the reductive elimination of **Int0** through **TS10** requires an activation free energy of 39.9 kcal/mol, which could not happen at the present temperature. Therefore, pathway II can be ruled out.

We also calculated the intermediate **Int2'** to give the *E*-type olefin via a *trans* concerted transition state **TS1'**, which is exergonic by 15.6 kcal/mol with a comparable activation energy to **TS2** (3.1 vs. 2.8 kcal/mol). However, the *E*-type olefin **Int2'** has a larger strain in the subsequent transition states, the activation free energy of CO insertion via **TS11** is as high as 44.1 kcal/mol. Therefore, we proposed that **In2'** could be a possible resting state of the [8+1] reaction. In addition, **Int1** could also undergo direct $\beta$-H elimination via **TS12** to give a methylene cyclopropane product, requiring an activation energy of 11.2 kcal/mol, but **TS11** is disfavored over **TS2** by 8.4 kcal/mol. Oxidative addition of the outer cyclopropane via **TS13** is more difficult, requiring an activation energy of 13.9 kcal/mol, so pathway III can also be ruled out.

**Table S3. Computed Energies of the Stationary Points**

| | E(hatree)[a] | TCG(hatree)[a] | E(hatree)[b] | E (hatree)[c] |
|---|---|---|---|---|

| | | | | |
|---|---|---|---|---|
| **CO** | -113.294361 | -0.01386 | -113.289565 | -113.1590663 |
| **1c** | -1032.295844 | 0.226835 | -1032.319178 | -1031.183309 |
| **2c** | -1145.644999 | 0.240206 | -1145.675643 | -1144.393671 |
| **3c** | -1032.317388 | 0.224699 | -1032.34103 | -1031.205871 |
| **Int0** | -1368.829089 | 0.238227 | -1368.930608 | -1367.780227 |
| **Int1** | -1368.809429 | 0.239354 | -1368.904768 | -1367.756514 |
| **Int2** | -1368.826177 | 0.243535 | -1368.918658 | -1367.775148 |
| **Int2’** | -1368.845081 | 0.244339 | -1368.934287 | -1367.792441 |
| **Int3** | -1482.125456 | 0.249545 | -1482.217841 | -1480.949756 |
| **Int3-UP** | -1368.799568 | 0.242663 | -1368.912226 | -1367.741519 |
| **Int4** | -1482.15316 | 0.252618 | -1482.251388 | -1480.965646 |
| **Int5** | -1368.809403 | 0.240427 | -1368.89997 | -1367.768068 |
| **Int6** | -1368.829615 | 0.238415 | -1368.917123 | -1367.779828 |
| **Int7** | -1482.173148 | 0.250866 | -1482.269721 | -1480.982942 |
| **Int8** | -1482.14476 | 0.247045 | -1482.233828 | -1480.964846 |
| ***trans*-Int1** | -1368.804927 | 0.240499 | -1368.9056 | -1367.750676 |
| ***trans*-Int0** | -1368.820145 | 0.240417 | -1368.912759 | -1367.766791 |
| ***trans*-Int2** | -1368.811043 | 0.240859 | -1368.916006 | -1367.761241 |
| ***trans*-Int3** | -1255.492749 | 0.237015 | -1255.611515 | -1254.571915 |
| ***trans*-Int4** | -1255.500529 | 0.236998 | -1255.617378 | -1254.578964 |
| **TS0** | -1368.804435 | 0.239375 | -1368.897418 | -1367.757845 |
| **TS1** | -1368.80448 | 0.240405 | -1368.899818 | -1367.754567 |
| **TS2** | -1482.098371 | 0.246295 | -1482.202213 | -1480.921117 |
| **TS2-UP** | -1482.103116 | 0.246934 | -1482.201779 | -1480.920979 |
| **TS3** | -1368.807408 | 0.239067 | -1368.898096 | -1367.765222 |
| **TS4** | -1368.792845 | 0.237659 | -1368.884753 | -1367.754016 |
| **TS5** | -1368.792233 | 0.237828 | -1368.881063 | -1367.753108 |
| **TS6** | -1368.795914 | 0.243317 | -1368.887283 | -1367.749043 |
| **TS7** | -1482.128031 | 0.253107 | -1482.225671 | -1480.940779 |
| **TS8** | -1368.780389 | 0.242018 | -1368.883788 | -1367.730087 |
| **TS8-UP** | -1368.780659 | 0.240038 | -1368.89683 | -1367.728114 |
| **TS7-UP** | -1482.102411 | 0.249652 | -1482.202984 | -1480.912561 |
| **TS9** | -1482.0956 | 0.247325 | -1482.192089 | -1480.917774 |
| **TS10** | -1368.779807 | 0.239968 | -1368.869951 | -1367.729798 |
| **TS11** | -1482.076091 | 0.248268 | -1482.17294 | -1480.889065 |
| **TS12** | -1368.790547 | 0.23653 | -1368.878753 | -1367.742933 |
| **TS13** | -1368.780295 | 0.238171 | -1368.88029 | -1367.728468 |
| ***trans*-TS1** | -1368.78936 | 0.238678 | -1368.895501 | -1367.736118 |
| ***trans*-TS2** | -1368.795368 | 0.239234 | -1368.898547 | -1367.743479 |
| ***trans*-TS2’** | -1368.793416 | 0.241295 | -1368.889069 | -1367.742715 |
| ***trans*-TS3** | -1255.442788 | 0.233769 | -1255.583298 | -1254.523926 |
| **TS2-six** | -1408.089326 | 0.264769 | -1408.185644 | -1406.999329 |
| **TS4-six** | -1521.401952 | 0.275837 | -1521.504751 | -1520.174091 |

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

[b]Computed at the SMD(PhCN)/BMK/6-311G(d,p) (def2-TZVP for Rh) level.

[c]Computed at the DLPNO-CCSD(T1)/def2-TZVPP//BMK/6-311G(d,p) (def2-TZVP for Rh) level. We used 3.1 mM[12] as the concentration of CO and 1.0 M for other species:

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

$$\Delta G_{\mathrm{CO}} = -RT\ln\left(\frac{V_1}{V_2}\right) - RT\ln\left(\frac{c_1}{c_2}\right) = -RT\ln\left(\frac{\frac{1}{24.46}}{1}\right) - RT\ln\left(\frac{1}{0.0031}\right) = -1.52\ \mathrm{kcal/mol}$$

## Cartesian coordinates of the stationary points

**1c**

| | | | |
|---|---|---|---|
| C | 0.405469 | -1.348951 | -0.688308 |
| C | -1.025963 | -1.047676 | -0.215575 |
| C | -0.899892 | -0.572712 | 1.234287 |
| C | 0.571091 | -0.668912 | 1.623961 |
| H | -1.646509 | -0.829194 | 1.979065 |
| C | -1.264497 | 0.436080 | 0.144247 |
| H | -0.480239 | 1.122163 | -0.174998 |
| C | -2.644716 | 1.020721 | 0.105263 |
| C | -2.993129 | 2.041588 | -0.979525 |
| C | -2.837206 | 2.492439 | 0.474516 |
| H | -3.442307 | 0.343092 | 0.396189 |
| H | -3.991322 | 2.017575 | -1.403159 |
| H | -2.207341 | 2.316136 | -1.676162 |
| H | -3.730640 | 2.769061 | 1.023938 |
| H | -1.950868 | 3.063757 | 0.731202 |
| C | -2.108577 | -1.915365 | -0.755778 |
| H | -2.179077 | -1.943259 | -1.843884 |
| C | -2.968435 | -2.630957 | -0.033404 |
| H | -2.933491 | -2.637783 | 1.052566 |
| H | -3.737457 | -3.232946 | -0.507315 |
| H | 0.624447 | -0.922020 | -1.670678 |
| H | 0.555582 | -2.435427 | -0.721119 |
| H | 0.751429 | -1.583754 | 2.201542 |
| H | 0.940769 | 0.186004 | 2.191891 |
| N | 1.283463 | -0.757487 | 0.333476 |
| S | 2.348496 | 0.432613 | -0.109953 |
| O | 2.695000 | 1.162964 | 1.085807 |
| O | 1.864190 | 1.137215 | -1.277672 |
| C | 3.797381 | -0.510573 | -0.641172 |
| H | 3.501783 | -1.165482 | -1.462608 |
| H | 4.537009 | 0.218053 | -0.979458 |
| H | 4.165378 | -1.080898 | 0.211757 |

**2c**

| | | | |
|---|---|---|---|
| C | 3.098020 | 1.797419 | -0.384750 |
| C | 4.102109 | 0.817607 | 0.277461 |
| C | 1.808636 | 1.917749 | 0.398537 |
| C | 0.647828 | 1.316843 | 0.127318 |
| C | 0.363137 | 0.374574 | -1.030380 |
| C | 0.440040 | -1.074969 | -0.550271 |
| C | 1.539266 | -1.815716 | -0.424062 |
| C | 2.940249 | -1.326088 | -0.736979 |
| H | 2.905865 | 1.493561 | -1.416609 |
| H | 3.579851 | 2.780199 | -0.437622 |
| H | 5.000668 | 0.746435 | -0.352275 |
| H | 4.409045 | 1.178680 | 1.263469 |
| H | 1.860773 | 2.533136 | 1.295402 |
| H | -0.192584 | 1.478444 | 0.801794 |
| H | 1.047919 | 0.551454 | -1.863029 |
| H | 1.455610 | -2.822491 | -0.021291 |
| H | 2.944749 | -0.682673 | -1.619809 |
| H | 3.590735 | -2.182445 | -0.947349 |
| C | 3.567688 | -0.603907 | 0.479468 |
| O | 3.660622 | -1.164402 | 1.535918 |
| C | -0.968494 | -1.543433 | -0.189021 |
| C | -1.110321 | 0.481126 | -1.492245 |
| N | -1.830690 | -0.416557 | -0.579562 |
| H | -1.237320 | -2.447372 | -0.749175 |
| H | -1.077103 | -1.745836 | 0.878989 |
| H | -1.214251 | 0.117254 | -2.521417 |
| H | -1.505472 | 1.494971 | -1.422078 |
| S | -2.997268 | 0.157165 | 0.437351 |
| O | -2.928034 | 1.600113 | 0.451492 |
| O | -2.928622 | -0.600855 | 1.663338 |
| C | -4.547324 | -0.287108 | -0.383523 |
| H | -5.357069 | 0.088514 | 0.245449 |
| H | -4.566749 | 0.189688 | -1.364524 |
| H | -4.590288 | -1.373685 | -0.465923 |

**3c**

| | | | |
|---|---|---|---|
| C | 3.575692 | -1.368258 | 0.229165 |
| C | 4.684066 | -2.074574 | -0.021500 |
| C | 2.379888 | -1.418060 | -0.617052 |
| C | 1.240912 | -0.729912 | -0.441689 |
| C | 0.943709 | 0.260102 | 0.663501 |
| C | 0.538759 | 1.611643 | 0.074479 |
| C | 1.339350 | 2.611642 | -0.287684 |
| C | 2.847149 | 2.601468 | -0.243631 |
| H | 3.244421 | 1.627586 | 0.051327 |
| H | 3.552477 | -0.727174 | 1.107372 |
| H | 5.553041 | -2.017763 | 0.625475 |
| H | 4.750858 | -2.731701 | -0.884962 |
| H | 2.441260 | -2.088251 | -1.473083 |
| H | 0.435369 | -0.870004 | -1.162769 |
| H | 1.790241 | 0.364159 | 1.343199 |
| H | 0.879089 | 3.523987 | -0.668866 |
| H | 3.224414 | 3.360566 | 0.452790 |
| H | 3.256139 | 2.842387 | -1.231671 |

|  |  |  |  |
|---|---|---|---|
| C | -0.987102 | 1.648659 | -0.028003 |
| C | -0.334779 | -0.125933 | 1.453087 |
| N | -1.447805 | 0.427851 | 0.660104 |
| H | -1.394980 | 2.537998 | 0.466750 |
| H | -1.313338 | 1.639492 | -1.072422 |
| H | -0.331733 | 0.365995 | 2.432323 |
| H | -0.460775 | -1.199268 | 1.592534 |
| S | -2.433896 | -0.614602 | -0.181751 |
| O | -2.395680 | -1.882071 | 0.506226 |
| O | -2.161858 | -0.551953 | -1.602316 |
| C | -4.060537 | 0.131885 | 0.074818 |
| H | -4.774016 | -0.475123 | -0.486189 |
| H | -4.277330 | 0.113487 | 1.142767 |
| H | -4.040515 | 1.152518 | -0.311516 |

**CO**

|  |  |  |  |
|---|---|---|---|
| C | 0.000000 | 0.000000 | -0.641380 |
| O | 0.000000 | 0.000000 | 0.481035 |

**Int0**

|  |  |  |  |
|---|---|---|---|
| Rh | 1.197866 | -0.909725 | 0.147891 |
| C | 2.911837 | -0.503336 | 1.043796 |
| O | 3.907124 | -0.274013 | 1.507864 |
| C | 2.541031 | 2.650395 | 0.530839 |
| C | 1.687485 | 3.449252 | -0.425989 |
| C | 1.893077 | 1.923282 | -0.658680 |
| C | 0.721586 | 1.038327 | -0.432835 |
| C | -0.112032 | 0.606804 | -1.649204 |
| C | -0.299561 | -0.921366 | -1.527522 |
| C | 0.718425 | -1.828226 | -1.827052 |
| C | 2.077573 | -1.380992 | -1.757973 |
| H | 2.132011 | 2.457801 | 1.518652 |
| H | 3.616487 | 2.789855 | 0.502211 |
| H | 0.710700 | 3.774149 | -0.084435 |
| H | 2.175127 | 4.112476 | -1.131987 |
| H | 2.549753 | 1.674037 | -1.487000 |
| H | 0.088658 | 1.411999 | 0.374075 |
| H | 0.410562 | 0.859667 | -2.577898 |
| H | 0.490956 | -2.894345 | -1.827370 |
| H | 2.345555 | -0.434410 | -2.219860 |
| H | 2.859193 | -2.134635 | -1.805685 |
| C | -1.793599 | -1.220818 | -1.485568 |
| C | -1.583739 | 1.123578 | -1.673865 |
| N | -2.401814 | 0.052021 | -1.083169 |
| S | -2.879727 | 0.216284 | 0.521439 |
| O | -2.115808 | 1.292581 | 1.123063 |
| O | -2.825940 | -1.101059 | 1.112016 |
| C | -4.596493 | 0.744426 | 0.394061 |
| H | -4.948018 | 0.895044 | 1.417241 |
| H | -5.156997 | -0.046236 | -0.105677 |
| H | -4.627320 | 1.677937 | -0.170173 |
| C | 0.070181 | -0.743616 | 1.856696 |
| O | -0.371399 | -0.728133 | 2.884089 |
| H | -2.138907 | -1.464464 | -2.498959 |
| H | -2.073844 | -2.030921 | -0.813688 |
| H | -1.712482 | 2.059665 | -1.130691 |
| H | -1.903520 | 1.264054 | -2.711169 |

**Int1**

|  |  |  |  |
|---|---|---|---|
| Rh | 1.661048 | -0.412479 | 0.025571 |
| C | 3.292813 | -1.445457 | -0.043909 |
| O | 4.250335 | -2.029790 | -0.130169 |
| C | 0.420289 | 3.157591 | 1.870782 |
| C | 1.513152 | 3.217905 | 0.828323 |
| C | 0.930848 | 1.850051 | 1.185092 |
| C | -0.082734 | 1.112631 | 0.352693 |
| C | -0.639741 | 1.707242 | -0.911082 |
| C | -0.065814 | 0.402673 | -1.385048 |
| C | 1.229200 | 0.133964 | -1.981131 |
| C | 2.370707 | 0.861928 | -1.613171 |
| H | -0.573003 | 3.490840 | 1.589251 |
| H | 0.675092 | 3.289091 | 2.916084 |
| H | 1.261156 | 3.661884 | -0.129054 |
| H | 2.527091 | 3.416057 | 1.159662 |
| H | 1.531495 | 1.242108 | 1.865691 |
| H | -0.800489 | 0.544731 | 0.936042 |
| H | -0.173200 | 2.621987 | -1.266567 |
| H | 1.289562 | -0.694430 | -2.682781 |
| H | 2.295049 | 1.868125 | -1.214739 |
| H | 3.315515 | 0.613274 | -2.084900 |
| C | -1.254669 | -0.530375 | -1.666970 |
| C | -2.163655 | 1.585926 | -1.111217 |
| N | -2.419692 | 0.138258 | -1.094202 |
| S | -3.109193 | -0.545796 | 0.289540 |
| O | -3.551639 | 0.545445 | 1.118758 |
| O | -2.169110 | -1.518902 | 0.811391 |
| C | -4.542539 | -1.428147 | -0.351861 |
| H | -5.020086 | -1.901496 | 0.509233 |
| H | -4.197777 | -2.177438 | -1.066017 |
| H | -5.204876 | -0.698544 | -0.818851 |
| C | 0.829850 | -1.727803 | 1.275130 |

| | | | |
|---|---|---|---|
| O | 0.427810 | -2.533866 | 1.942667 |
| H | -1.357071 | -0.579113 | -2.760189 |
| H | -1.135847 | -1.539006 | -1.273659 |
| H | -2.744755 | 2.087915 | -0.337683 |
| H | -2.435482 | 1.988645 | -2.092429 |

**Int2'**

| | | | |
|---|---|---|---|
| Rh | -1.468907 | 0.057824 | -0.135938 |
| C | -2.644472 | 0.665255 | -1.554477 |
| O | -3.362331 | 1.002133 | -2.348704 |
| C | -2.861910 | 0.768294 | 1.295276 |
| C | -2.045968 | 0.467631 | 2.562264 |
| C | -1.282905 | -0.744929 | 2.049330 |
| C | -0.016114 | -0.701302 | 1.531293 |
| C | 0.650404 | -1.867113 | 0.802775 |
| C | 0.376724 | -1.650936 | -0.695647 |
| C | -0.830436 | -1.804620 | -1.334428 |
| C | -2.092897 | -1.912330 | -0.599834 |
| H | -3.100004 | 1.822165 | 1.150630 |
| H | -3.764759 | 0.161307 | 1.236103 |
| H | -1.361589 | 1.283213 | 2.813083 |
| H | -2.653790 | 0.236316 | 3.440977 |
| H | -1.825517 | -1.685793 | 2.063494 |
| H | 0.616871 | 0.167165 | 1.707416 |
| H | 0.260213 | -2.828016 | 1.151594 |
| H | -0.846874 | -1.680728 | -2.416737 |
| H | -2.103709 | -2.567170 | 0.266034 |
| H | -2.980883 | -2.039814 | -1.213159 |
| C | 1.708033 | -1.395926 | -1.386875 |
| C | 2.205609 | -1.806950 | 0.869584 |
| N | 2.615682 | -1.012133 | -0.300852 |
| S | 2.914111 | 0.635125 | -0.095270 |
| O | 2.674385 | 0.962423 | 1.294370 |
| O | 2.180945 | 1.341612 | -1.124859 |
| C | 4.677685 | 0.787129 | -0.425554 |
| H | 4.923226 | 1.845112 | -0.308364 |
| H | 4.863317 | 0.450155 | -1.446129 |
| H | 5.211744 | 0.176432 | 0.303652 |
| C | -0.507577 | 1.893958 | 0.022687 |
| O | -0.120112 | 2.937448 | 0.131695 |
| H | 2.068983 | -2.336923 | -1.824175 |
| H | 1.659520 | -0.638117 | -2.167374 |
| H | 2.576886 | -1.369768 | 1.795695 |
| H | 2.621480 | -2.812595 | 0.756380 |

**Int2**

| | | | |
|---|---|---|---|
| Rh | -1.528943 | 0.210750 | -0.078795 |
| C | -2.834608 | 1.084055 | -1.198502 |
| O | -3.622018 | 1.575802 | -1.829880 |
| C | -2.326256 | -1.448520 | 2.031463 |
| C | -3.087118 | -0.348896 | 1.263877 |
| C | -0.975771 | -0.767348 | 2.002360 |
| C | 0.142122 | -0.871422 | 1.210671 |
| C | 0.635768 | -1.874072 | 0.182779 |
| C | 0.428242 | -1.198528 | -1.184798 |
| C | -0.776042 | -1.155134 | -1.833036 |
| C | -1.990509 | -1.551754 | -1.120164 |
| H | -2.342403 | -2.407994 | 1.516725 |
| H | -2.677159 | -1.595092 | 3.057116 |
| H | -3.948833 | -0.706104 | 0.703291 |
| H | -3.360113 | 0.487033 | 1.907667 |
| H | -0.923152 | 0.062954 | 2.708142 |
| H | 0.885996 | -0.112543 | 1.439963 |
| H | 0.129444 | -2.839813 | 0.250666 |
| H | -0.827385 | -0.720051 | -2.829714 |
| H | -1.914110 | -2.436922 | -0.495552 |
| H | -2.905256 | -1.551954 | -1.707909 |
| C | -0.794686 | 2.018246 | 0.660120 |
| O | -0.463397 | 2.993644 | 1.096523 |
| C | 1.782803 | -0.783804 | -1.735829 |
| C | 2.188579 | -2.005300 | 0.239778 |
| N | 2.703888 | -0.908782 | -0.599887 |
| H | 2.086480 | -1.491932 | -2.518412 |
| H | 1.782896 | 0.223620 | -2.153987 |
| H | 2.495121 | -2.951453 | -0.216520 |
| H | 2.599453 | -1.942744 | 1.247467 |
| S | 3.130292 | 0.534676 | 0.168938 |
| O | 3.417514 | 0.199211 | 1.541118 |
| O | 2.120883 | 1.540222 | -0.119137 |
| C | 4.654600 | 0.996611 | -0.672113 |
| H | 4.965573 | 1.948111 | -0.234812 |
| H | 5.388530 | 0.212845 | -0.482905 |
| H | 4.448864 | 1.109121 | -1.737861 |

**Int3-UP**

| | | | |
|---|---|---|---|
| Rh | -1.961140 | -0.176976 | -0.718121 |
| C | -2.360100 | -0.814315 | 1.045495 |
| O | -3.224779 | -1.548468 | 0.678574 |
| C | -2.109071 | 2.584101 | -0.335222 |
| C | -3.153032 | 1.451532 | -0.331626 |
| C | -1.013201 | 1.783450 | -1.013118 |

| | | | |
|---|---|---|---|
| C | -0.029423 | 1.029703 | -0.392421 |
| C | 0.440051 | 1.166280 | 1.049347 |
| C | 0.635905 | -0.153232 | 1.798918 |
| C | -0.303322 | -0.876992 | 2.405617 |
| C | -1.784131 | -0.527969 | 2.405535 |
| H | -1.827747 | 2.898055 | 0.671501 |
| H | -2.391346 | 3.470286 | -0.908049 |
| H | -3.757103 | 1.391248 | 0.576707 |
| H | -3.820719 | 1.498154 | -1.202847 |
| H | -0.992776 | 1.807960 | -2.106980 |
| H | 0.673798 | 0.530911 | -1.053697 |
| H | -0.224662 | 1.834595 | 1.603438 |
| H | -0.027942 | -1.786890 | 2.933064 |
| H | -1.942279 | 0.540441 | 2.598792 |
| H | -2.342878 | -1.108386 | 3.144655 |
| C | -0.712891 | -1.821094 | -1.252927 |
| O | -0.120814 | -2.731779 | -1.512578 |
| C | 2.132346 | -0.470490 | 1.848234 |
| C | 1.908828 | 1.720583 | 1.030113 |
| N | 2.766886 | 0.529217 | 0.977629 |
| H | 2.510400 | -0.340062 | 2.868690 |
| H | 2.349992 | -1.488001 | 1.518742 |
| H | 2.109316 | 2.240205 | 1.972385 |
| H | 2.123982 | 2.391794 | 0.198990 |
| S | 3.214164 | -0.010475 | -0.559760 |
| O | 3.231869 | 1.153071 | -1.411256 |
| O | 2.380085 | -1.141676 | -0.931477 |
| C | 4.894337 | -0.599978 | -0.292250 |
| H | 5.236162 | -0.981526 | -1.257078 |
| H | 5.496783 | 0.246862 | 0.036967 |
| H | 4.874821 | -1.397309 | 0.452622 |

**Int3**

| | | | |
|---|---|---|---|
| Rh | -1.528943 | 0.210750 | -0.078795 |
| C | -2.834608 | 1.084055 | -1.198502 |
| O | -3.622018 | 1.575802 | -1.829880 |
| C | -2.326256 | -1.448520 | 2.031463 |
| C | -3.087118 | -0.348896 | 1.263877 |
| C | -0.975771 | -0.767348 | 2.002360 |
| C | 0.142122 | -0.871422 | 1.210671 |
| C | 0.635768 | -1.874072 | 0.182779 |
| C | 0.428242 | -1.198528 | -1.184798 |
| C | -0.776042 | -1.155134 | -1.833036 |
| C | -1.990509 | -1.551754 | -1.120164 |
| H | -2.342403 | -2.407994 | 1.516725 |
| H | -2.677159 | -1.595092 | 3.057116 |
| H | -3.948833 | -0.706104 | 0.703291 |
| H | -3.360113 | 0.487033 | 1.907667 |
| H | -0.923152 | 0.062954 | 2.708142 |
| H | 0.885996 | -0.112543 | 1.439963 |
| H | 0.129444 | -2.839813 | 0.250666 |
| H | -0.827385 | -0.720051 | -2.829714 |
| H | -1.914110 | -2.436922 | -0.495552 |
| H | -2.905256 | -1.551954 | -1.707909 |
| C | -0.794686 | 2.018246 | 0.660120 |
| O | -0.463397 | 2.993644 | 1.096523 |
| C | 1.782803 | -0.783804 | -1.735829 |
| C | 2.188579 | -2.005300 | 0.239778 |
| N | 2.703888 | -0.908782 | -0.599887 |
| H | 2.086480 | -1.491932 | -2.518412 |
| H | 1.782896 | 0.223620 | -2.153987 |
| H | 2.495121 | -2.951453 | -0.216520 |
| H | 2.599453 | -1.942744 | 1.247467 |
| S | 3.130292 | 0.534676 | 0.168938 |
| O | 3.417514 | 0.199211 | 1.541118 |
| O | 2.120883 | 1.540222 | -0.119137 |
| C | 4.654600 | 0.996611 | -0.672113 |
| H | 4.965573 | 1.948111 | -0.234812 |
| H | 5.388530 | 0.212845 | -0.482905 |
| H | 4.448864 | 1.109121 | -1.737861 |

**Int4**

| | | | |
|---|---|---|---|
| Rh | -1.266280 | -0.309504 | 0.172056 |
| C | -2.213402 | -1.627268 | 1.250971 |
| O | -2.769439 | -2.374749 | 1.872486 |
| C | -2.062243 | 2.374971 | -1.214419 |
| C | -3.372148 | 1.567655 | -1.038176 |
| C | -0.948488 | 1.391817 | -1.473224 |
| C | 0.257877 | 1.197047 | -0.853478 |
| C | 0.900558 | 1.893828 | 0.332012 |
| C | 0.827483 | 0.915362 | 1.511740 |
| C | -0.310908 | 0.596837 | 2.186445 |
| C | -1.635142 | 1.050738 | 1.726648 |
| H | -1.853377 | 3.018728 | -0.360714 |
| H | -2.147279 | 3.025107 | -2.092348 |
| H | -3.978566 | 1.951412 | -0.209462 |
| H | -4.002137 | 1.579094 | -1.933610 |
| H | -1.085032 | 0.816034 | -2.390181 |
| H | 0.924013 | 0.500919 | -1.356323 |
| H | 0.423374 | 2.850467 | 0.560470 |
| H | -0.237648 | -0.090529 | 3.028487 |
| H | -1.684182 | 2.081712 | 1.390120 |

|  |  |  |  |
|---|---|---|---|
| H | -2.455266 | 0.824447 | 2.404629 |
| C | -3.091378 | 0.079120 | -0.725110 |
| O | -3.863241 | -0.787260 | -0.958092 |
| C | 2.234684 | 0.438649 | 1.834419 |
| C | 2.441523 | 2.035177 | 0.123408 |
| N | 3.025368 | 0.786323 | 0.645641 |
| H | 2.629132 | 1.002664 | 2.689852 |
| H | 2.281516 | -0.626354 | 2.065241 |
| H | 2.821198 | 2.860618 | 0.732729 |
| H | 2.737074 | 2.190850 | -0.914235 |
| S | 3.273386 | -0.469354 | -0.459179 |
| O | 3.411454 | 0.145567 | -1.756442 |
| O | 2.250015 | -1.484547 | -0.266649 |
| C | 4.858565 | -1.146303 | 0.062041 |
| H | 5.060417 | -1.989440 | -0.602570 |
| H | 5.607120 | -0.361645 | -0.050909 |
| H | 4.777028 | -1.480550 | 1.097624 |
| C | -0.593117 | -1.757537 | -1.175985 |
| O | -0.297506 | -2.534135 | -1.923515 |

**Int5**

|  |  |  |  |
|---|---|---|---|
| Rh | 1.819042 | -0.003442 | 0.027597 |
| C | 3.650450 | -0.539777 | -0.495557 |
| O | 4.681792 | -0.902583 | -0.745397 |
| C | 0.781415 | -1.499659 | -1.467962 |
| C | 0.697110 | -0.222745 | -1.990377 |
| C | -0.336757 | -2.249979 | -0.846261 |
| C | -0.965052 | -2.098437 | 0.318473 |
| C | -0.780609 | -1.097523 | 1.448738 |
| C | -0.088499 | 0.242040 | 1.155519 |
| C | 0.985615 | 0.788039 | 1.913485 |
| C | 2.166349 | 0.076415 | 2.220626 |
| H | 1.697983 | -1.490348 | 0.458682 |
| H | 1.602589 | -2.130544 | -1.808906 |
| H | 1.415367 | 0.095398 | -2.740708 |
| H | -0.245263 | 0.317131 | -1.925977 |
| H | -0.654257 | -3.085029 | -1.471636 |
| H | -1.763611 | -2.809346 | 0.518160 |
| H | -0.307136 | -1.606895 | 2.297047 |
| H | 1.029581 | 1.875337 | 1.985116 |
| H | 2.129584 | -0.967258 | 2.512318 |
| H | 3.009540 | 0.638834 | 2.610139 |
| C | 1.996427 | 2.001077 | -0.572224 |
| O | 2.091785 | 3.064564 | -0.909340 |
| C | -1.197683 | 1.241353 | 0.729200 |
| C | -2.194183 | -0.565259 | 1.851436 |
| N | -2.455557 | 0.512698 | 0.889170 |
| H | -1.185129 | 2.105195 | 1.405732 |
| H | -1.094488 | 1.600061 | -0.294344 |
| H | -2.165523 | -0.131181 | 2.856459 |
| H | -2.970929 | -1.327238 | 1.811068 |
| S | -3.338878 | 0.155224 | -0.507214 |
| O | -3.873282 | -1.173479 | -0.353387 |
| O | -2.519533 | 0.499997 | -1.653143 |
| C | -4.701404 | 1.333592 | -0.431079 |
| H | -5.307191 | 1.161154 | -1.323536 |
| H | -5.272793 | 1.130765 | 0.475320 |
| H | -4.289441 | 2.343558 | -0.429560 |

**Int6**

|  |  |  |  |
|---|---|---|---|
| Rh | -1.179138 | -0.479707 | -0.046970 |
| C | -2.183326 | -1.755624 | -1.109068 |
| O | -2.803426 | -2.460848 | -1.727327 |
| C | -1.415024 | 1.149620 | -1.789884 |
| C | -0.453153 | 0.233477 | -2.134645 |
| C | -1.097793 | 2.563308 | -1.487865 |
| C | -0.231472 | 3.080639 | -0.615055 |
| C | 0.585682 | 2.374603 | 0.442396 |
| C | 0.026565 | 1.164194 | 1.199555 |
| C | -1.205326 | 1.035618 | 1.793247 |
| C | -2.398329 | 1.955090 | 1.707138 |
| H | -2.400269 | 2.579450 | 0.817361 |
| H | -2.448913 | 0.956202 | -2.076367 |
| H | -0.696696 | -0.644719 | -2.723500 |
| H | 0.604788 | 0.469567 | -2.080466 |
| H | -1.642737 | 3.260035 | -2.124433 |
| H | -0.103753 | 4.160376 | -0.635092 |
| H | 0.739898 | 3.113972 | 1.241160 |
| H | -1.255106 | 0.337179 | 2.628557 |
| H | -2.378274 | 2.610120 | 2.589628 |
| H | -3.329769 | 1.384312 | 1.755691 |
| C | -1.272198 | -1.759507 | 1.409259 |
| O | -1.272245 | -2.522856 | 2.234078 |
| C | 1.284509 | 0.457853 | 1.715788 |
| C | 2.023424 | 1.917001 | -0.016801 |
| N | 2.247557 | 0.605042 | 0.623043 |
| H | 1.658792 | 1.008245 | 2.590177 |
| H | 1.151001 | -0.585347 | 1.999239 |
| H | 2.775011 | 2.629562 | 0.333080 |
| H | 2.110882 | 1.829460 | -1.099293 |
| S | 2.556012 | -0.737106 | -0.328967 |
| O | 2.733013 | -0.270469 | -1.683402 |

| | | | |
|---|---|---|---|
| O | 1.540198 | -1.736848 | -0.040319 |
| C | 4.135331 | -1.352678 | 0.282378 |
| H | 4.368175 | -2.239968 | -0.310748 |
| H | 4.879660 | -0.570260 | 0.130024 |
| H | 4.025789 | -1.606390 | 1.337885 |

**Int7**

| | | | |
|---|---|---|---|
| C | 3.098020 | 1.797419 | -0.384750 |
| C | 4.102109 | 0.817607 | 0.277461 |
| C | 1.808636 | 1.917749 | 0.398537 |
| C | 0.647828 | 1.316843 | 0.127318 |
| C | 0.363137 | 0.374574 | -1.030380 |
| C | 0.440040 | -1.074969 | -0.550271 |
| C | 1.539266 | -1.815716 | -0.424062 |
| C | 2.940249 | -1.326088 | -0.736979 |
| H | 2.905865 | 1.493561 | -1.416609 |
| H | 3.579851 | 2.780199 | -0.437622 |
| H | 5.000668 | 0.746435 | -0.352275 |
| H | 4.409045 | 1.178680 | 1.263469 |
| H | 1.860773 | 2.533136 | 1.295402 |
| H | -0.192584 | 1.478444 | 0.801794 |
| H | 1.047919 | 0.551454 | -1.863029 |
| H | 1.455610 | -2.822491 | -0.021291 |
| H | 2.944749 | -0.682673 | -1.619809 |
| H | 3.590735 | -2.182445 | -0.947349 |
| C | 3.567688 | -0.603907 | 0.479468 |
| O | 3.660622 | -1.164402 | 1.535918 |
| C | -0.968494 | -1.543433 | -0.189021 |
| C | -1.110321 | 0.481126 | -1.492245 |
| N | -1.830690 | -0.416557 | -0.579562 |
| H | -1.237320 | -2.447372 | -0.749175 |
| H | -1.077103 | -1.745836 | 0.878989 |
| H | -1.214251 | 0.117254 | -2.521417 |
| H | -1.505472 | 1.494971 | -1.422078 |
| S | -2.997268 | 0.157165 | 0.437351 |
| O | -2.928034 | 1.600113 | 0.451492 |
| O | -2.928622 | -0.600855 | 1.663338 |
| C | -4.547324 | -0.287108 | -0.383523 |
| H | -5.357069 | 0.088514 | 0.245449 |
| H | -4.566749 | 0.189688 | -1.364524 |
| H | -4.590288 | -1.373685 | -0.465923 |

**Int8**

| | | | |
|---|---|---|---|
| Rh | -1.247604 | -0.567523 | 0.002226 |
| C | -2.830629 | 0.200472 | -0.894987 |
| O | -3.755273 | 0.638036 | -1.353315 |
| C | -1.764906 | 3.257892 | -0.963421 |
| C | -0.779394 | 3.939368 | -0.020715 |
| C | -1.337166 | 2.546833 | 0.323141 |
| C | -0.403114 | 1.365502 | 0.252395 |
| C | 0.427944 | 1.108144 | 1.524818 |
| C | 0.354955 | -0.407744 | 1.734129 |
| C | -0.803868 | -1.053688 | 2.142046 |
| C | -2.073997 | -0.396161 | 1.972441 |
| H | -1.368907 | 2.884579 | -1.903950 |
| H | -2.773995 | 3.651688 | -1.020646 |
| H | 0.254166 | 4.001010 | -0.345712 |
| H | -1.126819 | 4.784750 | 0.562752 |
| H | -2.073913 | 2.535219 | 1.122942 |
| H | 0.274327 | 1.492115 | -0.594568 |
| H | 0.006306 | 1.638914 | 2.384760 |
| H | -0.760651 | -2.114685 | 2.384765 |
| H | -2.149917 | 0.657673 | 2.220177 |
| H | -2.964883 | -0.970773 | 2.209207 |
| C | 1.764993 | -0.974831 | 1.722681 |
| C | 1.959846 | 1.364403 | 1.424539 |
| N | 2.559238 | 0.065343 | 1.059679 |
| S | 2.996552 | -0.193229 | -0.541597 |
| O | 2.490783 | 0.902796 | -1.341008 |
| O | 2.605445 | -1.548144 | -0.870910 |
| C | 4.794424 | -0.093858 | -0.518410 |
| H | 5.122092 | -0.238708 | -1.550375 |
| H | 5.171400 | -0.884499 | 0.131036 |
| H | 5.076566 | 0.895579 | -0.155361 |
| C | -0.121240 | -0.757373 | -1.730063 |
| O | 0.317796 | -0.842051 | -2.754083 |
| H | 2.111280 | -1.071937 | 2.761128 |
| H | 1.864751 | -1.937273 | 1.222005 |
| H | 2.213893 | 2.131686 | 0.694182 |
| H | 2.357540 | 1.655287 | 2.401886 |
| C | -1.897648 | -2.589211 | -0.148946 |
| O | -2.245219 | -3.650176 | -0.217497 |

**TS0**

| | | | |
|---|---|---|---|
| Rh | -1.455435 | -0.573494 | 0.103351 |
| C | -3.206432 | -1.515226 | -0.264290 |
| O | -4.211106 | -1.976864 | -0.453032 |
| C | -0.879831 | 3.324599 | -1.661726 |
| C | -2.051861 | 3.000412 | -0.777980 |
| C | -1.212622 | 1.825895 | -1.293058 |
| C | -0.173751 | 1.111778 | -0.509906 |

| | | | |
|---|---|---|---|
| C | 0.366348 | 1.622643 | 0.801565 |
| C | 0.041099 | 0.294294 | 1.488128 |
| C | -1.161327 | -0.002258 | 2.204312 |
| C | -2.379323 | 0.564627 | 1.818686 |
| H | 0.006376 | 3.746802 | -1.200256 |
| H | -1.043826 | 3.604249 | -2.696088 |
| H | -1.971145 | 3.284408 | 0.266410 |
| H | -3.050886 | 3.095769 | -1.190047 |
| H | -1.625787 | 1.271205 | -2.130823 |
| H | 0.597459 | 0.660982 | -1.131246 |
| H | -0.155687 | 2.486874 | 1.214293 |
| H | -1.150303 | -0.843175 | 2.895753 |
| H | -2.431161 | 1.550006 | 1.366994 |
| H | -3.292454 | 0.206926 | 2.282649 |
| C | 1.372102 | -0.403555 | 1.789947 |
| C | 1.909089 | 1.723827 | 0.893139 |
| N | 2.366896 | 0.332898 | 1.012619 |
| S | 3.053221 | -0.422811 | -0.327284 |
| O | 2.930151 | 0.479420 | -1.449884 |
| O | 2.483452 | -1.749157 | -0.398624 |
| C | 4.797394 | -0.561340 | 0.102000 |
| H | 5.284921 | -1.038666 | -0.751222 |
| H | 4.882082 | -1.177239 | 0.997939 |
| H | 5.188643 | 0.443973 | 0.263568 |
| C | -0.473931 | -1.719579 | -1.158816 |
| O | 0.002459 | -2.426391 | -1.888306 |
| H | 1.580156 | -0.273752 | 2.861677 |
| H | 1.388644 | -1.465652 | 1.550089 |
| H | 2.357016 | 2.206936 | 0.024305 |
| H | 2.189346 | 2.269534 | 1.800217 |

**TS1'**

| | | | |
|---|---|---|---|
| Rh | -1.720836 | -0.270435 | -0.009460 |
| C | -3.403371 | -1.216634 | -0.154233 |
| O | -4.385076 | -1.764427 | -0.192000 |
| C | -0.688215 | 2.541592 | -2.054738 |
| C | -0.356543 | 3.532434 | -0.950975 |
| C | -0.869108 | 2.109146 | -0.600243 |
| C | 0.110129 | 1.142454 | 0.029193 |
| C | 0.667951 | 1.371919 | 1.408603 |
| C | 0.076224 | 0.000750 | 1.537279 |
| C | -1.224704 | -0.377514 | 2.048043 |
| C | -2.308539 | 0.512994 | 1.963569 |
| H | 0.149586 | 2.112151 | -2.596551 |
| H | -1.579671 | 2.705381 | -2.650364 |
| H | 0.692649 | 3.734741 | -0.761343 |
| H | -1.031845 | 4.359505 | -0.764064 |
| H | -1.894860 | 2.129490 | -0.223480 |
| H | 0.822815 | 0.724602 | -0.674465 |
| H | 0.218828 | 2.185568 | 1.974606 |
| H | -1.331580 | -1.374853 | 2.466826 |
| H | -2.142615 | 1.585671 | 1.922221 |
| H | -3.269628 | 0.207447 | 2.363064 |
| C | 1.242046 | -0.996578 | 1.533193 |
| C | 2.190495 | 1.175902 | 1.556833 |
| N | 2.418213 | -0.219850 | 1.146873 |
| S | 3.072771 | -0.522497 | -0.382894 |
| O | 3.562430 | 0.736116 | -0.884487 |
| O | 2.090399 | -1.270888 | -1.143848 |
| C | 4.463655 | -1.611361 | -0.030433 |
| H | 4.904277 | -1.865482 | -0.997226 |
| H | 4.087106 | -2.503917 | 0.471595 |
| H | 5.170334 | -1.064498 | 0.594631 |
| C | -0.979415 | -1.209579 | -1.605731 |
| O | -0.601781 | -1.784697 | -2.490594 |
| H | 1.353156 | -1.343996 | 2.570097 |
| H | 1.091990 | -1.856762 | 0.882122 |
| H | 2.777292 | 1.859913 | 0.944079 |
| H | 2.476553 | 1.291530 | 2.607417 |

**TS1**

| | | | |
|---|---|---|---|
| Rh | -1.621746 | -0.352777 | 0.000705 |
| C | -3.291314 | -1.371796 | 0.090472 |
| O | -4.249986 | -1.952536 | 0.184138 |
| C | -1.116579 | 3.167008 | -1.443382 |
| C | -2.312362 | 2.345157 | -1.106643 |
| C | -0.884072 | 1.643358 | -1.373168 |
| C | 0.062258 | 1.016943 | -0.400900 |
| C | 0.548723 | 1.593658 | 0.903468 |
| C | 0.168229 | 0.246596 | 1.477439 |
| C | -1.071126 | -0.133491 | 2.065959 |
| C | -2.220580 | 0.665893 | 1.824905 |
| H | -0.673082 | 3.760865 | -0.650976 |
| H | -1.036571 | 3.595895 | -2.436461 |
| H | -2.707601 | 2.410117 | -0.104801 |
| H | -3.047172 | 2.153686 | -1.879927 |
| H | -0.841451 | 1.172954 | -2.349024 |
| H | 0.831036 | 0.454801 | -0.919456 |
| H | 0.004377 | 2.457852 | 1.282417 |
| H | -1.110806 | -1.056408 | 2.638390 |
| H | -2.101379 | 1.737485 | 1.705280 |
| H | -3.156899 | 0.369034 | 2.286574 |

| | | | |
|---|---|---|---|
| C | 1.454668 | -0.559537 | 1.649717 |
| C | 2.084304 | 1.657050 | 1.057255 |
| N | 2.510063 | 0.247386 | 1.036240 |
| S | 3.237583 | -0.359958 | -0.363991 |
| O | 3.614620 | 0.779974 | -1.158572 |
| O | 2.360444 | -1.373844 | -0.917181 |
| C | 4.718390 | -1.174808 | 0.259019 |
| H | 5.222863 | -1.595476 | -0.614037 |
| H | 4.418858 | -1.964120 | 0.950264 |
| H | 5.337357 | -0.421346 | 0.746926 |
| C | -0.826004 | -1.653380 | -1.279089 |
| O | -0.397477 | -2.445975 | -1.947961 |
| H | 1.630265 | -0.638739 | 2.732162 |
| H | 1.410175 | -1.562307 | 1.224499 |
| H | 2.578634 | 2.218471 | 0.264214 |
| H | 2.340166 | 2.092968 | 2.028712 |

**TS10**

| | | | |
|---|---|---|---|
| Rh | -0.691510 | -0.969106 | 0.133736 |
| C | -1.919887 | -1.790507 | -1.164143 |
| O | -2.667012 | -2.268901 | -1.853054 |
| C | -3.522173 | 1.729325 | -1.124479 |
| C | -2.593299 | 2.922822 | -1.227629 |
| C | -2.552192 | 2.013477 | 0.025336 |
| C | -1.353652 | 1.152748 | 0.226065 |
| C | -0.234041 | 1.609203 | 1.167550 |
| C | 0.300733 | 0.301532 | 1.776299 |
| C | -0.674455 | -0.557102 | 2.262130 |
| C | -2.010463 | -0.168841 | 1.769754 |
| H | -3.311707 | 0.875353 | -1.761636 |
| H | -4.575971 | 1.905736 | -0.940181 |
| H | -1.764763 | 2.861969 | -1.925540 |
| H | -3.005927 | 3.916511 | -1.093532 |
| H | -2.979969 | 2.446264 | 0.926070 |
| H | -0.942991 | 0.896903 | -0.779153 |
| H | -0.644507 | 2.253070 | 1.955887 |
| H | -0.489820 | -1.440091 | 2.864930 |
| H | -2.408455 | 0.782903 | 2.110522 |
| H | -2.787539 | -0.933034 | 1.761185 |
| C | 1.805585 | 0.410004 | 1.861505 |
| C | 1.053245 | 2.258648 | 0.564111 |
| N | 2.124088 | 1.245920 | 0.682699 |
| S | 2.522935 | 0.416680 | -0.734368 |
| O | 1.432990 | 0.544908 | -1.686839 |
| O | 2.954685 | -0.902910 | -0.336599 |
| C | 3.928955 | 1.353746 | -1.357550 |
| H | 4.213140 | 0.886520 | -2.303172 |
| H | 4.731362 | 1.285771 | -0.622474 |
| H | 3.612951 | 2.386511 | -1.514620 |
| C | 0.515044 | -2.507392 | -0.028349 |
| O | 1.162883 | -3.423258 | -0.063503 |
| H | 2.098698 | 0.967981 | 2.760362 |
| H | 2.346229 | -0.535017 | 1.839118 |
| H | 0.925274 | 2.571629 | -0.472003 |
| H | 1.337607 | 3.127789 | 1.163504 |

**TS11**

| | | | |
|---|---|---|---|
| Rh | -1.689750 | -0.211868 | -0.041482 |
| C | -2.894932 | -1.707948 | -0.251393 |
| O | -3.588595 | -2.577690 | -0.406990 |
| C | -3.221250 | 1.679754 | 0.074158 |
| C | -2.174570 | 2.685399 | 0.577502 |
| C | -1.141321 | 1.839561 | 1.301115 |
| C | 0.057896 | 1.407160 | 0.822740 |
| C | 1.067258 | 0.728276 | 1.749749 |
| C | 1.185108 | -0.791493 | 1.652742 |
| C | 0.169074 | -1.669340 | 1.694209 |
| C | -1.267294 | -1.322708 | 1.843095 |
| H | -4.053574 | 2.091813 | -0.499238 |
| H | -3.661191 | 1.102349 | 0.894854 |
| H | -1.724056 | 3.232171 | -0.256280 |
| H | -2.617065 | 3.414984 | 1.262390 |
| H | -1.398466 | 1.587773 | 2.330604 |
| H | 0.427185 | 1.718399 | -0.153120 |
| H | 0.783656 | 0.993661 | 2.776396 |
| H | 0.406791 | -2.724812 | 1.560921 |
| H | -1.469923 | -0.582918 | 2.618105 |
| H | -1.879674 | -2.202107 | 2.032364 |
| C | 2.659065 | -1.130754 | 1.495253 |
| C | 2.538600 | 1.201714 | 1.478867 |
| N | 3.236885 | 0.065524 | 0.853752 |
| S | 3.216971 | 0.042475 | -0.836532 |
| O | 2.087044 | 0.826226 | -1.317788 |
| O | 3.335092 | -1.334437 | -1.241330 |
| C | 4.731875 | 0.925040 | -1.248891 |
| H | 4.764235 | 0.974960 | -2.339582 |
| H | 5.568967 | 0.349815 | -0.852765 |
| H | 4.691028 | 1.926322 | -0.817182 |
| C | -2.422111 | 1.022667 | -1.372665 |
| O | -2.618746 | 1.440997 | -2.428291 |
| H | 3.144340 | -1.240114 | 2.473477 |
| H | 2.848712 | -2.029556 | 0.908707 |

| | | | |
|---|---|---|---|
| H | 2.592322 | 2.096933 | 0.858283 |
| H | 3.037400 | 1.411667 | 2.429195 |
| C | -0.306195 | -1.081588 | -1.154452 |
| O | 0.355344 | -1.660096 | -1.846146 |

**TS12**

| | | | |
|---|---|---|---|
| Rh | -1.435807 | -0.413043 | -0.023665 |
| C | -2.655770 | -1.930978 | 0.221298 |
| O | -3.379075 | -2.779200 | 0.352827 |
| C | -1.995323 | 2.450458 | -2.037782 |
| C | -2.426345 | 2.847353 | -0.597842 |
| C | -1.452327 | 1.732085 | -0.827383 |
| C | -0.182101 | 1.356599 | -0.376756 |
| C | 0.396918 | 1.600510 | 1.015816 |
| C | 0.250901 | 0.242255 | 1.722035 |
| C | -0.946347 | -0.253148 | 2.192549 |
| C | -2.191607 | 0.378306 | 1.779424 |
| H | -1.293064 | 3.087956 | -2.566525 |
| H | -2.746632 | 1.978505 | -2.660013 |
| H | -2.033961 | 3.766568 | -0.171895 |
| H | -3.446210 | 2.609262 | -0.315565 |
| H | -2.423509 | 0.361519 | -1.006419 |
| H | 0.557390 | 1.095097 | -1.131509 |
| H | -0.117048 | 2.405540 | 1.547257 |
| H | -0.949242 | -1.188232 | 2.749652 |
| H | -2.214698 | 1.463504 | 1.727929 |
| H | -3.107237 | -0.045411 | 2.181767 |
| C | 1.637857 | -0.338265 | 1.943267 |
| C | 1.939102 | 1.797616 | 0.993164 |
| N | 2.506267 | 0.438934 | 1.052485 |
| S | 2.983705 | -0.291574 | -0.391116 |
| O | 2.851000 | 0.695988 | -1.438143 |
| O | 2.279130 | -1.552281 | -0.505390 |
| C | 4.733363 | -0.630744 | -0.131630 |
| H | 5.088945 | -1.118263 | -1.042198 |
| H | 4.831487 | -1.291417 | 0.730817 |
| H | 5.240890 | 0.320884 | 0.030580 |
| C | -0.449530 | -1.344869 | -1.588330 |
| O | -0.026742 | -1.842162 | -2.496709 |
| H | 1.937793 | -0.144547 | 2.982516 |
| H | 1.704185 | -1.408046 | 1.749164 |
| H | 2.295857 | 2.328217 | 0.110722 |
| H | 2.255940 | 2.336613 | 1.891435 |

**TS13**

| | | | |
|---|---|---|---|
| Rh | 2.328822 | 0.108268 | 0.096662 |
| C | 2.924922 | 1.942104 | -0.617504 |
| O | 3.204237 | 2.940417 | -1.042695 |
| C | 1.096160 | -2.637848 | 0.054166 |
| C | 2.014300 | -1.836336 | 0.974885 |
| C | 0.716786 | -1.295501 | -0.502278 |
| C | -0.598890 | -0.701053 | -0.077624 |
| C | -1.113662 | -0.753301 | 1.350960 |
| C | -0.705114 | 0.599251 | 0.757595 |
| C | 0.528939 | 1.351777 | 1.103063 |
| C | 1.437481 | 1.036959 | 2.072002 |
| H | 0.294164 | -3.190979 | 0.541156 |
| H | 1.631049 | -3.273586 | -0.651497 |
| H | 1.598017 | -1.681407 | 1.964529 |
| H | 3.049734 | -2.182859 | 1.012646 |
| H | 0.929184 | -1.139141 | -1.561469 |
| H | -1.342530 | -0.826556 | -0.867896 |
| H | -0.537090 | -1.237242 | 2.131711 |
| H | 0.614133 | 2.319858 | 0.607724 |
| H | 1.278308 | 0.206077 | 2.748939 |
| H | 2.224015 | 1.738112 | 2.340085 |
| C | -1.999644 | 1.408967 | 0.569638 |
| C | -2.638254 | -0.701628 | 1.507396 |
| N | -3.069019 | 0.411435 | 0.646433 |
| H | -2.097268 | 2.118079 | 1.401785 |
| H | -2.049643 | 1.954994 | -0.373866 |
| H | -2.894024 | -0.482715 | 2.549909 |
| H | -3.123653 | -1.630639 | 1.201942 |
| S | -3.945197 | 0.053400 | -0.746932 |
| O | -3.690606 | -1.322334 | -1.113663 |
| O | -3.679145 | 1.116787 | -1.682793 |
| C | -5.654162 | 0.171197 | -0.184054 |
| H | -5.835436 | 1.196977 | 0.137672 |
| H | -6.278067 | -0.091444 | -1.041231 |
| H | -5.800894 | -0.538796 | 0.631575 |
| C | 3.546703 | -0.783239 | -1.117572 |
| O | 4.267500 | -1.319034 | -1.791058 |

**TS2-UP**

| | | | |
|---|---|---|---|
| Rh | -1.773371 | -0.157600 | -0.183543 |
| C | -2.588522 | -0.526520 | 1.496514 |
| O | -3.368629 | -1.077618 | 2.146217 |
| C | -1.789438 | 2.552691 | -0.960076 |
| C | -2.915667 | 1.592454 | -0.517147 |
| C | -0.747304 | 1.594992 | -1.527938 |
| C | 0.348053 | 1.103805 | -0.882219 |

| | | | |
|---|---|---|---|
| C | 0.969401 | 1.627235 | 0.411619 |
| C | 1.054142 | 0.622477 | 1.573668 |
| C | 0.031850 | 0.150677 | 2.291402 |
| C | -1.395786 | 0.595725 | 2.091147 |
| H | -1.388676 | 3.117477 | -0.115023 |
| H | -2.116574 | 3.274460 | -1.713715 |
| H | -3.435368 | 1.905631 | 0.390063 |
| H | -3.658477 | 1.463030 | -1.304648 |
| H | -0.922370 | 1.248152 | -2.546077 |
| H | 0.953326 | 0.381203 | -1.426739 |
| H | 0.445189 | 2.532125 | 0.731050 |
| H | 0.215619 | -0.558696 | 3.095662 |
| H | -1.461511 | 1.583148 | 1.627000 |
| H | -1.919365 | 0.690491 | 3.046930 |
| C | -2.944667 | -0.979564 | -1.471101 |
| O | -3.657715 | -1.438660 | -2.206024 |
| C | 2.524234 | 0.281529 | 1.803575 |
| C | 2.486366 | 1.938987 | 0.158461 |
| N | 3.212398 | 0.734728 | 0.584932 |
| H | 2.921084 | 0.855210 | 2.649635 |
| H | 2.682381 | -0.780888 | 1.996184 |
| H | 2.801459 | 2.762065 | 0.807105 |
| H | 2.720008 | 2.193099 | -0.874529 |
| S | 3.433617 | -0.454653 | -0.598605 |
| O | 3.509764 | 0.229084 | -1.865387 |
| O | 2.435310 | -1.495926 | -0.418848 |
| C | 5.050624 | -1.121751 | -0.170644 |
| H | 5.239131 | -1.935755 | -0.874253 |
| H | 5.779486 | -0.319074 | -0.285242 |
| H | 5.020616 | -1.495788 | 0.853956 |
| C | -0.530285 | -1.865180 | -0.006100 |
| O | -0.020847 | -2.854116 | 0.086326 |

**TS2**

| | | | |
|---|---|---|---|
| Rh | -1.837105 | -0.407059 | 0.048330 |
| C | -3.887171 | -0.701893 | 0.161117 |
| O | -4.993078 | -0.854833 | 0.222397 |
| C | -1.332790 | 3.152526 | 0.033886 |
| C | -2.151725 | 1.901766 | 0.429101 |
| C | 0.109463 | 2.945935 | -0.378424 |
| C | 0.987806 | 2.037350 | 0.045344 |
| C | 0.807808 | 0.984898 | 1.131087 |
| C | 0.239102 | -0.353513 | 0.612433 |
| C | -0.408124 | -1.286882 | 1.528674 |
| C | -1.465989 | -0.915795 | 2.339124 |
| H | -1.381093 | 3.848559 | 0.882976 |
| H | -1.851422 | 3.643911 | -0.793913 |
| H | -1.903884 | 1.608012 | 1.448175 |
| H | -3.221844 | 2.112387 | 0.389938 |
| H | 0.461671 | 3.653334 | -1.125998 |
| H | 1.982809 | 2.067343 | -0.396457 |
| H | 0.253825 | 1.372882 | 1.989141 |
| H | -0.225899 | -2.351137 | 1.382207 |
| H | -1.572600 | 0.096380 | 2.715732 |
| H | -2.044930 | -1.679032 | 2.850393 |
| C | -1.952960 | 0.978126 | -1.242134 |
| O | -2.058703 | 1.554293 | -2.222177 |
| C | 1.369933 | -0.924033 | -0.244513 |
| C | 2.207308 | 0.469933 | 1.563250 |
| N | 2.571254 | -0.490167 | 0.501957 |
| H | 1.328070 | -2.015652 | -0.318278 |
| H | 1.355735 | -0.508355 | -1.256437 |
| H | 2.153832 | -0.038872 | 2.531629 |
| H | 2.934566 | 1.282663 | 1.618694 |
| S | 3.963847 | -0.218907 | -0.402795 |
| O | 4.279889 | 1.190250 | -0.373662 |
| O | 3.745993 | -0.904057 | -1.651188 |
| C | 5.231717 | -1.086812 | 0.542533 |
| H | 6.172698 | -0.921857 | 0.012638 |
| H | 5.275668 | -0.655148 | 1.543940 |
| H | 4.974176 | -2.145634 | 0.567640 |
| C | -1.508462 | -2.011496 | -1.061143 |
| O | -1.338787 | -2.893042 | -1.731353 |

**TS3**

| | | | |
|---|---|---|---|
| Rh | 1.779276 | -0.025713 | -0.004048 |
| C | 3.660530 | 0.263677 | 0.605074 |
| O | 4.712099 | 0.480808 | 0.927908 |
| C | 0.863639 | 1.550084 | 1.461171 |
| C | 0.790966 | 0.225618 | 1.943347 |
| C | -0.310435 | 2.314956 | 0.969704 |
| C | -1.001323 | 2.193768 | -0.161108 |
| C | -0.813304 | 1.261320 | -1.345014 |
| C | -0.066344 | -0.074448 | -1.156161 |
| C | 1.011819 | -0.464271 | -2.029951 |
| C | 2.123992 | 0.351812 | -2.253841 |
| H | 1.677988 | 1.557518 | -0.066792 |
| H | 1.667184 | 2.174045 | 1.854200 |
| H | 1.486769 | -0.078978 | 2.719980 |
| H | -0.178504 | -0.269081 | 1.926396 |
| H | -0.611506 | 3.096344 | 1.667016 |
| H | -1.837644 | 2.877596 | -0.285437 |

| | | | |
|---|---|---|---|
| H | -0.370345 | 1.838270 | -2.166468 |
| H | 1.096250 | -1.518169 | -2.295639 |
| H | 2.034141 | 1.432469 | -2.282643 |
| H | 2.996013 | -0.068701 | -2.744950 |
| C | 1.811659 | -2.066001 | 0.300920 |
| O | 1.823682 | -3.167931 | 0.502102 |
| C | -1.145049 | -1.156947 | -0.869653 |
| C | -2.215041 | 0.719660 | -1.777698 |
| N | -2.428936 | -0.459530 | -0.929956 |
| H | -1.111580 | -1.923508 | -1.654723 |
| H | -1.028366 | -1.642206 | 0.098995 |
| H | -2.187623 | 0.388567 | -2.821032 |
| H | -3.019166 | 1.442973 | -1.647447 |
| S | -3.266644 | -0.240761 | 0.522972 |
| O | -3.856127 | 1.072869 | 0.480103 |
| O | -2.391818 | -0.625258 | 1.613840 |
| C | -4.582636 | -1.468495 | 0.415639 |
| H | -5.165793 | -1.373480 | 1.334378 |
| H | -5.189516 | -1.237508 | -0.460292 |
| H | -4.130390 | -2.458489 | 0.342565 |

**TS4**

| | | | |
|---|---|---|---|
| Rh | -1.747545 | 0.046390 | -0.068927 |
| C | -3.637729 | 0.327532 | 0.532159 |
| O | -4.705264 | 0.429318 | 0.860719 |
| C | -0.970079 | -0.896678 | 1.939028 |
| C | -0.802625 | 0.479698 | 1.958417 |
| C | 0.138975 | -1.867174 | 1.775118 |
| C | 0.886107 | -2.202522 | 0.724527 |
| C | 0.829516 | -1.779087 | -0.730385 |
| C | 0.084799 | -0.490288 | -1.132810 |
| C | -1.070860 | -0.529361 | -1.990842 |
| C | -2.064367 | -1.515139 | -1.705632 |
| H | -2.082641 | -1.536360 | -0.056298 |
| H | -1.858145 | -1.304036 | 2.422412 |
| H | -1.525987 | 1.098645 | 2.481584 |
| H | 0.182900 | 0.903256 | 1.773308 |
| H | 0.353911 | -2.387434 | 2.709473 |
| H | 1.660760 | -2.943445 | 0.913143 |
| H | 0.445284 | -2.635869 | -1.297881 |
| H | -1.266518 | 0.236024 | -2.737699 |
| H | -1.754766 | -2.534576 | -1.481912 |
| H | -3.036656 | -1.437685 | -2.184300 |
| C | -1.499208 | 2.011776 | -0.404978 |
| O | -1.357937 | 3.112047 | -0.574282 |
| C | 1.164616 | 0.593902 | -1.400333 |
| C | 2.268848 | -1.458567 | -1.249959 |
| N | 2.439723 | -0.019935 | -1.032551 |
| H | 1.180326 | 0.837801 | -2.470804 |
| H | 1.019963 | 1.511143 | -0.831713 |
| H | 2.327066 | -1.643373 | -2.327798 |
| H | 3.045507 | -2.032154 | -0.746966 |
| S | 3.162012 | 0.487945 | 0.408690 |
| O | 3.728309 | -0.673127 | 1.044079 |
| O | 2.213208 | 1.330157 | 1.113788 |
| C | 4.503744 | 1.544116 | -0.169729 |
| H | 4.998734 | 1.928437 | 0.725039 |
| H | 5.184340 | 0.931097 | -0.761383 |
| H | 4.078244 | 2.357016 | -0.759575 |

**TS5**

| | | | |
|---|---|---|---|
| Rh | -1.567181 | 0.126304 | -0.083884 |
| C | -3.378260 | 0.779365 | 0.474579 |
| O | -4.407714 | 1.105301 | 0.778971 |
| C | -1.060343 | -0.977230 | 1.948237 |
| C | -0.605104 | 0.334077 | 1.963789 |
| C | -0.226163 | -2.183663 | 1.746491 |
| C | 0.490785 | -2.601922 | 0.702124 |
| C | 0.765454 | -2.035444 | -0.675162 |
| C | 0.098629 | -0.737114 | -1.200746 |
| C | -1.110416 | -0.719134 | -1.989572 |
| C | -2.196816 | -1.522845 | -1.572386 |
| H | -2.150580 | -1.348005 | 0.175665 |
| H | -2.014612 | -1.176444 | 2.436210 |
| H | -1.184375 | 1.088881 | 2.487414 |
| H | 0.443090 | 0.553740 | 1.799013 |
| H | -0.239795 | -2.837239 | 2.618461 |
| H | 1.015137 | -3.545575 | 0.850141 |
| H | 0.547534 | -2.845222 | -1.383953 |
| H | -1.248281 | -0.004308 | -2.797380 |
| H | -2.004576 | -2.524758 | -1.191574 |
| H | -3.178467 | -1.375131 | -2.013653 |
| C | -0.958586 | 2.018819 | -0.474099 |
| O | -0.674280 | 3.085865 | -0.662991 |
| C | 1.260915 | 0.131065 | -1.732739 |
| C | 2.312646 | -1.715511 | -0.793099 |
| N | 2.425811 | -0.264883 | -0.952201 |
| H | 1.454748 | -0.144185 | -2.778783 |
| H | 1.106557 | 1.206413 | -1.682840 |
| H | 2.721161 | -2.187008 | -1.691780 |
| H | 2.870551 | -2.058083 | 0.077491 |
| S | 2.795111 | 0.670274 | 0.396180 |

| | | | |
|---|---|---|---|
| O | 2.801013 | -0.177897 | 1.565534 |
| O | 1.917190 | 1.824595 | 0.358343 |
| C | 4.479065 | 1.222500 | 0.071658 |
| H | 4.770602 | 1.837024 | 0.926240 |
| H | 5.116594 | 0.341160 | -0.011940 |
| H | 4.474868 | 1.804179 | -0.850716 |

**TS6**

| | | | |
|---|---|---|---|
| Rh | 1.523896 | 0.360073 | -0.052655 |
| C | 2.787371 | 1.523718 | 0.850813 |
| O | 3.536350 | 2.183480 | 1.369749 |
| C | 2.244130 | -1.986409 | -1.578180 |
| C | 3.107532 | -1.248007 | -0.557267 |
| C | 1.090635 | -1.033459 | -1.849106 |
| C | -0.091784 | -0.972161 | -1.148766 |
| C | -0.602806 | -1.885859 | -0.041499 |
| C | -0.408277 | -1.131019 | 1.279160 |
| C | 0.797358 | -0.858481 | 1.836910 |
| C | 2.068088 | -1.385444 | 1.250843 |
| H | 1.888130 | -2.945993 | -1.193737 |
| H | 2.812388 | -2.187992 | -2.491818 |
| H | 1.179192 | -0.386095 | -2.718878 |
| H | -0.837231 | -0.273207 | -1.525376 |
| H | -0.093975 | -2.855047 | -0.044552 |
| H | 0.847886 | -0.267734 | 2.748150 |
| C | 0.702723 | 1.941619 | -0.856340 |
| O | 0.247393 | 2.844298 | -1.345591 |
| C | -1.771155 | -0.730882 | 1.816197 |
| C | -2.152455 | -2.038016 | -0.103522 |
| N | -2.683111 | -0.907901 | 0.678345 |
| H | -2.067545 | -1.423042 | 2.615741 |
| H | -1.792093 | 0.287242 | 2.206219 |
| H | -2.455075 | -2.963984 | 0.394795 |
| H | -2.555184 | -2.024051 | -1.116185 |
| S | -3.095279 | 0.496377 | -0.170428 |
| O | -3.264878 | 0.107665 | -1.549776 |
| O | -2.147576 | 1.543269 | 0.160647 |
| C | -4.697073 | 0.927283 | 0.531027 |
| H | -5.013102 | 1.844362 | 0.028666 |
| H | -5.383140 | 0.104934 | 0.326636 |
| H | -4.575499 | 1.094162 | 1.602575 |
| H | 2.924743 | -1.237468 | 1.902006 |
| H | 1.969838 | -2.424535 | 0.953368 |
| H | 3.668491 | -0.427789 | -1.006231 |
| H | 3.797061 | -1.870755 | 0.004663 |

**TS7-UP**

| | | | |
|---|---|---|---|
| Rh | -1.635749 | 0.539680 | 0.299568 |
| C | -2.445173 | -1.045684 | -0.944491 |
| O | -3.333825 | -0.686968 | -1.636823 |
| C | -1.838114 | -1.646584 | 2.030636 |
| C | -2.889513 | -1.108791 | 1.031265 |
| C | -0.742050 | -0.597861 | 2.034147 |
| C | 0.379445 | -0.592379 | 1.248195 |
| C | 0.969543 | -1.744509 | 0.445661 |
| C | 0.910969 | -1.523886 | -1.066856 |
| C | -0.163525 | -1.702037 | -1.831456 |
| C | -1.489289 | -2.196854 | -1.289326 |
| H | -1.462362 | -2.625806 | 1.729918 |
| H | -2.276792 | -1.756557 | 3.027607 |
| H | -3.483132 | -1.920765 | 0.603600 |
| H | -3.623103 | -0.428342 | 1.480038 |
| H | -0.848005 | 0.217681 | 2.752424 |
| H | 1.050779 | 0.252833 | 1.389203 |
| H | 0.486268 | -2.683963 | 0.725983 |
| H | -0.113418 | -1.512786 | -2.901026 |
| H | -1.340891 | -2.826739 | -0.412088 |
| H | -2.018207 | -2.778408 | -2.050615 |
| C | -3.131293 | 1.635849 | -0.355222 |
| O | -4.006193 | 2.275257 | -0.640097 |
| C | 2.305141 | -1.133494 | -1.556718 |
| C | 2.509924 | -1.821678 | 0.689813 |
| N | 3.102074 | -0.947870 | -0.333269 |
| H | 2.741051 | -1.951865 | -2.141108 |
| H | 2.292655 | -0.229560 | -2.168100 |
| H | 2.853074 | -2.843773 | 0.501594 |
| H | 2.823501 | -1.517348 | 1.687956 |
| S | 3.425202 | 0.641050 | 0.117047 |
| O | 3.588056 | 0.642178 | 1.550742 |
| O | 2.427836 | 1.514434 | -0.476654 |
| C | 5.011837 | 0.967056 | -0.669815 |
| H | 5.261911 | 2.003449 | -0.431954 |
| H | 5.741432 | 0.276437 | -0.246212 |
| H | 4.905688 | 0.831835 | -1.747485 |
| C | -0.430130 | 2.088661 | -0.106765 |
| O | 0.118363 | 3.020037 | -0.393991 |

**TS7**

| | | | |
|---|---|---|---|
| Rh | -1.144472 | 0.481289 | 0.061797 |
| C | -1.816536 | 2.027861 | -0.936191 |
| O | -2.201217 | 2.906446 | -1.514972 |

|  |  |  |  |
|---|---|---|---|
| C | -2.053603 | -2.301943 | 1.295306 |
| C | -3.349449 | -1.582693 | 0.907044 |
| C | -0.962592 | -1.300066 | 1.603198 |
| C | 0.256294 | -1.169805 | 0.982398 |
| C | 0.781502 | -1.934267 | -0.224870 |
| C | 0.619915 | -0.998495 | -1.424119 |
| C | -0.552560 | -0.576449 | -1.961343 |
| C | -1.933618 | -1.005503 | -1.532106 |
| H | -1.744640 | -3.007654 | 0.522747 |
| H | -2.230941 | -2.891203 | 2.202298 |
| H | -4.114819 | -2.274757 | 0.535997 |
| H | -3.783566 | -1.056431 | 1.765896 |
| H | -1.085229 | -0.767748 | 2.545834 |
| H | 1.000672 | -0.543290 | 1.470602 |
| H | 0.267353 | -2.888198 | -0.367725 |
| H | -0.504852 | 0.111956 | -2.802654 |
| H | -1.976517 | -2.069953 | -1.311045 |
| H | -2.651241 | -0.730667 | -2.300664 |
| C | -3.162546 | -0.491766 | -0.159580 |
| O | -4.040413 | 0.210033 | -0.532560 |
| C | 2.005768 | -0.573401 | -1.892229 |
| C | 2.329082 | -2.110031 | -0.149433 |
| N | 2.888293 | -0.894123 | -0.762632 |
| H | 2.308149 | -1.183678 | -2.753422 |
| H | 2.058335 | 0.480120 | -2.167900 |
| H | 2.632794 | -2.964599 | -0.761556 |
| H | 2.705260 | -2.244503 | 0.864112 |
| S | 3.280021 | 0.393020 | 0.266885 |
| O | 3.378759 | -0.156403 | 1.598655 |
| O | 2.363956 | 1.488642 | 0.016136 |
| C | 4.921627 | 0.867286 | -0.302411 |
| H | 5.228496 | 1.710006 | 0.321323 |
| H | 5.582336 | 0.010838 | -0.165630 |
| H | 4.855706 | 1.163154 | -1.350566 |
| C | -0.724002 | 1.670434 | 1.521453 |
| O | -0.488602 | 2.342803 | 2.392376 |

**TS8-UP**

|  |  |  |  |
|---|---|---|---|
| Rh | 1.762877 | -0.201326 | -0.216674 |
| C | 2.971680 | 1.223717 | -0.603858 |
| O | 3.970941 | 1.586176 | -1.072909 |
| C | 1.853568 | -0.901817 | 2.387256 |
| C | 2.954087 | -0.902349 | 1.310564 |
| C | 0.632193 | -1.426568 | 1.642535 |
| C | -0.412773 | -0.728706 | 1.134977 |
| C | -0.775053 | 0.738664 | 1.331983 |
| C | -0.588093 | 1.508036 | 0.015022 |
| C | 0.536302 | 2.093373 | -0.446638 |
| C | 1.876126 | 2.135123 | 0.267420 |
| H | 1.683499 | 0.099853 | 2.792307 |
| H | 2.110824 | -1.555285 | 3.229375 |
| H | 3.792167 | -0.228204 | 1.497311 |
| H | 3.330147 | -1.906484 | 1.111576 |
| H | 0.643480 | -2.496628 | 1.435914 |
| H | -1.148848 | -1.300905 | 0.571434 |
| H | -0.213125 | 1.186778 | 2.155622 |
| H | 0.493808 | 2.619536 | -1.399085 |
| H | 1.819501 | 1.905861 | 1.336653 |
| H | 2.357541 | 3.113038 | 0.179995 |
| C | 2.347975 | -1.609449 | -1.362229 |
| O | 2.730473 | -2.433201 | -2.022040 |
| C | -1.944707 | 1.613956 | -0.680025 |
| C | -2.316523 | 0.873963 | 1.542937 |
| N | -2.866351 | 0.878576 | 0.186211 |
| H | -2.237702 | 2.670450 | -0.734051 |
| H | -1.940958 | 1.195588 | -1.689036 |
| H | -2.537486 | 1.831784 | 2.026276 |
| H | -2.735917 | 0.063203 | 2.137699 |
| S | -3.645960 | -0.486421 | -0.418093 |
| O | -3.509538 | -1.532505 | 0.568359 |
| O | -3.164265 | -0.679749 | -1.764561 |
| C | -5.379245 | 0.002655 | -0.486403 |
| H | -5.925412 | -0.860097 | -0.874671 |
| H | -5.705907 | 0.247434 | 0.525036 |
| H | -5.469375 | 0.857123 | -1.158069 |

**TS8**

|  |  |  |  |
|---|---|---|---|
| Rh | -1.717183 | -0.324339 | -0.044509 |
| C | -1.747276 | -2.012760 | -1.019109 |
| O | -1.823205 | -2.976073 | -1.590077 |
| C | -1.753290 | 2.654049 | -0.388166 |
| C | -2.572849 | 1.781675 | 0.575920 |
| C | -0.709272 | 1.775955 | -1.078861 |
| C | 0.277427 | 1.077838 | -0.446211 |
| C | 0.570053 | 0.985673 | 1.057943 |
| C | 0.434778 | -0.523978 | 1.337200 |
| C | -0.585458 | -1.365046 | 1.726271 |
| C | -2.022102 | -1.102409 | 1.847017 |
| H | -1.274220 | 3.487601 | 0.138364 |
| H | -2.411062 | 3.088008 | -1.144720 |
| H | -2.071755 | 1.598045 | 1.527703 |
| H | -3.549463 | 2.191982 | 0.838457 |

| | | | |
|---|---|---|---|
| H | -0.686828 | 1.774837 | -2.166887 |
| H | 0.976756 | 0.537563 | -1.084006 |
| H | -0.068847 | 1.625395 | 1.664916 |
| H | -0.304180 | -2.419539 | 1.728137 |
| H | -2.349252 | -0.254569 | 2.445866 |
| H | -2.628484 | -1.986695 | 2.022760 |
| C | -3.353292 | 0.497686 | -0.449985 |
| O | -4.384204 | 0.658156 | -0.937389 |
| C | 1.829992 | -1.126321 | 1.097119 |
| C | 2.072798 | 1.228297 | 1.356359 |
| N | 2.731296 | 0.006866 | 0.884687 |
| H | 2.115215 | -1.685978 | 1.997147 |
| H | 1.852973 | -1.801384 | 0.236487 |
| H | 2.214675 | 1.325403 | 2.438371 |
| H | 2.476798 | 2.106860 | 0.853060 |
| S | 3.595259 | 0.069628 | -0.568316 |
| O | 3.736936 | 1.463882 | -0.899572 |
| O | 2.962921 | -0.843511 | -1.496719 |
| C | 5.205843 | -0.603553 | -0.122718 |
| H | 5.804198 | -0.590007 | -1.036709 |
| H | 5.641435 | 0.038703 | 0.643229 |
| H | 5.068345 | -1.625339 | 0.234367 |

**TS9**

| | | | |
|---|---|---|---|
| Rh | -1.258811 | -0.722286 | 0.057867 |
| C | -3.051362 | -0.804295 | -0.845144 |
| O | -4.056827 | -0.862736 | -1.336002 |
| C | -1.032218 | 3.948048 | -0.199605 |
| C | -2.275073 | 3.126448 | 0.139611 |
| C | -1.204806 | 2.540415 | -0.779763 |
| C | -0.240281 | 1.431496 | -0.404532 |
| C | 0.244050 | 1.277671 | 1.093360 |
| C | 0.184637 | -0.193603 | 1.553263 |
| C | -0.924108 | -0.732947 | 2.286993 |
| C | -2.204252 | -0.208860 | 2.147515 |
| H | -0.304796 | 4.090725 | 0.593542 |
| H | -1.127532 | 4.788991 | -0.877120 |
| H | -2.360175 | 2.774468 | 1.161880 |
| H | -3.220199 | 3.410278 | -0.310206 |
| H | -1.462580 | 2.519931 | -1.835690 |
| H | 0.689601 | 1.595137 | -0.965765 |
| H | -0.362897 | 1.920810 | 1.735129 |
| H | -0.796464 | -1.711533 | 2.748790 |
| H | -2.361574 | 0.847422 | 1.960368 |
| H | -3.055580 | -0.763083 | 2.528922 |
| C | 1.619832 | -0.690202 | 1.748340 |
| C | 1.761157 | 1.594163 | 1.246744 |
| N | 2.446032 | 0.303581 | 1.059840 |
| S | 2.993258 | -0.094861 | -0.488860 |
| O | 2.825167 | 1.084473 | -1.308081 |
| O | 2.364264 | -1.339762 | -0.877380 |
| C | 4.754427 | -0.388645 | -0.252064 |
| H | 5.152028 | -0.651485 | -1.235075 |
| H | 4.874759 | -1.213835 | 0.451232 |
| H | 5.203663 | 0.531692 | 0.122420 |
| C | -0.404756 | 0.029901 | -1.479034 |
| O | -0.183492 | 0.041802 | -2.607594 |
| H | 1.867894 | -0.664675 | 2.817614 |
| H | 1.798102 | -1.695920 | 1.369901 |
| H | 2.123306 | 2.335672 | 0.534142 |
| H | 1.971088 | 1.937711 | 2.265088 |
| C | -0.748966 | -2.614493 | -0.184114 |
| O | -0.432386 | -3.679689 | -0.332911 |

***trans*-Int0**

| | | | |
|---|---|---|---|
| Rh | 1.677636 | -0.091432 | 0.045920 |
| C | 3.255280 | 0.863900 | -0.613874 |
| O | 4.149679 | 1.375383 | -1.061442 |
| C | 0.401153 | 0.710713 | -1.362191 |
| C | -0.410004 | -0.533817 | -1.733224 |
| C | -0.190346 | -1.475209 | -0.538685 |
| C | 0.973357 | -2.199721 | -0.351965 |
| C | 2.171084 | -1.835624 | -1.067697 |
| H | -0.004554 | -0.971229 | -2.649476 |
| H | 1.023297 | -2.910991 | 0.471439 |
| H | 2.089345 | -1.584402 | -2.121804 |
| H | 3.080304 | -2.372357 | -0.812877 |
| C | -1.517439 | -1.715211 | 0.168310 |
| C | -1.956362 | -0.418385 | -1.826777 |
| N | -2.443692 | -0.793364 | -0.491512 |
| S | -3.404676 | 0.229479 | 0.405812 |
| O | -3.512054 | 1.462452 | -0.334295 |
| O | -2.870749 | 0.226989 | 1.750683 |
| C | -5.024385 | -0.561887 | 0.440236 |
| H | -5.674737 | 0.092094 | 1.025727 |
| H | -4.923036 | -1.537407 | 0.917876 |
| H | -5.382240 | -0.647899 | -0.586518 |
| C | 2.504961 | -0.743513 | 1.856023 |
| O | 2.957150 | -1.083486 | 2.822970 |
| H | -1.821308 | -2.759048 | 0.006384 |
| H | -1.482830 | -1.521357 | 1.243028 |
| H | -2.294818 | 0.586158 | -2.083577 |

| | | | |
|---|---|---|---|
| H | -2.334680 | -1.125823 | -2.572879 |
| H | 0.785223 | 1.308927 | -2.186826 |
| C | -0.133367 | 1.456108 | -0.202814 |
| C | 0.025029 | 2.901430 | 0.102137 |
| C | 0.901348 | 2.122923 | 1.051542 |
| H | -0.937478 | 0.999791 | 0.355196 |
| H | -0.849045 | 3.391106 | 0.520505 |
| H | 0.557789 | 3.495535 | -0.636554 |
| H | 0.504817 | 1.918210 | 2.038721 |
| H | 1.956927 | 2.354086 | 1.003361 |

### ***trans*-Int1**

| | | | |
|---|---|---|---|
| Rh | 2.121064 | -0.059855 | 0.011482 |
| C | 3.875015 | -0.241254 | 0.773859 |
| O | 4.905945 | -0.388457 | 1.198407 |
| C | 0.118016 | 0.200329 | -1.221988 |
| C | -0.594408 | -1.063643 | -1.668581 |
| C | 0.069004 | -1.320703 | -0.349827 |
| C | 1.331941 | -2.048626 | -0.160307 |
| C | 2.355489 | -1.996237 | -1.096057 |
| H | -0.198425 | -1.558680 | -2.551383 |
| H | 1.440123 | -2.634993 | 0.749303 |
| H | 2.185761 | -1.672221 | -2.120275 |
| H | 3.263606 | -2.564406 | -0.925059 |
| C | -1.022509 | -1.378584 | 0.723454 |
| C | -2.104604 | -1.163659 | -1.441590 |
| N | -2.251402 | -1.042564 | 0.012316 |
| S | -3.392779 | -0.036884 | 0.700034 |
| O | -3.983232 | 0.722935 | -0.371242 |
| O | -2.747464 | 0.618086 | 1.814773 |
| C | -4.647805 | -1.152732 | 1.359514 |
| H | -5.410967 | -0.520386 | 1.818958 |
| H | -4.181102 | -1.797944 | 2.105137 |
| H | -5.066371 | -1.725601 | 0.530965 |
| C | 1.851685 | 1.657346 | 0.969431 |
| O | 1.710344 | 2.591727 | 1.572596 |
| H | -1.041822 | -2.409556 | 1.104837 |
| H | -0.860474 | -0.698525 | 1.562541 |
| H | -2.668082 | -0.376281 | -1.944803 |
| H | -2.450054 | -2.141230 | -1.797408 |
| H | 0.981820 | 0.394027 | -1.878577 |
| C | -0.632588 | 1.428081 | -0.767023 |
| C | -1.445363 | 2.204105 | -1.808281 |
| C | -0.163929 | 2.808427 | -1.248558 |
| H | -1.051874 | 1.400398 | 0.233135 |
| H | -2.405865 | 2.592971 | -1.489803 |
| H | -1.412242 | 1.848936 | -2.834259 |
| H | -0.247317 | 3.637901 | -0.554647 |
| H | 0.695259 | 2.855725 | -1.912652 |

### ***trans*-Int2**

| | | | |
|---|---|---|---|
| Rh | -2.097513 | -0.147391 | -0.330793 |
| C | -3.697956 | -1.096832 | 0.225140 |
| O | -4.587279 | -1.692104 | 0.559265 |
| C | 0.008449 | 1.029629 | -0.830678 |
| C | 0.674169 | 1.499648 | 0.452697 |
| C | 0.731027 | 0.464865 | 1.565079 |
| C | -0.356846 | -0.111626 | 2.091022 |
| C | -1.729383 | 0.285383 | 1.695694 |
| H | 0.135793 | 2.394259 | 0.791441 |
| H | -0.247872 | -0.914803 | 2.816866 |
| H | -1.872748 | 1.368650 | 1.727356 |
| H | -2.488926 | -0.198944 | 2.308789 |
| C | 2.189096 | 0.186347 | 1.899171 |
| C | 2.185427 | 1.862980 | 0.232266 |
| N | 2.933378 | 0.714034 | 0.745936 |
| S | 3.597932 | -0.369842 | -0.357627 |
| O | 3.024158 | -0.109310 | -1.660820 |
| O | 3.492242 | -1.681754 | 0.234550 |
| C | 5.335930 | 0.106666 | -0.402687 |
| H | 5.819787 | -0.562183 | -1.117930 |
| H | 5.746141 | -0.022918 | 0.599139 |
| H | 5.402273 | 1.143733 | -0.734754 |
| C | -2.991697 | 1.745065 | -0.614475 |
| O | -3.494086 | 2.729326 | -0.793109 |
| H | 2.483441 | 0.746414 | 2.796662 |
| H | 2.411200 | -0.870010 | 2.058424 |
| H | 2.434114 | 2.063912 | -0.809457 |
| H | 2.432603 | 2.741329 | 0.836970 |
| H | -0.265178 | 1.845604 | -1.500601 |
| C | -0.067905 | -0.228636 | -1.369178 |
| C | -1.143842 | -1.995148 | -0.314042 |
| C | 0.265367 | -1.582170 | -0.768798 |
| H | -0.451785 | -0.266797 | -2.395223 |
| H | -1.648364 | -2.617923 | -1.063649 |
| H | -1.166354 | -2.511618 | 0.646657 |
| H | 0.710212 | -2.237191 | -1.522526 |
| H | 0.961899 | -1.515985 | 0.061639 |

### ***trans*-Int3**

| | | | |
|---|---|---|---|
| Rh | -2.297489 | -0.180203 | -0.400460 |

| | | | |
|---|---|---|---|
| C | -4.056787 | -0.228142 | 0.398696 |
| O | -5.066918 | -0.277799 | 0.883236 |
| C | -0.093162 | 0.181136 | -1.583341 |
| C | 0.615227 | 1.398438 | -1.019951 |
| C | 0.533348 | 1.584613 | 0.487886 |
| C | -0.613943 | 1.660184 | 1.170989 |
| C | -1.951142 | 1.608733 | 0.523911 |
| H | 0.200192 | 2.277121 | -1.529529 |
| H | -0.589553 | 1.733083 | 2.256224 |
| H | -2.022137 | 2.248021 | -0.374432 |
| H | -2.747769 | 1.876246 | 1.217682 |
| C | 1.948578 | 1.627676 | 1.046481 |
| C | 2.166842 | 1.341595 | -1.285607 |
| N | 2.767648 | 0.992738 | 0.003015 |
| S | 3.280700 | -0.595264 | 0.240934 |
| O | 2.779421 | -1.406056 | -0.848507 |
| O | 2.958847 | -0.938860 | 1.606263 |
| C | 5.072173 | -0.479790 | 0.081211 |
| H | 5.455419 | -1.493915 | 0.215117 |
| H | 5.439913 | 0.186531 | 0.862040 |
| H | 5.308428 | -0.103566 | -0.915215 |
| H | 2.278058 | 2.668484 | 1.163041 |
| H | 2.058468 | 1.114551 | 2.002569 |
| H | 2.443691 | 0.624500 | -2.057950 |
| H | 2.514718 | 2.337452 | -1.576405 |
| H | -0.329529 | 0.273789 | -2.645002 |
| C | -0.305434 | -1.054434 | -1.043418 |
| C | -1.565361 | -1.576974 | 0.878492 |
| C | -0.117970 | -1.562068 | 0.382428 |
| H | -0.691839 | -1.804645 | -1.742428 |
| H | -2.101942 | -2.503451 | 0.632696 |
| H | -1.712294 | -1.318871 | 1.928233 |
| H | 0.351331 | -2.551615 | 0.369479 |
| H | 0.502094 | -0.903609 | 0.983947 |

***trans*-Int4**

| | | | |
|---|---|---|---|
| Rh | -1.872683 | -0.156564 | -0.380574 |
| C | -3.323149 | -1.371081 | -0.692574 |
| O | -4.186228 | -2.062110 | -0.885797 |
| C | -2.119745 | 2.476437 | 0.223586 |
| C | -3.156073 | 1.445498 | -0.259703 |
| C | -0.905652 | 1.959385 | -0.533001 |
| C | 0.167846 | 1.226733 | -0.116219 |
| C | 0.633404 | 0.859008 | 1.278655 |
| C | 0.519269 | -0.666020 | 1.363971 |
| C | -0.645054 | -1.342698 | 1.506966 |
| C | -1.933189 | -0.624754 | 1.598885 |
| H | -1.980014 | 2.441398 | 1.306232 |
| H | -2.360526 | 3.506175 | -0.059687 |
| H | -3.977295 | 1.248850 | 0.430891 |
| H | -3.546003 | 1.693023 | -1.251348 |
| H | -0.945228 | 2.139217 | -1.610889 |
| H | 0.836546 | 0.891363 | -0.909365 |
| H | 0.058288 | 1.370709 | 2.054764 |
| H | -0.635945 | -2.430586 | 1.526962 |
| H | -1.912645 | 0.312629 | 2.157321 |
| H | -2.777953 | -1.240219 | 1.902456 |
| C | 1.914742 | -1.262964 | 1.273953 |
| C | 2.168341 | 1.080074 | 1.443772 |
| N | 2.790917 | -0.141372 | 0.911776 |
| H | 2.206350 | -1.643720 | 2.262023 |
| H | 1.975908 | -2.077998 | 0.549940 |
| H | 2.410868 | 1.154057 | 2.508566 |
| H | 2.546115 | 1.961716 | 0.926487 |
| S | 3.335072 | -0.099617 | -0.690390 |
| O | 3.551840 | 1.288602 | -1.008875 |
| O | 2.435607 | -0.892800 | -1.505400 |
| C | 4.918495 | -0.953270 | -0.594237 |
| H | 5.311415 | -0.974576 | -1.613364 |
| H | 5.569193 | -0.384563 | 0.070410 |
| H | 4.748903 | -1.966219 | -0.225499 |

***trans*-TS1**

| | | | |
|---|---|---|---|
| Rh | -1.882034 | -0.214659 | -0.102064 |
| C | -3.285107 | -1.197982 | -1.088640 |
| O | -4.051359 | -1.789004 | -1.656619 |
| C | -0.233241 | 0.816090 | 0.988213 |
| C | 0.565106 | -0.153603 | 1.902760 |
| C | 0.019263 | -1.186924 | 0.994154 |
| C | -1.236140 | -1.875884 | 1.031677 |
| C | -2.352150 | -1.254627 | 1.675867 |
| H | 0.215026 | -0.165321 | 2.933019 |
| H | -1.319578 | -2.834535 | 0.528535 |
| H | -2.204298 | -0.564056 | 2.502586 |
| H | -3.298158 | -1.786934 | 1.699389 |
| C | 1.121023 | -1.626390 | 0.040886 |
| C | 2.093596 | -0.216114 | 1.752622 |
| N | 2.294179 | -0.871103 | 0.452421 |
| S | 3.333686 | -0.252166 | -0.700802 |
| O | 3.864730 | 0.977294 | -0.173504 |
| O | 2.622023 | -0.286450 | -1.958610 |
| C | 4.675807 | -1.454563 | -0.788289 |

| | | | |
|---|---|---|---|
| H | 5.366458 | -1.085829 | -1.550363 |
| H | 4.262292 | -2.421263 | -1.079308 |
| H | 5.160747 | -1.496150 | 0.187782 |
| C | -2.673094 | 1.595443 | -0.548946 |
| O | -3.252172 | 2.541055 | -0.716807 |
| H | 1.245914 | -2.710979 | 0.189640 |
| H | 0.892189 | -1.452919 | -1.016543 |
| H | 2.567142 | 0.765427 | 1.757967 |
| H | 2.510539 | -0.824710 | 2.563004 |
| H | -0.933078 | 1.356032 | 1.632821 |
| C | 0.508520 | 1.704754 | 0.020194 |
| C | 1.348770 | 2.869204 | 0.556718 |
| C | 0.037380 | 3.155905 | -0.164384 |
| H | 0.893660 | 1.230637 | -0.877875 |
| H | 2.288886 | 3.075629 | 0.058304 |
| H | 1.353038 | 3.025483 | 1.631890 |
| H | 0.076254 | 3.577744 | -1.162829 |
| H | -0.787894 | 3.508786 | 0.448066 |

***trans*-TS2'**

| | | | |
|---|---|---|---|
| Rh | -1.447591 | -0.182768 | -0.043267 |
| C | -2.710728 | -1.487897 | -1.121483 |
| O | -3.419798 | -2.239610 | -1.554105 |
| C | -0.690914 | 1.349023 | 1.120595 |
| C | 0.281242 | 0.595727 | 2.027347 |
| C | -0.045913 | -0.840768 | 1.572837 |
| C | -1.298365 | -1.476360 | 1.693254 |
| C | -2.498211 | -0.684344 | 1.759195 |
| H | 0.037577 | 0.757885 | 3.081184 |
| H | -1.349939 | -2.545041 | 1.493438 |
| H | -2.545383 | 0.169856 | 2.427199 |
| H | -3.436644 | -1.228520 | 1.694987 |
| C | 1.268030 | -1.552397 | 1.287063 |
| C | 1.815569 | 0.716270 | 1.815561 |
| N | 2.217402 | -0.466701 | 1.036129 |
| S | 2.842829 | -0.271782 | -0.498094 |
| O | 2.485026 | 1.050584 | -0.973534 |
| O | 2.442316 | -1.435744 | -1.253647 |
| C | 4.628356 | -0.311720 | -0.264572 |
| H | 4.907717 | 0.498319 | 0.411097 |
| H | 5.067141 | -0.160989 | -1.253582 |
| H | 4.895598 | -1.288245 | 0.140599 |
| C | -0.180307 | -0.098071 | -1.721498 |
| O | 0.221065 | -0.051607 | -2.765614 |
| H | 1.564142 | -2.091947 | 2.199132 |
| H | 1.244024 | -2.253197 | 0.452686 |
| H | 2.098879 | 1.634766 | 1.301012 |
| H | 2.317345 | 0.688364 | 2.787473 |
| H | -1.545504 | 1.717104 | 1.689605 |
| C | -0.418678 | 2.254242 | -0.010814 |
| C | -1.176723 | 3.540663 | -0.170681 |
| C | -1.761185 | 2.416954 | -0.993437 |
| H | 0.514743 | 2.147304 | -0.556809 |
| H | -0.664663 | 4.317573 | -0.729897 |
| H | -1.758896 | 3.900621 | 0.671609 |
| H | -1.581221 | 2.413016 | -2.061437 |
| H | -2.732300 | 2.046203 | -0.669696 |

***trans*-TS2**

| | | | |
|---|---|---|---|
| Rh | 1.532196 | -0.487770 | -0.134341 |
| C | 3.056934 | 0.686488 | -0.714809 |
| O | 3.992736 | 1.261910 | -0.949490 |
| C | 0.582717 | 0.851029 | 1.559768 |
| C | -0.589462 | 1.771140 | 1.339409 |
| C | 0.075346 | 1.617325 | -0.004008 |
| C | 0.925486 | 2.688726 | -0.596693 |
| C | 1.355424 | 3.778569 | 0.039534 |
| H | -0.487537 | 2.726796 | 1.846510 |
| H | 1.173115 | 2.552950 | -1.648215 |
| H | 1.136355 | 3.980268 | 1.084151 |
| H | 1.953308 | 4.520248 | -0.479940 |
| C | -0.959459 | 0.945145 | -0.922639 |
| C | -2.024177 | 1.262265 | 1.209280 |
| N | -1.949704 | 0.436510 | 0.006323 |
| S | -3.202003 | -0.532698 | -0.479772 |
| O | -3.727360 | -1.103316 | 0.731722 |
| O | -2.654914 | -1.341391 | -1.540522 |
| C | -4.466612 | 0.546895 | -1.189149 |
| H | -5.282677 | -0.108596 | -1.502987 |
| H | -4.047186 | 1.068743 | -2.051179 |
| H | -4.813403 | 1.236384 | -0.417198 |
| C | 2.611000 | -2.043826 | -0.413767 |
| O | 3.234718 | -2.970592 | -0.545825 |
| H | -1.344099 | 1.754924 | -1.567282 |
| H | -0.594893 | 0.148008 | -1.580128 |
| H | -2.380383 | 0.678120 | 2.058857 |
| H | -2.683905 | 2.132797 | 1.080224 |
| H | 1.461467 | 1.415005 | 1.860363 |
| C | 0.682290 | -0.577629 | 1.859201 |
| C | 0.069277 | -1.975517 | 0.428362 |
| C | -0.422365 | -1.592205 | 1.826514 |
| H | 1.554145 | -0.831916 | 2.458659 |

| | | | |
|---|---|---|---|
| H | 0.521647 | -2.963144 | 0.401049 |
| H | -0.645199 | -1.820402 | -0.382961 |
| H | -0.288774 | -2.377574 | 2.569326 |
| H | -1.440640 | -1.218656 | 1.855104 |

***trans*-TS3**

| | | | |
|---|---|---|---|
| Rh | -2.610043 | 0.361696 | -0.198799 |
| C | -3.455507 | -1.280017 | -0.436212 |
| O | -3.930071 | -2.286029 | -0.599161 |
| C | 0.667072 | 1.925743 | 0.987212 |
| C | 1.035809 | 0.685061 | 1.786340 |
| C | 0.543937 | -0.708766 | 1.417236 |
| C | -0.723131 | -1.141900 | 1.422279 |
| C | -1.892654 | -0.256467 | 1.613624 |
| H | 0.719757 | 0.901328 | 2.815771 |
| H | -0.924202 | -2.190352 | 1.206476 |
| H | -1.635094 | 0.718855 | 2.049341 |
| H | -2.717711 | -0.720178 | 2.162598 |
| C | 1.761969 | -1.580384 | 1.122475 |
| C | 2.596922 | 0.494961 | 1.776849 |
| N | 2.846461 | -0.623438 | 0.858209 |
| S | 3.093348 | -0.217097 | -0.764481 |
| O | 3.604139 | 1.128440 | -0.795340 |
| O | 1.905137 | -0.555671 | -1.531510 |
| C | 4.402138 | -1.362563 | -1.238555 |
| H | 4.604872 | -1.175035 | -2.295354 |
| H | 4.049520 | -2.384037 | -1.087601 |
| H | 5.275256 | -1.145018 | -0.623165 |
| H | 2.038006 | -2.170176 | 2.005683 |
| H | 1.602669 | -2.261269 | 0.284724 |
| H | 3.143061 | 1.384477 | 1.467536 |
| H | 2.942922 | 0.186646 | 2.767953 |
| H | 1.099227 | 2.794567 | 1.485444 |
| C | 0.011762 | 2.264200 | -0.130858 |
| C | -1.055646 | 0.117074 | -1.422523 |
| C | -0.751838 | 1.604728 | -1.269342 |
| H | 0.034150 | 3.337510 | -0.319625 |
| H | -1.415658 | -0.110401 | -2.432136 |
| H | -0.279688 | -0.569825 | -1.108171 |
| H | -1.715724 | 2.178105 | -1.365238 |
| H | -0.266841 | 1.922155 | -2.207108 |

**TS2-six**

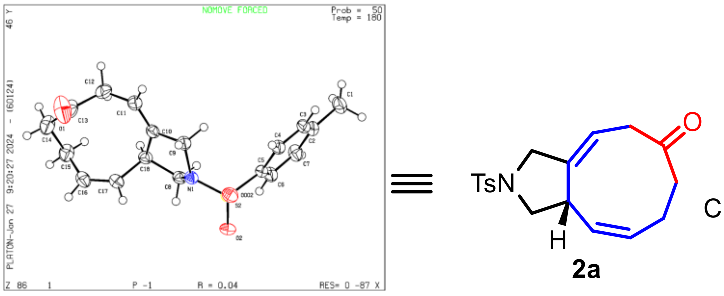
| | | | |
|---|---|---|---|
| Rh | -2.113622 | -0.309180 | 0.064088 |
| C | -4.134294 | -0.303762 | 0.506604 |
| O | -5.229015 | -0.288729 | 0.736890 |
| C | -1.105292 | 3.149520 | 0.175626 |
| C | -2.050540 | 1.997541 | 0.589185 |
| C | 0.237972 | 2.783481 | -0.420555 |
| C | 1.005907 | 1.722448 | -0.175195 |
| C | 0.771710 | 0.629104 | 0.851890 |
| C | 0.051193 | -0.615009 | 0.293038 |
| C | -0.620538 | -1.516834 | 1.217486 |
| C | -1.487140 | -1.078758 | 2.208015 |
| H | -0.958476 | 3.783779 | 1.060876 |
| H | -1.636421 | 3.765522 | -0.555414 |
| H | -1.760126 | 1.601020 | 1.561909 |
| H | -3.078404 | 2.355484 | 0.671760 |
| H | 0.611749 | 3.504062 | -1.144588 |
| H | 1.944633 | 1.658356 | -0.718282 |
| H | 0.228575 | 1.030785 | 1.710641 |
| H | -0.648711 | -2.574837 | 0.956781 |
| H | -1.371823 | -0.112659 | 2.688423 |
| H | -2.103221 | -1.800807 | 2.735212 |
| C | -2.175562 | 1.166312 | -1.123900 |
| O | -2.307535 | 1.813156 | -2.057257 |
| C | 2.245597 | -1.714956 | -0.214039 |
| C | 2.154167 | 0.136276 | 1.405171 |
| N | 2.907320 | -0.572149 | 0.388999 |
| H | 1.975247 | -0.529441 | 2.261255 |
| H | 2.725598 | 1.003084 | 1.741869 |
| S | 4.318867 | 0.034843 | -0.248394 |
| O | 4.324072 | 1.448601 | 0.031866 |
| O | 4.410048 | -0.471653 | -1.593723 |
| C | 5.643799 | -0.718240 | 0.723478 |
| H | 6.582663 | -0.338337 | 0.314265 |
| H | 5.527109 | -0.411867 | 1.764018 |
| H | 5.587175 | -1.802068 | 0.611335 |
| C | -2.249711 | -1.836487 | -1.177119 |
| O | -2.359655 | -2.674186 | -1.914189 |
| C | 0.872253 | -1.295806 | -0.799999 |
| H | 0.370748 | -2.190782 | -1.181114 |
| H | 1.036896 | -0.612719 | -1.638389 |
| H | 2.872516 | -2.120693 | -1.008694 |
| H | 2.093685 | -2.493707 | 0.548647 |

**TS4-six**

| | | | |
|---|---|---|---|
| Rh | 2.165375 | 0.037374 | 0.107545 |
| C | 4.123202 | -0.305000 | 0.120944 |
| O | 5.221029 | -0.528075 | 0.186576 |
| C | 1.428472 | -2.082282 | -0.780538 |

| | | | |
|---|---|---|---|
| C | 1.871211 | -1.278415 | -1.808729 |
| C | -0.011315 | -2.412376 | -0.595421 |
| C | -0.948119 | -1.839088 | 0.155529 |
| C | -0.761875 | -0.694634 | 1.139642 |
| C | 0.009342 | 0.516496 | 0.607998 |
| C | 0.951165 | 1.196148 | 1.438688 |
| C | 1.805200 | 0.428195 | 2.305556 |
| H | 2.101087 | -0.883076 | 1.441992 |
| H | 2.138599 | -2.777528 | -0.332458 |
| H | 2.881381 | -1.372489 | -2.195051 |
| H | 1.147190 | -0.779452 | -2.447229 |
| H | -0.303648 | -3.283826 | -1.183658 |
| H | -1.946162 | -2.268980 | 0.119229 |
| H | -0.257171 | -1.108759 | 2.019284 |
| H | 1.160508 | 2.254086 | 1.302928 |
| H | 1.376358 | -0.338645 | 2.947831 |
| H | 2.656926 | 0.932718 | 2.753232 |
| C | 2.366240 | 1.542293 | -1.210594 |
| O | 2.478453 | 2.385548 | -1.943434 |
| C | -2.141957 | -0.177495 | 1.669159 |
| N | -2.884002 | 0.609724 | 0.694967 |
| H | -1.961445 | 0.467252 | 2.538046 |
| H | -2.748908 | -1.023317 | 1.993095 |
| S | -3.935955 | -0.150645 | -0.367458 |
| O | -4.162961 | -1.475906 | 0.156022 |
| O | -3.447271 | 0.037524 | -1.714435 |
| C | -5.455716 | 0.806041 | -0.181924 |
| H | -6.177179 | 0.365402 | -0.873658 |
| H | -5.791551 | 0.711394 | 0.850794 |
| H | -5.256735 | 1.844935 | -0.449495 |
| C | -2.140439 | 1.757178 | 0.185678 |
| C | -0.778075 | 1.326671 | -0.414537 |
| H | -0.983347 | 0.719718 | -1.302382 |
| H | -0.224632 | 2.220595 | -0.720047 |
| H | -2.725889 | 2.275508 | -0.575964 |
| H | -1.981980 | 2.449767 | 1.022020 |

# VII. NMR Spectra and Crystal Structures of New Compounds

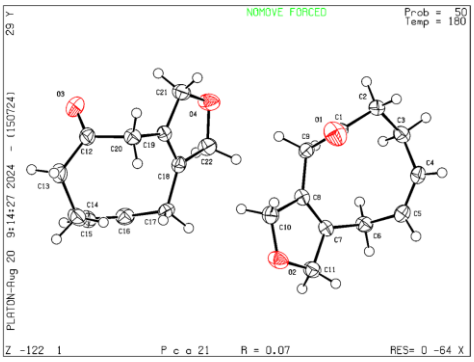


**2a**

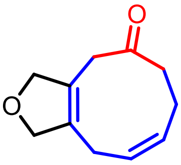
XRD of **2a**
CCDC:2380478

**Ellipsoids are drawn at 50% probability**

| | |
|---|---|
| **Crystal data** | |
| **Chemical formula** | $C_{18}H_{21}NO_3S$ |
| $M_r$ | 331.42 |
| **Crystal system, space group** | Triclinic, $P\bar{1}$ |
| **Temperature (K)** | 180 |
| ***a*, *b*, *c* (Å)** | 5.2763 (2), 11.9759 (3), 13.5796 (3) |
| **α, β, γ (°)** | 103.072 (2), 96.993 (2), 98.585 (2) |
| ***V* (Å3)** | 815.63 (4) |
| ***Z*** | 2 |
| **Radiation type** | Cu *K*α |
| **μ (mm−1)** | 1.89 |
| **Crystal size (mm)** | 0.4 × 0.1 × 0.1 |
| **Data collection** | |
| **Diffractometer** | XtaLAB Synergy R, DW system, HyPix |
| $T_{min}$, $T_{max}$ | 0.752, 1.000 |
| **No. of measured, independent and observed [*I* > 2σ(*I*)] reflections** | 6777, 3083, 2893 |
| $R_{int}$ | 0.021 |
| **(sin θ/λ)$_{max}$ (Å−1)** | 0.618 |
| **Refinement** | |
| ***R*[*F*2 > 2σ(*F*2)], *wR*(*F*2), *S*** | 0.037, 0.100, 1.05 |
| **No. of reflections** | 3083 |
| **No. of parameters** | 209 |
| **H-atom treatment** | H-atom parameters constrained |
| **Δρ$_{max}$, Δρ$_{min}$ (e Å−3)** | 0.31, −0.39 |



≡

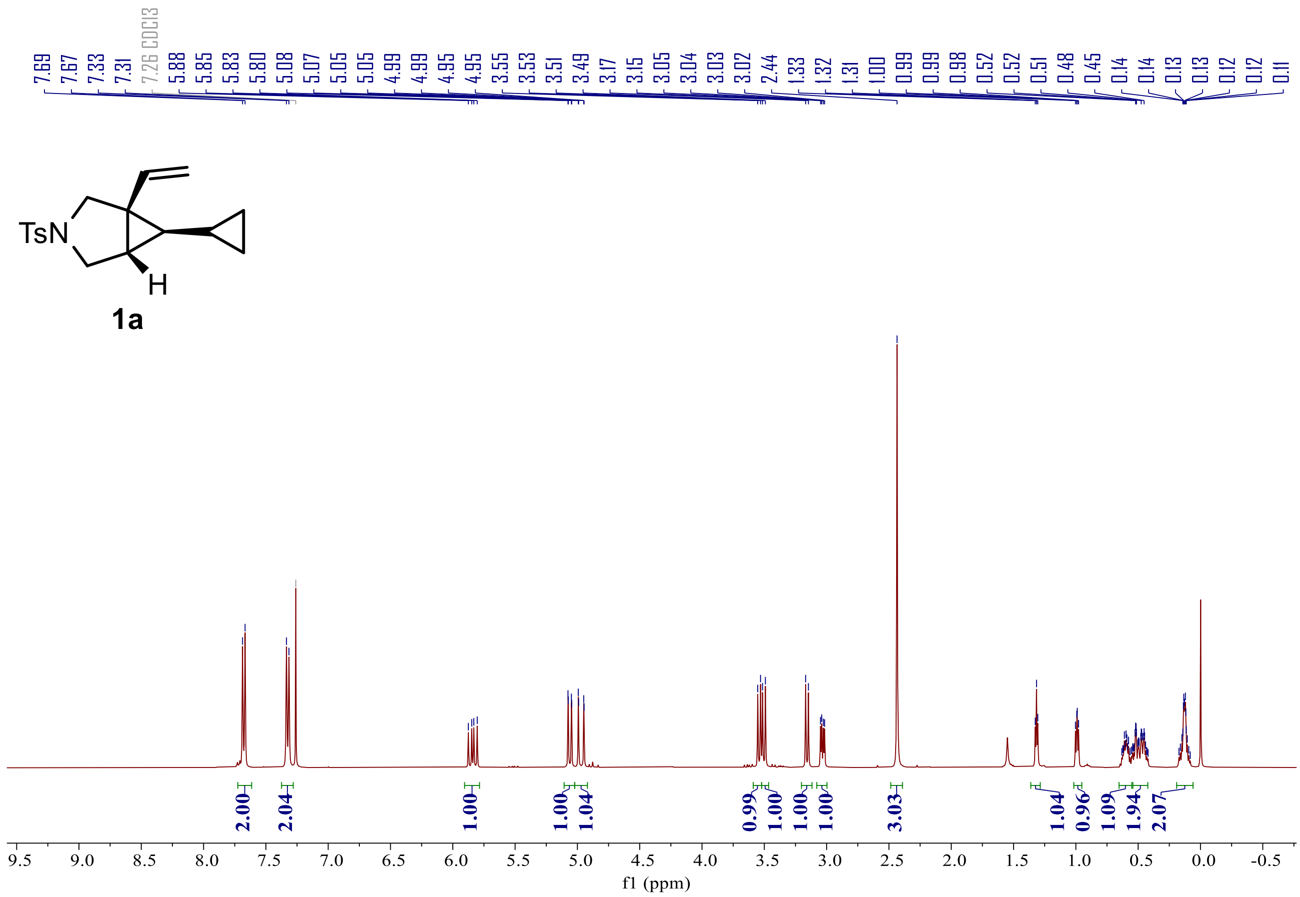


**5c**
CCDC:2380477

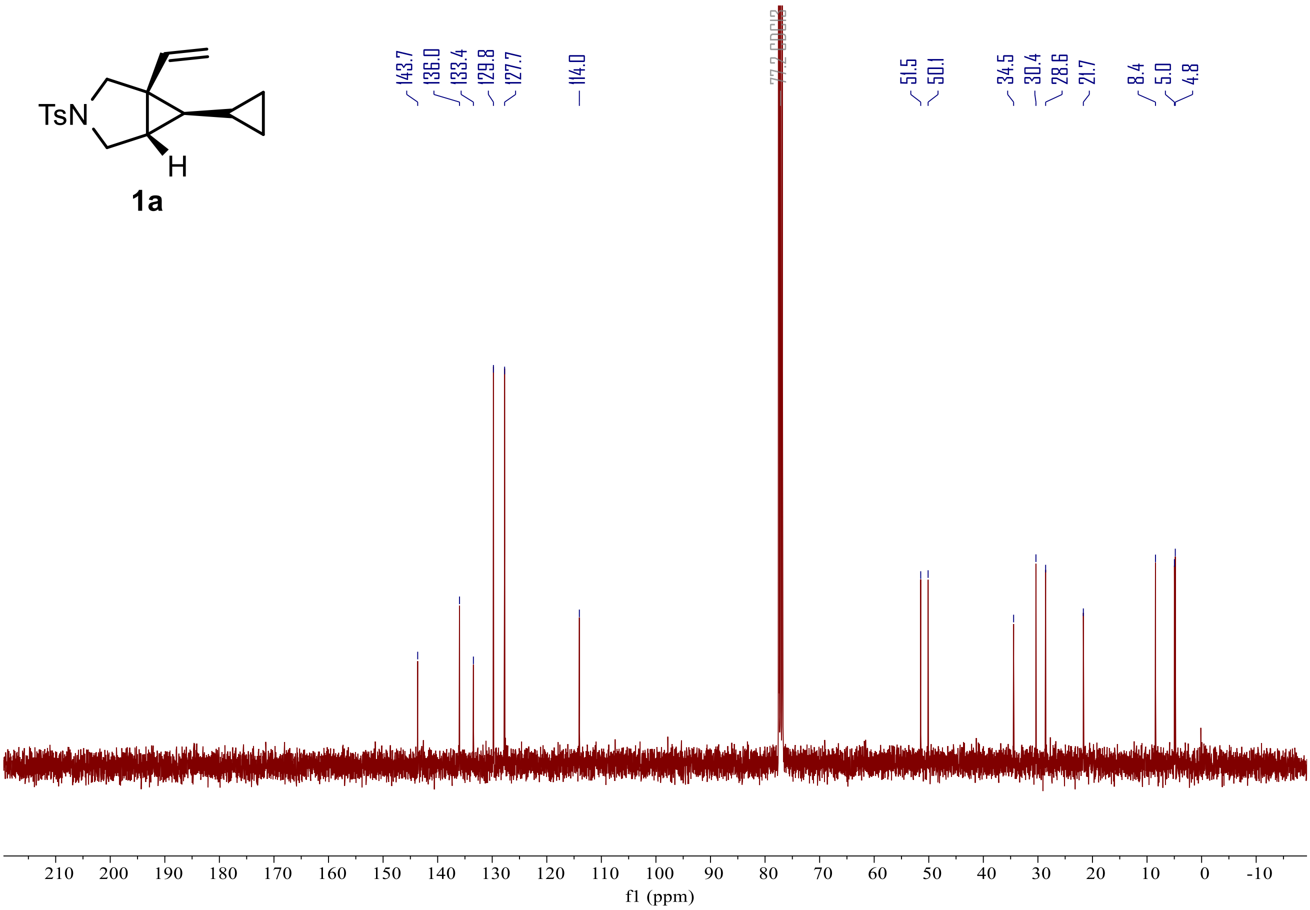
Ellipsoids are drawn at 50% probability

| **Crystal data** | |
|---|---|
| **Chemical formula** | $C_{11}H_{14}O_2$ |
| $M_r$ | 178.22 |
| **Crystal system, space group** | Orthorhombic, $Pca2_1$ |
| **Temperature (K)** | 180 |
| ***a*, *b*, *c* (Å)** | 12.8948 (5), 5.9984 (2), 24.2348 (11) |
| $V$ **(Å$^3$)** | 1874.52 (13) |
| $Z$ | 8 |
| **Radiation type** | Mo *K*α |
| **μ (mm$^{-1}$)** | 0.09 |
| **Crystal size (mm)** | 0.2 × 0.2 × 0.02 |
| **Data collection** | |
| **Diffractometer** | XtaLAB Synergy R, DW system, HyPix |
| $T_{min}$, $T_{max}$ | 0.747, 1.000 |
| **No. of measured, independent and observed [$I > 2\sigma(I)$] reflections** | 12244, 4391, 3484 |
| $R_{int}$ | 0.026 |
| **(sin θ/λ)$_{max}$ (Å$^{-1}$)** | 0.717 |
| **Refinement** | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.071, 0.195, 1.02 |
| **No. of reflections** | 4391 |
| **No. of parameters** | 235 |
| **No. of restraints** | 1 |
| **H-atom treatment** | H-atom parameters constrained |
| **Δρ$_{max}$, Δρ$_{min}$ (e Å$^{-3}$)** | 0.74, −0.22 |

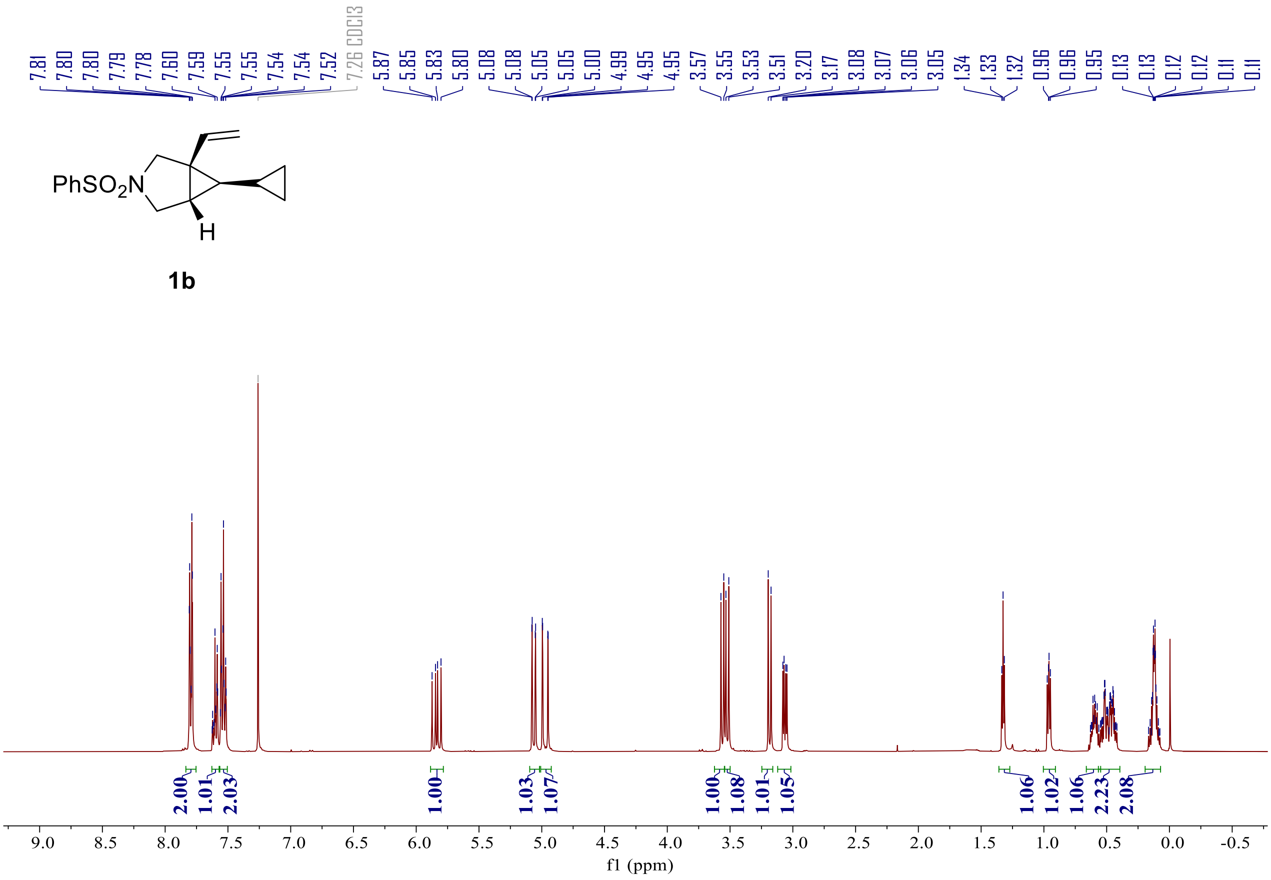
## $^1$H NMR (400 MHz, CDCl$_3$):



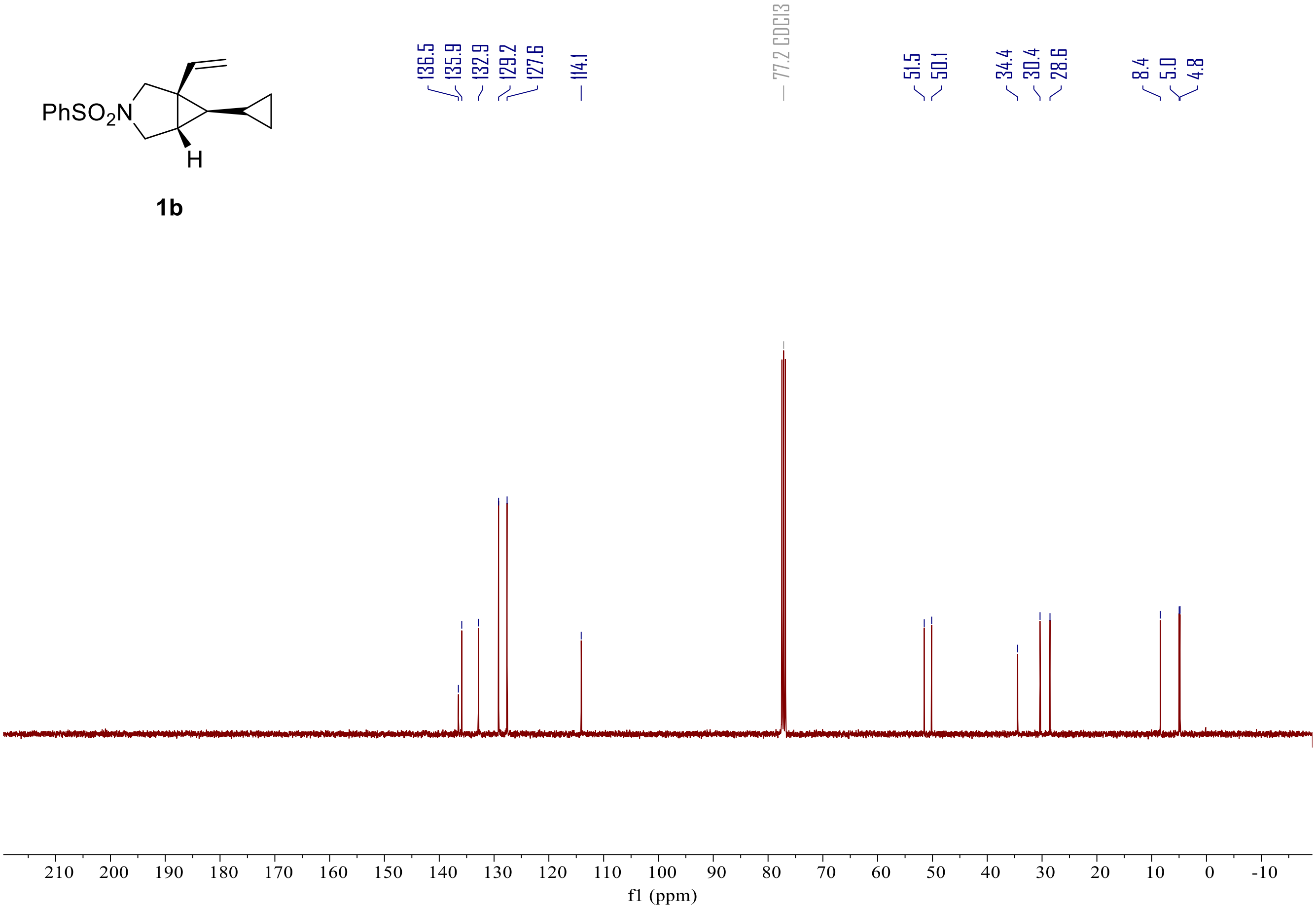
## $^{13}$C NMR (101 MHz, CDCl$_3$):



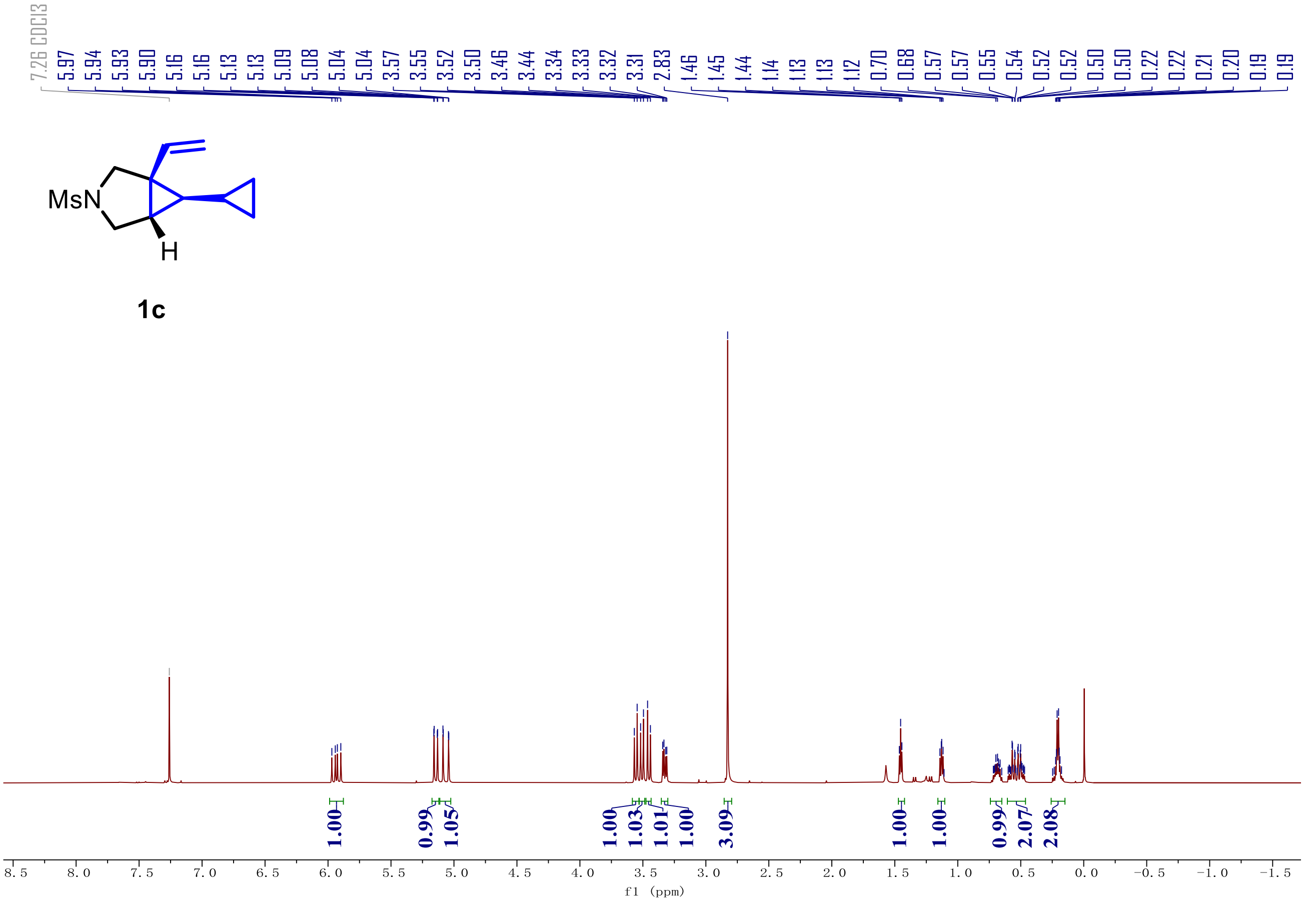
**$^1$H NMR (400 MHz, CDCl$_3$):**



**$^{13}$C NMR (101 MHz, CDCl$_3$):**

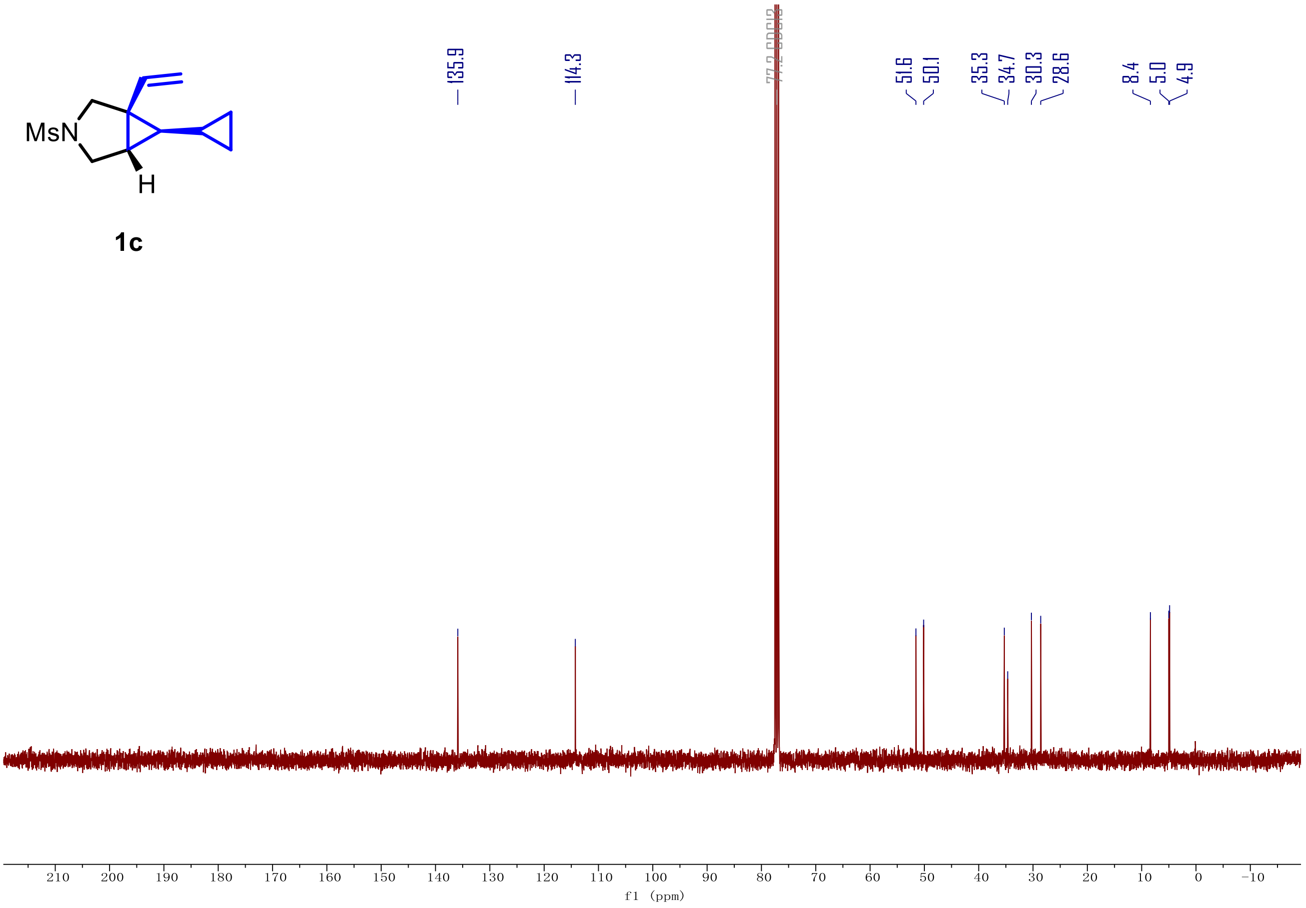


$^1$H NMR (400 MHz, CDCl$_3$):



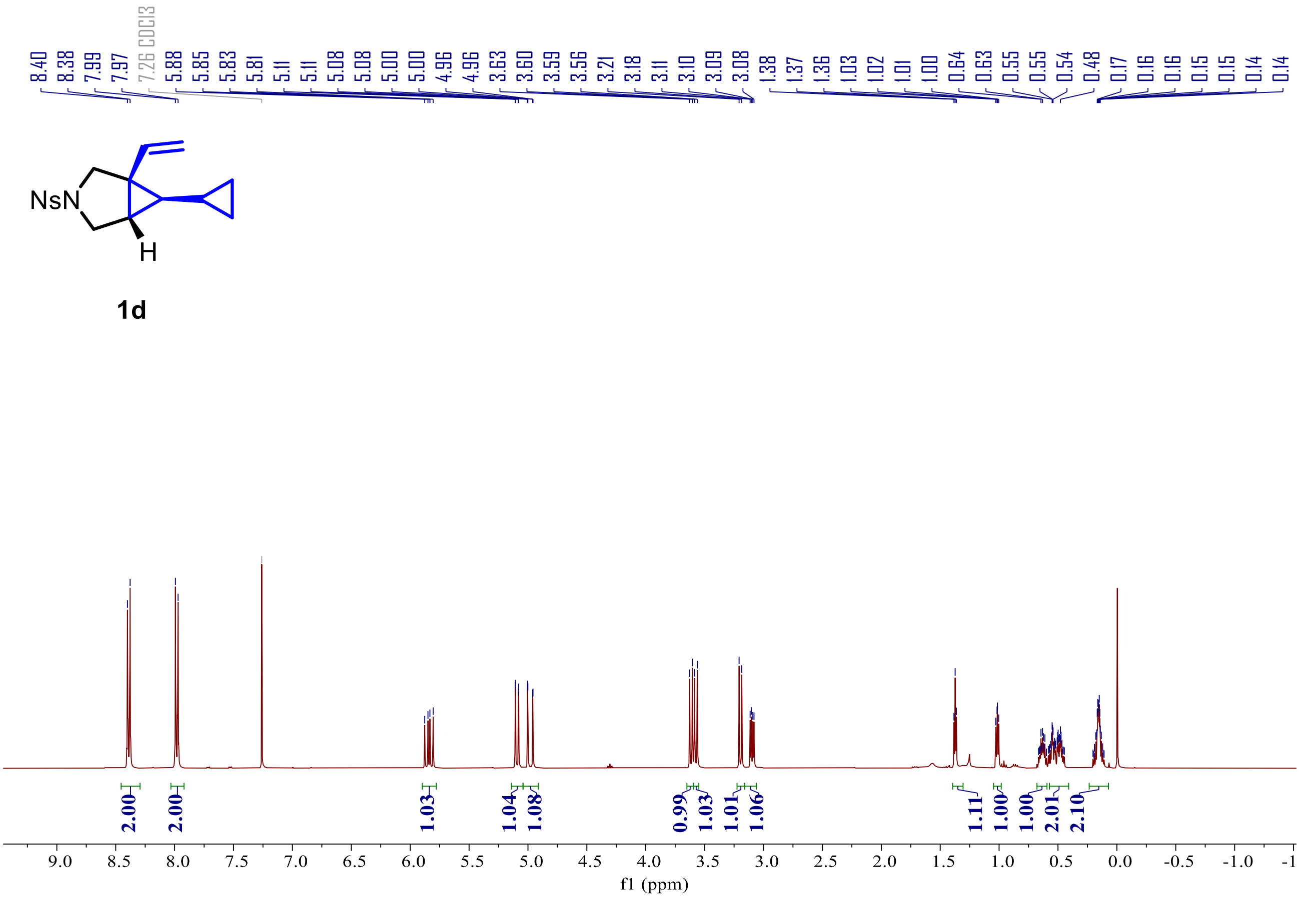
**1c**

$^{13}$C NMR (101 MHz, CDCl$_3$):



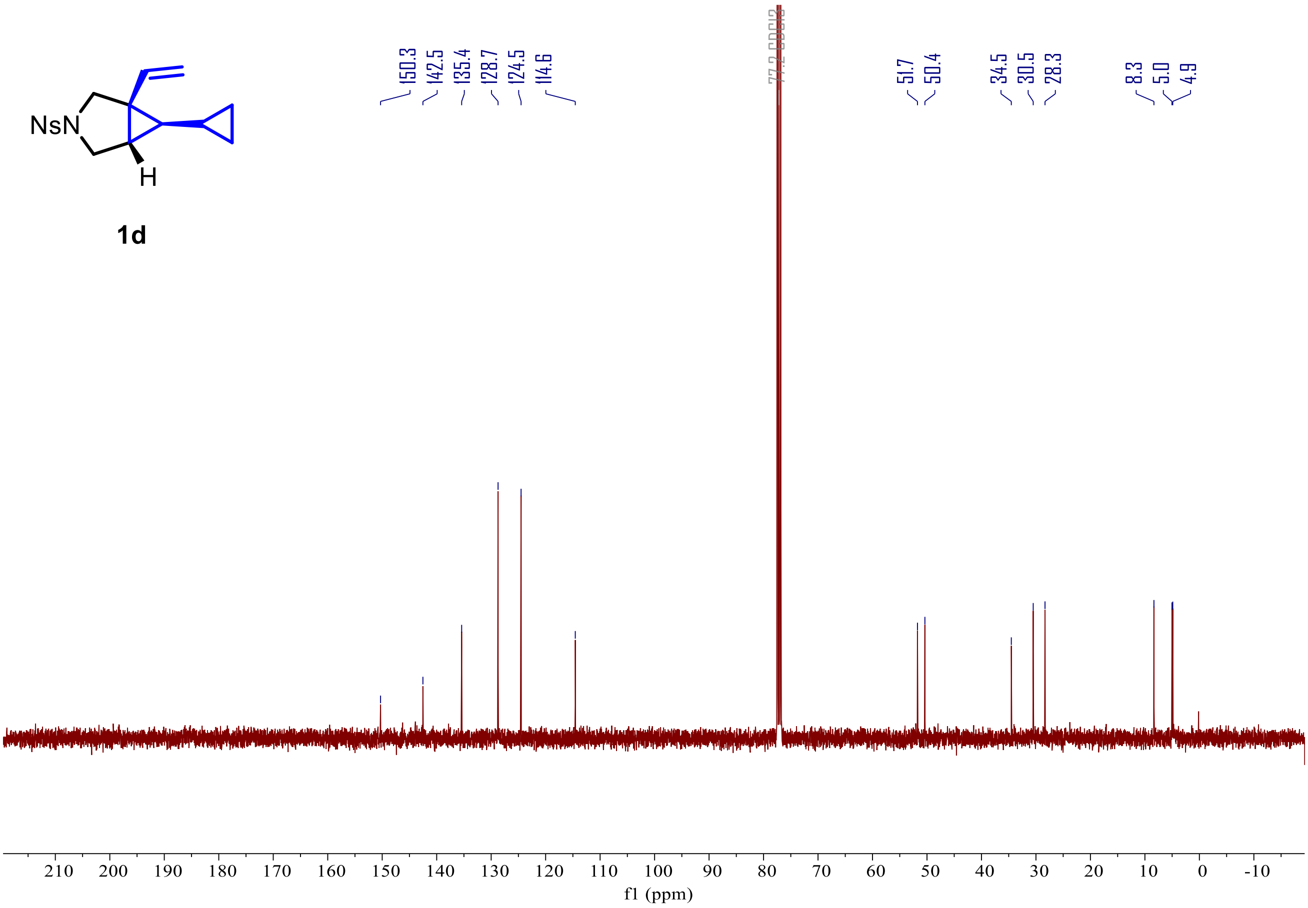
**1c**

## $^1$H NMR (400 MHz, $CDCl_3$):



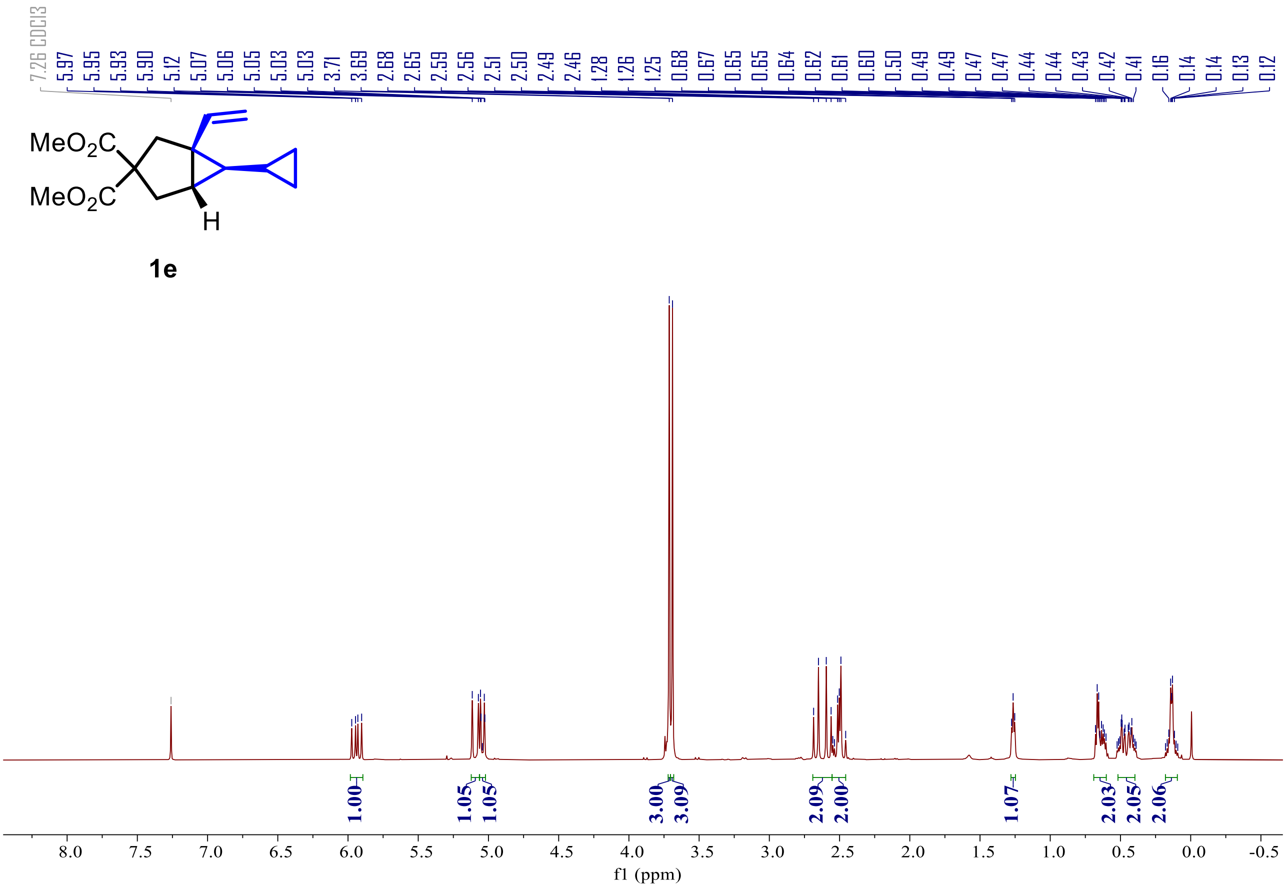
**1d**

## $^{13}$C NMR (101 MHz, $CDCl_3$):

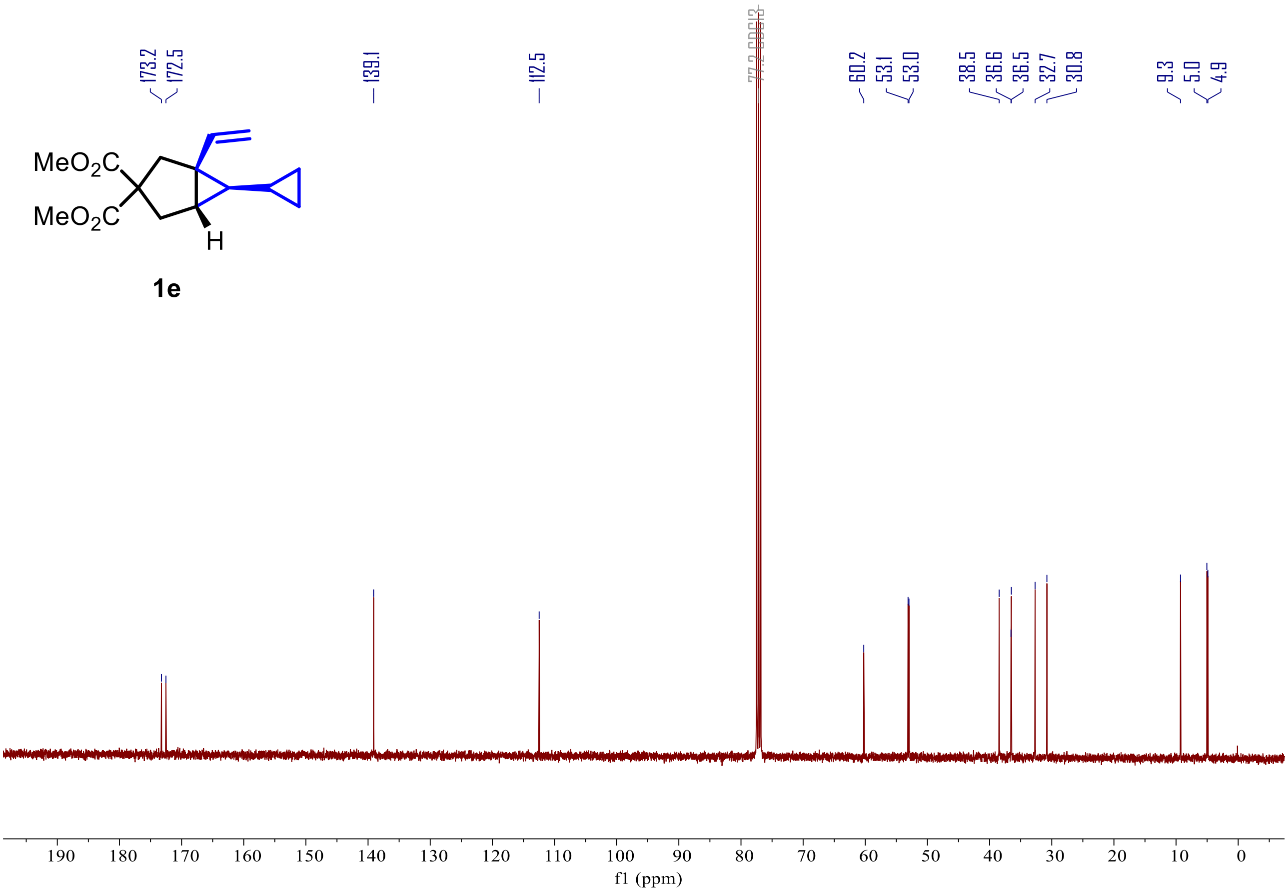


**1d**

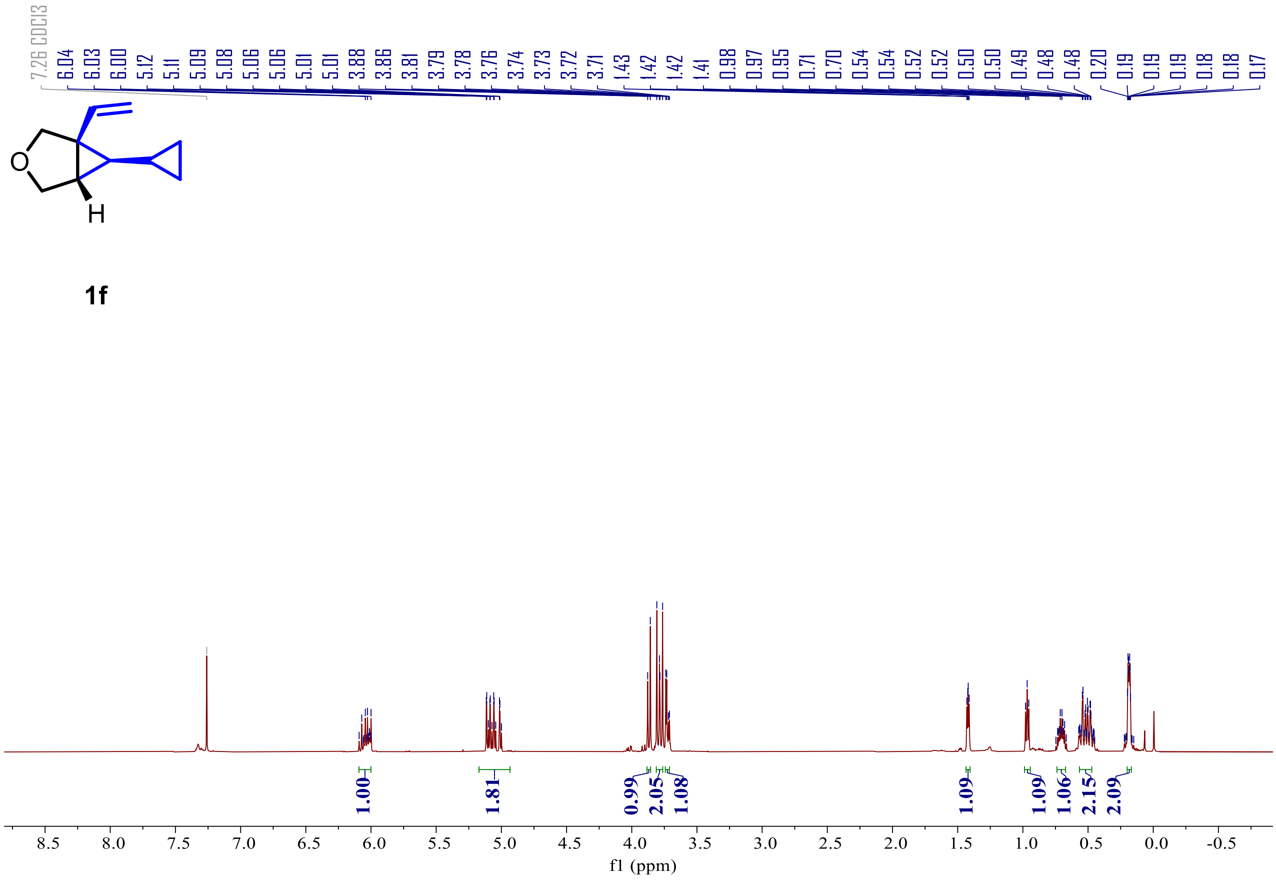
## $^1$H NMR (400 MHz, CDCl$_3$):



## $^{13}$C NMR (101 MHz, CDCl$_3$):

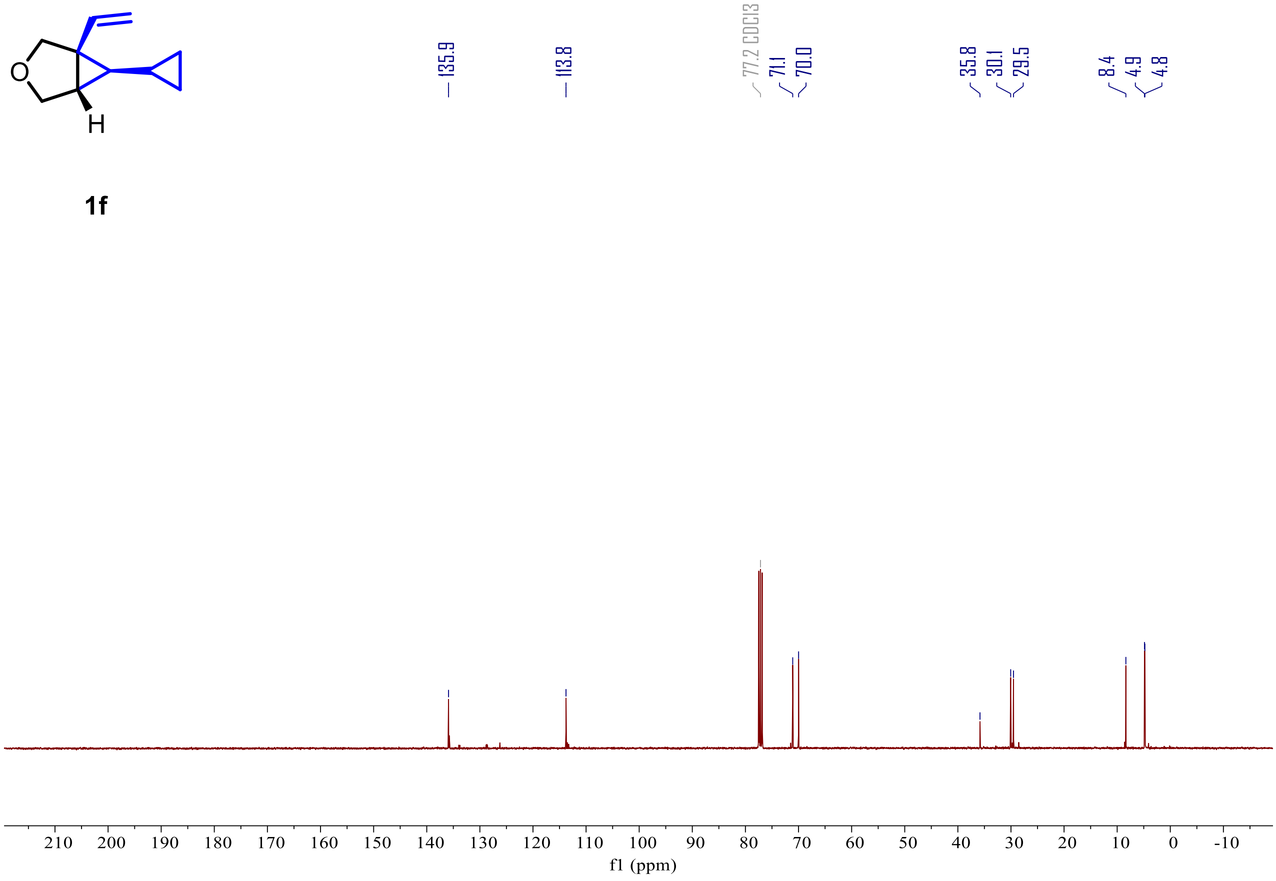


## $^1H$ NMR (400 MHz, $CDCl_3$):



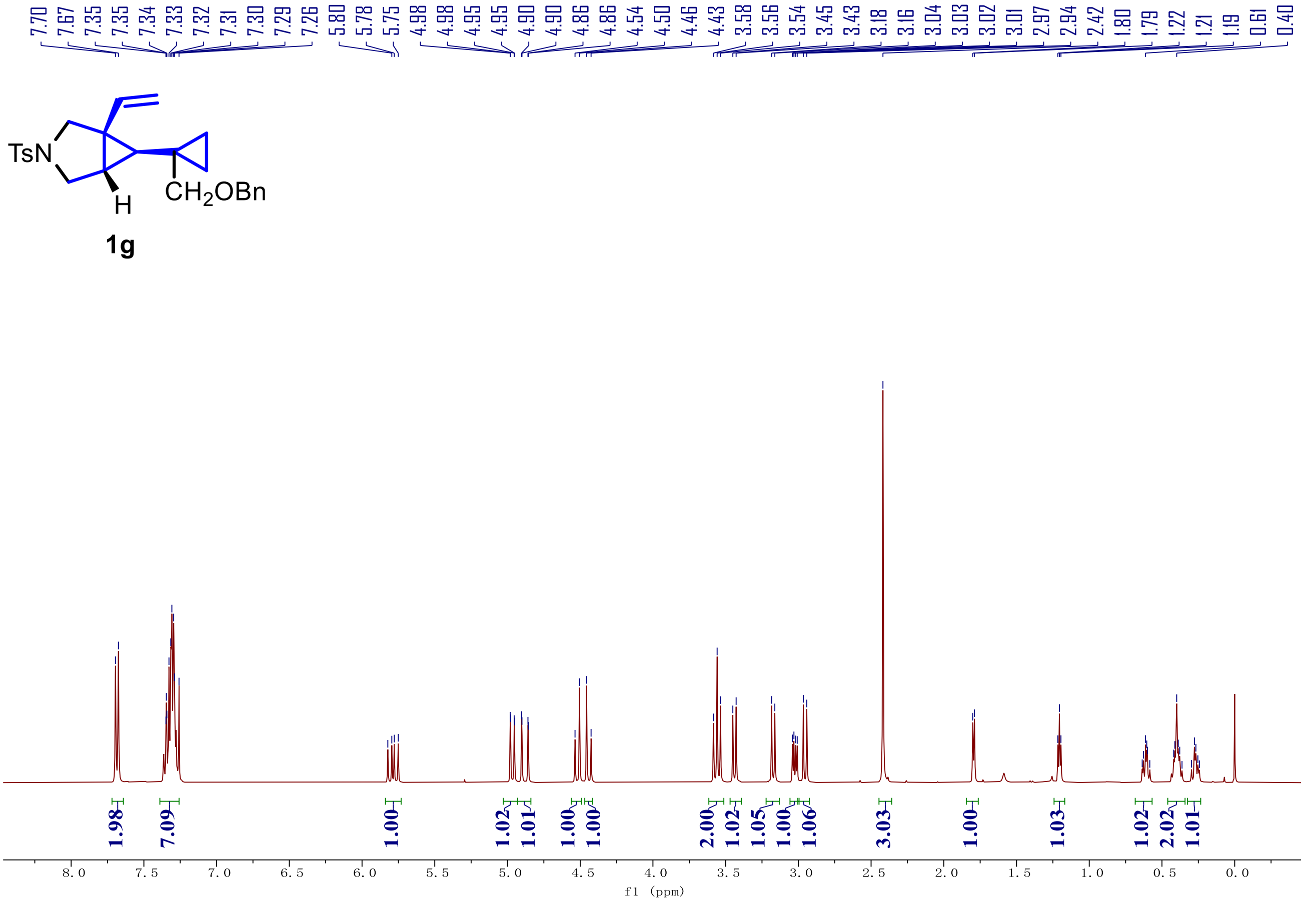
**1f**

## $^{13}C$ NMR (101 MHz, $CDCl_3$):

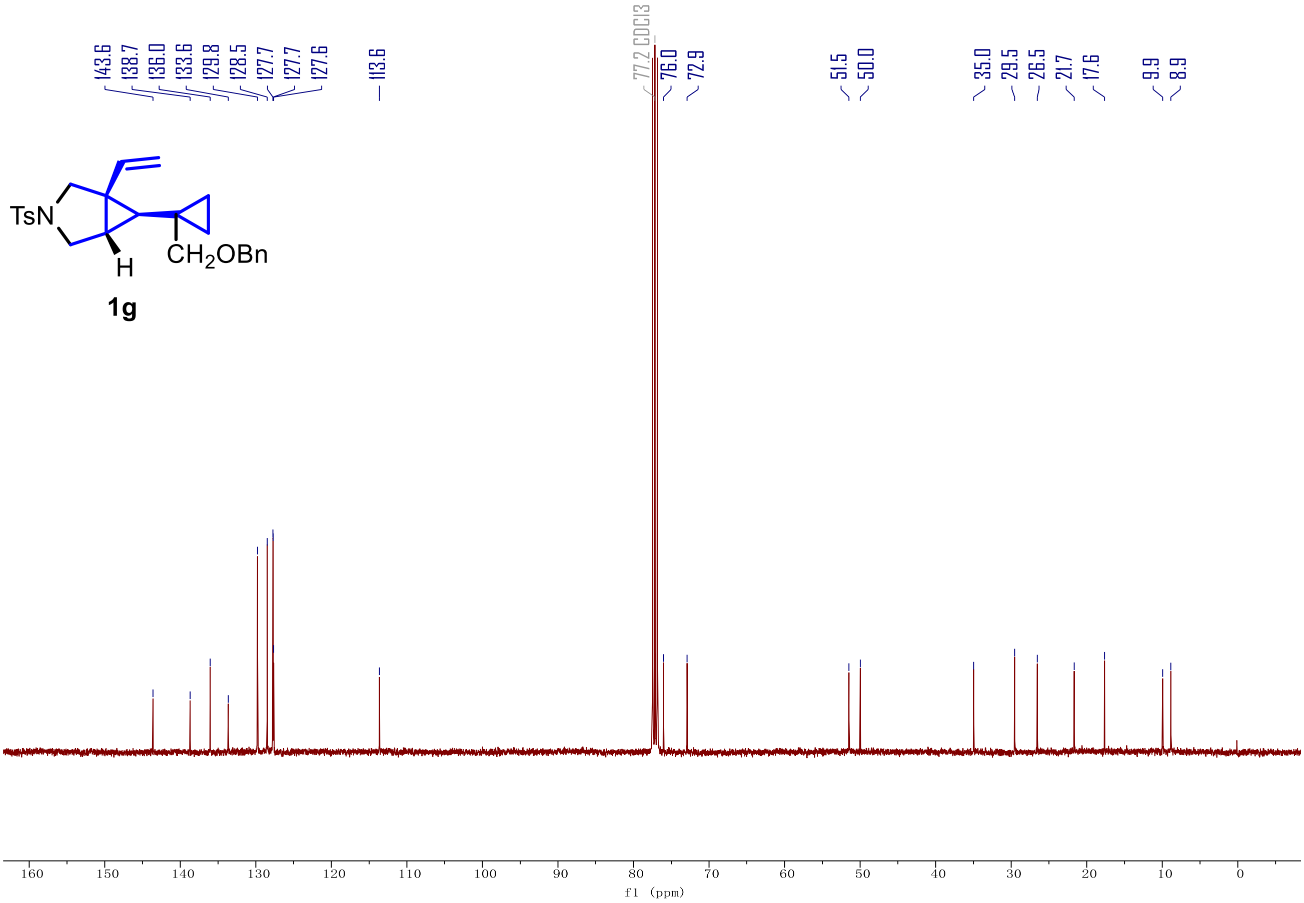


**1f**

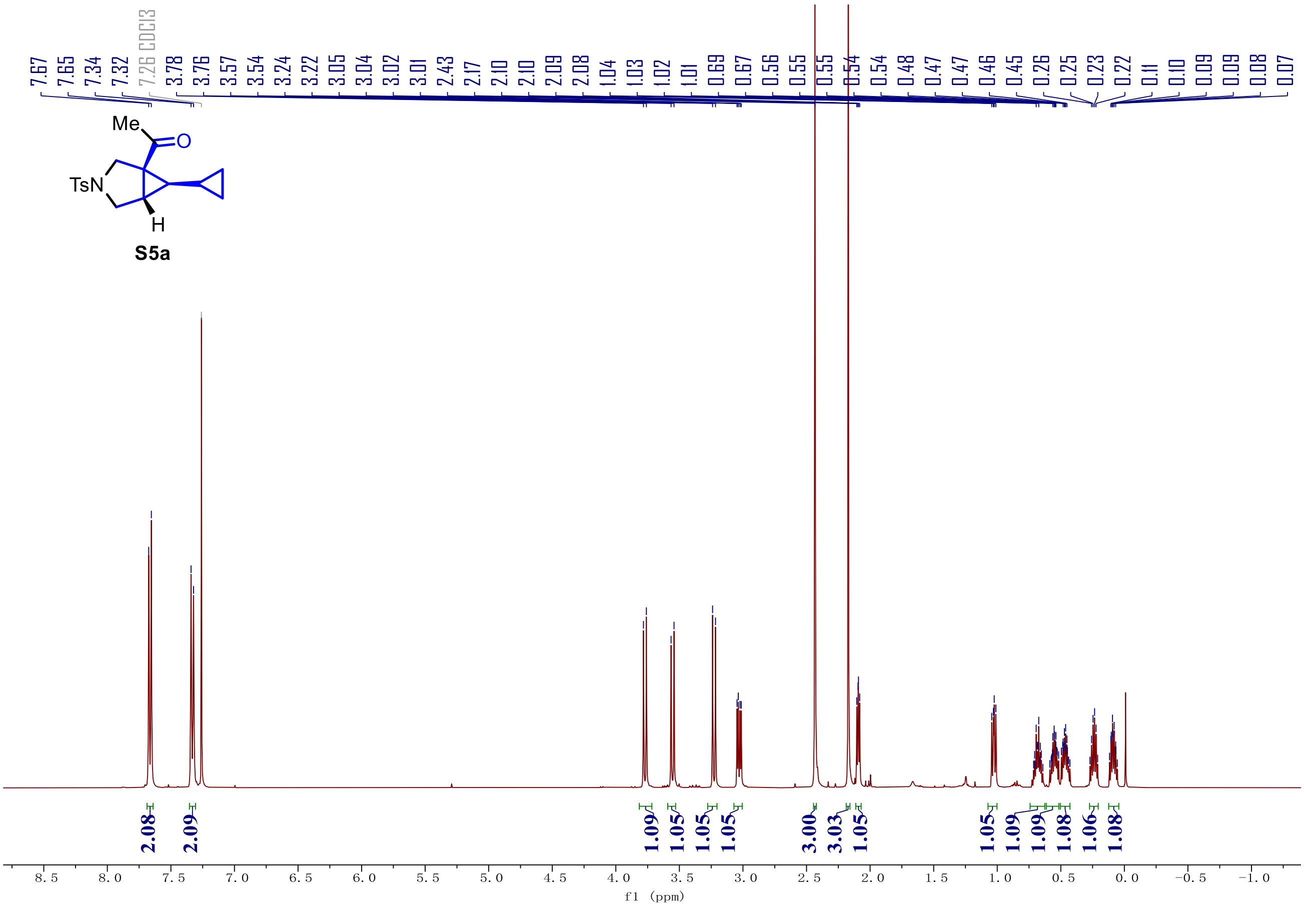
## $^1$H NMR (400 MHz, CDCl$_3$):



## $^{13}$C NMR (101 MHz, CDCl$_3$):

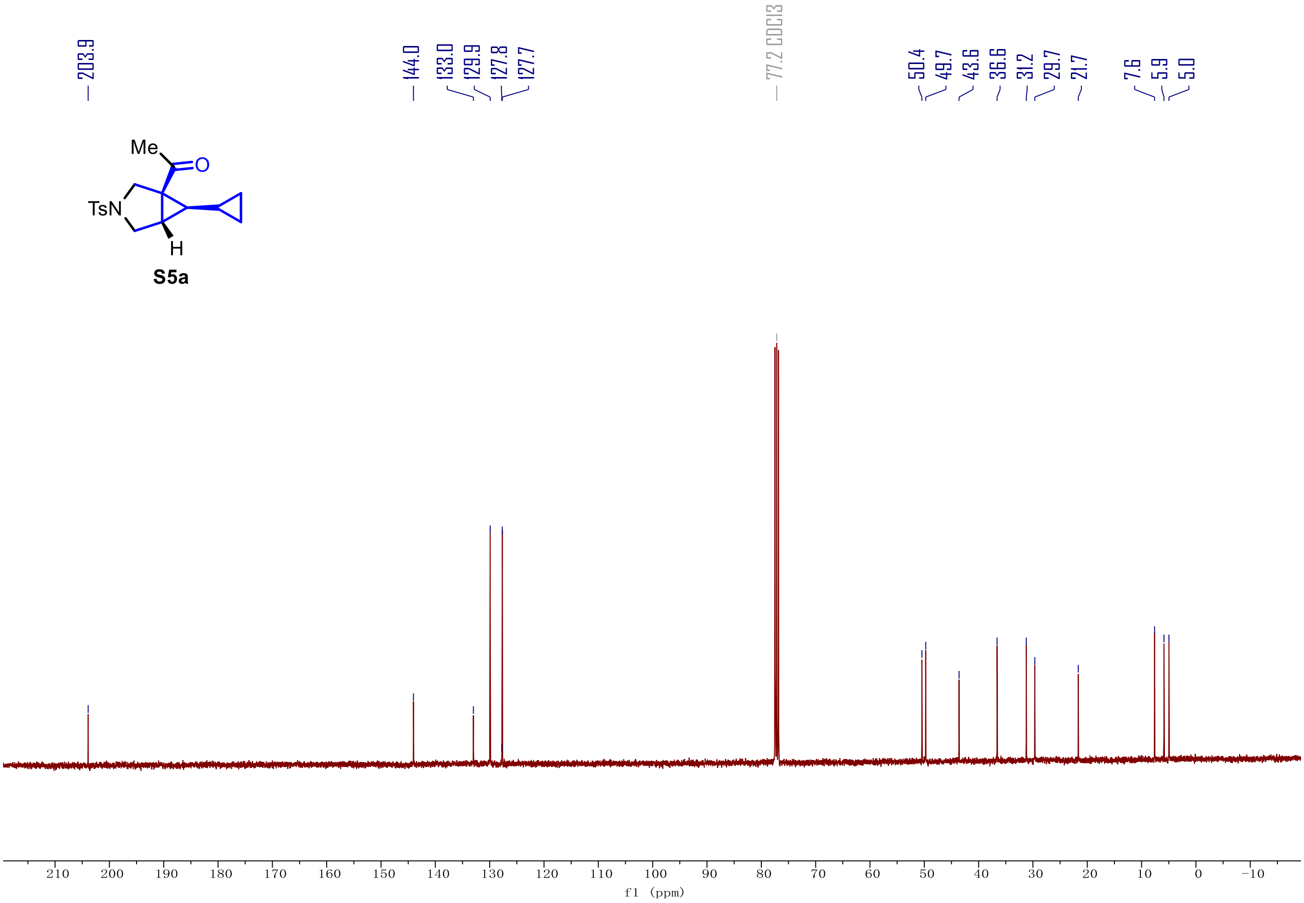


## $^1$H NMR (400 MHz, CDCl$_3$):



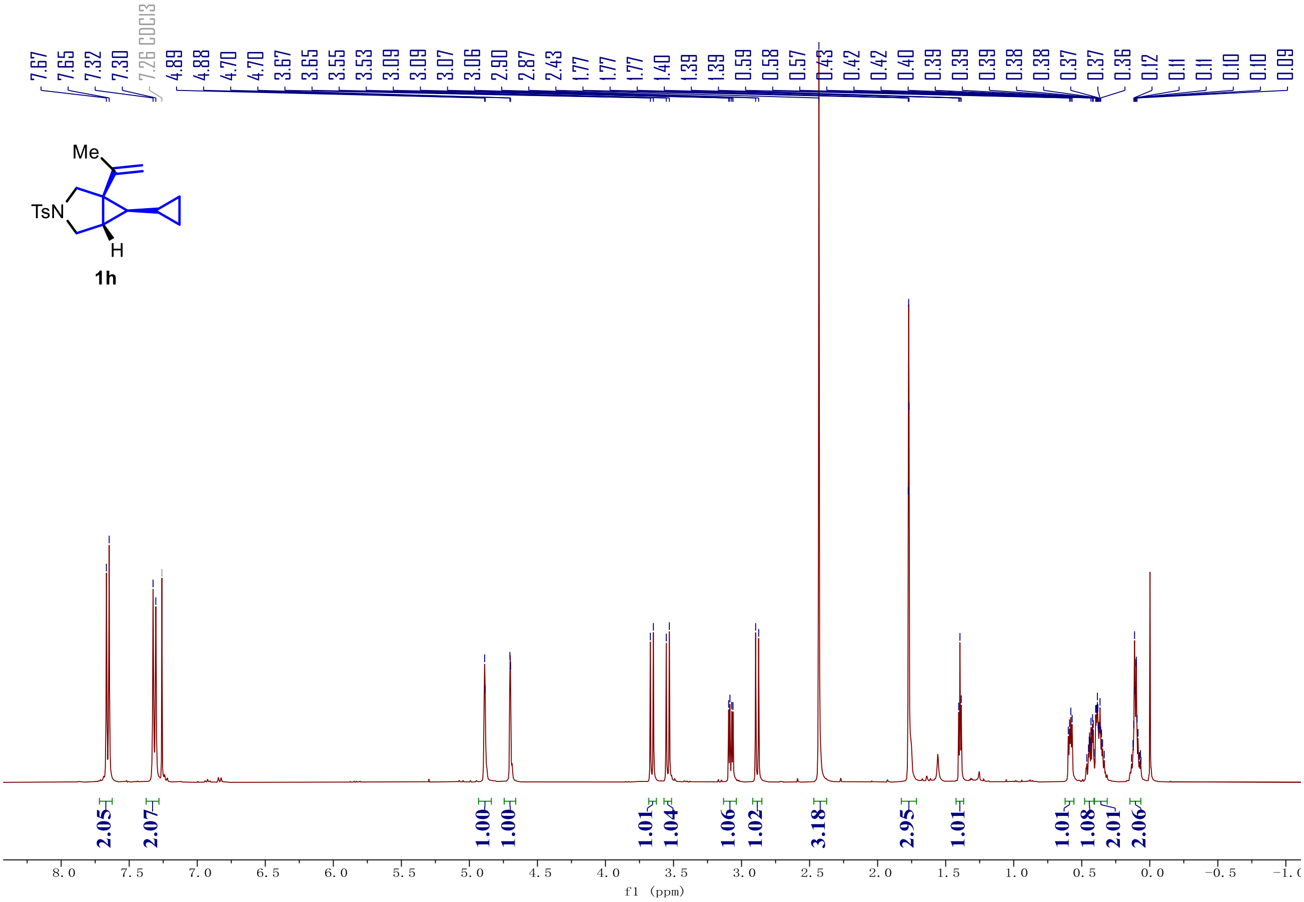
**S5a**

## $^{13}$C NMR (101 MHz, CDCl$_3$):

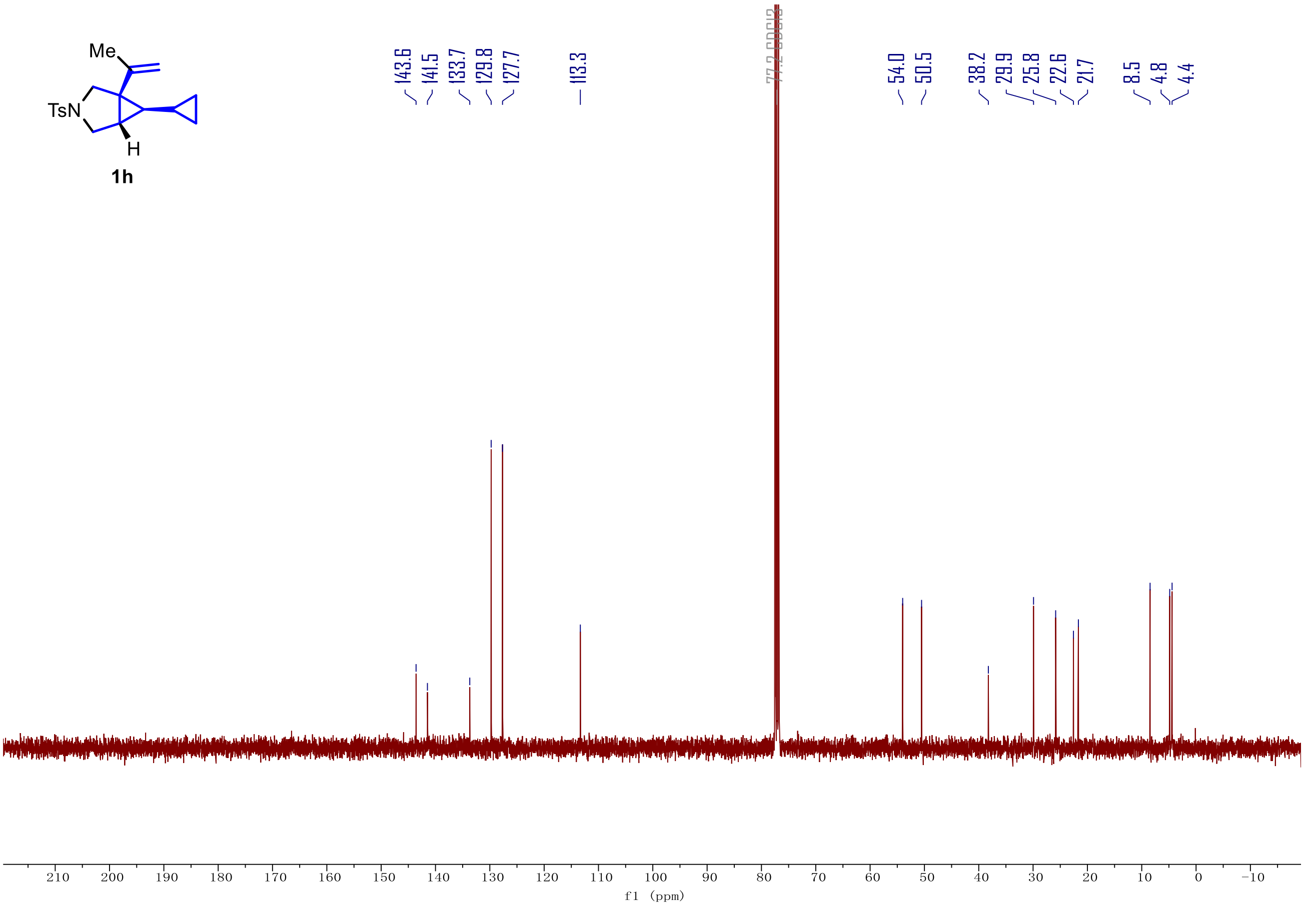


**S5a**

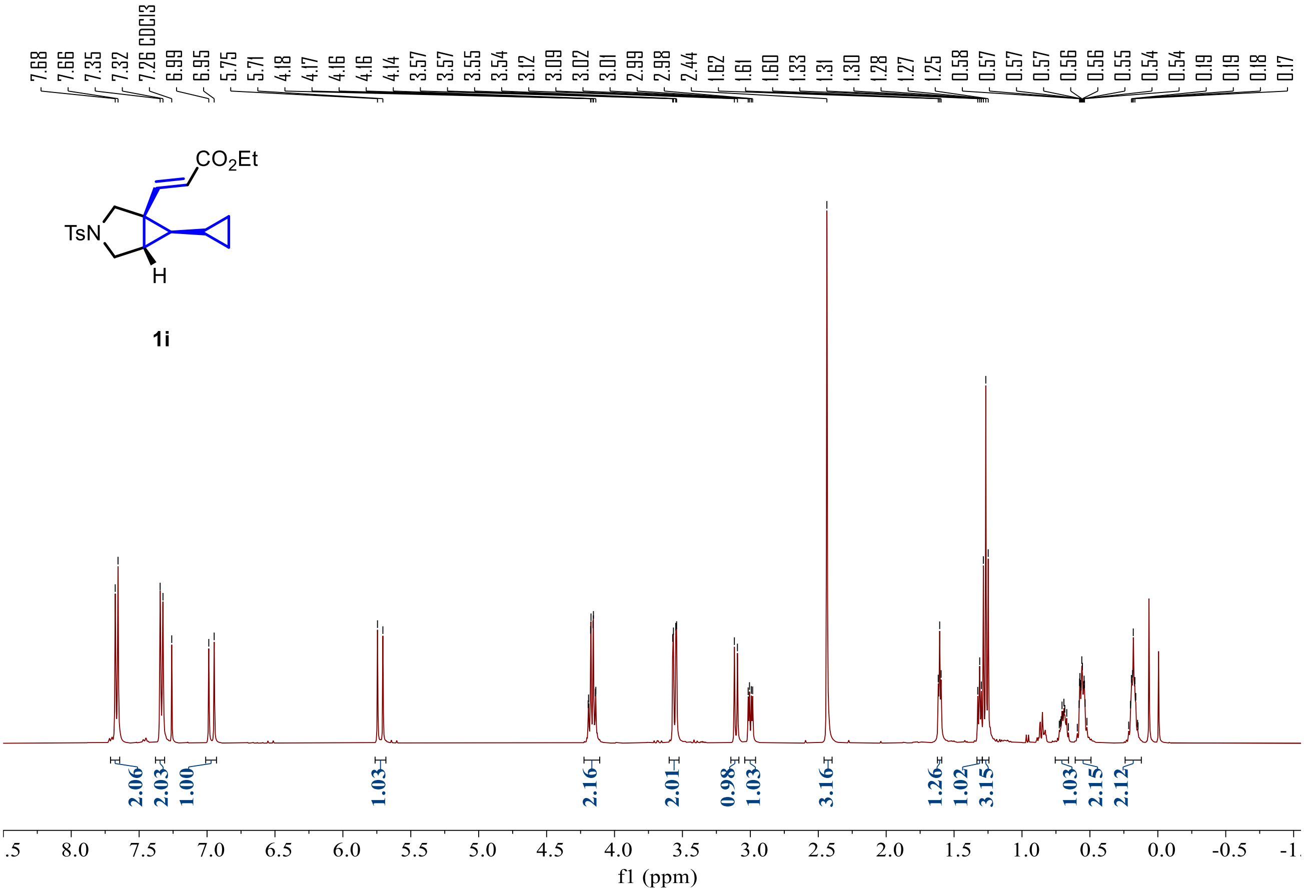
## $^1$H NMR (400 MHz, CDCl$_3$):



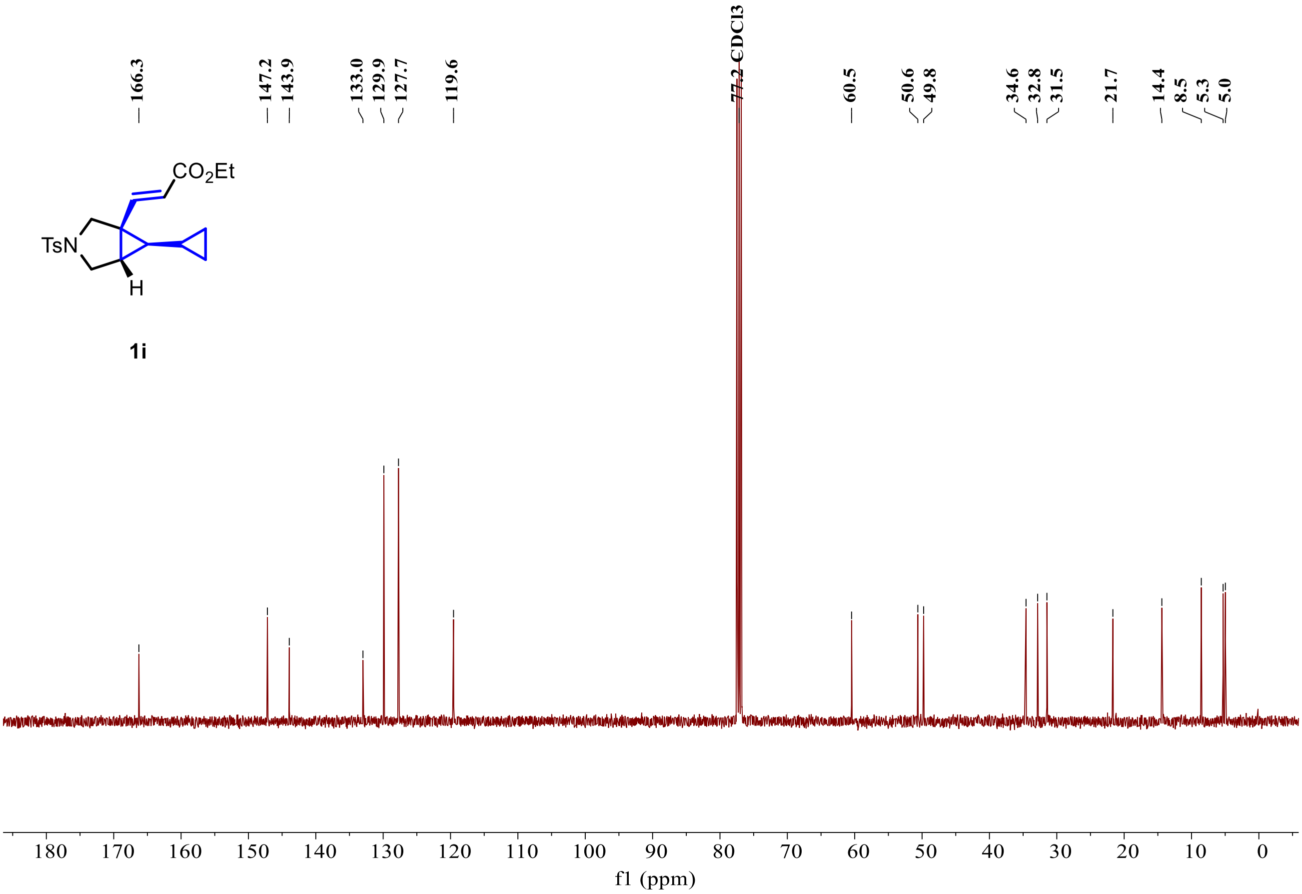
## $^{13}$C NMR (101 MHz, CDCl$_3$):



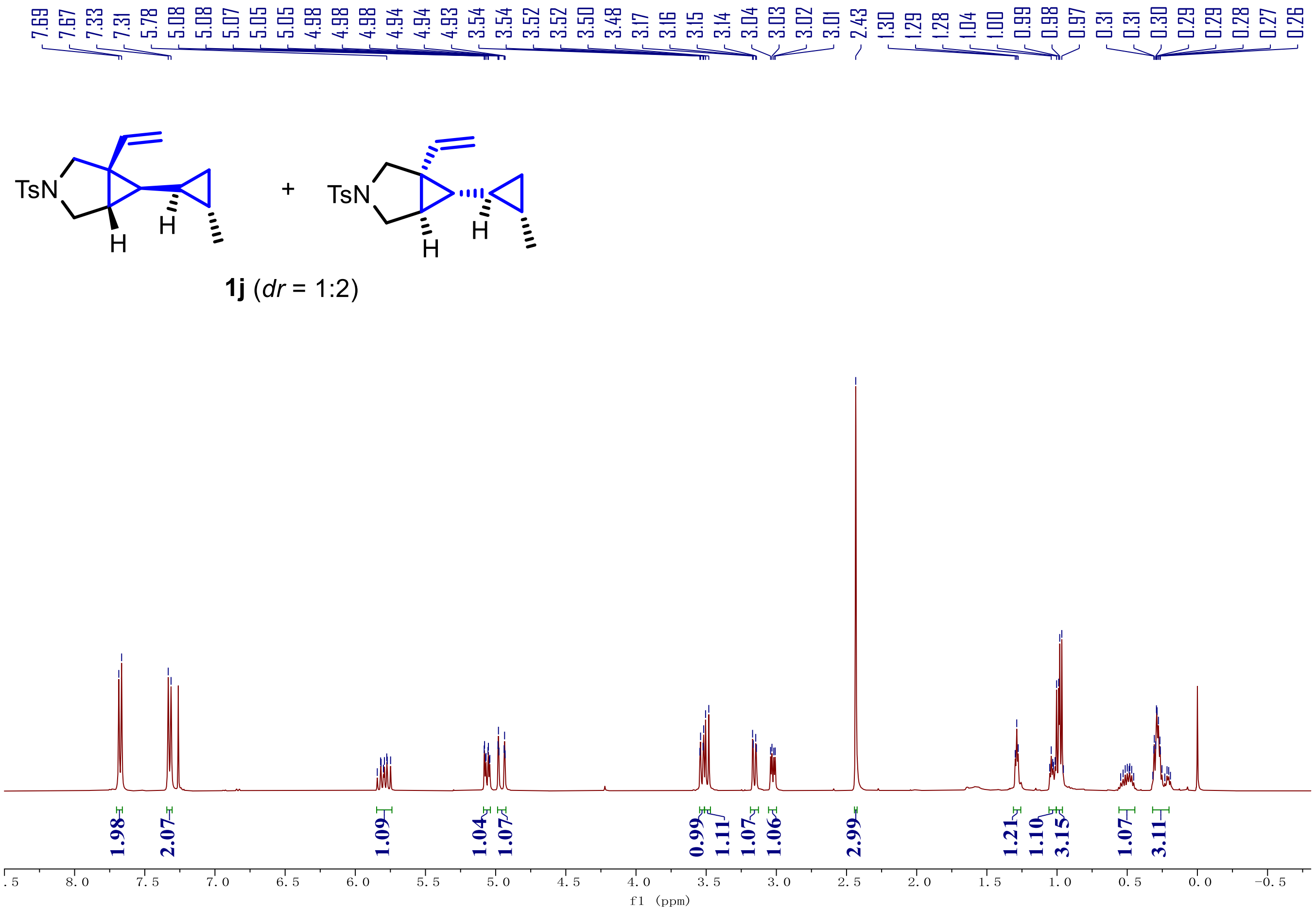
$^{1}$H NMR (400 MHz, CDCl$_3$):



$^{13}$C NMR (101 MHz, CDCl$_3$):

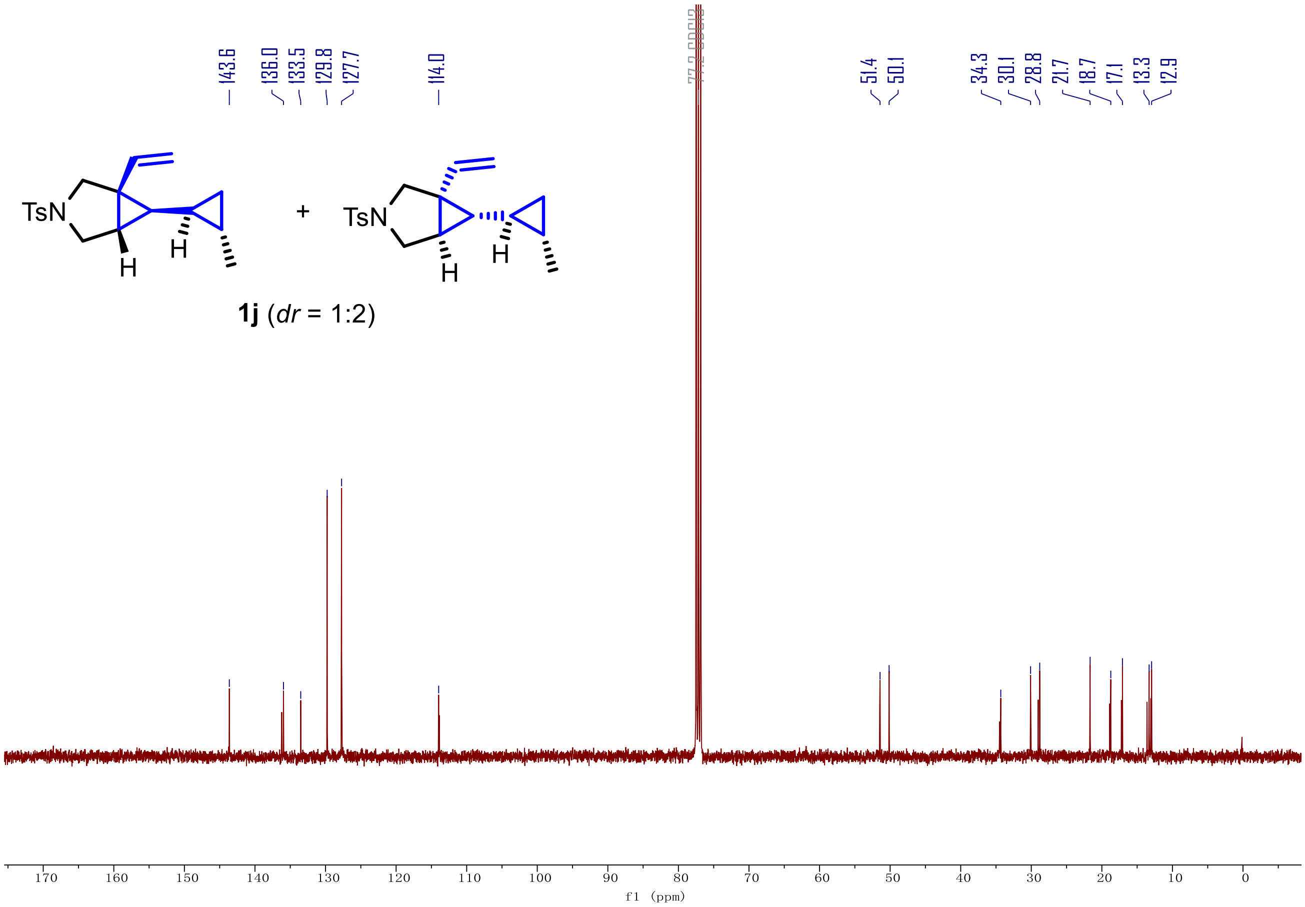


$^{1}$H NMR (400 MHz, CDCl$_3$):



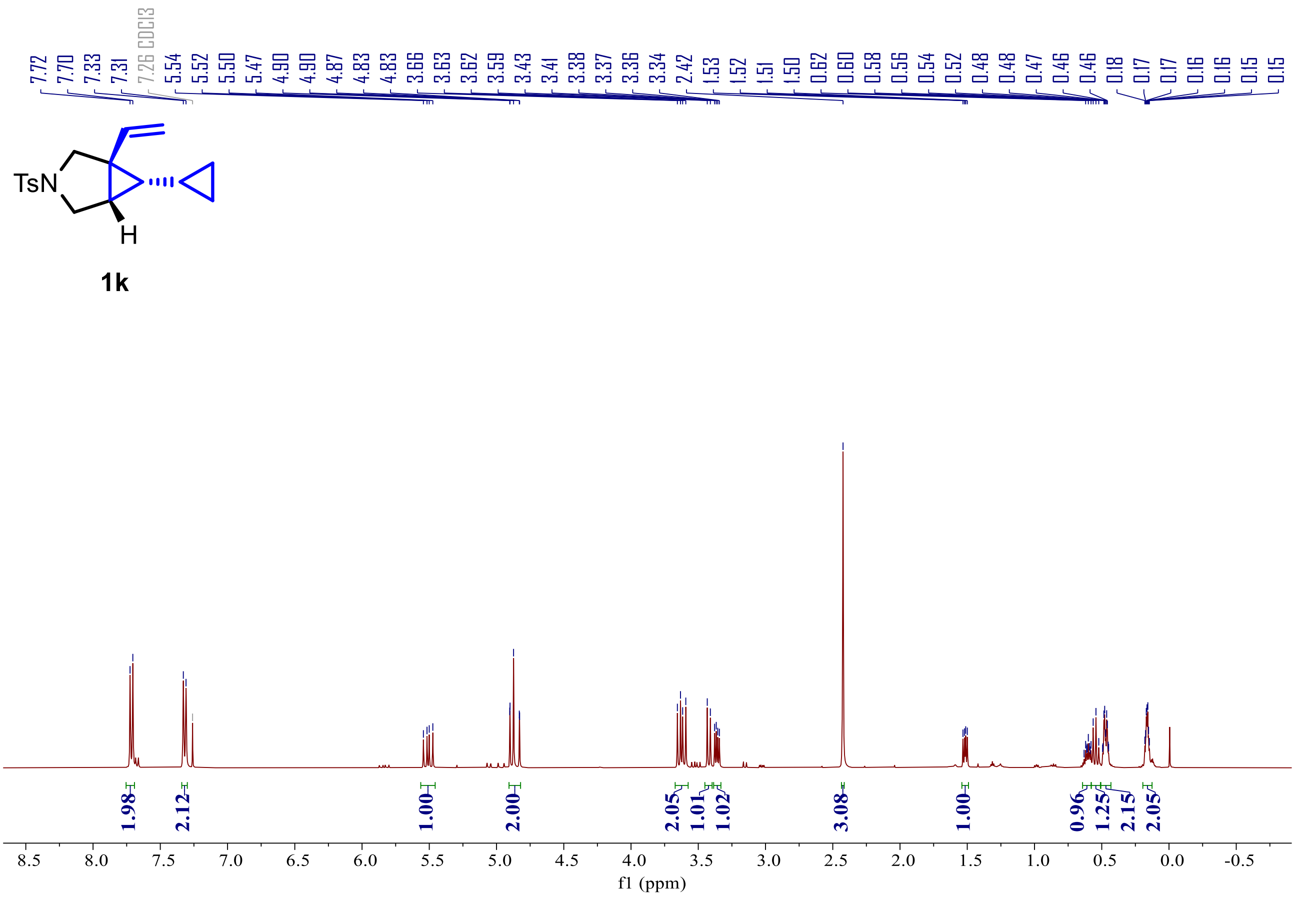
**1j** (*dr* = 1:2)

$^{13}$C NMR (101 MHz, CDCl$_3$):



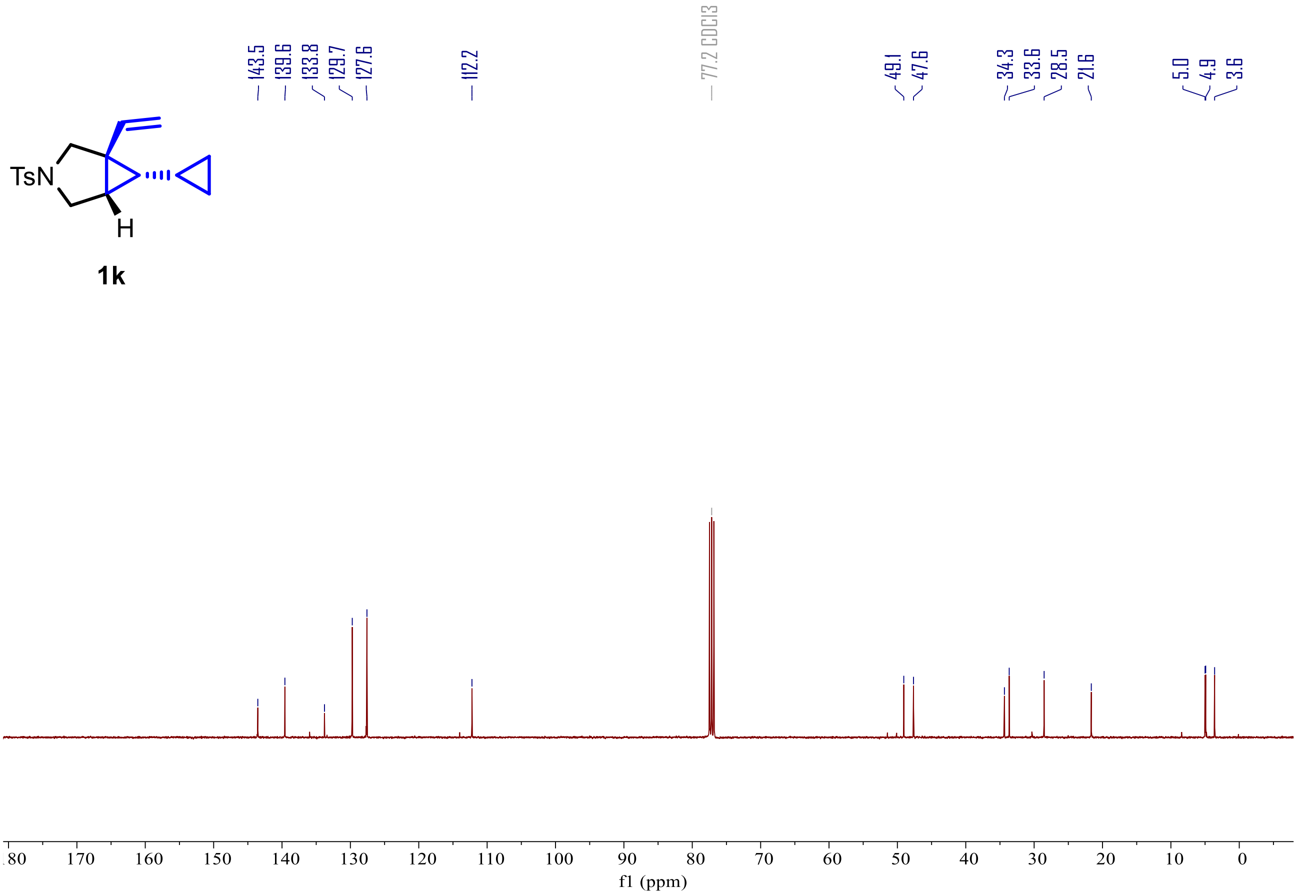
**1j** (*dr* = 1:2)

$^1$H NMR (400 MHz, CDCl$_3$):



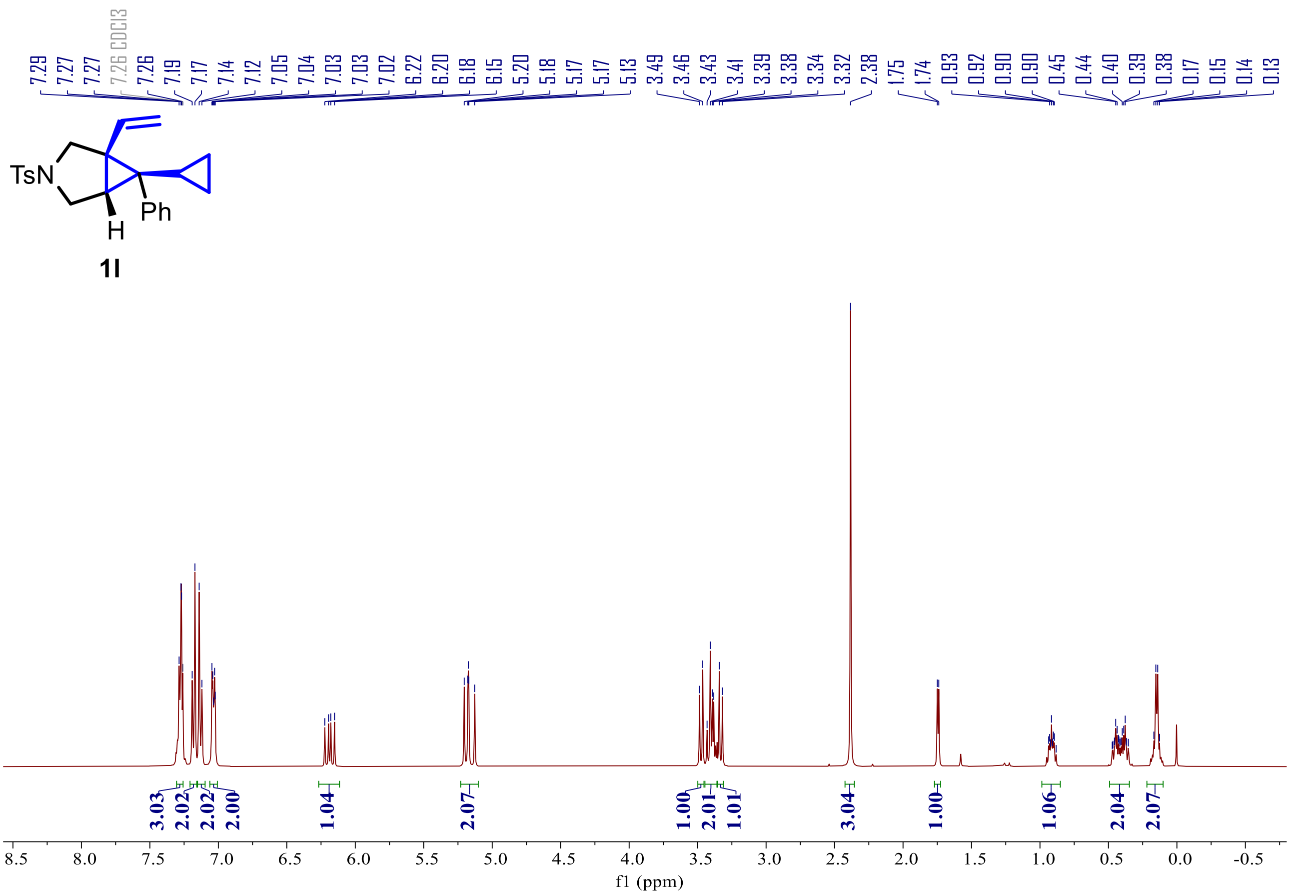
**1k**

$^{13}$C NMR (101 MHz, CDCl$_3$):



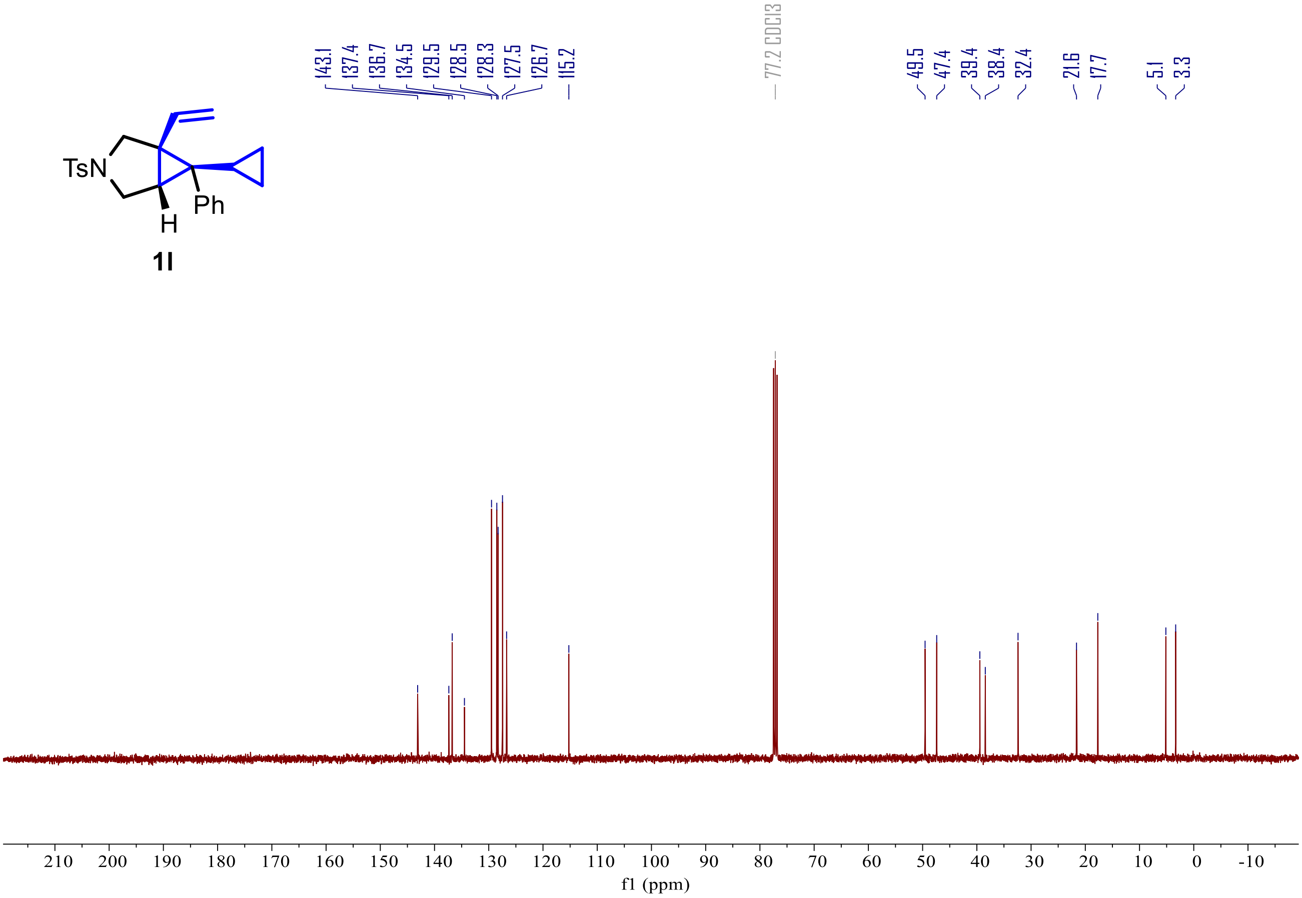
**1k**

## $^1$H NMR (400 MHz, CDCl$_3$):



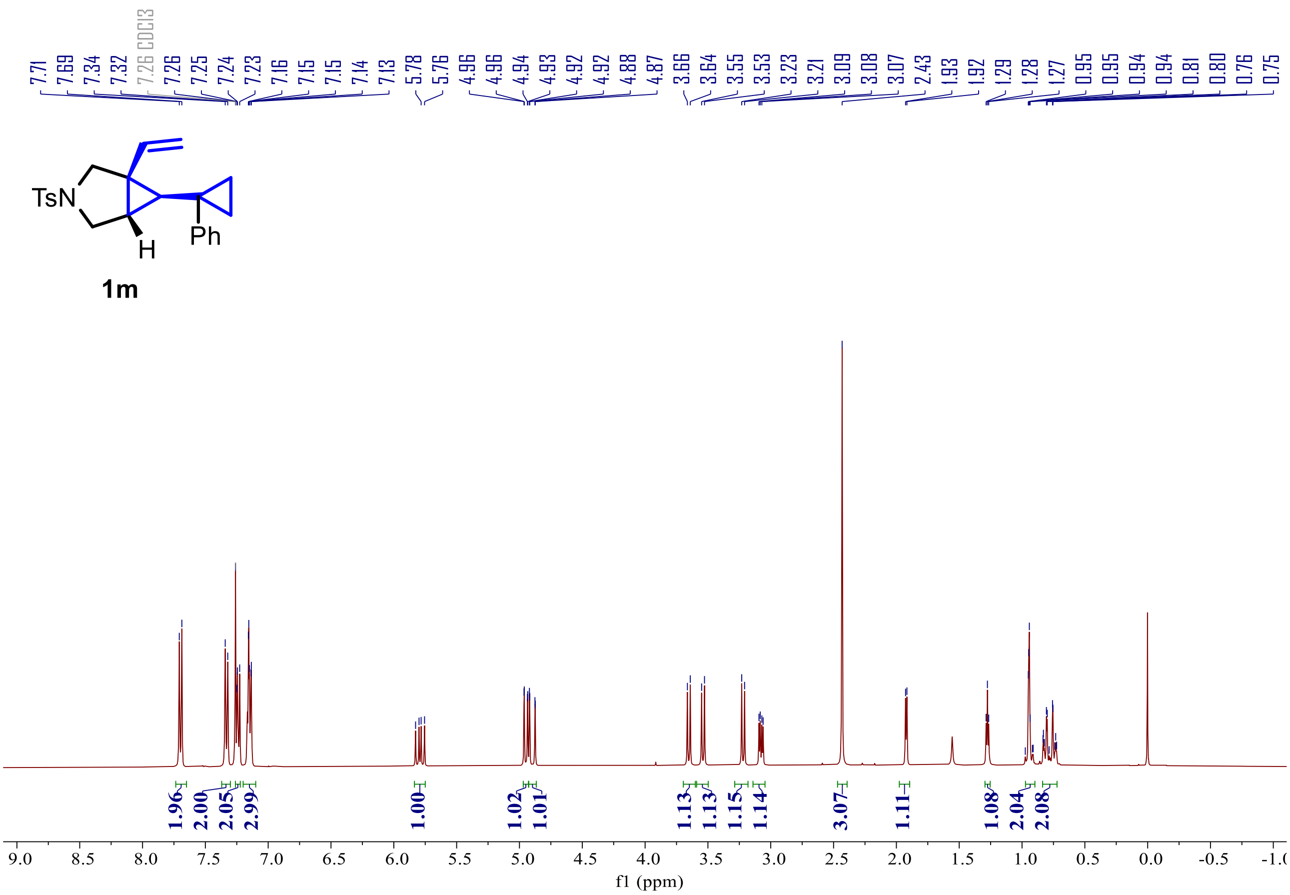
**1l**

## $^{13}$C NMR (101 MHz, CDCl$_3$):

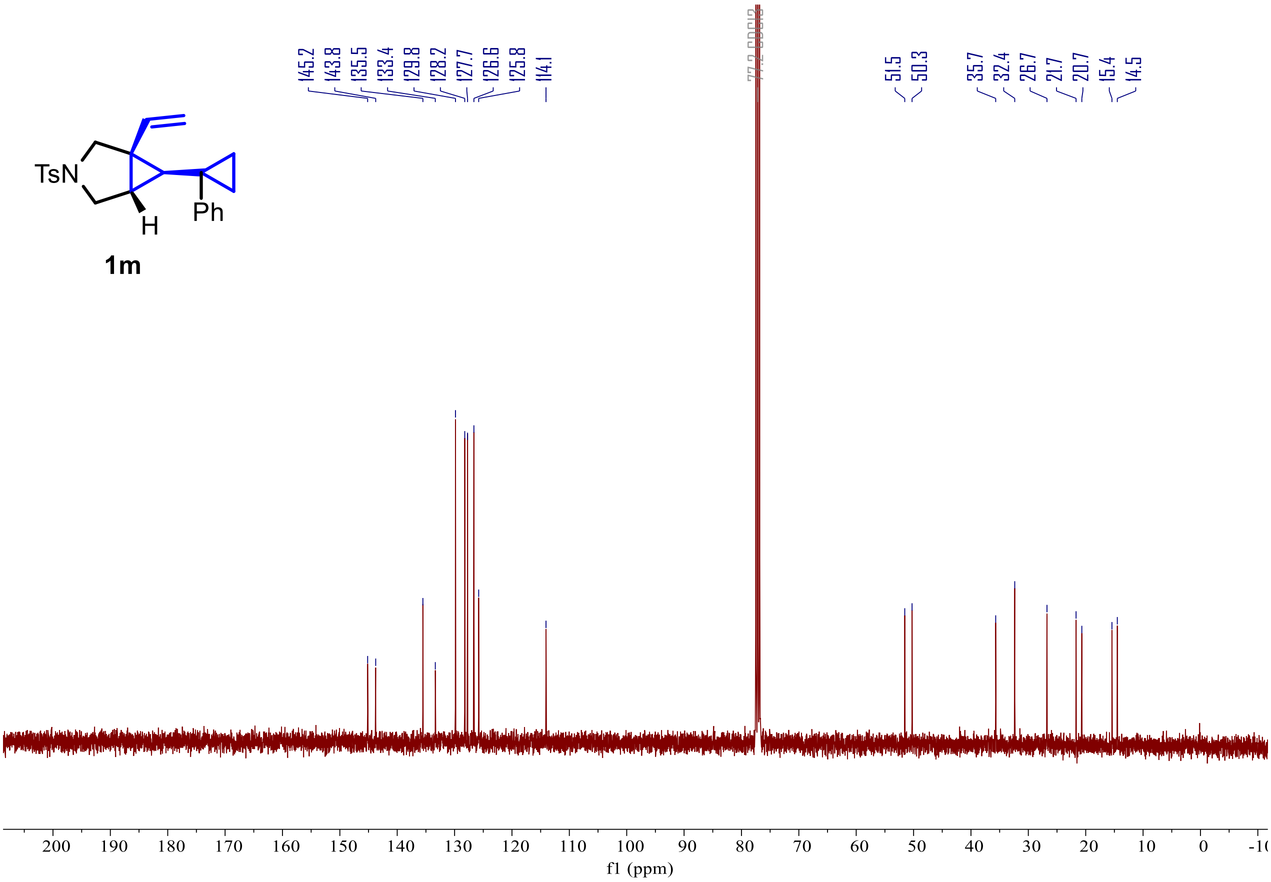


**1l**

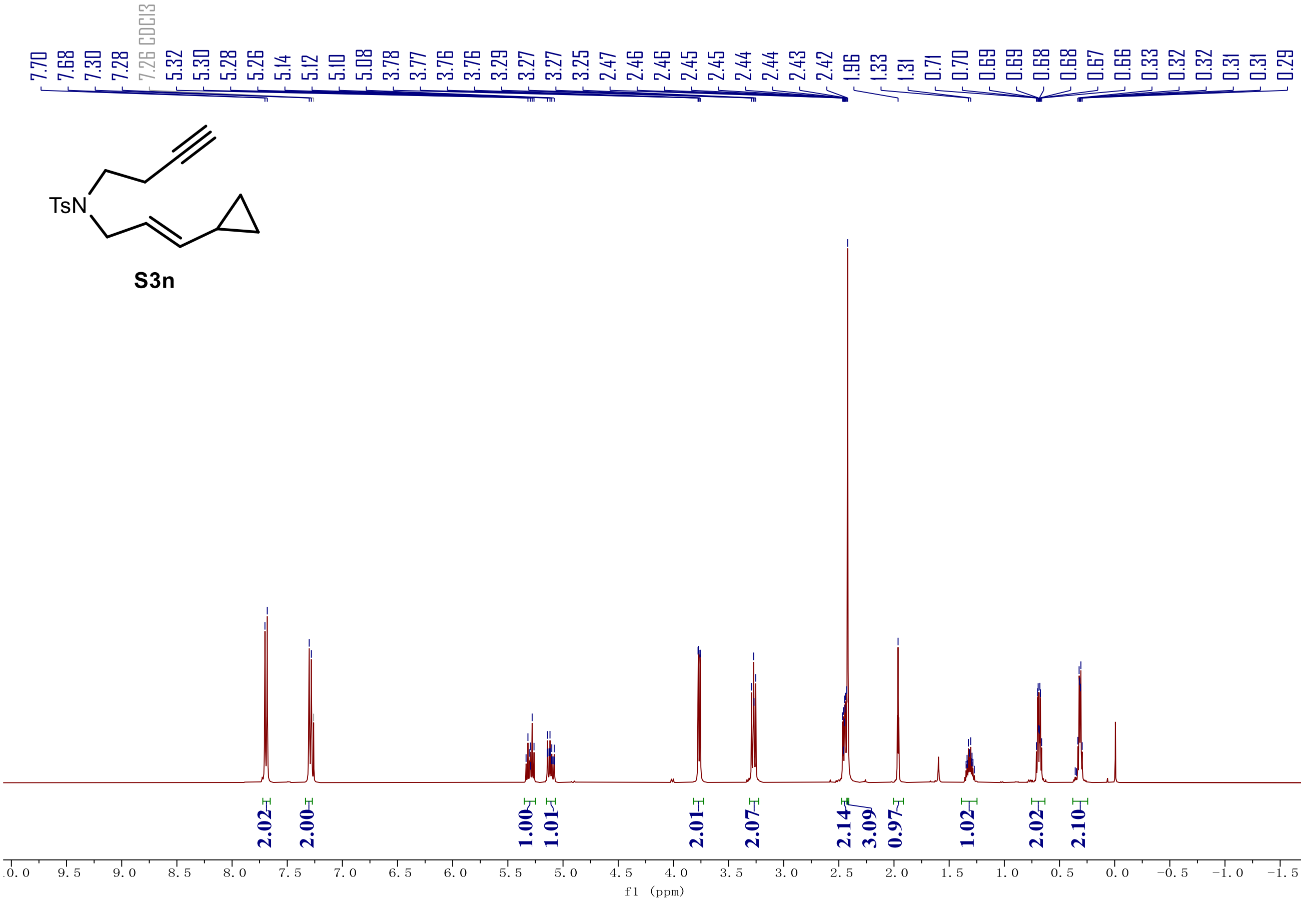
## $^1H$ NMR (400 MHz, $CDCl_3$):


**1m**

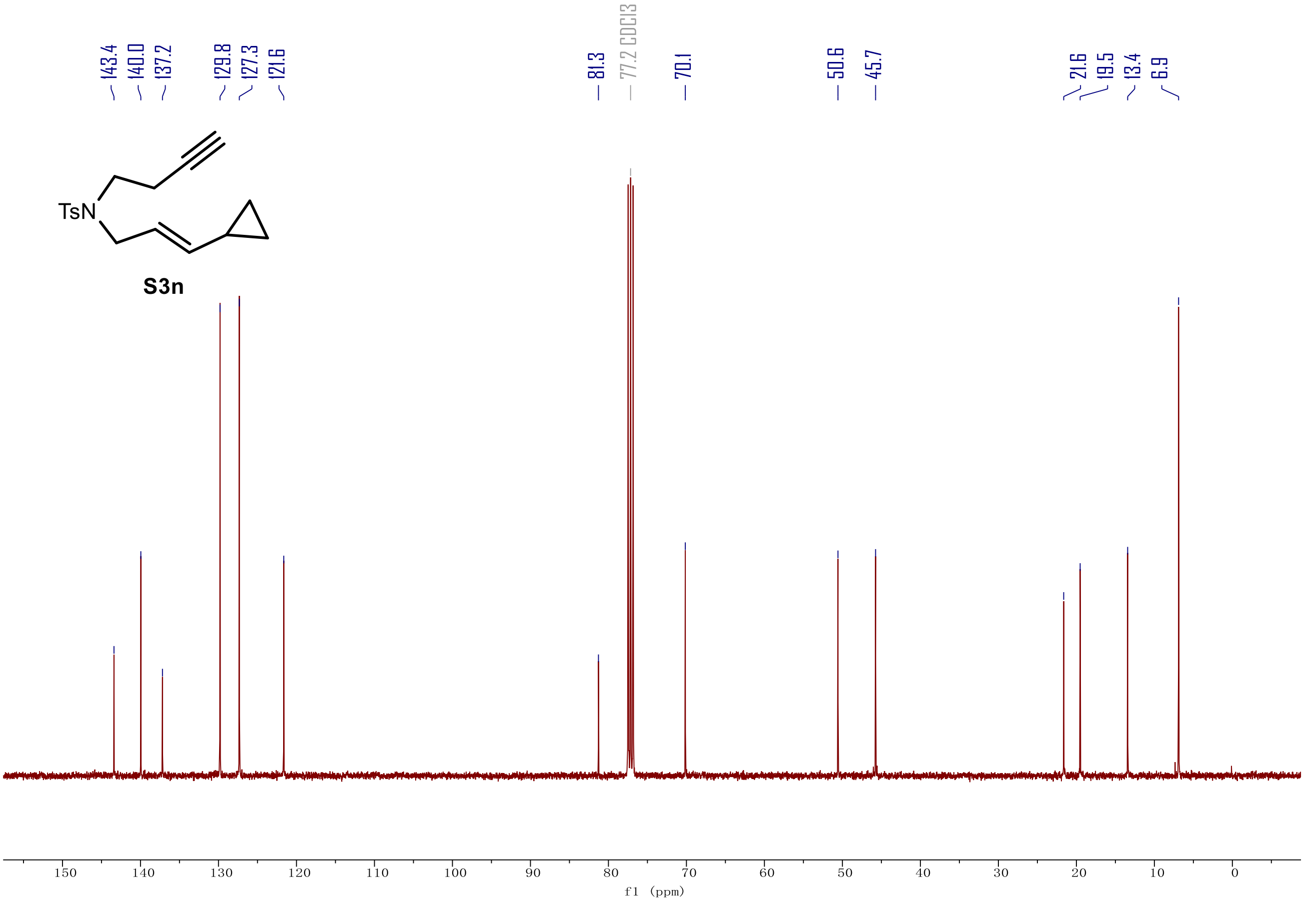
## $^{13}C$ NMR (101 MHz, $CDCl_3$):


**1m**

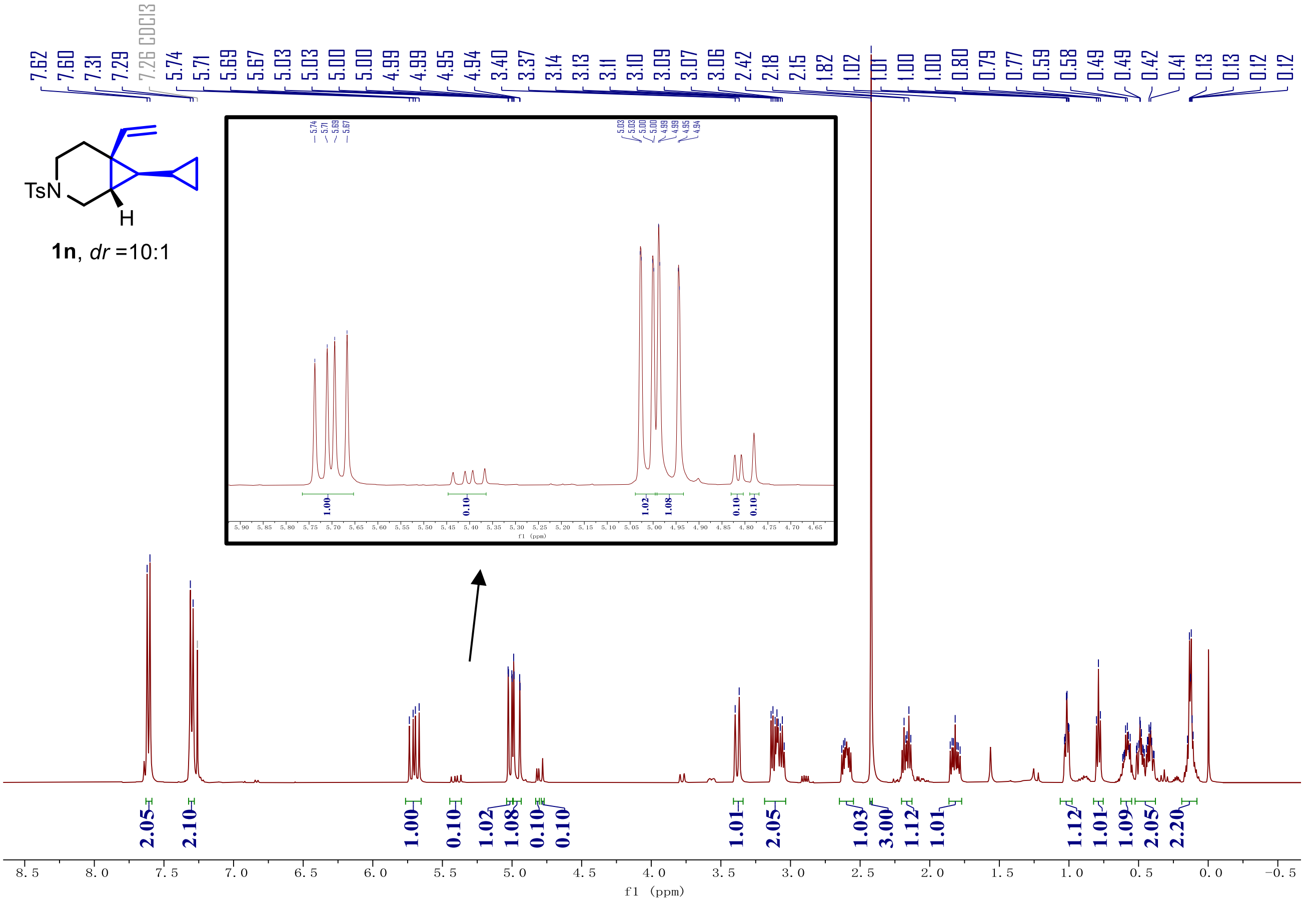
$^1$H NMR (400 MHz, CDCl$_3$):



$^{13}$C NMR (101 MHz, CDCl$_3$):

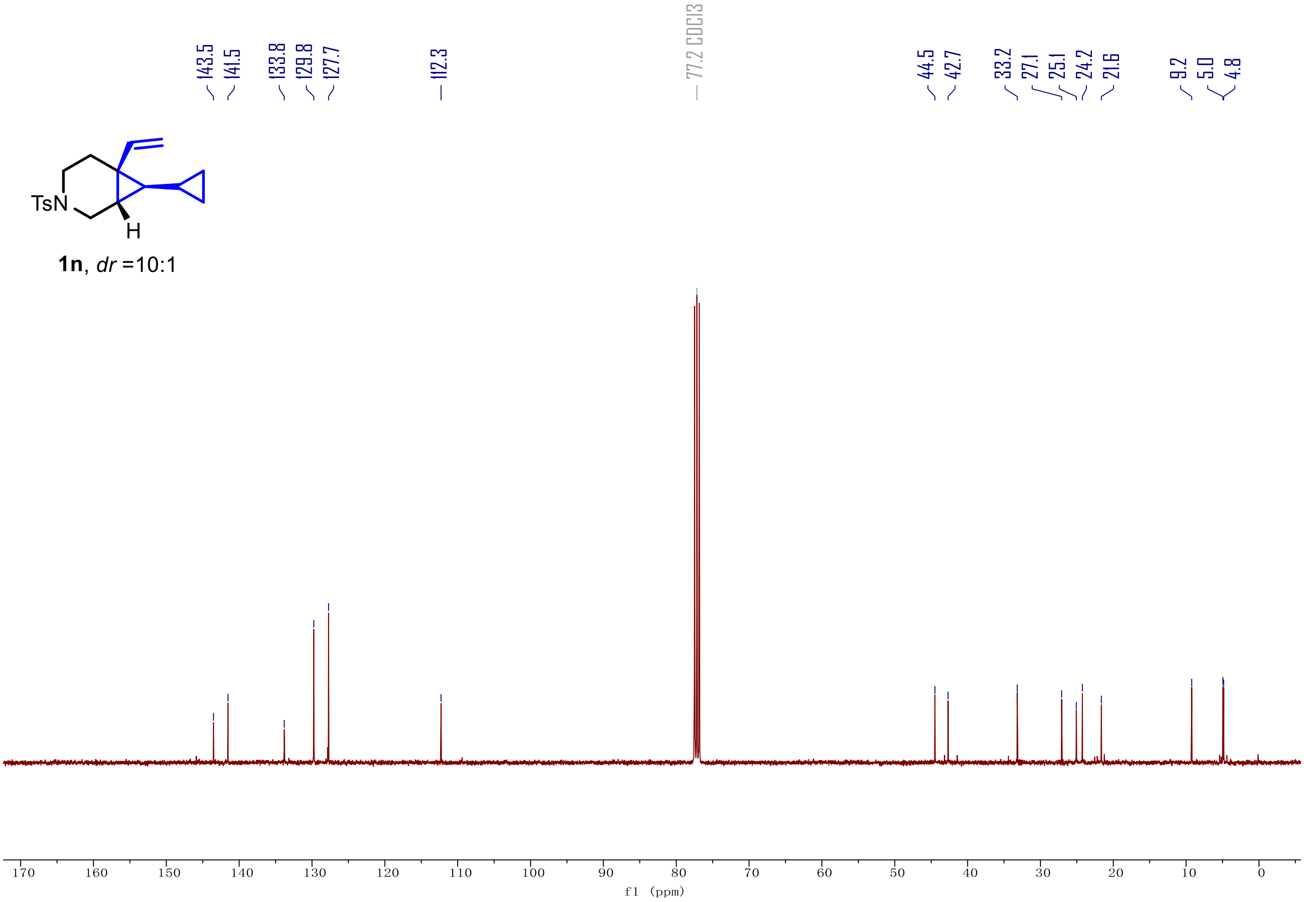


## $^{1}$H NMR (400 MHz, CDCl$_3$):



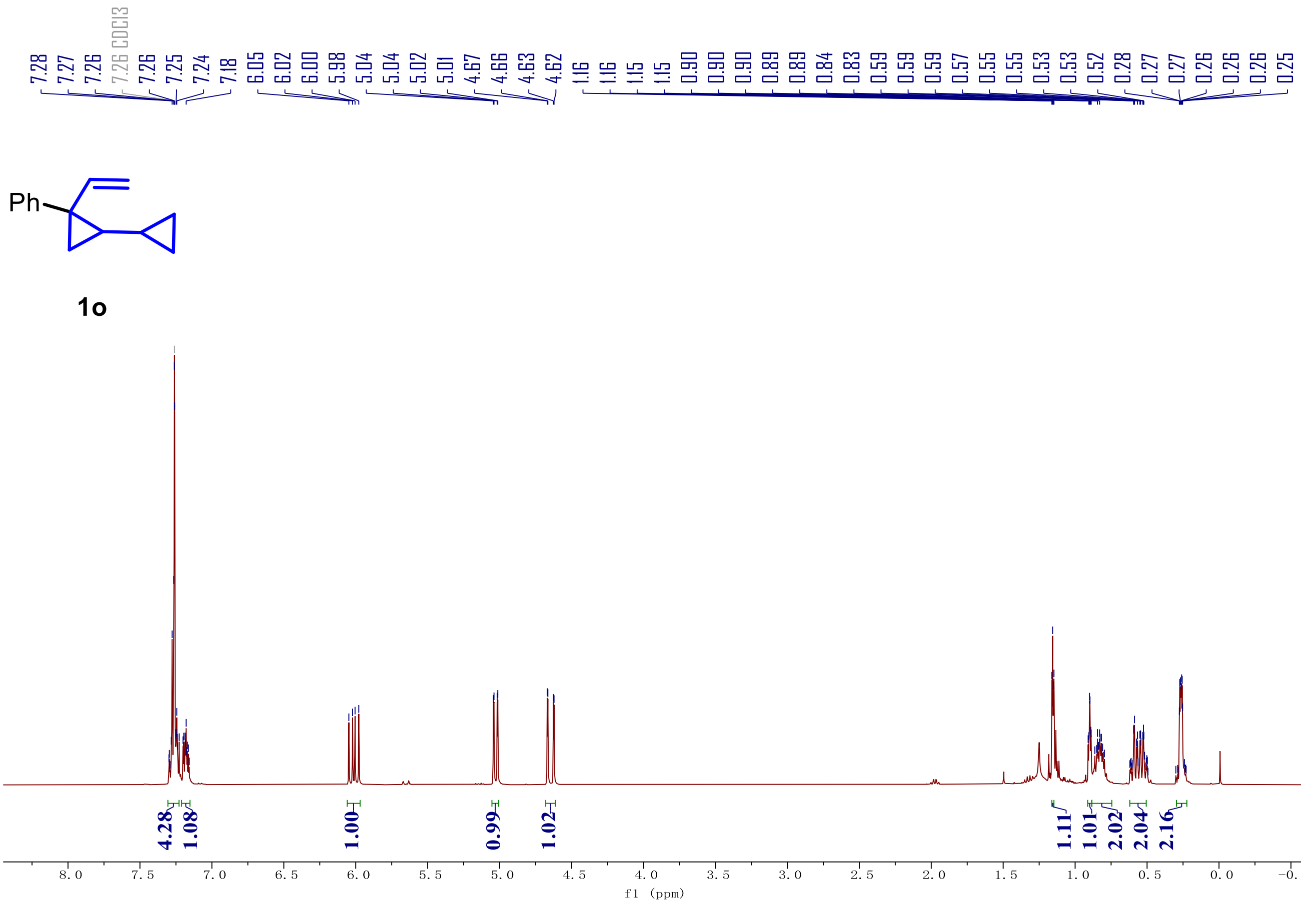
**1n**, *dr* =10:1

## $^{13}$C NMR (101 MHz, CDCl$_3$):



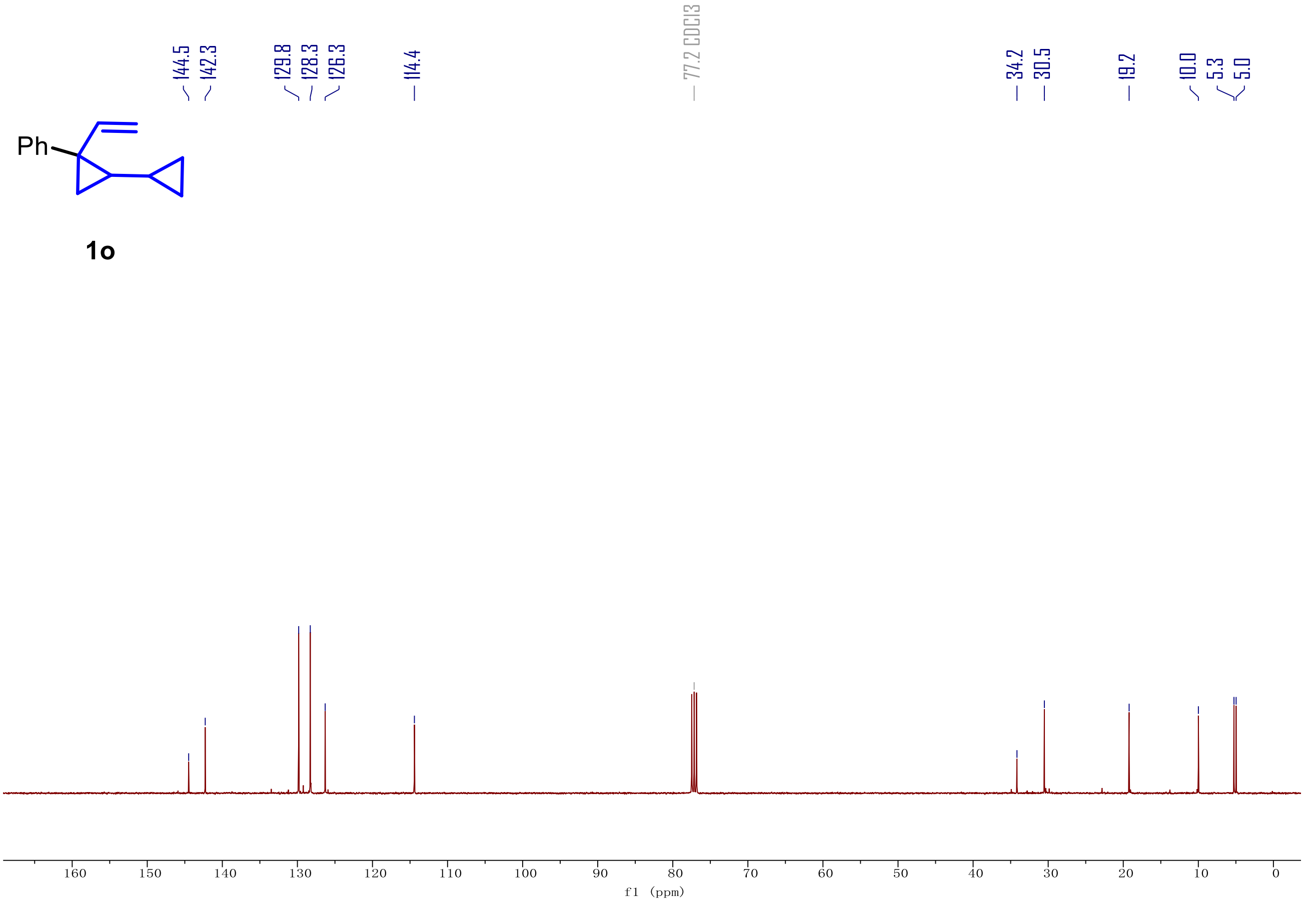
**1n**, *dr* =10:1

## $^1$H NMR (400 MHz, CDCl$_3$):



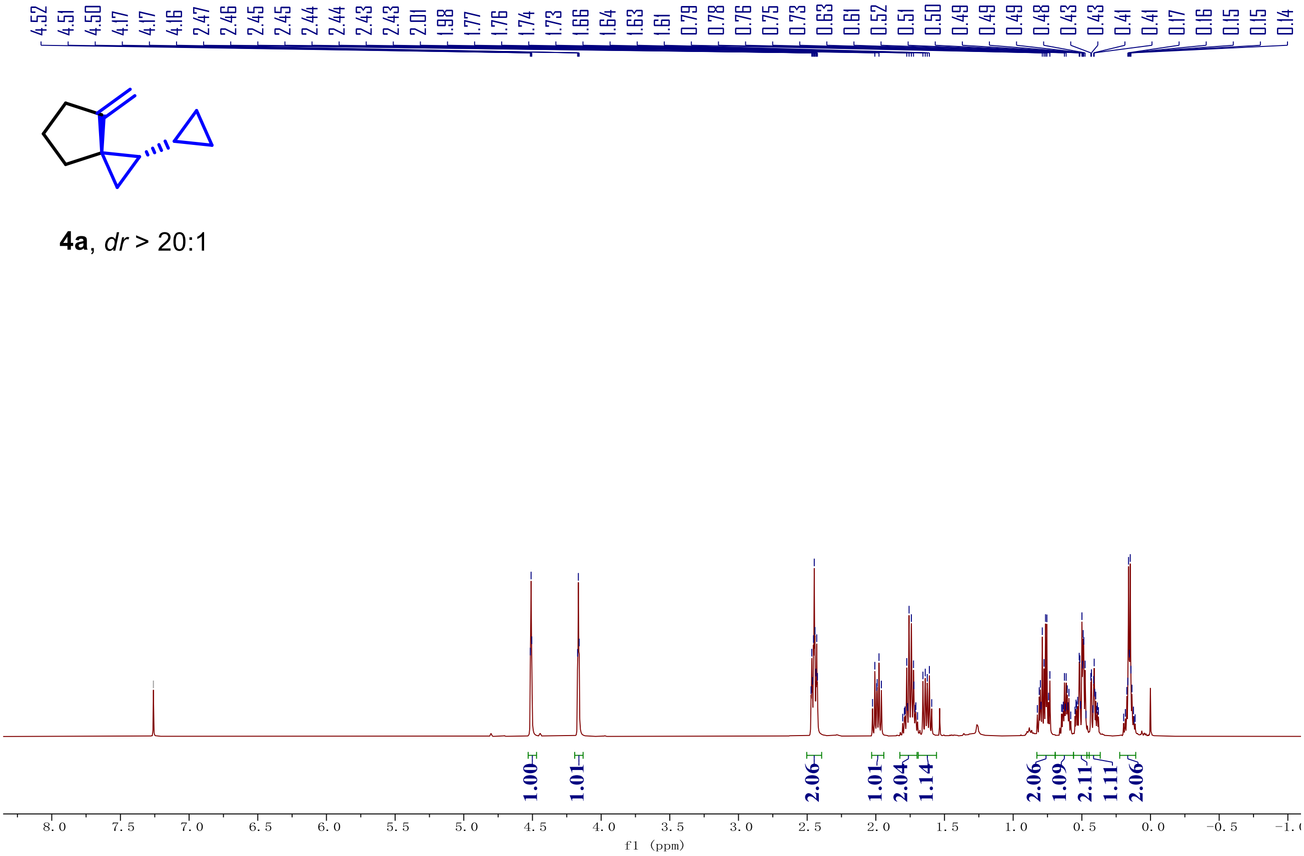
**1o**

## $^{13}$C NMR (101 MHz, CDCl$_3$):



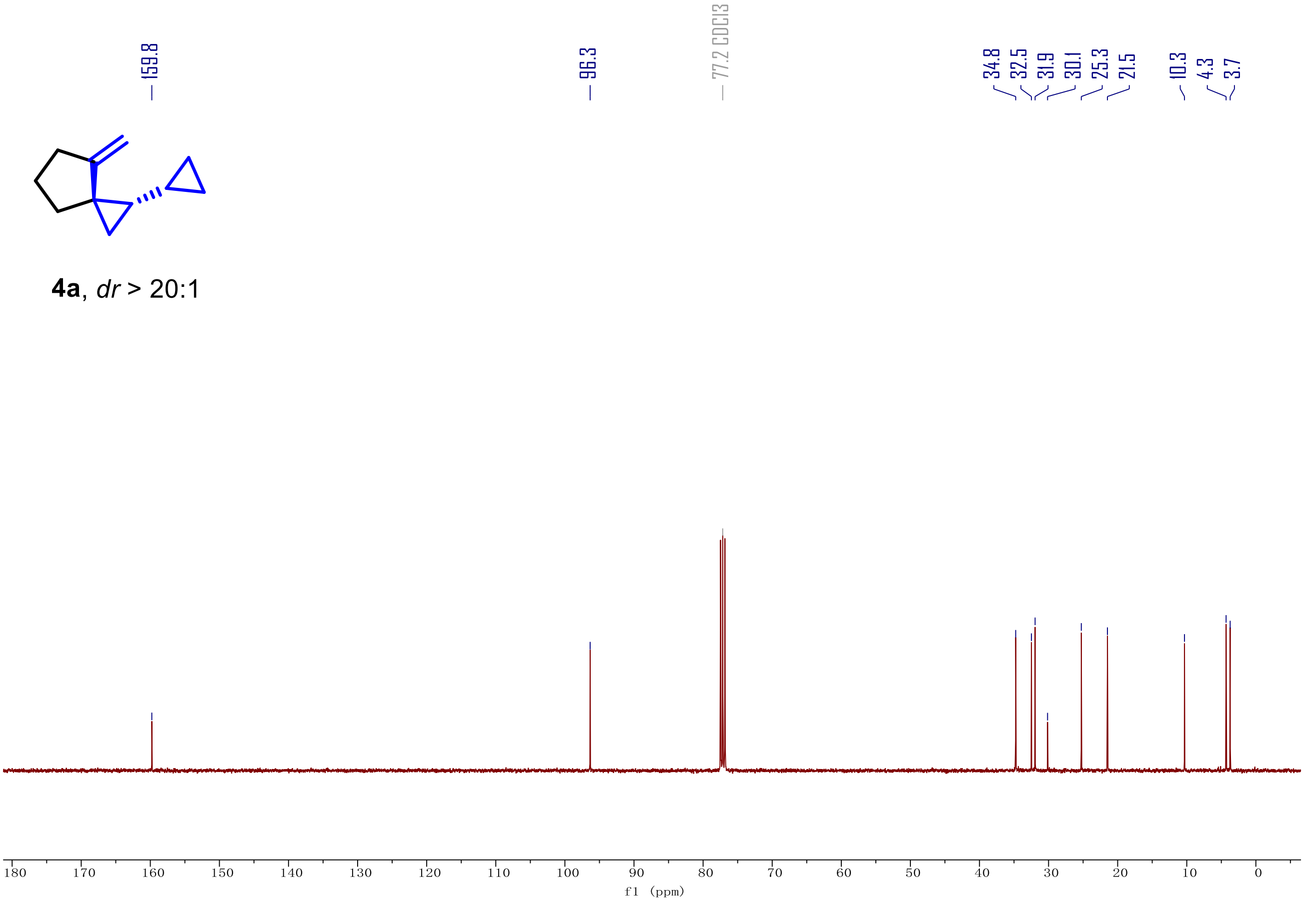
**1o**

## $^1$H NMR (400 MHz, CDCl$_3$):



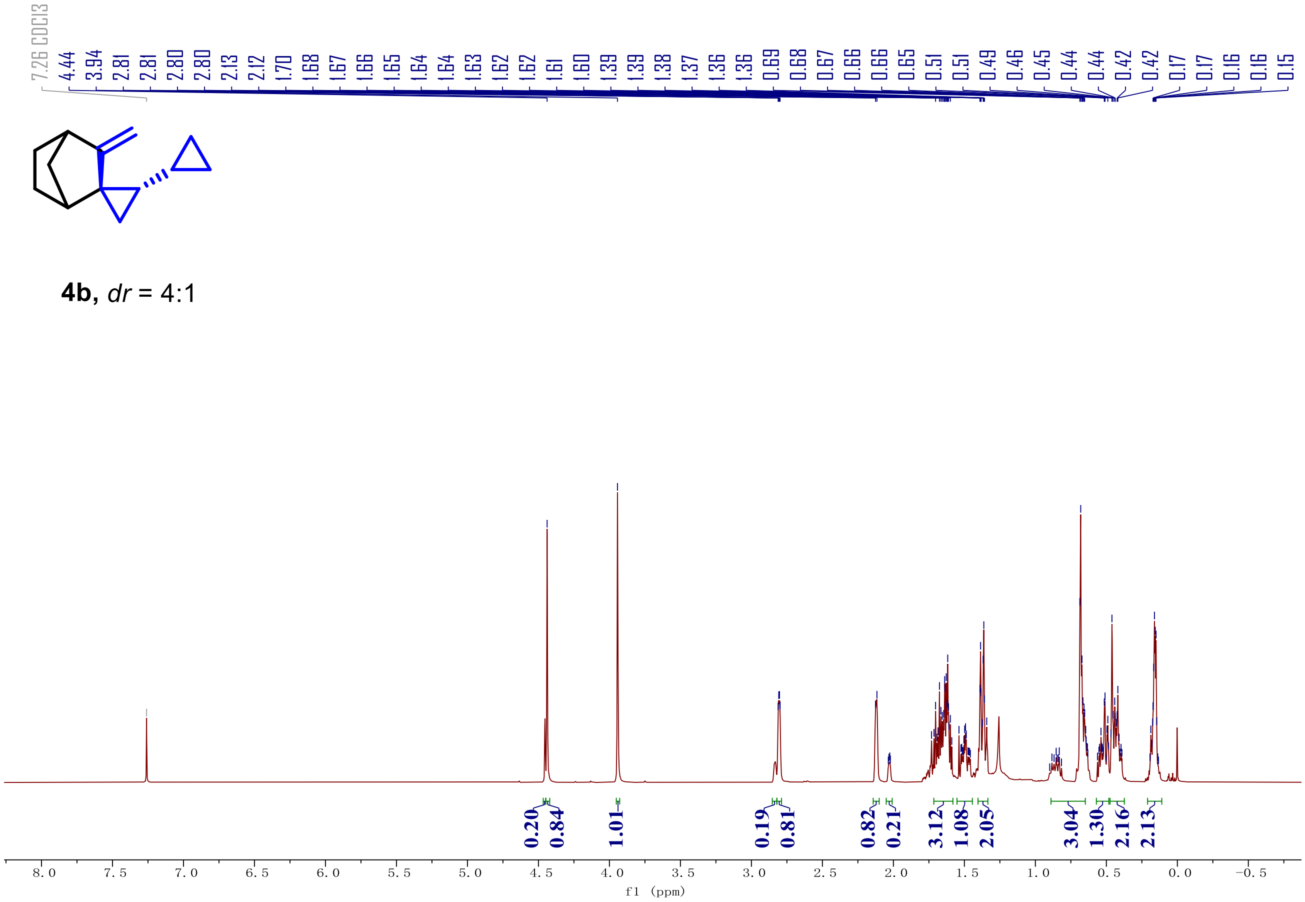
**4a**, *dr* > 20:1

## $^{13}$C NMR (101 MHz, CDCl$_3$):



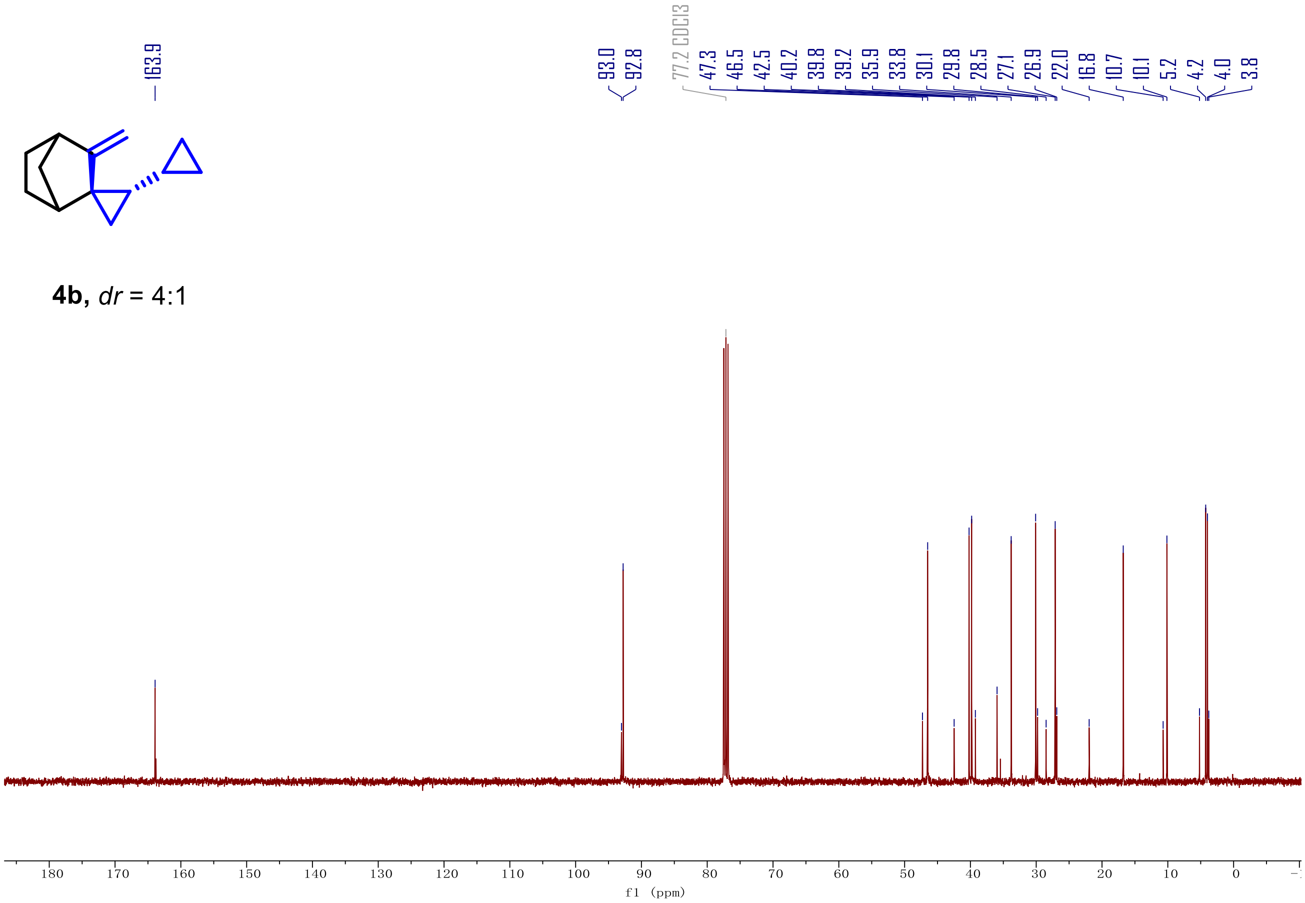
**4a**, *dr* > 20:1

$^{1}$H NMR (400 MHz, CDCl$_3$):



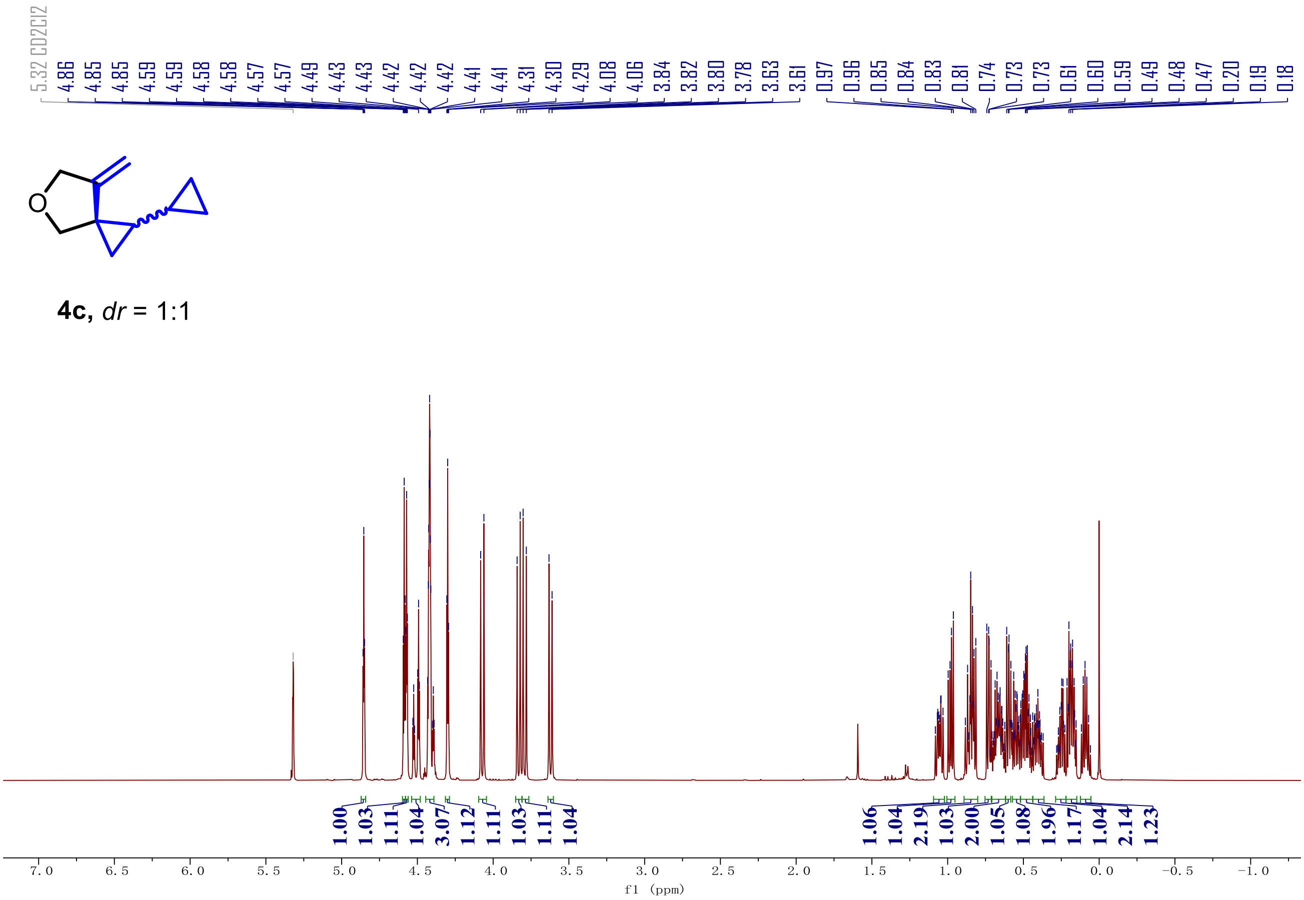
**4b,** *dr* = 4:1

$^{13}$C NMR (101 MHz, CDCl$_3$):



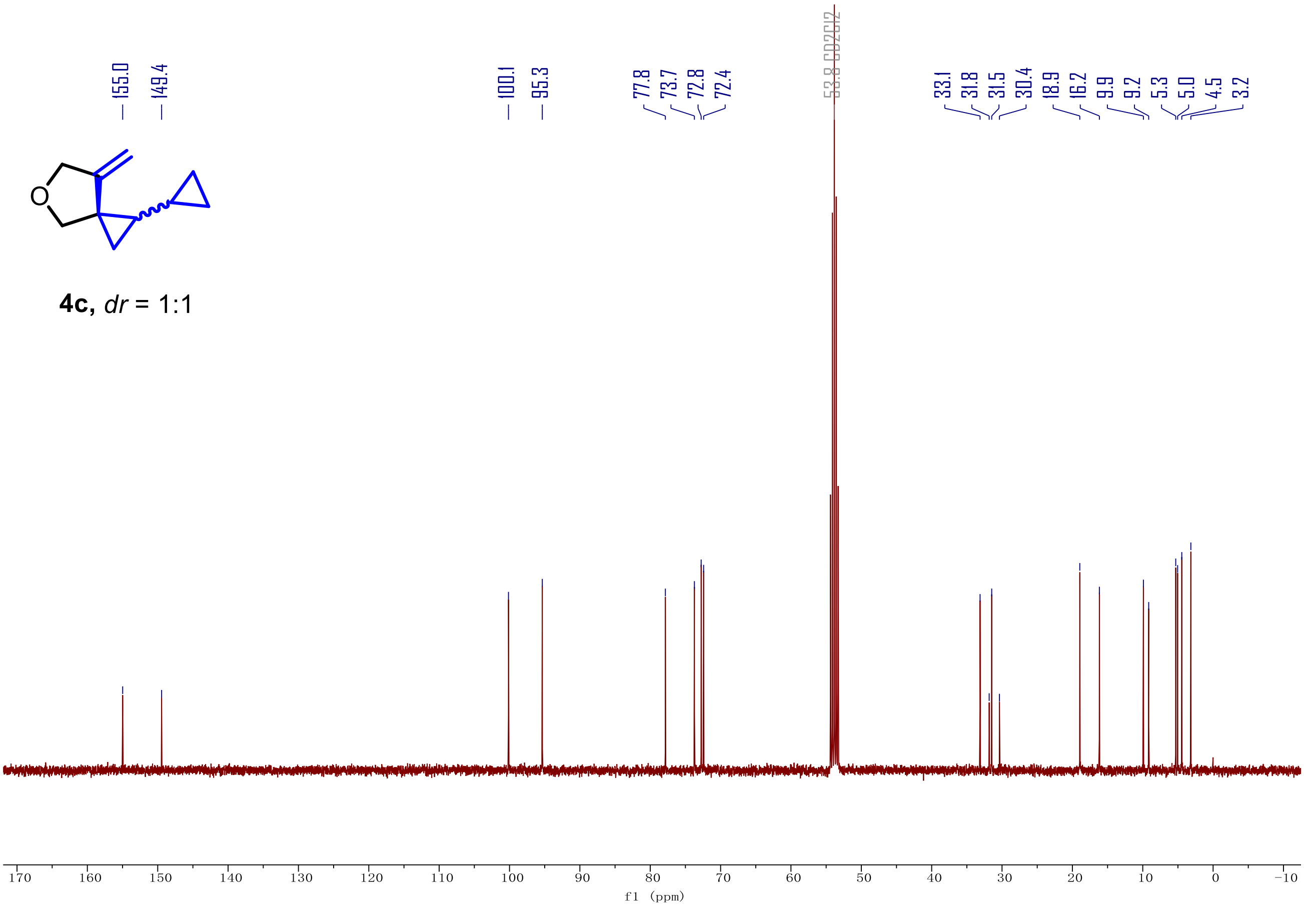
**4b,** *dr* = 4:1

### $^1$H NMR (400 MHz, CDCl$_3$):



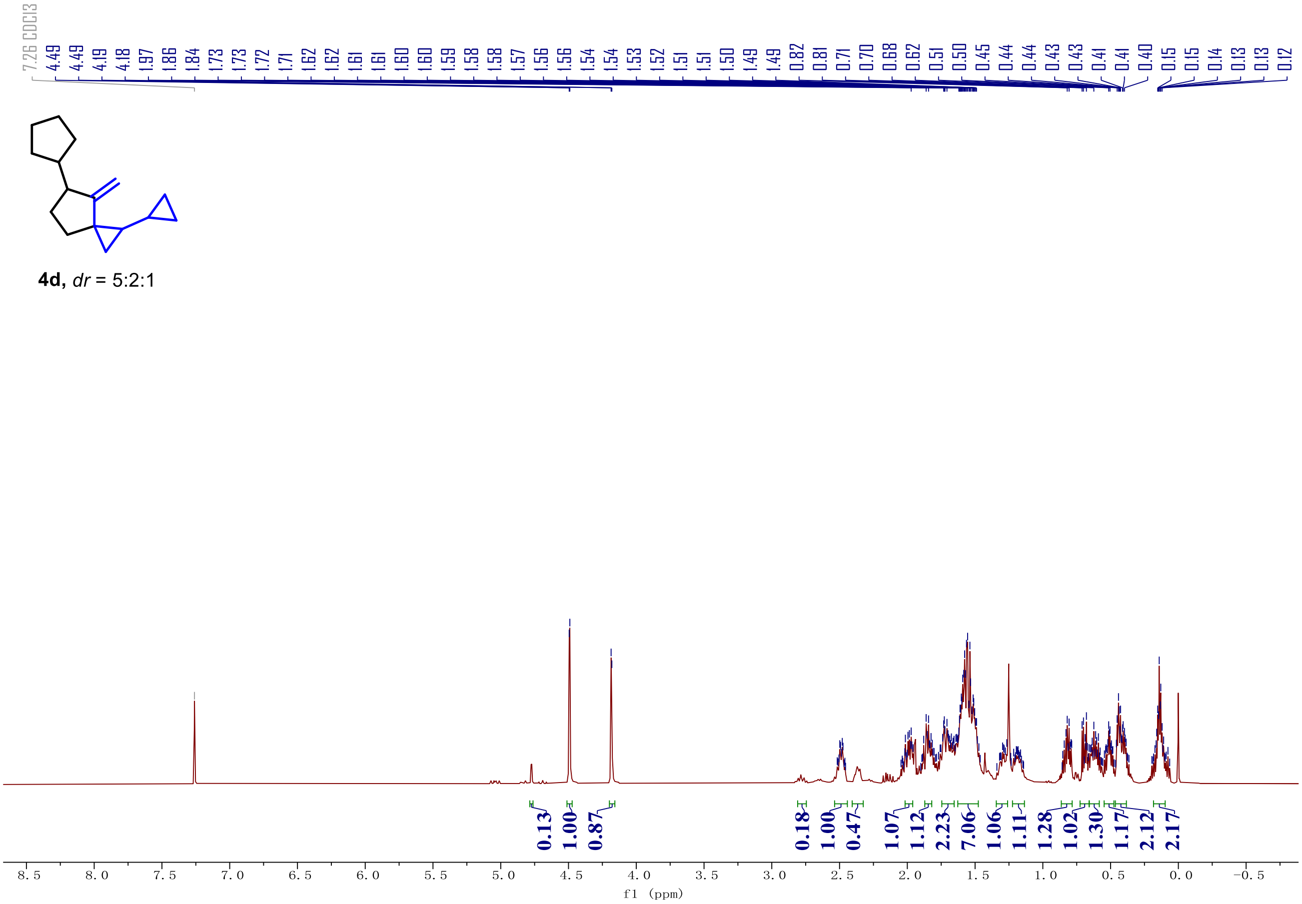
**4c**, *dr* = 1:1

### $^{13}$C NMR (101 MHz, CDCl$_3$):



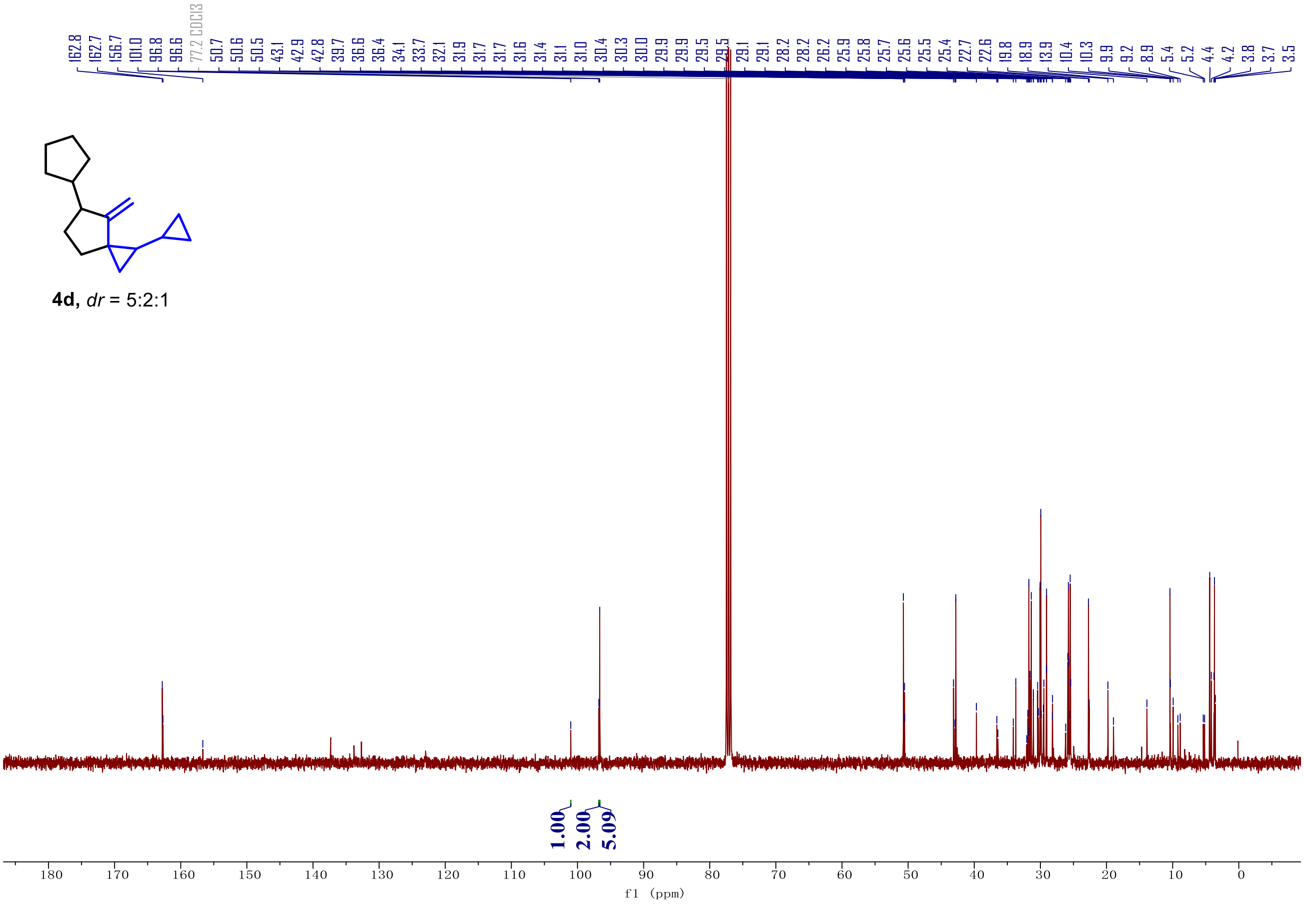
**4c**, *dr* = 1:1

## $^1$H NMR (400 MHz, CDCl$_3$):



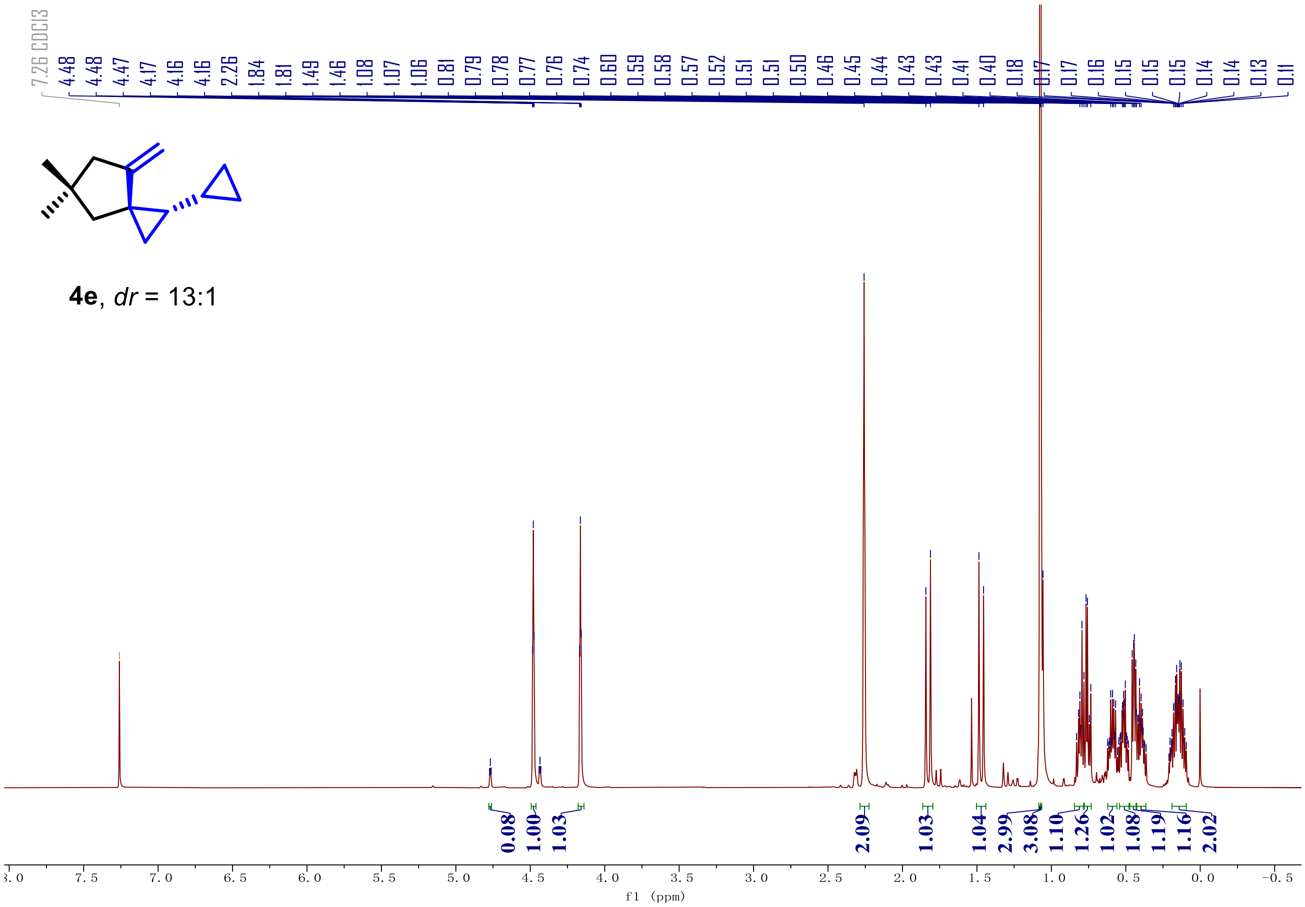
**4d,** *dr* = 5:2:1

## $^{13}$C NMR (101 MHz, CDCl$_3$):



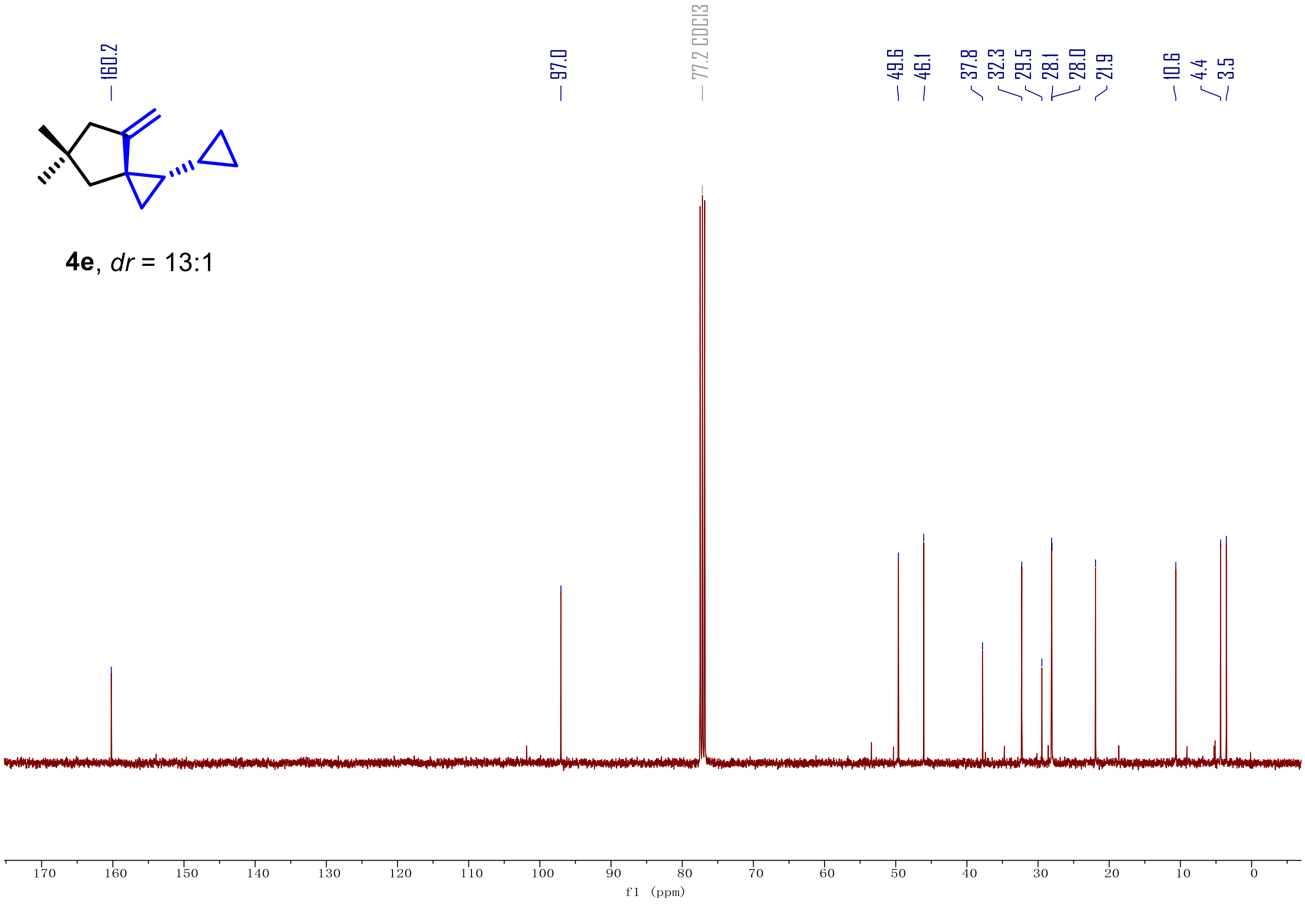
**4d,** *dr* = 5:2:1

$^1$H NMR (400 MHz, CDCl$_3$):



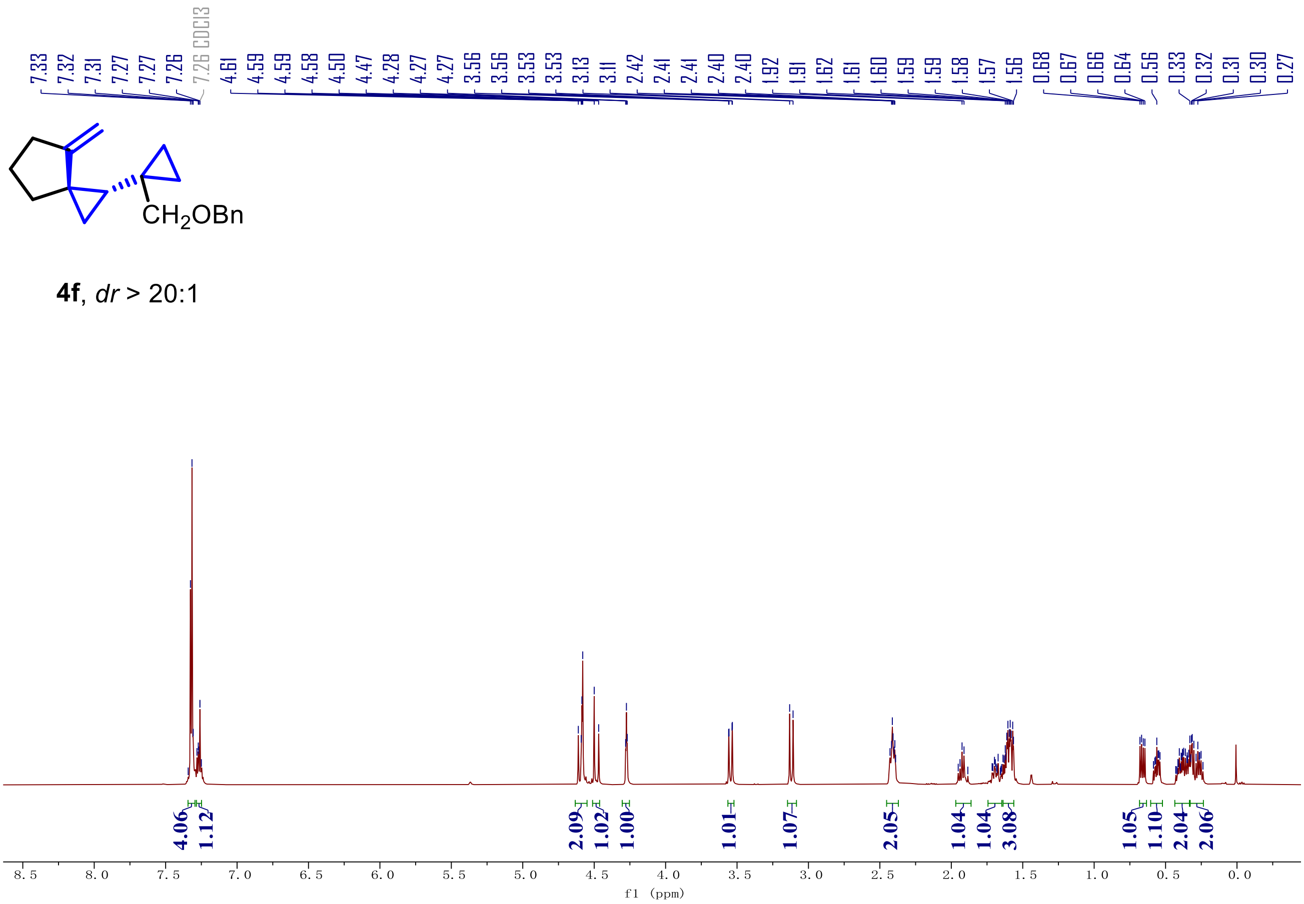
**4e**, *dr* = 13:1

$^{13}$C NMR (101 MHz, CDCl$_3$):



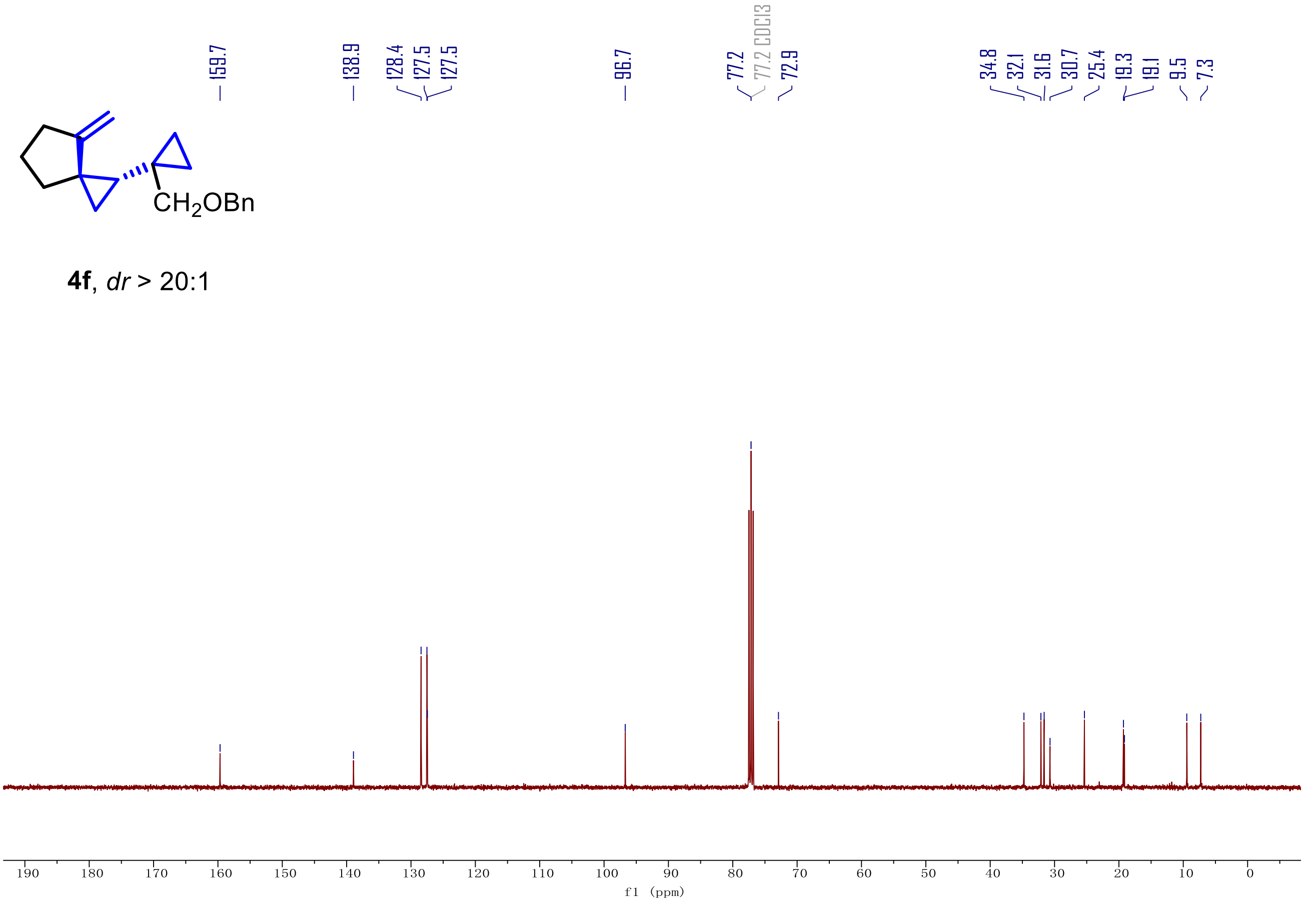
**4e**, *dr* = 13:1

$^{1}$H NMR (400 MHz, CDCl$_3$):



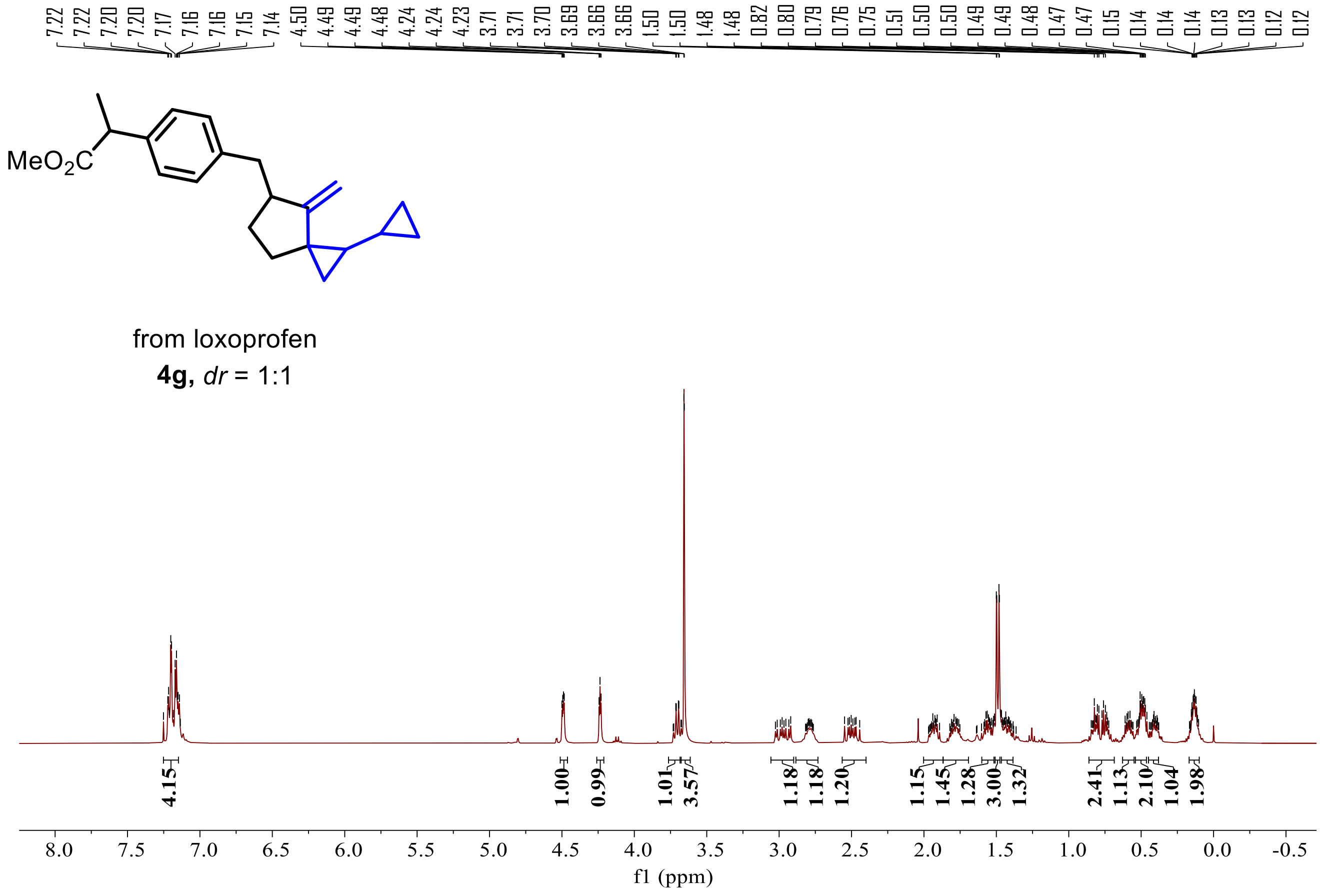
**4f**, *dr* > 20:1

$^{13}$C NMR (101 MHz, CDCl$_3$):



**4f**, *dr* > 20:1

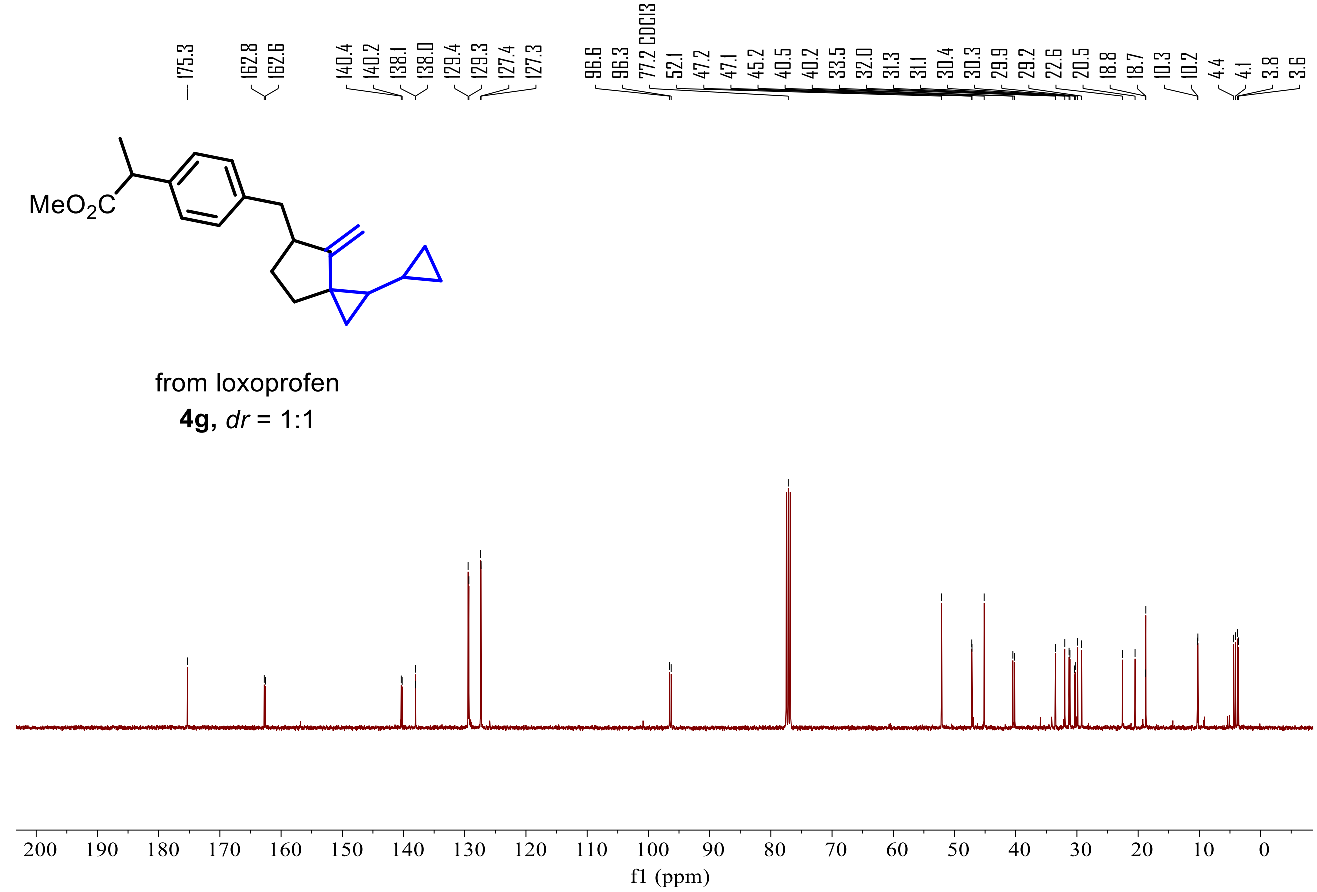
$^{1}H$ NMR (400 MHz, $CDCl_3$):



from loxoprofen

**4g**, *dr* = 1:1

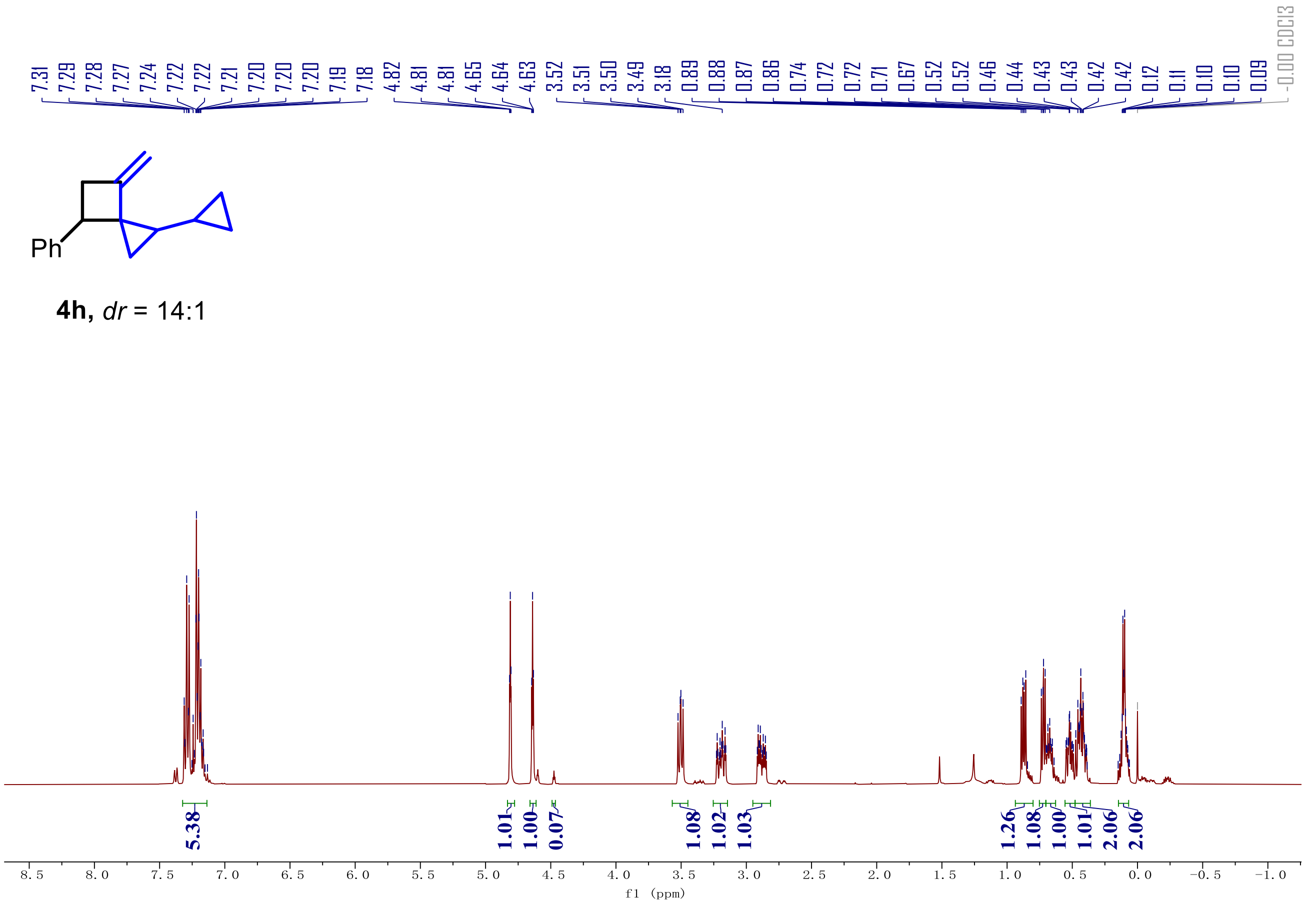
$^{13}C$ NMR (101 MHz, $CDCl_3$):



from loxoprofen

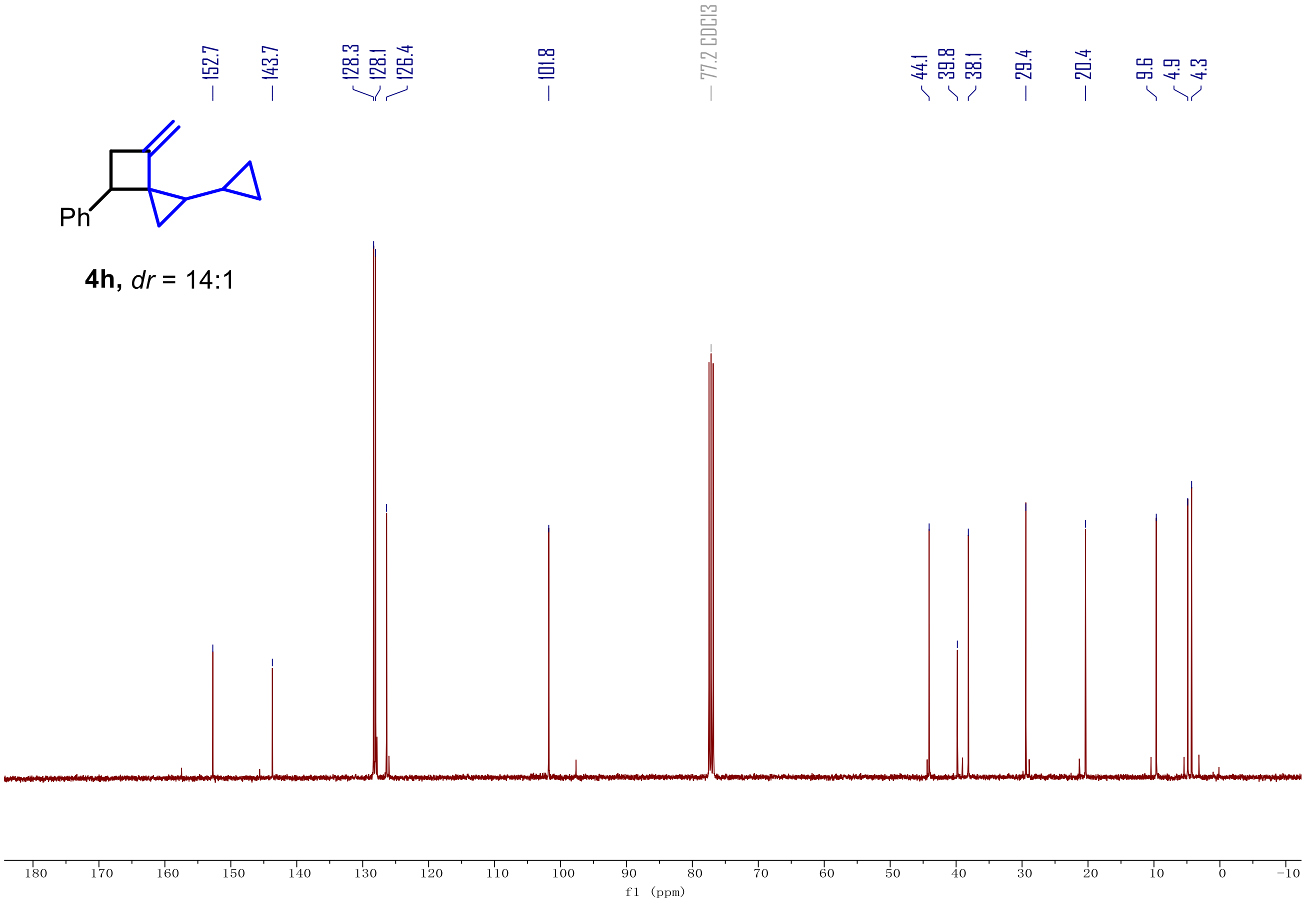
**4g**, *dr* = 1:1

$^1$H NMR (400 MHz, CDCl$_3$):



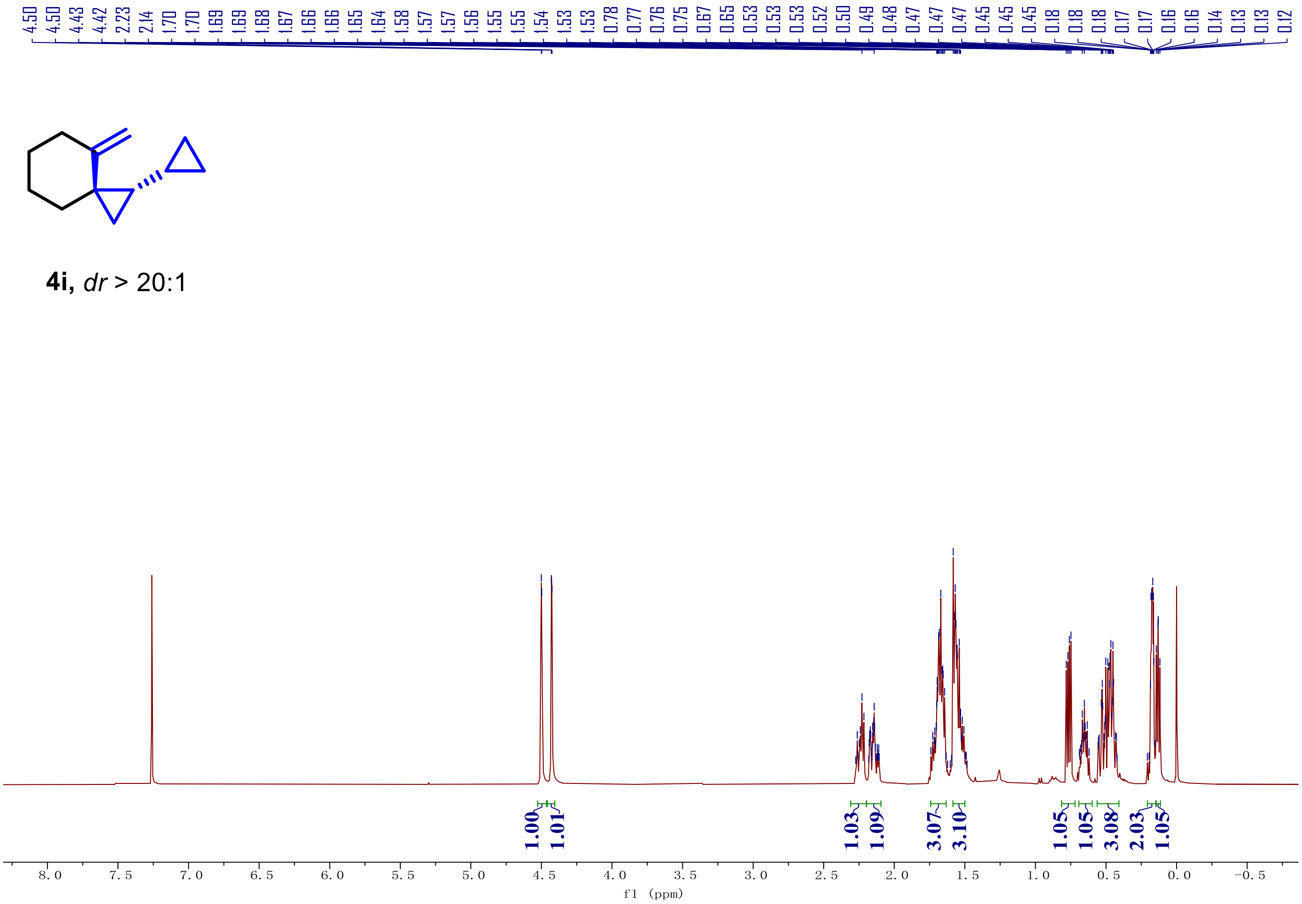
**4h,** *dr* = 14:1

$^{13}$C NMR (101 MHz, CDCl$_3$):



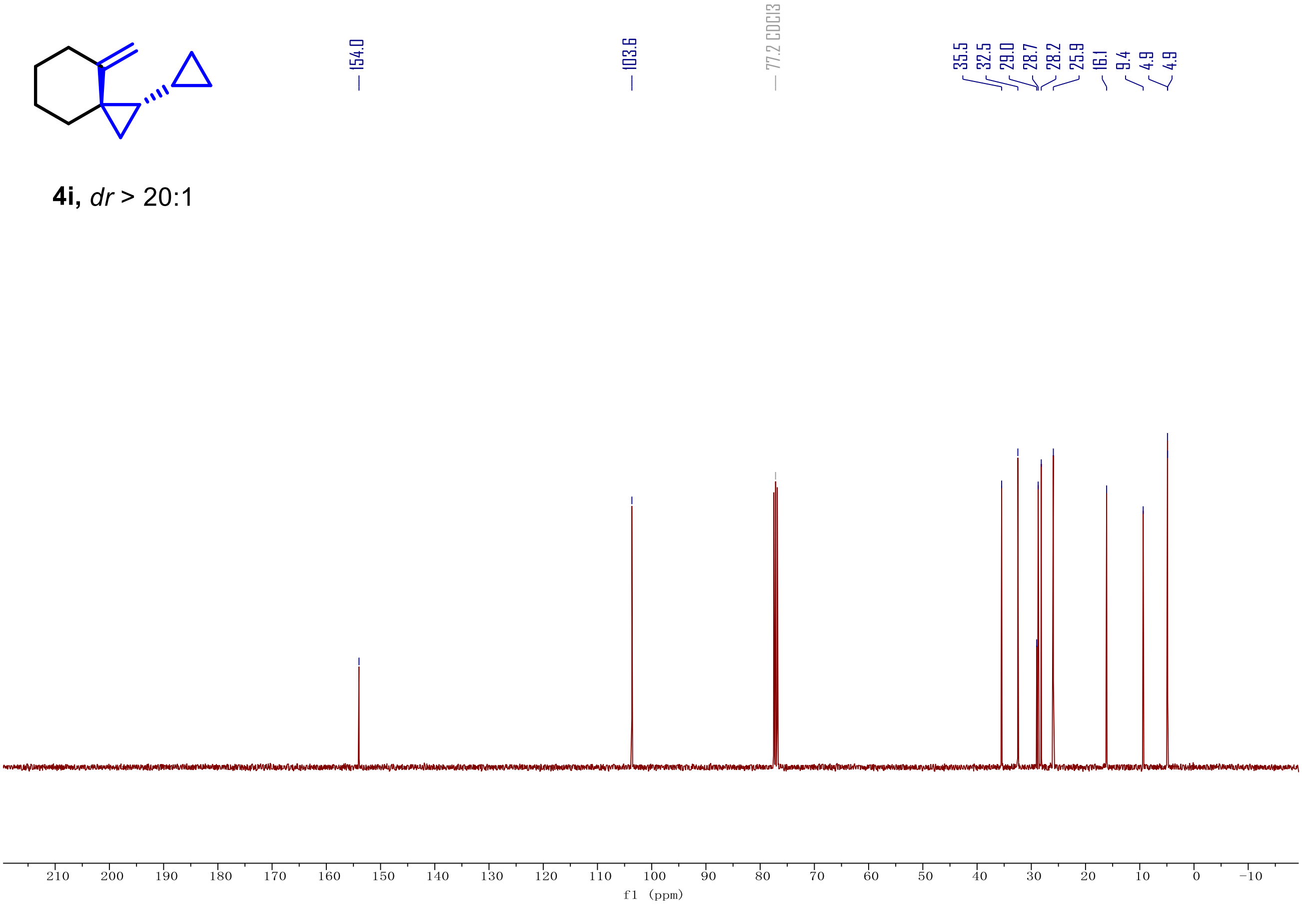
**4h,** *dr* = 14:1

$^1$H NMR (400 MHz, $CDCl_3$):



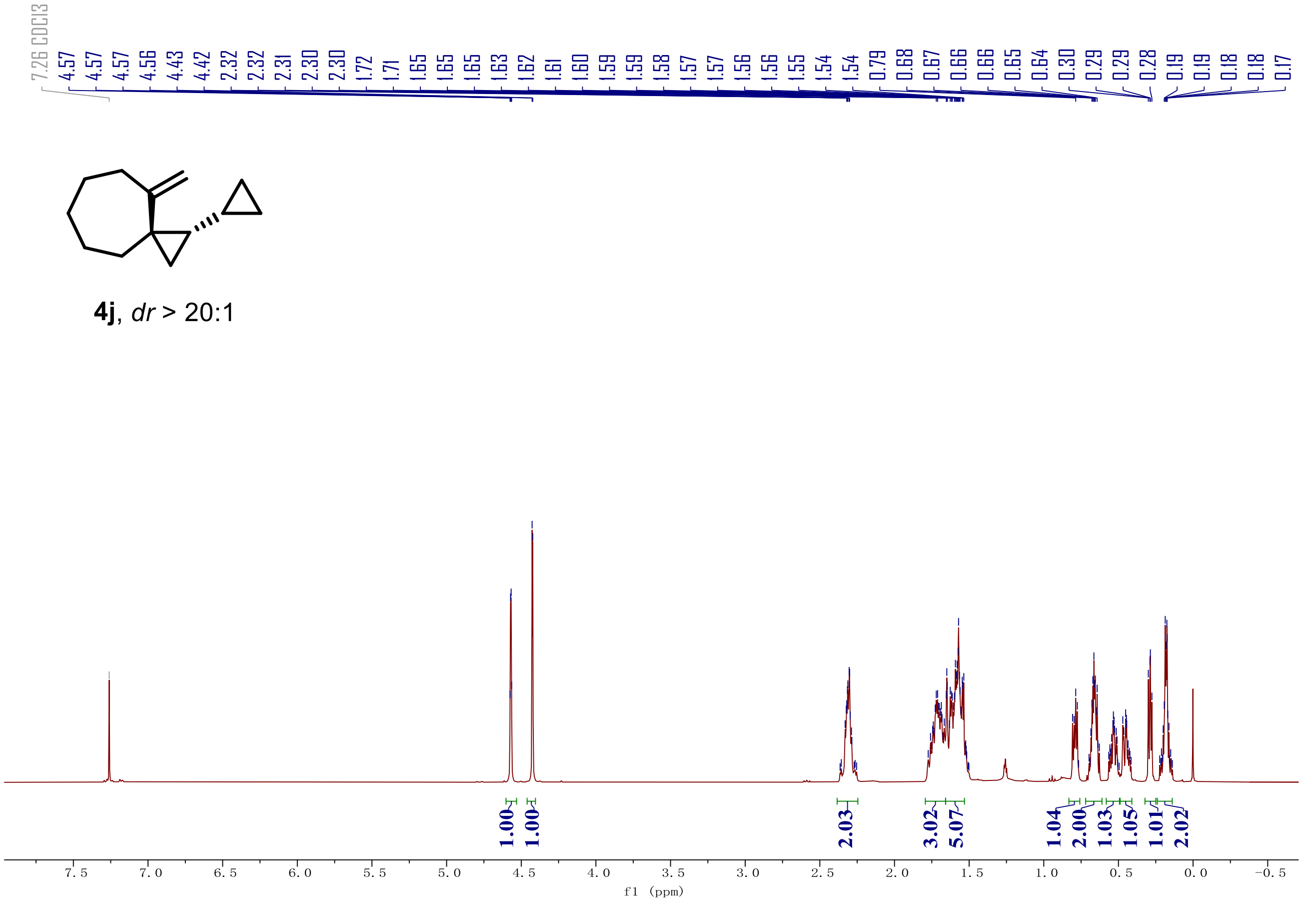
**4i,** *dr* > 20:1

$^{13}$C NMR (101 MHz, $CDCl_3$):



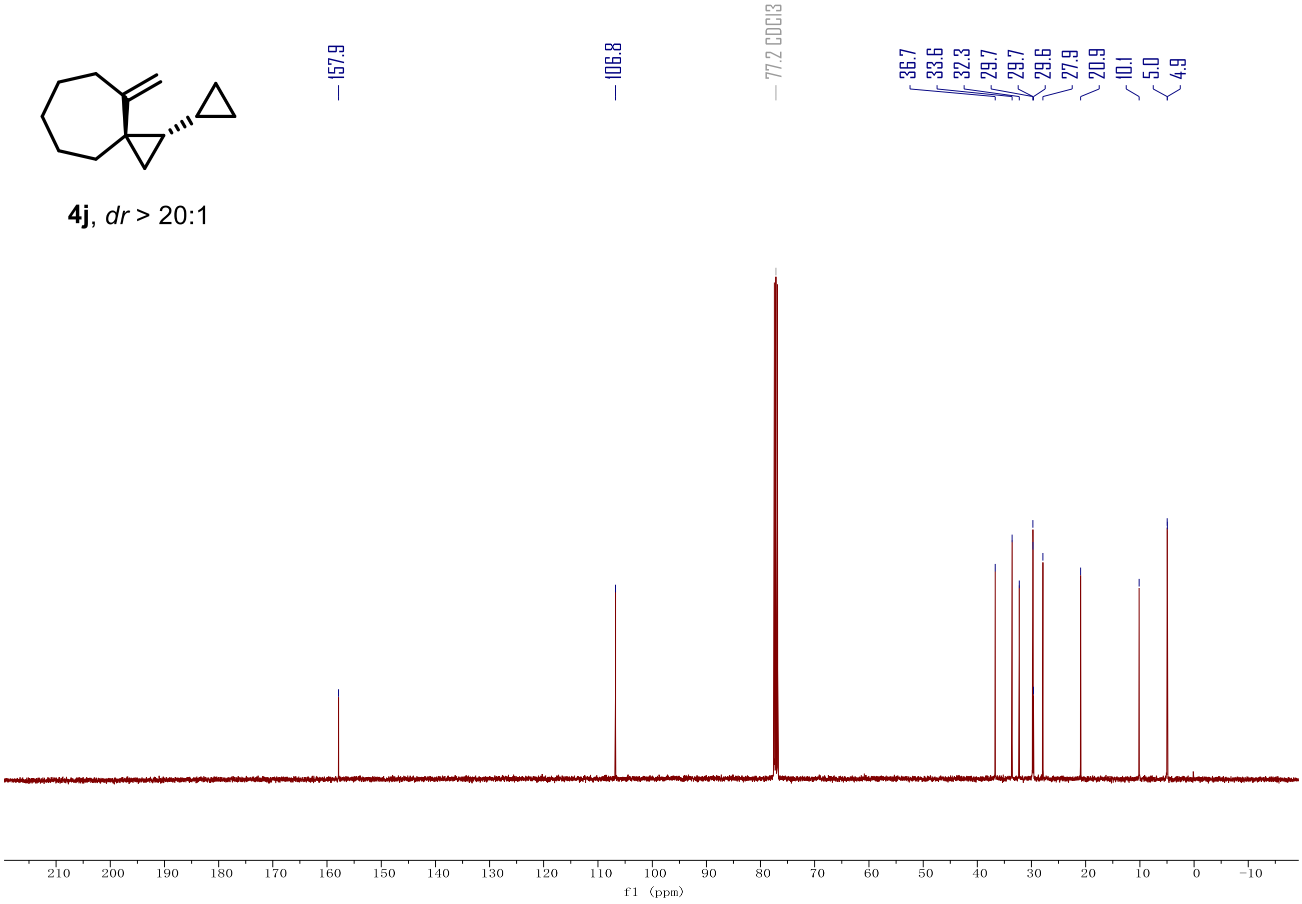
**4i,** *dr* > 20:1

## $^1$H NMR (400 MHz, $CDCl_3$):



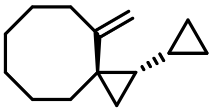
**4j**, *dr* > 20:1

## $^{13}$C NMR (101 MHz, $CDCl_3$):

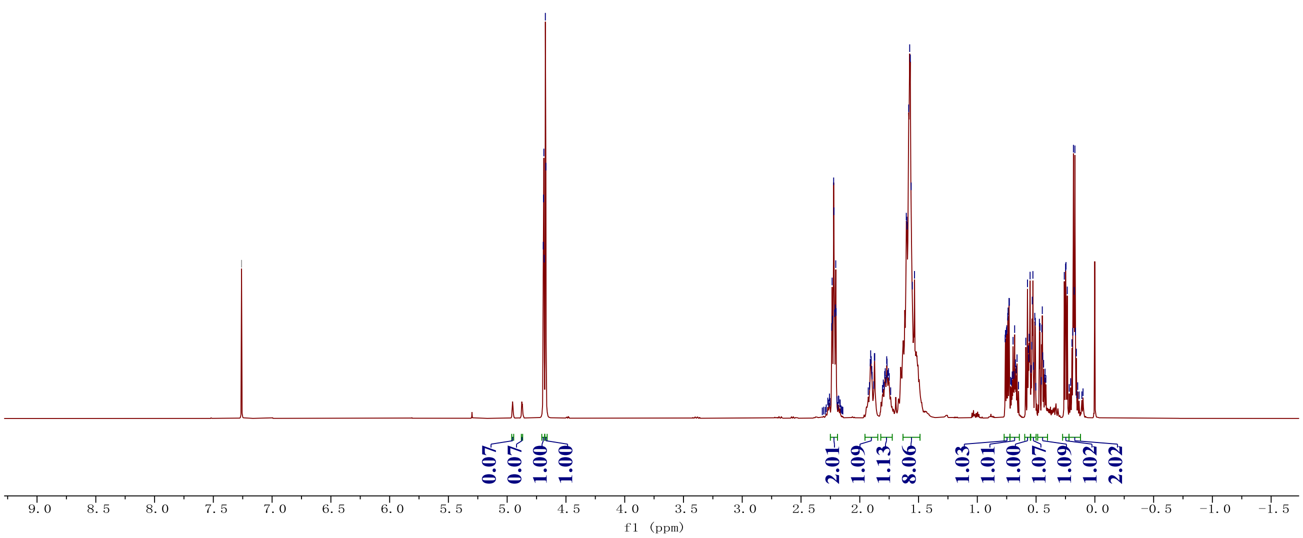


**4j**, *dr* > 20:1

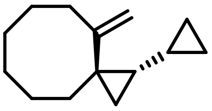
$^1$H NMR (400 MHz, CDCl$_3$):



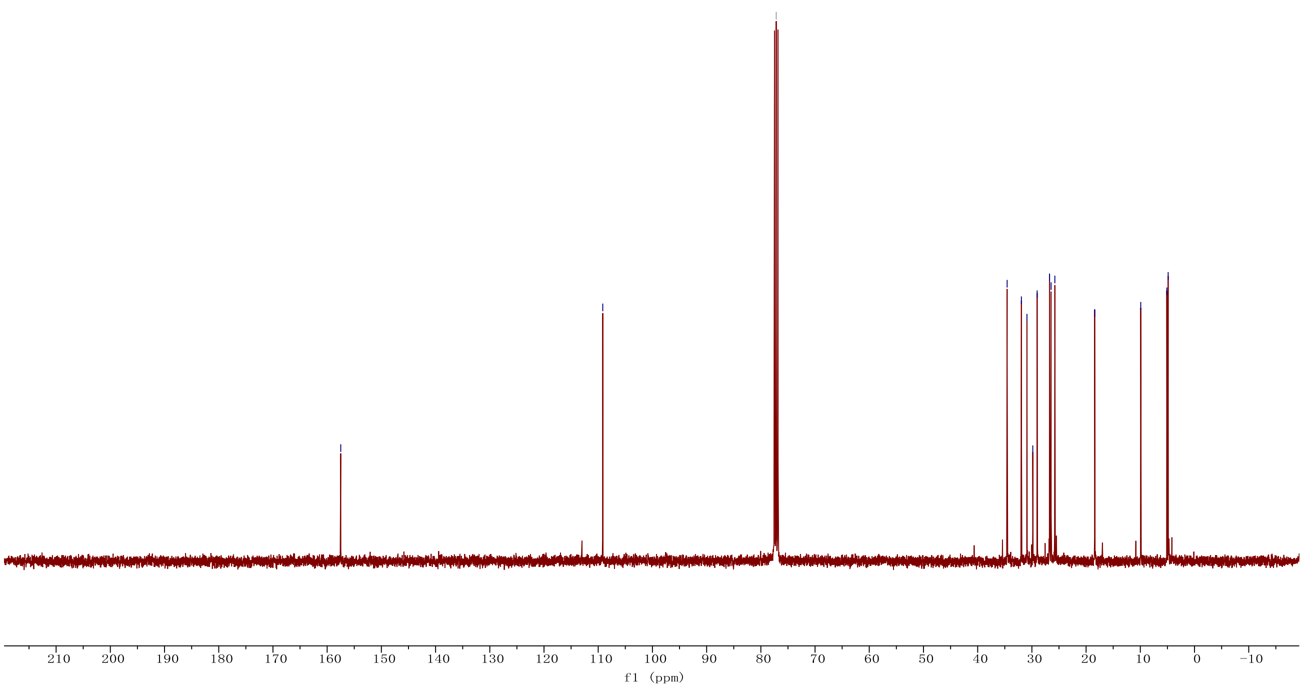
**4k**, *dr* = 14:1



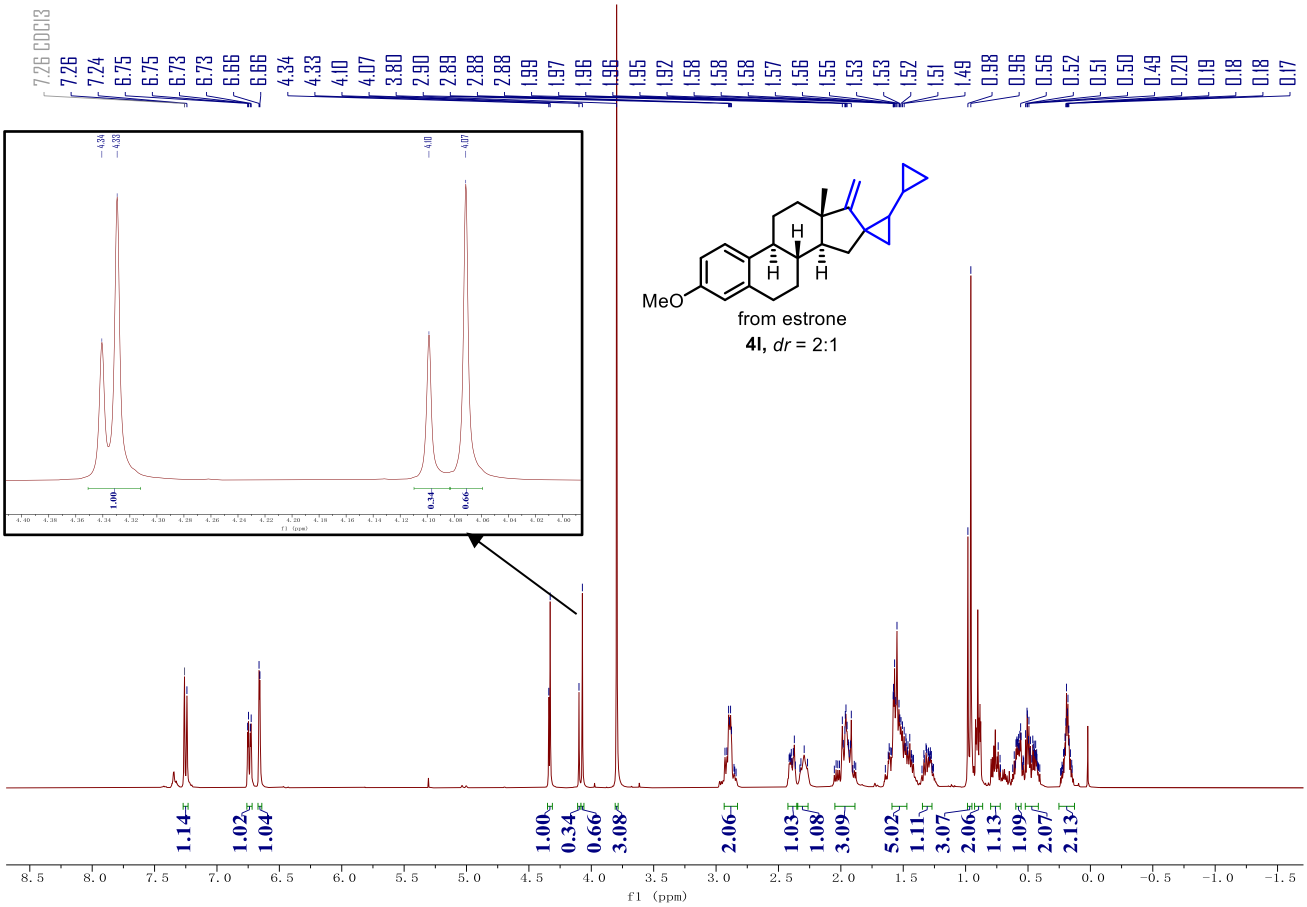
$^{13}$C NMR (101 MHz, CDCl$_3$):



**4k**, *dr* = 14:1



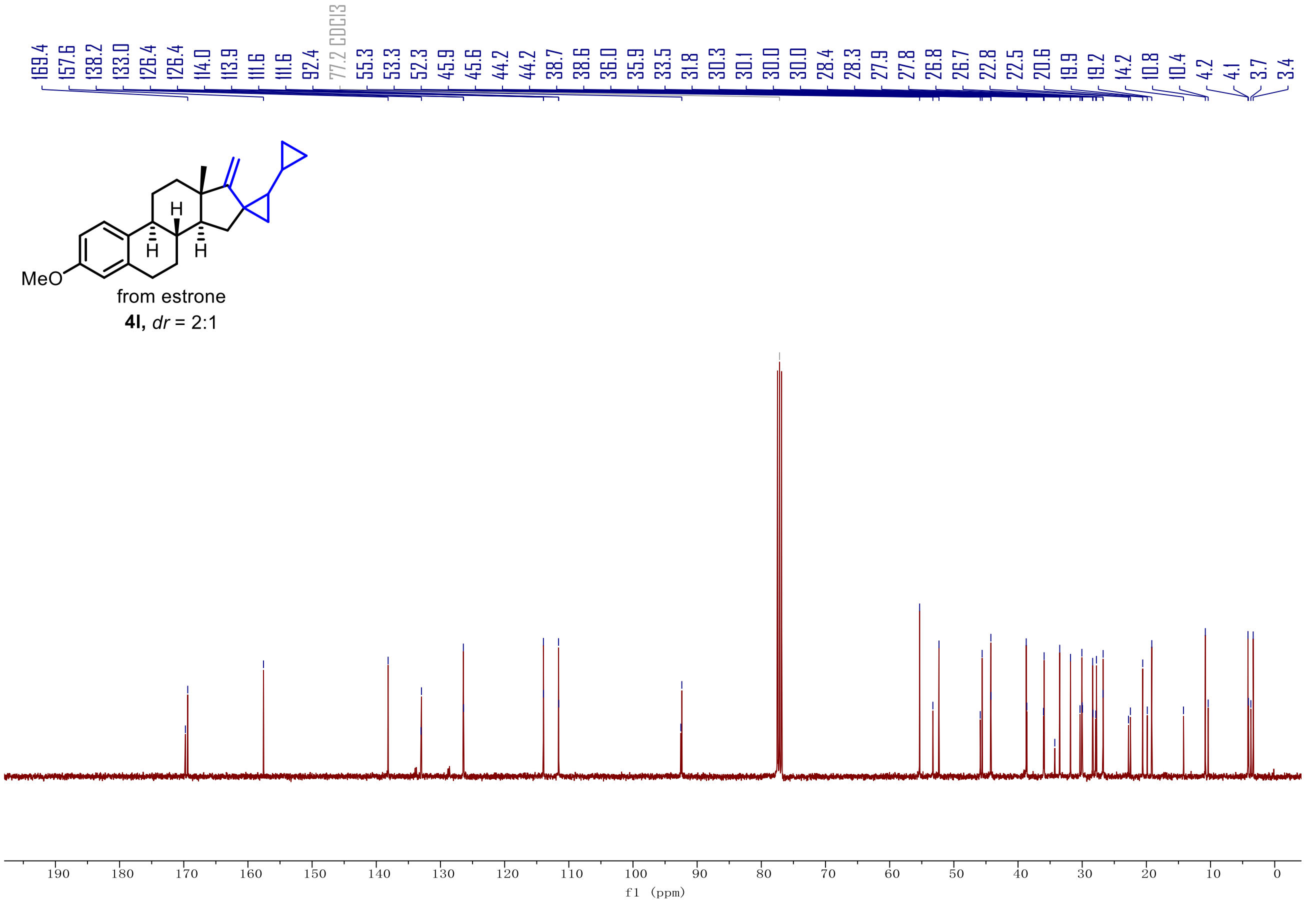
## $^{1}$H NMR (400 MHz, CDCl$_3$):



from estrone

**4l,** *dr* = 2:1

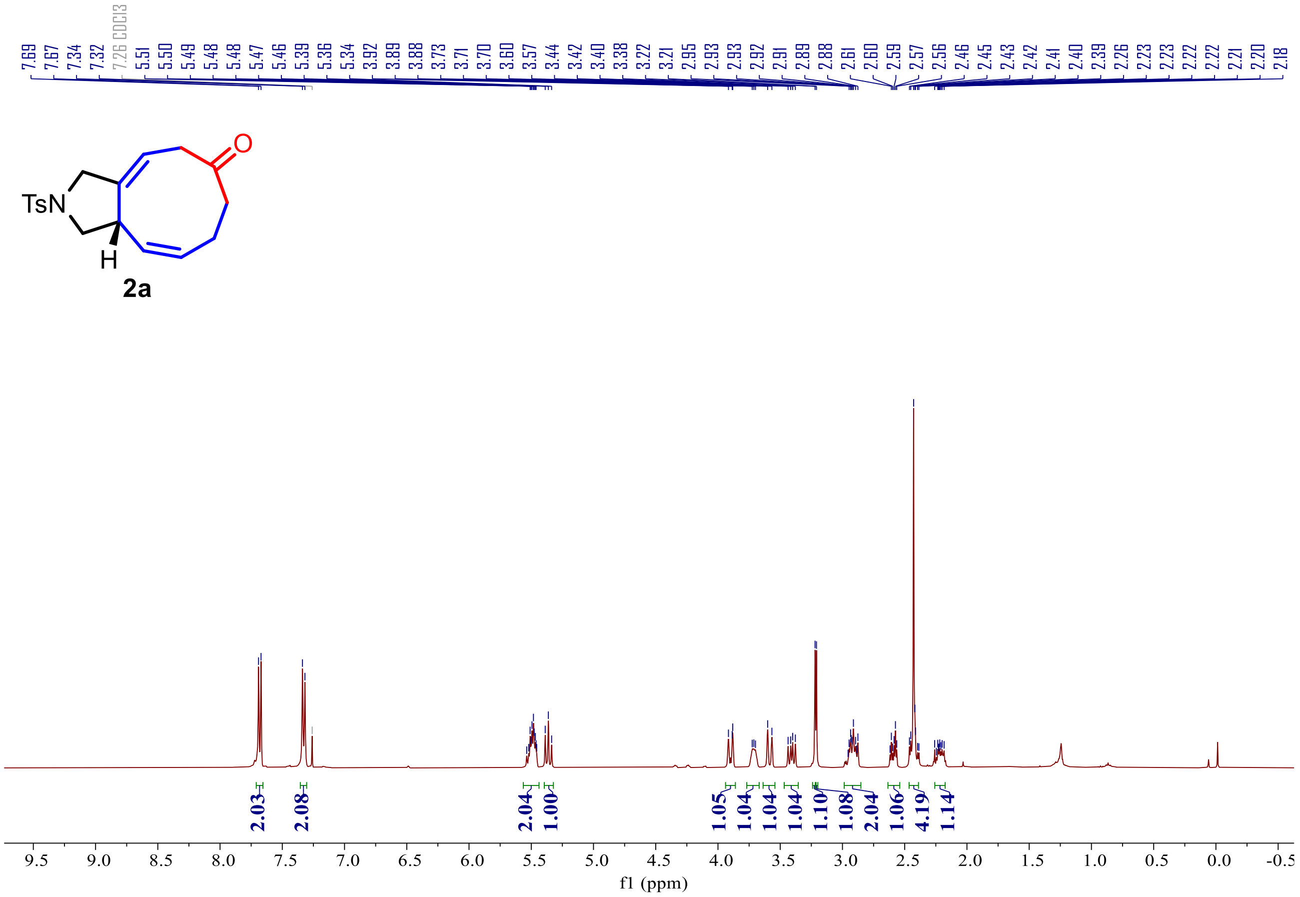
## $^{13}$C NMR (101 MHz, CDCl$_3$):



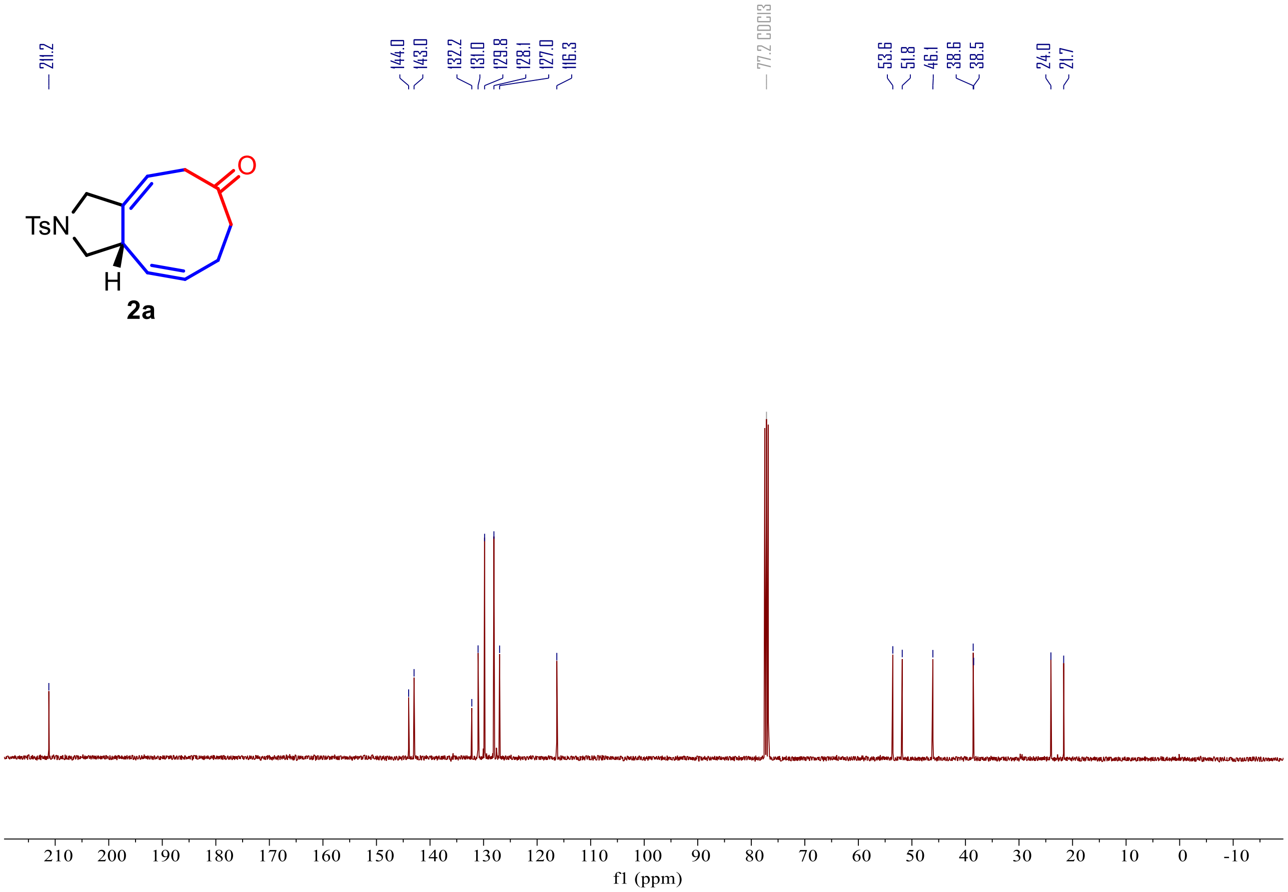
from estrone

**4l,** *dr* = 2:1

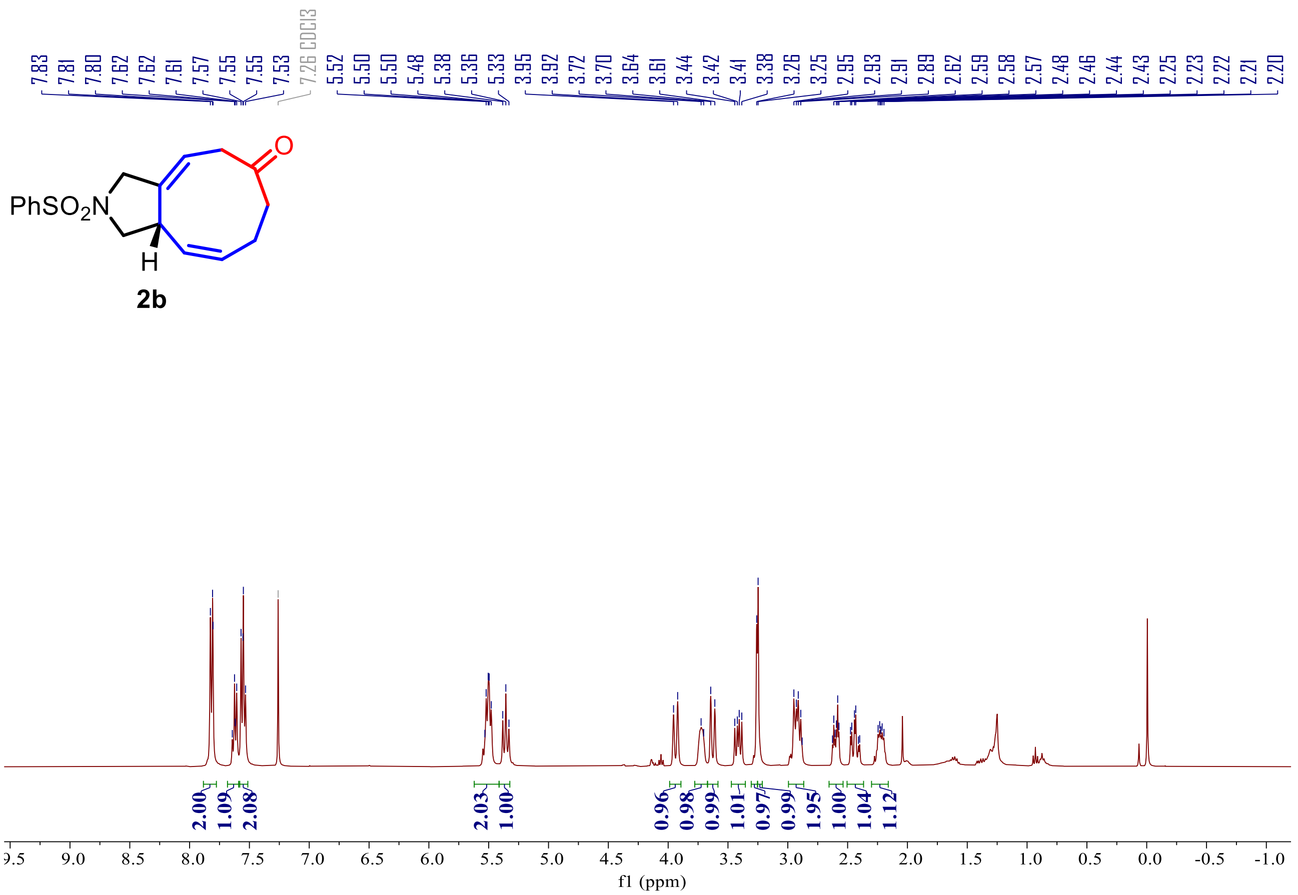
## $^1$H NMR (400 MHz, CDCl$_3$):



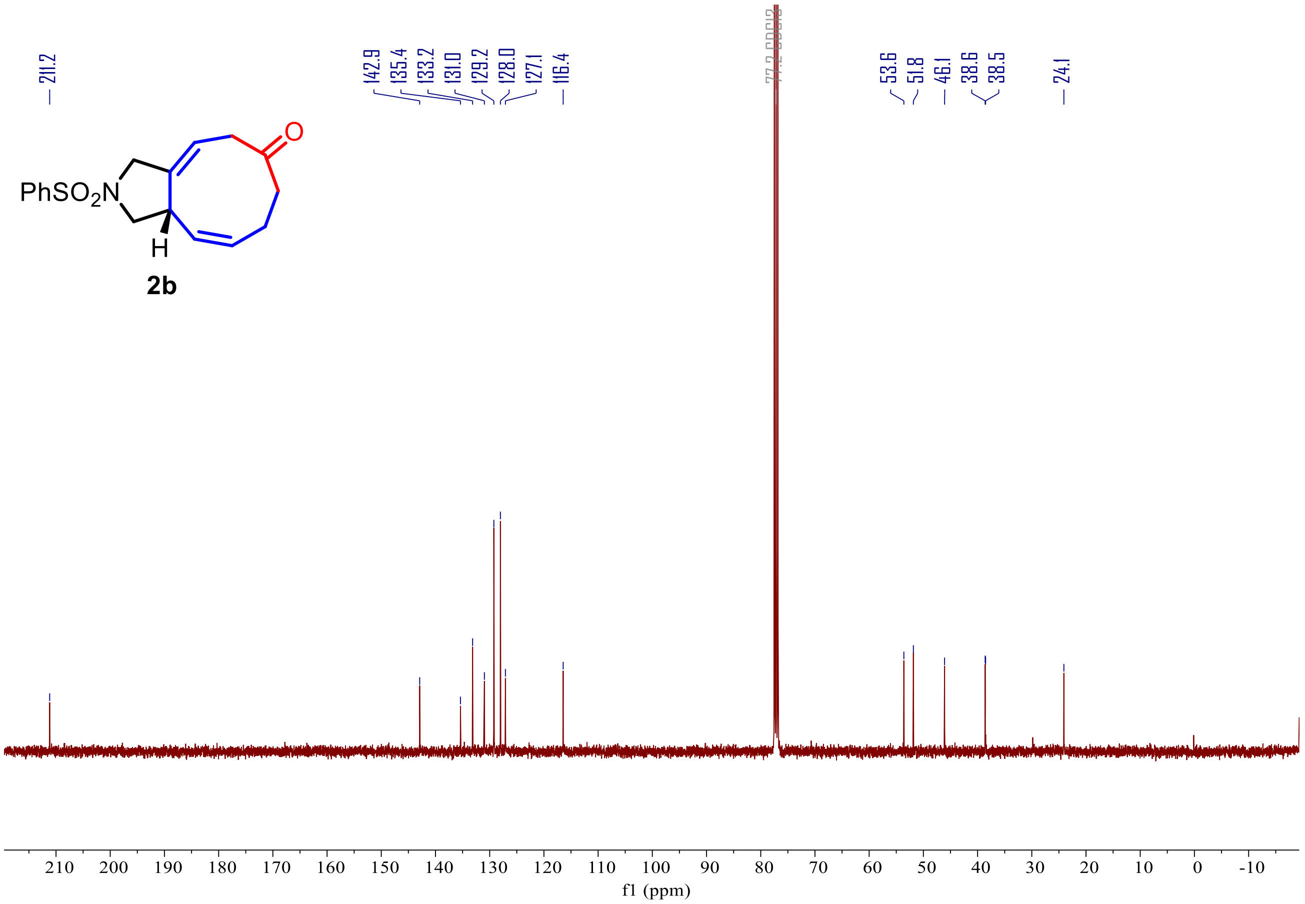
## $^{13}$C NMR (101 MHz, CDCl$_3$):



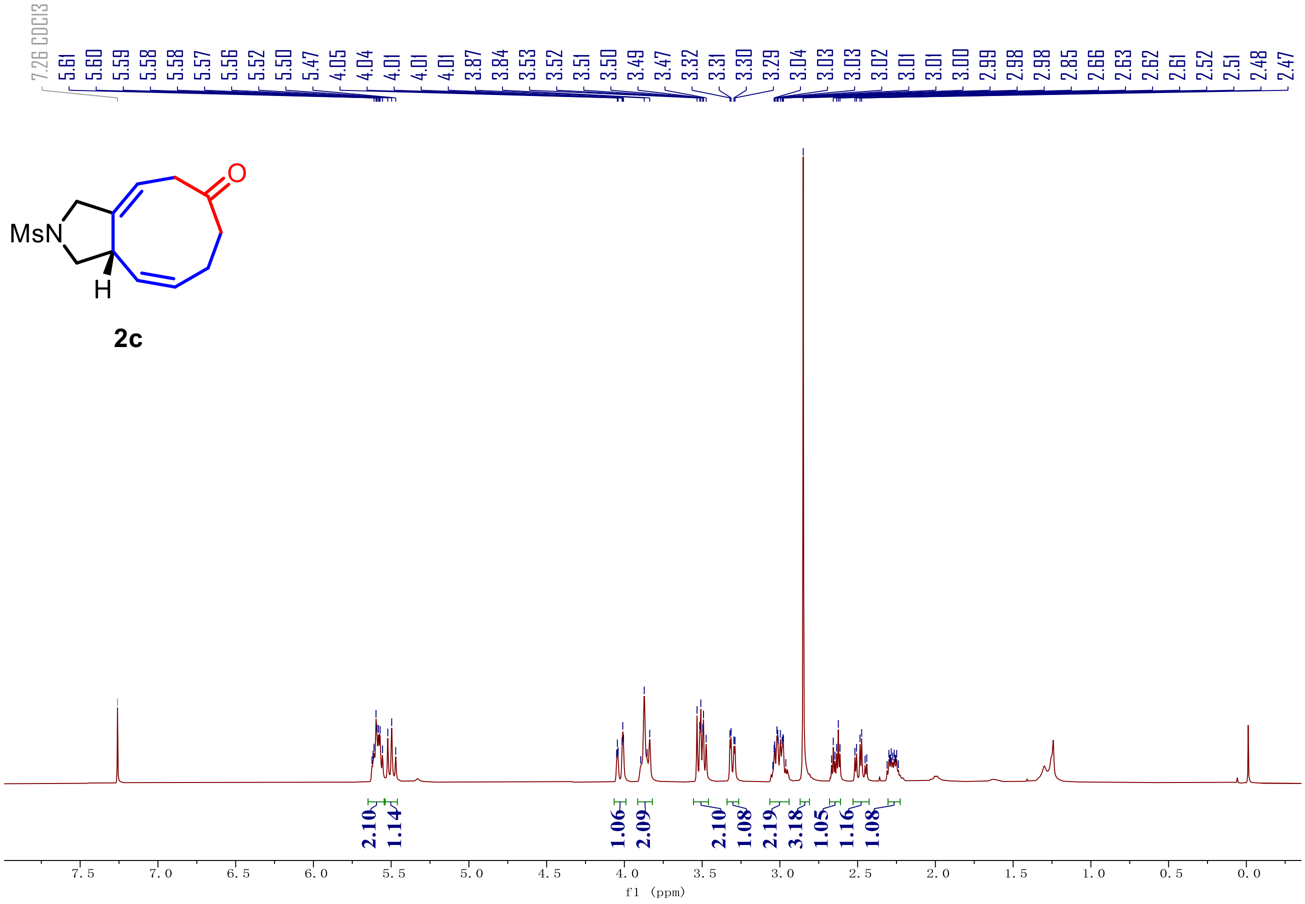
$^1$H NMR (400 MHz, $CDCl_3$):



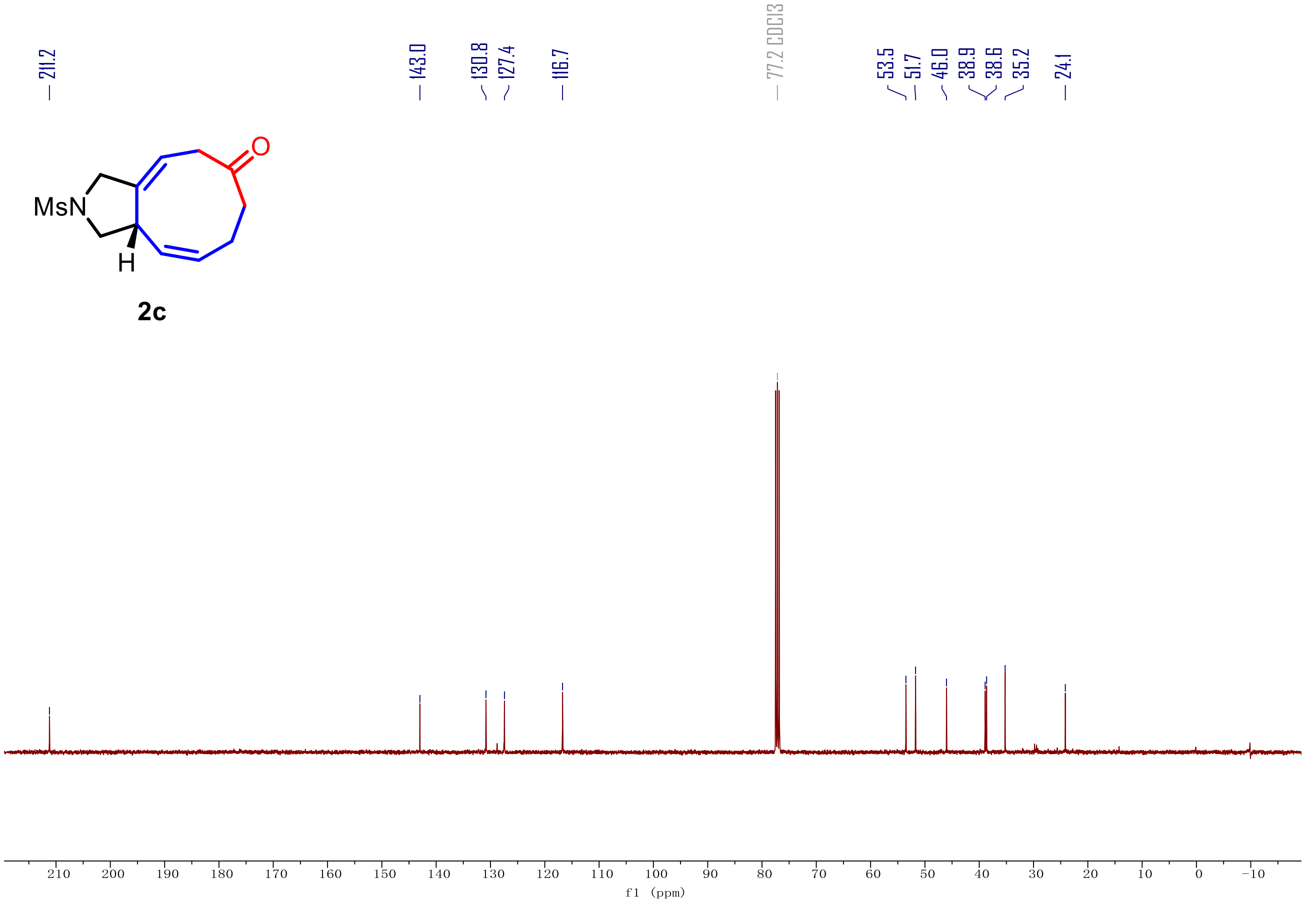
$^{13}$C NMR (101 MHz, $CDCl_3$):



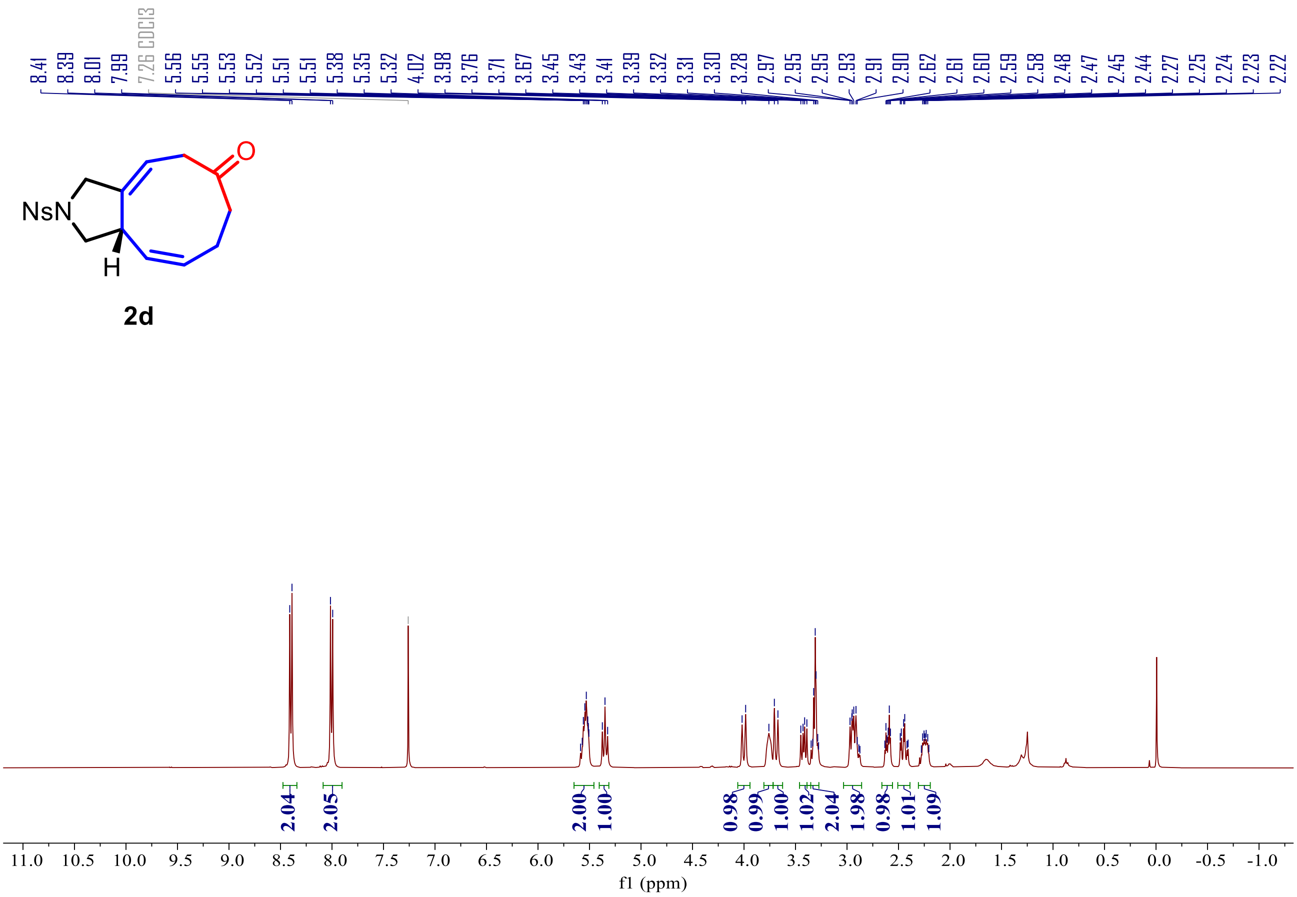
$^1$H NMR (400 MHz, CDCl$_3$):



$^{13}$C NMR (101 MHz, CDCl$_3$):

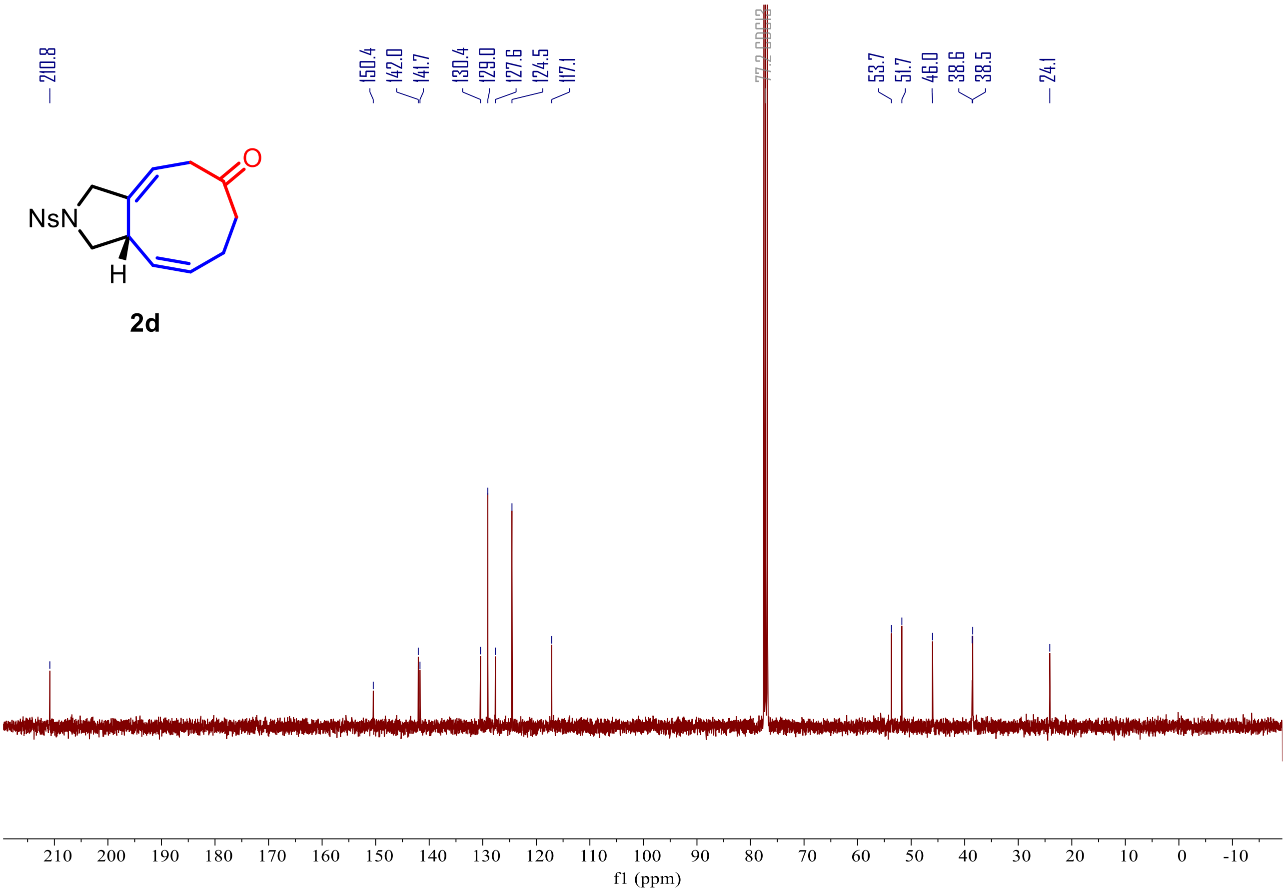


## $^1H$ NMR (400 MHz, $CDCl_3$):



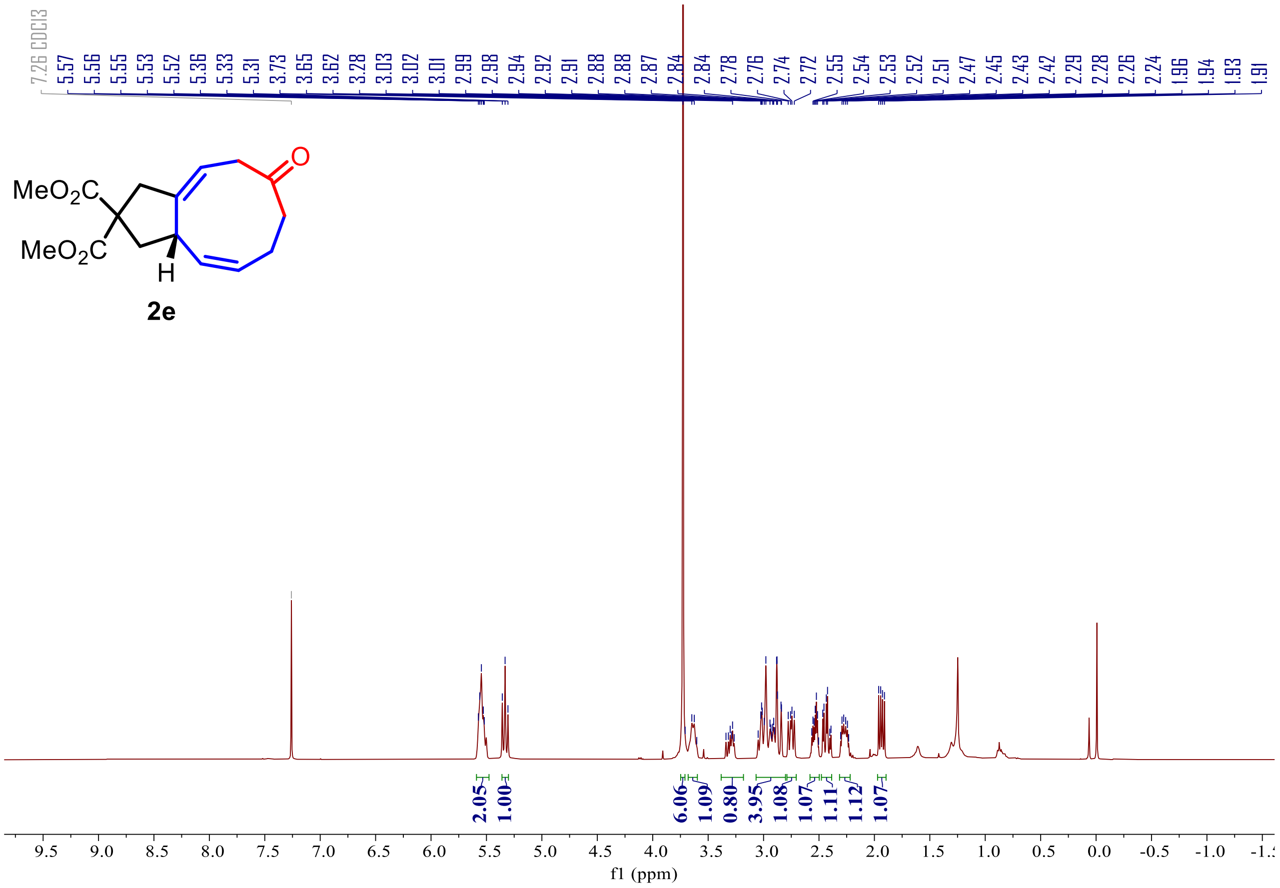
**2d**

## $^{13}C$ NMR (101 MHz, $CDCl_3$):

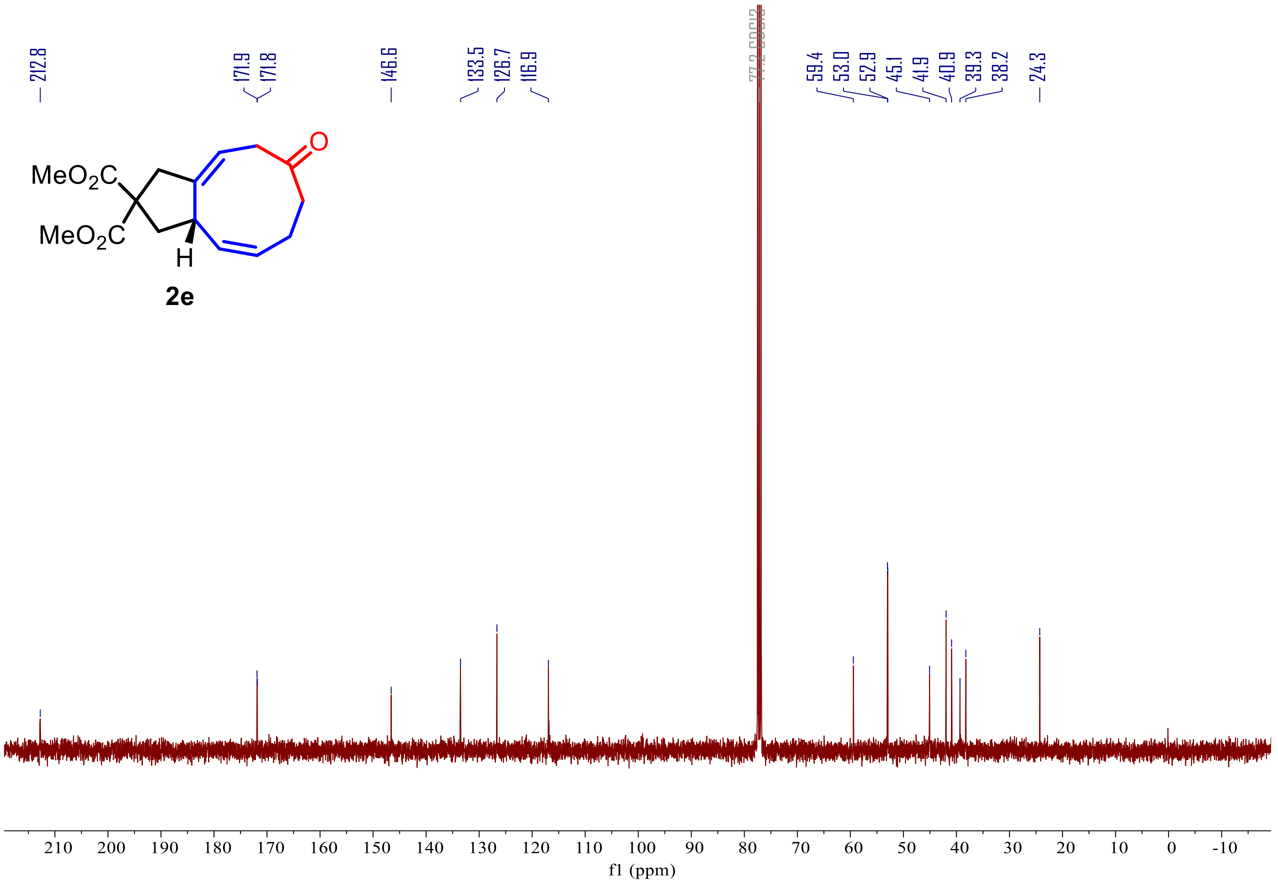


**2d**

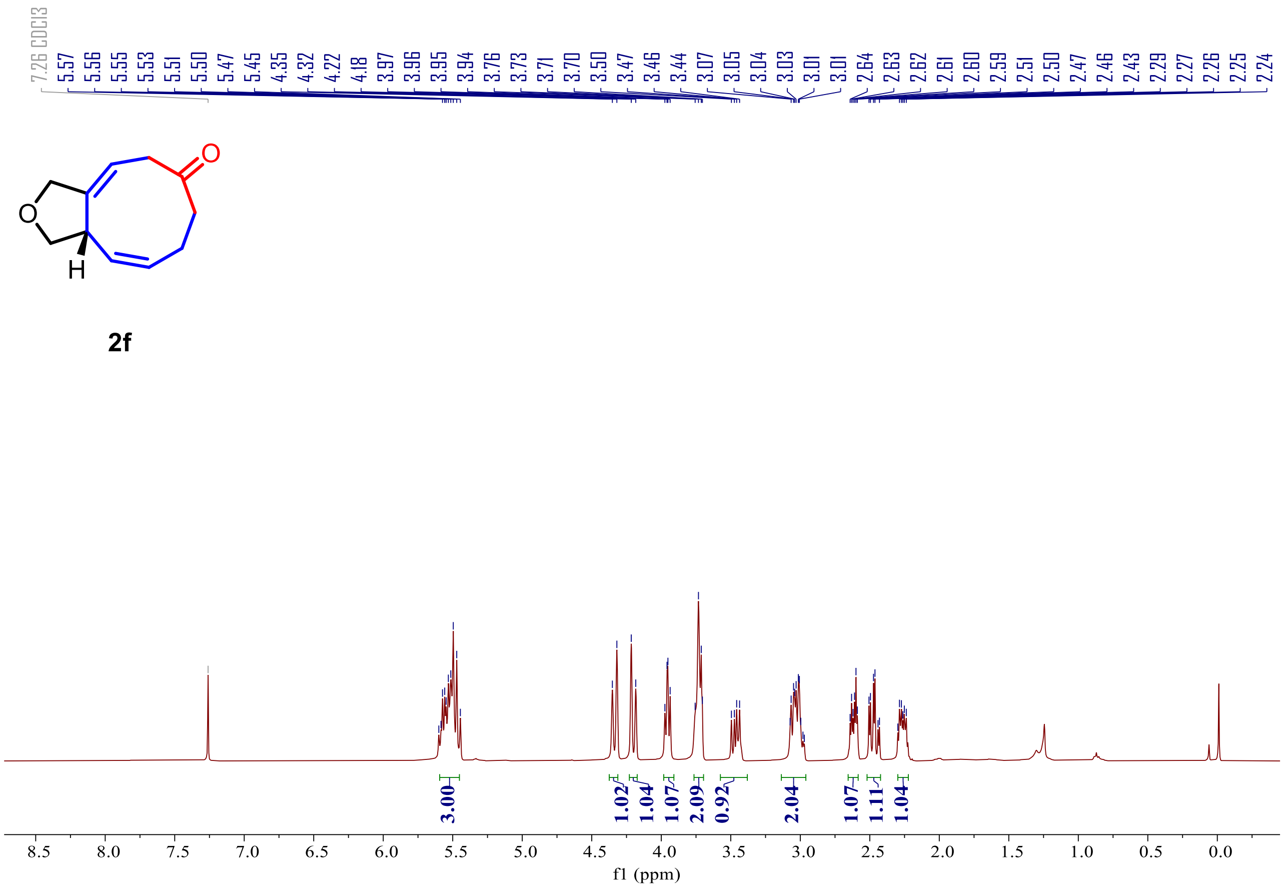
$^1$H NMR (400 MHz, CDCl$_3$):



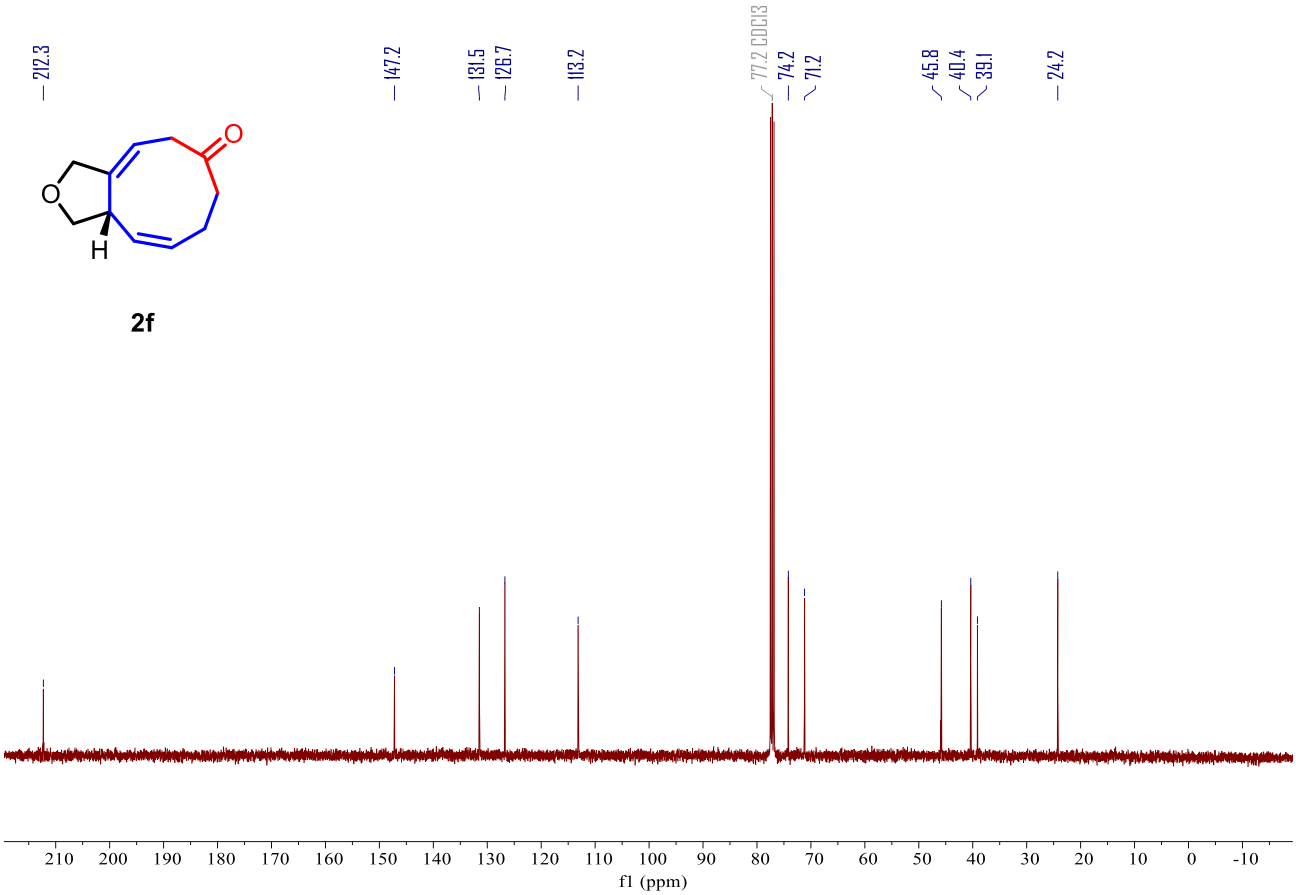
$^{13}$C NMR (101 MHz, CDCl$_3$):



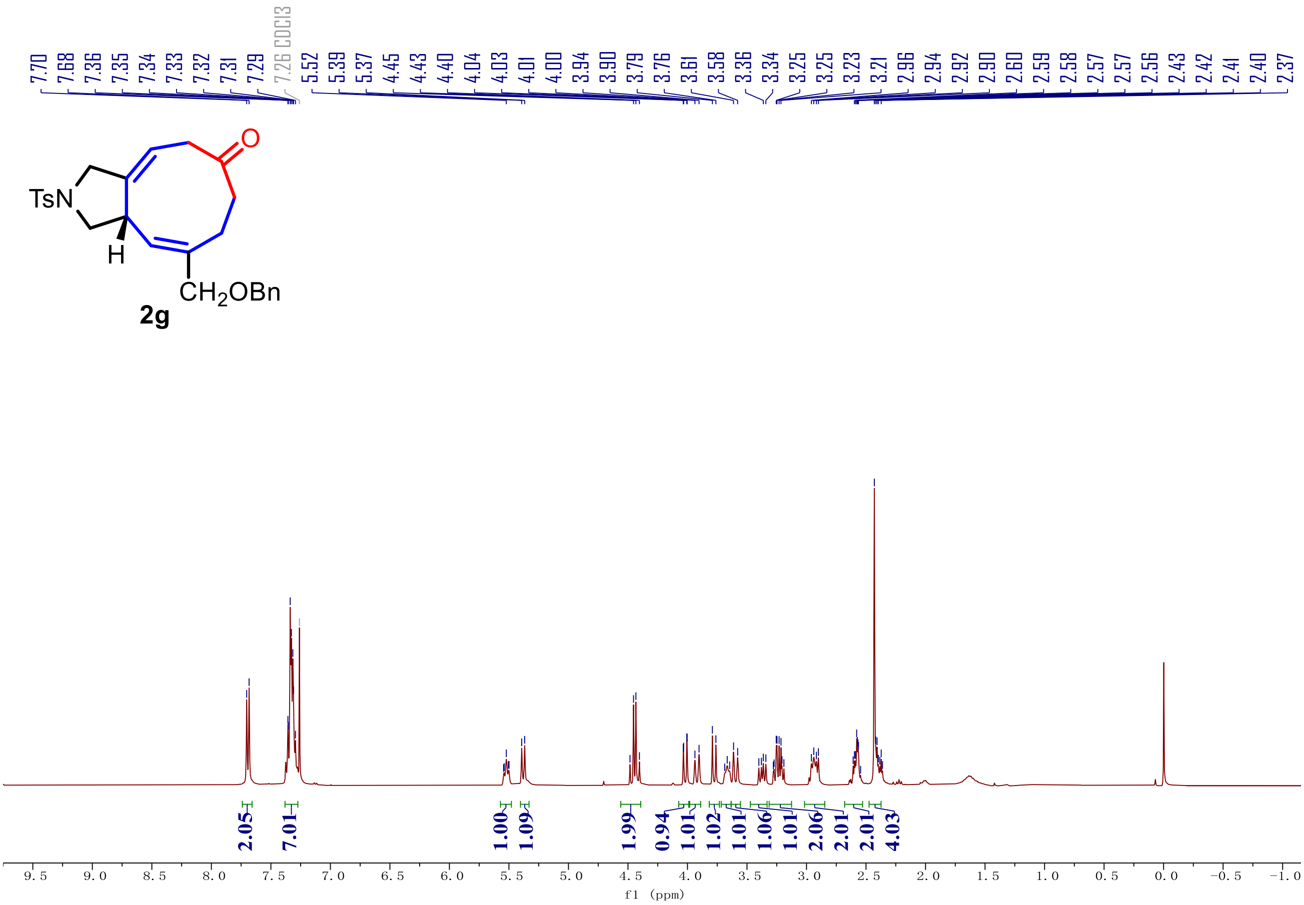
## $^1$H NMR (400 MHz, $CDCl_3$):



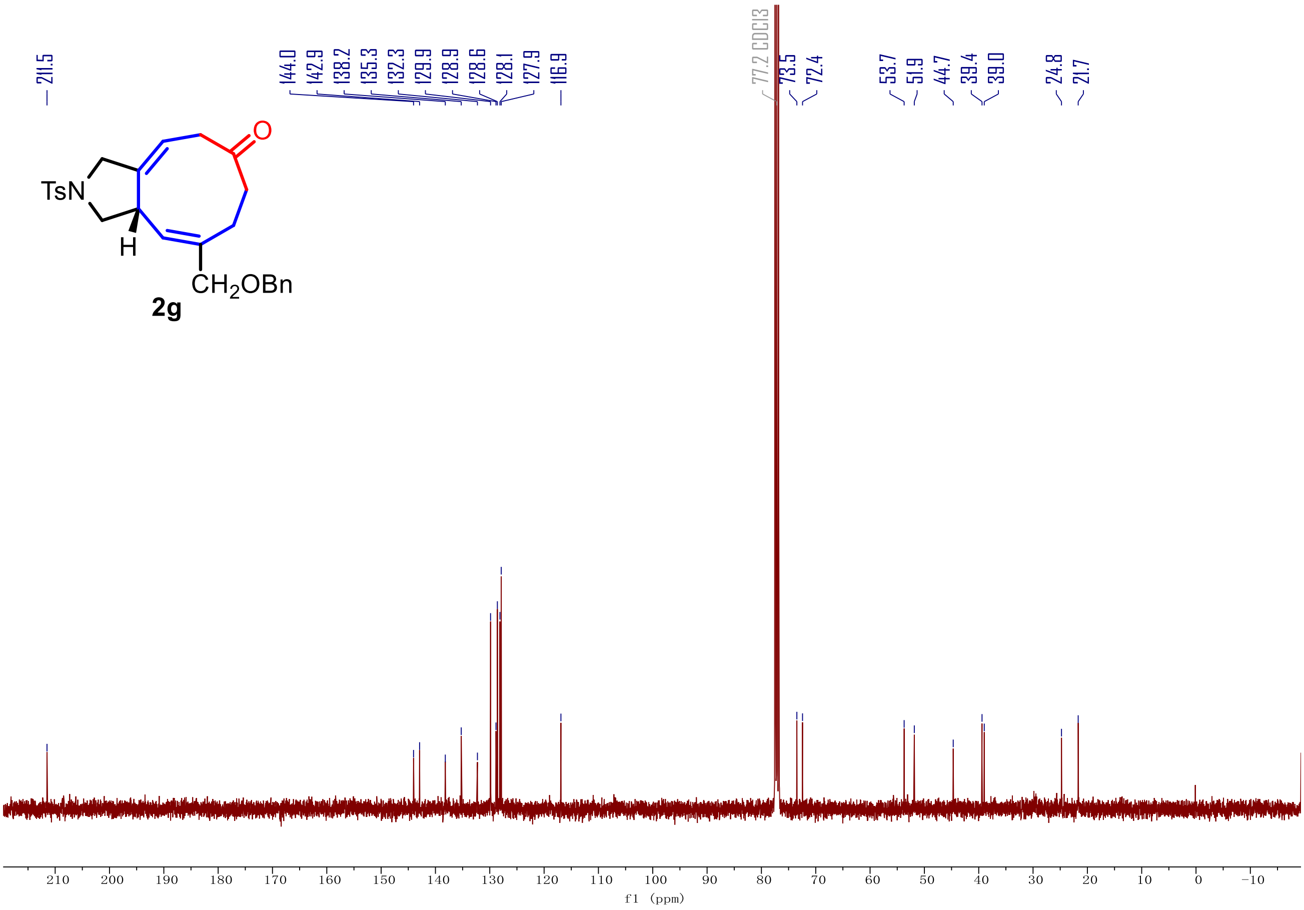
## $^{13}$C NMR (101 MHz, $CDCl_3$):



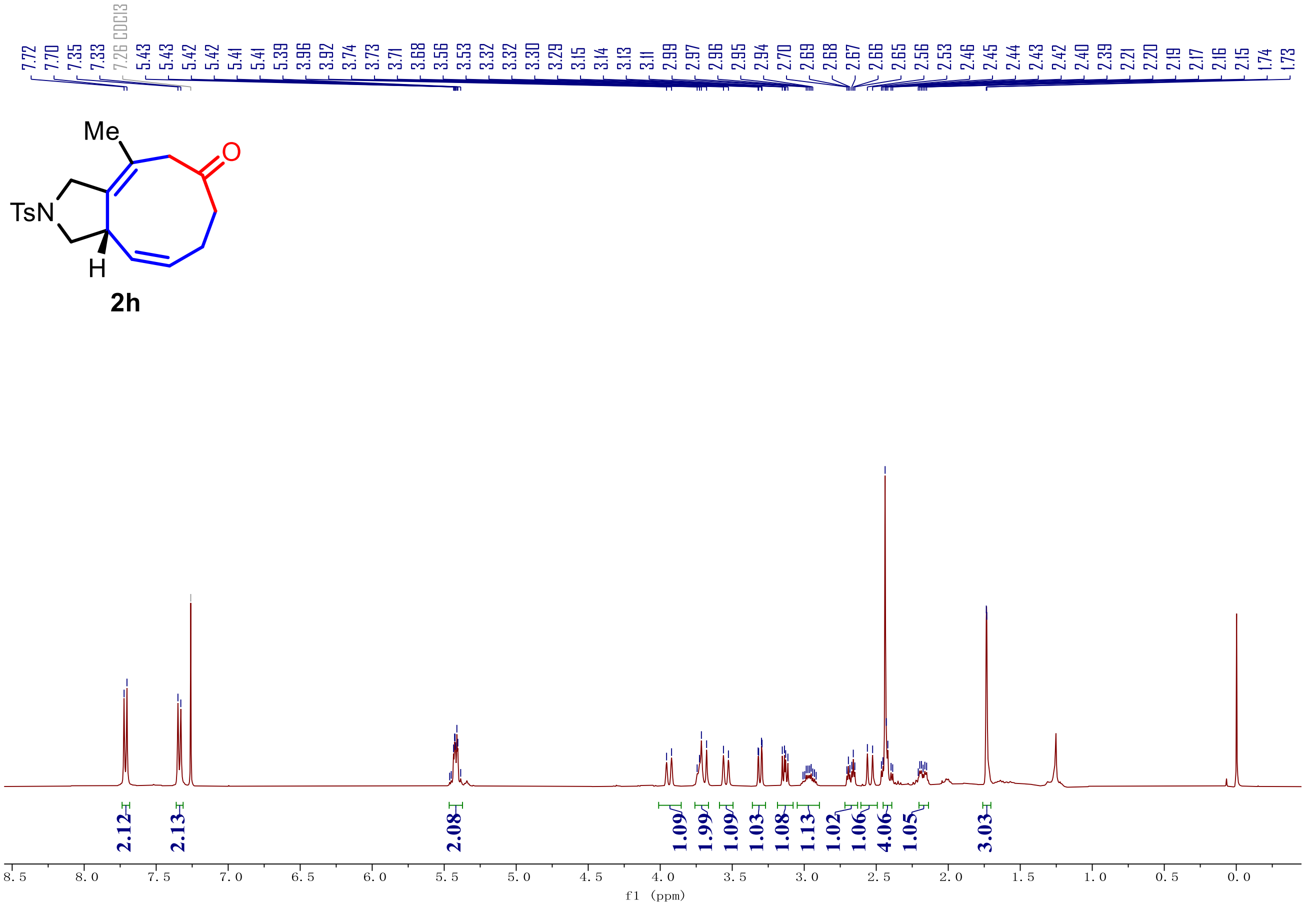
### $^1$H NMR (400 MHz, $CDCl_3$):



### $^{13}$C NMR (101 MHz, $CDCl_3$):

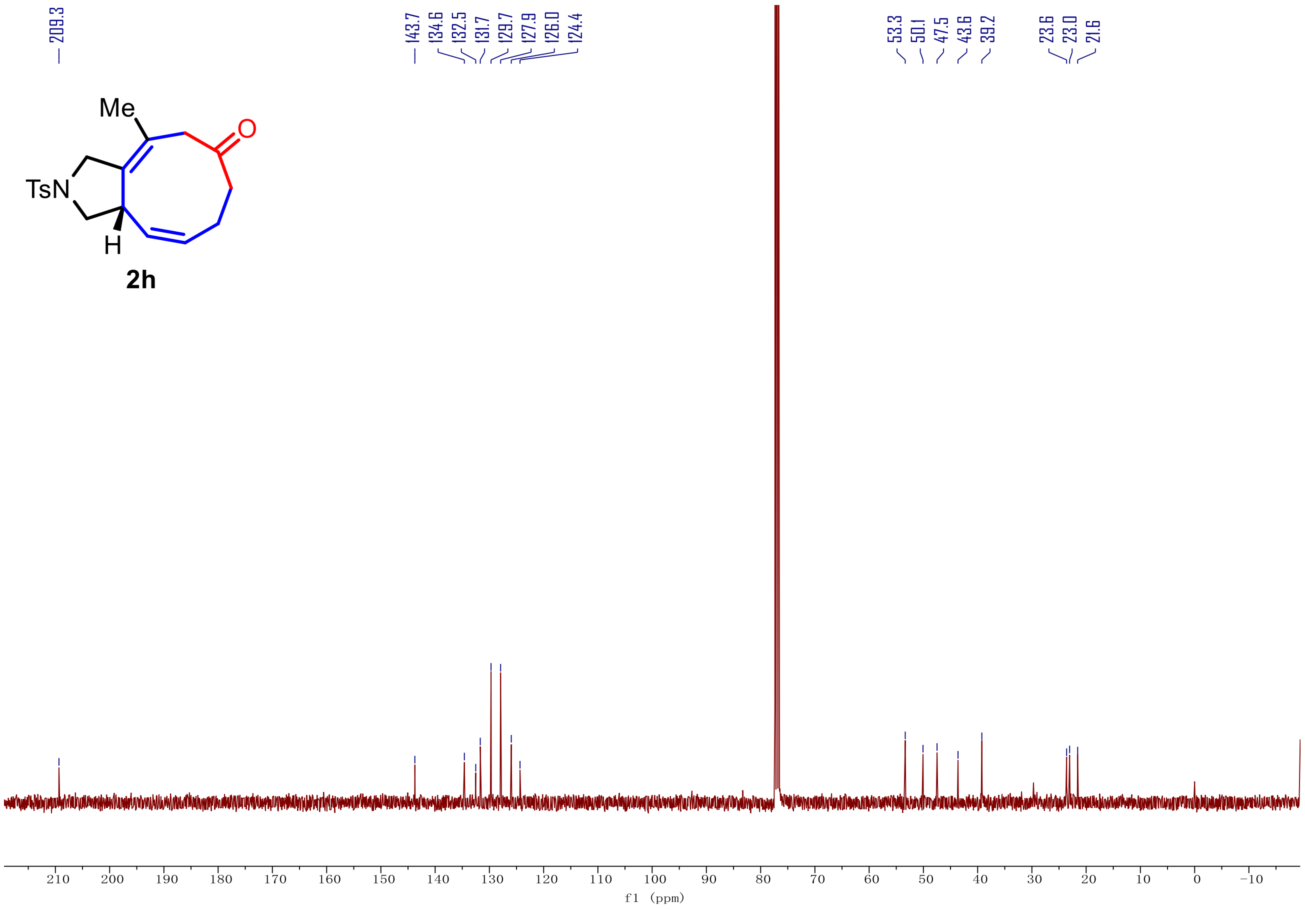


## $^1$H NMR (400 MHz, CDCl$_3$):



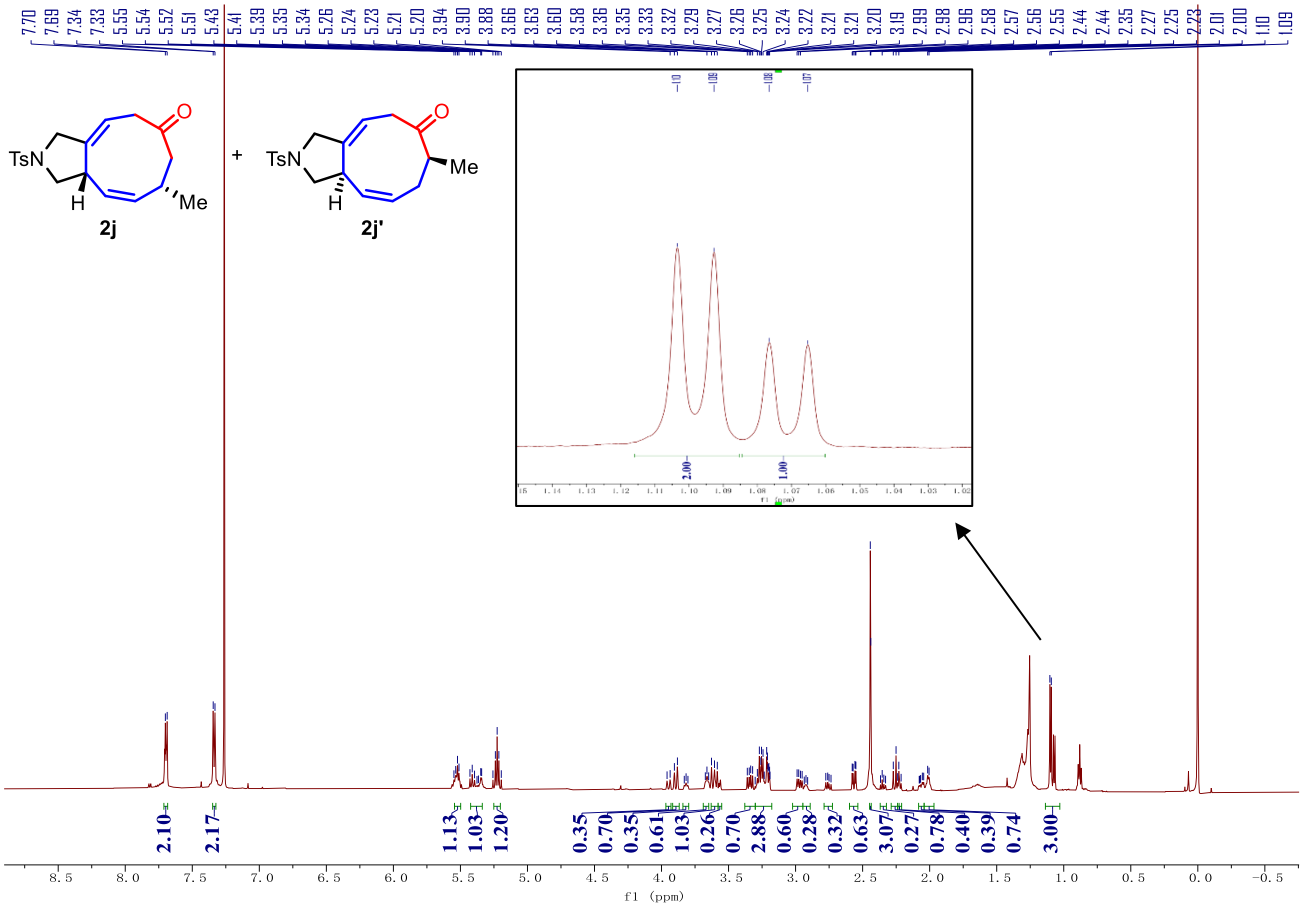
**2h**

## $^{13}$C NMR (101 MHz, CDCl$_3$):

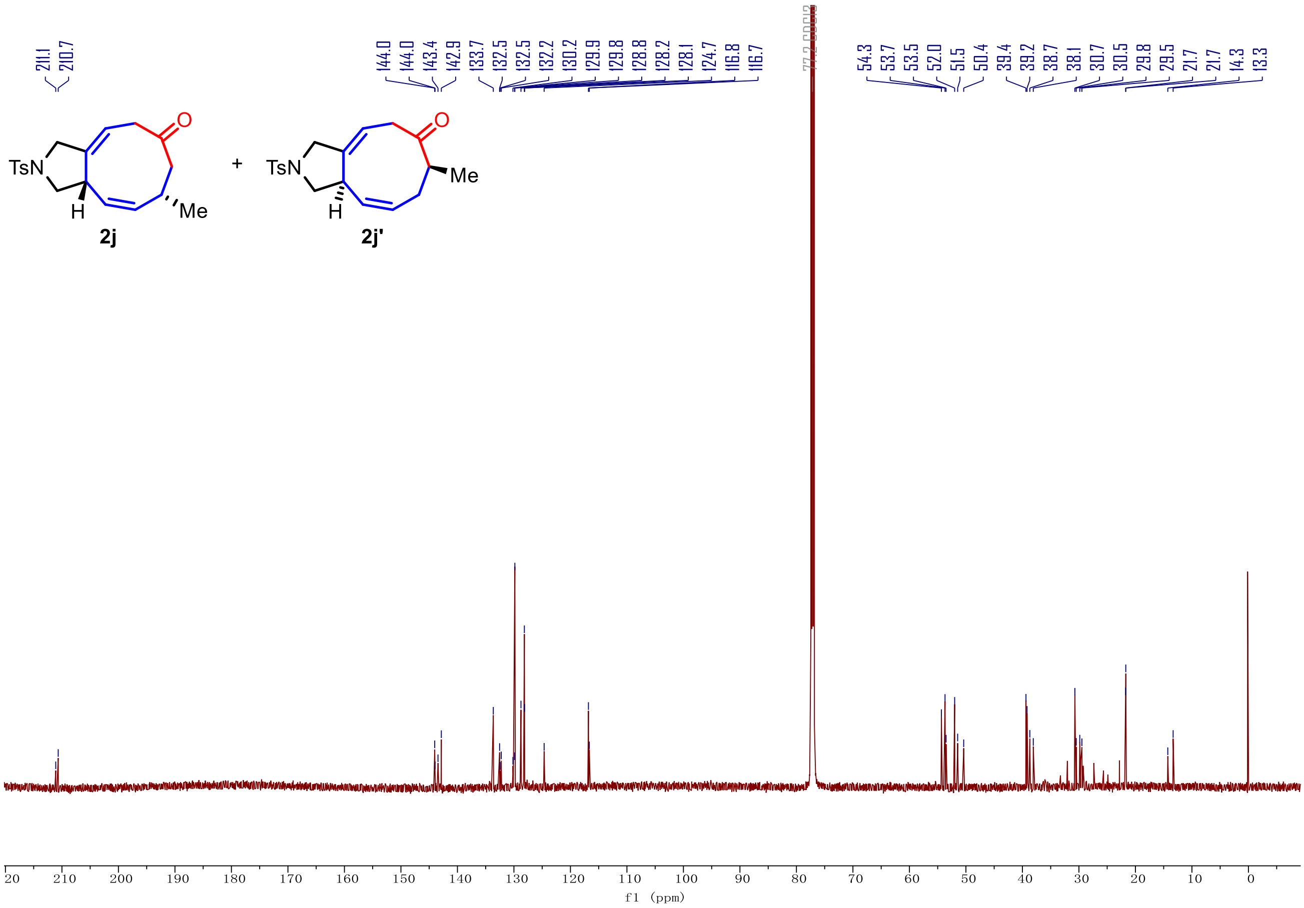


**2h**

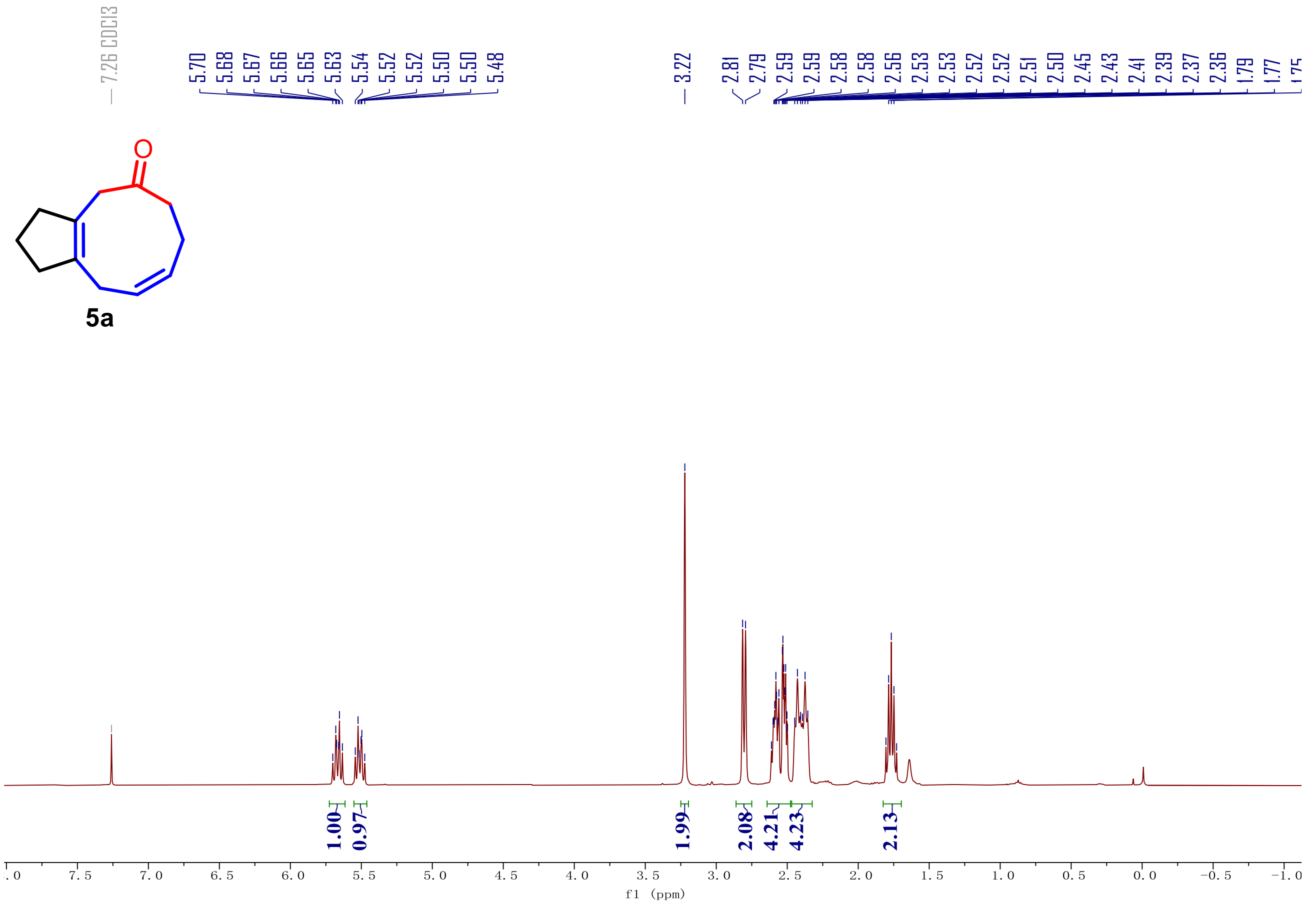
## $^1$H NMR (600 MHz, CDCl$_3$):



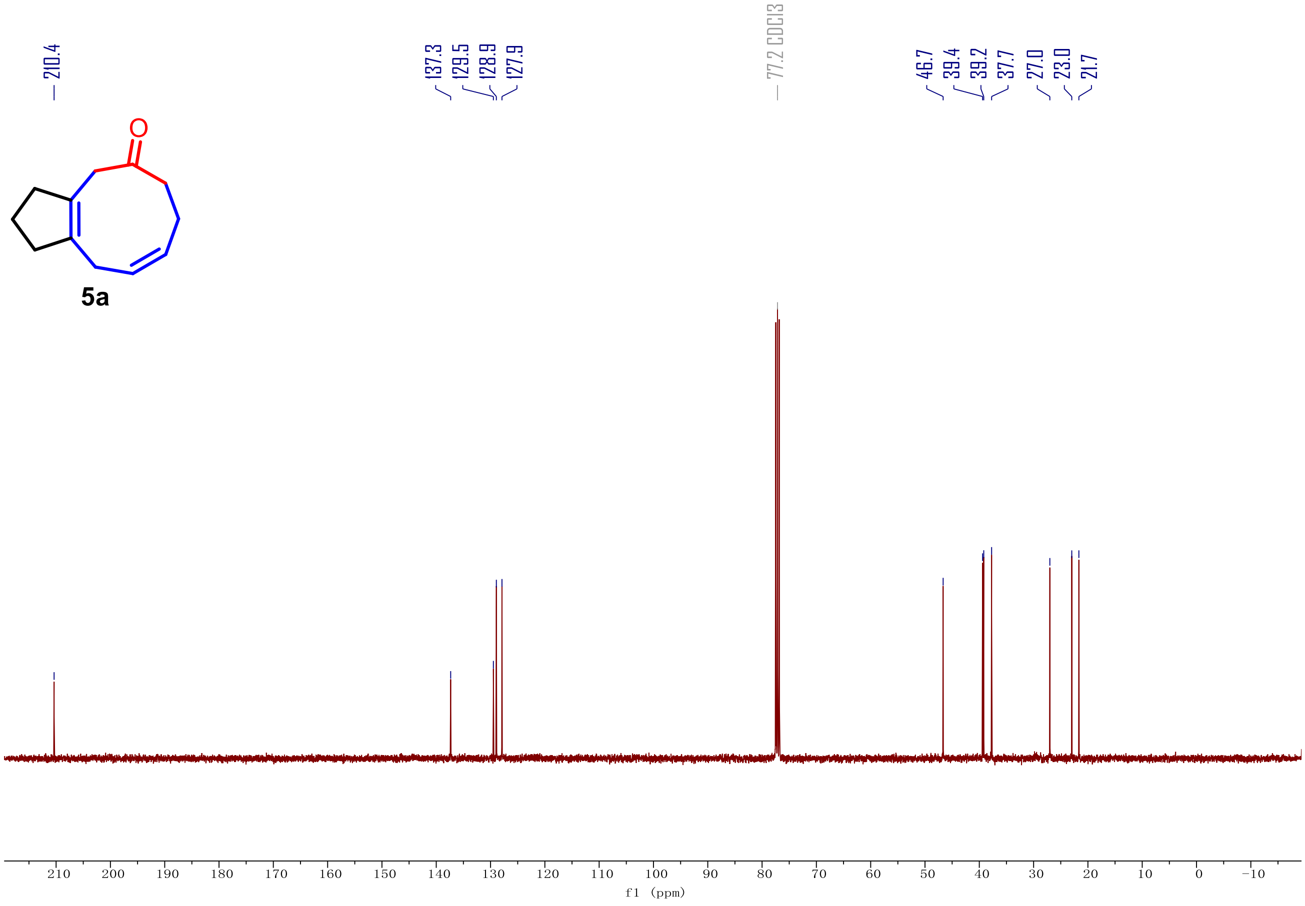
## $^{13}$C NMR (151 MHz, CDCl$_3$):



$^{1}$H NMR (400 MHz, $CDCl_3$):



$^{13}$C NMR (101 MHz, $CDCl_3$):



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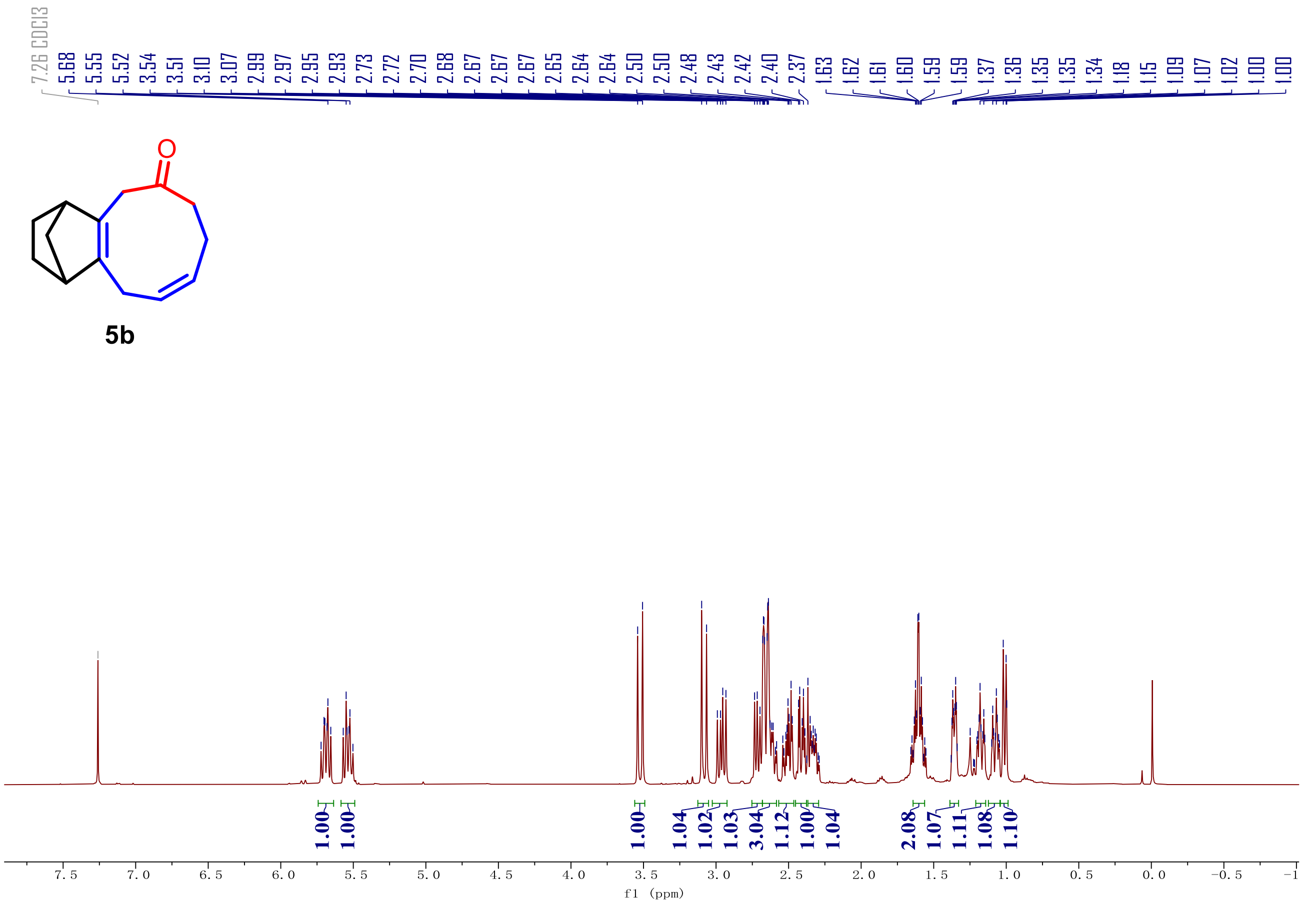

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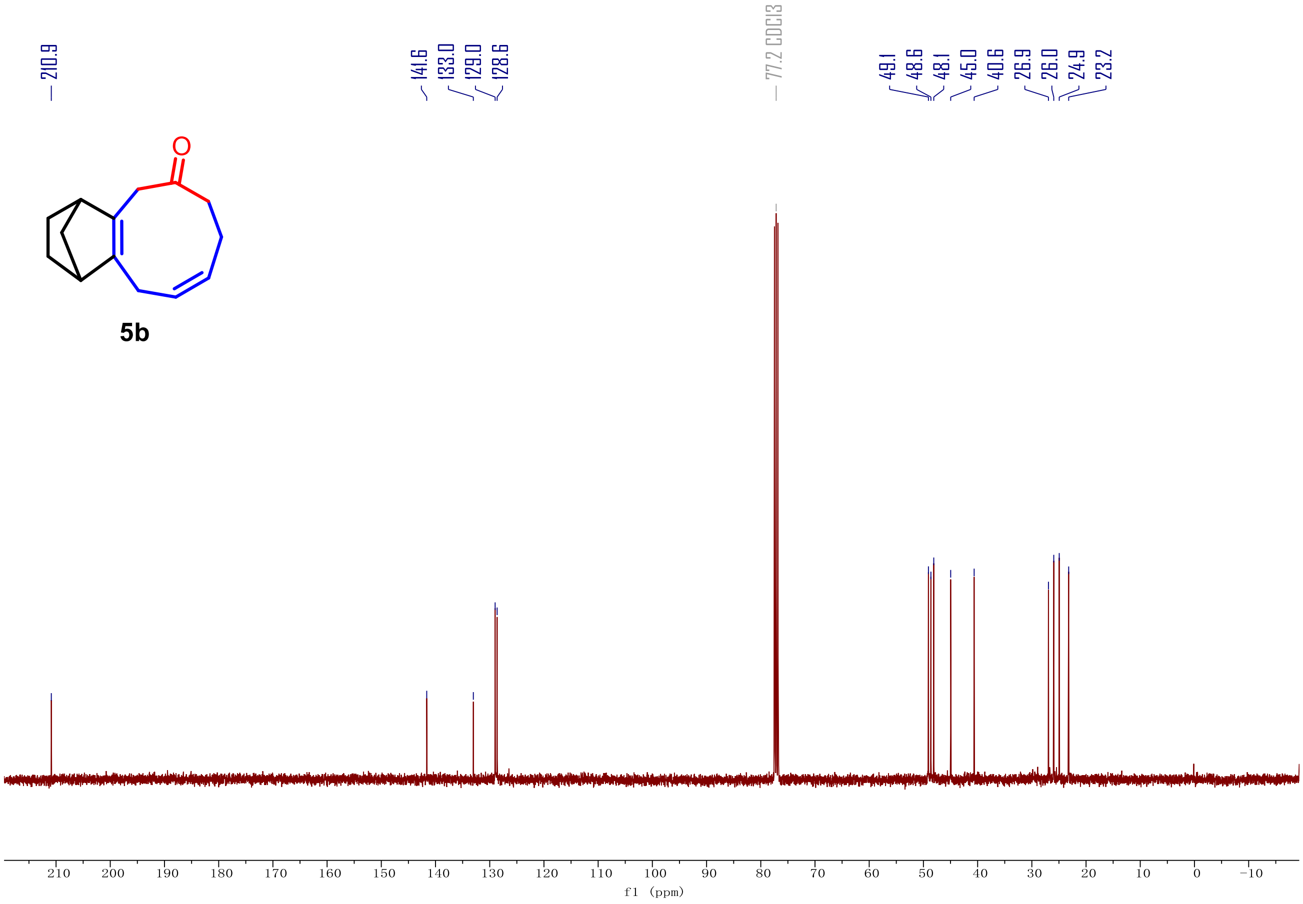

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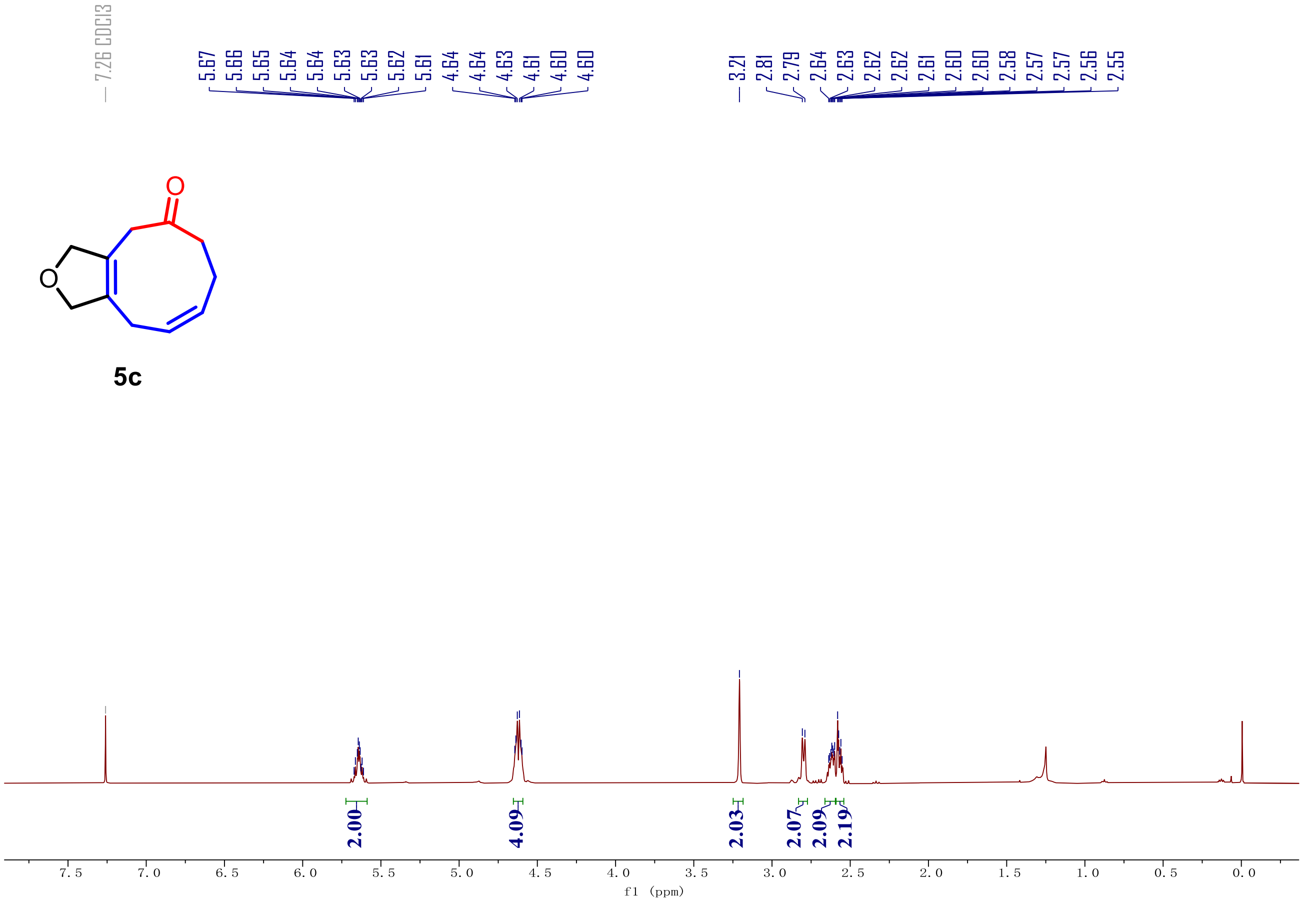
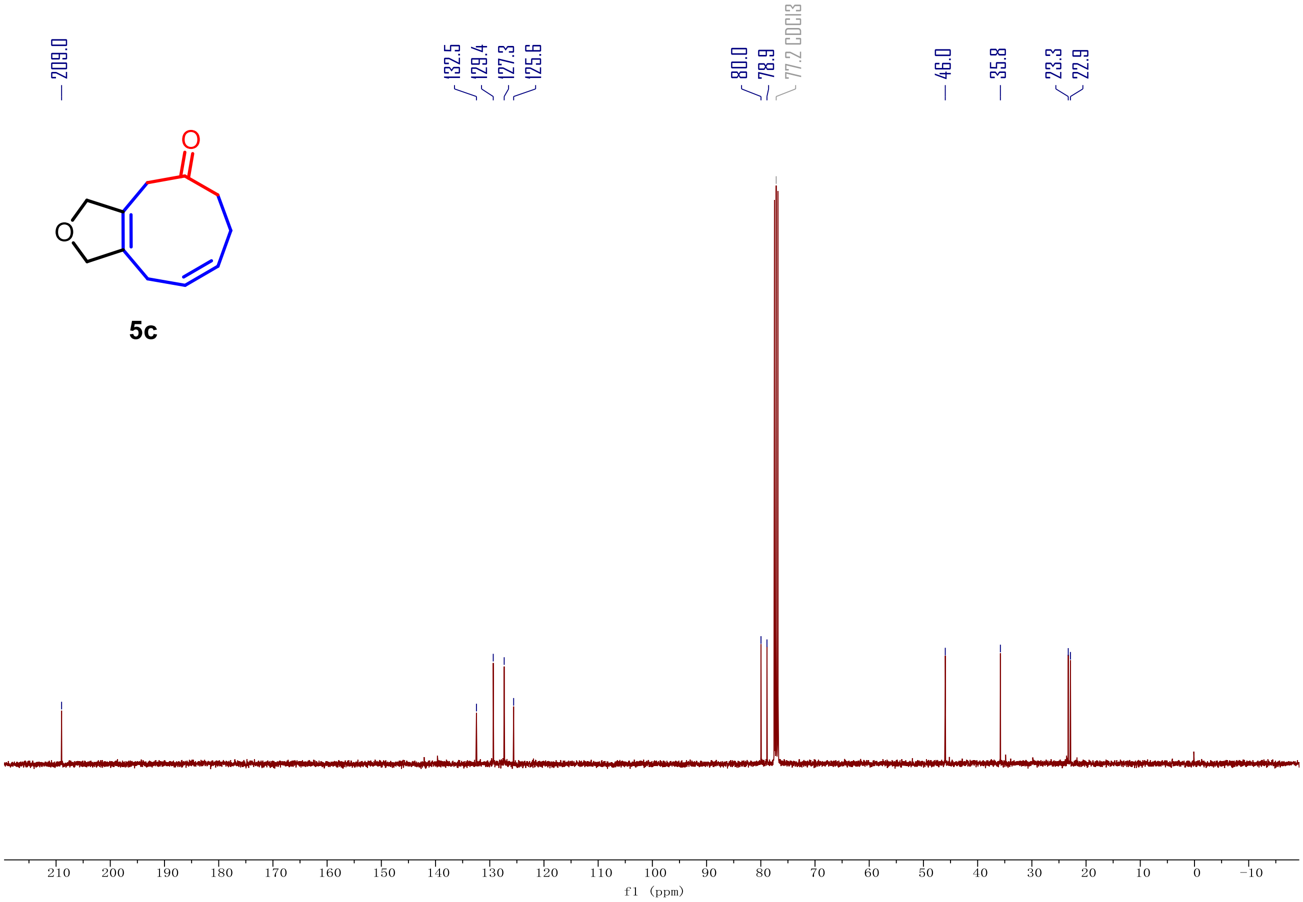
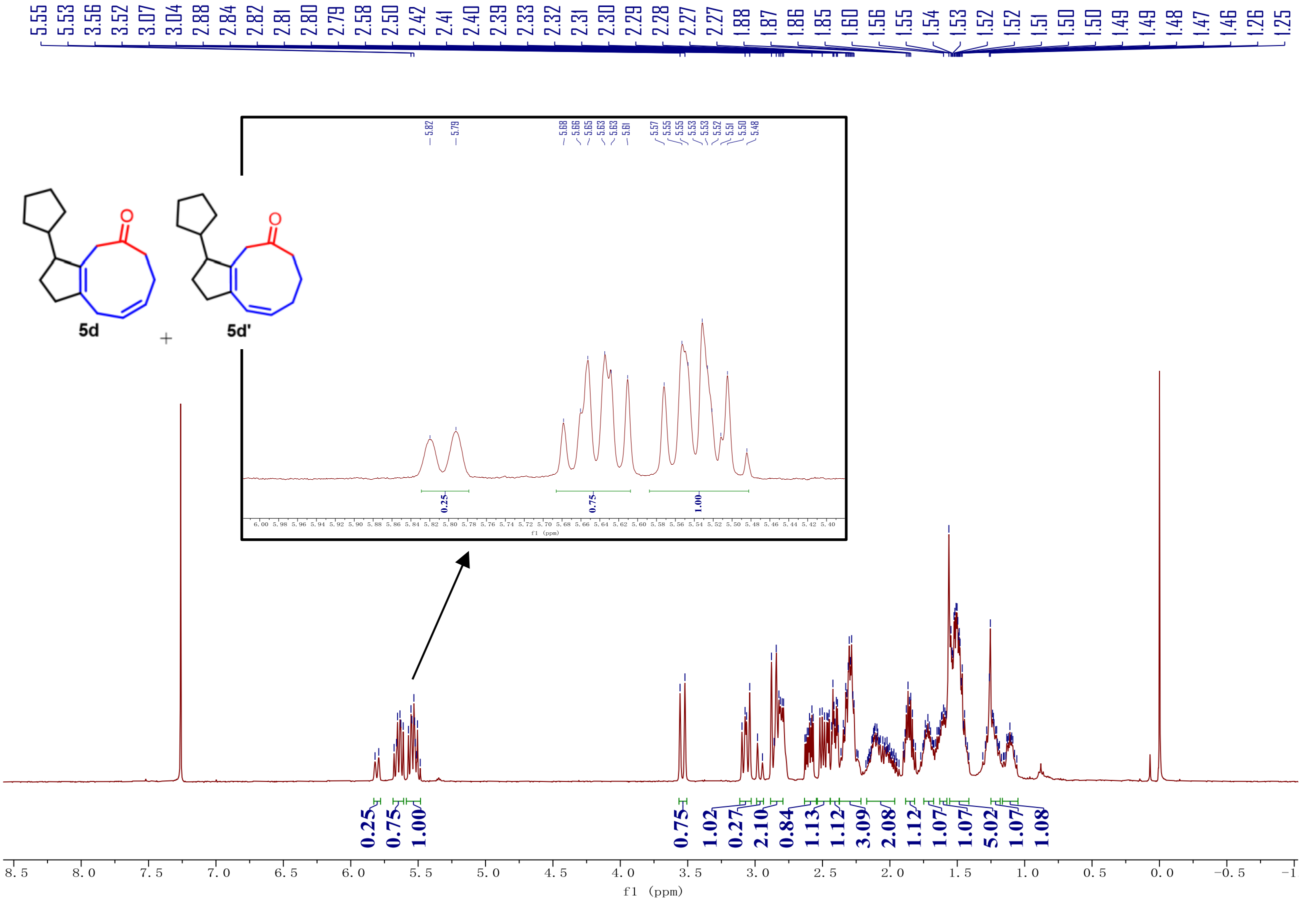


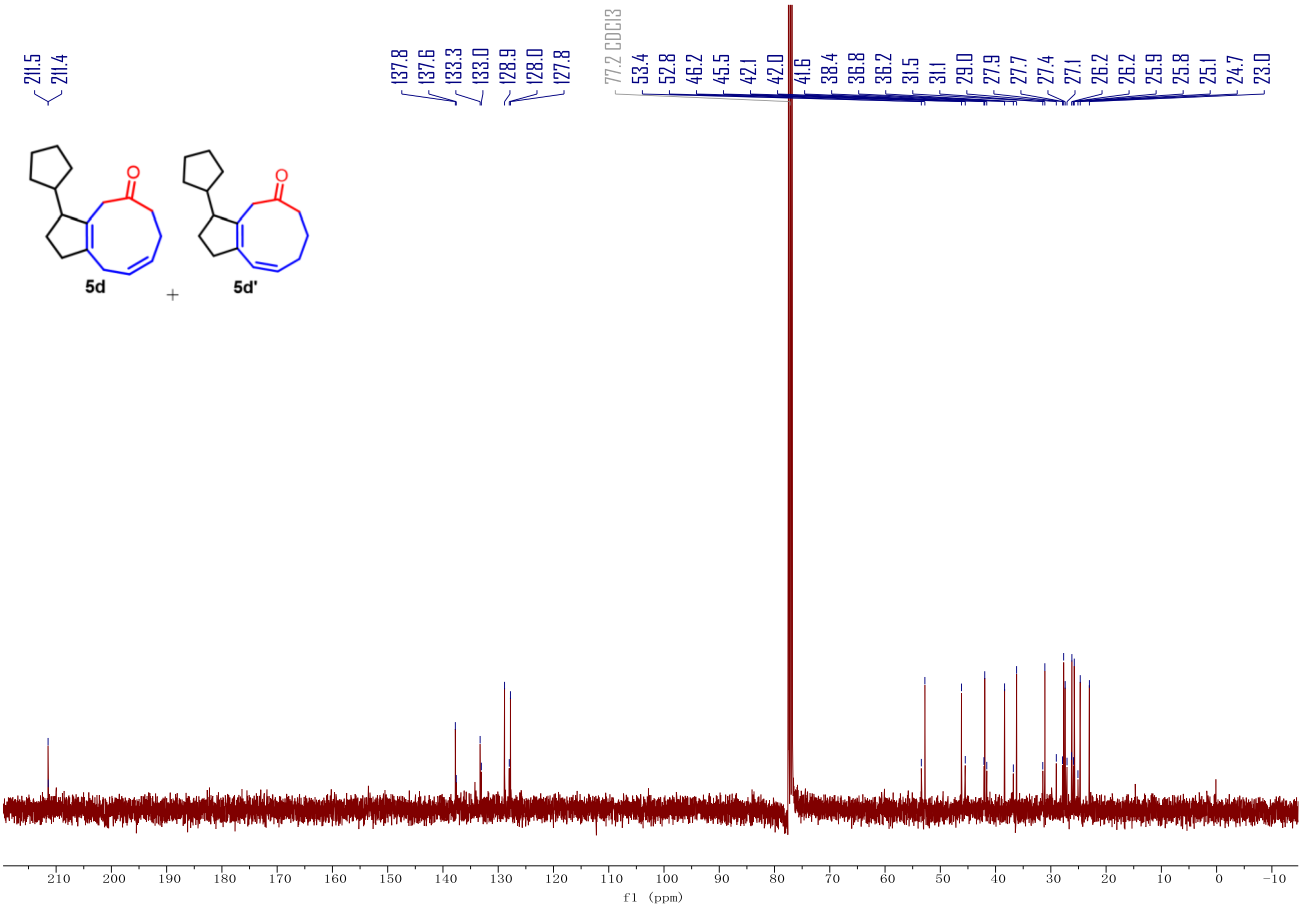
$^{13}$C NMR (101 MHz, CDCl$_3$):



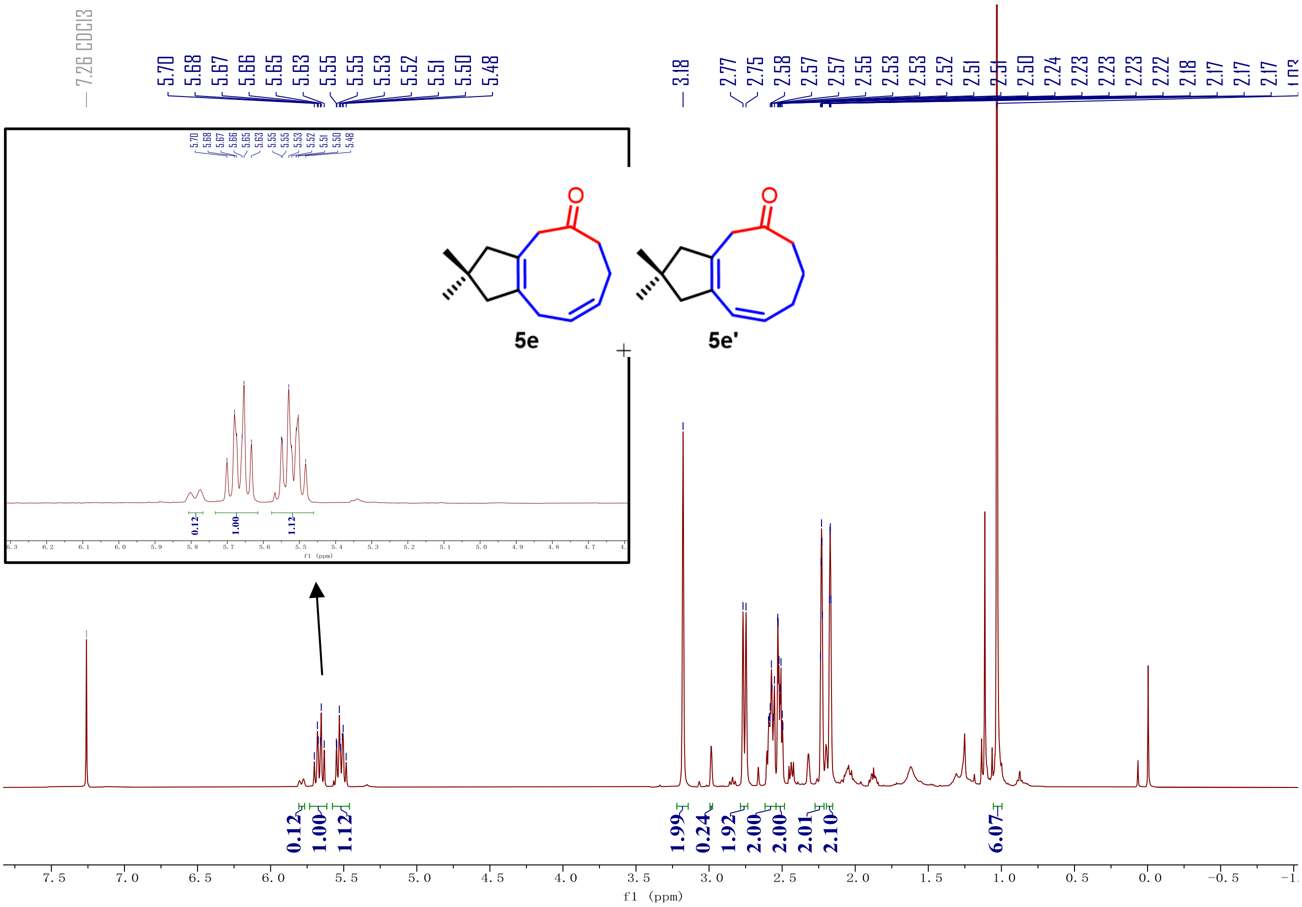
**$^{1}$H NMR** (400 MHz, CDCl$_3$):



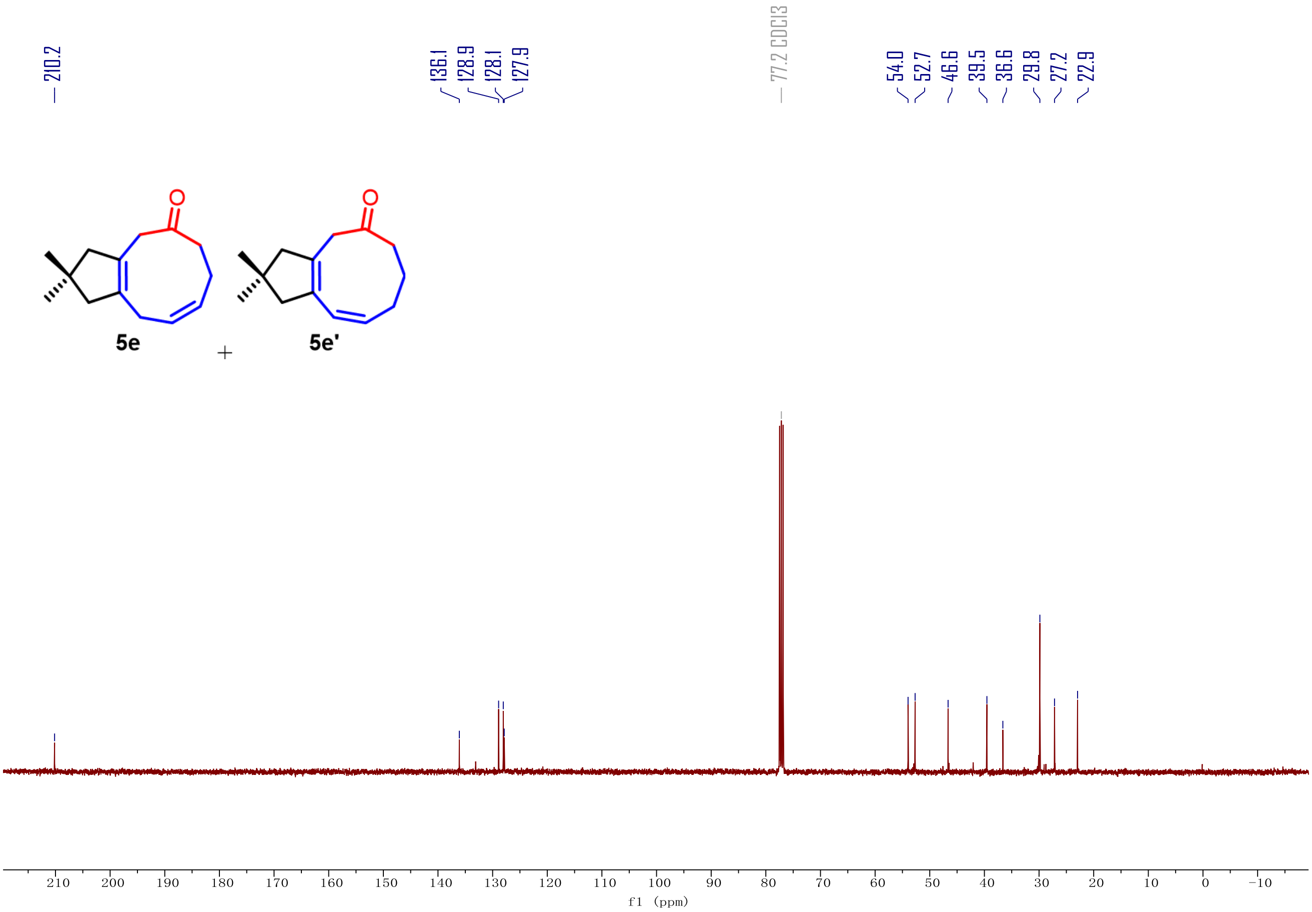
**$^{13}$C NMR** (101 MHz, CDCl$_3$):



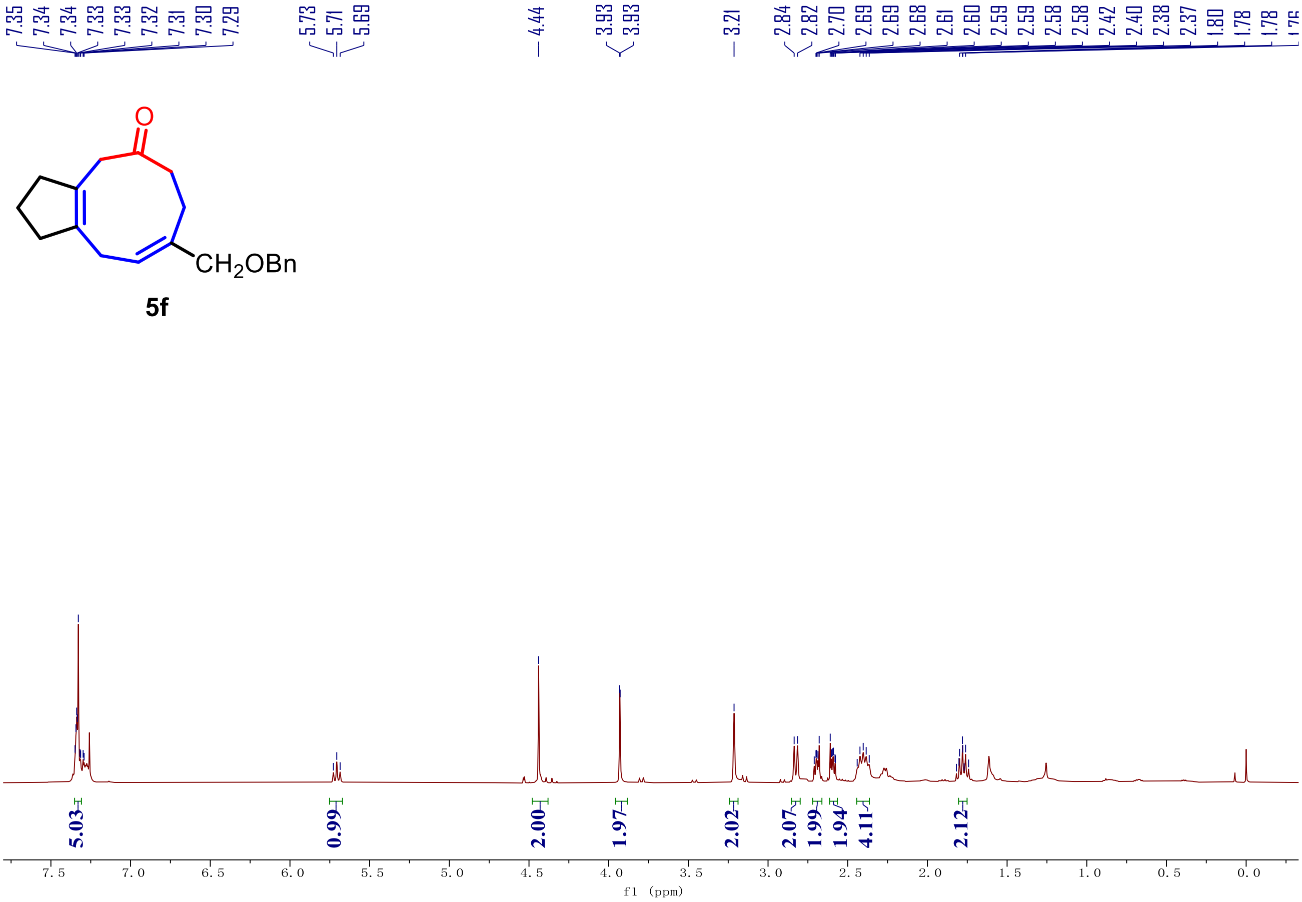
$^1$**H NMR** (400 MHz, CDCl$_3$):



$^{13}$**C NMR** (101 MHz, CDCl$_3$):

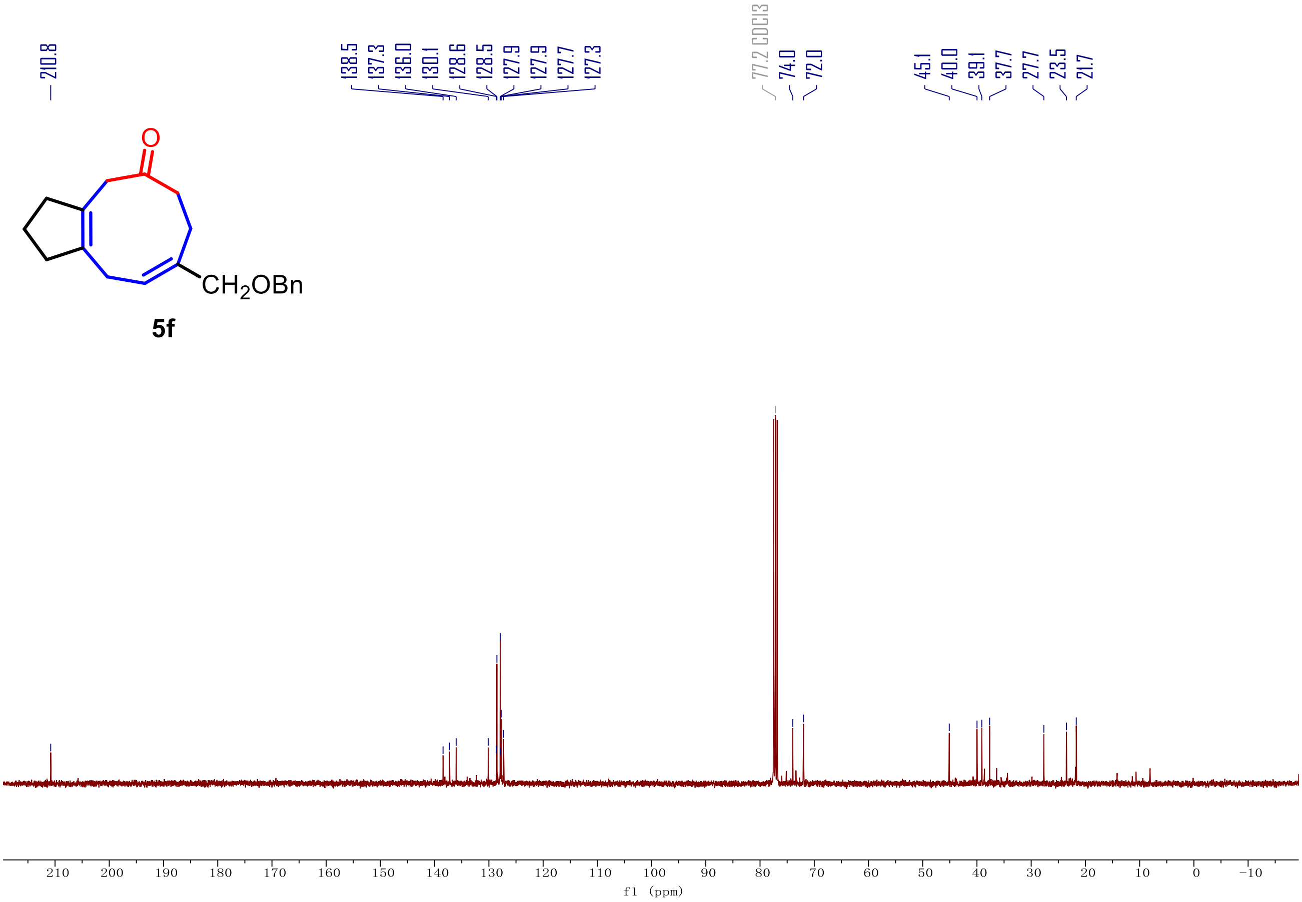


## $^1$H NMR (400 MHz, CDCl$_3$):



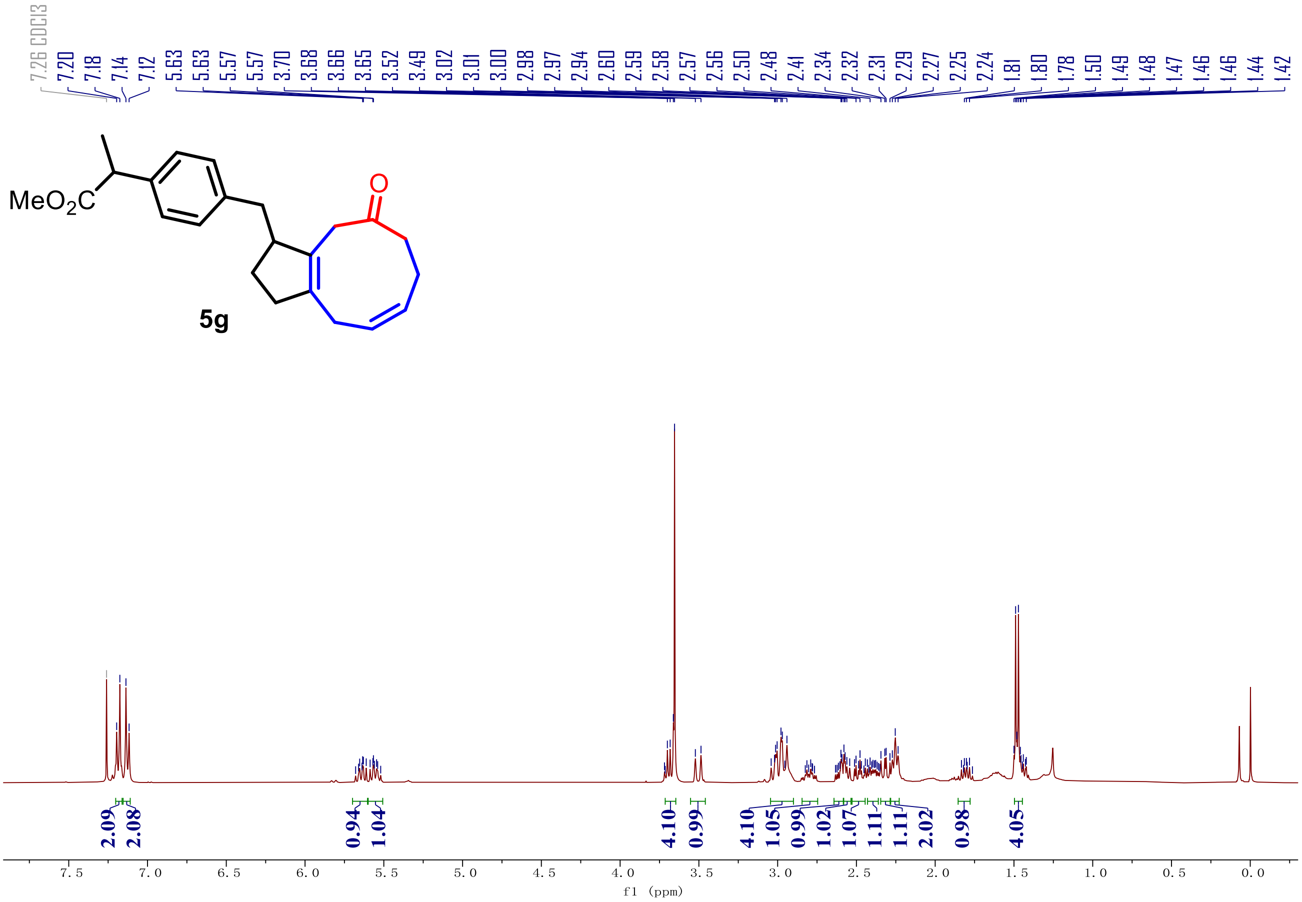
**5f**

## $^{13}$C NMR (101 MHz, CDCl$_3$):

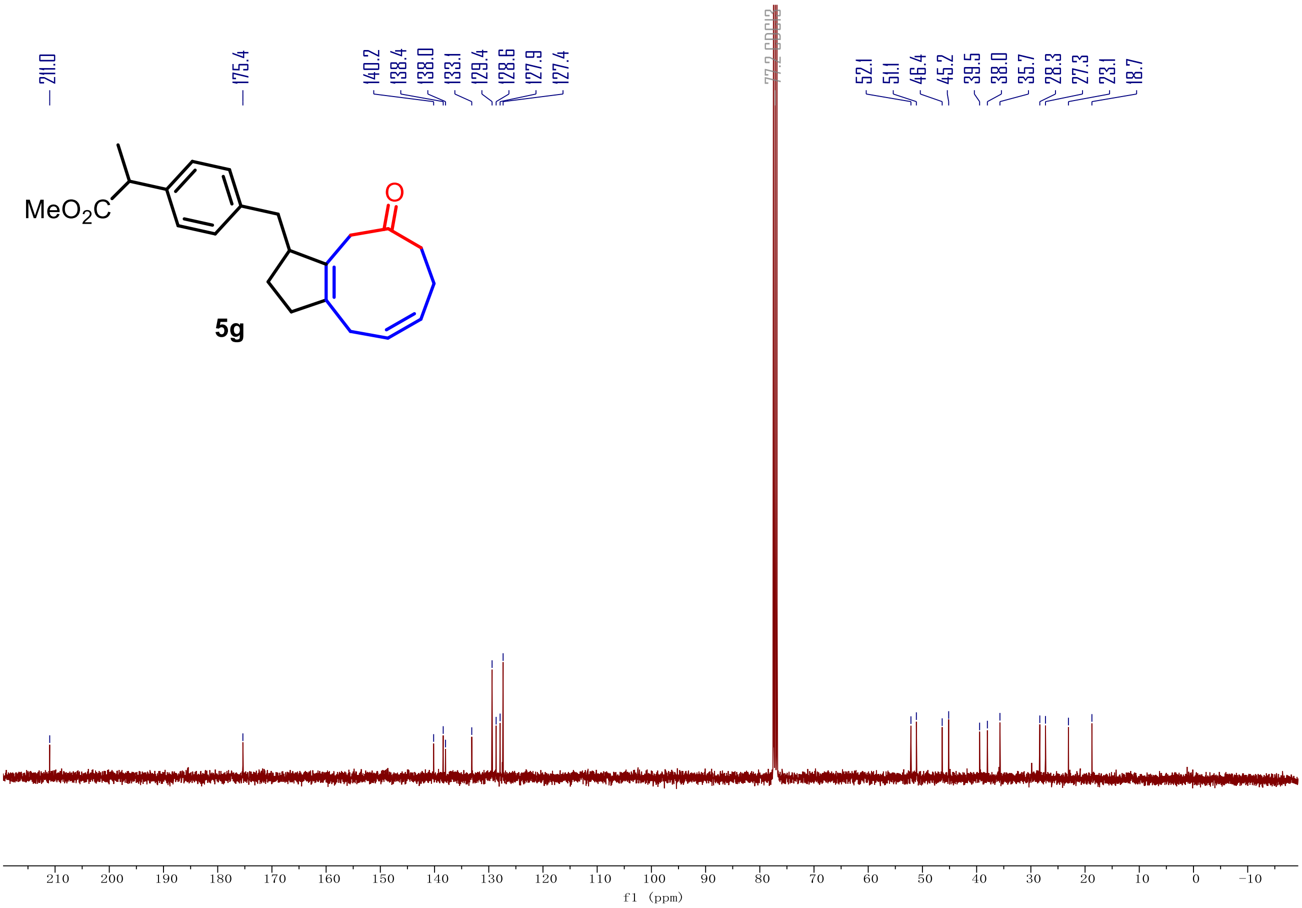


**5f**

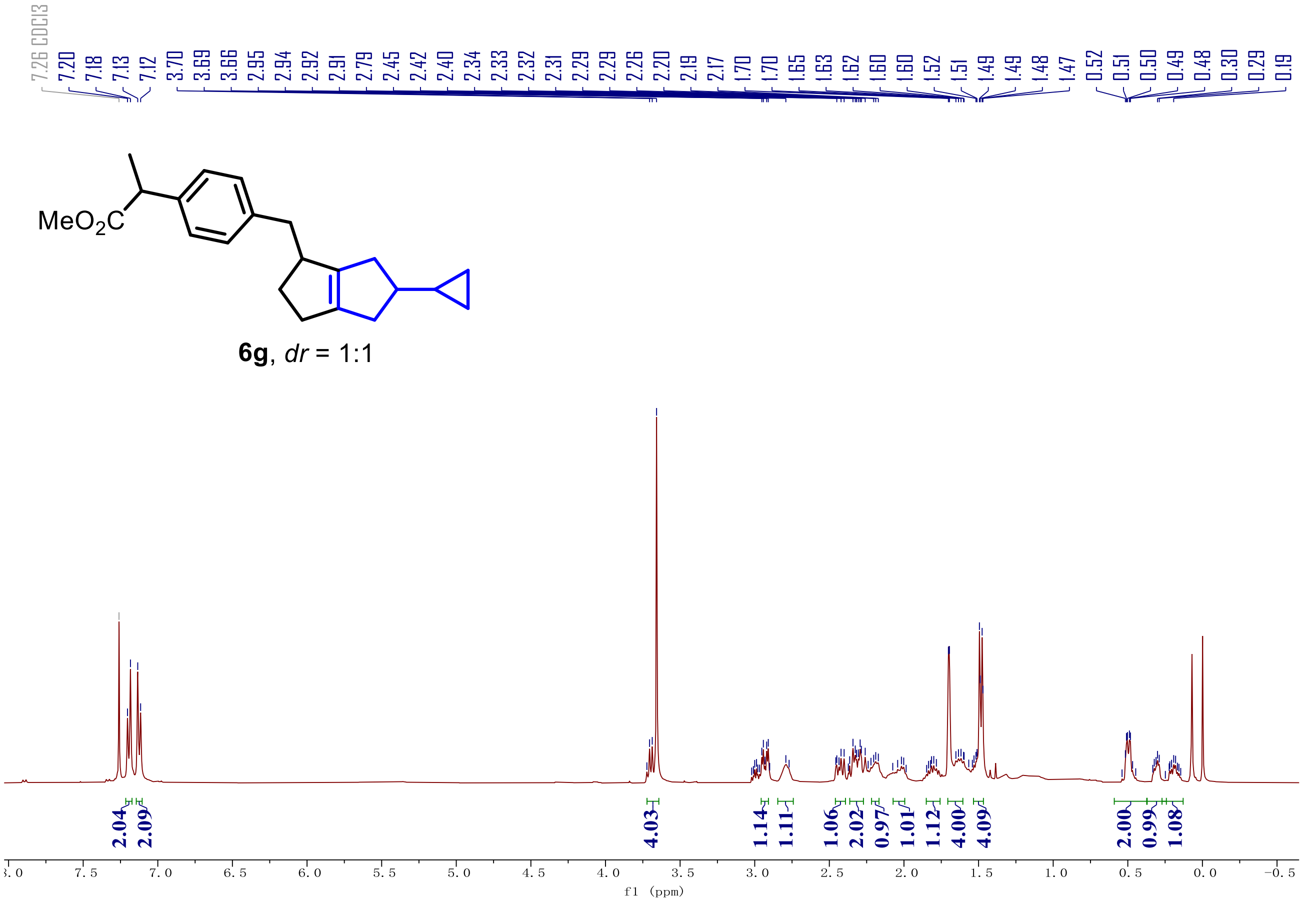
## $^1$H NMR (400 MHz, CDCl$_3$):



## $^{13}$C NMR (101 MHz, CDCl$_3$):

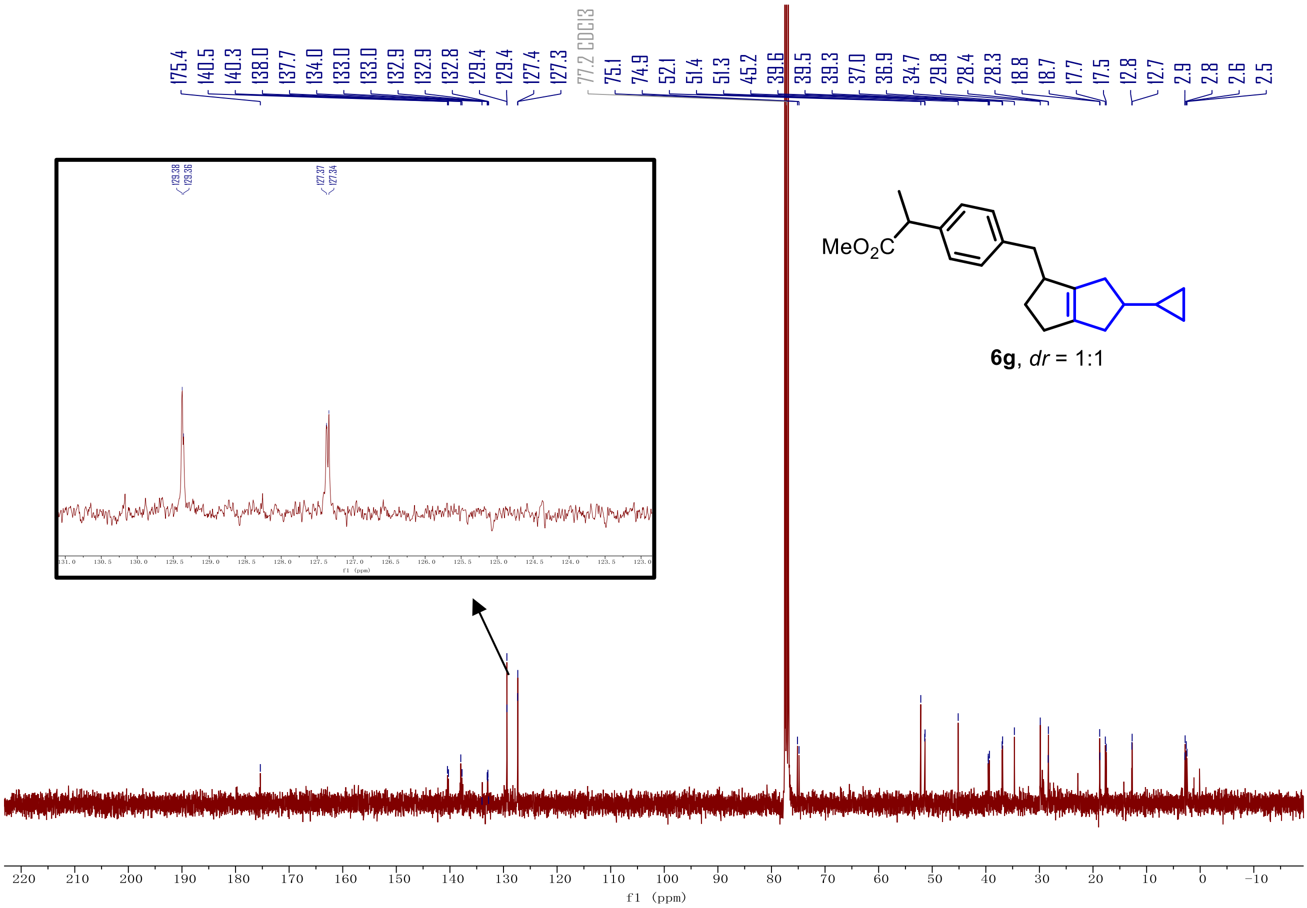


## $^1$H NMR (400 MHz, CDCl$_3$):



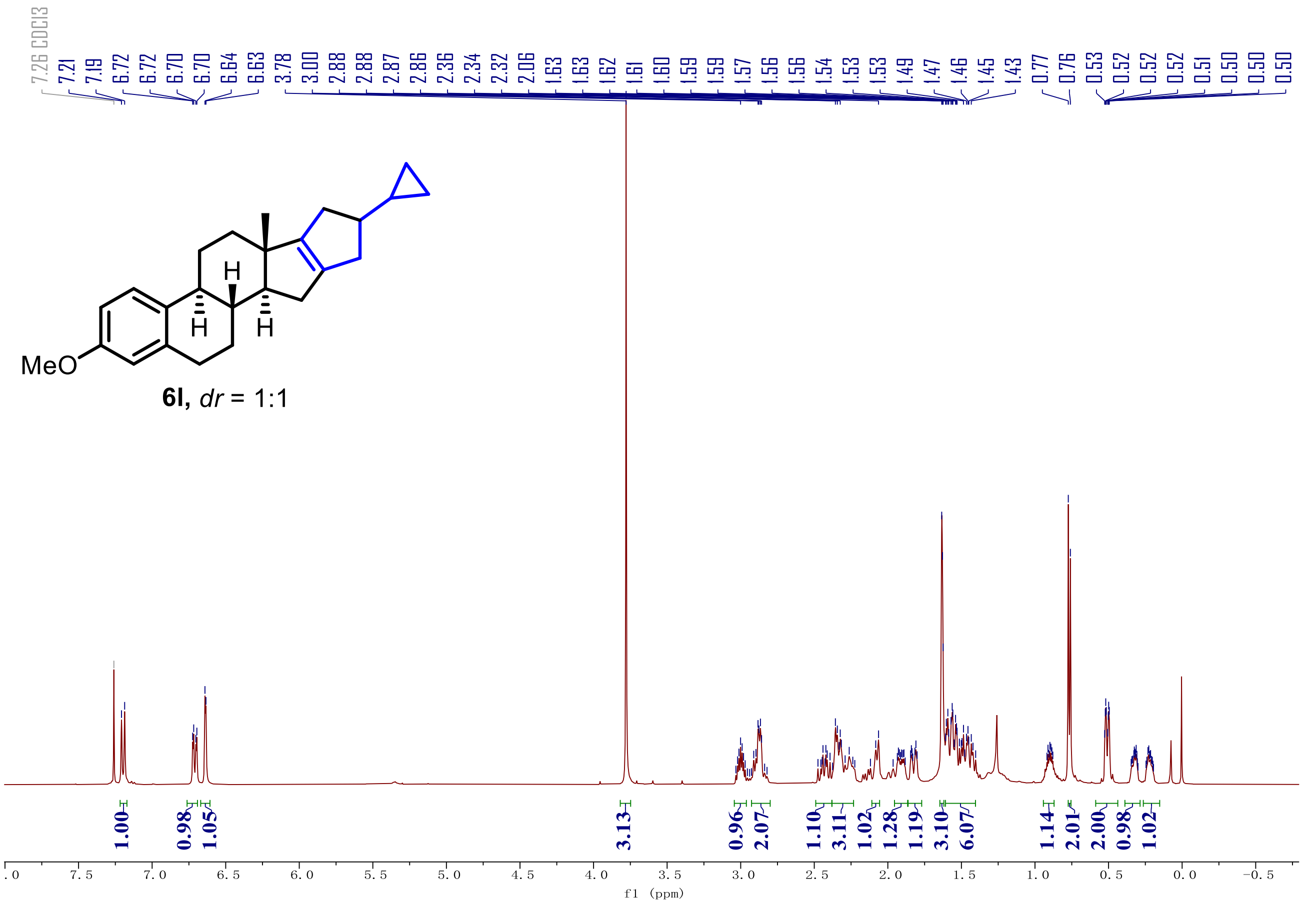
**6g**, *dr* = 1:1

## $^{13}$C NMR (101 MHz, CDCl$_3$):



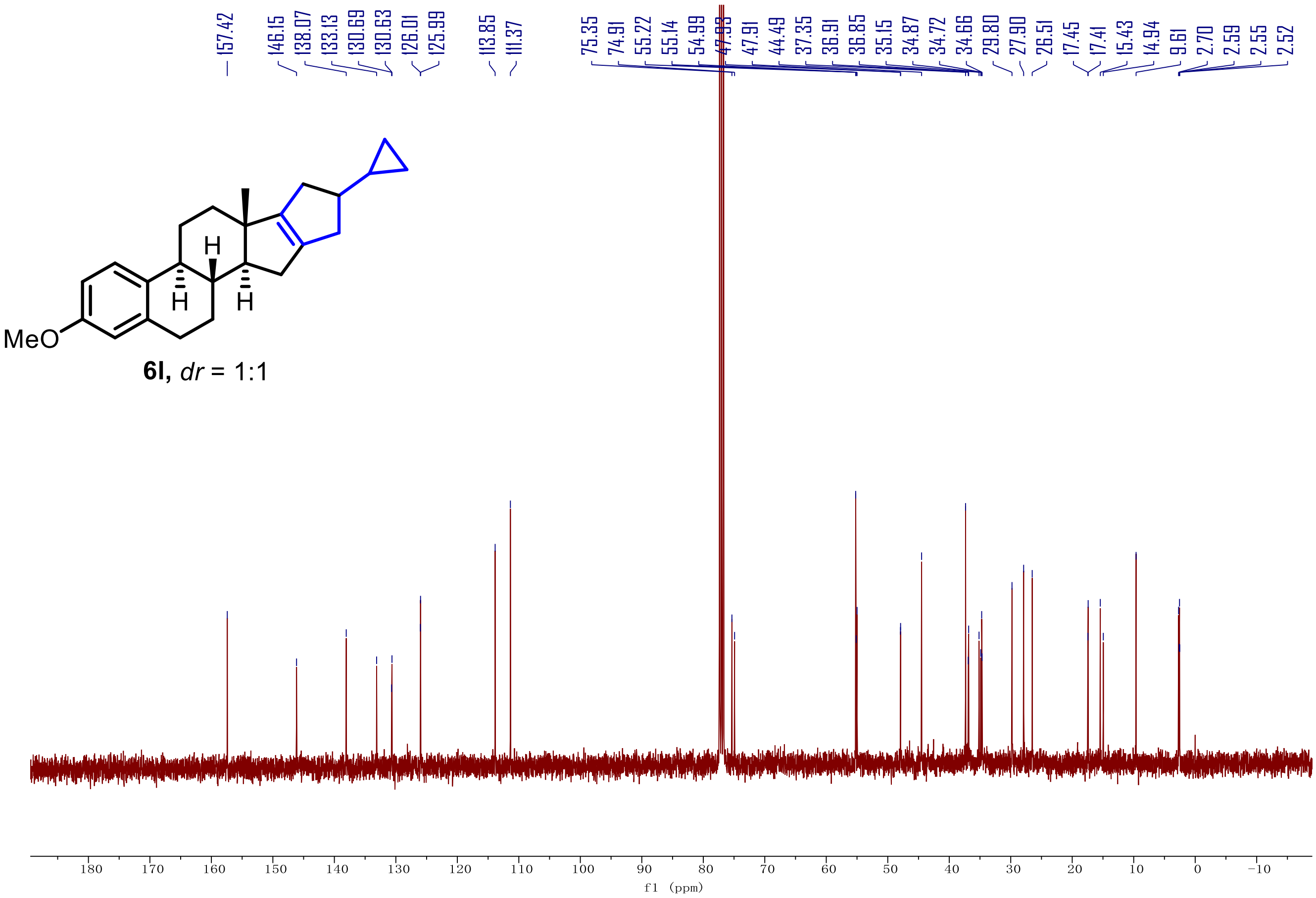
**6g**, *dr* = 1:1

### $^{1}H$ NMR (400 MHz, $CDCl_3$):



**6l**, *dr* = 1:1

### $^{13}C$ NMR (101 MHz, $CDCl_3$):



**6l**, *dr* = 1:1

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