Supporting Information

Rhodium-Catalyzed [7 + 1] Cycloaddition of Exocyclic 1,3-Dienylcyclopropanes and Carbon Monoxide

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1. General Information

All chemicals were used as received without further purification. DCE (with molecular sieves) was purchased from J&K. Reaction tubes (25 mL) were purchased from Synthware. $[Rh(CO)_2Cl]_2$ was purchased from J&K. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Analytical TLCs were performed with 0.25 mm silica gel HSGF254. The TLC plates were visualized by ultraviolet light and treatment with anisaldehyde-H_2SO_4 or phosphomolybdic acid stain followed by gentle heating. Purification of products was accomplished by flash chromatography on silica gel (200-300 mesh) purchased from Yantai Huayang New Material Technology Co. Ltd. and the purified compounds show a single spot by analytical TLC. Generally, the exocyclic-1,3-dienylcyclopropanes are unstable, so they are purified by SiliaFlash P60 (Particle size: 40-63um, Pore size 60A) purchased from Innochem. Organic solutions were concentrated using a Büchi or Eyela rotary evaporator with a desktop vacuum pump. Nuclear magnetic resonance (NMR) spectra were measured on Bruker AVANCE III 400 (^1H at 400 MHz, $^{13}C\{^1H\}$ at 101 MHz). Data for ^1H NMR spectrum are reported as follows: chemical shift δ (ppm) referenced to tetramethylsilane (TMS, 0.00 ppm), C_6D_5H (7.16 ppm), or $CHDCl_2$ (5.32 ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, ddd = doublet of doublet of doublets, dddq = doublet of doublet of doublet of quartets, dtdt = doublet of triplet of doublet of triplets, tq = triplet of quartets, qdd = quartet of doublet of doublets, m = multiplet), coupling constant *J* (Hz), and integration. Data for $^{13}C\{^1H\}$ NMR spectrum are reported as follows: chemical shift δ (ppm) referenced to $CDCl_3$ (77.16 ppm), C_6D_6 (128.06 ppm), or CD_2Cl_2 (53.84 ppm). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer (ESI or EI) with an FT-ICR analyzer.

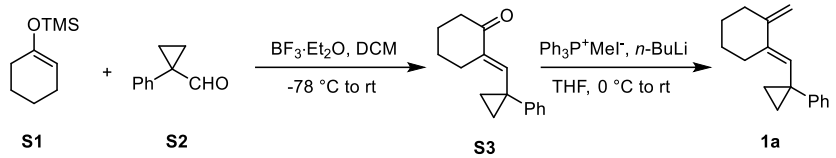
Abbreviations

atm	Atmosphere
Bn	benzyl group
Bu	Butyl
d	density
DCM	Dichloromethane
DCE	1,2-dichloroethane
DFT	density functional theory
EA	ethyl acetate
EI	electron impact ion source
ESI	electron spray ionization
Et	Ethyl
HRMS	high-resolution mass spectroscopy
INT	intermediate
Me	methyl
m.p.	melting point
PE	petroleum ether
Ph	phenyl
PTLC	preparative thin-layer chromatography
rpm	revolutions per minute
rt	room temperature
THF	Tetrahydrofuran
TLC	thin layer chromatography
TS	transition state

2. Substrates preparations

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

S1 is commercially available, **S2** is a known compound and was synthesized according to the reported literature.[1]



To a 250 mL flask with **S2** (4.389 g, 30 mmol) in DCM (100 mL) was added $BF_3{\cdot}Et_2O$ (13.25 mL, *d* = 1.125 g/mL, 105 mmol) under an argon atmosphere at -78 °C. Then a solution of **S1** (5.634 g, 33 mmol) in DCM (4 mL) was added by syringe pump in 1 h. The obtained mixture was then stirred for 5.5 h at 0 °C to rt, quenched with saturated aqueous NH_4Cl solution, and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 to 25:1 PE/EA) afforded compound **S3** (3.0026 g) as a yellow oil.

To a 250 mL flask with $Ph_3P^+MeI^-$ (10.7391 g, 26.6 mmol) was added THF (120 mL) under an argon atmosphere. *n*-BuLi (11 mL, 2.4 M in hexane, 26.4 mmol) was added dropwise at 0 °C. An hour later, a solution of **S3** (3.0026 g, 13.3 mmol) in THF (12 mL) was added. The obtained mixture was then stirred for 1 h at rt, filtered, washed with PE, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 1:0 PE/EA) afforded compound **1a** (2.0093 g, 31%, two steps) as a colorless oil.

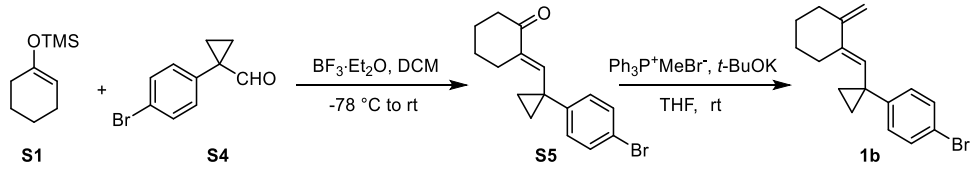
TLC (10:1 PE/EA, R_f): 0.9.

^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.28 – 7.22 (m, 2H), 7.20 – 7.15 (m, 2H), 7.15 – 7.09 (m, 1H), 5.82 (s, 1H), 4.88 (s, 1H), 4.61 (s, 1H), 2.32 – 2.23 (m, 4H), 1.66 – 1.59 (m, 2H), 1.58 – 1.50 (m, 2H), 1.17 – 1.11 (m, 2H), 1.06 – 1.00 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, *δ*): 150.9, 145.9, 145.3, 128.3, 126.2, 125.8, 125.2, 107.7, 35.6, 30.3, 27.1, 26.0, 22.6, 18.9.

HRMS (EI) m/z: calcd. for $C_{17}H_{20}$ ($[M\cdot]^+$): 224.1560, found: 224.1558.

S4 is a known compound and was synthesized according to the reported literature.[1]



To a flask with **S4** (1.13 g, 5 mmol) in DCM (20 mL) was added $BF_3{\cdot}Et_2O$ (2.2 mL, *d* = 1.125 g/mL, 17.4 mmol) under an argon atmosphere at -78 °C. Then a solution of **S1** (936.8 mg, 5.5 mmol) in DCM (4 mL) was added by syringe pump in 0.5 h. The obtained mixture was then stirred for 10.5 h

at -78 °C to rt, quenched with saturated aqueous NH_4Cl solution, and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 PE/EA) afforded compound **S5** (749.5 mg) as a yellow oil.

To a flask with $Ph_3P^+MeBr^-$ (4.47 g, 12.5 mmol) and *t*-BuOK (1.4 g, 12.5 mmol) was added THF (30 mL) under an argon atmosphere at rt. 30 min later, a solution of **S5** (749.5 mg, 2.46 mmol) in THF (5 mL) was added. The obtained mixture was then stirred for 2.5 h at rt, quenched with water, and extracted with EA. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 1:0 PE/EA) afforded compound **1b** (667.9 mg, 44%, two steps) as a colorless oil.

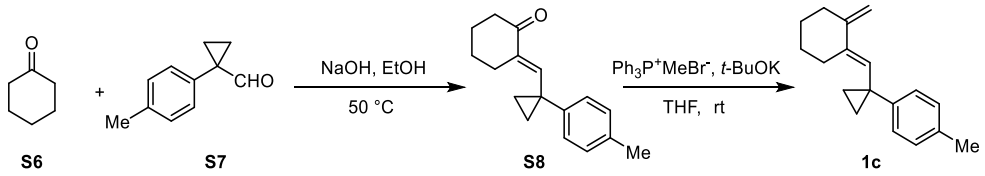
TLC (10:1 PE/EA, R_f): 1.0.

^{1}H NMR (400 MHz, C_6D_6, δ): 7.28 – 7.20 (m, 2H), 6.84 – 6.76 (m, 2H), 5.85 – 5.79 (m, 1H), 5.00 – 4.95 (m, 1H), 4.69 – 4.64 (m, 1H), 2.21 – 2.13 (m, 4H), 1.50 – 1.40 (m, 2H), 1.43 – 1.31 (m, 2H), 0.87 (s, 4H).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, δ): 150.5, 145.9, 145.1, 131.6, 127.9, 126.1, 119.3, 108.2, 35.8, 30.5, 27.2, 26.1, 22.5, 18.9.

HRMS (EI) m/z: calcd. for $C_{17}H_{19}Br$ ($[M\cdot]^+$): 302.0665, found: 302.0660.

S6 is commercially available. **S7** is a known compound and was synthesized according to the reported literature.[1]



To a sealed tube with **S6** (9.81 g, 100 mmol) and **S7** (1.6 g, 10 mmol) in EtOH (30 mL) was added NaOH (400 mg, 10 mmol) under an argon atmosphere. The obtained mixture was then stirred for 11 h at 50 °C, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 100:1 to 50:1 to 25:1 PE/EA) afforded compound **S8** (468 mg) as a light yellow oil.

To a flask with $Ph_3P^+MeBr^-$ (2.07 g, 5.8 mmol) and *t*-BuOK (651 mg, 5.8 mmol) was added THF (20 mL) under an argon atmosphere at rt. 30 min later, a solution of **S8** (468 mg, 1.9 mmol) in THF (5 mL) was added. The obtained mixture was then stirred for 45 min at rt, quenched with water, and extracted with EA. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 1:0 PE/EA) afforded compound **1c** (258 mg, 11%, two steps) as a colorless oil.

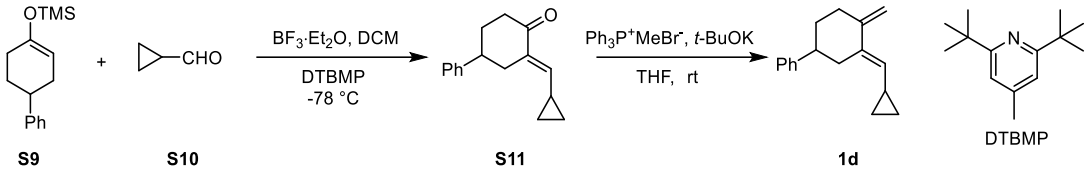
TLC (10:1 PE/EA, R_f): 0.9.

^{1}H NMR (400 MHz, CD_2Cl_2, δ): 6.77 – 6.69 (m, 4H), 5.51 – 5.45 (m, 1H), 4.57 – 4.51 (m, 1H), 4.30 – 4.25 (m, 1H), 1.97 – 1.90 (m, 4H), 1.95 (s, 3H), 1.34 – 1.25 (m, 2H), 1.25 – 1.18 (m, 2H), 0.79 – 0.74 (m, 2H), 0.68 – 0.64 (m, 2H).

$^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, δ): 151.3, 145.3, 143.1, 135.0, 129.2, 126.7, 126.1, 107.6, 35.9, 30.6, 27.4, 26.3, 22.5, 21.0, 18.6.

HRMS (EI) m/z: calcd. for $C_{18}H_{22}$ ($[M\cdot]^+$): 238.1716, found: 238.1712.

S9 is a known compound and was synthesized according to the reported literature.[2] **S10** is commercially available.



S9 **S10** **S11** **1d**

To a flask with **S10** (0.12 mL, d = 0.938 g/mL, 1.6 mmol) and DTBMP (308 mg, 1.5 mmol) in DCM (8 mL) was added $BF_3{\cdot}Et_2O$ (0.44 mL, d = 1.125 g/mL, 3.5 mmol) under an argon atmosphere at -78 °C. Then a solution of **S9** (246 mg, 1 mmol) in DCM (8 mL) was added dropwise. The obtained mixture was then stirred for 2.5 h at -78 °C, quenched with saturated aqueous NH_4Cl solution, and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 10:1 PE/EA) afforded compound **S11** (136.8 mg).

To a flask with $Ph_3P^+MeBr^-$ (2.858 g, 8 mmol) and *t*-BuOK (974 mg, 8 mmol) was added THF (30 mL) under an argon atmosphere at rt. 30 min later, a solution of **S11** (910 mg, 4 mmol) in THF (10 mL) was added dropwise. The obtained mixture was then stirred for 15 h at rt, quenched with water, and extracted with ether. The combined organic layer was washed with brine, and dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 100:1 PE/EA) afforded compound **1d** (889 mg, 59%, two steps) as a colorless oil.

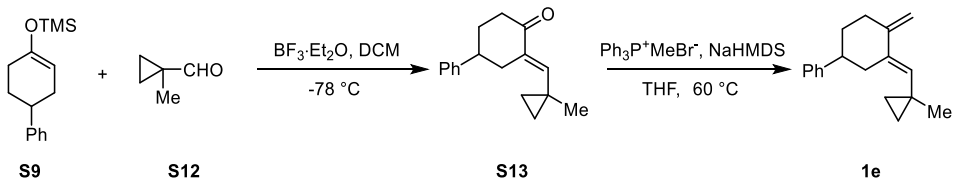
TLC (10:1 PE/EA, R_f): 0.8.

^1H NMR (400 MHz, CD_2Cl_2, δ): 7.35 – 7.27 (m, 4H), 7.24 – 7.17 (m, 1H), 4.97 (dd, J = 9.7, 2.2 Hz, 1H), 4.85 (dd, J = 2.3, 2.3 Hz, 1H), 4.63 (dd, J = 2.2, 2.2 Hz, 1H), 2.98 (ddd, J = 13.8, 4.0, 2.2 Hz, 1H), 2.84 – 2.73 (m, 1H), 2.49 (ddd, J = 13.7, 3.7, 3.7 Hz, 1H), 2.36 – 2.24 (m, 1H), 2.18 (ddd, J = 14.2, 12.2, 2.2 Hz, 1H), 2.07 – 1.97 (m, 1H), 1.73 (ddd, J = 12.6, 12.6, 4.1 Hz, 1H), 1.59 – 1.46 (m, 1H), 0.80 – 0.71 (m, 2H), 0.45 – 0.34 (m, 2H).

$^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, δ): 150.3, 147.1, 138.0, 129.0, 128.8, 127.3, 126.5, 107.3, 44.2, 36.8, 35.2, 34.8, 10.2, 7.41, 7.36.

HRMS (EI) m/z: calcd. for $C_{17}H_{20}$ ($[M\cdot]^+$): 224.1560, found: 224.1560.

S12 is a known compound and was synthesized according to the reported literature.[1]



S9 **S12** **S13** **1e**

To a flask with **S12** (1.68 g, 20 mmol) in DCM (90 mL) was added $BF_3{\cdot}Et_2O$ (6.8 mL, *d* = 1.125 g/mL, 54 mmol) under an argon atmosphere at -78 °C. Then a solution of **S9** (15 mmol) in DCM (30 mL) was added dropwise. The obtained mixture was then stirred for 2.5 h at -78 °C, quenched with saturated aqueous NH_4Cl solution, and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 10:1 PE/EA) afforded compound **S13** (1.61 g).

To a flask with $Ph_3P^+MeBr^-$ (857.3 mg, 2.4 mmol) was added THF (20 mL) and NaHMDS (1.2 mL, 2M, 2.4 mmol) under an argon atmosphere at rt. 3.5 h later, a solution of **S13** (480.3 mg, 2 mmol) in THF (8 mL) was added dropwise. The obtained mixture was then stirred for 9 h at 60 °C, quenched with water, and extracted with ether. The combined organic layer was washed with brine, and dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 1:0 to 20:1 PE/EA) afforded compound **1e** (311.9 mg, 29%, two steps) as a white solid.

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

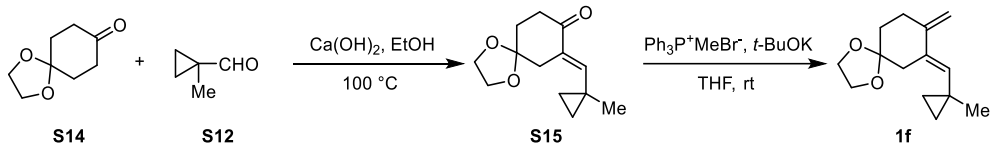
Melting Point: 53.2 – 54.8 °C

^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.38 – 7.29 (m, 2H), 7.31 – 7.18 (m, 3H), 5.72 (s, 1H), 4.88 – 4.82 (m, 1H), 4.66 – 4.60 (m, 1H), 3.16 (dd, *J* = 13.8, 2.2 Hz, 1H), 2.77 – 2.64 (m, 1H), 2.49 (dd, *J* = 13.7, 3.3 Hz, 1H), 2.35 – 2.22 (m, 1H), 2.09 (ddd, *J* = 14.3, 12.2, 1.9 Hz, 1H), 2.05 – 1.96 (m, 1H), 1.78 – 1.63 (m, 1H), 1.12 (s, 3H), 0.56 – 0.47 (m, 2H), 0.48 – 0.39 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, *δ*): 150.0, 146.8, 142.2, 129.1, 128.6, 127.0, 126.4, 107.8, 44.1, 37.4, 35.1, 34.4, 25.2, 14.9, 14.74, 14.67.

HRMS (EI) m/z: calcd. for $C_{18}H_{22}$ ($[M\cdot]^+$): 238.1716, found: 238.1716.

S14 is commercially available. The reaction condition of this aldol condensation was modified according to the reported literature.[3]



To a sealed tube with **S12** (632.5 mg, 66.5% in DCM, 5 mmol) in EtOH (15 mL) was added **S14** (1.56 g, 10 mmol) and $Ca(OH)_2$ (37 mg, 0.5 mmol) under an argon atmosphere. The obtained mixture was then refluxed for 24 h at 100 °C, quenched with water, and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 30:1 PE/EA) and PTLC (3:1 PE/EA) afforded compound **S15** (168 mg).

To a flask with $Ph_3P^+MeBr^-$ (1.36 g, 3.8 mmol) and *t*-BuOK (426.4 mg, 3.8 mmol) was added THF (15 mL) under an argon atmosphere at rt. 30 min later, a solution of **S15** (168 mg, 0.76 mmol) in THF (5 mL) was added dropwise. The obtained mixture was then stirred for 3 h at rt, quenched with water, and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 100:1 PE/EA) afforded compound **1f** (130 mg, 12%, two

steps) as a light yellow oil.

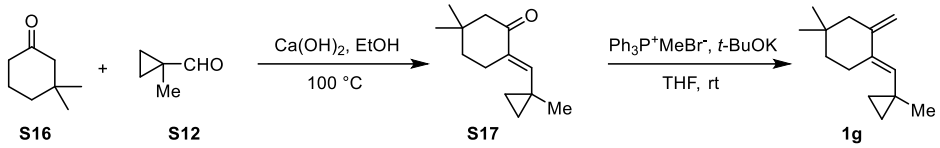
TLC (10:1 PE/EA, R_f): 0.8.

^{1}H NMR (400 MHz, C_6D_6, δ): 5.96 – 5.91 (m, 1H), 5.05 – 4.99 (m, 1H), 4.69 – 4.64 (m, 1H), 3.65 – 3.54 (m, 2H), 3.57 – 3.47 (m, 2H), 2.82 (s, 2H), 2.45 – 2.36 (m, 2H), 1.84 – 1.75 (m, 2H), 1.14 (s, 3H), 0.65 – 0.58 (m, 2H), 0.45 – 0.38 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, δ): 148.9, 140.3, 130.6, 109.3, 108.5, 64.5, 39.1, 35.7, 31.8, 25.2, 15.0, 14.8.

HRMS (ESI) m/z: calcd. for $C_{14}H_{21}O_2$ ($[M+H]^+$): 221.1536, found: 221.1536.

S16 is commercially available.



S16 **S12** **S17** **1g**

To a sealed tube with **S12** (673 mg, 8 mmol) in EtOH (24 mL) was added **S16** (2.02 g, 16 mmol) and $Ca(OH)_2$ (59.3 mg, 0.8 mmol). The obtained mixture was then refluxed for 24 h at 100 °C. The mixture was concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 80:1 to 70:1 PE/EA) afforded compound **S17** (149 mg).

To a flask with $Ph_3P^+MeBr^-$ (1.39 g, 3.9 mmol) and *t*-BuOK (437.6 mg, 3.9 mmol) was added THF (15 mL) under an argon atmosphere at rt. 30 min later, a solution of **S17** (149 mg, 0.77 mmol) in THF (5 mL) was added dropwise. The obtained mixture was then stirred for 1 h at rt, quenched with water, and extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, washed with ether, and concentrated by rotary evaporation at low temperature. Purification of the crude product by flash column chromatography (silica gel, *n*-pentane) afforded compound **1g** (26.4 mg, 2%, two steps) as a colorless oil.

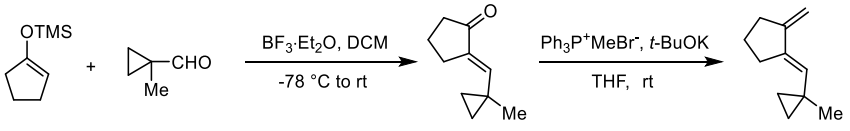
TLC (10:1 PE/EA, R_f): 0.9.

^{1}H NMR (400 MHz, C_6D_6, δ): 5.87 – 5.82 (m, 1H), 5.05 – 4.98 (m, 1H), 4.66 – 4.60 (m, 1H), 2.50 – 2.42 (m, 2H), 2.02 – 1.96 (m, 2H), 1.38 – 1.34 (m, 2H), 1.13 (s, 3H), 0.90 (s, 6H), 0.59 – 0.53 (m, 2H), 0.45 – 0.39 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, δ): 149.4, 142.7, 128.4, 109.0, 48.9, 39.0, 31.9, 28.1, 25.9, 25.2, 15.1, 14.9.

HRMS (EI) m/z: calcd. for $C_{14}H_{22}$ ($[M\cdot]^+$): 190.1716, found: 190.1715.

S18 is commercially available.



S18 **S12** **S19** **1h**

To a flask with **S12** (412 mg, 4.9 mmol) in DCM (20 mL) was added $BF_3{\cdot}Et_2O$ (2.2 mL, d = 1.125 g/mL, 17.4 mmol) under an argon atmosphere at -78 °C. Then a solution of **S18** (1001 mg, 5 mmol) in DCM (4 mL) was added by syringe pump in 1 h. The obtained mixture was then stirred for 3.5 h at

-78 °C, then for 6 h at 0 °C to rt, quenched with saturated aqueous $NaHCO_3$ solution, and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 100:1 to 50:1 PE/EA) afforded compound **S19** (109.8 mg).

To a flask with $Ph_3P^+MeBr^-$ (1.999 g, 5.6 mmol) and *t*-BuOK (683 mg, 5.6 mmol) was added THF (10 mL) under an argon atmosphere at rt. 30 min later, a solution of **S19** (279 mg, 1.86 mmol) in THF (5 mL) was added dropwise. The obtained mixture was then stirred for 3.5 h at rt, quenched with water, and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, washed with ether, and concentrated by rotary evaporation at low temperature. Purification of the crude product by flash column chromatography (silica gel, 1:0 PE/EA) afforded compound **1h** (116.1 mg, 6%, two steps) as a colorless oil.

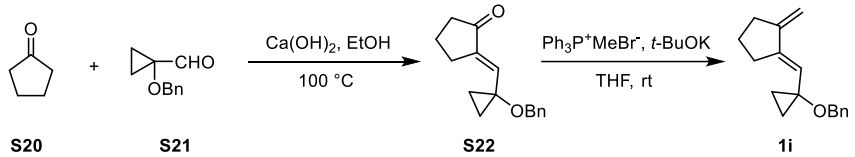
TLC (10:1 PE/EA, R_f): 0.9.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.85 (t, *J* = 2.6 Hz, 1H), 5.18 (t, *J* = 2.4 Hz, 1H), 4.74 (t, *J* = 2.1 Hz, 1H), 2.52 (td, *J* = 7.2, 2.5 Hz, 2H), 2.36 (tdd, *J* = 7.2, 2.2, 2.2 Hz, 2H), 1.67 (tt, *J* = 7.2, 7.2 Hz, 2H), 1.19 (s, 3H), 0.61 – 0.54 (m, 2H), 0.51 – 0.46 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 150.6, 140.8, 125.5, 100.8, 34.1, 30.8, 24.4, 24.1, 16.3, 15.2.

HRMS (EI) m/z: calcd. for $C_{11}H_{16}$ ($[M\cdot]^+$): 148.1246, found: 148.1246.

S20 and **S21** are commercially available.



S20 **S21** **S22** **1i**

To a flask with **S21** (1156 mg, 6.56 mmol) in EtOH (20 mL) was added **S20** (1.74 mL, *d* = 0.951 g/mL, 19.7 mmol) and $Ca(OH)_2$ (100 mg, 1.3 mmol). The obtained mixture was then refluxed for 7 h at 100 °C. The mixture was concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 to 25:1 PE/EA) afforded compound **S22** (699.4 mg).

To a flask with $Ph_3P^+MeBr^-$ (1.537 g, 4.3 mmol) and *t*-BuOK (533 mg, 4.4 mmol) was added THF (10 mL) under an argon atmosphere at rt. 10 min later, a solution of **S22** (0.86 mmol) in THF (2 mL) was added dropwise. The obtained mixture was then stirred for 40 min at rt, quenched with water, and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, washed with ether, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 PE/EA) afforded compound **1i** (186 mg, 40%, two steps) as a light yellow oil.

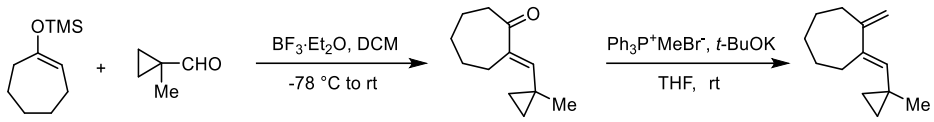
TLC (10:1 PE/EA, R_f): 0.9.

^{1}H NMR (400 MHz, C_6D_6, δ): 7.26 (d, *J* = 7.1 Hz, 2H), 7.15 – 7.12 (m, 2H), 7.09 – 7.03 (m, 1H), 5.89 (t, *J* = 2.5 Hz, 1H), 5.35 (t, *J* = 2.4 Hz, 1H), 4.87 (t, *J* = 2.2 Hz, 1H), 4.42 (s, 2H), 2.60 (td, *J* = 7.2, 2.5 Hz, 2H), 2.24 (tdd, *J* = 7.3, 2.2, 2.2 Hz, 2H), 1.47 (tt, *J* = 7.2, 7.2 Hz, 2H), 1.08 – 1.02 (m, 2H), 0.60 – 0.53 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, δ): 150.1, 144.2, 139.6, 128.5, 127.6, 127.4, 119.8, 102.6, 69.9, 60.3, 34.1, 31.7, 24.6, 15.0.

HRMS (ESI) m/z: calcd. for $C_{17}H_{21}O$ ($[M+H]^+$): 241.1587, found: 241.1587.

S23 is a known compound and was synthesized according to the reported literature.[4]



S23 **S12** **S24** **1j**

To a flask with **S12** (504.7 mg, 6 mmol) in DCM (20 mL) was added $BF_3{\cdot}Et_2O$ (0.63 mL, *d* = 1.125 g/mL, 5 mmol) under an argon atmosphere at -78 °C. Then a solution of **S23** (921.7 mg, 5 mmol) in DCM (5 mL) was added dropwise. The obtained mixture was then stirred for 17 h at -78 °C to rt, quenched with saturated aqueous NH_4Cl solution, and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 PE/EA) afforded compound **S24** (177 mg).

To a flask with $Ph_3P^+MeBr^-$ (714.4 mg, 2 mmol) and *t*-BuOK (224.4 mg, 2 mmol) was added THF (10 mL) under an argon atmosphere at rt. 30 min later, a solution of **S24** (177 mg, 1 mmol) in THF (5 mL) was added dropwise. The obtained mixture was then stirred for 15 h at rt, quenched with water, and extracted with EA. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, washed with ether, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 100:1 *n*-pentane/Et_3N) afforded compound **1j** (84.8 mg, 15%, two steps) as a colorless oil.

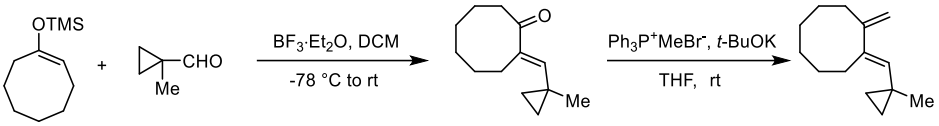
TLC (10:1 PE/EA, R_f): 0.9.

^{1}H NMR (400 MHz, C_6D_6, *δ*): 5.95 (s, 1H), 5.13 (d, *J* = 2.4 Hz, 1H), 4.74 – 4.69 (m, 1H), 2.55 – 2.48 (m, 2H), 2.27 – 2.21 (m, 2H), 1.61 – 1.45 (m, 6H), 1.13 (s, 3H), 0.59 – 0.54 (m, 2H), 0.44 – 0.39 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, *δ*): 153.9, 146.1, 129.6, 109.6, 36.7, 32.0, 30.9, 30.2, 28.8, 25.0, 15.3, 15.2.

HRMS (EI) m/z: calcd. for $C_{13}H_{20}$ ($[M\cdot]^+$): 176.1560, found: 176.1559.

S25 is a known compound and was synthesized according to the reported literature.[5]



S25 **S12** **S26** **1k**

To a flask with **S12** (352.6 mg, 4.2 mmol) in DCM (30 mL) was added $BF_3{\cdot}Et_2O$ (0.53 mL, *d* = 1.125 g/mL, 4.2 mmol) under an argon atmosphere at -78 °C. Then a solution of **S25** (833.2 mg, 4.2 mmol) in DCM (5 mL) was added dropwise. The obtained mixture was then stirred for 15.5 h at -78 °C to rt, quenched with saturated aqueous NH_4Cl solution, and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 PE/EA) afforded compound **S26** (176 mg).

To a flask with $Ph_3P^+MeBr^-$ (714.4 mg, 2 mmol) and *t*-BuOK (224.4 mg, 2 mmol) was added THF (10 mL) under an argon atmosphere at rt. 30 min later, a solution of **S26** (176 mg, 0.92 mmol) in THF (5 mL) was added dropwise. The obtained mixture was then stirred for 16 h at rt, quenched with water, and extracted with EA. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, washed with ether, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 100:1 *n*-pentane/Et_3N) afforded compound **1k** (89.6 mg, 11%, two steps) as a colorless oil.

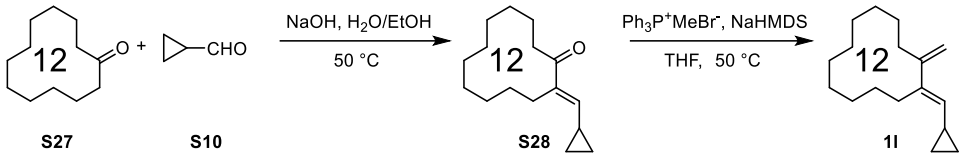
TLC (10:1 PE/EA, R_f): 1.0.

^{1}H NMR (400 MHz, CD_2Cl_2, δ): 5.60 (s, 1H), 4.85 (d, J = 2.4 Hz, 1H), 4.71 (dt, J = 2.2, 1.0 Hz, 1H), 2.56 – 2.50 (m, 2H), 2.29 – 2.20 (m, 2H), 1.66 – 1.57 (m, 4H), 1.57 – 1.50 (m, 4H), 1.17 (s, 3H), 0.57 – 0.51 (m, 2H), 0.51 – 0.45 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, δ): 154.7, 145.5, 130.8, 109.9, 35.6, 30.9, 28.1, 28.0, 26.8, 26.8, 25.4, 15.4, 15.2.

HRMS (EI) m/z: calcd. for $C_{14}H_{22}$ ([M·]$^+$): 190.1716, found: 190.1716.

S27 is commercially available.



To a flask with **S27** (3.6462 g, 20 mmol) in EtOH (7 mL) was added **S10** (2.1 g, 30 mmol) under an argon atmosphere at 50 °C. Then a solution of NaOH (1.2 g, 30 mmol) in water (12 mL) was added. The obtained mixture was then stirred for 16 h at 50 °C, and extracted with ester. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 20:1 PE/EA) afforded compound **S28** (2.5424 g, with impurity of **S27**).

To a flask with $Ph_3P^+MeBr^-$ (4.65 g, 13 mmol) was added THF (80 mL) and NaHMDS (6.5 mL, 2M, 13 mmol) under an argon atmosphere at rt. 2 h later, a solution of **S28** (2.5424 g, with impurity of **S27**) in THF (10 mL) was added dropwise. The obtained mixture was then stirred for 2.5 h at 50 °C, quenched with water, and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 15:1 PE/EA) afforded compound **1l** (1.5112 g, **1l**: methylenecyclodecane = 1:1.75, 14%, two steps) as a colorless oil.

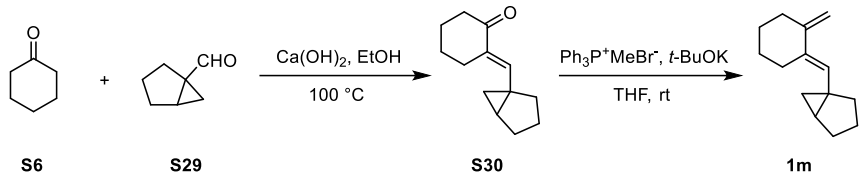
TLC (10:1 PE/EA, R_f): 0.9.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.02 – 4.95 (m, 2H), 4.87 (s, 1H), 2.55 – 2.46 (m, 2H), 2.35 – 2.27 (m, 2H), 1.66 – 1.56 (m, 1H), 1.48 – 1.40 (m, 2H), 1.39 – 1.17 (m, 14H), 0.82 – 0.74 (m, 2H), 0.42 – 0.35 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 146.0, 135.5, 133.9, 111.6, 34.8, 27.0, 26.83, 26.79, 24.4, 24.0, 23.53, 23.51, 22.41, 22.37, 11.2, 7.6.

HRMS (EI) m/z: calcd. for $C_{17}H_{28}$ ([M·]$^+$): 232.2186, found: 232.2184.

S29 is a known compound and was synthesized according to the reported literature.[6]



To a flask with **S29** (500.8 mg, 5 mmol) in EtOH (15 mL) was added **S28** (981.4 mg, 10 mmol) and $Ca(OH)_2$ (37.04 mg, 0.5 mmol) under an argon atmosphere. The obtained mixture was then refluxed for 24 h at 100 °C. The mixture was concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 100:1 PE/EA) afforded compound **S30** (277.6 mg).

To a flask with $Ph_3P^+MeBr^-$ (2.5 g, 7 mmol) and *t*-BuOK (785.5 mg, 7 mmol) was added THF (30 mL) under an argon atmosphere at rt. 30 min later, a solution of **S30** (277.6 mg, 1.4 mmol) in THF (5 mL) was added dropwise. The obtained mixture was then stirred for 4 h at rt, quenched with water, and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 1:0 PE/EA) afforded compound **1m** (194.6 mg, 21%, two steps) as a colorless oil.

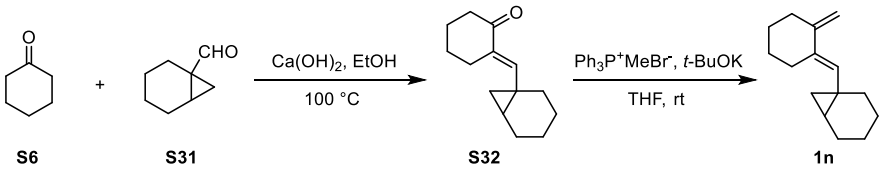
TLC (10:1 PE/EA, R_f): 0.9.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.65 (s, 1H), 4.78 (d, J = 2.7 Hz, 1H), 4.56 – 4.51 (m, 1H), 2.40 – 2.32 (m, 2H), 2.26 – 2.19 (m, 2H), 1.86 – 1.77 (m, 2H), 1.73 – 1.66 (m, 1H), 1.65 – 1.56 (m, 6H), 1.23 – 1.12 (m, 2H), 0.58 (dd, J = 4.4, 4.4 Hz, 1H), 0.46 (dd, J = 8.1, 4.6 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 151.3, 143.0, 126.5, 107.1, 35.6, 33.2, 29.8, 27.8, 27.4, 27.2, 26.4, 25.8, 21.5, 14.0.

HRMS (EI) m/z: calcd. for $C_{14}H_{20}$ ($[M\cdot]^+$): 188.1560, found: 188.1558.

S31 is a known compound and was synthesized according to the reported literature.[7]



To a flask with **S31** (808 mg, 6.5 mmol) in EtOH (19.5 mL) was added **S6** (1.283 g, 13 mmol) and $Ca(OH)_2$ (50.8 mg, 0.69 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, 100:1 to 50:1 PE/EA) afforded compound **S32** (301.5 mg).

To a flask with $Ph_3P^+MeBr^-$ (1.268 g, 3.5 mmol) and *t*-BuOK (438 mg, 3.6 mmol) was added THF (10 mL) under an argon atmosphere at rt. 10 min later, a solution of **S32** (301.5 mg, 1.47 mmol) in THF (2 mL) was added dropwise. The obtained mixture was then stirred for 13 h at rt, quenched with water, and extracted with ester. The combined organic layer was washed with brine, and dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 1:0 PE/EA) afforded compound

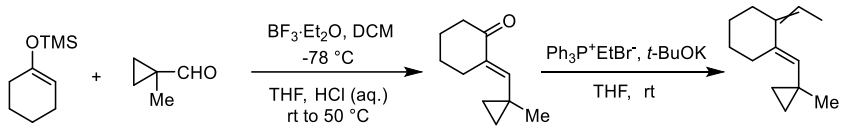
1n (118.8 mg, 9%, two steps) as a colorless oil.

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

^{1}H NMR (400 MHz, C_6D_6, δ): 5.90 (s, 1H), 4.99 (d, J = 2.7 Hz, 1H), 4.68 – 4.64 (m, 1H), 2.46 – 2.37 (m, 2H), 2.25 – 2.19 (m, 2H), 1.97 – 1.87 (m, 1H), 1.86 – 1.71 (m, 2H), 1.63 – 1.47 (m, 5H), 1.32 – 1.21 (m, 1H), 1.20 – 1.11 (m, 2H), 1.10 – 1.01 (m, 1H), 1.01 – 0.93 (m, 1H), 0.69 (dd, J = 9.2, 4.1 Hz, 1H), 0.41 (dd, J = 5.6, 4.2 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, δ): 151.0, 142.6, 131.4, 107.5, 35.9, 30.7, 30.1, 27.4, 26.6, 24.3, 21.9, 21.6, 19.7, 19.3, 18.9.

HRMS (EI) m/z: calcd. for $C_{15}H_{22}$ ([M·]$^+$): 202.1716, found: 202.1714.



S1 **S12** **S33** **1o**

To a flask with **S12** (437 mg, 5.2 mmol) in DCM (20 mL) was added BF_3·Et_2O (2.2 mL, d = 1.125 g/mL, 17.4 mmol) under an argon atmosphere at -78 °C. Then a solution of **S1** (978 mg, 5.7 mmol) in DCM (4 mL) was added by syringe pump in 1 h. The obtained mixture was then stirred for 3 h at -78 °C, quenched with saturated aqueous NH_4Cl solution, and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Then 15 mL THF and 30 mL 1M HCl were added, and the mixture was stirred for 3.25 h at rt and for 0.5 h at 50 °C, and extracted with ester. The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 PE/EA) afforded compound **S33** (355.4 mg).

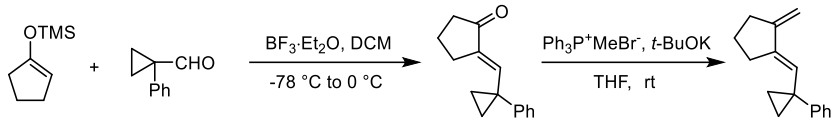
To a flask with $Ph_3P^+EtBr^-$ (1.608 g, 4.3 mmol) and *t*-BuOK (533 mg, 4.4 mmol) was added THF (10 mL) under an argon atmosphere at rt. 20 min later, a solution of **S33** (355.4 mg, 2.16 mmol) in THF (3 mL) was added dropwise. The obtained mixture was then stirred for 1 h at rt, quenched with water, and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 1:0 PE/EA) afforded compound **1o** (120.1 mg, 13%, two steps) as a colorless oil.

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

^{1}H NMR for the major isomer (400 MHz, $CDCl_3$, δ): 5.33 (s, 1H), 5.19 (qt, J = 6.7, 1.3 Hz, 1H), 2.36 (t, J = 5.6 Hz, 2H), 2.16 – 2.09 (m, 2H), 1.64 – 1.58 (m, 4H), 1.60 (dt, J = 6.1, 1.4 Hz, 3H), 1.16 (s, 3H), 0.53 – 0.50 (m, 2H), 0.48 – 0.46 (m, 2H).

^{13}C{^{1}H} NMR for the major isomer (101 MHz, $CDCl_3$, δ): 142.3, 140.0, 130.7, 117.1, 38.3, 30.6, 28.2, 27.6, 25.6, 14.9, 14.8, 14.4.

HRMS (EI) m/z: calcd. for $C_{13}H_{20}$ ([M·]$^+$): 176.1560, found: 176.1559.



S18 **S2** **S34** **1p**

To a flask with **S2** (442 mg, 3 mmol) in DCM (15 mL) was added $BF_3{\cdot}Et_2O$ (1.3 mL, *d* = 1.125 g/mL, 10 mmol) under an argon atmosphere at -78 °C. Then **S18** (0.64 mL, *d* = 0.878 g/mL, 3.6 mmol) was added by syringe pump in 1 h. The obtained mixture was then stirred for 4 h at -20 °C, then for 7 h at 0 °C, quenched with saturated aqueous NH_4Cl solution, and extracted with DCM. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 PE/EA) afforded compound **S34** (351.9 mg).

To a flask with $Ph_3P^+MeBr^-$ (1.189 g, 3.3 mmol) and *t*-BuOK (406 mg, 3.3 mmol) was added THF (7 mL) under an argon atmosphere at rt. 30 min later, a solution of **S34** (351.9 mg, 1.66 mmol) in THF (1.3 mL) was added dropwise. The obtained mixture was then stirred for 18 h at rt, quenched with water, and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 100:1 to 20:1 PE/EA) afforded compound **1p** (258.6 mg, 41%, two steps) as a colorless oil.

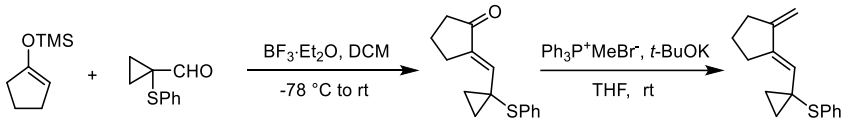
TLC (10:1 PE/EA, R_f): 0.9.

^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.26 – 7.20 (m, 4H), 7.17 – 7.09 (m, 1H), 6.07 (t, *J* = 2.6 Hz, 1H), 5.29 – 5.24 (m, 1H), 4.82 – 4.77 (m, 1H), 2.34 (tdd, *J* = 7.3, 2.2, 2.2 Hz, 2H), 2.18 (td, *J* = 7.3, 2.5 Hz, 2H), 1.57 (tt, *J* = 7.2, 7.2 Hz, 2H), 1.15 – 1.10 (m, 2H), 1.05 – 1.00 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, *δ*): 150.2, 145.2, 143.1, 128.3, 127.3, 125.6, 123.7, 101.5, 34.1, 31.1, 25.0, 24.2, 17.4.

HRMS (EI) m/z: calcd. for $C_{16}H_{18}$ ($[M\cdot]^+$): 210.1403, found: 210.1401.

S35 is a known compound and was synthesized according to the reported literature.[1]



S18 **S35** **S36** **1q**

To a flask with **S35** (895 mg, 5 mmol) in DCM (20 mL) was added $BF_3{\cdot}Et_2O$ (1.3 mL, *d* = 1.125 g/mL, 10 mmol) under an argon atmosphere at -78 °C. Then the solution of **S18** (898 mg, 5.7 mmol) in DCM (4 mL) was added dropwise. The obtained mixture was then stirred for 1 h at -78 °C, then for 17 h at -78 °C to rt, quenched with saturated aqueous $NaHCO_3$ solution, and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 PE/EA) afforded compound **S36** (170.8 mg).

To a flask with $Ph_3P^+MeBr^-$ (1.824 g, 3 mmol) and *t*-BuOK (625 mg, 3 mmol) was added THF (15 mL) under an argon atmosphere at rt. 30 min later, a solution of **S36** (1.7 mmol) in THF (2 mL) was added dropwise. The obtained mixture was then stirred for 3 h at rt, quenched with water, and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous

Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 1:0 PE/EA) afforded compound **1q** (232.2 mg, 8%, two steps) as a colorless oil.

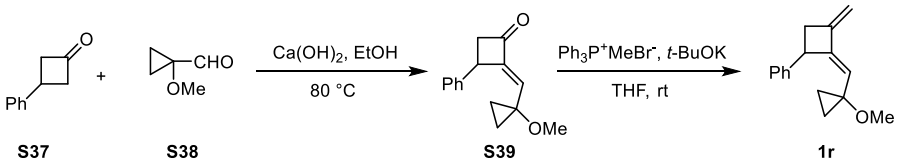
TLC (10:1 PE/EA, R_f): 0.9.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.42 (d, J = 7.5 Hz, 2H), 7.29 – 7.24 (m, 2H), 7.23 – 7.17 (m, 1H), 6.14 – 6.08 (m, 1H), 5.23 (s, 1H), 4.79 (s, 1H), 2.34 – 2.22 (m, 4H), 1.51 (tt, J = 7.2, 7.2 Hz, 2H), 1.22 – 1.16 (m, 2H), 1.09 – 1.03 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 149.8, 144.0, 136.5, 131.0, 128.7, 126.6, 121.0, 102.3, 34.0, 31.0, 26.1, 24.2, 17.5.

HRMS (ESI) m/z: calcd. for $C_{16}H_{19}S$ ($[M+H]^+$): 243.1202, found: 243.1203.

S37 and **S38** are commercially available.



To a flask with **S38** (353 mg, 3.5 mmol) in EtOH (10 mL) was added **S37** (437 mg, 3 mmol) and $Ca(OH)_2$ (66 mg, 0.9 mmol). The obtained mixture was then refluxed for 23 h at 80 °C. The mixture was concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 100:1 to 50:1 to 25:1 to 10:1 PE/EA) afforded compound **S39** (223.3 mg).

To a flask with $Ph_3P^+MeBr^-$ (714.3 mg, 2 mmol) and *t*-BuOK (244.3 mg, 2 mmol) was added THF (7 mL) under an argon atmosphere at rt. 30 min later, a solution of **S39** (223.3 mg, 0.98 mmol) in THF (3 mL) was added dropwise. The obtained mixture was then stirred for 40 min at rt, quenched with water, and extracted with ester. The combined organic layer was washed with brine, and dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 100:1 to 50:1 PE/EA) afforded compound **1r** (81.2 mg, 12%, two steps) as a yellow oil.

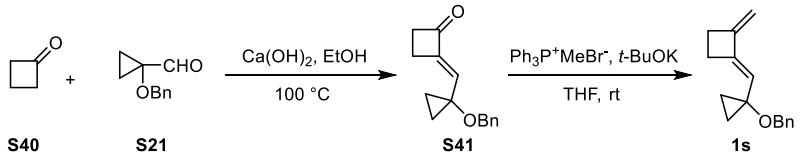
TLC (10:1 PE/EA, R_f): 0.8.

^{1}H NMR (400 MHz, CD_2Cl_2, δ): 7.33 – 7.27 (m, 4H), 7.22 – 7.16 (m, 1H), 5.77 (d, J = 2.5 Hz, 1H), 5.24 (dd, J = 2.9, 2.9 Hz, 1H), 4.75 (dd, J = 2.4, 2.4 Hz, 1H), 4.17 (ddd, J = 9.4, 5.5, 2.5 Hz, 1H), 3.27 – 3.18 (m, 1H), 3.04 (s, 3H), 2.58 – 2.50 (m, 1H), 0.82 – 0.74 (m, 2H), 0.62 – 0.57 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, δ): 148.0, 145.4, 144.3, 128.6, 127.4, 126.4, 121.5, 102.5, 60.8, 55.4, 45.6, 40.2, 15.4, 14.1.

HRMS (ESI) m/z: calcd. for $C_{16}H_{19}O$ ($[M+H]^+$): 227.1430, found: 227.1430.

S37 and **S38** are commercially available.



To a flask with **S21** (882 mg, 5 mmol) in EtOH (15 mL) was added **S40** (1064 mg, 15.2 mmol) and $Ca(OH)_2$ (37.6 mg, 0.51 mmol). The obtained mixture was then refluxed for 20.5 h at 100 °C. The mixture was concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 to 25:1 PE/EA) afforded compound **S41** (109.4 mg).

To a flask with $Ph_3P^+MeBr^-$ (859 mg, 2.4 mmol) and *t*-BuOK (296 mg, 2.4 mmol) was added THF (5 mL) under an argon atmosphere at rt. 10 min later, a solution of **S41** (109.4 mg, 0.48 mmol) in THF (2 mL) was added dropwise. The obtained mixture was then stirred for 70 min at rt, quenched with water, and extracted with ester. The combined organic layer was washed with brine, and dried over anhydrous Na_2SO_4, filtered, washed with EA, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 1:0 to 100:1 to 50:1 to 20:1 PE/EA) afforded compound **1s** (78.9 mg, 7%, two steps) as a yellow oil.

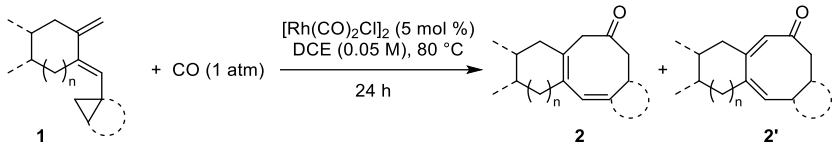
TLC (10:1 PE/EA, R_f): 0.8.

^{1}H NMR (400 MHz, C_6D_6, δ): 7.25 (d, J = 7.1 Hz, 2H), 7.15 – 7.11 (m, 2H), 7.09 – 7.03 (m, 1H), 5.56 (t, J = 2.7 Hz, 1H), 5.12 (t, J = 2.9 Hz, 1H), 4.63 (t, J = 2.4 Hz, 1H), 4.43 (s, 2H), 2.68 – 2.59 (m, 2H), 2.50 – 2.40 (m, 2H), 1.04 – 0.96 (m, 2H), 0.59 – 0.52 (m, 2H).

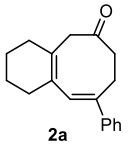
^{13}C{^{1}H} NMR (101 MHz, C_6D_6, δ): 149.8, 142.3, 139.5, 128.5, 127.40, 127.38, 120.0, 102.0, 70.2, 60.7, 29.0, 28.0, 14.8.

HRMS (ESI) m/z: calcd. for $C_{16}H_{19}O$ ($[M+H]^+$): 227.1430, found: 227.1430.

3. General procedure for [7 + 1] cycloaddition



To a reaction tube with **1** and $[Rh(CO)_2Cl]_2$ (5 mol %) was added DCE (0.05 M of **1**) under an argon atmosphere. The reaction mixture was charged with CO three times and bubbled with balloon pressured (slightly higher than 1 atm) gas of CO at room temperature for 5 min and then stirred at 80 °C for 24 h under balloon pressured gas of CO, 600 rpm for the magnetic stir bars. After cooling, purification of the crude product by flash column chromatography (silica gel, PE/EA) afforded [7 + 1] cycloadduct **2**.



run 1: Following general procedure. Substrate: **1a** (45.5 mg, 0.203 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), DCE (4 mL), flash column chromatography (silica gel, 100:1 to 10:1 PE/EA); product: **2a** (27.2 mg, 53%).

run 2: Following general procedure. Substrate: **1a** (45.4 mg, 0.202 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), DCE (4 mL), flash column chromatography (silica gel, 100:1 to 10:1 PE/EA); product: **2a** (26.2 mg, 51%).

The average yield of two runs: 52%.

1 mmol scale experiments:

run 1: Following general procedure with 100 mL flask, the reaction time is 24 h. Substrate: **1a** (224.1 mg, 1 mmol), $[Rh(CO)_2Cl]_2$ (19.4 mg, 0.02 mmol), DCE (20 mL), flash column chromatography (silica gel, 50:1 PE/EA); product: **2a** (111.9 mg, 44%).

run 2: Following general procedure with 100 mL flask, the reaction time is 24 h. Substrate: **1a** (223.2 mg, 1 mmol), $[Rh(CO)_2Cl]_2$ (19.4 mg, 0.02 mmol), DCE (20 mL), flash column chromatography (silica gel, 50:1 PE/EA); product: **2a** (100.7 mg, 40%).

The average yield of two runs: 42%.

run 3: Following general procedure with 100 mL flask, the reaction time is 72 h. Substrate: **1a** (223.6 mg, 1 mmol), $[Rh(CO)_2Cl]_2$ (7.8 mg, 0.02 mmol), DCE (20 mL), flash column chromatography (silica gel, 50:1 PE/EA); product: **2a** (64 mg, 25%).

run 4: Following general procedure with 100 mL flask, the reaction time is 72 h. Substrate: **1a** (223.4 mg, 1 mmol), $[Rh(CO)_2Cl]_2$ (7.8 mg, 0.02 mmol), DCE (20 mL), flash column chromatography (silica gel, 50:1 PE/EA); product: **2a** (66.7 mg, 27%).

run 5: Following general procedure with 100 mL flask, the reaction time is 24 h. Substrate: **1a** (222.5

mg, 1 mmol), $[Rh(CO)_2Cl]_2$ (7.9 mg, 0.02 mmol), DCE (20 mL), flash column chromatography (silica gel, 20:1 PE/EA); product: **2a** (79.8 mg, 32%).

Note: longer time leads to decompose of the products

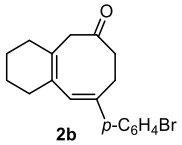
Physical Form: colorless oil

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

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.51 (d, J = 7.7 Hz, 2H), 7.37 (dd, J = 8.6, 6.6 Hz, 2H), 7.33 – 7.27 (m, 1H), 6.24 (s, 1H), 3.19 (s, 2H), 2.87 – 2.77 (m, 2H), 2.41 – 2.34 (m, 2H), 2.25 – 2.16 (m, 2H), 2.09 – 2.00 (m, 2H), 1.70 – 1.62 (m, 4H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 209.8, 141.7, 139.9, 134.2, 130.1, 129.3, 128.7, 127.7, 126.5, 50.0, 38.4, 29.9, 29.6, 28.3, 23.2, 22.8.

HRMS (ESI) m/z: calcd. for $C_{18}H_{21}O$ ($[M+H]^+$): 253.1587, found: 253.1586.



2b

run 1: Following general procedure. Substrate: **1b** (60.6 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), DCE (4 mL), flash column chromatography (silica gel, 100:1 to 50:1 PE/EA); product: **2b** (21.5 mg, 32%).

run 2: Following general procedure. Substrate: **1b** (61.3 mg, 0.202 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.0103 mmol), DCE (4 mL), flash column chromatography (silica gel, 100:1 to 50:1 PE/EA); product: **2b** (18.6 mg, 28%).

The average yield of two runs: 30%.

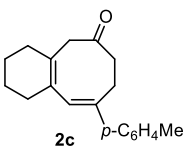
Physical Form: yellow oil

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

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.49 (d, J = 8.6 Hz, 2H), 7.36 (d, J = 8.6 Hz, 2H), 6.23 (s, 1H), 3.17 (s, 2H), 2.85 – 2.75 (m, 2H), 2.41 – 2.32 (m, 2H), 2.23 – 2.15 (m, 2H), 2.08 – 1.99 (m, 2H), 1.70 – 1.60 (m, 4H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 209.3, 140.5, 138.8, 133.9, 131.8, 130.5, 129.6, 128.1, 121.6, 50.0, 38.3, 29.9, 29.5, 28.2, 23.2, 22.7.

HRMS (ESI) m/z: calcd. for $C_{18}H_{20}BrO$ ($[M+H]^+$): 331.0692, found: 331.0696.



2c

run 1: Following general procedure. Substrate: **1c** (47.5 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), DCE (4 mL), flash column chromatography (silica gel, 100:1 PE/EA); product: **2c** (29.7 mg, 56%).

run 2: Following general procedure. Substrate: **1c** (47.3 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.8 mg, 0.01 mmol), DCE (4 mL), flash column chromatography (silica gel, 100:1 PE/EA); product: **2c** (31.4 mg, 59%).

The average yield of two runs: 58%.

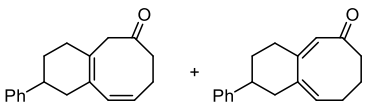
Physical Form: tan oil

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

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.40 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 7.9 Hz, 2H), 6.21 (s, 1H), 3.18 (s, 2H), 2.85 – 2.74 (m, 2H), 2.40 – 2.33 (m, 5H), 2.25 – 2.15 (m, 2H), 2.06 – 2.00 (m, 2H), 1.70 – 1.59 (m, 4H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 209.9, 139.7, 138.6, 137.5, 134.3, 129.4, 129.2, 129.1, 126.3, 50.0, 38.4, 29.8, 29.6, 28.2, 23.2, 22.8, 21.2.

HRMS (ESI) m/z: calcd. for $C_{19}H_{23}O$ ($[M+H]^+$): 267.1743, found: 267.1745.



2d **2d'**

run 1: Following general procedure, the solvent is *o*-DCB, temperature is 120 °C. Substrate: **1d** (46.2 mg, 0.206 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.0103 mmol), *o*-DCB (4 mL), flash column chromatography (silica gel, 50:1 to 20:1 PE/EA); product: **2d** (9.5 mg, 18%) and **2d'** (9.2 mg, 18%).

run 2: Following general procedure, the solvent is *o*-DCB, temperature is 120 °C. Substrate: **1d** (47.4 mg, 0.211 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.0103 mmol), *o*-DCB (4 mL), flash column chromatography (silica gel, 50:1 to 20:1 PE/EA); product: **2d** (9.7 mg, 18%) and **2d'** (8.3 mg, 16%).

The average yield of two runs: **2d** (18%) and **2d'** (17%).

Physical Form of 2d: colorless oil

Physical Form of 2d': white solid

Melting Point of 2d': 153.2 – 155.0 °C

TLC (10:1 PE/EA, R_f): **2d** (0.5) and **2d'** (0.4).

^{1}H NMR of **2d** (400 MHz, $CDCl_3$, δ): 7.30 (dd, J = 8.2, 6.7 Hz, 2H), 7.25 – 7.17 (m, 3H), 5.95 – 5.82 (m, 2H), 3.48 (d, J = 10.9 Hz, 1H), 2.96 (d, J = 10.9 Hz, 1H), 2.84 – 2.73 (m, 1H), 2.50 – 2.34 (m, 4H), 2.33 – 2.10 (m, 4H), 2.02 – 1.93 (m, 1H), 1.81 – 1.68 (m, 1H).

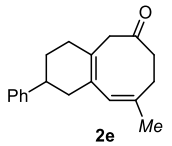
^{13}C{^{1}H} NMR of **2d** (101 MHz, $CDCl_3$, δ): 209.9, 146.5, 132.2, 131.9, 129.2, 128.6, 128.5, 127.0, 126.3, 49.6, 40.3, 38.1, 37.7, 30.7, 30.2, 26.1.

HRMS of **2d** (ESI) m/z: calcd. for $C_{18}H_{21}O$ ($[M+H]^+$): 253.1587, found: 253.1587.

^{1}H NMR of **2d'** (400 MHz, $CDCl_3$, δ): 7.37 – 7.29 (m, 2H), 7.26 – 7.19 (m, 3H), 5.98 (s, 1H), 5.88 (t, J = 7.9 Hz, 1H), 2.98 – 2.81 (m, 2H), 2.68 (d, J = 13.3 Hz, 1H), 2.63 – 2.50 (m, 2H), 2.44 (ddd, J = 16.2, 9.6, 3.6 Hz, 1H), 2.31 – 2.16 (m, 2H), 2.16 – 2.06 (m, 2H), 2.07 – 1.96 (m, 1H), 1.94 – 1.84 (m, 1H), 1.84 – 1.68 (m, 1H).

^{13}C{^{1}H} NMR of **2d'** (101 MHz, $CDCl_3$, δ): 204.5, 152.4, 145.4, 139.5, 129.0, 128.7, 128.4, 126.8, 126.6, 45.0, 44.5, 38.6, 38.5, 34.6, 30.1, 26.1.

HRMS of **2d'** (ESI) m/z: calcd. for $C_{18}H_{21}O$ ($[M+H]^+$): 253.1587, found: 253.1586.



2e

run 1: Following general procedure. Substrate: **1e** (48.5 mg, 0.203 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.0103 mmol), DCE (4 mL), flash column chromatography (silica gel, 100:1 to 10:1 PE/EA); product: **2e** (39.4 mg, 73%).

run 2: Following general procedure. Substrate: **1e** (47.6 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.0103 mmol), DCE (4 mL), flash column chromatography (silica gel, 50:1 PE/EA); product: **2e** (39.9 mg, 75%).

The average yield of two runs: 74%.

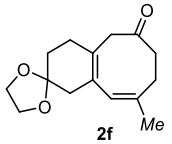
Physical Form: colorless oil

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

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.32 – 7.26 (m, 2H), 7.24 – 7.16 (m, 3H), 5.69 (s, 1H), 3.45 (d, J = 10.5 Hz, 1H), 2.85 (d, J = 10.4 Hz, 1H), 2.82 – 2.72 (m, 1H), 2.53 – 2.42 (m, 1H), 2.40 – 2.30 (m, 3H), 2.30 – 2.15 (m, 3H), 2.15 – 2.05 (m, 1H), 2.00 – 1.93 (m, 1H), 1.92 (d, J = 1.5 Hz, 3H), 1.79 – 1.67 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 210.3, 146.6, 137.4, 133.5, 128.5, 128.0, 127.3, 126.9, 126.2, 49.5, 40.4, 37.72, 37.69, 30.6, 30.5, 30.3, 24.4.

HRMS (ESI) m/z: calcd. for $C_{19}H_{23}O$ ($[M+H]^+$): 267.1743, found: 267.1741.



2f

run 1: Following general procedure. Substrate: **1f** (42.2 mg, 0.192 mmol), $[Rh(CO)_2Cl]_2$ (3.7 mg, 0.0095 mmol), DCE (3.8 mL), flash column chromatography (silica gel, 50:1 to 5:1 PE/EA); product: **2f** (34 mg, 71%).

run 2: Following general procedure. Substrate: **1f** (44.1 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), DCE (4 mL), flash column chromatography (silica gel, 20:1 to 4:1 PE/EA); product: **2f** (37.1 mg, 75%).

The average yield of two runs: 73%.

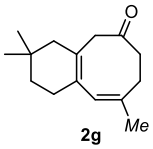
Physical Form: colorless oil

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

^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.64 (s, 1H), 3.98 (s, 4H), 3.12 (s, 2H), 2.40 – 2.29 (m, 6H), 2.23 – 2.19 (m, 2H), 1.91 (d, J = 1.6 Hz, 3H), 1.75 (t, J = 6.6 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 210.0, 138.0, 131.4, 127.5, 127.0, 107.9, 64.6, 49.1, 39.4, 37.5, 31.4, 30.5, 28.9, 24.4.

HRMS (ESI) m/z: calcd. for $C_{15}H_{21}O_3$ ($[M+H]^+$): 249.1485, found: 249.1483.



2g

run 1: Following general procedure. Substrate: **1g** (12.0 mg, 0.063 mmol), $[Rh(CO)_2Cl]_2$ (1.2 mg, 0.003 mmol), DCE (1.3 mL), flash column chromatography (silica gel, 100:1 PE/EA); product: **2g** (9.2 mg, 67%).

run 2: Following general procedure. Substrate: **1g** (15.7 mg, 0.082 mmol), $[Rh(CO)_2Cl]_2$ (1.6 mg, 0.004 mmol), DCE (1.6 mL), flash column chromatography (silica gel, 100:1 PE/EA); product: **2g** (12.4 mg, 69%).

The average yield of two runs: 68%.

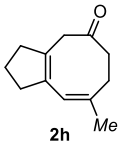
Physical Form: colorless oil

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

^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.69 (s, 1H), 3.08 (s, 2H), 2.35 – 2.25 (m, 4H), 2.01 – 1.95 (m, 2H), 1.92 – 1.88 (m, 4H), 1.26 (s, 3H), 0.89 (s, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 210.2, 136.9, 132.4, 127.5, 126.9, 49.9, 43.7, 37.7, 35.5, 30.6, 29.8, 29.4, 28.2, 27.5, 24.4.

HRMS (ESI) m/z: calcd. for $C_{15}H_{23}O$ ($[M+H]^+$): 219.1743, found: 219.1744.



2h

run 1: Following general procedure. Substrate: **1h** (30.0 mg, 0.202 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), DCE (4 mL), flash column chromatography (silica gel, 50:1 PE/EA); product: **2h** (14.6 mg, 41%).

run 2: Following general procedure. Substrate: **1h** (30.3 mg, 0.204 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.0103 mmol), DCE (4 mL), flash column chromatography (silica gel, 50:1 PE/EA); product: **2h** (14.1 mg, 39%).

The average yield of two runs: 40%.

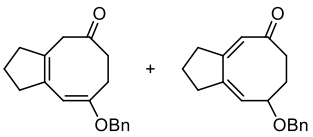
Physical Form: colorless oil

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

^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.59 (s, 1H), 3.15 (s, 2H), 2.64 – 2.57 (m, 2H), 2.55 – 2.48 (m, 2H), 2.47 – 2.39 (m, 2H), 2.39 – 2.32 (m, 2H), 1.85 – 1.76 (m, 2H), 1.82 (d, J = 1.7 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 210.2, 137.9, 134.8, 133.7, 122.4, 45.2, 43.7, 39.5, 38.3, 29.9, 24.0, 21.8.

HRMS (ESI) m/z: calcd. for $C_{12}H_{17}O$ ($[M+H]^+$): 177.1274, found: 177.1274.



2i **2i'**

run 1: Following general procedure. Substrate: **1i** (47.9 mg, 0.199 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), DCE (4 mL), flash column chromatography (silica gel, 50:1 to 20:1 PE/EA); product: **2i+2i'** (13.7 mg, 4:1, 26%).

run 2: Following general procedure. Substrate: **1i** (49.2 mg, 0.205 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.0103 mmol), DCE (4 mL), flash column chromatography (silica gel, 50:1 to 20:1 PE/EA); product: **2i+2i'** (13.4 mg, 4:1, 24%).

The average yield of two runs: 25%.

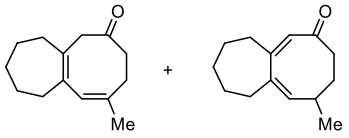
Physical Form: light yellow oil

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

^{1}H NMR for the major isomer (400 MHz, $CDCl_3$, δ): 7.39 – 7.35 (m, 4H), 7.34 – 7.30 (m, 1H), 5.00 (s, 1H), 4.78 (s, 2H), 3.22 – 3.12 (m, 3H), 2.69 – 2.65 (m, 1H), 2.65 – 2.62 (m, 3H), 2.48 – 2.40 (m, 3H), 1.91 – 1.78 (m, 2H).

^{13}C{^{1}H} NMR for the major isomer (101 MHz, $CDCl_3$, δ): 209.9, 157.4, 136.9, 134.0, 131.7, 128.6, 128.1, 127.7, 96.6, 69.7, 45.3, 42.7, 39.0, 38.7, 29.1, 21.9.

HRMS (ESI) m/z: calcd. for $C_{18}H_{21}O_2$ ($[M+H]^+$): 269.1536, found: 269.1536.



2j **2j'**

run 1: Following general procedure. Substrate: **1j** (35.5 mg, 0.201 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.0103 mmol), DCE (4 mL), flash column chromatography (silica gel, 50:1 PE/EA); product: **2j** (6.5 mg, 16%) and **2j'** (4.2 mg, 10%).

run 2: Following general procedure. Substrate: **1j** (32.6 mg, 0.185 mmol), $[Rh(CO)_2Cl]_2$ (3.7 mg, 0.0095 mmol), DCE (4 mL), flash column chromatography (silica gel, 50:1 to 20:1 PE/EA); product: **2j** (4 mg, 11%) and **2j'** (2 mg, 6%).

The average yield of two runs: **2j** (14%) and **2j'** (8%).

Physical Form of 2j: colorless oil

Physical Form of 2j': colorless oil

TLC (10:1 PE/EA, R_f): **2j** (0.6) and **2j'** (0.4).

^{1}H NMR of **2j** (400 MHz, $CDCl_3$, δ): 5.78 (s, 1H), 3.12 (s, 2H), 2.38 – 2.25 (m, 6H), 2.18 – 2.10 (m, 2H), 1.90 (d, J = 1.5 Hz, 3H), 1.77 – 1.68 (m, 2H), 1.53 – 1.41 (m, 4H).

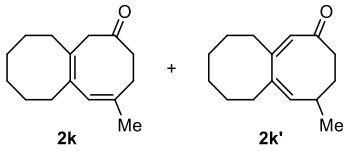
^{13}C{^{1}H} NMR of **2j** (101 MHz, $CDCl_3$, δ): 210.4, 139.6, 135.7, 134.5, 129.8, 52.2, 37.2, 34.5, 33.3, 32.2, 30.5, 26.5, 26.0, 24.3.

HRMS of **2j** (ESI) m/z: calcd. for $C_{14}H_{21}O$ ($[M+H]^+$): 205.1587, found: 205.1586.

^{1}H NMR of **2j'** (400 MHz, $CDCl_3$, δ): 5.99 – 5.93 (m, 1H), 5.63 (dd, *J* = 8.8, 1.6 Hz, 1H), 2.88 (ddd, *J* = 13.6, 10.8, 6.2 Hz, 1H), 2.58 – 2.44 (m, 3H), 2.43 – 2.34 (m, 2H), 2.22 (ddd, *J* = 8.8, 4.4, 2.1 Hz, 1H), 2.08 – 1.97 (m, 1H), 1.77 – 1.48 (m, 7H), 1.00 (d, *J* = 6.4 Hz, 3H).

^{13}C{^{1}H} NMR of **2j'** (101 MHz, $CDCl_3$, δ): 205.0, 157.3, 141.3, 139.3, 130.0, 39.7, 39.5, 39.2, 36.5, 32.5, 31.6, 29.9, 29.5, 20.9.

HRMS of **2j'** (ESI) m/z: calcd. for $C_{14}H_{21}O$ ($[M+H]^+$): 205.1587, found: 205.1587.



2k **2k'**

run 1: Following general procedure. Substrate: **1k** (35.6 mg, 0.187 mmol), $[Rh(CO)_2Cl]_2$ (3.7 mg, 0.0095 mmol), DCE (3.7 mL), flash column chromatography (silica gel, 50:1 PE/EA); product: **2k** (4.7 mg, 12%), **2k'** < 5%.

run 2: Following general procedure. Substrate: **1k** (39.2 mg, 0.206 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.0103 mmol), DCE (4 mL), flash column chromatography (silica gel, 50:1 PE/EA); product: **2k** (6.3 mg, 14%), **2k'** < 5%.

The average yield of two runs: 13%.

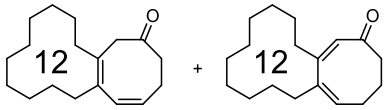
Physical Form: colorless oil

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

^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.81 (s, 1H), 3.14 (s, 2H), 2.37 – 2.27 (m, 6H), 2.22 – 2.15 (m, 2H), 1.91 (d, *J* = 1.6 Hz, 3H), 1.60 – 1.49 (m, 4H), 1.49 – 1.41 (m, 4H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 210.9, 136.7, 136.1, 131.0, 128.1, 49.9, 37.6, 32.0, 31.1, 30.4, 29.2, 28.7, 26.83, 26.80, 24.5.

HRMS (ESI) m/z: calcd. for $C_{15}H_{23}O$ ($[M+H]^+$): 219.1743, found: 219.1742.



2l **2l'**

run 1: Following general procedure, the solvent is *o*-DCB, temperature is 120 °C. Substrate: **1l** (110 mg, **1l**:methylenecyclododecane = 1:1.75, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), *o*-DCB (4 mL), flash column chromatography (silica gel, 50:1 to 10:1 PE/EA); product: **2l** (10.7 mg, 20%) and **2l'** (15 mg, 29%).

run 2: Following general procedure, the solvent is *o*-DCB, temperature is 120 °C. Substrate: **1l** (109.1 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.8 mg, 0.0098 mmol), *o*-DCB (4 mL), flash column chromatography (silica gel, 50:1 to 10:1 PE/EA); product: **2l** (9.8 mg, 19%) and **2l'** (13.2 mg, 26%).

The average yield of two runs: **2l** (20%) and **2l'** (28%).

Physical Form of 2l: light yellow oil

Physical Form of 2l': light yellow oil

TLC (10:1 PE/EA, R_f): **2l** (0.5) and **2l'** (0.3).

^{1}H NMR of **2l** (400 MHz, $CDCl_3$, δ): 5.96 (d, J = 11.7 Hz, 1H), 5.85 (dt, J = 11.6, 5.9 Hz, 1H), 3.25 (s, 2H), 2.47 – 2.40 (m, 2H), 2.40 – 2.34 (m, 2H), 2.25 (t, J = 7.4 Hz, 2H), 2.20 (t, J = 7.3 Hz, 2H), 1.55 – 1.22 (m, 16H).

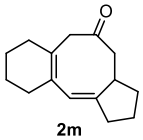
^{13}C{^{1}H} NMR of **2l** (101 MHz, $CDCl_3$, δ): 210.7, 136.0, 132.3, 131.1, 129.6, 50.2, 38.1, 30.5, 29.0, 26.3, 26.2, 25.6, 25.3, 25.2, 24.6, 22.6, 22.5.

HRMS of **2l** (ESI) m/z: calcd. for $C_{18}H_{29}O$ ($[M+H]^+$): 261.2213, found: 261.2214.

^{1}H NMR of **2l'** (400 MHz, $CDCl_3$, δ): 6.09 (s, 1H), 5.83 (t, J = 8.4 Hz, 1H), 2.88 (ddd, J = 13.5, 11.2, 6.0 Hz, 1H), 2.50 – 2.39 (m, 1H), 2.35 – 2.14 (m, 5H), 2.12 – 2.04 (m, 1H), 2.00 – 1.88 (m, 1H), 1.78 – 1.59 (m, 3H), 1.55 – 1.28 (m, 15H).

^{13}C{^{1}H} NMR of **2l'** (101 MHz, $CDCl_3$, δ): 203.9, 155.5, 141.6, 131.1, 128.6, 38.8, 33.4, 32.0, 29.4, 26.0 (2C), 25.7, 25.2, 25.1, 24.5, 24.1, 23.4, 23.2.

HRMS of **2l'** (ESI) m/z: calcd. for $C_{18}H_{29}O$ ($[M+H]^+$): 261.2213, found: 261.2213.



2m

run 1: Following general procedure. Substrate: **1m** (37.9 mg, 0.201 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), DCE (4 mL), flash column chromatography (silica gel, 50:1 PE/EA); product: **2m** (29.6 mg, 68%).

run 2: Following general procedure. Substrate: **1m** (37.7 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), DCE (4 mL), flash column chromatography (silica gel, 50:1 PE/EA); product: **2m** (27.2 mg, 64%).

The average yield of two runs: 66%.

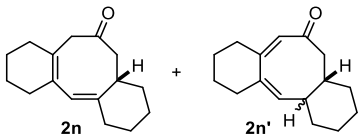
Physical Form: light yellow oil

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

^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.71 (s, 1H), 3.56 (d, J = 10.2 Hz, 1H), 2.70 – 2.58 (m, 2H), 2.56 – 2.37 (m, 3H), 2.36 – 2.25 (m, 1H), 2.08 (dd, J = 13.5, 2.5 Hz, 1H), 2.02 – 1.86 (m, 4H), 1.80 – 1.64 (m, 3H), 1.62 – 1.51 (m, 1H), 1.51 – 1.43 (m, 2H), 1.43 – 1.33 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 210.1, 147.5, 134.2, 127.1, 123.8, 49.5, 45.2, 39.1, 35.3, 33.5, 30.0, 29.8, 23.3, 23.1, 22.9.

HRMS (ESI) m/z: calcd. for $C_{15}H_{21}O$ ($[M+H]^+$): 217.1587, found: 217.1587.



2n **2n'**

run 1: Following general procedure, the reaction time is 3 h. Substrate: **1n** (31.1 mg, 0.154 mmol), $[Rh(CO)_2Cl]_2$ (3.1 mg, 0.008 mmol), DCE (3 mL), flash column chromatography (silica gel, 50:1

PE/EA); product: **2n** (6.5 mg, 18%).

run 2: Following general procedure, the reaction time is 3 h. Substrate: **1n** (31 mg, 0.153 mmol), $[Rh(CO)_2Cl]_2$ (3.1 mg, 0.008 mmol), DCE (3 mL), flash column chromatography (silica gel, 50:1 PE/EA); product: **2n** (6.5 mg, 18%).

The average yield of two runs: 18%.

run 3: Following general procedure. Substrate: **1n** (41.2 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), DCE (4 mL), flash column chromatography (silica gel, 50:1 PE/EA); product: **2n** (12.3 mg, 26%), **2n'** (7.7 mg, 16%).

run 4: Following general procedure. Substrate: **1n** (41.6 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), DCE (4 mL), flash column chromatography (silica gel, 50:1 PE/EA); product: **2n** (12.1 mg, 26%), **2n'** (8.2 mg, 17%).

The average yield of two runs: **2n** (26%), **2n'** (16%).

Physical Form: 2n (colorless oil), **2n'** (light yellow oil)

TLC (10:1 PE/EA, R_f): **2n** (0.6), **2n'** (0.5).

^{1}H NMR of 2n (400 MHz, $CDCl_3$, δ): 5.60 (s, 1H), 3.57 – 3.04 (m, 1H), 2.83 – 2.50 (m, 2H), 2.45 – 2.27 (m, 2H), 2.23 – 1.89 (m, 5H), 1.75 – 1.33 (m, 11H).

^{13}C{^{1}H} NMR of 2n (101 MHz, $CDCl_3$, δ): 210.6, 143.3, 132.5, 128.1, 125.1, 50.6 (2C), 44.8, 30.2 (3C), 28.2, 23.2 (2C), 22.9 (2C).

HRMS of 2n (ESI) m/z: calcd. for $C_{16}H_{23}O$ ($[M+H]^+$): 231.1743, found: 231.1743.

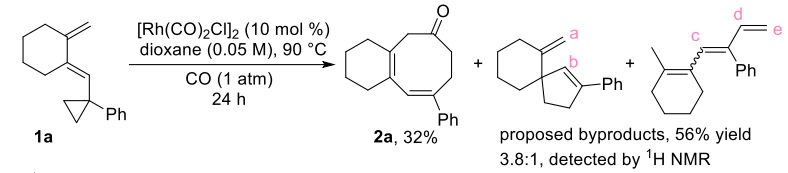
^{1}H NMR of 2n' (400 MHz, $CDCl_3$, δ): 5.99 – 5.84 (m, 3H), 5.56 (dd, J = 8.8, 2.1 Hz, 1H), 3.09 (dd, J = 10.9, 6.3 Hz, 1H), 2.67 – 2.55 (m, 2H), 2.55 – 2.22 (m, 8H), 2.12 – 1.86 (m, 8H), 1.81 – 1.52 (m, 15H), 1.49 – 1.37 (m, 2H), 1.23 – 1.03 (m, 4H).

^{13}C{^{1}H} NMR of 2n' (101 MHz, $CDCl_3$, δ): 204.2, 202.9, 154.2, 154.0, 138.7, 137.8, 134.6, 129.5, 129.2, 128.6, 47.4, 46.7, 46.4, 45.8, 42.0, 39.0, 38.9, 37.4, 36.9, 35.9, 32.6, 31.7, 29.5, 29.2, 27.5, 27.4, 27.3, 27.2, 26.3, 26.1, 25.7, 21.1.

HRMS of 2n' (ESI) m/z: calcd. for $C_{16}H_{23}O$ ($[M+H]^+$): 231.1743, found: 231.1744.

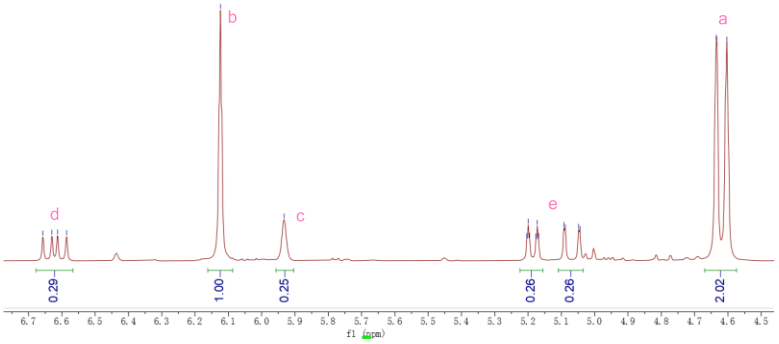
4. Byproduct Analysis and DFT Studies

(a) Detail in entry 5, table 1



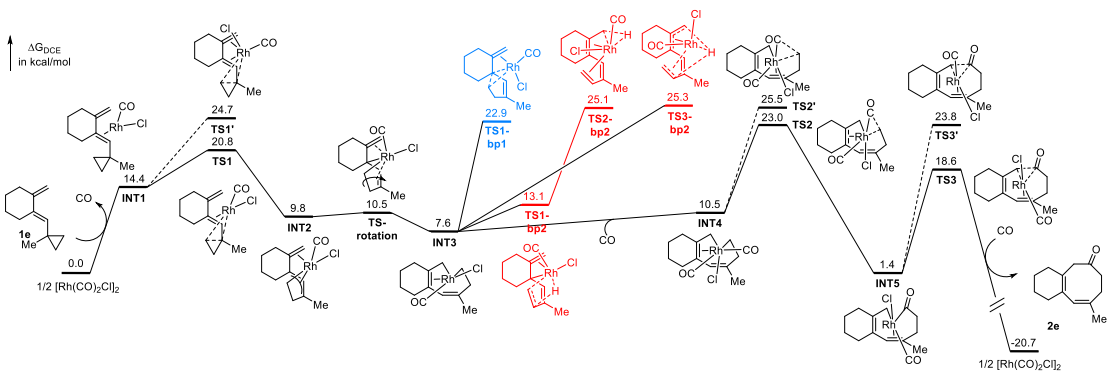
proposed byproducts, 56% yield
3.8:1, detected by ^{1}H NMR

(b) ^{1}H NMR crude spectrum of byproducts



On the basis of ^{1}H NMR crude spectrum, we thought that VCP rearrangement and "VCP to diene" were possible pathways of byproducts. Generally, it is difficult to form a spiral ring in mental catalyzed cycloaddition reactions because of the high energy barrier of reductive elimination. In this case, we thought extra exocyclic alkene group is crucial for this transformation. The coordination would decrease the energy barrier of reductive elimination significantly. This proposal is consistent with the DFT calculations shown below.

DFT calculations were performed by Gaussian 09 E.01.[8] DLPNO-CCSD(T)[9] single-point energy calculations were performed by ORCA 4.2.1.[10] Pruned integration grids with 99 radial shells and 590 angular points per shell were used in DFT calculations (int = ultrafine). Geometry optimizations of all the minima and transition states were carried out with the BMK functional[11] in the gas phase, and the def2-TZVP[12] basis set was used for all atoms. The BMK functional performed well in our previously reported [5 + 2 + 1] cycloaddition[13] and was used in this study as well. Enthalpy and Gibbs free energy corrections were obtained through frequency analyses at 298 K. Solvent effects were considered based on gas-phase-optimized structures using the same basis set and functional. Solvation energies in DCE were evaluated by a self-consistent reaction field employing the SMD model.[14] Based on the optimized structures, single-point energy refinements were performed at the DLPNO-CCSD(T)/def2-TZVPP[12] level (def2-TZVPP/C auxiliary basis set) with TightSCF and TightPNO keywords. In this paper, all discussed energies are Gibbs free energies in the solution phase (ΔG_{DCE} 298 K) unless otherwise specified. We have searched for all possible conformers for all intermediates and transition states, and the discussed ones in this paper are the most stable. We used 5.5 mM as the concentration of CO[15] in DCE and 1.0 M for other species.



In the oxidative addition step, we found **TS1** with ene-coordination is more favored than TS1' with diene-coordination in 3.9 kcal/mol. In the CO insertion step, **TS2** with the coordination of tetra-substituted double bond is more favored than **TS2'** in 2.5 kcal/mol. In the reductive elimination step, **TS3** is more favored in 5.2 kcal/mol.

For VCP rearrangement byproduct, the activation free energy of reductive elimination via **TS1-bp1** is 22.9 kcal/mol, and the overall activation free energy of "VCP to diene" byproduct is 25.1 kcal/mol through **TS2-bp2**. Besides, the concerted ligand to ligand H transfer transition state can be located (**TS3-bp2**, 25.3 kcal/mol), which is also a possible pathway for "VCP to diene" byproduct.

Energy and Cartesian Coordinates of the Stationary Points:

Computed Energies for the Stationary Points

Table S1. Thermal corrections to Gibbs energies (TCGs), single-point energies (SPEs) in gas phase and solvent

	Imaginary Frequencies (cm-1)	SPE[a] (a. u.)	TCG[a,b] (a. u.)	SPE[c] (a. u.)	SPE[d] (a. u.)
CO	none	-113.172745	-0.01386	-113.167302	-113.158173
$[Rh(CO)_2Cl]_2$	none	-1592.916752	-0.008309	-1592.918394	-1593.122136
1e	none	-467.35274	0.232054	-467.363892	-467.188120
INT1	none	-1150.59189	0.237014	-1150.615749	-1150.553544
TS1	-220.85	-1150.584272	0.238242	-1150.606268	-1150.546444
TS1'	-201.74	-1150.587307	0.237718	-1150.60844	-1150.540546
INT2	none	-1150.608035	0.238072	-1150.628477	-1150.565324
TS-rotation	-52.05	-1150.594718	0.237131	-1150.621013	-1150.557353
INT3	none	-1150.601234	0.237159	-1150.626355	-1150.563152
INT4	none	-1263.796469	0.244964	-1263.813322	-1263.743202
TS2	-258.36	-1263.780143	0.245739	-1263.798851	-1263.722171
TS2'	-204.06	-1263.776625	0.245707	-1263.797757	-1263.715677
INT5	none	-1263.807614	0.244137	-1263.837178	-1263.744166
TS3	-230.27	-1263.787386	0.24734	-1263.815218	-1263.721606
TS3'	-201.11	-1263.787938	0.247865	-1263.812442	-1263.717216
2e	none	-580.594541	0.245766	-580.609832	-580.399223
TS1-bp1	-219.16	-1150.577506	0.236826	-1150.598883	-1150.542248
TS1-bp2	-241.89	-1150.592613	0.235466	-1150.614957	-1150.555444
TS2-bp2	-679.80	-1150.567915	0.233559	-1150.585344	-1150.539462
TS3-bp2	-1346.85	-1150.566729	0.232945	-1150.588147	-1150.534462

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

[b]Computed at 1 atm and 298 K

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

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

Cartesian coordinates for the stationary points:

CO

C	0.00000000	0.00000000	-0.64339800
O	0.00000000	0.00000000	0.48254900

$[Rh(CO)_2Cl]_2$

C	2.78965400	1.35688400	0.50180500
O	3.46730700	2.19545200	0.85403300
C	2.78934000	-1.35711300	0.50172400
O	3.46672300	-2.19590200	0.85394200
Rh	1.62758700	0.00004600	-0.09761500

Cl	-0.00003500	1.66150600	-0.89947600
Cl	0.00004400	-1.66151100	-0.89943700
Rh	-1.62763600	-0.00007100	-0.09776600
C	-2.78958300	-1.35693200	0.50181200
C	-2.78938900	1.35703100	0.50171400
O	-3.46642300	2.19599500	0.85416800
O	-3.46736400	-2.19529900	0.85427400

1e

C	-2.75856500	0.29621700	-0.70385700
C	-2.98308400	-1.03716000	0.03386100
C	-1.68399800	-1.85431900	0.08013000
C	-0.55274000	-1.06124600	0.76405900
C	-0.35316500	0.30750700	0.13187200
C	-1.60950900	1.08520900	-0.09752700
C	-1.72074200	2.38480900	0.22563200
C	0.85161100	0.80862200	-0.21125900
C	2.18480200	0.15002600	0.02185100
C	2.54499400	-1.10053800	-0.79771200
C	3.21430100	0.24180700	-1.10655700
H	-3.67680200	0.90616800	-0.70904500
H	-2.50874700	0.07099200	-1.75932200
H	-3.32505300	-0.83093900	1.06527700
H	-3.78399800	-1.61168200	-0.46268500
H	-1.84525900	-2.80712000	0.61318900
H	-1.37740000	-2.11113600	-0.95112600
H	-0.82777400	-0.91237800	1.82726300
H	0.38664100	-1.63481600	0.75058700
H	-2.64796800	2.93704600	0.03771300
H	-0.89242800	2.92717100	0.69208100
H	0.87383500	1.80264000	-0.67773700
H	3.14468400	-1.87776500	-0.31058900
H	1.80344900	-1.47576100	-1.51059000
H	2.91747200	0.75648300	-2.02724800
H	4.26769000	0.36978800	-0.83444000
C	2.69964800	0.23274500	1.45596700
H	2.79194700	1.28443600	1.77748200
H	2.00743300	-0.27256200	2.15136300
H	3.69095600	-0.24265100	1.54906800

INT1

C	3.13221300	0.56023600	0.06410000
C	3.50630300	-0.12468300	-1.26305200
C	2.24259500	-0.56711600	-2.01025400
C	1.37322800	-1.49223400	-1.13998400
C	1.00114500	-0.85406700	0.20760500
C	2.23491100	-0.32993600	0.90771700
C	2.57105800	-0.67668100	2.16127000
C	-0.13899200	-1.16035500	1.00718500
C	-1.43013400	-1.76133400	0.54991300
C	-1.60148700	-2.77189300	-0.54509500
C	-1.94587900	-1.35568200	-0.97819300
H	4.03463600	0.82902800	0.63616300
H	2.60218000	1.50159600	-0.17073500
H	4.13815400	-1.00740900	-1.05255700
H	4.10453100	0.56167700	-1.88609600
H	2.51007200	-1.09101500	-2.94375200
H	1.64945500	0.32167400	-2.29552700
H	1.94860500	-2.41313600	-0.91486500
H	0.49493700	-1.80426900	-1.71670400
H	3.48250400	-0.28367200	2.62329100
H	1.96640900	-1.36253800	2.76176300
H	-0.06753500	-1.01884000	2.08998100
H	-2.44389800	-3.46211500	-0.42963300
H	-0.71234100	-3.23671200	-0.97725600
H	-1.30681000	-0.90839300	-1.75492000
H	-2.99602800	-1.06080800	-1.04962700
Rh	-0.66282600	0.53994500	-0.03619500
Cl	-2.23065100	2.02842600	-0.96091400
C	0.17328400	1.95739400	0.82656500
O	0.64785300	2.83151700	1.37710800
C	-2.52487500	-1.72660300	1.60930700
H	-3.50556400	-1.97885900	1.17702600
H	-2.29582400	-2.46975800	2.39297200

H	-2.59830500	-0.73161800	2.07540900

TS1

C	2.99545200	0.75276500	-0.06007900
C	3.44437400	-0.05457900	-1.29263200
C	2.24209100	-0.74721800	-1.94633200
C	1.48740000	-1.63238700	-0.93806600
C	1.03165100	-0.83888600	0.29615200
C	2.21552800	-0.12143700	0.90675800
C	2.60567800	-0.28780400	2.18131100
C	-0.05826700	-1.16641600	1.18225700
C	-1.33843200	-1.68337100	0.77002100
C	-1.61174300	-2.53678400	-0.42568200
C	-1.70792500	-1.20285400	-1.16354400
H	3.86041300	1.20229500	0.45357500
H	2.34947200	1.58189400	-0.40603100
H	4.18142100	-0.81636900	-0.97783800
H	3.95040200	0.60862200	-2.01459300
H	2.57137900	-1.36505400	-2.79917500
H	1.54819800	0.01473800	-2.34814700
H	2.17178200	-2.42681800	-0.57857100
H	0.65949300	-2.13347700	-1.44852400
H	3.48010400	0.24328200	2.57129900
H	2.08580400	-0.95951600	2.87101300
H	0.00371000	-0.84290000	2.22511300
H	-2.54882300	-3.10641300	-0.35613100
H	-0.79135900	-3.19736300	-0.72555300
H	-1.09839800	-1.11736800	-2.07715900
H	-2.73273900	-0.84649600	-1.31690300
Rh	-0.69984100	0.37494500	-0.06538100
Cl	-2.04669100	1.93011700	-1.24280500
C	-0.01292900	1.92140800	0.91802300
O	0.27866700	2.83699300	1.51731800
C	-2.49796900	-1.52185600	1.73073900
H	-3.42357700	-1.29246700	1.17910000
H	-2.65327200	-2.48338400	2.25485000
H	-2.32620400	-0.72714000	2.47141200

TS1'

C	2.74499800	-0.95399300	-0.71653400
C	3.75313000	0.04925100	-0.14034000
C	3.05112200	1.04129900	0.79329500
C	2.00686600	1.84664800	0.00794200
C	1.43904000	-0.33490000	-1.18181500
C	0.45288500	-1.18029500	-1.81929000
H	3.18274200	-1.50682900	-1.56488500
H	2.47238000	-1.70381700	0.05071900
H	4.24277100	0.60782900	-0.95986500
H	4.54867900	-0.49717500	0.39269800
H	3.78045300	1.72716100	1.25604200
H	2.54945800	0.48477400	1.60656400
H	2.51656400	2.47847700	-0.74649600
H	1.48297000	2.54406700	0.67176400
H	0.72116300	-2.24027100	-1.90101300
H	-0.11233900	-0.79809800	-2.67661800
Rh	-0.52050800	-0.42737100	-0.08010200
Cl	0.26346500	-1.96112000	1.67743000
O	-3.09345000	-2.04314900	-0.44900400
C	-2.14762600	-1.43104200	-0.31517000
C	-1.23125800	1.07428700	1.55755800
C	-1.10767000	2.53959400	1.16105300
C	-1.33412200	1.87402100	-0.14599800
C	-0.38417500	1.31451700	-1.11137200
C	1.02251900	0.95544900	-0.73255100
H	-2.21660100	0.76621100	1.91940000
H	-0.39134700	0.66757800	2.13444400
H	-1.92501900	3.19835200	1.48141100
H	-0.13432100	2.99235100	1.35683100
H	-0.69415800	1.34544300	-2.16330700
C	-2.76030500	1.99154000	-0.65911800
H	-3.49070700	1.85644400	0.15378700
H	-2.89639300	3.01150100	-1.06190000
H	-2.97717200	1.26368300	-1.45521100

INT2

C	-2.77216900	-0.68321900	0.97752700
C	-3.41377200	-0.25743700	-0.34974800
C	-3.37745500	1.27097900	-0.47369000
C	-1.92822500	1.77777600	-0.56768300
C	-1.43236100	-0.02196100	1.26256900
C	-0.52729700	-0.62808600	2.15636500
H	-3.44268700	-0.39366300	1.80890300
H	-2.66038300	-1.77903000	1.04399000
H	-4.45030200	-0.63094900	-0.39305500
H	-2.87495300	-0.71271900	-1.20171900
H	-3.87169200	1.71167000	0.41213300
H	-3.94408200	1.61076900	-1.35646600
H	-1.89698000	2.86576900	-0.38225000
H	-1.55887600	1.62492300	-1.59652700
H	-0.80444800	-1.59556600	2.58626000
H	0.22826400	-0.07190700	2.71292600
Rh	0.42795100	-0.43321900	0.02685000
Cl	2.55896100	-1.48459300	0.38746500
O	-0.56539100	-2.88093400	-1.42739300
C	-0.20624800	-1.95645400	-0.87749400
C	1.01304500	0.34193000	-1.82956400
C	1.28743700	1.81857800	-1.48811700
C	1.38274600	1.92245400	0.03250000
C	0.30703700	1.67719700	0.85876500
C	-0.99142900	1.07857700	0.41684800
H	1.93732700	-0.17428100	-2.12550900
H	0.26407000	0.23401500	-2.63103500
H	2.22455400	2.18553500	-1.93866300
H	0.48083400	2.48275300	-1.84066200
H	0.47982600	1.79197000	1.93477400
C	2.72704100	2.26352500	0.61074000
H	3.42640400	1.44494100	0.35562500
H	3.11307100	3.19237600	0.15571200
H	2.70294700	2.37064500	1.70546000

TS-rotation

C	2.66336600	0.59392600	-1.14001200
C	3.17644300	0.92620200	0.26609200
C	2.54049600	2.23600400	0.74437400
C	1.01167100	2.11544300	0.87715000
C	1.15042400	0.67999900	-1.27719200
C	0.49325000	-0.13577100	-2.21141900
H	3.08150100	1.32768600	-1.85632300
H	3.00748800	-0.39905000	-1.47474100
H	4.27592900	1.00803700	0.24800600
H	2.93207400	0.10396800	0.96446100
H	2.78399100	3.02865500	0.01239000
H	2.96993900	2.55481700	1.70894200
H	0.57174300	3.12635800	0.91121400
H	0.76589800	1.65238700	1.84844300
H	1.06044700	-0.79375200	-2.87557200
H	-0.54403800	0.07469800	-2.50242600
Rh	-0.07676900	-0.82254500	-0.10320300
Cl	-0.43575000	-3.10583000	-0.64363000
O	0.71637700	-1.35170400	2.72202400
C	0.39159400	-1.13664100	1.65409500
C	-1.93026500	-0.57626800	0.77197500
C	-2.27370300	0.87287300	1.13386600
C	-2.15527800	1.79067700	-0.06848600
C	-0.98357200	1.91097900	-0.71924500
C	0.32924800	1.32528500	-0.26612600
H	-2.54325700	-0.93038400	-0.07512700
H	-2.11320600	-1.25285500	1.62107700
H	-3.30757300	0.90173500	1.52605400
H	-1.62531600	1.22334500	1.95738700
H	-0.94591700	2.52197000	-1.63263800
C	-3.41191800	2.48190200	-0.53653400
H	-4.20487100	1.74147400	-0.74901800
H	-3.80487100	3.15043200	0.25112700
H	-3.23915900	3.08005700	-1.44480600

INT3

C	1.02013700	2.06982500	-1.48044900

C	1.55189500	2.84887300	-0.27056700	O	3.54777700	-0.16352500	-0.44828100
C	0.37726500	3.44487700	0.51040100	O	0.75125800	-3.66145700	-0.86247700
C	-0.54276600	2.34552300	1.06576400	C	2.42492700	-0.26499900	-0.40408600
C	-0.14690100	1.13174700	-1.17713800	C	0.66841300	-2.57159600	-0.56301000
C	-0.30613400	-0.01507100	-1.99879600	C	-1.35131200	-1.53214500	0.70366700
H	0.63739900	2.78368700	-2.23589100	C	-2.67981000	-1.30678900	-0.00988000
H	1.82579800	1.50427300	-1.98164300	C	-3.12840200	0.13449900	0.00701800
H	2.23807800	3.63971300	-0.61647800	C	-2.30419300	1.19366700	0.12077500
H	2.14495700	2.18333600	0.38426600	C	-0.82668600	1.41440900	0.06724200
H	-0.20118600	4.09726800	-0.17021600	C	-0.36282300	-0.00104100	-1.90288300
H	0.73348000	4.08386000	1.33573700	H	-1.36977400	-1.05211300	1.69523900
H	-1.50170200	2.79914200	1.37096900	H	-1.23246800	-2.61172400	0.89278000
H	-0.11186100	1.93176100	1.99368300	H	-3.46622200	-1.89835100	0.49954500
H	0.33929500	-0.11486600	-2.87705300	H	-2.66200300	-1.69847600	-1.04604100
H	-1.27361800	-0.51482600	-2.06530700	H	-2.79921200	2.17055100	0.23174400
Rh	0.61498100	-0.53024200	-0.05824800	H	0.23372000	-0.11894000	-2.81612400
Cl	2.09323600	-2.21428100	-0.81741900	H	-1.40462900	-0.31187900	-2.02007300
O	1.92638500	-0.57935700	2.72098200	C	-0.31983000	2.41556500	1.10776400
C	1.42838500	-0.57334100	1.70510500	C	0.57814900	3.51653800	0.52484100
C	-0.81729600	-1.72001000	0.78742200	C	1.67603800	2.90901900	-0.35539900
C	-2.15224900	-1.75385600	0.06579700	C	1.05002000	2.12026300	-1.51197700
C	-2.88977000	-0.43381600	0.07418400	C	-0.09046900	1.19001800	-1.11299800
C	-2.28554000	0.76834300	0.13648200	H	-0.03179600	4.21308900	-0.08060200
C	-0.84295500	1.19169700	0.08415700	H	-1.18485900	2.86213700	1.62442100
H	-0.33616700	-2.71097800	0.77831400	H	0.23355800	1.84225400	1.87601200
H	-0.98421500	-1.40686200	1.83172600	H	2.33697700	3.69379700	-0.76028400
H	-2.03310100	-2.13500900	-0.96579100	H	2.30770100	2.24862600	0.26558100
H	-2.78801600	-2.50586600	0.57578600	H	0.59106300	2.83455000	-2.22427400
H	-2.95392400	1.64039800	0.19438400	H	1.80988400	1.57300200	-2.09457500
C	-4.39836900	-0.53722400	0.02545500	H	1.02141000	4.10709000	1.34388100
H	-4.71575200	-1.11090500	-0.86462400	C	-4.62629600	0.34338000	-0.03670800
H	-4.78247500	-1.08235800	0.90684800	H	-4.89997000	1.40960900	-0.05887500
H	-4.88143800	0.45134800	-0.01215600	H	-5.05374400	-0.14304300	-0.93251300
				H	-5.10984100	-0.12578500	0.83938300

INT4

				TS2			
Rh	0.43404200	-0.74942200	-0.08958700				
Cl	1.32409900	-0.70795700	2.20447300	Rh	0.23721400	-0.85096600	-0.04018400

Cl	1.10895400	-0.89971000	2.24581300	Rh	0.98265700	-0.34052100	-0.10367500
O	3.01755000	-1.86245300	-0.79736200	Cl	2.98167400	0.66305600	-1.11393100
O	-1.38211900	-3.25975700	-0.69935400	O	1.18740900	-2.44009600	-2.27518000
C	1.99305800	-1.45123500	-0.55081900	O	2.60349300	-1.60090100	2.02800600
C	-0.89647500	-2.29840400	-0.27336200	C	1.08520700	-1.64614300	-1.47571800
C	-1.87680300	-1.09537600	0.75088900	C	1.94007700	-0.90366400	1.37865200
C	-2.95680400	-0.35594500	-0.03970800	C	1.42443400	0.68989500	1.94168100
C	-2.80871200	1.15549700	-0.04291900	C	0.15908000	1.56794800	1.62239700
C	-1.67618100	1.89320900	0.02435500	C	0.02005500	1.94941900	0.14772100
C	-0.19612000	1.68749400	-0.03704400	C	-0.90948900	1.39107400	-0.69119500
C	-0.19981900	0.05635200	-1.88842600	C	-2.08899100	0.54746300	-0.34597100
H	-1.46331000	-0.48629900	1.57285800	C	-0.70753800	-1.29267900	0.67945500
H	-2.27758400	-1.98437700	1.25909100	H	2.35347500	1.26677100	1.81737500
H	-3.94026000	-0.58046000	0.41070200	H	1.32799300	0.35685500	2.98505900
H	-3.02748200	-0.74621800	-1.07417100	H	0.26400900	2.48997300	2.22373400
H	-1.86230100	2.97344000	0.12254000	H	-0.74619400	1.04665900	1.96517100
H	0.32662000	-0.31202100	-2.77730500	H	-0.91381500	1.79183300	-1.71553400
H	-1.28127800	0.14235800	-2.04185000	H	-0.75085900	-2.35115000	0.36156000
C	0.57640700	2.51647300	0.98671000	H	-0.64281000	-1.34913300	1.78565200
C	1.91449800	3.07377900	0.47885600	C	-3.41000300	1.15997000	-0.79909100
C	2.70380300	2.00040600	-0.27990300	C	-4.58326700	0.17264700	-0.74175800
C	1.89114700	1.52203900	-1.48820500	C	-4.56269200	-0.59622400	0.58437100
C	0.45843400	1.13078100	-1.14444300	C	-3.26554900	-1.40780000	0.70113600
H	1.72919400	3.93055200	-0.19580400	C	-2.01757600	-0.63301300	0.30802400
H	-0.06653700	3.33619500	1.34919400	H	-5.53612500	0.71255700	-0.87266000
H	0.75594400	1.85544700	1.85762400	H	-3.62827400	2.04493900	-0.16880200
H	3.67805100	2.39347400	-0.61543500	H	-3.28969900	1.55219800	-1.82588200
H	2.90692700	1.15046400	0.39803000	H	-4.62629600	0.12284900	1.42213200
H	1.82040400	2.34105800	-2.23085900	H	-5.43650800	-1.26416900	0.66832000
H	2.39451000	0.69012000	-2.00873000	H	-3.13542500	-1.78594700	1.73208600
H	2.49918100	3.45783700	1.33119400	H	-3.32454800	-2.31242800	0.06333600
C	-4.14324500	1.87511500	-0.07718700	H	-4.50102600	-0.54520000	-1.57868700
H	-4.02713100	2.96843400	-0.12457900	C	0.90936700	3.07921200	-0.31259900
H	-4.72916600	1.55181800	-0.95702100	H	0.89798300	3.18866600	-1.40682800
H	-4.74521300	1.62328500	0.81490800	H	0.53910300	4.01618900	0.14491700
				H	1.95507700	2.92936500	-0.00399400

TS2’

INT5

Cl	1.78216100	-2.52299500	0.00861400
O	3.34783100	-0.05744300	-2.14745700
O	2.93148900	0.32713100	1.54479900
C	2.43723900	-0.08376400	-1.48444700
C	1.78674300	0.55822900	1.32373100
C	0.98550000	1.61774800	2.10484100
C	-0.20294700	2.11834500	1.26358300
C	0.07263800	1.81760700	-0.20276500
C	-0.73257200	0.97876100	-0.97050900
C	-2.01581700	0.34546400	-0.54359800
C	-0.69307500	-0.97018600	1.08005800
H	1.70360800	2.41431900	2.36215700
H	0.66700500	1.15531300	3.05440600
H	-0.32585000	3.20840100	1.38759400
H	-1.14118700	1.63870900	1.57032500
H	-0.56215200	1.01486900	-2.05860600
H	-0.63742900	-2.07180200	1.14458000
H	-0.63415600	-0.61006400	2.12605700
C	-3.26417500	0.76574900	-1.29936700
C	-4.44004700	-0.18917300	-1.03920600
C	-4.55669400	-0.50526600	0.45886600
C	-3.28407100	-1.20280500	0.96464000
C	-2.00881100	-0.55748000	0.46115600
H	-5.37585200	0.25182700	-1.42184300
H	-3.54107500	1.79832200	-1.00616000
H	-3.04044200	0.81394100	-2.38175900
H	-4.70612600	0.43821000	1.01637600
H	-5.43986500	-1.13578000	0.65698800
H	-3.25923800	-1.22215300	2.06996100
H	-3.27573100	-2.26616600	0.65335200
H	-4.27453800	-1.13003700	-1.59564000
Rh	0.85032200	-0.37977200	-0.16273900
C	1.08738400	2.73327500	-0.86466400
H	0.68814800	3.76398200	-0.86715400
H	2.04559300	2.75731200	-0.31783100
H	1.28575500	2.44494400	-1.90865500

TS3

Cl	1.76855000	-2.40204000	-0.71399500
O	3.28903800	0.57997000	-2.05161700
O	1.64922300	-1.10611100	2.35000000
C	2.39115300	0.30416300	-1.42001400
C	0.95335600	-0.27313500	1.86074000
C	0.74099500	1.11328900	2.47493400
C	-0.17255400	1.97009900	1.60773000
C	0.26219800	1.86728500	0.14901900
C	-0.52562900	1.19747300	-0.81342700
C	-1.80895900	0.48800600	-0.54639800
C	-0.63570800	-1.00811800	1.12661400
H	1.75399100	1.54562400	2.55189200
H	0.36976000	0.97680100	3.50622600
H	-0.12610700	3.02443800	1.92960700
H	-1.21635500	1.63912800	1.71620200
H	-0.36388400	1.47318200	-1.86562900
H	-0.41530400	-2.06959000	0.91482700
H	-0.90088300	-0.98646200	2.20017000
C	-3.00982500	0.91510200	-1.37231100
C	-4.15318300	-0.10801500	-1.32481900
C	-4.39584200	-0.56944700	0.11788800
C	-3.14176200	-1.25586900	0.67900300
C	-1.85739800	-0.50676200	0.36784900
H	-5.06873900	0.32829100	-1.75787500
H	-3.36373100	1.90069400	-1.00978000
H	-2.68470500	1.08088700	-2.41577600
H	-4.64650600	0.30798000	0.74248900
H	-5.25637000	-1.25713400	0.17169400
H	-3.22682300	-1.38301200	1.77416000
H	-3.04952500	-2.28129900	0.26980300
H	-3.88607800	-0.98267500	-1.94572800
Rh	0.94530500	-0.22927700	-0.25774400
C	1.25941400	2.93010600	-0.28446900
H	0.81669300	3.93252400	-0.13738300
H	2.18338900	2.88866300	0.31735500

H	1.53345900	2.83816700	-1.34695700	H	0.42247100	3.45648800	1.92289200
				H	1.82377200	2.35578800	1.91264800

TS3'

				2e			
Cl	2.65185400	1.43202500	-1.14603200				
O	3.04415700	-2.13024400	-1.51718400	O	0.71633600	-3.01355300	0.28931600
O	1.31621200	-2.28727400	1.46380900	C	1.06440800	-1.93860900	-0.13118700
C	2.30710500	-1.39926400	-1.07152400	C	2.29650400	-1.22713800	0.41816900
C	0.56337800	-1.33893200	1.37278800	C	1.98166500	0.15576100	1.04702600
C	0.31827800	-0.43106000	2.58130500	C	1.79305900	1.30960800	0.07130700
C	-0.49766500	0.82875000	2.28668400	C	0.59883000	1.65159000	-0.45749300
C	0.00174900	1.56205000	1.04570100	C	-0.68459300	0.93849900	-0.25443700
C	-0.61182600	1.40053700	-0.19110200	C	0.25215900	-1.20967200	-1.20258400
C	-1.84689500	0.59173800	-0.39073200	H	3.03117900	-1.10916600	-0.40092000
C	-0.67928300	-1.56295200	0.25654600	H	2.73230000	-1.89633100	1.17590800
H	1.32664800	-0.17883700	2.95160700	H	2.82411200	0.41216100	1.71255800
H	-0.15943000	-1.04896000	3.36411500	H	1.08909400	0.05432000	1.68686200
H	-0.42682200	1.51245800	3.14900700	H	0.55192200	2.56537400	-1.06839100
H	-1.55847100	0.56374900	2.16063300	H	0.91068000	-0.57657500	-1.81553300
H	-0.36259800	2.12729100	-0.97579800	H	-0.21441600	-1.98322000	-1.83464300
H	-0.28415200	-2.01311400	-0.67749500	C	-1.83108900	1.78556300	0.28046100
H	-1.01356500	-2.46207300	0.80087800	C	-3.20006500	1.10330100	0.15540400
C	-3.04375300	1.36549900	-0.91874300	C	-3.10592700	-0.35567800	0.62134000
C	-4.18728600	0.45262600	-1.37840400	C	-2.12591300	-1.13143600	-0.26783600
C	-4.44654700	-0.63419100	-0.32818100	C	-0.84169300	-0.37431800	-0.54979400
C	-3.19948100	-1.51161200	-0.14778700	H	-3.95418000	1.65811800	0.73883900
C	-1.90476500	-0.71829700	-0.06661200	H	-1.62490700	2.03115400	1.34097900
H	-5.09665100	1.04878900	-1.56186800	H	-1.82983600	2.75570800	-0.25077500
H	-3.39916700	2.05800900	-0.12985100	H	-2.75186700	-0.37938600	1.66863600
H	-2.70410500	2.01136000	-1.74887300	H	-4.09612000	-0.84139300	0.60713000
H	-4.70051400	-0.15332900	0.63462300	H	-1.85938700	-2.10242200	0.18944300
H	-5.30891400	-1.26077900	-0.61058900	H	-2.60403500	-1.38168500	-1.23640900
H	-3.29575700	-2.12906200	0.76508900	H	-3.52805200	1.12593300	-0.90046700
H	-3.11938400	-2.23477800	-0.98449600	C	3.04401700	2.10361300	-0.23288600
H	-3.91385900	-0.02403900	-2.33763100	H	2.85933900	2.89738100	-0.97317700
Rh	1.06832700	-0.08054100	-0.34104600	H	3.44543000	2.56768900	0.68671100
C	0.95944200	2.69994500	1.32039600	H	3.83988800	1.44426700	-0.62621200
H	1.33657400	3.16209100	0.39968900				

TS1-bp1

C	0.73240200	2.33958300	-0.94357500
C	1.22351900	2.80360600	0.43447600
C	0.05498600	2.84440300	1.42932800
C	-0.54160400	1.43844800	1.63018400
C	-0.13139800	1.09165500	-0.88476400
C	-0.28277600	0.17247600	-1.97366700
H	0.10461400	3.13613700	-1.39027700
H	1.57073800	2.17826300	-1.64313000
H	1.69371800	3.79720000	0.34500200
H	1.99722800	2.10922600	0.80986900
H	-0.72338200	3.53668000	1.05549800
H	0.38822500	3.23625400	2.40490400
H	-1.41804000	1.47568800	2.29729700
H	0.21079100	0.80039600	2.12271800
H	0.30997000	0.34879800	-2.87844600
H	-1.24424900	-0.32205500	-2.14457000
Rh	0.68193000	-0.67678800	-0.26952000
Cl	1.83996200	-1.66557100	1.60853600
O	3.53145200	-0.27412600	-1.36467800
C	2.47826400	-0.42311600	-0.97631600
C	-1.12237800	-1.49332200	0.62642300
C	-2.46502300	-1.65579300	-0.06019700
C	-3.19055800	-0.33727300	-0.13105700
C	-2.44037700	0.75243900	0.06149900
C	-0.96010200	0.79344200	0.29626400
H	-0.52534000	-2.42278500	0.54154400
H	-1.22752900	-1.27311800	1.69857300
H	-2.34698400	-2.08520000	-1.07390000
H	-3.07780200	-2.38510300	0.50649600
H	-2.88544800	1.75721300	0.01345300
C	-4.66764300	-0.31734500	-0.42057100
H	-4.88256300	-0.82696200	-1.37718500
H	-5.22430300	-0.86192000	0.36316900
H	-5.06134200	0.70926600	-0.47845500

TS1-bp2

C	2.55876700	-0.06707900	1.39724700
C	3.39195300	-0.11458800	0.11139400
C	3.16638200	-1.45249400	-0.59949100
C	1.70213300	-1.61240200	-1.03864900
C	1.12049200	-0.54605000	1.24972400
C	0.16254400	-0.10992800	2.16994600
H	3.02224700	-0.74341400	2.14112000
H	2.56355900	0.93972700	1.84758200
H	4.45709000	0.02222200	0.36221000
H	3.12067800	0.71983700	-0.55941600
H	3.43514000	-2.27233600	0.09312300
H	3.82716100	-1.54953500	-1.47743000
H	1.53081100	-2.65872100	-1.34523400
H	1.52125400	-1.01137200	-1.94722400
H	0.44389900	0.56998900	2.97880900
H	-0.76751500	-0.67382800	2.30611500
Rh	-0.36803600	0.65229400	0.04709900
Cl	-1.55545000	2.68867000	0.58172500
O	1.27575300	2.23557800	-1.87226000
C	0.67228600	1.60511700	-1.14446500
C	-1.61058500	0.04796300	-1.45249800
C	-2.31341700	-0.75169200	-0.36372600
C	-1.74223900	-2.13255800	-0.08149800
C	-0.42242800	-2.29521700	0.12253400
C	0.65537900	-1.23680400	0.03983400
H	-2.21608900	0.86814200	-1.86176900
H	-1.15447900	-0.56699400	-2.24054700
H	-2.24492900	-0.14659800	0.60200400
H	-3.40946400	-0.77046200	-0.50163300
H	-0.04647900	-3.31595300	0.28655400
C	-2.72530100	-3.27639200	-0.02399300
H	-3.48526000	-3.09887900	0.75857200
H	-3.26846400	-3.37023600	-0.98173700
H	-2.22672200	-4.23410800	0.19003600

TS2-bp2

C	-2.41951100	0.48947700	1.31787700

C	-3.26740400	0.86685100	0.09350600	C	-3.16879100	1.53964000	-0.54415800
C	-2.71498800	2.12411800	-0.58667000	C	-1.73957600	1.66821400	-1.09517100
C	-1.27872200	1.87538400	-1.07192200	C	-0.99813500	0.65202300	1.14656200
C	-0.92170100	0.73142800	1.17604100	C	0.04274100	0.36129700	2.08979400
C	-0.04159400	0.23150000	2.19202500	H	-2.81486800	0.86706400	2.20314800
H	-2.72956000	1.11223200	2.17944500	H	-2.38775900	-0.82248700	1.88711100
H	-2.59454800	-0.56060200	1.60727200	H	-4.39797100	0.11488900	0.56145500
H	-4.31109900	1.02188200	0.41517100	H	-3.15944600	-0.63022100	-0.45435800
H	-3.25411400	0.03346000	-0.62550700	H	-3.37434100	2.38290100	0.14190500
H	-2.72783100	2.97711300	0.11926000	H	-3.89335800	1.61884400	-1.37213800
H	-3.35066700	2.40628900	-1.44313700	H	-1.58456900	2.69342800	-1.47461400
H	-0.86211600	2.79260000	-1.52231800	H	-1.62038800	1.01015000	-1.97428700
H	-1.30015300	1.10617100	-1.86491700	H	-0.18169800	-0.32592200	2.91255400
H	-0.47022300	-0.41521000	2.96585400	H	0.75413800	1.16075100	2.33816600
H	0.77791100	0.87665400	2.53484900	Rh	0.33766100	-0.63184100	0.03756900
Rh	0.35246400	-0.71618500	0.16698000	Cl	1.46171600	-2.72003300	0.53647500
Cl	-1.35950500	-1.62837300	-1.35836400	O	-1.47804500	-2.45215500	-1.62801300
O	0.84857300	-3.72405700	0.56317200	C	-0.85922500	-1.73683800	-0.99943000
C	0.68626100	-2.60894000	0.44063600	C	1.79275400	-0.13051900	-1.44905600
C	1.69565600	-0.33487300	-1.57132800	C	2.19869000	0.60737600	-0.29075700
C	2.31194800	0.25072500	-0.45685400	C	1.80326400	2.04476200	-0.14919300
C	2.16234000	1.69504400	-0.09865200	C	0.49132300	2.35311200	-0.10587900
C	0.93357800	2.20482300	0.10889000	C	-0.63164500	1.35431000	-0.06989900
C	-0.33447800	1.40073900	0.04468700	H	2.36334400	-1.02343800	-1.72295100
H	2.07213700	-1.27986700	-1.97246800	H	1.30524800	0.41129600	-2.26609500
H	1.08519600	0.26969300	-2.24857000	H	1.37498100	0.07018200	1.10911200
H	1.31788200	-0.37772600	1.37819100	H	3.12365000	0.28741000	0.21030500
H	3.18187900	-0.26271500	-0.02563800	H	0.19050200	3.41034800	-0.14053900
H	0.81560600	3.29207100	0.22872000	C	2.91547100	3.06503200	-0.09782000
C	3.43630000	2.50504600	-0.02676400	H	3.56604000	2.88607900	0.77727800
H	4.11610800	2.09407500	0.74151100	H	3.55619400	2.99429700	-0.99436700
H	3.97894100	2.47228600	-0.98800000	H	2.52010200	4.08984400	-0.02766400
H	3.23067100	3.55678000	0.22419000				

TS3-bp2

C	-2.41789100	0.18102800	1.43011400
C	-3.35554600	0.22309900	0.21812500

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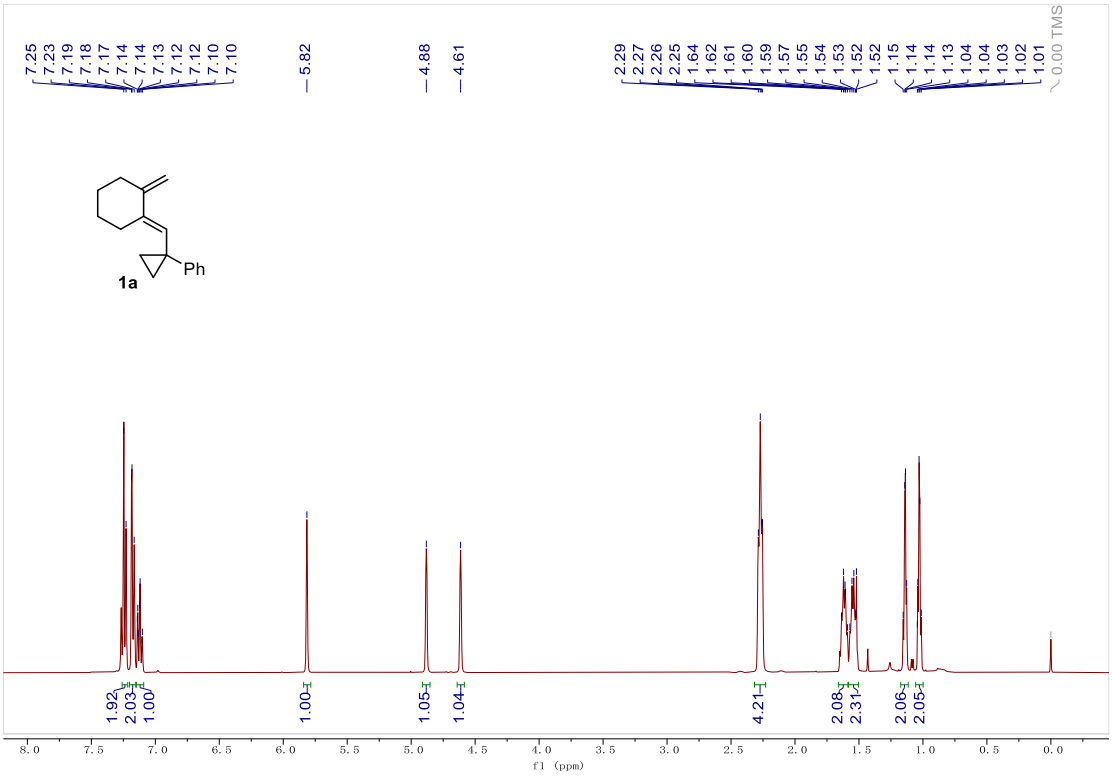
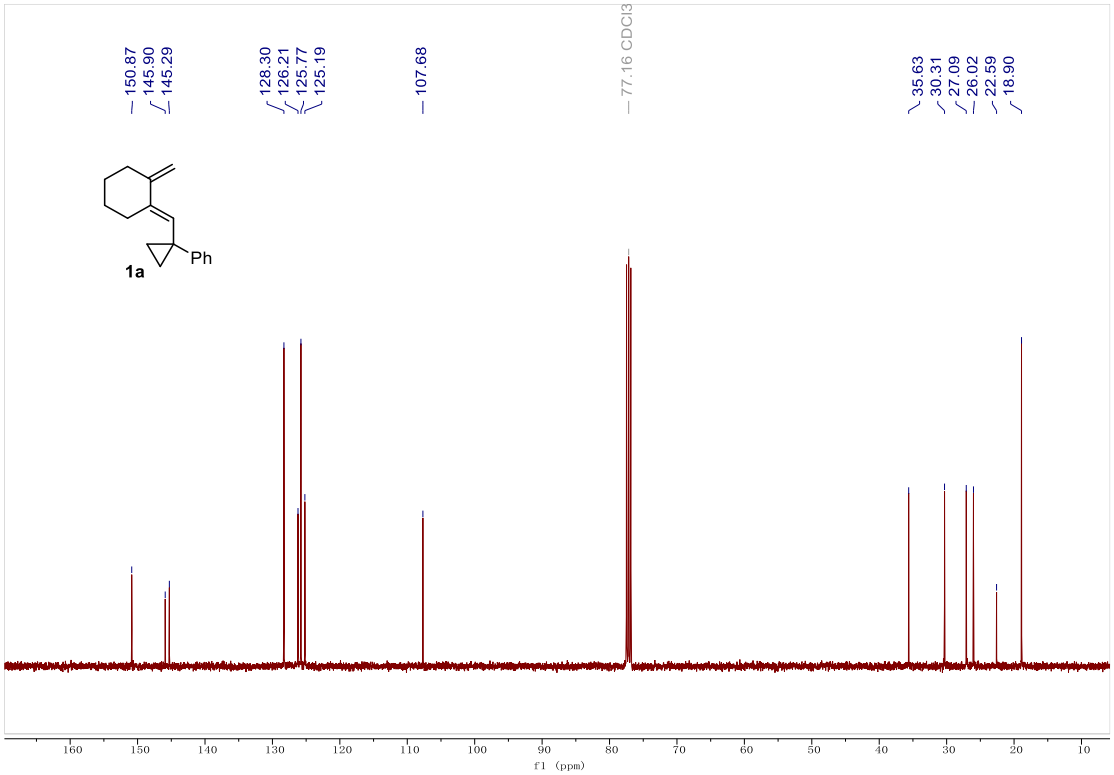
6. NMR Spectra of New Compounds

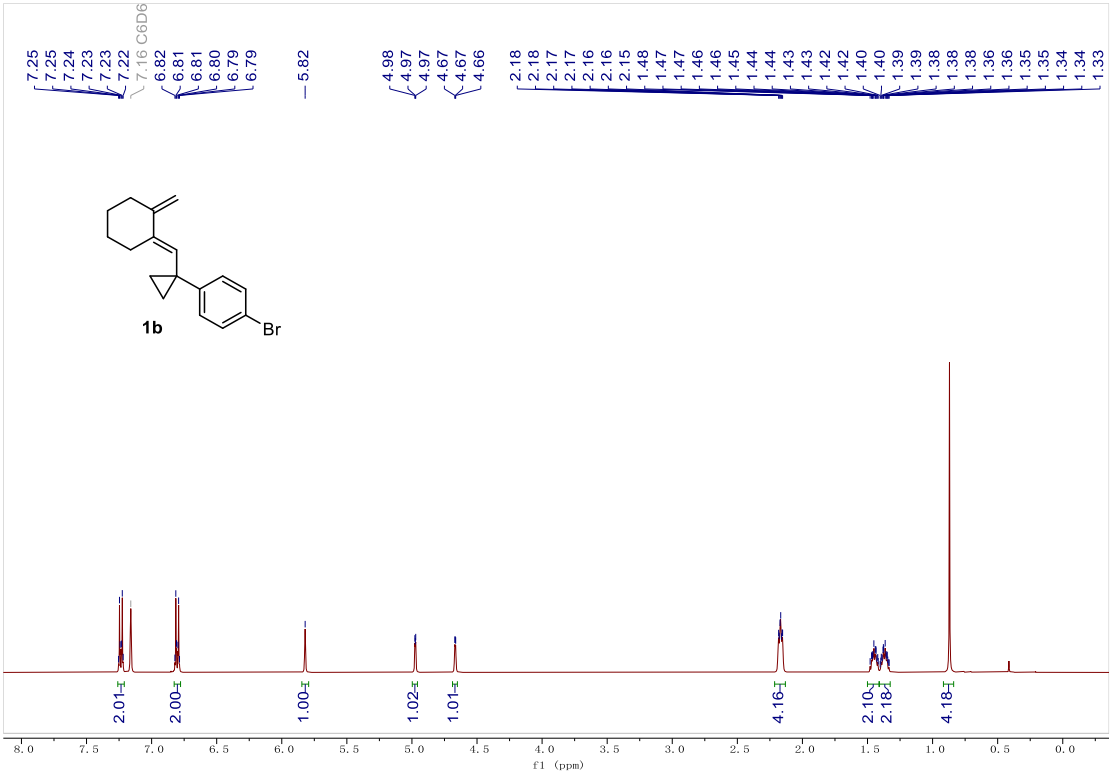
^{1}H NMR in $CDCl_3$, 400 MHz



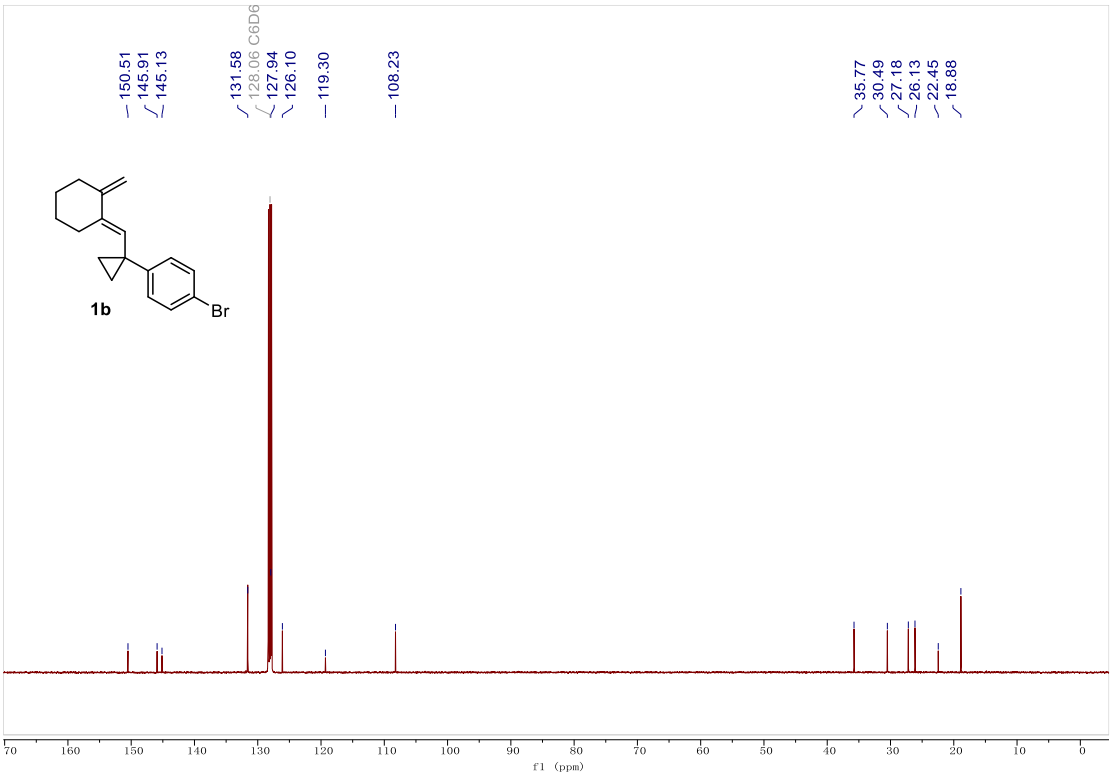
^{13}C NMR in $CDCl_3$, 101 MHz



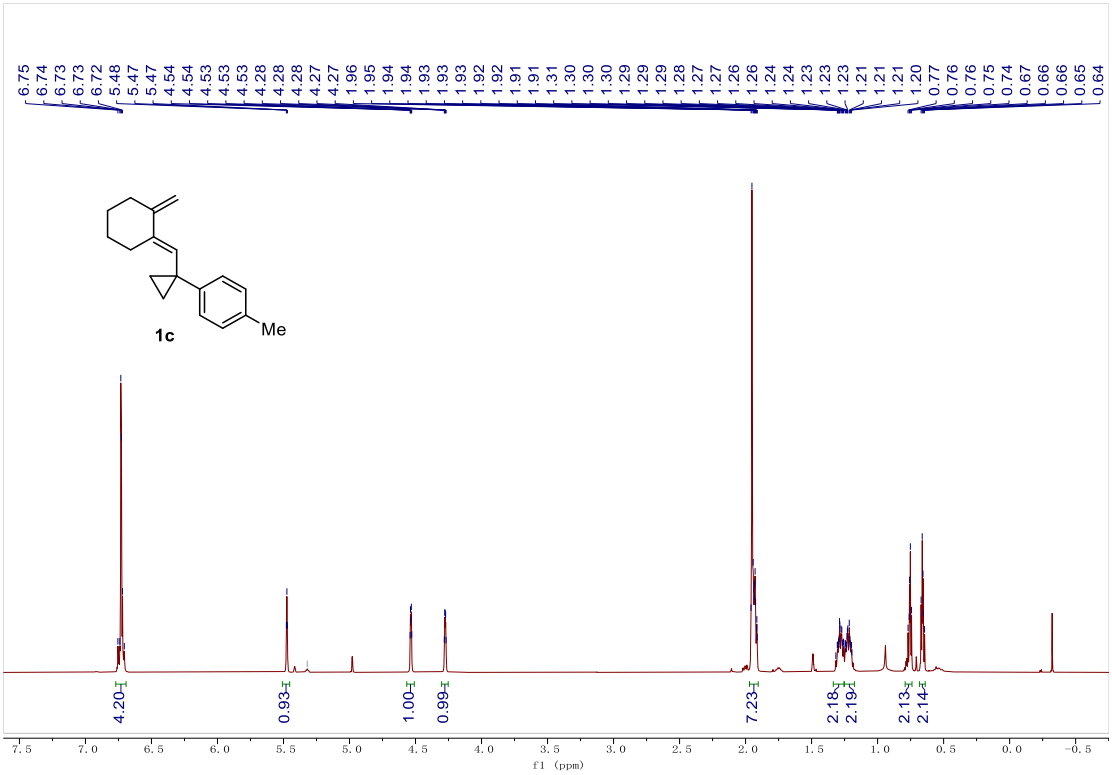
^{1}H NMR in C_6D_6, 400 MHz



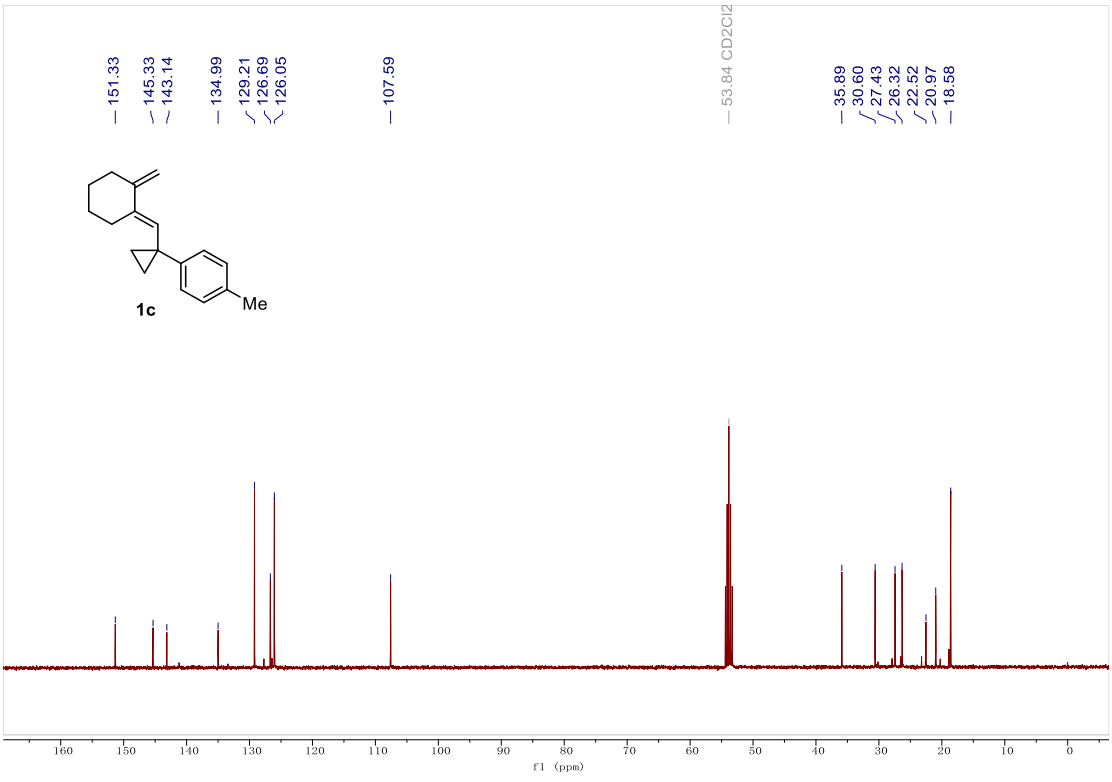
^{13}C NMR in C_6D_6, 101 MHz



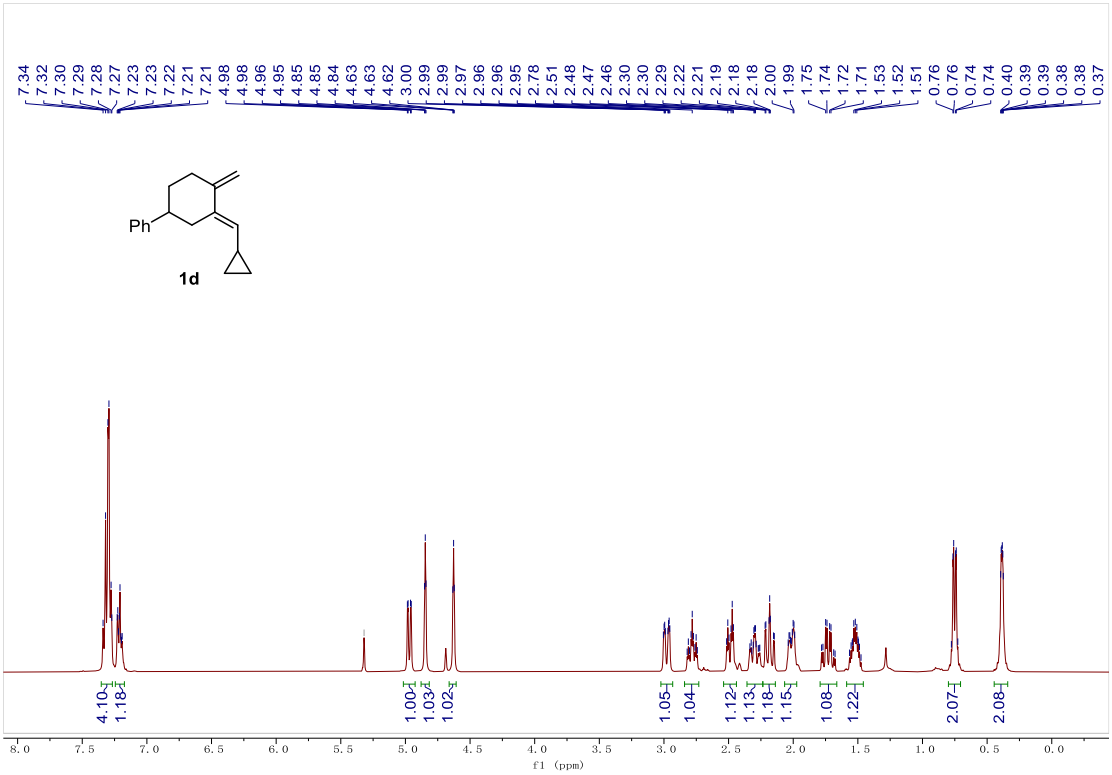
^{1}H NMR in CD_2Cl_2, 400 MHz



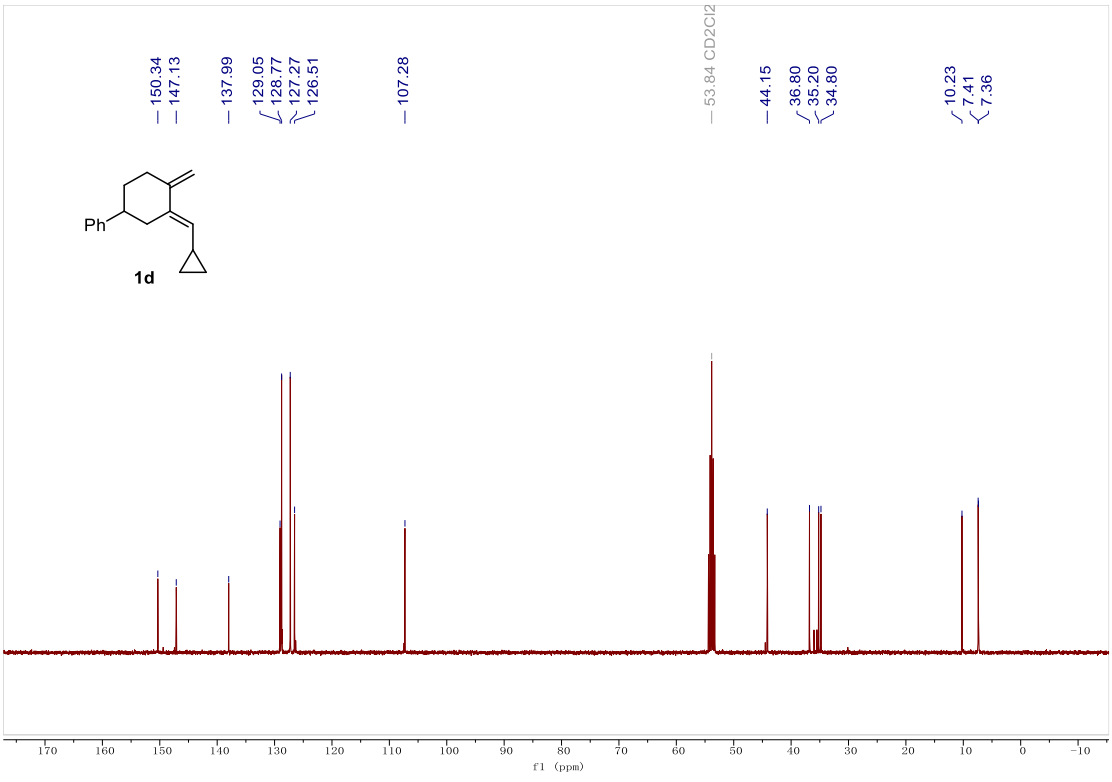
^{13}C NMR in CD_2Cl_2, 101 MHz



^{1}H NMR in CD_2Cl_2, 400 MHz



^{13}C NMR in CD_2Cl_2, 101 MHz



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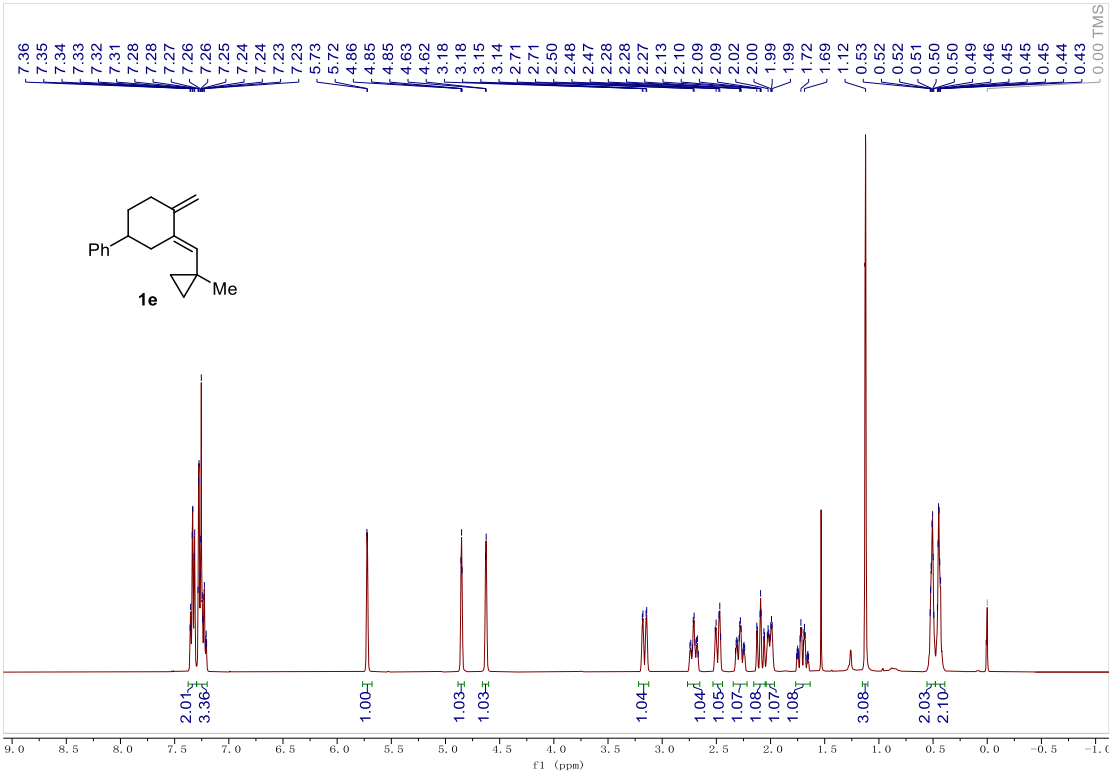
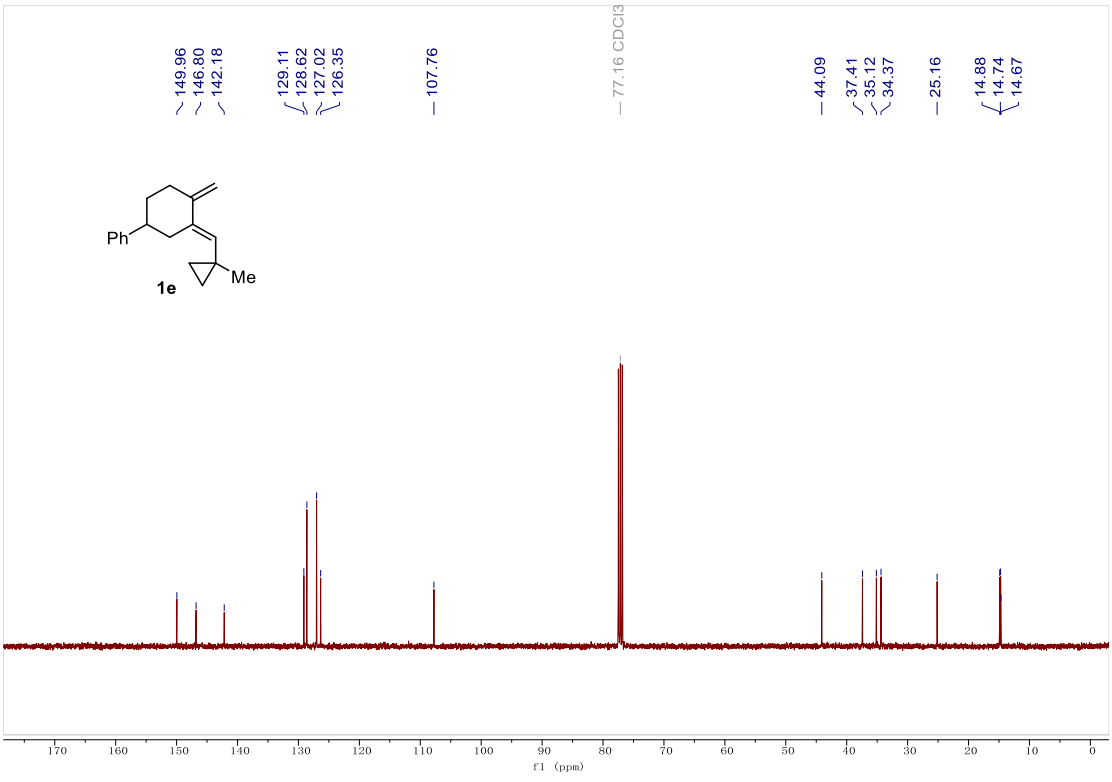
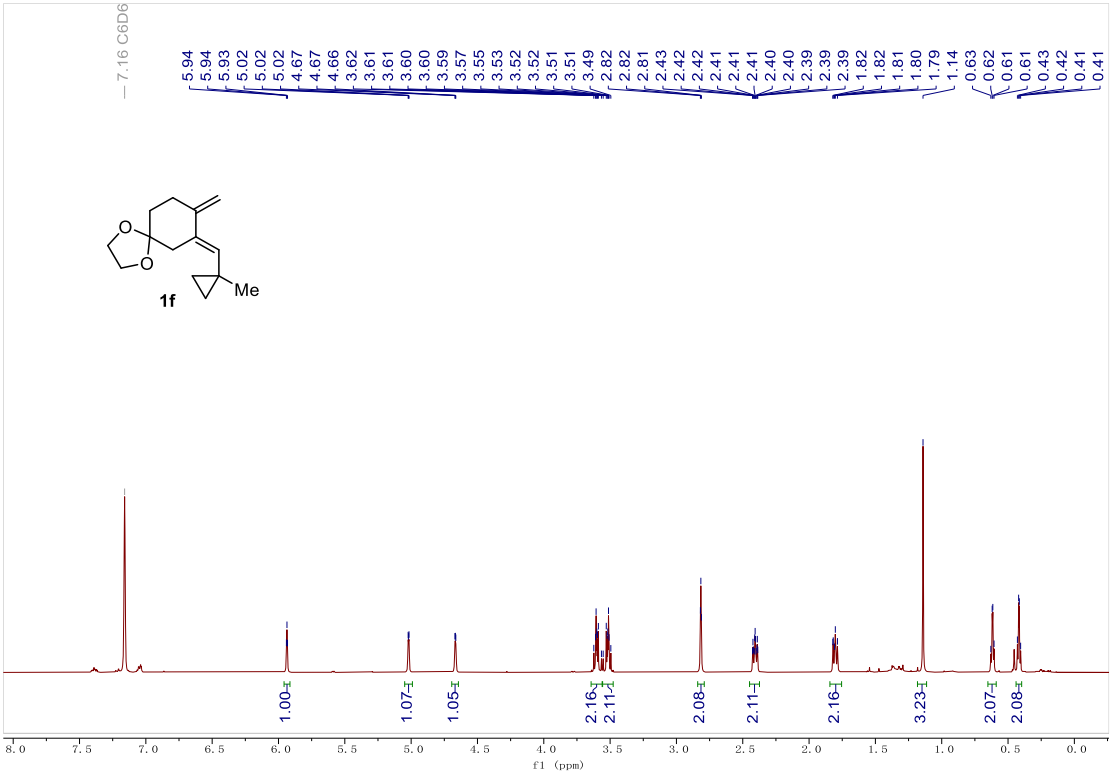


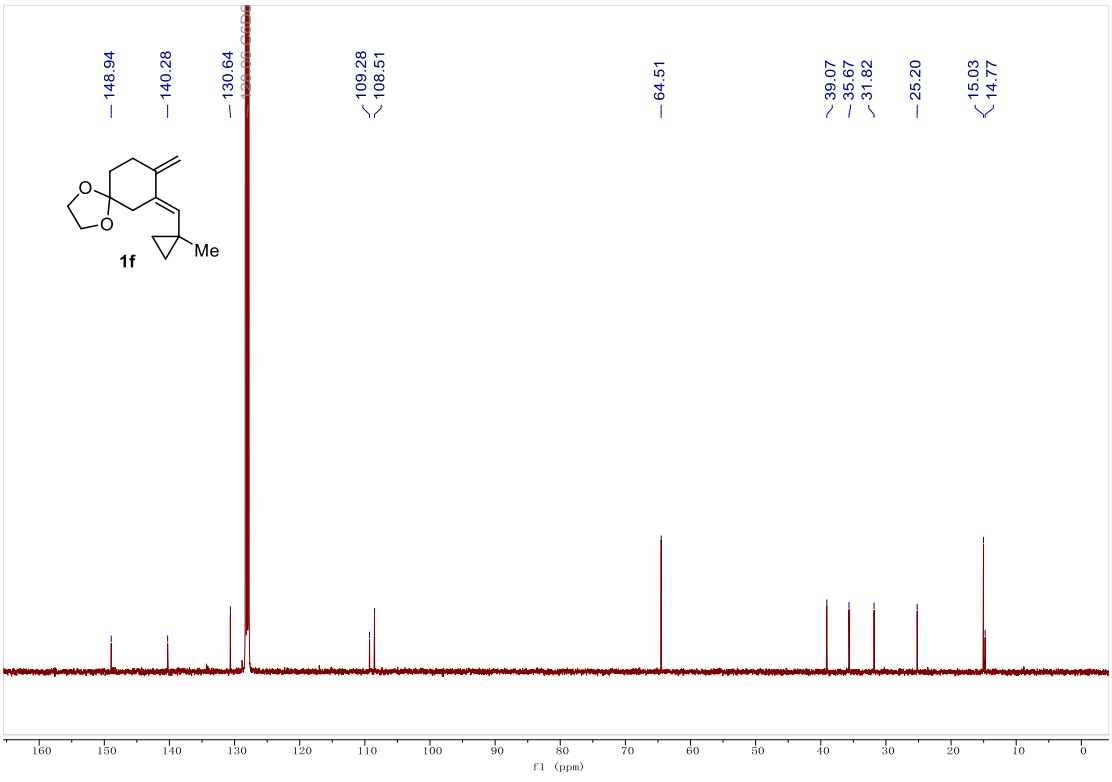
^{13}C NMR in $CDCl_3$, 101 MHz



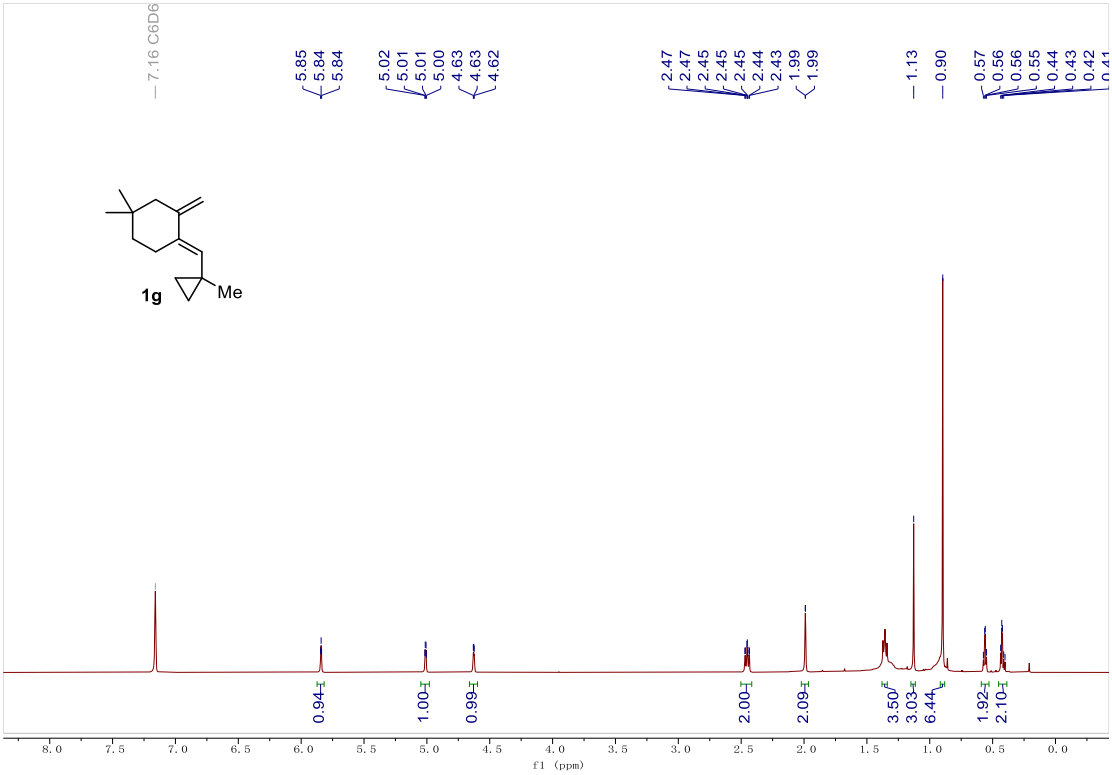
^{1}H NMR in C_6D_6, 400 MHz



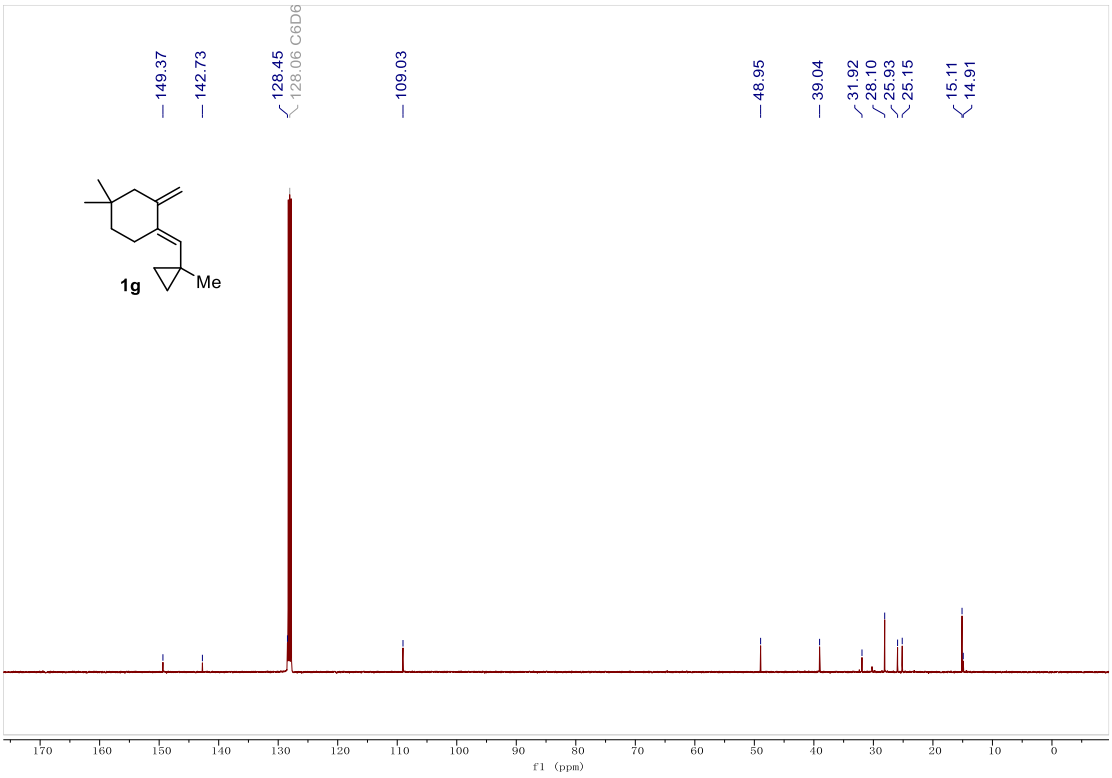
^{13}C NMR in C_6D_6, 101 MHz



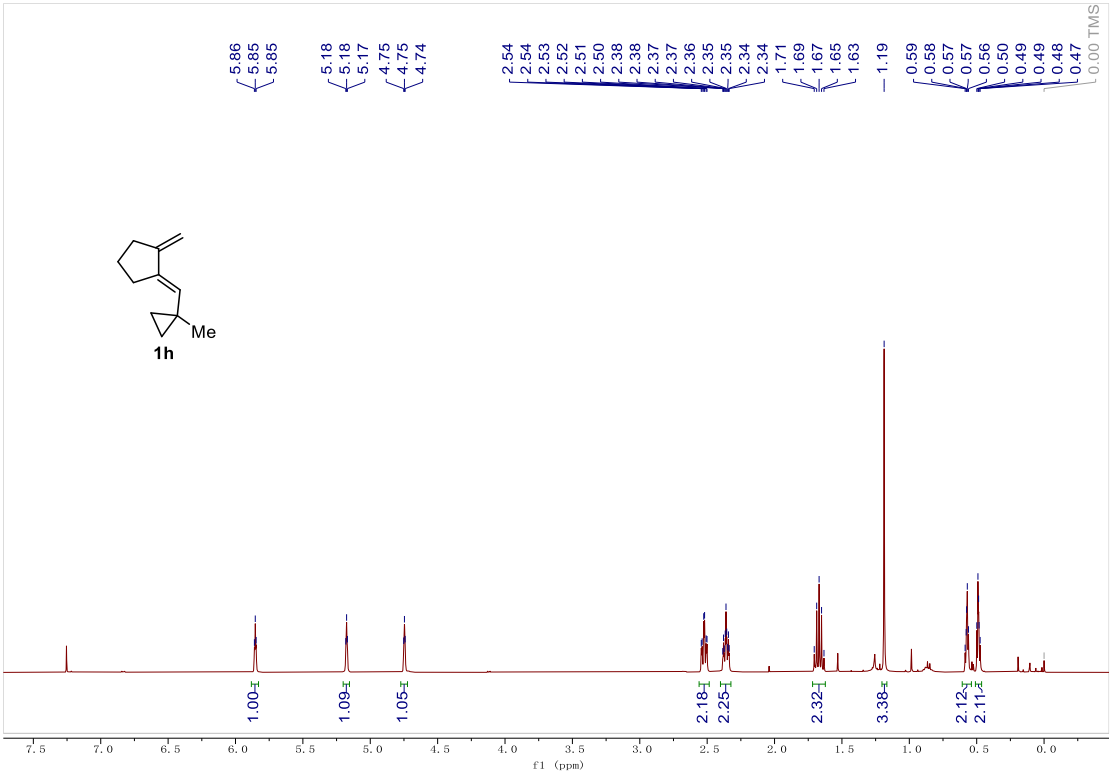
^{1}H NMR in C_6D_6, 400 MHz



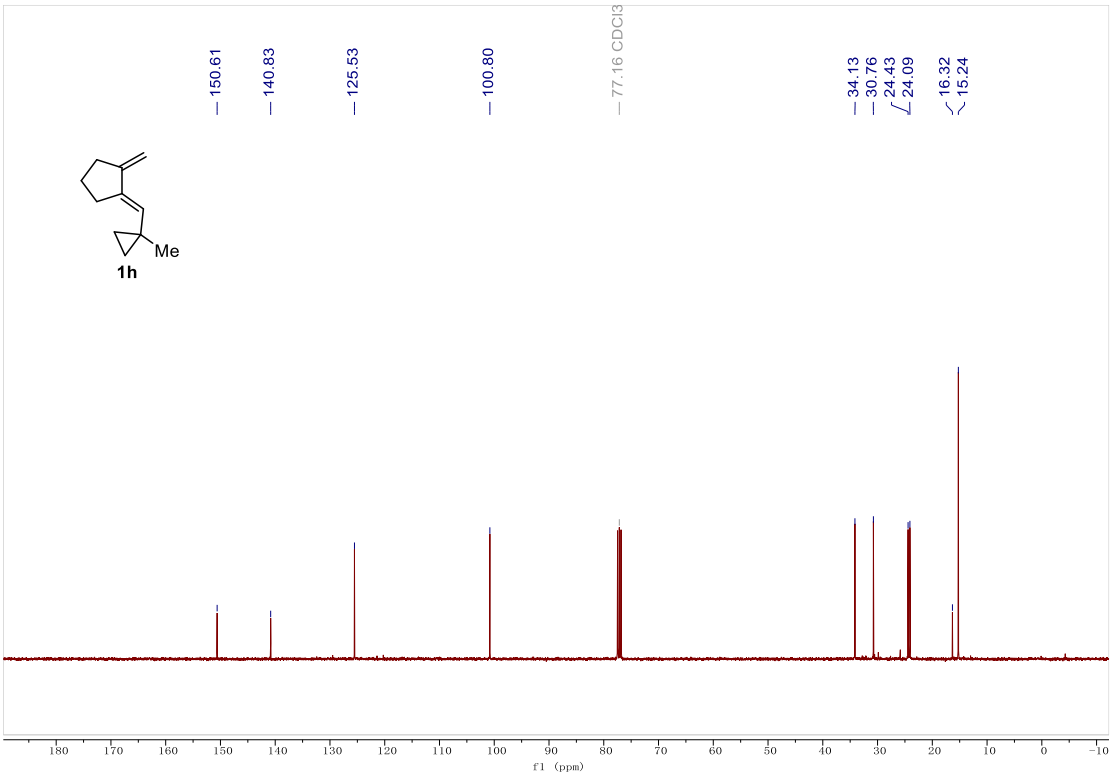
^{13}C NMR in C_6D_6, 101 MHz



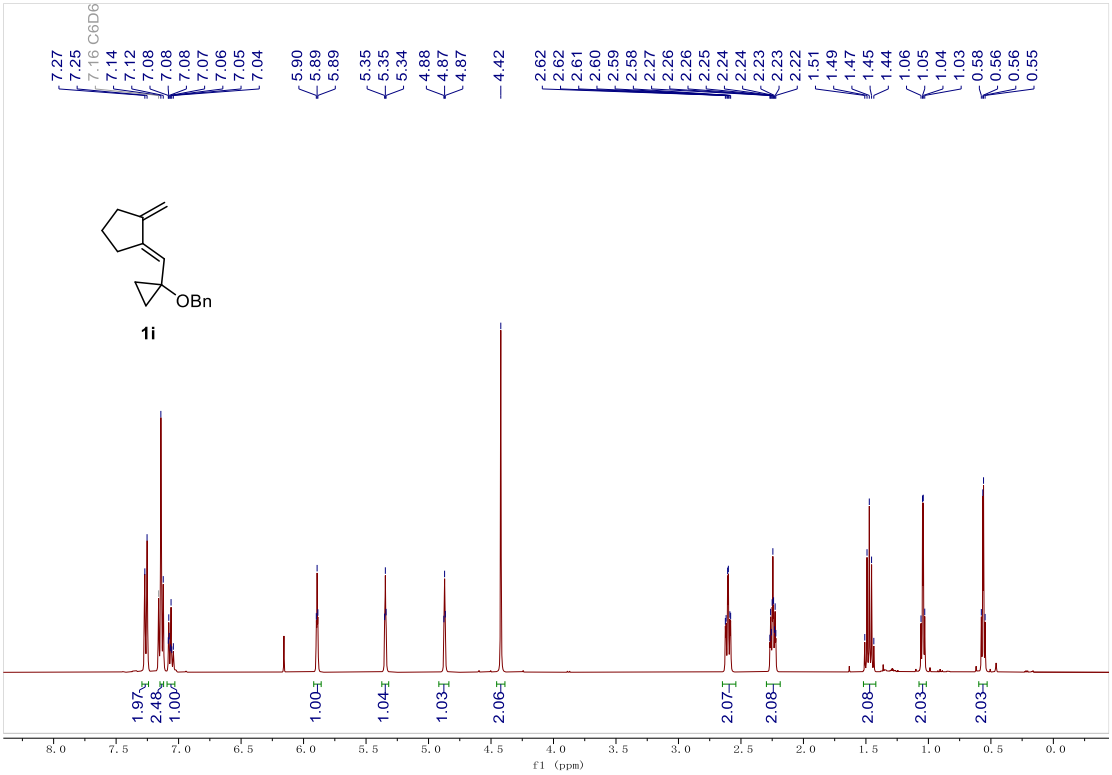
^{1}H NMR in $CDCl_3$, 400 MHz



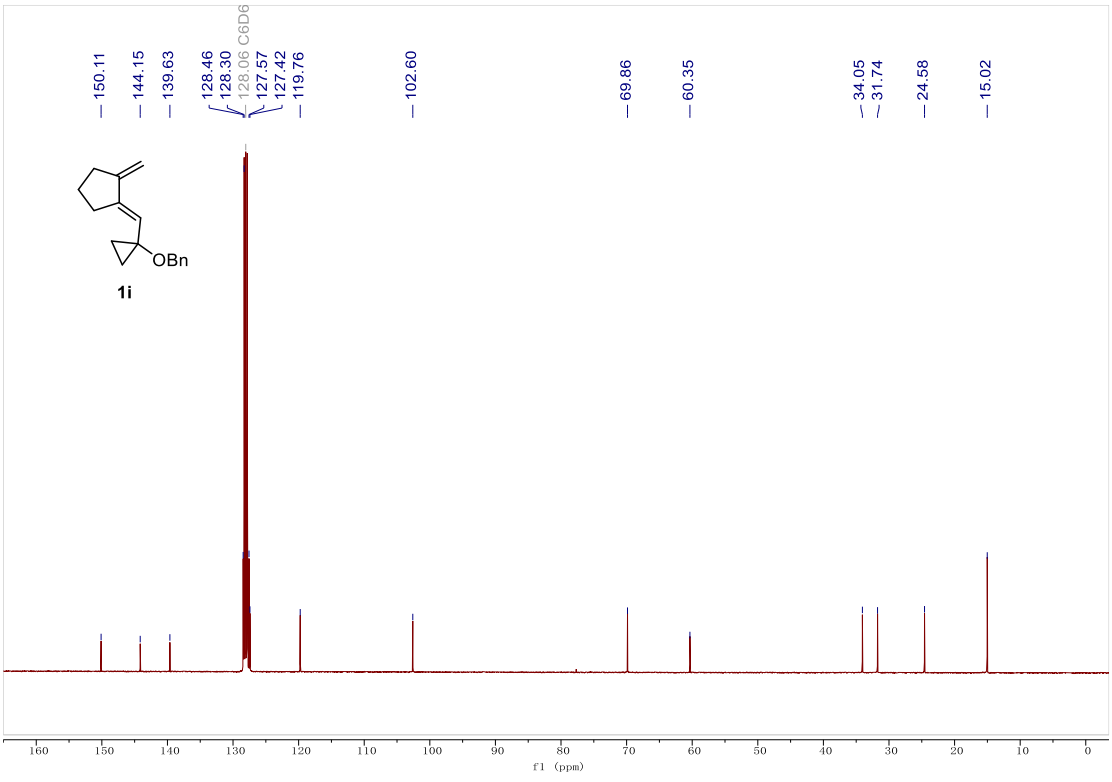
^{13}C NMR in $CDCl_3$, 101 MHz



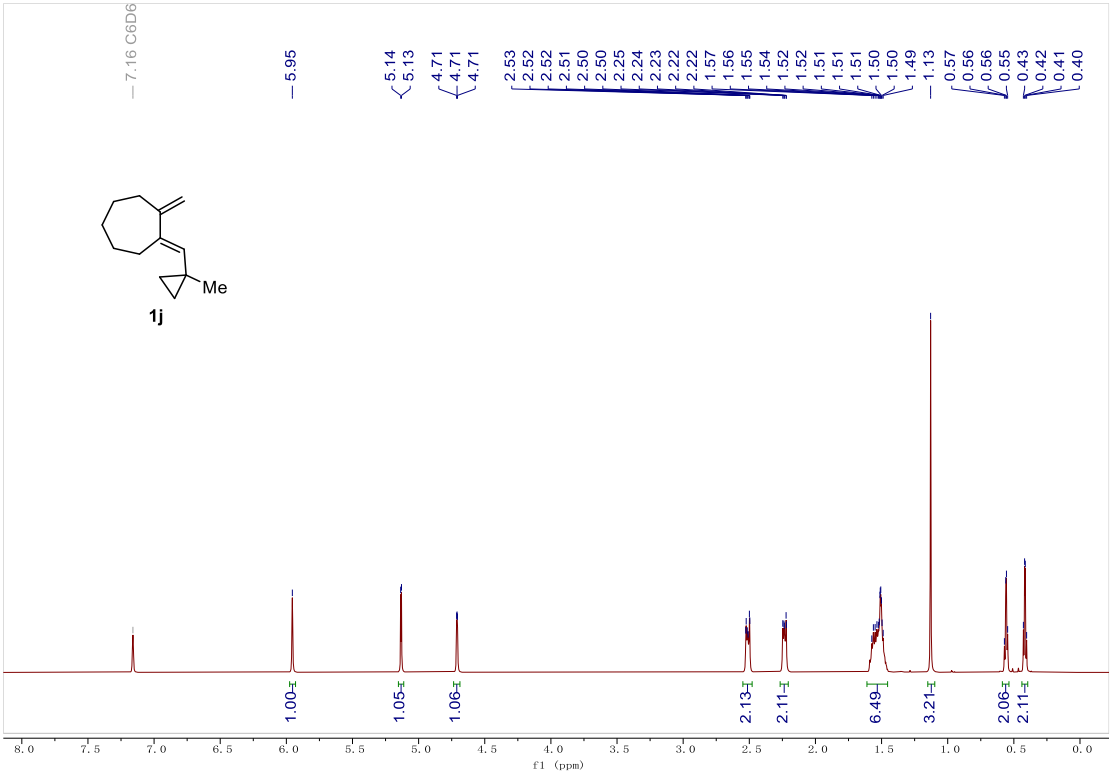
^{1}H NMR in C_6D_6, 400 MHz



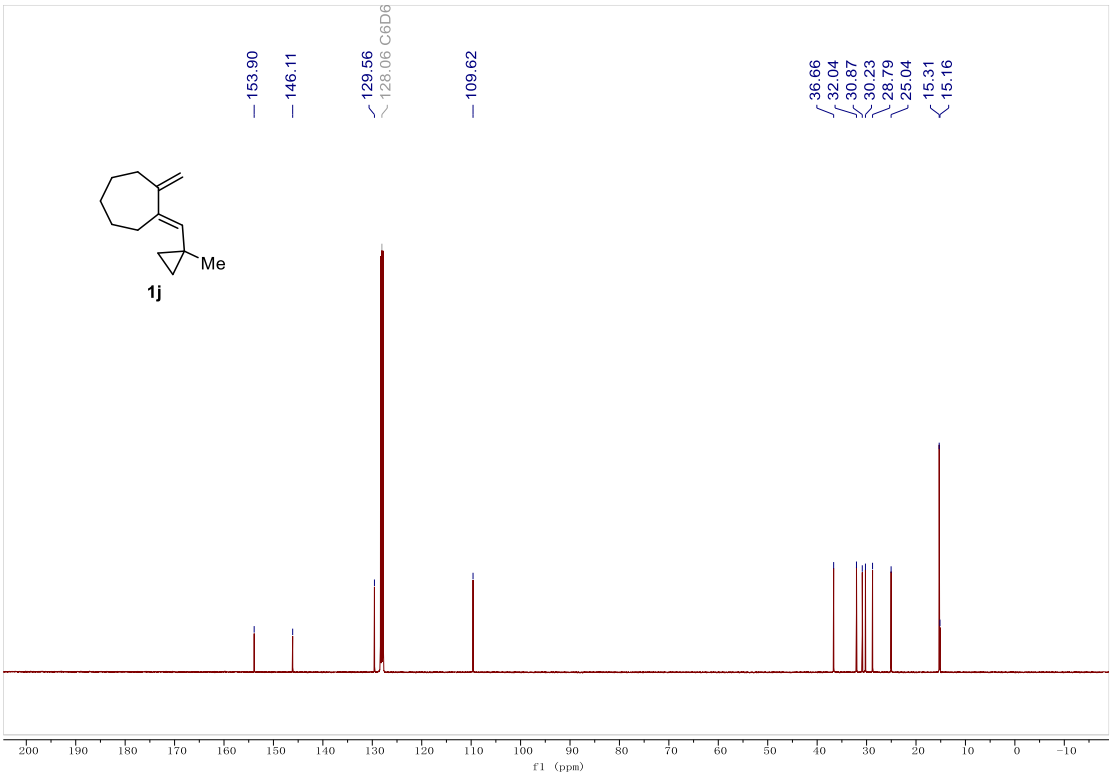
^{13}C NMR in C_6D_6, 101 MHz



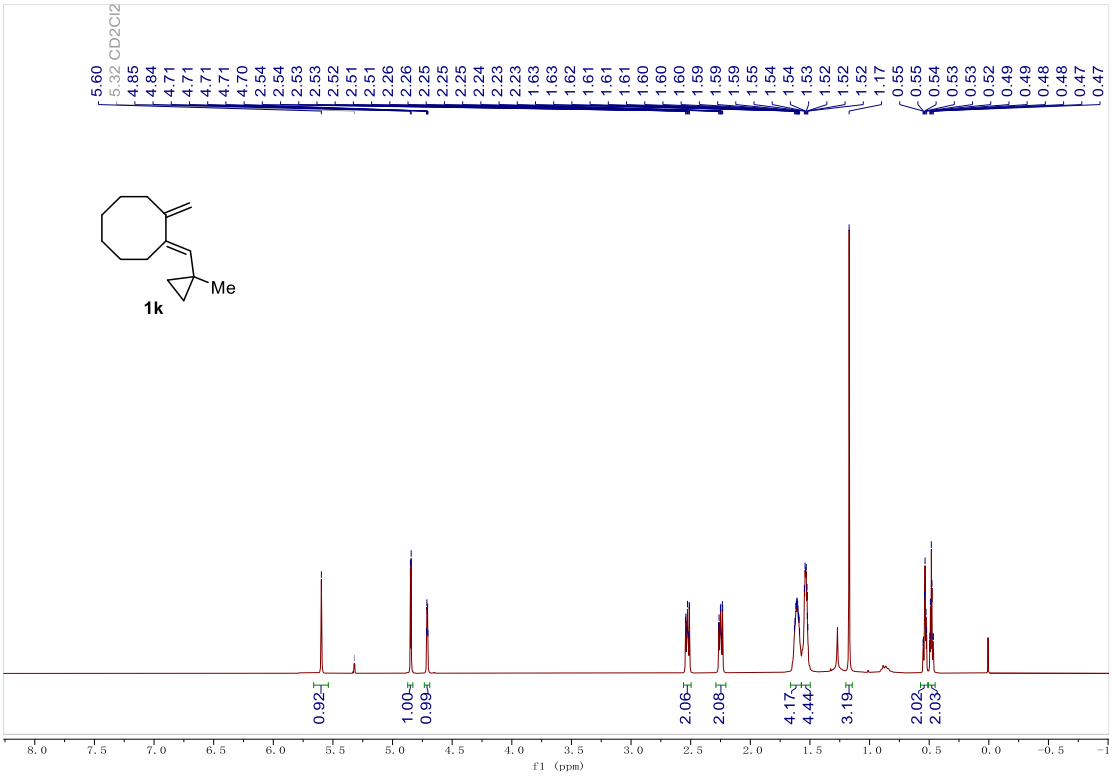
^{1}H NMR in C_6D_6, 400 MHz



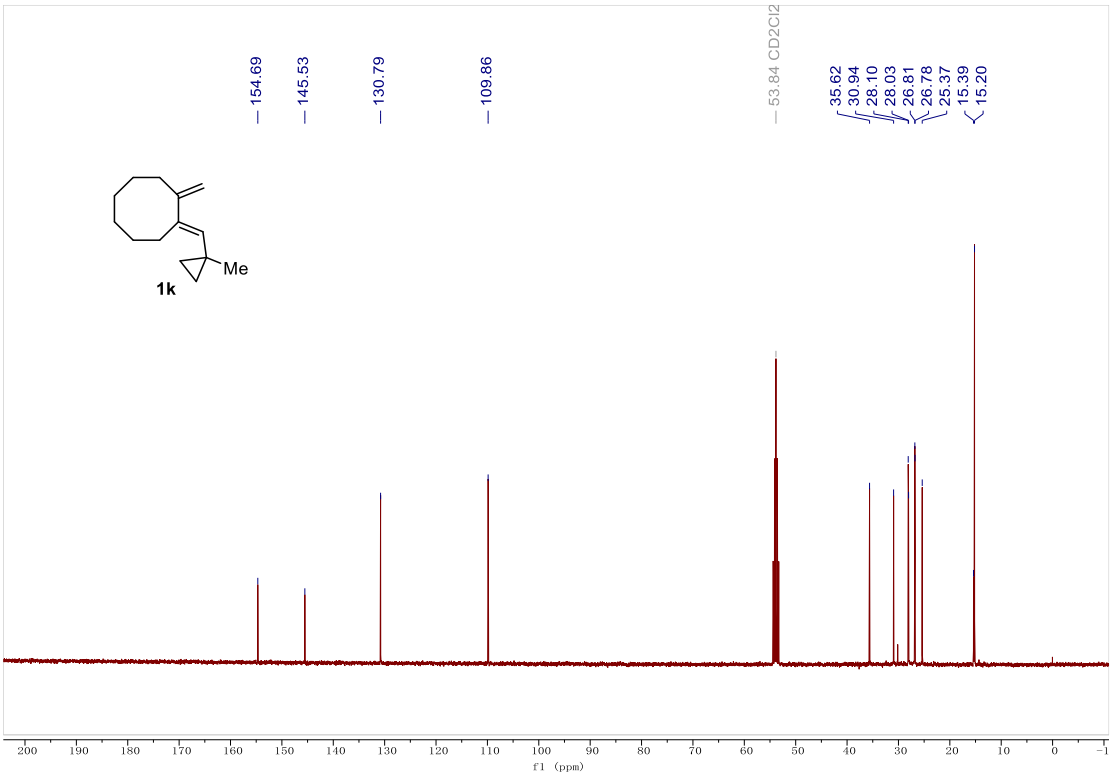
^{13}C NMR in C_6D_6, 101 MHz



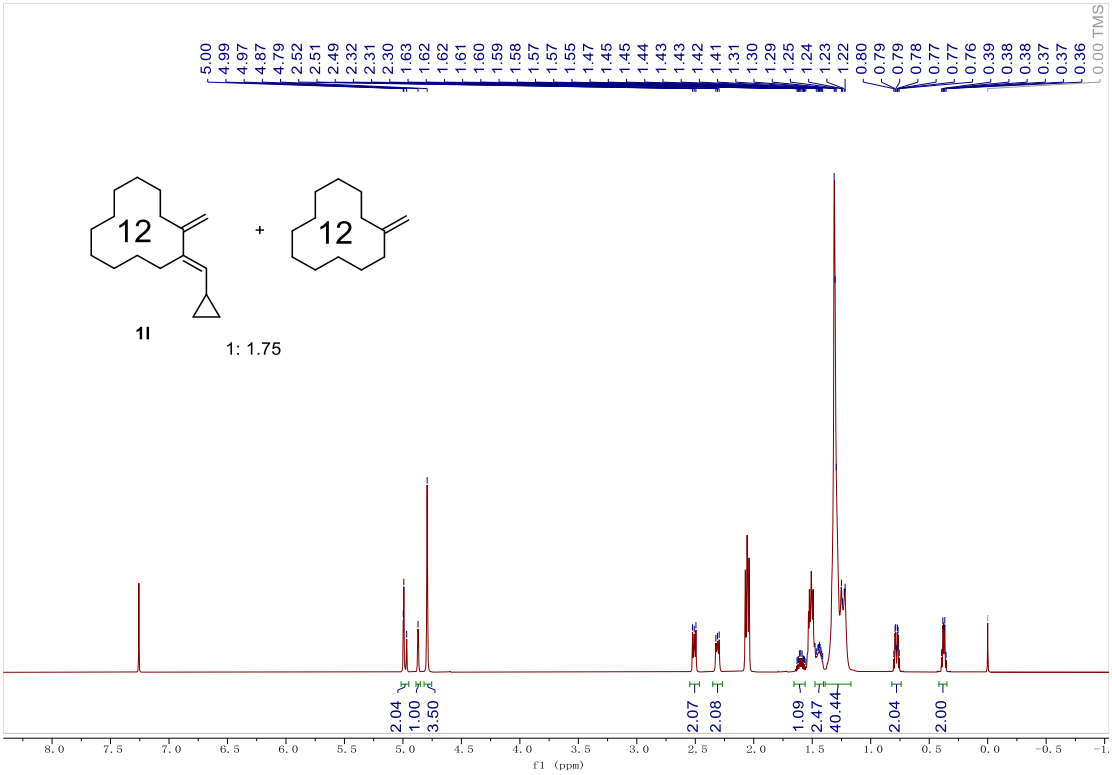
^{1}H NMR in CD_2Cl_2, 400 MHz



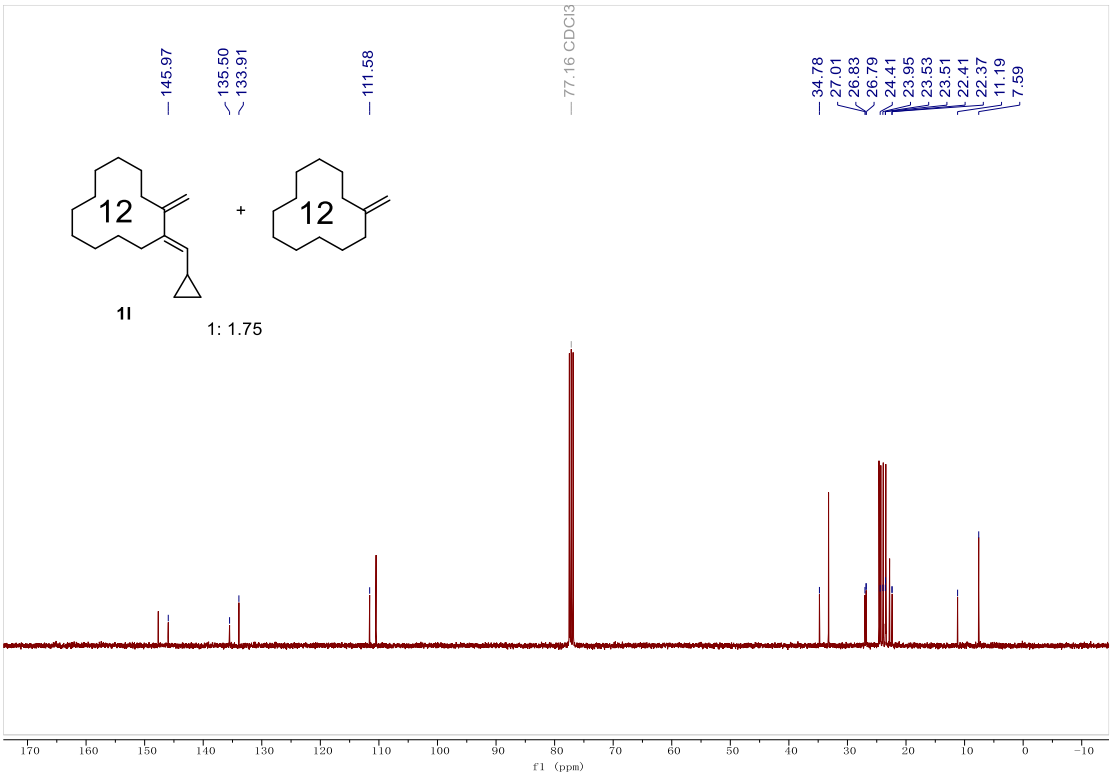
^{13}C NMR in CD_2Cl_2, 101 MHz



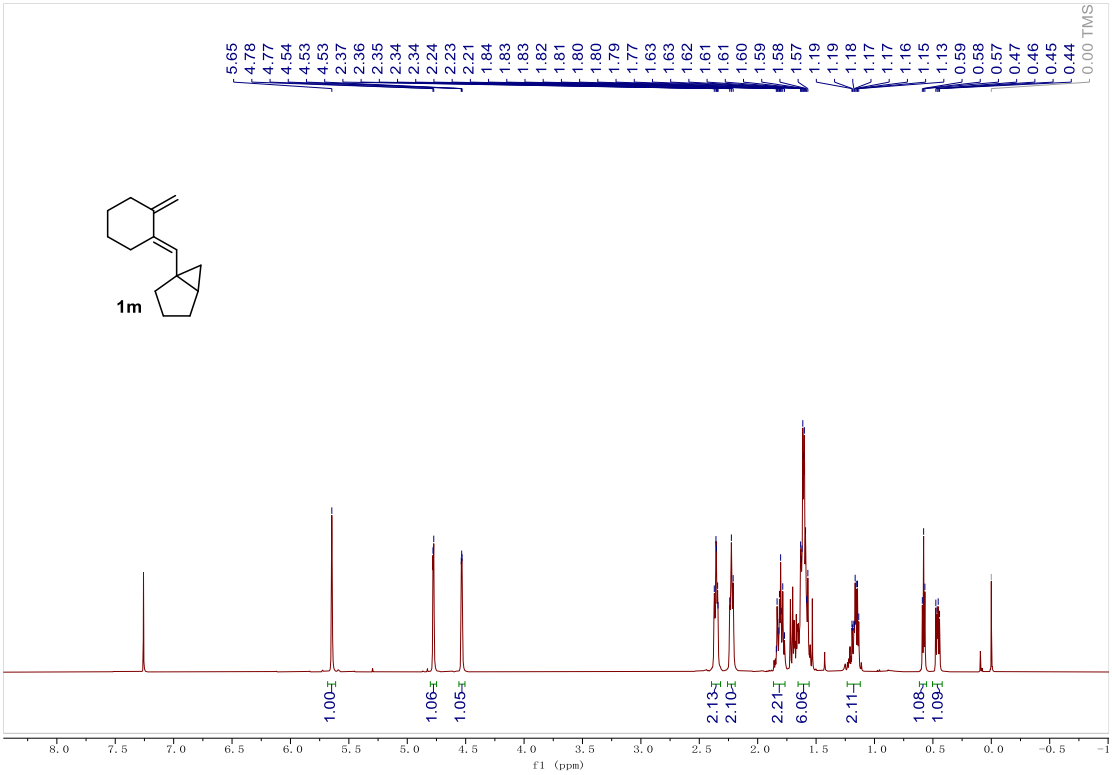
^{1}H NMR in $CDCl_3$, 400 MHz



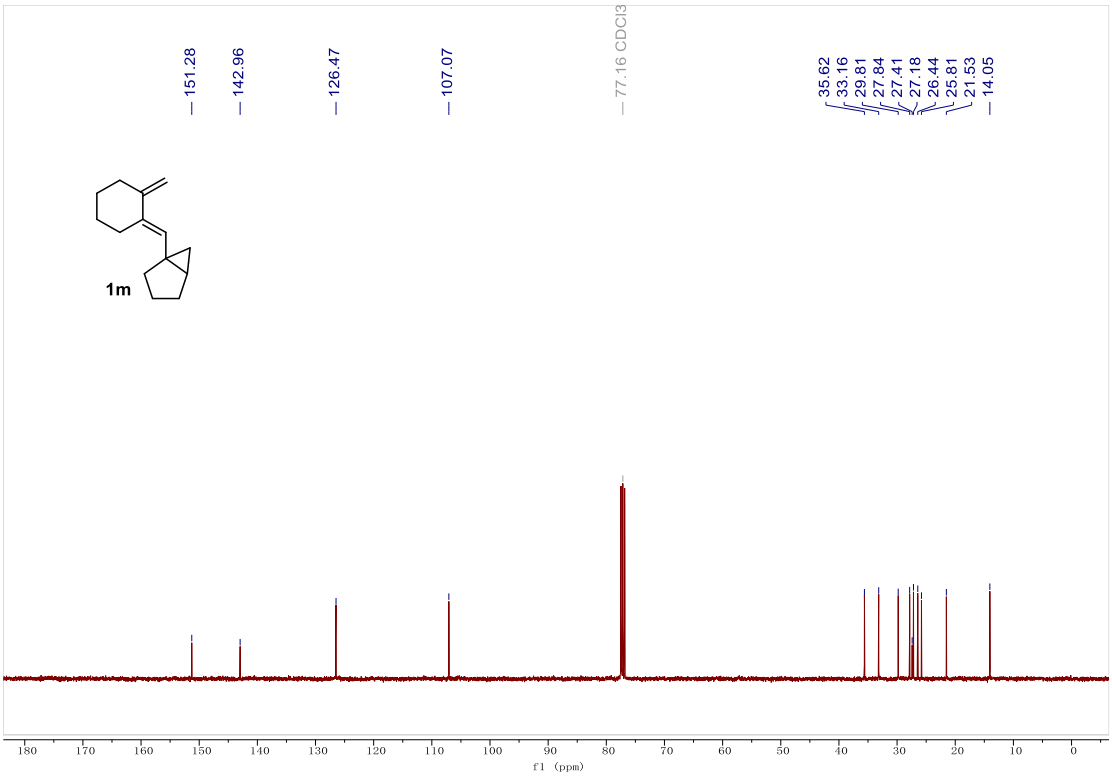
^{13}C NMR in $CDCl_3$, 101 MHz



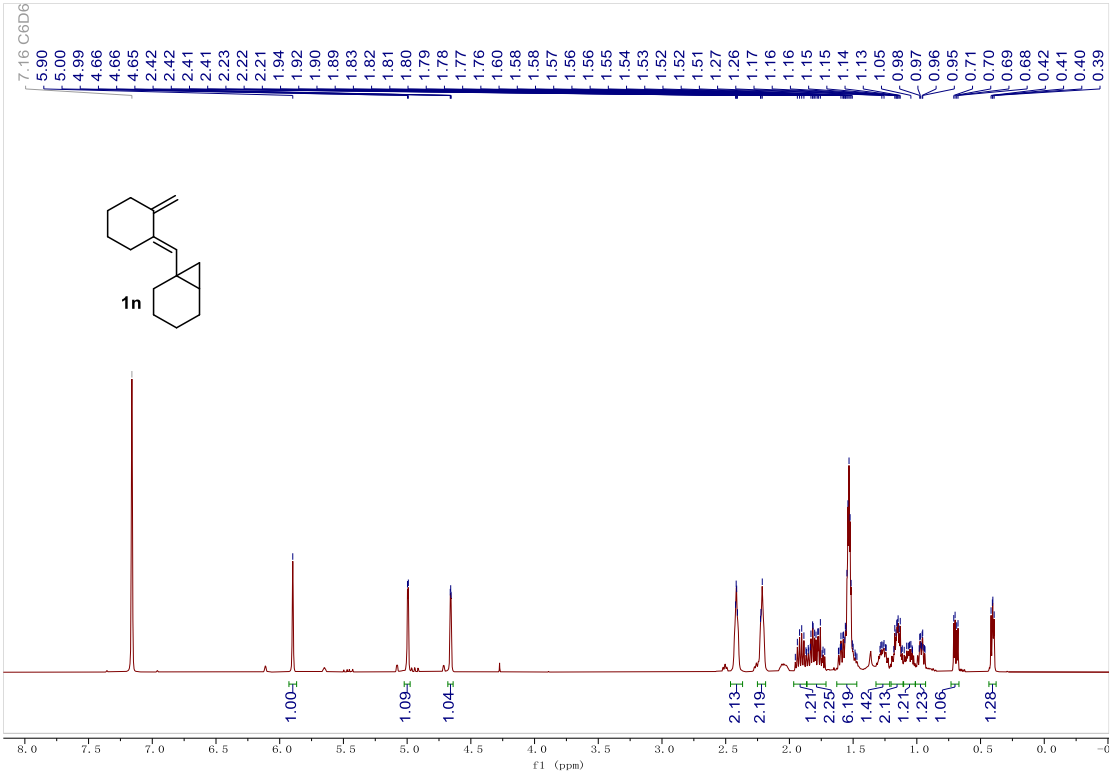
^{1}H NMR in $CDCl_3$, 400 MHz



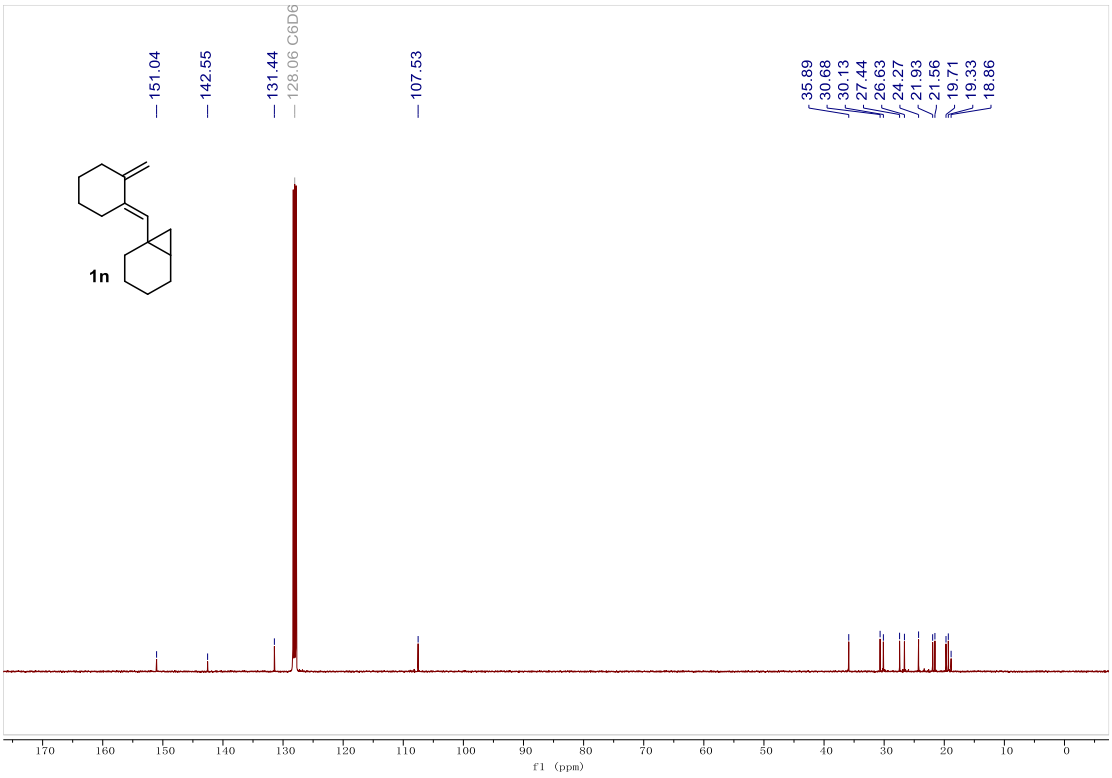
^{13}C NMR in $CDCl_3$, 101 MHz



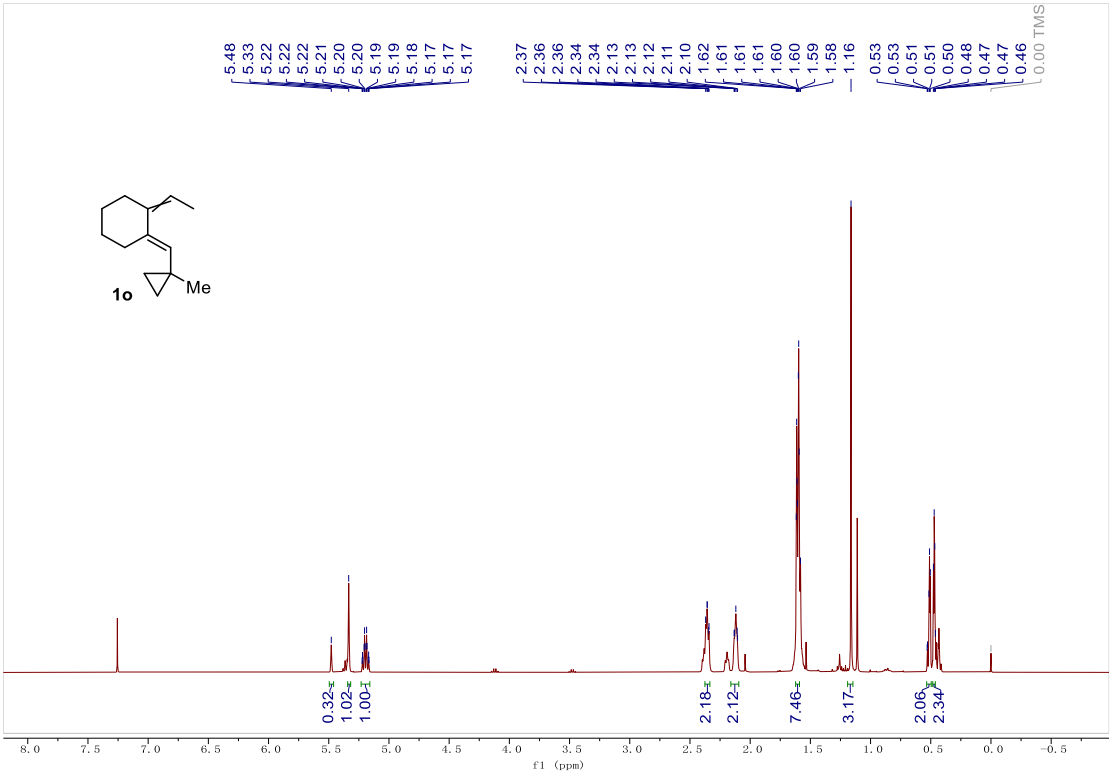
^{1}H NMR in C_6D_6, 400 MHz



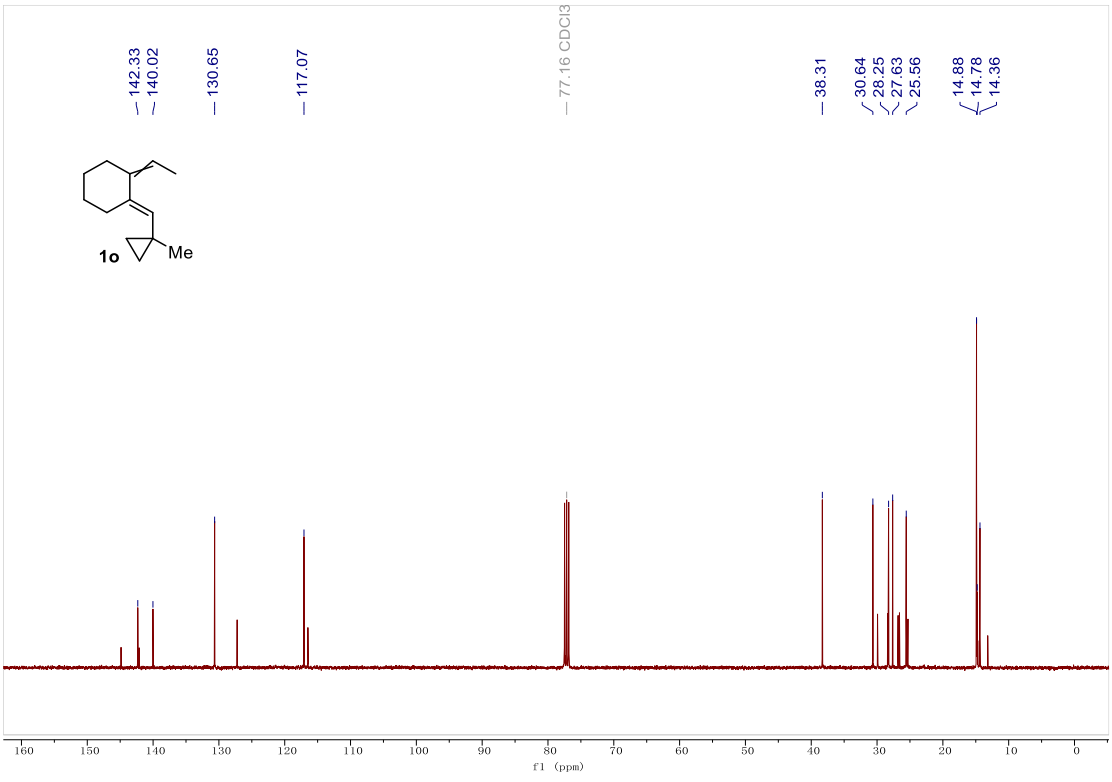
^{13}C NMR in C_6D_6, 101 MHz



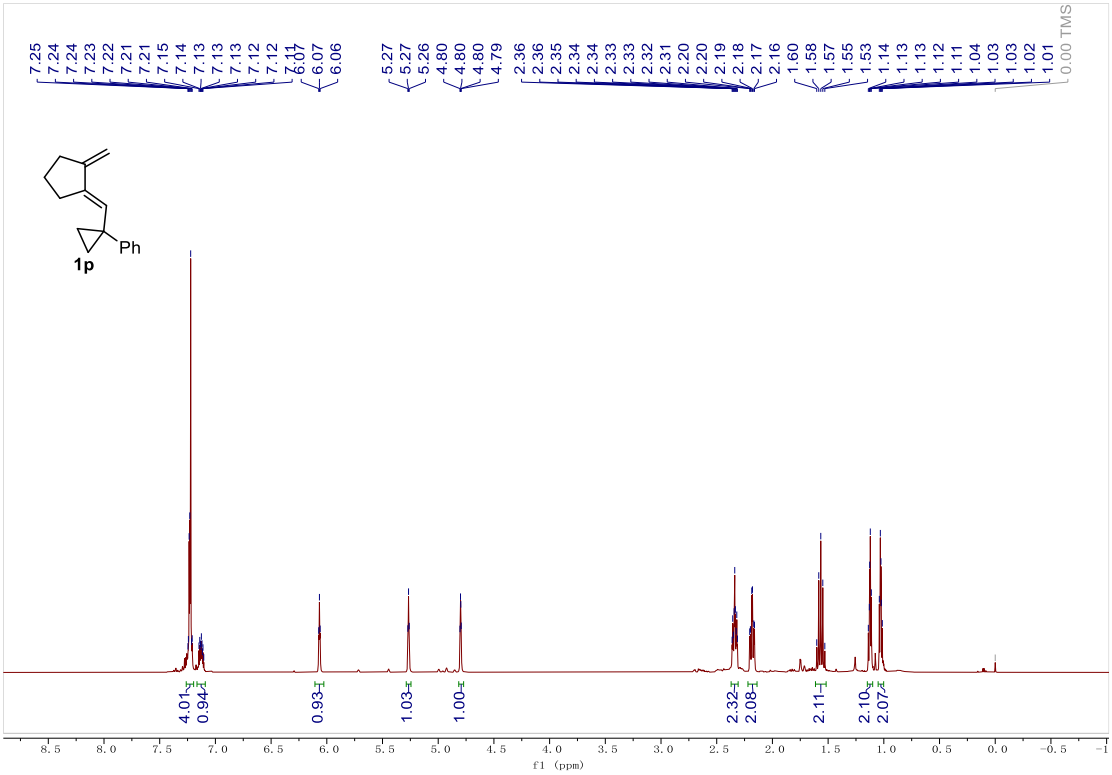
^{1}H NMR in $CDCl_3$, 400 MHz



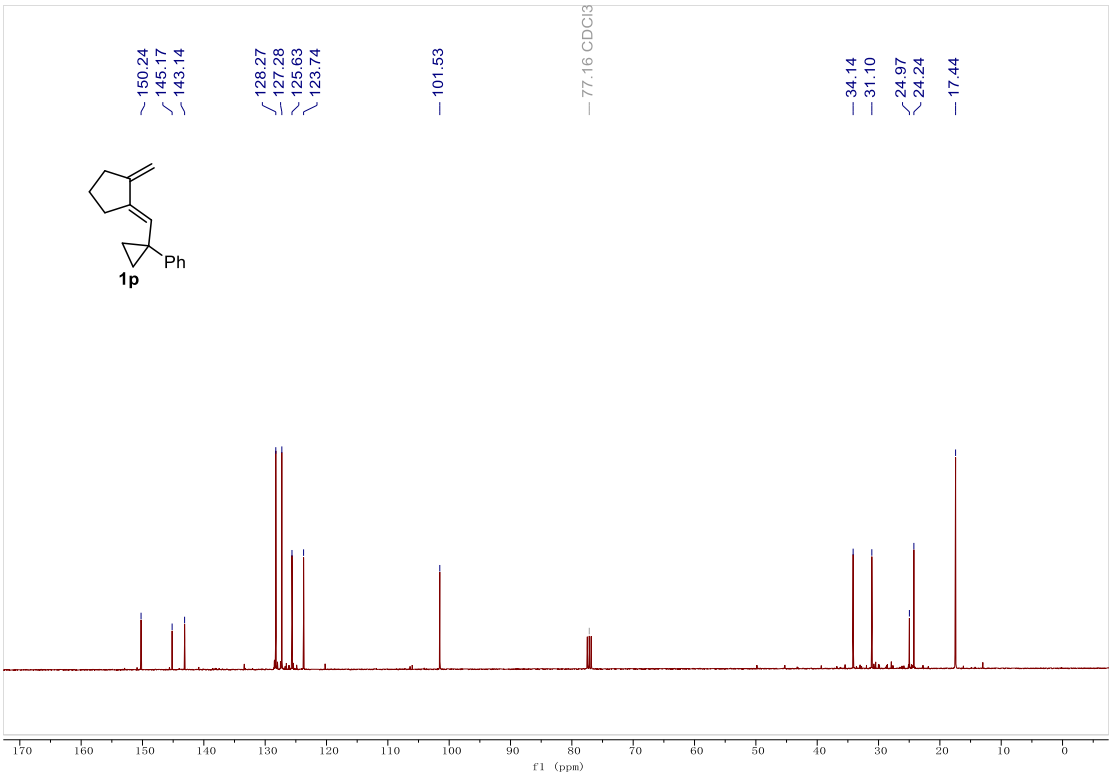
^{13}C NMR in $CDCl_3$, 101 MHz



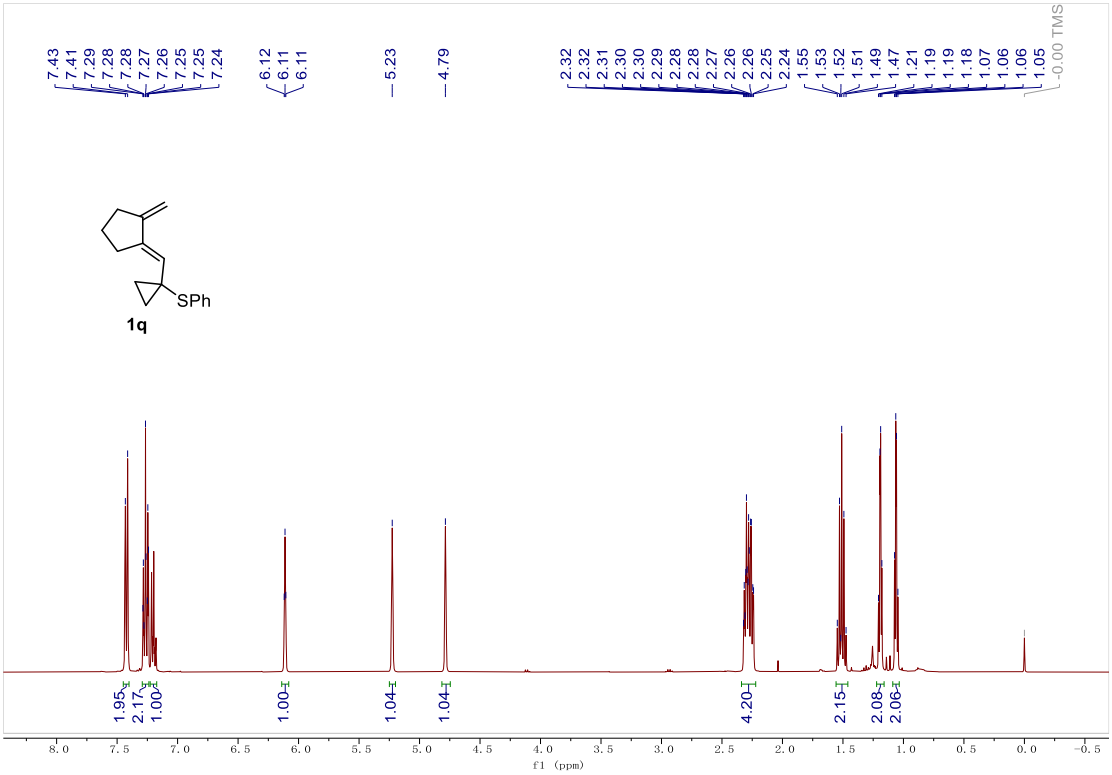
^{1}H NMR in $CDCl_3$, 400 MHz



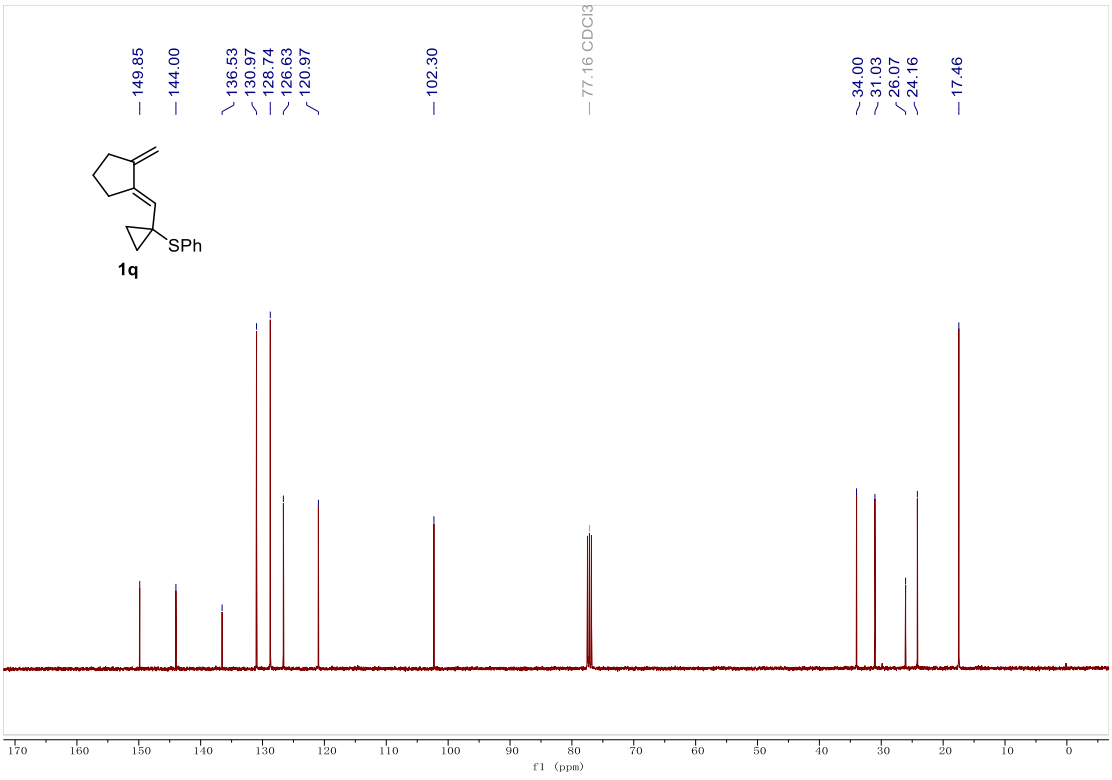
^{13}C NMR in $CDCl_3$, 101 MHz



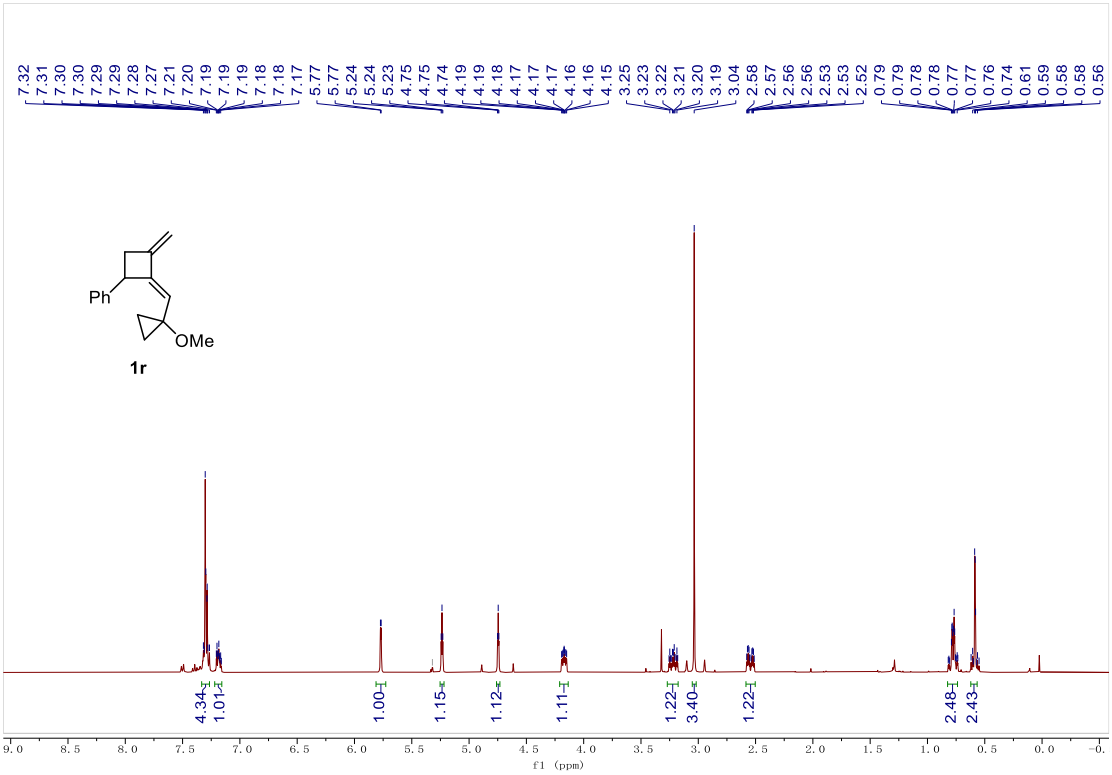
^{1}H NMR in $CDCl_3$, 400 MHz



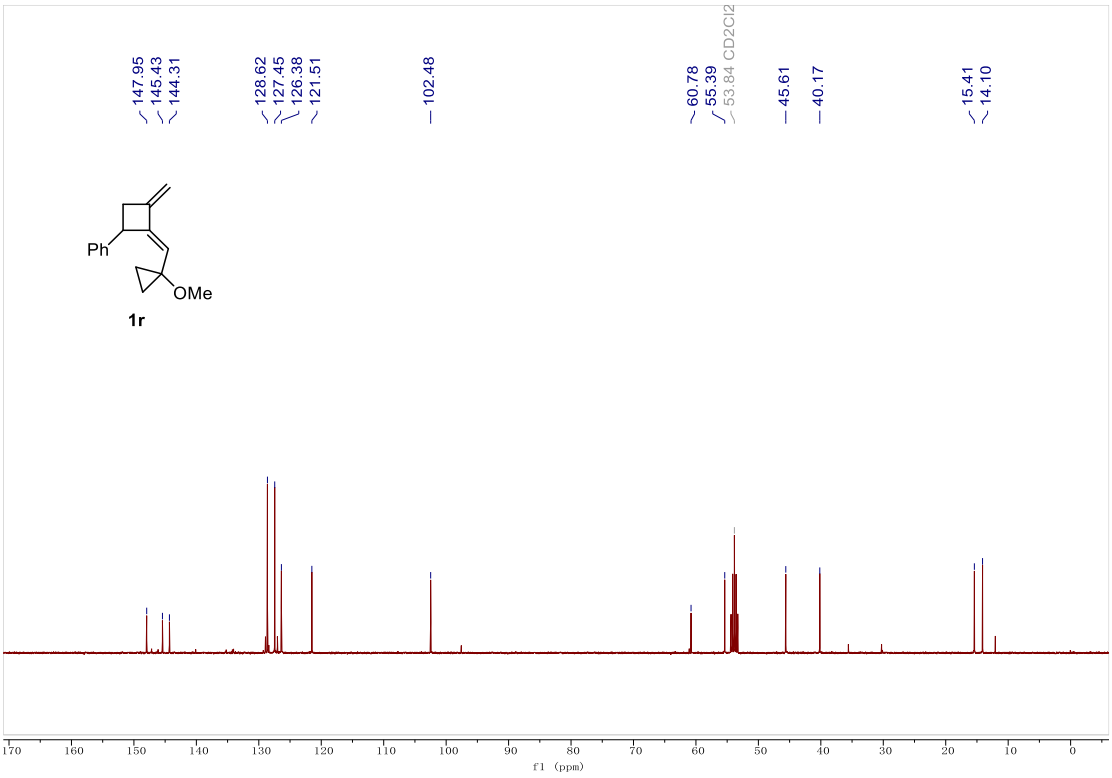
^{13}C NMR in $CDCl_3$, 101 MHz



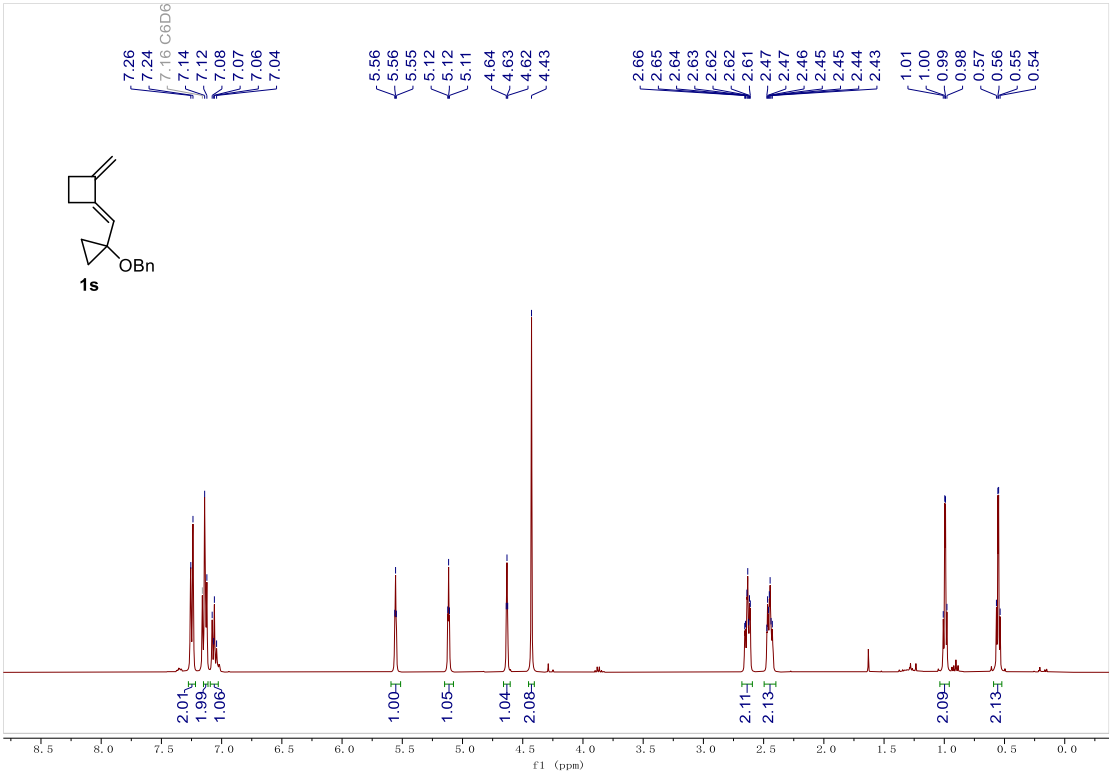
^{1}H NMR in CD_2Cl_2, 400 MHz



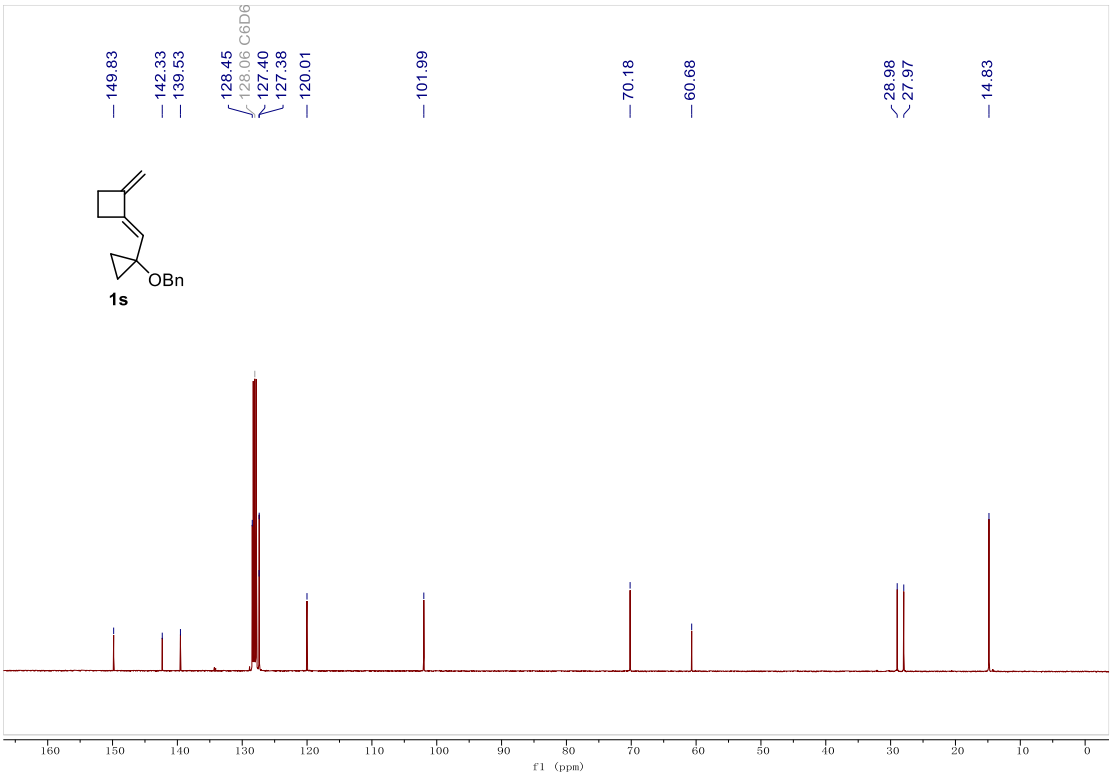
^{13}C NMR in CD_2Cl_2, 101 MHz



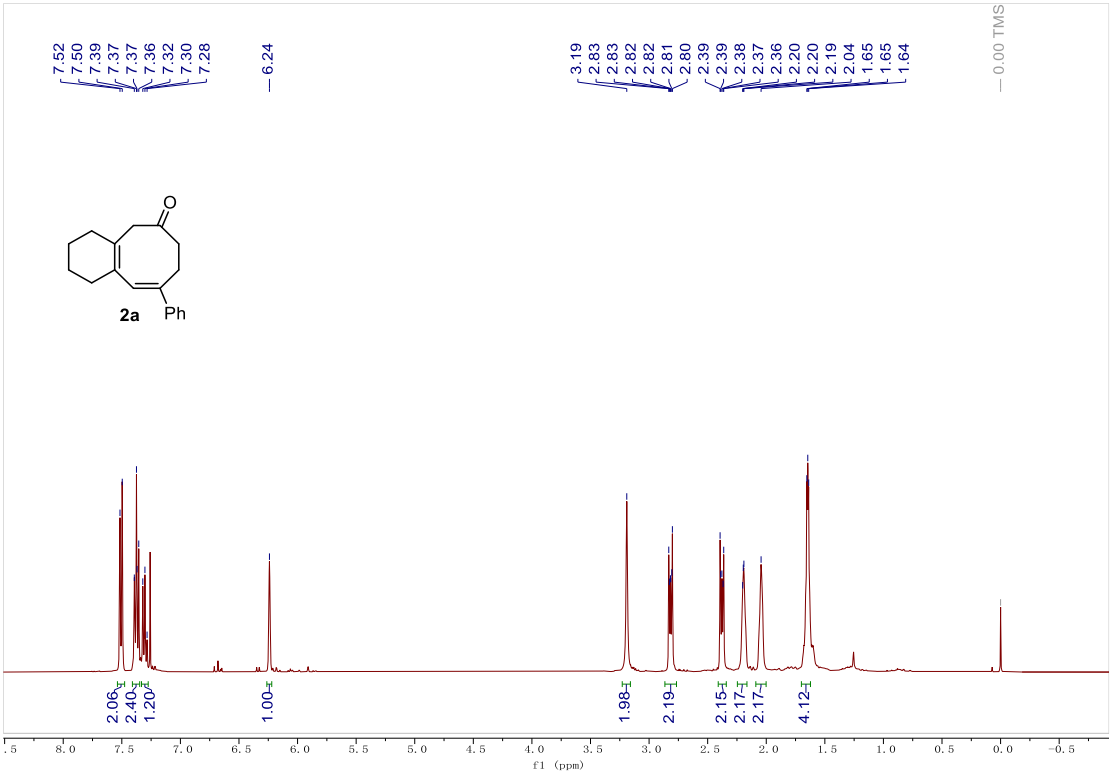
^{1}H NMR in C_6D_6, 400 MHz



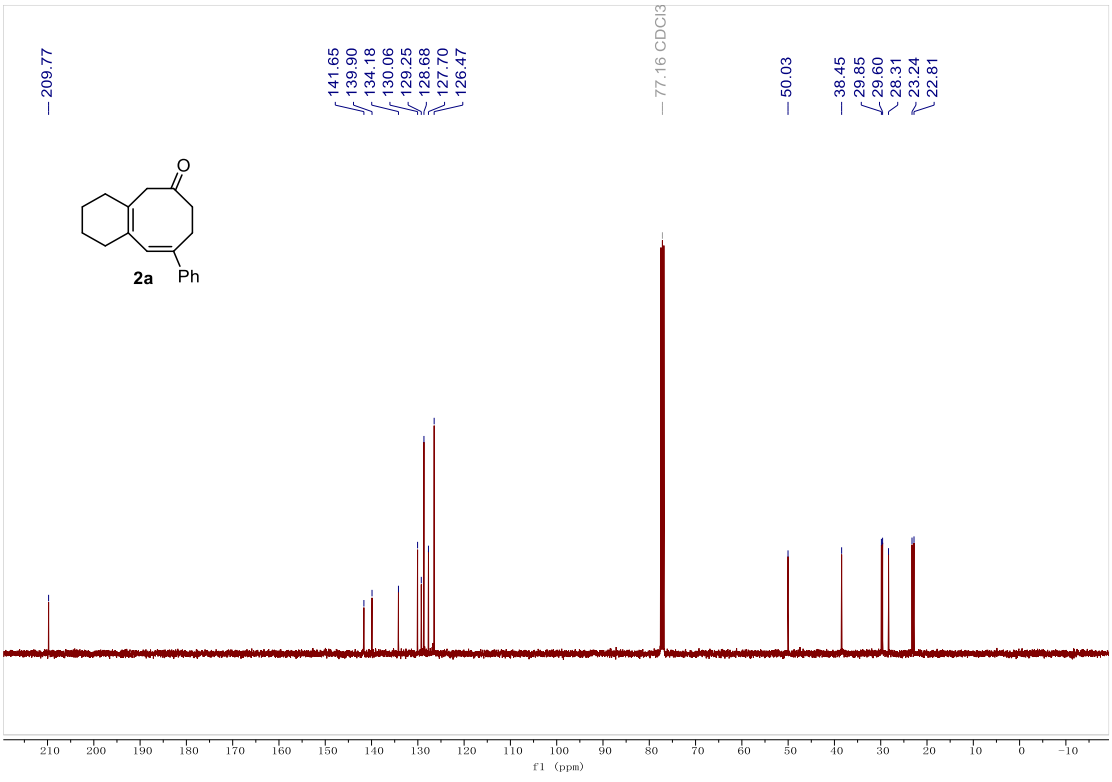
^{13}C NMR in C_6D_6, 101 MHz



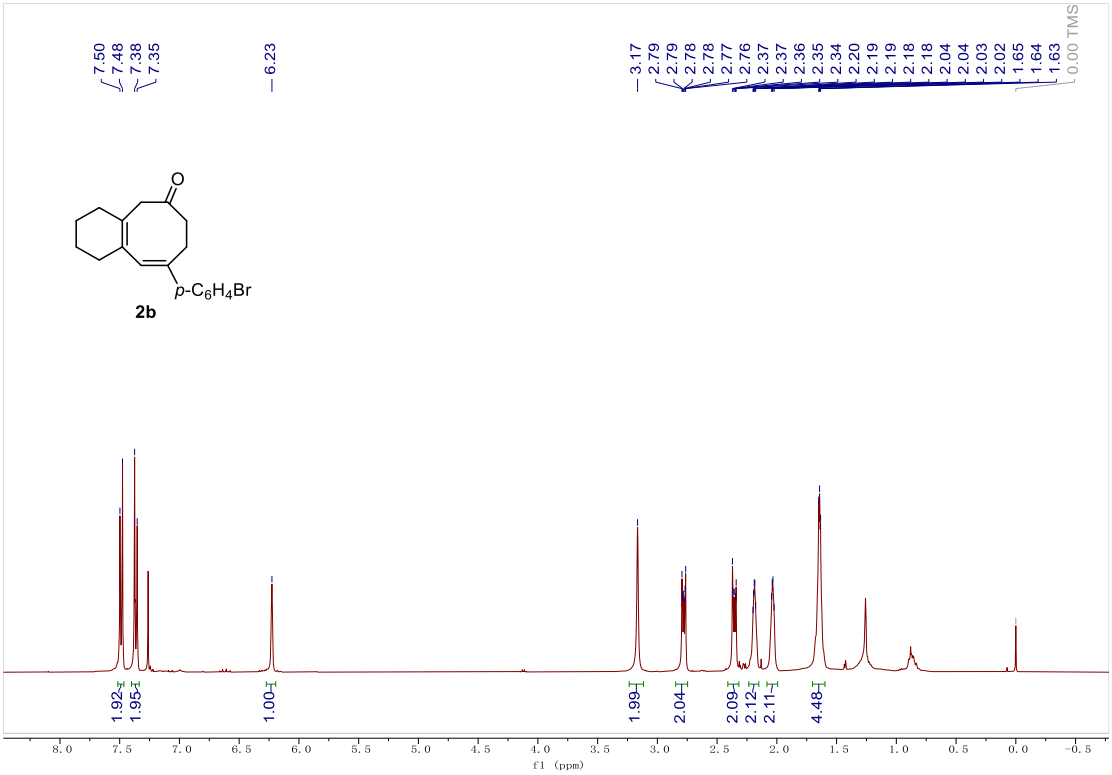
^{1}H NMR in $CDCl_3$, 400 MHz



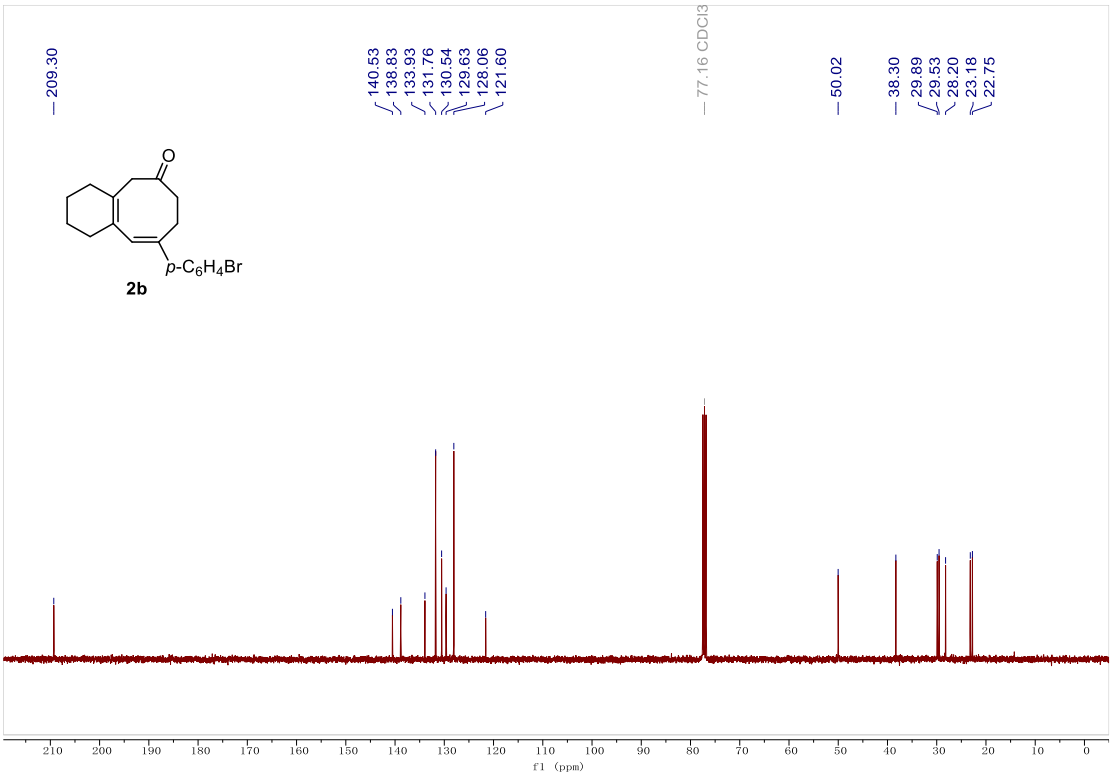
^{13}C NMR in $CDCl_3$, 101 MHz



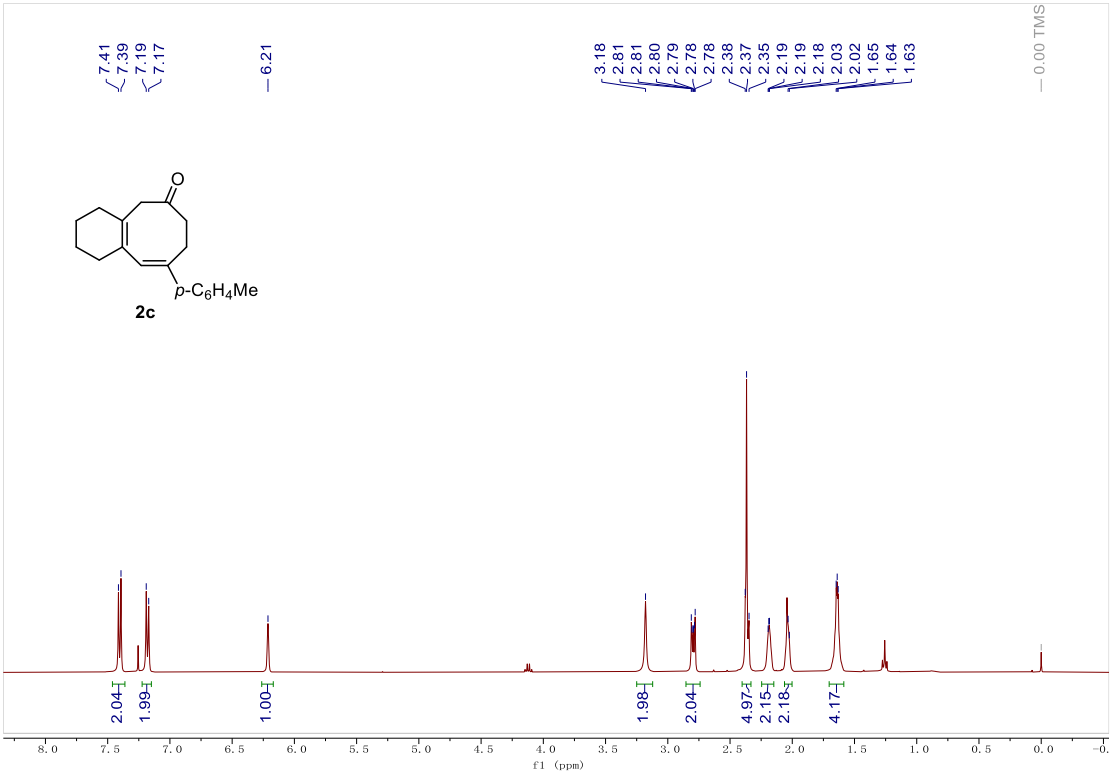
^{1}H NMR in $CDCl_3$, 400 MHz



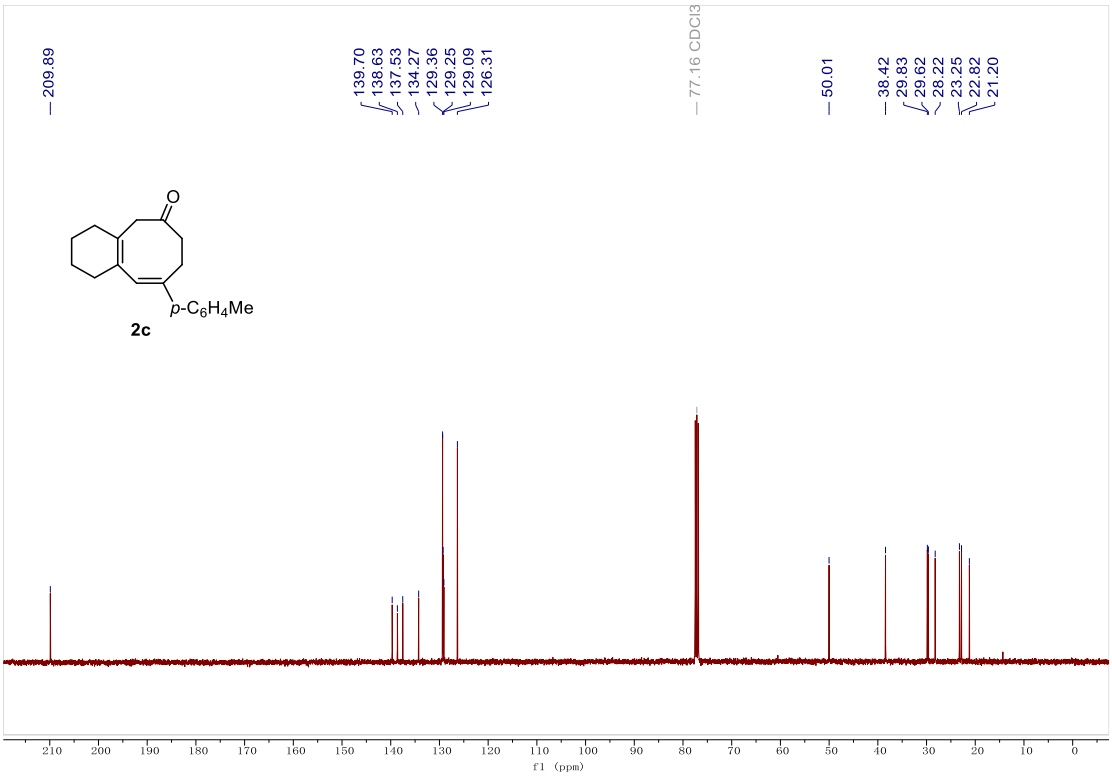
^{13}C NMR in $CDCl_3$, 101 MHz



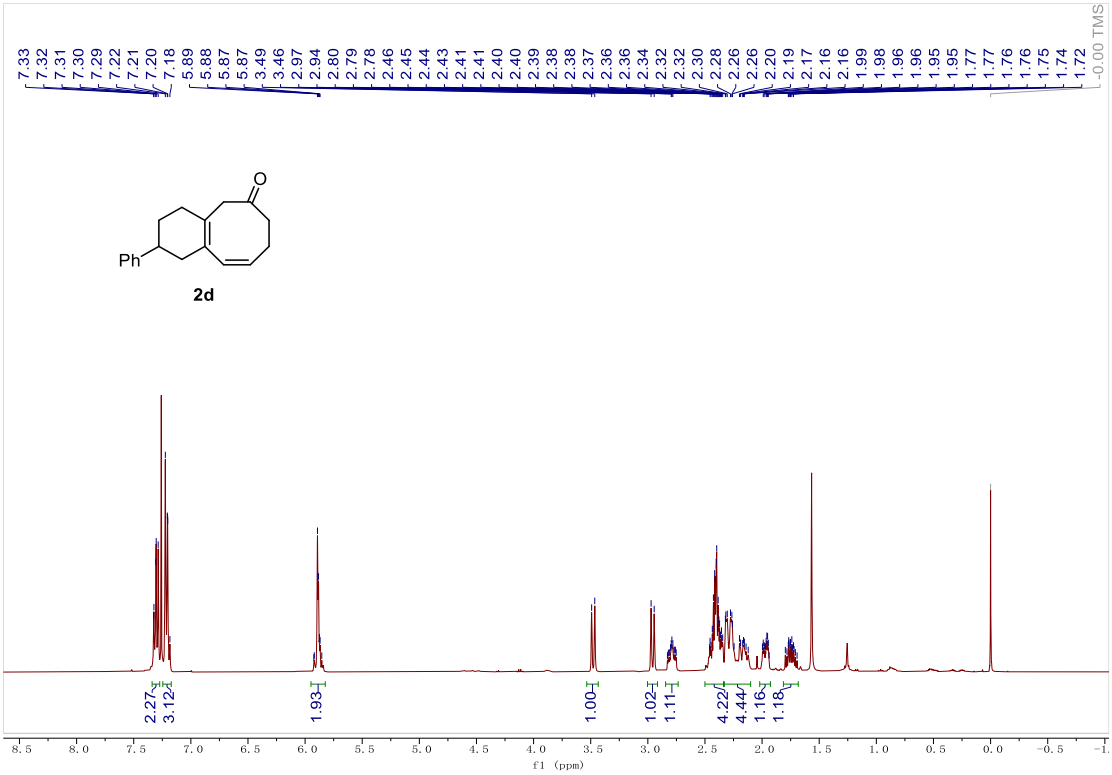
^{1}H NMR in $CDCl_3$, 400 MHz



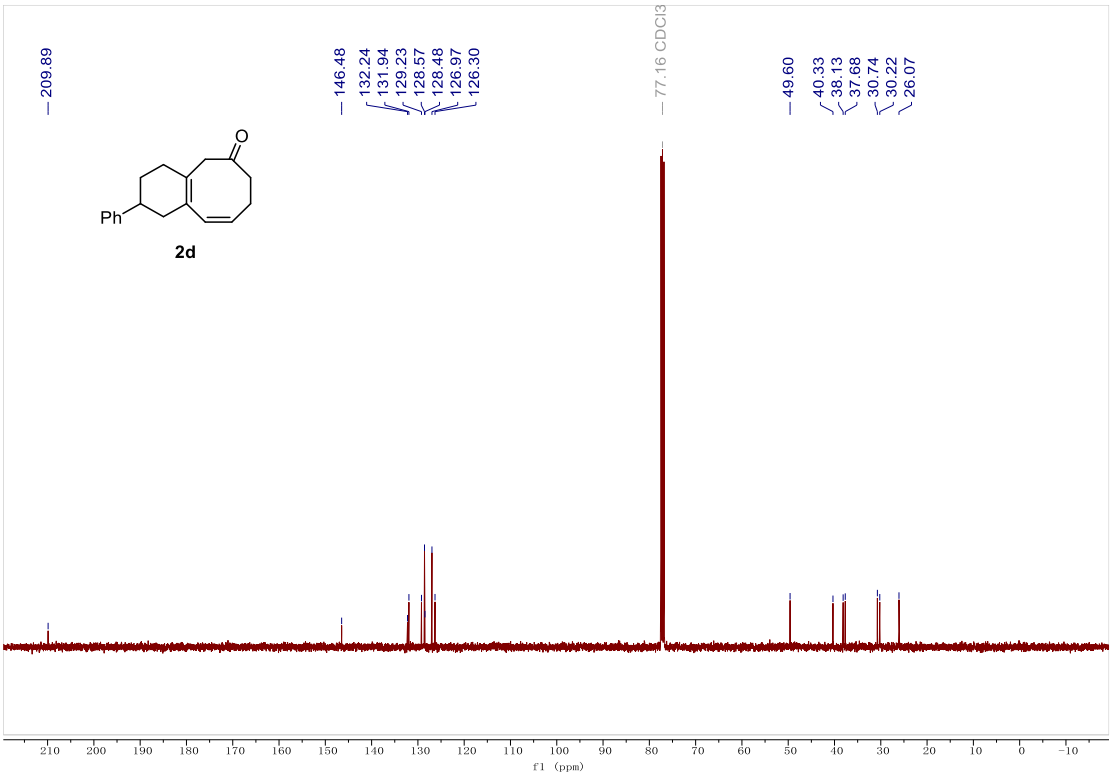
^{13}C NMR in $CDCl_3$, 101 MHz



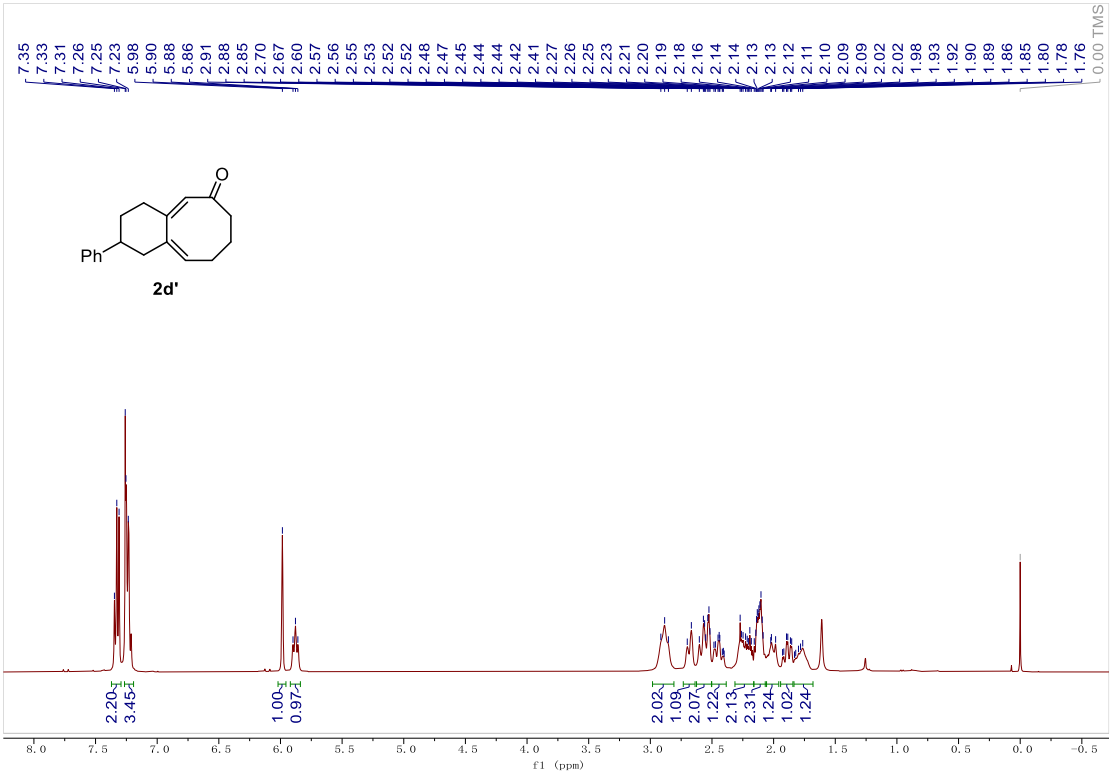
^{1}H NMR in $CDCl_3$, 400 MHz



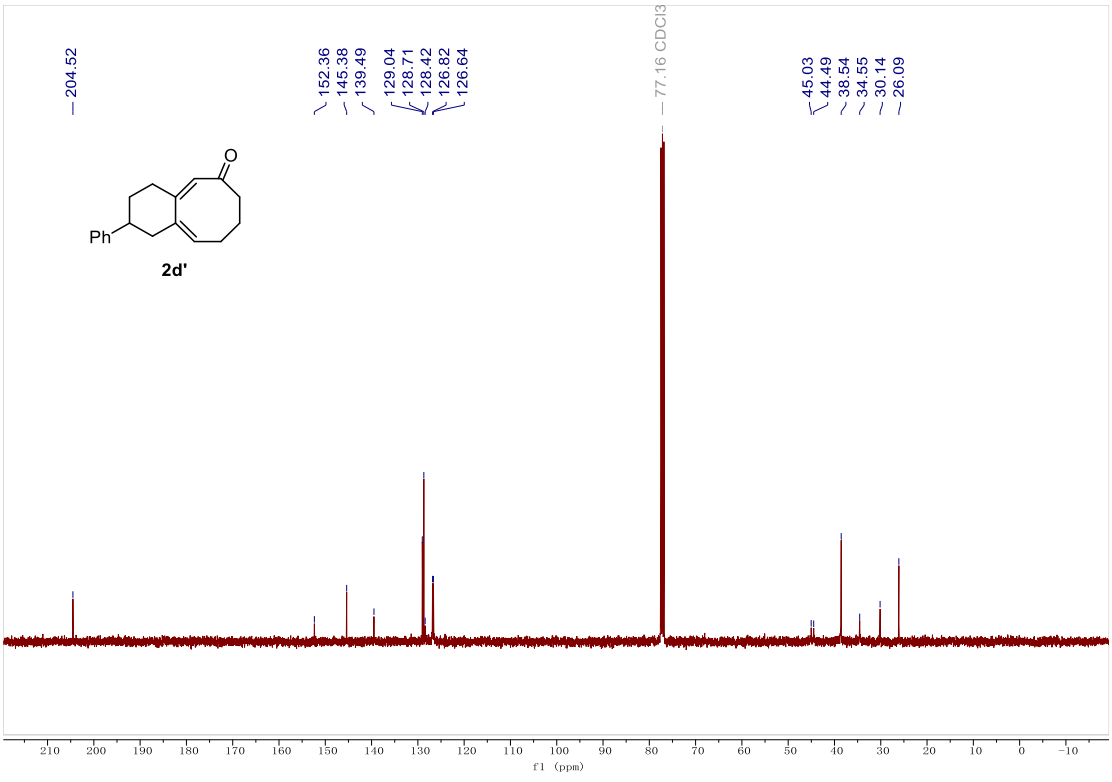
^{13}C NMR in $CDCl_3$, 101 MHz



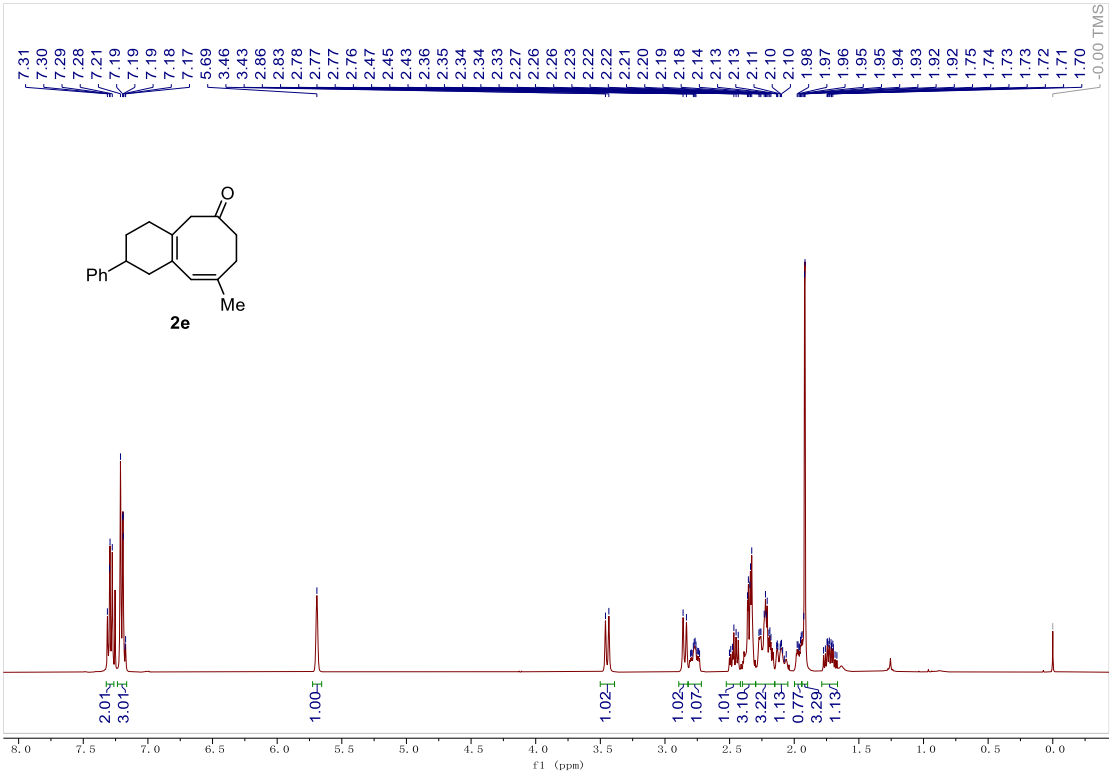
^{1}H NMR in $CDCl_3$, 400 MHz



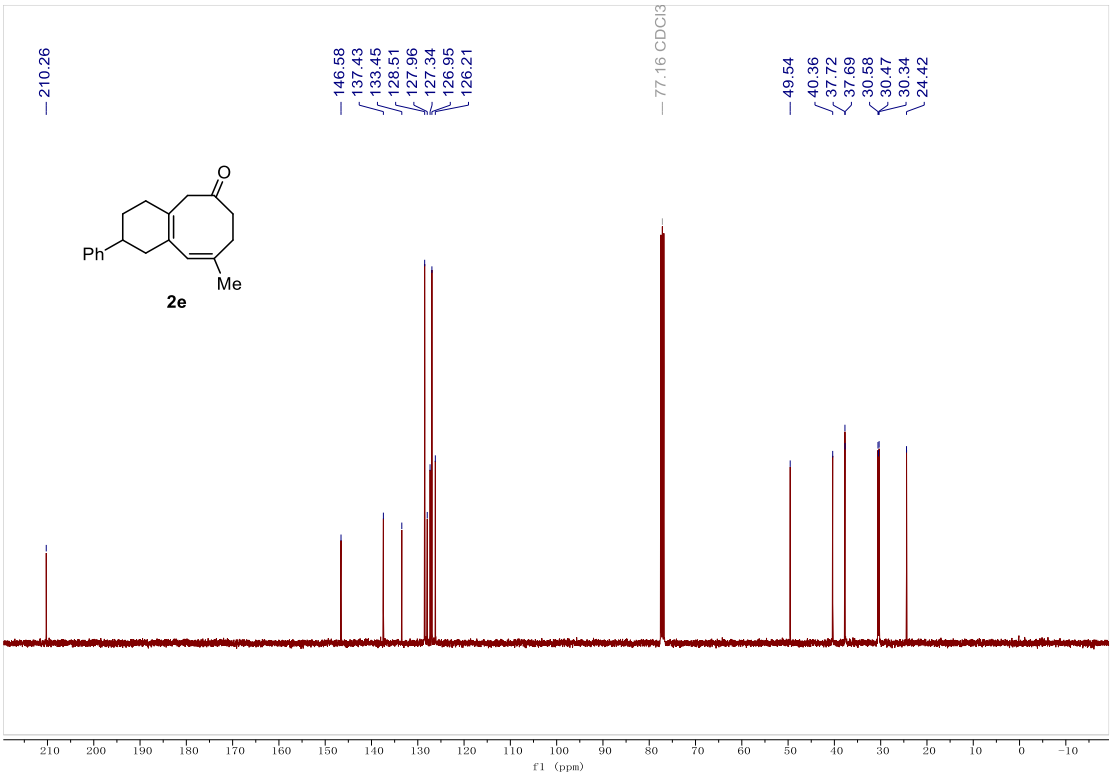
^{13}C NMR in $CDCl_3$, 101 MHz



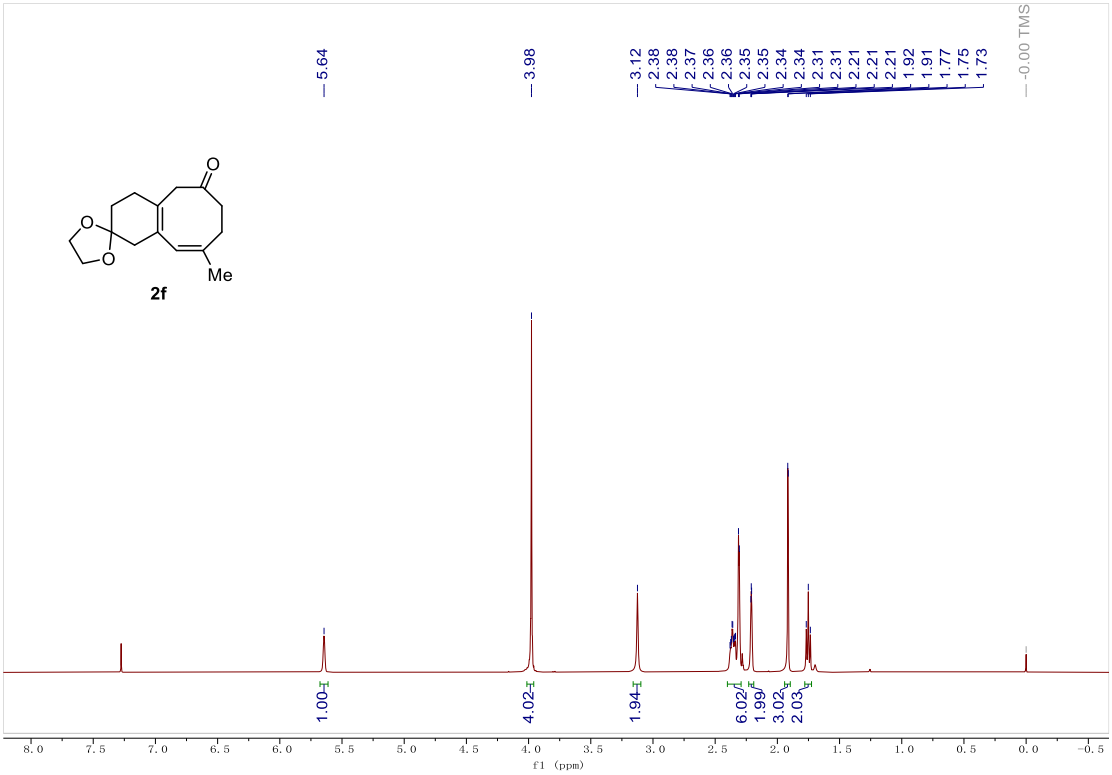
^{1}H NMR in $CDCl_3$, 400 MHz



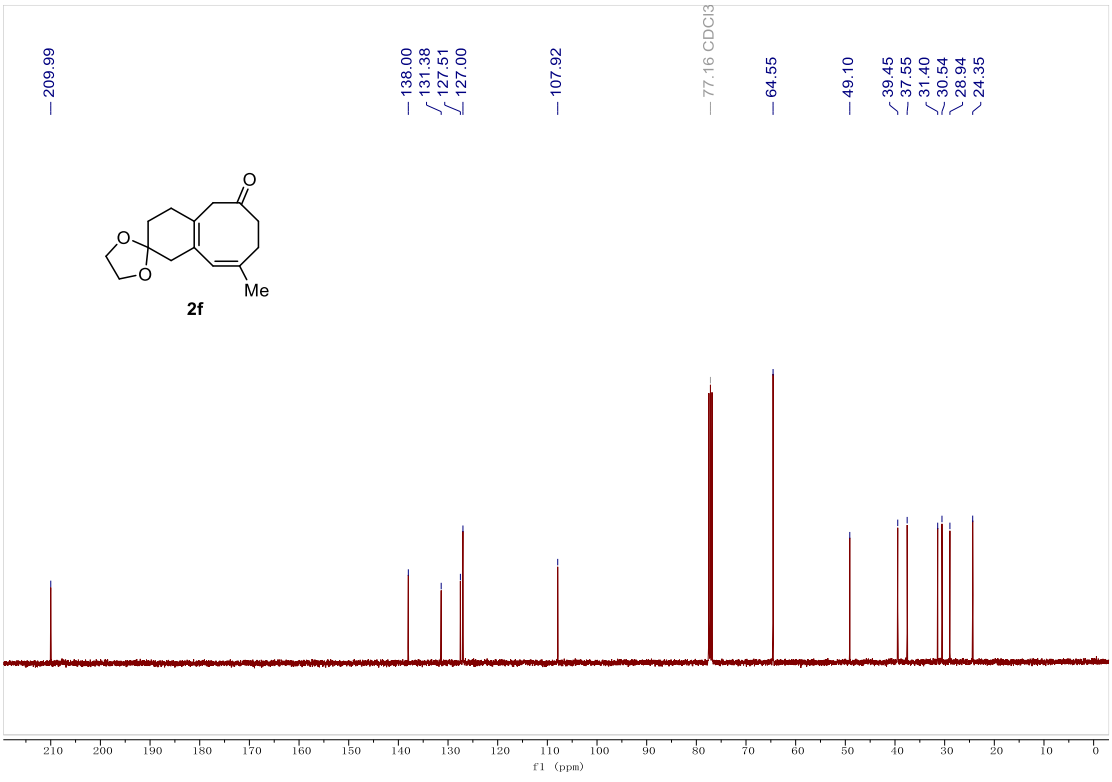
^{13}C NMR in $CDCl_3$, 101 MHz



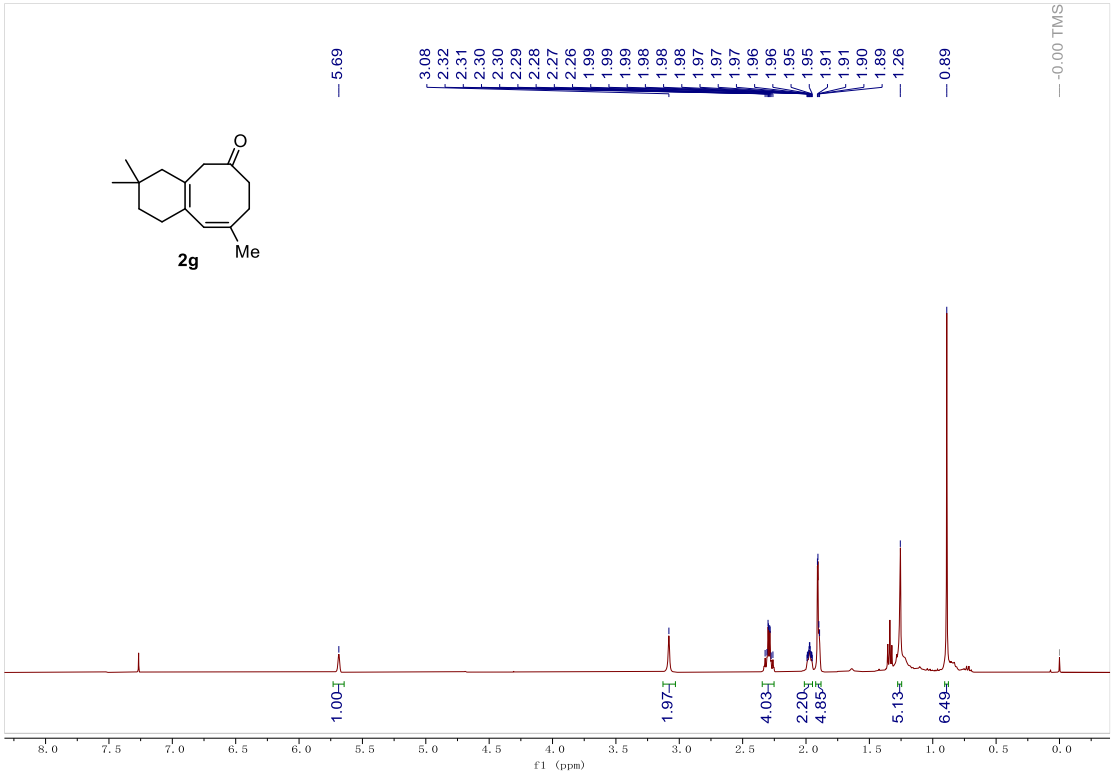
^{1}H NMR in $CDCl_3$, 400 MHz



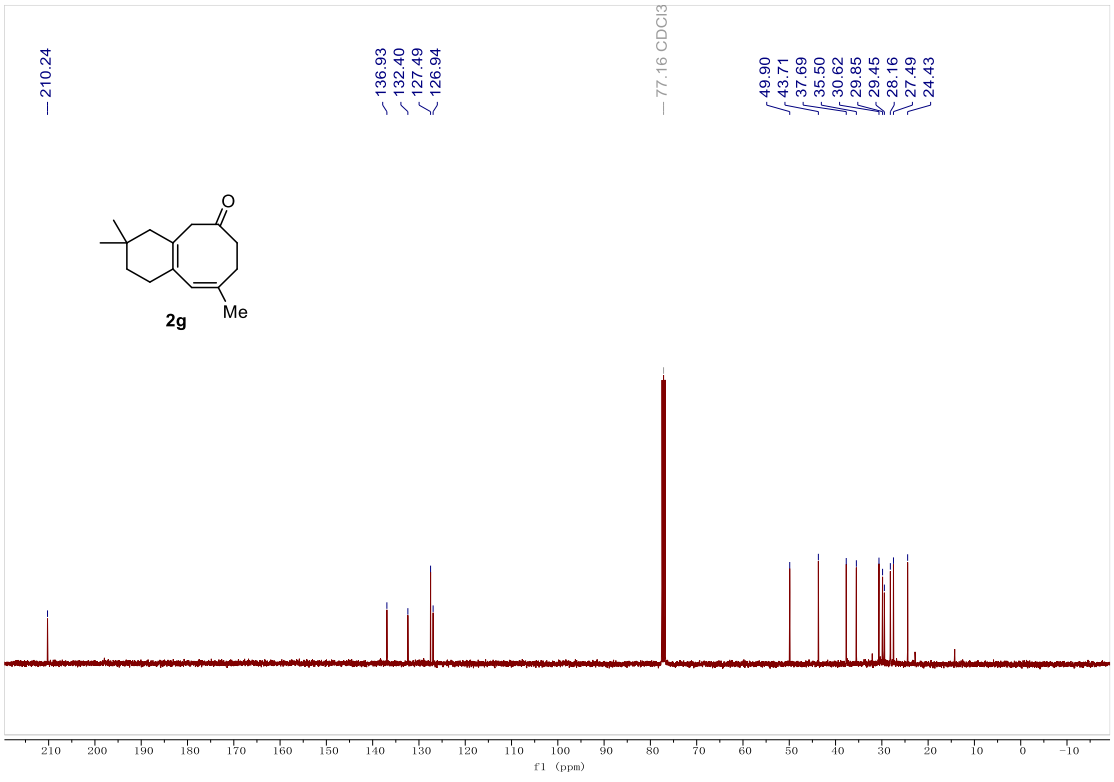
^{13}C NMR in $CDCl_3$, 101 MHz



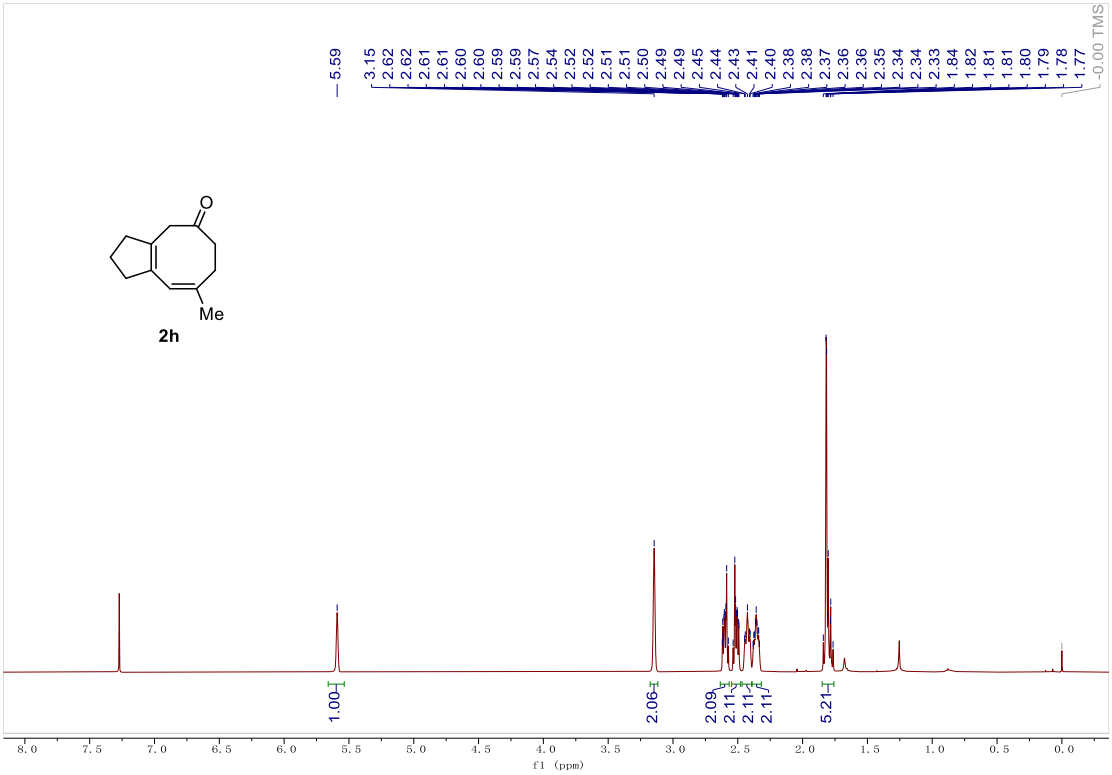
^{1}H NMR in $CDCl_3$, 400 MHz



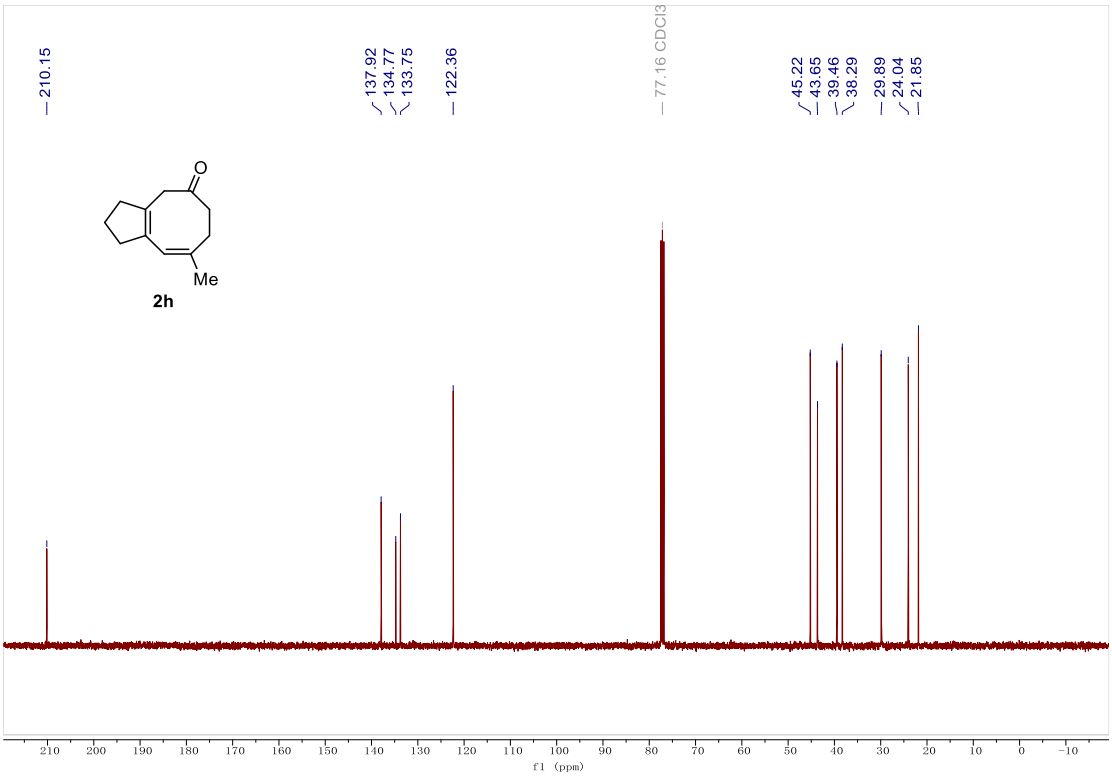
^{13}C NMR in $CDCl_3$, 101 MHz



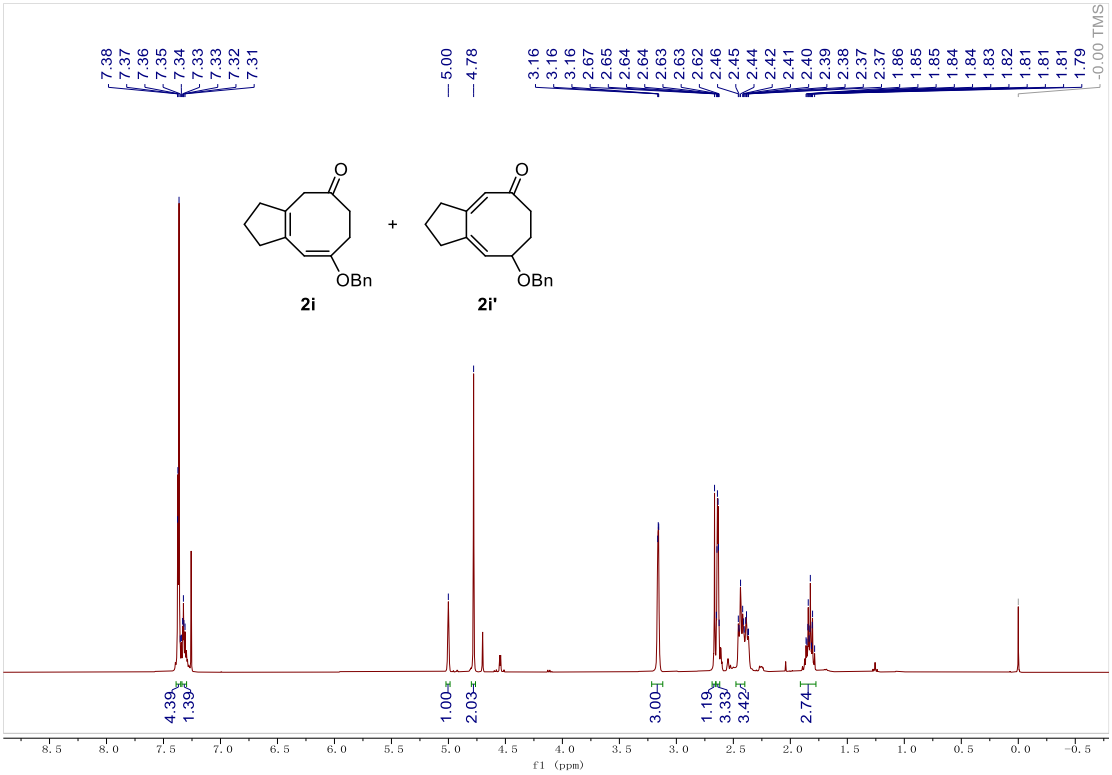
^{1}H NMR in $CDCl_3$, 400 MHz



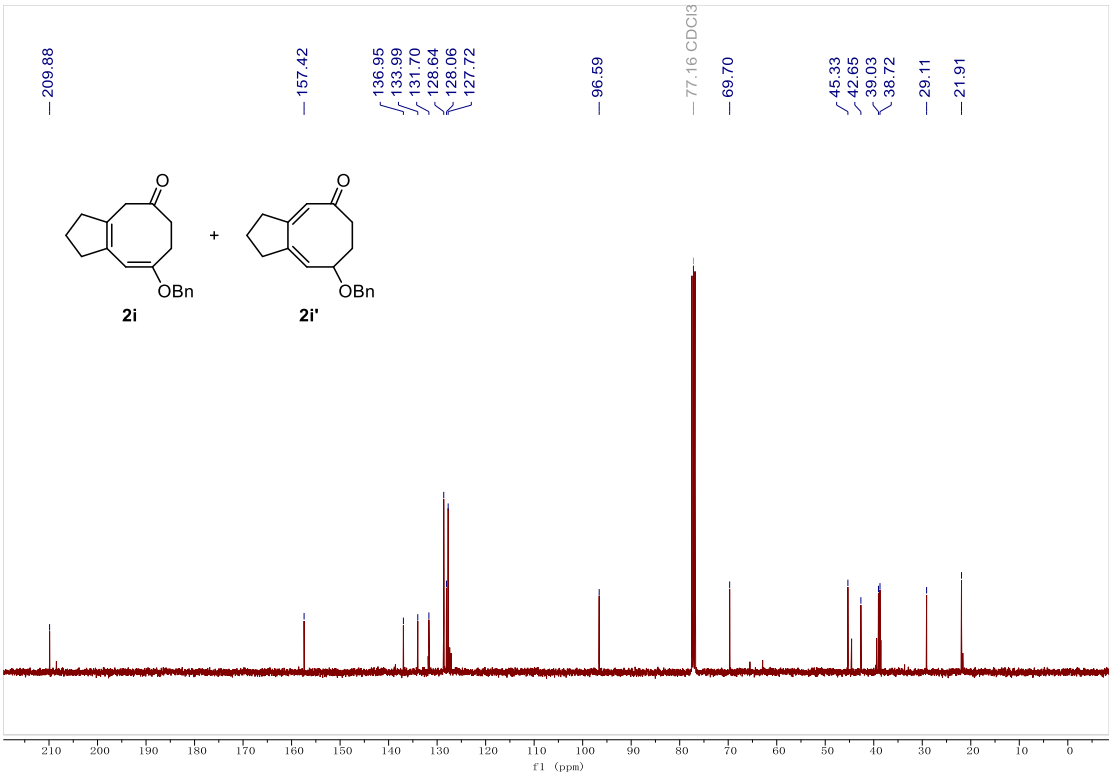
^{13}C NMR in $CDCl_3$, 101 MHz



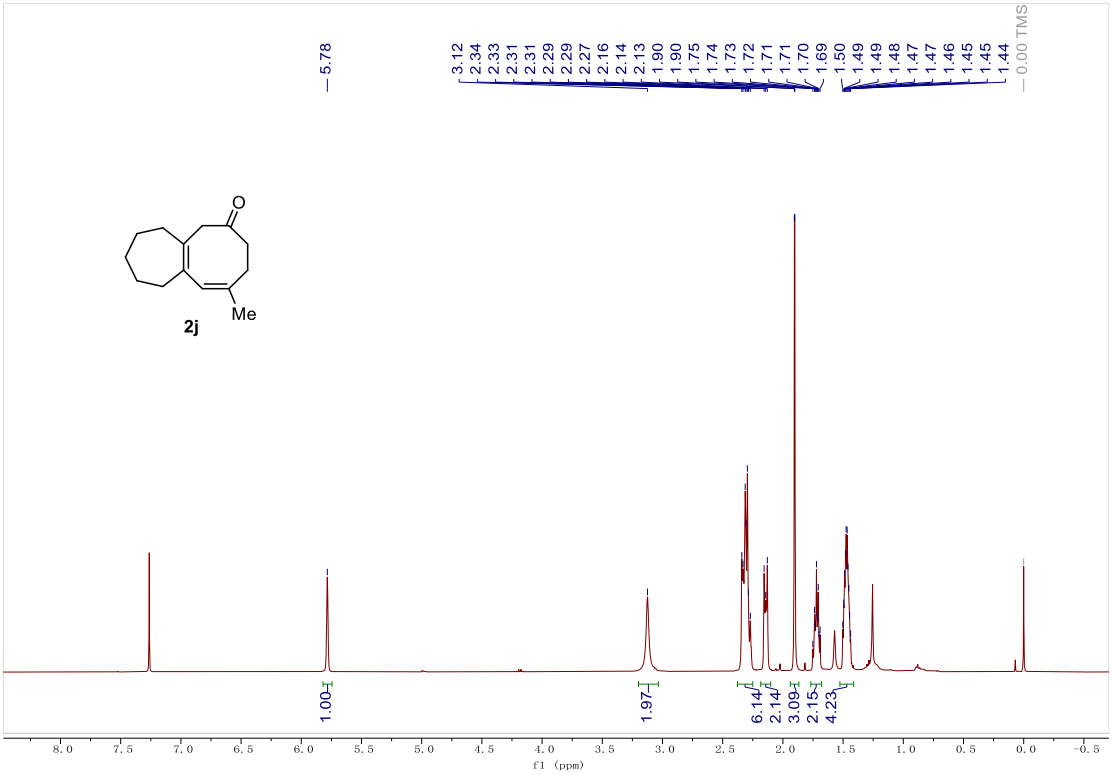
^{1}H NMR in $CDCl_3$, 400 MHz



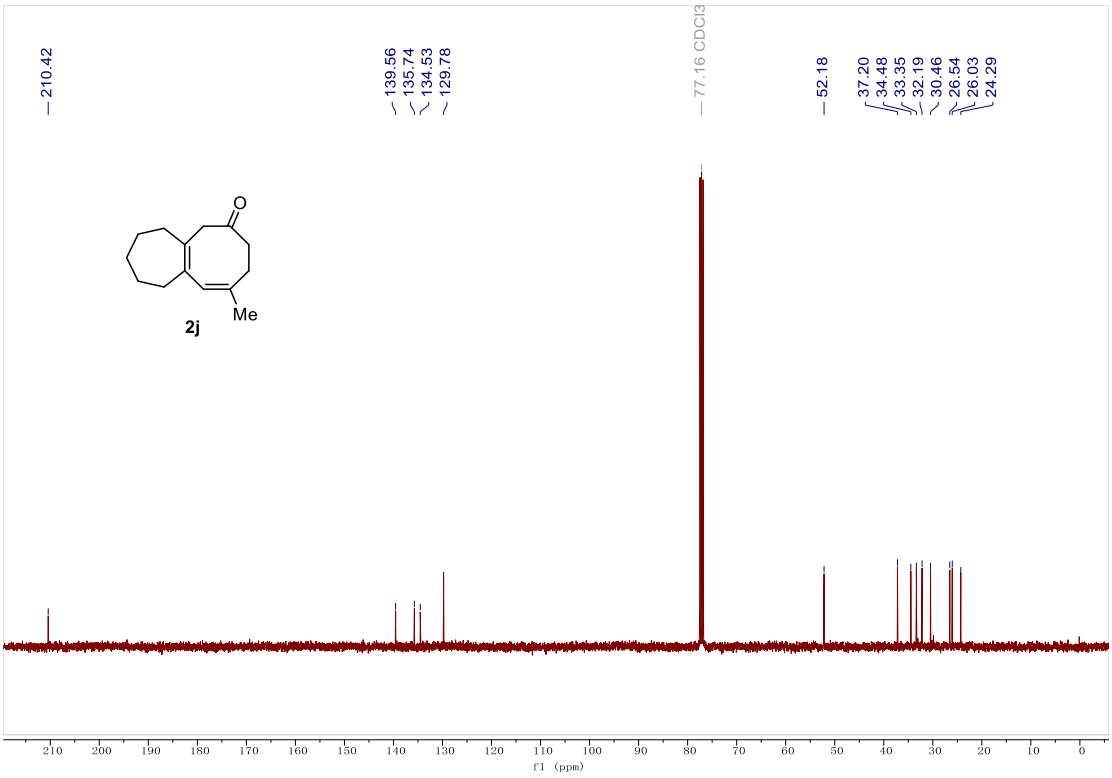
^{13}C NMR in $CDCl_3$, 101 MHz



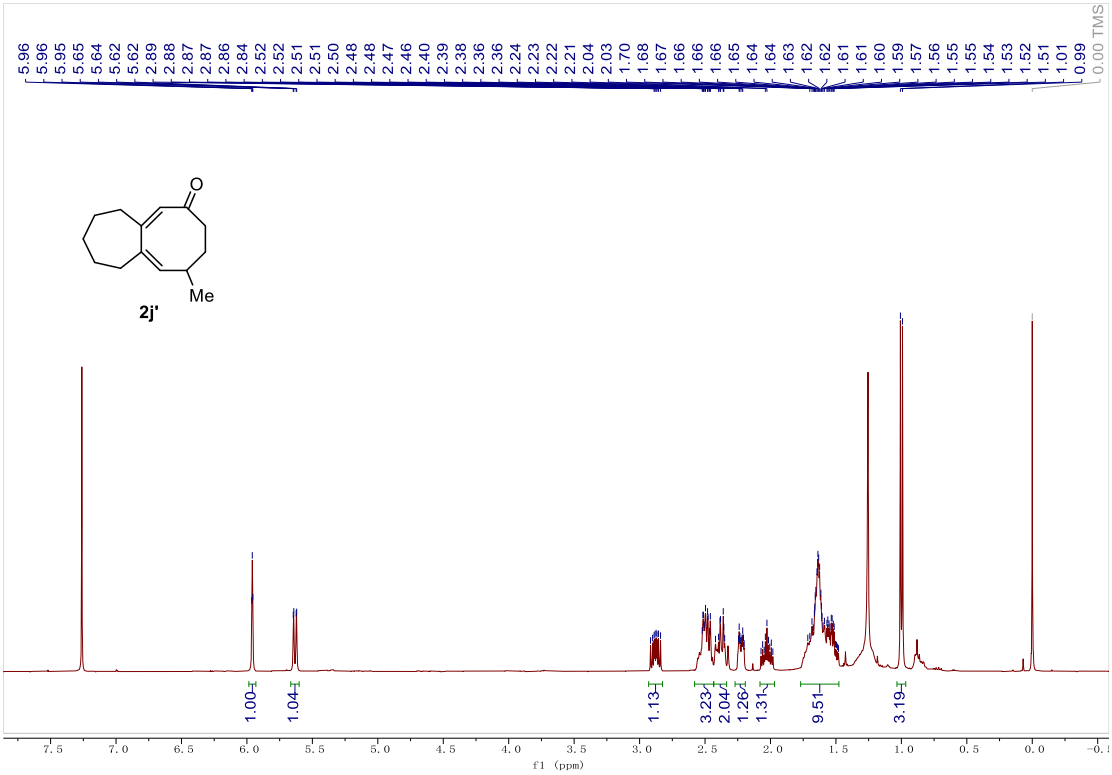
^{1}H NMR in $CDCl_3$, 400 MHz



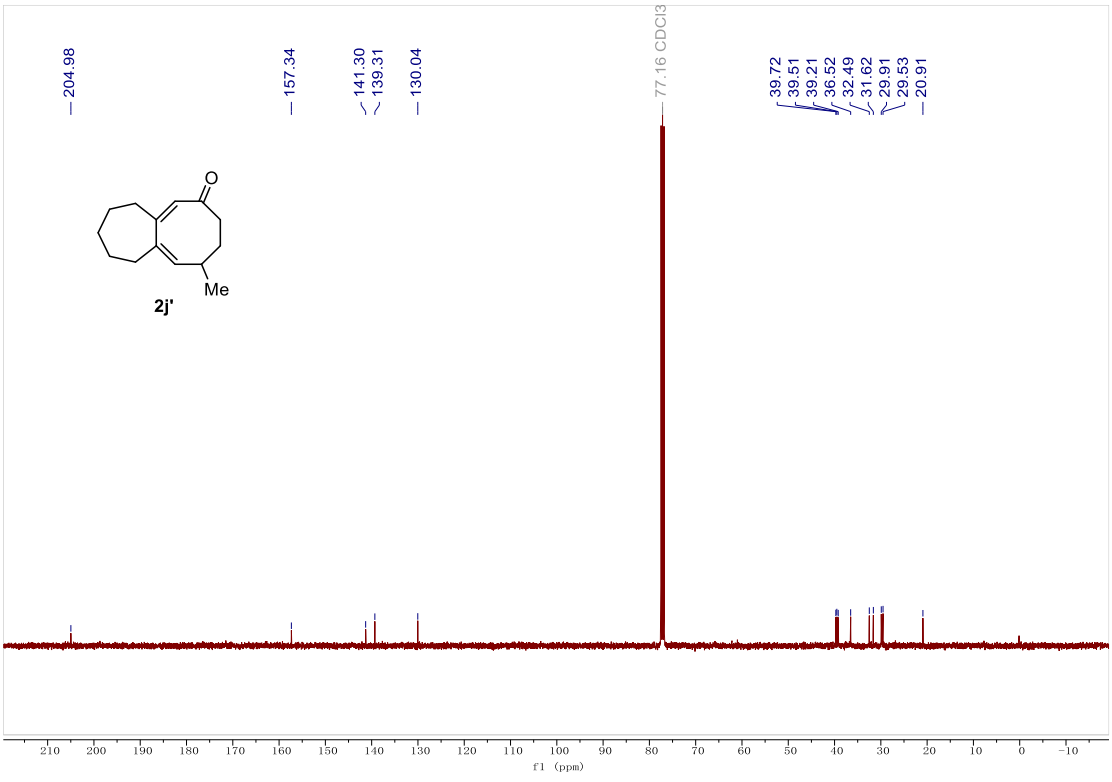
^{13}C NMR in $CDCl_3$, 101 MHz



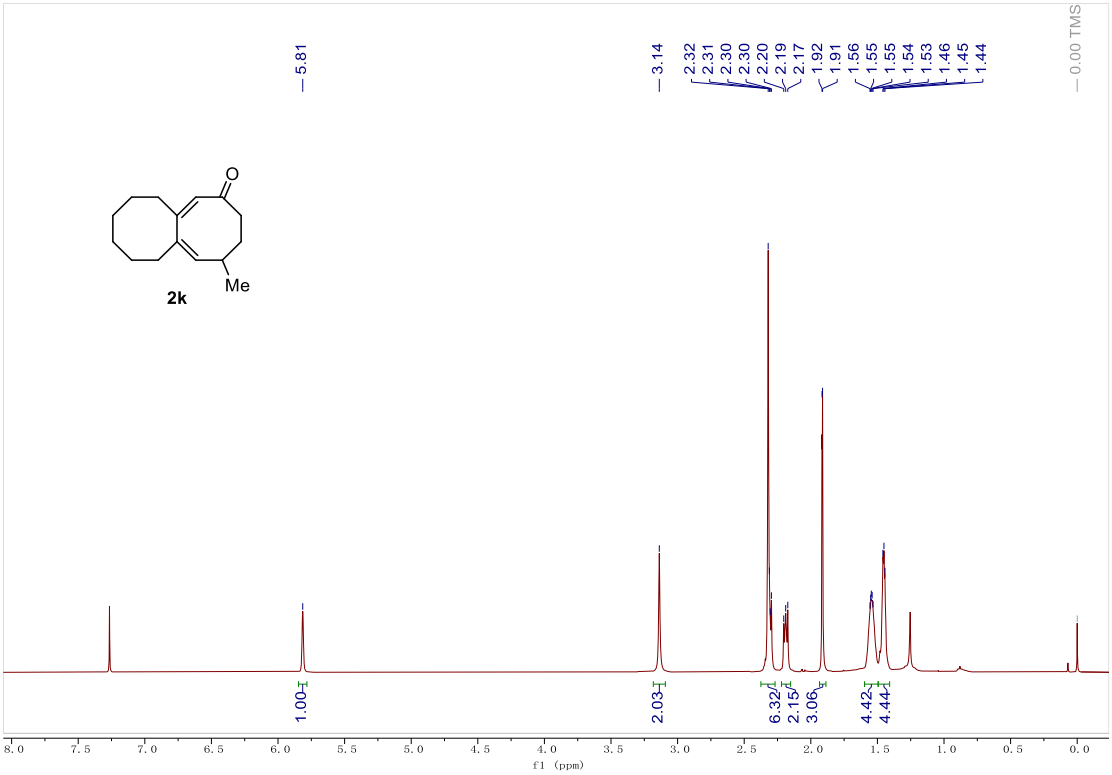
^{1}H NMR in $CDCl_3$, 400 MHz



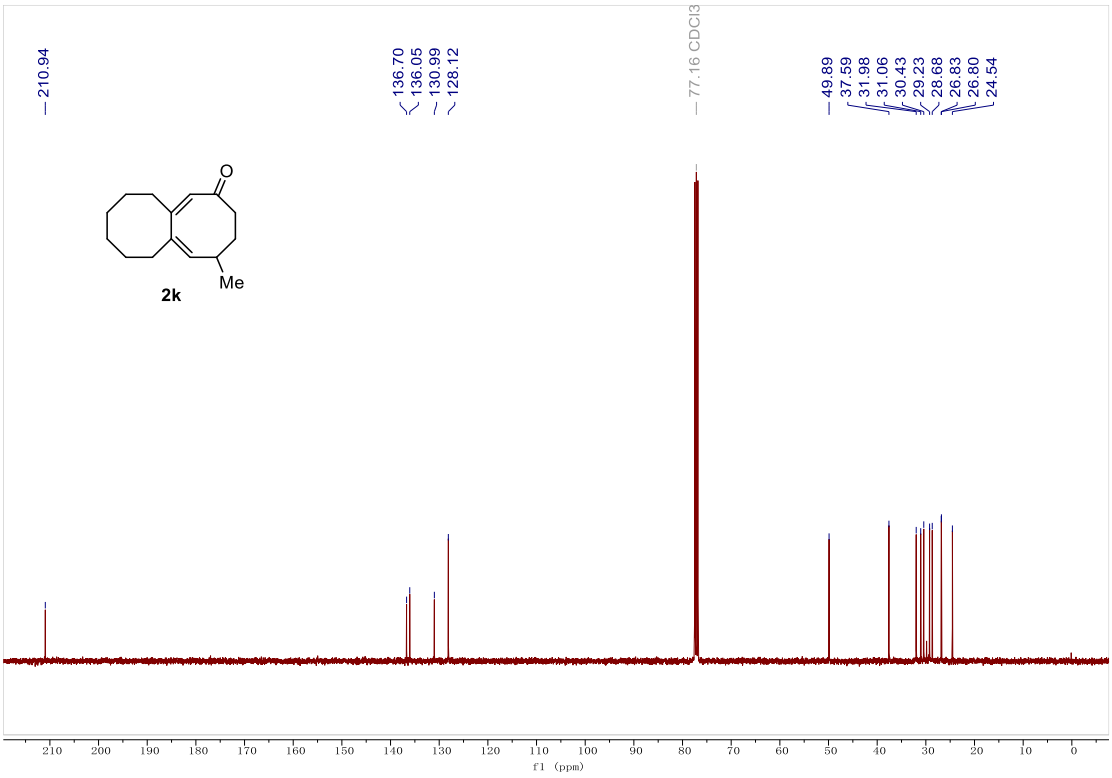
^{13}C NMR in $CDCl_3$, 101 MHz



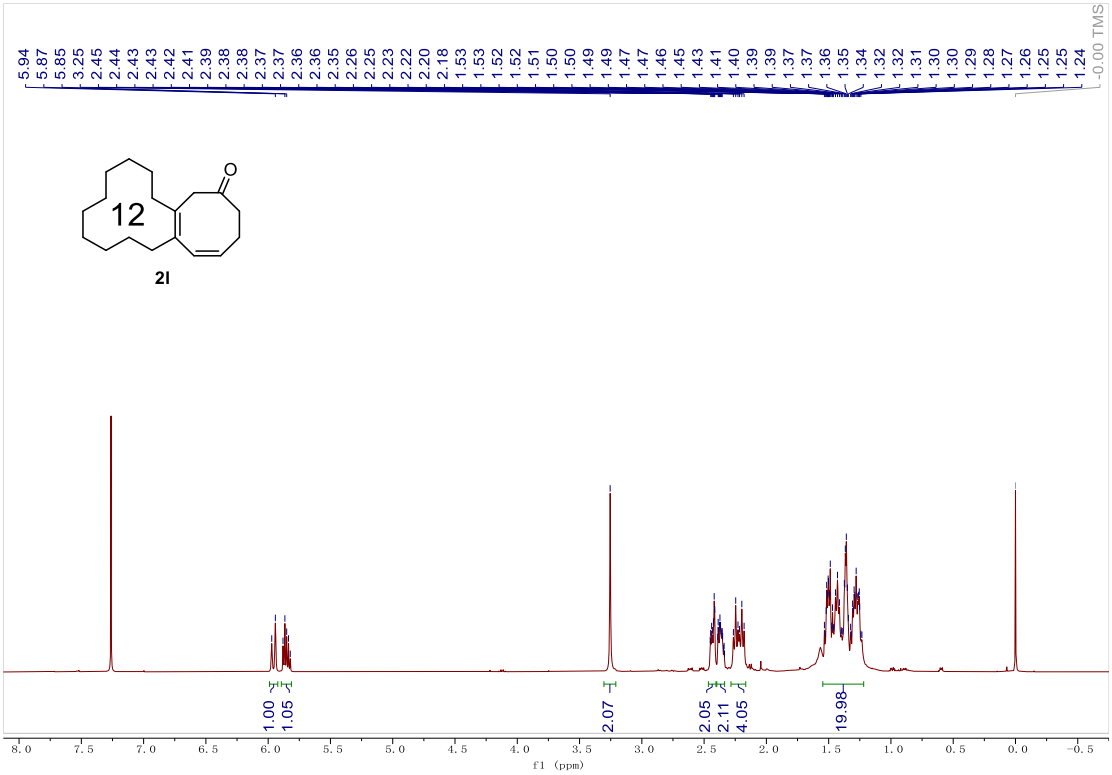
^{1}H NMR in $CDCl_3$, 400 MHz



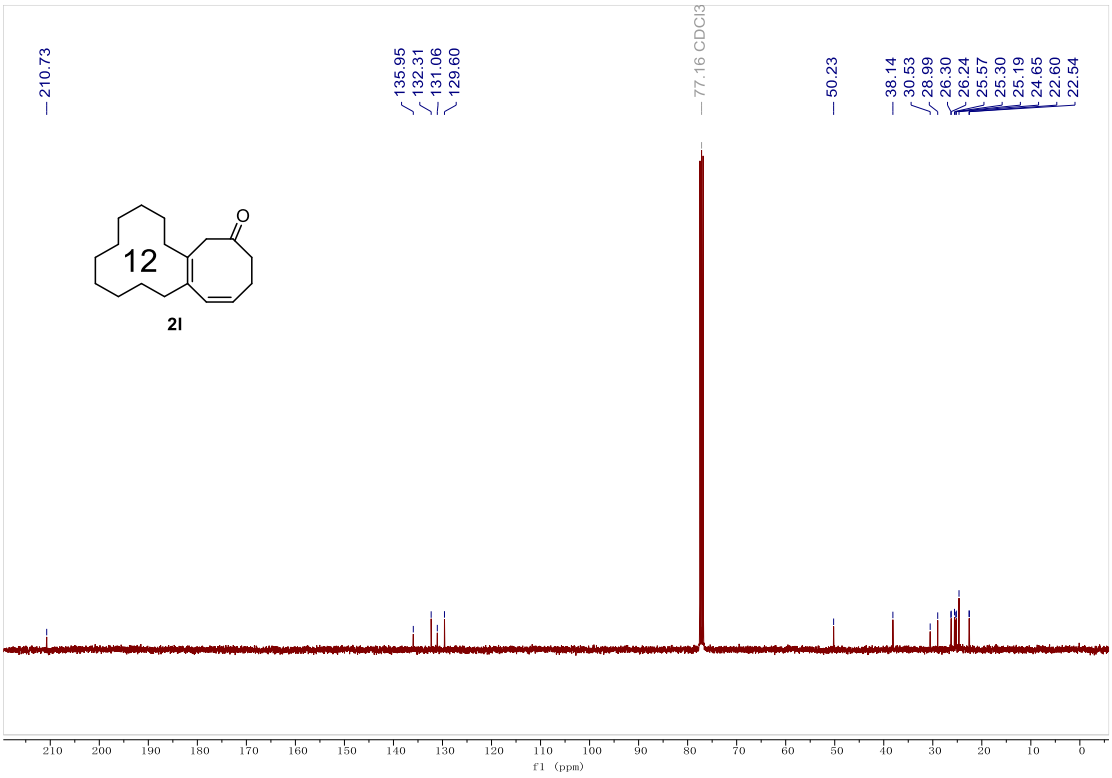
^{13}C NMR in $CDCl_3$, 101 MHz



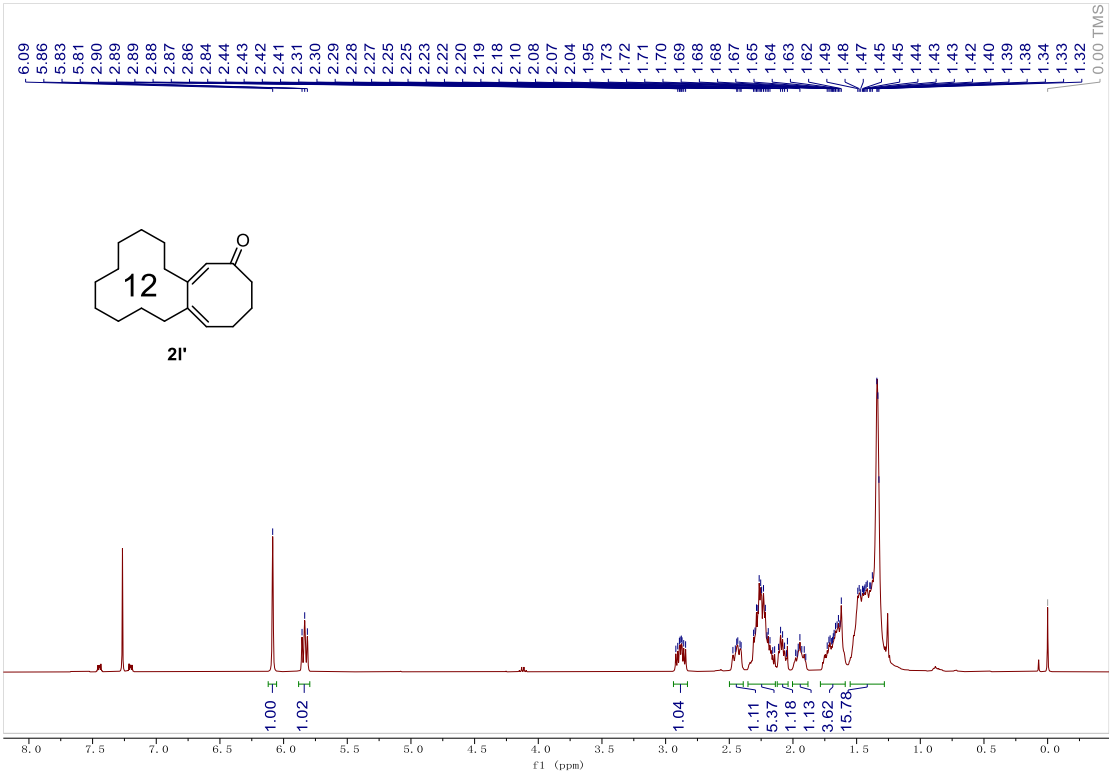
^{1}H NMR in $CDCl_3$, 400 MHz



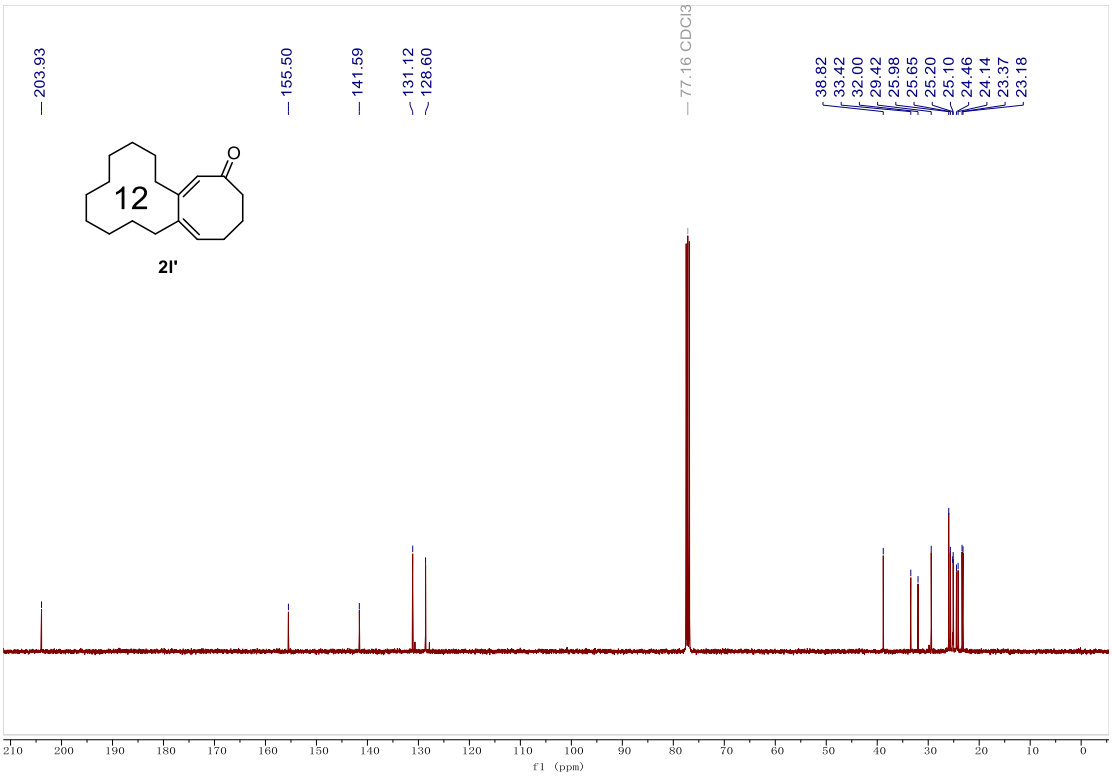
^{13}C NMR in $CDCl_3$, 101 MHz



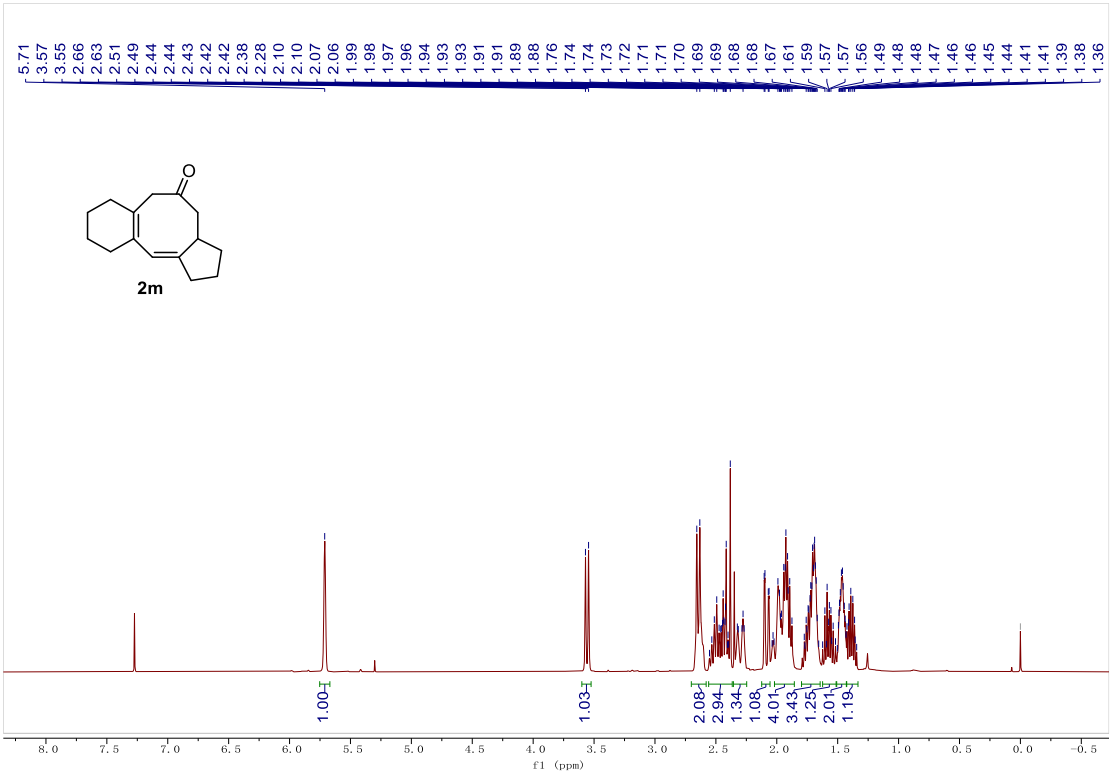
^{1}H NMR in $CDCl_3$, 400 MHz



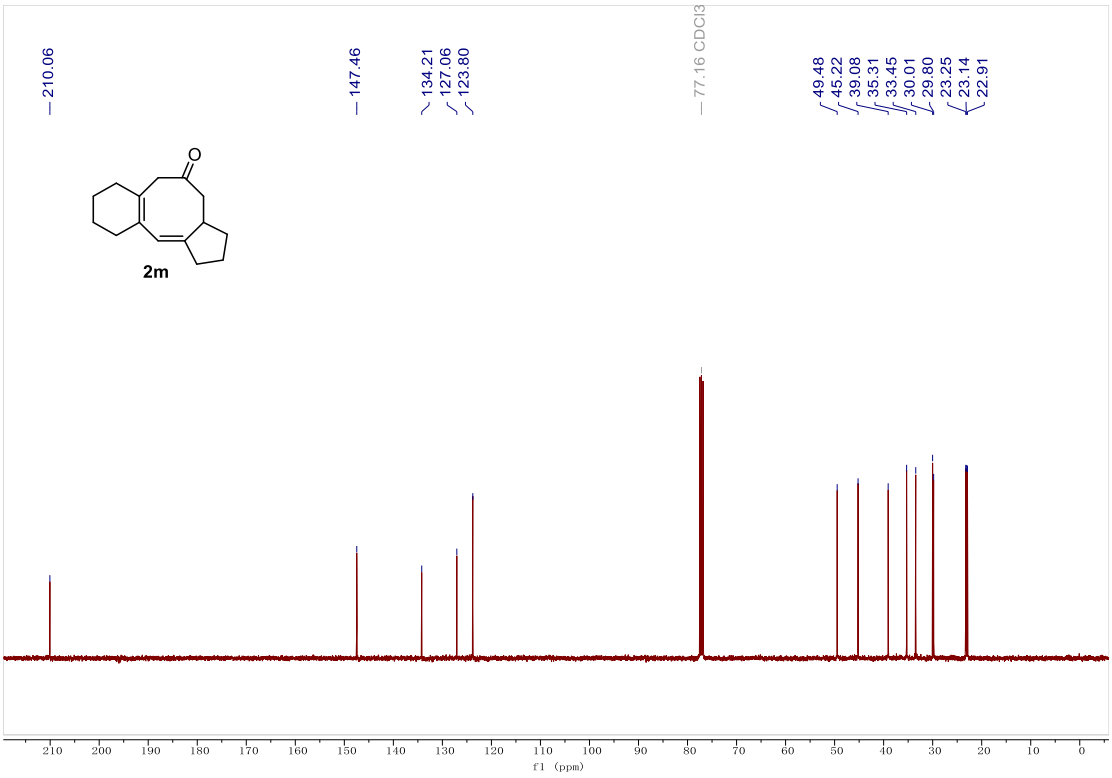
^{13}C NMR in $CDCl_3$, 101 MHz



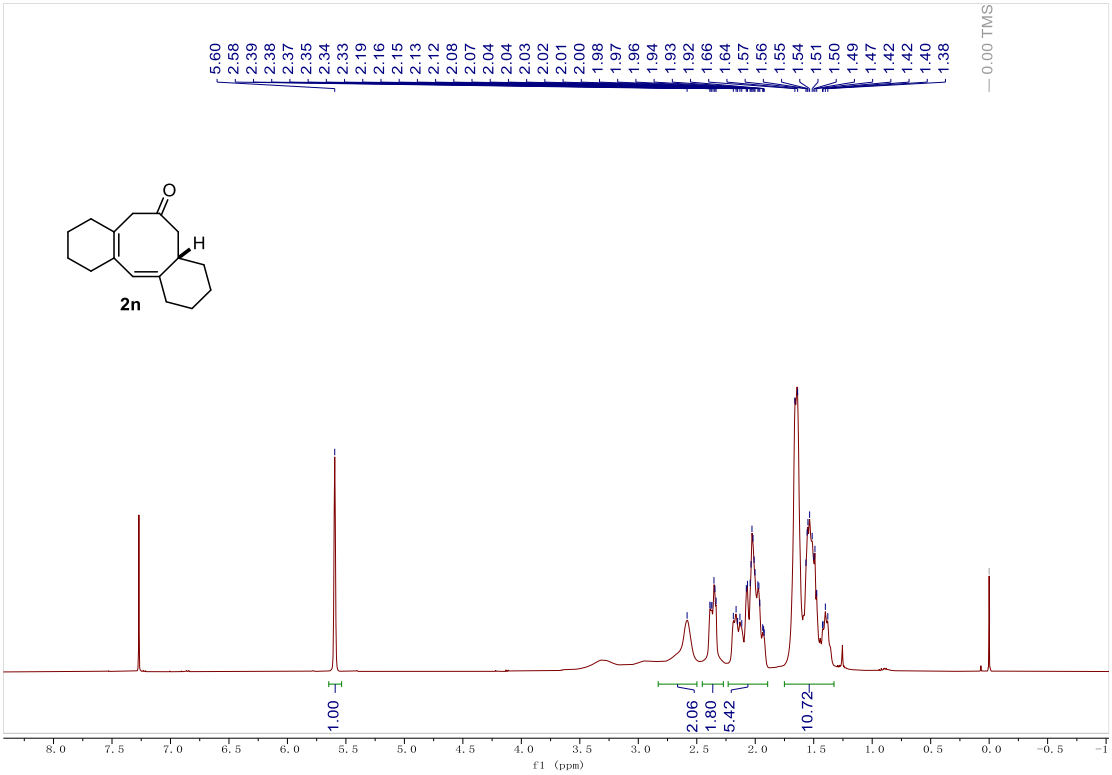
^{1}H NMR in $CDCl_3$, 400 MHz



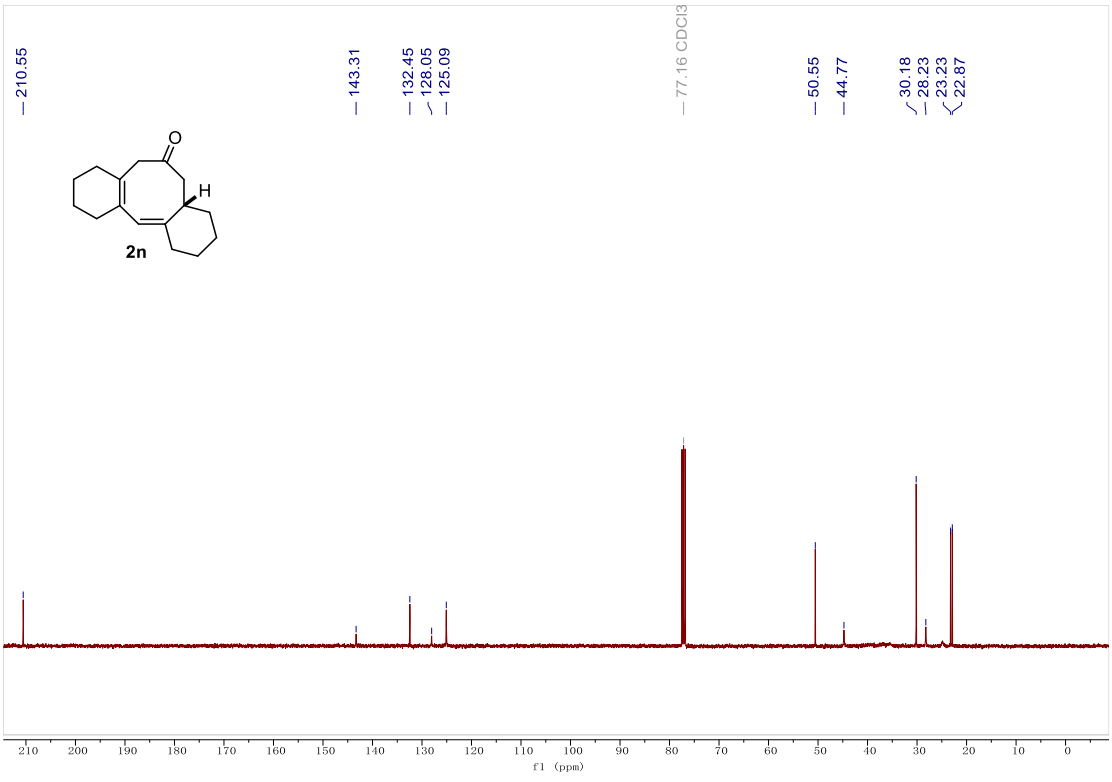
^{13}C NMR in $CDCl_3$, 101 MHz



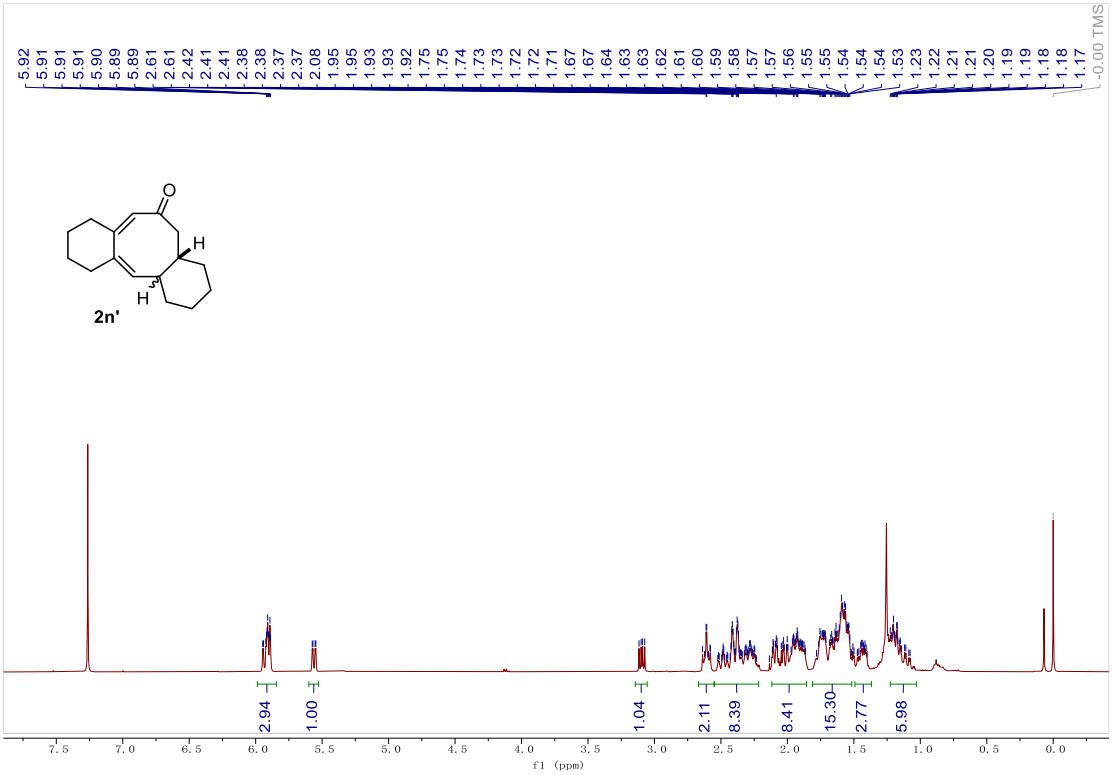
^{1}H NMR in $CDCl_3$, 400 MHz



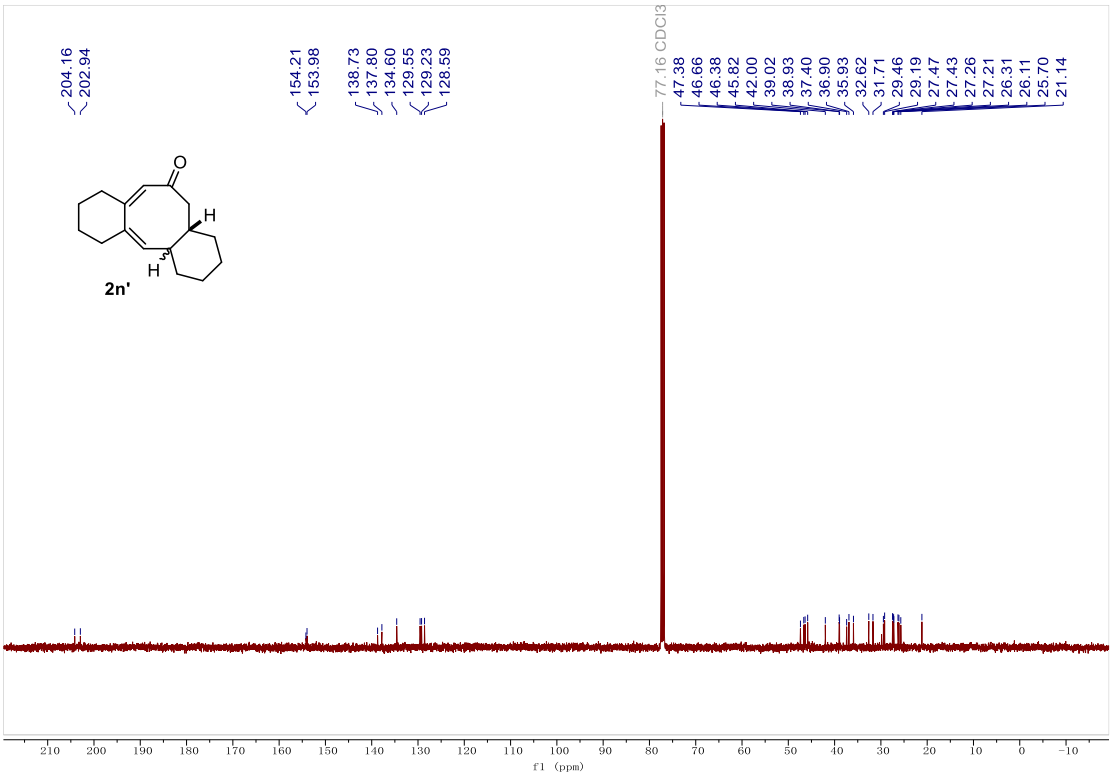
^{13}C NMR in $CDCl_3$, 101 MHz



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



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



^{1}H NMR crude spectrum of byproducts, entry 5, table 1 (^{1}H NMR in $CDCl_3$, 400 MHz)