Supporting Information

Rhodium-Catalyzed [5 + 1 + 2] Reaction of Yne-Vinylcyclopropenes and CO: The Application of Vinylcyclopropenes for Higher-Order Cycloaddition

Zhiqiang Huang, and Zhi-Xiang Yu*

Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

*E-mail: yuzx@pku.edu.cn

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1. General Information

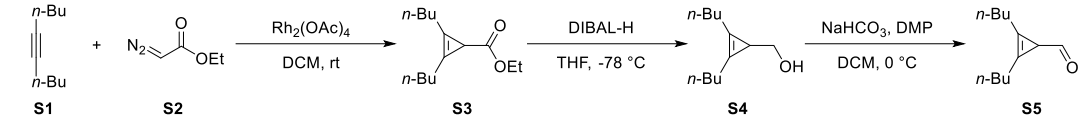
All chemicals were used as received without further purification. Reaction tubes (25 mL) were purchased from Synthware. $[Rh(CO)_2Cl]_2$ was purchased from J&K. Diethyl ether, NaCl, Na_2SO_4, and NH_4Cl were purchased from Bei Jing TongGuang Fine Chemicals Company. Ethyl acetate (EA), petroleum ether (PE), and dichloromethane (DCM) were purchased from Bei Jing TongGuang Fine Chemicals Company and Adamas-beta. Rhodium(II) acetate dimer (no. 1022762) and $MgSO_4$ (no. 1087059) were purchased from Leyan, Shanghai, China. Ethyl diazoacetate was purchased from Adamas-beta. Chloroform-d and DIBAL-H were purchased from Energy Chemical. Reactions were stirred using Teflon-coated magnetic stir bar. 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 (300-400 mesh, no. C200013) purchased from Leyan, Shanghai, China. and the purified compounds show a single spot by analytical TLC. Organic solutions were concentrated using a Büchi or Eyela rotary evaporator with a desktop vacuum pump. Nuclear magnetic resonance (NMR) spectra were measured on Bruker AVANCE III (^1H at 400 MHz, $^{13}C\{^1H\}$ at 101 MHz) nuclear magnetic resonance spectrometers. Data for ^1H NMR spectrum are reported as follows: chemical shift δ (ppm) referenced to tetramethylsilane (TMS, 0.00 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). High-resolution mass spectra (HRMS) were recorded on a Bruker Solarix XR Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (ESI). The crystal compound was obtained by adding petroleum ether to their ethyl acetate solution and then stilling and evaporating for several hours.

Abbreviations

Ac	acetyl
atm	atmosphere
Bn	benzyl group
Bu	butyl
BRSM	based on recovered starting materials
d	density
DCM	dichloromethane
DCE	1,2-dichloroethane
DFT	density functional theory
DIAD	diisopropyl azodicarboxylate
DMF	N, N-dimethylformamide
DMP	Dess-Martin periodinane
DMSO	dimethyl sulfoxide
d.r.	diastereomeric ratio
EA	ethyl acetate
ESI	electron spray ionization
Et	ethyl
HRMS	high-resolution mass spectroscopy
INT	intermediate
Me	methyl
m.p.	melting point
PE	petroleum ether
Ph	phenyl
Pr	propyl
PTLC	preparative thin-layer chromatography
rpm	revolutions per minute
rt	room temperature
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	trimethylsilyl
TS	transition state
Ts	tosyl

2. Substrates Preparations

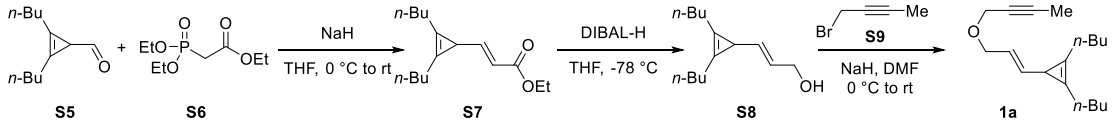
The synthesis of all substrates for the present study was not optimized.



To a mixture of $Rh_2(OAc)_4$ (65 mg, 0.147 mmol) in **S1** (5.239 g, 37.9 mmol) was added the solution of **S2** (3.977 g, 95% in DCM, 33.1 mmol) in DCM (5 mL) by syringe pump in 12 h under an argon atmosphere at room temperature (rt). Then the mixture was concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 to 100:1 to 50:1 PE/EA) to afford **S3** (6.18 g).

To a flask with **S3** (6.18 g, 27.5 mmol) in THF (70 mL) was added DIBAL-H (69 mL, 1 M in hexanes, 69 mmol) under an argon atmosphere at -78 °C. The mixture was stirred for 37 min at -78 °C. After that, the mixture was diluted with Et_2O and quenched with H_2O (2.8 mL), 15% NaOH (2.8 mL), and H_2O (8.4 mL). The reaction system was then warmed to rt, and stirred until milky white turbidity became clear. $MgSO_4$ (15 g) was added and stirred for 5 min. Filtered and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 100:1 to 50:1 to 25:1 PE/EA) to afford **S4** (1.9724 g, 10.8 mmol, 33% over two steps).

To a flask with **S4** (1.9724 g, 10.8 mmol) in DCM (50 mL) was added $NaHCO_3$ (2.73 g, 32.5 mmol) at 0 °C. Then, Dess–Martin periodinane (DMP, 5.53 g, 13 mmol) was added in portions slowly (ca. 20 min). The obtained mixture was stirred for 30 min at 0 °C. Then, 5% NaOH was added, and the mixture was allowed to stir at room temperature. The layers were separated, and the water phase was extracted with DCM. The combined organic solutions were dried over Na_2SO_4. Filtered through Celite, washed with EA, and concentrated by rotary evaporation. The crude **S5** was used for the next step without purification due to poor stability. **S5** is a known compound.[3e]



To a flask with **S6** (2.9 g, 13 mmol) in THF (40 mL) was added NaH (518 mg, 60% dispersion in mineral oil, 13 mmol) slowly at 0 °C, stirred for 5 min at 0 °C. Then, the solution of **S5** (~10.8 mmol) in THF (10 mL) was added. The obtained mixture was stirred for 50 min at rt. The reaction system was then quenched with saturated aqueous NH_4Cl solution and extracted with Et_2O. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 to 500:1 to 100:1 PE/EA) to afford **S7** (816.9 mg, 3.26 mmol, 30% over two steps).

To a flask with **S7** (816.9 mg, 3.26 mmol) in THF (9 mL) was added DIBAL-H (9 mL, 1 M in hexanes, 9 mmol) under an argon atmosphere at -78 °C. The mixture was stirred for 1 h at -78 °C. After that, the mixture was diluted with Et_2O and quenched with H_2O (0.4 mL), 15% NaOH (0.4

mL), and H_2O (1.2 mL). The reaction system was then warmed to rt, and stirred until milky white turbidity became clear. $MgSO_4$ (2.5 g) was added and stirred for 5 min. Filtered and concentrated by rotary evaporation. The crude **S8** was used for the next step without purification

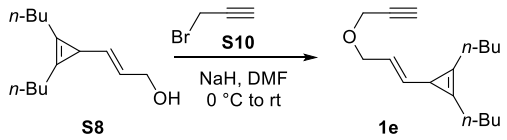
To a flask with NaH (262 mg, 60% dispersion in mineral oil, 6.55 mmol) was added **S8** (~3.26 mmol) in DMF (10 mL) under an argon atmosphere at 0 °C. After 10 min, **S9** (834 mg, 6.3 mmol) was added. The reaction mixture was stirred at rt for 8 h, quenched with saturated aqueous NH_4Cl solution, and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 500:1 to 200:1 PE/EA) to afford **1a** (681.9 mg, 2.62 mmol, 80% over two steps) as a colorless oil.

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

^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.56 (dt, J = 15.4, 6.7 Hz, 1H), 5.34 (ddt, J = 15.3, 7.8, 1.1 Hz, 1H), 4.06 (q, J = 2.3 Hz, 2H), 3.96 (dd, J = 6.7, 1.1 Hz, 2H), 2.42 – 2.33 (m, 4H), 1.97 (d, J = 7.8 Hz, 1H), 1.85 (t, J = 2.4 Hz, 3H), 1.56 – 1.44 (m, 4H), 1.42 – 1.28 (m, 4H), 0.91 (t, J = 7.3 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 144.9, 120.8, 113.4, 82.1, 75.6, 70.6, 57.1, 29.6, 25.0, 23.9, 22.6, 13.9, 3.7.

HRMS (ESI) m/z: calcd. for $C_{18}H_{29}O$ ($[M+H]^+$): 261.2213, found: 261.2209.



S8 **1e**

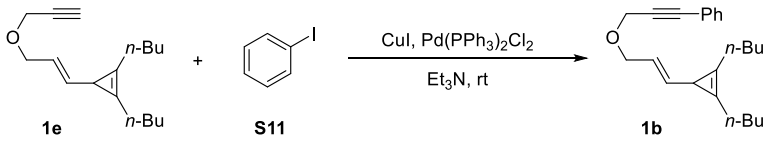
To a flask with NaH (167 mg, 60% dispersion in mineral oil, 4.2 mmol) in DMF (7 mL) was added **S8** (434 mg, 2.08 mmol) in DMF (3 mL) under an argon atmosphere at 0 °C. After 30 min, **S10** (639 mg, 80%, 4.3 mmol) was added. The reaction mixture was stirred at rt for 12 h, quenched with saturated aqueous NH_4Cl solution, and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 to 500:1 PE/EA) to afford **1e** (395.3 mg, 1.6 mmol, 77%) as a yellow oil.

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

^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.56 (dt, J = 15.3, 6.8 Hz, 1H), 5.36 (ddt, J = 15.3, 7.8, 1.1 Hz, 1H), 4.12 (d, J = 2.4 Hz, 2H), 3.99 (dd, J = 6.7, 1.1 Hz, 2H), 2.40 (t, J = 1.9 Hz, 1H), 2.39 – 2.35 (m, 4H), 1.97 (d, J = 7.8 Hz, 1H), 1.55 – 1.45 (m, 4H), 1.41 – 1.30 (m, 4H), 0.91 (t, J = 7.3 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 145.6, 120.4, 113.4, 80.2, 74.1, 70.7, 56.4, 29.7, 25.1, 23.9, 22.6, 14.0.

HRMS (ESI) m/z: calcd. for $C_{17}H_{27}O$ ($[M+H]^+$): 247.2056, found: 247.2049.



1e **S11** **1b**

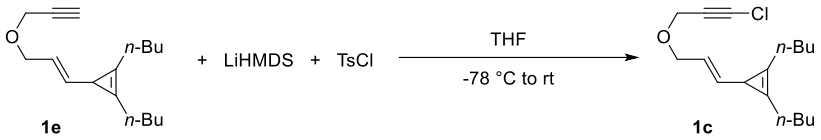
To a flask with CuI (4.5 mg, 0.0236 mmol) and $Pd(PPh_3)_2Cl_2$ (5.1 mg, 0.0073 mmol) in Et_3N (3 mL) was added **S11** (171 mg, 0.84 mmol) under an argon atmosphere at rt. Stirred for 5 min, **1e** (163.8 mg, 0.66 mmol) was added. The reaction mixture was stirred at rt for 13 h, quenched with saturated aqueous $NaHCO_3$ solution, and extracted with EA. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 to 100:1 PE/EA) to afford **1b** (207.4 mg, 0.64 mmol, 97%) as a yellow oil.

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

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.49 – 7.40 (m, 2H), 7.35 – 7.27 (m, 3H), 5.61 (dt, J = 15.3, 6.7 Hz, 1H), 5.39 (ddt, J = 15.4, 7.9, 1.1 Hz, 1H), 4.34 (s, 2H), 4.06 (dd, J = 6.7, 1.2 Hz, 2H), 2.38 (t, J = 7.3 Hz, 4H), 1.99 (d, J = 7.9 Hz, 1H), 1.56 – 1.46 (m, 4H), 1.40 – 1.30 (m, 4H), 0.91 (t, J = 7.3 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 145.4, 131.9, 128.4, 128.4, 123.0, 120.6, 113.4, 86.0, 85.7, 70.8, 57.3, 29.7, 25.1, 23.9, 22.6, 14.0.

HRMS (ESI) m/z: calcd. for $C_{23}H_{31}O$ ($[M+H]^+$): 323.2369, found: 323.2362.



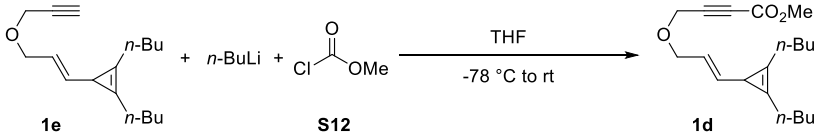
To a reaction tube with **1e** (100 mg, 0.4 mmol) in THF (1 mL) was added LiHMDS (0.5 mL, 1 M, 0.5 mmol) under an argon atmosphere at -78 °C. Stirred for 40 min, TsCl (93.4 mg, 0.49 mmol) was added. The reaction mixture was stirred at rt for 16.5 h, quenched with saturated aqueous NH_4Cl solution, and extracted with Et_2O. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 to 100:1 PE/EA) to afford **1c** (67.3 mg, 0.24 mmol, 59%) as a light yellow oil.

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

^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.55 (dt, J = 15.4, 6.7 Hz, 1H), 5.35 (ddt, J = 15.3, 7.9, 1.1 Hz, 1H), 4.11 (s, 2H), 3.97 (dd, J = 6.8, 1.1 Hz, 2H), 2.38 (t, J = 7.3 Hz, 4H), 1.97 (d, J = 7.8 Hz, 1H), 1.55 – 1.45 (m, 4H), 1.40 – 1.29 (m, 4H), 0.91 (t, J = 7.3 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 145.7, 120.3, 113.4, 70.9, 66.0, 64.1, 56.8, 29.7, 25.1, 23.9, 22.6, 14.0.

HRMS (ESI) m/z: calcd. for $C_{17}H_{26}ClO$ ($[M+H]^+$): 281.1667, found: 281.1666.



To a flask with **1e** (138 mg, 0.56 mmol) in THF (3 mL) was added *n*-BuLi (0.3 mL, 2.5 M, 0.75 mmol) under an argon atmosphere at -78 °C. Stirred for 25 min, **S12** (122 mg, 1.3 mmol) was added.

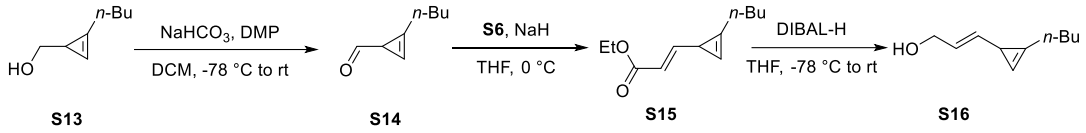
The reaction mixture was stirred at rt for 2 h, quenched with saturated aqueous NH_4Cl solution, and extracted with Et_2O. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 100:1 PE/EA) to afford **1d** (115.3 mg, 0.38 mmol, 68%) as a colorless oil.

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

^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.54 (dt, J = 15.4, 6.7 Hz, 1H), 5.37 (ddt, J = 15.3, 7.9, 1.1 Hz, 1H), 4.24 (s, 2H), 4.00 (dd, J = 6.7, 1.0 Hz, 2H), 3.78 (s, 3H), 2.38 (t, J = 7.3 Hz, 4H), 1.98 (d, J = 7.8 Hz, 1H), 1.55 – 1.44 (m, 4H), 1.41 – 1.29 (m, 4H), 0.91 (t, J = 7.3 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 153.8, 146.3, 119.8, 113.3, 84.4, 77.5, 71.2, 55.9, 52.9, 29.6, 25.0, 23.9, 22.6, 14.0.

HRMS (ESI) m/z: calcd. for $C_{19}H_{29}O_3$ ($[M+H]^+$): 305.2111, found: 305.2105.

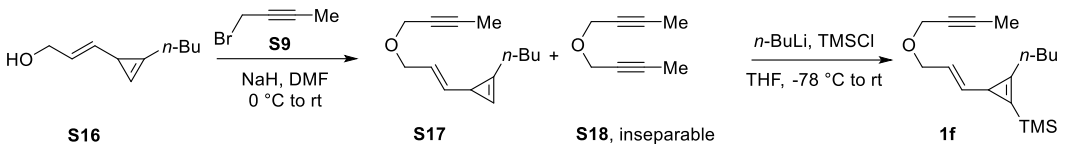


S13 **S14** **S15** **S16**

To a flask with **S13**[4e] (2.7 g, 21.4 mmol) in DCM (107 mL) was added $NaHCO_3$ (5.4 g, 64.3 mmol) at -78 °C. Then, Dess–Martin periodinane (DMP, 10.9 g, 25.7 mmol) was added slowly in portions. The obtained mixture was stirred for 70 min at 0 °C and stirred for 1 h at rt. Then, 15% NaOH was added, and the mixture was allowed to stir at room temperature. The layers were separated, and the water phase was extracted with DCM. The combined organic solutions were dried over Na_2SO_4. Filtered through Celite, washed with EA, and concentrated by rotary evaporation. The crude **S14** was used for the next step without purification.

To a flask with **S6** (6.2 g, 27.7 mmol) in THF (80 mL) was added NaH (1.29 g, 60% dispersion in mineral oil, 32.2 mmol) slowly at 0 °C, stirred for 10 min at 0 °C. Then, the solution of **S14** (~21.4 mmol) in THF (10 mL) was added. The obtained mixture was stirred for 30 min at 0 °C. The reaction system was then quenched with saturated aqueous NH_4Cl solution and extracted with Et_2O. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 to 500:1 to 200:1 to 100:1 PE/EA) to afford **S15** (1.48 g, 7.62 mmol).

To a flask with **S15** (1.48 g, 7.62 mmol) in THF (16 mL) was added DIBAL-H (20 mL, 1 M in hexanes, 20 mmol) under an argon atmosphere at -78 °C. The mixture was stirred for 10 h at 0 °C to rt. After that, the mixture was diluted with Et_2O and quenched with H_2O (0.8 mL), 15% NaOH (0.8 mL), and H_2O (2.4 mL). The reaction system was then warmed to rt, and stirred until milky white turbidity became clear. $MgSO_4$ (5 g) was added and stirred for 5 min. Filtered and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 300:1 to 100:1 to 50:1 to 25:1 to 10:1 PE/EA) to afford **S16** (863.6 mg, 5.67 mmol, 26% over three steps).



To a flask with NaH (456 mg, 60% dispersion in mineral oil, 11.4 mmol) in DMF (25 mL) was added **S16** (5.67 mmol) in DMF (3 mL) under an argon atmosphere at 0 °C. After 30 min, **S9** (1.49 g, 11.23 mmol) was added. The reaction mixture was stirred at rt for 5.5 h, quenched with saturated aqueous NH_4Cl solution, and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 to 300:1 PE/EA) to afford **S17** and **S18**[13] (885.4 mg, **S17**:**S18** = 8:1).

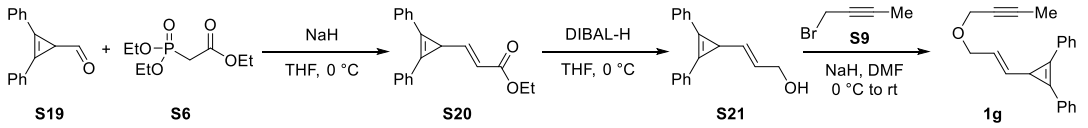
To a flask with **S17** (114 mg, 0.56 mmol, with inseparable **S18**) in THF (3 mL) was added *n*-BuLi (0.3 mL, 2.4 M, 0.72 mmol) under an argon atmosphere at -78 °C. Stirred for 8 min, TMSCl (95 mg, 0.87 mmol) was added. The reaction mixture was stirred at rt for 20 min, quenched with saturated aqueous NH_4Cl solution, and extracted with Et_2O. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 PE/EA) to afford **1f** (110.3 mg, 0.4 mmol, 55% over two steps) as a light yellow oil.

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

^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.53 (dt, J = 15.3, 6.7 Hz, 1H), 5.30 (ddt, J = 15.2, 7.8, 1.1 Hz, 1H), 4.05 (q, J = 2.3 Hz, 2H), 3.95 (dd, J = 6.7, 1.1 Hz, 2H), 2.50 (t, J = 7.2 Hz, 2H), 1.96 (d, J = 7.7 Hz, 1H), 1.85 (t, J = 2.3 Hz, 3H), 1.60 – 1.48 (m, 2H), 1.44 – 1.30 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H), 0.15 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 145.3, 137.1, 120.4, 110.5, 82.1, 75.6, 70.6, 56.9, 29.5, 27.2, 22.8, 22.5, 14.0, 3.7, -1.0.

HRMS (ESI) m/z: calcd. for $C_{17}H_{29}OSi$ ($[M+H]^+$): 277.1982, found: 277.1980.



To a flask with **S6** (556 mg, 2.5 mmol) in THF (5 mL) was added NaH (163 mg, 60% dispersion in mineral oil, 4.1 mmol) slowly at 0 °C, stirred for 5 min at 0 °C. Then, the solution of **S19**[3e] (2 mmol) in THF (5 mL) was added. The obtained mixture was stirred for 30 min at 0 °C. The reaction system was then quenched with saturated aqueous NH_4Cl solution and extracted with Et_2O. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 500:1 to 250:1 to 100:1 PE/EA) to afford **S20** (467.8 mg, 1.6 mmol).

To a flask with **S20** (467.8 mg, 1.6 mmol) in THF (6 mL) was added DIBAL-H (6 mL, 1 M in hexanes, 6 mmol) under an argon atmosphere at 0 °C. The mixture was stirred for 15 min at 0 °C. After that, the mixture was diluted with Et_2O and quenched with H_2O (0.24 mL), 15% NaOH (0.24 mL), and H_2O (0.72 mL). The reaction system was then warmed to rt, and stirred until milky white

turbidity became clear. $MgSO_4$ (1.5 g) was added and stirred for 5 min. Filtered and concentrated by rotary evaporation. The crude **S21** was used for the next step without purification

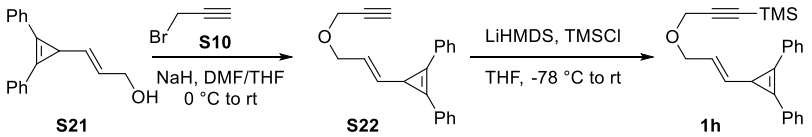
To a flask with NaH (128 mg, 60% dispersion in mineral oil, 3.2 mmol) in DMF (5 mL) was added **S21** (~1.6 mmol) in DMF (3 mL) under an argon atmosphere at 0 °C. After 10 min, **S9** (451 mg, 3.4 mmol) was added. The reaction mixture was stirred at rt for 10 h, quenched with saturated aqueous NH_4Cl solution, and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 100:1 PE/EA) to afford **1g** (322.1 mg, 1.07 mmol, 54 % over three steps) as a light yellow oil.

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

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.71 – 7.64 (m, 4H), 7.45 (dd, J = 8.4, 6.8 Hz, 4H), 7.39 – 7.32 (m, 2H), 5.90 (dt, J = 15.4, 6.6 Hz, 1H), 5.57 (ddt, J = 15.4, 8.0, 1.2 Hz, 1H), 4.09 (q, J = 2.4 Hz, 2H), 4.01 (dd, J = 6.6, 1.2 Hz, 2H), 2.79 (d, J = 7.8 Hz, 1H), 1.83 (t, J = 2.3 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 140.7, 129.7, 129.4, 128.9, 128.8, 123.9, 114.9, 82.4, 75.4, 70.5, 57.4, 23.0, 3.8.

HRMS (ESI) m/z: calcd. for $C_{22}H_{21}O$ ($[M+H]^+$): 301.1587, found: 301.1594.



To a flask with NaH (146 mg, 60% dispersion in mineral oil, 3.6 mmol) in DMF (5 mL) was added **S21** (446 mg, 1.8 mmol) in THF (2 mL) under an argon atmosphere at 0 °C. After 10 min, **S10** (569 mg, 80%, 3.8 mmol) was added. The reaction mixture was stirred at rt for 11 h, quenched with saturated aqueous NH_4Cl solution, and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 to 250:1 to 100:1 PE/EA) to afford **S22** (439.3 mg, 1.5 mmol).

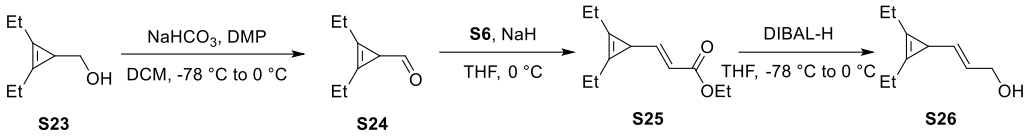
To a reaction tube with **S22** (201 mg, 0.7 mmol) in THF (3 mL) was added LiHMDS (1 mL, 1 M, 1 mmol) under an argon atmosphere at -78 °C. Stirred for 50 min, TMSCl (130 mg, 1.2 mmol) was added. The reaction mixture was stirred at -78 °C for 20 min and at rt for 30 min, quenched with saturated aqueous NH_4Cl solution, and extracted with Et_2O. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 100:1 PE/EA) to afford **1h** (228.1 mg, 0.64 mmol, 77% over two steps) as a yellow oil.

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

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.71 – 7.64 (m, 4H), 7.45 (dd, J = 8.3, 6.9 Hz, 4H), 7.39 – 7.32 (m, 2H), 5.91 (dt, J = 15.3, 6.6 Hz, 1H), 5.57 (ddt, J = 15.4, 8.0, 1.2 Hz, 1H), 4.13 (s, 2H), 4.03 (dd, J = 6.7, 1.2 Hz, 2H), 2.79 (d, J = 7.9 Hz, 1H), 0.16 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 141.1, 129.7, 129.3, 128.9, 128.8, 123.7, 114.9, 101.9, 91.2, 70.6, 57.6, 23.0, -0.0.

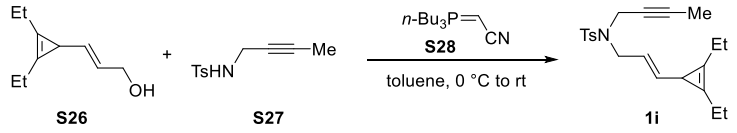
HRMS (ESI) m/z: calcd. for $C_{24}H_{27}OSi$ ($[M+H]^+$): 359.1826, found: 359.1819.



To a flask with **S23** (13.1 mmol) in DCM (50 mL) was added $NaHCO_3$ (3.32 g, 39.5 mmol) at -78 °C. Then, Dess–Martin periodinane (DMP, 6.66 g, 15.7 mmol) was added slowly in portions. The obtained mixture was stirred for 70 min at 0 °C. Then, 15% NaOH was added, and the mixture was allowed to stir at room temperature. The layers were separated, and the water phase was extracted with DCM. The combined organic solutions were dried over Na_2SO_4. Filtered through Celite, washed with EA, and concentrated by rotary evaporation. The crude **S24** was used for the next step without purification.

To a flask with **S6** (3.56 g, 15.9 mmol) in THF (50 mL) was added NaH (637 mg, 60% dispersion in mineral oil, 15.9 mmol) slowly at 0 °C, stirred for 10 min at 0 °C. Then, the solution of **S24** (~13.1 mmol) in THF (10 mL) was added. The obtained mixture was stirred for 15 min at 0 °C. The reaction system was then quenched with saturated aqueous NH_4Cl solution and extracted with Et_2O. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 500:1 to 250:1 to 100:1 PE/EA) to afford **S25** (1.02 g, 5.26 mmol).

To a flask with **S25** (1.02 g, 5.26 mmol) in THF (13 mL) was added DIBAL-H (13 mL, 1 M in hexanes, 13 mmol) under an argon atmosphere at -78 °C. The mixture was stirred for 30 min at 0 °C. After that, the mixture was diluted with Et_2O and quenched with H_2O (0.5 mL), 15% NaOH (0.5 mL), and H_2O (1.5 mL). The reaction system was then warmed to rt, and stirred until milky white turbidity became clear. $MgSO_4$ (3 g) was added and stirred for 5 min. Filtered and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 100:1 to 50:1 to 25:1 PE/EA) to afford **S26** (625.7 mg, 4.1 mmol, 31% over three steps).



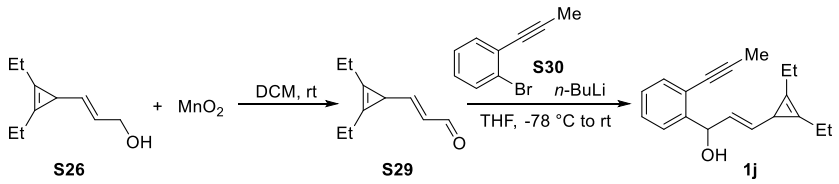
To a flask with **S26** (79.4 mg, 0.52 mmol) and **S27** (127 mg, 0.57 mmol) in toluene (2.5 mL) was added Tsunoda reagent[14] **S28** (160 mg, 0.66 mmol) under an argon atmosphere at 0 °C. The mixture was stirred for 18 h at 0 °C to rt. The mixture was purified by flash column chromatography (silica gel, 300:1 to 200:1 to 100:1 PE/EA) to afford **1i** (102.5 mg, 0.29 mmol, 55%, with inseparable impurity) as a yellow oil.

TLC (5:1 PE/EA, R_f): 0.5.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.75 – 7.71 (m, 2H), 7.29 – 7.26 (m, 2H), 5.34 – 5.29 (m, 2H), 4.01 – 3.98 (m, 2H), 3.74 – 3.68 (m, 2H), 2.41 (s, 3H), 2.39 – 2.33 (m, 4H), 1.98 – 1.94 (m, 1H), 1.52 (t, J = 2.4 Hz, 3H), 1.10 (t, J = 7.5 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 145.8, 143.1, 136.5, 129.2, 128.0, 118.2, 114.0, 81.1, 72.0, 48.5, 35.8, 23.7, 21.6, 18.8, 12.3, 3.3.

HRMS (ESI) m/z: calcd. for $C_{21}H_{28}NO_2S$ ([M+H]$^+$): 358.1835, found: 358.1841.



To a flask with **S26** (79.6 mg, 0.52 mmol) in DCM (3 mL) was added MnO_2 (488 mg, 92%, 5 mmol) at rt. The mixture was stirred for 3 h at rt. Then, MnO_2 (486 mg, 92%, 5 mmol) was added and stirred for 1 h at rt. Filtered through Celite, washed with EA, and concentrated by rotary evaporation. The crude **S29** was used for the next step without purification.

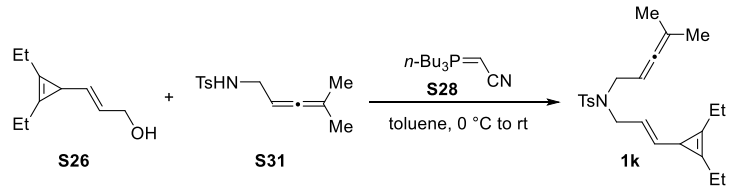
To a reaction tube with **S30** (107.3 mg, 0.55 mmol) in THF (2 mL) was added *n*-BuLi (0.23 mL, 2.4 M, 0.55 mmol) under an argon atmosphere at -78 °C. Stirred for 40 min, the solution of **S29** (~0.5 mmol) in THF (1 mL) was added. The reaction mixture was stirred at rt for 14 h, quenched with saturated aqueous NH_4Cl solution, and extracted with Et_2O. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 to 100:1 to 50:1 PE/EA) to afford **1j** (41.8 mg, 0.16 mmol, 30% over two steps) as a yellow oil.

TLC (5:1 PE/EA, R_f): 0.4.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.48 – 7.43 (m, 1H), 7.37 (dd, J = 7.7, 1.4 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.17 (ddd, J = 7.5, 1.4 Hz, 1H), 5.69 (dd, J = 15.3, 6.9 Hz, 1H), 5.54 (d, J = 6.9 Hz, 1H), 5.38 (ddd, J = 15.3, 7.9, 1.1 Hz, 1H), 2.45 – 2.31 (m, 4H), 2.25 – 2.16 (m, 1H), 2.07 (s, 3H), 2.01 (d, J = 7.9 Hz, 1H), 1.17 – 1.04 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 145.5, 141.6, 132.5, 128.1, 127.0, 126.4, 125.9, 121.9, 114.6, 114.6, 91.0, 77.9, 73.5, 24.2, 19.0, 18.9, 12.43, 12.40, 4.6.

HRMS (ESI) m/z: calcd. for $C_{19}H_{23}O$ ([M+H]$^+$): 267.1743, found: 267.1747.



To a flask with **S26** (76.2 mg, 0.5 mmol) and **S31** (130.6 mg, 0.52 mmol) in toluene (2.5 mL) was added Tsunoda reagent[14] **S28** (161 mg, 0.66 mmol) under an argon atmosphere at 0 °C. The mixture was stirred for 14 h at 0 °C to rt. The mixture was purified by flash column chromatography (silica gel, 300:1 to 200:1 to 100:1 PE/EA) to afford **1k** (60.4 mg, 0.16 mmol, 31%) as a yellow oil.

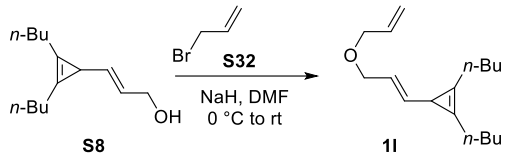
TLC (5:1 PE/EA, R_f): 0.5.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.70 (d, J = 8.3 Hz, 2H), 7.31 – 7.24 (m, 2H), 5.24 – 5.17 (m, 2H), 4.76 – 4.67 (m, 1H), 3.82 – 3.73 (m, 4H), 2.41 (s, 3H), 2.39 – 2.30 (m, 4H), 1.93 – 1.88 (m, 1H), 1.64 (s, 3H), 1.63 (s, 3H), 1.09 (t, J = 7.4 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 203.4, 145.1, 142.9, 138.3, 129.7, 127.3, 118.7, 114.2, 96.4,

84.5, 48.2, 45.7, 23.7, 21.6, 20.5, 18.8, 12.4.

HRMS (ESI) m/z: calcd. for $C_{23}H_{32}NO_2S$ ($[M+H]^+$): 386.2148, found: 386.2150.



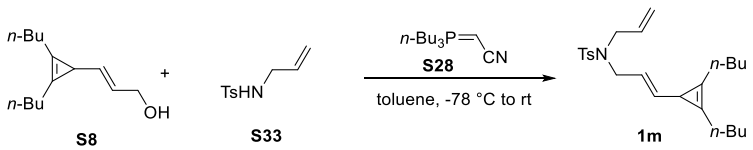
To a flask with NaH (81.8 mg, 60% dispersion in mineral oil, 2 mmol) in DMF (4 mL) was added **S8** (209.7 mg, 1 mmol) in DMF (1 mL) under an argon atmosphere at 0 °C. After 30 min, **S32** (249 mg, 2 mmol) was added. The reaction mixture was stirred at rt for 16.5 h, quenched with saturated aqueous NH_4Cl solution, and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 250:1 to 100:1 PE/EA) to afford **1l** (230.1 mg, 0.93 mmol, 92%) as a colorless oil.

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

^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.99 – 5.86 (m, 1H), 5.59 (ddd, J = 15.4, 6.6 Hz, 1H), 5.35 – 5.22 (m, 2H), 5.19 – 5.13 (m, 1H), 3.95 (d, J = 5.8 Hz, 2H), 3.91 (d, J = 6.6 Hz, 2H), 2.37 (t, J = 7.3 Hz, 4H), 1.97 (d, J = 7.8 Hz, 1H), 1.54 – 1.45 (m, 4H), 1.40 – 1.30 (m, 4H), 0.91 (t, J = 7.3 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 144.2, 135.3, 121.4, 116.9, 113.5, 71.3, 70.7, 29.7, 25.1, 23.9, 22.6, 14.0.

HRMS (ESI) m/z: calcd. for $C_{17}H_{29}O$ ($[M+H]^+$): 249.2213, found: 249.2206.



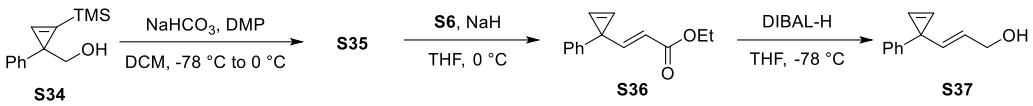
To a flask with **S8** (111 mg, 0.53 mmol) and **S33** (125 mg, 0.59 mmol) in toluene (2.5 mL) was added Tsunoda reagent[14] **S28** (149 mg, 0.62 mmol) under an argon atmosphere at -78 °C. The mixture was stirred for 4 h at -78 °C to rt. The mixture was purified by flash column chromatography (silica gel, 1:0 to 300:1 to 100:1 PE/EA) to afford **1m** (59.7 mg, 0.15 mmol, 28%) as a light yellow oil.

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

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.70 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 5.61 (ddt, J = 17.5, 9.8, 6.3 Hz, 1H), 5.23 – 5.07 (m, 4H), 3.79 (d, J = 6.3 Hz, 2H), 3.74 (d, J = 5.5 Hz, 2H), 2.42 (s, 3H), 2.33 (td, J = 7.3, 1.5 Hz, 4H), 1.88 – 1.84 (m, 1H), 1.52 – 1.42 (m, 4H), 1.38 – 1.29 (m, 4H), 0.90 (t, J = 7.3 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 145.2, 143.0, 137.9, 133.2, 129.7, 127.3, 118.8, 118.5, 113.2, 48.9, 48.7, 29.6, 25.0, 23.6, 22.6, 21.6, 14.0.

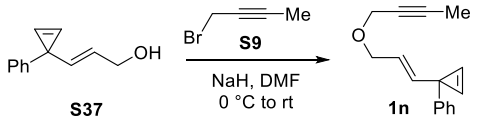
HRMS (ESI) m/z: calcd. for $C_{24}H_{36}NO_2S$ ($[M+H]^+$): 402.2461, found: 402.2464.



To a flask with **S34**[15] (8.5 mmol) in DCM (39 mL) was added $NaHCO_3$ (2.15 g, 25.6 mmol) at -78 °C. Then, Dess–Martin periodinane (DMP, 4.7 g, 11.2 mmol) was added slowly in portions. The obtained mixture was stirred for 40 min at 0 °C. Then, 5% NaOH was added, and the mixture was allowed to stir at room temperature. The layers were separated, and the water phase was extracted with DCM. The combined organic solutions were dried over Na_2SO_4. Filtered through Celite, washed with EA, and concentrated by rotary evaporation. The crude **S35** was used for the next step without purification.

To a flask with **S6** (1.9 g, 8.4 mmol) in THF (20 mL) was added NaH (351 mg, 60% dispersion in mineral oil, 8.8 mmol) slowly at 0 °C, stirred for 10 min at 0 °C. Then, the solution of **S35** (~8.5 mmol) in THF (10 mL) was added. The obtained mixture was stirred for 30 min at 0 °C. The reaction system was then quenched with saturated aqueous NH_4Cl solution and extracted with Et_2O. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 to 250:1 to 100:1 to 50:1 PE/EA) to afford **S36** (399.9 mg, 1.87 mmol).

To a flask with **S36** (399.9 mg, 1.87 mmol) in THF (5 mL) was added DIBAL-H (5 mL, 1 M in hexanes, 5 mmol) under an argon atmosphere at -78 °C. The mixture was stirred for 11 h at -78 °C. After that, the mixture was diluted with Et_2O and quenched with H_2O (0.2 mL), 15% NaOH (0.2 mL), and H_2O (0.6 mL). The reaction system was then warmed to rt, and stirred until milky white turbidity became clear. $MgSO_4$ (2 g) was added and stirred for 5 min. Filtered and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 100:1 to 50:1 to 20:1 to 10:1 PE/EA) to afford **S37** (195.1 mg, 1.13 mmol, 13% over three steps).



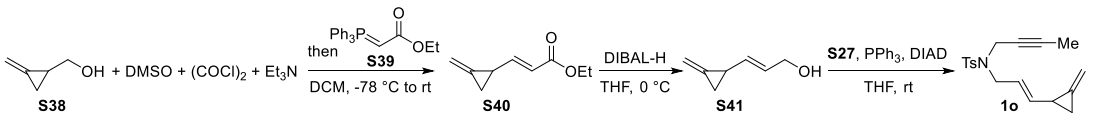
To a flask with NaH (53.5 mg, 60% dispersion in mineral oil, 1.3 mmol) in DMF (3 mL) was added **S37** (106 mg, 0.62 mmol) in DMF (2 mL) under an argon atmosphere at 0 °C. After 30 min, **S9** (179 mg, 1.3 mmol) was added. The reaction mixture was stirred at rt for 13 h, quenched with saturated aqueous NH_4Cl solution, and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 250:1 to 100:1 PE/EA) to afford **1n** (97.1 mg, 0.43 mmol, 70%) as a light yellow oil.

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

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.32 – 7.25 (m, 2H), 7.26 (s, 2H), 7.24 – 7.20 (m, 2H), 7.20 – 7.14 (m, 1H), 6.36 (dt, J = 15.4, 1.4 Hz, 1H), 5.42 (dt, J = 15.4, 6.4 Hz, 1H), 4.09 (q, J = 2.4 Hz, 2H), 4.06 (dd, J = 6.4, 1.3 Hz, 2H), 1.85 (t, J = 2.3 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 146.7, 142.0, 128.2, 127.2, 125.9, 125.8, 112.5, 82.5, 75.3, 70.1, 57.7, 28.7, 3.7.

HRMS (ESI) m/z: calcd. for $C_{16}H_{17}O$ ($[M+H]^+$): 225.1274, found: 225.1267.



To a flask with $(COCl)_2$ (0.47 mL, density (*d*) = 1.488 g/mL, 5.5 mmol) in DCM (50 mL) was added DMSO (0.85 mL, *d* = 1.1 g/mL, 12 mmol) dropwise under an argon atmosphere at -78 °C. Then, **S38**[16] (437 mg, 5.2 mmol) was added slowly. Et_3N (4.2 mL, *d* = 0.728 g/mL, 30 mmol) was added. The reaction mixture was stirred at -78 °C for 10 min and warmed to rt. **S39** (2.12 g, 6.1 mmol) was added. The reaction mixture was stirred at rt for 4 h, quenched with water, and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 to 300:1 PE/EA) to afford **S40** (587.2 mg, 3.86 mmol).

To a flask with **S40** (587.2 mg, 3.86 mmol) in THF (10 mL) was added DIBAL-H (10 mL, 1 M in hexanes, 10 mmol) under an argon atmosphere at 0 °C. The mixture was stirred for 10 min at 0 °C. After that, the mixture was diluted with Et_2O and quenched with H_2O (0.4 mL), 15% NaOH (0.4 mL), and H_2O (1.2 mL). The reaction system was then warmed to rt, and stirred until milky white turbidity became clear. $MgSO_4$ (4 g) was added and stirred for 5 min. Filtered and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 300:1 to 150:1 to 100:1 to 50:1 PE/EA) to afford **S41** (268.7 mg, 2.44 mmol).

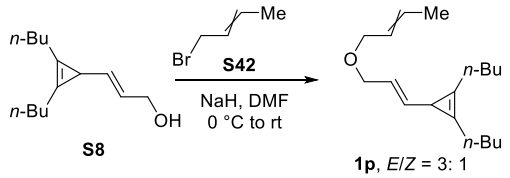
To a flask with **S41** (58 mg, 0.53 mmol), PPh_3 (204 mg, 0.78 mmol), and **S27** (126 mg, 0.57 mmol) in THF (5 mL) was added DIAD (156 mg, 0.77 mmol) at rt. The mixture was stirred for 1 h at rt. The mixture was concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 300:1 to 100:1 to 50:1 PE/EA) to afford **1o** (134.1 mg, 0.43 mmol, 38% over three steps) as a colorless oil.

TLC (5:1 PE/EA, R_f): 0.5.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.72 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 5.50 – 5.40 (m, 3H), 5.35 (dd, *J* = 15.3, 7.8 Hz, 1H), 4.09 – 3.93 (m, 2H), 3.79 – 3.66 (m, 2H), 2.42 (s, 3H), 2.10 – 2.02 (m, 1H), 1.53 (t, *J* = 2.4 Hz, 3H), 1.52 – 1.47 (m, 1H), 1.05 – 0.98 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 143.3, 136.9, 136.5, 134.7, 129.3, 128.0, 122.6, 104.6, 81.5, 71.9, 48.2, 36.2, 21.6, 18.4, 12.1, 3.4.

HRMS (ESI) m/z: calcd. for $C_{18}H_{22}NO_2S$ ($[M+H]^+$): 316.1366, found: 316.1368.



To a flask with NaH (83 mg, 60% dispersion in mineral oil, 2.1 mmol) in DMF (4 mL) was added **S8** (204 mg, 1 mmol) in DMF (1 mL) under an argon atmosphere at 0 °C. After 30 min, **S42** (326 mg, 2.4 mmol, E/Z = 0.85: 0.15) was added. The reaction mixture was stirred at rt for 13 h, quenched with saturated aqueous NH_4Cl solution, and extracted with Et_2O. The combined organic layer was

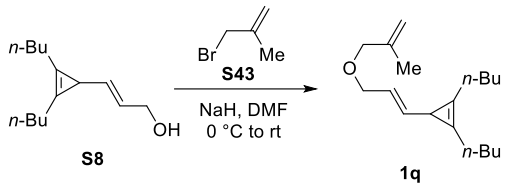
washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 to 250:1 PE/EA) to afford **1p** (220.2 mg, 0.84 mmol, 86%, *E*/*Z* = 3: 1) as a colorless oil.

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

^{1}H NMR for the major isomer (400 MHz, $CDCl_3$, δ): 5.75 – 5.65 (m, 1H), 5.64 – 5.54 (m, 2H), 5.35 – 5.25 (m, 1H), 3.92 – 3.84 (m, 4H), 2.41 – 2.33 (m, 4H), 1.97 (d, *J* = 7.8 Hz, 1H), 1.70 (dd, *J* = 6.2, 1.2 Hz, 3H), 1.55 – 1.45 (m, 4H), 1.40 – 1.29 (m, 4H), 0.91 (t, *J* = 7.3 Hz, 6H).

^{13}C{^{1}H} NMR for the major isomer (101 MHz, $CDCl_3$, δ): 144.0, 129.4, 128.0, 121.6, 113.5, 71.1, 70.4, 29.7, 25.1, 23.9, 22.6, 17.9, 14.0.

HRMS (ESI) m/z: calcd. for $C_{18}H_{31}O$ ($[M+H]^+$): 263.2369, found: 263.2362.



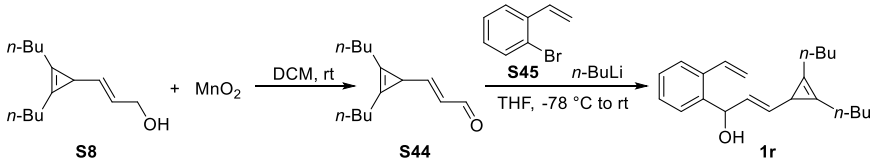
To a flask with NaH (87 mg, 60% dispersion in mineral oil, 2.2 mmol) in DMF (4 mL) was added **S8** (199 mg, 0.96 mmol) in DMF (1 mL) under an argon atmosphere at 0 °C. After 30 min, **S43** (299 mg, 2.2 mmol) was added. The reaction mixture was stirred at rt for 13 h, quenched with saturated aqueous NH_4Cl solution, and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 to 300:1 PE/EA) to afford **1q** (220.8 mg, 0.84 mmol, 88%) as a colorless oil.

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

^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.59 (dt, *J* = 15.4, 6.6 Hz, 1H), 5.30 (ddt, *J* = 15.3, 7.8, 1.2 Hz, 1H), 4.97 – 4.93 (m, 1H), 4.89 – 4.86 (m, 1H), 3.88 (dd, *J* = 6.6, 1.2 Hz, 2H), 3.86 (s, 2H), 2.38 (t, *J* = 7.3 Hz, 4H), 1.97 (d, *J* = 7.8 Hz, 1H), 1.74 (s, 3H), 1.55 – 1.45 (m, 4H), 1.41 – 1.29 (m, 4H), 0.91 (t, *J* = 7.3 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 144.0, 142.7, 121.5, 113.5, 111.9, 73.6, 71.0, 29.7, 25.1, 23.9, 22.6, 19.7, 14.0.

HRMS (ESI) m/z: calcd. for $C_{18}H_{31}O$ ($[M+H]^+$): 263.2369, found: 263.2364.



To a flask with **S8** (209.5 mg, 1 mmol) in DCM (10 mL) was added MnO_2 (1.75 g, 92%, 18 mmol) at rt. The mixture was stirred for 2.5 h at rt. Filtered through Celite, washed with EA, and concentrated by rotary evaporation. The crude **S44** was used for the next step without purification.

To a reaction tube with **S45** (208 mg, 1.1 mmol) in THF (4 mL) was added *n*-BuLi (0.46 mL, 2.4 M, 1.1 mmol) under an argon atmosphere at -78 °C. Stirred for 15 min, the solution of **S44** (~1

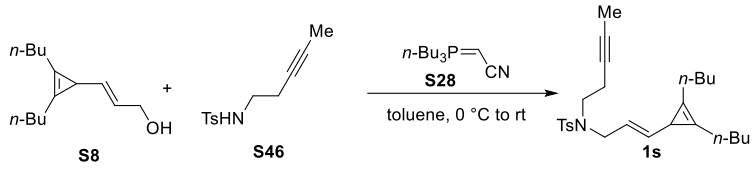
mmol) in THF (2 mL) was added. The reaction mixture was stirred at rt for 70 min, quenched with saturated aqueous NH_4Cl solution, and extracted with Et_2O. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by flash column chromatography (silica gel, 1:0 to 300:1 to 100:1 to 50:1 PE/EA) to afford **1r** (136 mg, 0.44 mmol, 44% over two steps) as a yellow oil.

TLC (5:1 PE/EA, R_f): 0.5.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.50 (dd, J = 7.6, 1.6 Hz, 1H), 7.45 (dd, J = 7.5, 1.6 Hz, 1H), 7.32 – 7.21 (m, 2H), 7.06 (dd, J = 17.4, 11.0 Hz, 1H), 5.69 (dd, J = 15.3, 6.8 Hz, 1H), 5.60 (dd, J = 17.4, 1.5 Hz, 1H), 5.42 (dd, J = 7.2, 2.4 Hz, 1H), 5.32 – 5.24 (m, 2H), 2.43 – 2.27 (m, 4H), 1.95 (d, J = 7.9 Hz, 1H), 1.86 – 1.82 (m, 1H), 1.53 – 1.41 (m, 4H), 1.39 – 1.27 (m, 4H), 0.94 – 0.85 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 142.3, 140.7, 136.1, 134.7, 128.0, 127.5, 126.8, 126.2, 126.0, 116.1, 113.5, 113.4, 72.3, 29.7, 29.6, 25.09, 25.07, 24.0, 22.59, 22.57, 14.0, 13.9.

HRMS (ESI) m/z: calcd. for $C_{22}H_{31}O$ ($[M+H]^+$): 311.2369, found: 311.2362.



To a flask with **S8** (171 mg, 0.82 mmol) and **S46** (211 mg, 0.89 mmol) in toluene (5 mL) was added Tsunoda reagent[14] **S28** (234 mg, 0.97 mmol) under an argon atmosphere at 0 °C. The mixture was stirred for 4 h at rt. The mixture was purified by flash column chromatography (silica gel, 1:0 to 300:1 to 100:1 PE/EA) and PTLC (10:1 PE/EA) to afford **1s** (61.6 mg, 0.14 mmol, 18%) as a light yellow oil.

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

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.70 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 5.31 – 5.16 (m, 2H), 3.80 – 3.69 (m, 2H), 3.26 – 3.16 (m, 2H), 2.42 (s, 3H), 2.40 – 2.30 (m, 6H), 1.91 – 1.85 (m, 1H), 1.73 (t, J = 2.6 Hz, 3H), 1.53 – 1.42 (m, 4H), 1.40 – 1.28 (m, 4H), 0.91 (t, J = 7.3 Hz, 6H).

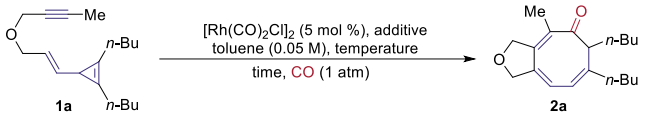
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 145.3, 143.1, 137.4, 129.7, 127.3, 119.1, 113.1, 77.3, 76.0, 50.7, 46.0, 29.6, 24.9, 23.6, 22.6, 21.6, 19.6, 13.9, 3.5.

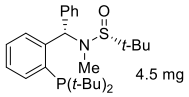
HRMS (ESI) m/z: calcd. for $C_{26}H_{38}NO_2S$ ($[M+H]^+$): 428.2618, found: 428.2621.

3. Reaction Optimization

All reactions were conducted on a 0.1 mmol scale. All yields are NMR yields, and 1,3,5-trimethoxybenzene was used as the internal standard.

Table S1. More reaction optimization study.



entry	additive	T (°C)	t (h)	yield (%)
1	-	30–50	3	79
2	AgBr (8.9 mg)	30–50	3	79
3	AgF (1.3 mg)	30	6	57
4	PPh_3 (2.6 mg)	30	6	31
5	 4.5 mg	30	6	74

In entry 1, this reaction was conducted at 30 °C for 2 h, we found that the [5 + 1 + 2] reaction was completed and produced two isomers (detected by TLC and crude ^{1}H NMR, Figure S1 and S2, one was assigned as **2a**, and the other one was its precursor **2a'**). Then, this reaction was heated to 50 °C and stirred for 1 h, **2a** can be the only product (79% NMR yield). We used AgBr as the additive and found that it has no effect on the reaction outcome (entry 2). When AgF was used, a slight decrease in yield was observed (entry 3). We also attempted to use PPh_3 as a ligand, but the yield significantly decreased (entry 4). TY-Phos did not affect the reaction yield either (entry 5).

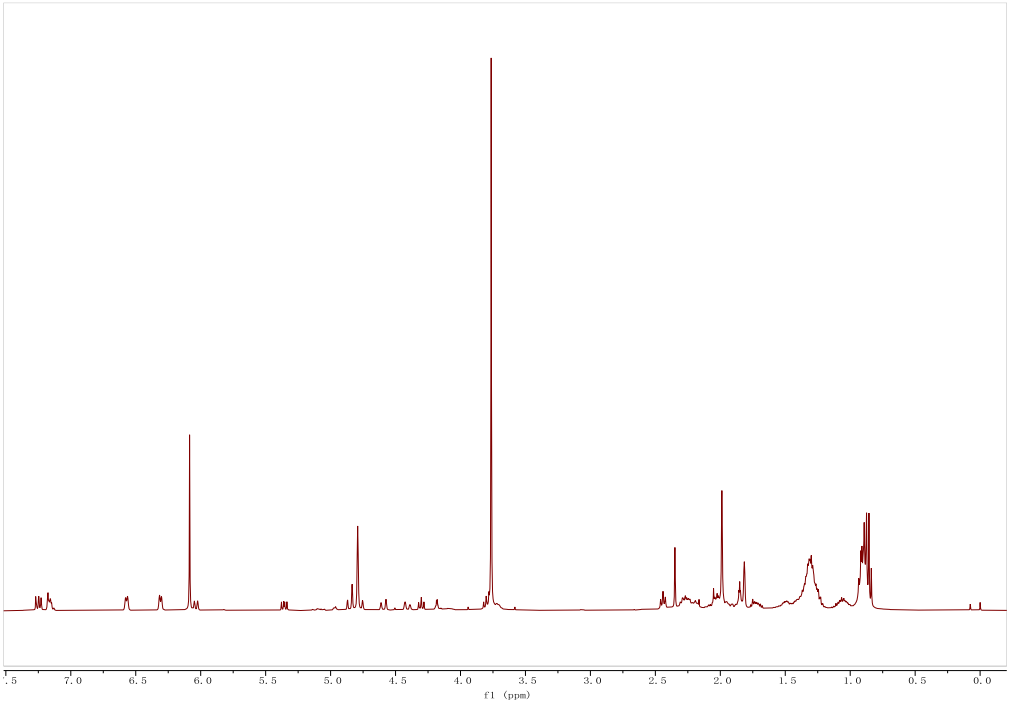


Figure S1

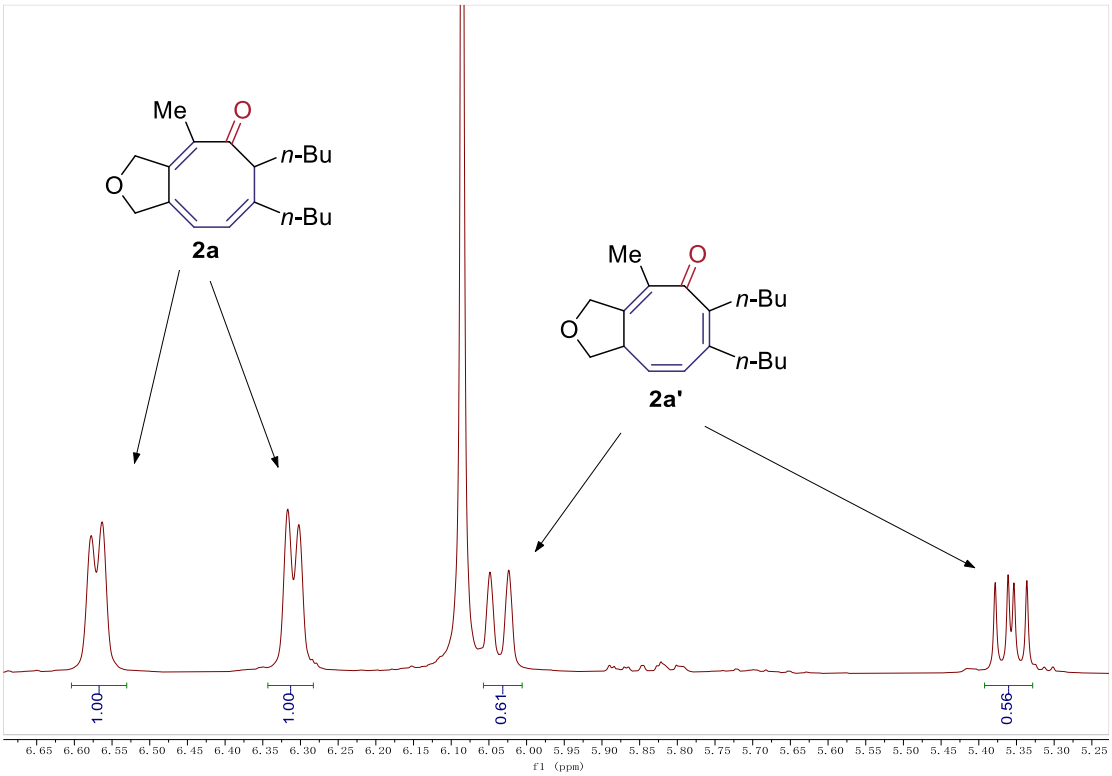
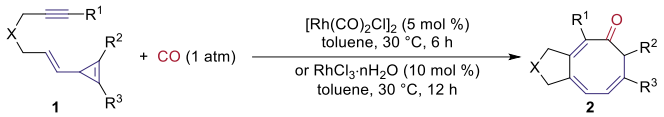

Me
O
n-Bu
n-Bu
O
2a
Me
O
n-Bu
n-Bu
O
2a'
1.00
1.00
0.61
0.56
6.65 6.60 6.55 6.50 6.45 6.40 6.35 6.30 6.25 6.20 6.15 6.10 6.05 6.00 5.95 5.90 5.85 5.80 5.75 5.70 5.65 5.60 5.55 5.50 5.45 5.40 5.35 5.30 5.25
f1 (ppm)

Figure S2

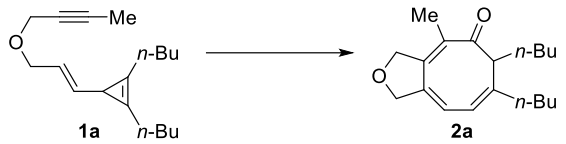
4. General Procedure for [5 + 1 + 2] Reaction



General procedure A: To a reaction tube with **1** (0.1 mmol) and $[Rh(CO)_2Cl]_2$ (5 mol %) was added toluene (2 mL or 4 mL) 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 30 °C for 6 h under balloon-pressured gas of CO, 600 rpm for the magnetic stir bar. After cooling, purification of the crude product by flash column chromatography (silica gel, PE/EA) afforded [5 + 1 + 2] cycloadducts **2**.

Note: some substrates need higher temperatures to promote [1,5]-H shift when the [5 + 1 + 2] reaction is completed.

General procedure B: To a reaction tube with **1** (0.1 mmol) and $RhCl_3 \cdot nH_2O$ (10 mol %) was added toluene (2 mL) 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 30 °C for 12 h under balloon-pressured gas of CO, 600 rpm for the magnetic stir bar. After cooling, purification of the crude product by flash column chromatography (silica gel, PE/EA) afforded [5 + 1 + 2] cycloadducts **2**.



Run 1: Following general procedure A. Substrate: **1a** (26.4 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (1.9 mg, 0.005 mmol), toluene (2 mL), flash column chromatography (silica gel, 50:1 PE/EA); product: **2a** (22.5 mg, 77%).

Run 2: Following general procedure A. Substrate: **1a** (52.9 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.8 mg, 0.01 mmol), mesitylene (4 mL), 30 °C for 2 h and 50 °C for 1 h, flash column chromatography (silica gel, 50:1 to 20:1 PE/EA); product: **2a** (43.1 mg, 74%).

Run 3: Following general procedure A. Substrate: **1a** (263.0 mg, 1 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), toluene (10 mL), 800 rpm, 30 °C for 24 h and 50 °C for 12 h. flash column chromatography (silica gel, 50:1 PE/EA); product: **2a** (132.6 mg, 46%), recover of **1a** (105.9 mg, 40%), yield based on recovered starting materials (BRSM): 77%.

Run 4: Following general procedure B. Substrate: **1a** (26.4 mg, 0.1 mmol), $RhCl_3 \cdot nH_2O$ (2.6 mg, 0.01 mmol), toluene (2 mL), flash column chromatography (silica gel, 50:1 PE/EA); product: **2a** (19.4 mg, 66%).

Physical Form: yellow oil.

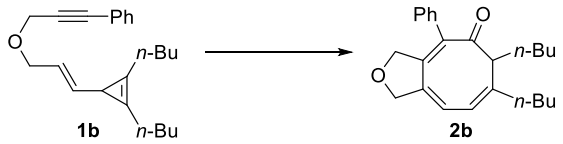
TLC (10:1 PE/EA, R_f): 0.6.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.58 (d, J = 6.0 Hz, 1H), 6.31 (d, J = 6.0 Hz, 1H), 4.89 – 4.74 (m, 4H), 2.44 (t, J = 7.2 Hz, 1H), 2.28 – 2.16 (m, 1H), 2.09 – 1.89 (m, 2H), 1.99 (s, 3H), 1.78 – 1.67 (m,

1H), 1.55 – 1.44 (m, 1H), 1.37 – 1.21 (m, 5H), 1.14 – 0.98 (m, 2H), 0.94 – 0.82 (m, 6H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 188.2, 146.7, 145.7, 140.6, 135.4, 125.8, 124.7, 77.3, 75.2, 53.1, 30.8, 30.0, 29.3, 26.8, 22.9, 22.6, 16.6, 14.1 (2C).

HRMS (ESI) m/z: calcd. for $C_{19}H_{29}O_2$ ($[M+H]^+$): 289.2162, found: 289.2155.



Run 1: Following general procedure A. Substrate: **1b** (32.7 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (1.9 mg, 0.005 mmol), toluene (4 mL), 18 h, flash column chromatography (silica gel, 100:1 to 25:1 PE/EA); product: **2b** (24.9 mg, 70%).

Run 2: Following general procedure A. Substrate: **1b** (32.2 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), toluene (2 mL), 15 h, flash column chromatography (silica gel, 100:1 to 25:1 PE/EA); product: **2b** (26.3 mg, 75%).

Run 3: Following general procedure A. Substrate: **1b** (34.5 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (1.9 mg, 0.005 mmol), toluene (2 mL), CO (0.2 atm), 18 h, flash column chromatography (silica gel, 100:1 to 25:1 PE/EA); product: **2b** (27.1 mg, 72%).

Run 4: Following general procedure B. Substrate: **1b** (32.5 mg, 0.1 mmol), $RhCl_3 \cdot nH_2O$ (5.2 mg, 0.02 mmol), toluene (2 mL), 15 h, flash column chromatography (silica gel, 100:1 to 25:1 PE/EA); product: **2b** (17.7 mg, 50%).

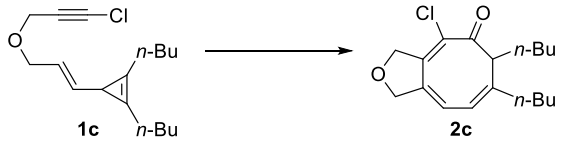
Physical Form: yellow oil.

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

^1H NMR (400 MHz, $CDCl_3$, δ): 7.40 – 7.34 (m, 2H), 7.33 – 7.28 (m, 1H), 7.07 – 7.01 (m, 2H), 6.66 (d, J = 5.9 Hz, 1H), 6.41 (d, J = 6.1 Hz, 1H), 4.88 – 4.78 (m, 2H), 4.54 (d, J = 14.2 Hz, 1H), 4.35 (d, J = 14.2 Hz, 1H), 2.67 (dd, J = 8.3, 6.1 Hz, 1H), 2.29 – 2.18 (m, 1H), 2.18 – 2.09 (m, 1H), 2.02 – 1.90 (m, 1H), 1.79 – 1.67 (m, 1H), 1.58 – 1.47 (m, 1H), 1.38 – 1.24 (m, 6H), 1.18 – 1.08 (m, 1H), 0.95 – 0.84 (m, 6H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 188.2, 148.0, 147.1, 146.3, 139.4, 136.0, 129.1, 128.5, 127.8, 127.1, 124.9, 76.6, 75.7, 53.7, 30.9, 30.2, 29.2, 26.9, 23.0, 22.6, 14.18, 14.16.

HRMS (ESI) m/z: calcd. for $C_{24}H_{31}O_2$ ($[M+H]^+$): 351.2319, found: 351.2317.



Run 1: Following general procedure A. Substrate: **1c** (28.2 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (1.9 mg, 0.005 mmol), toluene (4 mL), 42 h, flash column chromatography (silica gel, 100:1 to 50:1 PE/EA); product: **2c** (12.5 mg, 40%).

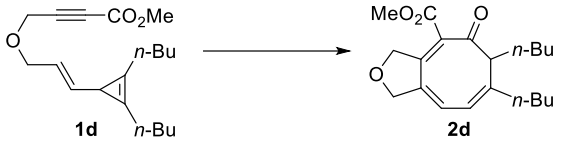
Physical Form: yellow oil.

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

^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.71 (d, J = 6.1 Hz, 1H), 6.39 (d, J = 6.0 Hz, 1H), 5.01 (d, J = 15.5 Hz, 1H), 4.91 (d, J = 15.6 Hz, 1H), 4.87 (apparent s, 2H), 2.45 (t, J = 7.2 Hz, 1H), 2.28 – 2.16 (m, 1H), 2.11 – 2.02 (m, 1H), 2.01 – 1.90 (m, 1H), 1.83 – 1.71 (m, 1H), 1.56 – 1.45 (m, 1H), 1.37 – 1.22 (m, 5H), 1.17 – 1.00 (m, 2H), 0.89 (t, J = 7.1 Hz, 3H), 0.86 (t, J = 7.3 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 182.4, 147.1, 146.7, 138.5, 135.4, 128.3, 125.7, 77.7, 76.6, 53.0, 30.8, 29.8, 29.3, 26.7, 22.9, 22.6, 14.1 (2C).

HRMS (ESI) m/z: calcd. for $C_{18}H_{26}ClO_2$ ($[M+H]^+$): 309.1616, found: 309.1616.



Run 1: Following general procedure A. Substrate: **1d** (31.2 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (1.9 mg, 0.005 mmol), toluene (4 mL), 30 °C for 22 h and 80 °C for 1 h, flash column chromatography (silica gel, 25:1 to 10:1 PE/EA); product: **2d** (8.8 mg, 26%).

Run 2: Following general procedure A. Substrate: **1d** (30.8 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.01 mmol), toluene (4 mL), 30 °C for 11 h and 80 °C for 1 h, flash column chromatography (silica gel, 25:1 to 10:1 PE/EA); product: **2d** (11.6 mg, 34%).

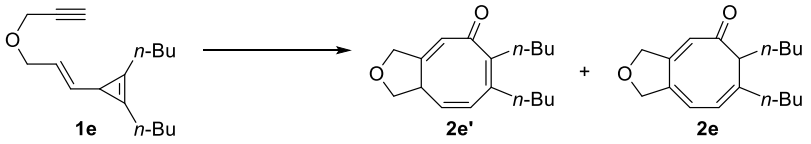
Physical Form: yellow oil.

TLC (5:1 PE/EA, R_f): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.76 (d, J = 6.2 Hz, 1H), 6.39 (d, J = 6.2 Hz, 1H), 4.84 – 4.72 (m, 4H), 3.84 (s, 3H), 2.48 (t, J = 7.2 Hz, 1H), 2.29 – 2.16 (m, 1H), 2.13 – 2.03 (m, 1H), 2.03 – 1.93 (m, 1H), 1.80 – 1.69 (m, 1H), 1.57 – 1.45 (m, 1H), 1.39 – 1.23 (m, 5H), 1.21 – 1.03 (m, 2H), 0.90 (t, J = 7.1 Hz, 3H), 0.87 (t, J = 7.3 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 186.3, 168.4, 148.6, 148.3, 138.2, 135.0, 129.9, 125.3, 76.5, 74.4, 53.9, 52.7, 31.3, 29.9, 29.2, 26.3, 22.9, 22.6, 14.1 (2C).

HRMS (ESI) m/z: calcd. for $C_{20}H_{29}O_4$ ($[M+H]^+$): 333.2060, found: 333.2058.



Run 1: Following general procedure A. Substrate: **1e** (24.9 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (1.9 mg, 0.005 mmol), toluene (2 mL), flash column chromatography (silica gel, 50:1 to 25:1 PE/EA); products: **2e'** and **2e** (11.7 mg, 42%, **2e'**:**2e** = 3:2).

Run 2: Following general procedure A. Substrate: **1e** (23.9 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (1.9 mg, 0.005 mmol), toluene (4 mL), 30 °C for 24 h and 50 °C for 1 h, flash column chromatography (silica gel, 50:1 to 20:1 PE/EA); product: **2e** (11.7 mg, 44%). Pure **2e** can be obtained if heated to 50 °C for 1 h when the [5 + 1 + 2] reaction is completed.

Run 3: Following general procedure B. Substrate: **1e** (25.0 mg, 0.1 mmol), $RhCl_3 \cdot nH_2O$ (2.6 mg, 0.01 mmol), toluene (2 mL), flash column chromatography (silica gel, 25:1 PE/EA); products: **2e'**

and **2e** (14.0 mg, 50%, **2e'**:**2e** = 2:3).

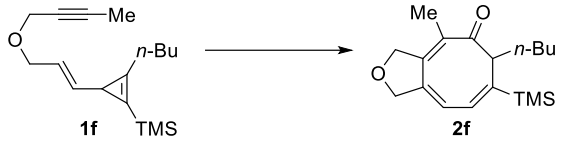
Physical Form: yellow oil.

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

^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.71 – 6.66 (m, 2H), 6.34 (d, J = 6.0 Hz, 1H), 4.81 – 4.74 (m, 4H), 2.47 (dd, J = 7.9, 6.5 Hz, 1H), 2.27 – 2.15 (m, 1H), 2.10 – 2.00 (m, 1H), 2.00 – 1.88 (m, 1H), 1.76 – 1.65 (m, 1H), 1.54 – 1.43 (m, 1H), 1.39 – 1.23 (m, 5H), 1.22 – 1.01 (m, 2H), 0.91 – 0.84 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 189.2, 149.4, 147.1, 135.7, 131.7, 128.5, 125.1, 76.7, 75.6, 53.9, 31.3, 30.0, 29.4, 26.1, 22.9, 22.6, 14.15, 14.12.

HRMS (ESI) m/z: calcd. for $C_{18}H_{27}O_2$ ([M+H]$^+$): 275.2006, found: 275.1998.



Run 1: Following general procedure A. Substrate: **1f** (27.6 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (1.9 mg, 0.005 mmol), toluene (4 mL), 30 °C for 1 h and 50 °C for 14.5 h and 100 °C for 6 h, flash column chromatography (silica gel, 50:1 PE/EA); product: **2f** (4.6 mg, 15%). The structure was assigned by the ^{1}H NMR, and the peak shape between 2.37 – 2.25 is almost a triplet.

Run 2: Following general procedure A. Substrate: **1f** (56.6 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (7.9 mg, 0.02 mmol), toluene (4 mL), 50 °C for 24 h, flash column chromatography (silica gel, 100:1 to 50:1 to 20:1 to 10:1 PE/EA); product: **2f** (6.3 mg, 10%).

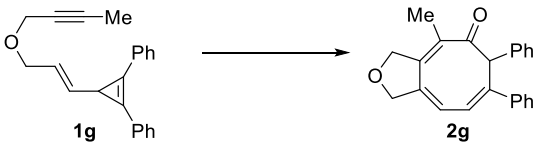
Physical Form: yellow oil.

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

^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.52 (d, J = 6.2 Hz, 1H), 6.30 (d, J = 6.2 Hz, 1H), 4.92 – 4.73 (m, 4H), 2.37 – 2.25 (m, 1H), 2.19 – 2.09 (m, 1H), 2.00 (s, 3H), 1.58 – 1.48 (m, 1H), 1.41 – 1.24 (m, 4H), 0.90 (t, J = 7.0 Hz, 3H), 0.12 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 187.9, 146.2, 145.6, 141.9, 133.9, 125.7, 124.6, 77.7, 75.5, 48.4, 35.8, 29.2, 22.6, 16.8, 14.1, -0.6.

HRMS (ESI) m/z: calcd. for $C_{18}H_{29}O_2Si$ ([M+H]$^+$): 305.1931, found: 305.1933.



Run 1: Following general procedure A. Substrate: **1g** (30.5 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (1.9 mg, 0.005 mmol), toluene (4 mL), 23 h, flash column chromatography (silica gel, 20:1 PE/EA); product: **2g** (14.7 mg, 44%).

Run 2: Following general procedure A. Substrate: **1g** (30.8 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), toluene (4 mL), 23 h, flash column chromatography (silica gel, 20:1 PE/EA); product: **2g** (18.3 mg, 54%).

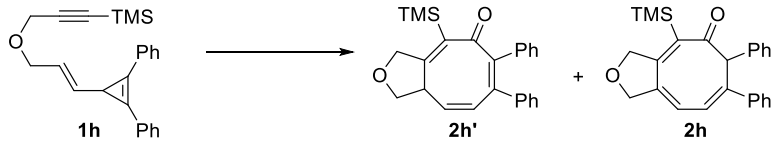
Physical Form: yellow oil.

TLC (5:1 PE/EA, R_f): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.48 – 7.41 (m, 2H), 7.24 – 7.10 (m, 8H), 6.92 (d, J = 6.3 Hz, 1H), 6.72 (d, J = 6.3 Hz, 1H), 4.98 – 4.70 (m, 4H), 4.59 – 4.41 (m, 1H), 2.12 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 187.7, 145.9, 142.7, 140.7, 138.5, 137.4, 136.7, 129.3, 128.7, 128.1, 127.9, 127.85, 127.75, 126.4, 125.3, 77.4, 75.2, 55.5, 16.9.

HRMS (ESI) m/z: calcd. for $C_{23}H_{21}O_2$ ([M+H]$^+$): 329.1536, found: 329.1537.



Run 1: Following general procedure A. Substrate: **1h** (35.3 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (1.9 mg, 0.005 mmol), toluene (4 mL), 49 h, flash column chromatography (silica gel, 50:1 to 20:1 PE/EA); products: **2h'** and **2h** (20.5 mg, 54%, **2h'**:**2h** = 5:4), recover of **1h** (9.3 mg, 26%), yield based on recovered starting materials (BRSM): 73%.

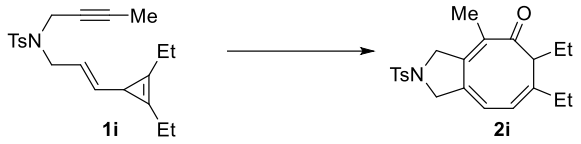
Physical Form: yellow oil.

TLC (5:1 PE/EA, R_f): 0.3.

^{1}H NMR for the major isomer **2h'** (400 MHz, $CDCl_3$, δ): 7.31 – 7.27 (m, 2H), 7.25 – 7.10 (m, 8H), 6.45 (d, J = 9.8 Hz, 1H), 5.52 (ddd, J = 9.9, 7.0, 1.3 Hz, 1H), 4.51 (s, 1H), 4.45 (dd, J = 8.3, 8.3 Hz, 1H), 4.42 – 4.35 (m, 1H), 4.08 – 4.00 (m, 1H), 3.90 – 3.82 (m, 1H), 0.04 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 202.9, 192.9, 163.2, 152.8, 148.1, 146.2, 140.4, 139.7, 136.8, 136.4, 136.3, 135.0, 134.4, 134.1, 133.9, 130.3, 130.1, 129.8, 129.4, 128.9, 128.5, 128.2, 128.1, 128.0, 127.92, 127.89, 127.85, 127.8, 126.9, 123.4, 77.4, 76.0, 74.2, 72.0, 59.8, 46.3, 1.0, -0.2.

HRMS (ESI) m/z: calcd. for $C_{25}H_{27}O_2Si$ ([M+H]$^+$): 387.1775, found: 387.1780.



Run 1: Following general procedure A. Substrate: **1i** (35.5 mg, 0.1 mmol, with inseparable impurity), $[Rh(CO)_2Cl]_2$ (1.8 mg, 0.005 mmol), toluene (4 mL), 30 °C for 22 h and 80 °C for 1 h, flash column chromatography (silica gel, 50:1 to 20:1 to 10:1 PE/EA); product: **2i** (20.8 mg, 54%).

Physical Form: yellow oil.

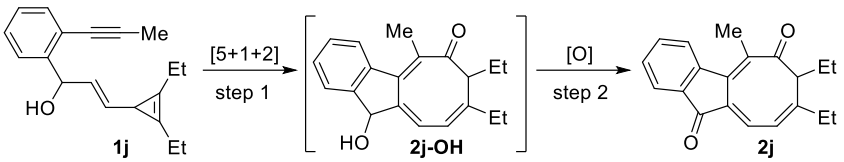
TLC (5:1 PE/EA, R_f): 0.2.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.76 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 6.54 (d, J = 5.9 Hz, 1H), 6.19 (d, J = 5.9 Hz, 1H), 4.36 (d, J = 12.9 Hz, 1H), 4.32 – 4.21 (m, 3H), 2.43 (s, 3H), 2.27 – 2.14 (m, 2H), 1.98 (s, 3H), 1.96 – 1.84 (m, 2H), 1.76 – 1.64 (m, 1H), 0.99 (t, J = 7.2 Hz, 3H), 0.67 (t, J = 7.3 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 187.8, 148.7, 144.2, 142.8, 142.6, 133.0, 132.3, 130.0, 128.2,

128.0, 123.8, 57.3, 55.6, 54.8, 23.7, 21.7, 19.9, 17.1, 12.0, 11.4.

HRMS (ESI) m/z: calcd. for $C_{22}H_{28}NO_3S$ ($[M+H]^+$): 386.1784, found: 386.1785.



Run 1: Following general procedure A. Substrate: **1j** (27.1 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol), toluene (4 mL), 30 °C for 4 h and 50 °C for 0.5 h. When step 1 was finished, the mixture was concentrated by rotary evaporation, DCM (2 mL), PDC (76.7 mg), and 4Å molecular (85.1 mg) sieve were added, stirred at rt for 30 min, purified by flash column chromatography (silica gel, 100:1 to 50:1 PE/EA); product: **2j** (17.3 mg, 58% over two steps).

Physical Form: yellow solid.

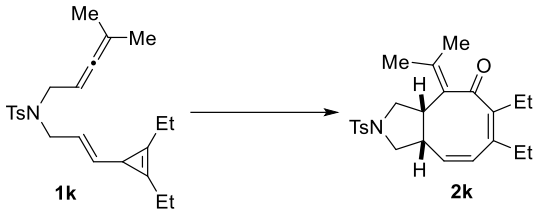
Melting Point: 128 – 130 °C.

TLC (5:1 PE/EA, R_f): 0.4.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.10 (d, J = 8.1 Hz, 1H), 7.96 (d, J = 7.4 Hz, 1H), 7.72 – 7.64 (m, 2H), 7.53 (dd, J = 7.4 Hz, 1H), 6.52 (d, J = 6.3 Hz, 1H), 3.04 (dd, J = 8.4, 6.1 Hz, 1H), 2.63 (s, 3H), 2.46 – 2.32 (m, 1H), 2.26 – 2.04 (m, 2H), 1.84 – 1.72 (m, 1H), 1.13 (t, J = 7.2 Hz, 3H), 0.75 (t, J = 7.3 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 192.6, 188.8, 155.7, 149.1, 145.2, 142.5, 135.0, 134.9, 134.5, 133.6, 130.2, 127.7, 124.6, 123.9, 56.0, 24.8, 20.9, 19.3, 12.2, 11.1.

HRMS (ESI) m/z: calcd. for $C_{20}H_{21}O_2$ ($[M+H]^+$): 293.1536, found: 293.1535.



Run 1: Following general procedure A. Substrate: **1k** (38.5 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol), toluene (4 mL), 30 °C for 5 h and 50 °C for 4 h, flash column chromatography (silica gel, 50:1 to 20:1 to 10:1 PE/EA); product: **2k** (17.8 mg, 43%).

Physical Form: white solid.

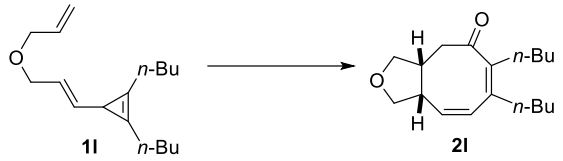
Melting Point: 138 – 140 °C.

TLC (5:1 PE/EA, R_f): 0.2.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.70 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 5.96 (d, J = 11.8 Hz, 1H), 5.50 – 5.32 (m, 1H), 3.62 – 3.53 (m, 1H), 3.32 – 3.14 (m, 4H), 3.07 – 2.98 (m, 1H), 2.44 (s, 3H), 2.30 – 2.12 (m, 4H), 1.58 (s, 3H), 1.51 (s, 3H), 1.04 – 0.95 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 202.9, 143.7, 139.2, 135.1, 133.8, 133.1, 132.0, 129.9 (3C), 127.8, 127.6 (2C), 51.3, 49.6, 41.3 (2C), 28.1, 22.5, 21.7, 21.6, 20.7, 14.3, 12.9.

HRMS (ESI) m/z: calcd. for $C_{24}H_{32}NO_3S$ ([M+H]$^+$): 414.2097, found: 414.2104.



Run 1: Following general procedure A. Substrate: **1l** (24.4 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (1.9 mg, 0.005 mmol), toluene (2 mL), 70 °C for 12 h, flash column chromatography (silica gel, 20:1 PE/EA); product: **2l** (7.6 mg, 28%).

Run 2: Following general procedure A. Substrate: **1l** (25.1 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (1.9 mg, 0.005 mmol), mesitylene (2 mL), 70 °C for 12 h, flash column chromatography (silica gel, 20:1 PE/EA); product: **2l** (6.7 mg, 24%).

Run 3: Following general procedure B. Substrate: **1l** (24.5 mg, 0.1 mmol), $RhCl_3 \cdot nH_2O$ (2.6 mg, 0.01 mmol), toluene (2 mL), 70 °C for 12 h, flash column chromatography (silica gel, 20:1 PE/EA); product: **2l** (6.8 mg, 25%).

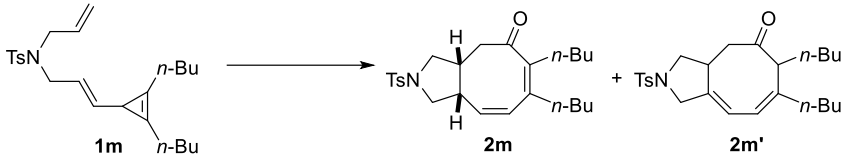
Physical Form: light yellow oil.

TLC (5:1 PE/EA, R_f): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.26 (dt, J = 11.8, 1.2 Hz, 1H), 5.81 (dd, J = 11.7, 7.5 Hz, 1H), 3.93 (dd, J = 8.0 Hz, 1H), 3.86 (d, J = 2.8 Hz, 2H), 3.30 (dd, J = 10.3, 8.0 Hz, 1H), 3.02 (dd, J = 12.7, 11.3 Hz, 1H), 2.94 (ddd, J = 9.5, 4.8, 2.2 Hz, 1H), 2.81 – 2.69 (m, 1H), 2.51 – 2.42 (m, 1H), 2.41 – 2.26 (m, 3H), 2.18 – 2.07 (m, 1H), 1.48 – 1.28 (m, 8H), 0.99 – 0.87 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 202.7, 148.2, 138.1, 134.9, 134.3, 73.7, 71.2, 48.2, 41.6, 41.5, 36.0, 32.6, 31.0, 28.8, 23.3, 23.1, 14.11, 14.09.

HRMS (ESI) m/z: calcd. for $C_{18}H_{29}O_2$ ([M+H]$^+$): 277.2162, found: 277.2160.



Run 1: Following general procedure A. Substrate: **1m** (40 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol), toluene (2 mL), 100 °C for 14 h, flash column chromatography (silica gel, 100:1 to 50:1 to 20:1 PE/EA); product: **2m** (5.1 mg, 12%) and **2m'** (3.3 mg, 8%).

Characterization of **2m**:

Physical Form: light yellow oil.

TLC (5:1 PE/EA, R_f): 0.2.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.72 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 6.20 (d, J = 11.7 Hz, 1H), 5.53 (dd, J = 11.8, 7.7 Hz, 1H), 3.49 – 3.37 (m, 2H), 3.20 (dd, J = 9.9, 5.0 Hz, 1H), 2.94 (dd, J = 12.5, 10.9 Hz, 1H), 2.89 – 2.77 (m, 2H), 2.50 – 2.38 (m, 2H), 2.45 (s, 3H), 2.36 – 2.18 (m, 3H), 2.15 – 2.04 (m, 1H), 1.38 – 1.22 (m, 8H), 0.94 – 0.86 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 202.2, 148.3, 143.8, 138.3, 134.7, 134.0, 133.6, 130.0, 127.5, 53.1, 50.7, 47.6, 41.4, 40.4, 36.2, 32.5, 31.1, 28.7, 23.3, 23.1, 21.7, 14.07, 14.05.

HRMS (ESI) m/z: calcd. for $C_{25}H_{36}NO_3S$ ($[M+H]^+$): 430.2410, found: 430.2414.

Characterization of **2m'**:

Physical Form: colorless oil.

TLC (5:1 PE/EA, R_f): 0.2.

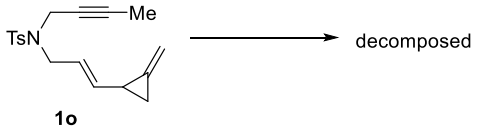
^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.72 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 7.9 Hz, 2H), 5.87 (d, J = 6.5 Hz, 1H), 5.73 (d, J = 6.2 Hz, 1H), 4.23 (d, J = 14.1 Hz, 1H), 3.85 – 3.77 (m, 2H), 3.72 – 3.64 (m, 1H), 2.90 – 2.84 (m, 1H), 2.83 – 2.73 (m, 1H), 2.44 (s, 3H), 2.09 – 2.02 (m, 1H), 1.97 – 1.90 (m, 2H), 1.90 – 1.79 (m, 1H), 1.54 – 1.44 (m, 1H), 1.36 – 1.18 (m, 8H), 1.11 – 1.01 (m, 1H), 0.91 – 0.82 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 206.8, 143.9, 140.6, 139.4, 133.6, 130.0, 127.8, 122.5, 120.7, 55.0, 53.9, 53.7, 41.0, 38.5, 33.0, 29.98, 29.95, 25.8, 22.9, 22.7, 21.7, 14.1, 14.0.

HRMS (ESI) m/z: calcd. for $C_{25}H_{36}NO_3S$ ($[M+H]^+$): 430.2410, found: 430.2407.

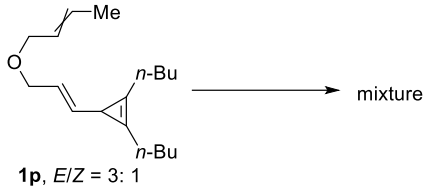
1n

Run 1: Following general procedure A. Substrate: **1n** (22.2 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (1.9 mg, 0.005 mmol), toluene (4 mL), 12.5 h, gave side products.



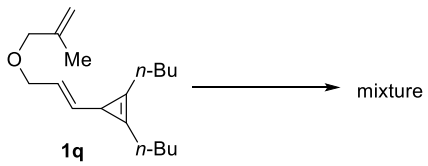
1o

Run 1: Following general procedure A. Substrate: **1o** (31.6 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (1.9 mg, 0.005 mmol), toluene (2 mL), 70 °C for 11.5 h, decomposed.



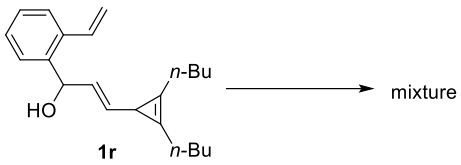
1p, *E*/*Z* = 3: 1

Run 1: Following general procedure A. Substrate: **1p** (25.9 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol), toluene (2 mL), 70 °C for 33 h, gave a mixture.

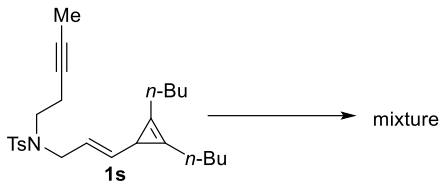


1q

Run 1: Following general procedure A. Substrate: **1q** (26.4 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.005 mmol), toluene (2 mL), 70 °C for 33 h, gave a mixture.



Run 1: Following general procedure A. Substrate: **1r** (61.8 mg, 0.2 mmol), $[Rh(CO)_2Cl]_2$ (3.9 mg, 0.01 mmol), toluene (4 mL), 70 °C for 8 h, gave a mixture.



Run 1: Following general procedure A. Substrate: **1s** (43.2 mg, 0.1 mmol), $[Rh(CO)_2Cl]_2$ (1.9 mg, 0.005 mmol), toluene (2 mL), 80 °C for 10 h, gave a mixture.

5. DFT Studies

DFT calculations were performed with Gaussian 16 C.02 program package.[17] Geometry optimizations of all of the minima and transition states were carried out with the PW6B95 functional[17] with D3(BJ) dispersion correction[19] in the gas phase, The def2-TZVP basis set with corresponding effective core potential (ECP)[20] was used for Rh, and the 6-311G(d,p)[21] basis set was used for all other atoms. PRuned integration grids with 99 radial shells and 590 angular points per shell were used in DFT calculations (int = ultrafine). Enthalpy and Gibbs free energy corrections at 298 K were obtained through frequency analyses. Solvent effects were considered based on gas-phase-optimized structures using the same basis set and functional. Solvation energies in mesitylene were evaluated by a self-consistent reaction field employing the SMD model of toluene.[22] Single-point energy calculations were performed with ORCA 5.0.4[23] based on the optimized structures. The ωB97M-V functional,[24] and def2-QZVP basis sets were utilized. The SCF convergence criterion was set via the 'TightSCF' keyword in ORCA. In this paper, all discussed energies are Gibbs free energies in the solution phase ($\Delta G_{\text{toluene}}$ 298 K). Standard state concentrations of 7.4 mM[11b] and 1.0 M[25] were used for CO and the other species, respectively. All of the 3D structures were prepared with CYLview.[26]

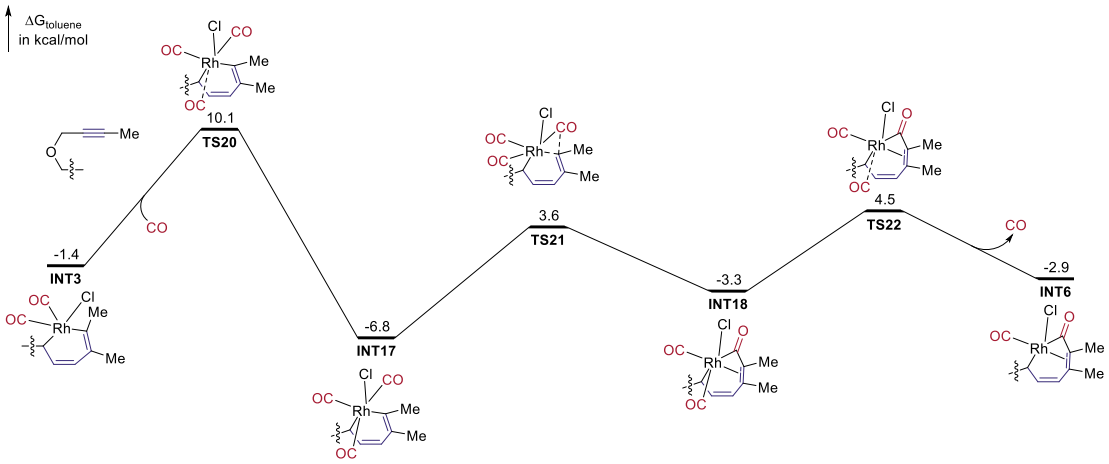


Figure S3. An alternative pathway for the CO insertion step in the [5 + 1 + 2] pathway

In Scheme 3, the oxygen tether promotes the CO insertion step (**TS4**). There is an alternative pathway for the CO insertion step for common substrates (independent of the tether groups). For **INT3**, coordination of another CO occurs via **TS20** with an activation free energy of 11.5 kcal/mol to give **INT17**, followed by the CO insertion step via **TS21** with an activation free energy of 10.4 kcal/mol. Then, dissociation of CO (**TS22**, 7.8 kcal/mol) occurs to generate **INT6**. **TS20** is still favored over **TS14** by 1.5 kcal/mol. Therefore, the [5 + 1 + 2] pathway is favored for common yne-VCPEs (independent of the tether groups).

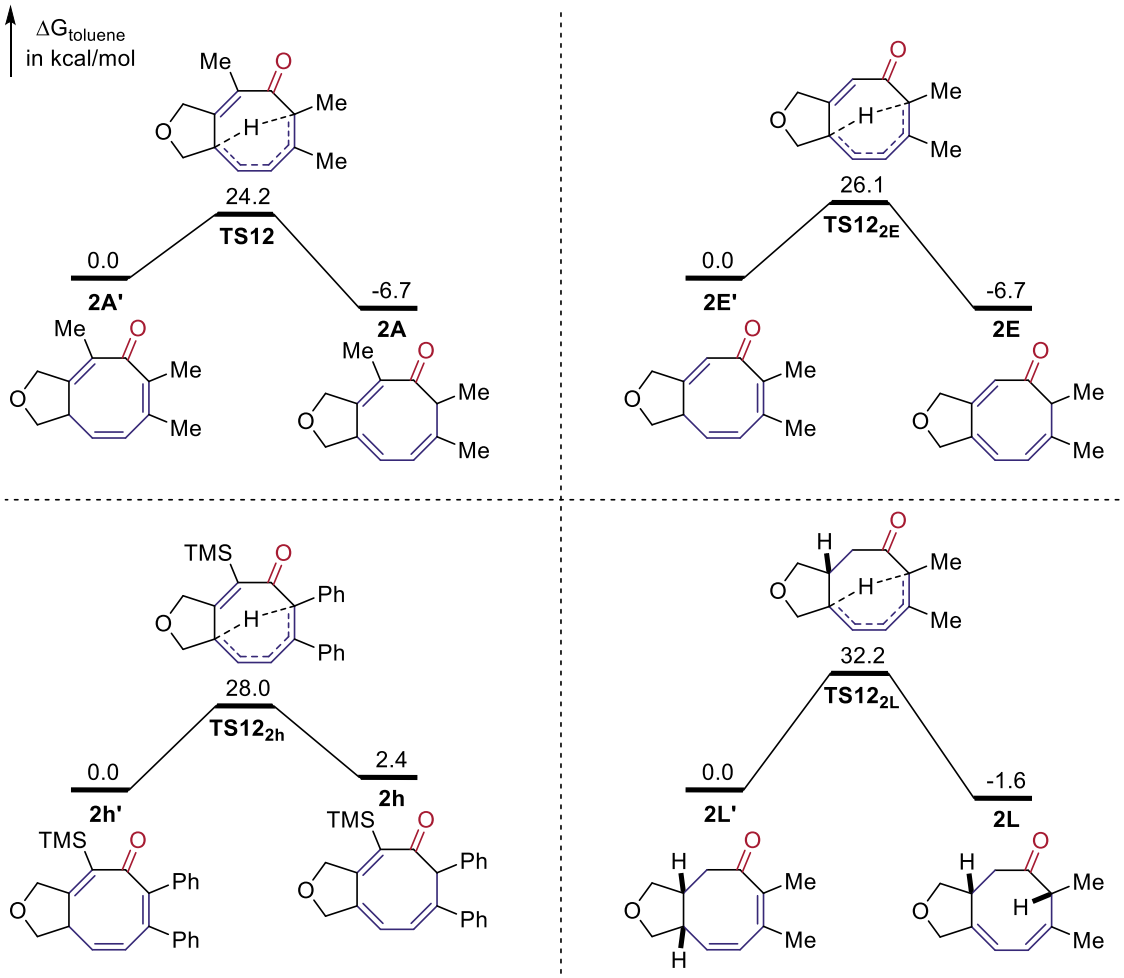


Figure S4. Calculations of [1,5]-H shift

The activation free energy of [1,5]-H shift of **2A'** (model substrate representing **2a'** except that Me instead of *n*-Bu group was used in the cyclopropene moiety) is 24.2 kcal/mol (**TS12**), **2A** is more stable than **2A'** by 6.7 kcal/mol. Therefore, this [1,5]-H shift is completed within 6 h at 30 °C, and **2A** can be obtained as the sole product. The activation free energy of **2E'** (model substrate representing **2e'** except that Me instead of *n*-Bu group was used in the cyclopropene moiety) is 26.1 kcal/mol (**TS12$_{2E}$**), higher than **TS12,** showing that the alkyl group can decrease the energy barrier, but do not affect the thermodynamic stability (**2E'** and **2E**). For substrate **1e**, a higher reaction temperature is needed (50 °C) to give the pure **2e**. However, the TMS-substituted product **2h'** is more stable than **2h** by 2.4 kcal/mol. Therefore, **2h'** is the major product. As for **2L'** (model substrate representing **2l** except that Me instead of *n*-Bu group was used in the cyclopropene moiety), the activation free energy of [1,5]-H shift is high (32.2 kcal/mol, **TS12$_{2L}$**), and we can only obtain **2l** at 70 °C. However, **1m** can deliver **2m** and **2m'** at 100 °C, which is consistent with the calculations.

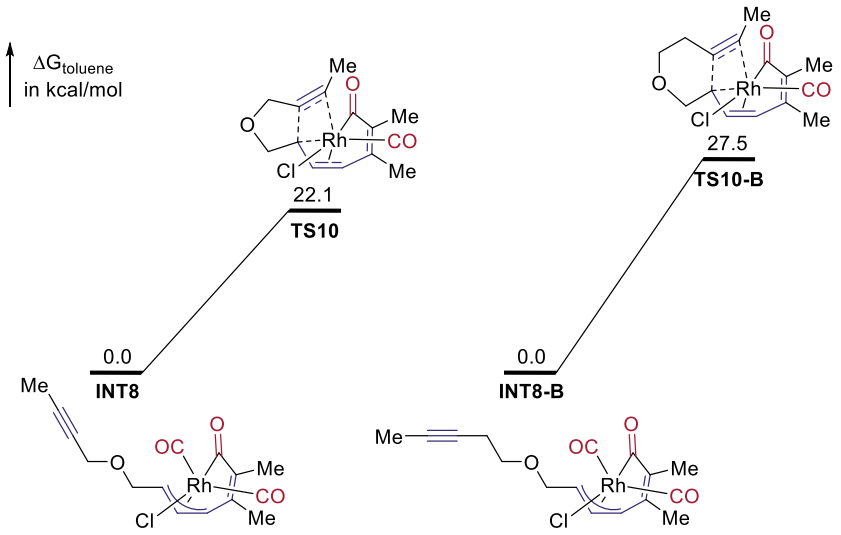


Figure S5. Calculations of the substrate with a longer tether

The migratory insertion of alkyne is more difficult for the substrate with a longer tether (**TS10-B**, 27.5 kcal/mol). The VCPEs are highly active and can undergo many reactions, such as rearrangement, [5 + 1], and carbene-type reactions (scheme 1). Therefore, a mixture was obtained for **1s**.

More discussions of Scheme 5 and chemoselectivity of yne-VCP and yne-VCPE:

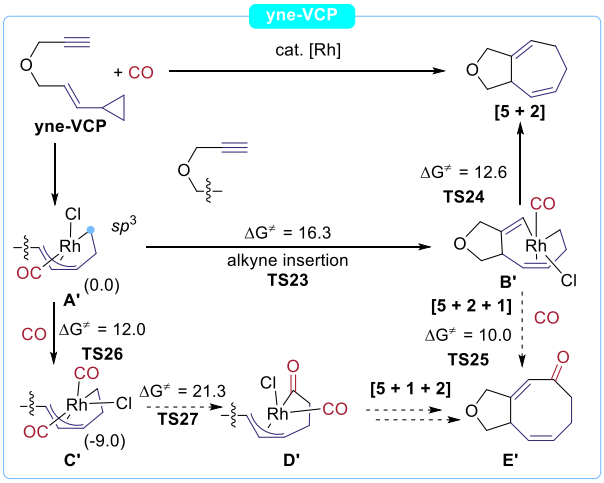


Figure S6. New reaction energies of yne-VCP

The calculation methods for reactions shown in Scheme 5 of the main text are different. We aim to understand the different chemoselectivity of different substrates. Therefore, the relative energies shown in Scheme 5 are more important. Here we show that the conclusion in the main text is kept even when we use the same computational method for both reactions in Scheme 5.

In Scheme 5, the computational method for yne-VCP is DLPNO-CCSD(T)/def2-TZVPP:SMD(mesitylene)//BMK/def2-SVP, and these computational results agreed with experiment.[8a] Figure S6 shows the new reaction energies for yne-VCP using the method applied for yen-VCPE, which is ωB97M-V/def2-QZVP:SMD(toluene)//PW6B95-D3(BJ)/6-311G(d,p), (def2-TZVP for Rh). In this case, the alkyne insertion is disfavored over CO insertion, disagreeing with

the experimental result. This could be two reasons: 1, DFT calculations here introduce errors and DLPNO-CCSD(T) is required, which is the case of the results in Scheme 5, left; 2, the steps for controlling selectivity could be changed to other steps, considering that many steps having similar energies are involved in the reaction.

Despite this, Figure S6 supports that the activation free energies for CO insertion from **C'** to **D'** are very close (21.3 and 22.6 kcal/mol) using both computational methods. More importantly, C(sp^2) promotes the CO insertion step, which is supported by comparing Scheme 5, right, and Figure S6 and agrees with the conclusion in the main text.

In addition, we must point out that the activation energies in Scheme 5 are related to the highest transition states of the discussed processes. For example, the CO rotation is the most difficult step for the alkyne insertion step (Scheme 5, left, 10.1 kcal/mol), and oxygen coordination is the most difficult step for the CO insertion step (Scheme 5, right, 16.1 kcal/mol).

Discussion of the substituent effect in yne-VCP:

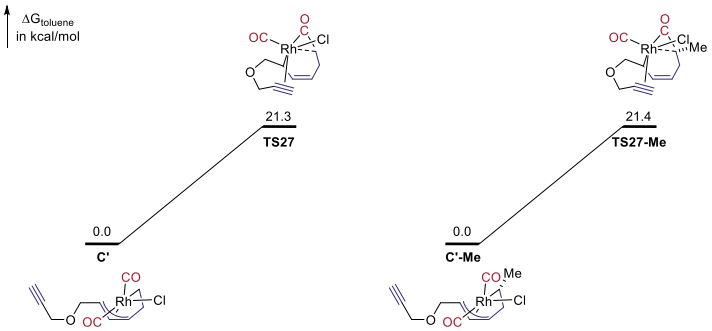


Figure S7. Discussion of the steric effect

The energies in Figure S7 were computed at the ωB97M-V/def2-QZVP:SMD(toluene)//PW6B95-D3(BJ)/6-311G(d,p), (def2-TZVP for Rh) level, the same as the computation method of [5 + 1 + 2] reaction of yne-VCPEs. When H is replaced with Me, there is no significant change in the energy barrier of the CO insertion step. Therefore, the discussion of Scheme 5 can be compared, even though there is an additional Me group for yne-VCPE.

Discussion of the chemoselectivity of yne-3-acyloxy-1,4-enyne (yne-ACE):

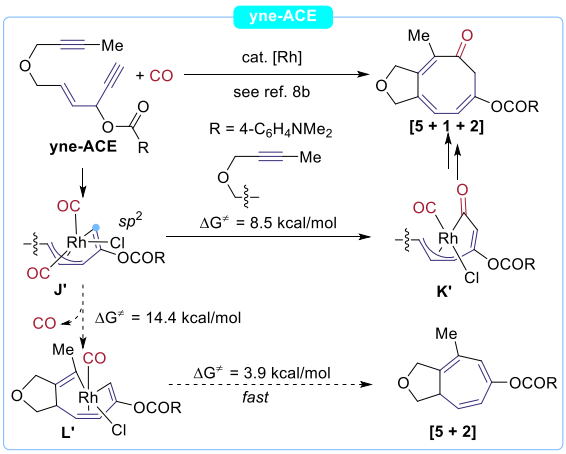


Figure S8. The [5 + 1 + 2] and [5 + 2] pathways of yne-ACE

Previously, we found that yne-ACEs can undergo [5 + 1 + 2] reaction,[8b] and the key steps in this reaction and the competing [5 + 2] pathway with the computed energies (DLPNO–CCSD(T)/def2-TZVPP:SMD(1,4-dioxane)//SMD(1,4-dioxane)/BMK/def2-SVP) are given in Figure S8. Here, intermediate **J'** is generated from yne-ACE, which features a sp^2 carbon. The CO insertion step with an activation free energy of 8.5 kcal/mol is easier compared with yne-VCP (22.6 kcal/mol) due to the presence of C(sp^2). The CO insertion is favored over the alkyne insertion by 5.9 kcal/mol. Therefore, comparison of Scheme 5 and Figures S6, S8 leads to the conclusion that C(sp^2) helps CO insertion.

Computed Energies for the Stationary Points:

Table S2. 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] (a. u.)	SPE[b] (a. u.)	SPE[c] (a. u.)
CO	none	-113.478262	-0.01398	-113.473793	-113.344211
$[Rh(CO)_2Cl]_2$	none	-1596.615168	-0.008113	-1596.616333	-1595.091125
1A	none	-542.801752	0.200944	-542.816646	-541.951301
INT0	none	-1341.116089	0.211899	-1341.133434	-1339.499217
TS1	-119.53	-1341.08752	0.205987	-1341.105491	-1339.472834
INT1	none	-1341.109899	0.208231	-1341.127832	-1339.492203
TS2	-46.18	-1341.092311	0.207176	-1341.109972	-1339.472476
INT2	none	-1341.141629	0.215289	-1341.160797	-1339.525105
TS3	-58.16	-1341.124101	0.209759	-1341.14385	-1339.505302
INT3	none	-1341.125972	0.20994	-1341.145831	-1339.506275
TSco	-76.54	-1341.119657	0.213012	-1341.135749	-1339.500119
INT4	none	-1341.131148	0.214336	-1341.147454	-1339.513076
TS4	-262.43	-1341.122807	0.213591	-1341.140858	-1339.502523
INT5	none	-1341.131677	0.212408	-1341.152828	-1339.5085
TS5	-25.01	-1341.127074	0.212852	-1341.148819	-1339.505826
INT6	none	-1341.127809	0.211487	-1341.150141	-1339.507766
TS6	-68.70	-1341.121943	0.214237	-1341.144757	-1339.500897
INT7	none	-1341.154104	0.212536	-1341.178814	-1339.53251
TS7	-76.67	-1454.629309	0.213214	-1454.649692	-1452.871636
INT8	none	-1454.666447	0.218426	-1454.687025	-1452.91032
INT8-B	none	-1494.043818	0.244904	-1494.065861	-1492.219995
TS8	-50.37	-1454.633987	0.21448	-1454.652706	-1452.876588
INT9	none	-1341.149311	0.212639	-1341.172239	-1339.528196
TS9	-13.04	-1341.148884	0.216614	-1341.169632	-1339.527786

INT10	none	-1341.169374	0.22048	-1341.188715	-1339.54862
TS10	-239.22	-1341.142434	0.221013	-1341.163395	-1339.522035
TS10-B	-230.04	-1380.512793	0.249187	-1380.533998	-1378.825924
INT11	none	-1341.195319	0.222685	-1341.215186	-1339.576788
TS11	-241.86	-1341.185075	0.223375	-1341.204729	-1339.566958
INT12	none	-1341.213132	0.226231	-1341.233264	-1339.59694
2A'	none	-656.410307	0.222317	-656.42479	-655.4228396
TS12	-1376.95	-656.370452	0.217637	-656.38512	-655.379371
2A	none	-656.42572	0.223687	-656.439701	-655.435358
TS13	-103.07	-1341.10446	0.205552	-1341.121254	-1339.488897
INT13	none	-1227.626404	0.204512	-1227.646142	-1226.146482
TS14	-235.10	-1227.606331	0.202018	-1227.622772	-1226.125783
INT14	none	-1227.628325	0.204782	-1227.645748	-1226.147393
TS15	-26.06	-1227.617013	0.20862	-1227.636188	-1226.137272
INT15	none	-1227.648114	0.213065	-1227.665584	-1226.169243
TS16	-216.12	-1227.624299	0.21283	-1227.642632	-1226.145236
INT16	none	-1227.666829	0.214382	-1227.684757	-1226.189941
TS17	-288.84	-1227.659964	0.214555	-1227.67839	-1226.182777
TS18	-239.65	-1454.64468	0.225782	-1454.661082	-1452.892768
TS19	-302.77	-1341.158667	0.221275	-1341.178532	-1339.539883
2E'	none	-617.030581	0.196111	-617.045224	-616.1119635
$TS12_{2E}$	-1385.18	-616.988974	0.191875	-617.003612	-616.0661072
2E	none	-617.045914	0.197683	-617.060172	-616.1245503
2h'	none	-1410.266987	0.387619	-1410.289794	-1408.284336
$TS12_{2h}$	-1309.23	-1410.226797	0.382773	-1410.248915	-1408.235598
2h	none	-1410.26741	0.387265	-1410.290006	-1408.280365
2L'	none	-618.261371	0.219877	-618.2751	-617.3318527
$TS12_{2L}$	-1486.58	-618.210098	0.216206	-618.22389	-617.2767633
2L	none	-618.263095	0.220257	-618.277017	-617.3346259
TS20	-167.58	-1454.601199	0.212461	-1454.619701	-1452.847122
INT17	none	-1454.62811	0.214375	-1454.645473	-1452.877123
TS21	-222.82	-1454.615699	0.216218	-1454.634856	-1452.86062
INT18	none	-1454.631347	0.22008	-1454.650576	-1452.875447
TS22	-25.62	-1454.613136	0.214086	-1454.633297	-1452.856099
A'	none	-1110.702694	0.1518	-1110.723314	-1109.420644
TS23	-152.88	-1110.686024	0.152601	-1110.702278	-1109.399825

B'	none	-1110.754167	0.159525	-1110.772373	-1109.469501
TS24	-407.82	-1110.734806	0.159837	-1110.75134	-1109.451327
TS25	-200.90	-1224.238011	0.167368	-1224.25744	-1222.815575
TS26	-62.12	-1224.184898	0.15255	-1224.198619	-1222.764463
C'	none	-1224.222865	0.15755	-1224.237951	-1222.801676
TS27	-336.45	-1224.195747	0.16292	-1224.212255	-1222.771756
C'-Me	none	-1263.598486	0.184432	-1263.614414	-1262.108511
TS27-Me	-282.57	-1263.572545	0.190048	-1263.588477	-1262.079977

[a]Computed at the PW6B95-D3(BJ)/6-311G(d,p), (def2-TZVP for Rh) level

[b]Computed at the SMD(toluene)/PW6B95-D3(BJ)/6-311G(d,p), (def2-TZVP for Rh)//PW6B95-D3(BJ)/6-311G(d,p), (def2-TZVP for Rh) level

[c]Computed at the ωB97M-V/def2-QZVP//PW6B95-D3(BJ)/6-311G(d,p), (def2-TZVP for Rh) level

Cartesian coordinates of the stationary points:

CO

C	0.00000000	0.00000000	-0.64163400
O	0.00000000	0.00000000	0.48122500

$[Rh(CO)_2Cl]_2$

C	-2.62923400	1.31956100	-0.57637400
O	-3.28472600	2.13953200	-1.00285200
C	-2.62961600	-1.31931400	-0.57590100
O	-3.28570500	-2.13907400	-1.00186700
Rh	-1.53741500	0.00008800	0.12052400
Cl	0.00012000	1.61678800	1.03130600
Cl	-0.00007600	-1.61673400	1.03140900
Rh	1.53733600	-0.00009700	0.12030900
C	2.62914000	-1.31959100	-0.57656700
C	2.62970900	1.31925600	-0.57594000
O	3.28586900	2.13899700	-1.00183300
O	3.28491800	-2.13945100	-1.00281900

1A

O	-2.63619400	-1.77407500	0.24047800
C	2.53998600	0.56084200	0.72711800
C	3.07621900	0.00852300	-0.30499100
C	1.97457800	-0.78859000	0.35121400
C	0.63946900	-0.87534200	-0.26190100
C	-0.22906400	-1.87142700	-0.10827400
C	-1.58952600	-1.86290200	-0.72137100
C	-2.56696300	-0.62393800	1.05518200
H	2.24511700	-1.65451700	0.95645900
H	0.34834500	-0.02537300	-0.87505400
H	0.02409600	-2.71972400	0.51918900
H	-1.66776600	-1.03453400	-1.43144400
H	-1.79435100	-2.79067400	-1.25200800
H	-3.43173500	-0.68194400	1.71298200
H	-1.66711600	-0.64593600	1.67757700
C	-2.58758200	0.63652500	0.31530600
C	-2.57791400	1.66468000	-0.30498200
C	-2.58085300	2.91113900	-1.04829000
H	-3.25962000	2.85655600	-1.89820000
H	-2.90485100	3.73757300	-0.41712100
H	-1.58722600	3.14869000	-1.42604900
C	2.37754100	1.65199600	1.69794000
H	2.57055200	1.29493700	2.70989100
H	3.05210500	2.47930800	1.48774800
H	1.35242200	2.02284900	1.68018600
C	4.02405000	-0.02279400	-1.42813500
H	4.62196600	0.88511800	-1.47115000

H	4.69565000	-0.87682700	-1.33681600	H	-1.59355800	1.94119800	2.07818800
H	3.49232400	-0.13517400	-2.37290500	H	-1.32392400	3.68430900	2.27209600

INT0

O	2.41519100	-1.45441600	-2.18709000	O	3.79339700	-2.07001100	-1.31727200
C	0.88094800	3.07597000	0.20773900	C	0.24563400	2.08628400	-0.50851200
C	-0.28548900	2.77486300	0.65490500	C	-0.78384400	1.83778100	0.22368300
C	0.14021900	2.01102900	-0.57620300	C	0.05584700	0.64868400	-0.79974500
C	0.57738000	0.61540900	-0.45497700	C	1.07506600	-0.28628700	-0.30285900
C	0.41223000	-0.36147300	-1.40288900	C	1.49998400	-1.35914000	-0.96720100
C	1.23804500	-1.61783800	-1.41243100	C	2.64621500	-2.18850400	-0.48857100
C	3.33031400	-0.50488100	-1.67595400	C	4.27575700	-0.74848600	-1.45150700
H	-0.33280400	2.25303400	-1.52354200	H	-0.38018300	0.41947500	-1.76899300
H	1.22427700	0.39889700	0.39099500	H	1.55775000	-0.01593900	0.63134400
H	-0.08190200	-0.09663800	-2.32933600	H	1.04718900	-1.62587400	-1.91517100
H	1.50675900	-1.91175000	-0.39555200	H	2.89583200	-1.91108600	0.53916600
H	0.70106400	-2.43556700	-1.88238700	H	2.40070800	-3.24796000	-0.51141400
H	4.21466900	-0.59318500	-2.30279000	H	5.18589500	-0.83276900	-2.04105400
H	2.94142300	0.51184000	-1.79775500	H	3.56598500	-0.13600300	-2.01687800
C	3.68069500	-0.71203300	-0.27344700	C	4.55973000	-0.08035200	-0.18380400
C	3.90497500	-0.89317900	0.89273000	C	4.75969800	0.46589900	0.86704000
Rh	-1.36448600	-0.63457800	0.01308000	Rh	-1.84104900	-0.24712400	0.16335200
Cl	-2.67400400	0.43076600	-1.62815600	Cl	-3.01432700	0.55418900	-1.71710600
C	-0.36527900	-1.46405600	1.32683500	C	-0.96233500	-0.83011200	1.69231800
C	-3.00772000	-1.11331800	0.82169000	C	-3.31145700	-1.38194700	0.47115800
O	0.25775800	-1.94556000	2.15080300	O	-0.43914000	-1.17425500	2.64231600
O	-4.00107800	-1.39231100	1.28277500	O	-4.21546000	-2.04133000	0.63634200
C	4.18124900	-1.12406600	2.29836300	C	5.02539900	1.12250900	2.13369900
H	4.47087900	-0.19951400	2.79535300	H	5.70109100	1.96554100	1.99708700
H	3.29828000	-1.51344400	2.80345300	H	4.10833600	1.49808700	2.58558500
H	4.98793000	-1.84370400	2.42688800	H	5.49015400	0.43422500	2.83786000
C	2.15061400	3.81562300	0.21324700	C	1.20795200	3.10700800	-0.95623800
H	2.20404000	4.50221300	1.05501700	H	1.03730000	4.05888600	-0.46066100
H	2.99284500	3.12548800	0.27102500	H	2.22735400	2.77863300	-0.75227900
H	2.26262900	4.38586900	-0.70883500	H	1.12227600	3.25406000	-2.03275400
C	-1.44507100	2.88227500	1.54784700	C	-1.77782900	2.49373500	1.11414000
H	-2.34629100	3.05627000	0.96061800	H	-2.76697900	2.46843800	0.66175200

TS1

H	-1.83592200	2.02024000	2.09076500	H	-1.52261700	3.85263200	-0.70653500
H	-1.47131100	3.53378800	1.24291100	H	-3.04234300	2.96475000	-0.54092500

INT1

O	4.00258100	-2.10777200	-0.74804000	O	3.35508800	-1.48045000	-0.21534900
C	-0.25672300	1.39891900	-1.03642400	C	-0.65449100	1.83095000	-0.53342500
C	-1.31396300	1.76255300	-0.32578100	C	-1.85018400	1.72020600	0.06673800
C	-0.14217100	-0.07998500	-0.83183500	C	-0.30211700	0.53255200	-1.17757400
C	1.03020900	-0.60655400	-0.14853800	C	0.94054000	-0.12437200	-0.83655800
C	1.62717700	-1.76206200	-0.45253800	C	1.52759100	0.01444500	0.36638900
C	2.92036500	-2.17929400	0.16757300	C	2.72547600	-0.75841600	0.81528100
C	4.21364900	-0.82150900	-1.30041800	C	4.19353400	-0.68360000	-1.03468900
H	-0.46737400	-0.68491500	-1.67636100	H	-0.69853200	0.38000600	-2.17220400
H	1.48432300	0.02900400	0.60518600	H	1.35448500	-0.84700700	-1.52970500
H	1.21842100	-2.39321600	-1.23393000	H	1.12026400	0.72376900	1.07945900
H	3.12648600	-1.55682000	1.04225400	H	3.44062500	-0.08904700	1.30647400
H	2.89151300	-3.22087900	0.47974600	H	2.42654500	-1.49570900	1.56277900
H	5.12378700	-0.90953500	-1.88911000	H	4.52754300	-1.34139700	-1.83391400
H	3.39844000	-0.55701700	-1.98188800	H	3.62236400	0.13162600	-1.49053800
C	4.35247800	0.24340900	-0.31153700	C	5.34383800	-0.13233300	-0.32691700
C	4.42001700	1.11754900	0.50936700	C	6.29057500	0.32145800	0.25501300
Rh	-1.86440400	-0.06251300	0.39407000	Rh	-1.72460200	-0.24298900	0.18727700
Cl	-3.27129000	-0.28685300	-1.46312800	Cl	-3.24663300	-0.39091300	-1.60465000
C	-0.85841000	0.39572300	1.90332400	C	-3.08288400	-0.45159700	1.58684500
C	-2.19305400	-2.04973000	0.77228400	C	-1.16263300	-2.18588600	0.09408600
O	-0.26914800	0.72664600	2.81525700	O	-3.94809100	-0.47917700	2.31496800
O	-2.30430000	-3.16618900	0.86715300	O	-0.85637600	-3.26396700	-0.04231800
C	4.51445800	2.17782400	1.49542700	C	7.44084200	0.86218800	0.95442900
H	5.20746700	1.91052300	2.29150500	H	8.33861300	0.77933000	0.34373900
H	4.87139900	3.09869400	1.03679900	H	7.29651700	1.91296700	1.20080100
H	3.54440700	2.38349200	1.94611900	H	7.61854400	0.31947000	1.88162600
C	0.65277600	2.14969600	-1.94993000	C	0.26042000	3.02162900	-0.54604200
H	1.69583800	2.01211700	-1.65662100	H	-0.06496700	3.78438000	0.15693000
H	0.55324300	1.79124900	-2.97599200	H	1.28064000	2.73545700	-0.30121600
H	0.43086800	3.21414800	-1.94142300	H	0.27709100	3.45957300	-1.54572400
C	-2.02414300	3.05180700	-0.16110700	C	-2.81770800	2.70597900	0.58556800
H	-2.09279600	3.34382900	0.88705900	H	-3.08913500	2.51073000	1.62161300

H	-2.44016600	3.72602900	0.50399600	H	-3.59020400	-1.17430300	2.26820900
H	-3.73233800	2.63935300	-0.00580900	H	-2.60166300	-2.28587200	1.31235500

INT2

O	1.95839800	2.15386200	-0.14201900	O	-2.24606800	-0.49660900	0.33098400
C	-2.90088700	0.75469000	0.41048800	C	2.21610400	2.01152400	-0.31394100
C	-2.20142800	-0.25669300	0.91791000	C	2.04698300	1.10161800	0.67976500
C	-2.06978800	1.46453900	-0.58881400	C	1.55703100	1.76576700	-1.56596400
C	-0.82237600	1.99987400	-0.29169700	C	0.37768200	1.09123200	-1.68820300
C	-0.11861400	1.59910800	0.88551200	C	-0.45093000	0.78125400	-0.54713000
C	1.29434300	2.04950800	1.10011400	C	-1.79056700	0.16578100	-0.82519200
C	3.34527300	1.88447000	-0.07673900	C	-3.54990500	-1.02902100	0.19330900
H	-2.48932200	1.67180600	-1.56580200	H	2.05361400	2.09925500	-2.46941900
H	-0.28114000	2.52828300	-1.06469800	H	0.04741500	0.77926100	-2.67064500
H	-0.70136700	1.49972900	1.79386500	H	-0.48672200	1.56909100	0.19971800
H	1.31081200	3.02450300	1.60295100	H	-1.72338400	-0.53810400	-1.66445200
H	1.80300100	1.33146400	1.74689100	H	-2.49817800	0.95469400	-1.10490200
H	3.73710200	2.11693300	-1.06468800	H	-3.72691000	-1.60567500	1.09827500
H	3.83251400	2.55475600	0.63876900	H	-3.58119000	-1.72175300	-0.65550100
C	3.63722800	0.49509200	0.26331000	C	-4.58164800	-0.01089700	0.03598400
C	3.85877100	-0.65507300	0.52862600	C	-5.42469700	0.83342900	-0.09402800
Rh	-0.50883700	-0.18179500	-0.20690900	Rh	0.98552500	-0.55935600	0.16187100
Cl	-1.56633900	-1.81638100	-1.69682200	Cl	2.92821600	-1.37674000	-1.02417400
C	0.39292700	-1.45851100	0.85697400	C	0.14875700	-0.54776700	1.81170900
C	0.93914800	-0.04699800	-1.64648900	C	0.11737400	-2.27243300	-0.46166900
O	0.91042900	-2.21122700	1.52766200	O	-0.32839400	-0.56154200	2.84244000
O	1.67166800	-0.04769500	-2.50136300	O	-0.32147900	-3.25530500	-0.79543100
C	4.15042400	-2.04309000	0.83324800	C	-6.44968700	1.84909800	-0.24189800
H	5.21370900	-2.24294900	0.71116500	H	-6.69416000	2.01398800	-1.28997300
H	3.87437700	-2.28746900	1.85724200	H	-7.36161800	1.55437900	0.27500300
H	3.60405900	-2.71102100	0.16950800	H	-6.11851800	2.79615600	0.18124800
C	-4.32719700	1.14369700	0.62337000	C	3.14073400	3.19845600	-0.21277100
H	-4.80281500	0.50770500	1.36524100	H	3.27736200	3.66148900	-1.18766500
H	-4.41306100	2.17926000	0.95528400	H	2.73696700	3.96210200	0.45288300
H	-4.89072200	1.05120400	-0.30659200	H	4.12199800	2.91572600	0.16290000
C	-2.59697700	-1.33608500	1.84901000	C	2.70362800	1.22060900	2.00961500
H	-1.88888700	-1.43144400	2.67399800	H	3.18577900	2.18502100	2.16357700

H	1.98519900	1.06779400	2.81692900	H	2.82390900	-0.12346800	2.51152800
H	3.45641800	0.43791800	2.11734600	H	4.16445200	0.40952500	1.53244400

INT3

O	-2.17012600	-0.36479000	0.44412600
C	2.41561400	1.89825700	-0.17344900
C	2.28338100	0.80717700	0.62868600
C	1.58263000	2.08252200	-1.32647200
C	0.36687800	1.50973500	-1.47513500
C	-0.32076900	0.87134400	-0.38204400
C	-1.68950400	0.33632800	-0.67986600
C	-3.47064700	-0.89078800	0.25895800
H	1.98373700	2.66965300	-2.14278600
H	-0.09930300	1.49798400	-2.45239800
H	-0.30528900	1.47257800	0.52302300
H	-1.66741500	-0.31723200	-1.56053100
H	-2.35597500	1.17745100	-0.90464700
H	-3.67592400	-1.48510900	1.14642800
H	-3.47713300	-1.56625700	-0.60441900
C	-4.49458500	0.13338100	0.09135800
C	-5.33198500	0.98183200	-0.04759700
Rh	0.99901400	-0.70786500	0.18165700
Cl	2.17451300	-1.20748100	-1.81986800
C	0.28671800	-0.57274400	1.90485000
C	-0.15802500	-2.27514100	-0.35359600
O	-0.12639000	-0.50635300	2.95867000
O	-0.79312600	-3.14460500	-0.68830700
C	-6.34851100	2.00385700	-0.20922300
H	-6.63987200	2.10864100	-1.25303000
H	-7.23892700	1.75822800	0.36735500
H	-5.98290000	2.96906200	0.13778000
C	3.50749600	2.90965200	0.07023700
H	3.60654900	3.58872300	-0.77323400
H	3.29427400	3.51433700	0.95403200
H	4.47204100	2.43076700	0.23332600
C	3.14987000	0.67183400	1.84556200
H	3.22117000	1.59875200	2.41879200

TSco

C	-0.64655000	1.64817000	-1.99786100
C	0.02884800	0.41990000	-1.59425100
Rh	-0.94653800	-0.67309300	-0.08199600
H	0.19435700	-0.25486400	-2.42930300
C	-1.44858300	1.06525900	0.87194700
C	-1.42686300	2.29034500	0.28028800
H	-0.68851900	1.87172500	-3.05662400
C	-1.20638300	2.50838800	-1.13128600
H	-1.58280400	3.44514400	-1.52443000
C	1.32154600	0.66397600	-0.84085700
H	2.09297700	1.03687300	-1.52209700
H	1.16501400	1.40692300	-0.05565000
O	1.71141000	-0.57555100	-0.27711000
C	2.61325200	-0.45367100	0.81114800
H	2.72970000	-1.45770100	1.20933800
H	2.15209300	0.15440800	1.59528500
C	3.89574200	0.11013000	0.41234100
C	4.94394600	0.58791300	0.07496000
C	6.21886400	1.15368200	-0.32378000
H	6.19717800	2.24178200	-0.28754300
H	6.47638700	0.85424100	-1.33861600
H	7.01478100	0.81137100	0.33597400
Cl	-0.28546300	-1.76512500	1.98887100
C	-0.35960400	-2.46631300	-0.86489000
O	-0.01376900	-3.46622300	-1.24610100
C	-2.50707300	-0.36710600	-0.95543900
O	-3.51032600	-0.20007200	-1.46294200
C	-1.71919100	3.53845200	1.08378400
H	-1.50476100	4.43262000	0.50392200
H	-2.76485500	3.58275300	1.39209700
H	-1.11577800	3.57699900	1.98882400
C	-1.82351400	0.93920600	2.31635300
H	-0.93246300	0.95452600	2.94696800

H	-2.47812800	1.75120200	2.63139700	H	-0.83821000	2.09463600	2.80552400
H	-2.31321600	-0.00692400	2.52395900	H	-1.69368200	0.54648300	2.70897300

INT4

C	-0.91258700	1.66597500	-2.15520100	C	-0.68434500	1.55159700	-2.22530600
C	-0.16318100	0.44399300	-1.84419700	C	-0.02332700	0.30085400	-1.86971900
Rh	-0.75244100	-0.59417900	-0.13762100	Rh	-0.77151400	-0.64314900	-0.15296600
H	-0.14379100	-0.24152500	-2.68567700	H	0.00282600	-0.38791400	-2.70724500
C	-0.92262800	1.21848100	0.83456000	C	-1.10359600	1.25380900	0.77800300
C	-1.10343000	2.40605700	0.21055800	C	-0.92050600	2.41826800	0.08855700
H	-1.17974300	1.84660100	-3.18872500	H	-0.92979400	1.71183000	-3.26837500
C	-1.27882400	2.55704200	-1.22541000	C	-0.97961700	2.52709200	-1.34865800
H	-1.76273700	3.46892700	-1.55146200	H	-1.33225900	3.47678800	-1.73116900
C	1.23654200	0.68527800	-1.29255700	C	1.35825100	0.46287800	-1.24585000
H	2.04060000	0.58546000	-2.02037700	H	2.17684600	0.41340200	-1.96430200
H	1.29126900	1.65860000	-0.80849000	H	1.41759800	1.40188400	-0.69635800
O	1.39499300	-0.34113200	-0.27527900	O	1.47692500	-0.63174300	-0.31252300
C	2.21250000	0.02481900	0.84235300	C	2.25192400	-0.34758200	0.85352200
H	2.03649900	-0.74822400	1.58779400	H	2.11662600	-1.20819400	1.50320900
H	1.85177800	0.97807900	1.23693400	H	1.81945800	0.52329500	1.35705200
C	3.60939200	0.11702200	0.46576200	C	3.64903300	-0.11776800	0.53417800
C	4.76449600	0.20809200	0.15394500	C	4.80104000	0.08561900	0.26650600
C	6.16307100	0.30510200	-0.21574100	C	6.19745200	0.31587700	-0.04945900
H	6.45787700	1.34060200	-0.37714700	H	6.43864300	1.37725300	-0.02308500
H	6.35760600	-0.24954100	-1.13232900	H	6.43359400	-0.05978400	-1.04386000
H	6.79710900	-0.11029100	0.56587900	H	6.84327700	-0.19626600	0.66197700
Cl	-0.70294700	-2.01406600	1.89892900	Cl	-0.80556300	-1.90808400	1.93173300
C	-0.56765100	-2.45569500	-0.98245500	C	-0.93707600	-2.36398900	-1.04420500
O	-0.49537300	-3.50339900	-1.38488500	O	-1.11709100	-3.36439600	-1.53514700
C	-2.56225500	-0.38025000	-0.29734600	C	-2.41958500	0.15545000	-0.07054700
O	-3.67988200	-0.22115700	-0.39093500	O	-3.54201200	0.39387800	-0.12504400
C	-1.20815000	3.69641600	0.99966500	C	-0.78574900	3.71962000	0.83651200
H	-1.39142300	4.53795300	0.33654100	H	-0.46794900	4.52086400	0.17533200
H	-2.01877400	3.66154600	1.72615500	H	-1.73790700	4.00732300	1.28627900
H	-0.29045700	3.90774500	1.54756400	H	-0.06403200	3.63567900	1.64636900
C	-0.84870800	1.11852200	2.32528500	C	-1.24374100	1.24987600	2.26966600
H	0.02661000	0.56054500	2.65344800	H	-0.27245800	1.12527600	2.75284000

TS4

H	-1.69012000	2.17500000	2.63325900	H	-2.81045700	2.26710200	2.17144700
H	-1.84517200	0.41118600	2.60457700	H	-2.77532000	0.50181400	2.32572100

INT5

C	-0.47391700	1.40048800	-2.26496400	C	-0.01370000	2.13854600	-1.30679100
C	0.20432500	0.19305900	-1.79612600	C	0.53449900	0.77034800	-1.14715600
Rh	-0.70270400	-0.65800600	-0.11081600	Rh	-0.77351500	-0.45869800	-0.09398200
H	0.36607100	-0.51264800	-2.60372300	H	0.85110300	0.35812300	-2.10307500
C	-1.75753200	1.27402300	0.60545500	C	-2.59435200	0.80384200	0.00004500
C	-1.09447400	2.29796100	-0.02073000	C	-1.75464600	1.79870700	0.44995500
H	-0.56348800	1.55131100	-3.33481400	H	0.42341000	2.79811900	-2.04902600
C	-0.91510800	2.37603700	-1.45365200	C	-0.95990900	2.60121700	-0.49762200
H	-1.18079500	3.33381500	-1.88666600	H	-1.23556800	3.65041600	-0.51978700
C	1.50833600	0.46524400	-1.04951600	C	1.71159500	0.79746700	-0.18334600
H	2.37569800	0.53650500	-1.70933500	H	2.57460300	1.30944000	-0.62470000
H	1.42874200	1.39279600	-0.47604300	H	1.43457100	1.34107100	0.72927900
O	1.66955800	-0.63172000	-0.14680400	O	2.05195800	-0.53693900	0.14174300
C	2.48295000	-0.36315100	0.98854200	C	3.05253900	-0.64005900	1.13676000
H	2.38496600	-1.23768900	1.62644100	H	3.11731600	-1.69770600	1.38103000
H	2.06813100	0.49110300	1.53390700	H	2.73160300	-0.10878900	2.03933200
C	3.87033300	-0.11453800	0.63221500	C	4.35038900	-0.13903900	0.70056300
C	5.01195200	0.10036700	0.33082800	C	5.41442600	0.27650800	0.33213100
C	6.39621100	0.34451900	-0.02644900	C	6.70569500	0.76725200	-0.11063500
H	6.63314600	1.40652300	0.01242600	H	6.85282400	1.80759200	0.17513000
H	6.60164900	-0.01056300	-1.03515600	H	6.79432900	0.69844200	-1.19378300
H	7.06808700	-0.17717900	0.65324700	H	7.51193900	0.18035800	0.32677600
Cl	-0.91914000	-1.57581900	2.09097500	Cl	-1.58849300	-1.79000900	1.71779800
C	-0.98663100	-2.25484200	-1.02606300	C	-0.02797100	-1.92963200	-1.01311700
O	-1.24218500	-3.21323500	-1.57388400	O	0.34834400	-2.81253700	-1.60848600
C	-2.39347200	0.17194500	-0.21413100	C	-2.20309000	0.11750500	-1.24563600
O	-3.48924200	-0.00555000	-0.60520400	O	-2.61473500	-0.10683900	-2.32363900
C	-0.74173700	3.52297600	0.77242900	C	-1.93554900	2.36604400	1.82795000
H	-0.09589500	4.18978300	0.20936900	H	-1.07542300	2.96804600	2.10753200
H	-1.64411200	4.06933900	1.05397800	H	-2.82166900	3.00199300	1.87516000
H	-0.24049200	3.24952000	1.69896200	H	-2.05504400	1.56996600	2.55940600
C	-2.19879600	1.37325700	2.03761900	C	-3.81214900	0.31370700	0.71839600
H	-1.34857000	1.42763000	2.71478000	H	-3.68178400	0.33191100	1.79507900

H	-4.64717100	0.96364000	0.44879400	H	4.74915500	0.91723100	0.43242400
H	-4.05366900	-0.70499900	0.43354000	H	4.10234500	-0.72741800	0.37293400

INT6

C	-0.18948100	2.22036400	0.75969100
C	-0.60828200	0.79584400	0.83682100
Rh	0.86642500	-0.41480100	0.01865400
H	-0.86489800	0.52440800	1.86112500
C	2.64494000	0.84423100	0.31140600
C	1.92584000	1.72064000	-0.47630100
H	-0.83020500	2.96884600	1.21566700
C	0.90026700	2.60758800	0.11037400
H	1.11627800	3.66418200	-0.00742400
C	-1.81596200	0.55358000	-0.04636500
H	-2.59111900	1.30340900	0.15806900
H	-1.54506600	0.65365400	-1.10779400
O	-2.31859200	-0.73673400	0.20988400
C	-3.37514200	-1.11071100	-0.65108600
H	-3.58465700	-2.15384400	-0.42503100
H	-3.04295500	-1.05487100	-1.69381700
C	-4.57969400	-0.30695900	-0.47445700
C	-5.56541000	0.36147500	-0.32591900
C	-6.76378300	1.15871000	-0.14493200
H	-6.76697500	2.02358600	-0.80647800
H	-6.83917600	1.51702800	0.88059400
H	-7.65440400	0.56927800	-0.35751000
Cl	1.92212500	-1.69494300	-1.69823100
C	0.01260200	-1.92116300	0.78971700
O	-0.36770500	-2.84405000	1.31771500
C	1.93198700	0.29988500	1.47727500
O	2.02379500	0.20132300	2.64461100
C	2.42331500	2.08703800	-1.84399800
H	1.64733100	2.60476500	-2.40095900
H	3.29135100	2.74599900	-1.78257900
H	2.70858700	1.19459500	-2.39716700
C	3.98962600	0.27775900	-0.02167200
H	4.15424200	0.23521100	-1.09257000

TS6

C	-0.10020500	2.00804100	-0.74524800
C	-0.68877300	0.95003100	0.08313900
Rh	0.90799900	-0.38071600	-0.19002500
H	-0.82440900	1.24477000	1.12201100
C	2.40598300	0.90786900	1.02371200
C	2.35617300	1.64062400	-0.14556900
H	-0.74616600	2.55570000	-1.42515100
C	1.21513300	2.29422900	-0.79776300
H	1.51664200	3.05042000	-1.50948900
C	-2.00319200	0.43871300	-0.44542900
H	-2.72742400	1.26202000	-0.50354400
H	-1.88420200	0.02998400	-1.45762400
O	-2.47074500	-0.55294400	0.43121100
C	-3.65861000	-1.17999400	-0.00738700
H	-3.83931100	-1.99048000	0.69476300
H	-3.50268600	-1.62459900	-0.99716600
C	-4.80834800	-0.28301200	-0.04920500
C	-5.74948800	0.46104600	-0.08302400
C	-6.89317300	1.35294800	-0.11547600
H	-7.02973400	1.78545200	-1.10540000
H	-6.76785800	2.16826600	0.59540600
H	-7.80548300	0.81983400	0.14772300
Cl	2.55813300	-1.60594000	-1.40079700
C	-0.09325600	-1.89969300	0.12786800
O	-0.58187800	-2.89635600	0.35549100
C	1.21949800	0.31155800	1.62793100
O	0.76967800	0.15464800	2.70379500
C	3.66679800	1.85450400	-0.85184700
H	3.53994100	2.43763000	-1.75761400
H	4.38310900	2.36592500	-0.20922200
H	4.09200900	0.88795400	-1.12460300
C	3.70197700	0.34123400	1.53864400
H	4.10692000	-0.39537600	0.84458400

H	4.43323900	1.13841300	1.66143200	H	-2.43495500	-3.55497000	1.89053700
H	3.54764400	-0.13406800	2.50249700	H	-1.40013700	-2.49781900	2.85575900

INT7

C	-0.30035300	-0.76829800	-1.69294900	C	0.15654700	0.45839100	-1.65937800
C	0.67993200	-0.66415700	-0.68983000	C	-0.80361900	0.60914200	-0.61663900
Rh	-0.98181100	0.71947100	-0.36547500	Rh	0.76029100	-0.68285400	-0.00483900
H	0.63912200	-1.34218300	0.15348700	H	-0.79550900	1.52460000	-0.03846100
C	-1.89373500	-1.69611700	0.94667200	C	1.64951100	1.99614100	0.71679000
C	-2.08094300	-2.00353500	-0.34699700	C	1.91756300	1.97154600	-0.60105900
H	-0.09101700	-0.33463100	-2.66527800	H	-0.05018900	-0.20036000	-2.49278400
C	-1.65377900	-1.05584800	-1.39574000	C	1.48511700	0.83864200	-1.44100700
H	-2.35205100	-0.93416700	-2.21365500	H	2.19968300	0.50308200	-2.18292700
C	2.04007000	-0.13111300	-1.00094700	C	-2.14994900	-0.02438600	-0.75148200
H	2.75705800	-0.95430200	-1.09284500	H	-2.84048700	0.67432900	-1.23950400
H	2.03363800	0.41897700	-1.94996900	H	-2.08981900	-0.93034100	-1.36530200
O	2.43321000	0.72013000	0.05249000	O	-2.61335700	-0.33223000	0.54057800
C	3.75532900	1.20092500	-0.08121900	C	-3.89688900	-0.92529200	0.54518600
H	3.87950200	1.93638100	0.71037000	H	-4.08002500	-1.21603400	1.57685700
H	3.87165400	1.72066700	-1.03949000	H	-3.88951800	-1.83738900	-0.06229000
C	4.77165100	0.16077200	0.03722200	C	-4.95258000	-0.03361100	0.07775000
C	5.60264700	-0.69929100	0.13939600	C	-5.81700300	0.70383800	-0.30913100
C	6.61278700	-1.73185400	0.27335500	C	-6.86839300	1.59241500	-0.76681800
H	6.89728000	-2.13578700	-0.69695900	H	-7.26901400	1.26805100	-1.72590700
H	6.24699800	-2.55324300	0.88758800	H	-6.49124200	2.60710900	-0.88532400
H	7.50857900	-1.33492700	0.74854300	H	-7.68836300	1.62396200	-0.05107000
Cl	-3.07434600	1.79521600	-0.37223500	Cl	1.61157800	-2.54769500	-1.28217800
C	-0.08634600	2.12581600	0.66080300	C	-0.16334100	-1.78194100	1.30161200
O	0.42477800	2.93432900	1.25792500	O	-0.73352800	-2.42045600	2.03481800
C	-1.34212600	-0.36191400	1.24557200	C	1.02861900	0.78373800	1.30670700
O	-1.13076000	0.07835200	2.32762000	O	0.84286300	0.64506000	2.48126800
C	-2.73231000	-3.25117100	-0.84279800	C	2.70343600	3.01469200	-1.32530100
H	-2.05160900	-3.80086000	-1.49377700	H	2.13324300	3.41673600	-2.16301000
H	-3.06067300	-3.90740300	-0.04435900	H	3.00836400	3.83239500	-0.68145000
H	-3.60161100	-2.98871300	-1.44722500	H	3.60247300	2.55957900	-1.74546000
C	-2.22636300	-2.52178300	2.14809000	C	2.00451900	3.08249500	1.68084200
H	-3.09298600	-2.10894800	2.66359600	H	2.96961400	2.88476100	2.14873700

TS7

H	2.04721800	4.05800700	1.20546000
H	1.26997400	3.10897400	2.48168800
C	3.72932300	-0.62108400	0.41552800
O	4.53108900	-0.37069900	-0.33242400

INT8

C	0.24270400	0.59755000	-1.64689800
C	-0.66560900	0.76397500	-0.59492800
Rh	0.97629000	-0.62004000	-0.04000000
H	-0.53506700	1.57889100	0.10581900
C	2.04844200	2.07603600	0.60185500
C	2.12245000	2.04958100	-0.73685600
H	-0.04023400	-0.04613000	-2.46864000
C	1.62499400	0.86869300	-1.48452900
H	2.25167500	0.54241900	-2.30561900
C	-2.04354900	0.20044400	-0.69350000
H	-2.73679800	0.95884000	-1.07508300
H	-2.04889700	-0.65724500	-1.37327700
O	-2.43583100	-0.19448900	0.60203400
C	-3.70209700	-0.82345000	0.62794300
H	-3.82385000	-1.19452500	1.64308400
H	-3.70190000	-1.68649700	-0.04640600
C	-4.80240300	0.07102600	0.28444000
C	-5.70214200	0.81117400	-0.00422200
C	-6.79660000	1.70090300	-0.34368300
H	-7.03412200	1.64819000	-1.40504100
H	-6.54549000	2.73316000	-0.10435400
H	-7.69380300	1.43904800	0.21518800
Cl	0.28473200	-2.51195700	-1.56254100
C	-0.02361300	-1.57829300	1.37095300
O	-0.55972600	-2.15888200	2.17102300
C	1.55541500	0.83775300	1.24925200
O	1.50792800	0.70226400	2.43975100
C	2.65803700	3.14428300	-1.60054300
H	1.87280300	3.52959600	-2.25248100
H	3.06911000	3.96950800	-1.02949200
H	3.44122100	2.75479400	-2.25214000
C	2.41992000	3.19024100	1.52332400
H	3.21522100	2.87157200	2.19566700
H	2.74138100	4.08190500	0.99527900
H	1.57145900	3.44801000	2.15554400
C	2.68354600	-1.52519100	0.13970200
O	3.67598300	-2.05824300	0.18860300

INT8-B

C	-0.93791500	-0.56053800	-1.73741000
C	-0.06738300	-1.10858500	-0.78744700
Rh	-1.12254300	0.66353300	0.01509500
H	-0.40932200	-1.90498400	-0.13856300
C	-2.98171600	-1.59104200	0.55842100
C	-3.12791500	-1.41200000	-0.76250600
H	-0.51346800	0.03517200	-2.53412900
C	-2.31866800	-0.38763800	-1.46718900
H	-2.85501200	0.20212300	-2.20060100
C	1.41144300	-0.99732700	-0.97171900
H	1.78826500	-1.89397000	-1.47839000
H	1.63997400	-0.12311500	-1.58813400
O	1.99578400	-0.86673500	0.30365200
C	4.33117200	-1.45472900	-0.11296900
H	4.11564000	-1.80507200	-1.12425900
H	4.20801500	-2.31011600	0.55271400
C	5.69338900	-0.95398300	-0.05183800
C	6.80205900	-0.49929800	0.01259800
C	8.14725700	0.04106200	0.08564700
H	8.72116600	-0.44228400	0.87506200
H	8.12669400	1.10978200	0.29412300
H	8.67930700	-0.10552100	-0.85329800
Cl	0.07178300	2.36543800	-1.41814000
C	0.22650400	1.10181500	1.39304500
O	0.97796800	1.39646100	2.17623100
C	-2.06854600	-0.64708400	1.24412600
O	-1.90342700	-0.65040200	2.43177000
C	-4.04841800	-2.18537400	-1.64893300
H	-3.47755000	-2.73826900	-2.39626000

H	-4.67150800	-2.88496500	-1.10269200
H	-4.69916000	-1.50222500	-2.19617300
C	-3.64092100	-2.60940800	1.42845100
H	-4.24787500	-2.11804600	2.18760300
H	-4.26608900	-3.29748300	0.86906000
H	-2.88706600	-3.18320800	1.96547900
C	-2.41854400	2.05214300	0.41610900
O	-3.17275300	2.87098100	0.59489000
C	3.32072800	-0.37977200	0.28881100
H	3.39832900	0.48212600	-0.37935600
H	3.52804200	-0.04326200	1.30139600

TS8

C	0.42667900	1.20430300	-1.52458300
C	-0.43792500	1.27076400	-0.45010000
Rh	0.94503100	-0.53646700	-0.41352400
H	-0.11788200	1.74584300	0.46888800
C	2.48461500	1.58793800	1.00997100
C	2.50955700	1.99446700	-0.26698600
H	0.05205200	0.90801600	-2.49543500
C	1.84829500	1.13018600	-1.27843500
H	2.45064200	0.92966000	-2.15756600
C	-1.89332100	0.97232700	-0.54313700
H	-2.48174400	1.89617200	-0.58128300
H	-2.10232600	0.38613700	-1.44086800
O	-2.20896700	0.23605800	0.61767100
C	-3.40322100	-0.51175400	0.48667500
H	-3.48871100	-1.08936700	1.40338100
H	-3.29961000	-1.21436500	-0.34615900
C	-4.58536500	0.32336500	0.29997500
C	-5.54728400	1.02161100	0.13129200
C	-6.71876600	1.85547600	-0.06277800
H	-6.93028100	2.00074700	-1.12115100
H	-6.57819200	2.83561300	0.39084500
H	-7.59612500	1.40092100	0.39521000
Cl	-0.63071500	-1.98932500	-1.54460300
C	-0.22636100	-2.76914300	1.74112500
O	-1.23200000	-2.62592500	2.22262000
C	1.78798200	0.29953200	1.18316100
O	1.60548100	-0.26248800	2.22255100
C	3.13081200	3.24827100	-0.78246300
H	2.36941800	3.88834800	-1.23005900
H	3.64133000	3.81135100	-0.00817400
H	3.84819300	3.01677100	-1.57058300
C	3.01142400	2.26572500	2.22846000
H	3.65471500	1.58652600	2.78526100
H	3.57238500	3.16432700	1.99092500
H	2.19353200	2.53586200	2.89559500
C	2.33277200	-1.85766400	-0.50738300
O	3.17161000	-2.60457900	-0.62544100

INT9

O	-2.70937100	-1.15412200	-0.80199600
C	1.21375600	2.25945800	-0.55545900
C	1.72432400	2.07255000	0.66925900
C	0.85028900	1.06155100	-1.35004800
C	-0.39971000	0.39276200	-1.13085200
C	-0.88340600	0.14508900	0.14320600
C	-2.05432500	-0.76914300	0.38655300
C	-3.59947000	-0.17518300	-1.30401200
H	1.17387400	1.09531300	-2.38381000
H	-0.83388400	-0.17336100	-1.94612700
H	-0.62140700	0.81493900	0.95322700
H	-2.75820700	-0.28600500	1.06978900
H	-1.70390300	-1.68645000	0.85741700
H	-3.95572900	-0.56549900	-2.25506000
H	-3.06946100	0.76272200	-1.50907500
C	-4.72935400	0.09656700	-0.42246700
C	-5.66030700	0.31327600	0.30340600
Rh	1.20773600	-0.69729100	-0.22421200
Cl	0.76049100	-2.73444600	0.88784300
C	1.93725700	0.66258700	1.04170400
C	2.99233600	-1.16472900	-0.70130800
O	2.45530000	0.27013400	2.03280900

O	4.04678100	-1.42671500	-1.01537600	H	1.22878000	-1.71933200	1.26981700
C	-6.78889200	0.56441300	1.17950200	C	5.14185000	0.46453700	0.55185400
H	-7.72410100	0.54746500	0.62195500	H	5.52689000	0.75124300	1.52940800
H	-6.84970700	-0.19814200	1.95445100	H	5.97716800	0.10388000	-0.04643900
H	-6.70353200	1.53427500	1.66710000	H	4.72892900	1.35170500	0.07363600
C	0.95618200	3.57943500	-1.19895500	C	-4.07093600	-1.03234100	-1.28264900
H	-0.10954900	3.69248200	-1.40221900	H	-3.74795900	-1.70654200	-2.07696400
H	1.28463500	4.41905000	-0.59554900	H	-4.79453600	-1.55247800	-0.66373700
H	1.46432200	3.62815700	-2.16265100	H	-4.57087600	-0.19339400	-1.76791800
C	2.12350200	3.08670300	1.68999900	C	-3.43962700	-1.56920500	1.77689700
H	3.18248500	2.99022600	1.92438500	H	-4.38981400	-1.90276700	1.37148800
H	1.93062500	4.10078600	1.35523300	H	-2.87549900	-2.44479100	2.09662500
H	1.58229500	2.92134900	2.62046700	H	-3.62796000	-0.97717700	2.67084300

TS9

Rh	-0.26690300	0.78215900	-0.08992700
Cl	1.80885300	1.69053500	-0.88826500
O	-0.90182600	-0.27549600	2.33471200
C	-1.38449400	-0.17154500	1.24375300
C	-2.65132700	-0.77459500	0.79236200
C	-2.89139400	-0.55078300	-0.50837100
C	-1.88527300	0.23684600	-1.26783300
C	-0.70054700	-0.38401400	-1.82322800
C	-0.01217300	-1.30371000	-1.06027100
C	1.34386500	-1.86004200	-1.38195700
C	3.21967400	-1.34220800	0.77342900
C	4.11123900	-0.54520800	0.68021100
H	-0.23477900	0.06493100	-2.69055300
H	-0.56800300	-1.88918900	-0.33607700
H	1.30043700	-2.39940100	-2.32846000
H	2.07749700	-1.05497200	-1.47913800
C	2.08569200	-2.24999100	0.83519700
O	1.73690500	-2.81144200	-0.42268700
C	-0.82968300	2.48375700	0.57662200
O	-1.20823100	3.49860600	0.89873200
H	-2.30621700	1.03142400	-1.87393700
H	2.30009100	-3.10173700	1.47649800

INT10

Rh	-0.27203800	-0.37881800	-0.11099300
Cl	-2.07363600	-1.06122000	-1.74767100
O	0.88620100	0.35754000	2.38857000
C	1.14655400	0.08815400	1.24689300
C	2.53046900	0.08558200	0.71155700
C	2.64641100	-0.24330700	-0.58323600
C	1.43355500	-0.51751700	-1.38823200
C	0.56631200	0.51757000	-1.84863100
C	0.24166800	1.58646900	-1.01219300
C	-0.93091700	2.47535200	-1.27698200
C	-1.70870900	1.07809200	1.04568900
C	-2.17958600	-0.02775900	1.25853700
H	-0.07014100	0.29697900	-2.69419500
H	1.00046100	1.97941600	-0.34444100
H	-0.68486700	3.24580600	-2.00728700
H	-1.75544000	1.87036900	-1.66644200
C	-1.31098500	2.48583800	1.10020600
O	-1.33209900	3.19121800	-0.12212800
C	-0.27852400	-2.21572400	0.46738200
O	-0.25638900	-3.31066000	0.74661200
H	1.49525200	-1.37847200	-2.04319000
H	-2.00825700	3.00983500	1.75150500

H	-0.32257700	2.53131300	1.56596400	H	-2.70181900	2.03478000	2.27914800
C	-3.00770000	-1.17170600	1.60525000	C	-1.99104700	-1.46256500	2.18134700
H	-2.48674000	-1.84099400	2.28762900	H	-2.62815100	-1.02458700	2.94876200
H	-3.92276300	-0.82775100	2.08376400	H	-2.56748200	-2.18544700	1.60643400
H	-3.26563000	-1.71486200	0.69757300	H	-1.16393000	-1.97940900	2.66445200
C	3.94626700	-0.34071500	-1.31099700	C	3.57148000	0.36334000	1.70566700
H	3.98687500	0.39401300	-2.11659400	H	3.89754000	-0.61352300	2.05997500
H	4.79664200	-0.18142700	-0.65520000	H	4.43534100	0.92710600	1.37015600
H	4.04640700	-1.32146600	-1.77785700	H	3.14160300	0.86949000	2.56877400
C	3.65296700	0.44916800	1.63324700	C	3.79917500	1.24822400	-1.26616500
H	4.37344300	-0.36361100	1.71848900	H	3.58167800	2.28202200	-1.53862000
H	4.18907400	1.33259600	1.28827600	H	4.67306900	1.23668100	-0.62458300
H	3.25337500	0.65401900	2.62174600	H	4.04847400	0.72789700	-2.19153900

TS10

Rh	-0.20015500	-0.61002700	-0.29533700
Cl	-2.13191500	-0.80043100	-1.87732600
O	1.21331400	-0.99653900	2.16538800
C	1.30288600	-0.51958900	1.06461700
C	2.53333700	0.20249800	0.64446200
C	2.60230500	0.61163100	-0.63110400
C	1.45612600	0.48234200	-1.55271300
C	0.25396500	1.15176400	-1.43205700
C	-0.28235000	1.70374100	-0.17651800
C	-1.25456000	2.84410800	-0.41914800
C	-1.49548700	0.81751700	1.00962200
C	-1.45119300	-0.43125000	1.28877100
H	-0.39929200	1.19399100	-2.29205400
H	0.48362800	1.95417700	0.55089800
H	-0.71403700	3.73059900	-0.74077800
H	-1.97442000	2.54919000	-1.19051300
C	-2.45958300	1.94392100	1.22332300
O	-1.89027300	3.14595000	0.78892700
C	-0.00201200	-2.45874100	-0.37162900
O	0.09099000	-3.58498300	-0.45202300
H	1.69649100	0.13177700	-2.54944000
H	-3.36966600	1.72672300	0.65447100

TS10-B

Rh	-0.16360400	0.77947200	-0.26325300
Cl	1.61069500	1.75264600	-1.73454500
O	-1.60163700	0.54368100	2.19969500
C	-1.52193700	0.10303200	1.08415900
C	-2.38618200	-1.02395800	0.64343500
C	-2.39819800	-1.31720900	-0.66521000
C	-1.48249900	-0.66201500	-1.61824500
C	-0.11720100	-0.83126600	-1.65732200
C	0.72395100	-1.34116500	-0.55275900
C	2.07606800	-1.77118700	-1.12765100
C	1.41961000	-0.38596000	1.03325300
C	1.13754900	0.83911200	1.26955000
H	0.41407400	-0.50494200	-2.54083900
H	0.22139200	-2.10231000	0.03667000
H	1.88876600	-2.32852800	-2.04316500
H	2.64731100	-0.87190200	-1.37947600
C	2.20428100	-1.45596500	1.69630700
O	2.79914400	-2.64167100	-0.30367300
C	-0.90427500	2.48831400	-0.16815000
O	-1.33218400	3.53659400	-0.13637100
H	-1.93835500	-0.30116900	-2.53279600
H	2.61237000	-1.02149400	2.61029400

H	1.55219500	-2.28203700	1.98638000	O	3.19405200	-1.89276700	0.94657600
C	1.42919200	1.92584300	2.21166000	H	0.55667400	1.79244200	-1.92056800
H	2.15436000	1.60959500	2.96221500	H	-2.86871200	-2.97494300	0.34221700
H	1.82865900	2.78413000	1.67433100	H	-3.42731800	-1.80625300	1.55020200
H	0.50786200	2.22232000	2.71030000	C	-0.14915300	-2.38565500	1.69099100
C	-3.19216500	-1.66776900	1.72308800	H	-1.02823800	-2.81477000	2.17201300
H	-3.83438900	-0.92816400	2.19856400	H	0.41764900	-3.19865700	1.23535300
H	-3.79957100	-2.49149100	1.36355100	H	0.47640700	-1.94626800	2.46893400
H	-2.53209500	-2.04201800	2.50460700	C	-0.31137400	2.75872500	2.45339400
C	-3.30588500	-2.31514900	-1.31517000	H	0.64620800	3.04930800	2.88255500
H	-2.72977300	-3.15505700	-1.70617000	H	-0.91697000	3.64640300	2.30521200
H	-4.06248300	-2.69926300	-0.64018000	H	-0.80033400	2.12326500	3.18979300
H	-3.80949400	-1.85881200	-2.16792400	C	-1.07618400	3.66833900	-0.43632900
C	3.32508600	-1.99802000	0.82975400	H	-2.07414100	3.49396900	-0.84240200
H	3.90067800	-2.74547500	1.36993100	H	-1.15579100	4.36120700	0.39383000
H	3.99185600	-1.18325300	0.52996500	H	-0.49652800	4.14454600	-1.22756800

INT11

Rh	0.92666900	-0.32441900	-0.32487400
Cl	2.45846200	0.05186400	-2.14125400
O	1.16025400	0.41348500	2.39319300
C	0.65243700	0.72409200	1.35532900
C	-0.10179400	1.99475200	1.18640000
C	-0.44153600	2.37197300	-0.05366400
C	-0.16395800	1.46387600	-1.18206000
C	-0.93672500	0.37074100	-1.45782300
C	-2.13327000	-0.01907600	-0.65478000
C	-3.28813000	-0.69356800	-1.39013100
C	-1.77335100	-1.11074700	0.30547300
C	-0.52035200	-1.34367000	0.68752200
H	-0.75153500	-0.16595200	-2.38245800
H	-2.52431500	0.84238500	-0.10735000
H	-3.98186400	-0.00650700	-1.86640500
H	-2.90248400	-1.39419200	-2.14055900
C	-3.02950200	-1.91133600	0.54025600
O	-3.98614400	-1.37061800	-0.36349100
C	2.33822700	-1.32671600	0.48169400

TS11

Rh	1.01999300	-0.22334600	-0.27976600
Cl	2.54877700	0.07507100	-2.03963200
O	3.30278900	-1.51438600	1.24981600
O	0.72155800	0.49796900	2.51442200
C	2.44171900	-1.04838000	0.68908400
C	0.14627700	0.57993700	1.44948600
C	-0.63891400	1.81489800	1.13362700
C	-0.64710700	2.29204900	-0.11932500
C	-0.12272000	1.46453900	-1.21760400
C	-0.74902100	0.30304000	-1.58849000
C	-1.98741100	-0.17590300	-0.89267600
C	-2.91866100	-1.09090500	-1.69087000
C	-2.68614500	-2.15175300	0.30009200
C	-1.63387600	-1.08424400	0.24056200
C	-0.48754200	-1.02832200	0.94109100
H	0.61848300	1.89502900	-1.87830100
H	-0.44334700	-0.19487500	-2.50041700
H	-2.56514700	0.67050400	-0.50987700
H	-3.64023700	-0.55988600	-2.30339200

H	-2.33488300	-1.76785200	-2.32559000	H	1.01034200	-1.51839300	-3.09083100
H	-3.19434700	-2.19458400	1.26375400	H	1.37770400	-3.23336600	0.14649700
H	-2.24501000	-3.13730800	0.10625200	H	2.26383200	-2.03423700	-0.82339500
O	-3.62611900	-1.80793300	-0.69885000	O	0.77285800	-3.10281900	-1.78539800
C	-0.17356900	-2.06943700	1.97320800	C	0.48430000	-1.72187800	2.17626600
H	-1.03315300	-2.25818200	2.61778600	H	-0.04650300	-2.62943400	2.46068400
H	0.09954700	-3.00774900	1.48972000	H	1.51824500	-1.97239800	1.95894500
H	0.64549100	-1.74565900	2.60699200	H	0.45556600	-1.05930300	3.03675900
C	-1.16717800	2.50733200	2.34841500	C	-3.98783700	-0.08394500	0.94149400
H	-0.34376600	2.83391000	2.98101900	H	-4.23381600	0.62210700	1.73634500
H	-1.79302000	3.35874200	2.10330500	H	-4.68491100	0.07033100	0.12251300
H	-1.75460700	1.80943200	2.94420800	H	-4.13603300	-1.07562400	1.35495900
C	-1.14698700	3.63816300	-0.54044300	C	-3.32105900	1.97131100	-0.92630000
H	-1.99915100	3.54099400	-1.21480500	H	-3.91658600	1.49541200	-1.70813500
H	-1.43802000	4.26062600	0.29815300	H	-3.99876400	2.27284200	-0.13203500
H	-0.36676400	4.15996000	-1.09564500	H	-2.87581300	2.86385900	-1.35724400

INT12 **2A'**

Rh	0.86615500	0.60464500	0.12699000	C	1.37045600	0.40518700	0.09203600
Cl	1.75667000	2.69323500	-0.41921300	C	1.02835500	-1.00280900	0.49488900
O	3.35270100	0.19830100	1.78404400	C	0.53984500	-1.67034100	-0.74800400
O	-2.00964100	-1.03927100	2.42049800	C	-0.73643000	-1.62044200	-1.12665000
C	2.39574300	0.33256500	1.19472300	C	0.52504500	1.40298200	-0.18330700
C	-1.60405200	-0.68370300	1.32973500	H	0.25975400	-1.02705700	1.26628900
C	-2.56436800	0.08652400	0.48820100	H	1.27964900	-2.16332800	-1.36583100
C	-2.25563400	1.02907600	-0.42534800	C	-1.81307000	-1.03548100	-0.33831400
C	-0.96748500	1.25795600	-1.08375500	C	-1.82116200	0.17352400	0.27291200
C	-0.26979500	0.30683400	-1.77845400	C	2.87339300	0.45673800	-0.01310000
C	-0.50633500	-1.15634600	-1.58594800	C	2.38083800	-1.52293500	0.96391900
C	0.21858400	-2.07258300	-2.57314700	O	3.31852400	-0.87762600	0.12521400
C	1.28164300	-2.47759700	-0.62724600	H	2.55007700	-1.25663900	2.01295700
C	0.25140900	-1.41541800	-0.29322500	H	2.50331100	-2.59616100	0.84563800
C	-0.19520400	-1.07927100	0.99040900	H	-1.03498500	-2.15577200	-2.01980800
H	-0.73257600	2.28960600	-1.30928900	C	-0.95013000	1.35666600	-0.02591100
H	0.47508700	0.62491600	-2.49604200	O	-1.54227100	2.42305700	-0.10981100
H	-1.56691600	-1.39508700	-1.49512600	H	3.28665600	1.09009400	0.78265800
H	-0.43600900	-2.52608700	-3.31011200	H	3.22733400	0.83561900	-0.96907900

C	1.02401600	2.75720200	-0.59335300
H	0.56559900	3.06119100	-1.53289700
H	0.73014900	3.50615000	0.13968300
H	2.10429000	2.77839100	-0.70441200
C	-3.02611400	-1.92726700	-0.22862700
H	-3.05088300	-2.42629800	0.74201600
H	-3.95590100	-1.37171500	-0.33283300
H	-3.00099200	-2.70483600	-0.98786100
C	-3.01278100	0.56642900	1.10808700
H	-3.84222700	0.89754300	0.48123400
H	-3.36008100	-0.26718700	1.71417500
H	-2.76535800	1.39984800	1.75737200

TS12

C	1.35910000	0.36719700	-0.12429400
C	0.95099300	-0.99399800	0.29311100
C	0.38972900	-1.82360300	-0.71704200
C	-0.88236600	-1.62703700	-1.19976800
C	0.53932100	1.39669400	-0.35795400
H	0.92023900	-2.72368000	-1.00353800
C	-1.81997300	-0.89295700	-0.46868300
C	-1.44519100	0.00706700	0.56866500
C	2.86235500	0.37343900	-0.13895100
H	3.27180600	0.52630300	-1.13782000
H	3.24371100	1.16907600	0.51025600
C	2.18453600	-1.50207400	1.00575800
O	3.27617700	-0.89756000	0.32696700
H	2.17500300	-1.21025100	2.06109600
H	2.30247800	-2.58131400	0.94251800
H	-1.25300800	-2.28920700	-1.96978600
C	-0.85508300	1.31029700	0.07327900
O	-1.55083100	2.30809400	0.12610700
H	-0.20329100	-0.63873000	0.91259800
C	1.00159800	2.74510400	-0.80904700
H	0.41553800	3.07636900	-1.66492900
H	0.84431600	3.48645100	-0.02696600
H	2.05212500	2.74087300	-1.08877500
C	-2.44108300	0.24371300	1.67909400
H	-3.31719100	0.77680200	1.31193400
H	-2.76369800	-0.69600400	2.12289200
H	-1.99740600	0.86203500	2.45517900
C	-3.26898300	-1.23780300	-0.64074600
H	-3.42164200	-1.85235700	-1.52380200
H	-3.64498900	-1.79034800	0.22146600
H	-3.87646900	-0.33653400	-0.72745100

2A

C	1.31985600	0.38849200	-0.04093400
C	1.36152500	-1.04697100	0.14153300
C	0.52255300	-2.03426400	-0.25135300
C	-0.80987900	-1.93921000	-0.76172700
C	0.34049800	1.31272100	-0.21400400
H	0.95017000	-3.03143500	-0.25710400
C	-1.76776800	-1.08757000	-0.34740200
C	-1.52139800	-0.14523300	0.79323900
C	2.77037700	0.82426000	-0.05444900
H	3.03537000	1.36354700	-0.96296800
H	2.96294400	1.49113000	0.79712500
C	2.76561100	-1.35187400	0.59385300
O	3.56417900	-0.33703200	0.02398200
H	-1.07732300	-2.66713200	-1.51916900
C	-1.08995000	1.12498600	0.07301700
O	-1.91935700	1.96366000	-0.22463400
H	-0.68919000	-0.52070600	1.38477000
H	2.83364100	-1.32675500	1.68970900
H	3.12673600	-2.31728300	0.24808300
C	0.72110700	2.71865200	-0.58269300
H	1.30710600	3.19307500	0.20742200
H	1.32648500	2.73831000	-1.48863900
H	-0.17411600	3.30718500	-0.74803900
C	-2.73341100	0.10659500	1.67590500
H	-3.12488500	-0.82993200	2.06938500
H	-2.45620700	0.73951500	2.51632100
H	-3.51509000	0.61889300	1.12296500

C	-3.09939800	-1.01159400	-1.01267300	C	3.13266500	1.04406000	1.66840700
H	-3.13696300	-1.63006900	-1.90498200	H	3.77554200	0.18363100	1.48887800
H	-3.89725600	-1.32057000	-0.33669600	H	3.75463800	1.93221000	1.78731300
H	-3.30833400	0.02526100	-1.28681900	H	2.61873400	0.86075400	2.61316000

TS13

O	-2.37505600	-0.44709500	-0.40553900
C	1.96799100	2.20579700	-0.28531600
C	2.16458400	1.18135600	0.55457400
C	0.99100400	1.72090400	-1.27527600
C	-0.31616300	1.28998100	-0.93175900
C	-0.61482500	0.92736700	0.38947100
C	-1.90187500	0.24869900	0.72115000
C	-3.57381300	-1.15625700	-0.16446800
H	1.19625300	1.85607300	-2.33171000
H	-1.00866300	1.02108400	-1.71591100
H	-0.16572500	1.48363900	1.20119600
H	-2.63582400	1.00208700	1.03408800
H	-1.75587500	-0.43646500	1.56219000
H	-3.43059500	-1.85686600	0.66555100
H	-3.75513500	-1.74104000	-1.06338600
C	-4.71398900	-0.29012900	0.11333900
C	-5.64666100	0.42920700	0.34408100
Rh	1.03874300	-0.23324700	-0.35662900
Cl	2.88450900	-1.71817400	-0.33365500
C	0.78473700	-1.60362100	2.12718300
C	0.04964200	-1.58807000	-1.47840100
O	1.47545300	-1.71035500	3.00780700
O	-0.42326300	-2.37864800	-2.13008500
C	-6.77972300	1.29304900	0.61653800
H	-7.63959100	1.00621100	0.01329500
H	-7.07012200	1.24309700	1.66469300
H	-6.53950900	2.32905600	0.38253700
C	2.63062100	3.53827000	-0.40468500
H	3.40941800	3.65777700	0.34377700
H	3.08874900	3.65571400	-1.38849800
H	1.91536300	4.35320900	-0.28320800

INT13

O	-2.18460400	-0.35858800	-0.37689600
C	2.38933800	1.84308500	-0.37599300
C	2.39751300	0.90793500	0.59448600
C	1.33540200	1.51757700	-1.34430300
C	0.01840200	1.19931400	-0.99149000
C	-0.31048300	0.89560800	0.36097400
C	-1.65400600	0.35057200	0.71524500
C	-3.41108300	-0.99919000	-0.08856100
H	1.53849300	1.64232300	-2.40267300
H	-0.70176100	0.98601900	-1.76746200
H	0.13227400	1.50059000	1.14234500
H	-2.32058900	1.18011500	0.98412900
H	-1.56353900	-0.29830900	1.59254200
H	-3.28583400	-1.67327800	0.76564800
H	-3.63677500	-1.60866600	-0.96069600
C	-4.50270000	-0.06774300	0.17354700
C	-5.39393500	0.70562000	0.39296500
Rh	1.17624900	-0.43642600	-0.23639100
Cl	1.85280100	-2.10606000	1.24405900
C	0.08263000	-1.81488900	-1.22039700
O	-0.48379900	-2.64935700	-1.72865200
C	-6.47790900	1.63406700	0.65259800
H	-7.41284900	1.26194300	0.23650700
H	-6.62088100	1.78471000	1.72141600
H	-6.27421600	2.60296000	0.19924100
C	3.30145400	3.00715000	-0.60247300
H	4.09475000	3.03616700	0.13922000
H	3.76495900	2.94841000	-1.58864700
H	2.75741500	3.95193700	-0.55928000
C	3.24011100	0.80728700	1.80649800
H	3.90659200	-0.05121300	1.73005700

H	3.83082300	1.70790400	1.97912900
H	2.62115400	0.61579100	2.68295200

TS14

O	1.98220800	0.11981800	-0.74460500
C	-2.66082200	-1.47780300	-0.38734000
C	-2.16860100	-0.92649700	0.72916900
C	-1.83304700	-1.01602900	-1.51616200
C	-0.43024000	-1.06472700	-1.45562500
C	0.17588500	-1.29933100	-0.17561700
C	1.62253900	-0.99345000	0.04612500
C	3.03181300	0.88387700	-0.18400600
H	-2.29475100	-0.77139100	-2.46522700
H	0.16268800	-0.75815200	-2.30386400
H	-0.20422800	-2.12069600	0.42182700
H	2.24812600	-1.85806800	-0.20718800
H	1.77144000	-0.77359000	1.10645500
H	2.73260600	1.23628900	0.80852500
H	3.14107600	1.75375600	-0.82809200
C	4.29426800	0.15686400	-0.10188500
C	5.32099000	-0.46023500	-0.02581100
Rh	-0.96997500	0.42279600	-0.07328800
Cl	-0.32041600	1.41040400	1.95391600
C	-1.29915900	2.31160000	-1.01156100
O	-1.64099300	3.26584300	-1.50071500
C	6.56797300	-1.19649800	0.06322800
H	6.53365000	-2.09214100	-0.55548100
H	7.40359500	-0.58788800	-0.27929500
H	6.77243600	-1.50328800	1.08786200
C	-3.85772700	-2.35413000	-0.56956400
H	-4.35219600	-2.54363000	0.37967600
H	-4.58329800	-1.88828200	-1.23803600
H	-3.58068700	-3.31298200	-1.00985500
C	-2.42344700	-1.12357100	2.16943600
H	-2.74783100	-0.19681400	2.63783300
H	-3.17467200	-1.89901900	2.32765600
H	-1.50428500	-1.41248300	2.67882700

INT14

O	-1.94620000	0.03981800	-0.53812300
C	2.59101800	1.57617200	0.01795000
C	2.39395700	0.44854700	0.68124600
C	1.55222700	1.62025900	-1.05297200
C	0.18667800	1.68561500	-0.74496400
C	-0.29900600	1.28032700	0.52556500
C	-1.72751200	0.84744800	0.61738300
C	-3.00243600	-0.89276200	-0.38349000
H	1.84982500	1.78824000	-2.08064000
H	-0.51374200	1.74492200	-1.56807000
H	0.20494800	1.59661600	1.42851100
H	-2.44331400	1.67475300	0.63114900
H	-1.86499200	0.24827000	1.51933700
H	-2.77870300	-1.54947600	0.46190600
H	-2.99624900	-1.49759100	-1.28751800
C	-4.30264000	-0.25716400	-0.20881500
C	-5.36739900	0.27387200	-0.05079400
Rh	0.83107600	-0.32339000	-0.28621500
Cl	0.07223000	-1.92719800	1.29312300
C	1.99387300	-1.57040100	-1.22591700
O	2.70462000	-2.27411900	-1.75531300
C	-6.65817400	0.90925700	0.13626700
H	-7.39411800	0.50819700	-0.55904700
H	-7.03020100	0.75441900	1.14789600
H	-6.58896400	1.98255100	-0.03530000
C	3.60061700	2.65714800	0.21768400
H	3.11585900	3.61028200	0.43253100
H	4.26952700	2.42122600	1.04173300
H	4.20550500	2.79643500	-0.67962000
C	3.00483800	-0.20338500	1.85575300
H	3.83863300	0.39322400	2.22972300
H	2.26801600	-0.33313600	2.64637300
H	3.36802000	-1.19918200	1.60571900

TS15

Rh	-0.73518200	-0.52923500	-0.25277200
Cl	0.27944200	-2.56501700	-0.99735800
O	-2.92655800	-0.64556700	-2.32238200
C	-2.06925700	-0.58698600	-1.58419600
C	-1.14483200	1.43275100	0.04432200
C	-1.73201800	1.42676800	1.23013900
C	-1.80240900	-0.03635700	1.50202300
C	-0.65628100	-0.79008000	1.91326900
C	0.61980400	-0.34994900	1.63840100
C	1.81621800	-1.22179300	1.88308200
C	2.91193500	0.66512500	-0.54316500
C	2.79560100	1.75998500	-1.02422400
H	-0.80468000	-1.81775700	2.22261700
H	0.80810200	0.70808100	1.50084700
H	1.93197100	-1.35583000	2.95996900
H	1.65197200	-2.20701500	1.43475200
C	3.20277100	-0.63983300	0.04350500
O	3.02801400	-0.66093500	1.45300800
H	2.59652300	-1.41334400	-0.43126700
H	4.25118400	-0.87308200	-0.14047300
H	-2.77154800	-0.50022700	1.64309100
C	2.71431900	3.08618000	-1.60910800
H	3.71027600	3.49374300	-1.77622700
H	2.19642700	3.06647600	-2.56731800
H	2.17986500	3.77207200	-0.95298100
C	-0.84744000	2.48765300	-0.95185500
H	-0.90706400	3.47970400	-0.50088300
H	0.14244100	2.35598400	-1.37870400
H	-1.56342200	2.44739300	-1.77444100
C	-2.25860300	2.49786000	2.12016500
H	-2.11770700	3.48037000	1.67568100
H	-3.32502600	2.36150900	2.30733000
H	-1.75714100	2.48685100	3.08868600

INT15

Rh	-0.08166200	0.23837200	-0.28650700
Cl	1.73535000	0.61755200	-1.95203200
O	-1.36022000	2.80935500	-1.31843500
C	-0.89425000	1.86065500	-0.91445200
C	-1.70197700	-0.22307100	0.86548800
C	-2.37430800	-1.00619900	0.02944100
C	-1.54132500	-1.10677400	-1.20504900
C	-0.27758400	-1.72827200	-1.17771300
C	0.39930000	-1.89440400	0.04313000
C	1.82264600	-2.34107600	0.09664100
C	1.62003100	0.42276300	1.21520200
C	0.95408900	1.44488200	1.35173500
H	0.27224900	-1.81816800	-2.10492600
H	-0.18619700	-2.09500000	0.93162700
H	1.87534300	-3.42707600	0.16977400
H	2.35812900	-2.01607400	-0.80011100
C	2.76936500	-0.49346000	1.17674200
O	2.46638000	-1.86001300	1.26156900
H	3.31607700	-0.27284300	0.25447600
H	3.40502100	-0.26910200	2.03135900
H	-1.97029200	-0.88718200	-2.17527000
C	0.49986400	2.76006400	1.79084700
H	1.11999200	3.10715200	2.61552200
H	0.57226700	3.47812800	0.97571700
H	-0.53349500	2.73224200	2.12749700
C	-2.01430400	0.22779400	2.24201900
H	-2.30704100	1.27933500	2.25133000
H	-2.83534500	-0.34486700	2.67543100
H	-1.14568400	0.12993300	2.89328700
C	-3.68331800	-1.71058900	0.16794500
H	-4.13312300	-1.51968400	1.13938100
H	-4.38815500	-1.38148800	-0.59759100
H	-3.56458000	-2.78902300	0.05293500

TS16

Rh	-0.28031600	0.47170500	-0.27642400
Cl	1.33609200	1.57608600	-1.77771600
O	-2.09840700	2.83747700	-0.37549000
C	-1.41580300	1.93106500	-0.33775700

C	-1.63678300	-0.63272000	0.76913400
C	-2.06464200	-1.54147200	-0.10950900
C	-1.32850400	-1.38361200	-1.38584100
C	0.04625400	-1.36482400	-1.43324000
C	0.89128500	-1.50450000	-0.23525800
C	2.30557500	-1.92896100	-0.54375500
C	1.52305300	-0.13122000	1.04978700
C	0.82900900	0.89226600	1.36507600
H	0.54759600	-1.19607000	-2.37588300
H	0.41761800	-2.09747200	0.54095100
H	2.31350700	-2.94791800	-0.92367300
H	2.73995800	-1.25405000	-1.28933100
C	2.92262600	-0.63373700	1.17747000
O	3.04124600	-1.92475600	0.65058800
H	3.57210500	0.05980000	0.63214500
H	3.21920900	-0.66092900	2.22343100
H	-1.86979600	-1.34746500	-2.32428500
C	0.77590400	2.04530800	2.27631200
H	1.54163300	1.97491500	3.04779400
H	0.92758900	2.96274100	1.70940000
H	-0.19778000	2.11052000	2.76001800
C	-2.07882300	-0.38592800	2.16342700
H	-2.79906700	-1.12772800	2.50947500
H	-1.22508800	-0.39791100	2.84215100
H	-2.53985400	0.59924300	2.25399900
C	-3.11872200	-2.59305800	0.02633200
H	-3.59927300	-2.55343500	1.00017800
H	-3.89159600	-2.46547500	-0.73370700
H	-2.70138000	-3.59235000	-0.10627700

INT16

Rh	0.89379400	-0.16845900	-0.26119900
Cl	2.13134900	-0.19404600	-2.29973100
O	3.02683600	-1.77313500	1.09577600
C	2.20594200	-1.19526200	0.57273900
C	0.46985200	1.05508300	1.28194800
C	0.11128900	2.17227700	0.64205700
C	-0.00578000	1.86766400	-0.80492900
C	-0.92420000	0.96665700	-1.26236400
C	-2.09603900	0.50655100	-0.45076700
C	-3.34668400	0.10348700	-1.22597900
C	-1.82950400	-0.76965900	0.28952800
C	-0.61068800	-1.18001500	0.61348000
H	-0.89770600	0.69570200	-2.31126200
H	-2.36742900	1.28055800	0.27191500
H	-3.97551900	0.93644000	-1.52727500
H	-3.07235700	-0.48055400	-2.11256000
C	-3.15378900	-1.48262700	0.41784200
O	-4.07772400	-0.67915900	-0.30178200
H	-3.10526200	-2.49053300	-0.00594600
H	-3.50757000	-1.55874400	1.44644600
H	0.67929700	2.32374700	-1.51114900
C	-0.33057000	-2.41799000	1.40217700
H	0.24893600	-3.14054500	0.82784200
H	0.24131400	-2.18920300	2.30293400
H	-1.25630600	-2.90078100	1.71646400
C	0.72146000	0.81407400	2.72280200
H	1.74056300	0.46854800	2.89626700
H	0.56799800	1.71895100	3.31056000
H	0.04721200	0.04871100	3.10634100
C	-0.05841000	3.56005300	1.16794700
H	0.15351300	3.61495900	2.23208900
H	0.61401400	4.24801700	0.65333900
H	-1.07450900	3.92075000	1.00254500

TS17

C	-1.83496600	-0.55867900	0.43268100
C	-2.09694700	0.38533900	-0.69114900
C	-0.86095100	0.63359500	-1.50283600
C	0.01562500	1.62755900	-1.14786200
C	-0.64377400	-0.65518200	1.03007400
Rh	0.90182100	-0.22854900	-0.23801700
Cl	2.14773400	-0.67719600	-2.18970200
H	-2.45442800	1.33345700	-0.27200300

H	-0.77233400	0.17707400	-2.47989500
C	0.03692100	2.16021400	0.22134400
C	0.23979500	1.16795100	1.12622600
C	-3.08280300	-1.36808200	0.64375400
H	-2.89520200	-2.43570600	0.48111900
H	-3.51263700	-1.24769700	1.63916000
C	-3.25902300	-0.32475400	-1.37895700
O	-4.00797200	-0.86688700	-0.30608000
H	-3.91353600	0.33284700	-1.94277800
H	-2.88478400	-1.11576000	-2.03901000
C	2.20331000	-1.13961600	0.74675200
O	3.01513100	-1.66443800	1.33866800
H	0.71840200	2.01201400	-1.87822100
C	-0.42245400	-1.55741100	2.20770000
H	-1.29379300	-1.57737000	2.86358100
H	-0.23389400	-2.57589100	1.86564700
H	0.43335200	-1.25936700	2.80581200
C	0.55585400	1.34732500	2.57245000
H	0.78993900	2.38662100	2.79156000
H	-0.27471900	1.04830400	3.21096600
H	1.42098200	0.75201800	2.85939500
C	0.06636500	3.63715000	0.45258100
H	0.25830800	3.89274700	1.48988200
H	0.84242200	4.09707300	-0.16113400
H	-0.88050000	4.09482000	0.16435600

TS18

C	1.99212700	-0.95869400	-0.20919000
C	2.46678000	0.46845000	-0.23448600
C	2.18777000	1.12391900	1.08195700
C	1.23027900	2.02932300	1.27173800
C	0.76919800	-1.46404900	-0.38340000
H	1.99015100	1.02283400	-1.03935300
H	2.83493000	0.82940100	1.89906400
C	0.35541800	2.51450800	0.19793900
C	-0.42249200	1.72896400	-0.55603300
C	3.21238300	-1.80246000	0.06816200
H	3.09482300	-2.45771900	0.92931900
H	3.43063100	-2.42830300	-0.80836600
C	3.96885800	0.25999100	-0.43611800
O	4.26371200	-0.89842000	0.32015300
H	4.19496300	0.09977900	-1.49585400
H	4.57740000	1.07611800	-0.05845500
H	1.15383200	2.51393700	2.23963800
Rh	-1.01343500	-0.21358000	-0.02266800
C	-0.88780500	0.15177800	1.99448300
O	-0.85658200	0.25651700	3.11376700
C	-0.33416700	-0.76243600	-1.68525400
O	-0.15651300	-0.90882800	-2.81386000
Cl	-2.29379900	-2.19580000	0.74429300
C	-2.83047500	0.43676300	-0.23795900
O	-3.90596800	0.73898600	-0.38738000
C	0.54989500	-2.95070400	-0.33972400
H	1.40034200	-3.46763900	-0.78690600
H	0.42815600	-3.29396300	0.68625500
H	-0.35064500	-3.24931400	-0.86617300
C	-1.14007300	2.27875700	-1.76174300
H	-2.08863500	2.74583100	-1.48218000
H	-0.54388000	3.03322900	-2.27314100
H	-1.37284100	1.50307500	-2.48647600
C	0.47259900	4.00168100	-0.04705300
H	1.33778100	4.23204400	-0.67250700
H	-0.41126400	4.42085300	-0.51907300
H	0.62446100	4.51875000	0.89992500

TS19

Rh	-1.04562600	-0.30474200	-0.35396100
Cl	-1.51937100	-1.79269700	-2.09124500
O	-3.65554000	1.13963100	-0.98660100
O	-0.74456800	2.48984700	-0.01598000
C	-2.66959600	0.63369600	-0.77219600
C	-0.07041800	1.48481400	0.06674000
C	-0.60012800	0.51731300	1.60095300
C	-0.34187200	-0.73015200	2.07997200

C	-0.13192700	-1.71659900	1.02274900
C	0.83067100	-1.52217500	0.05872300
C	2.07708700	-0.74888500	0.35971300
C	3.34372700	-1.47497300	-0.11389200
C	3.67470200	0.65577000	-0.76790700
C	2.24680700	0.58313900	-0.29500100
C	1.33865200	1.55222800	-0.40209900
H	-0.73991200	-2.61395500	1.02225500
H	0.87486300	-2.22296000	-0.76481100
H	2.14753200	-0.59187800	1.43936000
H	3.69546200	-2.23690900	0.57480600
H	3.16363400	-1.93225800	-1.09427900
H	4.19552000	1.55171200	-0.43797400
H	3.71321900	0.61697600	-1.86408200
O	4.31980900	-0.46490500	-0.20013900
C	1.65501300	2.86670500	-1.05408800
H	0.98197200	3.04332300	-1.89086000
H	1.49432200	3.68465900	-0.35419900
H	2.67795600	2.90222900	-1.41627300
C	-1.23928000	1.57078900	2.44673600
H	-1.77487100	1.13381300	3.28612700
H	-0.49946400	2.27487200	2.83008900
H	-1.93220900	2.14990400	1.84455600
C	-0.55264400	-1.17292100	3.49427500
H	0.08812600	-2.01931200	3.73207200
H	-0.33962300	-0.37158800	4.19581100
H	-1.58643900	-1.48845900	3.65052500

2E'

C	1.38533800	0.76292600	-0.02039200
C	1.22079300	-0.64091000	0.49298500
C	0.75266500	-1.45479300	-0.66984900
C	-0.53246900	-1.55751200	-1.00226300
C	0.42179700	1.60727600	-0.37860800
H	0.49126800	-0.68429800	1.30147900
H	1.51474600	-1.92990800	-1.27433500
C	-1.65159000	-1.00533600	-0.24456000
C	-1.79463300	0.26276700	0.20651900
C	2.86603500	1.00715500	-0.12864200
C	2.64420400	-0.97272400	0.93026300
O	3.46974900	-0.26132900	0.02820000
H	2.81614900	-0.63671000	1.95858700
H	2.89158800	-2.02784600	0.85511700
H	-0.79921900	-2.19687100	-1.83547900
C	-1.03612800	1.47630500	-0.23862000
O	-1.70278300	2.47678900	-0.45196800
H	3.18963600	1.69077300	0.66678100
H	3.16863100	1.42153500	-1.08653700
C	-2.75150900	-2.00792600	0.00889000
H	-2.71873200	-2.36184700	1.04101300
H	-3.73980800	-1.58359800	-0.15757100
H	-2.63610700	-2.87781700	-0.63254500
C	-3.02073100	0.63382700	0.99888200
H	-3.88288500	0.77498100	0.34486800
H	-3.27179900	-0.13821600	1.72271200
H	-2.86951900	1.57449300	1.51799200
H	0.68769400	2.58532300	-0.75957400

TS12$_{2E}$

C	1.37776900	0.67176200	-0.35801300
C	1.11144100	-0.60464800	0.34173300
C	0.61383500	-1.66882100	-0.46222700
C	-0.67887700	-1.69424700	-0.92732600
C	0.44417400	1.53065400	-0.76834700
H	1.22779600	-2.55258600	-0.58686400
C	-1.67417900	-0.91719200	-0.32726800
C	-1.37716700	0.21200700	0.48553500
C	2.87147900	0.82611900	-0.41513200
H	3.25190100	0.83206400	-1.43588100
H	3.17098900	1.76090400	0.06955000
C	2.40381800	-0.84354500	1.09202400
O	3.41629200	-0.29023700	0.26348300
H	2.38736200	-0.34775700	2.06817100
H	2.62589100	-1.89777700	1.23884400

H	-0.99370200	-2.53176500	-1.53401500
C	-0.92505400	1.43609000	-0.28963800
O	-1.70770300	2.35794500	-0.41161300
H	-0.06722600	-0.22976600	0.91101800
C	-2.37351100	0.58091900	1.55822000
H	-3.30324200	0.94240500	1.12071300
H	-2.59572300	-0.27118300	2.19745400
H	-1.98094100	1.38634700	2.17352100
C	-3.08254200	-1.42971500	-0.37007100
H	-3.18554000	-2.22905100	-1.09883800
H	-3.38586700	-1.82063500	0.60214200
H	-3.78028600	-0.63013700	-0.62030100
H	0.69276000	2.45097400	-1.27740400

2E

C	-1.34664300	-0.66832700	-0.17423500
C	-1.49111500	0.71850500	0.20954800
C	-0.69846900	1.79417400	-0.00935200
C	0.64191000	1.85339400	-0.50674400
C	-0.29509100	-1.46262500	-0.46368300
H	-1.18229500	2.75736900	0.11628400
C	1.65673400	1.01098100	-0.22979500
C	1.49464900	-0.11409800	0.74712800
C	-2.76106000	-1.20770000	-0.25194800
H	-2.96582100	-1.71411100	-1.19239400
H	-2.92309700	-1.91878000	0.56802900
C	-2.93310300	0.86820700	0.62504600
O	-3.62714400	-0.10239000	-0.13073400
H	0.86122900	2.70471400	-1.14120700
C	1.11847800	-1.28285400	-0.16059100
O	1.96684300	-2.04144000	-0.58520200
H	0.65105100	0.10757000	1.39867200
H	-3.05136100	0.67689600	1.70010200
H	-3.34630400	1.84764200	0.39935100
C	2.73796100	-0.42805200	1.56259300
H	3.08739600	0.45546600	2.09394300
H	2.51610300	-1.20110600	2.29508500
H	3.53308600	-0.80118500	0.92369700
C	2.98017500	1.12875500	-0.90566700
H	2.96526100	1.88075400	-1.68934700
H	3.76739800	1.37756900	-0.19345900
H	3.24911200	0.16342800	-1.34153500
H	-0.50591700	-2.44774500	-0.86352800

2h'

C	1.83621400	-1.39096200	0.46979900
C	0.65343100	-2.34580800	0.48515600
C	0.06596900	-2.67037600	-0.84981200
C	-0.92510000	-1.98529700	-1.41885000
C	1.93027800	-0.24736400	-0.21906800
H	-0.11509600	-1.89556300	1.11944500
H	0.46773300	-3.54114000	-1.35462500
C	-1.46192800	-0.75674000	-0.82333500
C	-0.60681300	0.24037700	-0.52591400
C	2.88009400	-2.01226300	1.36270800
C	1.25087400	-3.56117700	1.19626400
O	2.22173400	-3.03953400	2.07192000
H	0.52985500	-4.12378700	1.78151100
H	1.71252600	-4.23352500	0.46141600
H	-1.37029100	-2.33924000	-2.33995600
C	0.80520400	0.23253100	-1.05954000
O	1.02064400	0.78347100	-2.12112200
H	3.29112000	-1.31693400	2.08637100
H	3.70546400	-2.41997300	0.76337200
Si	3.48377900	0.82728700	-0.43287400
C	4.31758400	0.32689900	-2.03238100
H	4.62821800	-0.71727100	-2.00593500
H	3.62218500	0.45437600	-2.85920100
H	5.20139300	0.93694300	-2.22044000
C	2.98209500	2.63009100	-0.48304100
H	2.41265300	2.85106700	-1.38257600
H	2.37473900	2.90088600	0.38004900
H	3.87145500	3.26060100	-0.47956000
C	4.69868400	0.61933700	0.98604200

H	4.24365900	0.82205000	1.95486400	H	-4.02615600	1.04037100	1.43749700
H	5.15939400	-0.36606000	1.01859900	C	-1.85045400	2.93228600	1.69065400
H	5.50002200	1.34607800	0.84596300	O	-3.21680200	2.94310600	1.31249900
C	-0.94053300	1.45511200	0.24585200	H	-1.72582600	2.51397100	2.69502900
C	-1.58192700	1.34498300	1.48030700	H	-1.48935200	3.95798200	1.69260200
C	-0.59609900	2.72158500	-0.22432600	H	0.92516500	2.61871200	-1.98691300
C	-1.88073100	2.47443800	2.22031400	C	-0.63397600	-0.67114300	-0.20910100
H	-1.84772700	0.36483300	1.84871600	O	-0.40271600	-1.81627300	-0.57213600
C	-0.90148300	3.85162800	0.51716800	H	-0.21981200	1.16768700	0.95448800
H	-0.10447400	2.81084400	-1.18116200	C	2.44192500	0.58225300	-1.23592300
C	-1.54278800	3.73229000	1.74044600	C	2.77923800	-0.76509100	-1.38895600
H	-2.37667500	2.37375700	3.17457100	C	3.35927300	1.55604900	-1.63257700
H	-0.63712300	4.82735100	0.13656300	C	4.00090600	-1.12326100	-1.92861600
H	-1.77664000	4.61390200	2.31893800	H	2.06339300	-1.52047500	-1.09696700
C	-2.92161200	-0.70290700	-0.59886400	C	4.58440400	1.19324300	-2.16481800
C	-3.59156300	-1.84216100	-0.15454000	H	3.12295700	2.60112700	-1.49318000
C	-3.66336300	0.45054400	-0.85725000	C	4.90844300	-0.14711000	-2.31473300
C	-4.96060600	-1.82224800	0.05813300	H	4.24561800	-2.16824200	-2.04899300
H	-3.02664900	-2.74482300	0.03181800	H	5.29098000	1.95703500	-2.45495400
C	-5.03081000	0.46749300	-0.65202500	H	5.86529800	-0.42935200	-2.72878900
H	-3.15980600	1.33068800	-1.22718900	C	1.40117400	-0.50633300	1.35493400
C	-5.68388000	-0.66597100	-0.18720700	C	2.47472600	0.23803400	1.85111100
H	-5.46213200	-2.71092500	0.41260000	C	1.14432900	-1.75368700	1.92436100
H	-5.59108300	1.36716100	-0.86031800	C	3.28566000	-0.25720900	2.85481900
H	-6.75179300	-0.64900700	-0.02620200	H	2.66924800	1.21816500	1.43906600
				C	1.95358100	-2.24475400	2.93581200
TS12$_{2h}$				H	0.32766600	-2.35255500	1.55781200
C	-2.21588300	1.07829300	0.29420900	C	3.02965200	-1.50602500	3.40193200
C	-1.16737900	2.06453600	0.65965700	H	4.11417000	0.33483600	3.21523200
C	-0.48449900	2.71883700	-0.40675100	H	1.74300200	-3.21686600	3.35747800
C	0.47465400	2.08737900	-1.16148800	H	3.65969800	-1.89641100	4.18753900
C	-1.99460400	-0.13813100	-0.23502900	Si	-3.26547900	-1.39595800	-0.86331200
H	-0.63776000	3.78307100	-0.53803700	C	-4.99244900	-0.65250300	-0.91487700
C	1.11415100	0.92907300	-0.70233400	H	-5.66730700	-1.39752300	-1.33832800
C	0.52623900	0.13485100	0.33781600	H	-5.38048100	-0.38813700	0.06725500
C	-3.52221100	1.69655400	0.72018600	H	-5.04460400	0.22768200	-1.55473600
H	-4.19816200	1.87044100	-0.11384000	C	-2.80714400	-1.87568900	-2.61348200

H	-2.78022500	-1.00065300	-3.26231000
H	-1.82870800	-2.34796200	-2.63439500
H	-3.54044300	-2.57168600	-3.02165000
C	-3.29482400	-2.88586700	0.27093800
H	-3.53127900	-2.59840500	1.29521400
H	-4.04811500	-3.60273800	-0.05641400
H	-2.32570400	-3.37883500	0.26730200

2h

C	-2.44305600	-0.84755100	-0.47888400
C	-1.94457300	-2.08489700	-1.05809100
C	-0.82171000	-2.82576400	-0.89539400
C	0.43530300	-2.57461700	-0.26112200
C	-1.85907800	0.11367900	0.28192200
H	-0.89985900	-3.83270700	-1.29649500
C	1.10593400	-1.40478300	-0.18450200
C	0.47996400	-0.15595100	-0.73920700
C	-3.92213900	-0.84784200	-0.81738600
H	-4.50810700	-1.24958000	0.02047300
H	-4.29964800	0.13575400	-1.06659600
C	-3.10529100	-2.69031900	-1.82196300
O	-4.05253100	-1.66222200	-1.95767300
H	0.95017500	-3.45424000	0.10434400
C	-0.41180900	0.26081600	0.44545600
O	0.08221600	0.76221100	1.43945800
H	-0.16774500	-0.44423200	-1.56392100
H	-2.82571900	-3.03480500	-2.81477300
H	-3.52358700	-3.53877300	-1.26353100
Si	-2.73192400	1.46051800	1.32404600
C	-4.55926400	1.69316300	0.94201300
H	-4.74267800	2.06113400	-0.06616800
H	-5.15847500	0.79893800	1.10030300
H	-4.92645000	2.45411600	1.63281900
C	-1.90159500	3.10810500	1.00480400
H	-1.95152600	3.37229100	-0.05143200
H	-2.40913300	3.89275700	1.56647500
H	-0.85715700	3.09287600	1.30338300
C	-2.59724600	0.94486100	3.11954000
H	-3.09464600	-0.00970300	3.28968800
H	-1.55305200	0.84573700	3.40262000
H	-3.06879500	1.68802400	3.76340600
C	2.38619800	-1.34081500	0.54402000
C	2.41075200	-1.59624600	1.91311000
C	3.57877200	-1.03970100	-0.11255700
C	3.60549200	-1.55401300	2.61342200
H	1.48165000	-1.80135800	2.42418100
C	4.77285800	-1.01348800	0.58669600
H	3.56524900	-0.83156000	-1.17204300
C	4.78849000	-1.26622100	1.95087800
H	3.61106000	-1.74279400	3.67685800
H	5.69221500	-0.78901200	0.06631700
H	5.72065100	-1.23582500	2.49583500
C	1.39501800	0.93746500	-1.22244000
C	1.46652400	1.17072400	-2.59255200
C	2.17243000	1.71768400	-0.36844500
C	2.29691500	2.15419000	-3.10688100
H	0.86416700	0.57213000	-3.26259500
C	2.99613600	2.70560600	-0.88301400
H	2.12560600	1.54422500	0.69381200
C	3.06522900	2.92633000	-2.25041800
H	2.33869900	2.31844500	-4.17378200
H	3.59255800	3.30275500	-0.20869900
H	3.71246600	3.69575400	-2.64543200

2L'

C	1.43841400	0.87090700	-0.01554000
C	1.19505900	-0.46959100	0.70335800
C	0.73805900	-1.50252000	-0.27060000
C	-0.51130800	-1.66750700	-0.70986600
C	0.31853900	1.25697100	-0.96946800
H	0.46934700	-0.34725900	1.50849100
H	1.51207800	-2.13999000	-0.68231500
C	-1.72911600	-0.99500000	-0.25394700
C	-1.92013000	0.31331800	0.04784200

C	2.79844100	0.62482200	-0.66399200
C	2.60379500	-0.74921900	1.19347600
O	3.44411700	-0.38288200	0.11000500
H	2.82895200	-0.15112400	2.08193500
H	2.78836200	-1.79708200	1.42130100
H	-0.68629600	-2.48019600	-1.40562200
C	-0.96512500	1.43425400	-0.18974900
O	-1.21765100	2.53905500	0.24846300
H	3.41438200	1.52382900	-0.68661400
H	2.68531300	0.25621700	-1.68632100
C	-2.88121800	-1.95058200	-0.06917700
H	-3.01496900	-2.18518100	0.98884400
H	-3.81992700	-1.53092900	-0.42497200
H	-2.69928700	-2.88865000	-0.58684500
C	-3.23003200	0.75235300	0.64238700
H	-4.02556500	0.73839900	-0.10574900
H	-3.54063300	0.09952300	1.45617800
H	-3.14061900	1.76587600	1.01460200
H	1.53174800	1.64688500	0.74560500
H	0.53182000	2.22261200	-1.42229100
H	0.22129500	0.50844800	-1.75231500

$TS12_{2L}$

C	1.38809600	0.78318500	-0.15511700
C	1.09333100	-0.61403800	0.38550800
C	0.57900700	-1.64565800	-0.43022800
C	-0.72956200	-1.69791800	-0.88757900
C	0.34087500	1.24750200	-1.13990000
H	1.15793200	-2.55776000	-0.52071800
C	-1.72851400	-0.92002800	-0.31674900
C	-1.41607400	0.23013300	0.47102000
C	2.82956000	0.59263700	-0.57816300
H	2.88890500	0.04770100	-1.52626100
H	3.38463600	1.52391300	-0.66555400
C	2.37205400	-0.91280300	1.13492500
O	3.40131200	-0.16229900	0.48303300
H	2.31666500	-0.59619600	2.17822400
H	2.61894500	-1.97498200	1.11064300
H	-1.03110100	-2.56096500	-1.46550300
C	-0.91271000	1.41474200	-0.31703800
O	-1.47622300	2.47926000	-0.22014700
H	-0.12787800	-0.23231500	0.93353900
C	-2.40087900	0.64033500	1.53683500
H	-3.33086100	1.00051100	1.09673400
H	-2.63078800	-0.19144000	2.19921600
H	-1.99693200	1.46018100	2.12400800
C	-3.13602000	-1.43856800	-0.33225200
H	-3.24254900	-2.24564400	-1.05239800
H	-3.42076300	-1.82667900	0.64692600
H	-3.84836400	-0.65135700	-0.57896900
H	0.57501200	2.21336500	-1.57831200
H	0.21145000	0.50879000	-1.93052300
H	1.39999400	1.47005300	0.69828700

2L

C	-1.32671000	-0.71300200	0.02552600
C	-1.51137700	0.77398200	0.16696600
C	-0.70509900	1.80513100	-0.10795000
C	0.69113200	1.85310700	-0.51159900
C	-0.22110600	-1.20900400	-0.88972200
H	-1.17626400	2.78318400	-0.06582500
C	1.70052300	1.04162400	-0.16905600
C	1.49254800	-0.15236700	0.73311500
C	-2.73454000	-1.09448100	-0.42479700
H	-2.86204400	-0.87704100	-1.49252100
H	-2.97813800	-2.13853400	-0.24543500
C	-2.96267100	0.96203000	0.54127800
O	-3.58906000	-0.29903500	0.36843200
H	0.93909400	2.69630900	-1.14692500
C	1.13533800	-1.28864400	-0.21933800
O	1.91298700	-2.17238400	-0.47525900
H	0.62247700	0.06121600	1.35478100
H	-3.09374500	1.26064400	1.58226700
H	-3.43157500	1.72116200	-0.09200600

C	2.68610500	-0.50603900	1.60244300
H	2.98862800	0.34589400	2.20845300
H	2.43340500	-1.32844500	2.26802400
H	3.52810700	-0.82874400	0.99648000
C	3.07414600	1.22677300	-0.73024400
H	3.09751900	2.03797100	-1.45293700
H	3.79938600	1.44300400	0.05474300
H	3.41251500	0.31234500	-1.22265300
H	-1.20140200	-1.14741400	1.02482900
H	-0.44152700	-2.20991300	-1.25668700
H	-0.13758000	-0.55494900	-1.75969300

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O	-2.38467000	-0.59065400	0.16212300
C	1.86260000	2.28305400	-0.08358200
C	1.68713300	1.34116500	0.85747000
C	1.29616100	2.05740400	-1.41282800
C	0.12790100	1.41503100	-1.63150500
C	-0.69379400	0.92078800	-0.52753300
C	-1.98183000	0.24550500	-0.90403900
C	-3.64675900	-1.19580900	-0.04427500
H	1.85526400	2.43046400	-2.26366700
H	-0.18047400	1.20757200	-2.64963200
H	-0.82967500	1.66770400	0.25212700
H	-1.85084900	-0.35375700	-1.81539900
H	-2.76191300	0.98850300	-1.10094700
H	-3.77150100	-1.90142900	0.77411900
H	-3.63715700	-1.76829000	-0.97908900
C	-4.75333700	-0.24645300	-0.06056600
C	-5.65964800	0.54024900	-0.07036900
Rh	0.79231500	-0.36171600	0.14119900
Cl	2.80763300	-1.70273500	0.77781900
C	-0.03707000	-0.55658600	1.75688500
C	0.02619500	-2.11965600	-0.61699000
O	-0.53476600	-0.68471700	2.76492600
O	-0.35836400	-3.12473700	-0.94403400
C	-6.75989300	1.48554400	-0.07410400
H	-7.68524600	0.99962900	0.23145000
H	-6.56924100	2.30421300	0.61800000
H	-6.91370900	1.90892800	-1.06535700
C	2.64874300	3.55419500	0.07996800
H	3.40644300	3.63015900	-0.70148900
H	2.00131300	4.42697500	-0.01592700
H	3.15373300	3.61391600	1.03781200
C	2.18362300	1.37705000	2.25779200
H	2.81090000	2.24227500	2.46191200
H	1.34697400	1.40515200	2.96022800
H	2.75213400	0.47264300	2.47032800
C	2.43712800	-0.75338700	-2.03306100
O	3.41107000	-0.61732800	-2.57688200

INT17

Rh	-1.02819000	-0.47355600	-0.19329500
C	0.63820100	0.40244000	-1.14058100
C	0.30667300	1.73274900	-1.71088300
C	-0.38362600	2.67870800	-1.06826100
C	-1.01610900	2.52956600	0.23634600
C	-1.37231100	1.34640800	0.76790000
H	0.70386100	1.95829600	-2.69408200
H	0.90696300	-0.28418000	-1.94150600
C	-0.71554200	-2.26324700	-1.10416900
O	-0.56748100	-3.27071800	-1.58024400
Cl	-3.02208000	-1.66944100	0.75066300
C	-2.22391000	0.29279600	-1.51100300
O	-2.98875600	0.72559500	-2.21347300
C	1.83306800	0.50886700	-0.21840800
H	2.67610800	0.94926000	-0.76045200
H	1.60410000	1.15713600	0.63557100
O	2.18780100	-0.78790900	0.22313100
C	3.28061200	-0.79501300	1.12158300
H	3.05515000	-0.15992100	1.98642600
H	3.36553200	-1.81964900	1.47753000
C	4.53556700	-0.36935200	0.51412100
C	5.56770600	-0.01901100	0.01206400

H	-0.49065900	3.64689500	-1.54222100
C	6.81771500	0.39920600	-0.59351100
H	7.01120100	1.45486300	-0.41006700
H	7.65250800	-0.17187800	-0.19014300
H	6.79647900	0.24190000	-1.67078700
C	-2.00968600	1.25775900	2.11856400
H	-2.63886600	2.12464000	2.31922700
H	-2.61855600	0.36497900	2.21962800
H	-1.24435700	1.22965700	2.90143000
C	-1.29396700	3.81952700	0.97707500
H	-0.85539800	3.80695100	1.97411600
H	-0.87864900	4.67112000	0.44399600
H	-2.36397400	3.99197000	1.09836000
C	-0.07209700	-0.98437100	1.43449500
O	0.31952500	-1.25368400	2.45533300

TS21

Rh	-1.05066200	-0.49650500	-0.21081000
C	0.66292900	0.26017500	-1.19091200
C	0.38561700	1.58213800	-1.77340100
C	-0.08912300	2.62708400	-1.07675600
C	-0.69968000	2.53976800	0.22675900
C	-1.42093800	1.45249400	0.63036300
H	0.66710400	1.74353700	-2.80803300
H	0.93726700	-0.44134700	-1.97427000
C	-1.09469000	-2.02273600	-1.42640400
O	-1.16816600	-2.88782700	-2.14576000
Cl	-3.00983200	-1.59187600	0.86462600
C	-2.26766700	0.81545400	-0.86583300
O	-3.15430500	1.30643100	-1.40779000
C	1.84150700	0.34206700	-0.23431100
H	2.68004700	0.84151400	-0.73065500
H	1.58323400	0.92516700	0.65732600
O	2.22816400	-0.96630900	0.12215500
C	3.29104000	-1.00400500	1.05383900
H	3.01336900	-0.45017200	1.95855600
H	3.40475200	-2.05007100	1.33007800
C	4.54687600	-0.48391000	0.52622600
C	5.58018600	-0.05706600	0.09001300
H	-0.08080600	3.61033400	-1.53110400
C	6.83257300	0.45082800	-0.43711700
H	6.97668900	1.49745300	-0.17375400
H	7.67516700	-0.11513600	-0.04285400
H	6.85592300	0.36926200	-1.52272100
C	-2.20999100	1.48010600	1.90201000
H	-2.73844900	2.42702500	2.02268300
H	-2.92807300	0.66880700	1.93886900
H	-1.54165900	1.36120700	2.75831500
C	-0.68190800	3.78186600	1.07079800
H	-0.43274300	3.54627400	2.10404900
H	0.03708200	4.50467000	0.69616300
H	-1.66702600	4.25270100	1.08360800
C	-0.01971000	-1.39561300	1.28297200
O	0.35217200	-1.88960600	2.22540600

INT18

Rh	-0.86787600	-0.27479800	-0.13317600
C	0.67511600	1.15573700	-0.26250600
C	0.18594500	2.41734200	0.35944000
C	-1.01250500	2.47951000	0.92099900
C	-2.00117300	1.37082000	0.85124000
C	-2.58228200	1.09121500	-0.41061500
H	0.83526800	3.28742400	0.35997100
H	0.89660000	1.31402000	-1.32001900
C	0.03831600	-1.38548100	-1.44962100
O	0.51906800	-2.03722300	-2.23294900
Cl	-2.49045800	-2.11922400	0.16635700
C	-1.68328300	1.08731300	-1.50577700
O	-1.39589600	1.49378500	-2.56814400
C	1.94867700	0.69561100	0.41967100
H	2.76234100	1.39158900	0.18466200
H	1.82521400	0.69468700	1.51017400
O	2.28837500	-0.59801700	-0.02906900
C	3.45189000	-1.11620700	0.58461300

H	3.31709700	-1.13540900	1.67282800
H	3.53212300	-2.14582800	0.24278500
C	4.66668600	-0.38137700	0.25154600
C	5.66296500	0.22653300	-0.02809000
H	-1.35229800	3.38041200	1.42047000
C	6.87049300	0.95380000	-0.37043000
H	7.17711200	1.61384300	0.43946100
H	7.69061700	0.26751700	-0.57566100
H	6.71481400	1.56157700	-1.26046900
C	-3.96234700	0.55819200	-0.64614000
H	-4.61190800	1.41910900	-0.81872700
H	-3.99935300	-0.08732400	-1.51783200
H	-4.32883000	-0.01022600	0.19999600
C	-2.80073000	1.10141000	2.09728400
H	-3.24624100	0.11001100	2.07103000
H	-2.15728100	1.16478900	2.97117400
H	-3.59705500	1.83897600	2.21768300
C	-0.09826000	-1.06012400	1.54692500
O	0.31057100	-1.53832200	2.48217300

TS22

Rh	-0.92838800	-0.18405600	-0.25290800
C	0.58759200	1.23948500	-0.26945000
C	0.11809200	2.48438700	0.39495000
C	-1.03948700	2.55269900	1.03744600
C	-2.08865200	1.51322400	1.05444300
C	-2.71104600	1.10735400	-0.10860400
H	0.77345600	3.35014700	0.38822500
H	0.94065200	1.45726800	-1.27831500
C	0.05502600	-1.18087600	-1.53176700
O	0.52363000	-1.76221300	-2.37811600
Cl	-2.26054700	-2.08111900	0.36968200
C	-1.87918700	1.12655400	-1.32154700
O	-1.85263700	1.56016200	-2.41237300
C	1.73674400	0.63858000	0.51495000
H	2.52050400	1.39402600	0.65591800
H	1.40737100	0.31609600	1.51198500
O	2.26190700	-0.45879200	-0.20078400
C	3.45817600	-0.96631900	0.35621400
H	3.30674100	-1.20529700	1.41501700
H	3.65787800	-1.89882500	-0.16757600
C	4.58915200	-0.05581900	0.21737300
C	5.51939200	0.69284900	0.09633300
H	-1.30170200	3.44509400	1.59613600
C	6.64761300	1.59199300	-0.05512800
H	6.79305300	2.19824300	0.83758500
H	7.56457800	1.03314200	-0.23588900
H	6.49571100	2.26341300	-0.89886900
C	-4.08200200	0.51651400	-0.20423600
H	-4.78084900	1.33263600	-0.39991000
H	-4.14939400	-0.20153200	-1.01517000
H	-4.37159700	0.01366600	0.71147000
C	-2.72539600	1.22916300	2.38375300
H	-3.05057800	0.19224200	2.43737500
H	-2.01661200	1.41132100	3.18674200
H	-3.59389900	1.86968000	2.54839500
C	0.81244700	-2.58399900	1.70486900
O	1.06968100	-3.43221800	1.01446500

A’

Rh	-1.31864300	-0.20510500	-0.01722100
Cl	-3.56524600	-0.58763200	-0.46631700
O	-0.77472300	-3.05513700	0.51745600
O	3.04598100	0.02285300	-0.12223500
C	-0.99332100	-1.95923000	0.30013200
C	-1.64085100	2.19421500	-0.42583900
C	-0.59576500	3.18299700	-0.02736300
C	-0.78106300	2.03345200	0.89783600
C	0.13583400	0.88291100	0.97366100
C	0.73085000	0.36993700	-0.18255800
C	1.81061000	-0.65862300	-0.10724200
C	4.13639000	-0.87158400	-0.14967100
H	-2.68325500	2.42709800	-0.29168600
H	-1.42295800	1.61992100	-1.32633100

H	-0.93727000	4.14524400	0.31889700
H	0.31401400	3.20240700	-0.60757700
H	-1.35240900	2.22545300	1.79188800
H	0.42081700	0.52529100	1.95250300
H	0.77272000	0.97646800	-1.08128100
H	1.70963800	-1.25450700	0.80797900
H	1.74649400	-1.34289600	-0.96049400
H	4.11676200	-1.52458900	0.73096900
H	4.07650500	-1.51813400	-1.03323500
C	5.38395300	-0.13042000	-0.17457800
C	6.42546800	0.45817700	-0.19552800
H	7.34435500	0.98501300	-0.21417300

TS23

Rh	-1.06795200	0.14475700	-0.03327900
Cl	-2.99765700	1.43643300	-0.34535600
O	0.77120400	2.64868500	0.61013000
O	2.31828500	0.14577100	-0.46004500
C	0.07026200	1.82752600	0.28249200
C	-2.25382700	-1.24605600	0.99402600
C	-1.99953500	-2.51494400	0.23117700
C	-1.29270400	-1.78526300	-0.88141700
C	0.08160000	-1.41957800	-0.77608400
C	0.59356000	-1.15731900	0.50349500
C	1.97237700	-0.60634900	0.68006000
C	3.52798200	0.85666900	-0.31973000
H	-3.25400200	-0.84873600	0.89973700
H	-1.84965500	-1.16763700	1.99910700
H	-2.90112200	-3.01970800	-0.10087100
H	-1.35866800	-3.23544800	0.73450300
H	-1.75854000	-1.73996100	-1.85538500
H	0.65670200	-1.15008800	-1.64924400
H	0.23382400	-1.71739000	1.35766700
H	2.01435400	0.02263200	1.57762500
H	2.68970400	-1.42251100	0.82302700
H	3.62738600	1.45954800	-1.21927700
H	3.46500600	1.53936200	0.53531300
C	4.69505100	-0.00697100	-0.17015900
C	5.64602700	-0.72384000	-0.04356500
H	6.49235200	-1.35238900	0.06395200

B’

Rh	-0.85222200	0.16921800	-0.13793400
Cl	-2.63513800	-1.13406700	-1.12034200
O	-2.69532400	2.51263200	0.01866000
C	-1.99275700	1.63041400	-0.06559100
C	-1.02712800	-0.17434400	1.87616800
C	-0.07987500	-1.35252200	1.99410700
C	-0.00532500	-1.85664000	0.57338800
C	0.94697800	-1.46356900	-0.30913200
C	2.18776400	-0.71919100	0.07701200
C	3.35147600	-0.72268000	-0.90893400
C	1.96391700	0.76226200	0.17825900
C	0.75301100	1.31215400	0.21201200
H	-2.07225500	-0.43978300	2.00190000
H	-0.75375500	0.69125800	2.46616600
H	-0.45388600	-2.12050200	2.67058400
H	0.89632700	-1.02185800	2.34026200
H	0.87596500	-1.82711100	-1.32848000
H	2.57011000	-1.09603000	1.03036800
H	3.95655500	-1.62499600	-0.88656300
H	2.98409800	-0.56053100	-1.92931400
C	3.31955900	1.39681200	0.00535700
O	4.16280900	0.35173400	-0.47304100
H	3.28582800	2.22345800	-0.70741100
H	3.74232900	1.76410400	0.94142000
H	0.66725000	2.39358800	0.26261200
H	-0.79682600	-2.50837600	0.23047100

TS24

Rh	-0.91956900	0.05958800	0.03094900
Cl	-2.13125800	-1.64065700	-1.02405800
O	-2.88952900	2.04951000	-1.06958000
C	0.03639000	-1.31192100	1.53718300

C	0.80624700	-1.45875500	0.42306100
C	2.07729400	-0.68569900	0.22677800
C	2.89374600	-0.99378900	-1.02469000
C	1.82503900	0.77650400	-0.02161000
C	-0.25139800	1.05908800	1.86679300
C	0.31339600	-0.19651200	2.51804300
C	-2.14173000	1.30596600	-0.65624900
C	0.64234600	1.37053100	0.16152900
H	3.52093900	-1.87699800	-0.94029900
H	2.22983500	-1.09950800	-1.88942600
H	2.73848800	-0.81514200	1.09121200
H	0.57690500	-2.26075300	-0.26648400
H	1.38380600	-0.09238600	2.69189300
H	-0.16585700	-0.38084500	3.47705200
H	-1.30947100	1.21067100	2.08379500
H	0.26349000	1.96752600	2.15717700
O	3.74617500	0.12941600	-1.15766200
C	3.02572800	1.29198100	-0.76677200
H	3.68577700	1.89996500	-0.14501400
H	2.73370500	1.88152600	-1.63910500
H	0.50446500	2.41134200	-0.09771200
H	-0.76559000	-2.01146600	1.72672000

TS25

Rh	-1.01974800	-0.21054200	0.04152600
Cl	-1.55778400	-2.23592300	-0.91372000
O	-3.77126800	0.76900200	-0.85656300
O	-0.93230000	2.61059800	-0.61569900
C	-2.73436700	0.44022600	-0.55618800
C	-0.16424600	1.76802200	-0.20162400
C	-0.42941200	1.48192800	1.48885700
C	0.02434300	0.36800900	2.47711200
C	0.02865500	-0.95091400	1.76526500
C	0.90814900	-1.16040200	0.73080000
C	2.14717900	-0.34041000	0.50918500
C	3.33595000	-1.18194500	0.02485000
C	3.43156900	0.64267200	-1.28126000
C	2.12083700	0.73330400	-0.54449300
C	1.16340500	1.61349800	-0.81961600
H	-1.44530200	1.81714700	1.66470200
H	0.19809400	2.35484800	1.66508800
H	-0.67853700	0.35415700	3.30549900
H	1.00656700	0.59844000	2.89100000
H	-0.60439400	-1.75556700	2.11025300
H	0.88938100	-2.12499100	0.24048400
H	2.44986700	0.14137100	1.44291200
H	3.84489200	-1.71725700	0.82007800
H	2.99544000	-1.89849200	-0.73205200
H	3.94998800	1.59468700	-1.36221500
H	3.25745100	0.25182900	-2.29130200
O	4.22985900	-0.24674800	-0.53035400
H	1.30484800	2.32218000	-1.62626300

TS26

Rh	0.96875700	-0.13034000	0.28828400
Cl	2.80946500	1.27105600	0.60535600
O	-0.51907700	1.58604900	2.49468700
O	-2.45358400	0.15085900	0.35226900
C	-0.04719700	0.95493900	1.68757000
C	2.10584600	-1.26028700	-1.00661500
C	1.73559700	-2.63322900	-0.45465300
C	0.86072500	-2.21062700	0.70047300
C	-0.44036300	-1.70165400	0.49156300
C	-0.70943600	-1.04280400	-0.71842600
C	-1.96505700	-0.25631500	-0.90376500
C	-3.61082600	0.95255500	0.27336800
H	3.14446000	-0.99236500	-0.85939600
H	1.80896700	-1.09318200	-2.04039700
H	2.59770200	-3.19367000	-0.10387500
H	1.18944000	-3.26767100	-1.15295300
H	1.13144000	-2.49297100	1.70833200
H	-1.12018900	-1.57509000	1.32094000
H	-0.27911700	-1.41084900	-1.64030000
H	-1.76695400	0.61360900	-1.53809300

H	-2.71101400	-0.87764700	-1.41459000
H	-3.79828100	1.30924300	1.28345400
H	-3.42479500	1.82558100	-0.36117700
C	-4.77753500	0.22916800	-0.22332500
C	-5.72597000	-0.37499600	-0.63539400
H	-6.57096700	-0.90428500	-0.99428000
C	0.79641900	1.80403800	-2.10372600
O	1.61155000	1.95707900	-2.86119200

C'

Rh	0.92847800	-0.05646800	0.07188400
Cl	2.98352000	-0.74586800	-1.01973000
O	-0.42506500	-2.34791900	-1.64895400
O	-2.42954700	-0.40679700	-0.05068100
C	-0.00986400	-1.50647300	-1.02634600
C	2.00980100	1.48996100	0.93642800
C	1.79267800	2.50129200	-0.17813100
C	0.81358700	1.84705000	-1.13370600
C	-0.45713100	1.44312400	-0.75924900
C	-0.77279400	1.15824600	0.60143800
C	-2.10293800	0.55278600	0.93042900
C	-3.71159200	-0.97062300	0.11261100
H	3.03774400	1.15876300	1.01576500
H	1.62955400	1.79736400	1.90662900
H	2.72192400	2.68288200	-0.71027400
H	1.41224800	3.46683800	0.16222700
H	1.05372100	1.82604700	-2.18672900
H	-1.12900700	1.06613100	-1.51939900
H	-0.40579100	1.83085400	1.36552400
H	-2.07460900	0.08892200	1.92152600
H	-2.87245500	1.33390900	0.95145500
H	-3.77457900	-1.78577200	-0.60475900
H	-3.81476500	-1.39903100	1.11539000
C	-4.79301100	-0.01880100	-0.12375000
C	-5.67134700	0.77118900	-0.32089400
H	-6.45359400	1.46364400	-0.49869400
C	1.20585300	-1.09624800	1.63270900
O	1.39821400	-1.66263200	2.59372600

TS27

Rh	-0.29909600	-0.37322200	-0.03082400
C	0.78313900	1.30176500	-0.79605500
C	0.70909400	2.38236200	0.21809400
C	-0.41159800	2.96791800	0.63681100
C	-1.76983600	2.52157200	0.19615300
C	-1.99060900	1.04819800	0.51354900
H	-1.66508700	0.80266300	1.52192000
H	-2.53757500	3.10864200	0.69975500
H	-1.91173000	2.69553700	-0.87461500
H	1.64834200	2.72466700	0.63988000
H	0.23755800	1.60792100	-1.68898600
C	0.76246400	-1.69216900	-0.93140700
O	1.24018400	-2.52862000	-1.52010300
Cl	-1.62098800	-2.16154900	0.98273400
C	-1.66148300	0.10319700	-1.14588500
O	-2.34775900	0.28461000	-2.04854900
C	2.19669800	0.94492400	-1.23076700
H	2.19186800	0.56897500	-2.24991200
H	2.82381400	1.84509100	-1.20066000
O	2.85029200	-0.07664000	-0.48807200
C	2.89103500	0.14508600	0.89365300
H	3.66087300	-0.51309200	1.29227900
H	3.17794500	1.17599800	1.12434000
C	1.62924200	-0.17381800	1.57625800
C	0.68224200	-0.48070900	2.26241800
H	-0.10435700	-0.79135400	2.90510600
H	-0.34951000	3.76002300	1.36970900
H	-3.02009100	0.71151700	0.43862200

C'-Me

Rh	0.83127000	-0.19824300	-0.01872500
Cl	2.70100300	-1.52615100	-0.82492800
O	-0.78489500	-2.87228300	-0.58276500
O	-2.53711400	-0.33594300	0.12888100

C	-0.28603500	-1.88187500	-0.38657900
C	2.14633000	1.43838700	0.07095000
C	1.71089500	2.09497100	-1.23059800
C	0.74715900	1.11560700	-1.86707800
C	-0.52048400	0.92662600	-1.34516100
C	-0.77253700	1.24203400	0.02225300
C	-2.10503400	0.91352300	0.62114600
C	-3.82841300	-0.70097200	0.56132200
H	2.55218900	2.28864800	-1.89207400
H	1.20457800	3.04804000	-1.05805700
H	0.98575100	0.67282700	-2.82244300
H	-1.23243100	0.30466800	-1.87078100
H	-0.33591200	2.14884300	0.41794000
H	-2.03647000	0.88898900	1.71341600
H	-2.83490900	1.68640200	0.35160700
H	-3.97301800	-1.72994400	0.23968800
H	-3.88384300	-0.68154400	1.65507600
C	-4.88134600	0.14388400	0.00548100
C	-5.73616500	0.84359300	-0.45722700
H	-6.49799300	1.45567700	-0.86704600
C	1.13976400	-0.55526200	1.81563700
O	1.34411000	-0.71853600	2.91767100
C	2.18843400	2.33807700	1.28241000
H	1.22047900	2.77751100	1.52566400
H	2.54099700	1.80708300	2.16487500
H	2.87817700	3.16855400	1.10746100
H	3.09599000	0.93227200	-0.06457700

TS27-Me

Rh	-0.07836800	-0.41435800	-0.06509300
C	0.79801400	1.39509800	-0.78691900
C	0.52870100	2.45502500	0.21409700
C	-0.68262200	2.88088000	0.56609500
C	-1.93704500	2.24950500	0.05776100
C	-2.01441400	0.76994300	0.42830700
H	-1.60332800	0.62329100	1.42550100
H	-2.80669300	2.74879300	0.48862300
H	-2.03452200	2.36751700	-1.02614500
H	1.38920100	2.91916200	0.68435700
H	0.26394600	1.62680800	-1.70868600
C	1.22177900	-1.57127700	-0.88537000
O	1.83775300	-2.33618700	-1.44202900
Cl	-1.10206000	-2.41470700	0.90423900
C	-1.40540300	-0.14176700	-1.28143900
O	-2.06230900	-0.04845000	-2.21655400
C	2.26756500	1.23289200	-1.14621700
H	2.36677100	0.84929400	-2.15773600
H	2.76058800	2.21233900	-1.10141200
O	3.01905500	0.32088300	-0.35486700
C	2.94917100	0.54964700	1.02432300
H	3.77595600	0.00164100	1.47245500
H	3.08178100	1.61021300	1.26075000
C	1.70450200	0.06626400	1.63915100
C	0.77139000	-0.35601300	2.28189500
H	0.00082800	-0.76373100	2.88845900
H	-0.77123500	3.66990400	1.29972900
C	-3.40683900	0.17575300	0.38461500
H	-4.01278000	0.63943800	1.16467800
H	-3.89264400	0.36108300	-0.57162300
H	-3.38107200	-0.89526900	0.56795900

6. References

[1] a) Souillart, L.; Cramer, N. Catalytic C–C Bond Activations via Oxidative Addition to Transition Metals. *Chem. Rev.* **2015**, *115*, 9410–9464; b) Chen, P. H.; Billett, B. A.; Tsukamoto, T.; Dong, G. Cut and Sew Transformations via Transition-Metal-Catalyzed Carbon-Carbon Bond Activation. *ACS Catal.* **2017**, *7*, 1340–1360; c) Dian, L.; Marek, I. Asymmetric Preparation of Polysubstituted Cyclopropanes Based on Direct Functionalization of Achiral Three-Membered Carbocycles. *Chem. Rev.* **2018**, *118*, 8415–8434;

[2] a) Jiao, L.; Yu, Z.-X. Vinylcyclopropane Derivatives in Transition-Metal-Catalyzed Cycloadditions for the Synthesis of Carbocyclic Compounds. *J. Org. Chem.* **2013**, *78*, 6842–6848; b) Brownsey, D. K.; Gorobets, E.; Derksen, D. J. Beyond Geminal Diesters: Increasing the Scope of Metal-Mediated Vinylcyclopropane Annulations While Decreasing Pre-activation. *Org. Biomol. Chem.* **2018**, *16*, 3506–3523; c) Wang, J.; Blaszczyk, A. A.; Li, X.; Tang, W. Transition Metal-Catalyzed Selective C–C Bond Cleavage of Vinylcyclopropanes in Cycloaddition Reactions. *Chem. Rev.* **2021**, *121*, 110–139. d) Zhang, P.; Yu, Z.-X. Vinylcyclopropanes as Three-Carbon Synthons in Rhodium-Catalyzed Cycloadditions: Reaction Development, Mechanistic Studies, New Inspirations, and Synthetic Applications. *Acc. Chem. Res.* **2025**, *58*, 1065–1080.

[3] a) Rubin, M.; Rubina, M.; Gevorgyan, V. Transition Metal Chemistry of Cyclopropenes and Cyclopropanes. *Chem. Rev.* **2007**, *107*, 3117–3179; b) Archambeau, A.; Miege, F.; Meyer, C.; Cossy, J. Intramolecular Cyclopropanation and C–H Insertion Reactions with Metal Carbenoids Generated from Cyclopropenes. *Acc. Chem. Res.* **2015**, *48*, 1021–1031; c) Li, P.; Zhang, X.; Shi, M. Recent Developments in Cyclopropene Chemistry. *Chem. Commun.* **2020**, *56*, 5457–5471; d) Vicente, R. C–C Bond Cleavages of Cyclopropenes: Operating for Selective Ring-Opening Reactions. *Chem. Rev.* **2021**, *121*, 162–226; e) Li, C.; Zeng, Y.; Zhang, H.; Feng, J.; Zhang, Y.; Wang, J. Gold(I)-Catalyzed Cycloisomerization of Enynes Containing Cyclopropenes. *Angew. Chem. Int. Ed.* **2010**, *49*, 6413–6417; f) Han, J.; Fan, Y.; Yang, X.; Zhu, Y.; Zhang, X.; Zhang, F.; Hao, G.; Jiang, Y. Synthesis of Functionalized Cycloheptadienones Starting from Phenols and Using a Rhodium/Boron Asymmetric Catalytic System. *Angew. Chem. Int. Ed.* **2024**, e202416468; g) Akiyama, T.; Kusamoto, T.; Mashima, K.; Tsurugi, H. Synthesis of Multisubstituted Cyclopentadiene Derivatives from 3,3-Disubstituted Cyclopropenes and Internal Alkynes Catalyzed by Low-Valent Niobium Complexes. *J. Am. Chem. Soc.* **2024**, *146*, 33338–33348.

[4] a) Fumagalli, G.; Stanton, S.; Bower, J. F. Recent Methodologies That Exploit C–C Single-Bond Cleavage of Strained Ring Systems by Transition Metal Complexes. *Chem. Rev.* **2017**, *117*, 9404–9432; For selected work for cyclopropenes in transition metal-catalyzed cycloadditions, see: b) Padwa, A.; Xu, S. L. A New Phenol Synthesis from the Rhodium(I) Catalyzed Reaction of Cyclopropenes and Alkynes. *J. Am. Chem. Soc.* **1992**, *114*, 5881–5882; c) Eisch, J. J.; Qian, Y.; Singh, M. Nickel(O)-Induced Geminal Bond Cleavages Leading to Carbon-Carbon Double Bonds: Intermediacy of Nickel(O)-Carbene Complexes as a Unifying Hypothesis. *J. Organomet. Chem.* **1996**, *512*, 207–217; d) Isobe, H.; Sato, S.; Tanaka, T.; Tokuyama, H.; Nakamura, E. Thermal and Palladium-Catalyzed [3 + 2] Synthesis of Cyclopentadienone Acetals from Cyclopropenone Acetals and Acetylenes. *Org. Lett.* **2004**, *6*, 3569–3571; e) Li, C.; Zhang, H.; Feng, J.; Zhang, Y.; Wang, J. Rh(I)-Catalyzed Carbonylative Carbocyclization of Tethered Ene− and Yne−cyclopropenes. *Org. Lett.* **2010**, *12*, 3082−3085; f) Cheng, X.; Zhu, L.; Lin, M.; Chen, J.; Huang, X. Rapid Access to Cyclopentadiene Derivatives through Gold-Catalyzed Cycloisomerization of Ynamides with Cyclopropenes by Preferential Activation of Alkenes over Alkynes. *Chem. Commun.* **2017**, *53*, 3745–3748; g) Dai, P.; Ogunlana, A. A.; Bao, X. Mechanistic Insights into Cyclopropenes-Involved Carbonylative Carbocyclization Catalyzed by Rh(I) Catalyst: A DFT Study. *J. Org. Chem.* **2018**, *83*, 12734−12743; h) Huang, J.-Q.; Ho, C.-Y. [(NHC)NiIIH]-

Catalyzed Cross-Hydroalkenylation of Cyclopropenes with Alkynes: Cyclopentadiene Synthesis by [(NHC)NiII]-Assisted C−C Rearrangement. *Angew. Chem., Int. Ed.* **2019**, *58*, 5702–5706; i) Kikuchi, T.; Yasui, T.; Yamamoto, Y. Cycloaddition of Cyclopropenes with Alkynes via Carbon–Carbon Double Bond Cleavage Enabled by a Ruthenium Catalyst: Synthesis of Cyclopentadienes and Cycloheptatrienes. *ACS Catal.* **2023**, *13*, 9656–9666.

[5] a) Cho, S. H.; Liebeskind, L. S. Practical Organic Synthesis with Strained Ring Molecules. Rhodium Catalyzed Carbonylation of Cyclopropenecarboxylate Esters and Cyclopropenyl Ketones to α-Pyrones and of Vinylcyclopropenes to Phenols. *J. Org. Chem.* **1987**, *52*, 2631−2634; b) Hemond, R. C.; Hughes, R. P. The First Transition Metal Complex Containing a Co-ordinated Vinylcyclopropene and Its Photochemical Ring Expansion to Give an η4-Cyclobutadiene Ligand. *J. Chem. Soc., Chem. Commun.* **1988**, 319–320; c) Huang, J. Q.; Yu, M.; Yong, X.; Ho, C. Y. NHC-Ni(II)-Catalyzed Cyclopropene-Isocyanide [5 + 1] Benzannulation. *Nat. Commun.* **2022**, *13*, 4145–4155; d) Semmelhack, M. F.; Ho, S.; Steigerwald, M.; Lee, M. C. Metal Carbonyl-Promoted Rearrangement of Cyclopropenes to Naphthols. *J. Am. Chem. Soc.* **1987**, *109*, 4397−4399.

[6] a) Inglesby, P. A.; Evans, P. A. Stereoselective Transition Metal-Catalysed Higher-Order Carbocyclisation Reactions. *Chem. Soc. Rev.* **2010**, *39*, 2791–2805; b) McLeod, D.; Thøgersen, M. K.; Jessen, N. I.; Jørgensen, K. A.; Jamieson, C. S.; Xue, X.-S.; Houk, K. N.; Liu, F.; Hoffmann, R. Expanding the Frontiers of Higher-Order Cycloadditions. *Acc. Chem. Res.* **2019**, *52*, 3488–3501; c) Feliciano, A.; Vázquez, J. L.; Benítez-Puebla, L. J.; Velazco-Cabral, I.; Cruz, D. C.; Delgado, F.; Vázquez, M. A. Fischer Carbene Complexes: A Glance at Two Decades of Research on Higher-Order Cycloaddition Reactions. *Chem. Eur. J.* **2021**, *27*, 8233–8251. d) Jessen, N. I.; McLeod, D.; Jørgensen, K. A. Higher-Order Cycloadditions in the Age of Catalysis. *Chem.* **2022**, *8*, 20–30. For selected examples of transition metal-mediated/catalyzed higher-order cycloadditions, see: e) Pettit, R.; Ward, J. S. Cycloaddition Reactions between Cyclobutadiene and Unsaturated Molecules Coordinated to Iron. *J. Am. Chem. Soc.* **1971**, *93*, 262–264; f) Wender, P. A.; Ihle, N. C. Nickel-Catalyzed Intramolecular [4 + 4]-Cycloadditions: A New Method for the Synthesis of Polycycles Containing Eight-Membered Rings. *J. Am. Chem. Soc.* **1986**, *108*, 4678–4679; g) Wender, P. A.; Takahashi, H.; Witulski, B. Transition Metal Catalyzed [5+2] Cycloadditions of Vinylcyclopropanes and Alkynes: A Homolog of the Diels-Alder Reaction for the Synthesis of Seven-Membered Rings. *J. Am. Chem. Soc.* **1995**, *117*, 4720–4721; h) Bennacer, B.; Fujiwara, M.; Ojima, I. Novel [2 + 2 + 2 + 1] Cycloaddition of Enediynes Catalyzed by Rhodium Complexes. *Org. Lett.* **2004**, *6*, 3589–3591; i) Evans, P. A.; Inglesby, P. A. Intermolecular Rhodium-Catalyzed [3+2+2] Carbocyclization of Alkenylidenecyclopropanes with Activated Alkynes: Regio- and Diastereoselective Construction of cis-Fused Bicycloheptadienes. *J. Am. Chem. Soc.* **2008**, *130*, 12838–12839; j) Shu, X.; Huang, S.; Shu, D.; Guzei, I. A.; Tang, W. Interception of a Rautenstrauch Intermediate by Alkynes for [5+2] Cycloaddition: Rhodium-Catalyzed Cycloisomerization of 3-Acyloxy-4-ene-1,9-diynes to Bicyclo[5.3.0]decatrienes. *Angew. Chem., Int. Ed.* **2011**, *50*, 8153–8156; k) Yang, L.-C.; Wang, Y.-N.; Liu, R.; Luo, Y.; Ng, X. Q.; Yang, B.; Rong, Z.-Q.; Lan, Y.; Shao, Z.; Zhao, Y. Stereoselective Access to [5.5.0] and [4.4.1] Bicyclic Compounds Through Pd-catalysed Divergent Higher-order Cycloadditions. *Nat. Chem.* **2020**, *12*, 860–868; l) Braconi, E.; Götzinger, A. C.; Cramer, N. Enantioselective Iron-Catalyzed Cross-[4 + 4]-Cycloaddition of 1,3-Dienes Provides Chiral Cyclooctadienes. *J. Am. Chem. Soc.* **2020**, *142*, 19819–19824; m) Zhou, J.-L.; Xiao, Y.; He, L.; Gao, X.-Y.; Yang, X.-C.; Wu, W.-B.; Wang, G.; Zhang, J.; Feng, J.-J. Palladium-Catalyzed Ligand-Controlled Switchable Hetero-(5 + 3)/Enantioselective [2σ+2σ] Cycloadditions of Bicyclobutanes with Vinyl Oxiranes. *J. Am. Chem. Soc.* **2024**, *146*, 19621–19628; n) Shi, B.; Xiao, M.; Zhao, J.-P.; Zhang, Z.; Xiao, W.-J.; Lu, L.-Q. Synthesis of Chiral Endocyclic Allenes and Alkynes via Pd-Catalyzed Asymmetric Higher-Order Dipolar Cycloaddition. *J. Am. Chem. Soc.* **2024**, *146*, 26622–26629.

[7] a) Maier, M. E. Synthesis of Medium-Sized Rings by the Ring-Closing Metathesis Reaction. *Angew. Chem. Int. Ed.* **2000**, *39*, 2073–2077; b) Yet, L. Metal-Mediated Synthesis of Medium-Sized Rings. *Chem. Rev.* **2000**, *100*, 2963–3008; c) Yu, Z.-X.; Wang, Y.; Wang, Y. Transition-Metal-Catalyzed Cycloadditions for the Synthesis of Eight-Membered Carbocycles. *Chem. - Asian J.* **2010**, *5*, 1072–1088; d) Hussain, A.; Yousuf, S. K.; Mukherjee, D. Importance and Synthesis of Benzannulated Medium-Sized and Macrocyclic Rings (BMRs). *RSC Adv.* **2014**, *4*, 43241; e) Donald, J. R.; Unsworth, W. P. Ring-Expansion Reactions in the Synthesis of Macrocycles and Medium-Sized Rings. *Chem. Eur. J.* **2017**, *23*, 8780–8799; f) Hu, Y.-J.; Li, L.-X.; Han, J.-C.; Min, L.; Li, C.-C. Recent Advances in the Total Synthesis of Natural Products Containing Eight-Membered Carbocycles (2009–2019). *Chem. Rev.* **2020**, *120*, 5910–5953; g) Wang, L.-N.; Yu, Z.-X. Transition-Metal-Catalyzed Cycloadditions for the Synthesis of Eight-Membered Carbocycles: An Update from 2010 to 2020. *Chin. J. Org. Chem.* **2020**, *40*, 3536–3558; h) Clarke, A. K.; Unsworth, W. P. A Happy Medium: the Synthesis of Medicinally Important Medium-Sized Rings via Ring Expansion. *Chem. Sci.* **2020**, *11*, 2876–2881; i) Reyes, R. L.; Iwai, T.; Sawamura, M. Construction of Medium-Sized Rings by Gold Catalysis. *Chem. Rev.* **2021**, *121*, 8926–8947; j) Yao, T.; Li, J.; Jiang, C.; Zhao, C. Recent Advances for the Catalytic Asymmetric Construction of Medium-Sized Rings. *Chem. Catal.* **2022**, *11*, 2929–2964; k) Otevrel, J.; Eugui, M.; Ričko, S.; Jørgensen, K. A. Enantioselective Organocatalytic Cycloadditions for the Synthesis of Medium-Sized Rings. *Nat. Synth.* **2023**, *2*, 1142–1158; l) Wootton, J. M.; Tam, J. K. F.; Unsworth, W. P. Cascade Ring Expansion Reactions for the Synthesis of Medium-Sized Rings and Macrocycles. *Chem. Commun.* **2024**, *60*, 4999–5009.

[8] a) Huang, Z.; Jin, Y.; Zhao, S.; Zhang, P.; Liao, W.; Yu, Z.-X. How to Suppress C(sp^2)–Rh–C(sp^3) Reductive Elimination and Insert CO to Achieve Rhodium-Catalyzed [5 + 2 + 1] Cycloaddition of Yne-Vinylcyclopropanes and CO: Answers from Experimental and Computational Investigation. *ACS Catal.* **2024**, *14*, 12734–12742; b) Cui, Q.; Zhang, P.; Li, B.-W.; Jin, Y.; Zhang, Q.; Bai, H.-X.; Yu, Z.-X. Rhodium-Catalyzed [5 + 1 + 2] Cycloaddition of Yne-3-acyloxy-1,4-enynes (YACEs) and Carbon Monoxide: Reaction Development and Mechanism. *ACS Catal.* **2024**, *14*, 14595–14605.

[9] a) Gibson, S. E. née Thomas; Stevenazzi, A. The Pauson–Khand Reaction: the Catalytic Age Is Here! *Angew. Chem. Int. Ed.* **2003**, *42*, 1800–1810; b) Blanco-Urgoiti, J.; Añorbe, L.; Pérez-Serrano, L.; Domínguez, G.; Pérez-Castells, J. The Pauson–Khand Reaction, A Powerful Synthetic Tool for the Synthesis of Complex Molecules. *Chem. Soc. Rev.* **2004**, *33*, 32–42.

[10] a) Deng, Y.; Doyle, M. P. Versatile Donor-Acceptor Cyclopropenes in Metal Carbene Transformations. *Isr. J. Chem.* **2016**, *56*, 399–408; b) Zhu, D.; Chen, L.; Fan, H.; Yao, Q.; Zhu, S. Recent Progress on Donor and Donor–Donor Carbenes. *Chem. Soc. Rev.* **2020**, *49*, 908–950; c) Li, D.; Zang, W.; Bird, M. J.; Hyland, C. J. T.; Shi, M. Gold-Catalyzed Conversion of Highly Strained Compounds. *Chem. Rev.* **2021**, *121*, 8685–8755.

[11] a) Wang, Y.; Liao, W.; Wang, Y.; Jiao, L.; Yu, Z.-X. Mechanism and Stereochemistry of Rhodium-Catalyzed [5 + 2 + 1] Cycloaddition of Ene-Vinylcyclopropanes and Carbon Monoxide Revealed by Visual Kinetic Analysis and Quantum Chemical Calculations. *J. Am. Chem. Soc.* **2022**, *144*, 2624–2636; b) Li, C.-L.; Yang, Y.; Zhou, Y.; Duan, Z.-C.; Yu, Z.-X. Strain-Release-Controlled [4 + 2 + 1] Reaction of Cyclopropyl-Capped Diene-ynes/Diene-enes and Carbon Monoxide Catalyzed by Rhodium. *J. Am. Chem. Soc.* **2023**, *145*, 5496–5505; c) Yang, J.; Zhang, P.; Shen, Z.-Y.; Zhou, Y.; Yu, Z.-X. Unprecedented *endo*-Oxidative Cyclometallation and [4 + 3] Cycloaddition of Diene-Vinylcyclopropanes. *Chem.* **2023**, *9*, 1477–1494.

[12] We computed the key steps for the substrate of yne-VCP by using the same method as that for yne-VCPE, finding that the reason for the chemoselectivity is the same. See Supporting Information for details.

[13] Jin, C. H.; Lee, H. Y.; Lee, S. H.; Kim, I. S.; Jung, Y. H. Direct Etherification of Alkyl Halides by Sodium Hydride in the Presence of N, N-Dimethylformamide. *Synlett* **2007**, 2695–2698.

[14] Tsunoda, T.; Ozaki, F.; Ito, S. Novel Reactivity of Stabilized Methylenetributylphosphorane: A New Mitsunobu Reagent. *Tetrahedron Lett.* **1994**, *35*, 5081–5082.

[15] Edwards, A.; Benin, T.; Rubina, M.; Rubin, M. Synthesis of 1,5-Dioxocanes via the Two-Fold C-O Bond Forming Nucleophilic 4 + 4-Cyclodimerization of Cycloprop-2-en-1-ylmethanols. *RSC Adv.* **2015**, *5*, 71849–71853.

[16] Melnykov, K. P.; Voloshyna, O. V.; Vashchenko, B. V.; Demchuk, O. P.; Hryshchuk, O. V.; Grygorenko, O. O. 4,4-Difluorospiro[2.2]pentan-1-yl – A Fluorinated Substituent To Expand the Synthetic and Medicinal Chemists' Toolbox. *Eur. J. Org. Chem.* **2022**, e202200863.

[17] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.

[18] Zhao, Y.; Truhlar, D. G. Design of Density Functionals That Are Broadly Accurate for Thermochemistry, Thermochemical Kinetics, and Non-Bonded Interactions. *J. Phys. Chem. A* **2005**, *109*, 5656–5667.

[19] a) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104; b) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.* **2011**, *32*, 1456–1465.

[20] a) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305; b) Weigend, F. Accurate Coulomb-Fitting Basis Sets for H to Rn. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057–1065.

[21] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*, Wiley: New York, 1986.

[22] Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009**, *113*, 6378–6396.

[23] a) Neese, F. The ORCA Program System. *WIREs Comput. Mol. Sci.* **2012**, *2*, 73–78; b) Neese, F. Software Update: The ORCA Program System—Version 5.0. *WIREs Comput. Mol. Sci.* **2022**, *12*, e1606.

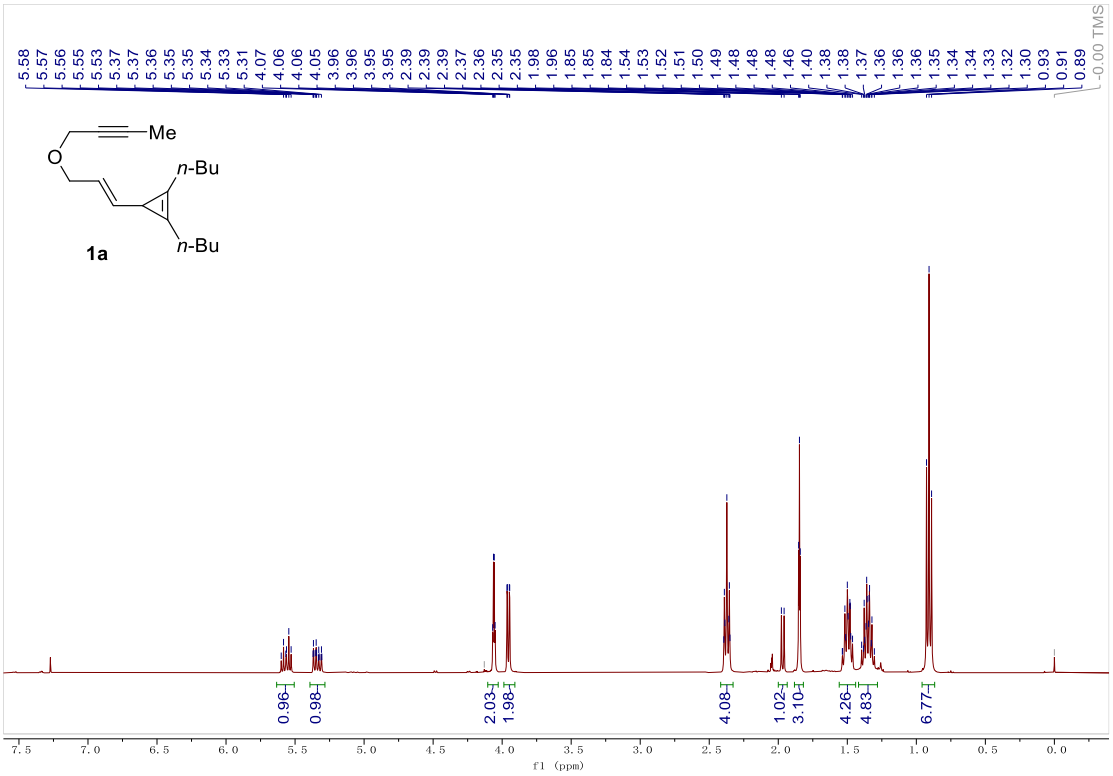
[24] Mardirossian, N.; Head-Gordon, M. ωB97M-V: A Combinatorially Optimized, Range-Separated Hybrid, Meta-GGA Density Functional with VV10 Nonlocal Correlation. *J. Chem. Phys.* **2016**, *144*, 214110.

[25] Keith, J. A.; Carter, E. A. Quantum Chemical Benchmarking, Validation, and Prediction of Acidity Constants for Substituted Pyridinium Ions and Pyridinyl Radicals. *J. Chem. Theory Comput.* **2012**, *8*, 3187–3206.

[26] Legault, C. Y. *CYLview20*; Université de Sherbrooke, 2020; http://www.cylview.org (accessed 17 April, 2022).

7. NMR Spectra

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



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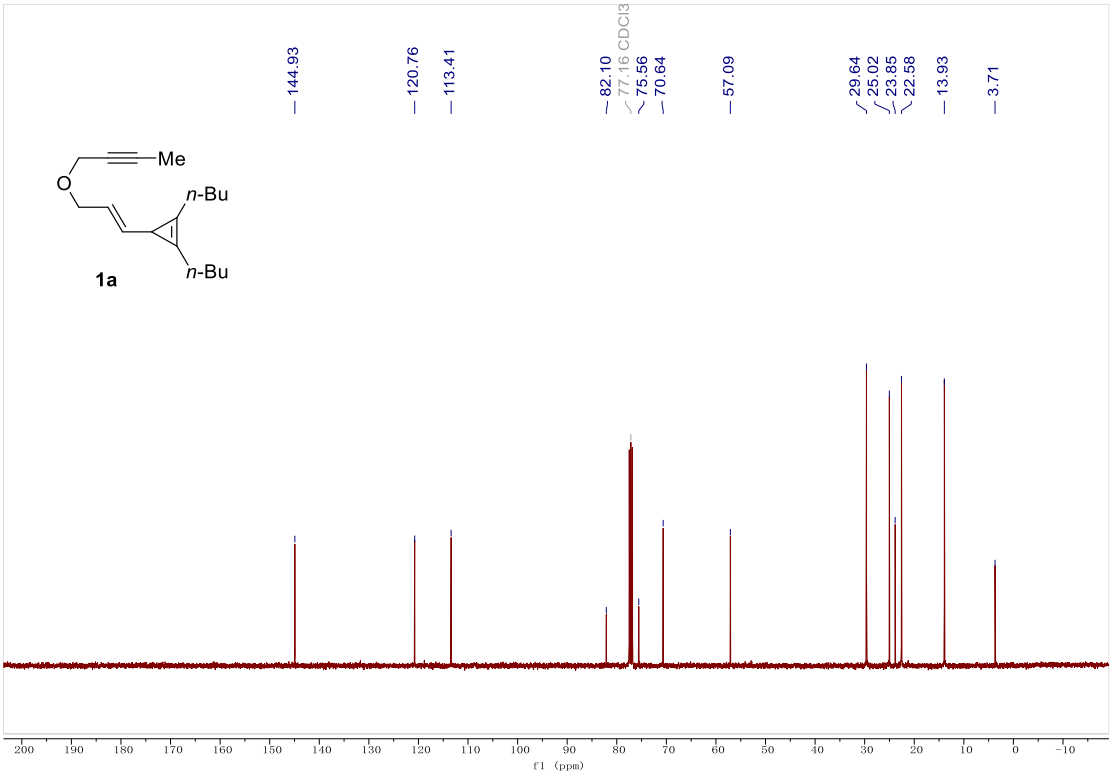

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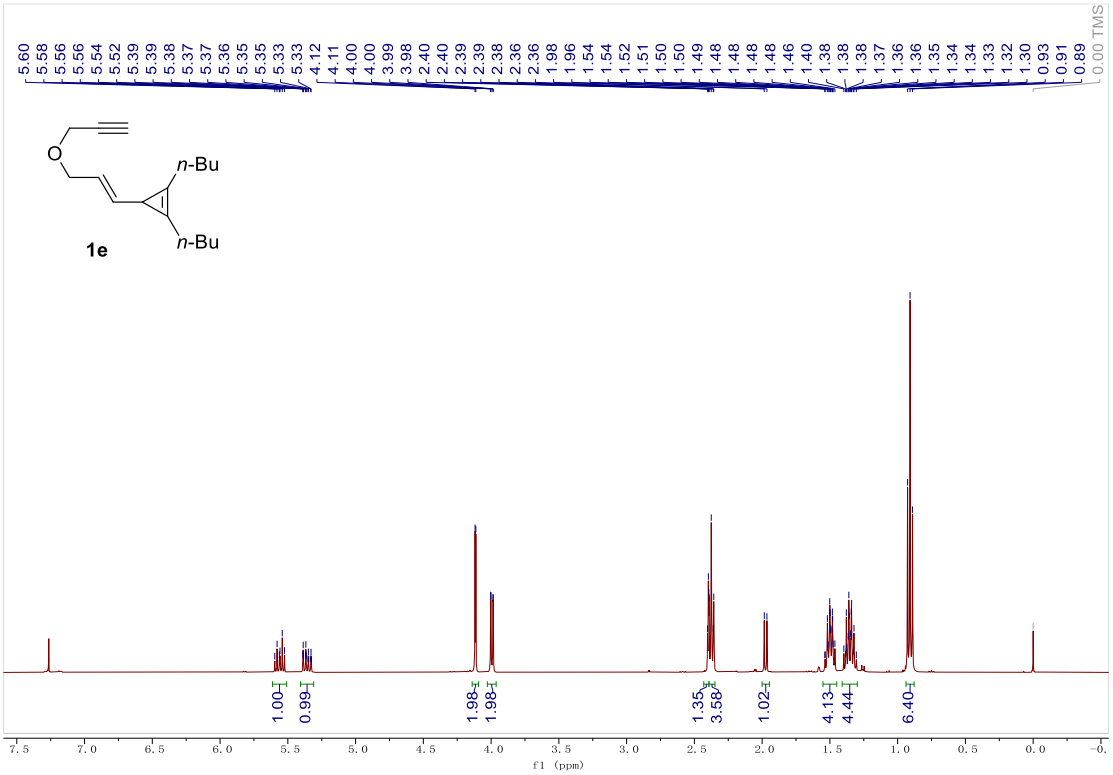

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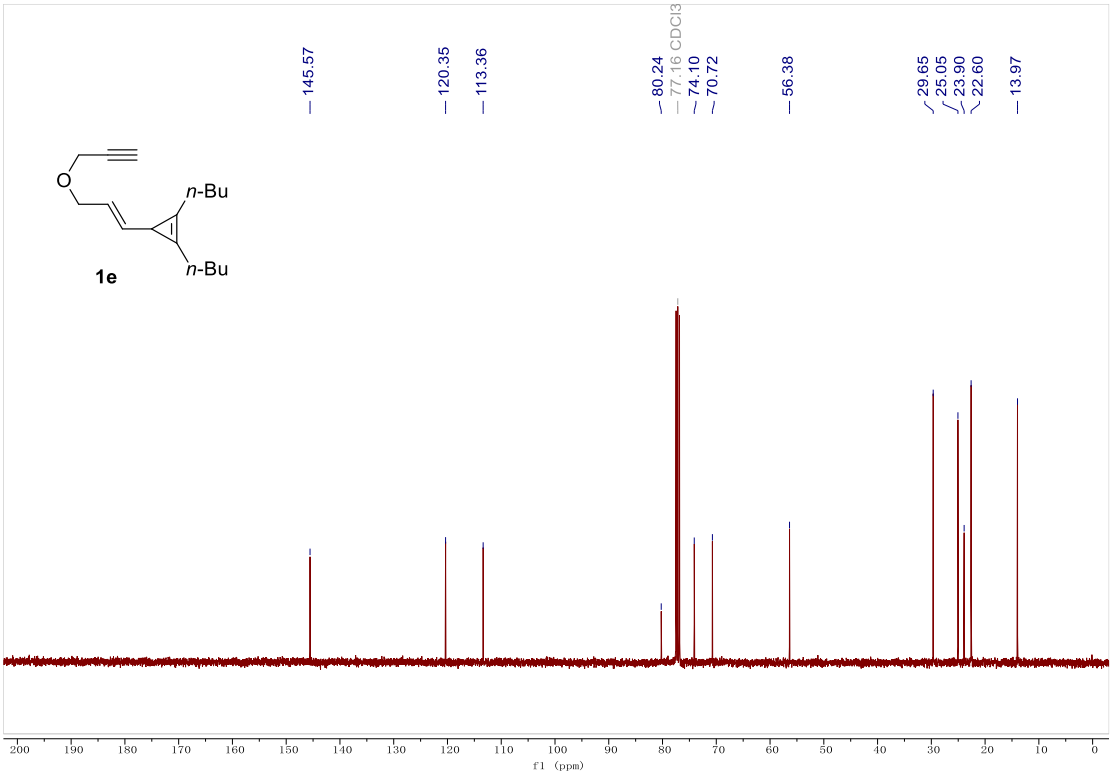
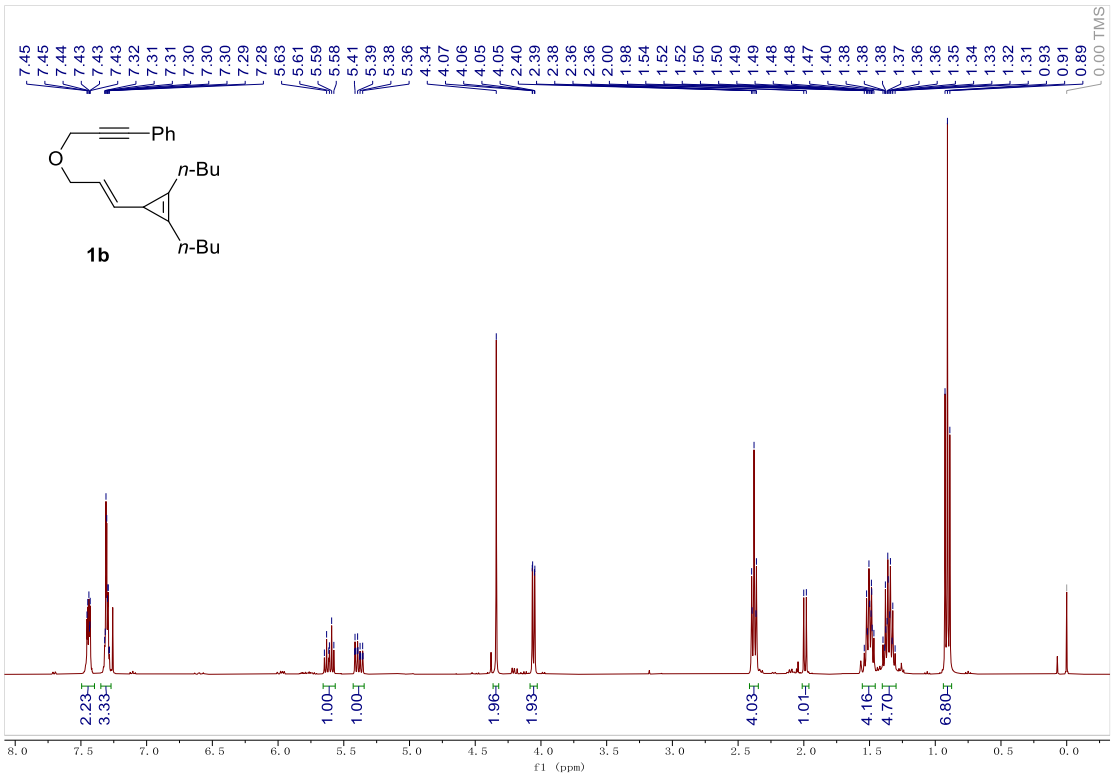
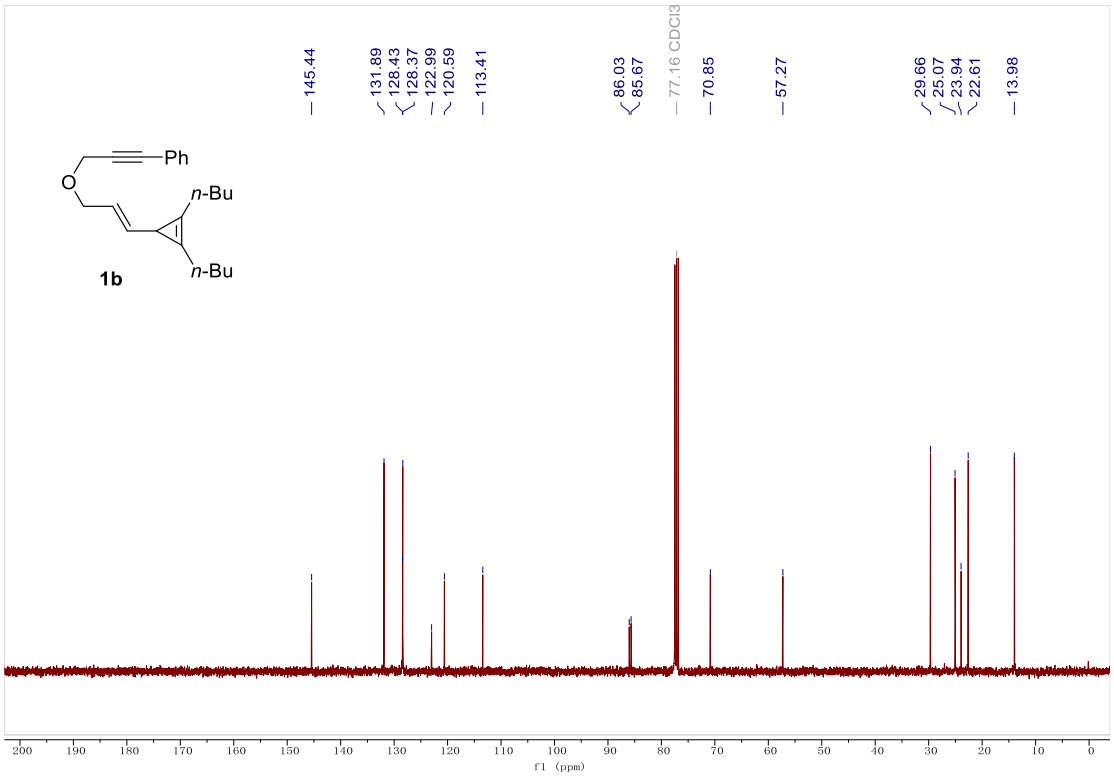


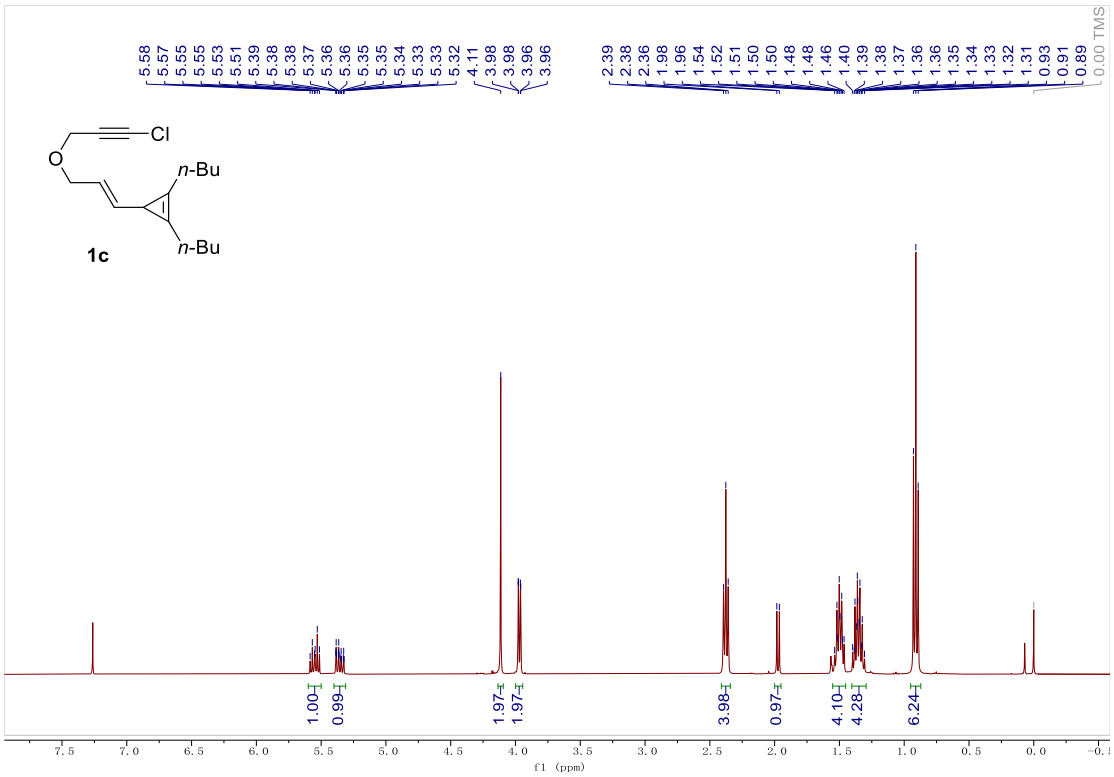
^{1}H NMR in $CDCl_3$, 400 MHz



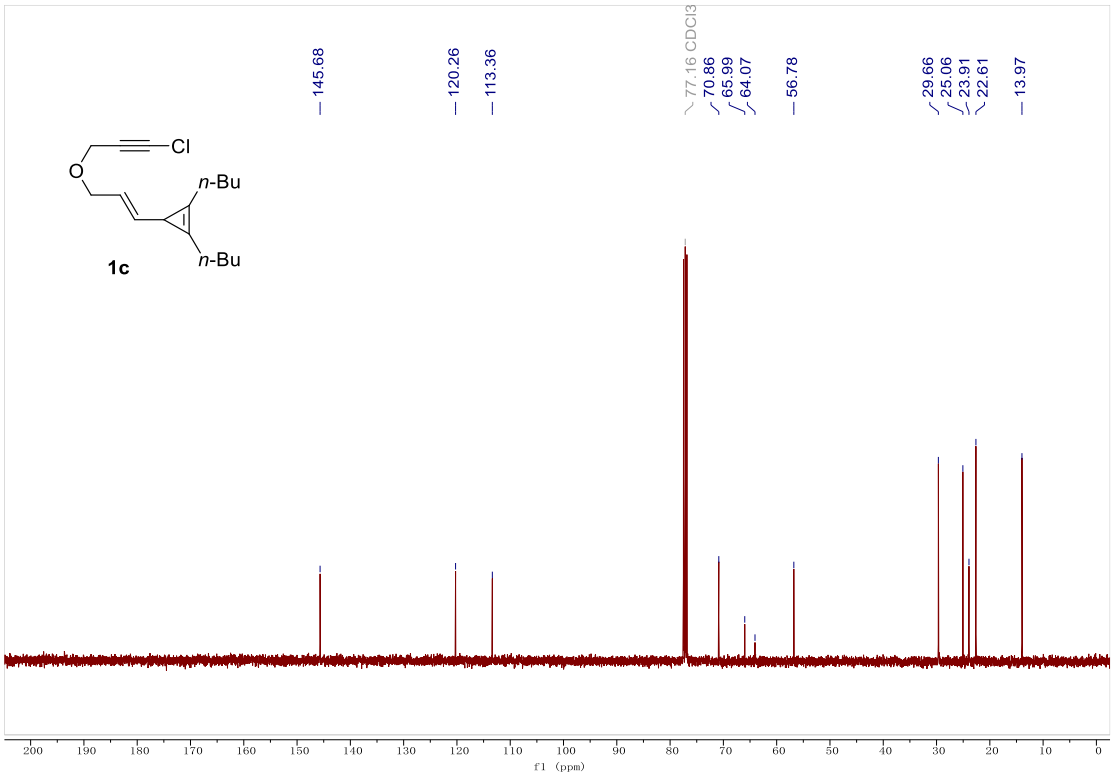
^{13}C NMR in $CDCl_3$, 101 MHz



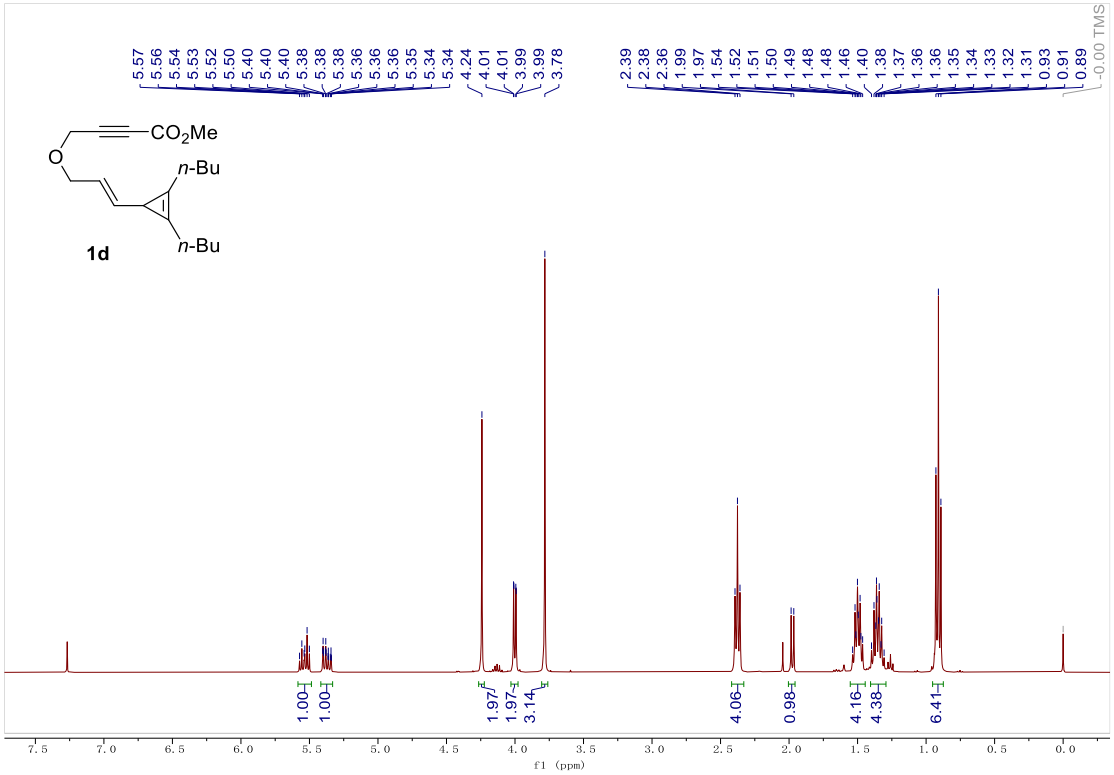
^{1}H NMR in $CDCl_3$, 400 MHz



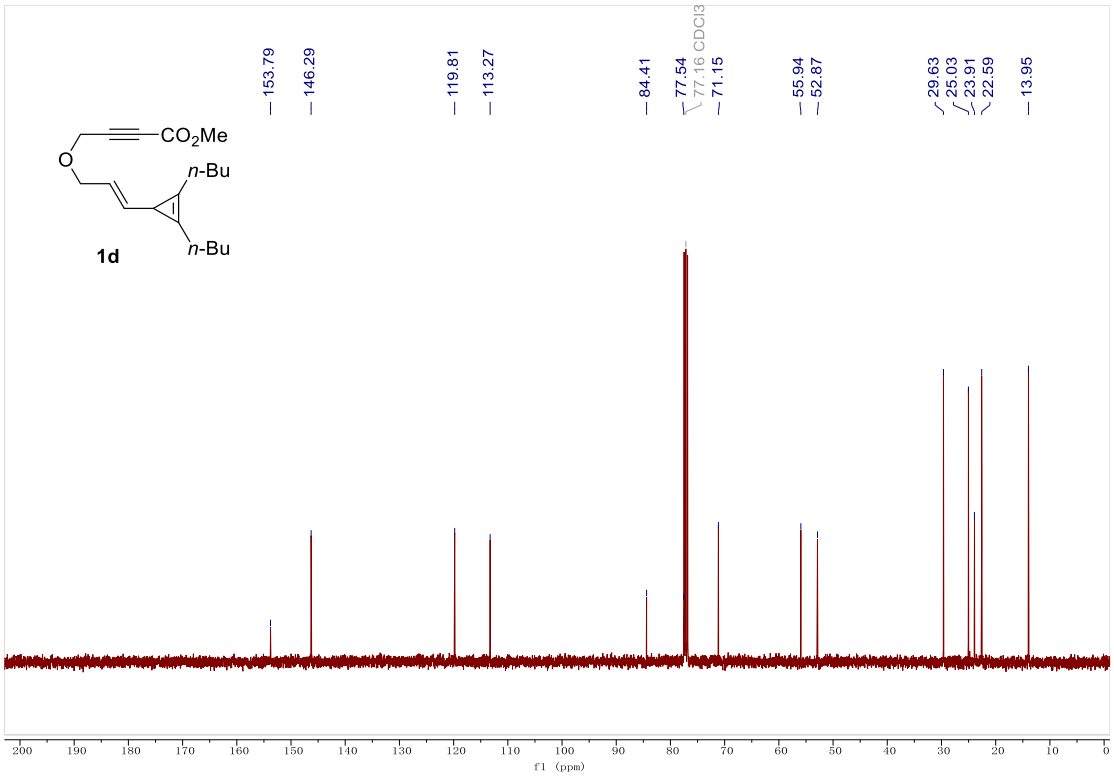
^{13}C NMR in $CDCl_3$, 101 MHz



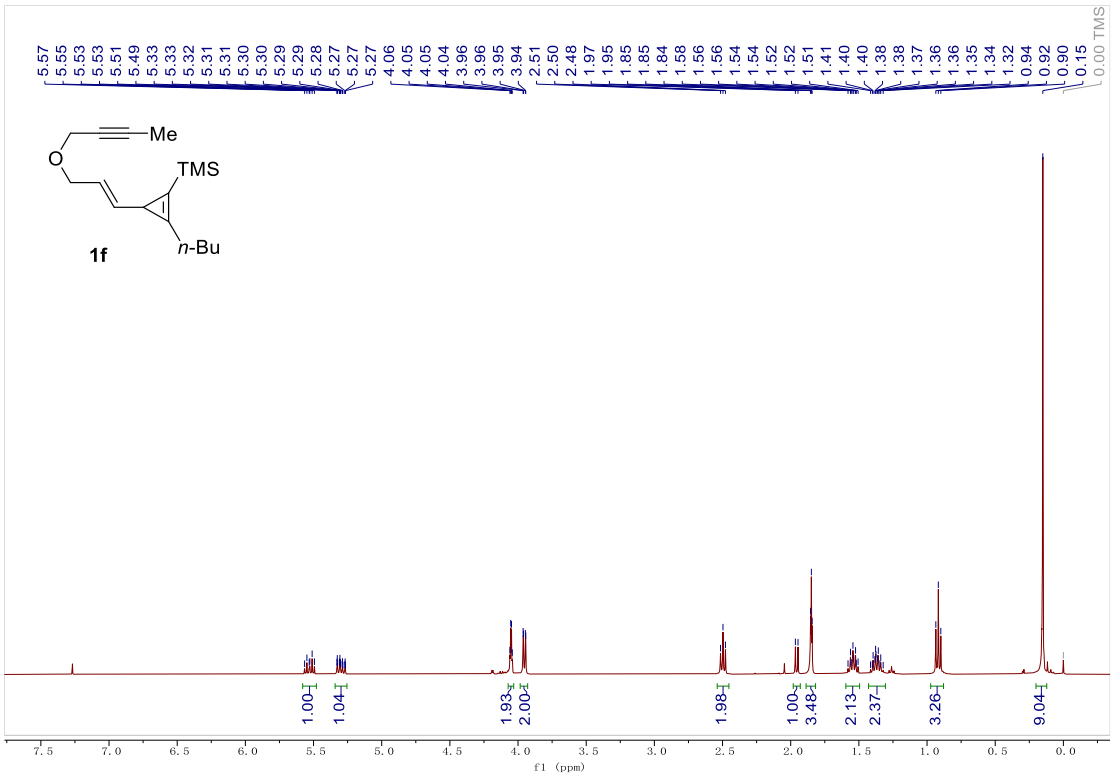
^{1}H NMR in $CDCl_3$, 400 MHz



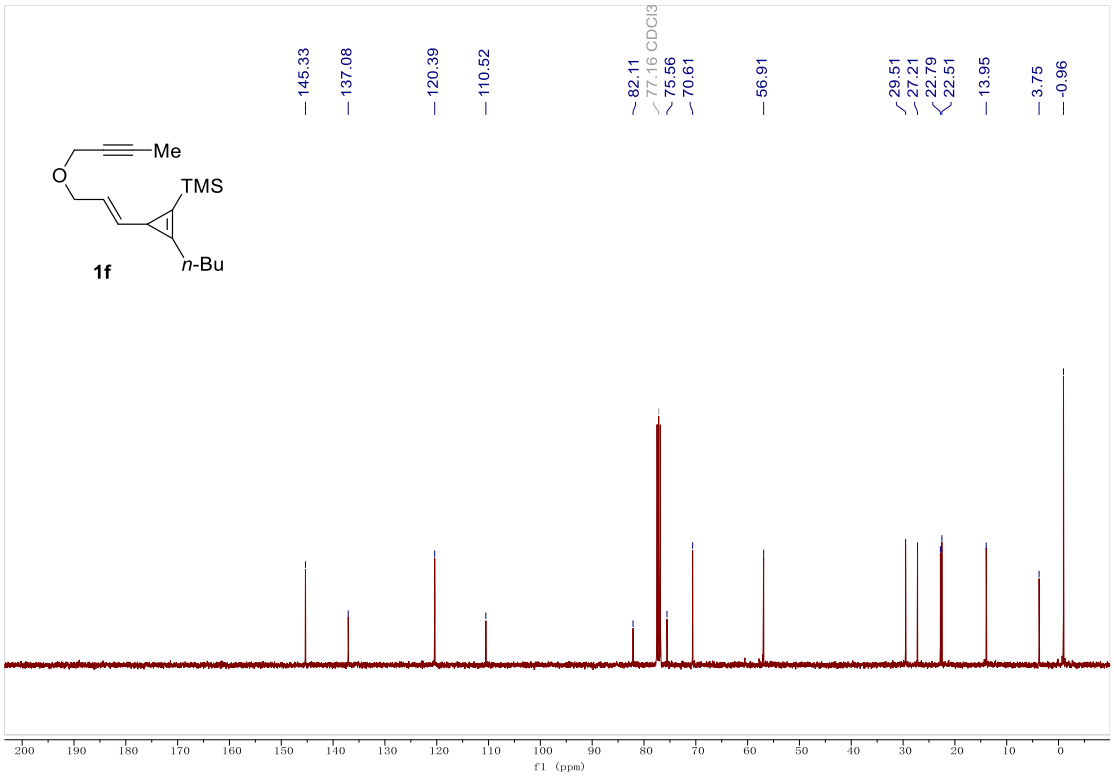
^{13}C NMR in $CDCl_3$, 101 MHz



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



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



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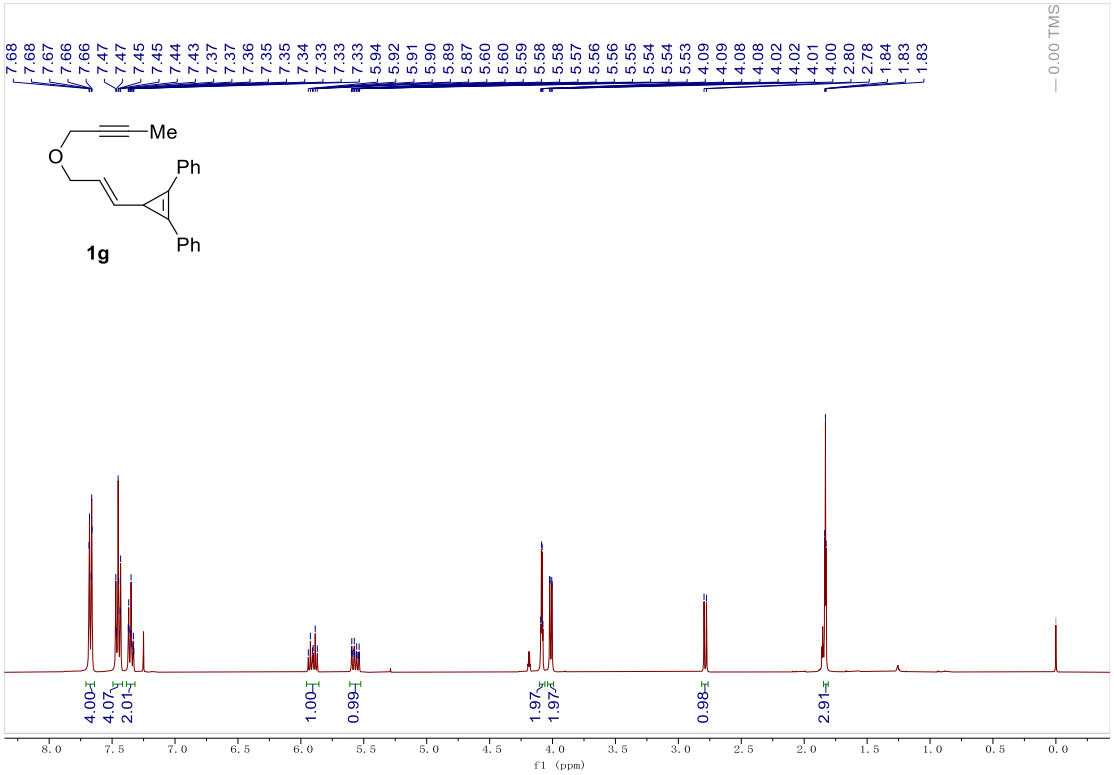
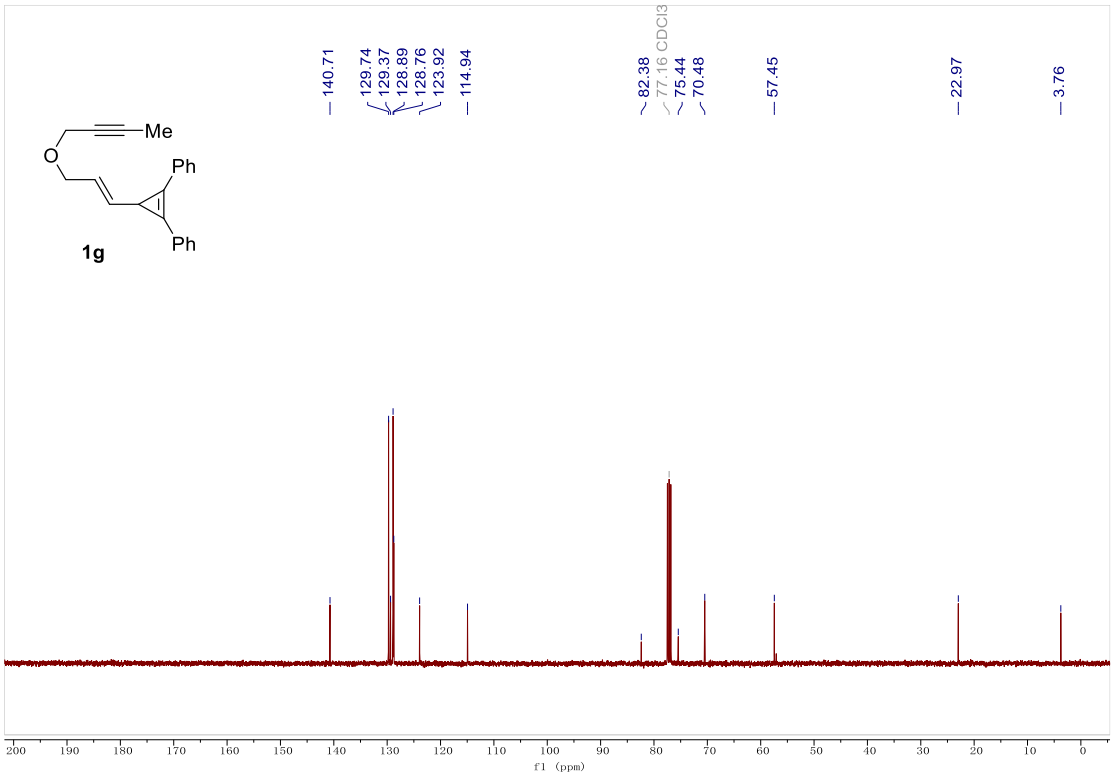
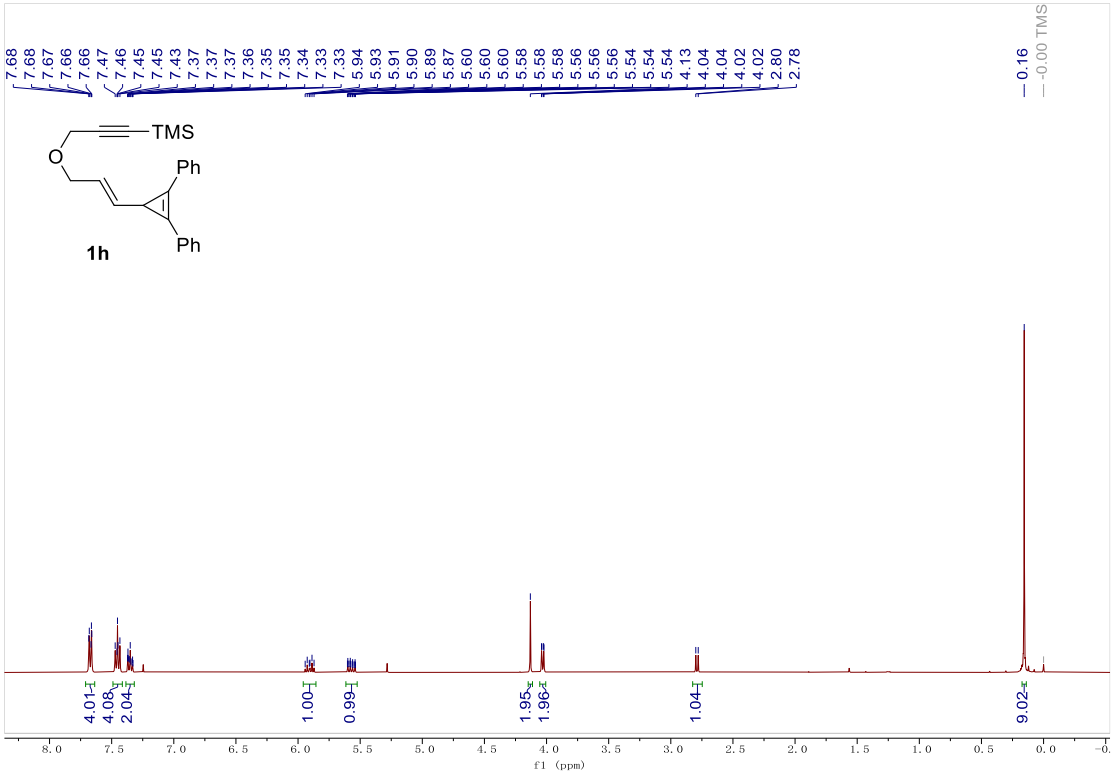


^{13}C NMR in $CDCl_3$, 101 MHz



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



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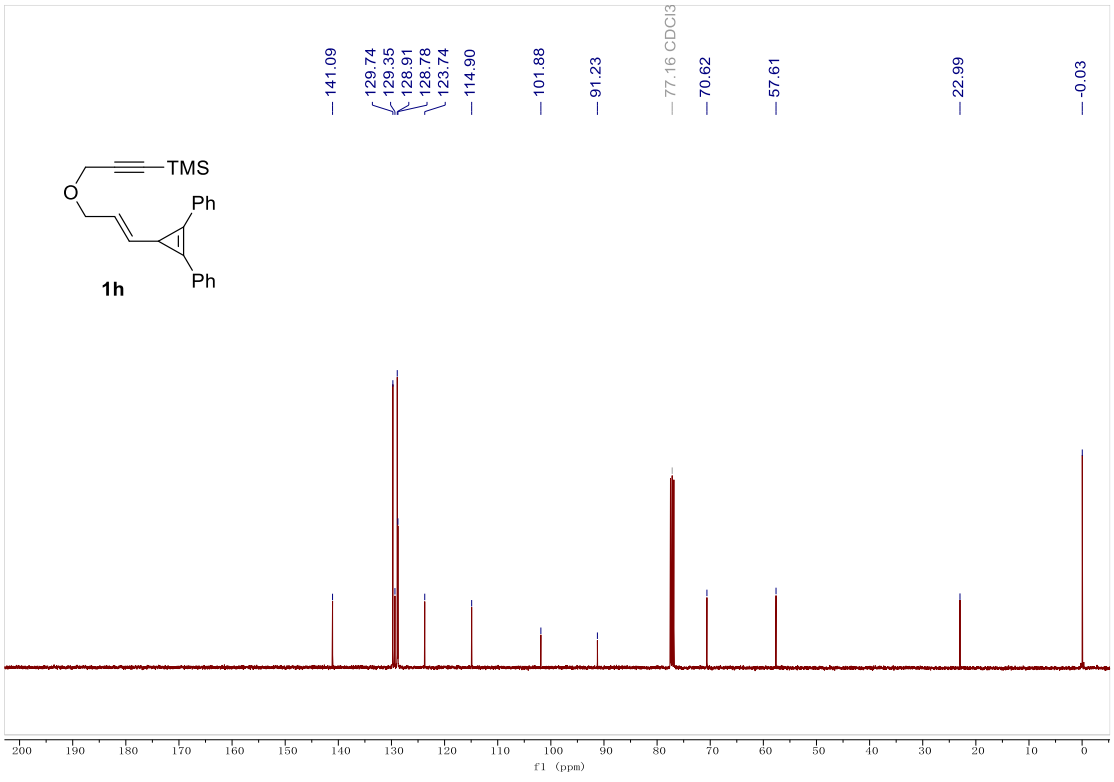
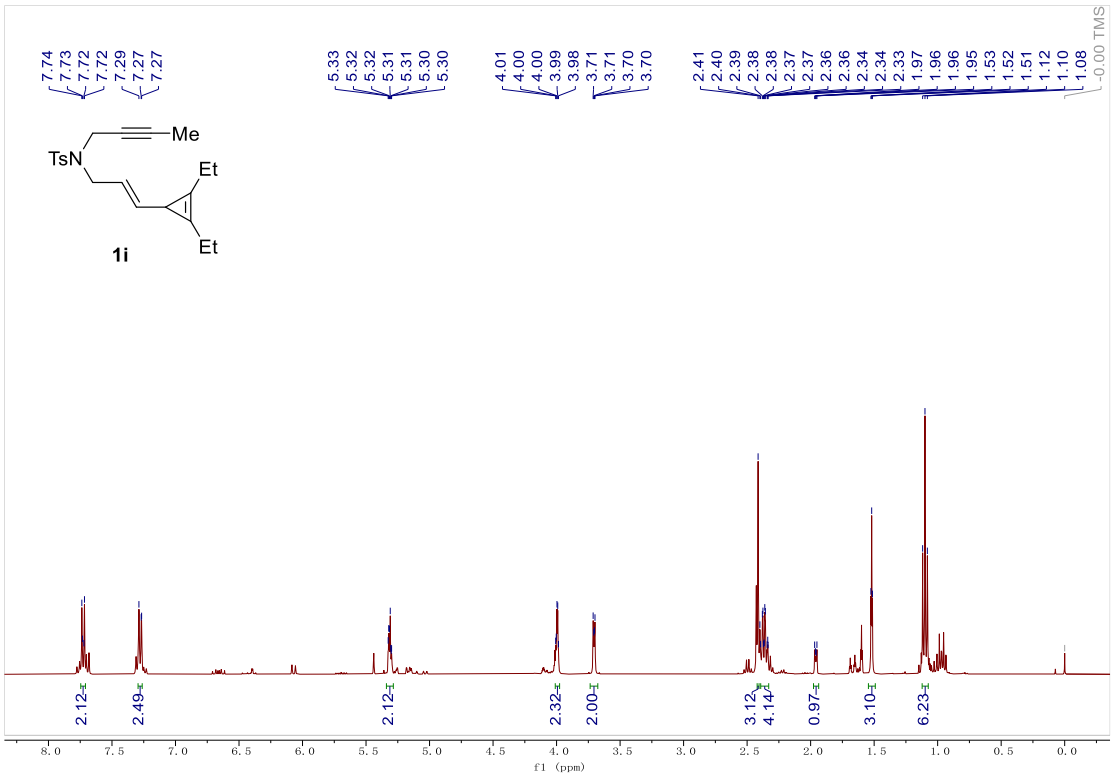
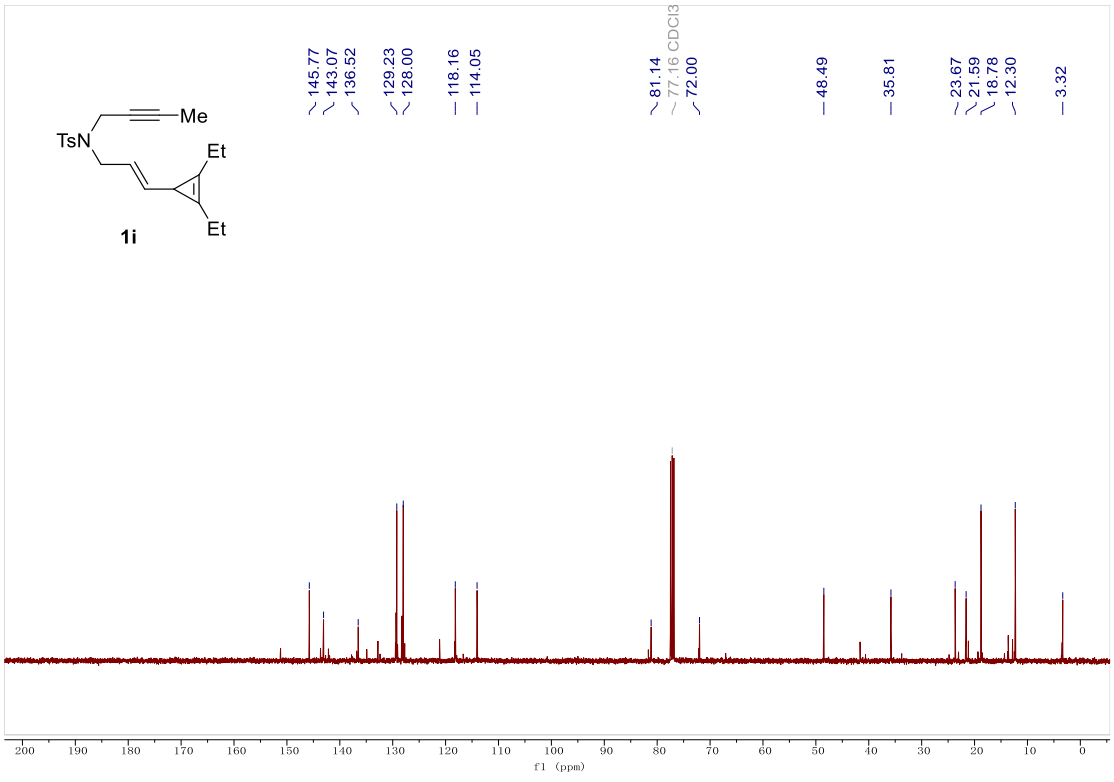


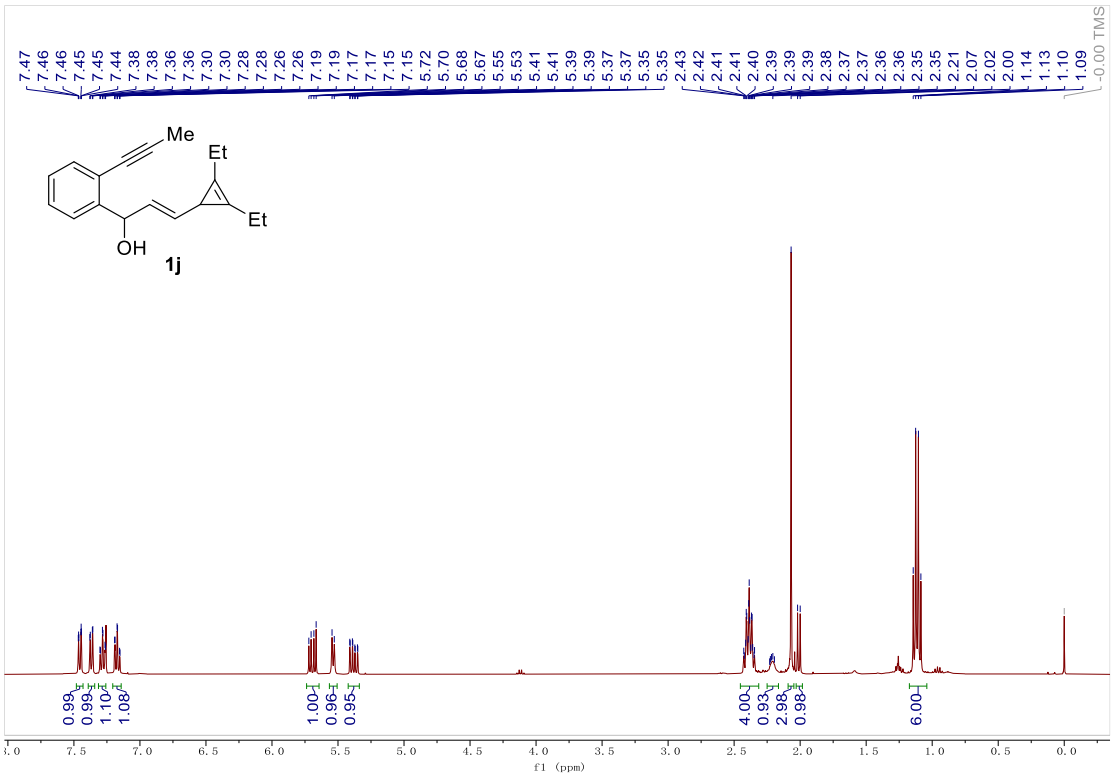
^{1}H NMR in $CDCl_3$, 400 MHz



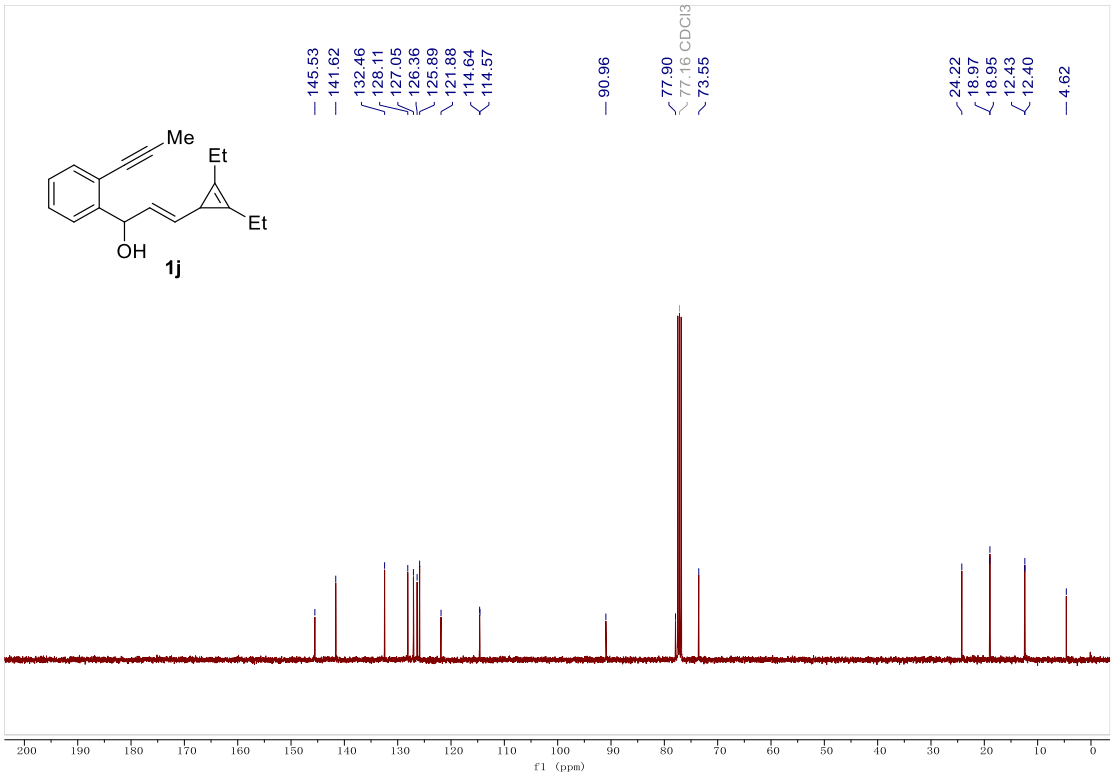
^{13}C NMR in $CDCl_3$, 101 MHz



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



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



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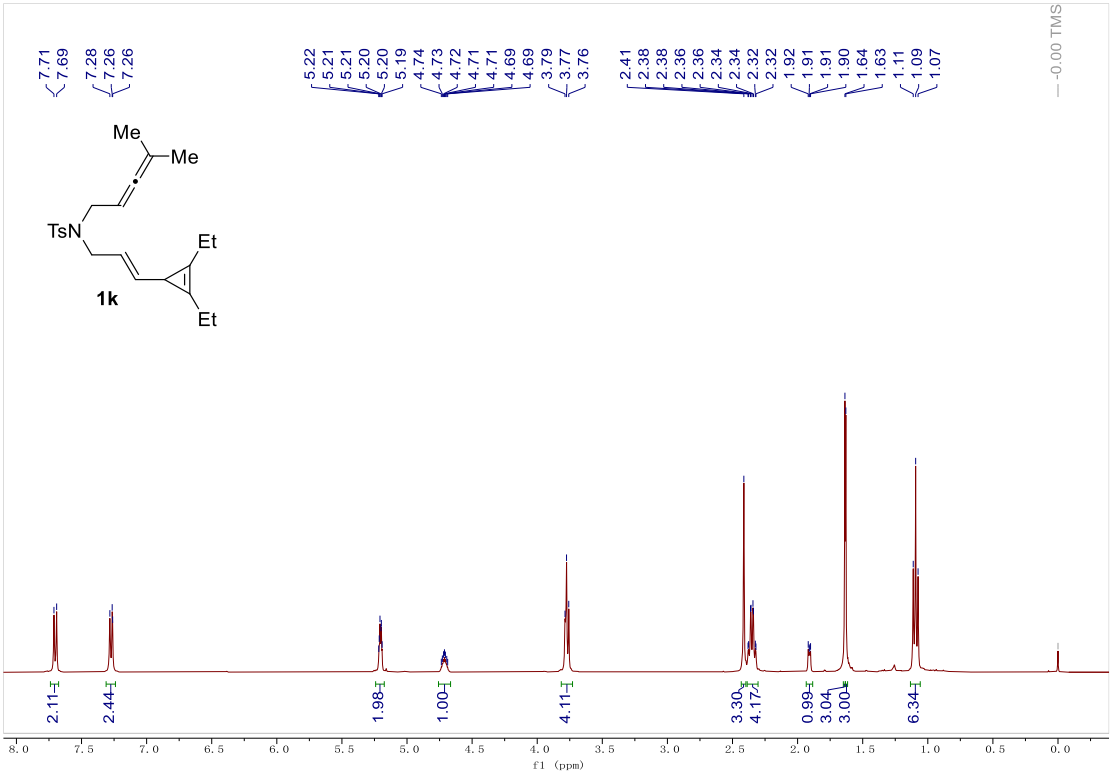
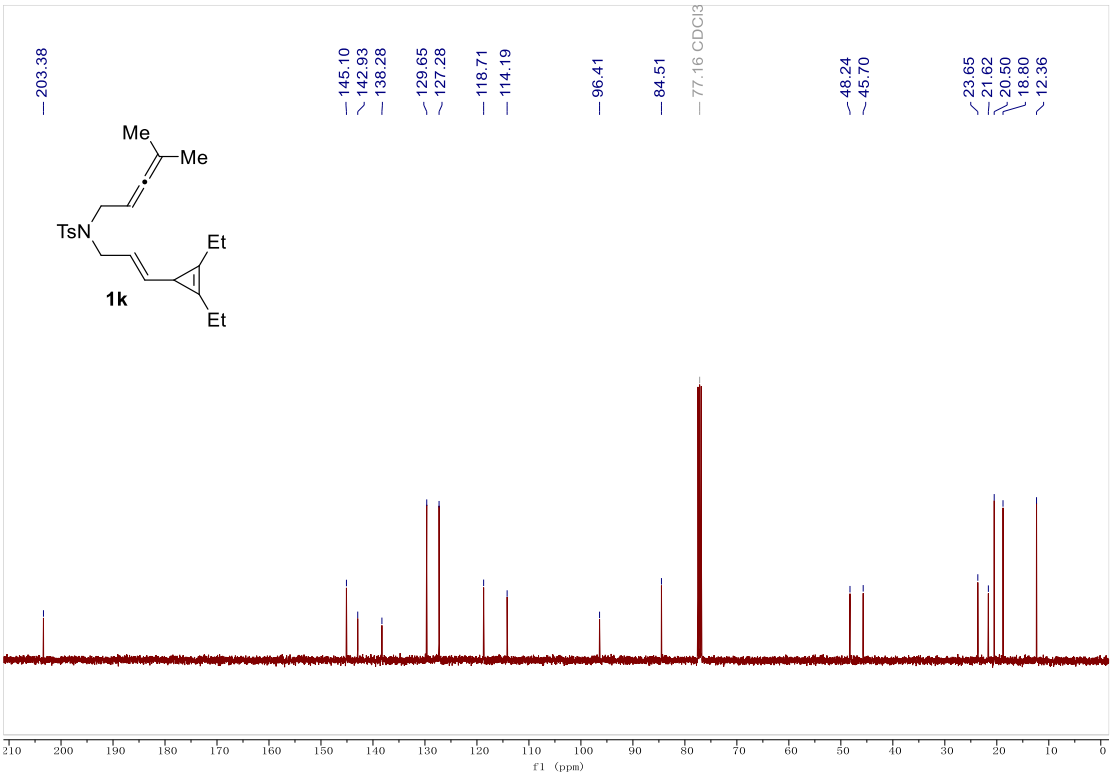
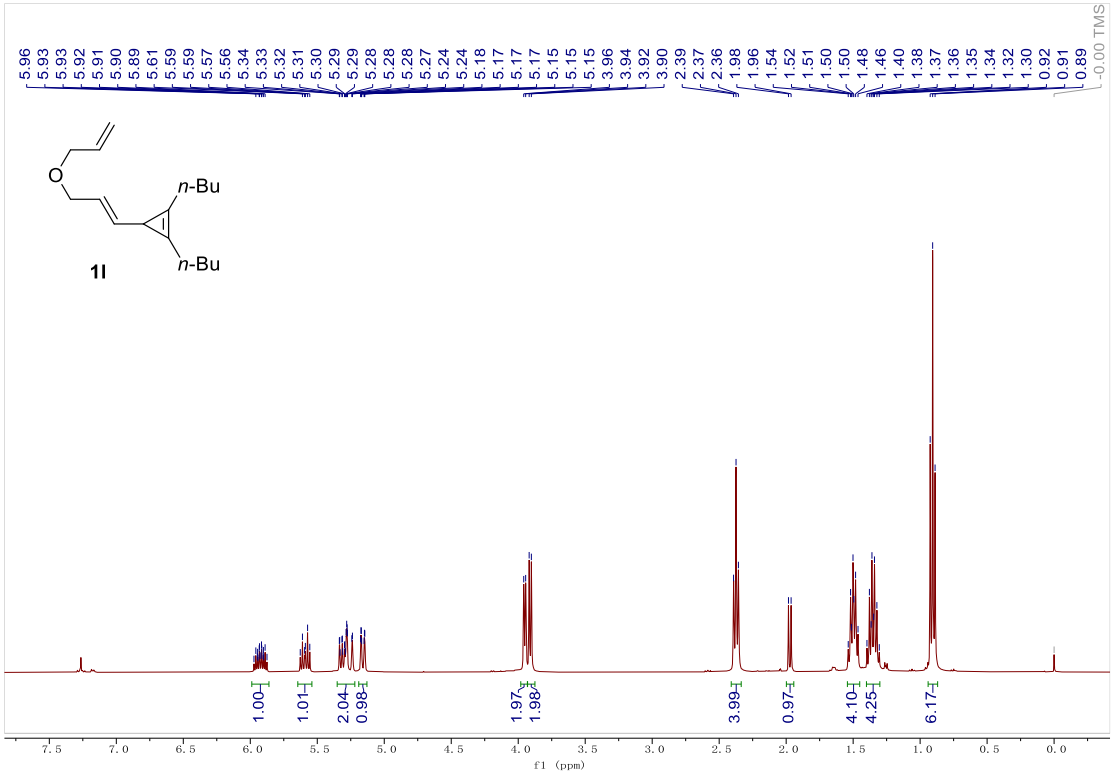


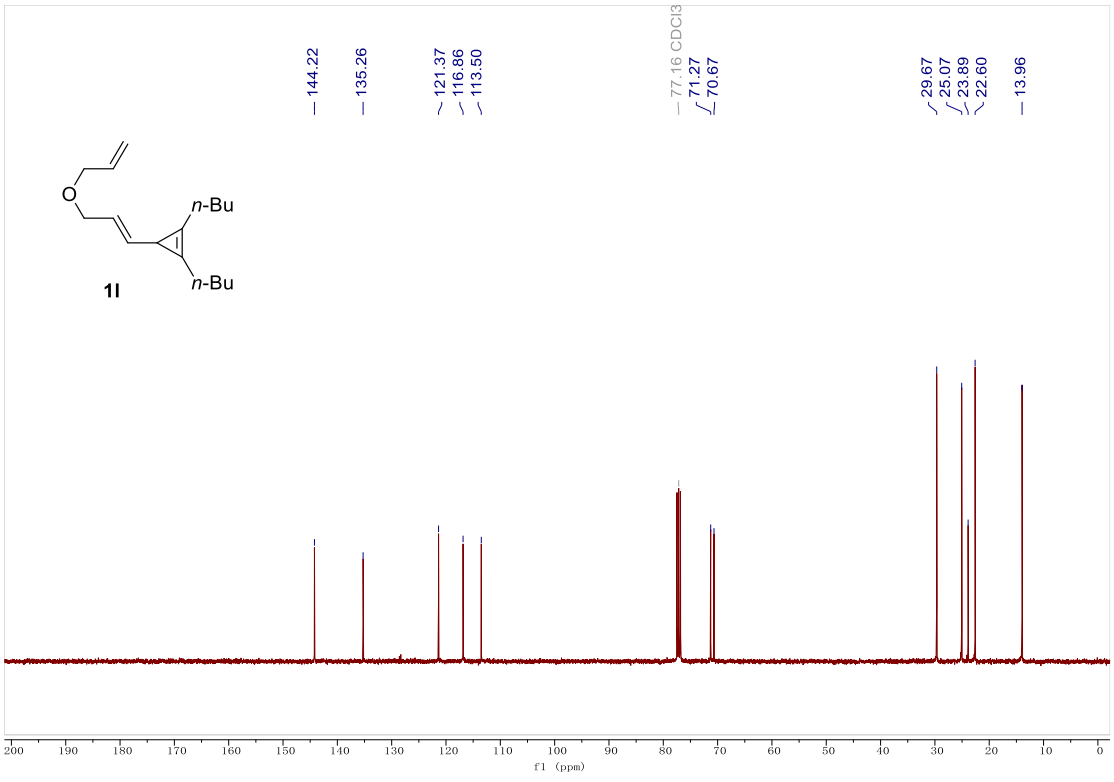
^{13}C NMR in $CDCl_3$, 101 MHz



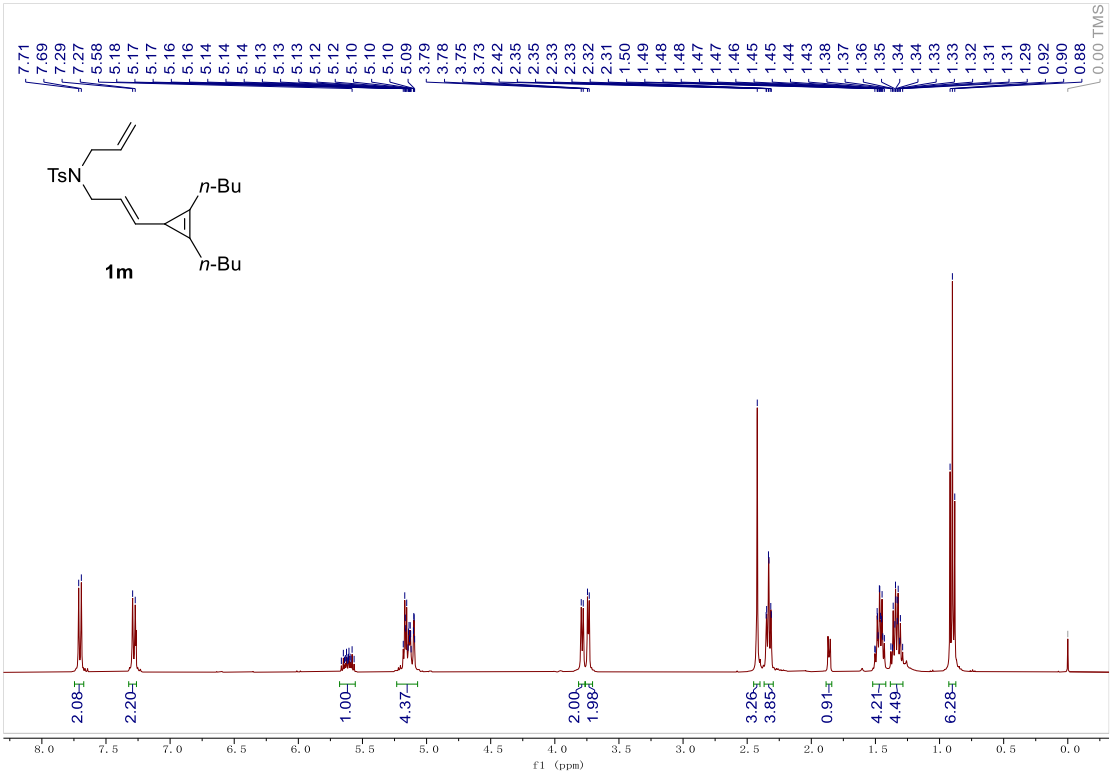
^{1}H NMR in $CDCl_3$, 400 MHz



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



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



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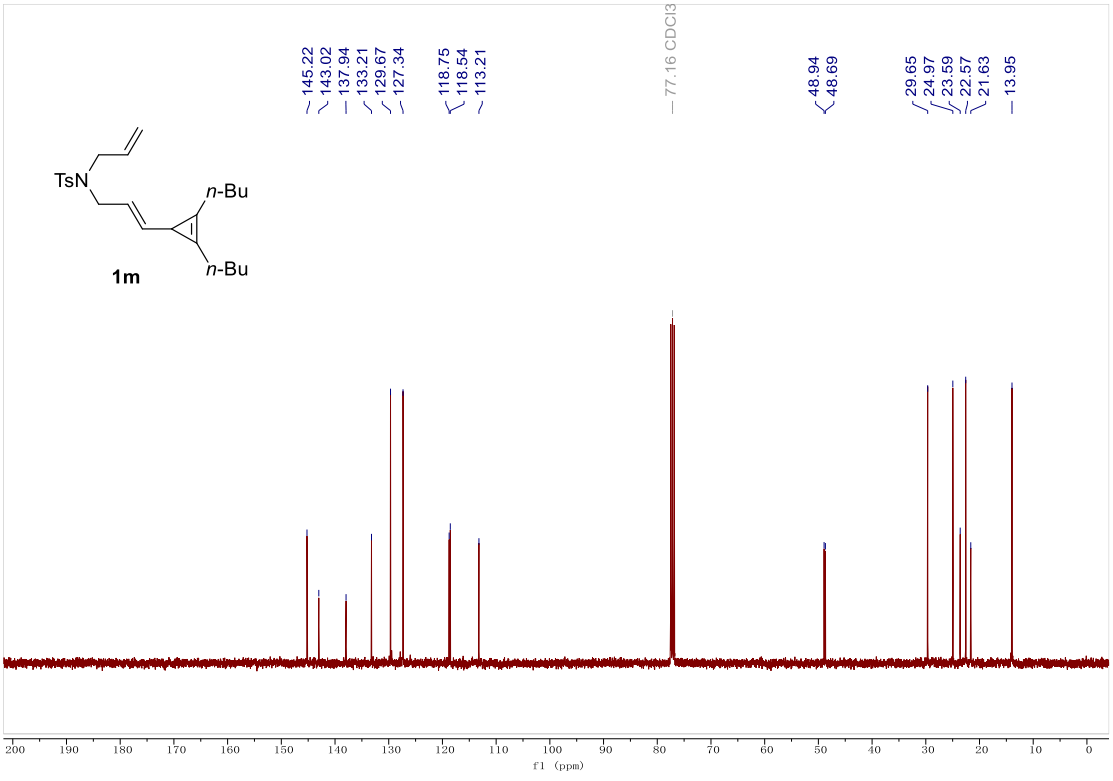

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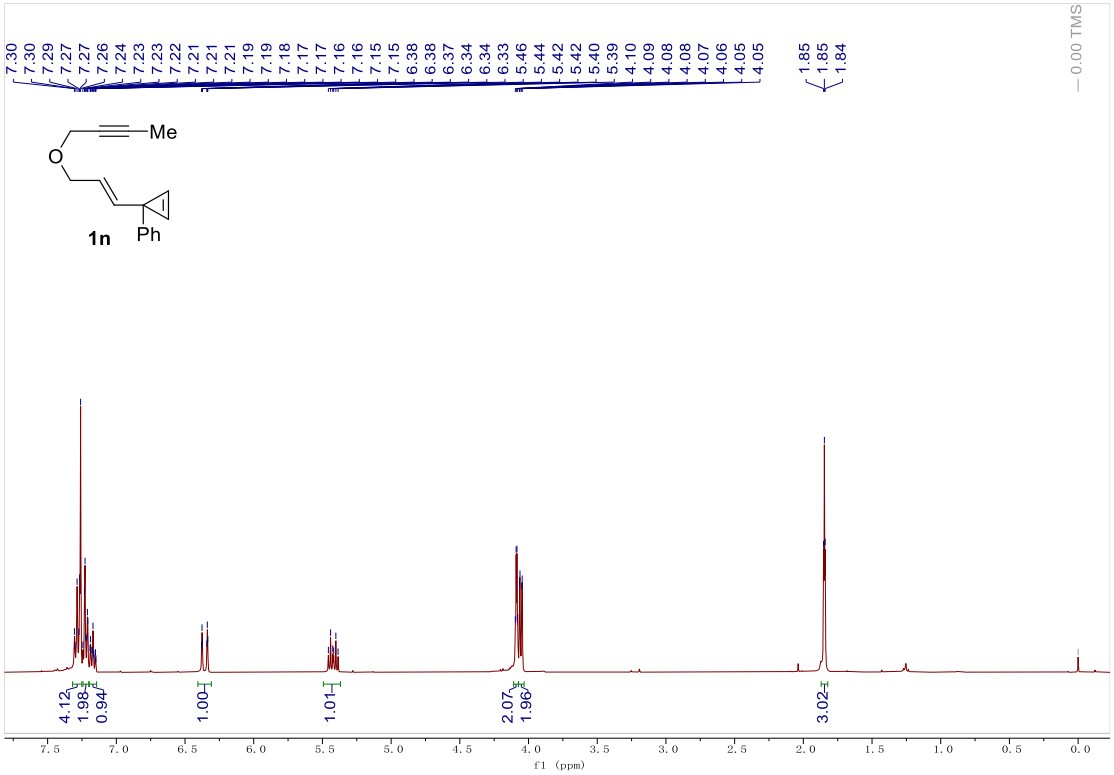
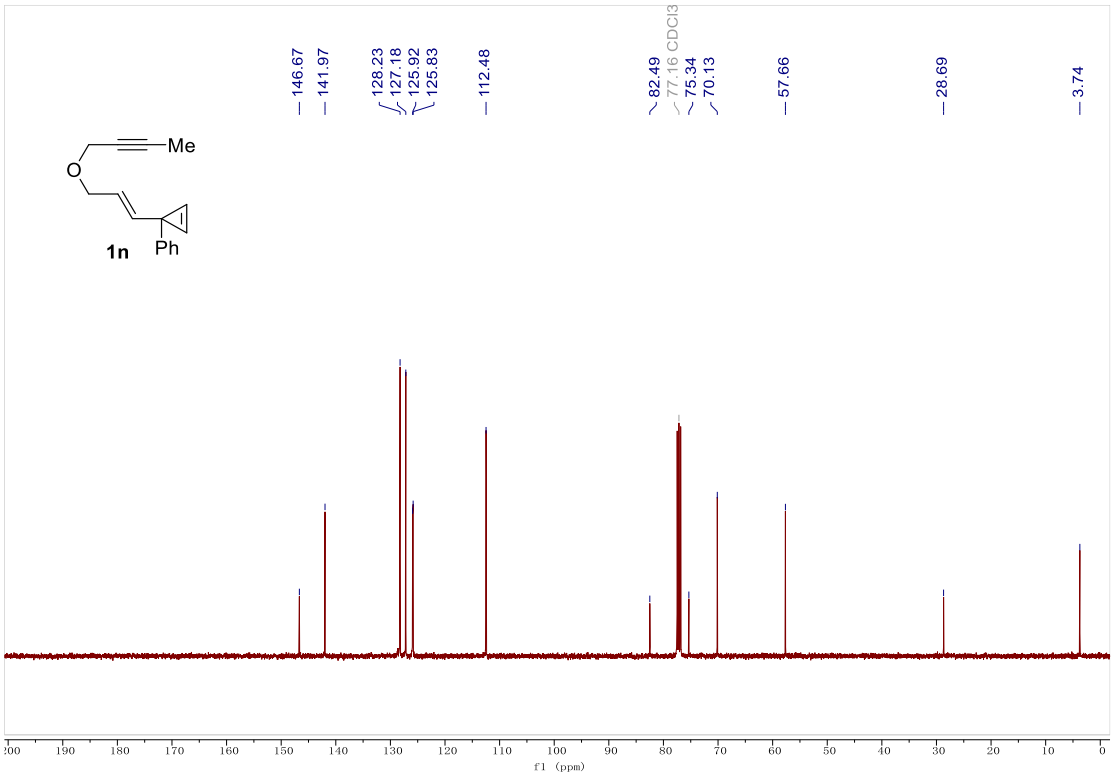
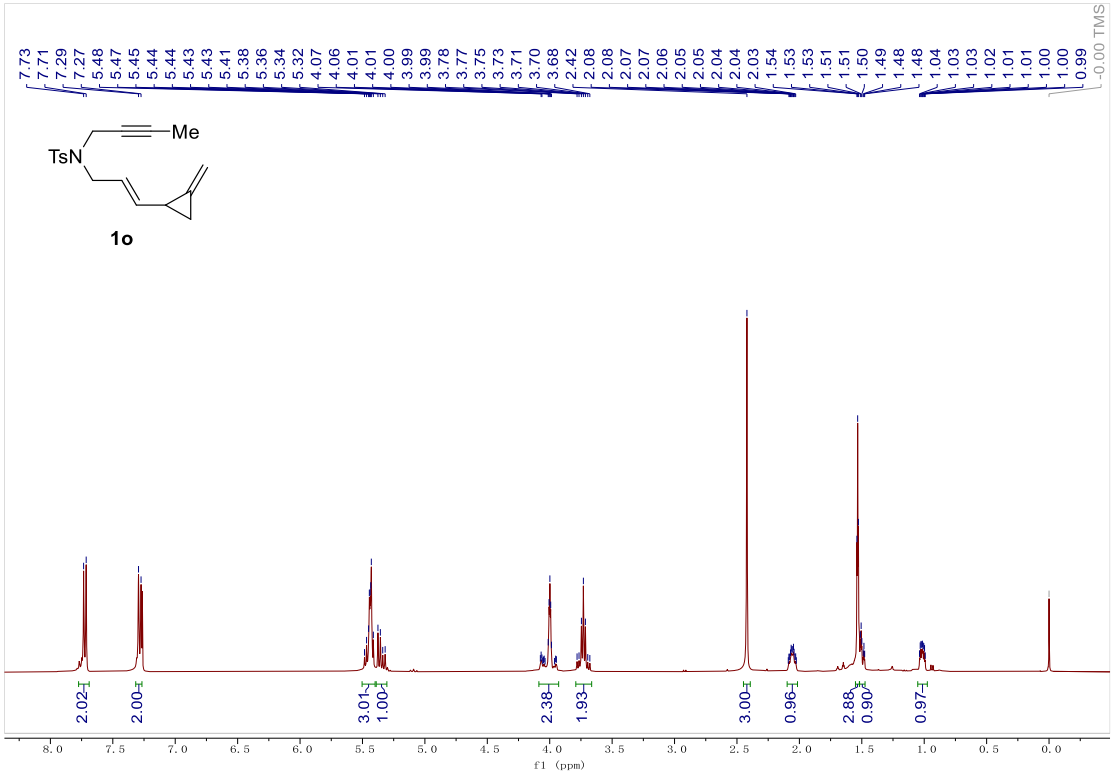


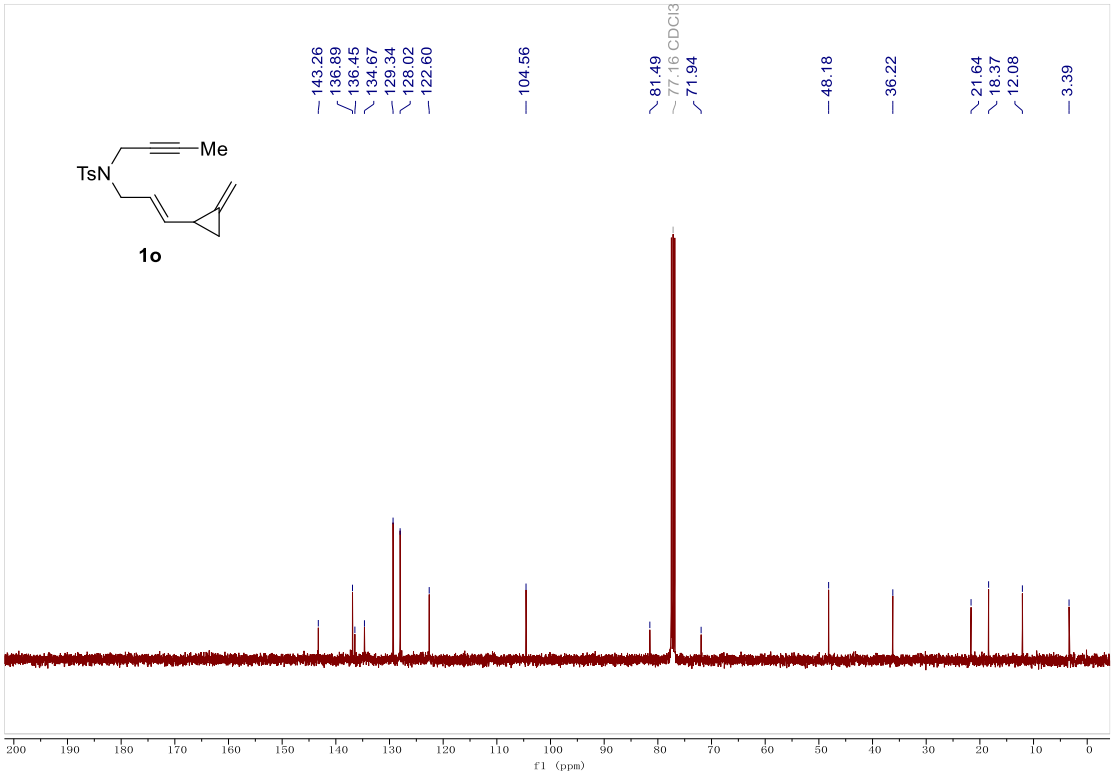
^{13}C NMR in $CDCl_3$, 101 MHz



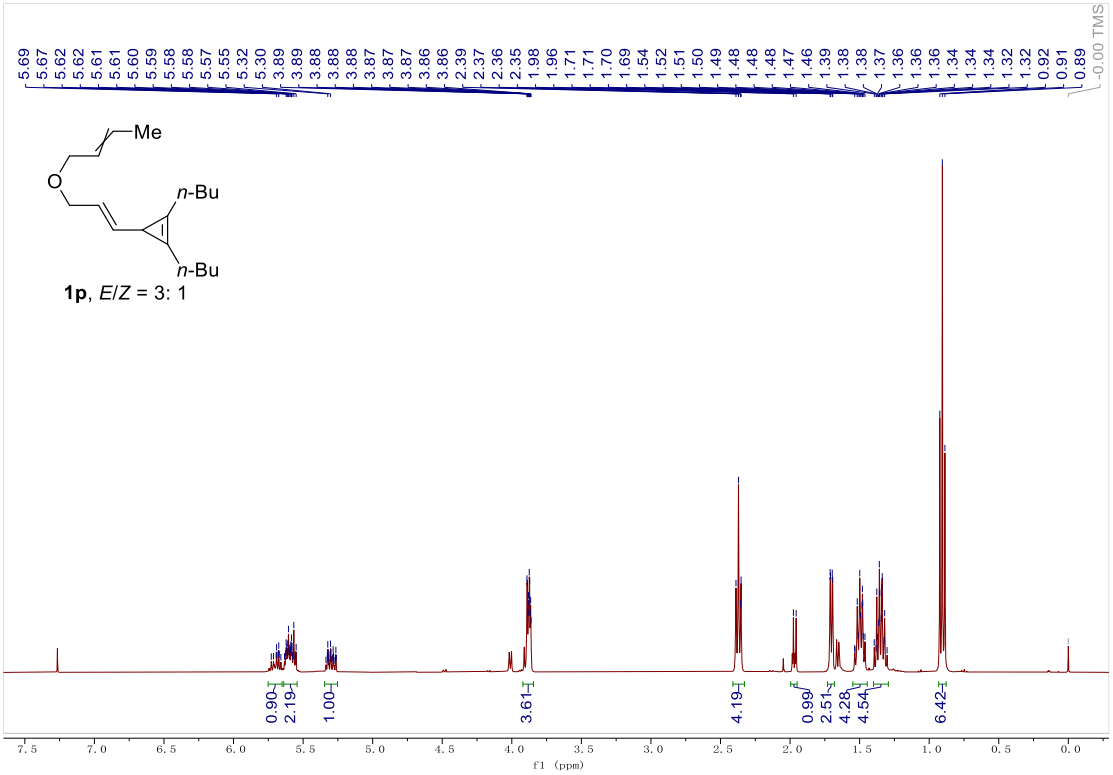
^{1}H NMR in $CDCl_3$, 400 MHz



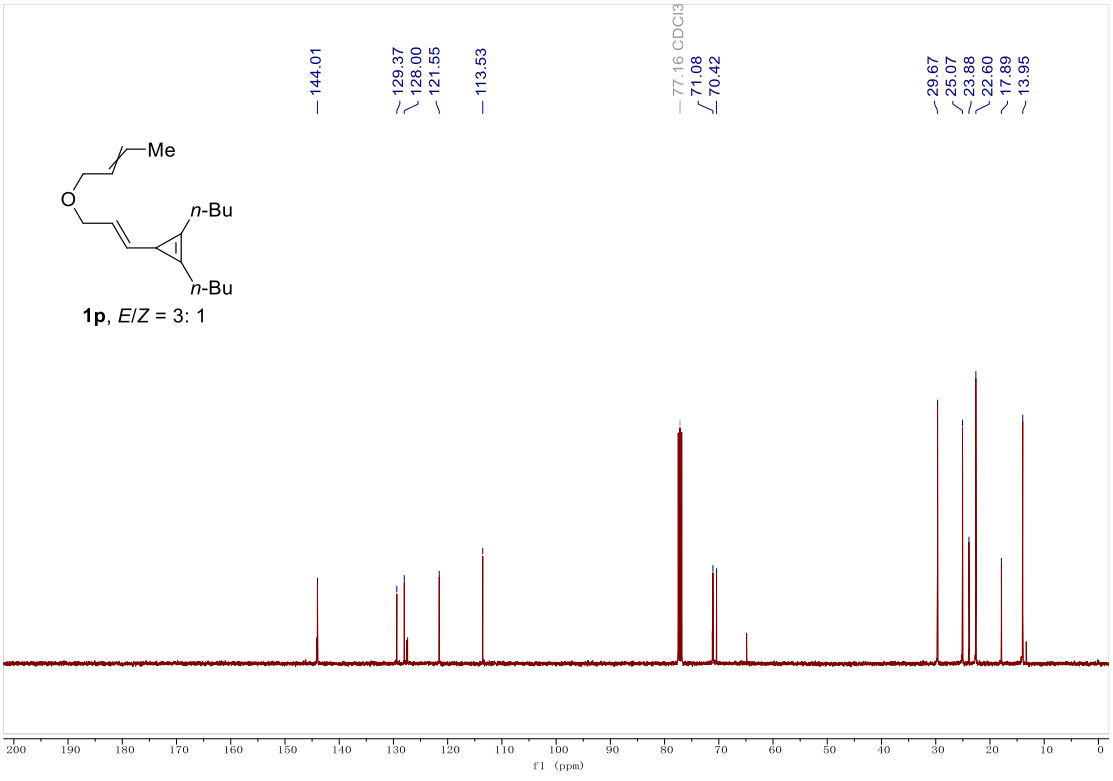
^{13}C NMR in $CDCl_3$, 101 MHz



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



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



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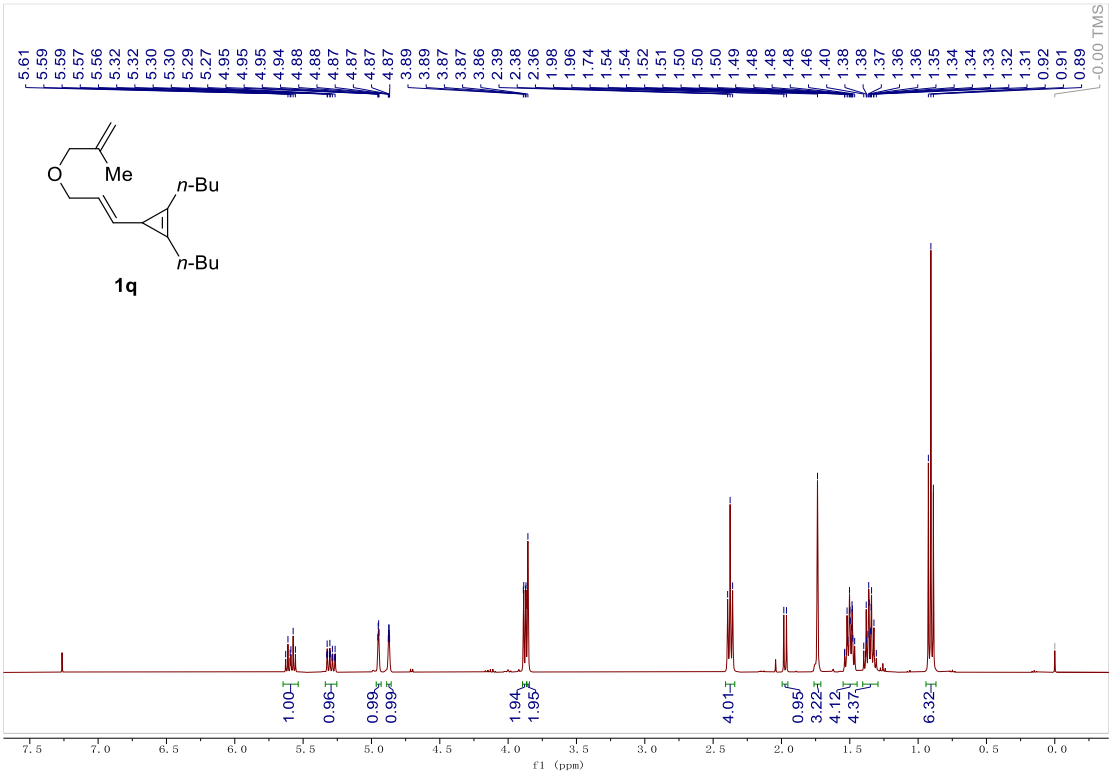

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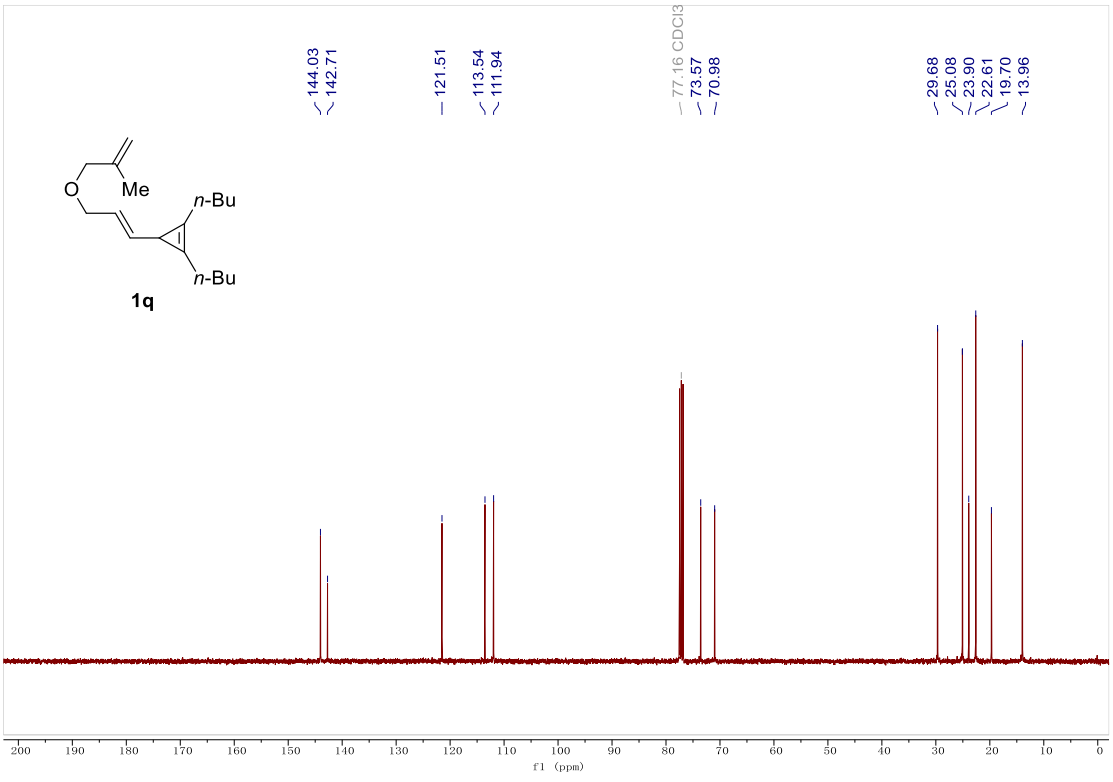
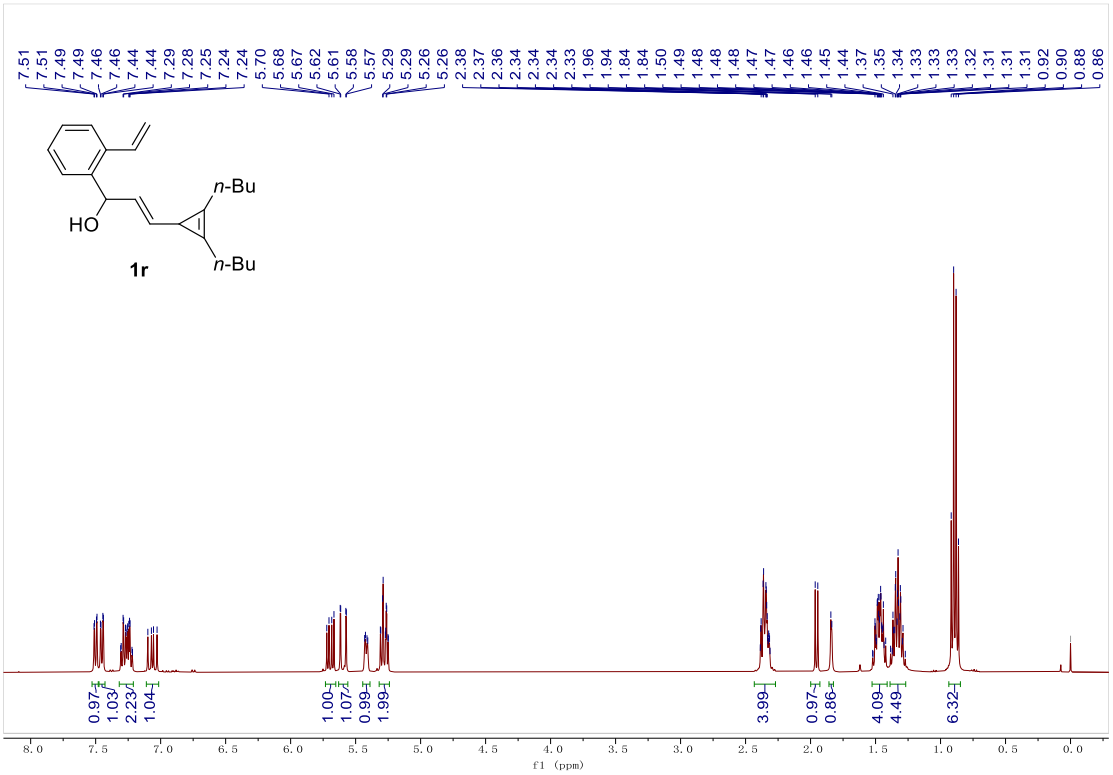


^{1}H NMR in $CDCl_3$, 400 MHz



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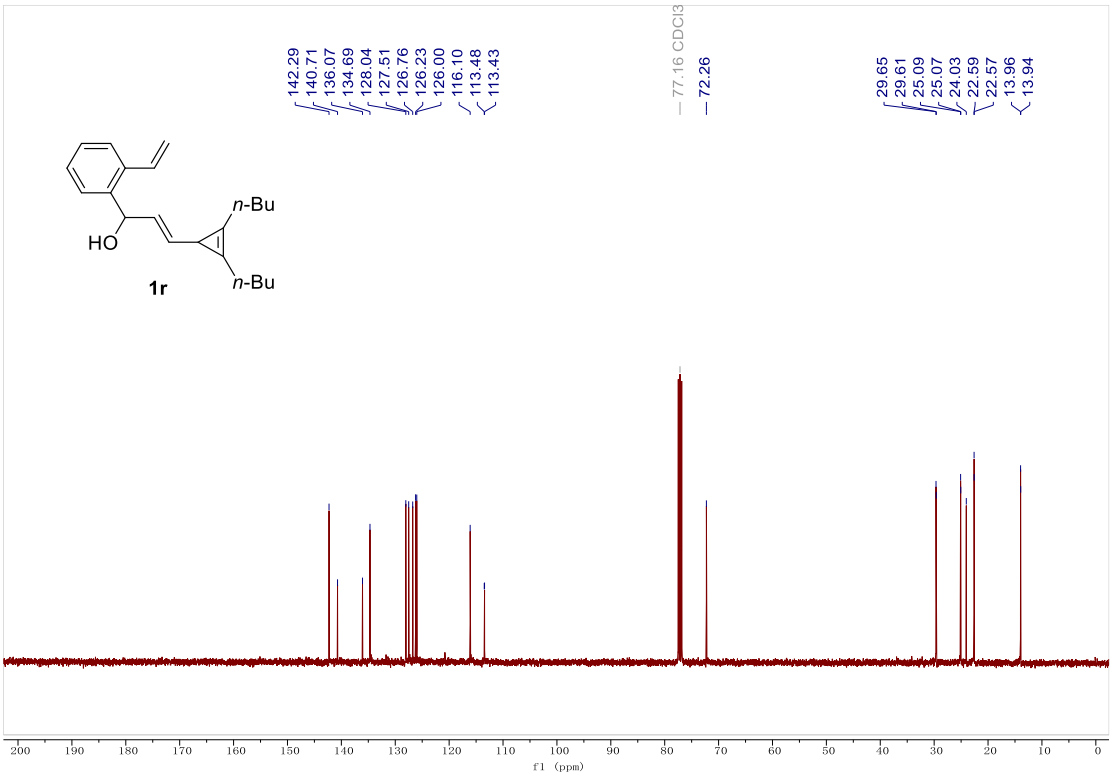
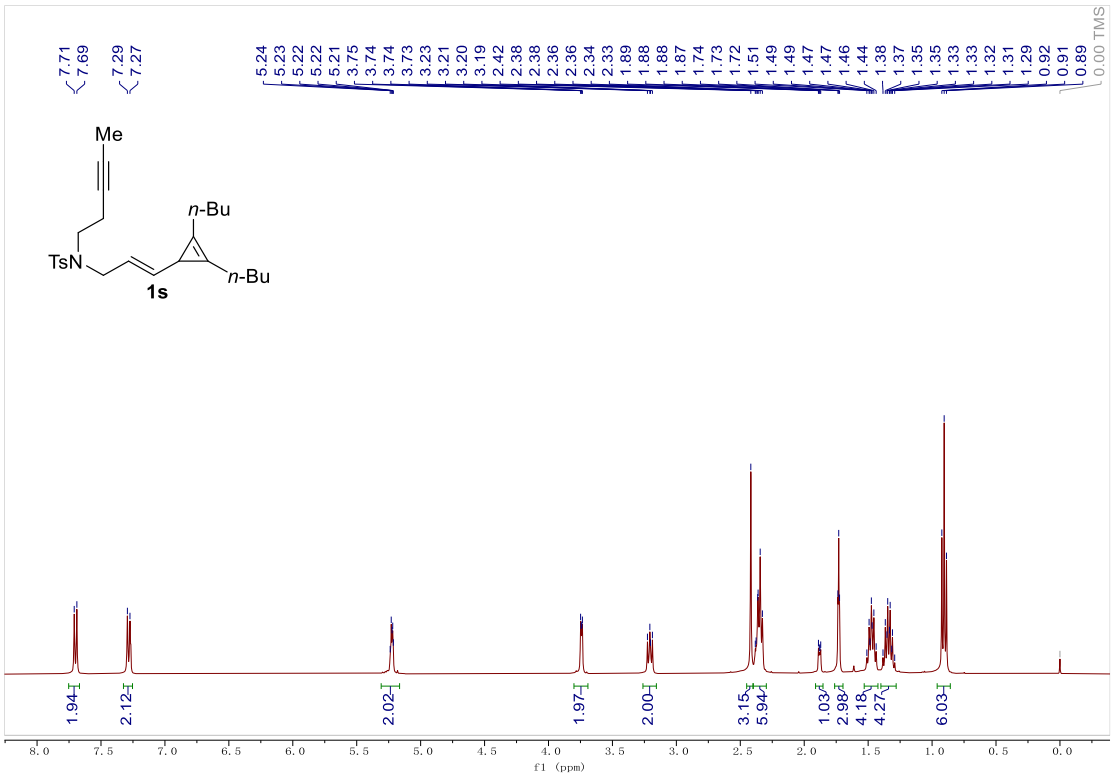
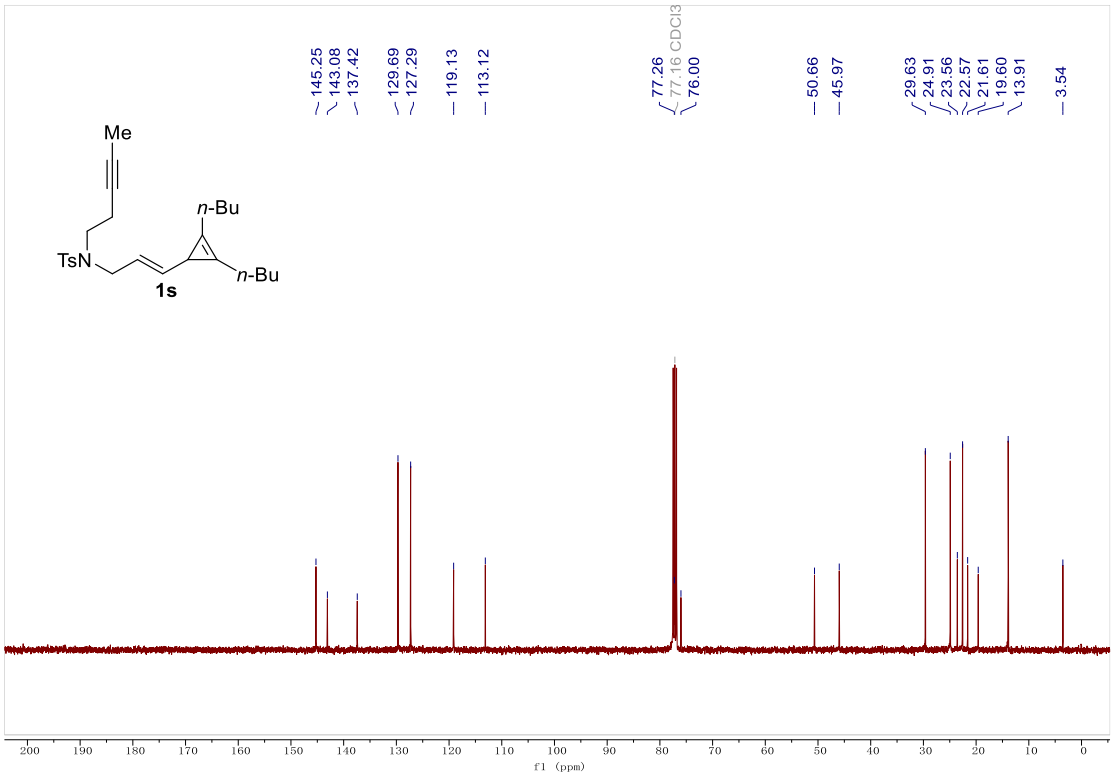


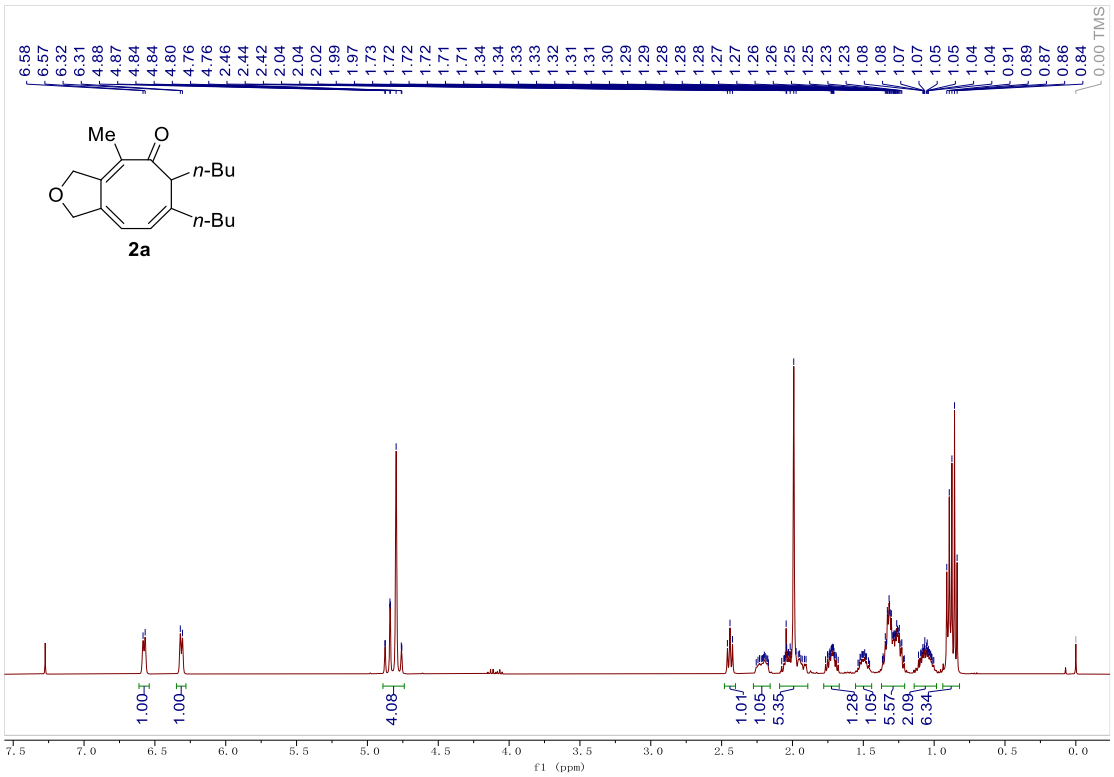
^{1}H NMR in $CDCl_3$, 400 MHz



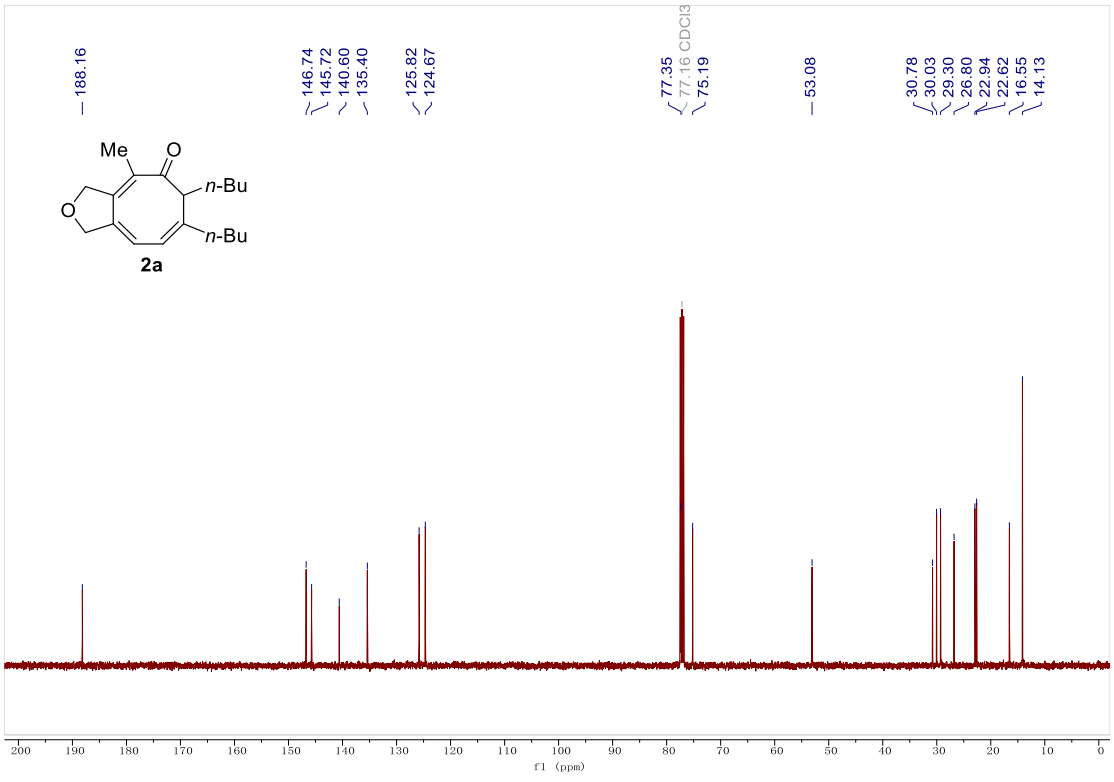
^{13}C NMR in $CDCl_3$, 101 MHz



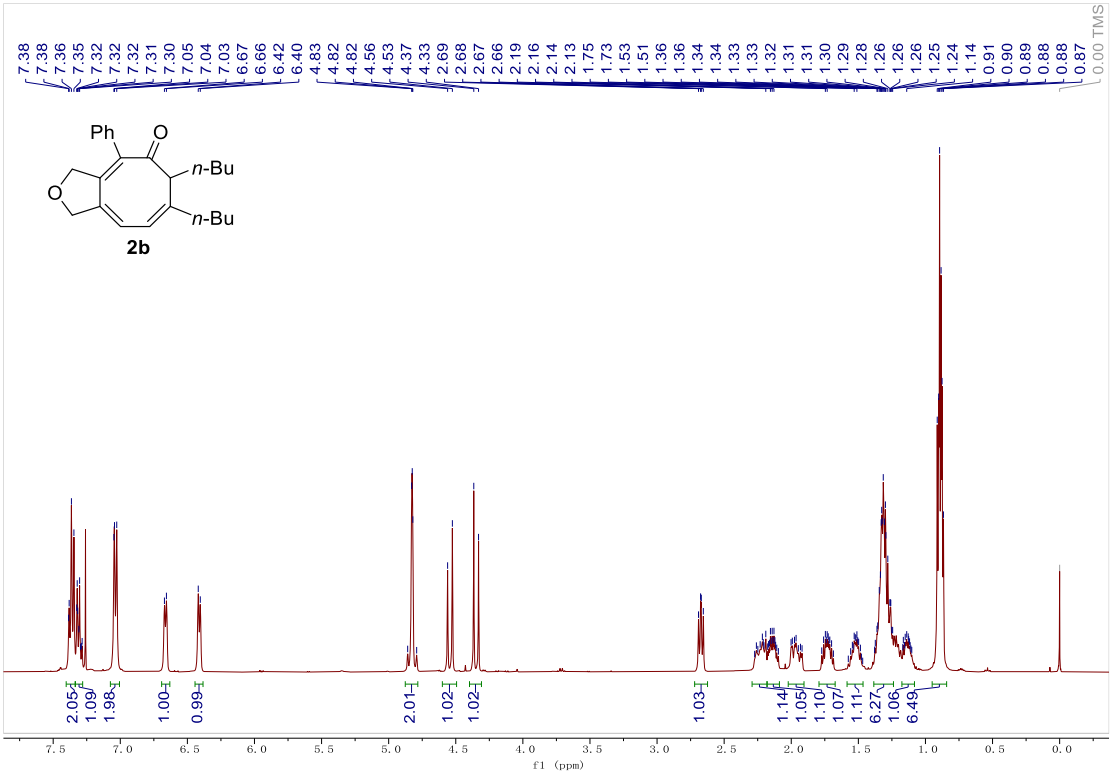
^{1}H NMR in $CDCl_3$, 400 MHz



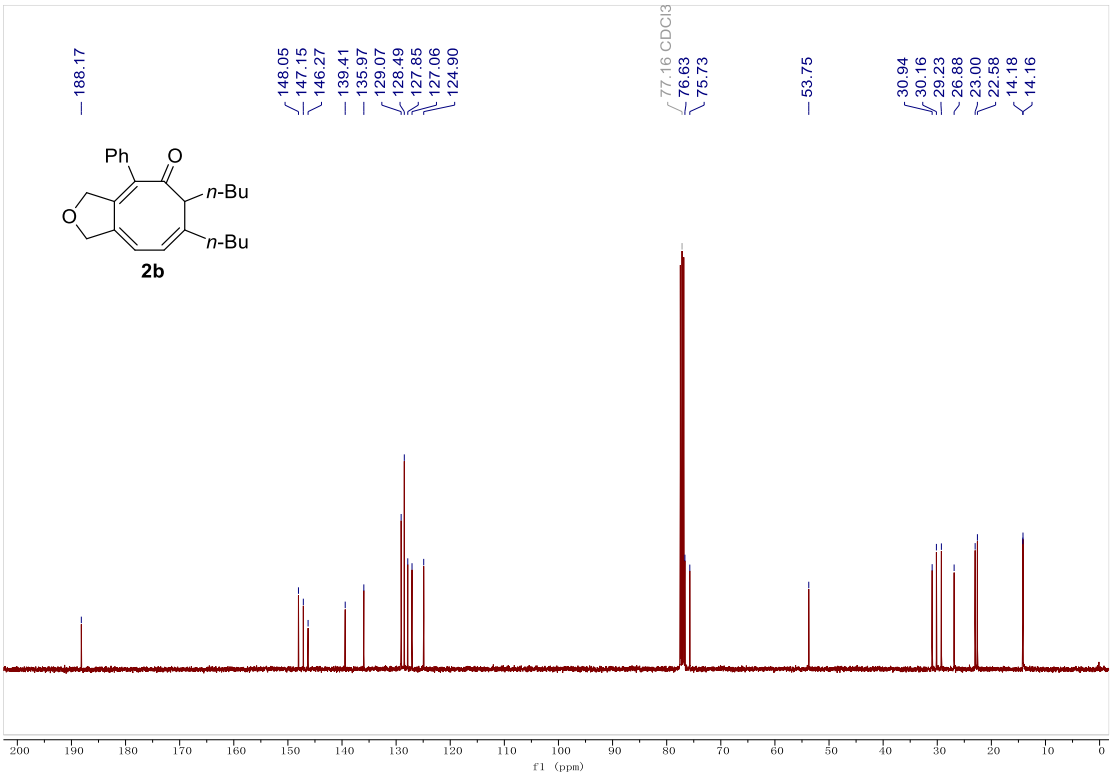
^{13}C NMR in $CDCl_3$, 101 MHz



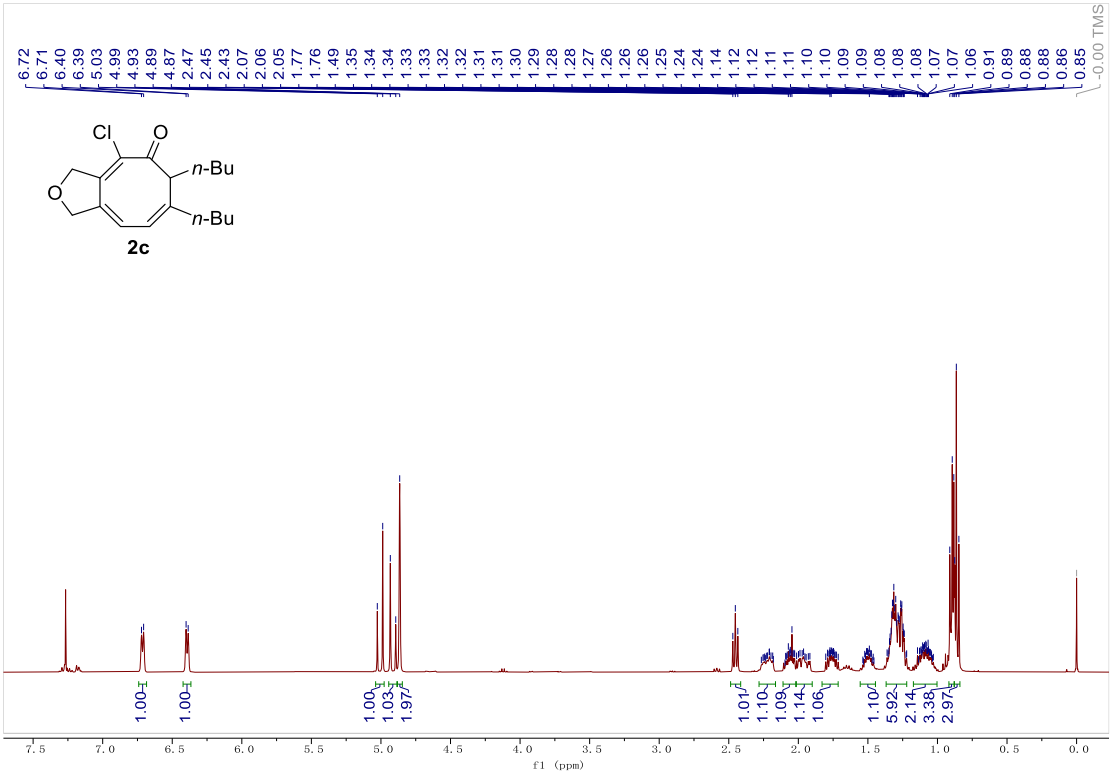
^{1}H NMR in $CDCl_3$, 400 MHz



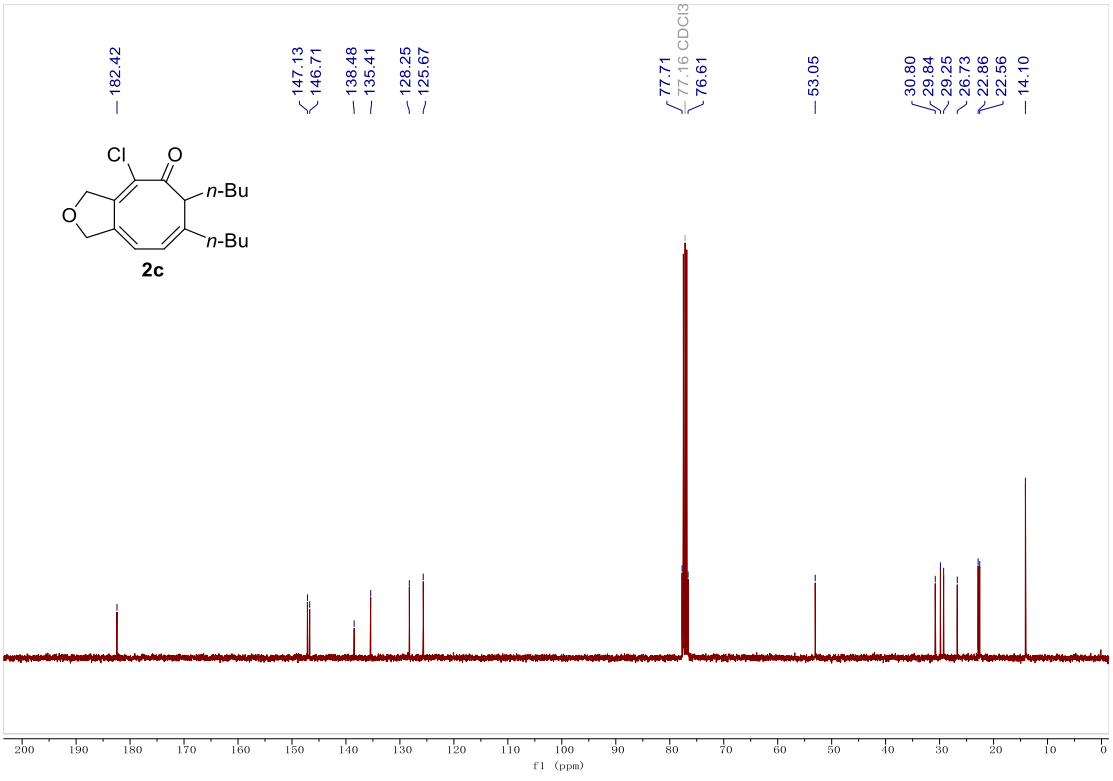
^{13}C NMR in $CDCl_3$, 101 MHz



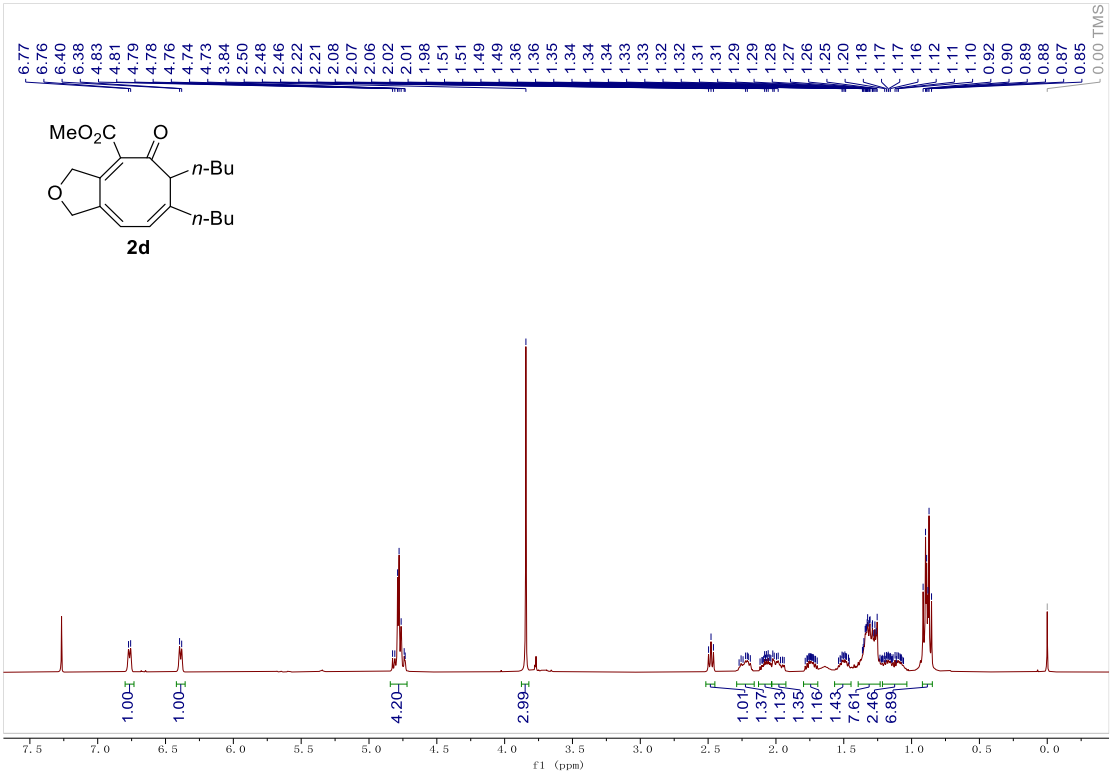
^{1}H NMR in $CDCl_3$, 400 MHz



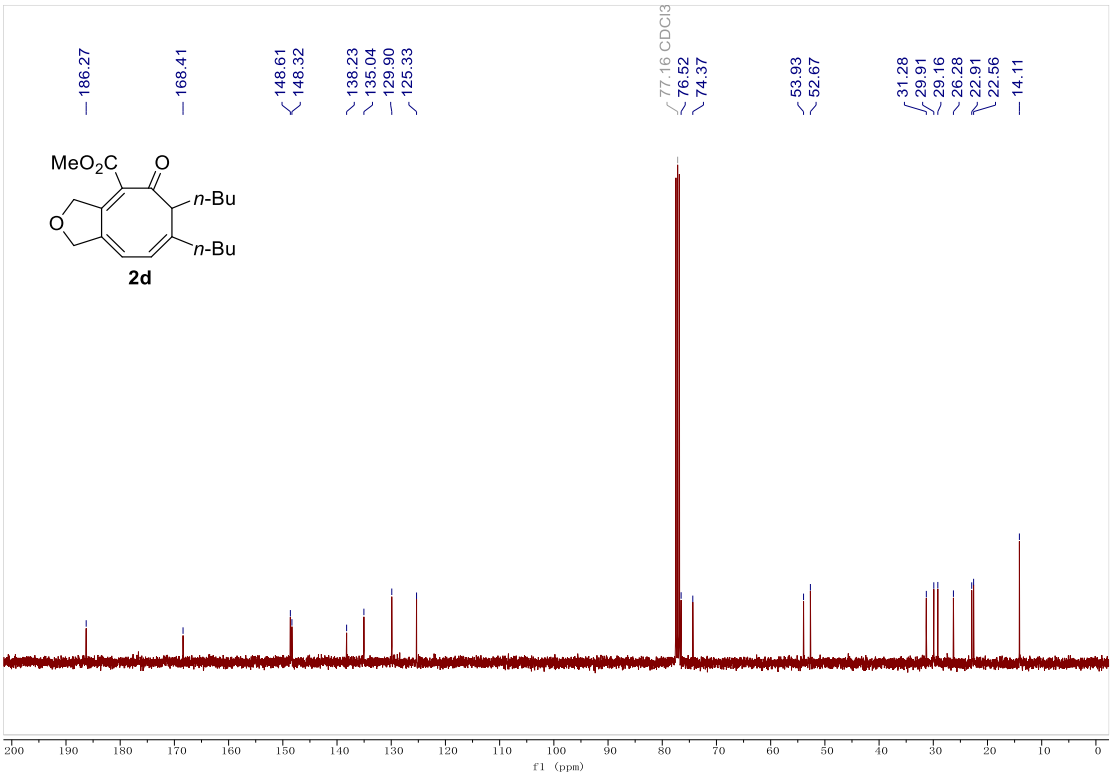
^{13}C NMR in $CDCl_3$, 101 MHz



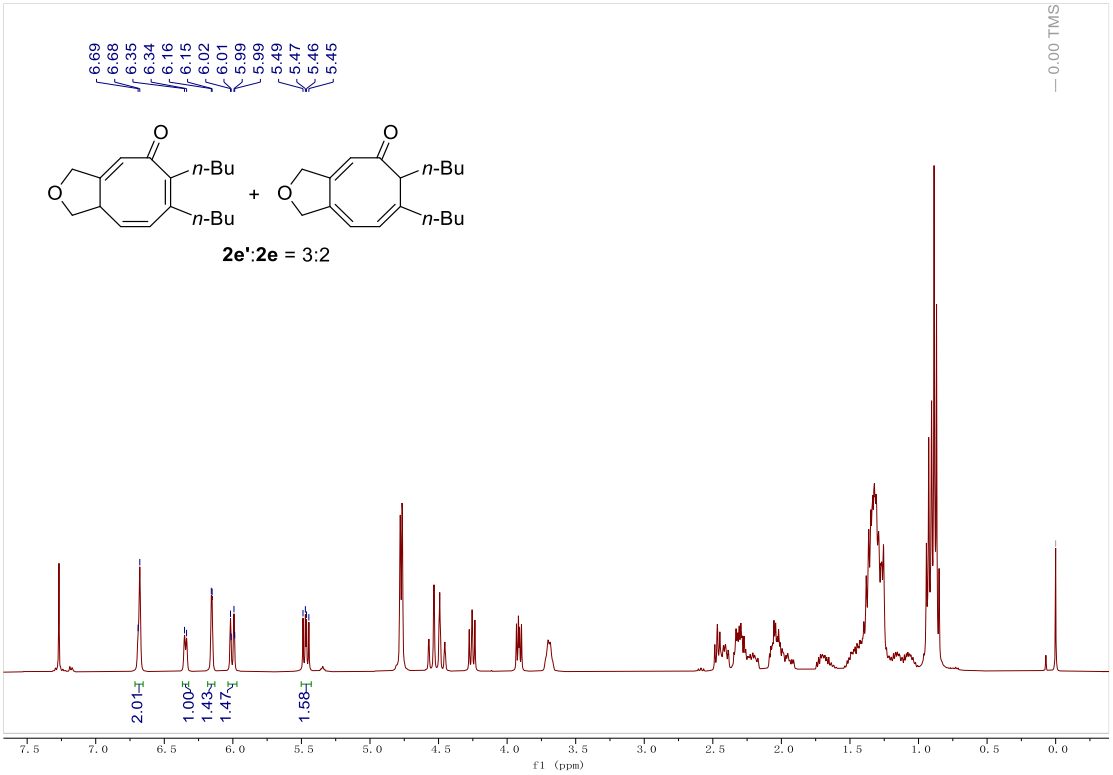
^{1}H NMR in $CDCl_3$, 400 MHz



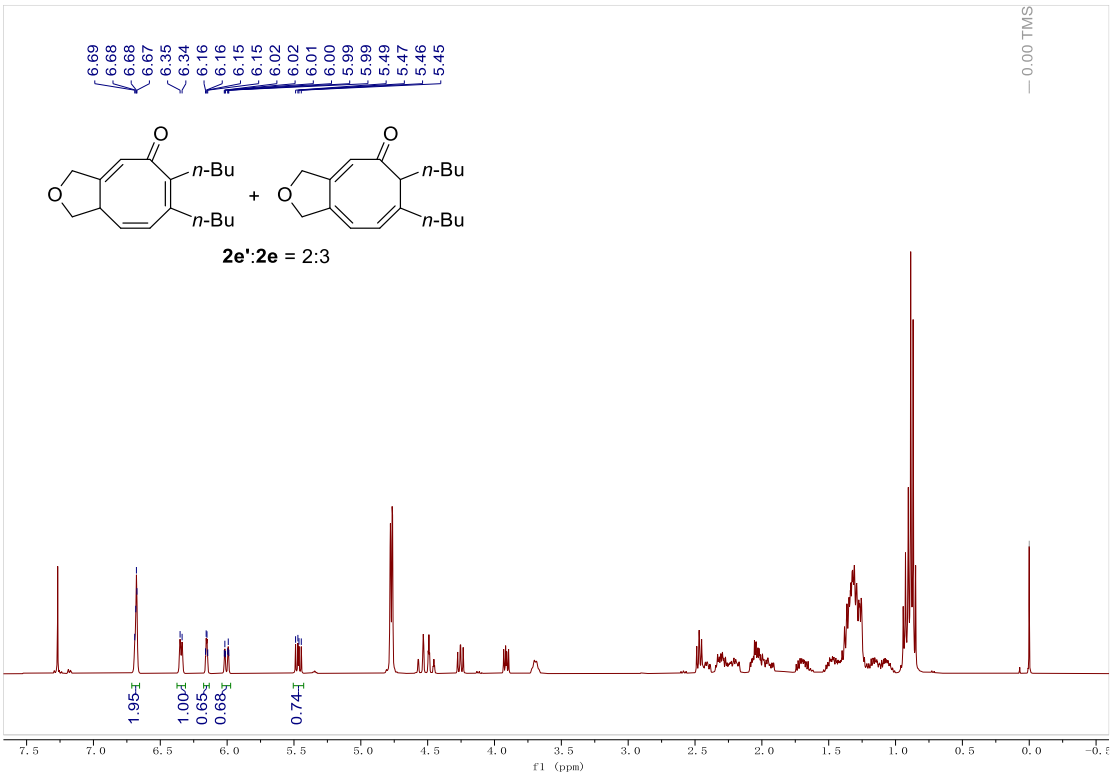
^{13}C NMR in $CDCl_3$, 101 MHz



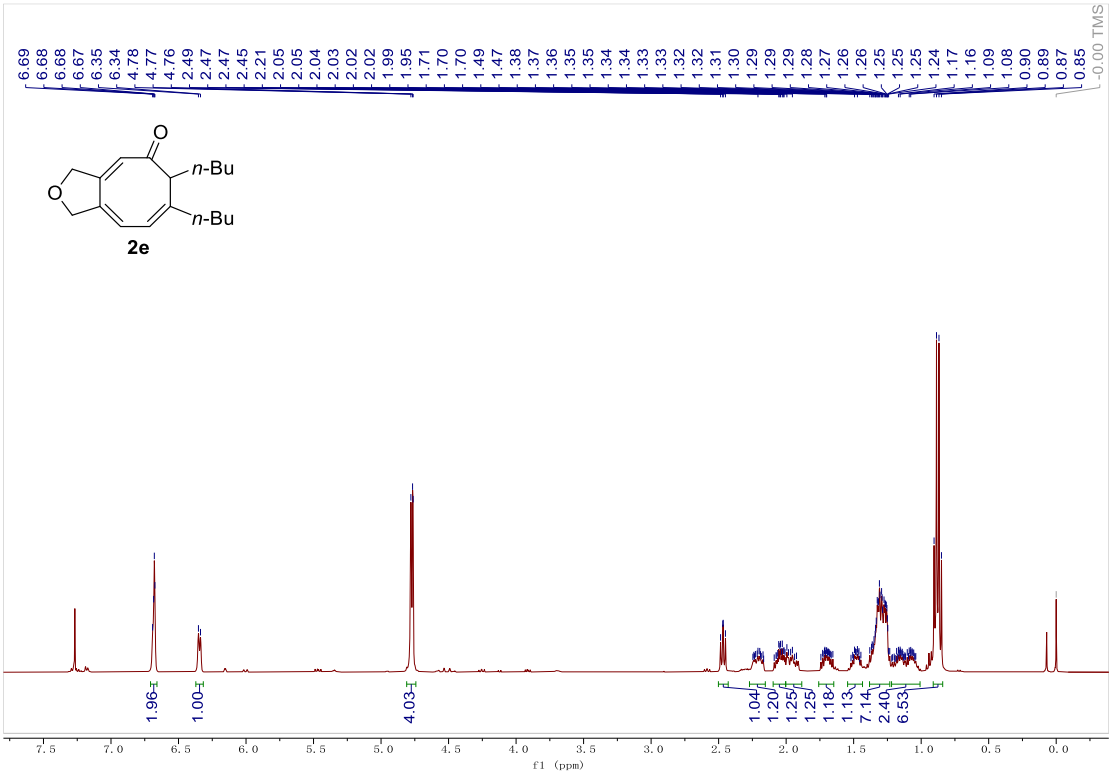
^{1}H NMR in $CDCl_3$, 400 MHz



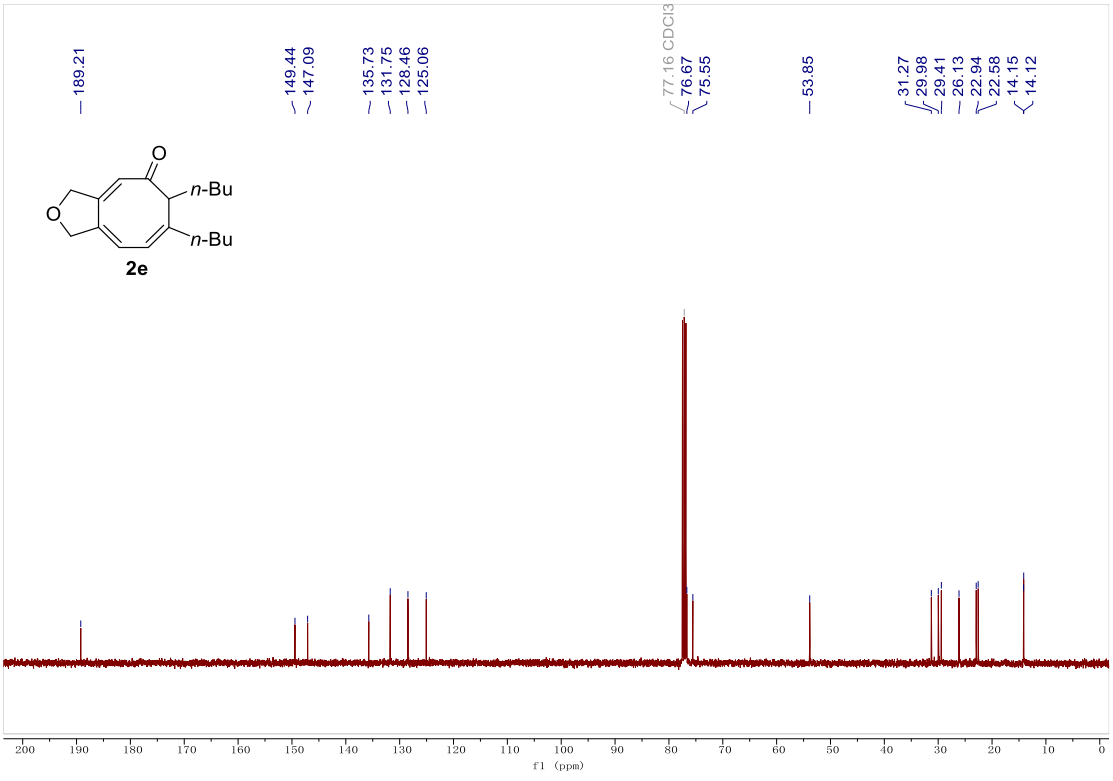
^{1}H NMR in $CDCl_3$, 400 MHz



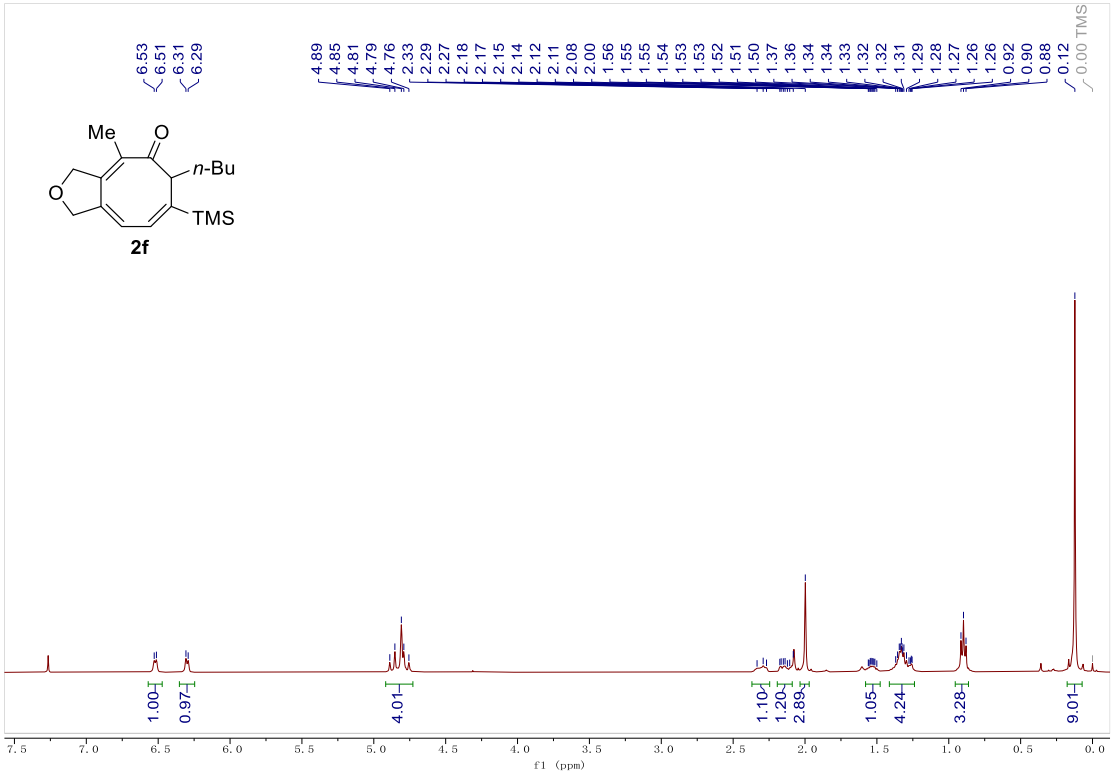
^{1}H NMR in $CDCl_3$, 400 MHz



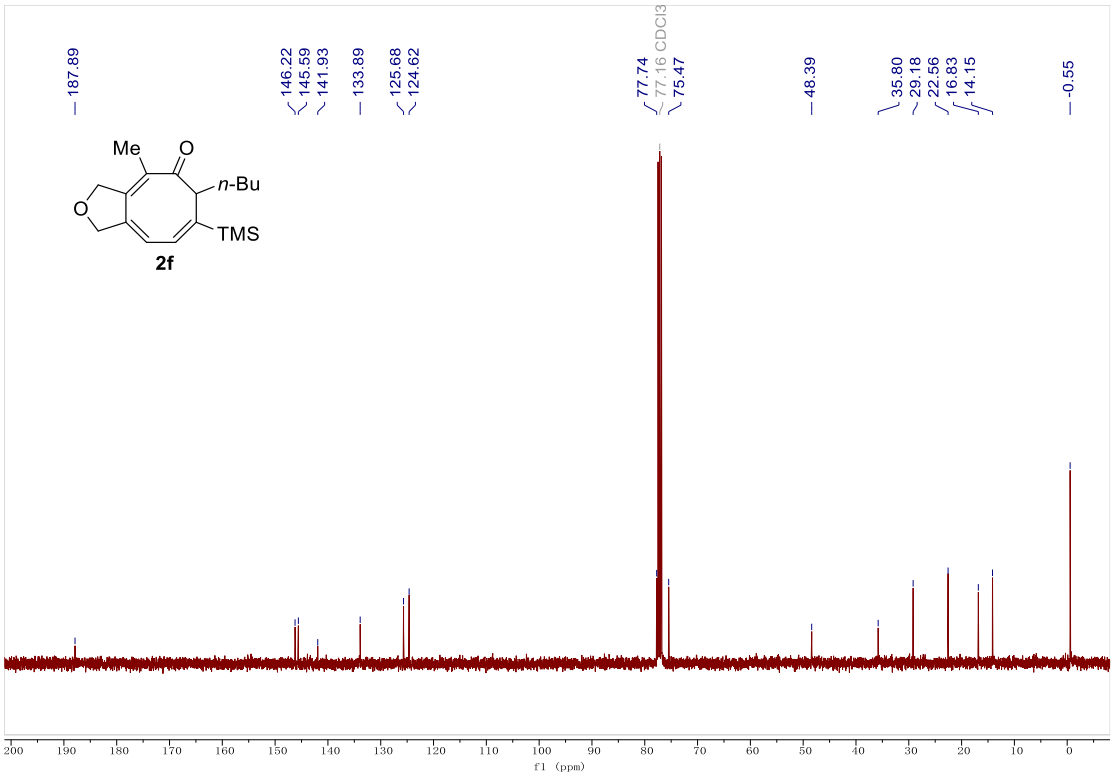
^{13}C NMR in $CDCl_3$, 101 MHz



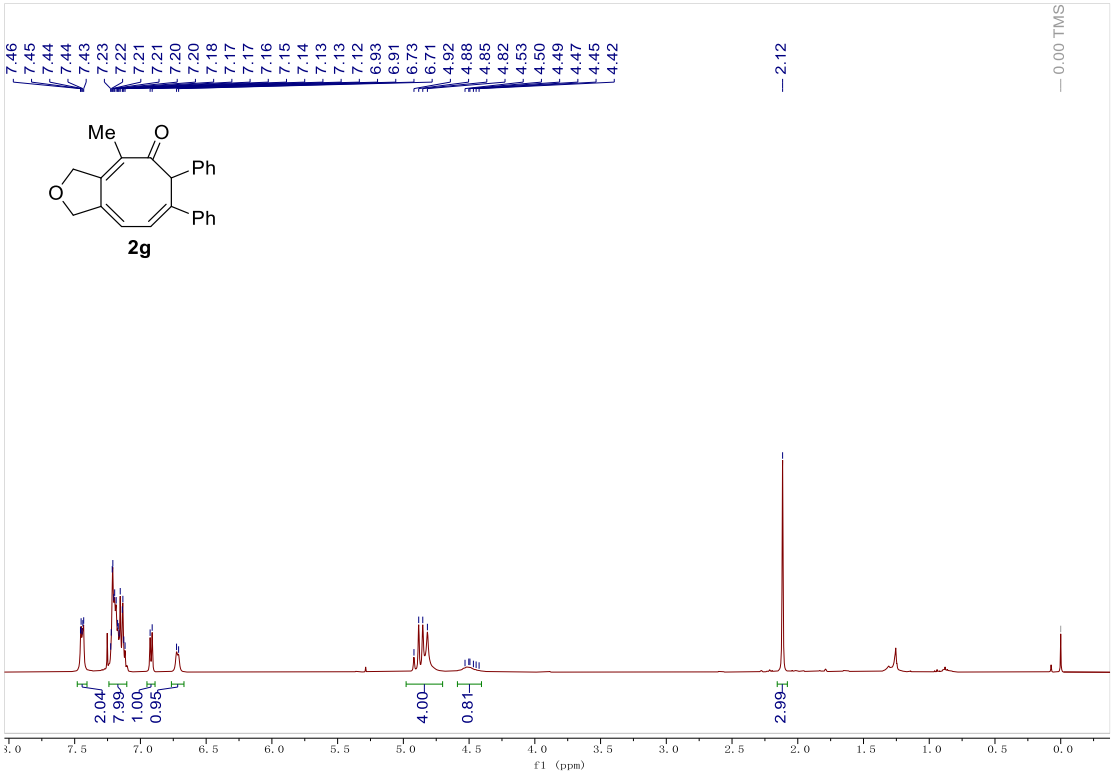
^{1}H NMR in $CDCl_3$, 400 MHz



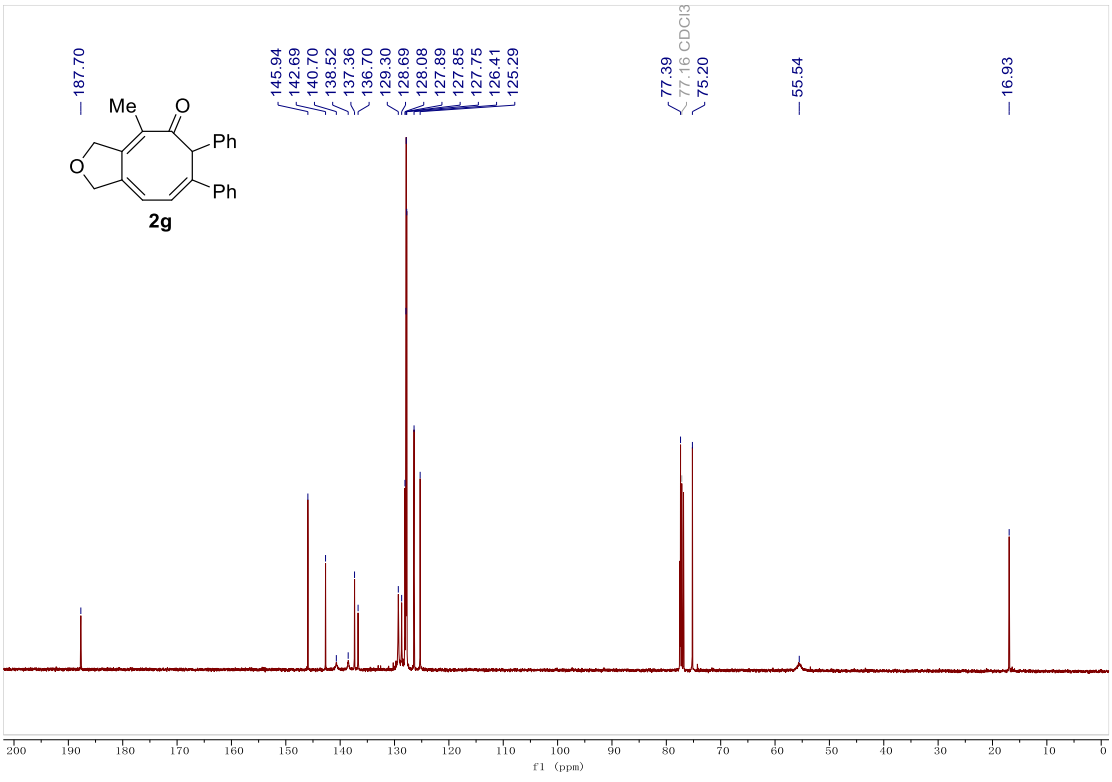
^{13}C NMR in $CDCl_3$, 101 MHz



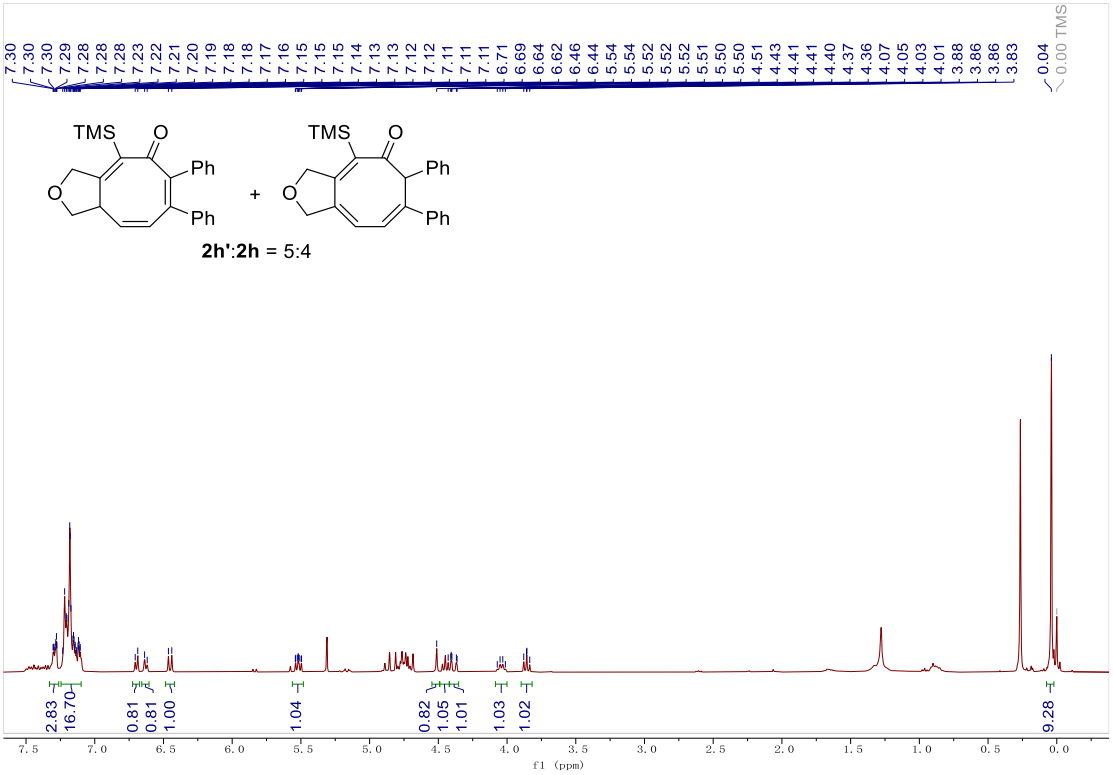
^{1}H NMR in $CDCl_3$, 400 MHz



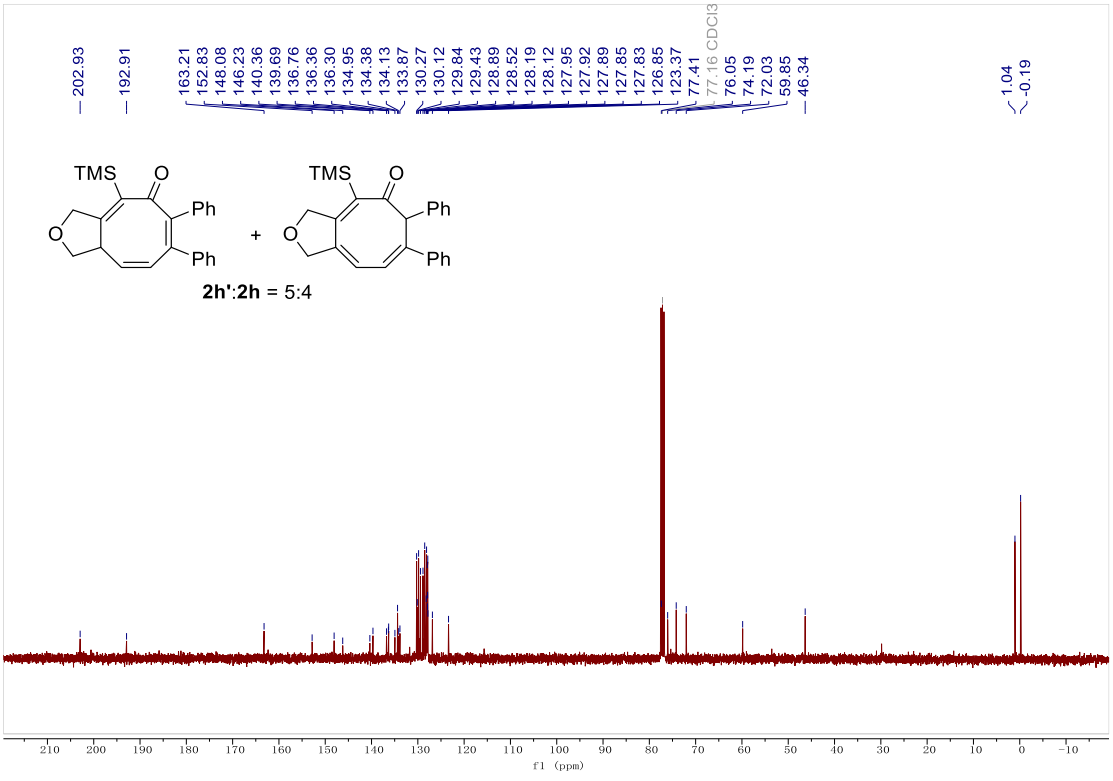
^{13}C NMR in $CDCl_3$, 101 MHz



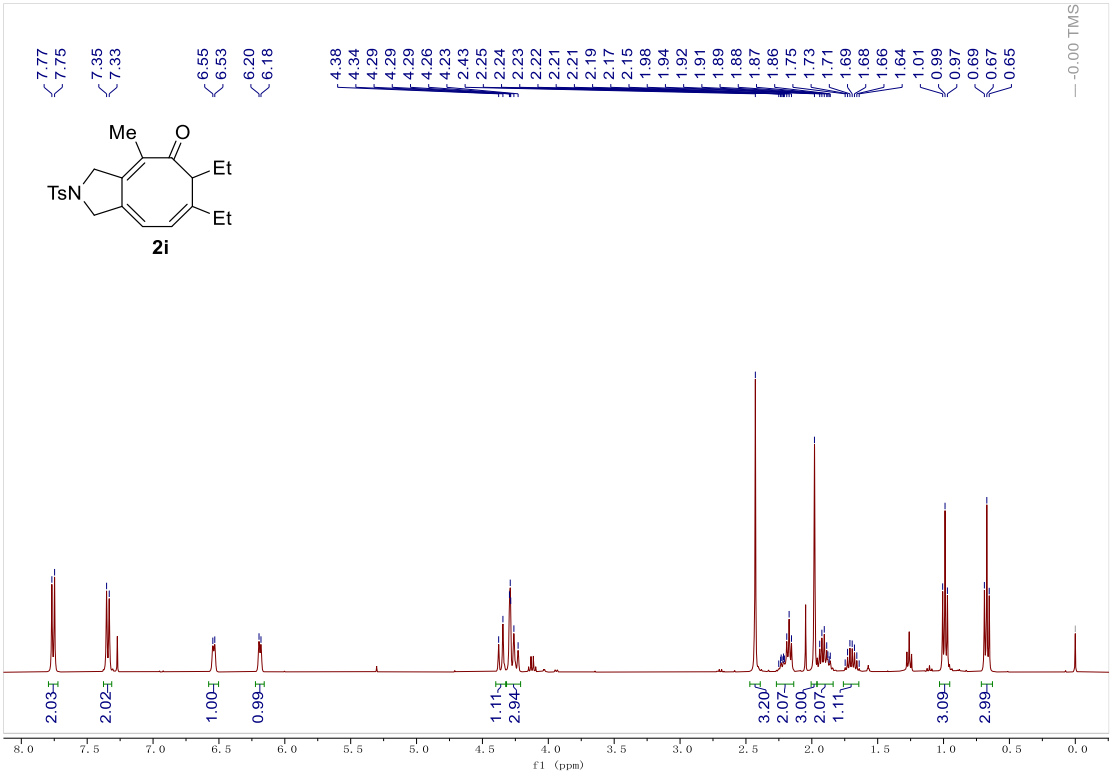
^{1}H NMR in $CDCl_3$, 400 MHz



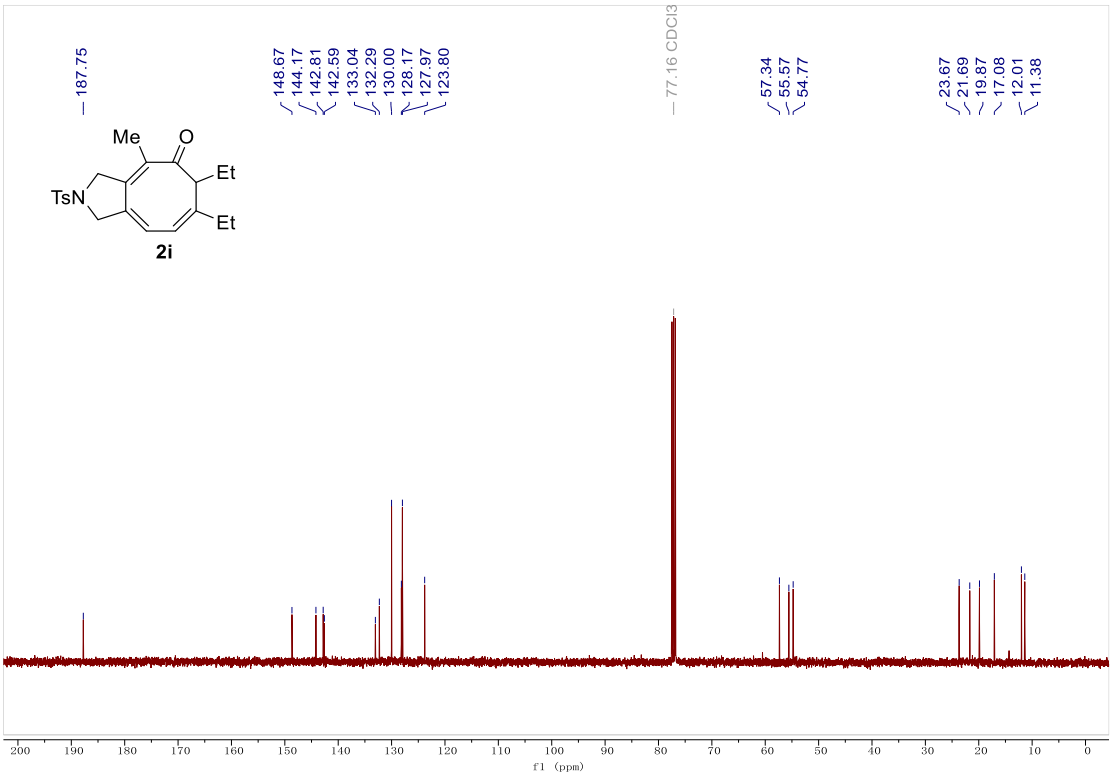
^{13}C NMR in $CDCl_3$, 101 MHz



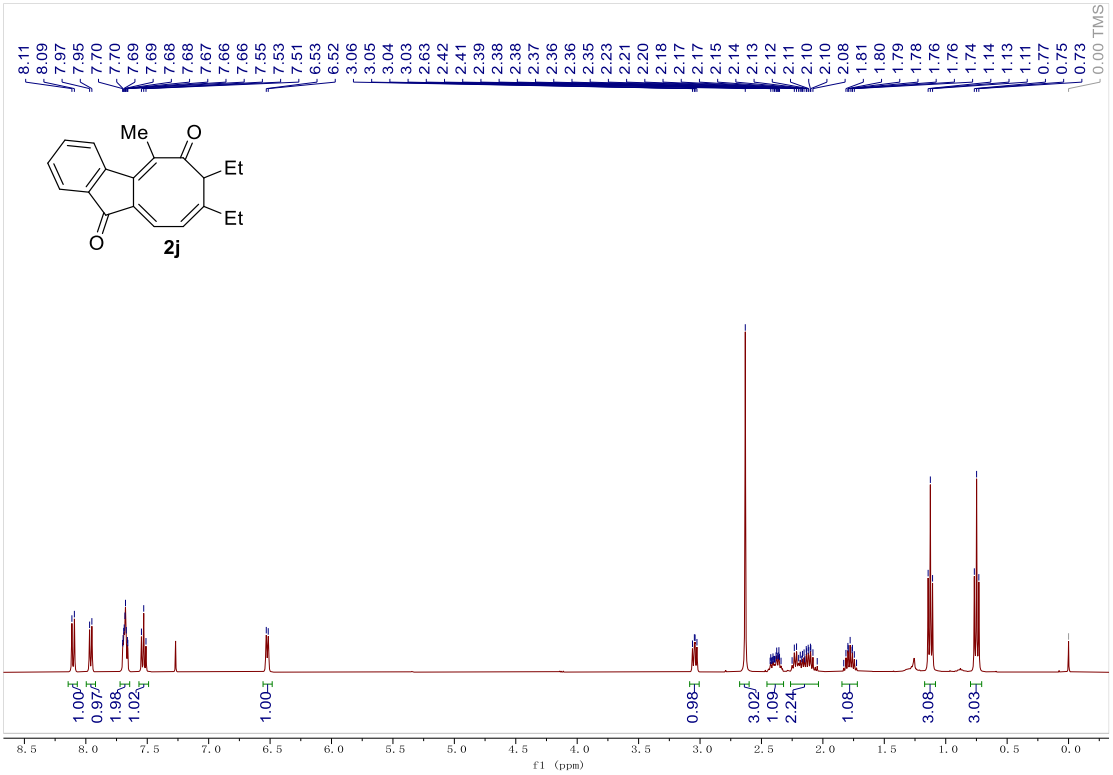
^{1}H NMR in $CDCl_3$, 400 MHz



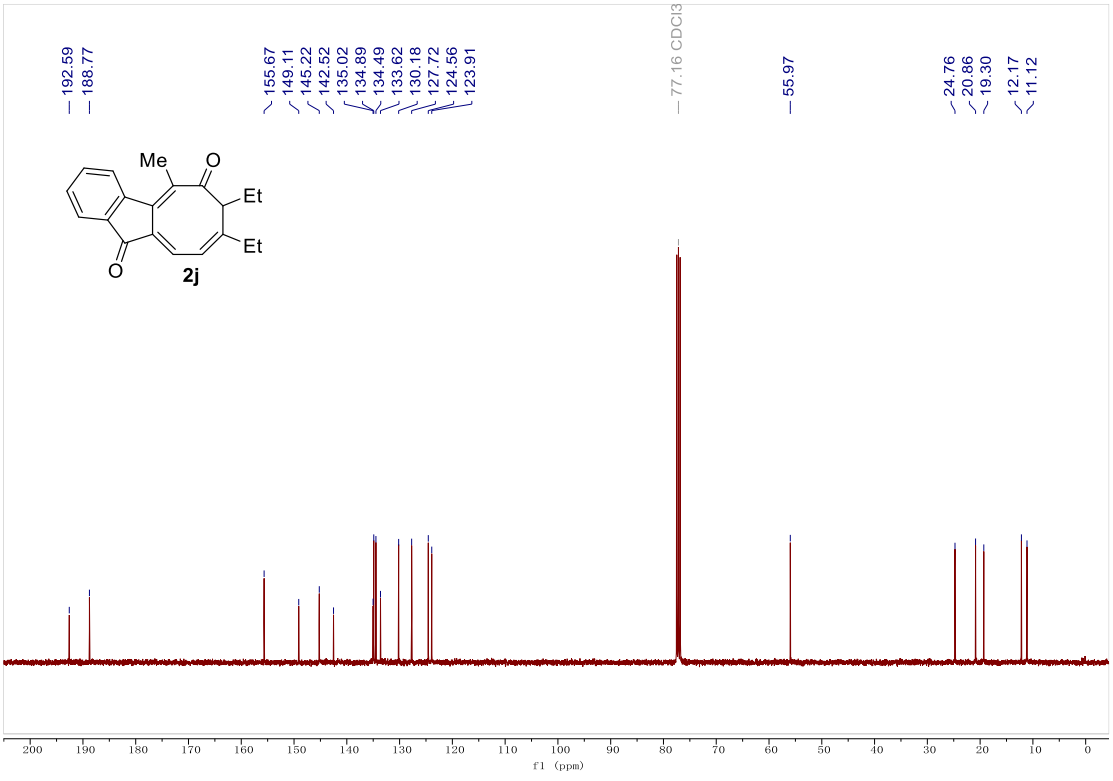
^{13}C NMR in $CDCl_3$, 101 MHz



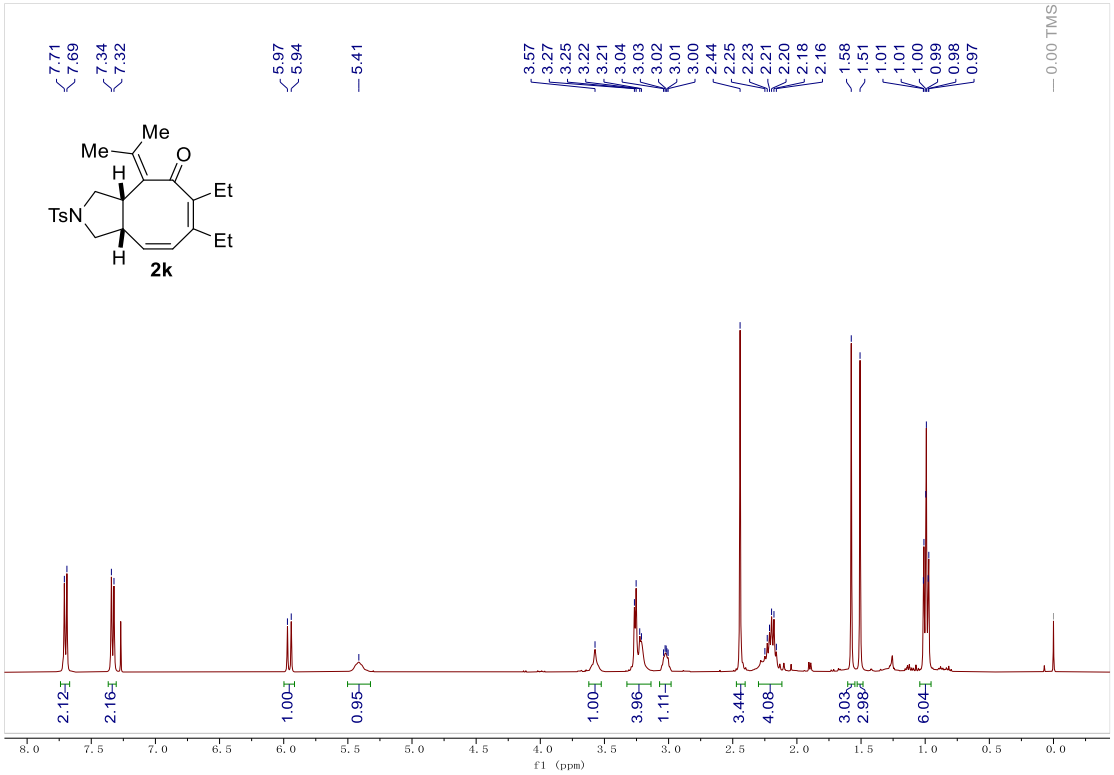
^{1}H NMR in $CDCl_3$, 400 MHz



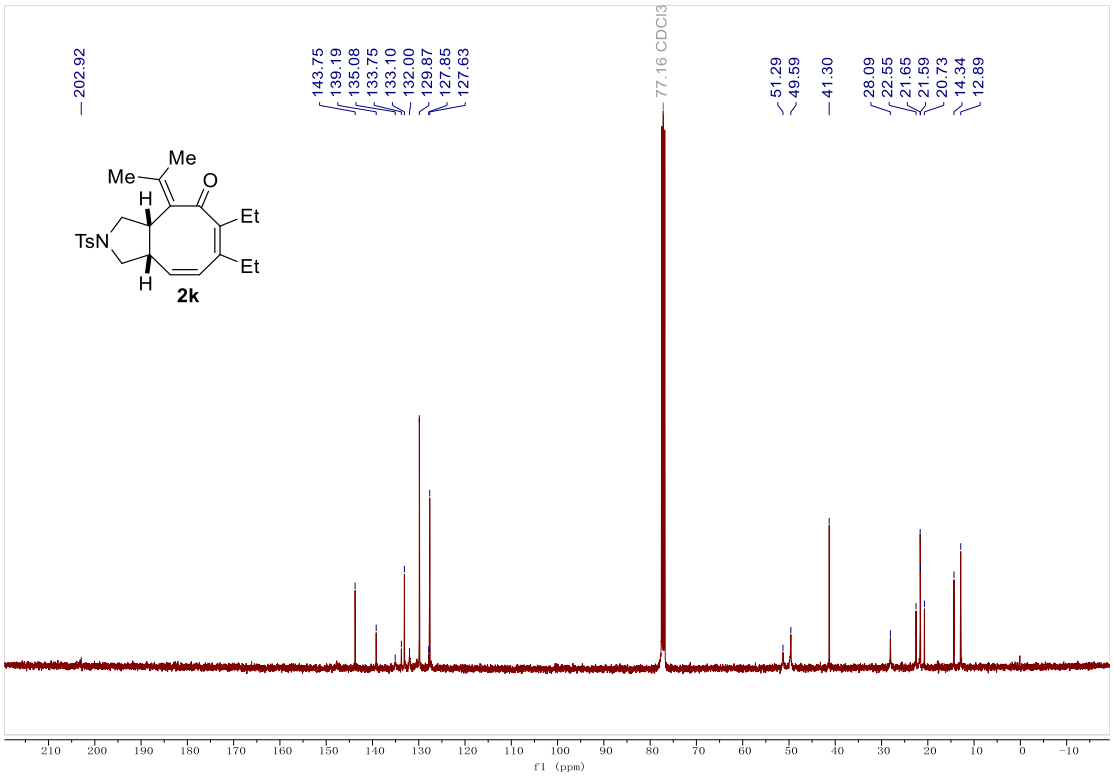
^{13}C NMR in $CDCl_3$, 101 MHz



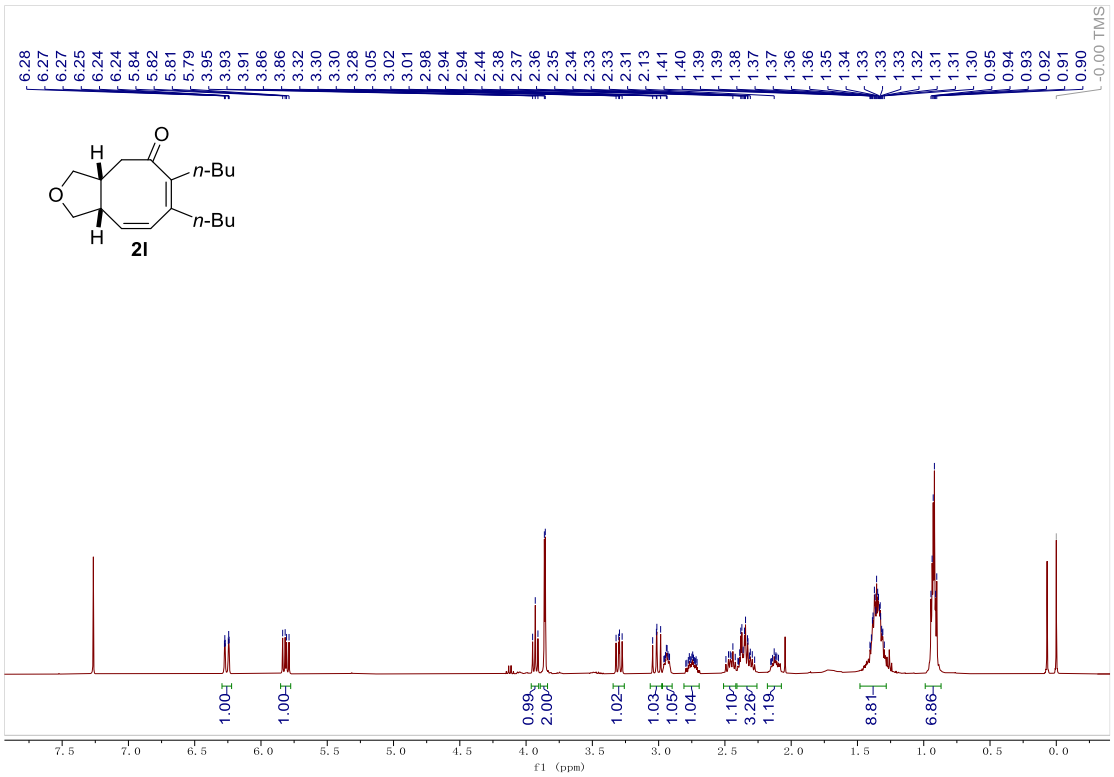
^{1}H NMR in $CDCl_3$, 400 MHz



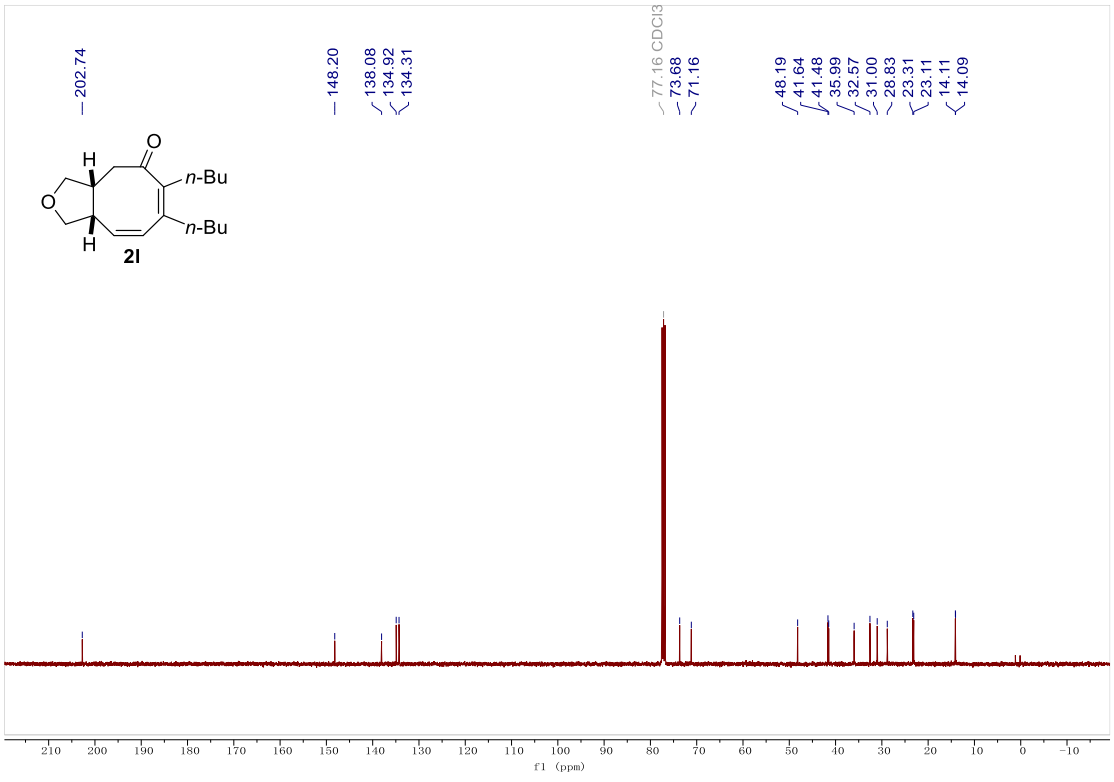
^{13}C NMR in $CDCl_3$, 101 MHz



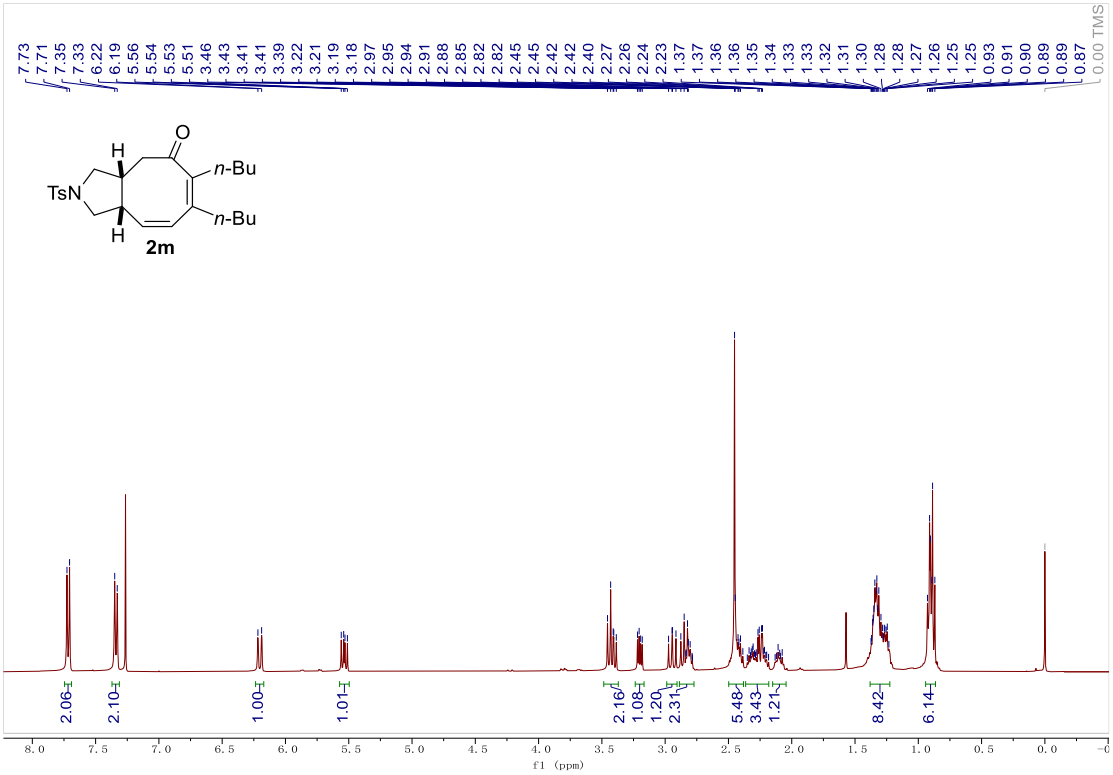
^{1}H NMR in $CDCl_3$, 400 MHz



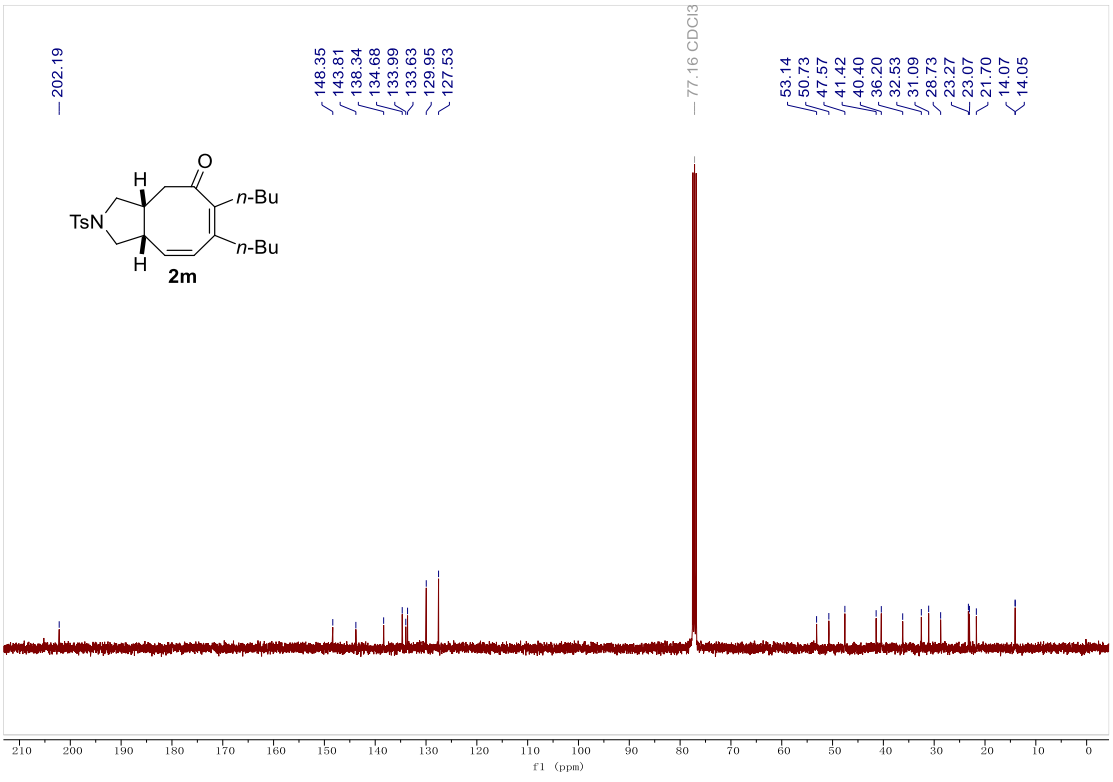
^{13}C NMR in $CDCl_3$, 101 MHz



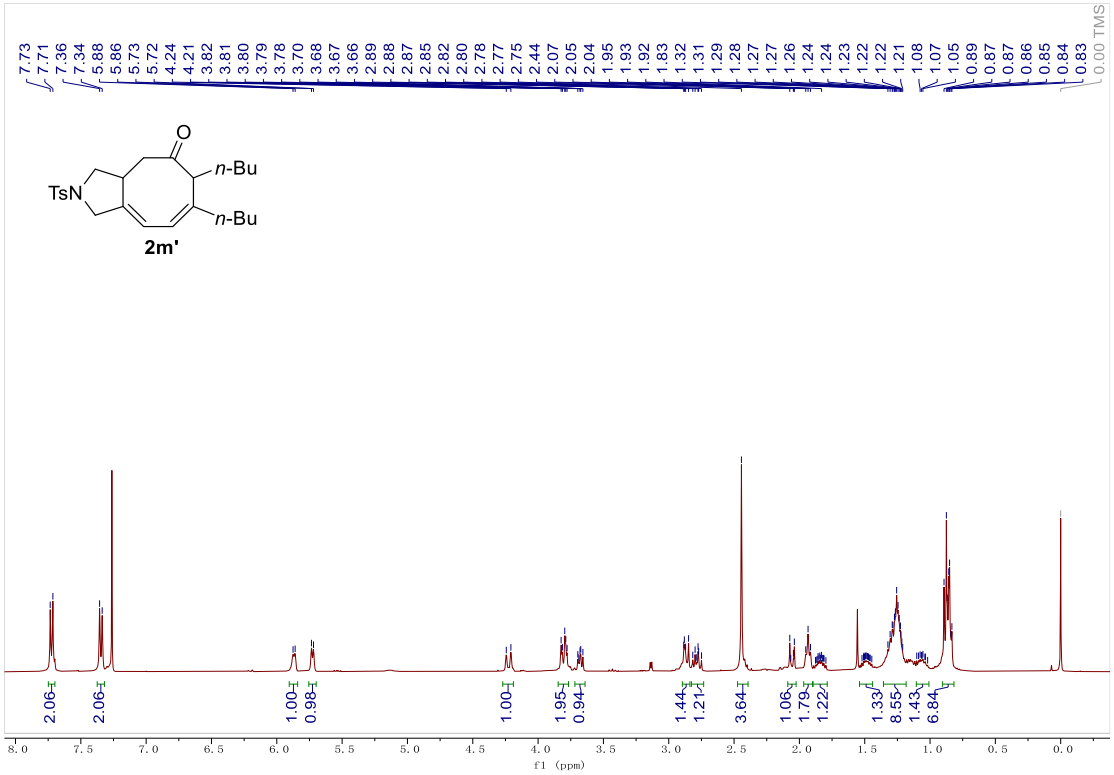
^{1}H NMR in $CDCl_3$, 400 MHz



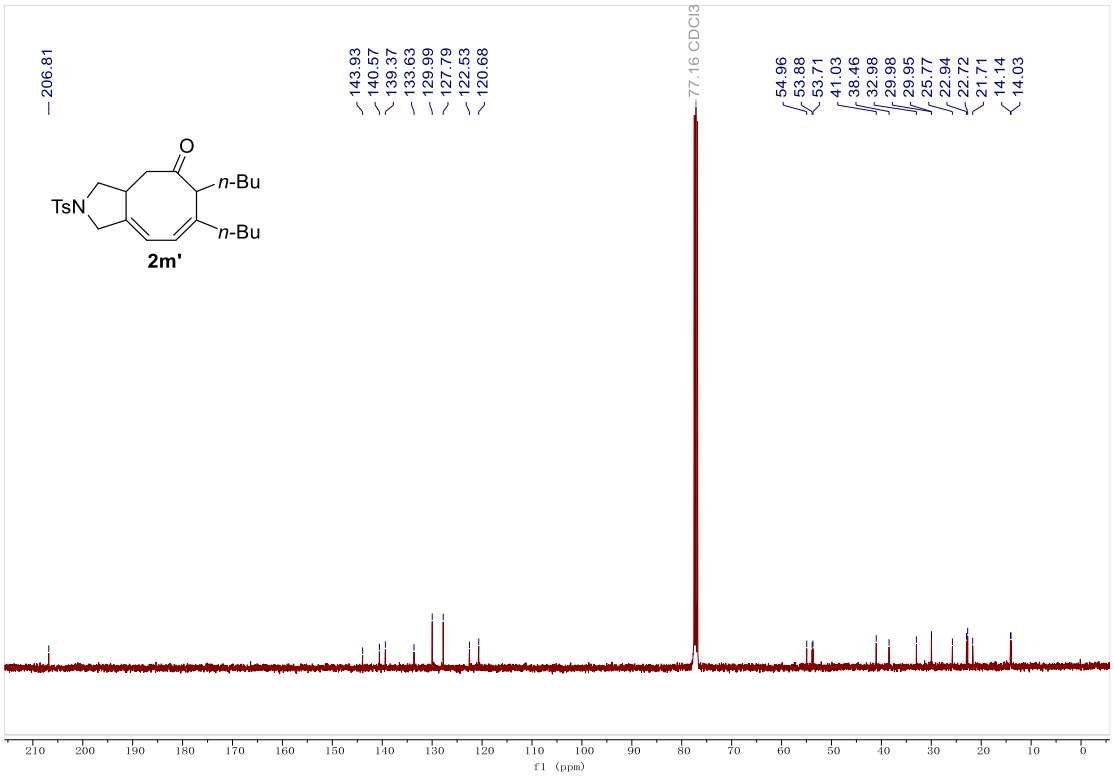
^{13}C NMR in $CDCl_3$, 101 MHz



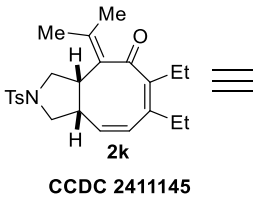
^{1}H NMR in $CDCl_3$, 400 MHz



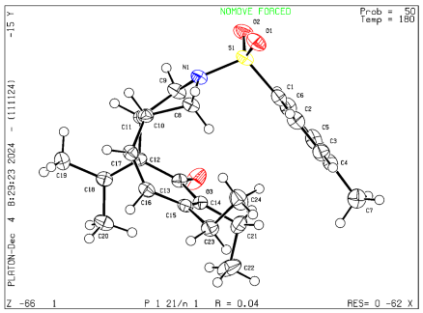
^{13}C NMR in $CDCl_3$, 101 MHz



8. X-Ray Crystal Structure of 2k



CCDC 2411145



Ellipsoids are drawn at 50% probability

Crystallographic Data of Compound **2k**:

Crystal data	
Chemical formula	$C_{24}H_{31}NO_3S$
M_r	413.56
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	180
a, b, c (Å)	9.6250 (4), 7.6640 (4), 29.3841 (13)
β (°)	92.837 (4)
V (Å^3)	2164.89 (17)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.18
Crystal size (mm)	0.6 × 0.05 × 0.02
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.113, 1.05
No. of reflections	5570
No. of parameters	267
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.28, −0.42