Supporting Information

Synthesis of Polycyclic n/5/8 and n/5/5/5 Skeletons Using Rhodium-Catalyzed [5 + 2 + 1] Cycloaddition of Exocyclic-Ene-Vinylcyclopropanes and Carbon Monoxide

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1. General Information

All chemicals were used as received without further purification. 1,4-Dioxane and DCE (with molecular sieves) were purchased from J&K. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Analytical TLCs were performed with 0.25 mm silica gel HSGF254. The TLC plates were visualized by ultraviolet light and treatment with anisaldehyde-H_2SO_4 or phosphomolybdic acid stain followed by gentle heating. Purification of products was accomplished by flash chromatography on silica gel (200-300 mesh) and the purified compounds show a single spot by analytical TLC. Organic solutions were concentrated using a Büchi or Eyela rotary evaporator with a desktop vacuum pump. Nuclear magnetic resonance (NMR) spectra were measured on Bruker AVANCE III 400 (^{1}H at 400 MHz, ^{13}C{^{1}H} at 101 MHz). Data for ^{1}H NMR spectrum are reported as follows: chemical shift δ (ppm) referenced to tetramethylsilane (TMS, 0.00 ppm) or $CHDCl_2$ (5.32 ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, ddd = doublet of doublet of doublets, dddq = doublet of doublet of doublet of quartets, dtdt = doublet of triplet of doublet of triplets, tq = triplet of quartets, qdd = quartet of doublet of doublets, m = multiplet), coupling constant *J* (Hz), and integration. Data for ^{13}C{^{1}H} NMR spectrum are reported as follows: chemical shift δ (ppm) referenced to $CDCl_3$ (77.16 ppm) or CD_2Cl_2 (53.84 ppm). High-resolution mass spectrometry (HRMS) data were recorded on Bruker Apex IV and Bruker Solarix XR fourtier transform ion cyclotron resonance (FTICR) mass spectrometers (electrospray ionization, ESI). Single crystal X-ray diffractometer was measured on XtaLAB PRO 007HF(Mo). All crystal compounds were obtained by adding *n*-hexane/petroleum ether to their dichloromethane/EA solutions and then stilling for several days. X-ray structures were prepared with CYLview.

Abbreviations

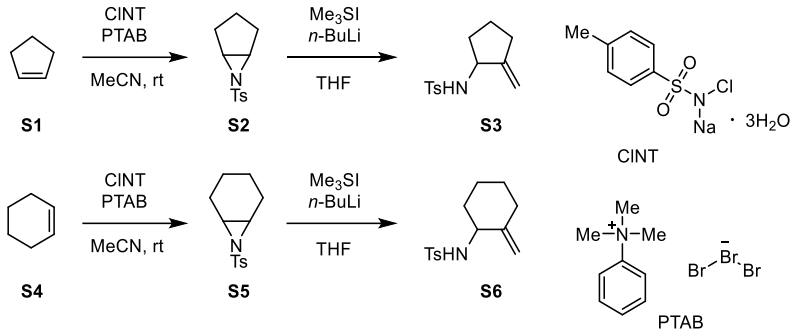
Ac	Acetyl
atm	Atmosphere
Bu	Butyl
Bn	benzyl group
ClNT	Sodium *p*-toluenesulfonchloramide trihydrate
DCM	Dichloromethane
DFT	density functional theory
DIAD	Diisopropyl azodicarboxylate
DMF	N,N-Dimethylformamide
DMP	Dess-Martin periodinane
DIBAL-H	diisobutylaluminum hydride
EA	ethyl acetate
Et	Ethyl
EI	electron impact ion source
ESI	electron spray ionization
HRMS	high-resolution mass spectroscopy
m-CPBA	m-chloro-peroxybenzoic acid
Me	methyl
m.p.	melting point
MsCl	Methanesulfonyl chloride
PE	petroleum ether
Ph	phenyl
PTAB	Phenyltrimethylammonium tribromide
rt	room temperature
THF	Tetrahydrofuran
TLC	thin layer chromatography
Ts	Tosyl
TS	transition state
VCP	vinylcyclopropane

2. Substrates preparations

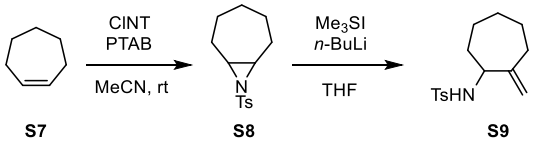
The synthesis of all substrates for the present study was not optimized.

Synthesis of Exo-Enes:

The following synthetic intermediates are known compounds and were synthesized according to the reported literature.[1,2]



The following synthetic intermediates were synthesized according to the reported literature.[1,2]



To a flask with **S7** (3.49 g, 36.29 mmol) was added MeCN (150 mL). Then ClNT (11.35 g, 40.29 mmol) and PTAB (1.3709 g, 3.65 mmol) were added. The reaction mixture was stirred vigorously at room temperature for 17 h, and then filtered (wash with EA) and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 5:1 petroleum ether/EtOAc) afforded compound **S8** (8.867 g, 92%).

To a flask with Me_3SI (13.77 g, 67.47 mmol) in THF (50 mL) was added *n*-BuLi (28 mL, 2.4 M in hexanes, 67,2 mmol) under an argon atmosphere at 0 °C. Then a solution of **S8** (2.98 g, 11.24 mmol) in THF (10 mL) was added and stirred for 18 h at 0 °C, quenched with saturated aqueous NH_4Cl solution, and extracted with EA. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 10:1 to 5:1 petroleum ether/EtOAc) afforded compound **S9** (781 mg, 25%) as a white solid.

TLC (5:1 petroleum ether/EtOAc, R_f): 0.5.

Melting Point: 55.9 – 57.4 °C

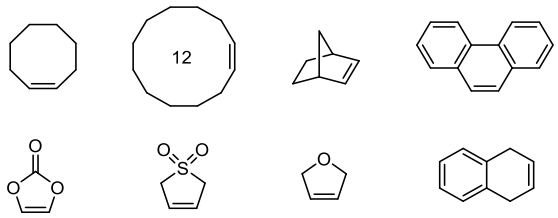
^{1}H NMR (400 MHz, CD_2Cl_2, δ): 7.70 (d, J = 7.9 Hz, 2H), 7.29 (d, J = 7.9 Hz, 2H), 4.77 – 4.73 (m, 1H), 4.72 – 4.69 (m, 1H), 3.91 – 3.79 (m, 1H), 2.40 (s, 3H), 2.12 – 1.99 (m, 2H), 1.92 – 1.80 (m, 1H), 1.66 – 1.55 (m, 1H), 1.54 – 1.35 (m, 5H), 1.33 – 1.20 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, δ): 150.6, 143.7, 138.4, 129.9, 127.5, 114.3, 58.7, 35.8, 33.0, 30.0,

29.4, 24.8, 21.6.

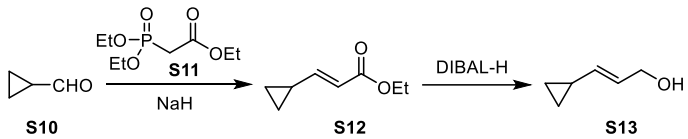
HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{22}NO_2S^+$: 280.1366, found: 280.1354.

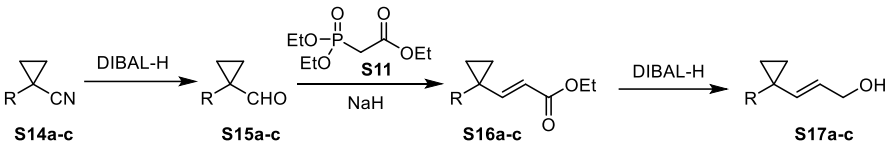
The following substrates failed to access exo-enes by the same procedure discussed above:

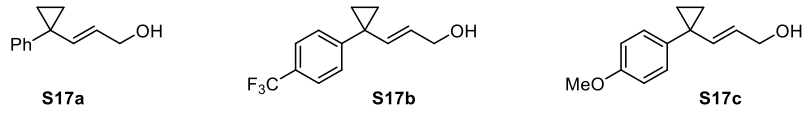


Synthesis of VCPs:

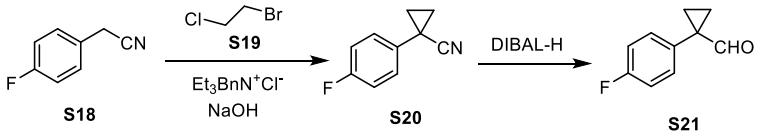
The following synthetic intermediates are known compounds and were synthesized according to the reported literature.[3,4]

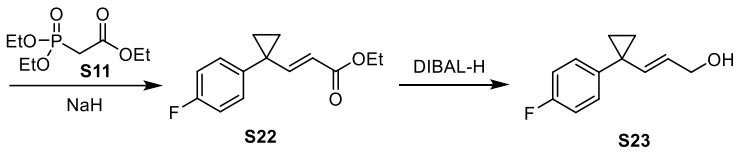






S18-**S23** are known compounds and were synthesized according to the literature procedures.[5]





To a flask with **S18** (4.92 g, 36.4 mmol), **S19** (7.92 g, 54.6 mmol) and $Et_3BnN^+Cl^-$ (169 mg, 0.728 mmol) was added a solution of NaOH (8.77 g) in water (29 mL). The mixture was stirred for 13 h at 50 °C, then poured into water after cooling to room temperature, extracted with DCM. The combined organic layer was washed with 2 M HCl, saturated aqueous Na_2CO_3 solution, and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 10:1 petroleum ether/EtOAc) afforded

compound **S20** (968.7 mg, 16%) as a colorless oil.

To a flask with **S20** (968.7 mg, 6.01 mmol) in DCM (12 mL) was added DIBAL-H (12 mL, 1 M in hexanes, 12 mmol) under an argon atmosphere at 0 °C. The mixture was stirred for 16.5 h at 0 °C to rt, quenched with saturated aqueous citric acid solution slowly and kept stirring until the upper organic phase was clarified, extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 2:1 petroleum ether/ether) afforded compound **S21** (968.3 mg, 98%) as a colorless oil.

To a flask with **S11** (1.62 g, 7.23 mmol) in THF (40 mL) was added NaH (713.3 mg, 60% dispersion in mineral oil, 17.83 mmol) slowly at 0 °C. A solution of **S21** (968.3 mg, 5.9 mmol) in THF (20 mL) was added after 30 min. The mixture was stirred for 3 h at 0 °C to rt, quenched with saturated aqueous NH_4Cl solution, and extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 10:1 petroleum ether/EtOAc) afforded compound **S22**, which was used for the next step directly.

To a flask with **S22** in DCM (18 mL) was added DIBAL-H (18 mL, 1 M in hexanes, 18 mmol) under an argon atmosphere at 0 °C. The mixture was stirred for 1 h at 0 °C to rt, quenched with saturated aqueous potassium sodium tartrate solution slowly and kept stirring until the upper organic phase was clarified, extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 5:1 petroleum ether/ EtOAc) afforded compound **S23** (722.6 mg, 64% over two steps) as a colorless oil.

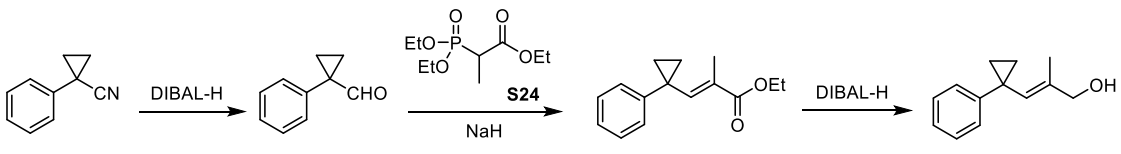
TLC (2:1 petroleum ether/EtOAc, R_f): 0.5.

^{1}H NMR (400 MHz, CD_2Cl_2, δ): 7.32 – 7.24 (m, 2H), 7.05 – 6.95 (m, 2H), 5.54 (d, J = 15.3 Hz, 1H), 5.15 (dt, J = 15.3, 5.9 Hz, 1H), 3.99 (d, J = 5.9 Hz, 2H), 1.60 – 1.53 (m, 1H), 1.08 – 1.03 (m, 2H), 1.00 – 0.95 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, δ): 161.8 (d, J = 244.4 Hz), 139.8, 139.6 (d, J = 3.0 Hz), 131.9 (d, J = 8.1 Hz), 127.8, 115.2 (d, J = 21.2 Hz), 63.5, 27.3, 15.0.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{14}FO^+$: 193.1023, found: 193.1021.

S14a and **S15a** are known compounds.[4]



S14a **S15a** **S25** E/Z = 3.6:1 **S26** E/Z = 3.6:1

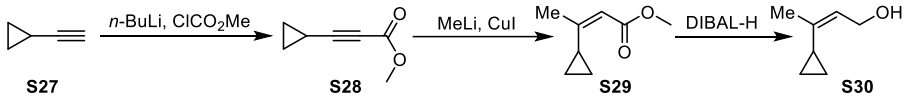
To a flask with **S14a** (3.0379 g, 21.2 mmol) in DCM (42 mL) was added DIBAL-H (42 mL, 1 M in hexanes, 42 mmol) under an argon atmosphere at 0 °C. The mixture was stirred for 17 h at 0 °C to rt, quenched with saturated aqueous citric acid solution slowly and kept stirring until the upper organic phase was clarified, extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude

product by flash column chromatography (silica gel, 2:1 petroleum ether/ether) afforded compound **S15a** as a light yellow oil.

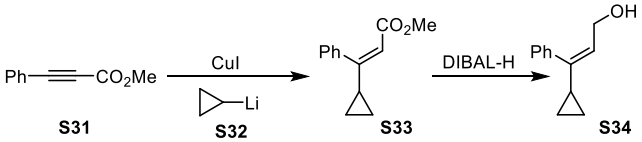
To a flask with **S24** (5.55 g, 23.3 mmol) in THF (100 mL) was added NaH (2.554 g, 60% dispersion in mineral oil, 63.85 mmol) slowly at 0 °C. A solution of **S15a** in THF (5 mL) was added after 30 min. The mixture was stirred for 2.7 h at 0 °C to rt, quenched with saturated aqueous NH_4Cl solution, and extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 20:1 petroleum ether/EtOAc) afforded compound **S25** as a colorless oil, which was used for the next step directly.

To a flask with **S25** in DCM (63 mL) was added DIBAL-H (63 mL, 1 M in hexanes, 63 mmol) under an argon atmosphere at 0 °C. The mixture was stirred for 2 h at 0 °C to rt, quenched with saturated aqueous potassium sodium tartrate solution slowly and kept stirring until the upper organic phase was clarified, extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 5:1 petroleum ether/ EtOAc) afforded compound **S26** (3.8455 g, 96% over three steps) as a colorless oil.

The following synthetic intermediates are known compounds and were synthesized according to the reported literature.[6]



S31-**S34** are known compounds.[6]

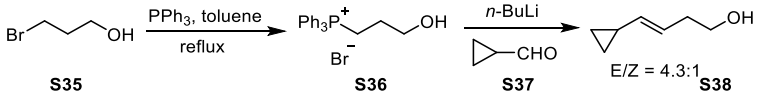


To a flask B with CuI (2.479 g, 13 mmol) was added THF (95 mL) under argon atmosphere at −78 °C. Then all newly prepared solution of **S32** in flask A was transferred to flask B. Flask B was stirred at 0 °C for another 17 min, giving cyclopropyl copper lithium solution as a brown solution.

Then flask B was cooled at −78 °C. A solution of **S31** (1.591 g, 9.93 mmol) in THF (5 mL) was added to flask B. The reaction mixture was stirred at −78 °C for 1 h, then was stirred at room temperature for 14 h, quenched with saturated aqueous NH_4Cl solution, and then extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 to 20:1 petroleum ether/EtOAc) afforded compound **S33** (936.3 mg) as a yellow oil for the next step.

To a solution of **S33** (936.3 mg) in DCM (12 mL) was added DIBAL-H (1.0 M in hexanes, 12 mL, 12 mmol) under argon atmosphere at 0 °C. The reaction mixture was stirred at 0 °C to rt for 2.5 h, quenched with saturated aqueous Rochelle salt (potassium sodium tartrate) 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. Purification of the crude product by flash column chromatography (silica gel, 10:1 to 4:1 petroleum ether/EtOAc) afforded compound **S34** (780 mg, 45% for 2 steps).



To a flask with **S35** (3.4879 g, 25.1 mmol) in toluene (10 mL) was added PPh_3 (7.2172 g, 27.52 mmol), then this mixture was refluxed for 13.5 h. After cooling to room temperature, the mixture was filtered (wash with cold ether) to afford compound **S36** (9.3211 g, 92%) as a white solid.

To a suspension of **S36** (9.3211 g) in THF (30 mL) was added *n*-BuLi (2.4 M in hexanes, 18 mL, 43.2 mmol) under argon atmosphere at 0 °C. A solution of **S37** (1.359 g, 19.39 mmol) in THF (5 mL) was added after 30 min. The reaction mixture was stirred at 0 °C to rt for 2 h, quenched with saturated aqueous NH_4Cl 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. Purification of the crude product by flash column chromatography (silica gel, 10:1 to 5:1 petroleum ether/EtOAc) afforded compound **S38** (841.8 mg, 39%) as a colorless oil.

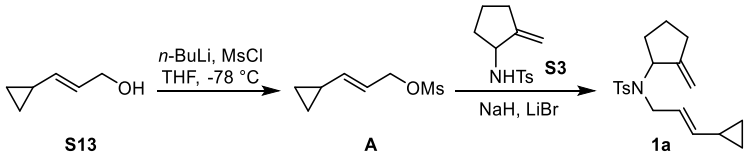
TLC (5:1 petroleum ether/EtOAc, R_f): 0.3.

^{1}H NMR for main isomer (400 MHz, $CDCl_3$, δ): 5.47 (dt, *J* = 15.3, 7.1 Hz, 1H), 5.09 (dd, *J* = 15.3, 8.7 Hz, 1H), 3.66 – 3.59 (m, 2H), 2.26 (dt, *J* = 6.5 Hz, 6.5 Hz, 2H), 1.48 (s, 1H), 1.43 – 1.33 (m, 1H), 0.72 – 0.64 (m, 2H), 0.37 – 0.32 (m, 2H).

^{13}C{^{1}H} NMR for main isomer (101 MHz, $CDCl_3$, δ): 137.8, 123.6, 62.2, 36.0, 13.8, 6.7.

Synthesis of Exo-Ene-VCPs:

We here used the Mitsunobu reaction of nucleophile and VCP-type alcohols to obtain the final substrates. This reaction could give the SN2 and SN2' products and in most cases, two products can be separated. Therefore, we just isolated the desired substrates for the [5+2+1] reaction and tested their reactions.



To a solution of **S13** (775.8 mg, 7.91 mmol) in THF (79 mL) was added *n*-BuLi (1.6 M in hexanes, 6.92 mL, 11.1 mmol) under argon atmosphere at -78 °C. Then MsCl (0.8 mL, d = 1.48 g/mL, 10.3 mmol) was added after 5 min. The mixture was stirred at -78 °C for 30 min to afford intermediate **A**, which was used for the next step directly.

To a flask with NaH (569.3 mg, 60% dispersion in mineral oil, 23.7 mmol) and LiBr (4.12 g, 47.4 mmol) in DMF (59 mL) was added a solution of **S3** (2.9815 g, 11.86 mmol) in DMF (59 mL) under argon atmosphere at 0 °C. Then the solution of **A** was added after 30 min and stirred at 0 °C for 12 h, quenched with saturated aqueous NH_4Cl solution, and then extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by

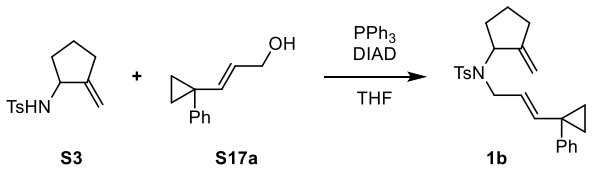
rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 5:1 petroleum ether/EtOAc) afforded compound **1a** (2.0157 g, 77% over two steps) as a colorless oil.

TLC (5:1 petroleum ether/EtOAc, R_f): 0.7.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.72 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 5.40 (dt, J = 15.3, 6.6 Hz, 1H), 5.06 (dd, J = 15.3, 8.7 Hz, 1H), 5.00 – 4.96 (m, 1H), 4.72 – 4.67 (m, 2H), 3.86 – 3.77 (m, 1H), 3.65 – 3.56 (m, 1H), 2.42 (s, 3H), 2.28 – 2.20 (m, 1H), 1.86 – 1.79 (m, 1H), 1.74 – 1.66 (m, 1H), 1.64 – 1.57 (m, 1H), 1.49 – 1.41 (m, 1H), 1.34 – 1.22 (m, 2H), 0.70 – 0.62 (m, 2H), 0.33 – 0.27 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 148.5, 142.9, 138.8, 137.5, 129.5, 127.4, 124.9, 108.5, 62.2, 46.4, 31.5, 30.7, 22.6, 21.6, 13.3, 6.5.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{26}O_2NS^+$: 332.1679, found: 332.1694.



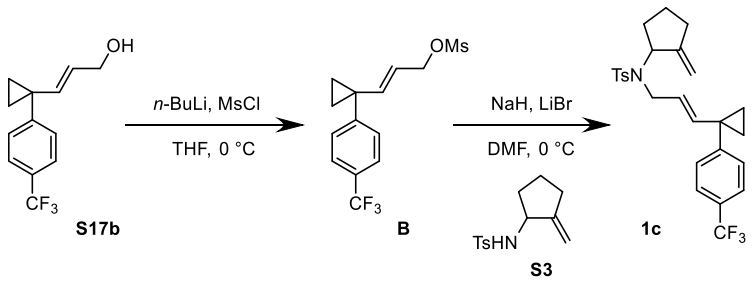
To a solution of **S3** (1.0101 g, 4.02 mmol), **S17a** (830.6 mg, 4.77 mmol) and PPh_3 (1.568 g, 5.97 mmol) in THF (30 mL) was added DIAD (1.2239 g, 6.05 mmol) dropwise under argon atmosphere at 0 °C. The mixture was stirred at 0 °C to rt for 21.5 h, quenched with water, and then extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 to 10:1 petroleum ether/EtOAc) afforded compound **1b** (825.0 mg, 50%) as a colorless oil.

TLC (10:1 petroleum ether/EtOAc, R_f): 0.4.

^{1}H NMR (400 MHz, CD_2Cl_2, δ): 7.64 (d, J = 8.0 Hz, 2H), 7.30 – 7.23 (m, 4H), 7.22 – 7.15 (m, 3H), 5.41 (d, J = 15.3 Hz, 1H), 4.97 – 4.93 (m, 1H), 4.91 (dt, J = 15.3, 6.7 Hz, 1H), 4.68 – 4.64 (m, 1H), 4.64 – 4.59 (m, 1H), 3.78 (ddd, J = 15.7, 6.7 Hz, 1H), 3.64 (ddd, J = 15.7, 6.7 Hz, 1H), 2.42 (s, 3H), 2.36 – 2.27 (m, 1H), 2.25 – 2.14 (m, 1H), 1.73 – 1.61 (m, 2H), 1.57 – 1.35 (m, 2H), 1.04 – 0.99 (m, 2H), 0.91 – 0.86 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, δ): 149.1, 143.6, 143.4, 140.4, 139.1, 129.92, 129.90, 128.5, 127.4, 126.7, 125.8, 108.4, 62.3, 46.5, 31.7, 30.6, 27.9, 22.8, 21.6, 14.73, 14.70.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{30}O_2NS^+$: 408.1992, found: 408.1976.



To a solution of **S17b** (503.2 mg, 2.078 mmol) in THF (20 mL) was added *n*-BuLi (2.4 M in hexanes, 1.3 mL, 3.118 mmol) under argon atmosphere at 0 °C. Then MsCl (333.1 mg, 2.909 mmol) was added after 15 min. The mixture was stirred at 0 °C for 30 min to afford intermediate **B**, which was used for the next step directly.

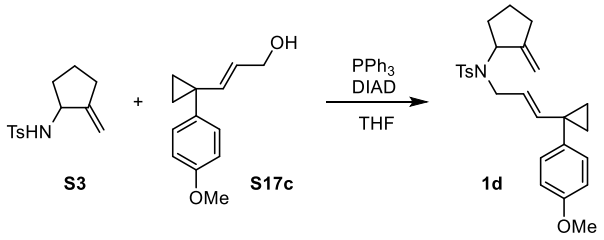
To a flask with NaH (277.2 mg, 60% dispersion in mineral oil, 6.928 mmol) and LiBr (902.1 mg, 10.392 mmol) was added a solution of **S3** (435.2 mg, 1.732 mmol) in DMF (20 mL) under argon atmosphere at 0 °C. Then the solution of **B** was added after 30 min and stirred at 0 °C for 6 h, quenched with saturated aqueous NH_4Cl solution, and then extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 petroleum ether/EtOAc) afforded compound **1c** (403.2 mg, 49%) as a colorless oil.

TLC (5:1 petroleum ether/EtOAc, R_f): 0.7.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.67 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.22 (m, 4H), 5.45 (d, *J* = 15.4 Hz, 1H), 4.97 (dt, *J* = 15.4 ,6.4 Hz, 1H), 4.95– 4.92 (m, 1H), 4.72 – 4.63 (m, 2H), 3.81 (dd, *J* = 15.9, 6.4 Hz, 1H), 3.66 (dd, *J* = 15.9, 6.4 Hz, 1H), 2.42 (s, 3H), 2.37 – 2.29 (m, 1H), 2.23 – 2.13 (m, 1H), 1.80 – 1.72 (m, 1H), 1.70 – 1.64 (m, 1H), 1.51 – 1.41 (m, 2H), 1.07 – 1.02 (m, 2H), 0.99 – 0.93 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 148.3, 147.5, 143.0, 138.9, 138.7, 129.8, 129.6, 128.7 (q, *J* = 32.4 Hz), 127.2, 126.4, 125.2 (q, *J* = 3.7 Hz), 124.4 (q, *J* = 272.8 Hz), 108.7, 62.0, 46.1, 31.5, 30.6, 27.5, 22.6, 21.6, 14.89, 14.87.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{29}O_2NF_3S^+$: 476.1866, found: 476.1860.



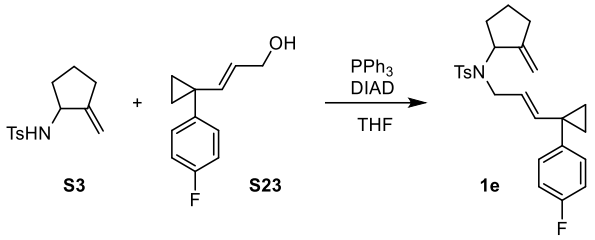
To a solution of **S3** (513.4 mg, 2.043 mmol), **S17c** (500.9 mg, 2.452 mmol) and PPh_3 (1.0718 g, 4.086 mmol) in THF (20 mL) was added DIAD (0.81 mL, 4.086 mmol) dropwise under argon atmosphere at 0 °C. The mixture was stirred at 0 °C to rt for 4 h, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 petroleum ether/EtOAc) afforded compound **1d** (428.1 mg, 48%) as a colorless oil.

TLC (5:1 petroleum ether/EtOAc, R_f): 0.6.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.66 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 5.35 (d, *J* = 15.3 Hz, 1H), 4.95 (s, 1H), 4.91 (dt, *J* = 15.3, 6,6 Hz, 1H), 4.71 – 4.60 (m, 2H), 3.85 – 3.76 (m, 1H), 3.80 (s, 3H), 3.64 (dd, *J* = 15.6, 6.6 Hz, 1H), 2.42 (s, 3H), 2.32 (dd, *J* = 16.6, 7.2 Hz, 1H), 2.25 – 2.13 (m, 1H), 1.79 – 1.62 (m, 2H), 1.56 – 1.36 (m, 2H), 1.02 – 0.95 (m, 2H), 0.88 – 0.79 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 158.2, 148.4, 142.8, 140.9, 138.8, 135.2, 130.8, 129.6, 127.2, 125.1, 113.6, 108.6, 61.9, 55.4, 46.2, 31.5, 30.6, 27.0, 22.6, 21.6, 14.6, 14.5.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{32}O_3NS^+$: 438.2097, found: 438.2080.



S3 S23 1e

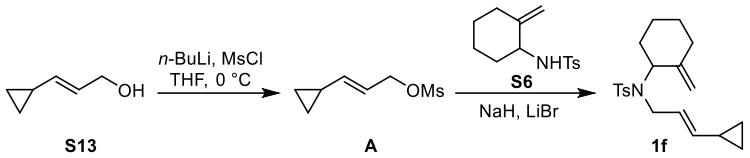
To a solution of **S3** (1.039 g, 4.13 mmol), **S23** (668 mg, 3.47 mmol) and PPh_3 (1.6987 g, 6.48 mmol) in THF (30 mL) was added DIAD (1.3558 g, 6.70 mmol) dropwise under argon atmosphere at 0 °C. The mixture was stirred at 0 °C to rt for 31 h, quenched with water, and then extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 to 20:1 petroleum ether/EtOAc) afforded compound **1e** (628.2 mg, 38%) as a colorless oil.

TLC (10:1 petroleum ether/EtOAc, R_f): 0.6.

^{1}H NMR (400 MHz, CD_2Cl_2, δ): 7.59 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.14 – 7.06 (m, 2H), 6.96 – 6.87 (m, 2H), 5.29 – 5.28 (m, 1H), 4.94 – 4.88 (m, 1H), 4.80 (dt, J = 15.3, 6.6 Hz, 1H), 4.66 – 4.55 (m, 2H), 3.74 (dd, J = 16.0 Hz, 8.0 Hz, 1H), 3.60 (dd, J = 16.0 Hz, 8.0 Hz, 1H), 2.39 (s, 3H), 2.33 – 2.24 (m, 1H), 2.21 – 2.11 (m, 1H), 1.69 – 1.57 (m, 2H), 1.49 – 1.33 (m, 2H), 0.99 – 0.92 (m, 2H), 0.87 – 0.81 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, δ): 161.8 (d, J = 244.8 Hz), 149.2, 143.4, 140.4, 139.3 (d, J = 3.3 Hz), 139.1, 131.7 (d, J = 8.1 Hz), 129.9, 127.4, 125.9, 115.1 (d, J = 21.3 Hz), 108.4, 62.3, 46.4, 31.7, 30.6, 27.3, 22.8, 21.6, 14.72, 14.68.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{29}O_2NFS^+$: 426.1898, found: 426.1886.



S13 A 1f

To a solution of **S13** (257.1 mg, 2.62 mmol) in THF (30 mL) was added *n*-BuLi (1.6 M in hexanes, 2.3 mL, 3.67 mmol) under argon atmosphere at 0 °C. Then MsCl (0.26 mL, 3.41 mmol) was added after 10 min. The mixture was stirred at 0 °C for 30 min to afford intermediate **A**, which was used for the next step directly.

To a flask with NaH (314.3 mg, 60% dispersion in mineral oil, 7.86 mmol) and LiBr (1.3645 g, 15.72 mmol) was added a solution of **S6** (1.0428 g, 3.93 mmol) in DMF (30 mL) under argon atmosphere at 0 °C. Then the solution of **A** was added after 30 min and stirred at 0 °C for 5 h, quenched with saturated aqueous NH_4Cl solution, and then extracted with EA. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 10:1 petroleum ether/EtOAc) afforded compound **1f** (508.6 mg, 56% over two steps) as a colorless oil.

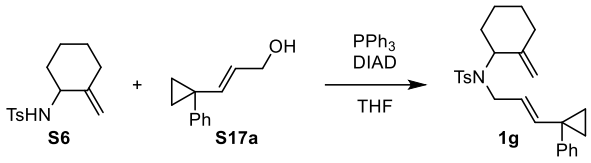
TLC (10:1 petroleum ether/EtOAc, R_f): 0.6.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.69 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.2 Hz, 2H), 5.37 (dt, J = 15.3, 6.5 Hz, 1H), 5.10 (dd, J = 15.3, 8.7 Hz, 1H), 4.71 (d, J = 1.8 Hz, 1H), 4.52 (d, J = 1.8 Hz, 1H), 4.43 – 4.36

(m, 1H), 4.01 (dd, *J* = 16.1, 7.1 Hz, 1H), 3.65 (ddd, *J* = 16.1, 5.9, 1.4 Hz, 1H), 2.41 – 2.35 (m, 1H), 2.40 (s, 3H), 2.10 – 1.99 (m, 1H), 1.87 – 1.79 (m, 1H), 1.79 – 1.66 (m, 2H), 1.55 – 1.35 (m, 2H), 1.30 – 1.11 (m, 2H), 0.69 – 0.61 (m, 2H), 0.34 – 0.25 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, *δ*): 145.8, 142.7, 139.1, 137.6, 129.3, 127.4, 124.9, 108.0, 61.6, 47.0, 35.4, 33.1, 26.9, 26.2, 21.6, 13.3, 6.5.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{28}O_2NS^+$: 346.1835, found: 346.1826.



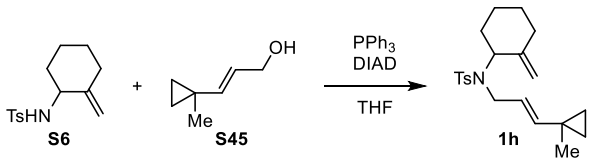
To a solution of **S6** (553 mg, 2.08 mmol), **S17a** (431.5 mg, 2.48 mmol) and PPh_3 (1.206 g, 4.60 mmol) in THF (25 mL) was added DIAD (921.6 mg, 4.56 mmol) dropwise under argon atmosphere at 0 °C. The mixture was stirred at 0 °C to rt for 18 h, quenched with water, and then extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 petroleum ether/EtOAc) afforded compound **1g** (387.9 mg, 44%) as a colorless oil.

TLC (10:1 petroleum ether/EtOAc, R_f): 0.4.

^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.64 (d, *J* = 8.2 Hz, 2H), 7.28 – 7.11 (m, 7H), 5.47 (d, *J* = 15.3 Hz, 1H), 4.91 (dt, *J* = 15.2, 6.6 Hz, 1H), 4.72 (s, 1H), 4.55 (s, 1H), 4.39 – 4.29 (m, 1H), 4.03 (dd, *J* = 16.1, 7.1 Hz, 1H), 3.67 (dd, *J* = 16.0, 6.0 Hz, 1H), 2.42 (s, 3H), 2.40 – 2.34 (m, 1H), 2.09 – 1.97 (m, 1H), 1.82 – 1.74 (m, 1H), 1.74 – 1.65 (m, 1H), 1.65 – 1.56 (m, 1H), 1.47 – 1.33 (m, 2H), 1.20 – 1.10 (m, 1H), 1.05 – 0.98 (m, 2H), 0.91 – 0.84 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, *δ*): 145.9, 143.3, 142.7, 140.4, 139.3, 129.6, 129.4, 128.2, 127.3, 126.4, 125.4, 108.1, 61.6, 46.9, 35.4, 32.9, 27.6, 26.9, 26.3, 21.6, 14.70, 14.67.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{32}O_2NS^+$: 422.2148, found: 422.2150.



S45 is known compound and was synthesized according to the literature procedures.[4]

To a solution of **S6** (2.387 mg, 8.99 mmol), **S45** (836 mg, 7.45 mmol) and PPh_3 (3.941 g, 15.03 mmol) in THF (37.5 mL) was added DIAD (3.05 g, 15.08 mmol) dropwise under argon atmosphere at 0 °C. The mixture was stirred at 0 °C to rt for 8 h, concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 to 25:1 petroleum ether/EtOAc) afforded compound **1h** and inseparable by product (524.7 mg, 20%) as a light yellow oil. The ratio of **1h** and by product, which was proposed as the competing Mitsunobu reaction is 5:1, which is determined by ^{1}H NMR.

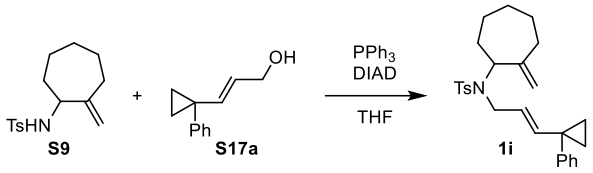
TLC (5:1 petroleum ether/EtOAc, R_f): 0.7.

^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.69 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 5.17 – 5.13 (m, 2H),

4.74 (d, *J* = 1.9 Hz, 1H), 4.58 (d, *J* = 1.8 Hz, 1H), 4.47 – 4.38 (m, 1H), 4.07 – 3.99 (m, 1H), 3.72 – 3.64 (m, 1H), 2.39 (s, 3H), 2.38 – 2.37 (m, 1H), 2.11 – 2.00 (m, 1H), 1.87 – 1.80 (m, 1H), 1.79 – 1.68 (m, 2H), 1.56 – 1.37 (m, 2H), 1.24 – 1.11 (m, 1H), 1.00 (s, 3H), 0.54 – 0.46 (m, 4H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, *δ*): 145.9, 142.6, 141.5, 139.3, 129.3, 127.4, 122.8, 108.0, 61.6, 47.2, 35.4, 33.0, 26.8, 26.2, 21.5, 21.2, 16.9, 14.9, 14.8.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{30}O_2NS^+$: 360.1992, found: 360.1986.



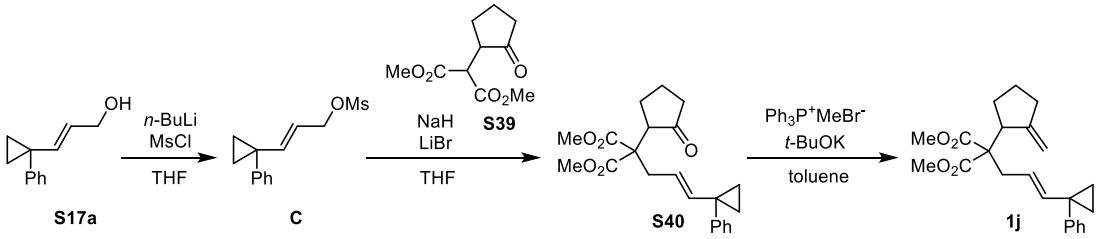
To a solution of **S9** (998.5 mg, 3.57 mmol), **S17a** (755.5 mg, 4.45 mmol) and PPh_3 (3.7495 g, 14.29 mmol) in THF (30 mL) was added DIAD (2.884 g, 14.26 mmol) dropwise under argon atmosphere at 0 °C. The mixture was stirred at 0 °C to rt for 23 h, quenched with water, and then extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 petroleum ether/EtOAc) afforded compound **1i** (435.4 mg, 28%) as a colorless oil.

TLC (10:1 petroleum ether/EtOAc, R_f): 0.4.

^{1}H NMR (400 MHz, CD_2Cl_2, *δ*): 7.61 (d, *J* = 8.3 Hz, 2H), 7.29 – 7.23 (m, 4H), 7.22 – 7.17 (m, 3H), 5.43 (d, *J* = 15.4 Hz, 1H), 4.93 (dt, *J* = 15.3, 6.6 Hz, 1H), 4.92– 4.88 (m, 1H), 4.63 (s, 1H), 4.44 (dd, *J* = 10.1, 5.9 Hz, 1H), 3.79 (ddd, *J* = 15.8, 6.4, 1.3 Hz, 1H), 3.66 (ddd, *J* = 15.8, 7.1, 1.3 Hz, 1H), 2.41 (s, 3H), 2.27 (dd, *J* = 13.7, 7.2 Hz, 1H), 2.12 – 2.03 (m, 1H), 1.86 – 1.76 (m, 1H), 1.77 – 1.68 (m, 2H), 1.68 – 1.60 (m, 2H), 1.25 – 1.15 (m, 2H), 1.15 – 1.06 (m, 1H), 1.06 – 1.01 (m, 2H), 0.93 – 0.89 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2, *δ*): 150.2, 143.6, 143.3, 140.2, 139.3, 129.9, 129.8, 128.5, 127.4, 126.7, 126.1, 116.4, 62.5, 46.9, 35.9, 33.0, 31.3, 31.1, 27.9, 27.2, 21.6, 14.69, 14.68.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{34}O_2NS^+$: 436.2305, found: 436.2294.



Compound **S39** is known and synthesized according to the reported literature.[7]

To a solution of **S17a** (2.183 g, 12.5 mmol) in THF (25 mL) was added *n*-BuLi (2.4 M in hexanes, 6.25 mL, 15 mmol) under argon atmosphere at -78 °C. Then MsCl (1.711 g, 12.9 mmol) was added after 10 min. The mixture was stirred at -78 °C for 30 min to afford intermediate **C**, which was used for the next step directly.

To a flask with NaH (196 mg, 60% dispersion in mineral oil, 4.9 mmol) and LiBr (1.404 g, 16.2 mmol) was added THF (15 mL) under argon atmosphere at 0 °C, then a solution of **S39** (861 mg, 4.02 mmol)

in THF (5 mL) was added. The mixture was stirred for 1 h at 0 °C and the solution of **C** (ca. 5.6 mmol) was added, stirred at 0 °C to rt for 23.5 h, quenched with saturated aqueous NH_4Cl solution, and then extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 20:1 to 10:1 to 5:1 petroleum ether/EtOAc) afforded a mixture of **S40** and **S39** (ca. 1:1.2, 926.2 mg) as a colorless oil.

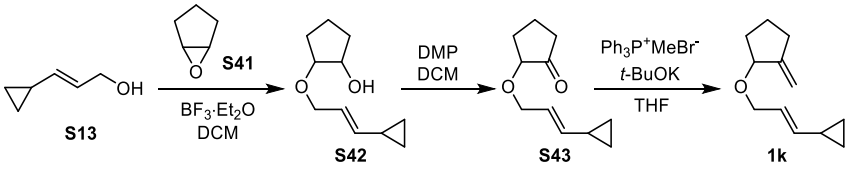
To a flask with *t*-BuOK (1.794 g, 14.7 mmol) and $Ph_3P^+MeBr^-$ (5.360 g, 15.0 mmol) was added toluene (75 mL) under an argon atmosphere at room temperature. The reaction mixture was refluxed at 130 °C for 1 h to get the yellow solution. Then the solution of **S40** and **S39** (ca. 1:1.2, 926.2 mg) in toluene (15 mL) was added. The reaction mixture was refluxed at 130 °C for 4 h, quenched with water, and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 petroleum ether/EtOAc) afforded compound **1j** (131.5 mg, 9% over two steps) as a light yellow oil.

TLC (10:1 petroleum ether/EtOAc, R_f): 0.7.

^{1}H NMR (400 MHz, CD_2Cl_2, δ): 7.26 – 7.18 (m, 4H), 7.17 – 7.12 (m, 1H), 5.46 (d, *J* = 15.2 Hz, 1H), 5.07 (dt, *J* = 15.2, 7.4 Hz, 1H), 4.90 (s, 1H), 4.75 (s, 1H), 3.57 (s, 6H), 3.07 – 2.98 (m, 1H), 2.62 – 2.50 (m, 2H), 2.21 (dd, *J* = 15.6, 7.2 Hz, 1H), 2.16 – 2.04 (m, 1H), 1.96 – 1.87 (m, 1H), 1.67 – 1.55 (m, 2H), 1.41 – 1.30 (m, 1H), 0.99 – 0.96 (m, 2H), 0.90 – 0.86 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, δ): 171.4, 171.3, 152.6, 144.3, 140.7, 129.6, 128.5, 126.5, 123.9, 108.3, 62.7, 52.10, 52.08, 47.1, 38.1, 36.1, 30.1, 28.0, 24.8, 15.0.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{29}O_4^+$: 369.2060, found: 369.2060.



S42 and **S43** were synthesized according to the reported literature.[8]

To a flask with **S13** (1.132 g, 10.1 mmol) in DCM (10 mL) was added BF_3•Et_2O (78 mg, 0.55 mmol) under argon atmosphere at 0 °C, then a solution of **S41** (425 mg, 5.05 mmol) in DCM (5 mL) was added by syringe pump in 1 h. Then the mixture was stirred for 2 h at 0 °C to rt, quenched with Et_3N (172 mg, 1.7 mmol), concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 20:1 to 5:1 petroleum ether/EtOAc) afforded compound **S42** (575.2 mg, 62%) as a colorless oil.

To a flask with **S42** (575.2 mg, 3.16 mmol) in DCM (32 mL) was added DMP (2.686 g, 6.33 mmol) at rt. Then the mixture was stirred for 11.5 h at rt, quenched with saturated aqueous $Na_2S_2O_3$ solution, diluted with saturated $NaHCO_3$ solution and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 20:1 petroleum ether/EtOAc) afforded compound **S43** (252.1 mg, 44%) as a colorless oil.

To a flask with *t*-BuOK (842 mg, 6.89 mmol) and $Ph_3P^+MeBr^-$ (2.499 g, 7.0 mmol) was added THF

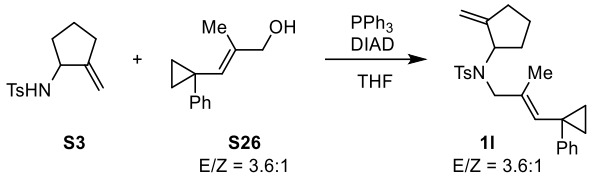
(15 mL) under an argon atmosphere at room temperature. The reaction mixture was stirred at rt for 1 h to get the yellow solution. Then the solution of **S43** (252.1 mg, 1.4 mmol) in THF (5 mL) was added dropwise. The reaction mixture was stirred at 50 °C for 17 h, quenched with water, and extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 petroleum ether/EtOAc) afforded compound **1k** (102.2 mg, 41%) as a light yellow oil.

TLC (10:1 petroleum ether/EtOAc, R_f): 0.7.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.65 (dt, J = 15.3, 6.4 Hz, 1H), 5.22 (dd, J = 15.3, 8.9 Hz, 1H), 5.08 (s, 1H), 5.03 (s, 1H), 4.10 – 4.04 (m, 1H), 3.98 – 3.86 (m, 2H), 2.46 – 2.36 (m, 1H), 2.29 – 2.18 (m, 1H), 1.90 – 1.78 (m, 2H), 1.76 – 1.66 (m, 1H), 1.65 – 1.55 (m, 1H), 1.46 – 1.35 (m, 1H), 0.73 – 0.66 (m, 2H), 0.40 – 0.35 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 151.8, 138.1, 124.5, 109.2, 81.4, 69.1, 32.8, 30.3, 22.4, 13.6, 6.8.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{19}O^+$: 179.1430, found: 179.1431.



S3 **S26** E/Z = 3.6:1 **1l** E/Z = 3.6:1

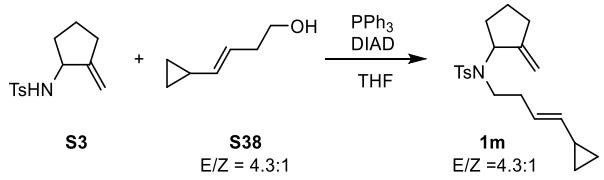
To a solution of **S3** (766.1 mg, 3.05 mmol), **S26** (686.1 mg, 3.64 mmol) and PPh_3 (1.600 g, 6.1 mmol) in THF (30 mL) was added DIAD (1.257 g, 6.22 mmol) dropwise under argon atmosphere at 0 °C. The mixture was stirred at 0 °C to rt for 24 h, quenched with water, and then extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 30:1 petroleum ether/EtOAc) afforded compound **1l** (399.7 mg, 31%) as a colorless oil, E/Z = 3.6:1.

TLC (10:1 petroleum ether/EtOAc, R_f): 0.5.

^{1}H NMR for main isomer (400 MHz, CD_2Cl_2, δ): 7.68 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.26 – 7.18 (m, 3H), 7.17 – 7.13 (m, 2H), 5.61 (s, 1H), 4.93 – 4.89 (m, 1H), 4.71 – 4.63 (m, 1H), 4.48 – 4.44 (m, 1H), 3.83 (d, J = 15.4 Hz, 1H), 3.66 (d, J = 15.4 Hz, 1H), 2.41 (s, 3H), 2.31 – 2.22 (m, 1H), 2.19 – 2.09 (m, 1H), 1.79 – 1.71 (m, 1H), 1.63 (s, 3H), 1.59 – 1.46 (m, 2H), 1.45 – 1.31 (m, 1H), 1.10 – 1.05 (m, 2H), 0.91 – 0.86 (m, 2H).

^{13}C{^{1}H} NMR for main isomer (101 MHz, CD_2Cl_2, δ): 148.6, 145.6, 143.6, 138.7, 137.6, 131.0, 130.0, 128.5, 127.4, 126.8, 125.7, 108.7, 62.2, 51.7, 32.3, 31.0, 23.5, 23.1, 21.6, 17.7, 17.6, 15.9.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{32}O_2NS^+$: 422.2148, found: 422.2147.



S3 **S38** E/Z = 4.3:1 **1m** E/Z =4.3:1

To a solution of **S3** (1.3715 g, 5.46 mmol), **S38** (741.5 mg, 6.6 mmol) and PPh_3 (3.1718 g, 12.09 mmol) in THF (50 mL) was added DIAD (2.4853 g, 12.29 mmol) dropwise under argon atmosphere at 0 °C. The mixture was stirred at 0 °C to rt for 20 h, quenched with water, and then extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 petroleum ether/EtOAc) afforded compound **1m** (1.1508 g, 61%) as a white solid, E/Z = 4.3:1.

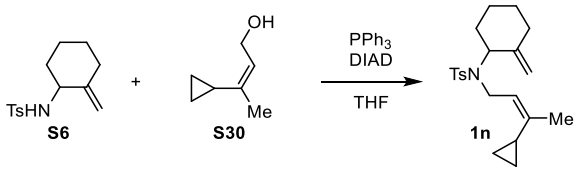
Melting Point: 57.5 – 59.3 °C

TLC (10:1 petroleum ether/EtOAc, R_f): 0.6.

^{1}H NMR for main isomer (400 MHz, $CDCl_3$, δ): 7.74 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 5.37 (dt, *J* = 15.3, 7.0 Hz, 1H), 5.00 – 4.93 (m, 2H), 4.70 – 4.67 (m, 1H), 4.66 – 4.57 (m, 1H), 3.12 – 2.96 (m, 2H), 2.41 (s, 3H), 2.40 – 2.20 (m, 4H), 1.84 – 1.75 (m, 1H), 1.75 – 1.66 (m, 1H), 1.53 – 1.43 (m, 2H), 1.35 – 1.27 (m, 1H), 0.68 – 0.61 (m, 2H), 0.34 – 0.27 (m, 2H).

^{13}C{^{1}H} NMR for main isomer (101 MHz, $CDCl_3$, δ): 148.4, 143.0, 138.3, 136.4, 129.7, 127.2, 124.2, 108.6, 62.3, 45.1, 34.6, 31.3, 30.5, 22.5, 21.6, 13.7, 6.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{28}O_2NS^+$: 346.1835, found: 346.1822.



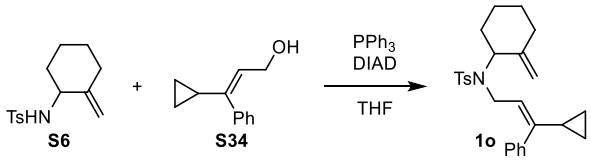
To a solution of **S6** (1.3273 g, 5 mmol), **S30** (628.9 mg, 5.61 mmol) and PPh_3 (2.6215 g, 9.99 mmol) in THF (50 mL) was added DIAD (2.0179 g, 9.98 mmol) dropwise under argon atmosphere at 0 °C. The mixture was stirred at 0 °C to 50 °C for 24 h, quenched with water, and then extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 50:1 petroleum ether/EtOAc) afforded compound **1n** (825.6 mg, 46%) as a light yellow oil.

TLC (10:1 petroleum ether/EtOAc, R_f): 0.6.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.70 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 5.13 (t, *J* = 6.6 Hz, 1H), 4.72 (s, 1H), 4.55 (s, 1H), 4.44 (dd, *J* = 12.3, 4.2 Hz, 1H), 4.26 (dd, *J* = 16.8, 6.6 Hz, 1H), 3.83 (dd, *J* = 16.8, 6.6 Hz, 1H), 2.40 (s, 3H), 2.11 – 2.00 (m, 1H), 1.87 – 1.76 (m, 2H), 1.76 – 1.68 (m, 1H), 1.66 – 1.60 (m, 1H), 1.60 – 1.57 (m, 1H), 1.55 – 1.46 (m, 1H), 1.46 – 1.39 (m, 1H), 1.31 (s, 3H), 1.24 – 1.11 (m, 1H), 0.67 – 0.60 (m, 2H), 0.59 – 0.53 (m, 1H), 0.52 – 0.44 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 146.0, 142.7, 139.3, 136.7, 129.3, 127.4, 124.0, 108.0, 61.6, 42.7, 35.5, 32.9, 27.0, 26.3, 21.6, 18.8, 12.3, 4.3, 4.2.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{30}O_2NS^+$: 360.1992, found: 360.1991.



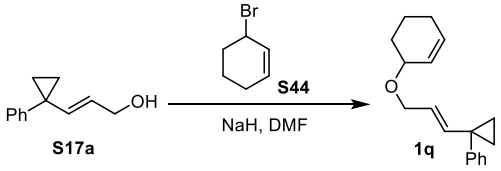
To a solution of **S6** (1.3063 g, 4.92 mmol), **S34** (780 mg, 4.48 mmol) and PPh_3 (2.3508 g, 8.96 mmol) in THF (45 mL) was added DIAD (1.8119 g, 8.96 mmol) dropwise under argon atmosphere at 0 °C. The mixture was stirred at 0 °C to rt for 21 h and at 50 °C for 12 h, quenched with water, and then extracted with ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 20:1 petroleum ether/EtOAc) afforded compound **1o** (660.1 mg, 35%) as a colorless oil.

TLC (10:1 petroleum ether/EtOAc, R_f): 0.5.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.61 (d, J = 8.2 Hz, 2H), 7.35 – 7.29 (m, 2H), 7.30 – 7.22 (m, 1H), 7.20 (d, J = 8.2 Hz, 2H), 7.16 – 7.10 (m, 2H), 5.40 (t, J = 6.2 Hz, 1H), 4.57 (d, J = 1.8 Hz, 1H), 4.41 – 4.32 (m, 1H), 4.28 (d, J = 1.8 Hz, 1H), 3.86 (dd, J = 16.9, 6.2 Hz, 1H), 3.56 (dd, J = 16.9, 6.2 Hz, 1H), 2.38 (s, 3H), 2.32 – 2.24 (m, 1H), 2.02 – 1.90 (m, 1H), 1.81 – 1.71 (m, 1H), 1.73 – 1.61 (m, 2H), 1.55 – 1.44 (m, 1H), 1.41 – 1.21 (m, 2H), 1.09 – 0.93 (m, 1H), 0.66 – 0.56 (m, 2H), 0.39 – 0.30 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 145.6, 143.0, 142.8, 139.3, 138.7, 129.4, 128.6, 128.1, 127.24, 127.16, 123.3, 108.0, 61.6, 43.7, 35.4, 32.8, 26.8, 26.1, 21.5, 18.3, 5.5, 5.4.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{32}O_2NS^+$: 422.2148, found: 422.2142.



To a flask with NaH (1.3848 mg, 60% dispersion in mineral oil, 34.6 mmol) in DMF (100 mL) was added a solution of **S17a** (2.0102 g, 11.5 mmol) in DMF (175 mL) at room temperature. **S44** (2.68 mL, d= 1.38, 23.0 mmol) was added after 15 min. The reaction mixture was stirred at 0 °C for 4 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. Purification of the crude product by flash column chromatography (silica gel, 50:1 petroleum ether/EtOAc) afforded compound **1q** (1.5324 g, 52%) as a colorless oil.

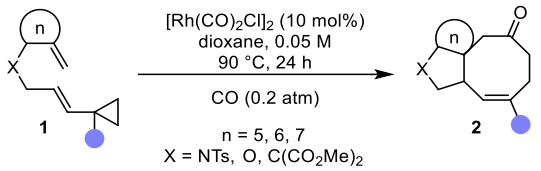
TLC (50:1 petroleum ether/EtOAc, R_f): 0.5.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.24 – 7.18 (m, 4H), 7.17 – 7.09 (m, 1H), 5.79 – 5.72 (m, 1H), 5.69 – 5.62 (m, 1H), 5.53 (d, J = 15.4 Hz, 1H), 5.10 (dt, J = 15.4, 6.1 Hz, 1H), 3.94 – 3.81 (m, 2H), 3.80 – 3.72 (m, 1H), 2.01 – 1.91 (m, 1H), 1.90 – 1.80 (m, 1H), 1.77 – 1.61 (m, 2H), 1.60 – 1.52 (m, 1H), 1.51 – 1.39 (m, 1H), 1.04 – 0.98 (m, 2H), 0.94 – 0.88 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 143.5, 140.5, 130.9, 130.0, 128.3, 128.1, 126.5, 125.3, 72.3, 68.8, 28.5, 27.8, 25.3, 19.4, 14.9.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{23}O^+$: 255.1743, found: 255.1744.

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

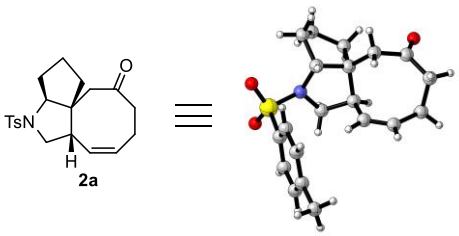


To a flask with **1** and $[Rh(CO)_2Cl]_2$ (10 mol%) was added dioxane (0.05 M of **1**) under an argon atmosphere. The reaction mixture was bubbled with balloon pressured (slightly higher than 1 atm) mix gas of CO and N_2 (1:4, V/V) at room temperature for 5 min and then stirred at 90 °C for 24 h under balloon pressured mix gas of CO and N_2 (1:4, V/V). After cooling, the reaction mixture was concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, petroleum ether/EtOAc) afforded [5 + 2 + 1] cycloadduct **2**.

Note:

1, We emphasize here that the quality of catalyst from different companies could be different and the yields of the reactions could be varied.[4]

2, We just used the previous optimized conditions, except the catalyst loading which was raised from 5% to 10% and the temperature which was raised from 80°C to 90°C for the present [5+2+1] reactions.



run 1: Following general procedure. Substrate: **1a** (34.1 mg, 0.103 mmol), $[Rh(CO)_2Cl]_2$ (4.0 mg, 0.0103 mmol), dioxane (2.0 mL), flash column chromatography (silica gel, 25:1 to 10:1 petroleum ether/EtOAc); product: **2a** (17.6 mg, 48%).

run 2: Following general procedure. Substrate: **1a** (201.2 mg, 0.607 mmol), $[Rh(CO)_2Cl]_2$ (23.6 mg, 0.061 mmol), dioxane (12.2 mL), flash column chromatography (silica gel, 20:1 petroleum ether/EtOAc); product: **2a** (109.9 mg, 50%).

The average yield of two runs: 49%.

1 mmol scale experiments:

run 1: Following general procedure. Substrate: **1a** (339 mg, 1.02 mmol), $[Rh(CO)_2Cl]_2$ (19.9 mg, 0.051 mmol), dioxane (20 mL), flash column chromatography (silica gel, 5:1 petroleum ether/EtOAc); product: **2a** (130.9 mg, 36%).

run 2: Following general procedure. Substrate: **1a** (339.8 mg, 1.03 mmol), $[Rh(CO)_2Cl]_2$ (19.9 mg, 0.051 mmol), dioxane (20 mL), flash column chromatography (silica gel, 5:1 petroleum ether/EtOAc); product: **2a** (152.3 mg, 41%).

The average yield of two runs: 38%.

Catalyst loading control experiments:

run 1: Following general procedure. Substrate: **1a** (198.3 mg, 0.6 mmol), $[Rh(CO)_2Cl]_2$ (23.3 mg, 0.06 mmol), dioxane (12 mL), flash column chromatography (silica gel, 5:1 petroleum ether/EtOAc); product: **2a** (104.3 mg, 49%).

run 2: Following general procedure. Substrate: **1a** (199 mg, 0.6 mmol), $[Rh(CO)_2Cl]_2$ (11.8 mg, 0.03 mmol), dioxane (12 mL), flash column chromatography (silica gel, 5:1 petroleum ether/EtOAc); product: **2a** (90.8 mg, 42%).

Physical Form: white solid

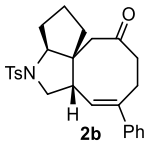
Melting Point: 131.2 – 132.1 °C

TLC (5:1 petroleum ether/EtOAc, R_f): 0.4

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.74 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 5.81 – 5.72 (m, 1H), 4.89 – 4.80 (m, 1H), 3.57 – 3.54 (m, 1H), 3.54 – 3.45 (m, 2H), 2.73 – 2.66 (m, 2H), 2.47 – 2.31 (m, 3H), 2.45 (s, 3H), 2.26 – 2.13 (m, 3H), 2.02 (d, J = 6.0 Hz, 1H), 1.78 – 1.71 (m, 2H), 1.66 – 1.56 (m, 1H), 1.39 – 1.30 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 211.5, 143.4, 137.0, 132.1, 130.1, 129.8, 127.2, 70.8, 56.1, 53.5, 46.7, 46.2, 44.2, 33.5, 32.9, 23.9, 23.5, 21.7.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{26}NO_3S^+$: 360.1628; found: 360.1626.



2b

run 1: Following general procedure. Substrate: **1b** (247.6 mg, 0.61 mmol), $[Rh(CO)_2Cl]_2$ (22.7 mg, 0.058 mmol), dioxane (12.0 mL), flash column chromatography (silica gel, 10:1 to 5:1 petroleum ether/EtOAc); product: **2b** (175.8 mg, 66%).

run 2: Following general procedure. Substrate: **1b** (248.4 mg, 0.61 mmol), $[Rh(CO)_2Cl]_2$ (22.8 mg, 0.059 mmol), dioxane (12.0 mL), flash column chromatography (silica gel, 10:1 to 5:1 petroleum ether/EtOAc); product: **2b** (166.2 mg, 63%).

The average yield of two runs: 64%.

Physical Form: white solid

Melting Point: 168.5 – 170.5 °C

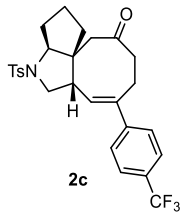
TLC (5:1 petroleum ether/EtOAc, R_f): 0.3

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.79 (d, J = 8.1 Hz, 2H), 7.36 – 7.27 (m, 5H), 7.10 – 7.03 (m, 2H), 4.90 (d, J = 8.8 Hz, 1H), 3.70 (dd, J = 11.2, 4.7 Hz, 1H), 3.58 – 3.49 (m, 2H), 2.73 (dd, J = 8.8, 4.7 Hz, 1H), 2.68 – 2.52 (m, 4H), 2.51 – 2.41 (m, 2H), 2.39 (s, 3H), 2.36 – 2.29 (m, 1H), 2.03 (d, J = 10.8 Hz, 1H),

1.86 – 1.76 (m, 3H), 1.47 – 1.36 (m, 1H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 210.7, 143.5, 140.9, 140.7, 136.4, 130.0, 128.6, 128.5, 127.7, 127.3, 125.9, 71.0, 56.6, 53.9, 46.6, 46.3, 45.7, 33.2, 33.0, 26.5, 23.6, 21.8.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{30}NO_3S^+$: 436.1941; found: 436.1943.



run 1: Following general procedure. Substrate: **1c** (285.4 mg, 0.60 mmol), $[Rh(CO)_2Cl]_2$ (23.4 mg, 0.060 mmol), dioxane (12.0 mL), flash column chromatography (silica gel, 10:1 to 5:1 petroleum ether/EtOAc); product: **2c** (165.6 mg, 55%).

run 2: Following general procedure. Substrate: **1c** (288.6 mg, 0.61 mmol), $[Rh(CO)_2Cl]_2$ (23.7 mg, 0.061 mmol), dioxane (12.0 mL), flash column chromatography (silica gel, 10:1 to 5:1 petroleum ether/EtOAc); product: **2c** (171.8 mg, 56%).

The average yield of two runs: 56%.

Physical Form: white solid

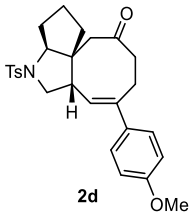
Melting Point: 240.1 – 241.2 °C

TLC (5:1 petroleum ether/EtOAc, R_f): 0.3

^1H NMR (400 MHz, $CDCl_3$, δ): 7.79 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 4.98 (d, J = 8.0 Hz, 1H), 3.70 (dd, J = 11.2, 4.8 Hz, 1H), 3.59 – 3.51 (m, 2H), 2.75 (dd, J = 8.4, 4.4 Hz, 1H), 2.68 – 2.55 (m, 4H), 2.50 – 2.41 (m, 2H), 2.37 (s, 3H), 2.35 – 2.28 (m, 1H), 2.08 (d, J = 11.2 Hz, 1H), 1.86 – 1.76 (m, 3H), 1.46 – 1.38 (m, 1H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 210.2, 144.7, 143.6, 139.8, 136.5, 131.0, 130.0, 129.7 (q, J = 32.8 Hz), 127.3, 126.3, 125.5 (q, J = 3.7 Hz), 124.3 (q, J = 272.9 Hz), 71.0, 56.5, 53.7, 46.7, 46.2, 45.9, 33.25, 33.18, 26.5, 23.6, 21.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{29}NO_3F_3S^+$: 504.1815; found: 504.1797.



run 1: Following general procedure. Substrate: **1d** (262.6 mg, 0.60 mmol), $[Rh(CO)_2Cl]_2$ (23.3 mg, 0.060 mmol), dioxane (12.0 mL), flash column chromatography (silica gel, 5:1 petroleum ether/EtOAc); product: **2d** (196 mg, 70%).

run 2: Following general procedure. Substrate: **1d** (273 mg, 0.62 mmol), $[Rh(CO)_2Cl]_2$ (24.2 mg, 0.062 mmol), dioxane (12.4 mL), flash column chromatography (silica gel, 5:1 petroleum

ether/EtOAc); product: **2d** (210.4 mg, 72%).

The average yield of two runs: 71%.

Physical Form: light yellow solid

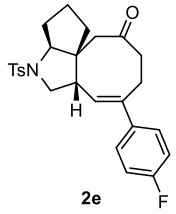
Melting Point: 225.0 – 226.8 °C

TLC (5:1 petroleum ether/EtOAc, R_f): 0.2

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.79 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.7 Hz, 2H), 6.82 (d, J = 8.7 Hz, 2H), 4.85 (d, J = 8.7 Hz, 1H), 3.83 (s, 3H), 3.69 (dd, J = 11.1, 4.7 Hz, 1H), 3.58 – 3.49 (m, 2H), 2.72 (dd, J = 8.7, 4.7 Hz, 1H), 2.65 – 2.52 (m, 4H), 2.49 – 2.40 (m, 2H), 2.43 (s, 3H), 2.36 – 2.28 (m, 1H), 2.02 (d, J = 11.0 Hz, 1H), 1.84 – 1.75 (m, 3H), 1.45 – 1.36 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 210.8, 159.3, 143.4, 140.0, 136.5, 133.2, 130.0, 127.4, 126.98, 126.95, 113.9, 71.0, 56.6, 55.5, 53.9, 46.6, 46.2, 45.7, 33.2, 33.0, 26.3, 23.6, 21.8.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{32}NO_4S^+$: 466.2047; found: 466.2028.



2e

run 1: Following general procedure. Substrate: **1e** (201.6 mg, 0.47 mmol), $[Rh(CO)_2Cl]_2$ (18.3 mg, 0.047 mmol), dioxane (9.0 mL), flash column chromatography (silica gel, 5:1 petroleum ether/EtOAc); product: **2e** (139.6 mg, 65%).

run 2: Following general procedure. Substrate: **1e** (200.7 mg, 0.47 mmol), $[Rh(CO)_2Cl]_2$ (18.2 mg, 0.047 mmol), dioxane (9.0 mL), flash column chromatography (silica gel, 5:1 petroleum ether/EtOAc); product: **2e** (136 mg, 64%).

The average yield of two runs: 64%.

Physical Form: white solid

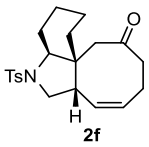
Melting Point: 204.2 – 206.0 °C

TLC (5:1 petroleum ether/EtOAc, R_f): 0.2

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.78 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.08 – 6.93 (m, 4H), 4.88 (d, J = 8.2 Hz, 1H), 3.68 (dd, J = 11.2, 4.4 Hz, 1H), 3.58 – 3.49 (m, 2H), 2.72 (dd, J = 8.2, 4.4 Hz, 1H), 2.65 – 2.52 (m, 4H), 2.47 – 2.38 (m, 2H), 2.40 (s, 3H), 2.35 – 2.26 (m, 1H), 2.05 (d, J = 11.2 Hz, 1H), 1.85 – 1.73 (m, 3H), 1.46 – 1.36 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 210.5, 162.4 (d, J = 248.5 Hz), 143.5, 139.8, 137.1 (d, J = 3.3 Hz), 136.5, 130.0, 128.64, 128.63, 127.6 (d, J = 8.1 Hz), 127.3, 115.4 (d, J = 22.2 Hz), 71.0, 56.6, 53.8, 46.7, 46.1, 45.8, 33.2, 33.1, 26.6, 23.6, 21.8.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{29}FNO_3S^+$: 454.1847; found: 454.1851.



2f

run 1: Following general procedure. Substrate: **1f** (210 mg, 0.61 mmol), $[Rh(CO)_2Cl]_2$ (23.6 mg, 0.061 mmol), dioxane (12.0 mL), flash column chromatography (silica gel, 20:1 petroleum ether/EtOAc); product: **2f** (105.4 mg, 46%).

run 2: Following general procedure. Substrate: **1f** (210.3 mg, 0.61 mmol), $[Rh(CO)_2Cl]_2$ (23.7 mg, 0.061 mmol), dioxane (12.0 mL), flash column chromatography (silica gel, 20:1 petroleum ether/EtOAc); product: **2f** (111.4 mg, 49%).

The average yield of two runs: 48%.

Physical Form: colorless oil

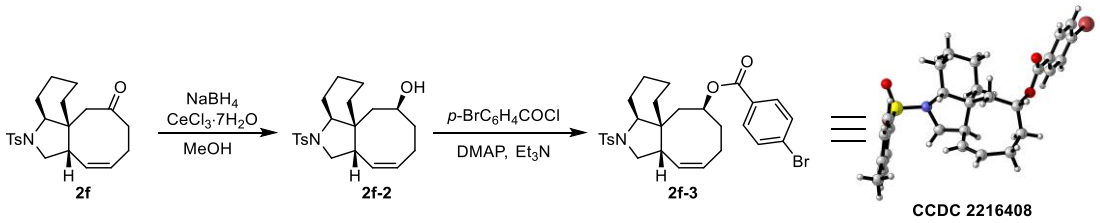
TLC (5:1 petroleum ether/EtOAc, R_f): 0.3

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.73 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 5.74 – 5.62 (m, 1H), 4.54 – 4.46 (m, 1H), 3.80 (dd, J = 11.3, 5.6 Hz, 1H), 3.40 (d, J = 11.3 Hz, 1H), 2.91 (s, 1H), 2.53 (d, J = 14.7 Hz, 1H), 2.46 (s, 3H), 2.42 (dd, J = 8.4, 4.0 Hz, 1H), 2.39 – 2.30 (m, 4H), 2.18 – 2.10 (m, 2H), 1.79 (d, J = 13.4 Hz, 1H), 1.64 – 1.58 (m, 1H), 1.55 – 1.42 (m, 3H), 1.37 – 1.28 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 211.1, 143.6, 134.7, 131.0, 130.4, 129.8, 127.6, 63.8, 53.9, 46.2, 46.0, 43.3, 43.1, 28.1, 25.5, 23.2, 21.7, 21.6, 19.8.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{28}NO_3S^+$: 374.1784; found: 374.1784.

Prepare the derivatives of 2f for XRD analysis:



To a flask with **2f** (83.5 mg, 0.22 mmol), $CeCl_3·7H_2O$ (90.7 mg, 0.24 mmol) and $NaBH_4$ (42.4 mg, 1.1 mmol) was added MeOH (2.0 mL) at 0 °C. $NaBH_4$ (42.4 mg, 1.1 mmol) was added after 2 h, and this reaction was completed after 30 min, quenched with 1 N HCl, and then extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 10:1 to 5:1 petroleum ether/EtOAc) afforded compound **2f-2** (56.3 mg, 67%).

To a flask with **2f-2** (53.8 mg, 0.143 mmol), *p*-BrC_6H_4COCl (47.3 mg, 0.215 mmol) and DMAP (35.2 mg, 0.288 mmol) was added DCM (3mL) and Et_3N (2.86 mmol). The mixture was stirred at rt for 24 h, quenched with water, and then extracted with EA. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 10:1 petroleum ether/EtOAc)

afforded compound **2f-3** (31.5 mg, 40%) as a white solid.

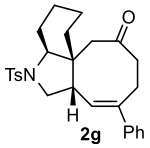
Melting Point: 199.5 – 201.4 °C

TLC (5:1 petroleum ether/EtOAc, R_f): 0.6.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.88 – 7.79 (m, 2H), 7.75 – 7.67 (m, 2H), 7.62 – 7.53 (m, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 5.37 – 5.29 (m, 1H), 5.28 – 5.19 (m, 1H), 4.23 – 4.11 (m, 1H), 3.86 (dd, *J* = 11.4, 6.0 Hz, 1H), 3.38 (d, *J* = 11.4 Hz, 1H), 3.04 – 2.93 (m, 1H), 2.84 – 2.75 (m, 1H), 2.53 (d, *J* = 14.2 Hz, 1H), 2.44 (s, 3H), 2.42 – 2.38 (m, 1H), 2.37 – 2.21 (m, 2H), 2.17 – 2.00 (m, 2H), 1.90 – 1.81 (m, 1H), 1.65 (ddd, *J* = 16.0, 4.3, 1.4 Hz, 1H), 1.51 (m, 3H), 1.45 – 1.38 (m, 2H), 1.32 – 1.27 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 165.1, 143.5, 134.4, 131.9, 131.2, 131.1, 129.7, 129.5, 128.5, 128.3, 127.7, 76.2, 64.1, 55.3, 47.9, 44.5, 32.8, 30.8, 29.4, 27.4, 25.4, 22.1, 21.7, 19.9.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{33}BrNO_4S^+$: 558.1308; found: 558.1328.



2g

run 1: Following general procedure. Substrate: **1g** (252.9 mg, 0.60 mmol), $[Rh(CO)_2Cl]_2$ (23.3 mg, 0.060 mmol), dioxane (12.0 mL), flash column chromatography (silica gel, 5:1 petroleum ether/EtOAc); product: **2g** (151.2 mg, 56%).

run 2: Following general procedure. Substrate: **1g** (71.4 mg, 0.169 mmol), $[Rh(CO)_2Cl]_2$ (6.6 mg, 0.017 mmol), dioxane (4 mL), flash column chromatography (silica gel, 5:1 petroleum ether/EtOAc); product: **2g** (38.3 mg, 50%).

The average yield of two runs: 53%.

Physical Form: white solid

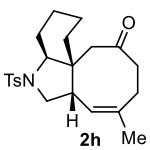
Melting Point: 200.1 – 202.0 °C

TLC (5:1 petroleum ether/EtOAc, R_f): 0.2

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.77 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.26 (m, 3H), 7.03 – 6.96 (m, 2H), 4.62 (d, *J* = 8.0 Hz, 1H), 3.92 (dd, *J* = 11.6, 5.2 Hz, 1H), 3.47 (d, *J* = 11.6 Hz, 1H), 2.94 (s, 1H), 2.69 – 2.60 (m, 2H), 2.57 – 2.47 (m, 2H), 2.46 – 2.34 (m, 3H), 2.39 (s, 3H), 2.29 (d, *J* = 8.0 Hz, 1H), 1.85 (d, *J* = 13.2 Hz, 1H), 1.70 – 1.60 (m, 2H), 1.58 – 1.47 (m, 2H), 1.44 – 1.30 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 210.5, 143.7, 140.9, 140.7, 133.9, 129.9, 128.5, 127.8, 127.7, 127.6, 125.8, 64.2, 54.3, 46.5, 46.3, 45.1, 43.3, 28.0, 26.2, 25.6, 21.8, 21.6, 19.7.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{32}NO_3S^+$: 450.2097; found: 450.2098.



2h

Since 1h and its another isomer from the previous step cannot be seprated, we just used the mixture for the reaction.

run 1: Following general procedure. Substrate: **1h** and the isomer (107.7 mg, 0.3 mmol), $[Rh(CO)_2Cl]_2$ (11.7 mg, 0.03 mmol), dioxane (6 mL), flash column chromatography (silica gel, 20:1 to 10:1 petroleum ether/EtOAc); product: **2h** (56.1 mg, 48%).

run 2: Following general procedure. Substrate: **1h** the isomer (107.1 mg, 0.3 mmol), $[Rh(CO)_2Cl]_2$ (11.7 mg, 0.03 mmol), dioxane (6 mL), flash column chromatography (silica gel, 20:1 to 10:1 petroleum ether/EtOAc); product: **2h** (61.3 mg, 53%).

The average yield of two runs: 50%.

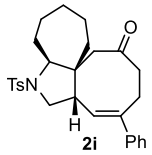
Physical Form: light yellow oil

TLC (5:1 petroleum ether/EtOAc, R_f): 0.3

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.75 (d, J = 8.3 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 3.94 (dt, J = 8.6, 1.5 Hz, 1H), 3.78 (dd, J = 11.4, 5.5 Hz, 1H), 3.33 (d, J = 11.4 Hz, 1H), 2.88 (s, 1H), 2.56 (dt, J = 14.7, 2.7 Hz, 1H), 2.47 (s, 3H), 2.44 – 2.37 (m, 1H), 2.37 – 2.28 (m, 2H), 2.28 – 2.19 (m, 2H), 2.16 (dd, J = 8.7, 5.5 Hz, 1H), 1.90 (ddd, J = 13.6, 6.5, 2.6 Hz, 1H), 1.80 – 1.73 (m, 1H), 1.64 – 1.56 (m, 1H), 1.56 – 1.50 (m, 1H), 1.53 (s, 3H), 1.50 – 1.41 (m, 2H), 1.36 – 1.27 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 210.9, 143.6, 137.5, 134.4, 129.7, 127.8, 124.8, 63.9, 54.1, 46.1, 45.3, 44.4, 43.3, 28.1, 28.0, 25.6, 24.1, 21.63, 21.59, 19.8.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{30}NO_3S^+$: 388.1941; found: 388.1942.



2i

run 1: Following general procedure. Substrate: **1i** (297.8 mg, 0.68 mmol), $[Rh(CO)_2Cl]_2$ (24.6 mg, 0.063 mmol), dioxane (14.0 mL), flash column chromatography (silica gel, 10:1 petroleum ether/EtOAc); product: **2i** (85.7 mg, 27%).

run 2: Following general procedure. Substrate: **1i** (100.7 mg, 0.23 mmol), $[Rh(CO)_2Cl]_2$ (8.8 mg, 0.023 mmol), dioxane (4.6 mL), flash column chromatography (silica gel, 10:1 petroleum ether/EtOAc); product: **2i** (32.4 mg, 30%).

The average yield of two runs: 28%.

Physical Form: white solid

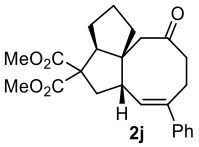
Melting Point: 174.3 – 176.2 °C

TLC (5:1 petroleum ether/EtOAc, R_f): 0.3

^{1}H NMR (400 MHz, CD_2Cl_2, δ): 7.76 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.31 – 7.23 (m, 3H), 7.04 (dd, J = 7.4, 2.1 Hz, 2H), 4.84 (d, J = 9.0 Hz, 1H), 3.76 (dd, J = 11.1, 5.9 Hz, 1H), 3.56 (dd, J = 11.1, 3.6 Hz, 1H), 3.08 (dd, J = 7.5, 1.8 Hz, 1H), 2.73 (ddd, J = 14.2, 7.9, 3.7 Hz, 1H), 2.57 – 2.46 (m, 2H), 2.39 (s, 3H), 2.37 – 2.33 (m, 1H), 2.33 – 2.28 (m, 1H), 2.28 – 2.21 (m, 1H), 2.21 – 2.13 (m, 2H), 2.04 – 1.91 (m, 1H), 1.75 – 1.64 (m, 3H), 1.62 – 1.52 (m, 4H), 1.51 – 1.41 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, δ): 209.8, 144.2, 142.6, 141.9, 134.8, 130.2, 128.7, 127.9, 127.8, 127.2, 126.3, 69.5, 52.9, 51.9, 47.5, 46.3, 44.8, 33.2, 29.2, 28.3, 26.7, 22.6, 21.8, 21.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{34}NO_3S^+$: 464.2254; found: 464.2241.



2j

run 1: Following general procedure. Substrate: **1j** (35.4 mg, 0.096 mmol), $[Rh(CO)_2Cl]_2$ (3.7 mg, 0.0095 mmol), dioxane (2.0 mL), flash column chromatography (silica gel, 20:1 to 5:1 petroleum ether/EtOAc); product: **2j** (17.9 mg, 47%).

run 2: Following general procedure. Substrate: **1j** (26.8 mg, 0.073 mmol), $[Rh(CO)_2Cl]_2$ (2.8 mg, 0.0072 mmol), dioxane (1.5 mL), flash column chromatography (silica gel, 20:1 to 5:1 petroleum ether/EtOAc); product: **2j** (15.1 mg, 52%).

The average yield of two runs: 50%.

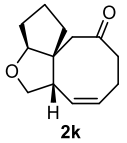
Physical Form: colorless oil

TLC (5:1 petroleum ether/EtOAc, R_f): 0.5

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.38 – 7.32 (m, 4H), 7.31 – 7.27 (m, 1H), 5.41 (d, J = 7.3 Hz, 1H), 3.77 (s, 3H), 3.72 (s, 3H), 3.03 – 2.95 (m, 2H), 2.94 – 2.84 (m, 2H), 2.71 – 2.55 (m, 3H), 2.43 – 2.33 (m, 2H), 2.28 (d, J = 12.0 Hz, 1H), 2.25 – 2.17 (m, 1H), 1.96 – 1.86 (m, 1H), 1.77 – 1.62 (m, 2H), 1.36 – 1.20 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 211.8, 173.5, 170.8, 142.2, 140.9, 131.3, 128.7, 127.6, 126.3, 64.2, 57.2, 55.7, 53.1, 52.7, 49.5, 46.7, 44.2, 39.4, 38.0, 30.6, 25.9, 25.7.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{29}O_5^+$: 397,2010; found: 397.2010.



2k

run 1: Following general procedure. Substrate: **1k** (54.7 mg, 0.307 mmol), $[Rh(CO)_2Cl]_2$ (11.7 mg, 0.0301 mmol), dioxane (6.0 mL), flash column chromatography (silica gel, 20:1 to 10:1 petroleum ether/EtOAc); product: **2k** (29.5 mg, 47%).

run 2: Following general procedure. Substrate: **1k** (55.7 mg, 0.312 mmol), $[Rh(CO)_2Cl]_2$ (11.8 mg, 0.0303 mmol), dioxane (6.0 mL), flash column chromatography (silica gel, 20:1 to 10:1 petroleum ether/EtOAc); product: **2k** (28.9 mg, 45%).

The average yield of two runs: 46%.

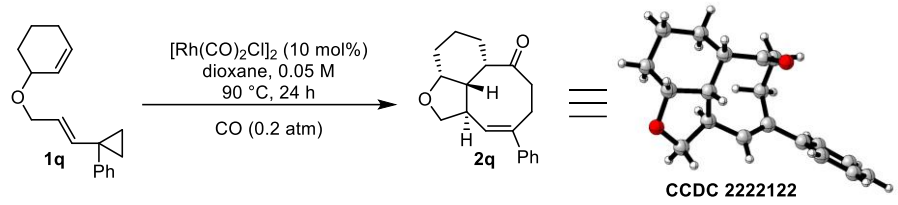
Physical Form: light yellow oil

TLC (10:1 petroleum ether/EtOAc, R_f): 0.2

^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.01 – 5.89 (m, 1H), 5.67 – 5.54 (m, 1H), 4.02 (dd, J = 8.6, 4.4 Hz, 1H), 3.91 (d, J = 3.8 Hz, 1H), 3.81 (d, J = 8.6 Hz, 1H), 2.91 – 2.83 (m, 1H), 2.82 (d, J = 11.5 Hz, 1H), 2.63 – 2.53 (m, 1H), 2.46 (ddd, J = 12.1, 12.1, 3.3 Hz, 1H), 2.43 – 2.19 (m, 3H), 2.04 (d, J = 11.5 Hz, 1H), 1.89 – 1.81 (m, 1H), 1.82 – 1.69 (m, 3H), 1.43 – 1.31 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 212.0, 133.9, 130.0, 90.0, 74.1, 55.2, 47.6, 46.6, 45.8, 34.5, 33.5, 24.8, 23.6.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{19}O_2^+$: 207.1380; found: 207.1377.



run 1: Following general procedure. Substrate: **1q** (253.7 mg, 1.0 mmol), $[Rh(CO)_2Cl]_2$ (38.6 mg, 0.1 mmol), dioxane (20.0 mL), flash column chromatography (silica gel, 20:1 to 5:1 to 2:1 petroleum ether/EtOAc); product: **2q** (80.1 mg, 28%).

run 2: Following general procedure. Substrate: **1q** (255.1 mg, 1.0 mmol), $[Rh(CO)_2Cl]_2$ (38.8 mg, 0.1 mmol), dioxane (20.0 mL), flash column chromatography (silica gel, 20:1 to 5:1 to 2:1 petroleum ether/EtOAc); product: **2q** (75.1 mg, 26%).

The average yield of two runs: 27%.

Physical Form: white solid

Melting Point: 89.5 – 91.5 °C

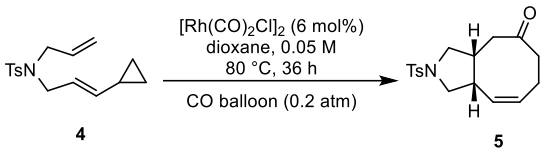
TLC (5:1 petroleum ether/EtOAc, R_f): 0.2

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.25 – 7.21 (m, 4H), 7.19 – 7.14 (m, 1H), 5.61 (d, J = 7.2 Hz, 1H), 4.20 (dd, J = 8.2, 8.2 Hz, 1H), 4.10 – 4.12 (m, 1H), 3.67 (dd, J = 8.8, 8.8 Hz, 1H), 3.48 – 3.34 (m, 1H), 3.21 (ddd, J = 13.8, 13.8, 5.9 Hz, 1H), 2.99 (ddd, J = 12.6, 5.9, 2.7 Hz, 1H), 2.69 – 2.58 (m, 2H), 2.49 (ddd, J = 13.2, 13.2, 6.3 Hz, 1H), 2.24 – 2.16 (m, 1H), 1.97 – 1.88 (m, 1H), 1.84 – 1.78 (m, 2H), 1.41 – 1.29 (m, 1H), 1.23 – 1.12 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 212.1, 142.6, 141.4, 128.6, 128.3, 127.5, 126.1, 78.8, 73.4, 51.7, 45.1, 44.6, 37.9, 29.7, 26.7, 23.3, 22.7.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{23}O_2^+$: 283.1693; found: 283.1692.

4. General procedure for [5+2+1] cycloaddition with $(CH_2O)_n$ as carbonyl source



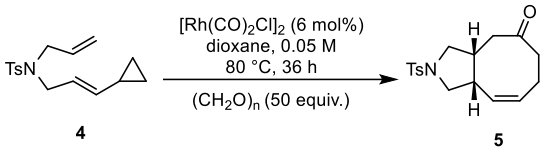
4 5

To a reaction tube with **4** (59.9 mg, 0.206 mmol) and $[Rh(CO)_2Cl]_2$ (4.9 mg, 0.0126 mmol) was added dioxane (4 mL) under an argon atmosphere. The reaction mixture was bubbled with balloon pressured (slightly higher than 1 atm) mix gas of CO and N_2 (1:4, V/V) at room temperature for 5 min and then stirred at 80 °C for 36 h under balloon pressured mix gas of CO and N_2 (1:4, V/V). After cooling, the reaction mixture was concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 5:1 petroleum ether/EtOAc) afforded [5 + 2 + 1] cycloadduct **5** (45.4 mg, 69%). Besides, small amount of substrate **4** and unknown by-product were detected by ^1H NMR.

run 2: Following general procedure. Substrate: **4** (59.1 mg, 0.203 mmol), $[Rh(CO)_2Cl]_2$ (4.8 mg, 0.0123 mmol), dioxane (4 mL), flash column chromatography (silica gel, 5:1 petroleum ether/EtOAc); product: **5** (42.4 mg, 65%).

The average yield of two runs: 67%.

Note: In our previous report, the reaction condition is substrate: **4** (150 mg, 0.515 mmol), $[Rh(CO)_2Cl]_2$ (15 ± 2 mg), dioxane (0.5 mL), reaction time: 108 h; product: **5** (134 mg, 81%).[3]

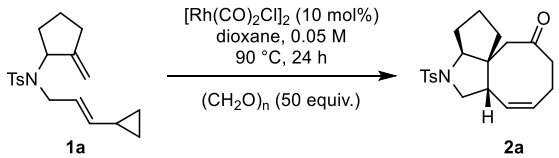


4 5

Compound **4** (60.3 mg, 0.207 mmol), $(CH_2O)_n$ (315 mg, 10.5 mmol), $[Rh(CO)_2Cl]_2$ (4.8 mg, 0.0123 mmol) and dioxane (4 mL) were sealed in a tube filled with argon. The reaction mixture was stirred at 80 °C for 36 h. After cooling, the reaction mixture was concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 5:1 petroleum ether/EtOAc) afforded [5 + 2 + 1] cycloadduct **5** (37.5 mg, 57%).

run 2: Following general procedure. Substrate: **4** (60.9 mg, 0.209 mmol), $(CH_2O)_n$ (308.6 mg, 10.3 mmol), $[Rh(CO)_2Cl]_2$ (4.9 mg, 0.0126 mmol), dioxane (4 mL), flash column chromatography (silica gel, 5:1 petroleum ether/EtOAc); product: **5** (40.0 mg, 60%).

The average yield of two runs: 58%.



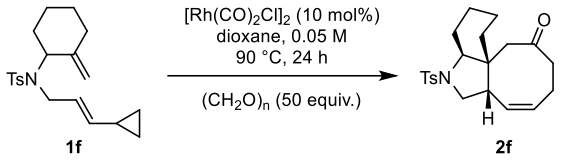
1a 2a

Compound **1a** (100.3 mg, 0.30 mmol), $(CH_2O)_n$ (453 mg, 15.1 mmol), $[Rh(CO)_2Cl]_2$ (11.8 mg, 0.03 mmol) and dioxane (6 mL) were sealed in a tube in glove box. The reaction mixture was stirred at

90 °C for 24 h. After cooling, the reaction mixture was concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 5:1 petroleum ether/EtOAc) afforded [5 + 2 + 1] cycloadduct **2a** (61.7 mg, 57%).

run 2: Following general procedure. Substrate: **1a** (99.9 mg, 0.30 mmol), $(CH_2O)_n$ (449 mg, 15.0 mmol), $[Rh(CO)_2Cl]_2$ (11.5 mg, 0.03 mmol), dioxane (6 mL), flash column chromatography (silica gel, 5:1 petroleum ether/EtOAc); product: **2a** (58.7 mg, 54%).

The average yield of two runs: 56%.

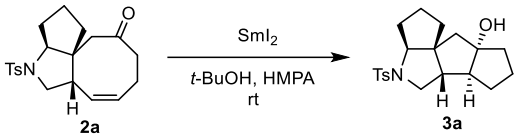


Compound **1f** (114.6 mg, 0.33 mmol), $(CH_2O)_n$ (473.9 mg, 15.8 mmol), $[Rh(CO)_2Cl]_2$ (13.6 mg, 0.035 mmol) and dioxane (6 mL) were sealed in a tube in glove box. The reaction mixture was stirred at 90 °C for 24 h. After cooling, the reaction mixture was concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 5:1 petroleum ether/EtOAc) afforded [5 + 2 + 1] cycloadduct **2f** (51.7 mg, 42%).

run 2: Following general procedure. Substrate: **1f** (105.8 mg, 0.31 mmol), $(CH_2O)_n$ (460 mg, 15.3 mmol), $[Rh(CO)_2Cl]_2$ (11.9 mg, 0.031 mmol), dioxane (6 mL), flash column chromatography (silica gel, 5:1 petroleum ether/EtOAc); product: **2f** (42.9 mg, 38%).

The average yield of two runs: 40%.

5. General procedure for transformations to tetracycles



To a flask with **2a** (36.0 mg, 0.1 mmol) was added *t*-BuOH (0.2 mL) and HMPA (0.8 mL) under argon atmosphere. Then the solution of SmI_2 (0.1 M in THF, 5 mL, 0.5 mmol) was added under 0 °C, and stirred at 0 °C for 5 min, quenched with water, and then extracted with ether. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. Purification of the crude product by flash column chromatography (silica gel, 3:1 petroleum ether/EtOAc) afforded compound **3a** (20.0 mg, 55%) as a colorless oil.

run 2: Following general procedure. Substrate: **2a** (36.0 mg, 0.1 mmol), *t*-BuOH (0.2 mL), HMPA (0.8 mL), SmI_2 (0.1 M in THF, 5 mL, 0.5 mmol), flash column chromatography (silica gel, 3:1 petroleum ether/EtOAc); product: **3a** (21.0 mg, 58%).

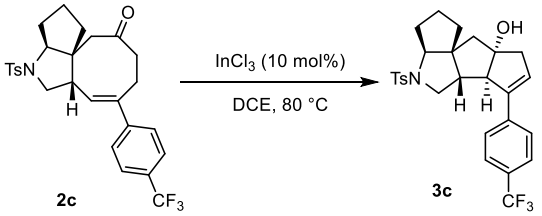
The average yield of two runs: 56%.

TLC (3:1 petroleum ether/EtOAc, R_f): 0.3

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.78 – 7.73 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.92 (dd, *J* = 5.9, 2.3 Hz, 1H), 3.52 (dd, *J* = 10.4, 6.1 Hz, 1H), 3.29 (dd, *J* = 10.4, 3.6 Hz, 1H), 2.43 (s, 3H), 2.07 – 1.98 (m, 1H), 1.96 – 1.90 (m, 1H), 1.90 – 1.47 (m, 12H), 1.34 – 1.22 (m, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 143.3, 135.6, 129.6, 127.8, 91.4, 71.2, 63.4, 58.5, 56.9, 54.8, 52.1, 42.0, 39.0, 34.2, 32.4, 25.4, 25.3, 21.7.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{28}NO_3S^+$: 362.1784; found: 362.1784.



To a flask with **2c** (50.4 mg, 0.1 mmol) and $InCl_3$ (2.2 mg, 0.01 mmol) was added DCE (2.0 mL) in glove box. Then mixture was stirred at 80 °C for 12 h. Purification of the crude product by flash column chromatography (silica gel, 1.5:1 petroleum ether/EtOAc) afforded compound **3c** (31.1 mg, 62%) as a white solid.

run 2: Following general procedure. Substrate: **2c** (50.3 mg, 0.1 mmol), $InCl_3$ (2.2 mg, 0.01 mmol), DCE (2.0 mL), flash column chromatography (silica gel, 1.5:1 petroleum ether/EtOAc); product: **3c** (33.9 mg, 67%).

The average yield of two runs: 64%.

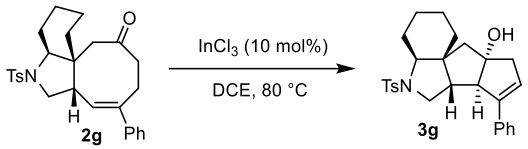
Melting Point: 208.2 – 209.1 °C

TLC (1:1 petroleum ether/EtOAc, R_f): 0.6

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.78 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.40 – 7.31 (m, 4H), 6.07 – 6.00 (m, 1H), 3.85 (dd, *J* = 6.6, 2.0 Hz, 1H), 3.72 (dd, *J* = 9.8, 7.0 Hz, 1H), 3.27 (dd, *J* = 9.8, 6.6 Hz, 1H), 3.05 (s, 1H), 2.80 (d, *J* = 18.6 Hz, 1H), 2.66 (d, *J* = 18.6 Hz, 1H), 2.45 (s, 3H), 2.08 – 1.87 (m, 5H), 1.75 – 1.66 (m, 1H), 1.64 – 1.57 (m, 1H), 1.57 – 1.47 (m, 2H), 1.44 – 1.35 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 143.7, 143.2, 139.1, 134.6, 129.8, 129.4 (q, *J* = 32.8 Hz), 128.0, 126.34, 126.27, 125.7 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 272.7 Hz), 90.6, 71.2, 64.0, 63.2, 55.5, 52.7, 51.7, 48.8, 38.9, 33.9, 25.3, 21.7.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{29}F_3NO_3S^+$: 504.1815; found: 504.1814.



To a flask with **2g** (45.1 mg, 0.10 mmol) and $InCl_3$ (2.2 mg, 0.01 mmol) was added DCE (2.0 mL) in glove box. Then mixture was stirred at 80 °C for 12 h. Purification of the crude product by flash column chromatography (silica gel, 3:1 petroleum ether/EtOAc) afforded compound **3g** (32.7 mg, 73%) as a white solid.

run 2: Following general procedure. Substrate: **2g** (45.5 mg, 0.1 mmol), $InCl_3$ (2.2 mg, 0.01 mmol), DCE (2.0 mL), flash column chromatography (silica gel, 3:1 petroleum ether/EtOAc); product: **3g** (33.4 mg, 73%).

The average yield of two runs: 73%.

Melting Point: 209.5 – 211.0 °C

TLC (3:1 petroleum ether/EtOAc, R_f): 0.1

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.78 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.32 – 7.28 (m, 2H), 7.26 – 7.24 (m, 1H), 7.21 – 7.16 (m, 2H), 5.82 – 5.76 (m, 1H), 3.74 (dd, *J* = 10.6, 8.8 Hz, 1H), 3.57 (dd, *J* = 6.1, 6.1 Hz, 1H), 3.34 (dd, *J* = 10.6, 4.8 Hz, 1H), 2.96 (s, 1H), 2.79 – 2.63 (m, 2H), 2.43 (s, 3H), 2.14 (ddd, *J* = 8.5, 4.3, 4.3 Hz, 1H), 1.98 (d, *J* = 14.1 Hz, 1H), 1.83 – 1.74 (m, 3H), 1.74 – 1.64 (m, 2H), 1.57 – 1.47 (m, 1H), 1.29 – 1.13 (m, 4H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 144.5, 143.5, 135.8, 135.3, 129.7, 128.7, 127.7, 127.6, 126.2, 123.4, 90.3, 65.5, 64.1, 55.0, 53.4, 53.1, 50.3, 48.9, 34.2, 28.4, 22.5, 21.8, 21.7.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{32}NO_3S^+$: 450.2097; found: 450.2096.

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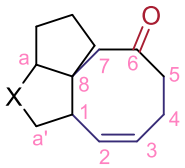
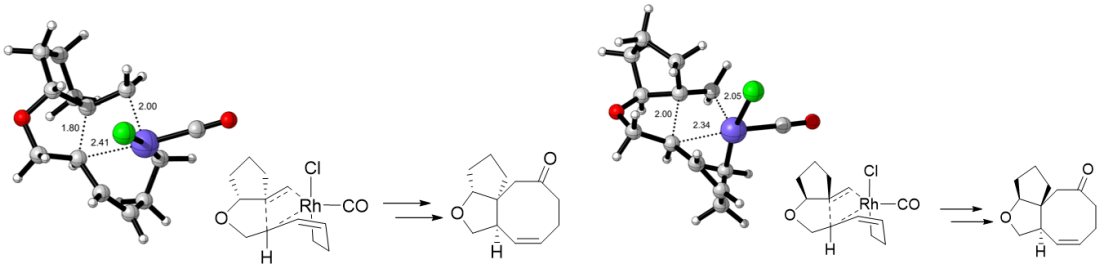
6. DFT Studies

Unless otherwise stated, all DFT calculations were performed with the Gaussian 09 software package.[9] Pruned integration grids with 99 radial shells and 590 angular points per shell were used. Geometry optimizations of all the stationary points were carried out in the gas phase at the BMK[10]/def2-SVP[11,12] level. Unscaled harmonic frequency calculations at the same level were performed to validate each structure as either a minimum or a transition state and to evaluate its zero-point energy and thermal corrections at 298 K. All discussed energy differences are based on Gibbs energies at 298 K. All the 3D structures were prepared with CYLview.[13]

The origin of stereochemistry of 5/5/8 tricyclic products:

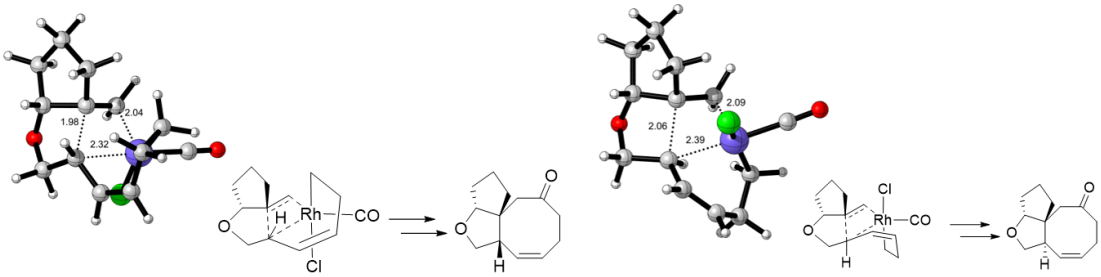


TS1 ($cis_{8,a}cis_{8,1}$) have the lowest energy with a relative energy of 0.0 kcal/mol compared with **TS2** ($cis_{8,a}trans_{8,1}$) with 9.1 kcal/mol, **TS3** ($trans_{8,a}cis_{8,1}$) with 20.4 kcal/mol and **TS4** ($trans_{8,a}trans_{8,1}$) with 41.8 kcal/mol. In our previous work, the alkene insertion step is irreversible and thus determines the stereochemistry.[14] Thus, this reaction prefers **TS1** ($cis_{9,10}cis_9$) to give the cis-cis-5/5/8 tricyclic product, which is consistent with the experiment.



TS1 ($cis_{8,a}cis_{8,1}$)
0.0 kcal/mol

TS2 ($cis_{8,a}trans_{8,1}$)
9.1 kcal/mol

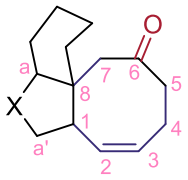


TS3 ($trans_{8,a}cis_{8,1}$)
20.4 kcal/mol

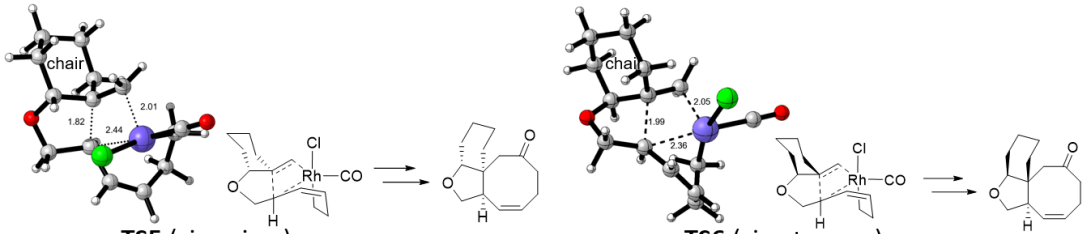
TS4 ($trans_{8,a}trans_{8,1}$)
41.8 kcal/mol

TS3 and **TS4,** compared with **TS1** and **TS2**, are much higher in energy, which may be derived from the strain on the trans five-membered ring, and according to the literature, the trans-5/5 ring structure is about 10 kcal/mol higher energy than the cis-5/5 ring structure.[15,16]

The origin of stereochemistry of 6/5/8 tricyclic products:

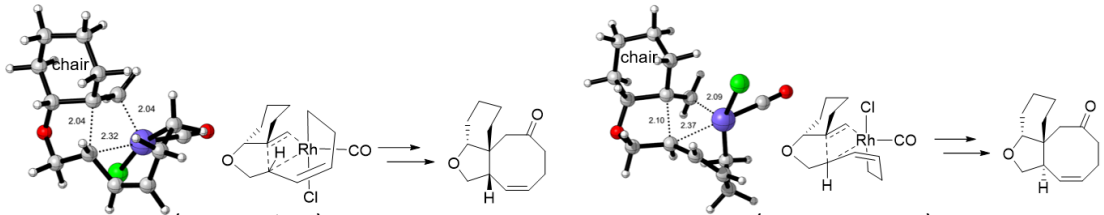


TS5 ($cis_{8,a}cis_{8,1}$)-chair have the lowest energy with a relative energy of 0.0 kcal/mol compared with **TS6** ($cis_{8,a}trans_{8,1}$)-chair (9.6 kcal/mol), **TS7** ($trans_{8,a}cis_{8,1}$)-chair (14.2 kcal/mol) and **TS8** ($trans_{8,a}trans_{8,1}$)-chair (37.0 kcal/mol). Thus, this reaction favors **TS5** ($cis_{9,10}cis_9$)-chair to give the cis-cis-6/5/8 tricyclic product, which is consistent with the experiment.



TS5 ($cis_{8,a}cis_{8,1}$)
chair: 0.0 kcal/mol
boat: 5.7 kcal/mol

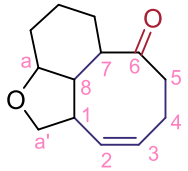
TS6 ($cis_{8,a}trans_{8,1}$)
chair: 9.6 kcal/mol
boat: 14.7 kcal/mol



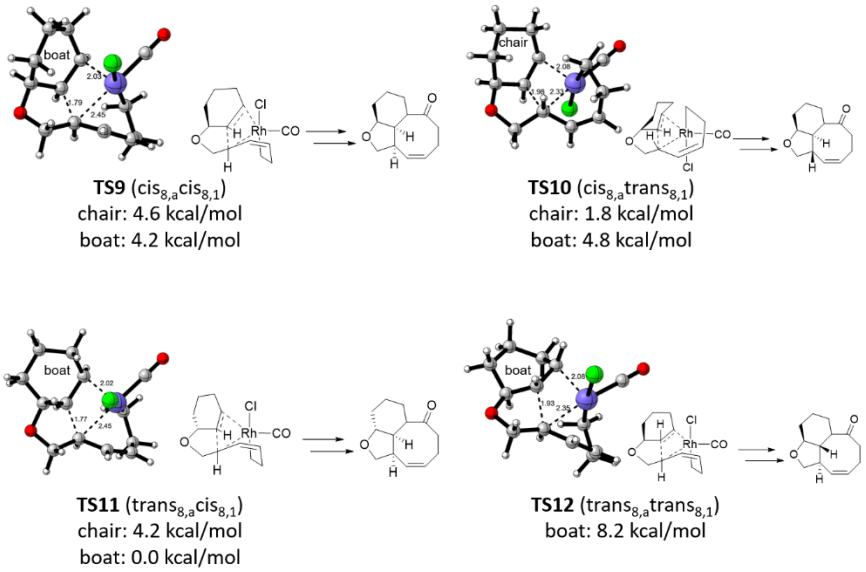
TS7 ($trans_{8,a}cis_{8,1}$)
chair: 14.2 kcal/mol

TS8 ($trans_{8,a}trans_{8,1}$)
chair: 37.0 kcal/mol
boat: 37.9 kcal/mol

The origin of stereochemistry of 6/5/8 tricyclic product:

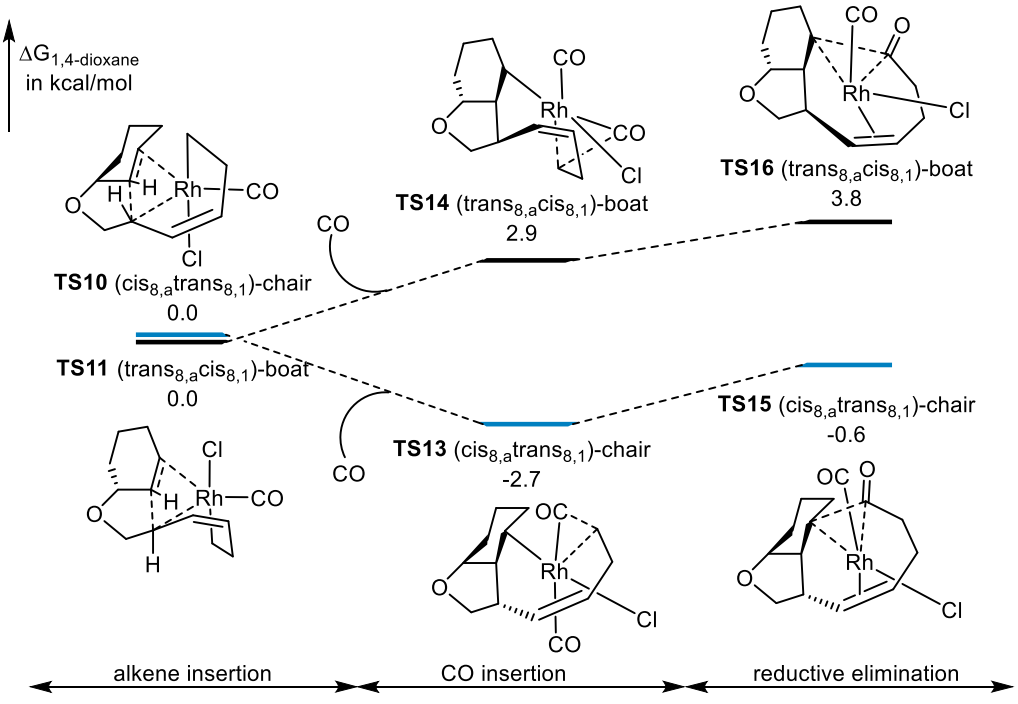


In this reaction, **TS11** ($trans_{8,a}cis_{8,1}$)-boat is favored than **TS10** ($cis_{8,a}trans_{8,1}$)-chair in energies of $1.8\ \mathrm{kcal/mol}$, which is not consistent with the experiment. We speculated that the alkene insertion step would be reversible so this step cannot determine the diastereoselectivity because the six-membered ring was introduced into the C_7 and C_8 positions.



To verify this conjecture, we calculated alkene insertion, CO insertion and reductive elimination at higher level. On basis of the optimized structures at the BMK[10]/def2-SVP[11,12] level, Gibbs energies of solvation in 1,4-dioxane were computed at the SMD[17]/BMK/def2-SVP level and single-point energy refinements were performed with ORCA 5.0.3[18,19] at the DLPNO-CCSD(T)[20,21]/def2-TZVPP[11,12] level (using the def2- TZVPP/C auxiliary basis set and tight thresholds). All discussed energy differences are based on Gibbs energies in 1,4-dioxane at 298 K. Standard state concentrations of 1.5 mM[22] and 1.0 M[23] were used for CO and the other species, respectively.

In the $cis_{8,a}trans_{8,1}$ pathway, alkene insertion is irreversible, while the alkene insertion step in the $trans_{8,a}cis_{8,1}$ pathway is reversible. The $cis_{8,a}trans_{8,1}$ pathway is favored over $trans_{8,a}cis_{8,1}$ pathway by 3.8 kcal/mol, suggesting that this reaction occurs via **TS10**, **TS13**, and **TS15** to give the $cis_{8,a}trans_{8,1}$ product which is consistent with the experiment.



DLPNO-CCSD(T)/def2-TZVPP:SMD(1,4-dioxane)//BMK/def2-SVP level

Energy and Cartesian Coordinates of the Stationary Points:

Computed Energies for the Stationary Points

Thermal corrections to Gibbs energies (TCGs), single-point energies (SPEs) in gas phase (Computed at the BMK/def2-SVP level).

	Imaginary Frequencies (cm^{-1})	SPEs (in gas phase) (hartree)	TCGs (in gas phase) (hartree)
TS1 ($cis_{8,a}cis_{8,1}$)	-96.36	-1225.709766	0.246713
TS2 ($cis_{8,a}trans_{8,1}$)	-227.78	-1225.695326	0.246729
TS3 ($trans_{8,a}cis_{8,1}$)	-222.28	-1225.676635	0.246134
TS4 ($trans_{8,a}trans_{8,1}$)	-268.24	-1225.643343	0.246889
TS5 ($cis_{8,a}cis_{8,1}$)-chair	-113.50	-1264.972142	0.276050
TS5 ($cis_{8,a}cis_{8,1}$)-boat	-127.73	-1264.962913	0.275863
TS6 ($cis_{8,a}trans_{8,1}$)-chair	-207.55	-1264.955780	0.275033
TS6 ($cis_{8,a}trans_{8,1}$)-boat	-207.13	-1264.949174	0.276505
TS7 ($trans_{8,a}cis_{8,1}$)-chair	-196.20	-1264.948552	0.275147
TS8 ($trans_{8,a}trans_{8,1}$)-chair	-272.97	-1264.912128	0.274977
TS8 ($trans_{8,a}trans_{8,1}$)-boat	-267.98	-1264.910172	0.274492
TS9 ($cis_{8,a}cis_{8,1}$)-chair	-98.16	-1225.703374	0.248428
TS9 ($cis_{8,a}cis_{8,1}$)-boat	-97.13	-1225.705470	0.249812
TS10 ($cis_{8,a}trans_{8,1}$)-chair	-231.03	-1225.707682	0.248201
TS10 ($cis_{8,a}trans_{8,1}$)-boat	-277.88	-1225.701913	0.247264
TS11 ($trans_{8,a}cis_{8,1}$)-chair	-94.13	-1225.704245	0.248595
TS11 ($trans_{8,a}cis_{8,1}$)-boat	-70.99	-1225.710342	0.247998
TS12 ($trans_{8,a}trans_{8,1}$)-boat	-203.27	-1225.696804	0.247584

Thermal corrections to Gibbs energies (TCGs), single-point energies (SPEs) in gas phase and solvent ([a]Computed at the BMK/def2-SVP level; [b]Computed at the SMD(1,4-Dioxane)/BMK/def2-SVP//BMK/def2-SVP level; [c]Computed at the DLPNO-CCSD(T)/def2-TZVPP//BMK/def2-SVP level).

	Imaginary Frequencies (cm^{-1})	SPEs (in gas phase) (hartree)[a]	TCGs (in gas phase) (hartree)[a]	SPEs (in dioxane) (hartree)[b]	SPEs (in gas phase) (hartree)[c]
CO	none	-113.172745	-0.013860	-113.167803	-113.158173

TS10 ($cis_{8,a}trans_{8,1}$)-chair	-231.03	-1225.707682	0.248201	-1225.720676	-1225.662259
TS11 ($trans_{8,a}cis_{8,1}$)-boat	-70.99	-1225.710342	0.247998	-1225.722811	-1225.662655
TS13 ($cis_{8,a}trans_{8,1}$)-chair	-189.60	-1338.908843	0.255311	-1338.924827	-1338.840813
TS14 ($trans_{8,a}cis_{8,1}$)-boat	-177.71	-1338.898850	0.254915	-1338.915487	-1338.830881
TS15 ($cis_{8,a}trans_{8,1}$)-chair	-137.46	-1338.916691	0.257522	-1338.933270	-1338.839159
TS16 ($trans_{8,a}cis_{8,1}$)-boat	-90.22	-1338.913007	0.256729	-1338.929956	-1338.830942

Cartesian coordinates for the stationary points:

TS1 ($cis_{8,a}cis_{8,1}$)

Rh	-1.08873000	-0.14348900	-0.09238400
Cl	-0.77686000	-1.86150700	1.65079500
O	-3.25420400	-1.76159600	-1.37603600
O	2.89983200	0.22608100	1.29728400
C	-2.43920700	-1.14138100	-0.88660900
C	-1.42183800	1.46299700	-1.39028700
C	-1.60535800	2.65326200	-0.41690500
C	-1.65202200	2.05085400	0.97971400
C	-0.60803900	1.33679300	1.50507800
C	0.73697400	1.13876600	0.81305700
C	1.77618000	0.76708000	1.90432100
C	2.43449900	-0.71459000	0.36811700
C	1.34008200	0.01625100	-0.45219900
C	0.40873300	-0.91556100	-1.17905800
H	-2.32664900	1.32418800	-2.00178800
H	-0.57632400	1.60779600	-2.08241000
H	-2.52793400	3.22099800	-0.61444200
H	-0.77036400	3.37637200	-0.47642900
H	-2.54161200	2.18669000	1.60650700
H	-0.71295900	0.89034500	2.49908500
H	0.97548400	2.08221300	0.30470400
H	2.07476400	1.65824800	2.47915500
H	1.30107800	0.03205500	2.58269100
H	2.01926800	-1.59983400	0.88416100
H	0.33370600	-0.73503200	-2.26021800
H	0.53969600	-1.97763300	-0.93098200
C	3.54265200	-1.02688100	-0.65017600
H	4.51363900	-0.82526500	-0.17202300
H	3.52464900	-2.08971300	-0.93630000
C	2.18628200	0.88618800	-1.40844800
H	1.59740300	1.31035900	-2.23692100
H	2.65446100	1.71338700	-0.85232100
C	3.27807500	-0.10035300	-1.87466600
H	2.90958900	-0.69448900	-2.72706000
H	4.18445300	0.42551500	-2.21323900

TS2 ($cis_{8,a}trans_{8,1}$)

C	-2.50321600	-1.05938400	-0.77132700

Rh	-1.02205400	-0.10603900	-0.12324400
Cl	-0.98581900	-1.88498100	1.60543000
O	-3.38137700	-1.65590100	-1.16986900
C	0.70567900	1.32834500	0.53720500
C	-1.93230200	2.52613400	-0.27979400
C	-1.46193800	1.51488500	-1.35476600
C	0.39243500	-0.82079700	-1.43115700
C	1.34869400	-0.29469400	-0.44153200
C	2.55469300	0.52278200	-0.94073500
H	-0.58867100	1.86645700	-1.93022400
H	-1.41486300	3.50323800	-0.32959900
H	-2.26186500	1.30368100	-2.08129600
H	-3.00836500	2.73845000	-0.37589700
H	2.32569600	1.12246400	-1.84137700
H	0.35751300	-0.31676300	-2.40634200
H	0.35367700	-1.91404400	-1.49895000
H	0.60082400	2.03077600	-0.29672800
C	-1.68496800	1.86875700	1.07994100
H	-2.48600100	1.85409700	1.82805700
O	3.02069400	1.35434200	0.09680500
C	2.09334400	1.53288600	1.12429600
H	2.28618000	0.86340600	1.98442200
H	2.17029400	2.57365600	1.48448000
C	-0.44797600	1.39137100	1.46659500
H	-0.33109500	0.94983600	2.46295800
C	1.96627900	-1.35466500	0.50598200
H	1.43488200	-2.30548200	0.37890400
H	1.83803900	-1.09880500	1.56674800
C	3.59391200	-0.57687000	-1.17850900
H	4.59813600	-0.14816900	-1.32311700
H	3.32309800	-1.14656800	-2.08367400
C	3.46638900	-1.43819400	0.09684000
H	3.79028600	-2.47738100	-0.06668600
H	4.10293500	-1.01325000	0.88824500
O	3.08518900	0.08381700	-2.33207500
O	-2.24367700	-1.74059800	0.59526800
C	2.30834400	0.08838800	-1.50614400
C	1.11818200	2.15740000	0.03002400
C	1.08708600	2.33757900	1.56231700
C	1.55042600	0.99656000	2.10676500
C	0.75450600	-0.12111300	2.05352500
C	-0.63688900	-0.12605400	1.48550700
C	-1.32897000	-1.50992300	1.64450000
C	-2.64240400	-0.49437700	0.18703300
C	-1.42755700	0.33360000	-0.26765700
C	-0.62433100	-0.12308500	-1.41014200
H	0.35224600	2.74645000	-0.49290800
H	2.10036500	2.48433100	-0.34820000
H	0.06068500	2.54086200	1.91906700
H	1.72453500	3.16080100	1.92472100
H	2.55089300	0.89677300	2.54386200
H	1.16051900	-1.08433100	2.37963400
H	-1.20110400	0.71654100	1.90907000
H	-0.58100300	-2.31353700	1.62068800
H	-1.86295600	-1.51838300	2.61689900
H	-3.08987900	0.04935500	1.05139800
H	-0.60530800	0.55961100	-2.26860700
H	-0.70158700	-1.18686900	-1.67072800
C	-3.60400600	-0.28043600	-0.97244500
H	-3.28860300	-0.86466800	-1.85098600
H	-4.63986100	-0.55601400	-0.72315400
C	-2.09322000	1.69411600	-0.46590400
H	-1.50607000	2.38779600	-1.07913000
H	-2.31500100	2.18606700	0.49649400
C	-3.42243800	1.26035000	-1.19781000
H	-4.27966800	1.82367100	-0.79706600
H	-3.35849600	1.49220400	-2.27184400

TS3 ($trans_{8,a}cis_{8,1}$)

Rh	0.98242800	0.06795400	-0.16530400
Cl	1.31215100	-2.38837400	-0.18373500

TS4 ($trans_{8,a}trans_{8,1}$)

Rh	-0.98317100	-0.15642200	-0.12579500
Cl	-1.05828900	-1.55551100	1.91981200

O	-2.85104500	-2.21865800	-1.24124700
O	2.88799100	1.70757100	-0.28902200
C	-2.16012700	-1.42510100	-0.81540700
C	-1.67014600	1.26096600	-1.48856900
C	-2.20376800	2.34563200	-0.52211600
C	-1.79104700	1.97556300	0.90146100
C	-0.49768100	1.70615100	1.28097500
C	0.61842500	1.55354400	0.33343700
C	1.96976300	2.21453400	0.63515300
C	2.83844100	0.35287700	-0.05016500
C	1.42193700	-0.27415400	-0.17968000
C	0.63616300	-0.50402700	-1.39683400
H	-2.48236300	0.86477900	-2.11781300
H	-0.89710700	1.64705500	-2.17268900
H	-3.30281600	2.39860900	-0.55919000
H	-1.83382400	3.35945500	-0.76712200
H	-2.54595600	2.00420100	1.69565700
H	-0.29685200	1.48067900	2.33488700
H	0.37387700	1.89550800	-0.67701900
H	1.87094400	3.30042600	0.48015700
H	2.30360800	2.02941400	1.67635800
H	3.08837000	0.20819100	1.02267200
H	0.63029400	-1.53799900	-1.76352700
H	0.70034600	0.23539500	-2.20520100
C	3.69914900	-0.64965200	-0.79681900
H	3.53759500	-0.57886900	-1.88452300
H	4.77265800	-0.51875100	-0.59168700
C	1.75642200	-1.61468600	0.51171700
H	0.98366000	-2.37623800	0.36018400
H	1.87105100	-1.49713700	1.59859000
C	3.11622300	-1.97467000	-0.19612300
H	3.81716600	-2.42640200	0.52333900
H	2.94489200	-2.71882400	-0.98911200

TS5 ($cis_{8,a}cis_{8,1}$)-chair

Rh	-1.26124500	-0.13168700	-0.16273100
Cl	-1.06909200	-2.13939500	1.25769100
O	-3.21706900	-1.53883400	-1.93333700
O	2.60101600	-0.03219500	1.61557800
C	-2.48125200	-0.99866700	-1.25853800
C	-1.58493400	1.68110700	-1.15795400
C	-1.76483900	2.68691200	0.00489300
C	-1.92619900	1.84098700	1.25859500
C	-0.92165100	1.03772200	1.72900200
C	0.47830200	0.98486200	1.13497300
C	1.44116900	0.43483000	2.22027700
C	2.17481300	-0.79618700	0.52125200
C	1.22360300	0.12539300	-0.28506000
C	0.35205500	-0.63581300	-1.24584900
H	-2.50252000	1.64177200	-1.76577900
H	-0.75670300	1.95093800	-1.83345000
H	-2.63683400	3.34577600	-0.13105600
H	-0.88333600	3.34474000	0.11935700
H	-2.87216400	1.85590400	1.81320200
H	-1.10645400	0.40775600	2.60501800
H	0.72865700	2.00757900	0.82893800
H	1.70440600	1.22327400	2.94324900
H	0.91984200	-0.38849500	2.74673100
H	1.58917800	-1.66733200	0.87288300
H	0.34834100	-0.24202200	-2.27147700
H	0.48724400	-1.72587300	-1.21341000
C	4.12364400	-0.12994300	-0.99042100
H	4.58828600	0.51748800	-0.22590900
H	4.93939900	-0.53471400	-1.61298300
C	2.02031500	1.26148000	-0.96406400
H	1.33567500	1.89348800	-1.55435300
H	2.47966200	1.89970900	-0.19110900
C	3.15565400	0.70522300	-1.84165700
H	2.73889900	0.08402400	-2.65597000
H	3.68655000	1.54499900	-2.32200800
C	3.37824500	-1.27585400	-0.29370700
H	4.04672800	-1.82978000	0.38673300
H	3.01059900	-1.99769100	-1.04483800

TS5 ($cis_{8,a}cis_{8,1}$)-boat

Rh	-1.27694800	-0.02978900	-0.14086600
Cl	-1.25276100	-2.31135400	0.80636000
O	-3.58647100	-0.84663400	-1.86942300
O	2.58635100	-0.78526200	1.26970000
C	-2.72011800	-0.52842600	-1.20922100
C	-1.45339100	1.95838100	-0.77626900
C	-1.35241000	2.74658600	0.54908000
C	-1.61246100	1.71702900	1.63646900
C	-0.72939100	0.70104800	1.89393700
C	0.61398600	0.54186700	1.20695400
C	1.47169000	-0.44119800	2.02224000
C	2.14460200	-1.09813700	-0.01848600
C	1.16434800	0.01003600	-0.50746500
C	0.14587900	-0.51570400	-1.47331700
H	-2.43983800	2.13154600	-1.23468000
H	-0.69034300	2.25026700	-1.51589300
H	-2.06695500	3.58250000	0.61571300
H	-0.34252200	3.17551800	0.69085000
H	-2.52830800	1.76822300	2.23731900
H	-0.98129100	-0.05304500	2.64706100
H	1.07804200	1.53387000	1.14053300
H	1.81376800	0.03355700	2.95657900
H	0.85761800	-1.32934100	2.26236700
H	1.58815600	-2.05518700	-0.00508200
H	0.07941500	0.03504800	-2.42001700
H	0.15840800	-1.60518500	-1.61030300
C	4.20477700	0.13330300	-0.86588500
H	4.99247500	0.01510300	-0.10539300
H	4.71786400	0.28213600	-1.83142000
C	1.92033000	1.25134700	-1.05432800
H	1.96952100	1.15122800	-2.15255700
H	1.34548800	2.17141500	-0.85991400
C	3.35611600	1.38121000	-0.52133400
H	3.81676800	2.28555000	-0.95305400
H	3.33992700	1.52461600	0.57029700
C	3.36029800	-1.16287700	-0.94316000
H	3.97156300	-2.03804900	-0.66917400
H	2.99526100	-1.33788100	-1.96990100

TS6 ($cis_{8,a}trans_{8,1}$)-chair

C	-2.51002600	-1.22111700	-0.90016300
Rh	-1.18286200	-0.14272700	-0.13870000
Cl	-1.25424100	-1.86378500	1.65175800
O	-3.29565000	-1.89150800	-1.36886200
C	0.40943500	1.43049200	0.59388300
C	-2.22360800	2.42904900	-0.45020600
C	-1.62554100	1.40908700	-1.45347900
C	0.39857000	-0.80680800	-1.26375400
C	1.26491400	-0.14323100	-0.26662000
C	2.34165600	0.83370500	-0.77129200
H	-0.73887500	1.79265300	-1.98699800
H	-1.76176800	3.43318800	-0.50932300
H	-2.36339500	1.12845300	-2.22116900
H	-3.30090500	2.57250400	-0.62630600
H	1.91810100	1.47830600	-1.56869000
H	0.40633600	-0.38675200	-2.27923000
H	0.44727600	-1.90301400	-1.24663000
H	0.28485600	2.07567400	-0.28024200
C	-2.03579400	1.84621900	0.95334300
H	-2.88828600	1.81146200	1.64156200
O	2.75759300	1.61059400	0.32670000
C	1.72608700	1.83880000	1.24606300
H	1.90775600	1.31001900	2.19962700
H	1.67216000	2.91975200	1.46843900
C	-0.80915100	1.44643100	1.44148900
H	-0.73868000	1.05015400	2.46095600
C	1.85903400	-1.10191500	0.77947500
H	1.09018600	-1.81008700	1.11539800
H	2.20782500	-0.55748100	1.66887600
C	4.14955800	-0.89444600	-0.32498000
H	4.56305400	-0.32733900	0.52665400
H	4.98421000	-1.45143900	-0.78350200
C	3.06459100	-1.85612000	0.17604300

H	2.71923800	-2.49309100	-0.65932700
H	3.47166300	-2.53713800	0.94261400
C	3.56107400	0.09480800	-1.33850800
H	4.30632600	0.85211900	-1.63590300
H	3.24348400	-0.43327300	-2.25564400

TS6 ($cis_{8,a}trans_{8,1}$)-boat

C	2.54126400	-1.19387000	0.88686000
Rh	1.18591700	-0.14227600	0.13974700
Cl	1.18443400	-1.91313700	-1.59774600
O	3.34544400	-1.84808000	1.34708800
C	-0.43536900	1.40699000	-0.59380800
C	2.21711000	2.44310000	0.35745100
C	1.64994600	1.44711300	1.40194200
C	-0.36585000	-0.78422800	1.31446600
C	-1.24080100	-0.15017300	0.30175400
C	-2.31977100	0.80612300	0.83268600
H	0.77225800	1.83929200	1.94409800
H	1.74985700	3.44564200	0.39924200
H	2.40704800	1.19331300	2.16012300
H	3.29734800	2.59809600	0.50304700
H	-1.88424500	1.46121500	1.61304700
H	-0.35891800	-0.32288500	2.31170300
H	-0.41392200	-1.87921800	1.34048800
H	-0.29947600	2.09063000	0.24953400
C	1.99921600	1.81827200	-1.02347000
H	2.83533700	1.76623800	-1.73044300
O	-2.76769200	1.58712500	-0.25333000
C	-1.77816900	1.75474900	-1.22883400
H	-1.98888800	1.14467000	-2.12779400
H	-1.75313800	2.81497000	-1.53662100
C	0.76297400	1.39980300	-1.47088600
H	0.67181800	0.97228700	-2.47605700
C	-1.80687500	-1.11382500	-0.77409600
H	-1.35718700	-2.10120000	-0.60295300
H	-1.46928800	-0.83475000	-1.78192800
C	-3.84649600	-1.26805300	0.71134900
H	-4.93114200	-1.46044100	0.75149700
H	-3.35757300	-2.11260800	1.23032000
C	-3.34666900	-1.23219600	-0.73854700
H	-3.63396600	-2.15413400	-1.27073300
H	-3.81727900	-0.38739100	-1.26704600
C	-3.51617500	0.05274300	1.44154600
H	-4.36599200	0.75413900	1.39414200
H	-3.31230300	-0.13378600	2.50884400

TS7 ($trans_{8,a}cis_{8,1}$)-chair

Rh	-1.13134900	-0.10078000	-0.19884300
Cl	-1.52609200	2.33283100	-0.43765600
O	-3.01281500	-0.28441400	-2.55351600
O	1.76785700	1.97613300	0.67052600
C	-2.32038200	-0.22690800	-1.65752700
C	-1.27450600	-2.17768700	0.09038100
C	-1.26980100	-2.29686000	1.62649100
C	-1.85361900	-0.97168900	2.08194400
C	-1.13195600	0.19435000	2.03810700
C	0.29826100	0.27570100	1.59382300
C	0.86646800	1.70928500	1.71276700
C	2.38287500	0.78484300	0.36431700
C	1.33261600	-0.25566700	-0.07920800
C	0.57665800	-0.01754200	-1.31380600
H	-0.51639400	-2.80036900	-0.40814500
H	-2.25817900	-2.50767700	-0.28343300
H	-0.23810700	-2.39757100	2.01114300
H	-1.84914600	-3.15217200	2.01265600
H	-2.89389800	-0.92339400	2.42518600
H	-1.62939200	1.13950800	2.28013000
H	0.88837900	-0.49340100	2.11004000
H	0.05710500	2.44739800	1.64711500
H	1.38534000	1.80071000	2.69014000
H	2.86220300	0.37545400	1.28409000
H	0.62473200	-0.82276700	-2.05762900
H	0.64318800	0.99480700	-1.73351900
C	4.18149700	-0.50187300	-0.74412800

H	4.93205700	-0.51983900	-1.55197200
H	4.73535700	-0.65362400	0.20087000
C	1.98162800	-1.63206100	0.04385800
H	1.29165000	-2.44759800	-0.20706500
H	2.34022900	-1.79927800	1.07574400
C	3.18766200	-1.66585000	-0.93667300
H	3.71415700	-2.62884300	-0.82171100
H	2.79682300	-1.64332300	-1.96907400
C	3.48720600	0.87444200	-0.68645300
H	3.06002500	1.15760300	-1.66332500
H	4.20014300	1.66267900	-0.39260700

TS8 ($trans_{8,a}trans_{8,1}$)-chair

Rh	-1.13159300	-0.19815900	-0.14868300
Cl	-1.29538500	-1.63025600	1.88258600
O	-2.74362300	-2.40087000	-1.39145500
O	2.44978900	2.14569600	-0.12672400
C	-2.14623900	-1.55841600	-0.92048300
C	-1.80623800	1.15789100	-1.57734500
C	-2.52253300	2.17405500	-0.65501700
C	-2.22272600	1.78833300	0.79408000
C	-0.94867100	1.63548200	1.29490900
C	0.25331100	1.63636100	0.44808300
C	1.49643400	2.42278500	0.85249800
C	2.65950300	0.78222000	-0.02076200
C	1.35219500	-0.07879800	-0.06619000
C	0.60641800	-0.45777200	-1.27237700
H	-2.51547700	0.69636400	-2.28196600
H	-1.00777700	1.61889800	-2.18134100
H	-3.61293200	2.14264600	-0.80338500
H	-2.21070400	3.21982200	-0.83787000
H	-3.05095200	1.71524200	1.50824300
H	-0.82611300	1.39565000	2.35732400
H	0.05513400	1.98613200	-0.56953900
H	1.26167900	3.49844800	0.81794400
H	1.86284100	2.16648000	1.86757600
H	3.04624600	0.61188400	1.00473100
H	0.69698400	-1.51045800	-1.56583500
H	0.64947000	0.22481400	-2.13131000
C	4.11286300	-1.16229900	-0.32744300
H	4.77539800	-1.72578000	-1.00580700
H	4.70563300	-0.94402100	0.57947000
C	1.72513200	-1.31233300	0.78125800
H	0.89137000	-2.01410400	0.89141700
H	2.01799100	-1.01305300	1.80121900
C	2.89990800	-2.03748400	0.05441700
H	3.23443600	-2.87390900	0.69183000
H	2.49333800	-2.49847400	-0.86281800
C	3.70236400	0.18508300	-0.95990300
H	3.29074300	0.05814100	-1.97596000
H	4.56625300	0.86750600	-1.02605100

TS8 ($trans_{8,a}trans_{8,1}$)-boat

Rh	-1.11324200	-0.19491300	-0.15213400
Cl	-1.27400500	-1.61479500	1.88411100
O	-2.76214100	-2.38080200	-1.38116800
O	2.47852000	2.12586000	-0.05314500
C	-2.15202600	-1.54434700	-0.91605300
C	-1.74862400	1.16058400	-1.60068500
C	-2.48293400	2.18124900	-0.69777200
C	-2.21564000	1.79391100	0.75703800
C	-0.95224700	1.62902100	1.28156900
C	0.26864200	1.62250400	0.45950800
C	1.51261800	2.37733000	0.91979500
C	2.66810400	0.75649600	-0.00384100
C	1.34810800	-0.08812700	-0.04724300
C	0.62852600	-0.49567100	-1.25924800
H	-2.44136200	0.70182000	-2.32330100
H	-0.93215800	1.61702000	-2.18373800
H	-3.56988300	2.15229400	-0.87026600
H	-2.16468500	3.22621300	-0.87436200
H	-3.05775400	1.72860300	1.45556900
H	-0.85222000	1.38474600	2.34532700
H	0.10138300	1.99914700	-0.55434300

H	1.29288900	3.45663100	0.92525100	H	-0.88824200	1.67286600	2.04499800
H	1.85497800	2.07421700	1.93064100	H	0.18748800	2.59833600	-0.59784400
H	3.07440000	0.54350100	1.00374600	H	1.71985000	3.09882600	1.11089400
H	0.72034500	-1.55772600	-1.51530500	H	1.26011800	1.66620000	2.10057300
H	0.68192700	0.16401700	-2.13513300	H	0.71930400	1.15482900	-1.98949500
C	3.65161800	-1.35682500	-0.87699400	H	0.19860300	-1.02058100	-2.18139800
H	3.01186800	-1.78933400	-1.66320000	C	1.60161700	-1.94089100	-0.77373800
H	4.66273500	-1.76221600	-1.04453200	H	1.80739000	-2.53799600	-1.68140100
C	1.68646900	-1.29788900	0.84866100	H	1.12124400	-2.61394200	-0.04712000
H	0.95088100	-2.09578900	0.69907000	C	3.44412800	-0.21796600	-0.95906700
H	1.62031100	-1.03224700	1.91628400	H	3.50483200	-0.42198700	-2.04395200
C	3.13295000	-1.81100000	0.50727400	H	4.44984800	0.07944900	-0.61877300
H	3.84496500	-1.47739200	1.28131500	C	2.93531600	-1.44358200	-0.19171100
H	3.12917700	-2.91205500	0.55450200	H	3.67595800	-2.25949200	-0.22942600
C	3.66200300	0.19242700	-1.01171800	H	2.79714900	-1.16672200	0.86550000
H	3.39217500	0.51161500	-2.03232800	C	2.50273200	0.96297300	-0.71246400
H	4.65756800	0.61107700	-0.78629100	H	2.80054600	1.83532100	-1.33496500

TS9 ($cis_{8,a}cis_{8,1}$)-chair

Rh	-0.90140300	-0.24141100	0.00999800
Cl	0.15673300	-0.98713400	2.11256900
O	-2.41190700	-2.83708300	-0.07503500
O	2.58898800	1.28706700	0.63635000
C	-1.85245700	-1.85016900	-0.04368900
C	-1.98985100	0.52476400	-1.61187600
C	-2.49448600	1.88523000	-1.07677300
C	-2.26010800	1.83161300	0.42364200
C	-1.00123300	1.76944100	0.96116200
C	0.28239400	1.79944800	0.14962000
C	1.49371100	2.01251200	1.08246600
C	1.02944600	0.62333200	-1.08366000
C	0.63348600	-0.82048900	-1.19331900
H	-2.84528500	-0.12258200	-1.86019200
H	-1.37932000	0.62493000	-2.52601600
H	-3.55720600	2.07008800	-1.29956900
H	-1.92756800	2.73246900	-1.50483600
H	-3.11083800	1.83762100	1.11537200

TS9 ($cis_{8,a}cis_{8,1}$)-boat

Rh	-0.88695700	-0.14980300	-0.00169900
Cl	-0.06940800	-1.29908700	2.03030700
O	-2.77904400	-2.44471100	-0.33041800
O	2.99778500	1.65893900	-0.18169000
C	-2.06957600	-1.56760700	-0.20407200
C	-1.87328400	1.02221100	-1.42188600
C	-2.34292100	2.22993300	-0.57043700
C	-1.79094100	2.02068300	0.83545200
C	-0.46585100	1.78551500	1.08793500
C	0.61593400	1.78593500	0.02177900
C	1.98756200	2.09954400	0.66576700
C	1.16937700	0.52786600	-1.12793400
C	0.44965700	-0.77402400	-1.38962400
H	-2.72844600	0.51332800	-1.89267500
H	-1.18918000	1.32436900	-2.23407900
H	-3.44133300	2.28423600	-0.51837700
H	-2.00151600	3.20411100	-0.97064300
H	-2.46916900	2.06156100	1.69618000

H	-0.14809500	1.58891000	2.11723700
H	0.34227700	2.54884100	-0.71795000
H	2.10338000	3.18598000	0.80674600
H	2.03870700	1.61342900	1.65879600
H	1.10864200	1.16962900	-2.01530300
H	-0.05324200	-0.76227900	-2.36667800
C	1.28465500	-2.05221300	-1.25847200
H	1.79910900	-2.15786200	-2.23414500
H	0.61174700	-2.92298700	-1.18705200
C	2.85015700	-0.72725200	0.34143100
H	3.92386700	-0.76050900	0.58893000
H	2.30494000	-0.47419200	1.26284900
C	2.34617600	-2.11019200	-0.13504000
H	3.19005700	-2.71838500	-0.50163800
H	1.92449200	-2.62829900	0.73799900
C	2.63469600	0.39640100	-0.67755600
H	3.25300000	0.22109700	-1.57615100
H	-0.95634100	-3.39624900	0.00585700
H	-0.88768300	-2.25172300	-1.33450600
C	-3.22401900	-0.80746900	-0.59554200
H	-4.32009200	-0.72071100	-0.68278500
H	-2.79445900	-0.45458600	-1.55115200
C	-2.79273700	-2.25751100	-0.31915400
H	-3.20582700	-2.57874200	0.65551400
H	-3.21549700	-2.93565900	-1.07922900
C	-2.74825900	0.09213000	0.54669700
H	-3.25422500	-0.23989300	1.47625100
H	-1.12616900	1.17998600	-1.28954800
C	0.64585100	-0.29734900	-2.06155700
H	-0.41396300	-0.41166000	-2.33959800
H	1.18943700	-1.15013000	-2.49847400
C	1.23912500	1.05485100	-2.52505900
H	0.57715700	1.62499000	-3.20467900
H	2.18990000	0.91192900	-3.06191100

TS10 ($cis_{8,a}trans_{8,1}$)-chair

Rh	0.91261700	-0.07883300	-0.00200900
Cl	1.51367600	0.43235100	2.34712600
O	3.17311200	-2.07114300	-0.02195100
O	-3.05837400	1.44691000	0.33640400
C	2.32902200	-1.31335600	-0.02492600
C	1.51490800	1.85805200	-1.25387600
C	0.55280300	2.11017300	-0.29200400
C	-0.78994300	1.48539200	-0.29233000
C	-1.92120000	2.25382100	0.38171400
C	-1.25786700	-0.06398000	0.85360300
C	-0.59955000	-1.36230600	0.63769600
H	2.48337700	2.35626800	-1.12996400
H	0.82545800	2.71409200	0.58112800
H	-1.64385400	2.54971100	1.41342800
H	-2.13656300	3.16892000	-0.19432900
H	-0.98513300	0.37161300	1.82226200
H	-0.20999000	-1.77667800	1.57653600
C	-1.25375300	-2.38079900	-0.30378600

TS10 ($cis_{8,a}trans_{8,1}$)-boat

Rh	0.92870700	0.06212000	-0.00696800
Cl	1.52903900	-0.66678300	-2.30309200
O	3.24469100	1.97851600	-0.18838100
O	-3.12472100	-1.26438400	-0.16391500
C	2.37728800	1.25115600	-0.11148200
C	1.42283200	-1.79893000	1.39817900
C	0.44166600	-2.08056100	0.46319300
C	-0.85864400	-1.38175300	0.40922000
C	-2.04881100	-2.14368400	-0.16613000
C	-1.24499100	0.06552100	-0.93563800
C	-0.56578900	1.34540800	-0.72833500
H	2.36230400	-2.35780600	1.31744300
H	0.67625300	-2.77090700	-0.35542500
H	-1.81981900	-2.54976500	-1.17272800
H	-2.30505900	-2.98405700	0.49919900
H	-0.88743600	-0.44976900	-1.83432500
H	-0.11044700	1.74207500	-1.64469700
C	-1.23305600	2.38020400	0.18167000

H	-1.56487300	3.22893600	-0.44607000	H	-2.91061300	1.75074500	1.41562900
H	-0.50251300	2.79527900	0.89585500	H	-0.57411800	1.77483700	1.98087800
C	-3.42440600	1.13977000	-0.04429000	H	-0.07260500	2.43252300	-0.97048700
H	-3.76014200	1.87912200	-0.79288800	H	1.57503000	3.60833600	0.33863400
H	-4.32438800	0.76421500	0.46933200	H	1.49879300	2.38039000	1.64754200
C	-2.45934100	1.82495200	0.93129600	H	2.13281000	0.22389900	1.01822600
H	-2.97244300	2.64611200	1.45929800	H	1.33779300	1.09773300	-1.78966600
H	-2.15255800	1.10308900	1.70714500	H	0.22676000	-0.86986200	-2.24820900
C	-2.77920700	-0.04710600	-0.77615600	C	1.53252600	-2.06539900	-0.96703500
H	-3.14712100	-0.06767800	-1.82163700	H	1.72795600	-2.50886800	-1.95954400
H	-1.16798600	-0.94687500	1.36675000	H	0.99492400	-2.83079300	-0.38513800
C	0.72497000	0.47730900	2.02700800	C	3.45836000	-0.37717400	-0.53150800
H	-0.30369800	0.73202300	2.31992700	H	4.40443400	-0.23230000	0.01544800
H	1.37253600	1.29836900	2.37339600	H	3.65423800	-0.19356800	-1.60417000
C	1.19132200	-0.88324900	2.60020700	C	2.89487900	-1.79180500	-0.27491100
H	0.46291500	-1.34377100	3.29445900	H	3.61730300	-2.55713300	-0.60295200
H	2.13621800	-0.78593700	3.15698600	H	2.76563700	-1.91089100	0.81359100

TS11 (trans$_{8,a}$cis$_{8,1}$)-chair

Rh	-0.88331700	-0.22881400	-0.00019000
Cl	0.16495900	-1.09847500	2.06613500
O	-2.55564400	-2.71894100	-0.05438100
O	2.70424200	1.93576500	0.04172400
C	-1.93580200	-1.76831900	-0.03008200
C	-1.93899000	0.62974400	-1.57988600
C	-2.68854000	1.77149500	-0.85045200
C	-2.18796100	1.76198500	0.59103300
C	-0.85597000	1.81656900	0.92334300
C	0.26786200	1.88410500	-0.08406300
C	1.54954600	2.52817800	0.55088500
C	2.39587100	0.56839600	0.00079600
C	1.15411800	0.51393700	-0.87641500
C	0.61507500	-0.84616000	-1.22141600
H	-2.63975300	-0.05597400	-2.08033100
H	-1.24307300	1.00381000	-2.35153400
H	-3.77638800	1.60156500	-0.84930300
H	-2.52880600	2.76837400	-1.30483800

TS11 (trans$_{8,a}$cis$_{8,1}$)-boat

Rh	-0.93823300	-0.23922700	0.01483900
Cl	-0.10569100	-0.74653200	2.28969700
O	-2.61622700	-2.71387100	0.01858600
O	2.76539400	1.79013500	0.21242700
C	-1.98857800	-1.76742900	0.01987300
C	-1.78552200	0.46440000	-1.75671400
C	-2.47274000	1.77136700	-1.28730600
C	-2.15997900	1.92219000	0.19718800
C	-0.88592000	1.92109700	0.70039800
C	0.37467700	1.82609000	-0.14261200
C	1.59082000	2.39023600	0.65956300
C	2.44718300	0.43219500	0.08791400
C	1.20486200	0.40937200	-0.79542000
C	0.64792200	-0.98592000	-0.98624600
H	-2.51128000	-0.22626600	-2.21233800
H	-0.99809800	0.65253500	-2.50767200
H	-3.56455300	1.72701000	-1.42168300
H	-2.12566700	2.66584900	-1.83926400

H	-2.98138100	2.05311700	0.91190400
H	-0.74768200	1.98685900	1.78427100
H	0.19961900	2.38237400	-1.07290900
H	1.67109400	3.48085300	0.53055900
H	1.42469400	2.16167700	1.73064800
H	2.17382700	0.02229900	1.07878300
H	1.43798000	0.86153900	-1.77010800
H	0.39000000	-1.18249600	-2.03729700
C	3.55895000	-0.41400000	-0.52651800
H	4.39299200	-0.47659200	0.19067300
H	3.94188000	0.10801500	-1.42026500
C	1.56025400	-2.07649500	-0.41786400
H	1.21709300	-3.06280800	-0.77138500
H	1.50915400	-2.08950000	0.68050600
C	3.01903500	-1.83301500	-0.89309500
H	3.67017100	-2.61077100	-0.46204800
H	3.05828100	-1.96808300	-1.98805000

TS12 (trans$_{8,a}$trans$_{8,1}$)-boat

Rh	-0.93685800	-0.14556000	0.00563500
Cl	-1.17271400	-0.23009300	2.46902300
O	-3.02793400	-2.29728700	-0.22811100
O	2.93854200	1.61368900	0.24908500
C	-2.25253000	-1.47308100	-0.14639200
C	-1.85668600	1.94522700	-0.64241900
C	-0.80342200	2.09843500	0.24353400
C	0.56927600	1.66090200	-0.09040000
C	1.77494900	2.35053400	0.56254500
C	2.58654700	0.34102800	-0.22463600
C	1.30362100	-0.03058400	0.48286500
C	0.74452000	-1.35272200	0.17172800
H	-2.84793400	2.26144900	-0.29786600
H	-1.00920900	2.43255400	1.26648000
H	0.72975900	1.64081900	-1.17317000
H	1.64001300	2.43770200	1.65728600
H	1.87253800	3.36711900	0.14389100
H	2.42453000	0.37928300	-1.32068300
H	1.33259800	0.18069500	1.55924500
H	0.56445100	-1.94886100	1.07617700
C	3.59604500	-0.77741200	0.03507600
H	4.56499000	-0.51623400	-0.41986600
H	3.75690000	-0.85837200	1.12320600
C	1.51579000	-2.07679300	-0.92387400
H	1.14431600	-3.10566300	-1.05438000
H	1.38446500	-1.56895000	-1.89289200
C	3.03712200	-2.11564400	-0.55440800
H	3.60539900	-2.39625500	-1.45701100
H	3.20254500	-2.92194700	0.17868200
C	-0.93576800	0.14126100	-2.05759200
H	-1.47774500	-0.62915100	-2.62735000
H	0.08554900	0.19213200	-2.47193100
C	-1.67261700	1.50438300	-2.09819400
H	-2.66724600	1.40591600	-2.56006300
H	-1.13712600	2.28511700	-2.67151600

CO

C	0.00000000	0.00000000	-0.64339800
O	0.00000000	0.00000000	0.48254900

TS13 (cis$_{8,a}$trans$_{8,1}$)-chair

Rh	1.12847700	-0.01094500	0.22362600
Cl	3.29924800	1.14526100	0.14290700
O	1.50971600	-0.04252700	3.23480100
O	-3.95074100	1.14233000	0.49607500
C	1.33345800	-0.00203600	2.11852700
C	0.49657100	1.74045500	-1.44767800
C	-0.54141300	2.06448100	-0.63413600
C	-1.82371400	1.29193000	-0.49902100
C	-3.08983000	2.07705700	-0.11812400
C	-1.77746600	0.28542400	0.67496600
C	-0.78332500	-0.87739400	0.51128700
H	1.38751100	2.37659500	-1.42606800
H	-0.42632000	2.95479700	0.00019300
H	-2.83616600	2.89188500	0.59087900

H	-3.59851600	2.52888500	-0.98656300
H	-1.50674200	0.86549500	1.57796400
H	-0.75234100	-1.40720400	1.48171800
C	-1.28524500	-1.92539800	-0.50040600
H	-0.61386600	-2.80113700	-0.49520200
H	-1.28060000	-1.53177600	-1.53400500
C	-3.69478800	-1.18246500	-0.19256600
H	-4.72579400	-1.49908400	0.03961600
H	-3.72273800	-0.76310700	-1.21425200
C	-2.72149500	-2.37097800	-0.15385700
H	-2.72360400	-2.82616100	0.85482300
H	-3.05773700	-3.15608700	-0.85289800
C	-3.27669000	-0.06914000	0.78502000
H	-3.53330000	-0.37233200	1.81642900
H	-2.02103000	0.73457800	-1.42783700
C	1.48821300	-0.63425300	-1.97921200
H	1.16794500	-1.52138000	-2.54394700
H	2.53577500	-0.39041600	-2.21037500
C	0.54185800	0.55050400	-2.40033900
H	-0.46914100	0.14950700	-2.55079000
H	0.90290900	0.89280900	-3.38638500
C	1.78952600	-1.57775100	-0.48215500
O	2.24991300	-2.64047900	-0.52084000

TS14 ($trans_{8,a}cis_{8,1}$)-boat

Rh	-0.99508500	-0.10473300	0.16409700
Cl	-3.02825600	0.59458000	1.36354700
O	-0.37850500	-1.62005700	2.70956200
O	-2.40622200	-2.20919200	-1.36490100
O	3.65671700	1.11861600	0.60896400
C	-0.56426600	-1.04967000	1.74960800
C	-1.92986400	-1.21659000	-0.99143800
C	-2.06695900	0.27671900	-1.87992400
C	-1.16988900	1.57574500	-1.91474800
C	-0.92364600	2.18670900	-0.54100700
C	0.26568300	2.23442400	0.11888500
C	1.63426000	1.86374400	-0.42311400
C	2.77900700	2.20748300	0.59196400
C	2.86549300	-0.02258800	0.43565100
C	1.90722100	0.35460100	-0.70284900
C	0.76382000	-0.67861900	-0.84364300
H	-3.11612700	0.53767800	-1.67351700
H	-1.97913500	-0.19901000	-2.86801200
H	-1.70187800	2.30318800	-2.55381500
H	-0.21423200	1.34279400	-2.40685800
H	-1.80546600	2.58773300	-0.02935000
H	0.23955500	2.70192000	1.11273500
H	1.78546400	2.43421700	-1.35554400
H	3.34625500	3.11108500	0.32081800
H	2.33983000	2.36380300	1.59976600
H	2.26615500	-0.20195800	1.35861000
H	2.52365800	0.31513800	-1.61973900
H	0.48838700	-0.71233100	-1.91361400
C	1.32689900	-2.09176300	-0.49548900
H	1.19900300	-2.32633900	0.57481700
H	0.75239100	-2.85897200	-1.04135400
C	3.67889800	-1.27249700	0.08435200
H	4.00361600	-1.78591400	1.00456500
H	4.58979600	-0.94495200	-0.44471500
C	2.83392800	-2.22161600	-0.80836600
H	3.00345100	-1.98932100	-1.87441500
H	3.15903500	-3.26503400	-0.66333800

TS15 ($cis_{8,a}trans_{8,1}$)-chair

O	-3.16524400	-1.91500600	-0.94121000
O	0.86977400	2.69524600	0.09277600
C	0.70183800	-0.97413200	1.88360000
C	-1.41898100	-0.38398000	-0.64253700
C	-0.91484200	1.05683000	-0.32871700
C	0.04023700	-1.71149100	0.92373900
C	-1.38262900	-1.42172700	0.49882100
C	-2.88573300	-0.54173400	-1.12532000
C	-2.17588000	-2.55500700	-0.16529700
C	0.43947300	1.67322100	0.58796800

C	0.47652500	1.52643600	2.12483000
C	0.07518800	0.15568200	2.68224500
C	-2.02370500	1.87394800	0.40433400
C	-3.88003300	0.34156300	-0.36702600
C	-3.37094900	1.78667300	-0.33020800
H	-0.80642300	-0.80040100	-1.46284500
H	-0.73552400	1.56739800	-1.28739600
H	0.52637700	-2.61357600	0.53093200
H	-1.96148700	-1.03706000	1.35435900
H	-2.95346700	-0.31074600	-2.20454300
H	-2.66336900	-3.22863700	0.55860600
H	-1.50717300	-3.16357300	-0.80766000
H	1.52533100	1.75457200	2.37923100
H	-0.13480500	2.33790700	2.55865200
H	-1.02127800	0.05525800	2.69363800
H	0.40849200	0.07938200	3.73031400
H	-1.69494900	2.92244600	0.47390900
H	-2.16267600	1.50198500	1.43461000
H	-4.87142800	0.26818500	-0.84463100
H	-3.99485500	-0.04145100	0.66292700
H	-4.10077900	2.44015400	0.17701100
H	-3.25844600	2.17793100	-1.35866900
H	1.69645800	-1.31700900	2.18987700
Rh	1.24442500	-0.13692300	-0.18954500
Cl	3.23709000	-1.33759000	-0.08732500
C	2.06385600	0.79088700	-1.70529600
O	2.57224100	1.29535700	-2.57795400

TS16 (trans$_{8,a}$cis$_{8,1}$)-boat

Rh	-1.06517800	0.03167100	-0.28983500
Cl	-3.02325500	-0.85530300	-1.16577300
O	-0.90648600	1.55542000	-2.99308900
O	-0.49997600	2.70334500	0.62008800
O	2.60644600	-2.11021000	-0.71073400
C	-0.94842300	1.03461800	-1.99111500
C	-0.25274800	1.66047200	1.18371800
C	-0.96140100	1.30328100	2.49655500
C	-0.90083800	-0.19050000	2.81657100
C	-1.42417500	-1.00941000	1.64664200
C	-0.61897700	-1.77321500	0.81071300
C	0.89190700	-1.84150900	0.92803200
C	1.49281600	-2.76920400	-0.17928200
C	2.29993900	-0.74870400	-0.71178700
C	1.69708000	-0.51523400	0.69660100
C	1.18949000	0.97618400	0.89440700
H	-2.00244900	1.64823300	2.38728300
H	-0.49838500	1.91632400	3.29348900
H	-1.50768700	-0.40603900	3.71203400
H	0.13410500	-0.48437200	3.05982800
H	-2.50479900	-1.19097600	1.61237800
H	-1.10079700	-2.55263000	0.20928800
H	1.14350100	-2.23888500	1.92714600
H	1.81525700	-3.74849300	0.20563800
H	0.73067900	-2.93311400	-0.96746600
H	1.51769400	-0.53830900	-1.47473200
H	2.56704500	-0.59040800	1.37012300
H	1.55019000	1.21197700	1.91689500
C	1.97231000	1.90351700	-0.07310900
H	1.46933400	1.93357400	-1.05447100
H	1.92498400	2.93166000	0.31398600
C	3.54555600	0.09997700	-0.97427900
H	3.67622900	0.24051700	-2.05971900
H	4.41971500	-0.46744700	-0.61391100
C	3.43389500	1.46213300	-0.25080700
H	3.91074400	1.40401900	0.74442900
H	3.98455900	2.23647000	-0.80879000

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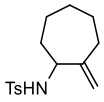
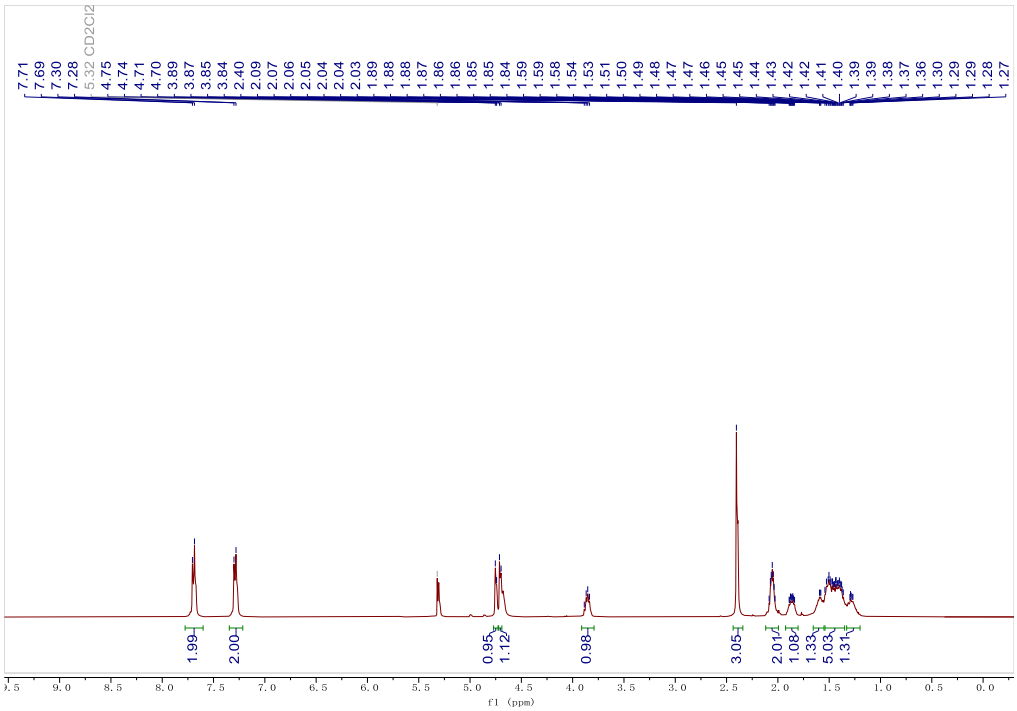
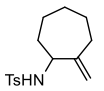
8. NMR Spectra and Crystal Structures of New Compounds

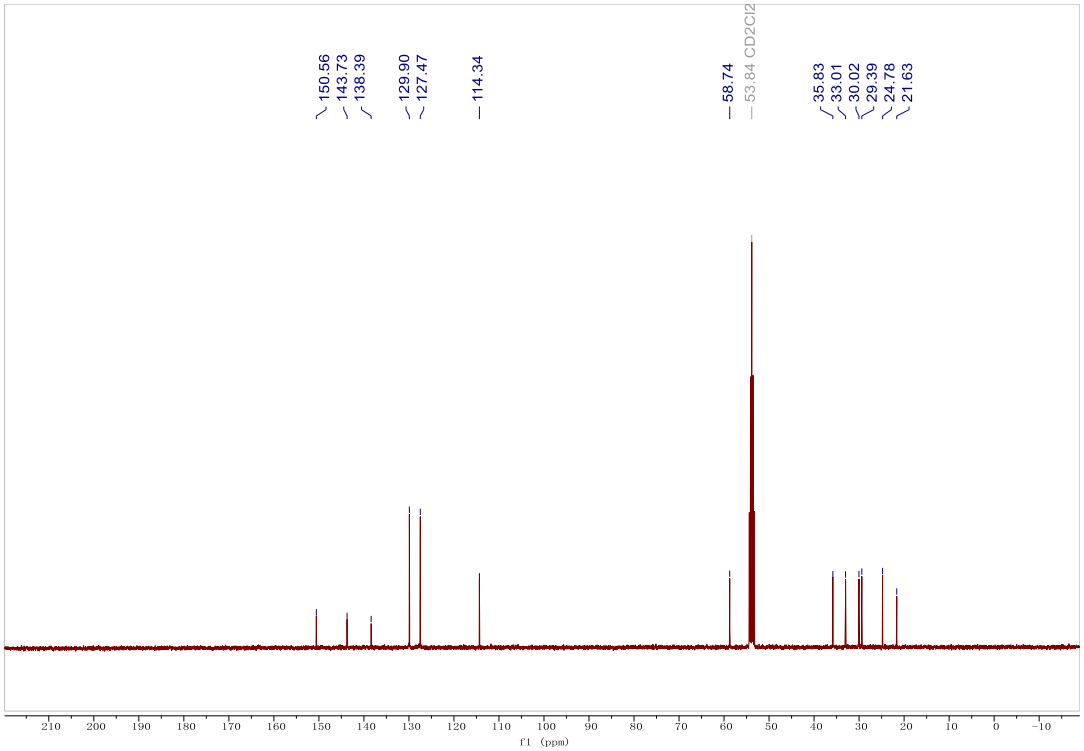


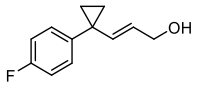
S9 ^{1}H NMR in CD_2Cl_2, 400 MHz





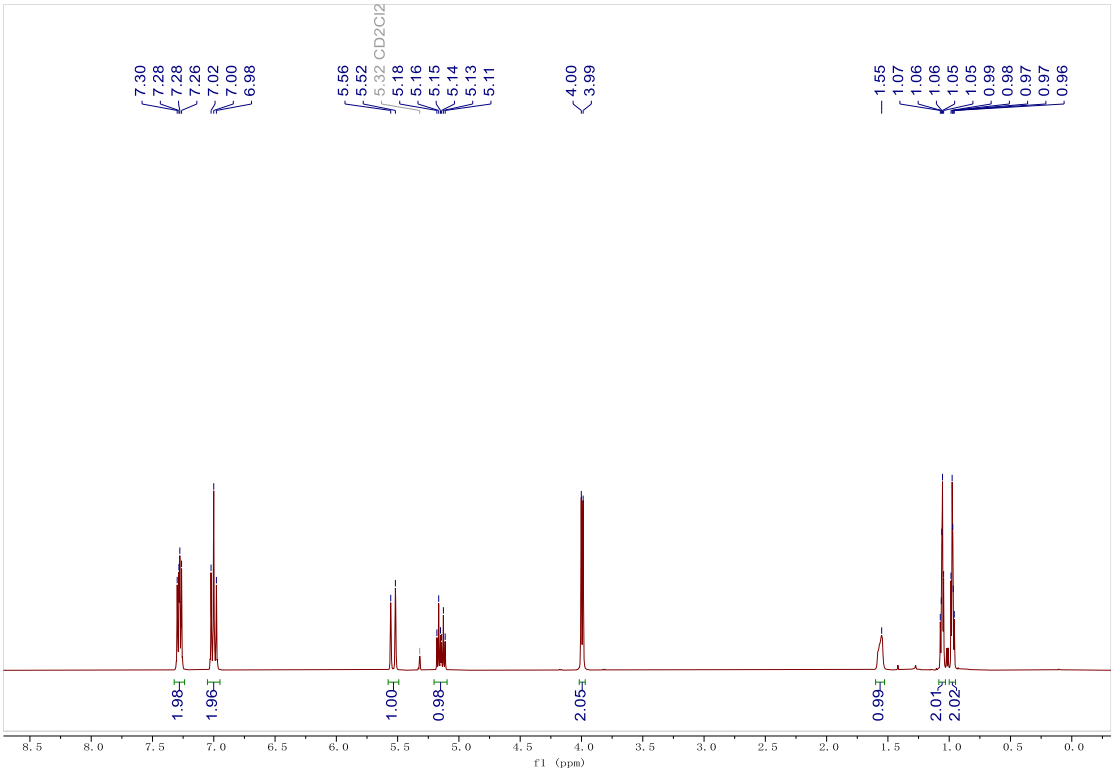
S9 ^{13}C NMR in CD_2Cl_2, 101 MHz

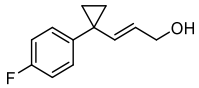




S23

^{1}H NMR in CD_2Cl_2, 400 MHz





S23

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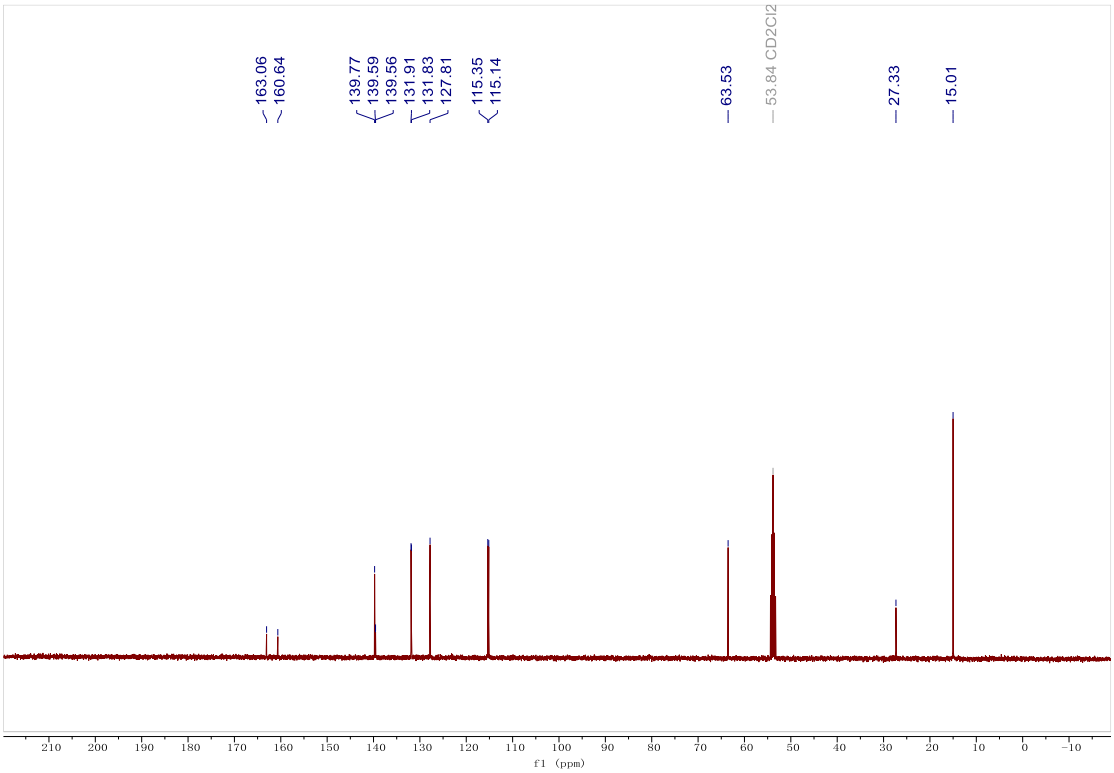
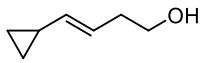
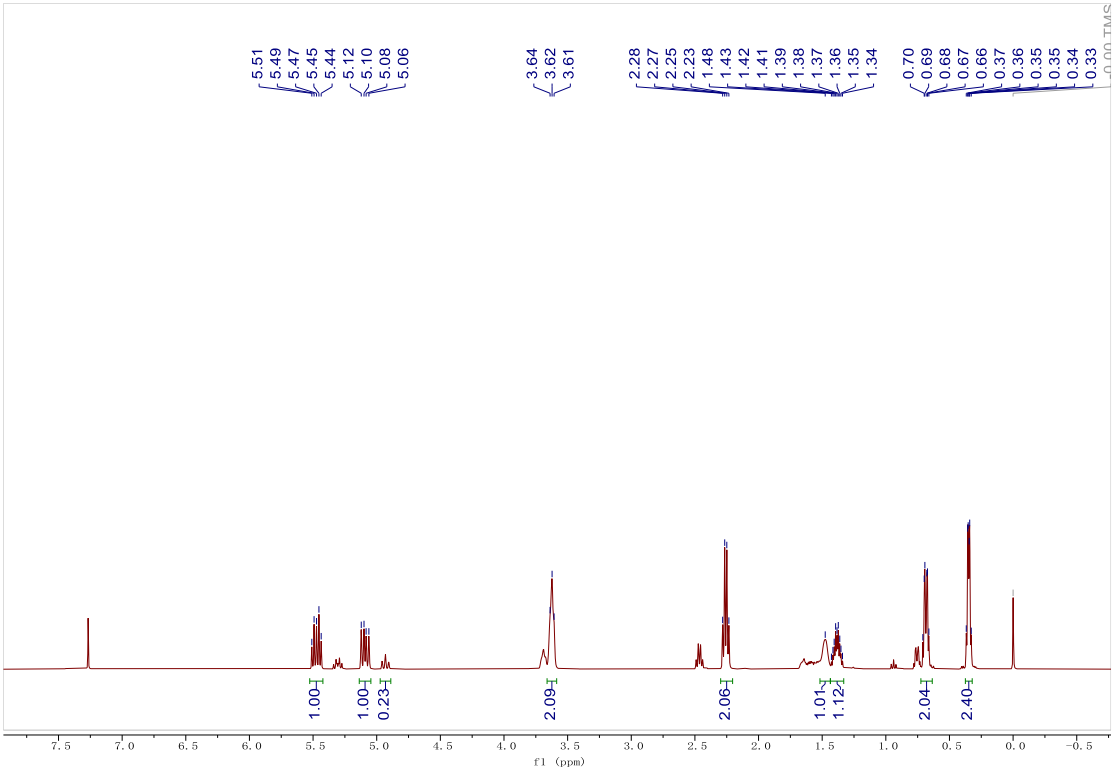
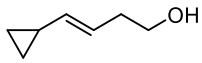




E/Z = 4.3:1 **S38**

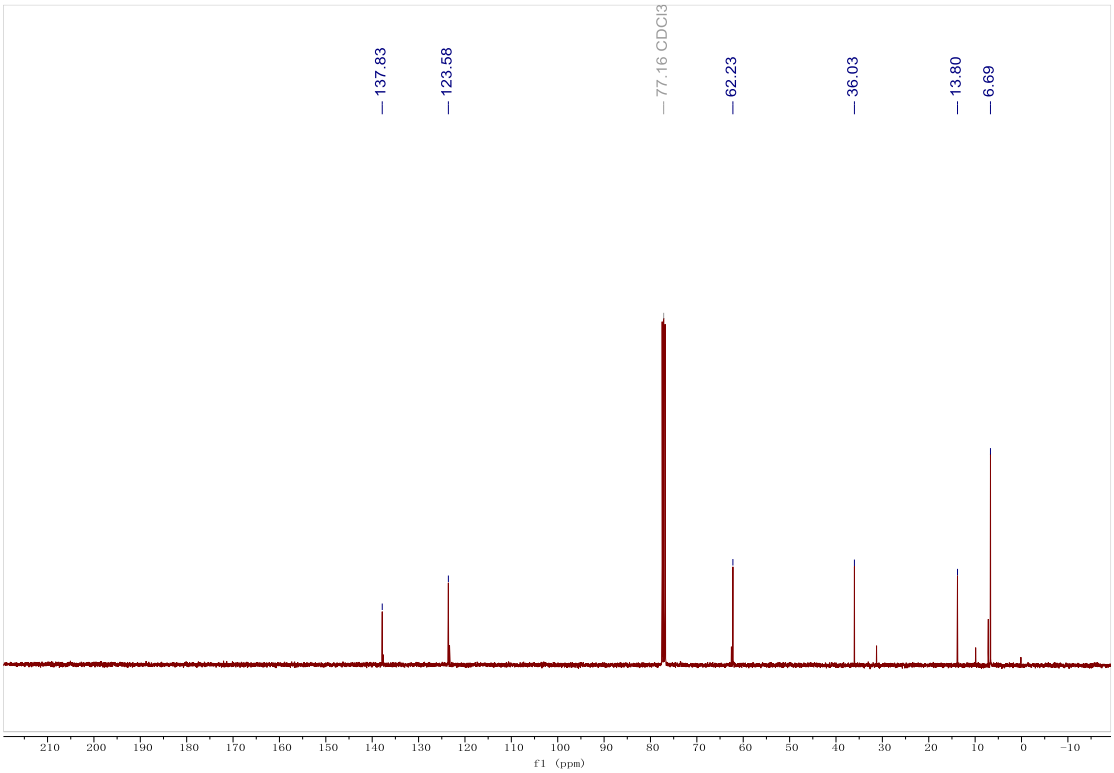
^{1}H NMR in $CDCl_3$, 400 MHz

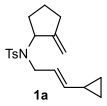




E/Z = 4.3:1 **S38**

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





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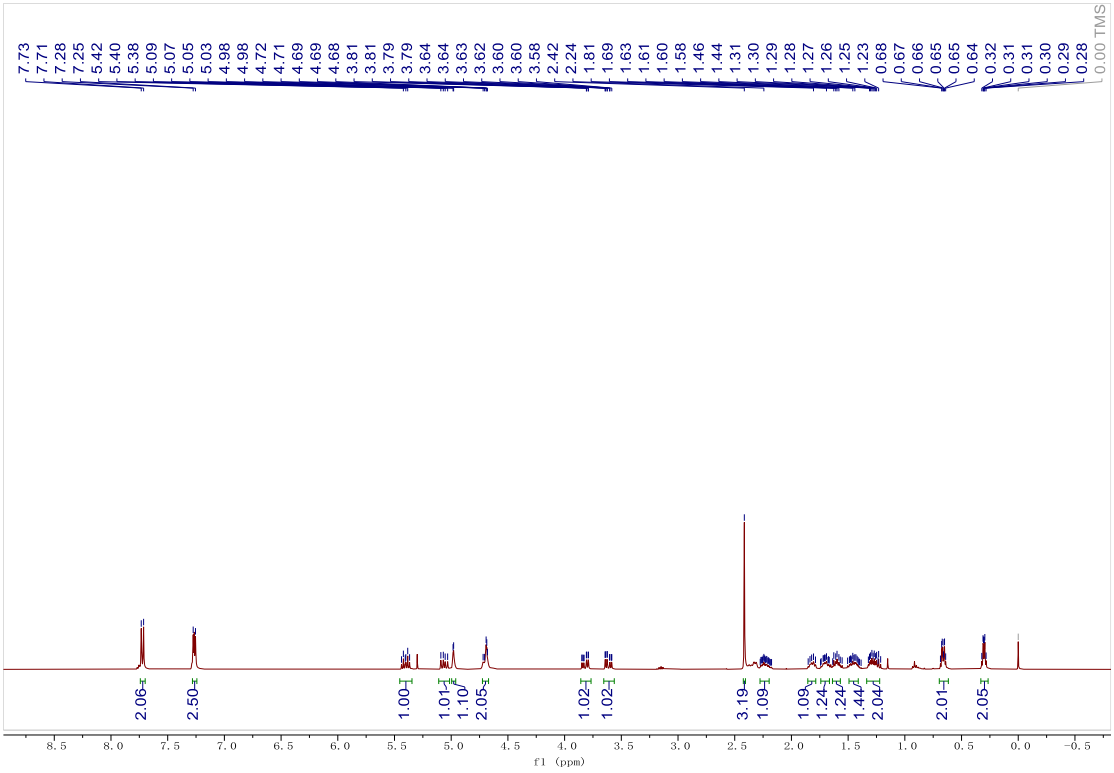
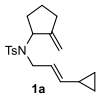
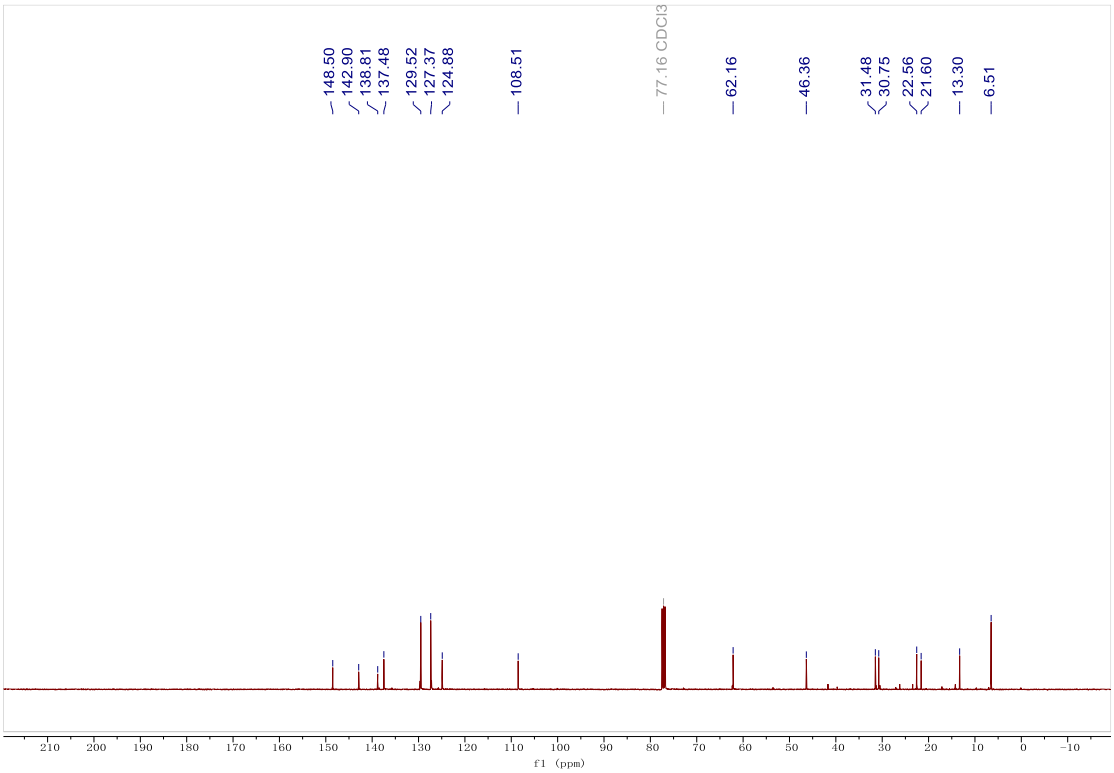
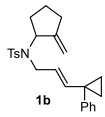




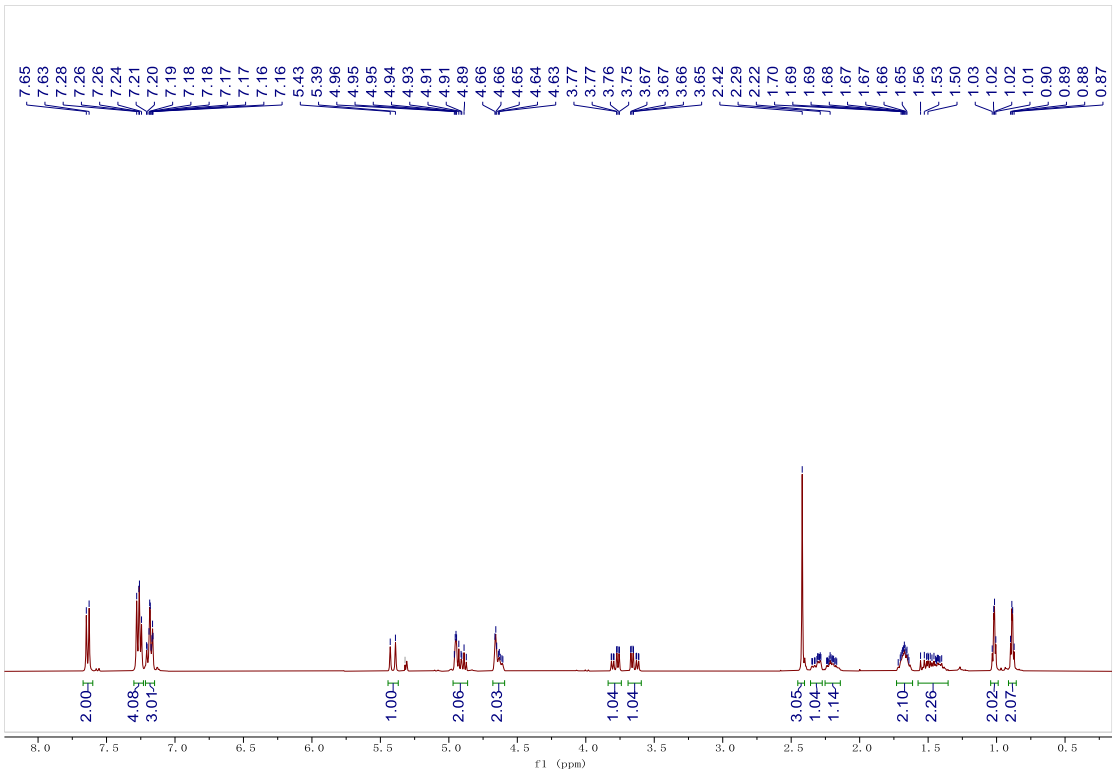
^{13}C NMR in $CDCl_3$, 101 MHz

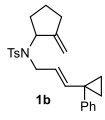




1b

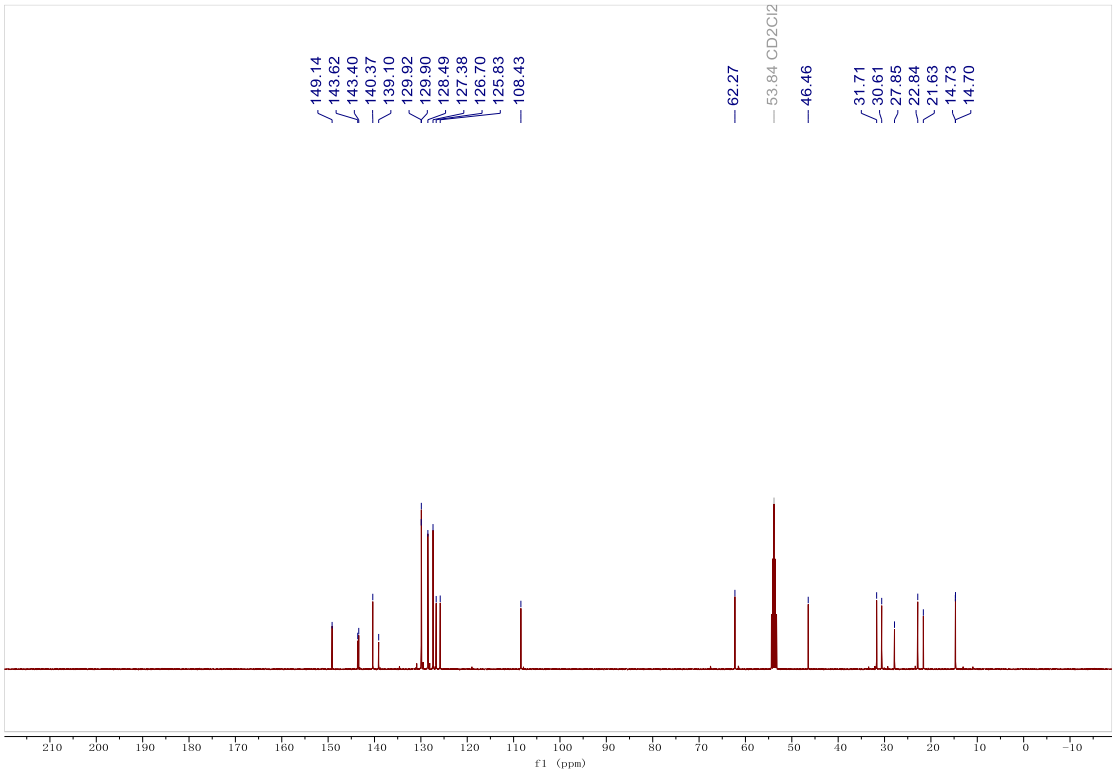
^{1}H NMR in CD_2Cl_2, 400 MHz

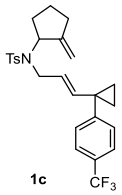




1b

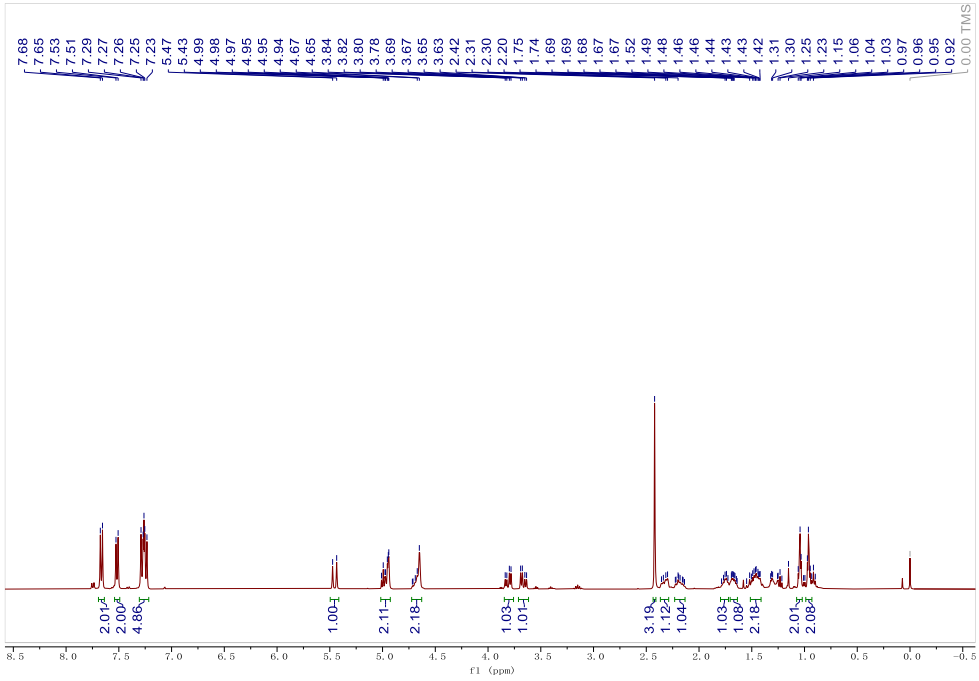
^{13}C NMR in CD_2Cl_2, 101 MHz

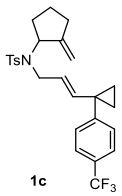




1c

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





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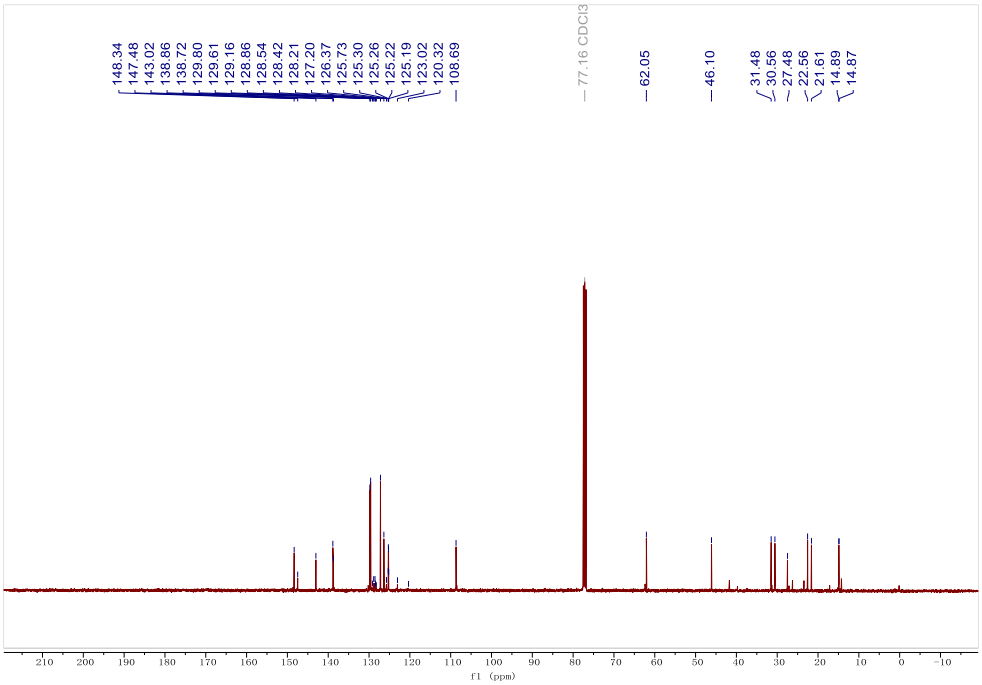

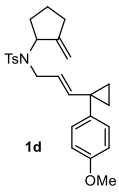

1d

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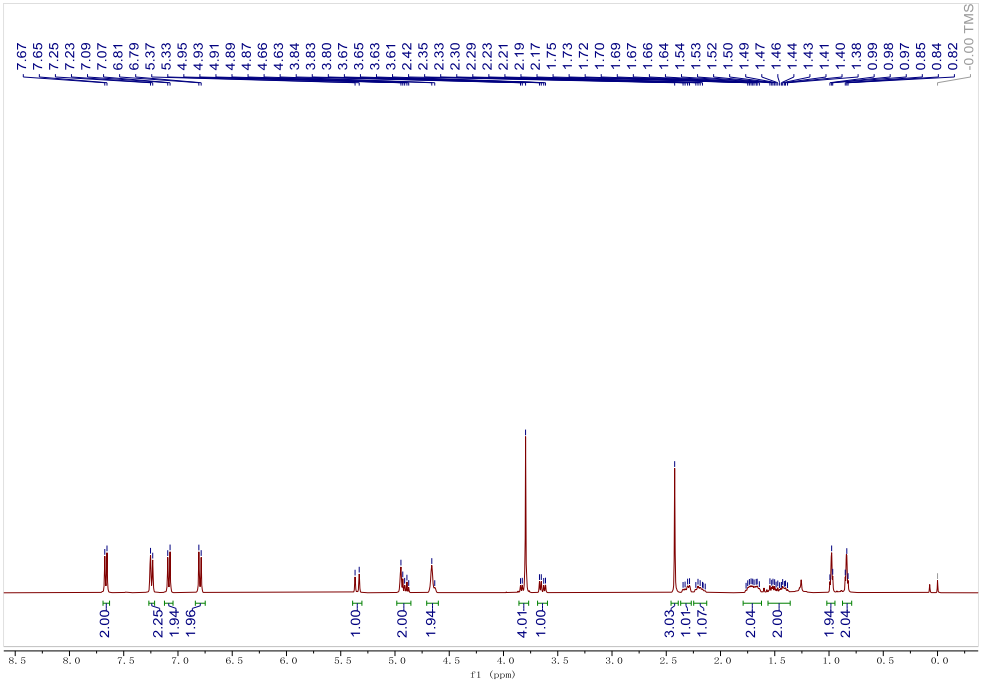

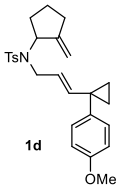

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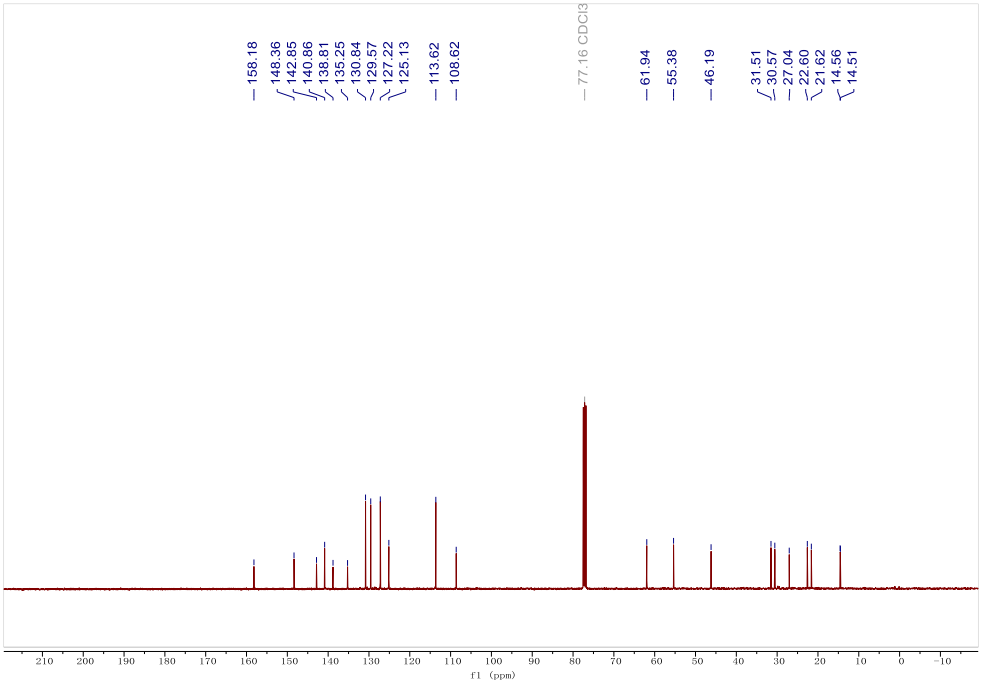

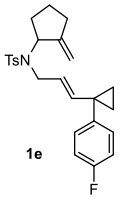

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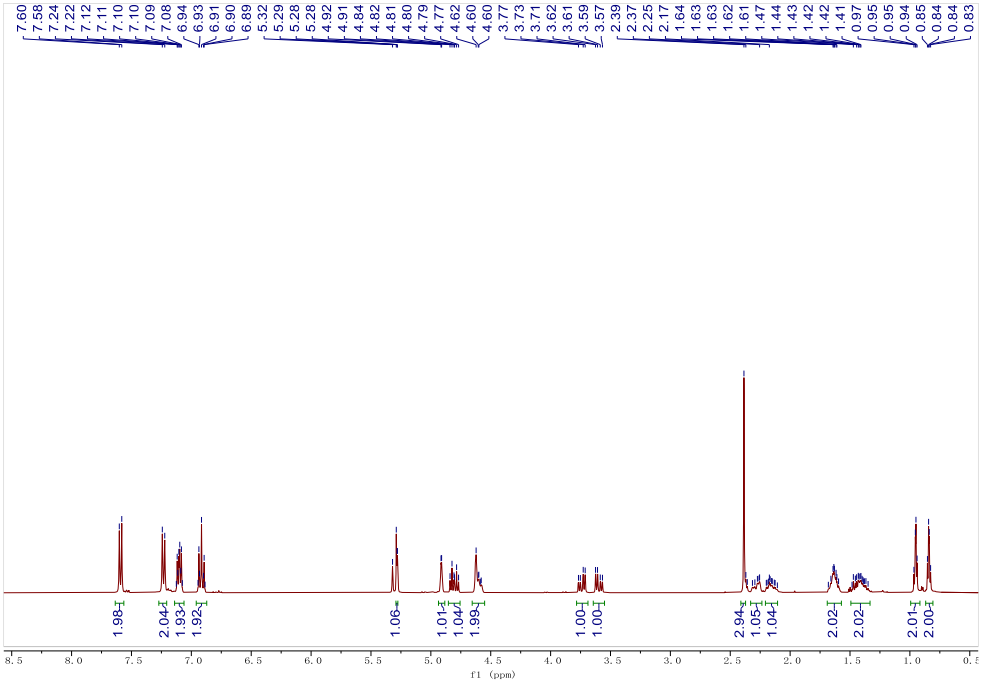
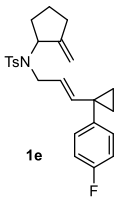
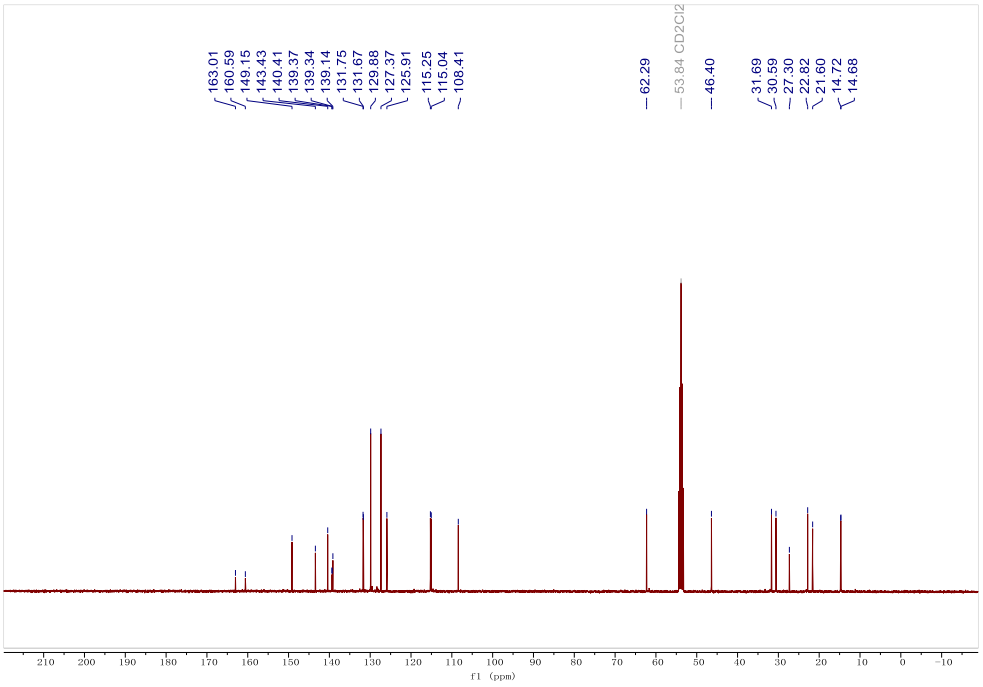
^{1}H NMR in CD_2Cl_2, 400 MHz

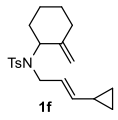




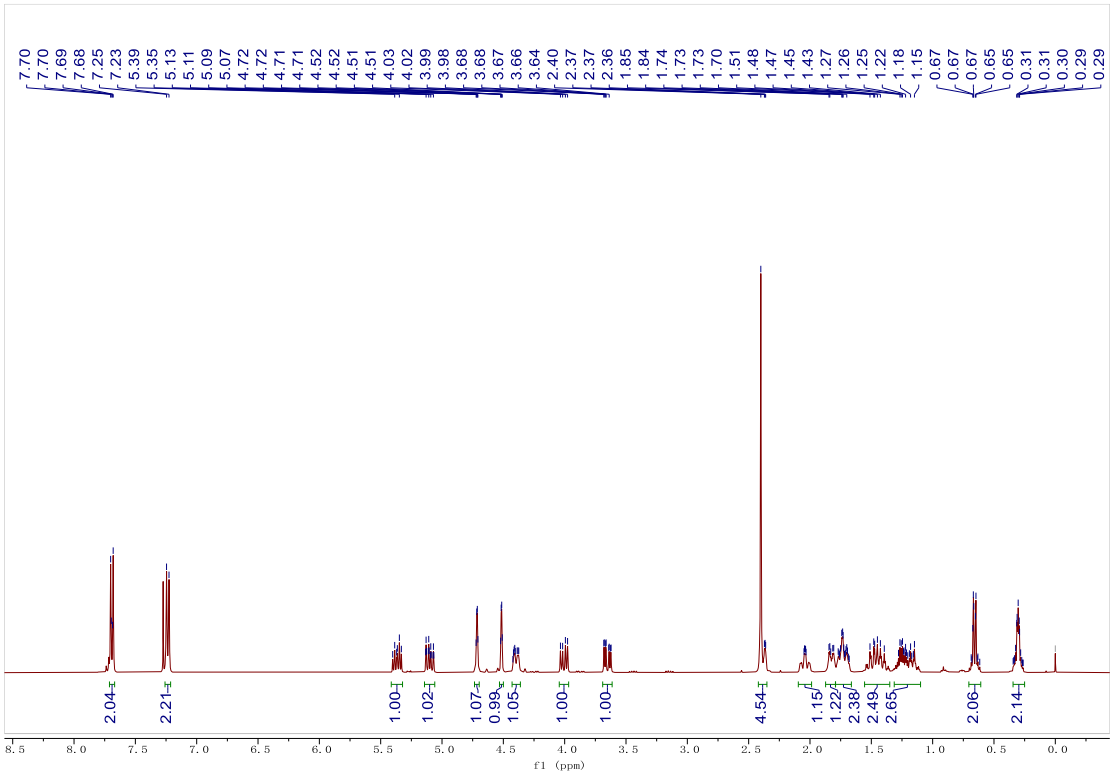
1e

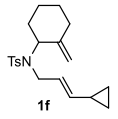
^{13}C NMR in CD_2Cl_2, 101 MHz



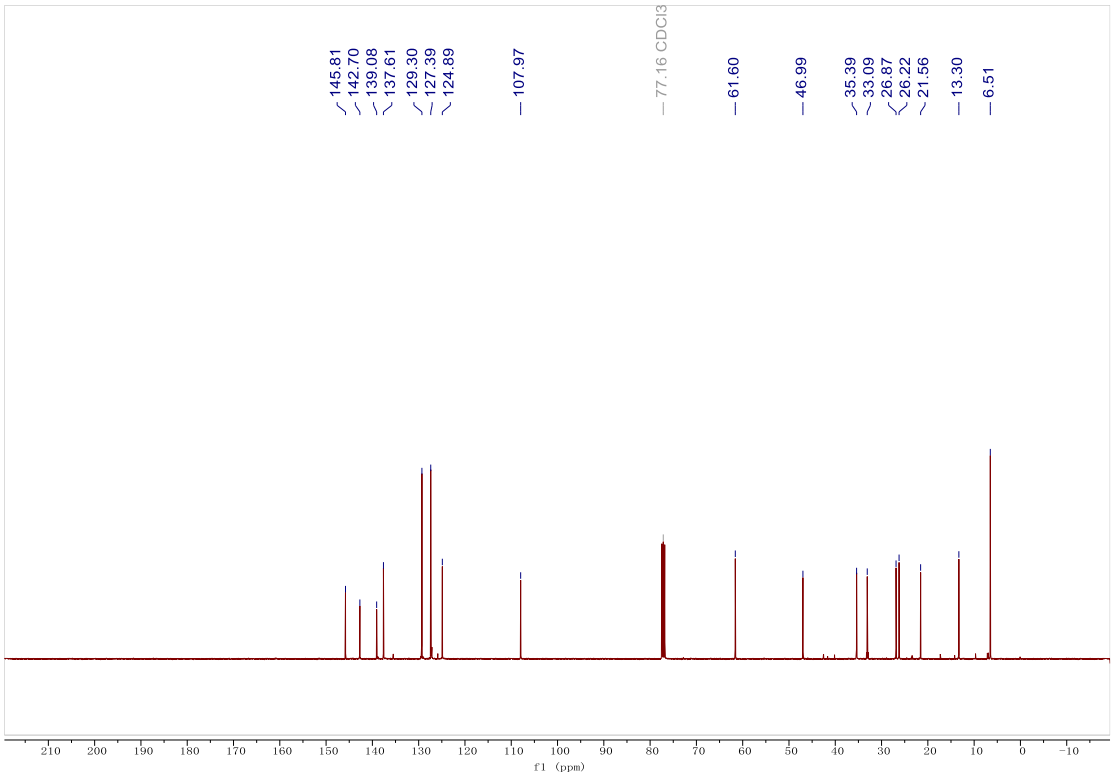


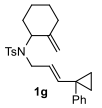
^{1}H NMR in $CDCl_3$, 400 MHz



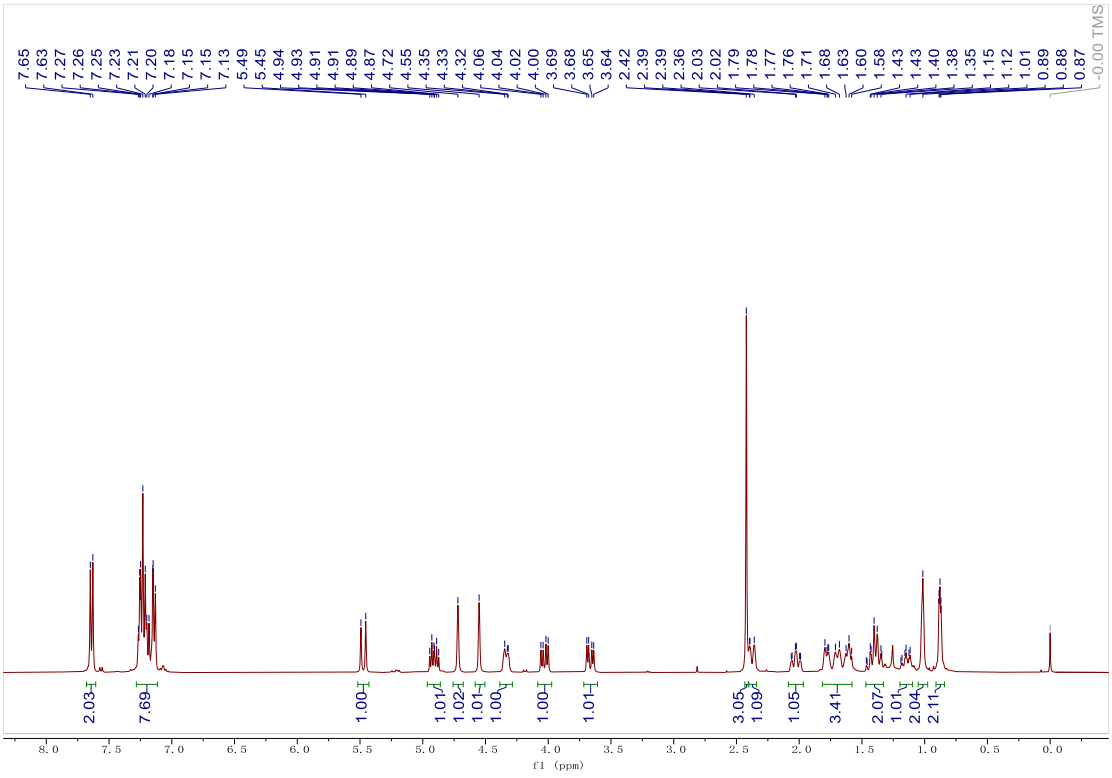


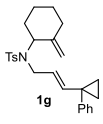
^{13}C NMR in $CDCl_3$, 101 MHz



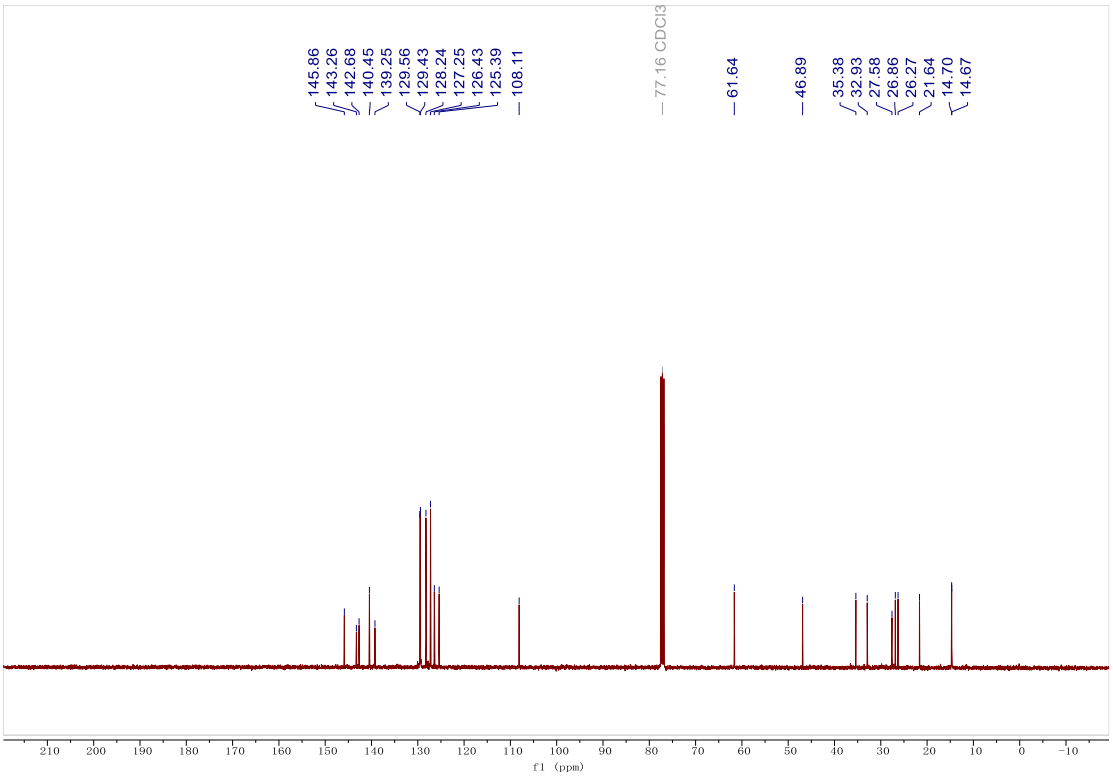


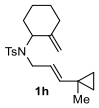
^{1}H NMR in $CDCl_3$, 400 MHz



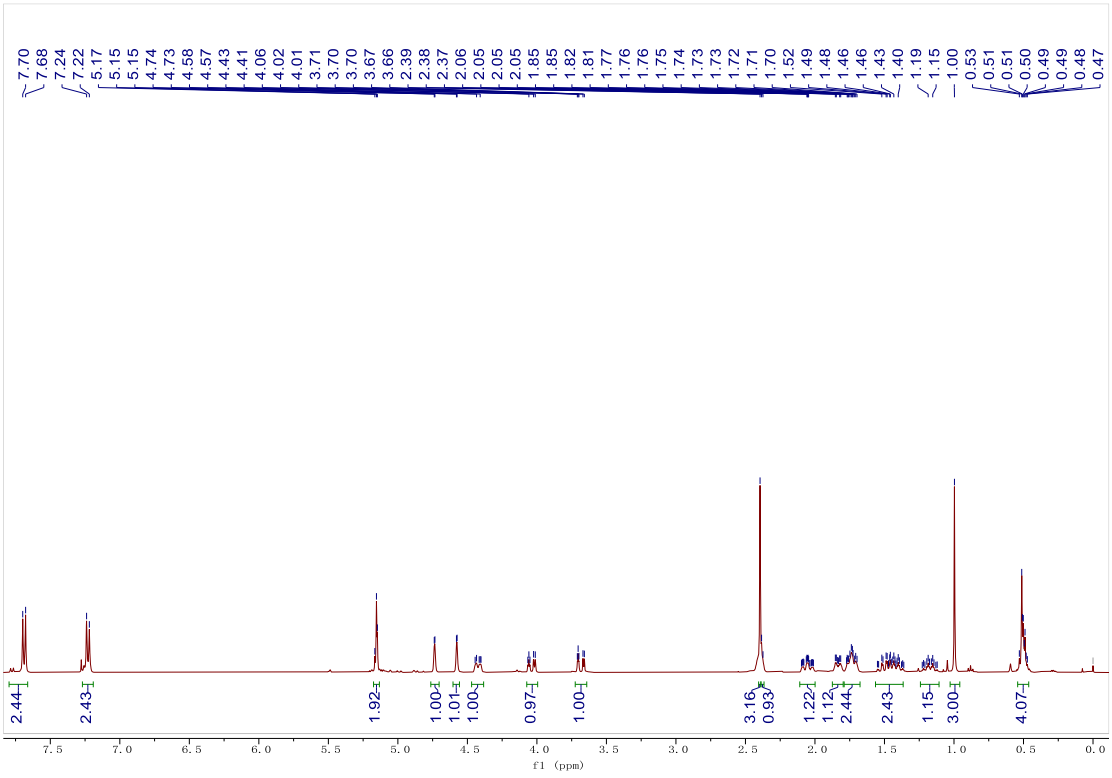


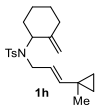
^{13}C NMR in $CDCl_3$, 101 MHz



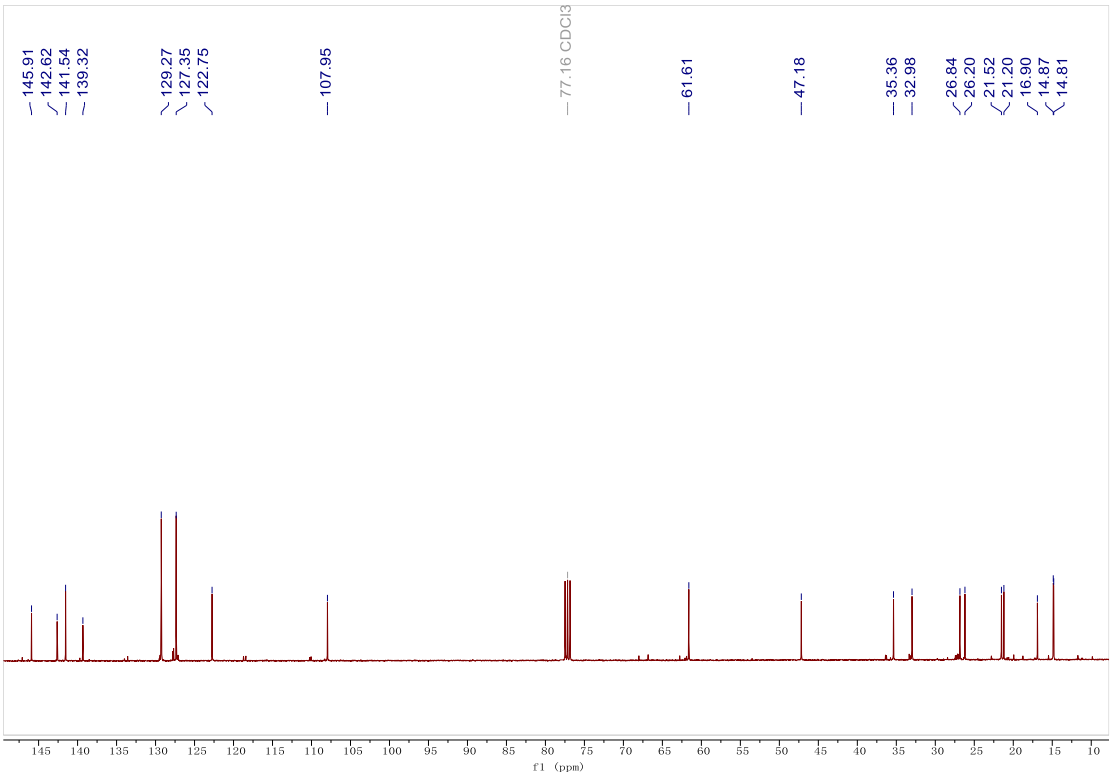


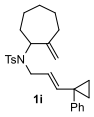
^{1}H NMR in $CDCl_3$, 400 MHz



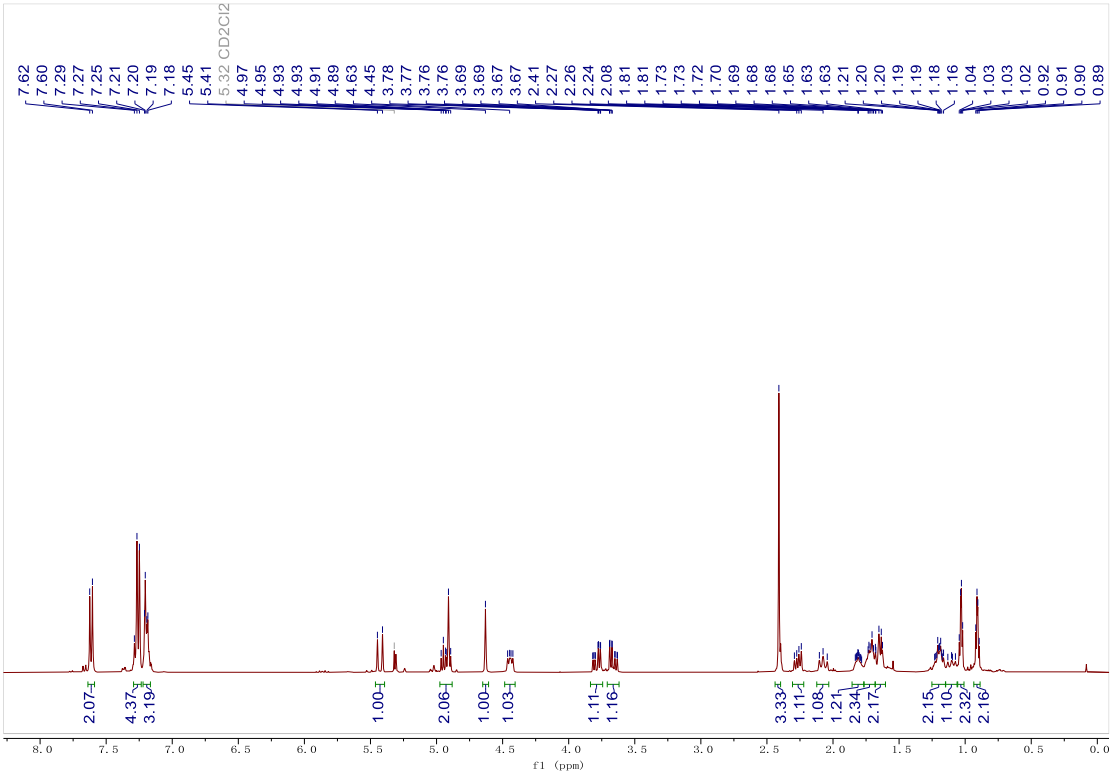


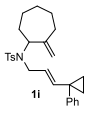
^{13}C NMR in $CDCl_3$, 101 MHz



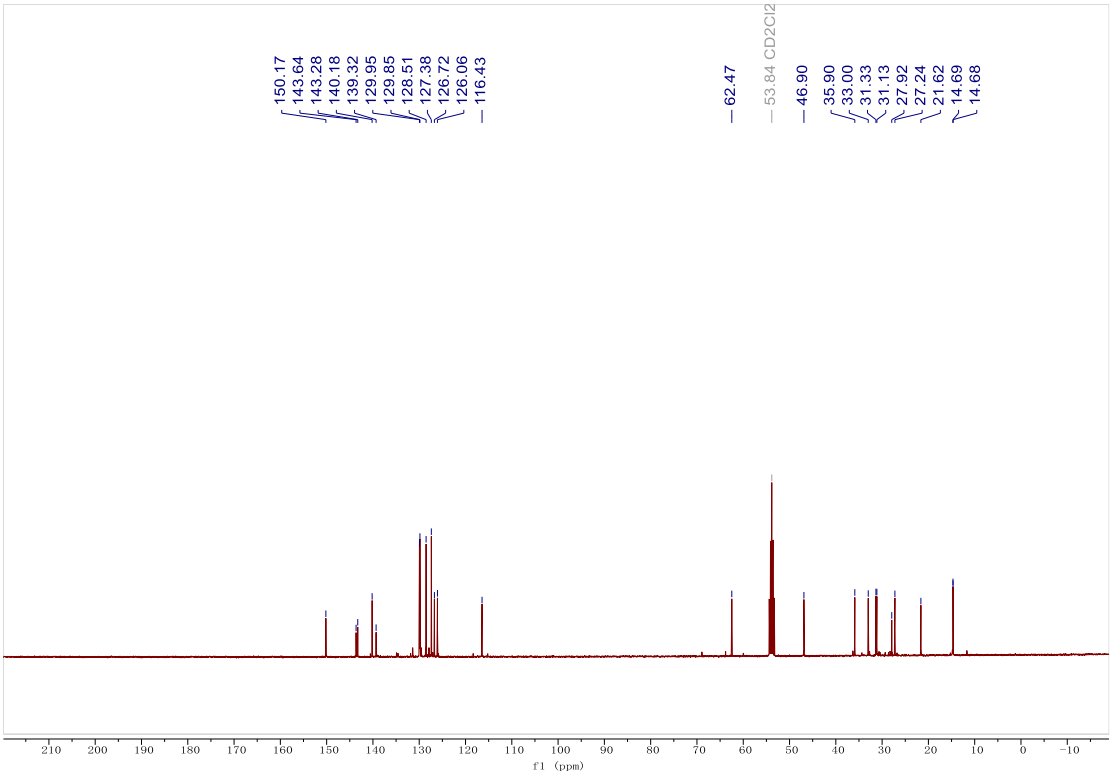


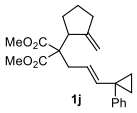
^{1}H NMR in CD_2Cl_2, 400 MHz



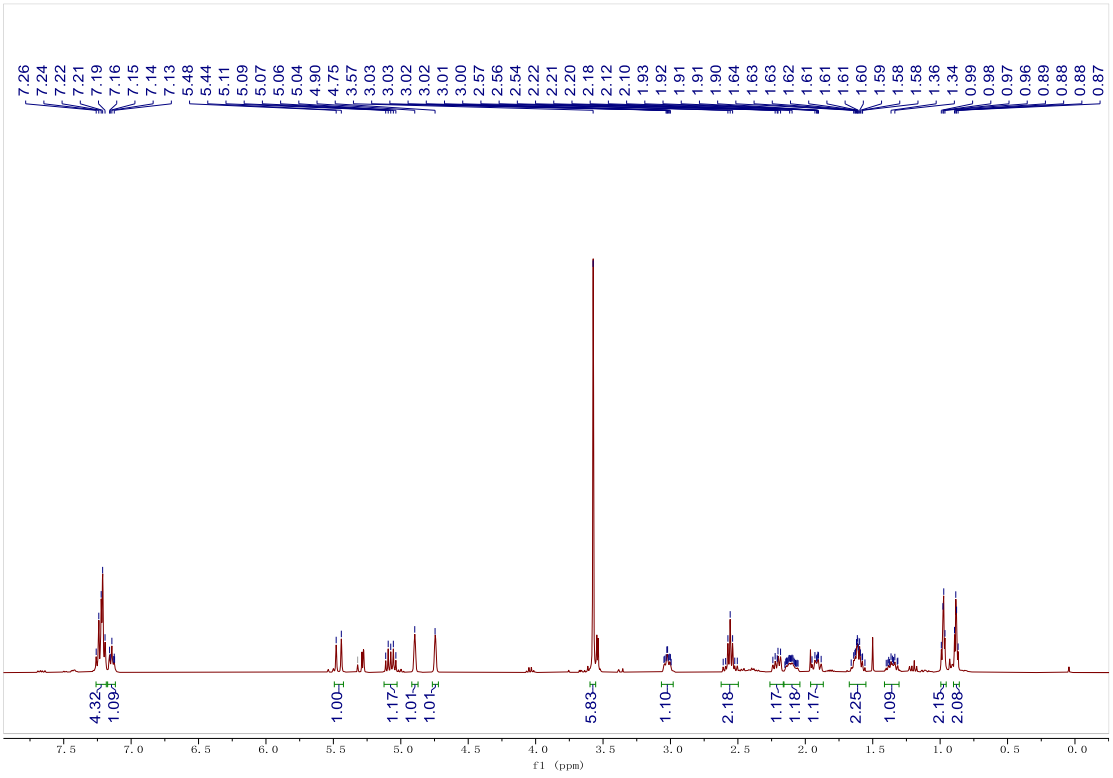


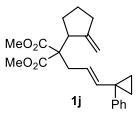
^{13}C NMR in CD_2Cl_2, 101 MHz



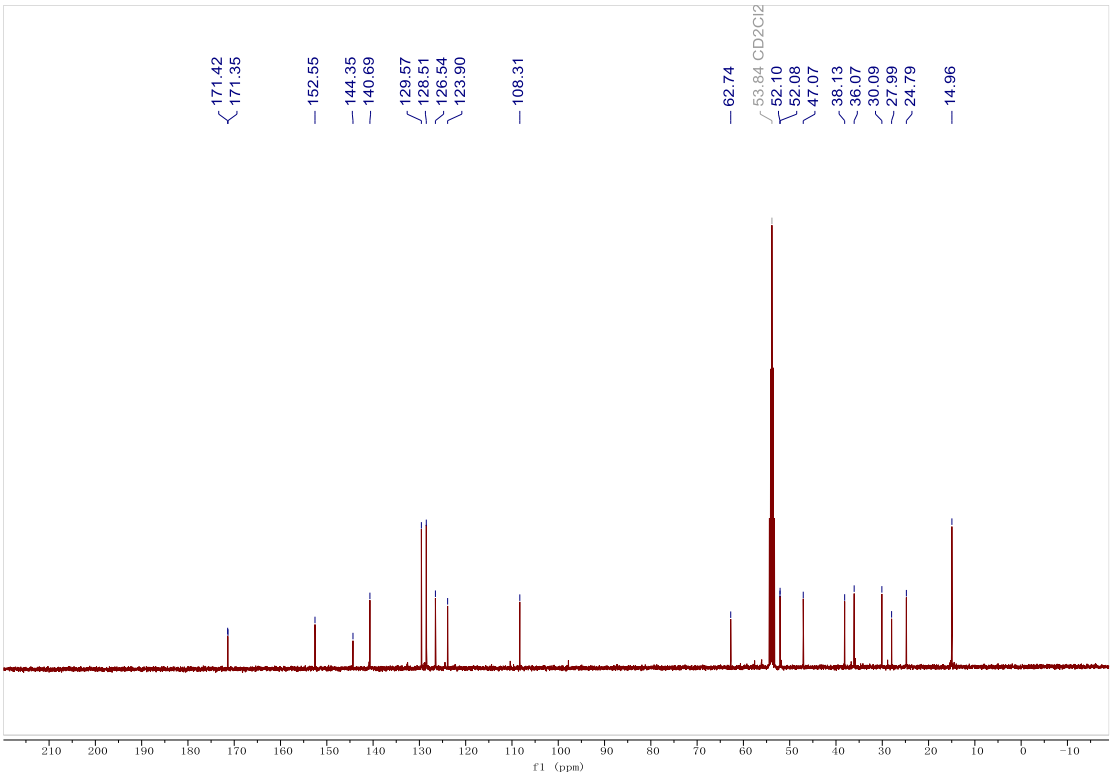


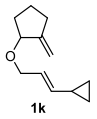
^{1}H NMR in CD_2Cl_2, 400 MHz





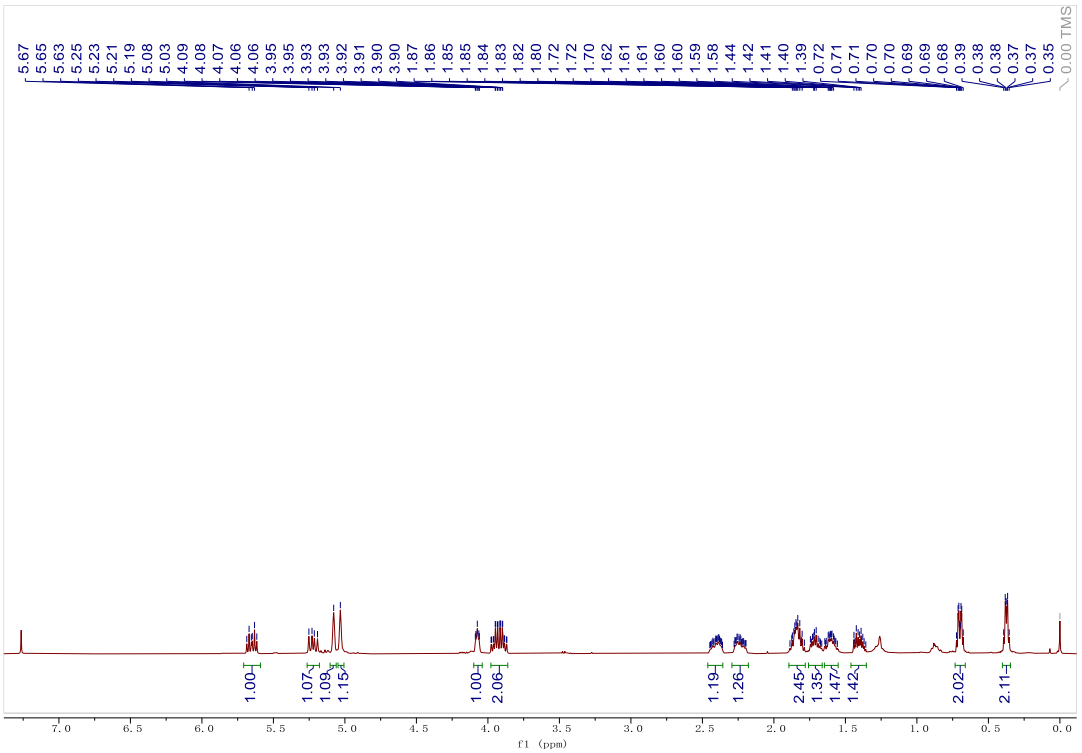
^{13}C NMR in CD_2Cl_2, 101 MHz

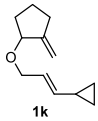




1k

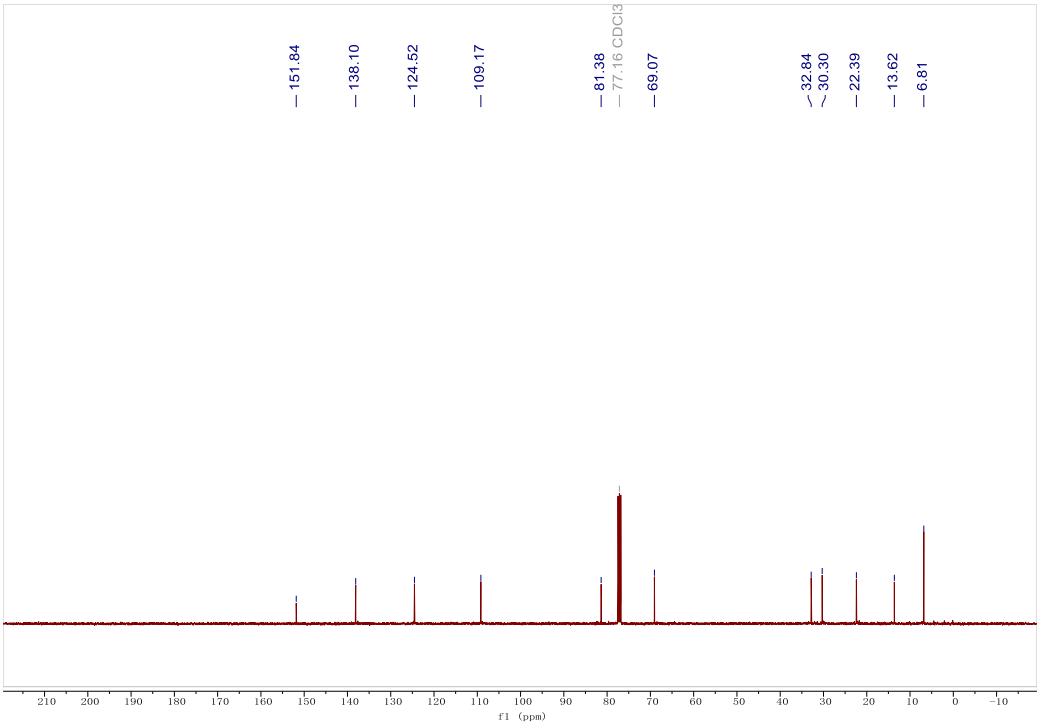
^{1}H NMR in $CDCl_3$, 400 MHz

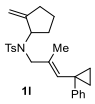




1k

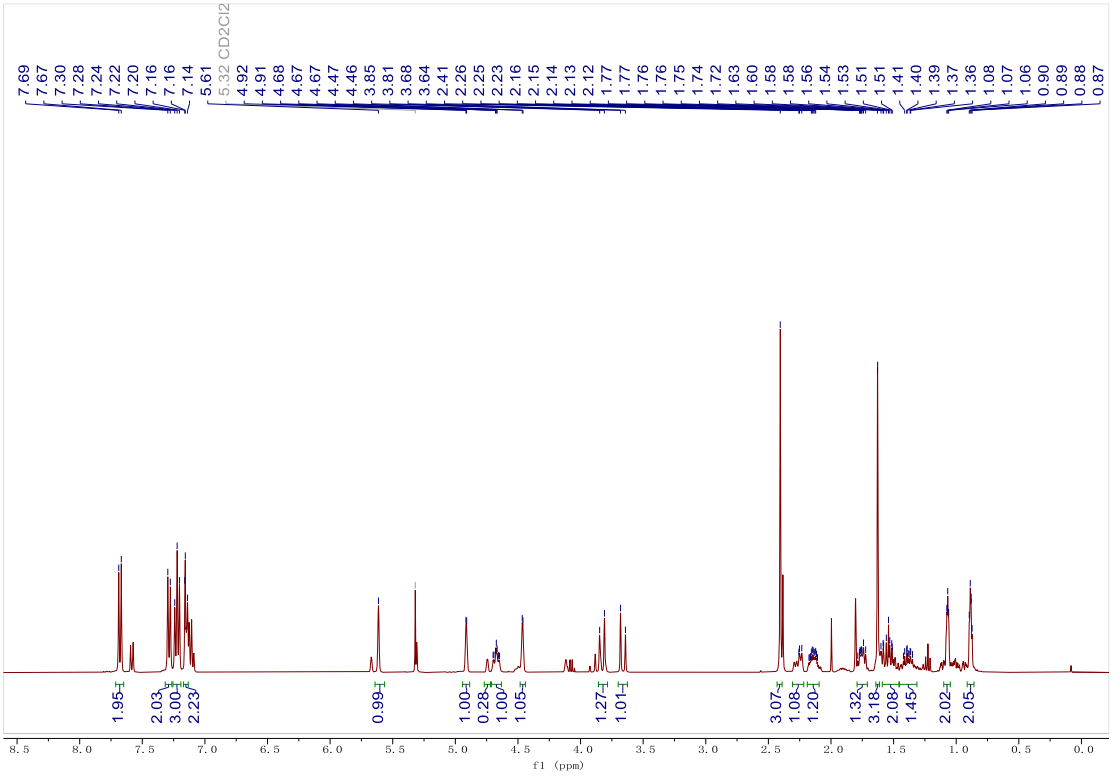
^{13}C NMR in $CDCl_3$, 101 MHz

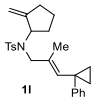




1l

^{1}H NMR in CD_2Cl_2, 400 MHz





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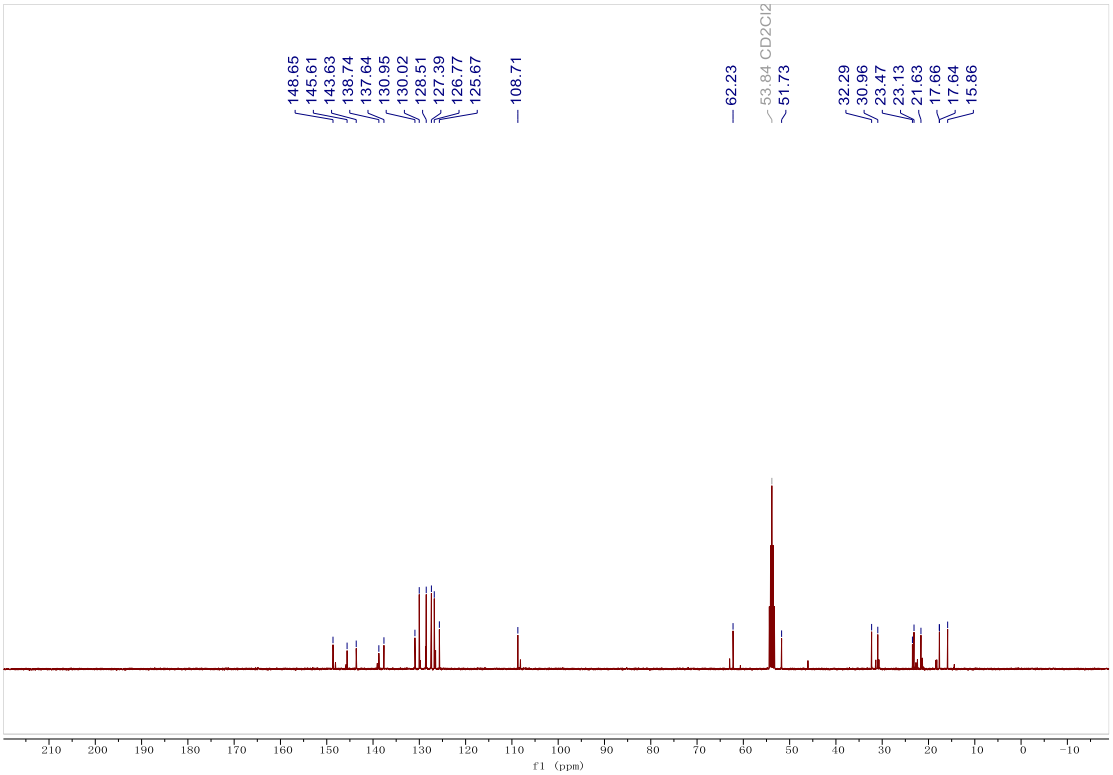
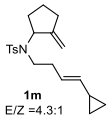
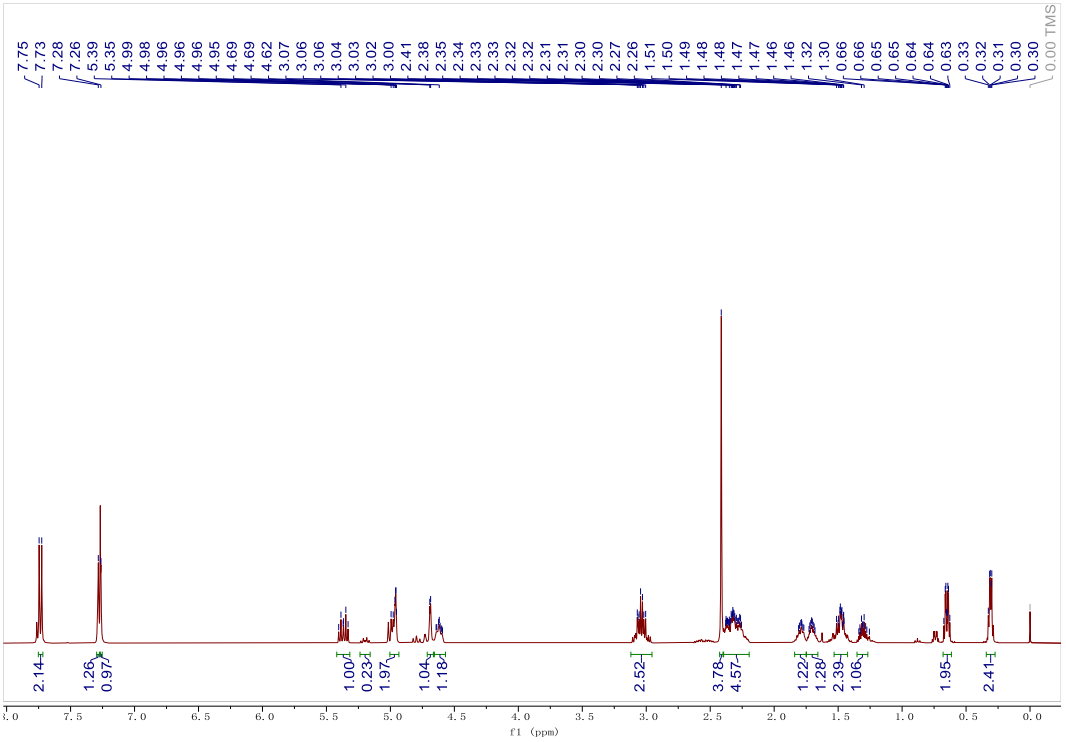
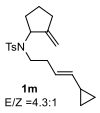
^{13}C NMR in CD_2Cl_2, 101 MHz



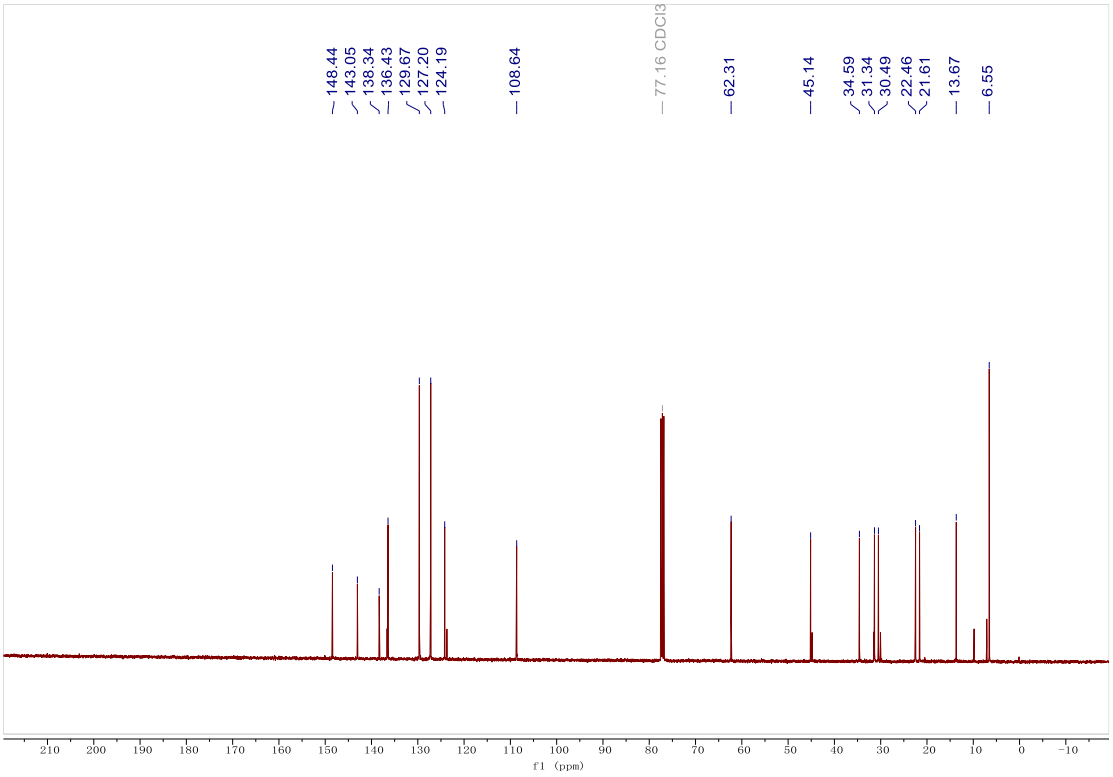


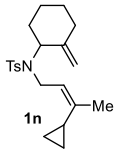
^{1}H NMR in $CDCl_3$, 400 MHz



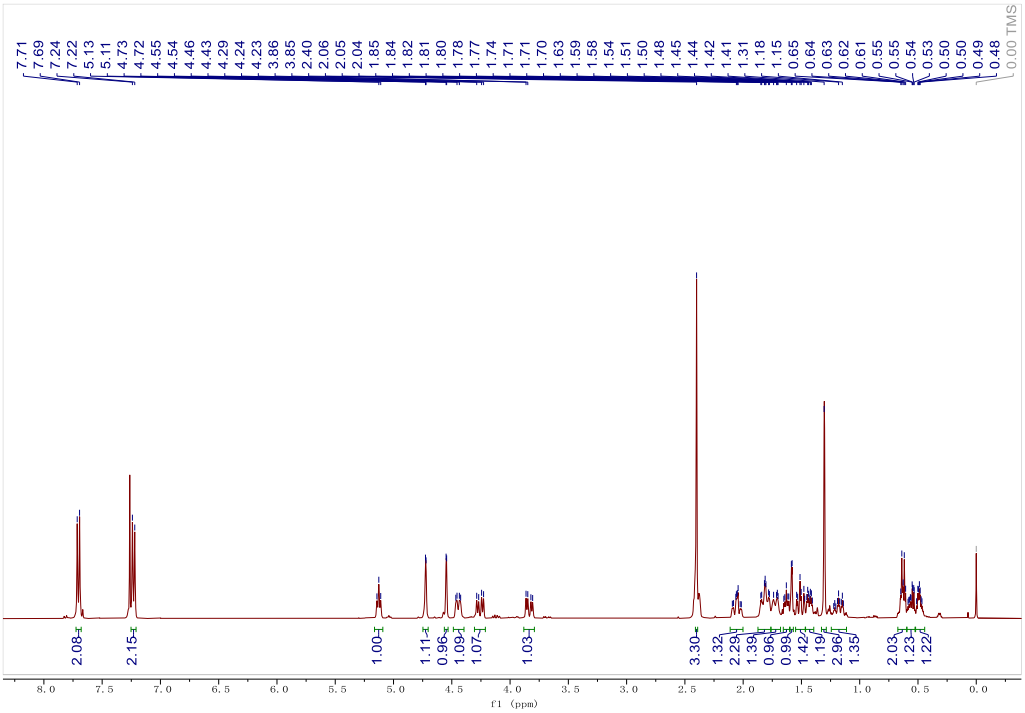


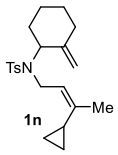
^{13}C NMR in $CDCl_3$, 101 MHz



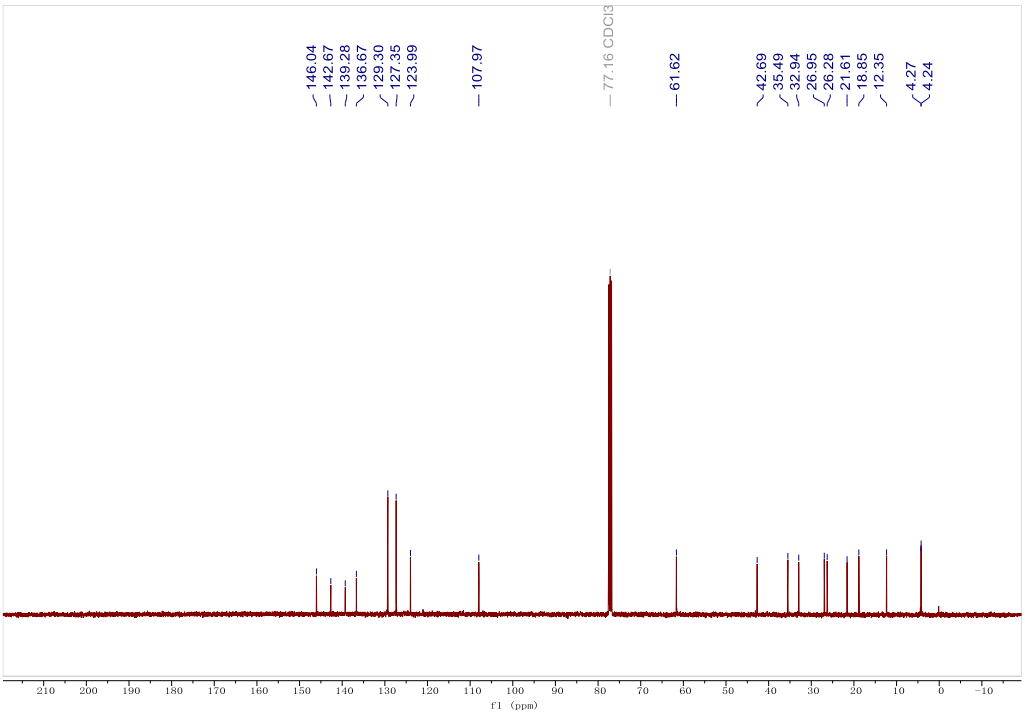


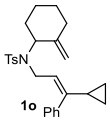
^{1}H NMR in $CDCl_3$, 400 MHz



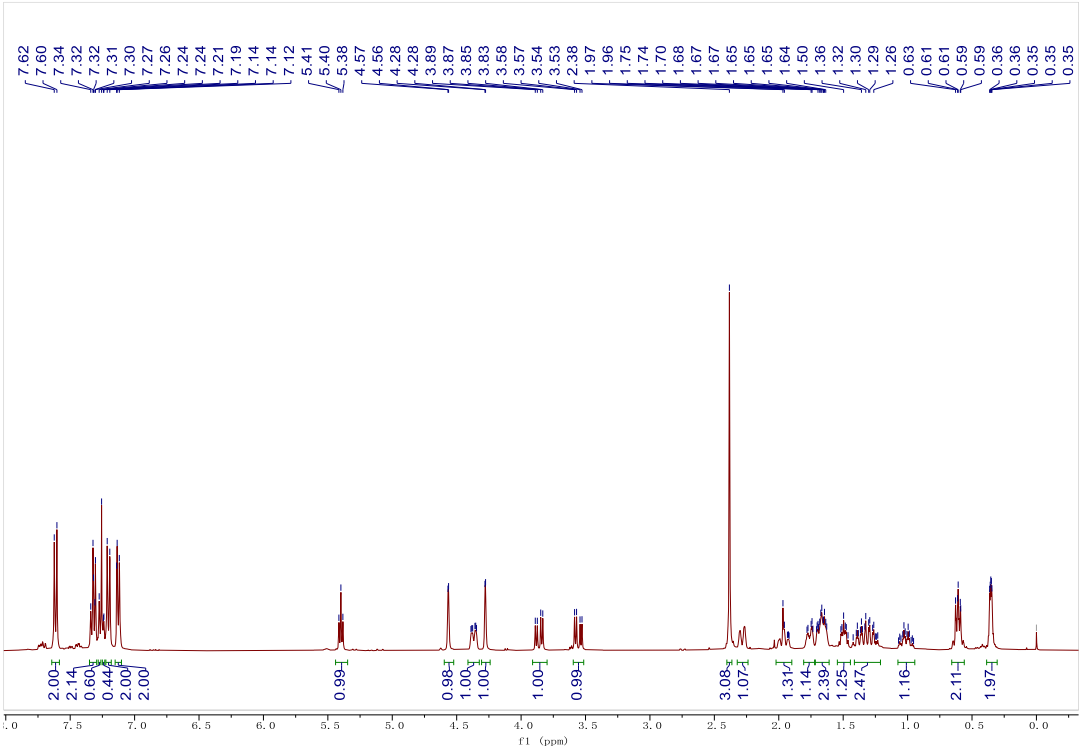


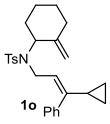
^{13}C NMR in $CDCl_3$, 101 MHz



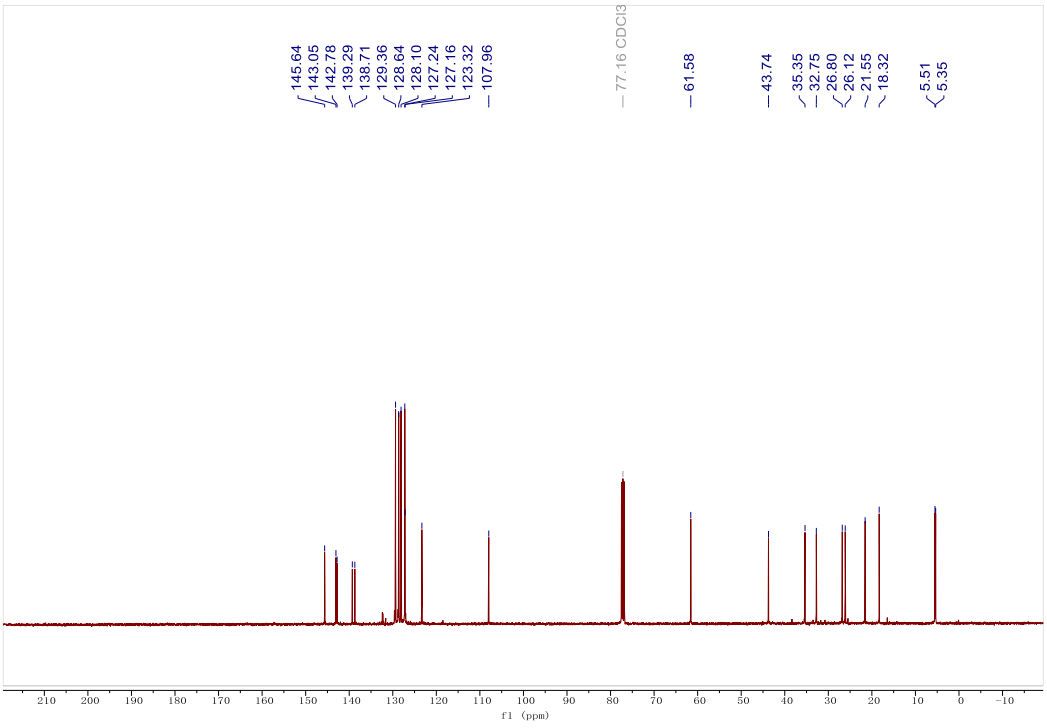


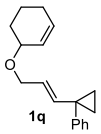
^{1}H NMR in $CDCl_3$, 400 MHz



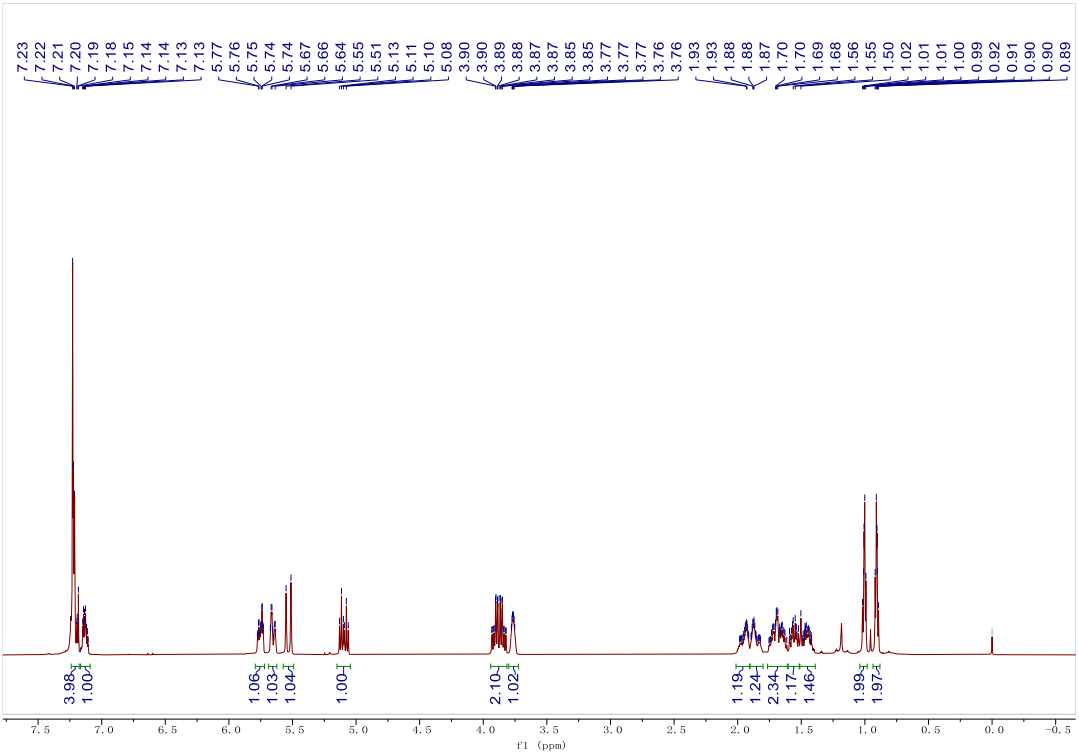


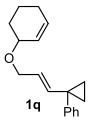
^{13}C NMR in $CDCl_3$, 101 MHz



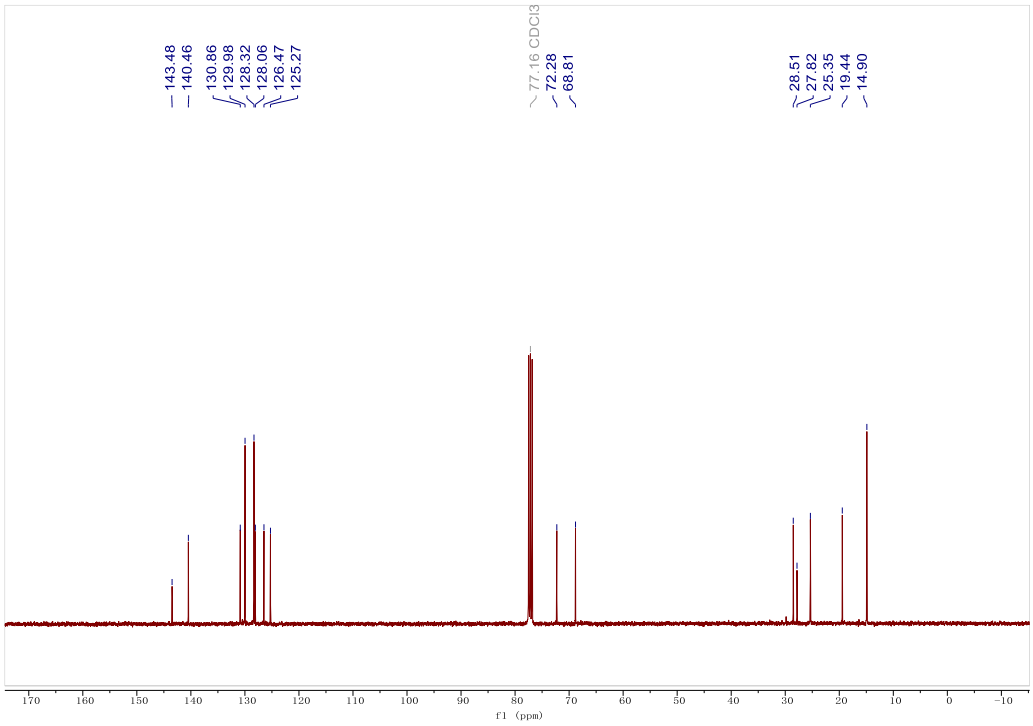


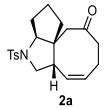
^{1}H NMR in $CDCl_3$, 400 MHz





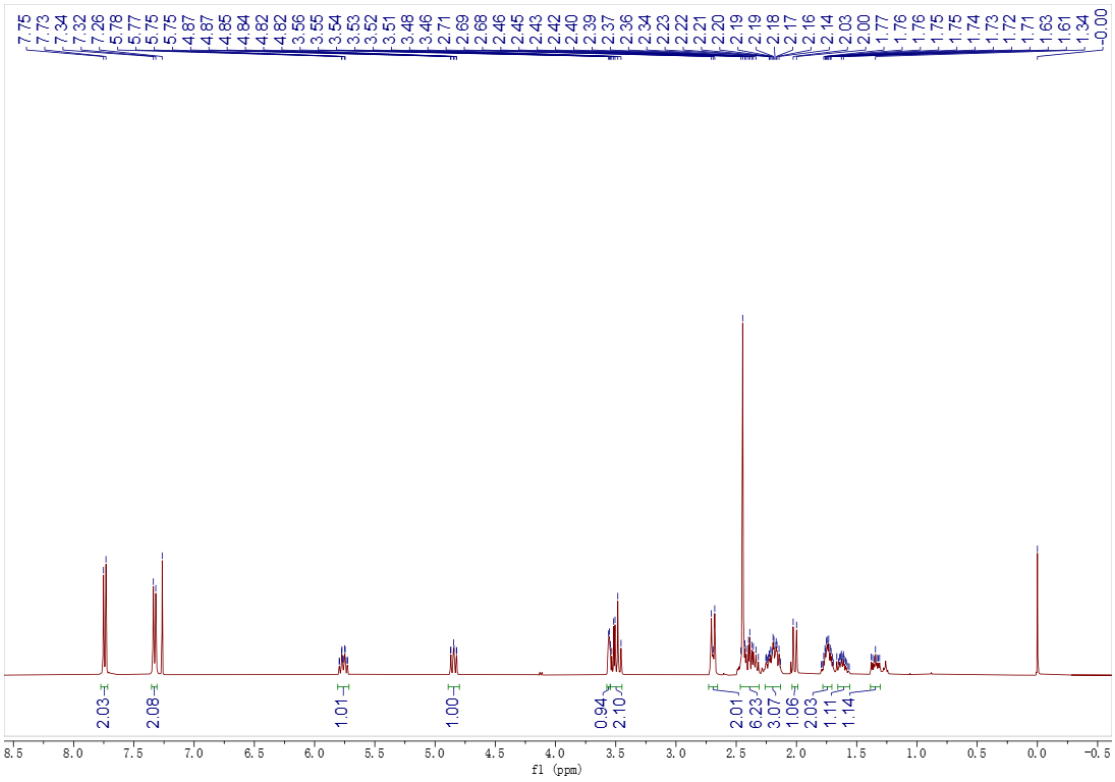
^{13}C NMR in $CDCl_3$, 101 MHz

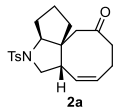




2a

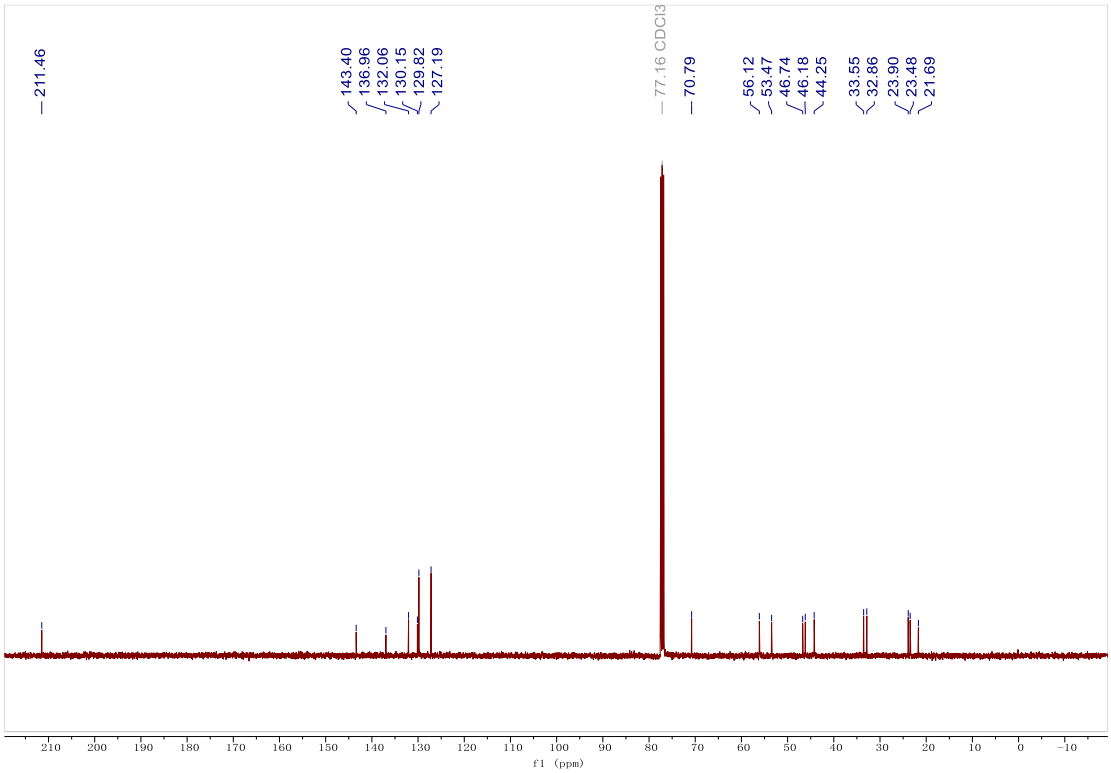
^{1}H NMR in $CDCl_3$, 400 MHz

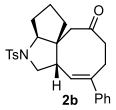




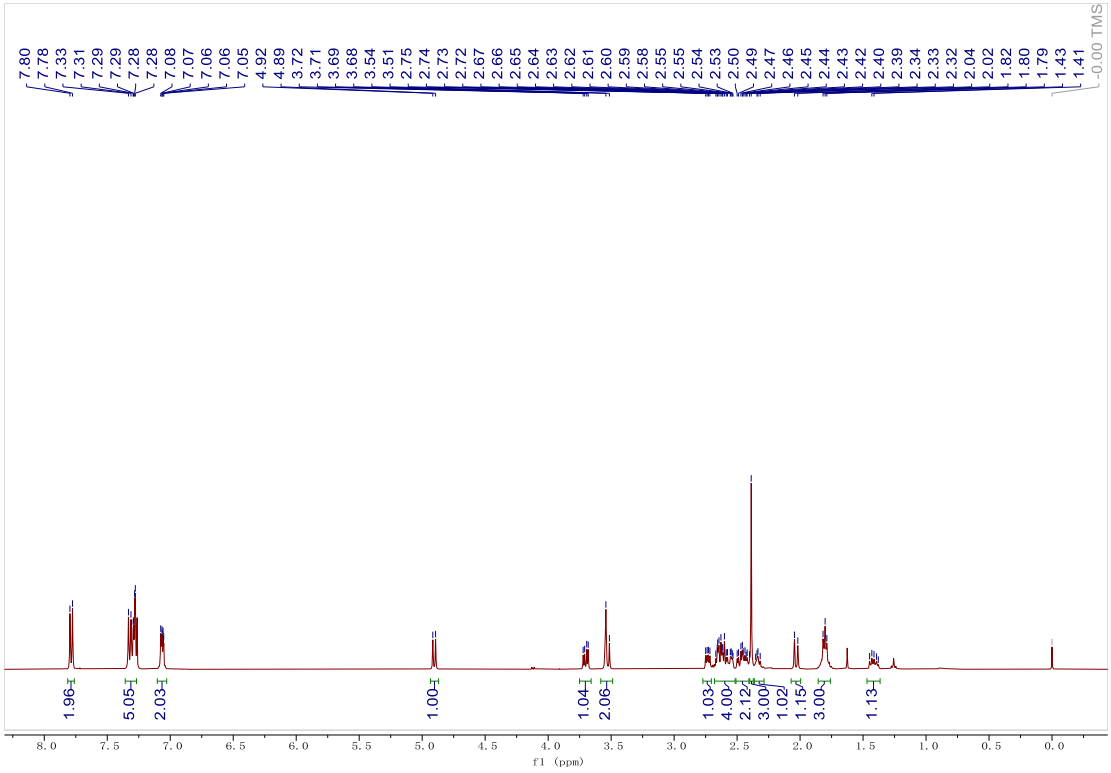
2a

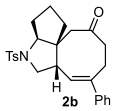
^{13}C NMR in $CDCl_3$, 101 MHz



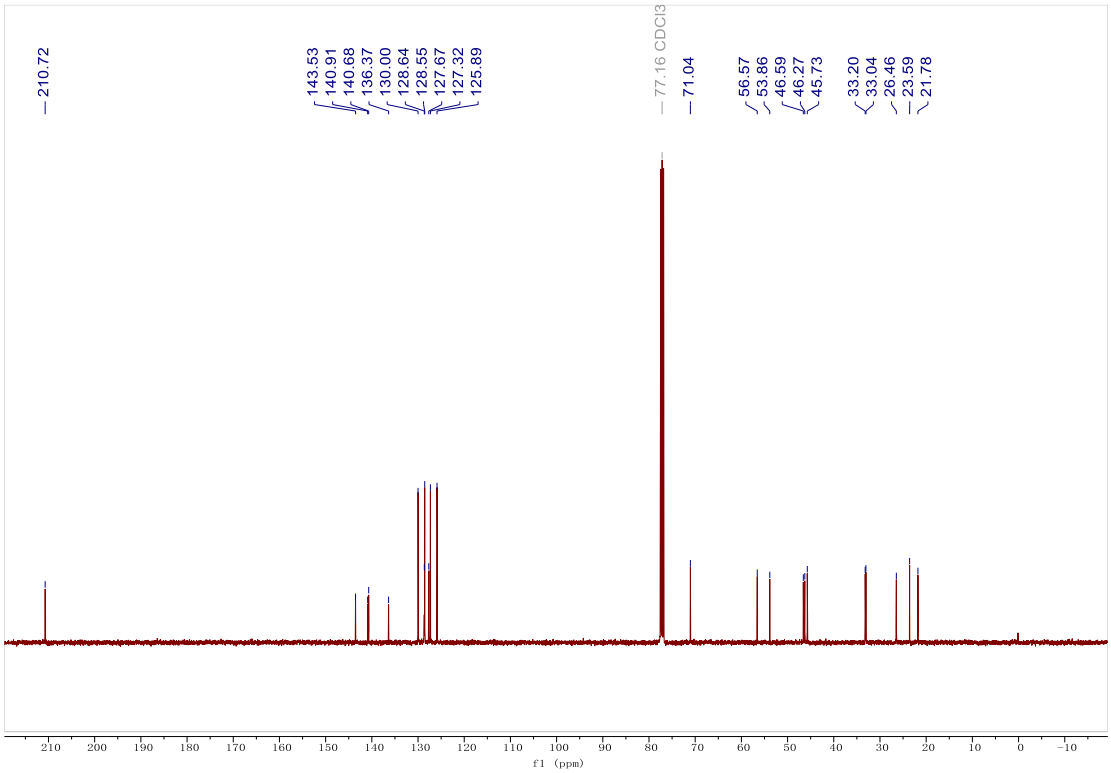


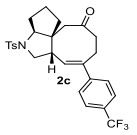
^{1}H NMR in $CDCl_3$, 400 MHz



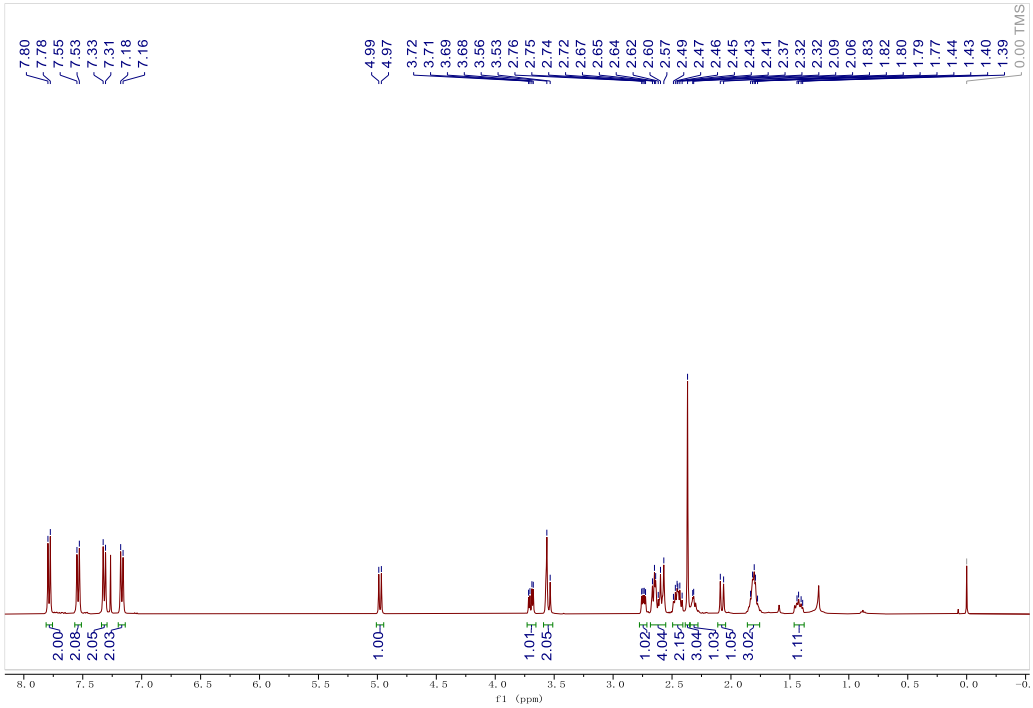


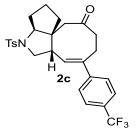
^{13}C NMR in $CDCl_3$, 101 MHz



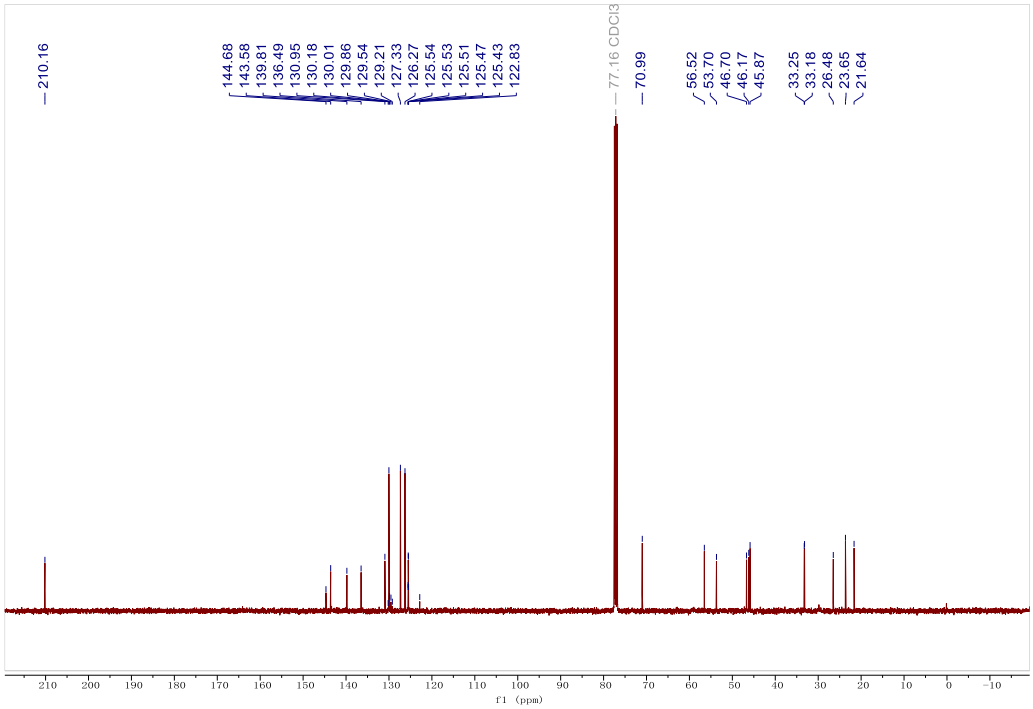


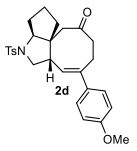
^{1}H NMR in $CDCl_3$, 400 MHz



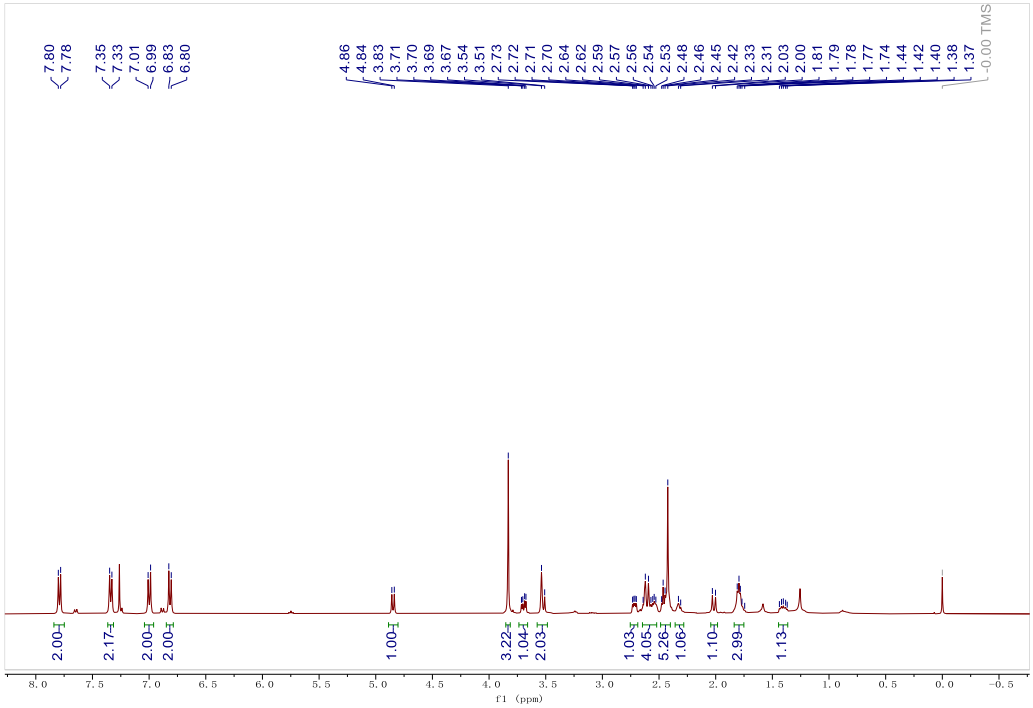


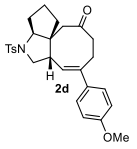
^{13}C NMR in $CDCl_3$, 101 MHz



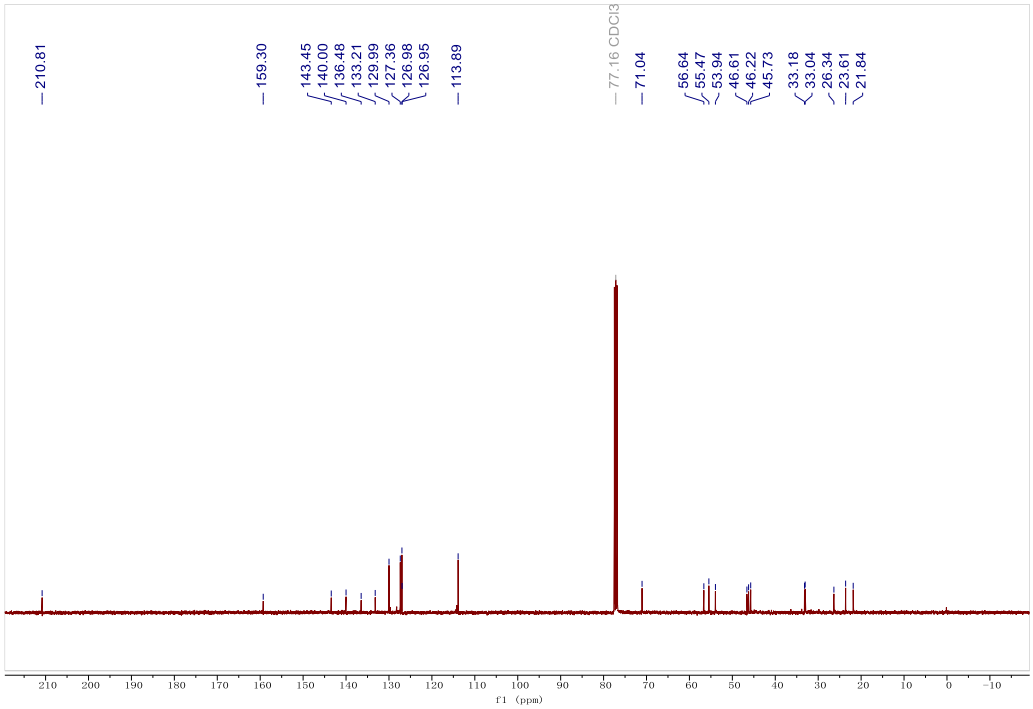


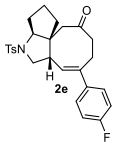
^{1}H NMR in $CDCl_3$, 400 MHz



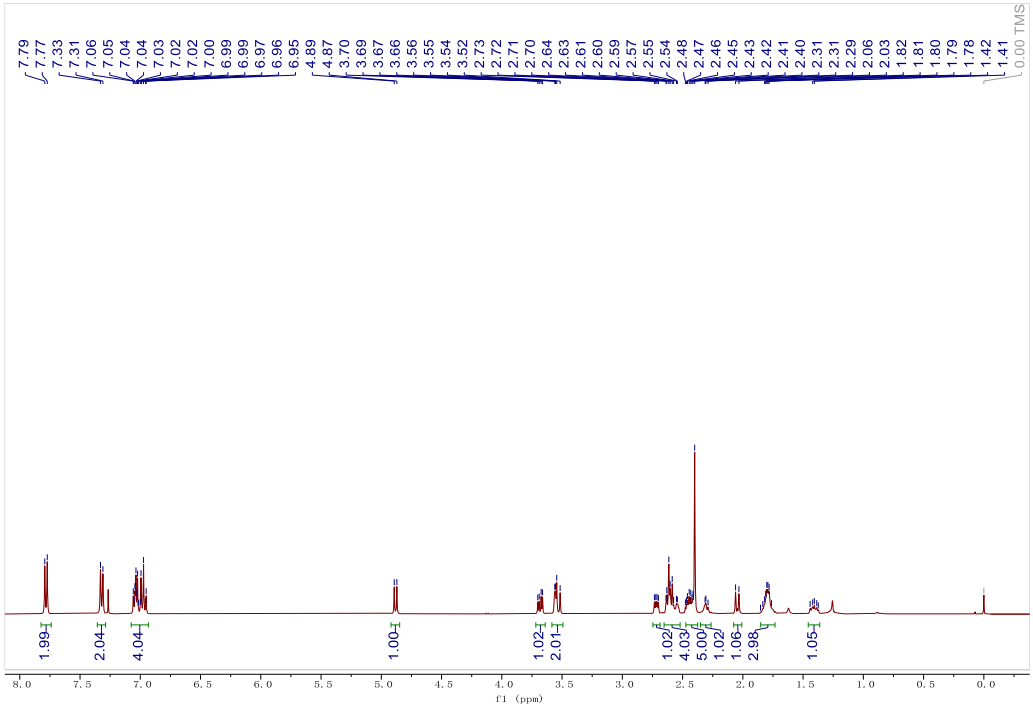


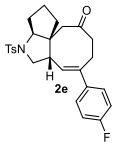
^{13}C NMR in $CDCl_3$, 101 MHz



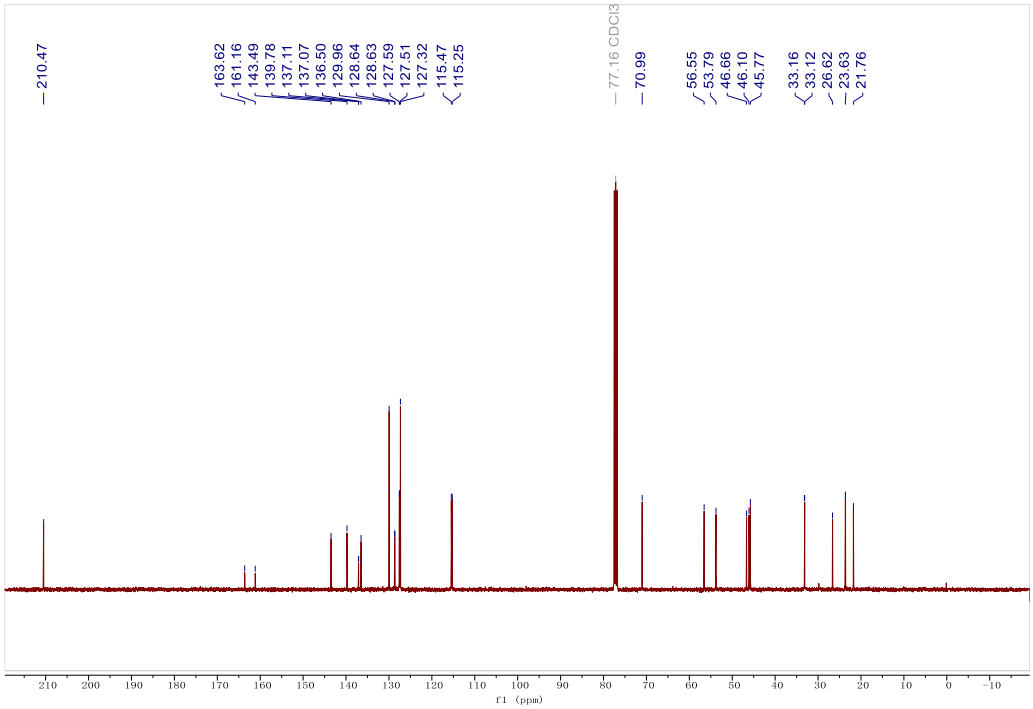


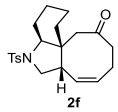
^{1}H NMR in $CDCl_3$, 400 MHz





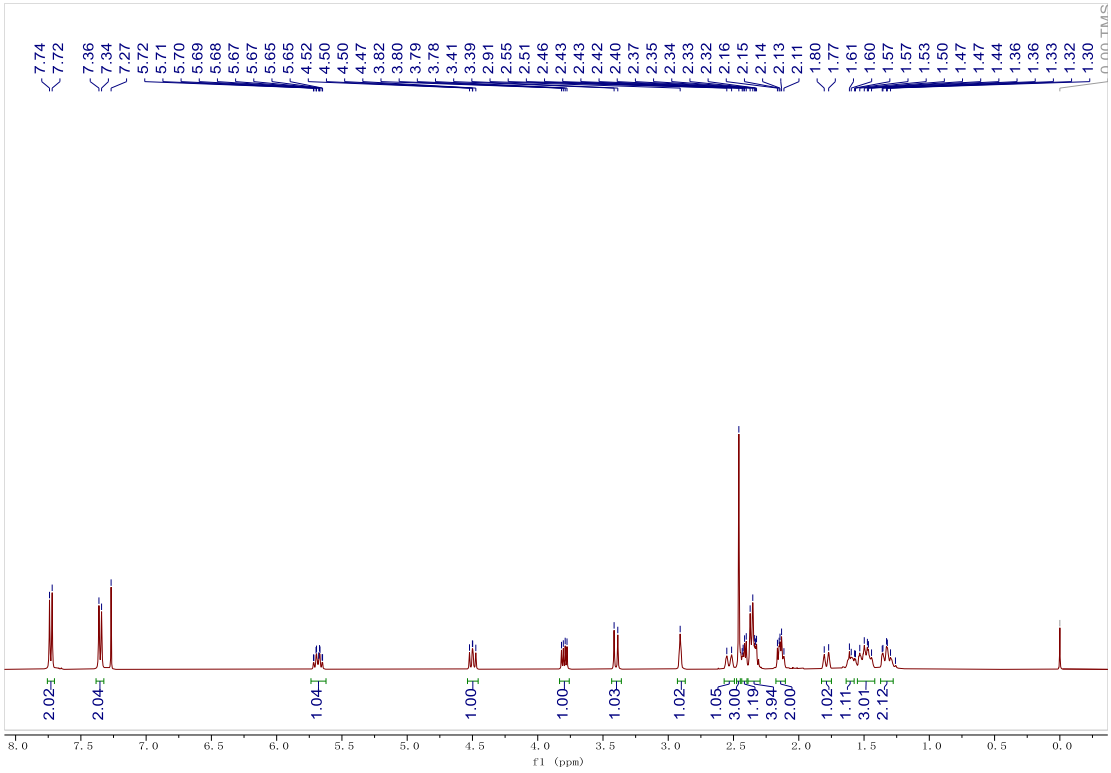
^{13}C NMR in $CDCl_3$, 101 MHz

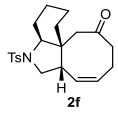




2f

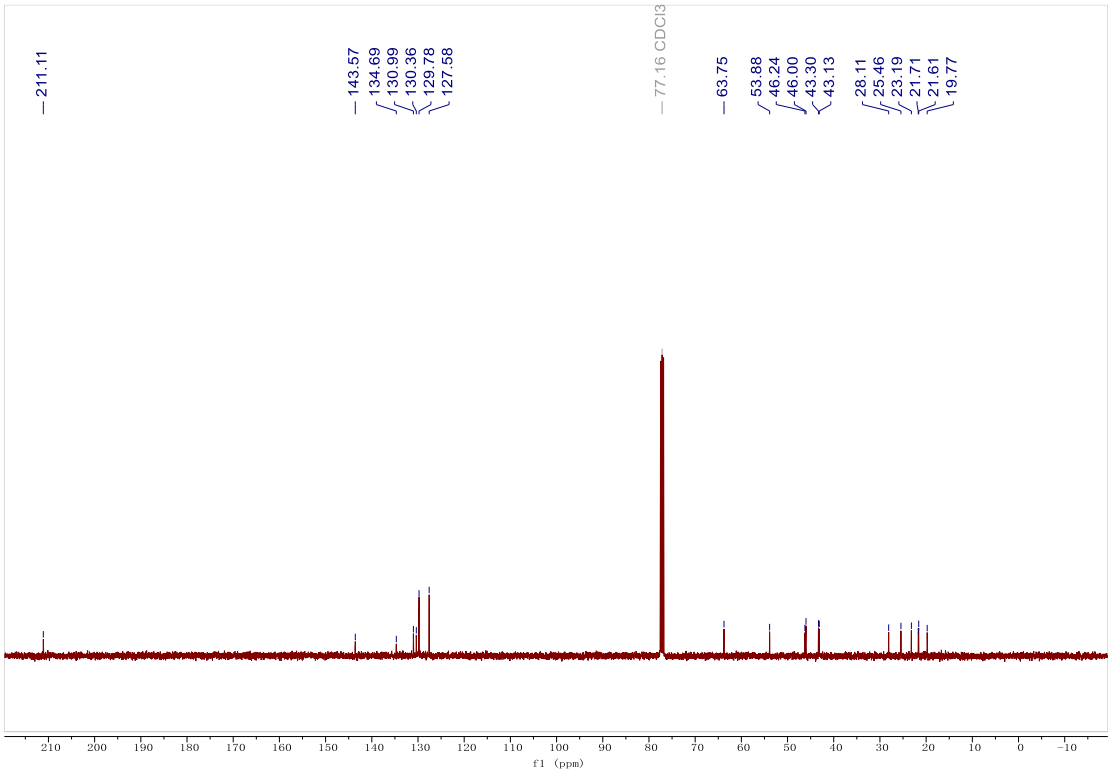
^{1}H NMR in $CDCl_3$, 400 MHz

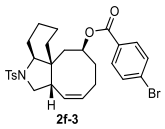




2f

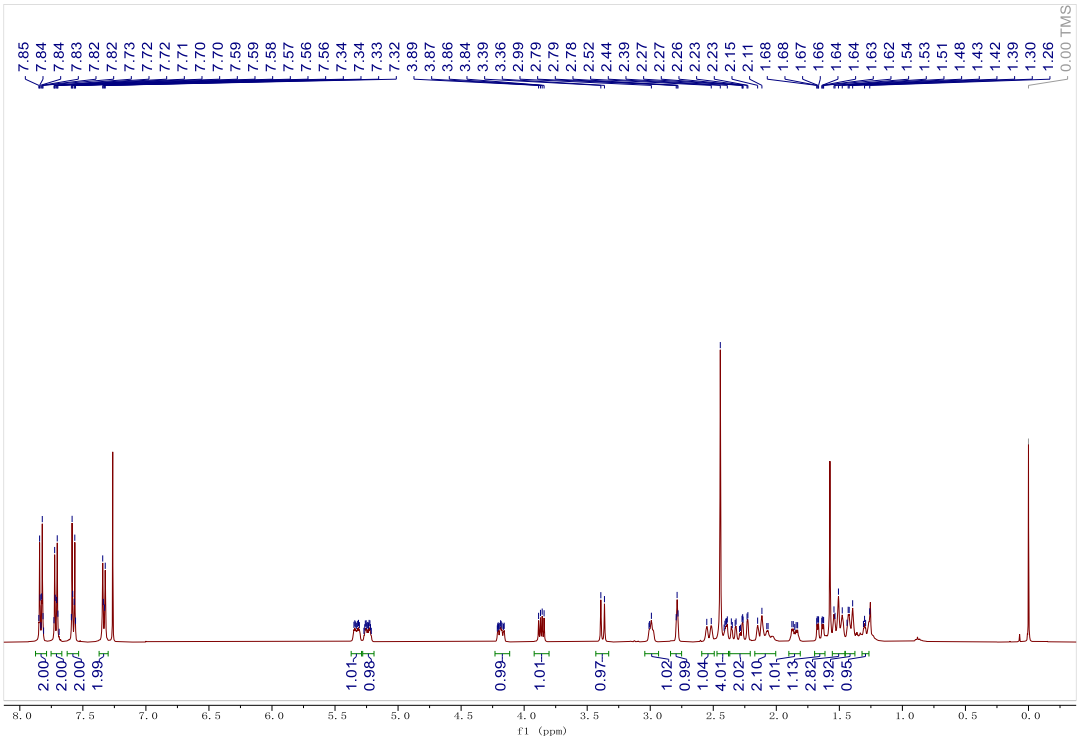
^{13}C NMR in $CDCl_3$, 101 MHz

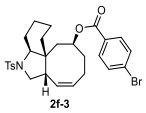




2f-3

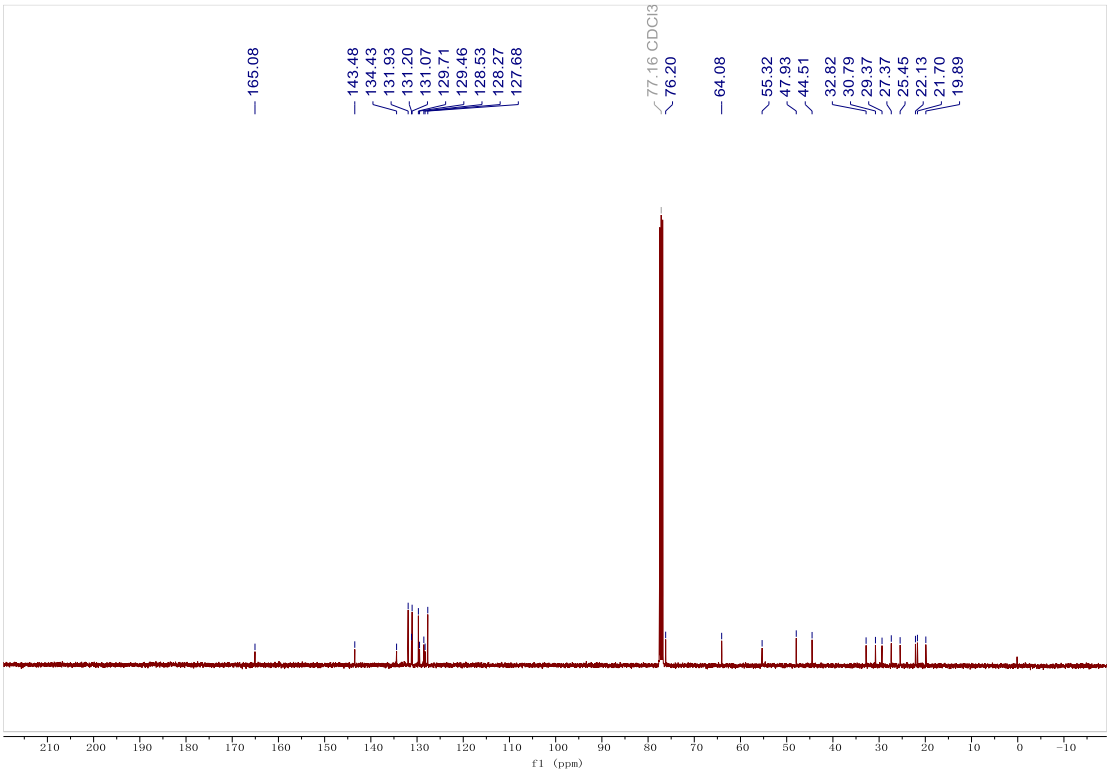
^{1}H NMR in $CDCl_3$, 400 MHz

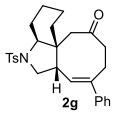




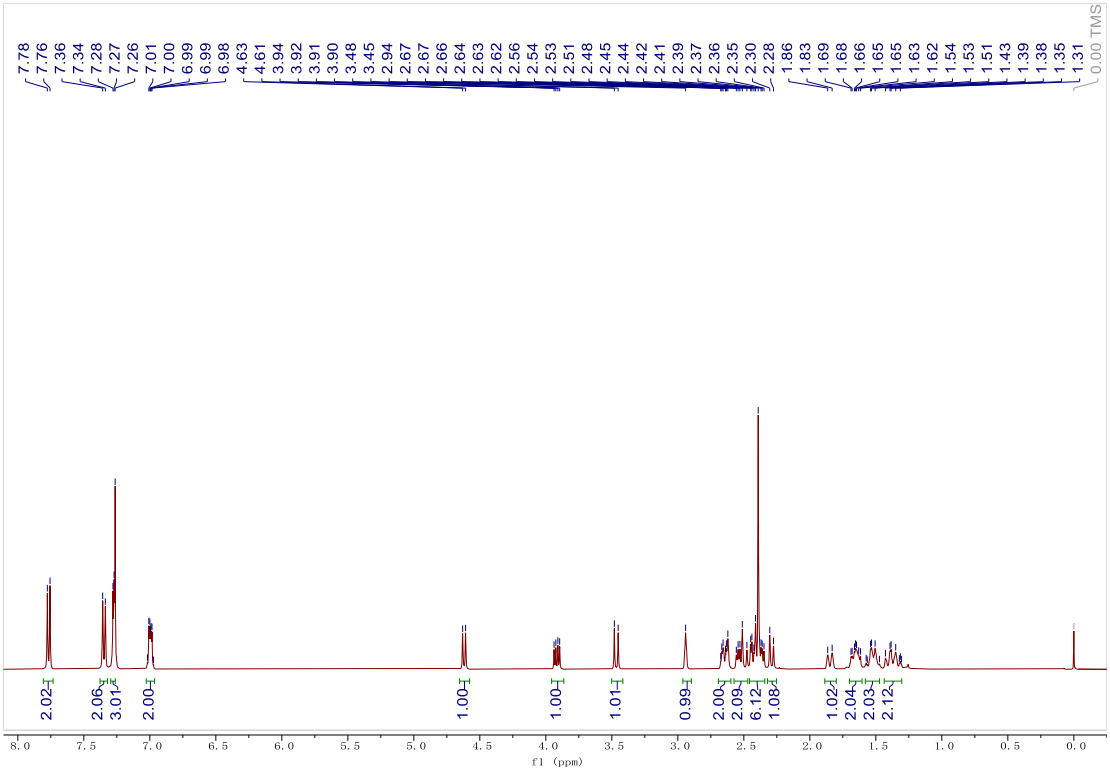
2f-3

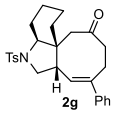
^{13}C NMR in $CDCl_3$, 101 MHz



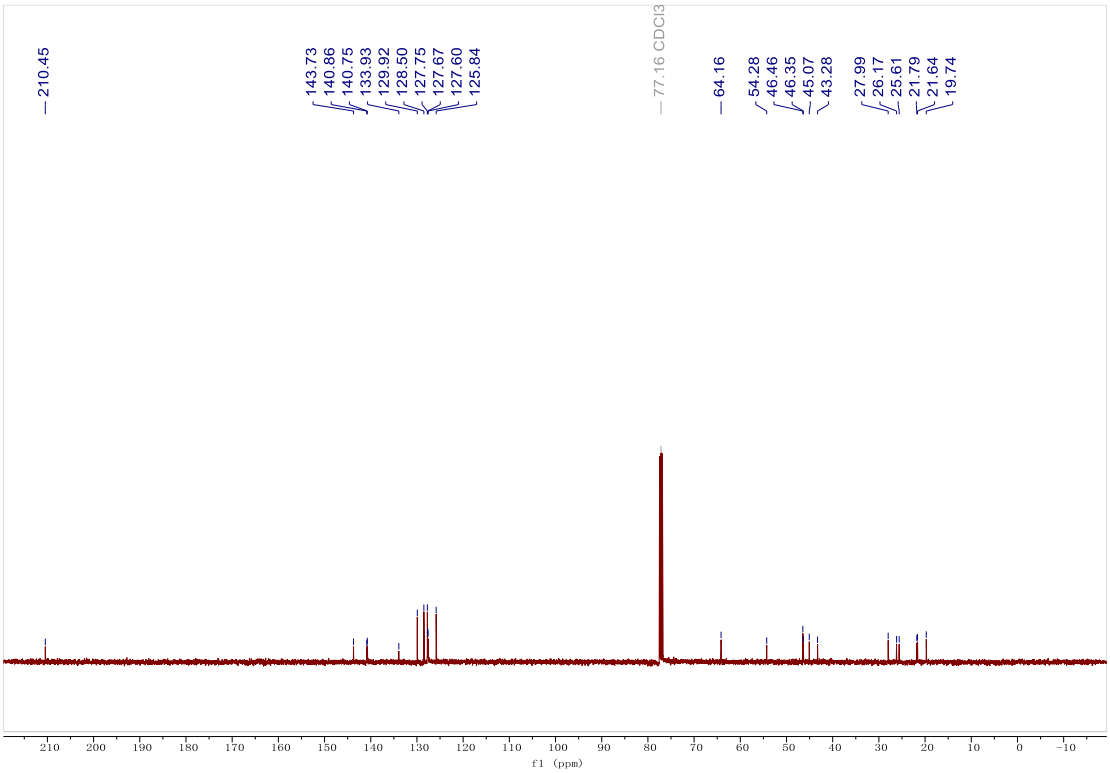


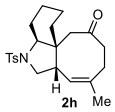
^{1}H NMR in $CDCl_3$, 400 MHz



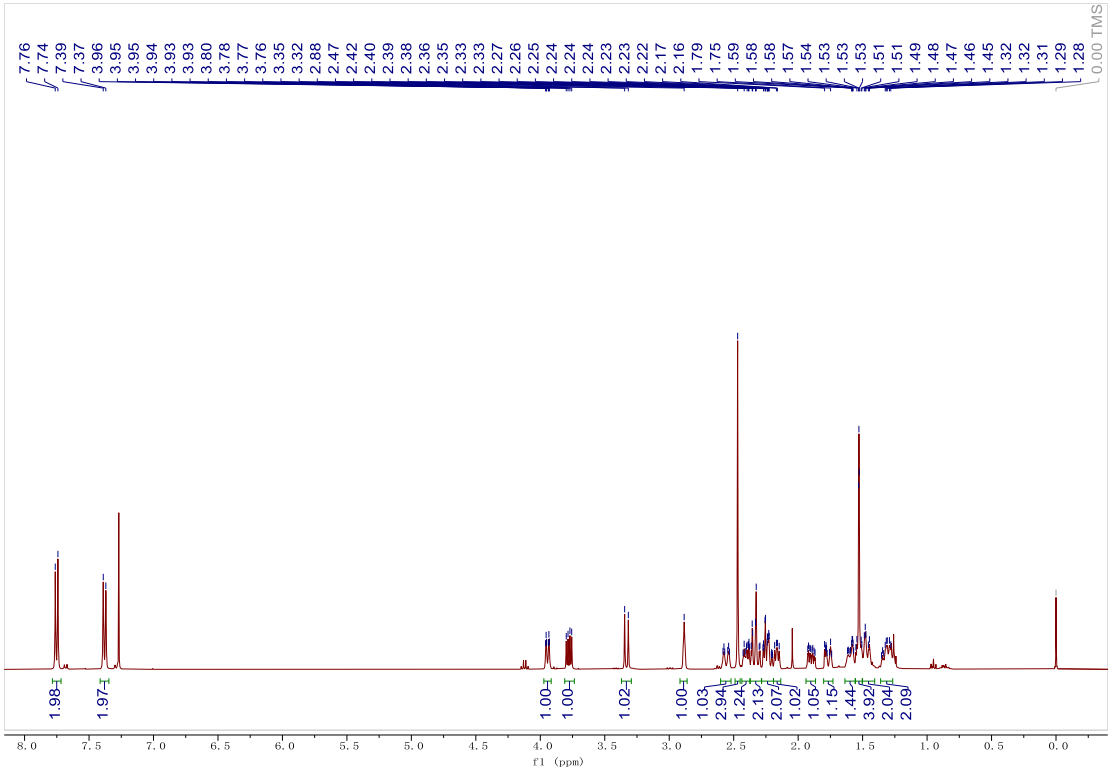


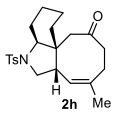
^{13}C NMR in $CDCl_3$, 101 MHz



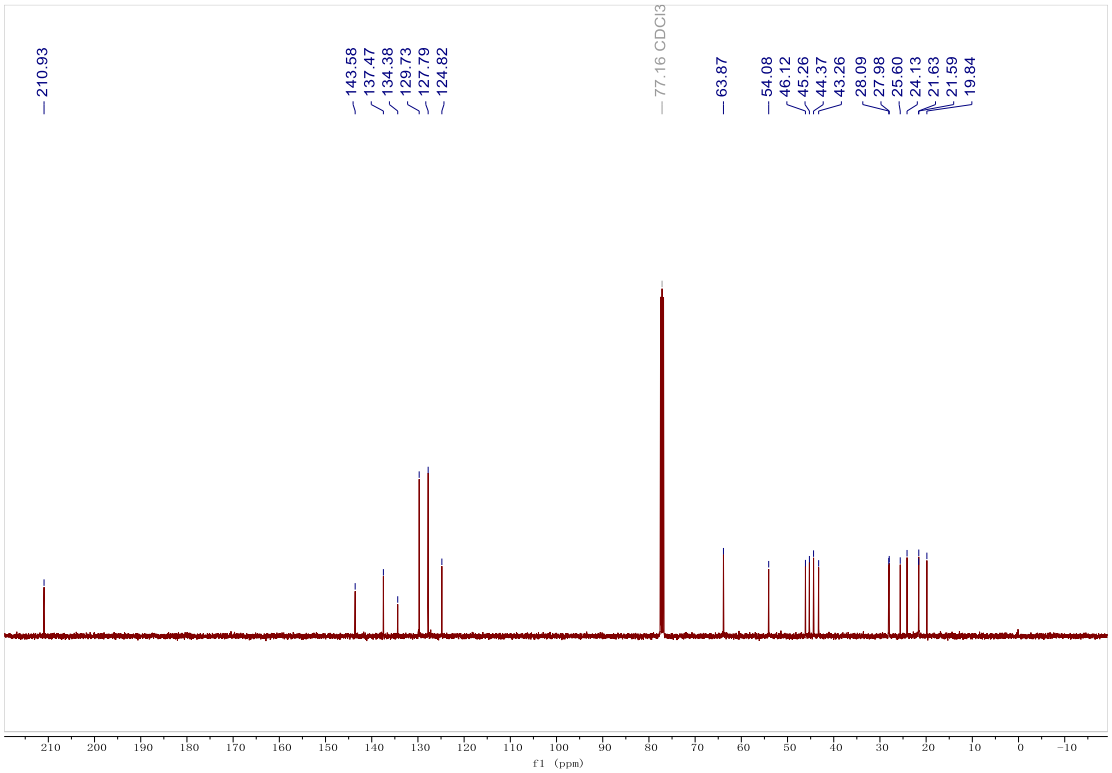


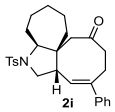
^{1}H NMR in $CDCl_3$, 400 MHz



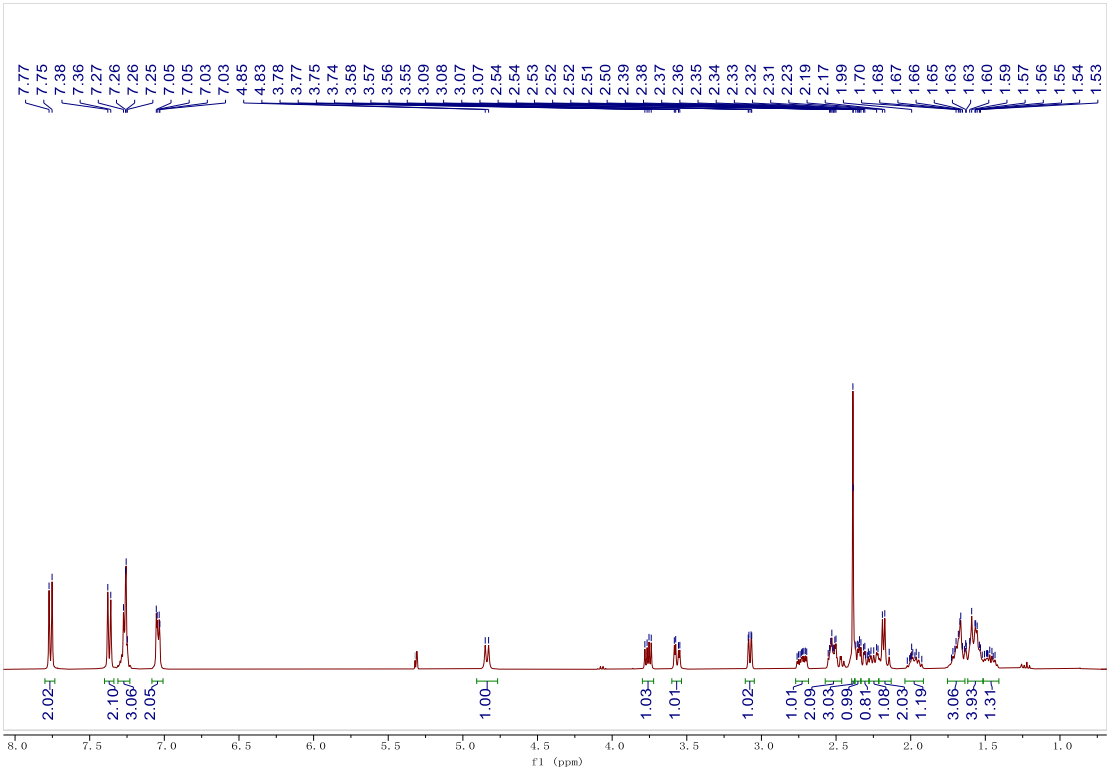


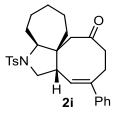
^{13}C NMR in $CDCl_3$, 101 MHz



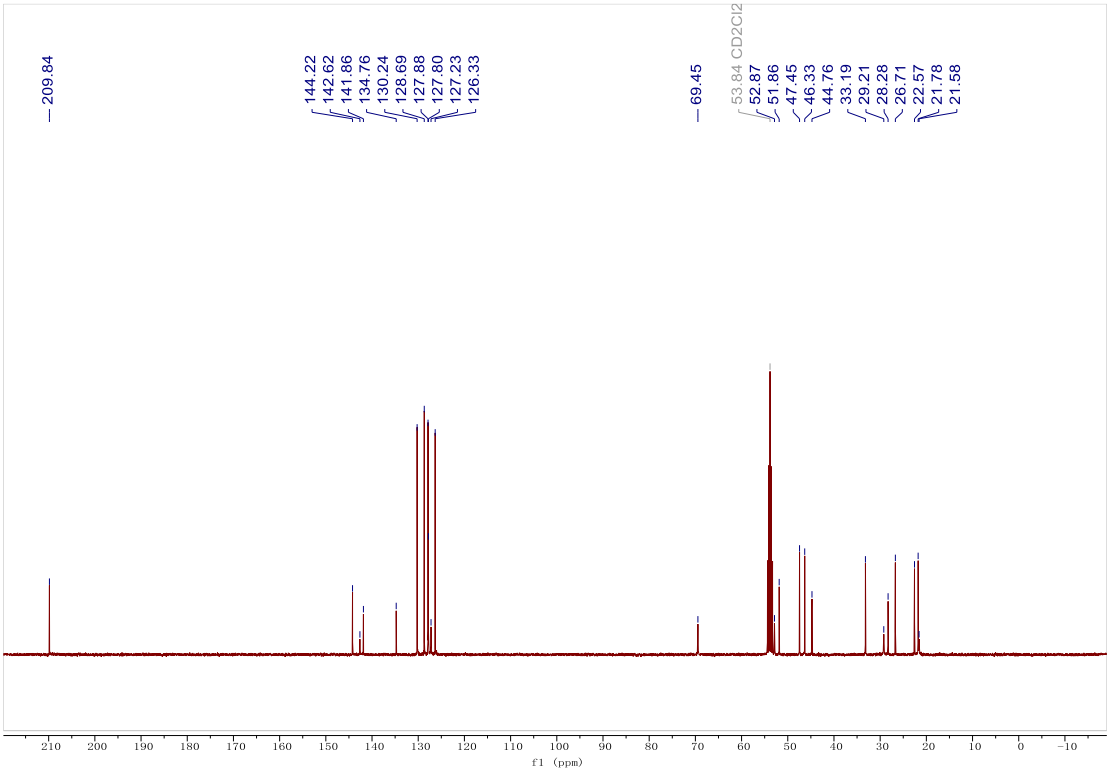


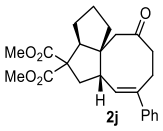
^{1}H NMR in CD_2Cl_2, 400 MHz





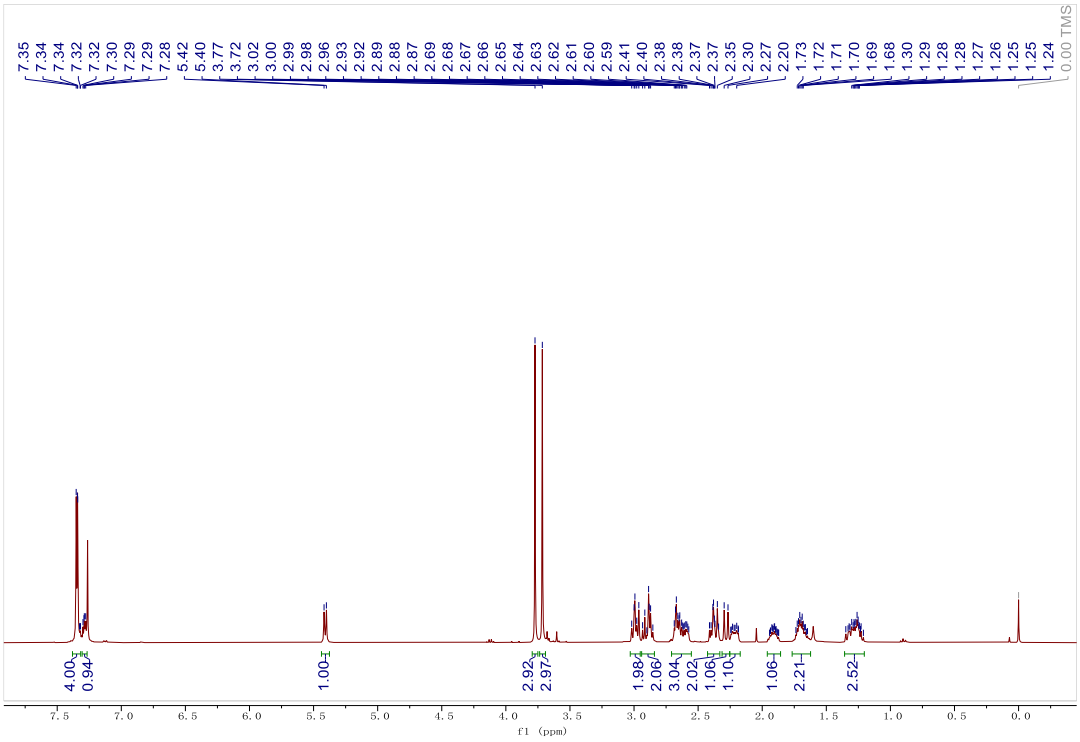
^{13}C NMR in CD_2Cl_2, 101 MHz

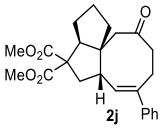




2j

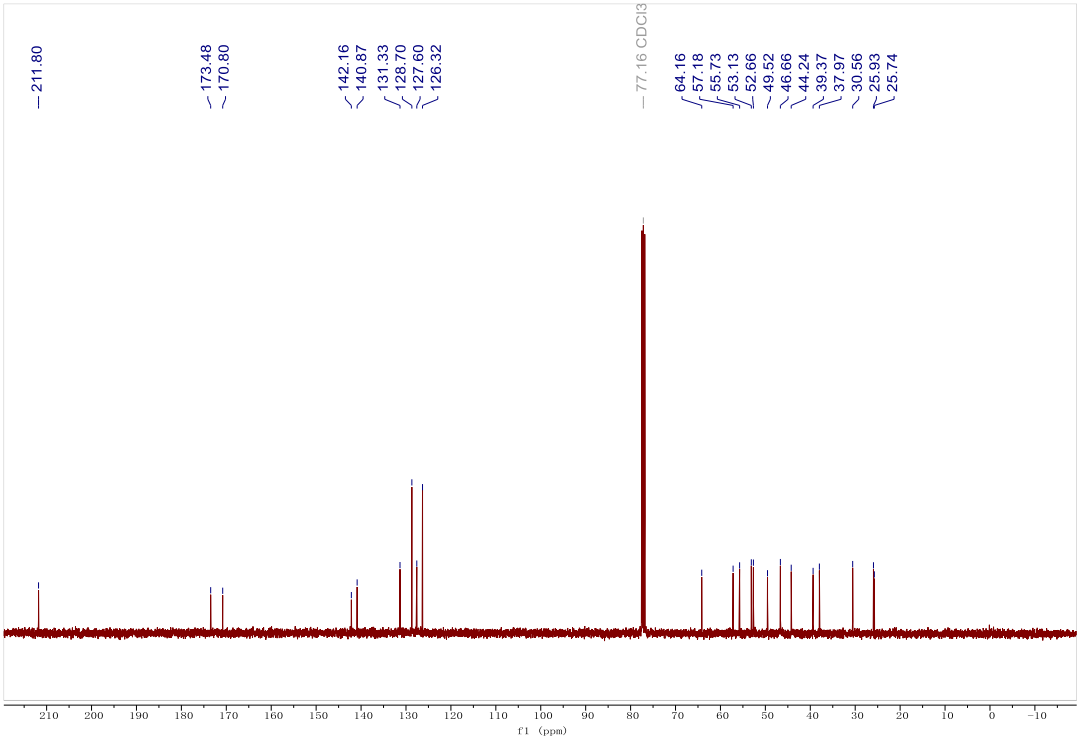
^{1}H NMR in $CDCl_3$, 400 MHz

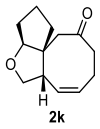




2j

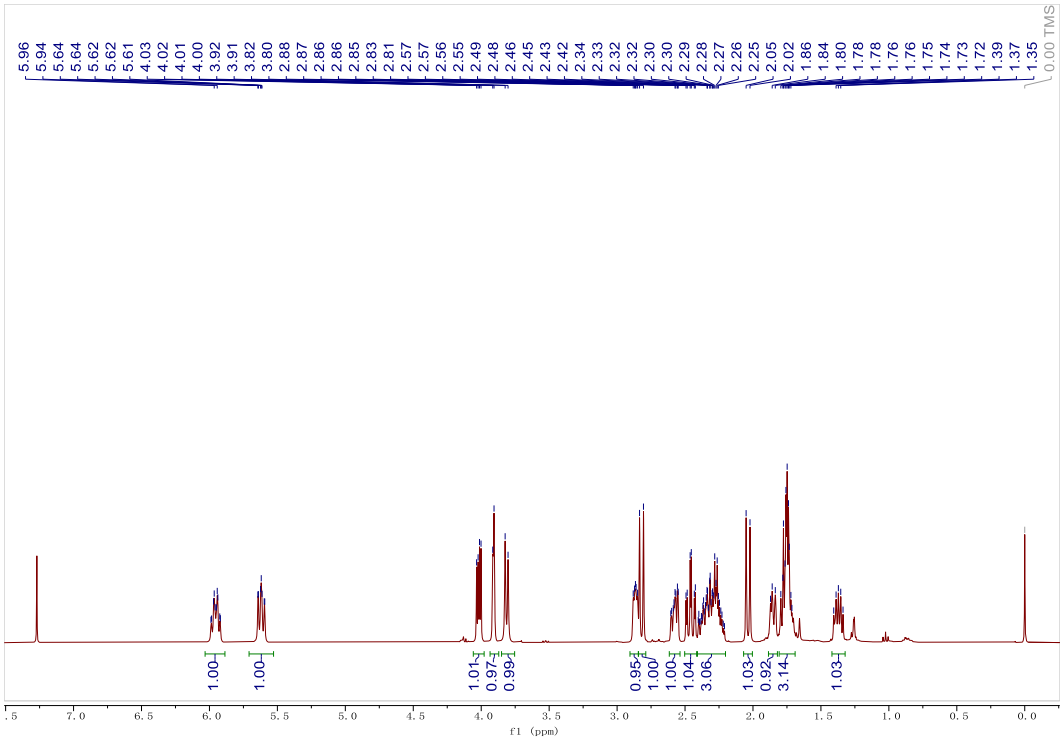
^{13}C NMR in $CDCl_3$, 101 MHz

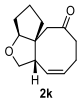




2k

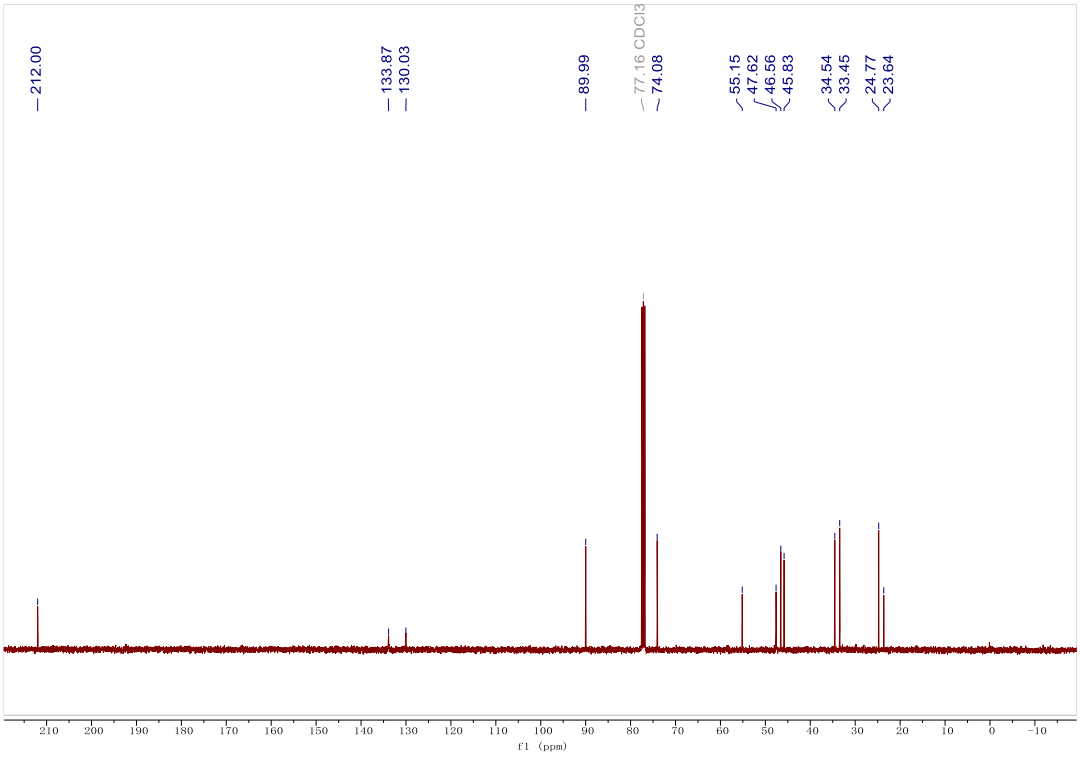
^{1}H NMR in $CDCl_3$, 400 MHz

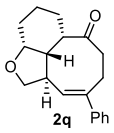




2k

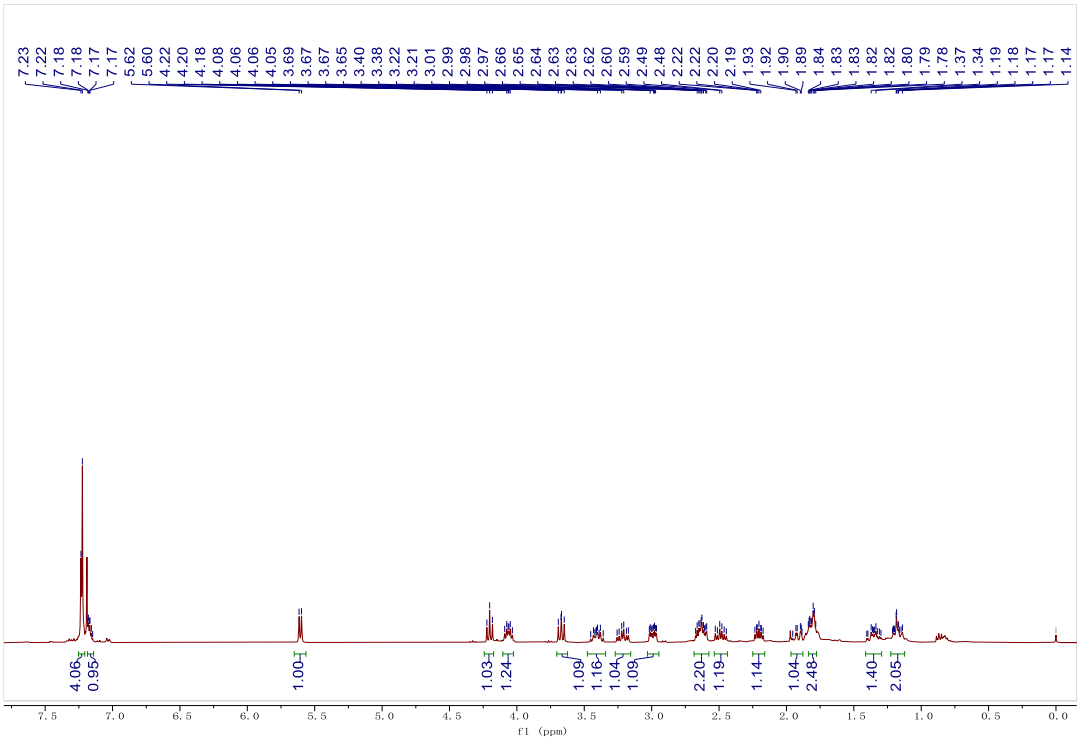
^{13}C NMR in $CDCl_3$, 101 MHz

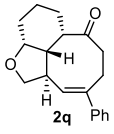




2q

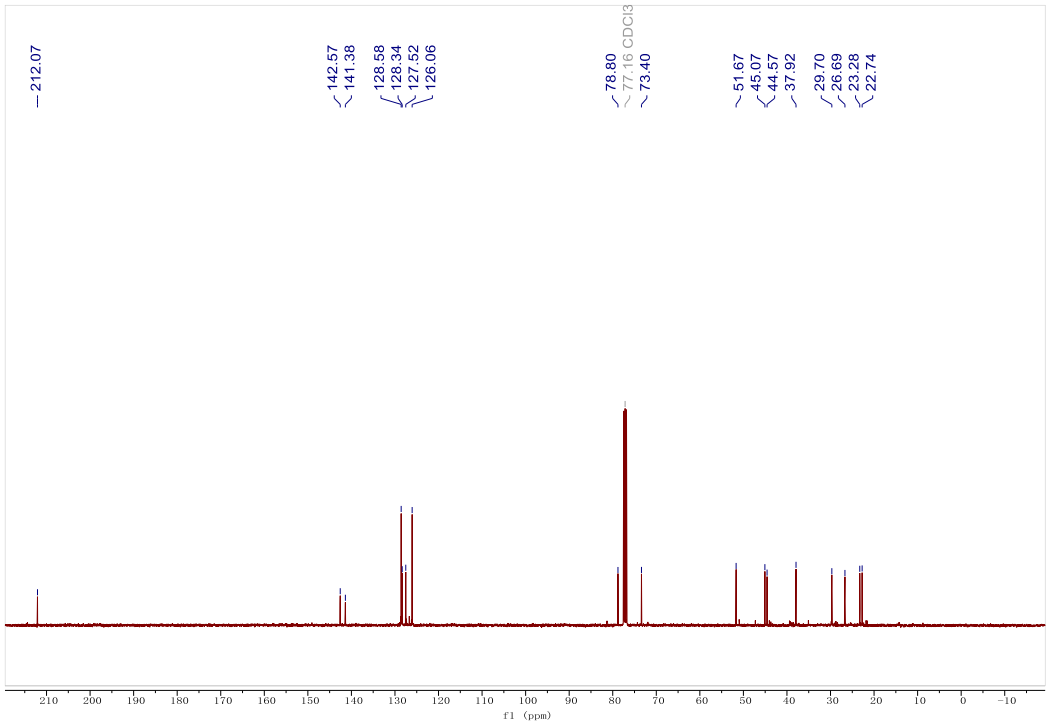
^{1}H NMR in $CDCl_3$, 400 MHz

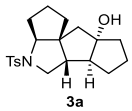




2q

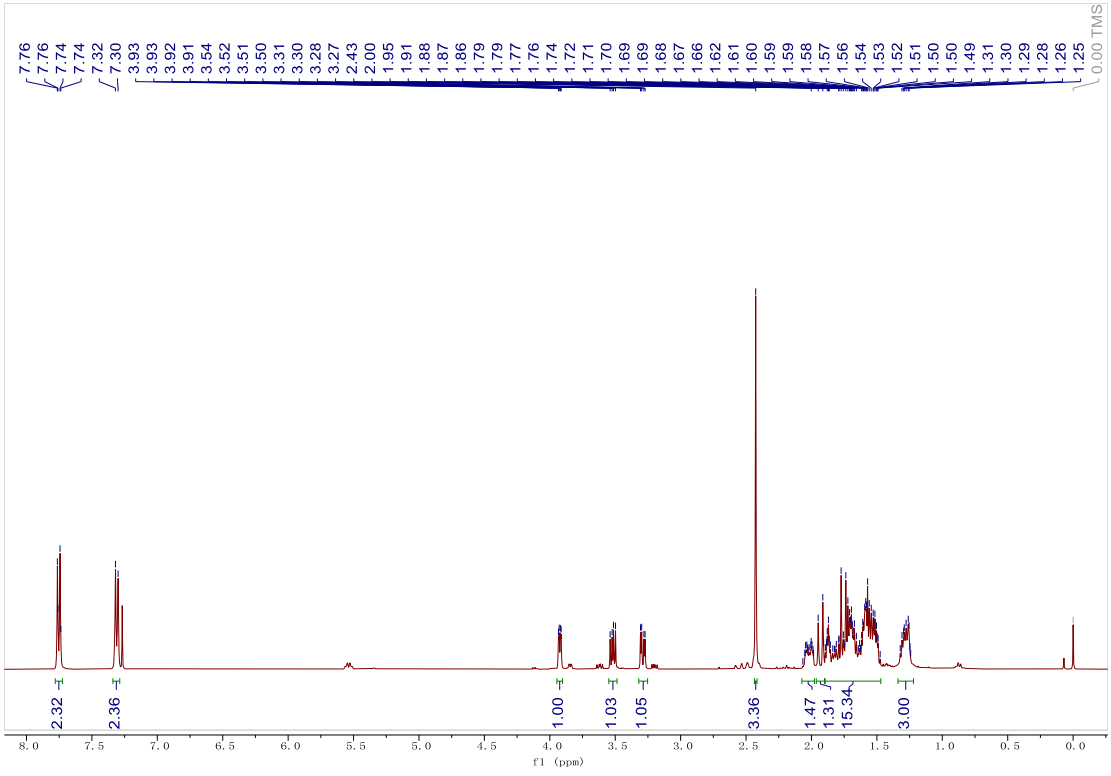
^{13}C NMR in $CDCl_3$, 101 MHz

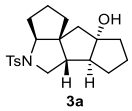




3a

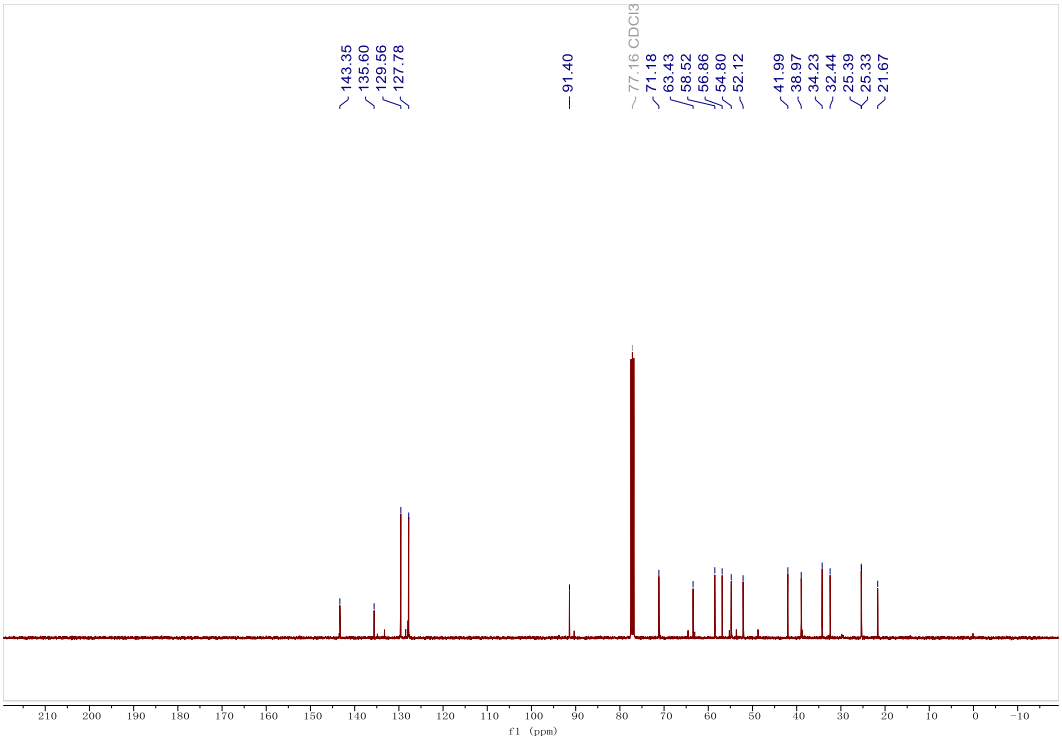
^{1}H NMR in $CDCl_3$, 400 MHz

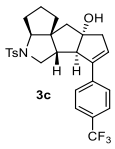




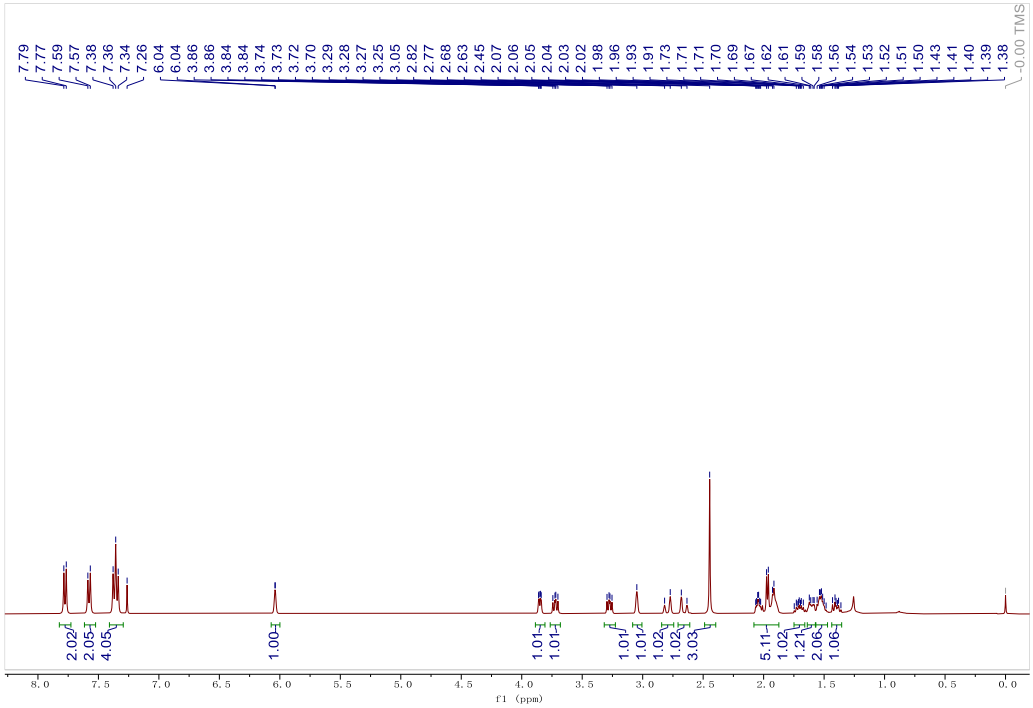
3a

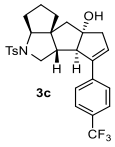
^{13}C NMR in $CDCl_3$, 101 MHz



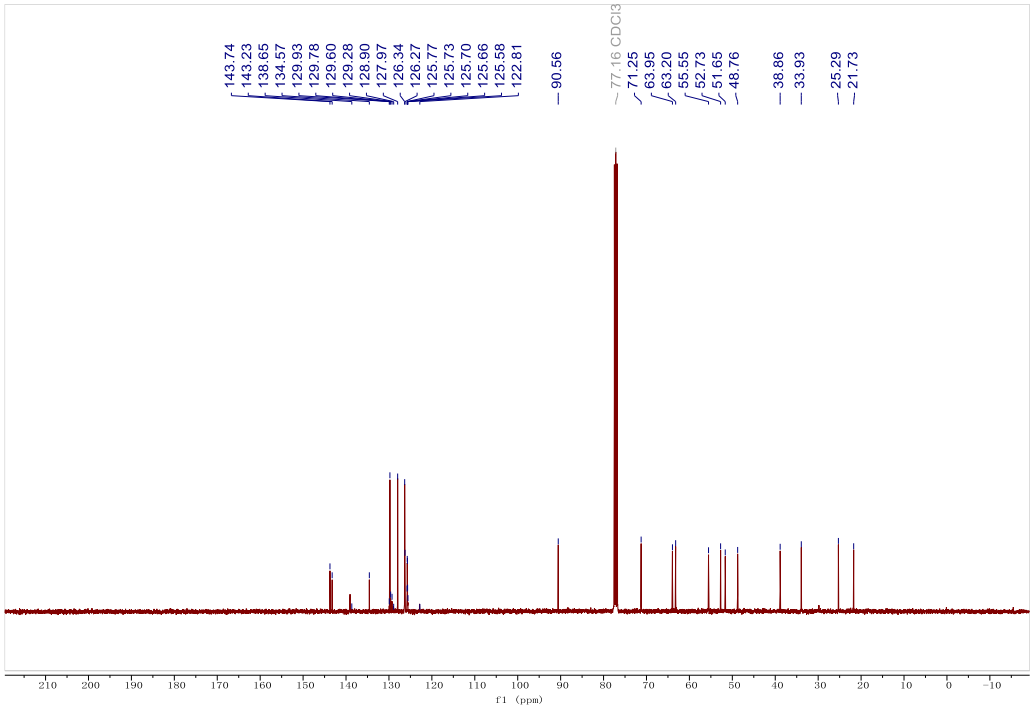


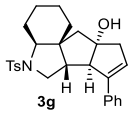
^{1}H NMR in $CDCl_3$, 400 MHz



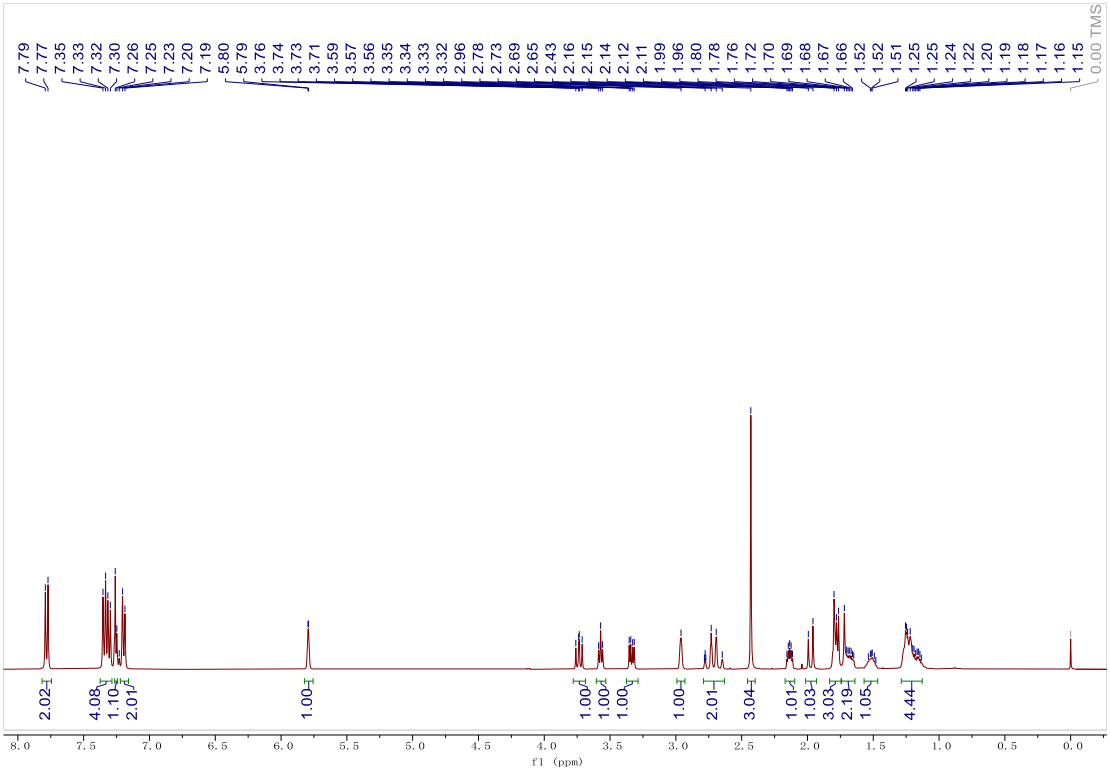


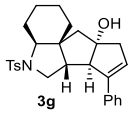
^{13}C NMR in $CDCl_3$, 101 MHz



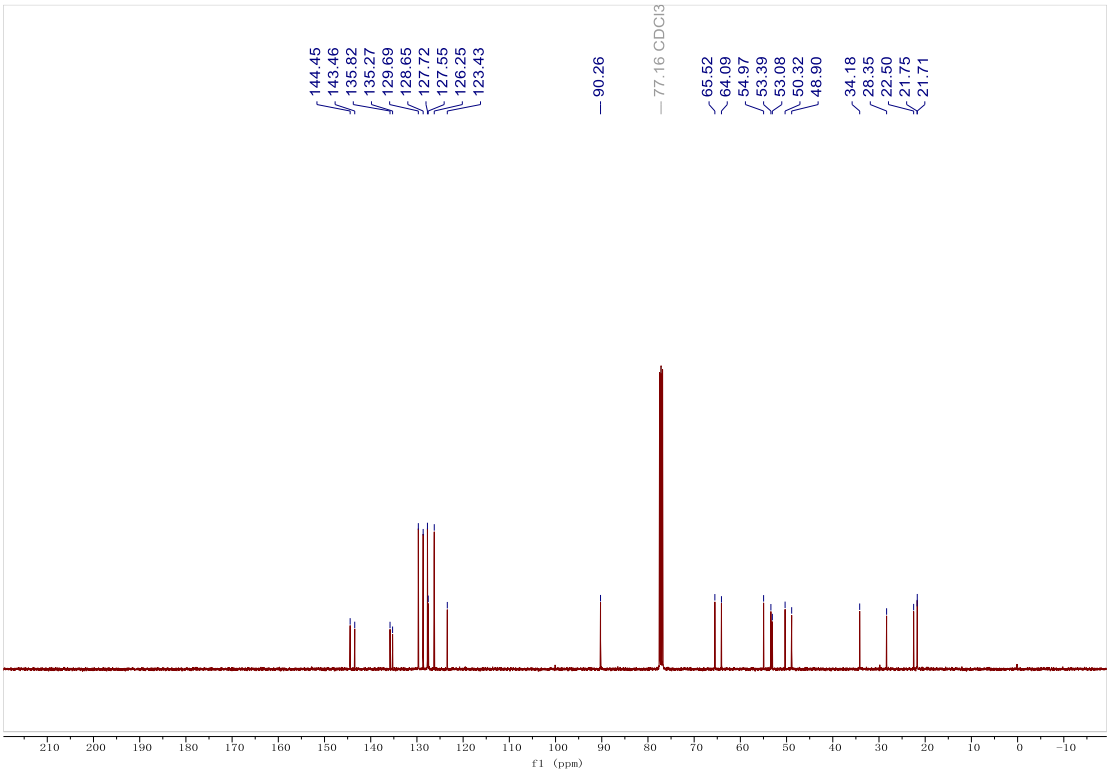


^{1}H NMR in $CDCl_3$, 400 MHz

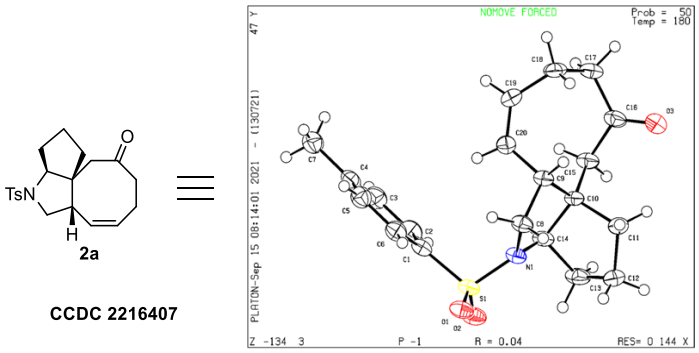




^{13}C NMR in $CDCl_3$, 101 MHz



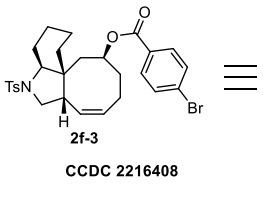
X-ray Crystal Analysis:

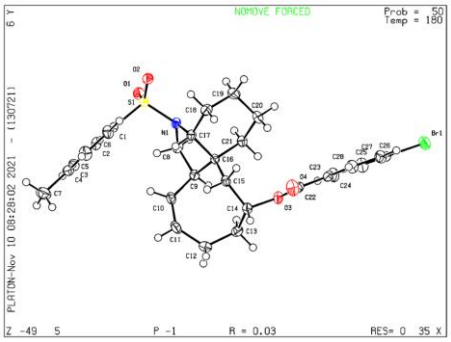


Ellipsoids are drawn at 50% probability

Crystallographic Data of Compound **2a**:

Crystal data	
Chemical formula	$C_{20}H_{25}NO_3S$
M_r	359.47
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	180
a, *b*, *c* (Å)	7.1764 (3), 8.8034 (3), 15.1715 (8)
α, β, γ (°)	95.439 (4), 95.044 (4), 107.991 (4)
V (Å^3)	900.54 (7)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.20
Crystal size (mm)	0.23 × 0.21 × 0.06
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.044, 0.133, 1.08
No. of reflections	4712
No. of parameters	227
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.36, −0.42

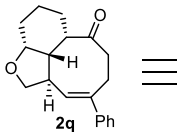




Ellipsoids are drawn at 50% probability

Crystallographic Data of Compound **2f-3**:

Crystal data	
Chemical formula	$C_{28}H_{32}BrNO_4S$
M_r	558.51
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	180
a, *b*, *c* (Å)	9.6222 (3), 11.2622 (4), 12.6918 (6)
α, β, γ (°)	89.485 (3), 81.586 (4), 68.813 (3)
V (Å^3)	1267.17 (9)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	1.74
Crystal size (mm)	0.20 × 0.05 × 0.03
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.030, 0.074, 1.05
No. of reflections	14458
No. of parameters	318
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.49, −0.38



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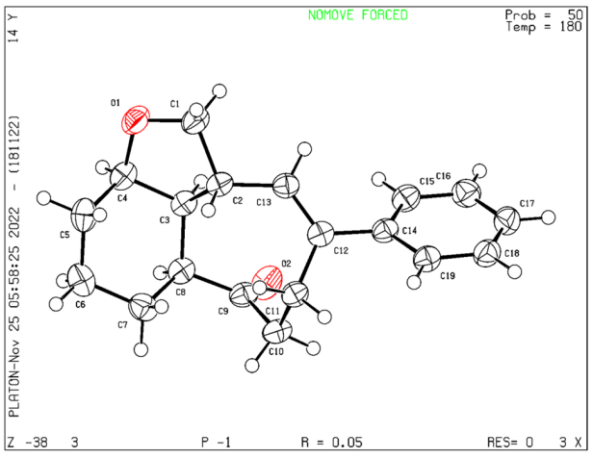

Ellipsoids are drawn at 50% probability

Crystallographic Data of Compound **2q**:

Crystal data	
Chemical formula	$C_{19}H_{22}O_2$
M_r	282.36
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	180
a, b, c (Å)	8.4311 (4), 8.8337 (4), 10.7283 (4)
α, β, γ (°)	105.842 (4), 102.440 (4), 95.246 (4)
V (Å^3)	740.96 (6)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	0.63
Crystal size (mm)	0.15 × 0.06 × 0.03
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.053, 0.157, 1.05
No. of reflections	2779
No. of parameters	190
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.35, −0.20