Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Gold-catalyzed cycloisomerization of alcohol or amine tethered-vinylidenecyclopropanes accessing to morpholine, piperazine or oxazepane derivatives: carbene versus non-carbene process

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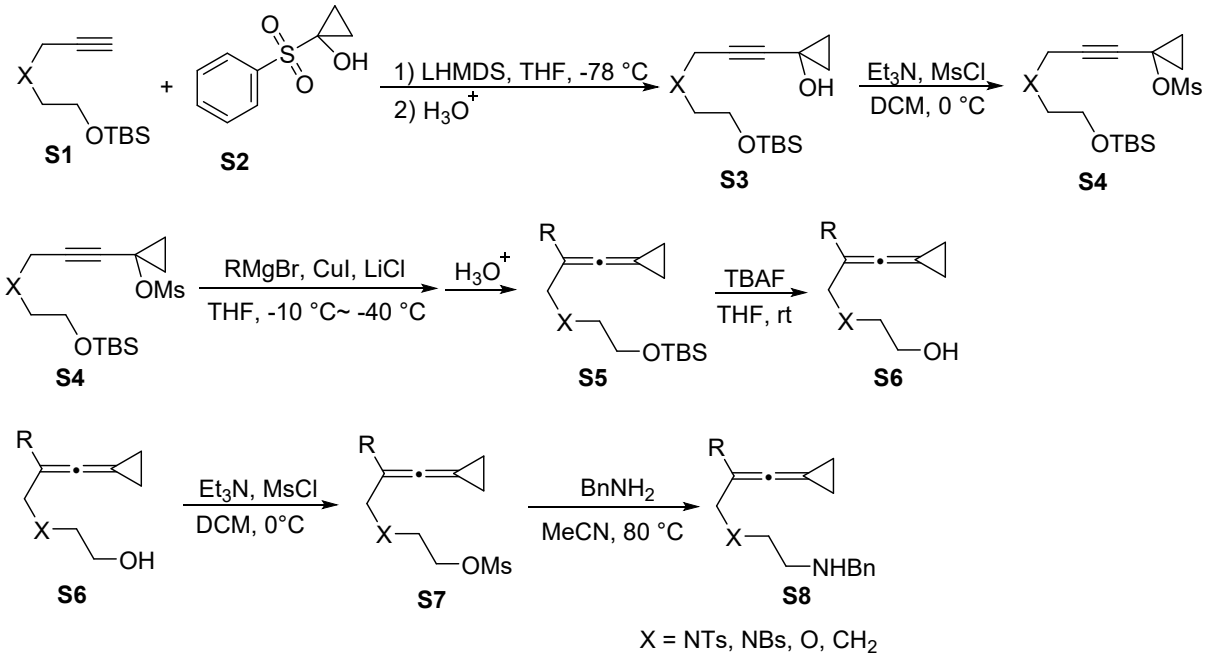
Contents

1 General methods

Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. ^{1}H NMR spectra were measured on a Brucker AC 400 or Agilent (400 MHz) spectrometer. Data were reported as follows: chemical shifts in ppm referenced to the internal solvent signal (peak at 0.00 ppm in the case of $CDCl_3$ with tetramethylsilane as an internal standard), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz), and assignment. ^{13}C NMR spectra were measured on a Brucker AC 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in ppm from the internal solvent signal (peak at 77.000 ppm in the case of $CDCl_3$). Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Flash column chromatography was performed using 300-400 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF254) were used. Chiral HPLC analysis was performed on a SHIMADZU SPD-10A vp series with chiral columns (Chiralpak IC, column 4.6 × 250 mm, (Daicel Chemical Ind., Ltd.)). Mass spectra were recorded by ESI, and HRMS was measured on a HP-5989 instrument. The employed solvents were dry up by standard methods when necessary. Commercially obtained reagents were used without further purification.

2 Preparation of the starting materials



The procedure of preparing compounds **S6** was slightly modified according to the previous literature.[1] To the solution of compounds **S1** (20 mmol) in THF (30 mL) was added LMHDS (22 mmol, 1.0 M in THF) within 20 min at -78 ℃ under argon. The resulting solution was allowed to stir at -78 ℃ for 0.5 h before a solution of **S2** (10 mmol) in THF (10 mL) was added into the above mixture. Consequently, the reaction mixture was allowed to warm up to room temperature and was stirred for 8 h. Then, saturated NH_4Cl solution was added to quench the reaction. Extracted with ethyl ether, dried over anhydrous Na_2SO_4, and filtered, the organic phase was purified by a flash column chromatography on silica gel to give the corresponding products **S3** (PE/EA: 4:1~2:1).

Under argon atmosphere, compound **S3** (4.0 mmol) was dissolved in DCM (10.0 mL) at 0 ℃, Et_3N (8.0 mmol) and MsCl (6.0 mmol) was added. After stirring for 1.0 h, the reaction was quenched with H_2O (10.0 mL), extracted with DCM (10 mL x 3), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding product **S4** (PE/EA: 4:1).

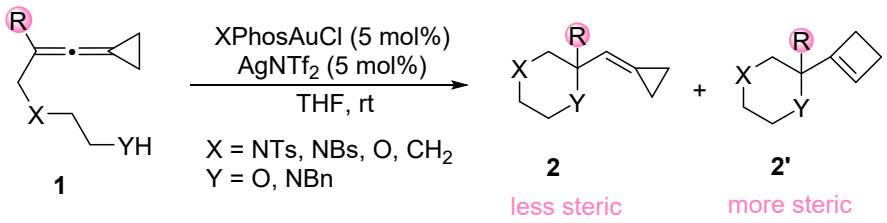
Under argon atmosphere, CuI (2.2 mmol) and LiCl (2.2 mmol) in a three-necked bottle was dried upon heating. Then THF (10 mL) was added. At -5 ℃, RMgBr (1.0 mol/L in THF, 2.0 mmol, 2.0 mL) was added to the reaction mixture. 10 minutes later, the flask was moved into a - 40 ℃ bath and the reaction mixture was stirred for a while before a solution of **S4** (1.0 mmol) in THF (10 mL) was added dropwise into the above flask. After stirring at -40 ℃ for 8.0 h, the reaction was quenched with saturated NH_4Cl solution, extracted with EA (10 mL x 3), and dried over anhydrous

Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding product **S5** (PE/EA: 10:1).In a flame dried 20 mL vial, compound **S5** (2 mmol, 1.0 eq.) was combined with anhydrous THF (10 mL) under argon, and then TBAF (1.0 M solution in THF, 3.0 mL, 3.0 mmol, 1.5 eq.) was added all at once. The reaction solution was left to stir at 0 ℃ for 1.0 h, and then was concentrated under reduced pressure and purified directly by a flash chromatography (SiO_2) to give product **S6** (PE/EA: 2:1).

Under argon atmosphere, compound **S6** (2.0 mmol) was dissolved in DCM (10.0 mL) at 0 ℃, Et_3N (4.0 mmol) and MsCl (3.0 mmol) was added. After stirring for 1.0 h, the reaction was quenched with H_2O (5.0 mL), extracted with DCM (5 mL x 3), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding product **S7** (PE/EA: 2:1).

To the solution of **S7** (1.5 mmol) in acetonitrile (10 ml) was added $BnNH_2$ (1.8 mmol). The resulting solution was warmed to 70 ℃ and stirred for 8 h. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding product **S8** (PE/EA: 1:1).

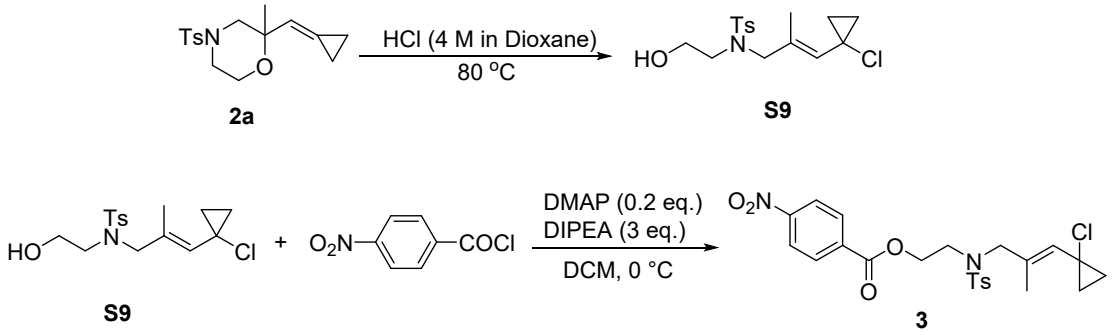
3 General procedure for the synthesis of compounds 2 and 2'



To a mixture of **1** (0.2 mmol), XPhosAuCl (7.1 mg, 5 mol%) and $AgNTf_2$ (3.9 mg, 5 mol%) was added THF (4.0 mL). The reaction mixture was stirred at room temperature until the substrates were completely consumed under ambient atmosphere. The solvent was evaporated and the residue was purified by a silica gel chromatography (PE/EA = 10/1) to furnish the desired product.

4 Experimental procedures for the transformations of the cyclization products 2a and 2q'

Experimental procedure for the synthesis of compound **3**

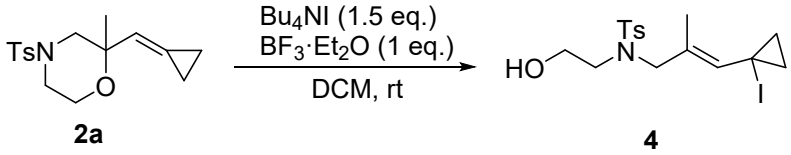


In a 10 mL vial, compound **2a** (61.4 mg, 0.2 mmol) was combined with 4.0 M HCl in Dioxane (0.2 mL). After stirring for 1.0 h, the reaction mixture was diluted with EtOAc (1.0 mL) and water (0.5 mL). The organic phase was collected, and the aqueous phase was washed with more EtOAc (2 x 1 mL). The combined organic phases were dried over sodium sulfate, concentrated under reduced pressure, and the residue was purified by a flash column chromatography (SiO_2, PE/EA: 2:1) to give the corresponding product **S9** (61.8 mg, 90%).

In a flame dried 2-dram vial, compound **S9** (61.8 mg, 0.18 mmol, 1.0 eq.) was combined with anhydrous DCM (1.0 mL), DMAP (13.5 mg, 0.036 mmol, 0.2 eq.) and DIPEA (0.32 mL, 0.54 mmol, 3.0 eq.) under an argon atmosphere. The reaction solution was cooled to 0 °C, and then a solution of *para*-nitrobenzoyl chloride (82.8 mg, 0.45 mmol, 2.5 eq.) in DCM (1.0 mL) was added slowly over a 5-min period (the reaction solution turned to yellow color). The resulting solution was left to stir at 0 °C for another 15 min, and then was warmed to room temperature for 45 min. The reaction was then quenched with water (1.0 mL), diluted with EtOAc (2.0 mL), and washed with

water (1.0 mL) and brine (1.0 mL). The organic phase was collected, dried over sodium sulfate, filtered and concentrated under reduced pressure to give a yellow oil, which was purified by a flash chromatography (PE/EA: 4:1) to give compound **3** (77.0 mg, 87%) as a colorless solid.

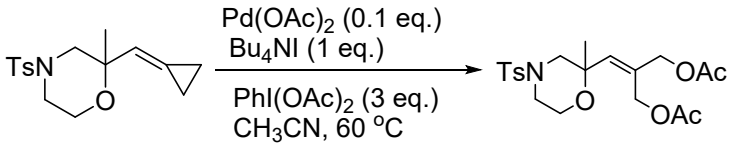
Experimental procedure for the synthesis of compound **4**



2a **4**

In a 10 mL vial, compound **2a** (30.7 mg, 0.1 mmol, 1.0 eq.) was combined with DCM (1.0 mL), Bu_4NI (55.4 mg, 0.15 mmol, 1.5 eq.) and $BF_3{\cdot}Et_2O$ (1.0 eq.). After stirring at room temperature for 6.0 h, the reaction mixture was concentrated under reduced pressure, and diluted with water (1.0 mL) and EtOAc (2.0 mL). The organic phase was collected, and then the aqueous phase was washed with more EtOAc (2 x 2 mL). The combined organic phases were dried over sodium sulfate, concentrated under reduced pressure, and the residue was purified by a flash column chromatography (SiO_2, PE/EA: 2:1) to give the corresponding product **4** (29.1 mg, 67%).

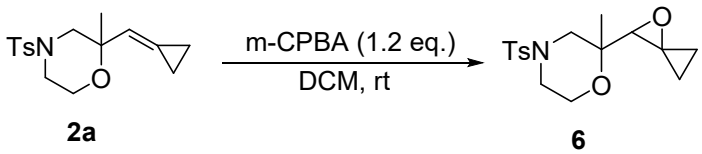
Experimental procedure for the synthesis of compound **5**



2a **5**

The procedure of preparing compound **5** was slightly modified according to the previous literature.[2] Under ambient atmosphere, compound **2a** (0.1 mmol), $PhI(OAc)_2$ (0.3 mmol), $Pd(OAc)_2$ (0.01 mmol), Bu_4NI (0.1 mmol), and CH_3CN (1.0 mL) were added into an Schlenk tube. The reaction mixture was stirred at 60 ℃ until the reaction was complete. Then, the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2, PE/EA: 2:1) to give the product **5** (17.5 mg, 42%) as a colorless oil.

Experimental procedure for the synthesis of compound **6**

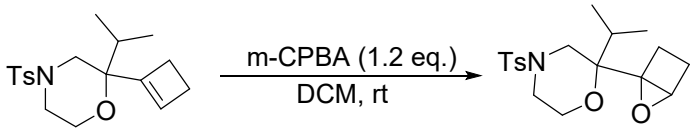


2a **6**

In a 10 mL vial, compound **2a** (30.7 mg, 0.1 mmol, 1.0 eq.) was combined with DCM (1.0 mL) and m-CPBA (0.12 mmol, 1.2 eq.). After stirring at room temperature for 12 h, the reaction mixture was

concentrated under reduced pressure, and diluted with water (1.0 mL) and EtOAc (2.0 mL). The organic phase was collected, and then the aqueous phase was washed with more EtOAc (2 x 2 mL). The combined organic phases were dried over sodium sulfate, concentrated under reduced pressure, and the residue was purified by a flash column chromatography (SiO_2, PE/EA: 10:1) to give the corresponding product **6** (20.9 mg, 68%).

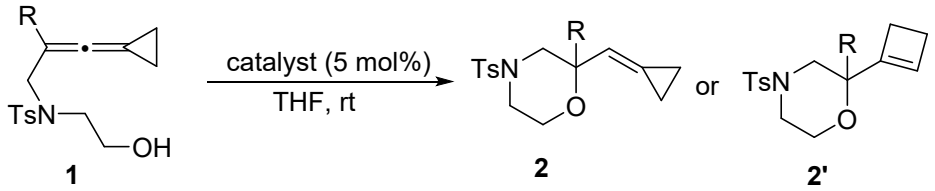
Experimental procedure for the synthesis of compound **7**



2q' **7**

In a 10 ml vial, compound **2q'** (33.5 mg, 0.1 mmol, 1.0 eq.) was combined with DCM (1.0 mL) and m-CPBA (0.12 mmol, 1.2 eq.). After stirring at room temperature for 1.0 h, the reaction mixture was concentrated under reduced pressure, and diluted with water (1.0 mL) and EtOAc (2.0 mL). The organic phase was collected, and then the aqueous phase was washed with more EtOAc (2 x 2 mL). The combined organic phases were dried over sodium sulfate, concentrated under reduced pressure, and the residue was purified by a flash column chromatography (SiO_2, PE/EA: 10:1) to give the corresponding product **7** (33.0 mg, 94%).

5 Control experiments

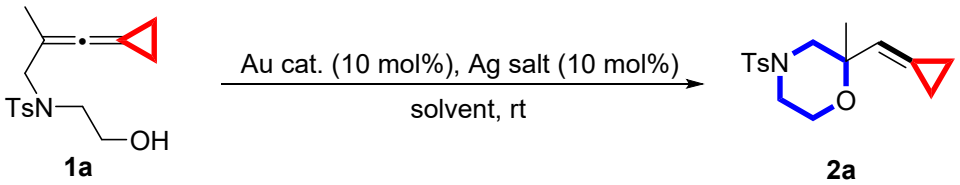


substrate	catalyst (5 mol%)	yield/%
1a	XPhosAuCl	NR
1a	$AgNTf_2$	NR
1a	$HNTf_2$	NR
1q	XPhosAuCl	NR
1q	$AgNTf_2$	NR
1q	$HNTf_2$	NR

All reactions were carried out using **1a** or **1q** (0.2 mmol), catalyst (5 mol%) in THF (4.0 mL) at room temperature.

6 Asymmetric studies

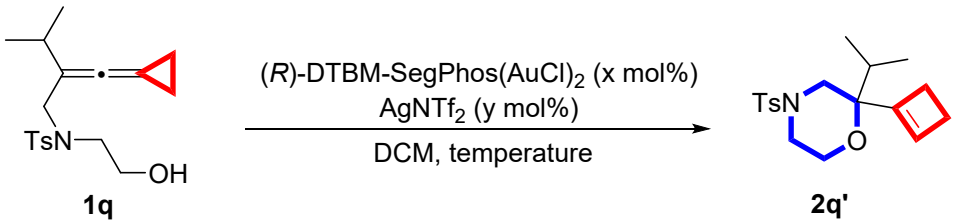
Using **1a** as substrate to screen the reaction conditions:



entry[a]	Au cat.	Ag salt (mol%)	solvent	yield (%)[b]	ee (%)
1	(*R*)-xyl-PHANEPhos$(AuSbF_6)_2$	-	THF	49	4
2	(*R*)-Xyl-BINAP$(AuCl)_2$	$AgNTf_2$, 10	THF	76	-
3	(*R*)-DTBM-SegPhos$(AuCl)_2$	$AgNTf_2$, 10	THF	62	26
4	(*R*)-DTBM-SegPhos$(AuCl)_2$	$AgNTf_2$, 10	Toluene	87	21
5	(*R*)-DTBM-SegPhos$(AuCl)_2$	$AgNTf_2$, 10	DCM	78	55
6	(*R*)-DTBM-SegPhos$(AuCl)_2$	$AgNTf_2$, 10	DCE	49	49
7	(*R*)-DTBM-SegPhos$(AuCl)_2$	AgOTs, 10	DCM	90	10
8	(*R*)-DTBM-SegPhos$(AuCl)_2$	$AgSbF_6$, 10	DCM	61	52
9[c]	(*R*)-DTBM-SegPhos$(AuCl)_2$	$AgNTf_2$, 5	DCM	65	40
10[c]	(*R*)-DTBM-SegPhos$(AuCl)_2$	$AgNTf_2$, 10	DCM	70	49

[a] All reactions were carried out using **1a** (0.1 mmol), Au cat. (5 mol%). [b] Isolated yields. [c] Temperature: - 5 °C

Using **1q** as substrate to screen the reaction conditions:

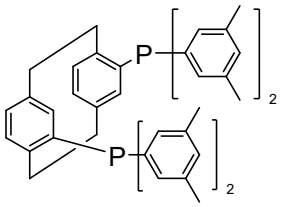


1q **2q'**

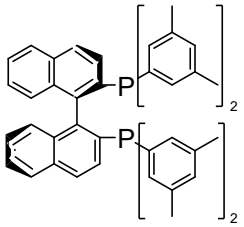
entry[a]	Au cat. (x mol%)	Ag salt (y mol%)	temperature	yield (%)[b]	ee (%)
1	(*R*)-DTBM-SegPhos(AuCl)$_2$, 5	AgNTf$_2$, 10	rt	84	55
2	(*R*)-DTBM-SegPhos(AuCl)$_2$, 5	AgNTf$_2$, 5	- 5 °C	88	72

[a] All reactions were carried out using **1q** (0.1 mmol), Au cat. (5 mol%). [b] Isolated yields.

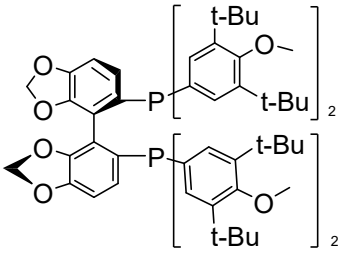
Chiral Ligands:



(*R*)-xyl-PHANEPhos

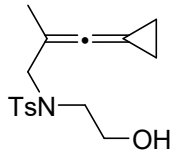


(*R*)-Xyl-BINAP

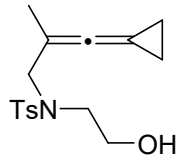


(*R*)-DTBM-SegPhos

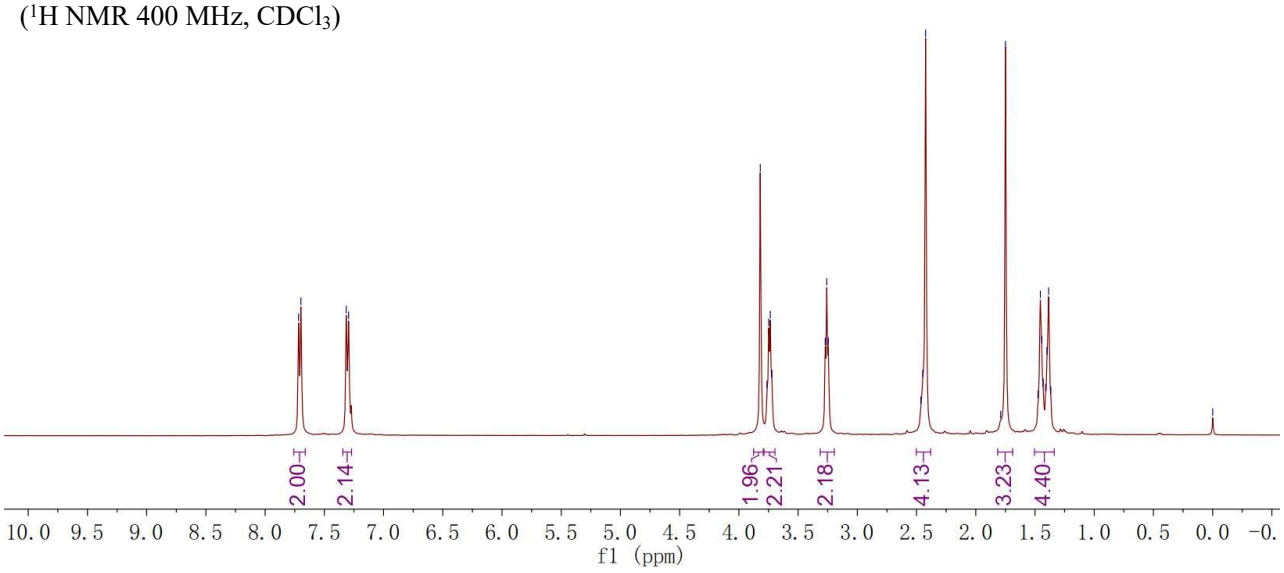
7 Spectroscopic data

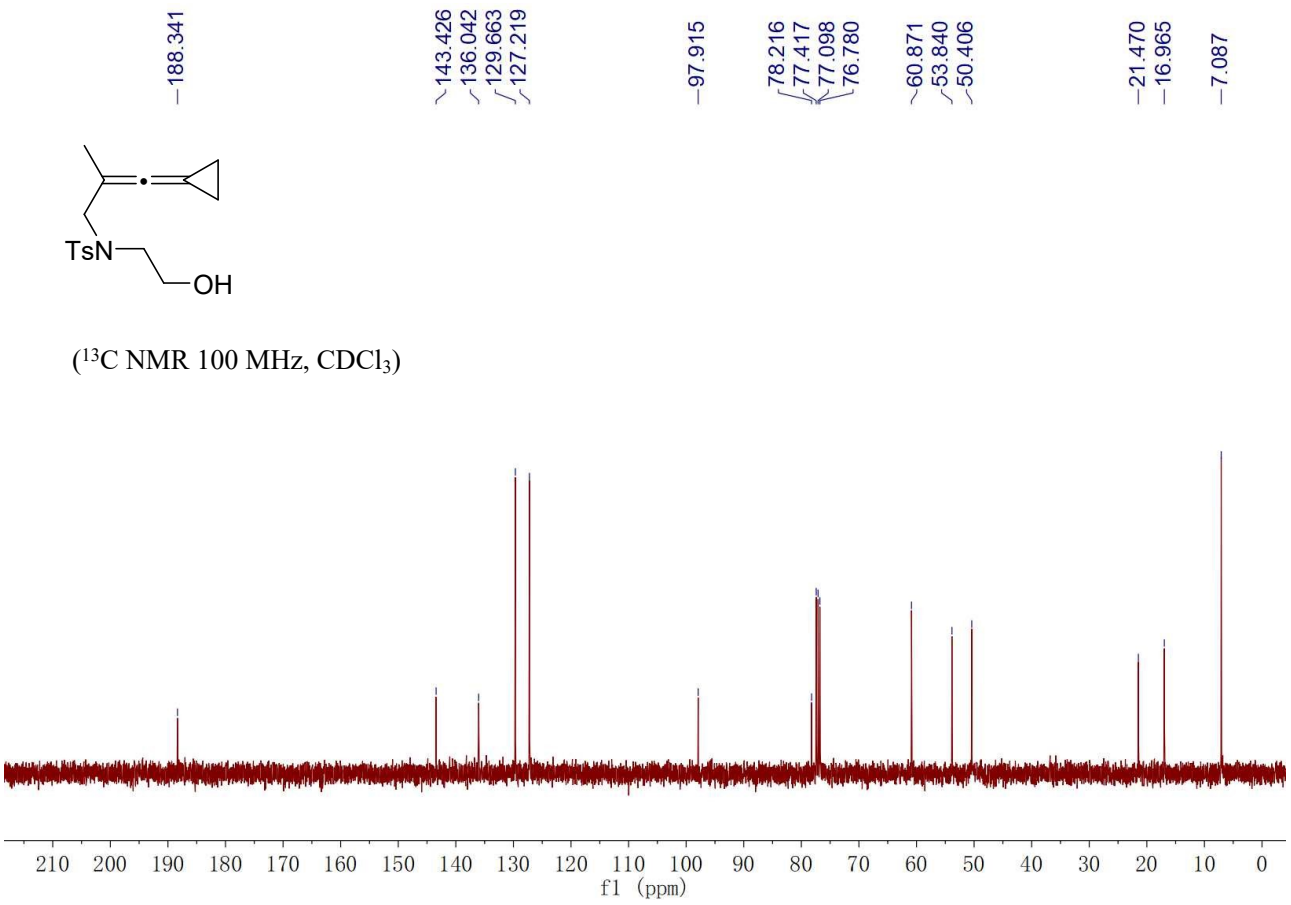


Compound 1a: Yield: 589.4 mg, 96%; A colorless solid; Mp: 63 – 65 ℃; Eluent: PE/EA = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.82 (s, 2H), 3.76 – 3.72 (m, 2H), 3.26 (t, *J* = 5.6 Hz, 2H), 2.46 – 2.42 (m, 4H), 1.75 (s, 3H), 1.50 - 1.34 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 188.3, 143.4, 136.0, 129.7, 127.2, 97.9, 78.2, 60.9, 53.8, 50.4, 21.5, 17.0, 7.1; IR (neat): ν 3520, 2990, 2912, 2023, 1600, 1328, 1154, 1098, 909, 813, 729 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{16}H_{21}NO_3NaS$ $[M+Na]^+$: 330.11344, found: 330.11427.

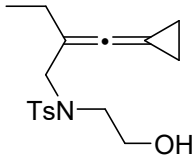


(^{1}H NMR 400 MHz, $CDCl_3$)

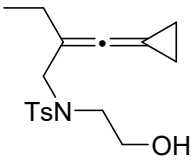




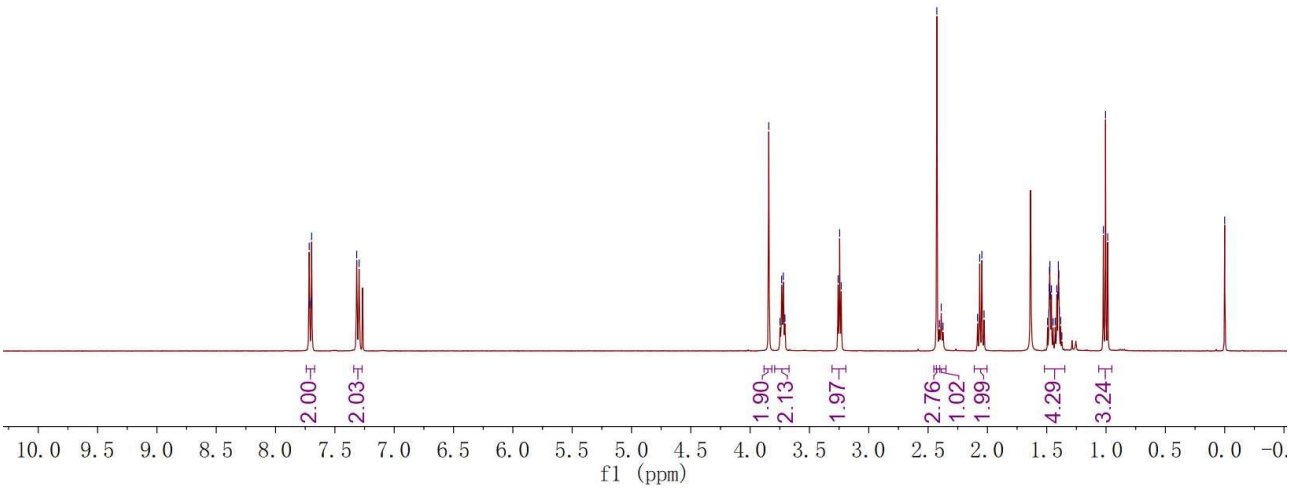
(^{13}C NMR 100 MHz, $CDCl_3$)

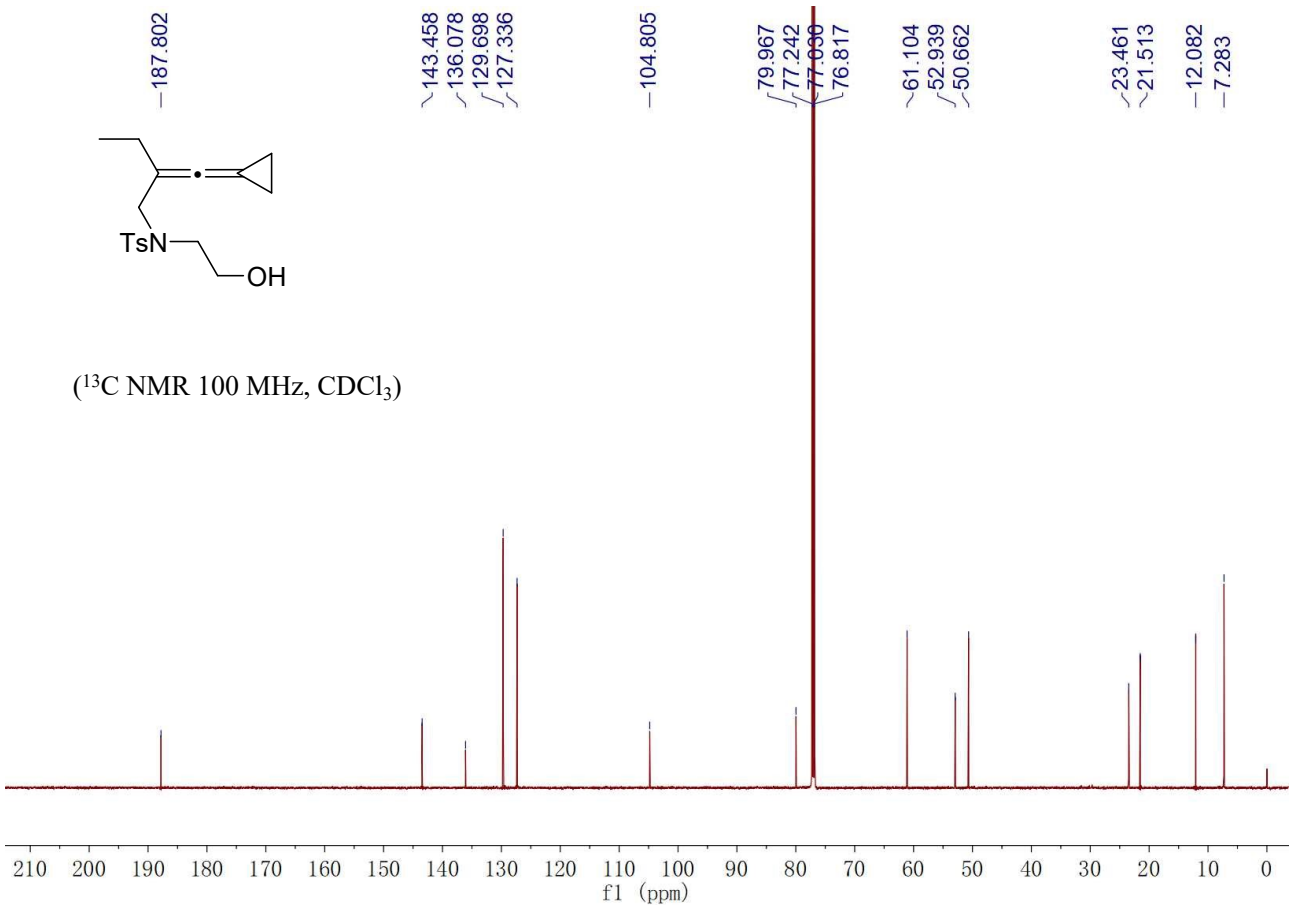


Compound 1b: Yield: 597.1 mg, 93%; A colorless solid; Mp: 62 – 64 ℃; Eluent: PE/EA = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.84 (s, 2H), 3.75 – 3.71 (m, 2H), 3.25 (t, *J* = 5.5 Hz, 2H), 2.43 (s, 3H), 2.39 (t, *J* = 6.0 Hz, 1H), 2.06 (q, *J* = 7.4 Hz, 2H), 1.52 – 1.42 (m, 2H), 1.45 – 1.35 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 187.8, 143.5, 136.1, 129.7, 127.3, 104.8, 80.0, 61.1, 52.9, 50.7, 23.5, 21.5, 12.1, 7.3; IR (neat): ν 3276, 2959, 2913, 2849, 2023, 1527, 1454, 1355, 1086, 966, 809 ,753 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{17}H_{23}NO_3NaS$ $[M+Na]^+$: 344.12909, found:344.12927.

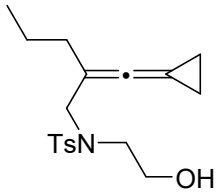


(^{1}H NMR 400 MHz, $CDCl_3$)

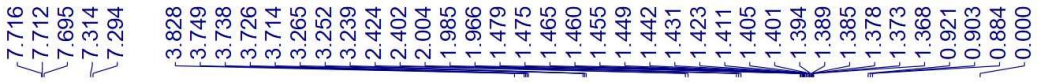


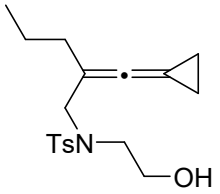


(^{13}C NMR 100 MHz, $CDCl_3$)

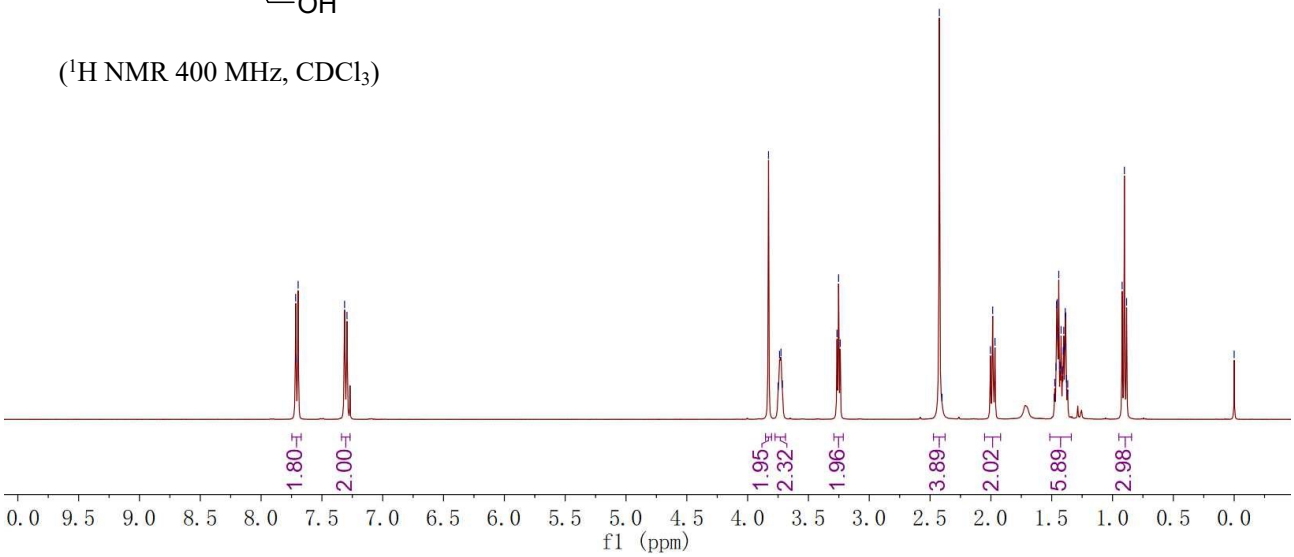


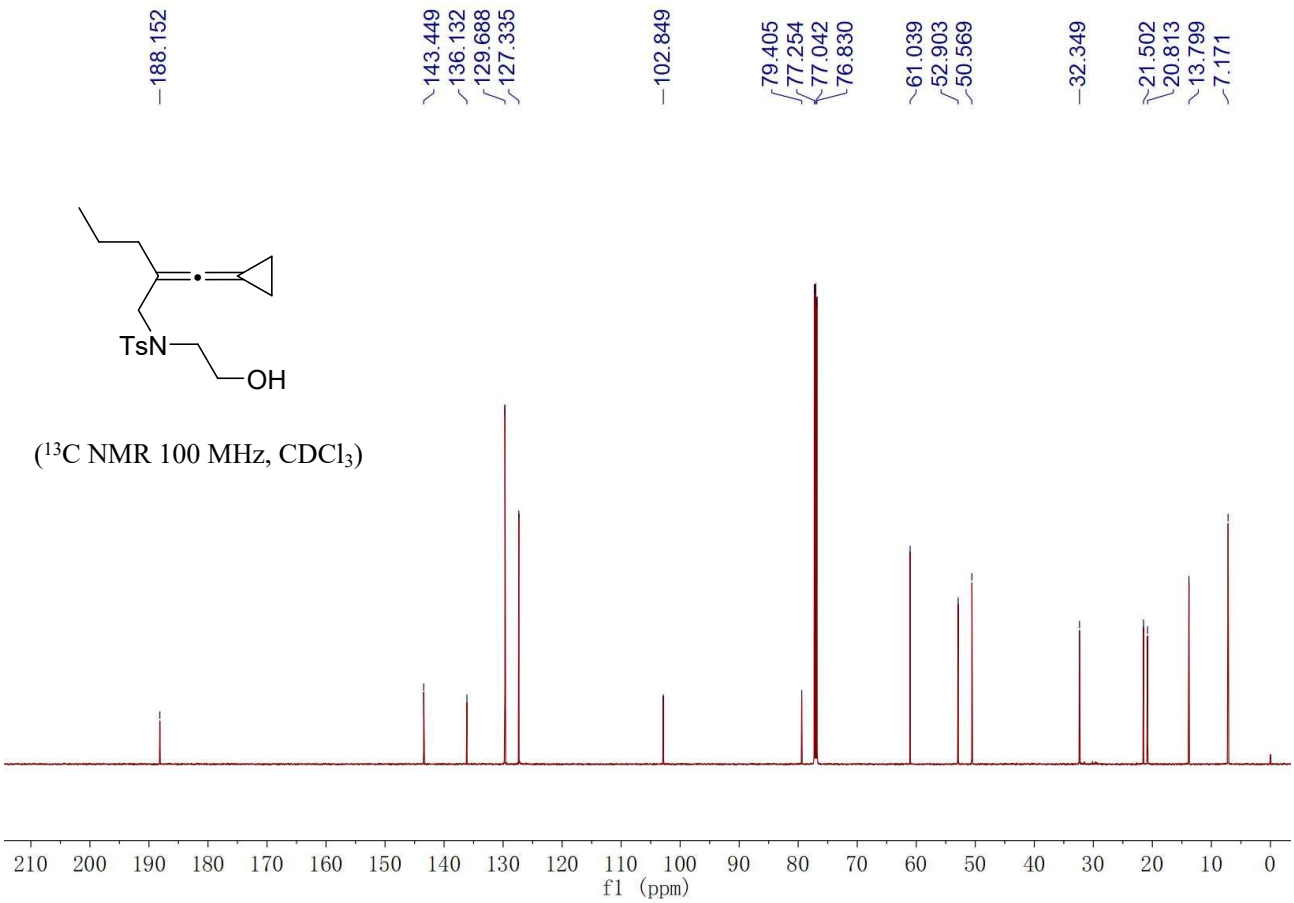
Compound 1c: Yield: 616.4 mg, 92%; A colorless solid; Mp: 59 – 61 ℃; Eluent: PE/EA = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.83 (s, 2H), 3.75 – 3.71 (m, 2H), 3.25 (t, *J* = 5.2 Hz, 2H), 2.42 – 2.40 (m, 4H), 1.99 (t, *J* = 7.5 Hz, 2H), 1.36 - 1.49 (m, 6H), 0.90 (t, *J* = 7.5 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 188.2, 143.4, 136.1, 129.7, 127.3, 102.8, 79.4, 61.0, 52.9, 50.6, 32.3, 21.5, 20.8, 13.8, 7.2; IR (neat): ν 3259, 2926, 2904, 2024, 1446, 1335, 1281, 1017, 989, 806, 829, 661 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{18}H_{25}NO_3NaS$ $[M+Na]^+$: 358.14474, found: 358.14484.



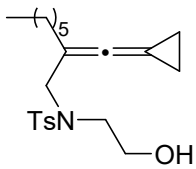


(^{1}H NMR 400 MHz, $CDCl_3$)

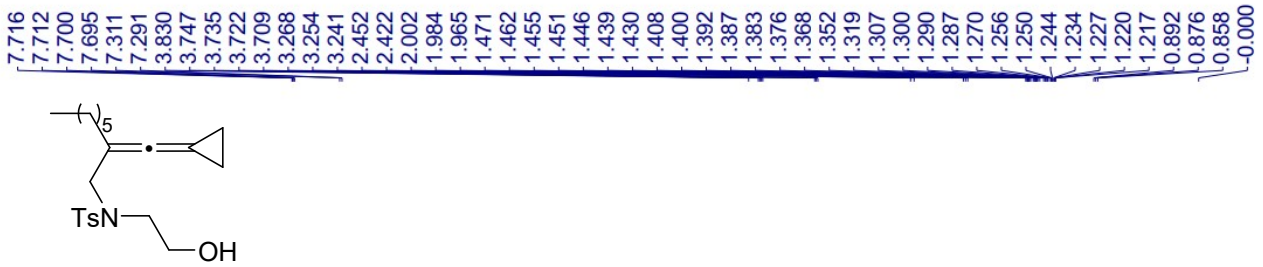




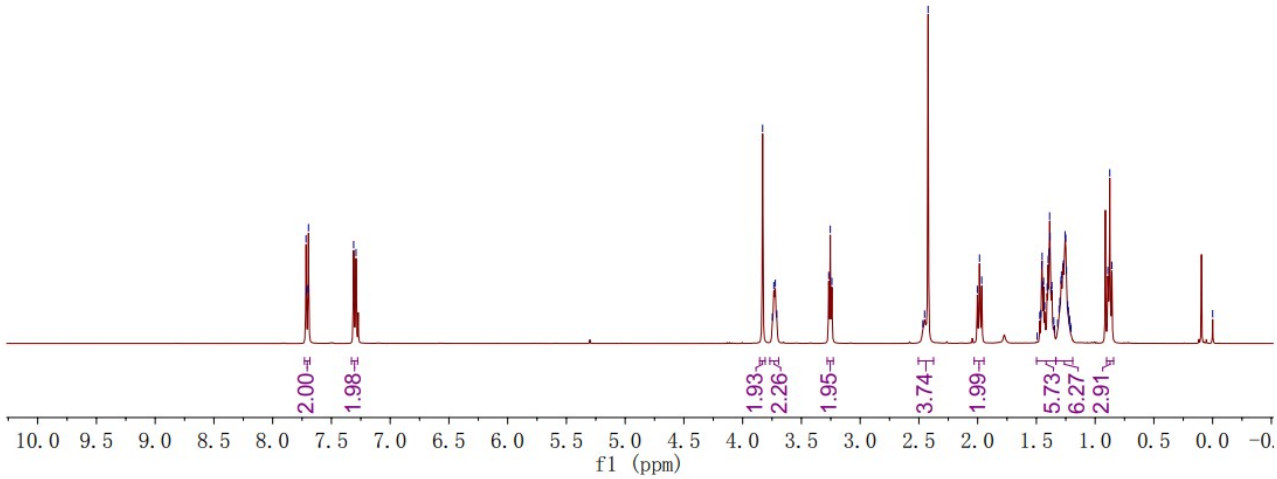
(^{13}C NMR 100 MHz, $CDCl_3$)

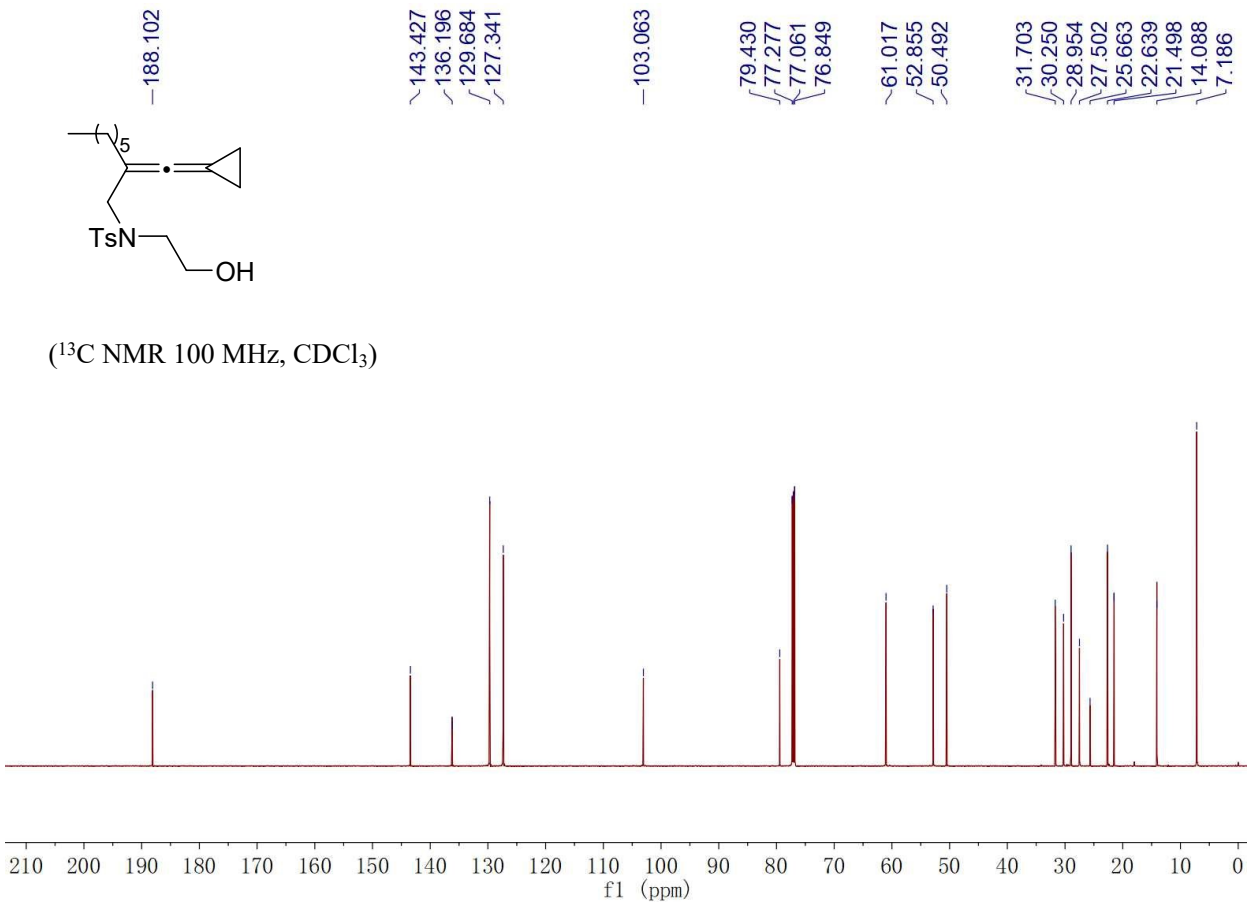


Compound 1d: Yield: 708.8 mg, 94%; A yellow oil; Eluent: PE/EA = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.73 – 7.68 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.83 (s, 2H), 3.75 – 3.71 (m, 2H), 3.25 (t, *J* = 5.4 Hz, 2H), 2.47 – 2.42 (m, 4H), 1.98 (t, *J* = 7.5 Hz, 2H), 1.50 – 1.34 (m, 6H), 1.33 – 1.19 (m, 6H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 188.1, 143.4, 136.2, 129.7, 127.3, 103.1, 79.4, 61.0, 52.9, 50.5, 31.7, 30.3, 29.0, 27.5, 25.7, 22.6, 21.5, 14.1, 7.2; IR (neat): ν 3531, 2925, 2855, 2023, 1602, 1448, 1331, 1044, 988, 813, 730 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{21}H_{31}NO_3NaS$ $[M+Na]^+$: 400.19169, found: 400.19187.

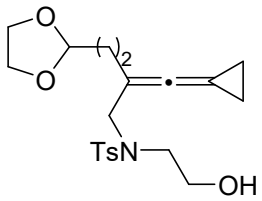


(^{1}H NMR 400 MHz, $CDCl_3$)

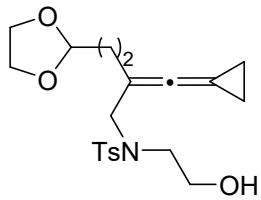




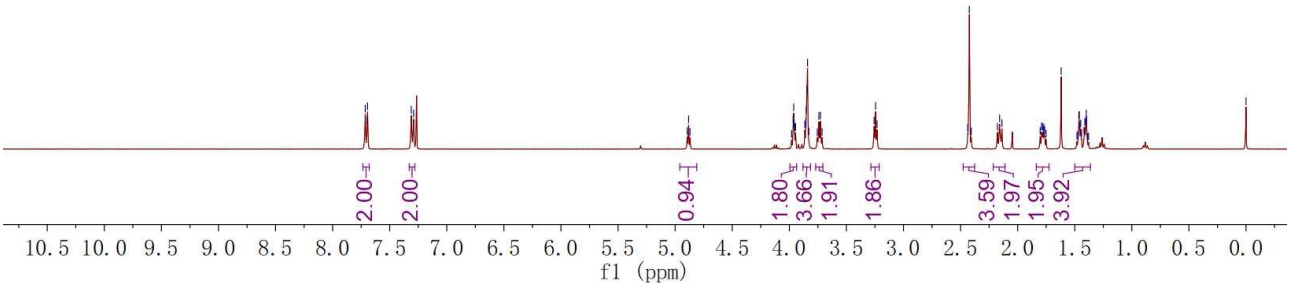
(^{13}C NMR 100 MHz, $CDCl_3$)

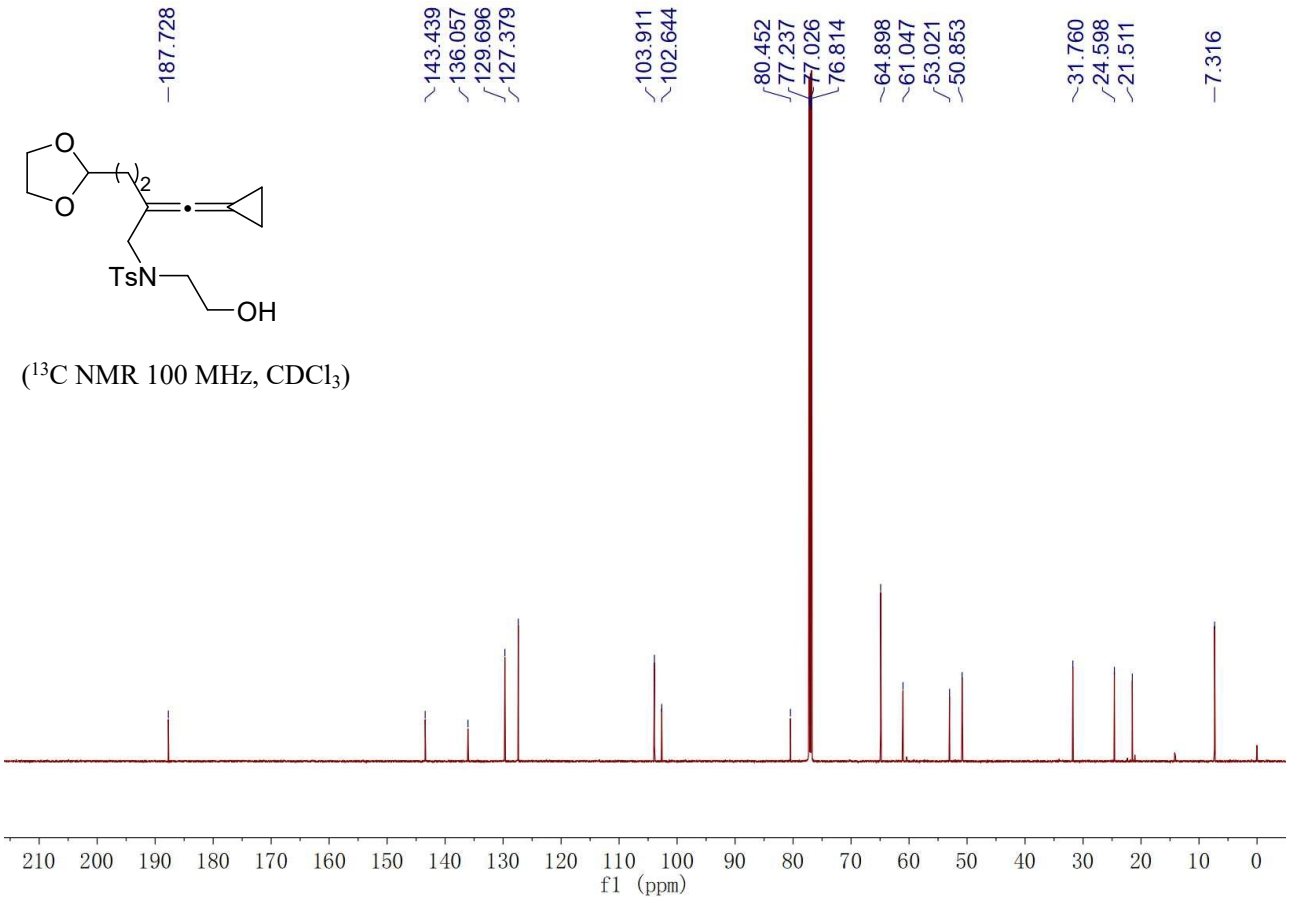


Compound 1e: Yield: 746.7 mg, 95%; A colorless solid; Mp: 80 – 84 ℃; Eluent: PE/EA = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.75 – 7.67 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.88 (t, *J* = 4.7 Hz, 1H), 4.00 – 3.89 (m, 2H), 3.91 – 3.80 (m, 4H), 3.76 – 3.71 (m, 2H), 3.24 (t, *J* = 5.2 Hz, 2H), 2.44 – 2.40 (m, 4H), 2.21 – 2.11 (m, 2H), 1.85 – 1.73 (m, 2H), 1.52 – 1.35 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 187.7, 143.4, 136.1, 129.7, 127.4, 103.9, 102.6, 80.5, 64.9, 61.0, 53.0, 50.9, 31.8, 24.6, 21.5, 7.3; IR (neat): ν 3512, 2961, 2024, 1445, 1331, 1088, 1261, 1042, 990, 836, 892, 730 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{27}NO_5NaS$ $[M+Na]^+$: 416.15021, found: 416.14994.

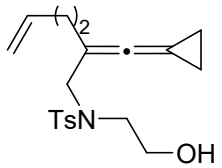


(^{1}H NMR 400 MHz, $CDCl_3$)

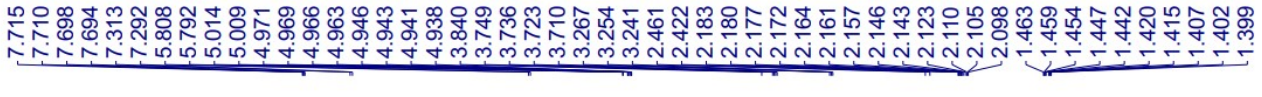


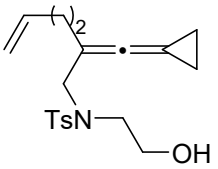


(^{13}C NMR 100 MHz, $CDCl_3$)

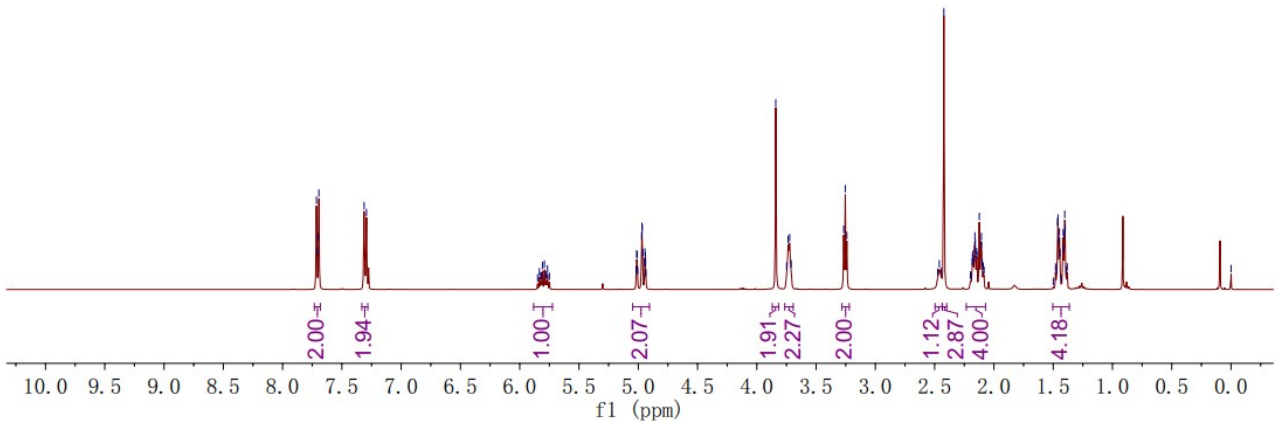


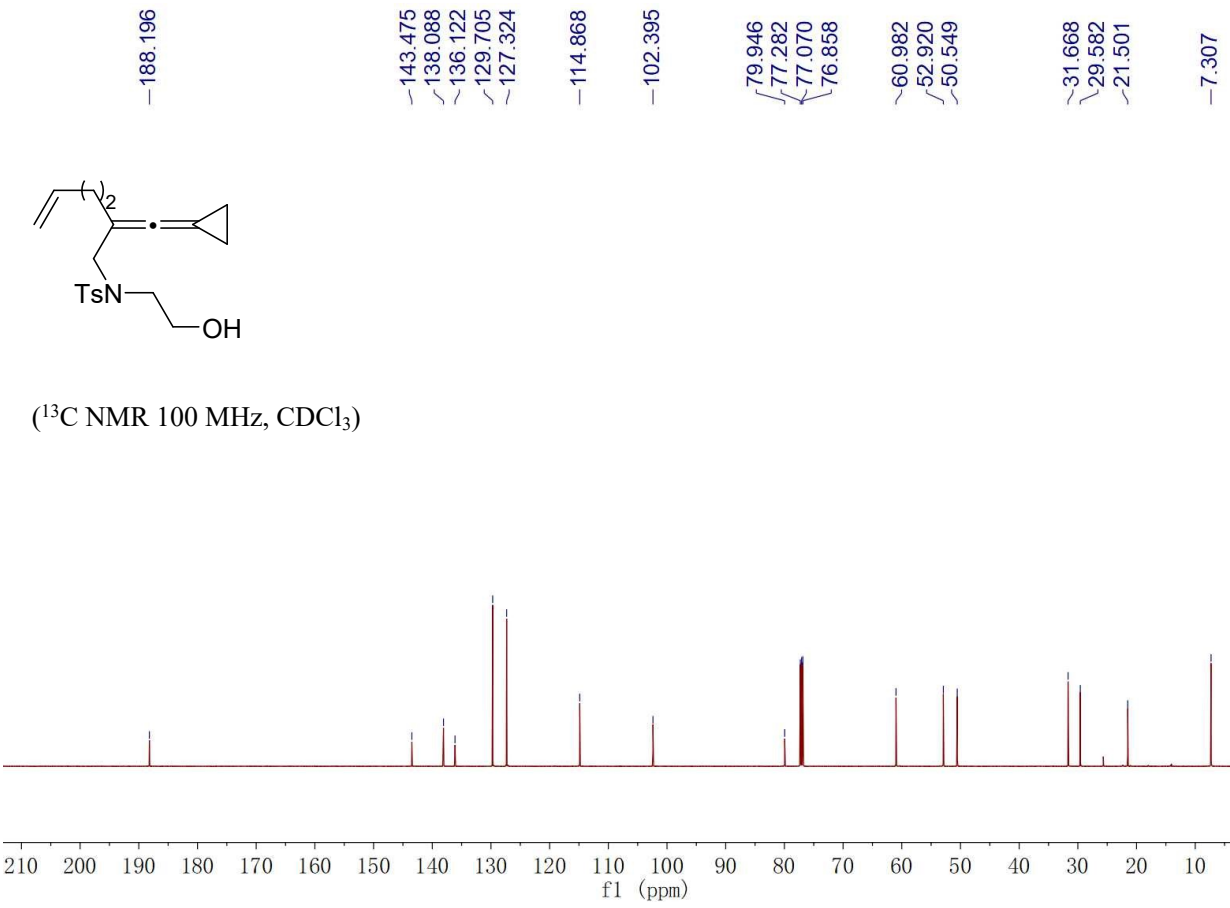
Compound 1f: Yield: 652.4 mg, 94%; A yellow oil; Eluent: PE/EA = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.73 – 7.68 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.85 – 5.75 (m, 1H), 5.05 – 4.91 (m, 2H), 3.84 (s, 2H), 3.75 – 3.71 (m, 2H), 3.25 (t, *J* = 5.4 Hz, 2H), 2.45 (d, *J* = 7.0 Hz, 1H), 2.42 (s, 3H), 2.23 – 2.07 (m, 4H), 1.50 – 1.36 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 188.2, 143.5, 138.1, 136.1, 129.7, 127.3, 114.9, 102.4, 79.9, 61.0, 52.9, 50.5, 31.7, 29.6, 21.5, 7.3; IR (neat): ν 3514, 2982, 2021, 1445, 1300, 1153, 1081, 1032, 919, 816, 729 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{19}H_{25}NO_3NaS$ $[M+Na]^+$: 370.14474, found: 370.14547.



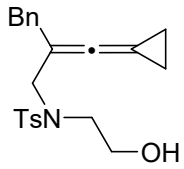


(^{1}H NMR 400 MHz, $CDCl_3$)

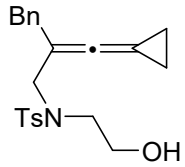




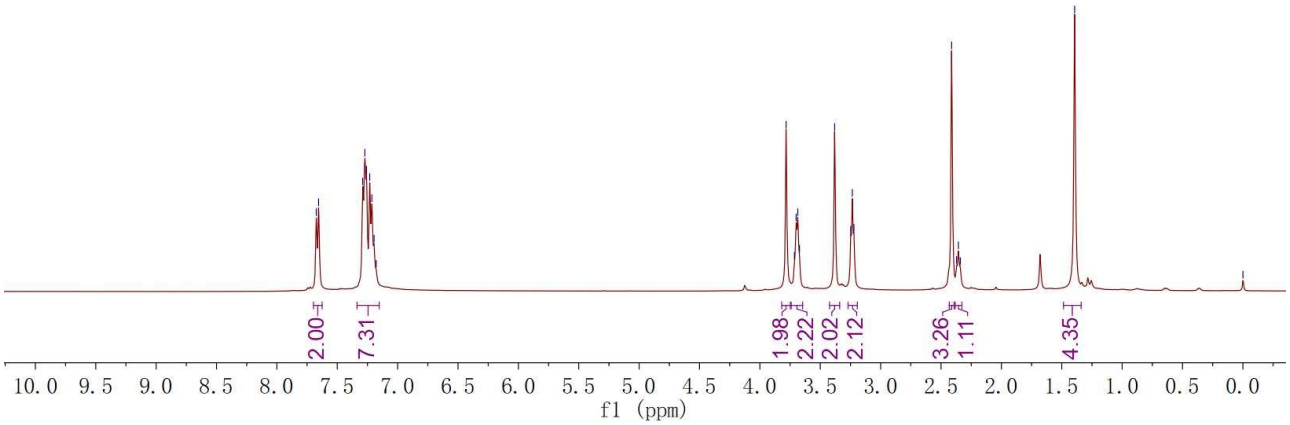
(^{13}C NMR 100 MHz, $CDCl_3$)

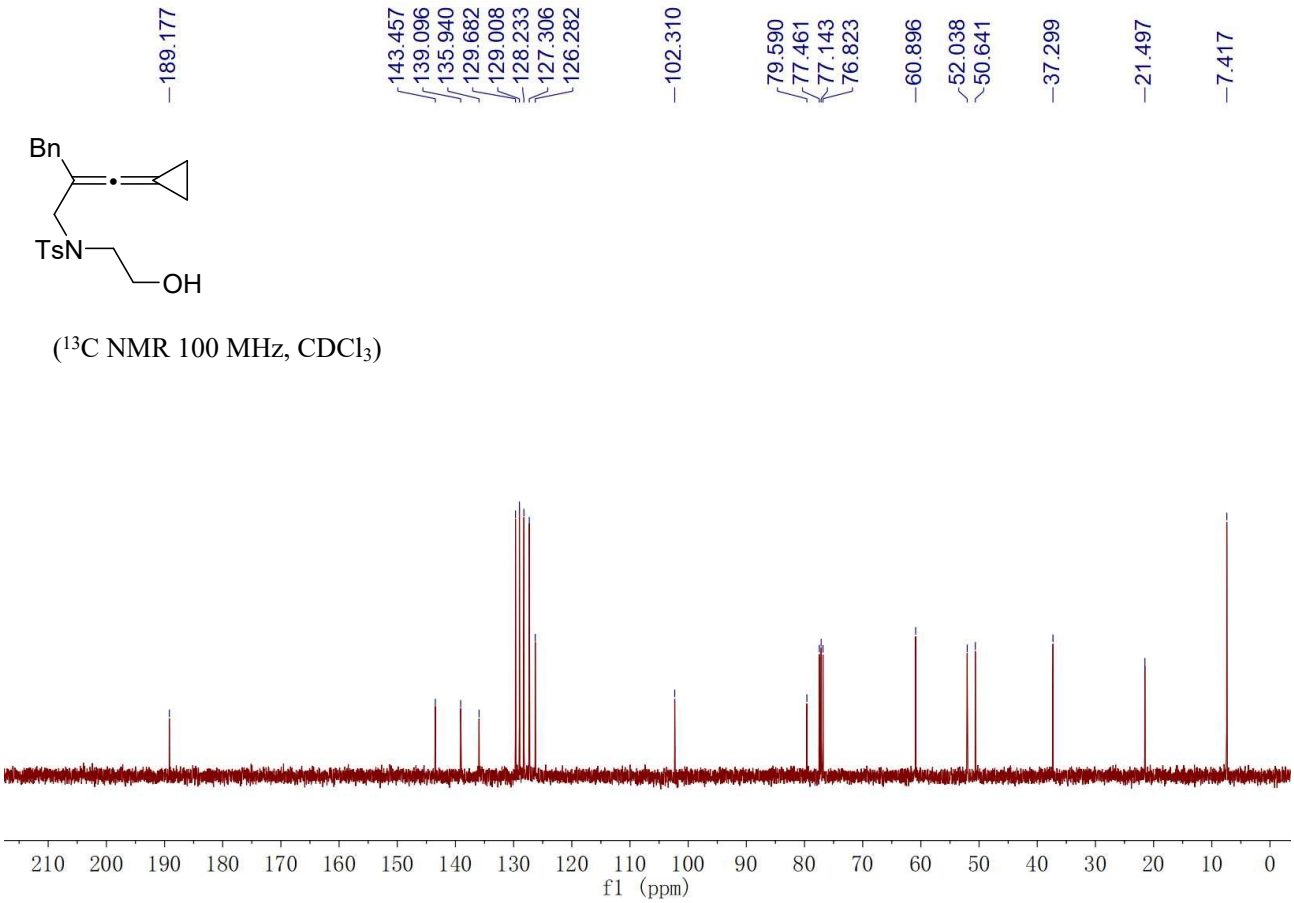


Compound 1g: Yield: 750.7 mg, 98%; A colorless solid; Mp: 76 – 79 ℃; Eluent: PE/EA = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.66 (d, *J* = 7.8 Hz, 2H), 7.29 – 7.18 (m,7H), 3.78 (s, 2H), 3.61 – 3.67 (m, 2H), 3.38 (s, 2H), 3.23 (t, *J* = 5.4 Hz, 2H), 2.41 (s, 3H), 2.35 (t, *J* = 5.6 Hz, 1H), 1.39 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 189.2, 143.5, 139.1, 135.9, 129.7, 129.0, 128.2, 127.3, 126.3, 102.3, 79.6, 60.9, 52.0, 50.6, 37.3, 21.5, 7.4; IR (neat): ν 3506, 3026, 2964, 1594, 2021, 1355, 1088, 965, 836, 829, 728 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{22}H_{25}NO_3NaS$ $[M+Na]^+$: 406.14474, found: 406.14409.

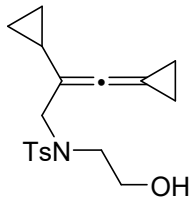


(^{1}H NMR 400 MHz, $CDCl_3$)

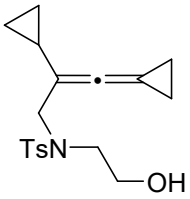




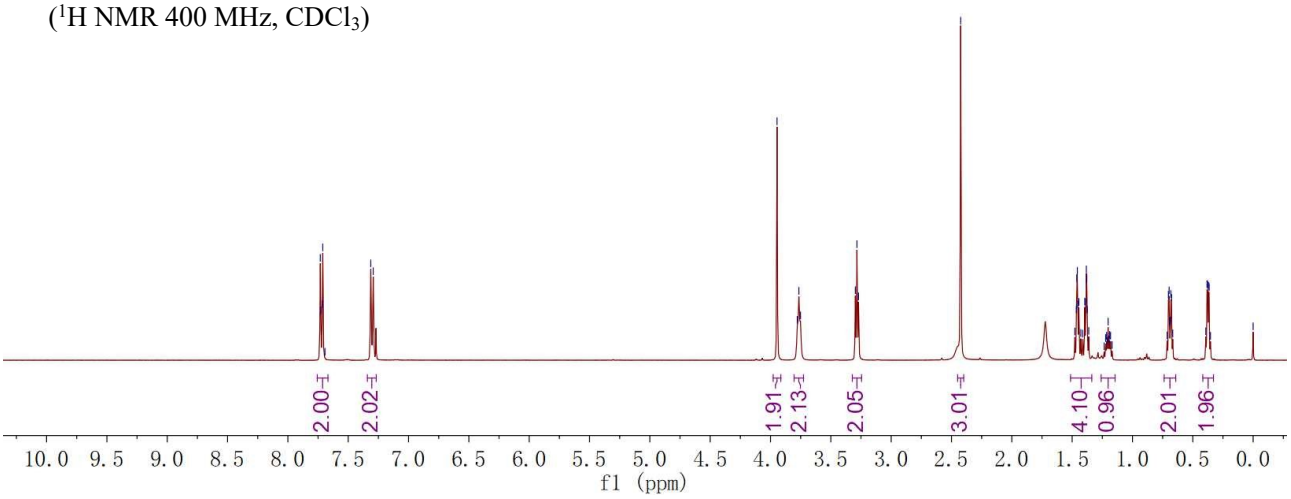
(^{13}C NMR 100 MHz, $CDCl_3$)

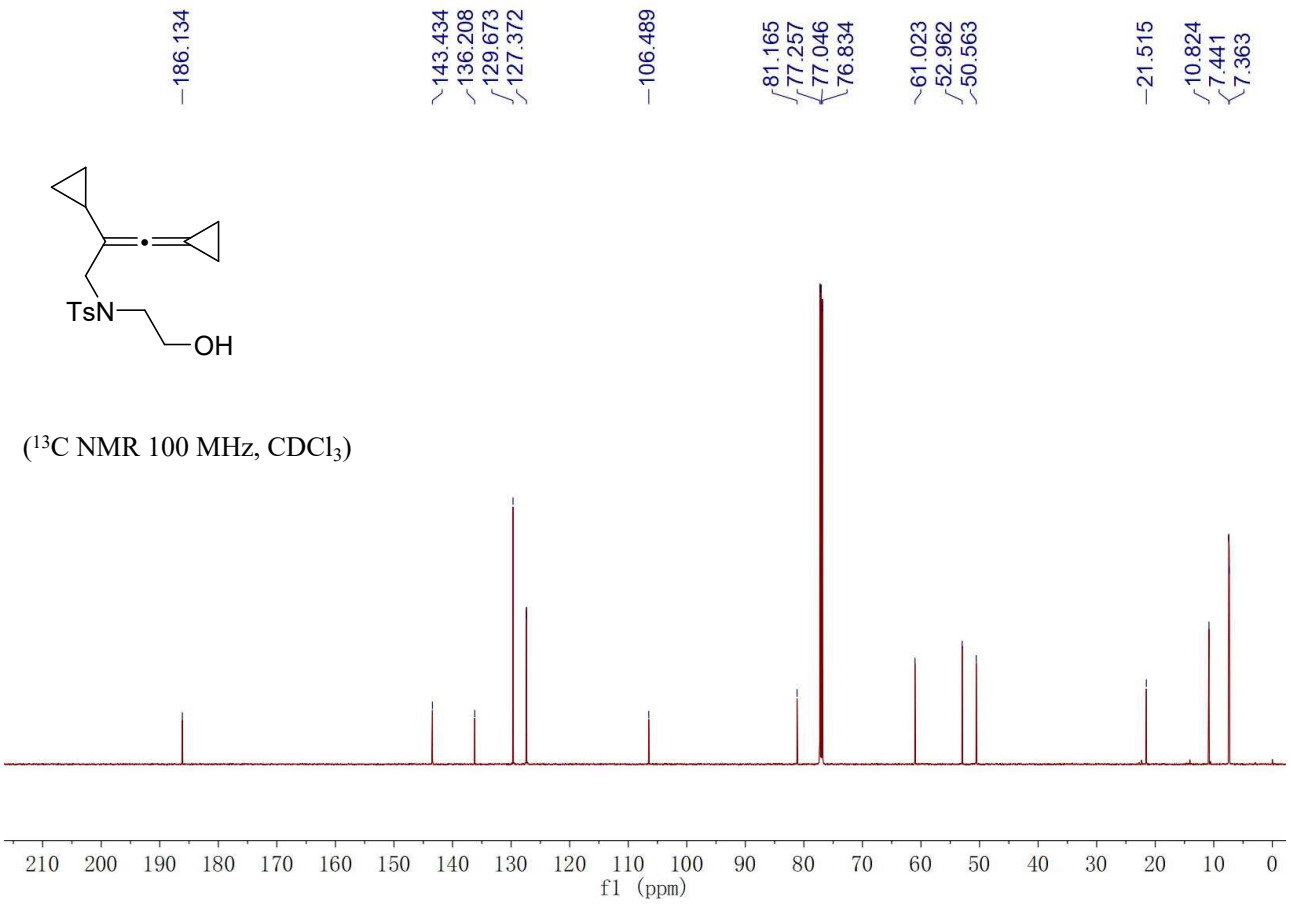


Compound 1h: Yield: 592.7 mg, 89%; A colorless solid; Mp: 81 – 83 ℃; Eluent: PE/EA = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.76 – 7.67 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.95 (s, 2H), 3.76 (t, *J* = 5.3 Hz, 2H), 3.28 (t, *J* = 5.3 Hz, 2H), 2.42 (s, 3H), 1.51 – 1.34 (m, 4H), 1.67 – 1.24 (m, 1H), 0.74 – 0.64 (m, 2H), 0.42 – 0.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 186.1, 143.4, 136.2, 129.7, 127.4, 106.5, 81.2, 61.0, 53.0, 50.6, 21.5, 10.8, 7.44, 7.36; IR (neat): ν 3514, 2973, 2892, 1442, 1342, 1163, 1083, 976, 957, 880, 829, 744 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{18}H_{23}NO_3NaS$ $[M+Na]^+$: 356.12909, found: 356.12926.

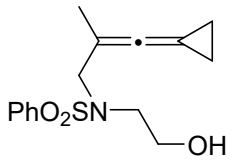


(^{1}H NMR 400 MHz, $CDCl_3$)

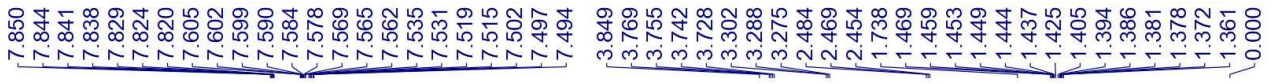


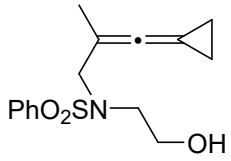


(^{13}C NMR 100 MHz, $CDCl_3$)

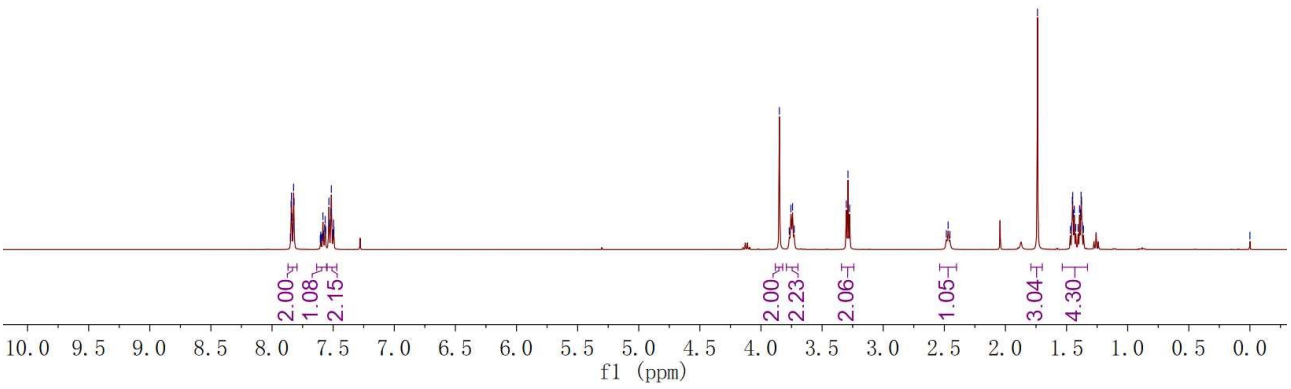


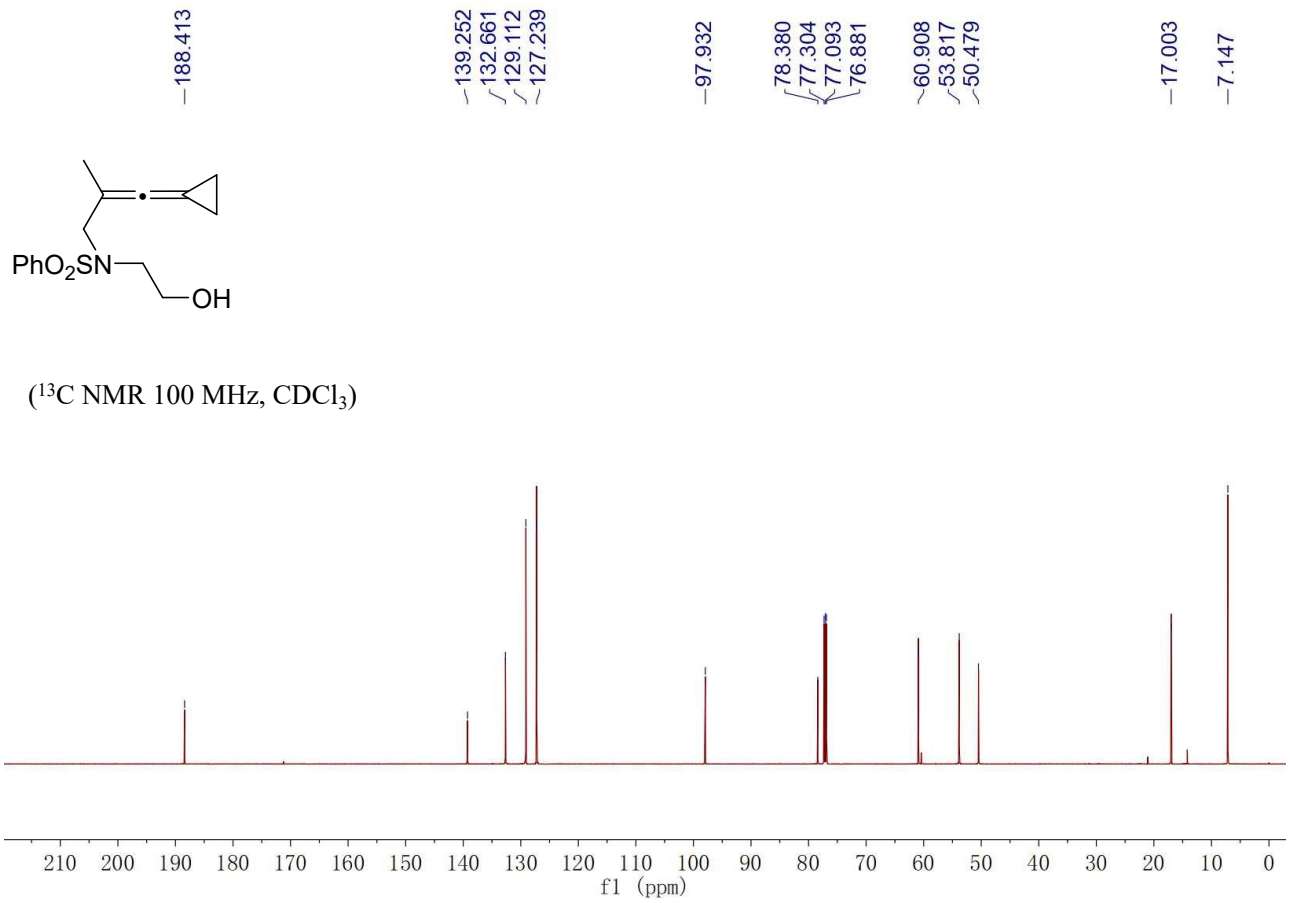
Compound 1i: Yield: 533.3 mg, 91%; A yellow oil; Eluent: PE/EA = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.87 – 7.80 (m, 2H), 7.63 – 7.55 (m, 1H), 7.54 – 7.49 (m, 2H), 3.85 (s, 2H), 3.77 – 3.73 (m, 2H), 3.29 (t, *J* = 5.6 Hz, 2H), 2.47 (t, *J* = 5.9 Hz, 1H), 1.74 (s, 3H), 1.54 – 1.33 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 188.4, 139.3, 132.7, 129.1, 127.2, 97.9, 78.4, 60.9, 53.8, 50.5, 17.0, 7.1; IR (neat): ν 3512, 2979, 2909, 2022, 1446, 1372, 1154, 1088, 989, 888, 689 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{15}H_{19}NO_3NaS$ $[M+Na]^+$: 316.09779, found: 316.09850.



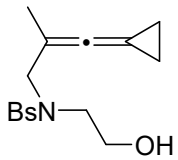


(^{1}H NMR 400 MHz, $CDCl_3$)

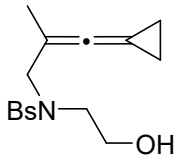




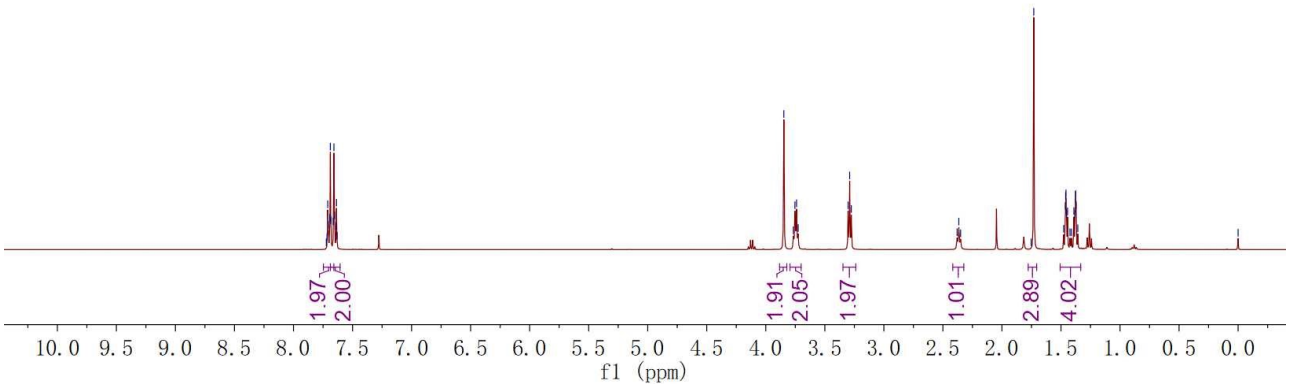
(^{13}C NMR 100 MHz, $CDCl_3$)

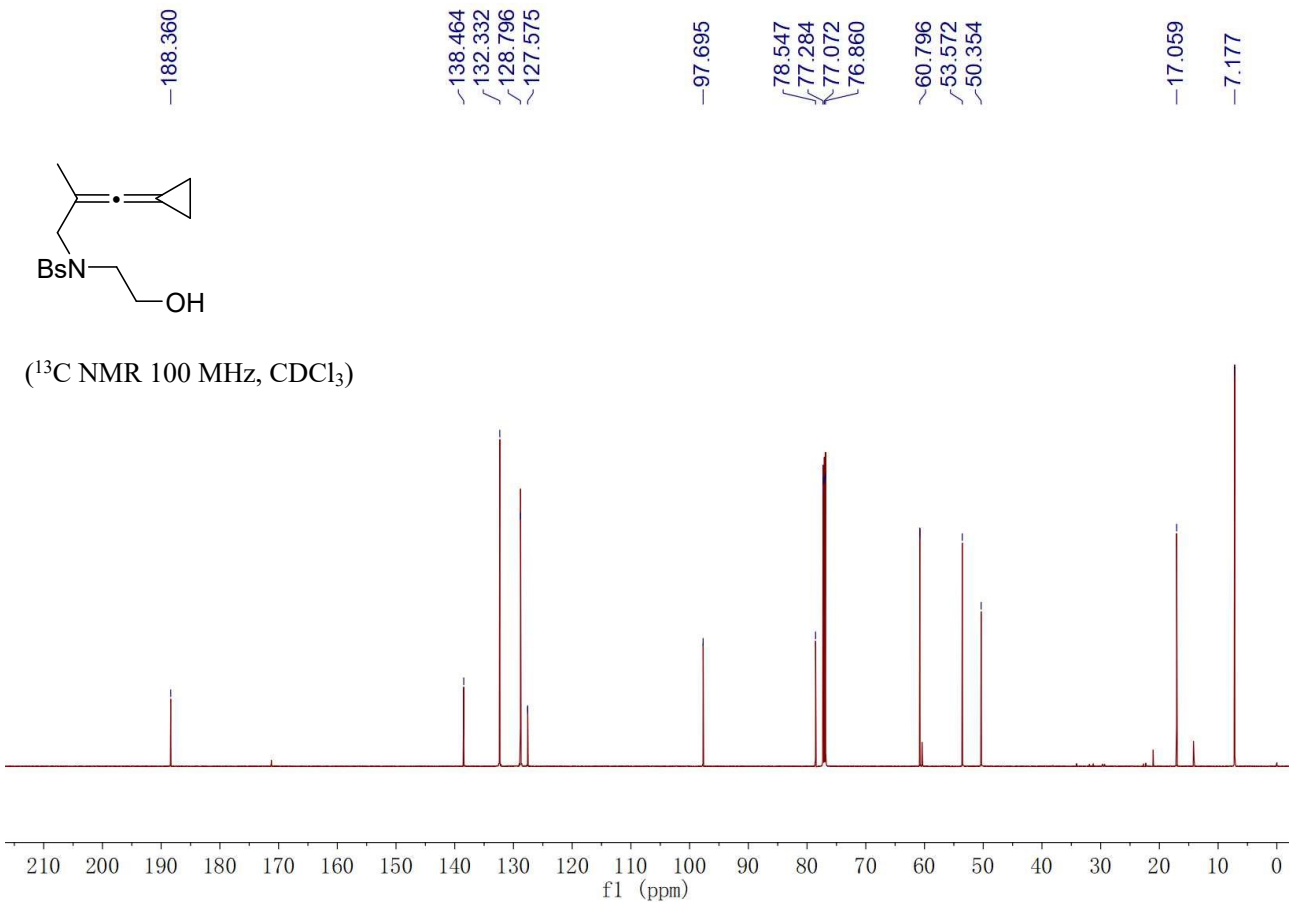


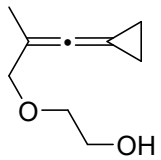
Compound 1j: Yield: 712.3 mg, 96%; A colorless solid; Mp: 71 – 74 ℃; Eluent: PE/EA = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.75 – 7.66 (m, 2H), 7.69 – 7.61 (m, 2H), 3.85 (s, 2H), 3.77 – 3.73 (m, 2H), 3.29 (t, *J* = 5.4 Hz, 2H), 2.36 (t, *J* = 5.9 Hz, 1H), 1.73 (s, 3H), 1.51 – 1.33 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 188.4, 138.5, 132.3, 128.8, 127.6, 97.7, 78.5, 60.8, 53.6, 50.4, 17.1, 7.2; IR (neat): ν 3523, 2987, 2909, 2023, 1574, 1388, 1332, 1086, 990, 836, 889, 753, 729 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{15}H_{18}NO_3NaSBr$ $[M+Na]^+$: 394.00830, found: 394.00756.



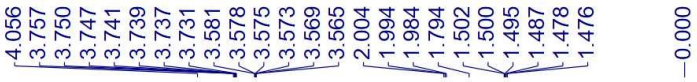
(^{1}H NMR 400 MHz, $CDCl_3$)

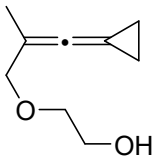



188.360
138.464
132.332
128.796
127.575
97.695
78.547
77.284
77.072
76.860
60.796
53.572
50.354
17.059
7.177
BsN
OH
(13C NMR 100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

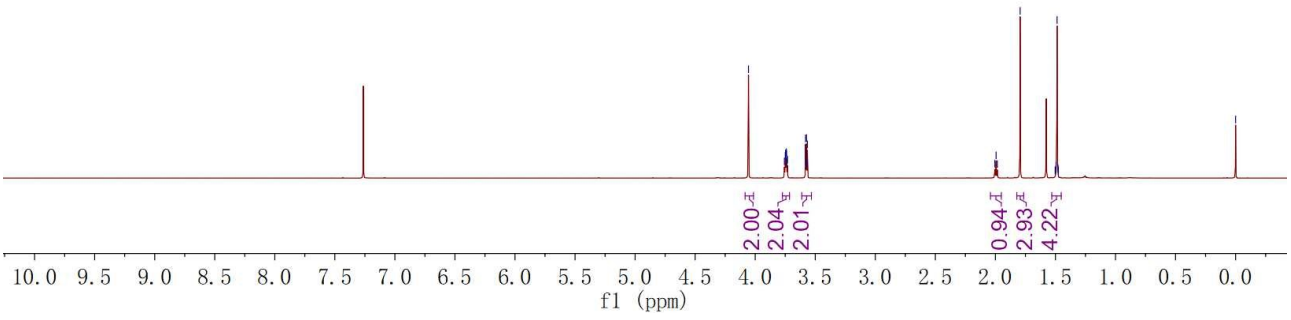


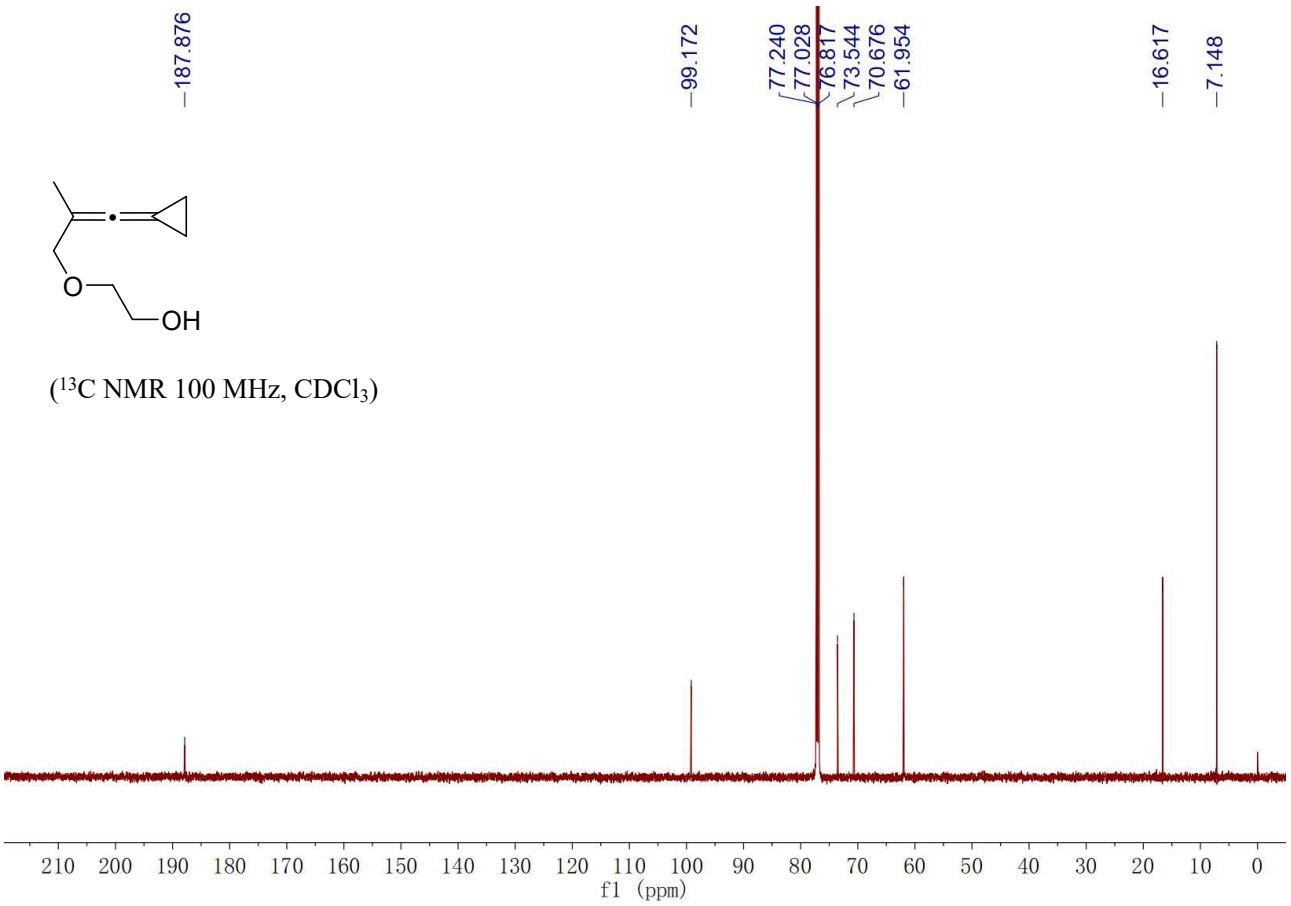
Compound 1k: Yield: 268.0 mg, 87%; A yellow oil; Eluent: PE/EA = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 4.06 (s, 2H), 3.76 – 3.73 (m, 2H), 3.61 – 3.53 (m, 2H), 1.99 (t, *J* = 6.2 Hz, 1H), 1.79 (s, 3H), 1.49 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 187.9, 99.2, 73.5, 70.7, 62.0, 16.6, 7.1; IR (neat): ν 3416, 2908, 2857, 2022, 1369, 1344, 1096, 1059, 972, 890, 835 cm^{-1}; HRMS (FI) Calcd for $C_9H_{14}O_2$: 154.0988, found: 154.0989.



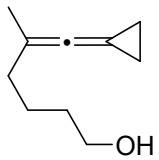


(^{1}H NMR 400 MHz, $CDCl_3$)

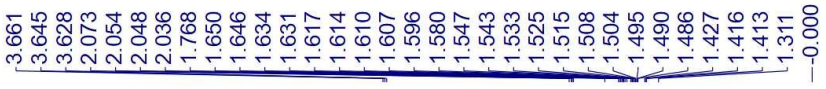


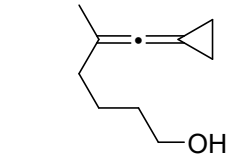


(^{13}C NMR 100 MHz, $CDCl_3$)

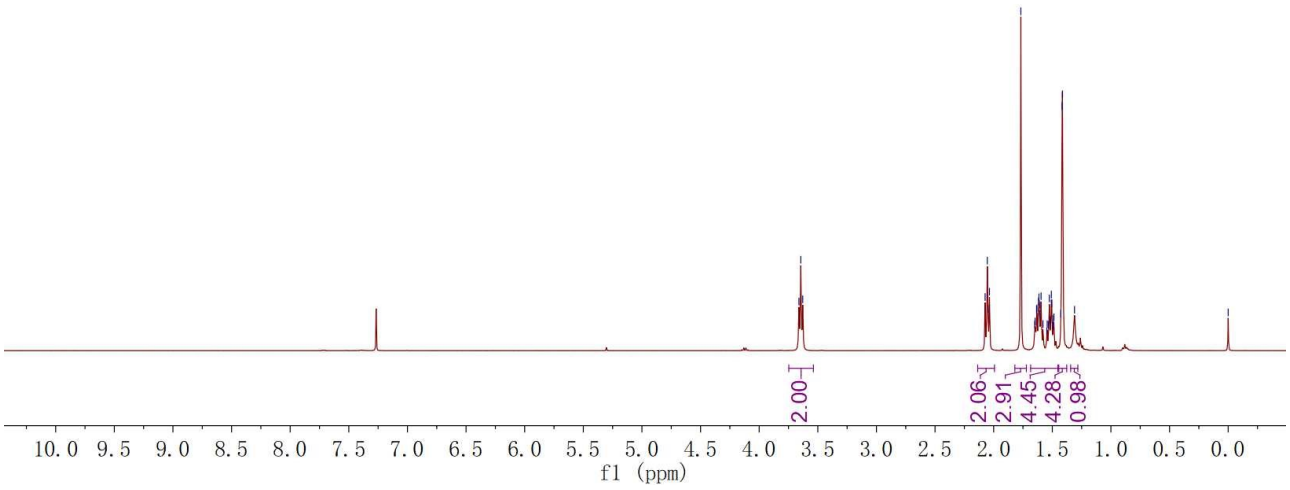


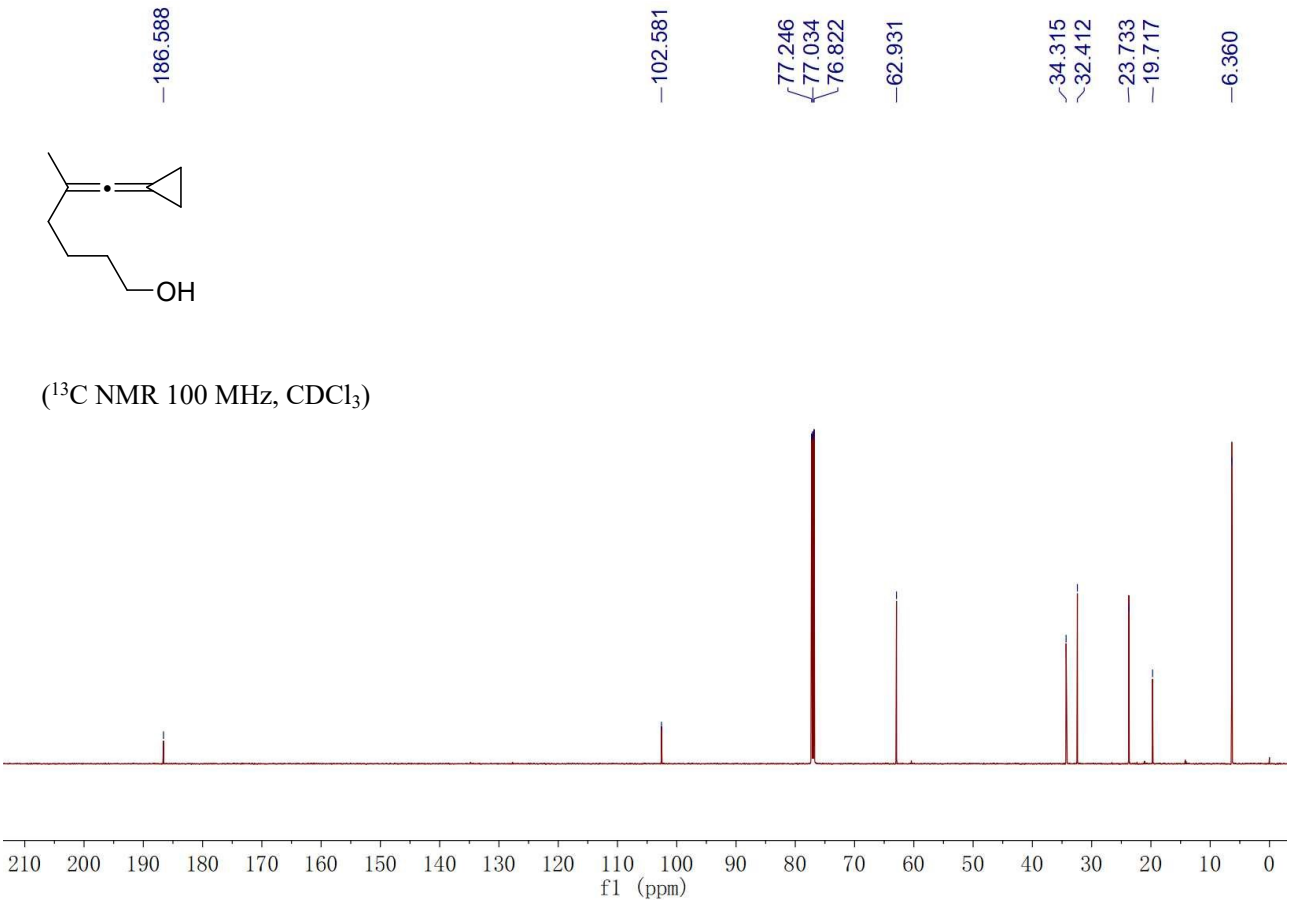
Compound 1l: Yield: 270.6 mg, 89%; A yellow oil; Eluent: PE/EA = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.64 (t, *J* = 6.4 Hz, 2H), 2.05 (t, *J* = 7.4 Hz, 2H), 1.77 (s, 3H), 1.68 – 1.44 (m, 4H), 1.45 – 1.38 (m, 4H), 1.31 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 186.6, 102.6, 62.9, 34.3, 32.4, 23.7, 19.7, 6.4; IR (neat): ν 3344, 2967, 2931, 2863, 2020, 1440, 1261, 1088, 909, 733 cm^{-1}; HRMS (FI) Calcd for $C_{10}H_{16}O$: 152.1196, found: 152.1199.



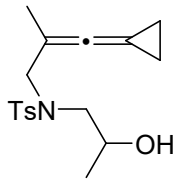


(^{1}H NMR 400 MHz, $CDCl_3$)

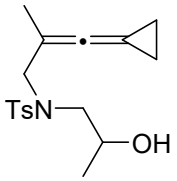




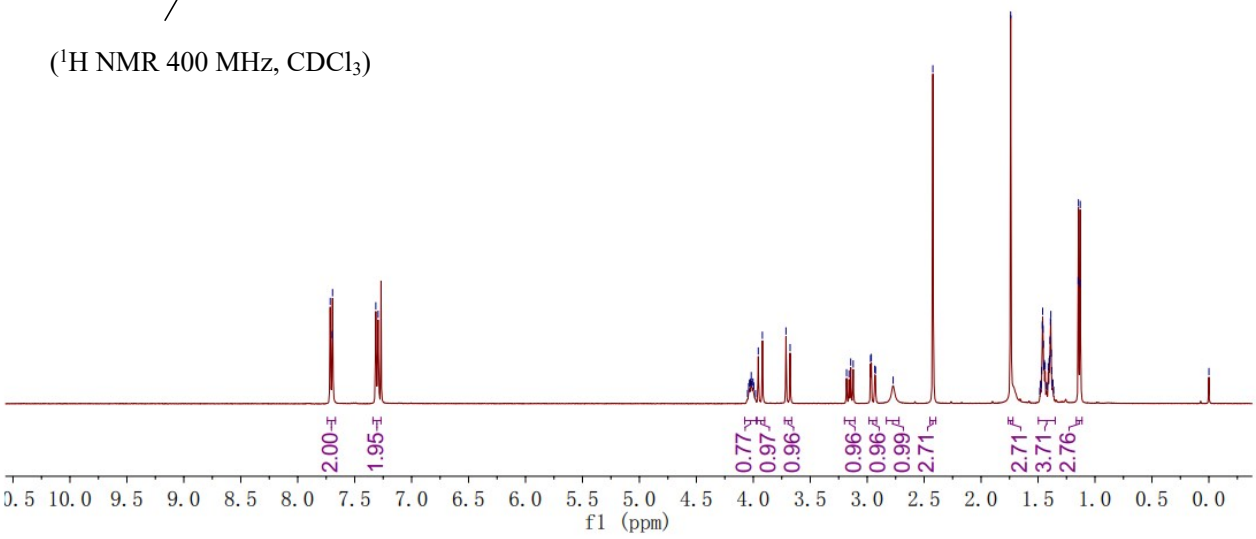
(^{13}C NMR 100 MHz, $CDCl_3$)



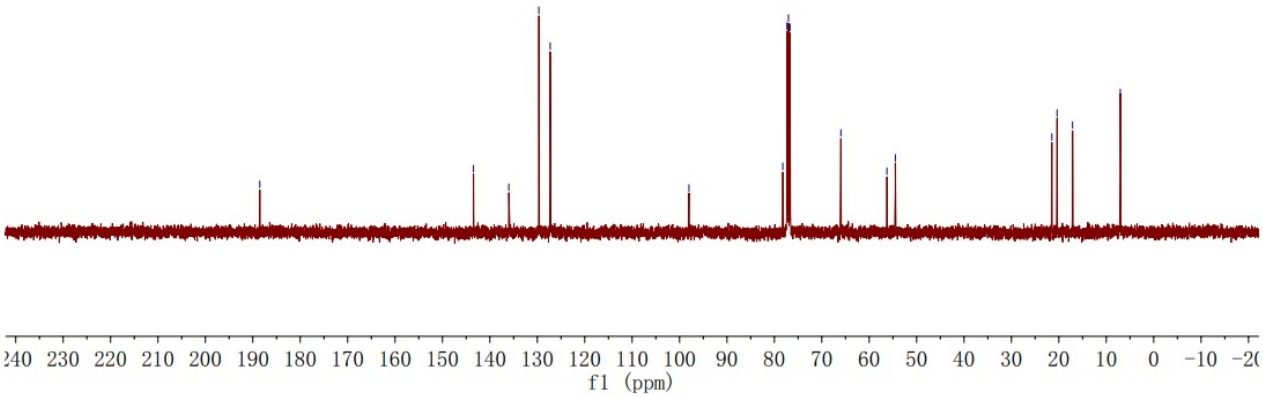
Compound 1m: Yield: 420.0 mg, 98%; A yellow oil; Eluent: PE/EA = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.05 – 4.00 (m, 1H), 3.94 (d, *J* = 14.5 Hz, 1H), 3.69 (d, *J* = 14.5 Hz, 1H), 3.18 – 3.12 (m, 1H), 2.97 – 2.93 (m, 1H), 2.77 (s, 1H), 2.42 (s, 3H), 1.74 (s, 3H), 1.50 – 1.35 (m, 4H), 1.14 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 188.5, 143.5, 136.0, 129.7, 127.3, 98.0, 78.2, 66.0, 56.3, 54.5, 21.5, 20.4, 17.1, 7.0; IR (neat): ν 3520, 2990, 2912, 2033, 1600, 1338, 1154, 1096, 919, 813, 719 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{17}H_{23}NO_3NaS$ $[M+Na]^+$: 344.12909, found: 344.12853.

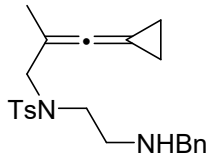


(^{1}H NMR 400 MHz, $CDCl_3$)

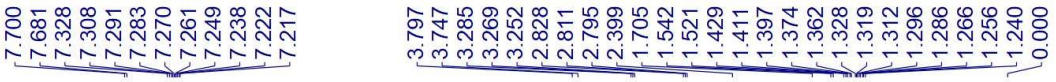


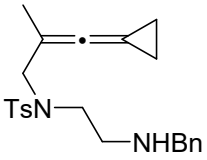
(^{13}C NMR 100 MHz, $CDCl_3$)



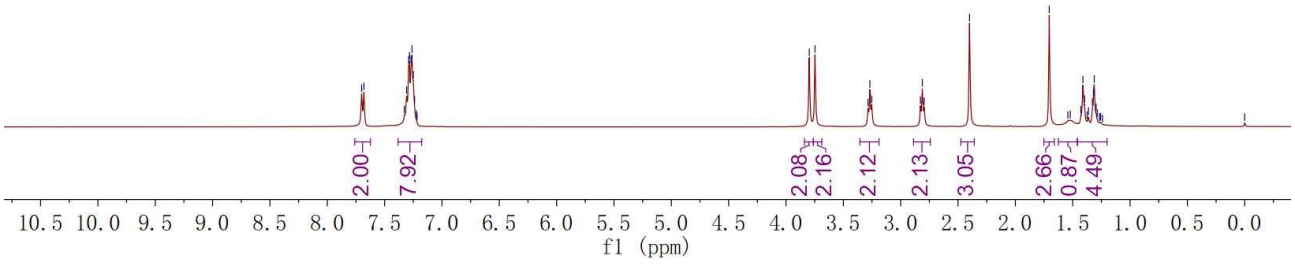


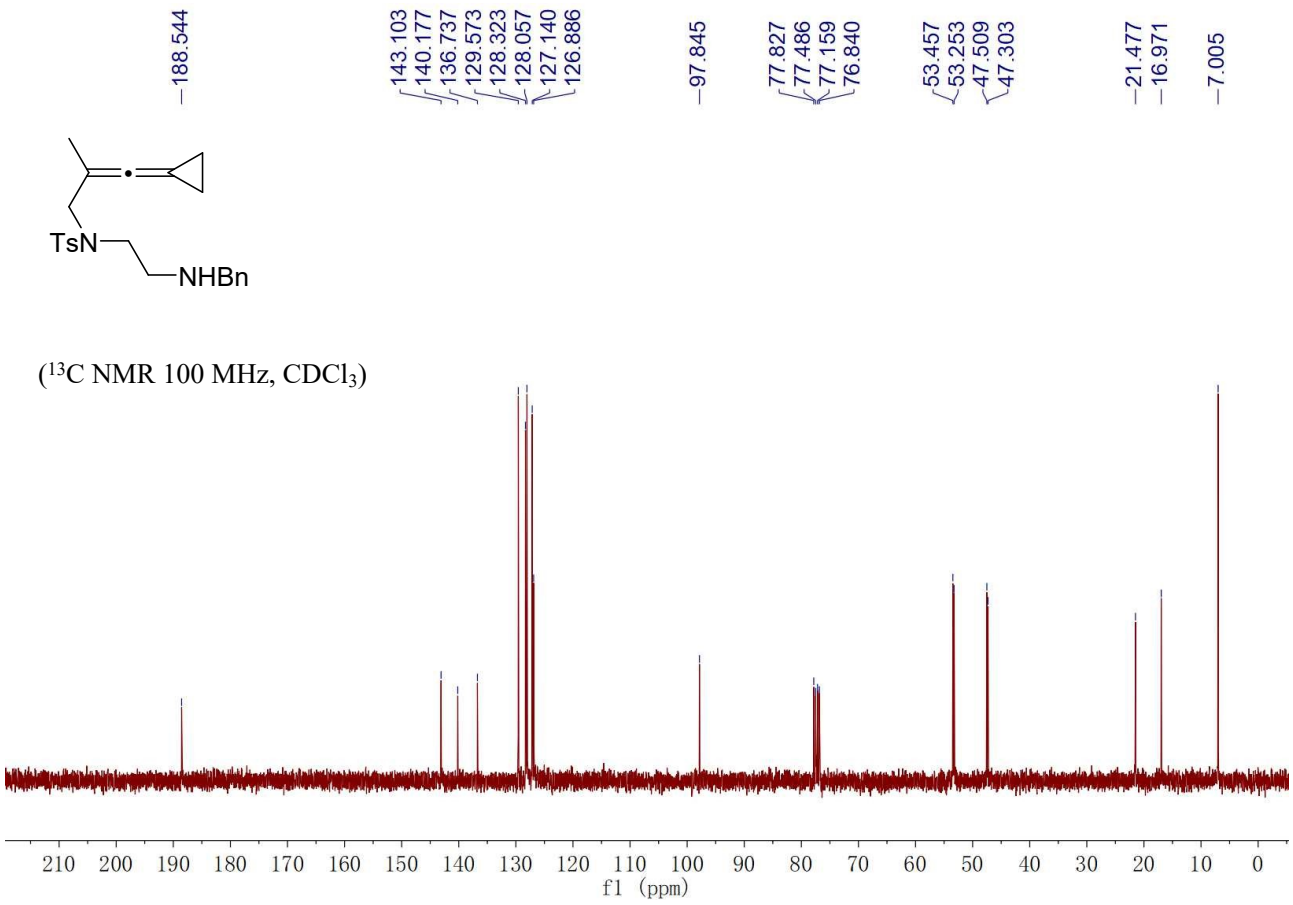
Compound 1n: Yield: 641.5 mg, 81%; A yellow oil; Eluent: PE/EA = 1/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.69 (d, *J* = 7.9 Hz, 2H), 7.33 – 7.22 (m, 7H), 3.80 (s, 2H), 3.75 (s, 2H), 3.27 (t, *J* = 6.6 Hz, 2H), 2.81 (t, *J* = 6.5 Hz, 2H), 2.40 (s, 3H), 1.70 (s, 3H), 1.53 (s, 1H), 1.46 – 1.20 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 188.5, 143.1, 140.2, 136.7, 129.6, 128.3, 128.1, 127.1, 126.9, 97.8, 77.8, 53.5, 53.3, 47.5, 47.3, 21.5, 17.0, 7.0; IR (neat): ν 3061, 3026, 2982, 2306, 2255, 2022, 1808, 1597, 1088, 847, 813, 728, 657 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{23}H_{29}N_2O_2S$ $[M+H]^+$: 397.19443, found: 397.19440.

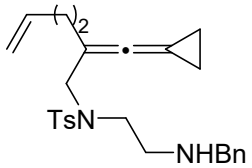




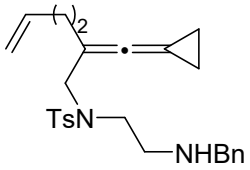
(^{1}H NMR 400 MHz, $CDCl_3$)



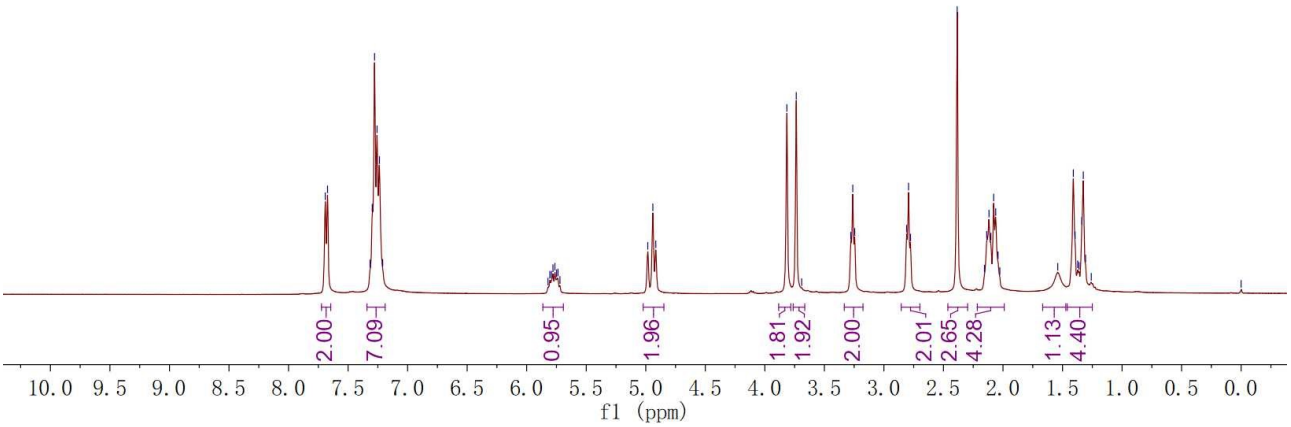

188.544
143.103
140.177
136.737
129.573
128.323
128.057
127.140
126.886
97.845
77.827
77.486
77.159
76.840
53.457
53.253
47.509
47.303
21.477
16.971
7.005
TsN
NHBn
(13C NMR 100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

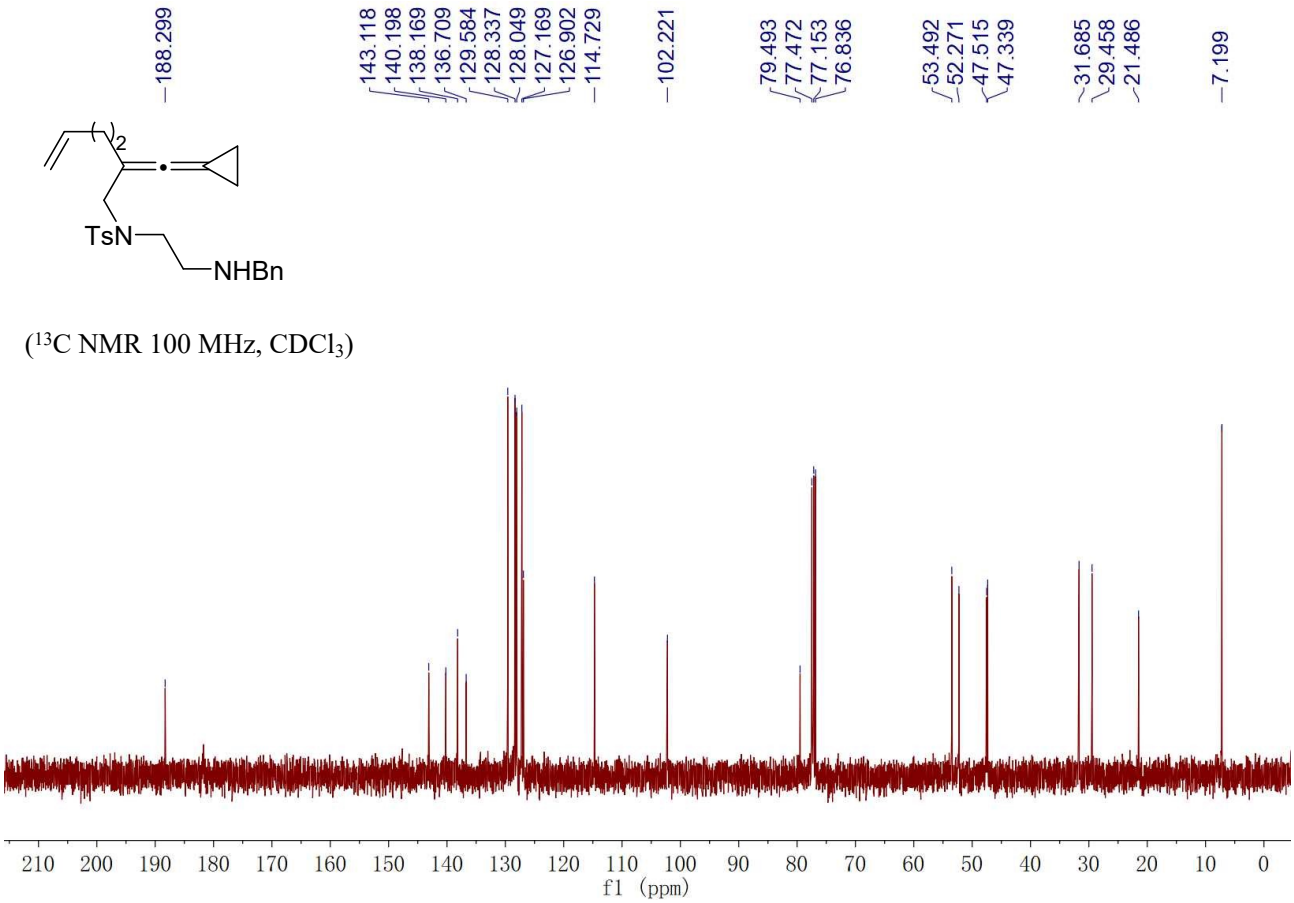


Compound 1o: Yield: 802.2 mg, 92%; A yellow oil; Eluent: PE/EA = 1/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.68 (d, *J* = 7.8 Hz, 2H), 7.31 – 7.20 (m, 7H), 5.81 – 5.71 (m, 1H), 4.97 – 4.90 (m, 2H), 3.82 (s, 2H), 3.74 (s, 2H), 3.26 (t, *J* = 6.6 Hz, 2H), 2.79 (t, *J* = 6.6 Hz, 2H), 2.38 (s, 3H), 2.15 – 2.02 (m, 4H), 1.54 (s, 1H), 1.46 – 1.25 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 188.3, 143.1, 140.2, 138.2, 136.7, 129.6, 128.3, 128.0, 127.2, 126.9, 114.7, 102.2, 79.5, 53.5, 52.3, 47.5, 47.3, 31.7, 29.5, 21.5, 7.2; IR (neat): ν 2917, 2843, 2020, 1639, 1597, 1493, 1333, 1155, 993, 813, 732, 657 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{26}H_{33}N_2O_2S$ $[M+H]^+$: 437.22573, found: 437.22558.

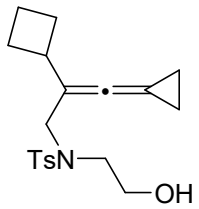


(^{1}H NMR 400 MHz, $CDCl_3$)

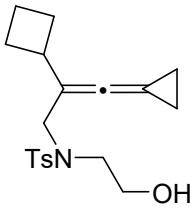




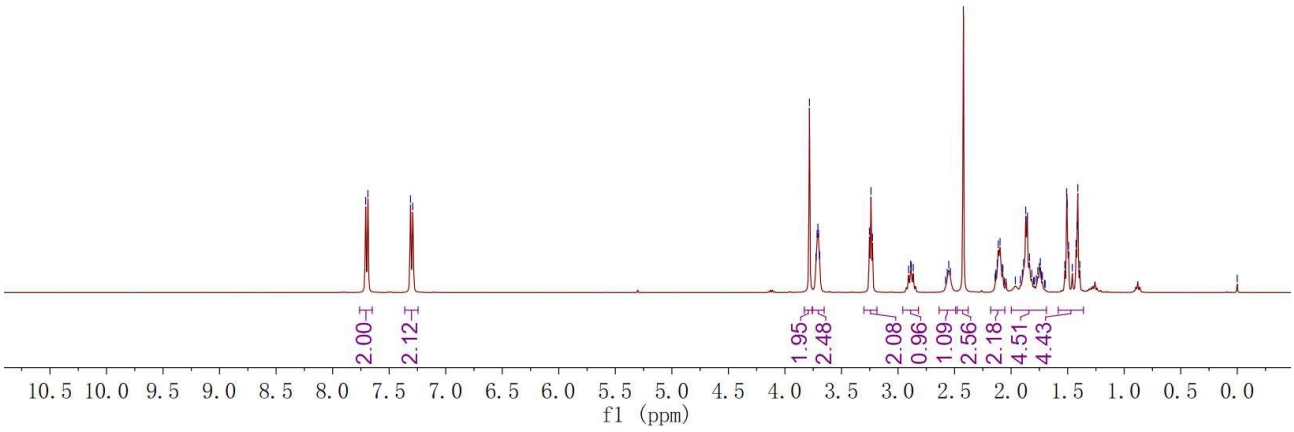
(^{13}C NMR 100 MHz, $CDCl_3$)

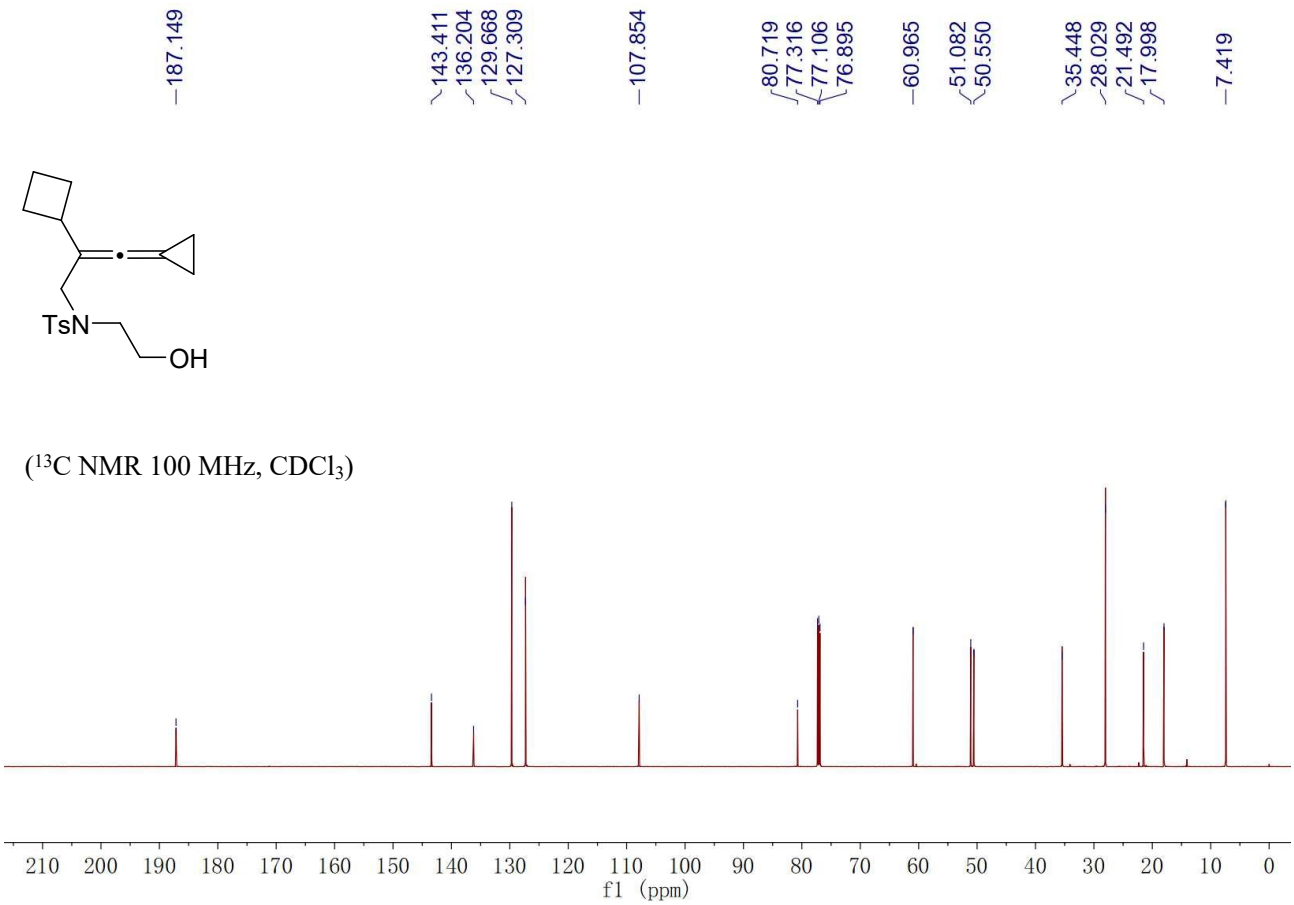


Compound 1p: Yield: 610.7 mg, 88%; A colorless solid; Mp: 73 –75 ℃; Eluent: PE/EA = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.70 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.78 (s, 2H), 3.73 – 3.69 (m, 2H), 3.24 (t, *J* = 5.4 Hz, 2H), 2.96 – 2.82 (m, 1H), 2.56 – 2.54 (m, 1H), 2.42 (s, 3H), 2.18 – 2.06 (m, 2H), 2.00 – 1.69 (m, 5H), 1.58 – 1.36 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 187.1, 143.4, 136.2, 129.7, 127.3, 107.9, 80.7, 61.0, 51.1, 50.6, 35.4, 28.0, 21.5, 18.0, 7.4; IR (neat): ν 3066, 3026, 2964, 1594, 1506, 1355, 1261, 1088, 965, 836, 829 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{19}H_{25}NO_3NaS$ $[M+Na]^+$: 370.14474, found: 370.14562.

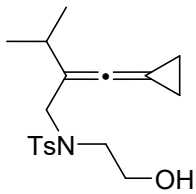


(^{1}H NMR 400 MHz, $CDCl_3$)

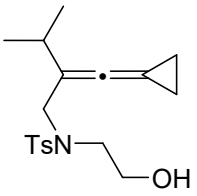




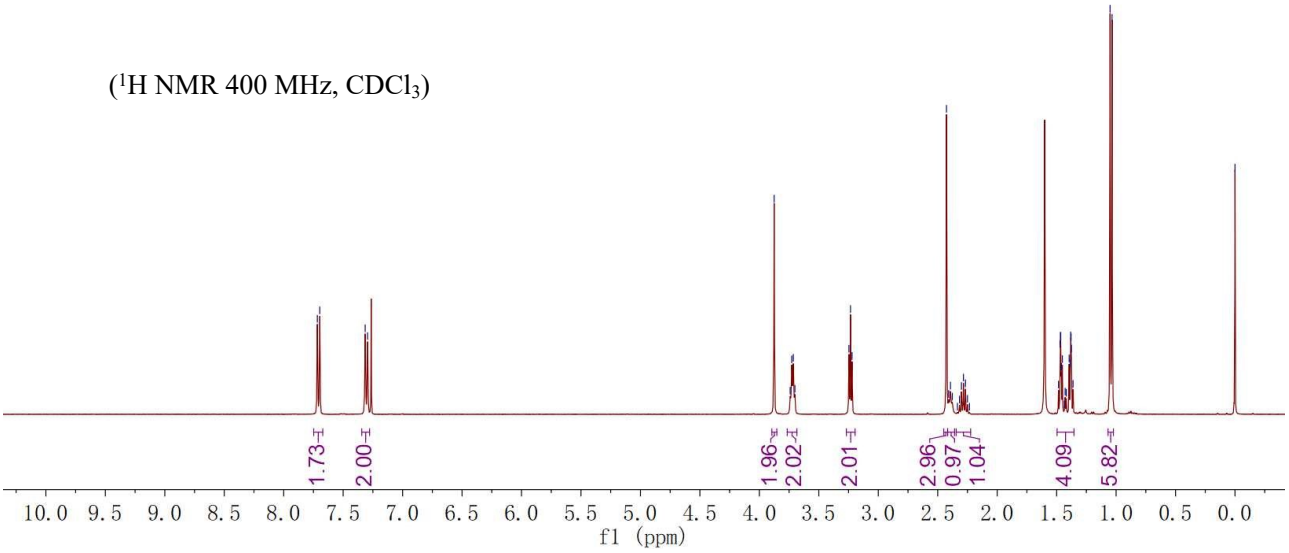
(^{13}C NMR 100 MHz, $CDCl_3$)

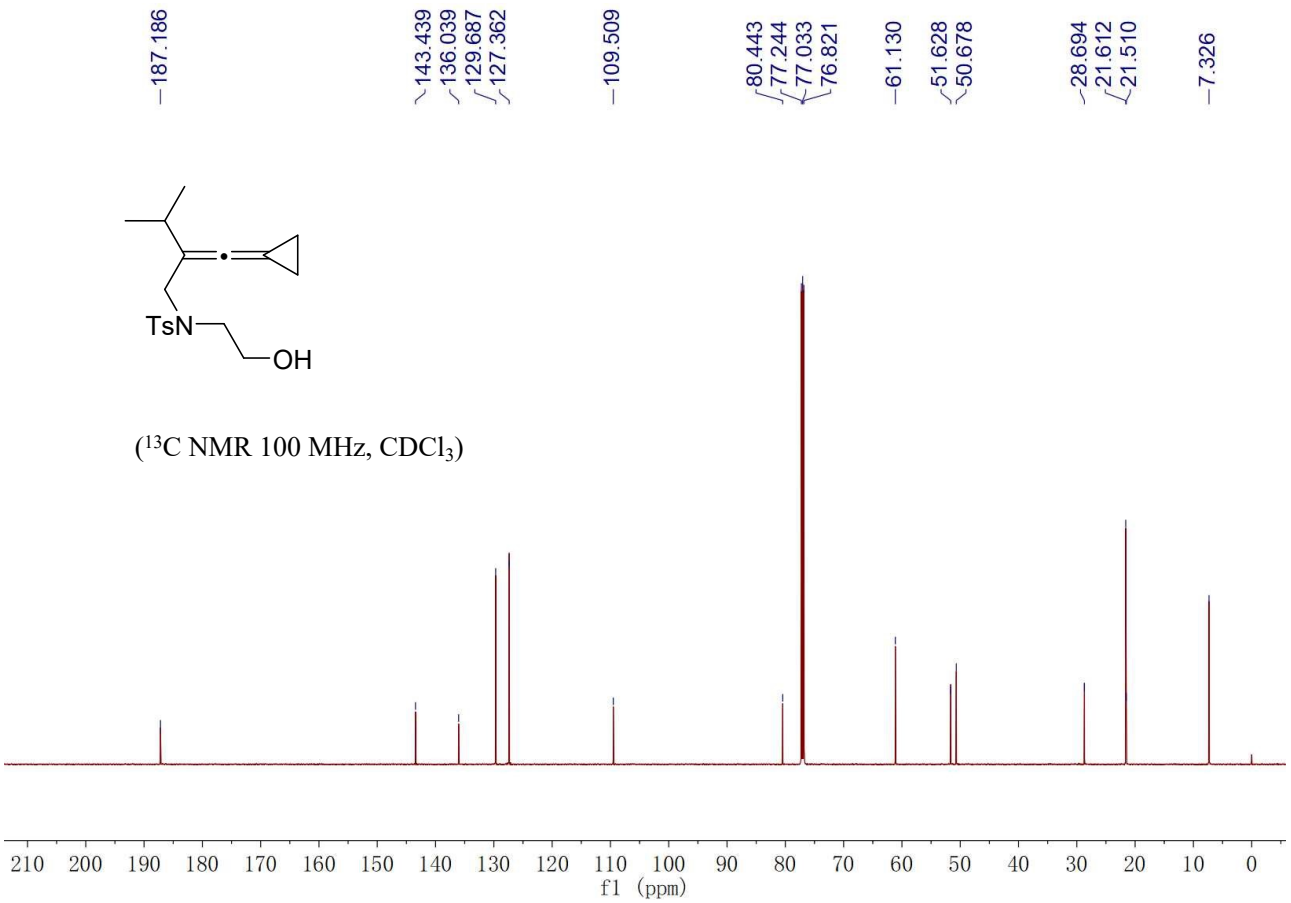


Compound 1q: Yield: 649.9 mg, 97%; A colorless solid; Mp: 89 – 91 ℃; Eluent: PE/EA = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.75 – 7.67 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.88 (s, 2H), 3.74 – 3.70 (m, 2H), 3.23 (t, *J* = 5.3 Hz, 2H), 2.43 (s, 3H), 2.28 (hept, *J* = 6.7 Hz, 1H), 1.51 – 1.44 (m, 2H), 1.43 – 1.34 (m, 2H), 1.04 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 187.2, 143.4, 136.0, 129.7, 127.4, 109.5, 80.4, 61.1, 51.6, 50.7, 28.7, 21.6, 21.5, 7.3; IR (neat): ν 3566, 3026, 2957, 2924, 1445, 1355, 1300, 1088, 981, 928, 809 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{18}H_{25}NO_3NaS$ $[M+Na]^+$: 358.14474, found: 358.14493.

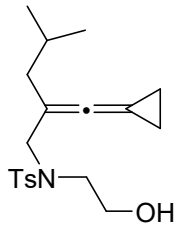


(^{1}H NMR 400 MHz, $CDCl_3$)

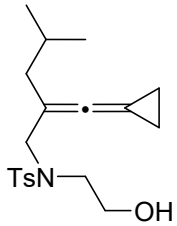




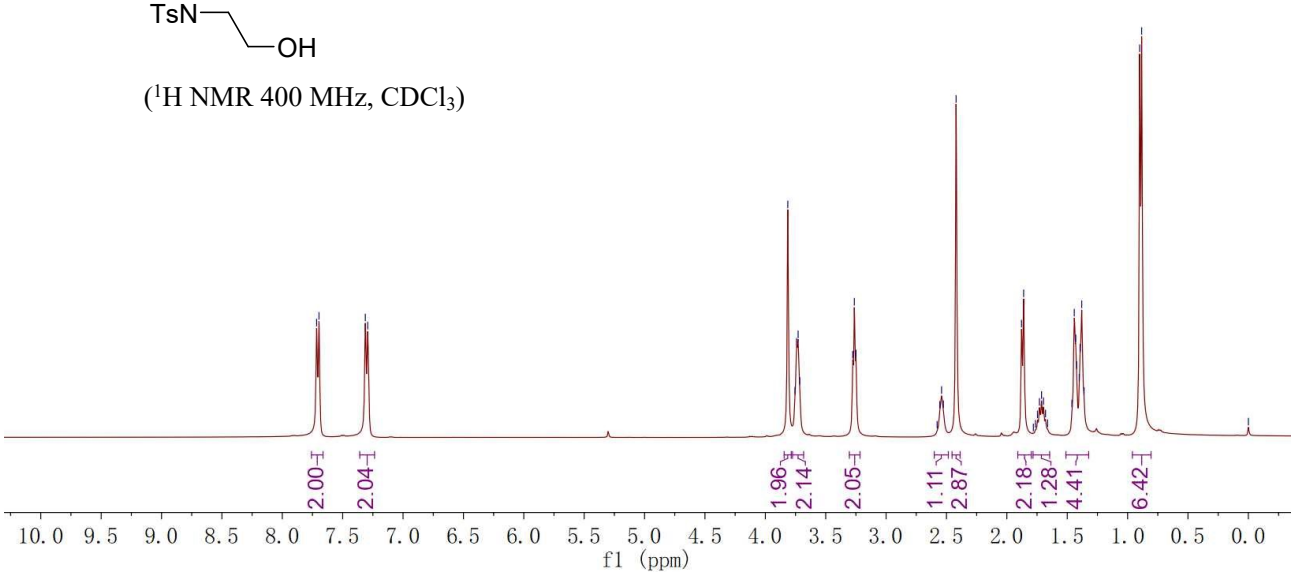
(^{13}C NMR 100 MHz, $CDCl_3$)

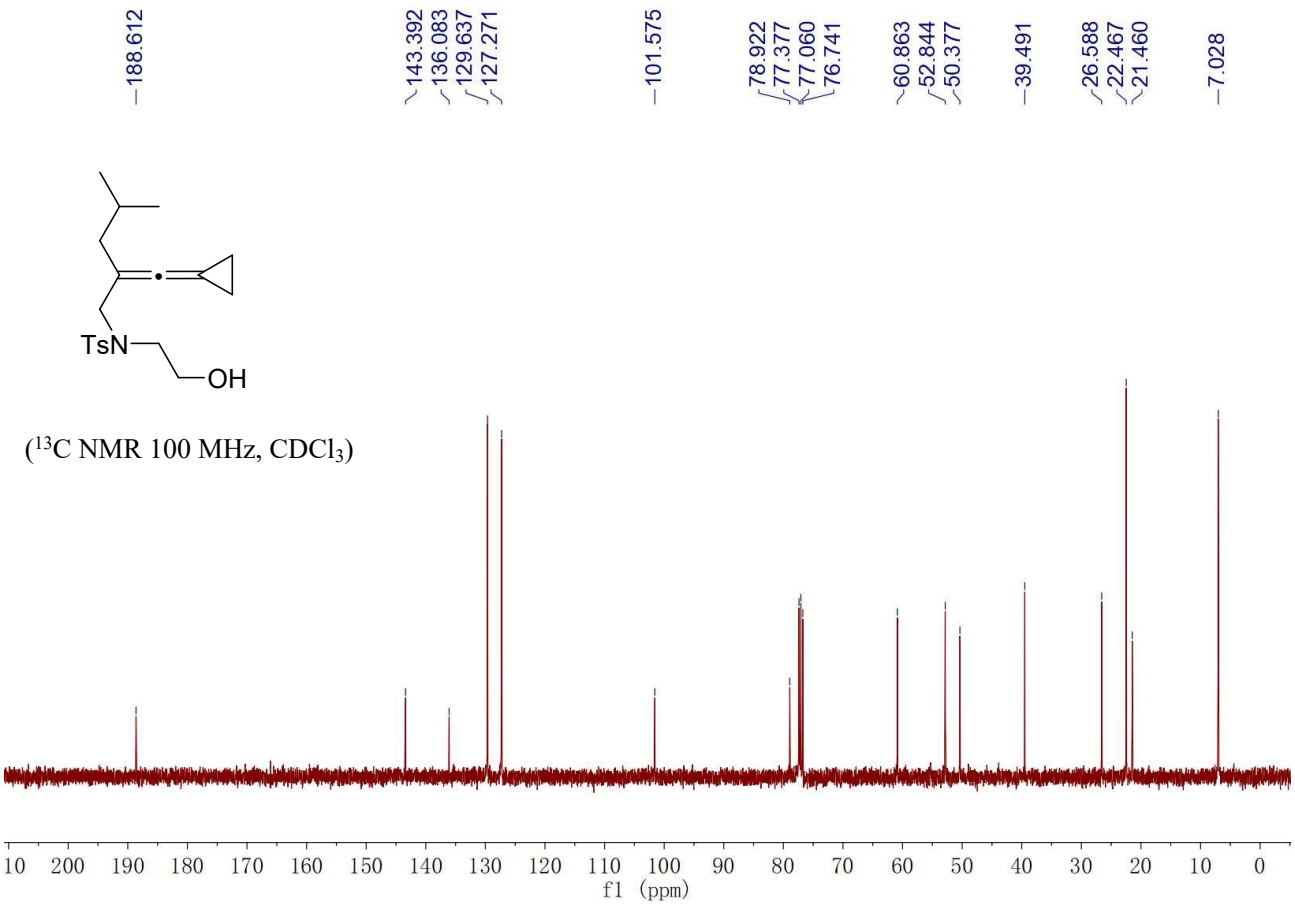


Compound 1r: Yield: 691.0 mg, 99%; A yellow oil; Eluent: PE/EA = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.71 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 3.81 (s, 2H), 3.76 – 3.72 (m, 2H), 3.26 (t, *J* = 5.6 Hz, 2H), 2.54 (t, *J* = 5.6 Hz, 1H), 2.42 (s, 3H), 1.87 (d, *J* = 7.0 Hz, 2H), 1.78 – 1.65 (m, 1H), 1.44 – 1.34 (m, 4H), 0.90 – 0.88 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 188.6, 143.4, 136.1, 129.6, 127.3, 101.6, 78.9, 60.9, 52.8, 50.4, 39.5, 26.6, 22.5, 21.5, 7.0; IR (neat): ν 3066, 3026, 2964, 1594, 1506, 1355, 1261, 1088, 965, 836, 829 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{19}H_{27}NO_3NaS$ $[M+Na]^+$: 372.16039, found: 372.16039.

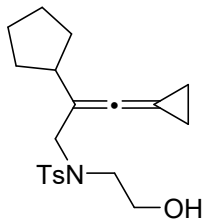


(^{1}H NMR 400 MHz, $CDCl_3$)

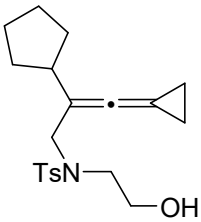




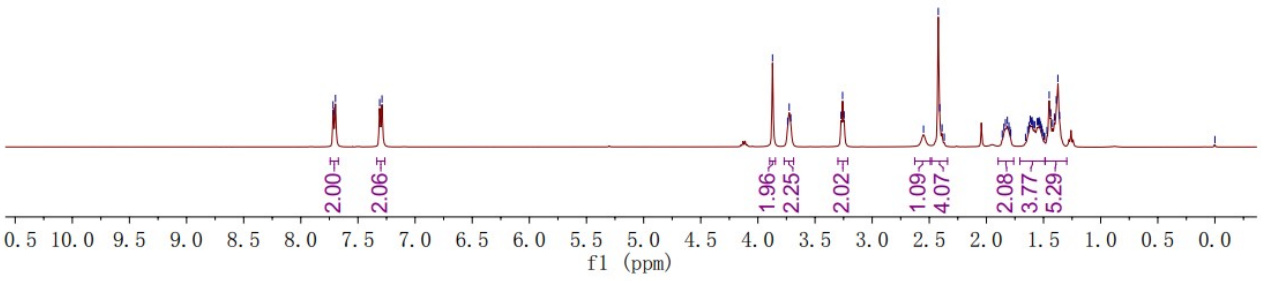
(^{13}C NMR 100 MHz, $CDCl_3$)

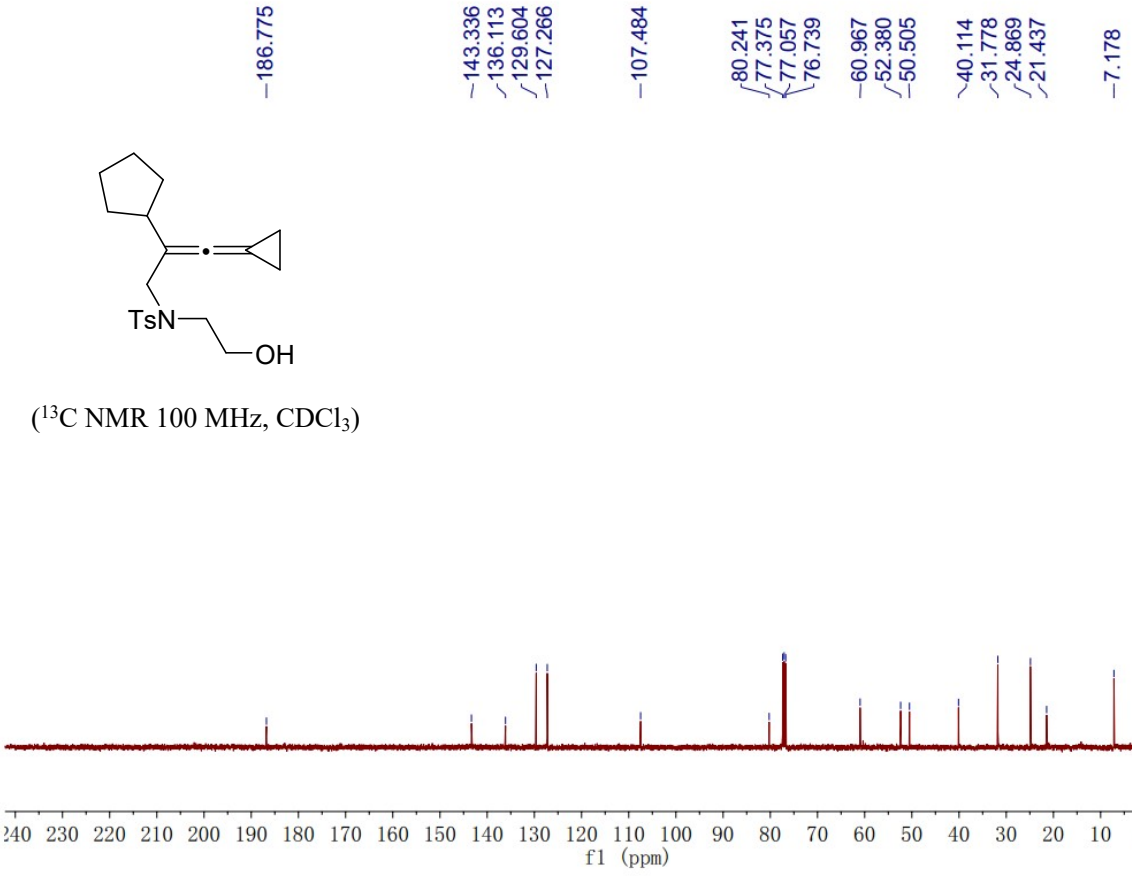


Compound 1s: Yield: 648.9 mg, 90%; A yellow oil; Eluent: PE/EA = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.74 – 7.67 (m, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 3.87 (s, 2H), 3.74 – 3.71 (m, 2H), 3.26 (t, *J* = 5.5 Hz, 2H), 2.55 (s, 1H), 2.42 – 2.37 (m, 4H), 1.86 – 1.79 (m, 2H), 1.66 – 1.58 (m, 4H), 1.56 – 1.36 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 186.8, 143.3, 136.1, 129.6, 127.3, 107.5, 80.2, 61.0, 52.4, 50.5, 40.1, 31.8, 24.9, 21.4, 7.2; IR (neat): ν 3066, 3026, 2964, 1594, 1506, 1355, 1261, 1088, 965, 836, 829 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{27}NO_3NaS$ $[M+Na]^+$: 384.16039, found: 384.16088.

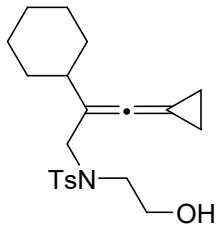


(^{1}H NMR 400 MHz, $CDCl_3$)

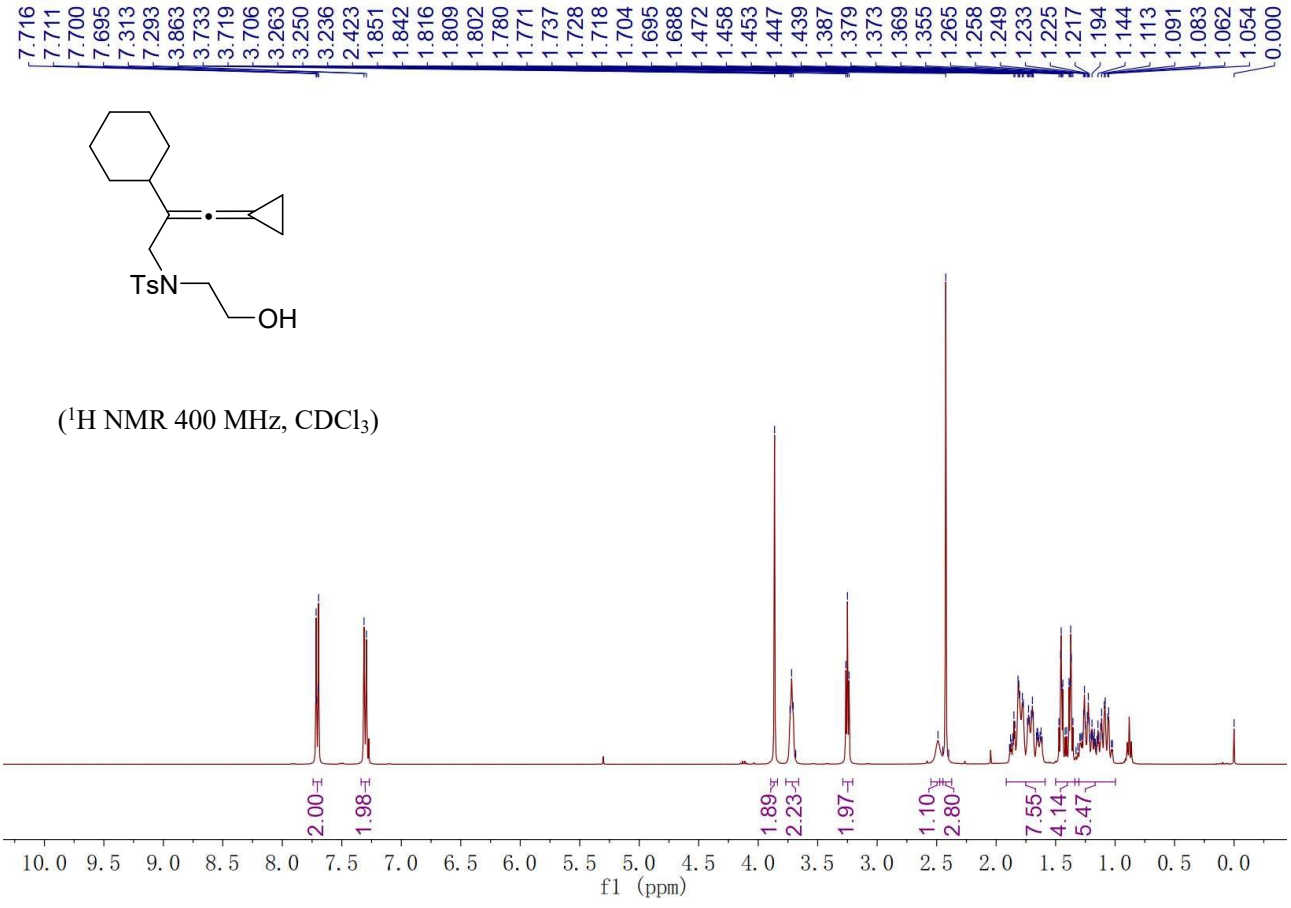




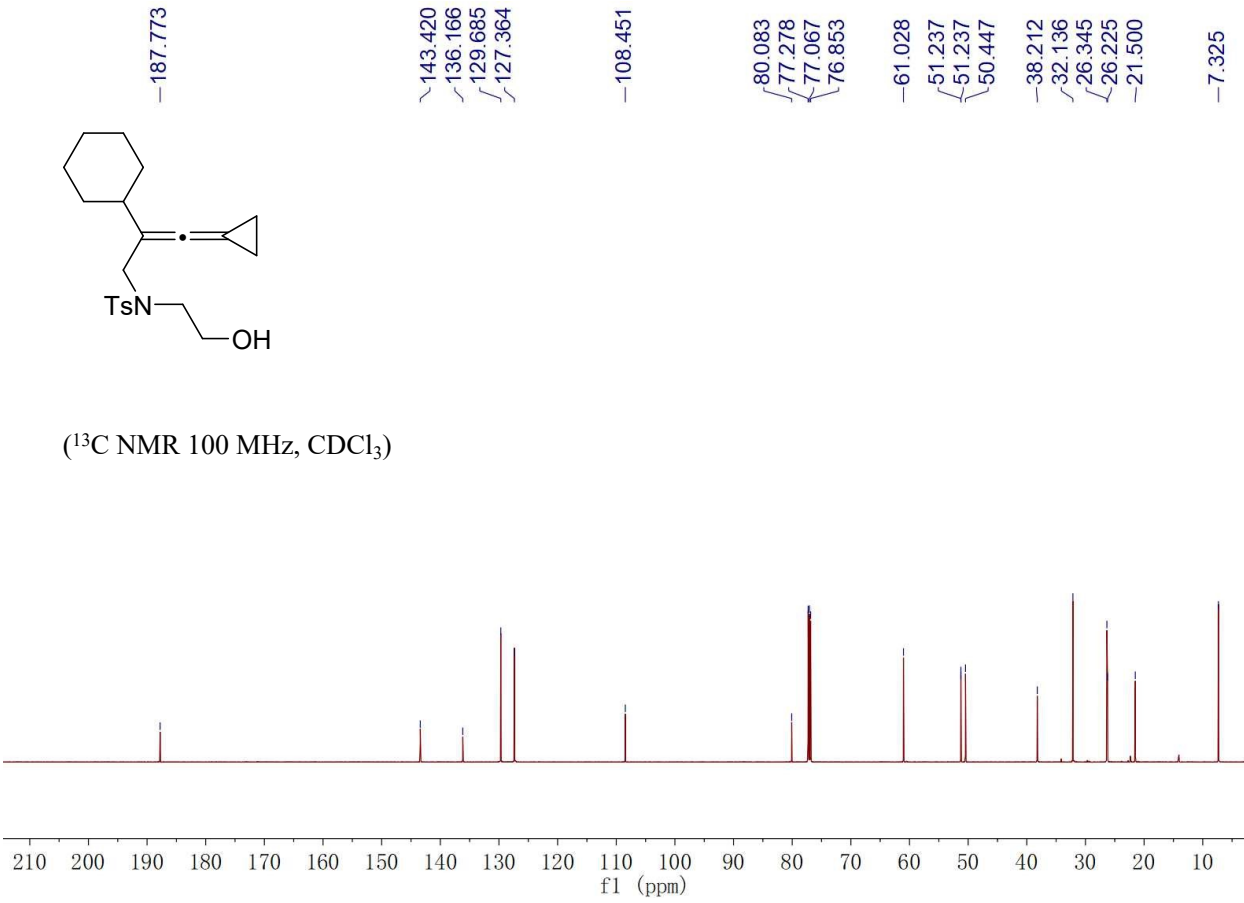
(^{13}C NMR 100 MHz, $CDCl_3$)



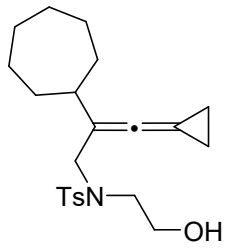
Compound 1t: Yield: 660.0 mg, 83%; A yellow oil; Eluent: PE/EA = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.74 – 7.67 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.86 (s, 2H), 3.72 (t, *J* = 5.3 Hz, 2H), 3.25 (t, *J* = 5.3 Hz, 2H), 2.49 (s, 1H), 2.42 (s, 3H), 1.91 – 1.59 (m, 8H), 1.50 – 1.30 (m, 4H), 1.34 – 1.00 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 187.8, 143.4, 136.2, 129.7, 127.4, 108.5, 80.1, 61.0, 51.3, 50.4, 38.2, 32.1, 26.3, 26.2, 21.5, 7.3; IR (neat): ν 3523, 2850, 2017, 1594, 1496, 1355, 1301, 1088, 965, 909, 829, 706 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{21}H_{29}NO_3NaS$ $[M+Na]^+$: 398.17604, found: 398.17640.



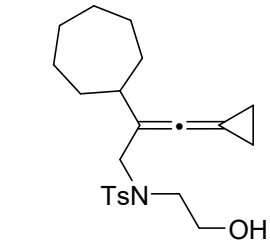
(^{1}H NMR 400 MHz, $CDCl_3$)



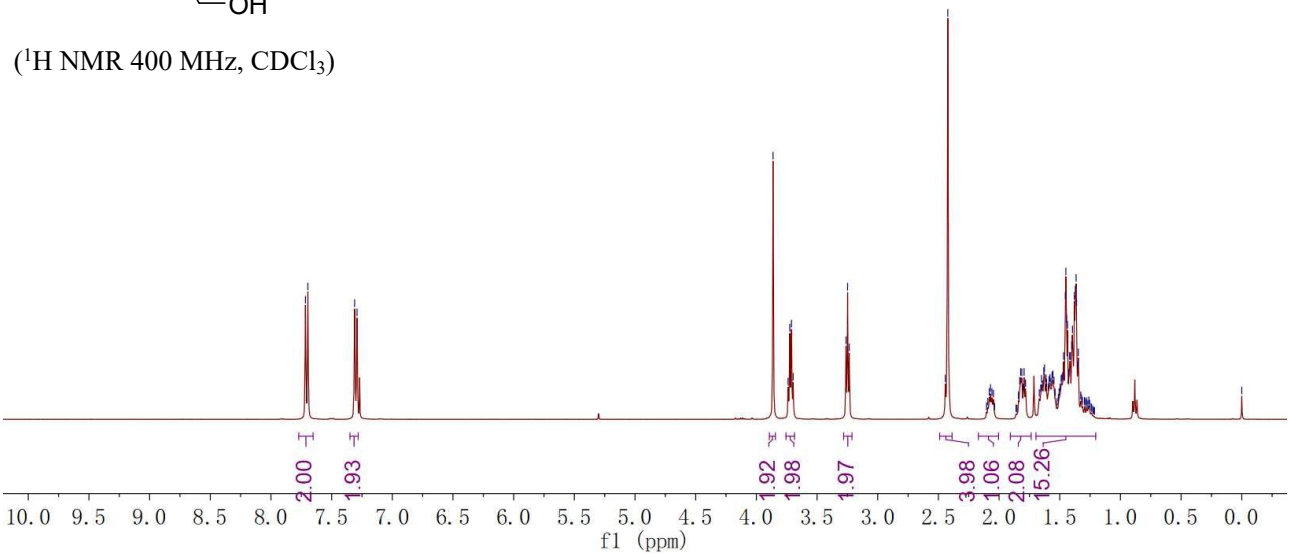
(^{13}C NMR 100 MHz, $CDCl_3$)



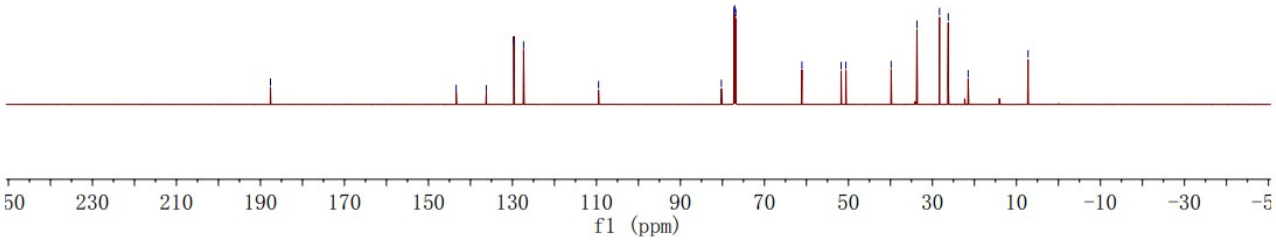
Compound 1u: Yield: 575.7 mg, 74%; A yellow oil; Eluent: PE/EA = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.86 (s, 2H), 3.74 – 3.70 (m, 2H), 3.25 (t, *J* = 5.3 Hz, 2H), 2.44 – 2.42 (m, 4H), 2.10 – 2.03 (m, 1H), 1.86 – 1.78 (m, 2H), 1.70 – 1.20 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 187.6, 143.4, 136.2, 129.7, 127.4, 109.5, 80.3, 61.1, 51.7, 50.6, 39.8, 33.7, 28.3, 26.2, 21.5, 7.2; IR (neat): ν 3520, 2853, 2017, 1445, 1339, 1305, 1088, 991, 888, 728 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{22}H_{31}NO_3NaS$ $[M+Na]^+$:412.19169, found: 412.19264.

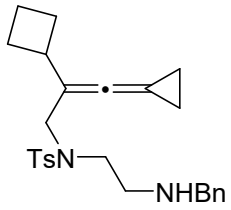


(^{1}H NMR 400 MHz, $CDCl_3$)

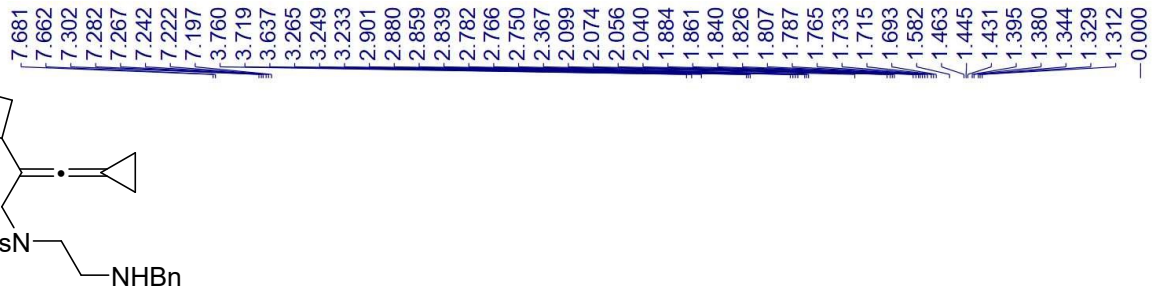


(^{13}C NMR 100 MHz, $CDCl_3$)

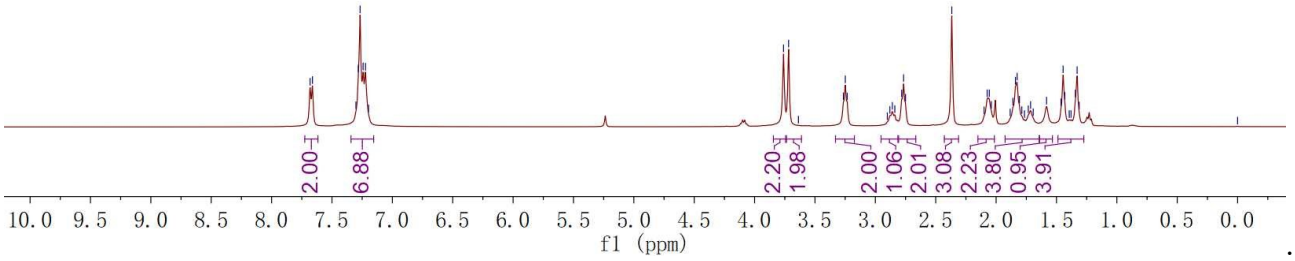


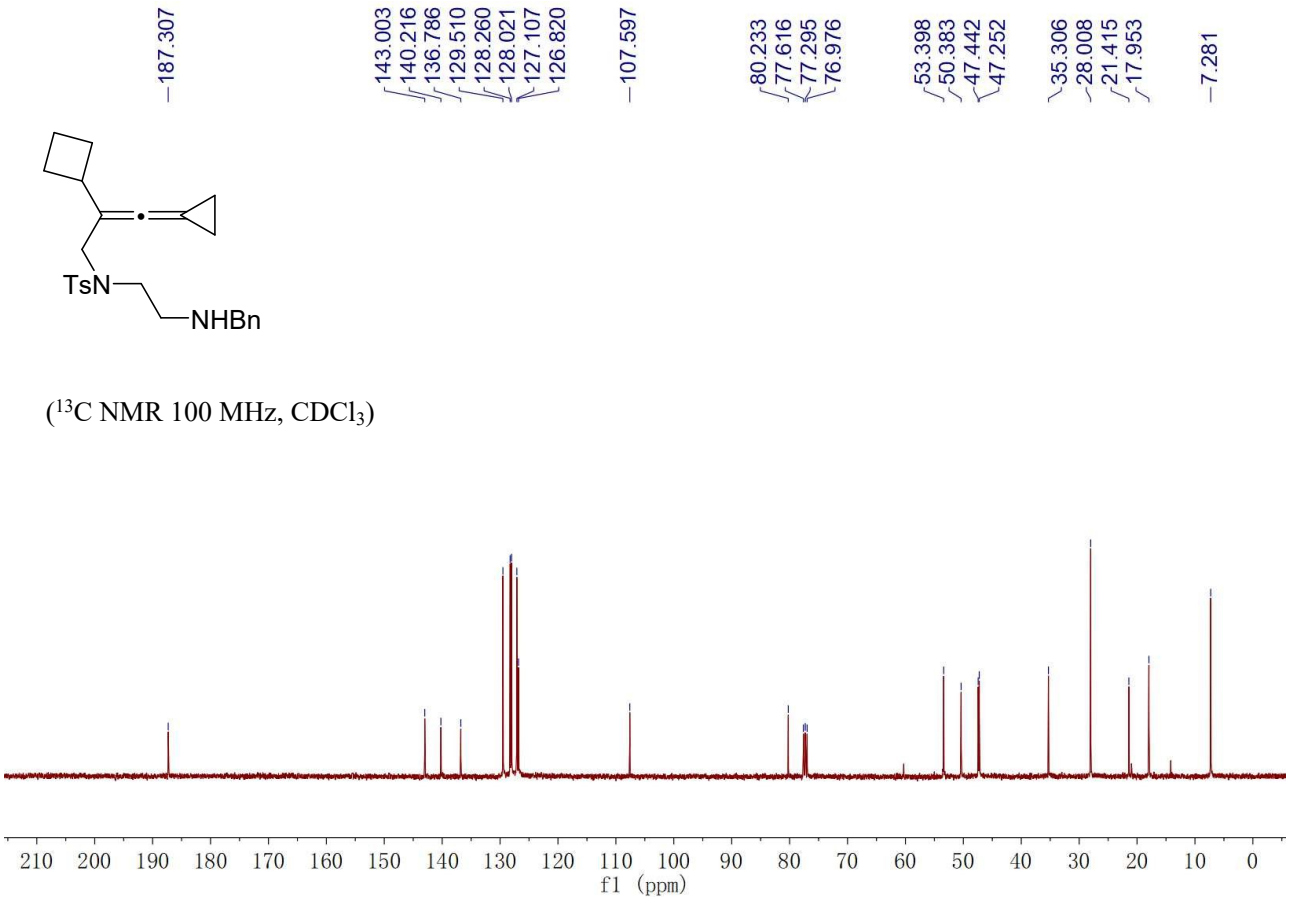


Compound 1v: Yield: 767.4 mg, 88%; A yellow oil; Eluent: PE/EA = 1/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.67 (d, *J* = 7.8 Hz, 2H), 7.28 – 7.18 (m, 7H), 3.76 (s, 2H), 3.72 (s, 2H), 3.25 (t, *J* = 6.4 Hz, 2H), 2.86 (t, *J* = 8.2 Hz, 1H), 2.77 (t, *J* = 6.4 Hz, 2H), 2.37 (s, 3H), 2.08 – 2.02 (m, 2H), 1.93 – 1.64 (m, 4H), 1.58 (s, 1H), 1.49 – 1.27 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 187.3, 143.0, 140.2, 136.8, 129.5, 128.3, 128.0, 127.1, 126.8, 107.6, 80.2, 53.4, 50.4, 47.4, 47.3, 35.3, 28.0, 21.4, 18.0, 7.3; IR (neat): ν 2974, 2932, 2859, 2017, 1597, 1493, 1333, 1154, 908, 813, 733, 698, 649 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{26}H_{33}N_2O_2S$ $[M+H]^+$: 437.22573, found: 437.22591

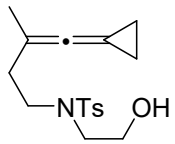


(^{1}H NMR 400 MHz, $CDCl_3$)

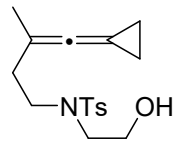




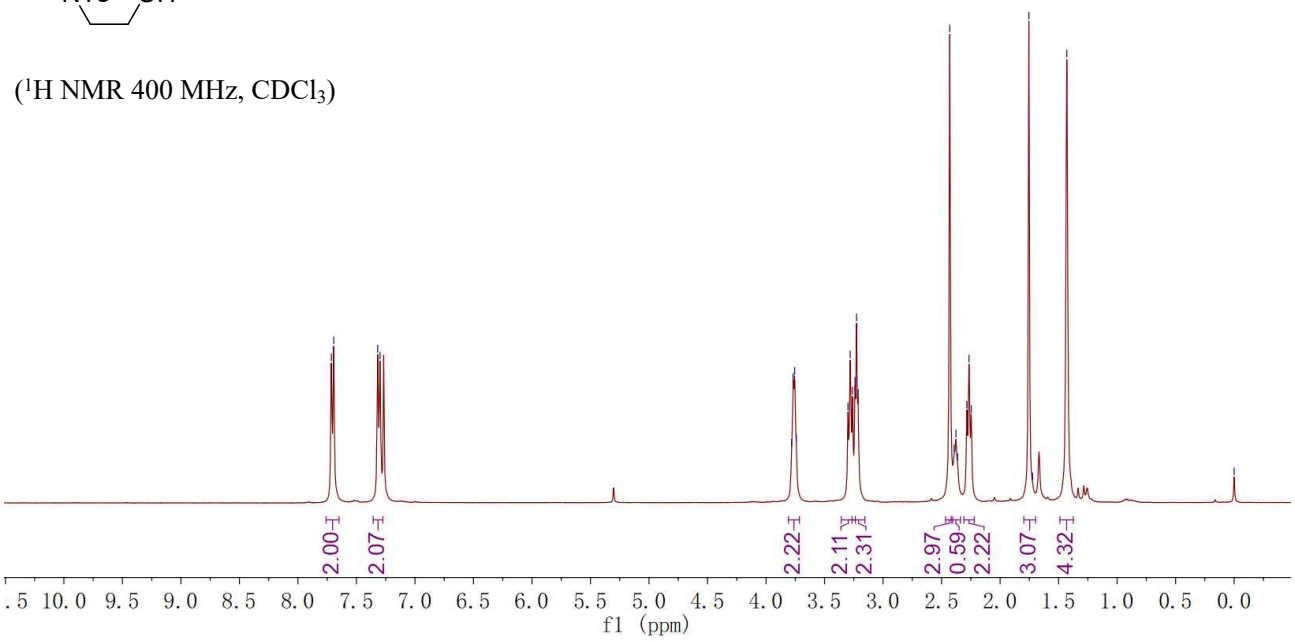
(^{13}C NMR 100 MHz, $CDCl_3$)

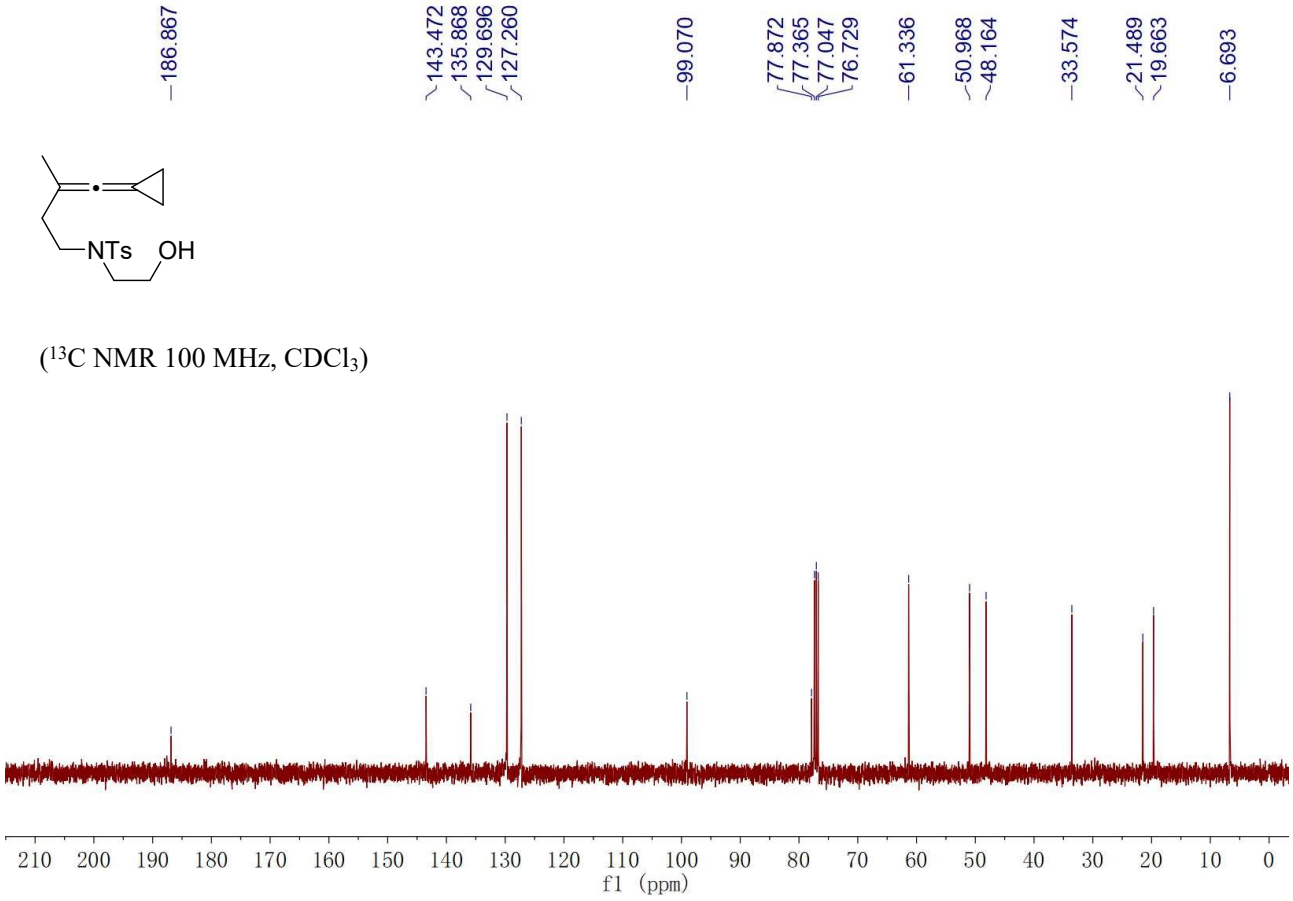


Compound 1w: Yield: 577.8 mg, 96%; A yellow oil; Eluent: PE/EA = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.70 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.78 – 3.74 (m, 2H), 3.28 (t, *J* = 7.6 Hz, 2H), 3.23 (t, *J* = 5.4 Hz, 2H), 2.43 (s, 3H), 2.39 (t, *J* = 5.6 Hz, 1H), 2.27 (t, *J* = 7.6 Hz, 2H), 1.75 (s, 3H), 1.43 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 186.9, 143.5, 135.9, 129.7, 127.3, 99.1, 77.9, 61.3, 51.0, 48.2, 33.6, 21.5, 19.7, 6.7; IR (neat): ν 3512, 2964, 1594, 1526, 1355, 1088, 989, 826, 829, 726 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{17}H_{23}NO_3NaS$ $[M+Na]^+$: 344.12909, found: 344.12938.

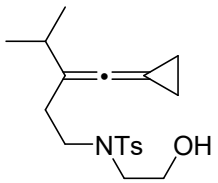


(^{1}H NMR 400 MHz, $CDCl_3$)

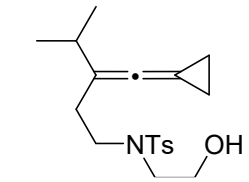




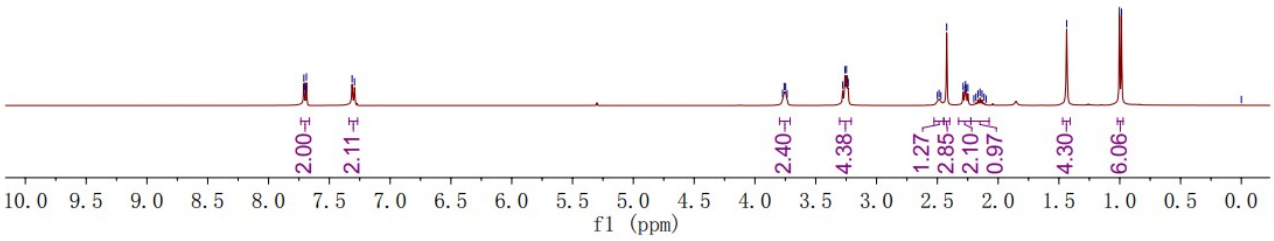
(^{13}C NMR 100 MHz, $CDCl_3$)

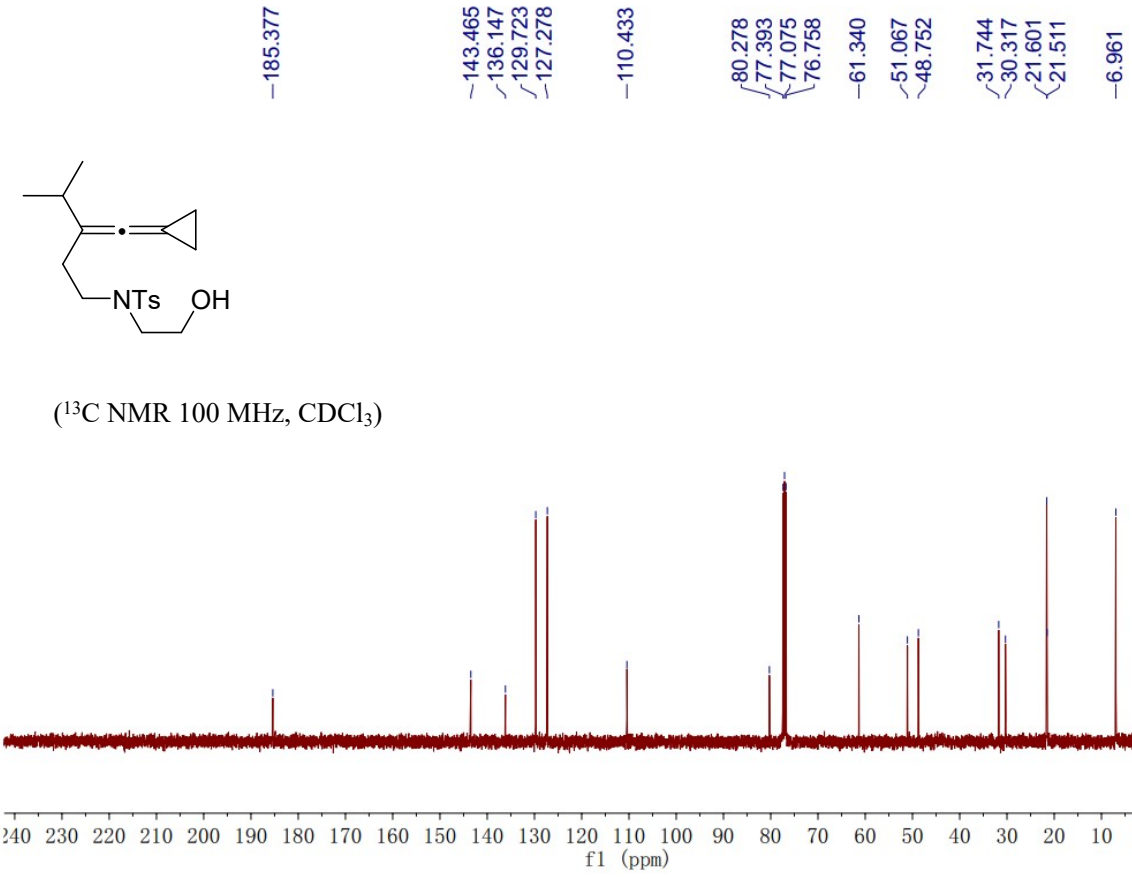


Compound 1x: Yield: 644.2 mg, 92%; A yellow oil; Eluent: PE/EA = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.73 – 7.66 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.77 – 3.74 (m, 2H), 3.30 – 3.21 (m, 4H), 2.40 – 2.47 (m, 1H), 2.42 (s, 3H), 2.33 – 2.22 (m, 2H), 2.15 (hept, *J* = 6.7 Hz, 1H), 1.44 (s, 4H), 0.99 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 185.4, 143.5, 136.1, 129.7, 127.3, 110.4, 80.3, 61.3, 51.1, 48.8, 31.7, 30.3, 21.6, 21.5, 7.0; IR (neat): ν 3535, 2959, 2011, 1445, 1332, 1153, 966, 814, 731 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{19}H_{27}NO_3NaS$ $[M+Na]^+$: 372.16039, found: 372.15969.

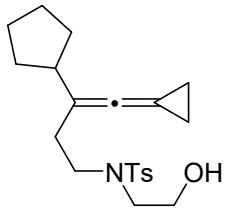


(^{1}H NMR 400 MHz, $CDCl_3$)

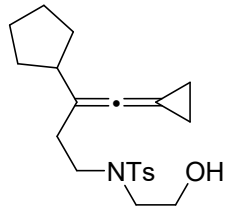




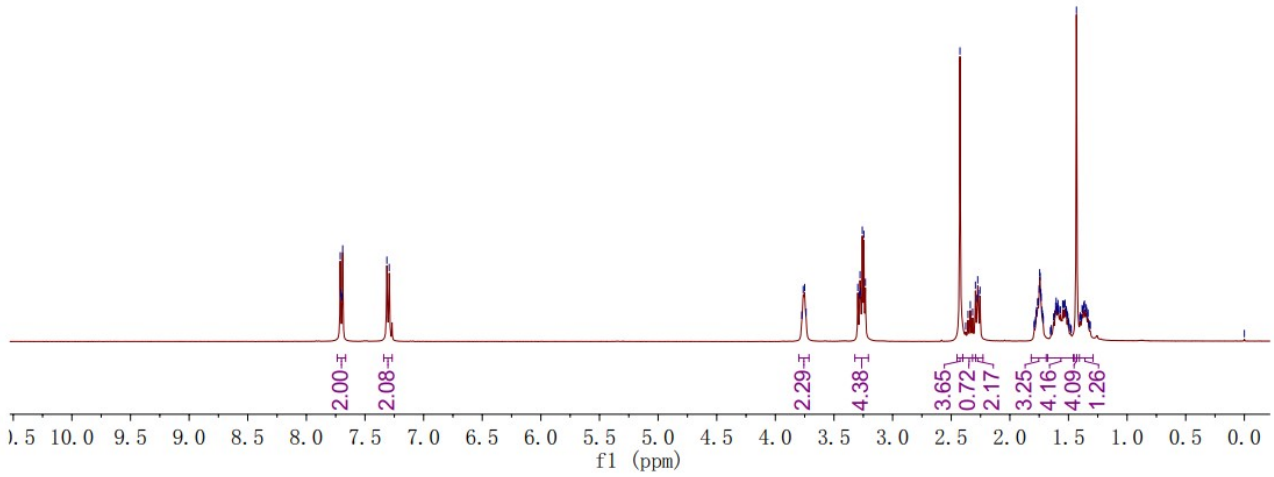
(^{13}C NMR 100 MHz, $CDCl_3$)

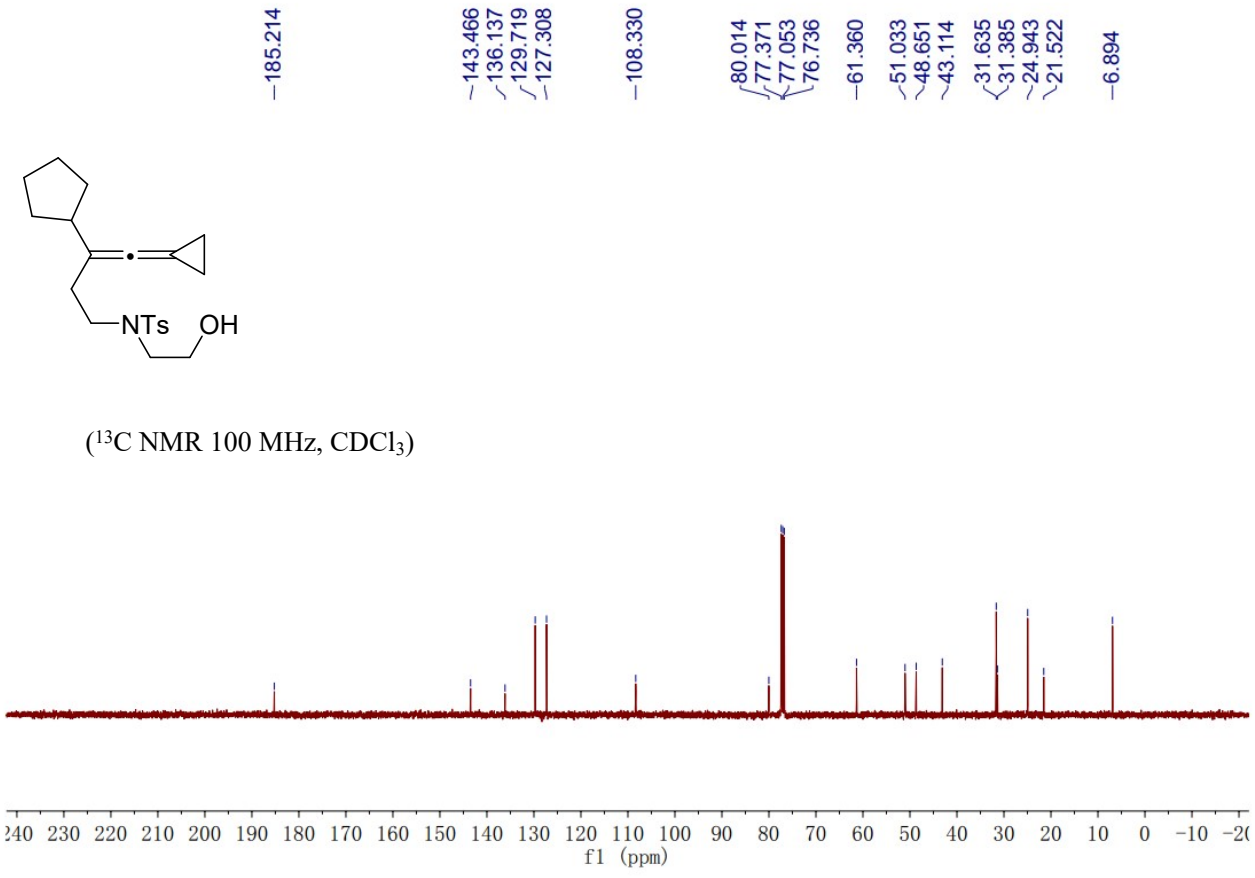


Compound 1y: Yield: 697.5 mg, 93%; A colorless oil; Eluent: PE/EA = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.74 – 7.67 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.78 – 3.74 (m, 2H), 3.32 – 3.21 (m, 4H), 2.43 (s, 3H), 2.38 – 2.32 (m, 1H), 2.29 – 2.25 (m, 2H), 1.79 – 1.73 (m, 3H), 1.65 – 1.48 (m, 4H), 1.43 (s, 4H), 1.40 – 1.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 185.2, 143.5, 136.1, 129.7, 127.3, 108.3, 80.0, 61.4, 51.0, 48.7, 43.1, 31.6, 31.4, 24.9, 21.5, 6.9; IR (neat): ν 3525, 2949, 2014, 1591, 1332, 1108, 970, 813, 736, 659 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{21}H_{29}NO_3NaS$ $[M+Na]^+$: 398.17604, found: 398.17607.

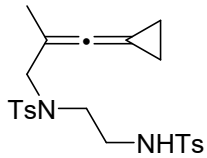


(^{1}H NMR 400 MHz, $CDCl_3$)

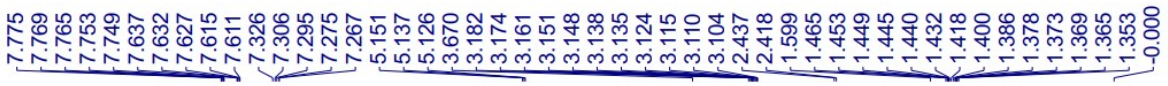


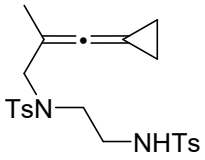


(^{13}C NMR 100 MHz, $CDCl_3$)

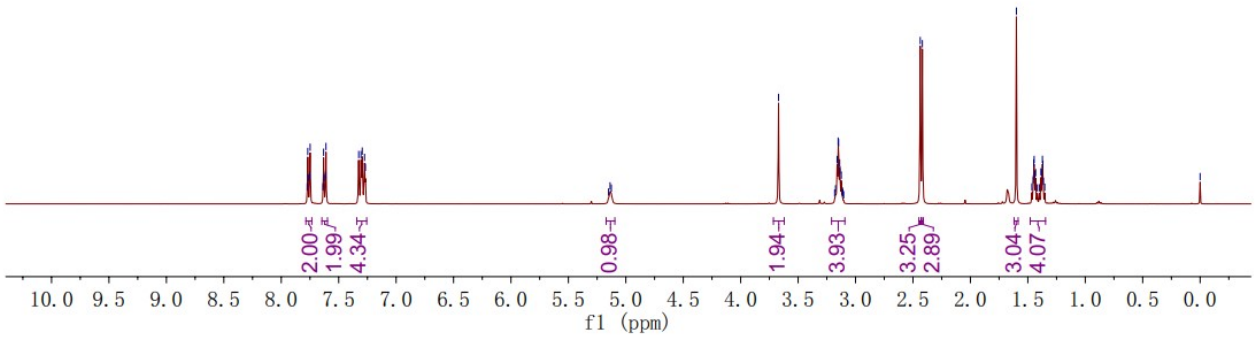


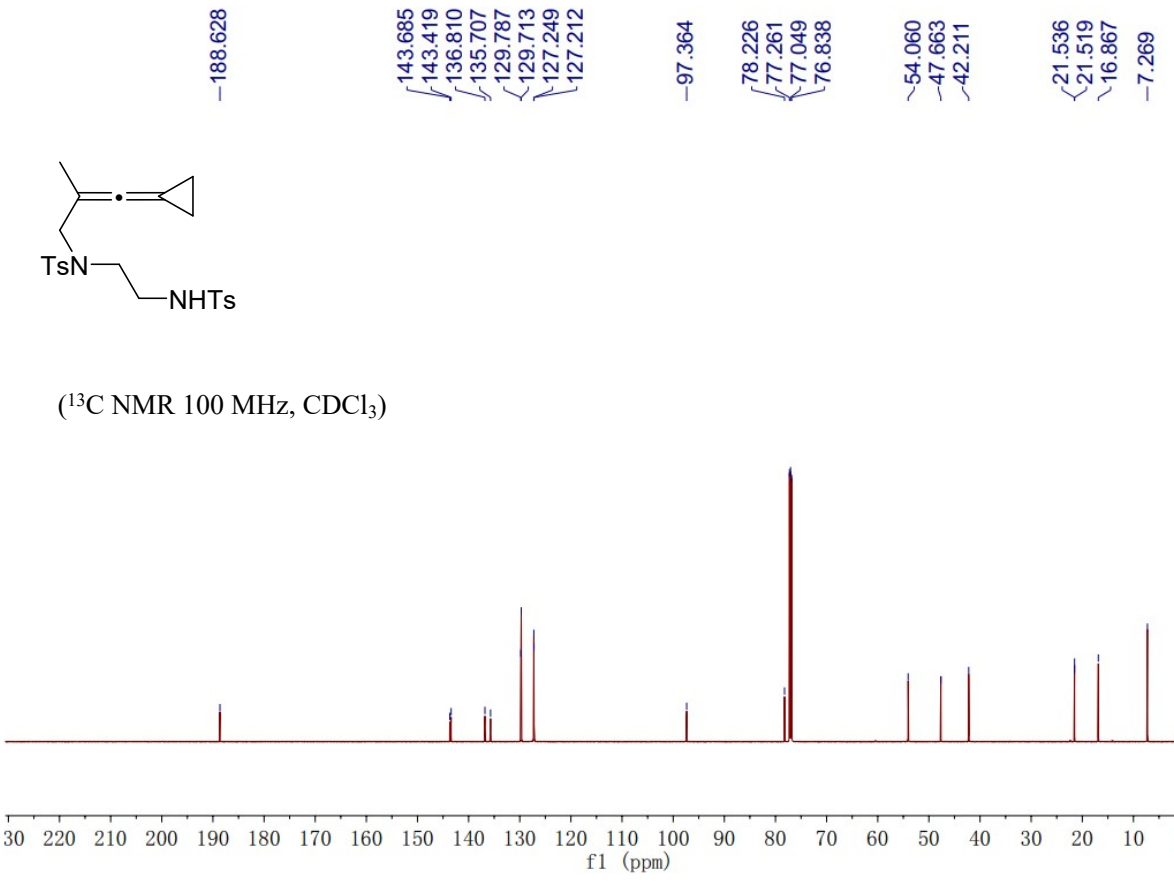
Compound 1z: Yield: 901.6 mg, 98%; A yellow oil; Eluent: PE/EA = 4/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.79 – 7.73 (m, 2H), 7.65 – 7.60 (m, 2H), 7.34 – 7.26 (m, 4H), 5.15 – 5.13 (m, 1H), 3.67 (s, 2H), 3.18 – 3.10 (m, 4H), 2.44 (s, 3H), 2.42 (s, 3H), 1.60 (s, 3H), 1.48 – 1.35 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 188.6, 143.7, 143.4, 136.8, 135.7, 129.8, 129.7, 127.25, 127.21, 97.4, 78.2, 54.1, 47.7, 42.2, 21.54, 21.52, 16.9, 7.3; IR (neat): ν 3287, 2900, 2026, 1585, 1337, 1080, 1001, 816, 763, 655 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{23}H_{28}N_2O_4NaS$ $[M+Na]^+$: 483.13827, found: 483.13815.



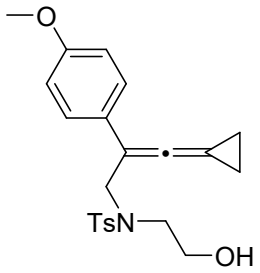


(^{1}H NMR 400 MHz, $CDCl_3$)

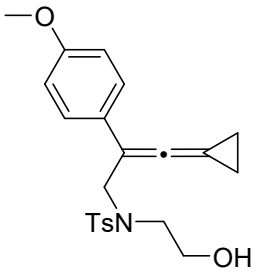




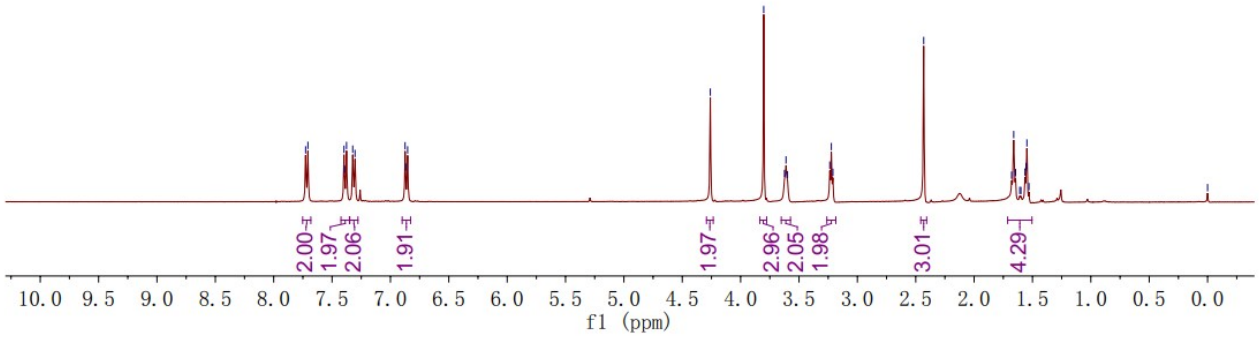
(^{13}C NMR 100 MHz, $CDCl_3$)

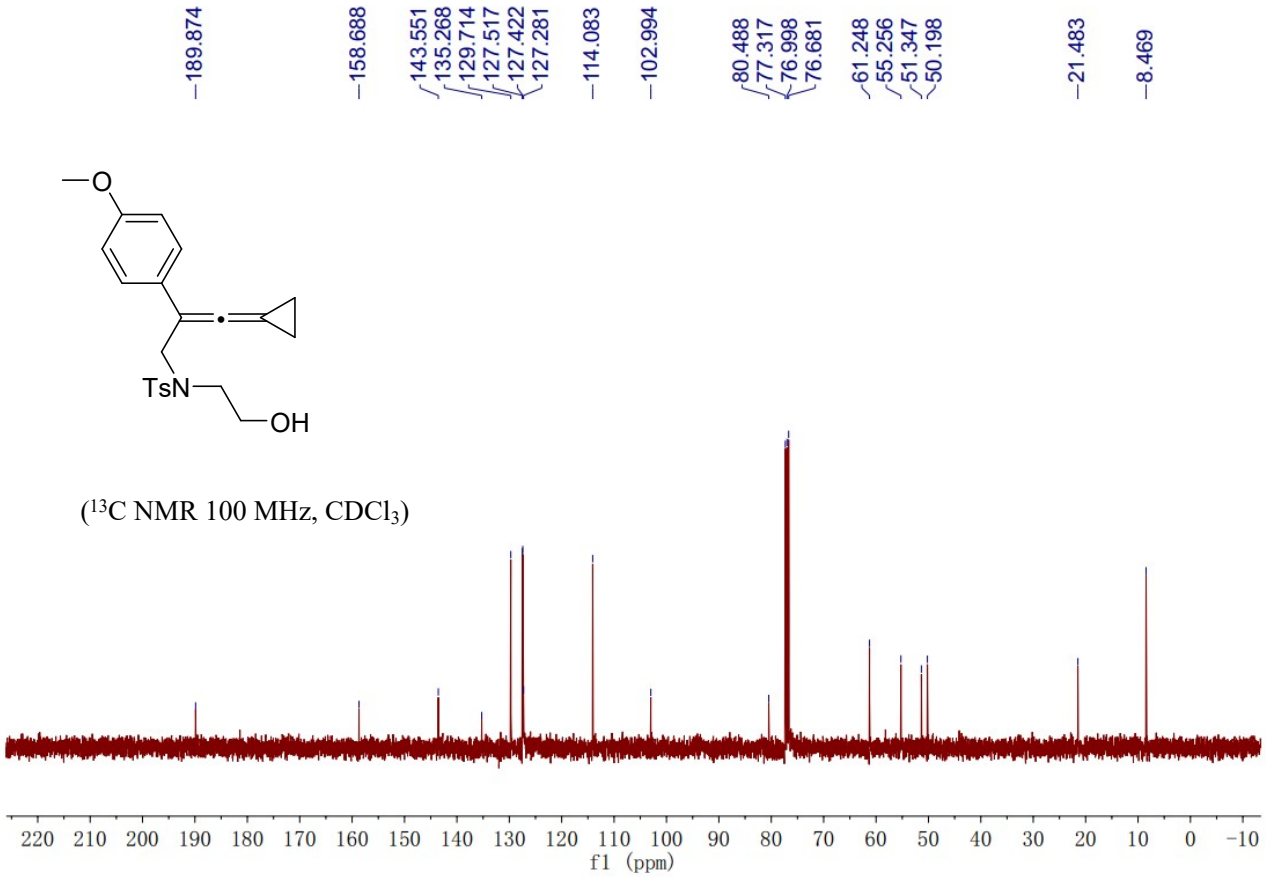


Compound 1aa: Yield: 95.8 mg, 12%; A colorless solid; Mp: 196 – 198 ℃; Eluent: PE/EA = 1/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.72 (d, *J* = 7.9 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 4.26 (s, 2H), 3.80 (s, 3H), 3.61 (t, *J* = 5.2 Hz, 2H), 3.22 (t, *J* = 5.2 Hz, 2H), 2.43 (s, 3H), 1.71 – 1.50 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 189.9, 158.7, 143.6, 135.3, 129.7, 127.5, 127.4, 127.3, 114.1, 103.0, 80.5, 61.2, 55.3, 51.3, 50.2, 21.5, 8.5; IR (neat): ν 3663, 2979, 2001, 1599, 1516, 1323, 1247, 1069, 827, 709, 756, 712 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{22}H_{25}NO_4NaS$ $[M+Na]^+$: 422.13965, found: 422.14017.

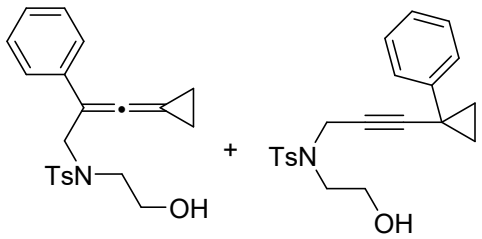


(^{1}H NMR 400 MHz, $CDCl_3$)



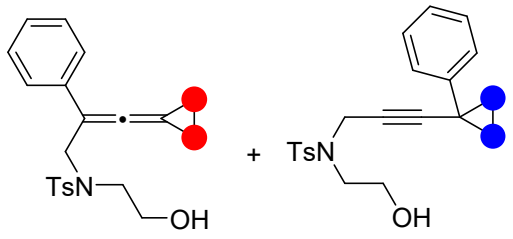


(^{13}C NMR 100 MHz, $CDCl_3$)



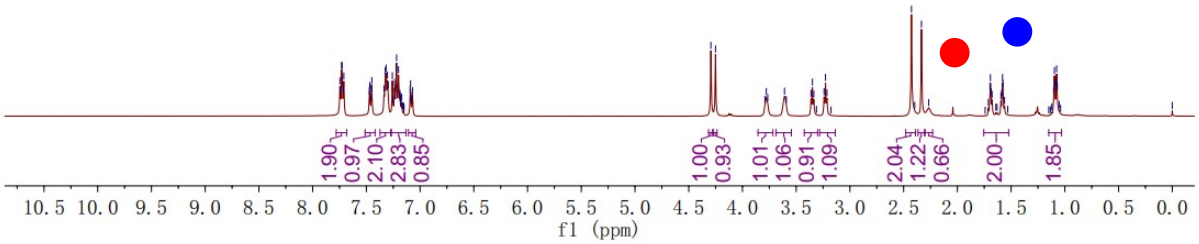
1ab **1ab'**

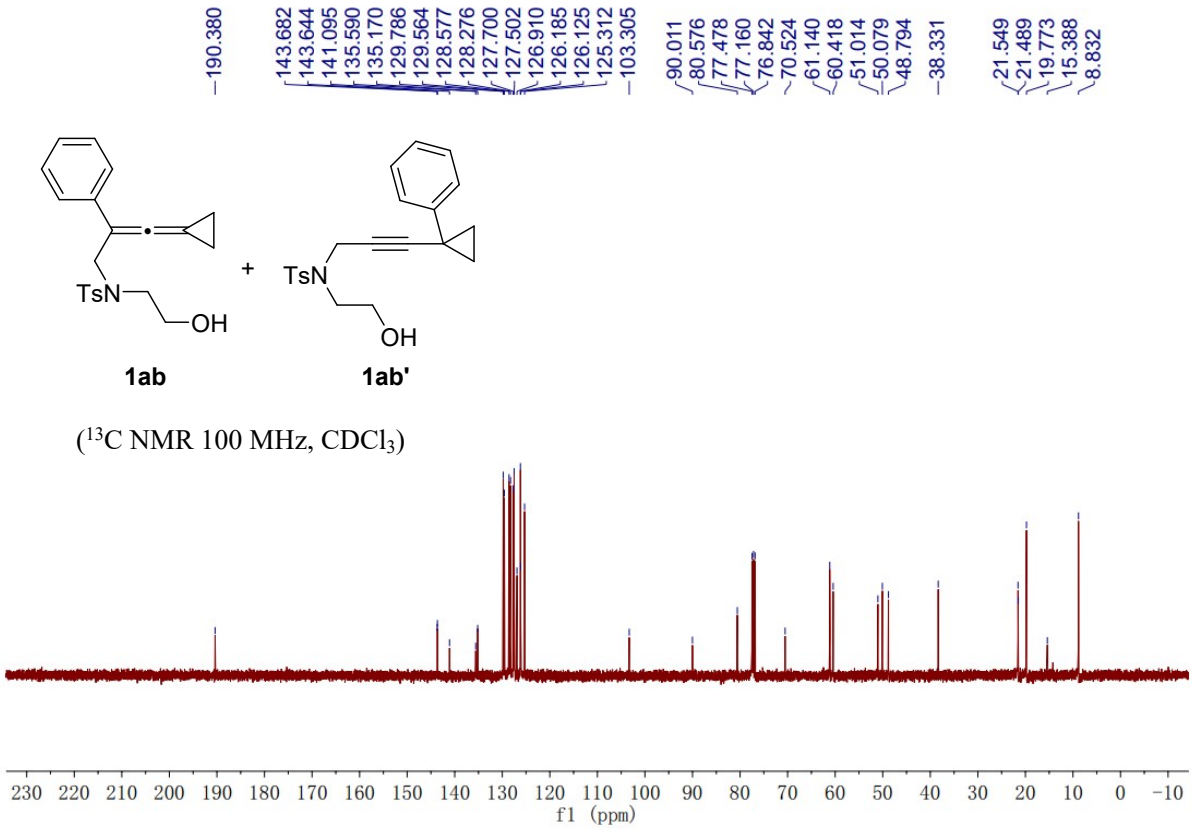
Compound 1ab: An inseparable mixture of **1ab** and **1ab'** in a 1:0.93 ratio determined by ^{1}H NMR analysis; a yellow oil; Eluent: PE/EA = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, detectable signals of **1ab** are marked with an asterisk) δ 7.78 – 7.68 (m, 2H), 7.47 – 7.45 (m, 1H), 7.34 – 7.30 (m, 2H), 7.28 – 7.12 (m, 3H), 7.10 – 7.07 (m, 1H), 4.29* (s, 1H), 4.25 (s, 1H), 3.79 – 3.77 (m, 1H), 3.61 – 3.59* (m, 1H), 3.35 (t, *J* = 5.2 Hz, 1H), 3.23* (t, *J* = 5.4 Hz, 1H), 2.43* (s, 2H), 2.33 (s, 1H), 1.77 – 1.51* (m, 2H), 1.14 – 1.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 190.4, 143.7, 143.6, 141.1, 135.6, 135.2, 129.8, 129.6, 128.6, 128.3, 127.7, 127.5, 126.9, 126.2, 126.1, 125.3, 103.3, 90.0, 80.6, 70.5, 61.1, 60.4, 51.0, 50.1, 48.8, 38.3, 21.55, 21.49, 19.8, 15.4, 8.8.



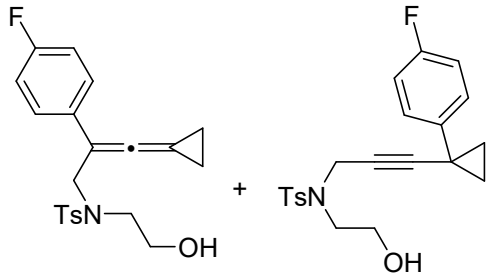
1ab **1ab'**

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



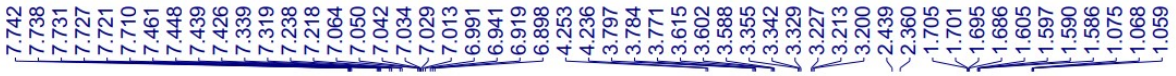


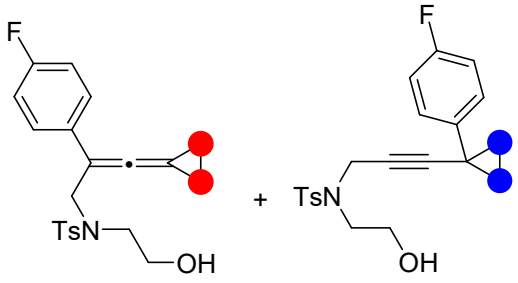
(^{13}C NMR 100 MHz, $CDCl_3$)



1ac **1ac'**

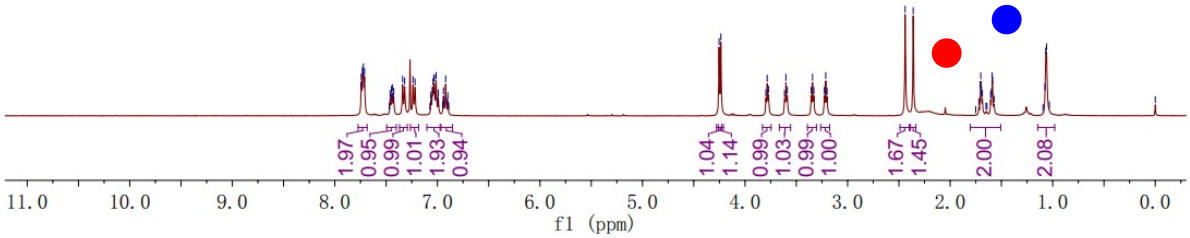
Compound 1ac: An inseparable mixture of **1ac** and **1ac'** in a 1:1.04 ratio determined by ^{1}H NMR analysis; a yellow oil; Eluent: PE/EA = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, detectable signals of **1ac** are marked with an asterisk) δ 7.77 – 7.69 (m, 2H), 7.49 – 7.40 (m, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.10 – 6.97 (m, 2H), 6.95 – 6.89 (m, 1H), 4.25* (s, 1H), 4.24 (s, 1H), 3.78* (t, *J* = 5.2 Hz, 1H), 3.60 (t, *J* = 5.4 Hz, 1H), 3.34* (t, *J* = 5.2 Hz, 1H), 3.21 (t, *J* = 5.4 Hz, 1H), 2.44* (s, 2H), 2.36 (s, 1H), 1.80 – 1.51* (m, 2H), 1.10 – 1.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 190.2, 163.0, 162.5, 160.5, 143.8, 143.7, 136.9, 135.6, 134.9, 131.1, 129.8, 129.5, 127.9, 127.8, 127.7, 127.5, 127.2, 127.1, 115.6, 115.4, 115.1, 114.9, 110.0, 102.3, 89.8, 80.7, 70.5, 61.2, 60.4, 51.4, 50.1, 48.8, 38.3, 21.54, 21.48, 19.4, 14.9, 8.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.4, -116.8.

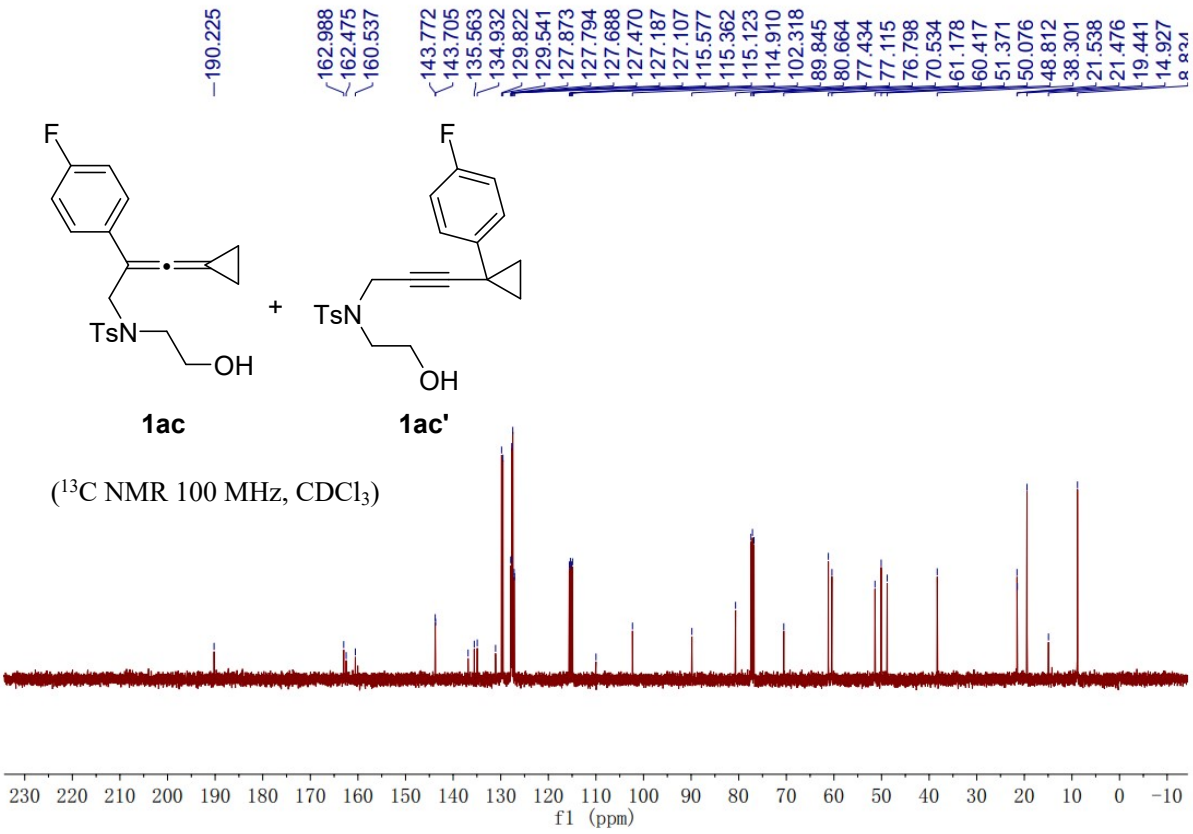




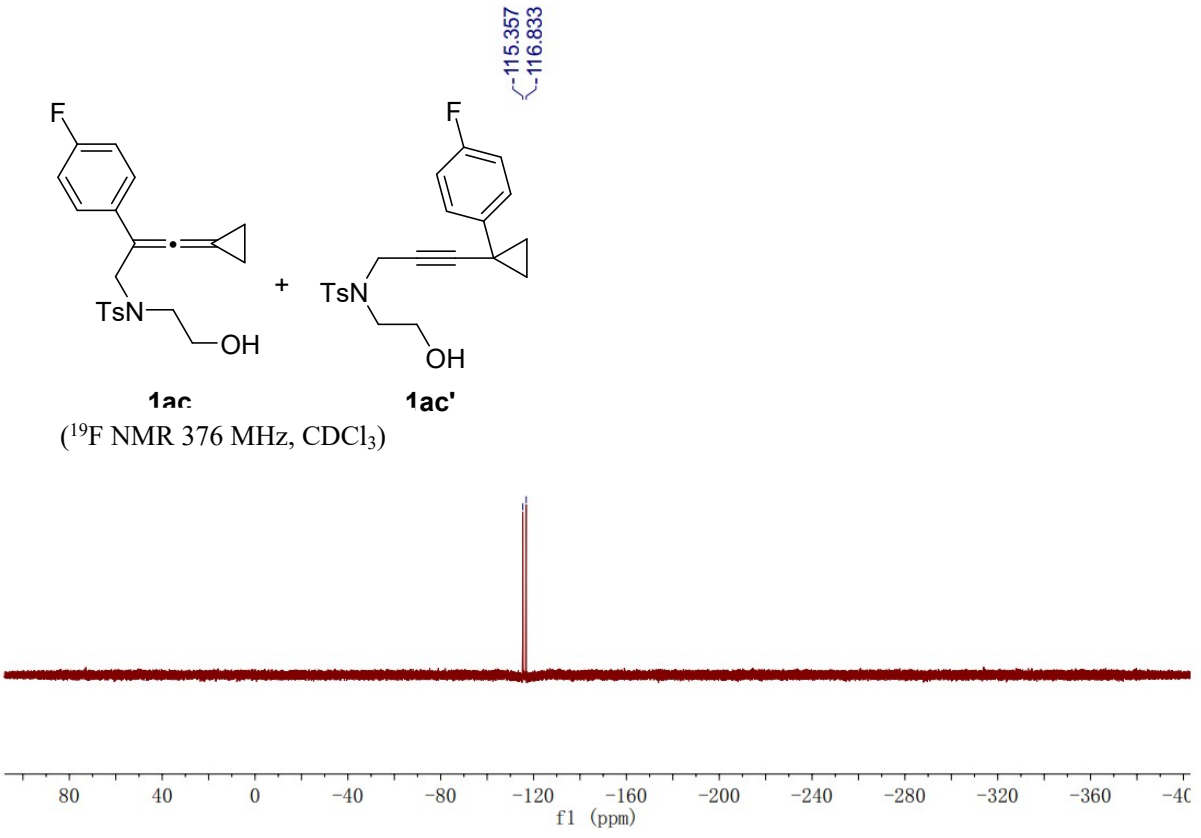
1ac **1ac'**

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

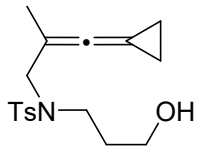




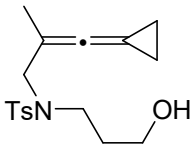
(^{13}C NMR 100 MHz, $CDCl_3$)



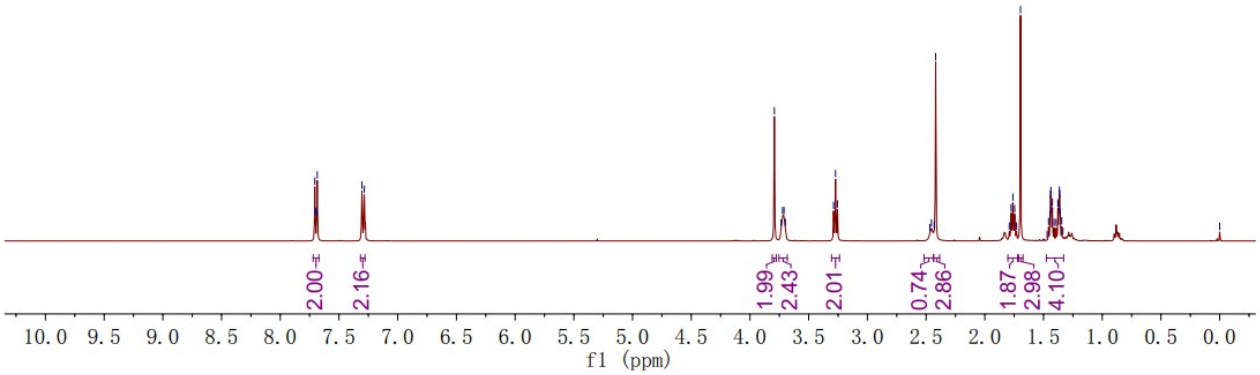
(^{19}F NMR 376 MHz, $CDCl_3$)



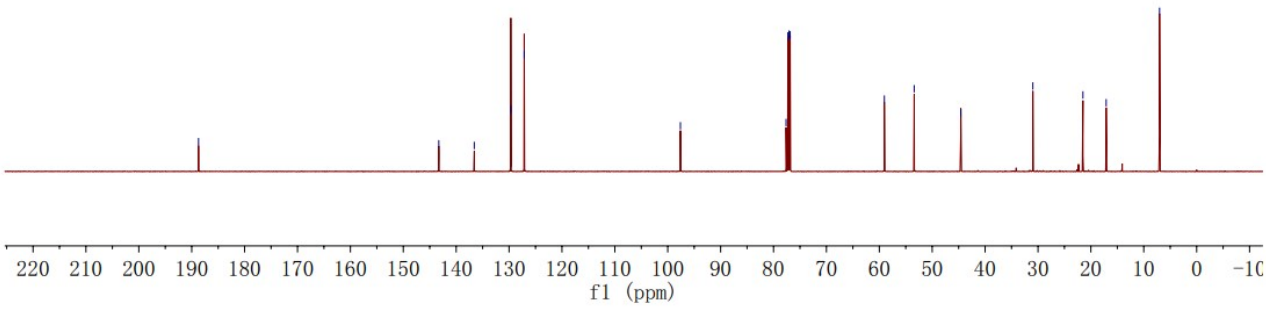
Compound 1ad: Yield: 500.8 mg, 78%; A yellow oil; Eluent: PE/EA = 1/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.72 – 7.67 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.79 (s, 2H), 3.74 – 3.70 (m, 2H), 3.27 (t, *J* = 6.6 Hz, 2H), 2.47 – 2.43 (m, 1H), 2.42 (s, 3H), 1.79 – 1.73 (m, 2H), 1.70 (s, 3H), 1.48 – 1.33 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 188.7, 143.3, 136.6, 129.7, 127.1, 97.6, 77.6, 59.0, 53.4, 44.6, 31.0, 21.5, 17.1, 7.0; IR (neat): ν 3530, 2917, 2027, 1589, 1320, 1036, 973, 806, 733, 691 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{17}H_{23}NO_3NaS$ $[M+Na]^+$: 344.12909, found: 344.12857.

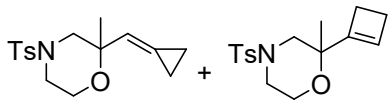


(^{1}H NMR 400 MHz, $CDCl_3$)



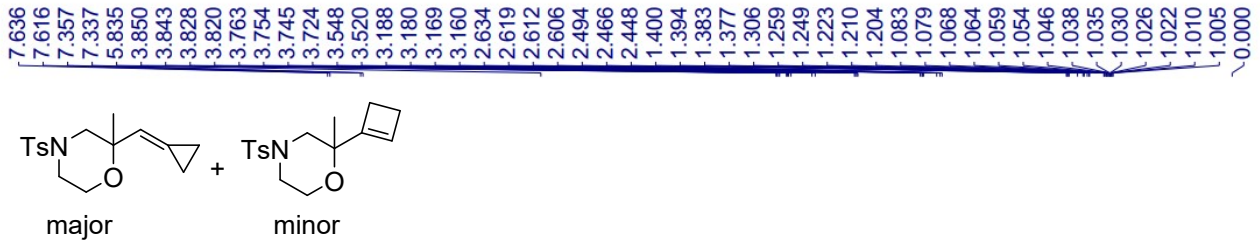
(^{13}C NMR 100 MHz, $CDCl_3$)



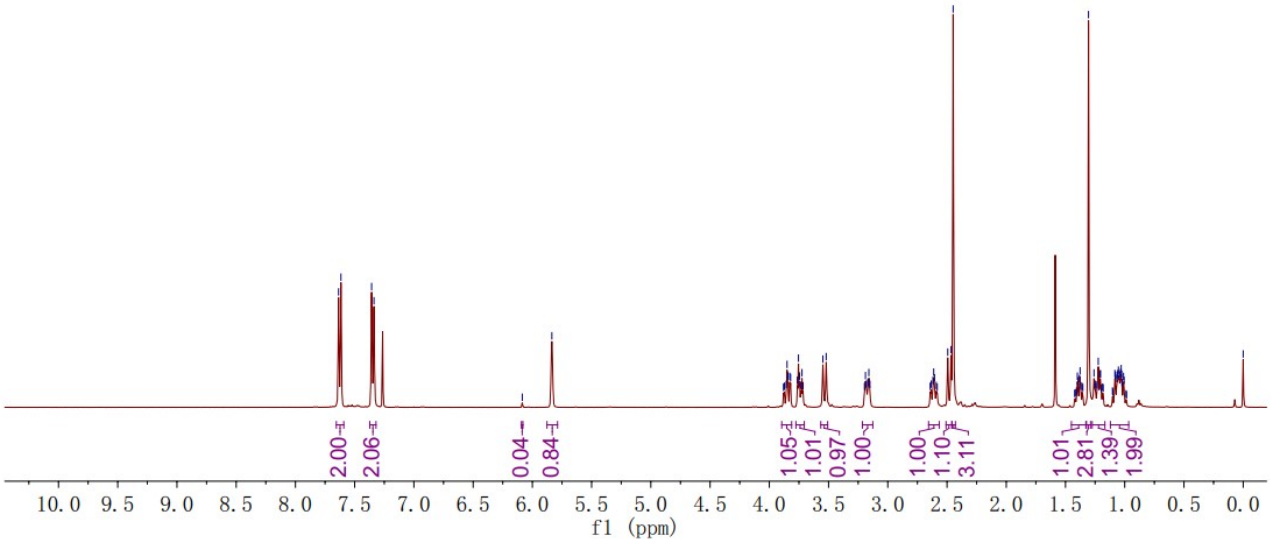


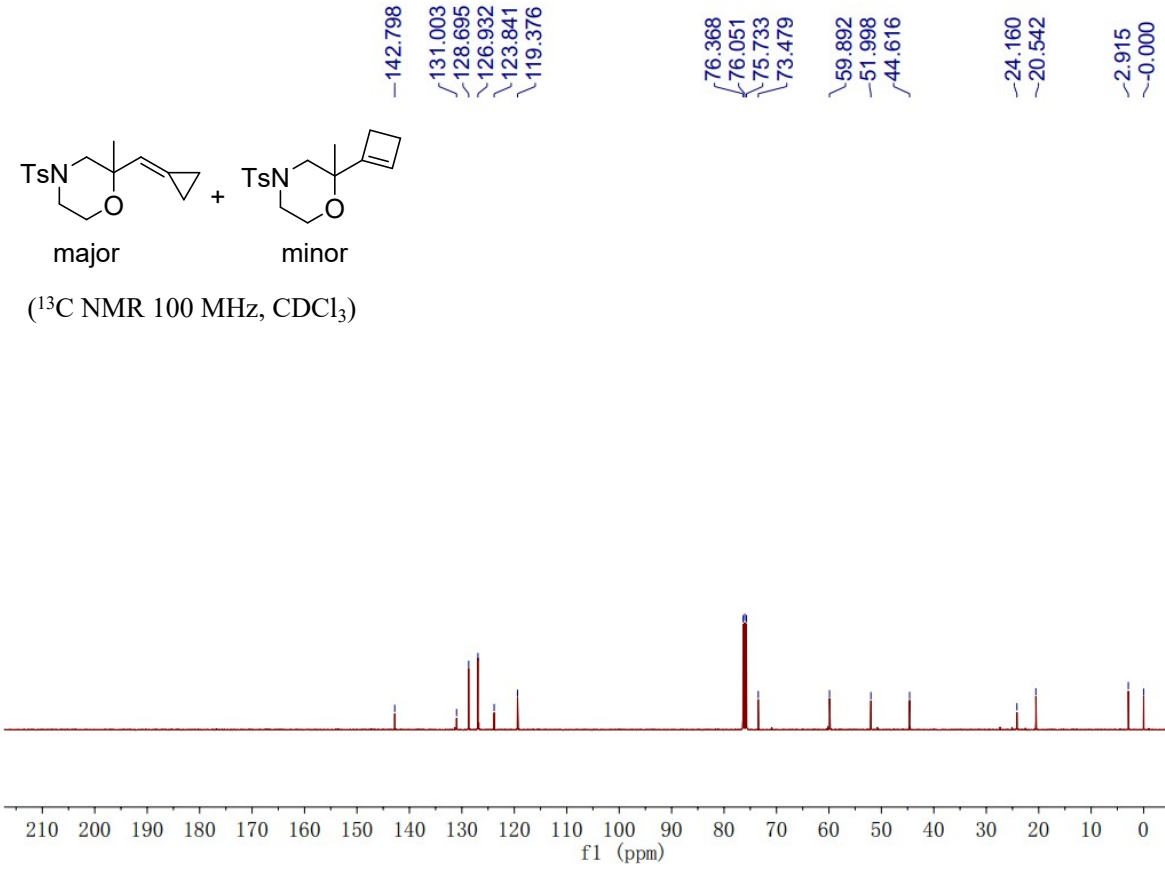
2a, major **2a'**, minor

Compound 2a: An inseparable mixture of **2a** and **2a'** in a 21:1 ratio determined by ^{1}H NMR analysis**;** Yield: 53.4 mg, 87%; A colorless solid; Mp: 89 – 92 ℃; Eluent: PE/EA = 10/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 5.84 (s, 1H), 3.88 – 3.82 (m, 1H), 3.76 – 3.71 (m, 1H), 3.53 (d, *J* = 11.2 Hz, 1H), 3.20 – 3.15 (m, 1H), 2.63 – 2.56 (m, 1H), 2.50 – 2.47 (m, 1H), 2.45 (s, 3H), 1.42 – 1.35 (m, 1H), 1.31 (s, 3H), 1.27 – 1.17 (m, 1H), 1.12 – 0.97 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 131.0, 128.7, 126.9, 123.8, 119.4, 73.5, 59.9, 52.0, 44.6, 24.2, 20.5, 2.9, 0.0; IR (neat): ν 2965, 2847, 2357, 1597, 1453, 1353, 1161, 1128, 990, 947, 864, 771, 656 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{16}H_{21}NO_3NaS$ $[M+Na]^+$: 330.11344, found: 330.11408; Enantiomeric excess was determined by HPLC with a Chiralpak IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 1.0 mL/min; t_{minor} = 16.55 min, t_{major} = 18.38 min; ee% = 55%].

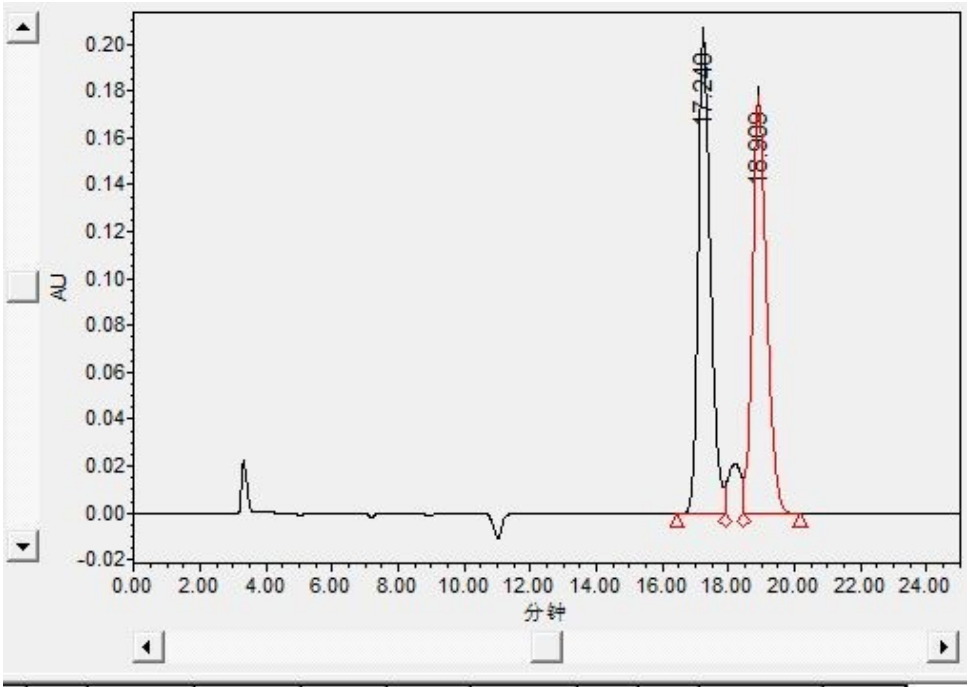


(^{1}H NMR 400 MHz, $CDCl_3$)

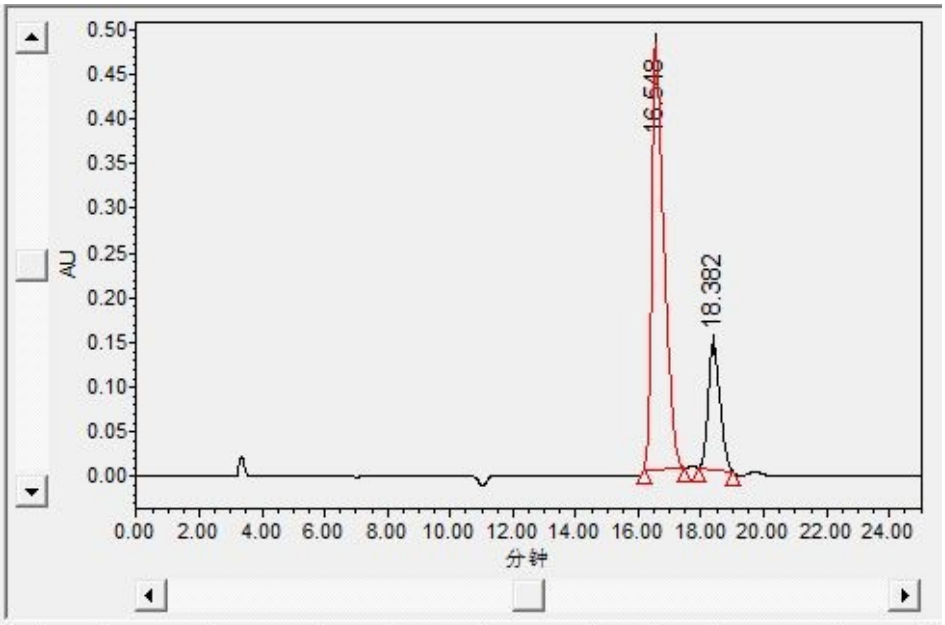




(^{13}C NMR 100 MHz, $CDCl_3$)

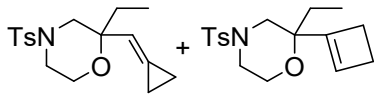


	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码
1		17.240	5298371	49.98	203236	Bv			未知	
2		18.909	5302398	50.02	177860	VB			未知	



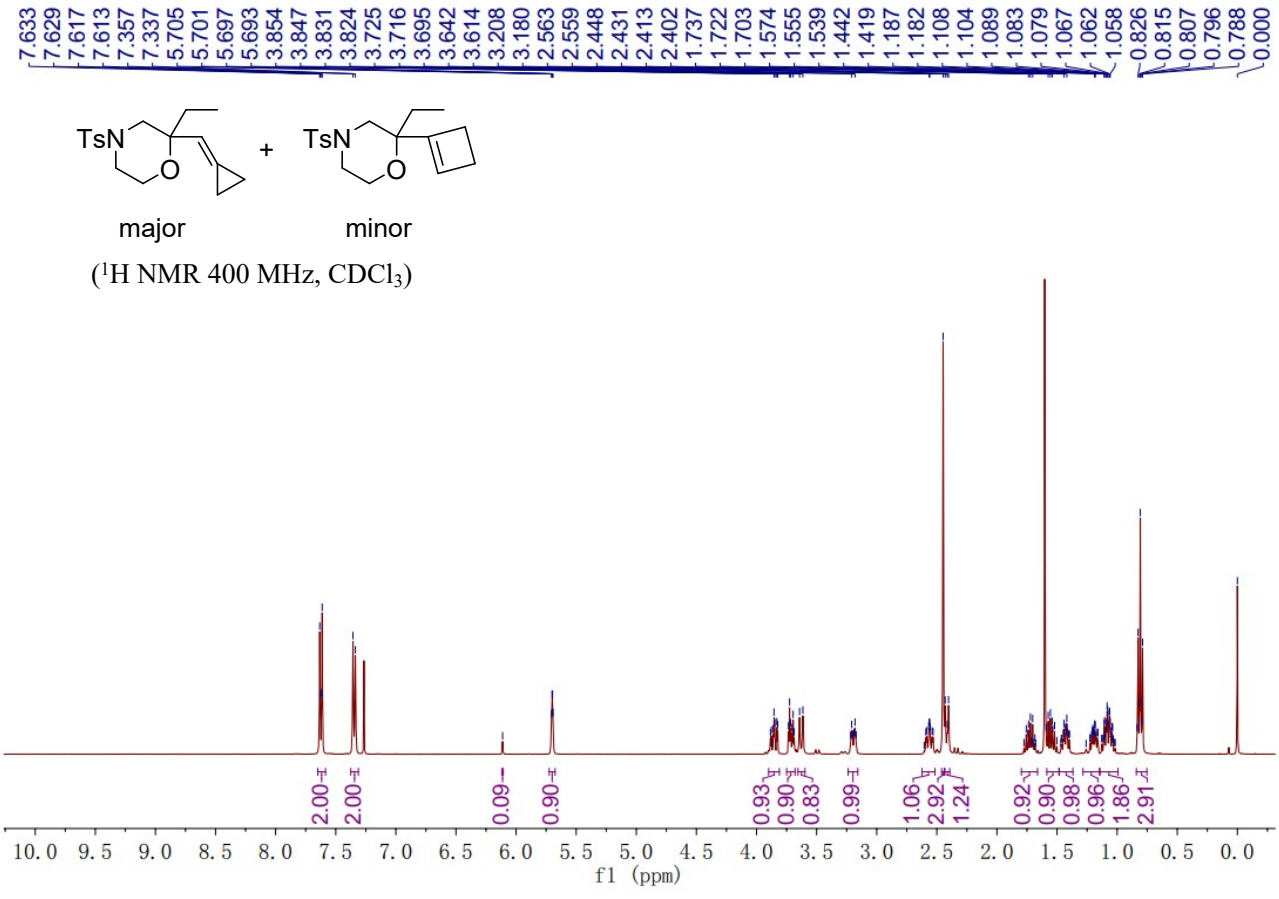
	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码
1		16.548	12857882	77.51	474879	BB			未知	
2		18.382	3731239	22.49	140924	BB			未知	

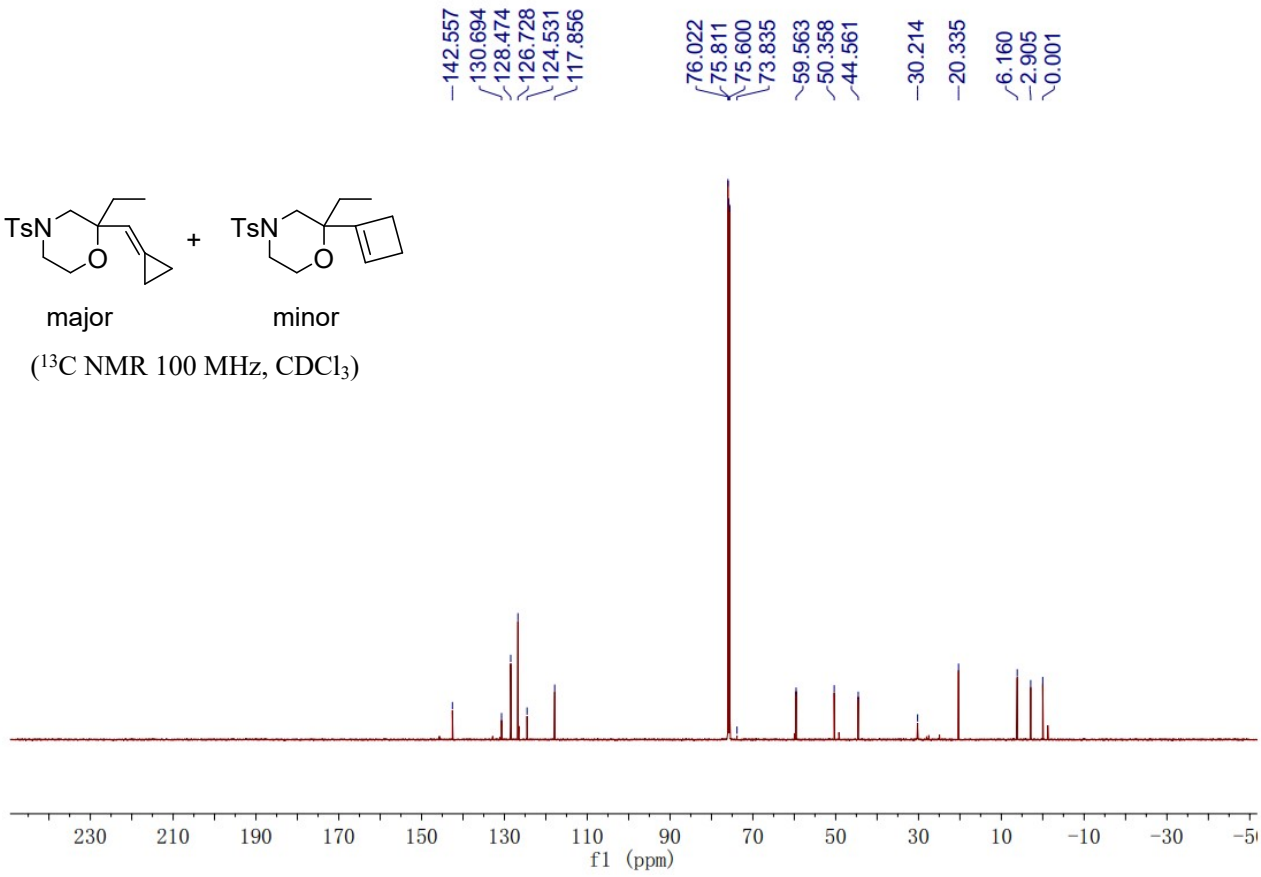
Translation: Enantiomeric excess was determined by HPLC with a Chiralpak IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 1.0 mL/min; t_{minor} = 16.55 min, t_{major} = 18.38 min; ee% = 55%].



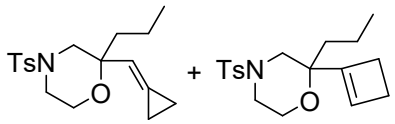
2b, major **2b'**, minor

Compound 2b: An inseparable mixture of **2b** and **2b'** in a 10:1 ratio determined by ^{1}H NMR analysis; Yield: 52.3 mg, 81%; a yellow oil; Eluent: PE/EA = 10/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.65 – 7.58 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 5.70 (s, 1H), 3.88 – 3.82 (m, 1H), 3.73 – 3.68 (m, 1H), 3.63 (d, *J* = 11.2 Hz, 1H), 3.21 – 3.17 (m, 1H), 2.60 – 2.53 (m, 1H), 2.45 (s, 3H), 2.43 – 2.39 (m, 1H), 1.80 – 1.66 (m, 1H), 1.59 – 1.50 (m, 1H), 1.46 – 1.39 (m, 1H), 1.28 – 1.15 (m, 1H), 1.12 – 1.01 (m, 2H), 0.81 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 130.7, 128.5, 126.7, 124.5, 117.9, 73.8, 59.6, 50.4, 44.6, 30.2, 20.3, 6.2, 2.9, 0.0; IR (neat): ν 2955, 2870, 2846, 2026, 1995, 1450, 1350, 1163, 1086, 976, 899, 815, 799, 734, 656 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{17}H_{23}NO_3NaS$ $[M+Na]^+$: 344.12909, found: 344.13002.



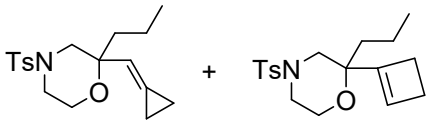


(^{13}C NMR 100 MHz, $CDCl_3$)



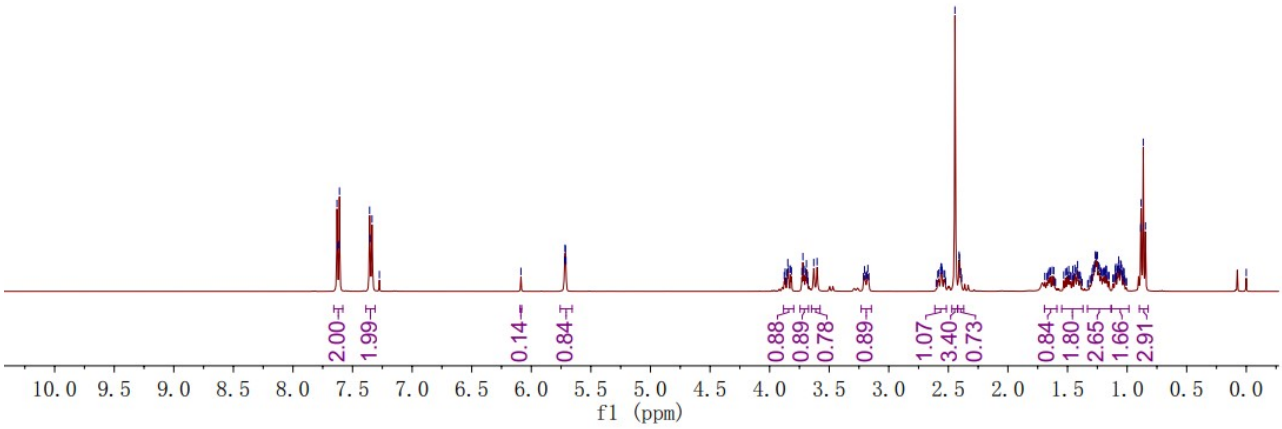
2c, major **2c'**, minor

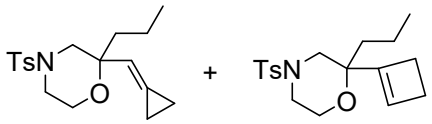
Compound 2c: An inseparable mixture of **2c** and **2c'** in a 6:1 ratio determined by ^{1}H NMR analysis; Yield: 56.3 mg, 84%; a yellow oil; Eluent: PE/EA = 10/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.66 – 7.58 (m, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 5.76 – 5.66 (m, 1H), 3.87 – 3.81 (m, 1H), 3.72 – 3.67 (m, 1H), 3.62 (d, *J* = 11.2 Hz, 1H), 3.21 – 3.16 (m, 1H), 2.61 – 2.52 (m, 1H), 2.44 (s, 3H), 2.41 – 2.38 (m, 1H), 1.69 – 1.60 (m, 1H), 1.55 – 1.37 (m, 2H), 1.33 – 1.13 (m, 3H), 1.11 – 1.10 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 130.7, 128.5, 126.8, 124.2, 118.3, 75.8, 73.5, 59.6, 50.7, 44.6, 20.4, 15.1, 13.3, 2.9, 0.0; IR (neat): ν 2958, 2871, 1597, 1454, 1359, 1305, 1261, 1278,1165, 1088, 980, 966, 916, 815, 802, 751, 661 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{18}H_{25}NO_3NaS$ $[M+Na]^+$: 358.14474, found: 358.14474.



major minor

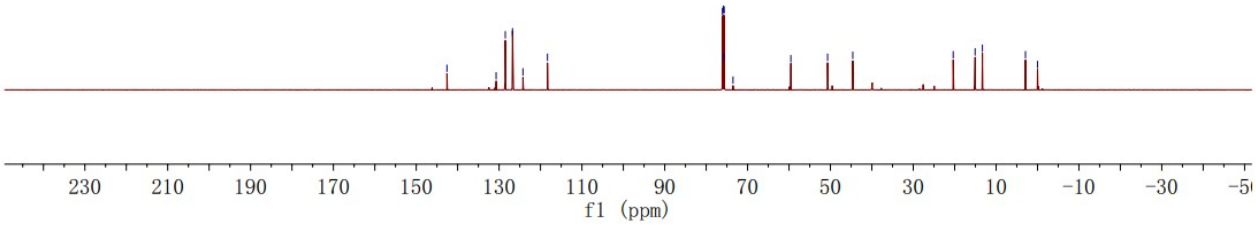
(^{1}H NMR 400 MHz, $CDCl_3$)

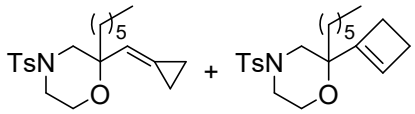




major minor

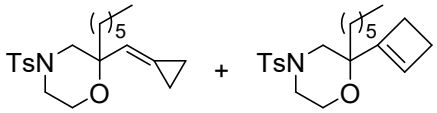
(^{13}C NMR 100 MHz, $CDCl_3$)





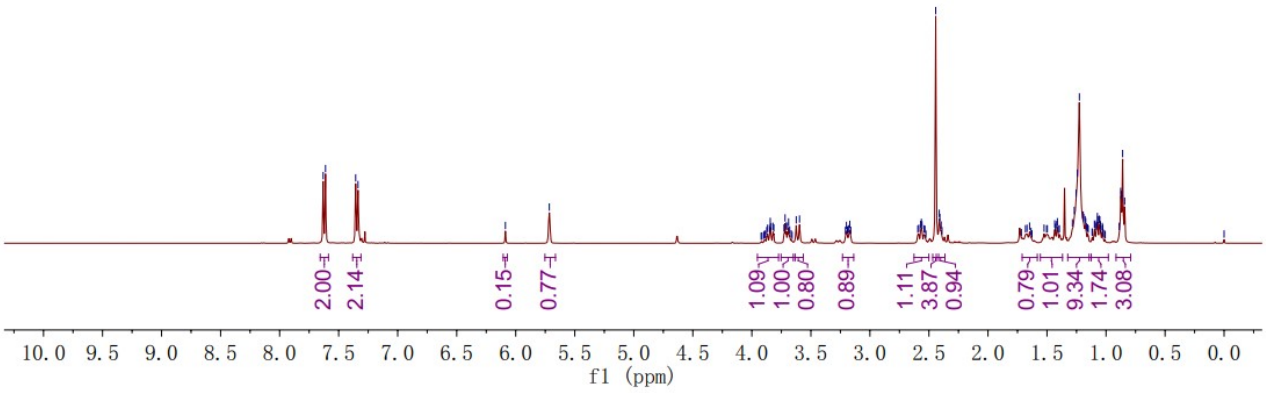
2d, major **2d'**, minor

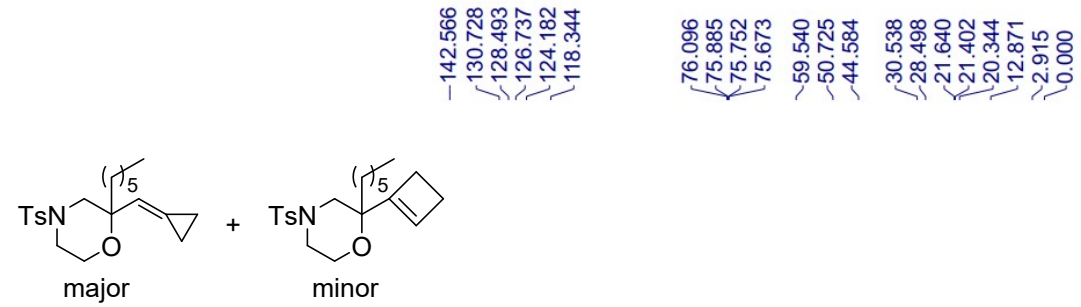
Compound 2d: An inseparable mixture of **2d** and **2d'** in a 5:1 ratio determined by ^{1}H NMR analysis; Yield: 54.2 mg, 72%; a yellow oil; Eluent: PE/EA = 10/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 5.72 (s, 1H), 3.92 – 3.81(m, 1H), 3.72 – 3.65 (m, 1H), 3.61 (d, *J* = 11.2 Hz, 1H), 3.21 – 3.16 (m, 1H), 2.59 – 2.52 (m, 1H), 2.44 (s, 3H), 2.41 – 2.39 (m, 1H), 1.71 – 1.58 (m, 1H), 1.56 – 1.37 (m, 1H), 1.32 – 1.13 (m, 6H), 1.13 – 0.98 (m, 2H), 0.92 – 0.79 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 130.7, 128.5, 126.7, 124.2, 118.3, 75.75, 59.5, 50.7, 44.6, 30.5, 28.5, 21.6, 21.4, 20.3, 12.9, 2.9, 0.0; IR (neat): ν 2926, 2855, 1454, 1351, 1305, 1278, 1125, 1089,1048, 979, 948, 815, 802, 751, 731, 661 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{21}H_{31}NO_3NaS$ $[M+Na]^+$: 400.19169, found: 400.19253.



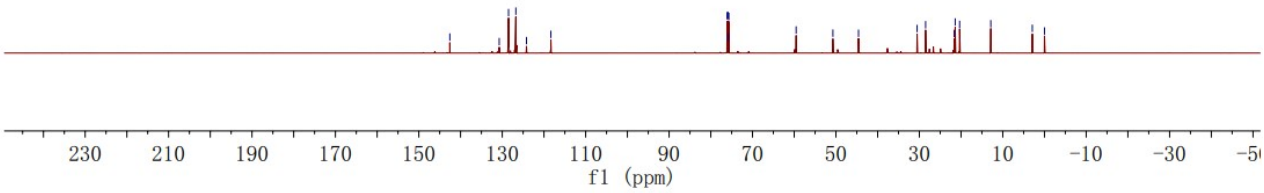
major minor

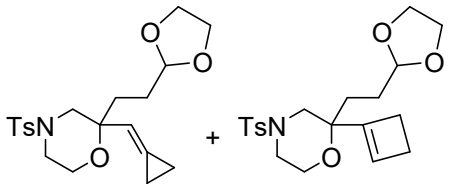
(^{1}H NMR 400 MHz, $CDCl_3$)





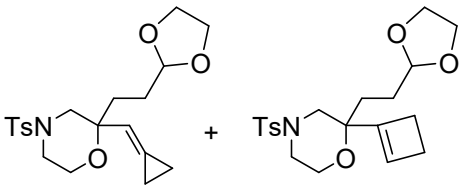
(^{13}C NMR 100 MHz, $CDCl_3$)





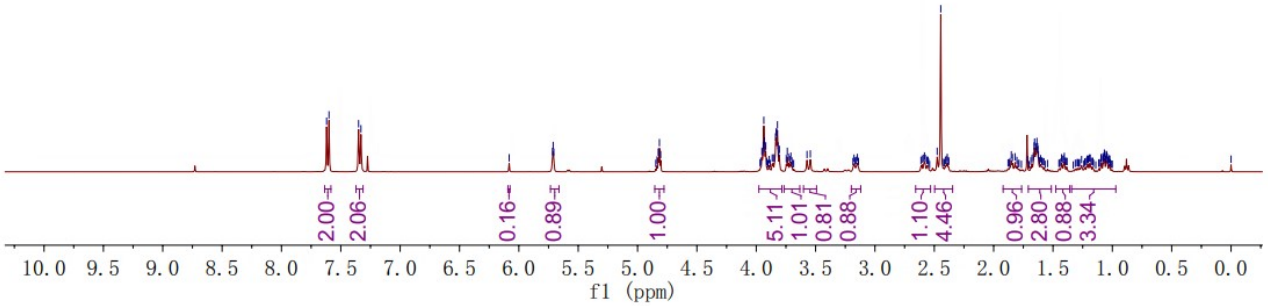
2e, major **2e'**, minor

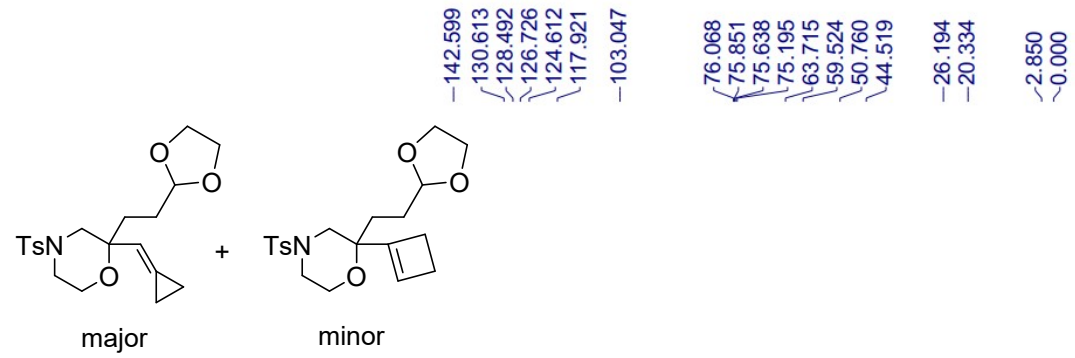
Compound 2e: An inseparable mixture of **2e** and **2e'** in a 5.6:1 ratio determined by ^{1}H NMR analysis; Yield: 58.9 mg, 75%; a yellow oil; Eluent: PE/EA = 10/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.71 (s, 1H), 4.84 – 4.80 (m, 1H), 3.98 – 3.78 (m, 5H), 3.74 – 3.68 (m, 1H), 3.56 (d, *J* = 11.1 Hz, 1H), 3.18 – 3.16 (m, 1H), 2.61 – 2.54 (m, 1H), 2.50 – 2.35 (m, 4H), 1.92 – 1.76 (m, 1H), 1.71 – 1.51 (m, 3H), 1.45 – 1.38 (m, 1H), 1.34 – 0.97 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 130.6, 128.5, 126.7, 124.6, 117.9, 103.0, 75.2, 63.7, 59.5, 50.8, 44.5, 26.2, 20.3, 2.8, 0.0; IR (neat): ν 2962, 2917, 2883, 2250, 1602, 1451, 1349, 1088,1035, 978, 948, 908, 816, 729, 659 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{27}NO_5NaS$ $[M+Na]^+$: 416.15021, found: 416.15041.



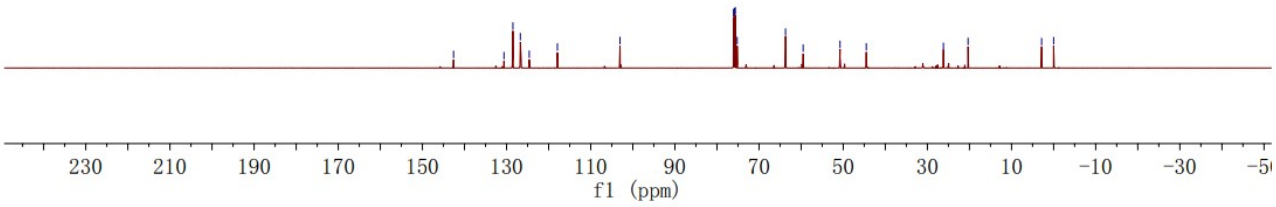
major minor

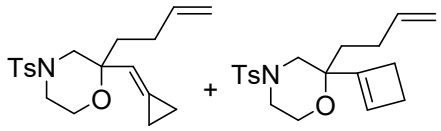
(^{1}H NMR 400 MHz, $CDCl_3$)





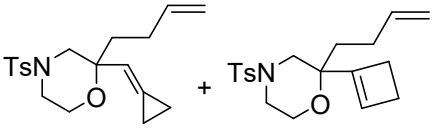
(^{13}C NMR 100 MHz, $CDCl_3$)





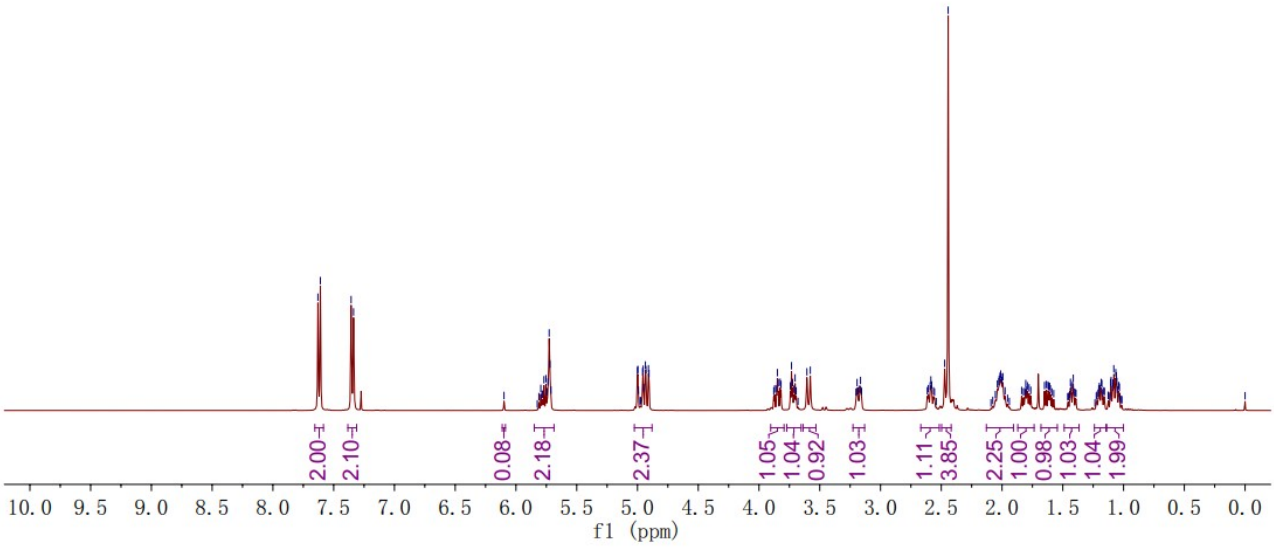
2f, major **2f'**, minor

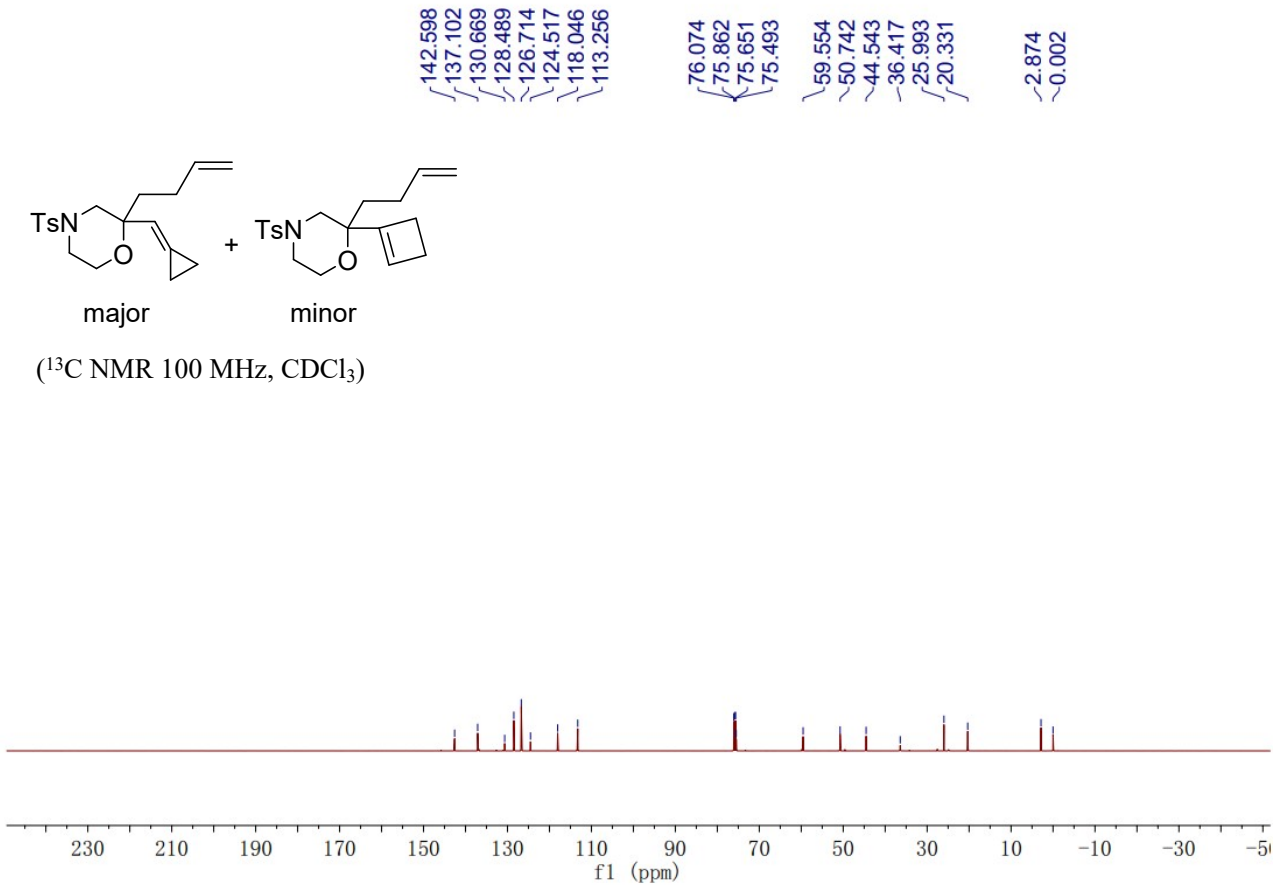
Compound 2f: An inseparable mixture of **2f** and **2f'** in a 11:1 ratio determined by ^{1}H NMR analysis**;** Yield: 52.7 mg, 76%; a yellow oil; Eluent: PE/EA = 10/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 5.85 – 5.69 (m, 2H), 5.03 – 4.88 (m, 2H), 3.87 – 3.81 (m, 1H), 3.74 – 3.67 (m, 1H), 3.59 (d, *J* = 11.2 Hz, 1H), 3.20 – 3.15 (m, 1H), 2.61 – 2.54 (m, 1H), 2.47 – 2.44 (m, 4H), 2.13 – 1.91 (m, 2H), 1.83 – 1.76 (m, 1H), 1.65 – 1.57 (m, 1H), 1.46 – 1.39 (m, 1H), 1.24 – 1.16 (m, 1H), 1.14 – 1.00 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 137.1, 130.7, 128.5, 126.7, 124.5, 118.0, 113.3, 75.5, 59.6, 50.7, 44.5, 36.4, 26.0, 20.3, 2.9, 0.0; IR (neat): ν 2982, 2917, 2839, 1597, 1454, 1348, 1165, 1088, 978, 908, 815, 750, 733, 665 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{19}H_{25}NO_3NaS$ $[M+Na]^+$: 370.14474, found: 370.14562.



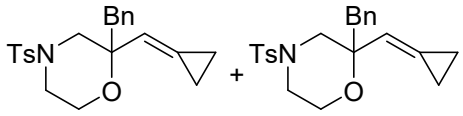
major minor

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



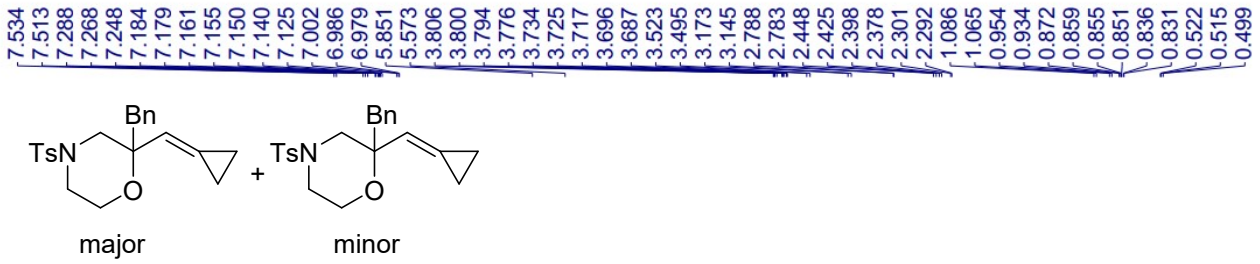


(^{13}C NMR 100 MHz, $CDCl_3$)

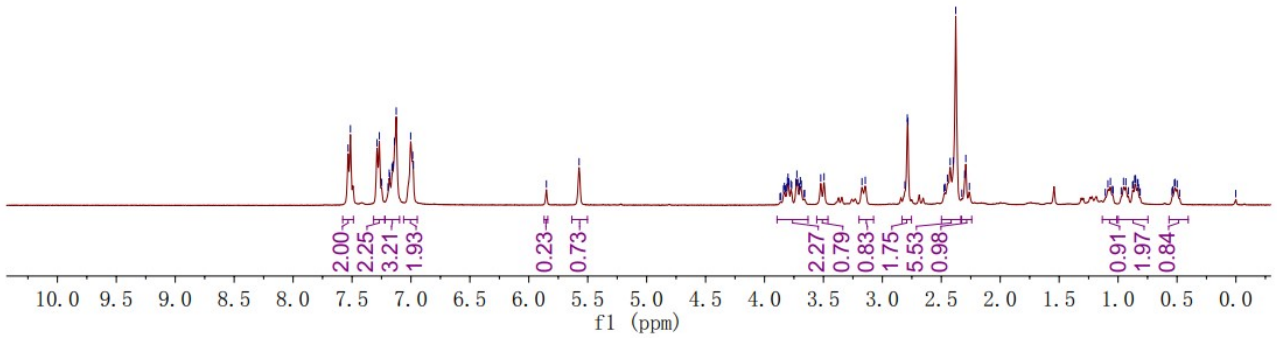


2g, major **2g'**, minor

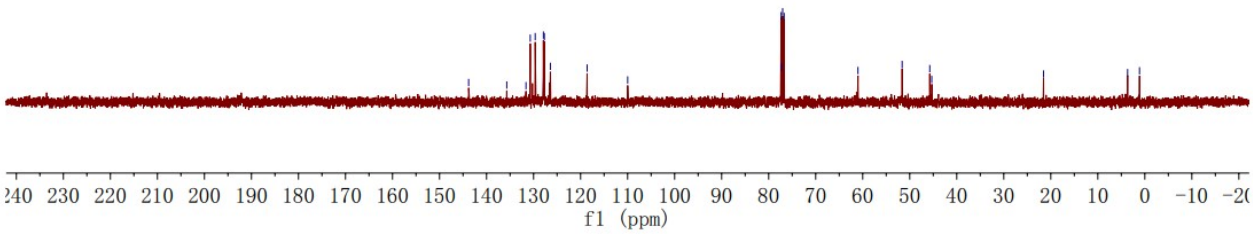
Compound 2g: An inseparable mixture of **2g** and **2g'** in a 3.2:1 ratio determined by ^{1}H NMR analysis**;** Yield: 23.0 mg, 30%; a yellow oil; Eluent: PE/EA = 10/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.22 – 7.10 (m, 3H), 7.00 – 6.98 (m, 2H), 5.57 (s, 1H), 3.89 – 3.63 (m, 2H), 3.51 (d, *J* = 11.2 Hz, 1H), 3.16 (d, *J* = 11.2 Hz, 1H), 2.83 – 2.75 (m, 2H), 2.48 – 2.38 (m, 4H), 2.33 – 2.24 (m, 1H), 1.11 – 1.04 (m, 1H), 1.00 – 0.75 (m, 2H), 0.54 – 0.48 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 135.7, 131.6, 130.7, 129.7, 127.9, 127.7, 126.4, 118.6, 110.0, 77.3, 61.0, 51.6, 45.7, 45.3, 21.5, 3.7, 1.1; IR (neat): ν 2912, 1583, 1457, 1366, 1322, 1215, 1191, 1088,1067, 981, 965, 830, 781 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{22}H_{26}NO_3S$ $[M+H]^+$: 384.1634, found: 384.1634.

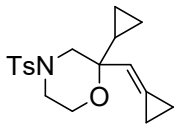


(^{1}H NMR 400 MHz, $CDCl_3$)

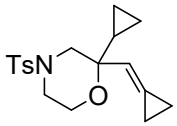


(^{13}C NMR 100 MHz, $CDCl_3$)

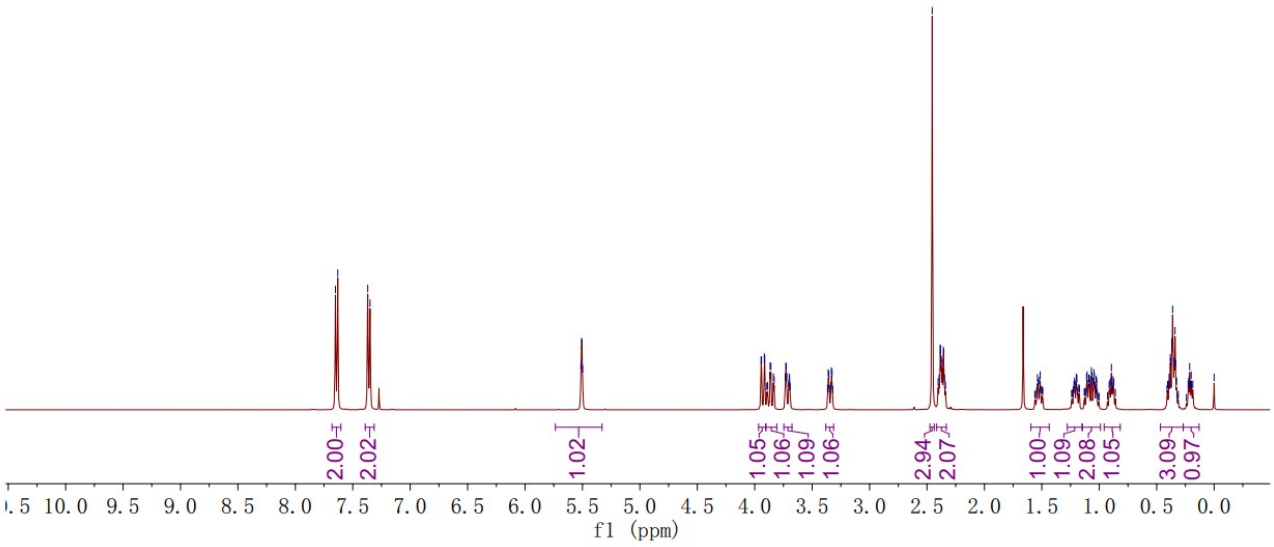


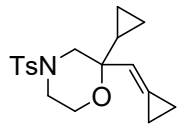


Compound 2h: Yield: 49.3 mg, 74%; A colorless solid; Mp: 143 – 145 ℃; Eluent: PE/EA = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS)δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 5.51 (s, 1H), 3.94 – 3.91 (m, 1H), 3.89 – 3.83 (m, 1H), 3.73 – 3.69 (m, 1H), 3.36 – 3.32 (m, 1H), 2.45 (s, 3H), 2.42 – 2.33 (m, 2H), 1.56 – 1.49 (m, 1H), 1.24 – 1.17 (m, 1H), 1.15 – 0.99 (m, 2H), 0.92 – 0.85 (m, 1H), 0.47 – 0.27 (m, 3H), 0.24 – 0.18 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 131.8, 129.6, 127.9, 127.3, 116.5, 61.0, 52.3, 45.7, 21.5, 18.6, 4.2, 1.3, 0.0, - 0.1; IR (neat): ν 2973, 2892, 2836, 1442, 1351, 1342, 1163, 1083,1046, 979, 957, 880, 744, 654 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{18}H_{23}NO_3NaS$ $[M+Na]^+$: 356.12909, found: 356.12932.

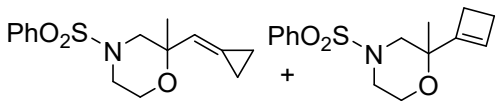


(^{1}H NMR 400 MHz, $CDCl_3$)



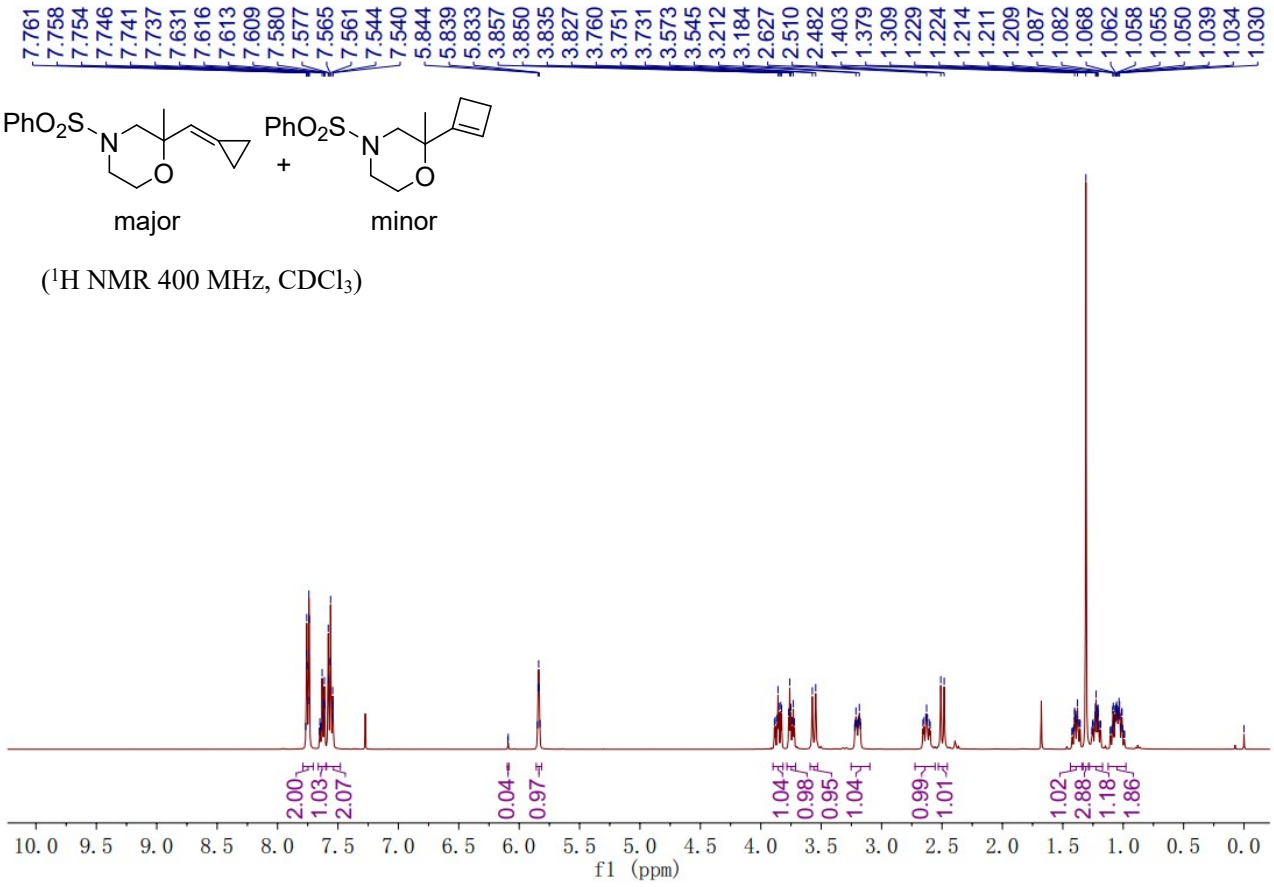


(^{13}C NMR 100 MHz, $CDCl_3$)

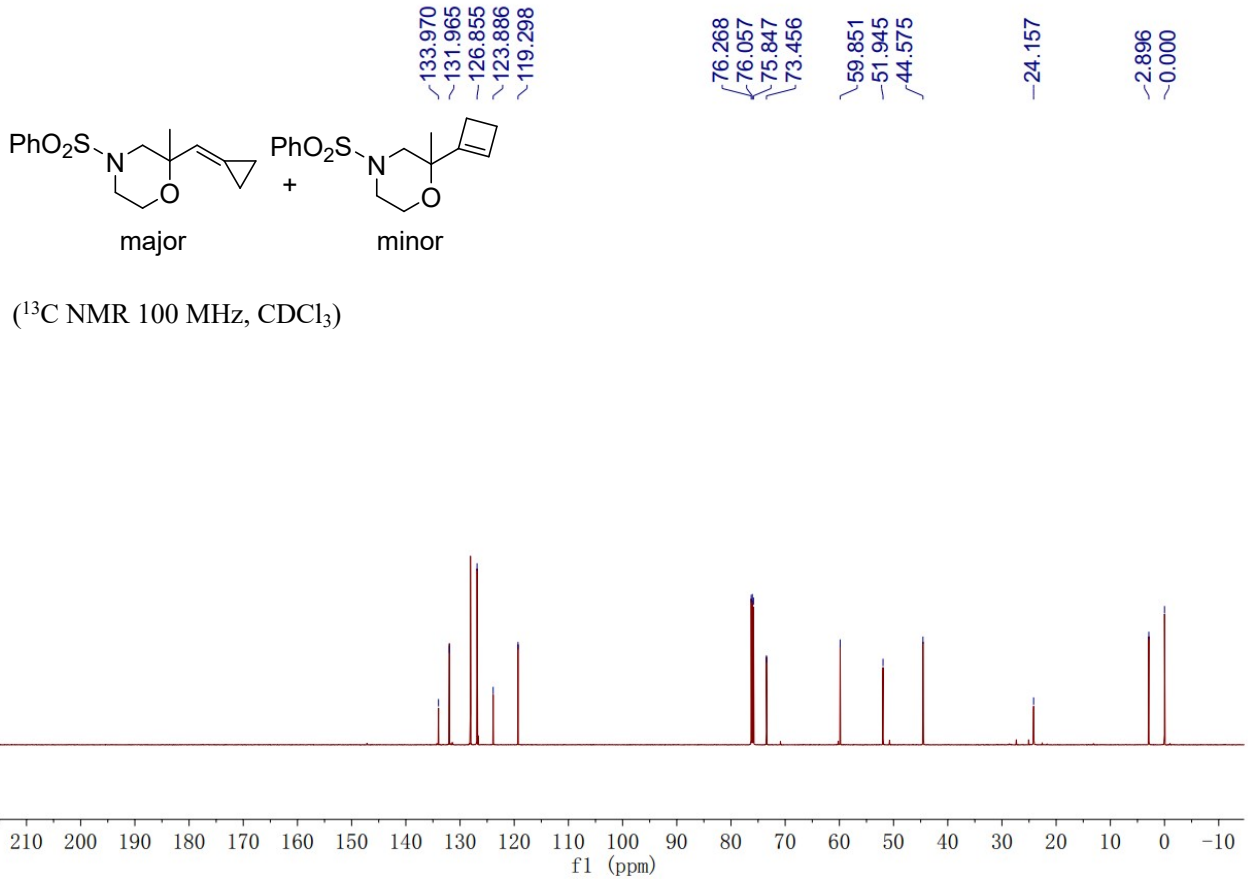


2i, major **2i'**, minor

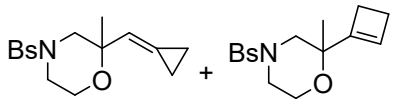
Compound 2i: An inseparable mixture of **2i** and **2i'** in a 32:1 ratio determined by ^{1}H NMR analysis**;** Yield: 57.4 mg, 98%; a yellow oil; Eluent: PE/EA = 10/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.79 – 7.70 (m, 2H), 7.66 – 7.60 (m, 1H), 7.58 – 7.54 (m, 2H), 5.84 (s, 1H), 3.88 – 3.82 (m, 1H), 3.77 – 3.72 (m, 1H), 3.56 (d, *J* = 11.2 Hz, 1H), 3.25 – 3.10 (m, 1H), 2.65 – 2.59 (m, 1H), 2.50 (d, *J* = 11.2 Hz, 1H), 1.44 – 1.34 (m, 1H), 1.31 (s, 3H), 1.28 – 1.17 (m, 2H), 1.10 – 0.99 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.0, 132.0, 128.1, 126.9, 123.9, 119.3, 73.5, 59.9, 51.9, 44.6, 24.2, 2.9, 0.0; IR (neat): ν 2971, 2842, 2359, 1446, 1342, 1309, 1280, 1168,1129, 1081, 1013, 979, 921, 775, 751, 709, 689 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{15}H_{19}NO_3NaS$ $[M+Na]^+$: 316.09779, found: 316.09880.



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

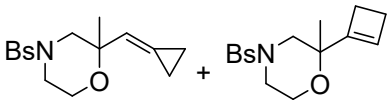


(^{13}C NMR 100 MHz, $CDCl_3$)



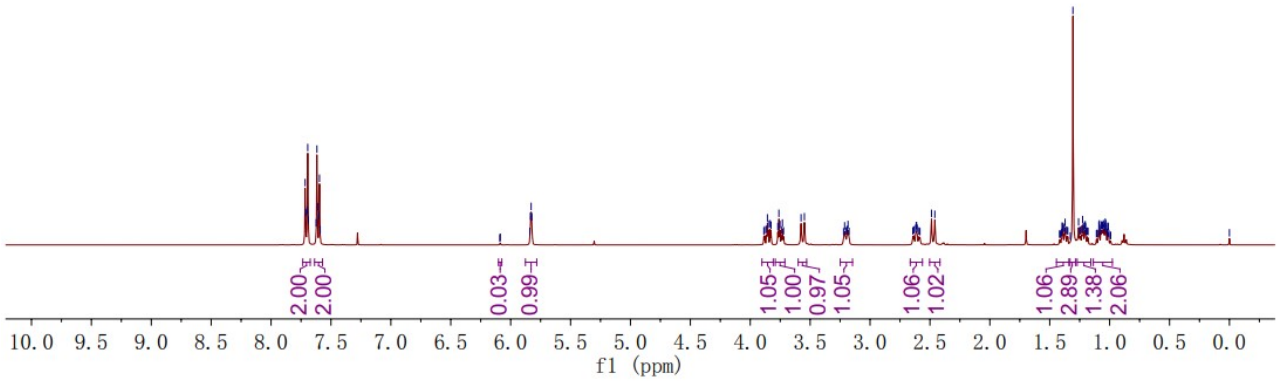
2j, major **2j'**, minor

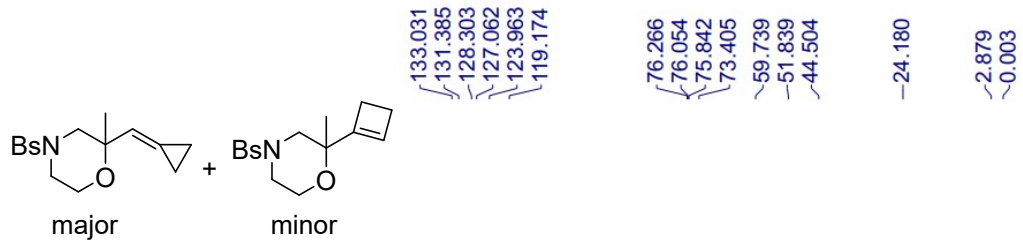
Compound 2j: An inseparable mixture of **2j** and **2j'** in a 33:1 ratio determined by ^{1}H NMR analysis**;** Yield: 64.6 mg, 87%; a yellow oil; Eluent: PE/EA = 10/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.74 – 7.67 (m, 2H), 7.64 – 7.57 (m, 2H), 5.83 (s, 1H), 3.88 – 3.82 (m, 1H), 3.77 – 3.72 (m, 1H), 3.56 (d, *J* = 11.2 Hz, 1H), 3.22 – 3.17 (m, 1H), 2.66 – 2.56 (m, 1H), 2.47 (d, *J* = 11.2 Hz, 1H), 1.44 – 1.33 (m, 1H), 1.31 (s, 3H), 1.27 – 1.16 (m, 1H), 1.11 – 0.99 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.0, 131.4, 128.3, 127.1, 124.0, 119.2, 73.4, 59.7, 51.8, 44.5, 24.2, 2.9, 0.0; IR (neat): ν 2968, 2917, 1573, 1452, 1354, 1165, 1126, 1015, 978, 948, 925, 810, 706 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{15}H_{18}NO_3NaSBr$ $[M+Na]^+$: 394.00830, found: 394.00916.



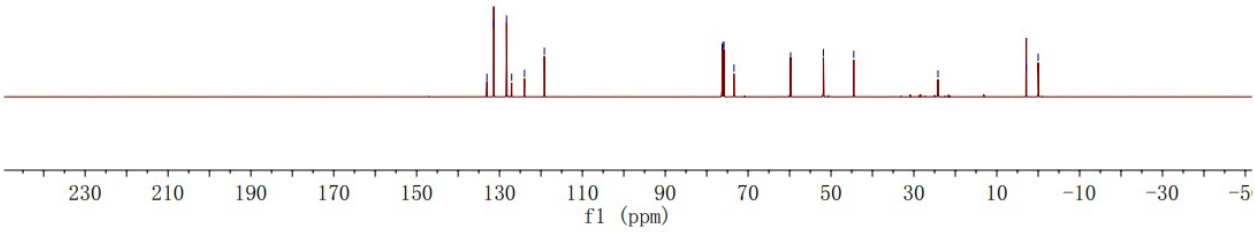
major minor

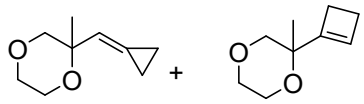
(^{1}H NMR 400 MHz, $CDCl_3$)





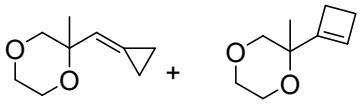
(^{13}C NMR 100 MHz, $CDCl_3$)





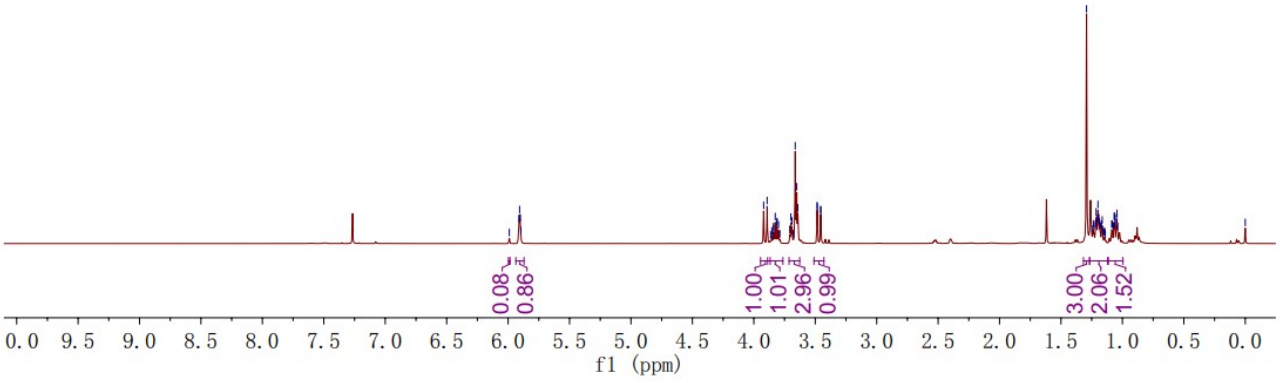
2k, major **2k'**, minor

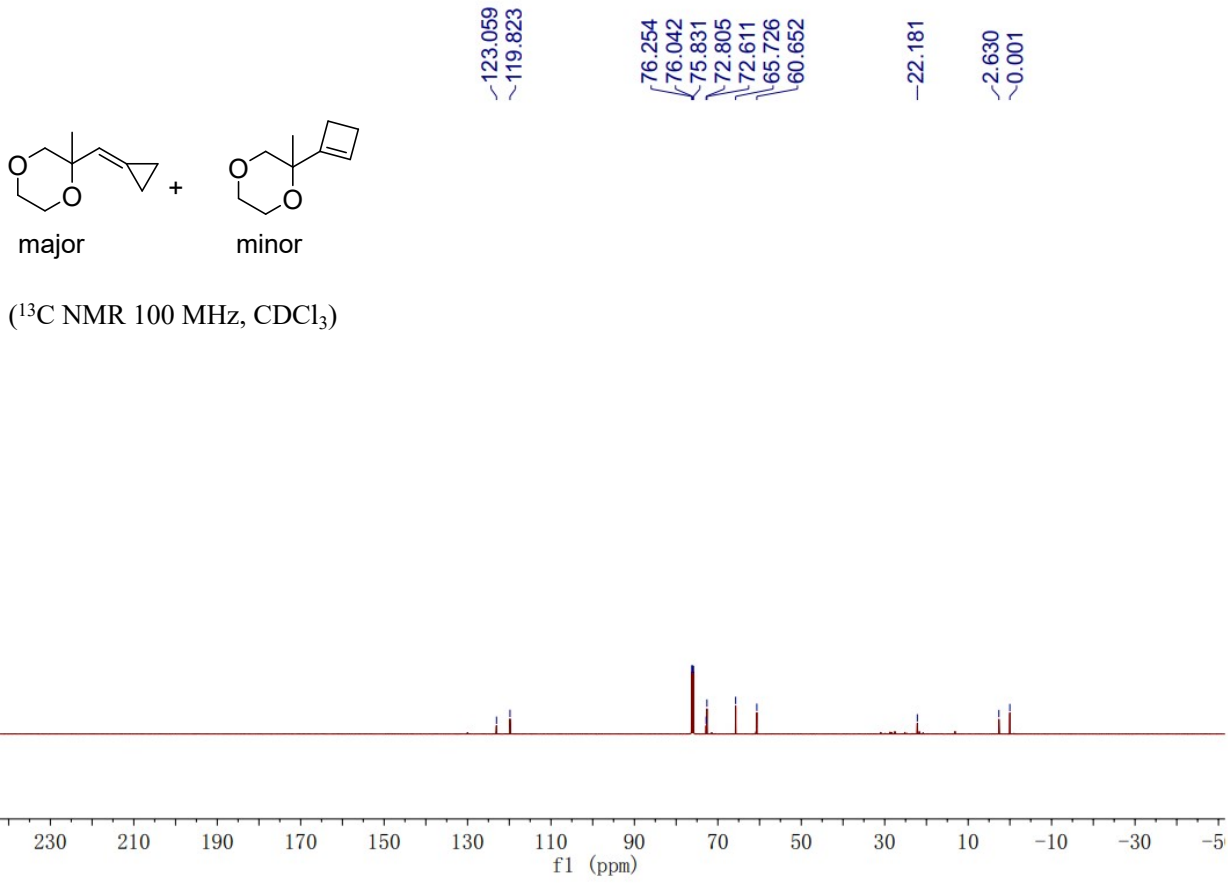
Compound 2k: An inseparable mixture of **2k** and **2k'** in a 10:1 ratio determined by ^{1}H NMR analysis**;** Yield: 30.5 mg, 99%; a yellow oil; Eluent: PE/EA = 10/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 5.91 (s, 1H), 3.91 (d, *J* = 11.4 Hz, 1H), 3.88 – 3.82 (m, 1H), 3.71 – 3.63 (m, 3H), 3.51 – 3.43 (m, 1H), 1.29 (s, 3H), 1.27 – 1.11 (m, 2H), 1.12 – 1.00 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 123.1, 119.8, 72.8, 72.6, 65.7, 60.7, 22.2, 2.6, 0.0; IR (neat): ν 2955, 1450, 1447, 1221, 1086, 989, 971, 930,780, 753 cm^{-1}; HRMS (FI) Calcd for $C_9H_{14}O_2$: 154.0988, found: 154.0989.



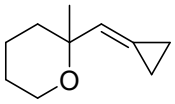
major minor

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

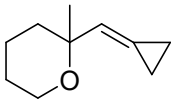




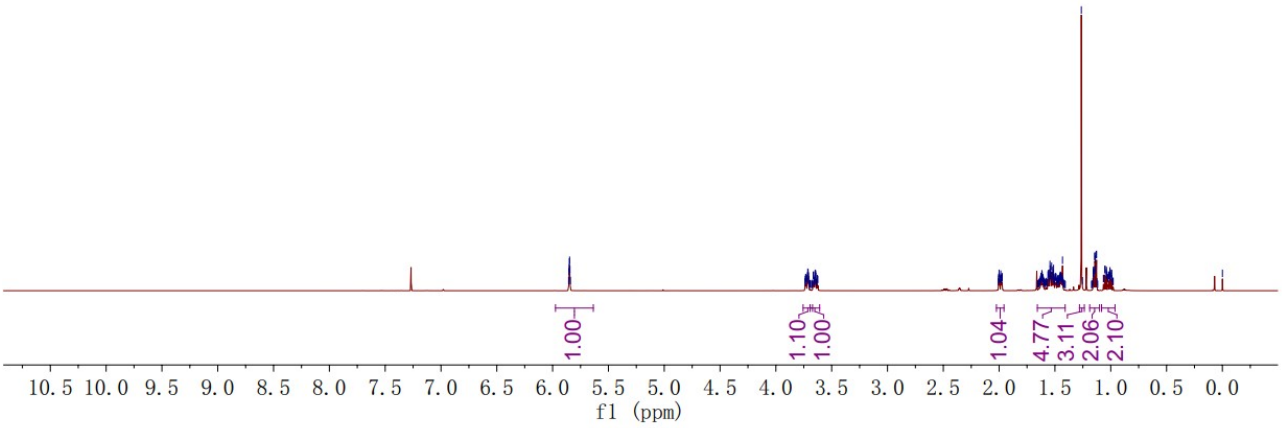
(^{13}C NMR 100 MHz, $CDCl_3$)

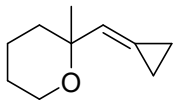


Compound 2l: Yield: 27.4 mg, 90%; a yellow oil; Eluent: PE/EA = 10/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 5.86 – 5.84 (m, 1H), 3.74 – 3.69 (m, 1H), 3.68 – 3.62 (m, 1H), 2.02 – 1.96 (m, 1H), 1.66 – 1.41 (m, 5H), 1.26 (s, 3H), 1.19 – 1.10 (m, 2H), 1.08 – 0.96 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 122.7, 120.8, 74.4, 62.2, 33.9, 27.9, 25.0, 19.4, 2.7, 0.0; IR (neat): ν 2932, 1449, 1353, 1208, 1173, 1102, 1086, 1043,962, 938, 924, 812, 751, 734 cm^{-1}; HRMS (FI) Calcd for $C_{10}H_{16}O$: 152.1196, found: 152.1199.

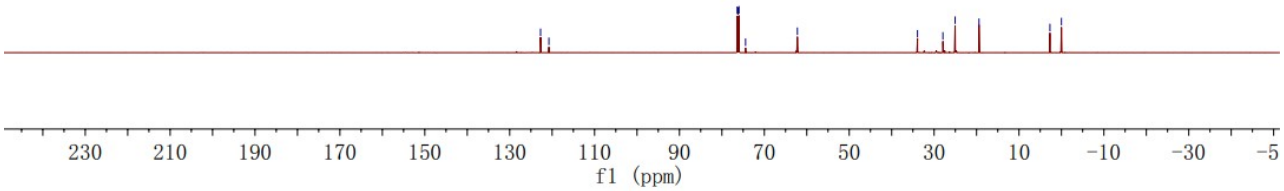


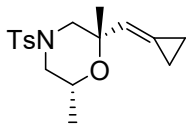
(^{1}H NMR 400 MHz, $CDCl_3$)



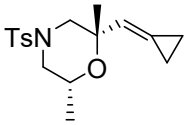


(^{13}C NMR 100 MHz, $CDCl_3$)

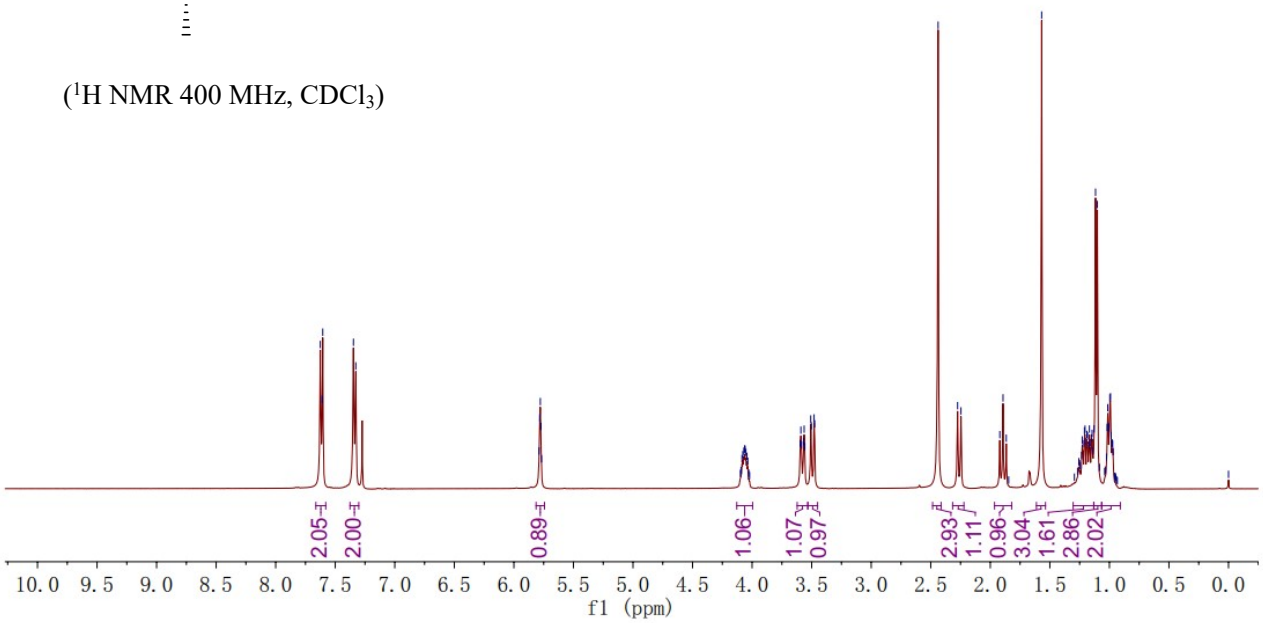


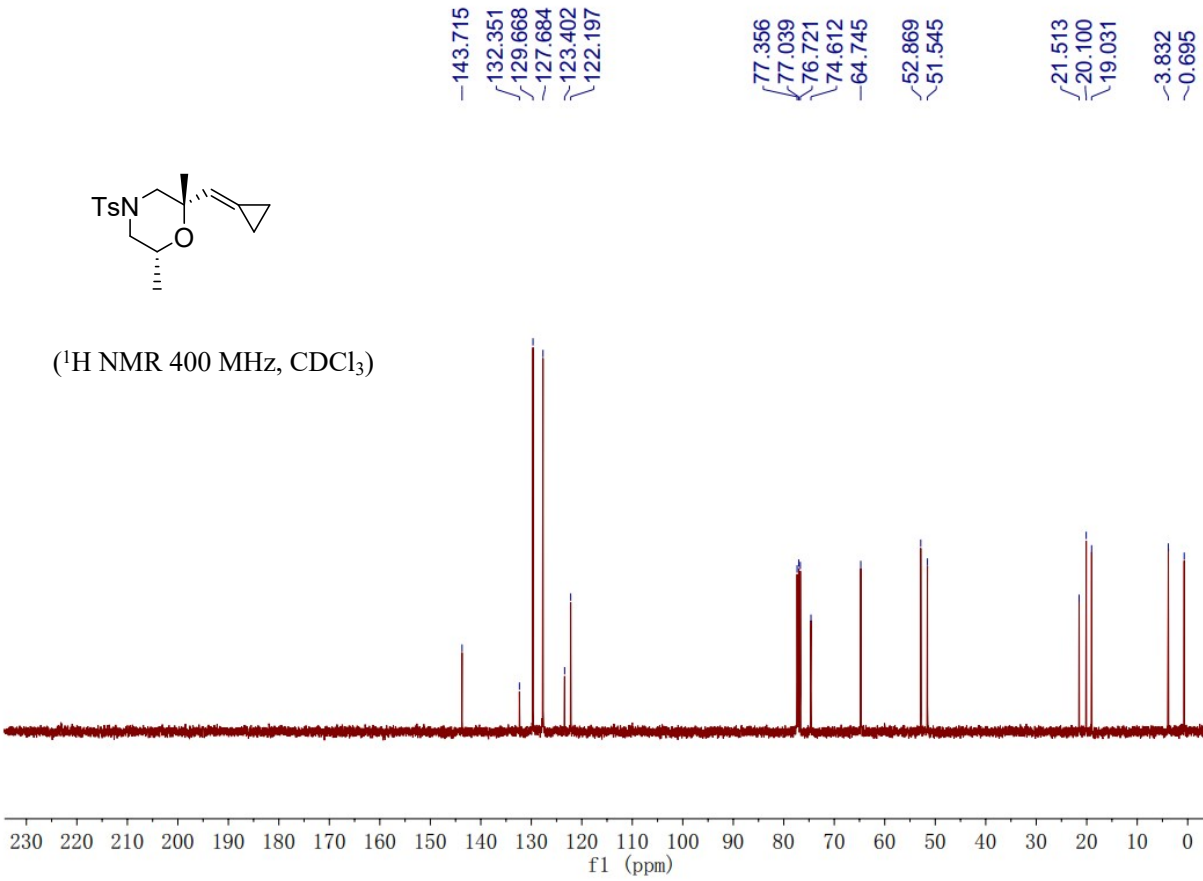


Compound 2m: Yield: 58.8 mg, 92%; a yellow oil; Eluent: PE/EA = 10/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.79 – 5.76 (m, 1H), 4.10 – 4.02 (m, 1H), 3.60 – 3.56 (m, 1H), 3.51 – 3.48 (m, 1H), 2.44 (s, 3H), 2.26 (d, *J* = 11.3 Hz, 1H), 1.89 (t, *J* = 10.8 Hz, 1H), 1.57 (s, 3H), 1.30 – 1.13 (m, 2H), 1.11 (d, *J* = 6.2 Hz, 3H), 1.02 – 0.97 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 132.4, 129.7, 127.7, 123.4, 122.2, 74.6, 64.7, 52.9, 51.5, 21.5, 20.1, 19.0, 3.8, 0.7; IR (neat): ν 2232, 1349, 1313, 1218, 1173, 1102, 1086, 1043,962, 812, 751, 734 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{17}H_{23}NO_3NaS$ $[M+Na]^+$: 344.12909, found: 344.12869.

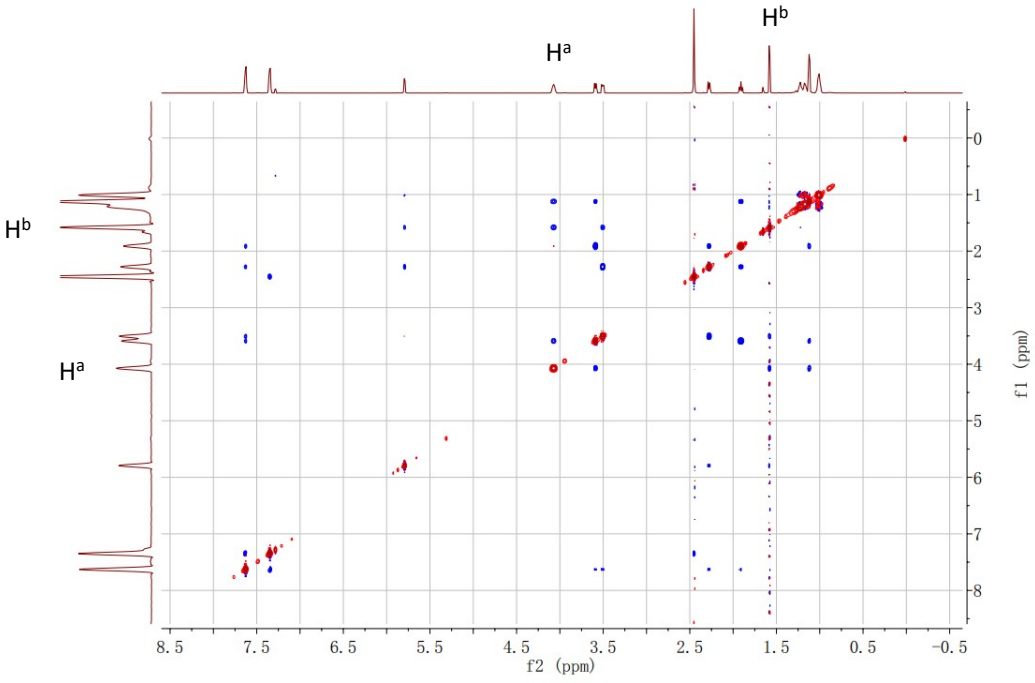


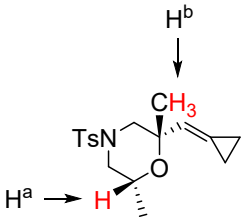
(^{1}H NMR 400 MHz, $CDCl_3$)





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

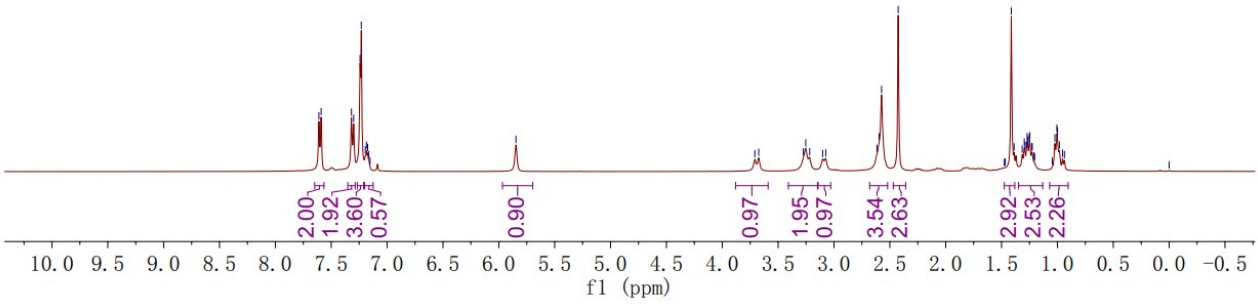


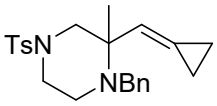


2m-NOESY
(500 MHz, $CDCl_3$)

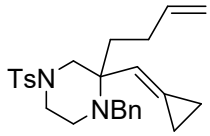
Compound 2n: Yield: 61.0 mg, 77%; a yellow oil; Eluent: PE/EA = 10/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.60 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.24 – 7.23 (m, 4H), 7.19 – 7.15 (m, 1H), 5.85 (s, 1H), 3.69 (d, *J* = 13.8 Hz, 1H), 3.27 – 3.21 (m, 2H), 3.09 (d, *J* = 10.9 Hz, 1H), 2.61 – 2.57 (m, 4H), 2.43 (s, 3H), 1.41 (s, 3H), 1.32 – 1.20 (m, 2H), 1.07 – 0.90 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 139.8, 132.5, 129.6, 128.4, 128.1, 127.8, 126.8, 124.7, 122.0, 59.1, 56.5, 54.3, 46.8, 44.9, 21.5, 4.4, 0.8; IR (neat): ν 2967, 2847, 2243, 1698, 14593, 1365, 1167, 1102,1021, 987, 825, 734, 629, 559, 543 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{23}H_{29}N_2O_2S$ $[M+H]^+$: 397.1949, found: 397.1949.

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

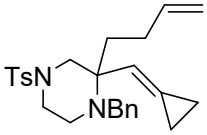




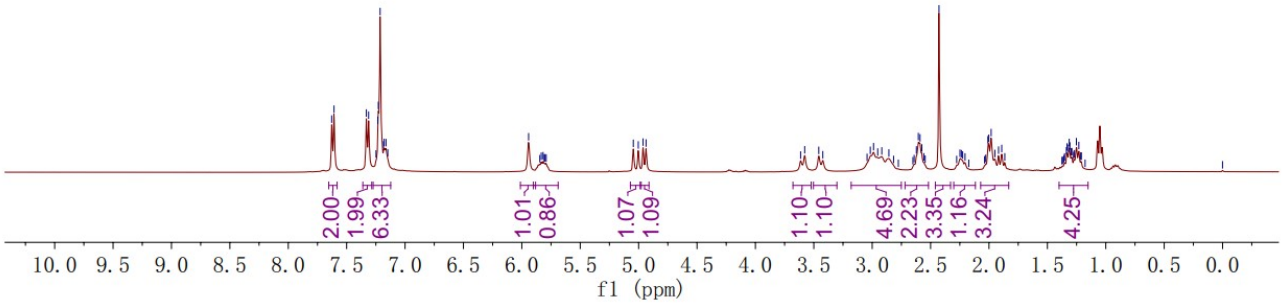
(^{13}C NMR 100 MHz, $CDCl_3$)

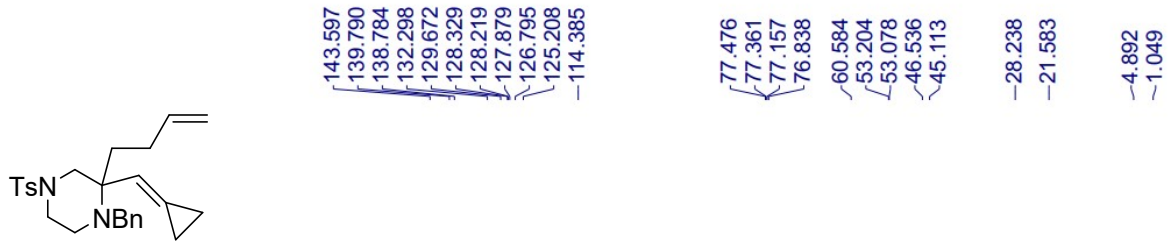


Compound 2o: Yield: 74.1 mg, 85%; a yellow oil; Eluent: PE/EA = 10/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.62 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1Hz, 2H), 7.27 – 7.12 (m, 5H), 5.94 (s, 1H), 5.85 – 5.79 (m, 1H), 5.02 (d, *J* = 17.0 Hz, 1H), 4.95 (d, *J* = 10.2 Hz, 1H), 3.60 (d, *J* = 14.0 Hz, 1H), 3.44 (d, *J* = 14.0 Hz, 1H), 3.04 – 2.78 (m, 4H), 2.65 – 2.55 (m, 2H), 2.43 (s, 3H), 2.30 – 2.12 (m, 1H), 2.07 – 1.83 (m, 3H), 1.40 – 1.15 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 139.8, 138.8, 132.3, 129.7, 128.3, 128.2, 127.9, 126.8, 125.2, 114.4, 77.4, 60.6, 53.2, 53.1, 46.5, 45.1, 28.2, 21.6, 4.9, 1.0; IR (neat): ν 2956, 1727, 1602, 1492, 1448, 1271, 1121, 1070,1001, 962, 910, 815, 768, 729, 661, 522 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{26}H_{33}N_2O_2S$ $[M+H]^+$: 437.22573, found: 437.22585.

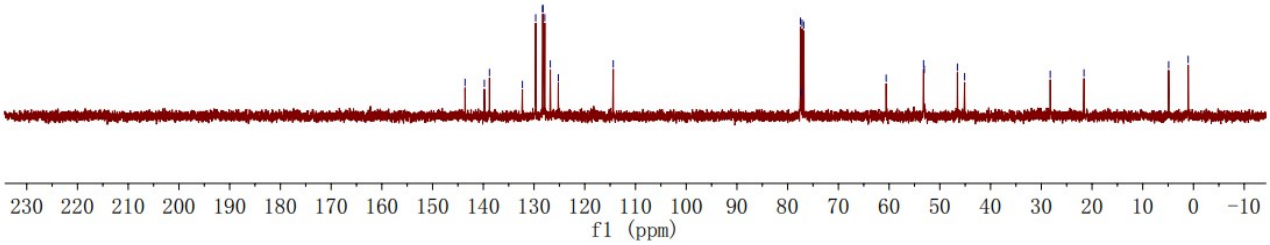


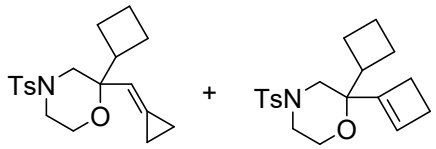
(^{1}H NMR 400 MHz, $CDCl_3$)





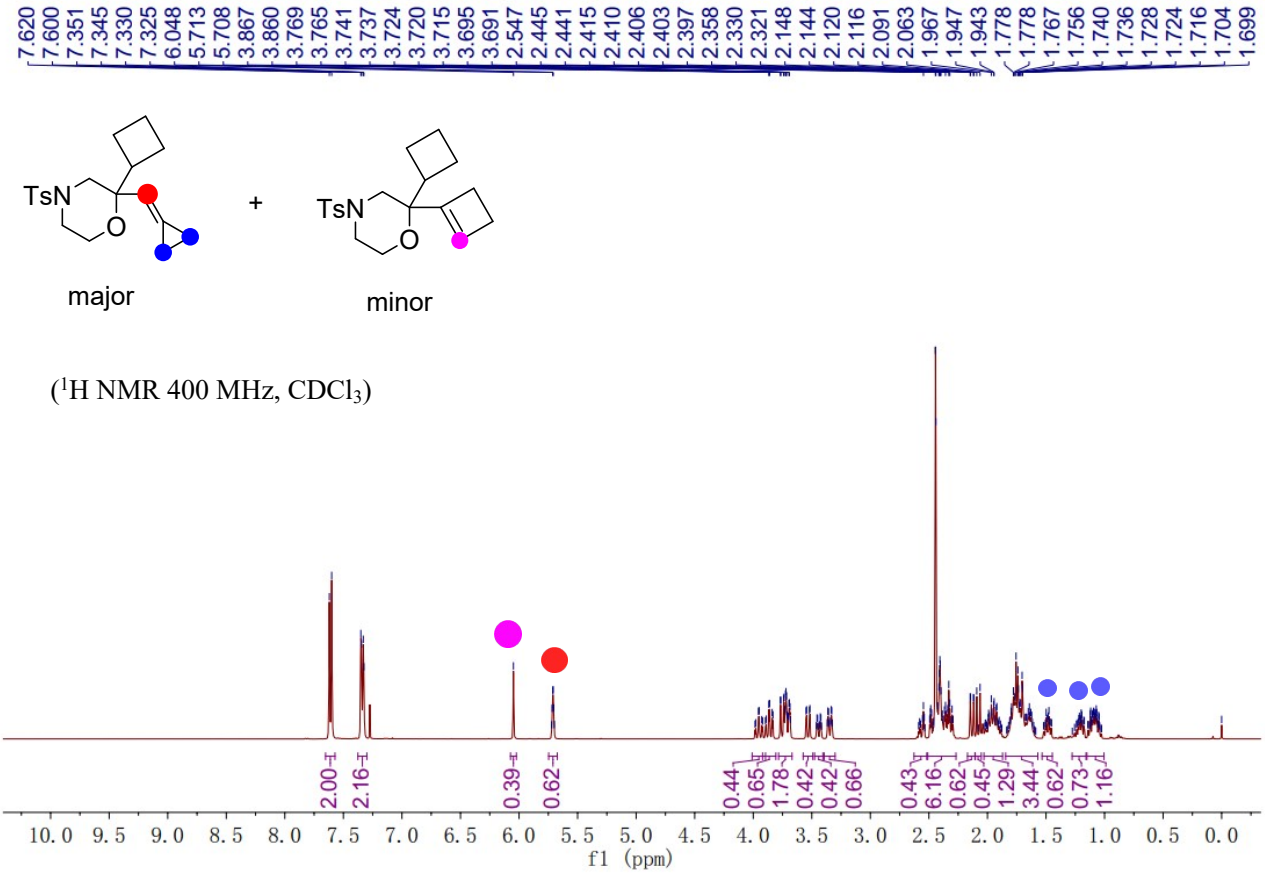
(^{13}C NMR 100 MHz, $CDCl_3$)

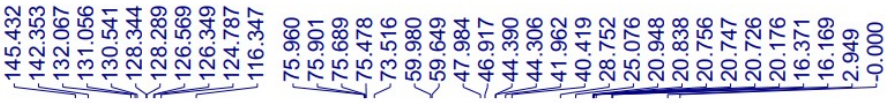


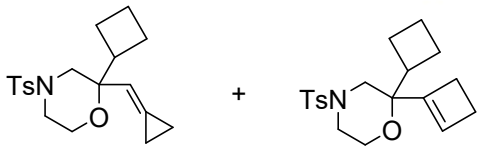


2p, major **2p'**, minor

Compound 2p: An inseparable mixture of **2p** and **2p'** in a 1.6:1 ratio determined by ^{1}H NMR analysis; Yield: 52.7 mg, 76%; a yellow oil; Eluent: PE/EA = 10/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.33 (m, 2H), 6.05 (s,1H, minor), 5.72 – 5.70 (m, 1H, major), 3.95 (td, *J* = 11.6, 2.8 Hz, 1H, minor), 3.87 (td, *J* = 11.6, 2.8 Hz, 1H, major), 3.77 – 3.68 (m, 3H, major 2H + minor 1H), 3.55 – 3.52 (m, 1H, minor), 3.46 – 3.42 (m, 1H, minor), 3.37 – 3.32 (m, 1H, major), 2.59 – 2.54(m, 1H, minor), 2.49 – 2.29 (m, 8H), 2.15 – 2.12 (m, 1H, major), 2.08 (d, *J* = 11.3 Hz, 1H, minor), 2.05 – 1.89 (m, 2H), 1.82 – 1.61 (m, 5H), 1.52 – 1.45 (m, 1H, major), 1.24 – 1.17 (m, 1H, major), 1.14 – 1.04 (m, 2H, major); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 142.4, 132.1, 131.1, 130.5, 128.3, 128.3, 126.6, 126.3, 124.8, 116.3, 76.0, 75.9, 75.7, 75.5, 73.5, 60.0, 59.6, 48.0, 46.9, 44.4, 44.3, 42.0, 40.4, 28.8, 25.1, 20.9, 20.8, 20.8, 20.7, 20.7, 20.2, 16.4, 16.2, 2.9, 0.0; IR (neat): ν 2912, 1588, 1447, 1346, 1323, 1165, 1091, 1088,1065, 971, 955, 810, 751 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{19}H_{25}NO_3NaS$ $[M+Na]^+$: 370.14474, found: 370.14555.

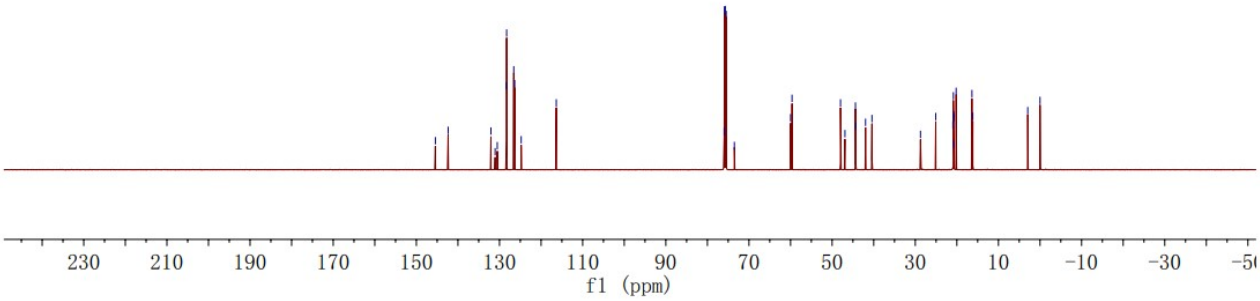


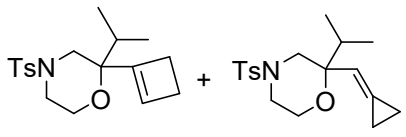




major minor

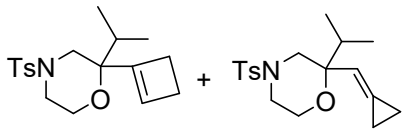
(^{13}C NMR 100 MHz, $CDCl_3$)





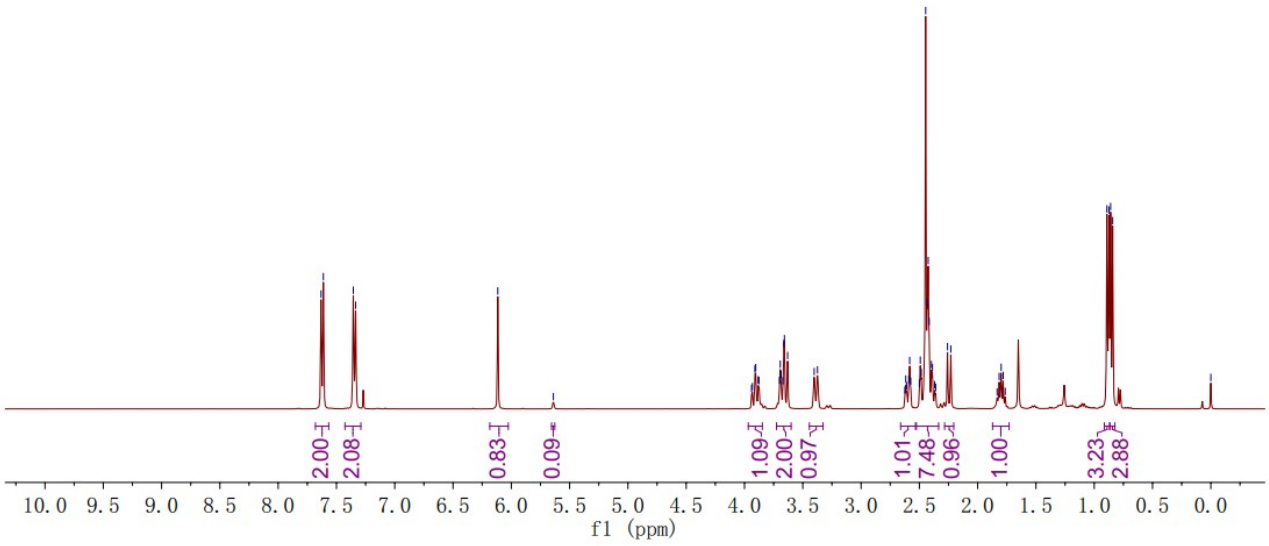
2q, major **2q'**, minor

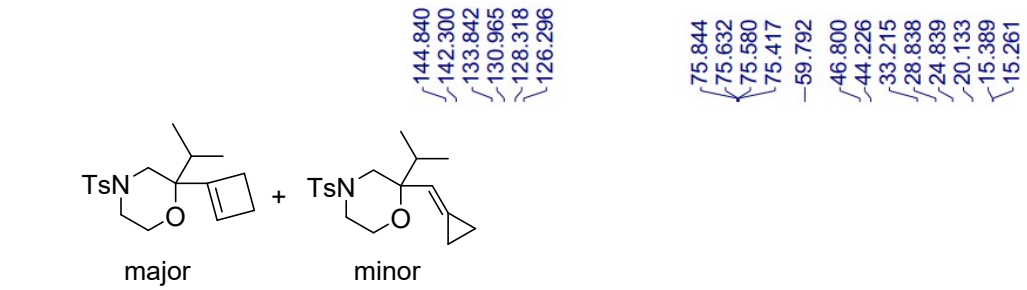
Compound 2q': An inseparable mixture of **2q'** and **2q** in a 9.2:1 ratio determined by ^{1}H NMR analysis**;** Yield: 57.2 mg, 86%; a yellow oil; Eluent: PE/EA = 10/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.62 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 6.12 (s, 1H), 3.93 – 3.87 (m, 1H), 3.72 – 3.60 (m, 2H), 3.39 (d, *J* = 11.3 Hz, 1H), 2.62 – 2.57(m, 1H), 2.51 – 2.35 (m, 6H), 2.24 (d, *J* = 11.3 Hz, 1H), 1.83 – 1.76 (m, 1H), 0.88 (d, *J* = 7.0, 3H), 0.85 (d, *J* = 7.0, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 142.3, 133.8, 131.0, 128.3, 126.3, 75.58, 59.8, 46.8, 44.2, 33.2, 28.8, 24.8, 20.1, 15.4, 15.3; IR (neat): ν 2912, 1588, 1447, 1346, 1323, 1165, 1091, 1088,1065, 971, 955, 810, 751 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{18}H_{25}NO_3NaS$ $[M+Na]^+$: 358.14471, found: 358.1147; Enantiomeric excess was determined by HPLC with a Chiralpak IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 1.0 mL/min; t_{minor} = 11.47 min, t_{major} = 10.13 min; ee% = 72%].



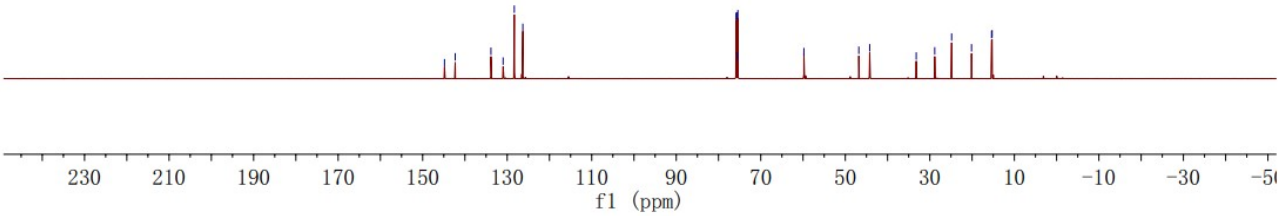
major minor

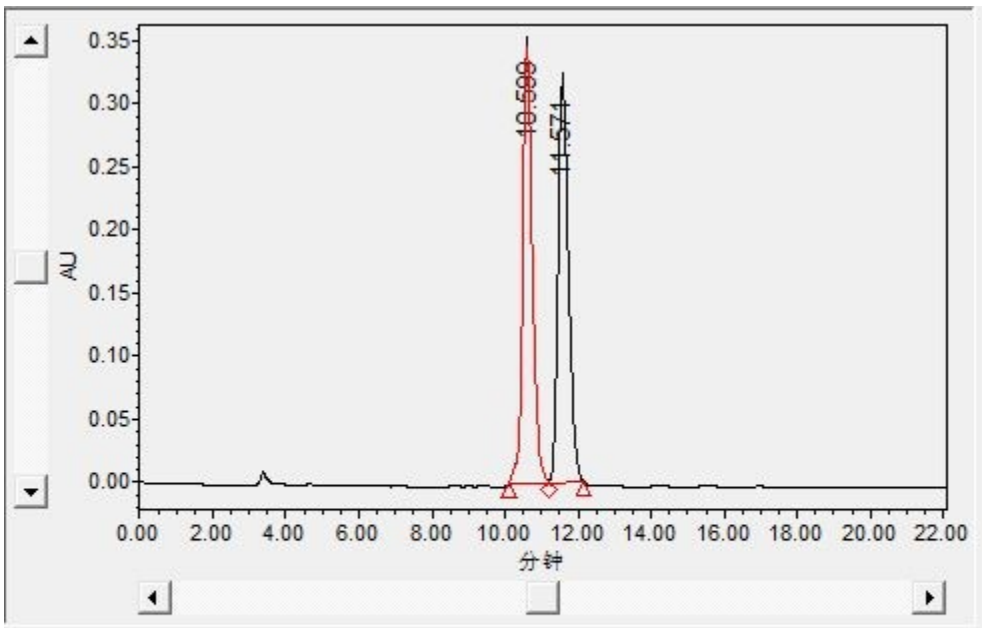
(^{1}H NMR 400 MHz, $CDCl_3$)



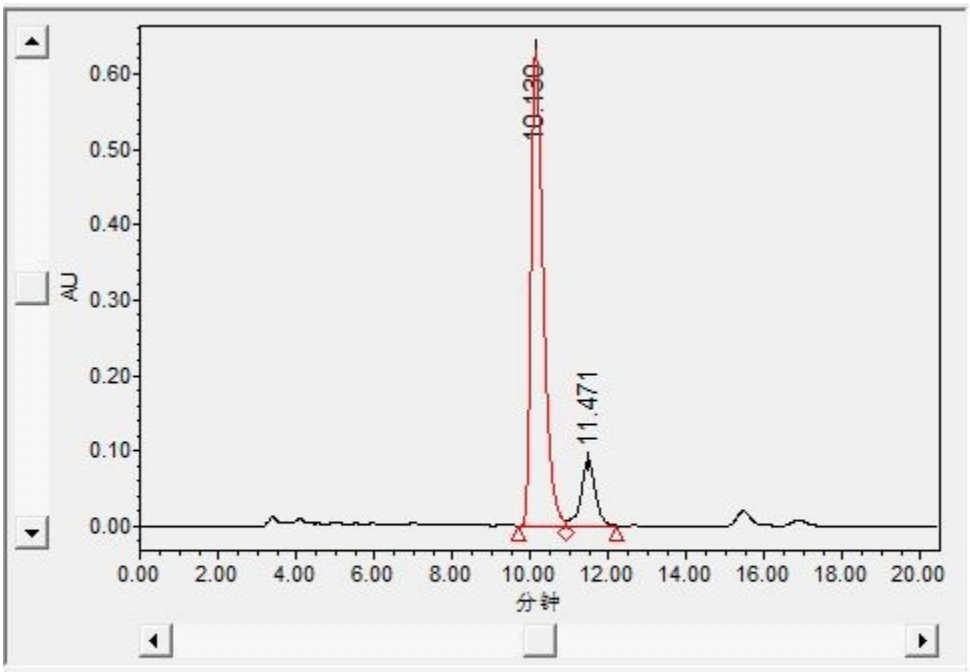


(^{13}C NMR 100 MHz, $CDCl_3$)



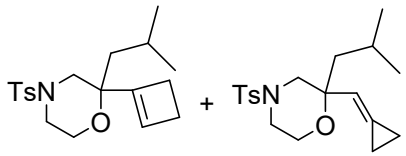


	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码
1		10.599	6347155	49.93	345847	BV			未知	
2		11.571	6363850	50.07	315930	VB			未知	



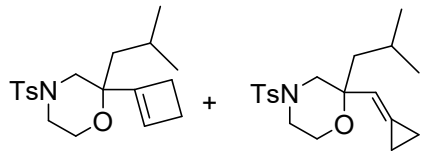
	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码
1		10.130	13443098	86.04	631001	BV			未知	
2		11.471	2181526	13.96	86688	VB			未知	

Translation ： Enantiomeric excess was determined by HPLC with a Chiralpak IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 1.0 mL/min; t_{minor} = 11.47 min, t_{major} = 10.13 min; ee% = 72%].



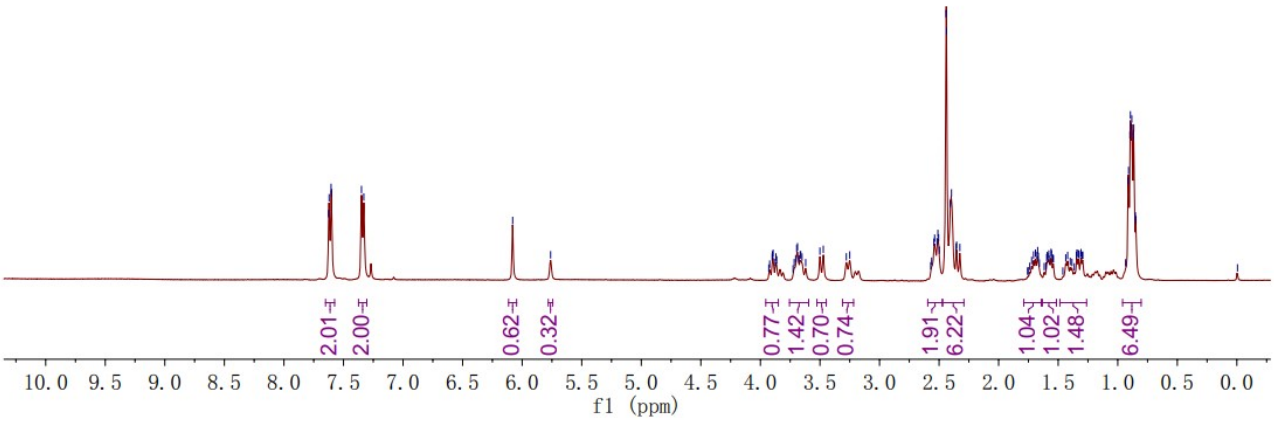
2r', major **2r**, minor

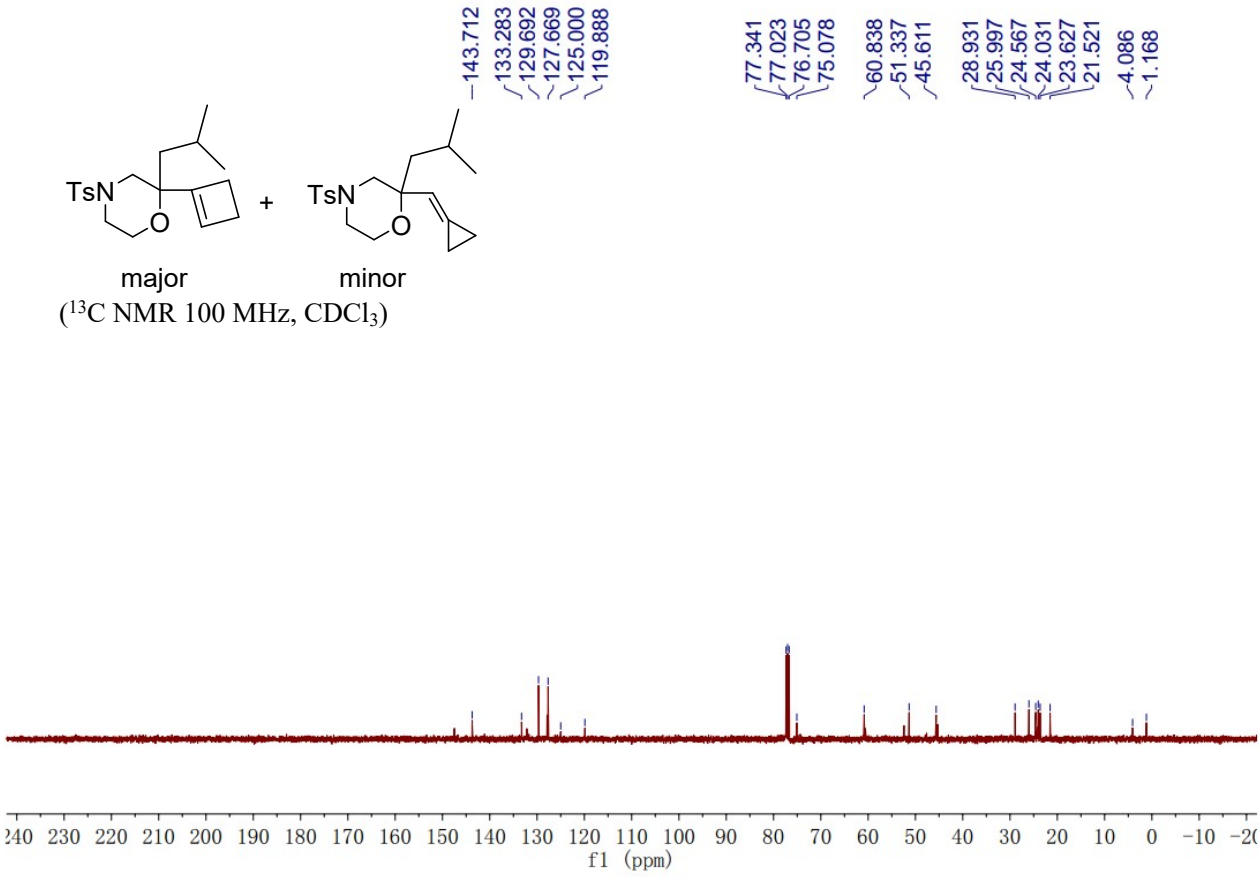
Compound 2r': An inseparable mixture of **2r'** and **2r** in a 2:1 ratio determined by ^{1}H NMR analysis**;** Yield: 47.4 mg, 68%; a yellow oil; Eluent: PE/EA = 10/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.65 – 7.57 (m, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 6.08 (s, 1H), 3.93 – 3.86 (m, 1H), 3.76 – 3.59 (m, 2H), 3.49 (d, *J* = 11.4 Hz, 1H), 3.26 (d, *J* = 11.4 Hz, 1H), 2.57 – 2.50 (m, 2H), 2.44 – 2.33 (m, 6H), 1.76 – 1.66 (m, 1H), 1.62 – 1.54 (m, 1H), 1.46 – 1.29 (m, 1H), 0.93 – 0.85 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 133.3, 129.7, 127.7, 125.0, 119.9, 75.1, 60.8, 51.3, 45.6, 28.9, 26.0, 24.6, 24.0, 23.6, 21.5, 4.1, 1.2; IR (neat): ν 2922, 1568, 1467, 1445, 1345, 1175, 1061, 1057,1032, 971, 945, 820, 771 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{19}H_{27}NO_3NaS$ $[M+Na]^+$: 372.16039, found: 372.16076.



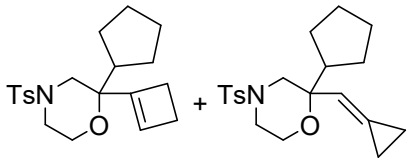
major minor

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



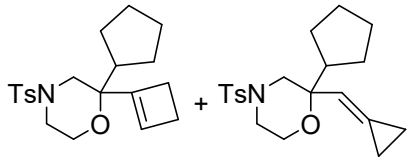


(^{13}C NMR 100 MHz, $CDCl_3$)



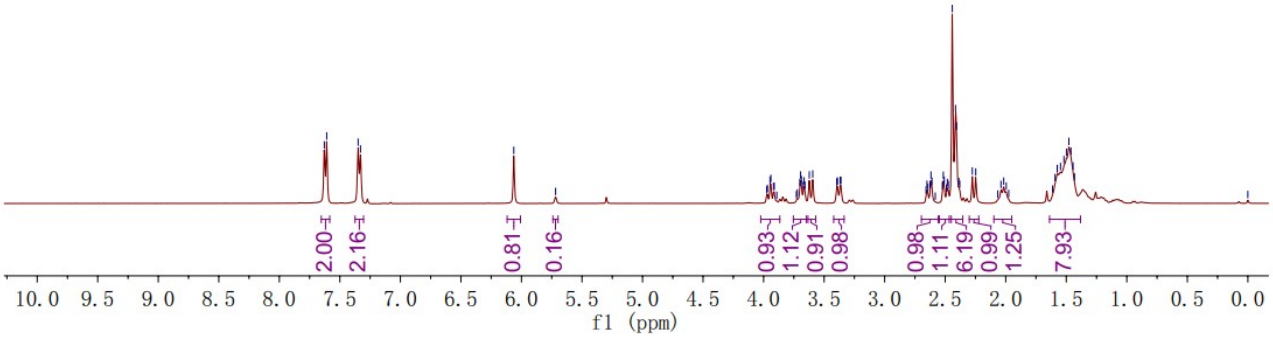
2s', major **2s**, minor

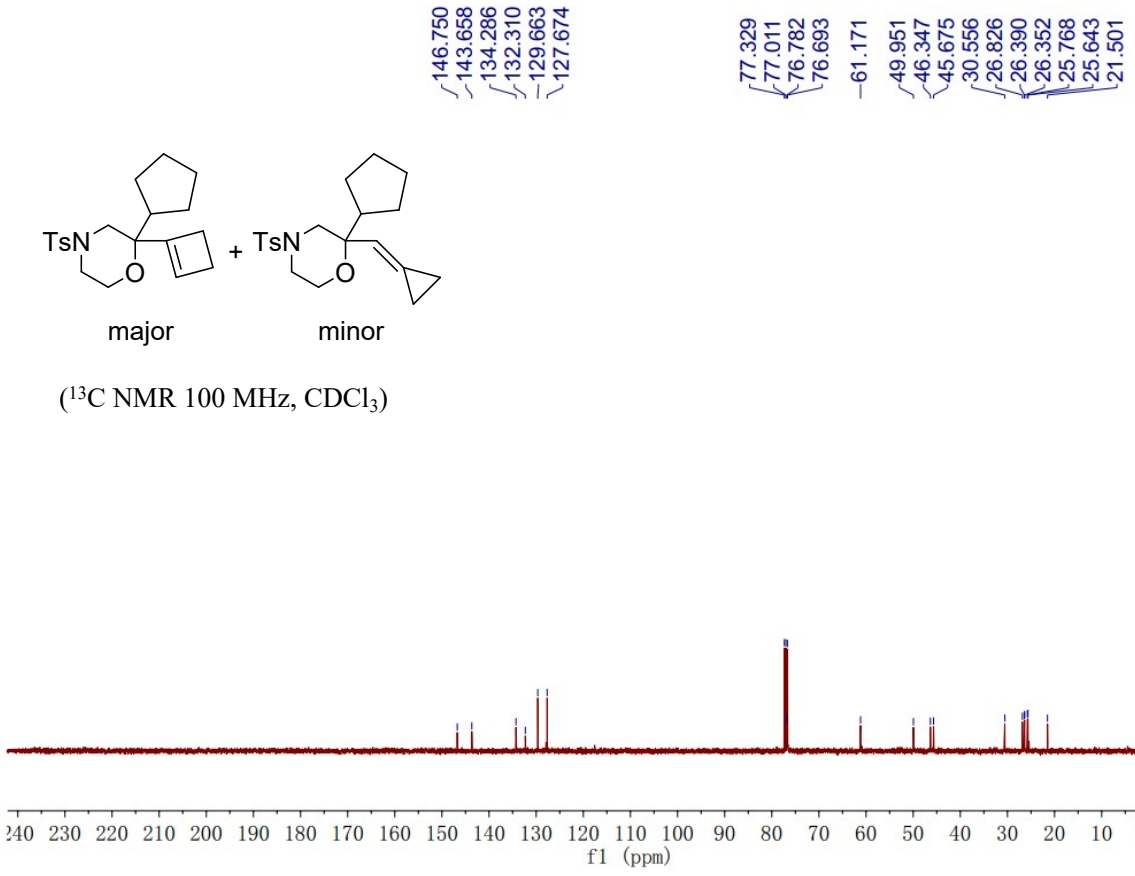
Compound 2s': An inseparable mixture of **2s'** and **2s** in a 5:1 ratio determined by ^{1}H NMR analysis**;** Yield: 52.7 mg, 76%; a yellow oil; Eluent: PE/EA = 10/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.62 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 6.06 (s, 1H), 3.96 – 3.89 (m, 1H), 3.73 – 3.67 (m, 1H), 3.61 (d, *J* = 11.4 Hz, 1H), 3.42 – 3.33 (m, 1H), 2.66 – 2.58 (m, 1H), 2.52 – 2.47 (m, 1H), 2.44 – 2.38 (m, 6H), 2.26 (d, *J* = 11.4 Hz, 1H), 2.07 – 1.98 (m, 1H), 1.64 – 1.38 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 143.7, 134.3, 132.3, 129.7, 127.7, 76.8, 61.2, 50.0, 46.3, 45.7, 30.6, 26.8, 26.39, 26.35, 25.8, 25.6, 21.5.; IR (neat): ν 2961, 2867, 1448, 1338, 1080, 973, 910, 811,751, 751 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{27}NO_3NaS$ $[M+Na]^+$: 384.16039, found: 384.16085.



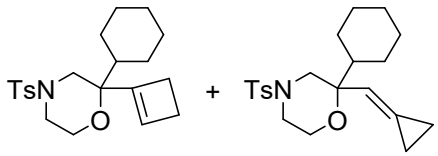
major minor

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



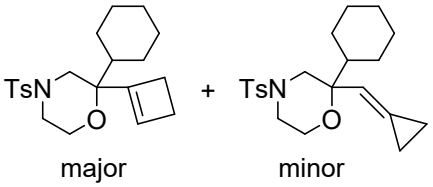


(^{13}C NMR 100 MHz, $CDCl_3$)



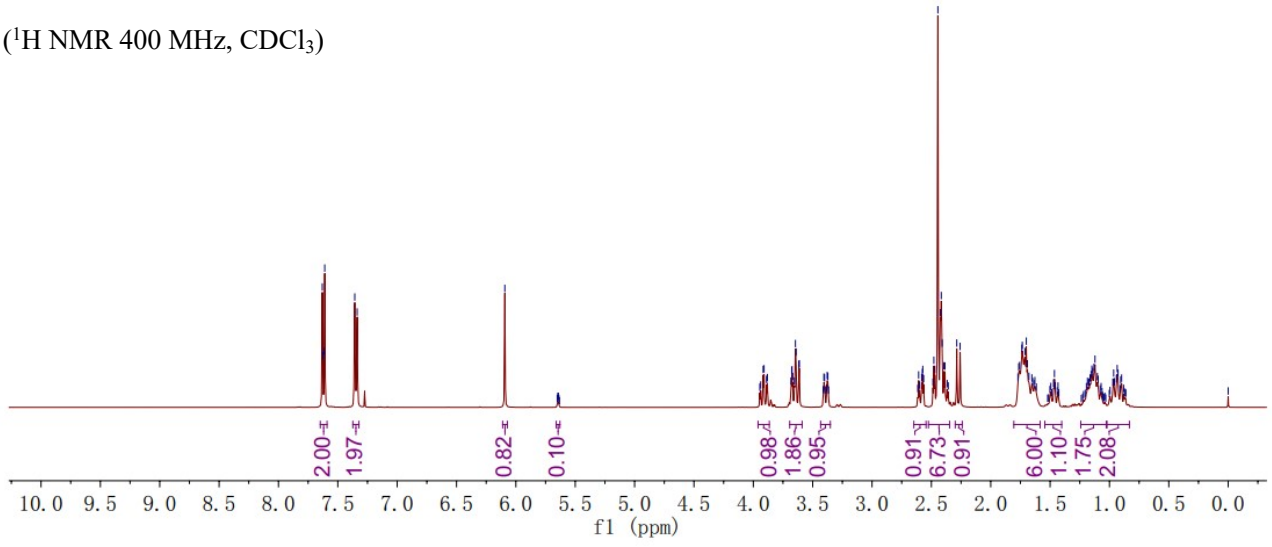
2t', major **2t**, minor

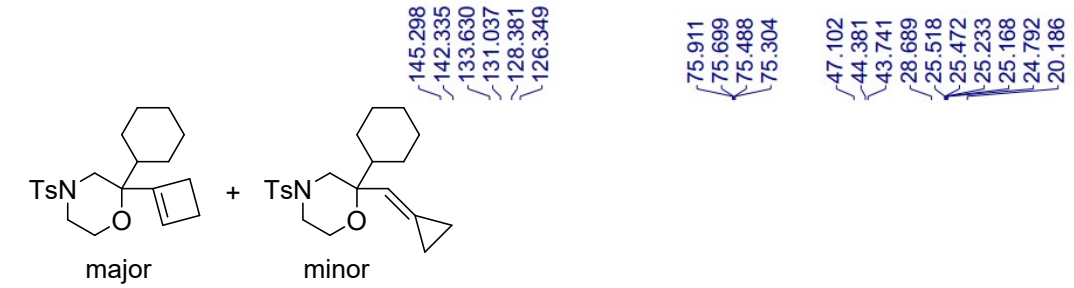
Compound 2t': An inseparable mixture of **2t'** and **2t** in a 8.3:1 ratio determined by ^{1}H NMR analysis**;** Yield: 52.5 mg, 70%; a yellow oil; Eluent: PE/EA = 10/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.65 – 7.59 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.09 (s, 1H), 3.94 – 3.88 (m, 1H), 3.69 – 3.59 (m, 2H), 3.41 – 3.36 (m, 1H), 2.65 – 2.55 (m, 1H), 2.53 – 2.35 (m, 7H), 2.27 (d, *J* = 11.3 Hz, 1H), 1.81 – 1.58 (m, 6H), 1.52 – 1.42 (m, 1H), 1.24 – 1.03 (m, 2H), 1.02 – 0.83 (m, 2H); ^{13}C NMR (101 MHz, CDCl3) δ 145.3, 142.3, 133.6, 131.0, 128.4, 126.3, 75.3, 47.1, 44.4, 43.7, 28.7, 25.52, 25.47, 25.23, 25.17, 24.8, 20.2; IR (neat): ν 2923, 2850, 2017, 1549, 1490, 1447, 1330, 1088,1019, 980, 909, 813, 706 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{21}H_{29}NO_3NaS$ $[M+Na]^+$: 398.17604, found: 398.17590.



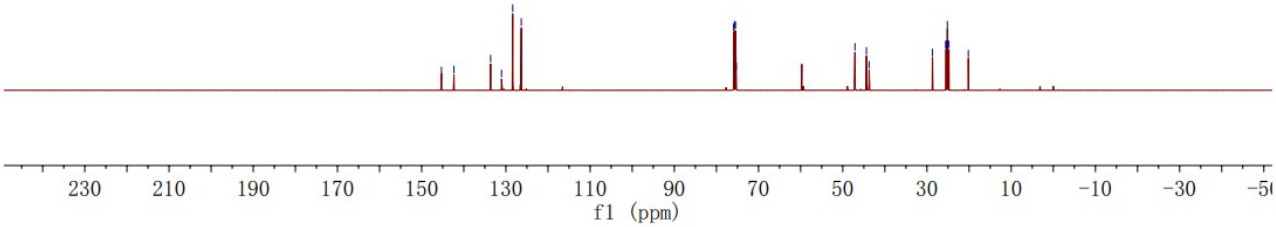
major minor

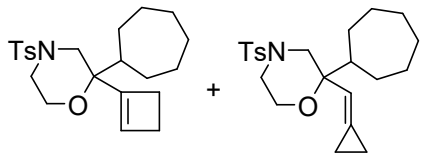
(^{1}H NMR 400 MHz, $CDCl_3$)





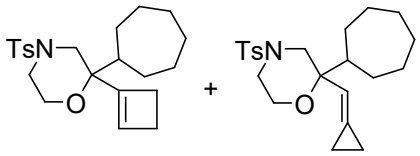
(^{13}C NMR 100 MHz, $CDCl_3$)





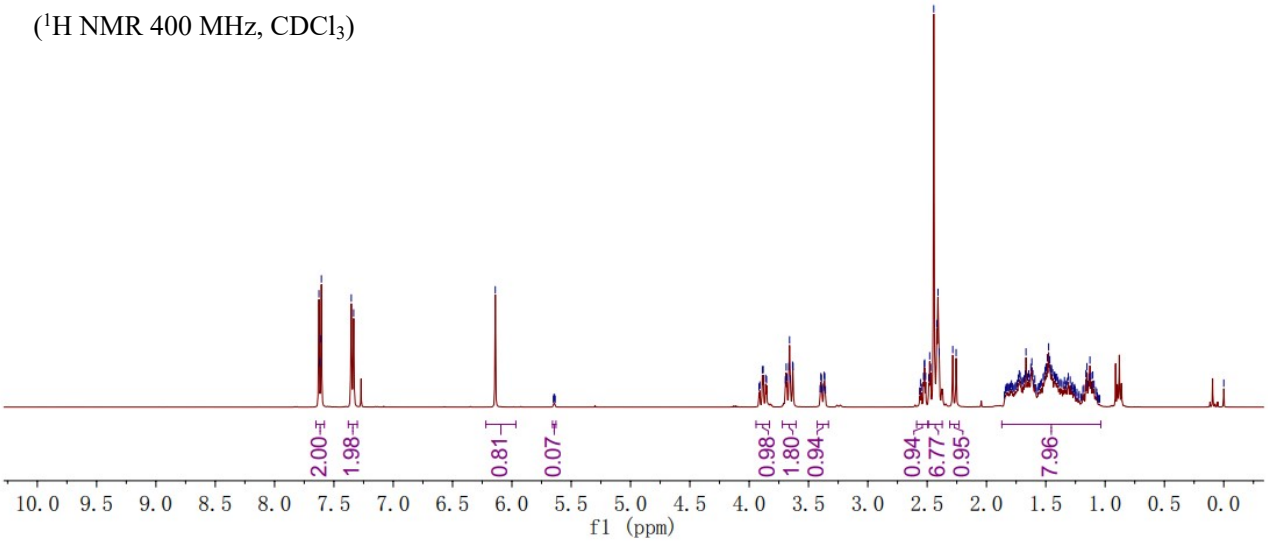
2u', major **2u**, minor

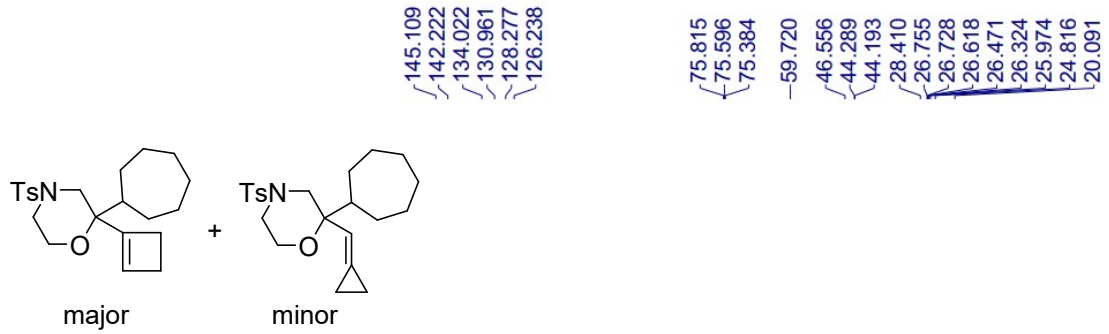
Compound 2u': An inseparable mixture of **2u'** and **2u** in a 11.5:1 ratio determined by ^{1}H NMR analysis**;** Yield: 66.1 mg, 85%; a yellow oil; Eluent: PE/EA = 10/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.65 – 7.58 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.14 (s, 1H), 3.91 – 3.85 (m, 1H), 3.72 – 3.61 (m, 2H), 3.40 – 3.35 (m, 1H), 2.59 – 2.49 (m, 1H), 2.49 – 2.37 (m, 7H), 2.27 (d, *J* = 11.4 Hz, 1H), 1.87 – 1.04 (m, 13H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 142.2, 134.0, 131.0, 128.3, 126.2, 59.7, 46.6, 44.3, 44.2, 28.4, 26.8, 26.7, 26.6, 26.5, 26.3, 26.0, 24.8, 20.1; IR (neat): ν 2920, 2853, 2017, 1594, 1445, 1330, 1305, 1088,1044, 991, 909, 888, 755, 662 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{22}H_{31}NO_2NaS$ $[M+Na]^+$: 412.19169, found: 412.19143.



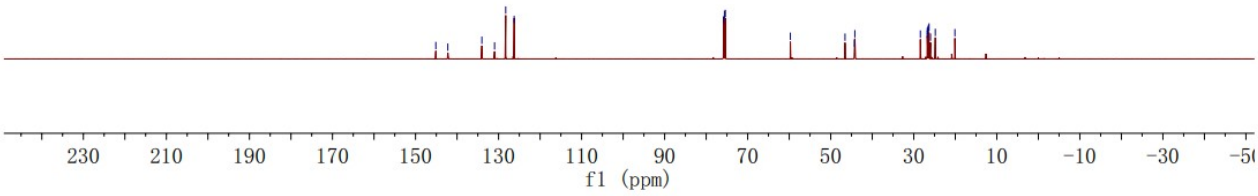
major minor

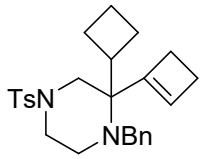
(^{1}H NMR 400 MHz, $CDCl_3$)



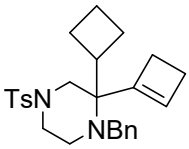


(^{13}C NMR 100 MHz, $CDCl_3$)

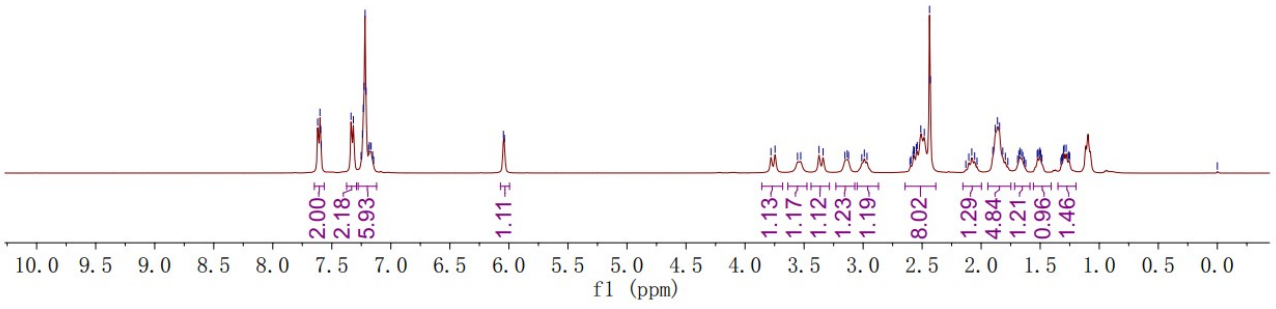


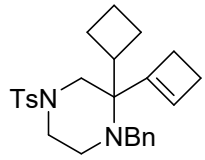


Compound 2v': Yield: 54.9 mg, 63%; a yellow oil; Eluent: PE/EA = 10/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.65 – 7.56 (m, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.28 – 7.12 (m, 5H), 6.04 (s, 1H), 3.76 (d, *J* = 13.8 Hz, 1H), 3.54 (d, *J* = 10.8 Hz, 1H), 3.36 (d, *J* = 13.8 Hz, 1H), 3.23 – 3.07 (m, 1H), 3.01 – 2.97 (m, 1H), 2.64 – 2.38 (m, 8H), 2.13 – 2.04 (m, 1H), 1.90 – 1.77 (m, 5H), 1.69 – 1.62 (m, 1H), 1.53 – 1.49 (m, 1H), 1.33 – 1.25 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 139.9, 132.1, 129.6, 128.3, 128.2, 127.9, 126.8, 126.0, 115.2, 61.8, 53.7, 51.0, 46.5, 45.6, 41.5, 25.7, 24.0, 21.6, 18.5, 5.4, 1.5; IR (neat): ν 2977, 2849, 2256, 1598, 1493, 1345, 1164, 1105,1021, 967, 815, 727,649, 599, 547 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{26}H_{33}N_2O_2S$ $[M+H]^+$: 437.22573, found: 437.22513.

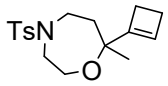


(^{1}H NMR 400 MHz, $CDCl_3$)

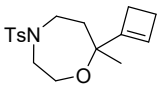




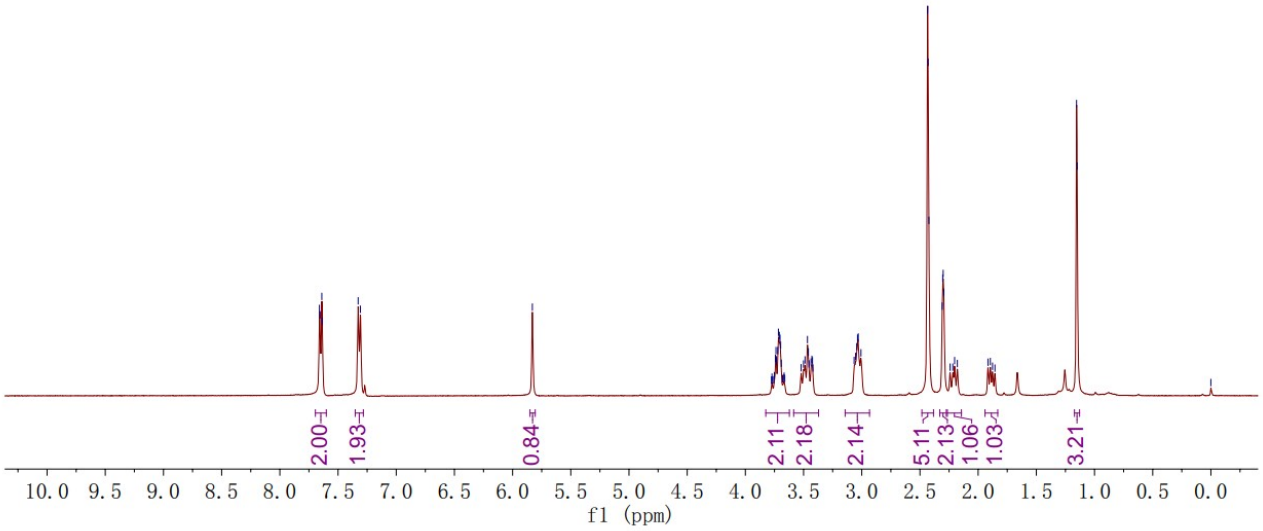
(^{13}C NMR 100 MHz, $CDCl_3$)

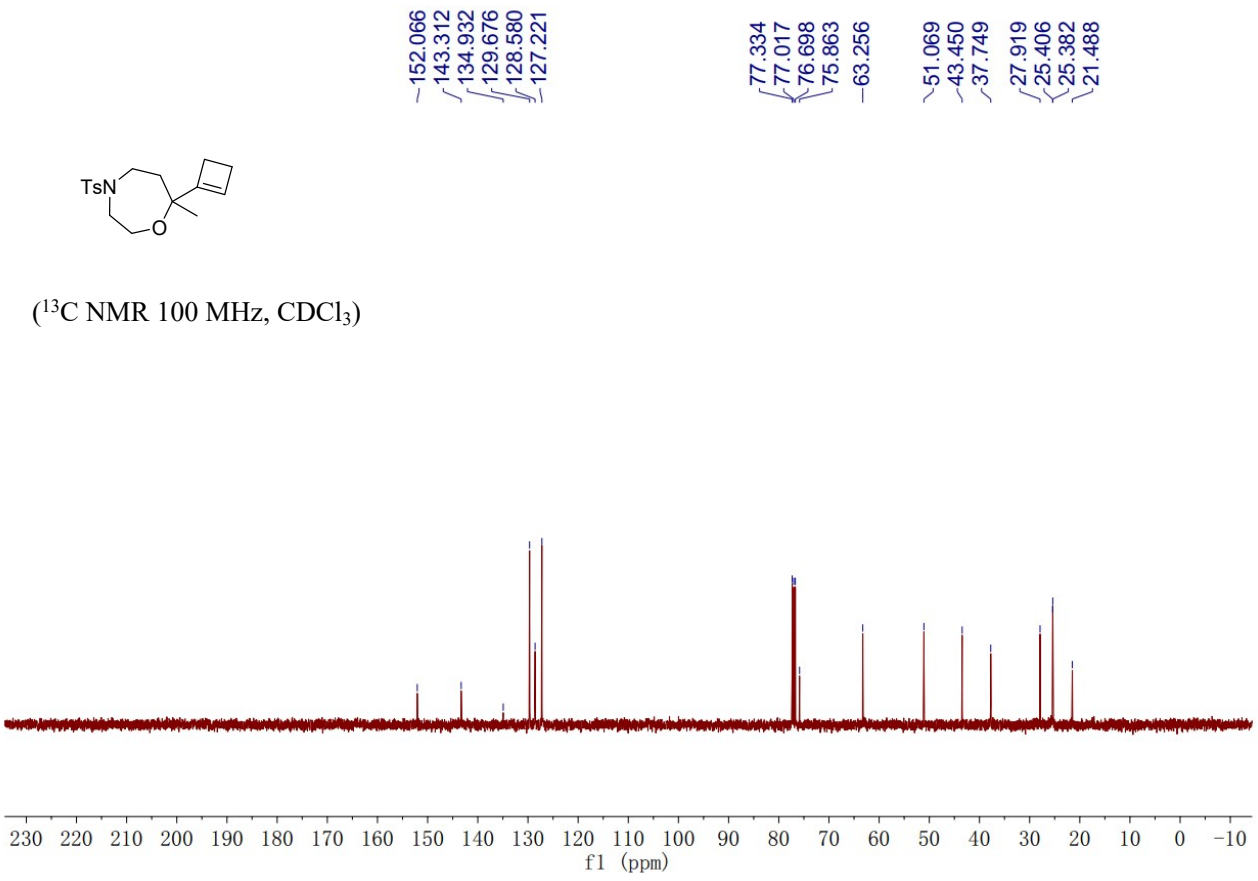


Compound 2w': Yield: 56.5 mg, 88%; a yellow oil; Eluent: PE/EA = 10/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.66 – 7.63 (m, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 5.83 (s, 1H), 3.82 – 3.62 (m, 2H), 3.59 – 3.37 (m, 2H), 3.14 – 2.93 (m, 2H), 2.44 – 2.42 (m, 5H), 2.33 – 2.27 (m, 2H), 2.24 – 2.18 (m, 1H), 1.92 – 1.86 (m, 1H), 1.15 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 143.3, 134.9, 129.7, 128.6, 127.2, 75.9, 63.3, 51.1, 43.5, 37.7, 27.9, 25.41, 25.38, 21.5; IR (neat): ν 2965, 2847, 2357, 1597, 1453, 1353, 1161, 1128, 990, 947, 864, 771, 656 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{17}H_{23}NO_3NaS$ $[M+Na]^+$: 344.1296, found: 344.1298.

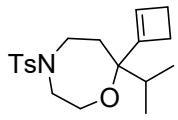


(^{1}H NMR 400 MHz, $CDCl_3$)

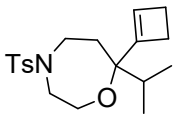




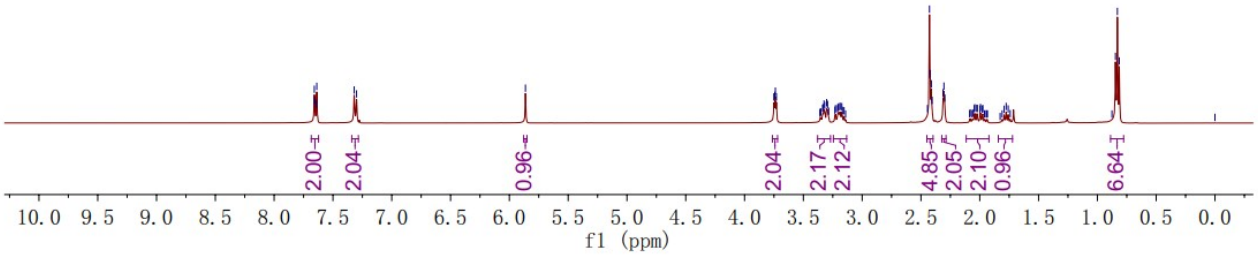
(^{13}C NMR 100 MHz, $CDCl_3$)

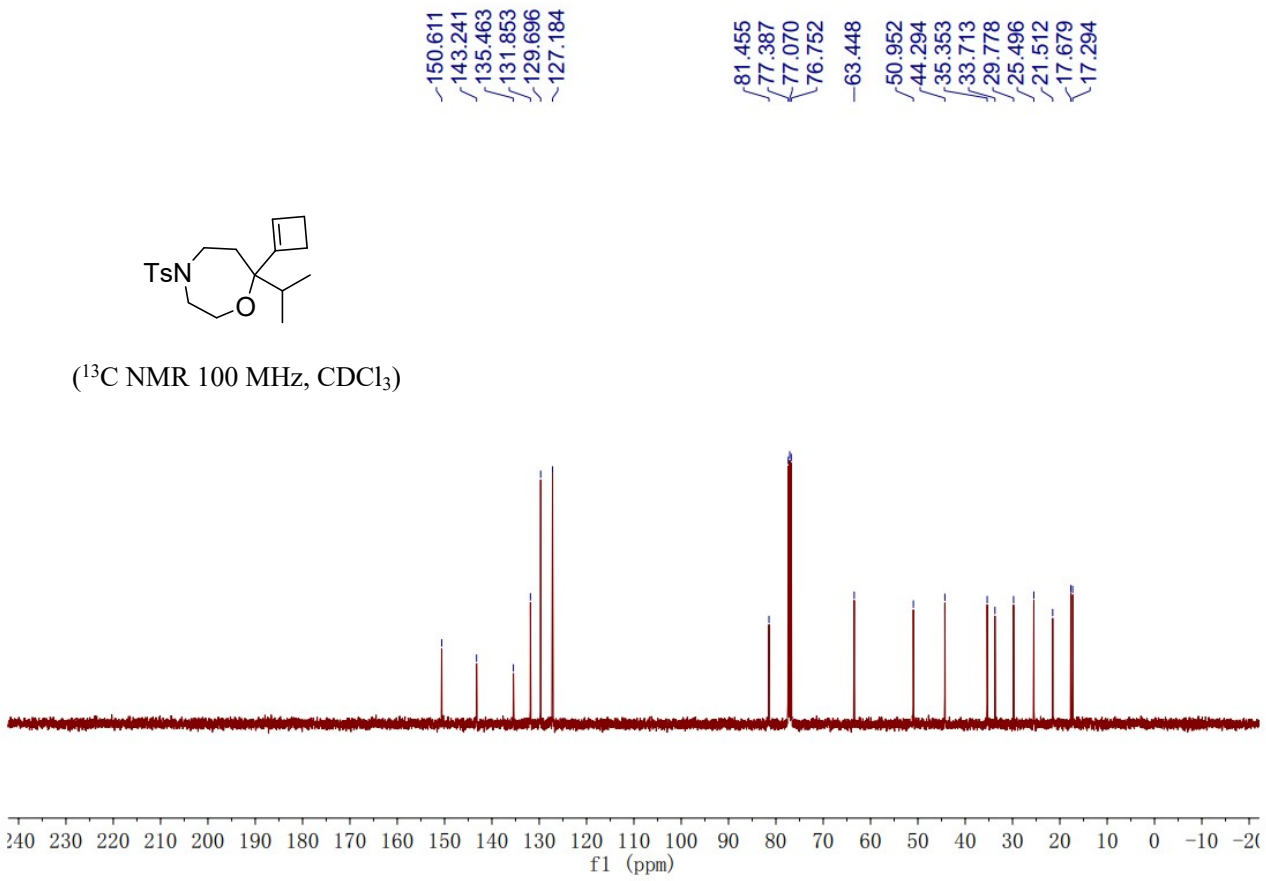


Compound 2x': Yield: 49.0 mg, 70%; A colorless solid; Mp: 116 – 118 ℃; Eluent: PE/EA = 10/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.68 – 7.62 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.86 (s, 1H), 3.75 – 3.73 (m, 2H), 3.38 – 3.27 (m, 2H), 3.24 – 3.13 (m, 2H), 2.44 – 2.41 (m, 5H), 2.31 – 2.30 (m, 2H), 2.09 – 1.94 (m, 2H), 1.83 – 1.74 (m, 1H), 0.88 – 0.81 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 143.2, 135.5, 131.9, 129.7, 127.2, 81.5, 63.4, 51.0, 44.3, 35.4, 33.7, 29.8, 25.5, 21.5, 17.7, 17.3; IR (neat): ν 2956, 1460, 1356, 1333, 1163, 1105, 1074, 978, 889, 811, 713 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{19}H_{27}NO_3NaS$ $[M+Na]^+$: 372.16039, found: 372.15994.

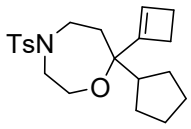


(^{1}H NMR 400 MHz, $CDCl_3$)

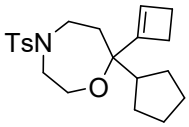




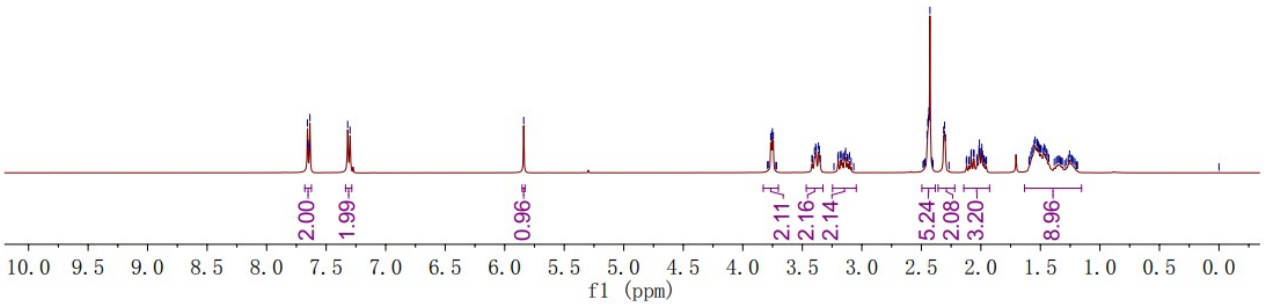
(^{13}C NMR 100 MHz, $CDCl_3$)

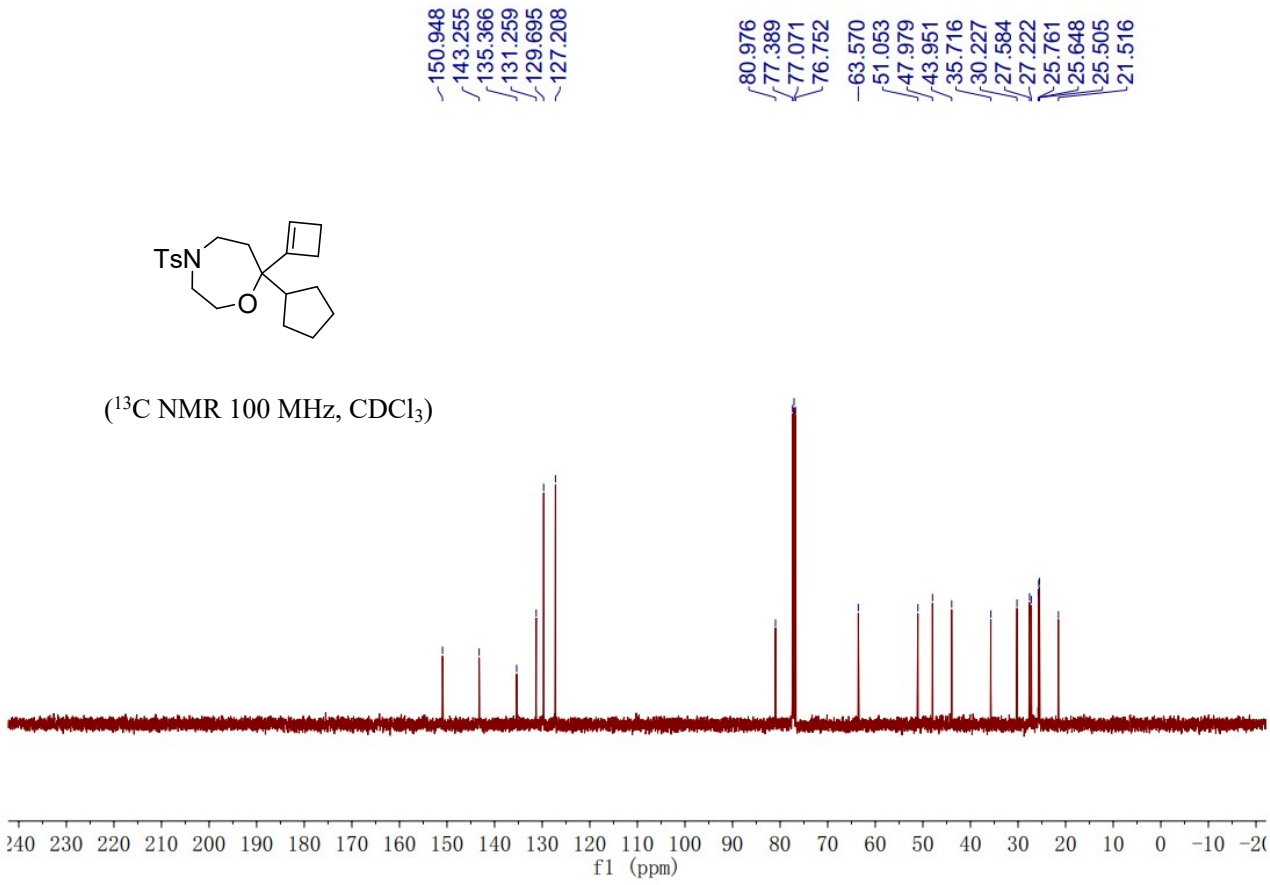


Compound 2y': Yield: 49.9 mg, 67%; A colorless solid; Mp: 125 – 127 ℃; Eluent: PE/EA = 10/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.68 – 7.62 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.84 (s, 1H), 3.77 – 3.74 (m, 2H), 3.47 – 3.33 (m, 2H), 3.25 – 3.05 (m, 2H), 2.45 – 2.40 (m, 5H), 2.36 – 2.22 (m, 2H), 2.14 – 1.93 (m, 3H), 1.63 – 1.15 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9, 143.3, 135.4, 131.3, 129.7, 127.2, 81.0, 63.6, 51.1, 48.0, 44.0, 35.7, 30.2, 27.6, 27.2, 25.8, 25.6, 25.5, 21.5; IR (neat): ν 2929, 1448, 1356, 1337, 1115, 1029, 888, 711, 668 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{21}H_{29}NO_3NaS$ $[M+Na]^+$: 398.17604, found: 398.17624.

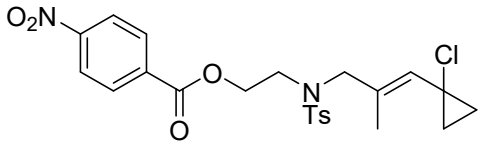


(^{1}H NMR 400 MHz, $CDCl_3$)

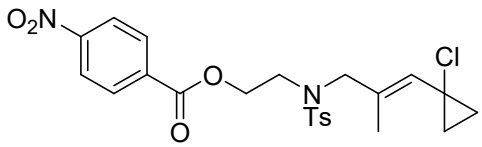




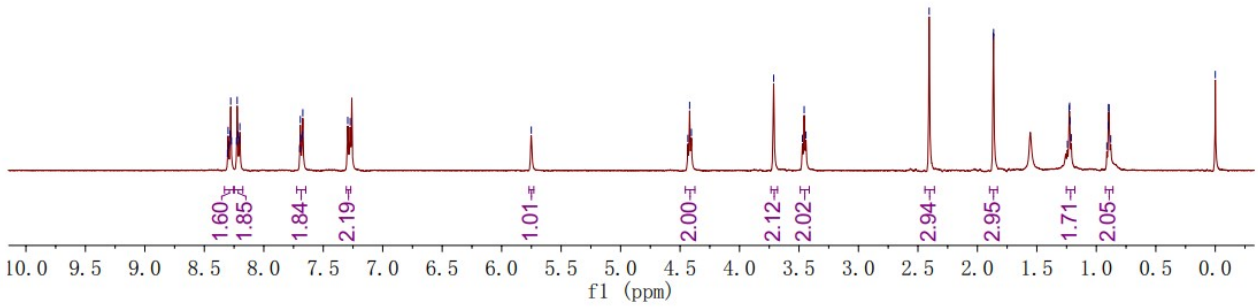
(^{13}C NMR 100 MHz, $CDCl_3$)

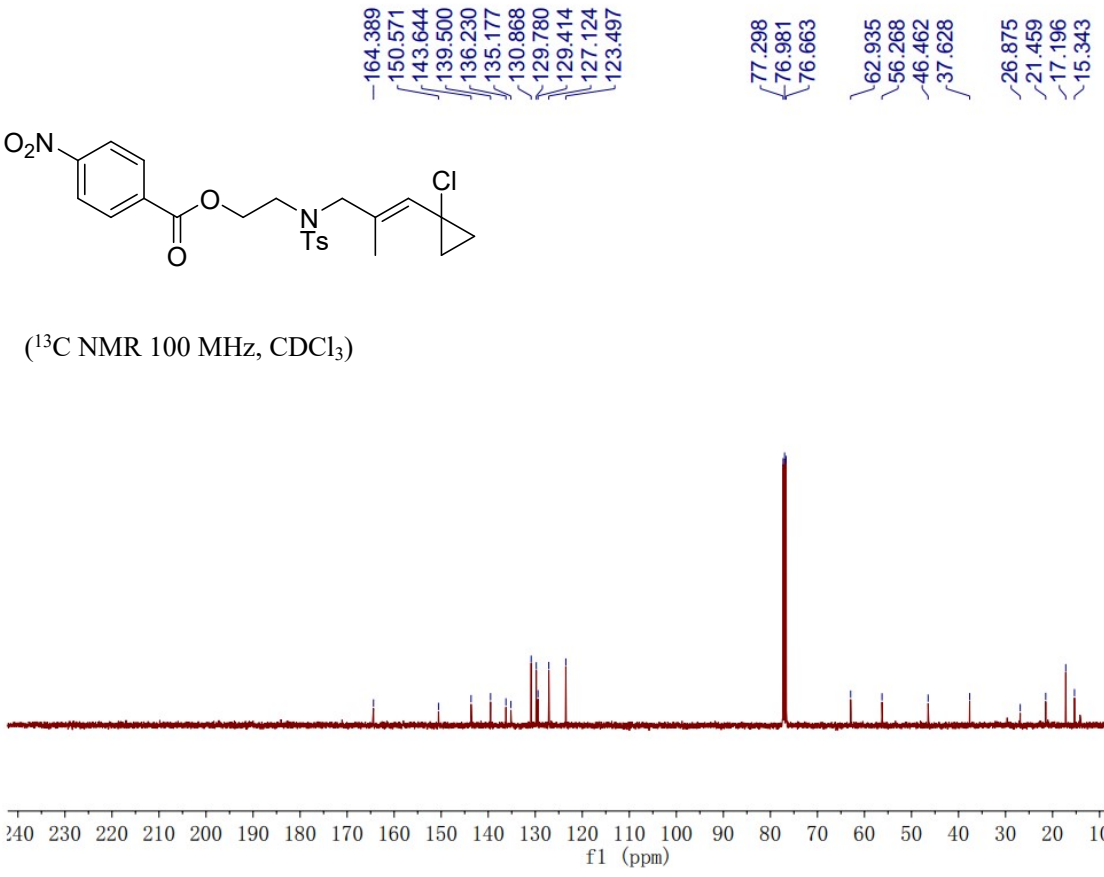


Compound 3: Yield: 77.0 mg, 78% for two steps; A colorless solid; Mp: 245 – 248 ℃; Eluent: PE/EA = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.33 – 8.25 (m, 2H), 8.25 – 8.18 (m, 2H), 7.72 – 7.65 (m, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 5.75 (s, 1H), 4.42 (t, *J* = 5.9 Hz, 2H), 3.71 (s, 2H), 3.46 (t, *J* = 5.9 Hz, 2H), 2.41 (s, 3H), 1.87 (d, *J* = 1.4 Hz, 3H), 1.25 – 1.18 (m, 2H), 0.92 – 0.86 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 164.4, 150.6, 143.6, 139.5, 136.2, 135.2, 130.9, 129.8, 129.4, 127.1, 123.5, 62.9, 56.3, 46.5, 37.6, 26.9, 21.5, 17.2, 15.3; IR (neat): ν 2927, 2853, 1724, 1594, 1529, 1459, 1161, 1088, 996, 712, 657 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{23}H_{25}N_2O_6NaSCl$ $[M+Na]^+$: 515.10141, found: 515.10144.

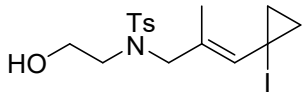


(^{1}H NMR 400 MHz, $CDCl_3$)

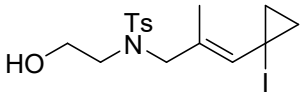




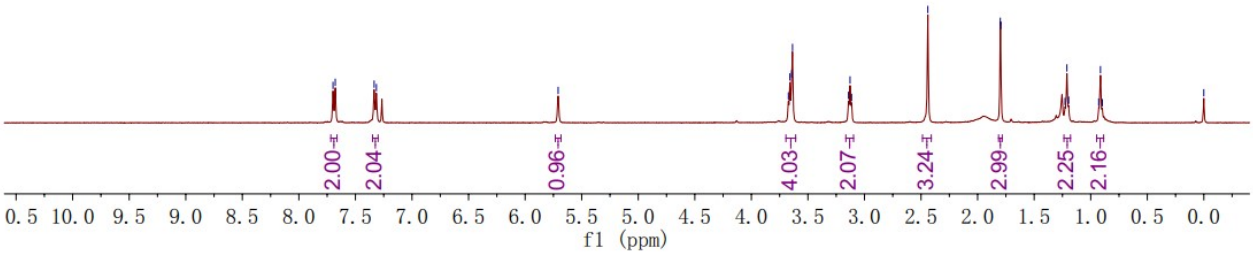
(^{13}C NMR 100 MHz, $CDCl_3$)

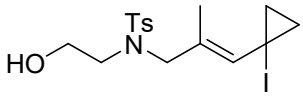


Compound 4: Yield: 29.1 mg, 67%; A yellow oil; Eluent: PE/EA = 1/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.71 (s, 1H), 3.67 – 3.64 (m, 4H), 3.13 (t, *J* = 5.4 Hz, 2H), 2.44 (s, 3H), 1.80 (s, 3H), 1.23 – 1.20 (m, 2H), 0.93 – 0.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 143.7, 137.7, 135.8, 133.7, 129.8, 127.2, 61.0, 56.9, 50.5, 21.6, 19.2, 15.5; IR (neat): ν 3525, 2956, 2922, 2849, 1599, 1450, 1335, 1088, 991, 815, 753 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{16}H_{22}NO_3NaSI$ $[M+Na]^+$: 458.02573, found: 458.02661.

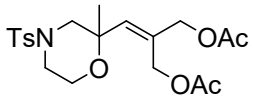


(^{1}H NMR 400 MHz, $CDCl_3$)

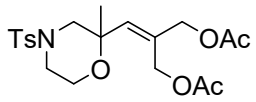




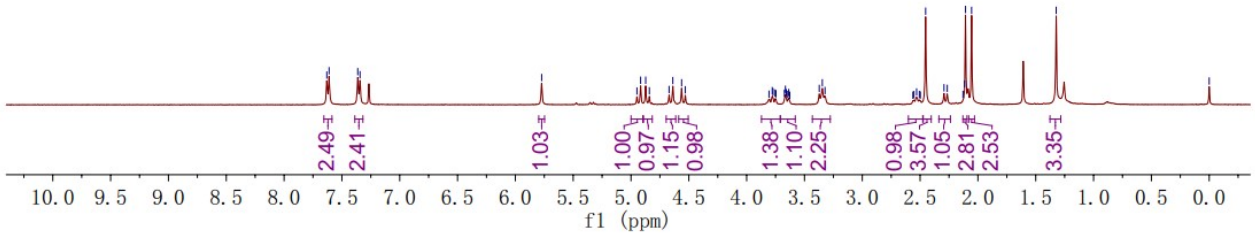
(^{13}C NMR 100 MHz, $CDCl_3$)

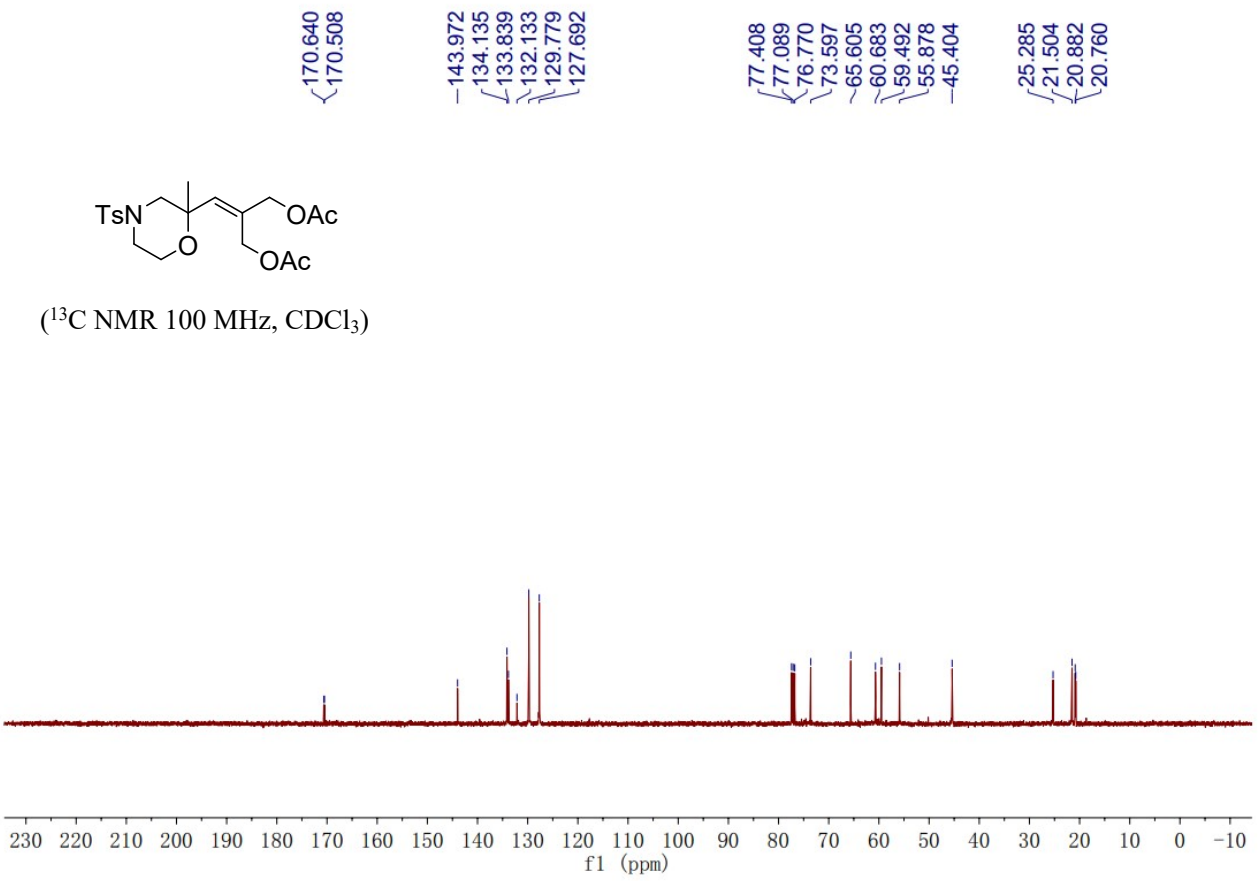


Compound 5: Yield: 17.5 mg, 42%; A colorless oil; Eluent: PE/EA = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.62 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 5.77 (s, 1H), 4.93 (d, *J* = 12.7 Hz, 1H), 4.86 (d, *J* = 12.7 Hz, 1H), 4.65 (d, *J* = 12.9 Hz, 1H), 4.55 (d, *J* = 12.9 Hz, 1H), 3.87 – 3.71 (m, 1H), 3.71 – 3.58 (m, 1H), 3.37 – 3.32 (m, 2H), 2.60 – 2.47 (m, 1H), 2.45 (s, 3H), 2.28 (d, *J* = 11.3 Hz, 1H), 2.11 (s, 3H), 2.05 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.6, 170.5, 144.0, 134.1, 133.8, 132.1, 129.8, 127.7, 73.6, 65.6, 60.7, 59.5, 55.9, 45.4, 25.3, 21.5, 20.9, 20.8; IR (neat): ν 2974, 2846, 1735, 1591, 1450, 1350, 1132, 1023, 919, 757, 657 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{27}NO_7NaS$ $[M+Na]^+$: 448.14004, found: 448.14025.

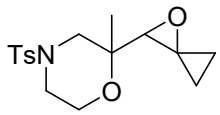


(^{1}H NMR 400 MHz, $CDCl_3$)

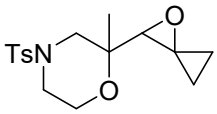




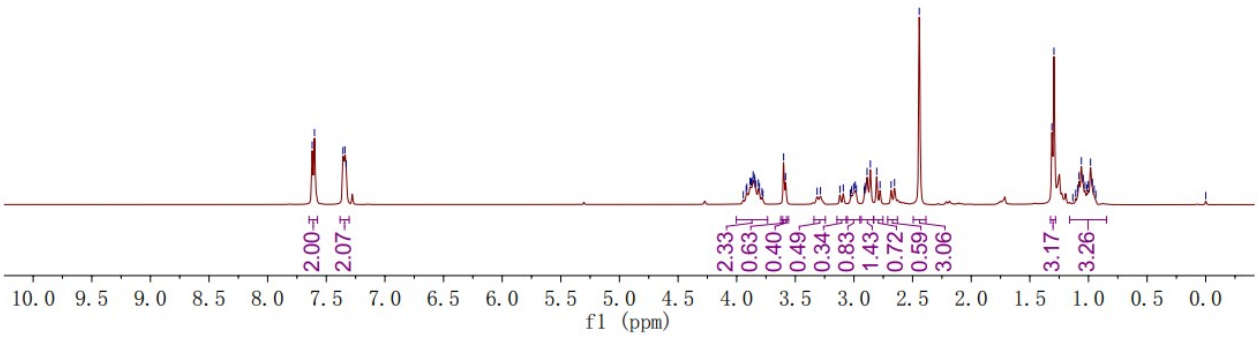
(^{13}C NMR 100 MHz, $CDCl_3$)

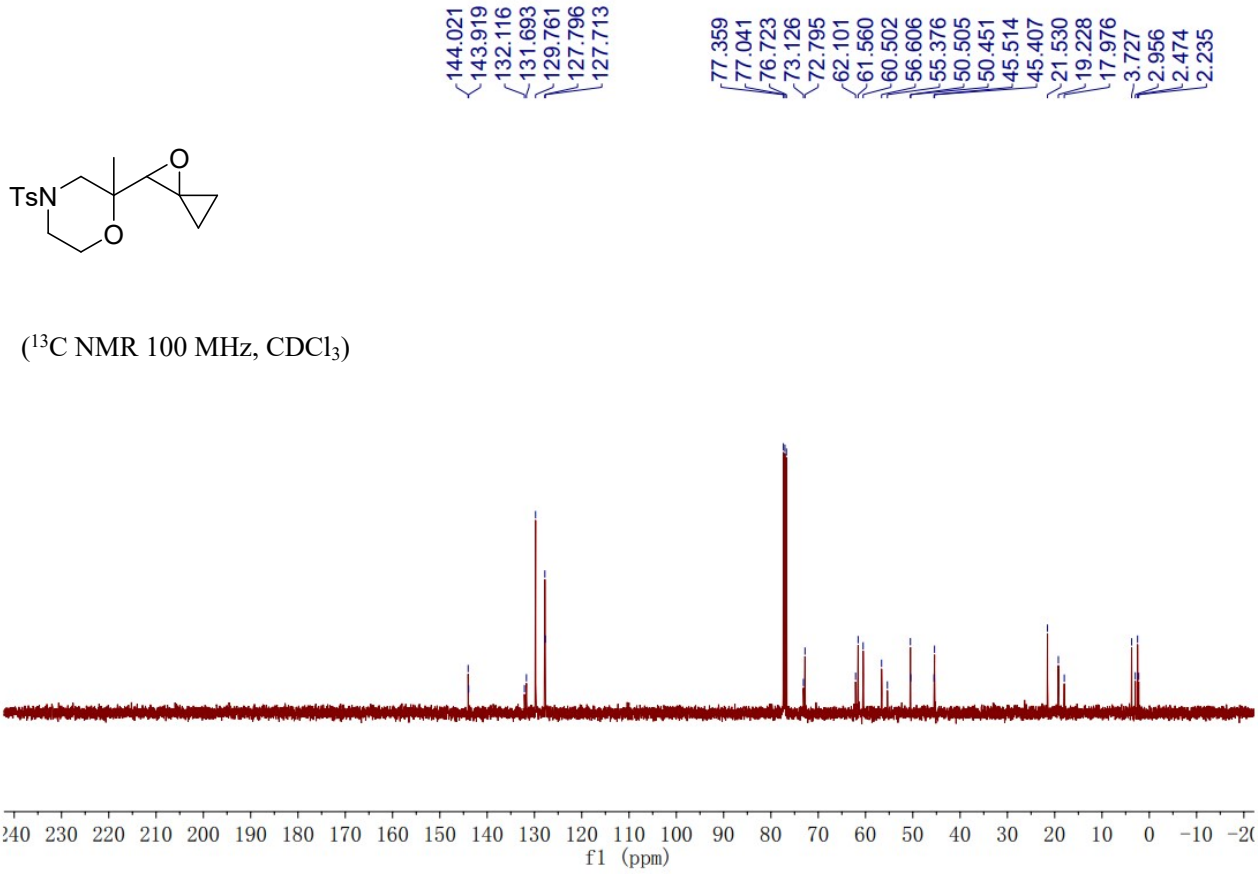


Compound 6: Yield: 20.9 mg, 68%; A colorless oil; Eluent: PE/EA = 2/1; The diastereomer ratio was 3:1, which was determined by ^{1}H NMR analysis. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, detectable signals of minor diastereomer are marked with an asterisk) δ 7.61 (d, *J* = 7.9 Hz, 2H), 7.38 – 7.30 (m, 2H), 4.00 – 3.74 (m, 2H), 3.60 (s, 1H), 3.58* (s, 1H), 3.30* (d, *J* = 11.4 Hz, 1H), 3.11* (d, *J* = 11.4 Hz, 1H), 3.03 – 2.98 (m, 1H), 2.94 – 2.83 (m, 1H), 2.79 (d, *J* = 11.4 Hz, 1H), 2.67 (d, *J* = 11.4 Hz, 1H), 2.44 (s, 3H), 1.31* (s, 3H), 1.29 (s, 3H), 1.16 – 0.85 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, mixture of diastereomers.) δ 144.0, 143.9, 132.1, 131.7, 129.8, 127.8, 127.7, 73.1, 72.8, 62.1, 61.6, 60.5, 56.6, 55.4, 50.5, 50.5, 45.5, 45.4, 21.5, 19.2, 18.0, 3.7, 3.0, 2.5, 2.2; IR (neat): ν 2982, 2930, 2251, 1591, 1351, 1164, 1088, 1010, 987, 861, 727 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{16}H_{21}NO_4NaS$ $[M+Na]^+$: 346.10385, found: 346.10869.

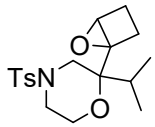


(^{1}H NMR 400 MHz, $CDCl_3$)

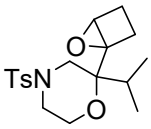




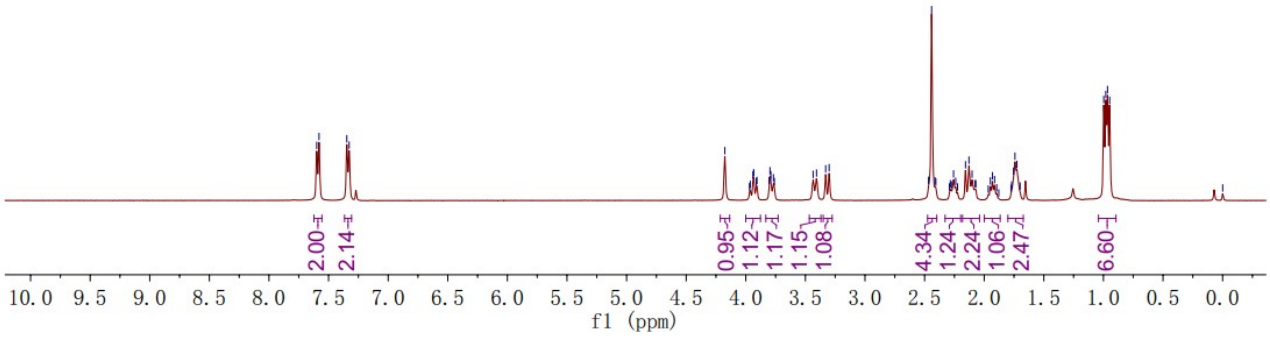
(^{13}C NMR 100 MHz, $CDCl_3$)

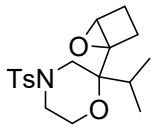


Compound 7: Yield: 33.0 mg, 94%; A colorless solid; Mp: 63 – 65 ℃; Eluent: PE/EA = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.59 (d, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 4.18 (s, 1H), 3.97 – 3.91 (m, 1H), 3.80 – 3.76 (m, 1H), 3.42 (d, *J* = 11.4 Hz, 1H), 3.32 (d, *J* = 11.5 Hz, 1H), 2.47 – 2.41 (m, 4H), 2.33 – 2.20 (m, 1H), 2.18 – 2.04 (m, 2H), 1.97 – 1.88 (m, 1H), 1.80 – 1.67 (m, 2H), 0.99 (d, *J* = 7.2 Hz, 3H), 0.96 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 143.8, 132.0, 129.7, 127.6, 74.7, 64.1, 61.1, 59.8, 45.6, 45.3, 35.1, 27.8, 26.2, 21.5, 17.0, 16.8; IR (neat): ν 2938, 2872, 1594, 1448, 1348, 1091, 972, 757, 655 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{18}H_{25}NO_4NaS$ $[M+Na]^+$: 374.13965, found: 374.13956.



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





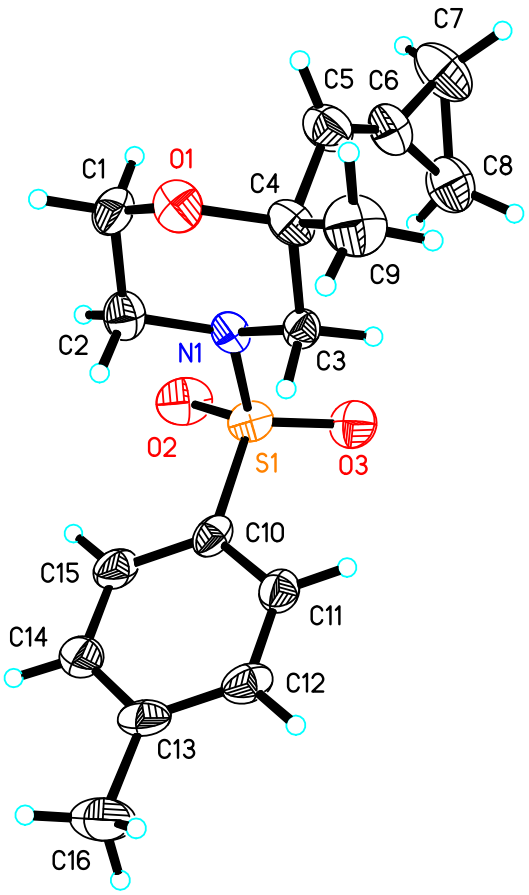
(^{13}C NMR 100 MHz, $CDCl_3$)

8 X-ray crystal data

X-ray crystal data of compound **2a**

Single crystals suitable for XRD were obtained by evaporation experiment:

Compound **2a** (50 mg) was dissolved in 0.5 mL of dichloromethane, and then 5 mL n-pentane was added, allowing this mixed solution evaporate slowly in a dry environment. Crystals were obtained in about 3-5 days with the evaporation of the solvent.

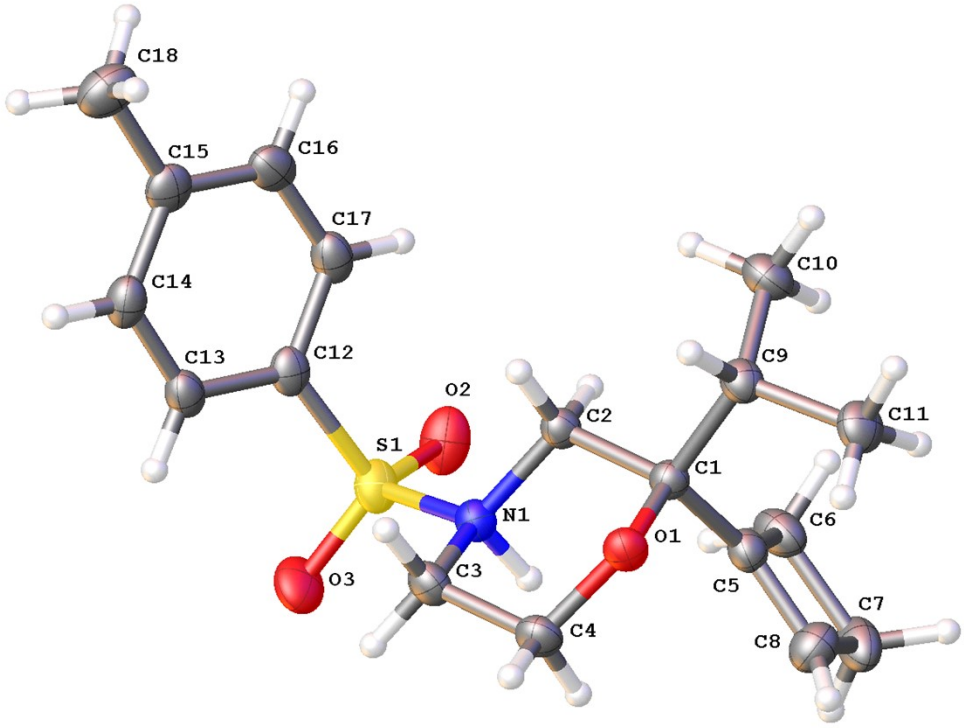


The crystal data of **2a** have been deposited in CCDC with number 1537103. Empirical Formula: $C_{16}H_{21}NO_3S$; Formula Weight: 307.40; Crystal Color, Habit: colorless; Crystal Dimensions: 0.200 x 0.110 x 0.080 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 11.797(6)Å, b = 6.533(3)Å, c = 11.917(6)Å, α = 90°, β = 117.243(9)°, γ = 90°, V = 816.6(7)$Å^3$; Space group: P 21; Z = 2; D_{calc} = 1.250 g/cm^3; F_{000} = 328; Final R indices [I>2sigma(I)] R1 = 0.0891, wR2 = 0.1649.

X-ray crystal data of compound **2q'**

Single crystals suitable for XRD were obtained by evaporation experiment:

Compound **2q'** (50 mg) were dissolved in 0.5 mL of dichloromethane, and then 5 mL n-pentane was added, allowing this mixed solution evaporate slowly in a dry environment. Crystals were obtained in about 3-5 days with the evaporation of the solvent.

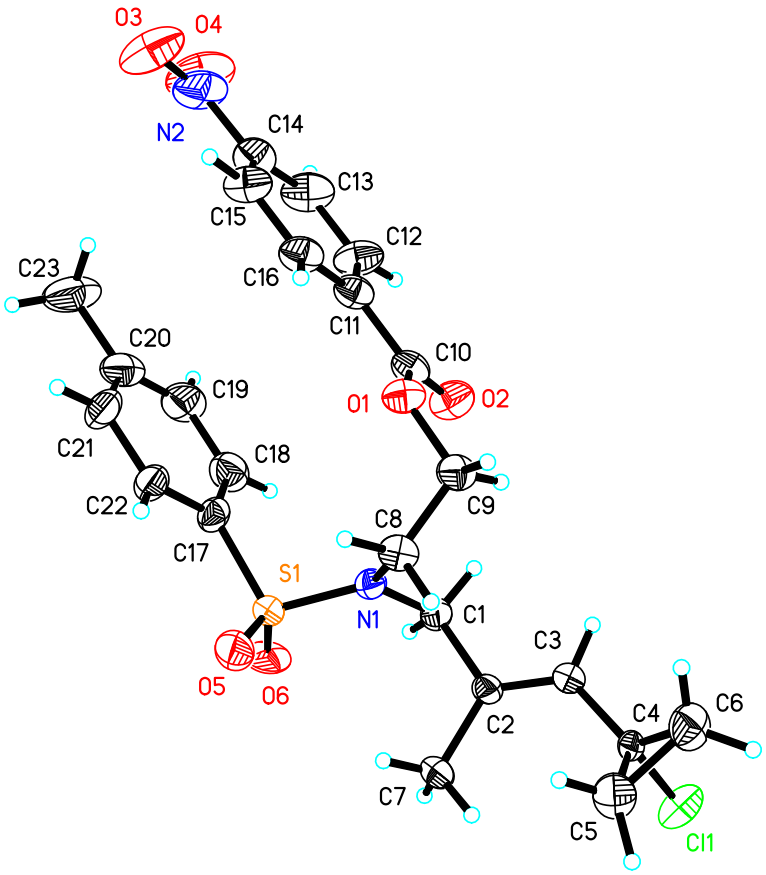


The crystal data of **2q'** have been deposited in CCDC with number 2178224. Empirical Formula: $C_{18}H_{26}NO_3S$; Formula Weight: 336.46; Crystal Color, Habit: colorless; Crystal Dimensions: 0.07 x 0.07 x 0.05 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 11.7615(3)Å, b = 7.0280(2)Å, c = 21.1943(6)Å, α = 90°, β = 93.4420(10)°, γ = 90°, V = 1748.76(8)$Å^3$; Space group: P 1 21/n 1; Z = 4; D_{calc} = 1.278 g/cm^3; F_{000} = 724; Final R indices [I>2sigma(I)] R1 = 0.0641, wR2 = 0.1811.

X-ray crystal data of compound **3**

Single crystals suitable for XRD were obtained by evaporation experiment:

Compound **3** (50 mg) were dissolved in 0.5 mL of dichloromethane, and then 5 mL n-pentane was added, allowing this mixed solution evaporate slowly in a dry environment. Crystals were obtained in about 3-5 days with the evaporation of the solvent.



The crystal data of **3** have been deposited in CCDC with number 2178226. Empirical Formula: $C_{23}H_{25}ClN_2O_6S$; Formula Weight: 492.96; Crystal Color, Habit: colorless; Crystal Dimensions: 0.150 x 0.100 x 0.050 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 6.5010(10)Å, b = 7.4457(11)Å, c = 24.493(4)Å, α = 90°, β = 95.467(6)°, γ = 90°, V = 1180.2(3)$Å^3$; Space group: P 21; Z = 2; D_{calc} = 1.387 g/cm^3; F_{000} = 516; Final R indices [I>2sigma(I)] R1 = 0.0948, wR2 = 0.2520.

9 Calculation details

The geometries of compounds not involving Au atom have been optimized at B3LYP/6-31G(d) level; and the geometries of compounds involving Au atom have been optimized at B3LYP/6-31G(d)/SDD level. Geometry optimizations were conducted without any constraint using implicit solvation model (SMD) in THF (ε = 7.4257). The nature of all stationary points was verified through calculation of the vibrational frequency spectrum. Thermochemical corrections to 298.15 K have been calculated for all minima from unscaled vibrational frequencies obtained at this same level. The thermochemical corrections were calculated at SMD(THF)/B3LYP/6-31G(d)/SDD level to yield free energy $G_{298,THF}$ at 298.15 K. All DFT calculations were performed with Gaussian 16 program.[3]

Computational Energies

	E_{tot}	H_{298}	G_{298}
1a	-1300.803547	-1300.434843	-1300.516437
IntA-1a	-3064.896189	-3063.734220	-3063.900285
IntC-1a	-3064.895471	-3063.733309	-3063.898754
1q	-1379.430754	-1379.002427	-1379.088720
IntA-1q	-3143.519232	-3142.297750	-3142.469338
IntC-1q	-3143.520690	-3142.298781	-3142.470700

The total energies, enthalpies and free energies of all species in toluene calculated at SMD(THF)/ B3LYP/6-31G(d)/SDD.

Computational Coordinates

1a

Opt @ SMD(THF)/B3LYP/6-31G(d)/SDD
SCF Done: E(B3LYP) = -1300.80354707 a.u.
Zero-point correction = 0.344594 Hartree/Particle
Sum of electronic and thermal Free Energies = -1300.516437 a.u.

C	2.23117000	-1.22970700	-0.44149700
C	4.70817900	-1.03976800	0.35724600
C	6.15007800	-1.22781000	0.06808500
C	5.68466900	-0.67517500	1.41110500
C	1.58856000	-0.08124100	-1.20254400
C	0.63037600	1.11022400	0.81644300
C	1.35681500	2.45545300	0.75639500
O	1.51455600	2.87780400	2.11116200
C	1.39062800	-2.46768800	-0.21879100
C	3.47908900	-1.13415900	-0.02939200
N	0.41320500	0.45686800	-0.48141400
C	-2.29815100	0.13394700	-0.43613800
C	-2.49698600	-1.24729300	-0.54656200
C	-3.54550000	-1.83889500	0.14928500
C	-4.40608100	-1.07563300	0.95808300
C	-4.18732800	0.30442700	1.04540200
C	-3.14133400	0.91673900	0.35141600
C	-5.53986800	-1.73665200	1.70126300
S	-0.95652300	0.90109500	-1.34753400
O	-1.16837200	2.35814900	-1.28242100
O	-0.85523800	0.24998200	-2.66340700
H	6.53830100	-2.24491000	0.03775700
H	6.62595100	-0.54253500	-0.63198300
H	5.84760300	0.38207400	1.61570300
H	5.75911400	-1.32007000	2.28557200
H	2.32552200	0.70758800	-1.38902900
H	1.22844500	-0.43990600	-2.16979000
H	-0.33526900	1.24312800	1.31387600
H	1.21318400	0.41836300	1.43330600
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H	-4.84432800	0.91362400	1.66072500
H	-2.98743700	1.98843400	0.41538200
H	-5.17203600	-2.54141700	2.34965200
H	-6.08260100	-1.01922600	2.32404800
H	-6.25640400	-2.18957700	1.00427000

IntA-1a

Opt @ SMD(THF)/B3LYP/6-31G(d)/SDD
SCF Done: E(B3LYP) = -3064.89618883 a.u.
Zero-point correction = 1.098439 Hartree/Particle
Sum of electronic and thermal Free Energies = -3063.900285 a.u.

C -1.57528100 -1.03352300 0.80595300
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C -0.04007800 -0.88882700 4.55382500
C -1.52210300 -1.21991300 4.64542200
C -2.30860900 0.21720500 0.31117000
C -4.32507000 -0.11028400 1.81134600
C -4.26615100 1.15020200 2.67914200
O -4.58778700 0.72762300 4.00504500
C -1.83633400 -2.32485400 0.05136900
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C -7.78553000 -2.78551400 -1.43671900
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C -7.26893900 -0.57375700 -0.55308500
C -8.77345100 -3.89450200 -1.69786600
S -4.78426600 0.61883200 -0.74611400
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C 3.95099400 0.72870100 -0.53274800
C 5.35107000 0.57874200 -0.62011300
C 6.19225700 1.64294000 -0.93307600
C 5.64130300 2.89968800 -1.17402100
C 4.26272400 3.06911500 -1.07973300
C 1.94210000 2.41653800 -0.63030000
C 1.09626700 2.42853700 -1.76844600
C -0.16232900 3.03284000 -1.66743600
C -0.61355100 3.64426200 -0.49101000
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C 1.49727300 3.00362900 0.57996500
H 5.80339600 -0.38947900 -0.44510300
H 7.26519300 1.48368700 -0.99044500
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H 3.83479700 4.05281700 -1.24811900

H -0.80608200 3.05954100 -2.54348600
H -0.09197200 4.06479900 1.55192800
C 1.54690000 1.87760700 -3.12206900
C 0.50345100 0.94981600 -3.77060600
H 0.91152600 0.50576600 -4.68678300
H 0.21527700 0.13249400 -3.09826200
H -0.40910100 1.48915800 -4.04917000
C -1.94931500 4.38351600 -0.49937100
H -2.63311800 3.80115000 -1.13163800
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C 3.12935200 -2.43746900 2.16189200
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C 4.99791300 -4.05999500 2.75436800
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H 4.49068800 -2.25480600 3.83166500
H 6.57163100 -4.14687500 1.25501700
H 6.49043400 -2.62206200 2.13475500
H 5.61961800 -4.44252300 3.57358600
H 4.47373900 -4.92593500 2.32384000
C 2.83781400 -1.69523600 -1.84580100
C 4.12756900 -1.87600300 -2.67271800
C 2.06161900 -3.02541300 -1.72578800
H 2.19672200 -0.98974000 -2.39310600
C 3.79526600 -2.44883200 -4.06304100
H 4.80965300 -2.56380100 -2.16224200
H 4.65261200 -0.92163300 -2.78315500
C 1.75288400 -3.60712200 -3.11672000

H 2.65391200 -3.75095400 -1.15386200
H 1.12688100 -2.86860300 -1.17247300
C 3.02303100 -3.77094700 -3.96237800
H 4.72631300 -2.59148000 -4.62599800
H 3.19652900 -1.71690000 -4.62428200
H 1.24165000 -4.57139700 -3.00166000
H 1.05308700 -2.93816100 -3.63842800
H 2.76504300 -4.13749000 -4.96399300
H 3.66892600 -4.53416300 -3.50373900
Au 0.76180900 -0.64897100 0.61469800

IntC-1a
Opt @ SMD(THF)/B3LYP/6-31G(d)/SDD
SCF Done: E(B3LYP) = -3064.89547103 a.u.
Zero-point correction = 1.098916 Hartree/Particle
Sum of electronic and thermal Free Energies = -3063.898754 a.u.

C 3.67495900 0.67334500 1.75685700
C 3.47394000 -0.71356000 1.54449400
C 4.21645700 -1.63051100 2.31897500
C 5.13953700 -1.21494700 3.27467000
C 5.34367500 0.14821600 3.47927800
C 4.61652600 1.06714900 2.72797000
C 2.95723500 1.80420000 1.06770300
C 3.52627900 2.41679900 -0.07530700
C 2.92274100 3.57216600 -0.59247300
C 1.79214600 4.15251300 -0.00997800
C 1.25627100 3.53731900 1.12735400
C 1.81751600 2.38133600 1.68529400
H 4.08066900 -2.69610000 2.17664300
H 5.69103700 -1.95379600 3.84900200
H 6.05857300 0.49686900 4.21936400
H 4.76773600 2.12930500 2.89479800
H 3.36602400 4.05697400 -1.45910800
H 0.39454900 3.98649400 1.61347600
C 4.83140600 1.91608100 -0.69800200
C 4.77601400 1.79265900 -2.23090400
H 5.71222000 1.36107200 -2.60551400
H 3.95495700 1.14355500 -2.55732600
H 4.64996700 2.76618700 -2.71865500
C 1.22240400 5.45532500 -0.56016300
H 1.68703500 5.62056900 -1.54157500
C -0.30077400 5.40939400 -0.76804500
H -0.65012100 6.34153800 -1.22840600
H -0.59233600 4.57961700 -1.42265300
H -0.83502700 5.29184700 0.18224500
C 1.61161800 6.64464500 0.34048800
H 2.69936900 6.71808400 0.45522300
H 1.25089300 7.58818300 -0.08746600
H 1.17465300 6.54048600 1.34139400
C 1.23718800 1.83310000 2.99140200
H 1.69188500 0.85585100 3.18108600
C -0.28488900 1.61825600 2.93430900
H -0.83080200 2.56175400 2.81737600
H -0.56207900 0.96299000 2.10118400
H -0.63512500 1.15077000 3.86279500
C 1.60632200 2.74596800 4.17801200
H 1.22448700 2.32706100 5.11730500

H 2.69181200 2.85937000 4.27533700
H 1.17343700 3.74634700 4.05552400
C 6.01045700 2.81903300 -0.28082100
H 6.95265500 2.43519700 -0.69138800
H 5.87294200 3.84189500 -0.65233100
H 6.11205300 2.86814700 0.80887000
H 5.03368200 0.91668800 -0.29938700
P 2.32963700 -1.46403300 0.29097700
C 1.56686600 -2.94643400 1.20091300
C 0.03752500 -3.00317300 0.99968100
C 2.19332500 -4.33261000 0.92695200
H 1.74587500 -2.69633200 2.25462600
C -0.59806200 -4.08809800 1.88627400
H -0.19123200 -3.20906900 -0.05522100
H -0.40556300 -2.02797800 1.23504500
C 1.55043300 -5.41139500 1.81697200
H 2.04365700 -4.60167600 -0.12566000
H 3.27280700 -4.32164400 1.10139700
C 0.02897100 -5.46587500 1.63982300
H -1.67952500 -4.12032400 1.70580500
H -0.46423300 -3.81079400 2.94205900
H 2.00058900 -6.38444100 1.58302600
H 1.78753000 -5.19900000 2.86956900
H -0.40714800 -6.20847500 2.31972200
H -0.20654700 -5.79636200 0.61699000
C 3.43579000 -1.93506100 -1.16726700
C 4.74227500 -2.69798500 -0.86809300
C 2.64045700 -2.61977500 -2.30169000
H 3.72220200 -0.93519300 -1.52564000
C 5.59459200 -2.81837000 -2.14538400
H 4.51551900 -3.70378000 -0.49842900
H 5.31802600 -2.18885100 -0.08862900
C 3.50194900 -2.75397900 -3.56945900
H 2.31919800 -3.61772400 -1.97874100
H 1.72916000 -2.04949800 -2.52441300
C 4.81930400 -3.48924400 -3.28721200
H 6.50687600 -3.38417200 -1.91795800
H 5.91681400 -1.81560000 -2.46178100
H 2.92891200 -3.27782300 -4.34505400
H 3.72376400 -1.75091900 -3.96282900
H 5.43476900 -3.52350400 -4.19504400
H 4.60142700 -4.53223800 -3.01427100
Au 0.65972400 -0.11067000 -0.75476000
C -2.36617500 1.13850000 -1.11323200
C -0.16187400 1.05327400 -2.52962000
C 0.74729900 1.95861500 -3.28144100
C 0.19680600 0.68894900 -3.92727200
C -2.77708100 0.51508800 0.20539400
C -4.10599700 -1.36042900 -0.82121100
C -3.42953700 -2.62339500 -0.27128800
O -2.93677300 -3.35032700 -1.39966500
C -3.39063700 2.00205200 -1.82183600
C -1.16832600 0.99206000 -1.65468700
N -4.06897700 -0.18241900 0.06033700
C -6.72207300 -0.01214700 0.61547600
C -7.07571900 1.21207000 0.03493000
C -8.33476000 1.34894500 -0.53918400
C -9.25388500 0.28386000 -0.54344400

C -8.87466600 -0.92653000 0.05027100
C -7.61516100 -1.08315900 0.63302600
C -10.61548500 0.45470600 -1.16911700
S -5.11561100 -0.18528000 1.38568400
O -5.09095000 -1.48842900 2.07416300
O -4.81251300 1.03254200 2.15401200
H 0.33440700 2.92407500 -3.56714000
H 1.80494400 1.96665800 -3.03821700
H 0.90396800 -0.12028900 -4.09147500
H -0.59723800 0.76402100 -4.66772800
H -1.98748400 -0.15617600 0.56543200
H -2.91833800 1.30106000 0.95164900
H -5.14569500 -1.56054100 -1.09695800
H -3.58636300 -1.07170800 -1.74064400
H -2.61082000 -2.34330000 0.40186900
H -4.14344800 -3.22444700 0.30376500
H -2.69460400 -4.23870400 -1.09178800
H -2.98694800 2.43951200 -2.73839900
H -4.28134700 1.41670500 -2.07529600
H -3.71085900 2.81691100 -1.15929100
H -6.38073500 2.04555900 0.03752900
H -8.61398800 2.29802900 -0.99007200
H -9.57238300 -1.75975300 0.06170500
H -7.33260300 -2.02076800 1.09910800
H -10.53188400 0.76015800 -2.21950200
H -11.19430300 -0.47293800 -1.12931700
H -11.18961000 1.23521800 -0.65391900

1q

Opt @ SMD(THF)/B3LYP/6-31G(d)/SDD
SCF Done: E(B3LYP) = -1379.43075420 a.u.
Zero-point correction = 0.401657 Hartree/Particle
Sum of electronic and thermal Free Energies = -1379.088720 a.u.

C 2.13215400 -0.85168600 -0.36601400
C 4.56976700 -0.38198400 0.44090700
C 6.02781000 -0.45209400 0.18182400
C 5.48860900 0.15062400 1.47484000
C 1.42296500 0.20783100 -1.20001700
C 0.41872900 1.49545500 0.73836000
C 1.07563900 2.86735900 0.57335800
O 1.21772600 3.39638500 1.89198900
C 1.38243800 -2.15555000 -0.09013700
C 3.36199600 -0.62359600 0.04952800
N 0.22763300 0.73912100 -0.50654200
C -2.46460800 0.26179500 -0.41983500
C -2.61556300 -1.12858500 -0.48015500
C -3.62559000 -1.73384600 0.25977900
C -4.49461100 -0.97544900 1.06387900
C -4.32576300 0.41393600 1.09910000
C -3.31900500 1.03976400 0.36069300
C -5.58114900 -1.65190500 1.86170300
S -1.17158200 1.04590200 -1.38549500
O -1.46659100 2.48963800 -1.40681900
O -1.04039700 0.32088800 -2.65955400
H 6.51130300 -1.42670600 0.23218800
H 6.44959800 0.22239000 -0.56211800

H 5.54722500 1.23078500 1.60162100
H 5.60853000 -0.41804800 2.39590000
H 2.11983800 1.01741500 -1.44255300
H 1.07581100 -0.22264500 -2.14115000
H -0.54941500 1.61615900 1.23376200
H 1.03908900 0.88074300 1.39844600
H 2.05521000 2.76427700 0.08326300
H 0.44620500 3.51043400 -0.05476900
H 1.61417300 4.27840400 1.80783100
H 0.34868300 -1.87118800 0.15196200
H -1.96201900 -1.72595000 -1.10750400
H -3.74786200 -2.81312100 0.20997900
H -4.99221400 1.01974700 1.70755800
H -3.20631100 2.11823700 0.38299500
H -5.15574300 -2.34555700 2.59803500
H -6.19553300 -0.92344700 2.39930200
H -6.24068900 -2.24043600 1.21201700
C 1.33756100 -3.04302600 -1.35037100
H 0.73181200 -3.93896000 -1.16600800
H 0.90219700 -2.52008700 -2.20926600
H 2.34690300 -3.36907000 -1.63075000
C 1.94908500 -2.93629600 1.10117300
H 1.34503400 -3.83123800 1.29192000
H 2.97848800 -3.26293300 0.91069200
H 1.95288200 -2.32926400 2.01375600

IntA-1q
Opt @ SMD(THF)/B3LYP/6-31G(d)/SDD
SCF Done: E(B3LYP) = -3143.51923242 a.u.
Zero-point correction = 1.155251 Hartree/Particle
Sum of electronic and thermal Free Energies = -3142.469338 a.u.

C -1.58765800 -1.07427500 0.65129900
C -0.82781300 -1.26980200 3.15707000
C -0.01154800 -1.21394800 4.38424900
C -1.50543700 -1.49295800 4.46295300
C -2.27471700 0.25120200 0.28796900
C -4.24169700 -0.03642900 1.86345700
C -4.11330100 1.19247600 2.76785300
O -4.38873200 0.73479200 4.09250300
C -1.95019100 -2.30953000 -0.18633900
C -1.00823200 -1.16190200 1.87836900
N -3.72911900 0.12813300 0.49440900
C -5.97564200 -0.51127800 -0.93687300
C -5.60544400 -1.62575700 -1.69891200
C -6.54407100 -2.62480800 -1.93673200
C -7.85244400 -2.53142500 -1.43004700
C -8.19549200 -1.40255400 -0.67472200
C -7.26852800 -0.38841700 -0.42673000
C -8.86363200 -3.61259100 -1.71818400
S -4.78107800 0.79217700 -0.64663400
O -5.50981200 1.93034600 -0.06302300
O -3.99053200 0.99256500 -1.87212100
H 0.66947900 -2.04043800 4.57959100
H 0.35100100 -0.23817000 4.70310000
H -2.17835900 -0.70993100 4.80795700
H -1.82180400 -2.50834500 4.69506000
H -1.85584700 1.05879100 0.89519800

H -2.11129300 0.50198800 -0.75856400
H -5.28800300 -0.35139500 1.81214700
H -3.69274000 -0.86402000 2.32273200
H -3.09963500 1.61337900 2.70246000
H -4.82354200 1.96701600 2.45508900
H -4.44829100 1.51596900 4.66615100
H -3.04245000 -2.38005200 -0.07224800
H -4.60387200 -1.70724100 -2.10829400
H -6.26089400 -3.49082900 -2.52985900
H -9.20249400 -1.30969600 -0.27666300
H -7.54759700 0.48804600 0.14771300
H -8.42754700 -4.61014900 -1.59182500
H -9.73534900 -3.53147200 -1.06154200
H -9.22018300 -3.54622400 -2.75475700
C 3.38590700 2.17593400 -0.53188300
C 3.98073900 0.90035100 -0.36708800
C 5.38874700 0.80401600 -0.39231300
C 6.20572900 1.91390100 -0.58686600
C 5.62252500 3.16618800 -0.76800400
C 4.23600700 3.28190800 -0.73673200
C 1.92157600 2.52925500 -0.46949300
C 1.14297300 2.57917200 -1.65379400
C -0.13012700 3.15796400 -1.60019400
C -0.65812600 3.71144200 -0.42648000
C 0.11513600 3.62395700 0.73412800
C 1.39490100 3.04742500 0.73881100
H 5.86742000 -0.15881200 -0.26584500
H 7.28511000 1.79363700 -0.60006900
H 6.23762900 4.04766400 -0.92629600
H 3.78114500 4.25987500 -0.86201100
H -0.72208800 3.21464500 -2.51058900
H -0.26729100 4.03911500 1.66147700
C 1.68887600 2.10558800 -3.00145300
C 0.70564800 1.20228700 -3.76715900
H 1.18015200 0.81642700 -4.67765900
H 0.38814500 0.34467500 -3.16197700
H -0.19532600 1.74494900 -4.07549500
C -2.00325400 4.43201100 -0.48138000
H -2.66135500 3.83262000 -1.12489600
C -2.69721700 4.58848100 0.87816600
H -3.69994300 5.00793300 0.73806000
H -2.80773700 3.62904000 1.39627100
H -2.14685700 5.26912000 1.53944500
C -1.83995500 5.81105800 -1.15540900
H -1.40230700 5.72095400 -2.15594000
H -2.81260600 6.30826600 -1.25542700
H -1.18651100 6.46086200 -0.55934000
C 2.19657100 3.05469300 2.04255500
H 3.13228300 2.51494600 1.86849200
C 1.46184200 2.32499700 3.18238400
H 0.52858800 2.83164400 3.45648700
H 1.21601300 1.29545500 2.89630000
H 2.09364600 2.28817600 4.07879300
C 2.57056900 4.48759600 2.46872400
H 3.18433700 4.46855700 3.37785000
H 3.14139500 5.00137300 1.68692900
H 1.67732200 5.08746100 2.68111800
C 2.10671000 3.30462200 -3.87640700

H 2.53483100 2.95740700 -4.82504200
H 1.24441500 3.94123500 -4.10936800
H 2.85720700 3.92534000 -3.37429400
H 2.59120600 1.51587700 -2.80888900
P 3.07141200 -0.70403100 -0.16869700
C 4.09386400 -1.66681000 1.11740300
C 3.18831100 -2.40354800 2.13011500
C 5.17284100 -2.63672600 0.58149200
H 4.60163200 -0.85828000 1.66027800
C 4.01053500 -3.01387400 3.27793200
H 2.63285900 -3.19921400 1.61420600
H 2.44474200 -1.71114200 2.54007300
C 5.99751900 -3.23270800 1.73691800
H 4.68871300 -3.45316600 0.03251500
H 5.84771800 -2.14212300 -0.12217100
C 5.10989700 -3.94944000 2.76078900
H 3.33891500 -3.55165700 3.95934400
H 4.46830700 -2.20141900 3.86114900
H 6.74336200 -3.92413400 1.32486900
H 6.55563200 -2.42702600 2.23573500
H 5.71604700 -4.32193700 3.59613000
H 4.64744700 -4.82868800 2.28851800
C 3.07646600 -1.49115500 -1.88466900
C 4.40379100 -1.48281700 -2.67059000
C 2.44944400 -2.90252700 -1.87456600
H 2.38062300 -0.82504600 -2.41520900
C 4.18006400 -2.00029200 -4.10368000
H 5.13990000 -2.12271300 -2.17126600
H 4.82508600 -0.47328600 -2.70736600
C 2.23909800 -3.41813300 -3.30874600
H 3.10825600 -3.59671800 -1.33850400
H 1.49455600 -2.88984400 -1.33607700
C 3.54440300 -3.39678800 -4.11591500
H 5.13931400 -2.01185400 -4.63651500
H 3.52878100 -1.29810600 -4.64402800
H 1.82716900 -4.43472600 -3.27291500
H 1.48985000 -2.79019100 -3.81234100
H 3.35611300 -3.71864700 -5.14793200
H 4.25042500 -4.12098000 -3.68342400
Au 0.79133900 -0.70347200 0.51353200
C -1.34562000 -3.61474300 0.34063100
H -1.70791600 -4.45789800 -0.25801700
H -0.25044400 -3.60405800 0.27660100
H -1.62248100 -3.80058000 1.38364700
C -1.66453200 -2.12660300 -1.68632900
H -2.03404300 -2.99677400 -2.24111100
H -2.15138100 -1.23828100 -2.09978900
H -0.58790700 -2.04388800 -1.87358700

IntC-1q
Opt @ SMD(THF)/B3LYP/6-31G(d)/SDD
SCF Done: E(B3LYP) = -3143.52068970 a.u.
Zero-point correction = 1.156018 Hartree/Particle
Sum of electronic and thermal Free Energies = -3142.470700 a.u.

C 3.80443300 0.46826700 1.79223400
C 3.54463600 -0.89813500 1.52247500
C 4.26029200 -1.87759200 2.24415200

C 5.20978400 -1.54302300 3.20538200
C 5.46802900 -0.19964500 3.47084900
C 4.77004700 0.77985100 2.77035500
C 3.14055200 1.66450200 1.16101800
C 3.74914000 2.30901600 0.05703200
C 3.23350600 3.53901700 -0.37517200
C 2.14862400 4.15921900 0.25101400
C 1.55792900 3.49916300 1.33498500
C 2.03423000 2.27044200 1.81008000
H 4.08043700 -2.92925200 2.05573800
H 5.73880100 -2.32845200 3.73744500
H 6.20293100 0.08665900 4.21801200
H 4.96472600 1.82690600 2.98233900
H 3.71186700 4.04776000 -1.20877900
H 0.72327800 3.96910800 1.84839100
C 4.99953900 1.74928600 -0.62407200
C 4.87964500 1.69624100 -2.15773100
H 5.76458600 1.21102100 -2.58744400
H 3.99751800 1.12790600 -2.47598900
H 4.81146000 2.69744700 -2.59891000
C 1.68305200 5.53973500 -0.19834200
H 2.19809200 5.76149300 -1.14271100
C 0.16997300 5.60715300 -0.46657100
H -0.10578400 6.59697900 -0.85012000
H -0.13788800 4.86001800 -1.20732000
H -0.40920300 5.43543000 0.44856300
C 2.10229300 6.61867700 0.81972700
H 3.18605300 6.61120900 0.98464000
H 1.82021400 7.61684800 0.46243800
H 1.61387400 6.45874800 1.78895900
C 1.39373200 1.66373400 3.06058400
H 1.82109200 0.66760800 3.21108300
C -0.12847300 1.48489800 2.92301100
H -0.64777200 2.44529000 2.82335600
H -0.37713300 0.87510100 2.04672000
H -0.53282600 0.98253800 3.81053200
C 1.72893900 2.49673000 4.31349700
H 1.30237900 2.02929800 5.20963200
H 2.81165500 2.58223700 4.46026500
H 1.31935100 3.51129700 4.23672800
C 6.25287700 2.54856700 -0.21451500
H 7.15072500 2.11777500 -0.67493800
H 6.17710500 3.59374800 -0.53855200
H 6.39460600 2.54294200 0.87190600
H 5.14300700 0.72191400 -0.27426900
P 2.35315700 -1.55539700 0.26099400
C 1.54743300 -3.03460200 1.14107600
C 0.01274800 -3.01832700 0.98037600
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