Supporting Information

Construction of Polysubstituted Spiro[2.3] or [3.3] Cyclic Frameworks Fused with a Tosylated Pyrrolidine Promoted by Visible-Light-Induced Photosensitization

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(1) General Information.

Melting points were determined on a digital melting point apparatus, and temperatures were uncorrected. NMR spectra were measured on a Brucker AC 400 or Agilent (400 MHz) spectrometer. Proton nuclear magnetic resonance (^{1}H NMR) spectra, carbon nuclear magnetic resonance (^{13}C NMR) spectra, and fluorine nuclear magnetic resonance (^{19}F NMR) spectra were recorded at 400, 100 MHz and 376 MHz, respectively. Data are presented as follows: chemical shift (ppm), multiplicity (s =singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet), coupling constants in Hertz (Hz) and integration. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Mass and High resolution mass spectra (HRMS) spectra were recorded by ESI method. The employed solvents were dry up by standard methods when necessary. Commercially obtained reagents were used without further purification. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF254) were used. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure. Fluorescence spectra for emission and excitation were obtained on a Hitachi F-4600 FL Spectrophotometer.

(2) Reaction Setup.

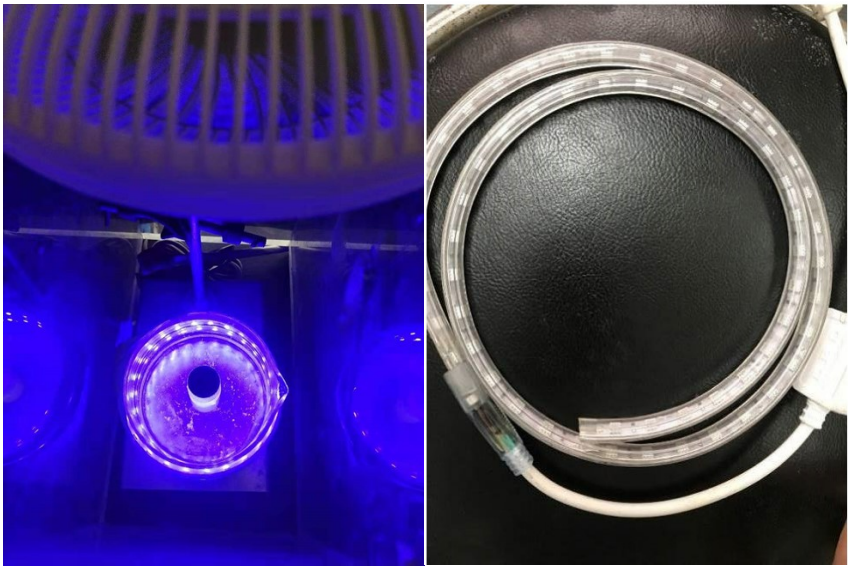


Figure S1. 8 W LEDs (450–470 nm) strip and reaction setup.

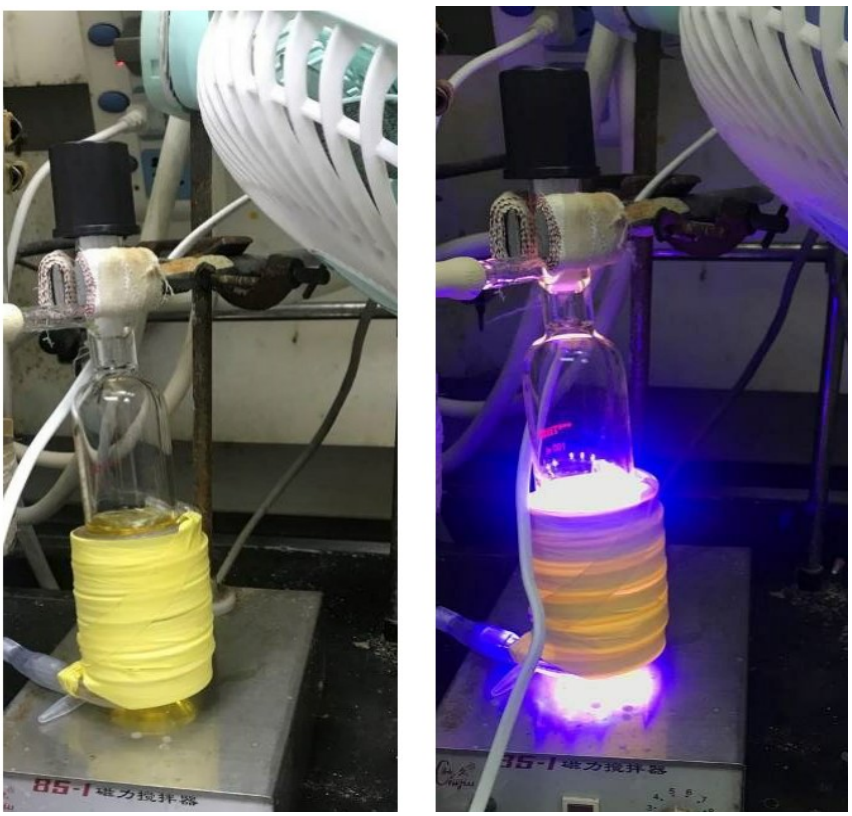
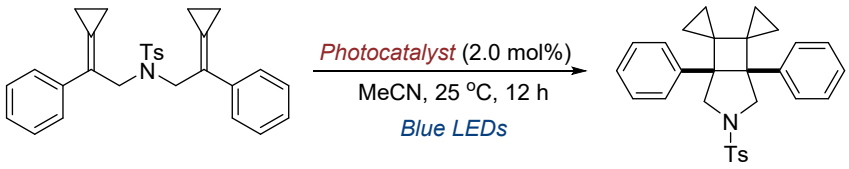


Figure S2. Reaction setup for scale-up synthesis.

As depicted in the pictures, the reactions were carried out in oven-dried sealed tubes. Each reaction setup is equipped with a fan to maintain the reaction temperature. The range of light source wavelength is 450-470 nm.

(3) Optimization of Reaction Conditions.

Table S1. Optimization of the Photocatalyst.

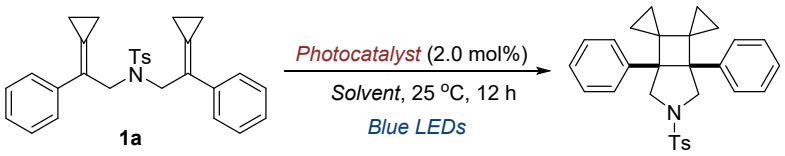


1a **2a**

Entry[a]	*Photocatalyst*	E_T (kcal/mol)	Yield (%)[b]
1	$[Ir(dtbbpy)[dF(CF_3)ppy]_2]PF_6$	60.8	97
2	fac-$Ir(ppy)_3$	57.8	< 5
3	$[Ru(bpy)_3](PF_6)_2$	46.5	< 5
4	$[Ru(bpz)_3](PF_6)_2$	48.4	< 5
5	$[Ir(ppy)_2(4,4'\text{-dtb-bpy})]PF_6$	49.2	< 5
6	$[Ru(phen)_3](PF_6)_2$	48.4	< 5
7	Xanthone	74.3	< 5
8	Thioxanthene	63.4	< 5
9	$[Ir(2',4'\text{-dF-5-}CF_3\text{-ppy})_2(bpy)]PF_6$	60.4	92
10	$Ir(dFppy)_2pic$	61.1	95

[a] **1a** (0.2 mmol), and PC (0.004 mmol, 2.0 mol%) in solvent (4.0 mL) at 25 °C, 8 W blue LEDs. [b] Determined by ^{1}H-NMR spectroscopy of crude reaction mixtures with 1,3,5-trimethoxybenzene as an internal standard.

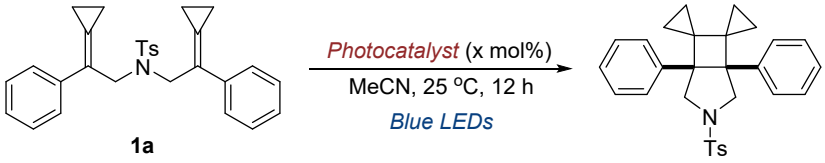
Table S2. Optimization of the Solvent.



Entry[a]	*Photocatalyst*	Solvent	Yield (%)[b]
1	$[Ir(dtbbpy)[dF(CF_3)ppy]_2]PF_6$	MeCN	97
2	$[Ir(dtbbpy)[dF(CF_3)ppy]_2]PF_6$	THF	81
3	$[Ir(dtbbpy)[dF(CF_3)ppy]_2]PF_6$	DCE	96
4	$[Ir(dtbbpy)[dF(CF_3)ppy]_2]PF_6$	Toluene	55
5	$[Ir(dtbbpy)[dF(CF_3)ppy]_2]PF_6$	Et_2O	80
6	$[Ir(dtbbpy)[dF(CF_3)ppy]_2]PF_6$	DMSO	60
7	$[Ir(dtbbpy)[dF(CF_3)ppy]_2]PF_6$	DCM	71
8	$[Ir(dtbbpy)[dF(CF_3)ppy]_2]PF_6$	DMF	57

[a] **1a** (0.2 mmol), and PC (0.004 mmol, 2.0 mol%) in solvent (4.0 mL) at 25 °C, 8 W blue LEDs. [b] Determined by ^{1}H-NMR spectroscopy of crude reaction mixtures with 1,3,5-trimethoxybenzene as an internal standard.

Table S3. Optimization of the Employed Amount of Photocatalyst.

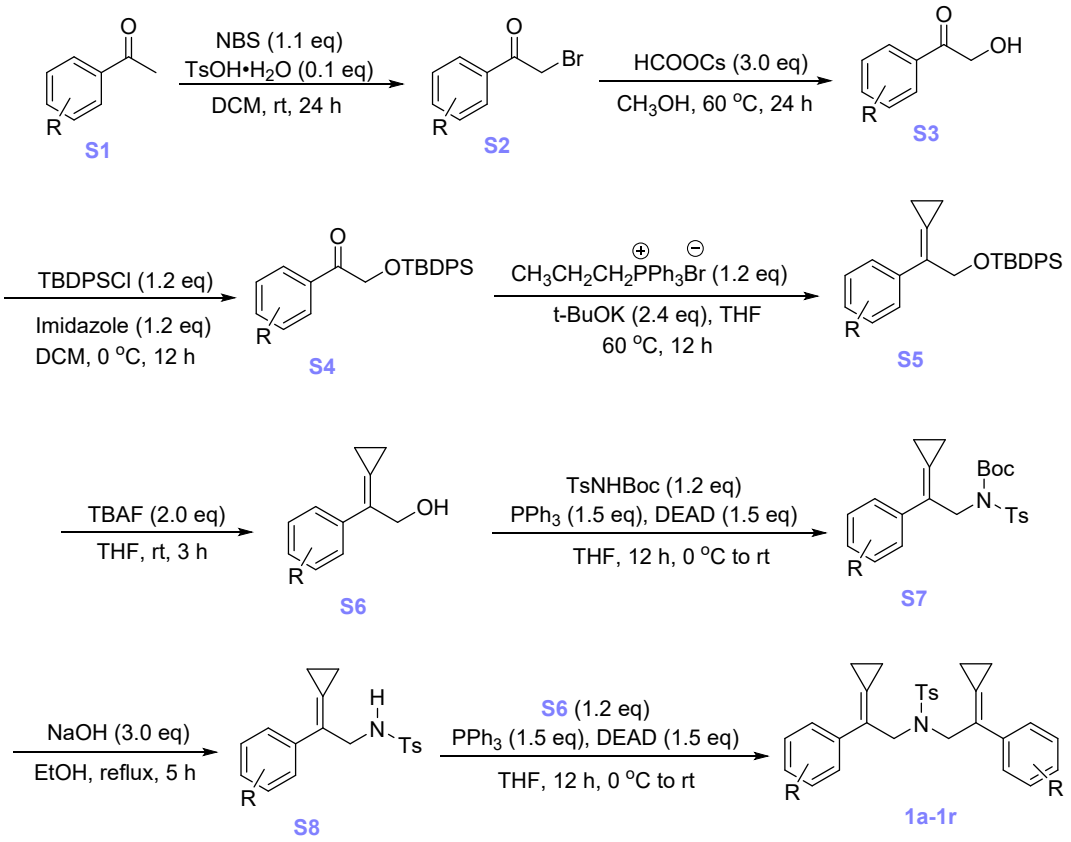


Entry	*Photocatalyst*	Yield (%)[b]
1	$[Ir(dtbbpy)[dF(CF_3)ppy]_2]PF_6$ (2.0 mol%)	97
2	$[Ir(dtbbpy)[dF(CF_3)ppy]_2]PF_6$ (1.5 mol%)	96
3	$[Ir(dtbbpy)[dF(CF_3)ppy]_2]PF_6$ (1.0 mol%)	91
4	$[Ir(dtbbpy)[dF(CF_3)ppy]_2]PF_6$ (0.5 mol%)	81
5	-	0
6[c]	$[Ir(dtbbpy)[dF(CF_3)ppy]_2]PF_6$ (2.0 mol%)	0

[a] **1a** (0.2 mmol), and PC (x mol%) in solvent (4.0 mL) at 25 °C, 12 h, 8 W blue LEDs. [b] Determined by ^{1}H-NMR spectroscopy of crude reaction mixtures with 1,3,5-trimethoxybenzene as an internal standard. [c] Under dark conditions.

(4) General Procedure for the Preparation of Starting Materials.

4.1 General Procedure for the Synthesis of Compounds 1a-1s.



Compound S1 to Compound S2:

A solution of **S1** (30.0 mmol) and $TsOH \cdot H_2O$ (3.0 mmol) in CH_2Cl_2 (100.0 mL) was stirred at room temperature. Then, *N*-bromosuccinimide (33.0 mmol) is gradually added. After stirring at room temperature for 24 hours, the starting material disappeared as evidenced by TLC and was quenched by the addition of water. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10 / 1) to afford the products **S2** in moderate yields.

Compound S2 to Compound S3:

A solution of **S2** (25.0 mmol) and cesium formate (HCO_2Cs, 3.0 equiv) in dry MeOH (80.0 mL) was heated under reflux for 24 hours. When the reaction was completed, the reaction mixture was washed by water and extracted with CH_2Cl_2 for 3 times. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue was used

directly into the next reaction without further purification.[1]

Compound S3 to Compound S4:

Tert-Butylchlorodiphenylsilane (30.0 mmol) was added dropwise to a stirred solution of **S3** and imidazole (30.0 mmol) in CH_2Cl_2 (50.0 mL) at 0 °C under argon. Then, the resulting mixture was stirred at 0 °C for 12 hours. The reaction mixture was treated with water and extracted with CH_2Cl_2. The organic layer was separated, dried over anhydrous Na_2SO_4 and the solvents was partially evaporated in vacuo. The solvent was completely removed under vacuum and the residue was purified by a flash column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 20 / 1) to afford the products **S4** in moderate yields.[2]

Compound S4 to Compound S5:

A solution of 3-bromopropyltriphenylphosphonium bromide (24.0 mmol) and *tert*-BuOK (48.0 mmol) in dry THF (30.0 mL) was stirred at 60 °C in an oil bath under argon for 0.5 h. Afterward compound **S4** (20.0 mmol) in dry THF (30.0 mL) was added and the reaction solution was stirred at 60 °C in an oil bath for another 12 hours. Upon completion, the reaction mixture was cooled to room temperature and the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether / ethyl acetate = 80 / 1) to afford the products **S5** in moderate yields.

Compound S5 to Compound S6:

To a solution of **S5** (15.0 mmol) in THF (20.0 mL) was added a 1.0 M solution of TBAF in THF (30.0 mL, 30.0 mmol) at room temperature. The resulting solution was stirred for 3 hours. The reaction mixture was evaporated in vacuo and the crude mixture was purified by a silica gel flash column chromatography (eluent: petroleum ether / ethyl acetate = 4 / 1) to afford the products **S6** in moderate yields.

Compound S6 to Compound S7:

N-Boc p-toluenesulfonamide (1.2 equiv) was dissolved in dry THF (20.0 mL) and triphenylphosphine (1.5 equiv) was added. The reaction solution was stirred under argon atmosphere and the **S6** (10.0 mmol, 1.0 equiv) was added. Immediately afterward, diethyl azodicarboxylate (12.0 mmol, 1.2 equiv)

was added dropwise at 0 °C, and then the reaction mixture was naturally restored to room temperature for 12 hours. The reaction mixture was evaporated in vacuo and the crude mixture was purified by a silica gel flash column chromatography (eluent: petroleum ether / ethyl acetate = 10 / 1) to afford the products **S7** in moderate yields.[3]

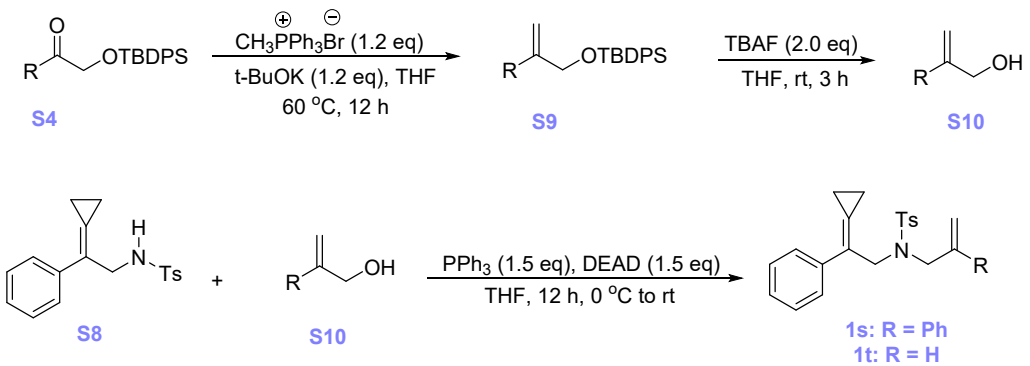
Compound S7 to Compound S8:

Product **S7** (8.0 mmol) was dissolved in ethanol (30.0 mL) and stirred continuously, then NaOH (3.0 equiv) was added and the resulting mixture was stirred under reflux for 3 hours. The starting material disappears as evidenced by TLC. The mixture was treated with water and extracted with CH_2Cl_2. The organic layer was separated, dried over anhydrous Na_2SO_4 and the solvent was evaporated in vacuo and the residue was used directly into the next reaction without further purification.

Compound S8 to 1a-1s:

Compound **S8** (1.2 equiv) was dissolved in dry THF (8.0 mL) and triphenylphosphine (1.5 equiv) was added. The reaction solution was stirred under argon atmosphere and the compound **S6** (1.0 mmol, 1.0 equiv) was added. Immediately afterward, diethyl azodicarboxylate (1.2 equiv) was added dropwise at 0 °C, and then the reaction mixture was naturally restored to room temperature for 12 hours. The reaction mixture was evaporated in vacuo and the crude mixture was purified by a silica gel flash column chromatography (eluent: petroleum ether / ethyl acetate = 10 / 1) to afford the products **1a-1s** in moderate yields.

4.2 General Procedure for the Synthesis of Compounds 1t and 1u.



Compound S4 to Compound S9:

A solution of methyltriphenylphosphine bromide (24.0 mmol) and *tert*-BuOK (24.0 mmol) in THF (30.0 mL) was stirred at 60 °C in an oil bath under argon for 0.5 h. Afterwards compound **S4** (20.0 mmol) in THF (30.0 mL) was added and the reaction solution was stirred at 60 °C in an oil bath for another 12 h. Upon completion, the reaction was cooled to room temperature and the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether / ethyl acetate = 80 / 1) to afford the products **S9** in moderate yields.

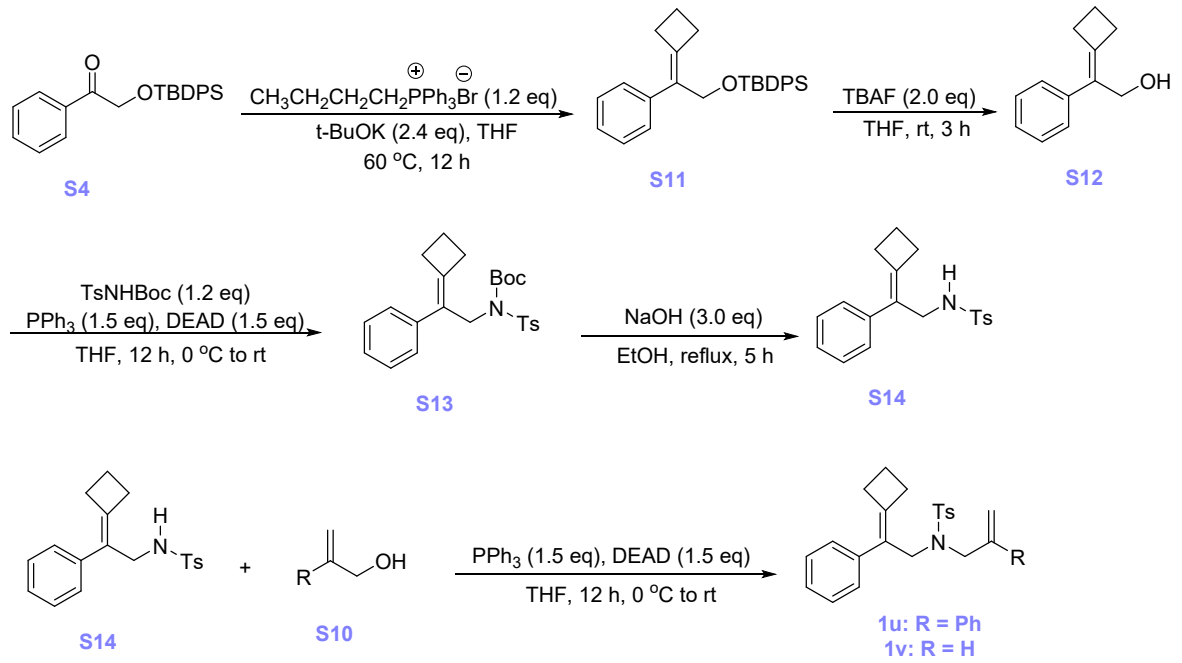
Compound S9 to Compound S10:

To a solution of **S9** (15.0 mmol) in THF (20.0 mL) was added a 1.0 M solution of TBAF in THF (30.0 mL, 30.0 mmol) at room temperature. The resulting solution was stirred for 3 h. The reaction mixture was evaporated in vacuo and the crude mixture was purified by a silica gel flash column chromatography (eluent: petroleum ether / ethyl acetate = 4 / 1) to afford the products **S10** in moderate yields.

Compound S10 to 1t and 1u:

Compound **S8** (1.2 eq) was dissolved in dry THF (8.0 mL) and triphenylphosphine (1.5 equiv) was added. The reaction solution was stirred under argon atmosphere and the compound **S10** (1.0 mmol, 1.0 equiv) was added. Immediately afterward, diethyl azodicarboxylate (1.2 equiv) was added dropwise at 0 °C, and then the reaction mixture was naturally restored to room temperature for 12 hours. The reaction mixture was evaporated in vacuo and the crude mixture was purified by a silica gel flash column chromatography (eluent: petroleum ether / ethyl acetate = 10 / 1) to afford the products **1t** and **1u** in moderate yields of 88% and 69%.

4.3 General Procedure for the Synthesis of Compounds 1v and 1w.



Compound S4 to Compound S11:

A solution of butyltriphenyl-phosphoniubromide (24.0 mmol) and *tert*-BuOK (48.0 mmol) in THF (30.0 mL) was stirred at 60 °C in an oil bath under argon for 0.5 h. Afterward compound **S4** (20.0 mmol) in THF (30.0 mL) was added and the reaction solution was stirred at 60 °C in an oil bath for another 12 h. Upon completion, the reaction was cooled to room temperature and the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether / ethyl acetate = 80 / 1) to afford the products **S11** in moderate yields.

Compound S11 to Compound S12:

To a solution of **S11** (15.0 mmol) in THF (20.0 mL) was added a 1.0 M solution of TBAF in THF (30.0 mL, 30.0 mmol) at room temperature. The resulting solution was stirred for 3 h. The reaction mixture was evaporated in vacuo and the crude mixture was purified by a silica gel flash column chromatography (eluent: petroleum ether / ethyl acetate = 4 / 1) to afford the products **S12** in moderate yields.

Compound S12 to Compound S13:

N-Boc p-toluenesulfonamide (1.2 equiv) was dissolved in dry THF (20.0 mL) and triphenylphosphine (1.5 equiv) was added. The resulting solution was stirred under argon atmosphere and the compound

S12 (10.0 mmol, 1.0 equiv) was added. Immediately afterward, diethyl azodicarboxylate (12.0 mmol, 1.2 equiv) was added dropwise at 0 °C, and then the reaction mixture was naturally restored to room temperature for 12 hours. The reaction mixture was evaporated in vacuo and the crude mixture was purified by a silica gel flash column chromatography (eluent: petroleum ether / ethyl acetate = 10 / 1) to afford the products **S13** in moderate yields.

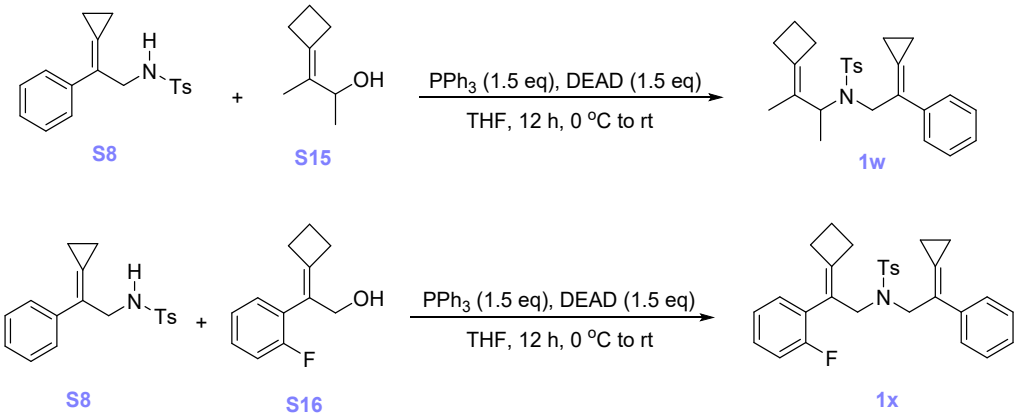
Compound S13 to Compound S14:

Product **S13** (8.0 mmol) was dissolved in ethanol (30.0 mL) and stirred continuously, then NaOH (3.0 equiv) was added and the reaction mixture was stirred under reflux for 3 hours. The starting material disappeared as evidenced by TLC. Then, the reaction mixture was treated with water and extracted with CH_2Cl_2. The organic layer was separated, dried over anhydrous Na_2SO_4 and the solvent was evaporated in vacuo and the residue was used directly into the next reaction without further purification.

Compound S14 to 1v and 1w:

Compound **S14** (1.2 equiv) was dissolved in dry THF (8.0 mL) and triphenylphosphine (1.5 equiv) was added. The reaction solution was stirred under argon atmosphere and the compound **S10** (1.0 mmol, 1.0 equiv) was added. Immediately afterward, diethyl azodicarboxylate (1.2 equiv) was added dropwise at 0 °C, and then the reaction mixture was naturally restored to room temperature for 12 hours. The reaction mixture was evaporated in vacuo and the crude mixture was purified by a silica gel flash column chromatography (eluent: petroleum ether / ethyl acetate = 10 / 1) to afford the products **1v** and **1w** in moderate yields of 86% and 75%.

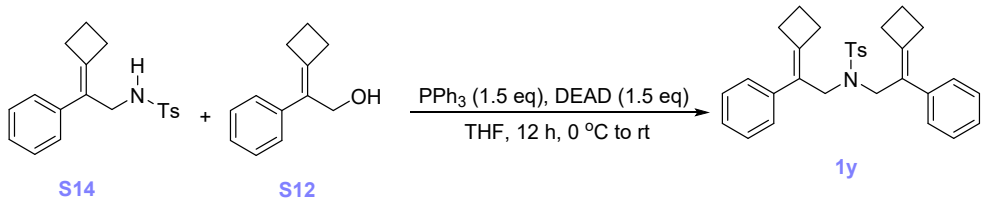
4.4 General Procedure for the Synthesis of Compounds 1x and 1y.



Compound S8 to 1x and 1y:

Compound **S8** (1.2 equiv) was dissolved in dry THF (8.0 mL) and triphenylphosphine (1.5 equiv) was added. The solution mixture was stirred under argon atmosphere and the compound **S15** or **S16** (1.0 mmol, 1.0 equiv) was added. Immediately afterward, diethyl azodicarboxylate (1.2 equiv) was added dropwise at 0 °C, and then the reaction mixture was naturally restored to room temperature for 12 hours. The reaction mixture was evaporated in vacuo and the crude mixture was purified by a silica gel flash column chromatography (eluent: petroleum ether / ethyl acetate = 10 / 1) to afford the products **1x** and **1y** in good yields of 81% and 89%.

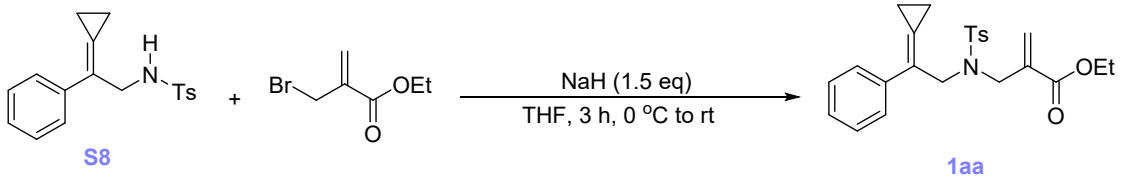
4.5 General Procedure for the Synthesis of Compound 1z.



Compound S14 to Compound 1z:

Compound **S14** (1.2 equiv, 1.2 mmol) was dissolved in dry THF (8.0 mL) and triphenylphosphine (1.5 equiv) was added. The reaction solution was stirred under argon atmosphere and the compound **S12** (1.0 mmol, 1.0 equiv) was added. Immediately afterward, diethyl azodicarboxylate (1.2 equiv) was added dropwise at 0 °C, and then the reaction mixture was naturally restored to room temperature for 12 hours. The reaction mixture was evaporated in vacuo and the crude mixture was purified by a silica gel flash column chromatography (eluent: petroleum ether / ethyl acetate = 10 / 1) to afford the product **1z** in 83% yield.

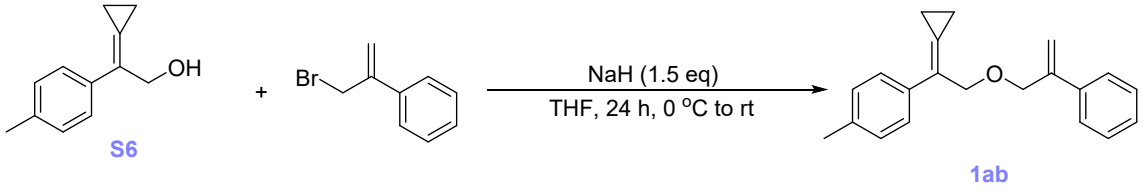
4.6 General Procedure for the Synthesis of Compound 1aa.



Compound S8 to Compound 1aa:

Compound **S8** (1.5 equiv, 1.5 mmol) was dissolved in dry THF (8.0 mL), and then NaH (1.5 equiv) was added at 0 °C. The reaction mixture was stirred for 5 min. Immediately afterward, 3-bromo-2-methyl-2-propenoic acid ethyl ester (1.0 equiv) was added at 0 °C, and then the reaction mixture was naturally restored to room temperature for 3 hours. The reaction mixture was evaporated in vacuo and the crude mixture was purified by a silica gel flash column chromatography (eluent: petroleum ether / ethyl acetate = 40 / 1) to afford the product **1aa** in 67% yield.

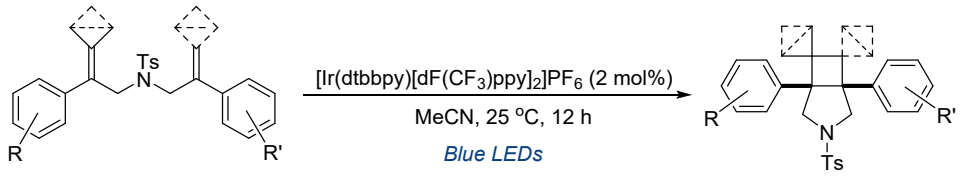
4.7 General Procedure for the Synthesis of Compound 1ab.



Compound S6 to Compound 1ab:

Compound **S6** (1.5 equiv, 1.5 mmol) was dissolved in dry THF (8.0 mL), and then NaH (1.5 equiv) was added at 0 °C. The reaction mixture was stirred for 5 min. Immediately afterward, (3-bromoprop-1-en-2-yl)benzene (1.0 equiv) was added at 0 °C, and then the reaction mixture was naturally restored to room temperature for 24 hours. The reaction mixture was evaporated in vacuo and the crude mixture was purified by a silica gel flash column chromatography (eluent: petroleum ether / ethyl acetate = 40 / 1) to afford the product **1ab** in 85% yield.

(5) General Procedure for the Preparation of 2a – 2ab.



An oven-dried 5.0 mL sealed tube equipped with a Teflon septum and a magnetic stir bar was charged with the photocatalyst (0.004 mmol, 0.02 equiv, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$), and the corresponding starting materials **1a-1z** (0.2 mmol). Then, 2.0 mL of degassed CH_3CN was added via a syringe and the mixture was degassed via argon bubbling for 10 min. The reaction tube was sealed with a Teflon septum. Then, the vail was placed in blue light from an 8 W blue LEDs strip at room temperature (a fan was employed to maintain this temperature). After the indicated time period, the reaction mixture was evaporated in vacuo and the crude mixture was purified by a silica gel flash column chromatography (eluent: petroleum ether / ethyl acetate = 4 / 1) to afford the products in up to 95% yield.

(6) Stern-Volmer Quenching Studies.

The measurements were performed using a 0.2 mM solution of photocatalyst $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$) in 2.0 mL of degassed CH_3CN with varying concentrations of a quencher. The samples were excited at 400 nm and emission intensity was recorded from 425 nm to 575 nm for $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$. Experiments showed that the excited state $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6^*$ was quenched by **1a**.

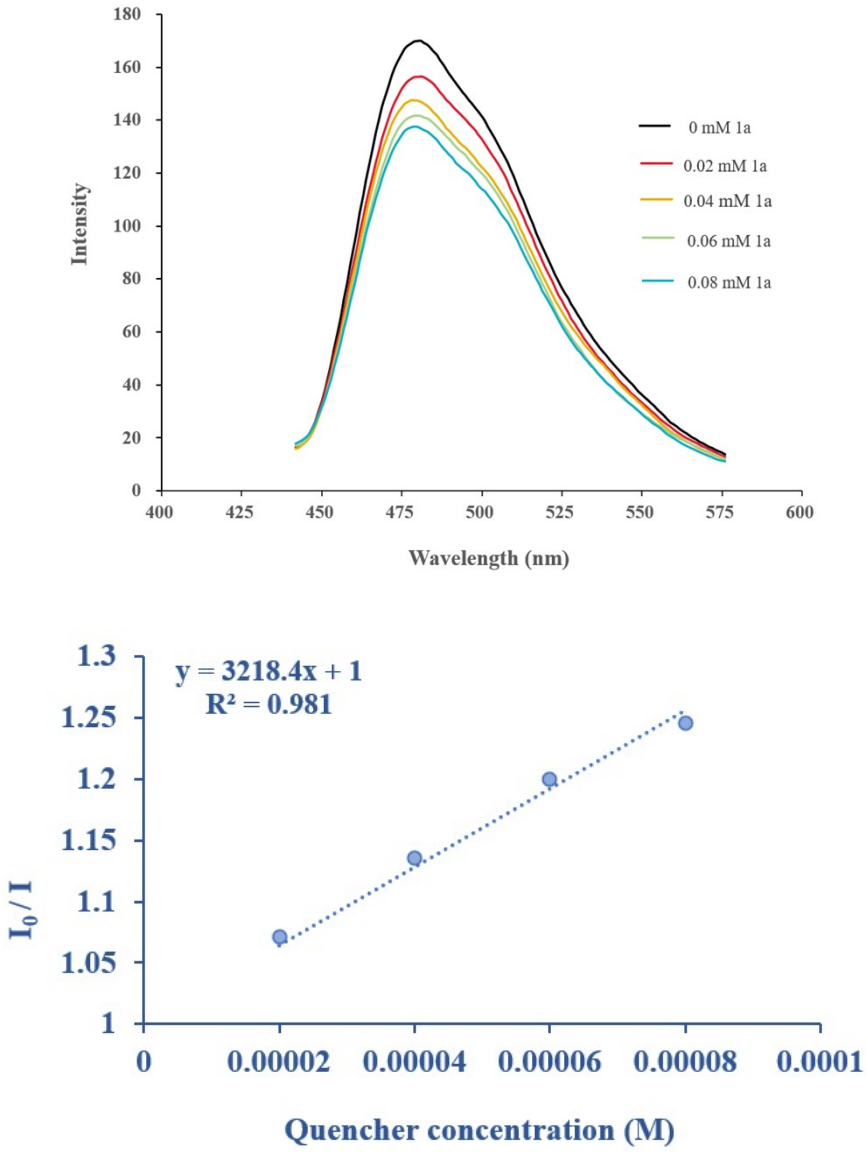


Figure S3. $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ emission quenching with substrate **1a**.

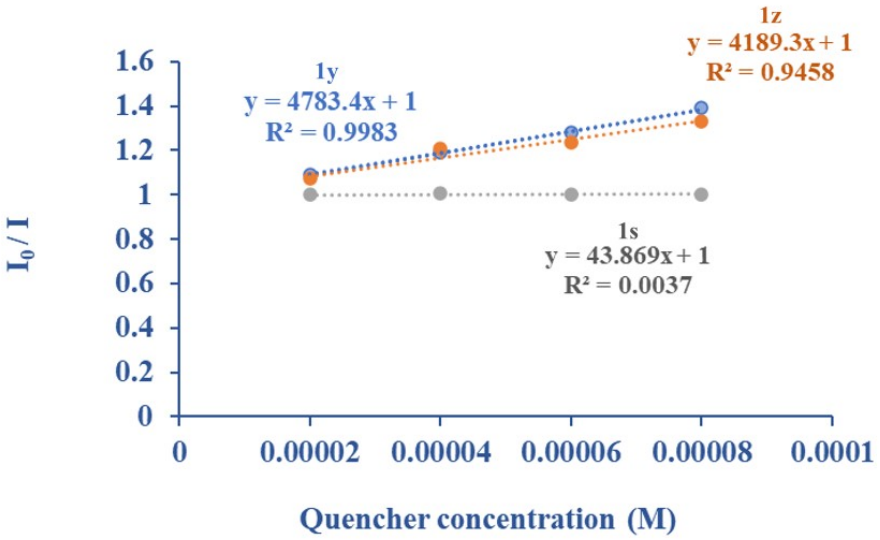
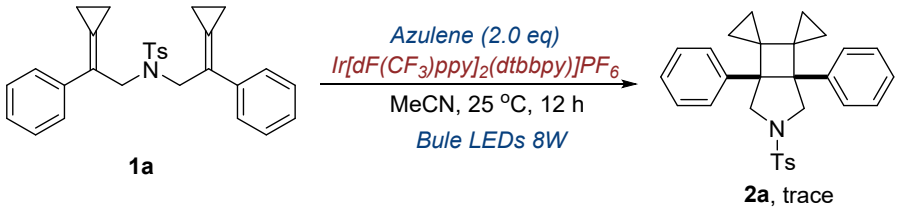


Figure S4. Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 emission quenching with substrates **1s**, **1y**, and **1z**.

(7) Mechanistic Experiment.

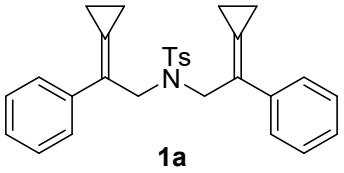


[a] reaction was carried out using **1a** (0.2 mmol, 1.0 eq), Ir[dF(CF_3)ppy]$_2$(dtbbpy)]PF_6 (2.0 mol%), Azulene (0.4 mmol, 2.0 eq) in MeCN (degassed) (2.0 mL) at 25 °C for 12 h.

An oven-dried 5.0 mL sealed tube equipped with a Teflon septum and a magnetic stir bar was charged with the photocatalyst (0.004 mmol, 0.02 equiv, Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6), and the corresponding starting materials **1a** (0.2 mmol) and azulene (2.0 equiv, 51.3 mg). Then, 2.0 mL of degassed CH_3CN was added via a syringe and the mixture was degassed via argon bubbling for 10 min. The reaction tube was sealed with a Teflon septum. Then, the vail was placed in blue light from an 8 W blue LEDs strip at 25 °C for 12 hours. After the indicated time period, the reaction mixture was evaporated in vacuo and the crude mixture was purified by a silica gel flash column chromatography (eluent: petroleum ether / ethyl acetate = 4 / 1). The result showed that the **1a** remained unchanged and the expected product **2a** was not obtained.

(8) Cyclic Voltammetry.

Cyclic voltammogram was recorded using a CHI660E potentiostat and a Pt working electrode (area = 0.03 cm^2), an $Ag/AgNO_3$ reference electrode and a Pt sheet auxiliary electrode. The voltammogram was recorded at room temperature in 0.1 M tetrabutylammonium tetrafluoroborate in MeCN containing **1a** (0.05 mM). The scan rate was 100 mV s^{-1}. Within the range of the diagram, no peaks of **1a** appeared. The oxidation potential of **1a** was determined as that **1a** = E_p^{ox} > + 2.50 V vs $Ag/AgNO_3$.



1a

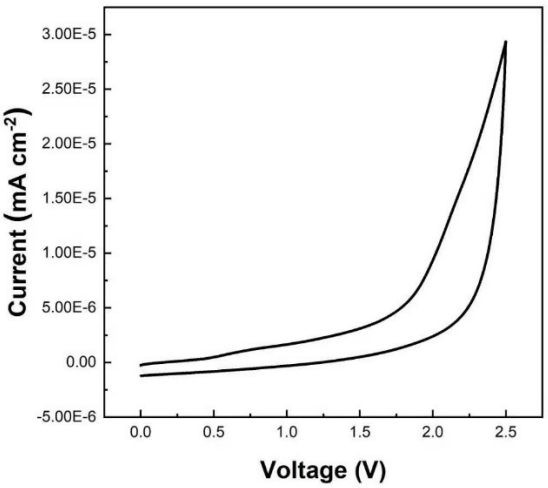
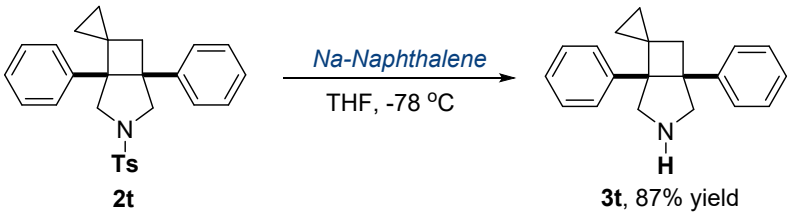


Figure S5. Cyclic voltammetry of **1a**

(9) Transformation of the Product 2t.

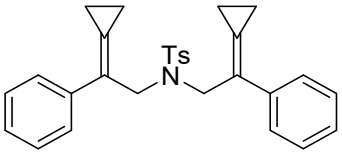


A solution 1 M of sodium naphthalide in THF was prepared as follows: to a stirred solution of naphthalene (5.0 g, 39.0 mmol) in 39 mL of THF, sodium metal (1.1 g, 47.0 mmol) was added under nitrogen atmosphere, and the solution was stirred for 1 h. A solution of **2t** (85.8 mg, 0.2 mmol) in anhydrous THF (4.0 mL) was cooled to -78 °C under nitrogen atmosphere and 1.0 mL (1.0 mmol) of 1 M sodium naphthalenide in THF was added dropwise. The mixture was stirred for 40 min at -78 °C and then 15.0 mL of saturated NH_4Cl aqueous solution was added. The solution was left to warm up to room temperature and the aqueous layer was extracted with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4. Then the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (eluent: ethyl acetate / triethylamine = 25 / 1) to give the corresponding product **3t** (48.1 mg) in 87% yield.[4]

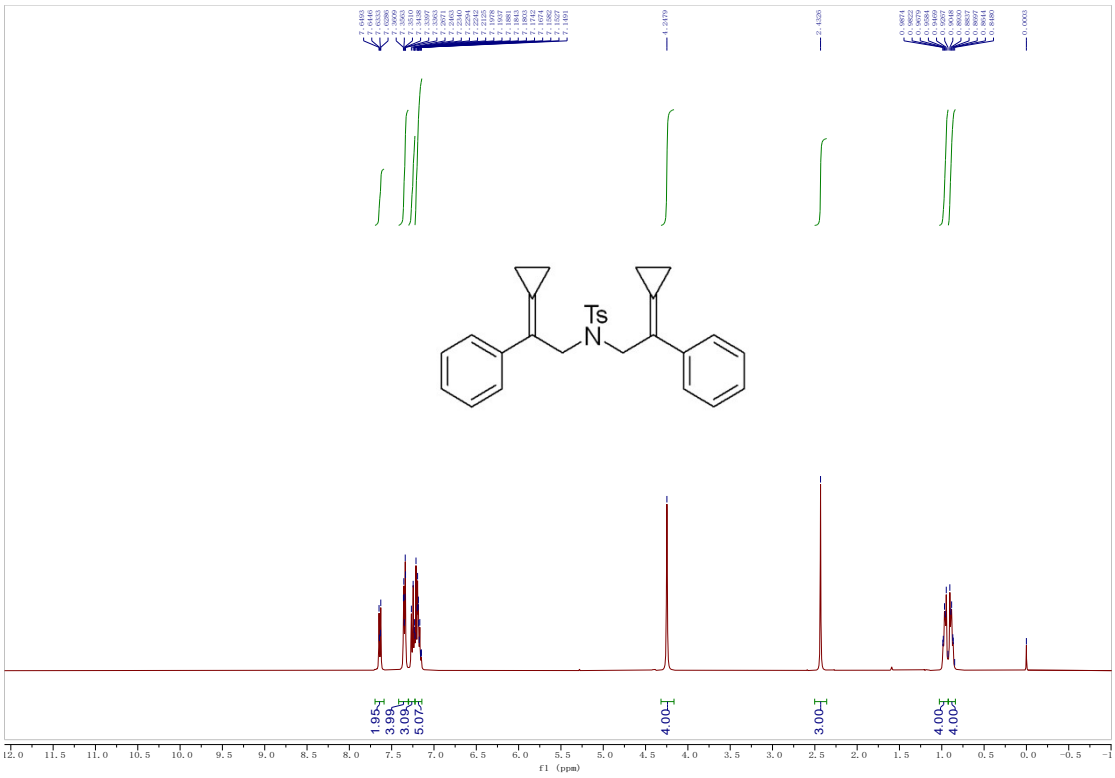
(10) Scale-up Synthesis of 1j.

An oven-dried 100.0 mL sealed tube equipped with a Teflon septum and a magnetic stir bar was charged with the photocatalyst (44.88 mg, 0.04 mmol, 0.01 equiv, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$), and the corresponding starting materials **1j** (4 mmol, 1.96g). Then, 40.0 mL of degassed CH_3CN was added via a syringe and the reaction mixture was degassed via argon bubbling for 20 min. The reaction tube was sealed with a Teflon septum. Then, the vail was placed in blue light from an 8 W blue LEDs strip at 25 °C (a fan was employed to maintain this temperature) for 12 hours. After the indicated time period, the reaction mixture was evaporated in vacuo and the crude mixture was purified by a silica gel flash column chromatography (eluent: petroleum ether / ethyl acetate = 4 / 1) to afford the product **2j** in 84% yield (1.65 g).

(11) Spectroscopic Data of Substrates and Products.



Compound 1a: Yield: 339 mg, 71%; A white solid; M.p.: 158 - 160 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.59 (m, 2H), 7.42 – 7.30 (m, 4H), 7.30 – 7.22 (m, 3H), 7.22 – 7.14 (m, 5H), 4.25 (s, 4H), 2.43 (s, 3H), 1.03 – 0.93 (m, 4H), 0.92 – 0.84 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 138.2, 135.9, 129.1, 127.4, 126.9, 126.2, 126.1, 125.4, 121.6, 51.2, 21.1, 3.7, 1.4; IR (neat): ν 2916, 1709, 1496, 1446, 1333, 1247, 1159, 766, 690 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{29}H_{29}NO_2SNa$ $[M+Na]^+$: 478.1811, Found: 478.1806.


Ts
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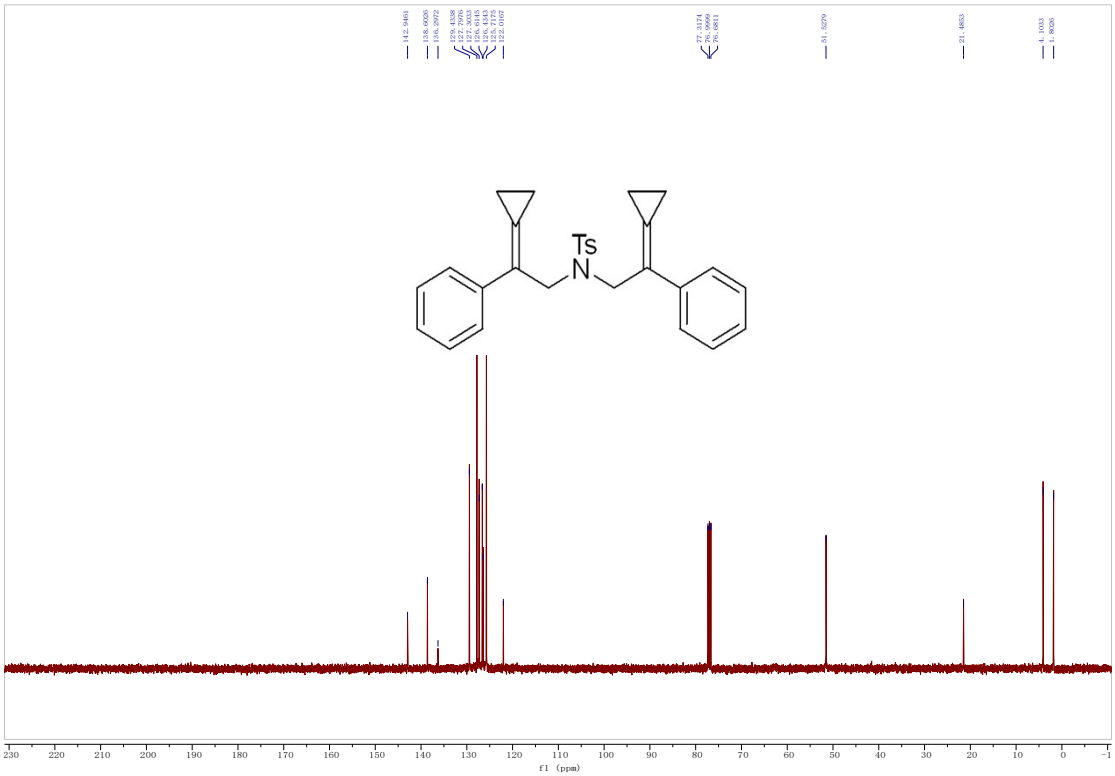
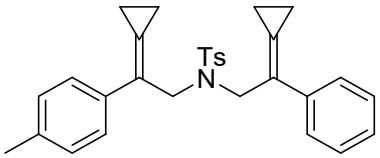
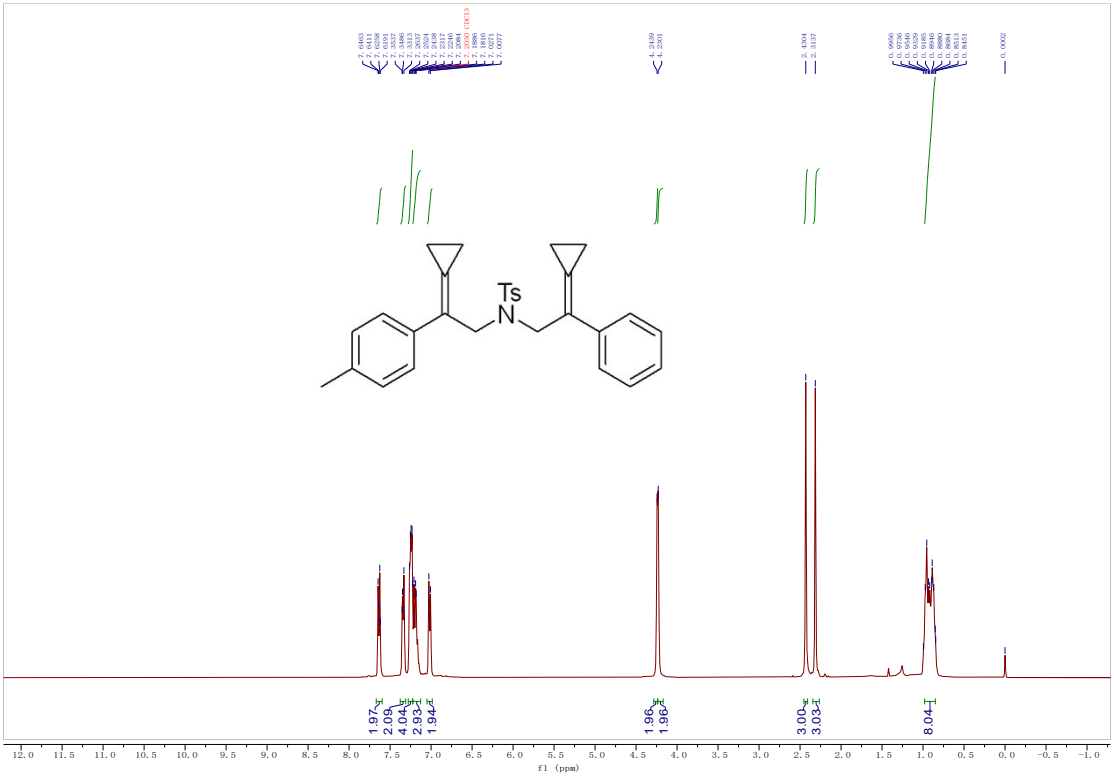
3.99
3.09
5.07
4.00
3.00
4.00
4.00
f1 (ppm)


Ts
N
f1 (ppm)



Compound 1b: Yield: 375 mg, 76%; A white solid; M.p.: 167 - 169 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.60 (m, 2H), 7.38 – 7.31 (m, 2H), 7.28 – 7.23 (m, 4H), 7.22 – 7.13 (m, 3H), 7.02 (d, J = 7.7 Hz, 2H), 4.24 (s, 2H), 4.23 (s, 2H), 2.43 (s, 3H), 2.31 (s, 3H), 0.98 – 0.85 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 138.7, 136.5, 136.31, 135.8, 129.5, 128.6, 127.8, 127.3, 126.6, 126.3, 125.8, 125.7, 125.4, 122.1, 122.0, 51.52, 51.45, 21.5, 21.1, 4.1, 4.1, 1.9, 1.84; IR (neat): ν 2972, 1712, 1514, 1340, 1162, 1092, 1018, 752, 697cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{30}H_{31}NO_2SNa$ $[M+Na]^+$: 492.1968, Found: 492.1969.


Ts
N
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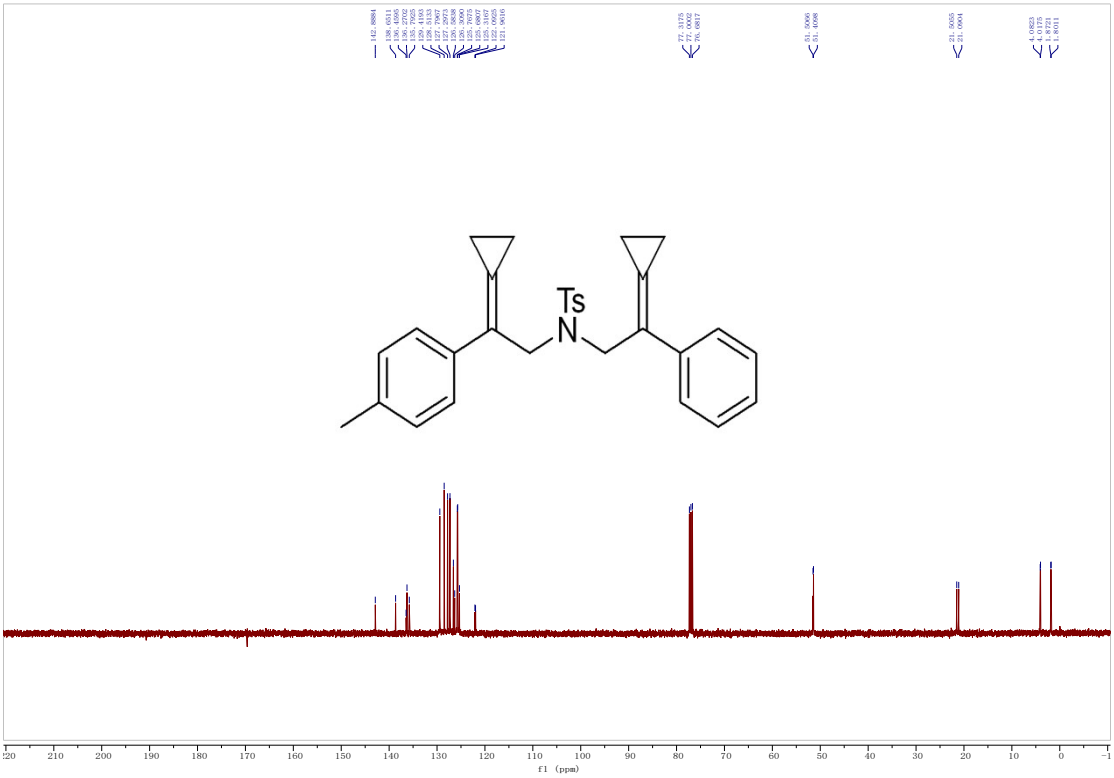
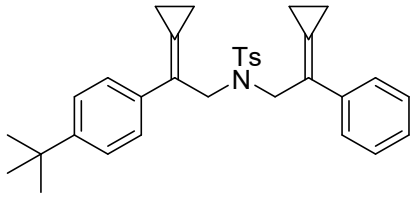
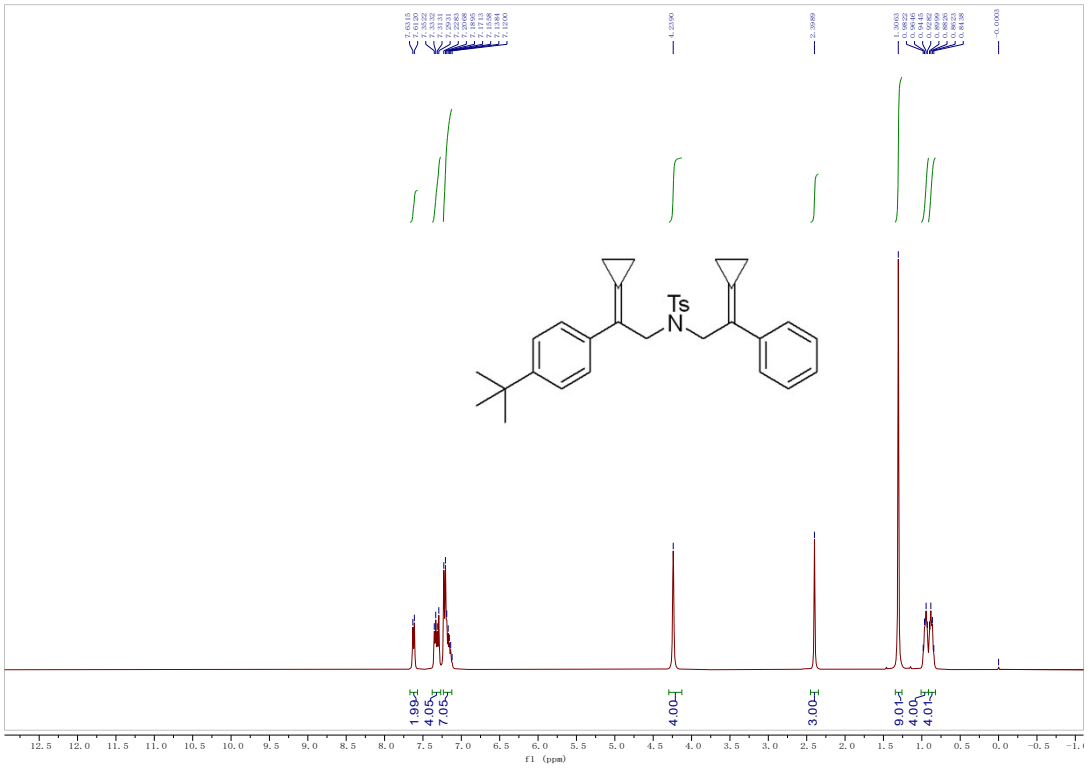
2.09
4.04
2.93
1.94
1.96
1.96
3.00
3.03
8.04
f1 (ppm)


Ts
N
f1 (ppm)



Compound 1c: Yield: 423 mg, 81%; A white solid; M.p.: 152 - 154 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.8 Hz, 2H), 7.38 – 7.27 (m, 4H), 7.23 – 7.12 (m, 7H), 4.24 (s, 4H), 2.40 (s, 3H), 1.31 (s, 9H), 1.01 – 0.91 (m, 4H), 0.91 – 0.82 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 139.7, 130.4, 128.8, 128.3, 127.5, 127.3, 126.7, 126.5, 126.4, 125.6, 123.0, 122.8, 52.7, 52.5, 35.4, 32.3, 22.5, 5.2, 5.0, 2.8, 2.6; IR (neat): ν 2965, 1341, 1106, 1092, 1047, 759, 697, 662 cm^{-1}; HRMS(ESI - TOF) Calcd. for $C_{33}H_{37}NO_2SNa$ $[M+Na]^+$: 534.2437, Found: 534.2434.


Ts
N
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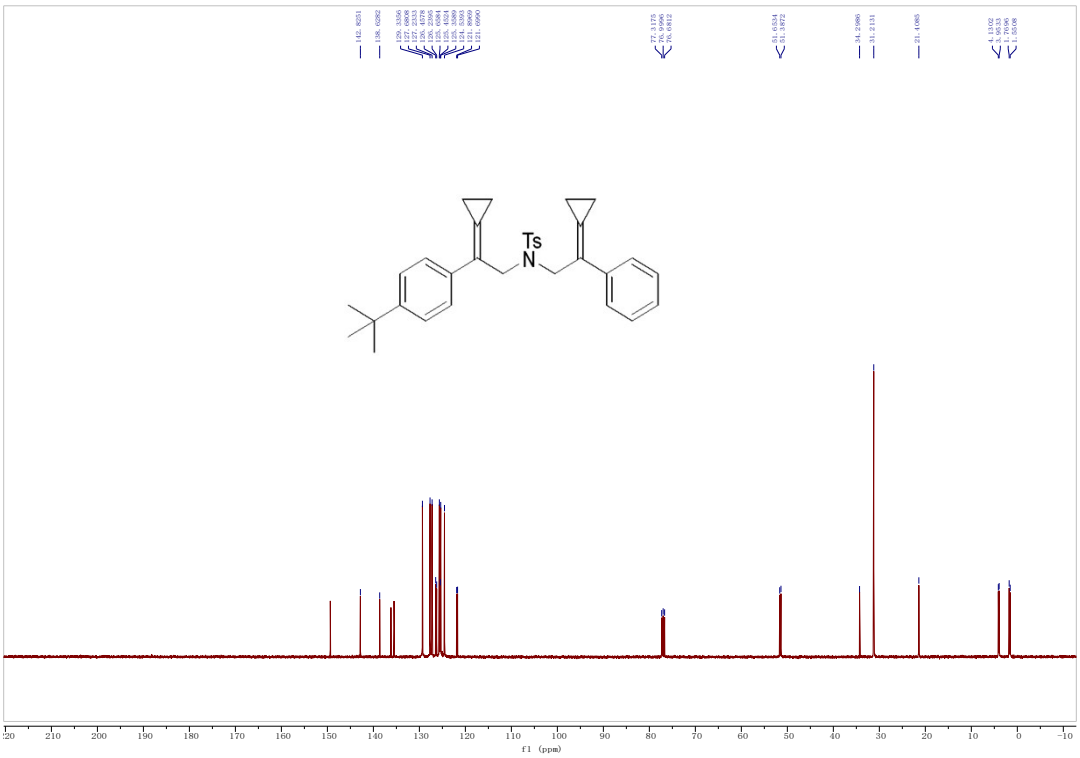
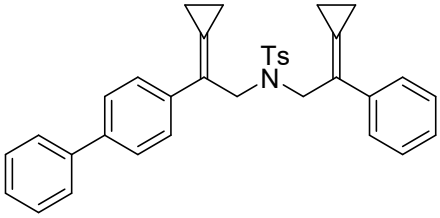
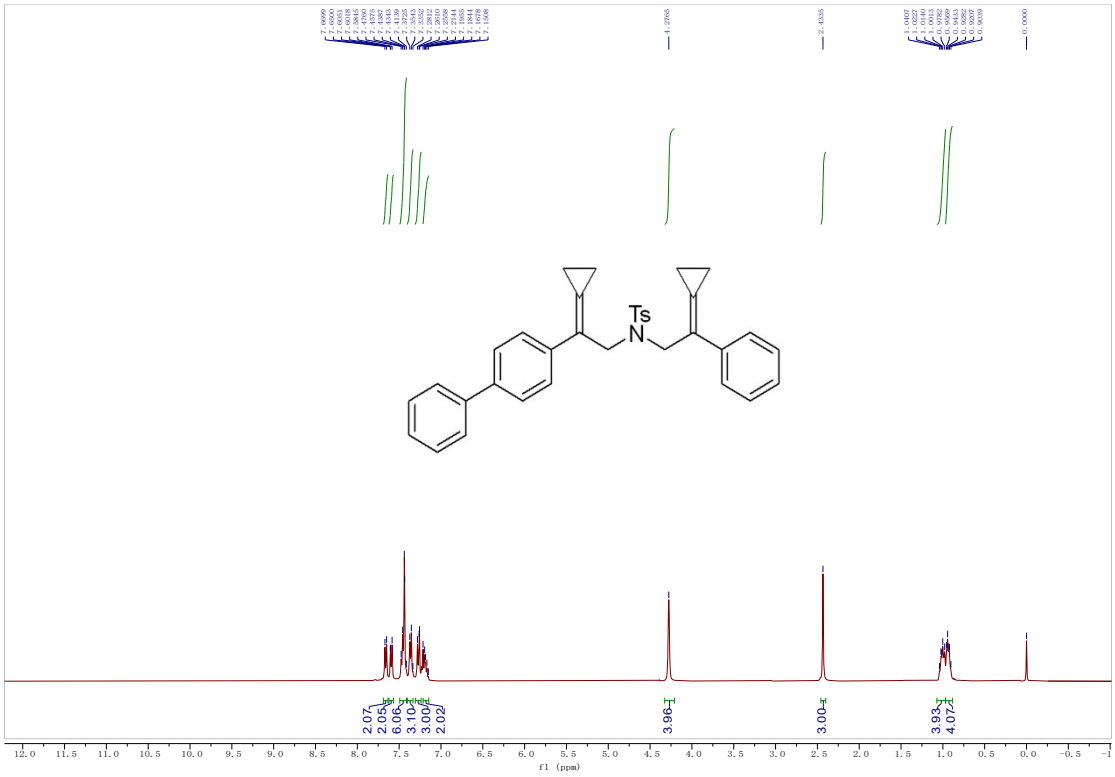
7.05
4.00
3.00
9.01
4.00
4.01
f1 (ppm)


Ts
N
f1 (ppm)



Compound 1d: Yield: 434 mg, 80%; A white solid; M.p.: 124 - 126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.9 Hz, 2H), 7.62 – 7.57 (m, 2H), 7.49 – 7.41 (m, 6H), 7.40 – 7.33 (m, 3H), 7.31 – 7.24 (m, 3H), 7.21 – 7.15 (m, 2H), 4.28 (s, 4H), 2.43 (s, 3H), 1.07 – 0.97 (m, 4H), 0.97 – 0.89 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 140.9, 139.4, 138.8, 137.7, 136.3, 129.6, 128.9, 128.0, 127.5, 127.3, 127.0, 126.8, 126.8, 126.63, 126.59, 126.3, 125.9, 122.2, 121.9, 51.8, 51.7, 21.7, 4.5, 4.4, 2.04, 1.95; IR (neat): ν 2972, 1712, 1597, 1487, 1339, 1220, 1017, 964, 697, 656 cm^{-1}; HRMS(ESI - TOF) Calcd. for $C_{35}H_{33}NO_2SNa$ $[M+Na]^+$: 554.2124, Found: 554.2128.


Ts
N
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6.06
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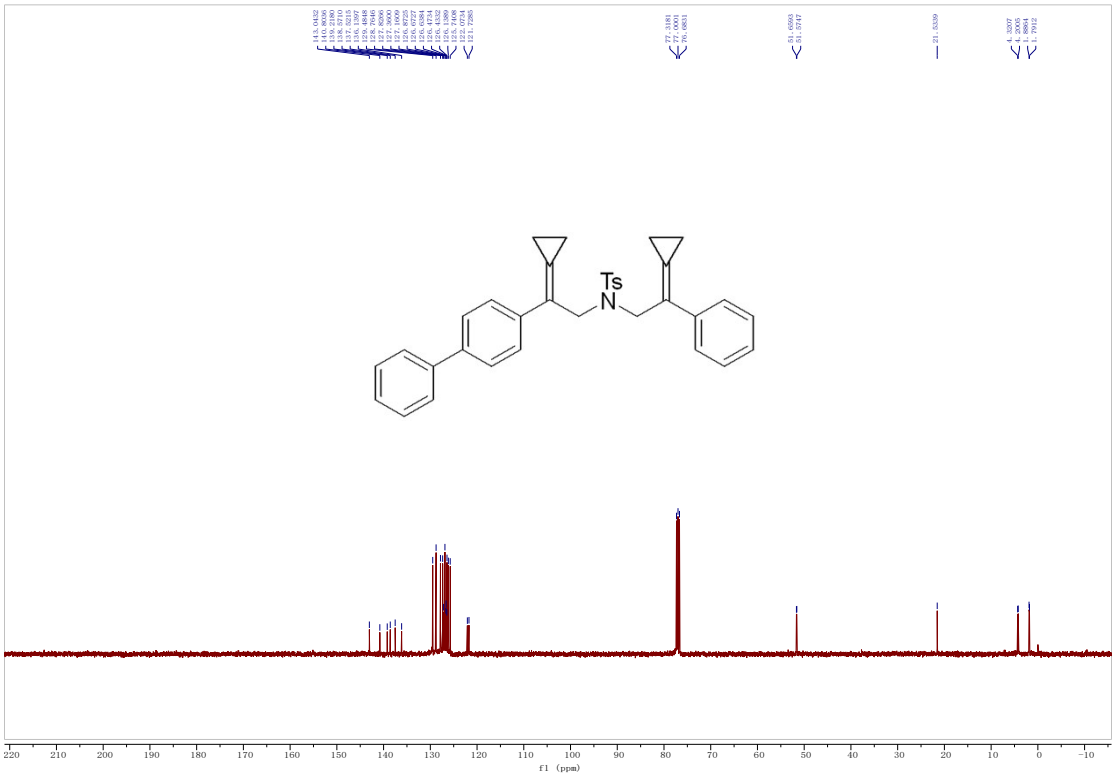
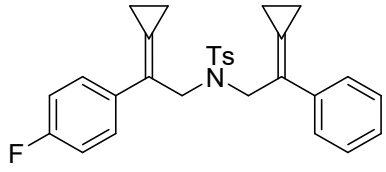
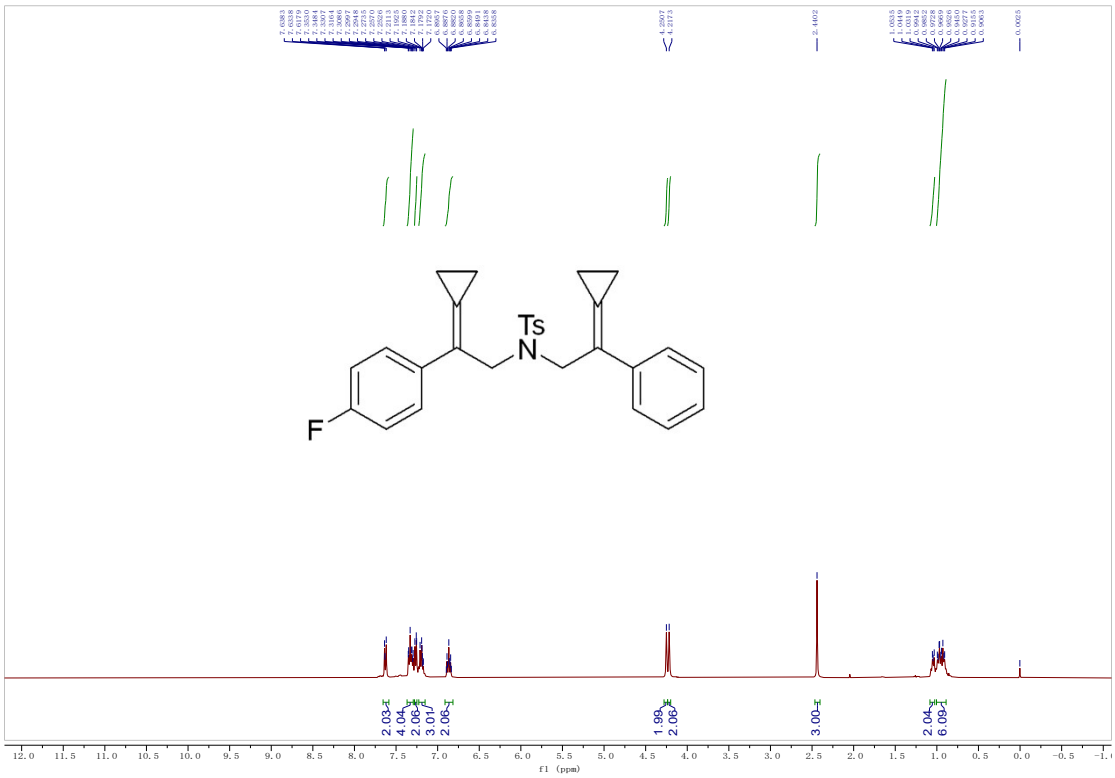
2.02
3.96
3.00
3.93
4.07
f1 (ppm)


Ts
N
f1 (ppm)



Compound 1e: Yield: 357 mg, 72%; A white solid; M.p.: 147 - 149 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.59 (m, 2H), 7.37 – 7.29 (m, 4H), 7.28 – 7.25 (m, 2H), 7.23 – 7.15 (m, 3H), 6.91 – 6.82 (m, 2H), 4.25 (s, 2H), 4.22 (s, 2H), 2.44 (s, 3H), 1.08 – 1.03 (m, 2H), 1.00 – 0.89 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 158.4 (d, J = 244.5 Hz), 141.1, 136.5, 134.1, 132.52, 132.49 (d, J = 3.4 Hz), 127.5, 125.9, 125.47, 125.39 (d, J = 7.7 Hz), 125.36, 124.7, 124.4, 124.1, 124.0 (d, J = 1.7 Hz), 123.7, 120.2, 119.4, 112.7, 112.5 (d, J = 21.1 Hz), 51.9, 51.6, 21.5, 4.3, 1.9, 1.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.8; IR (neat): ν 2973, 1597, 1450, 1337, 1229, 1093, 833, 709, 697 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{29}H_{28}NO_2SFNa$ $[M+Na]^+$: 496.1717, Found: 496.1708.


Ts
N
F
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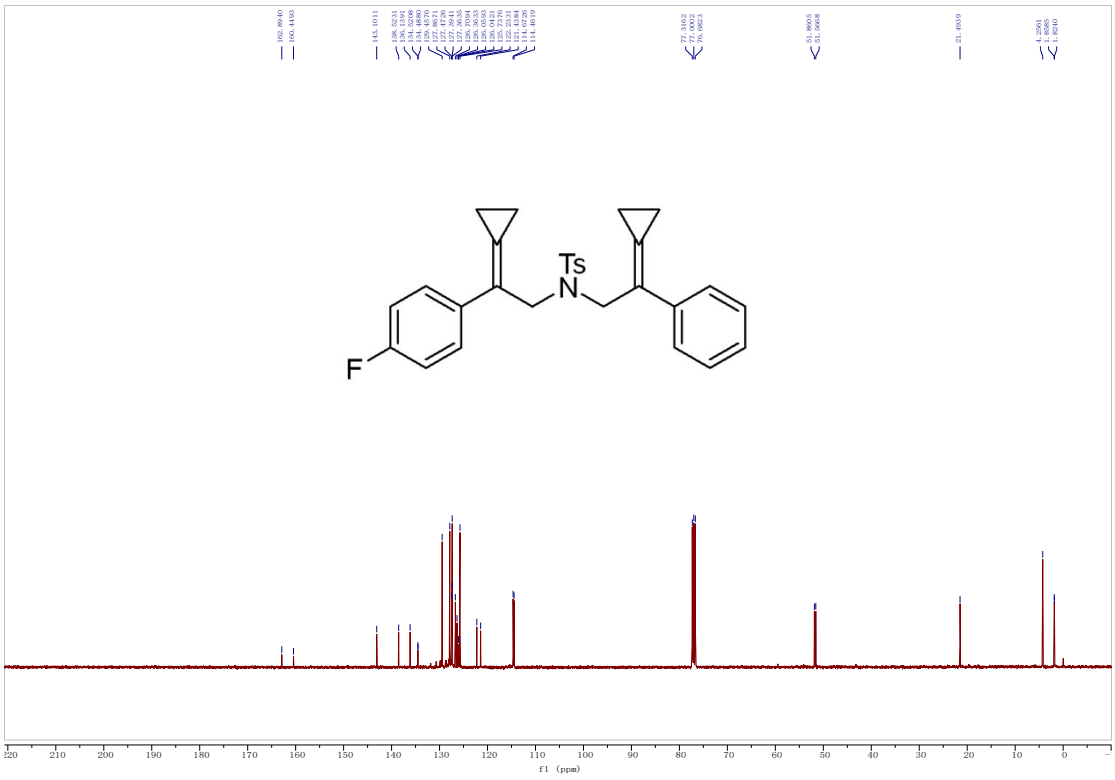
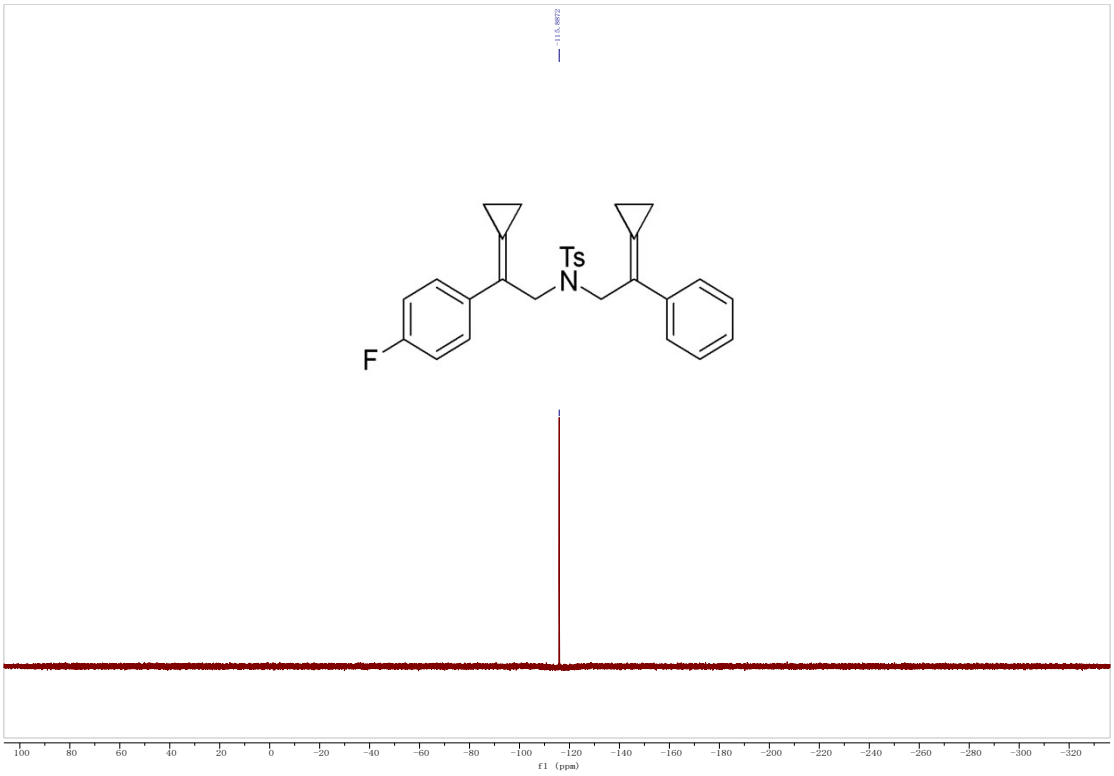
4.04
2.06
3.01
2.06
1.99
2.06
3.00
2.04
6.09
f1 (ppm)


Ts
N
F
f1 (ppm)


-115.88772
Ts
N
F
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
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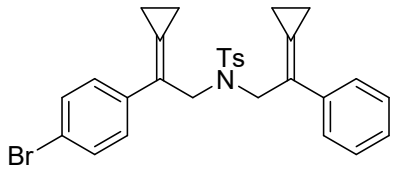
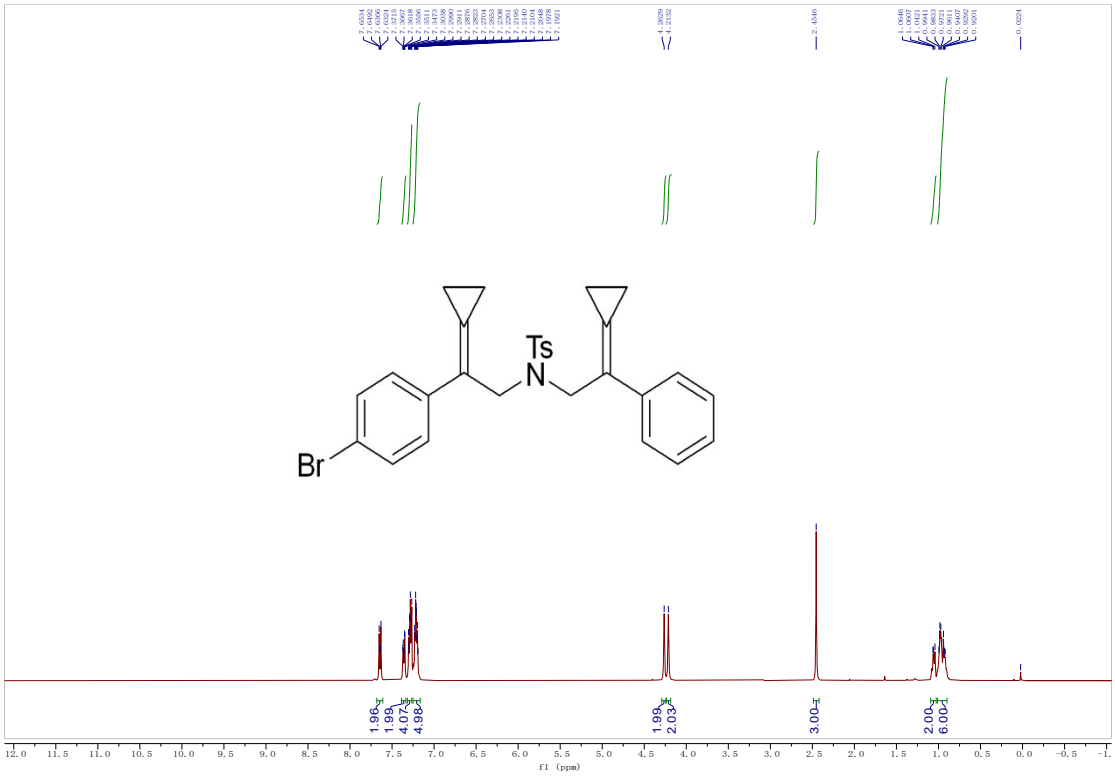
-240
-260
-280
-300
-320
f1 (ppm)



Compound 1f: Yield: 428 mg, 80%; A white solid; M.p.: 155 - 157 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.61 (m, 2H), 7.39 – 7.34 (m, 2H), 7.32 – 7.26 (m, 4H), 7.25 – 7.17 (m, 5H), 4.26 (s, 2H), 4.21 (s, 2H), 2.45 (s, 3H), 1.09 – 1.03 (m, 2H), 1.01 – 0.90 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 139.3, 138.3, 136.9, 131.7, 130.5, 128.8, 128.4, 128.3, 128.1, 127.7, 127.4, 126.7, 123.1, 122.4, 121.4, 78.3, 78.0, 77.7, 52.6, 52.5, 22.5, 5.3, 2.8; IR (neat): ν 2967, 1766, 1347, 1161, 1090, 1008, 700, 663 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{29}H_{29}NO_2SBr$ $[M+H]^+$: 534.1097, Found: 534.1094.


Ts
N
Br
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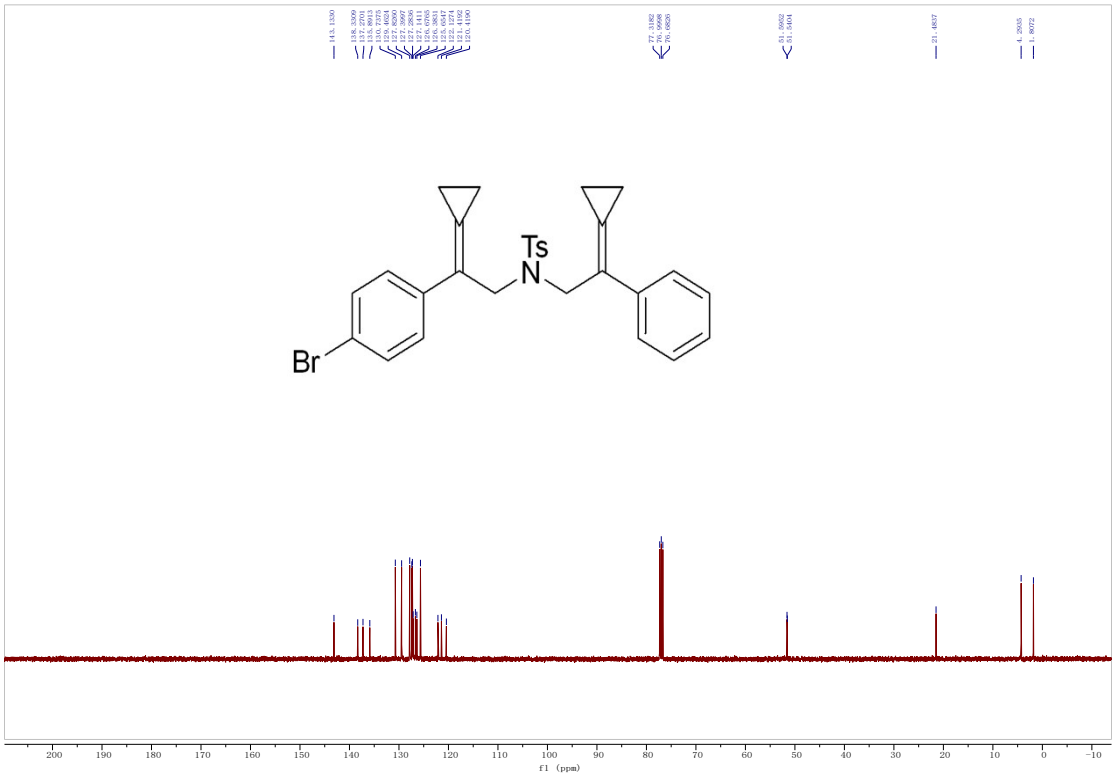
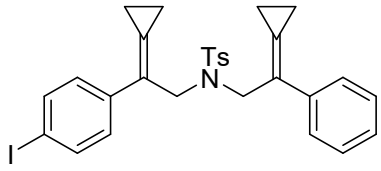
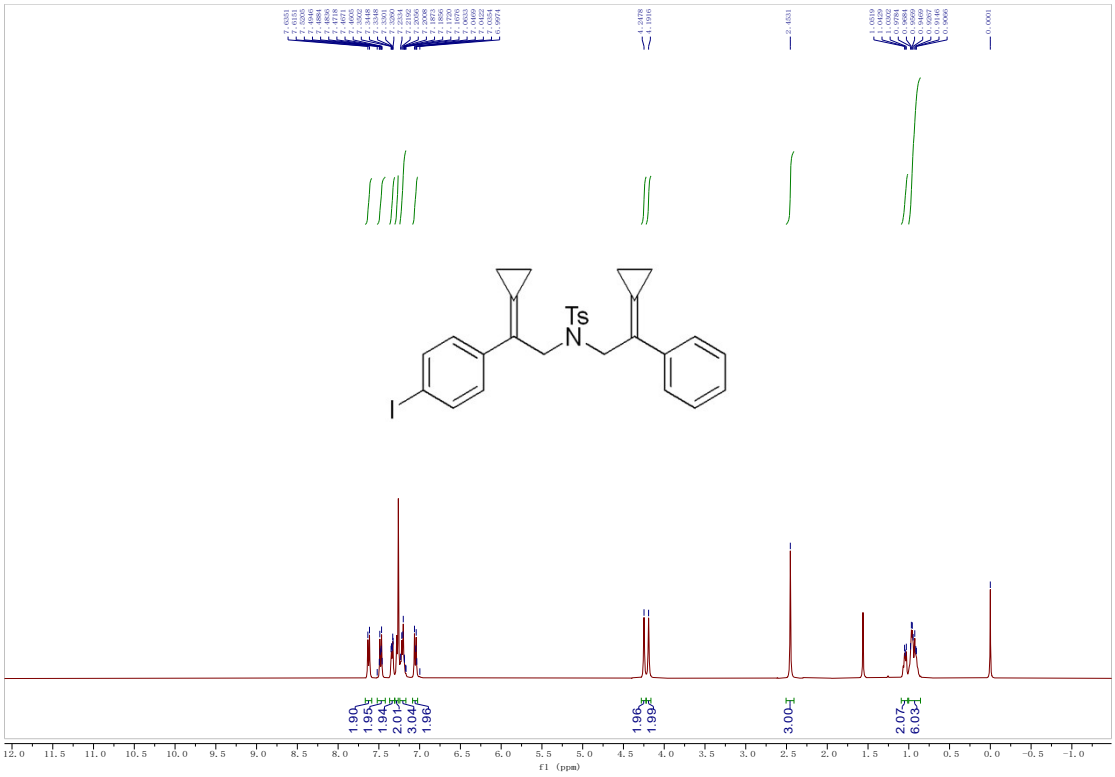
1.99
4.07
4.98
1.99
2.03
3.00
2.00
6.00
f1 (ppm)


Ts
N
Br
f1 (ppm)



Compound 1g: Yield: 418 mg, 69%; A white solid; M.p.: 159 - 161 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.52 – 7.42 (m, 2H), 7.36 – 7.30 (m, 2H), 7.30 – 7.26 (m, 2H), 7.24 – 7.16 (m, 3H), 7.08 – 7.02 (m, 2H), 4.24 (s, 2H), 4.19 (s, 2H), 2.45 (s, 3H), 1.09 – 1.01 (m, 2H), 1.00 – 0.85 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 138.4, 138.0, 136.8, 136.1, 129.5, 127.9, 127.7, 127.4, 127.3, 126.8, 126.5, 125.8, 122.3, 121.7, 92.0, 51.6, 51.5, 21.6, 4.4, 4.3, 1.9; IR (neat): ν 2928, 2076, 1733, 1718, 1495, 1334, 1091, 1005, 697, 654 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{29}H_{28}NO_2NaSI$ $[M+Na]^+$: 604.0778, Found: 604.0796.


Ts
N
I
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1.95
1.94
2.01
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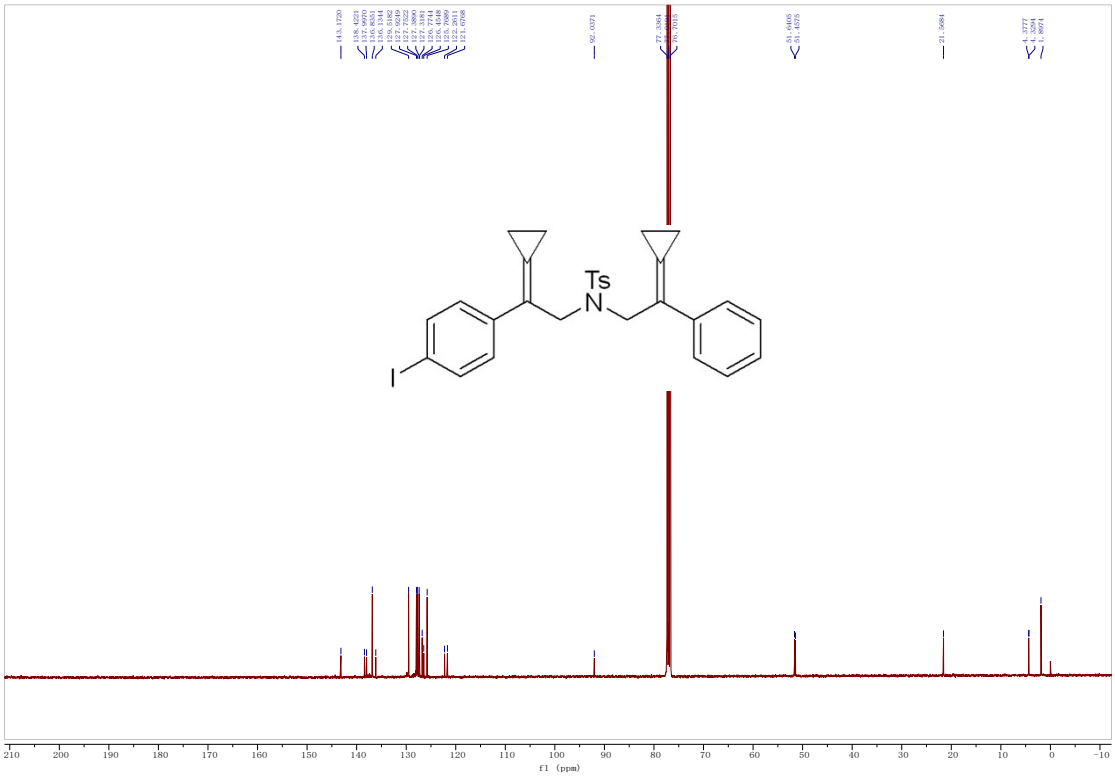
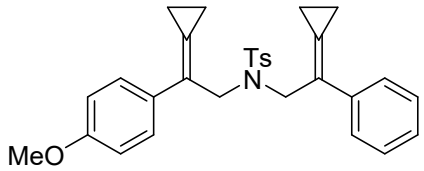
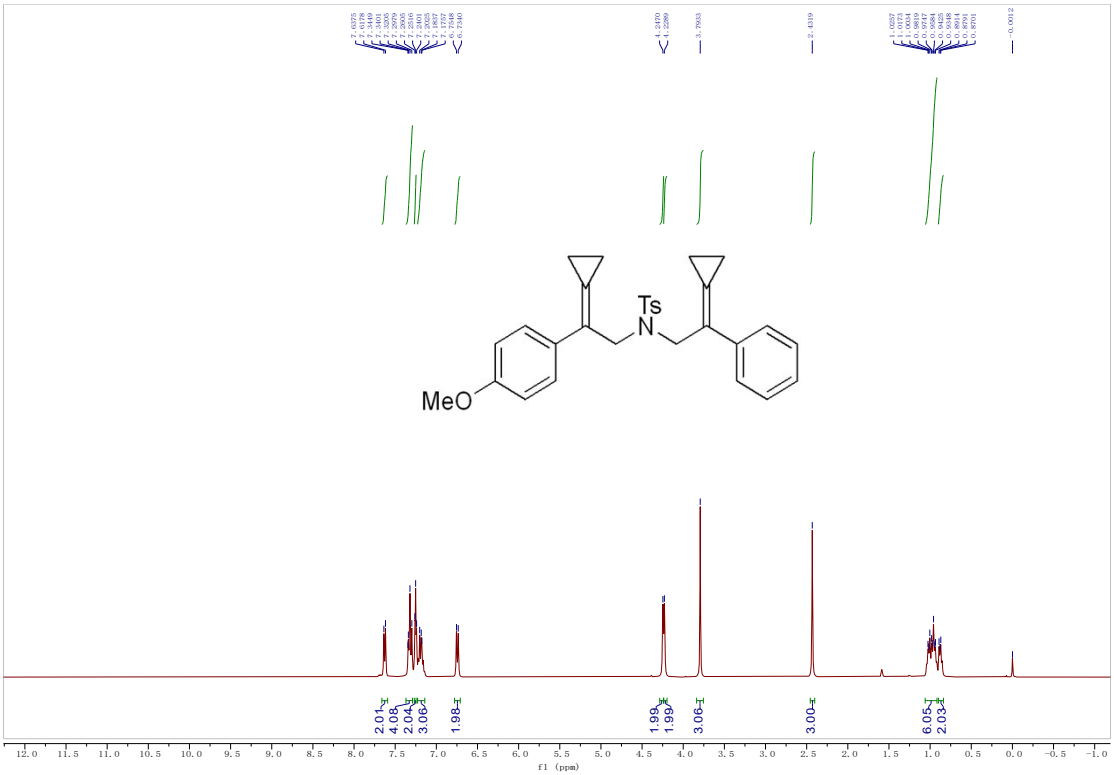
1.96
1.96
1.99
3.00
2.07
6.03
f1 (ppm)


Ts
N
I
f1 (ppm)



Compound 1h: Yield: 364 mg, 75%; A white solid; M.p.: 122 - 124 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.9 Hz, 2H), 7.37 – 7.29 (m, 4H), 7.28 – 7.23 (m, 2H), 7.23 – 7.14 (m, 3H), 6.74 (d, *J* = 8.3 Hz, 2H), 4.25 (s, 2H), 4.23 (s, 2H), 3.79 (s, 3H), 2.43 (s, 3H), 1.06 – 0.92 (m, 6H), 0.90 – 0.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 143.9, 139.6, 137.3, 132.1, 130.4, 128.8, 128.3, 127.9, 127.5, 127.2, 126.7, 125.2, 123.1, 122.5, 114.1, 56.2, 52.8, 52.3, 22.4, 5.1, 5.0, 2.9, 2.6; IR (neat): ν 2918, 1605, 1512, 1339, 1248, 1162, 1032, 825, 751 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{30}H_{32}NO_3S$ $[M+H]^+$: 486.2097, Found: 486.2099.


Ts
N
MeO
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2.04
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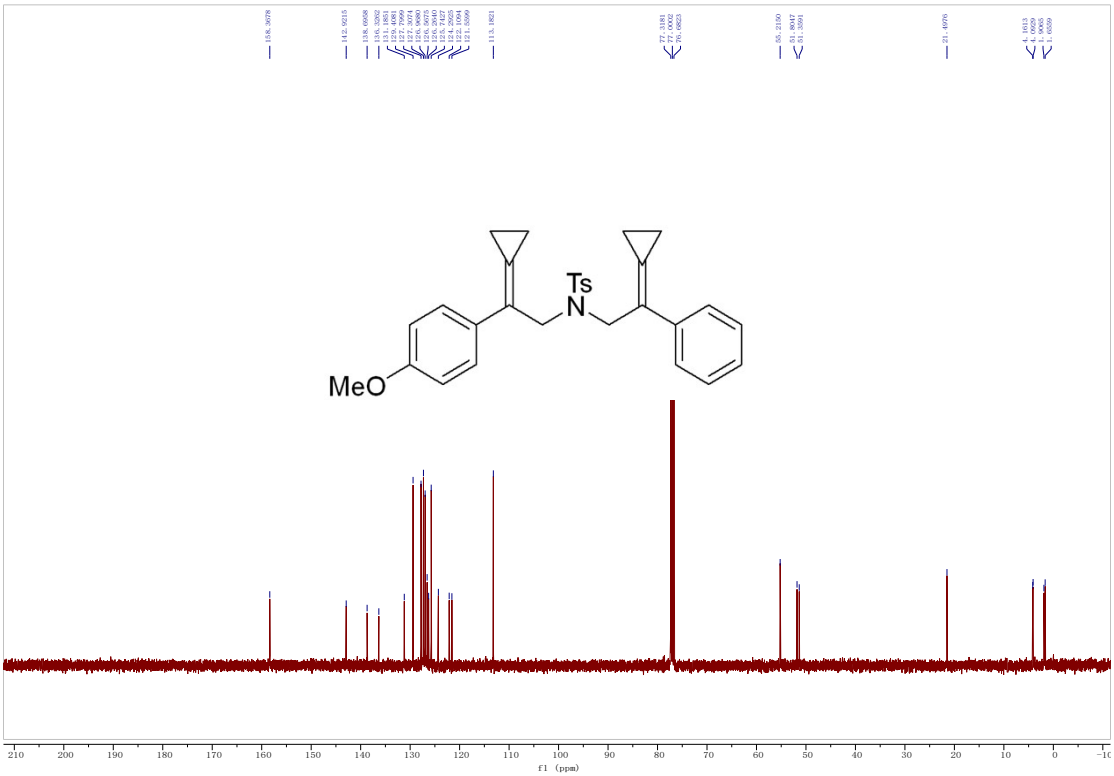
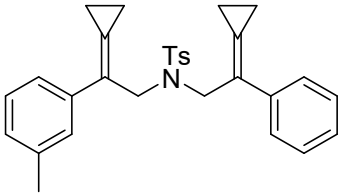
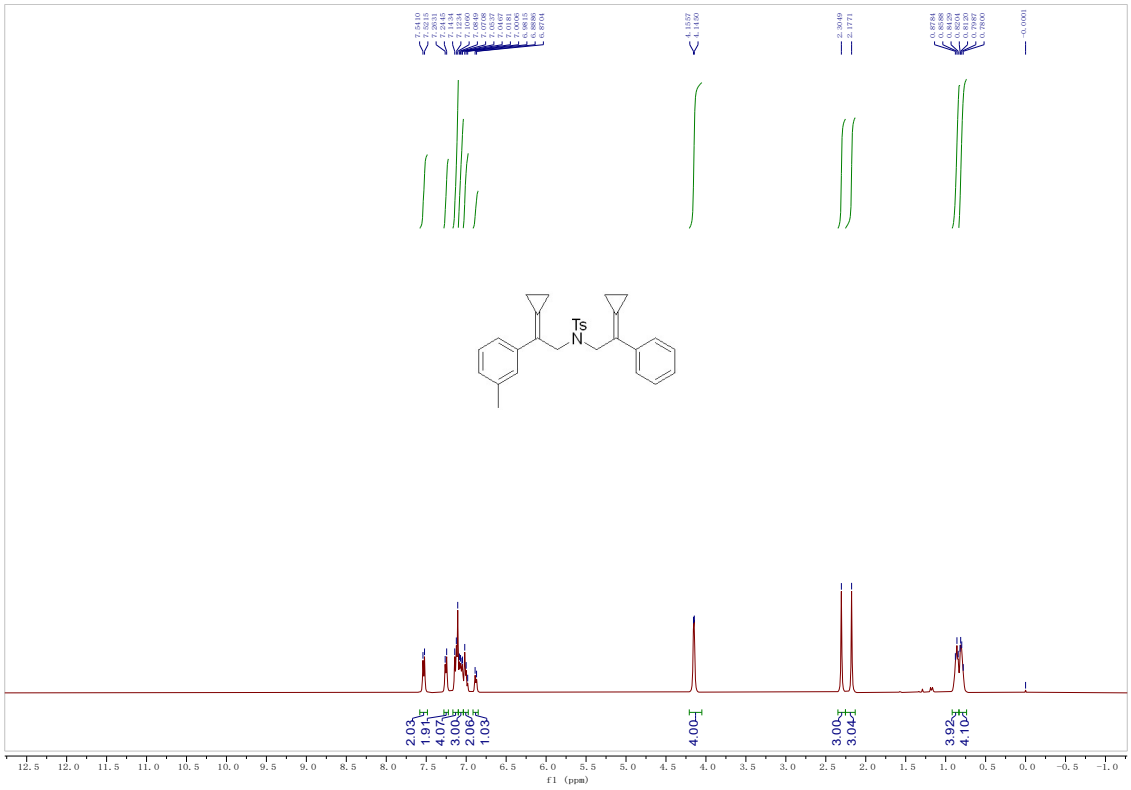
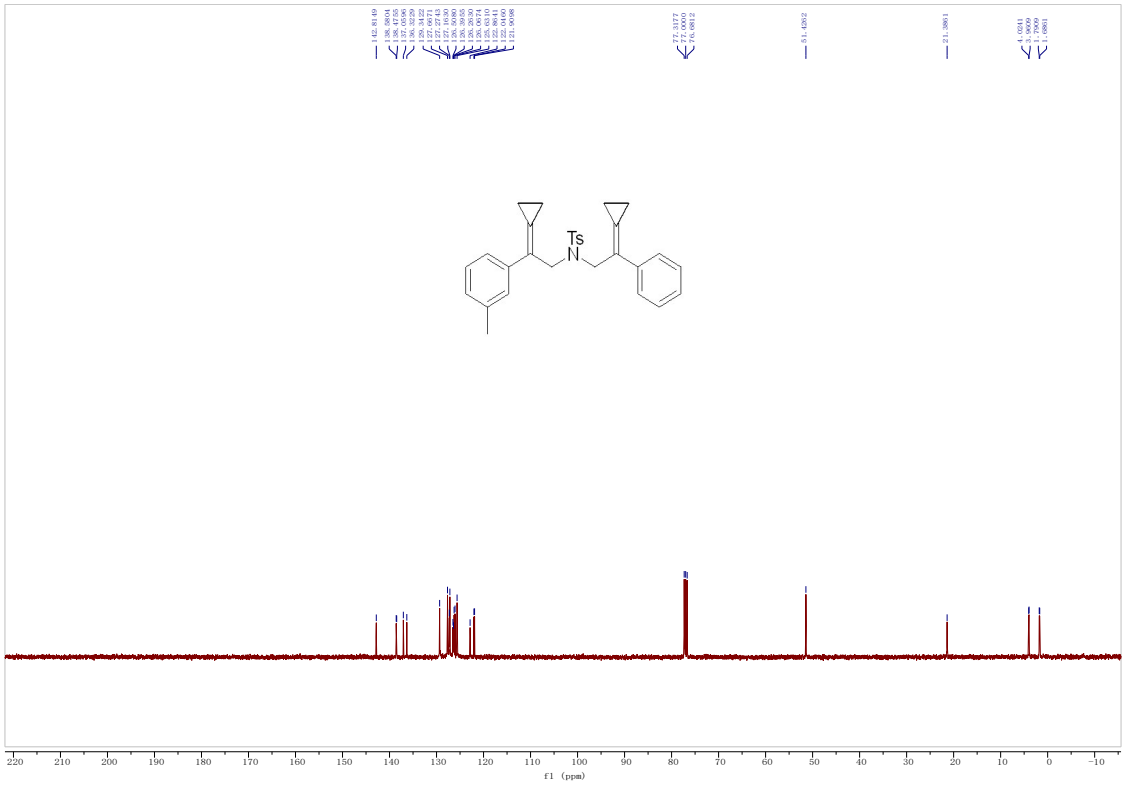
1.99
1.99
3.06
3.00
6.05
2.03
f1 (ppm)

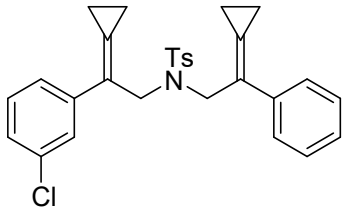

Ts
N
MeO
f1 (ppm)



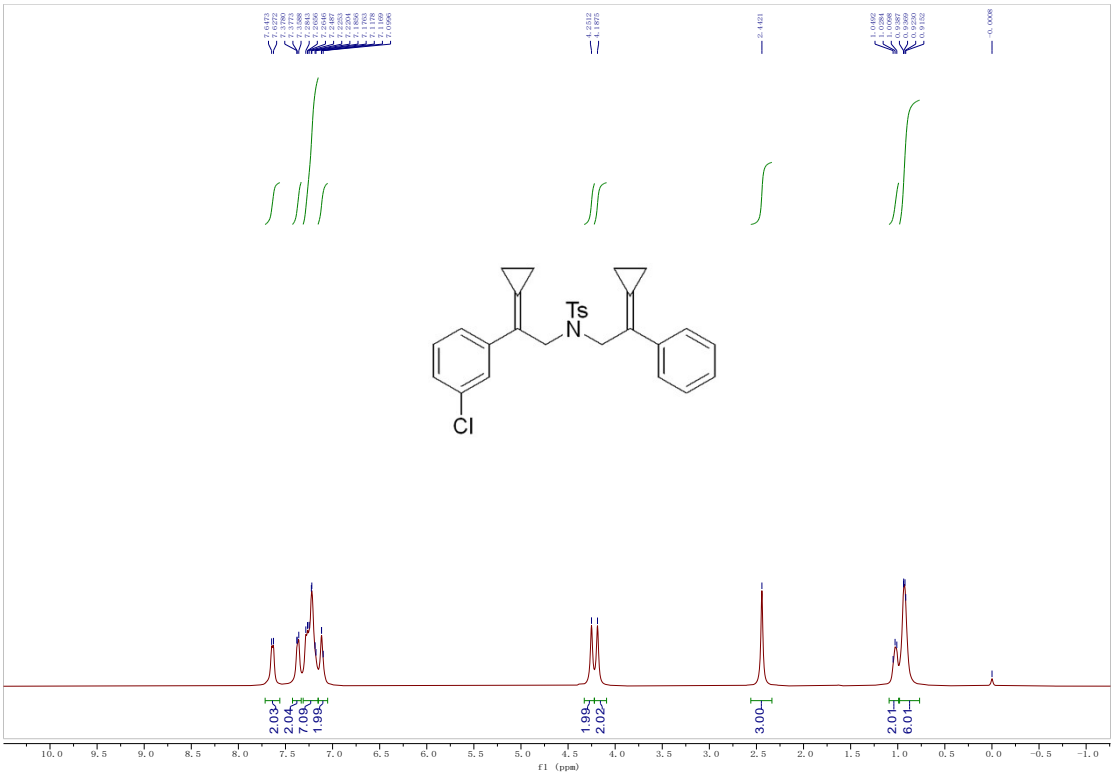
Compound 1i: Yield: 380 mg, 81%; A white solid; M.p.: 121 - 119 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 7.17 – 7.10 (m, 4H), 7.10 – 7.03 (m, 3H), 7.04 – 6.97 (m, 2H), 6.91 – 6.85 (m, 1H), 4.21 – 4.05 (m, 4H), 2.30 (s, 3H), 2.18 (s, 3H), 0.92 – 0.83 (m, 4H), 0.84 – 0.74 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 138.6, 138.5, 137.1, 136.3, 129.3, 127.7, 127.3, 127.2, 126.5, 126.4, 126.3, 126.1, 125.6, 122.9, 122.0, 121.9, 51.4, 21.4, 4.02, 3.96, 1.8, 1.7; IR (neat): ν 2962, 1790, 1504, 1329, 1236, 1187, 1160, 1078, 772, 699cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{30}H_{31}NO_2SNa$ $[M+Na]^+$: 492.1968, Found: 492.1963.

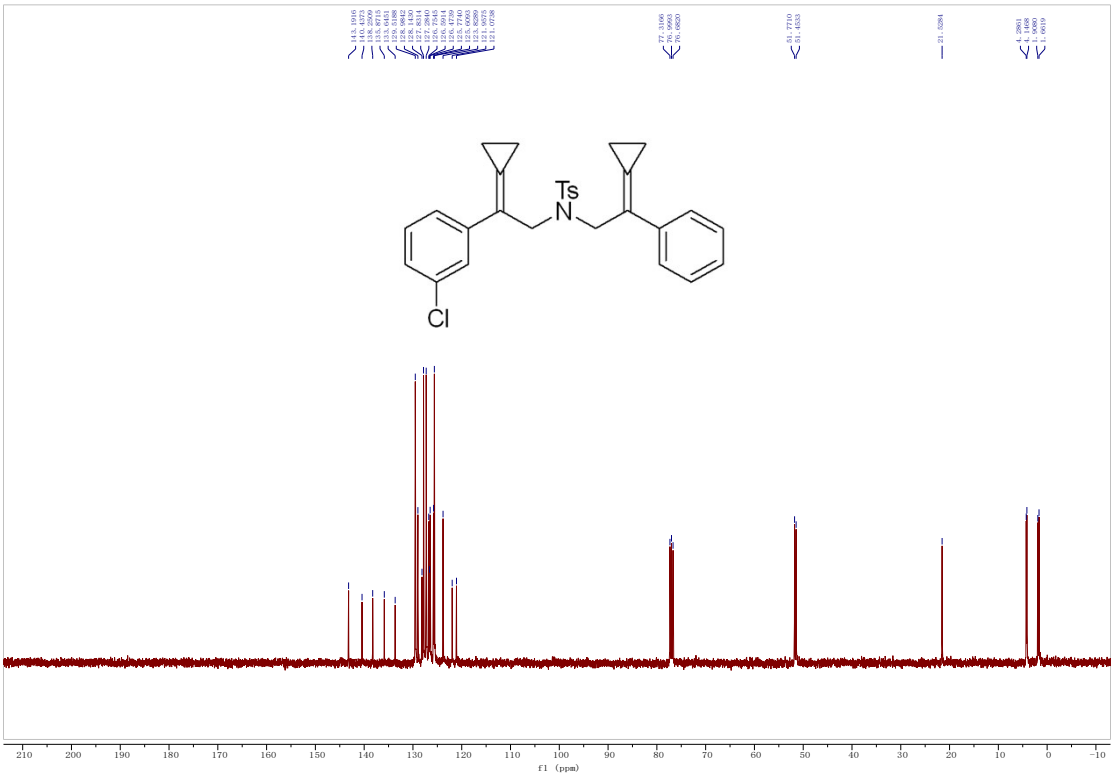

Ts
N
f1 (ppm)

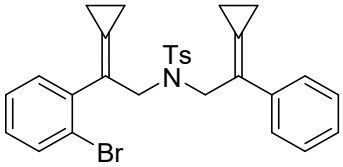

Ts
N
f1 (ppm)



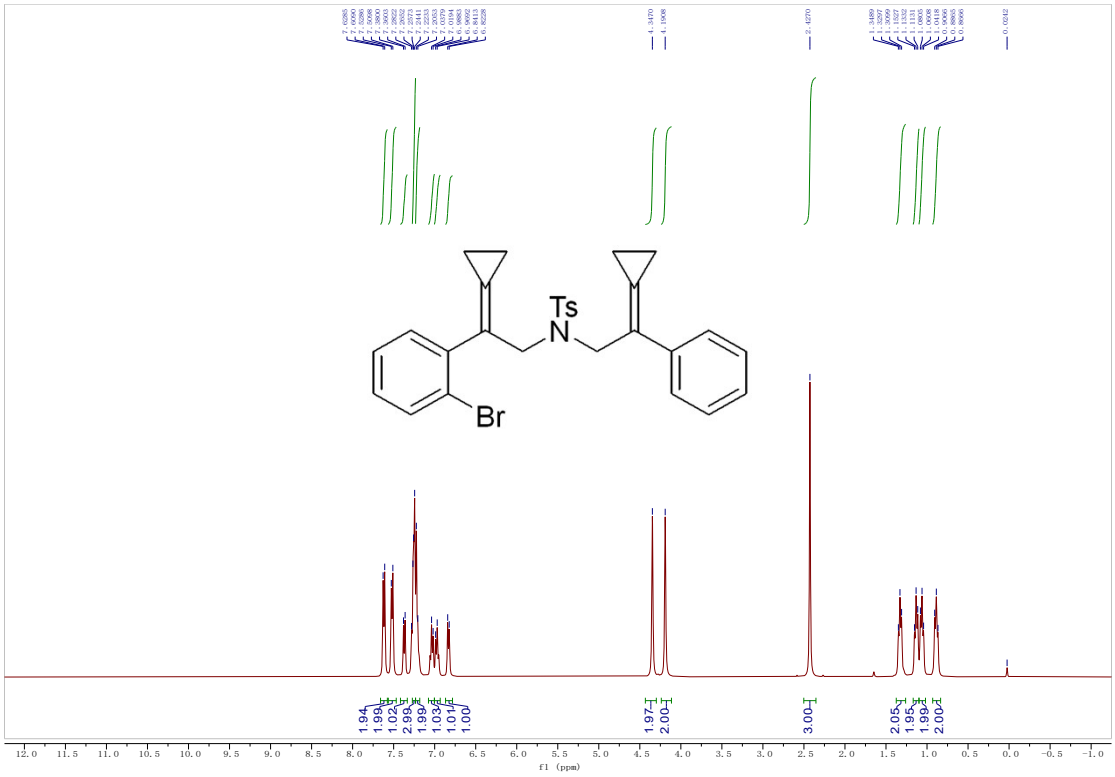
Compound 1j: Yield: 380 mg, 77%; A white solid; M.p.: 130 - 132 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.42 – 7.33 (m, 2H), 7.31 – 7.15 (m, 7H), 7.15 – 7.05 (m, 2H), 4.25 (s, 2H), 4.18 (s, 2H), 2.44 (s, 3H), 1.09 – 0.99 (m, 2H), 0.98 – 0.76 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 140.6, 138.4, 136.1, 133.8, 129.7, 129.2, 128.3, 128.1, 127.5, 126.9, 126.8, 126.7, 125.9, 125.8, 124.0, 122.1, 121.3, 77.5, 77.2, 76.9, 51.9, 51.6, 21.7, 4.5, 4.3, 2.1, 1.9; IR (neat): ν 2972, 1713, 1594, 1564, 1447, 1338, 1161, 1092, 905, 710, 692 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{29}H_{28}NO_2NaSCl$ $[M+Na]^+$: 512.1422, Found: 512.1422.

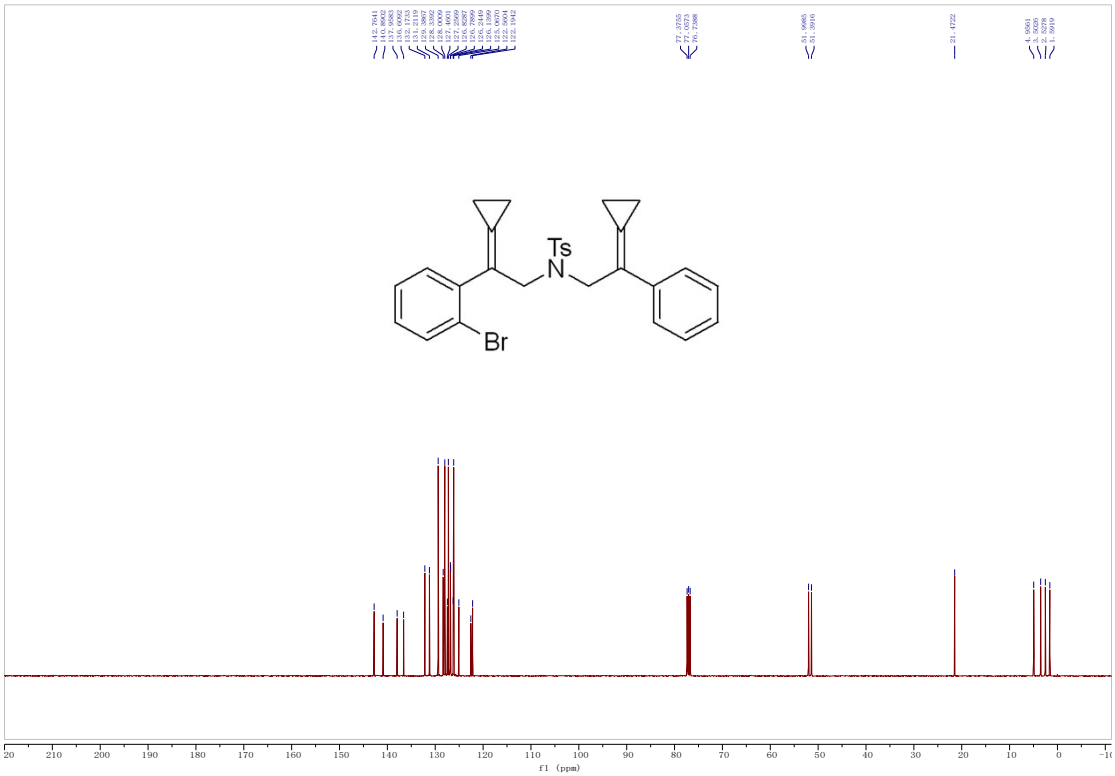

Ts
N
Cl
2.03
2.04
7.09
1.99
1.99
2.02
3.00
2.01
6.01
f1 (ppm)

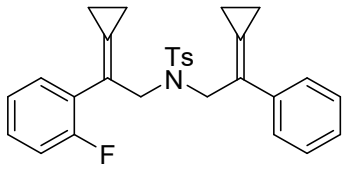

Ts
N
Cl
f1 (ppm)



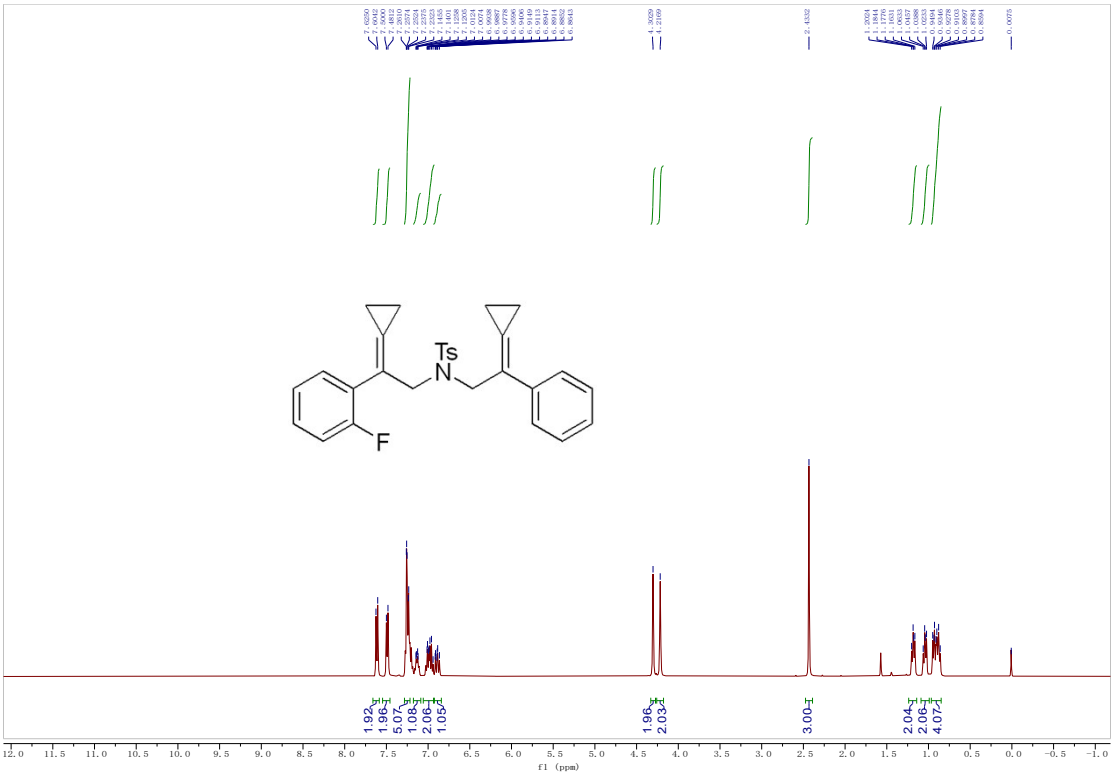
Compound 1k: Yield: 472 mg, 85%; A white solid; M.p.: 140 - 142 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.8 Hz, 2H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.27 – 7.23 (m, 3H), 7.23 – 7.18 (m, 2H), 7.08 – 7.00 (m, 1H), 7.00 – 6.93 (m, 1H), 6.83 (d, *J* = 7.4 Hz, 1H), 4.35 (s, 2H), 4.19 (s, 2H), 2.43 (s, 3H), 1.37 – 1.26 (m, 2H), 1.17 – 1.10 (m, 2H), 1.10 – 1.02 (m, 2H), 0.93 – 0.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 140.9, 137.9, 136.6, 132.2, 131.2, 129.4, 128.3, 128.0, 127.5, 127.3, 126.8, 126.8, 126.2, 126.1, 125.1, 122.6, 122.2, 52.0, 51.4, 21.4, 4.9, 3.5, 2.5, 1.6; IR (neat): ν 2959, 1756, 1457, 1356, 1099, 1052, 899, 710, 688 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{29}H_{28}NO_2NaSBr$ $[M+Na]^+$: 556.0916, Found: 556.0915.

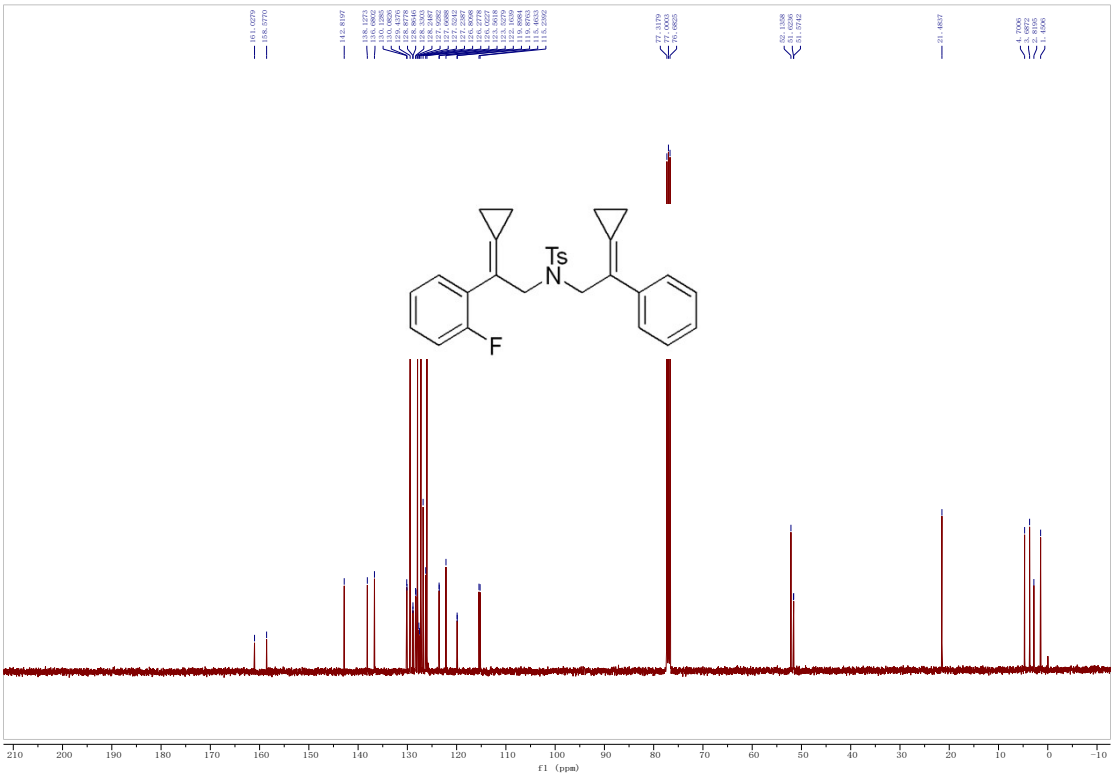

Ts
N
Br
1.94
1.99
1.02
2.98
1.99
1.03
1.01
1.00
1.97
2.00
3.00
2.05
1.95
1.99
2.00
f1 (ppm)

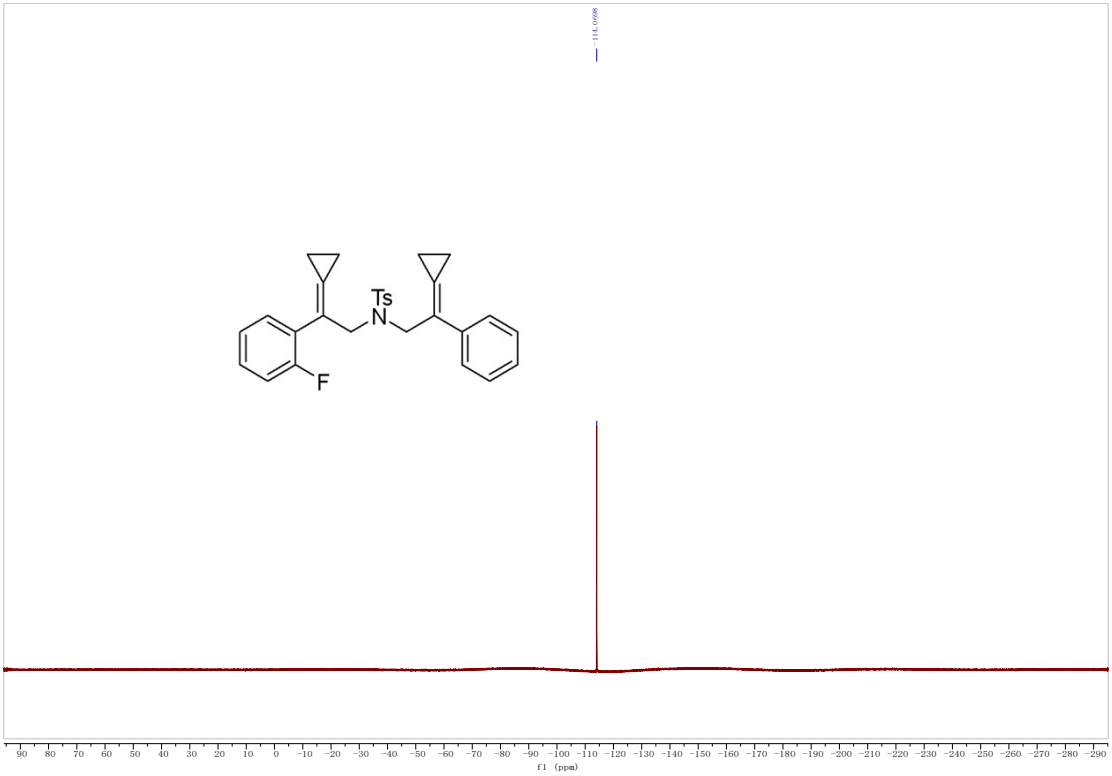

Ts
N
Br
f1 (ppm)

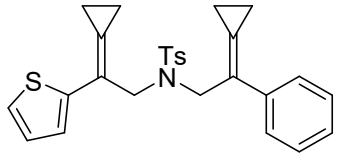


Compound 1l: Yield: 401 mg, 81%; A white solid; M.p.: 162 - 164 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.6 (d, *J* = 8.3 Hz, 2H), 7.5 (d, *J* = 7.5 Hz, 2H), 7.3–7.2 (m, 5H), 7.2 – 7.1 (m, 1H), 7.1 – 6.9 (m, 2H), 6.9 – 6.8 (m, 1H), 4.3 (s, 2H), 4.2 (s, 2H), 2.4 (s, 3H), 1.2 – 1.1 (m, 2H), 1.1 – 1.0 (m, 2H), 1.0 – 0.8 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 158.6 (d, *J* = 245.1 Hz), 142.8, 138.1, 136.7, 130.12, 130.08 (d, *J* = 4.6 Hz), 129.4, 128.88, 128.86 (d, *J* = 1.3 Hz), 128.3, 128.2 (d, *J* = 8.2 Hz), 127.9, 127.7, 127.5, 127.2, 126.8, 126.3, 126.0, 123.6, 123.5 (d, *J* = 3.4 Hz), 122.2, 119.89, 119.88 (d, *J* = 2.2 Hz), 115.5, 115.2 (d, *J* = 22.4 Hz), 52.1, 51.62, 51.57, 21.5, 4.7, 3.7, 2.8, 1.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.1; IR (neat): ν 2979, 1780, 1598, 1489, 1448, 1339, 1092, 815, 756, 669 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{29}H_{28}NO_2NaSF$ $[M+Na]^+$ 496.1717, Found: 496.1709.

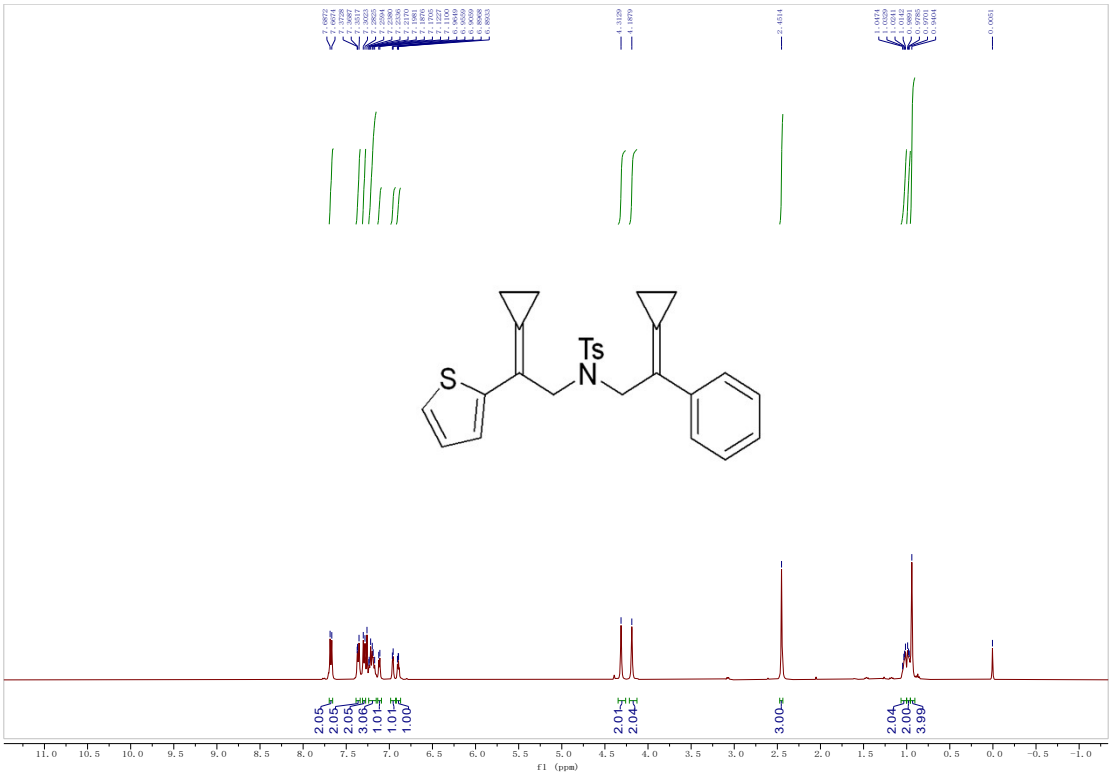

Ts
N
F
1.92
1.96
5.07
1.08
2.06
1.05
1.96
2.03
3.00
2.04
2.06
4.07
f1 (ppm)

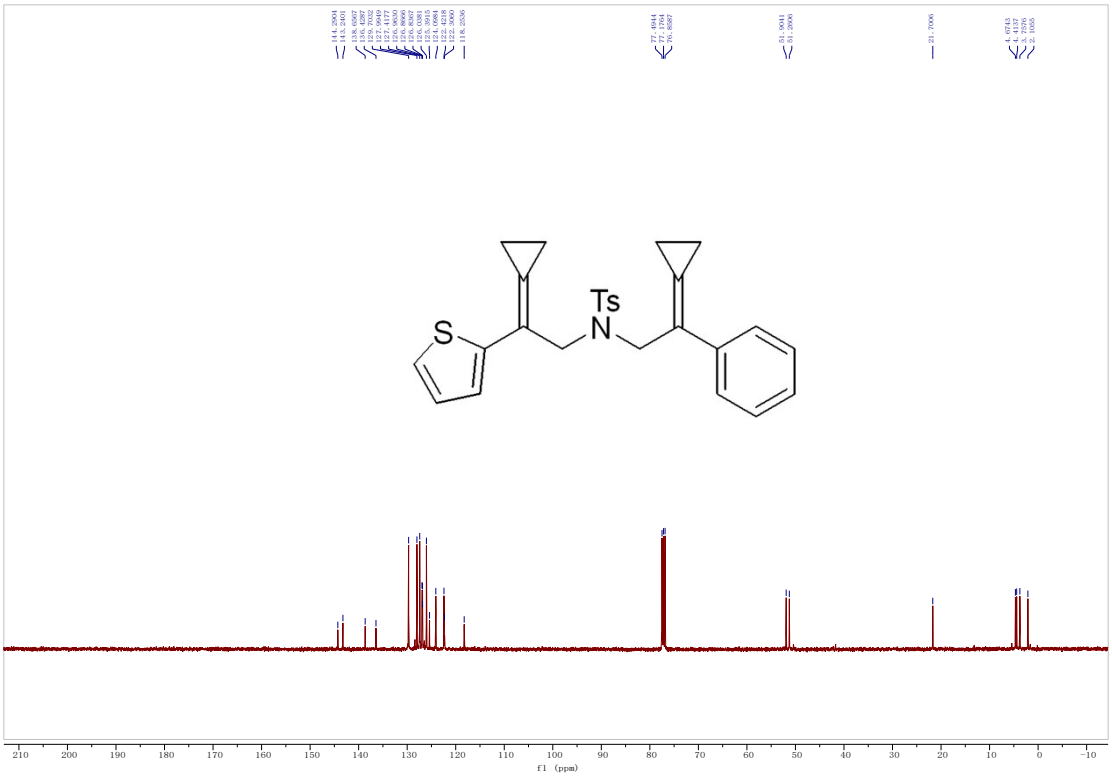

Ts
N
F
f1 (ppm)

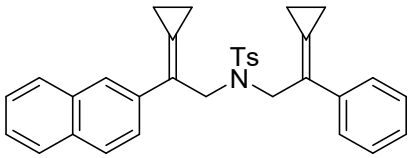

-114.0698
Ts
N
F
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290
f1 (ppm)



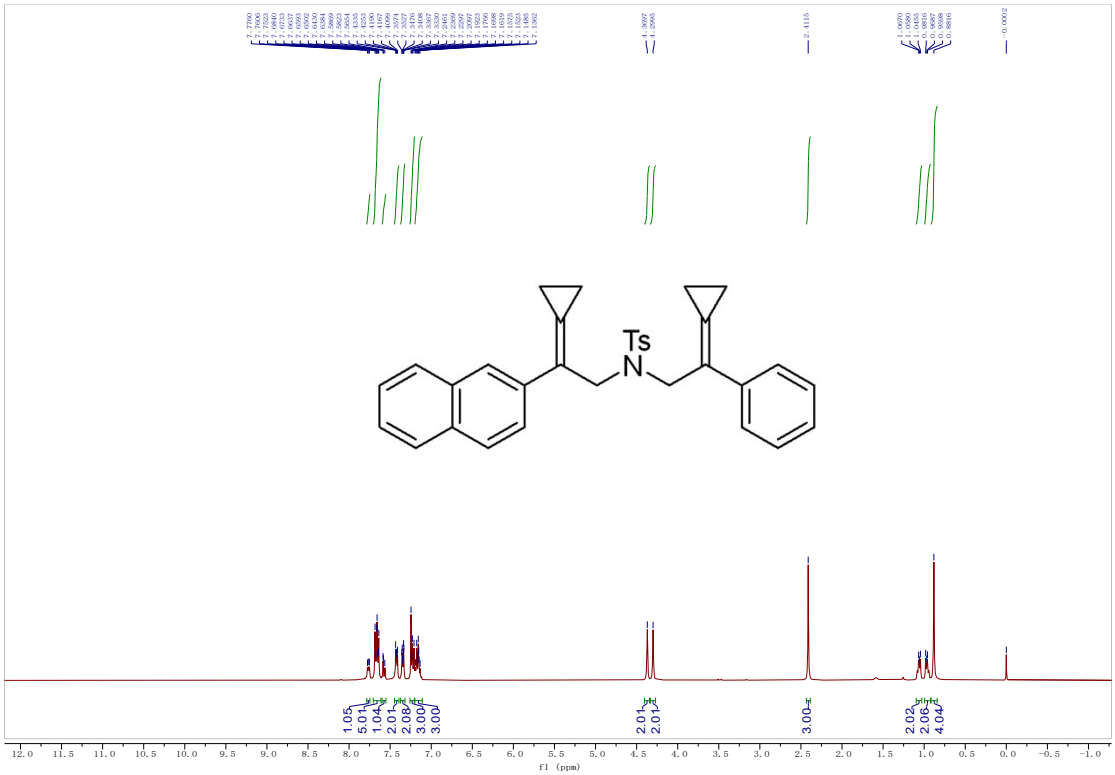
Compound 1m: Yield: 343 mg, 71%; A white solid; M.p.: 155 - 157 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.9 Hz, 2H), 7.39 – 7.34 (m, 2H), 7.31 – 7.27 (m, 2H), 7.24 – 7.15 (m, 3H), 7.13 – 7.09 (m, 1H), 6.99 – 6.93 (m, 1H), 6.92 – 6.87 (m, 1H), 4.31 (s, 2H), 4.19 (s, 2H), 2.45 (s, 3H), 1.07 – 1.00 (m, 2H), 1.00 – 0.96 (m, 2H), 0.96 – 0.90 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 143.2, 138.7, 136.4, 129.7, 128.0, 127.4, 126.9, 126.9, 126.8, 126.0, 125.4, 124.1, 122.4, 122.3, 118.3, 51.9, 51.3, 21.7, 4.7, 4.4, 3.8, 2.1; IR (neat): ν 2973, 1594, 1353, 1333, 1163, 1090, 817, 743, 709, 697 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{27}H_{27}NO_2NaS_2$ $[M+Na]^+$: 484.1375, Found: 484.1384.

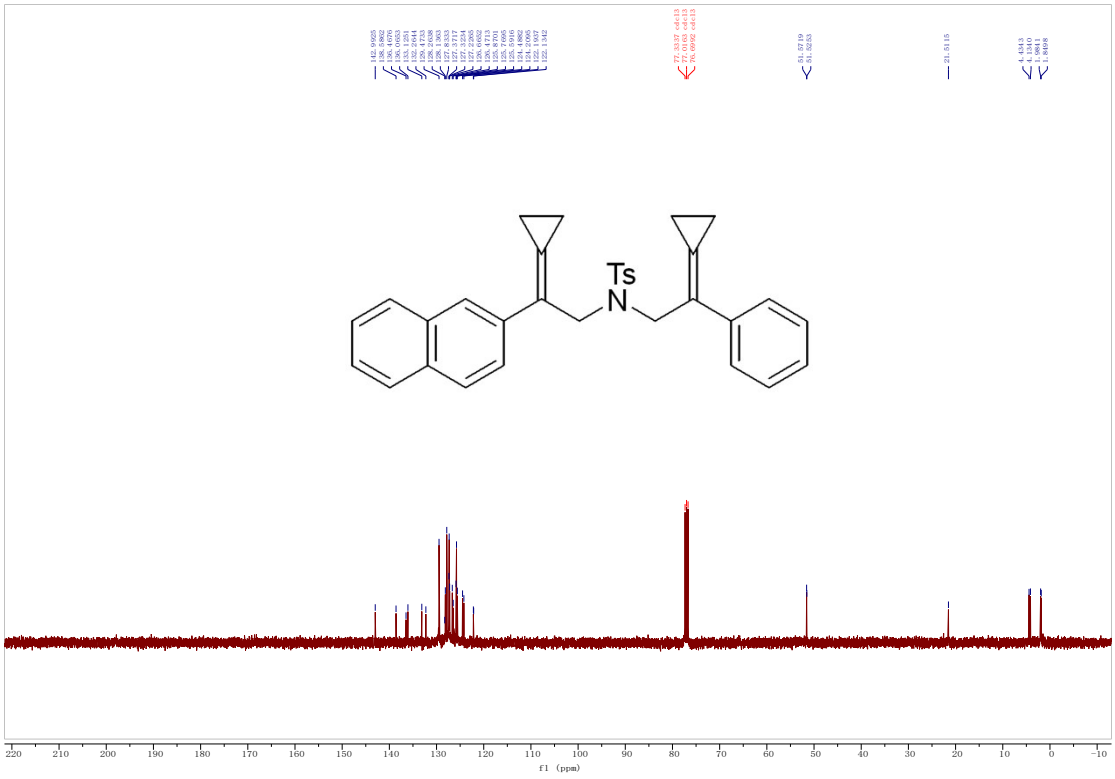

Ts
N
S
f1 (ppm)

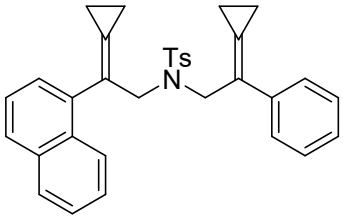

Ts
N
S
f1 (ppm)



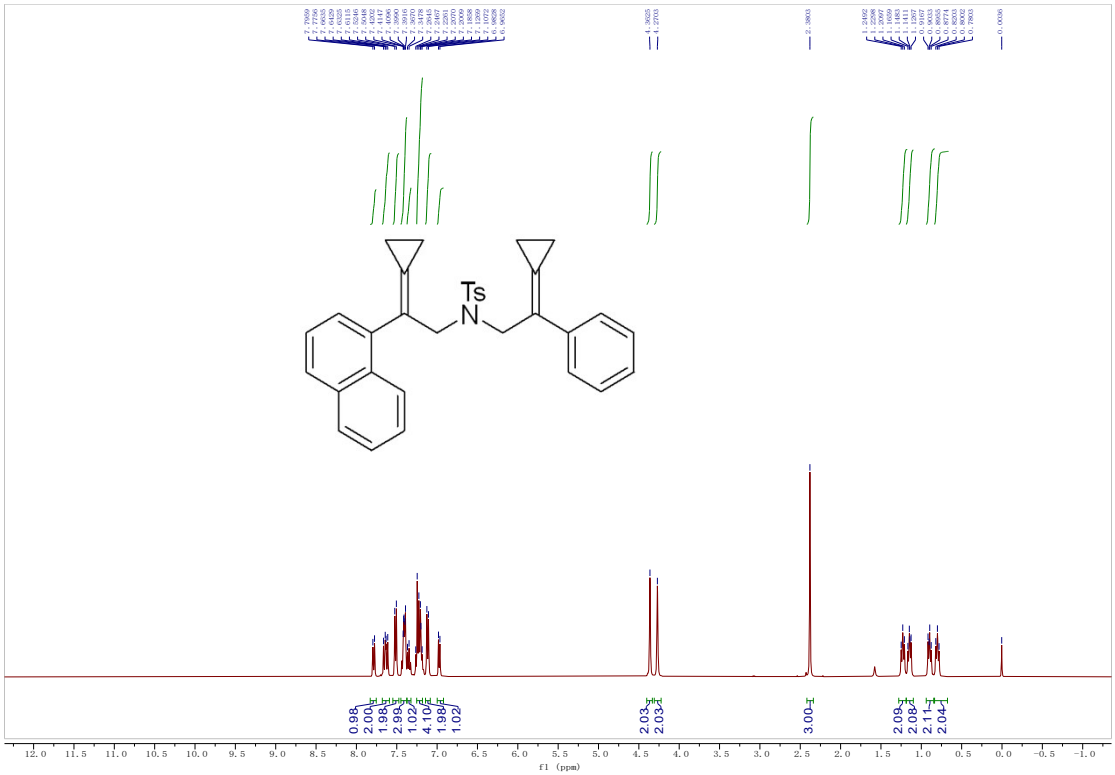
Compound 1n: Yield: 375 mg, 71%; A white solid; M.p.: 112 - 114 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.8 Hz, 2H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.27 – 7.23 (m, 3H), 7.23 – 7.18 (m, 2H), 7.08 – 7.00 (m, 1H), 7.00 – 6.93 (m, 1H), 6.83 (d, *J* = 7.4 Hz, 1H), 4.35 (s, 2H), 4.19 (s, 2H), 2.43 (s, 3H), 1.37 – 1.26 (m, 2H), 1.17 – 1.10 (m, 2H), 1.10 – 1.02 (m, 2H), 0.93 – 0.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 138.6, 136.5, 136.1, 133.1, 132.3, 129.5, 128.3, 128.1, 127.8, 127.4, 127.3, 127.2, 126.7, 126.5, 125.9, 125.8, 125.6, 124.5, 124.2, 122.2, 122.1, 77.3, 77.0, 76.7, 51.6, 51.5, 21.5, 4.4, 4.1, 2.0, 1.9; IR (neat): ν 2972, 1775, 1711, 1597, 1447, 1160, 1091, 1018, 747, 654 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{33}H_{31}NO_2NaS$ $[M+Na]^+$: 528.1968, Found: 528.1976.


Ts
N
1.05
5.01
1.04
2.01
2.08
3.00
3.00
2.01
2.01
3.00
2.02
2.06
4.04
f1 (ppm)


Ts
N
f1 (ppm)



Compound 1o: Yield: 438 mg, 83%; A white solid; M.p.: 109 - 111 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.1 Hz, 1H), 7.68 – 7.59 (m, 2H), 7.51 (d, *J* = 7.9 Hz, 2H), 7.45 – 7.38 (m, 3H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.25 – 7.18 (m, 4H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.97 (d, *J* = 7.0 Hz, 1H), 4.36 (s, 2H), 4.27 (s, 2H), 2.38 (s, 3H), 1.28 – 1.19 (m, 2H), 1.19 – 1.10 (m, 2H), 0.94 – 0.85 (m, 2H), 0.84 – 0.68 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 138.2, 138.2, 137.1, 133.7, 131.4, 129.3, 128.3, 128.1, 127.2, 127.03, 126.95, 126.87, 126.23, 126.15, 125.8, 125.6, 125.5, 125.4, 125.1, 123.5, 122.4, 52.6, 51.6, 21.5, 4.5, 3.9, 2.6, 1.6; IR (neat): ν 3053, 1711, 1597, 1496, 1337, 1157, 1091, 740, 709, 694 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{33}H_{31}NO_2NaS$ $[M+Na]^+$: 528.1968, Found: 528.1963.


Ts
N
0.98
2.00
1.95
2.99
1.02
4.10
1.98
1.02
2.03
2.03
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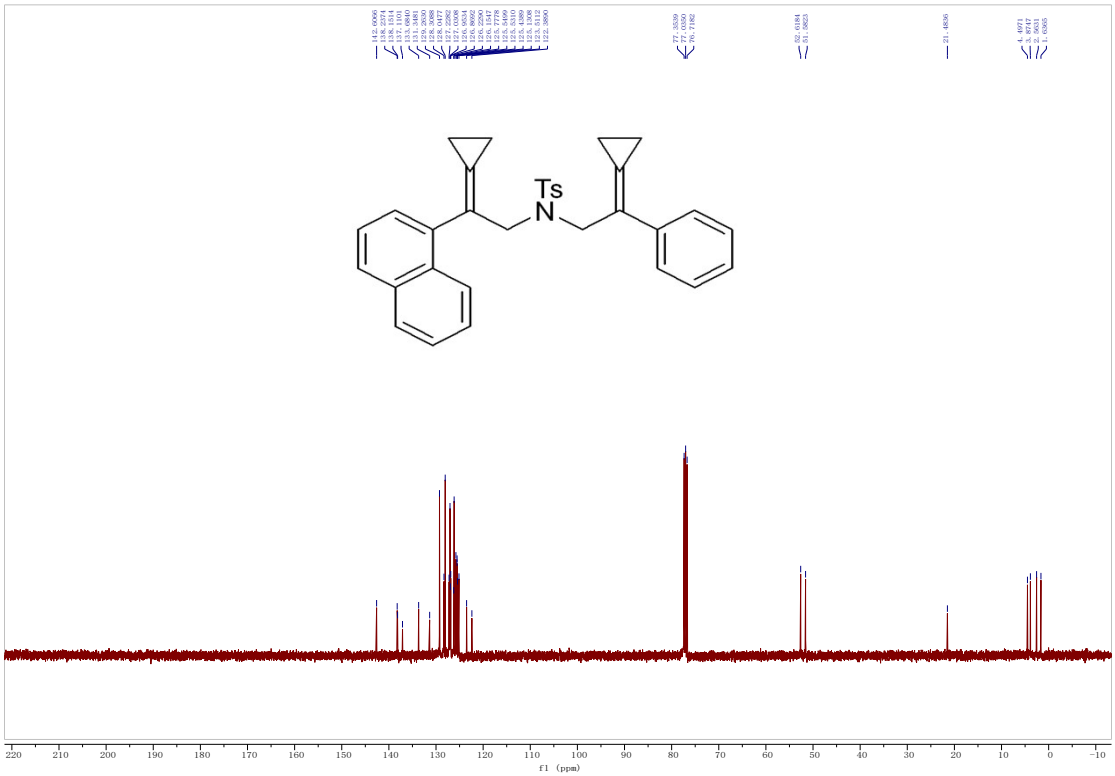
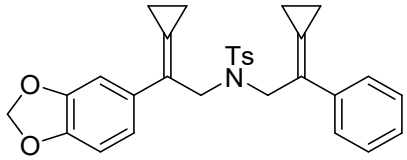
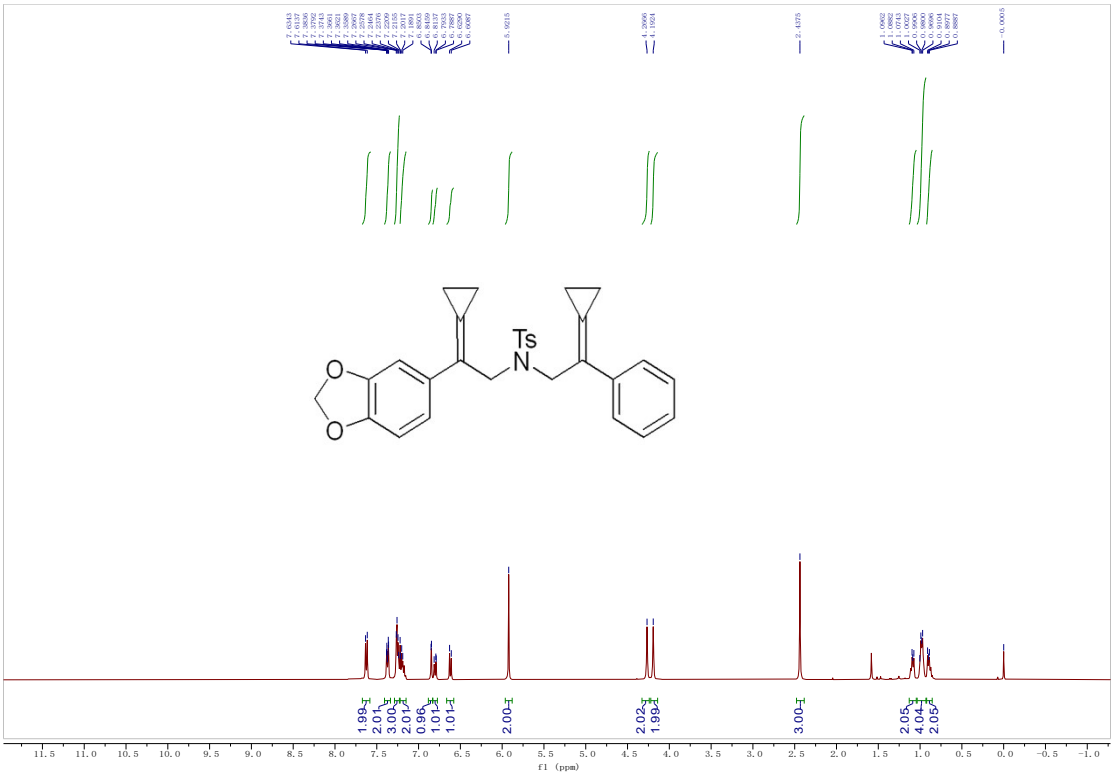
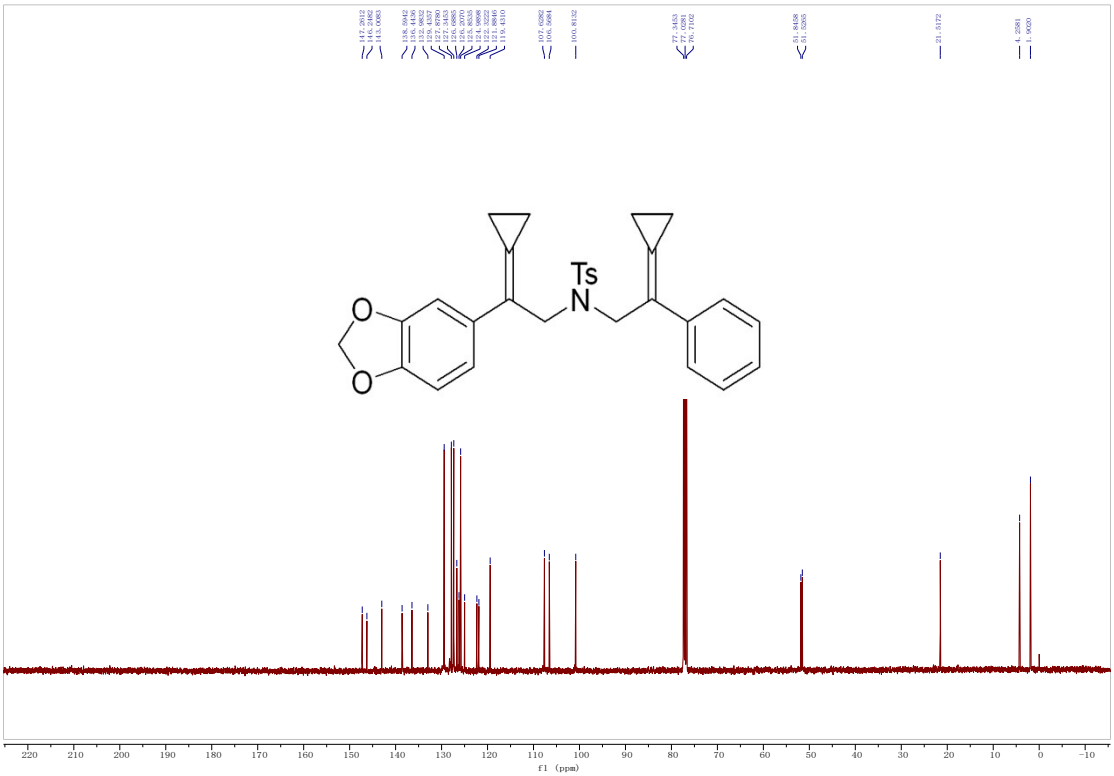
2.09
2.08
2.11
2.04
f1 (ppm)

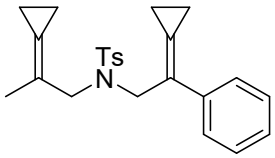

Ts
N
f1 (ppm)



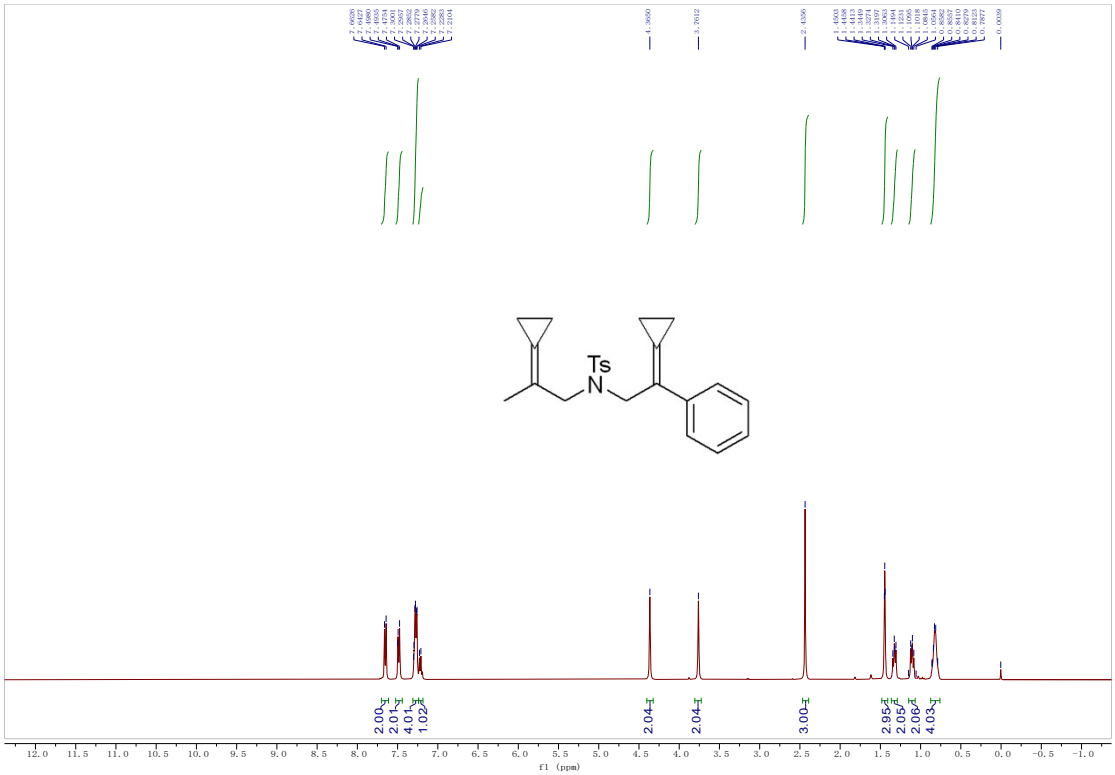
Compound 1p: Yield: 407 mg, 78%; A white solid; M.p.: 166 - 168 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.41 – 7.34 (m, 2H), 7.29 – 7.23 (m, 3H), 7.22 – 7.15 (m, 2H), 6.88 – 6.83 (m, 1H), 6.83 – 6.77 (m, 1H), 6.62 (d, *J* = 8.1 Hz, 1H), 5.92 (s, 2H), 4.27 (s, 2H), 4.19 (s, 2H), 2.44 (s, 3H), 1.13 – 1.05 (m, 2H), 1.04 – 0.93 (m, 4H), 0.92 – 0.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 146.3, 143.0, 138.6, 136.4, 133.0, 129.4, 127.9, 127.4, 126.7, 126.2, 125.9, 125.0, 122.3, 121.9, 119.4, 107.6, 106.6, 100.8, 51.9, 51.5, 21.5, 4.3, 1.9; IR (neat): ν 2968, 1712, 1489, 1440, 1338, 1222, 1161, 1091, 935, 954, 694 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{30}H_{29}NO_4NaS$ $[M+Na]^+$: 522.1709, Found: 522.1707.

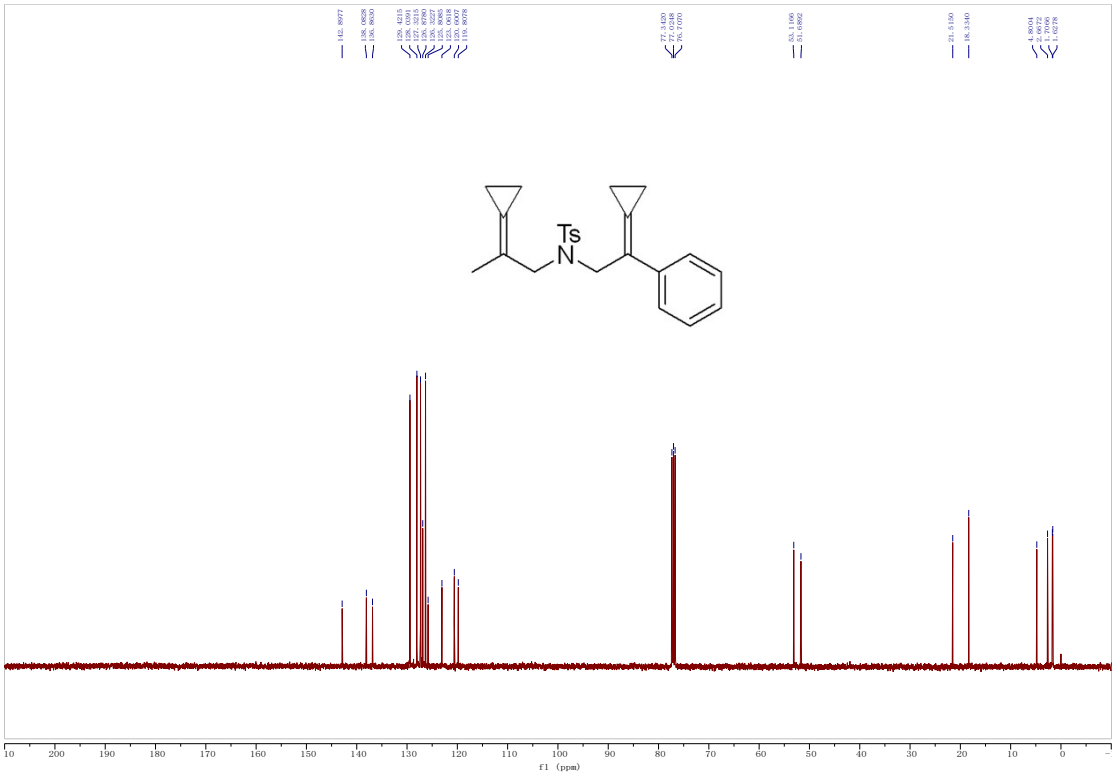

Ts
N
O
O
1.99
2.01
3.00
2.01
0.96
1.01
1.01
2.00
2.02
1.99
3.00
2.05
4.04
2.05
f1 (ppm)

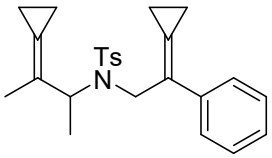

Ts
N
O
O
f1 (ppm)



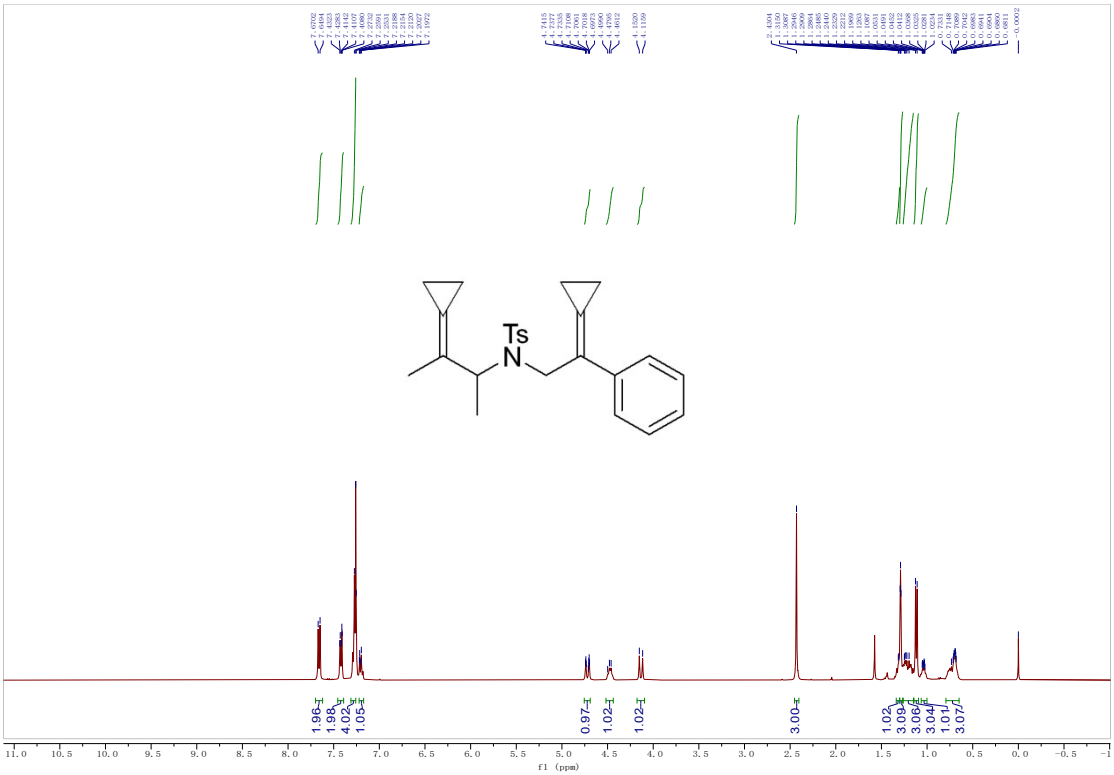
Compound 1q: Yield: 366 mg,88%; A white solid; M.p.: 152 - 154 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.52 – 7.44 (m, 2H), 7.31 – 7.24 (m, 4H), 7.22 (d, *J* = 7.2 Hz, 1H), 4.36 (s, 2H), 3.76 (s, 2H), 2.44 (s, 3H), 1.45 (t, *J* = 1.8 Hz, 3H), 1.36–1.29 (m, 2H), 1.15 – 1.07 (m, 2H), 0.87 – 0.76 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 138.1, 136.9, 129.4, 128.0, 127.3, 126.9, 126.3, 125.8, 123.1, 120.6, 119.8, 53.1, 51.7, 21.5, 18.3, 4.8, 2.7, 1.7, 1.6; IR (neat): ν 2975, 1597, 1448, 1162, 1091, 757, 666, 657 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{24}H_{27}NO_2SNa$ $[M+Na]^+$: 416.1655, Found: 416.1660.

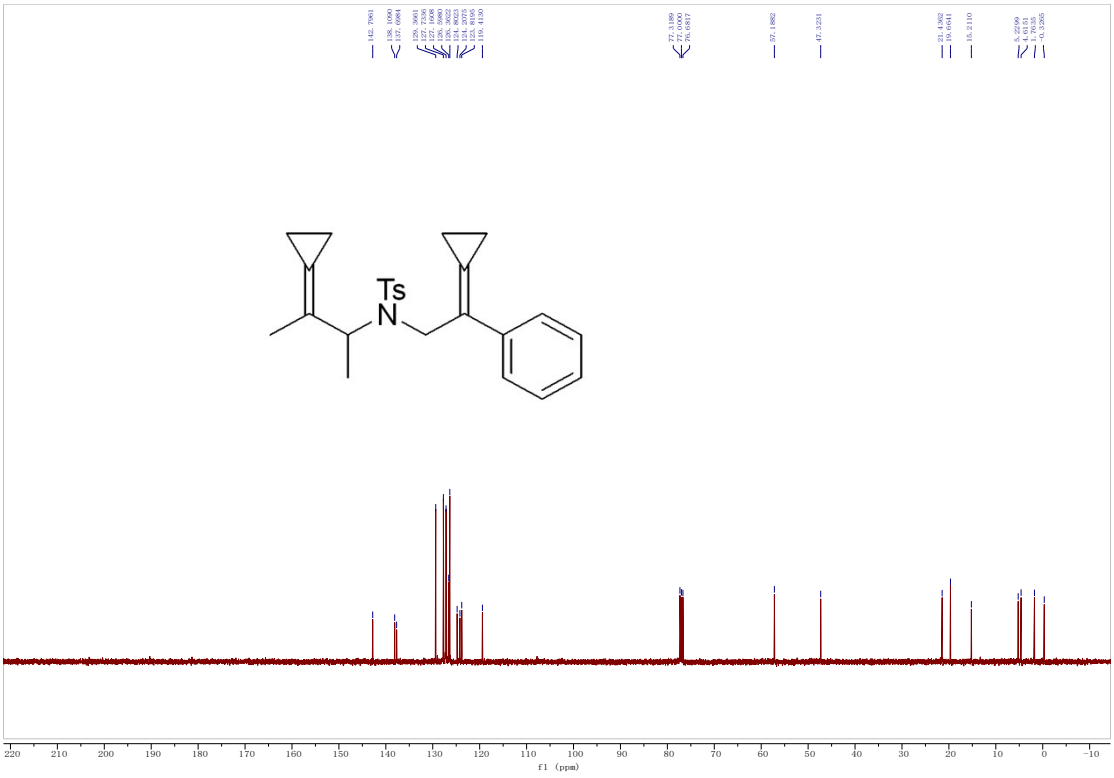

Ts
N
2.00
2.01
4.01
1.02
2.04
2.04
3.00
2.95
2.05
2.06
4.03
f1 (ppm)

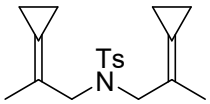

Ts
N
f1 (ppm)



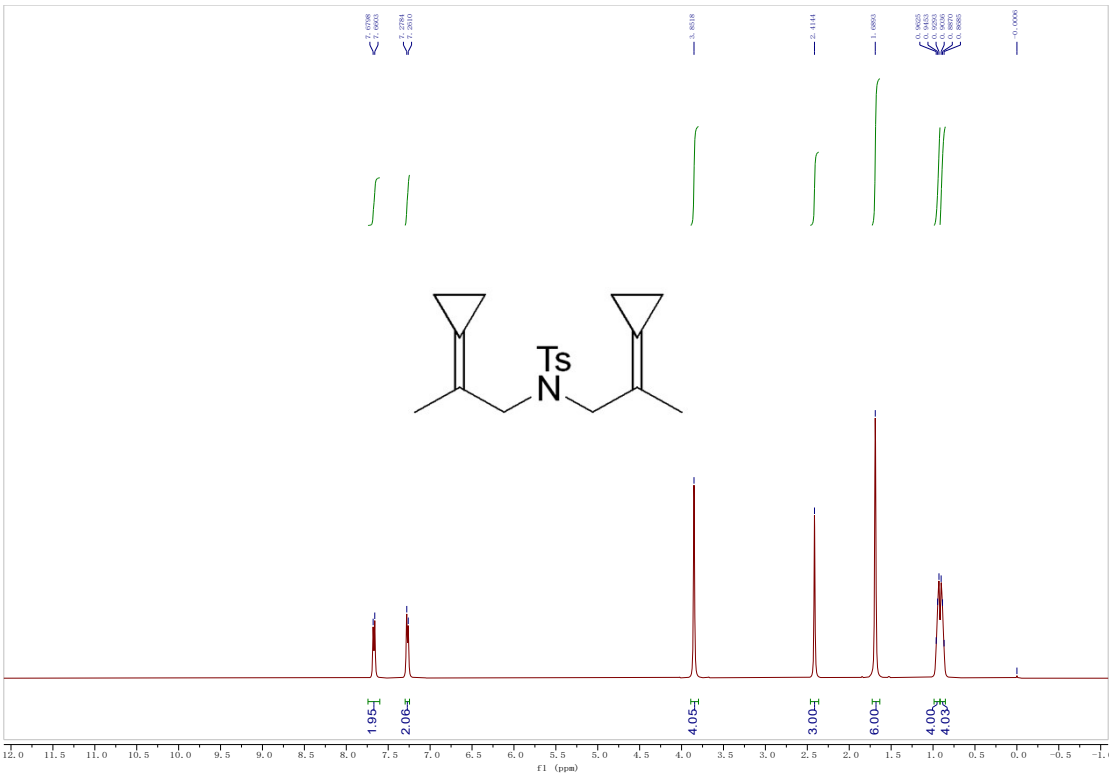
Compound 1r: Yield: 378mg, 88%; A white solid; M.p.: 146 - 148 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.46 – 7.39 (m, 2H), 7.31 – 7.26 (m, 4H), 7.22 – 7.17 (m, 1H), 4.76 – 4.69 (m, 1H), 4.52 – 4.44 (m, 1H), 4.13 (d, *J* = 14.4 Hz, 1H), 2.43 (s, 3H), 1.34 – 1.30 (m, 1H), 1.30 – 1.27 (m, 3H), 1.26 – 1.15 (m, 3H), 1.12 (d, *J* = 7.0 Hz, 3H), 1.06 – 1.00 (m, 1H), 0.79 – 0.65 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 138.2, 137.8, 129.5, 127.8, 127.2, 126.7, 126.5, 124.9, 124.3, 123.9, 119.5, 57.3, 47.4, 21.5, 19.8, 15.3, 5.3, 4.7, 1.9, -0.2; IR (neat): ν 2970, 2365, 2326, 1336, 1153, 1091, 821, 650 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{25}H_{29}NO_2SNa$ $[M+Na]^+$: 430.1811, Found: 430.1813.

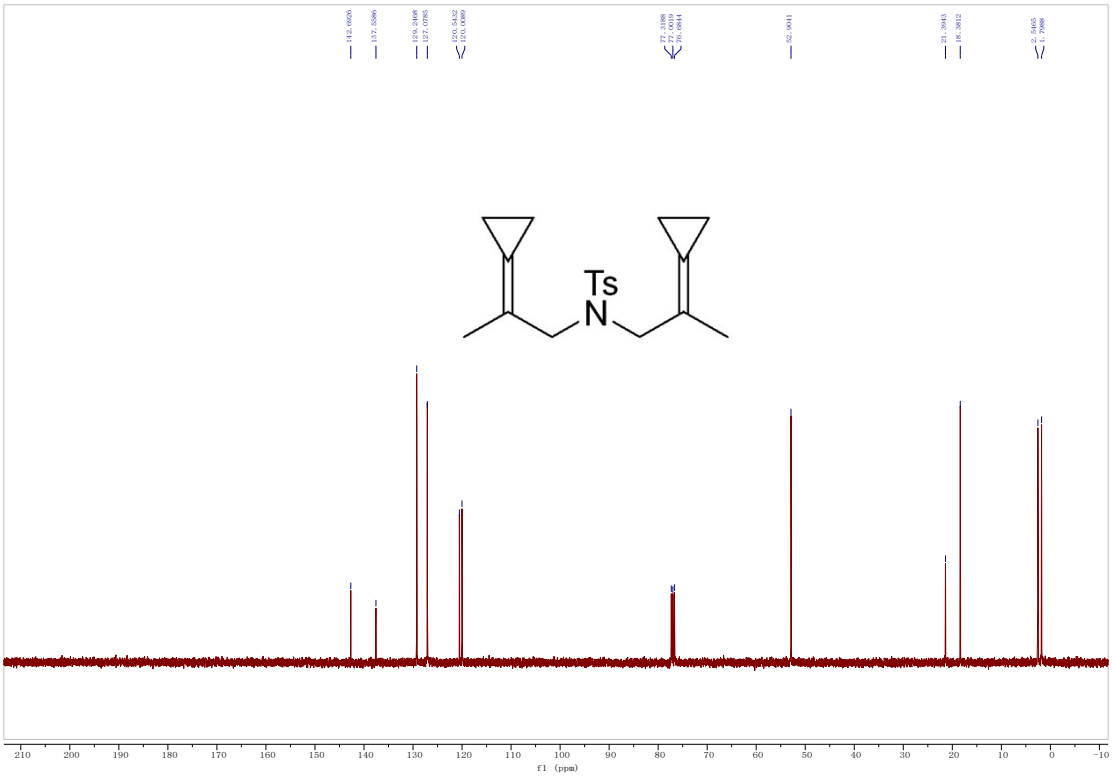

Ts
N
1.96
1.98
4.02
1.05
0.97
1.02
1.02
3.00
1.02
3.09
3.06
3.04
1.01
3.07
f1 (ppm)

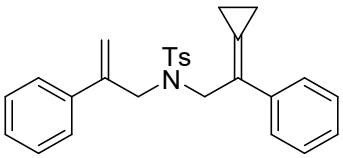

Ts
N
f1 (ppm)



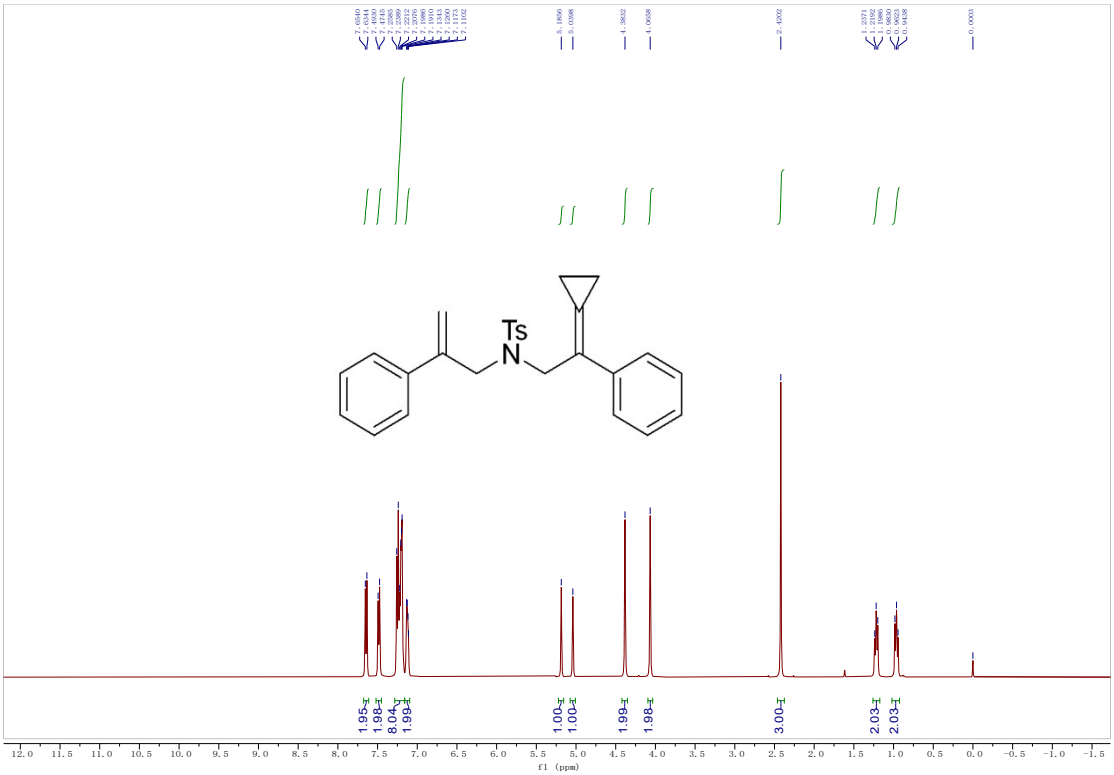
Compound 1s: Yield: 255mg, 72%; A white solid; M.p.: 98 - 100 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.4 Hz, 2H), 7.27 (d, *J* = 7.4 Hz, 2H), 3.85 (s, 4H), 2.41 (s, 3H), 1.69 (s, 6H), 0.99 – 0.92 (m, 4H), 0.92 – 0.85 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 137.6, 129.3, 127.1, 120.5, 120.0, 52.9, 21.4, 18.4, 2.6, 1.8; IR (neat): ν 1326, 1204, 1038, 821, 786, 670 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{19}H_{25}NO_2SNa$ $[M+Na]^+$: 354.1504, Found: 354.1511.

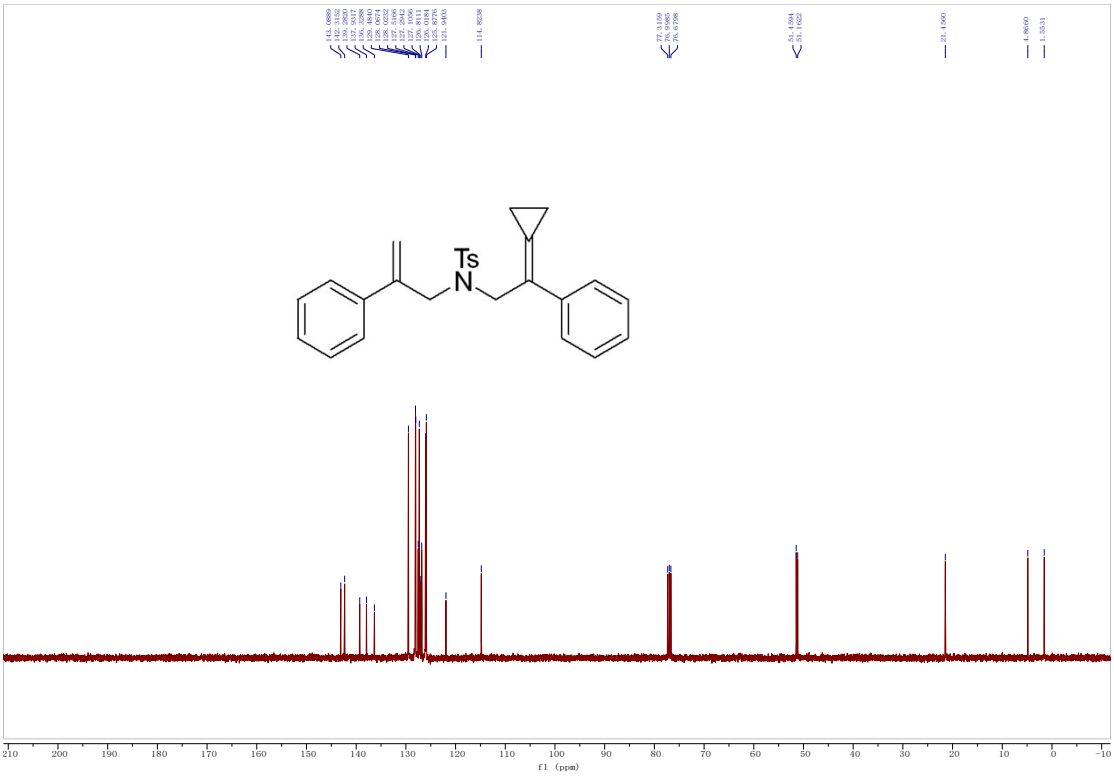

Ts
N
1.95
2.06
4.05
3.00
6.00
4.00
4.03
f1 (ppm)

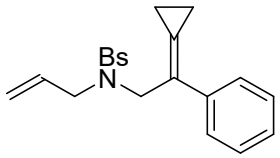

Ts
N
f1 (ppm)



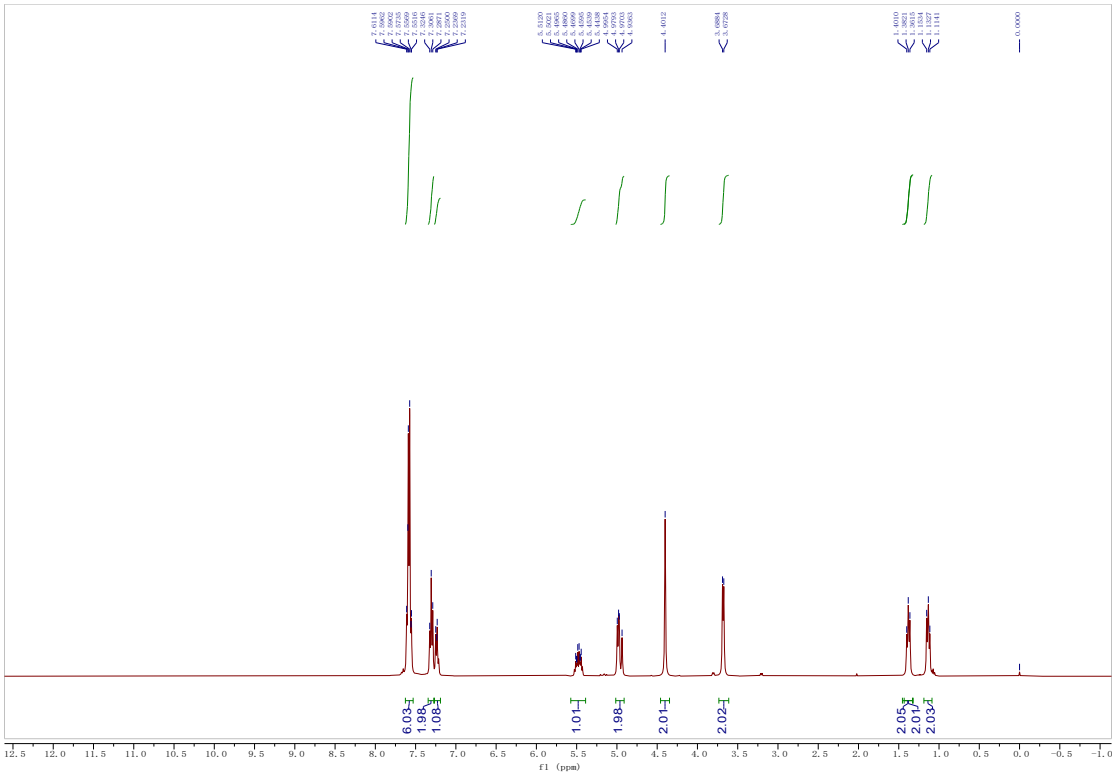
Compound 1t: Yield: 398 mg, 88%; A white solid; M.p.: 125 - 127 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 7.4 Hz, 2H), 7.31 – 7.18 (m, 8H), 7.18 – 7.12 (m, 2H), 5.21 (s, 1H), 5.06 (s, 1H), 4.41 (s, 2H), 4.09 (s, 2H), 2.44 (s, 3H), 1.28 – 1.19 (m, 2H), 1.04 – 0.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 142.3, 139.3, 137.9, 136.3, 129.5, 128.1, 128.0, 127.5, 127.3, 127.1, 126.8, 126.0, 125.9, 121.9, 114.8, 51.5, 51.2, 21.5, 4.9, 1.6; IR (neat): ν 3054, 1711, 1597, 1444, 1388, 1160, 1091, 815, 773 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{27}H_{27}NO_2SNa$ $[M+Na]^+$: 452.1655, Found: 452.1659.

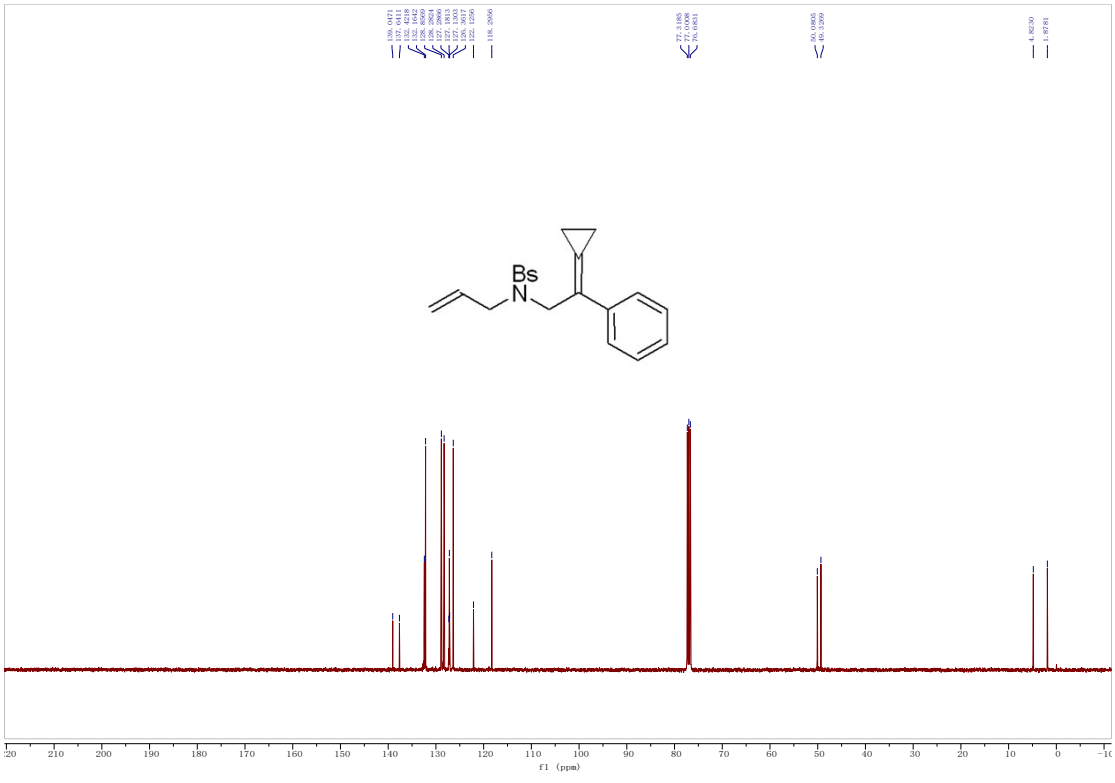

Ts
N
1.95
1.98
8.04
1.99
1.00
1.00
1.99
1.98
3.00
2.03
2.03
f1 (ppm)

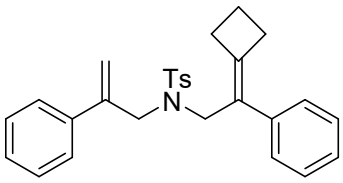

Ts
N
f1 (ppm)



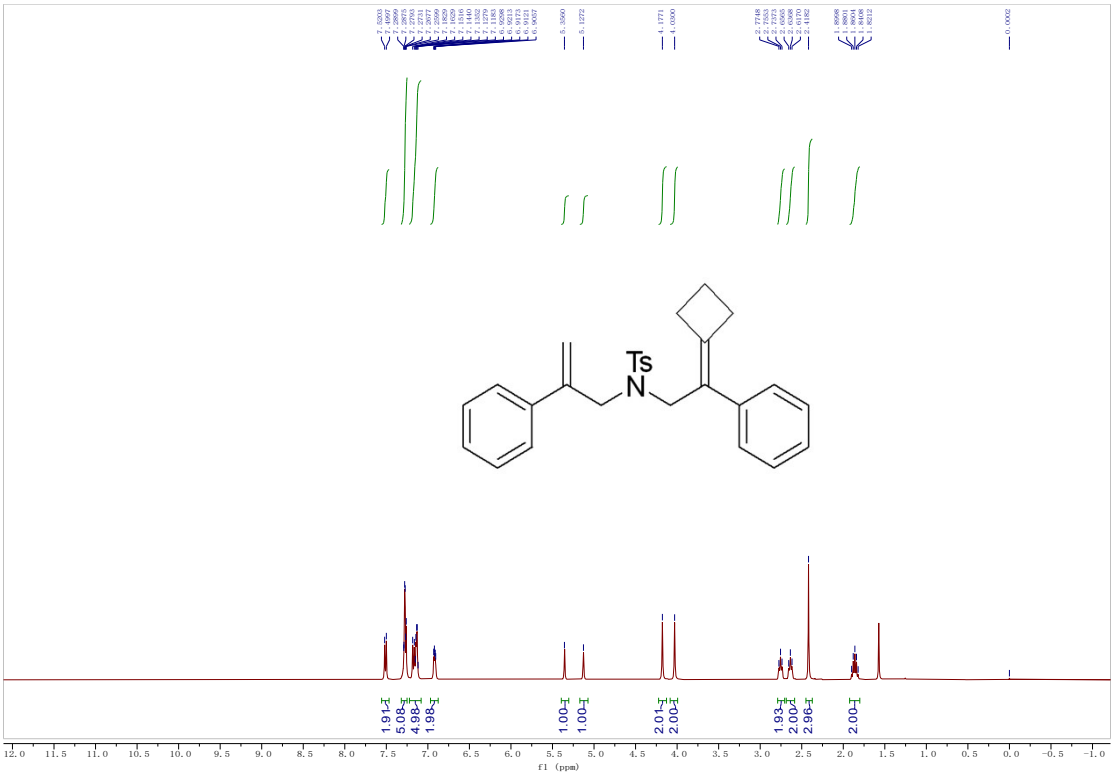
Compound 1u: Yield: 304 mg, 69%; A yellow solid; M.p.: 136 - 138 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.53 (m, 6H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.19 (m, 1H), 5.57 – 5.39 (m, 1H), 5.01 – 4.91 (m, 2H), 4.40 (s, 2H), 3.68 (d, *J* = 6.3 Hz, 2H), 1.38 (t, *J* = 7.9 Hz, 2H), 1.13 (t, *J* = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 137.6, 132.4, 132.2, 128.9, 128.3, 127.3, 127.2, 127.1, 126.4, 122.1, 118.3, 50.1, 49.3, 4.8, 1.2; IR (neat): ν 2913, 1574, 1346, 1162, 1088, 1067, 1008, 901, 823, 732, 695 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{20}H_{20}NO_2SNaBr$ $[M+Na]^+$: 440.0290, Found: 440.0297.

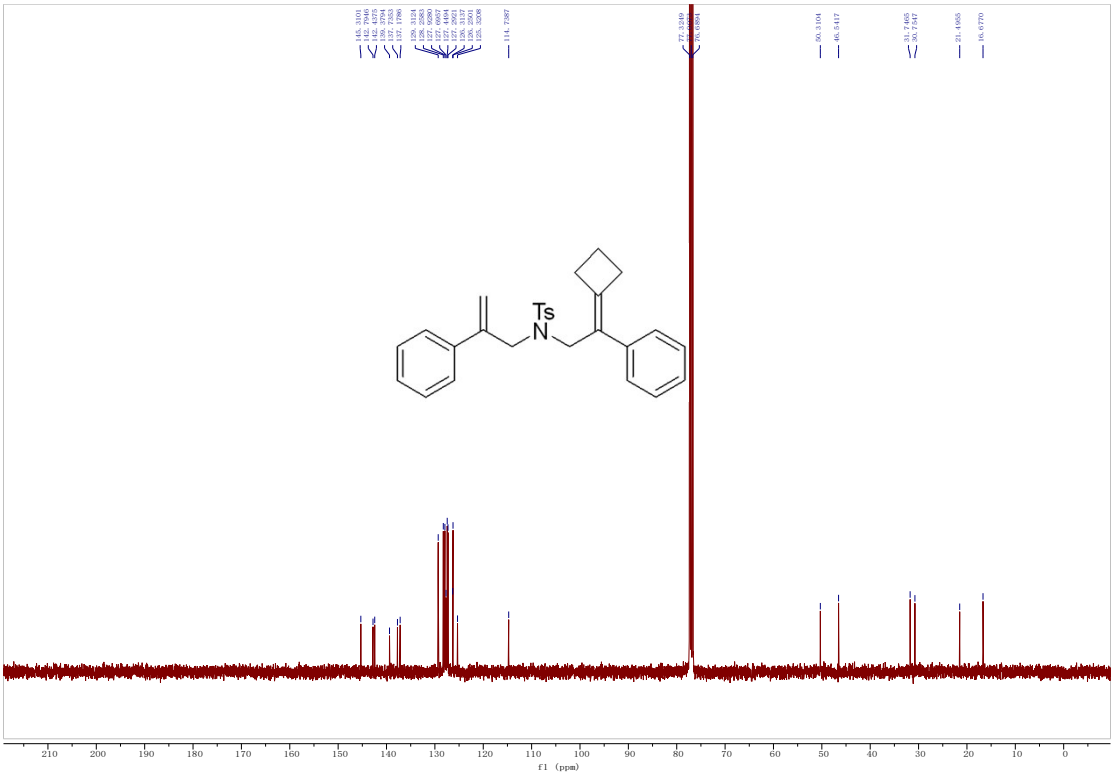

6.03
1.98
1.08
1.01
1.98
2.01
2.02
2.05
2.01
2.03
f1 (ppm)

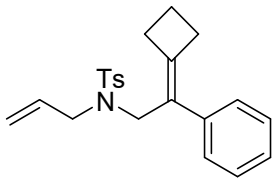

Bs
N
f1 (ppm)



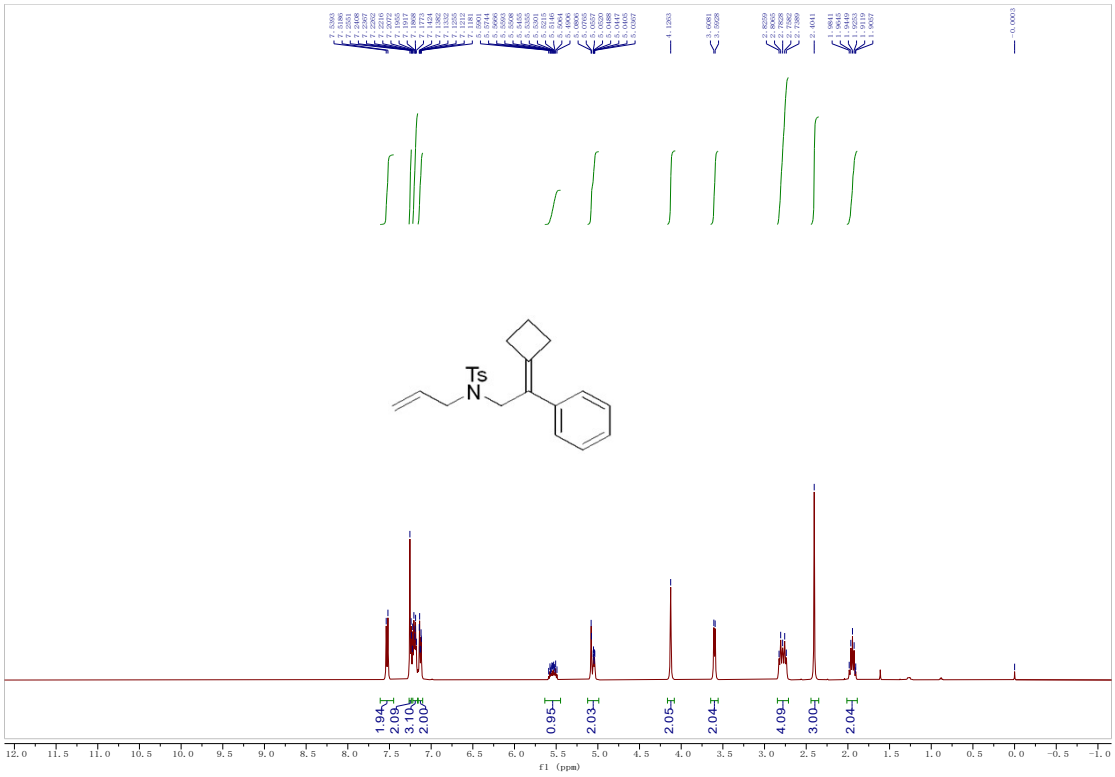
Compound 1v: Yield: 401 mg, 86%; A white solid; M.p.: 138 - 140 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.24 (m, 5H), 7.22 – 7.08 (m, 5H), 6.97 – 6.88 (m, 2H), 5.36 (s, 1H), 5.13 (s, 1H), 4.18 (s, 2H), 4.03 (s, 2H), 2.76 (t, *J* = 7.5 Hz, 2H), 2.64 (t, *J* = 7.9 Hz, 2H), 2.42 (s, 3H), 1.92 – 1.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 142.8, 142.4, 139.4, 137.7, 137.2, 129.3, 128.3, 127.9, 127.7, 127.5, 127.3, 126.3, 126.3, 125.3, 114.7, 50.3, 46.5, 31.8, 30.8, 21.5, 16.7; IR (neat): ν 2916, 2001, 1260, 1157, 1093, 1019, 802, 762, 700, 652 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{28}H_{29}NO_2SNa$ $[M+Na]^+$: 466.1811, Found: 466.1817.

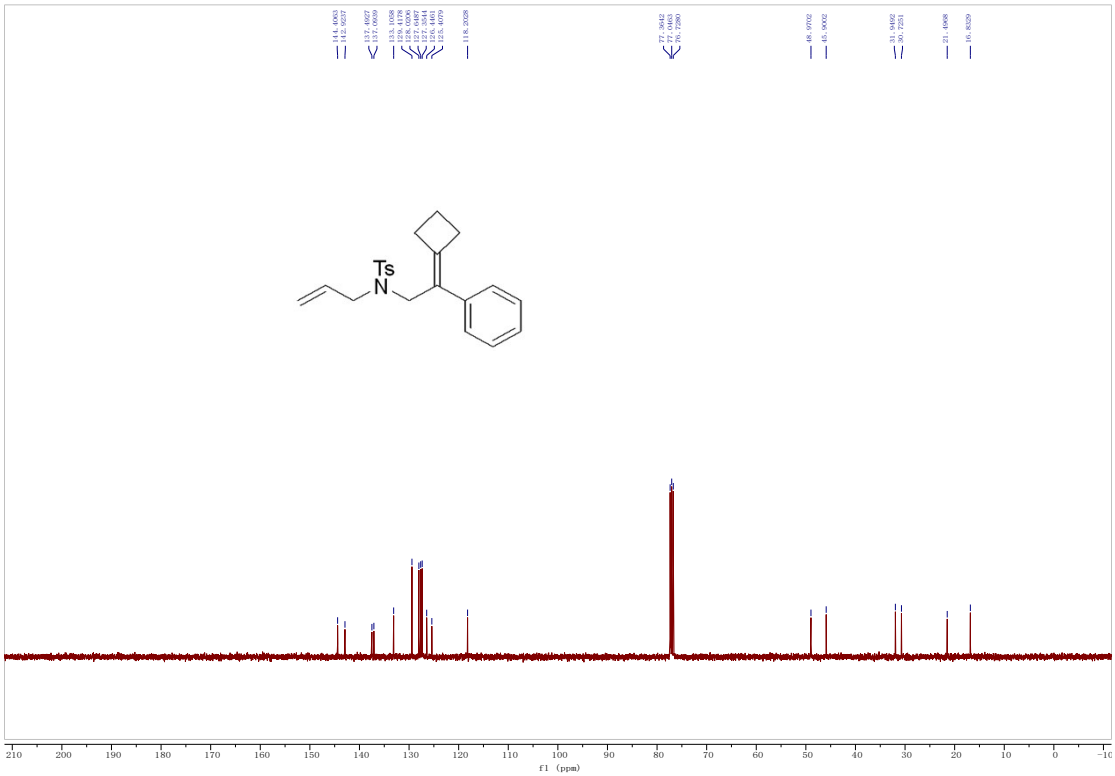

Ts
N
1.91
5.08
4.98
1.98
1.00
1.00
2.01
2.00
1.93
2.00
2.96
2.00
f1 (ppm)

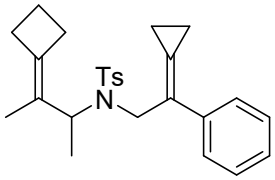

Ts
N
f1 (ppm)



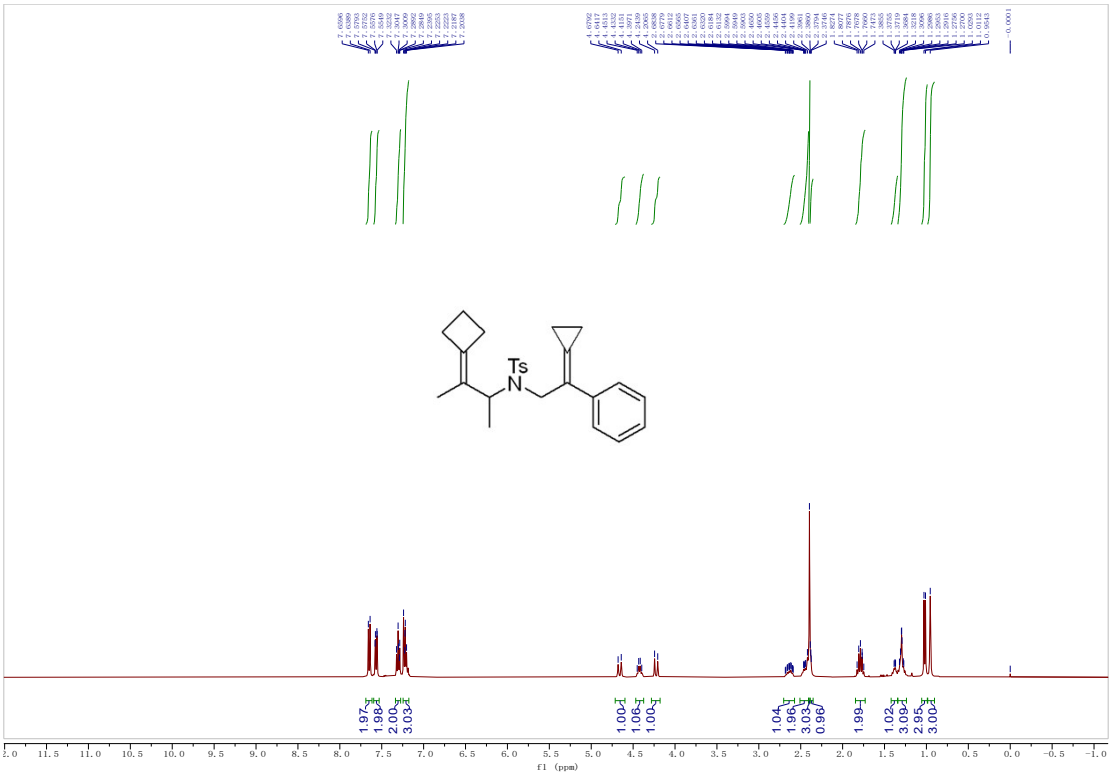
Compound 1w: Yield: 297 mg, 75%; A white solid; M.p.: 128 - 130 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.26 – 7.24 (m, 2H), 7.22 – 7.16 (m, 3H), 7.16 – 7.10 (m, 2H), 5.64 – 5.45 (m, 1H), 5.12 – 4.99 (m, 2H), 4.13 (s, 2H), 3.60 (d, *J* = 6.1 Hz, 2H), 2.85 – 2.71 (m, 4H), 2.40 (s, 3H), 2.01 – 1.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 142.9, 137.5, 137.1, 133.1, 129.4, 128.0, 127.7, 127.4, 126.5, 125.4, 118.2, 49.0, 45.9, 31.9, 30.7, 21.5, 16.8; IR (neat): ν 2956, 2011, 1187, 1031, 852, 756, 705, 649 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{28}H_{29}NO_2SNa$ $[M+Na]^+$: 390.1504, Found: 390.1516.

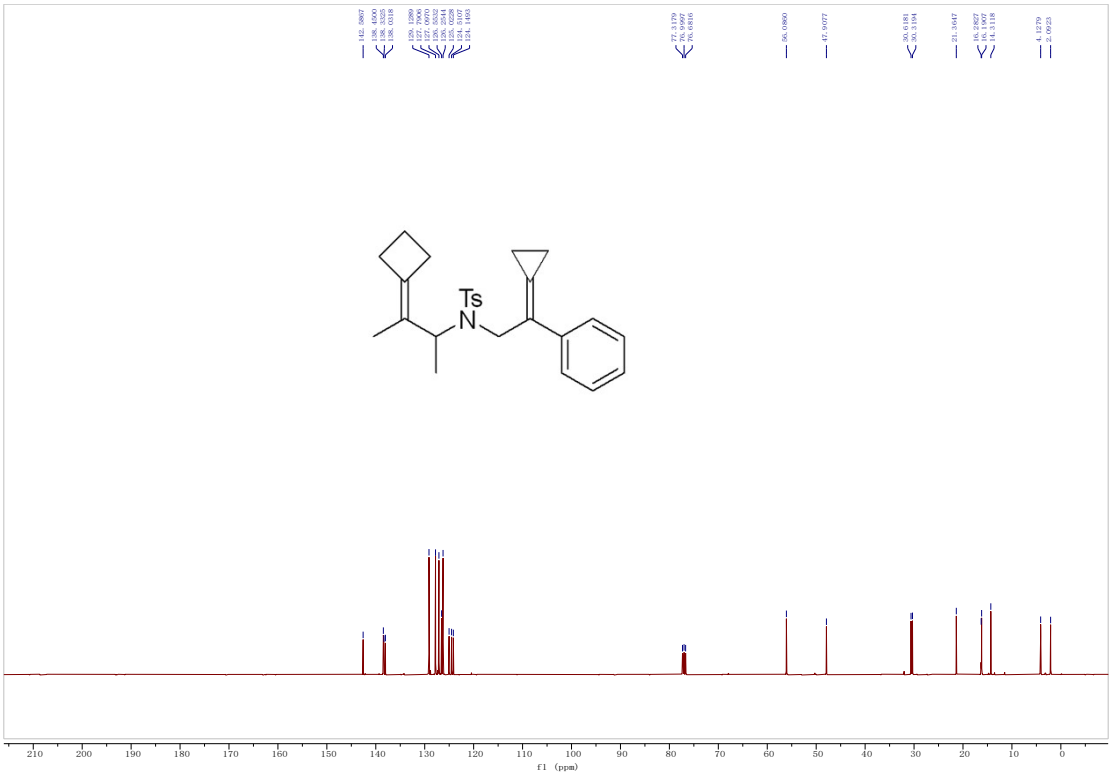

Ts
N
1.94
2.09
3.10
2.00
0.95
2.03
2.05
2.04
4.09
3.00
2.04
f1 (ppm)

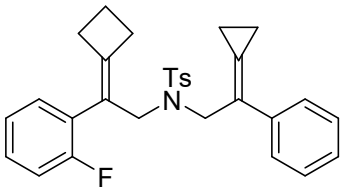

Ts
N
f1 (ppm)



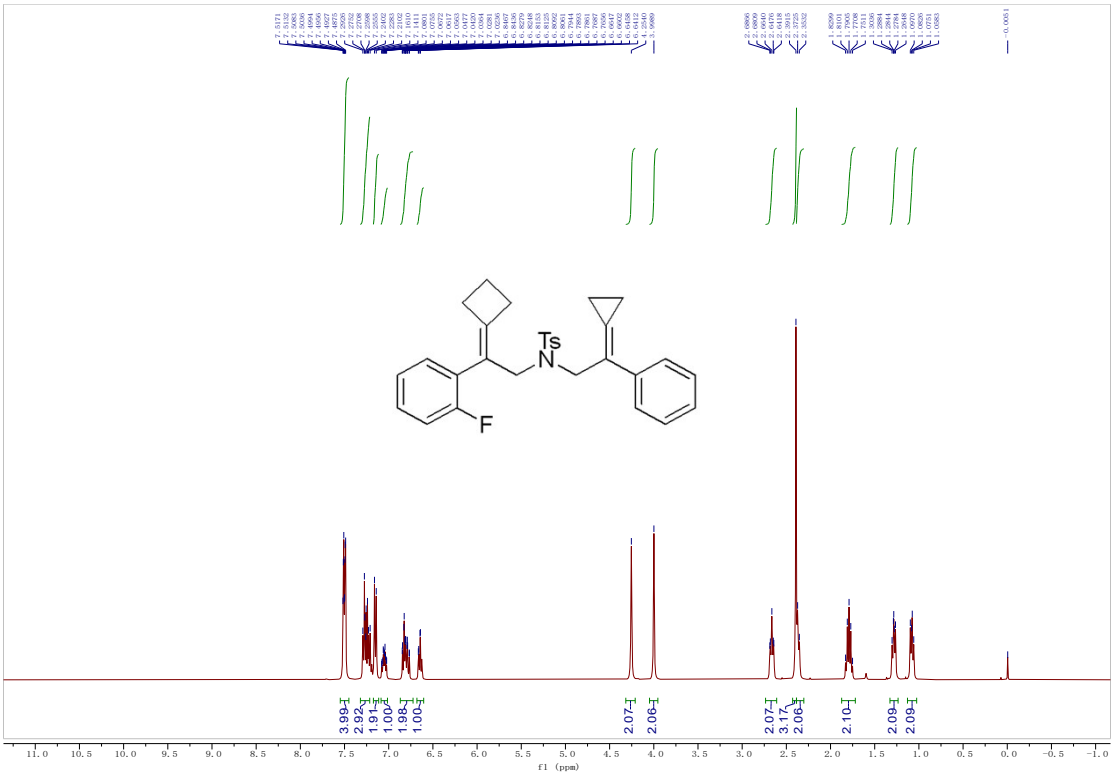
Compound 1x: Yield: 360 mg, 81%; A white solid; M.p.: 120 - 122 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.60 – 7.53 (m, 2H), 7.34 – 7.27 (m, 2H), 7.24 – 7.18 (m, 3H), 4.66 (d, *J* = 15.0 Hz, 1H), 4.42 (q, *J* = 7.2 Hz, 1H), 4.23 (d, *J* = 15.0 Hz, 1H), 2.70 – 2.57 (m, 1H), 2.51 – 2.41 (m, 2H), 2.40 (s, 3H), 2.39 – 2.35 (m, 1H), 1.85 – 1.73 (m, 2H), 1.42 – 1.34 (m, 1H), 1.34 – 1.24 (m, 3H), 1.02 (d, *J* = 7.2 Hz, 3H), 0.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 138.5, 138.3, 138.0, 129.1, 127.8, 127.1, 126.6, 126.3, 125.0, 124.5, 124.2, 56.1, 47.9, 30.6, 30.3, 21.4, 16.3, 16.2, 14.3, 4.1, 2.1; IR (neat): ν 2972, 1744, 1440, 1336, 1159, 1090, 903, 816, 661 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{26}H_{31}NO_2SNa$ $[M+Na]^+$: 444.1968, Found: 444.1974.

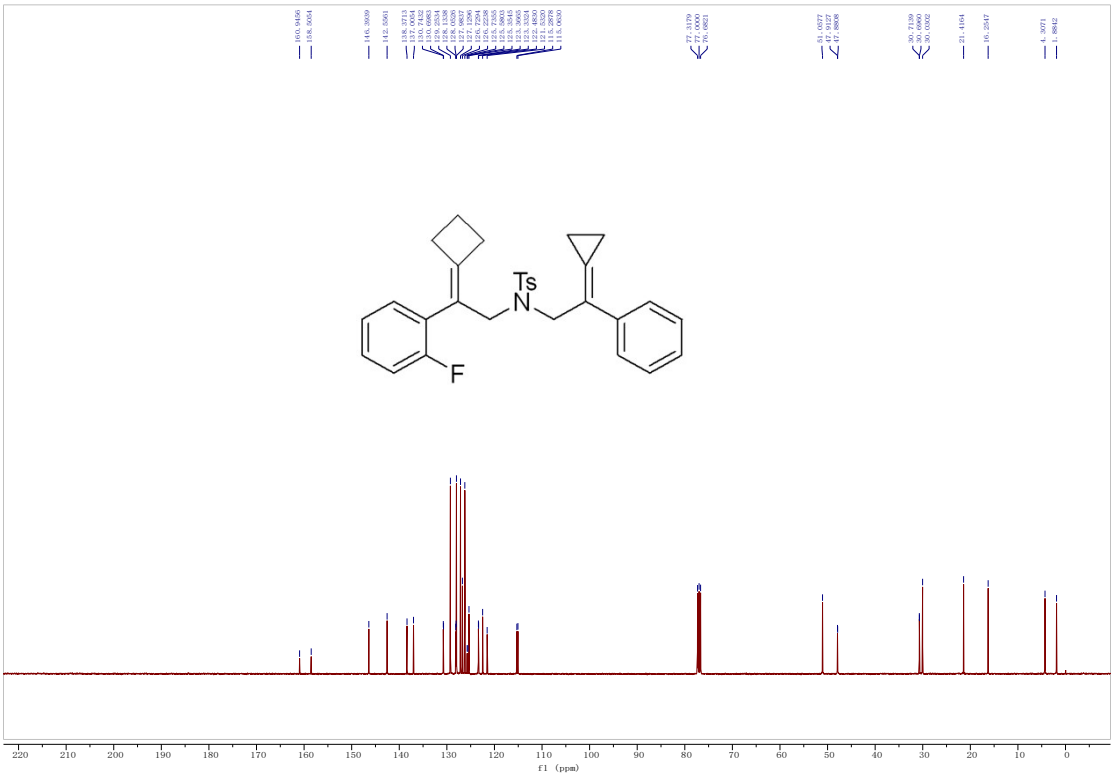

Ts
N
1.97
1.98
2.00
3.03
1.00
1.06
1.00
1.04
1.96
3.03
0.96
1.99
1.02
3.09
2.95
3.00
f1 (ppm)

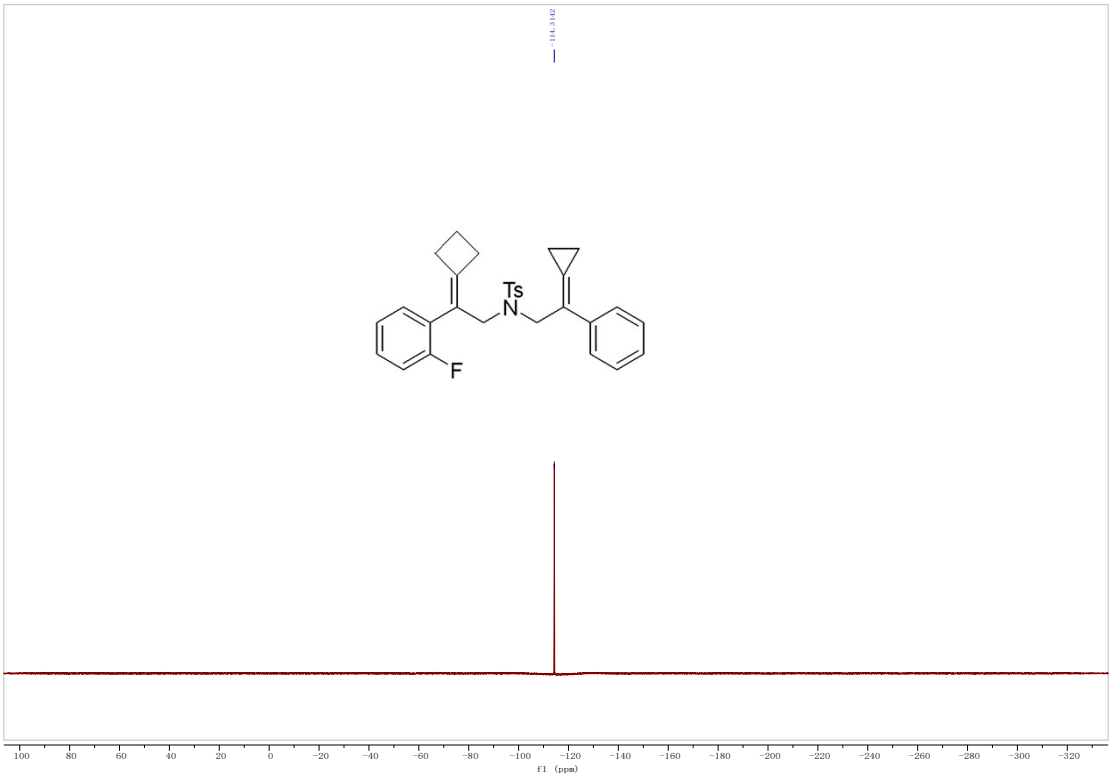

Ts
N
f1 (ppm)



Compound 1y: Yield: 449 mg, 87%; A white solid; M.p.: 124 - 126 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.5 – 7.5 (m, 4H), 7.3 – 7.2 (m, 3H), 7.2 (d, *J* = 8.0 Hz, 2H), 7.1 – 7.0 (m, 1H), 6.9 – 6.7 (m, 2H), 6.7 – 6.6 (m, 1H), 4.3 (s, 2H), 4.0 (s, 2H), 2.7 – 2.6 (m, 2H), 2.4 (s, 3H), 2.4 – 2.3 (m, 2H), 1.9 – 1.7 (m, 2H), 1.3 – 1.2 (m, 2H), 1.1 – 1.0 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 158.5 (d, *J* = 224.2 Hz), 146.4, 142.6, 138.4, 137.0, 130.74, 130.69 (d, *J* = 4.5 Hz), 129.3, 128.13, 128.05 (d, *J* = 8.1 Hz), 127.98, 127.1, 126.7, 126.2, 125.7, 125.6 (d, *J* = 15.5 Hz), 125.4, 123.4, 123.3 (d, *J* = 3.4 Hz), 122.5, 121.5, 115.3, 115.1 (d, *J* = 22.5 Hz), 51.1, 47.91, 47.88, 30.71, 30.69, 30.0, 21.4, 16.3, 4.3, 1.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.3; IR (neat): ν 2968, 1814, 1387, 1269, 1052, 934, 626 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{30}H_{30}NO_2SNaF$ $[M+Na]^+$: 510.1874, Found: 510.1882.


Ts
N
F
3.99
2.92
1.91
1.00
1.98
1.00
2.07
2.06
2.07
3.17
2.06
2.10
2.09
2.09
f1 (ppm)


Ts
N
F
f1 (ppm)


-114.3142
Ts
N
F
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
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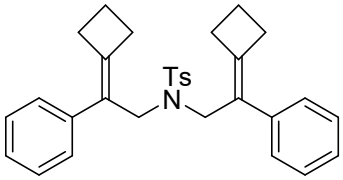
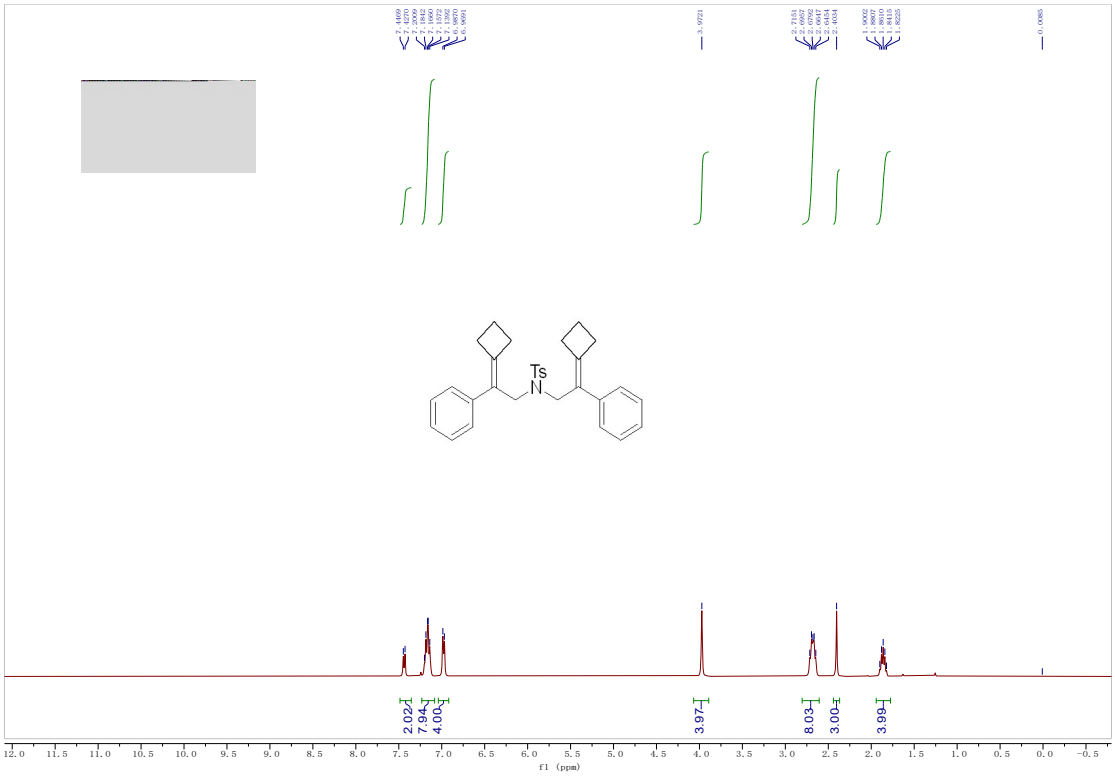
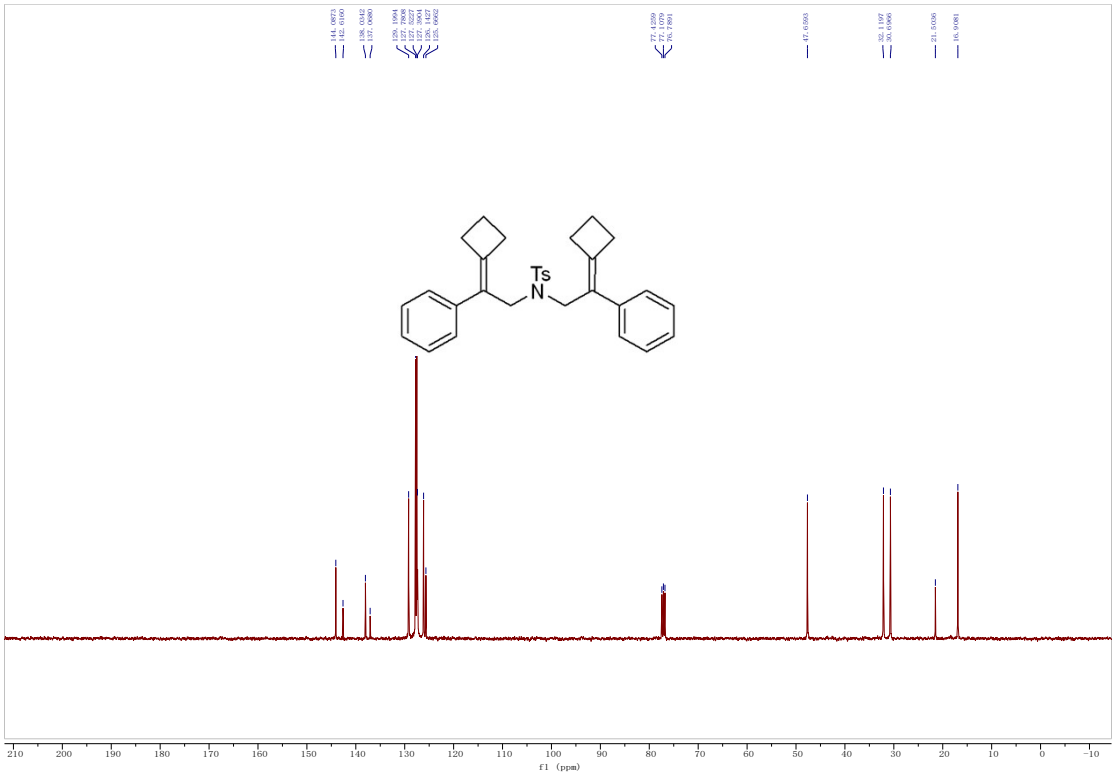
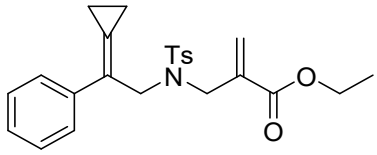
-180
-200
-220
-240
-260
-280
-300
-320
f1 (ppm)



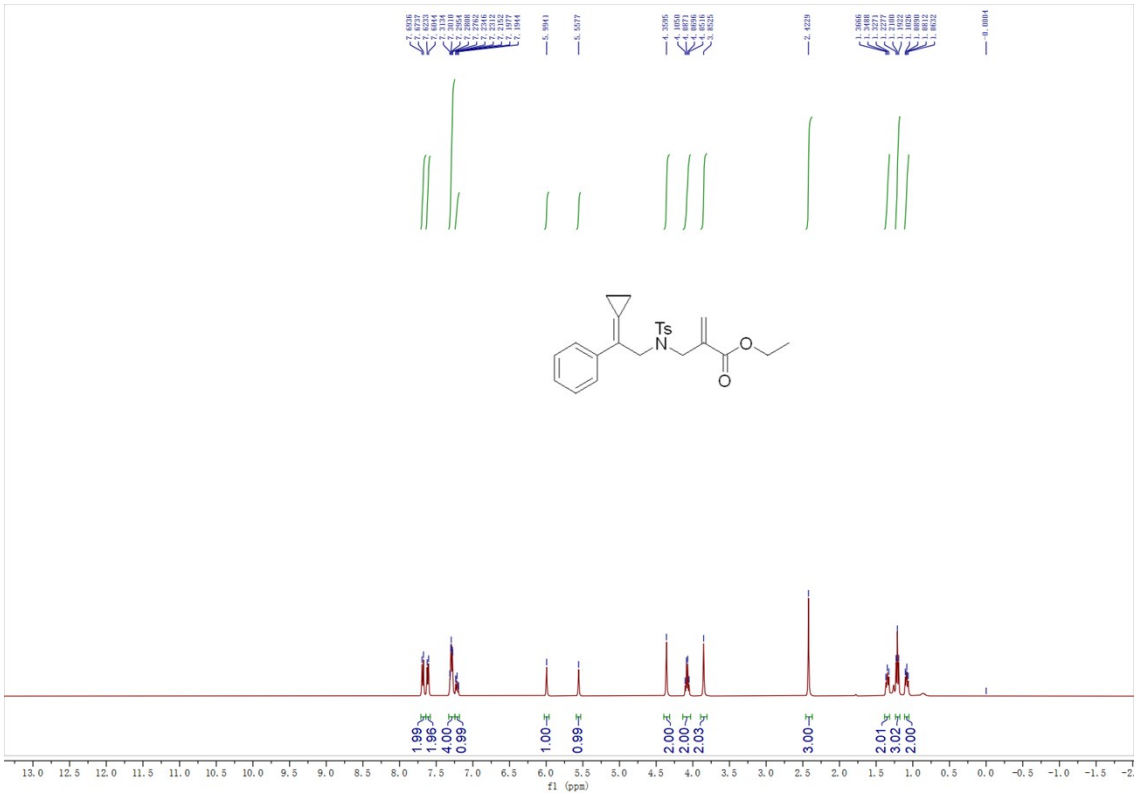
Compound 1z: Yield: 420 mg, 83%; A white solid; M.p.: 164 - 166 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.9 Hz, 2H), 7.23 – 7.08 (m, 8H), 6.98 (d, *J* = 7.1 Hz, 4H), 3.97 (s, 4H), 2.80 – 2.61 (m, 8H), 2.40 (s, 3H), 1.94 – 1.78 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 142.6, 138.0, 137.1, 129.2, 127.8, 127.5, 127.4, 126.1, 125.7, 47.7, 32.1, 30.7, 21.5, 16.9; IR (neat): ν 2968, 1805, 1503, 1305, 1164, 1112, 934, 625 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{31}H_{33}NO_2SNaF$ $[M+Na]^+$: 506.2130, Found: 506.2133.

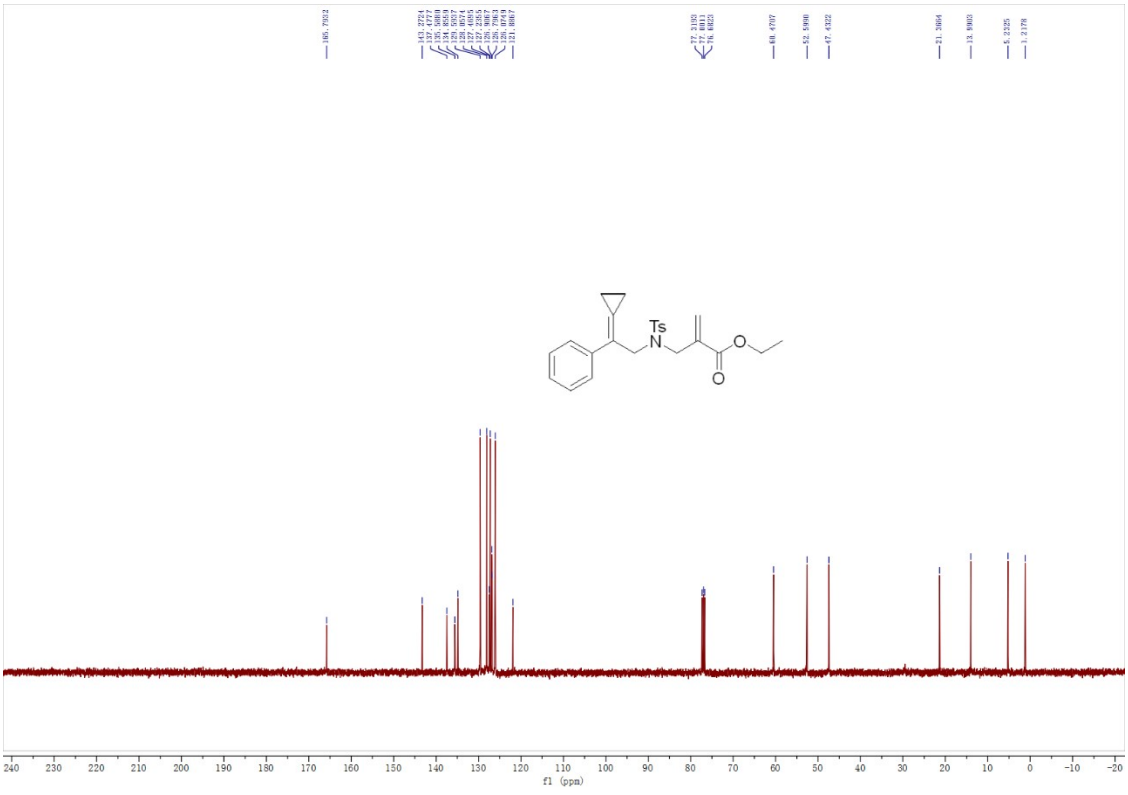

Ts
N
2.02
7.94
4.00
3.97
8.03
3.00
3.99
f1 (ppm)

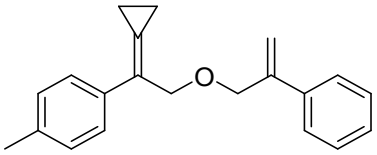

Ts
N
f1 (ppm)



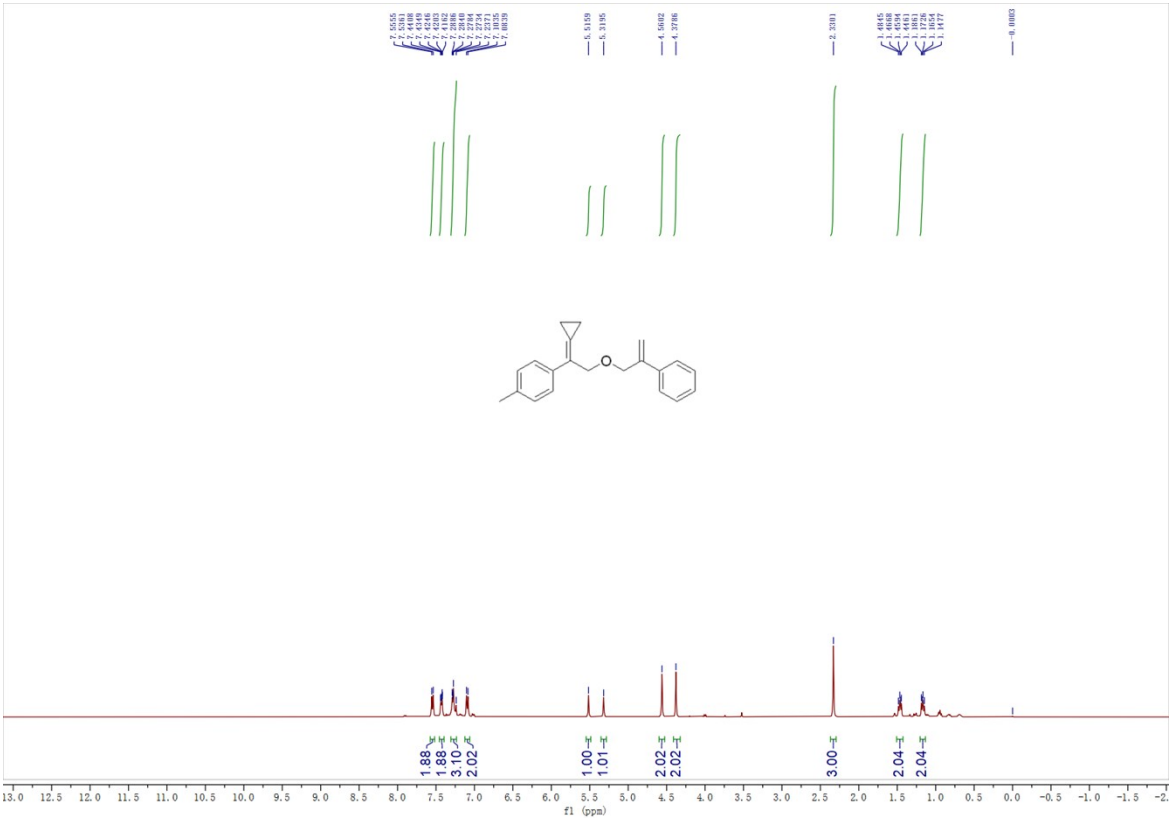
Compound 1aa: Yield: 285 mg, 67%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.24 (m, 4H), 7.24 – 7.18 (m, 1H), 5.99 (s, 1H), 5.56 (s, 1H), 4.36 (s, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 2H), 2.42 (s, 3H), 1.38 – 1.32 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.11 – 1.05 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 143.3, 137.5, 135.6, 134.9, 129.6, 128.1, 127.5, 127.2, 126.9, 126.8, 126.1, 121.9, 60.5, 52.6, 47.4, 21.4, 14.0, 5.2, 1.2; IR (neat): ν 2966, 1849, 1749, 1722, 1486, 1343, 1298, 1245, 1184, 769 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{24}H_{27}NO_4SNa$ $[M+Na]^+$: 448.1553, Found: 448.1553.

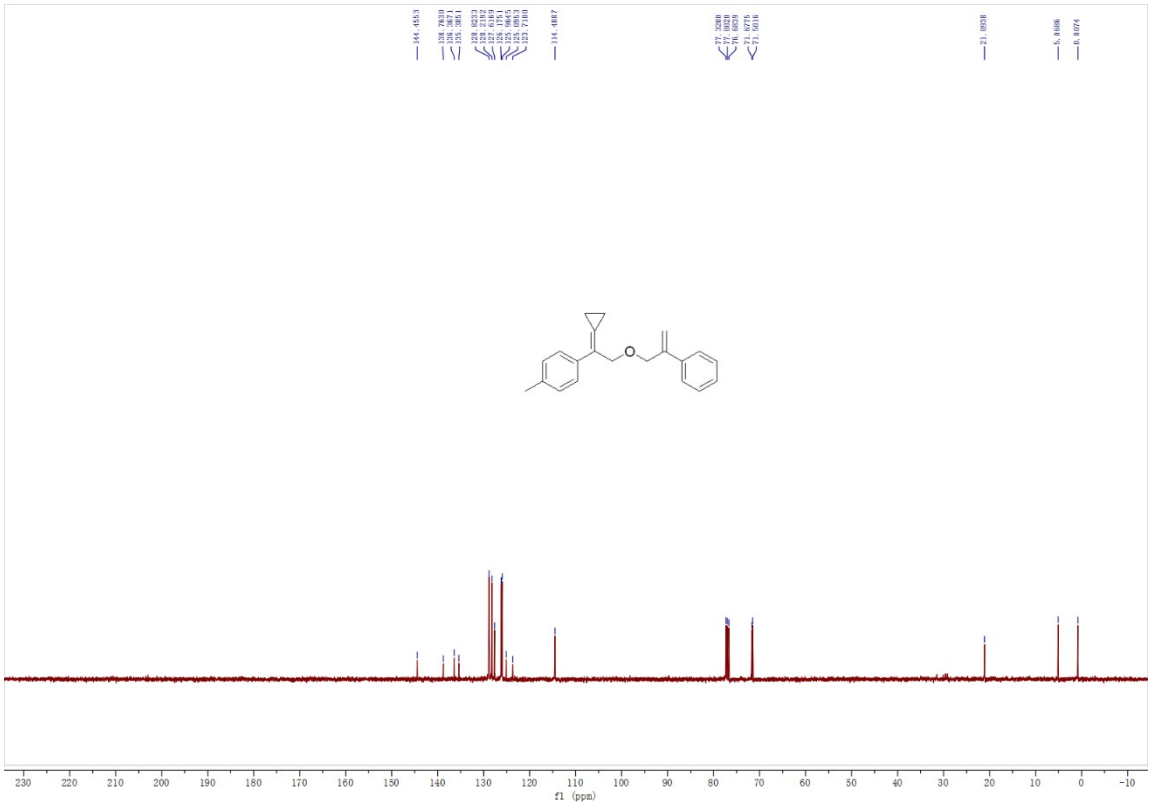

Ts
N
O
O
1.99
1.96
4.00
0.99
1.00
0.99
2.00
2.00
2.03
3.00
2.01
3.02
2.00
f1 (ppm)

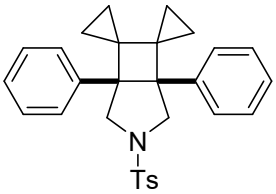

Ts
N
O
O
f1 (ppm)



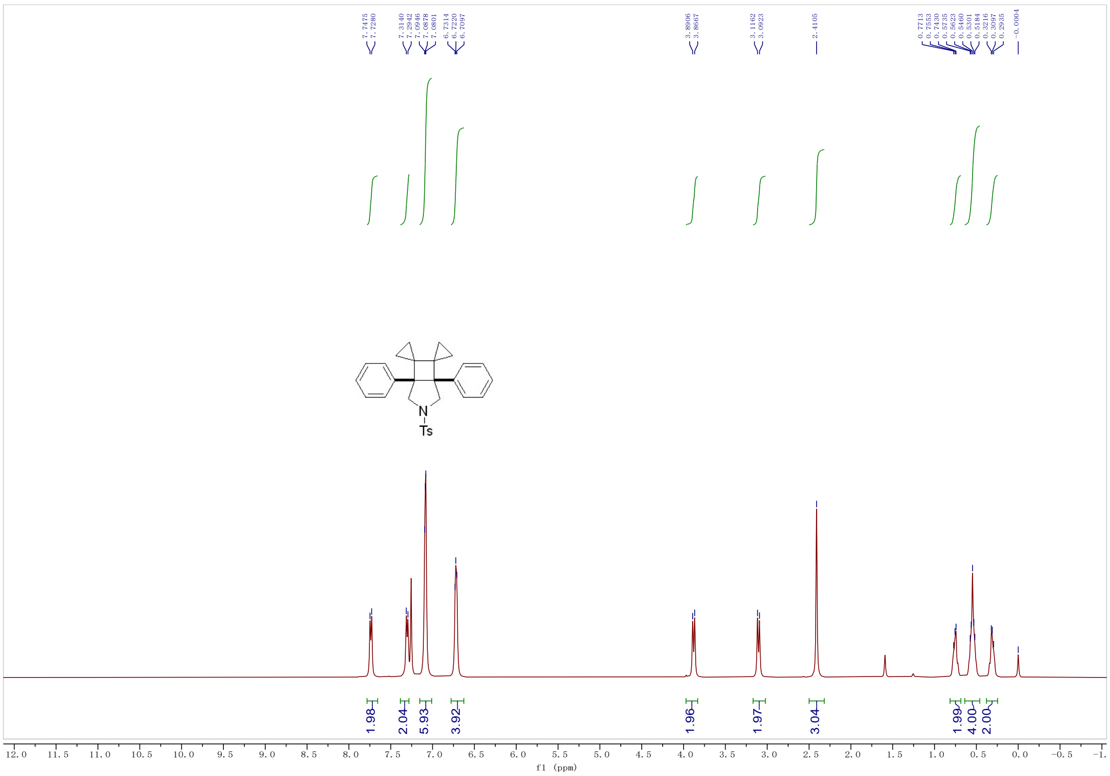
Compound 1ab: Yield: 245 mg, 85%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.8 Hz, 2H), 7.46 – 7.40 (m, 2H), 7.31 – 7.23 (m, 3H), 7.09 (d, *J* = 7.8 Hz, 2H), 5.52 (s, 1H), 5.32 (s, 1H), 4.56 (s, 2H), 4.38 (s, 2H), 2.33 (s, 3H), 1.51 – 1.43 (m, 2H), 1.20 – 1.13 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 138.8, 136.4, 135.4, 128.8, 128.2, 127.6, 126.2, 126.0, 125.1, 123.7, 114.5, 71.7, 71.5, 21.1, 5.1, 0.8; IR (neat): ν 2987, 1878, 1866, 1788, 1333, 1288, 1219, 1184, 785, 698 cm^{-1}; HRMS (EI - FI) Calcd. for $C_{21}H_{22}O$ $[M]^+$: 290.1665, Found: 290.1662.

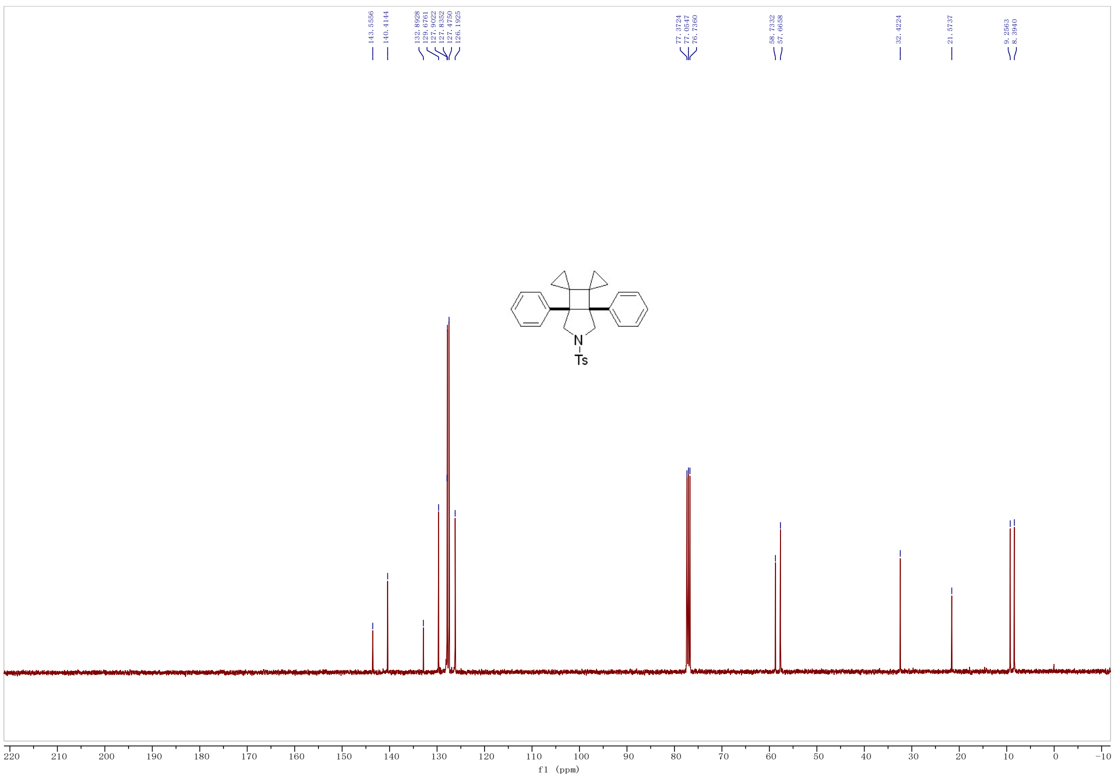


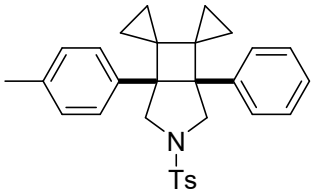




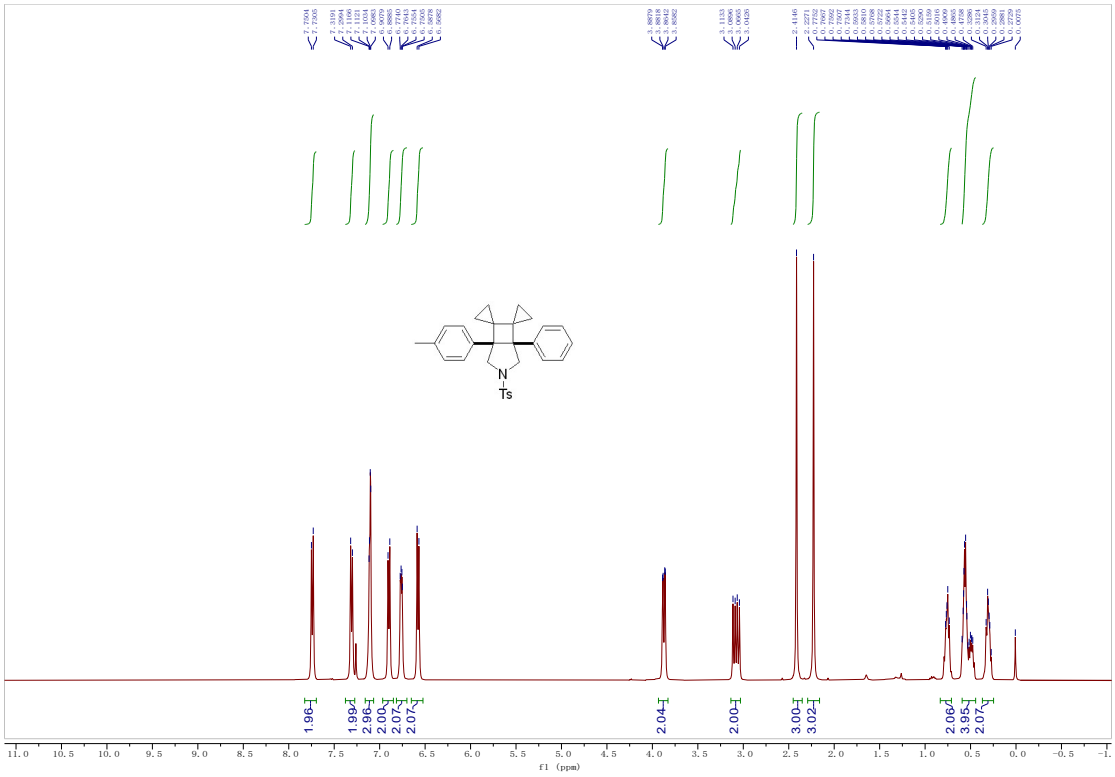
Compound 2a: Yield: 86.5 mg, 95%; A white solid; M.p.: 167 - 169 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.15 – 7.01 (m, 6H), 6.78 – 6.63 (m, 4H), 3.88 (d, *J* = 9.5 Hz, 2H), 3.10 (d, *J* = 9.5 Hz, 2H), 2.41 (s, 3H), 0.81 – 0.69 (m, 2H), 0.64 – 0.46 (m, 4H), 0.38 – 0.25 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 140.4, 132.9, 129.7, 127.9, 127.8, 127.5, 126.2, 58.7, 57.7, 32.4, 21.6, 9.3, 8.4; IR (neat): ν 2846, 1712, 1598, 1496, 1347, 1167, 1023, 830, 816, 702 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{29}H_{29}NO_2SNa$ $[M+Na]^+$: 478.1811, Found: 478.1805.

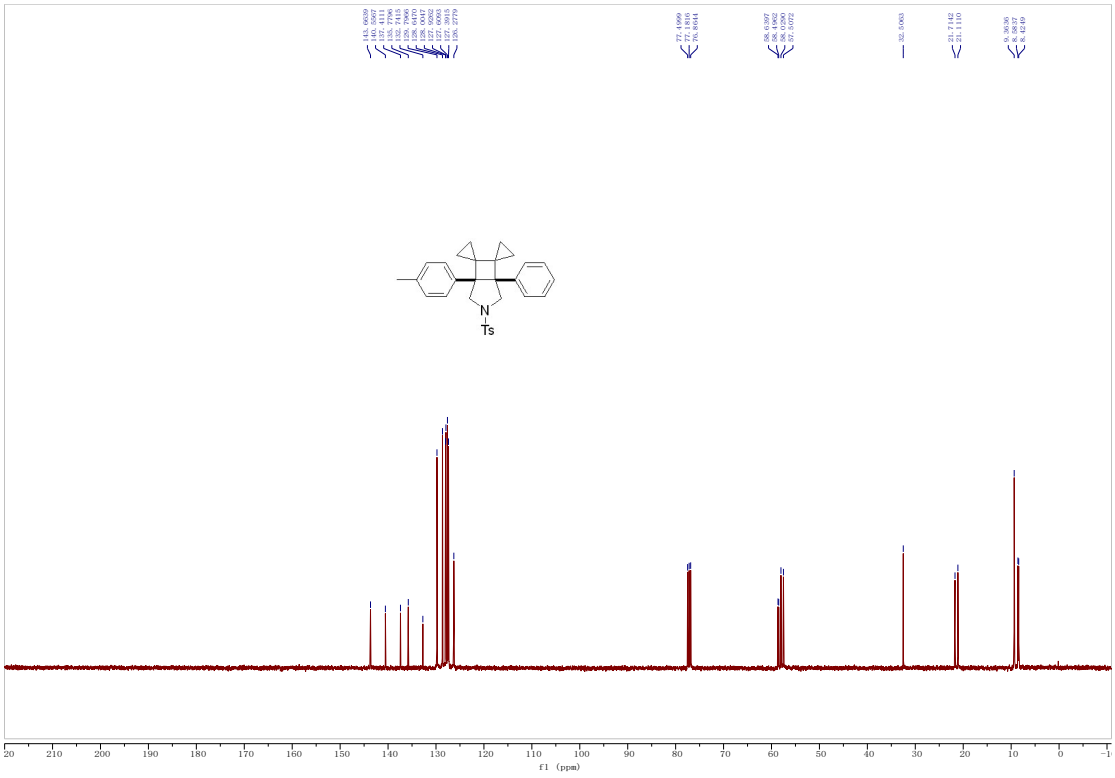

N
Ts
f1 (ppm)

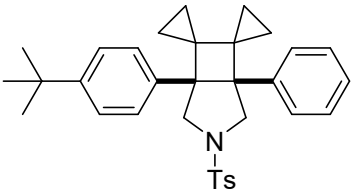

N
Ts
f1 (ppm)



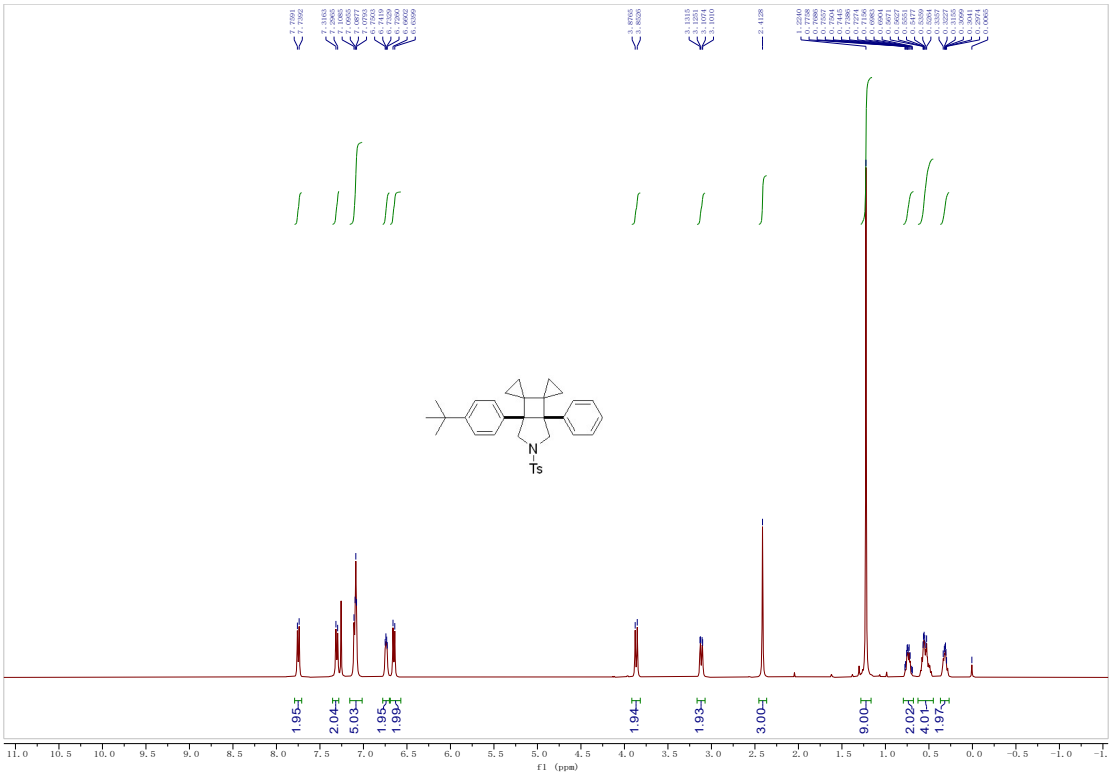
Compound 2b: Yield: 77.8 mg, 82%; A white solid; M.p.: 137 - 139^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.25 – 7.14 (m, 3H), 6.89 (d, *J* = 7.8 Hz, 2H), 6.77 – 6.75 (m, 2H), 6.57 (d, *J* = 7.8 Hz, 2H), 3.87 (dd, *J* = 9.5, 2.4 Hz, 2H), 3.11 – 3.04 (m, 2H), 2.41 (s, 3H), 2.23 (s, 3H), 0.77 – 0.69 (m, 2H), 0.67 – 0.44 (m, 4H), 0.42 – 0.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 140.6, 137.4, 135.8, 132.7, 129.8, 128.6, 128.0, 127.9, 127.6, 127.4, 126.3, 58.6, 58.5, 58.0, 57.5, 32.5, 21.7, 21.1, 9.4, 8.6, 8.4; IR (neat): ν 2924, 1724, 1598, 1468, 1446, 1347, 1287, 1166, 1106, 812, 706 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{30}H_{32}NO_2S$ $[M+H]^+$: 470.2148, Found: 470.2158.

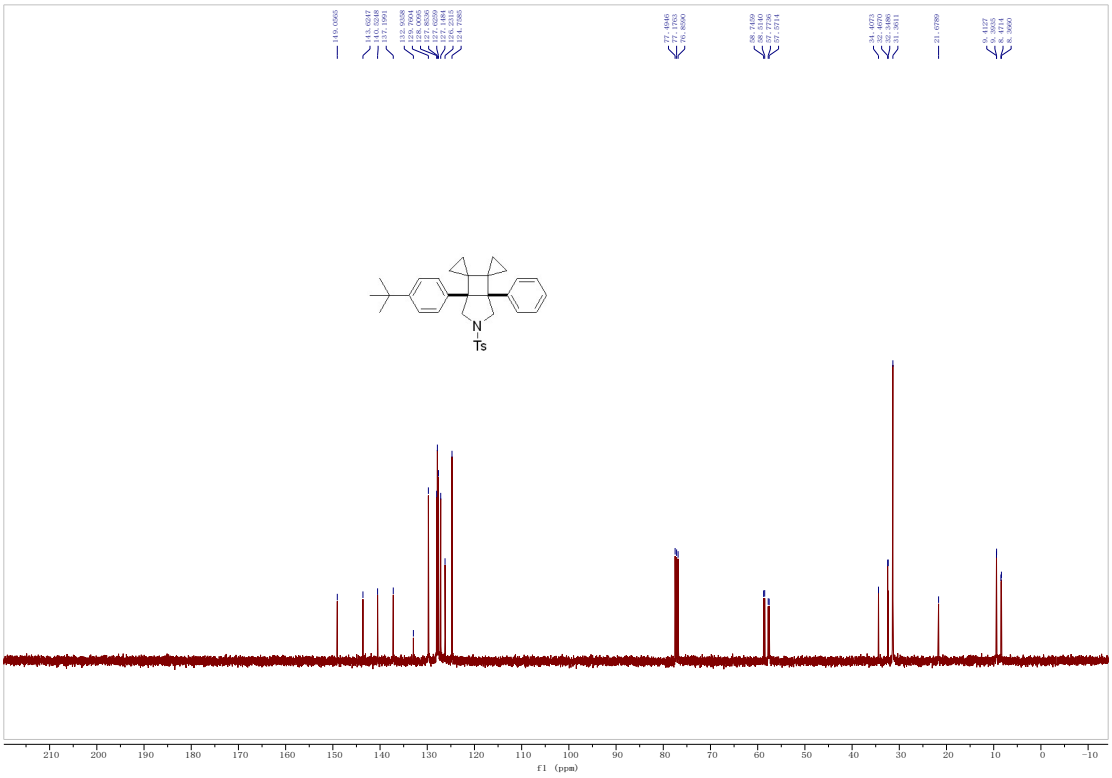

N
Ts
1.96
1.99
2.96
2.00
2.07
2.07
2.04
2.00
3.00
3.02
2.06
3.95
2.07
f1 (ppm)

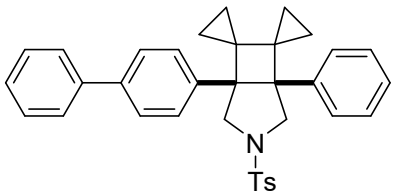

N
Ts
f1 (ppm)



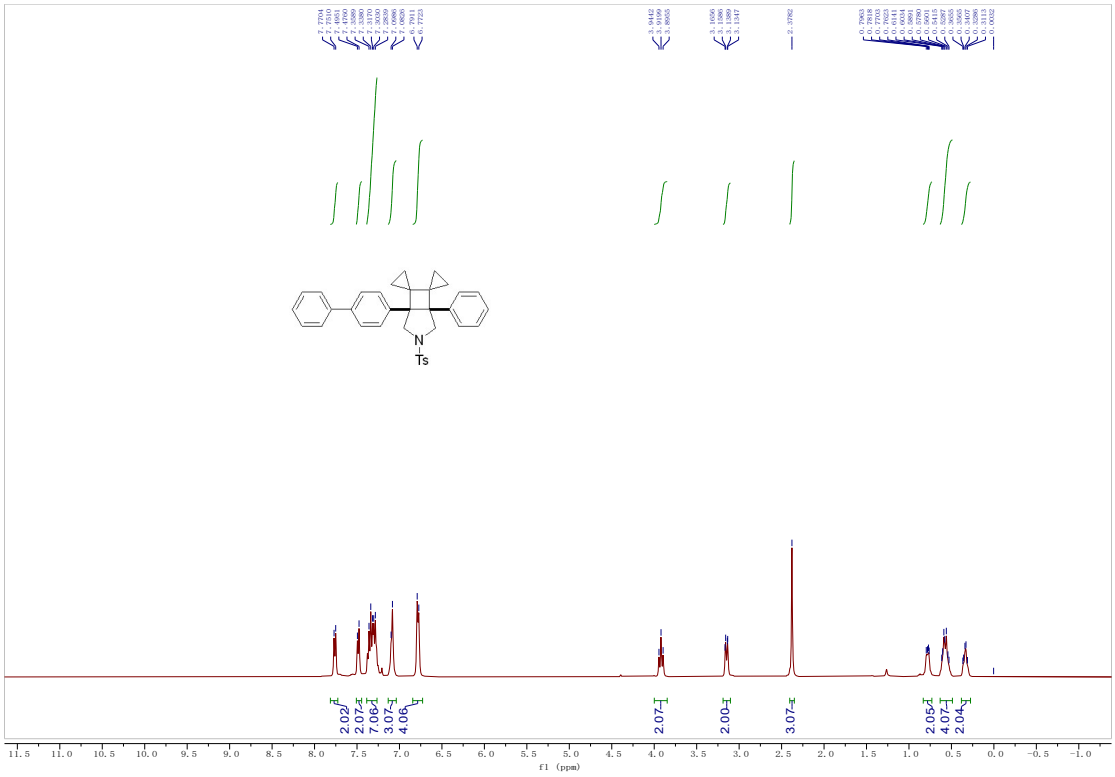
Compound 2c: Yield: 81.8 mg, 80%; A white solid; M.p.: 123 - 125 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.11 – 7.07 (m, 5H), 6.75 – 6.73 (m, 2H), 6.65 (d, *J* = 8.1 Hz, 2H), 3.86 (d, *J* = 9.5 Hz, 2H), 3.13 – 3.10 (m, 2H), 2.41 (s, 3H), 1.22 (s, 9H), 0.78 – 0.72 (m, 2H), 0.69 – 0.48 (m, 4H), 0.42 – 0.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 143.6, 140.5, 137.2, 132.9, 129.8, 128.0, 127.9, 127.6, 127.1, 126.2, 124.8, 58.7, 58.5, 57.8, 57.6, 34.4, 32.5, 32.3, 31.4, 21.7, 9.41, 9.39, 8.5, 8.4; IR (neat): ν 2945, 2020, 1652, 1614, 1351, 1166, 1107, 1014, 813, 705, 664 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{33}H_{38}NO_2S$ $[M+H]^+$: 512.2618, Found: 512.2622.

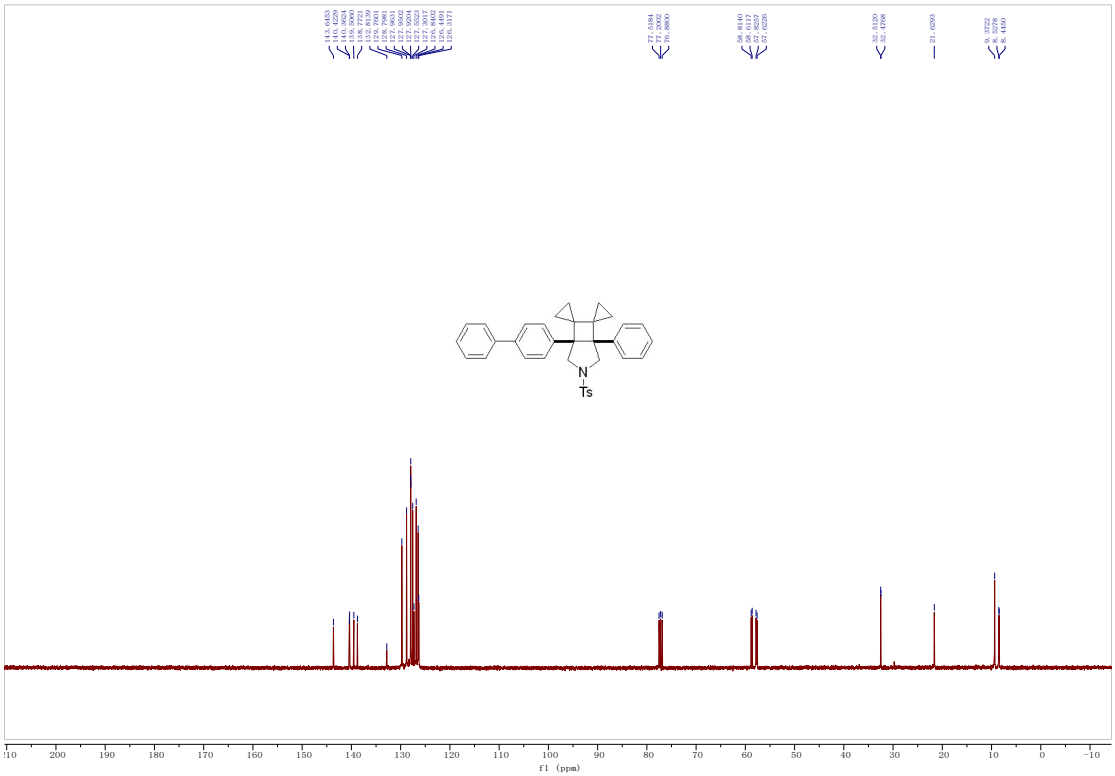

N
Ts
1.95
2.04
5.03
1.95
1.99
1.94
1.93
3.00
9.00
2.02
4.01
1.97
f1 (ppm)

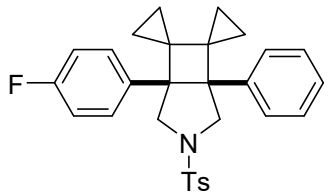

N
Ts
f1 (ppm)



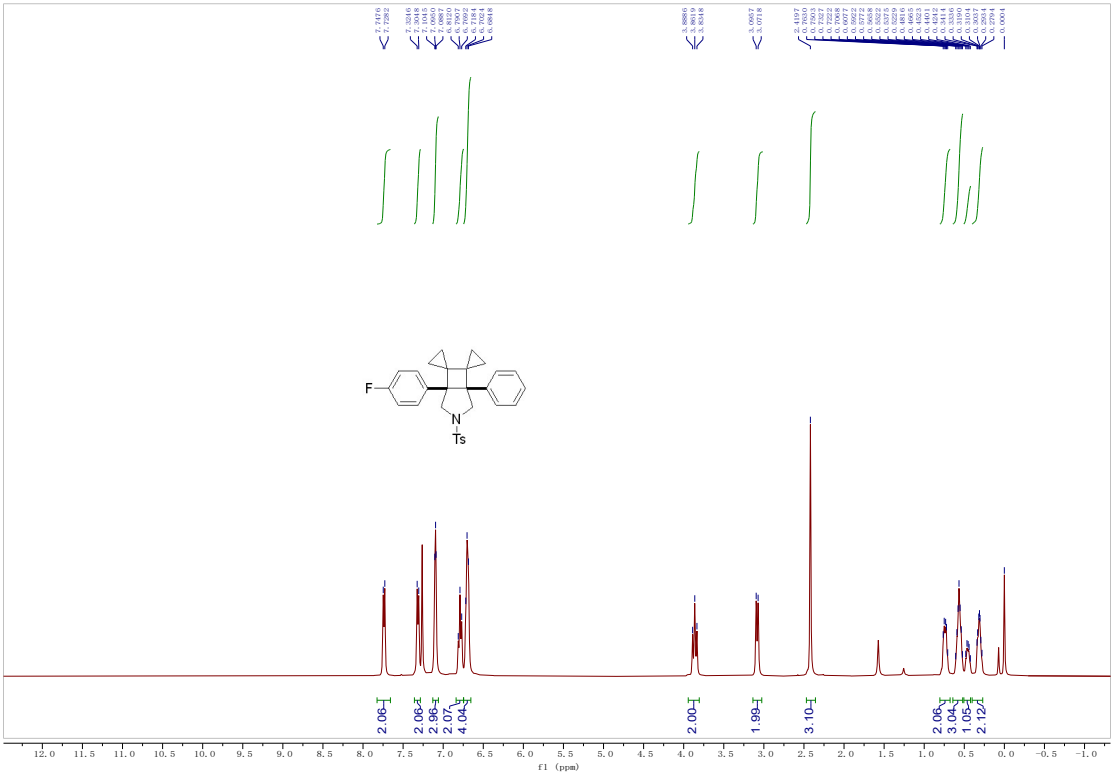
Compound 2d: Yield: 96.9 mg, 90%; A white solid; M.p.: 141 - 143 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.8 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 2H), 7.41 – 7.33 (m, 7H), 7.15 – 7.13 (m, 3H), 6.84 – 6.82 (m, 4H), 3.99 – 3.95 (m, 2H), 3.22 – 3.19 (m, 2H), 2.43 (s, 3H), 0.85–0.81 (m, 2H), 0.67–0.58 (m, 4H), 0.42–0.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 140.42, 140.36, 139.5, 138.8, 132.8, 129.8, 128.8, 127.96, 127.95, 127.92, 127.6, 127.3, 126.8, 126.4, 126.3, 58.8, 58.6, 57.8, 57.6, 32.51, 32.48, 21.6, 9.4, 8.5, 8.4; IR (neat): ν 3029, 1711, 1600, 1488, 1330, 1164, 1108, 1021, 838, 765, 698 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{35}H_{33}NO_2SNa$ $[M+Na]^+$: 554.2128, Found: 554.2109.

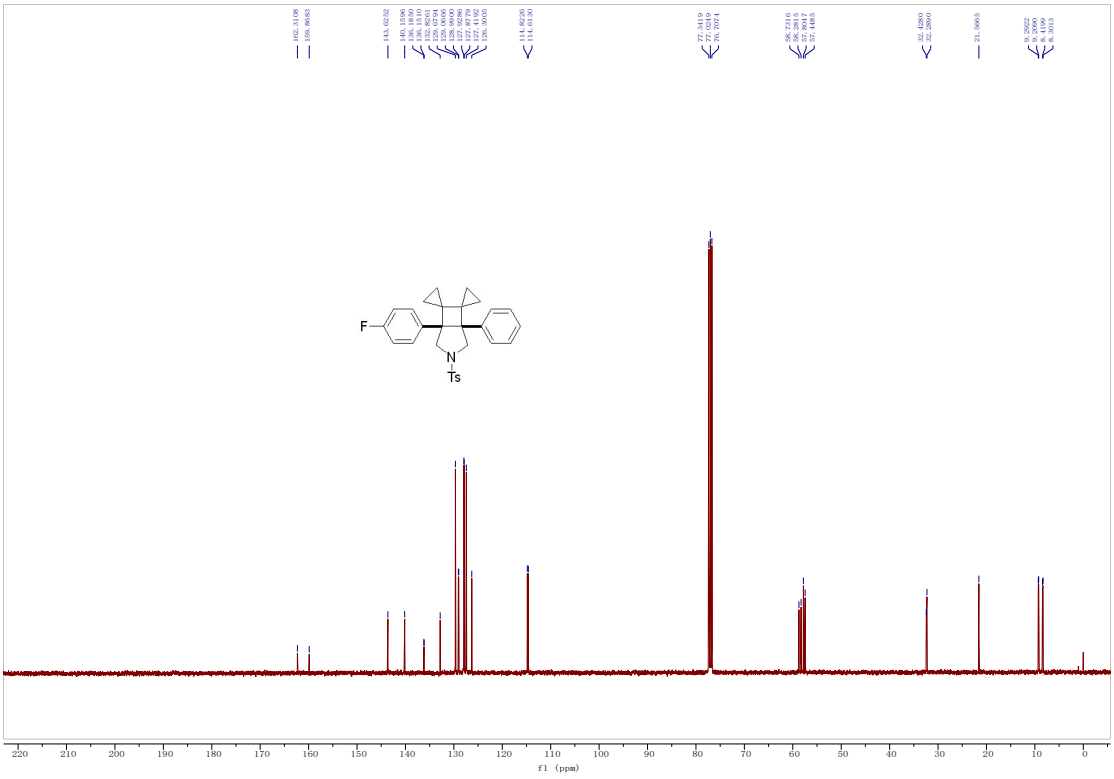

N
Ts
2.02
2.07
7.06
3.07
4.06
2.07
2.00
3.07
2.05
4.07
2.04
f1 (ppm)

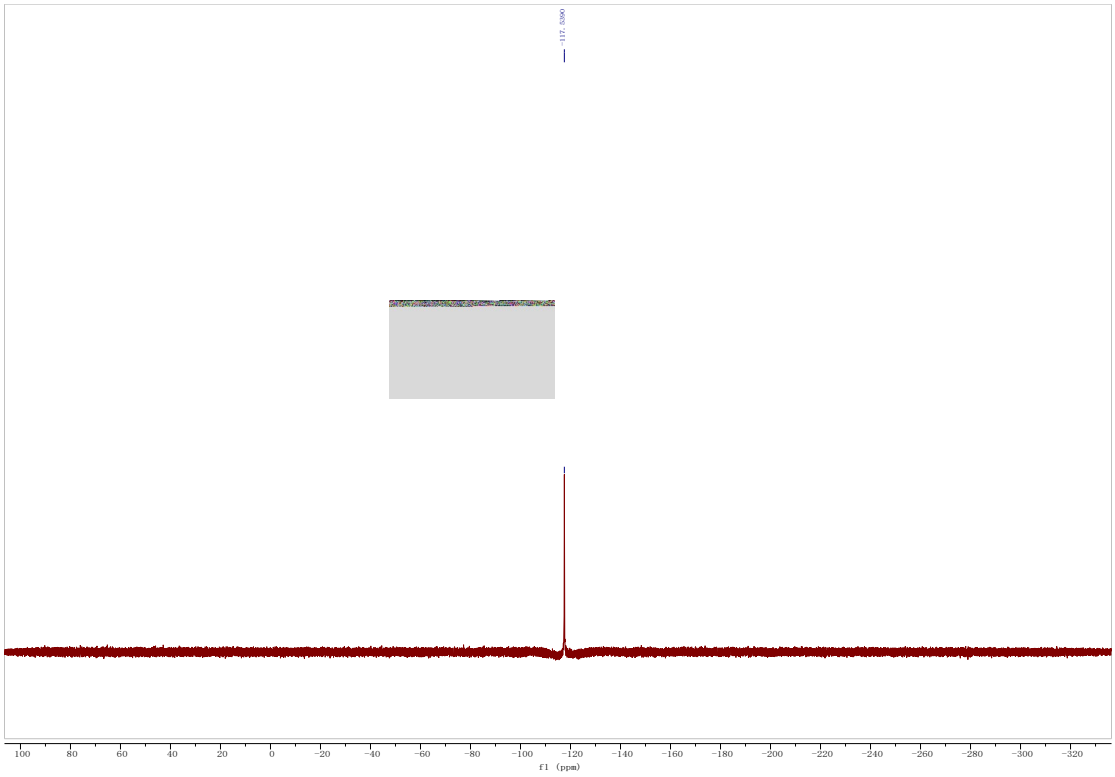

N
Ts
f1 (ppm)



Compound 2e: Yield: 75.7 mg, 79%; A white solid; M.p.: 152 - 154 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.10 – 7.08 (m, 3H), 6.81 – 6.77 (m, 2H), 6.72 – 6.68 (m, 4H), 3.89 – 3.83 (m, 2H), 3.08 (d, *J* = 9.6 Hz, 2H), 2.4 (s, 3H), 0.76 – 0.72 (m, 2H), 0.61 – 0.53 (m, 3H), 0.48 – 0.42 (m, 1H), 0.40 – 0.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 159.9 (d, *J* = 244.3 Hz), 143.6, 140.2, 136.18, 136.15 (d, *J* = 3.4 Hz), 132.8, 129.7, 129.1, 129.0 (d, *J* = 7.7 Hz), 127.92, 127.87, 127.4, 126.3, 114.8, 114.6 (d, *J* = 20.9 Hz), 58.7, 58.3, 57.8, 57.4, 32.4, 32.3, 21.6, 9.3, 9.2, 8.4, 8.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.5; IR (neat): ν 2918, 1714, 1511, 1338, 1161, 1023, 836, 664 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{29}H_{28}NO_2SFNa$ $[M+Na]^+$: 496.1717, Found: 496.1716.


F
N
Ts
2.06
2.06
2.96
2.07
4.04
2.00
1.99
3.10
2.06
3.04
1.05
2.12
f1 (ppm)


F
N
Ts
f1 (ppm)


-117.5300
100
80
60
40
20
0
-20
-40
-60
-80
-100
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-140
-160
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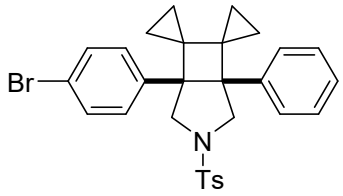
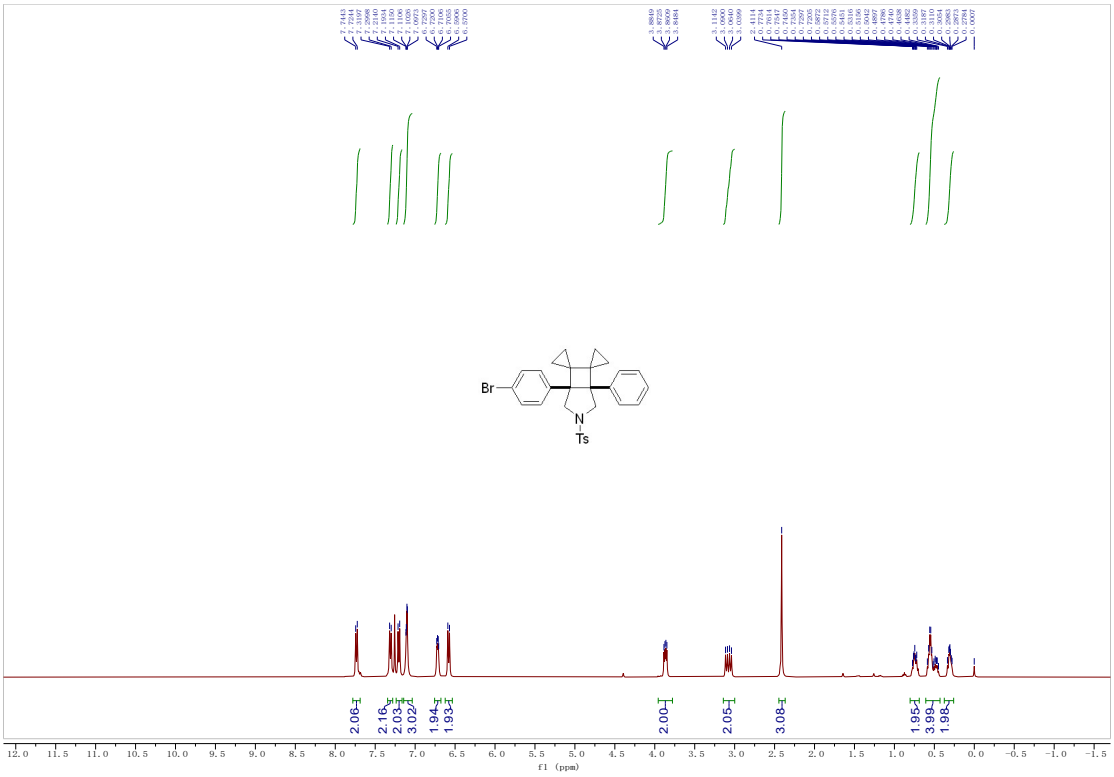
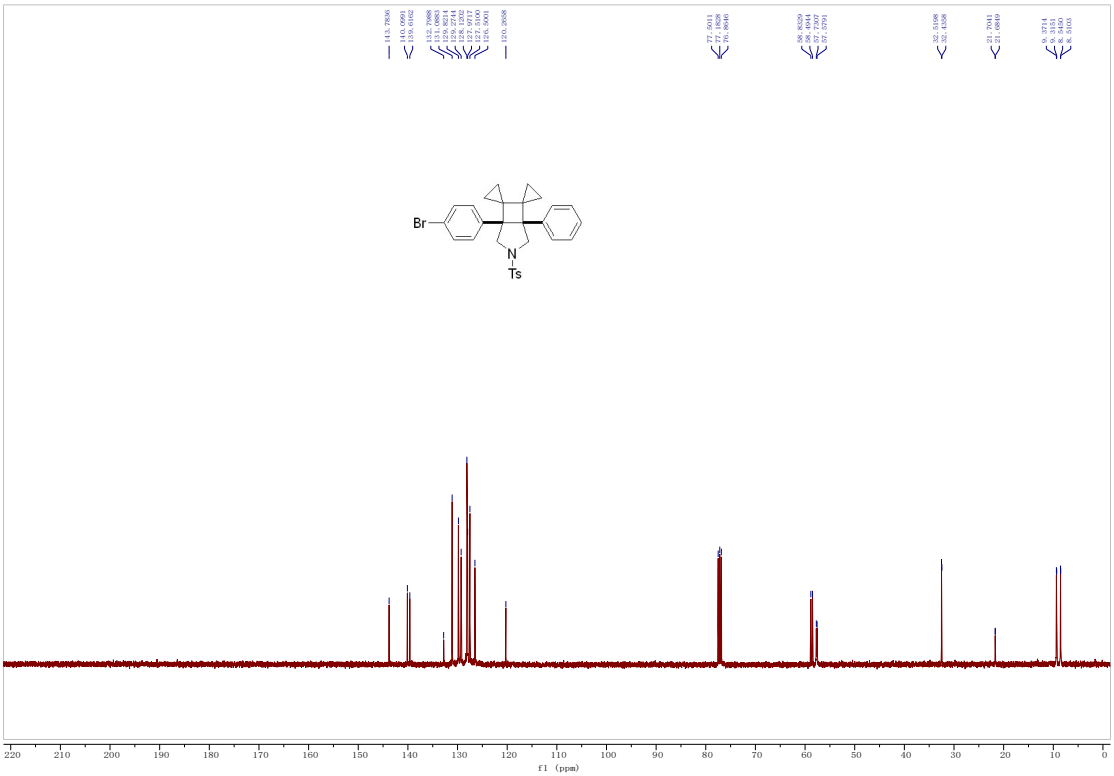
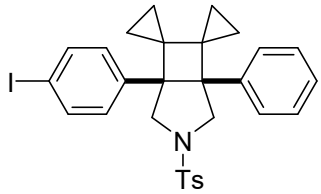
-240
-260
-280
-300
-320
f1 (ppm)



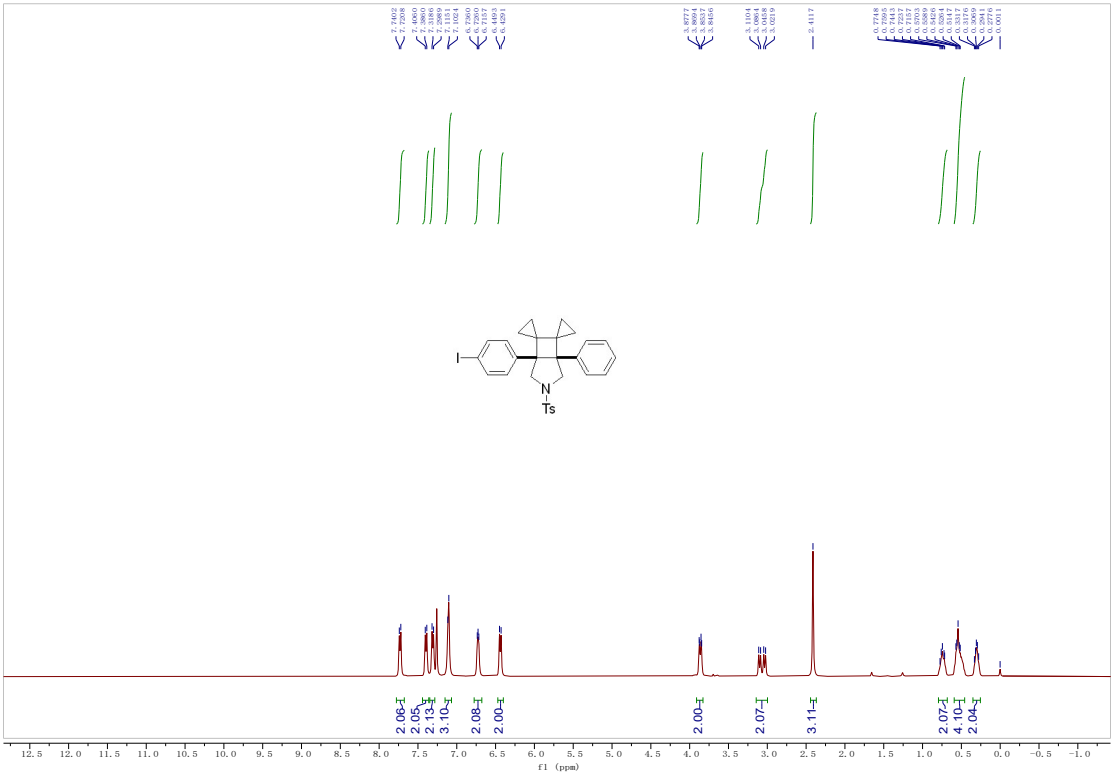
Compound 2f: Yield: 91.6 mg, 86%; A yellow solid; M.p.: 158 - 160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.11 – 7.09 (m, 3H), 6.73 – 6.71 (m, 2H), 6.58 (d, *J* = 8.2 Hz, 2H), 3.88 – 3.85 (m, 2H), 3.11 – 3.04 (m, 2H), 2.41 (s, 3H), 0.77 – 0.72 (m, 2H), 0.58 – 0.48 (m, 4H), 0.34 – 0.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 140.1, 139.6, 132.8, 131.1, 129.8, 129.3, 128.1, 128.0, 127.5, 126.5, 120.3, 58.8, 58.5, 57.7, 57.6, 32.5, 32.4, 21.70, 21.68, 9.4, 9.3, 8.54, 8.51; IR (neat): ν 2969, 1847, 1160, 1121, 1043, 706, 684, 659 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{29}H_{29}NO_2SBr$ $[M+H]^+$: 534.1097, Found: 534.1101.

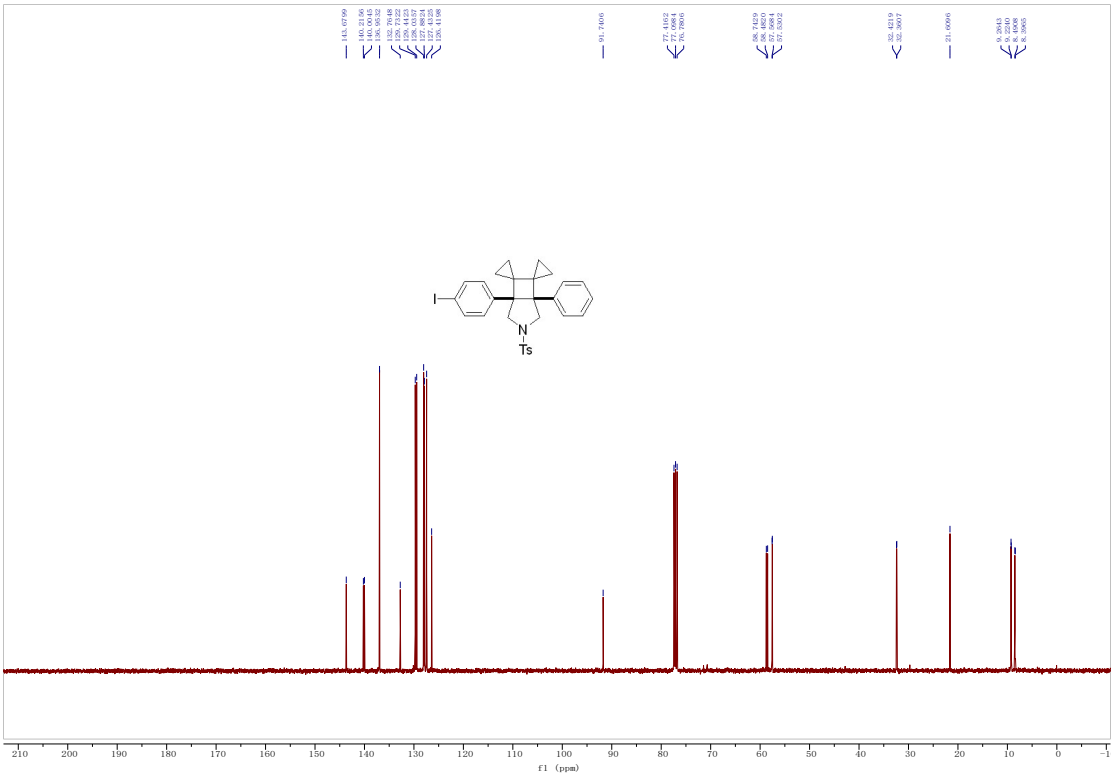

Br
N
Ts
2.06
2.16
2.03
3.02
1.94
1.93
2.00
2.05
3.08
1.95
3.99
1.98
f1 (ppm)

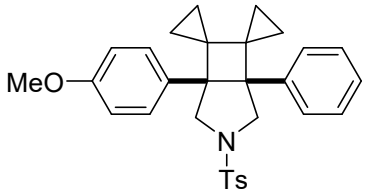

Br
N
Ts
f1 (ppm)



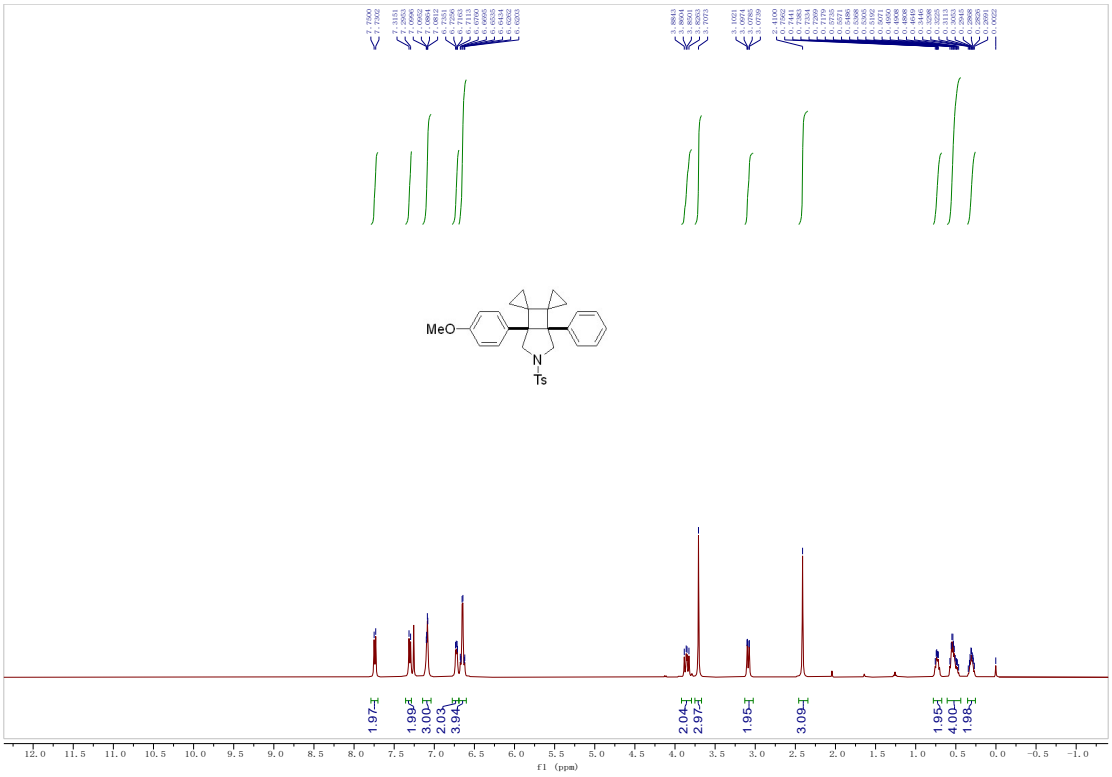
Compound 2g: Yield: 99.1 mg, 85%; A white solid; M.p.: 163 - 165 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.12 – 7.10 (m, 3H), 6.74 – 6.72 (m, 2H), 6.43 (d, *J* = 8.0 Hz, 2H), 3.88 – 3.85 (m, 2H), 3.10 (m, 2H), 2.41 (s, 3H), 0.77 – 0.72 (m, 2H), 0.57 – 0.51 (m, 4H), 0.33 – 0.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 140.2, 140.0, 137.0, 132.8, 129.7, 129.4, 128.0, 127.9, 127.4, 126.4, 91.7, 58.7, 58.5, 57.6, 57.5, 32.42, 32.36, 21.6, 9.3, 9.2, 8.5, 8.4; IR (neat): ν 2844, 1711, 1598, 1487, 1346, 1165, 1001, 816, 706, 663 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{29}H_{28}NO_2SNaI$ $[M+Na]^+$: 604.0778, Found: 604.0779.

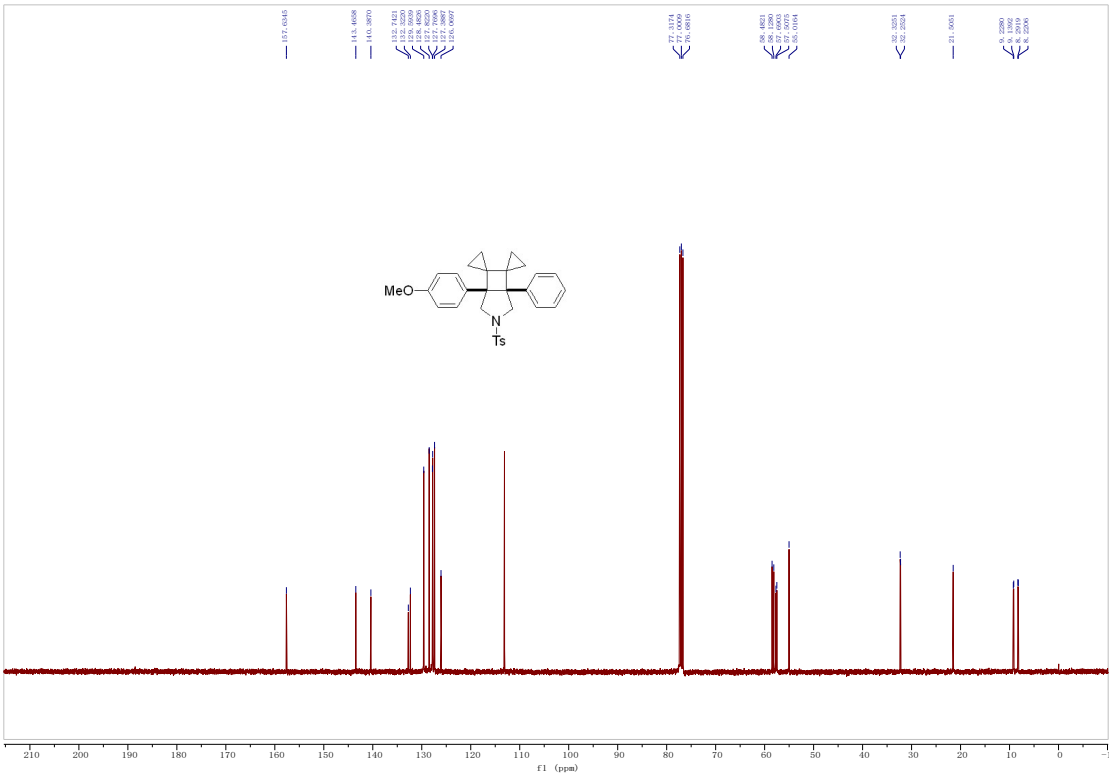

I
N
Ts
f1 (ppm)

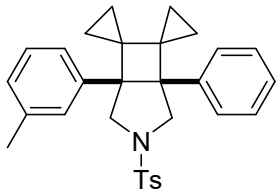

I
N
Ts
f1 (ppm)



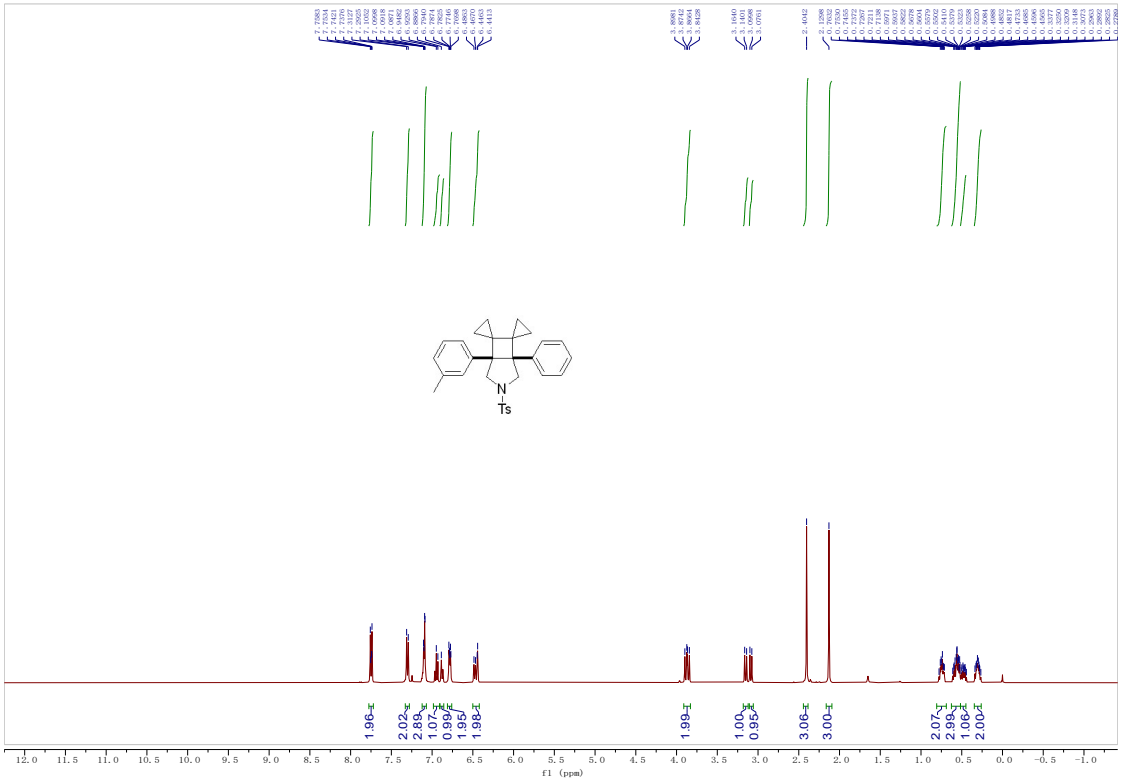
Compound 2h: Yield: 85.1 mg, 88%; A white solid; M.p.: 118 - 120 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.10 – 7.08 (m, 3H), 6.74 – 6.71 (m, 2H), 6.67 – 6.62 (m, 4H), 3.85 (m, 2H), 3.70 (s, 3H), 3.08 (dd, *J* = 9.4, 1.9 Hz, 2H), 2.41 (s, 3H), 0.76 – 0.71 (m, 2H), 0.58 – 0.48 (m, 4H), 0.46 – 0.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 143.5, 140.4, 132.7, 132.3, 129.6, 128.5, 127.82, 127.76, 127.4, 126.1, 58.5, 58.1, 57.7, 57.5, 55.0, 32.32, 32.25, 21.5, 9.2, 9.1, 8.3, 8.2; IR (neat): ν 2918, 1514, 1345, 1249, 1166, 1023, 816, 664 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{30}H_{32}NO_3S$ $[M+H]^+$: 486.2097, Found: 486.2108.

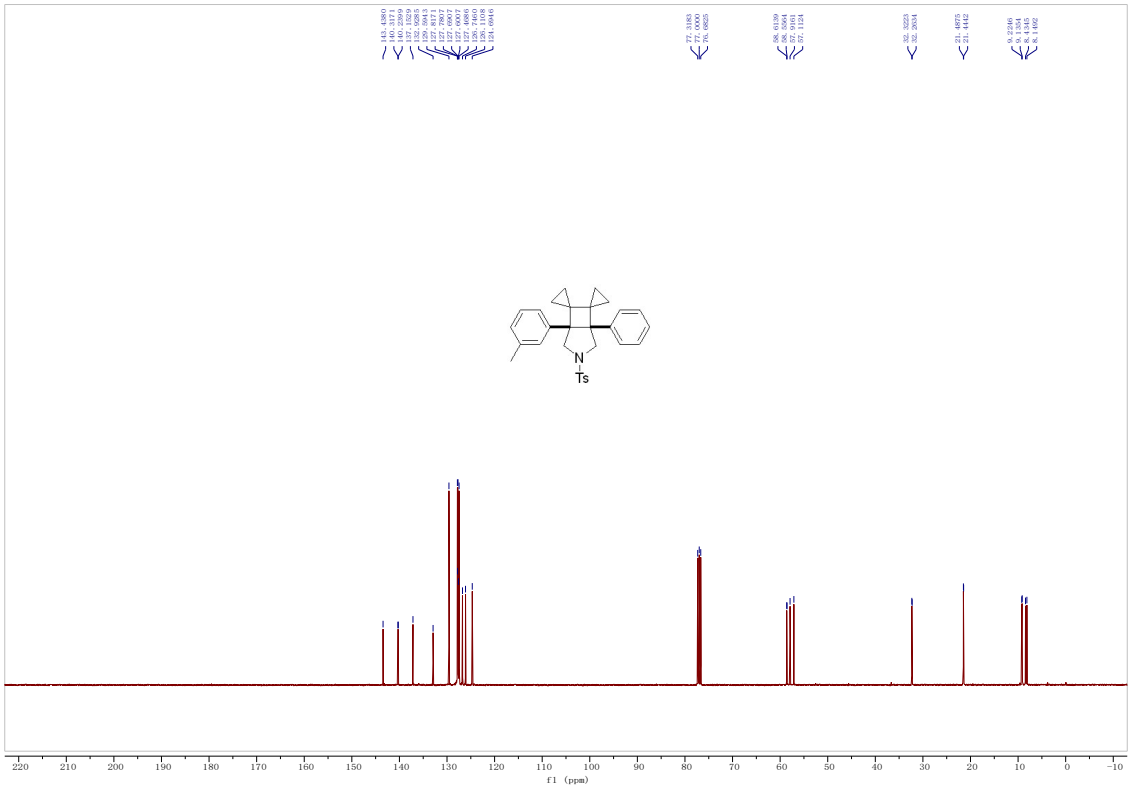

MeO
N
Ts
1.97
1.99
3.00
2.03
3.94
2.04
2.97
1.95
3.09
1.95
4.00
1.98
f1 (ppm)

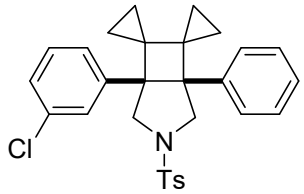

MeO
N
Ts
f1 (ppm)



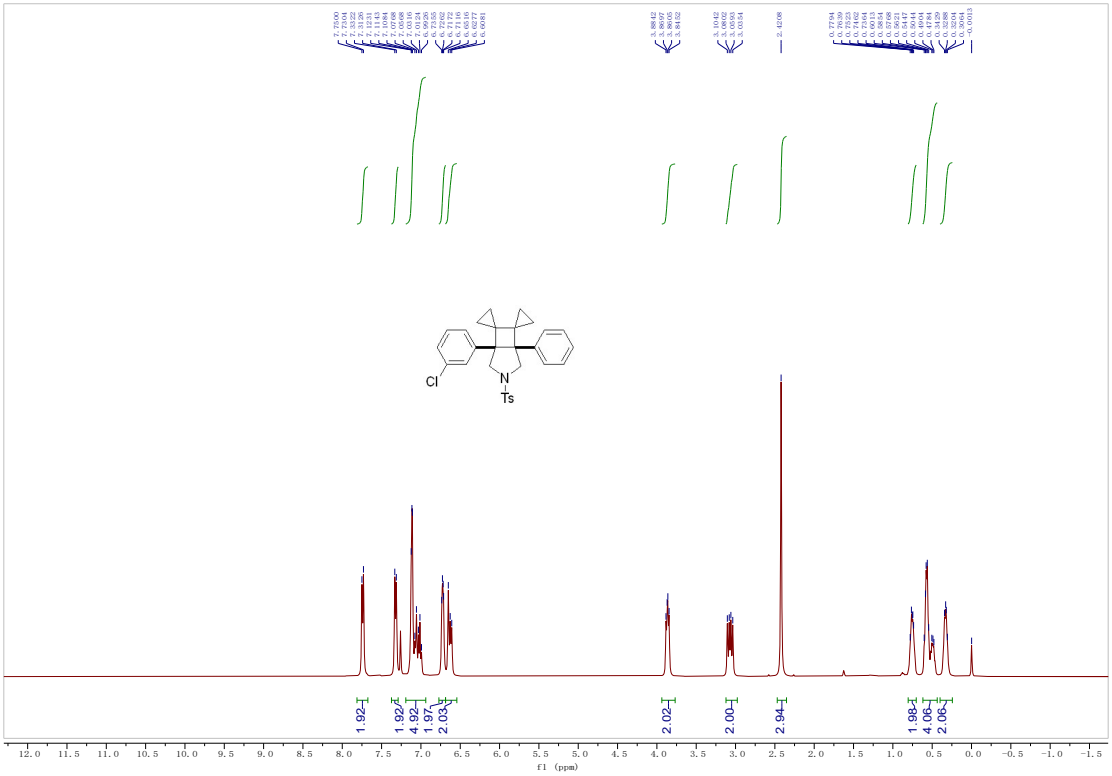
Compound 2i: Yield: 87.8 mg, 93%; A white solid; M.p.: 107 - 109°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.72 (m, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.13 – 7.06 (m, 3H), 6.99 – 6.91 (m, 1H), 6.91 – 6.86 (m, 1H), 6.82 – 6.75 (m, 2H), 6.51 – 6.42 (m, 2H), 3.92 – 3.82 (m, 2H), 3.15 (d, *J* = 9.5 Hz, 1H), 3.09 (d, *J* = 9.5 Hz, 1H), 2.40 (s, 3H), 2.13 (s, 3H), 0.81 – 0.69 (m, 2H), 0.63 – 0.50 (m, 3H), 0.53 – 0.43 (m, 2H), 0.36 – 0.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 140.3, 140.2, 137.2, 132.9, 129.6, 127.82, 127.78, 127.7, 127.6, 127.5, 126.7, 126.1, 124.7, 58.61, 58.56, 57.9, 57.1, 32.3, 32.3, 21.5, 21.4, 9.2, 9.1, 8.4, 8.1; IR (neat): ν 2932, 1607, 1488, 1455, 1337, 1298, 1176, 1117, 822, 777, 716 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{30}H_{32}NO_2S$ $[M+H]^+$: 470.2148, Found: 470.2152.

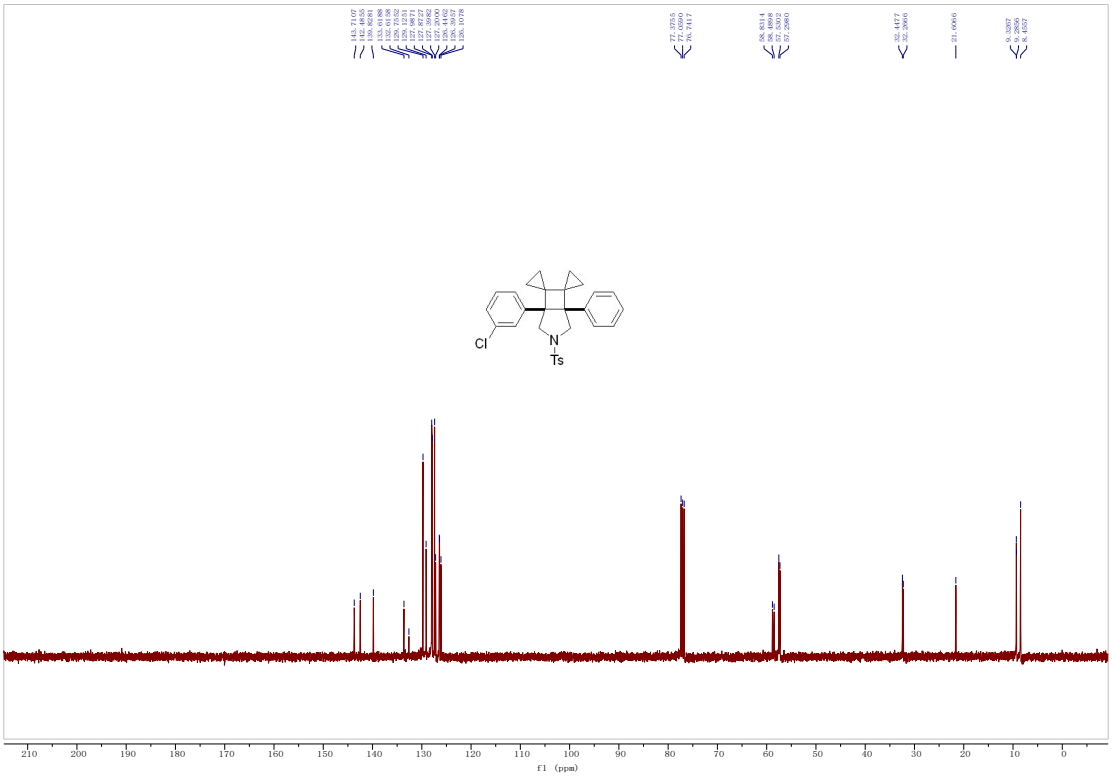

N
Ts
1.96
2.02
2.89
1.07
0.99
1.95
1.98
1.99
1.00
0.95
3.06
3.00
2.07
2.99
1.06
2.00
f1 (ppm)

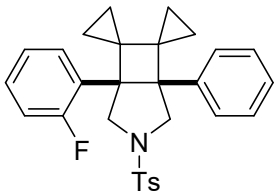

N
Ts
f1 (ppm)



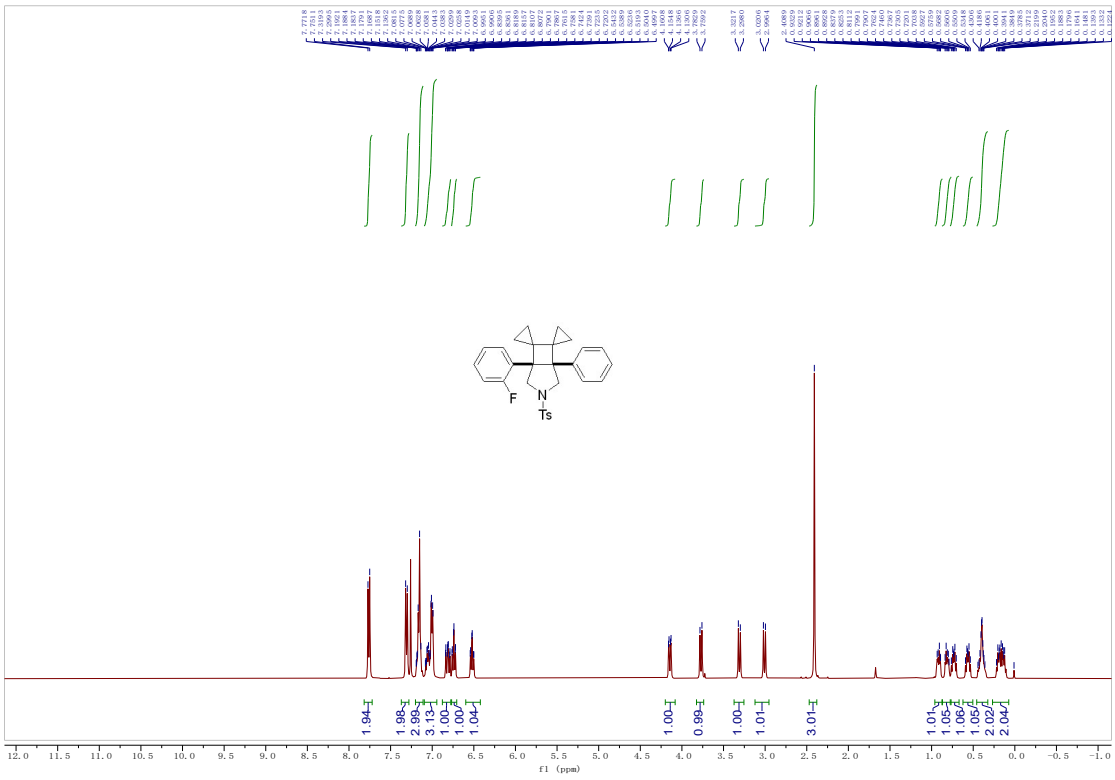
Compound 2j: Yield: 87.5 mg, 89%; A white solid; M.p.: 171 - 173 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.12 – 6.99 (m, 5H), 6.74 – 6.71 (m, 2H), 6.65 – 6.61 (m, 2H), 3.88 – 3.85 (m, 2H), 3.10 – 3.04 (m, 4H), 2.43 (s, 3H), 0.78 – 0.74 (m, 2H), 0.60 – 0.49 (m, 4H), 0.47 – 0.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 142.5, 139.8, 133.6, 132.6, 129.8, 129.1, 128.0, 127.9, 127.4, 127.2, 126.44, 126.40, 126.1, 58.8, 58.5, 57.5, 57.3, 32.4, 32.3, 21.6, 9.33, 9.29, 8.5; IR (neat): ν 2846, 1712, 1596, 1344, 1163, 1025, 830, 707, 664 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{29}H_{29}NO_2SCl$ $[M+H]^+$: 490.1602, Found: 490.1600.

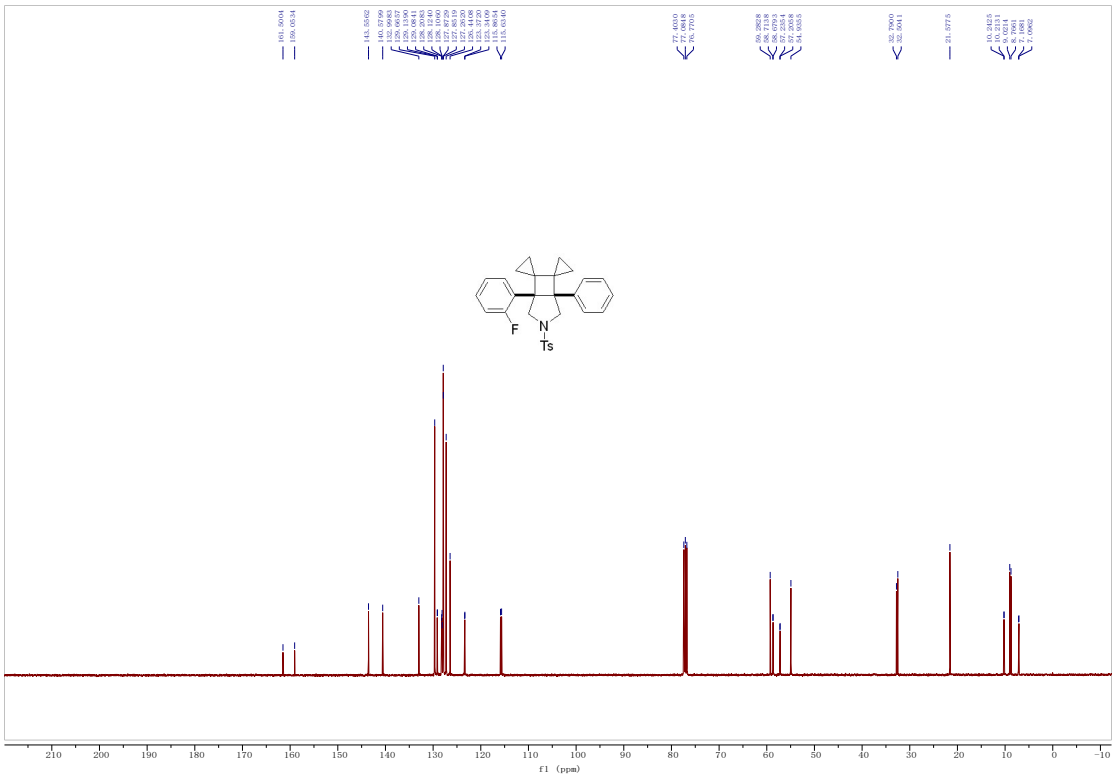

Cl
N
Ts
1.92
1.92
4.92
1.97
2.03
2.02
2.00
2.94
1.98
4.06
2.06
f1 (ppm)

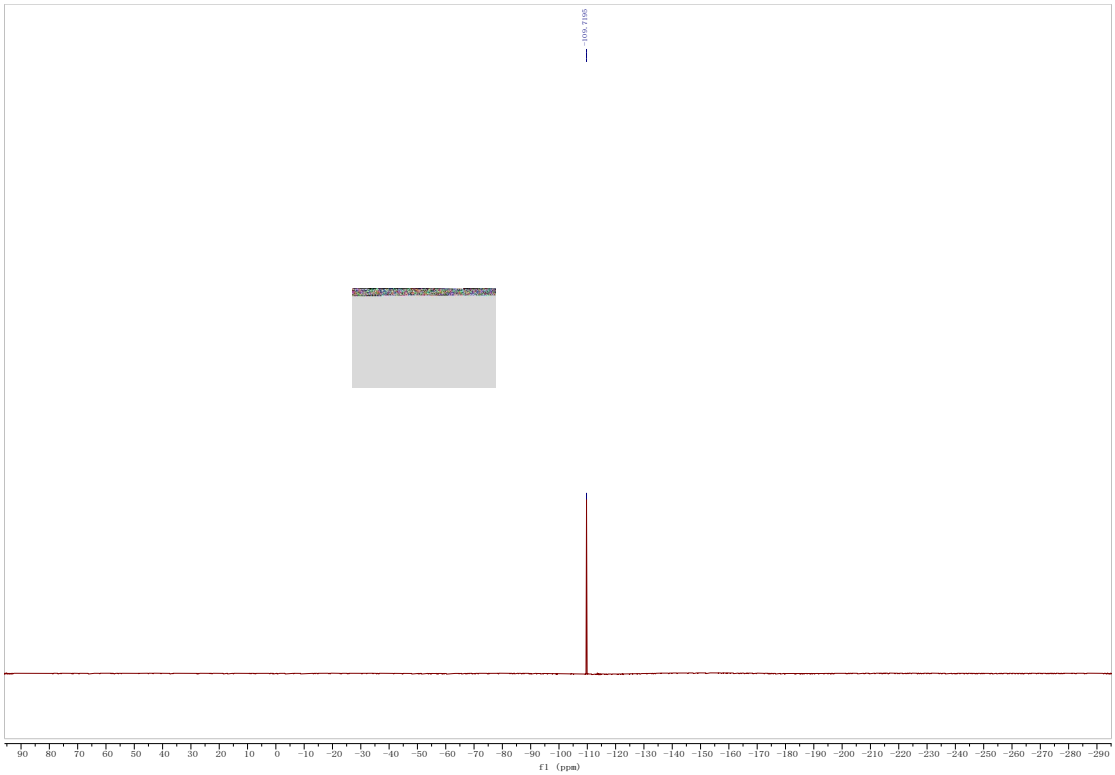

Cl
N
Ts
f1 (ppm)

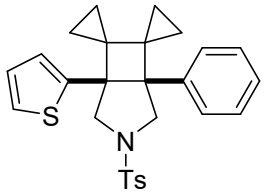


Compound 2l: Yield: 72.6 mg, 79%; A white solid; M.p.: 185 - 187 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.19 – 7.13 (m, 3H), 7.08 – 6.99 (m, 3H), 6.94 – 6.82 (m, 1H), 6.80 – 6.78 (m, 1H), 6.54 – 6.49 (m, 1H), 4.14 (dd, *J* = 9.7, 2.4 Hz, 1H), 3.77 (d, *J* = 9.5 Hz, 1H), 3.31 (d, *J* = 9.5 Hz, 1H), 3.01 (d, *J* = 9.7 Hz, 1H), 2.41 (s, 3H), 0.93 – 0.92 (m, 1H), 0.89 – 0.81 (m, 1H), 0.79 – 0.70 (m, 1H), 0.59 – 0.53 (m, 1H), 0.45 – 0.37 (m, 2H), 0.35 – 0.12 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 159.1 (d, *J* = 244.7 Hz), 143.6, 140.6, 133.0, 129.7, 129.13, 129.08 (d, *J* = 5.5 Hz), 128.2, 128.12 (d, *J* = 8.4 Hz), 128.11, 127.87, 127.85 (d, *J* = 2.1 Hz), 127.3, 126.4, 123.4, 123.3 (d, *J* = 3.1 Hz), 115.9, 115.6 (d, *J* = 23.0 Hz), 59.3, 58.71, 58.67, 57.24, 57.20 , 54.9, 32.8, 32.5, 21.6, 10.24, 10.21, 9.0, 8.8, 7.2, 7.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.7; IR (neat): ν 2999, 1489, 1447, 1165, 1102, 1024, 830, 760, 665 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{29}H_{28}NO_2FNaS$ $[M+Na]^+$: 496.1717, Found: 496.1714.

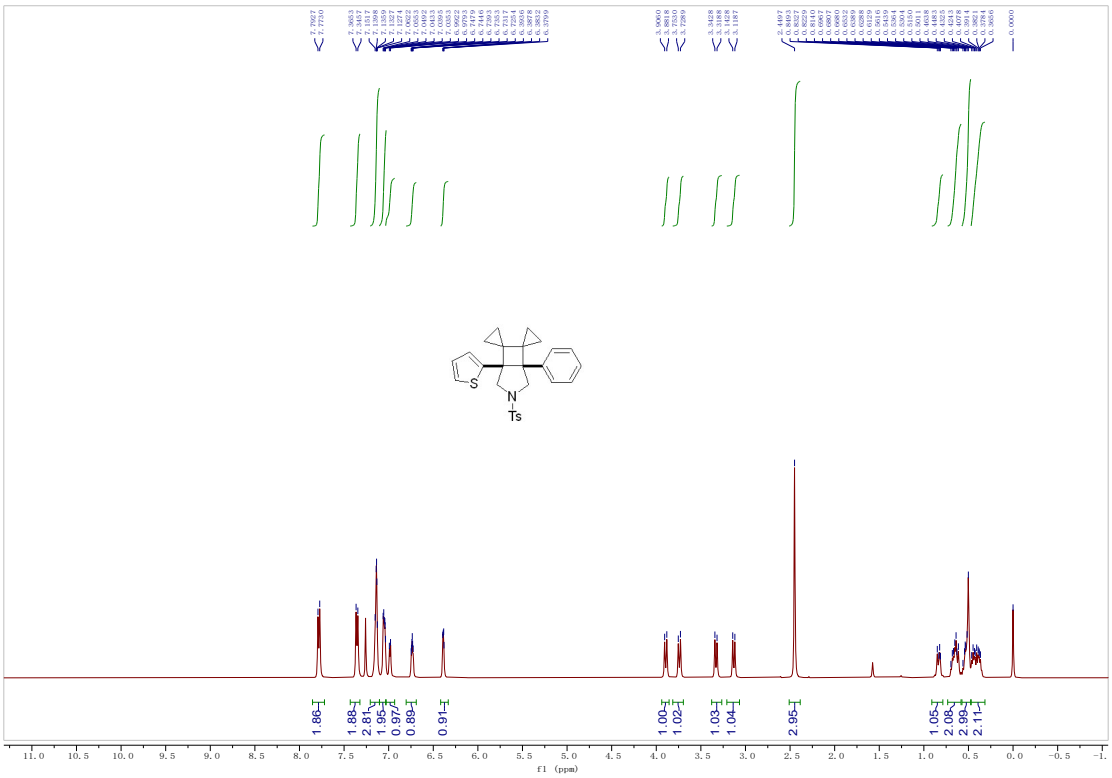

F
N
Ts
1.94
1.98
2.99
3.13
1.00
1.00
1.04
1.00
0.99
1.00
1.01
3.01
1.01
1.05
1.06
1.05
2.02
2.04
f1 (ppm)

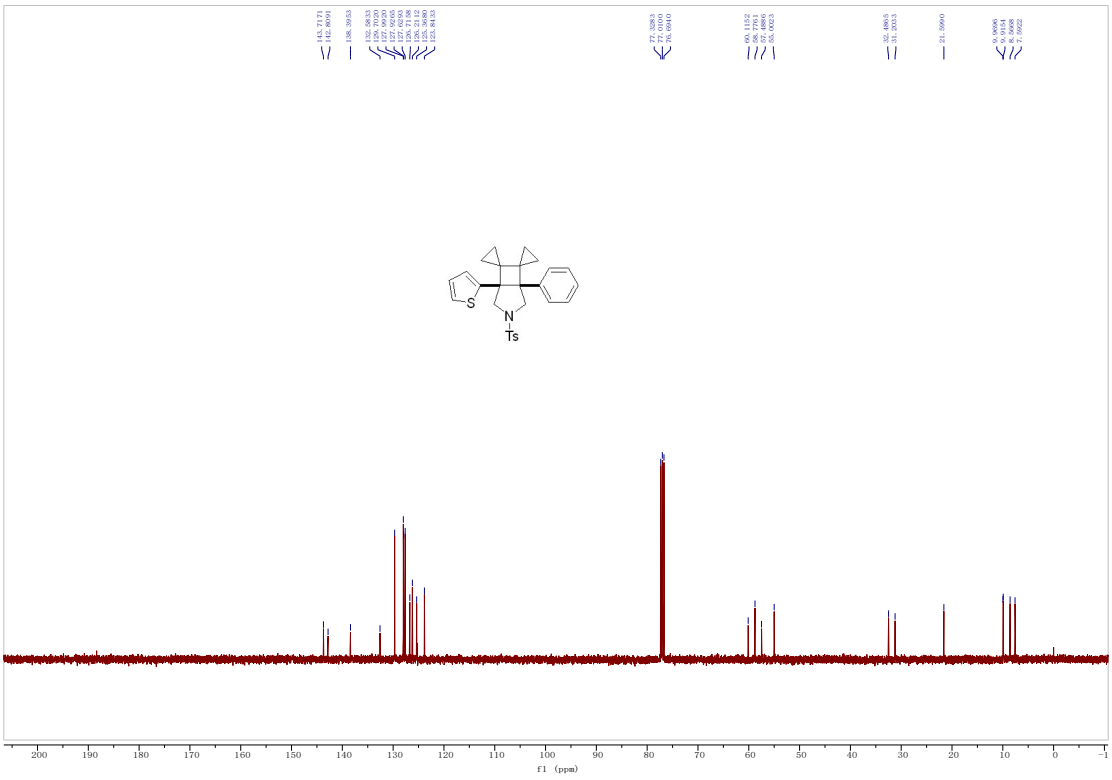

F
N
Ts
f1 (ppm)

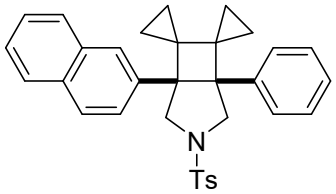

-109.7195
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290
f1 (ppm)



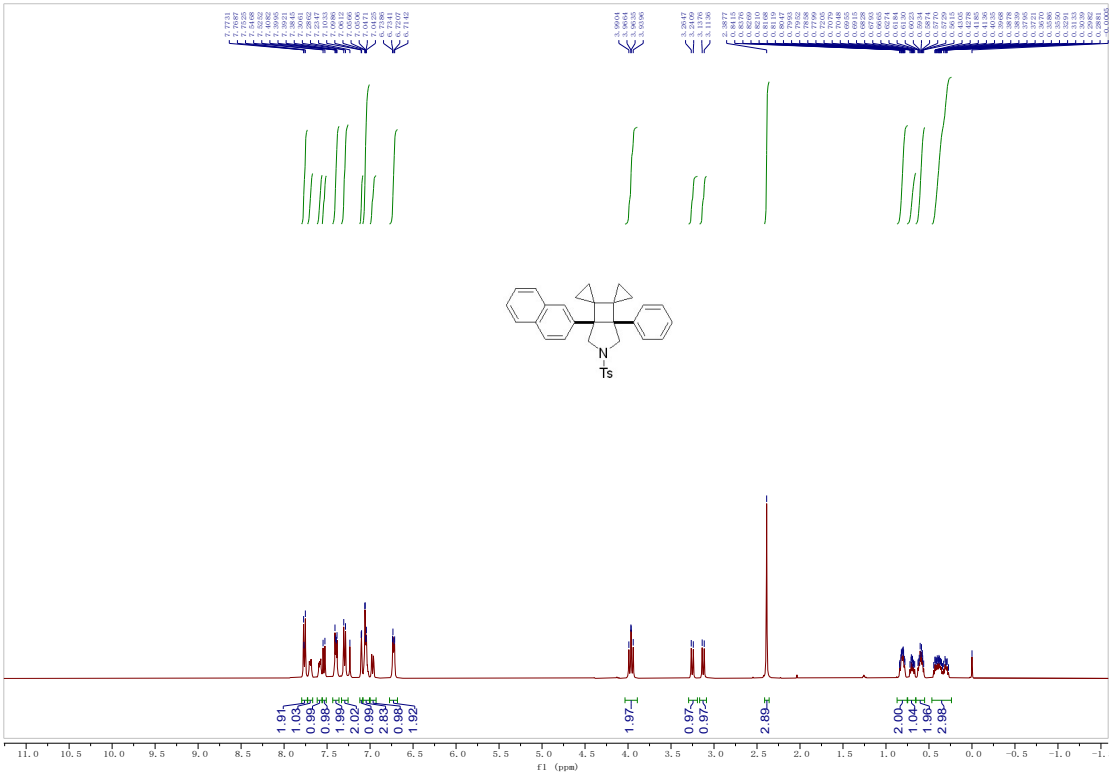
Compound 2m: Yield: 73.1 mg, 79%; A white solid; M.p.: 138 - 140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.15 – 7.12 (m, 3H), 7.06 – 7.03 (m, 2H), 6.99 – 6.97 (m, 1H), 6.75 – 6.73 (m, 1H), 6.39 – 6.38 (m, 1H), 3.89 (d, *J* = 9.6 Hz, 1H), 3.74 (d, *J* = 9.6 Hz, 1H), 3.33 (d, *J* = 9.6 Hz, 1H), 3.13 (d, *J* = 9.6 Hz, 1H), 2.45 (s, 3H), 0.85 – 0.82 (m, 1H), 0.69 – 0.64 (m, 2H), 0.62 – 0.53 (m, 3H), 0.51 – 0.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 142.8, 138.4, 132.6, 129.7, 128.0, 127.9, 127.6, 126.7, 126.2, 125.4, 123.8, 60.1, 58.8, 57.5, 55.0, 32.5, 31.2, 21.6, 10.0, 9.9, 8.6, 7.6; IR (neat): ν 2995, 1712, 1597, 1496, 1470, 1445, 1104, 1010, 815, 698 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{27}H_{27}NO_2NaS_2$ $[M+Na]^+$: 484.1375, Found: 484.1370.

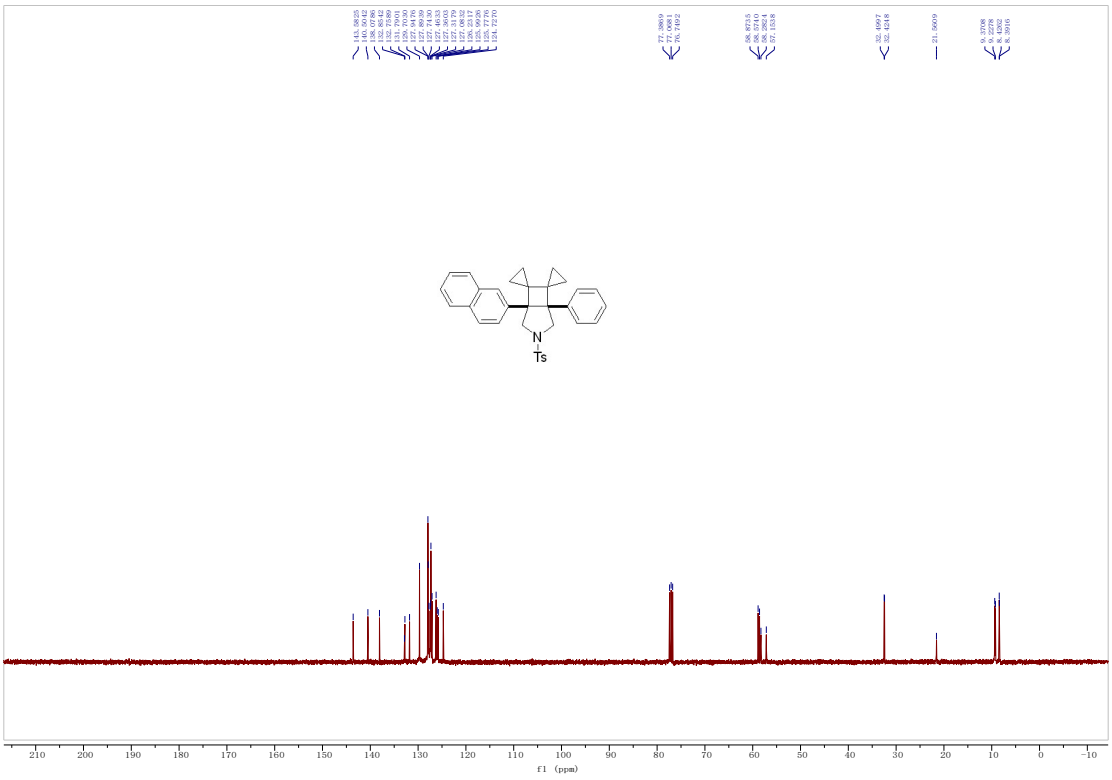

S
N
Ts
1.86
1.88
2.81
1.95
0.97
0.89
0.91
1.00
1.02
1.03
1.04
2.95
1.05
2.08
2.99
2.11
f1 (ppm)

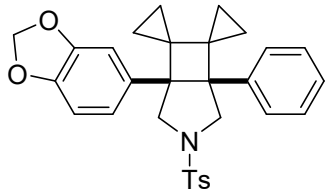

S
N
Ts
f1 (ppm)



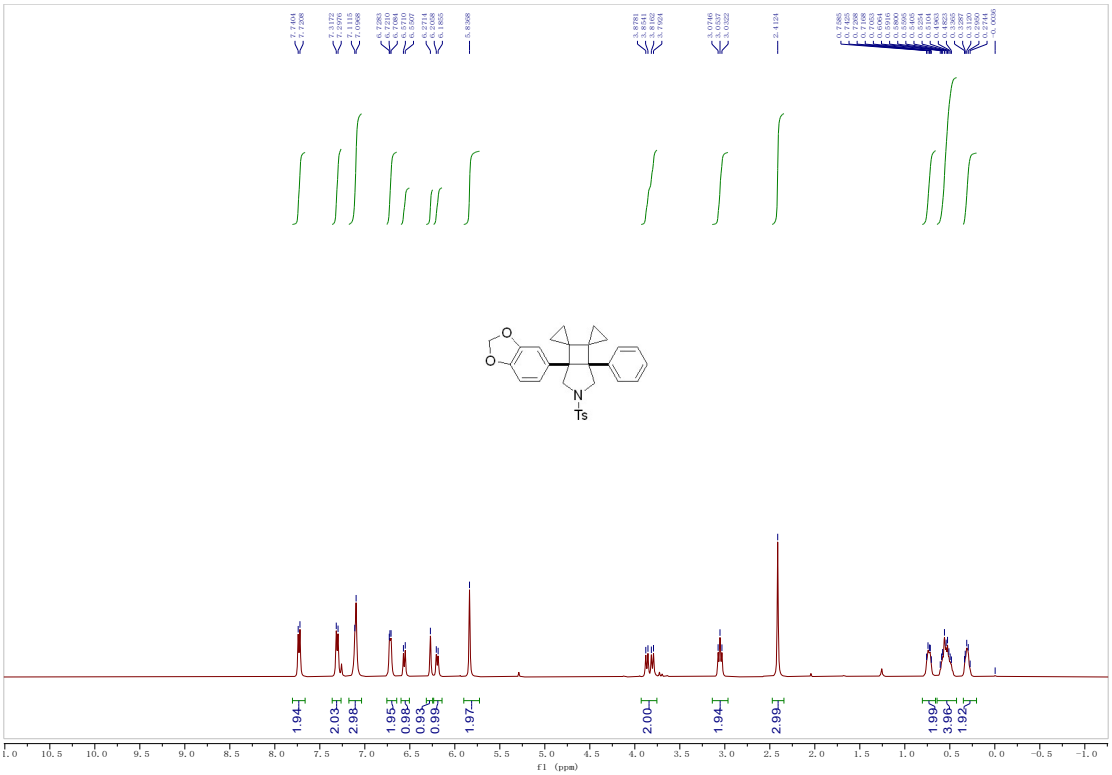
Compound 2n: Yield: 89.9 mg, 89%; A white solid; M.p.: 112 - 114 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.76 – 7.75 (m, 1H), 7.69 – 7.62 (m, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.39 – 7.38 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.09 – 7.06 (m, 1H), 7.06 – 7.05 (m, 3H), 7.05 – 7.04 (m, 1H), 6.74 – 6.71 (m, 2H), 3.99 – 3.94 (m, 2H), 3.25 (d, *J* = 9.6 Hz, 1H), 3.12 (d, *J* = 9.6 Hz, 1H), 2.39 (s, 3H), 0.84 – 0.76 (m, 2H), 0.76 – 0.64 (m, 1H), 0.62 – 0.56 (m, 2H), 0.48 – 0.25 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 140.5, 138.1, 132.9, 132.8, 131.8, 129.7, 127.95, 127.89, 127.7, 127.5, 127.4, 127.3, 127.1, 126.2, 126.0, 125.8, 124.7, 58.9, 58.6, 58.3, 57.2, 32.5, 32.4, 21.6, 9.4, 9.2, 8.42, 8.39; IR (neat): ν 3065, 2840, 1598, 1347, 1167, 1107, 1023, 753, 703 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{33}H_{32}NO_2S$ $[M+H]^+$: 506.2148, Found: 506.2153.

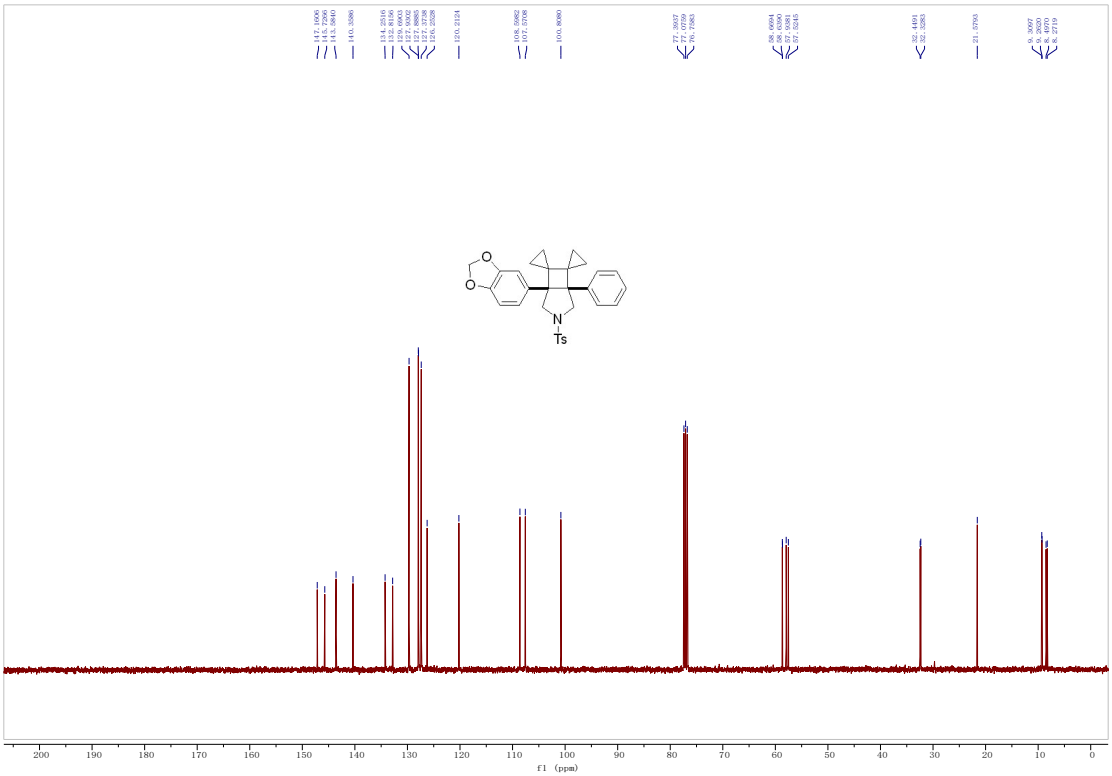

N
Ts
1.91
1.03
0.99
0.98
1.99
2.02
0.99
2.83
0.98
1.92
1.97
0.97
0.97
2.89
2.00
1.04
1.96
2.98
f1 (ppm)

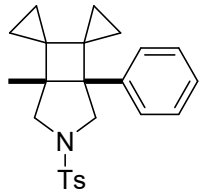

N
Ts
f1 (ppm)



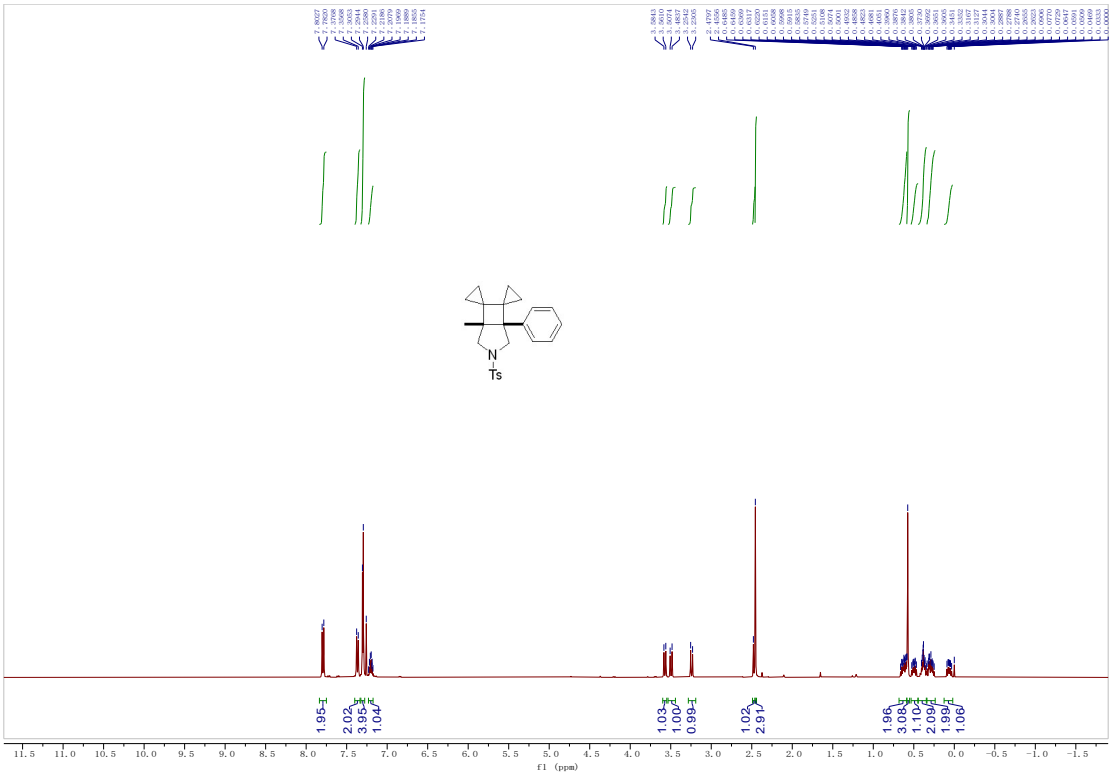
Compound 2p: Yield: 69.1 mg, 81%; A white solid; M.p.: 171 - 173°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.11 – 7.10 (m, 3H), 6.73 – 6.71 (m, 2H), 6.56 (d, *J* = 8.1 Hz, 1H), 6.27 (s, 1H), 6.19 (d, *J* = 8.1 Hz, 1H), 5.84 (s, 2H), 3.83 (m, 2H), 3.07 – 3.03 (m, 2H), 2.41 (s, 3H), 0.76 – 0.71 (m, 2H), 0.61 – 0.48 (m, 4H), 0.34 – 0.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 145.7, 143.6, 140.4, 134.3, 132.8, 129.7, 127.93, 127.89, 127.4, 126.3, 120.2, 108.6, 107.6, 100.8, 58.7, 58.6, 57.9, 57.5, 32.4, 32.3, 21.6, 9.31, 9.26, 8.5, 8.3; IR (neat): ν 2848, 1712, 1598, 1490, 1345, 1232, 1038, 1024, 935, 814, 701 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{30}H_{29}NO_4SNa$ $[M+Na]^+$: 522.1709, Found: 522.1714.

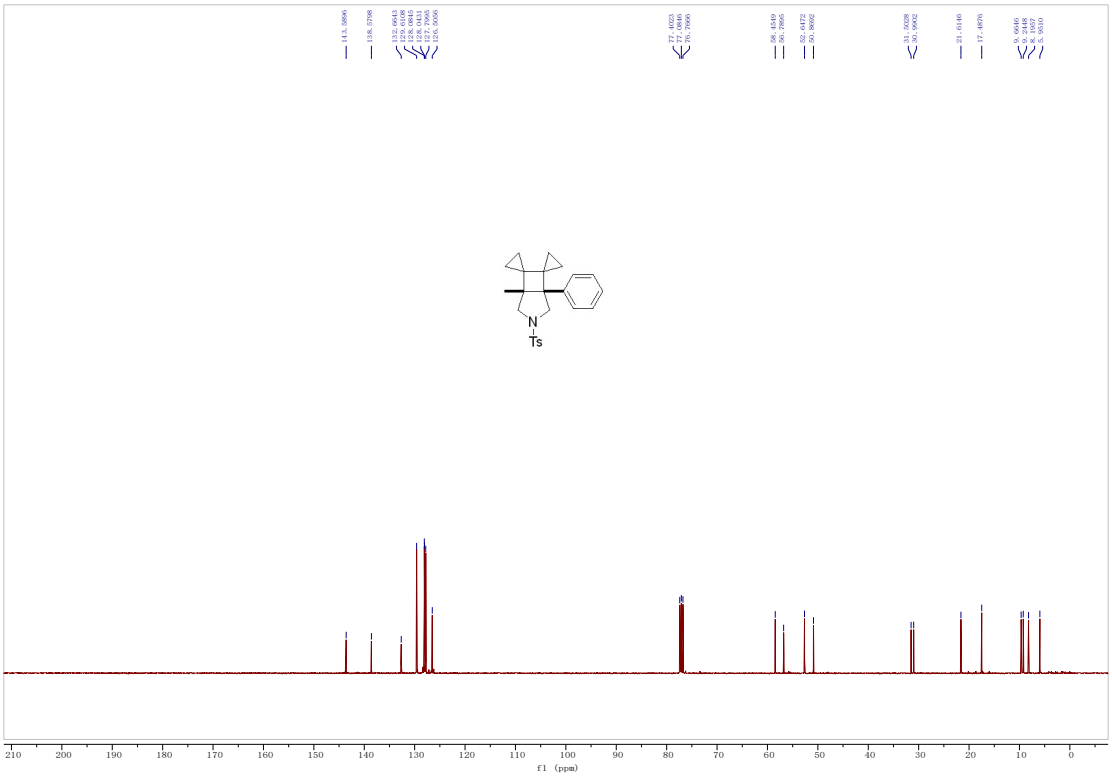

O
O
N
Ts
1.94
2.03
2.98
1.95
0.98
0.93
0.99
1.97
2.00
1.94
2.99
1.99
3.96
1.92
f1 (ppm)

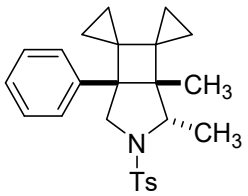

O
O
N
Ts
f1 (ppm)



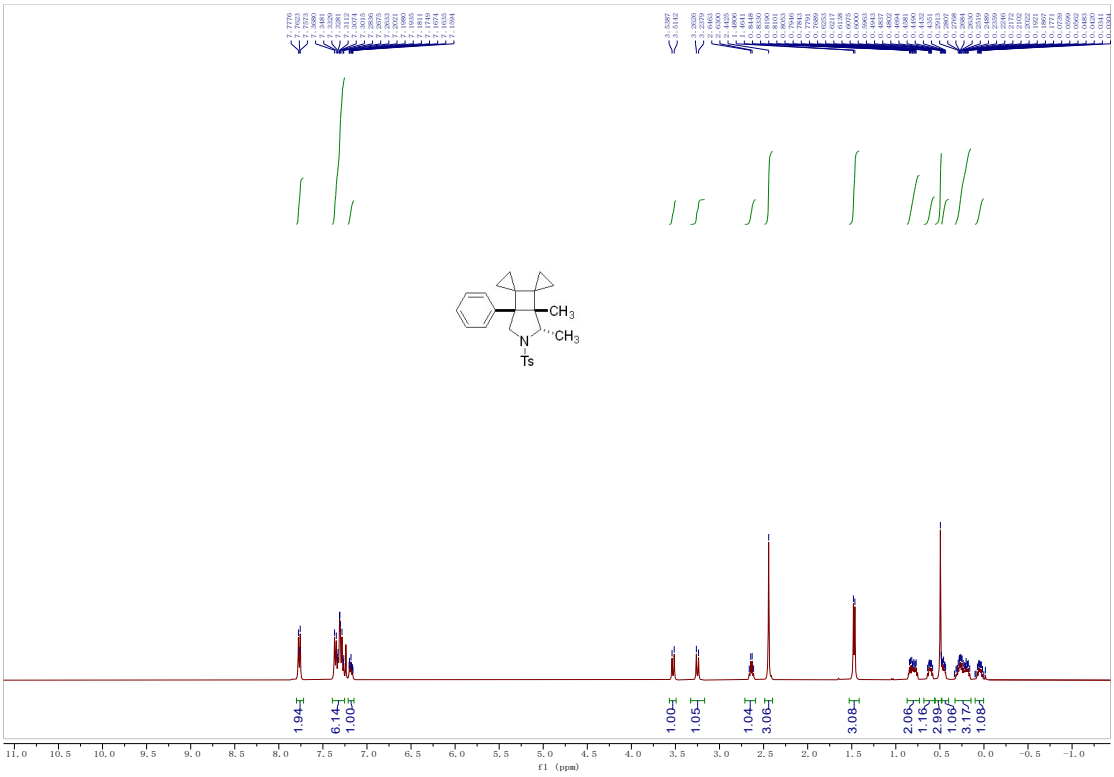
Compound 2q: Yield: 58.1 mg, 74%; A white solid; M.p.: 161 - 163 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.29 (m, 4H), 7.25 – 7.21 (m, 1H), 3.57 (d, *J* = 9.3 Hz, 1H), 3.50 (d, *J* = 9.5 Hz, 1H), 3.24 (d, *J* = 9.5 Hz, 1H), 2.46 (d, *J* = 9.3 Hz, 1H), 2.45 (s, 3H), 0.66 – 0.59 (m, 2H), 0.57 (s, 3H), 0.51 – 0.42 (m, 1H), 0.42 – 0.35 (m, 2H), 0.32 – 0.24 (m, 2H), 0.10 – 0.0 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 138.6, 132.7, 129.6, 128.1, 128.0, 127.8, 126.5, 58.5, 56.8, 52.6, 50.9, 31.5, 31.0, 21.6, 17.5, 9.7, 9.2, 8.2, 6.0; IR (neat): ν 2920, 2359, 1347, 1167, 1091, 1024, 815, 706 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{24}H_{27}NO_2SNa$ $[M+Na]^+$: 416.1655, Found: 416.1656.

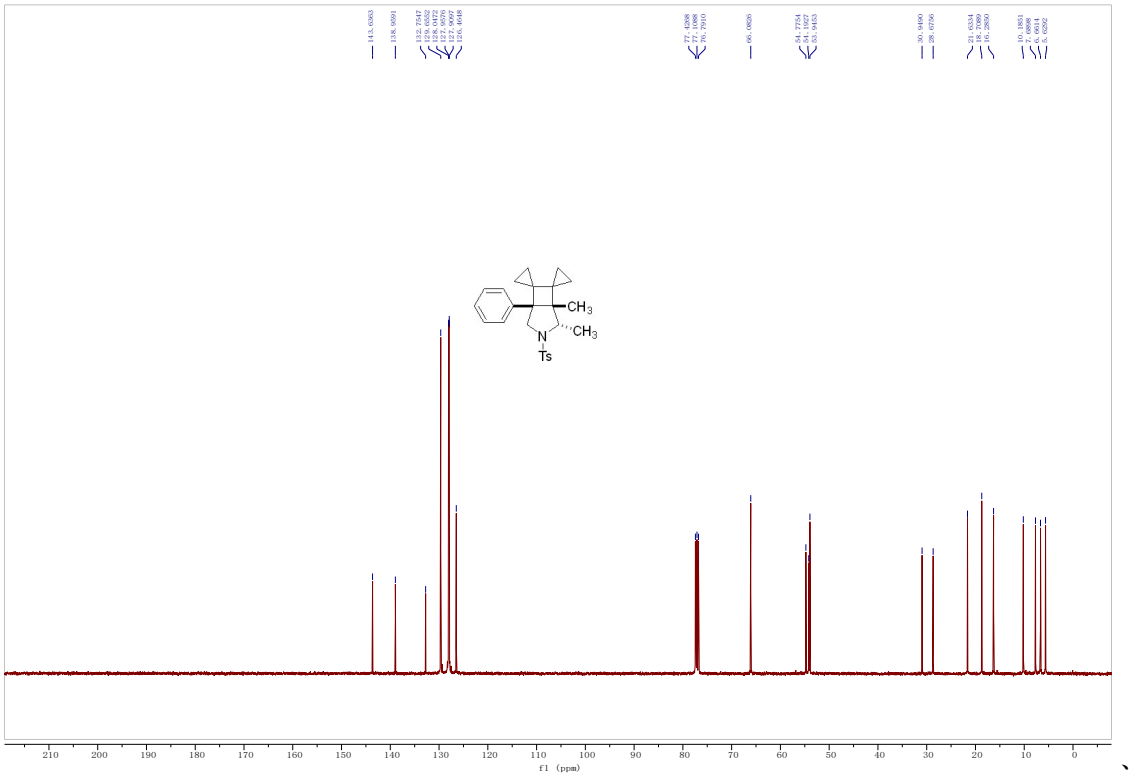

N
Ts
1.95
2.02
3.95
1.04
1.03
1.00
0.99
1.02
2.91
1.96
3.08
1.10
2.09
1.99
1.06
f1 (ppm)

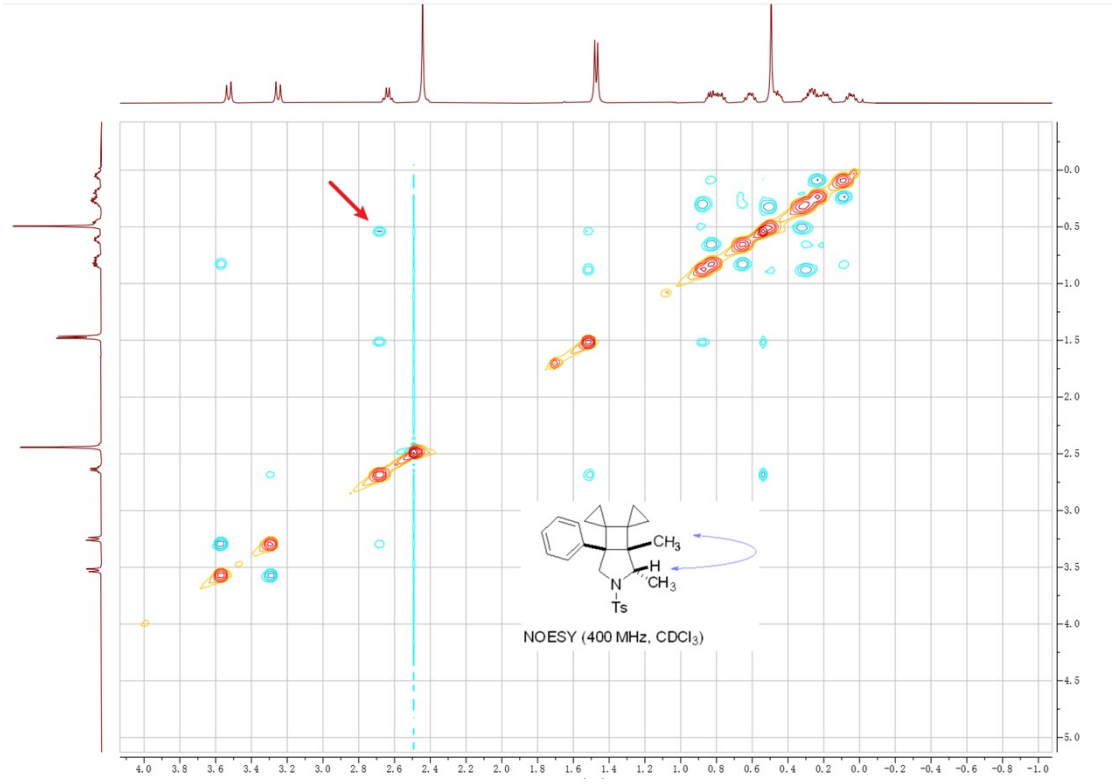

N
Ts
f1 (ppm)

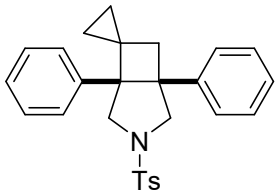


Compound 2r: Yield: 57.9 mg, 71%; A white solid; M.p.: 142 - 144 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.26 (m, 6H), 7.20 – 7.16 (m, 1H), 3.52 (d, *J* = 9.8 Hz, 1H), 3.25 (d, *J* = 9.8 Hz, 1H), 2.64 (q, *J* = 6.6 Hz, 1H), 2.44 (s, 3H), 1.46 (d, *J* = 6.6 Hz, 3H), 0.85 – 0.78 (m, 2H), 0.76 – 0.61 (m, 1H), 0.49 (s, 3H), 0.48 – 0.44 (m, 1H), 0.30 – 0.18 (m, 3H), 0.17 – 0.03 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 139.0, 132.8, 129.7, 128.04, 127.95, 127.91, 126.5, 66.1, 54.8, 54.2, 53.9, 30.9, 28.7, 21.6, 18.7, 16.3, 10.2, 7.7, 6.7, 5.6; IR (neat): ν 2988, 2359, 1351, 1207, 1106, 1090, 761, 661 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{25}H_{29}NO_2SNa$ $[M+Na]^+$: 430.1811, Found: 430.1816.

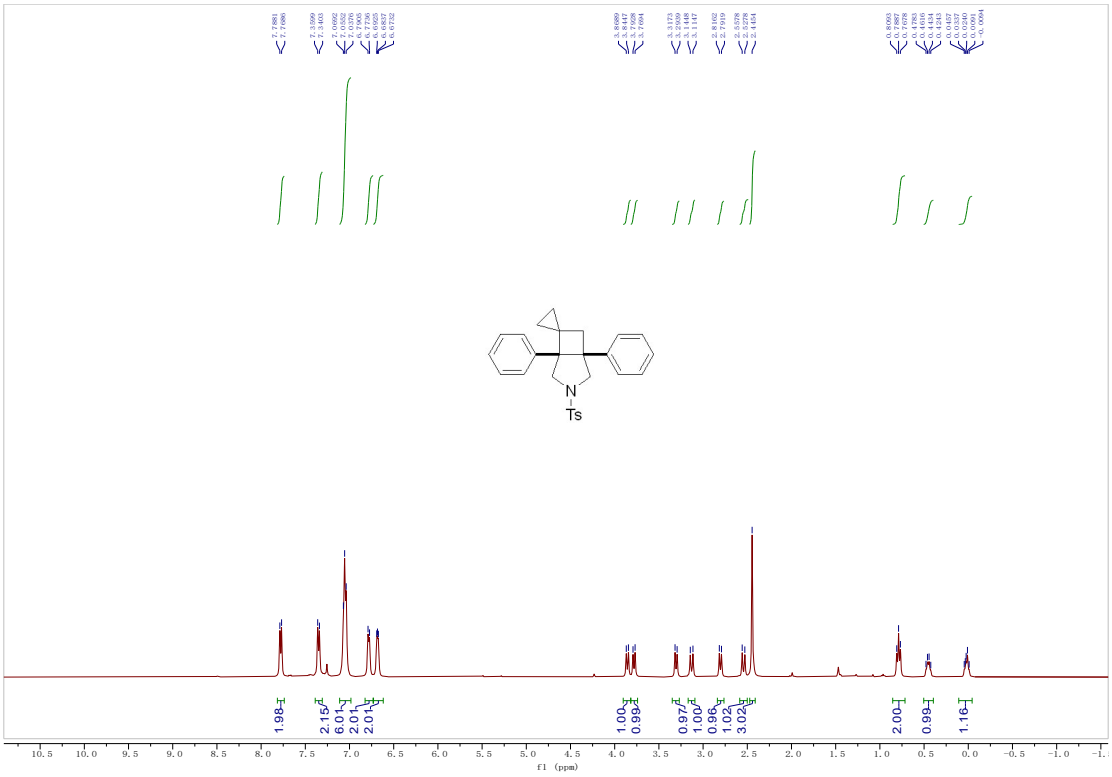

CH3
CH3
N
Ts
1.94
6.14
1.00
1.00
1.05
1.04
3.06
3.08
2.06
1.16
2.99
1.06
3.17
1.08
f1 (ppm)

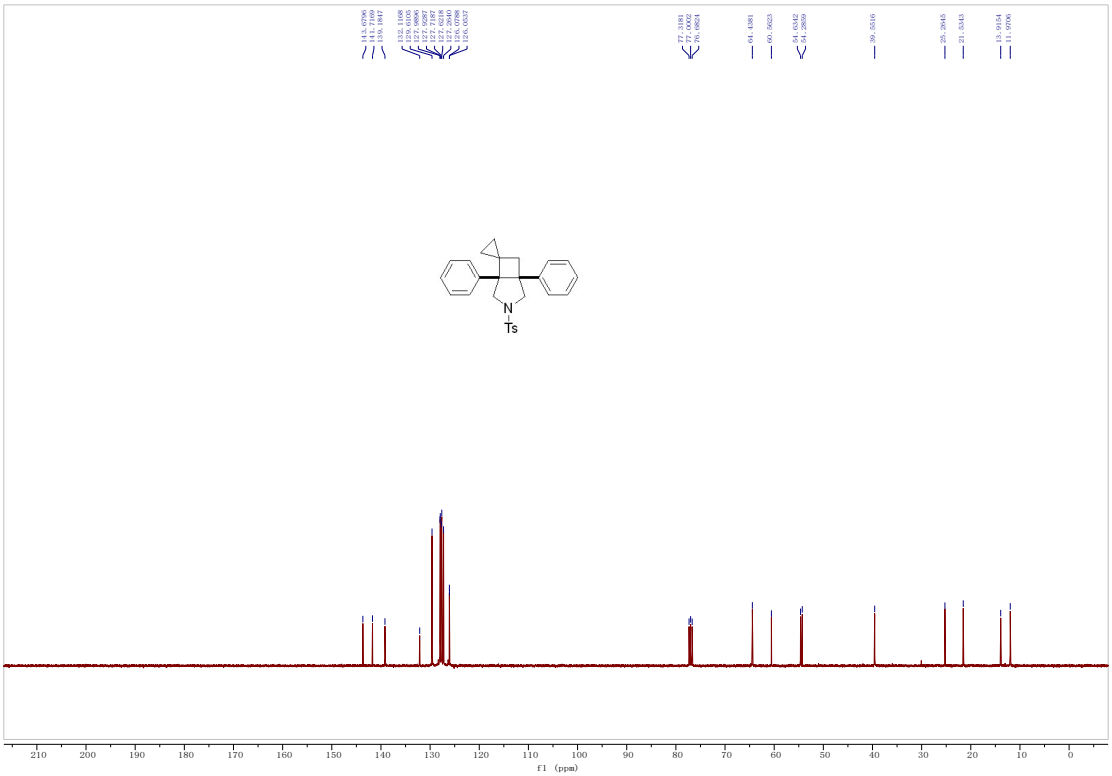

CH3
CH3
N
Ts
f1 (ppm)

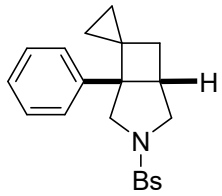

CH3
H
CH3
N
Ts
NOESY (400 MHz, CDCl3)



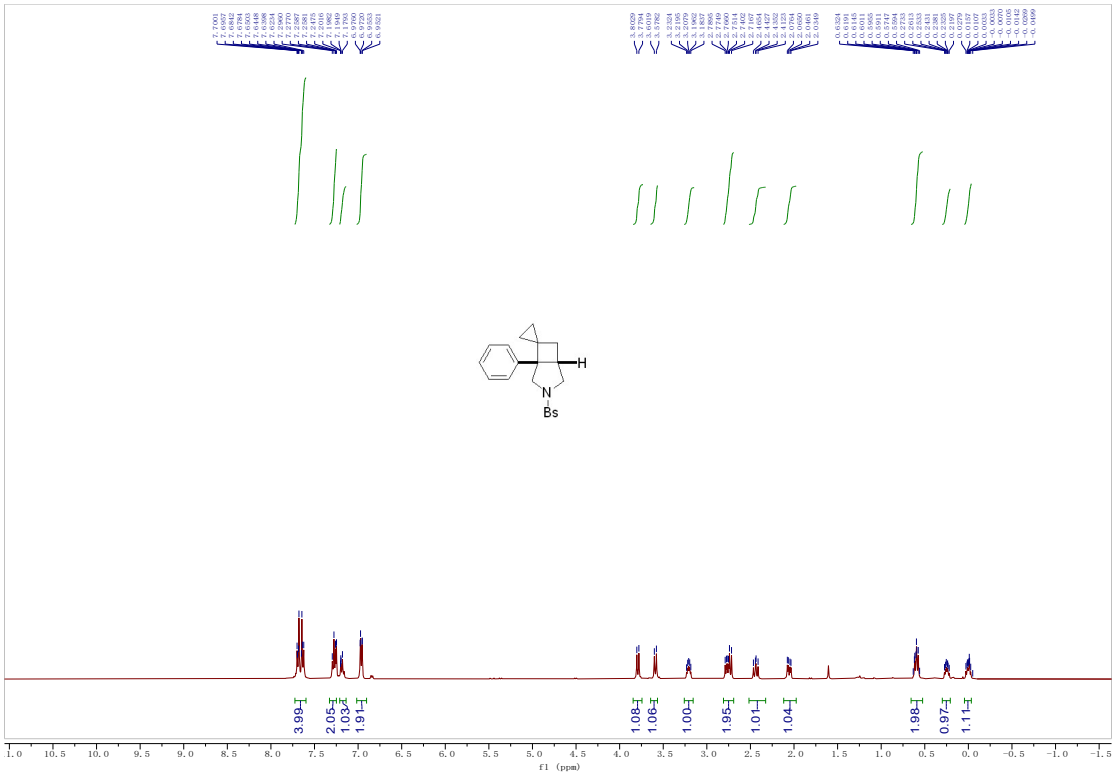
Compound 2t: Yield: 78.8 mg, 91%; A white solid; M.p.: 150 - 152 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.07 – 7.04 (m, 6H), 6.79 – 6.77 (m, 2H), 6.69 – 6.67 (m, 2H), 3.85 (d, *J* = 9.7 Hz, 1H), 3.78 (d, *J* = 9.4 Hz, 1H), 3.30 (d, *J* = 9.4 Hz, 1H), 3.13 (d, *J* = 12.0 Hz, 1H), 2.80 (d, *J* = 9.7 Hz, 1H), 2.53 (d, *J* = 12.0 Hz, 1H), 2.45 (s, 3H), 0.81 – 0.77 (m, 2H), 0.48 – 0.43 (m, 1H), 0.05 – 0.00 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 141.7, 139.2, 132.1, 129.6, 128.0, 127.9, 127.7, 127.6, 127.3, 127.07, 127.05, 64.4, 60.6, 54.6, 54.3, 39.5, 25.3, 21.5, 13.9, 12.0; IR (neat): ν 3047, 1712, 1347, 1166, 1013, 816, 701, 663 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{27}H_{27}NO_2SNa$ $[M+Na]^+$: 452.1655, Found: 452.1650.

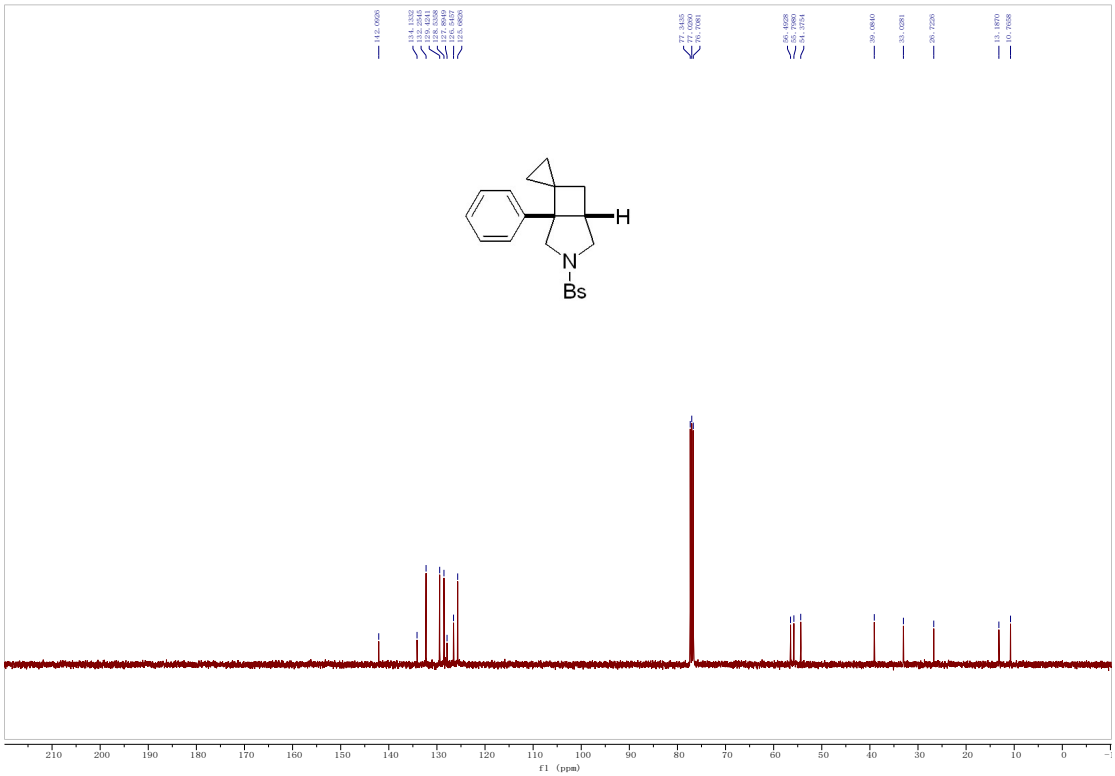

N
Ts
1.98
2.15
6.01
2.01
2.01
1.00
0.99
0.97
1.00
0.96
1.02
3.02
2.00
0.99
1.16
f1 (ppm)

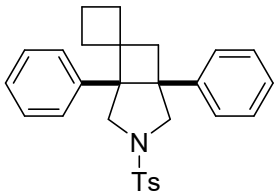

N
Ts
f1 (ppm)



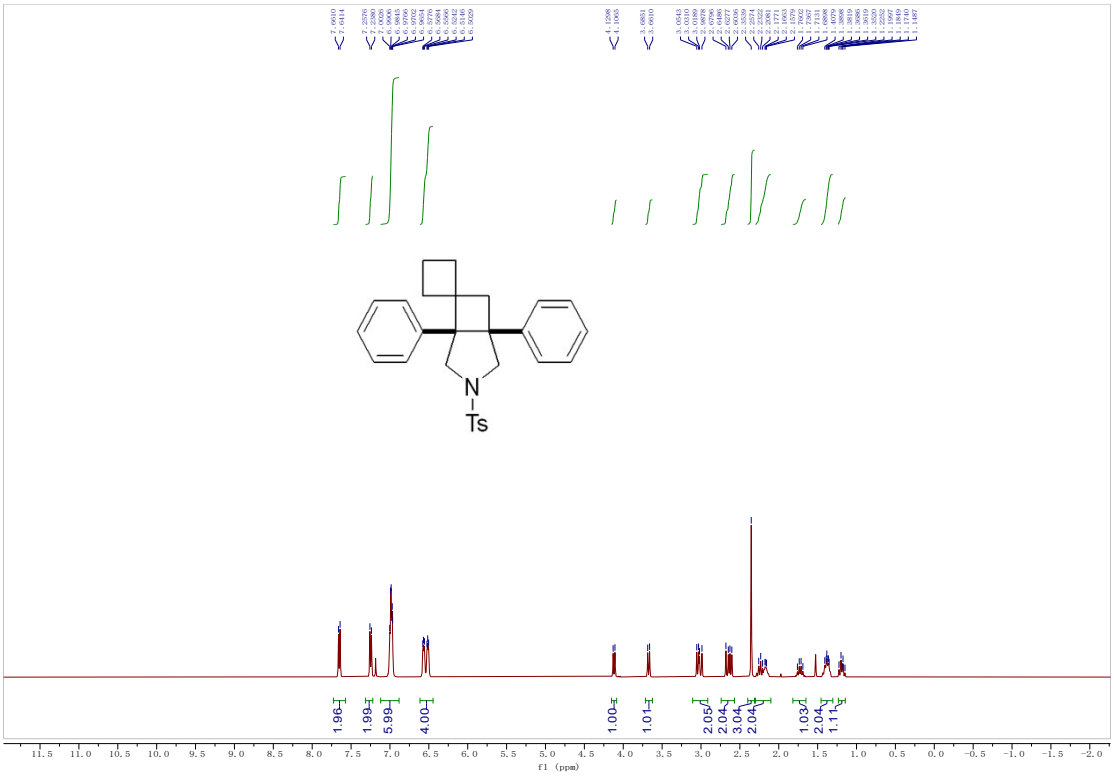
Compound 2u: Yield: 67.7 mg, 81%; A white solid; M.p.: 142 - 144 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.62 (m, 4H), 7.29 – 7.25 (m, 2H), 7.20 – 7.18 (m, 1H), 6.98 – 6.95 (m, 2H), 3.79 (d, *J* = 9.4 Hz, 1H), 3.59 (d, *J* = 9.4 Hz, 1H), 3.23 – 3.18 (m, 1H), 2.79 – 2.72 (m, 2H), 2.47 – 2.41 (m, 1H), 2.05 (dd, *J* = 12.1, 4.5 Hz, 1H), 0.63 – 0.56 (m, 2H), 0.27 – 0.22 (m, 1H), 0.03 – 0.00 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 134.1, 132.3, 129.4, 128.5, 127.9, 126.5, 125.7, 56.5, 55.8, 54.4, 39.1, 33.0, 26.7, 13.2, 10.8; IR (neat): ν 2922, 1969, 1350, 1168, 1021, 1007, 818, 737, 701 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{20}H_{20}NO_2SBrNa$ $[M+Na]^+$: 440.0290, Found: 440.0294.

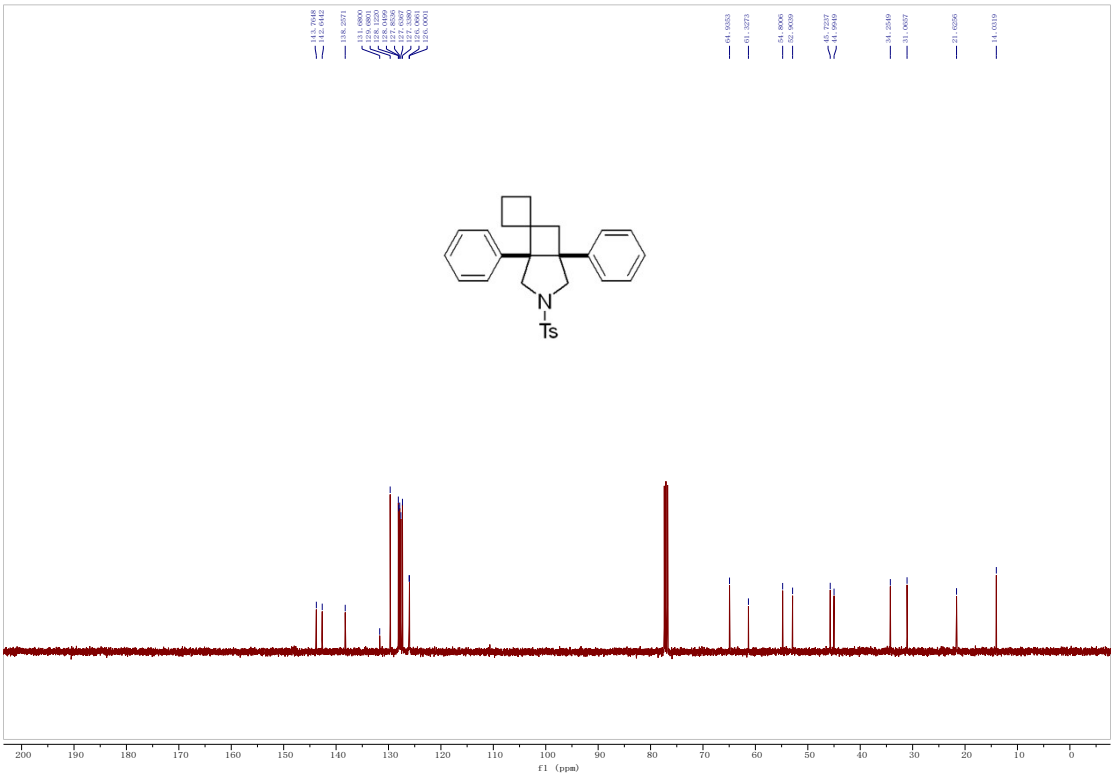

H
N
Bs
3.99
2.05
1.03
1.91
1.08
1.06
1.00
1.95
1.01
1.04
1.98
0.97
1.11
f1 (ppm)

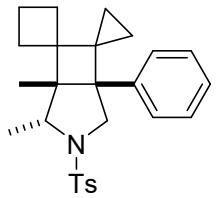

H
N
Bs
f1 (ppm)



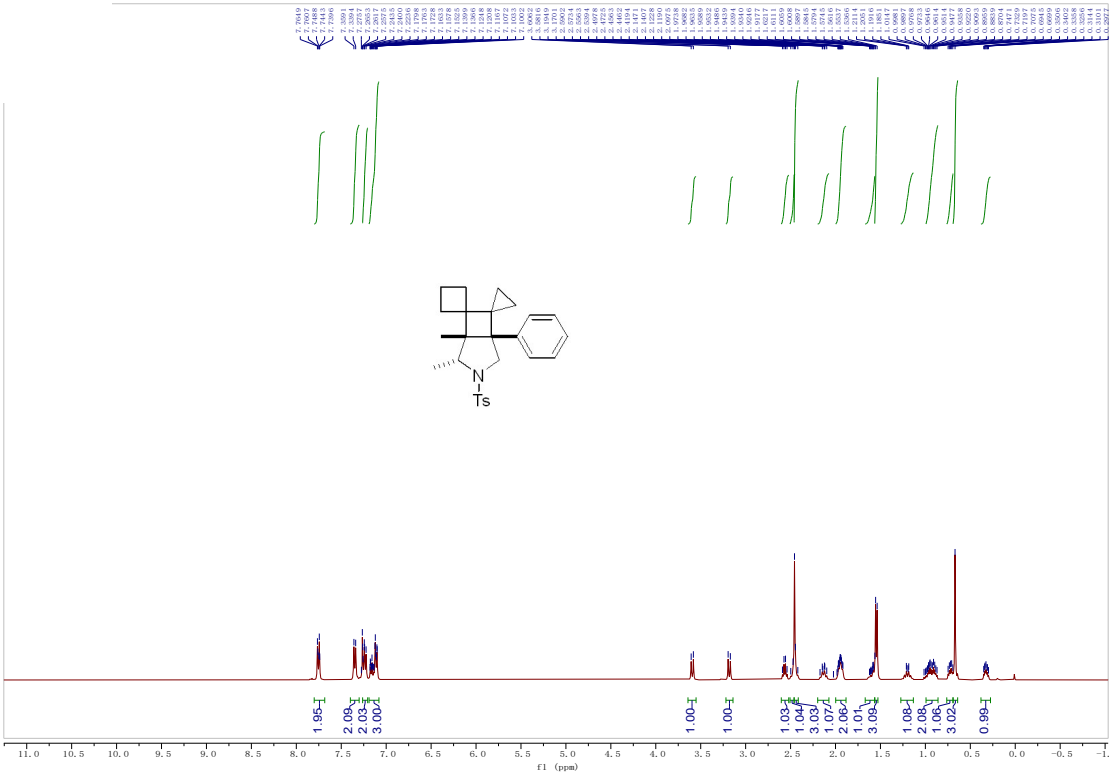
Compound 2v: Yield: 70.6 mg, 79%; A white solid; M.p.: 141 - 143 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.08 – 7.04 (m, 6H), 6.65 – 6.58 (m, 4H), 4.19 (d, *J* = 9.3 Hz, 1H), 3.75 (d, *J* = 9.6 Hz, 1H), 3.13 – 3.06 (m, 2H), 2.75 – 2.68 (m, 2H), 2.43 (s, 3H), 2.34 – 2.23 (m, 2H), 1.84 – 1.76 (m, 1H), 1.48 – 1.43 (m, 2H), 1.30 – 1.22 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 142.6, 138.3, 131.7, 129.7, 128.1, 128.0, 127.9, 127.6, 127.3, 126.1, 126.0, 64.9, 61.3, 54.8, 52.9, 45.7, 45.0, 34.3, 31.1, 21.6, 14.0 cm^{-1}; IR (neat): ν 2919, 1738, 1466, 1349, 1167, 1013, 702, 663 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{28}H_{29}NO_2SNa$ $[M+Na]^+$: 466.1811, Found: 466.1817.

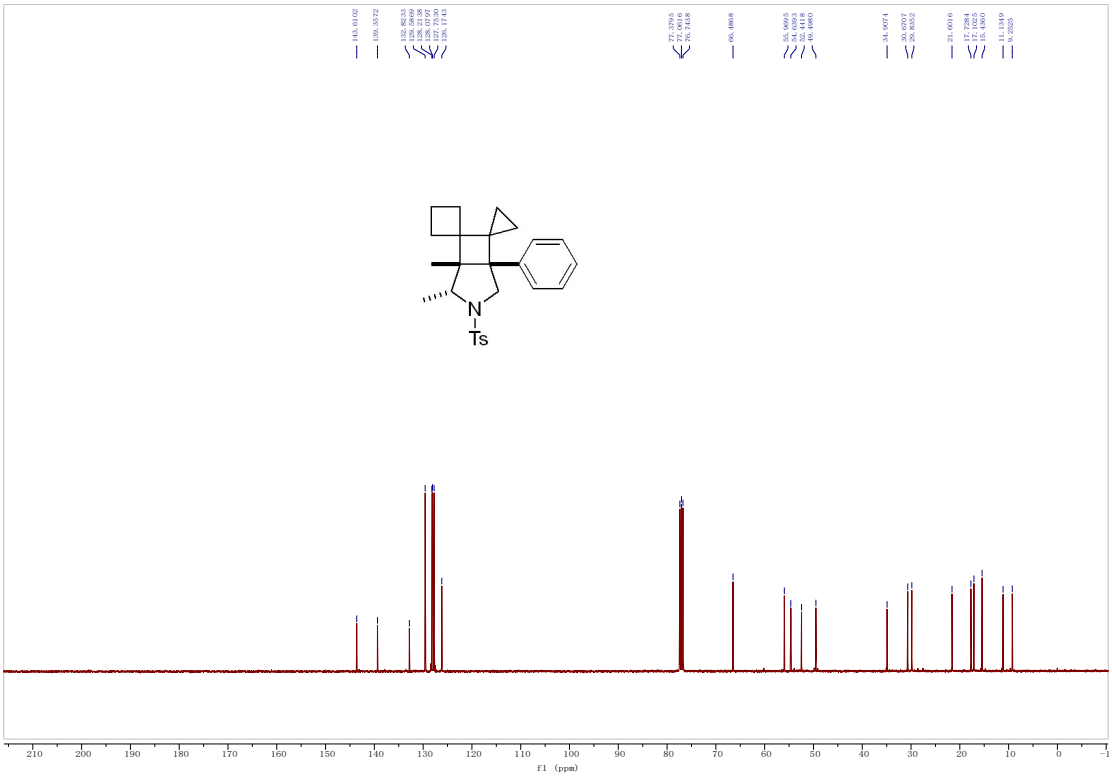

N
Ts
1.96
1.99
5.99
4.00
1.00
1.01
2.05
2.04
3.04
2.04
1.03
2.04
1.11
f1 (ppm)

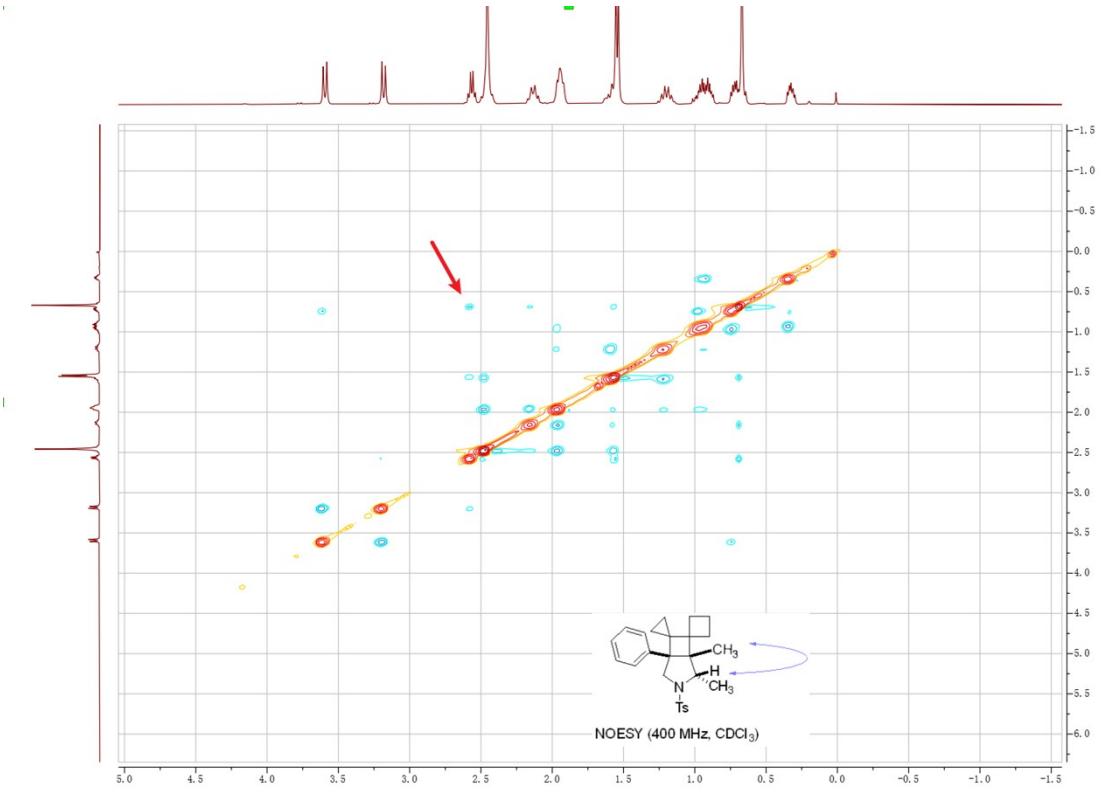

N
Ts
f1 (ppm)

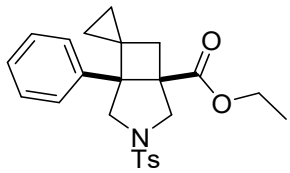


Compound 2x: Yield: 65.6 mg, 77%; A white solid; M.p.: 182 - 184 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.74 (m, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.27 – 7.22 (m, 2H), 7.17 – 7.10 (m, 3H), 3.59 (d, *J* = 9.8 Hz, 1H), 3.18 (d, *J* = 9.8 Hz, 1H), 2.56 (q, *J* = 6.8 Hz, 1H), 2.49 – 2.47 (m, 1H), 2.46 (s, 3H), 2.17 – 2.11 (m, 1H), 2.02 – 1.91 (m, 2H), 1.62 – 1.58 (m, 1H), 1.55 (d, *J* = 6.8 Hz, 3H), 1.22 – 1.19 (m, 1H), 1.01 – 0.87 (m, 2H), 0.75 – 0.69 (m, 1H), 0.72 (s, 3H), 0.35 – 0.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 139.4, 132.8, 129.6, 128.2, 128.1, 127.8, 126.2, 66.5, 56.0, 54.6, 52.4, 49.5, 34.9, 30.7, 29.8, 21.6, 17.7, 17.1, 15.4, 11.1, 9.3; IR (neat): ν 2962, 2359, 1457, 1339, 1164, 1018, 768, 701, 662 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{26}H_{31}NO_2SNa$ $[M+Na]^+$: 444.1968, Found: 444.1974.

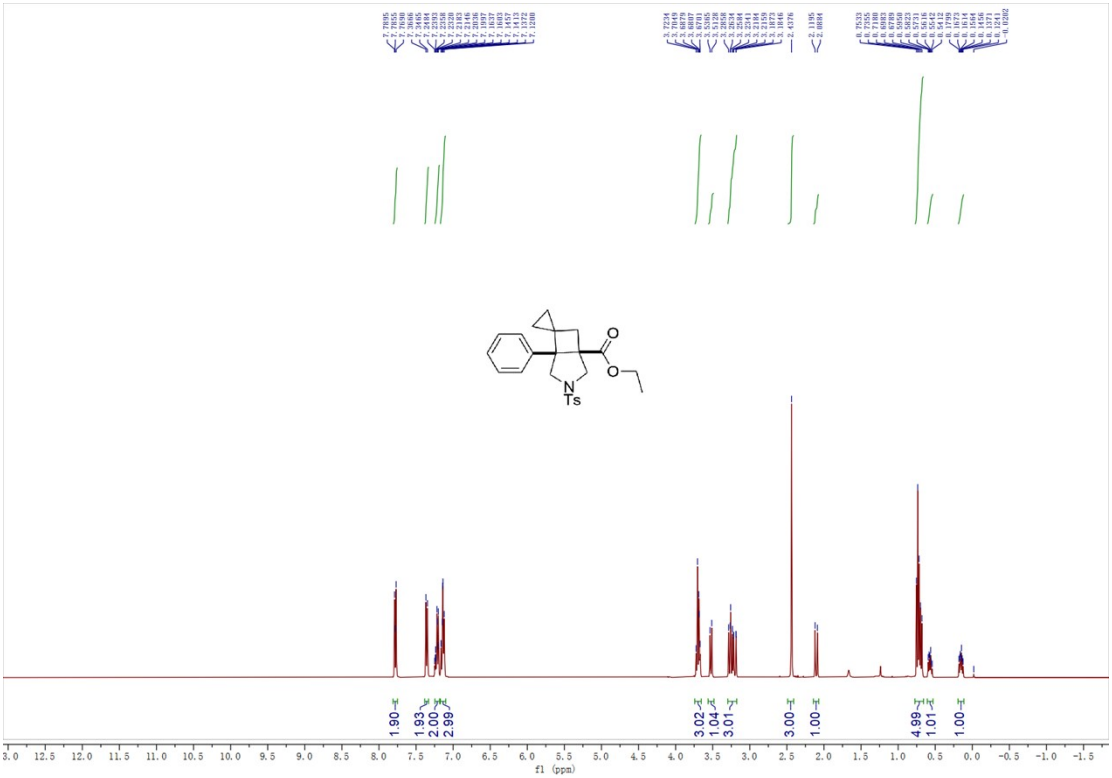

N
Ts
1.95
2.09
2.03
3.00
1.00
1.00
1.03
1.04
3.03
1.07
2.06
1.01
3.09
1.08
2.08
1.06
3.02
0.99
f1 (ppm)

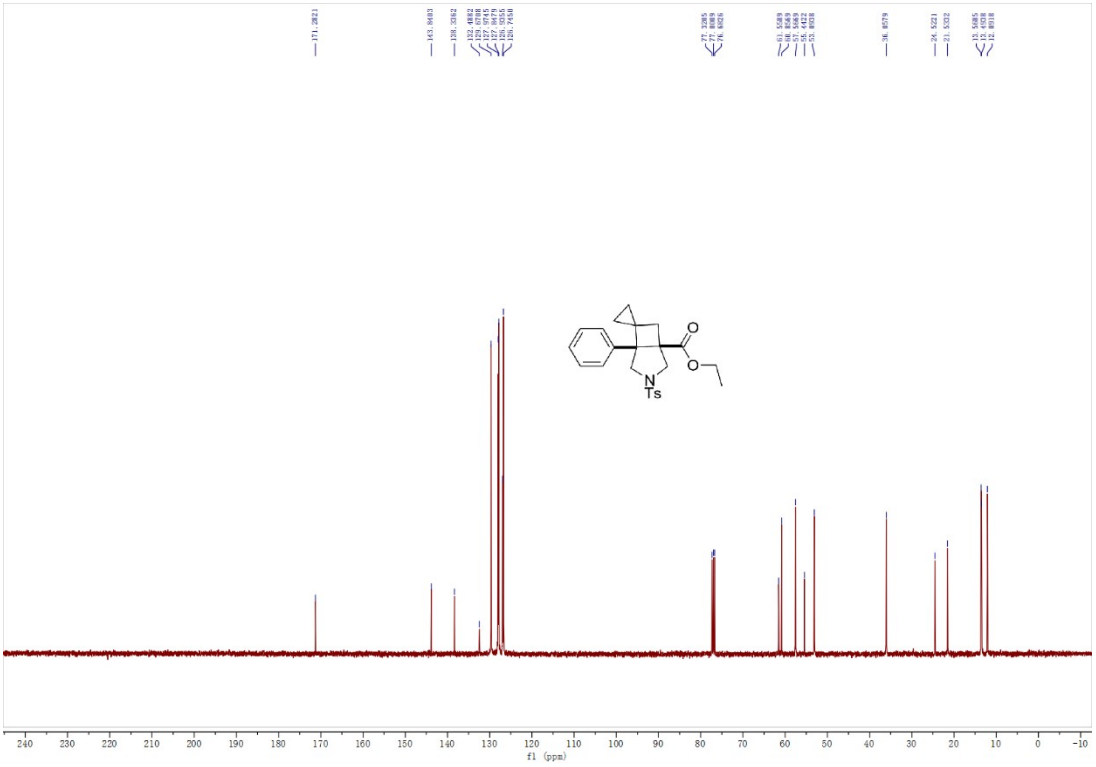

N
Ts
f1 (ppm)

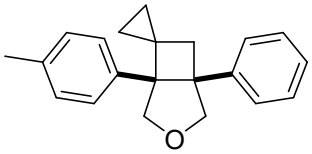

CH3
H
CH3
N
Ts
NOESY (400 MHz, CDCl3)



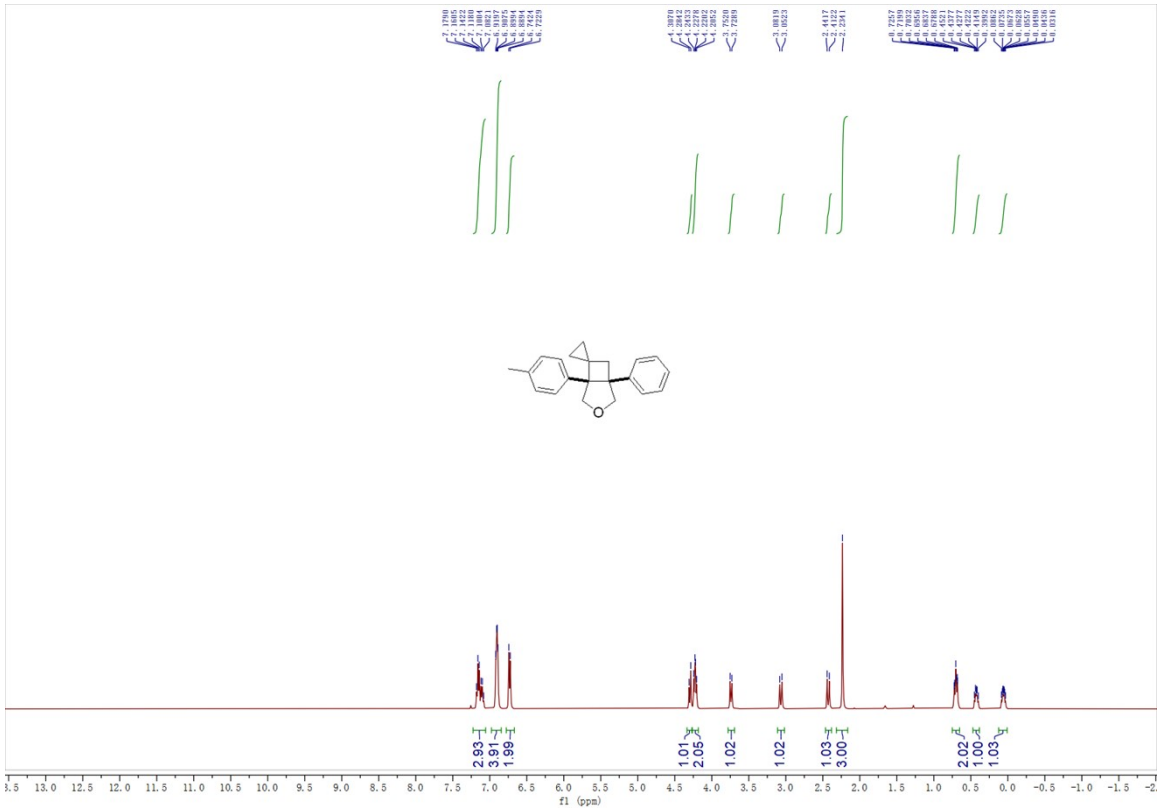
Compound 2aa: Yield: 74.8 mg, 88%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.18 (m, 2H), 7.17 – 7.10 (m, 3H), 3.74 – 3.65 (m, 3H), 3.52 (d, *J* = 9.5 Hz, 1H), 3.30 – 3.18 (m, 3H), 2.44 (s, 3H), 2.10 (d, *J* = 12.4 Hz, 1H), 0.77 – 0.66 (m, 5H), 0.61 – 0.53 (m, 1H), 0.19 – 0.11 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 143.8, 138.3, 132.5, 129.7, 128.0, 127.8, 126.9, 126.7, 61.6, 60.9, 57.6, 55.4, 53.1, 36.1, 24.5, 21.5, 13.6, 13.5, 12.1; IR (neat): ν 2976, 1838, 1751, 1762, 1488, 1309, 1285, 1184, 773, cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{24}H_{27}NO_4SNa$ $[M+Na]^+$: 448.1553, Found: 448.1555.

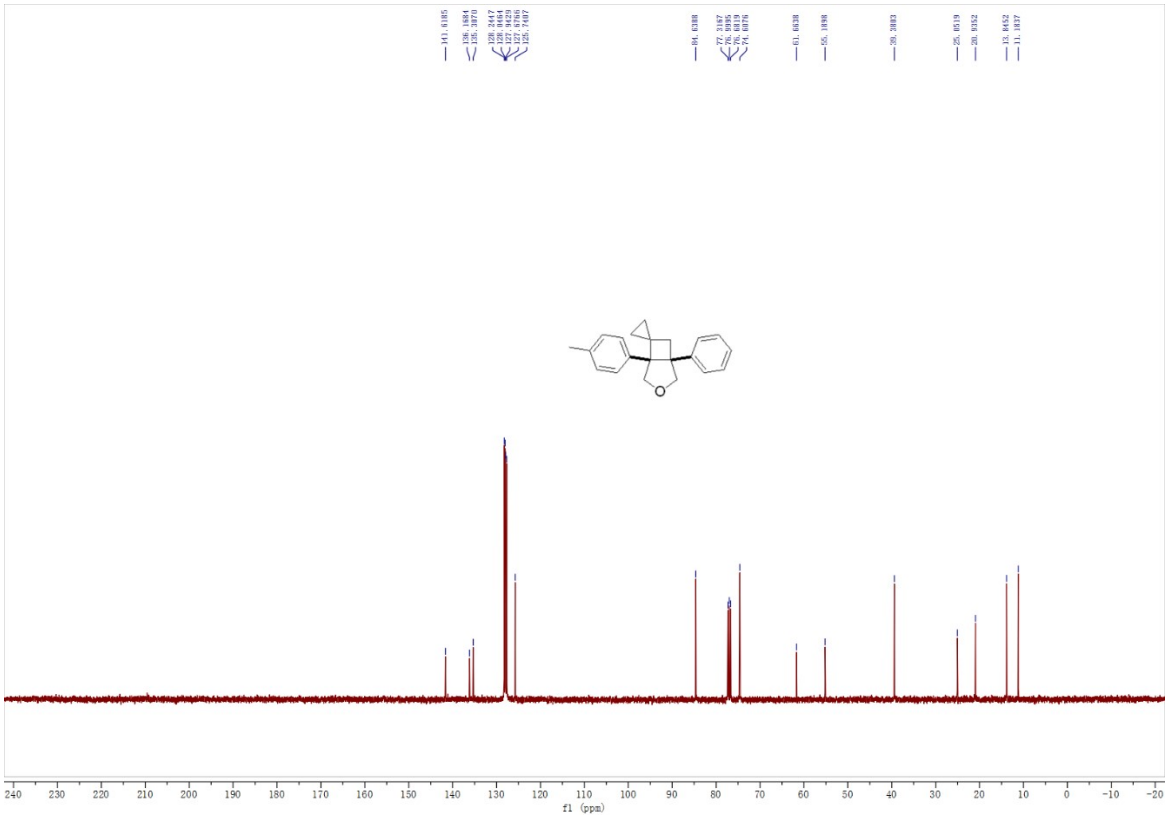

O
O
N
Ts
1.90
1.93
2.00
2.99
3.02
1.04
3.01
3.00
1.00
4.99
1.01
1.00
f1 (ppm)

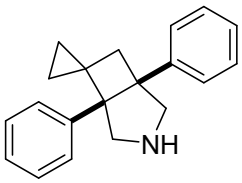

O
O
N
Ts
f1 (ppm)



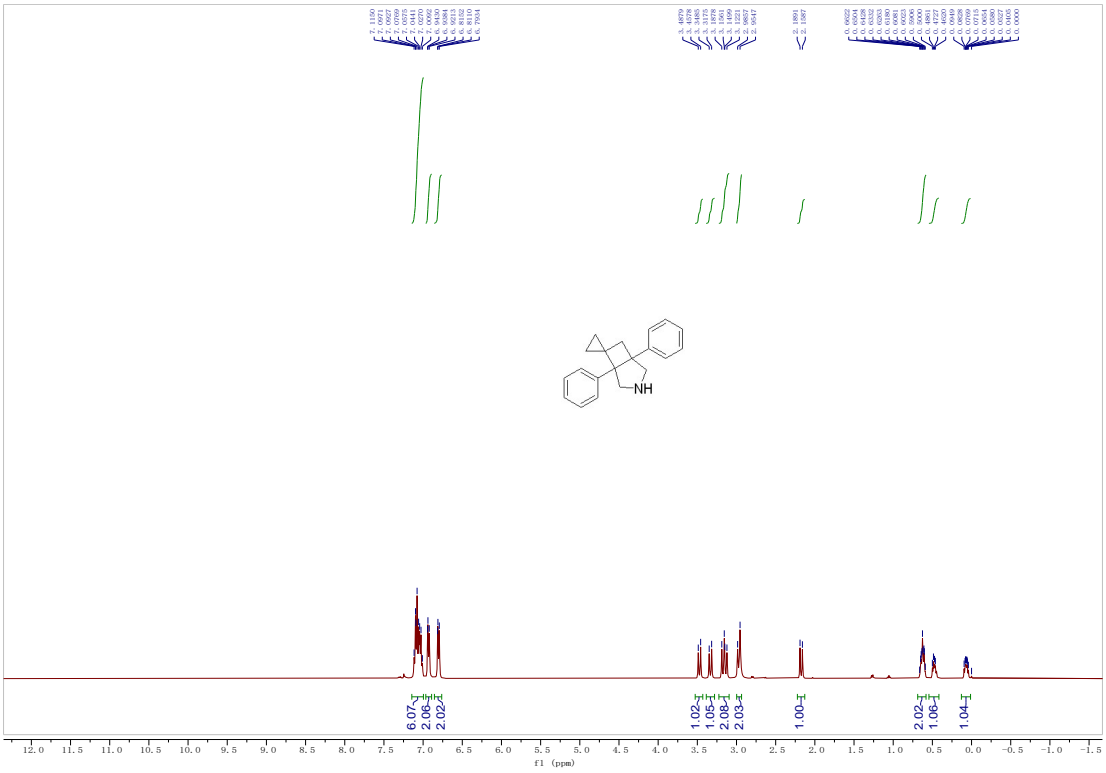
Compound 2ab: Yield: 51.1 mg, 88%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.06 (m, 3H), 6.98 – 6.84 (m, 4H), 6.73 (d, *J* = 7.8 Hz, 2H), 4.30 (d, *J* = 9.1 Hz, 1H), 4.26 – 4.18 (m, 2H), 3.74 (d, *J* = 9.1 Hz, 1H), 3.07 (d, *J* = 11.8 Hz, 1H), 2.43 (d, *J* = 11.8 Hz, 1H), 2.23 (s, 3H), 0.75 – 0.65 (m, 2H), 0.47 – 0.38 (m, 1H), 0.12 – 0.01 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 136.2, 135.3, 128.2, 128.0, 127.9, 127.7, 125.7, 84.6, 74.6, 61.7, 55.2, 39.4, 25.1, 20.9, 13.8, 11.2; IR (neat): ν 2966, 1978, 1856, 1734, 1323, 1297, 1239, 1184, 1136, 691, 683 cm^{-1}; HRMS (EI - FI) Calcd. for $C_{21}H_{22}O$ $[M]^+$: 290.1665, Found: 290.1668.

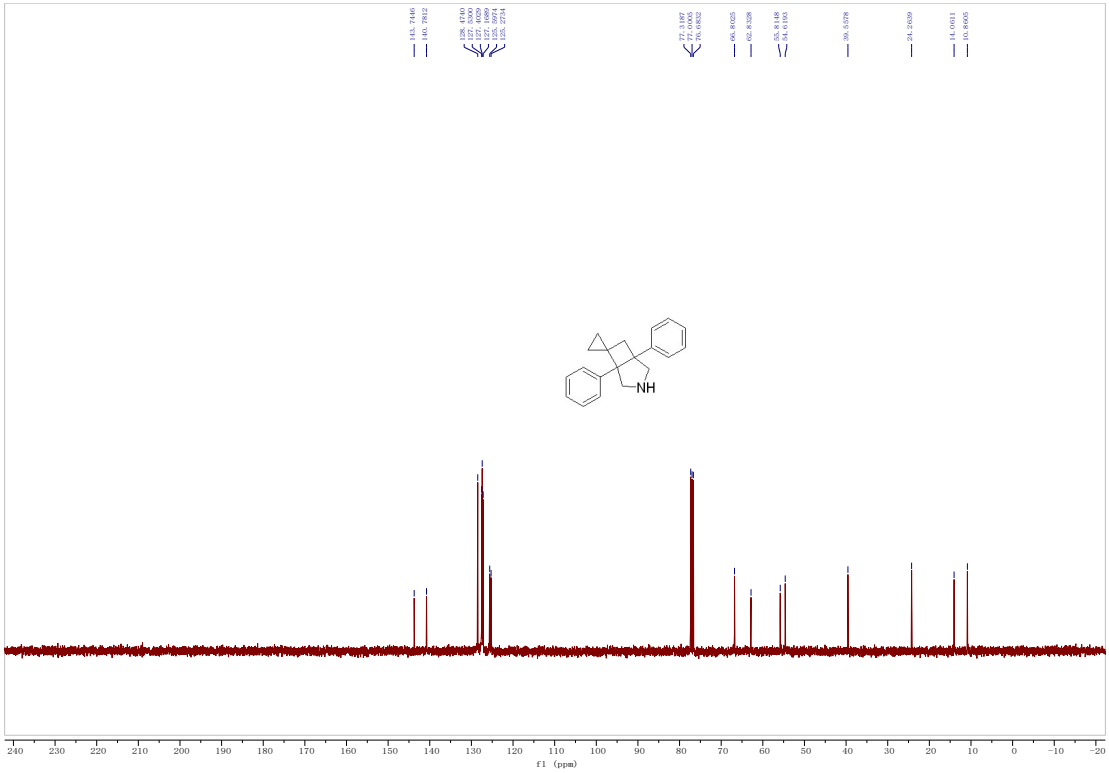

f1 (ppm)


f1 (ppm)



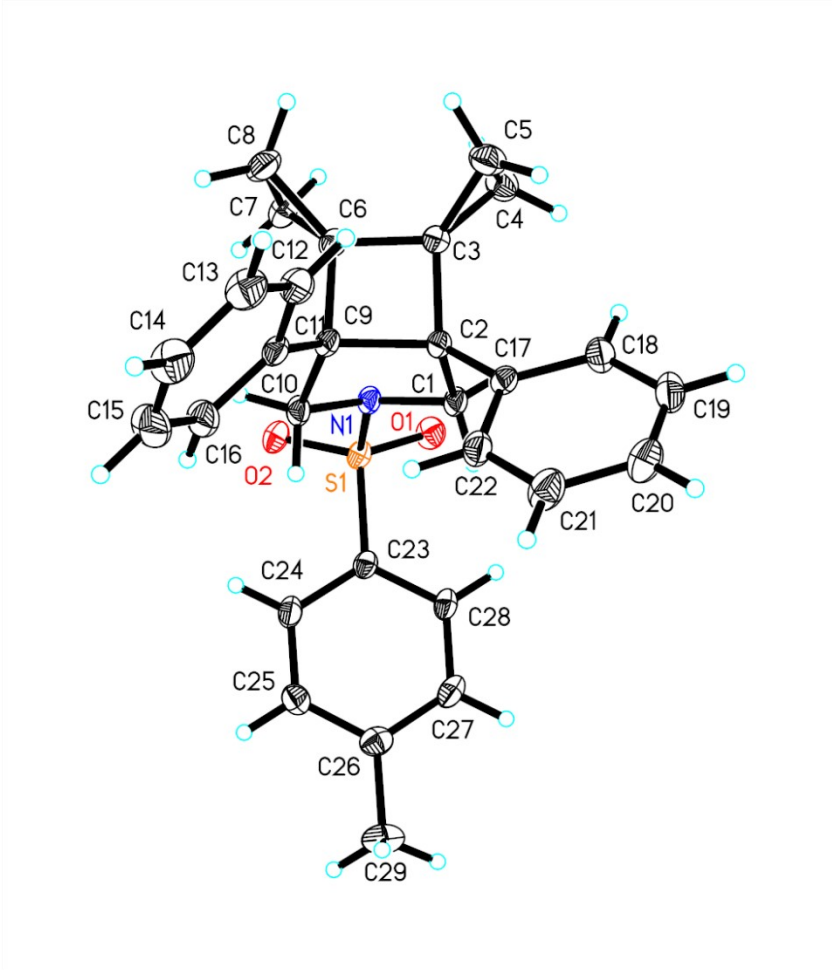
Compound 3t: Yield: 48.1 mg, 87%; A white solid; M.p.: 103 - 105 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.00 (m, 6H), 6.97 – 6.89 (m, 2H), 6.86 – 6.76 (m, 2H), 3.47 (d, *J* = 12.0 Hz, 1H), 3.33 (d, *J* = 12.4 Hz, 1H), 3.22 – 3.09 (m, 2H), 3.00 – 2.94 (m, 2H), 2.17 (d, *J* = 12.0 Hz, 1H), 0.69 – 0.58 (m, 2H), 0.54 – 0.42 (m, 1H), 0.13 – 0.01 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 140.8, 128.5, 127.5, 127.4, 127.2, 125.6, 125.3, 66.8, 62.8, 55.8, 54.6, 39.6, 24.3, 14.1, 10.9; IR (neat): ν 3071, 2987, 2862, 1602, 1500, 1417, 999, 811, 780 cm^{-1}; HRMS (ESI - TOF) Calcd. for $C_{20}H_{22}N$ $[M+H]^+$: 276.1747, Found: 276.1744.


NH
6.07
2.06
2.02
1.02
1.05
2.08
2.03
1.00
2.02
1.06
1.04
f1 (ppm)


NH
f1 (ppm)

(12) X-ray Crystal Data of 2a.

Single crystals of **2a** were grown in dichloromethane and hexanes. Hexanes (2.0 mL) were added to **2a** (20.0 mg in a 4.0 mL vial) followed by five drops of dichloromethane. The 4.0 mL vial was capped and placed at room temperature in the experimental cabinet for seven days or longer if necessary, whereupon crystals were formed.



The crystal data of **2a** have been deposited in CCDC with number 2064517. Empirical Formula: $C_{62}H_{68}N_2O_5S_2$ (2 x **2a** · EtOEt); Formula Weight: 985.30; Crystal Color, Habit: colorless, Crystal Dimensions: 0.200 x 0.150 x 0.060 mm^3; Crystal System: Triclinic; Lattice Parameters: a = 11.1766(4)Å, b = 14.1911(7)Å, c = 17.3803(7)Å, α = 79.0480(10)°, β = 84.9910(10)°, γ = 89.9570(10)°, V = 2695.8(2)$Å^3$; Space group: P -1; Z = 4; D_{calc} = 1.214 g/cm^3; F_{000} = 1052; Final R indices [I>2sigma(I)] R1 = 0.0621, wR2 = 0.1537. The thermal ellipsoids are set at a 30% probability level.

(13) References.

1. F. F. Wong, P.-W. Chang, H.-C. Lin, B.-J. You, J.-J. Huang and S.-K. Lin, *J. Organomet. Chem.*, 2009, **694**, 3452-3455.
2. O. Delgado, A. Monteagudo, M. Van Gool, A. A. Trabanco and S. Fustero, *Org. & Biomol. Chem.*, 2012, **10**, 6758-6766.
3. J. F. Teichert, S. Zhang, A. W. v. Zijl, J. W. Slaa, A. J. Minnaard and B. L. Feringa, *Org. Lett*., 2010, **12**, 4658-4660.
4. B. V. S. Reddy, D. N. Chaya, J. S. Yadav, R. Grée, *Synthesis*., 2012, **44**, 297-303.