Supporting Information

Atom-Controlled Divergent Synthesis of Spiro and Fused Rings via Base-Catalyzed Chemoselective Annulation

Gang Chen,[a‡] Guangjie Nie,[a‡] Linxuan Li,[a,b,*] Jie Fu,[a] Hui Yao,[a,b] Nianyu Huang,[a,b,*] and Nengzhong Wang[a,b,*]

[a]Hubei Key Laboratory of Natural Products Research and Development, College of Biological and Pharmaceutical Sciences, China Three Gorges University, Yichang Hubei 443002, China.

[b]Hubei Three Gorges Laboratory, Yichang Hubei 443007, China.

[‡]These authors contributed equally.

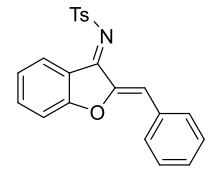
*Corresponding authors. E–mail: lilinxuan@ctgu.edu.cn, huangny@ctgu.edu.cn, wangnz@ctgu.edu.cn

Table of Contents

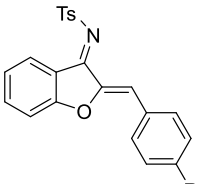
I. General Information

Unless otherwise specified, **all reactions** were carried out under a nitrogen atmosphere at room temperature. **All solvents** were purified according to the standard procedures. **All chemicals** which are commercially available were employed without further purification. **Thin-layer chromatography (TLC)** was performed on silica gel plates (GF254) using UV-light (254 and 365 nm). Flash chromatography was conducted on silica gel (200–300 mesh). **^{1}H and ^{13}C{^{1}H} NMR spectra** were recorded on a Bruker 400 MHz spectrometer. Chemical shifts were reported in parts per million (ppm). The **^{1}H NMR** (400 MHz) chemical shifts were measured relative to residual non-deuterated solvent resonance ($CDCl_3$: δ = 7.260 ppm). The **^{13}C{^{1}H} NMR** (100 MHz) chemical shifts were given using $CDCl_3$ as the internal standard ($CDCl_3$: δ = 77.00 ppm). **All high–resolution mass spectra (HR–MS)** were obtained on a Bruker microTOFQ II (ESI). **Crystal measurement** was performed by a Bruker D8 Venture X–ray diffractionmeter. Azadienes **1**[1-3] and unsaturated compounds **2**[4] were synthesized according to reported procedures. Some azadienes (**1aa-1an**, **1ba-1bg**, **1bi-1bk**, **1ca-1ce, 1cg-1ch**) have been reported earlier.[1-3] In addition, **1aa-1ac**, **1ae**, **1ag-1aj** and **1al** have previously been reported by our group.[1c] Only **1bh** and **1cf** are new compounds. Some unsaturated compounds (**2a-2i**, **2k**) have been reported earlier.[4] **2j**, **2l**, **2m** are new compounds.

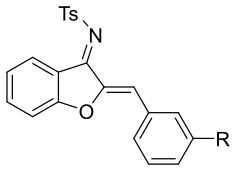
II. Substrate Scope of 1 and 2



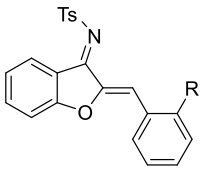
1aa



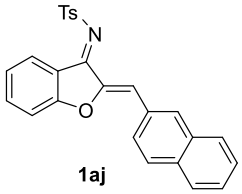
1ab, R = CN
1ac, R = CF_3
1ad, R = Me



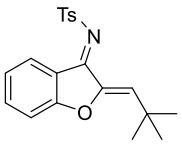
1ae, R = Me
1af, R = OMe



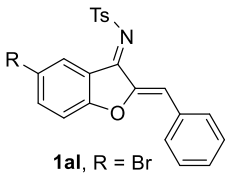
1ag, R = F
1ah, R = Cl
1ai, R = Br



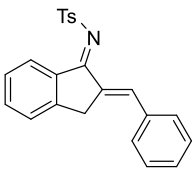
1aj



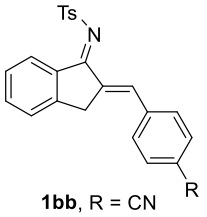
1ak



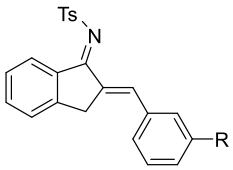
1al, R = Br
1am, R = Me
1an, R = OMe



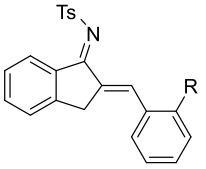
1ba



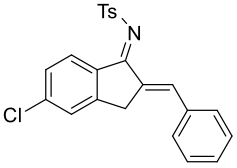
1bb, R = CN
1bc, R = OMe



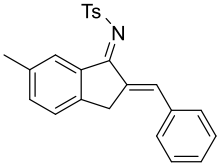
1bd, R = Cl
1be, R = OMe



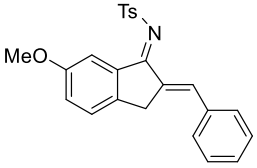
1bf, R = Cl
1bg, R = Me
1bh, R = OMe



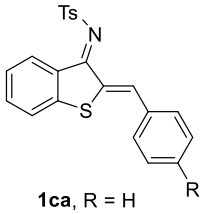
1bi



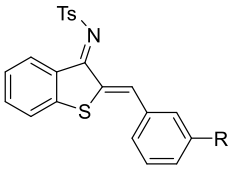
1bj



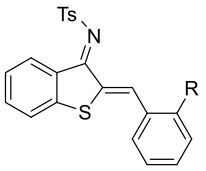
1bk



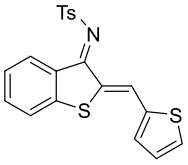
1ca, R = H
1cb, R = Br
1cc, R = Me



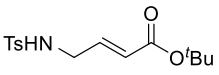
1cd, R = Br
1ce, R = Me



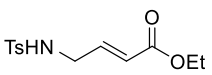
1cf, R = Br
1cg, R = Me



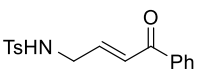
1ch



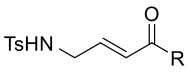
2a



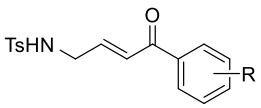
2b



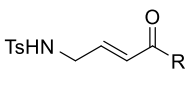
2c



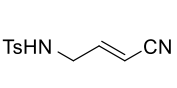
2d, R = OBn
2e, R = $OCHPh_2$



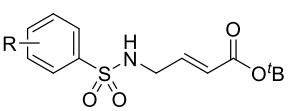
2f, R = 4-Cl
2g, R = 3-OMe
2h, R = 2-OMe



2i, R = Me
2j, R = Cyclopropyl

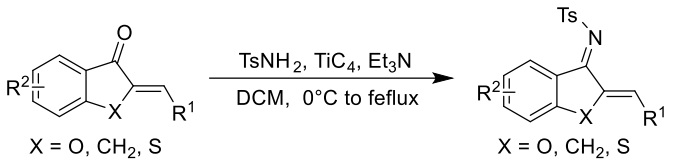


2k

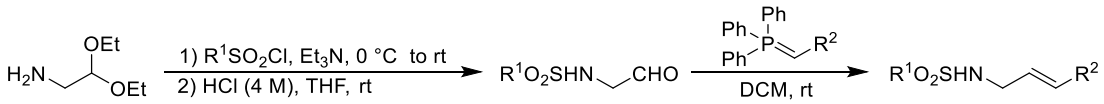


2l, R = H
2m, R = 4-NO_2

III. General Procedure for the Preparation of 1 and 2



To a solution of unsaturated ketones in DCM (0.1 M) were successively added triethylamine (2.0 equiv.) and benzenesulfonamides (1.1 equiv.) at 0 °C under argon. Titanium tetrachloride (1.0 M in DCM, 1.0 equiv.) was then added and the reaction mixture was heated under reflux overnight. The solution was then cooled to room temperature, quenched with water and extracted with DCM. Combined organic layers were dried over Na_2SO_4, filtered and concentrated to afford the crude product. Purification by silica gel column chromatography or recrystallization from ethanol afforded the desired products **1**.



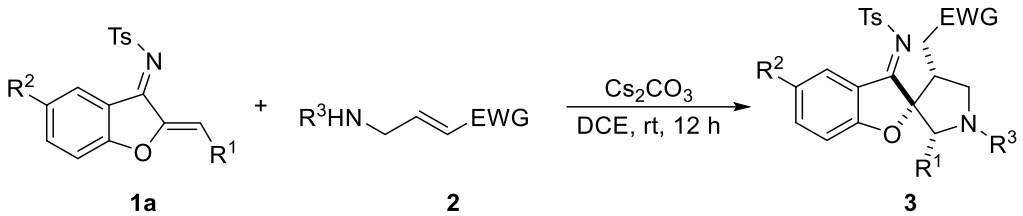
To a stirred solution of aminoacetaldehyde diethyl acetal (1.0 equiv.) and anhydrous Et_3N (1.2 equiv.) in CH_2Cl_2 (0.2 M) was added dropwise a solution of *p*-toluenesulfonyl chloride (1.1 equiv.) in CH_2Cl_2 over 30 min at 0 ^oC. After 5 h the reaction mixture was diluted with water. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The organic extracts were combined, washed with water and saturated $NaHCO_3$ (aq.), dried (Na_2SO_4), and concentrated under vacuum. Purification of the residue by silica gel column chromatography (petroleum ether/EtOAc 5:1) afforded the sulfonamides.

To a solution of the sulfonamides (10.0 mmol) in THF (10 mL) was added 4 M aq. HCl (6 mL) at room temperature. and the reaction mixture was stirred for 5 h at room temperature. Add excess sodium bicarbonate solid into the reaction, fully stir and filter. The filtrate was then diluted with DCM and washed with water. The organic portion was then dried (Na_2SO_4) and concentrated under vacuum to afford the

aldehydes which was used without further purification.

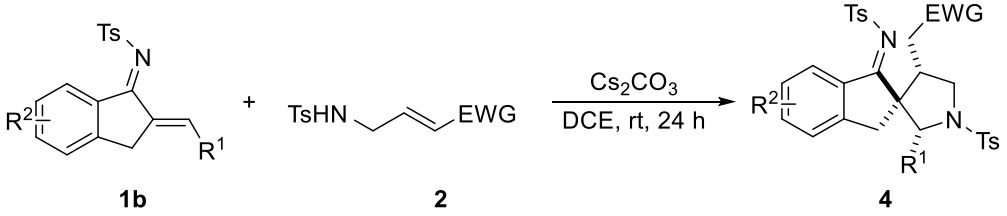
Wittig reagent (5.0 mmol, 1.0 equiv.) was added to a solution of the aldehydes (5.0 mmol, 1.0 equiv.) in CH_2Cl_2 (25 mL) in round bottom flask. The solution was stirred at room temperature for 24 h. After concentration reduced pressure, the residue was purified by flash chromatography (petroleum ether/EtOAc 3:1) to afford **2**.

IV. Representative Procedure of the Reaction



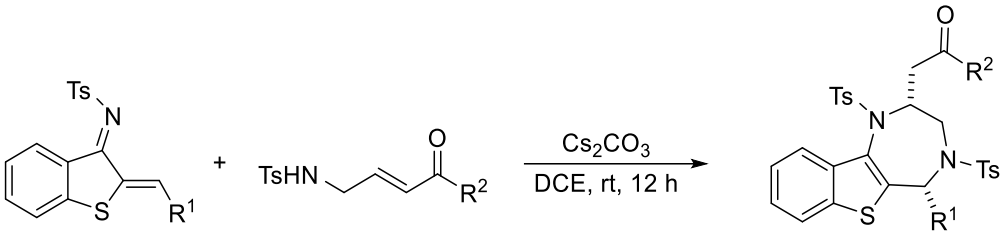
1a **2** **3**

To a stirred solution of benzofuran–derived azadienes **1a**[1] (0.12 mmol, 1.2 equiv) and unsaturated compounds **2**[4] (0.10 mmol, 1.0 equiv) in DCE (1 mL) was added Cs_2CO_3 (10 mol %) at room temperature for 12 h. The reaction mixture was stirred at room temperature until the completion of the reaction (monitored by TLC). The reaction mixture was then quenched with NH_4Cl (aq.), and extracted with DCM (10 mL × 3). The combined organic phase was dried over Na_2SO_4 and concentrated under vacuum, and the residue was purified by flash column chromatography on silica gel with PE/EA/DCM (5:1:1, v/v) to afford the compounds **3**.



1b **2** **4**

To a stirred solution of indanone–derived azadienes **1b**[2] (0.12 mmol, 1.2 equiv) and unsaturated compounds **2** (0.10 mmol, 1.0 equiv) in DCE (1 mL) was added Cs_2CO_3 (20 mol %) at room temperature for 24 h. The reaction mixture was stirred at room temperature until the completion of the reaction (monitored by TLC). The reaction mixture was then quenched with NH_4Cl (aq.), and extracted with DCM (10 mL × 3). The combined organic phase was dried over Na_2SO_4 and concentrated under vacuum, and the residue was purified by flash column chromatography on silica gel with PE/EA/DCM (5:1:1, v/v) to afford the compounds **4**.

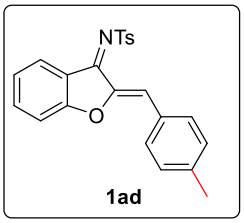


1c **2** **5**

To a stirred solution of benzothiophene–derived azadienes **1c**[3] (0.10 mmol, 1.0 equiv) and unsaturated compounds **2** (0.12 mmol, 1.2 equiv) in DCE (1 mL) was added Cs_2CO_3 (10 mol %) at room temperature for 12 h. The reaction mixture was stirred at room temperature until the completion of the reaction (monitored by TLC). The reaction mixture was then quenched with NH_4Cl (aq.), and extracted with DCM (10 mL × 3). The combined organic phase was dried over Na_2SO_4 and concentrated under vacuum, and the residue was purified by flash column chromatography on silica gel with PE/EA/DCM (5:1:1, v/v) to afford the compounds **5**.

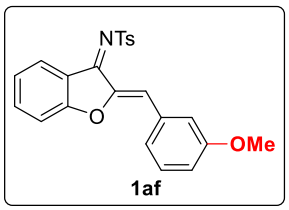
V. Analytical Data

4-methyl-N-((Z)-2-((Z)-4-methylbenzylidene)benzofuran-3(2H)-ylidene)benzenesulfonamide (1ad)[1a]



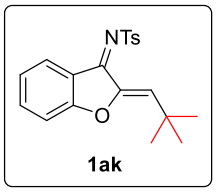
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 7.6 Hz, 2H), 7.69 – 7.64 (m, 1H), 7.37 (d, J = 8.0 Hz, 2H), 7.33 – 7.29 (m, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.11 (s, 1H), 2.47 (s, 3H), 2.39 (s, 3H).

N-((Z)-2-((Z)-3-methoxybenzylidene)benzofuran-3(2H)-ylidene)-4-methylbenzenesulfonamide (1af)[1d]



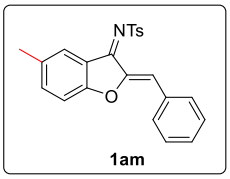
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.4 Hz, 2H), 7.70 – 7.65 (m, 1H), 7.47 – 7.44 (m, 2H), 7.39 – 7.28 (m, 5H), 7.06 (s, 1H), 6.96 – 6.93 (m, 1H), 3.84 (s, 3H), 2.47 (s, 3H).

N-((2Z,3Z)-2-(2,2-dimethylpropylidene)benzofuran-3(2H)-ylidene)-4-methylbenzenesulfonamide (1ak)[1a]



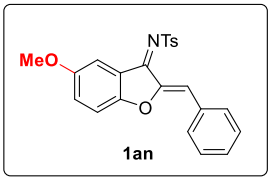
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, J = 8.0 Hz, 1H), 7.96 (d, J = 8.4 Hz, 2H), 7.66 – 7.62 (m, 1H), 7.36 (d, J = 8.4 Hz, 2H), 7.24 – 7.19 (m, 2H), 6.36 (s, 1H), 2.46 (s, 3H), 1.28 (s, 9H).

N-((Z)-2-((Z)-benzylidene)-5-methylbenzofuran-3(2H)-ylidene)-4-methylbenzenesulfonamide (1am)[1d]



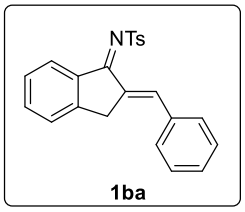
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.01 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 8.4 Hz, 2H), 7.50 – 7.37 (m, 6H), 7.21 (d, J = 8.4 Hz, 1H), 7.08 (s, 1H), 2.47 (s, 3H), 2.45 (s, 3H).

N-((Z)-2-((Z)-benzylidene)-5-methoxybenzofuran-3(2H)-ylidene)-4-methylbenzenesulfonamide (1an)[1d]



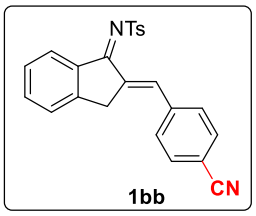
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 2.8 Hz, 1H), 8.00 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 6.8 Hz, 2H), 7.47 – 7.25 (m, 7H), 7.10 (s, 1H), 3.90 (s, 3H), 2.47 (s, 3H).

N-((E)-2-((E)-benzylidene)-2,3-dihydro-1H-inden-1-ylidene)-4-methylbenzenesulfonamide (1ba)[2b]



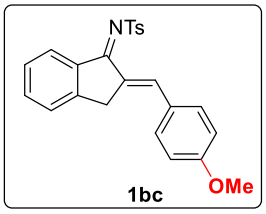
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, J = 7.6 Hz, 1H), 8.03 (d, J = 8.4 Hz, 2H), 7.82 (s, 1H), 7.63 – 7.36 (m, 10H), 4.03 (s, 2H), 2.47 (s, 3H).

N-((E)-2-((E)-4-cyanobenzylidene)-2,3-dihydro-1H-inden-1-ylidene)-4-methylbenzenesulfonamide (1bb)[2e]



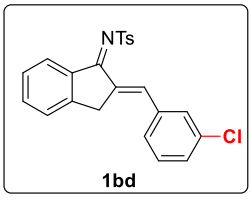
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, J = 8.0 Hz, 1H), 7.99 (d, J = 8.4 Hz, 2H), 7.72 – 7.61 (m, 6H), 7.52 – 7.46 (m, 2H), 7.37 (d, J = 8.0 Hz, 2H), 4.02 (s, 2H), 2.47 (s, 3H).

N-((E)-2-((E)-4-methoxybenzylidene)-2,3-dihydro-1H-inden-1-ylidene)-4-methylbenzenesulfonamide (1bc)[2a]



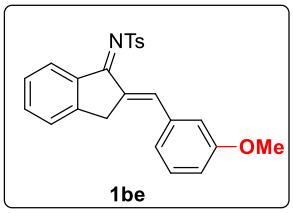
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 8.4 Hz, 2H), 7.80 (s, 1H), 7.61 – 7.54 (m, 3H), 7.51 – 7.43 (m, 2H), 7.36 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 3.98 (s, 2H), 3.84 (s, 3H), 2.46 (s, 3H).

N-((E)-2-((E)-3-chlorobenzylidene)-2,3-dihydro-1H-inden-1-ylidene)-4-methylbenzenesulfonamide (1bd)[2b]



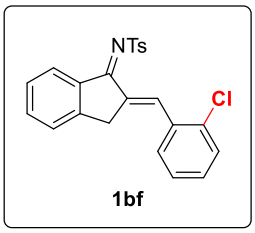
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.0 Hz, 2H), 7.70 (s, 1H), 7.64 – 7.61 (m, 1H), 7.54 – 7.44 (m, 4H), 7.39 – 7.34 (m, 4H), 4.01 (s, 2H), 2.47 (s, 3H).

N-((E)-2-((E)-3-methoxybenzylidene)-2,3-dihydro-1H-inden-1-ylidene)-4-methylbenzenesulfonamide (1be)[2a]



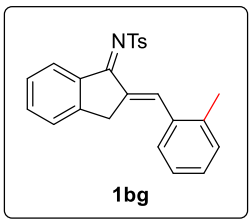
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 8.0 Hz, 2H), 7.77 (s, 1H), 7.62 – 7.59 (m, 1H), 7.52 – 7.44 (m, 2H), 7.38 – 7.31 (m, 3H), 7.18 (d, J = 7.6 Hz, 1H), 7.09 (s, 1H), 6.92 (dd, J = 8.4, 2.4 Hz, 1H), 4.01 (s, 2H), 3.83 (s, 3H), 2.47 (s, 3H).

N-((E)-2-((E)-2-chlorobenzylidene)-2,3-dihydro-1H-inden-1-ylidene)-4-methylbenzenesulfonamide (1bf)[2c]



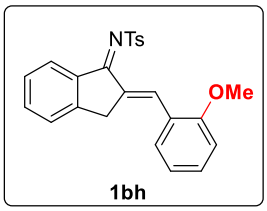
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.19 (s, 1H), 8.03 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 8.0 Hz, 1H), 7.63 – 7.60 (m, 2H), 7.50 – 7.44 (m, 3H), 7.37 – 7.29 (m, 3H), 3.96 (s, 2H), 2.46 (s, 3H).

4-Methyl-N-((E)-2-((E)-2-methylbenzylidene)-2,3-dihydro-1H-inden-1-ylidene)benzenesulfonamide (1bg)[2b]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.20 (s, 1H), 8.03 (d, J = 8.4 Hz, 2H), 7.62 – 7.44 (m, 4H), 7.35 (d, J = 8.4 Hz, 2H), 7.28 – 7.23 (m, 3H), 3.95 (s, 2H), 2.46 (s, 3H), 2.38 (s, 3H).

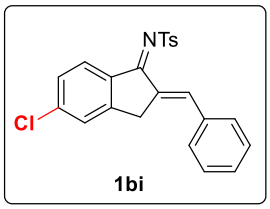
N-((E)-2-((E)-2-methoxybenzylidene)-2,3-dihydro-1H-inden-1-ylidene)-4-methylbenzenesulfonamide (1bh)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.20 (s, 1H), 8.03 (d, J = 8.4 Hz, 2H), 7.62 – 7.44 (m, 4H), 7.35 (d, J = 8.4 Hz, 2H), 7.28 – 7.23 (m, 3H), 3.95 (s, 2H), 2.46 (s, 3H), 2.38 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 175.8, 158.8, 150.5, 142.6, 140.2, 134.8, 131.3, 129.8, 129.6, 129.2, 127.7, 126.7, 126.4, 125.5, 124.5,

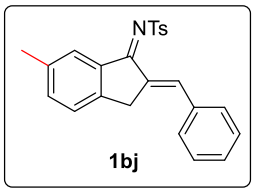
120.5, 111.0, 55.6, 34.1, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{24}H_{22}NO_3S^+$ $(M + H)^+$ 404.1315, found 404.1324.

N-((E)-2-((E)-benzylidene)-5-chloro-2,3-dihydro-1H-inden-1-ylidene)-4-methylbenzenesulfonamide (1bi)[2b]



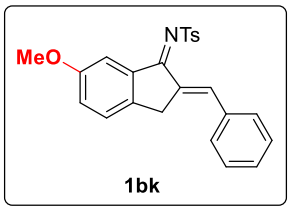
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, J = 8.8 Hz, 1H), 8.01 (d, J = 8.4 Hz, 2H), 7.80 (s, 1H), 7.56 (d, J = 8.0 Hz, 2H), 7.50 (s, 1H), 7.45 – 7.36 (m, 6H), 4.01 (s, 2H), 2.47 (s, 3H).

N-((E)-2-((E)-benzylidene)-6-methyl-2,3-dihydro-1H-inden-1-ylidene)-4-methylbenzenesulfonamide (1bj)[2b]



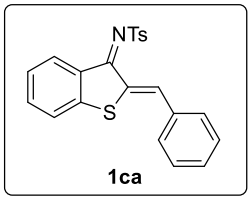
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.03 (d, J = 8.4 Hz, 2H), 7.81 (s, 1H), 7.58 (d, J = 8.4 Hz, 2H), 7.43 – 7.36 (m, 7H), 3.97 (s, 2H), 2.47 (s, 3H), 2.46 (s, 3H).

N-((E)-2-((E)-benzylidene)-6-methoxy-2,3-dihydro-1H-inden-1-ylidene)-4-methylbenzenesulfonamide (1bk)[2d]



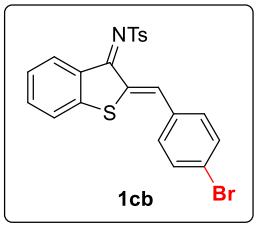
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.03 (d, J = 8.0 Hz, 2H), 7.80 (s, 1H), 7.58 (d, J = 8.0 Hz, 2H), 7.44 – 7.36 (m, 6H), 7.21 (dd, J = 8.4, 2.4 Hz, 1H), 3.96 (s, 2H), 3.91 (s, 3H), 2.47 (s, 3H).

N-((Z)-2-((Z)-benzylidene)benzo[b]thiophen-3(2H)-ylidene)-4-methylbenzenesulfonamide (1ca)[3a]



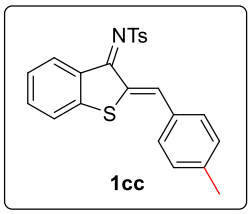
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (d, J = 8.0 Hz, 1H), 8.16 (s, 1H), 8.02 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 7.6 Hz, 2H), 7.58 – 7.54 (m, 1H), 7.48 – 7.32 (m, 7H), 2.47 (s, 3H).

N-((Z)-2-((Z)-4-bromobenzylidene)benzo[b]thiophen-3(2H)-ylidene)-4-methylbenzenesulfonamide (1cb)[3a]



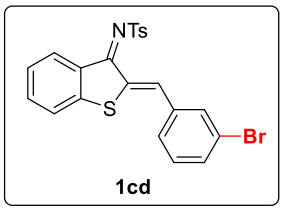
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, J = 8.4 Hz, 1H), 8.03 – 7.99 (m, 3H), 7.58 – 7.54 (m, 3H), 7.48 – 7.45 (m, 3H), 7.39 – 7.33 (m, 3H), 2.47 (s, 3H).

4-methyl-N-((Z)-2-((Z)-4-methylbenzylidene)benzo[b]thiophen-3(2H)-ylidene)benzenesulfonamide (1cc)[3a]



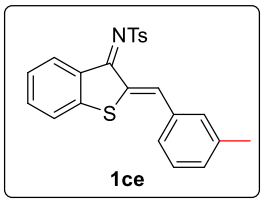
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, J = 8.0 Hz, 1H), 8.16 (s, 1H), 8.01 (d, J = 8.4 Hz, 2H), 7.57 – 7.54 (m, 3H), 7.47 (d, J = 8.0 Hz, 1H), 7.38 – 7.32 (m, 3H), 7.25 (d, J = 8.0 Hz, 2H), 2.47 (s, 3H), 2.39 (s, 3H).

N-((Z)-2-((Z)-3-bromobenzylidene)benzo[b]thiophen-3(2H)-ylidene)-4-methylbenzenesulfonamide (1cd)[3a]



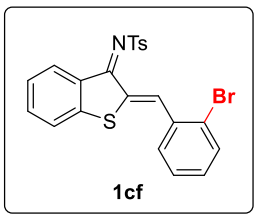
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 8.4 Hz, 3H), 7.73 (s, 1H), 7.59 – 7.55 (m, 2H), 7.51 – 7.46 (m, 2H), 7.40 – 7.28 (m, 4H), 2.48 (s, 3H).

4-methyl-N-((Z)-2-((Z)-3-methylbenzylidene)benzo[b]thiophen-3(2H)-ylidene)benzenesulfonamide (1ce)[3a]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, J = 8.0 Hz, 1H), 8.15 (s, 1H), 8.02 (d, J = 8.4 Hz, 2H), 7.58 – 7.54 (m, 1H), 7.48 – 7.44 (m, 3H), 7.39 – 7.32 (m, 4H), 7.22 (d, J = 7.6 Hz, 1H), 2.48 (s, 3H), 2.39 (s, 3H).

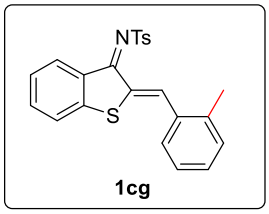
N-((Z)-2-((Z)-2-bromobenzylidene)benzo[b]thiophen-3(2H)-ylidene)-4-methylbenzenesulfonamide (1cf)



1cf

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, J = 8.4 Hz, 1H), 8.48 (s, 1H), 8.05 (d, J = 8.4 Hz, 2H), 7.74 (dd, J = 8.0, 1.6 Hz, 1H), 7.64 (dd, J = 8.0, 1.2 Hz, 1H), 7.58 – 7.54 (m, 1H), 7.45 – 7.33 (m, 5H), 7.25 – 7.20 (m, 1H), 2.46 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 169.8, 147.3, 143.1, 139.9, 135.5, 135.0, 134.5, 134.2, 133.5, 132.3, 131.2, 130.3, 129.3, 128.4, 127.7, 126.9, 126.6, 125.9, 123.4, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{22}H_{17}BrNO_2S_2^+$ $(M + H)^+$ 469.9879, found 469.9888.

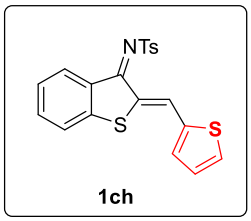
4-methyl-N-((Z)-2-((Z)-2-methylbenzylidene)benzo[b]thiophen-3(2H)-ylidene)benzenesulfonamide (1cg)[3b]



1cg

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, J = 8.0 Hz, 1H), 8.59 (s, 1H), 8.02 (d, J = 8.4 Hz, 2H), 7.73 – 7.70 (m, 1H), 7.57 – 7.53 (m, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.37 – 7.30 (m, 5H), 7.26 – 7.24 (m, 1H), 2.46 (s, 3H), 2.40 (s, 3H).

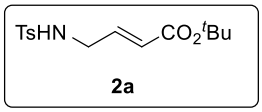
4-methyl-N-((2Z,3Z)-2-(thiophen-2-ylmethylene)benzo[b]thiophen-3(2H)-ylidene)benzenesulfonamide (1ch)[3b]



1ch

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, J = 8.4 Hz, 1H), 8.38 (s, 1H), 8.01 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 5.2 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.49 – 7.45 (m, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.35 – 7.30 (m, 1H), 7.15 (dd, J = 5.2, 3.6 Hz, 1H), 2.47 (s, 3H).

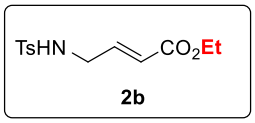
tert-Butyl (E)-4-((4-methylphenyl)sulfonamido)but-2-enoate (2a)[4a]



2a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 6.63 (dt, J = 15.6, 5.2 Hz, 1H), 5.84 (dt, J = 15.6, 2.0 Hz, 1H), 4.73 (t, J = 6.4 Hz, 1H), 3.74 – 3.71 (m, 2H), 2.42 (s, 3H), 1.44 (s, 9H).

Ethyl (E)-4-((4-methylphenyl)sulfonamido)but-2-enoate (2b)[4a]

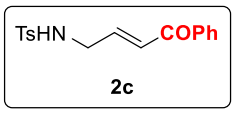


2b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 6.74 (dt, J = 15.6, 5.2 Hz, 1H), 5.91 (dt, J =

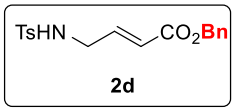
16.0, 1.6 Hz, 1H), 5.24 (t, *J* = 6.4 Hz, 1H), 4.16 – 4.11(m, 2H), 3.73 – 3.70 (m, 2H), 2.41 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H).

(E)-4-Methyl-N-(4-oxo-4-phenylbut-2-en-1-yl)benzenesulfonamide (2c)[4b]



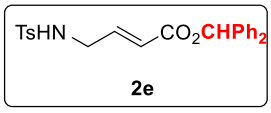
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.76 (m, 4H), 7.55 – 7.51 (m, 1H), 7.43 – 7.39 (m, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.01 (dt, *J* = 15.6, 1.6 Hz, 1H), 6.82 (dt, *J* = 15.6, 4.8 Hz, 1H), 5.54 (t, *J* = 6.4 Hz, 1H), 3.87 – 3.84 (m, 2H), 2.35 (s, 3H).

Benzyl (E)-4-((4-methylphenyl)sulfonamido)but-2-enoate (2d)[4c]



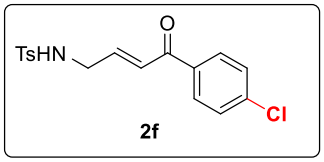
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.36 – 7.34 (m, 5H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.80 (dt, *J* = 15.6, 5.2 Hz, 1H), 5.98 (d, *J* = 15.6 Hz, 1H), 5.14 (s, 2H), 4.95 (t, *J* = 6.4 Hz, 1H), 3.74 (t, *J* = 6.4 Hz, 2H), 2.40 (s, 3H).

Benzhydryl (E)-4-((4-methylphenyl)sulfonamido)but-2-enoate (2e)[4c]



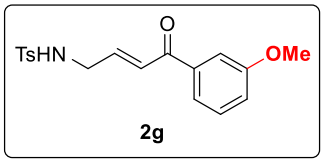
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.28 (m, 12H), 6.89 (s, 1H), 6.82 (dt, *J* = 16.0, 5.2 Hz, 1H), 6.03 (dt, *J* = 16.0, 1.6 Hz, 1H), 5.01 (t, *J* = 6.4 Hz, 1H), 3.76 – 3.73 (m, 2H), 2.37 (s, 3H).

(E)-N-(4-(4-chlorophenyl)-4-oxobut-2-en-1-yl)-4-methylbenzenesulfonamide (2f)[4d]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 4H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.00 (dt, *J* = 15.6, 2.0 Hz, 1H), 6.85 (dt, *J* = 15.6, 4.8 Hz, 1H), 5.59 (t, *J* = 6.4 Hz, 1H), 3.87 – 3.4 (m, 2H), 2.37 (s, 3H).

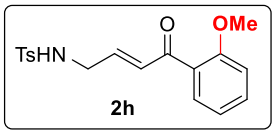
(E)-N-(4-(3-methoxyphenyl)-4-oxobut-2-en-1-yl)-4-methylbenzenesulfonamide (2g)[4b]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.37 (m, 2H), 7.32 – 7.26 (m, 3H), 7.09 – 7.06 (m, 1H), 6.97 (dt, *J* = 15.4, 1.6 Hz, 1H), 6.81 (dt, *J* = 15.4, 4.8

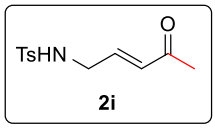
Hz, 1H), 5.49 (t, *J* = 6.4 Hz, 1H), 3.87 – 3.83 (m, 2H),3.82 (s, 3H). 2.36 (s, 3H).

(E)-N-(4-(2-methoxyphenyl)-4-oxobut-2-en-1-yl)-4-methylbenzenesulfonamide (2h)[4b]



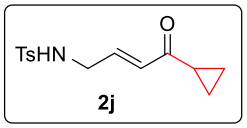
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.47 – 7.41 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.97 – 6.91 (m, 2H), 6.84 (dt, *J* = 15.6, 2.0 Hz, 1H), 6.63 (dt, *J* = 15.6, 5.2 Hz, 1H), 5.32 (t, *J* = 6.4 Hz, 1H), 3.82 (s, 3H), 3.79 – 3.76 (m, 2H), 2.36 (s, 3H).

(E)-4-methyl-N-(4-oxopent-2-en-1-yl)benzenesulfonamide (2i)[4b]



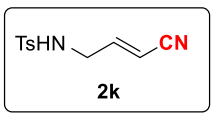
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.58 (dt, *J* = 16.0, 5.2 Hz, 1H), 6.12 (dt, *J* = 16.0, 2.0 Hz, 1H), 5.40 (t, *J* = 6.4 Hz, 1H), 3.76 - 3.72 (m, 2H), 2.41 (s, 3H), 2.15 (s, 3H).

(E)-N-(4-cyclopropyl-4-oxobut-2-en-1-yl)-4-methylbenzenesulfonamide (2j)



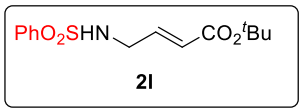
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.65 (dt, *J* = 15.6, 5.2 Hz, 1H), 6.29 (dt, *J* = 15.6, 1.6 Hz, 1H), 5.42 (t, *J* = 6.4 Hz, 1H), 3.76 – 3.73 (m, 2H), 2.40 (s, 3H), 2.03 – 1.97 (m, 2H), 1.03 – 1.00 (m, 2H), 0.91 – 0.86 (m, 2H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 199.8, 143.7, 139.9, 136.7, 130.6, 129.8, 127.1, 44.0, 21.5, 19.2, 11.4, 11.4. **HRMS (ESI)** m/z: calcd. for $C_{14}H_{17}NO_3SNa^+$ $(M + Na)^+$ 302.0821, found 302.0829.

(E)-N-(3-cyanoallyl)-4-methylbenzenesulfonamide (2k)[4a]



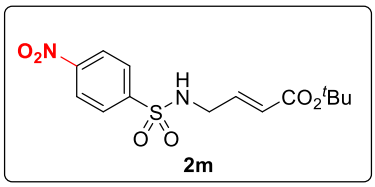
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.54 (dt, *J* = 16.4, 4.8 Hz, 1H), 5.53 (dt, *J* = 16.4, 2.0 Hz, 1H), 3.71 (dd, *J* = 4.8, 2.0 Hz, 2H), 2.43 (s, 3H).

tert-Butyl (E)-4-(phenylsulfonamido)but-2-enoate (2l)



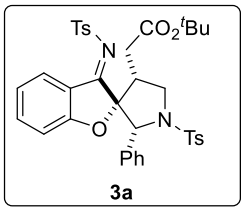
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.4 Hz, 2H), 7.56 – 7.49 (m, 3H), 6.60 (dt, J = 15.6, 5.2 Hz, 1H), 5.82 (dt, J = 15.6, 2.0 Hz, 1H), 5.39 (t, J = 6.4 Hz, 1H), 3.72 – 3.69 (m, 2H), 1.41 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.0, 141.0, 139.7, 132.8, 129.1, 127.0, 124.6, 80.7, 43.7, 27.9. **HRMS (ESI)** m/z: calcd. for $C_{14}H_{19}NO_4SNa^+$ $(M + Na)^+$ 320.0927, found 320.0935.

tert-butyl (E)-4-((4-nitrophenyl)sulfonamido)but-2-enoate (2m)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 8.4 Hz, 2H), 8.05 (d, J = 8.0 Hz, 2H), 6.61 (dt, J = 15.6, 5.2 Hz, 1H), 5.82 (d, J = 15.6 Hz, 1H), 5.48 (t, J = 6.0 Hz, 1H), 3.81 (t, J = 4.8 Hz, 2H), 1.42 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 164.9, 150.1, 145.8, 140.4, 128.3, 125.1, 124.5, 81.2, 43.8, 28.0. **HRMS (ESI)** m/z: calcd. for $C_{14}H_{18}N_2O_6SNa^+$ $(M + Na)^+$ 365.0778, found 365.0786.

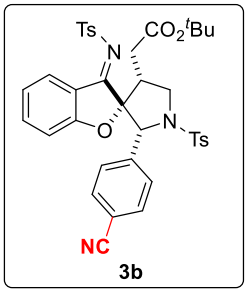
tert-Butyl (E)-2-(2'-phenyl-1'-tosyl-3-(tosylimino)-3H-spiro[benzofuran-2,3'-pyrrolidin]-4'-yl)acetate (3a)



According to the general procedure as described above, the reaction was carried out by using **1aa** (45.0 mg, 0.12 mmol), **2a** (31.1 mg, 0.1 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 81% total yield (55.9 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **3a** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 217.1 – 217.7 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.46 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.0 Hz, 1H), 7.46 – 7.41 (m, 3H), 7.15 – 7.08 (m, 5H), 7.04 – 6.98 (m, 3H), 6.71 (d, J = 8.8 Hz, 1H), 4.96 (s, 1H), 4.28 – 4.23 (m, 1H), 3.63 (t, J = 11.6 Hz, 1H), 2.56 (s, 3H), 2.35 (s,

4H), 2.15 – 2.08 (m, 1H), 2.00 – 1.94 (m, 1H), 1.33 (s, 9H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 177.1, 169.7, 169.5, 143.7, 143.6, 139.4, 138.4, 134.0, 133.7, 130.5, 129.59, 129.57, 128.0, 127.70, 127.66, 127.14, 127.07, 122.6, 118.1, 112.0, 98.6, 81.2, 74.7, 53.4, 44.2, 31.6, 27.9, 21.7, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{37}H_{38}N_2O_7S_2Na^+$ $(M + Na)^+$ 709.2013, found 709.2022.

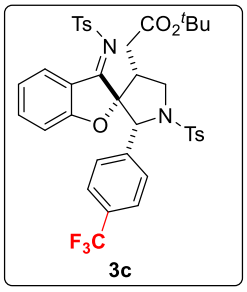
tert-Butyl (E)-2-(2'-(4-cyanophenyl)-1'-tosyl-3-(tosylimino)-3H-spiro[benzofuran-2,3'-pyrrolidin]-4'-yl)acetate (3b)



3b

According to the general procedure as described above, the reaction was carried out by using **1ab** (48.0 mg, 0.12 mmol), **2a** (31.1 mg, 0.1 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 77% total yield (55.1 mg) with 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **3b** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 196.5 – 197.2 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.47 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.50 – 7.40 (m, 5H), 7.29 (d, J = 7.6 Hz, 2H), 7.07 – 7.03 (m, 3H), 6.70 (d, J = 8.4 Hz, 1H), 4.98 (s, 1H), 4.26 – 4.21 (m, 1H), 3.62 (t, J = 11.6 Hz, 1H), 2.55 (s, 3H), 2.35 (s, 3H), 2.31 – 2.27 (m, 1H), 2.13 – 2.06 (m, 1H), 1.99 – 1.93 (m, 1H), 1.32 (s, 9H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 176.2, 169.2, 144.1, 143.9, 139.9, 139.8, 138.1, 133.2, 131.7, 130.7, 129.8, 129.6, 127.8, 127.6, 127.1, 123.1, 118.5, 117.9, 112.0, 111.8, 98.3, 81.4, 74.1, 53.5, 44.3, 31.3, 27.9, 21.7, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{38}H_{38}N_3O_7S_2^+$ $(M + H)^+$ 712.2146, found 712.2151.

tert-Butyl (E)-2-(1'-tosyl-3-(tosylimino)-2'-(4-(trifluoromethyl)phenyl)-3H-spiro[benzofuran-2,3'-pyrrolidin]-4'-yl)acetate (3c)

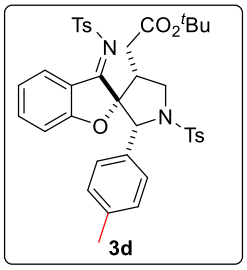


3c

According to the general procedure as described above, the reaction was carried out by using **1ac** (53.2 mg, 0.12 mmol), **2a** (31.1 mg, 0.1 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 88% total

yield (66.7 mg) with 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **3c** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 183.1 – 183.5 ^{o}C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.47 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.48 – 7.43 (m, 3H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.06 – 7.00 (m, 3H), 6.71 (d, *J* = 8.4 Hz, 1H), 5.00 (s, 1H), 4.29 – 4.24 (m, 1H), 3.64 (t, *J* = 12.0 Hz, 1H), 2.56 (s, 3H), 2.34 (s, 4H), 2.14 – 2.07 (m, 1H), 1.99 – 1.94 (m, 1H), 1.33 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 176.5, 169.3, 169.3, 143.9 (d, *J* = 4 Hz), 139.71, 138.3, 138.2, 133.4, 130.6, 130.1 (d, *J* = 4 Hz), 129.7, 129.6, 127.6, 127.1, 124.7 (q, *J* = 4 Hz), 123.8 (d, *J* = 270 Hz), 123.0, 117.9, 112.0, 98.4, 81.4, 74.1, 53.4, 44.3, 31.4, 27.9, 21.7, 21.5. **^{19}F NMR (376 MHz, $CDCl_3$)** δ –62.7. **HRMS (ESI)** m/z: calcd. for $C_{38}H_{37}F_3N_2O_7S_2Na^+$ $(M + Na)^+$ 777.1886, found 777.1891.

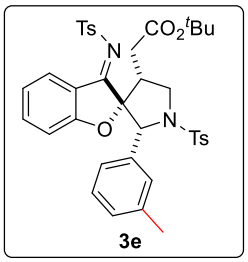
tert-Butyl (E)-2-(2'-(p-tolyl)-1'-tosyl-3-(tosylimino)-3H-spiro[benzofuran-2,3'-pyrrolidin]-4'-yl)acetate (3d)



According to the general procedure as described above, the reaction was carried out by using **1ad** (46.7 mg, 0.12 mmol), **2a** (31.1 mg, 0.1 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 84% total yield (58.8 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **3d** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 186.3 – 187.2 ^{o}C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.45 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.46 – 7.43 (m, 3H), 7.04 – 6.98 (m, 5H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.75 (d, *J* = 8.4 Hz, 1H), 4.90 (s, 1H), 4.26 – 4.21 (m, 1H), 3.62 (t, *J* = 12.0 Hz, 1H), 2.56 (s, 3H), 2.35 (s, 3H), 2.32 – 2.28 (m, 1H), 2.18 (s, 3H), 2.14 – 2.07 (m, 1H), 1.99 – 1.93 (m, 1H), 1.33 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 177.1, 169.7, 169.5, 143.7, 143.5, 139.4, 138.4, 137.6, 133.7, 130.9, 130.5, 129.5, 128.4, 127.7, 127.11, 127.06, 122.6, 118.0, 112.1, 98.6, 81.2, 74.5, 53.4, 44.2, 31.6, 27.9, 21.7, 21.5,

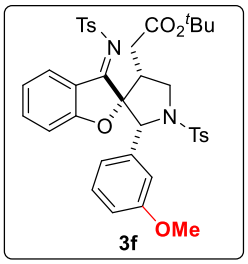
21.1. **HRMS (ESI)** m/z: calcd. for $C_{38}H_{41}N_2O_7S_2^+$ $(M + H)^+$ 701.2350, found 701.2357.

tert-Butyl (E)-2-(2'-(m-tolyl)-1'-tosyl-3-(tosylimino)-3H-spiro[benzofuran-2,3'-pyrrolidin]-4'-yl)acetate (3e)



According to the general procedure as described above, the reaction was carried out by using **1ae** (46.7 mg, 0.12 mmol), **2a** (31.1 mg, 0.1 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 83% total yield (56.7 mg) with 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **3e** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 173.4 – 174.2 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.45 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.46 – 7.41 (m, 3H), 7.03 – 6.86 (m, 7H), 6.71 (d, J = 8.4 Hz, 1H), 4.93 (s, 1H), 4.29 – 4.24 (m, 1H), 3.62 (t, J = 12.0 Hz, 1H), 2.56 (s, 3H), 2.34 (s, 4H), 2.16 (s, 3H), 2.14 – 2.07 (s, 1H), 2.00 – 1.94 (m, 1H), 1.34 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 177.1, 169.7, 169.5, 143.7, 143.5, 139.3, 138.4, 137.1, 134.0, 133.7, 130.5, 129.6, 129.5, 128.7, 127.8, 127.7, 127.5, 127.1, 124.2, 122.5, 118.2, 112.0, 98.7, 81.2, 74.7, 53.4, 44.1, 31.6, 27.9, 21.7, 21.5, 21.3. **HRMS (ESI)** m/z: calcd. for $C_{38}H_{41}N_2O_7S_2^+$ $(M + H)^+$ 701.2350, found 701.2354.

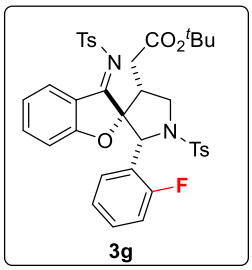
tert-Butyl (E)-2-(2'-(3-methoxyphenyl)-1'-tosyl-3-(tosylimino)-3H-spiro[benzofuran-2,3'-pyrrolidin]-4'-yl)acetate (3f)



According to the general procedure as described above, the reaction was carried out by using **1af** (48.6mg, 0.12 mmol), **2a** (31.1 mg, 0.1 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 91% total yield (64.8 mg) with 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **3f** was isolated as a white solid after flash

column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 187.2 – 187.9 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.47 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.46 – 7.42 (m, 3H), 7.03 – 7.00 (m, 4H), 6.67 – 6.61 (m, 4H), 4.98 (s, 1H), 4.28 – 4.23 (m, 1H), 3.65 – 3.59 (m, 4H), 2.55 (s, 3H), 2.33 (s, 4H), 2.13 – 2.07 (m, 1H), 1.99 – 1.94 (m, 1H), 1.33 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$)** δ 177.1, 169.7, 169.4, 158.9, 143.7, 143.6, 139.4, 138.4, 135.5, 133.9, 130.5, 129.6, 128.7, 127.7, 127.1, 122.6, 119.4, 118.2, 114.6, 112.1, 111.7, 98.7, 81.2, 74.7, 55.1, 53.4, 44.2, 31.5, 27.9, 21.7, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{38}H_{41}N_2O_8S_2^+$ $(M + H)^+$ 717.2299, found 717.2300.

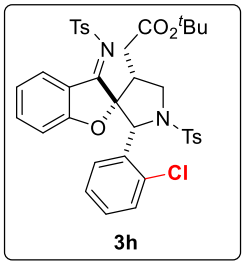
tert-Butyl (E)-2-(2'-(2-fluorophenyl)-1'-tosyl-3-(tosylimino)-3H-spiro[benzofuran-2,3'-pyrrolidin]-4'-yl)acetate (3g)



3g

According to the general procedure as described above, the reaction was carried out by using **1ag** (47.2 mg, 0.12 mmol), **2a** (31.1 mg, 0.1 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 90% total yield (63.6 mg) with 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **3g** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 212.2 – 212.6 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.49 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 7.6 Hz, 3H), 7.47 – 7.43 (m, 3H), 7.15 – 6.99 (m, 3H), 6.94 (d, J = 8.0 Hz, 2H), 6.81 – 6.73 (m, 2H), 5.33 (s, 1H), 4.25 – 4.20 (m, 1H), 3.63 (t, J = 12.0 Hz, 1H), 2.56 (s, 3H), 2.31 (s, 3H), 2.24 – 2.13 (m, 1H), 2.13 – 2.03 (m, 1H), 1.96 – 1.91 (m, 1H), 1.34 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$)** δ 176.3, 169.4, 169.1, 143.7, 143.5, 139.2, 138.5, 131.7 (d, J = 278 Hz), 130.8, 129.7, 129.6, 129.5, 127.7, 127.2, 123.6 (d, J = 3 Hz), 122.8, 122.0 (d, J = 13 Hz), 117.8, 114.7 (d, J = 21 Hz), 111.4, 98.1, 81.2, 67.2, 53.3, 44.9, 31.3, 27.9, 21.7, 21.5. **^{19}F NMR (376 MHz, CDCl$_3$)** δ –117.1. **HRMS (ESI)** m/z: calcd. for $C_{37}H_{38}FN_2O_7S_2^+$ $(M + H)^+$ 705.2099, found 705.2102.

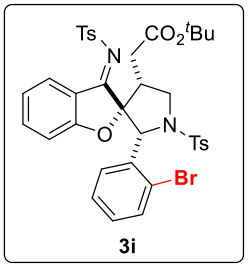
tert-Butyl (E)-2-(2'-(2-chlorophenyl)-1'-tosyl-3-(tosylimino)-3H-spiro[benzofuran-2,3'-pyrrolidin]-4'-yl)acetate (3h)



3h

According to the general procedure as described above, the reaction was carried out by using **1ah** (49.1 mg, 0.12 mmol), **2a** (31.1 mg, 0.1 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 97% total yield (69.8 mg) with 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **3h** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 194.8 – 195.2 °C.**^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.49 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 7.6 Hz, 1H), 7.45 – 7.42 (m, 3H), 7.22 – 7.18 (m, 1H), 7.07 – 6.98 (m, 5H), 6.71 (d, J = 8.4 Hz, 1H), 5.56 (s, 1H), 4.26 – 4.21 (m, 1H), 3.65 (t, J = 12.0 Hz, 1H), 2.55 (s, 3H), 2.32 (s, 3H), 2.30 – 2.25 (m, 1H), 2.14 – 2.07 (m, 1H), 1.99 – 1.93 (m, 1H), 1.34 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$)** δ 176.5, 169.4, 168.9, 143.7, 143.5, 139.2, 138.5, 133.5, 133.1, 132.4, 131.2, 130.8, 129.6, 129.5, 129.1, 128.8, 127.8, 127.2, 126.0, 122.8, 118.0, 111.9, 98.1, 81.2, 69.8, 53.2, 45.3, 31.3, 27.9, 21.7, 21.5. **HRMS (ESI)** m/z: calcd. For $C_{37}H_{37}ClN_2O_7S_2Na^+$ $(M + Na)^+$ 743.1623, found 743.1629.

tert-Butyl (E)-2-(2'-(2-bromophenyl)-1'-tosyl-3-(tosylimino)-3H-spiro[benzofuran-2,3'-pyrrolidin]-4'-yl)acetate (3i)

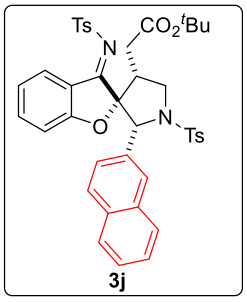


3i

According to the general procedure as described above, the reaction was carried out by using **1ai** (54.4 mg, 0.12 mmol), **2a** (31.1 mg, 0.1 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 92% total yield (70.3 mg) with 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **3i** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 217.1 – 217.8 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.49 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.0 Hz, 2H),

7.72 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 9.6 Hz, 1H), 7.45 – 7.41 (m, 3H), 7.25 – 7.21 (m, 2H), 7.04 – 6.96 (m, 4H), 6.69 (d, *J* = 8.4 Hz, 1H), 5.57 (s, 1H), 4.26 – 4.21 (m, 1H), 3.66 (t, *J* = 12.0 Hz, 1H), 2.54 (s, 3H), 2.33 (s, 4H), 2.15 – 2.08 (m, 1H), 1.99 – 1.94 (m, 1H), 1.34 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$)** δ 176.6, 169.4, 168.8, 143.6, 143.5, 139.1, 138.5, 134.9, 133.7, 132.1, 131.6, 130.8, 129.6, 129.4, 129.3, 127.8, 127.2, 126.5, 122.8, 122.6, 118.2, 111.9, 98.1, 81.2, 71.8, 53.1, 45.4, 31.3, 27.9, 21.7, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{37}H_{37}BrN_2O_7S_2Na^+$ $(M + Na)^+$ 787.1118, found 787.1128.

tert-Butyl (E)-2-(2'-(naphthalen-2-yl)-1'-tosyl-3-(tosylimino)-3H-spiro[benzofuran-2,3'-pyrrolidin]-4'-yl)acetate (3j)

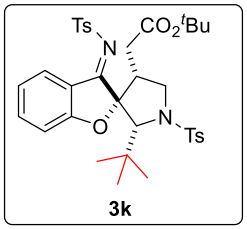


3j

According to the general procedure as described above, the reaction was carried out by using **1aj** (51.0 mg, 0.12 mmol), **2a** (31.1 mg, 0.1 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 74% total yield (54.2 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **3j** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 211.5 – 212.2 ^{o}C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.45 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.68 – 7.58 (m, 6H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.28 (m, 4H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.92 (t, *J* = 6.4 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 1H), 5.19 (s, 1H), 4.36 – 4.31 (m, 1H), 3.71 (t, *J* = 11.8 Hz, 1H), 2.57 (s, 3H), 2.43 – 2.41 (m, 1H), 2.33 (s, 3H), 2.17 – 2.11 (m, 1H), 2.02 – 1.97 (m, 1H), 1.35 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$)** δ 177.1, 169.6, 169.5, 143.8, 143.6, 139.4, 138.5, 134.0, 133.1, 132.6, 131.7, 130.6, 129.62, 129.56, 128.1, 127.7, 127.43, 127.36, 127.2, 126.5, 125.9, 125.7, 125.0, 122.6, 118.0, 112.0, 98.9, 81.3, 74.7, 53.5, 44.5, 31.6, 27.9, 21.7, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{41}H_{41}N_2O_7S_2^+$ $(M + H)^+$ 737.2350, found 737.2349.

tert-Butyl (E)-2-(2'-(tert-butyl)-1'-tosyl-3-(tosylimino)-3H-spiro[benzofuran-2,3'-

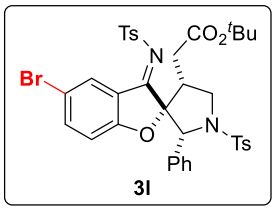
pyrrolidin]-4'-yl)acetate (3k)



3k

According to the general procedure as described above, the reaction was carried out by using **1ak** (42.6 mg, 0.12 mmol), **2a** (31.1 mg, 0.1 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 85% total yield (56.9 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **3k** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 214.3 – 215.1 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.63 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.69 – 7.62 (m, 3H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 2H), 4.30 (s, 1H), 4.03 – 3.98 (m, 1H), 3.27 (t, *J* = 12.0 Hz, 1H), 2.49 (s, 3H), 2.31 (s, 3H), 1.95 – 1.86 (m, 2H), 1.66 – 1.61 (m, 1H), 1.28 (s, 9H), 0.98 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 180.9, 169.6, 169.3, 144.0, 143.5, 139.4, 138.4, 135.2, 131.3, 129.6, 129.4, 128.5, 127.2, 122.9, 117.4, 112.3, 100.7, 80.9, 78.8, 54.4, 49.3, 37.4, 30.7, 28.1, 27.8, 21.6, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{35}H_{43}N_2O_7S_2^+$ $(M + H)^+$ 667.2507, found 667.2515.

tert-Butyl (E)-2-(5-bromo-2'-phenyl-1'-tosyl-3-(tosylimino)-3H-spiro[benzofuran-2,3'-pyrrolidin]-4'-yl)acetate (3l)

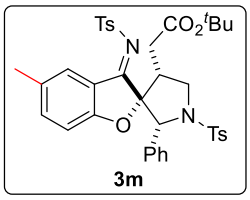


3l

According to the general procedure as described above, the reaction was carried out by using **1al** (54.4 mg, 0.12 mmol), **2a** (31.1 mg, 0.1 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 76% total yield (57.8 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **3l** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 216.3 – 216.9 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.60 (s, 1H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.51 – 7.45 (m, 3H), 7.12 – 7.03 (m, 7H), 6.62 (d, *J* = 8.8 Hz, 1H), 4.93 (s, 1H), 4.27 – 4.22 (m, 1H), 3.60 (t, *J* = 12.0 Hz, 1H), 2.56 (s, 3H), 2.35 (s, 4H), 2.13 – 2.06

(m, 1H), 1.99 – 1.94 (m, 1H), 1.33 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$)** δ 175.4, 169.3, 168.3, 144.0, 143.7, 142.0, 137.9, 133.8, 133.7, 132.6, 129.64, 129.60, 128.2, 127.8, 127.7, 127.2, 127.1, 115.0, 113.6, 99.4, 81.4, 74.8, 53.4, 44.4, 31.6, 27.9, 21.7, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{37}H_{38}BrN_2O_7S_2^+$ $(M + H)^+$ 765.1298, found 765.1293.

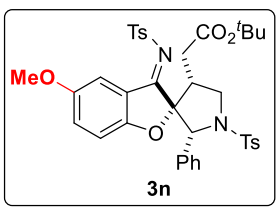
tert-Butyl (E)-2-(5-methyl-2'-phenyl-1'-tosyl-3-(tosylimino)-3H-spiro[benzofuran-2,3'-pyrrolidin]-4'-yl)acetate (3m)



3m

According to the general procedure as described above, the reaction was carried out by using **1am** (46.7 mg, 0.12 mmol), **2a** (31.1 mg, 0.1 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 87% total yield (60.9 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **3m** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 214.5 – 215.2 ^{o}C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.22 (s, 1H), 7.93 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 7.24 – 7.09 (m, 6H), 7.02 (d, J = 8.0 Hz, 2H), 6.61 (d, J = 8.4 Hz, 1H), 4.96 (s, 1H), 4.27 – 4.22 (m, 1H), 3.62 (t, J = 12.0 Hz, 1H), 2.55 (s, 3H), 2.34 (s, 3H), 2.27 (s, 4H), 2.12 – 2.05 (m, 1H), 1.97 – 1.92 (m, 1H), 1.34 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$)** δ 177.1, 169.5, 168.3, 143.6, 143.5, 141.1, 138.6, 134.1, 133.9, 132.3, 129.6, 129.5, 127.9, 127.69, 127.66, 127.1, 127.1, 118.0, 111.6, 98.8, 81.2, 74.6, 53.4, 44.4, 31.5, 27.9, 21.7, 21.5, 20.8. **HRMS (ESI)** m/z: calcd. for $C_{38}H_{41}N_2O_7S_2^+$ $(M + H)^+$ 701.2350, found 701.2340.

tert-Butyl (E)-2-(5-methoxy-2'-phenyl-1'-tosyl-3-(tosylimino)-3H-spiro[benzofuran-2,3'-pyrrolidin]-4'-yl)acetate (3n)

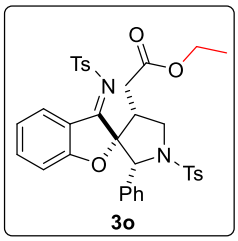


3n

According to the general procedure as described above, the reaction was carried out by using **1an** (48.6 mg, 0.12 mmol), **2a** (31.1 mg, 0.1 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving

the title compounds as a mixture of diastereoisomers in 77% total yield (55.3 mg) with 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **3n** was isolated as a pale yellow solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 229.8 – 230.5 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 (d, J = 8.4 Hz, 2H), 7.86 (d, J = 2.8 Hz, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.8 Hz, 2H), 7.14 – 7.01 (m, 8H), 6.63 (d, J = 8.8 Hz, 1H), 4.96 (s, 1H), 4.27 – 4.22 (m, 1H), 3.77 (s, 3H), 3.62 (t, J = 12.0 Hz, 1H), 2.55 (s, 3H), 2.34 (s, 4H), 2.13 – 2.06 (m, 1H), 1.98 – 1.93 (m, 1H), 1.34 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 177.2, 169.5, 165.5, 154.7, 143.7, 143.6, 138.5, 134.1, 133.8, 130.4, 129.6, 129.5, 128.0, 127.7, 127.6, 127.1, 127.0, 118.0, 112.8, 109.4, 99.2, 81.2, 74.7, 55.8, 53.4, 44.3, 31.5, 27.9, 21.7, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{38}H_{41}N_2O_8S_2^+$ $(M + H)^+$ 717.2299, found 717.2302.

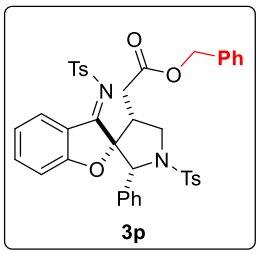
Ethyl (E)-2-(2'-phenyl-1'-tosyl-3-(tosylimino)-3H-spiro[benzofuran-2,3'-pyrrolidin]-4'-yl)acetate (3o)



3o

According to the general procedure as described above, the reaction was carried out by using **1aa** (45.0 mg, 0.12 mmol), **2b** (28.3 mg, 0.1 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 74% total yield (48.7 mg) with 10:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **3o** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 191.6 – 191.9 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.46 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.46 – 7.41 (m, 3H), 7.15 – 7.11 (m, 8H), 6.71 (d, J = 8.4 Hz, 1H), 4.97 (s, 1H), 4.28 – 3.95 (m, 1H), 4.04 – 3.95 (m, 2H), 3.63 (t, J = 12.0 Hz, 1H), 2.56 (s, 3H), 2.34 (s, 4H), 2.22 – 2.16 (m, 1H), 2.10 – 2.04 (m, 1H), 1.09 (t, J = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 176.9, 170.3, 169.6, 143.8, 143.6, 139.4, 138.3, 133.9, 133.7, 130.4, 129.6, 128.0, 127.7, 127.6, 127.1, 127.0, 122.6, 118.1, 112.0, 98.4, 74.8, 60.9, 53.4, 44.1, 30.3, 21.7, 21.5, 13.9. **HRMS (ESI)** m/z: calcd. for $C_{35}H_{34}N_2O_7S_2Na^+$ $(M + Na)^+$ 681.1700, found 681.1719.

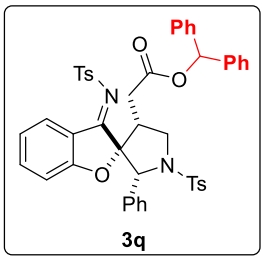
Benzyl (E)-2-(2'-phenyl-1'-tosyl-3-(tosylimino)-3H-spiro[benzofuran-2,3'-pyrrolidin]-4'-yl)acetate (3p)



3p

According to the general procedure as described above, the reaction was carried out by using **1aa** (45.0 mg, 0.12 mmol), **2d** (34.5 mg, 0.1 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 85% total yield (61.3 mg) with 15:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **3p** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 168.5 – 168.9 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.47 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), 7.50 – 7.40 (m, 3H), 7.36 – 7.32 (m, 3H), 7.08 – 7.22 (m, 7H), 6.99 – 6.95 (m, 3H), 6.71 (d, J = 8.4 Hz, 1H), 5.04 – 4.93 (m, 3H), 4.29 – 4.24 (m, 1H), 3.66 (t, J = 11.6 Hz, 1H), 2.59 (s, 3H), 2.36 (s, 4H), 2.28 – 2.22 (m, 1H), 2.15 – 2.10 (m, 1H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 176.9, 170.1, 169.5, 143.8, 143.6, 139.4, 138.3, 135.2, 133.9, 133.5, 130.4, 129.6, 128.6, 128.4, 128.3, 128.0, 127.7, 127.6, 127.1, 127.0, 122.7, 118.1, 112.0, 98.4, 74.7, 66.8, 53.4, 44.0, 30.3, 21.7, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{40}H_{36}N_2O_7S_2Na^+$ $(M + Na)^+$ 743.1856, found 743.1865.

Benzhydryl (E)-2-(2'-phenyl-1'-tosyl-3-(tosylimino)-3H-spiro[benzofuran-2,3'-pyrrolidin]-4'-yl)acetate (3q)

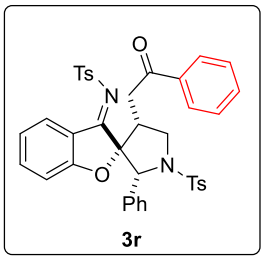


3q

According to the general procedure as described above, the reaction was carried out by using **1aa** (45.0 mg, 0.12 mmol), **2e** (42.1 mg, 0.10 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 87% total yield (68.9 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **3q** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 179.7 – 180.2 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.46 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.4 Hz, 2H),

7.55 (d, J = 8.0 Hz, 2H), 7.45 – 7.28 (m, 11H), 7.24 – 7.09 (m, 7H), 7.00 – 6.94 (m, 3H), 6.80 (s, 1H), 6.70 (d, J = 8.4 Hz, 1H), 4.94 (s, 1H), 4.29 – 4.24 (m, 1H), 3.66 (t, J = 11.6 Hz, 1H), 2.56 (s, 3H), 2.36 – 2.31 (m, 5H), 2.23 – 2.15 (m, 1H). **^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$)** δ 176.7, 169.5, 169.4, 143.7, 143.6, 139.6, 139.5, 139.4, 138.2, 133.9, 133.3, 130.4, 129.55, 129.53, 128.6, 128.5, 128.1, 128.0, 128.0, 127.7, 127.5, 127.1, 127.0, 126.8, 122.7, 118.0, 112.0, 98.5, 77.4, 74.6, 53.3, 43.9, 30.4, 21.7, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{46}H_{41}N_2O_7S_2^+$ $(M + H)^+$ 797.2350, found 797.2335.

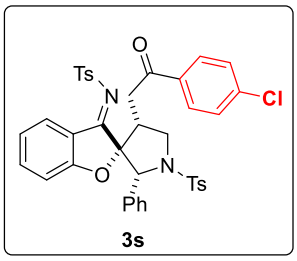
(E)-4-Methyl-N-(4'-(2-oxo-2-phenylethyl)-2'-phenyl-1'-tosyl-3H-spiro[benzofuran-2,3'-pyrrolidin]-3-ylidene)benzenesulfonamide (3r)



3r

According to the general procedure as described above, the reaction was carried out by using **1aa** (37.5 mg, 0.10 mmol), **2c** (37.8 mg, 0.12 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 58% total yield (40.1 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **3r** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 200.4 – 200.9 ^{o}C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.49 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 8.0 Hz, 2H), 7.69 (t, J = 8.4 Hz, 4H), 7.54 – 7.34 (m, 6H), 7.20 – 6.99 (m, 8H), 6.74 (d, J = 8.4 Hz, 1H), 4.96 (s, 1H), 4.41 – 4.36 (m, 1H), 3.61 (t, J = 12.0 Hz, 1H), 2.83 – 2.69 (m, 2H), 2.55 (s, 3H), 2.49 – 2.42 (m, 1H), 2.30 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$)** δ 196.5, 177.1, 169.7, 143.8, 143.6, 139.5, 138.3, 135.8, 134.1, 133.4, 130.6, 129.57, 129.55, 128.6, 128.01, 127.95, 127.7, 127.14, 127.07, 122.7, 118.3, 112.1, 99.1, 74.7, 53.6, 43.9, 34.3, 21.7, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{39}H_{35}N_2O_6S_2^+$ $(M + H)^+$ 691.1932, found 691.1939.

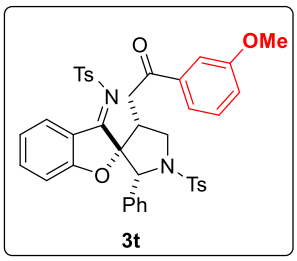
(E)-N-(4'-(2-(4-chlorophenyl)-2-oxoethyl)-2'-phenyl-1'-tosyl-3H-spiro[benzofuran-2,3'-pyrrolidin]-3-ylidene)-4-methylbenzenesulfonamide (3s)



3s

According to the general procedure as described above, the reaction was carried out by using **1aa** (37.5 mg, 0.10 mmol), **2f** (41.9 mg, 0.12 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 57% total yield (41.2 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **3s** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 207.8 – 208.5 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.48 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.4 Hz, 2H), 7.66 – 7.61 (m, 4H), 7.46 – 7.43 (m, 3H), 7.32 – 7.30 (m, 2H), 7.18 – 6.98 (m, 8H), 6.73 (d, J = 8.4 Hz, 1H), 4.95 (s, 1H), 4.35 – 4.30 (m, 1H), 3.61 (t, J = 12.0 Hz, 1H), 2.73 – 2.68 (m, 2H), 2.56 (s, 3H), 2.46 – 2.42 (m, 1H), 2.31 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 195.4, 177.0, 169.7, 143.9, 143.6, 139.9, 139.5, 138.3, 134.1, 134.0, 133.5, 130.6, 129.6, 129.5, 129.4, 128.9, 128.1, 127.72, 127.69, 127.13, 127.08, 122.7, 118.3, 112.1, 98.9, 74.8, 53.4, 43.9, 34.4, 21.7, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{39}H_{34}ClN_2O_6S_2^+$ $(M + H)^+$ 725.1541, found 725.1554.

(E)-N-(4'-(2-(3-methoxyphenyl)-2-oxoethyl)-2'-phenyl-1'-tosyl-3H-spiro[benzofuran-2,3'-pyrrolidin]-3-ylidene)-4-methylbenzenesulfonamide (3t)

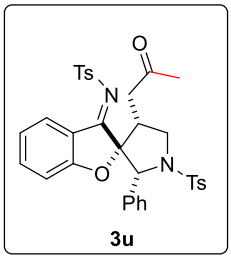


3t

According to the general procedure as described above, the reaction was carried out by using **1aa** (37.5 mg, 0.10 mmol), **2g** (41.4 mg, 0.12 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 43% total yield (31.2 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **3t** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 221.3 – 222.1 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.48 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.0 Hz, 2H), 7.47 – 7.42 (m, 3H), 7.26 – 7.00 (m, 12H), 6.73 (d, J = 8.4 Hz, 1H), 4.95 (s, 1H), 4.39 – 4.34 (m, 1H), 3.81 (s, 3H), 3.61 (t, J = 12.0 Hz, 1H), 2.80 – 2.67 (m, 2H), 2.55 (s, 3H), 2.48 – 2.43 (m, 1H), 2.31 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 196.4, 177.1, 169.7, 159.8, 143.8, 143.6, 139.5, 138.4, 137.2, 134.1, 133.5, 130.6, 129.56, 129.55, 128.0, 127.7, 127.14, 127.10, 122.7, 120.6, 119.9, 118.3, 112.2, 112.1, 99.0, 74.8, 55.4, 53.5, 43.9, 34.4, 21.7, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{40}H_{37}N_2O_7S_2^+$ $(M + H)^+$ 721.2037, found 721.2040.

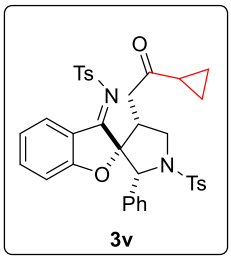
(E)-4-Methyl-N-(4'-(2-oxopropyl)-2'-phenyl-1'-tosyl-3H-spiro[benzofuran-2,3'-pyrrolidin]-3-ylidene)benzenesulfonamide (3u)



3u

According to the general procedure as described above, the reaction was carried out by using **1aa** (37.5 mg, 0.10 mmol), **2i** (30.4 mg, 0.12 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 76% total yield (47.7 mg) with 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **3u** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 186.2 – 186.9 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.47 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.46 – 7.42 (m, 3H), 7.17 – 6.99 (m, 8H), 6.71 (d, J = 8.4 Hz, 1H), 4.92 (s, 1H), 4.34 – 4.29 (m, 1H), 3.49 (t, J = 12.0 Hz, 1H), 2.56 (s, 3H), 2.33 (s, 3H), 2.32 – 2.24 (m, 2H), 2.16 – 2.13 (m, 1H), 1.94 (s, 3H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 204.9, 177.0, 169.6, 143.8, 143.6, 139.5, 138.3, 134.1, 133.5, 130.5, 129.59, 129.57, 128.0, 127.8, 127.7, 127.1, 127.0, 122.6, 118.2, 112.0, 98.9, 74.5, 53.4, 43.3, 39.0, 29.8, 21.7, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{34}H_{33}N_2O_6S_2^+$ $(M + H)^+$ 629.1775, found 629.1777.

(E)-N-(4'-(2-cyclopropyl-2-oxoethyl)-2'-phenyl-1'-tosyl-3H-spiro[benzofuran-2,3'-pyrrolidin]-3-ylidene)-4-methylbenzenesulfonamide (3v)

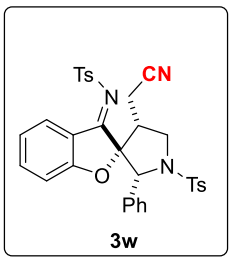


3v

According to the general procedure as described above, the reaction was carried out by using **1aa** (37.5 mg, 0.10 mmol), **2j** (33.5 mg, 0.12 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 48% total

yield (31.7 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **3v** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 218.6 – 219.2 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.47 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 7.46 – 7.43 (m, 3H), 7.15 – 6.99 (m, 8H), 6.73 (d, J = 8.4 Hz, 1H), 4.91 (s, 1H), 4.32 – 4.27 (m, 1H), 3.52 (t, J = 12.0 Hz, 1H), 2.55 (s, 3H), 2.46 – 2.29 (m, 6H), 1.66 – 1.62 (m, 1H), 0.92 – 0.72 (m, 4H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 207.0, 177.1, 169.7, 143.8, 143.6, 139.4, 138.4, 134.1, 133.6, 130.6, 129.6, 128.0, 127.73, 127.69, 127.11, 127.10, 122.6, 118.3, 112.0, 99.0, 74.5, 53.5, 43.4, 39.0, 21.7, 21.5, 20.5, 11.2, 11.1. **HRMS (ESI)** m/z: calcd. for $C_{36}H_{35}N_2O_6S_2^+$ $(M + H)^+$ 655.1931, found 655.1931.

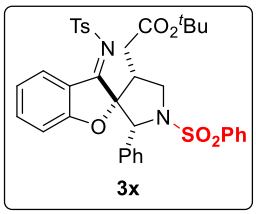
(E)-N-(4'-(cyanomethyl)-2'-phenyl-1'-tosyl-3H-spiro[benzofuran-2,3'-pyrrolidin]-3-ylidene)-4-methylbenzenesulfonamide (3w)



3w

According to the general procedure as described above, the reaction was carried out by using **1aa** (37.5 mg, 0.10 mmol), **2k** (33.5 mg, 0.12 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 77% total yield (47.1 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **3w** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 203.5 – 204.1 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.48 (d, J = 8.0 Hz, 1H), 7.96 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.49 – 7.42 (m, 3H), 7.11 – 7.01 (m, 8H), 6.72 (d, J = 8.4 Hz, 1H), 5.03 (s, 1H), 4.20 – 4.15 (m, 1H), 3.73 (t, J = 12.0 Hz, 1H), 2.56 (s, 3H), 2.35 (s, 4H), 2.25 – 2.12 (m, 2H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 175.7, 169.2, 144.12, 144.07, 139.8, 138.0, 133.8, 133.2, 130.7, 129.73, 129.70, 128.3, 127.8, 127.5, 127.3, 127.1, 123.2, 117.9, 116.1, 112.1, 97.3, 75.1, 52.3, 43.5, 21.7, 21.5, 13.7. **HRMS (ESI)** m/z: calcd. for $C_{33}H_{29}N_3O_5S_2Na^+$ $(M + Na)^+$ 634.1441, found 634.1430.

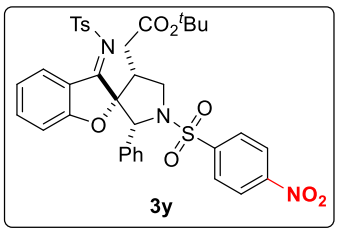
tert-Butyl (E)-2-(2'-phenyl-1'-(phenylsulfonyl)-3-(tosylimino)-3H-spiro[benzofuran-2,3'-pyrrolidin]-4'-yl)acetate (3x)



3x

According to the general procedure as described above, the reaction was carried out by using **1aa** (45.0 mg, 0.12 mmol), **2l** (29.7 mg, 0.1 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 53% total yield (35.4 mg) with 10:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **3x** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 202.8 – 203.4 ^{o}C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.44 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 9.6 Hz, 2H), 7.46 – 7.41 (m, 4H), 7.26 – 7.22 (m, 2H), 7.11 – 7.07 (m, 5H), 7.00 (t, J = 8.0 Hz, 1H), 6.70 (d, J = 8.4 Hz, 1H), 4.91 (s, 1H), 4.35 – 4.30 (m, 1H), 3.65 (t, J = 12.0 Hz, 1H), 2.56 (s, 3H), 2.32 – 2.29 (m, 1H), 2.15 – 2.08 (m, 1H), 2.00 – 1.95 (m, 1H), 1.34 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 177.0, 169.6, 169.5, 143.8, 139.4, 138.4, 136.7, 133.8, 132.9, 130.6, 129.6, 128.9, 128.1, 127.7, 127.6, 127.1, 122.6, 118.1, 112.0, 98.7, 81.3, 74.7, 53.6, 44.3, 31.5, 27.9, 21.7. **HRMS (ESI)** m/z: calcd. for $C_{36}H_{37}N_2O_7S_2^+$ $(M + H)^+$ 673.2037, found 673.2035.

tert-Butyl (E)-2-(1'-((4-nitrophenyl)sulfonyl)-2'-phenyl-3-(tosylimino)-3H-spiro[benzofuran-2,3'-pyrrolidin]-4'-yl)acetate (3y)

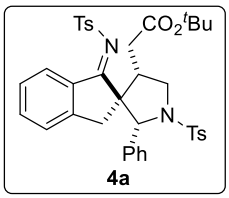


3y

According to the general procedure as described above, the reaction was carried out by using **1aa** (45.0 mg, 0.12 mmol), **2m** (34.2 mg, 0.1 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 67% total yield (48.1 mg) with 8:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **3y** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 227.7 – 228.1 ^{o}C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.46 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 8.8 Hz, 2H), 7.91 – 7.86 (m, 4H), 7.46-7.42 (m, 3H), 7.10 (s, 5H), 7.02 (t, J = 7.2 Hz, 1H) 6.70 (d,

J = 8.4 Hz, 1H), 4.97 (s, 1H), 4.41 – 4.36 (m, 1H), 3.68 (t, *J* = 12.0 Hz, 1H), 2.58 (s, 3H), 2.35 – 2.32 (m, 1H), 2.17 – 2.11 (m, 1H), 2.03 – 1.98 (m, 1H), 1.35 (s, 9H).**^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$)** δ 176.6, 169.5, 169.4, 150.1, 144.5, 142.9, 139.6, 138.0, 133.2, 129.7, 128.8, 128.4, 127.9, 127.1, 126.9, 124.1, 122.8, 112.0, 98.3, 81.6, 74.9, 53.6, 44.5, 31.2, 27.9, 21.6. **HRMS (ESI)** m/z: calcd. for $C_{36}H_{35}N_3O_9S_2Na^+$ $(M + Na)^+$ 740.1707, found 740.1695.

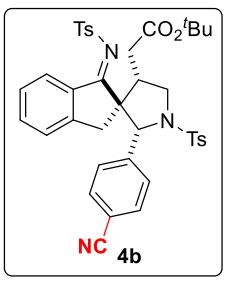
tert-Butyl (E)-2-(2'-phenyl-1'-tosyl-1-(tosylimino)-1,3-dihydrospiro[indene-2,3'-pyrrolidin]-4'-yl)acetate (4a)



4a

According to the general procedure as described above, the reaction was carried out by using **1ba** (44.8 mg, 0.12 mmol), **2a** (31.1 mg, 0.10 mmol), Cs_2CO_3 (6.5 mg, 0.02 mmol), giving the title compounds as a mixture of diastereoisomers in 74% total yield (50.3 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **4a** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 233.5 – 234.1 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.70 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.46 – 7.44 (m, 3H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.21 – 7.10 (m, 5H), 6.99 (d, *J* = 8.0 Hz, 2H), 5.12 (s, 1H), 4.07 – 4.03 (m, 1H), 3.35 (t, *J* = 12.0 Hz, 1H), 2.85 – 2.70 (m, 2H), 2.56 (s, 3H), 2.36 (s, 3H), 2.12 – 2.09 (m, 1H), 1.84 – 1.72 (m, 2H), 1.31 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$)** δ 184.5, 169.5, 152.8, 143.5, 143.4, 139.2, 137.7, 135.9, 133.1, 132.7, 130.6, 129.52, 129.48, 128.1, 128.0, 127.8, 127.6, 126.9, 125.4, 81.0, 72.5, 64.9, 53.4, 44.4, 32.8, 31.4, 27.9, 21.7, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{38}H_{41}N_2O_6S_2^+$ $(M + H)^+$ 685.2401, found 685.2397.

tert-Butyl (E)-2-(2'-(4-cyanophenyl)-1'-tosyl-1-(tosylimino)-1,3-dihydrospiro[indene-2,3'-pyrrolidin]-4'-yl)acetate (4b)

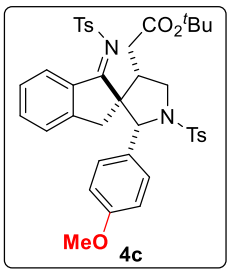


4b

According to the general procedure as described above, the reaction was carried out by using **1bb** (47.8 mg, 0.12 mmol), **2a** (31.1 mg, 0.10 mmol), Cs_2CO_3 (6.5 mg, 0.02 mmol), giving the title compounds as a mixture of diastereoisomers in 83% total

yield (58.8 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **4b** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 200.7 – 201.5 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.71 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.4 Hz, 2H), 7.60 – 7.36 (m, 10H), 7.12 (d, J = 7.6 Hz, 1H), 7.02 (d, J = 8.0 Hz, 2H), 5.09 (s, 1H), 4.07 – 4.02 (m, 1H), 3.34 (t, J = 12.0 Hz, 1H), 2.80 – 2.63 (m, 2H), 2.56 (s, 3H), 2.37 (s, 3H), 2.15 – 2.08 (m, 1H), 1.86 – 1.74 (m, 2H), 1.30 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 183.5, 169.3, 152.1, 144.0, 143.7, 143.2, 138.9, 136.3, 132.5, 131.9, 130.8, 129.7, 129.6, 128.2, 127.9, 126.9, 125.5, 118.5, 111.6, 81.2, 72.2, 64.6, 53.4, 44.3, 32.6, 31.2, 27.8, 21.7, 21.6. **HRMS (ESI)** m/z: calcd. for $C_{39}H_{39}N_3O_6S_2Na^+$ $(M + Na)^+$ 732.2172, found 732.2186.

tert-Butyl (E)-2-(2'-(4-methoxyphenyl)-1'-tosyl-1-(tosylimino)-1,3-dihydrospiro[indene-2,3'-pyrrolidin]-4'-yl)acetate (4c)

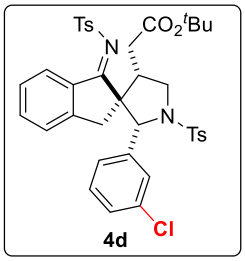


4c

According to the general procedure as described above, the reaction was carried out by using **1bc** (47.8 mg, 0.12 mmol), **2a** (31.1 mg, 0.10 mmol), Cs_2CO_3 (6.5 mg, 0.02 mmol), giving the title compounds as a mixture of diastereoisomers in 84% total yield (60.2 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **4c** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 223.4 – 224.2 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.69 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.48 – 7.23 (m, 6H), 7.14 (d, J = 7.6 Hz, 1H), 7.00 (d, J = 8.4 Hz, 2H), 6.71 (s, 2H), 5.04 (s, 1H), 4.07 – 4.02 (m, 1H), 3.70 (s, 3H), 3.33 (t, J = 12.0 Hz, 1H), 2.89 – 2.70 (m, 2H), 2.56 (s, 3H), 2.36 (s, 3H), 2.11 – 2.06 (m, 1H), 1.85 – 1.73 (m, 2H), 1.31 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 184.6, 169.6, 158.9, 153.0, 143.43, 143.36, 139.2, 135.9, 133.0, 132.7, 130.6, 129.6, 129.49, 129.45, 127.9, 127.8, 126.9, 125.5, 113.5, 81.0, 72.2, 65.0, 55.1, 53.4, 44.2, 32.8, 31.3, 27.8, 21.7, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{39}H_{43}N_2O_7S_2^+$ $(M + H)^+$

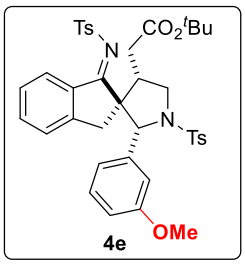
715.2506, found 715.2505.

tert-Butyl (E)-2-(2'-(3-chlorophenyl)-1'-tosyl-1-(tosylimino)-1,3-dihydrospiro[indene-2,3'-pyrrolidin]-4'-yl)acetate (4d)



According to the general procedure as described above, the reaction was carried out by using **1bd** (48.8 mg, 0.12 mmol), **2a** (31.1 mg, 0.10 mmol), Cs_2CO_3 (6.5 mg, 0.02 mmol), giving the title compounds as a mixture of diastereoisomers in 79% total yield (56.6 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **4d** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 191.8 – 192.4 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.69 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.0 Hz, 2H), 7.60 – 7.45 (m, 6H), 7.37 (t, J = 7.6 Hz, 1H), 7.16 – 6.66 (m, 6H), 5.06 (s, 1H), 4.10 – 4.05 (m, 1H), 3.33 (t, J = 12.0 Hz, 1H), 2.76 (s, 2H), 2.56 (s, 3H), 2.37 (s, 3H), 2.12 – 2.10 (m, 1H), 1.83 – 1.72 (m, 2H), 1.32 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 183.9, 169.4, 152.4, 143.7, 143.6, 139.9, 139.0, 136.1, 134.2, 132.9, 132.6, 130.7, 129.62, 129.57, 129.4, 128.00, 127.95, 127.9, 127.2, 127.0, 125.5, 81.2, 71.7, 64.9, 53.3, 44.3, 32.7, 31.4, 27.9, 21.7, 21.6. **HRMS (ESI)** m/z: calcd. for $C_{38}H_{39}ClN_2O_6S_2^+$ $(M + Na)^+$ 741.1830, found 741.1835.

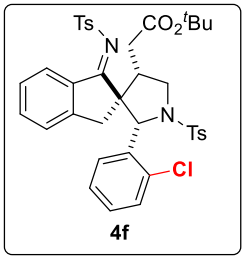
tert-Butyl (E)-2-(2'-(3-methoxyphenyl)-1'-tosyl-1-(tosylimino)-1,3-dihydrospiro[indene-2,3'-pyrrolidin]-4'-yl)acetate (4e)



According to the general procedure as described above, the reaction was carried out by using **1be** (48.4 mg, 0.12 mmol), **2a** (31.1 mg, 0.10 mmol), Cs_2CO_3 (6.5 mg, 0.02 mmol), giving the title compounds as a mixture of diastereoisomers in 84% total yield (60.1 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **4e** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 181.2 – 181.7 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.72 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 2H), 7.49 – 7.33 (m, 4H), 7.15 – 6.96 (m, 5H), 6.69 (s, 2H), 5.15

(s, 1H), 4.07 – 4.02 (m, 1H), 3.65 (s, 3H), 3.33 (t, J = 12.0 Hz, 1H), 2.85 – 2.69 (m, 2H), 2.56 (s, 3H), 2.35 (s, 3H), 2.10 – 2.06 (m, 1H), 1.83 – 1.71 (m, 2H), 1.31 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$)** δ 184.7, 169.5, 159.3, 153.1, 143.5, 143.4, 139.4, 139.2, 136.0, 133.1, 132.6, 130.6, 129.5, 129.2, 128.0, 127.8, 126.9, 125.5, 81.0, 72.5, 64.9, 55.1, 53.4, 44.5, 32.7, 31.5, 27.8, 21.7, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{39}H_{43}N_2O_7S_2^+$ $(M + H)^+$ 715.2506, found 715.2498.

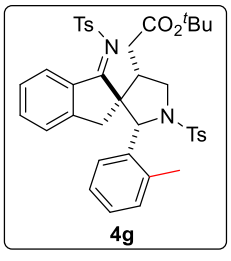
tert-Butyl (E)-2-(2'-(2-chlorophenyl)-1'-tosyl-1-(tosylimino)-1,3-dihydrospiro[indene-2,3'-pyrrolidin]-4'-yl)acetate (4f)



4f

According to the general procedure as described above, the reaction was carried out by using **1bf** (48.8 mg, 0.12 mmol), **2a** (31.1 mg, 0.10 mmol), Cs_2CO_3 (6.5 mg, 0.02 mmol), giving the title compounds as a mixture of diastereoisomers in 50% total yield (35.8 mg) with 10:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **4f** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 189.6 – 190.1 ^{o}C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.68 (d, J = 7.6 Hz, 1H), 7.88 (d, J = 8.4 Hz, 2H), 7.73 – 7.67 (m, 3H), 7.39 – 7.30 (m, 4H), 7.25 – 7.23 (m, 1H), 7.08 – 7.00 (m, 5H), 5.45 (s, 1H), 4.09 – 4.04 (m, 1H), 3.34 (t, J = 12.0 Hz, 1H), 2.89 – 2.68 (m, 2H), 2.51 (s, 3H), 2.33 (s, 4H), 1.88 – 1.86 (m, 2H), 1.30 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$)** δ 184.1, 169.7, 151.6, 143.6, 143.1, 139.3, 136.1, 135.5, 133.3, 132.9, 130.9, 129.8, 129.6, 129.3, 129.2, 128.8, 128.0, 127.7, 126.9, 126.2, 124.8, 80.9, 69.3, 65.0, 53.0, 44.2, 33.1, 31.5, 27.8, 21.6, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{38}H_{40}ClN_2O_6S_2^+$ $(M + H)^+$ 719.2011, found 719.2010.

tert-Butyl (E)-2-(2'-(o-tolyl)-1'-tosyl-1-(tosylimino)-1,3-dihydrospiro[indene-2,3'-pyrrolidin]-4'-yl)acetate (4g)

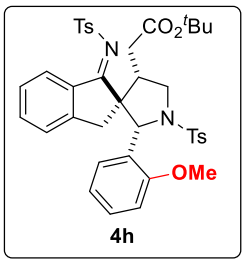


4g

According to the general procedure as described above, the reaction was carried out by using **1bg** (46.5 mg, 0.12 mmol), **2a** (31.1 mg, 0.10 mmol), Cs_2CO_3 (6.5 mg, 0.02 mmol), giving the title compounds as a mixture of diastereoisomers in 81% total

yield (56.5 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **4g** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 199.4 – 200.2 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.69 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.53 – 7.51 (m, 1H), 7.42 – 7.40 (m, 3H), 7.32 (t, J = 8.0 Hz, 1H), 7.13 (t, J = 7.6 Hz, 1H), 7.06 – 6.99 (m, 4H), 6.84 (d, J = 7.6 Hz, 1H), 5.36 (s, 1H), 4.13 – 4.08 (m, 1H), 3.34 (t, J = 12.0 Hz, 1H), 3.01 – 2.70 (m, 2H), 2.54 (s, 3H), 2.40 – 2.38 (m, 1H), 2.34 (s, 3H), 2.08 (s, 3H), 1.87 – 1.84 (m, 2H), 1.32 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$)** δ 184.9, 169.7, 152.7, 143.4, 143.3, 139.1, 136.5, 135.8, 135.3, 134.4, 132.3, 130.6, 130.4, 129.5, 128.7, 127.77, 127.76, 127.4, 127.0, 125.3, 125.2, 81.0, 68.7, 65.3, 53.0, 45.3, 33.1, 31.9, 27.9, 21.7, 21.5, 20.1. **HRMS (ESI)** m/z: calcd. for $C_{39}H_{43}N_2O_6S_2^+$ $(M + H)^+$ 699.2558, found 699.2594.

tert-Butyl (E)-2-(2'-(2-methoxyphenyl)-1'-tosyl-1-(tosylimino)-1,3-dihydrospiro[indene-2,3'-pyrrolidin]-4'-yl)acetate (4h)

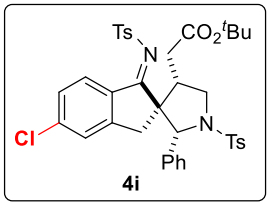


4h

According to the general procedure as described above, the reaction was carried out by using **1bh** (48.4 mg, 0.12 mmol), **2a** (31.1 mg, 0.10 mmol), Cs_2CO_3 (6.5 mg, 0.02 mmol), giving the title compounds as a mixture of diastereoisomers in 81% total yield (57.5 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **4h** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 176.3 – 177.2 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.71 (d, J = 7.6 Hz, 1H), 7.92 (d, J = 8.4 Hz, 2H), 7.71 – 7.64 (m, 3H), 7.41 – 7.31 (m, 4H), 7.13 – 7.09 (m, 1H), 7.00 – 6.88 (m, 4H), 6.47 (d, J = 8.4 Hz, 1H), 5.45 (s, 1H), 4.02 – 3.97 (m, 1H), 3.47 (s, 3H), 3.25 (t, J = 12.4 Hz, 1H), 2.71 – 2.55 (m, 2H), 2.52 (s, 3H), 2.29 (s, 3H), 2.26 – 2.19 (m, 1H), 1.83 – 1.81 (m, 2H), 1.28 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$)** δ 185.9, 169.8, 156.0, 152.0, 143.2, 143.0, 139.8, 135.1, 134.0, 133.0, 130.2, 129.39, 129.37, 128.6, 128.3, 128.0, 127.3, 126.9, 126.7, 125.1, 120.0, 109.2, 80.8, 68.7, 64.3, 54.4, 52.6,

44.7, 32.9, 31.8, 27.8, 21.6, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{39}H_{43}N_2O_7S_2^+$ $(M + H)^+$ 715.2506, found 715.2522.

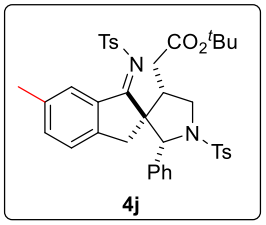
tert-Butyl (E)-2-(5-chloro-2'-phenyl-1'-tosyl-1-(tosylimino)-1,3-dihydrospiro[indene-2,3'-pyrrolidin]-4'-yl)acetate (4i)



4i

According to the general procedure as described above, the reaction was carried out by using **1bi** (6.5 mg, 0.02 mmol), **2a** (31.1 mg, 0.10 mmol), Cs_2CO_3 (6.5 mg, 0.02 mmol), giving the title compounds as a mixture of diastereoisomers in 65% total yield (46.8 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **4i** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 217.3 – 218.2 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.64 (d, J = 8.8 Hz, 1H), 7.93 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.8 Hz, 2H), 7.32 – 6.78 (m, 9H), 5.09 (s, 1H), 4.08 – 4.04 (m, 1H), 3.32 (t, J = 12.0 Hz, 1H), 2.83 – 2.67 (m, 2H), 2.56 (s, 3H), 2.35 (s, 3H), 2.13 – 2.06 (m, 1H), 1.85 – 1.73 (m, 2H), 1.32 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 183.0, 169.4, 154.3, 143.6, 143.5, 142.8, 138.9, 137.5, 133.0, 131.7, 131.1, 129.5, 128.5, 128.2, 127.9, 127.8, 126.9, 125.6, 81.2, 72.5, 65.2, 53.3, 44.4, 32.7, 31.2, 27.8, 21.7, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{38}H_{40}ClN_2O_6S_2^+$ $(M + H)^+$ 719.2011, found 719.2002.

tert-Butyl (E)-2-(6-methyl-2'-phenyl-1'-tosyl-1-(tosylimino)-1,3-dihydrospiro[indene-2,3'-pyrrolidin]-4'-yl)acetate (4j)

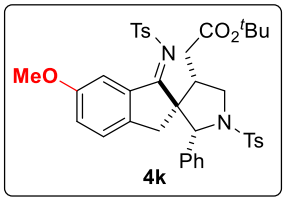


4j

According to the general procedure as described above, the reaction was carried out by using **1bj** (46.5 mg, 0.12 mmol), **2a** (31.1 mg, 0.10 mmol), Cs_2CO_3 (6.5 mg, 0.02 mmol), giving the title compounds as a mixture of diastereoisomers in 82% total yield (59.2 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **4j** was isolated as a white solid after flash column chromatography on

silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 221.2 – 221.8 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.49 (s, 1H), 7.94 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 7.29 – 6.82 (m, 9H), 5.13 (s, 1H), 4.06 – 3.97 (m, 1H), 3.34 (t, J = 12.0 Hz, 1H), 2.78 – 2.63 (m, 2H), 2.56 (s, 3H), 2.38 (s, 3H), 2.36 (s, 3H), 2.11 – 2.04 (m, 1H), 1.83 – 1.71 (m, 2H), 1.31 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 184.6, 169.6, 150.4, 143.5, 143.3, 139.3, 137.9, 137.8, 137.4, 133.1, 132.8, 130.4, 129.51, 129.47, 128.1, 127.9, 127.6, 126.9, 125.1, 81.0, 72.3, 65.2, 53.3, 44.6, 32.7, 31.0, 27.8, 21.6, 21.5, 21.3. **HRMS (ESI)** m/z: calcd. for $C_{39}H_{43}N_2O_6S_2^+$ $(M + H)^+$ 699.2557, found 699.2547.

tert-Butyl (E)-2-(6-methoxy-2'-phenyl-1'-tosyl-1-(tosylimino)-1,3-dihydrospiro[indene-2,3'-pyrrolidin]-4'-yl)acetate (4k)

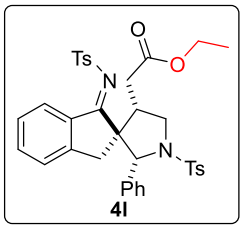


4k

According to the general procedure as described above, the reaction was carried out by using **1bk** (47.8 mg, 0.12 mmol), **2a** (31.1 mg, 0.10 mmol), Cs_2CO_3 (6.5 mg, 0.02 mmol), giving the title compounds as a mixture of diastereoisomers in 82% total yield (58.3 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **4k** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 227.4 – 228.3 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.20 (d, J = 2.4 Hz, 1H), 7.94 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 7.26 – 6.97 (m, 9H), 5.13 (s, 1H), 4.07 – 4.02 (m, 1H), 3.84 (s, 3H), 3.33 (t, J = 12.0 Hz, 1H), 2.75 – 2.61 (m, 2H), 2.56 (s, 3H), 2.35 (s, 3H), 2.12 – 2.05 (m, 1H), 1.84 – 1.72 (m, 2H), 1.32 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 184.7, 169.6, 159.1, 146.0, 143.5, 143.4, 139.3, 137.8, 133.6, 133.1, 129.51, 129.49, 128.1, 128.0, 127.6, 126.9, 126.0, 125.7, 111.7, 81.0, 72.4, 65.6, 55.6, 53.4, 44.6, 32.7, 30.7, 27.8, 21.6, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{39}H_{43}N_2O_7S_2^+$ $(M + H)^+$ 715.2506, found 715.2514.

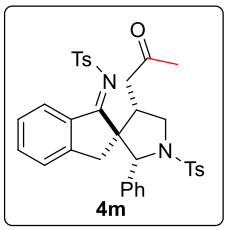
Ethyl (E)-2-(2'-phenyl-1'-tosyl-1-(tosylimino)-1,3-dihydrospiro[indene-2,3'-

pyrrolidin]-4'-yl)acetate (4l)



According to the general procedure as described above, the reaction was carried out by using **1ba** (44.8 mg, 0.12 mmol), **2b** (28.3 mg, 0.10 mmol), Cs_2CO_3 (6.5 mg, 0.02 mmol), giving the title compounds as a mixture of diastereoisomers in 87% total yield (57.2 mg) with 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **4l** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 206.2 – 206.8 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.69 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.46 – 7.44 (m, 3H), 7.34 (t, J = 8.0 Hz, 1H), 7.26 – 6.99 (m, 8H), 5.10 (s, 1H), 4.08 – 4.04 (m, 1H), 3.97 – 3.91 (m, 2H), 3.33 (t, J = 12.0 Hz, 1H), 2.87 – 2.74 (m, 2H), 2.56 (s, 3H), 2.36 (s, 3H), 2.21 – 2.15 (m, 1H), 1.97 – 1.82 (m, 2H), 1.03 (t, J = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 184.4, 170.2, 152.8, 143.6, 143.4, 139.2, 137.5, 135.9, 133.0, 132.7, 130.6, 129.51, 129.49, 128.1, 128.0, 127.8, 127.7, 127.0, 125.4, 72.7, 64.8, 60.8, 53.5, 44.0, 31.6, 31.3, 21.7, 21.6, 13.9. **HRMS (ESI)** m/z: calcd. for $C_{36}H_{37}N_2O_6S_2^+$ $(M + H)^+$ 657.2088, found 657.2095.

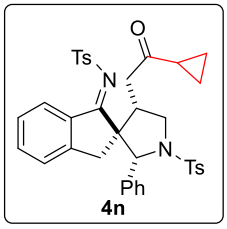
(E)-4-Methyl-N-(4'-(2-oxopropyl)-2'-phenyl-1'-tosylspiro[indene-2,3'-pyrrolidin]-1(3H)-ylidene)benzenesulfonamide (4m)



According to the general procedure as described above, the reaction was carried out by using **1ba** (37.3 mg, 0.10 mmol), **2i** (30.4 mg, 0.12 mmol), Cs_2CO_3 (6.5 mg, 0.02 mmol), giving the title compounds as a mixture of diastereoisomers in 48% total yield (30.2 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **4m** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 226.9 – 227.7 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.71 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H), 7.49 – 7.34 (m, 5H), 7.26 – 7.13 (m, 5H), 7.01 (d, J = 8.0 Hz, 2H), 5.09 (s, 1H), 4.13 – 4.08 (m, 1H), 3.21 (t, J = 12.0 Hz, 1H), 2.85 – 2.67 (m, 2H), 2.57 (s, 3H), 2.36

(s, 3H), 2.11 – 2.05 (m, 1H), 1.99 – 1.90 (m, 2H), 1.81 (s, 3H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 204.8, 184.5, 152.9, 143.6, 143.6, 139.1, 137.8, 136.0, 132.8, 132.7, 130.7, 129.6, 129.5, 128.2, 128.1, 127.9, 127.7, 126.9, 125.4, 72.2, 64.8, 53.3, 43.5, 39.9, 31.6, 29.7, 21.7, 21.6. **HRMS (ESI)** m/z: calcd. for $C_{35}H_{35}N_2O_5S_2^+$ $(M + H)^+$ 627.1982, found 627.1985.

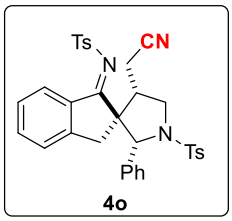
(E)-N-(4'-(2-Cyclopropyl-2-oxoethyl)-2'-phenyl-1'-tosylspiro[indene-2,3'-pyrrolidin]-1(3H)-ylidene)-4-methylbenzenesulfonamide (4n)



4n

According to the general procedure as described above, the reaction was carried out by using **1ba** (37.3 mg, 0.10 mmol), **2j** (33.5 mg, 0.12 mmol), Cs_2CO_3 (6.5 mg, 0.02 mmol), giving the title compounds as a mixture of diastereoisomers in 40% total yield (26.4 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **4n** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 235.7 – 236.1 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.70 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.55 – 7.27 (m, 5H), 7.22 – 6.85 (m, 7H), 5.08 (s, 1H), 4.10 – 4.06 (m, 1H), 3.25 (t, J = 11.6 Hz, 1H), 2.87 – 2.72 (m, 2H), 2.56 (s, 3H), 2.36 (s, 3H), 2.18 – 2.10 (m, 3H), 1.50 – 1.44 (m, 1H), 0.89 – 0.59 (m, 4H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 207.0, 184.6, 152.9, 143.46, 143.45, 139.1, 137.7, 135.9, 132.9, 132.8, 130.6, 129.48, 129.47, 128.1, 128.0, 127.8, 127.6, 126.9, 125.4, 72.2, 65.0, 53.4, 43.6, 40.0, 31.6, 21.6, 21.5, 20.2, 11.1, 11.0. **HRMS (ESI)** m/z: calcd. for $C_{37}H_{36}N_2O_5S_2Na^+$ $(M + Na)^+$ 675.1958, found 675.1967.

(E)-N-(4'-(cyanomethyl)-2'-phenyl-1'-tosylspiro[indene-2,3'-pyrrolidin]-1(3H)-ylidene)-4-methylbenzenesulfonamide (4o)

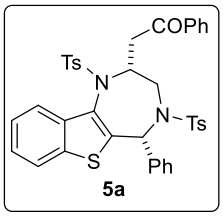


4o

According to the general procedure as described above, the reaction was carried out by using **1ba** (44.8 mg, 0.12 mmol), **2k** (23.6 mg, 0.10 mmol), Cs_2CO_3 (6.5 mg, 0.02 mmol), giving the title compounds as a mixture of diastereoisomers in 67% total

yield (41.1 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **4o** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 198.1 – 198.7 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.73 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.50 – 7.35 (m, 5H), 7.26 – 7.02 (m, 7H), 5.11 (s, 1H), 4.01 – 3.97 (m, 1H), 3.46 (t, J = 12.0 Hz, 1H), 2.89 – 2.72 (m, 2H), 2.58 (s, 3H), 2.38 (s, 3H), 2.07 – 2.02 (m, 1H), 1.95 – 1.93 (m, 2H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 183.0, 152.0, 144.1, 143.8, 138.8, 136.8, 136.3, 132.7, 132.3, 130.9, 129.8, 129.7, 128.23, 128.21, 128.0, 127.8, 127.0, 126.6, 125.5, 116.4, 73.0, 64.3, 52.5, 43.4, 30.8, 21.7, 21.6, 14.8. **HRMS (ESI)** m/z: calcd. for $C_{34}H_{32}N_3O_4S_2^+$ $(M + H)^+$ 610.1829, found 610.1825.

1-Phenyl-2-(5-phenyl-1,4-ditosyl-2,3,4,5-tetrahydro-1H-benzo[4,5]thieno[3,2-e][1,4]diazepin-2-yl)ethan-1-one (5a)

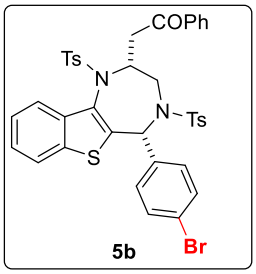


5a

According to the general procedure as described above, the reaction was carried out by using **1ca** (39.1 mg, 0.10 mmol), **2c** (37.8 mg, 0.12 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 90% total yield (63.2 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **5a** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 230.3 – 230.9 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.09 (d, J = 8.0 Hz, 1H), 8.01 – 7.98 (m, 2H), 7.80 (d, J = 8.4 Hz, 2H), 7.68 – 7.26 (m, 10H), 7.24 – 6.79 (m, 7H), 5.43 (s, 1H), 5.25 – 5.17 (m, 1H), 4.04 – 3.99 (m, 1H), 3.90 – 3.85 (m, 1H), 3.03 – 2.92 (m, 2H), 2.51 (s, 3H), 2.27 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 197.3, 144.2, 142.7, 141.2, 139.5, 139.1, 136.9, 136.8, 136.4, 136.0, 133.6, 130.2, 128.9, 128.8, 128.4, 128.3, 128.0, 127.0, 125.9, 125.2, 125.1, 123.5, 121.8, 61.2, 57.6, 47.6, 44.3, 21.7, 21.3. **HRMS (ESI)** m/z: calcd. for $C_{39}H_{35}N_2O_5S_3^+$ $(M + H)^+$ 707.1703, found 707.1704.

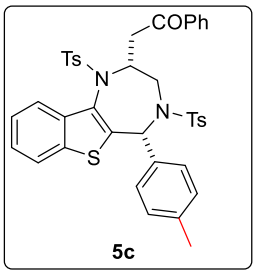
2-(5-(4-Bromophenyl)-1,4-ditosyl-2,3,4,5-tetrahydro-1H-benzo[4,5]thieno[3,2-

e][1,4]diazepin-2-yl)-1-phenylethan-1-one (5b)



According to the general procedure as described above, the reaction was carried out by using **1b** (40.5 mg, 0.10 mmol), **2c** (37.8 mg, 0.12 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 77% total yield (60.7 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **5b** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 181.2 – 181.9 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.06 (d, J = 8.0 Hz, 1H), 7.99 (d, J = 7.6 Hz, 2H), 7.78 (d, J = 8.0 Hz, 2H), 7.63 – 7.60 (m, 2H), 7.63 – 7.26 (m, 8H), 6.97 – 6.90 (m, 6H), 5.39 (s, 1H), 5.22 – 5.14 (m, 1H), 4.10 – 4.04 (m, 1H), 3.88 – 3.83 (m, 1H), 3.01 – 2.93 (m, 2H), 2.50 (s, 3H), 2.31 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 197.2, 144.2, 143.0, 140.0, 139.0, 138.3, 136.9, 136.8, 136.3, 135.9, 133.6, 131.4, 130.2, 129.0, 128.8, 128.2, 127.9, 126.8, 126.3, 125.3, 125.2, 123.5, 122.9, 121.8, 60.5, 57.6, 47.7, 44.2, 21.7, 21.4. **HRMS (ESI)** m/z: calcd. for $C_{39}H_{34}BrN_2O_5S_3^+$ $(M + H)^+$ 785.0808, found 785.0805.

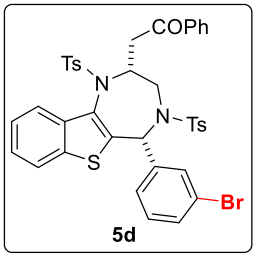
1-Phenyl-2-(5-(p-tolyl)-1,4-ditosyl-2,3,4,5-tetrahydro-1H-benzo[4,5]thieno[3,2-e][1,4]diazepin-2-yl)ethan-1-one (5c)



According to the general procedure as described above, the reaction was carried out by using **1cc** (40.5 mg, 0.10 mmol), **2c** (37.8 mg, 0.12 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 69% total yield (49.8 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **5c** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 194.3 – 195.2 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.08 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 7.2 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H), 7.63 – 7.33 (m, 8H), 7.12 – 6.88 (s, 8H), 5.39 (s, 1H), 5.23 – 5.15 (m, 1H), 4.03 – 3.98 (m, 1H), 3.89 – 3.84 (m, 1H), 3.02 – 2.91 (m, 2H), 2.50 (s,

3H), 2.36 (s, 3H), 2.28 (s, 3H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 197.3, 144.2, 142.6, 141.5, 139.2, 138.8, 136.87, 136.85, 136.6, 136.4, 136.0, 133.6, 130.2, 128.9, 128.8, 128.3, 127.9, 127.1, 125.8, 125.12, 125.07, 123.5, 121.8, 60.9, 57.7, 47.6, 44.3, 21.7, 21.3, 21.2. **HRMS (ESI)** m/z: calcd. for $C_{40}H_{37}N_2O_5S_3^+$ $(M + H)^+$ 721.1859, found 721.1849.

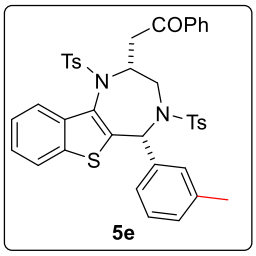
2-(5-(3-Bromophenyl)-1,4-ditosyl-2,3,4,5-tetrahydro-1H-benzo[4,5]thieno[3,2-e][1,4]diazepin-2-yl)-1-phenylethan-1-one (5d)



5d

According to the general procedure as described above, the reaction was carried out by using **1cd** (46.9 mg, 0.10 mmol), **2c** (37.8 mg, 0.12 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 61% total yield (47.5 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **5d** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 244.6 – 245.2 ^{o}C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.07 (d, J = 8.0 Hz, 1H), 7.99 (d, J = 7.6 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H), 7.62 – 7.34 (m, 10H), 6.98 – 6.92 (m, 6H), 5.37 (s, 1H), 5.22 – 5.16 (m, 1H), 4.14 – 4.09 (m, 1H), 3.89 – 3.84 (m, 1H), 3.00 – 2.93 (m, 2H), 2.51 (s, 3H), 2.31 (s, 3H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 197.2, 144.3, 143.2, 141.2, 140.0, 139.0, 136.8, 136.7, 136.3, 136.0, 133.6, 131.8, 130.2, 129.8, 129.1, 128.8, 128.3, 127.9, 126.7, 126.3, 125.4, 125.3, 123.5, 121.9, 60.5, 57.7, 47.8, 44.2, 21.7, 21.4. **HRMS (ESI)** m/z: calcd. for $C_{39}H_{34}BrN_2O_5S_3^+$ $(M + H)^+$ 785.0808, found 785.0817.

1-Phenyl-2-(5-(m-tolyl)-1,4-ditosyl-2,3,4,5-tetrahydro-1H-benzo[4,5]thieno[3,2-e][1,4]diazepin-2-yl)ethan-1-one (5e)

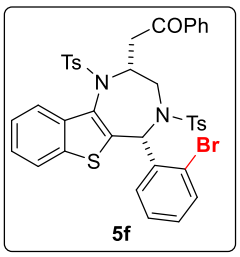


5e

According to the general procedure as described above, the reaction was carried out by using **1ce** (40.5 mg, 0.10 mmol), **2c** (37.8 mg, 0.12 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 62% total

yield (44.3 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **5e** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 214.9 – 215.6 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.08 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 7.2 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H), 7.62 – 7.33 (m, 8H), 7.12 – 7.10 (m, 2H), 6.91 – 6.84 (m, 6H), 5.39 (s, 1H), 5.22 – 5.14 (m, 1H), 4.06 – 4.01 (m, 1H), 3.91 – 3.86 (m, 1H), 3.04 – 2.92 (m, 2H), 2.50 (s, 3H), 2.27 (s, 3H), 2.04 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$)** δ 197.4, 144.2, 142.6, 141.4, 139.1, 138.1, 136.9, 136.8, 136.4, 136.0, 133.6, 130.2, 129.4, 128.8, 128.3, 128.2, 127.9, 127.1, 125.7, 125.14, 125.09, 123.4, 121.8, 61.2, 57.7, 47.8, 44.3, 21.7, 21.3, 21.2. **HRMS (ESI)** m/z: calcd. for $C_{40}H_{37}N_2O_5S_3^+$ $(M + H)^+$ 721.1859, found 721.1868.

2-(5-(2-Bromophenyl)-1,4-ditosyl-2,3,4,5-tetrahydro-1H-benzo[4,5]thieno[3,2-e][1,4]diazepin-2-yl)-1-phenylethan-1-one (5f)

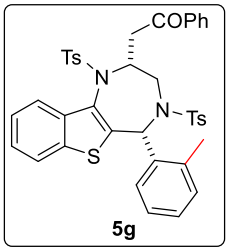


5f

According to the general procedure as described above, the reaction was carried out by using **1cf** (46.9 mg, 0.10 mmol), **2c** (37.8 mg, 0.12 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 62% total yield (48.9 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **5f** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 272.3 – 272.7 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.14 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 7.2 Hz, 2H), 7.85 (d, J = 8.4 Hz, 2H), 7.64 – 7.34 (m, 9H), 7.16 – 7.12 (m, 1H), 6.99 – 7.94 (s, 4H), 6.87 – 7.81 (m, 1H), 6.49 (d, J = 7.6 Hz, 1H), 6.16 (s, 1H), 5.29 – 5.21 (m, 1H), 4.15 – 4.10 (m, 1H), 3.96 – 3.91 (m, 1H), 3.00 – 2.90 (m, 2H), 2.46 (s, 3H), 2.30 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$)** δ 197.4, 144.3, 143.0, 139.4, 139.1, 136.9, 136.8, 136.3, 136.2, 133.6, 133.0, 130.4, 129.9, 129.1, 129.0, 128.8, 128.31, 128.28, 127.8, 127.4, 127.2, 126.1, 125.24, 125.17, 123.7, 123.5, 121.9, 59.7, 57.6, 47.9, 44.5, 21.7, 21.4. **HRMS (ESI)** m/z: calcd. for $C_{39}H_{34}BrN_2O_5S_3^+$ $(M + H)^+$ 785.0808, found

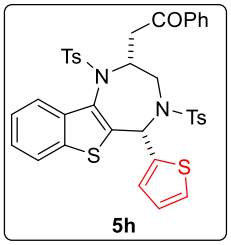
785.0810.

1-Phenyl-2-(5-(o-tolyl)-1,4-ditosyl-2,3,4,5-tetrahydro-1H-benzo[4,5]thieno[3,2-e][1,4]diazepin-2-yl)ethan-1-one (5g)



According to the general procedure as described above, the reaction was carried out by using **1cg** (40.5 mg, 0.10 mmol), **2c** (37.8 mg, 0.12 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 68% total yield (49.1 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **5g** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 222.6 – 223.2 ^{o}C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.15 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 7.2 Hz, 2H), 7.82 (d, J = 8.4 Hz, 2H), 7.64 – 7.47 (m, 5H), 7.40 – 7.33 (m, 3H), 7.18 (d, J = 4.0 Hz, 2H), 6.93 – 6.84 (m, 4H), 6.76 – 6.72 (m, 1H), 6.43 (d, J = 7.6 Hz, 1H), 5.64 (s, 1H), 5.35-5.28 (m, 1H), 4.09 – 4.03 (m, 1H), 3.91 – 3.86 (m, 1H), 3.02 – 2.93 (m, 2H), 2.47 (s, 3H), 2.29 (s, 3H), 2.24 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 197.3, 144.1, 142.8, 141.2, 139.2, 138.3, 136.9, 136.7, 136.4, 136.1, 133.6, 130.3, 130.2, 128.9, 128.8, 128.4, 128.3, 127.9, 127.7, 127.1, 126.1, 125.8, 125.1, 123.5, 121.8, 57.9, 56.0, 47.8, 44.6, 21.6, 21.4, 19.0. **HRMS (ESI)** m/z: calcd. for $C_{40}H_{37}N_2O_5S_3^+$ $(M + H)^+$ 721.1859, found 721.1848.

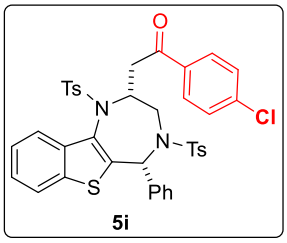
1-Phenyl-2-(5-(thiophen-2-yl)-1,4-ditosyl-2,3,4,5-tetrahydro-1H-benzo[4,5]thieno[3,2-e][1,4]diazepin-2-yl)ethan-1-one (5h)



According to the general procedure as described above, the reaction was carried out by using **1ch** (39.7 mg, 0.10 mmol), **2c** (37.8 mg, 0.12 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 63% total yield (45.2 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **5h** was isolated as a white solid after flash column chromatography

on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 245.1 – 245.7 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.06 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 7.2 Hz, 2H), 7.75 (d, J = 8.4 Hz, 2H), 7.64 – 7.58 (m, 2H), 7.51 – 7.44 (m, 3H), 7.39 – 7.34 (m, 3H), 7.13 (d, J = 5.1 Hz, 1H), 7.03 – 6.90 (m, 6H), 6.06 (s, 1H), 5.22 – 5.15 (m, 1H), 4.00 – 3.95 (m, 1H), 3.87 – 3.82 (m, 1H), 3.01 – 2.83 (m, 2H), 2.48 (s, 3H), 2.28 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 197.1, 144.1, 142.8, 142.5, 140.7, 139.2, 136.7, 136.4, 136.3, 135.6, 133.6, 130.1, 128.9, 128.8, 128.7, 128.2, 128.0, 126.9, 126.6, 125.5, 125.4, 125.3, 125.0, 123.7, 121.8, 57.8, 57.7, 46.7, 44.0, 21.7, 21.4. **HRMS (ESI)** m/z: calcd. for $C_{37}H_{33}N_2O_5S_4^+$ $(M + H)^+$ 713.1267, found 713.1276.

1-(4-Chlorophenyl)-2-(5-phenyl-1,4-ditosyl-2,3,4,5-tetrahydro-1H-benzo[4,5]thieno[3,2-e][1,4]diazepin-2-yl)ethan-1-one (5i)

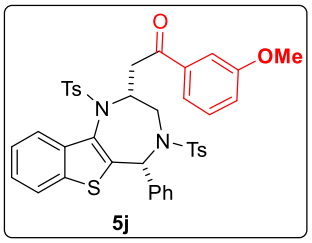


5i

According to the general procedure as described above, the reaction was carried out by using **1ca** (39.1 mg, 0.10 mmol), **2f** (41.4 mg, 0.12 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 73% total yield (53.9 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **5i** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 267.7 – 268.4 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.07 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.4 Hz, 2H), 7.78 (d, J = 8.0 Hz, 2H), 7.70 – 7.12 (m, 10H), 6.91 – 6.83 (m, 6H), 5.41 (s, 1H), 5.21 – 5.14 (m, 1H), 4.02 – 3.97 (m, 1H), 3.84 – 3.79 (m, 1H), 3.04 – 2.89 (m, 2H), 2.51 (s, 3H), 2.27 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 196.1, 144.3, 142.8, 141.2, 140.1, 139.4, 139.0, 136.9, 136.7, 135.9, 134.7, 130.2, 129.7, 129.1, 128.9, 128.8, 128.4, 127.9, 127.0, 125.8, 125.2, 125.1, 123.4, 121.8, 61.2, 57.6, 47.6, 44.2, 21.7, 21.3. **HRMS (ESI)** m/z: calcd. for $C_{39}H_{34}ClN_2O_5S_3^+$ $(M + H)^+$ 741.1313, found 741.1333.

1-(3-Methoxyphenyl)-2-(5-phenyl-1,4-ditosyl-2,3,4,5-tetrahydro-1H-

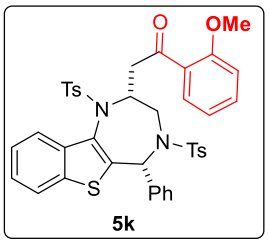
benzo[4,5]thieno[3,2-e][1,4]diazepin-2-yl)ethan-1-one (5j)



5j

According to the general procedure as described above, the reaction was carried out by using **1ca** (39.1 mg, 0.10 mmol), **2g** (41.4 mg, 0.12 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 74% total yield (54.1 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **5j** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 187.7 – 188.4 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.08 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 8.4 Hz, 2H), 7.60 – 7.31 (m, 10H), 7.18 – 6.82 (m, 8H), 5.41 (s, 1H), 5.25 – 5.17 (m, 1H), 4.00 – 3.95 (m, 1H), 3.90 (s, 3H), 3.88 – 3.83 (m, 1H), 3.04 – 2.90 (m, 2H), 2.51 (s, 3H), 2.27 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 197.1, 159.9, 144.2, 142.7, 141.2, 139.4, 139.1, 137.7, 136.9, 136.7, 136.0, 130.2, 129.8, 128.9, 128.8, 128.3, 127.9, 127.0, 125.9, 125.2, 125.1, 123.5, 121.8, 121.0, 120.4, 112.2, 61.2, 57.7, 55.5, 47.6, 44.5, 21.7, 21.3. **HRMS (ESI)** m/z: calcd. for $C_{40}H_{37}N_2O_6S_3^+$ $(M + H)^+$ 737.1808, found 737.1807.

1-(2-Methoxyphenyl)-2-(5-phenyl-1,4-ditosyl-2,3,4,5-tetrahydro-1H-benzo[4,5]thieno[3,2-e][1,4]diazepin-2-yl)ethan-1-one (5k)

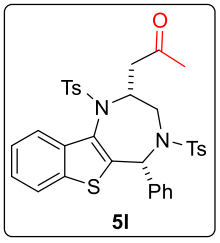


5k

According to the general procedure as described above, the reaction was carried out by using **1ca** (39.1 mg, 0.10 mmol), **2h** (41.4 mg, 0.12 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 77% total yield (56.8 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **5k** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 205.7 – 206.3 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.11 (d, J = 8.0 Hz, 1H), 7.80 – 7.76 (m, 3H), 7.59 – 7.30 (m, 8H), 7.21 – 6.81 (m, 9H), 5.40 (s, 1H), 5.28 – 5.20 (m, 1H), 4.04 – 3.99 (m, 1H), 3.92 (s, 3H), 3.80 – 3.75 (m, 1H), 3.07 – 2.92 (m, 2H), 2.50 (s, 3H), 2.27 (s, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.3, 159.0, 143.9, 142.6, 141.4, 139.5, 139.1, 136.87, 136.85, 136.3, 134.3, 130.7, 130.0, 128.8, 128.7, 128.3, 128.0, 127.1, 127.0, 126.1, 125.1, 124.9, 123.6, 121.7, 120.6, 111.7, 61.2, 57.5, 55.5, 49.5, 47.9, 21.7, 21.3. **HRMS (ESI)** m/z: calcd. for $C_{40}H_{37}N_2O_6S_3^+$ $(M + H)^+$ 737.1808, found 737.1818.

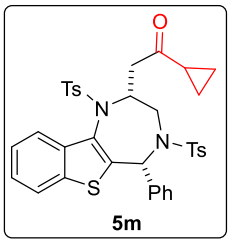
1-(5-Phenyl-1,4-ditosyl-2,3,4,5-tetrahydro-1H-benzo[4,5]thieno[3,2-e][1,4]diazepin-2-yl)propan-2-one (5l)



5l

According to the general procedure as described above, the reaction was carried out by using **1ca** (39.1 mg, 0.10 mmol), **2i** (30.4 mg, 0.12 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 71% total yield (45.8 mg) with > 20:1 *d.r.* (^1H NMR analysis of the crude product). The major diastereoisomer **5l** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 240.1 – 240.8 ºC. **^1H NMR (400 MHz, $CDCl_3$)** δ 8.05 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.0 Hz, 1H), 7.48 – 7.31 (m, 6H), 7.22 – 6.67 (m, 7H), 5.39 (s, 1H), 5.08 – 5.01 (m, 1H), 4.00 – 3.95 (m, 1H), 3.23 – 3.17 (m, 1H), 2.88 – 2.82 (m, 1H), 2.50 (s, 3H), 2.49 – 2.42 (m, 1H), 2.27 (s, 3H), 2.24 (s, 3H). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 205.7, 144.2, 142.8, 141.3, 139.4, 139.0, 136.8, 136.7, 135.9, 130.1, 128.9, 128.8, 128.4, 127.9, 127.0, 125.7, 125.2, 125.1, 123.5, 121.7, 61.1, 57.0, 48.8, 47.6, 30.3, 21.7, 21.3. **HRMS (ESI)** m/z: calcd. for $C_{34}H_{33}N_2O_5S_3^+$ $(M + H)^+$ 645.1546, found 645.1541.

1-Cyclopropyl-2-(5-phenyl-1,4-ditosyl-2,3,4,5-tetrahydro-1H-benzo[4,5]thieno[3,2-e][1,4]diazepin-2-yl)ethan-1-one (5m)

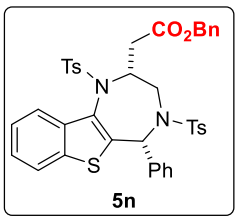


5m

According to the general procedure as described above, the reaction was carried out by using **1ca** (39.1 mg, 0.10 mmol), **2j** (33.5 mg, 0.12 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 85% total

yield (56.8 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **5m** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 215.7 – 216.2 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.06 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.0 Hz, 1H), 7.48 – 7.26 (m, 6H), 7.20 – 6.83 (m, 7H), 5.37 (s, 1H), 5.12 – 5.05 (m, 1H), 3.96 – 3.91 (m, 1H), 3.42 – 3.37 (m, 1H), 2.94 – 2.88 (m, 1H), 2.63 – 2.56 (m, 1H), 2.50 (s, 3H), 2.27 (s, 3H), 2.08 – 2.02 (m, 1H), 1.10 – 0.88 (m, 4H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 207.8, 144.1, 142.7, 141.2, 139.4, 139.0, 136.83, 136.80, 136.0, 130.2, 128.9, 128.8, 128.4, 127.9, 127.0, 125.9, 125.2, 125.0, 123.6, 121.7, 61.2, 57.2, 48.9, 47.6, 21.7, 21.3, 20.8, 11.8, 11.2. **HRMS (ESI)** m/z: calcd. for $C_{36}H_{34}N_2O_5S_3Na^+$ $(M + Na)^+$ 693.1522, found 693.1527.

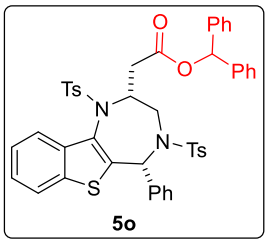
Benzyl 2-(5-phenyl-1,4-ditosyl-2,3,4,5-tetrahydro-1H-benzo[4,5]thieno[3,2-e][1,4]diazepin-2-yl)acetate (5n)



5n

According to the general procedure as described above, the reaction was carried out by using **1ca** (39.1 mg, 0.10 mmol), **2d** (41.4 mg, 0.12 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 85% total yield (62.3 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **5n** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 185.5 – 186.1 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.09 (d, J = 7.6 Hz, 1H), 7.78 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 7.6 Hz, 1H), 7.49 – 7.29 (m, 11H), 7.25 – 6.76 (m, 7H), 5.37 (s, 1H), 5.15 – 5.09 (m, 3H), 3.89 – 3.84 (m, 1H), 3.13 – 3.07 (m, 1H), 2.89 – 2.84 (m, 1H), 2.60 – 2.49 (m, 4H), 2.30 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 169.9, 144.1, 142.7, 141.1, 139.3, 139.0, 136.8, 136.7, 136.0, 135.4, 130.1, 128.9, 128.8, 128.59, 128.58, 128.4, 128.0, 126.9, 125.7, 125.2, 125.0, 123.8, 121.6, 67.0, 61.2, 57.7, 47.7, 39.6, 21.7, 21.3. **HRMS (ESI)** m/z: calcd. for $C_{40}H_{37}N_2O_6S_3^+$ $(M + H)^+$ 737.1808, found 737.1813.

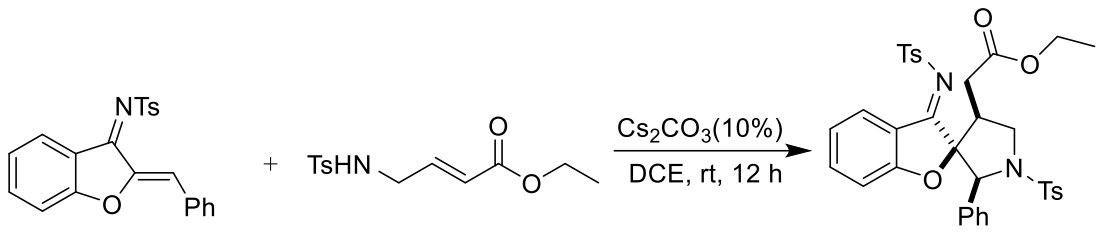
Benzhydryl 2-(5-phenyl-1,4-ditosyl-2,3,4,5-tetrahydro-1H-benzo[4,5]thieno[3,2-e][1,4]diazepin-2-yl)acetate (5o)



According to the general procedure as described above, the reaction was carried out by using **1ca** (39.1 mg, 0.10 mmol), **2e** (50.5 mg, 0.12 mmol), Cs_2CO_3 (3.3 mg, 0.01 mmol), giving the title compounds as a mixture of diastereoisomers in 58% total yield (46.8 mg) with > 20:1 *d.r.* (^{1}H NMR analysis of the crude product). The major diastereoisomer **5o** was isolated as a white solid after flash column chromatography on silica gel (PE:EtOAc:DCM = 5:1:1). M.p.: 188.1 – 188.8 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.97 – 7.95 (m, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.56 – 7.54 (m, 1H), 7.39 – 7.29 (m, 16H), 7.20 – 6.70 (m, 8H), 5.41 (s, 1H), 5.16 – 5.09 (m, 1H), 3.88 – 3.83 (m, 1H), 3.14 – 3.01 (m, 2H), 2.57 – 2.53 (m, 1H), 2.50 (s, 3H), 2.26 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 169.0, 144.1, 142.6, 141.2, 139.80, 139.75, 139.3, 138.9, 136.8, 136.7, 136.0, 130.1, 128.82, 128.75, 128.6, 128.5, 128.3, 128.1, 128.0, 127.9, 127.2, 127.0, 126.9, 125.7, 125.2, 125.1, 123.5, 121.7, 77.5, 61.2, 57.3, 47.5, 39.9, 21.7, 21.3. **HRMS (ESI)** m/z: calcd. for $C_{46}H_{41}N_2O_6S_3^+$ $(M + H)^+$ 813.2121, found 813.2134.

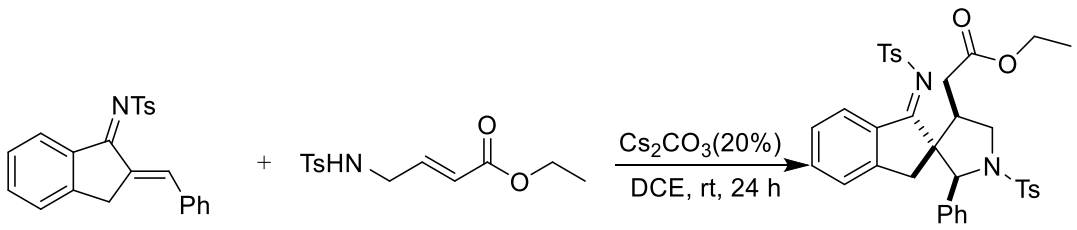
VI. Gram–Scale and Synthetic Manipulations

(a) Synthesis of 3o, 4l, 5a on gram–scale.



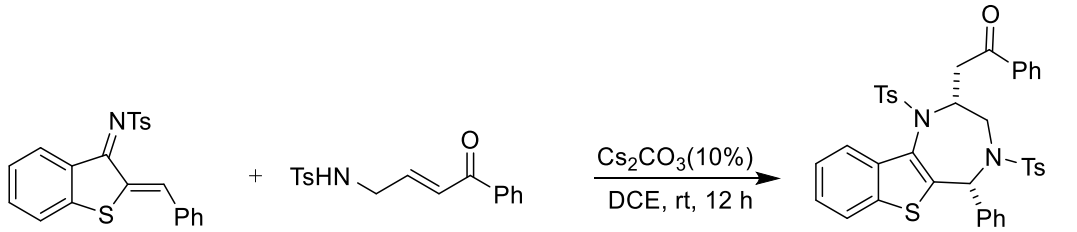
1aa, 1.80 g (4.8 mmol, 1.2 equiv) | **2b**, 1.13 g (4.0 mmol, 1.0 equiv) | **3o**, 1.89 g, 72%, 20:1 *d.r.*

To a stirred solution of benzofuran–derived azadiene **1aa** (1.80g, 4.8 mmol) and unsaturated esters **2b** (1.13g, 4.0 mmol) in DCE (40 mL) was added Cs_2CO_3 (130.4mg, 0.4 mmol) at room temperature for 12 h. The reaction mixture was purified via flash chromatography on silica gel (PE:EtOAc:DCM = 5:1:1 to afford product **3o** (1.89 g) in 72% yield with 20:1 *dr*.



1ba, 1.79 g (4.8 mmol, 1.2 equiv) | **2b**, 1.13 g (4.8 mmol, 1.0 equiv) | **4l**, 2.42 g, 92%, > 20:1 *d.r.*

To a stirred solution of indanone–derived azadiene **1ba** (1.79g, 4.8 mmol) and unsaturated esters **2b** (1.13g, 4.0 mmol) in DCE (40 mL) was added Cs_2CO_3 (260.8mg, 0.8 mmol) at room temperature for 24 h. The reaction mixture was purified via flash chromatography on silica gel (PE:EtOAc:DCM = 5:1:1 to afford product **4l** (2.42 g) in 92% yield with > 20:1 *d.r.*



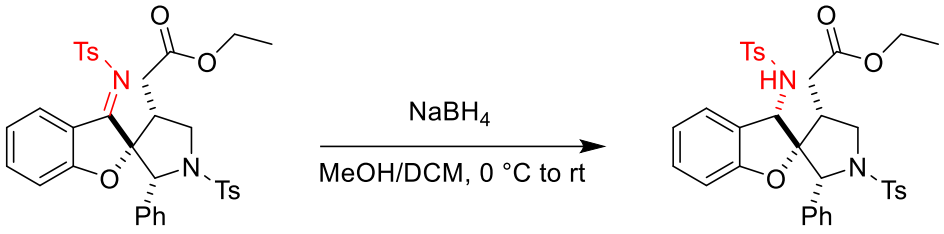
1ca, 0.78 g (2.0 mmol, 1.0 equiv) | **2c**, 0.76 g (2.4 mmol, 1.2 equiv) | **5a**, 1.14 g, 81%, > 20:1 *d.r.*

To a stirred solution of benzothiophene–derived azadiene **1ca** (0.78g, 2.0 mmol) and

unsaturated ketones **2c** (0.76g, 2.4 mmol) in DCE (20 mL) was added Cs_2CO_3 (65.2mg, 0.2 mmol) at room temperature for 12 h. The reaction mixture was purified via flash chromatography on silica gel (PE:EtOAc:DCM = 5:1:1 to afford product **5a** (1.14 g) in 81% yield with > 20:1 *d.r.*

(b) Synthetic manipulations of 6-10.

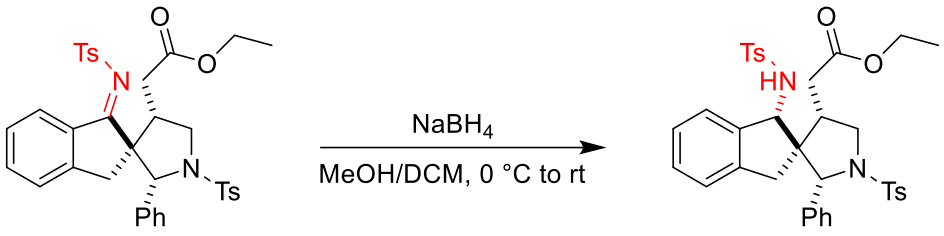
Ethyl 2-(3-((4-methylphenyl)sulfonamido)-2'-phenyl-1'-tosyl-3H-spiro[benzofuran-2,3'-pyrrolidin]-4'-yl)acetate (6)



3o **6**, 70%, 10:1 *d.r.*

According to the known procedure.[5] $NaBH_4$ (37.8mg, 1.0 mmol) were added to a solution of **3o** (65.8 mg, 0.1 mmol) in 2 mL MeOH/DCM (1:1) at 0 °C. The resulting reaction mixture was stirred at 0 ℃ for 5 min and then room temperature for 30 min. The reaction was quenched with saturated NH_4Cl (aq.) and the mixture was extracted with DCM. The combined organic phases were dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash column on silica gel (PE:EtOAc = 3:1) to afford a white solid **6** (46.4 mg, 70% yield, 10:1 *d.r.*). M.p.: 84.1 – 85.0 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.81 (d, J = 8.2 Hz, 2H), 7.68 (d, J = 8.2 Hz, 2H), 7.49 (d, J = 7.2 Hz, 2H), 7.38 – 7.32(m, 4H), 7.17 – 7.11 (m, 3H), 6.98 (t, J = 7.6 Hz, 1H), 6.57 – 6.54 (m, 2H), 6.12 (d, J = 7.6 Hz, 1H), 5.25 (s, 1H), 4.87 (d, J = 8.8 Hz, 1H), 4.64 (d, J = 8.8 Hz, 1H), 4.20 – 4.15 (m, 1H), 4.04 – 4.00 (m, 2H), 3.60 (t, J = 11.6 Hz, 1H), 2.47 (s, 3H), 2.44 (s, 3H), 2.39 – 2.35 (m, 1H), 2.23 – 2.12 (m, 2H), 1.17 (t, J = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 171.0, 157.6, 144.3, 143.5, 137.4, 136.2, 134.6, 130.8, 130.5, 130.1, 129.7, 127.61, 127.56, 127.5, 127.0, 124.2, 123.7, 121.3, 110.0, 96.2, 68.1, 60.8, 59.3, 53.0, 43.3, 30.7, 21.59, 21.56, 14.0. **HRMS (ESI)**: m/z calcd for $C_{35}H_{36}N_2O_7S_2Na^+$ $(M + Na)^+$ 683.1856, found 683.1851.

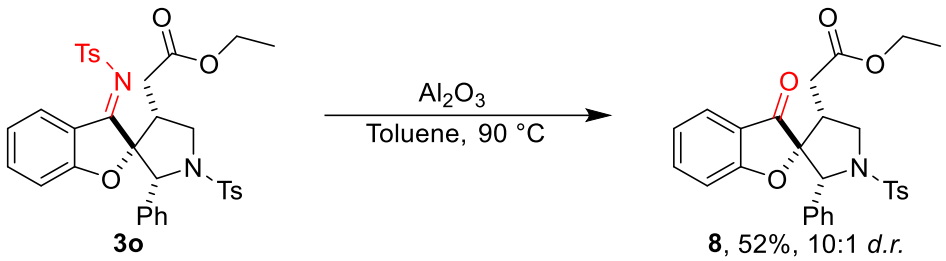
Ethyl 2-(1-((4-methylphenyl)sulfonamido)-2'-phenyl-1'-tosyl-1,3-dihydrospiro[indene-2,3'-pyrrolidin]-4'-yl)acetate (7)



4l **7**, 90%, > 20:1 *d.r.*

According to the known procedure.[5] $NaBH_4$ (37.8mg, 1.0 mmol) were added to a solution of **4l** (65.6 mg, 0.1 mmol) in 2 mL MeOH/DCM (1:1) at 0 °C. The resulting reaction mixture was stirred at 0 ℃ for 5 min and then room temperature for 30 min. The reaction was quenched with saturated NH_4Cl (aq.) and the mixture was extracted with DCM. The combined organic phases were dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash column on silica gel (PE:EtOAc = 3:1) to afford a white solid **6** (59.1 mg, 90% yield, > 20:1 *d.r.*). M.p.: 111.6 – 112.3 ^oC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 – 7.73 (m, 4H), 7.38 – 7.32 (m, 4H), 7.10 – 7.06 (m, 5H), 6.94 – 6.83 (m, 2H), 6.65 (d, J = 7.6 Hz, 1H), 6.17 (d, J = 7.6 Hz, 1H), 5.00 (s, 1H), 4.75 – 4.72 (m, 1H), 4.56 – 4.54 (m, 1H), 4.07 – 3.99 (m, 3H), 3.37 – 3.31 (m, 1H), 2.66 – 2.52 (m, 2H), 2.47 (s, 3H), 2.45 (s, 3H), 2.25 – 2.19 (m, 1H), 2.04 – 2.01 (m, 2H), 1.20 (t, J = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 171.1, 143.9, 143.7, 140.1, 139.9, 139.6, 137.7, 134.1, 130.0, 129.1, 128.6, 128.2, 127.8, 127.5, 127.2, 127.01, 126.98, 124.3, 122.5, 67.6, 64.3, 61.4, 60.7, 53.1, 40.9, 33.7, 33.3, 21.60, 21.58, 14.1. **HRMS (ESI)**: m/z calcd for $C_{36}H_{38}N_2O_6S_2Na^+$ $(M + Na)^+$ 681.2063, found 681.2068.

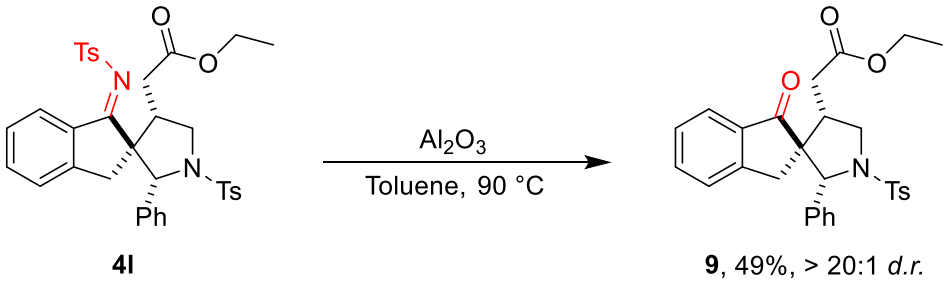
Ethyl 2-(3-oxo-2'-phenyl-1'-tosyl-3H-spiro[benzofuran-2,3'-pyrrolidin]-4'-yl)acetate (8)



3o **8**, 52%, 10:1 *d.r.*

According to the known procedure.[6] A solution of **3o** (65.8 mg, 0.1 mmol) in Toluene (2 mL) was added Al_2O_3 (816 mg, 8 mmol), The solution was stirred at 90 °C about 5 hours. After the reaction was completed as monitored by TLC, the solvent was removed under vacuum and the residue was purified by flash chromatography on silica gel(PE:EtOAc = 3:1) to afford a white solid **8** (26.4 mg, 52% yield, 10:1 *d.r.*). M.p.: 172.5 – 173.2 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (d, J = 8.0 Hz, 2H), 7.49 – 7.38 (m, 4H), 7.17 – 7.08 (m, 5H), 6.94 (t, J = 7.6 Hz, 1H), 6.77 (d, J = 8.4 Hz, 1H), 4.94 (s, 1H), 4.34 – 4.29 (m, 1H), 3.99 – 3.94 (m, 2H), 3.65 (t, J = 12.0 Hz, 1H), 2.62 – 2.54 (m, 1H), 2.48 (s, 3H), 2.30 – 2.23 (m, 1H), 2.10 – 2.05 (m, 1H), 1.12 (t, J = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 197.7, 171.2, 170.4, 144.2, 138.6, 134.2, 133.7, 129.9, 128.0, 127.8, 127.6, 127.4, 123.9, 122.3, 121.3, 112.8, 96.0, 71.7, 60.9, 53.8, 41.9, 30.7, 21.7, 14.0. **HRMS (ESI)**: m/z calcd for $C_{28}H_{28}NO_6S^+$ $(M + H)^+$ 506.1632, found 506.1627.

Ethyl 2-(1-oxo-2'-phenyl-1'-tosyl-1,3-dihydrospiro[indene-2,3'-pyrrolidin]-4'-yl)acetate (9)

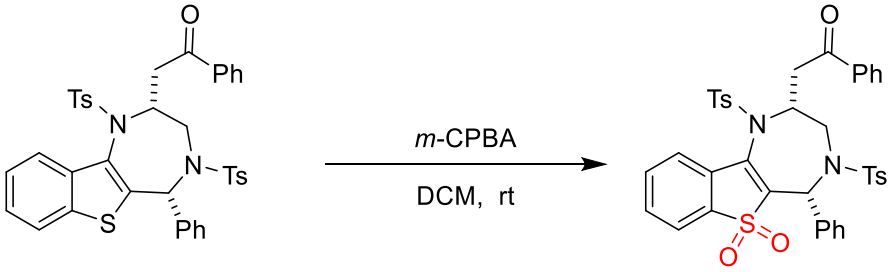


4l **9**, 49%, > 20:1 *d.r.*

According to the known procedure.[6] A solution of **4m** (65.8 mg, 0.1 mmol) in Toluene (2 mL) was added Al_2O_3 (816 mg, 8 mmol), The solution was stirred at 90 °C about 5 hours. After the reaction was completed as monitored by TLC, the solvent was removed under vacuum and the residue was purified by flash

chromatography on silica gel(PE:EtOAc = 3:1) to afford a white solid **9** (24.5 mg, 49% yield, > 20:1 *d.r.*). M.p.: 55.2 – 55.9 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 7.6 Hz, 1H), 7.48 – 7.42 (m, 3H), 7.30 – 7.26 (m, 3H), 7.19 – 7.06 (m, 4H), 5.13 (s, 1H), 4.22 – 4.17 (m, 1H), 3.99 – 3.89 (m, 2H), 3.36 (t, J = 12.0 Hz, 1H), 2.82 – 2.72 (m, 2H), 2.49 (s, 3H), 2.32 – 2.25 (m, 1H), 2.05 – 1.98 (m, 1H), 1.85 – 1.80 (m, 1H), 1.11 (t, J = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 204.8, 170.4, 152.6, 144.1, 137.8, 136.2, 135.6, 133.2, 129.9, 128.2, 128.1, 127.7, 127.6, 126.1, 123.9, 70.7, 63.5, 60.8, 54.1, 42.7, 31.6, 29.7, 21.7, 14.0. **HRMS (ESI)**: m/z calcd for $C_{29}H_{30}NO_5S^+$ $(M + H)^+$ 504.1839, found 504.1830.

2-(6,6-dioxido-5-phenyl-1,4-ditosyl-2,3,4,5-tetrahydro-1H-benzo[4,5]thieno[3,2-e][1,4]diazepin-2-yl)-1-phenylethan-1-one (10)



5a **10**, 88%, > 20:1 *d.r.*

According to the known procedure.[7] *m*-CPBA (43.1mg, 0.25 mmol) were added to a solution of **5a** (70.6 mg, 0.1 mmol) in 2 mL DCM at 0 °C. The resulting reaction mixture was stirred at 0 °C for 5 min and then room temperature for 6 h. The reaction was quenched with saturated $NaHCO_3$ (aq.) and the mixture was extracted with DCM. The combined organic phases were dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash column on silica gel (PE:EtOAc:DCM = 5:1:1) to afford a white solid **10** (64.6 mg, 88% yield, > 20:1 *d.r.*). M.p.: 227.2 – 227.9 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.95 – 7.88 (m, 4H), 7.74 – 7.51 (m, 10H), 7.13 – 6.95 (m, 4H), 6.86 – 6.79 (m, 4H), 5.44 (s, 1H), 4.95 – 4.90 (m, 1H), 3.93 – 3.88 (m, 1H), 3.68 – 3.59 (m, 2H), 3.48 – 3.41 (m, 1H), 2.52 (s, 3H), 2.25 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 196.8, 145.6, 142.9, 136.8, 136.6, 136.4, 136.1, 135.2, 134.1, 133.8, 133.0, 132.1, 130.7, 130.4, 129.2, 128.9, 128.8, 128.2, 128.1,

127.0, 125.4, 120.3, 59.8, 58.4, 47.2, 43.2, 21.8, 21.3. **HRMS (ESI)**: m/z calcd for $C_{36}H_{35}N_2O_7S_3^+$ $(M + H)^+$ 739.1601, found 739.1614.

VII. References

1. (a) Wang, Y.; Yang, L.; Rong, Z.; Liu, T.; Liu, R.; Zhao, Y. Pd-Catalyzed Enantioselective [6+4] Cycloaddition of Vinyl Oxetanes with Azadienes to Access Ten-Membered Heterocycles. *Angew. Chem. Int. Ed*. **2018**, *57*, 1596 – 1600. (b) Yan, J.; Li, X.; Chen, Y.; Li, Y.; Chen, W.; Zhan, R; Huang H. Organocatalytic 1,4-Addition of Azadienes with 3-Homoacyl Coumarins toward Highly Enantioenriched Benzofuran Coumarin Skeletons. *J. Org. Chem*. **2020**, *85*, 12175−12186. (c) Huang, Y.; Tan, M.; Wang, N.; Zhang, Y.; Yao, H.; Xiao, X.; Huang, N.; Zhou, K. Highly Regio- and Diastereoselective Phosphine-Catalyzed [2 + 4] Annulation of Benzofuran Derived Azadienes with Allyl Carbonates: Access to Spiro[benzofuran-cyclohexanes]. *J. Org. Chem*. **2023**, *88*, 13030−13041. (d) Shi, B.; Xiao, M.; Zhao, J.; Zhang, Z.; Xiao, W.; Lu, L. Synthesis of Chiral Endocyclic Allenes and Alkynes via Pd-Catalyzed Asymmetric Higher-Order Dipolar Cycloaddition. *J. Am. Chem. Soc*. **2024**, *146*, 26622−26629.
2. (a) Midya, S. P.; Gopi, E.; Satam, N.; Namboothiri, I. N. N. Synthesis of Fused Cyanopyrroles and Spirocyclopropanes via Addition of N-Ylides to Chalconimines. *Org. Biomol. Chem*. **2017**, *15*, 3616–3627. (b) Marques, A. S.; Duhail, T.; Marrot, J.; Chataigner, I.; Coeffard, V.; Vincent, G.; Moreau, X. A Fused Hexacyclic Ring System: Diastereo Selective Polycyclization of 2,4-Dienals through an Interrupted iso-Nazarov Reaction. *Angew. Chem. Int. Ed*. **2019**, *58*, 9969–9973. (c) Li, J.; Liu, S.; Zhong, R;Yang, Y.; Xu, J.; Yang, J.; Ding, H. Cascade Cyclization of Azadienes with Difluoroenoxysilanes: A One-Pot Formal [4 + 2] Approach to Fluorinated Polyfused Heterocycles. *Org. Lett*. **2021**, *23*, 9526−9532. (d) Wang, W.; Wang, Y.; Zhao, X.;Yuan, W.; Zhang, L.; Meng, X. Construction of Spiro[4.5]decanes via Annulations of Azadienes with Nazarov Reagent and DFT Studies. *Asian J. Org. Chem*. **2023**, *12*, e202300152. (e) Li, L.; Liu, T.; Ren, W.; Wang, Y. Catalyst-Free and Atom-Economical [4+3] Cycloaddition of Azadienes with Cyclic Azomethine Imines for Facile Synthesis of 1,2,4-Triazepines. *Green Synth. Catal.* **2024**, *5*, 57–61.
3. (a) Yan, R.; Liu, B.; Xiao, Ben.; Du, W.; Chen, Y. Asymmetric (4 + 3) and (4 + 1) Annulations of Isatin-derived Morita−Baylis−Hillman Carbonates to Construct

Diverse Chiral Heterocyclic Frameworks. *Org. Lett*. **2020**, *22*, 4240−4244. (b) Zhang, G.; Yu, A.; Liu, Y.; Meng, X.; Zhang. L. Synthesis of Novel Pyridinium 1,5-Zwitterions and Their Reactivity with Isatin-Based α-(Trifluoromethyl)imines: a Sulfur-Controlled Domino Reaction. *Org. Chem. Front*., **2021**, *8*, 3718–3723. (c) Song, Y.; Zhang, G.; Zhang, Y.; Zhang, Y.; Zhang, H.; Meng, X.; Zhang, L. Leaving-Group Controlled N- or C-Cyclization of Azadienes via Domino Sequences: Synthesis, Mechanism, and Chemoselectivity. *Org. Chem. Front*. **2022**, *9*, 4598–4605.

4. (a) Fritz, S. P.; Matlock, J. V.; McGarrigle, E. M.; Aggarwal, V. K. Efficient Synthesis of Cyclopropane-Fused Heterocycles with Bromoethylsulfonium Salt. *Chem. Eur. J*. **2013**, *19*, 10827–10831. (b) Shi, W.; Zhou, L.; Mao, B.; Wang, C.; Zhang, C.; Li, X.; Xiao, Y.; Guo, H. Phosphine-Catalyzed [3+2] Annulation of *β*-Sulfonamido-Substituted Enones with Sulfamate-Derived Cyclic Imines. *J. Org. Chem*. **2019**, *84*, 679−686. (c) Maddigan-Wyatt, J. T.; Blyth, M. T.; Ametovski, J.; Coote, M. L.; Hooper, J. F.; Lupton, D. W. Redox Isomerization/(3+2) Allenoate Annulation by Auto-Tandem Phosphine Catalysis. *Chem. Eur. J*. **2021**, *27*, 16232–16236. (d) No, J.; Yun, Y. J.; Kim, S. G. Chemodivergent 1,3-Dipolar Cycloadditions of *C,N*-Cyclic Azomethine Imines with *γ*-Sulfonamido-*α,β*-Unsaturated Ketones to Synthesize Tricyclic Dinitrogen-Fused Heterocycles. *J. Org. Chem*. **2023**, *88*, 1772−1785.
5. Gao, Z.; Xie, L.; Ji, L.; Ma, X.; Li, X.; Liu, H.; Guo, H. Phosphine-Catalyzed [3 + 2] Annulation of *β*-Sulfonamido-Substituted Enones with trans-α-Cyano-α,β-Unsaturated Ketones for the Synthesis of Highly Substituted Pyrrolidines. *RSC Adv*. **2021**, *11*, 40136.
6. Li, S.; Dong, Z.-H.; Dan, S.-Y.; Zheng, M.-J.; Long, T.; Zhan, J.; Zhou, Q.; Chu, W-D.; Liu, Q.-Z. Asymmetric [3 + 2] Cycloaddition of Donor–Acceptor Cyclopropanes with Azadienes Enabled by Brønsted Base Catalysis. *Org. Chem. Front*. **2024**, *11*, 2905–2910.
7. Li, K.; Aimin, Y.; Meng, X. Synthesis of Dibenzothiophene and 1,4-Dihydrodibenzothiophene Derivatives via Allylic Phosphonium Salt Initiated Domino Reactions. *Org. Lett.* **2018**, *20*, 1106−1109.

VIII. X–Ray Crystallographic Analysis

Crystal Growth Method: 10 mg of **3o** was added in a HPLC vial and dissolved by 1.0 mL EA, closed the lid. Then put it in a large bottle, added PE to the same level of the liquid in the HPLC vial, tighten the lid, put it in a fume hood and waited for growth.

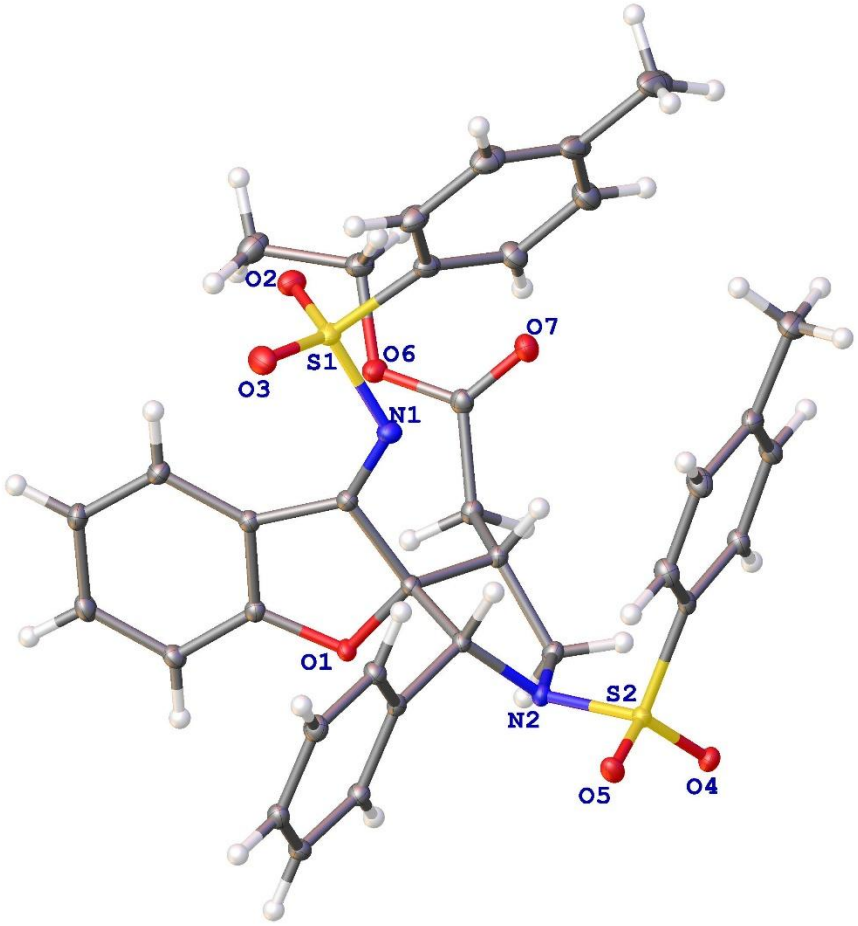


Figure S1. X–ray structure of **3o** (ellipsoid contour at 50% probability CCDC 2403335).

Crystal Growth Method: 10 mg of **4l** was added in a HPLC vial and dissolved by 1.0 mL DCM, closed the lid. Then put it in a large bottle, added PE to the same level of the liquid in the HPLC vial, tighten the lid, put it in a fume hood and waited for growth.

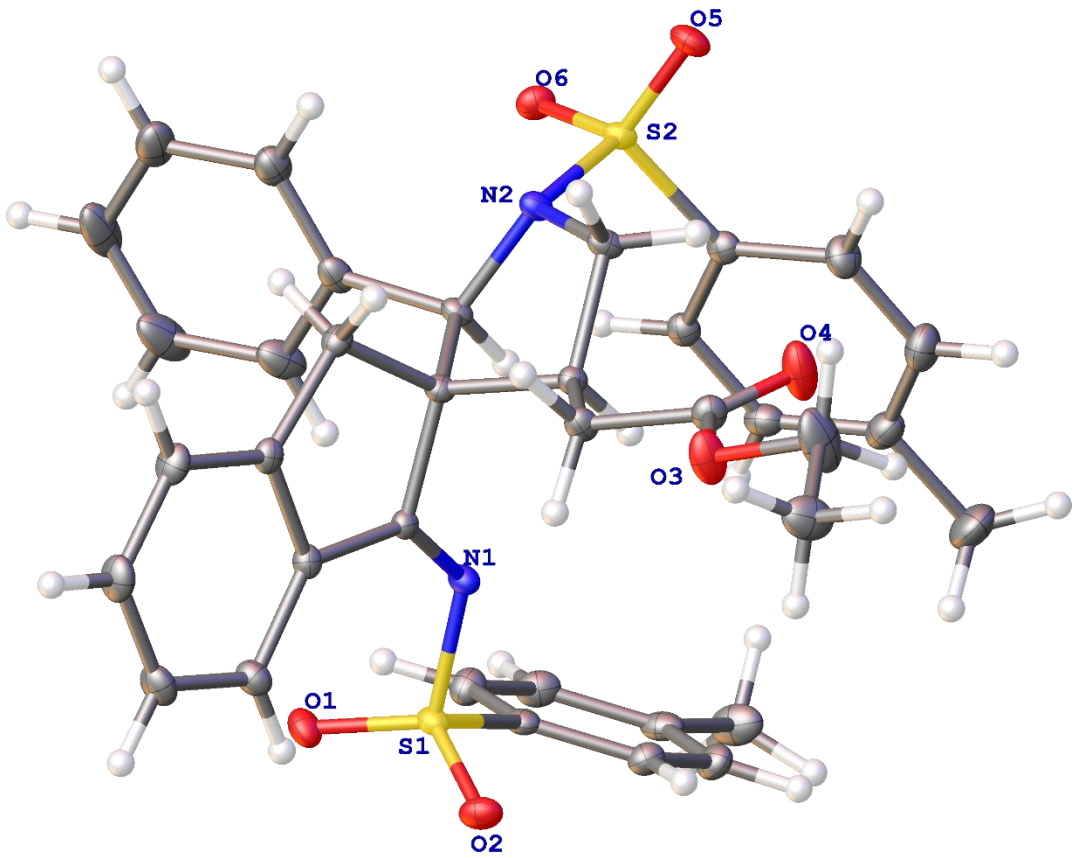


Figure S1. X–ray structure of **4l** (ellipsoid contour at 50% probability CCDC 2403336)

Crystal Growth Method: 6 mg of **5o** was added in a HPLC vial and dissolved by 1.0 mL DCM, closed the lid. Then put it in a large bottle, added PE to the same level of the liquid in the HPLC vial, tighten the lid, put it in a fume hood and waited for growth.

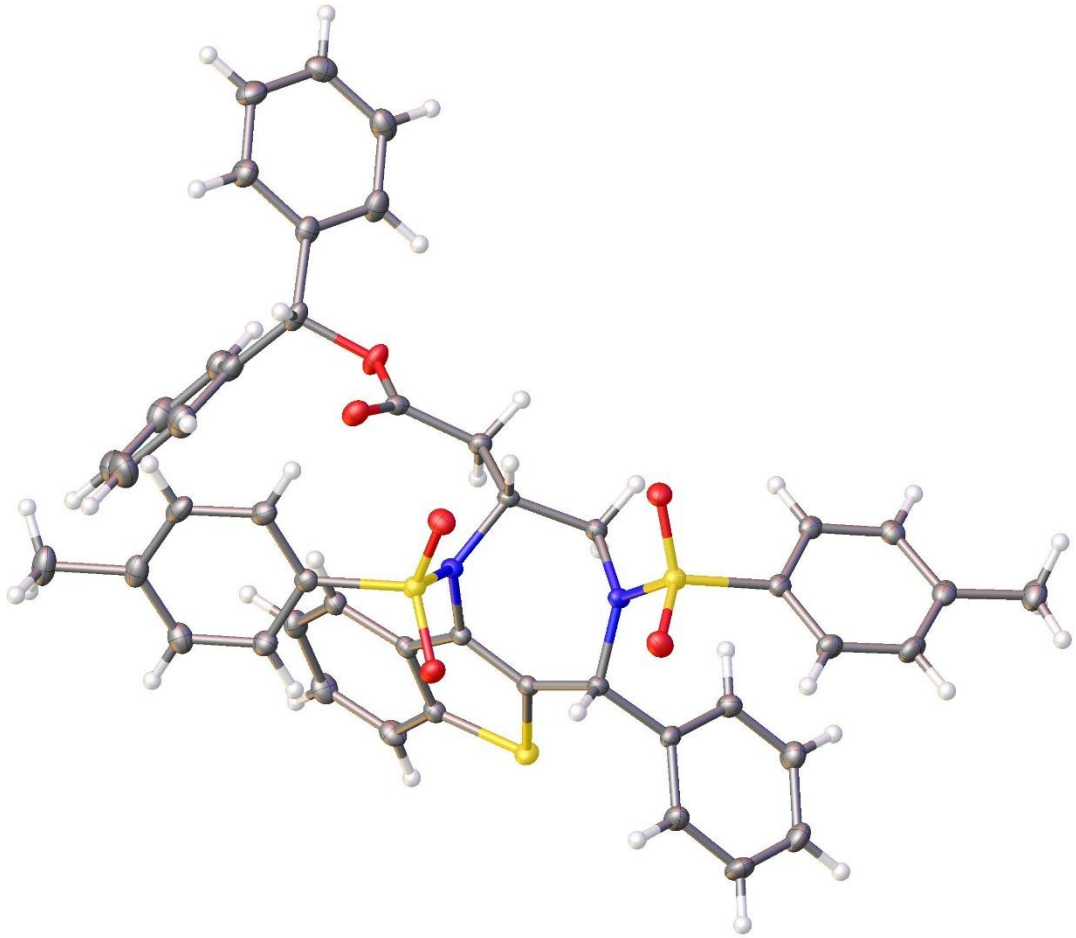


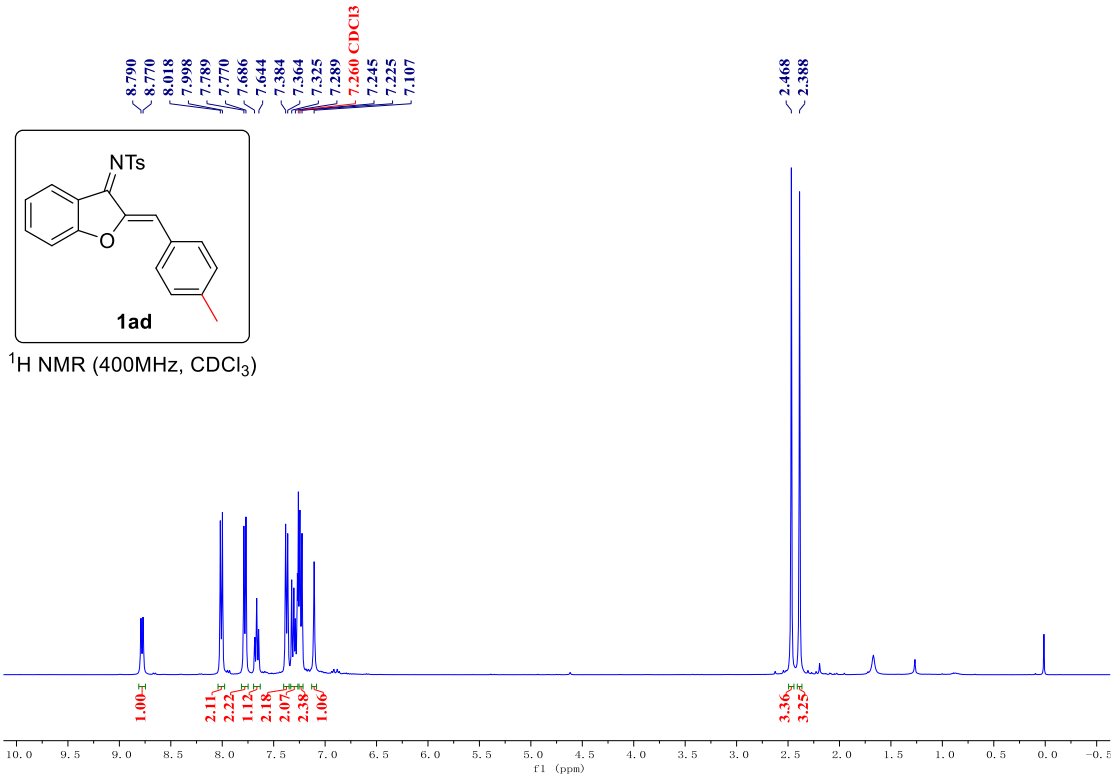
Figure S3. X–ray structure of **5o** (ellipsoid contour at 50% probability CCDC 2403337).

Table S1. Crystal data and structure refinement for **3o, 4l, 5o**.

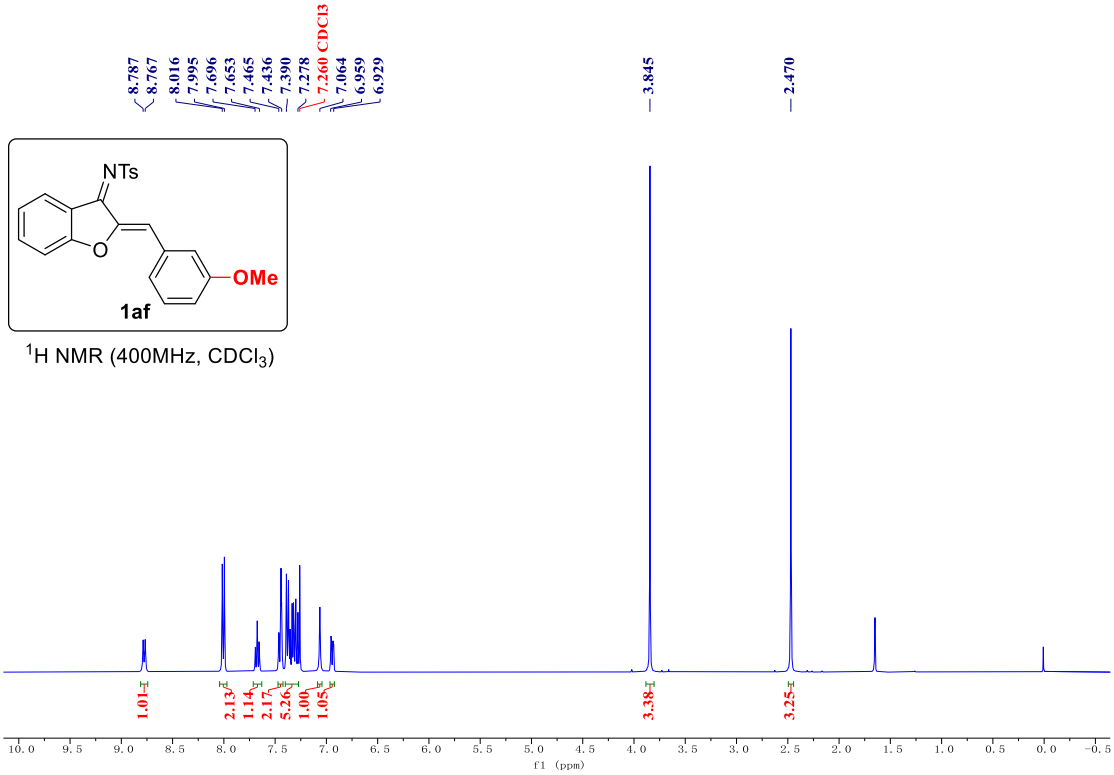
Identification code	**3o**	**4l**	**5o**
Empirical formula	$C_{35}H_{34}N_2O_7S_2$	$C_{36}H_{36}N_2O_6S_2$	$C_{46}H_{40}N_2O_6S_3$
Formula weight	658.76	656.79	812.20
Temperature/K	100.00(10)	99.98(10)	169.99(10)
Crystal system	triclinic	monoclinic	triclinic
Space group	P-1	$P2_1/c$	P-1
a/Å	9.0048(2)	10.6043(2)	10.1147(4)
b/Å	9.90340(10)	25.8400(5)	14.6674(7)
c/Å	17.6266(3)	13.0738(3)	16.0526(7)
α/°	83.5860(10)	90	105.603(4)
β/°	89.924(2)	112.814(2)	108.200(4)
γ/°	86.2460(10)	90	93.496(4)
Volume/$Å^3$	1558.69(5)	3302.16(13)	2151.46(17)
Z	2	4	2
$\rho_{calc}g/cm^3$	1.404	1.321	1.386
μ/mm^{-1}	1.999	1.862	0.349
F(000)	692.0	1384.0	936.0
Crystal size/mm^3	0.14 × 0.12 × 0.1	0.16 × 0.12 × 0.1	0.16 × 0.14 × 0.12
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.046 to 146.638	6.842 to 146.034	4.25 to 49.996
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 9, -21 ≤ l ≤ 21	-13 ≤ h ≤ 13, -30 ≤ k ≤ 31, -11 ≤ l ≤ 16	-12 ≤ h ≤ 11, -15 ≤ k ≤ 17, -18 ≤ l ≤ 19

Reflections collected	21278	28668	15418
Independent reflections	6050 [R_{int} = 0.0448, R_{sigma} = 0.0399]	6470 [R_{int} = 0.0504, R_{sigma} = 0.0326]	7570 [R_{int} = 0.0257, R_{sigma} = 0.0434]
Data/restraints/parameters	6050/0/418	6470/0/418	7570/0/543
Goodness – of – fit on F^2	1.057	1.073	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0442, wR_2 = 0.1266	R_1 = 0.0460, wR_2 = 0.1216	R_1 = 0.0510, wR_2 = 0.1106
Final R indexes [all data]	R_1 = 0.0470, wR_2 = 0.1288	R_1 = 0.0485, wR_2 = 0.1235	R_1 = 0.0624, wR_2 = 0.1185
Largest diff. peak/hole / e $Å^{-3}$	0.39/-0.72	0.56/-0.81	1.05/-0.86

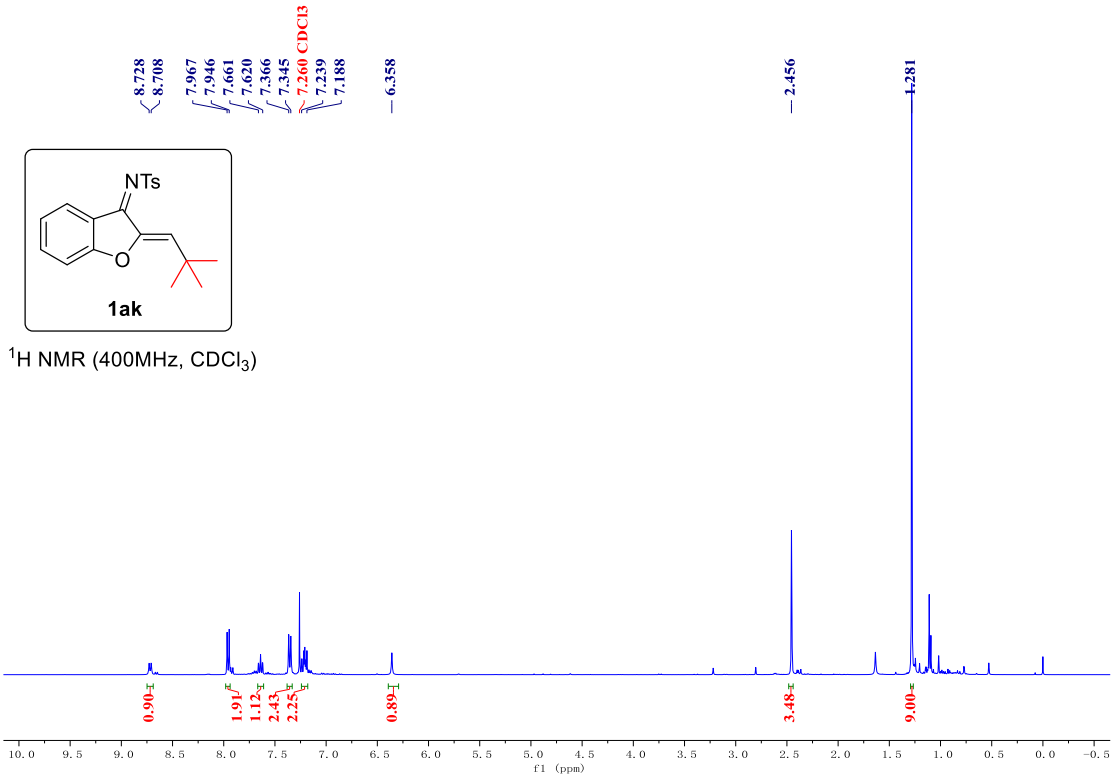
IX. Copies of ^{1}H, ^{19}F and ^{13}C NMR Spectra



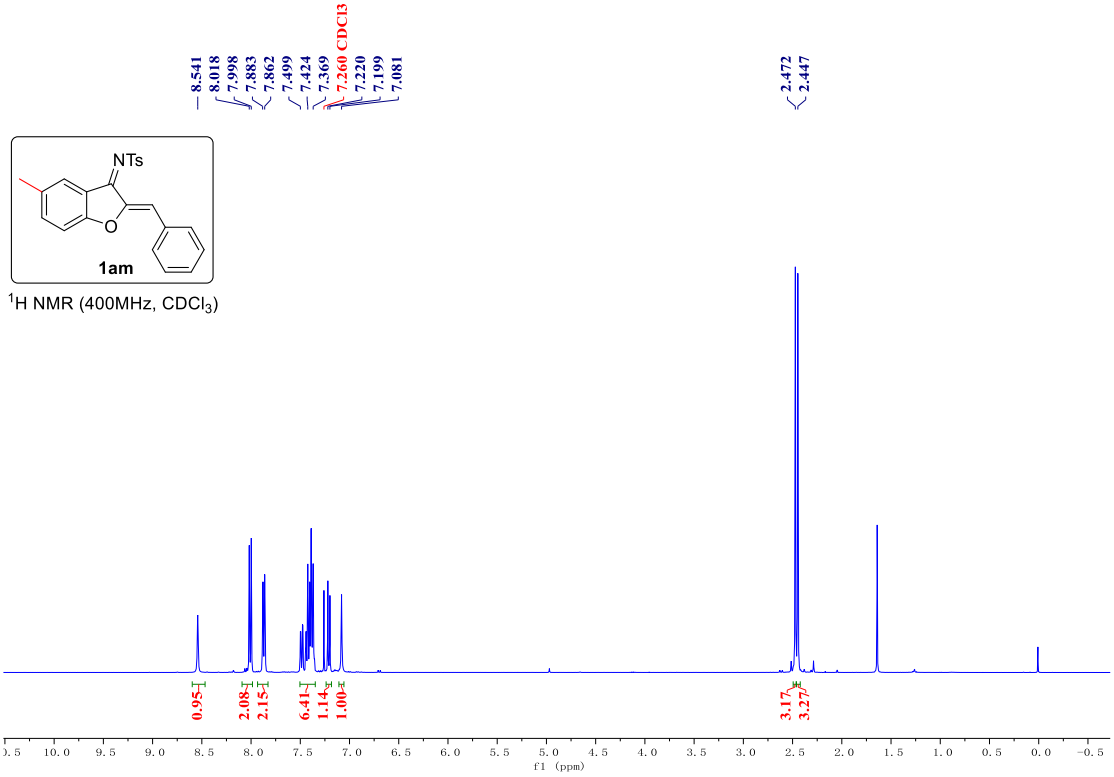
^{1}H NMR (400MHz, $CDCl_3$)



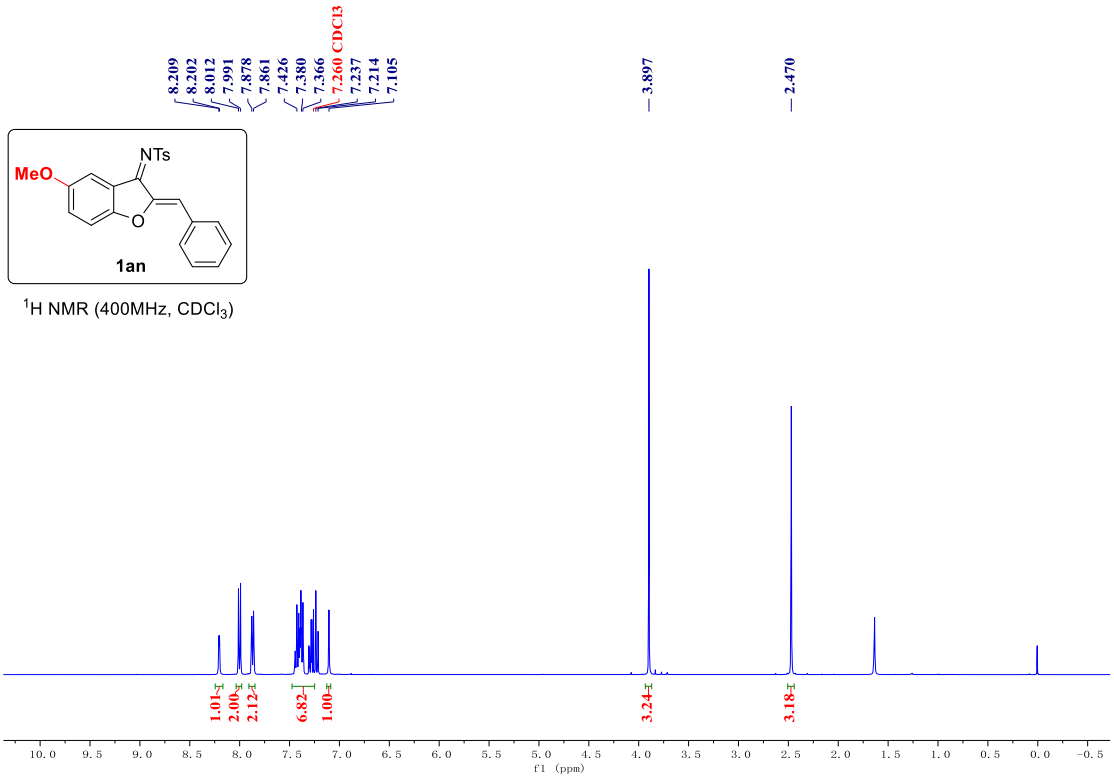
^{1}H NMR (400MHz, $CDCl_3$)

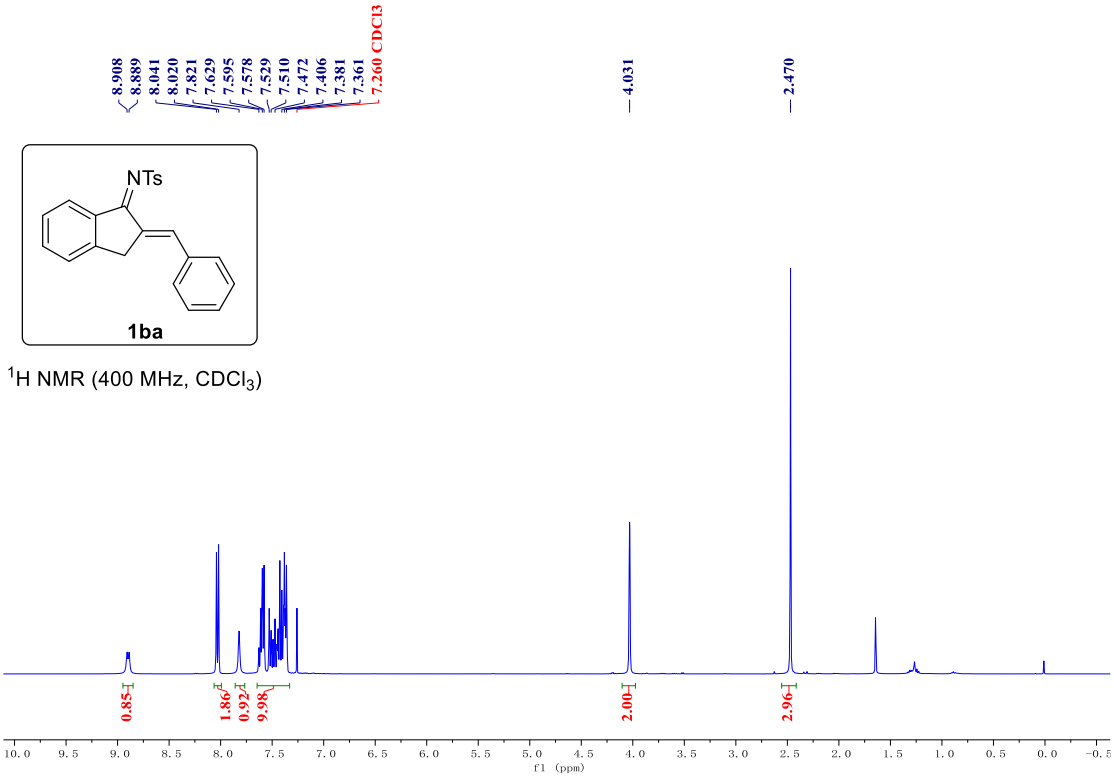


^{1}H NMR (400MHz, $CDCl_3$)

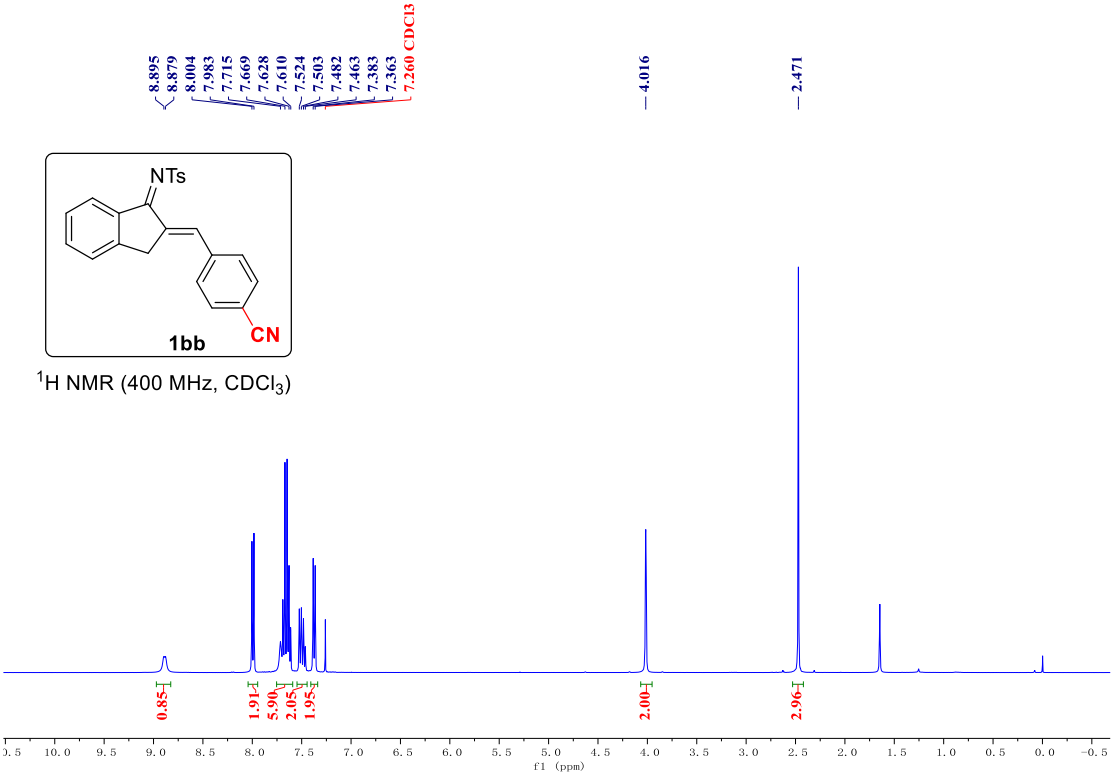


^{1}H NMR (400MHz, $CDCl_3$)

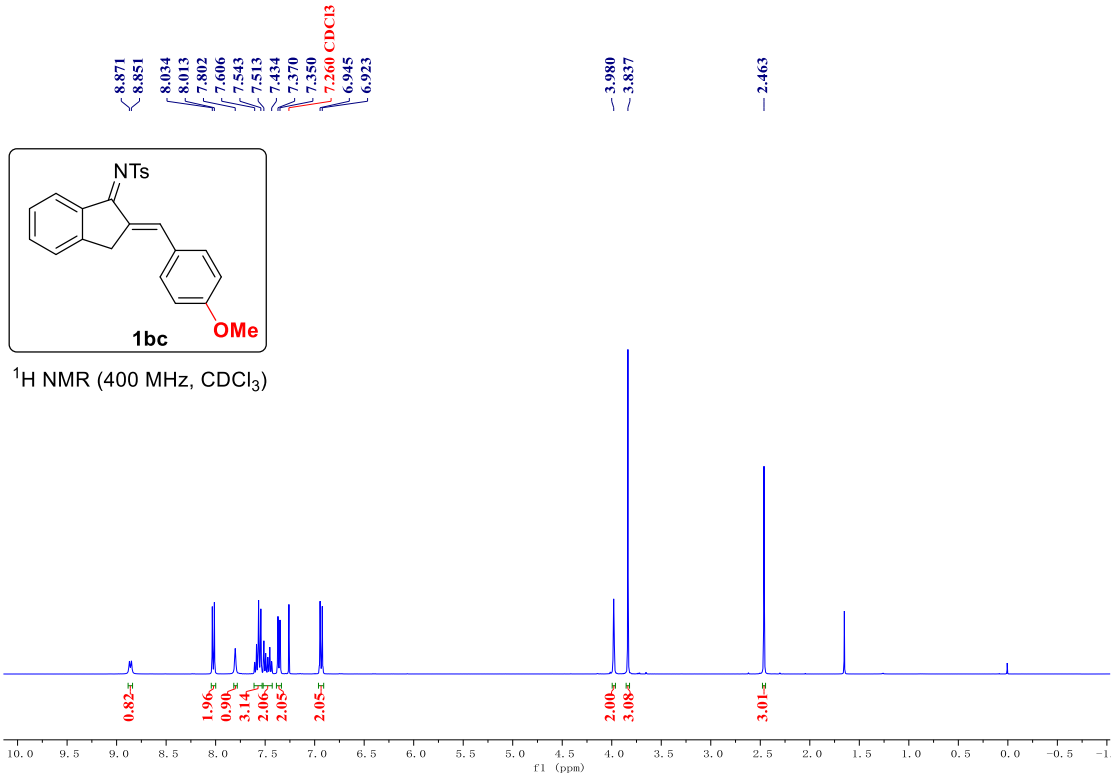

8.209
8.202
8.012
7.991
7.878
7.861
7.426
7.380
7.366
7.260 CDCl3
7.237
7.214
7.105
3.897
2.470
NTs
MeO
O
1an
1H NMR (400MHz, CDCl3)
1.01
2.00
2.12
6.82
1.00
3.24
3.18
f1 (ppm)



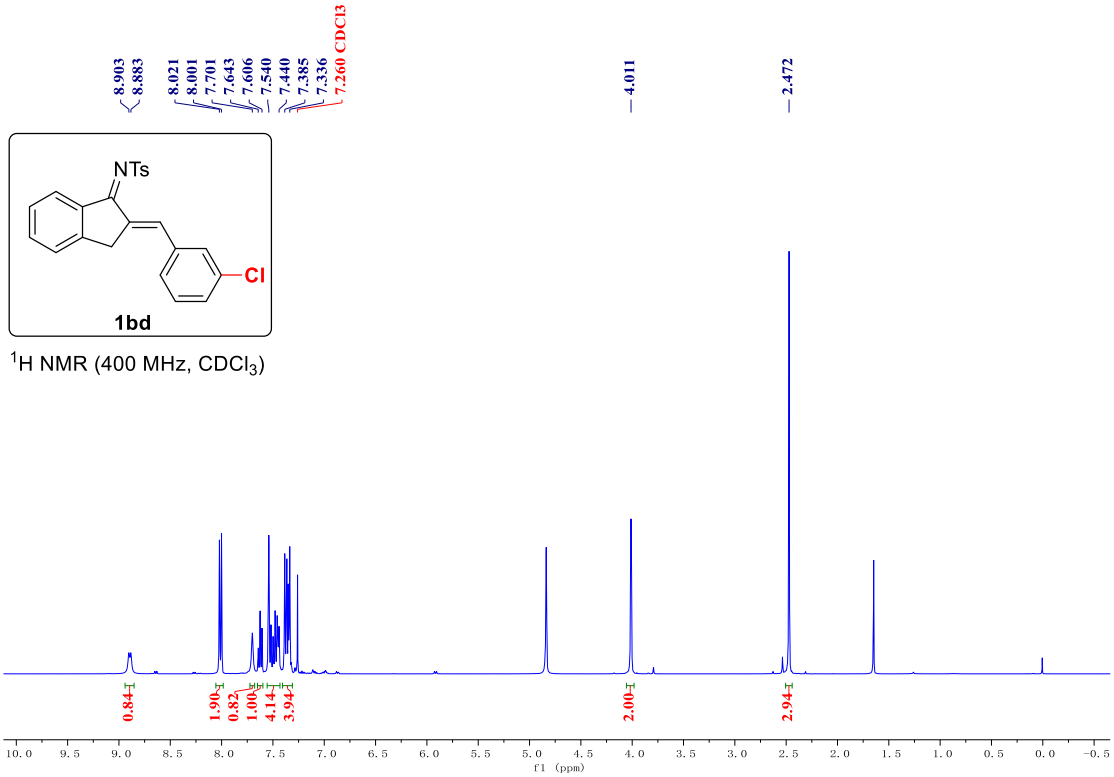
^{1}H NMR (400 MHz, $CDCl_3$)



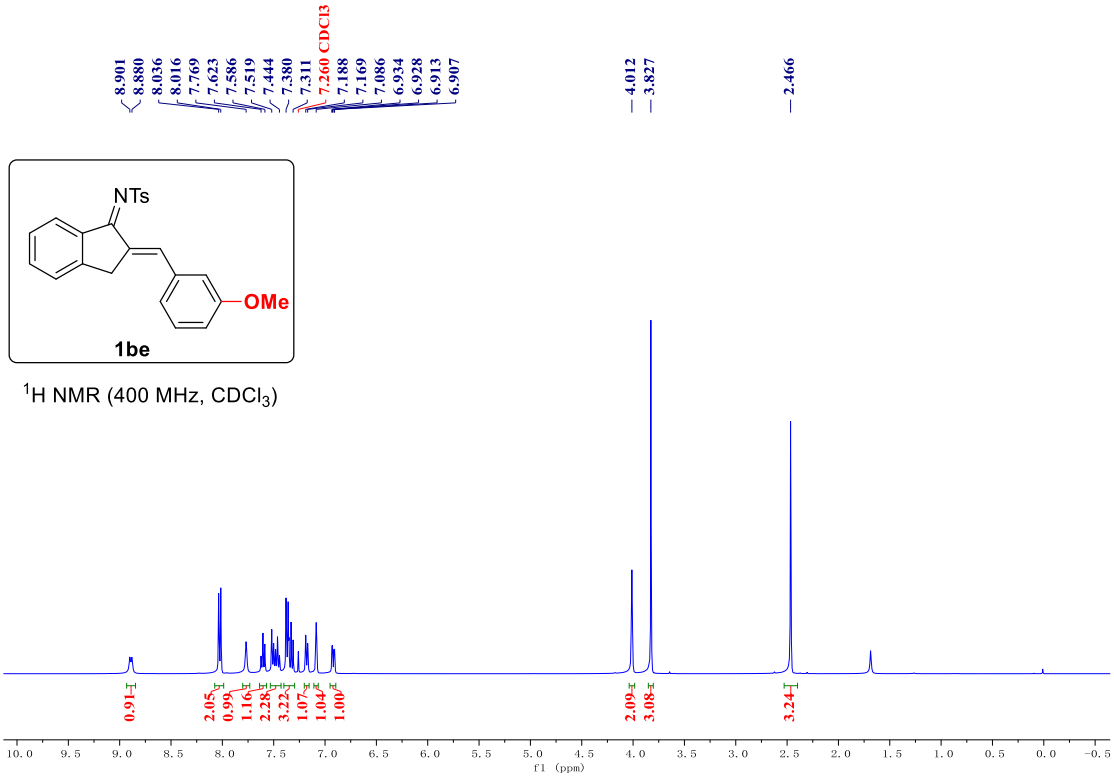
^{1}H NMR (400 MHz, $CDCl_3$)



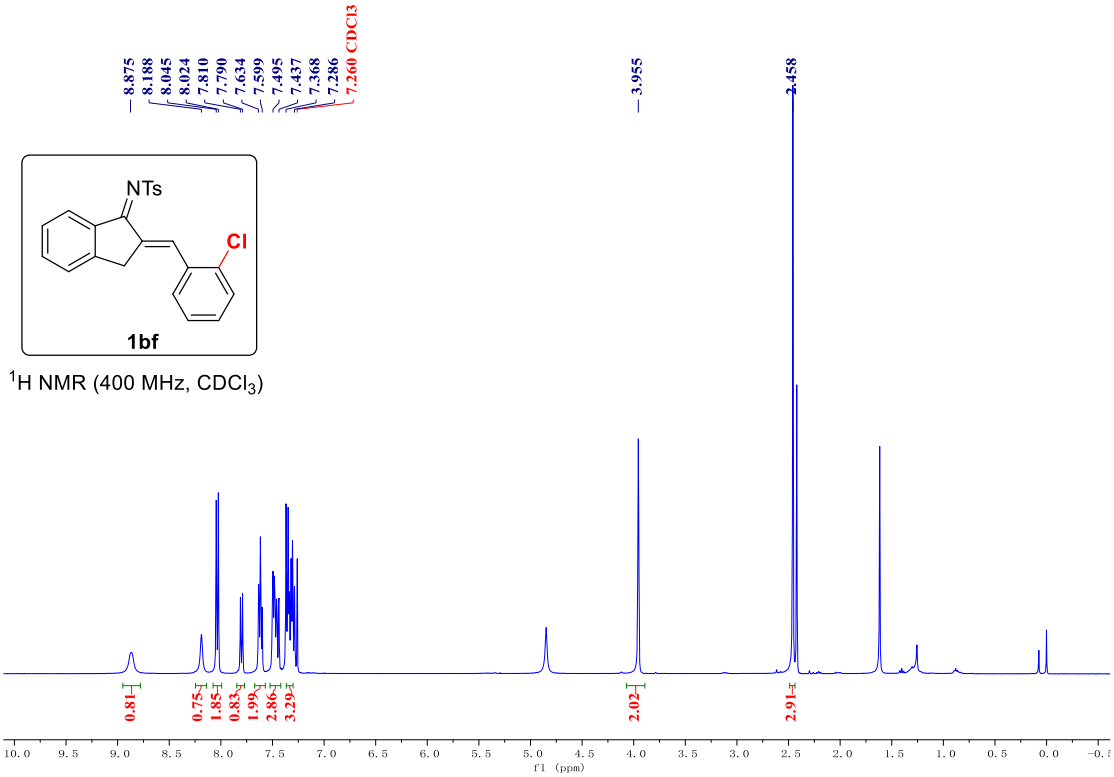
^{1}H NMR (400 MHz, $CDCl_3$)



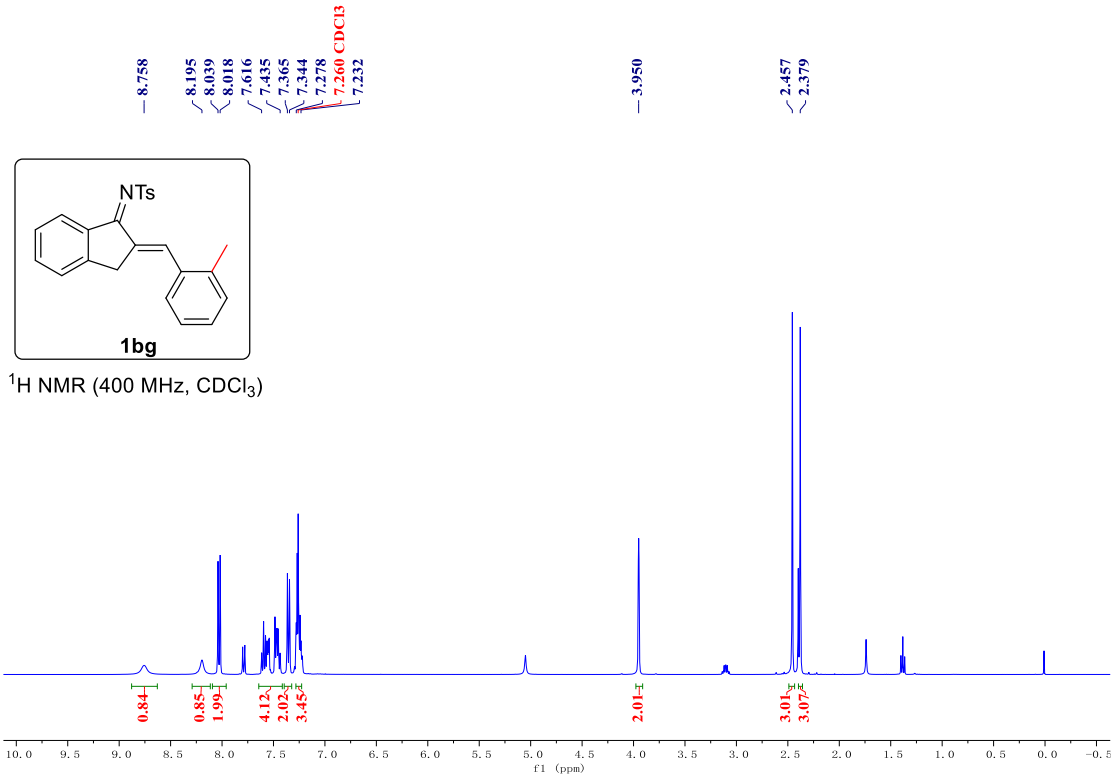
^{1}H NMR (400 MHz, $CDCl_3$)



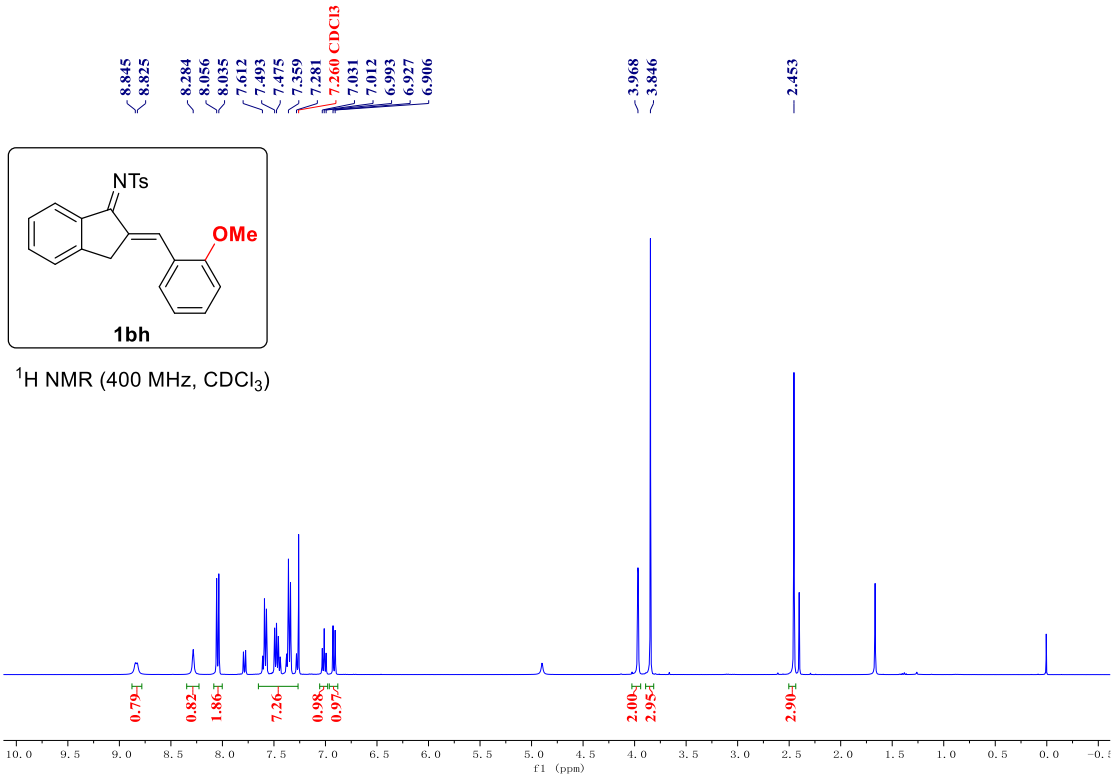
^{1}H NMR (400 MHz, $CDCl_3$)



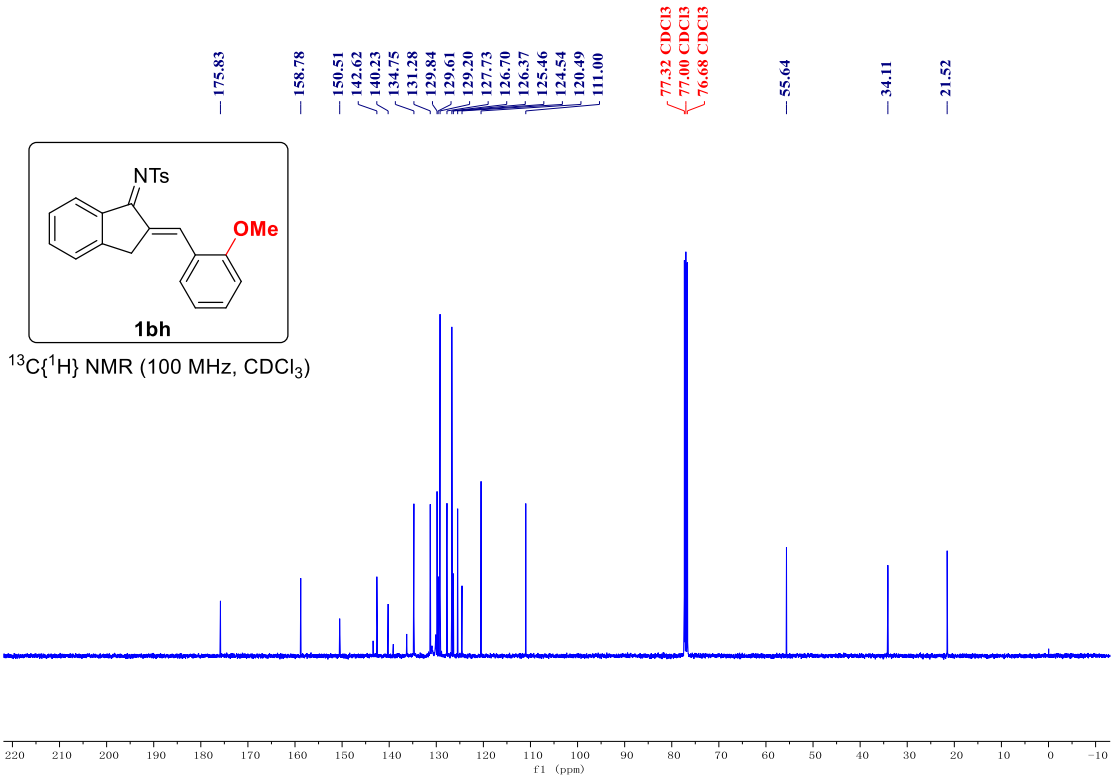
^{1}H NMR (400 MHz, $CDCl_3$)



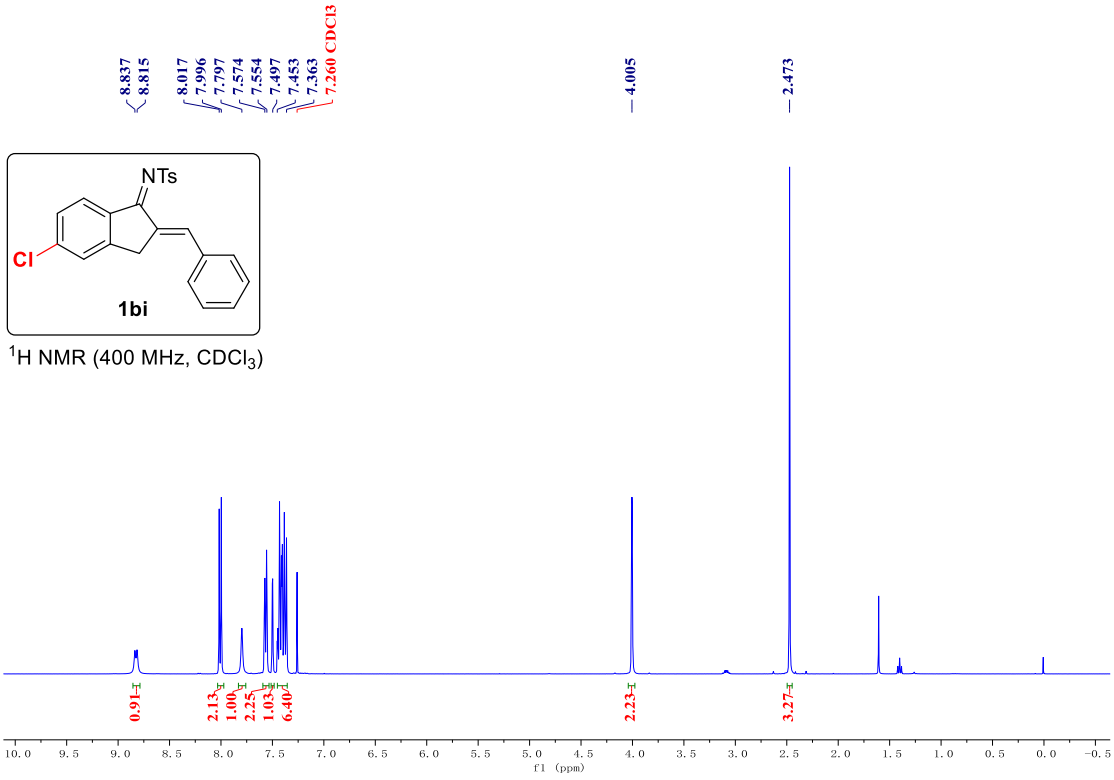
^{1}H NMR (400 MHz, $CDCl_3$)



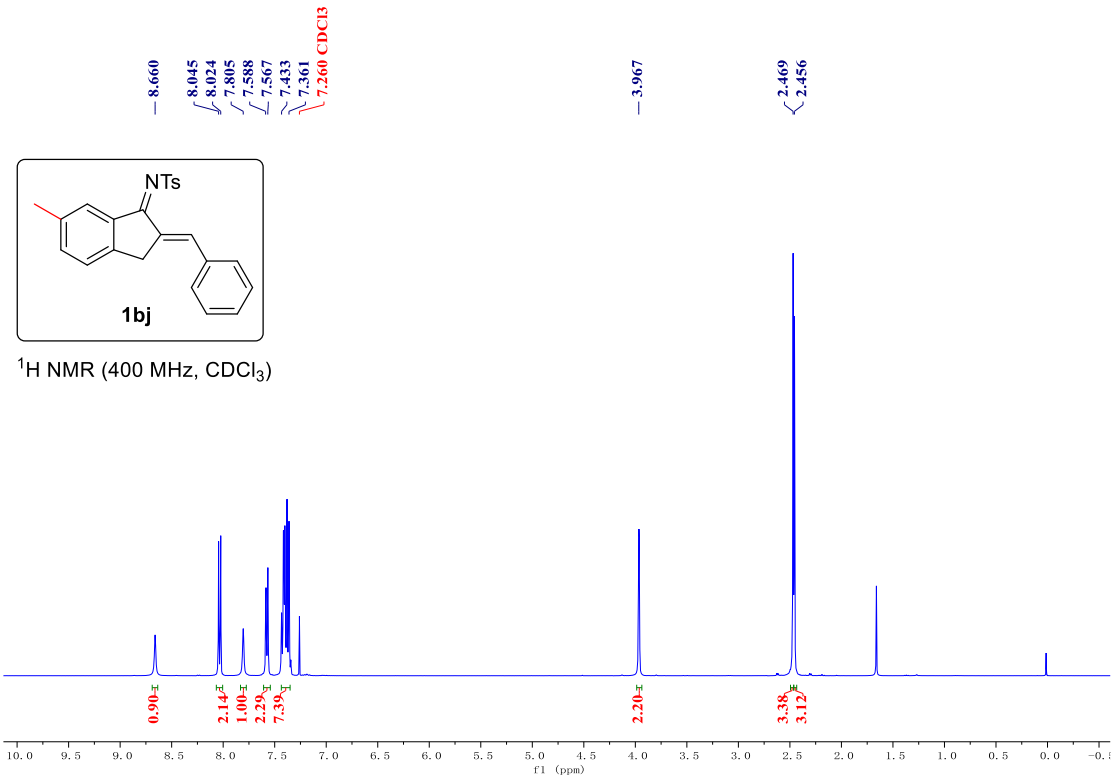
^{1}H NMR (400 MHz, $CDCl_3$)



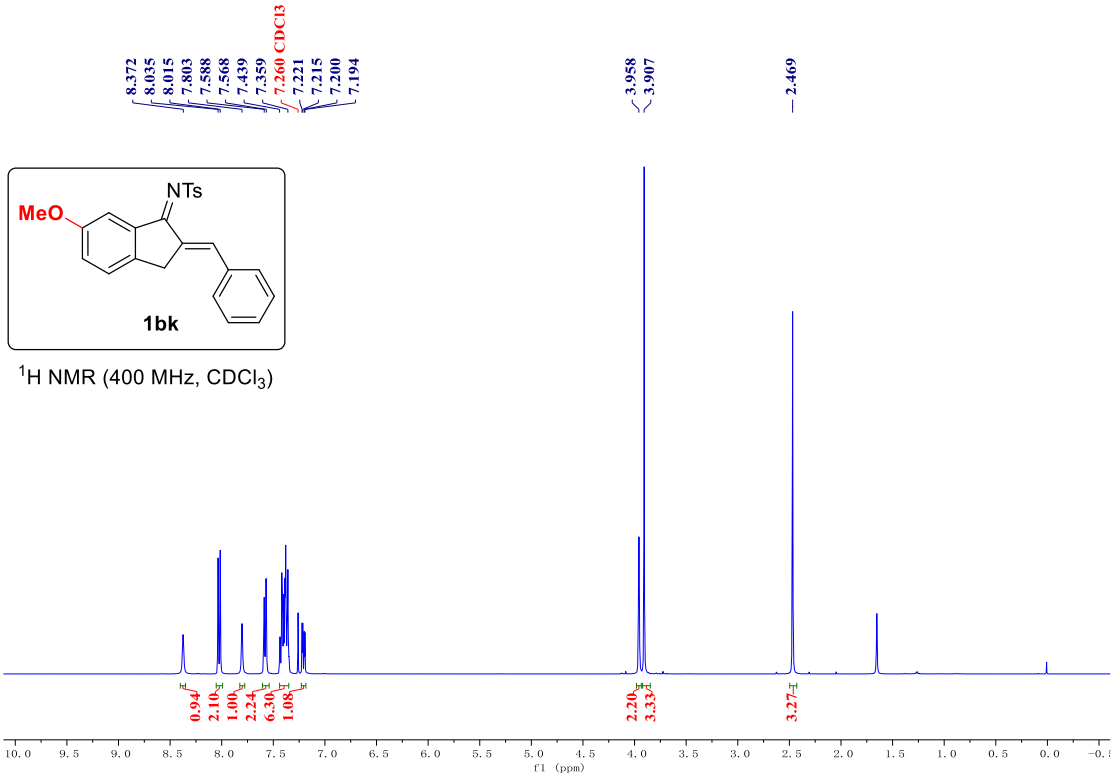
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



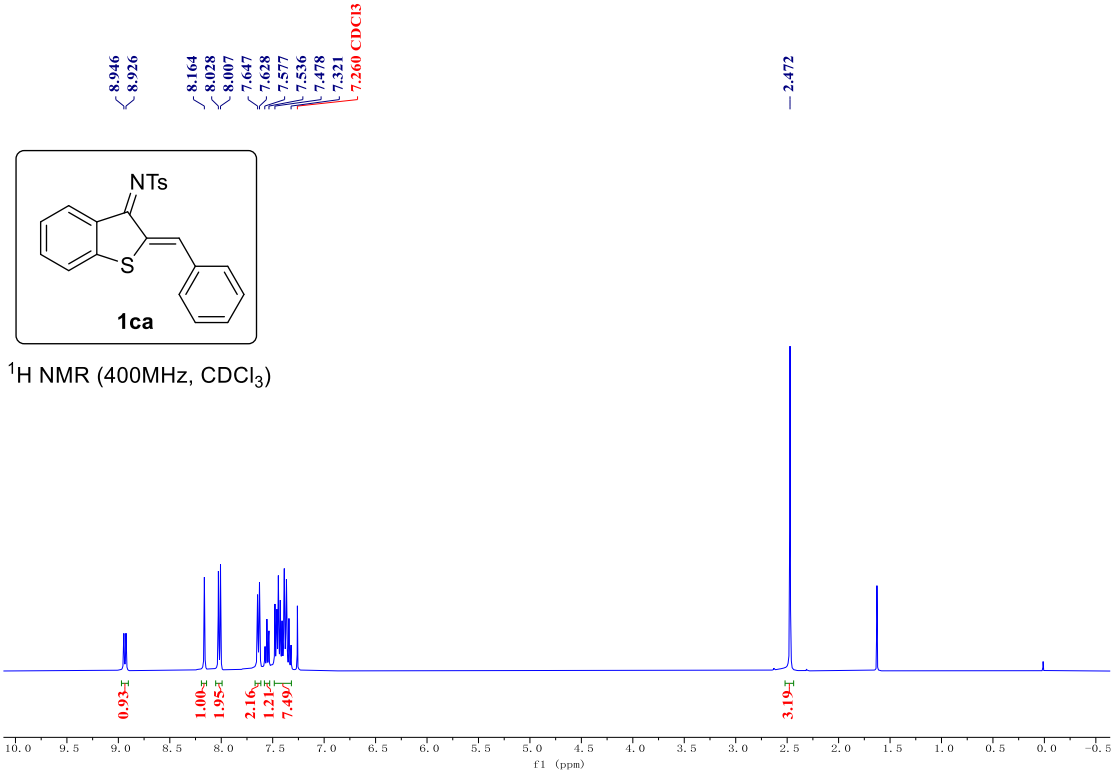
^{1}H NMR (400 MHz, $CDCl_3$)



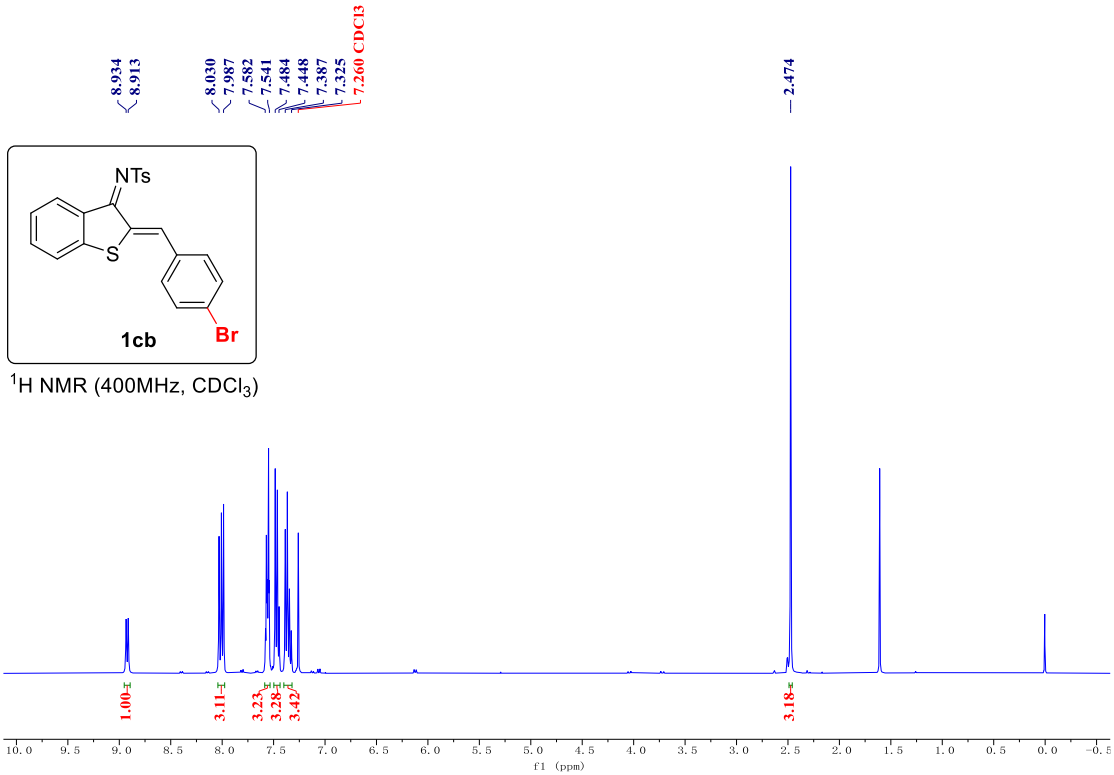
^{1}H NMR (400 MHz, $CDCl_3$)



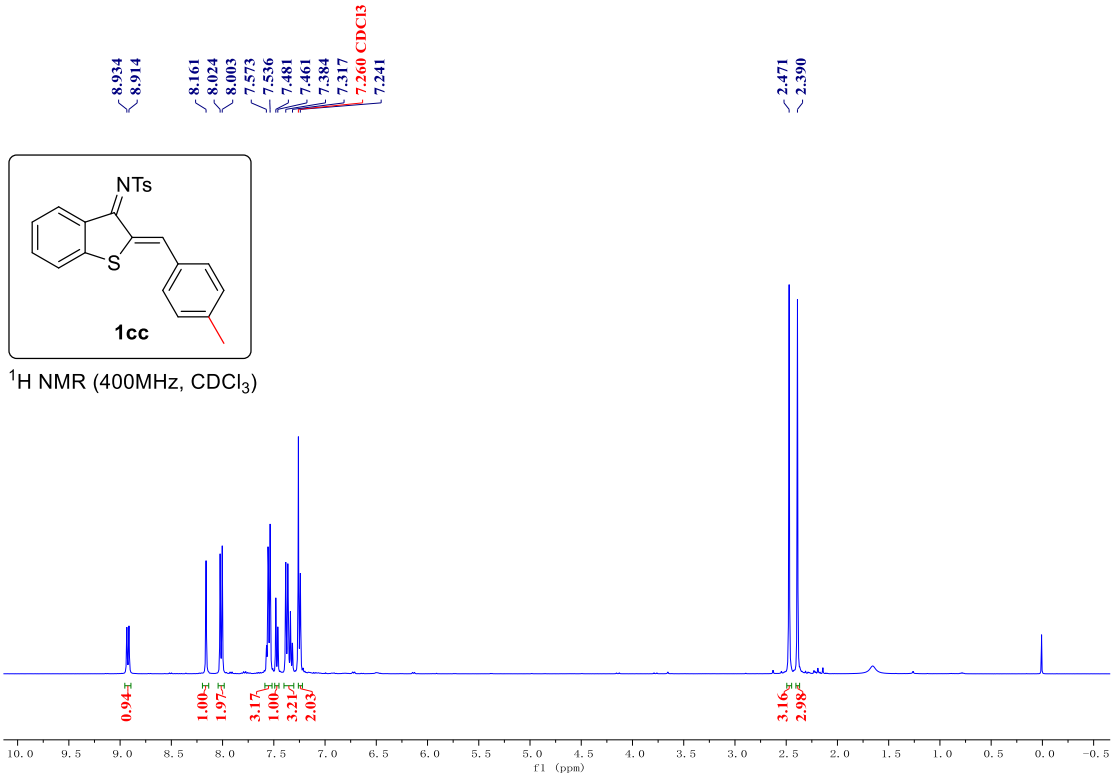
^{1}H NMR (400 MHz, $CDCl_3$)



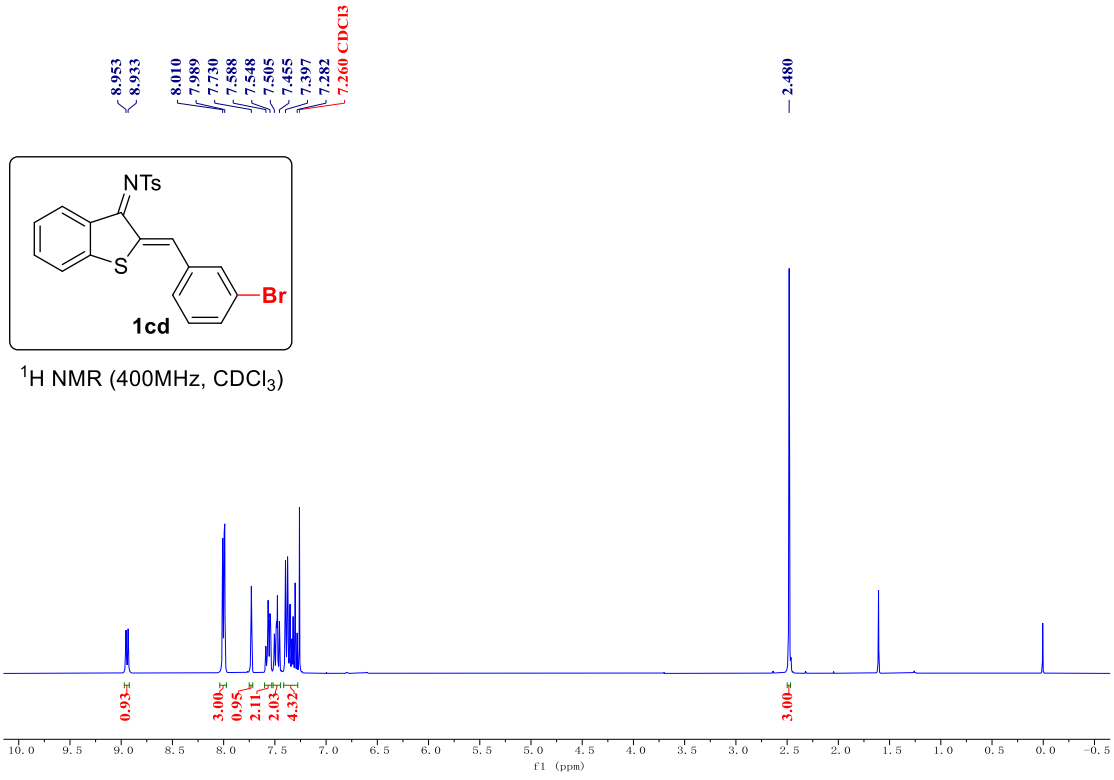
^{1}H NMR (400MHz, $CDCl_3$)



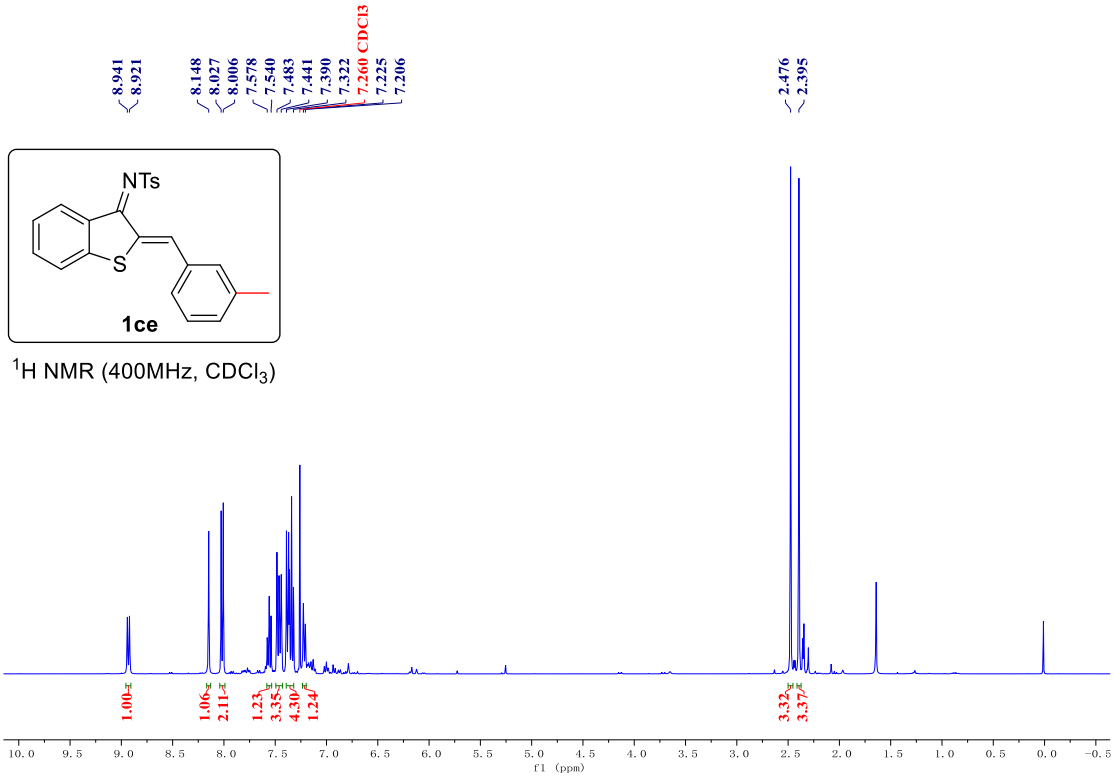
^{1}H NMR (400MHz, $CDCl_3$)

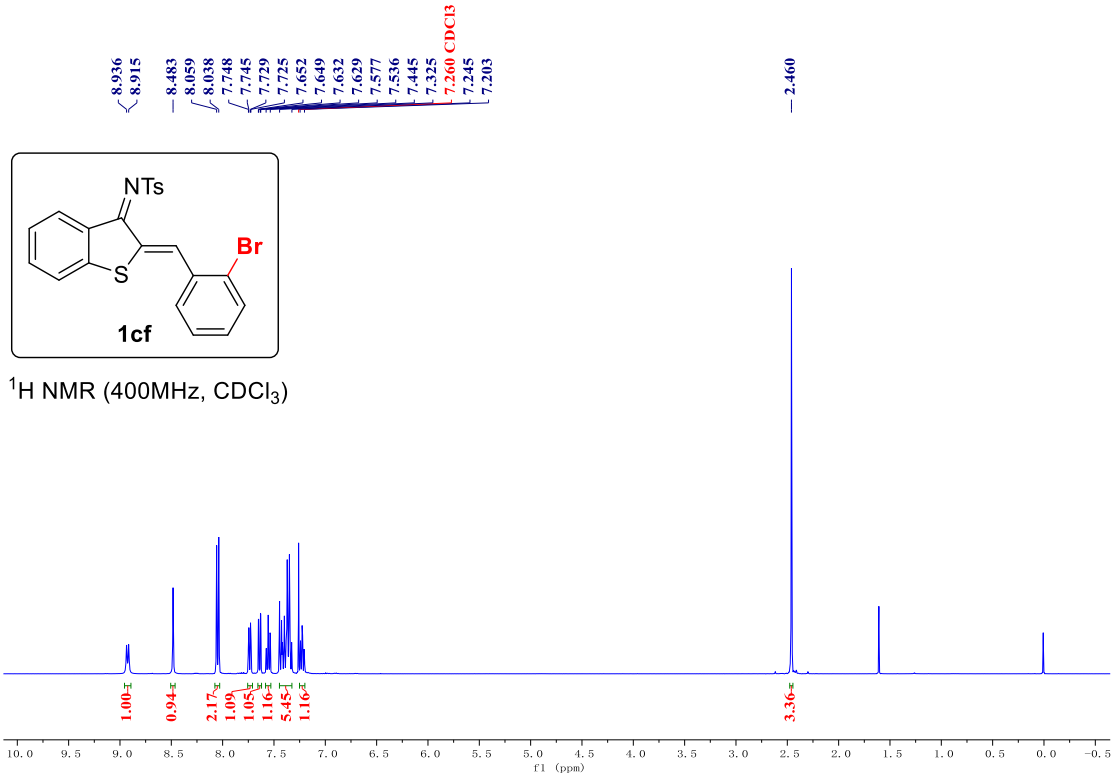


^{1}H NMR (400MHz, $CDCl_3$)

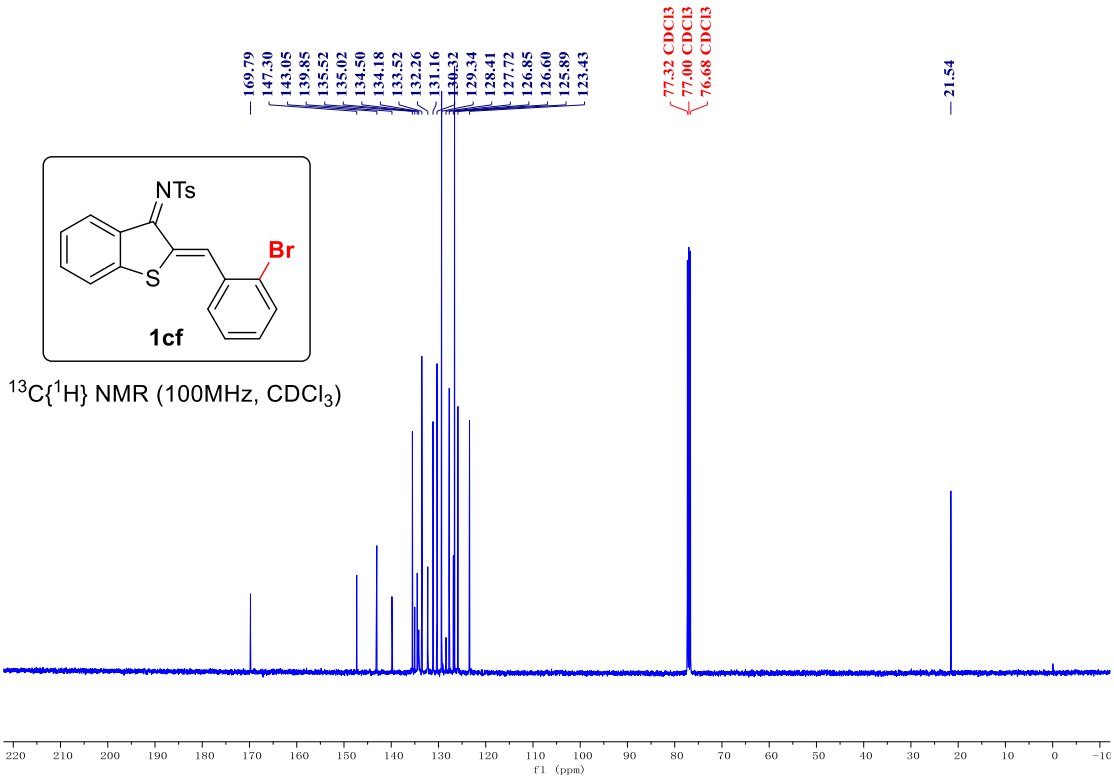


^{1}H NMR (400MHz, $CDCl_3$)

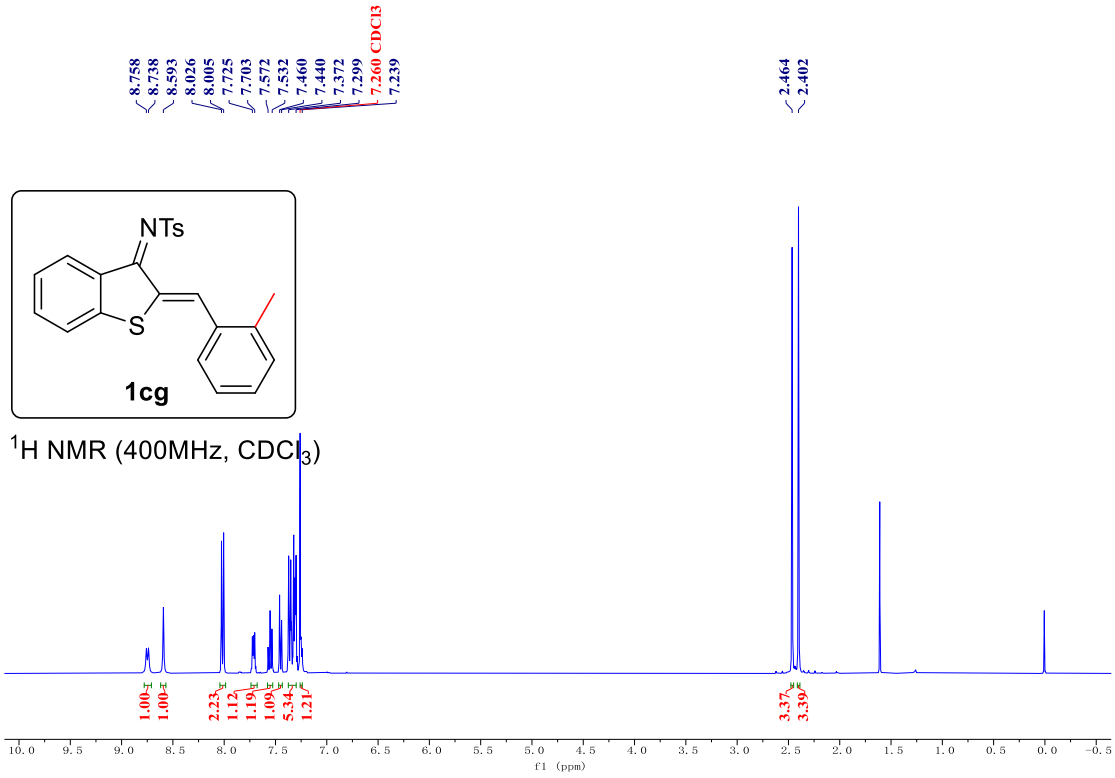

8.941
8.921
8.148
8.027
8.006
7.578
7.540
7.483
7.441
7.390
7.322
7.260 CDCl3
7.225
7.206
2.476
2.395
NTs
S
1ce
1H NMR (400MHz, CDCl3)
1.00
1.06
2.11
1.23
3.35
4.30
1.24
3.32
3.37
f1 (ppm)



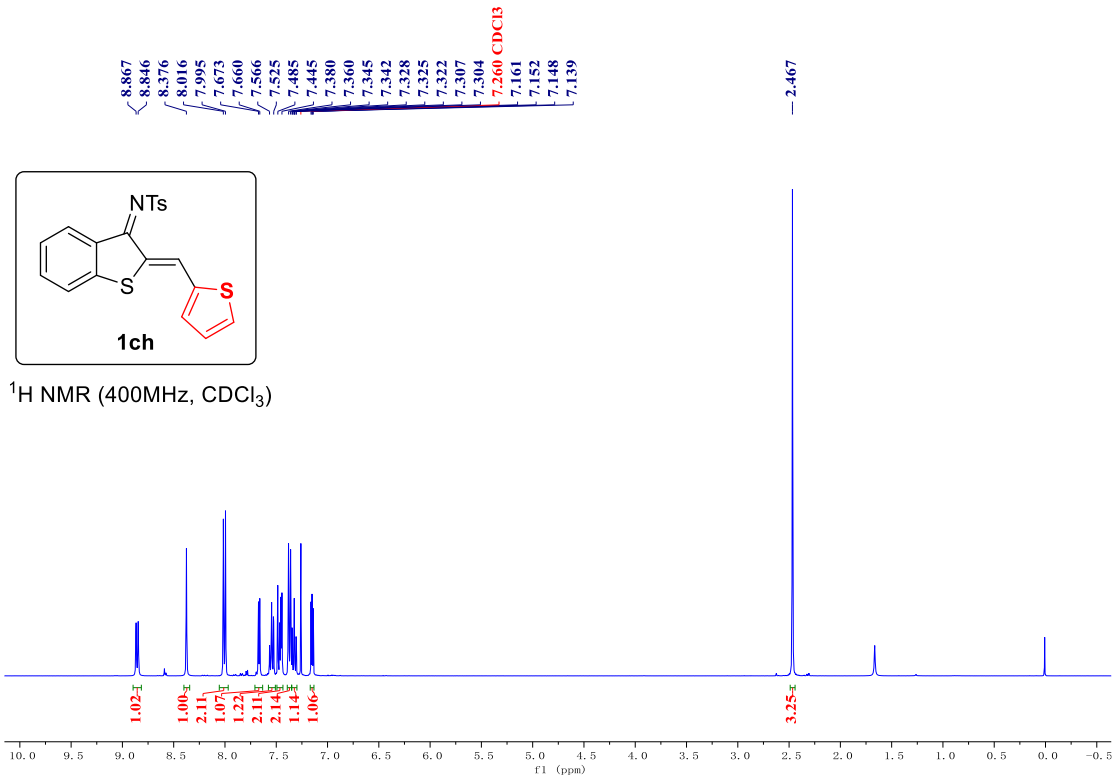
^{1}H NMR (400MHz, $CDCl_3$)



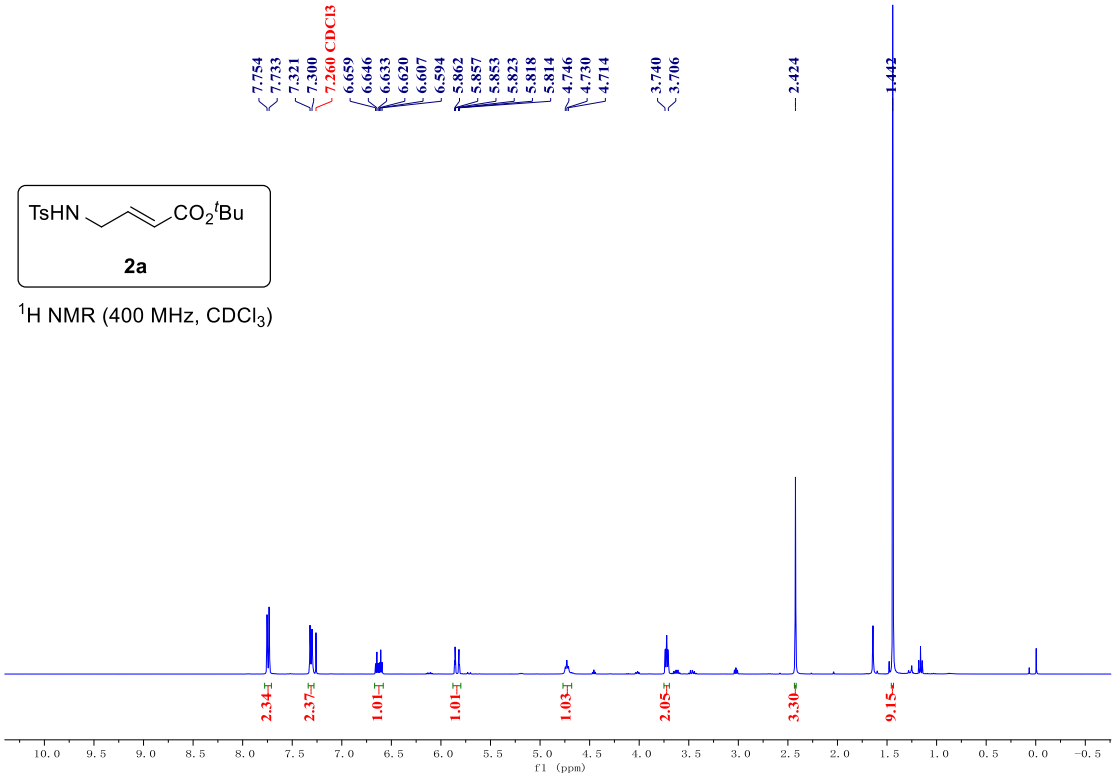
$^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$)



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



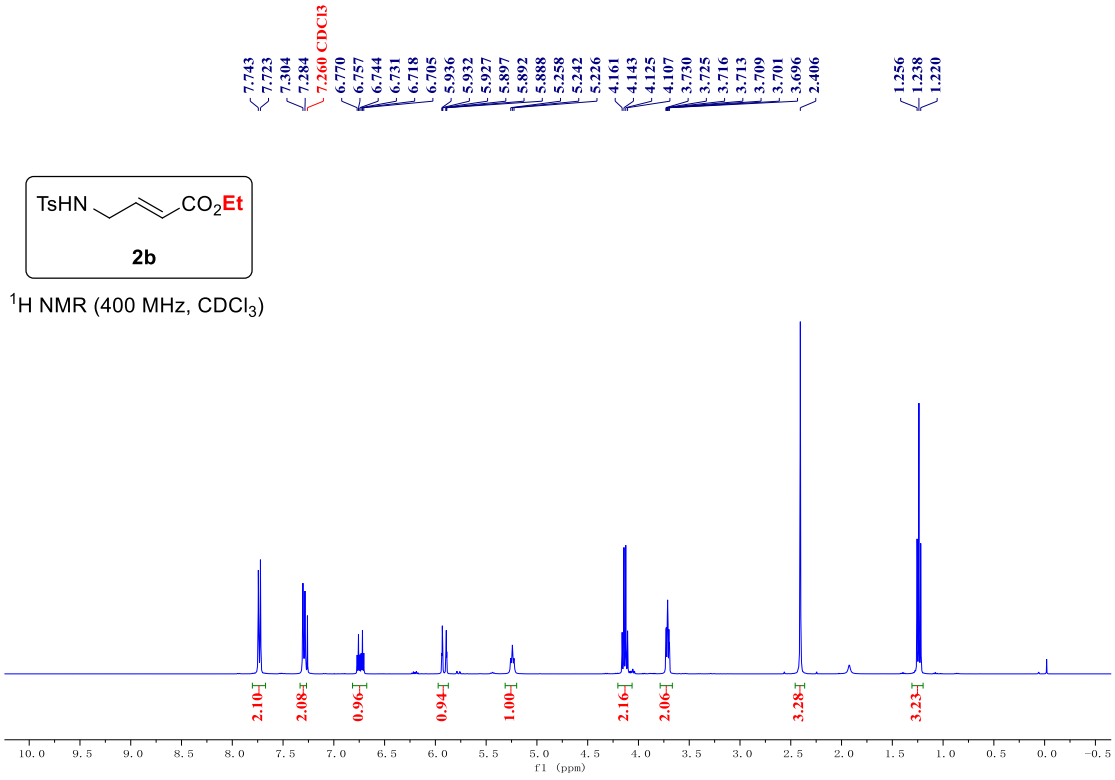
^{1}H NMR (400MHz, $CDCl_3$)



TsHN $CO_2{}^tBu$

2a

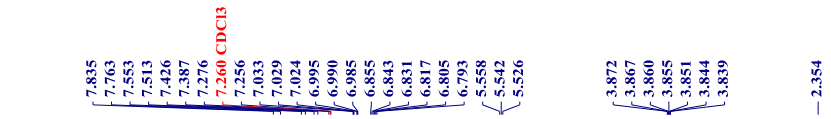
^{1}H NMR (400 MHz, $CDCl_3$)

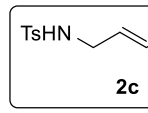


TsHN CO_2Et

2b

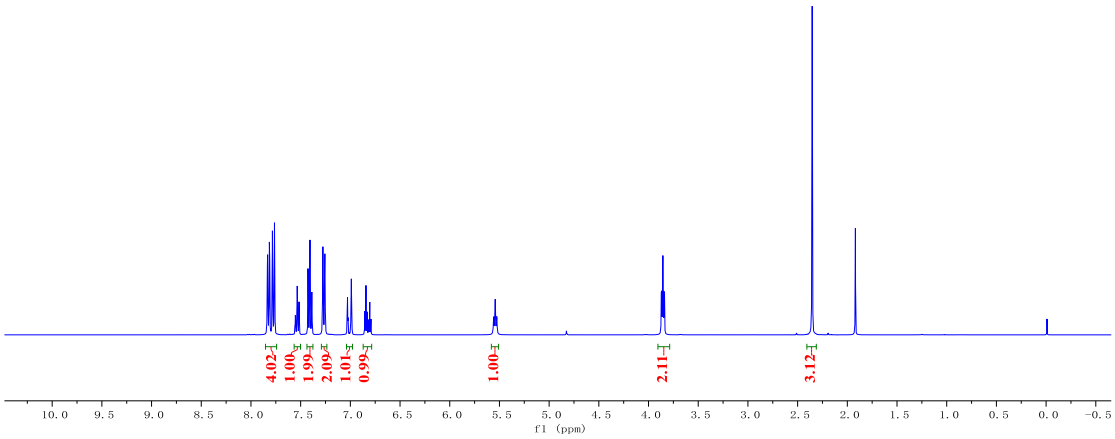
^{1}H NMR (400 MHz, $CDCl_3$)

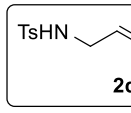




2c

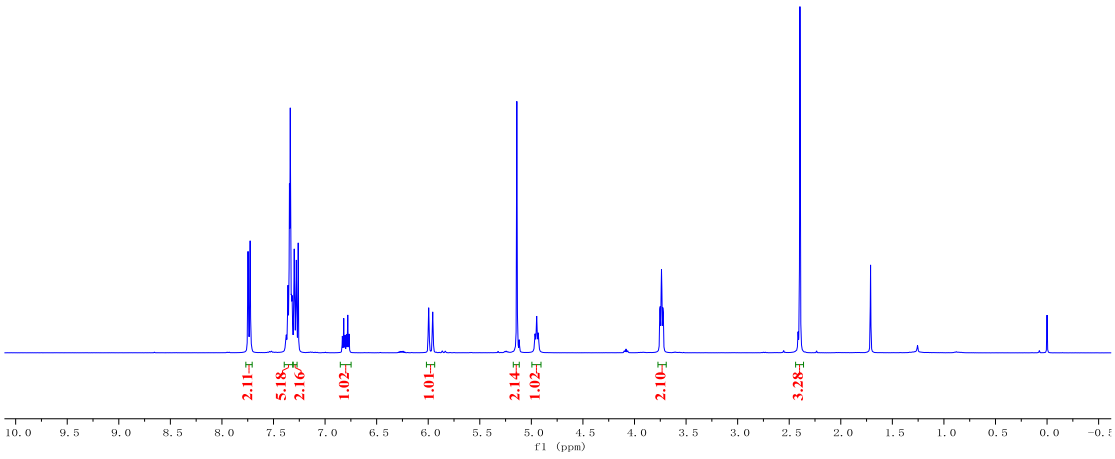
^{1}H NMR (400 MHz, $CDCl_3$)

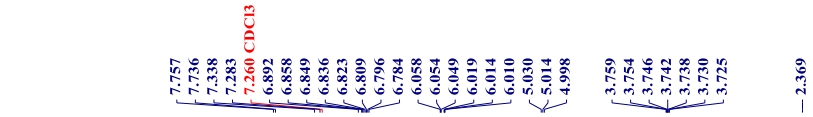


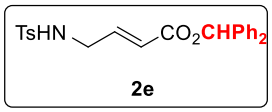


2d

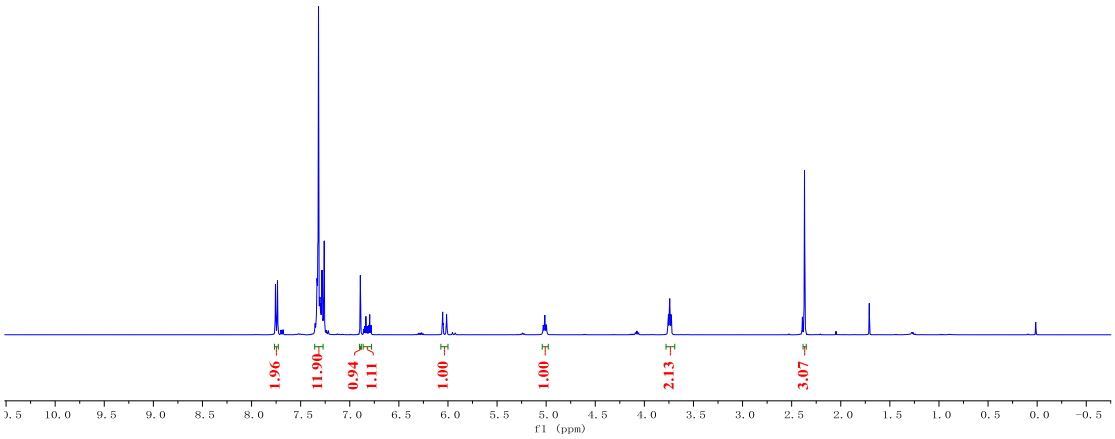
^{1}H NMR (400 MHz, $CDCl_3$)

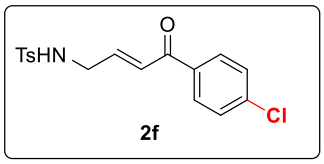




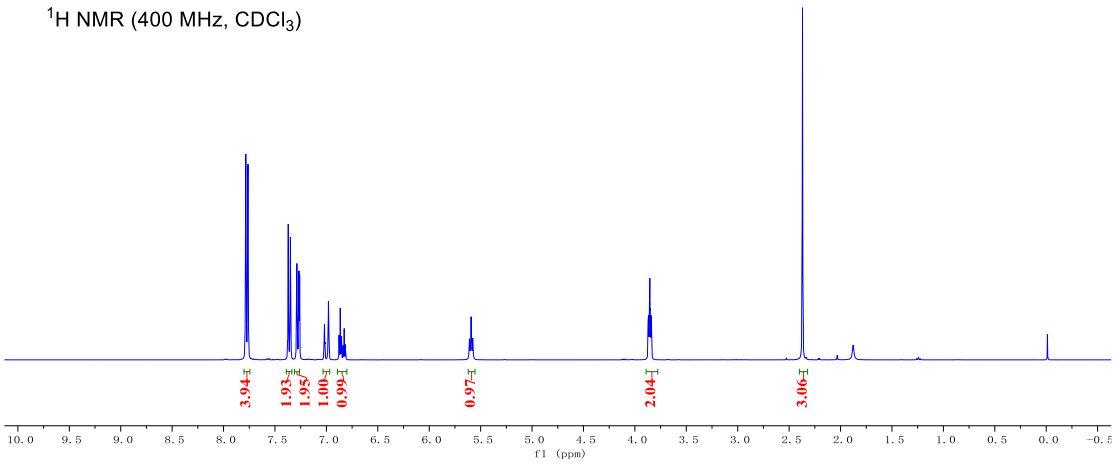


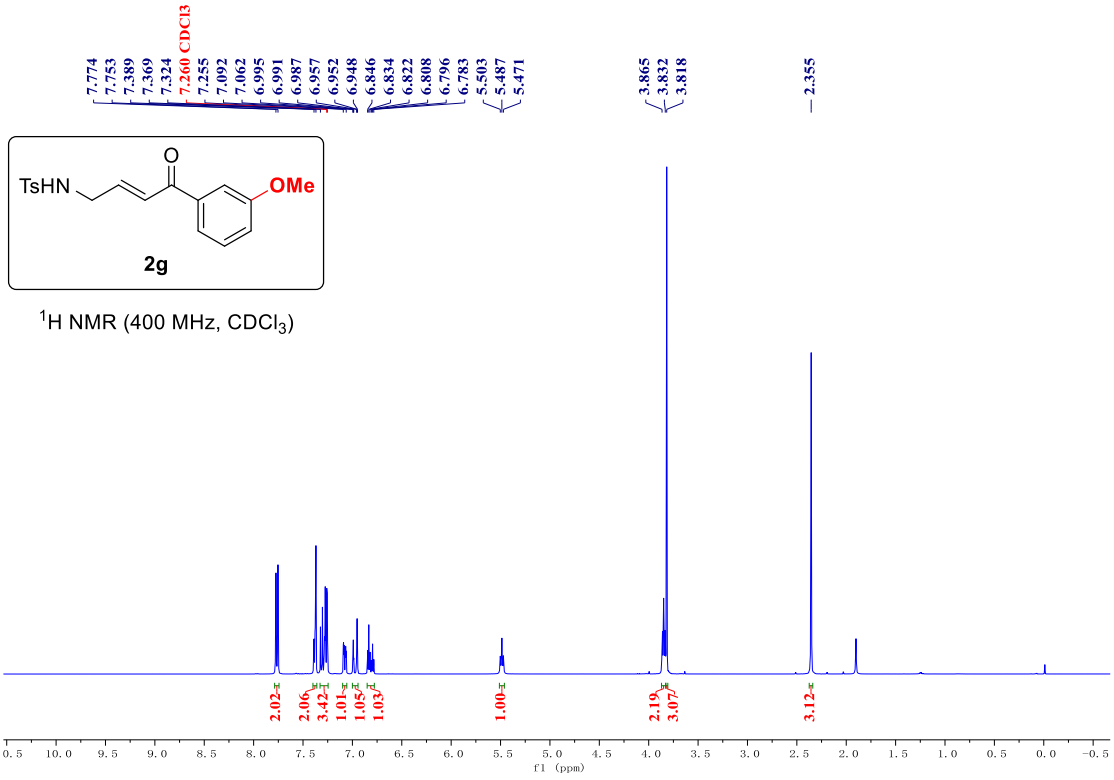
^{1}H NMR (400 MHz, $CDCl_3$)



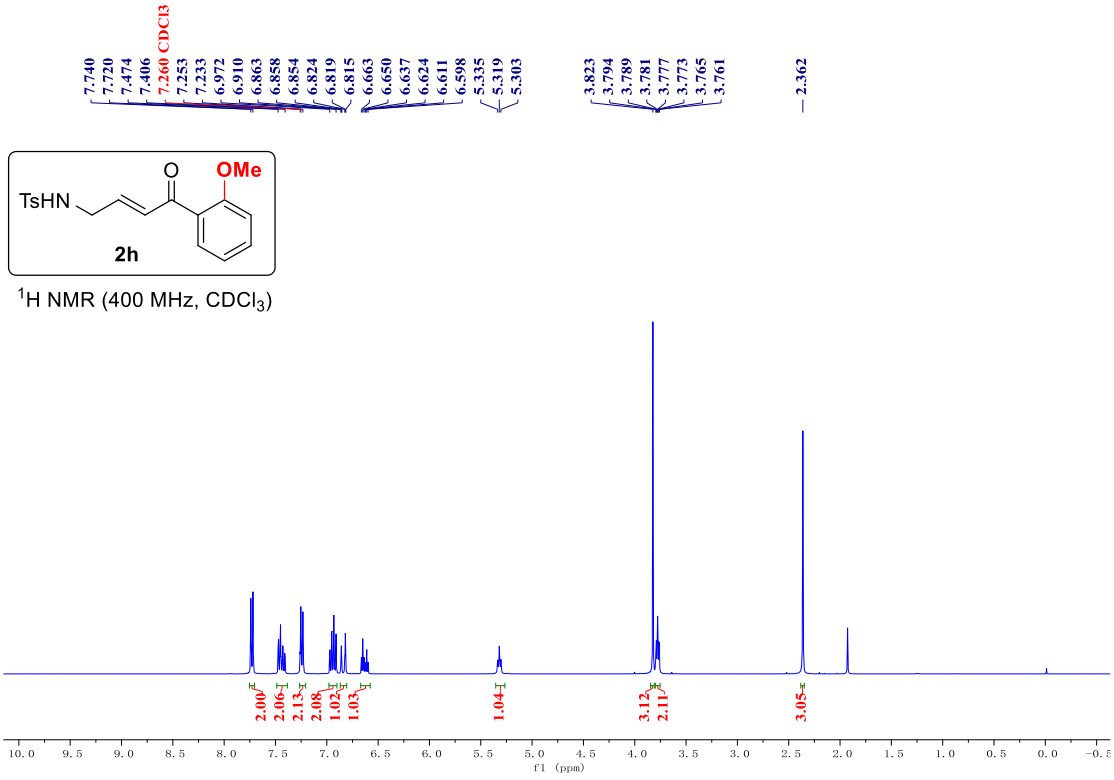


^{1}H NMR (400 MHz, $CDCl_3$)

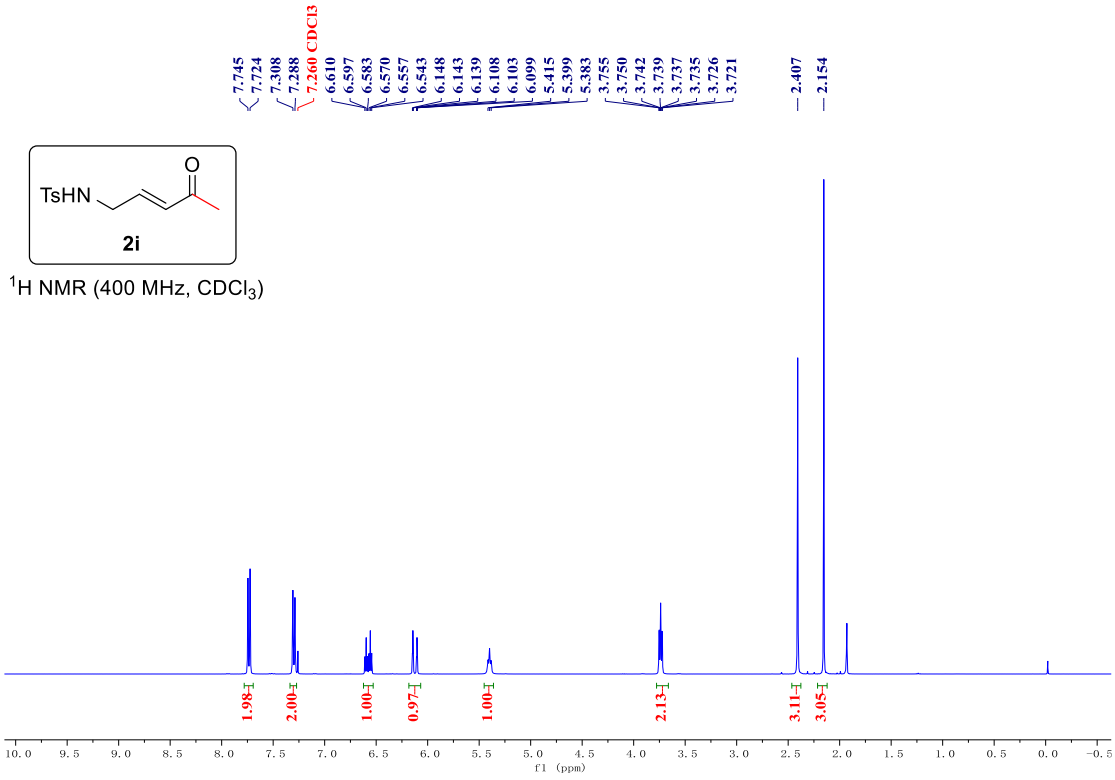


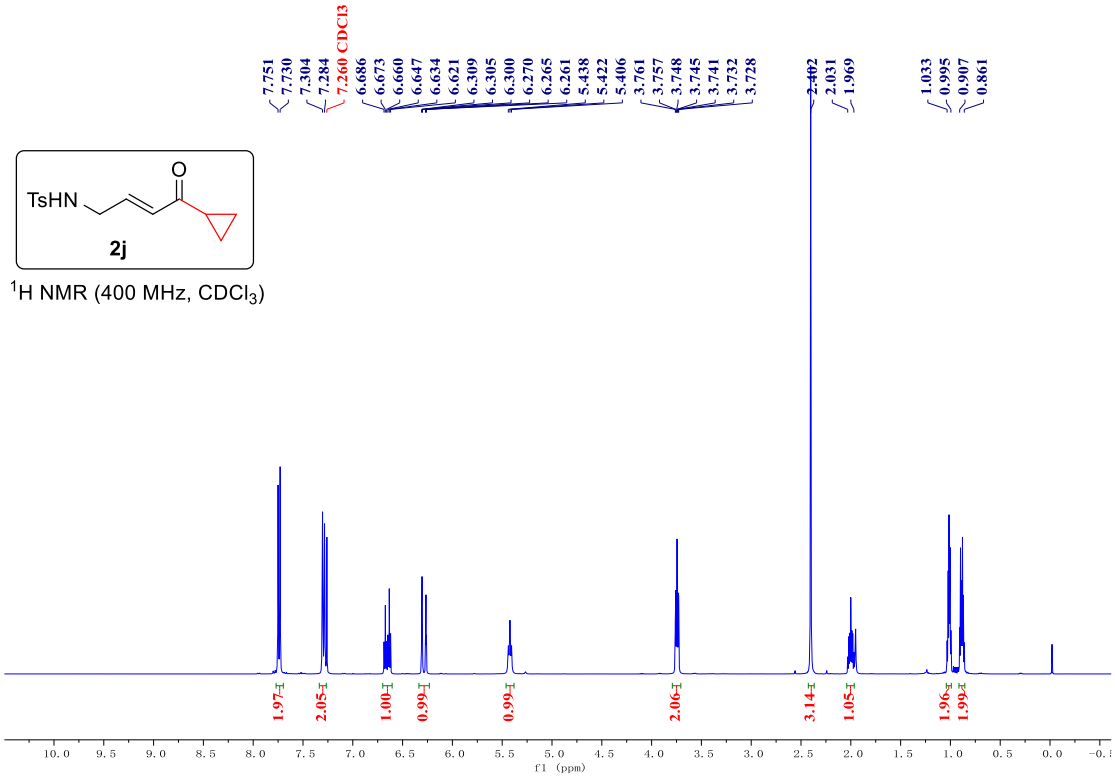


^{1}H NMR (400 MHz, $CDCl_3$)

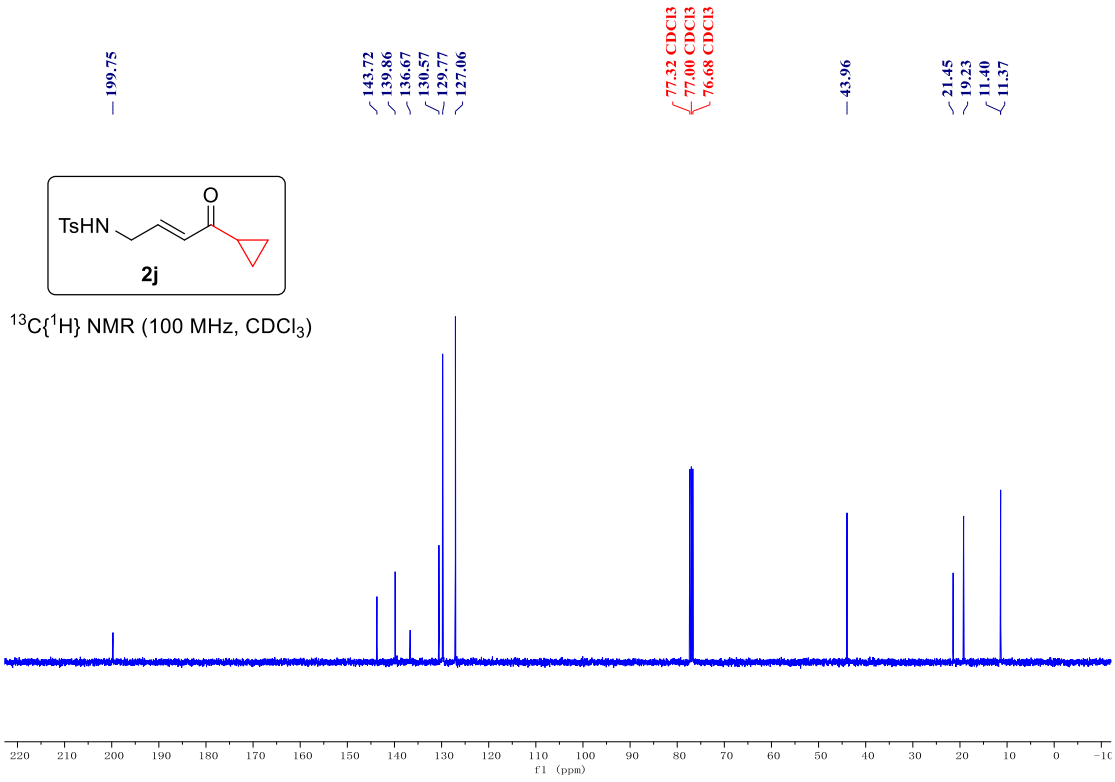


^{1}H NMR (400 MHz, $CDCl_3$)

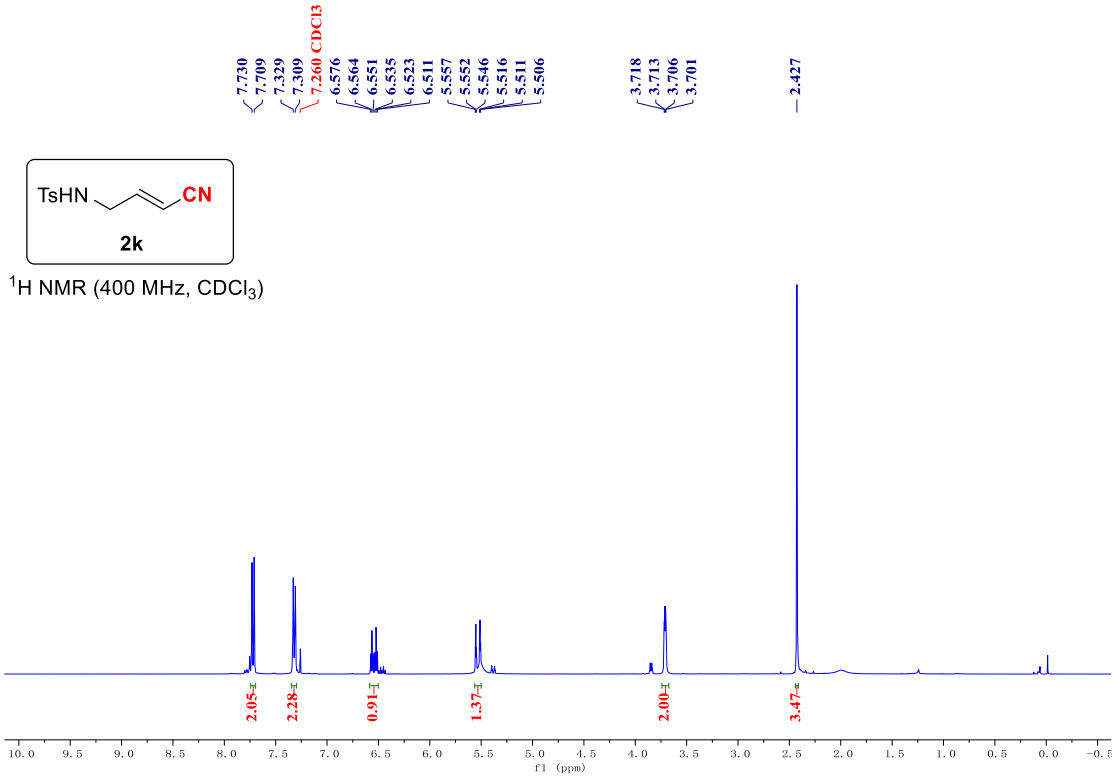

7.745
7.724
7.308
7.288
7.260 CDCl3
6.610
6.597
6.583
6.570
6.557
6.543
6.148
6.143
6.139
6.108
6.103
6.099
5.415
5.399
5.383
3.755
3.750
3.742
3.739
3.737
3.735
3.726
3.721
2.407
2.154
TsHN
O
2i
1H NMR (400 MHz, CDCl3)
1.98
2.00
1.00
0.97
1.00
2.13
3.11
3.05
f1 (ppm)

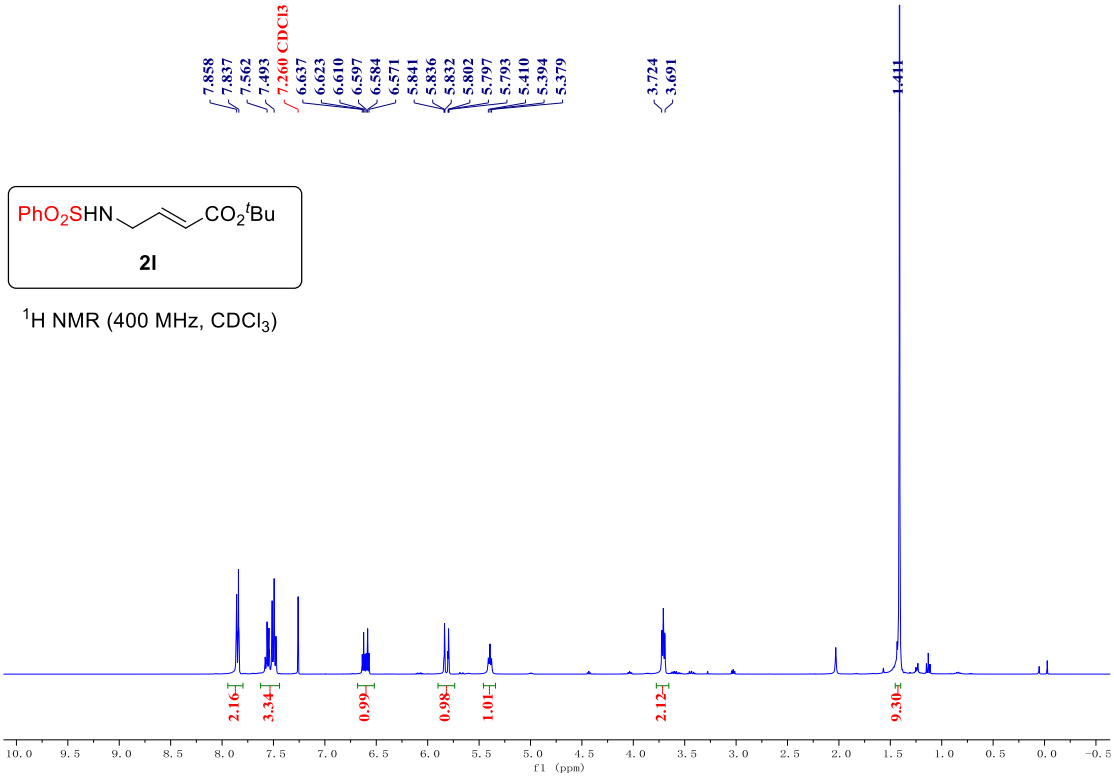


^{1}H NMR (400 MHz, $CDCl_3$)

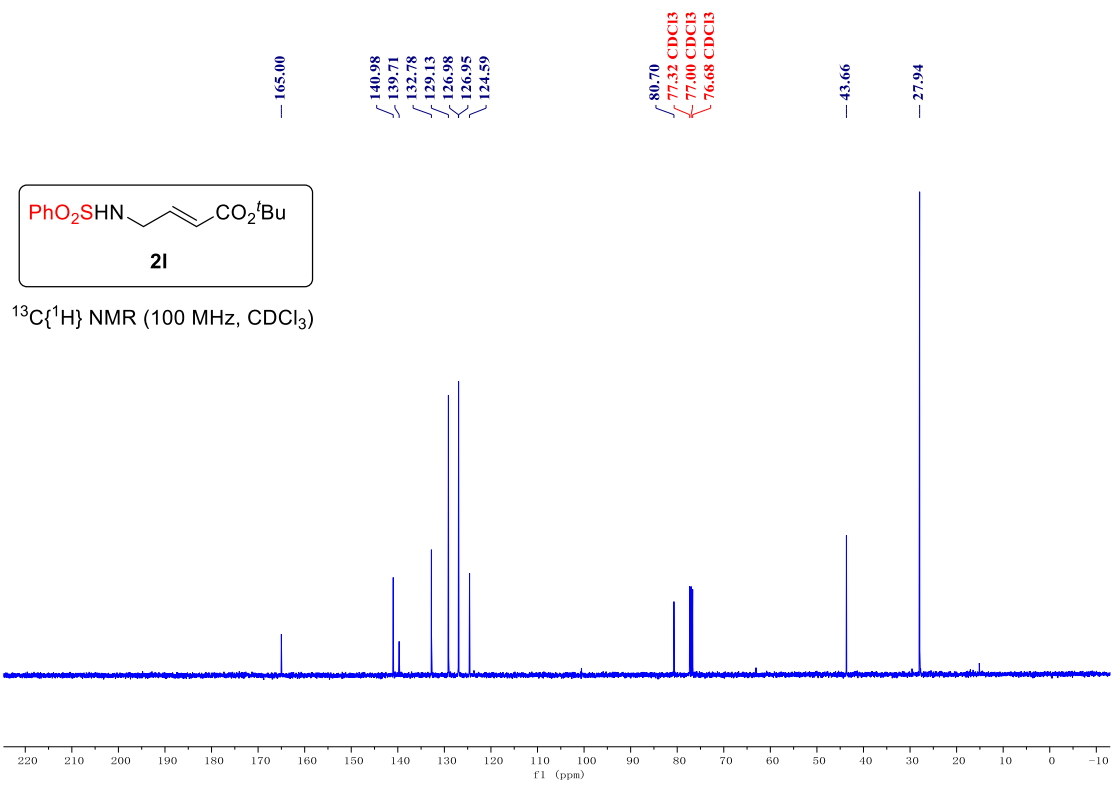


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

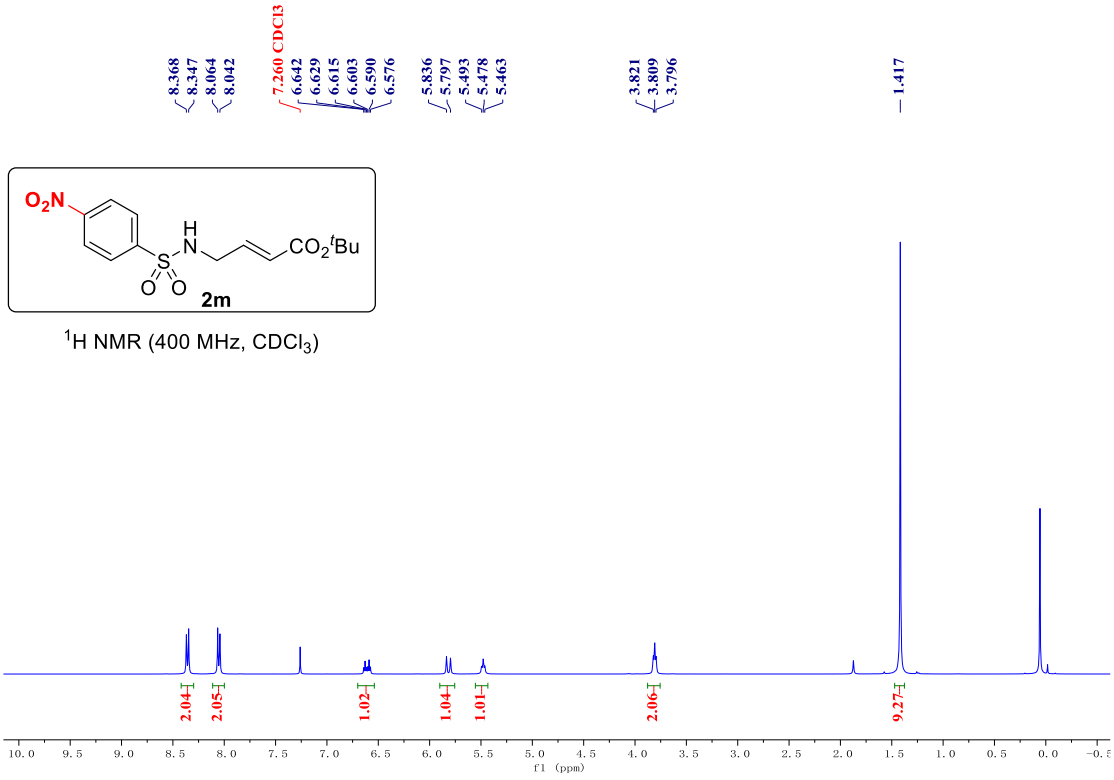

7.730
7.709
7.329
7.309
7.260 CDCl3
6.576
6.564
6.551
6.535
6.523
6.511
5.557
5.552
5.546
5.516
5.511
5.506
3.718
3.713
3.706
3.701
2.427
TsHN
CN
2k
1H NMR (400 MHz, CDCl3)
2.05
2.28
0.91
1.37
2.00
3.47
f1 (ppm)



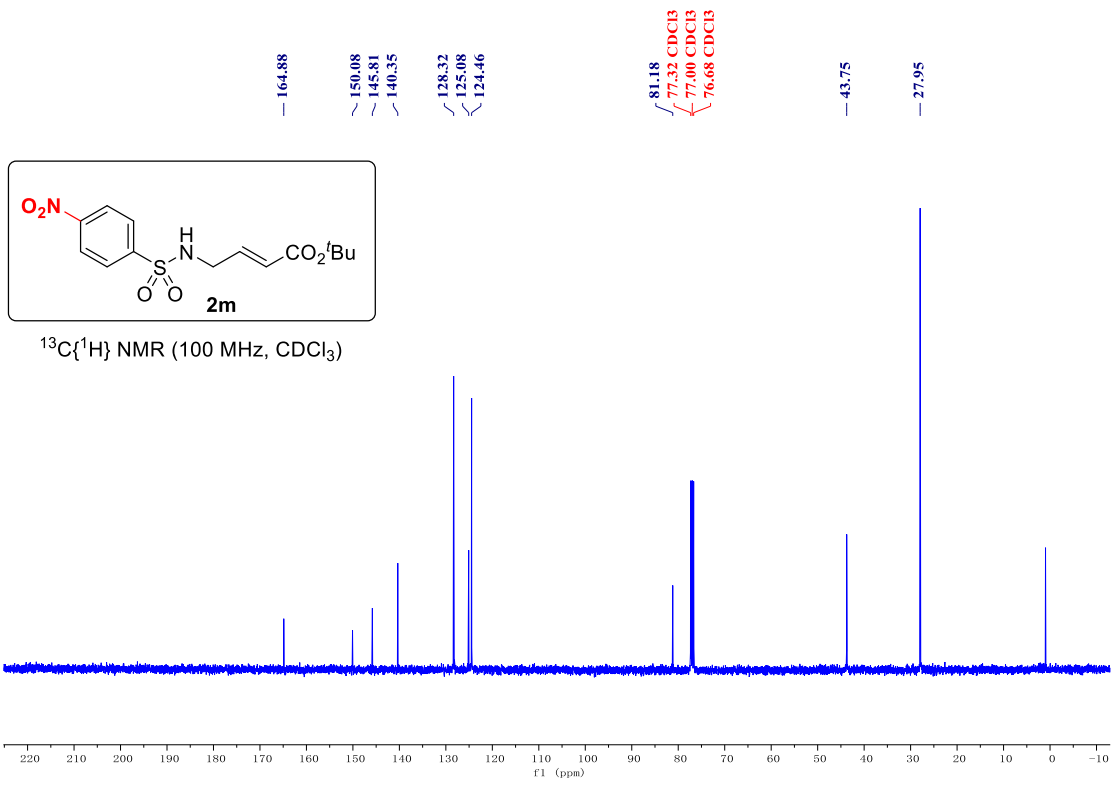
^{1}H NMR (400 MHz, $CDCl_3$)



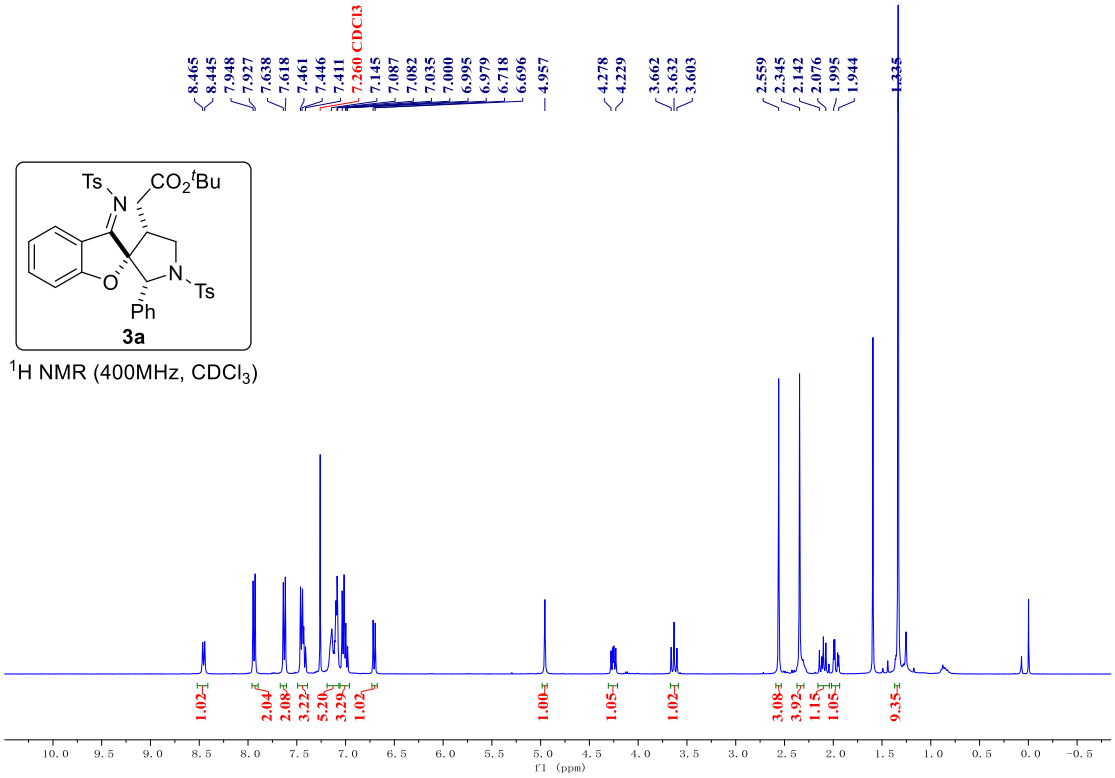
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



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

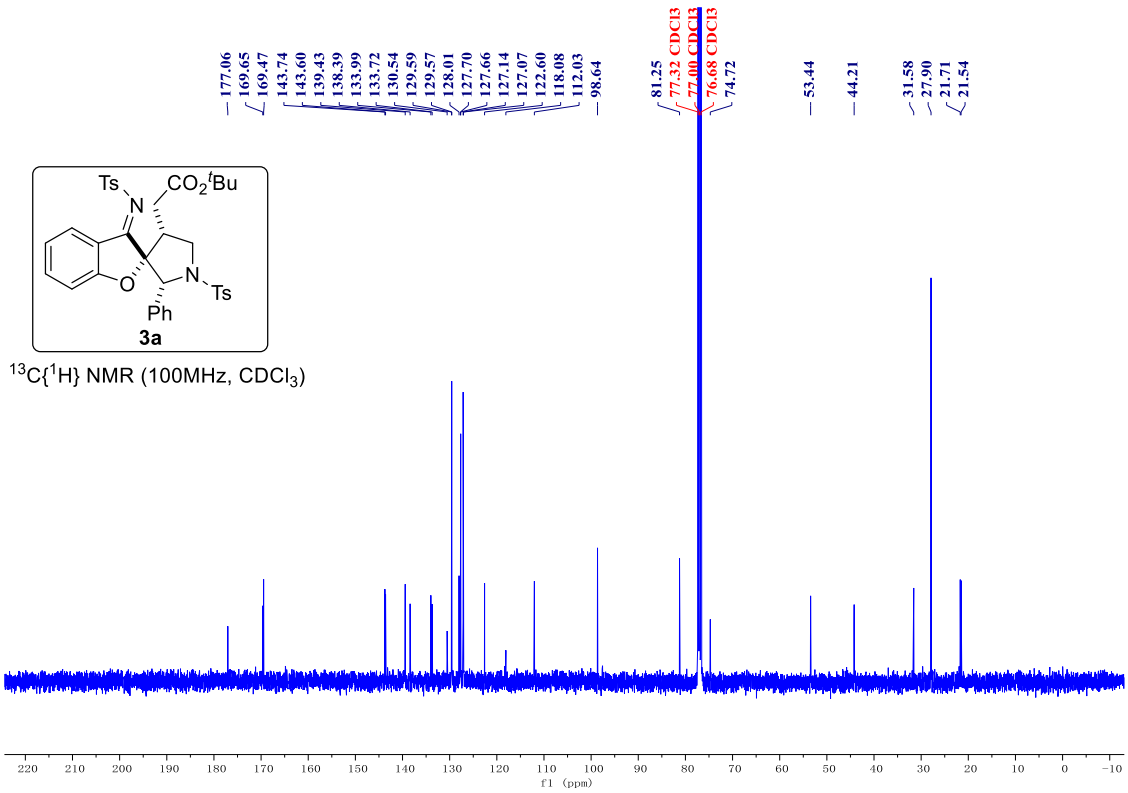


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



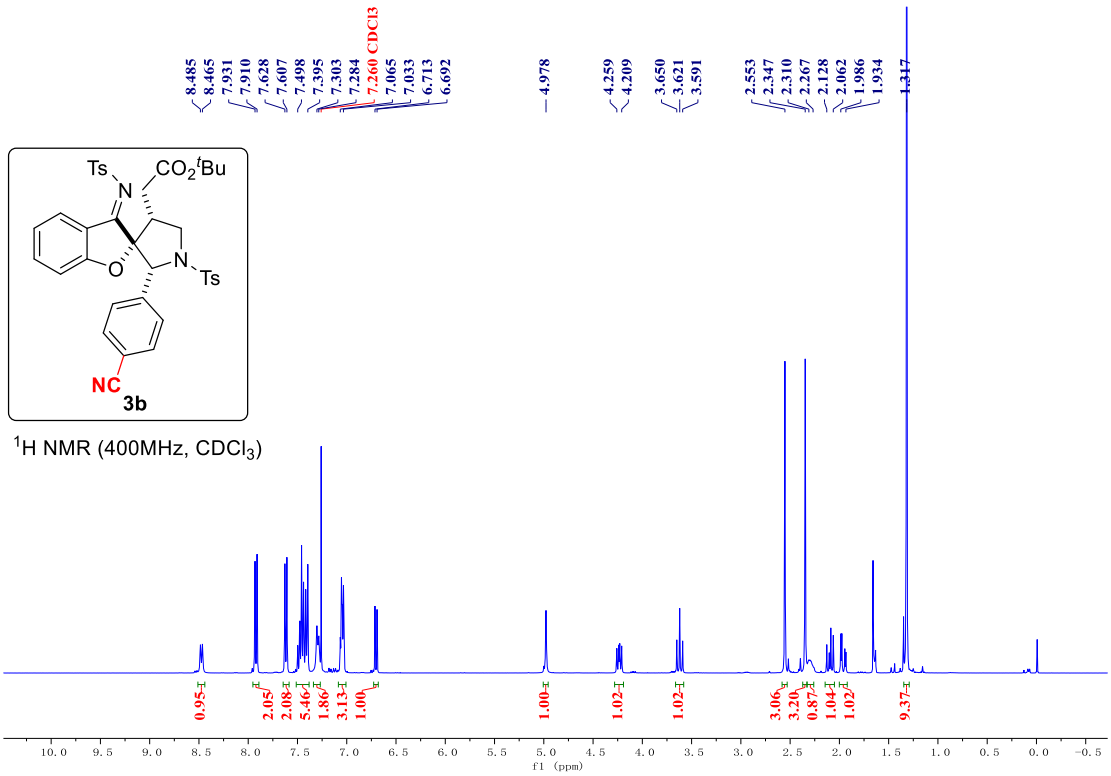
3a

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

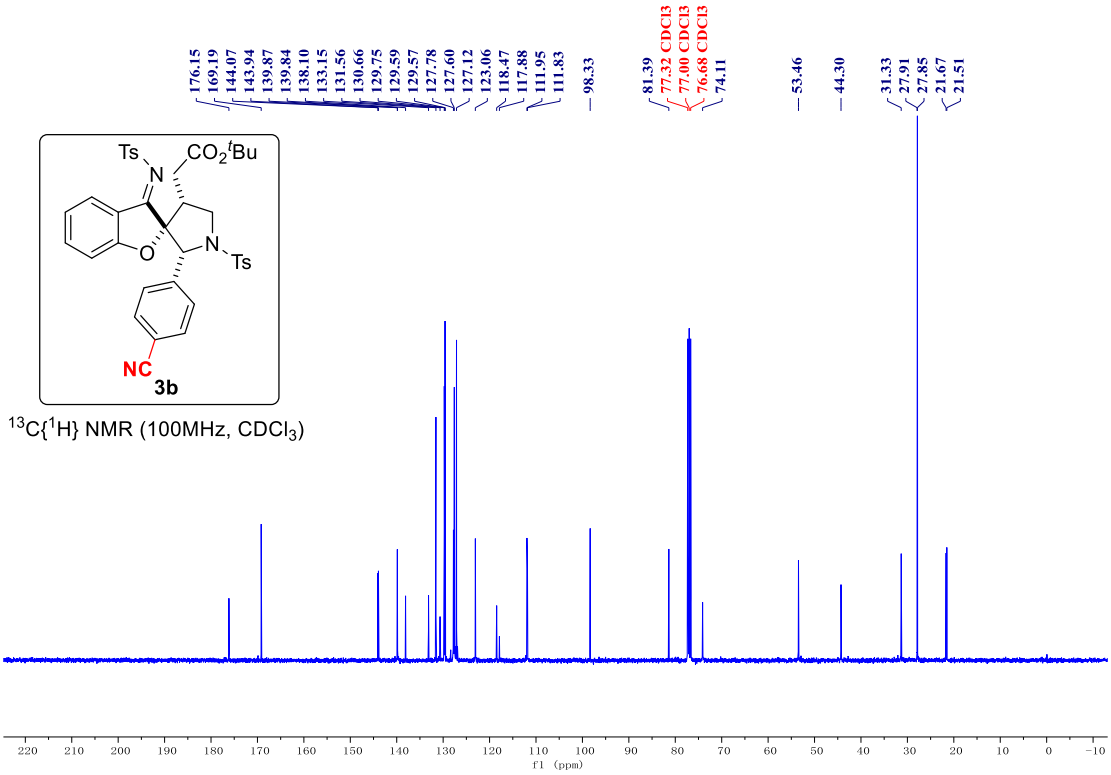


3a

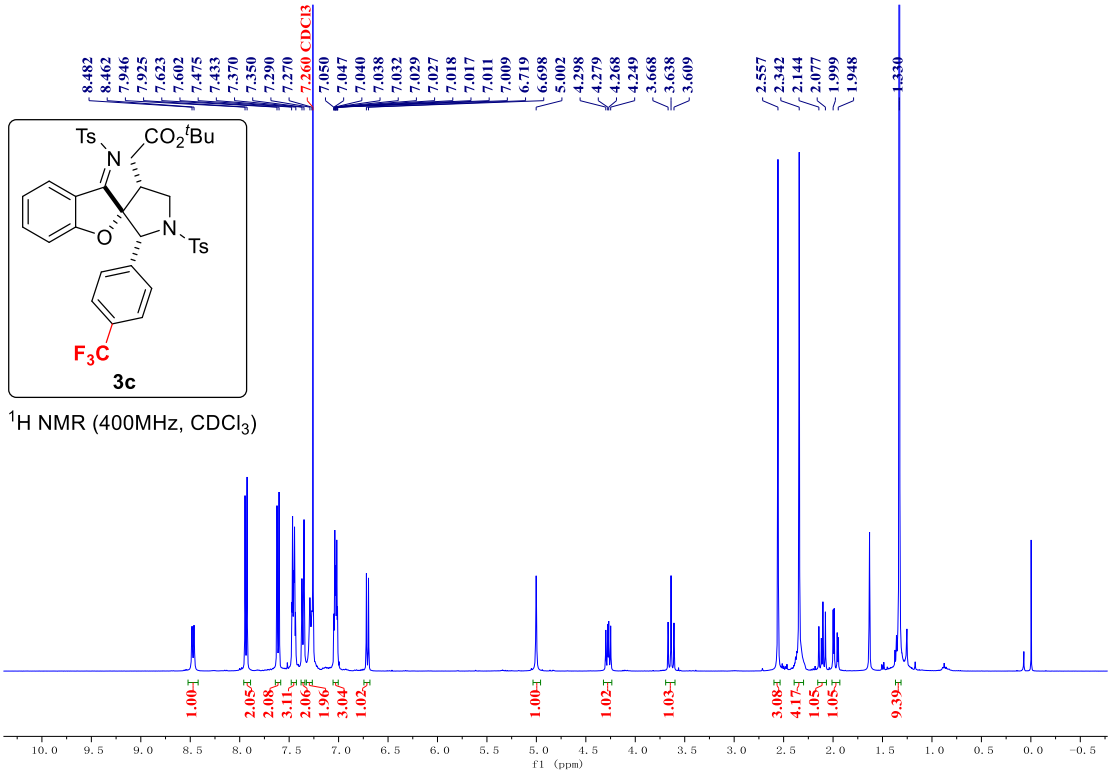
$^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$)



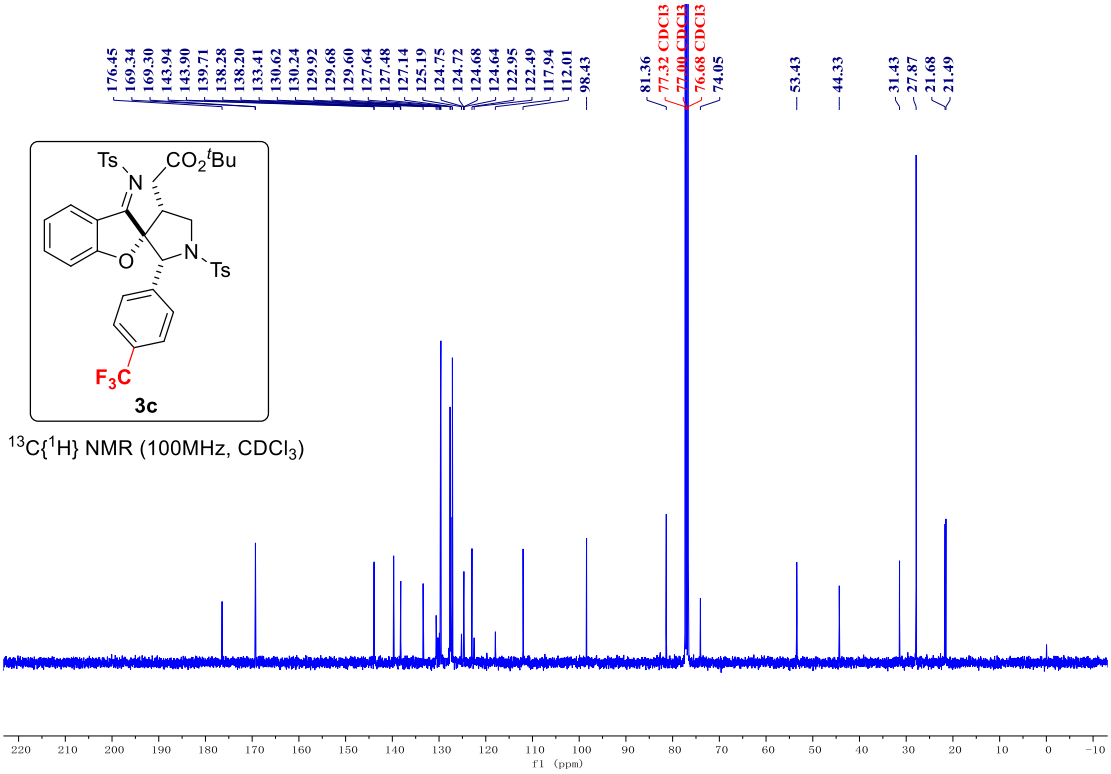
^{1}H NMR (400MHz, $CDCl_3$)



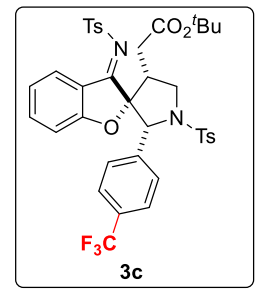
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$)



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

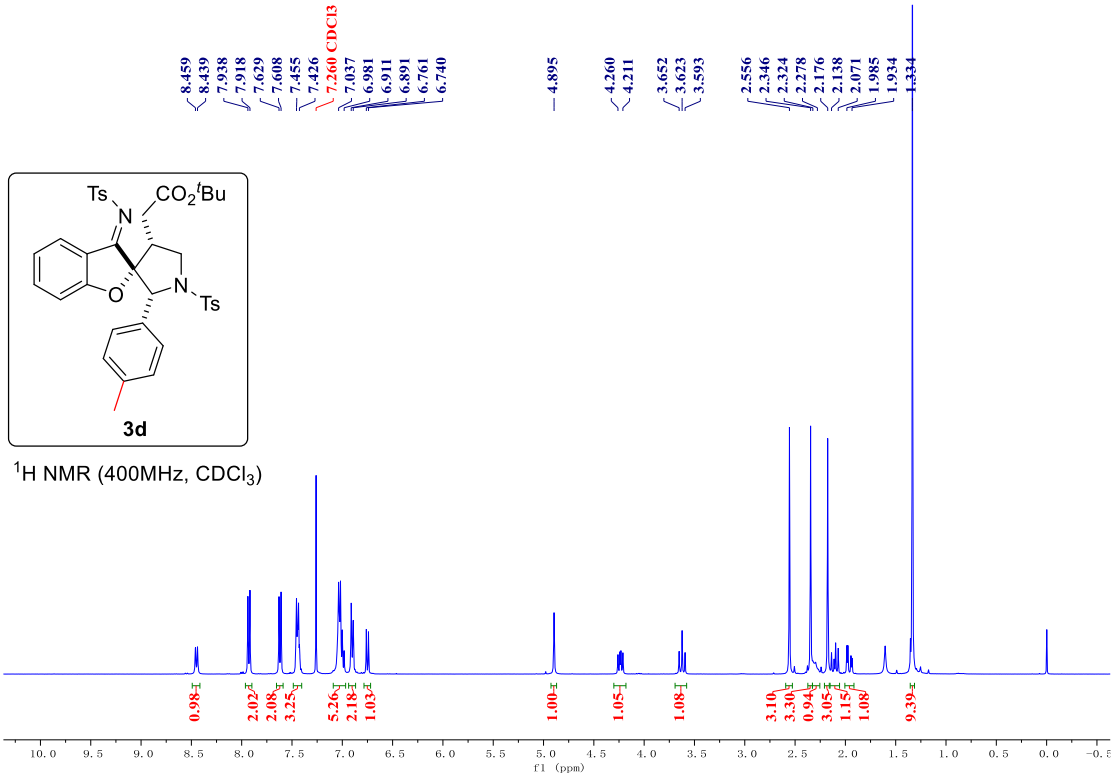


^{13}C{^{1}H} NMR (100MHz, $CDCl_3$)



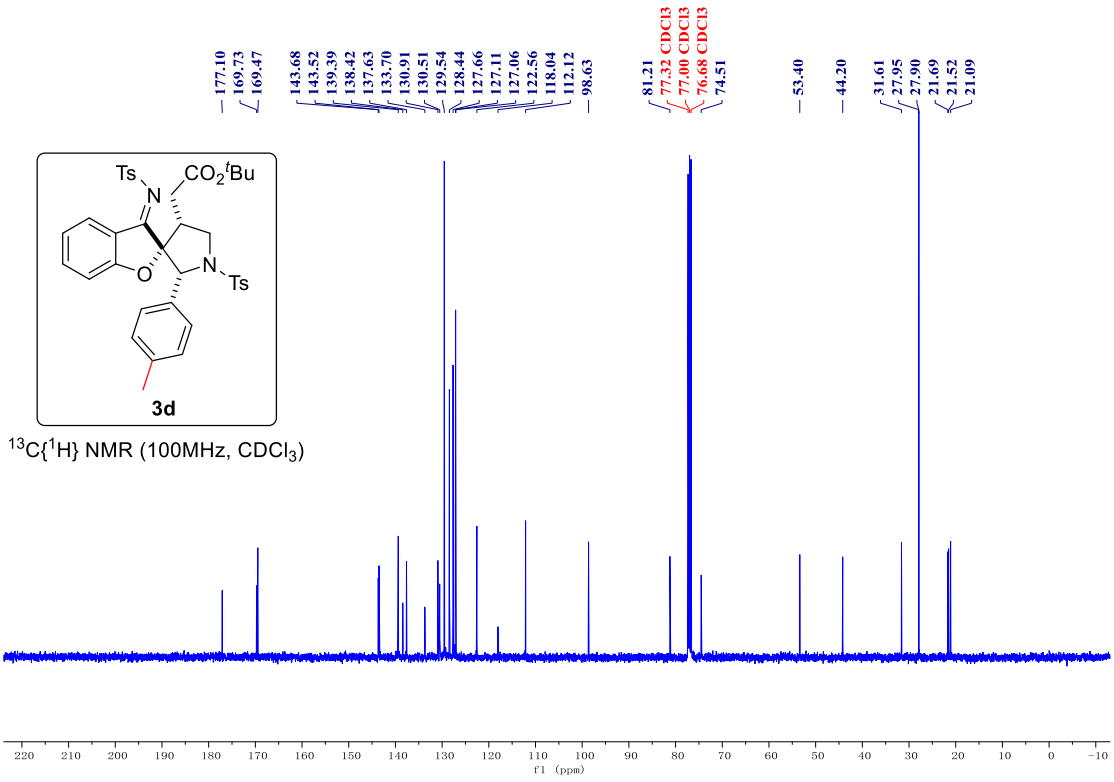
3c

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



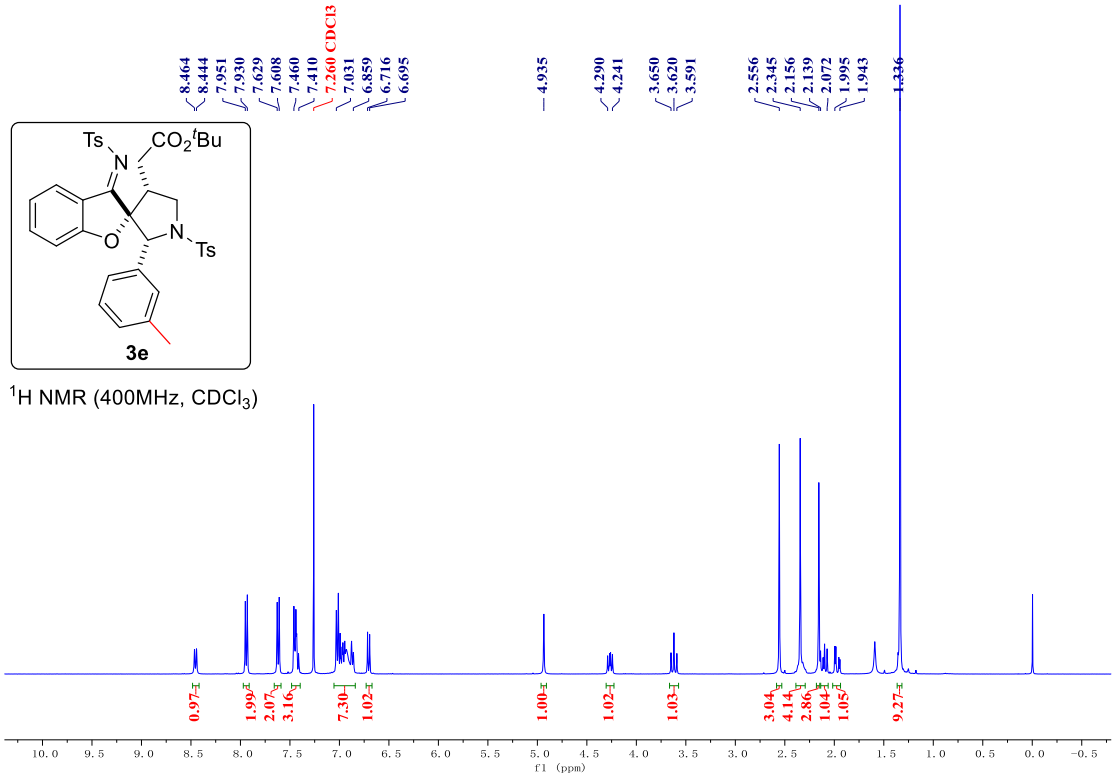
3d

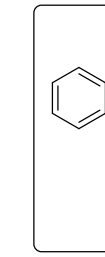
^{1}H NMR (400MHz, $CDCl_3$)



3d

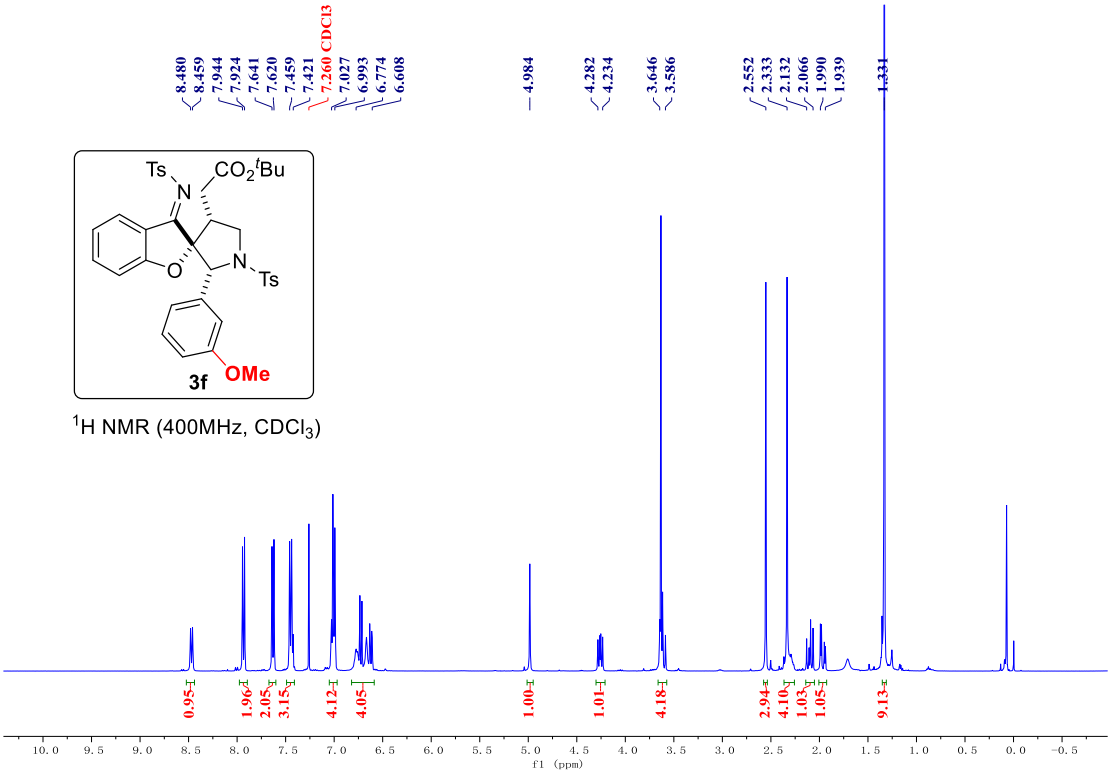
$^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$)





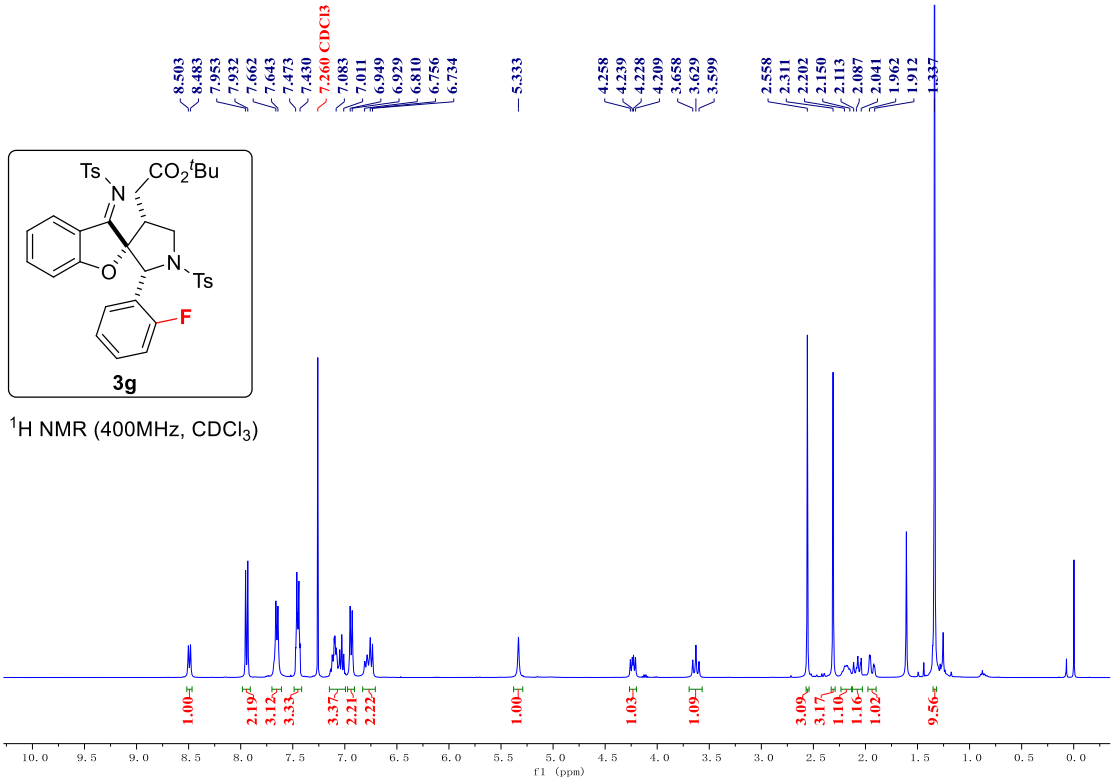
^{1}H NMR (400MHz, $CDCl_3$)

^{13}C{^{1}H} NMR (100MHz, $CDCl_3$)

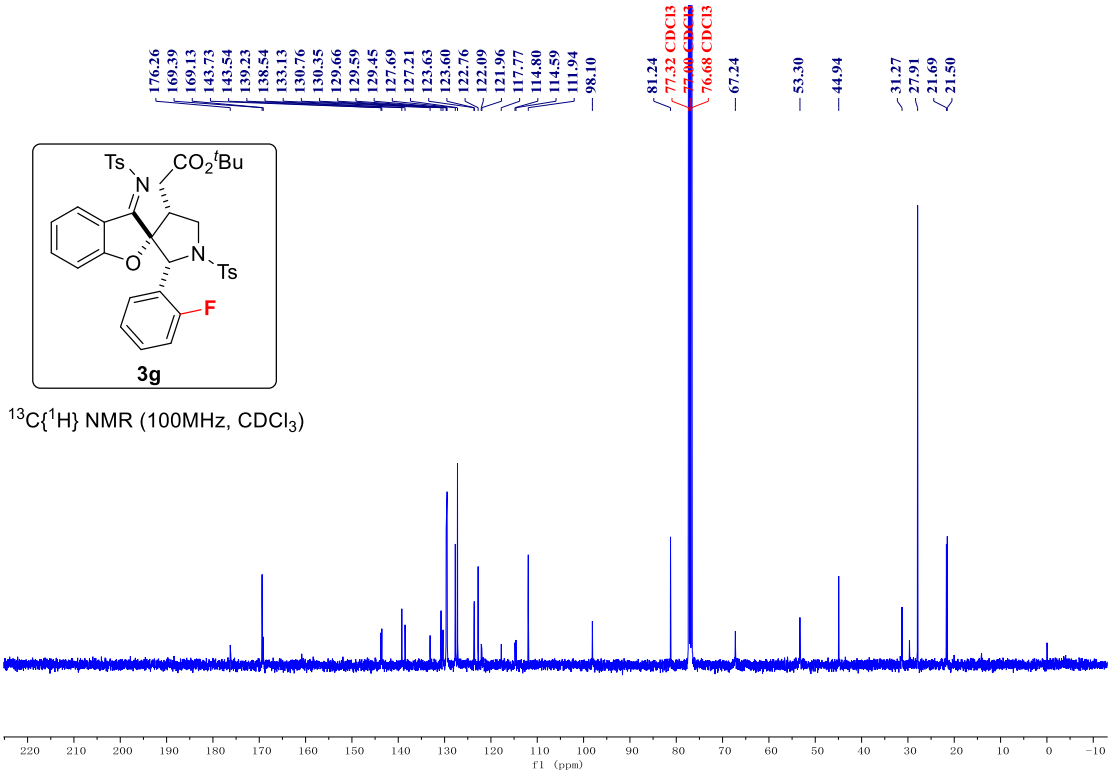


^{1}H NMR (400MHz, $CDCl_3$)

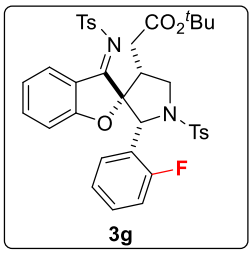
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$)



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

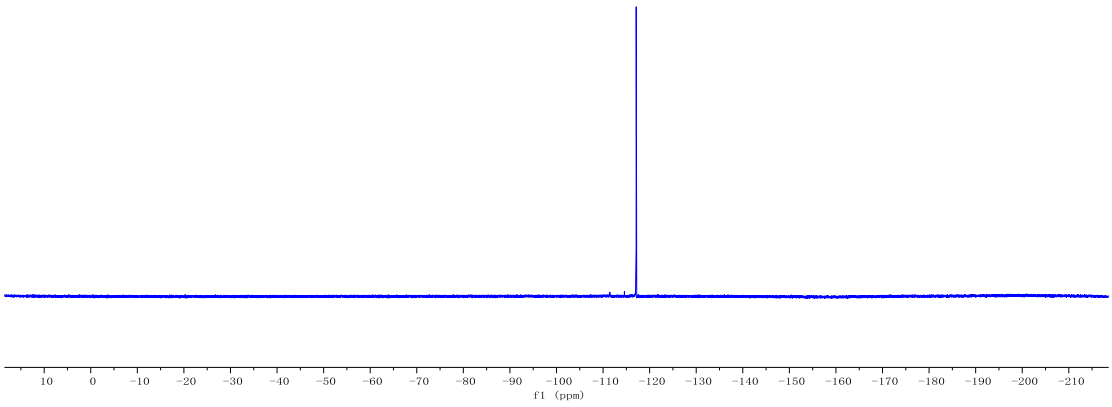


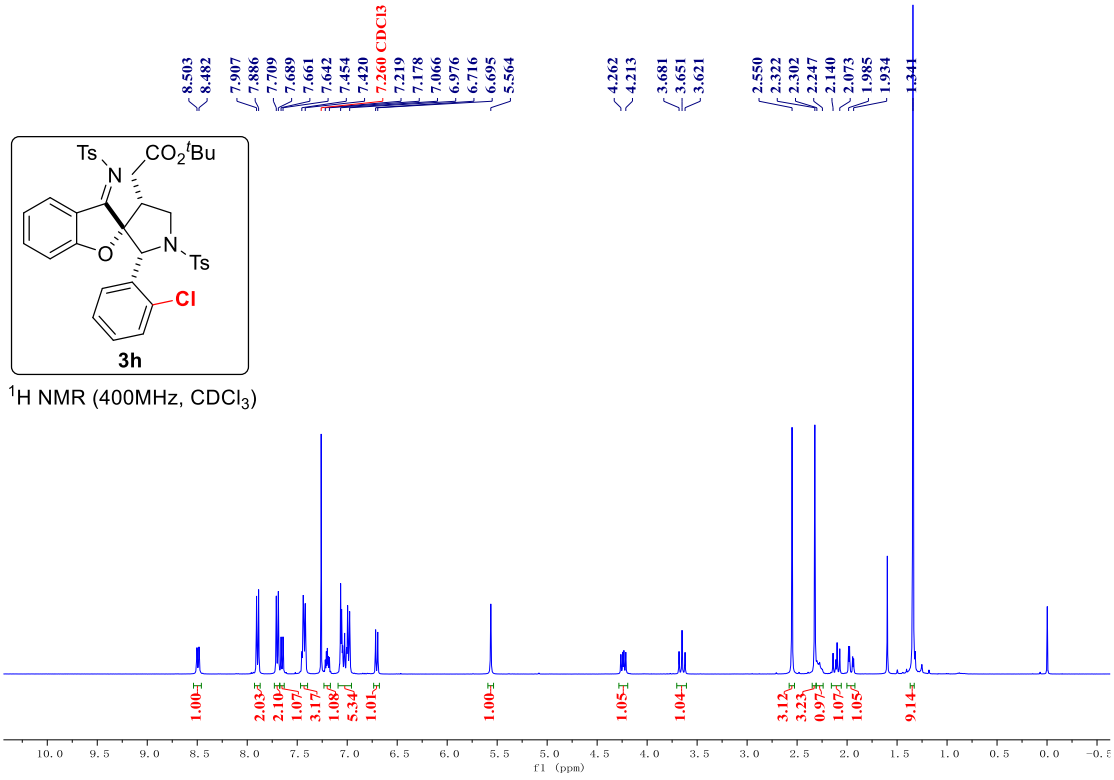
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$)



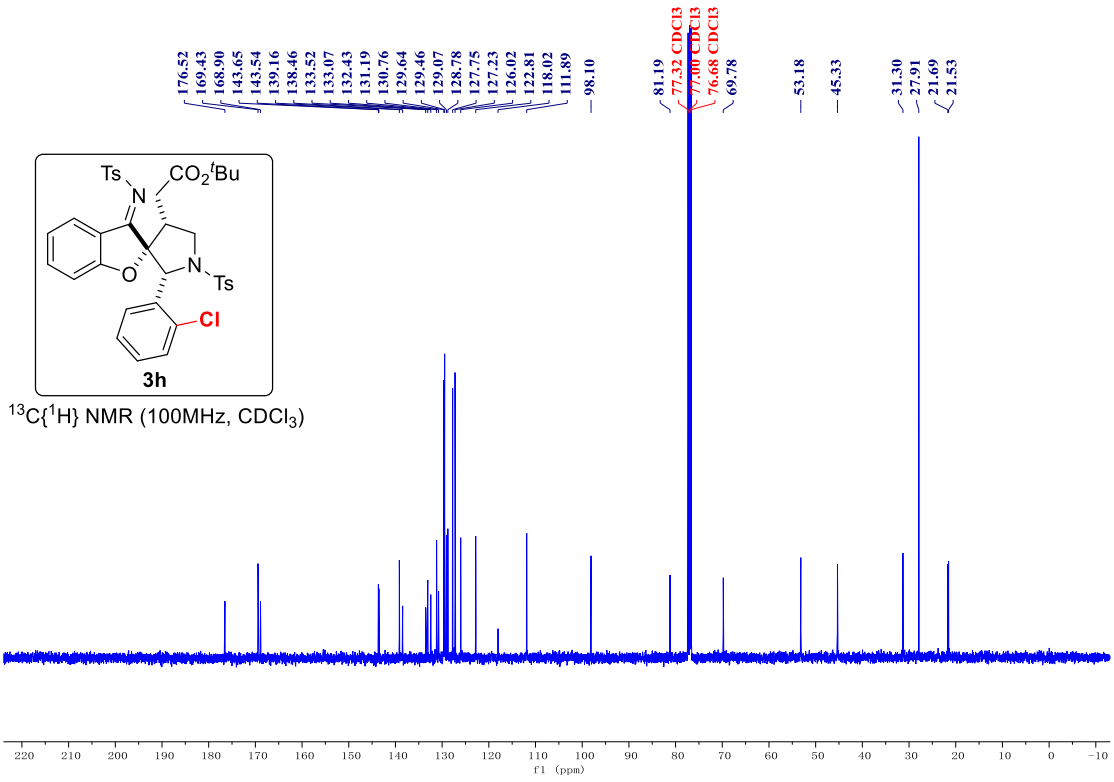
3g

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

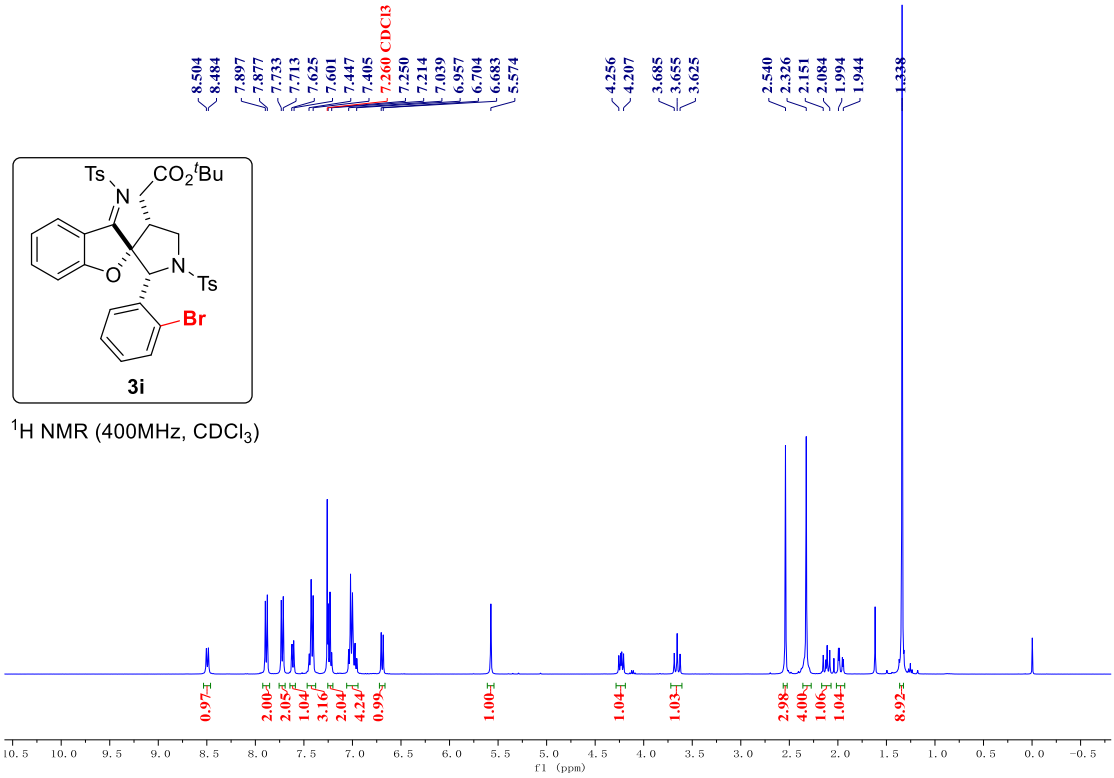




^{1}H NMR (400MHz, $CDCl_3$)

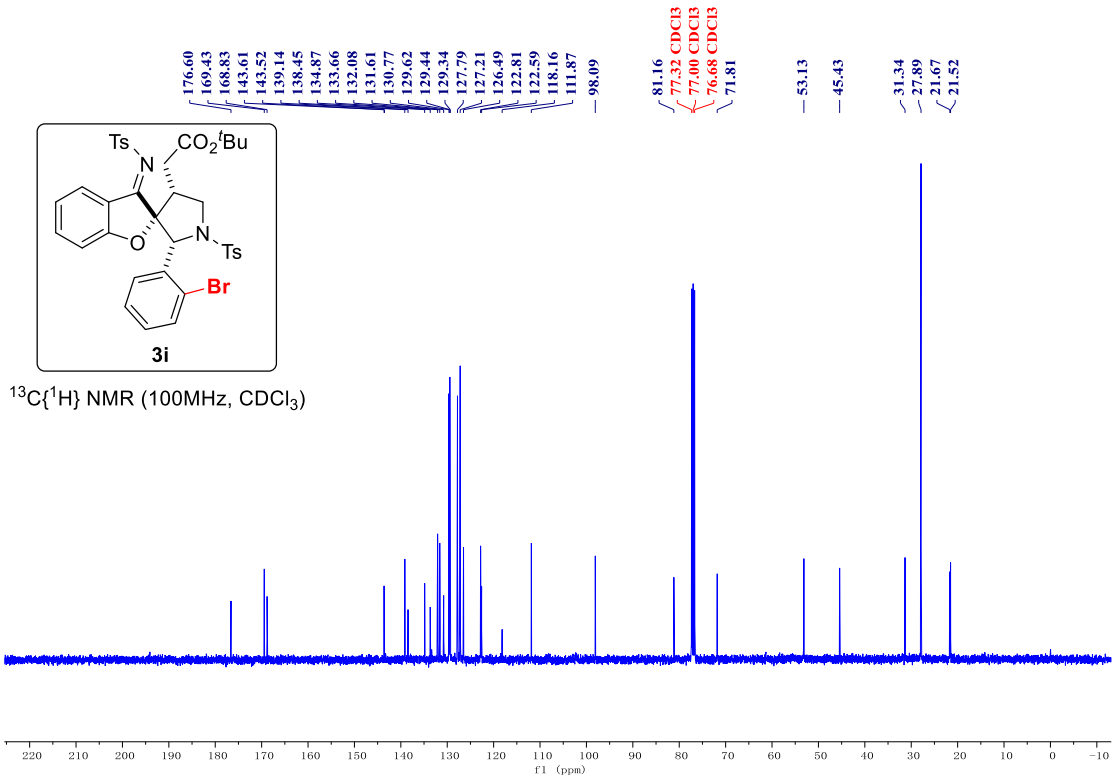


$^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$)



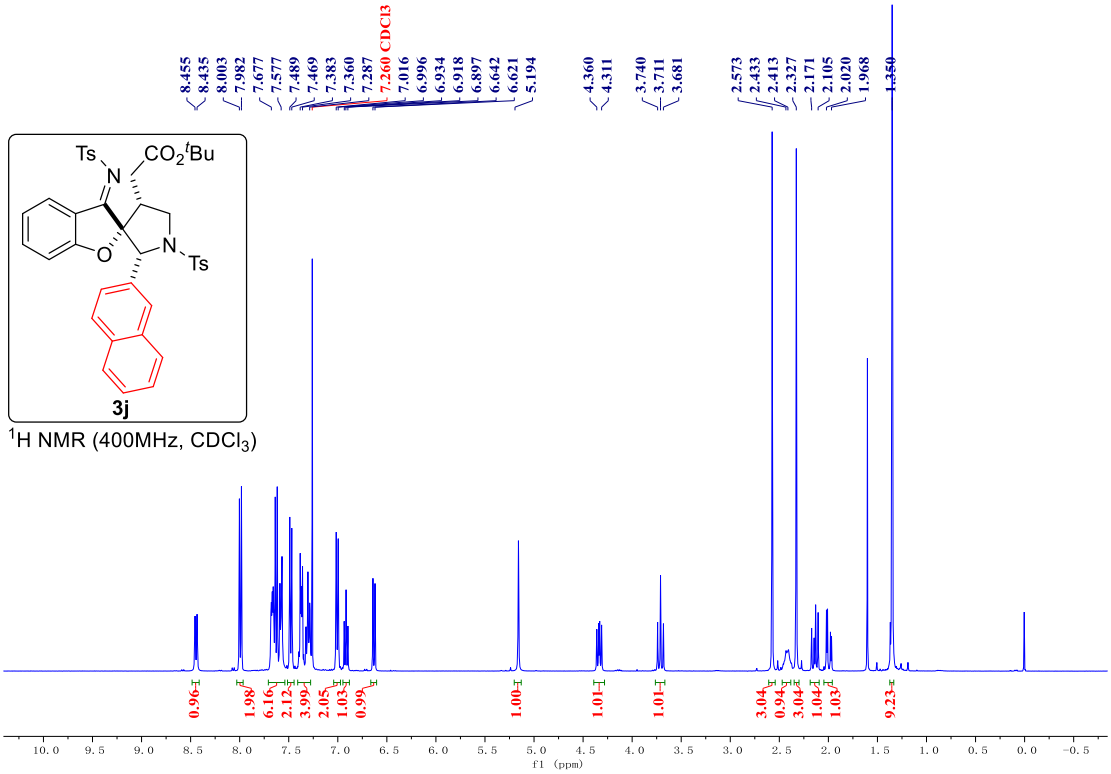
3i

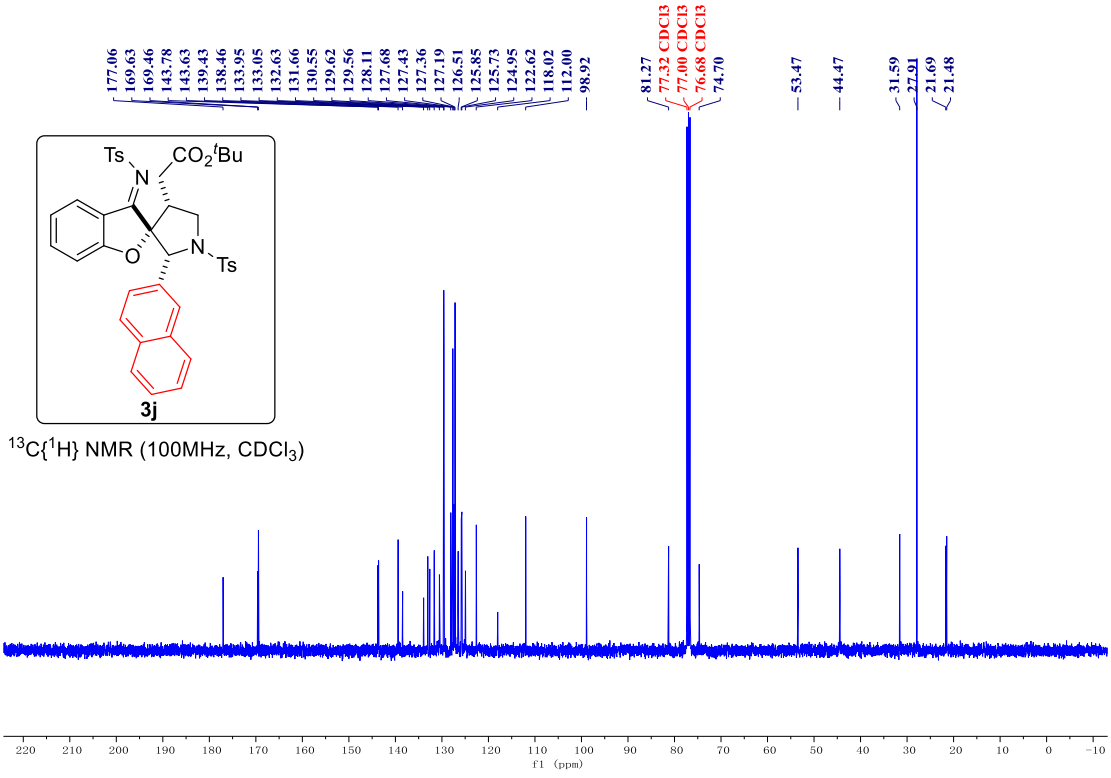
^{1}H NMR (400MHz, $CDCl_3$)

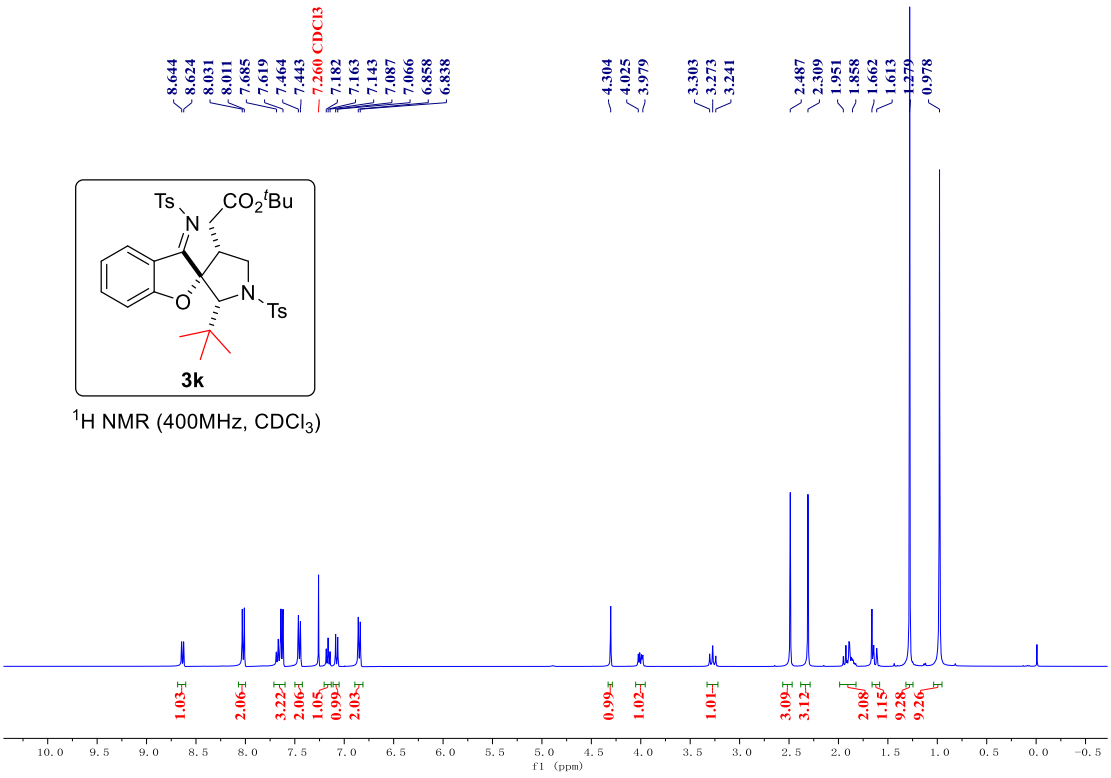


3i

$^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$)

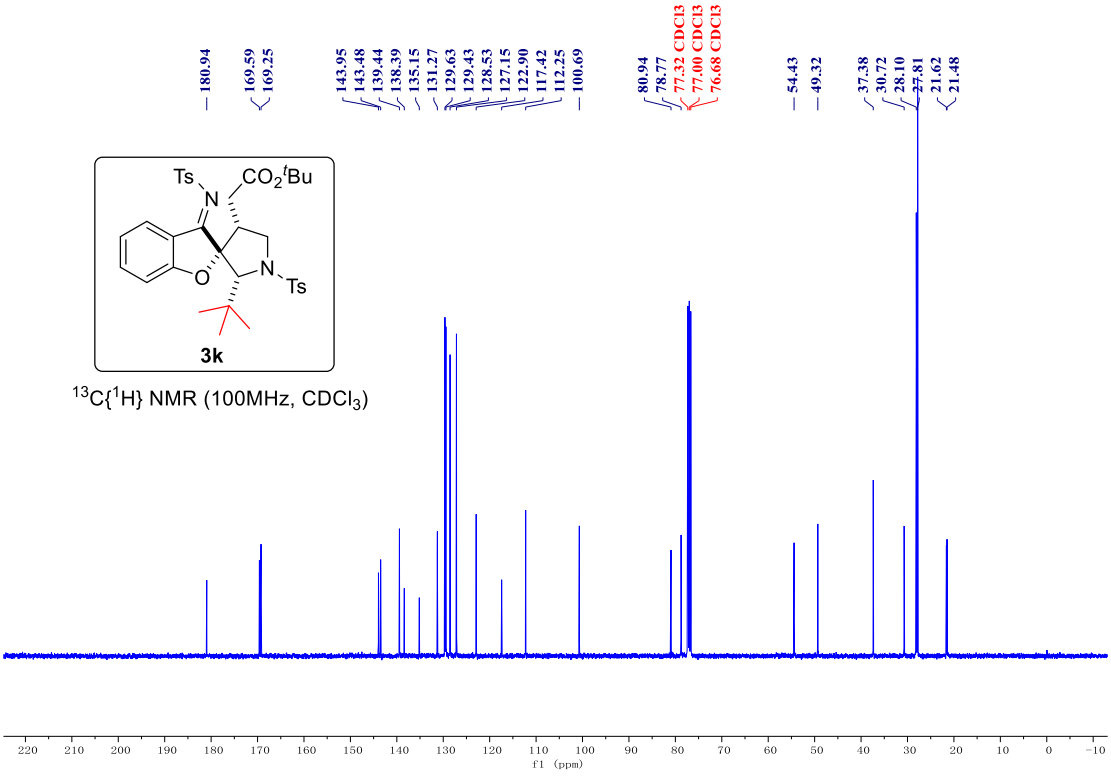

8.455
8.435
8.003
7.982
7.677
7.577
7.489
7.469
7.383
7.360
7.287
7.260 CDCl3
7.016
6.996
6.934
6.918
6.897
6.642
6.621
5.194
4.360
4.311
3.740
3.711
3.681
2.573
2.433
2.413
2.327
2.171
2.105
2.020
1.968
1.350
Ts
N
CO2tBu
O
N
Ts
3j
1H NMR (400MHz, CDCl3)
0.96
1.98
6.16
2.12
3.99
2.05
1.03
0.99
1.00
1.01
1.01
3.04
0.94
3.04
1.04
1.03
9.23
f1 (ppm)


177.06
169.63
169.46
143.78
143.63
139.43
138.46
133.95
133.05
132.63
131.66
130.55
129.62
129.56
128.11
127.68
127.43
127.36
127.19
126.51
125.85
125.73
124.95
122.62
118.02
112.00
98.92
81.27
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
74.70
53.47
44.47
31.59
27.91
21.69
21.48
Ts
N
CO2tBu
O
N
Ts
3j
13C{1H} NMR (100MHz, CDCl3)
f1 (ppm)



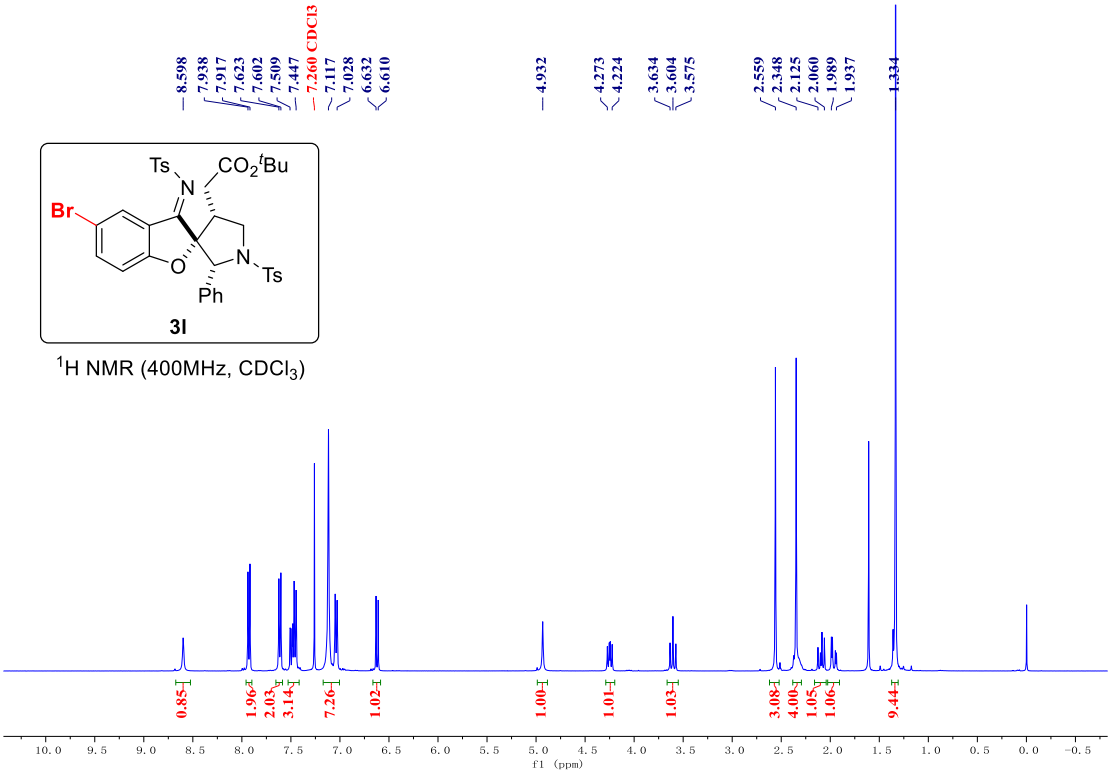
3k

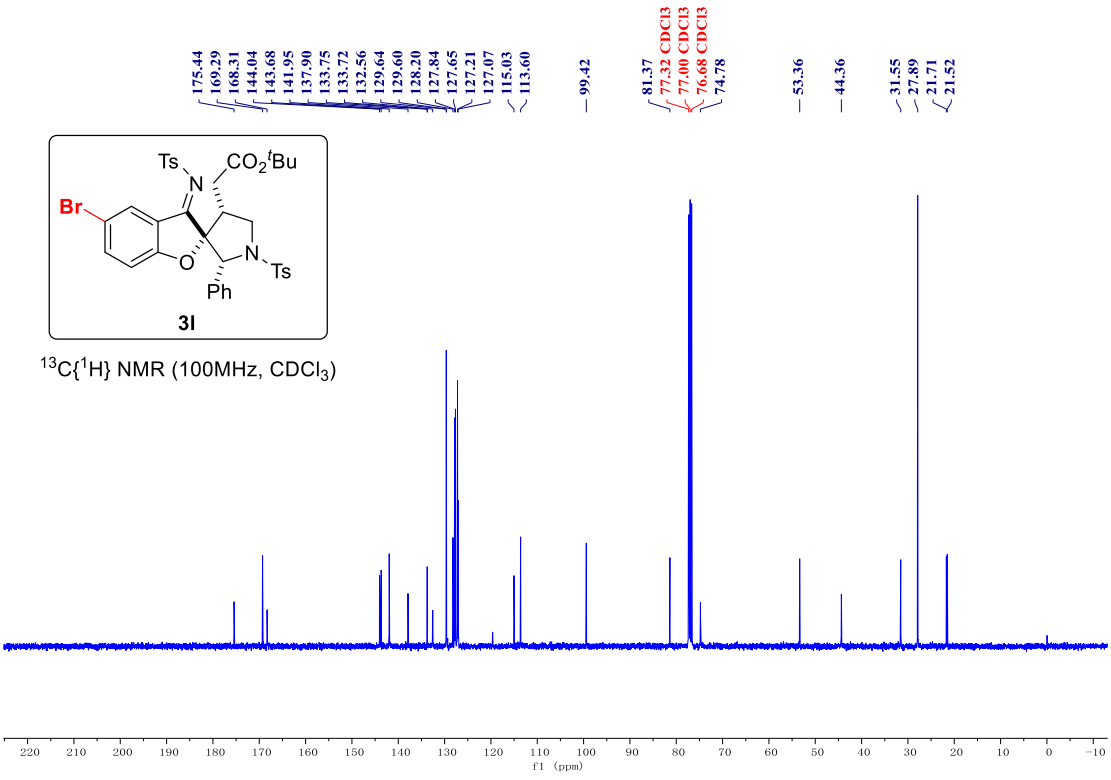
^{1}H NMR (400MHz, $CDCl_3$)

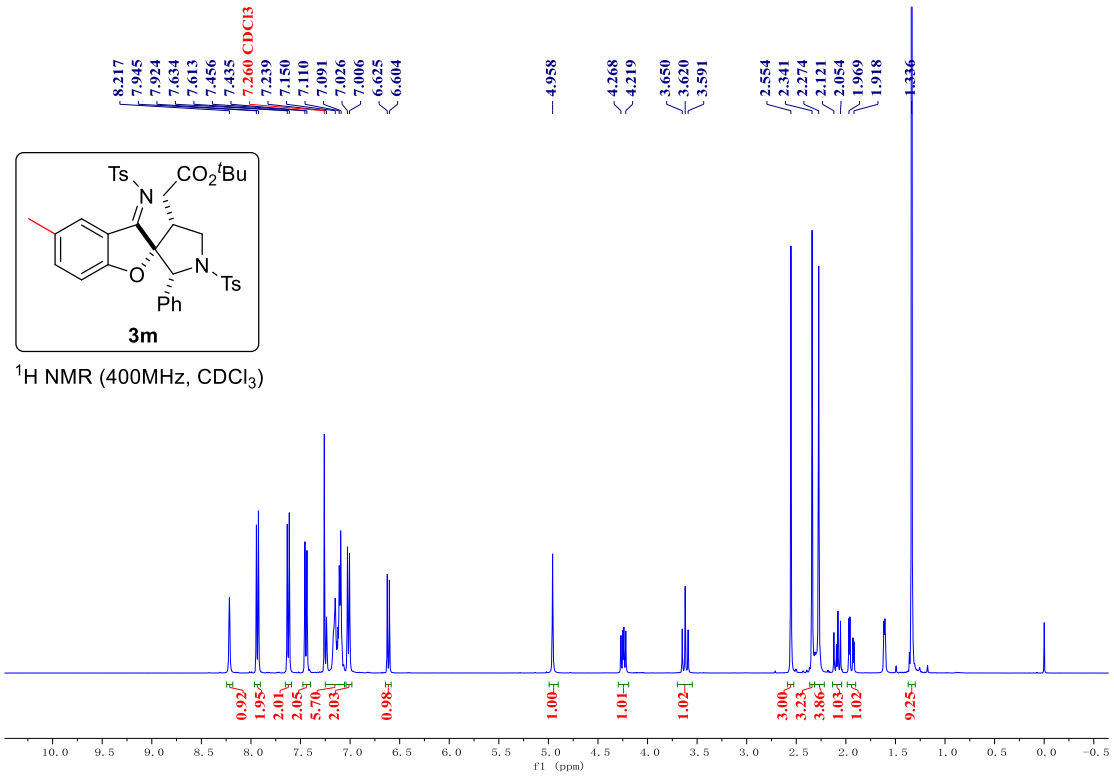


3k

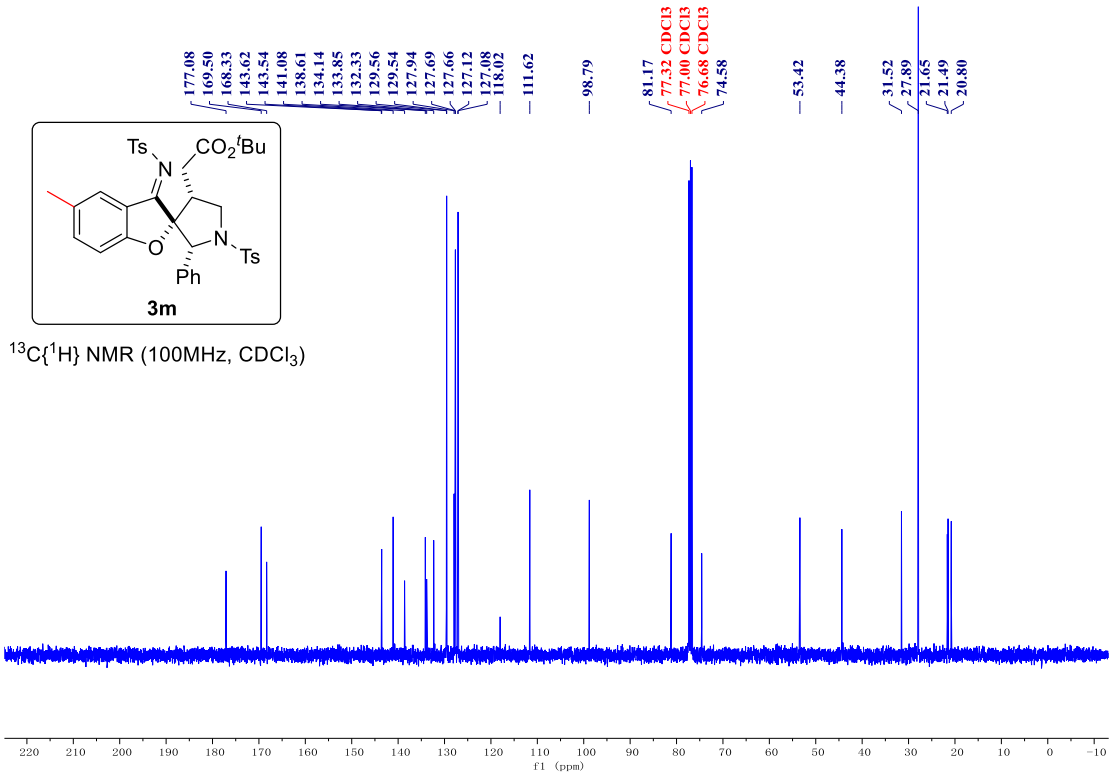
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$)


8.598
7.938
7.917
7.623
7.602
7.509
7.447
7.260 CDCl3
7.117
7.028
6.632
6.610
4.932
4.273
4.224
3.634
3.604
3.575
2.559
2.348
2.125
2.060
1.989
1.937
1.334
Ts
N
CO2tBu
Br
O
N
Ts
Ph
3l
1H NMR (400MHz, CDCl3)
0.85
1.96
2.03
3.14
7.26
1.02
1.00
1.01
1.03
3.08
4.00
1.05
1.06
9.44
f1 (ppm)

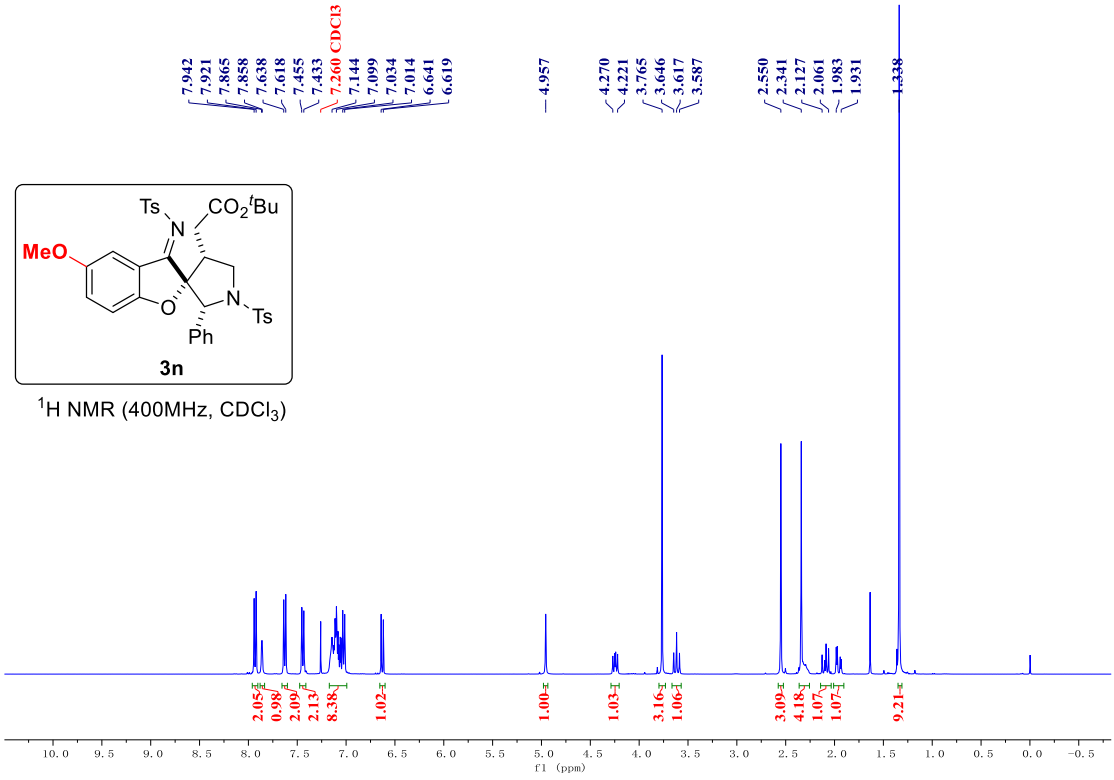

175.44
169.29
168.31
144.04
143.68
141.95
137.90
133.75
133.72
132.56
129.64
129.60
128.20
127.84
127.65
127.21
127.07
115.03
113.60
99.42
81.37
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
74.78
53.36
44.36
31.55
27.89
21.71
21.52
Ts
N
CO2tBu
Br
O
N
Ts
Ph
3l
13C{1H} NMR (100MHz, CDCl3)
f1 (ppm)



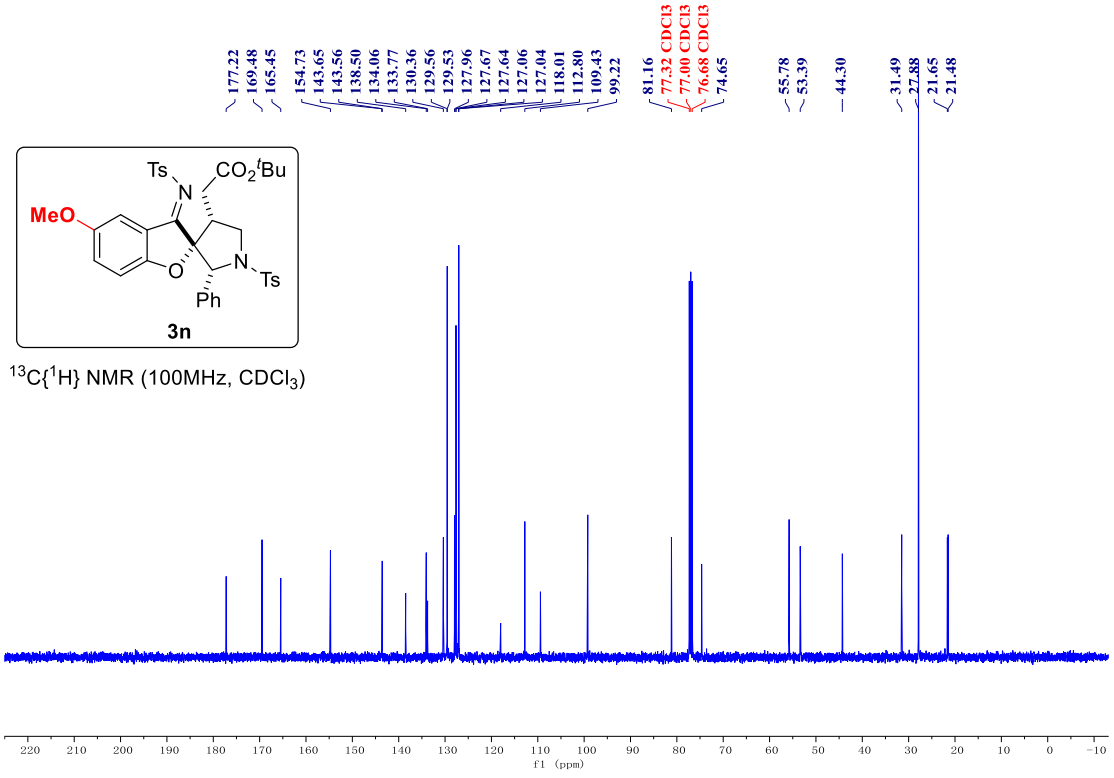
^{1}H NMR (400MHz, $CDCl_3$)



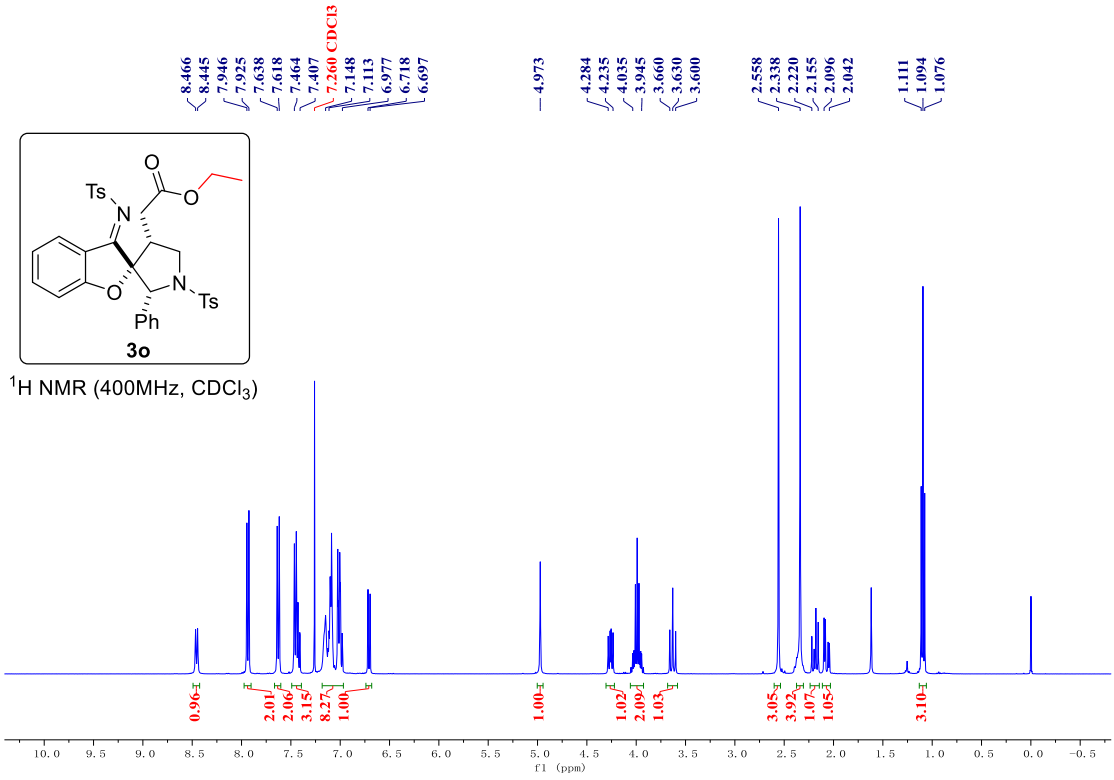
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$)



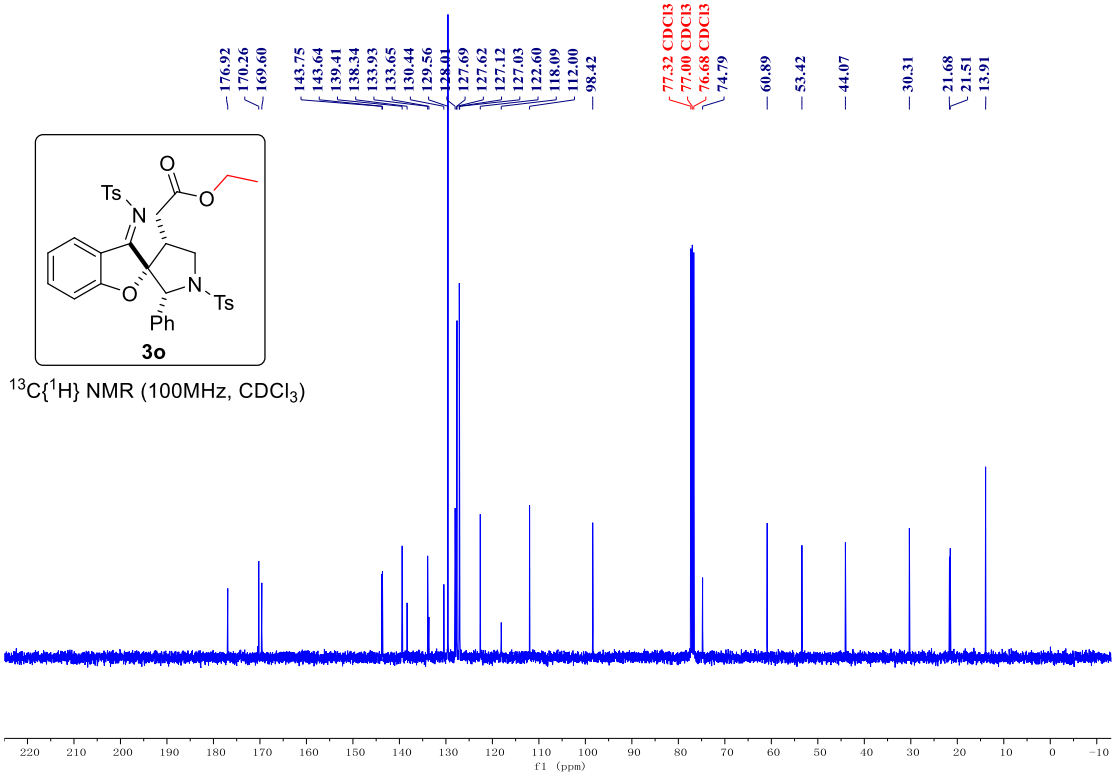
^{1}H NMR (400MHz, $CDCl_3$)



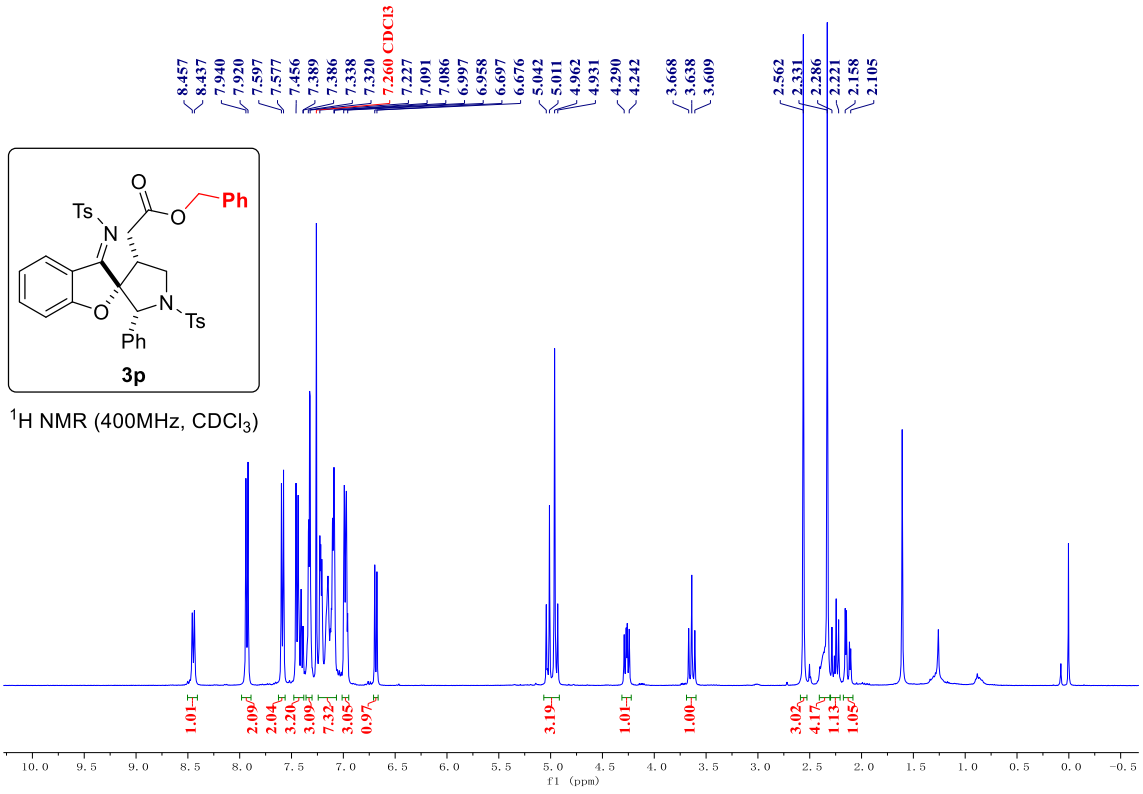
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$)

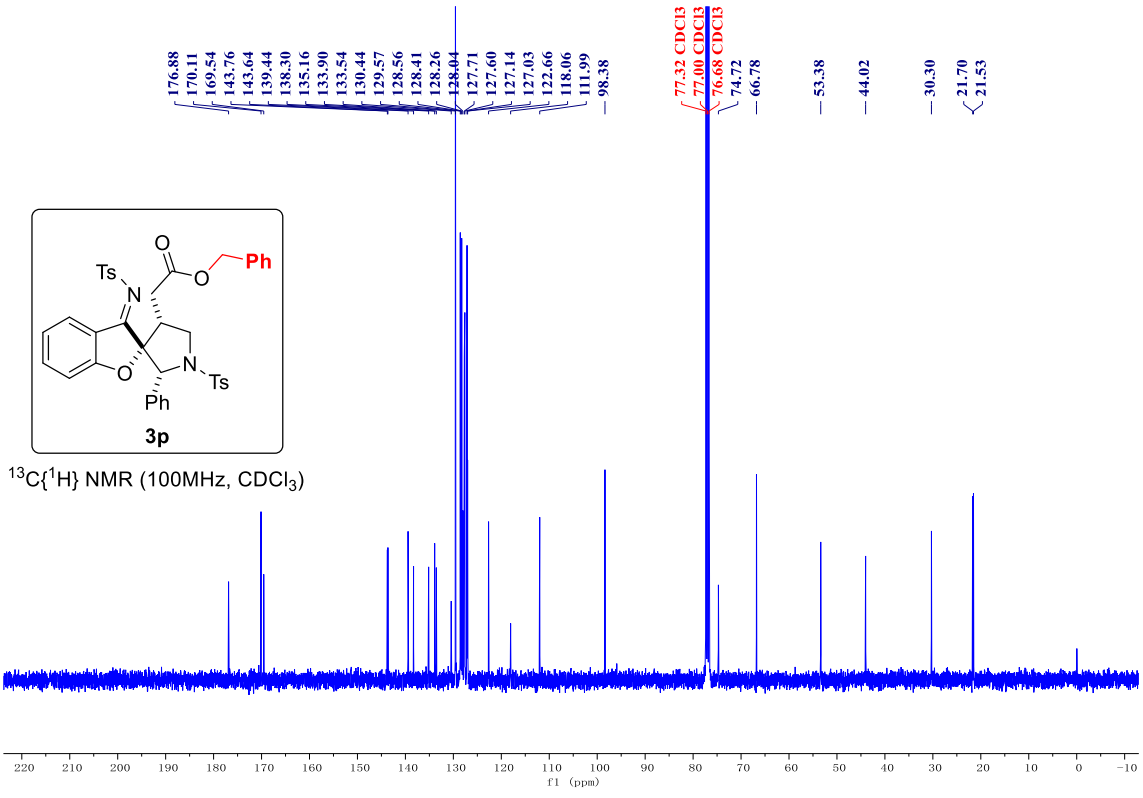


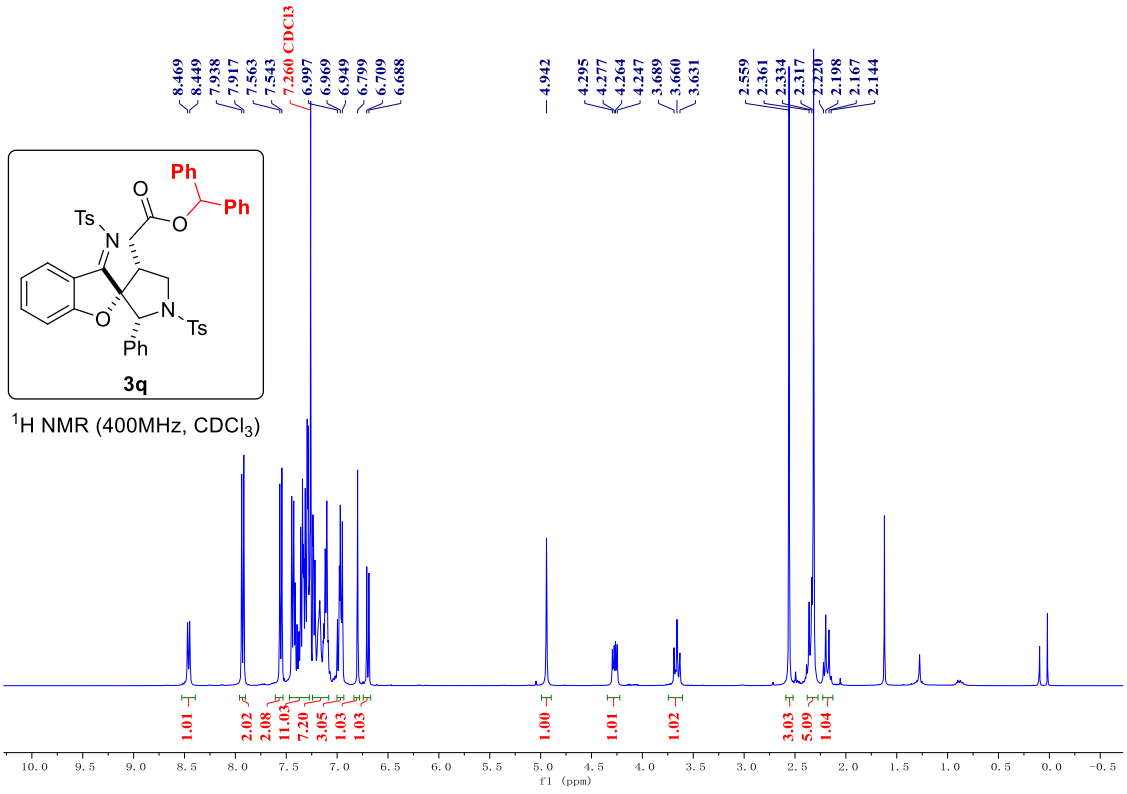
^{1}H NMR (400MHz, $CDCl_3$)



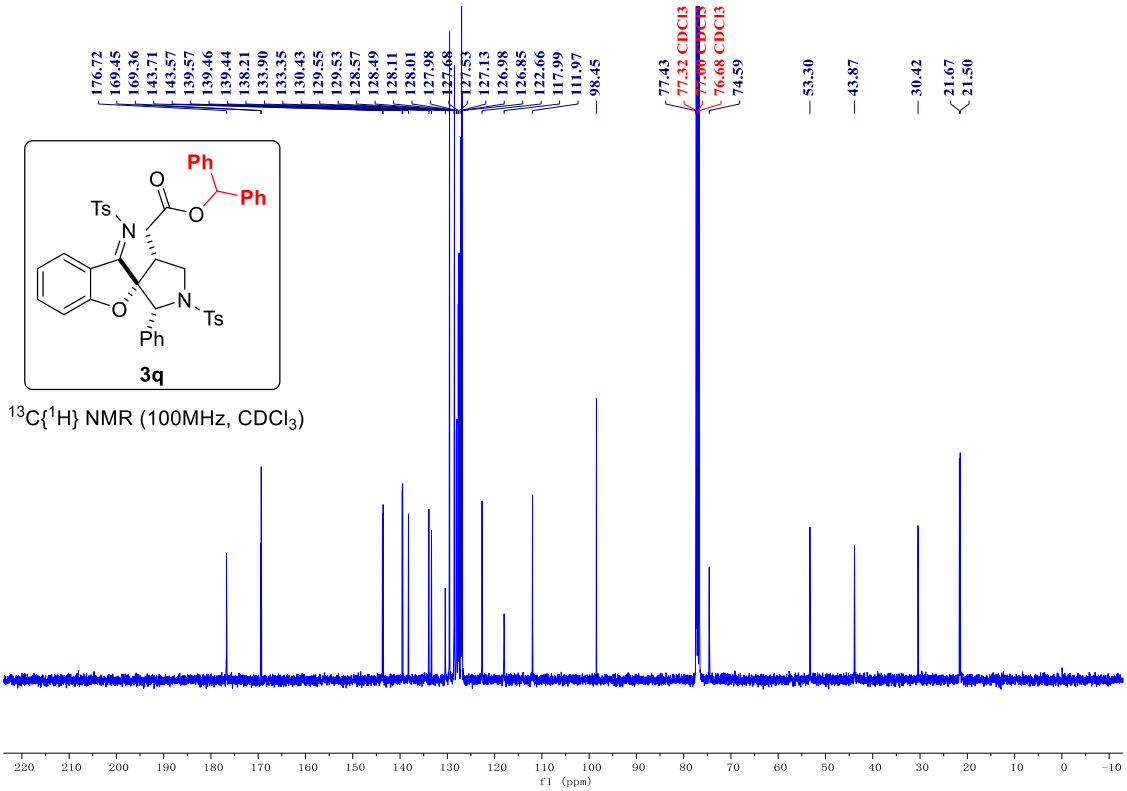
$^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$)


8.457
8.437
7.940
7.920
7.597
7.577
7.456
7.389
7.386
7.338
7.320
7.260 CDCl3
7.227
7.091
7.086
6.997
6.958
6.697
6.676
5.042
5.011
4.962
4.931
4.290
4.242
3.668
3.638
3.609
2.562
2.331
2.286
2.221
2.158
2.105
1.01
2.09
2.04
3.20
3.09
7.32
3.05
0.97
3.19
1.01
1.00
3.02
4.17
1.13
1.05
f1 (ppm)
Ts
N
O
Ph
O
N
Ts
Ph
3p
1H NMR (400MHz, CDCl3)

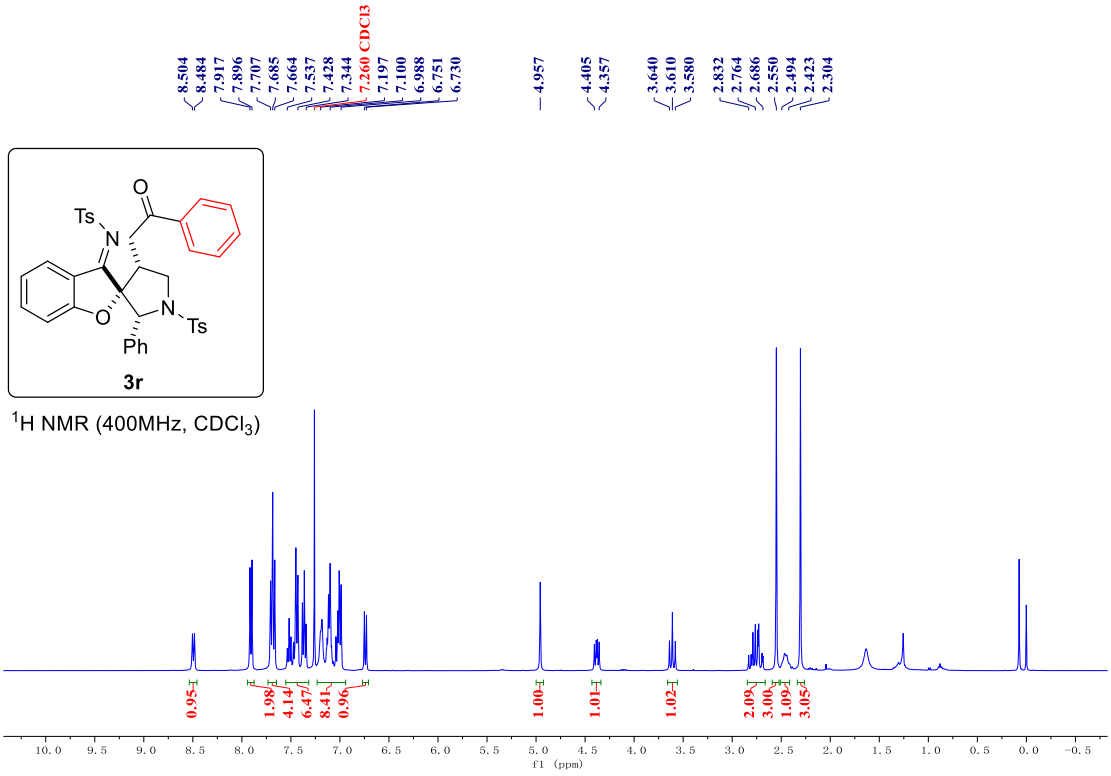

176.88
170.11
169.54
143.76
143.64
139.44
138.30
135.16
133.90
133.54
130.44
129.57
128.56
128.41
128.26
128.04
127.71
127.60
127.14
127.03
122.66
118.06
111.99
98.38
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
74.72
66.78
53.38
44.02
30.30
21.70
21.53
f1 (ppm)
Ts
N
O
Ph
O
N
Ts
Ph
3p
13C{1H} NMR (100MHz, CDCl3)



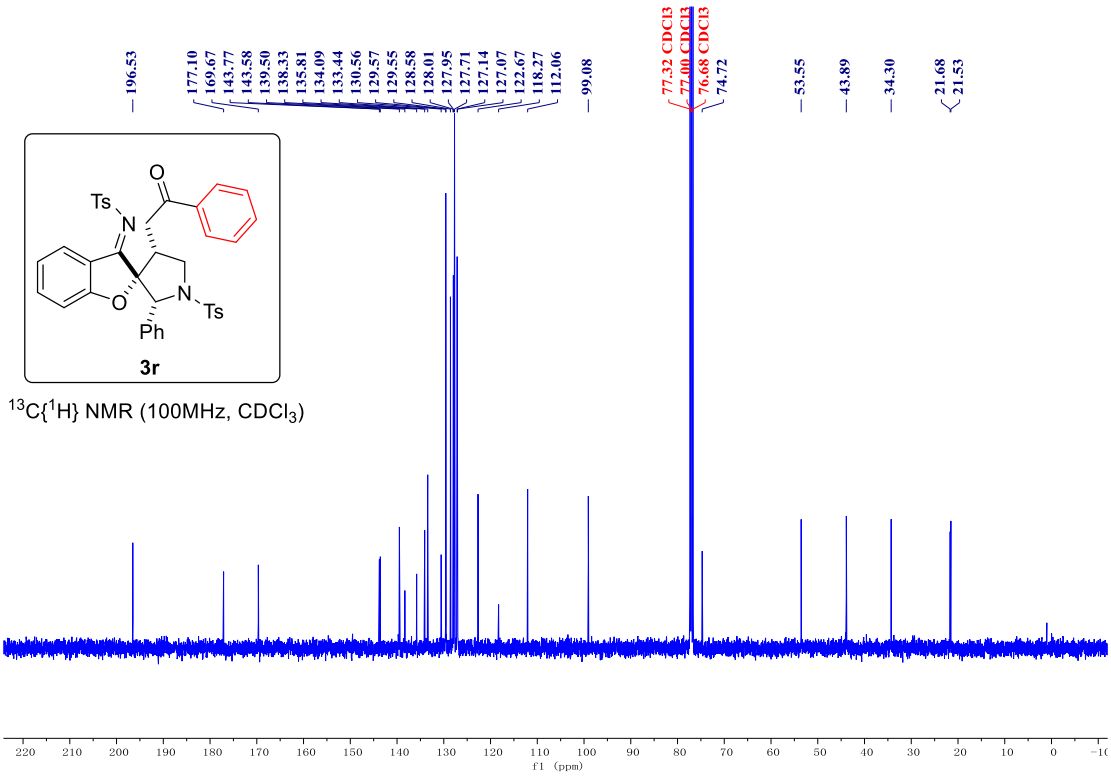
^{1}H NMR (400MHz, $CDCl_3$)



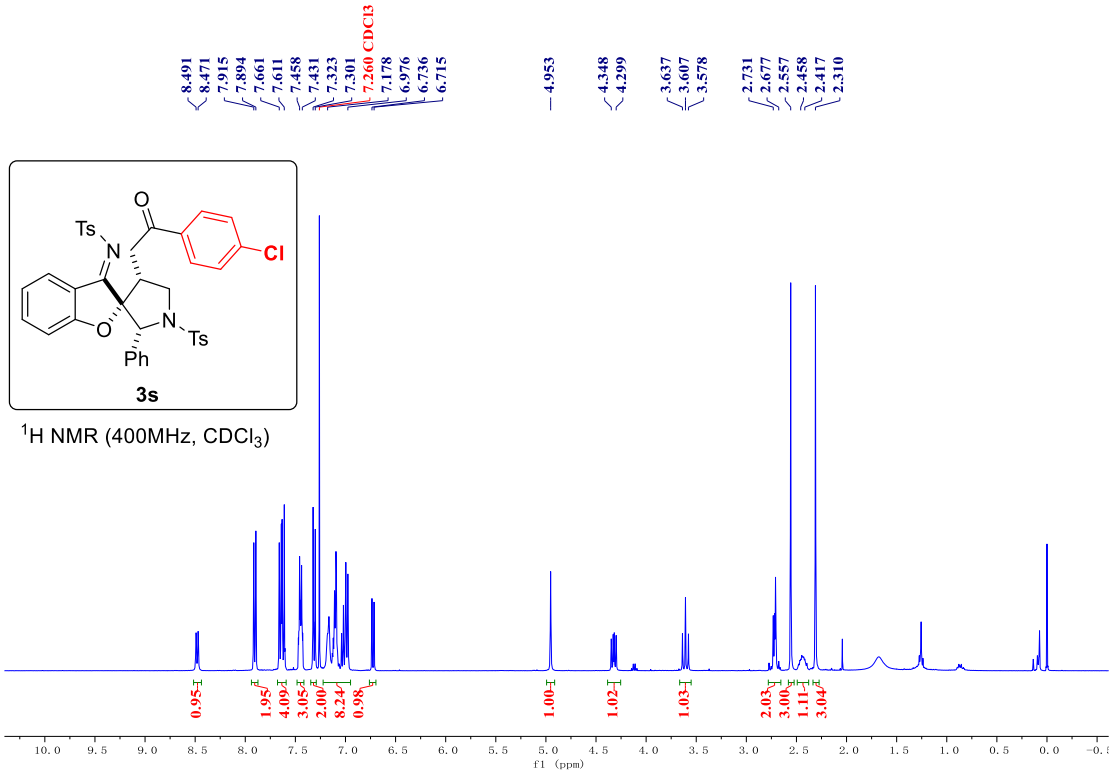
$^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$)



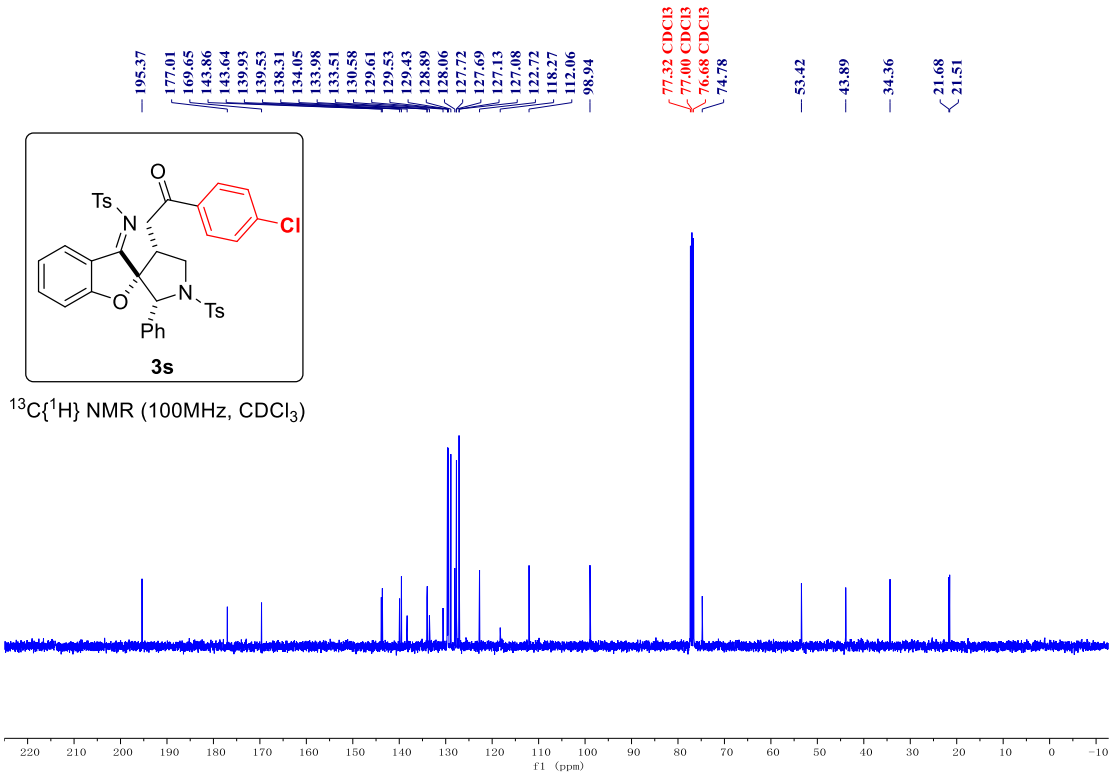
^{1}H NMR (400MHz, $CDCl_3$)



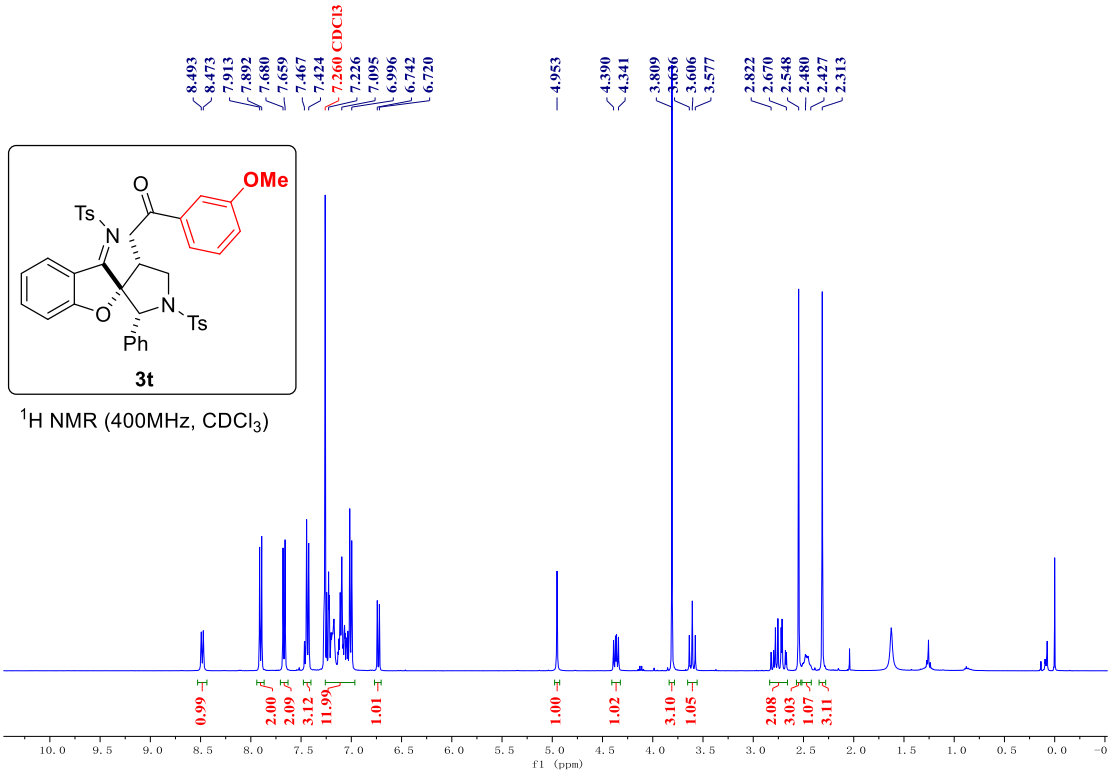
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$)



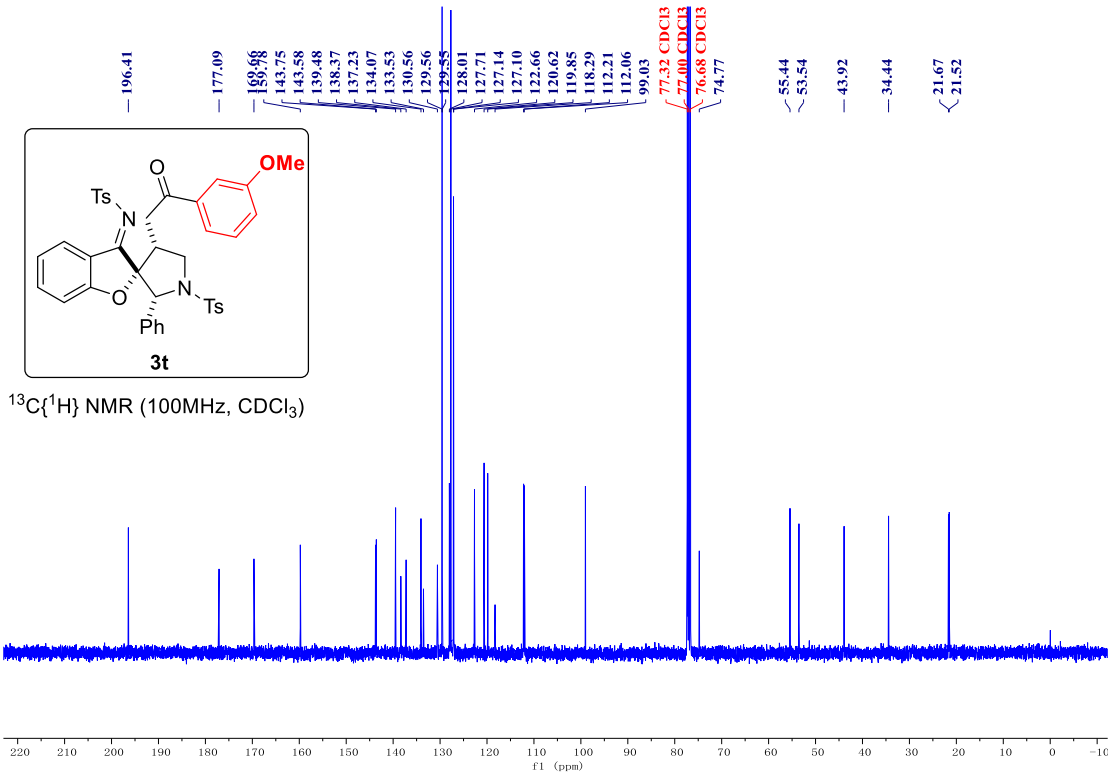
^{1}H NMR (400MHz, $CDCl_3$)



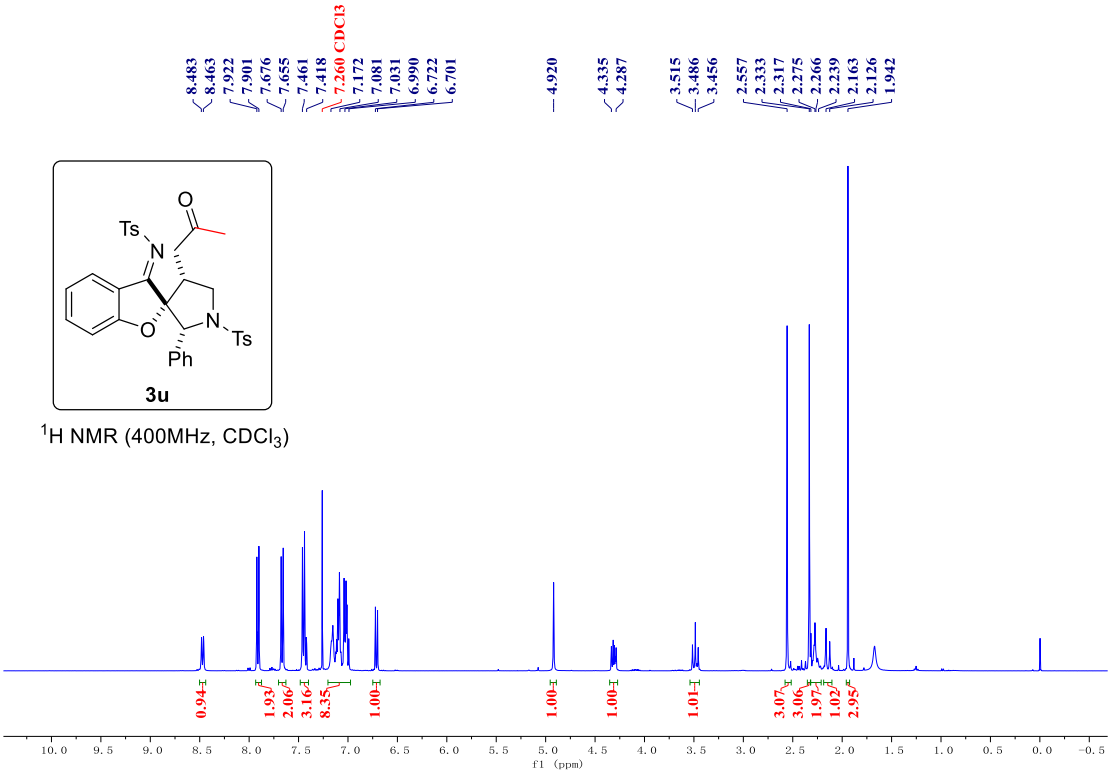
$^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$)



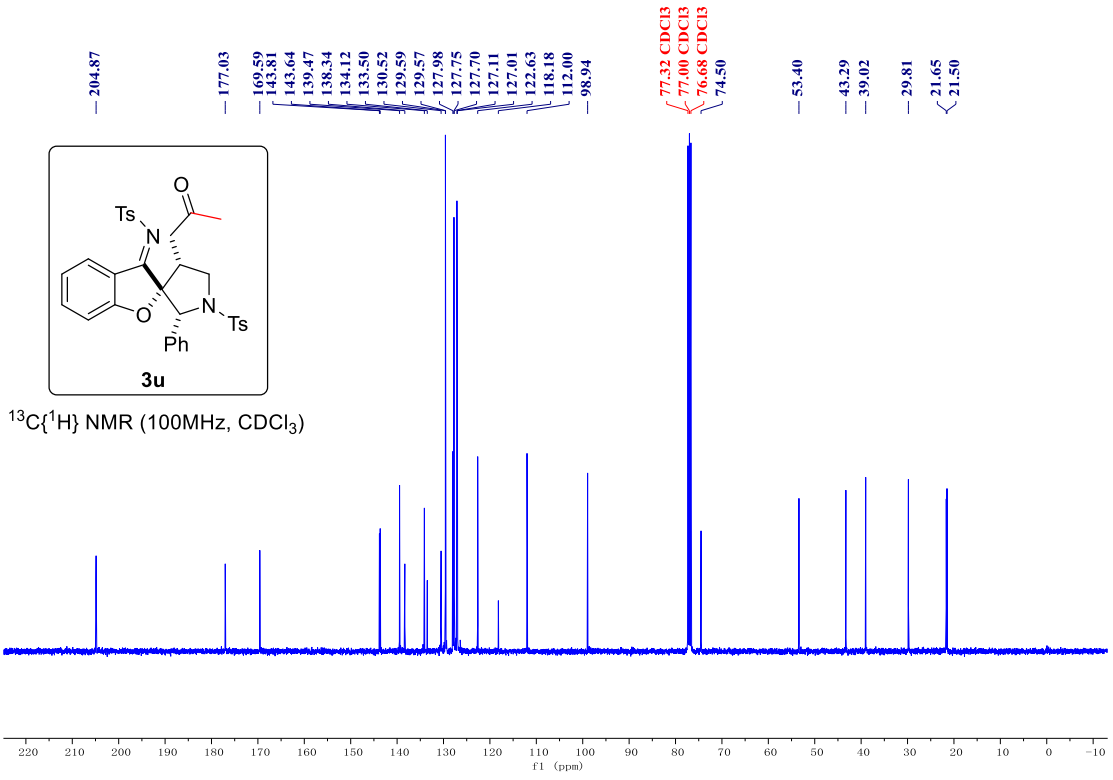
^{1}H NMR (400MHz, $CDCl_3$)



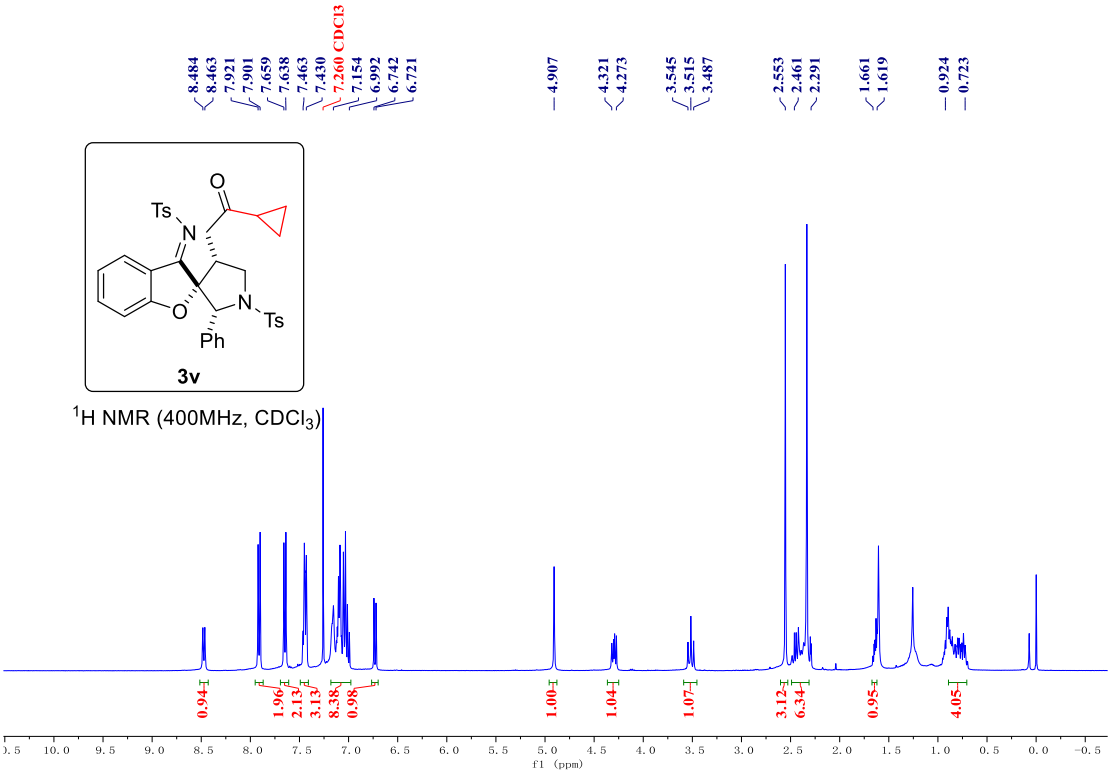
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$)



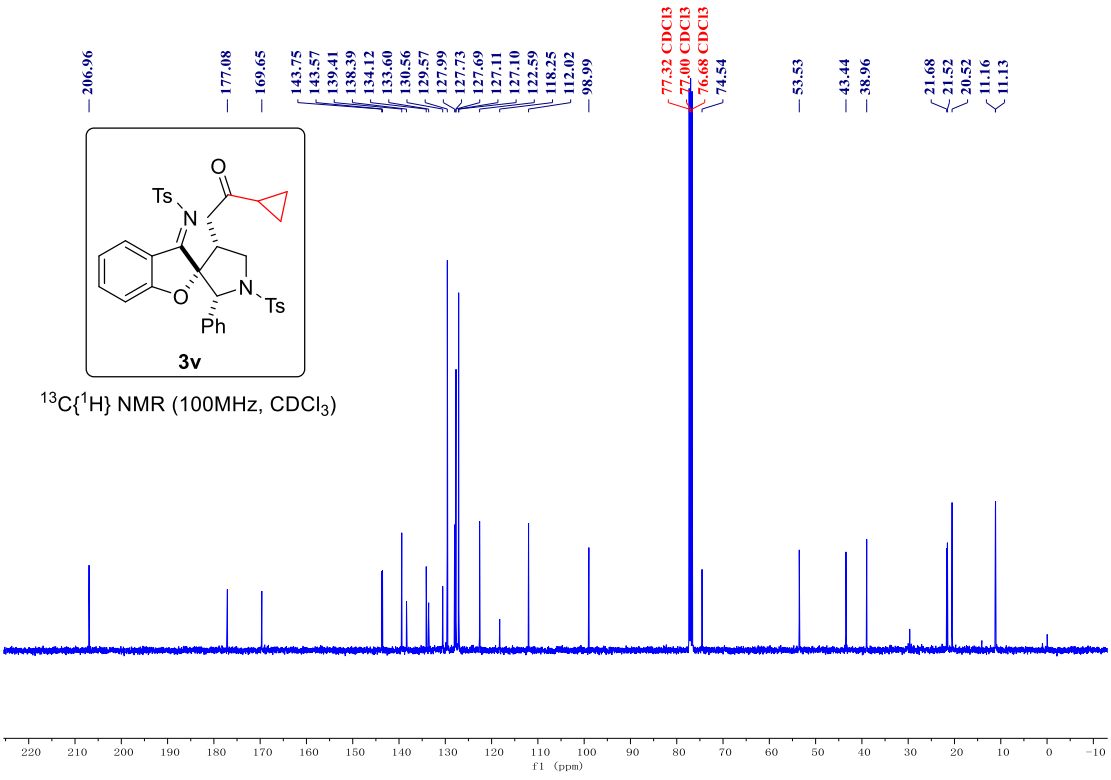
^{1}H NMR (400MHz, $CDCl_3$)



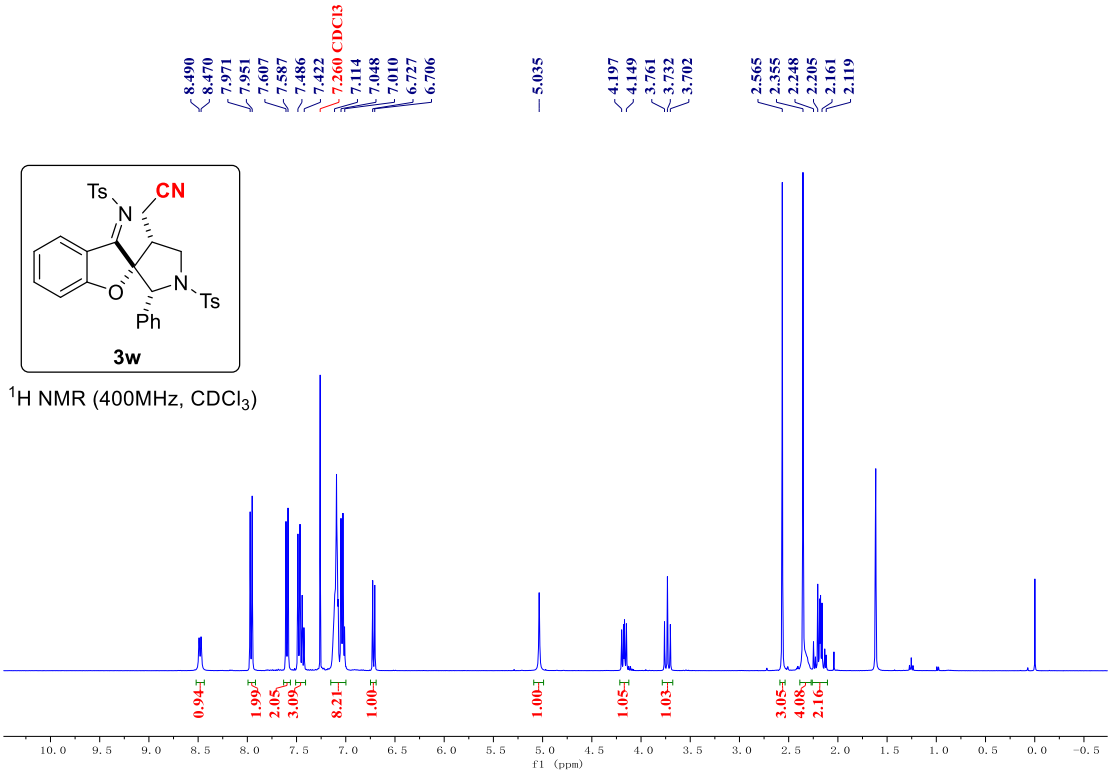
$^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$)



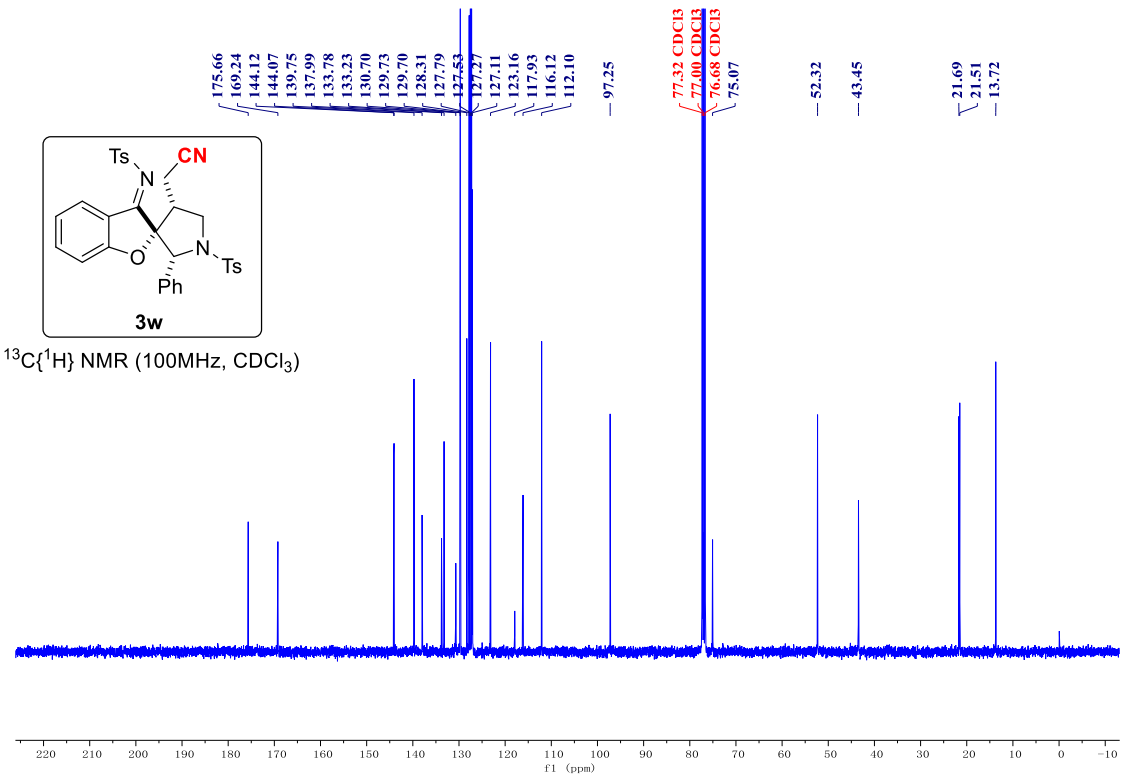
^{1}H NMR (400MHz, $CDCl_3$)



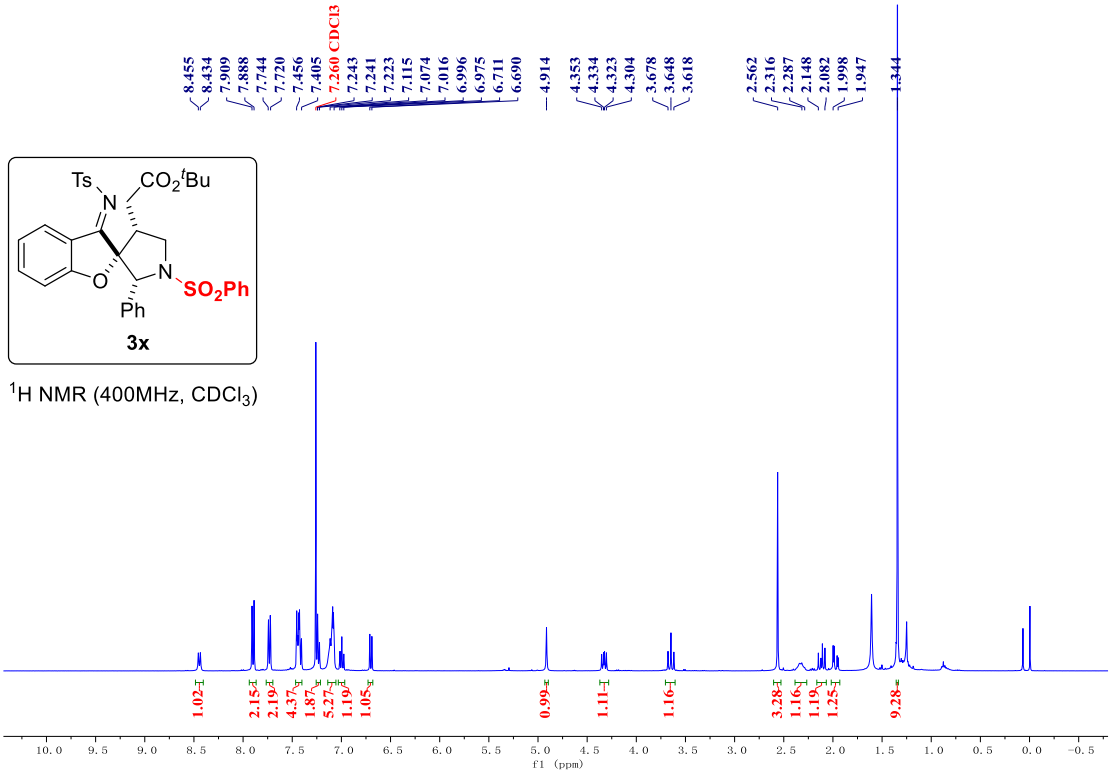
$^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$)

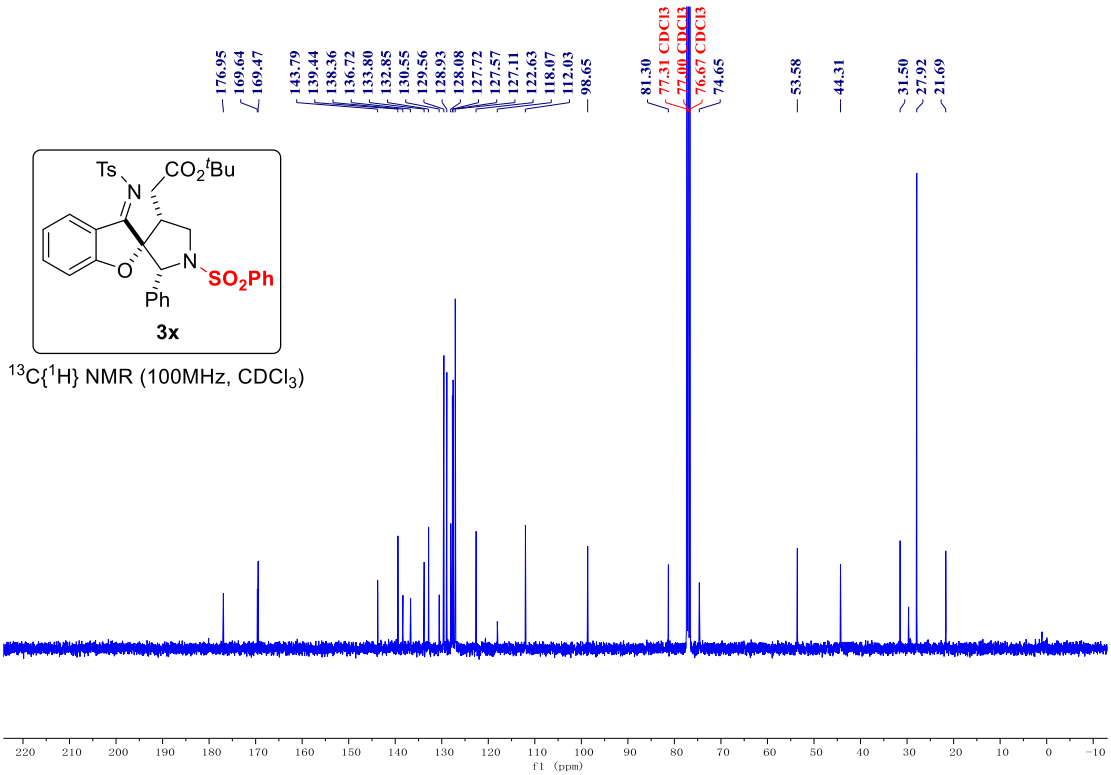


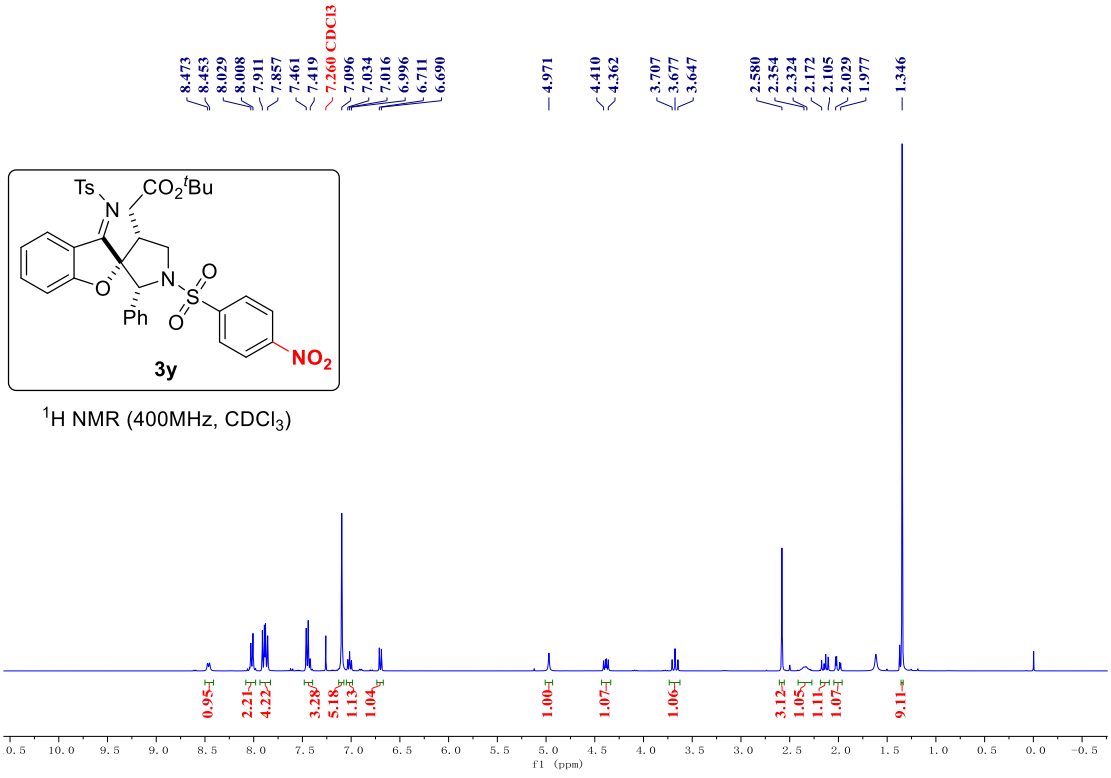
^{1}H NMR (400MHz, $CDCl_3$)



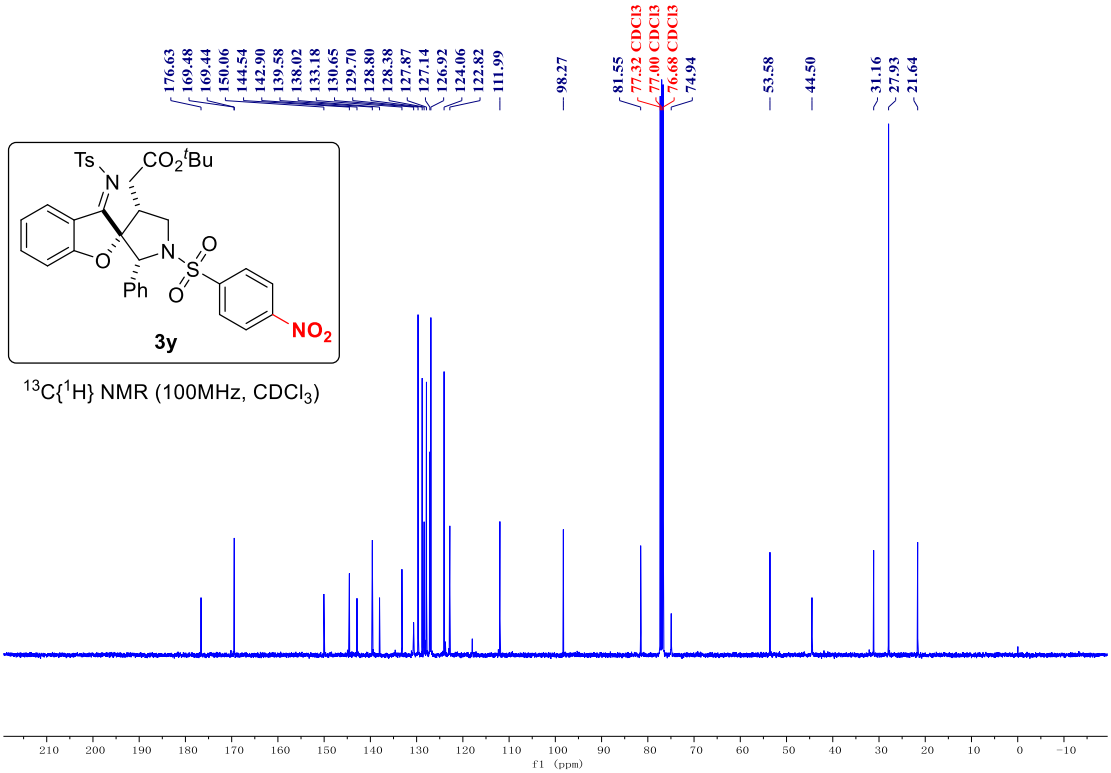
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$)


8.455
8.434
7.909
7.888
7.744
7.720
7.456
7.405
7.260 CDCl3
7.243
7.241
7.223
7.115
7.074
7.016
6.996
6.975
6.711
6.690
4.914
4.353
4.334
4.323
4.304
3.678
3.648
3.618
2.562
2.316
2.287
2.148
2.082
1.998
1.947
1.344
1.02
2.15
2.19
4.37
1.87
5.27
1.19
1.05
0.99
1.11
1.16
3.28
1.16
1.19
1.25
9.28
f1 (ppm)

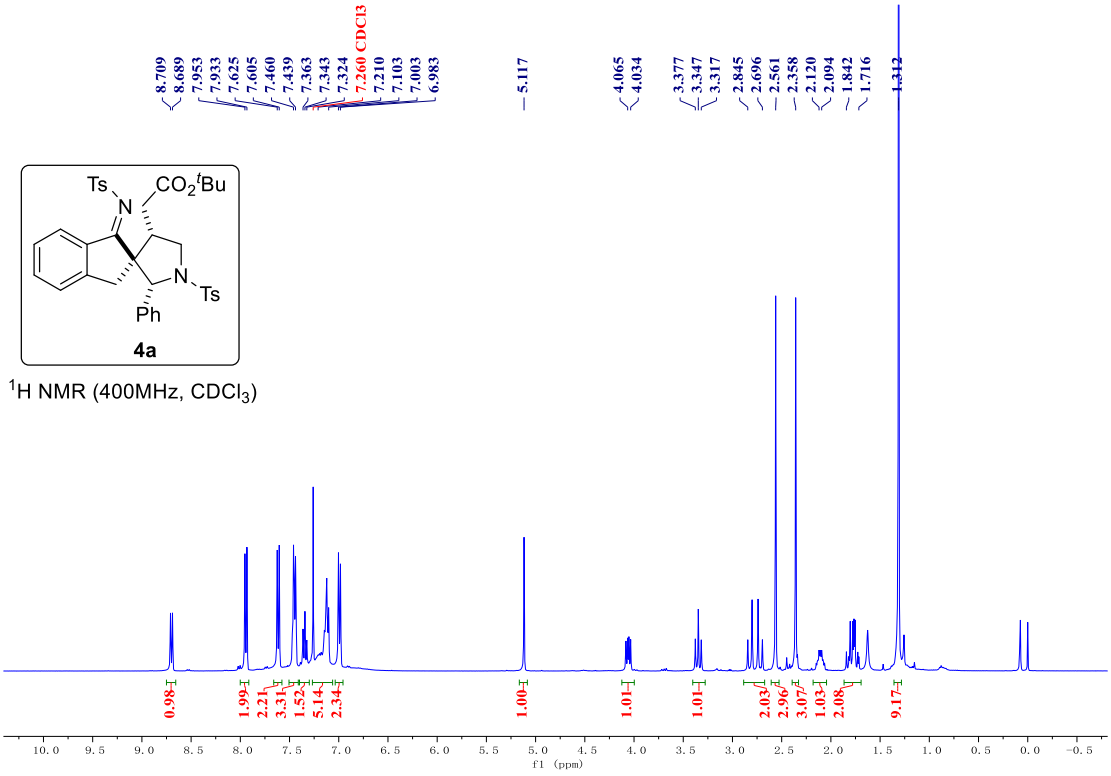

176.95
169.64
169.47
143.79
139.44
138.36
136.72
133.80
132.85
130.55
129.56
128.93
128.08
127.72
127.57
127.11
122.63
118.07
112.03
98.65
81.30
77.31 CDCl3
77.00 CDCl3
76.67 CDCl3
74.65
53.58
44.31
31.50
27.92
21.69
f1 (ppm)



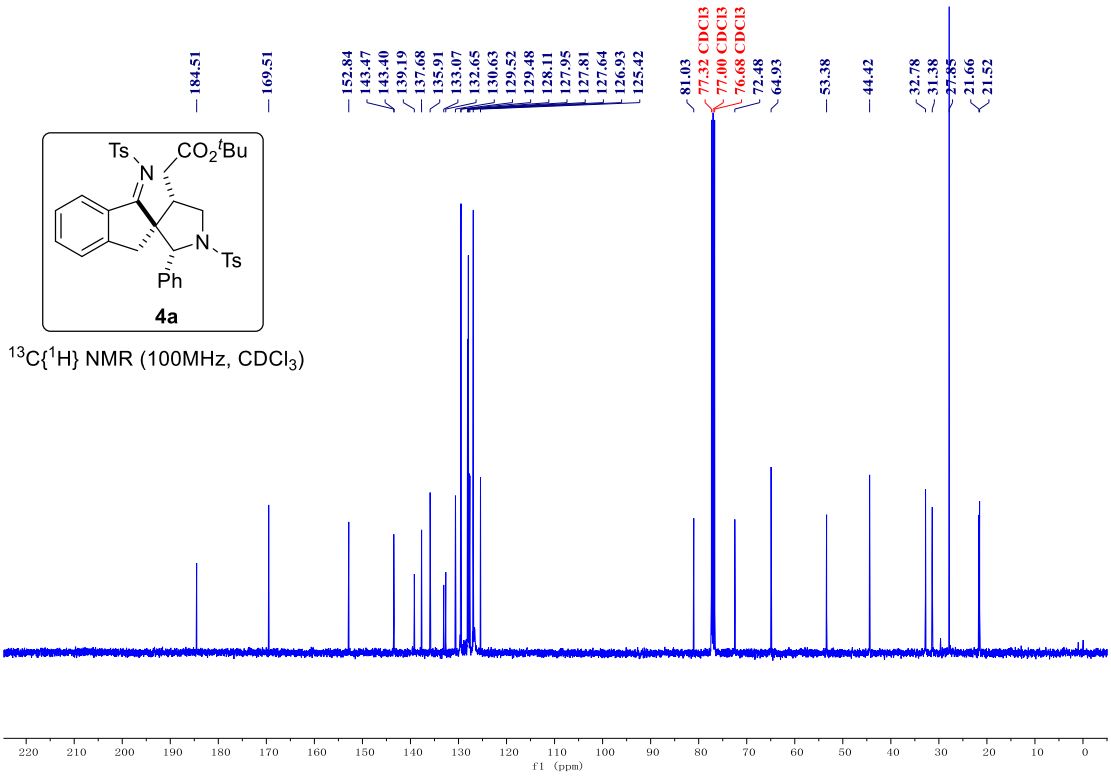
^{1}H NMR (400MHz, $CDCl_3$)



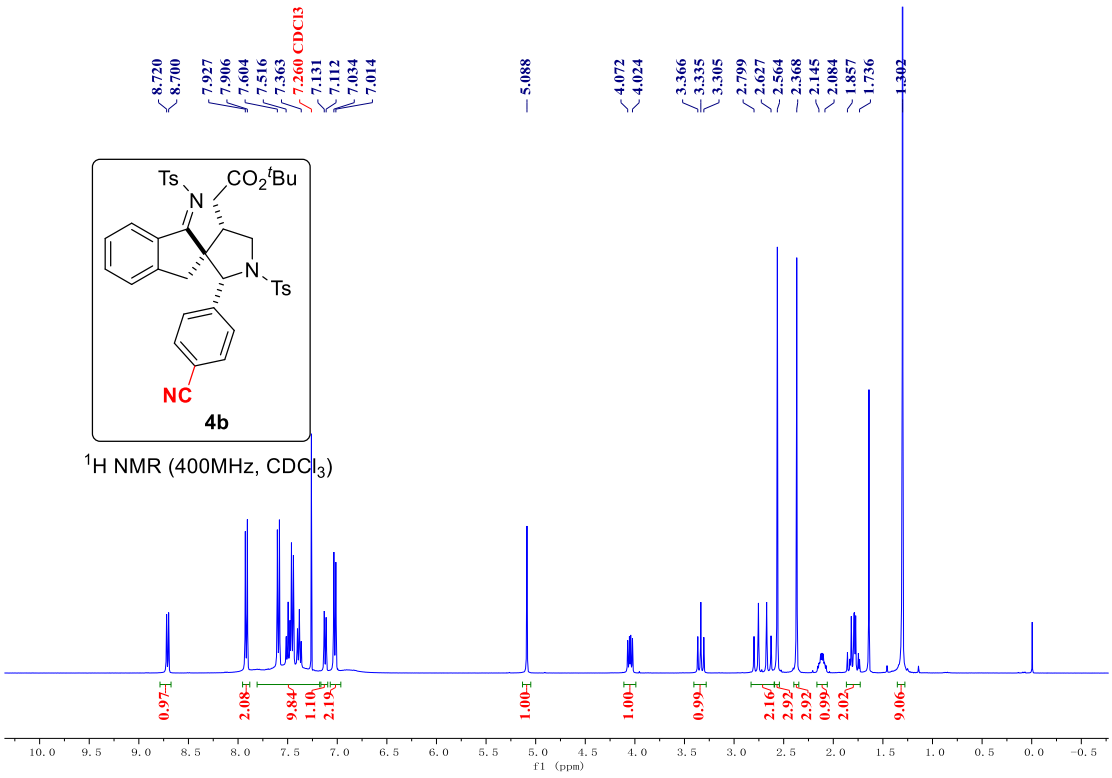
$^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$)

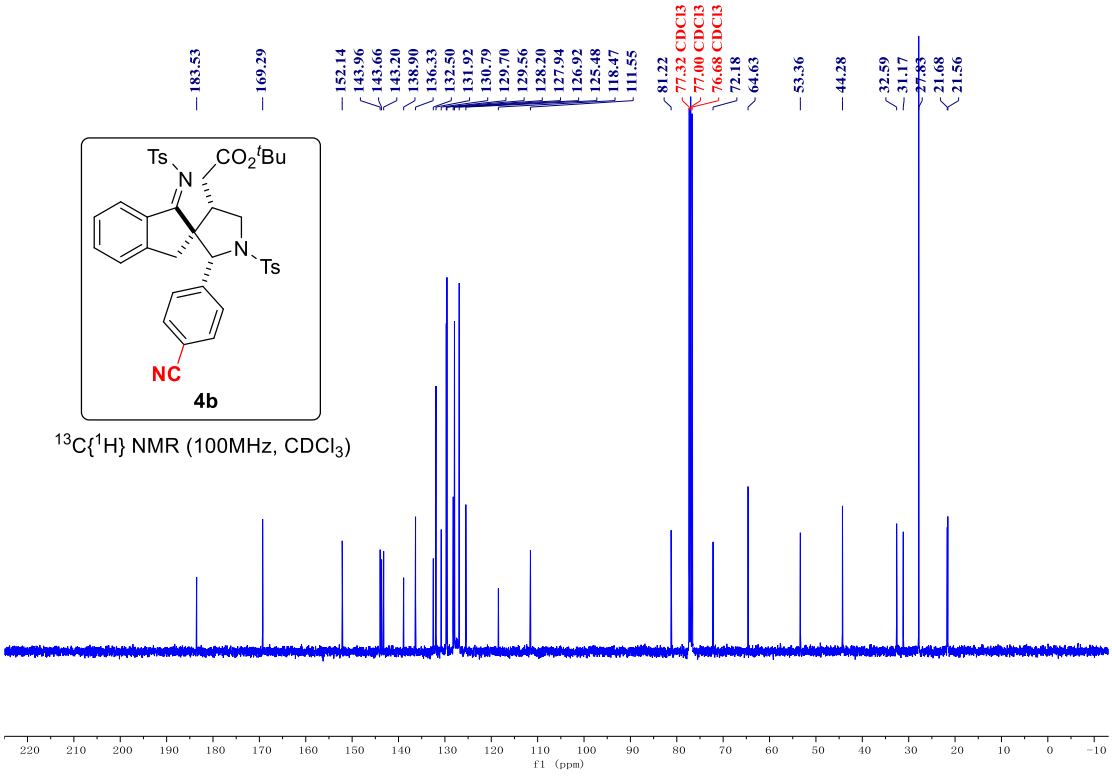


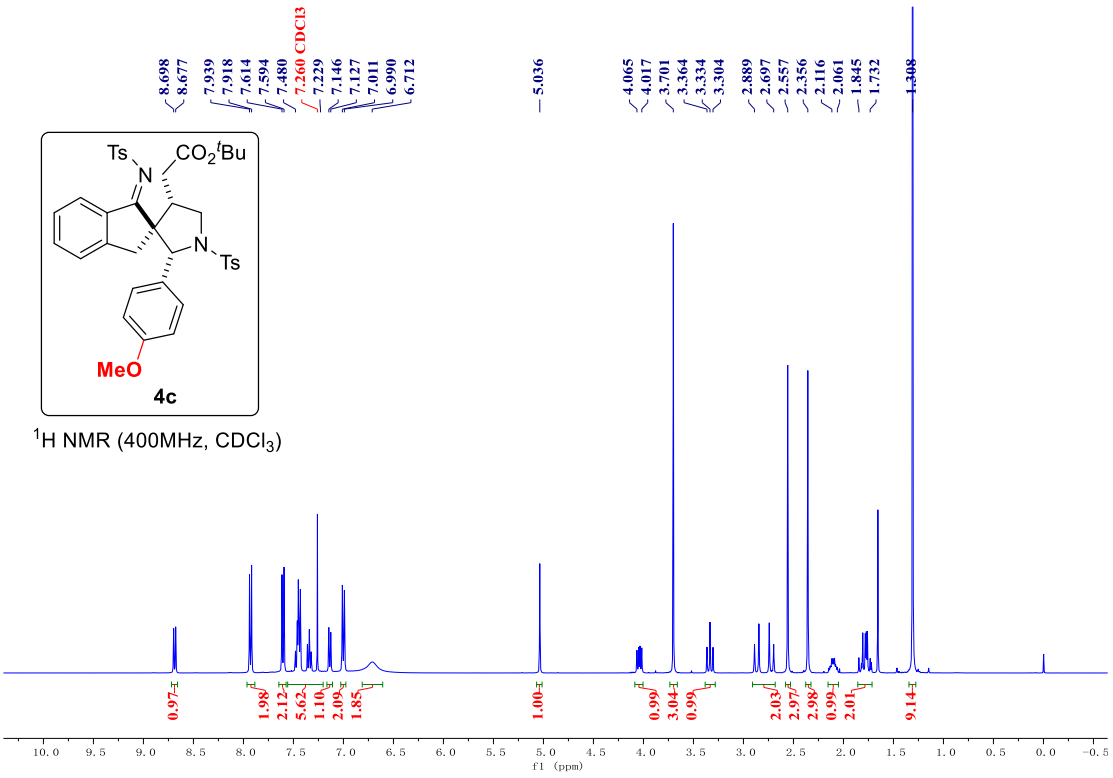
^{1}H NMR (400MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100MHz, $CDCl_3$)

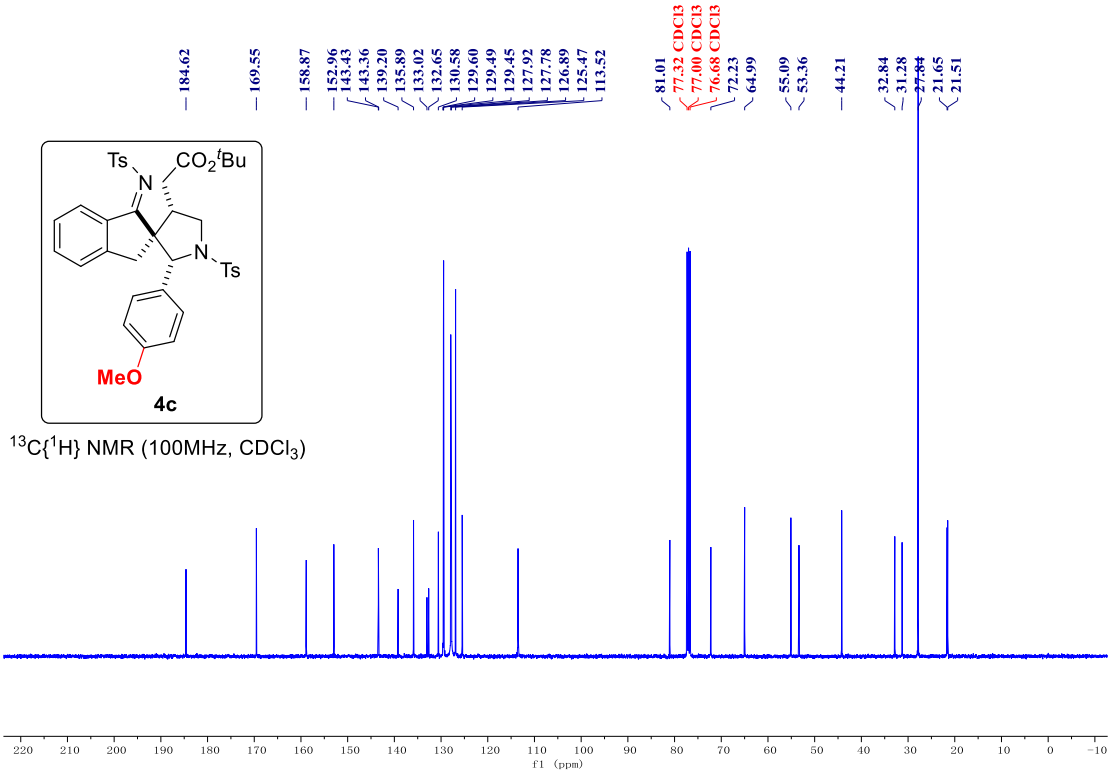

8.720
8.700
7.927
7.906
7.604
7.516
7.363
7.260 CDCl3
7.131
7.112
7.034
7.014
5.088
4.072
4.024
3.366
3.335
3.305
2.799
2.627
2.564
2.368
2.145
2.084
1.857
1.736
1.302
Ts
N
CO2tBu
N
Ts
NC
4b
1H NMR (400MHz, CDCl3)
0.97
2.08
9.84
1.10
2.19
1.00
1.00
0.99
2.16
2.92
2.92
0.99
2.02
9.06
f1 (ppm)


183.53
169.29
152.14
143.96
143.66
143.20
138.90
136.33
132.50
131.92
130.79
129.70
129.56
128.20
127.94
126.92
125.48
118.47
111.55
81.22
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
72.18
64.63
53.36
44.28
32.59
31.17
27.83
21.68
21.56
Ts
N
CO2tBu
N
Ts
NC
4b
13C{1H} NMR (100MHz, CDCl3)
f1 (ppm)



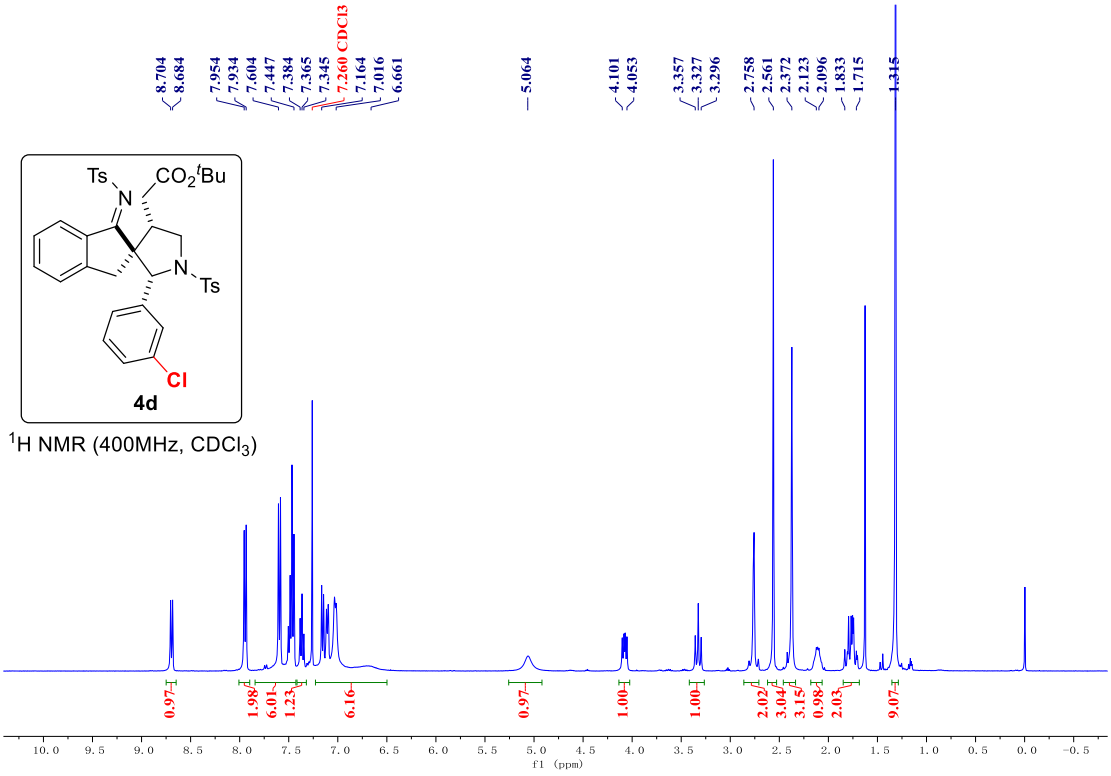
4c

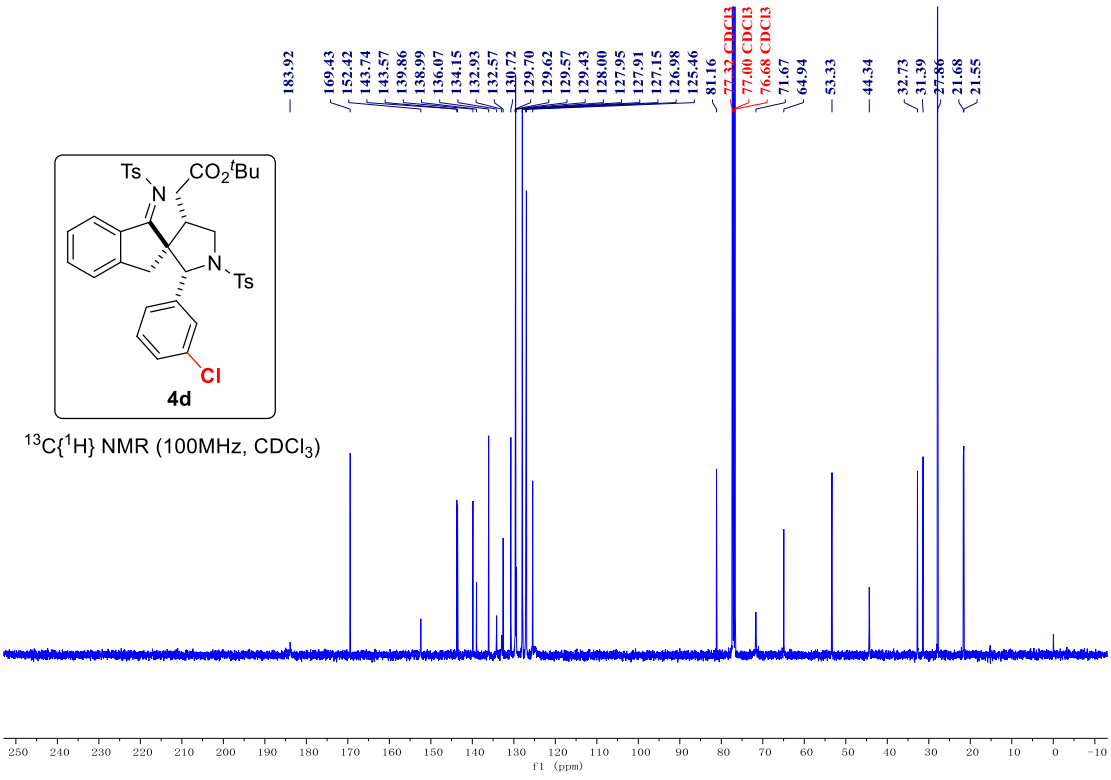
^{1}H NMR (400MHz, $CDCl_3$)

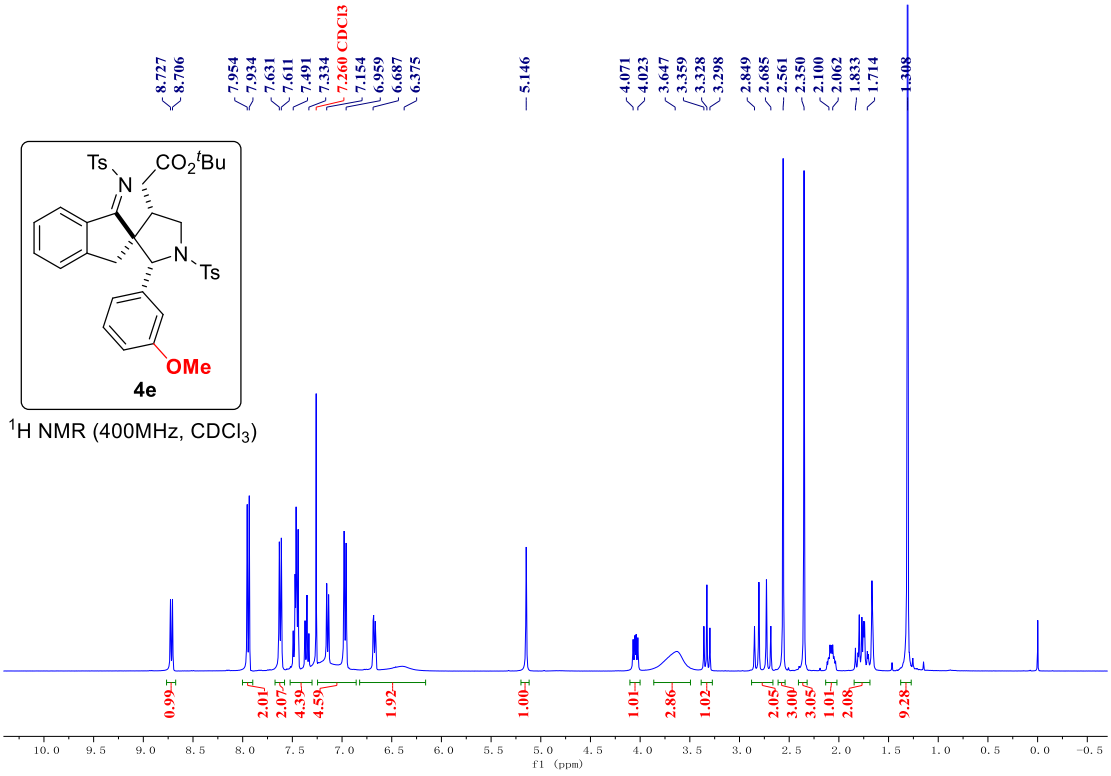


4c

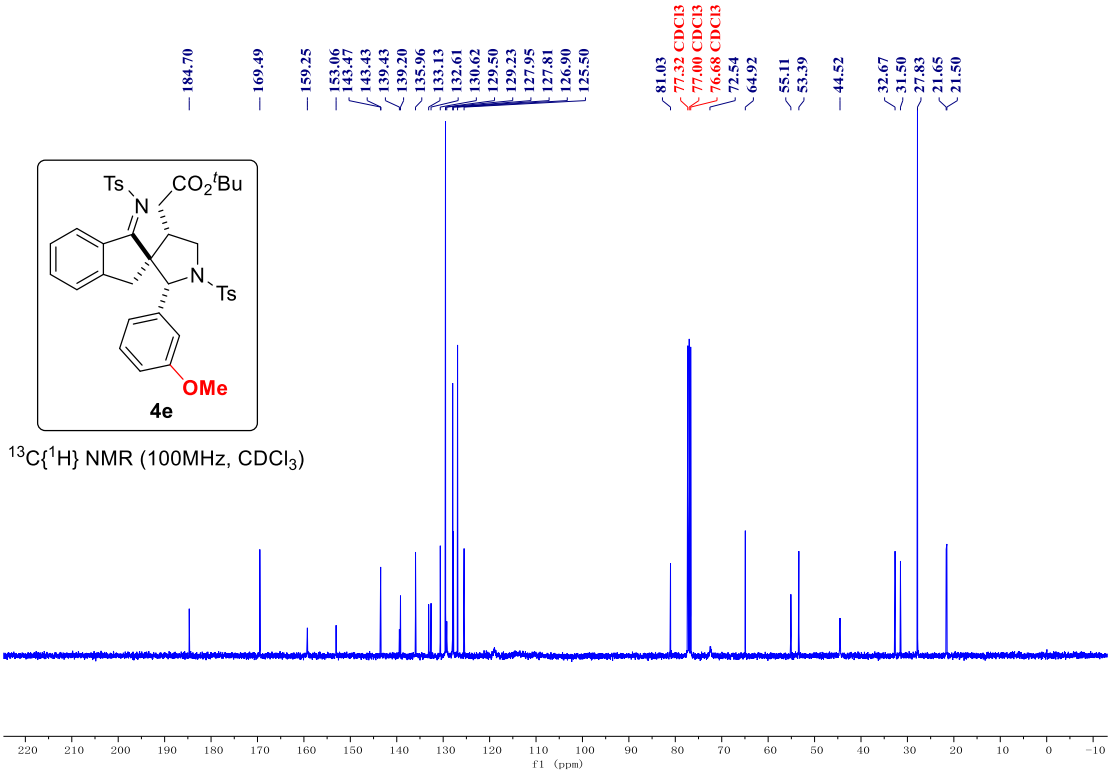
$^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$)


8.704
8.684
7.954
7.934
7.604
7.447
7.384
7.365
7.345
7.260 CDCl3
7.164
7.016
6.661
5.064
4.101
4.053
3.357
3.327
3.296
2.758
2.561
2.372
2.123
2.096
1.833
1.715
1.315
Ts
N
CO2tBu
N
Ts
Cl
4d
1H NMR (400MHz, CDCl3)
0.97
1.98
6.01
1.23
6.16
0.97
1.00
1.00
2.02
3.04
3.15
0.98
2.03
9.07
f1 (ppm)

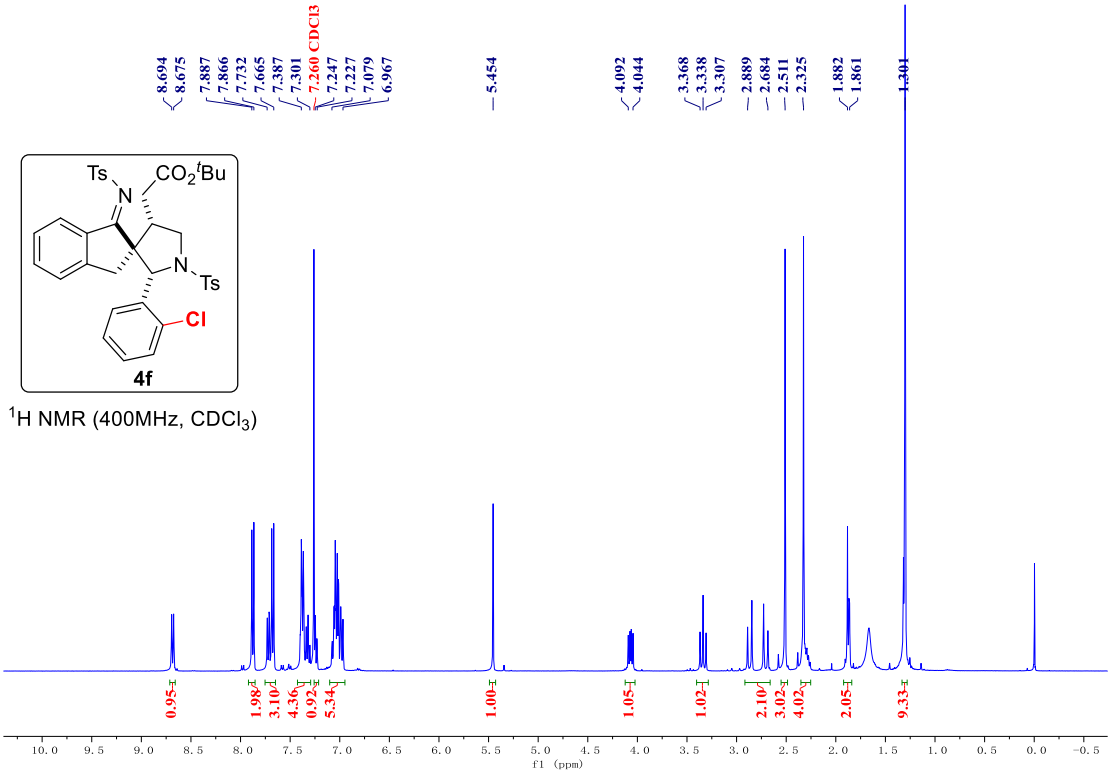

183.92
169.43
152.42
143.74
143.57
139.86
138.99
136.07
134.15
132.93
132.57
130.72
129.70
129.62
129.57
129.43
128.00
127.95
127.91
127.15
126.98
125.46
81.16
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
71.67
64.94
53.33
44.34
32.73
31.39
27.86
21.68
21.55
Ts
N
CO2tBu
N
Ts
Cl
4d
13C{1H} NMR (100MHz, CDCl3)
f1 (ppm)



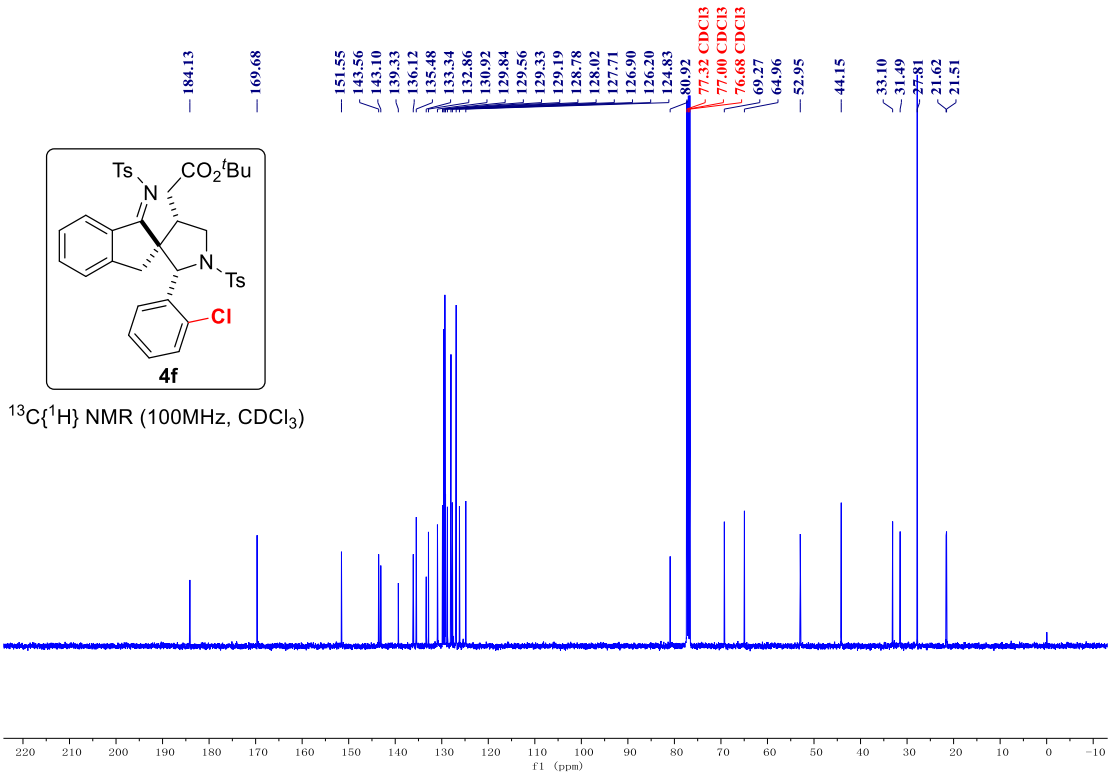
^{1}H NMR (400MHz, $CDCl_3$)



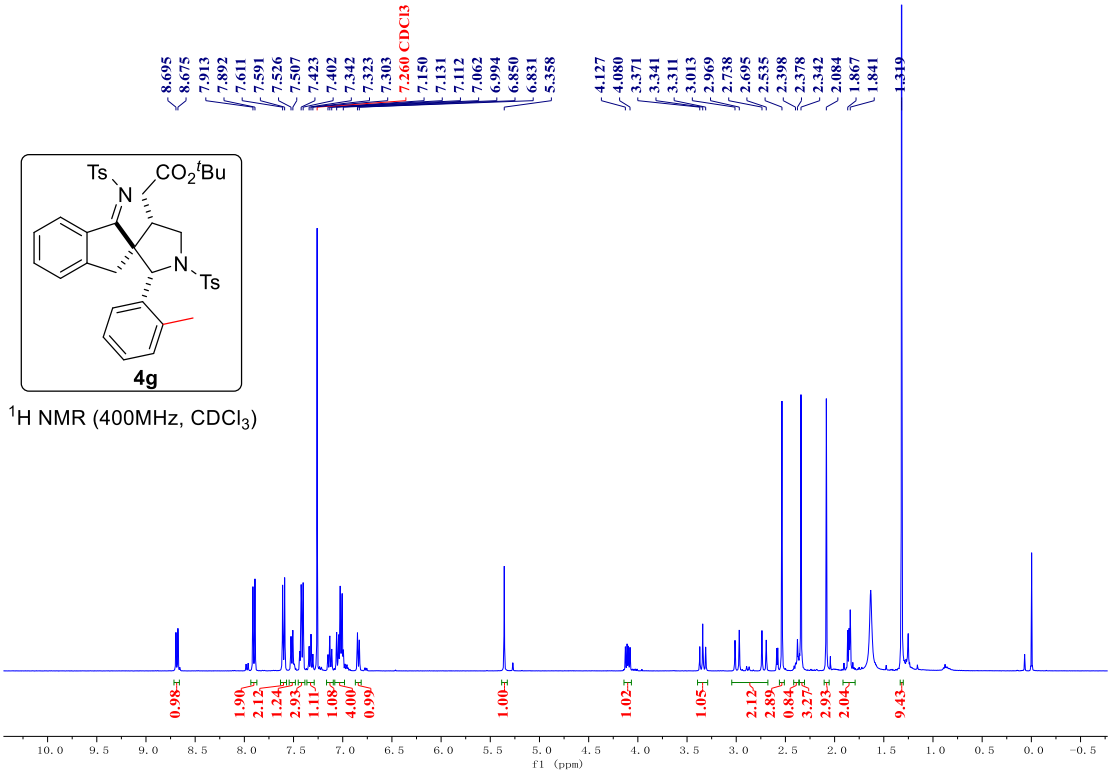
$^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$)



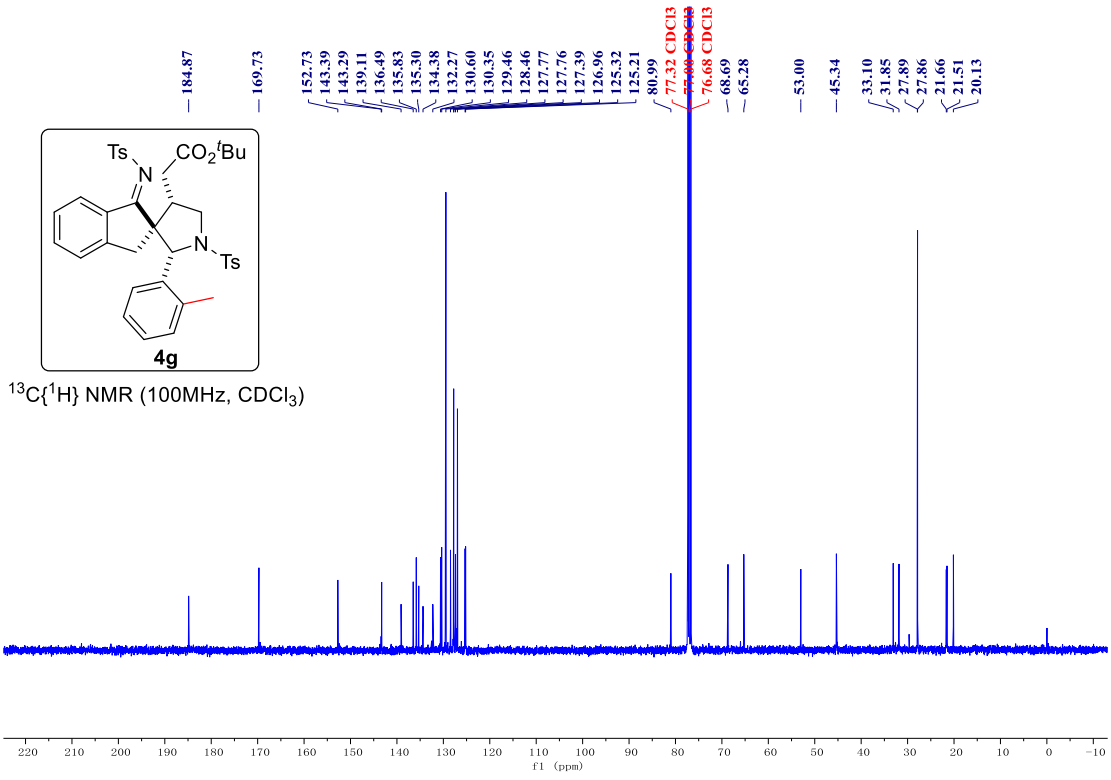
^{1}H NMR (400MHz, $CDCl_3$)



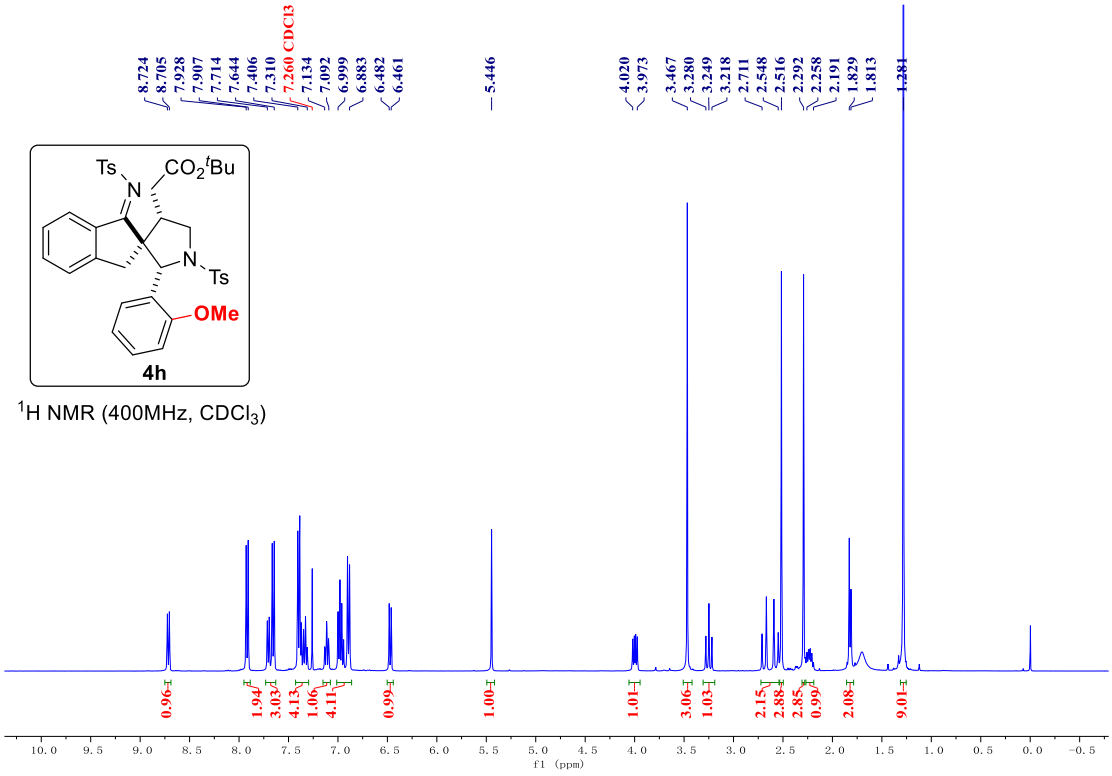
$^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$)



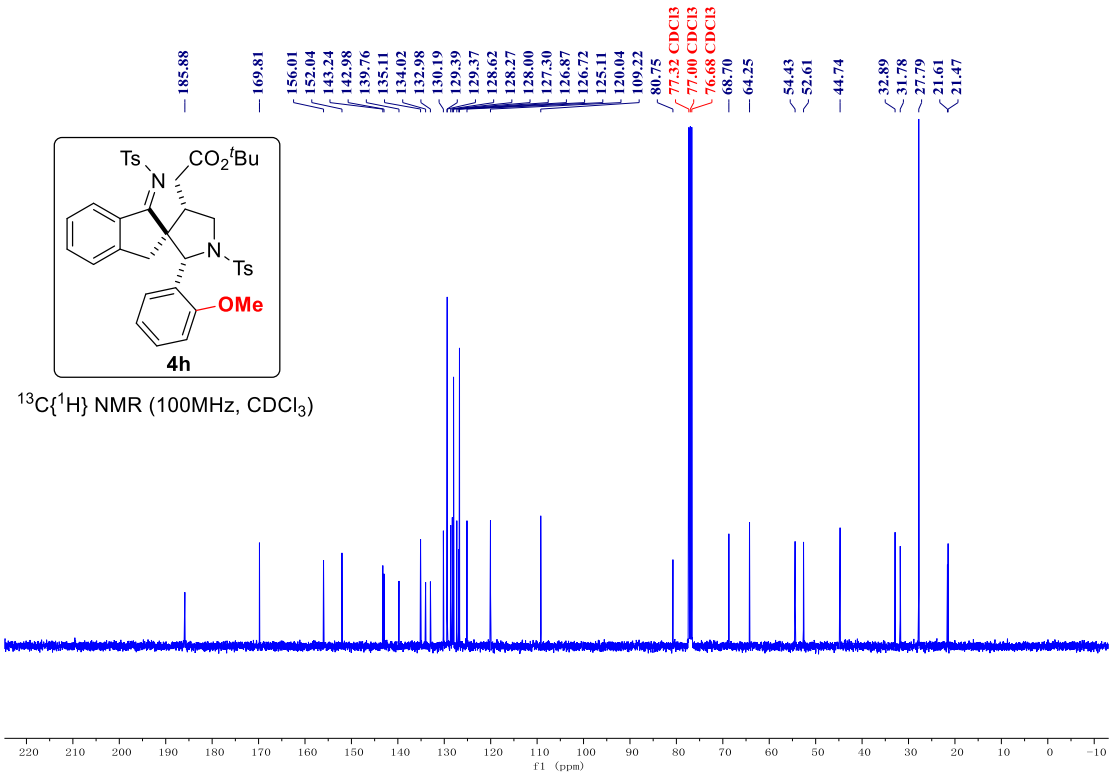
^{1}H NMR (400MHz, $CDCl_3$)



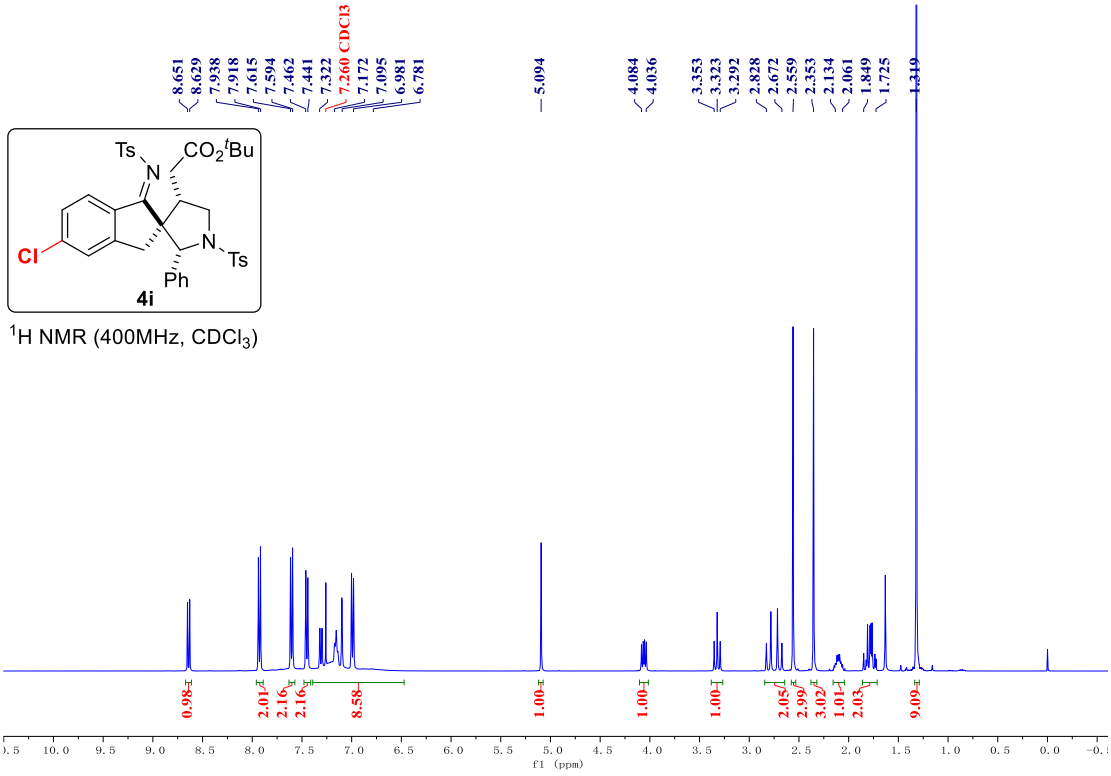
$^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$)



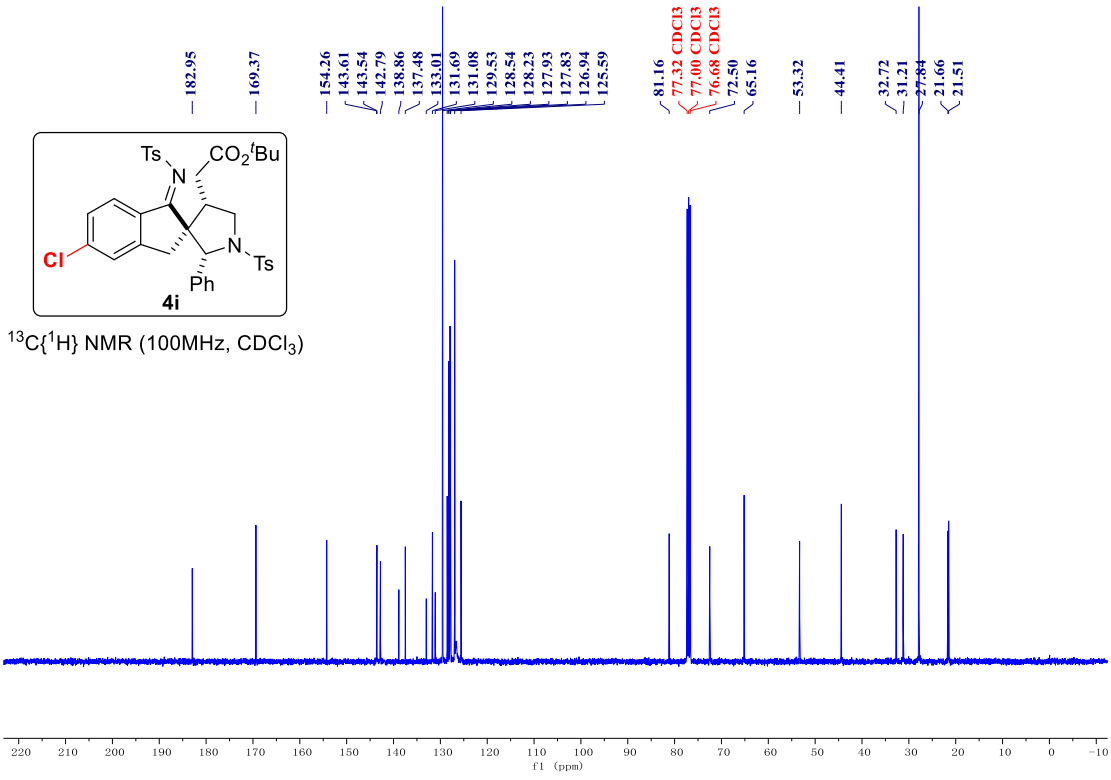
^{1}H NMR (400MHz, $CDCl_3$)



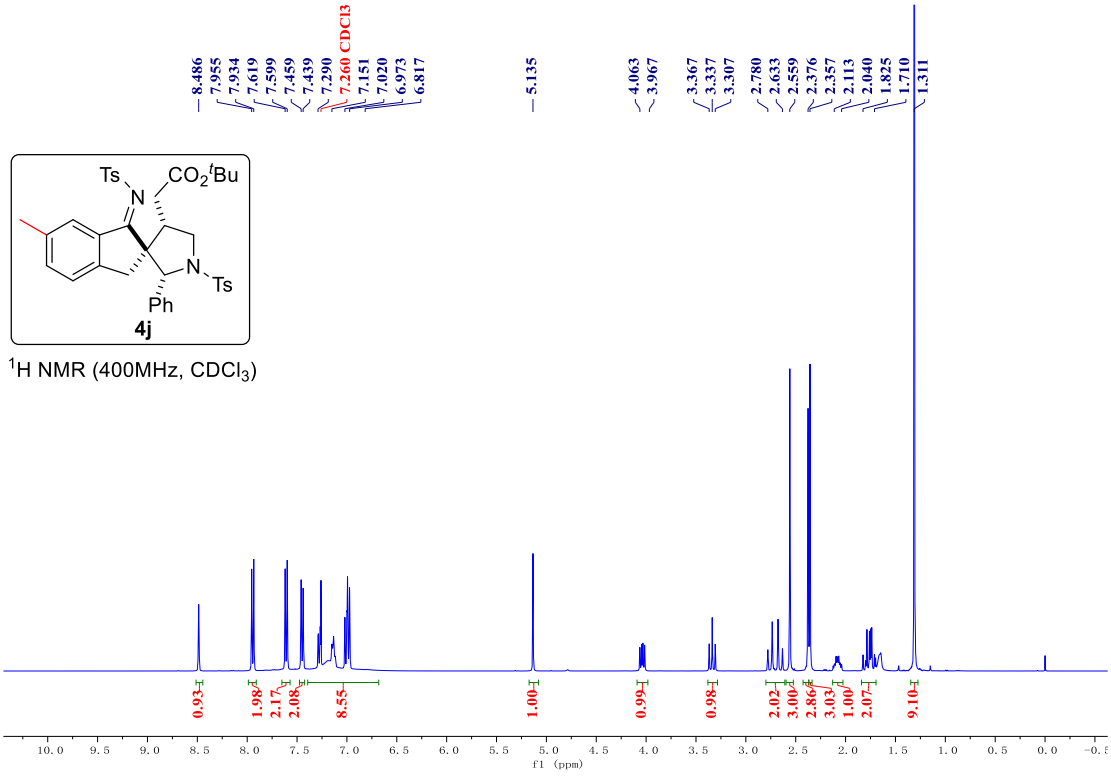
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$)

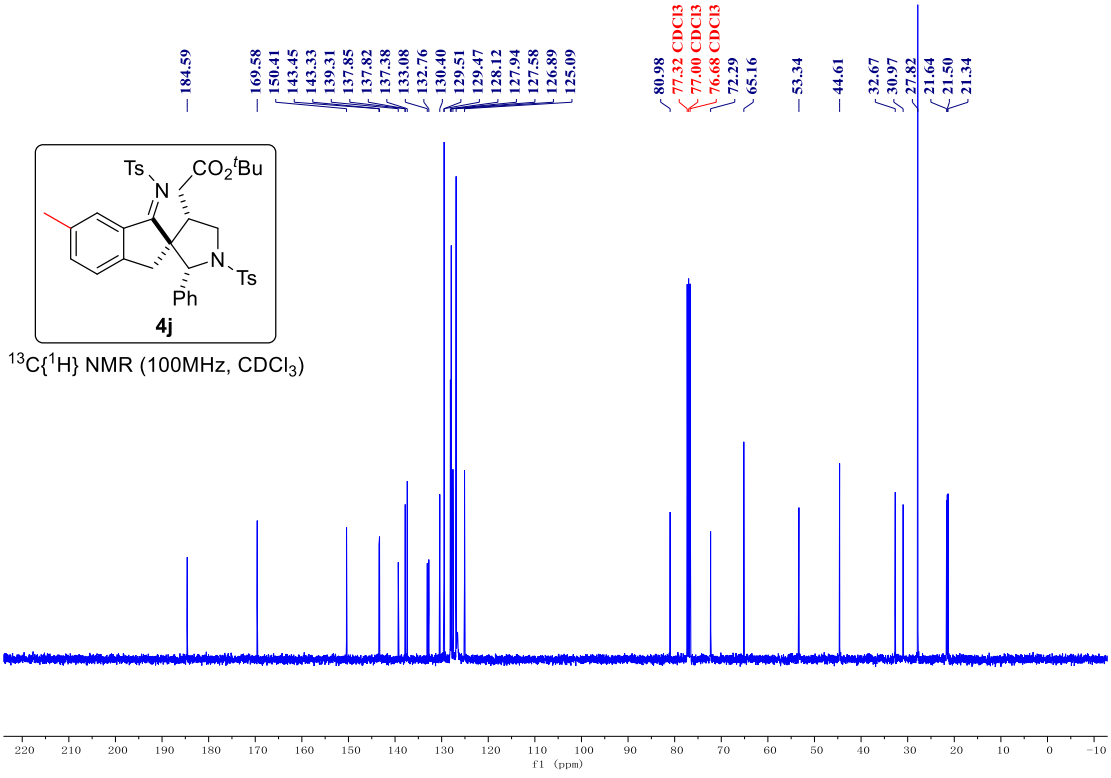


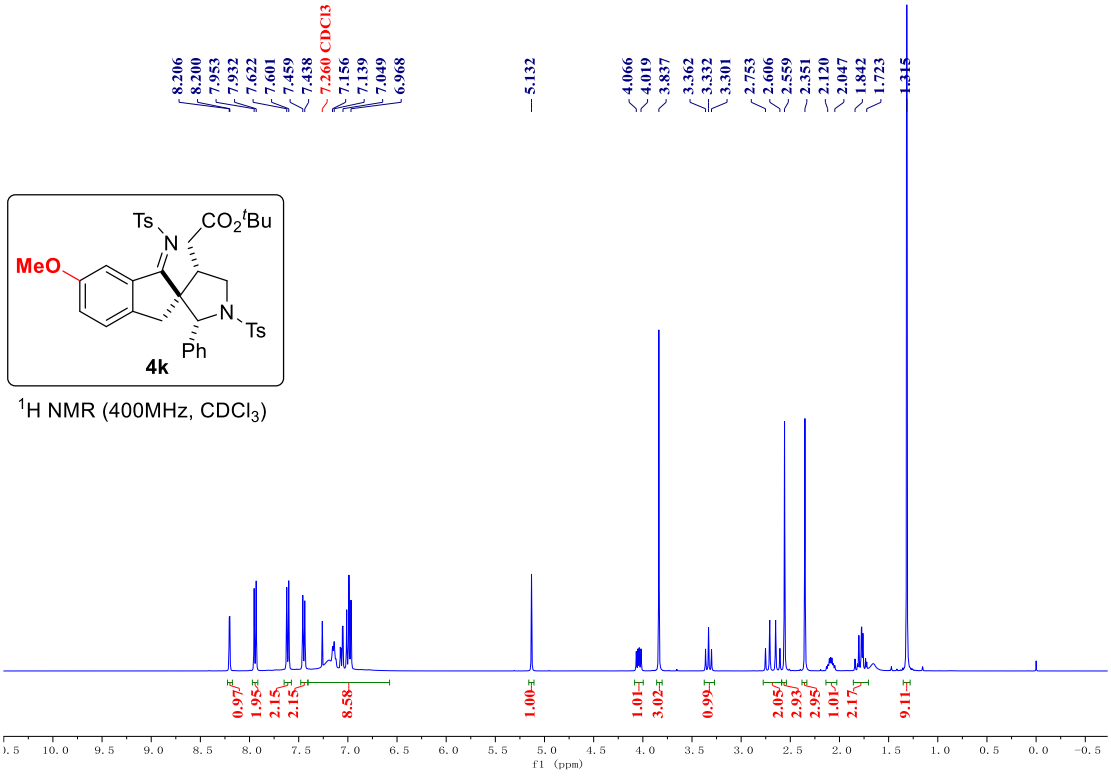
^{1}H NMR (400MHz, $CDCl_3$)



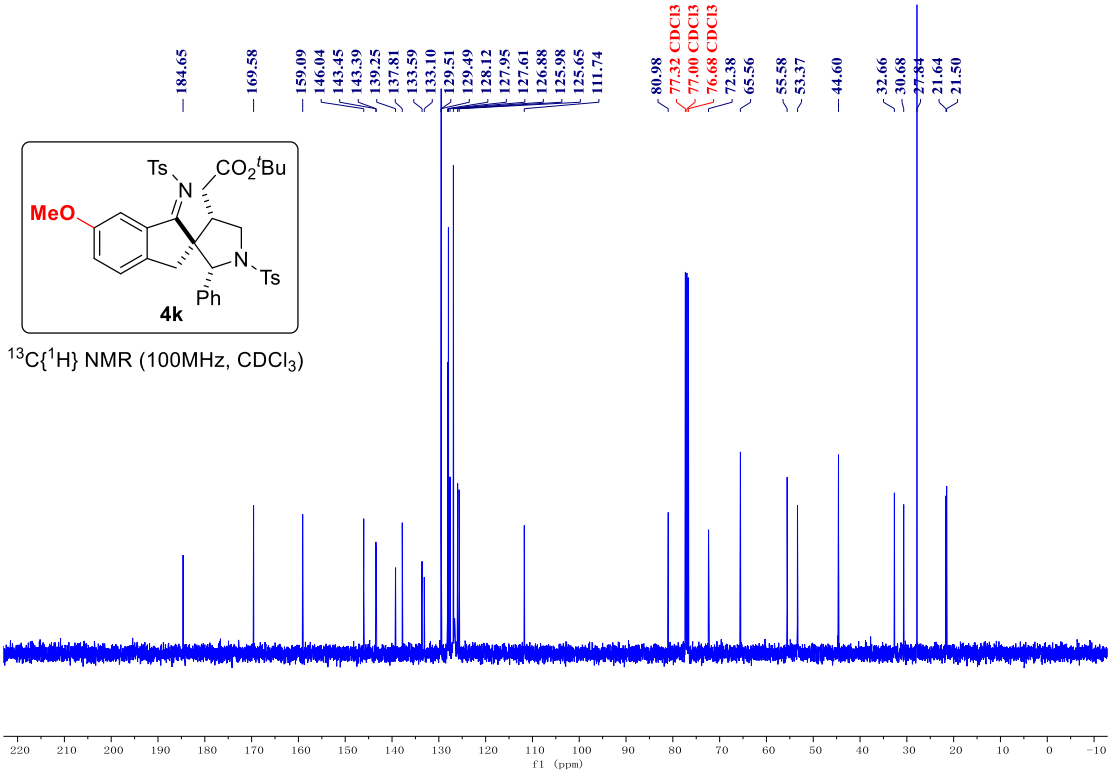
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$)


8.486
7.955
7.934
7.619
7.599
7.459
7.439
7.290
7.260 CDCl3
7.151
7.020
6.973
6.817
5.135
4.063
3.967
3.367
3.337
3.307
2.780
2.633
2.559
2.376
2.357
2.113
2.040
1.825
1.710
1.311
0.93
1.98
2.17
2.08
8.55
1.00
0.99
0.98
2.02
3.00
2.86
3.03
1.00
2.07
9.10
f1 (ppm)

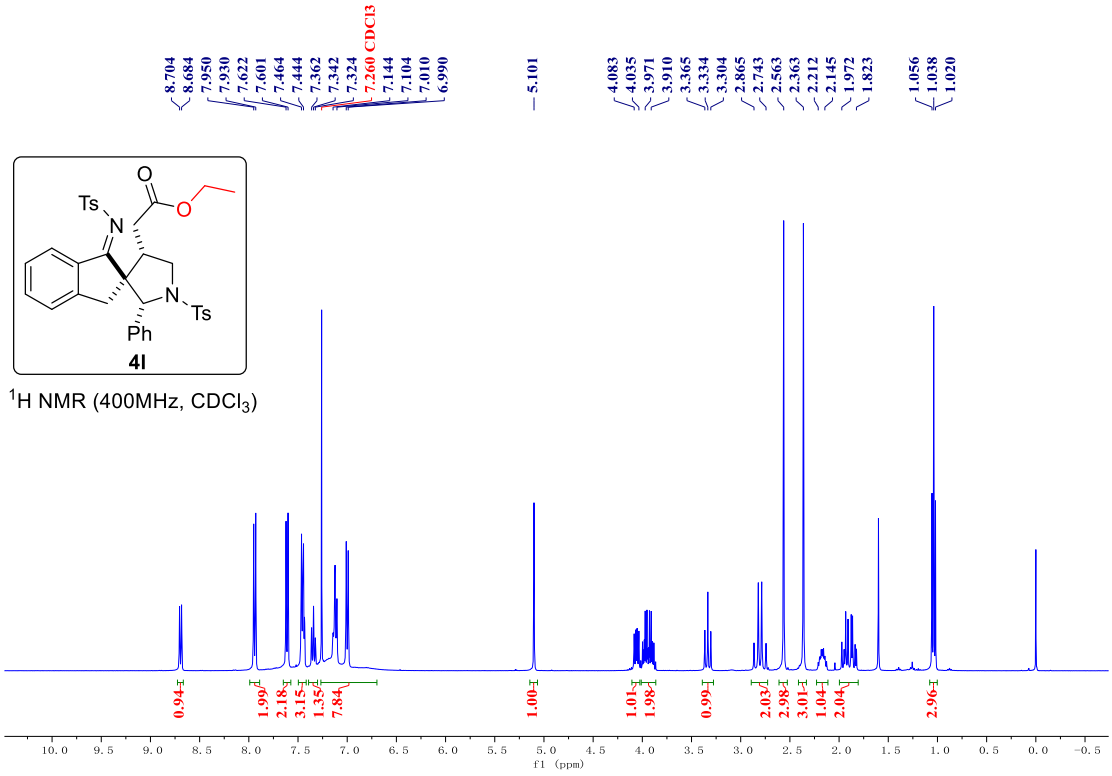

184.59
169.58
150.41
143.45
143.33
139.31
137.85
137.82
137.38
133.08
132.76
130.40
129.51
129.47
128.12
127.94
127.58
126.89
125.09
80.98
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
72.29
65.16
53.34
44.61
32.67
30.97
27.82
21.64
21.50
21.34
f1 (ppm)



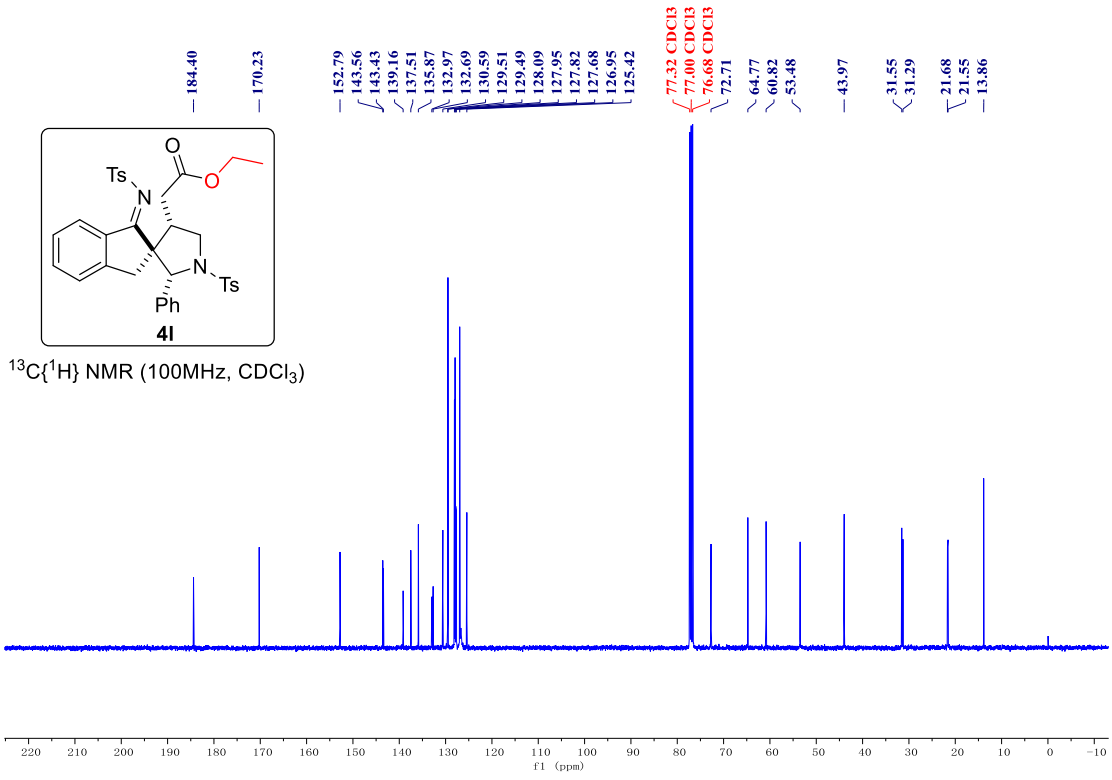
^{1}H NMR (400MHz, $CDCl_3$)



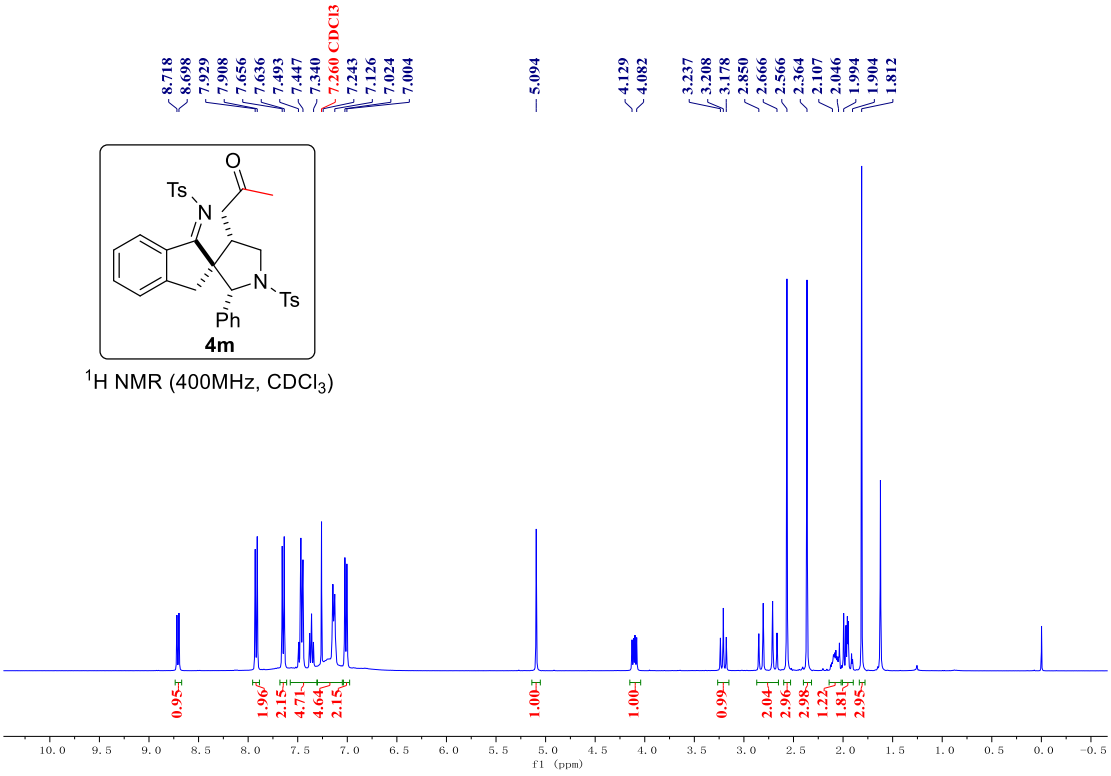
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$)



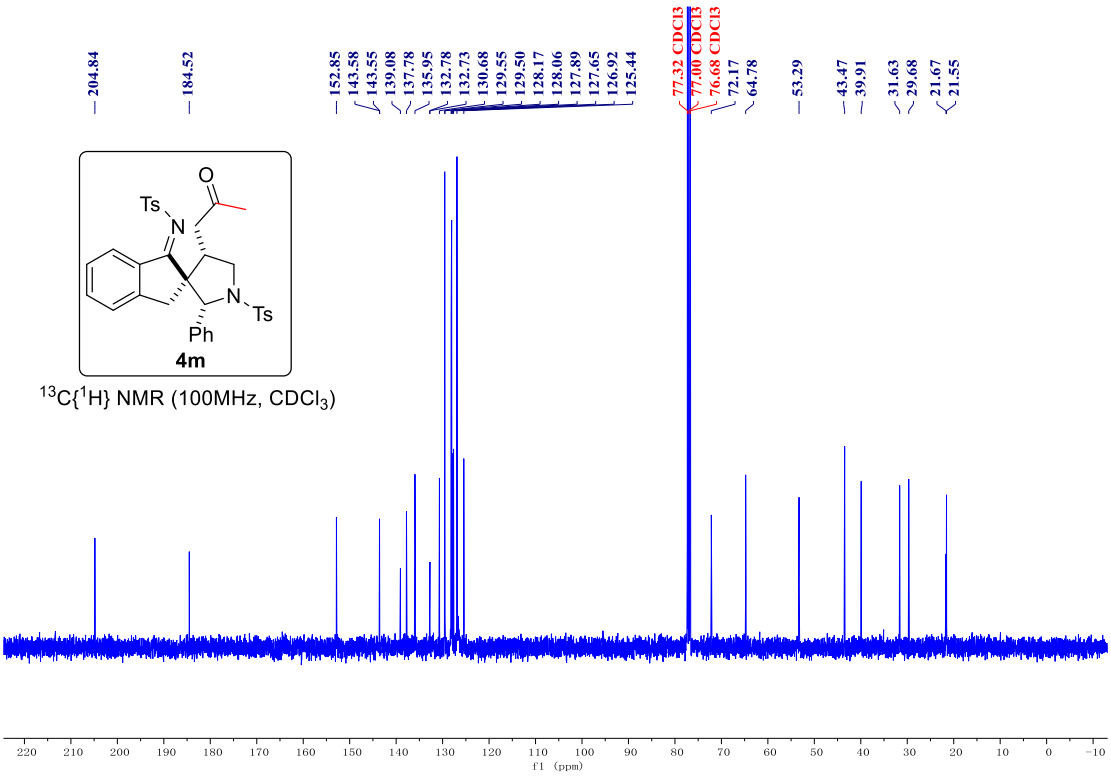
^{1}H NMR (400MHz, $CDCl_3$)



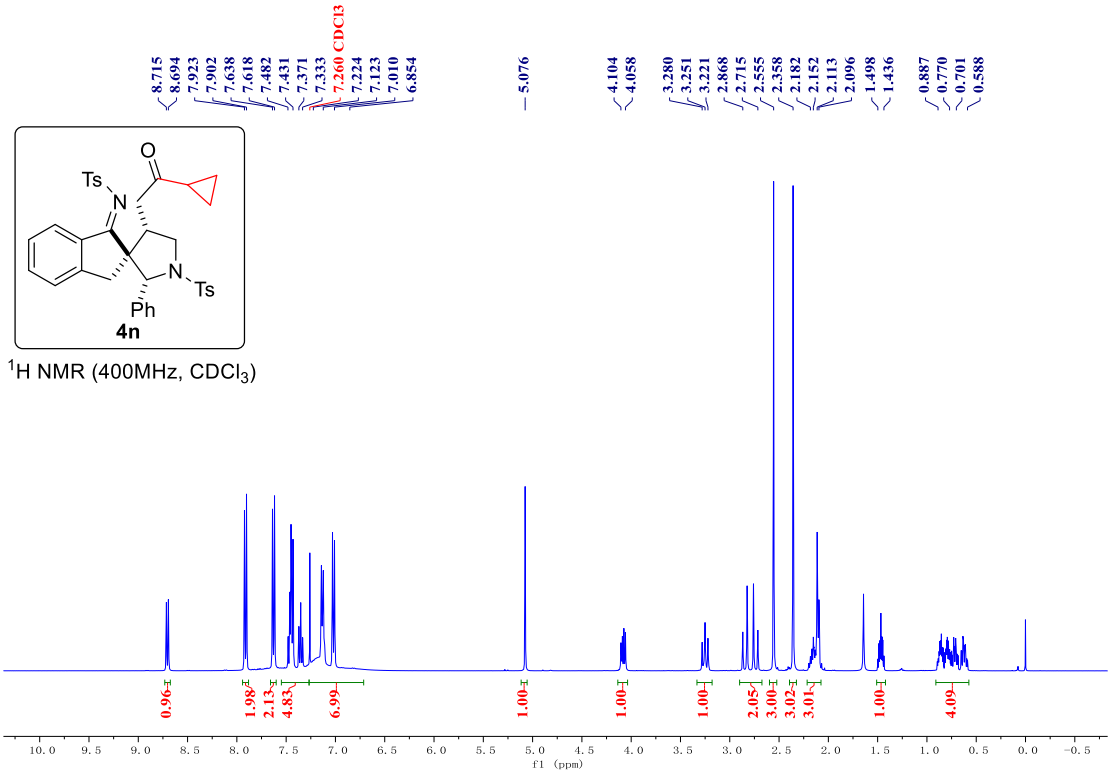
$^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$)



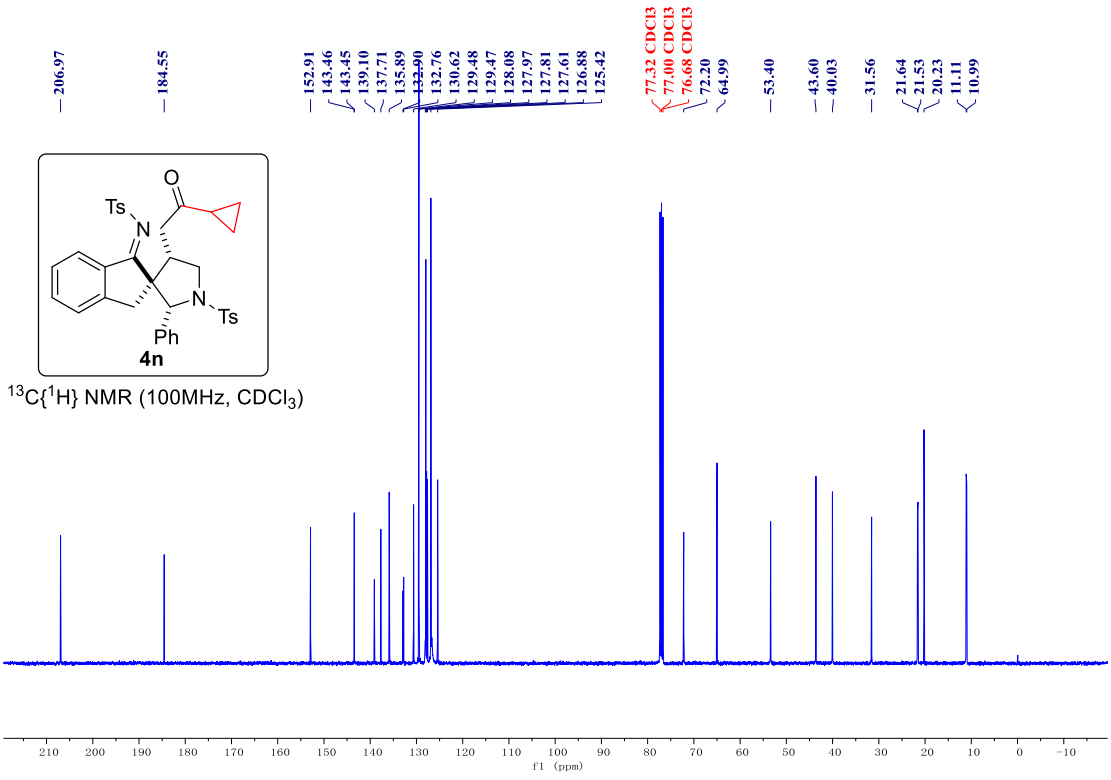
^{1}H NMR (400MHz, $CDCl_3$)



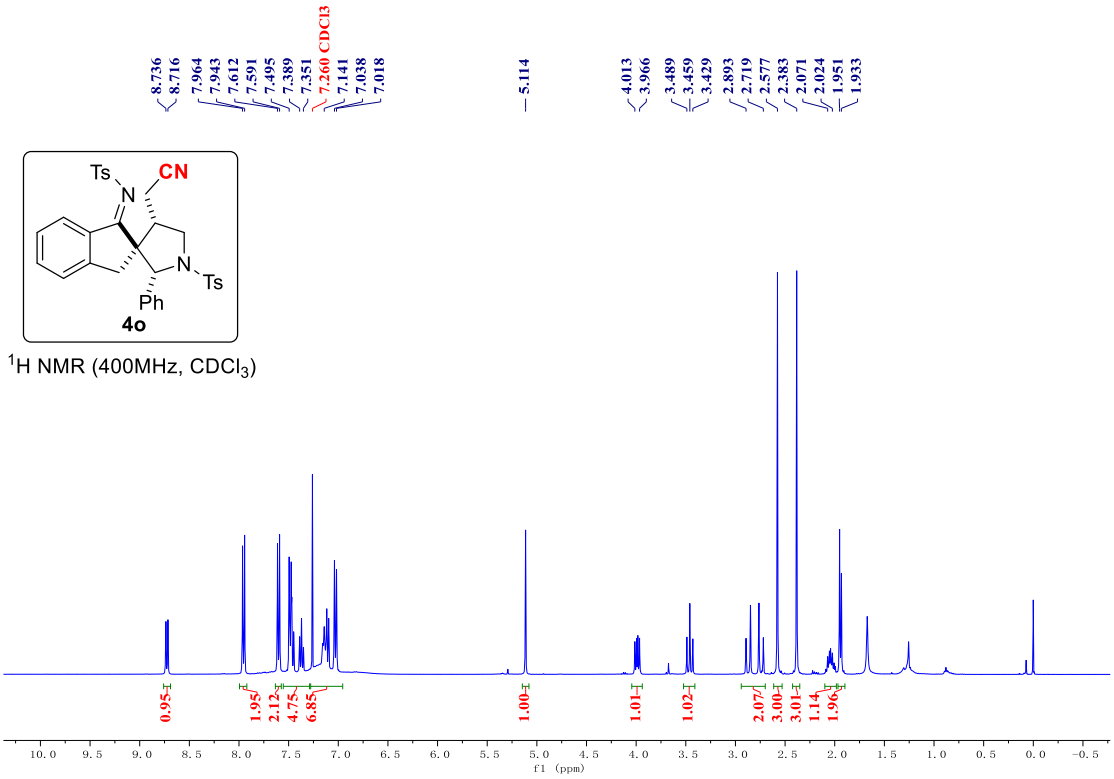
$^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$)



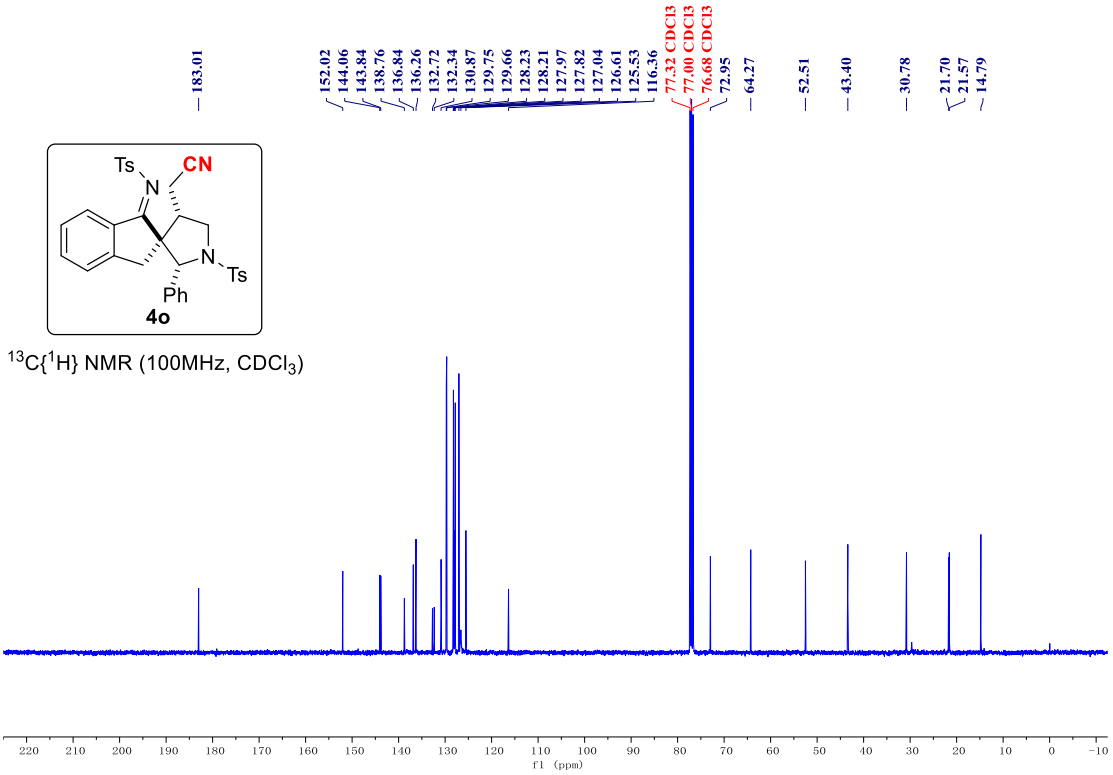
^{1}H NMR (400MHz, $CDCl_3$)



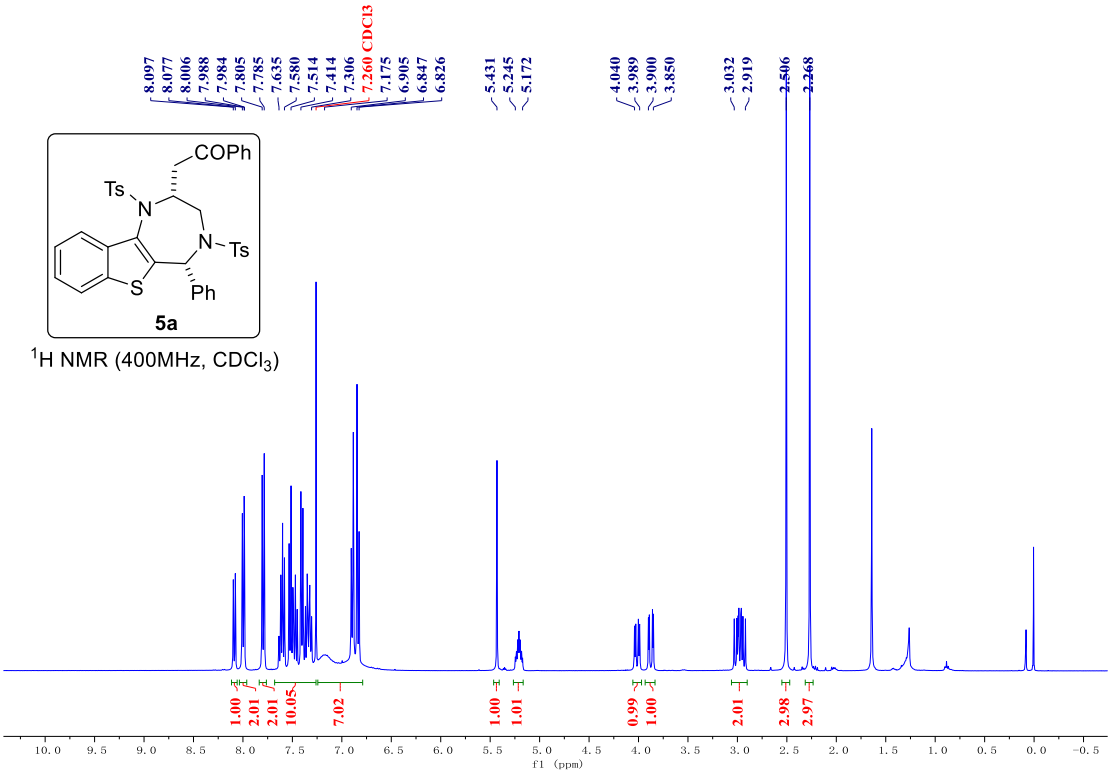
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$)

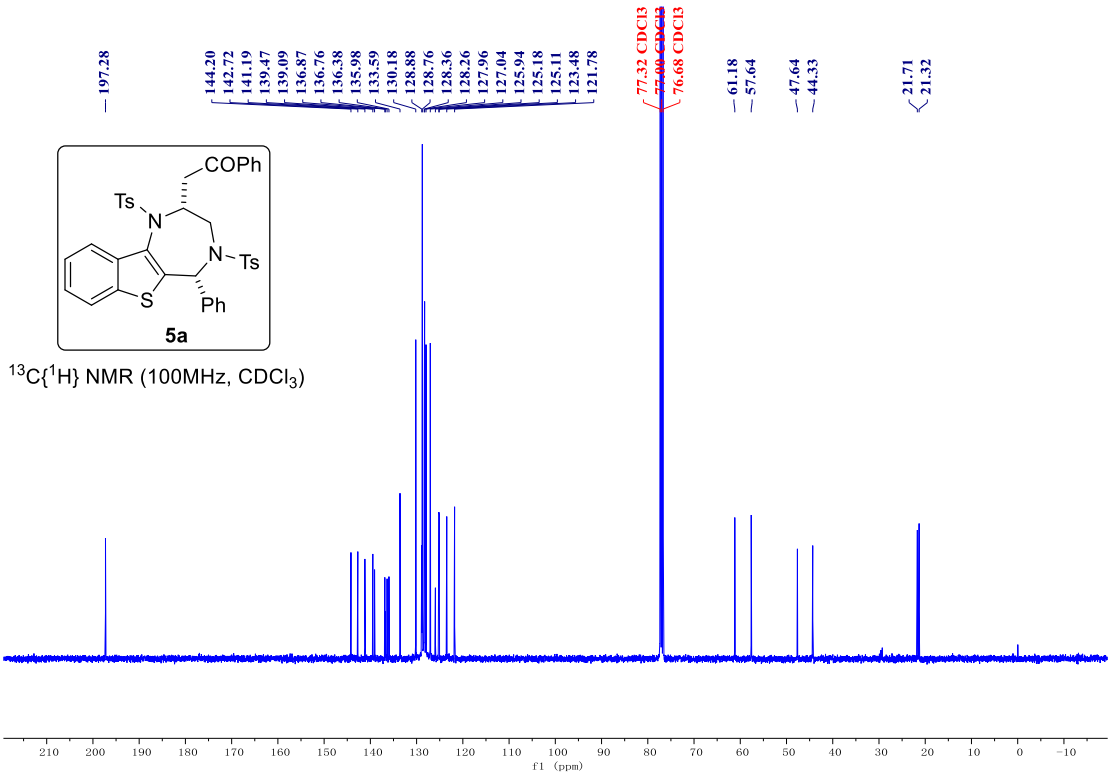


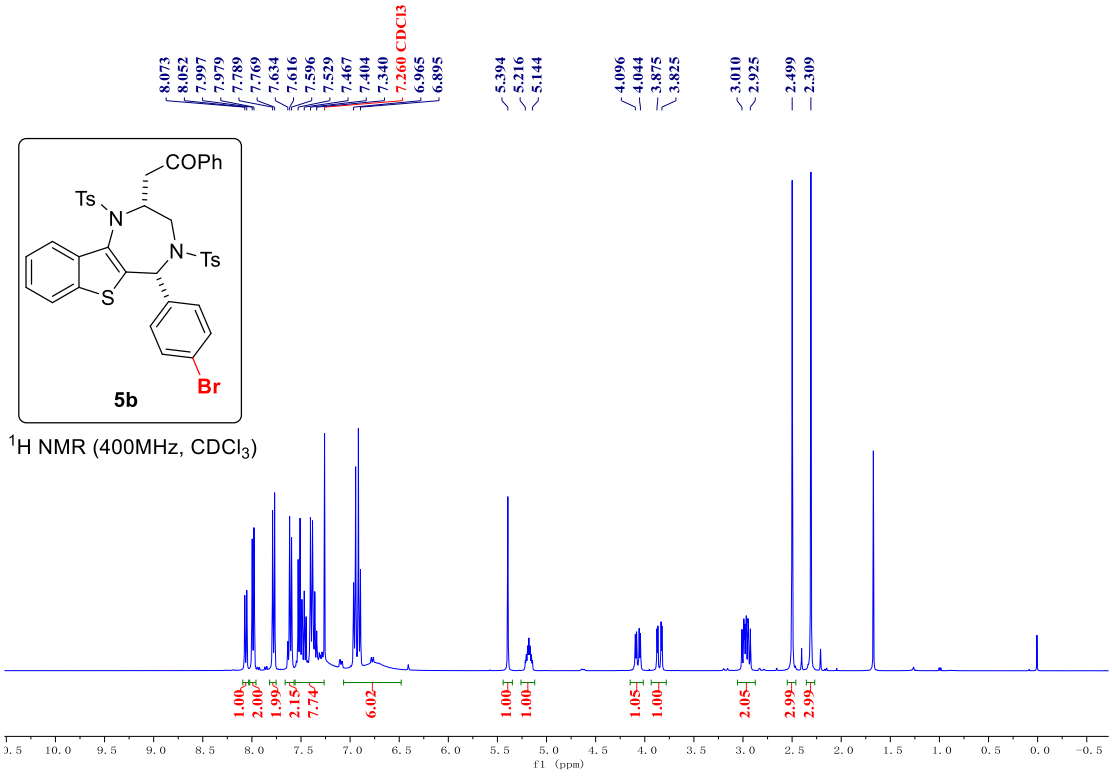
^{1}H NMR (400MHz, $CDCl_3$)

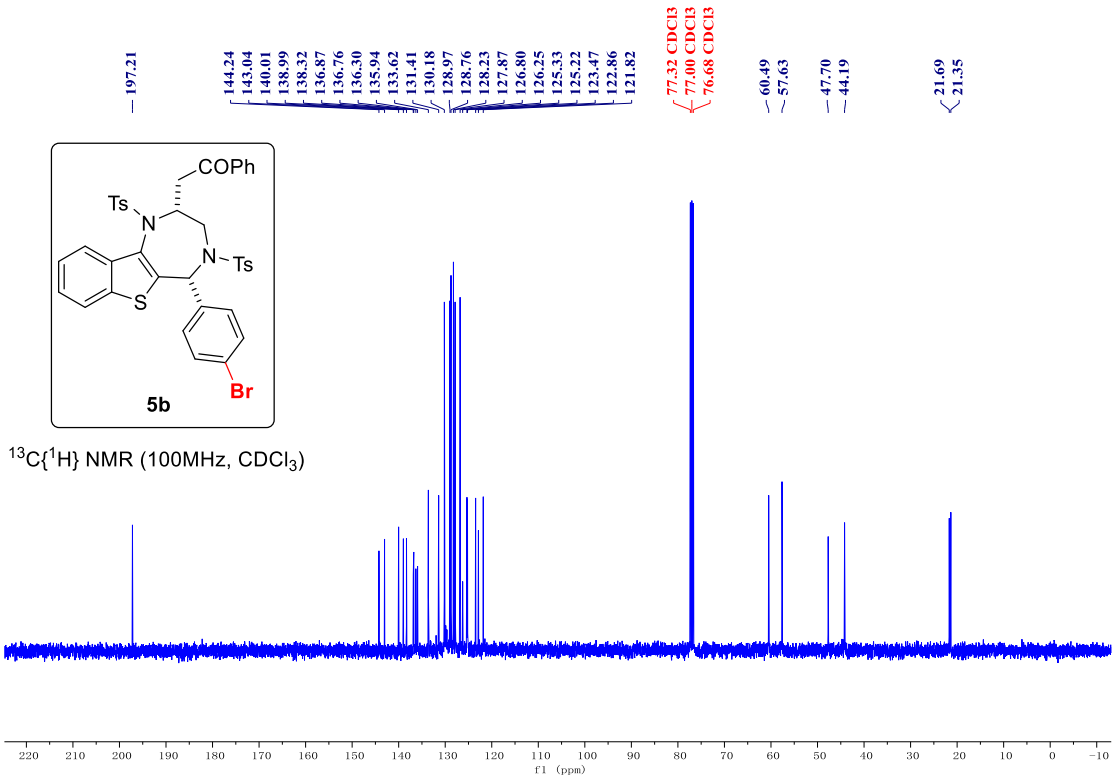


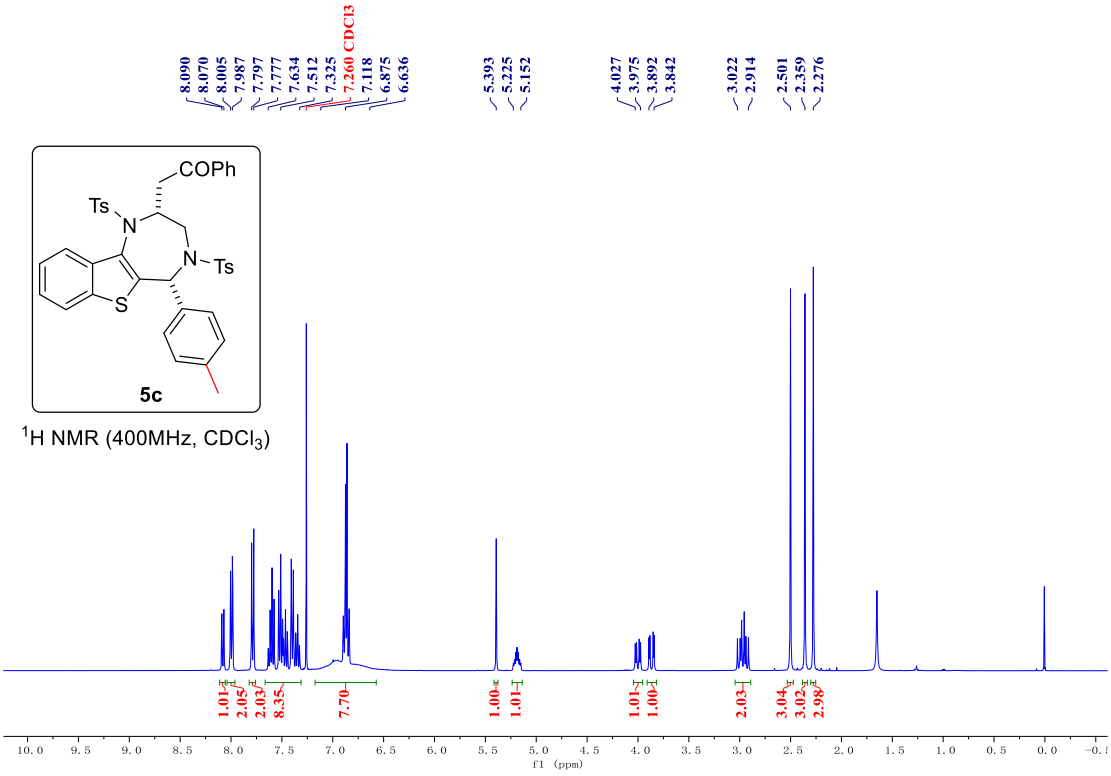
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$)

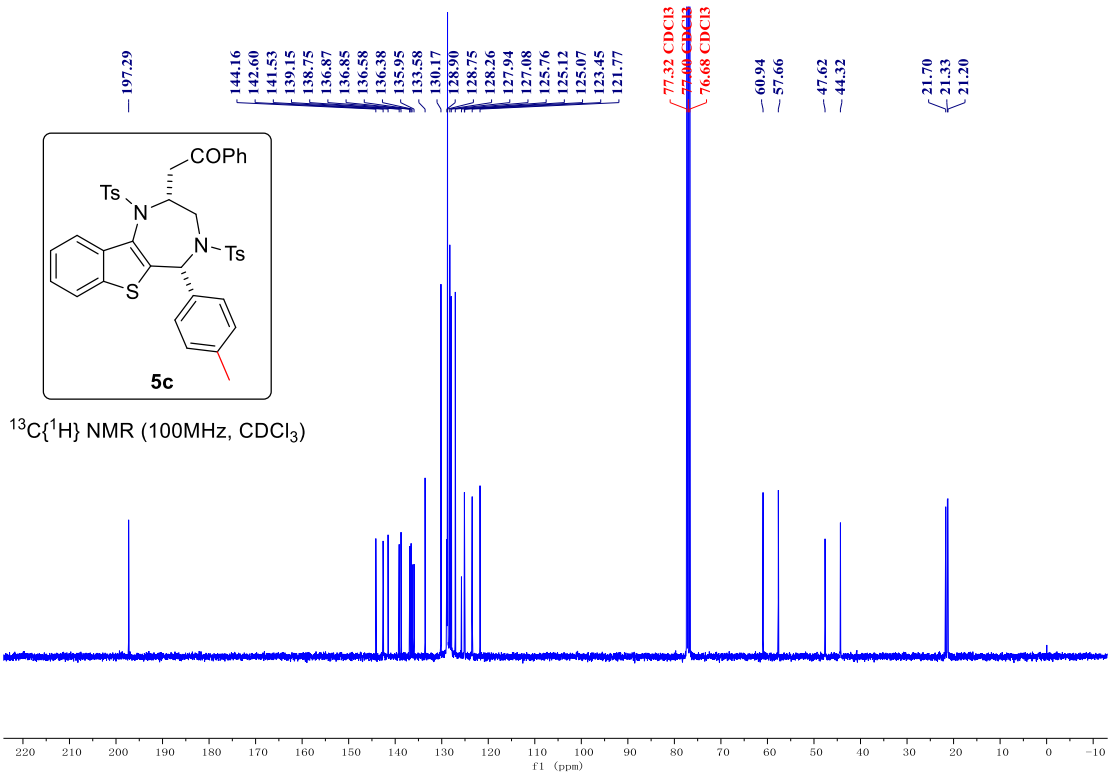

8.097
8.077
8.006
7.988
7.984
7.805
7.785
7.635
7.580
7.514
7.414
7.306
7.260 CDCl3
7.175
6.905
6.847
6.826
5.431
5.245
5.172
4.040
3.989
3.900
3.850
3.032
2.919
2.506
2.268
COPh
Ts
N
N
Ts
S
Ph
5a
1H NMR (400MHz, CDCl3)
1.00
2.01
2.01
10.05
7.02
1.00
1.01
0.99
1.00
2.01
2.98
2.97
f1 (ppm)

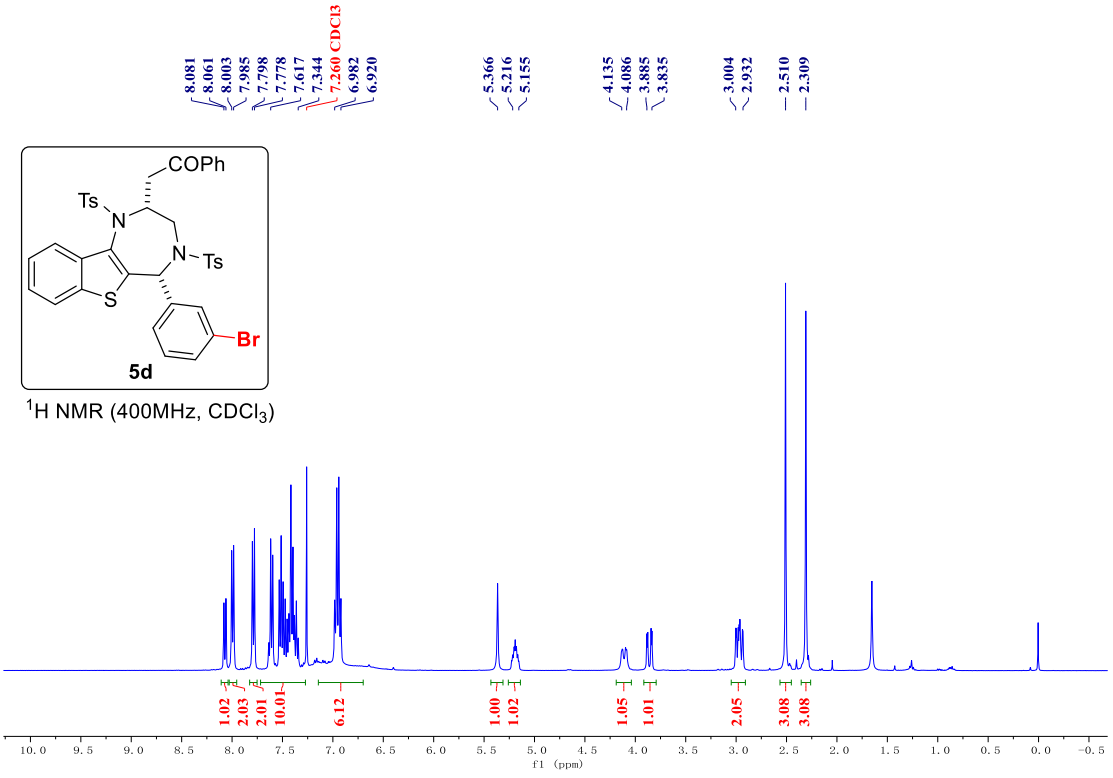

197.28
144.20
142.72
141.19
139.47
139.09
136.87
136.76
136.38
135.98
133.59
130.18
128.88
128.76
128.36
128.26
127.96
127.04
125.94
125.18
125.11
123.48
121.78
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
61.18
57.64
47.64
44.33
21.71
21.32
COPh
Ts
N
N
Ts
S
Ph
5a
13C{1H} NMR (100MHz, CDCl3)
f1 (ppm)


8.073
8.052
7.997
7.979
7.789
7.769
7.634
7.616
7.596
7.529
7.467
7.404
7.340
7.260 CDCl3
6.965
6.895
5.394
5.216
5.144
4.096
4.044
3.875
3.825
3.010
2.925
2.499
2.309
COPh
Ts
N
N
Ts
S
Br
5b
1H NMR (400MHz, CDCl3)
1.00
2.00
1.99
2.15
7.74
6.02
1.00
1.00
1.05
1.00
2.05
2.99
2.99
f1 (ppm)

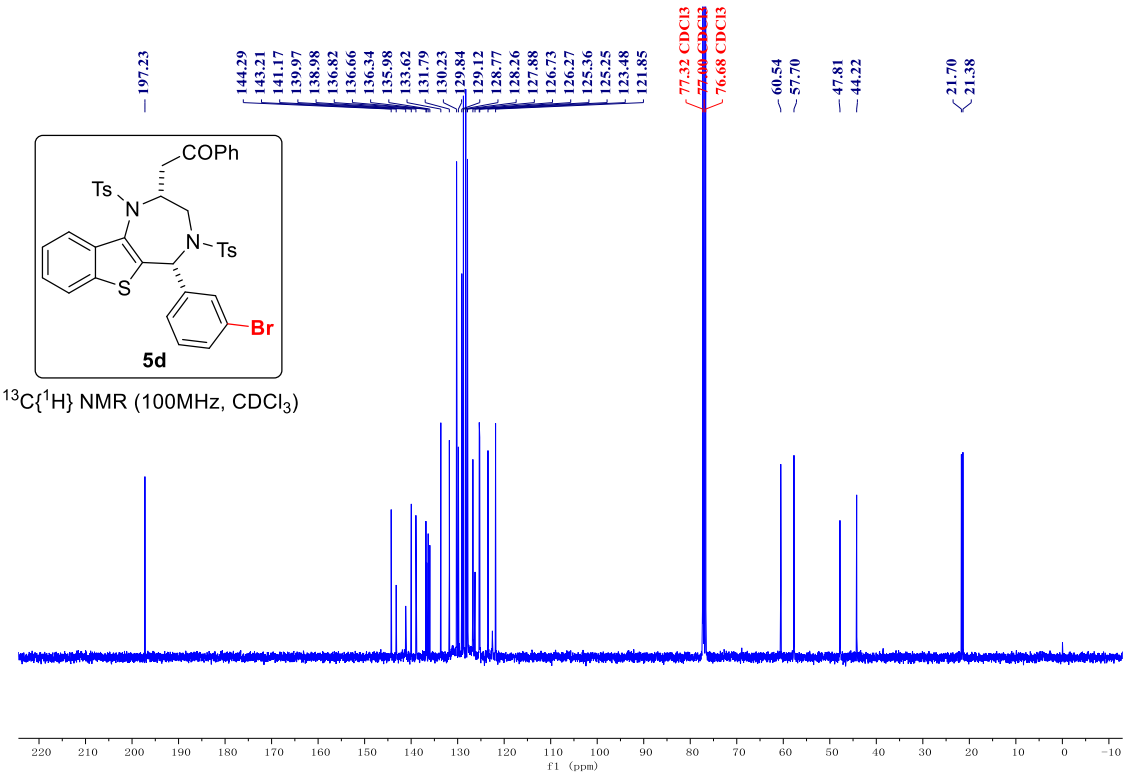

197.21
144.24
143.04
140.01
138.99
138.32
136.87
136.76
136.30
135.94
133.62
131.41
130.18
128.97
128.76
128.23
127.87
126.80
126.25
125.33
125.22
123.47
122.86
121.82
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
60.49
57.63
47.70
44.19
21.69
21.35
COPh
Ts
N
N
Ts
S
Br
5b
13C{1H} NMR (100MHz, CDCl3)
f1 (ppm)


8.090
8.070
8.005
7.987
7.797
7.777
7.634
7.512
7.325
7.260 CDCl3
7.118
6.875
6.636
5.393
5.225
5.152
4.027
3.975
3.892
3.842
3.022
2.914
2.501
2.359
2.276
COPh
Ts
N
N
Ts
S
5c
1H NMR (400MHz, CDCl3)
1.01
2.05
2.03
8.35
7.70
1.00
1.01
1.01
1.00
2.03
3.04
3.02
2.98
f1 (ppm)

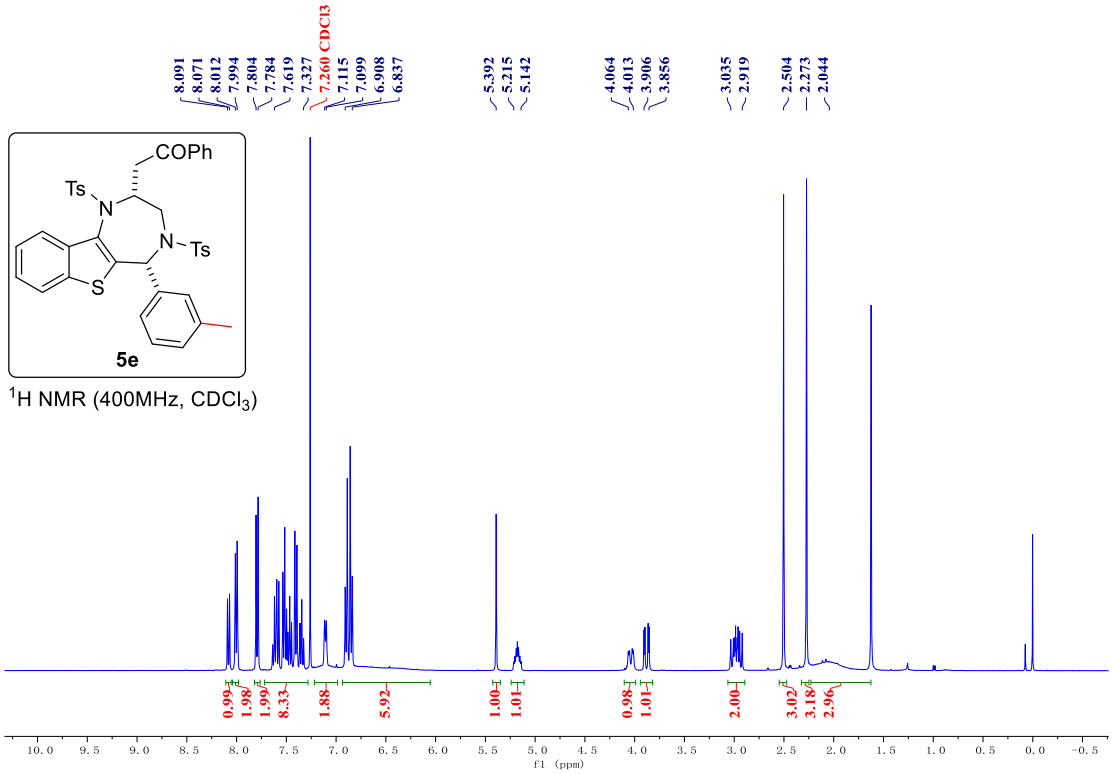

197.29
144.16
142.60
141.53
139.15
138.75
136.87
136.85
136.58
136.38
135.95
133.58
130.17
128.90
128.75
128.26
127.94
127.08
125.76
125.12
125.07
123.45
121.77
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
60.94
57.66
47.62
44.32
21.70
21.33
21.20
COPh
Ts
N
N
Ts
S
5c
13C{1H} NMR (100MHz, CDCl3)
f1 (ppm)



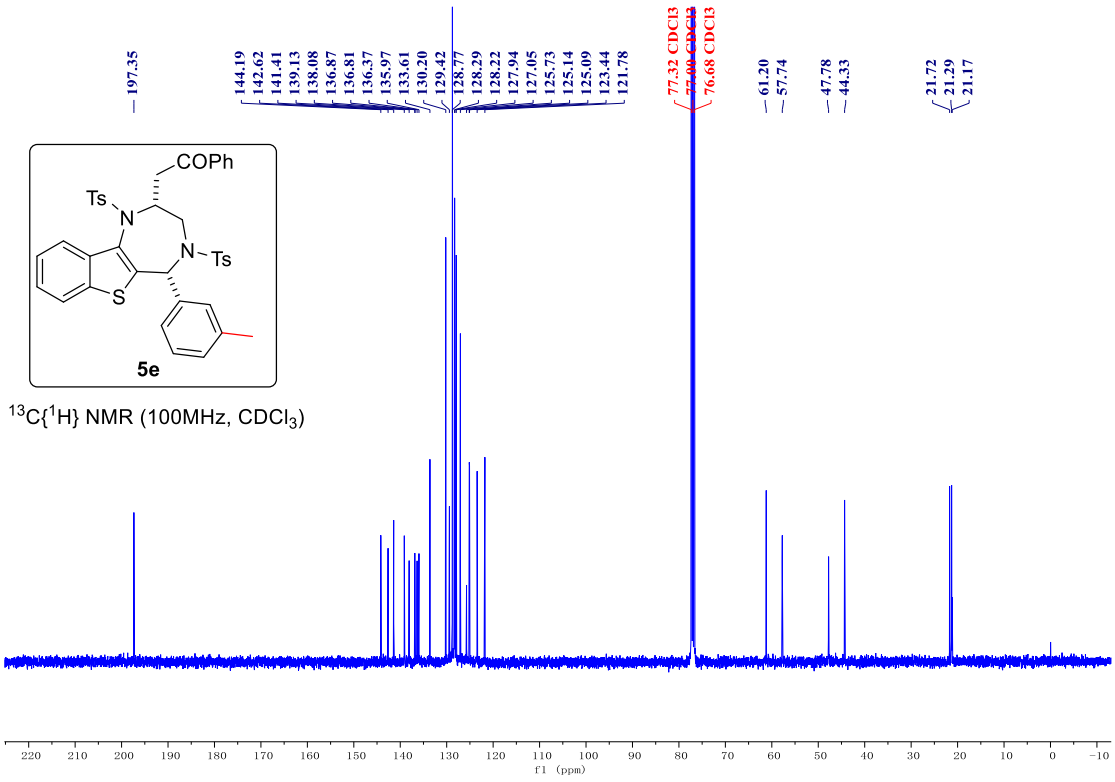
^{1}H NMR (400MHz, $CDCl_3$)



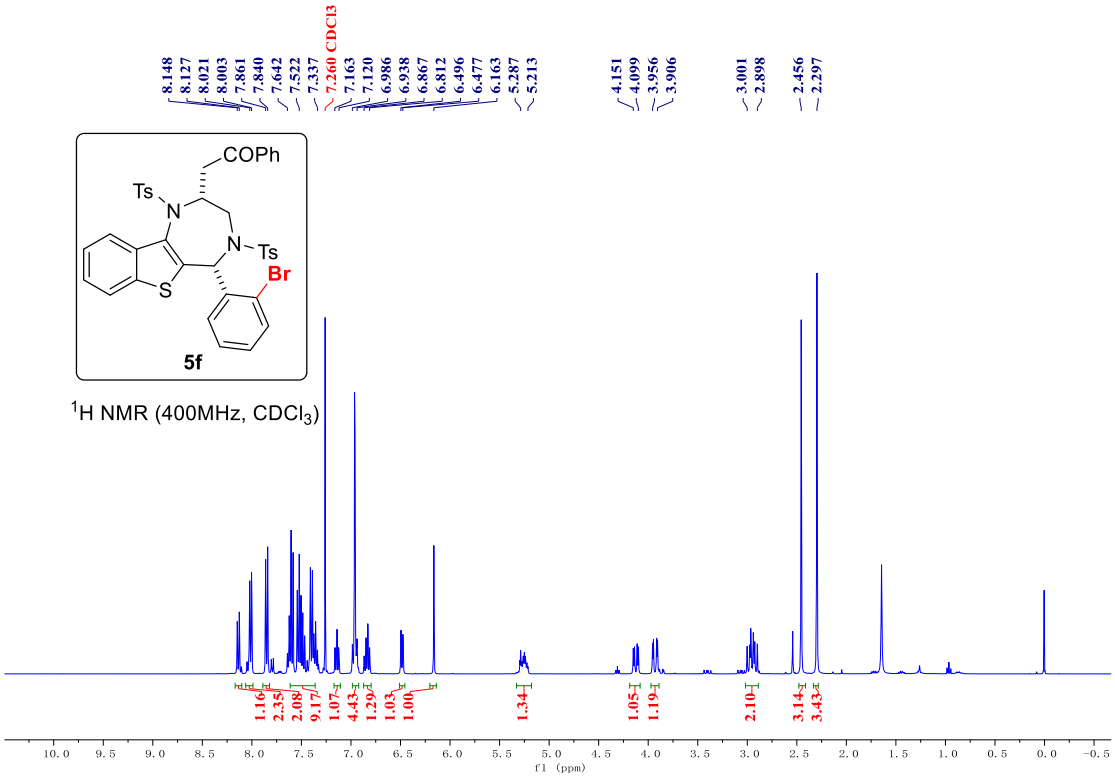
$^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$)



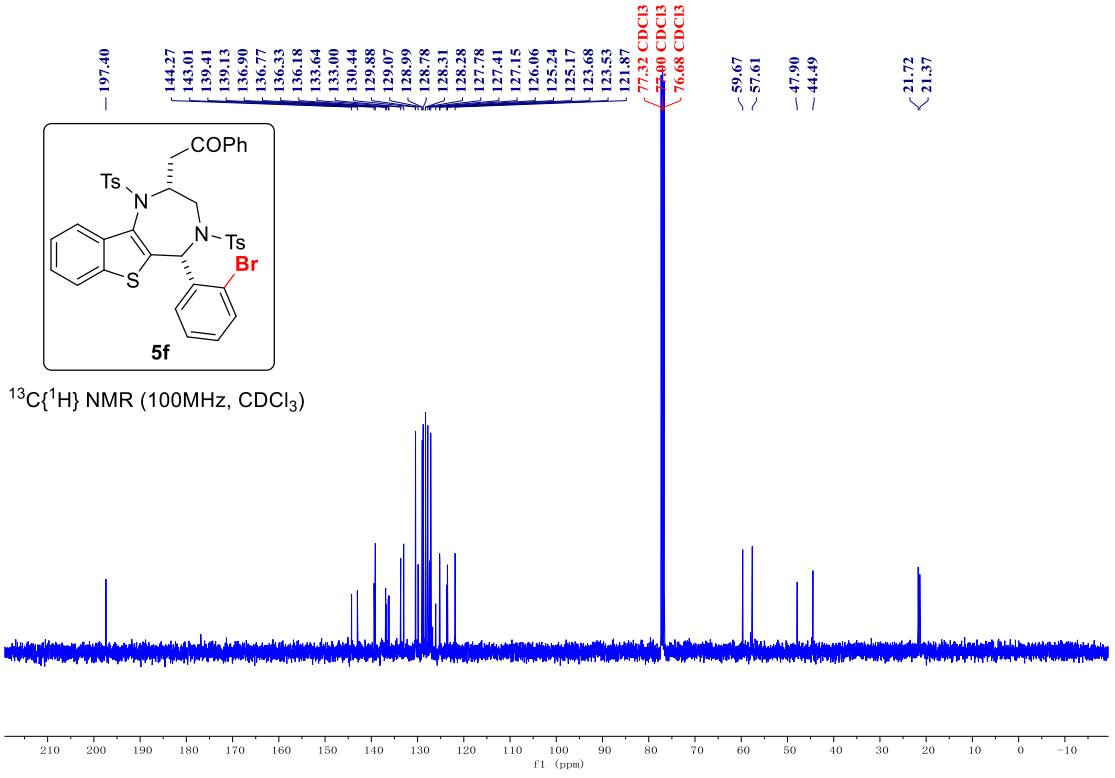
^{1}H NMR (400MHz, $CDCl_3$)



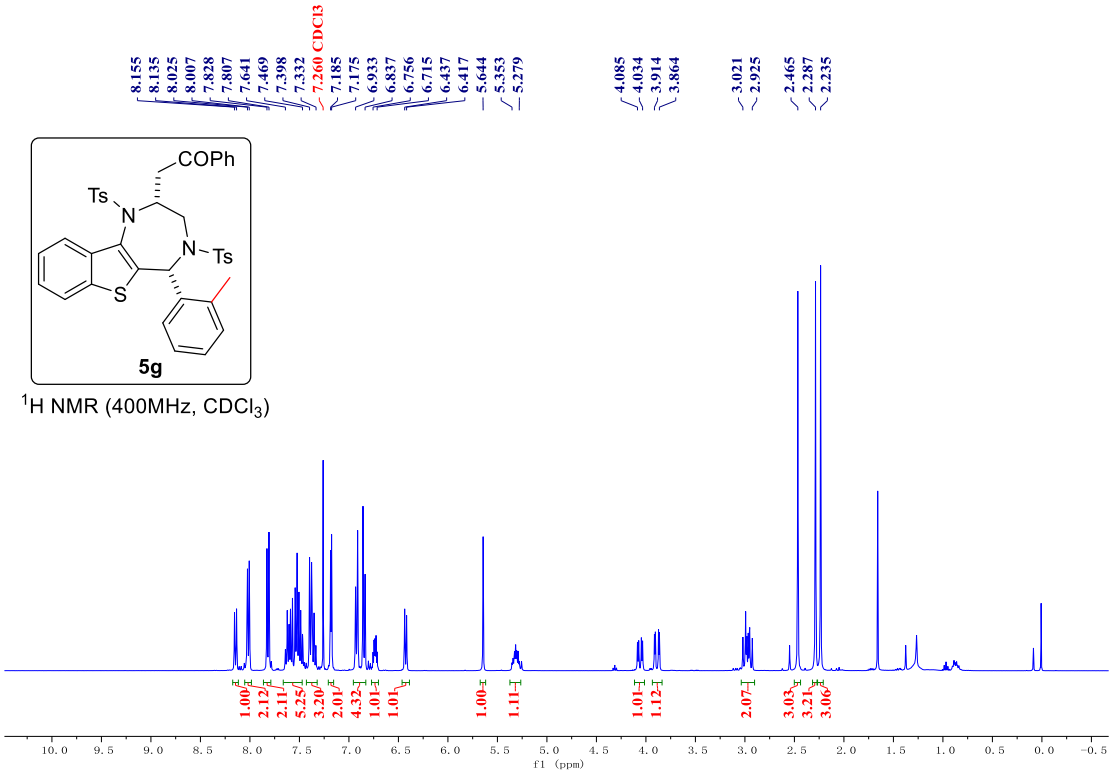
$^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$)

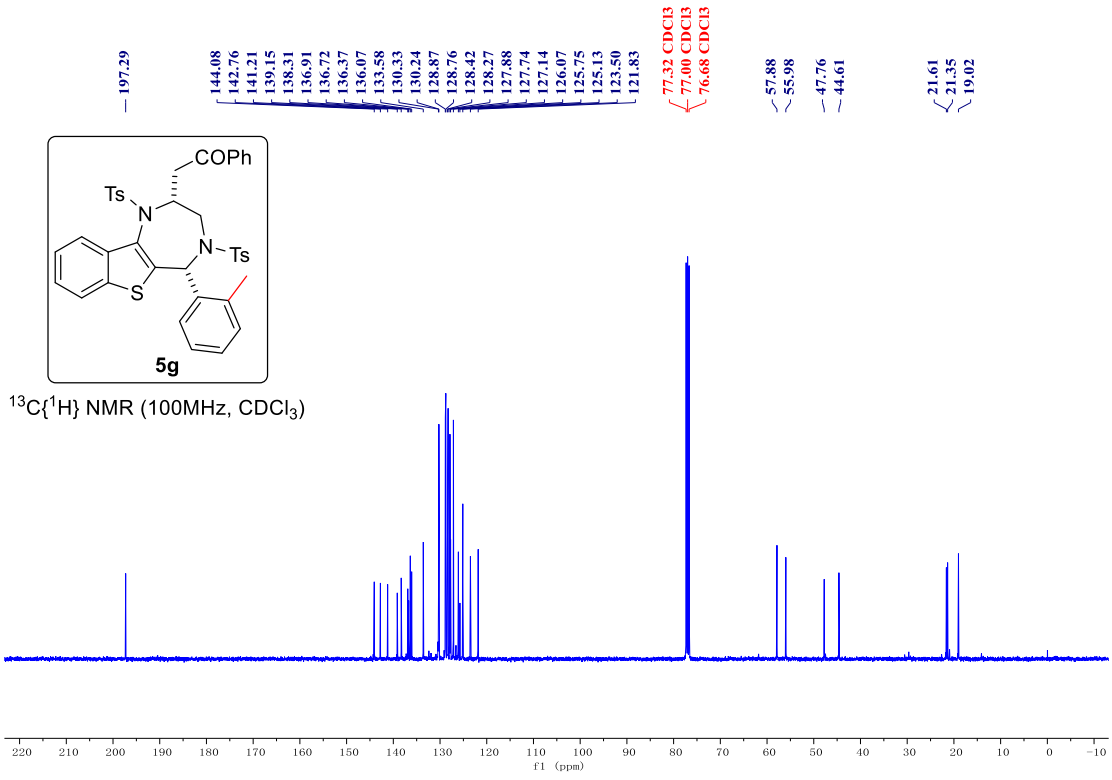


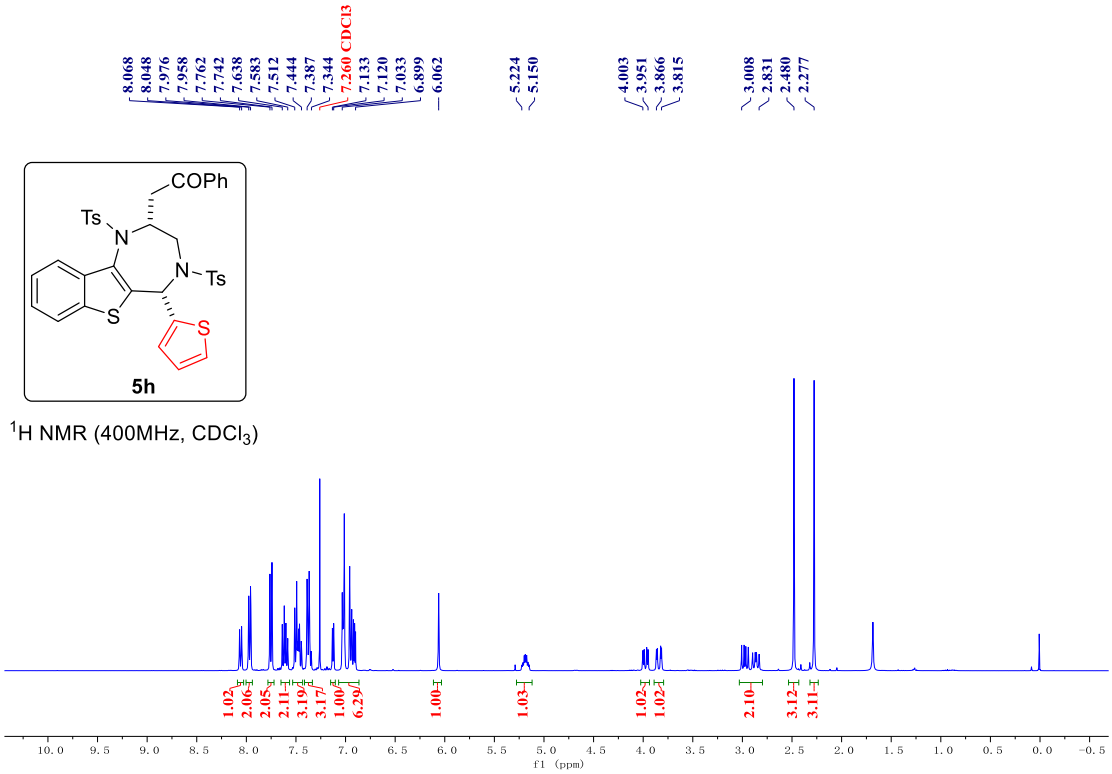
^{1}H NMR (400MHz, $CDCl_3$)

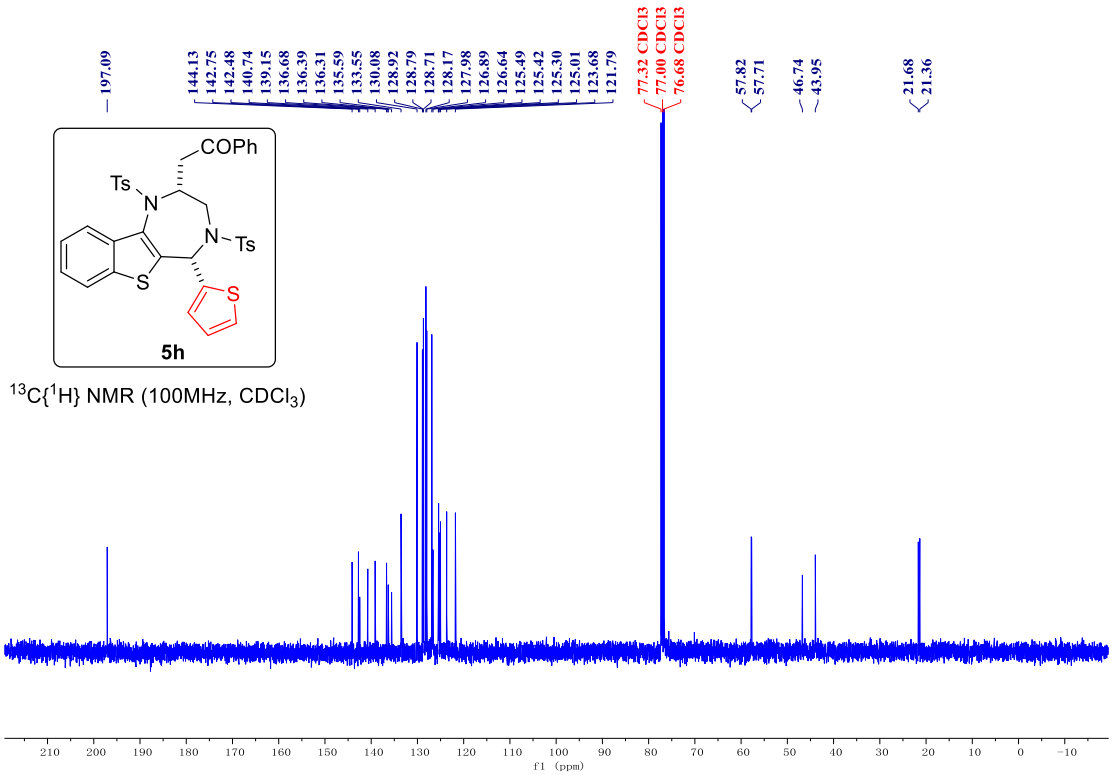


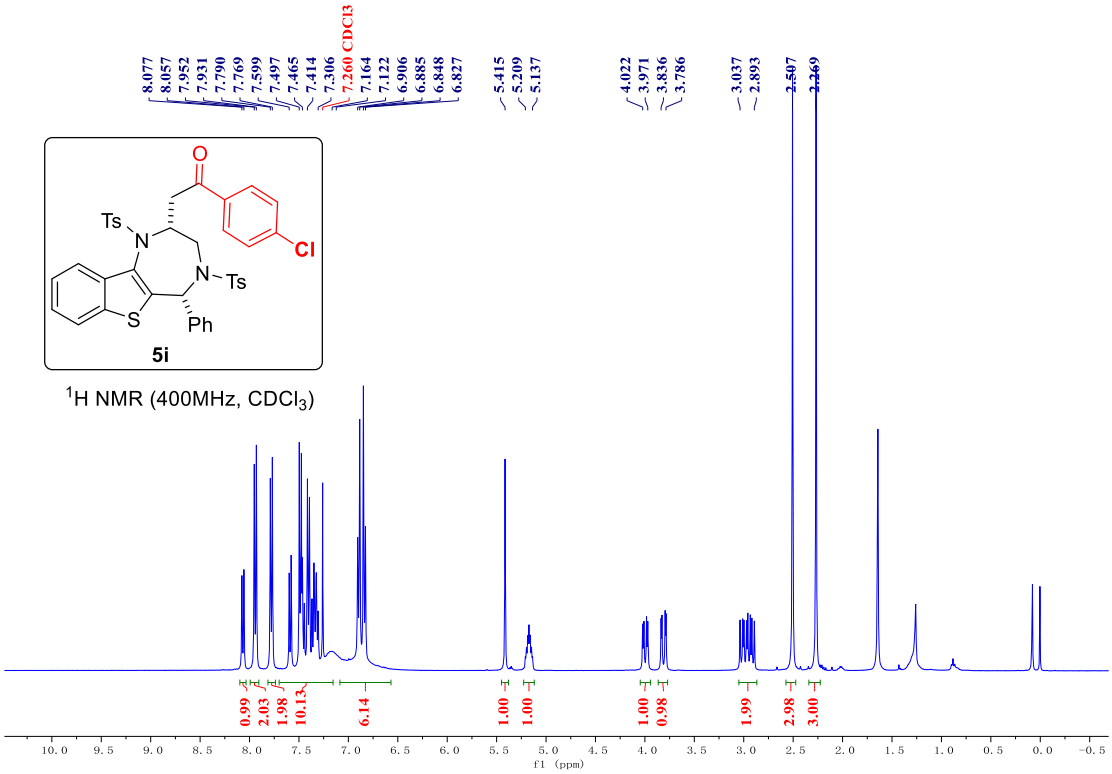
$^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$)

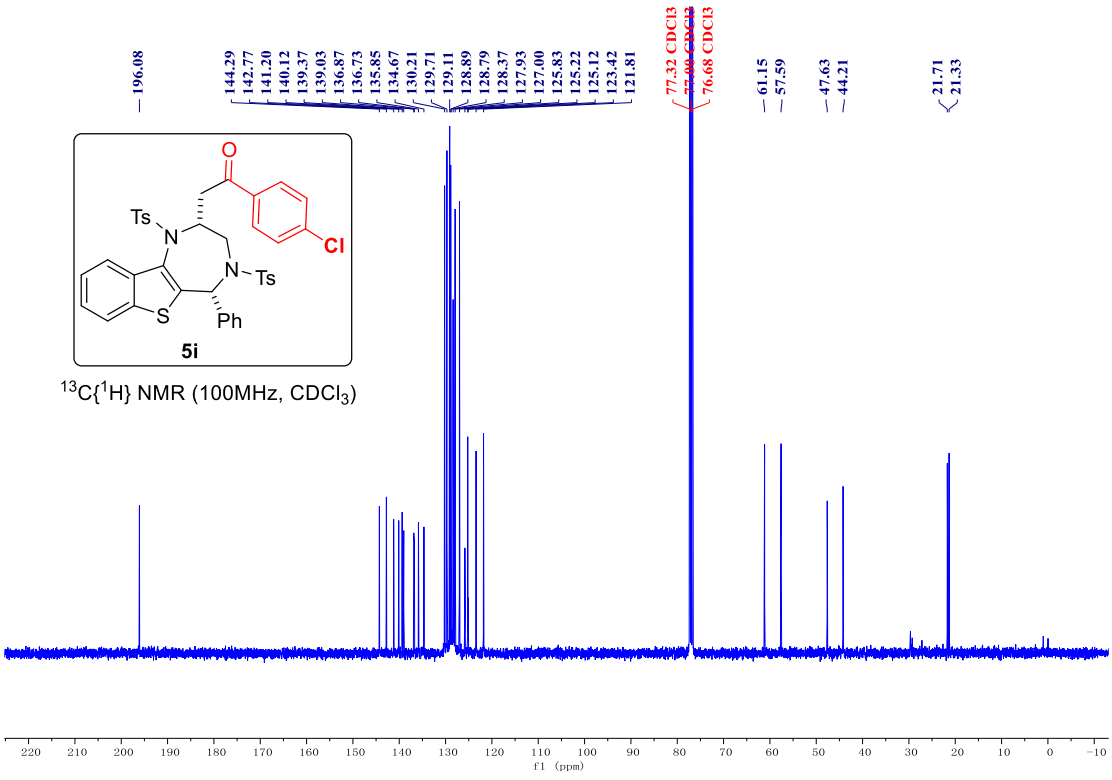

8.155
8.135
8.025
8.007
7.828
7.807
7.641
7.469
7.398
7.332
7.260 CDCl3
7.185
7.175
6.933
6.837
6.756
6.715
6.437
6.417
5.644
5.353
5.279
4.085
4.034
3.914
3.864
3.021
2.925
2.465
2.287
2.235
COPh
Ts
N
N
Ts
S
5g
1H NMR (400MHz, CDCl3)
1.00
2.12
2.11
5.25
3.20
2.01
4.32
1.01
1.01
1.00
1.11
1.01
1.12
2.07
3.03
3.21
3.06
f1 (ppm)

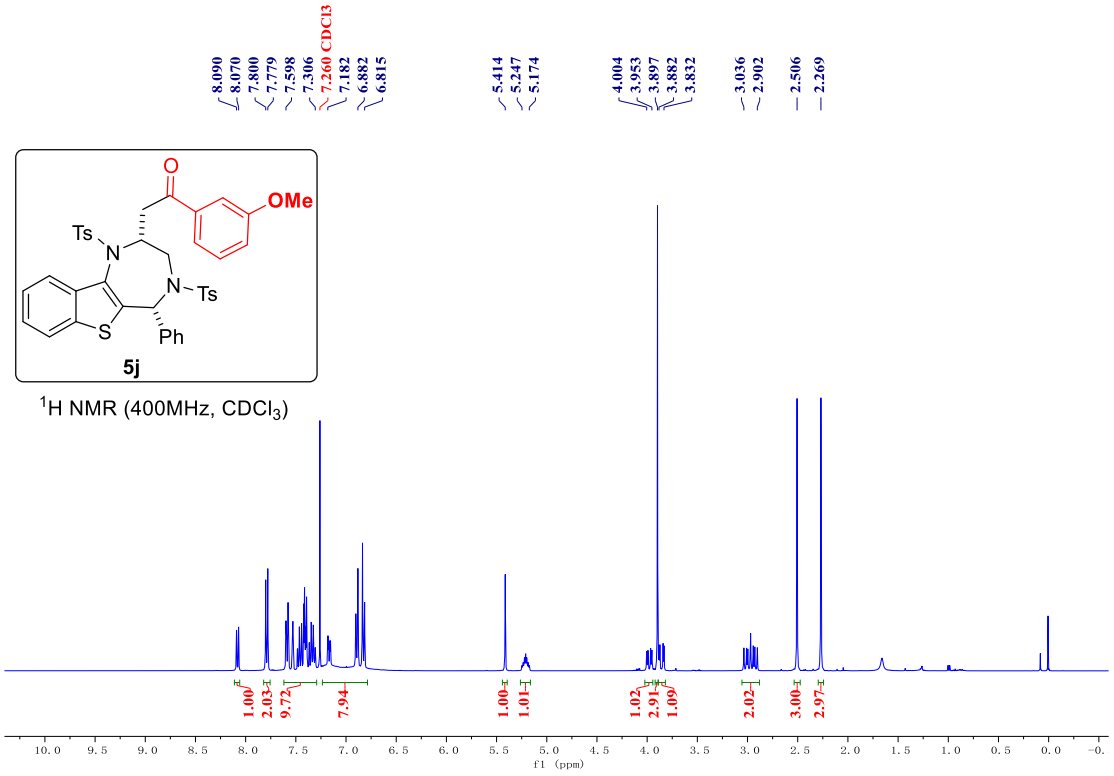

197.29
144.08
142.76
141.21
139.15
138.31
136.91
136.72
136.37
136.07
133.58
130.33
130.24
128.87
128.76
128.42
128.27
127.88
127.74
127.14
126.07
125.75
125.13
123.50
121.83
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
57.88
55.98
47.76
44.61
21.61
21.35
19.02
COPh
Ts
N
N
Ts
S
5g
13C{1H} NMR (100MHz, CDCl3)
f1 (ppm)

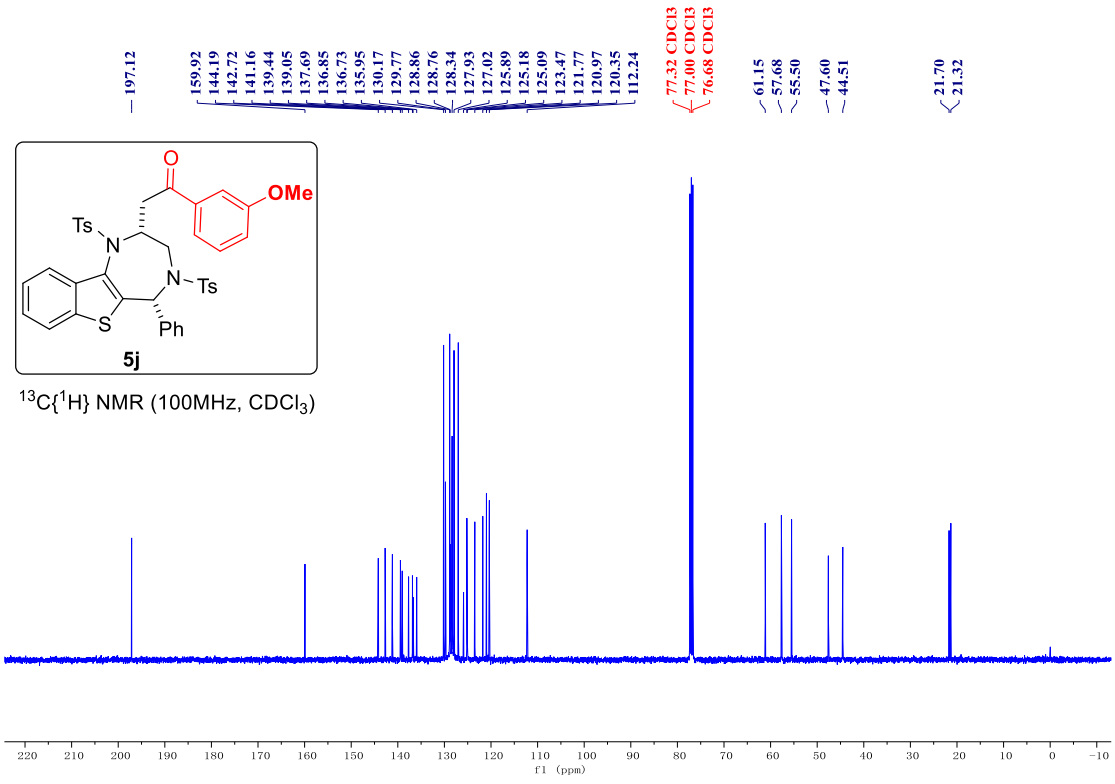

8.068
8.048
7.976
7.958
7.762
7.742
7.638
7.583
7.512
7.444
7.387
7.344
7.260 CDCl3
7.133
7.120
7.033
6.899
6.062
5.224
5.150
4.003
3.951
3.866
3.815
3.008
2.831
2.480
2.277
COPh
Ts
N
N
Ts
S
S
5h
1H NMR (400MHz, CDCl3)
1.02
2.06
2.05
2.11
3.19
3.17
1.00
6.29
1.00
1.03
1.02
1.02
2.10
3.12
3.11
f1 (ppm)

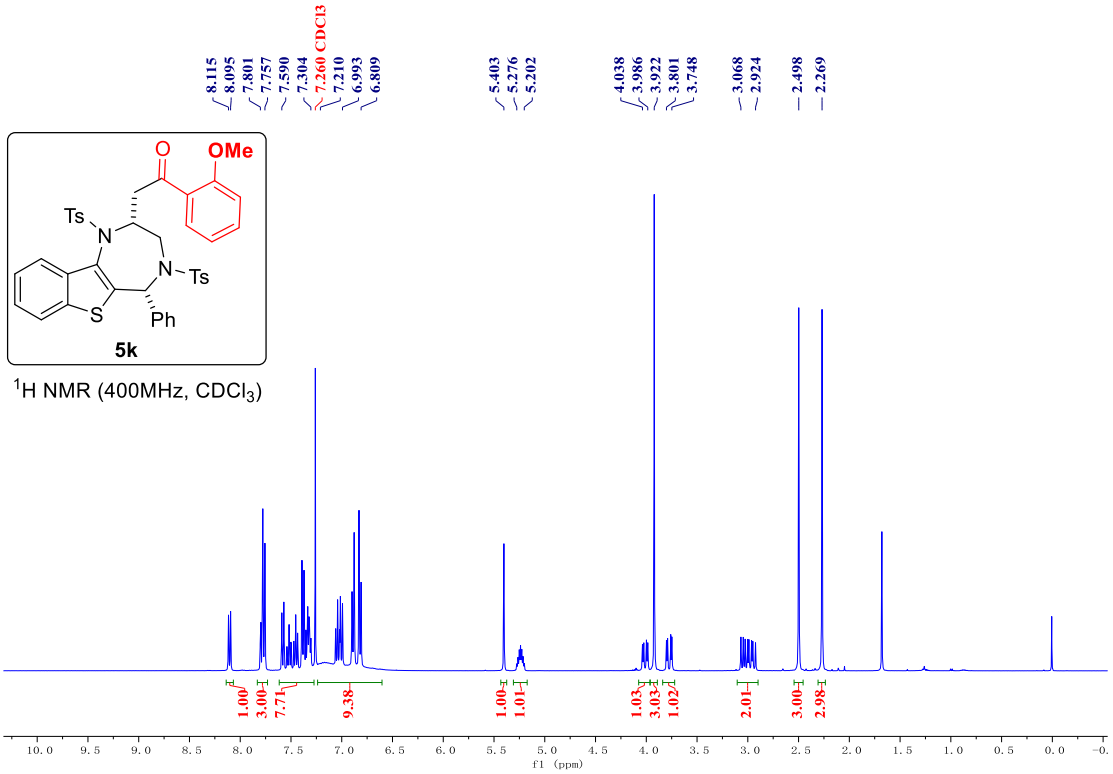

197.09
144.13
142.75
142.48
140.74
139.15
136.68
136.39
136.31
135.59
133.55
130.08
128.92
128.79
128.71
128.17
127.98
126.89
126.64
125.49
125.42
125.30
125.01
123.68
121.79
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
57.82
57.71
46.74
43.95
21.68
21.36
COPh
Ts
N
N
Ts
S
S
5h
13C{1H} NMR (100MHz, CDCl3)
f1 (ppm)

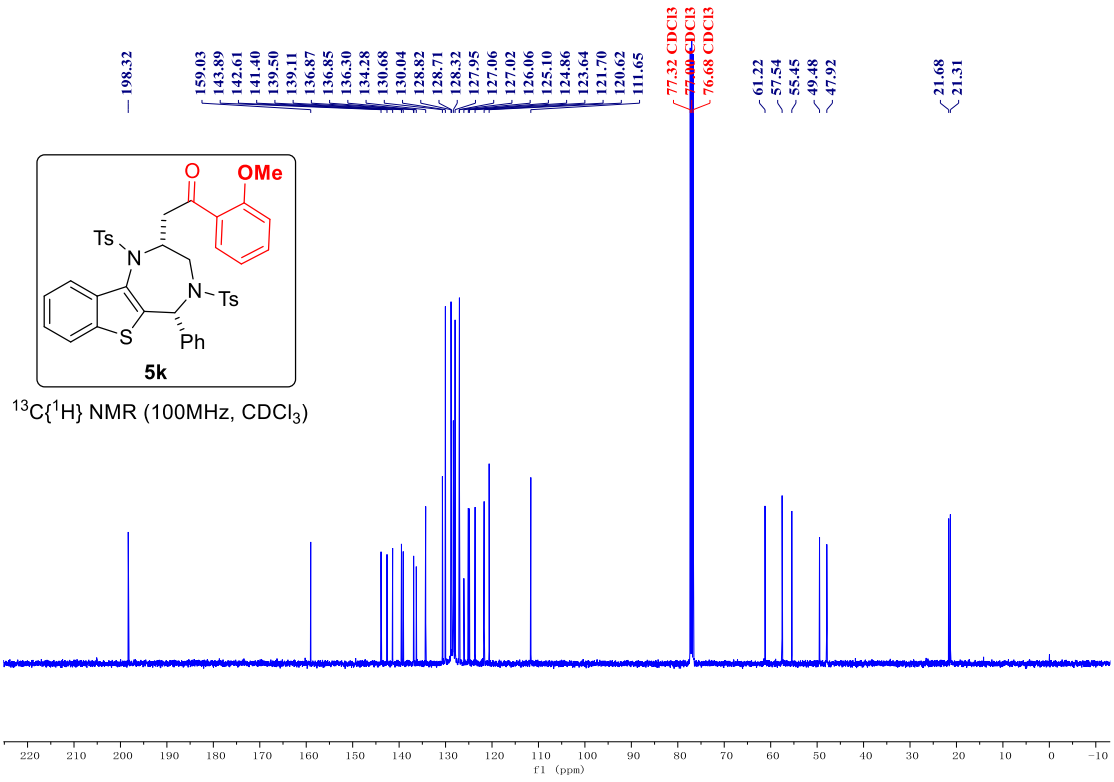

8.077
8.057
7.952
7.931
7.790
7.769
7.599
7.497
7.465
7.414
7.306
7.260 CDCl3
7.164
7.122
6.906
6.885
6.848
6.827
5.415
5.209
5.137
4.022
3.971
3.836
3.786
3.037
2.893
2.507
2.269
Ts
N
N
Ts
S
Ph
Cl
O
5i
1H NMR (400MHz, CDCl3)
0.99
2.03
1.98
10.13
6.14
1.00
1.00
1.00
0.98
1.99
2.98
3.00
f1 (ppm)

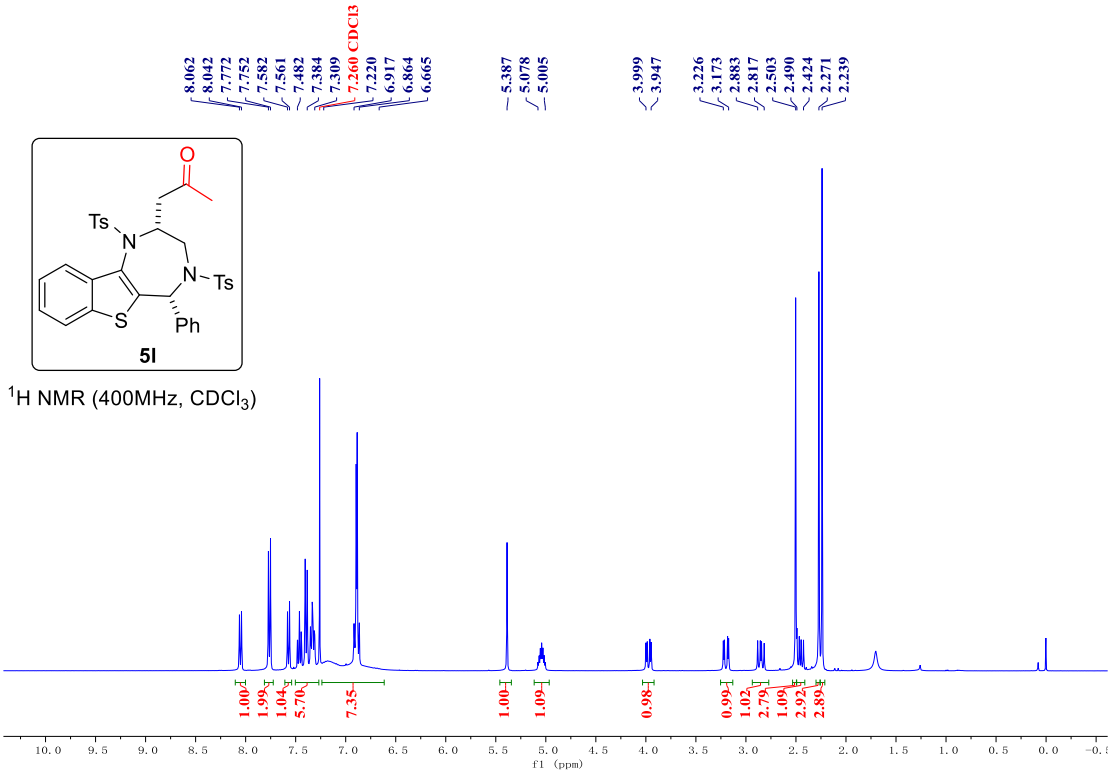

196.08
144.29
142.77
141.20
140.12
139.37
139.03
136.87
136.73
135.85
134.67
130.21
129.71
129.11
128.89
128.79
128.37
127.93
127.00
125.83
125.22
125.12
123.42
121.81
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
61.15
57.59
47.63
44.21
21.71
21.33
Ts
N
N
Ts
S
Ph
Cl
O
5i
13C{1H} NMR (100MHz, CDCl3)
f1 (ppm)


8.090
8.070
7.800
7.779
7.598
7.306
7.260 CDCl3
7.182
6.882
6.815
5.414
5.247
5.174
4.004
3.953
3.897
3.882
3.832
3.036
2.902
2.506
2.269
OMe
Ts
N
N
Ts
S
Ph
5j
1H NMR (400MHz, CDCl3)
1.00
2.03
9.72
7.94
1.00
1.01
1.02
2.91
1.09
2.02
3.00
2.97
f1 (ppm)

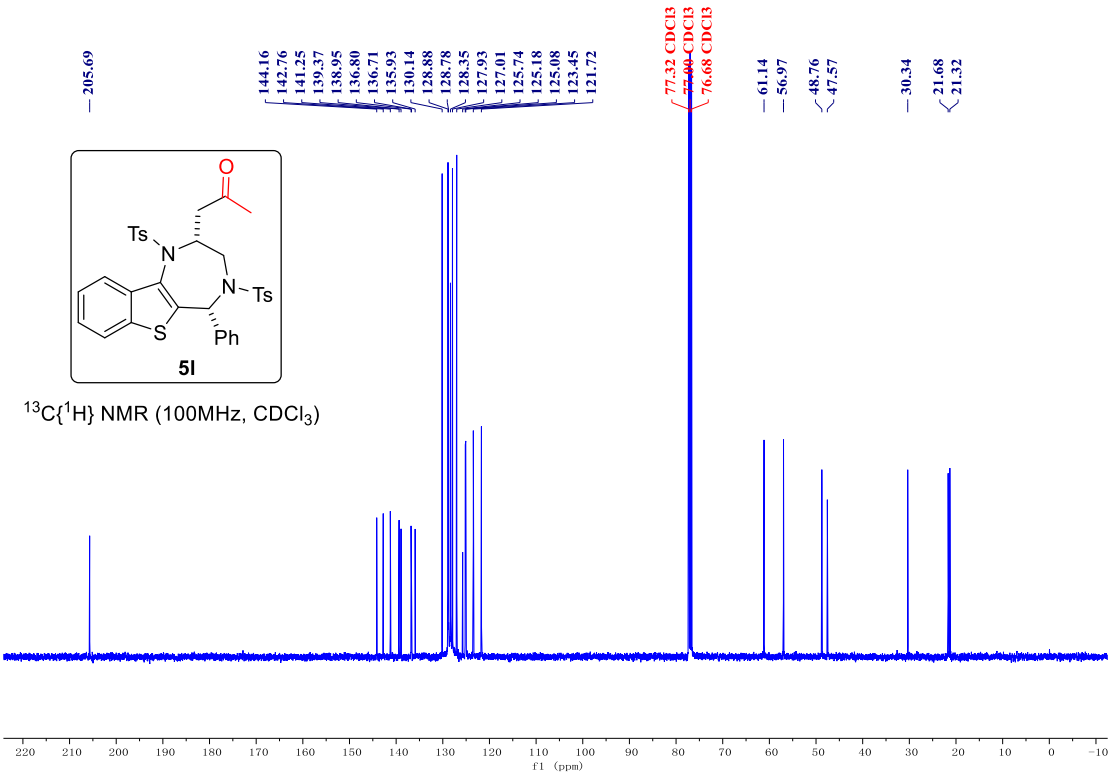

197.12
159.92
144.19
142.72
141.16
139.44
139.05
137.69
136.85
136.73
135.95
130.17
129.77
128.86
128.76
128.34
127.93
127.02
125.89
125.18
125.09
123.47
121.77
120.97
120.35
112.24
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
61.15
57.68
55.50
47.60
44.51
21.70
21.32
OMe
Ts
N
N
Ts
S
Ph
5j
13C{1H} NMR (100MHz, CDCl3)
f1 (ppm)


8.115
8.095
7.801
7.757
7.590
7.304
7.260 CDCl3
7.210
6.993
6.809
5.403
5.276
5.202
4.038
3.986
3.922
3.801
3.748
3.068
2.924
2.498
2.269
O
OMe
Ts
N
N
Ts
S
Ph
5k
1H NMR (400MHz, CDCl3)
1.00
3.00
7.71
9.38
1.00
1.01
1.03
3.03
1.02
2.01
3.00
2.98
f1 (ppm)

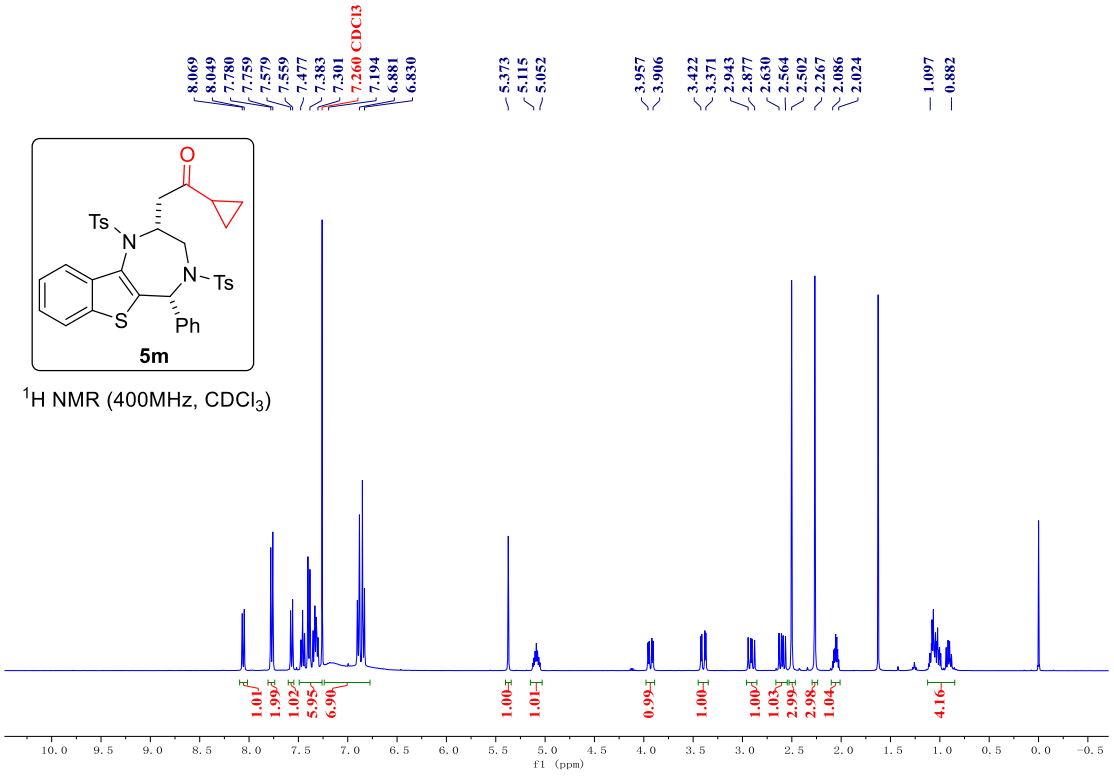

198.32
159.03
143.89
142.61
141.40
139.50
139.11
136.87
136.85
136.30
134.28
130.68
130.04
128.82
128.71
128.32
127.95
127.06
127.02
126.06
125.10
124.86
123.64
121.70
120.62
111.65
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
61.22
57.54
55.45
49.48
47.92
21.68
21.31
O
OMe
Ts
N
N
Ts
S
Ph
5k
13C{1H} NMR (100MHz, CDCl3)
f1 (ppm)

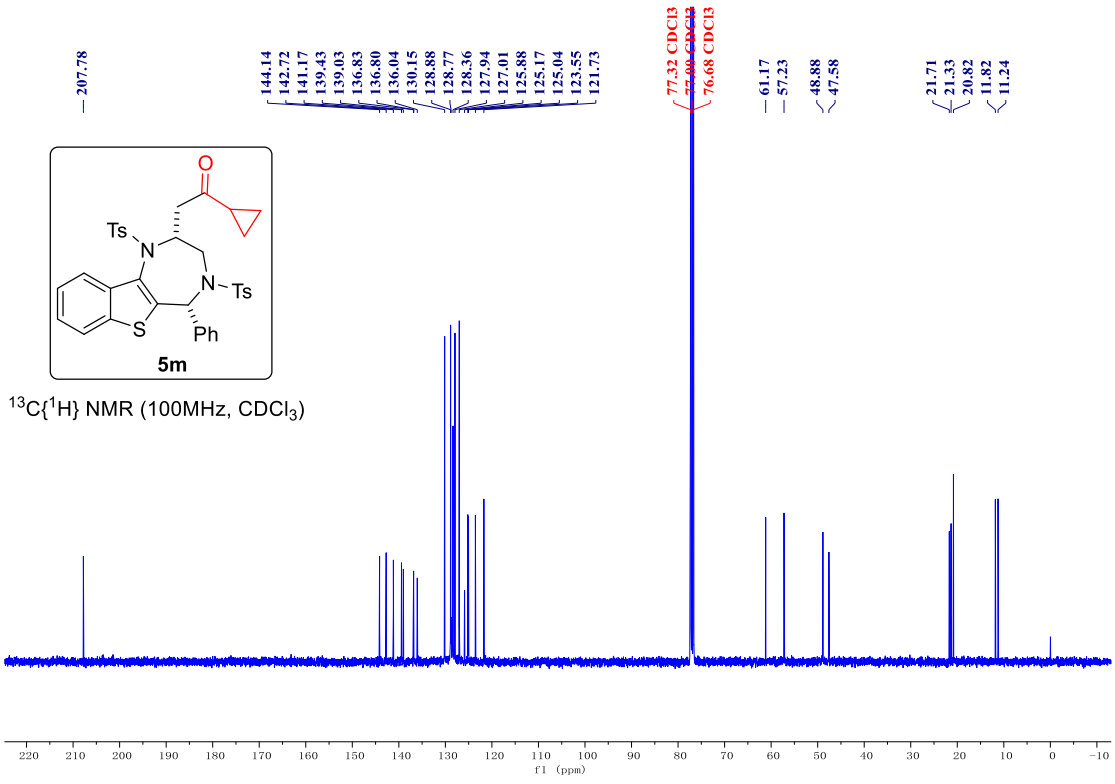


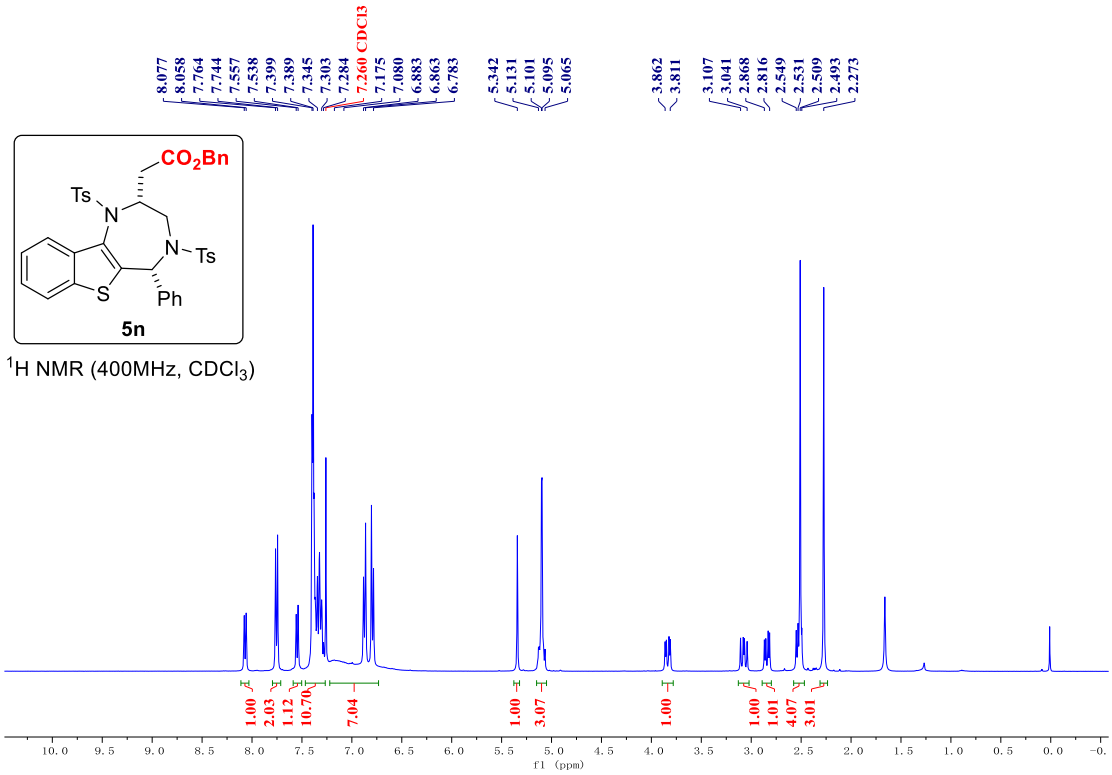
^{1}H NMR (400MHz, $CDCl_3$)

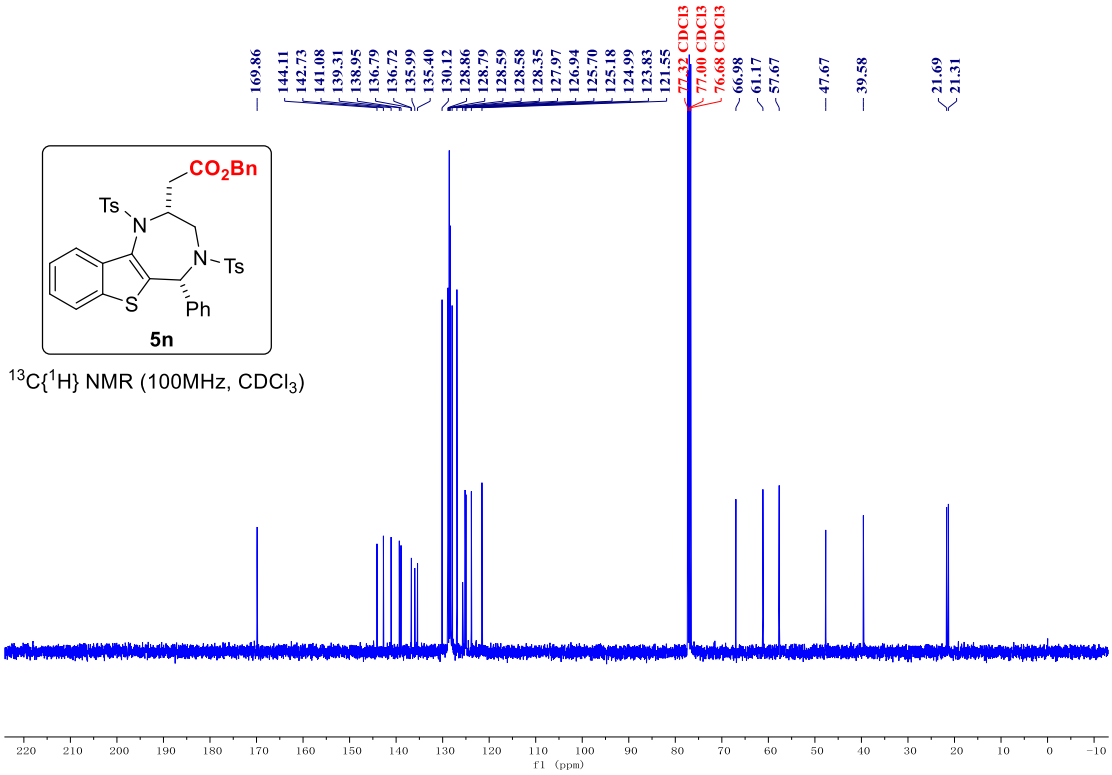


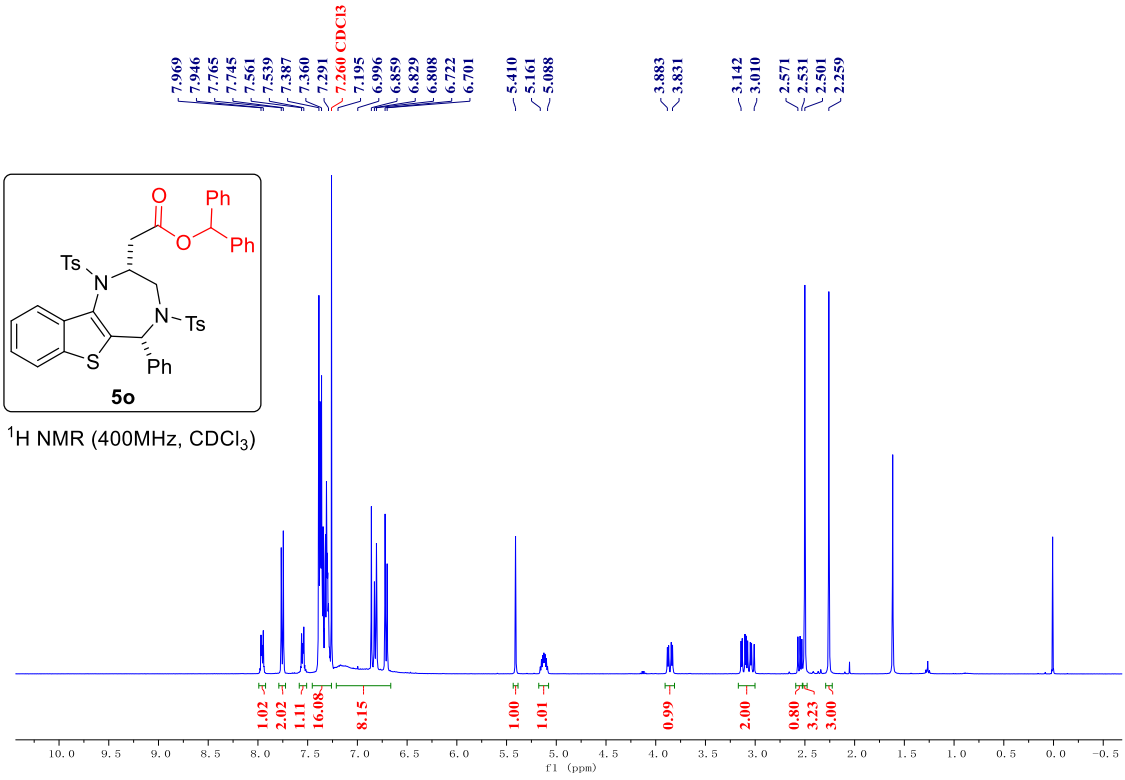
$^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$)


8.069
8.049
7.780
7.759
7.579
7.559
7.477
7.383
7.301
7.260 CDCl3
7.194
6.881
6.830
5.373
5.115
5.052
3.957
3.906
3.422
3.371
2.943
2.877
2.630
2.564
2.502
2.267
2.086
2.024
1.097
0.882
Ts
N
N
Ts
S
Ph
O
5m
1H NMR (400MHz, CDCl3)
1.01
1.99
1.02
5.95
6.90
1.00
1.01
0.99
1.00
1.00
1.03
2.99
2.98
1.04
4.16
f1 (ppm)

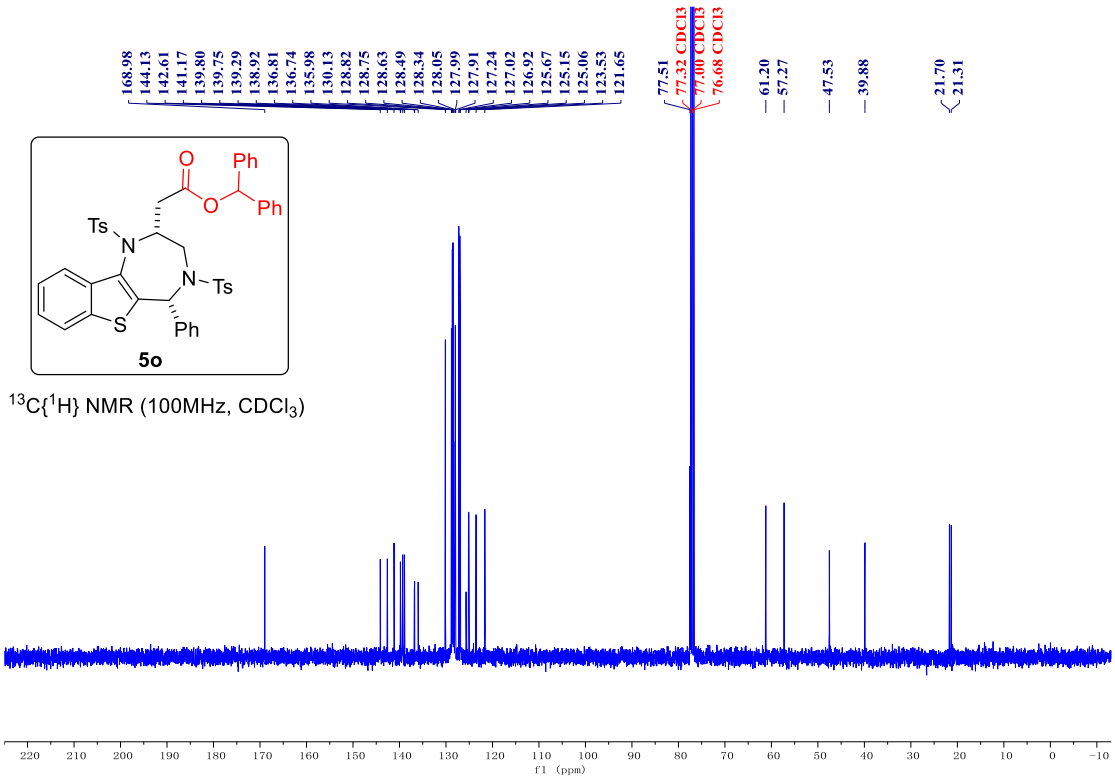

207.78
144.14
142.72
141.17
139.43
139.03
136.83
136.80
136.04
130.15
128.88
128.77
128.36
127.94
127.01
125.88
125.17
125.04
123.55
121.73
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
61.17
57.23
48.88
47.58
21.71
21.33
20.82
11.82
11.24
Ts
N
N
Ts
S
Ph
O
5m
13C{1H} NMR (100MHz, CDCl3)
f1 (ppm)


8.077
8.058
7.764
7.744
7.557
7.538
7.399
7.389
7.345
7.303
7.284
7.260 CDCl3
7.175
7.080
6.883
6.863
6.783
5.342
5.131
5.101
5.095
5.065
3.862
3.811
3.107
3.041
2.868
2.816
2.549
2.531
2.509
2.493
2.273
CO2Bn
Ts
N
N
Ts
S
Ph
5n
1H NMR (400MHz, CDCl3)
1.00
2.03
1.12
10.70
7.04
1.00
3.07
1.00
1.00
1.01
4.07
3.01
f1 (ppm)

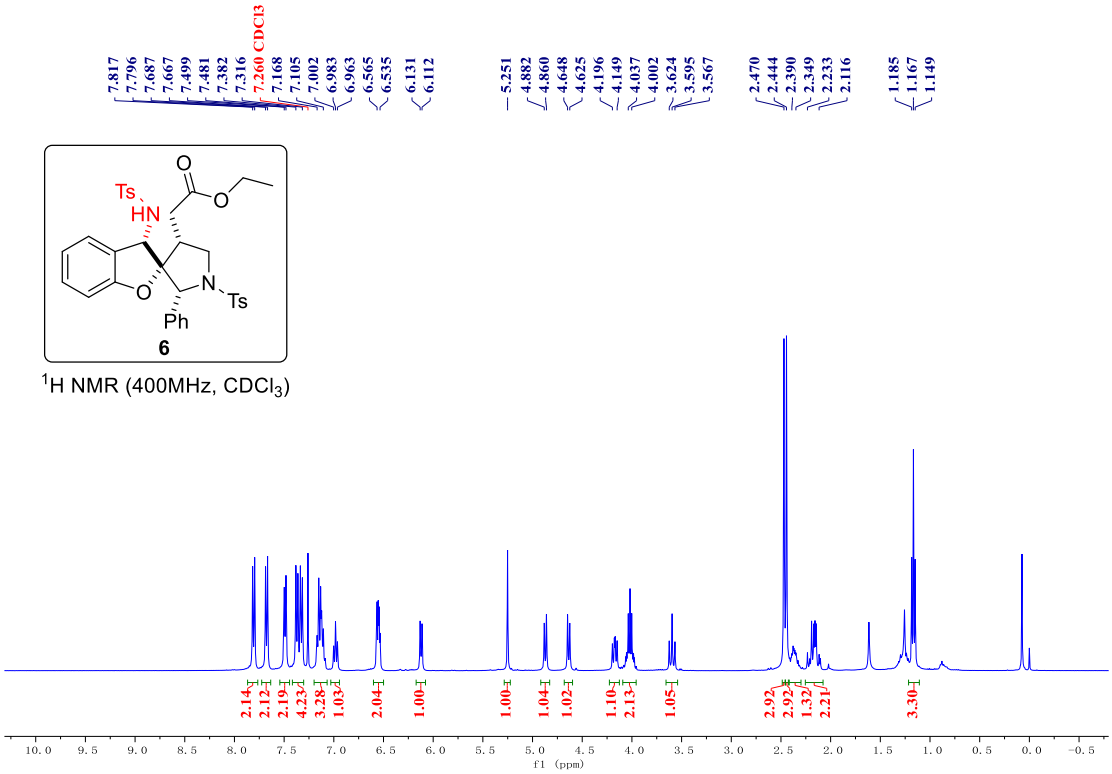

169.86
144.11
142.73
141.08
139.31
138.95
136.79
136.72
135.99
135.40
130.12
128.86
128.79
128.59
128.58
128.35
127.97
126.94
125.70
125.18
124.99
123.83
121.55
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
66.98
61.17
57.67
47.67
39.58
21.69
21.31
CO2Bn
Ts
N
N
Ts
S
Ph
5n
13C{1H} NMR (100MHz, CDCl3)
f1 (ppm)

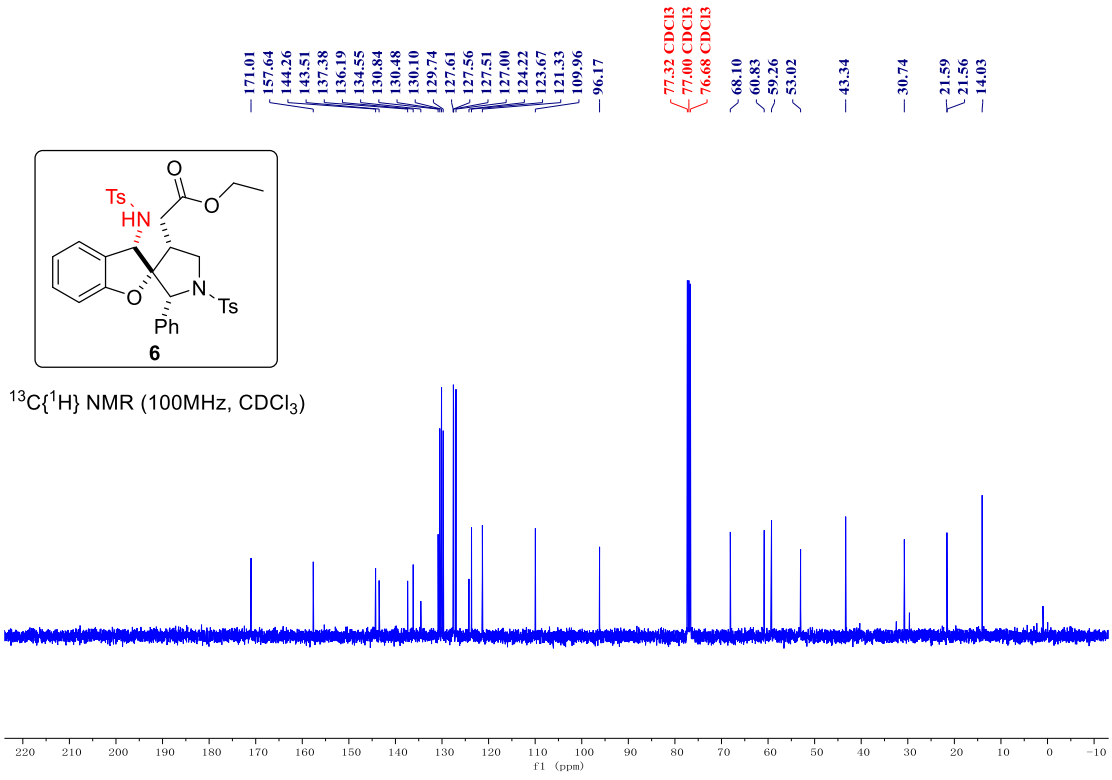


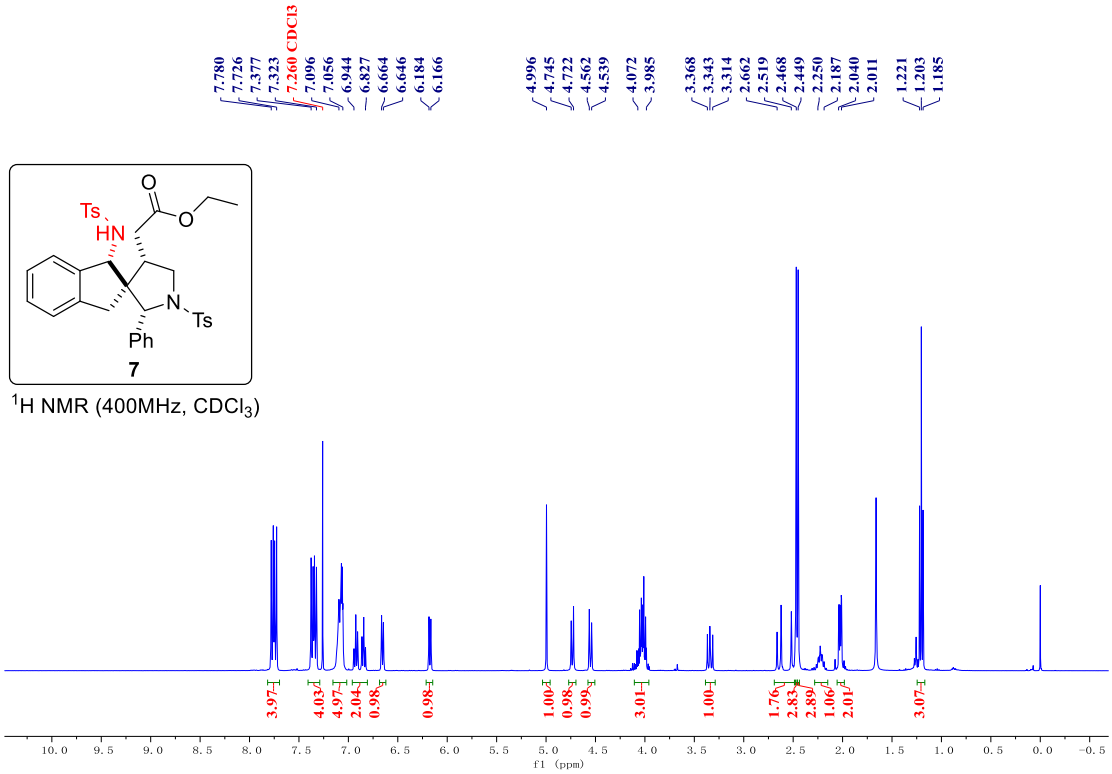
^{1}H NMR (400MHz, $CDCl_3$)



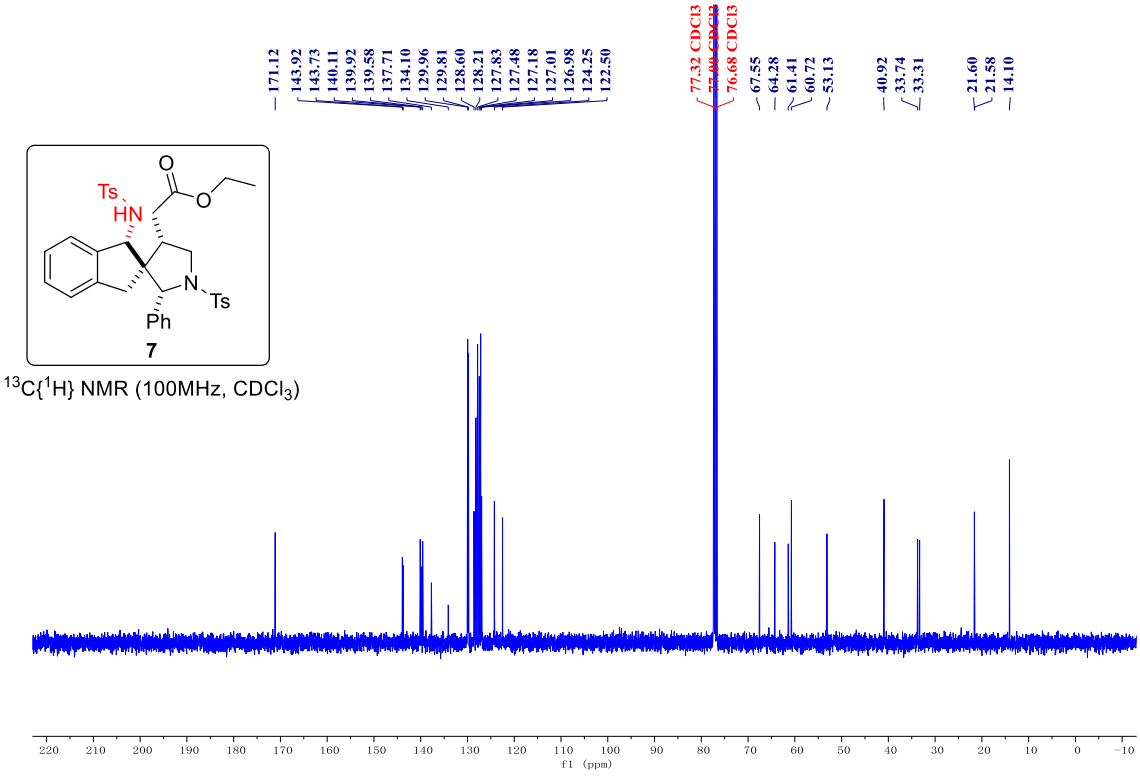
$^{13}C\{^1H\}$ NMR (100MHz, $CDCl_3$)


7.817
7.796
7.687
7.667
7.499
7.481
7.382
7.316
7.260 CDCl3
7.168
7.105
7.002
6.983
6.963
6.565
6.535
6.131
6.112
5.251
4.882
4.860
4.648
4.625
4.196
4.149
4.037
4.002
3.624
3.595
3.567
2.470
2.444
2.390
2.349
2.233
2.116
1.185
1.167
1.149
Ts
HN
O
O
N
Ts
O
Ph
6
1H NMR (400MHz, CDCl3)
2.14
2.12
2.19
4.23
3.28
1.03
2.04
1.00
1.00
1.04
1.02
1.10
2.13
1.05
2.92
2.92
1.32
2.21
3.30
f1 (ppm)

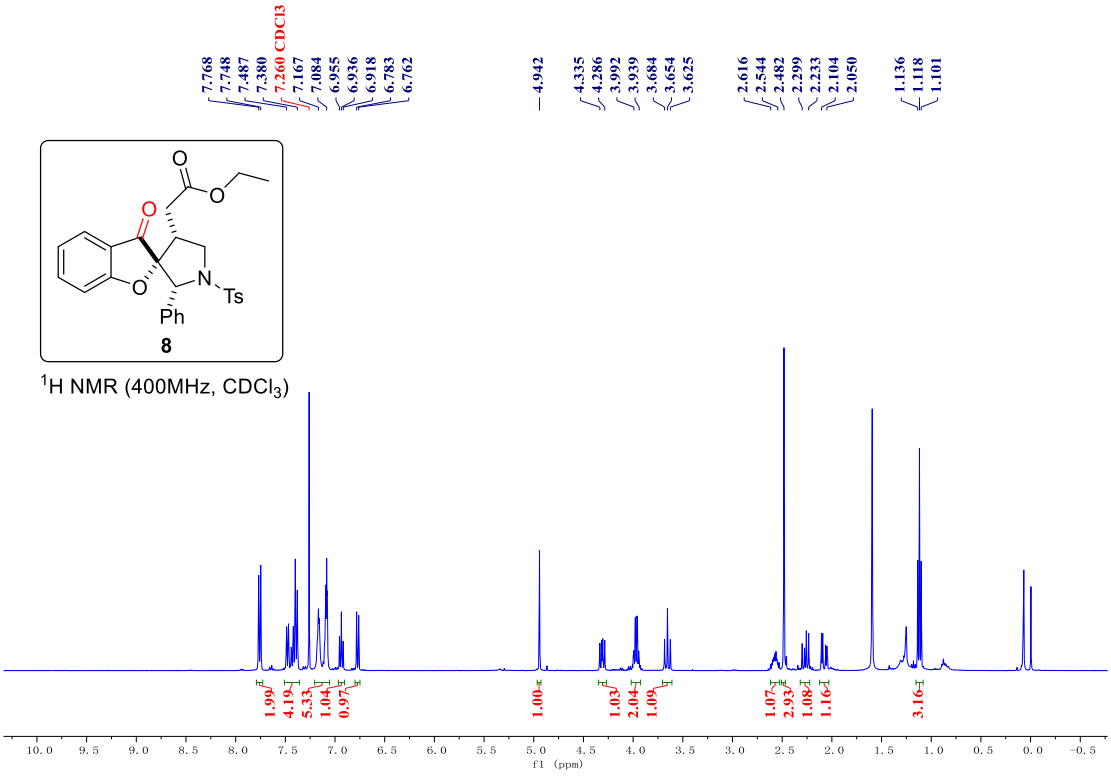

171.01
157.64
144.26
143.51
137.38
136.19
134.55
130.84
130.48
130.10
129.74
127.61
127.56
127.51
127.00
124.22
123.67
121.33
109.96
96.17
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
68.10
60.83
59.26
53.02
43.34
30.74
21.59
21.56
14.03
Ts
HN
O
O
N
Ts
O
Ph
6
13C{1H} NMR (100MHz, CDCl3)
f1 (ppm)

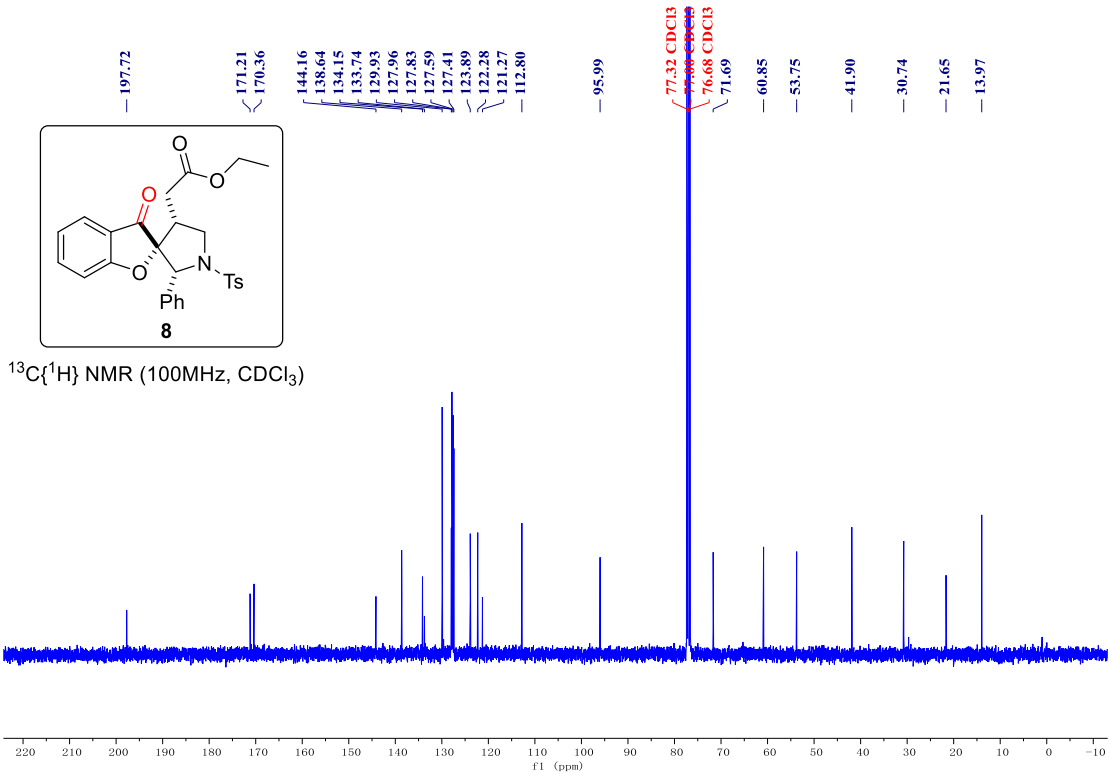


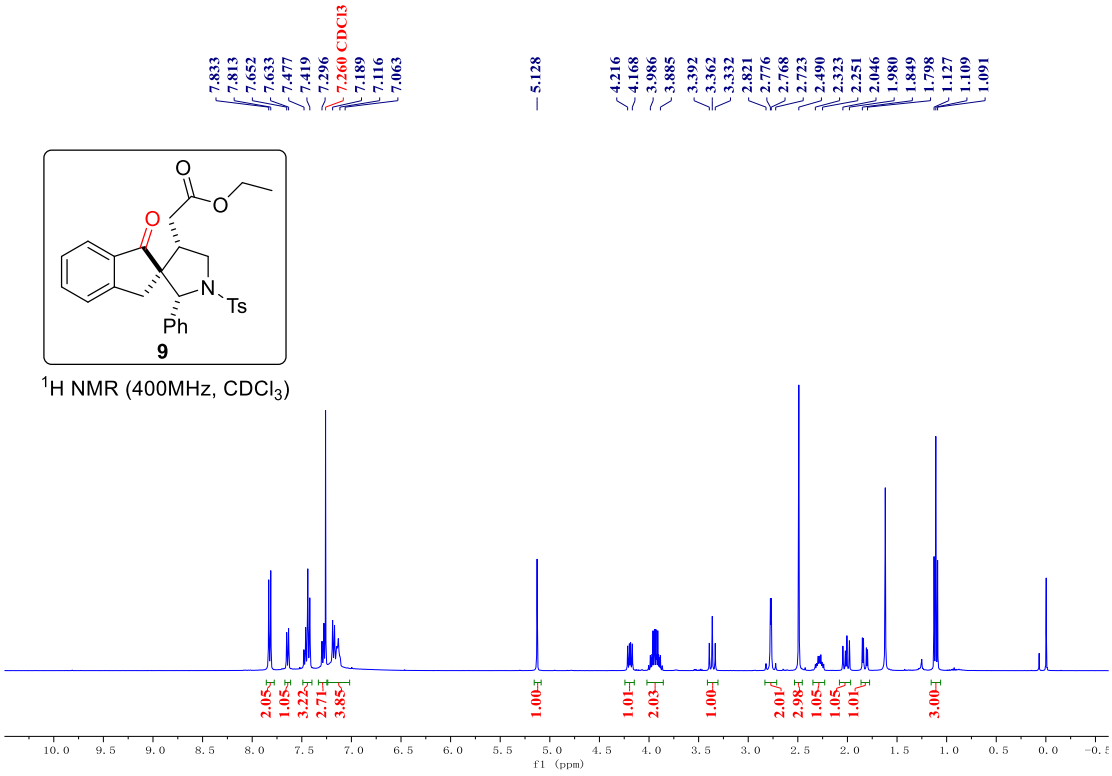
^{1}H NMR (400MHz, $CDCl_3$)

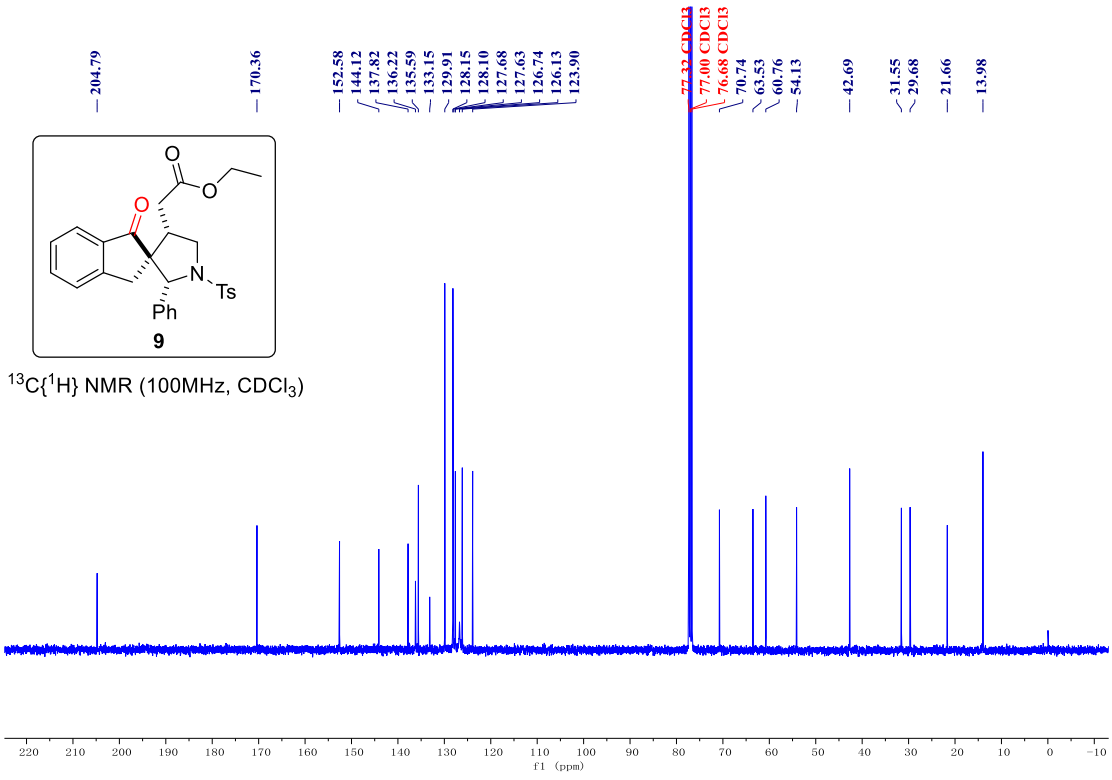


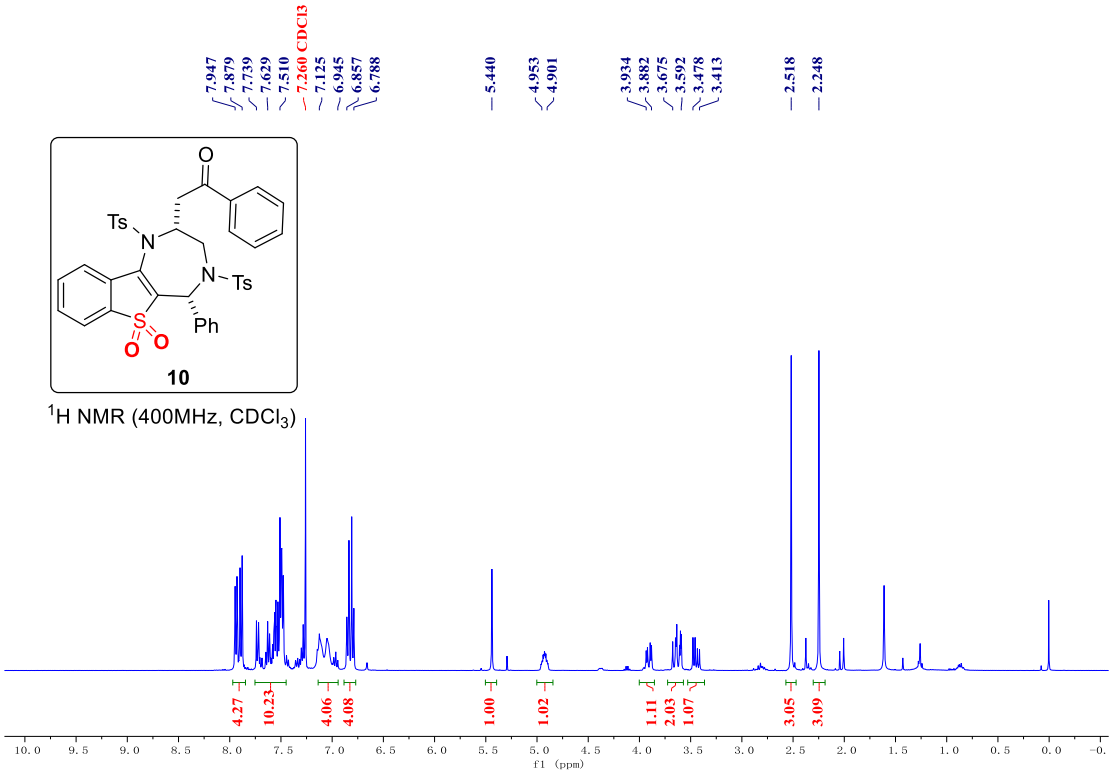
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$)

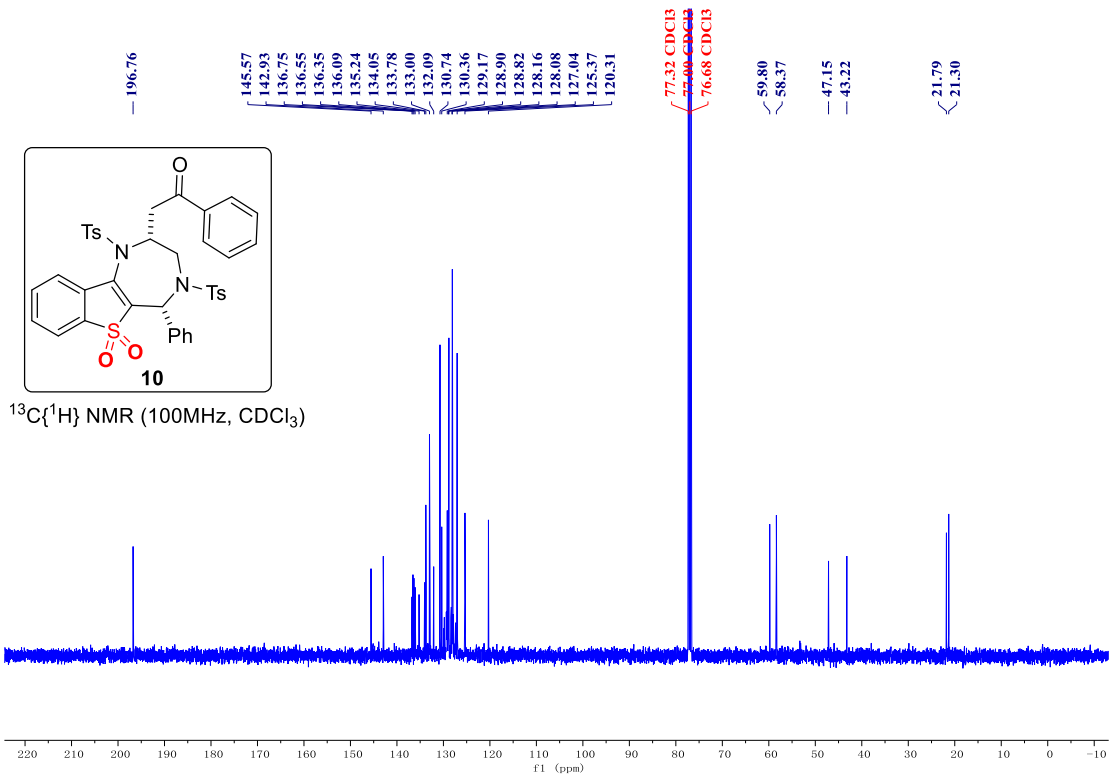

7.768
7.748
7.487
7.380
7.260 CDCl3
7.167
7.084
6.955
6.936
6.918
6.783
6.762
4.942
4.335
4.286
3.992
3.939
3.684
3.654
3.625
2.616
2.544
2.482
2.299
2.233
2.104
2.050
1.136
1.118
1.101
O
O
O
O
N
Ts
Ph
8
1H NMR (400MHz, CDCl3)
1.99
4.19
5.33
1.04
0.97
1.00
1.03
2.04
1.09
1.07
2.93
1.08
1.16
3.16
f1 (ppm)


197.72
171.21
170.36
144.16
138.64
134.15
133.74
129.93
127.96
127.83
127.59
127.41
123.89
122.28
121.27
112.80
95.99
77.32 CDCl3
76.68 CDCl3
71.69
60.85
53.75
41.90
30.74
21.65
13.97
O
O
O
O
N
Ts
Ph
8
13C{1H} NMR (100MHz, CDCl3)
f1 (ppm)


7.833
7.813
7.652
7.633
7.477
7.419
7.296
7.260 CDCl3
7.189
7.116
7.063
5.128
4.216
4.168
3.986
3.885
3.392
3.362
3.332
2.821
2.776
2.768
2.723
2.490
2.323
2.251
2.046
1.980
1.849
1.798
1.127
1.109
1.091
O
O
O
N
Ts
Ph
9
1H NMR (400MHz, CDCl3)
2.05
1.05
3.22
2.71
3.85
1.00
1.01
2.03
1.00
2.01
2.98
1.05
1.05
1.01
3.00
f1 (ppm)


204.79
170.36
152.58
144.12
137.82
136.22
135.59
133.15
129.91
128.15
128.10
127.68
127.63
126.74
126.13
123.90
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
70.74
63.53
60.76
54.13
42.69
31.55
29.68
21.66
13.98
O
O
O
N
Ts
Ph
9
13C{1H} NMR (100MHz, CDCl3)
f1 (ppm)


7.947
7.879
7.739
7.629
7.510
7.260 CDCl3
7.125
6.945
6.857
6.788
5.440
4.953
4.901
3.934
3.882
3.675
3.592
3.478
3.413
2.518
2.248
Ts
N
N
Ts
Ph
S
O
O
O
10
1H NMR (400MHz, CDCl3)
4.27
10.23
4.06
4.08
1.00
1.02
1.11
2.03
1.07
3.05
3.09
f1 (ppm)


196.76
145.57
142.93
136.75
136.55
136.35
136.09
135.24
134.05
133.78
133.00
132.09
130.74
130.36
129.17
128.90
128.82
128.16
128.08
127.04
125.37
120.31
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
59.80
58.37
47.15
43.22
21.79
21.30
Ts
N
N
Ts
Ph
S
O
O
O
10
13C{1H} NMR (100MHz, CDCl3)
f1 (ppm)