Supporting Information for

Straightforward regioselective construction of 3,4-dihydro-2H-1,4-thiazine by rhodium catalysed [3+3] cycloaddition of thiirane with 1-sulfonyl-1,2,3-triazole: a pronounced acid additive effect

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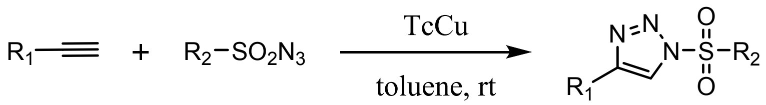
I. General Information and Materials

NMR spectra were recorded using Bruker AV - 300 / AV- 400 spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectra were acquired on an Agilent 6230 spectrometer and were obtained by peak matching. Gas Chromatography-Mass Spectra were acquired on an Agilent 7890A-5975C spectrometer. Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator and/or by exposure to phosphormolybdic acid/cerium (IV) sulfate/ ninhydrine followed by brief heating with a heat gun. Liquid chromatography (flash chromatography) was performed on 60Å (40 – 60 µm) mesh silica gel (SiO_2). All reactions were carried out under nitrogen or argon with anhydrous solvents in oven-dried glassware, unless otherwise noted. All reagents were commercially obtained and, where appropriate, purified prior to use.

III. Preparation of 1-sulfonyl-1,2,3-triazoles

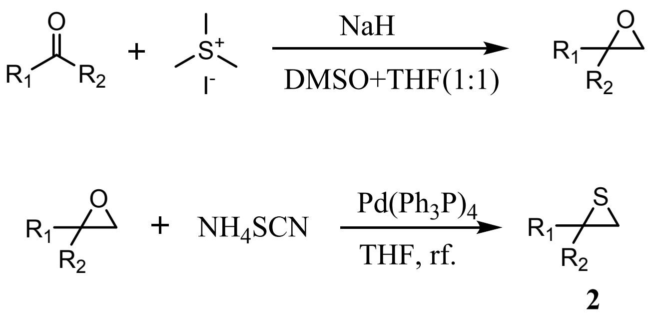
1-Sulfonyl-1,2,3-triazoles were prepared from the corresponding alkynes and sulfonyl azides according to previously reported synthetic procedures[1]and all data correspond to previously reported material.



1

Following the reported procedure[1], TcCu (0.3 mmol, 0.1 eq.), sulfonyl azide (3.6 mmol, 1.1 eq.), alkyne (3 mmol, 1 eq.) in wet toluene (10 mL) was stirred at room temperature under the protected of N_2. After the total consumption of alkyne by TLC, solvent was removed in vacuum, the residue was purified by column chromatography on silica gel to give the desired product of **1**.

III. Preparation of Substituted thiiranes

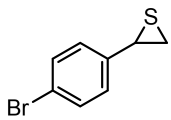


2

Following the reported procedure to obtain the epoxides[2].To a flame – dried 100 mL flask was added dropwise trimethyl sulfonium iodide (4.08 g, 20 mmol,2 eq.), sodium hydride (60% dispersion in oil, 0.96 g, 22 mmol, 1.1 eq.), DMSO (15 mL), and THF (15 mL), The solution was evacuated three times with N_2 and stirred for about 30 minutes at room temperature. Then the solution was cooled to 0 ºC, the aldehyde or ketone (10 mmol, 1 eq.) was added at 0 ºC slowly and allowed to stir at room temperature until the total consumption of aldehyde or ketone by TLC. The reaction was diluted with water, extracted with EtOAc. The combined organic layers were washed with water and brine, dried over $MgSO_4$, and concentrated under vacuum. The crude product was purified by column chromatography on silica gel to give the product of Epoxide.

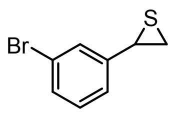
Following the modification procedure to obtain thiiranes from the reported procedure[3] and all data correspond to previously reported materials**.**

A flame dried 50 mL Schlenk tube was charged with $Pd(Ph_3P)_4$ (28mg, 0.025 mmol, 0.005 eq.), NH_4SCN (456 mg, 6 mmol, 1.2 eq.), epoxide (5mmol, 1 eq.) and THF (15 mL). Then the solution was evacuated three times with N_2 and stirred for 2.5 h at 80 ℃. After the total consumption of epoxide by TLC, the solvent was removed in vacuum. Then the crude product was purified by column chromatography on silica gel to give the desired product of **2**[3].



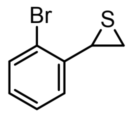
2d

2d: Light yellow oil (yield 58%):^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 3.83 (t, *J* = 6.0 Hz, 1H), 2.87 (dd, *J* = 6.5, 0.9 Hz, 1H), 2.58 (t, *J* = 2.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 131.7, 128.4, 121.4, 35.4, 27.4. GC-MS: m/z Calculated for C_8H_7BrS 213.9, found 213.9.



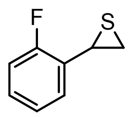
2e

2e: Light yellow oil (yield 54%):^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.22 - 7.14 (m, 2H), 3.82 (t, *J* = 6.0 Hz, 1H), 2.86 (dd, *J* = 6.5, 1.1 Hz, 1H), 2.59 (dd, *J* = 5.4, 1.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 130.7, 130.1, 129.8, 125.6, 122.7, 35.2, 27.5. GC-MS: m/z Calculated for C_8H_7BrS 213.9, found 213.9.



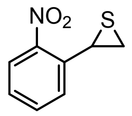
2f

2f: Light yellow oil (yield 51%):^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.29 – 7.22 (m, 1H), 7.19 (dd, *J* = 7.8, 2.1 Hz, 1H), 7.16 – 7.09 (m, 1H), 4.19 (t, *J* = 6.1 Hz, 1H), 2.90 (dd, *J* = 6.6, 1.4 Hz, 1H), 2.58 (dd, *J* = 5.6, 1.4 Hz, 1H).^{13}C NMR (75 MHz, $CDCl_3$) δ 138.3, 132.5, 128.9, 127.8, 127.7, 125.6, 36.2, 26.8. GC-MS: m/z Calculated for C_8H_7BrS 213.9, found 213.9.



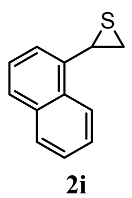
2g

2g: Colorless oil (yield 62%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.09 – 7.01 (m, 2H), 4.14 (t, *J* = 6.1 Hz, 1H), 2.86 (d, *J* = 6.5 Hz, 1H), 2.64 (d, *J* = 5.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161,9 (d, J_{CF} = 245 Hz) 129.0 (d, J_{CF} = 8 Hz), 127.0 (d, J_{CF} =3 Hz), 126.3 ,(d, J_{CF} =13 Hz) 124.4 (d, J_{CF} =4 Hz), 115.3 (d, J_{CF} =21 Hz), 29.3 (d, J_{CF} = 6 Hz), 26.2(d, J_{CF} = 1 Hz). GC-MS: m/z Calculated for C_8H_7FS ,154.0, found 154.0.



2h

2h: Light yellow oil (yield 56%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 4.43 (t, *J* = 6.1 Hz, 1H), 2.96 (d, *J* = 6.7 Hz, 1H), 2.50 (d, *J* = 5.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 134.4, 133.4, 129.9, 128.4, 124.5, 33.5, 27.2. GC-MS: m/z Calculated for $C_8H_7NO_2S$ 181.0, found 181.0.

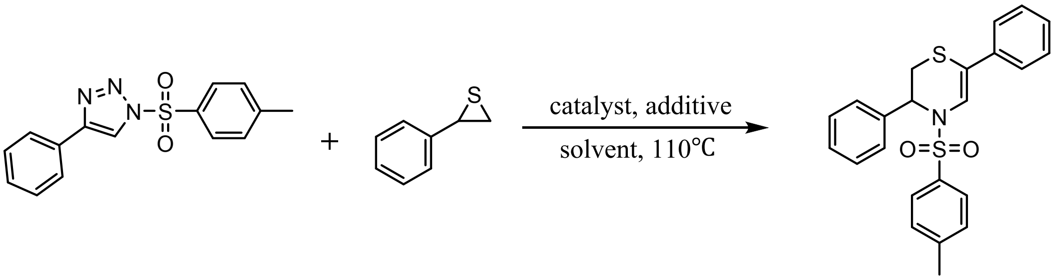


2i

2i: Colorless oil (yield 72%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.56 (dd, *J* = 7.8, 7.1 Hz, 1H), 7.46 - 7.40 (m, 2H), 4.51 (t, *J* = 6.1 Hz, 1H), 3.02 (d, *J* = 6.4 Hz, 1H), 2.89 (d, *J* = 5.8 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 134.8, 133.5, 132.7, 128.8, 128.5, 126.6, 126.0, 125.4, 123.9, 123.4, 34.6, 25.4. GC-MS: m/z Calculated for $C_{12}H_{10}S$ 186.0 , found 186.0.

IV. Synthesis and Characterization of Substituted 3,4-dihydro-2H-1,4-thiazine

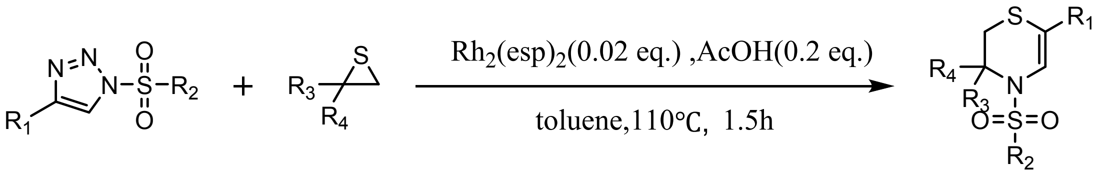
A, Conditions optimization for the reaction of 1-tosyl-1,2,3-triazole and 2-phenylthiirane.



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

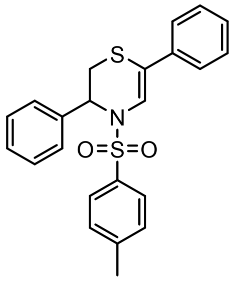
To a solution of 1-tosyl-1,2,3-triazole **1a** (0.5 mmol, 1 eq.) in 2mL toluene in a flame dried Schlenk tube was added dropwise 2-phenylthiirane **2a** (1 mmol, 2 eq.), additive and catalyst. Then the solution was evacuated three times with N_2 and stirred at 110 ℃until the total consumption of **1a** by TLC. After cooling to room temperature, solvent was removed in vacuum, the residue was purified by column chromatography on silica gel to give the product of **3aa**.

B, General Procedure for the synthesis of the Substituted 3,4-dihydro-2H-1,4-thiazine



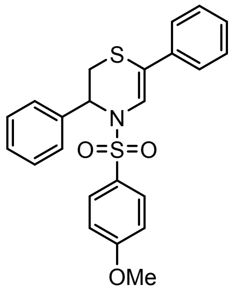
1 **2** **3**

To a solution of 1,2,3-triazole **1** (0.5 mmol, 1 eq.) in 2mL toluene in a flame dried Schlenk tube was added dropwise thiirane **2** (1 mmol, 2 eq.), AcOH (0.1 mmol, 0.2 eq.) and $Rh_2(esp)_2$ (0.01 mmol, 0.02 eq.). Then the solution was evacuated three times with N_2 and stirred for 1.5 h at 110 ℃. After cooling to room temperature, solvent was removed in vacuum, the residue was purified by column chromatography on silica gel to give the product of **3**.



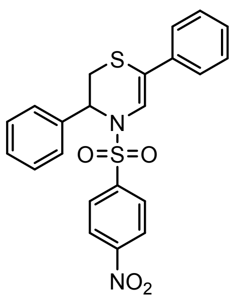
3aa

3aa: White solid, mp: 137 °C, (yield 85%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.56 (s, 1H), 7.49 – 7.46 (m, 2H), 7.37 – 7.19 (m, 10H), 5.58 (t, *J* = 3.0 Hz, 1H), 2.98 (dd, *J* = 13.1, 3.2 Hz, 1H), 2.63 (dd, *J* = 13.1, 3.2 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 139.0, 137.8, 135.2, 129.9, 128.6, 128.4, 127.8, 127.7, 127.1, 126.2, 126.0, 117.6, 115.7, 54.5, 31.1, 21.6. HRMS (ESI) *m/z* Calculated for $C_{23}H_{22}NO_2S_2^+$ $[M + H]^+$ 408.1086, found 408.1083.



3ba

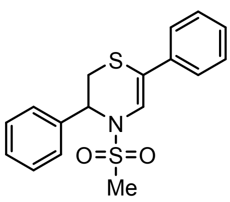
3ba: Light yellow solid, mp: 109 °C, (yield 93%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 – 7.63 (m, 2H), 7.56 (s, 1H), 7.49 – 7.45 (m, 2H), 7.37 – 7.19 (m, 8H), 6.92 – 6.87 (m, 2H), 5.57 (t, *J* = 3.0 Hz, 1H), 3.83 (s, 3H), 2.98 (dd, *J* = 13.1, 3.2 Hz, 1H), 2.66 (dd, *J* = 13.1, 3.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2, 139.0, 137.8, 129.7, 129.3, 128.6, 128.4, 127.8, 127.7, 126.2, 126.0, 117.6, 115.5, 114.4, 55.7, 54.4, 31.2. HRMS (ESI) *m/z* Calculated for $C_{23}H_{21}NNaO_3S_2^+$ $[M + Na]^+$ 446.0855, found 446.0852.



3ca

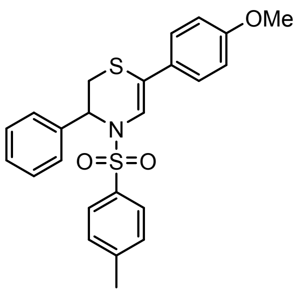
3ca: Brown solid, mp: 151 °C, (yield 31%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 – 8.19 (m, 2H), 7.84 – 7.79 (m, 2H), 7.50 – 7.46 (m, 3H), 7.40 – 7.32 (m, 3H), 7.25 –

7.18 (m, 3H), 7.16 – 7.12 (m, 2H), 5.67 (t, J = 3.1 Hz, 1H), 3.03 (dd, J = 13.2, 3.2 Hz, 1H), 2.91 (dd, J = 13.2, 3.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0, 143.8, 138.2, 137.3, 128.7, 128.4, 128.3, 128.2, 128.1, 126.3, 126.1, 124.3, 117.5, 116.6, 55.1, 31.8. HRMS (ESI) *m/z* Calculated for $C_{22}H_{18}N_2NaO_4S_2^+$ $[M + Na]^+$ 461.0600, found 461.0596.



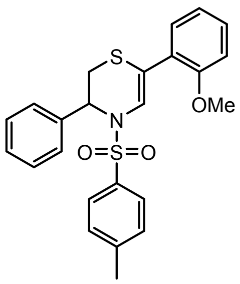
3da

3da: Yellow viscous oil, (yield 79%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, J = 1.5 Hz, 1H), 7.51 (s, 1H), 7.40 – 7.29 (m, 9H), 5.73 (t, J = 3.2 Hz, 1H), 3.31 (dd, J = 13.2, 3.3 Hz, 1H), 3.14 (dd, J = 13.2, 3.1 Hz, 1H), 2.80 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.4, 137.7, 128.7, 128.2, 127.8, 126.4, 126.0, 117.4, 114.5, 54.6, 40.4, 32.3. HRMS (ESI) *m/z* Calculated for $C_{17}H_{17}NNaO_2S_2^+$ $[M + Na]^+$ 354.0593, found 354.0592.



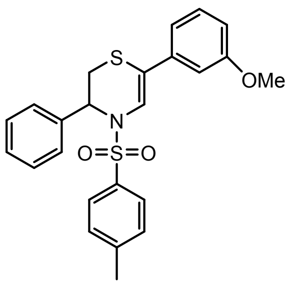
3ea

3ea: White solid, mp: 134 °C, (yield 73%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, J = 8.1 Hz, 2H), 7.44 (s, 1H), 7.42 – 7.37 (m, 2H), 7.28 – 7.21 (m, 7H), 6.89 – 6.86 (m, 2H), 5.56 (t, J = 3.0 Hz, 1H), 3.81 (s, 3H), 2.96 (dd, J = 13.1, 3.2 Hz, 1H), 2.62 (dd, J = 13.1, 3.2 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 144.1, 139.0, 135.1, 130.3, 129.9, 128.3, 127.6, 127.3, 127.1, 126.1, 116.3, 115.7, 114.0, 55.4, 54.3, 31.1, 21.6. HRMS (ESI) *m/z* Calculated for $C_{24}H_{24}NO_3S_2^+$ $[M + H]^+$ 438.1192, found 438.1184.



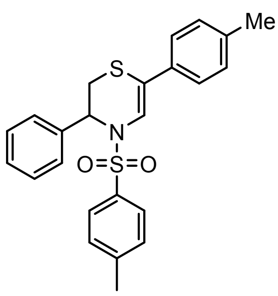
3fa

3fa: White solid, mp: 124 °C, (yield 33%): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.51 (s, 1H), 7.28 – 7.21 (m, 9H), 6.92 (t, *J* = 8.9 Hz, 2H), 5.56 (s, 1H), 3.85 (s, 3H), 2.88 (dd, *J* = 13.1, 2.9 Hz, 1H), 2.75 (dd, *J* = 13.0, 3.0 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.9, 143.8, 139.3, 135.6, 130.1, 129.7, 128.9, 128.2, 127.5, 127.2, 127.0, 126.7, 126.5, 120.6, 111.5, 111.0, 55.8, 54.3, 31.5, 21.6. HRMS (ESI) *m/z* Calculated for $C_{24}H_{24}NO_3S_2^+$ [M + H]$^+$ 438.1192, found 438.1189.



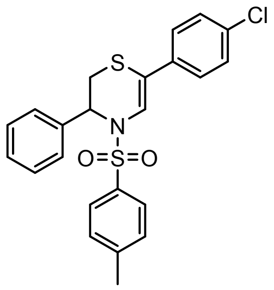
3ga

3ga: White solid, mp: 52 °C, (yield 64%): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.57 (s, 1H), 7.26 – 7.20 (m, 8H), 7.08 (d, *J* = 7.7 Hz, 1H), 7.01 (s, 1H), 6.83 (dd, *J* = 8.1, 1.9 Hz, 1H), 5.57 (s, 1H), 3.82 (s, 3H), 2.96 (dd, *J* = 13.1, 3.0 Hz, 1H), 2.64 (dd, *J* = 13.1, 3.0 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 159.8, 144.2, 139.3, 139.0, 135.1, 129.9, 129.6, 128.4, 127.7, 127.1, 126.1, 118.5, 117.7, 115.5, 113.2, 111.9, 55.4, 54.6, 31.1, 21.6. HRMS (ESI) *m/z* Calculated for $C_{24}H_{24}NO_3S_2^+$ [M + H]$^+$ 438.1192, found 438.1190.



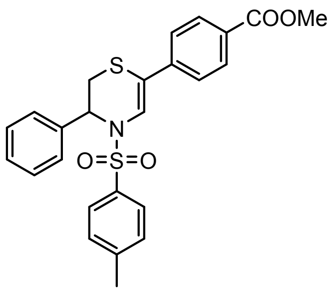
3ha

3ha: White solid, mp: 131 °C, (yield 72%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.52 (s, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.28 – 7.23 (m, 7H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.57 (t, *J* = 2.8 Hz, 1H), 2.96 (dd, *J* = 13.1, 3.2 Hz, 1H), 2.64 (dd, *J* = 13.1, 3.1 Hz, 1H), 2.40 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 139.0, 137.7, 135.2, 135.0, 129.9, 129.3, 128.4, 127.6, 127.1, 126.2, 125.9, 116.9, 115.9, 54.4, 31.1, 21.6, 21.1. HRMS (ESI) *m/z* Calculated for $C_{24}H_{23}NNaO_2S_2^+$ [M + Na]$^+$ 444.1062, found 444.1063.



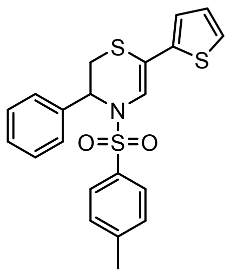
3ia

3ia: White solid, mp: 167 °C, (yield 81%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.53 (s, 1H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.31 – 7.23 (m, 7H), 7.20 – 7.18 (m, 2H), 5.58 (s, 1H), 2.98 (dd, *J* = 13.1, 3.1 Hz, 1H), 2.64 (dd, *J* = 13.1, 3.1 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 138.8, 136.3, 135.1, 133.5, 129.9, 128.7, 128.4, 127.7, 127.2, 127.1, 126.1, 117.9, 114.4, 54.5, 31.2, 21.6. HRMS (ESI) *m/z* Calculated for $C_{23}H_{21}ClNO_2S_2^+$ [M + H]$^+$ 442.0697, found 442.0692.



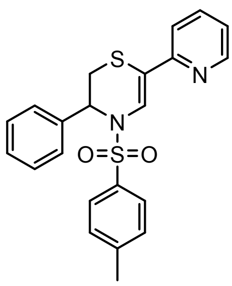
3ja

3ja: White solid, mp: 158 °C, (yield 83%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.69 (s, 1H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.29 – 7.22 (m, 5H), 7.19 – 7.16 (m, 2H), 5.60 (t, *J* = 2.8 Hz, 1H), 3.91 (s, 3H), 3.00 (dd, *J* = 13.1, 3.1 Hz, 1H), 2.66 (dd, *J* = 13.1, 3.1 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 144.4, 142.3, 138.8, 135.0, 130.0, 129.9, 129.1, 128.4, 127.8, 127.1, 126.1, 125.6, 119.3, 114.2, 54.7, 52.2, 31.2, 21.6. HRMS (ESI) *m/z* Calculated for $C_{25}H_{24}NO_4S_2^+$ [M + H]$^+$ 466.1141, found 466.1143.



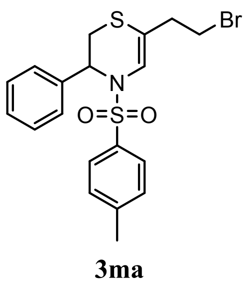
3ka

3ka: Brown solid, mp: 137 °C, (yield 89%):. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.3 Hz, 2H), 7.33 – 7.27 (m, 5H), 7.11 (d, J = 6.9 Hz, 2H), 6.97 (d, J = 5.2 Hz, 1H), 6.86 (d, J = 10.9 Hz, 1H), 6.54 (d, J = 10.7 Hz, 1H), 6.46 (d, J = 5.2 Hz, 1H), 4.31 (dd, J = 7.6, 4.2 Hz, 1H), 3.14 (dd, J = 13.0, 4.2 Hz, 1H), 2.97 (dd, J = 13.0, 7.7 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 142.3, 137.8, 137.0, 132.3, 130.0, 129.1, 128.6, 128.4, 127.3, 126.8, 121.5, 117.2, 110.4, 44.1, 34.9, 21.6. HRMS (ESI) *m/z* Calculated for $C_{21}H_{19}NNaO_2S_3^+$ $[M + Na]^+$ 436.0470, found 436.0472.



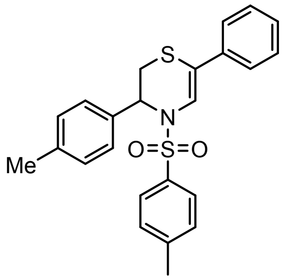
3la

3la: Light yellow solid, mp: 132 °C, (yield 62%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 4.7 Hz, 1H), 8.28 (s, 1H), 7.66 – 7.61 (m, 3H), 7.48 (d, J = 8.1 Hz, 1H), 7.20 (m, 7H), 7.13 (dd, J = 7.3, 5.0 Hz, 1H), 5.61 (t, J = 2.9 Hz, 1H), 3.00 (dd, J = 13.2, 3.1 Hz, 1H), 2.71 (dd, J = 13.2, 3.2 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 149.1, 144.2, 138.9, 136.4, 135.2, 129.9, 128.3, 127.7, 127.2, 126.2, 121.8, 120.9, 118.4, 114.4, 55.0, 30.9, 21.6. HRMS (ESI) *m/z* Calculated for $C_{22}H_{21}N_2O_2S_2^+$ $[M + H]^+$ 409.1039, found 409.1040.



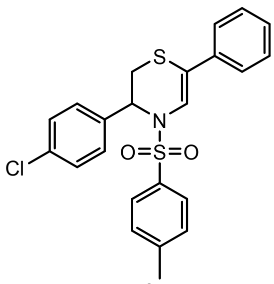
3ma

3ma: Yellow viscous oil, (yield 24%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.1 Hz, 2H), 7.31 – 7.23 (m, 5H), 7.19 – 7.18 (m, 2H), 7.11 (s, 1H), 5.45 (s, 1H), 3.47 – 3.44 (m, 2H), 2.85 (dd, J = 13.1, 3.0 Hz, 1H), 2.68 (t, J = 6.7 Hz, 2H), 2.47 (dd, J = 13.0, 2.7 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 138.7, 135.1, 129.8, 128.3, 127.6, 127.2, 126.1, 118.3, 112.4, 53.9, 38.8, 32.0, 30.1, 21.6. HRMS (ESI) *m/z* Calculated for $C_{19}H_{21}BrNO_2S_2^+$ $[M + H]^+$ 438.0192, found 438.0190.



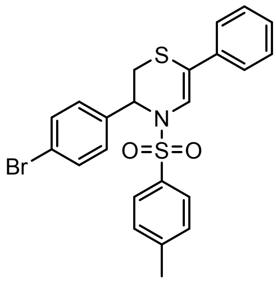
3ab

3ab: White solid, mp: 51 °C, (yield 88%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 – 7.60 (m, 2H), 7.55 (s, 1H), 7.49 – 7.45 (m, 2H), 7.36 – 7.23 (m, 5H), 7.12 – 7.05 (m, 4H), 5.53 (t, J = 3.0 Hz, 1H), 2.95 (dd, J = 13.1, 3.2 Hz, 1H), 2.60 (dd, J = 13.1, 3.2 Hz, 1H), 2.40 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1, 137.8, 137.4, 136.0, 135.1, 129.9, 129.1, 128.6, 127.8, 127.1, 126.03, 126.02, 117.6, 115.7, 54.3, 31.1, 21.6, 21.1. HRMS (ESI) *m/z* Calculated for $C_{24}H_{24}NO_2S_2^+$ $[M + H]^+$ 422.1243, found 422.1238.



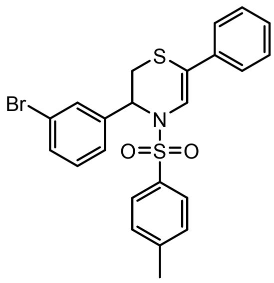
3ac

3ac: White solid, mp: 55 °C, (yield 97%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.2 Hz, 2H), 7.55 (s, 1H), 7.48 (d, J = 7.3 Hz, 2H), 7.36 (t, J = 7.4 Hz, 2H), 7.31 (d, J = 7.1 Hz, 1H), 7.27 – 7.23 (m, 4H), 7.16 (d, J = 8.5 Hz, 2H), 5.55 (s, 1H), 2.95 (dd, J = 13.2, 3.1 Hz, 1H), 2.65 (dd, J = 13.2, 3.1 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 137.6, 137.5, 135.0, 133.6, 130.0, 128.7, 128.5, 128.0, 127.7, 127.1, 126.0, 117.4, 115.8, 54.0, 30.9, 21.6. HRMS (ESI) *m/z* Calculated for $C_{23}H_{21}ClNO_2S_2^+$ $[M + H]^+$ 442.0697, found 442.0694.



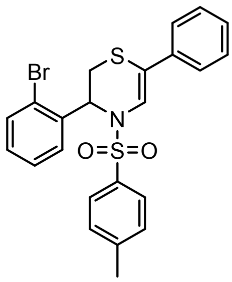
3ad

3ad: White solid, mp: 80 °C, (yield 85%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.53 (s, 1H), 7.46 (d, *J* = 7.3 Hz, 2H), 7.38 – 7.24 (m, 7H), 7.09 (d, *J* = 8.4 Hz, 2H), 5.52 (s, 1H), 2.93 (dd, *J* = 13.2, 3.1 Hz, 1H), 2.65 (dd, *J* = 13.2, 3.1 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 138.1, 137.6, 135.0, 131.5, 130.0, 128.7, 128.0, 127.9, 127.1, 126.0, 121.7, 117.4, 115.7, 54.0, 30.9, 21.6. HRMS (ESI) *m/z* Calculated for $C_{23}H_{21}BrNO_2S_2^+$ $[M + H]^+$ 486.0192, found 486.0194.



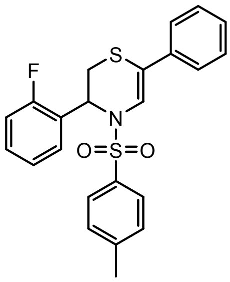
3ae

3ae: White solid, mp: 151 °C, (yield 76%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.53 (s, 1H), 7.47 (d, *J* = 7.4 Hz, 2H), 7.39 – 7.35 (m, 3H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.25 (dd, *J* = 7.9, 6.2 Hz, 3H), 7.17 – 7.11 (m, 2H), 5.55 (s, 1H), 2.95 (dd, *J* = 13.2, 3.1 Hz, 1H), 2.66 (dd, *J* = 13.2, 3.1 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 141.1, 137.6, 136.0, 130.8, 130.0, 129.9, 129.3, 128.7, 127.9, 126.9, 126.1, 125.0, 122.5, 117.4, 115.8, 54.0, 31.0, 21.6. HRMS (ESI) *m/z* Calculated for $C_{23}H_{21}BrNO_2S_2^+$ $[M + H]^+$ 486.0192, found 486.0189.



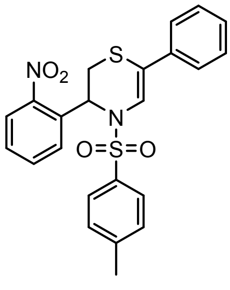
3af

3af: White solid, mp: 161 °C, (yield 33%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 5.4 Hz, 2H), 7.64 (s, 1H), 7.52 (t, J = 8.0 Hz, 3H), 7.36 (t, J = 7.6 Hz, 2H), 7.29 (t, J = 7.3 Hz, 1H), 7.26 – 7.23 (m, 2H), 7.13 – 7.08 (m, 3H), 5.87 (t, J = 3.0 Hz, 1H), 3.10 (dd, J = 13.3, 2.9 Hz, 1H), 2.59 (dd, J = 13.3, 3.4 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.3, 138.2, 137.6, 134.7, 132.5, 130.0, 129.3, 129.1, 128.7, 127.8, 127.3, 127.2, 126.0, 120.8, 118.3, 114.4, 54.9, 29.5, 21.6. HRMS (ESI) *m/z* Calculated for $C_{23}H_{21}BrNO_2S_2^+$ $[M + H]^+$ 486.0192, found 486.0191.



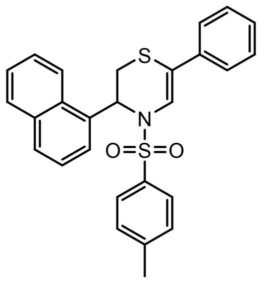
3ag

3ag: Brown solid, mp: 167 °C, (yield 44%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.1 Hz, 2H), 7.62 (s, 1H), 7.50 (d, J = 7.5 Hz, 2H), 7.36 (t, J = 7.4 Hz, 2H), 7.31 – 7.16 (m, 5H), 7.05 – 6.99 (m, 2H), 5.82 (s, 1H), 3.06 (dd, J = 13.2, 3.0 Hz, 1H), 2.53 (dd, J = 13.2, 3.0 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 137.7, 134.8, 130.1, 129.5, 129.4, 128.8 (d, J_{CF} =3 Hz), 128.7, 127.9, 127.2, 126.1, 124.1 (d, J_{CF} =3 Hz), 117.7, 115.5, 115.3, 115.0, 49.8, 30.1, 21.6. HRMS (ESI) *m/z* Calculated for $C_{23}H_{20}FNNaO_2S_2^+$ $[M + Na]^+$ 448.0812, found 448.0805.



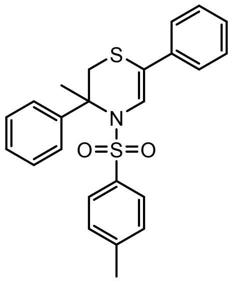
3ah

3ah: Light yellow solid, mp: 49 °C, (yield 38%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (dd, J = 7.4, 2.4 Hz, 1H), 7.71 (s, 1H), 7.66 – 7.63 (m, 2H), 7.57 – 7.51 (m, 3H), 7.47 – 7.39 (m, 4H), 7.37 – 7.32 (m, 3H), 6.27 (t, J = 3.1 Hz, 1H), 3.11 (dd, J = 13.6, 2.7 Hz, 1H), 2.62 (dd, J = 13.6, 3.7 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 144.6, 137.4, 135.2, 134.3, 133.6, 130.3, 130.2, 128.8, 128.2, 128.0, 127.2, 126.0, 124.9, 118.5, 115.0, 51.7, 30.4, 21.6. HRMS (ESI) *m/z* Calculated for $C_{23}H_{21}N_2O_4S_2^+$ $[M + H]^+$ 453.0937, found 453.0939.



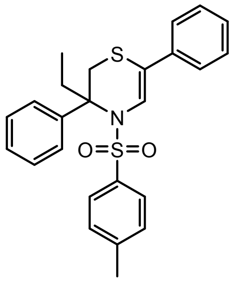
3ai

3ai: White solid, mp: 129 °C, (yield 83%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.62 – 7.48 (m, 6H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.20 (m, 5H), 6.38 (s, 1H), 3.12 (dd, *J* = 13.0, 2.8 Hz, 1H), 2.82 (dd, *J* = 13.0, 3.3 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 137.8, 135.2, 133.8, 133.7, 129.9, 129.5, 128.9, 128.7, 128.4, 127.7, 127.2, 126.7, 126.0, 125.5, 125.2, 125.1, 121.6, 118.4, 114.1, 52.0, 30.9, 21.6. HRMS (ESI) *m/z* Calculated for $C_{27}H_{24}NO_2S_2^+$ $[M + H]^+$ 458.1243, found 458.1241.



3aj

3aj: Light yellow viscous oil, (yield 49%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.7 Hz, 3H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 7.9 Hz, 2H), 7.35 – 7.31 (m, 3H), 7.29 – 7.25 (m, 5H), 3.17 (d, *J* = 13.5 Hz, 1H), 2.84 (d, *J* = 13.5 Hz, 1H), 2.42 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 143.6, 138.7, 137.8, 129.7, 128.6, 128.3, 127.7, 127.4, 127.0, 126.0, 125.7, 122.1, 115.9, 63.6, 42.4, 26.8, 21.6. HRMS (ESI) *m/z* Calculated for $C_{24}H_{24}NO_2S_2^+$ $[M + H]^+$ 422.1243, found 422.1239.



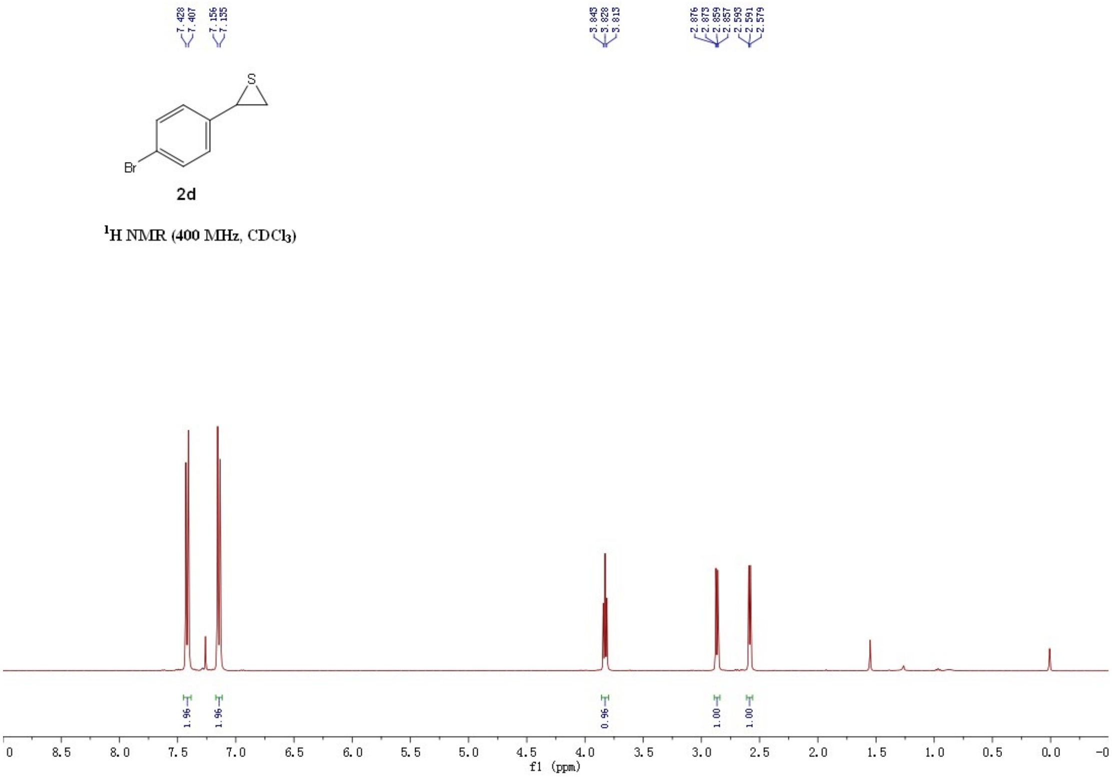
3ak

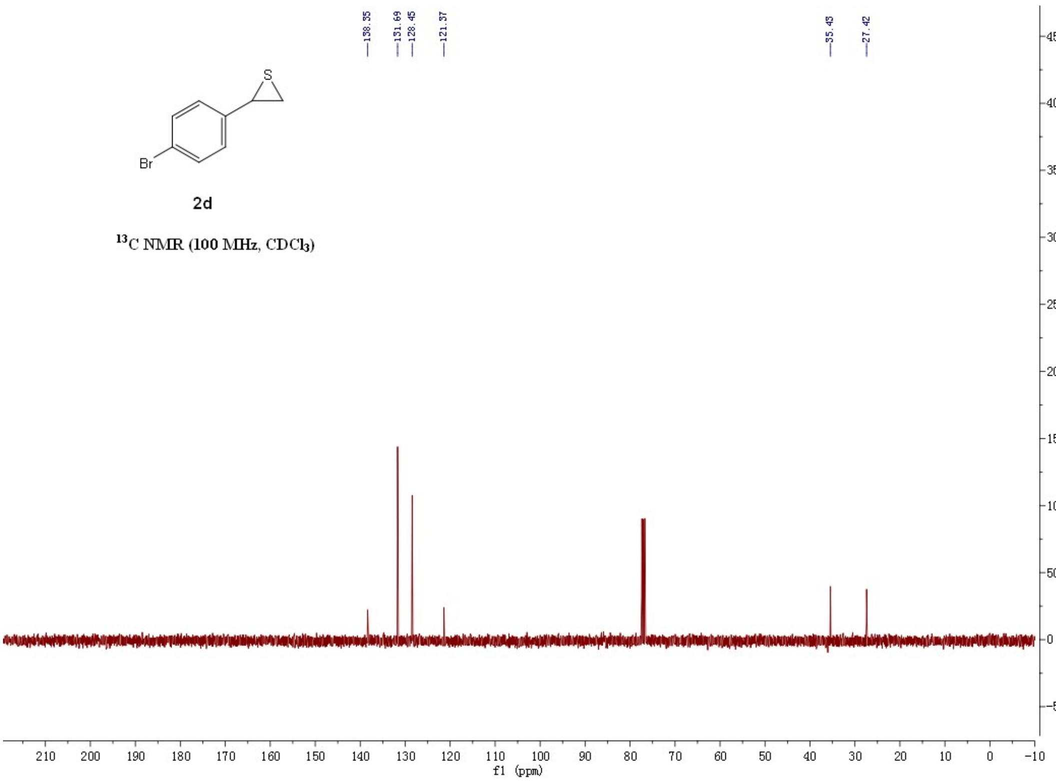
3ak: White solid, mp: 127 °C, (yield 38%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.46 – 7.40(m, 3H), 7.37 – 7.35 (m,1H), 7.33 – 7.28 (m, 4H), 7.27 – 7.24 (m, 1H), 7.22 – 7.15 (m, 5H), 3.20 (d, J = 13.6 Hz, 1H), 3.01 (d, J = 13.6 Hz, 1H), 2.80 – 2.68 (m, 1H), 2.55 – 2.42 (m, 1H), 2.40 (s, 3H), 0.97 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4, 140.0, 138.4, 137.8, 129.4, 128.6, 127.7, 127.6, 127.5, 127.1, 125.9, 122.2, 116.7, 66.3, 36.9, 30.5, 21.6, 8.9. HRMS (ESI) *m/z* Calculated for $C_{25}H_{25}NNaO_2S_2^+$ $[M + Na]^+$ 458.1219, found 458.1219.

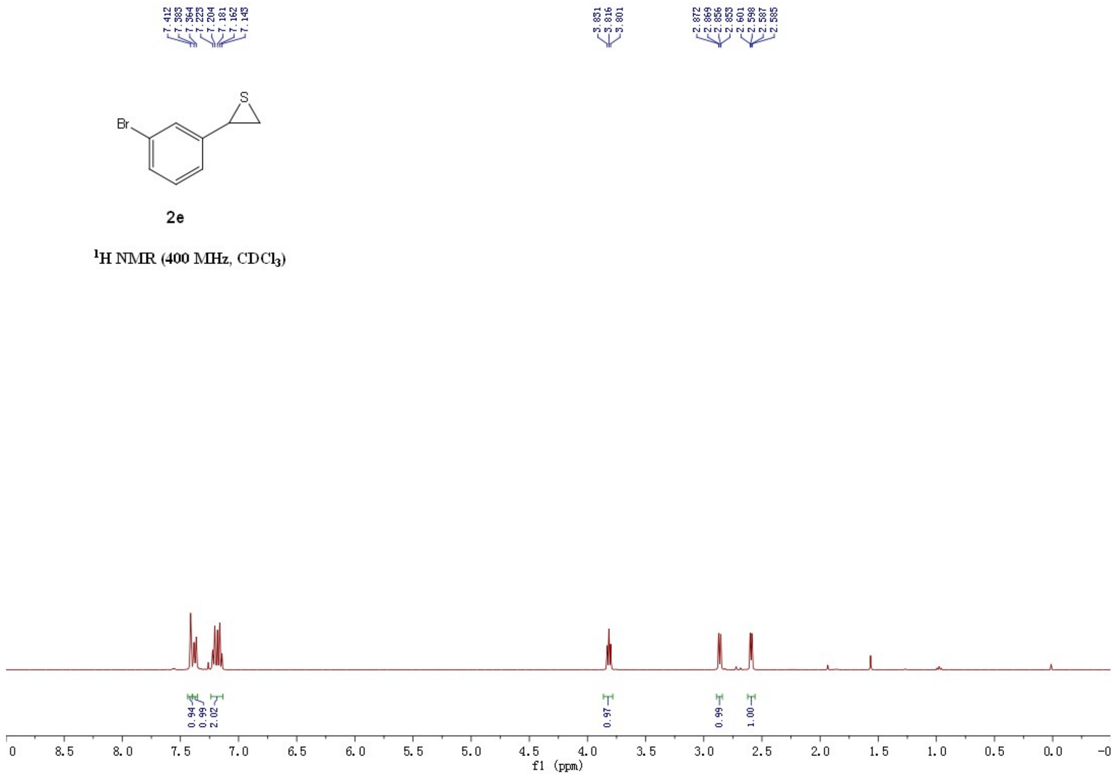
References.

1. (a) Jun He, Zeng-ming Man, Yin-ping Shi, Chuan-Ying Li. *J. Org. Chem*. 2015, 80, 4816−4823. (b) Rui-Qiao Ran, Shi-Dong Xiu, and Chuan-Ying Li. *Org. Lett*. 2014, 16, 6394−6396. (c) Forian Medina, Céline Besnard, Jérôme Lacour. *Org. Lett*. 2014, 16, 3232−3235. (d) Kai Wang, Xi-he Bi, Shuang-xi Xing, Pei-qiu Liao, Zhong-xue Fang, Xian-yu Meng, Qian Zhang, Qun Liu, Yu Ji. *Green Chem*. 2011, 13, 562-565.
2. Xue-ji Ma, Shan-fei Pan, Hang-xiang Wang, Wan-zhi Chen. *Org. Lett*. 2014, 16, 4554-4557.
3. (a)Hashem Sharghi, Alireza Salimi Beni, Reza Khalifeh. *Helvetica Chimica Acta*. 2007, 90, 1373-1385. (b) Hao Yu, Shengli Cao, Lei-lei Zhang ,Gang Liu, Jia-xi Xu. *Synthesis.* 2009, 13, 2205 - 2209.(c) Batool Akhlaghinia, Mohammad Rahimizadeh, Hosein Eshghi, Sara Zhaleh, Soodabeh Rezazadeh. *Journal of Sulfur Chemistry.* 2012, 33(3), 351-361.

NMR Spectra of compounds

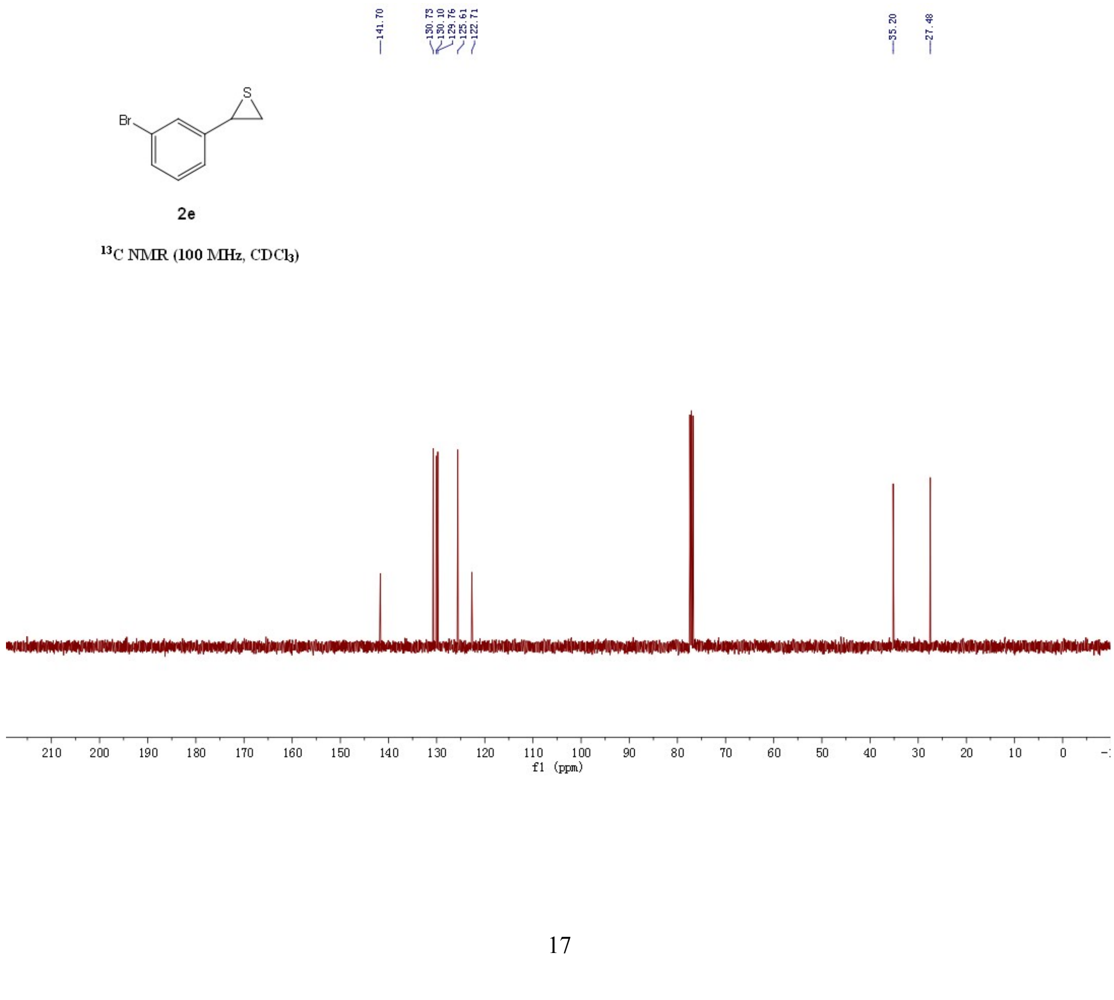






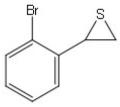
2e

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



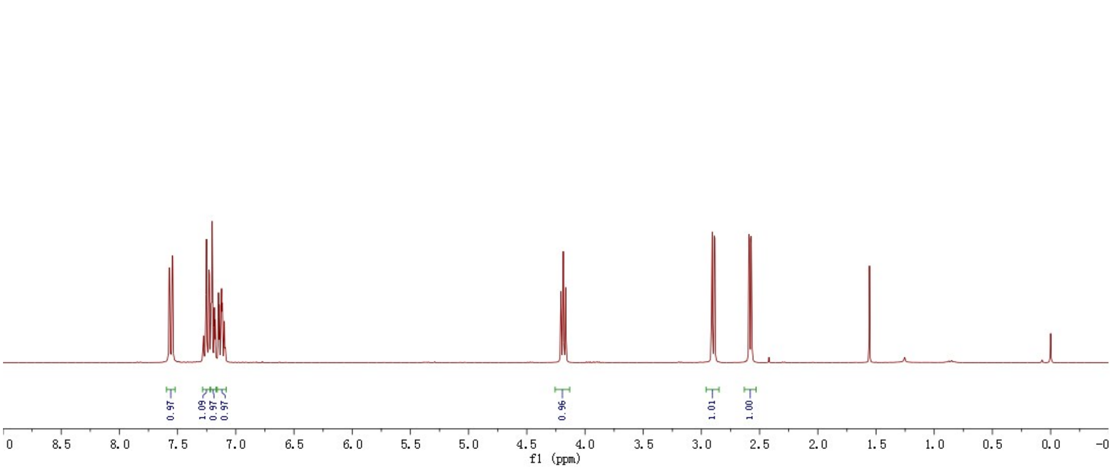
2e

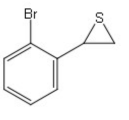
^{13}C NMR (100 MHz, $CDCl_3$)



2f

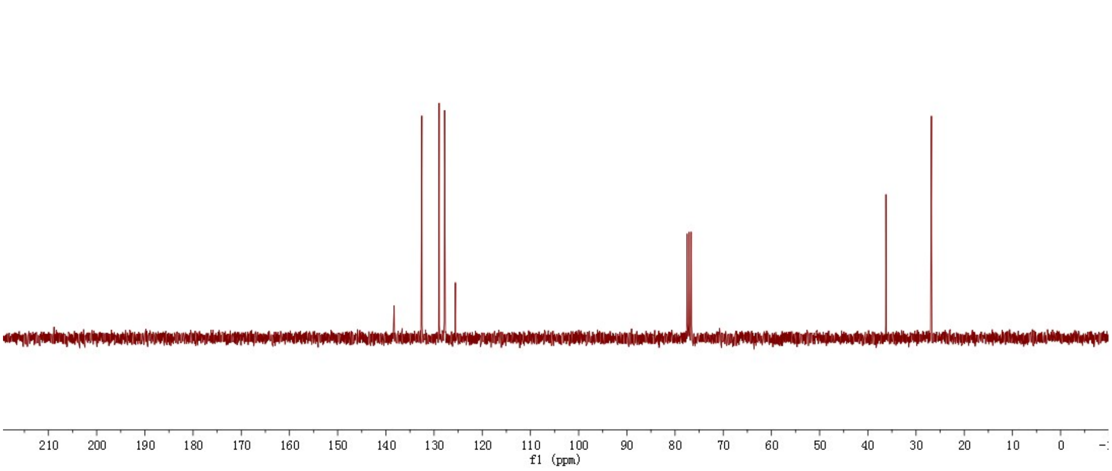
^{1}H NMR (300 MHz, CDCl$_3$)

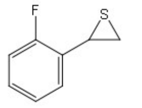




2f

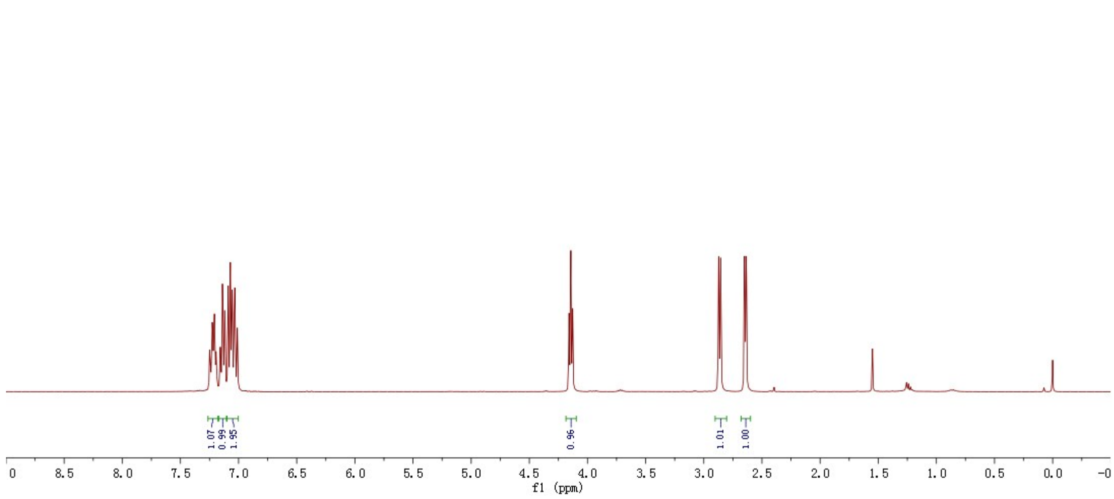
^{13}C NMR (75 MHz, CDCl$_3$)

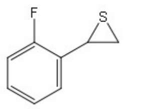




2g

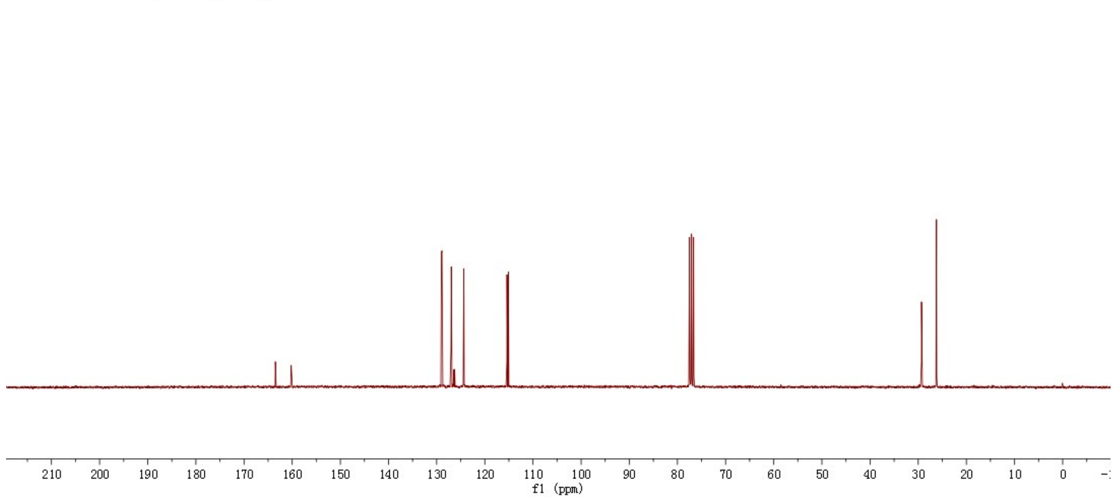
^{1}H NMR (400 MHz, CDCl$_3$)

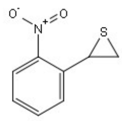




2g

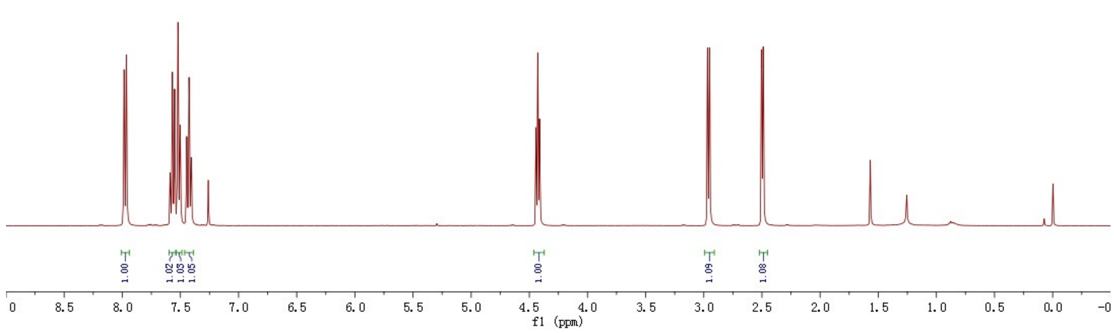
^{13}C NMR (75 MHz, CDCl$_3$)

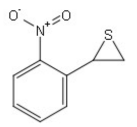




2h

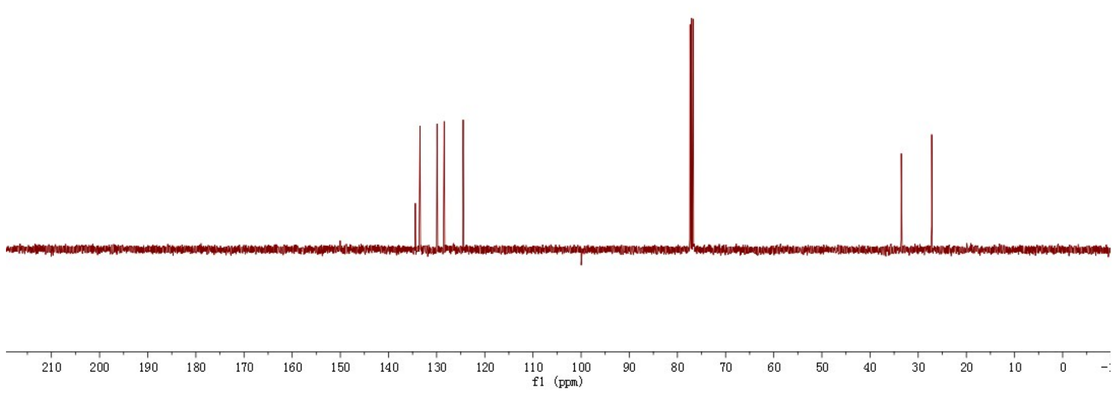
^{1}H NMR (400 MHz, $CDCl_3$)

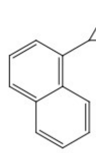




2h

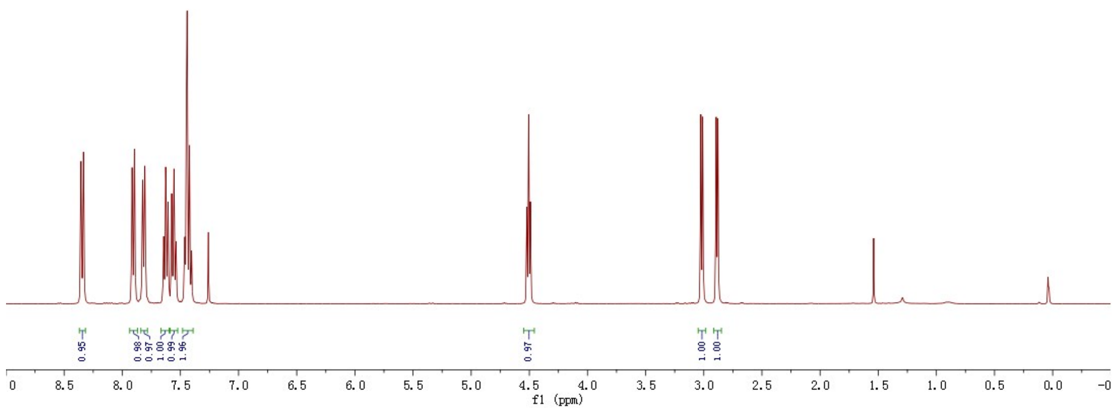
^{13}C NMR (100 MHz, $CDCl_3$)

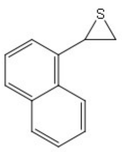




2i

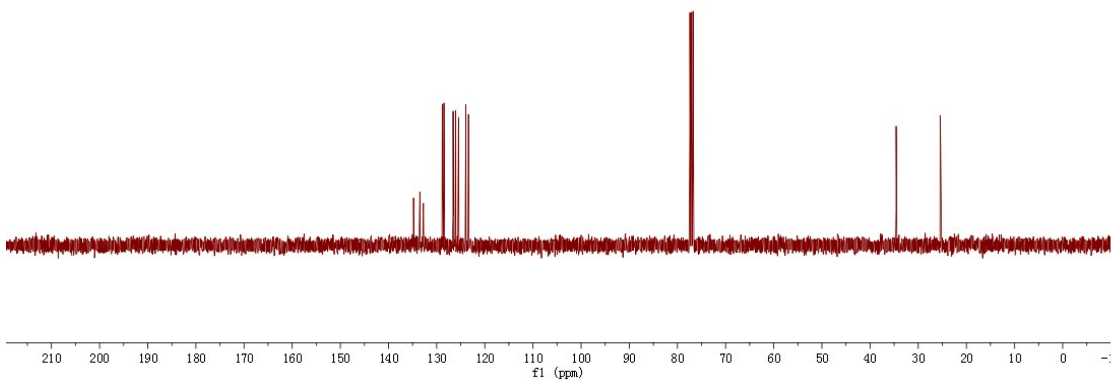
^{1}H NMR (400 MHz, $CDCl_3$)

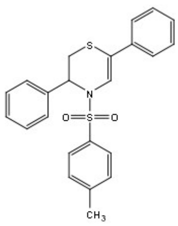




2i

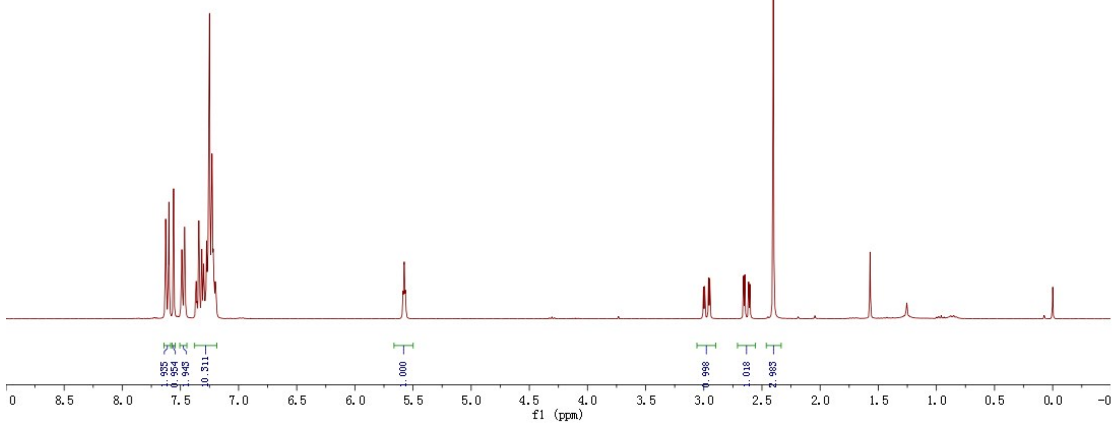
^{13}C NMR (100 MHz, $CDCl_3$)

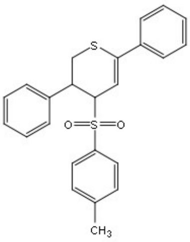




3aa

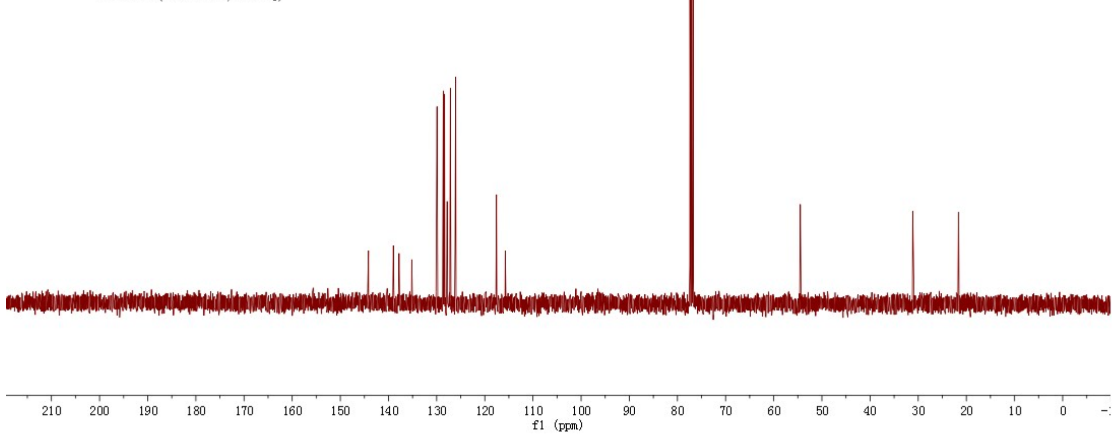
^{1}H NMR (300 MHz, $CDCl_3$)

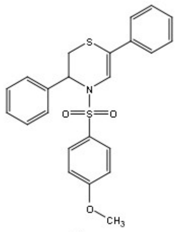




3aa

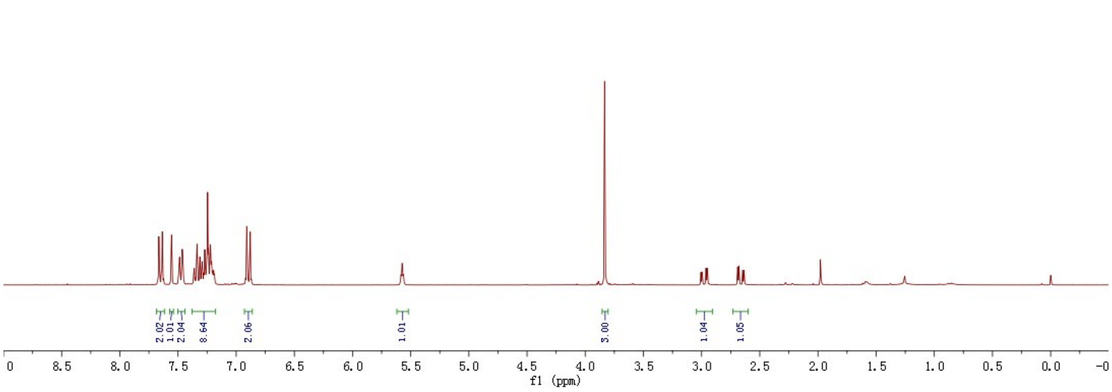
^{13}C NMR (100 MHz, $CDCl_3$)

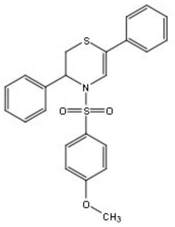




3ba

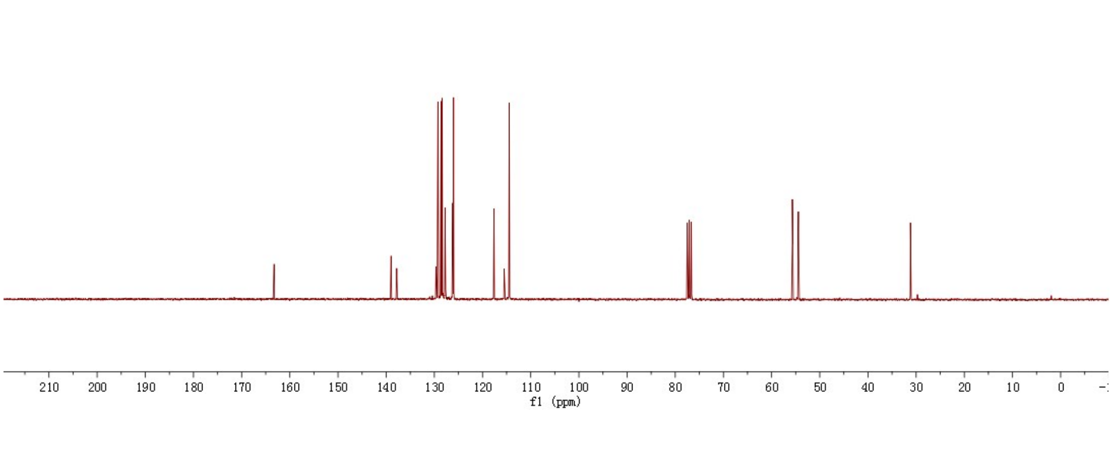
^{1}H NMR (300 MHz, $CDCl_3$)

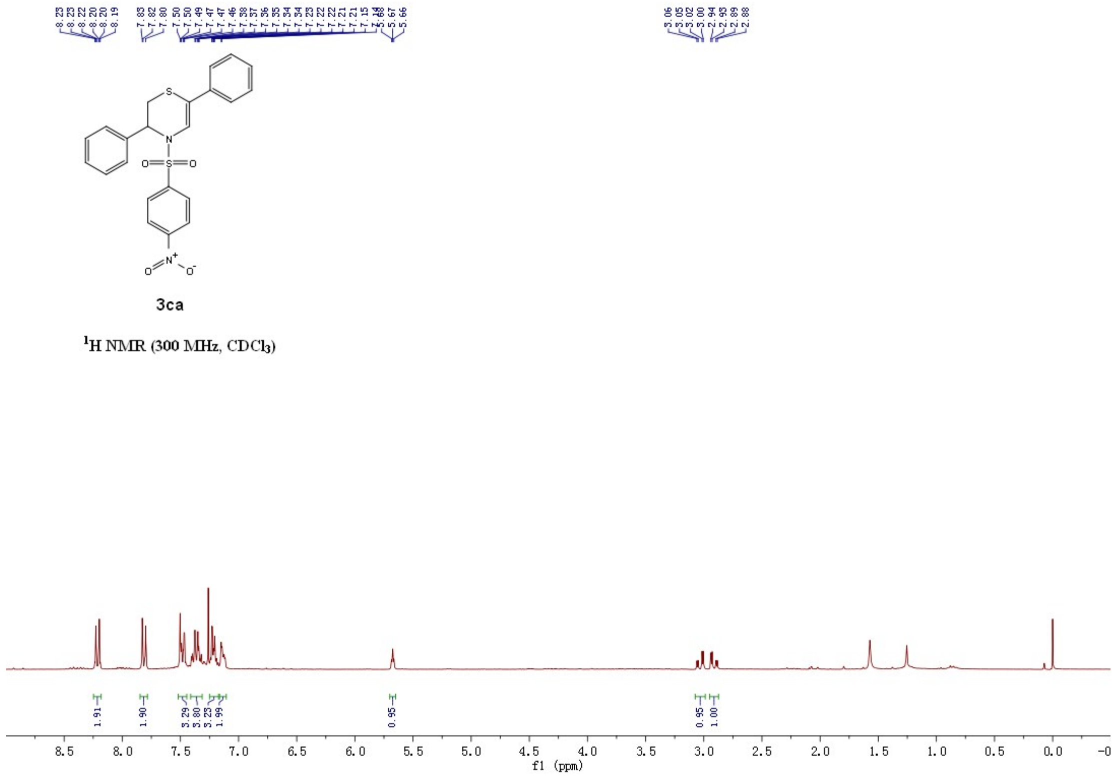




3ba

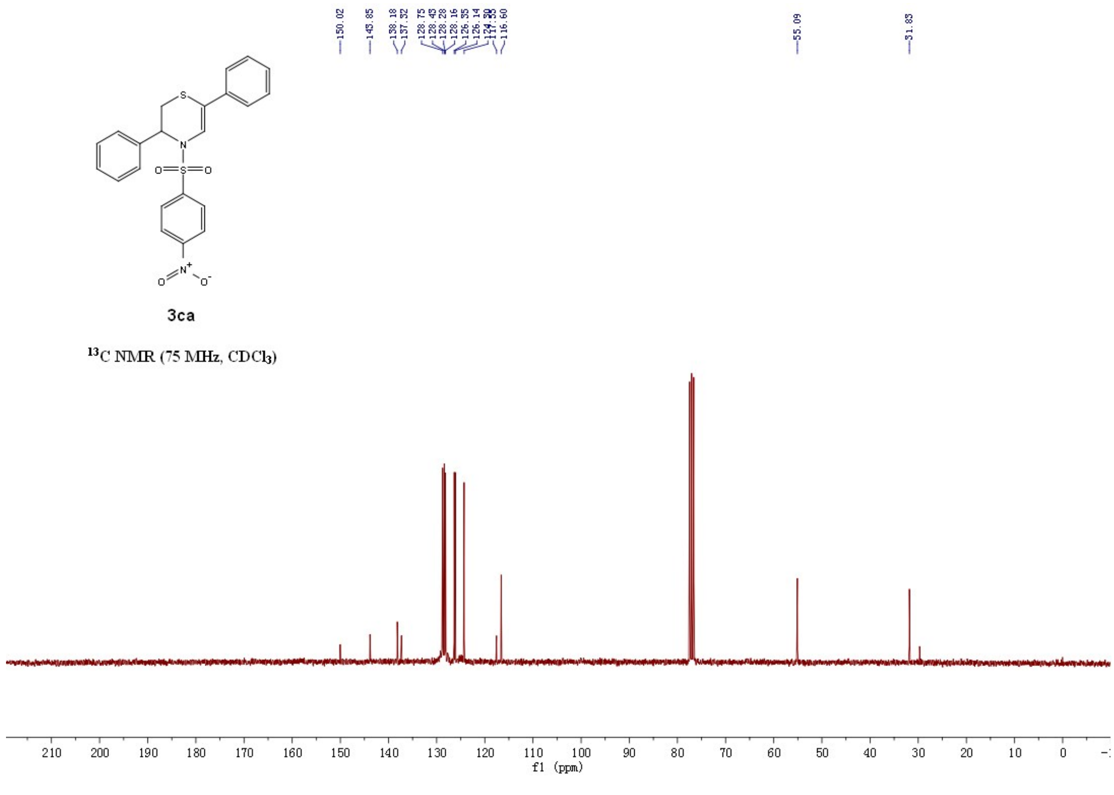
^{13}C NMR (75 MHz, $CDCl_3$)





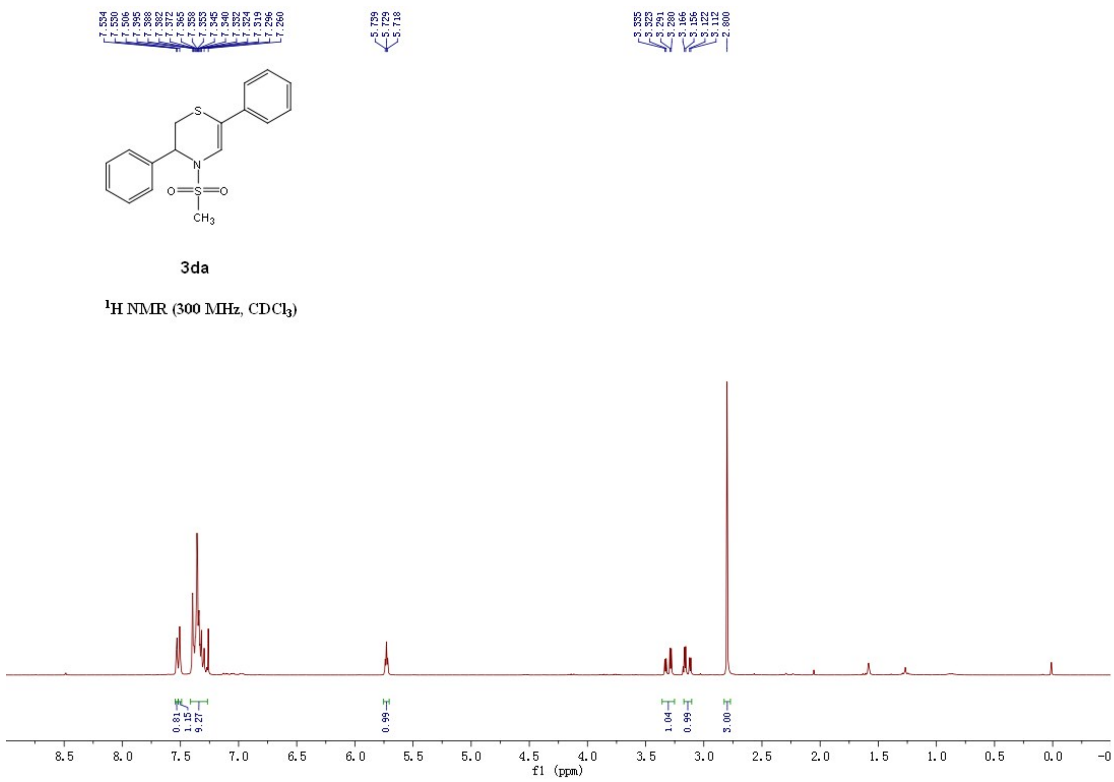
3ca

^{1}H NMR (300 MHz, CDCl$_3$)



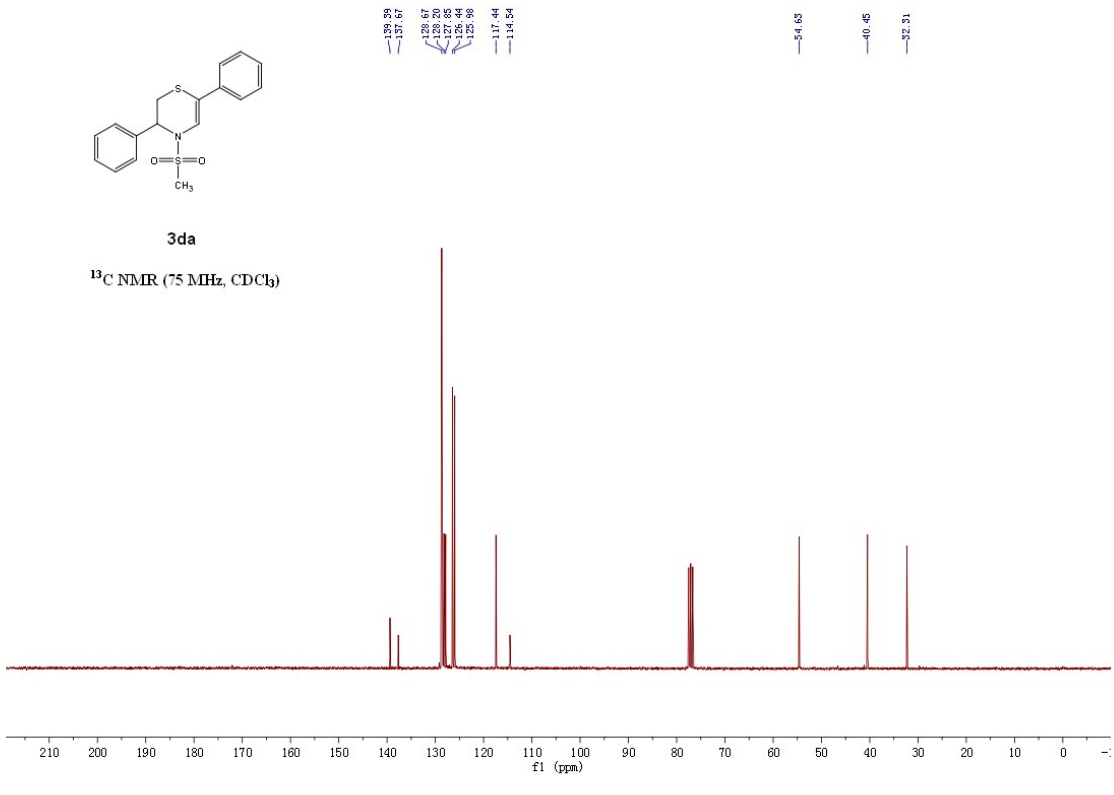
3ca

^{13}C NMR (75 MHz, CDCl$_3$)



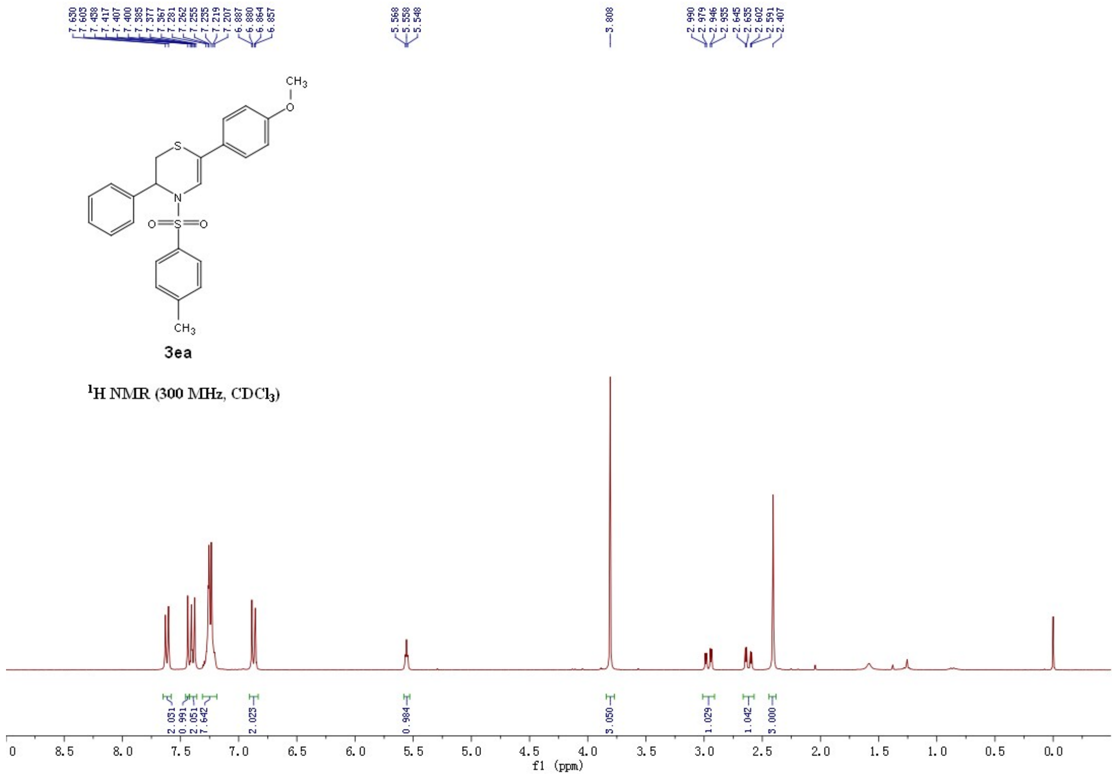
3da

^{1}H NMR (300 MHz, $CDCl_3$)



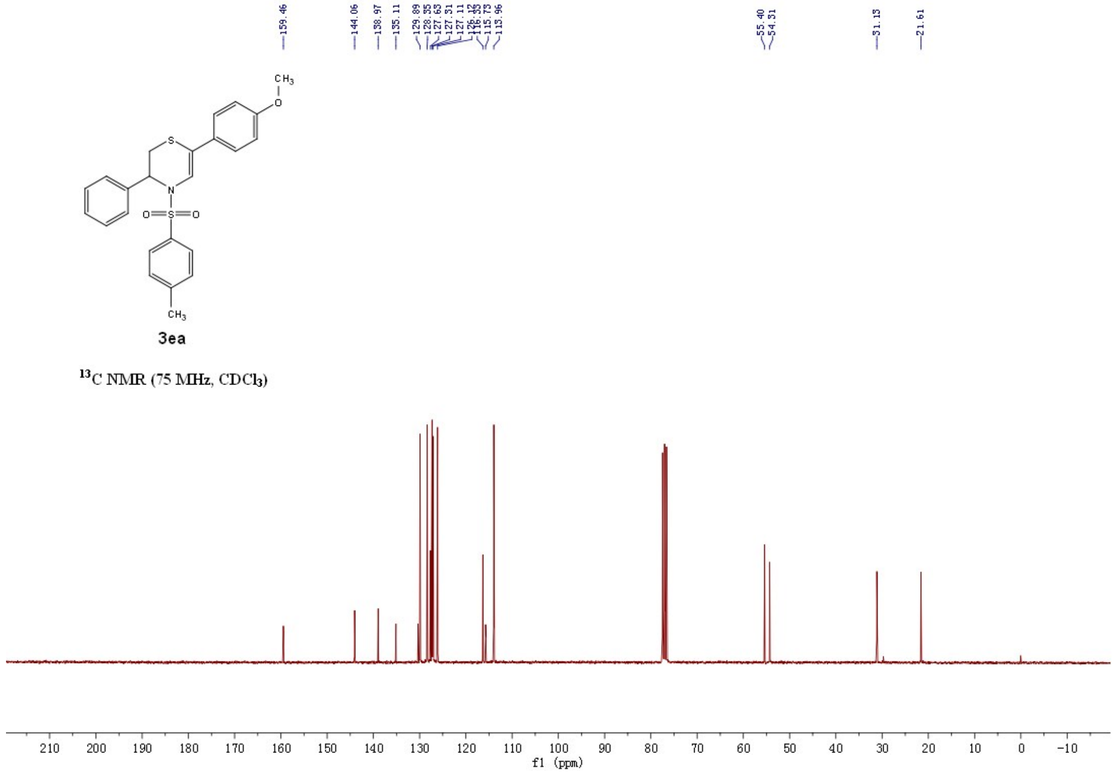
3da

^{13}C NMR (75 MHz, $CDCl_3$)



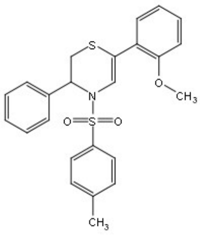
3ea

^{1}H NMR (300 MHz, $CDCl_3$)



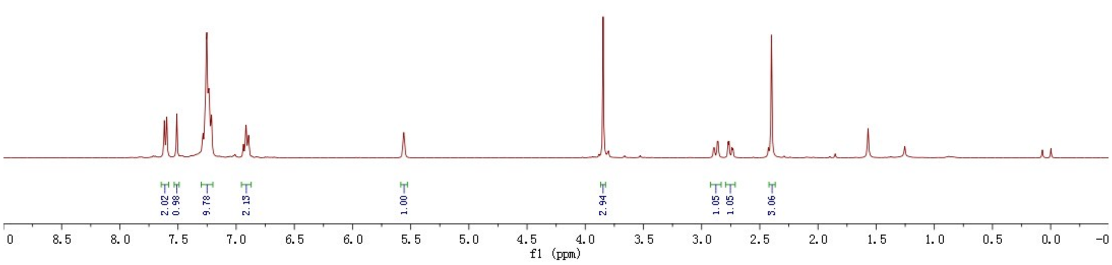
3ea

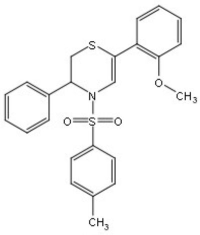
^{13}C NMR (75 MHz, $CDCl_3$)



3fa

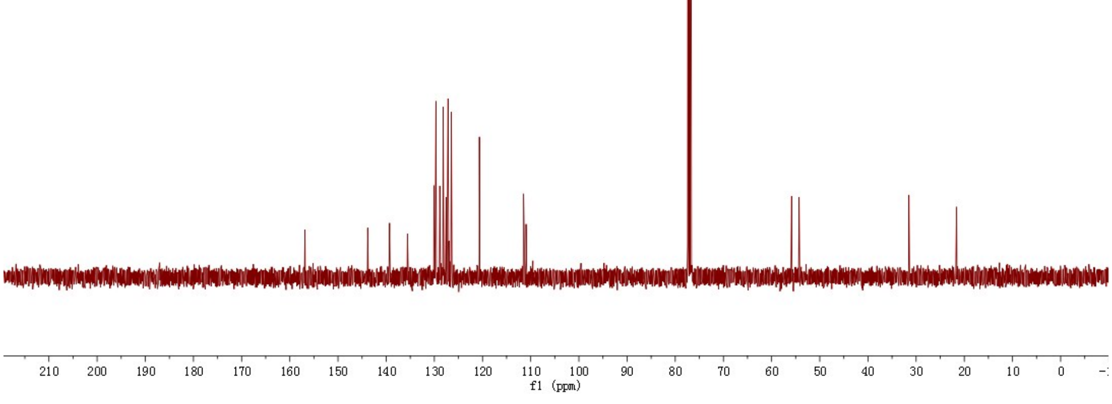
^{1}H NMR (400 MHz, $CDCl_3$)

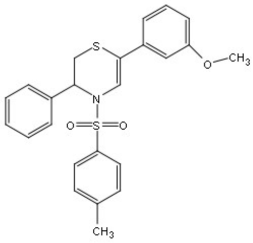




3fa

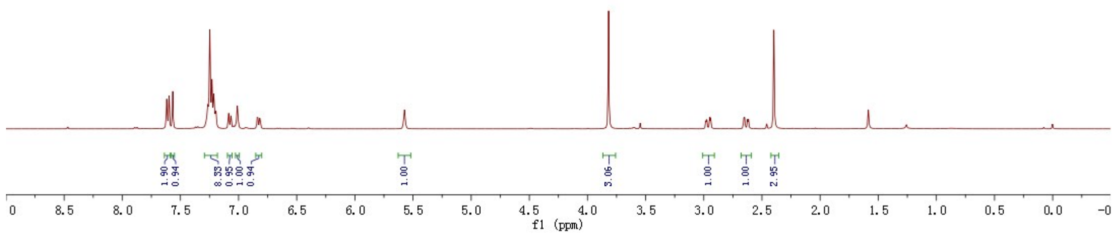
^{13}C NMR (100 MHz, $CDCl_3$)

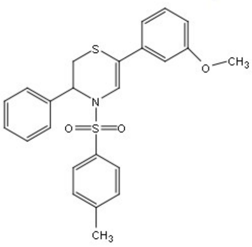




3ga

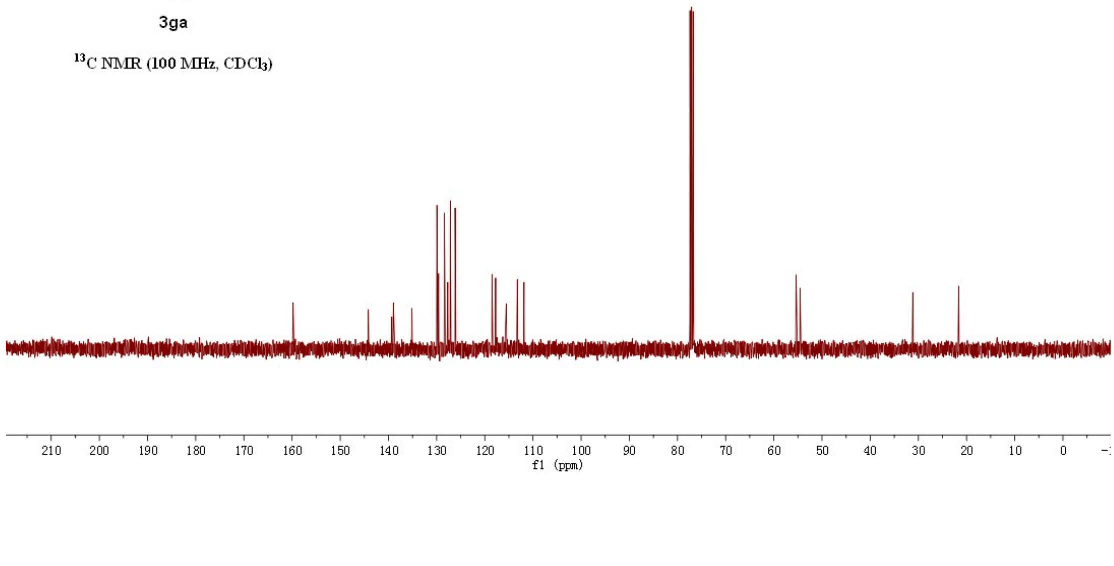
^{1}H NMR (400 MHz, CDCl$_3$)

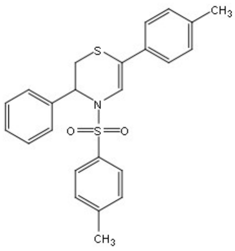




3ga

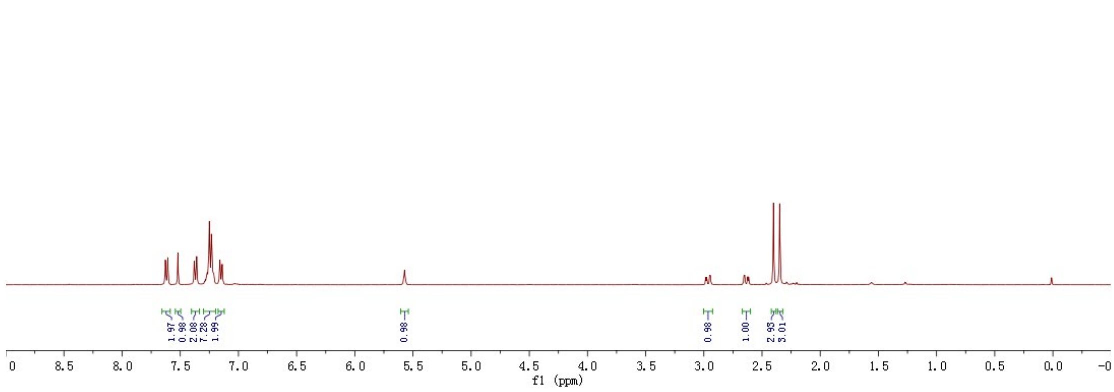
^{13}C NMR (100 MHz, CDCl$_3$)

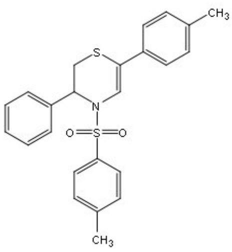




3ha

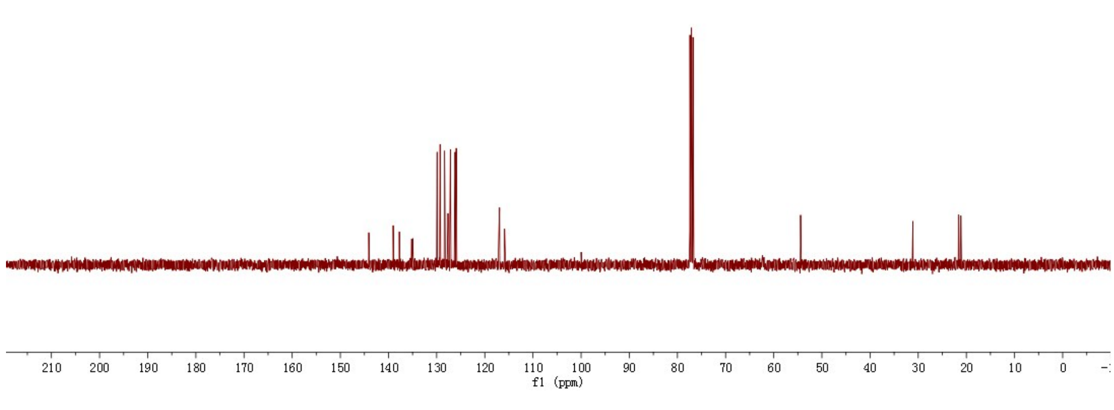
^{1}H NMR (400 MHz, $CDCl_3$)

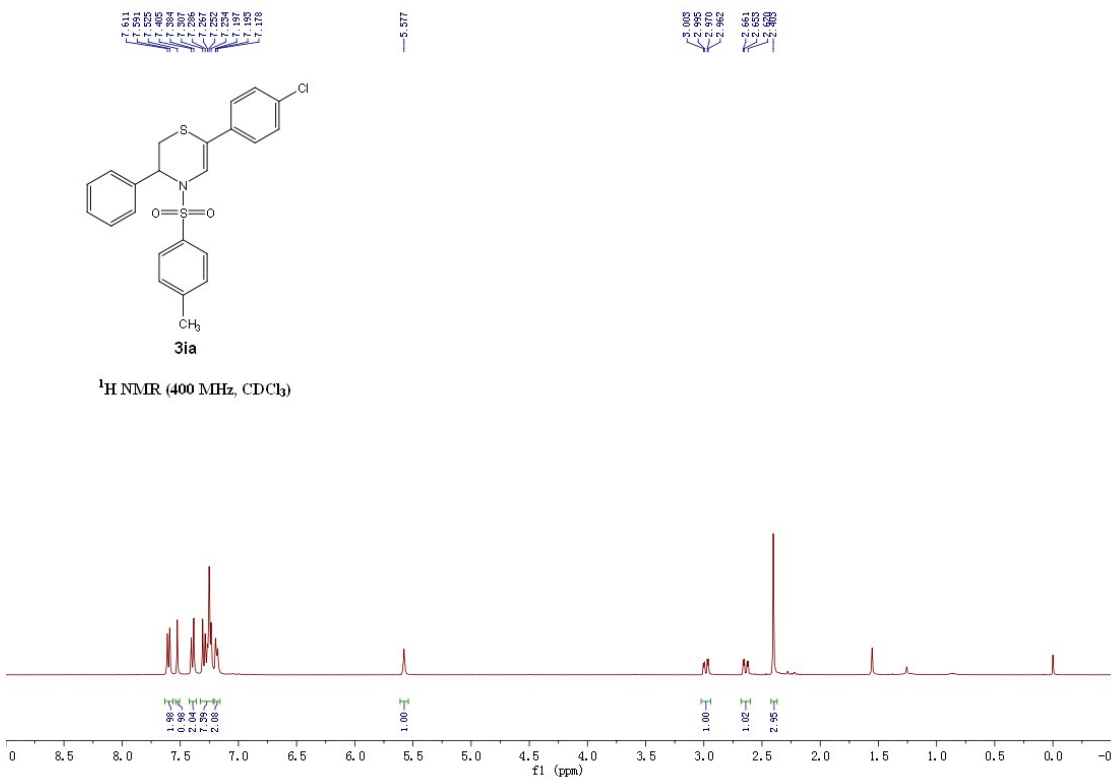




3ha

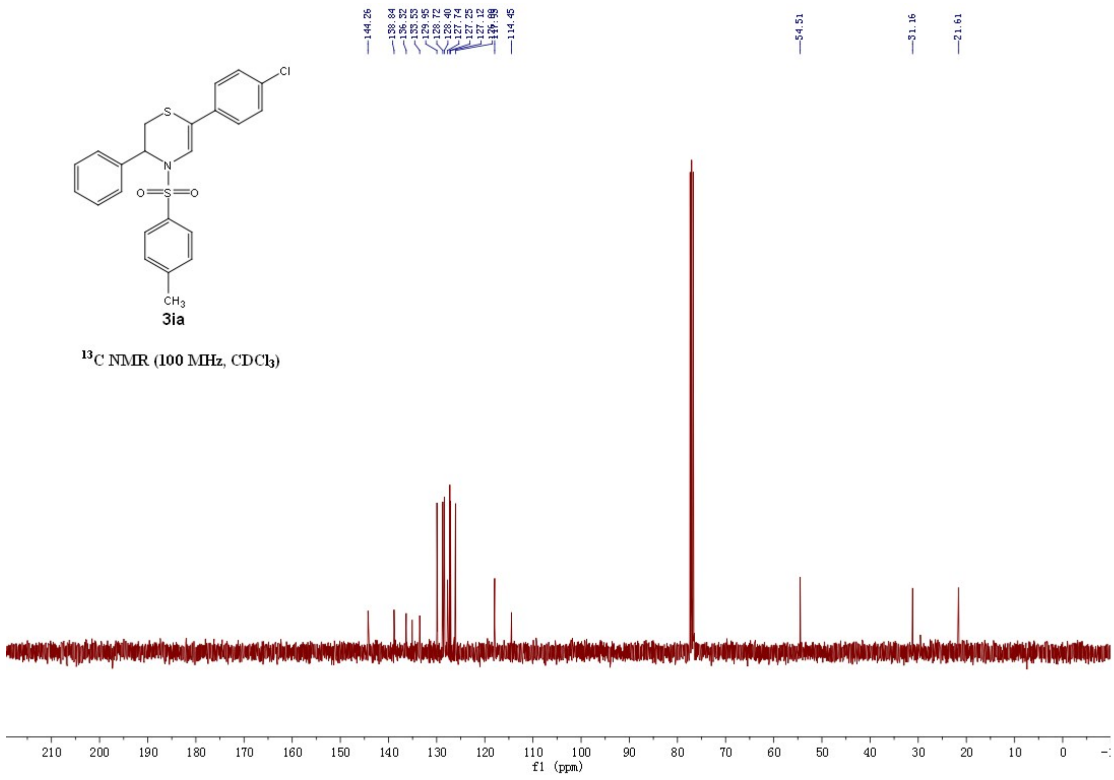
^{13}C NMR (100 MHz, $CDCl_3$)





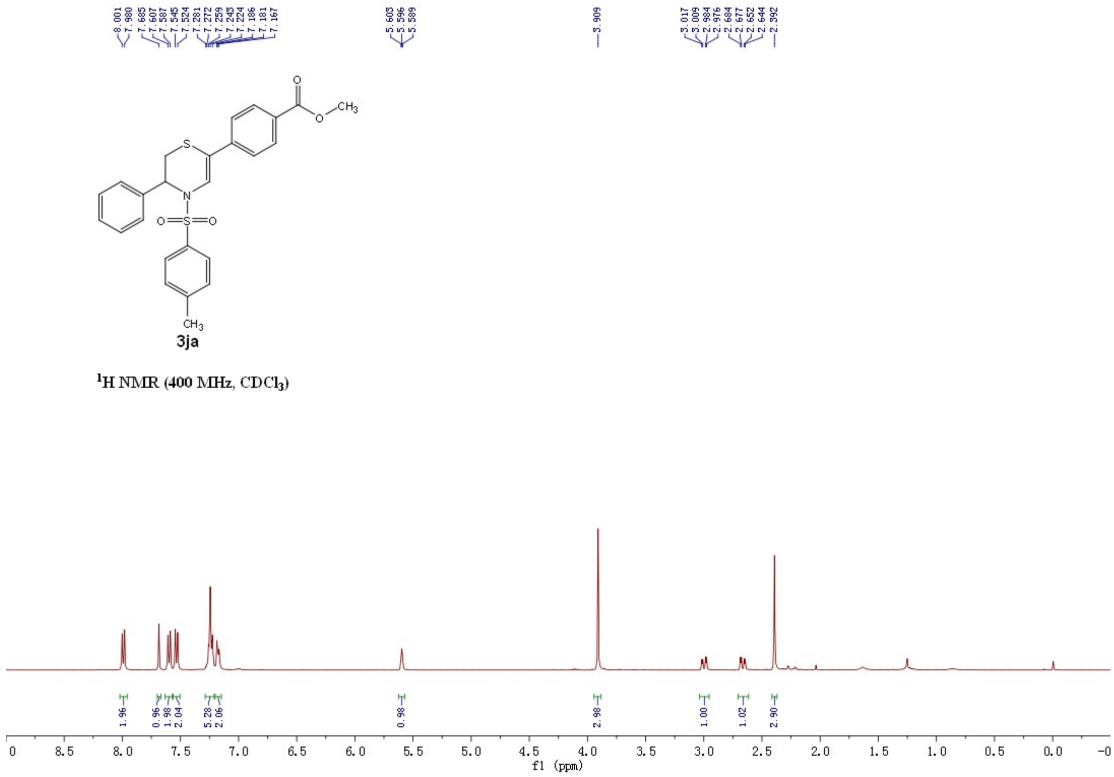
3ia

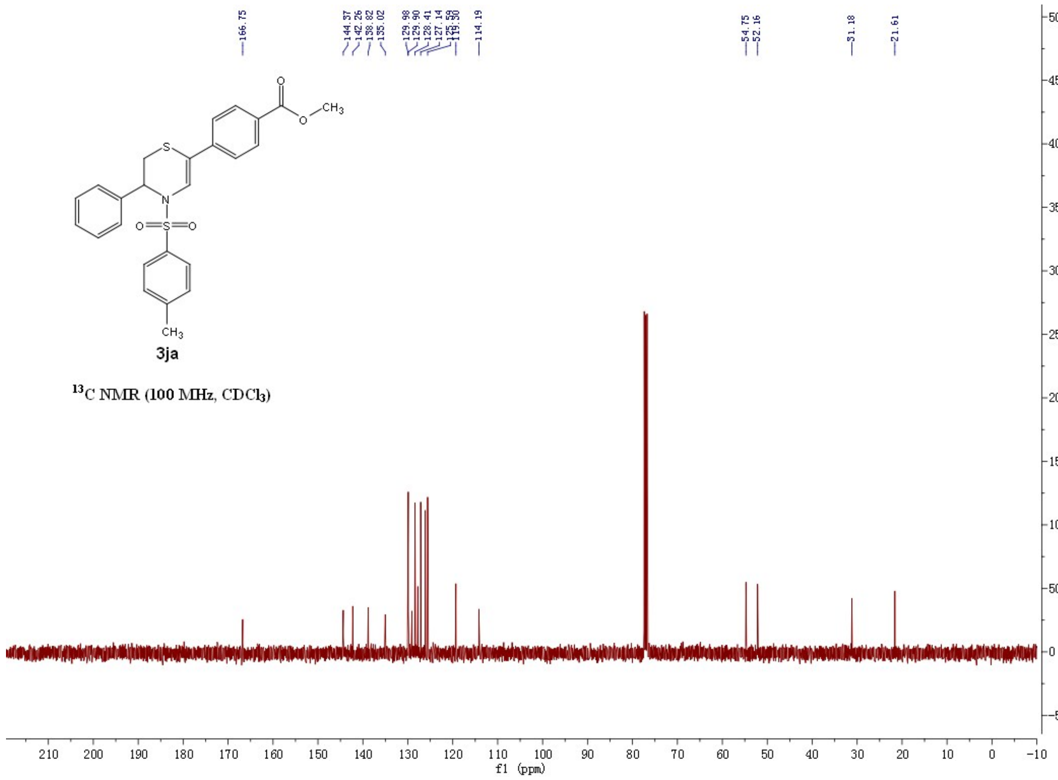
^{1}H NMR (400 MHz, $CDCl_3$)

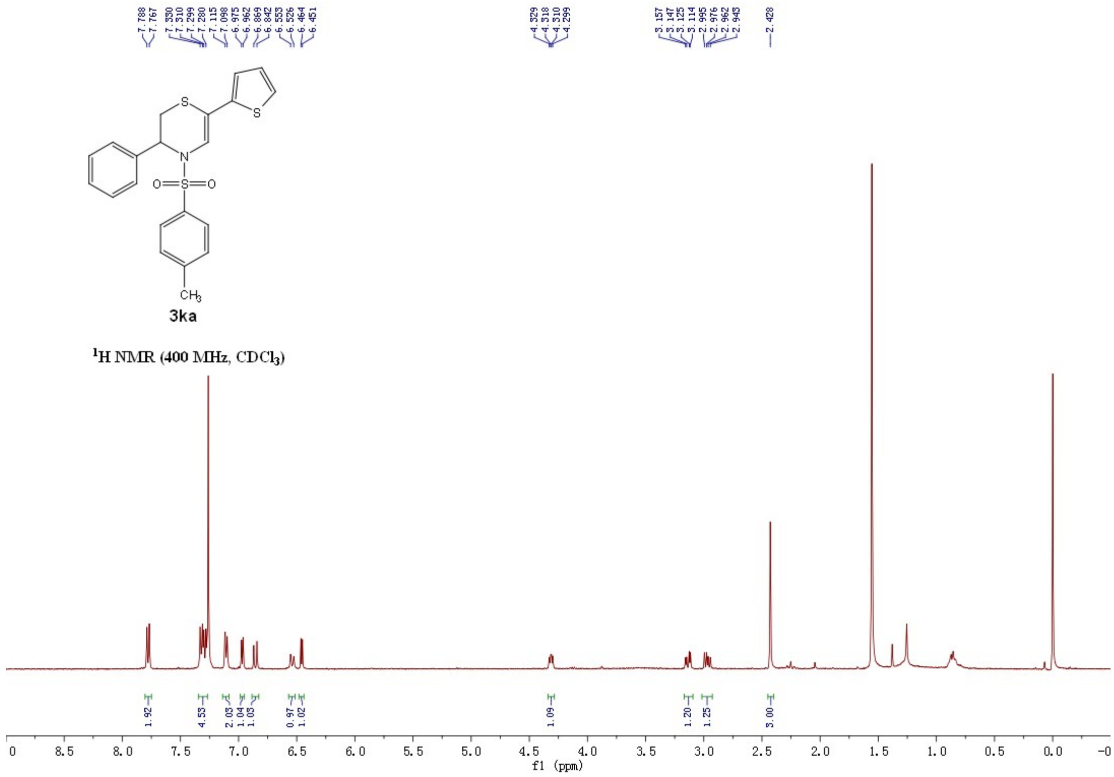


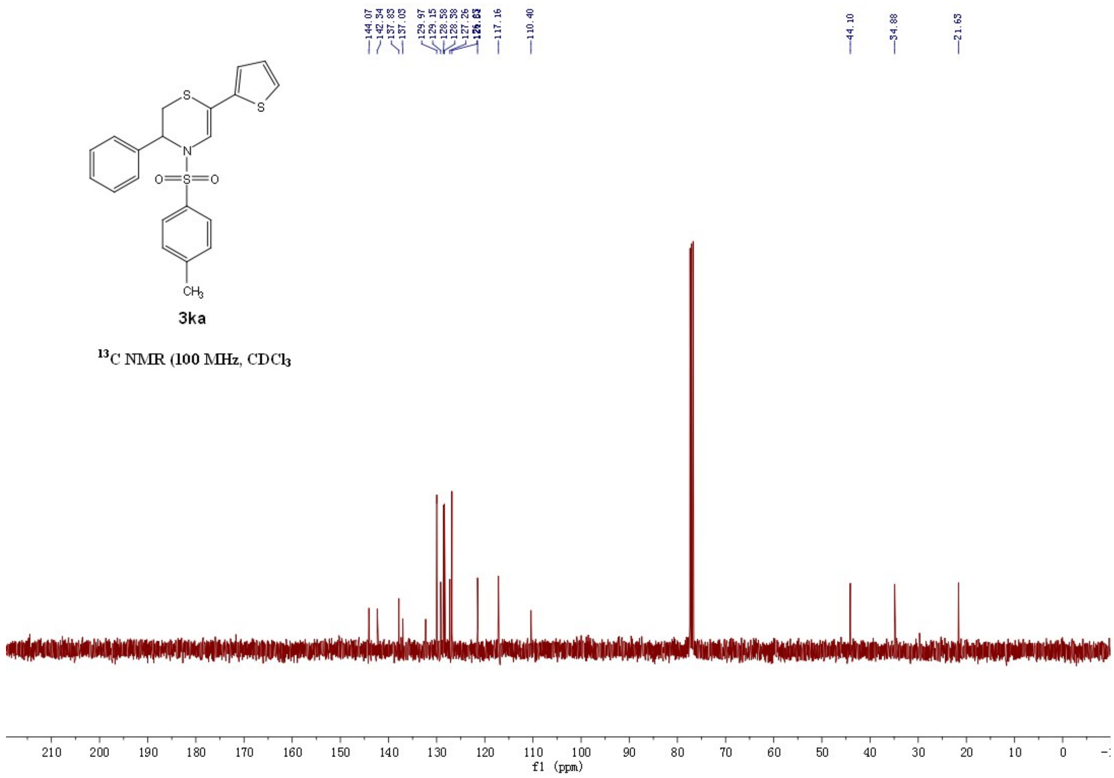
3ia

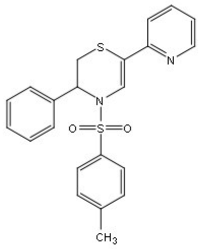
^{13}C NMR (100 MHz, $CDCl_3$)


3ja
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)


3ja
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

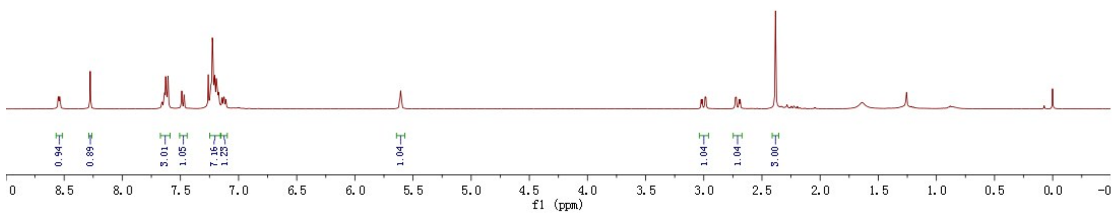

3ka
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

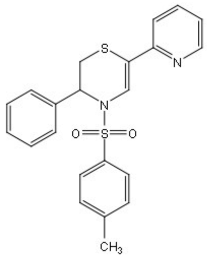

3ka
^{13}C NMR (100 MHz, CDCl$_3$
f1 (ppm)



3la

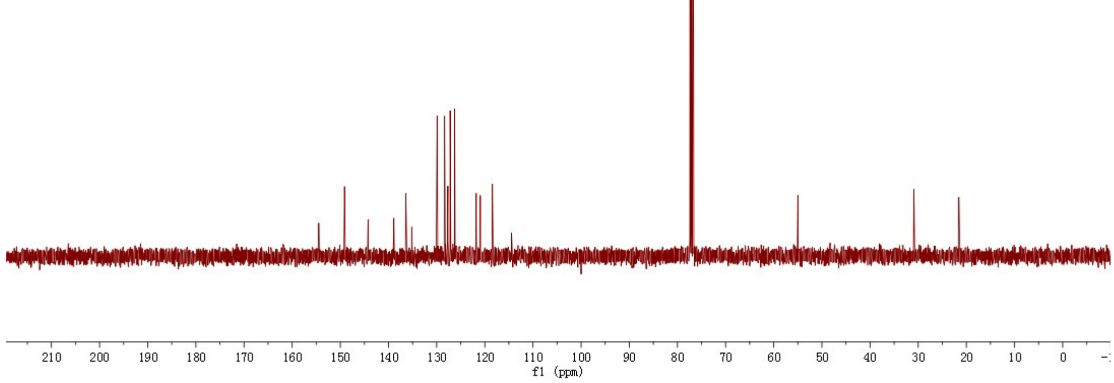
^{1}H NMR (400 MHz, CDCl$_3$)

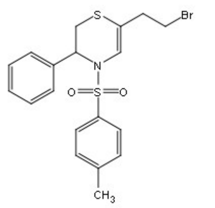




3la

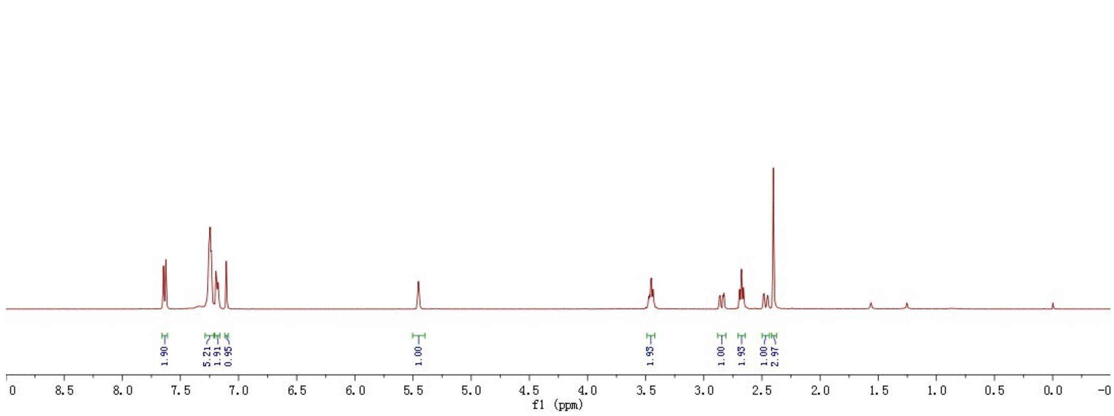
^{13}C NMR (100 MHz, CDCl$_3$)

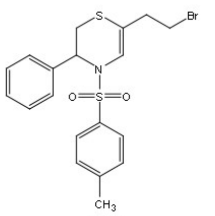




3ma

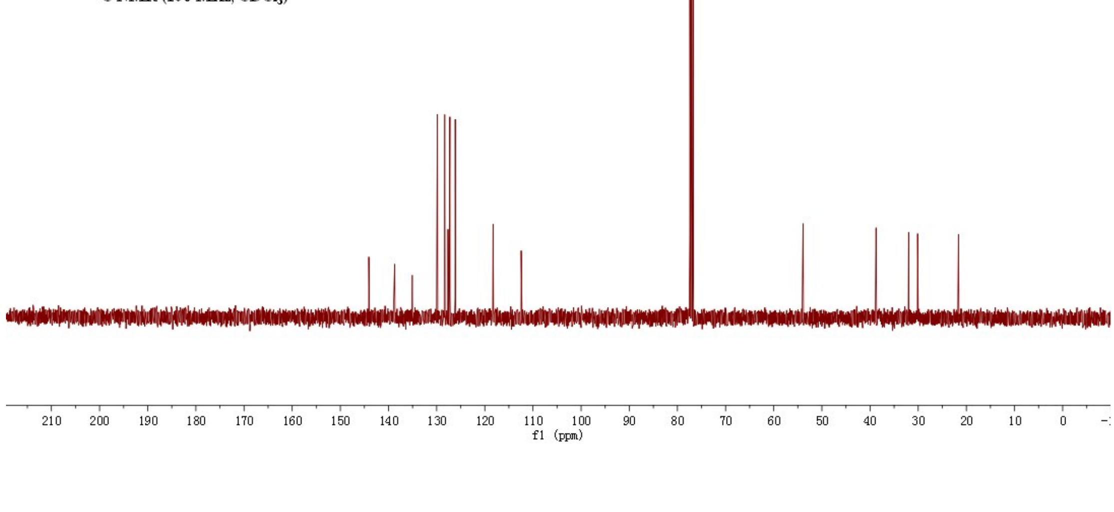
^{1}H NMR (400 MHz, $CDCl_3$)

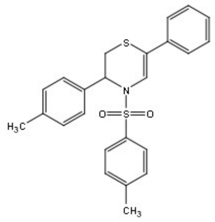




3ma

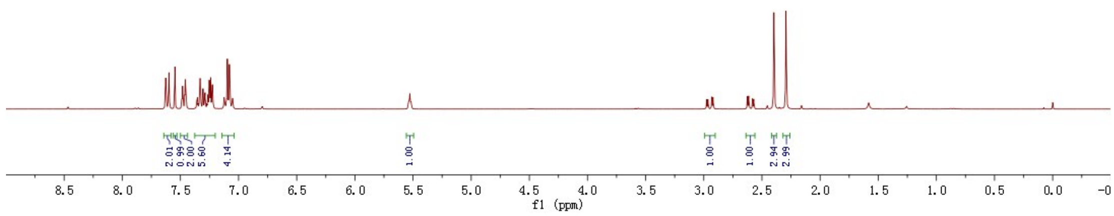
^{13}C NMR (100 MHz, $CDCl_3$)

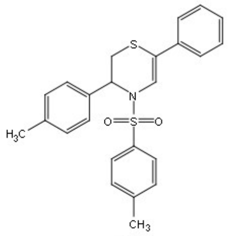




3ab

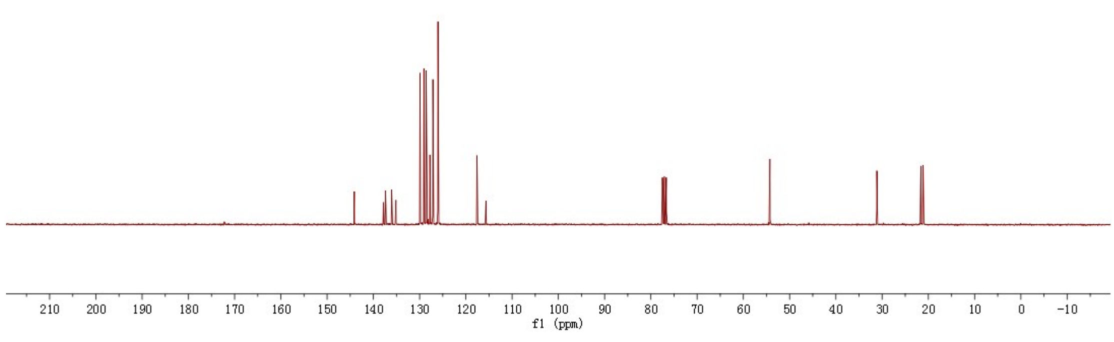
^{1}H NMR (300 MHz, $CDCl_3$)

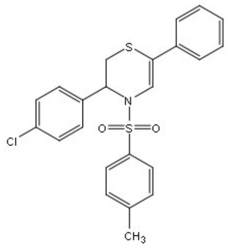




3ab

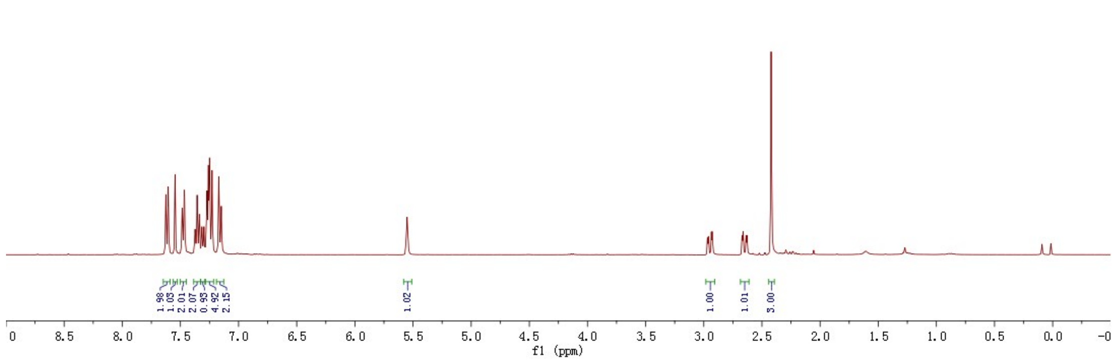
^{13}C NMR (75 MHz, $CDCl_3$)

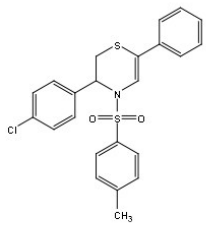




3ac

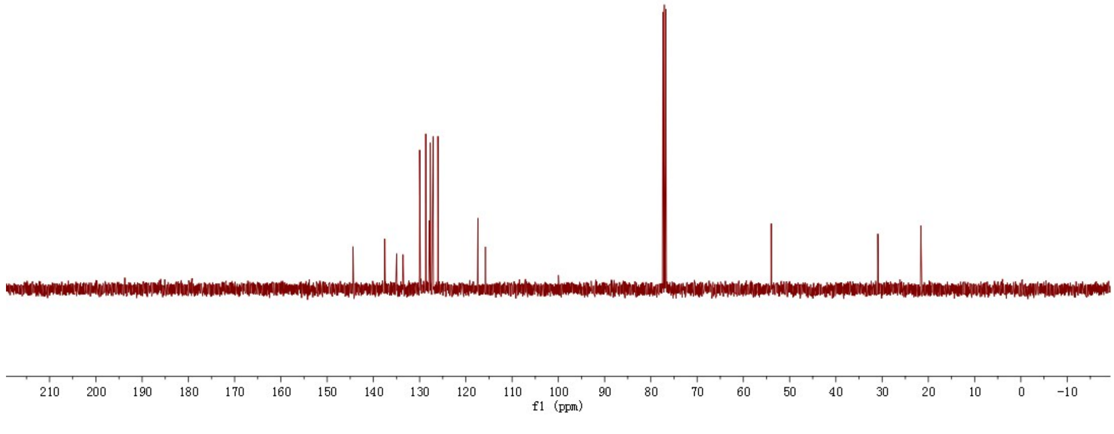
^{1}H NMR (400 MHz, CDCl$_3$)

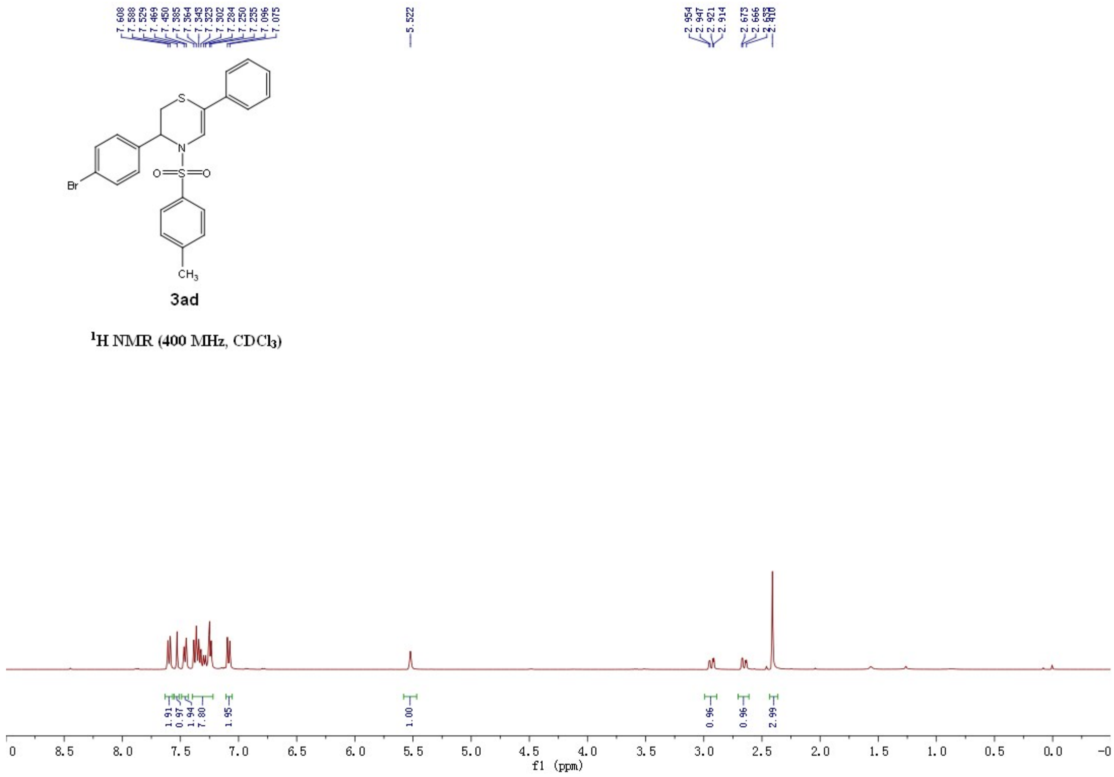




3ac

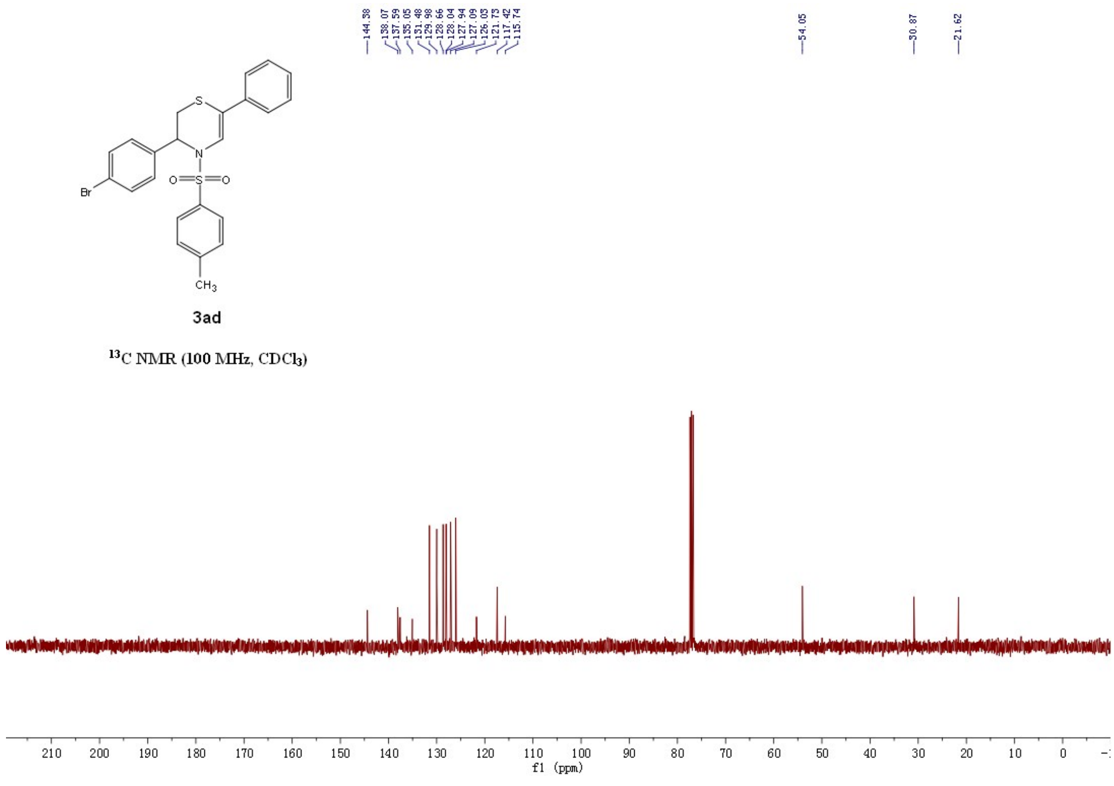
^{13}C NMR (100 MHz, CDCl$_3$)





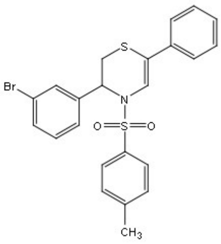
3ad

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



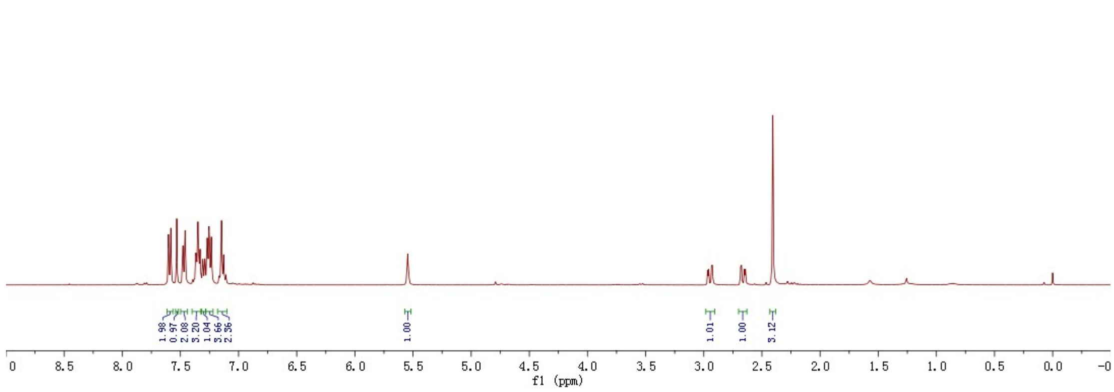
3ad

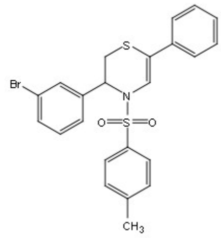
^{13}C NMR (100 MHz, $CDCl_3$)



3ae

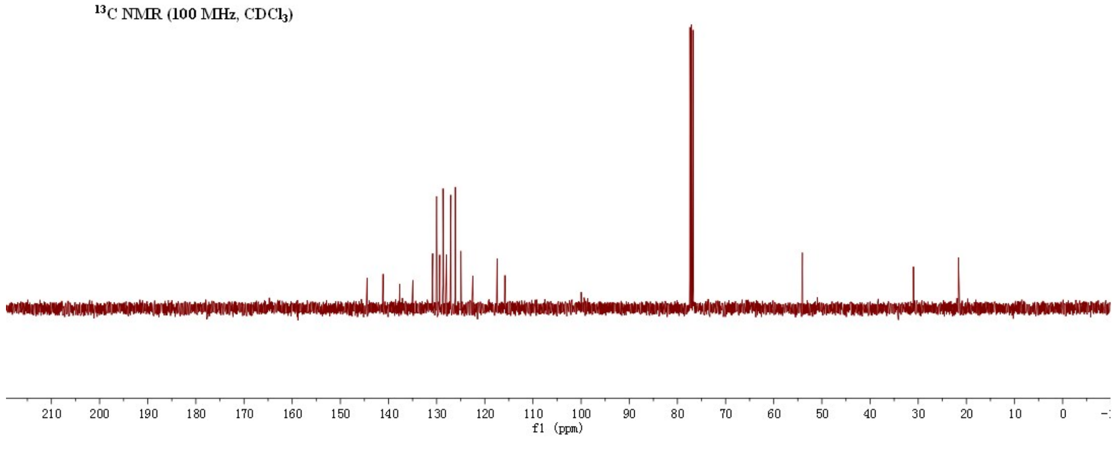
^{1}H NMR (400 MHz, $CDCl_3$)

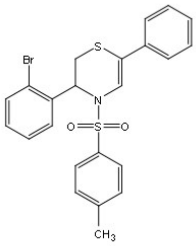




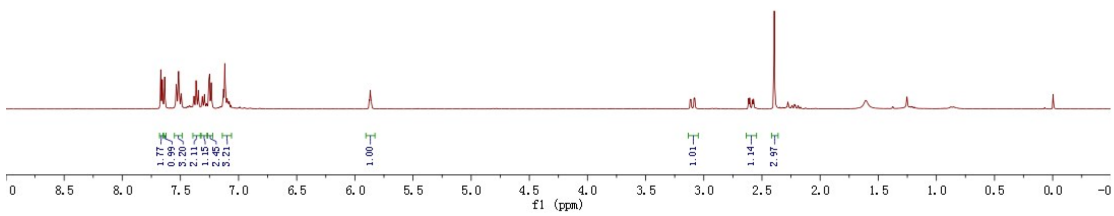
3ae

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

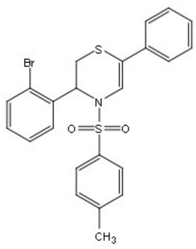




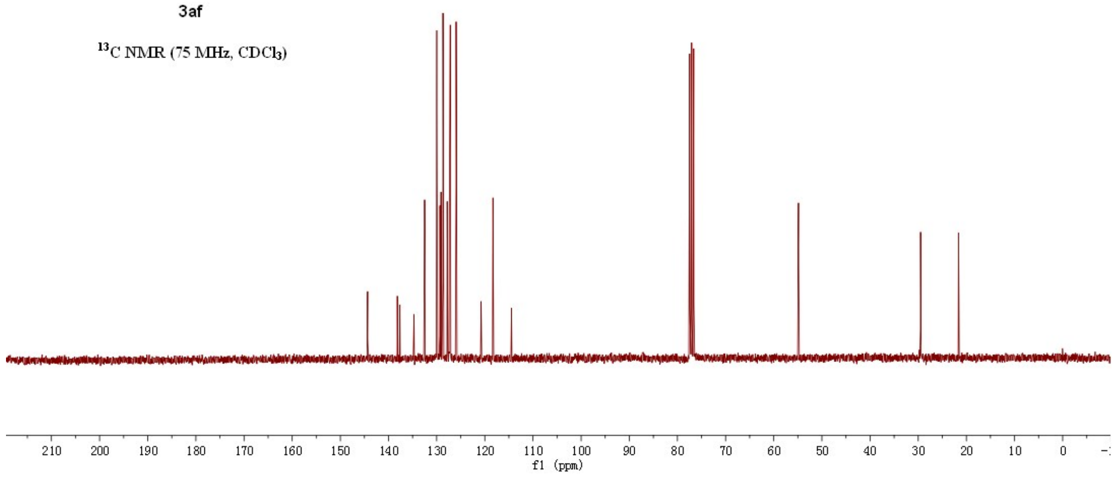
3af



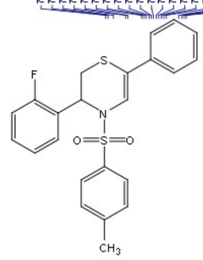
^{1}H NMR (400 MHz, CDCl$_3$)



3af

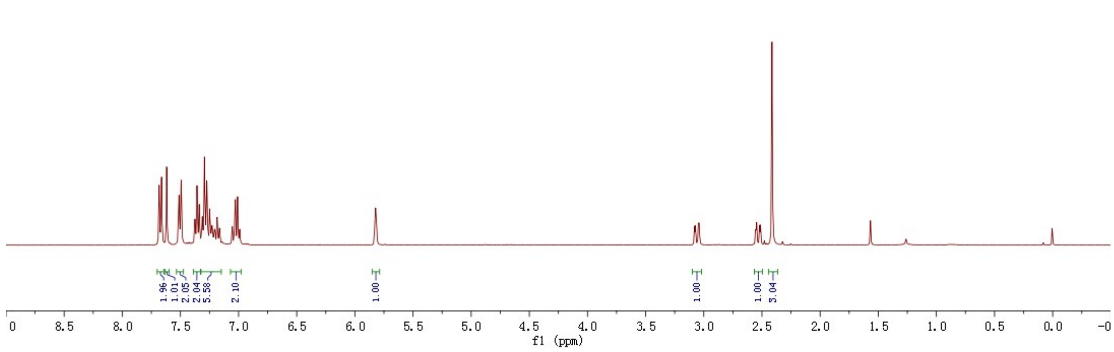


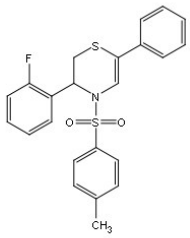
^{13}C NMR (75 MHz, CDCl$_3$)



3ag

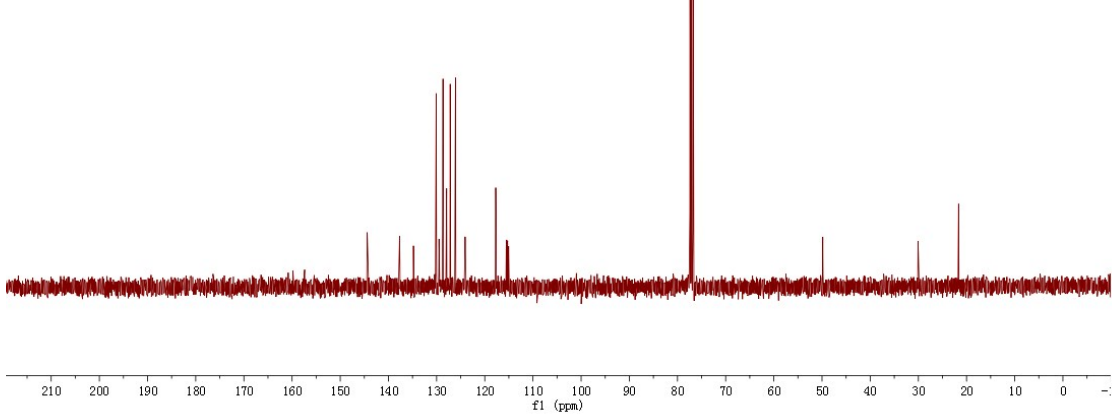
^{1}H NMR (400 MHz, $CDCl_3$)

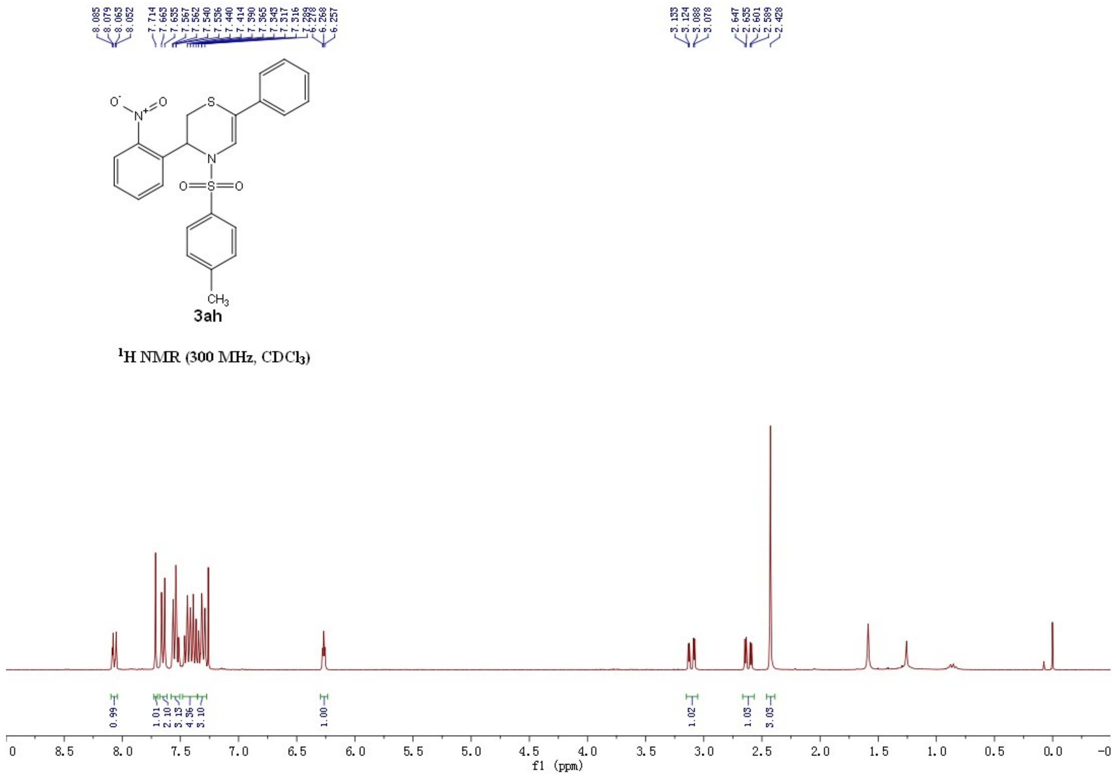




3ag

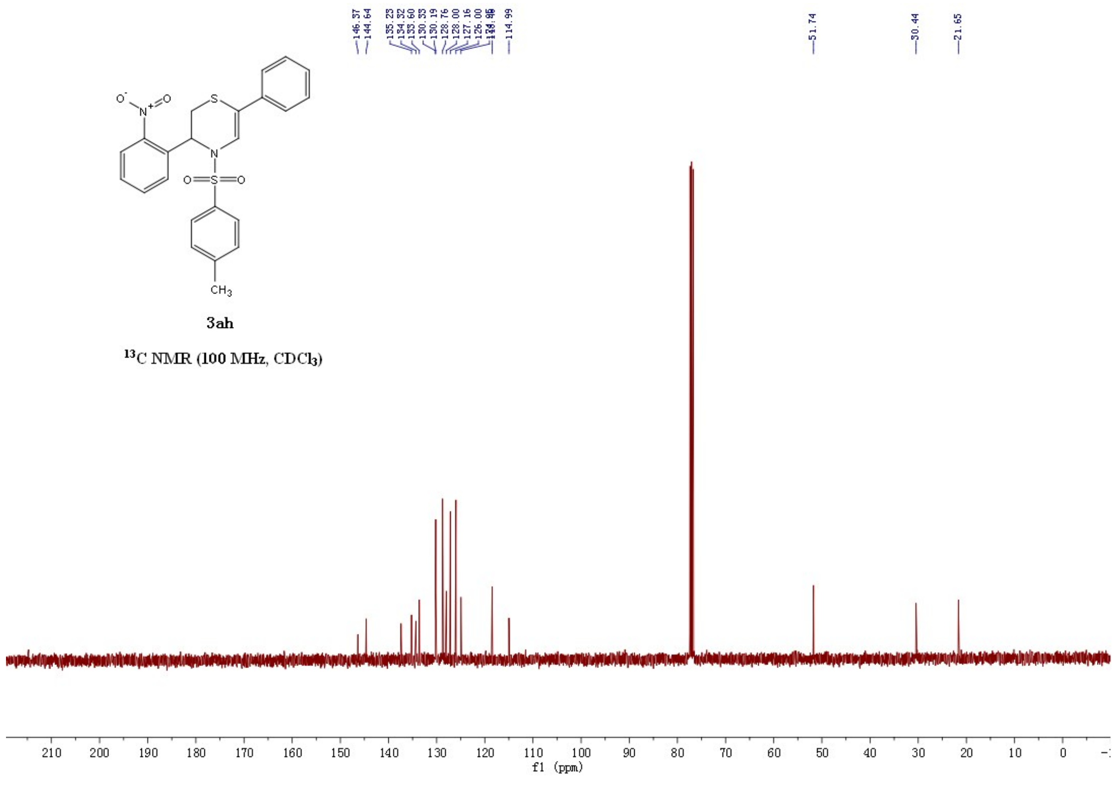
^{13}C NMR (100 MHz, $CDCl_3$)





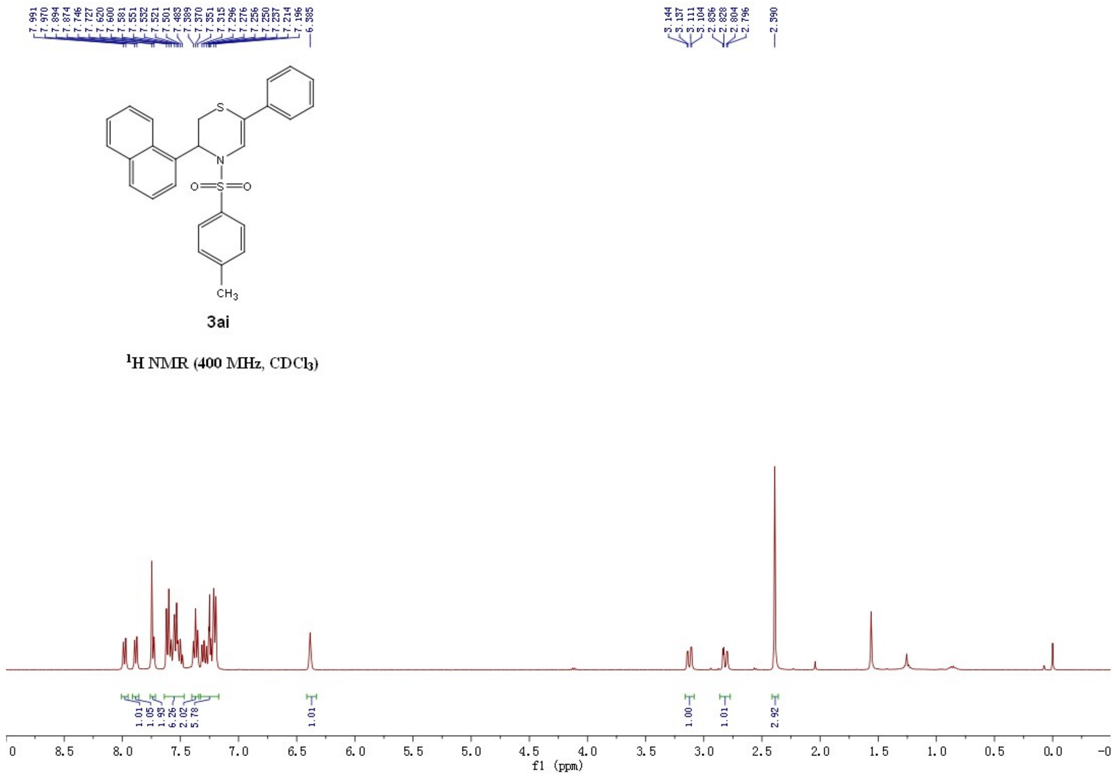
3ah

^{1}H NMR (300 MHz, $CDCl_3$)



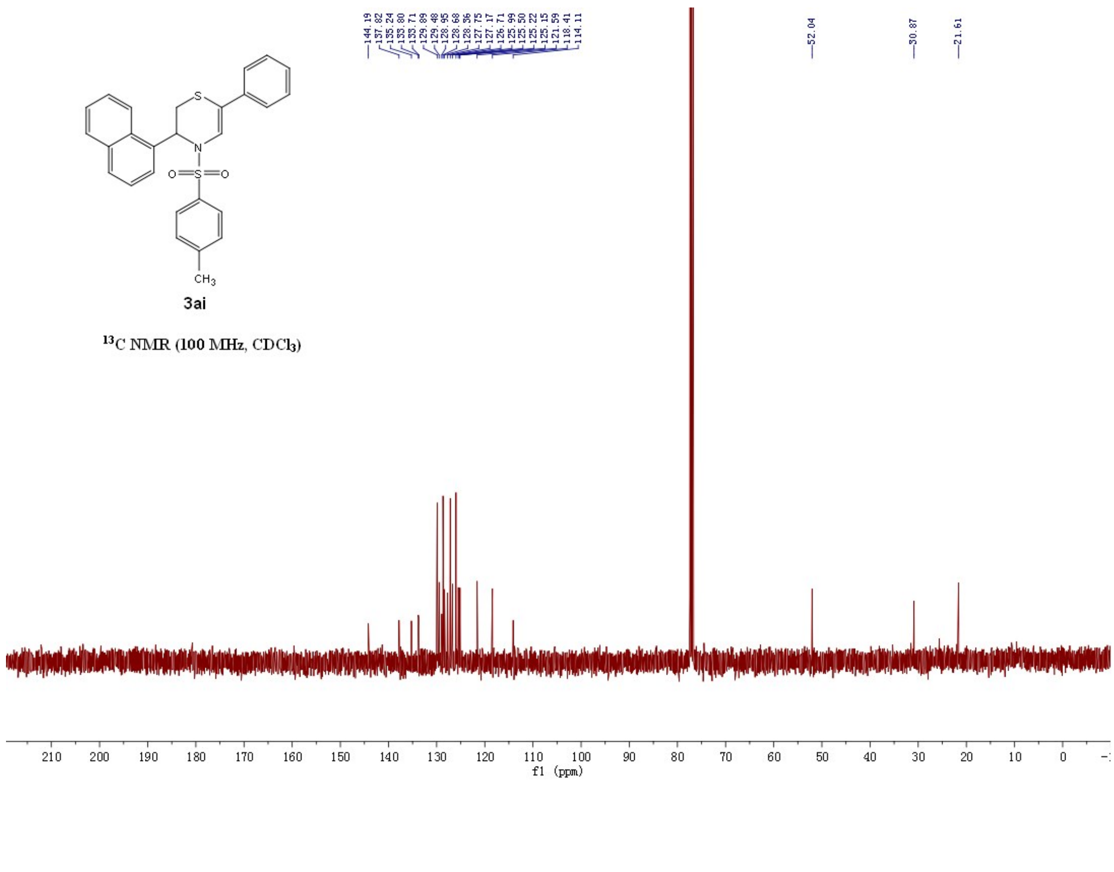
3ah

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



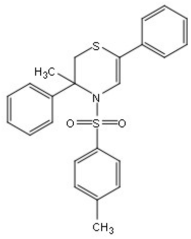
3ai

[1]H NMR (400 MHz, $CDCl_3$)



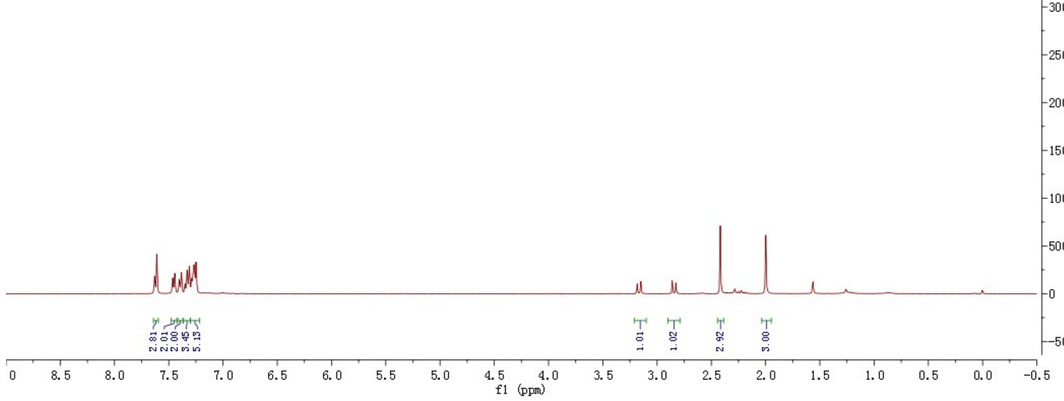
3ai

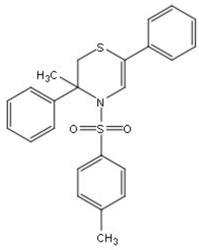
[13]C NMR (100 MHz, $CDCl_3$)



3aj

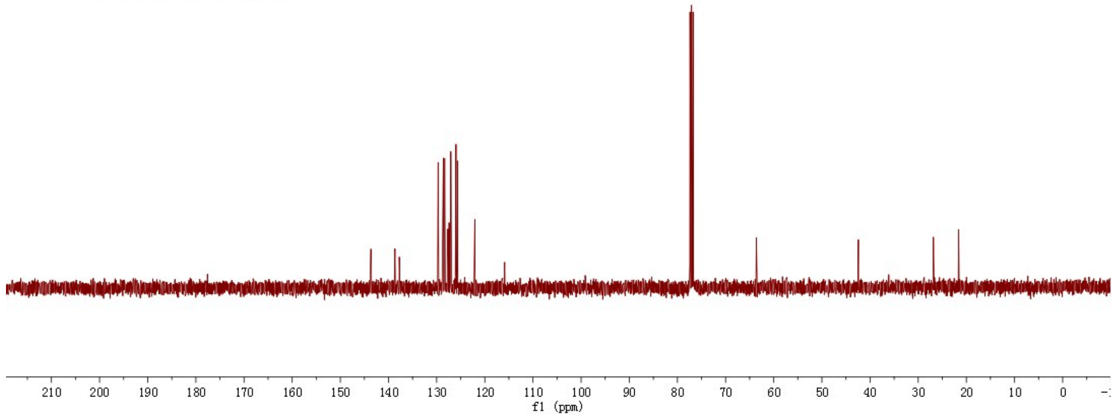
[1]H NMR (400 MHz, $CDCl_3$)

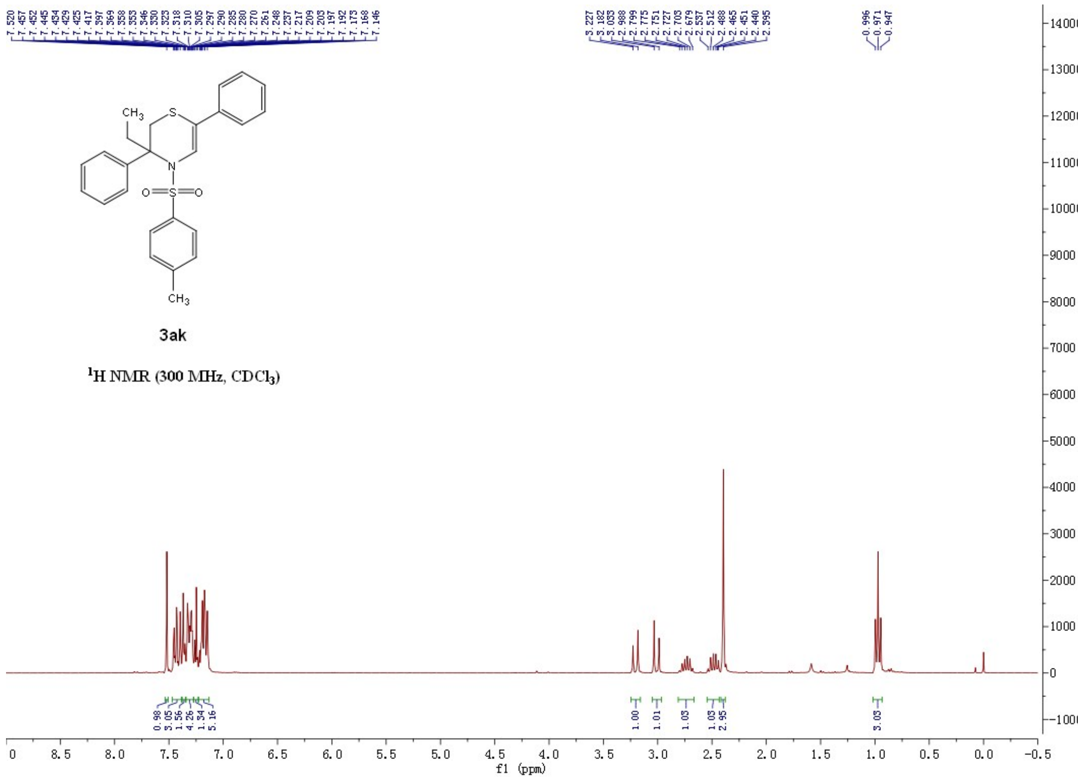


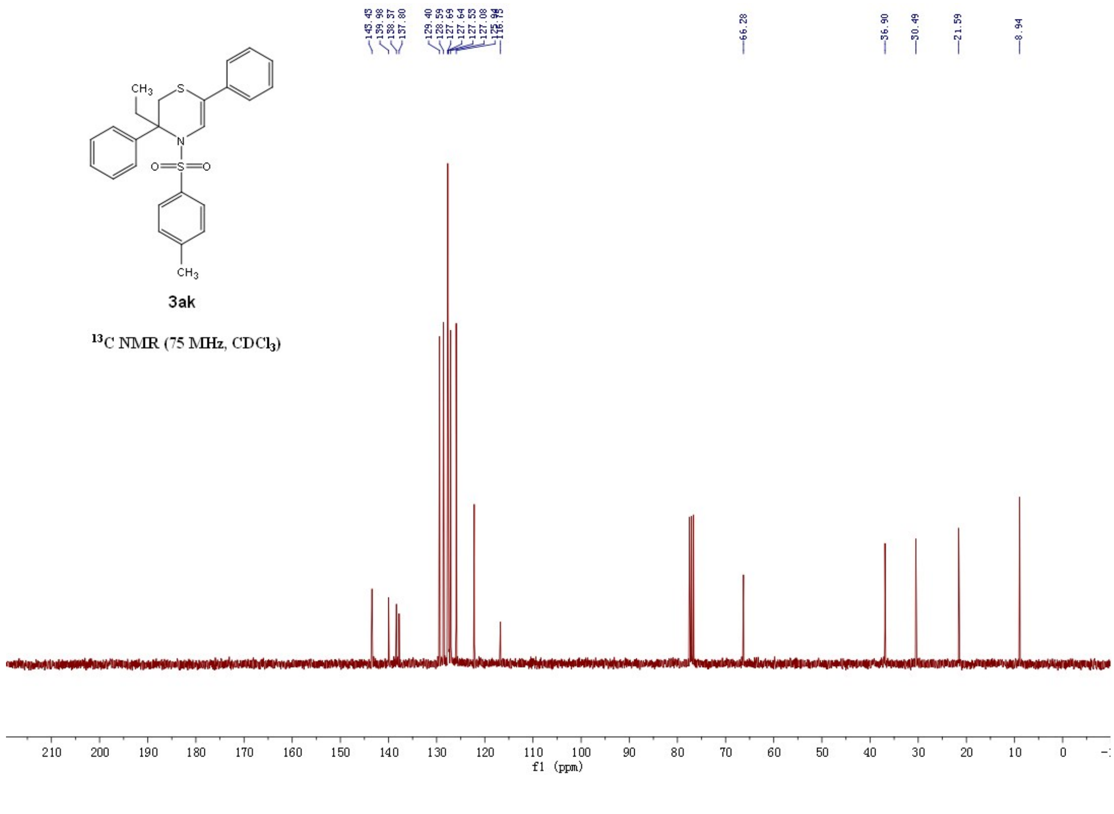


3aj

[13]C NMR (100 MHz, $CDCl_3$)




3ak
1H NMR (300 MHz, CDCl3)
f1 (ppm)


3ak
13C NMR (75 MHz, CDCl3)
f1 (ppm)