

Supporting Information

Regioselective Annulation of Alkylidenecyclopropanes by Rh(III)-Catalyzed C–H/C–C Activation to Access Spirocyclic Benzosultams

Qiuyun Li,^a Xin Yuan,^b Bin Li,^a and Baiquan Wang^{*,a,c,d}

^aState Key Laboratory of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, People's Republic of China

^bTanggu No. 1 High School, Tianjin 300450, People's Republic of China Collaborative

^cInnovation Center of Chemical Science and Engineering, Tianjin 300071, P. R. China

^dState Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China

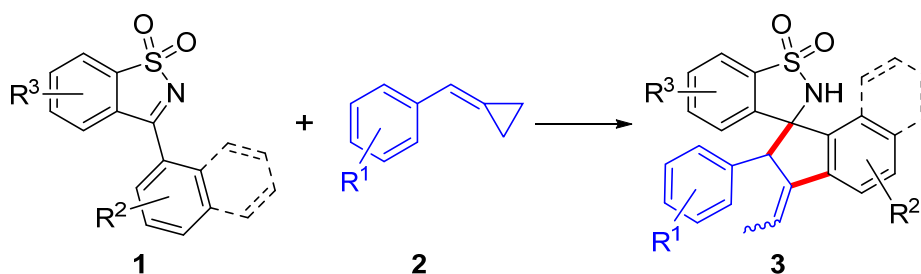
Contents

Table of Contents	S2
1. General Information	S3
2. General procedures for the Synthesis of 3	S3
3. Large scale reaction	S4
4. Mechanistic Studies	S4-S7
4.1 Deuterium-labeling experiments	S4-S6
4.2 KIE Experiments	S6-S7
5. Experimental Data	S7-S17
6. Molecular Structures of 3ac and 3al	S18
7. Copies of ¹ H, ¹³ C and ¹⁹ F NMR Spectra for Compounds	S19-S45
8. References	S46

1. General Information

All the reactions were carried out under argon atmosphere using standard sealed Schlenk technique. The substrates imine **1**^[1], ACP **2**^[2] were prepared following literature procedures. ¹H NMR (400 MHz), ¹³C NMR (101 MHz), and ¹⁹F (376 MHz) were recorded on a NMR spectrometer with DMSO-*d*₆ and CDCl₃ as solvent. Chemical shifts of ¹H, ¹³C and ¹⁹F NMR spectra are reported in parts per million (ppm). The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl₃: $\delta_{\text{H}} = 7.26$ ppm, $\delta_{\text{C}} = 77.16$ ppm; DMSO-*d*₆: $\delta_{\text{H}} = 2.50$ ppm, $\delta_{\text{C}} = 39.43$ ppm). All coupling constants (*J* values) were reported in Hertz (Hz). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of triplets (dt), triplet (t), triplet of doublets (td), quartet (q), and multiplet (m). Column chromatography was performed on silica gel 200–300 mesh. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm and 365 nm). High-resolution mass spectrometry (HRMS) was done on a FTICR-mass spectrometer (0.3 mm thickness). Column chromatography was performed on silica gel (200-300 mesh) using EtOAc/petroleum ether (PE).

2. General Procedure for the Synthesis of **3**



A mixture of **1** (0.1 mmol, 1.0 equiv), **2** (0.12 mmol, 1.2 equiv), [Cp*Rh(CH₃CN)₃](SbF₆)₂ (10.0 mol%), Cu(OAc)₂ (0.05 mmol, 0.5 equiv) was weighed in a sealed Schlenk tube equipped with a stir bar. Dry *t*-AmOH (1 mL) was added and the suspended mixture was stirred at 100 °C for 18 h under an Ar atmosphere. After the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure and the residue was purified by a silica gel column using PE/EtOAc (20/1-10/1) as eluent to give pure product **3**.

3. Large scale reaction

A mixture of **1a** (3 mmol, 1.0 equiv), **2d** (3.6 mmol, 1.2 equiv), [Cp*Rh(CH₃CN)₃](SbF₆)₂ (10.0 mol%), Cu(OAc)₂ (1.5 mmol, 0.5 equiv) was weighed in a sealed Schlenk tube equipped with a stir bar. Dry *t*-AmOH (5 mL) was added and the mixture was stirred at 100 °C for 18 h under an Ar atmosphere. After the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure and the residue was purified by a silica gel column using PE/EtOAc (20/1-10/1) as eluent to give pure product **3d**.

4. Mechanistic Studies

4.1. Deuterium-labeling experiments.

Procedures for the reaction without **2d**: A mixture of **1a** (0.1 mmol, 1.0 equiv), [Cp*Rh(CH₃CN)₃](SbF₆)₂ (10.0 mol%), Cu(OAc)₂ (0.05 mmol, 0.5 equiv), CD₃OD (10 equiv) was weighed in a sealed Schlenk tube equipped with a stir bar. Dry *t*-AmOH (1 mL) was added and the mixture was stirred at 100 °C for 18 h under Ar atmosphere. After the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure. The recovered **1a** were obtained by flash column chromatography on silica gel (eluent: EtOAc/PE = 1/10).

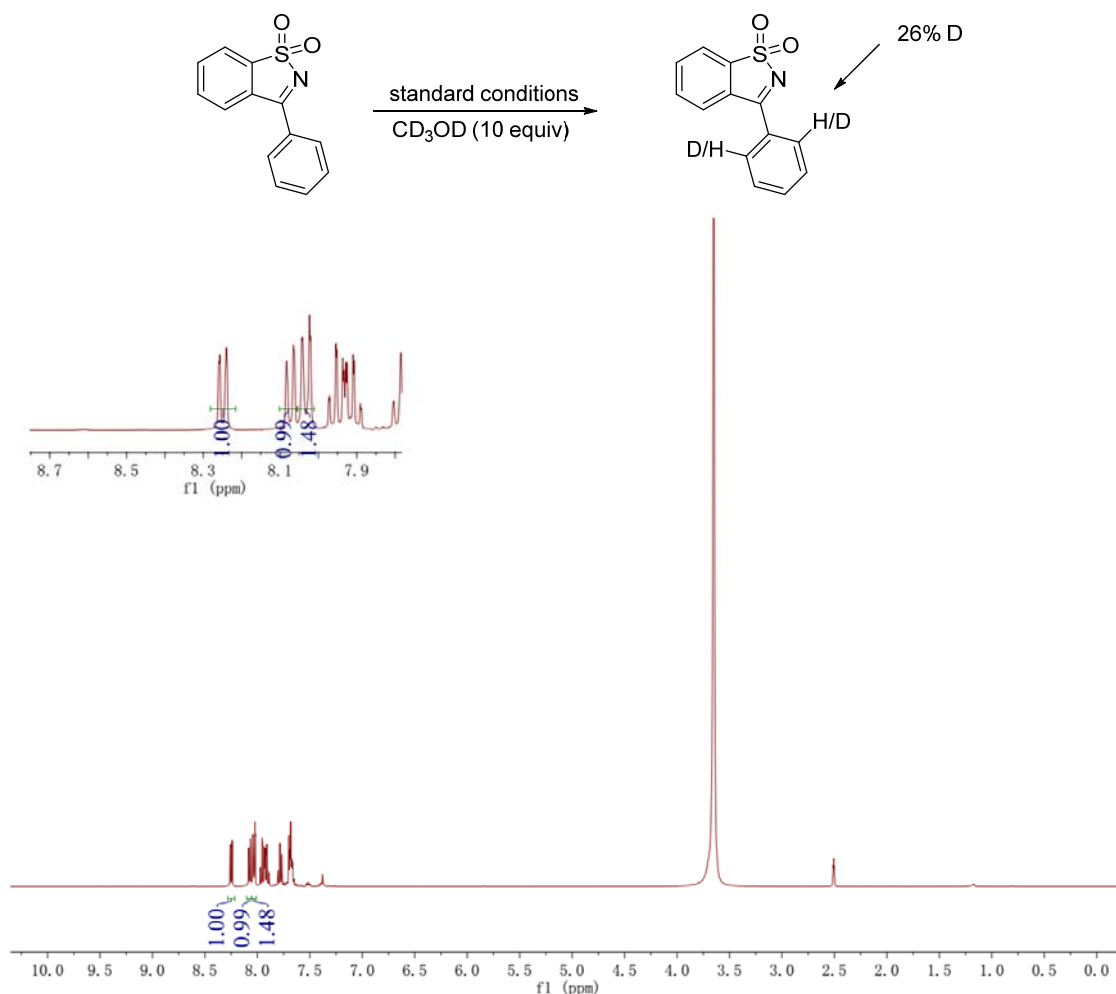
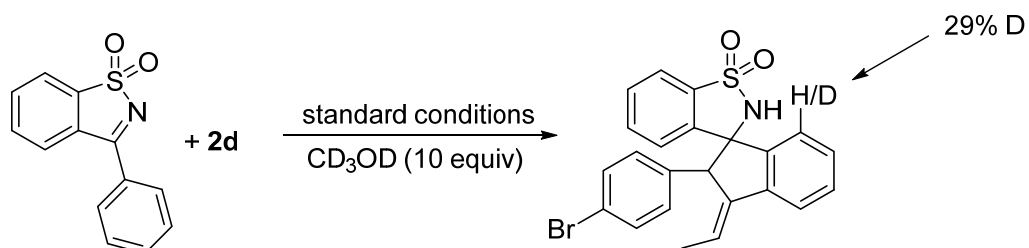


Figure S1 ^1H NMR spectra (400 MHz, DMSO) of *D-1a*

Procedures for the reaction in the presence of **2d**: A mixture of **1a** (0.1 mmol, 1.0 equiv), **2d** (0.12 mmol, 1.2 equiv), $[\text{Cp}^*\text{Rh}(\text{CH}_3\text{CN})_3](\text{SbF}_6)_2$ (10.0 mol%), $\text{Cu}(\text{OAc})_2$ (0.05 mmol, 0.5 equiv), CD_3OD (10 equiv) was weighed in a sealed Schlenk tube equipped with a stir bar. Dry *t*-AmOH (1 mL) was added and the mixture was stirred at 100 °C for 18 h under Ar atmosphere. After the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure. **3ad'** were obtained by flash column chromatography on silica gel (eluent: EtOAc/PE = 1/10).



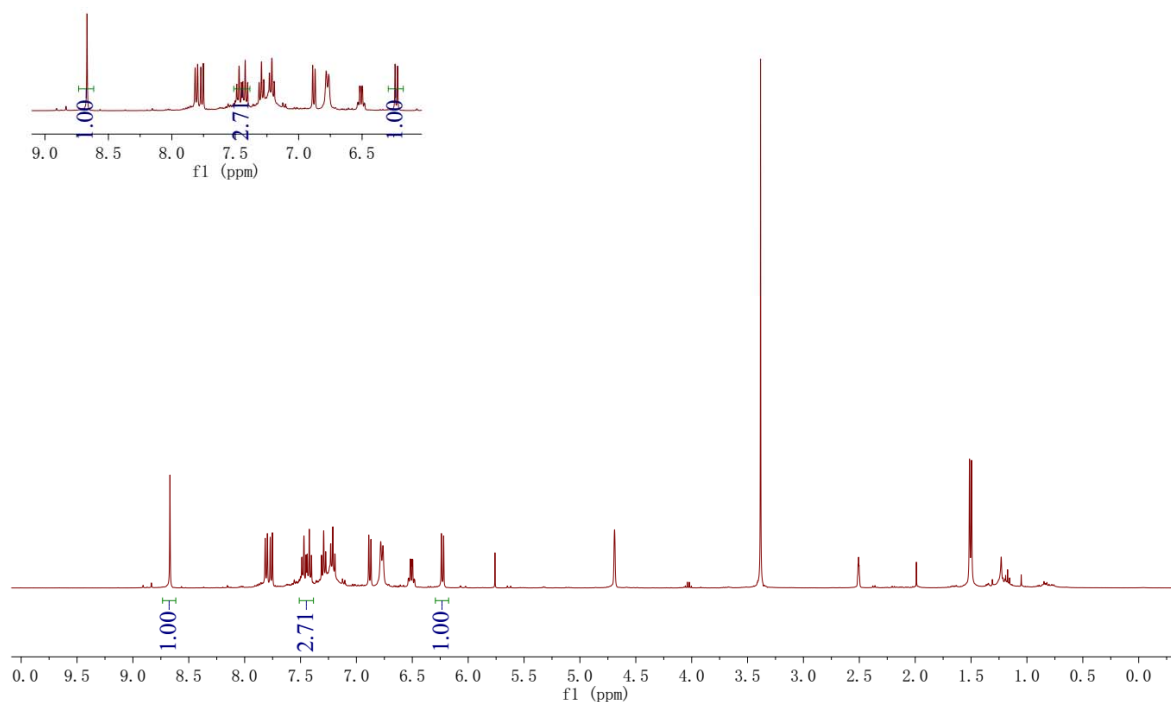
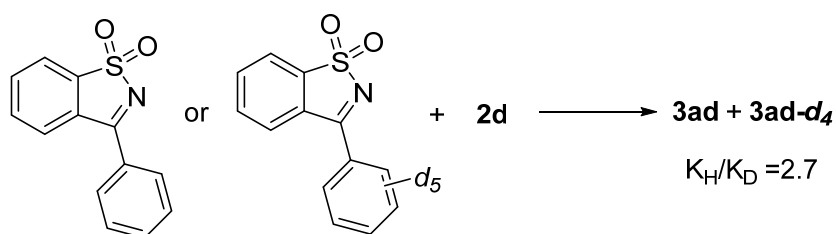


Figure S2 ^1H NMR spectra (400 MHz, DMSO) of *D-3ad'*

4.2 KIE Experiments



Procedure for independent reaction: A mixture of **1a** (0.1 mmol, 0.5 equiv), or **1a-d₅** (0.1 mmol, 0.5 equiv), **2d** (0.24 mmol, 1.2 equiv), $[\text{Cp}^*\text{Rh}(\text{CH}_3\text{CN})_3](\text{SbF}_6)_2$ (10.0 mol%), $\text{Cu}(\text{OAc})_2$ (0.1 mmol, 0.5 equiv) were separately weighted in two Schlenk tube equipped with a stir bar. Dry *t*-AmOH (1 mL) was added and the mixture was stirred at 60 °C for 45 minutes under Ar atmosphere. Afterwards, the two tubes were rapidly combined and the solvent was rapidly evaporated under reduced pressure. The residue was adsorbed onto small amounts of silica. The purification was performed by flash column chromatography on silica gel (eluent: EtOAc/PE= 1:10).

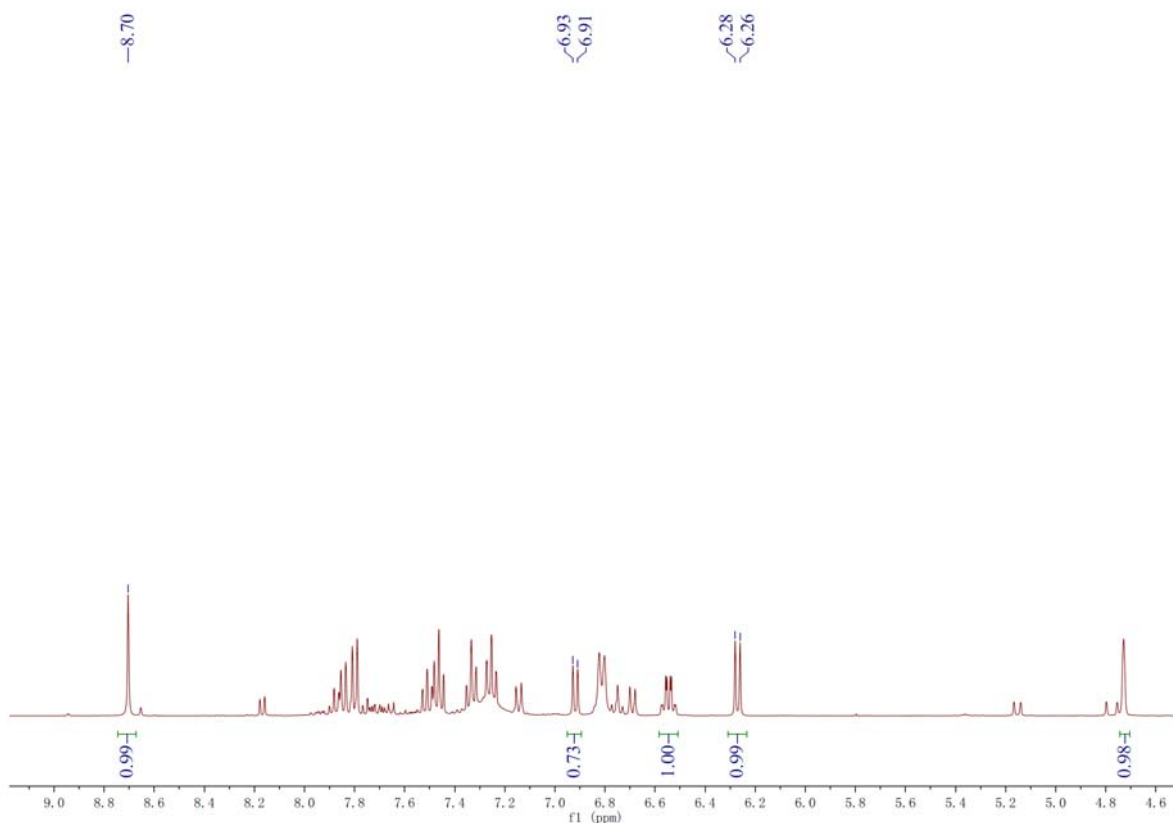
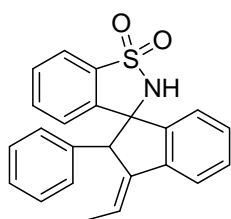
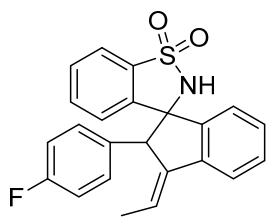


Figure S4 ^1H NMR of product obtained from the KIE experiment for independent reactions

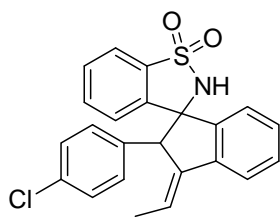
5. Experimental Data



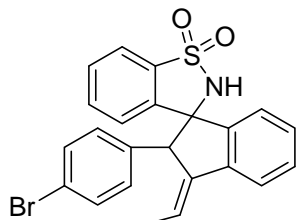
(E)-3'-Ethylidene-2'-phenyl-2',3'-dihydro-2H-spiro[benzo[*d*]isothiazole-3,1'-indene] 1,1-dioxide (3aa): White solid. M.p. 157 – 158 °C. ^1H NMR (400 MHz, DMSO) δ 8.60 (s, 1H), 7.81 (d, $J = 7.8$ Hz, 1H), 7.74 (d, $J = 7.7$ Hz, 1H), 7.50 – 7.44 (m, 1H), 7.40 – 7.34 (m, 1H), 7.28 (t, $J = 7.3$ Hz, 1H), 7.16 – 6.93 (m, 4H), 6.83 (dd, $J = 17.0, 6.7$ Hz, 3H), 6.49 (qd, $J = 7.0, 1.8$ Hz, 1H), 6.14 (d, $J = 7.9$ Hz, 1H), 4.71 (s, 1H), 1.52 (d, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 142.8, 142.6, 141.2, 140.8, 139.5, 136.9, 131.4, 129.8, 128.9, 128.8, 127.9, 126.6, 125.9, 125.7, 119.9, 119.7, 118.9, 74.8, 59.8, 14.9. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{20}\text{NO}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 374.1215, found 374.1212.



(E)-3'-Ethylidene-2'-(4-fluorophenyl)-2',3'-dihydro-2H-spiro[benzo[*d*]isothiazole-3,1'-indene] 1,1-dioxide (3ab): White solid. M.p. 110 – 112 °C. $^1\text{H NMR}$ (400 MHz, DMSO) δ 8.63 (s, 1H), 7.78 (dd, $J = 20.9, 7.8$ Hz, 2H), 7.43 (dt, $J = 24.2, 7.5$ Hz, 2H), 7.29 (t, $J = 7.5$ Hz, 1H), 7.19 (t, $J = 7.6$ Hz, 1H), 7.00 – 6.72 (m, 5H), 6.50 (q, $J = 6.7$ Hz, 1H), 6.18 (d, $J = 7.8$ Hz, 1H), 4.71 (s, 1H), 1.51 (d, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, DMSO) δ 161.2 (d, $J = 243.4$ Hz), 143.1, 142.9, 141.5, 141.3, 136.2 (d, $J = 2.4$ Hz), 132.0, 130.4, 129.5 (d, $J = 24.2$ Hz), 126.4, 126.2, 120.4, 120.3, 119.7, 115.2 (d, $J = 21.3$ Hz), 75.2, 59.4, 15.4. $^{19}\text{F NMR}$ (376 MHz, DMSO) δ -115.7. **HRMS (ESI)** calcd for $\text{C}_{23}\text{H}_{19}\text{FNO}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 392.1121, found 392.1114.

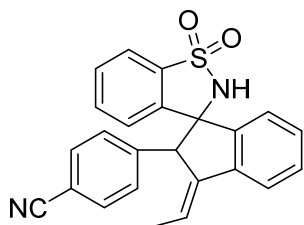


(E)-2'-(4-Chlorophenyl)-3'-ethylidene-2',3'-dihydro-2H-spiro[benzo[*d*]isothiazole-3,1'-indene] 1,1-dioxide (3ac): White solid. M.p. 162 – 163 °C. $^1\text{H NMR}$ (400 MHz, DMSO) δ 8.71 (s, 1H), 7.78 (dd, $J = 12.2, 7.8$ Hz, 2H), 7.43 (ddd, $J = 21.7, 11.4, 4.1$ Hz, 2H), 7.28 (t, $J = 7.4$ Hz, 1H), 7.21 – 6.98 (m, 3H), 6.88 (dd, $J = 16.9, 8.1$ Hz, 3H), 6.50 (tt, $J = 7.2, 3.5$ Hz, 1H), 6.23 (d, $J = 7.9$ Hz, 1H), 4.75 (s, 1H), 1.49 (d, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, DMSO) δ 143.1, 142.8, 141.3, 141.2, 138.9, 137.4, 132.0, 131.7, 130.4, 129.7, 129.4, 128.4, 126.5, 126.2, 120.4, 120.3, 119.9, 75.2, 59.6, 15.4. **HRMS (ESI)** calcd for $\text{C}_{23}\text{H}_{19}\text{ClNO}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 408.0825, found 408.0813.

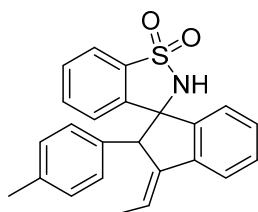


(E)-2'-(4-Bromophenyl)-3'-ethylidene-2',3'-dihydro-2H-spiro[benzo[*d*]isothiazole-3,1'-indene] 1,1-dioxide (3ad): White solid. M.p. 197 – 199 °C. $^1\text{H NMR}$ (400 MHz, DMSO) δ 8.66 (s, 1H), 7.78 (dd, $J = 18.5, 7.8$ Hz, 2H), 7.44 (dt, $J = 19.5, 7.6$ Hz, 2H), 7.25 (dt, $J = 32.5,$

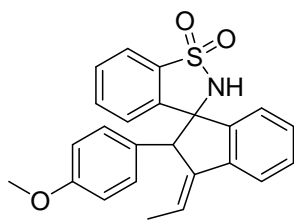
7.5 Hz, 4H), 6.82 (dd, $J = 43.2, 7.7$ Hz, 3H), 6.57 – 6.45 (m, 1H), 6.22 (d, $J = 7.8$ Hz, 1H), 4.68 (s, 1H), 1.50 (d, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 143.1, 142.8, 141.2, 141.1, 139.4, 137.3, 132.1, 131.4, 130.4, 129.7, 129.4, 126.5, 126.2, 120.5, 120.3, 120.1, 119.8, 75.1, 59.6, 15.4. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{19}\text{BrNO}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 452.0320, found 452.0306.



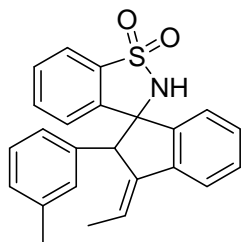
(E)-4-(3'-Ethylidene-1,1-dioxido-2',3'-dihydro-2H-spiro[benzo[*d*]isothiazole-3,1'-inden]-2'-yl)benzonitrile (3ae): White solid. M.p. 114 – 115 °C. ^1H NMR (400 MHz, DMSO) δ 8.77 (s, 1H), 7.79 (dd, $J = 23.8, 7.8$ Hz, 2H), 7.45 (dt, $J = 27.1, 7.6$ Hz, 4H), 7.30 (t, $J = 7.5$ Hz, 1H), 7.19 (t, $J = 7.6$ Hz, 1H), 7.01 (d, $J = 7.9$ Hz, 2H), 6.89 (d, $J = 7.7$ Hz, 1H), 6.55 (tt, $J = 7.1, 3.5$ Hz, 1H), 6.21 (d, $J = 7.9$ Hz, 1H), 4.79 (s, 1H), 1.48 (d, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 145.8, 142.8, 142.6, 140.8, 140.7, 137.2, 132.5, 132.2, 130.6, 129.9, 129.6, 126.3, 126.2, 120.5, 120.4, 120.3, 119.1, 109.8, 75.1, 60.1, 15.5. HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{19}\text{N}_2\text{O}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 399.1167, found 399.1157.



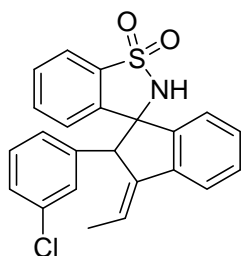
(E)-3'-Ethylidene-2'-(*p*-tolyl)-2',3'-dihydro-2H-spiro[benzo[*d*]isothiazole-3,1'-indene] 1,1-dioxide (3af): White solid. M.p. 174 – 175 °C. ^1H NMR (400 MHz, DMSO) δ 8.56 (s, 1H), 7.79 (d, $J = 7.8$ Hz, 1H), 7.73 (d, $J = 7.7$ Hz, 1H), 7.45 (t, $J = 7.5$ Hz, 1H), 7.38 (t, $J = 7.5$ Hz, 1H), 7.27 (t, $J = 7.5$ Hz, 1H), 7.14 (t, $J = 7.6$ Hz, 1H), 6.68 – 6.85 (m, 5H), 6.52 – 6.41 (m, 1H), 6.16 (d, $J = 7.9$ Hz, 1H), 4.65 (s, 1H), 2.11 (s, 3H), 1.50 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 143.5, 143.0, 141.8, 141.4, 137.3, 136.8, 135.9, 131.8, 130.2, 129.4, 129.2, 129.0, 126.5, 126.1, 120.3, 120.1, 119.3, 75.3, 59.9, 21.0, 15.4. HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{22}\text{NO}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 388.1371, found 388.1365.



(E)-3'-Ethylidene-2'-(4-methoxyphenyl)-2',3'-dihydro-2H-spiro[benzo[d]isothiazole-3,1'-indene] 1,1-dioxide (3ag): White solid. M.p. 224 – 225 °C. $^1\text{H NMR}$ (400 MHz, DMSO) δ 8.55 (s, 1H), 7.76 (dd, $J = 19.5, 7.8$ Hz, 2H), 7.43 (dt, $J = 22.6, 7.6$ Hz, 2H), 7.27 (t, $J = 7.4$ Hz, 1H), 7.18 (t, $J = 7.6$ Hz, 1H), 6.85 (d, $J = 7.6$ Hz, 1H), 6.76 – 6.42 (m, 5H), 6.17 (d, $J = 7.9$ Hz, 1H), 4.64 (s, 1H), 3.59 (s, 3H), 1.52 (d, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, DMSO) δ 158.2, 143.4, 143.0, 141.9, 141.5, 137.4, 131.9, 131.8, 130.3, 129.4, 129.2, 126.5, 126.1, 120.3, 120.2, 119.3, 113.8, 75.4, 59.5, 55.3, 15.3. **HRMS (ESI)** calcd for $\text{C}_{24}\text{H}_{22}\text{NO}_3\text{S}^+$ $[\text{M}+\text{H}]^+$ 404.1320, found 404.1312.

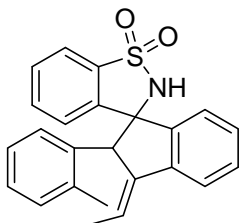


(E)-3'-Ethylidene-2'-(*m*-tolyl)-2',3'-dihydro-2H-spiro[benzo[d]isothiazole-3,1'-indene] 1,1-dioxide (3ah): White solid. M.p. 164 – 165 °C. $^1\text{H NMR}$ (400 MHz, DMSO) δ 8.58 (s, 1H), 7.77 (dd, $J = 24.4, 7.7$ Hz, 2H), 7.46 (t, $J = 7.5$ Hz, 1H), 7.38 (t, $J = 7.5$ Hz, 1H), 7.28 (t, $J = 7.5$ Hz, 1H), 7.13 (t, $J = 7.6$ Hz, 1H), 6.83 (dd, $J = 18.1, 7.3$ Hz, 3H), 6.61 (d, $J = 3.9$ Hz, 2H), 6.52 – 6.44 (m, 1H), 6.14 (d, $J = 6.5$ Hz, 1H), 4.66 (s, 1H), 2.02 (s, 3H), 1.53 (d, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, DMSO) δ 143.4, 143.0, 141.6, 141.3, 139.8, 137.3, 131.8, 130.3, 129.4, 129.2, 128.3, 127.7, 126.4, 126.1, 120.4, 120.1, 119.5, 75.4, 60.2, 15.4. **HRMS (ESI)** calcd for $\text{C}_{24}\text{H}_{22}\text{NO}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 388.1371, found 388.1362.



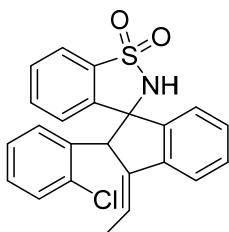
(E)-2'-(3-Chlorophenyl)-3'-ethylidene-2',3'-dihydro-2H-spiro[benzo[d]isothiazole-3,1'-indene] 1,1-dioxide (3ai): White solid. M.p. 199 – 200 °C. $^1\text{H NMR}$ (400 MHz, DMSO) δ 8.68 (s, 1H), 7.79 (dd, $J = 16.4, 7.8$ Hz, 2H), 7.44 (dt, $J = 23.9, 7.5$ Hz, 2H), 7.29 (t, $J = 7.4$

Hz, 1H), 7.19 (t, $J = 7.5$ Hz, 1H), 7.07 (d, $J = 5.7$ Hz, 2H), 6.88 (d, $J = 7.6$ Hz, 1H), 6.81 (s, 2H), 6.58 – 6.47 (m, 1H), 6.20 (d, $J = 7.8$ Hz, 1H), 4.71 (s, 1H), 1.52 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 142.9, 142.7, 142.3, 141.1, 140.8, 137.3, 133.1, 132.1, 130.5, 130.3, 129.7, 129.4, 127.1, 126.3, 126.2, 120.5, 120.5, 120.0, 75.2, 59.7, 15.5. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{19}\text{ClNO}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 408.0825, found 408.0818.



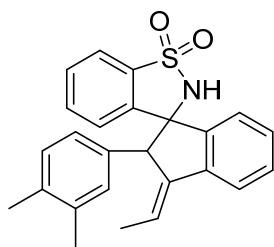
(E)-3'-(o-tolyl)-2',3'-dihydro-2H-spiro[benzo[d]isothiazole-3,1'-indene]

1,1-dioxide (3aj): White solid. M.p. 177 – 179 °C. ^1H NMR (400 MHz, DMSO) δ 8.71 (s, 1H), 7.80 (d, $J = 7.7$ Hz, 2H), 7.47 (dd, $J = 16.4, 8.1$ Hz, 2H), 7.25 (t, $J = 7.4$ Hz, 1H), 7.14 (t, $J = 7.6$ Hz, 1H), 7.01 (dd, $J = 4.8, 2.9$ Hz, 2H), 6.91 – 6.86 (m, 1H), 6.84 – 6.77 (m, 1H), 6.69 (d, $J = 7.7$ Hz, 1H), 6.43 (q, $J = 6.9$ Hz, 1H), 5.97 (d, $J = 7.9$ Hz, 1H), 4.79 (s, 1H), 1.87 (s, 3H), 1.52 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 145.0, 143.4, 142.9, 139.4, 138.3, 137.9, 137.7, 131.8, 130.5, 130.2, 123.0, 129.3, 127.6, 127.4, 126.4, 126.1, 125.5, 120.4, 120.3, 119.1, 75.0, 56.7, 19.8, 15.3. HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{22}\text{NO}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 388.1371, found 388.1369.

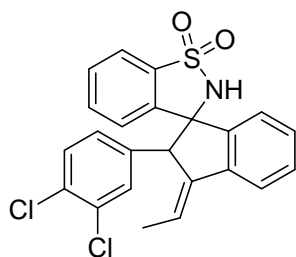


(E)-2'-(2-chlorophenyl)-3'-ethylidene-2',3'-dihydro-2H-spiro[benzo[d]isothiazole-3,1'-indene]

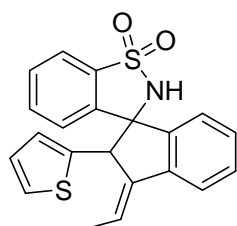
1,1-dioxide (3ak): White solid. M.p. 196 – 198 °C. ^1H NMR (400 MHz, DMSO) δ 8.72 (s, 1H), 7.80 (d, $J = 7.8$ Hz, 2H), 7.56 – 7.41 (m, 2H), 7.29 – 7.10 (m, 5H), 6.99 – 6.90 (m, 1H), 6.67 (d, $J = 7.6$ Hz, 1H), 6.49 (q, $J = 6.6$ Hz, 1H), 5.91 (d, $J = 7.9$ Hz, 1H), 5.03 (s, 1H), 1.53 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 145.0, 142.3, 142.1, 138.9, 138.2, 137.5, 135.4, 131.8, 130.3, 130.1, 129.6, 129.5, 129.3, 127.5, 125.8, 125.4, 120.7, 120.5, 119.9, 74.7, 57.1, 15.3. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{19}\text{ClNO}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 408.0825, found 408.0813.



(E)-2'-(3,4-Dimethylphenyl)-3'-ethylidene-2',3'-dihydro-2H-spiro[benzo[d]isothiazole-3,1'-indene] 1,1-dioxide (3al): White solid. M.p. 190 – 191 °C. $^1\text{H NMR}$ (400 MHz, DMSO) δ 8.53 (d, $J = 2.1$ Hz, 1H), 7.75 (dd, $J = 22.6, 6.8$ Hz, 2H), 7.51 – 7.33 (m, 2H), 7.26 (t, $J = 6.5$ Hz, 1H), 7.14 (t, $J = 6.7$ Hz, 1H), 6.81 (t, $J = 15.6$ Hz, 2H), 6.50 (dd, $J = 33.4, 8.8$ Hz, 3H), 6.16 (d, $J = 7.1$ Hz, 1H), 4.61 (s, 1H), 1.98 (d, $J = 35.2$ Hz, 6H), 1.51 (d, $J = 5.5$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, DMSO) δ 143.0, 142.5, 141.2, 140.9, 136.8, 136.6, 135.4, 134.1, 131.2, 129.7, 128.9, 128.7, 126.0, 125.5, 119.8, 119.6, 118.8, 74.9, 59.4, 18.9, 14.9. **HRMS (ESI)** calcd for $\text{C}_{25}\text{H}_{24}\text{NO}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 402.1528, found 402.1518.

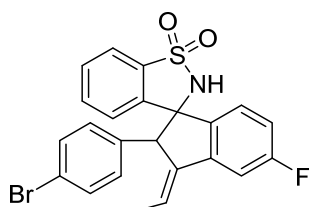


(E)-2'-(3,4-Dichlorophenyl)-3'-ethylidene-2',3'-dihydro-2H-spiro[benzo[d]isothiazole-3,1'-indene] 1,1-dioxide (3am): white solid. M.p. 210 – 211 °C. $^1\text{H NMR}$ (400 MHz, DMSO) δ 8.74 (s, 1H), 7.81 (dd, $J = 12.9, 7.8$ Hz, 2H), 7.53 – 7.41 (m, 2H), 7.28 (dt, $J = 19.1, 7.5$ Hz, 3H), 7.00 (s, 1H), 6.91 (d, $J = 7.7$ Hz, 1H), 6.82 (d, $J = 8.0$ Hz, 1H), 6.61 – 6.49 (m, 1H), 6.28 (d, $J = 7.7$ Hz, 1H), 4.71 (s, 1H), 1.52 (d, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, DMSO) δ 171.6, 150.9, 148.7, 142.7, 139.0, 138.3, 137.9, 137.1, 132.2, 131.3, 129.5, 129.1, 129.0, 127.9, 127.8, 126.5, 122.7, 122.5, 122.4, 122.0, 121.9, 121.8, 120.8, 110.5, 61.6, 60.7, 40.5, 39.4, 14.0. **HRMS (ESI)** calcd for $\text{C}_{23}\text{H}_{16}\text{Cl}_2\text{NO}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 440.0279, found 440.0287.



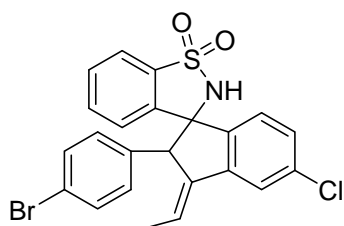
(E)-3'-Ethylidene-2'-(thiophen-2-yl)-2',3'-dihydro-2H-spiro[benzo[d]isothiazole-3,1'-indene] 1,1-dioxide (3an): White solid. M.p. 79 – 80 °C. $^1\text{H NMR}$ (400 MHz, DMSO) δ

8.59 (s, 1H), 7.78 (d, $J = 7.7$ Hz, 2H), 7.46 (t, $J = 7.5$ Hz, 2H), 7.26 (ddd, $J = 15.0, 10.7, 4.3$ Hz, 2H), 7.14 (dd, $J = 5.1, 1.1$ Hz, 1H), 6.87 (d, $J = 7.6$ Hz, 1H), 6.69 (dd, $J = 5.1, 3.5$ Hz, 1H), 6.47 (ddd, $J = 14.0, 9.5, 2.7$ Hz, 2H), 6.33 (d, $J = 7.8$ Hz, 1H), 4.90 (s, 1H), 1.61 (d, $J = 6.9$ Hz, 3H) ^{13}C NMR (101 MHz, DMSO) δ 142.4, 142.2, 141.7, 141.4, 140.7, 136.9, 131.7, 129.9, 129.3, 128.8, 126.5, 125.9, 125.6, 125.3, 124.7, 120.0, 119.8, 119.7, 74.7, 54.9, 14.8. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{18}\text{NO}_2\text{S}_2^+$ $[\text{M}+\text{H}]^+$ 380.0779, found 380.0773.



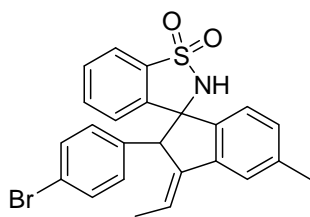
(E)-2'-(4-Bromophenyl)-3'-ethylidene-5'-fluoro-2',3'-dihydro-2H-

spiro[benzo[*d*]isothiazole-3,1'-indene] 1,1-dioxide (3bd): white solid. M.p. 221 – 222 °C. ^1H NMR (400 MHz, DMSO) δ 8.67 (s, 1H), 7.76 (d, $J = 7.7$ Hz, 1H), 7.67 (d, $J = 9.4$ Hz, 1H), 7.42 (t, $J = 7.2$ Hz, 1H), 7.16 (dt, $J = 17.4, 8.2$ Hz, 4H), 6.93 – 6.85 (m, 1H), 6.76 (s, 2H), 6.58 (q, $J = 6.8$ Hz, 1H), 6.25 (d, $J = 7.8$ Hz, 1H), 4.70 (s, 1H), 1.50 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 164.2 (d, $J = 245.0$ Hz), 145.3, 140.5 (d, $J = 3.1$ Hz), 139.2, 138.9, 137.3, 132.2, 131.4, 129.8, 128.2 (d, $J = 9.5$ Hz), 126.4, 121.9, 120.4, 120.2, 116.7 (d, $J = 23.9$ Hz), 107.2, 107.0, 74.5, 60.0, 15.4. ^{19}F NMR (376 MHz, DMSO) δ -111.98. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{18}\text{BrFNO}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 470.0226, found 470.0213.



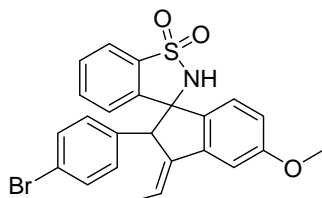
(E)-2'-(4-Bromophenyl)-5'-chloro-3'-ethylidene-2',3'-dihydro-2H-

spiro[benzo[*d*]isothiazole-3,1'-indene] 1,1-dioxide (3cd): White solid. M.p. 222 – 223 °C. ^1H NMR (400 MHz, DMSO) δ 8.72 (s, 1H), 7.93 (d, $J = 1.9$ Hz, 1H), 7.77 (d, $J = 7.7$ Hz, 1H), 7.47 – 7.39 (m, 1H), 7.37 – 7.05 (m, 4H), 6.88 (d, $J = 8.2$ Hz, 1H), 6.77 (d, $J = 5.7$ Hz, 2H), 6.62 (qd, $J = 6.9, 1.8$ Hz, 1H), 6.27 (d, $J = 7.8$ Hz, 1H), 4.70 (s, 1H), 1.50 (d, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 144.3, 141.2, 140.2, 139.6, 138.5, 136.8, 135.0, 131.7, 130.9, 129.4, 128.8, 127.5, 125.9, 121.6, 120.0, 119.9, 119.8, 74.0, 59.2, 15.0. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{18}\text{BrNO}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 485.9930, found 485.9905.



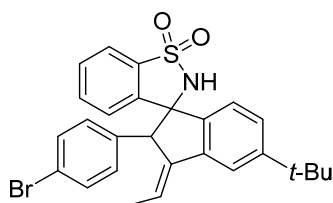
(E)-2'-(4-Bromophenyl)-3'-ethylidene-5'-methyl-2',3'-dihydro-2H-

spiro[benzo[d]isothiazole-3,1'-indene] 1,1-dioxide (3dd): White solid. M.p. 203 – 205 °C. $^1\text{H NMR}$ (400 MHz, DMSO) δ 8.57 (s, 1H), 7.74 (d, $J = 7.7$ Hz, 1H), 7.60 (s, 1H), 7.41 (t, $J = 7.3$ Hz, 1H), 7.34 – 7.07 (m, 4H), 6.82 – 6.68 (m, 3H), 6.45 (tt, $J = 7.1, 3.4$ Hz, 1H), 6.20 (d, $J = 7.8$ Hz, 1H), 4.67 (s, 1H), 2.38 (s, 3H), 1.49 (d, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, DMSO) δ 143.0, 141.4, 141.3, 140.3, 140.0, 139.6, 137.4, 132.0, 131.4, 130.4, 129.6, 126.4, 125.9, 120.6, 120.3, 120.1, 119.4, 74.9, 59.9, 21.6, 15.4. **HRMS (ESI)** calcd for $\text{C}_{24}\text{H}_{21}\text{BrNO}_2\text{S}^+ [\text{M}+\text{H}]^+$ 466.0476, found 466.0474.



(E)-2'-(4-Bromophenyl)-3'-ethylidene-5'-methoxy-2',3'-dihydro-2H-

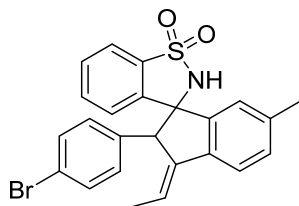
spiro[benzo[d]isothiazole-3,1'-indene] 1,1-dioxide (3ed): White solid. M.p. 203 – 204 °C. $^1\text{H NMR}$ (400 MHz, DMSO) δ 8.57 (s, 1H), 7.74 (d, $J = 7.7$ Hz, 1H), 7.60 (s, 1H), 7.41 (t, $J = 7.3$ Hz, 1H), 7.34 – 7.07 (m, 4H), 6.82 – 6.68 (m, 3H), 6.45 (tt, $J = 7.1, 3.4$ Hz, 1H), 6.20 (d, $J = 7.8$ Hz, 1H), 4.67 (s, 1H), 2.38 (s, 3H), 1.49 (d, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, DMSO) δ 143.0, 141.4, 141.3, 140.3, 140.0, 139.6, 137.4, 132.0, 131.4, 130.4, 129.6, 126.4, 126.0, 120.6, 120.3, 120.1, 119.4, 74.9, 59.9, 21.6, 15.4. **HRMS (ESI)** calcd for $\text{C}_{24}\text{H}_{21}\text{BrNO}_3\text{S}^+ [\text{M}+\text{H}]^+$ 482.0426, found 482.0423.



(E)-2'-(4-Bromophenyl)-5'-(tert-butyl)-3'-ethylidene-2',3'-dihydro-2H-

spiro[benzo[d]isothiazole-3,1'-indene] 1,1-dioxide (3fd): White solid. M.p. 208 – 209 °C. $^1\text{H NMR}$ (400 MHz, DMSO) δ 8.58 (s, 1H), 7.80 (d, $J = 1.3$ Hz, 1H), 7.75 (d, $J = 7.8$ Hz, 1H), 7.44 – 7.14 (m, 5H), 6.79 (dd, $J = 16.8, 8.0$ Hz, 3H), 6.60 – 6.49 (m, 1H), 6.23 (d, $J = 7.8$ Hz, 1H), 4.69 (s, 1H), 1.50 (d, $J = 7.1$ Hz, 3H), 1.35 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, DMSO) δ

153.2, 142.6, 141.4, 141.2, 140.5, 139.6, 137.4, 132.0, 131.4, 129.6, 127.0, 126.5, 125.7, 120.3, 120.0, 119.4, 116.7, 74.8, 60.0, 35.3, 31.7, 15.4. **HRMS (ESI)** calcd for $C_{27}H_{27}BrNO_2S^+$ $[M+H]^+$ 508.0946, found 508.0933.

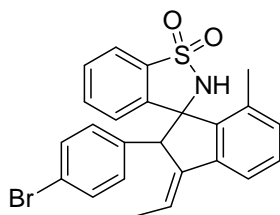


(E)-2'-(4-Bromophenyl)-3'-ethylidene-6'-methyl-2',3'-dihydro-2H-

spiro[benzo[d]isothiazole-3,1'-indene] 1,1-dioxide (3gd): White solid. M.p. 120 – 121 °C.

1H NMR (400 MHz, DMSO) δ 8.61 (s, 1H), 7.74 (d, $J = 7.7$ Hz, 1H), 7.69 (d, $J = 8.0$ Hz, 1H), 7.41 (t, $J = 7.5$ Hz, 1H), 7.34 – 7.14 (m, 4H), 6.75 (d, $J = 6.1$ Hz, 2H), 6.67 (s, 1H), 6.46 – 6.36 (m, 1H), 6.23 (d, $J = 7.8$ Hz, 1H), 4.65 (s, 1H), 2.24 (s, 3H), 1.48 (d, $J = 7.0$ Hz, 3H).

^{13}C NMR (101 MHz, DMSO) δ 142.8, 140.6, 139.8, 139.0, 138.5, 136.8, 131.6, 131.0, 130.8, 129.2, 126.0, 125.7, 119.8, 119.6, 118.1, 74.6, 59.3, 20.9, 14.9. **HRMS (ESI)** calcd for $C_{24}H_{21}BrNO_2S^+$ $[M+H]^+$ 466.0476, found 466.0440.

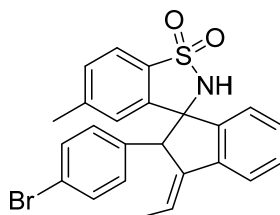


(E)-2'-(4-Bromophenyl)-3'-ethylidene-7'-methyl-2',3'-dihydro-2H-

spiro[benzo[d]isothiazole-3,1'-indene] 1,1-dioxide (3hd): White solid. M.p. 93 – 94 °C. **1H**

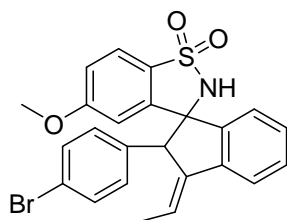
NMR (400 MHz, DMSO) δ 8.70 (s, 1H), 7.75 (d, $J = 7.7$ Hz, 1H), 7.65 (d, $J = 7.8$ Hz, 1H), 7.45 – 7.29 (m, 3H), 7.21 – 7.02 (m, 3H), 6.82 (d, $J = 8.3$ Hz, 1H), 6.72 (d, $J = 7.9$ Hz, 1H), 6.46 (qd, $J = 6.9, 1.9$ Hz, 1H), 6.21 (d, $J = 7.9$ Hz, 1H), 4.63 (s, 1H), 1.56 (s, 3H), 1.46 (d, $J = 7.1$ Hz, 3H).

^{13}C NMR (101 MHz, DMSO) δ 143.2, 141.6, 140.5, 139.8, 139.7, 136.7, 136.2, 132.3, 132.0, 131.6, 131.3, 130.5, 129.6, 129.3, 126.2, 120.6, 120.0, 119.3, 118.1, 75.0, 60.2, 17.9, 15.4. **HRMS (ESI)** calcd for $C_{24}H_{21}BrNO_2S^+$ $[M+H]^+$ 466.0476, found 466.0460.



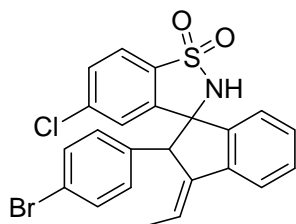
(E)-2'-(4-Bromophenyl)-3'-ethylidene-5-methyl-2',3'-dihydro-2H-

spiro[benzo[*d*]isothiazole-3,1'-indene] 1,1-dioxide (3id): White solid. M.p. 114 – 116 °C. ¹H NMR (400 MHz, DMSO) δ 8.57 (s, 1H), 7.80 (d, $J = 7.6$ Hz, 1H), 7.61 (d, $J = 7.8$ Hz, 1H), 7.46 (t, $J = 7.0$ Hz, 1H), 7.36 – 7.05 (m, 4H), 6.89 (d, $J = 7.6$ Hz, 1H), 6.73 (s, 2H), 6.51 (q, $J = 6.5$ Hz, 1H), 5.91 (s, 1H), 4.64 (s, 1H), 1.98 (s, 3H), 1.52 (d, $J = 6.5$ Hz, 3H). ¹³C NMR (101 MHz, DMSO) δ 143.0, 142.8, 142.4, 141.4, 141.1, 139.5, 134.7, 131.2, 130.4, 130.3, 129.4, 126.6, 126.3, 120.4, 120.1, 120.1, 119.8, 75.0, 59.7, 21.1, 15.5. HRMS (ESI) calcd for C₂₄H₂₁BrNO₂S⁺ [M+H]⁺ 466.0476, found 466.0460.



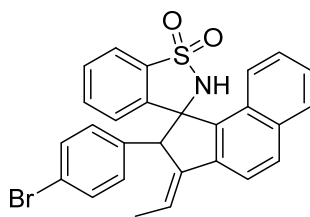
(E)-2'-(4-Bromophenyl)-3'-ethylidene-5-methoxy-2',3'-dihydro-2H-

spiro[benzo[*d*]isothiazole-3,1'-indene] 1,1-dioxide (3jd): White solid. M.p. 225 – 227 °C. ¹H NMR (400 MHz, DMSO) δ 8.51 (s, 1H), 7.80 (d, $J = 7.8$ Hz, 1H), 7.68 (d, $J = 8.6$ Hz, 1H), 7.51 – 7.44 (m, 1H), 7.28 (dd, $J = 27.3, 19.9$ Hz, 3H), 7.00 – 6.89 (m, 2H), 6.76 (s, 2H), 6.51 (qd, $J = 6.9, 1.6$ Hz, 1H), 5.52 (d, $J = 2.2$ Hz, 1H), 4.67 (s, 1H), 1.98 (s, 3H), 1.53 (d, $J = 7.1$ Hz, 3H). ¹³C NMR (101 MHz, DMSO) δ 161.6, 143.2, 142.4, 142.3, 140.8, 139.1, 131.0, 130.0, 129.5, 128.9, 125.9, 121.3, 119.9, 119.7, 119.4, 116.7, 109.3, 74.3, 59.2, 55.30 14.9. HRMS (ESI) calcd for C₂₄H₂₁BrNO₃S⁺ [M+H]⁺ 482.0426, found 482.0419.

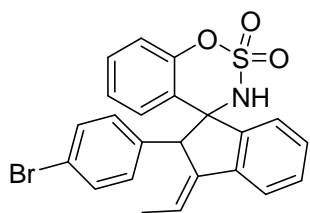


(E)-2'-(4-Bromophenyl)-5-chloro-3'-ethylidene-2',3'-dihydro-2H-

spiro[benzo[*d*]isothiazole-3,1'-indene] 1,1-dioxide (3kd): White solid. M.p. 225 – 226 °C. ¹H NMR (400 MHz, DMSO) δ 8.85 (s, 1H), 7.83 (t, $J = 8.9$ Hz, 2H), 7.54 – 7.45 (m, 2H), 7.43 – 7.09 (m, 3H), 6.94 (d, $J = 7.7$ Hz, 1H), 6.76 (s, 2H), 6.52 (qd, $J = 6.9, 1.6$ Hz, 1H), 6.09 (d, $J = 1.7$ Hz, 1H), 4.69 (s, 1H), 1.53 (d, $J = 7.1$ Hz, 3H). ¹³C NMR (101 MHz, DMSO) δ 143.0, 142.4, 141.6, 140.4, 138.8, 136.7, 135.8, 131.0, 130.2, 129.5, 129.1, 125.8, 125.6, 121.8, 120.0, 119.7, 74.3, 59.2, 14.9. HRMS (ESI) calcd for C₂₃H₁₈BrClNO₂S⁺ [M+H]⁺ 485.9930, found 485.9915.



(E)-2'-(4-Bromophenyl)-3'-ethylidene-2',3'-dihydro-2H-spiro[benzo[*d*]isothiazole-3,1'-cyclopenta[*a*]naphthalene] 1,1-dioxide (3ld): White solid. M.p. 224 – 225 °C. ¹H NMR (400 MHz, DMSO) δ 8.97 (s, 1H), 8.06 (d, J = 8.6 Hz, 1H), 8.01 – 7.93 (m, 2H), 7.83 (d, J = 7.7 Hz, 1H), 7.40 (dt, J = 14.6, 7.4 Hz, 2H), 7.32 – 7.24 (m, 1H), 7.23 – 7.07 (m, 3H), 6.98 (d, J = 8.5 Hz, 1H), 6.86 (d, J = 8.3 Hz, 2H), 6.68 – 6.52 (m, 1H), 6.18 (d, J = 7.8 Hz, 1H), 4.79 (s, 1H), 1.50 (d, J = 7.1 Hz, 3H). ¹³C NMR (101 MHz, DMSO) δ 141.9, 141.7, 140.8, 139.4, 135.9, 135.5, 134.7, 132.2, 132.0, 131.3, 129.8, 129.6, 127.2, 126.5, 126.1, 123.6, 120.8, 120.2, 118.7, 75.5, 60.5, 15.5. HRMS (ESI) calcd for C₂₇H₂₁BrNO₂S⁺ [M+H]⁺ 502.0476, found 502.0463.



(E)-2'-(4-bromophenyl)-3'-ethylidene-2',3'-dihydro-3H-spiro[benzo[*e*][1,2,3]oxathiazine-4,1'-indene] 2,2-dioxide (3md): White solid. M.p. 206 – 207 °C. ¹H NMR (400 MHz, DMSO) δ 9.00 (s, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.49 (t, J = 7.4 Hz, 1H), 7.24 (ddd, J = 15.3, 14.1, 8.8 Hz, 4H), 7.08 (d, J = 8.3 Hz, 1H), 6.93 (d, J = 7.7 Hz, 1H), 6.79 (d, J = 8.0 Hz, 2H), 6.65 (t, J = 7.5 Hz, 1H), 6.50 (q, J = 6.8 Hz, 1H), 5.88 (d, J = 7.9 Hz, 1H), 5.27 (s, 1H), 1.53 (d, J = 6.9 Hz, 3H). ¹³C NMR (101 MHz, DMSO) δ 151.7, 144.1, 142.7, 141.3, 139.2, 131.3, 130.7, 130.4, 130.1, 129.0, 127.5, 123.8, 122.5, 120.4, 120.27, 120.2, 118.3, 75.3, 57.2, 15.2. HRMS (ESI) calcd for C₂₃H₁₇BrNO₃S⁺ [M-H]⁺ 466.0113, found 466.0104.

6. Molecular Structures of 3ac and 3al

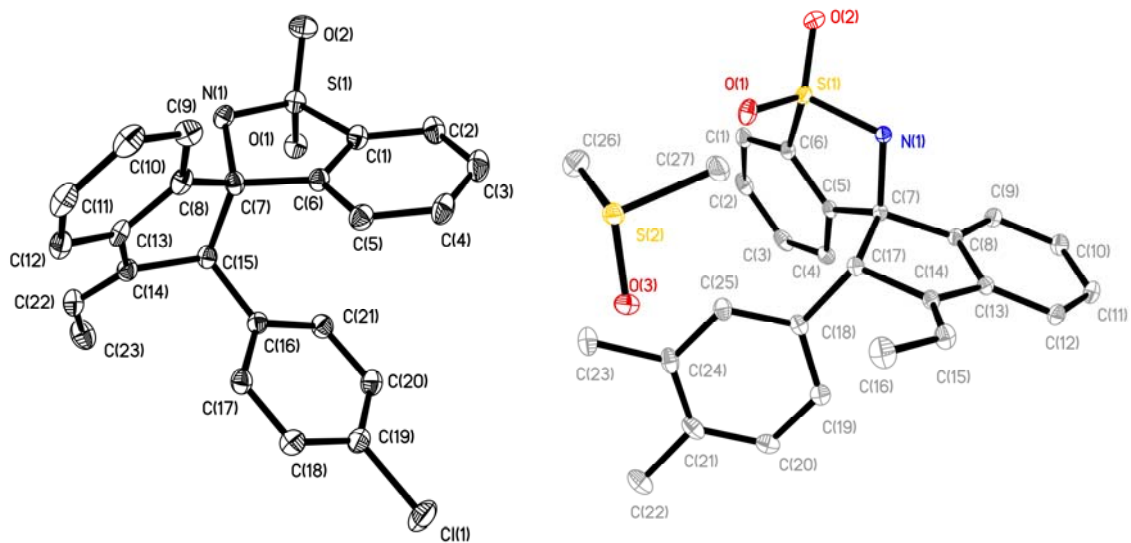
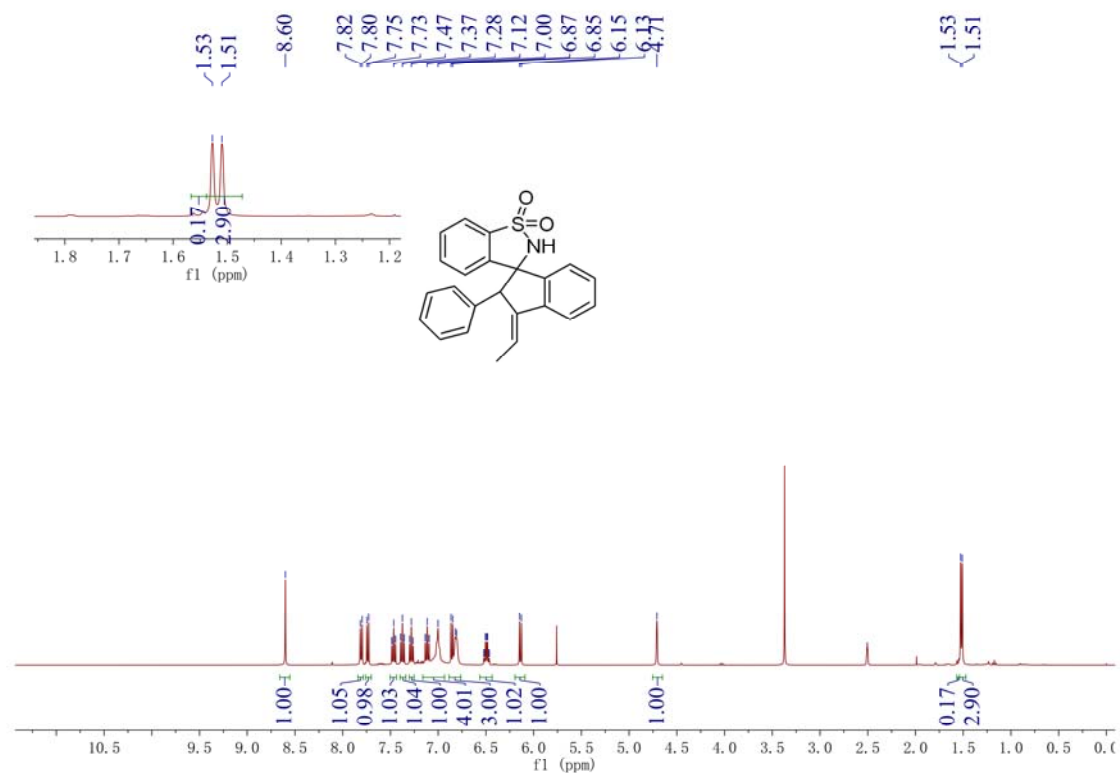


Figure S5. The molecular structures of **3ac** and **3al**.

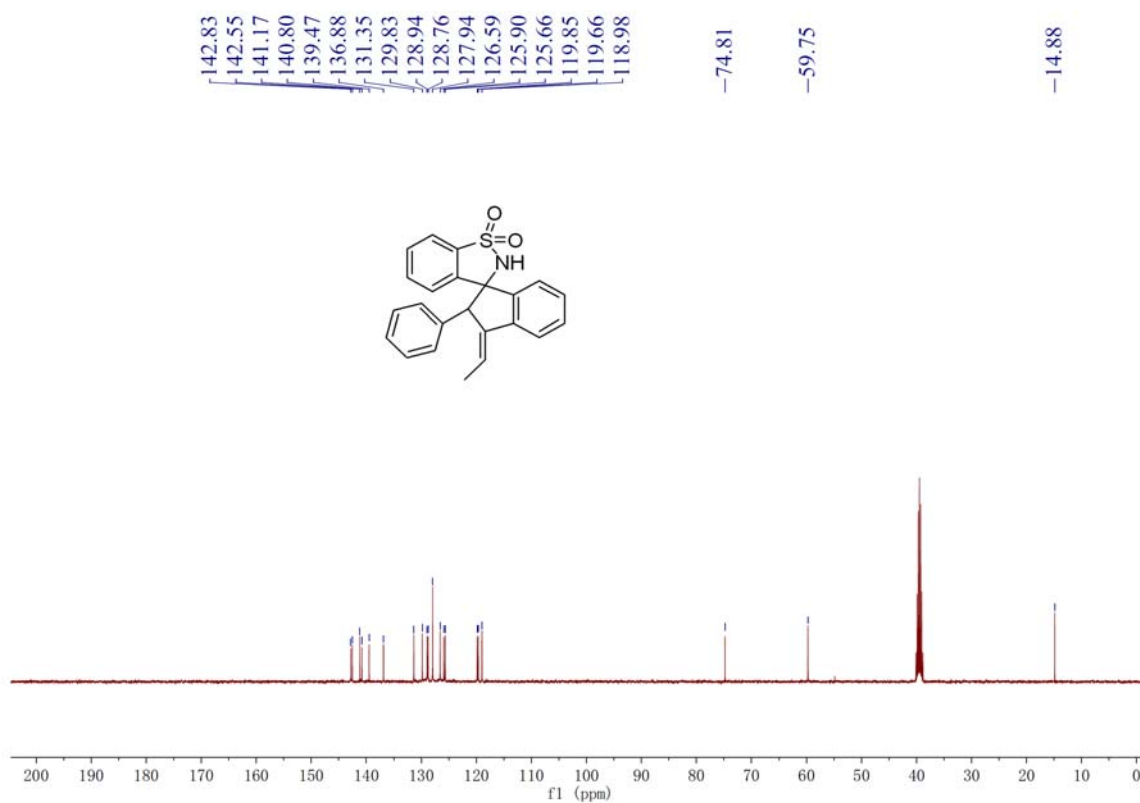
CCDC: 1942883 (3ac), 1951366 (3al)

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

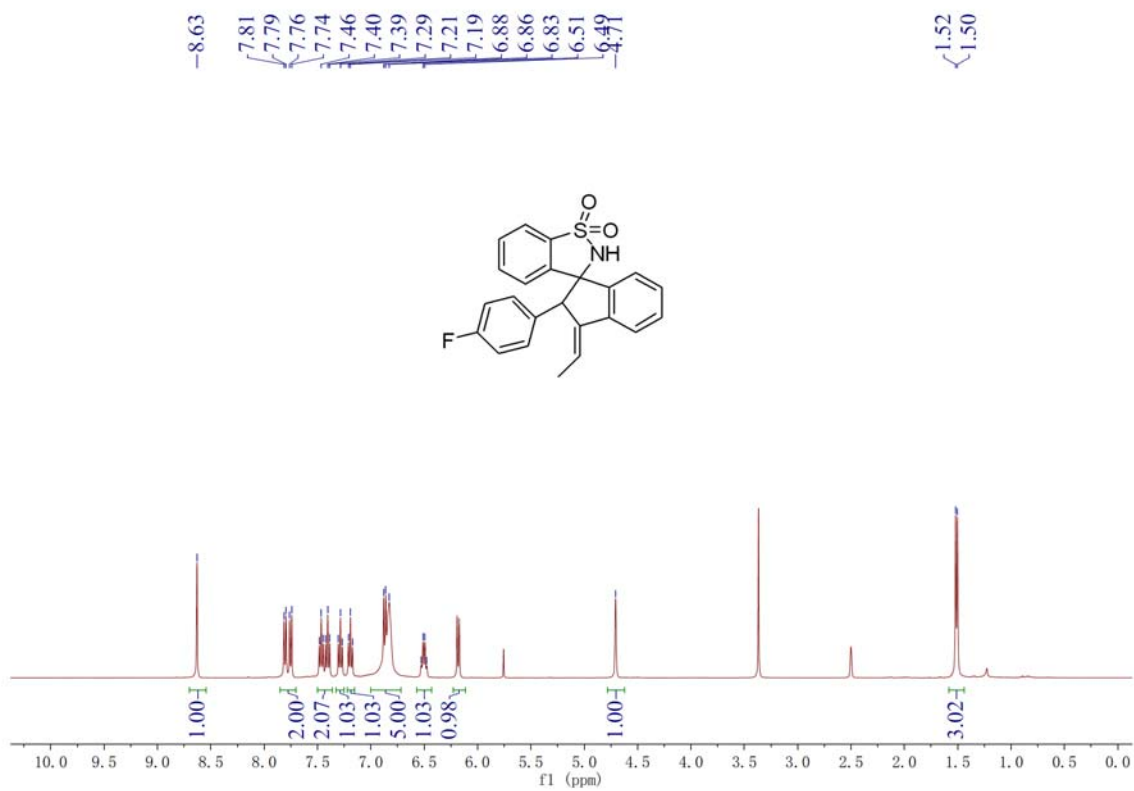
^1H NMR spectrum of **3aa**



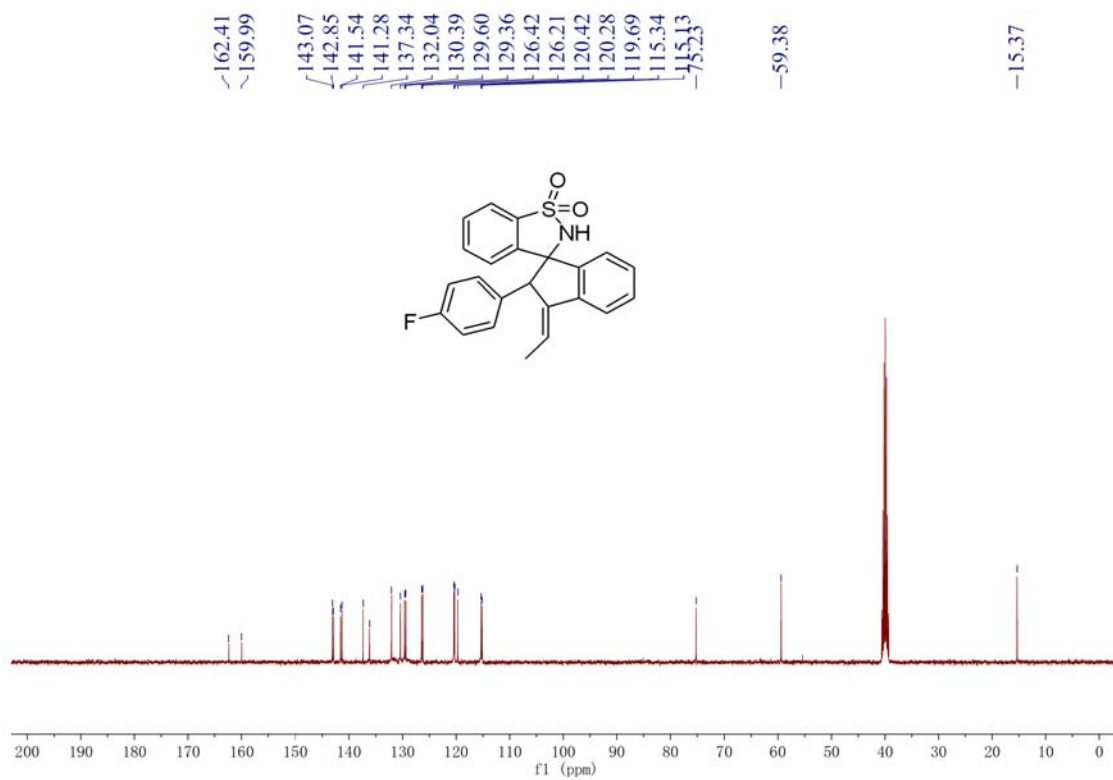
^{13}C NMR spectrum of **3aa**



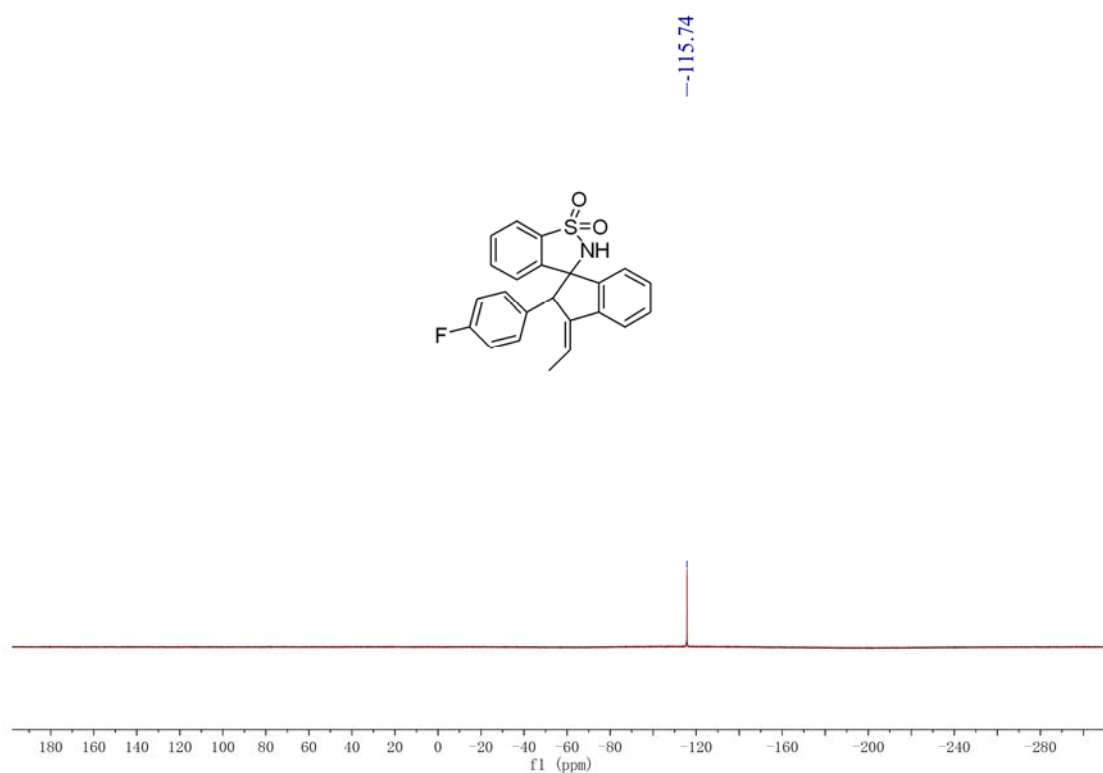
^1H NMR spectrum of **3ab**



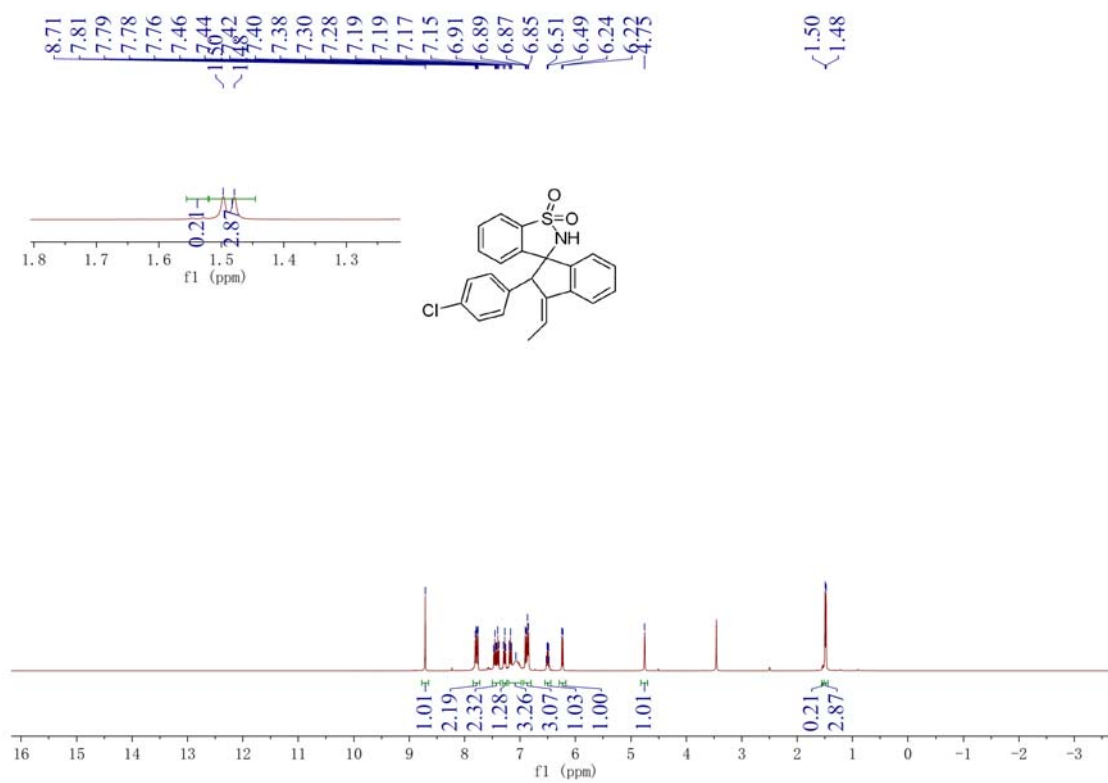
^{13}C NMR spectrum of **3ab**



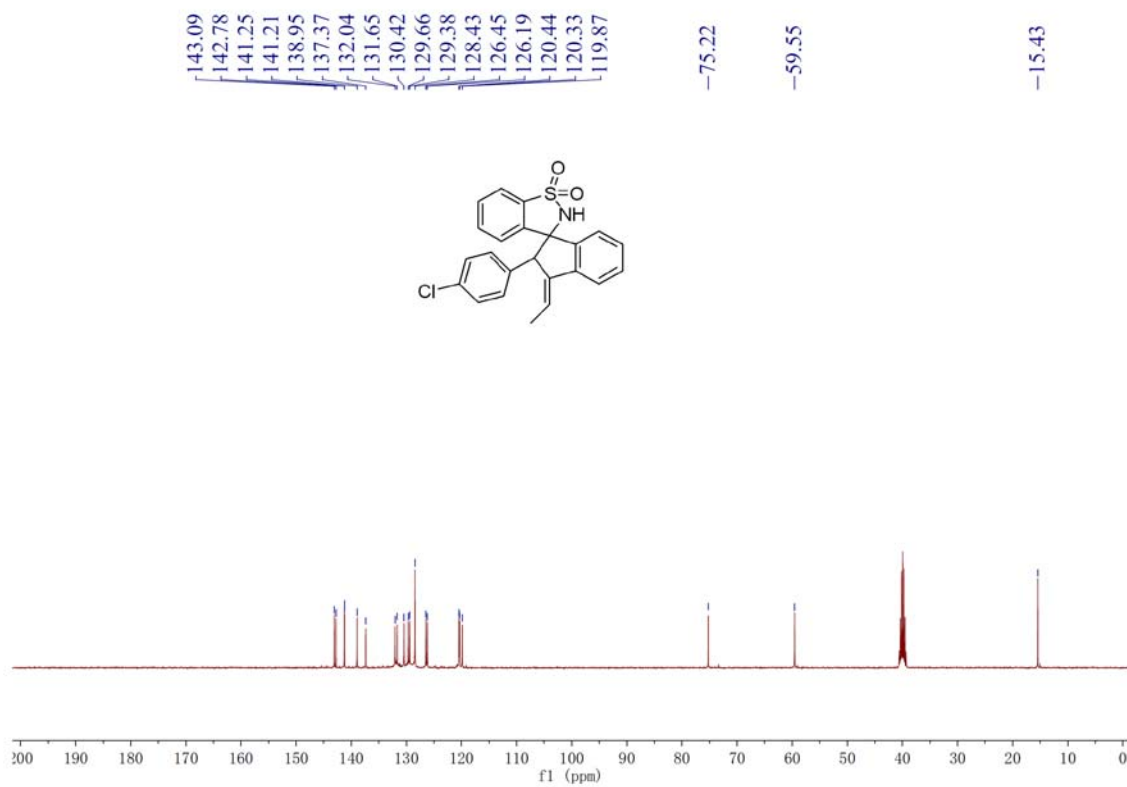
^{19}F NMR spectrum of **3ab**



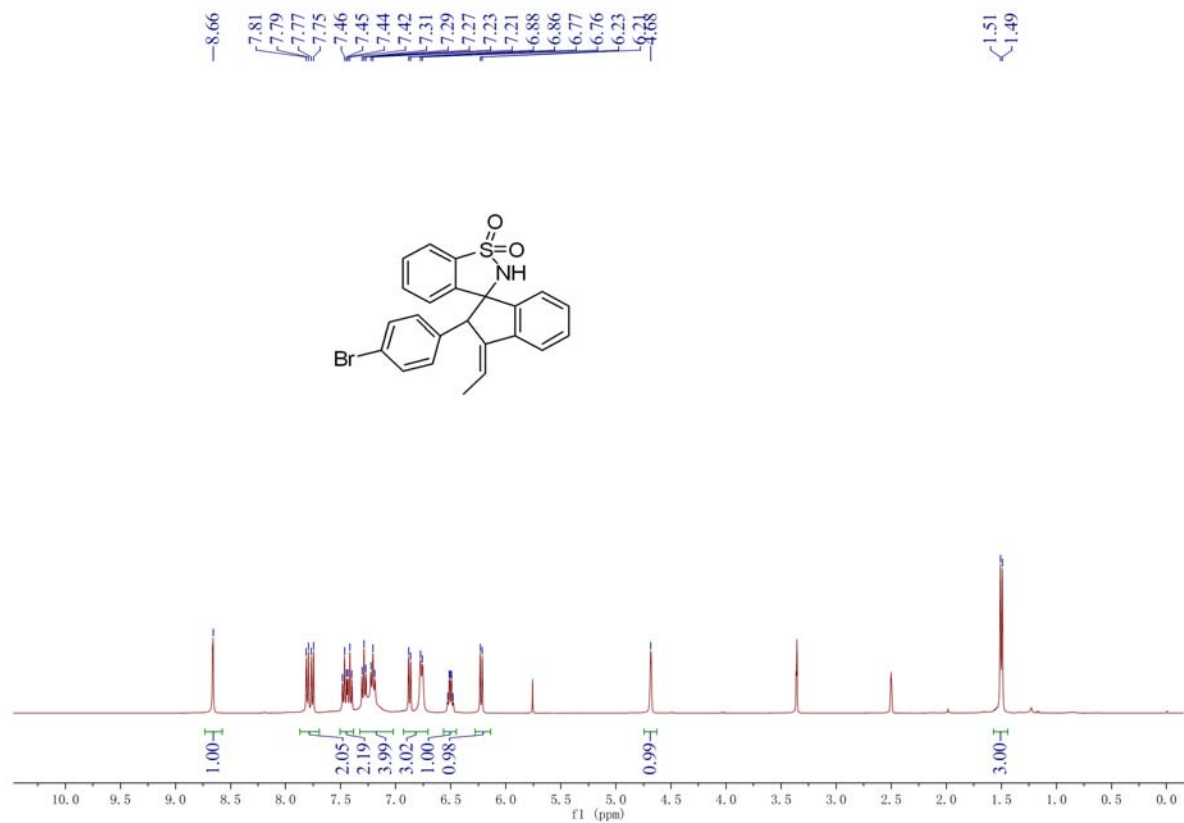
^1H NMR spectrum of **3ac**



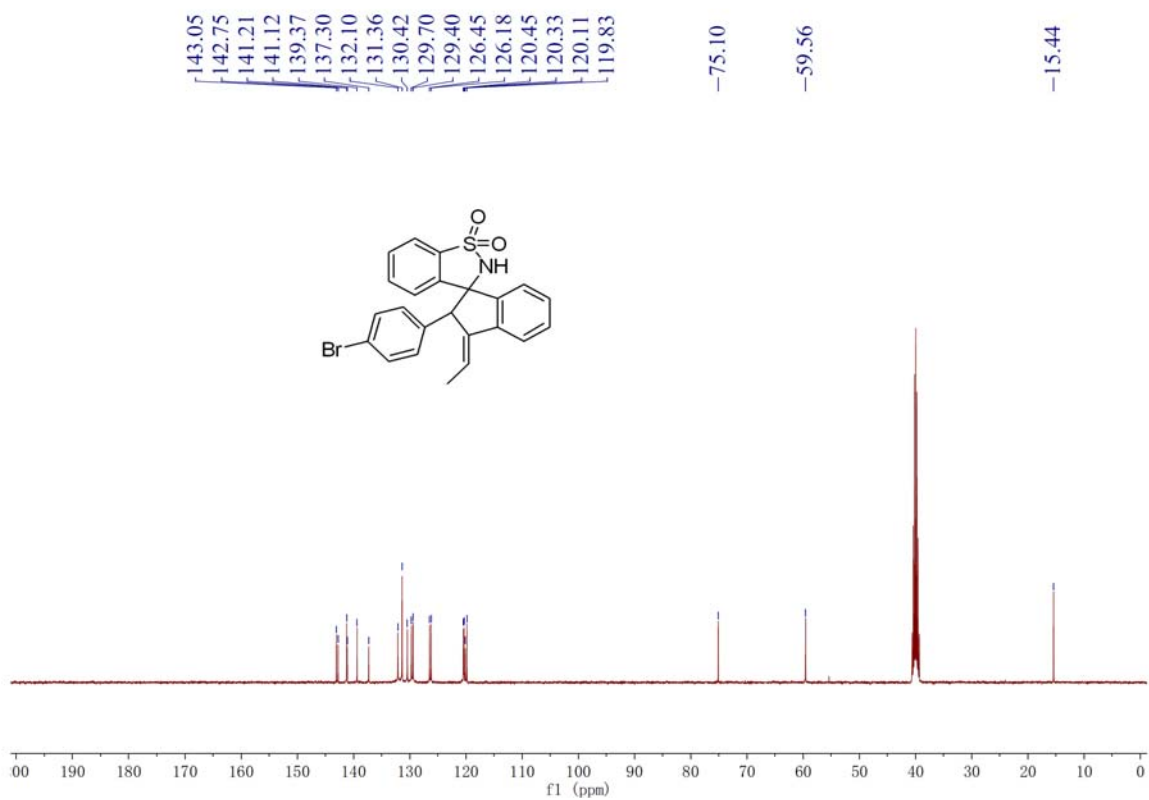
^{13}C NMR spectrum of **3ac**



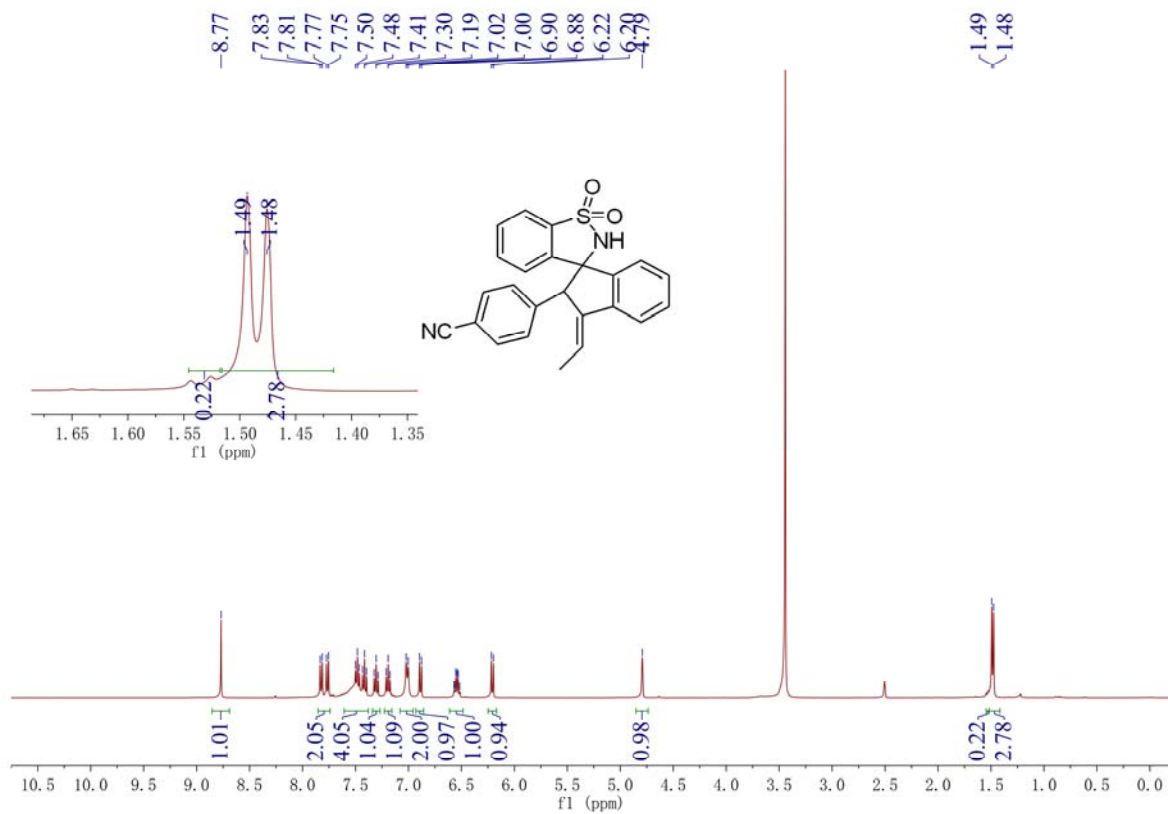
^1H NMR spectrum of **3ad**



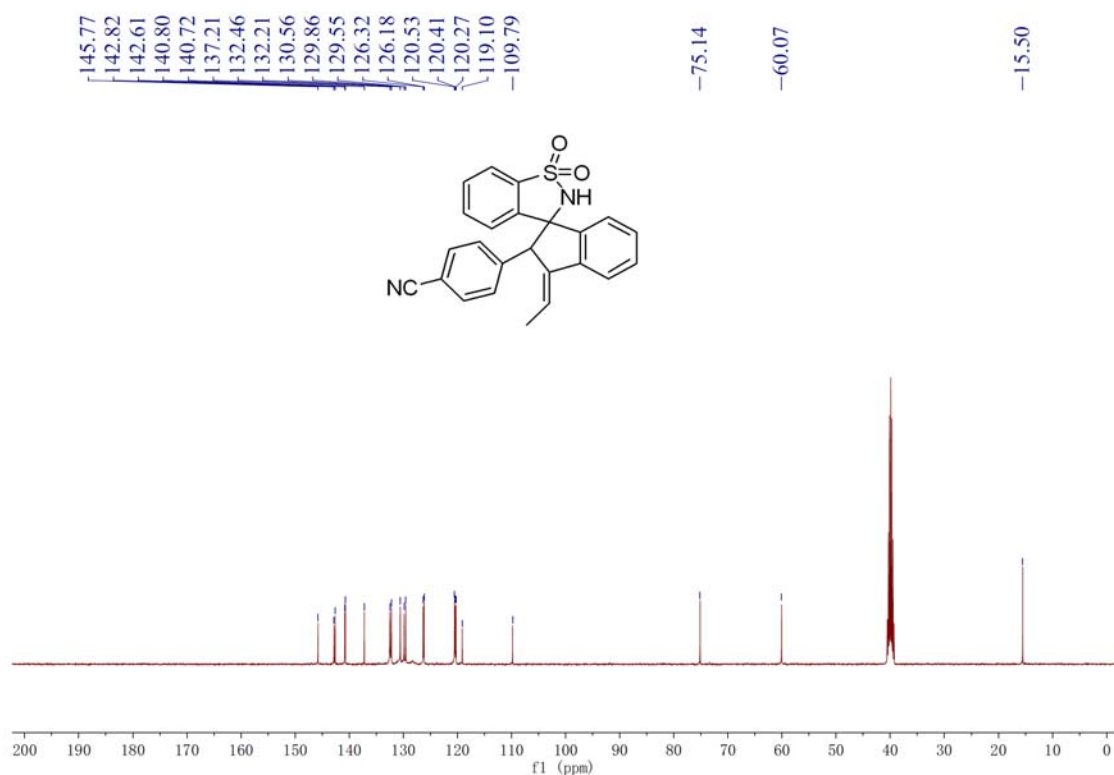
^{13}C NMR spectrum of **3ad**



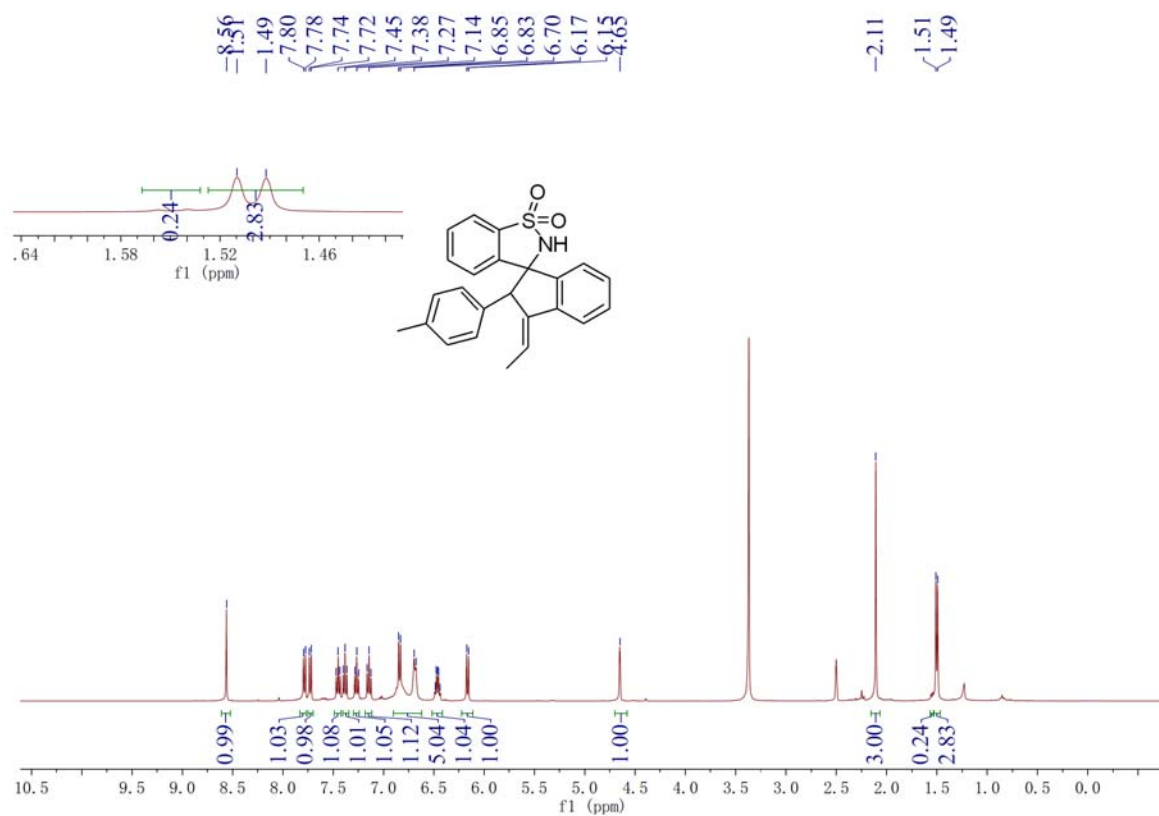
^1H NMR spectrum of **3ae**



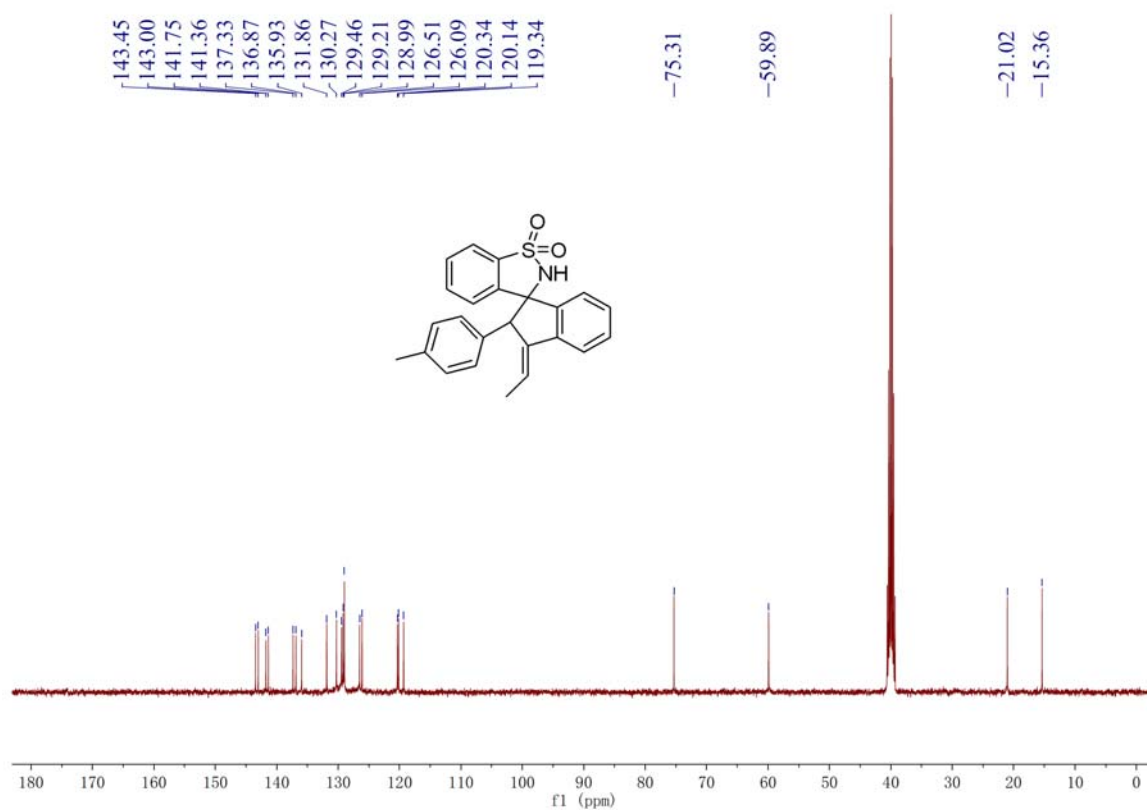
^{13}C NMR spectrum of **3ae**



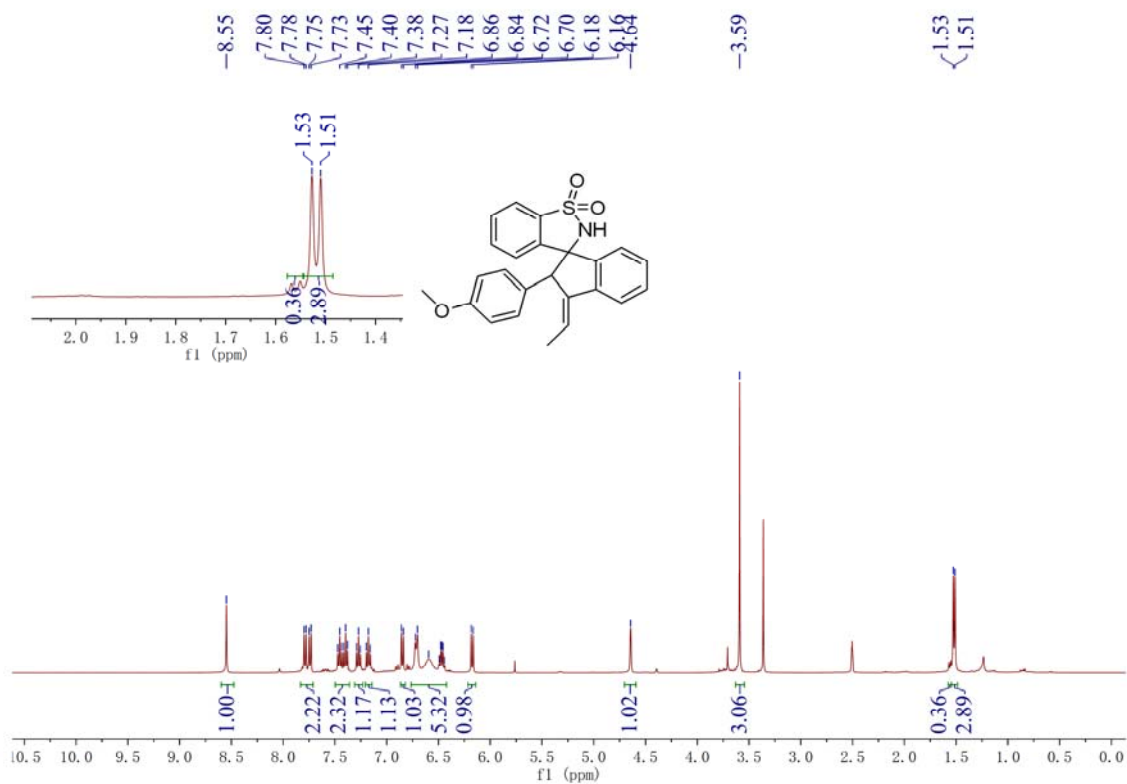
^1H NMR spectrum of **3af**



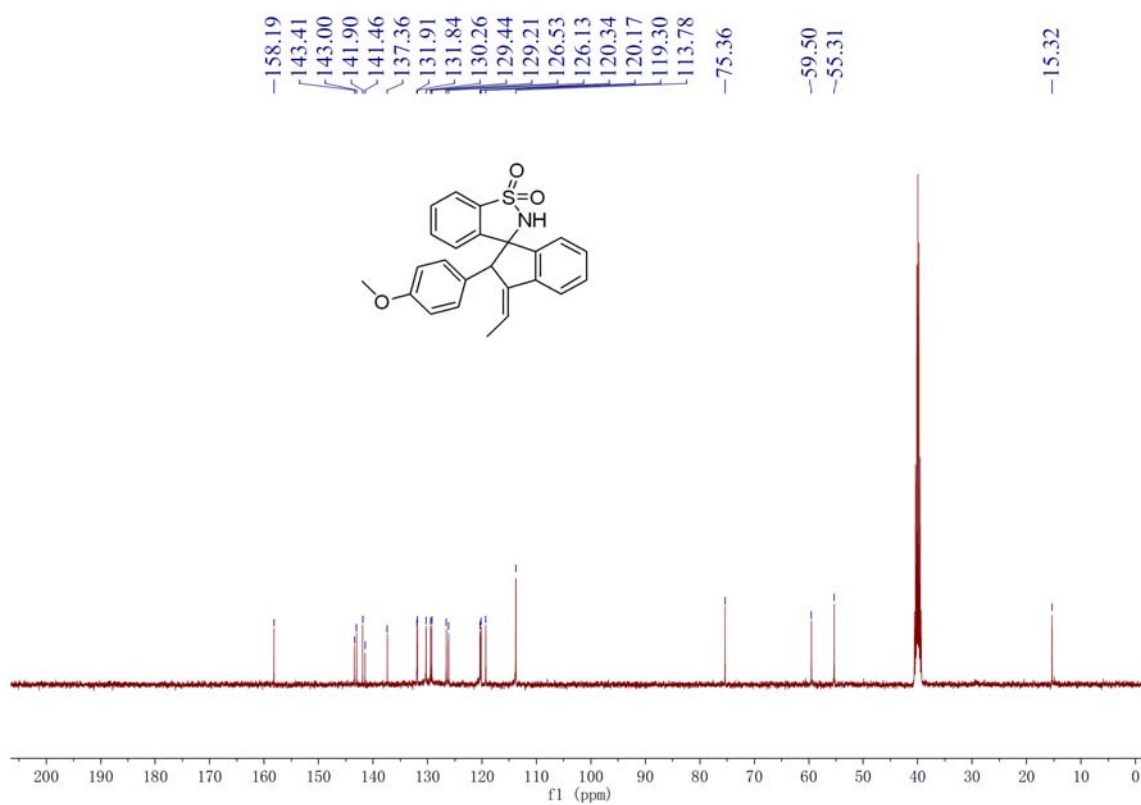
¹³C NMR spectrum of **3af**



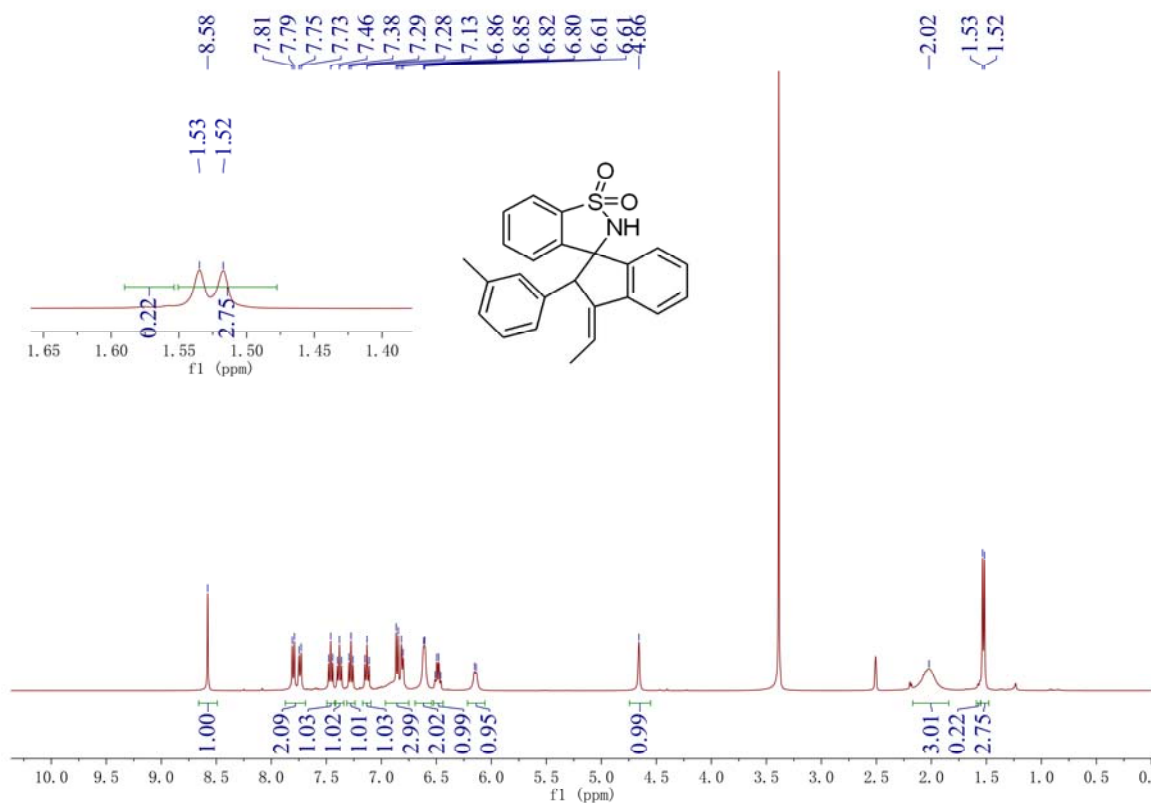
¹H NMR spectrum of **3ag**



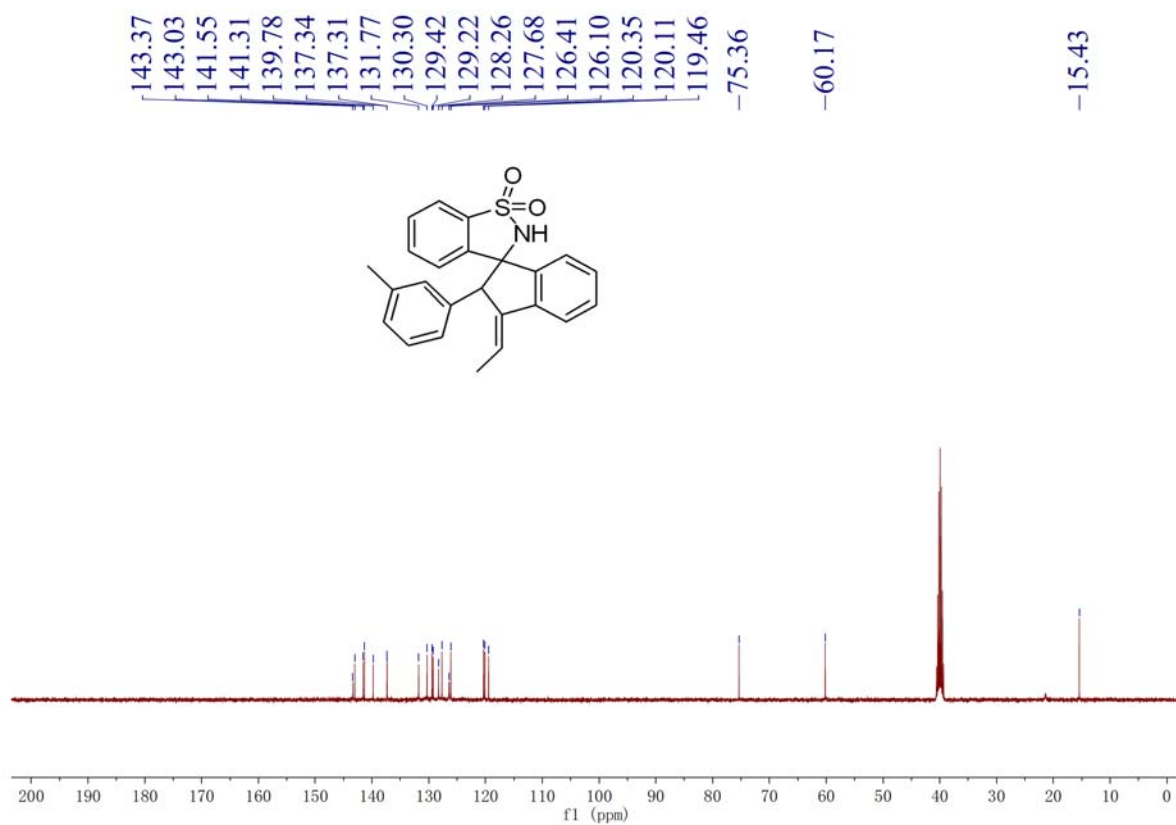
^{13}C NMR spectrum of **3ag**



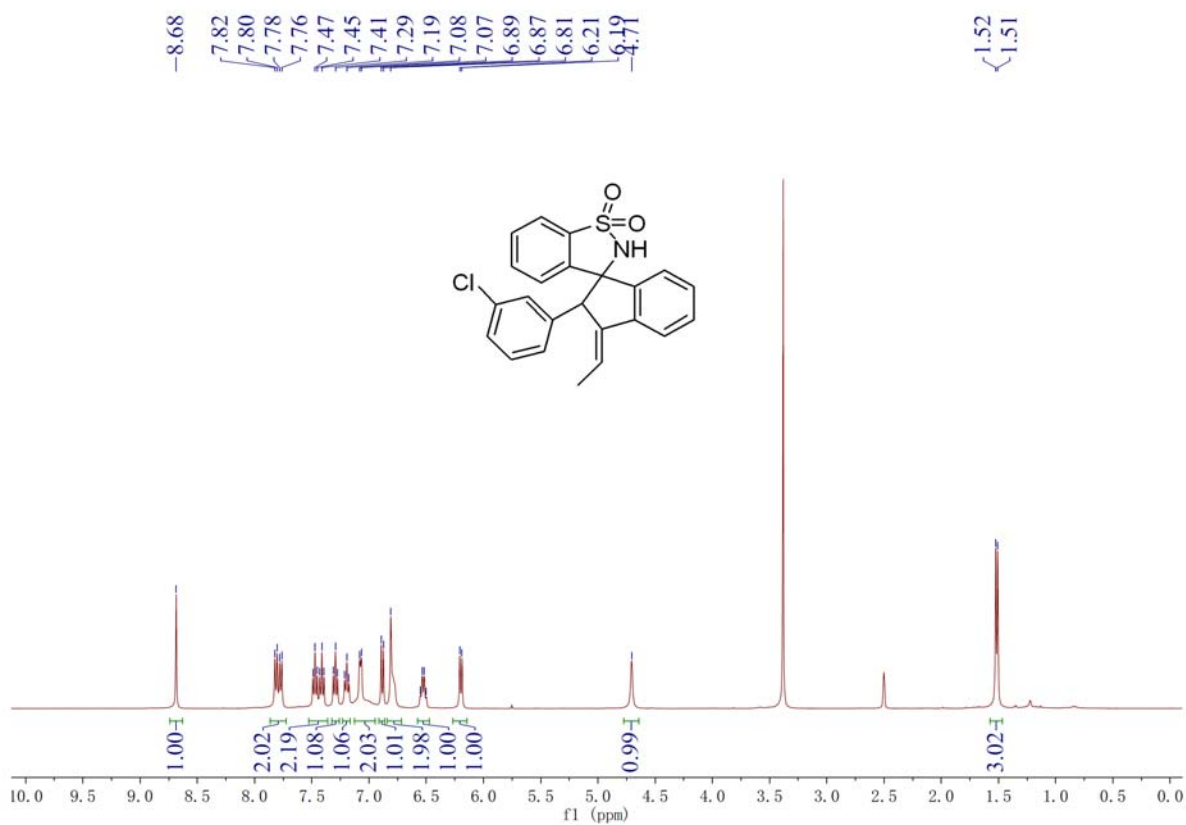
^1H NMR spectrum of **3ah**



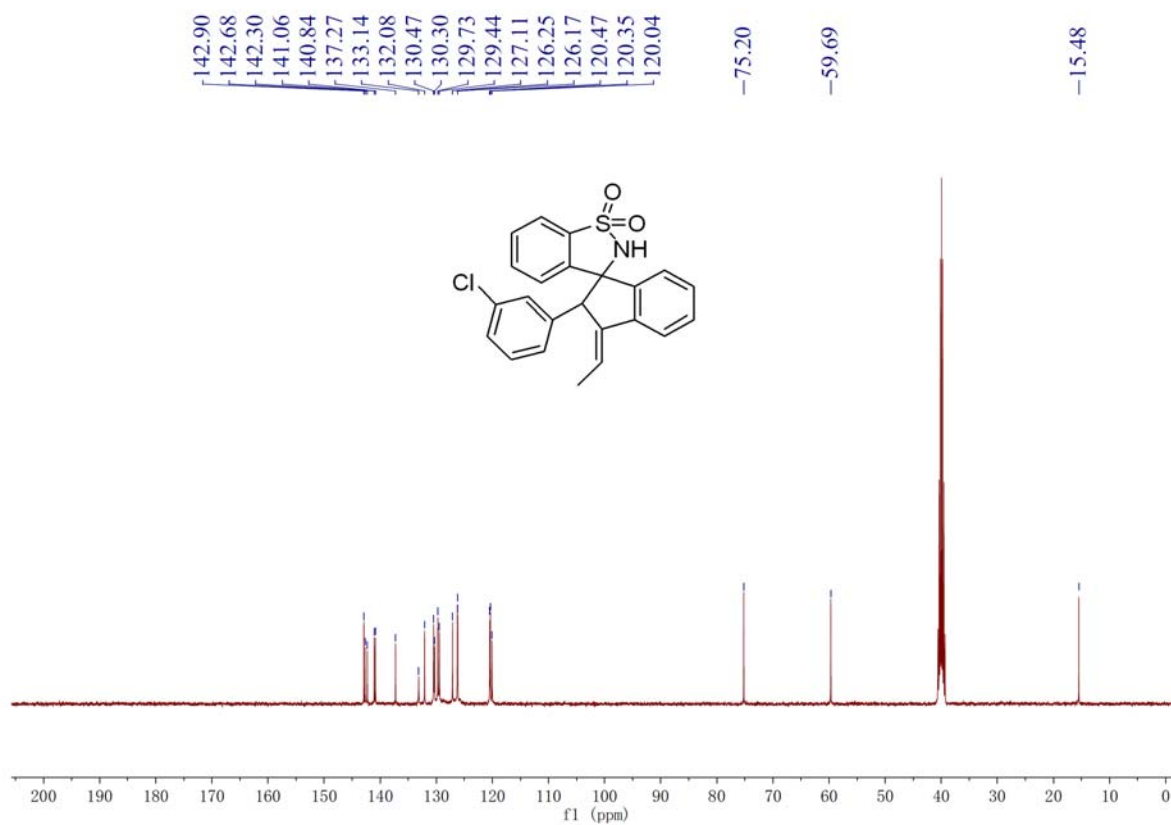
^{13}C NMR spectrum of **3ah**



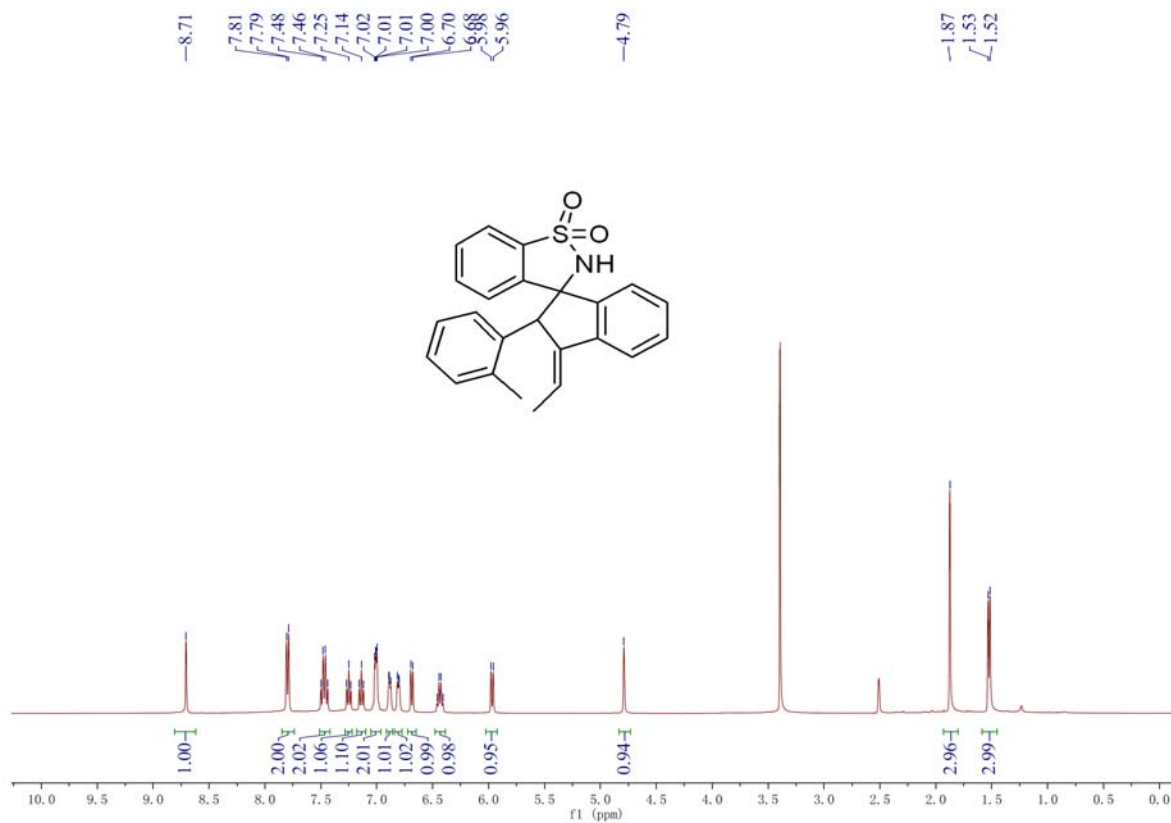
^1H NMR spectrum of **3ai**



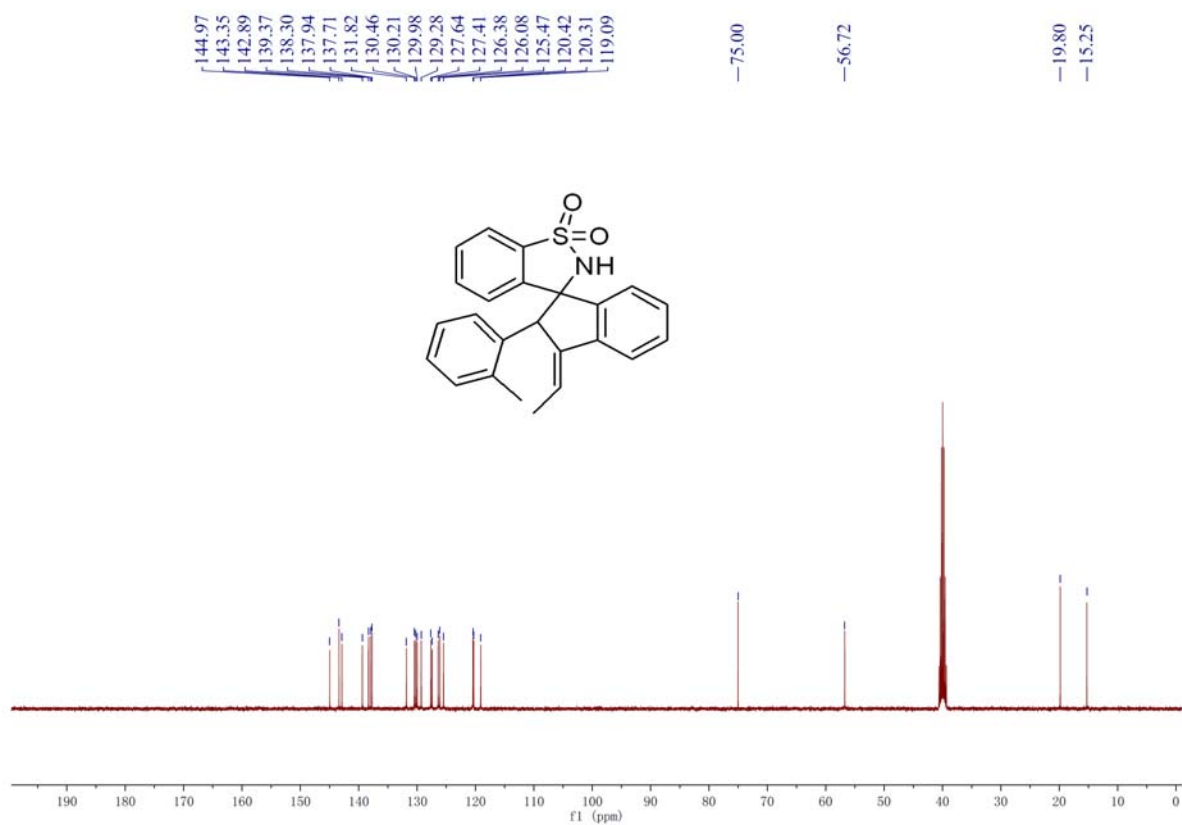
¹³C NMR spectrum of **3ai**



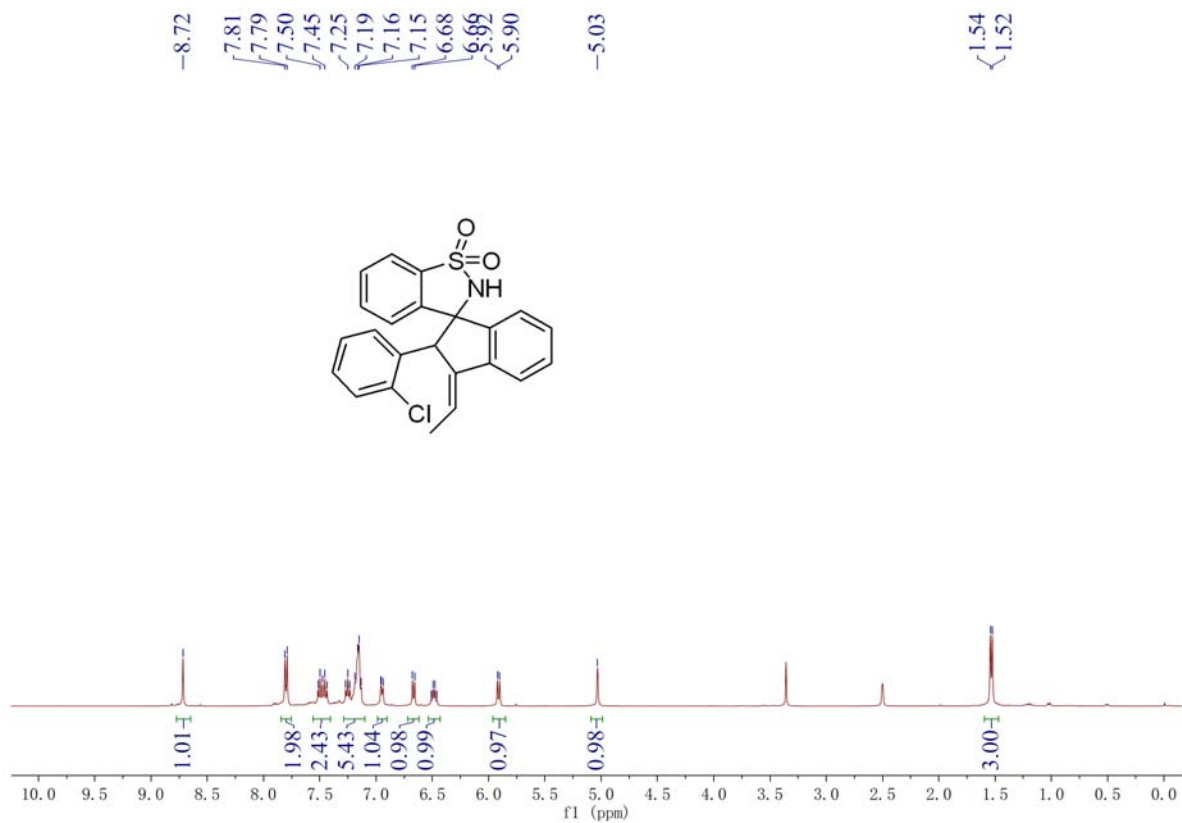
¹H NMR spectrum of **3aj**



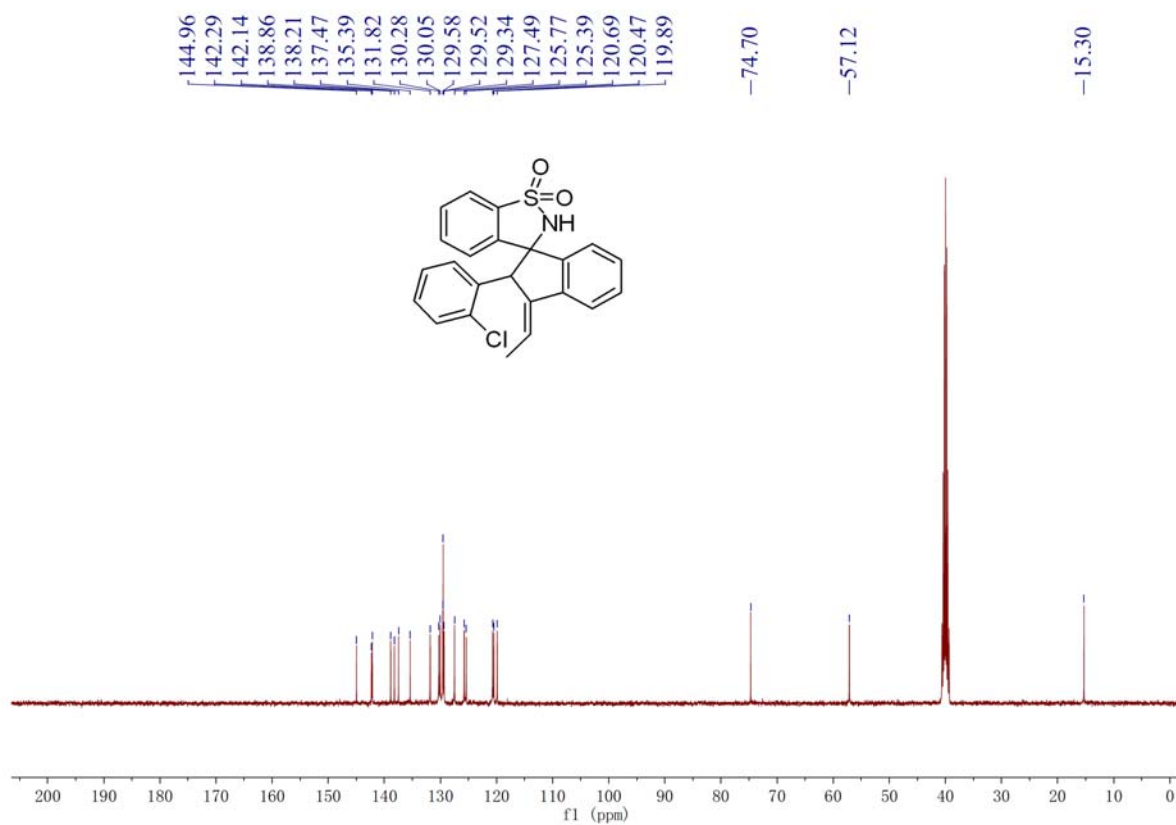
¹³C NMR spectrum of **3aj**



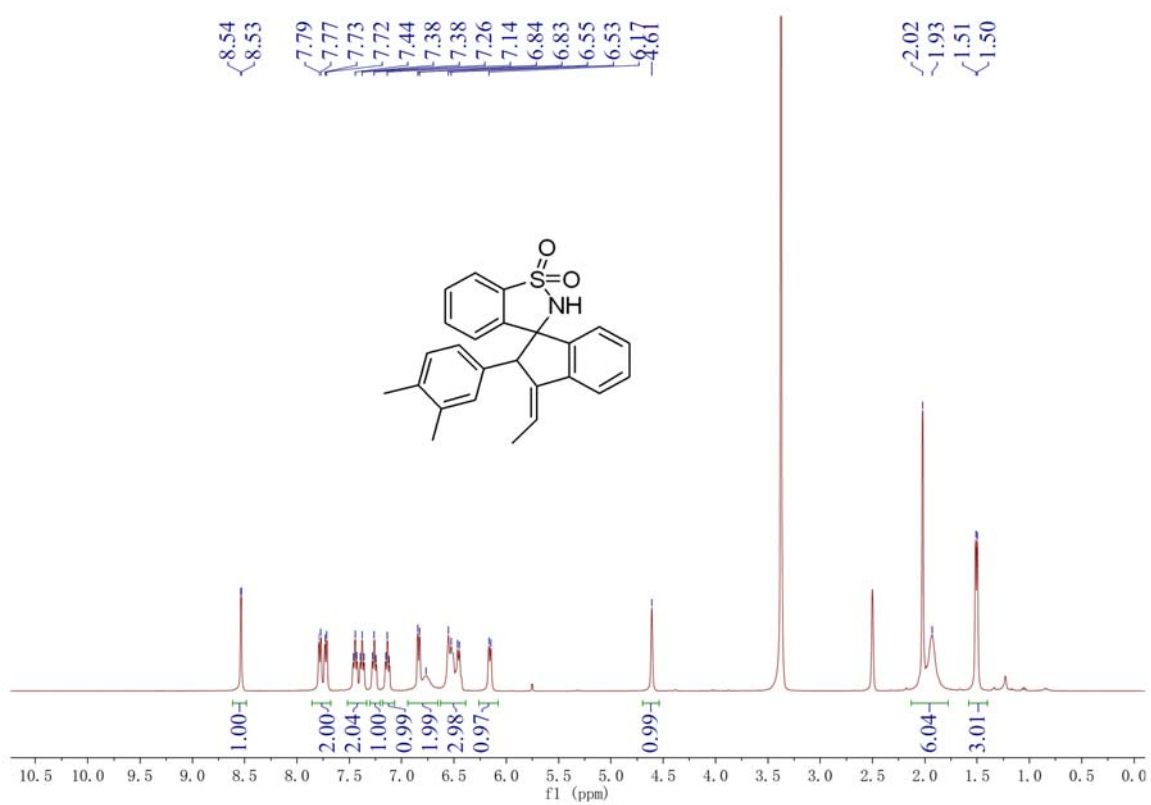
¹H NMR spectrum of **3ak**



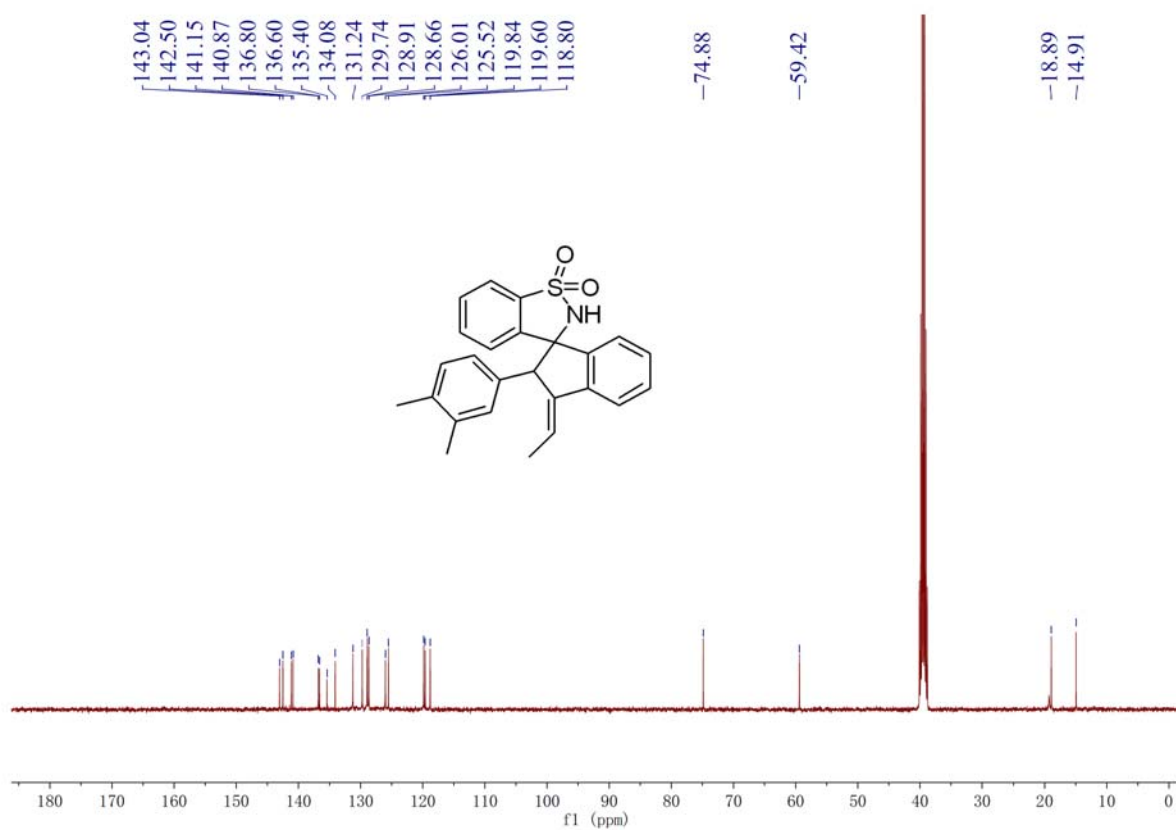
¹³C NMR spectrum of **3ak**



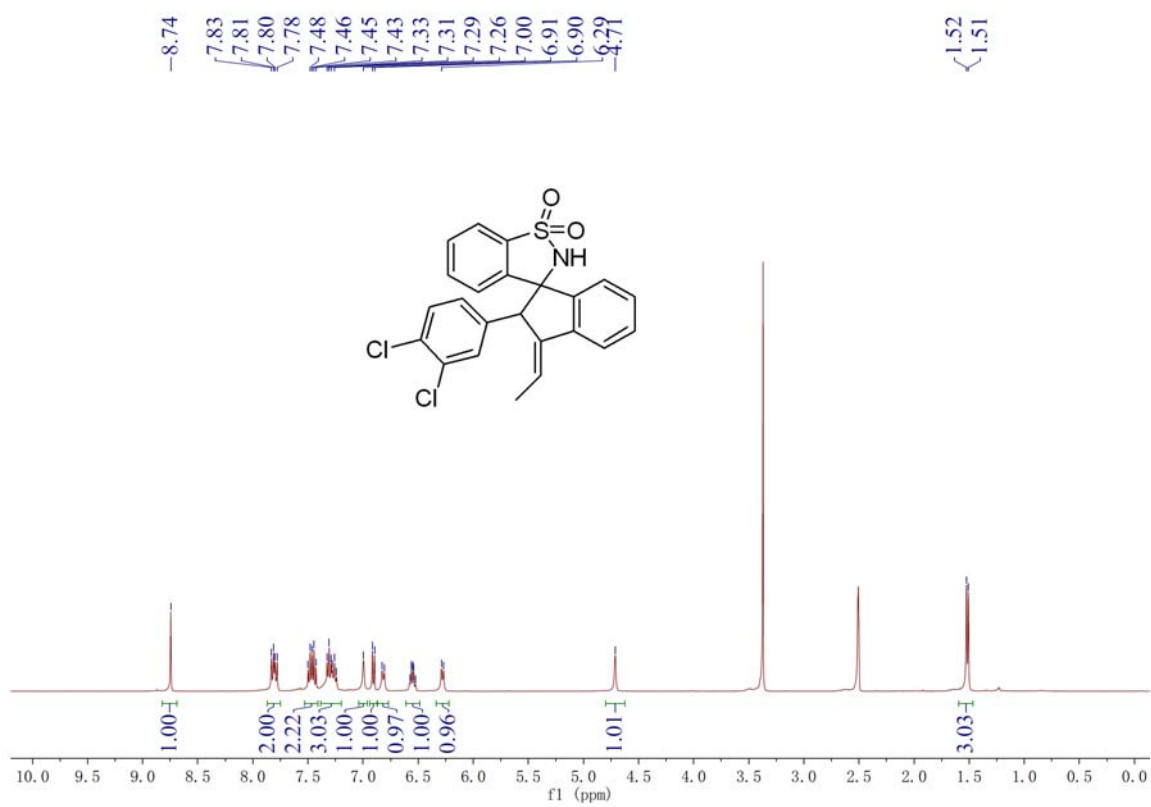
¹H NMR spectrum of **3al**



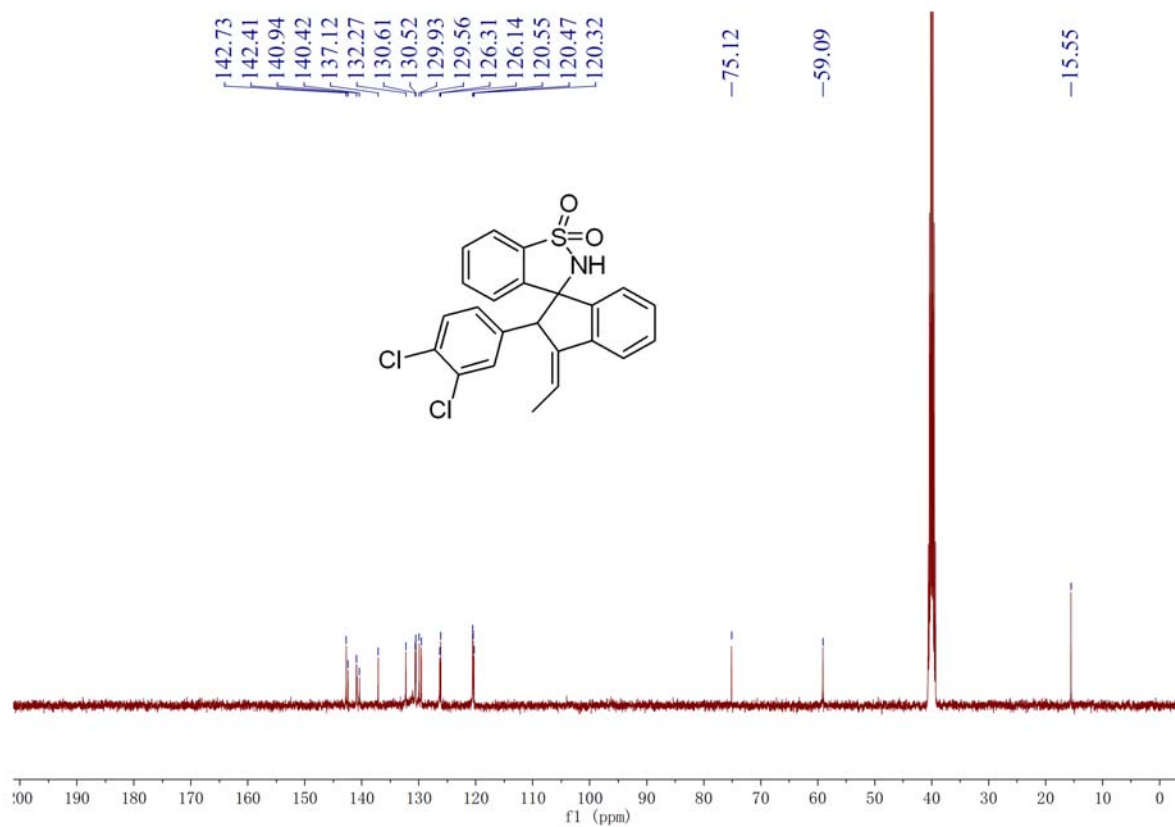
¹³C NMR spectrum of **3al**



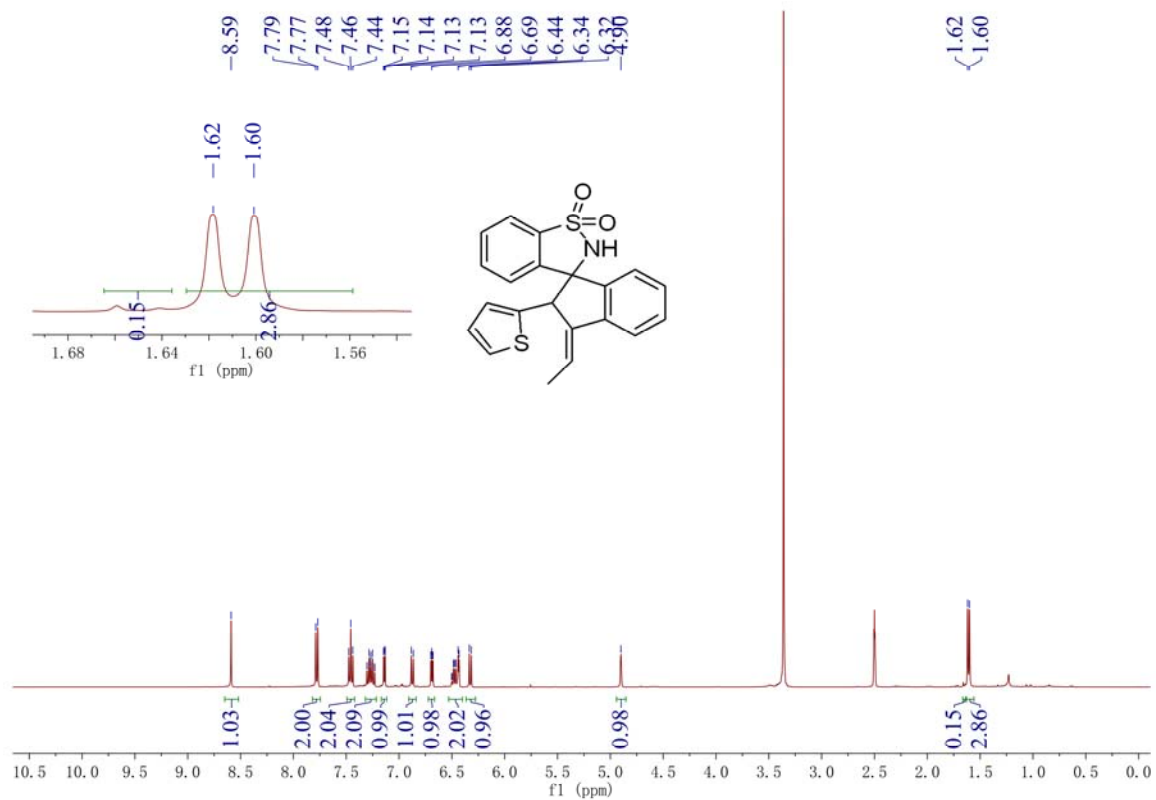
¹H NMR spectrum of **3am**



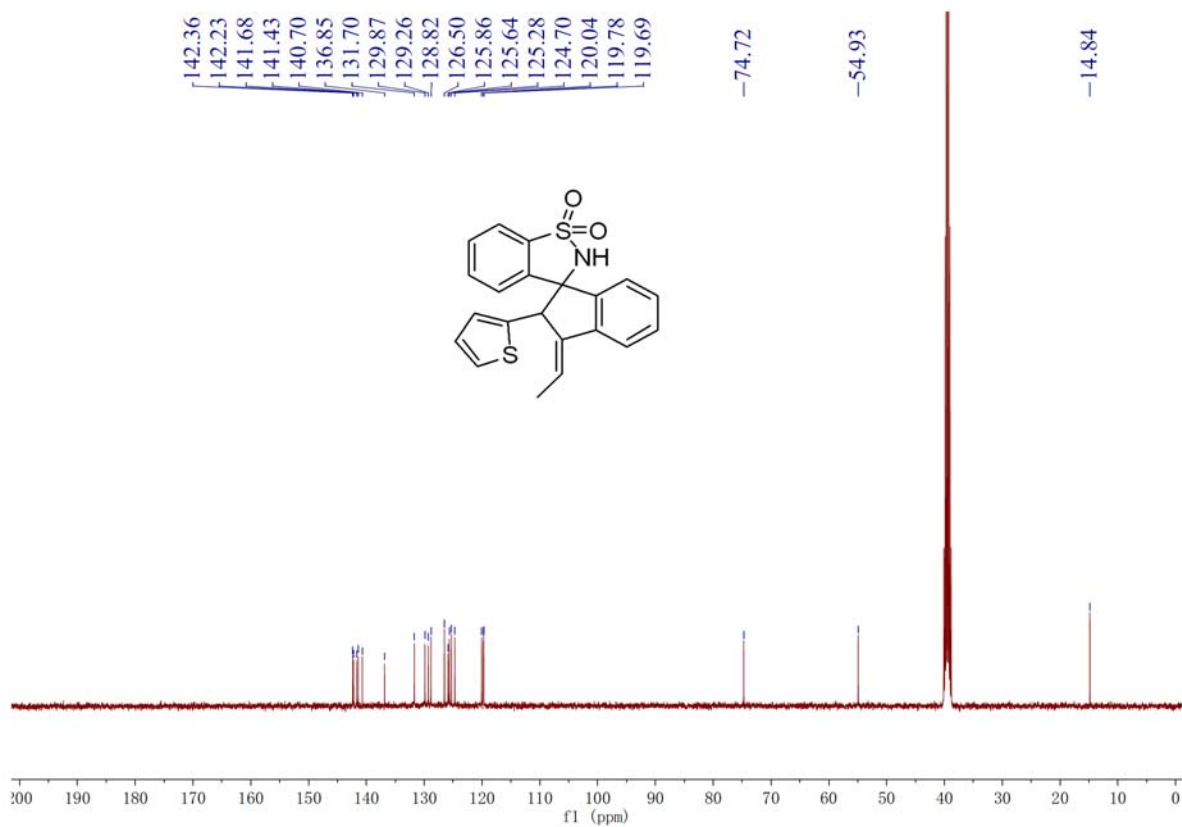
^{13}C NMR spectrum of **3am**



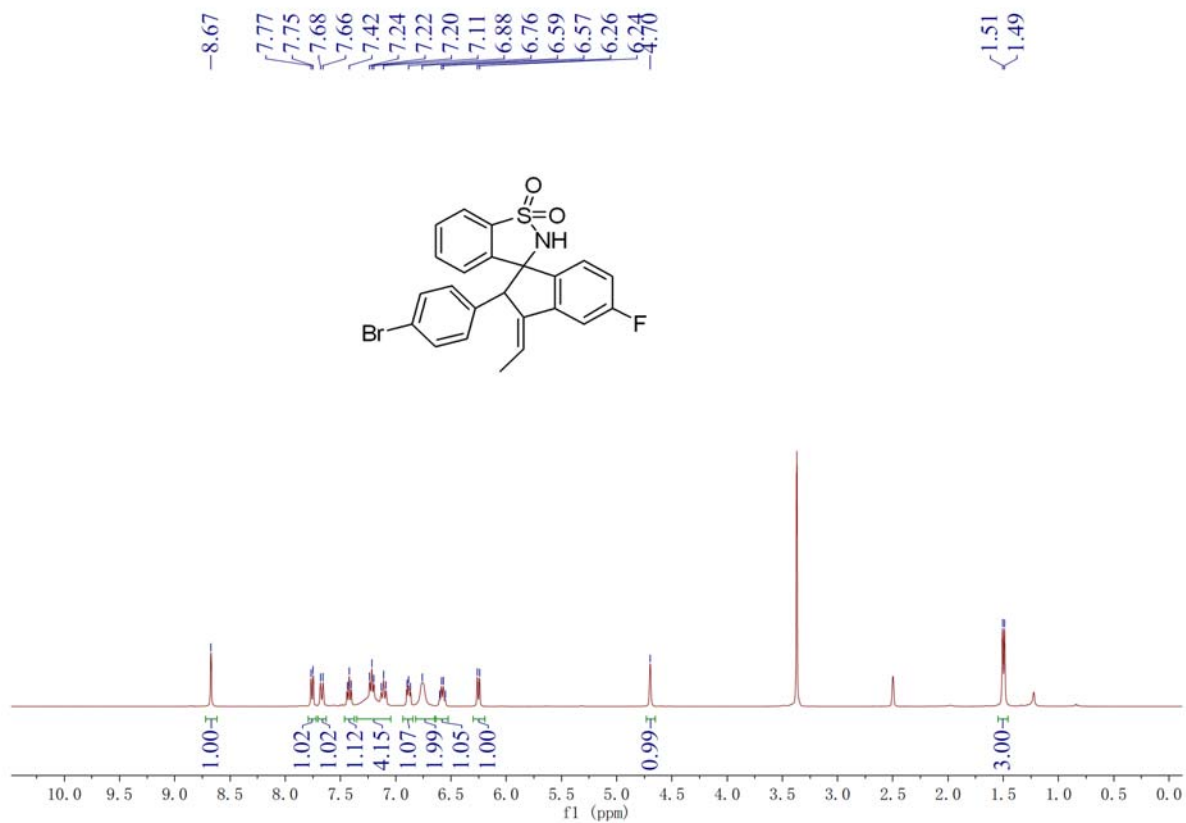
^1H NMR spectrum of **3an**



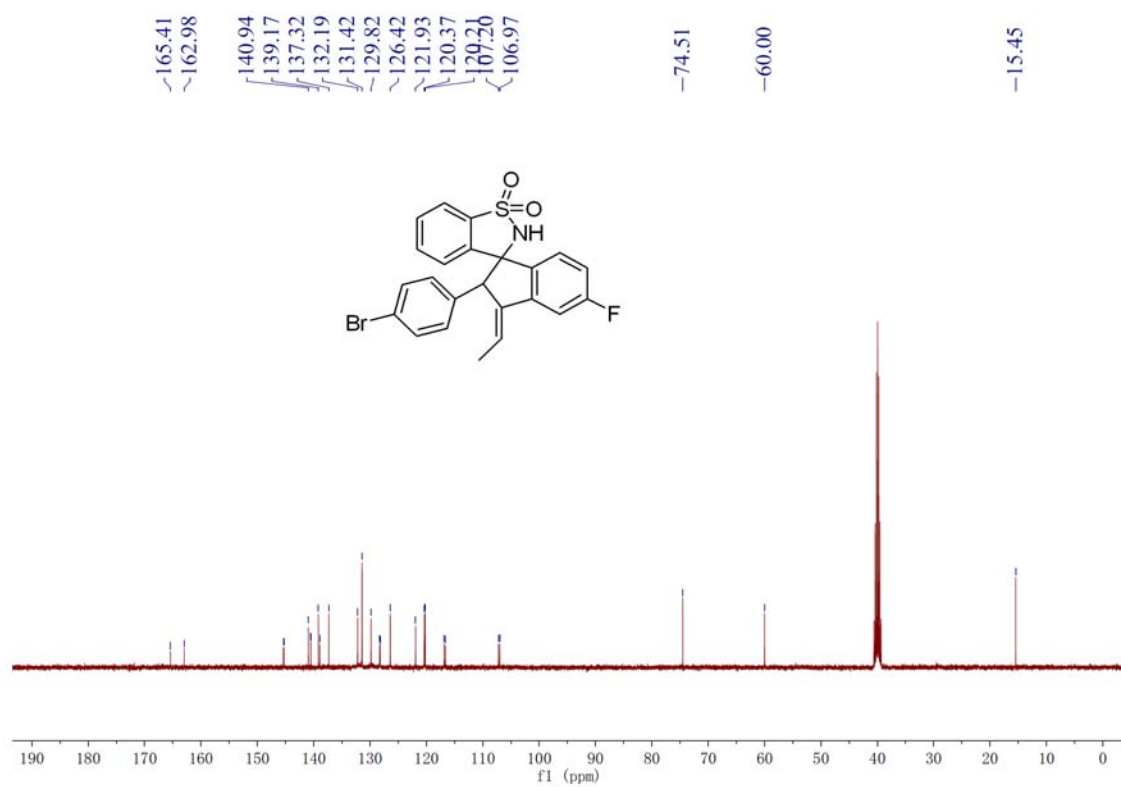
^{13}C NMR spectrum of **3an**



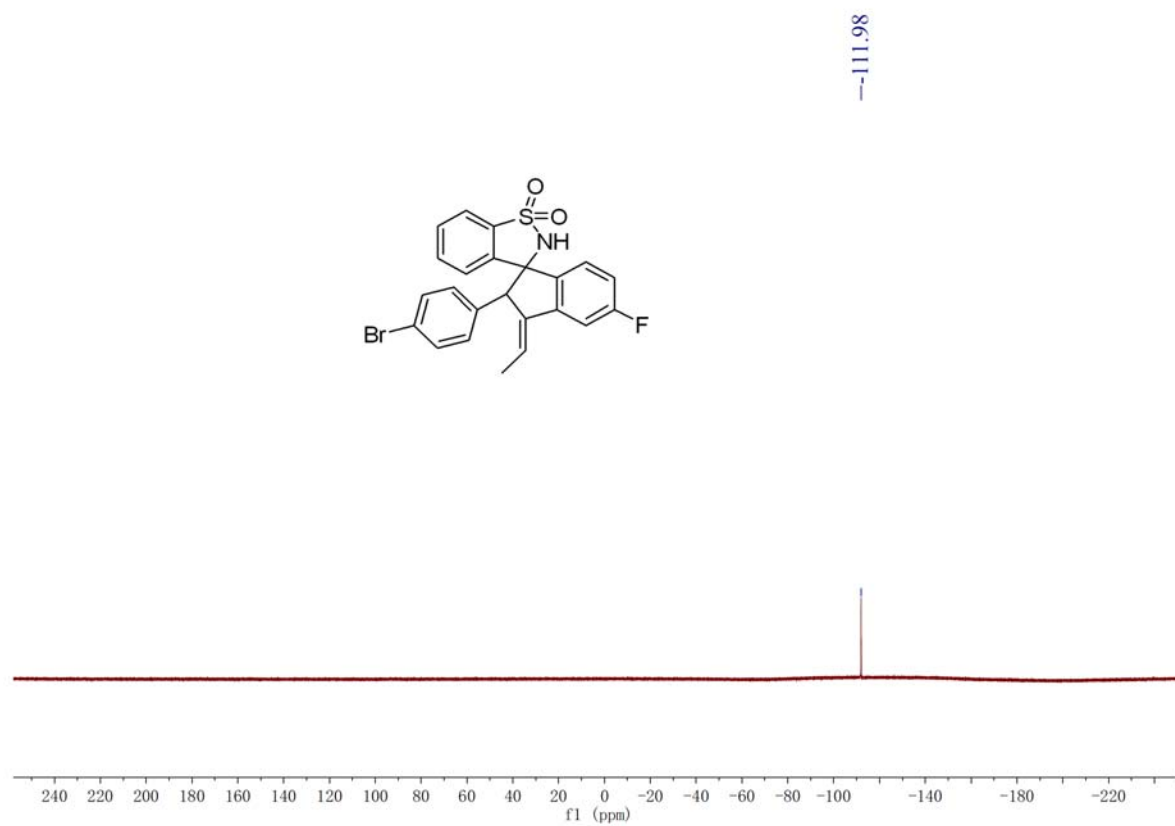
^1H NMR spectrum of **3bd**



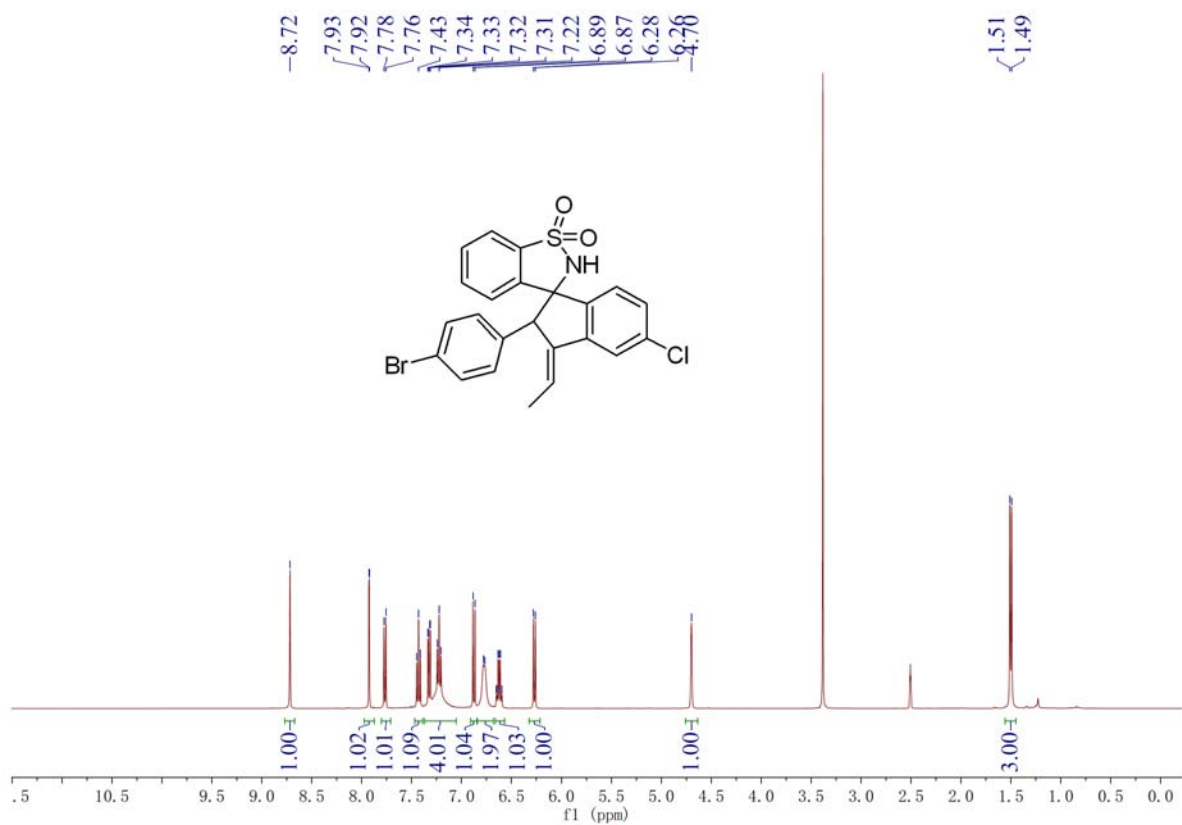
¹³C NMR spectrum of **3bd**



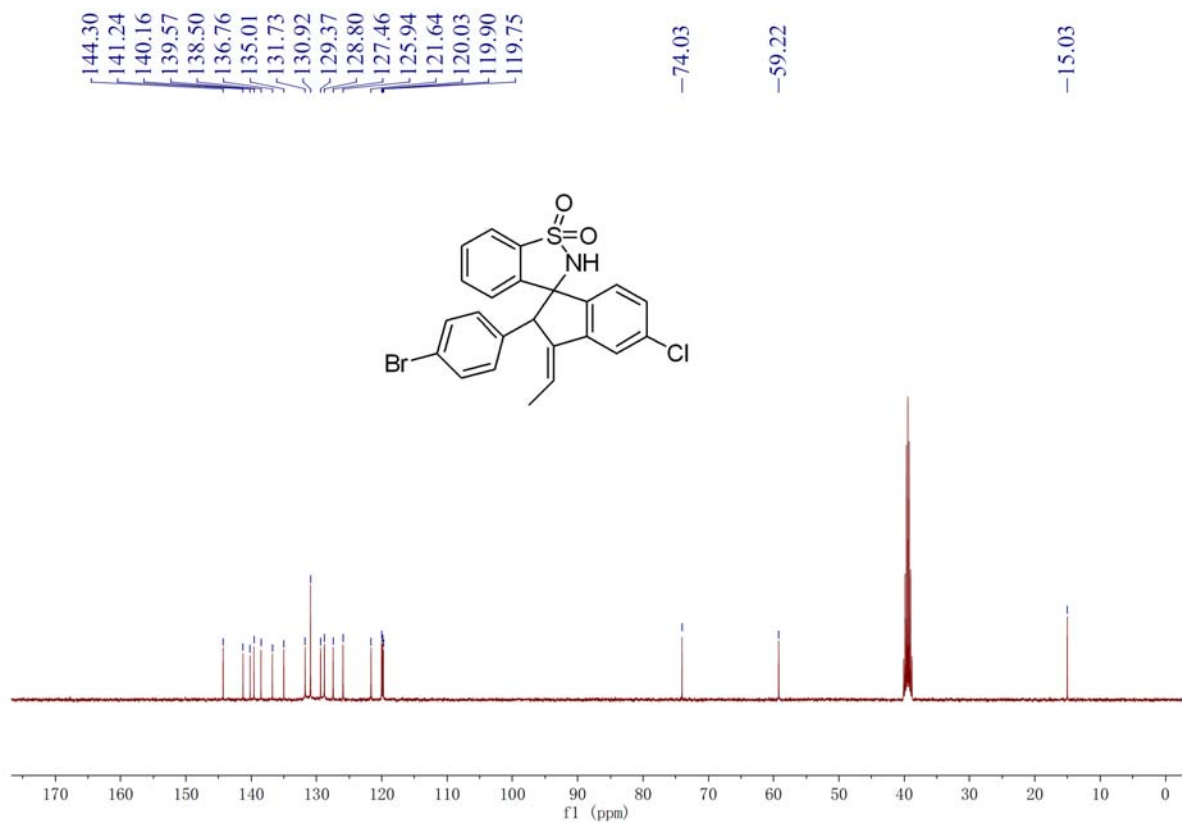
¹⁹F NMR spectrum of **3bd**



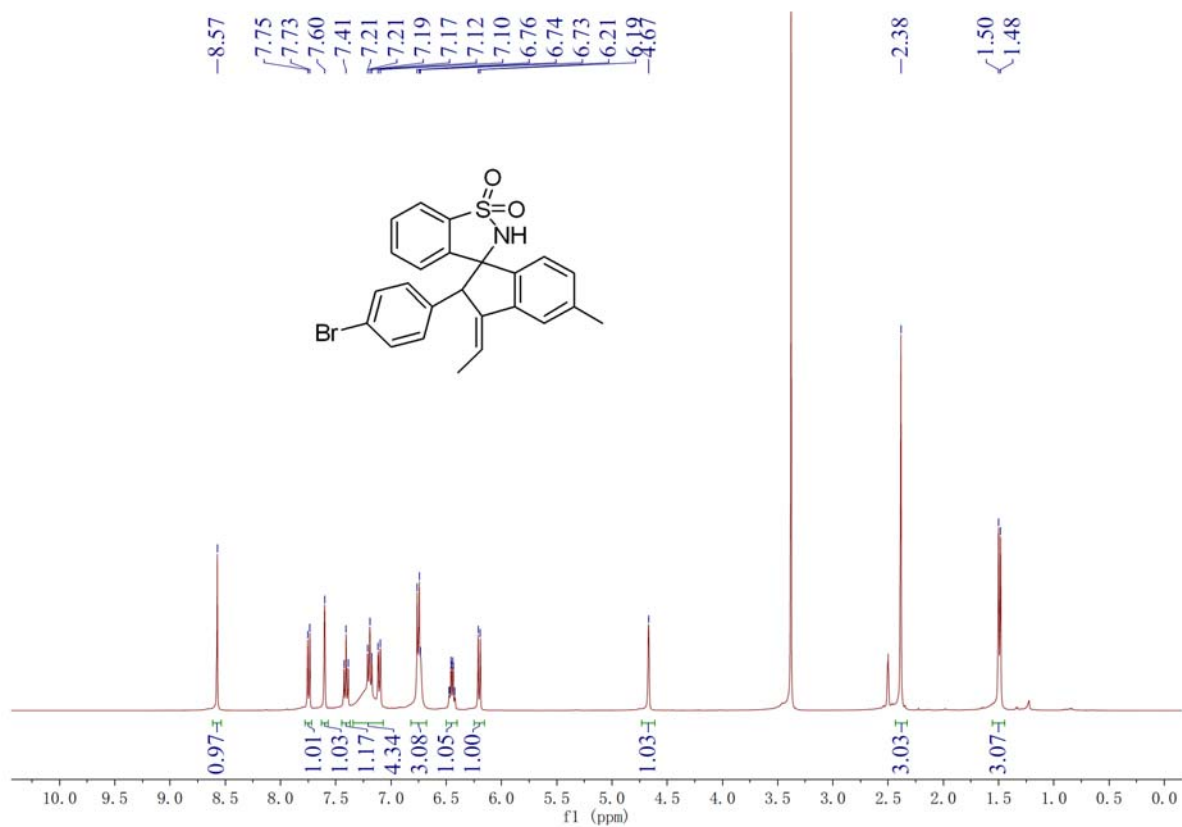
¹H NMR spectrum of **3cd**



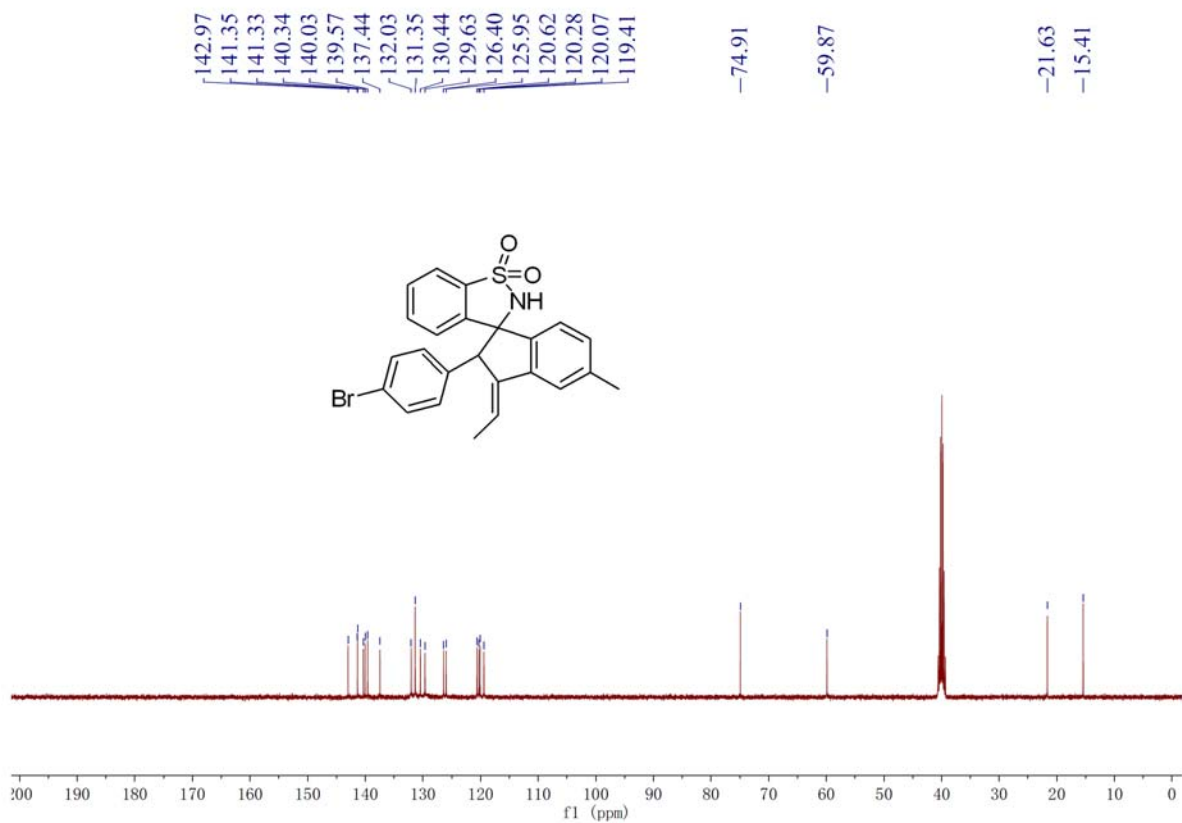
¹³C NMR spectrum of **3cd**



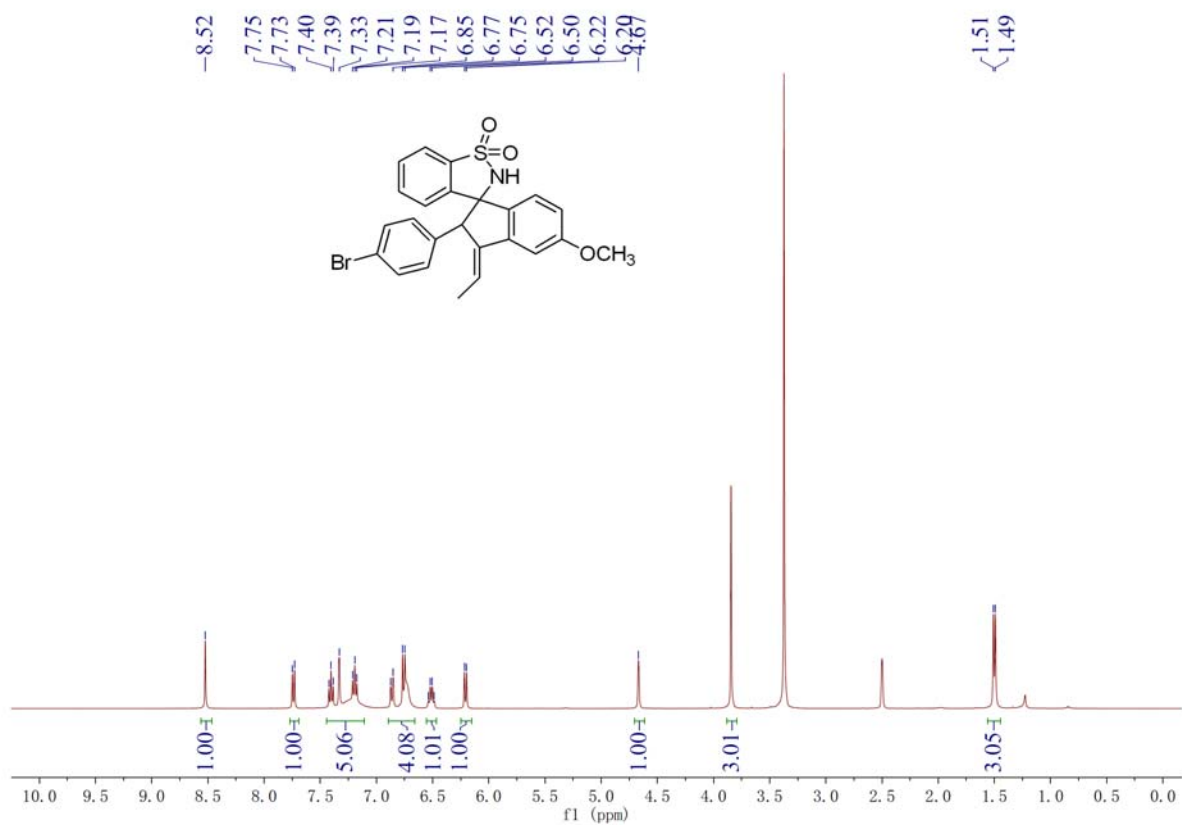
¹H NMR spectrum of **3dd**



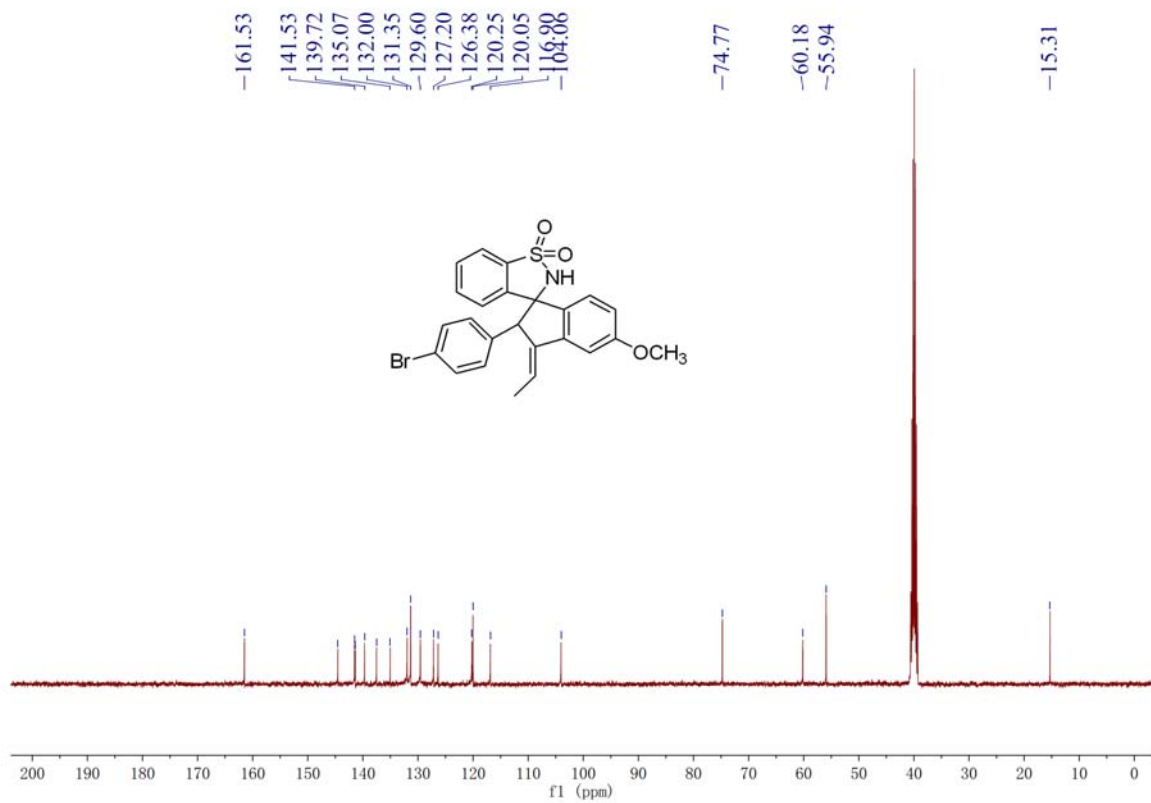
¹³C NMR spectrum of **3dd**



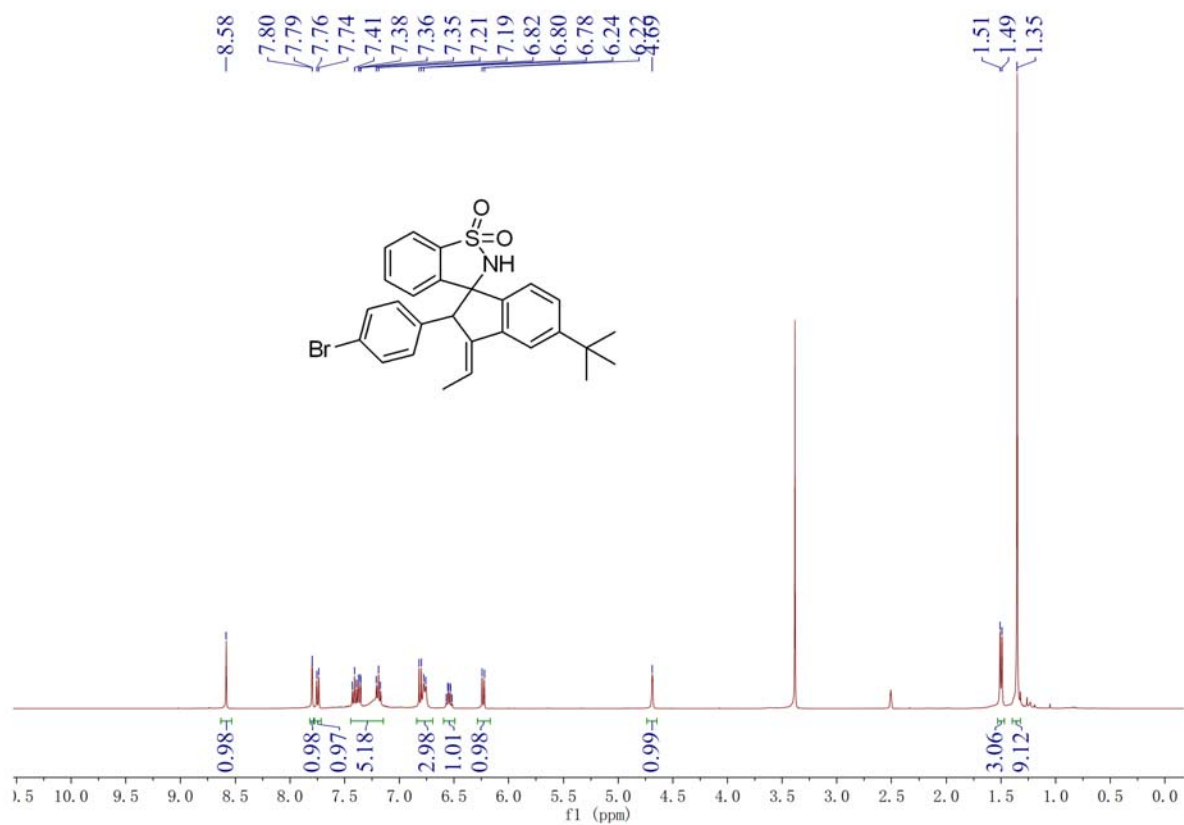
¹H NMR spectrum of **3ed**



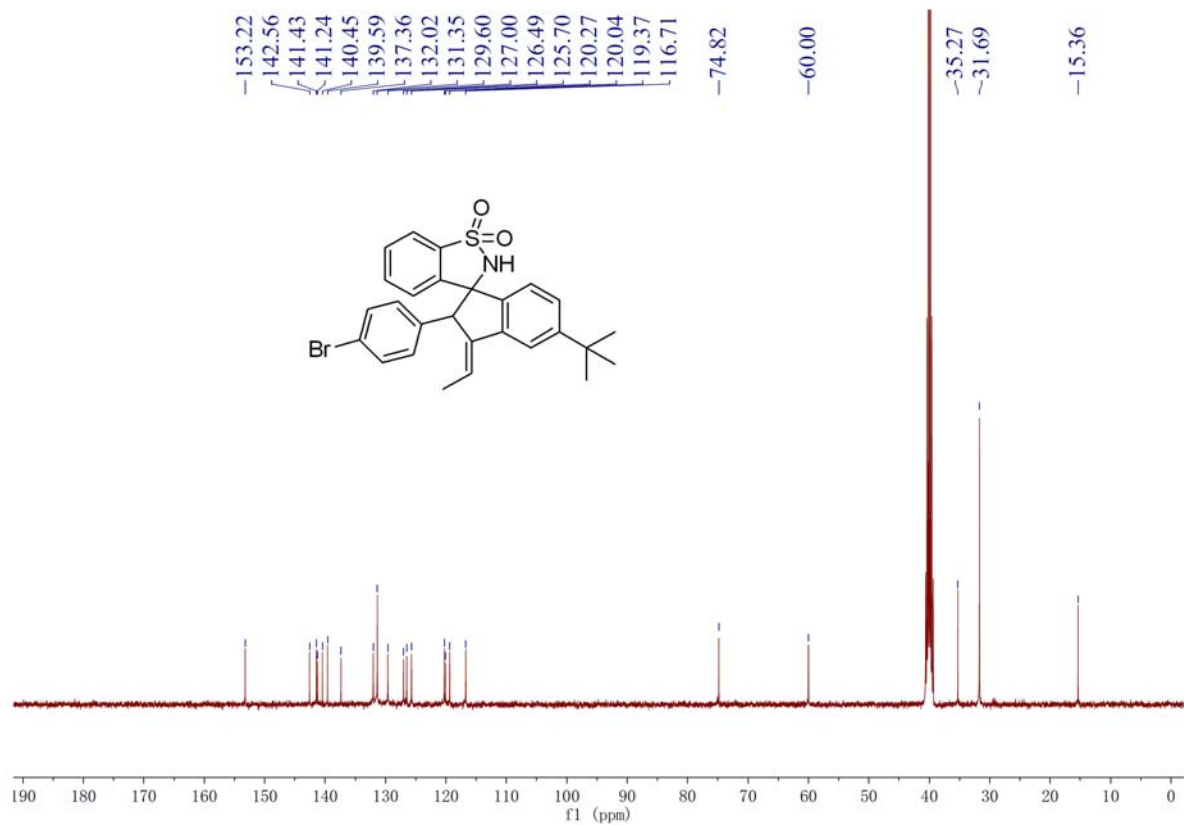
¹³C NMR spectrum of **3ed**



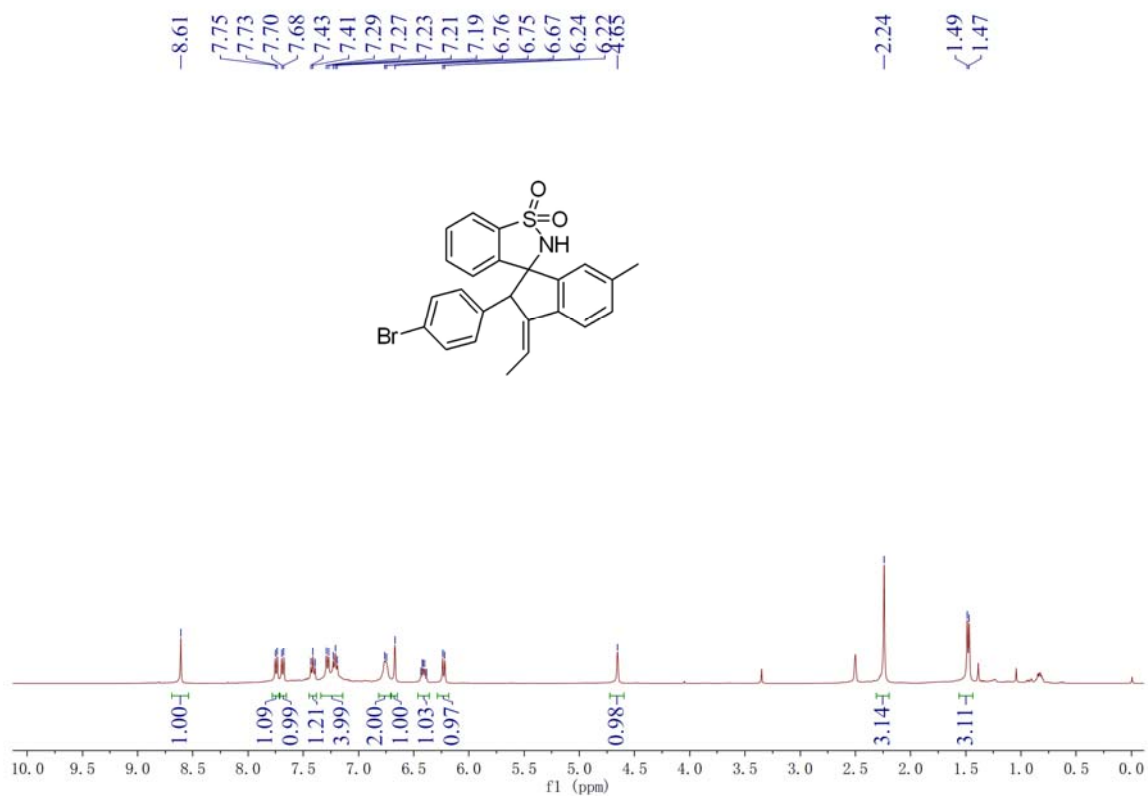
¹H NMR spectrum of **3fd**



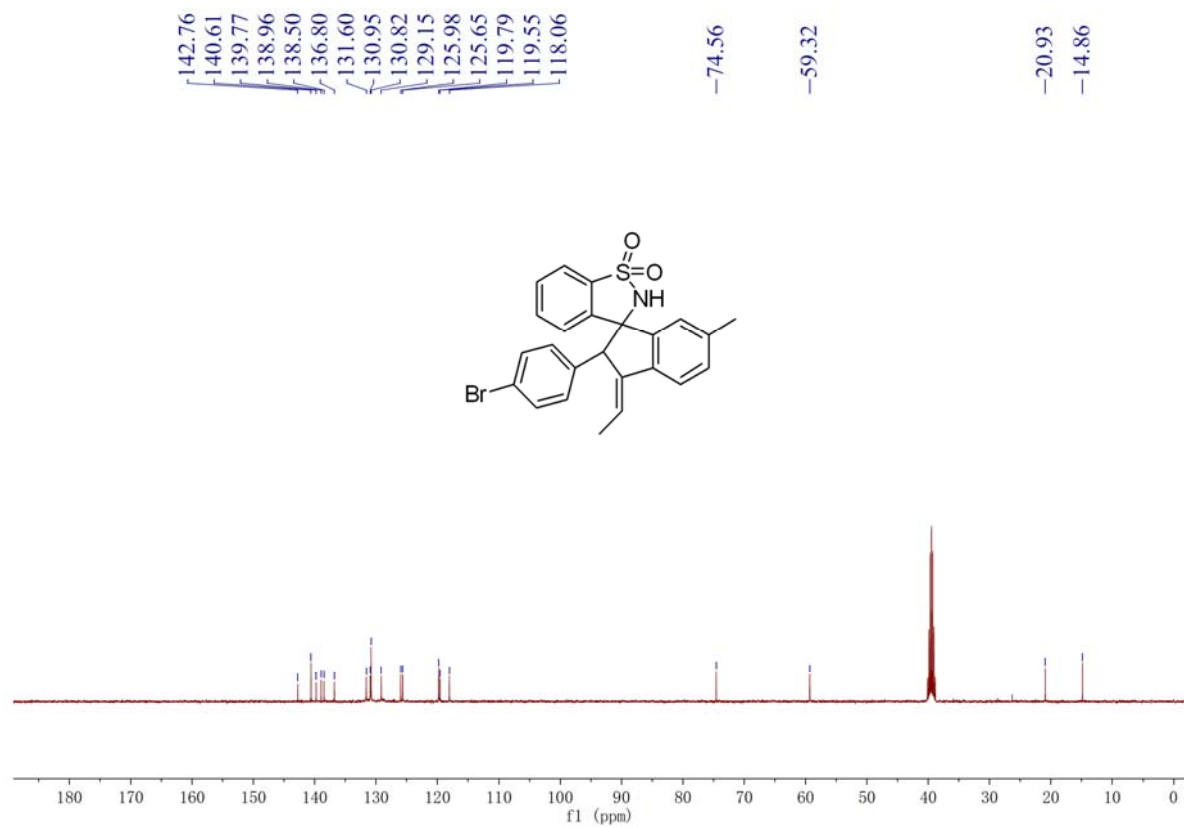
¹³C NMR spectrum of **3fd**



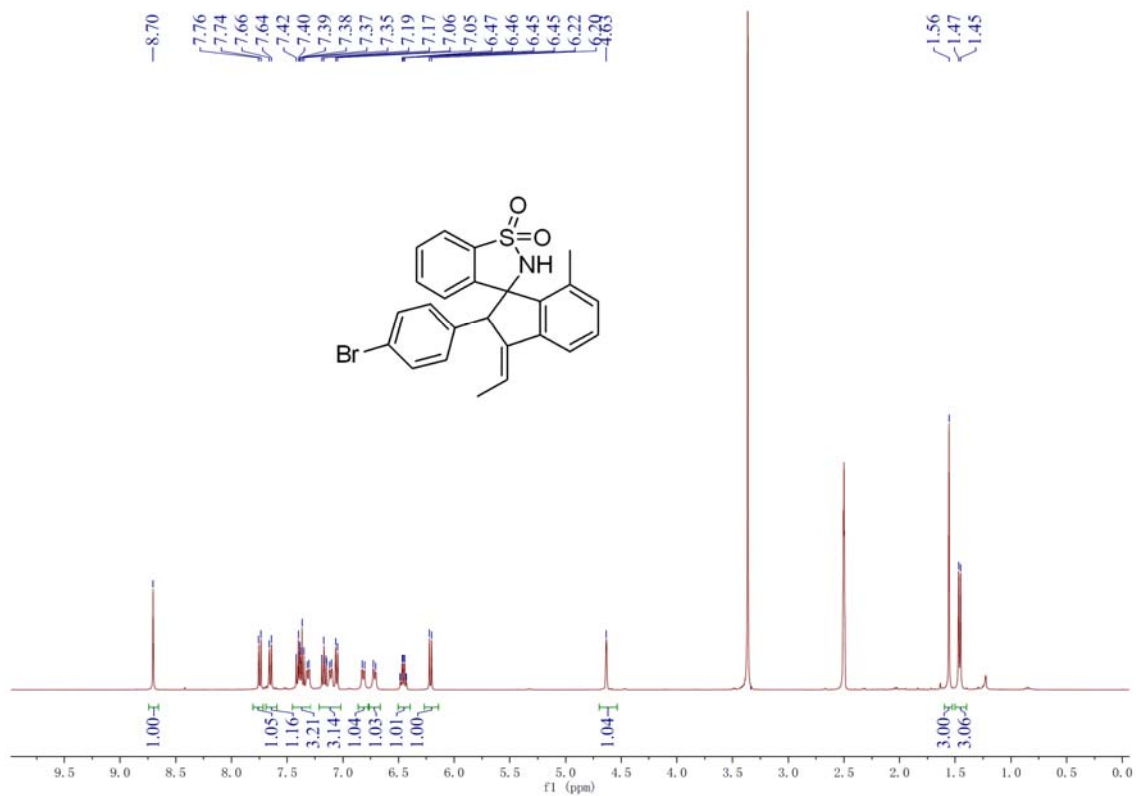
¹H NMR spectrum of **3gd**



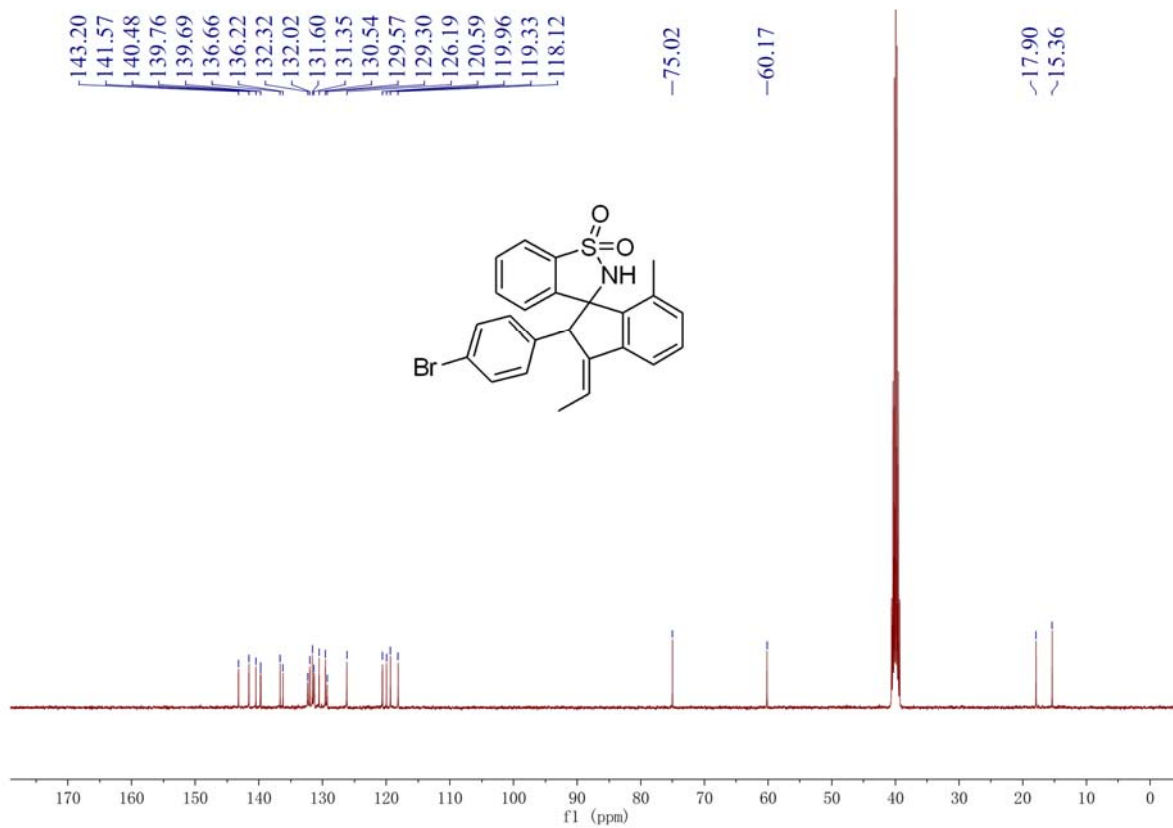
¹³C NMR spectrum of **3gd**



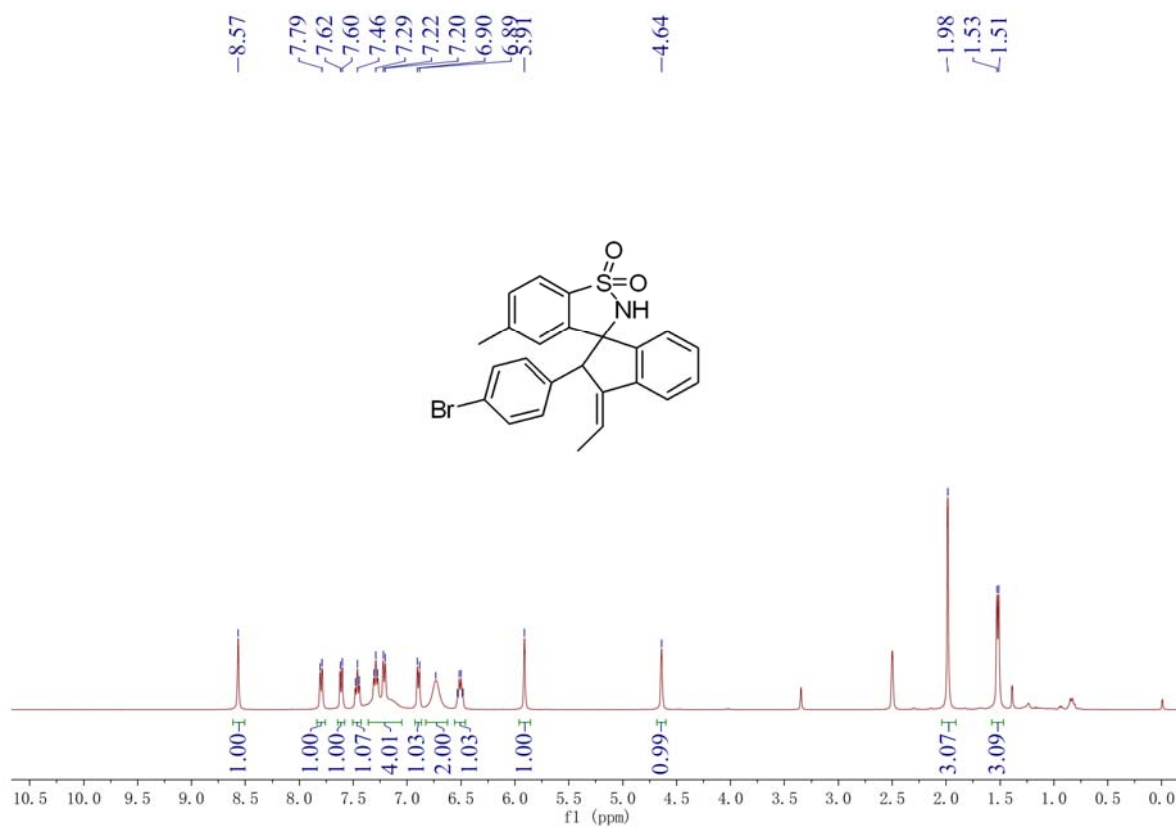
¹H NMR spectrum of **3hd**



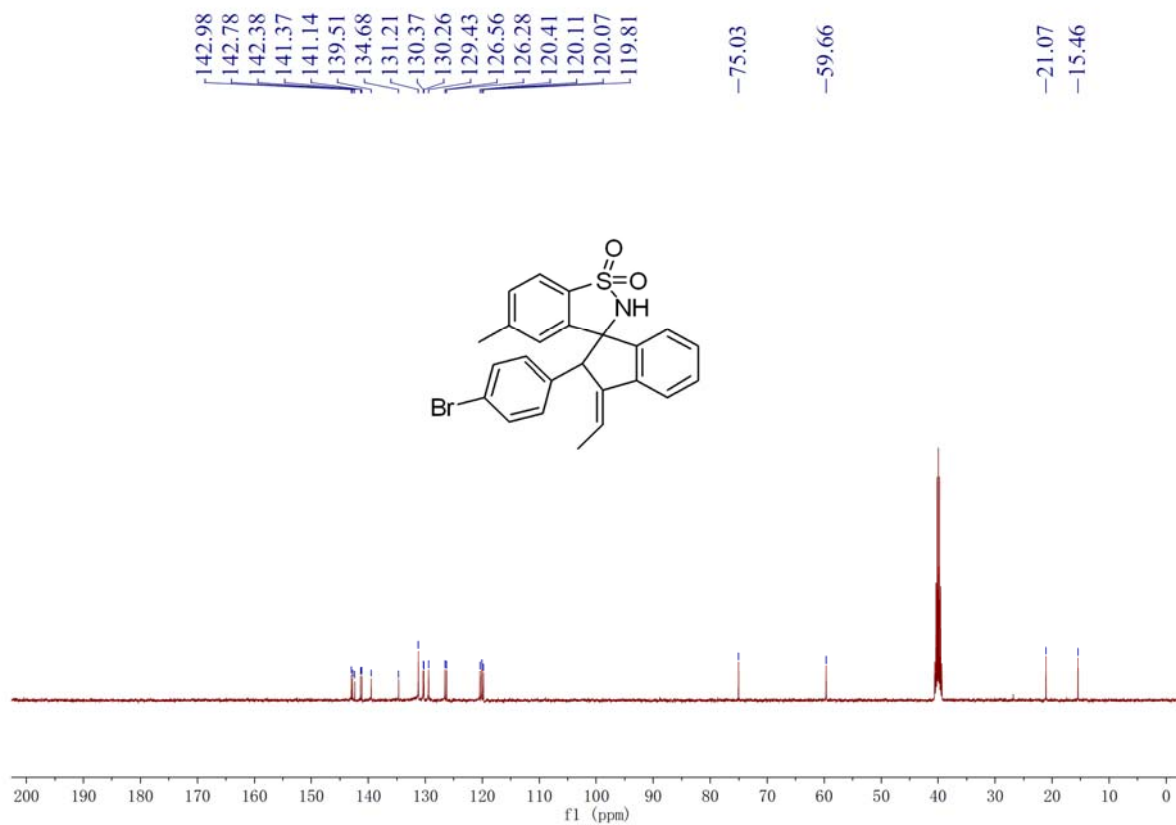
¹³C NMR spectrum of **3hd**



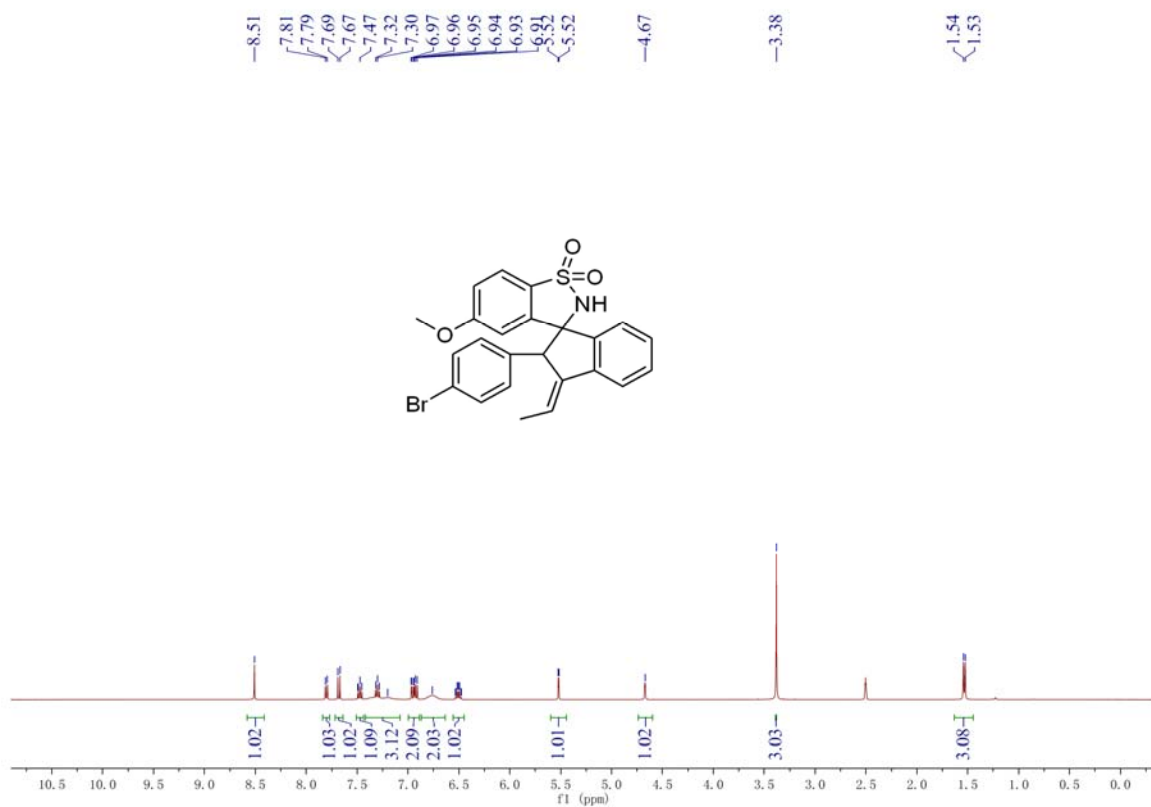
^1H NMR spectrum of **3id**



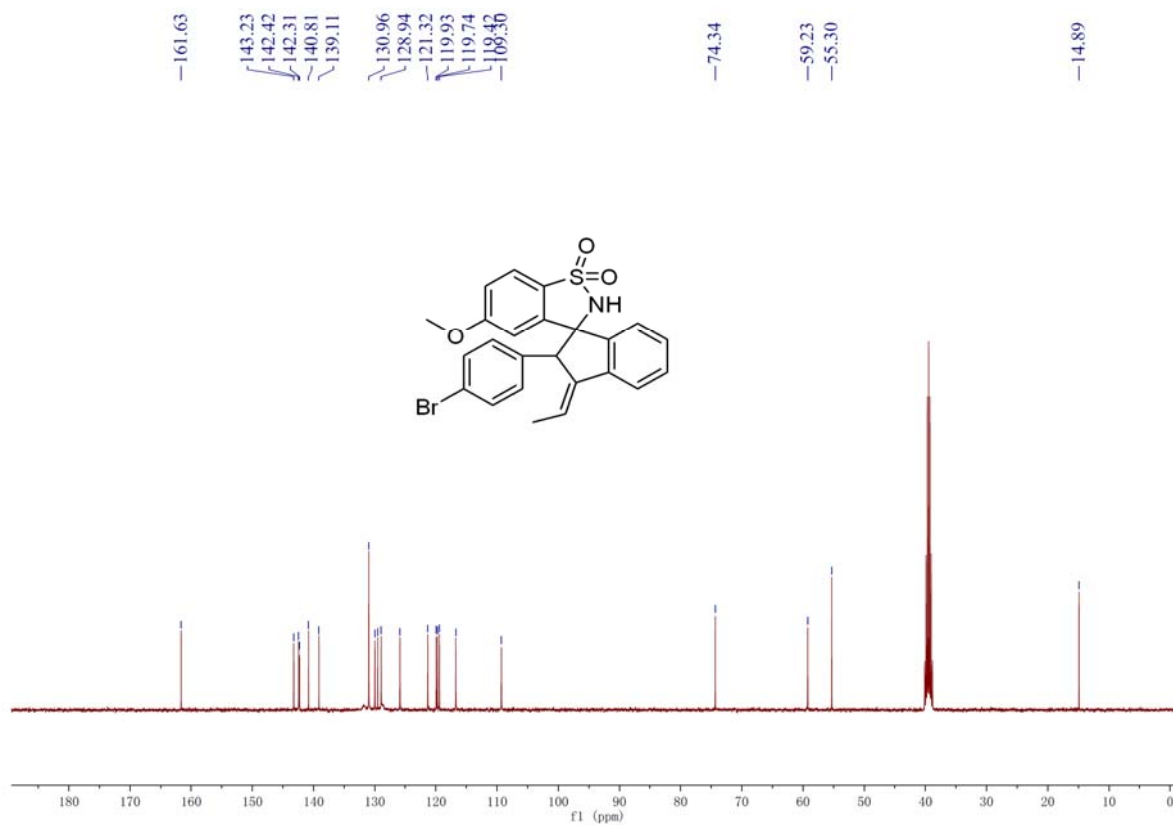
^{13}C NMR spectrum of **3id**



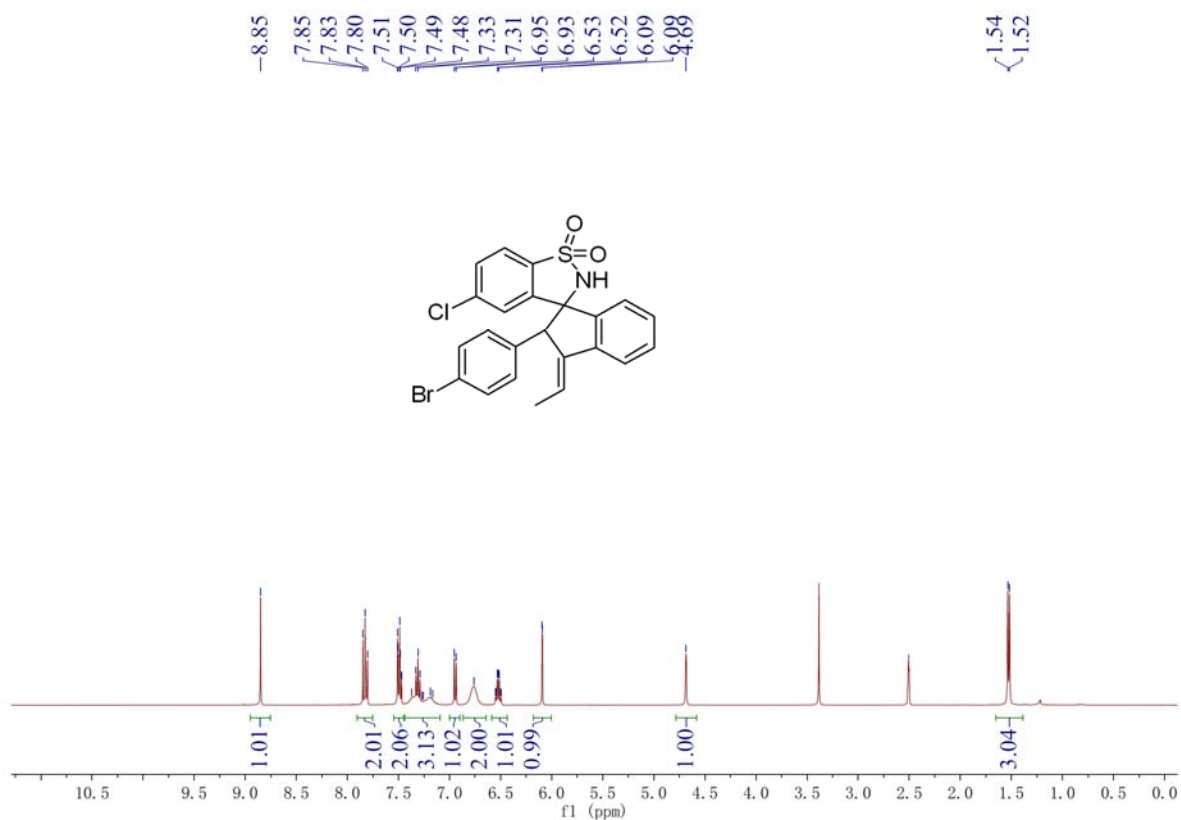
¹H NMR spectrum of **3jd**



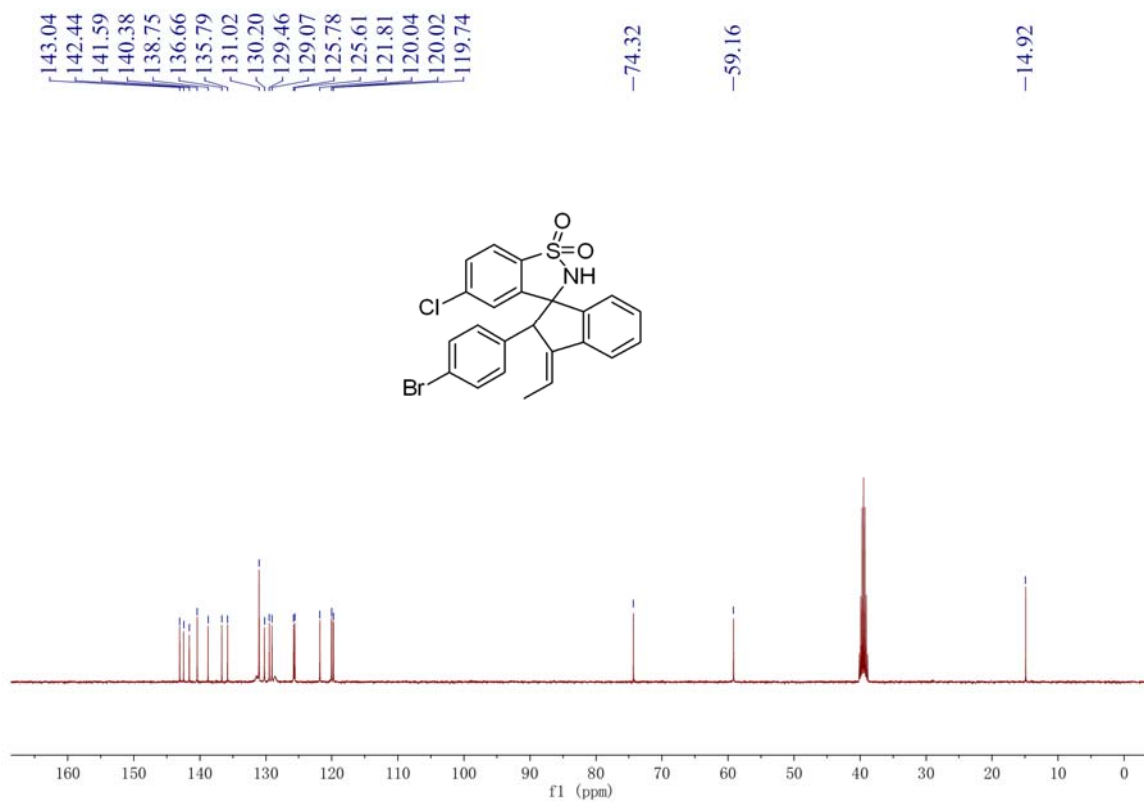
¹³C NMR spectrum of **3jd**



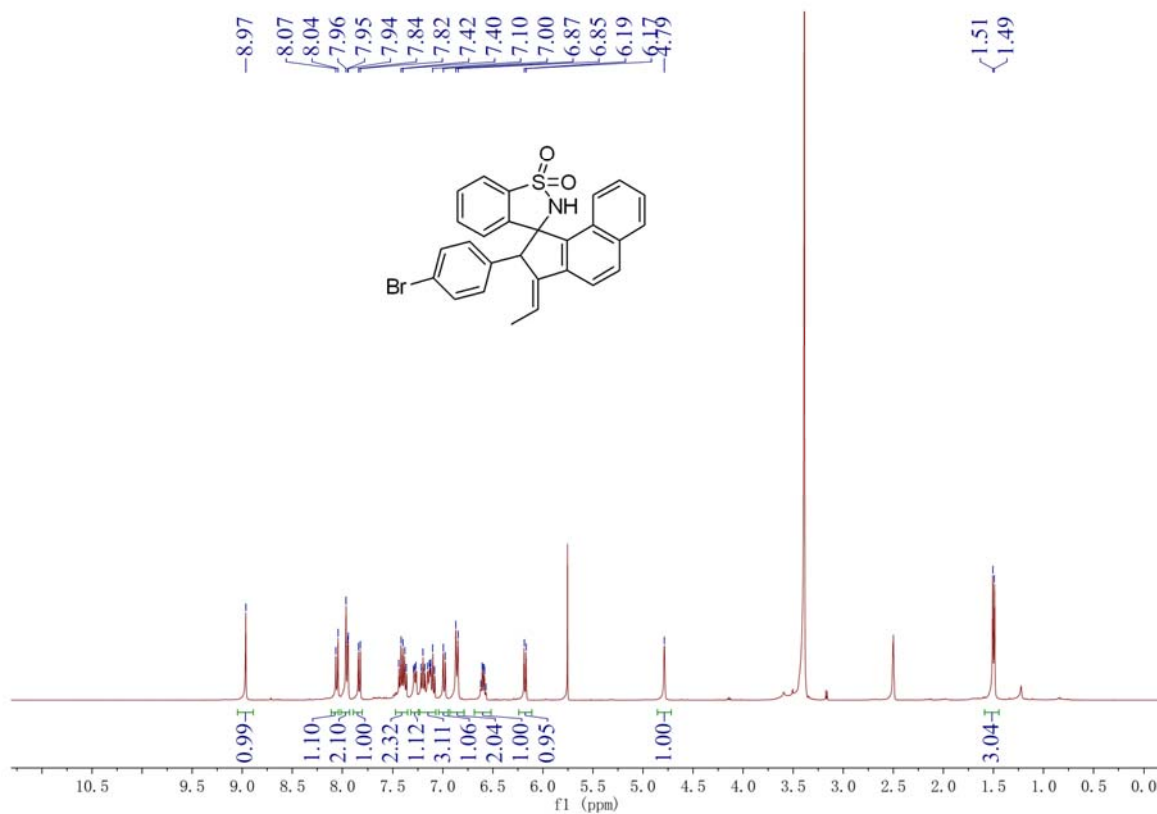
¹H NMR spectrum of **3kd**



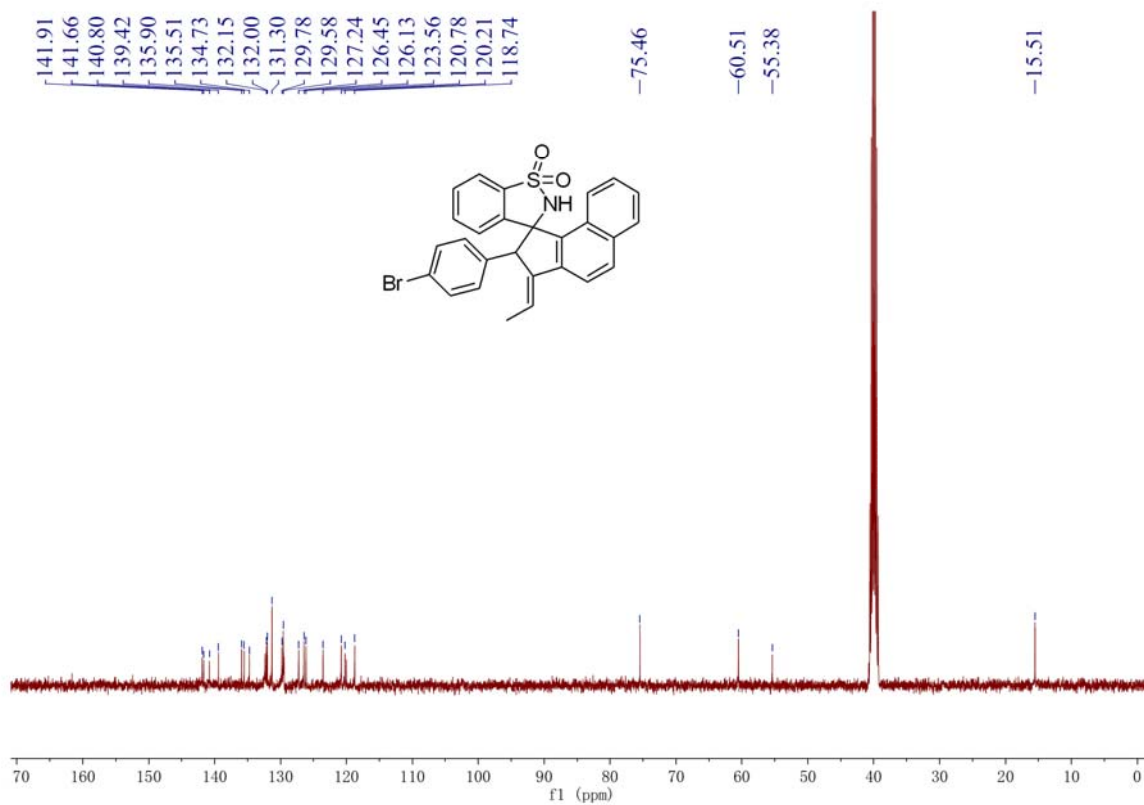
¹³C NMR spectrum of **3kd**



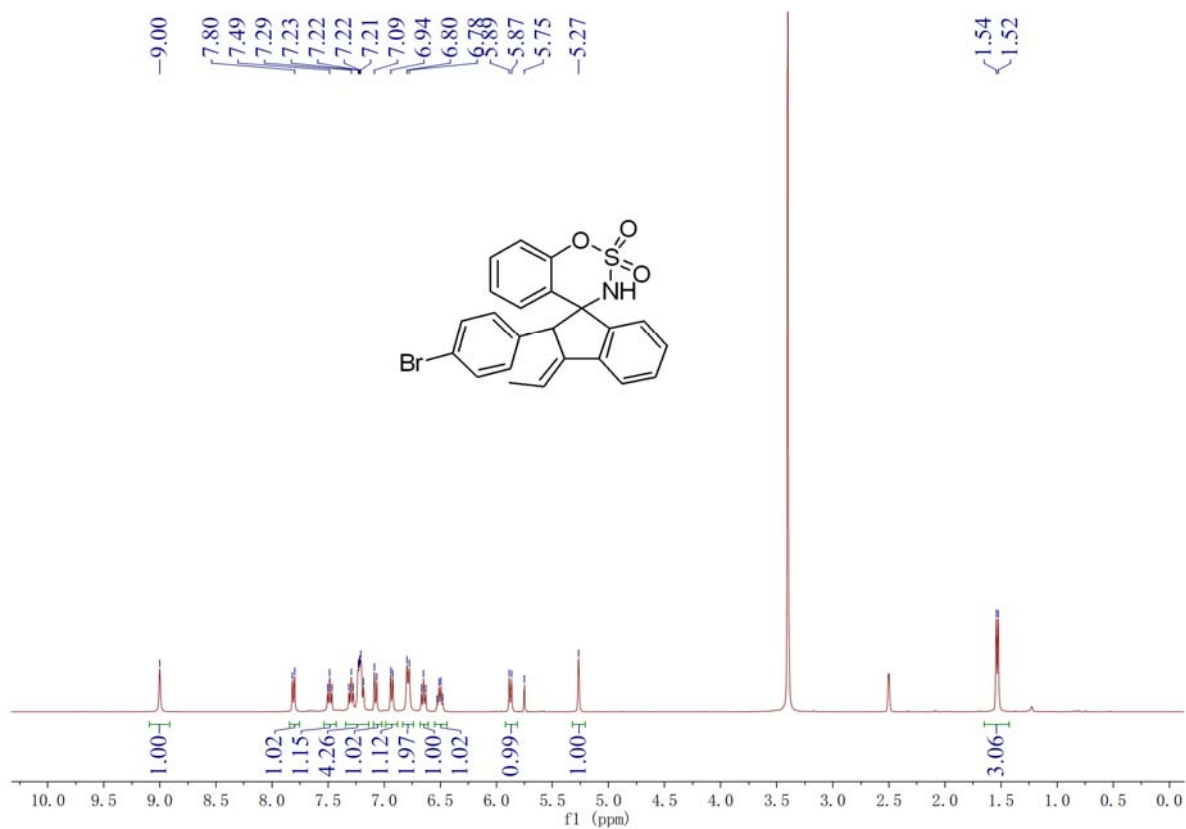
¹H NMR spectrum of **3ld**



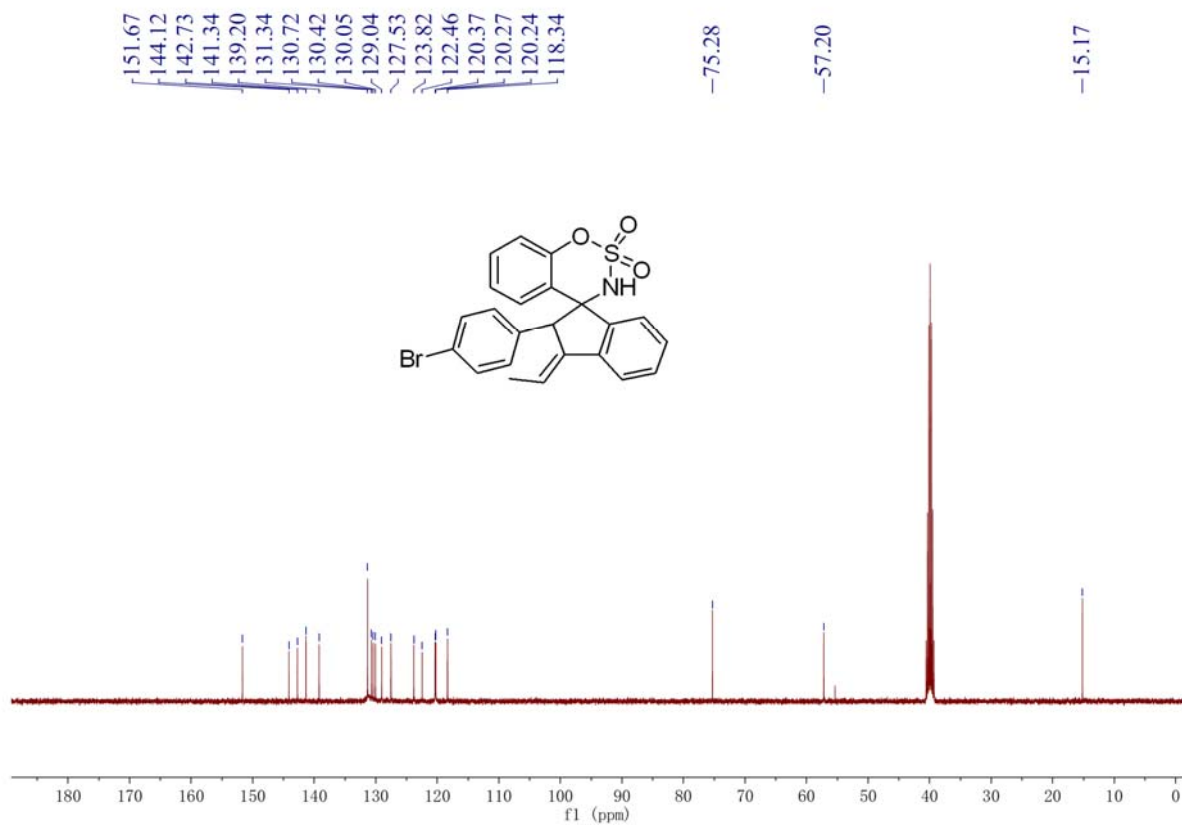
¹³C NMR spectrum of **3ld**



¹H NMR spectrum of **3md**



¹³C NMR spectrum of **3md**



8. References

- (1) (a) T. Nishimura, Y. Ebe and T. Hayashi, *J. Am. Chem. Soc.*, 2013, **135**, 2092; (b) Y.-Q. Wang, S.-M. Lu, Y.-G. Zhou, *J. Org. Chem.*, 2007, **72**, 3729; (c) C.-B. Yu, D.-W. Wang and Y.-G. Zhou, *J. Org. Chem.*, 2009, **74**, 5633.
- (2) (a) Y. Wang, M. E. Muratore, Z. Rong and A. M. Echavarren, *Angew. Chem., Int. Ed.*, 2014, **53**, 14022; (b) W. Ai, Y. Liu, Q. Wang, Z. Lu and Q. Liu, *Org. Lett.*, 2018, **20**, 409.