Electronic Supplementary Information

A rearrangement of saccharin-derived cyclic ketimines with 3-chlorooxindoles leading to spiro-1,3-benzothiazine oxindoles

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General Methods. Solvents and reagents were used as purchased without further purification. Reaction progress was monitored by thin-layer chromatography (TLC) on silica gel GF_{254} precoated plates. Visualization of developed plates was performed under a UV lamp. Chromatographic purification was performed with silica gel. Melting points were uncorrected. Nuclear magnetic resonance spectra (^1H and ^{13}C NMR) were recorded on Bruker DPX 400 MHz and 100 MHz spectrometers in $CDCl_3$ or DMSO-d_6 with chemical shift (δ) given in parts per million (ppm). Multiplicities were indicated as followed: s (singlet), d (doublet), t (triplet), m (multiplet), dd (doublet of doublets), and so forth; the coupling constant (*J*) was given in hertz (Hz). High-resolution mass spectra (HRMS) were recorded on a Thermo Fisher Scientific Q-Exactive Focus Orbitrap mass spectrometer. Saccharin-derived cyclic ketimines **1** and 3-chlorooxindoles **2** were prepared following the literature procedures.[1,2]

General Procedure for the Synthesis of Product 3. To a solution of saccharin-derived cyclic ketimines **1** (0.1 mmol) and 3-chlorooxindoles **2** (0.2 mmol) in DME (1 mL) were added Cs_2CO_3 (0.2 mmol). The reaction mixture was stirred at room temperature for 1 h. Upon completion of the reaction, the solid was filtered and washed with acetone, and the combined filtrate was concentrated under reduced pressure. The residue was purified using column chromatography to afford the product **3**.

4-Phenylspiro[benzo[e][1,3]thiazine-2,3'-indolin]-2'-one 1,1-dioxide (***3aa***). White solid (34 mg, 90% yield), ethyl acetate/petroleum ether = 1:5. mp 255-257 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 11.25 (s, 1H), 8.09-8.07 (m, 1H), 7.92-7.86 (m, 2H), 7.63-7.58 (m, 3H), 7.54-7.47 (m, 5H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.8, 167.5, 144.0, 137.8, 134.9, 134.0, 133.6, 132.4, 131.6, 131.4, 130.6,

129.7, 129.1, 128.3, 124.9, 123.3, 120.9, 111.3, 81.1. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{15}N_2O_3S$ 375.0803; found 375.0787.

4-(2-Methoxyphenyl)spiro[benzo[e][1,3]thiazine-2,3'-indolin]-2'-one 1,1-dioxide (***3ba***). White solid (36 mg, 89% yield), ethyl acetate/petroleum ether = 1:5. mp 239-241℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.24 (s, 1H), 8.07 (d, *J* = 6.8 Hz, 1H), 7.91-7.85 (m, 2H), 7.55-7.48 (m, 3H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.18-7.11 (m, 3H), 7.07-7.04 (m, 2H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.6, 167.5, 159.7, 144.0, 139.1, 134.9, 133.9, 133.6, 132.4, 131.5, 130.6, 130.3, 128.3, 124.9, 1234, 122.1, 120.8, 117.6, 114.4, 111.3, 81.1, 55.9. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{17}N_2O_4S$ 405.0909; found 405.0905.

4-(3-Methoxyphenyl)spiro[benzo[e][1,3]thiazine-2,3'-indolin]-2'-one 1,1-dioxide (***3ca***). White solid (36 mg, 90% yield), ethyl acetate/petroleum ether = 1:5. mp 241-242 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.24 (s, 1H), 8.08-8.06 (m, 1H), 7.92-7.85 (m, 2H), 7.56-7.48 (m, 3H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.19-7.11 (m, 3H), 7.08-7.04 (m, 2H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.5, 167.4, 159.7, 143.9, 139.1, 134.8, 133.8, 133.5, 132.3, 131.4, 130.5, 130.2, 128.2, 124.8, 123.2, 122.0, 120.7, 117.5, 114.4, 111.2, 81.0, 55.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{17}N_2O_4S$ 405.0909; found 405.0905.

4-(4-Methoxyphenyl)spiro[benzo[e][1,3]thiazine-2,3'-indolin]-2'-one 1,1-dioxide (***3da***). White solid (34 mg, 83% yield), ethyl acetate/petroleum ether = 1:5. mp 225-227 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-8.04 (m, 1H), 7.76 (s, 1H), 7.73-7.67 (m, 3H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.57-7.54 (m, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 7.6 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 167.7, 161.9, 141.7, 134.1, 133.5, 132.1, 131.6, 131.3, 131.0, 130.2, 128.6, 124.9, 123.9,

120.7, 113.8, 110.5, 80.7, 55.5. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{17}N_2O_4S$ 405.0909; found 405.0902.

4-(4-(Tert-butyl)phenyl)spiro[benzo[e][1,3]thiazine-2,3'-indolin]-2'-one 1,1-dioxide (***3ea***). White solid (37 mg, 86% yield), ethyl acetate/petroleum ether = 1:5. mp 264-266 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-8.05 (m, 1H), 7.96-7.93 (m, 1H), 7.73-7.67 (m, 3H), 7.58-7.55 (m, 3H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.82 (dd, *J* = 7.8, 2.8 Hz, 1H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 167.7, 154.4, 141.9, 135.0, 134.1, 133.6, 132.2, 131.7, 131.3, 131.2, 129.3, 128.6, 125.5, 124.8, 123.9, 120.6, 110.7, 80.9, 35.0, 31.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{25}H_{23}N_2O_3S$ 431.1429; found 431.1423.

4-(3-Fluorophenyl)spiro[benzo[e][1,3]thiazine-2,3'-indolin]-2'-one 1,1-dioxide (***3fa***). White solid (33 mg, 83% yield), ethyl acetate/petroleum ether = 1:5. mp 240-241 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-8.07 (m, 1H), 7.76-7.73 (m, 3H), 7.67 (s, 1H), 7.52-7.49 (m, 1H), 7.47-7.36 (m, 4H), 7.26-7.19 (m, 2H), 6.93 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.6 (*J* = 2.6 Hz), 167.3, 162.5 (*J* = 244 Hz), 144.0, 139.9 (*J* = 7.7 Hz), 135.0, 133.9, 133.8, 132.5, 131.4, 131.3 (*J* = 8.3 Hz), 130.2, 128.3, 126.0 (*J* = 2.8 Hz), 125.0, 123.4, 120.7, 118.6 (*J* = 20.9 Hz), 116.5 (*J* = 22.9 Hz), 111.4, 81.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{14}FN_2O_3S$ 393.0709 ; found 393.0703.

4-(4-Chlorophenyl)spiro[benzo[e][1,3]thiazine-2,3'-indolin]-2'-one 1,1-dioxide (***3ga***). White solid (33 mg, 82% yield), ethyl acetate/petroleum ether = 1:8. mp 252-254 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.08-8.06 (m, 1H), 7.89-7.88 (m, 2H), 7.64-7.54 (m, 5H), 7.51-7.46 (m, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz,

DMSO-d_6) δ 167.8, 167.4, 145.3, 136.6, 136.4, 134.9, 134.1, 133.6, 132.4, 131.6, 131.3, 130.3, 129.2, 128.1, 124.9, 122.9, 121.1, 111.6, 81.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{14}ClN_2O_3S$ 409.0414; found 409.0408.

4-(3,5-Dimethylphenyl)spiro[benzo[e][1,3]thiazine-2,3'-indolin]-2'-one 1,1-dioxide (***3ha***). White solid (35 mg, 86% yield), ethyl acetate/petroleum ether = 1:5. mp 278-280 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.22 (s, 1H), 8.06 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.91-7.85 (m, 2H), 7.52-7.47 (m, 3H), 7.23 (s, 1H), 7.17-7.14 (m, 3H), 7.04 (d, *J* = 8.0 Hz, 1H), 2.32 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.9, 167.6, 144.0, 138.4, 137.8, 134.9, 134.0, 133.5, 132.9, 132.4, 131.5, 130.8, 128.3, 127.3, 124.8, 123. 3, 120.9, 111.3, 81.0, 21.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{19}N_2O_3S$ 403.1116 ; found 403.1109.

4-(Naphthalen-2-yl)spiro[benzo[e][1,3]thiazine-2,3'-indolin]-2'-one 1,1-dioxide (***3ia***). White solid (36 mg, 84% yield), ethyl acetate/petroleum ether = 1:5. mp 236-238 ℃. ^{1}H NMR (400 MHz, DMSO-d_6 & $CDCl_3$) δ 11.28 (s, 1H), 8.24 (s, 1H), 8.12-8.01 (m, 4H), 7.92-7.90 (m, 2H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.66-7.58 (m, 3H), 7.54-7.49 (m, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6 & $CDCl_3$) δ 168.2, 167.0, 143.5 134.6, 134.4, 133.9, 133.5, 133.0, 132.2, 131.9, 131.1, 130.2, 129.6, 128.9, 128.2, 127.8, 127.7, 127.6 126.9, 125.9 124.4 122.8, 120.4, 110.8, 80.7. HRMS (ESI) m/z: $[M - H]^-$ calcd for $C_{25}H_{15}N_2O_3S$ 423.0803; found 423.0804.

5'-Methyl-4-phenylspiro[benzo[e][1,3]thiazine-2,3'-indolin]-2'-one 1,1-dioxide (***3ab***). White solid (33 mg, 84% yield), ethyl acetate/petroleum ether = 1:8. mp 209-210 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.03 (m, 1H), 7.95 (s, 1H), 7.72-7.67 (m, 2H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.55-7.43 (m, 5H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 2.33 (s,

3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 167.7, 139.4, 137.9, 134.1, 133.7, 133.6, 132.3, 132.2, 131.3, 131.1, 130.9, 129.5, 129.1, 128.5, 124.8, 120.3, 110.5, 81.0, 21.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{17}N_2O_3S$ 389.0960; found 389.0952.

6'-Methyl-4-phenylspiro[benzo[e][1,3]thiazine-2,3'-indolin]-2'-one 1,1-dioxide (***3ac***). White solid (33 mg, 86% yield), ethyl acetate/petroleum ether = 1:5. mp 239-241 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-8.05 (m, 1H), 8.03 (s, 1H), 7.71-7.68 (m, 2H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.55 (s, 1H), 7.53-7.43 (m, 4H), 7.15 (d, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6 & $CDCl_3$) δ 168.6, 167.4, 141.4, 137.7, 134.7, 134.0, 133.4, 132.5, 132.4, 131.5, 131.3, 130.5, 129.6, 129.0, 128.7, 124.8, 120.8, 111.0, 81.1, 21.0. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{17}N_2O_3S$ 389.0960; found 389.0952.

5'-Methoxy-4-phenylspiro[benzo[e][1,3]thiazine-2,3'-indolin]-2'-one 1,1-dioxide (***3ad***). White solid (31 mg, 76% yield), ethyl acetate/petroleum ether = 1:8. mp 215-216 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-8.00 (m, 2H), 7.71-7.68 (m, 2H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.54-7.43 (m, 4H), 7.29 (d, *J* = 1.6 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.73-6.69 (m, 1H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 167.5, 156.5, 137.8, 135.1, 134.1, 133.6, 132.3, 131.2, 131.1, 130.9, 129.4, 128.5, 124.7, 121.3, 117.8, 114.0, 111.4, 81.3, 55.9. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{17}N_2O_4S$ 405.0909; found 405.0904.

5'-Fluoro-4-phenylspiro[benzo[e][1,3]thiazine-2,3'-indolin]-2'-one 1,1-dioxide (***3ae***). White solid (22 mg, 57% yield), acetone/petroleum ether = 1:8. mp 212-213 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.07-8.03 (m, 1H), 7.73-7.69 (m, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.55-7.44 (m, 5H), 7.04 (td, *J* = 8.4, 2.4 Hz, 1H), 6.72 (dd, *J* = 8.4, 4.0 Hz, 1H). ^{13}C

NMR (100 MHz, $CDCl_3$) δ 169.6, 167.7, 159.5 (*J* = 241.9 Hz), 137.9 (*J* = 2.6 Hz), 137.7, 133.8, 132.5, 131.3, 131.1, 131.1, 129.4, 128.6, 124.9, 122.0 (*J* = 8.9 Hz), 118.4 (*J* = 23.8 Hz), 116.5 (*J* = 25.6 Hz), 111.5 (*J* = 8.0 Hz), 81.1 (*J* = 2.2 Hz). HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{14}FN_2O_3S$ 393.0709 ; found 393.0705.

5'-Chloro-4-phenylspiro[benzo[e][1,3]thiazine-2,3'-indolin]-2'-one 1,1-dioxide (***3af***). White solid (23 mg, 56% yield), acetone/petroleum ether = 1:8. mp 237-238 ℃. ^1H NMR (400 MHz, DMSO-d_6) δ 8.09 (d, *J* = 8.0 Hz, 1H), 7.94-7.87 (m, 2H), 7.64-7.51 (m, 7H), 7.49 (s, 1H), 7.10 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.0, 167.2, 143.0, 137.6, 135.1, 133.7, 133.6, 132.4, 131.8, 131.6, 130.5, 129.8, 129.1, 127.8, 127.2, 125.0, 122.8, 113.0, 81.1. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{14}ClN_2O_3S$ 409.0414 ; found 409.0409.

5'-Bromo-4-phenylspiro[benzo[e][1,3]thiazine-2,3'-indolin]-2'-one 1,1-dioxide (***3ag***). White solid (28 mg, 63% yield), acetone/petroleum ether = 1:8. mp 235-237 ℃. ^1H NMR (400 MHz, DMSO-d_6) δ 8.09 (d, *J* = 6.8 Hz, 1H), 7.93-7.89 (m, 2H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.63-7.53 (m, 7H), 7.06 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.9, 167.2, 144.0, 137.6, 135.2, 135.1, 133.7, 133.6, 131.7, 131.6, 130.6, 130.4, 129.7, 129.1, 125.0, 123.3, 114.5, 113.6, 81.1. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{14}BrN_2O_3S$ 452.9909 ; found 452.9905.

6'-Chloro-4-phenylspiro[benzo[e][1,3]thiazine-2,3'-indolin]-2'-one 1,1-dioxide (***3ah***). White solid (31 mg, 75% yield), ethyl acetate/petroleum ether = 1:5. mp 251-253 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ 8.03-8.00 (m, 1H), 7.71-7.66 (m, 2H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.52-7.40 (m, 5H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.79 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ

168.9, 167.6, 145.9, 137.7, 136.9, 135.0, 133.7, 133.6, 131.7, 131.5, 130.6, 129.7, 129.6, 129.1, 125.0, 123.1, 119.8, 111.6, 80.9. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{14}ClN_2O_3S$ 409.0414; found 409.0409.

6'-Bromo-4-phenylspiro[benzo[e][1,3]thiazine-2,3'-indolin]-2'-one 1,1-dioxide (***3ai***). White solid (32 mg, 70% yield), ethyl acetate/petroleum ether = 1:5. mp 253-255 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.43 (s, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.93-7.87 (m, 2H), 7.63-7.58 (m, 3H), 7.54-7.51 (m, 3H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.23 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.9, 167.3, 145.4, 137.5, 135.0, 133.6, 133.5, 131.7, 131.5, 130.4, 129.8, 129.6, 129.1, 126.1, 125.3, 124.9, 120.1, 114.2, 80.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{14}BrN_2O_3S$ 452.9909; found 452.9905.

1'-Methyl-4-phenylspiro[benzo[e][1,3]thiazine-2,3'-indolin]-2'-one 1,1-dioxide (***3aj***) White solid (17 mg, 43% yield), ethyl acetate/petroleum ether = 1:8. mp 244-246 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.04 (m, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.74-7.69 (m, 2H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.54-7.43 (m, 5H), 7.23 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 3.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 166.7, 144.9, 138.0, 134.3, 133.6, 132.3, 131.9, 131.3, 131.1, 130.9, 129.5, 128.5, 128.3, 124.8, 124.2, 120.1, 109.1, 80.6, 27.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{17}N_2O_3S$ 389.0960; found 389.0956.

5'-Methoxy-4-(3-methoxyphenyl)spiro[benzo[e][1,3]thiazine-2,3'-indolin]-2'-one 1,1-dioxide (***3cd***). White solid (32 mg, 73% yield), ethyl acetate/petroleum ether = 1:5. mp 147-149 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 8.05-8.02 (m, 1H), 7.71-7.67 (m, 2H), 7.52-7.47 (m, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 2.0 Hz, 1H), 7.17-7.14 (m, 2H), 7.06 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.88 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 3.79 (s,

3H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 167.6, 159.6, 156.5, 139.1, 135.1, 134.0, 133.6, 132.3, 131.2, 131.1, 129.5, 124.7, 121.8, 121.3, 117.8, 117.1, 114.3, 114.0, 111.4, 81.3, 55.9, 55.5. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{19}N_2O_5S$ 435.1015; found 435.1009.

4-(4-(Tert-butyl)phenyl)-6'-methylspiro[benzo[e][1,3]thiazine-2,3'-indolin]-2'-one 1,1-dioxide (***3ec***). White solid (39 mg, 87% yield), ethyl acetate/petroleum ether = 1:5. mp 251-253℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-8.05 (m, 1H), 7.76 (s, 1H), 7.72-7.68 (m, 2H), 7.58-7.54 (m, 4H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 2.33 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.3, 167.6, 154.5, 141.4, 135.1, 134.8, 134.1, 133.4, 132.6, 132.4, 131.4, 130.7, 129.6, 128.7, 125.9, 124.8, 121.1, 111.0, 81.1, 35.2, 31.5, 21.1. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{26}H_{25}N_2O_3S$ 445.1586 ; found 445.1579.

6'-Chloro-4-(3-methoxyphenyl)spiro[benzo[e][1,3]thiazine-2,3'-indolin]-2'-one 1,1-dioxide (***3bh***). White solid (38 mg, 86% yield), ethyl acetate/petroleum ether = 1:5. mp 213-215 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.05-8.06 (m, 1H), 7.92-7.86 (m, 2H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.21 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.17 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.13-7.08 (m, 3H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.7, 167.5, 159.7, 145.8, 139.0, 136.9, 135.0, 133.7, 133.6, 131.6, 130.6, 130.3, 129.6, 124.9, 123.1, 122.1, 119.8, 117.7, 114.5, 111.6, 80.8, 55.9. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{16}ClN_2O_4S$ 439.0519 ; found 439.0514.

4-(3-Fluorophenyl)-5'-methylspiro[benzo[e][1,3]thiazine-2,3'-indolin]-2'-one 1,1-dioxide (***3fb***). White solid (35 mg, 87% yield), ethyl acetate/petroleum ether = 1:5. mp

185-187 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.15 (s, 1H), 8.09-8.07 (m, 1H), 7.92-7.87 (m, 2H), 7.60-7.54 (m, 2H), 7.48-7.41 (m, 3H), 7.35 (s, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.4 (*J* = 2.4 Hz), 167.2, 162.4 (*J* = 243.8 Hz), 141.4, 139.9 (*J* = 7.5 Hz), 134.9, 133.9, 133.7, 132.6, 132.5, 131.3, 131.2, 130.2, 128.6, 125.9 (*J* = 2.5 Hz), 124.9, 120.6, 118.5 (*J* = 20.9 Hz), 116.3 (*J* = 22.9 Hz), 111.0, 81.2, 21.0. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{16}FN_2O_3S$ 407.0866; found 407.0860.

6'-Chloro-4-(3-fluorophenyl)spiro[benzo[e][1,3]thiazine-2,3'-indolin]-2'-one 1,1-dioxide (***3fh***). White solid (32 mg, 74% yield), ethyl acetate/petroleum ether = 1:5. mp 255-257 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.47 (s, 1H), 8.10-8.07 (m, 1H), 7.94-7.88 (m, 2H), 7.61-7.56 (m, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.49-7.43 (m, 3H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.10 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.8 (*J* = 2.7 Hz), 167.3, 162.5 (*J* = 244.1 Hz), 145.4, 139.8 (*J* = 7.6 Hz), 137.0, 135.2, 133.9, 133.6, 131.5, 131.3 (*J* = 8.3 Hz), 130.2, 129.6, 126.0 (*J* = 3.3 Hz), 125.1, 123.3, 119.5, 118.7 (*J* = 20.8 Hz), 116.5 (*J* = 22.9 Hz), 111.6, 80.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{13}ClFN_2O_3S$ 427.0319; found 427.0314.

2.0 mmol Scale Synthesis of 3aa. To a solution of compound **1a** (486 mg, 2.0 mmol) and 3-chlorooxindole **2a** (668 mg, 4.0 mmol) in DME (15 mL) were added Cs_2CO_3 (1.30 g, 4.0 mmol). The reaction mixture was stirred at room temperature for 1 h. Upon completion of the reaction, the solid was filtered and washed with acetone, and the combined filtrate was concentrated under reduced pressure. The residue was purified using column chromatography to afford the compound **3aa** as a white solid (598 mg, 80% yield).

Procedure for the Synthesis of Compound 4. To a solution of compound **3aa** (37 mg, 0.1 mmol) in THF (1 mL) was added NaH (3.6 mg, 0.15 mmol). After stirring at 0 ℃ for 40

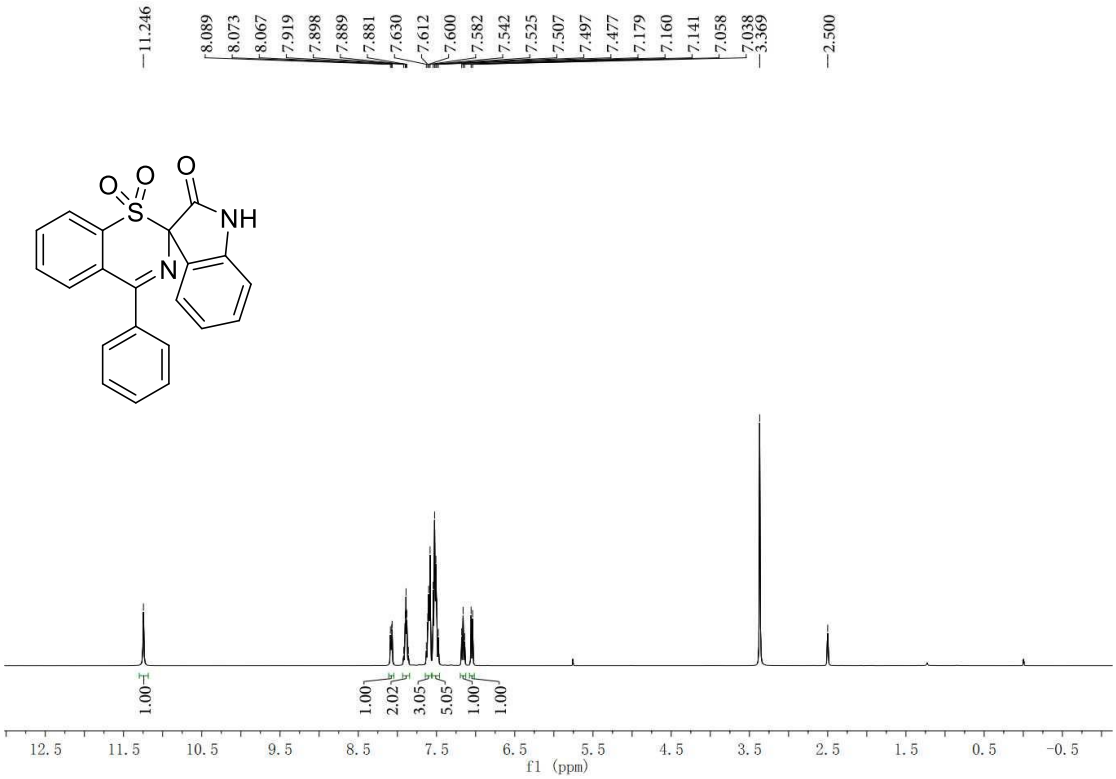
minutes, prenyl bromide (20 μL, 0.15 mmol) was added at 0 °C and the reaction mixture was warmed slowly to room temperature and stirred for additional 1 h. Then, the resulting mixture was quenched by water and extracted with DCM. The combined organic layers were dried and concentrated under reduced pressure followed by chromatography on silica gel to afford the compound **4.**

1'-(3-Methylbut-2-en-1-yl)-4-phenylspiro[benzo[e][1,3]thiazine-2,3'-indolin]-2'-one 1,1-dioxide (***4***). White solid (30 mg, 68% yield), ethyl acetate/petroleum ether = 1:8. mp 244-246 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-8.05 (m, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.74-7.69 (m, 2H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.54-7.43 (m, 5H), 7.21 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 5.17 (t, *J* = 6.4 Hz, 1H), 4.27 (d, *J* = 6.4 Hz, 2H), 1.77 (s, 3H), 1.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 166.2, 144.3, 138.0, 137.5, 134.3, 133.4, 132.2, 131.6, 131.3, 131.0, 130.8, 129.4, 128.4, 128.3, 124.7, 123.8, 120.2, 117.5, 109.8, 80.7, 39.3, 25.6, 18.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{26}H_{23}N_2O_3S$ 443.1429; found 443.1423.

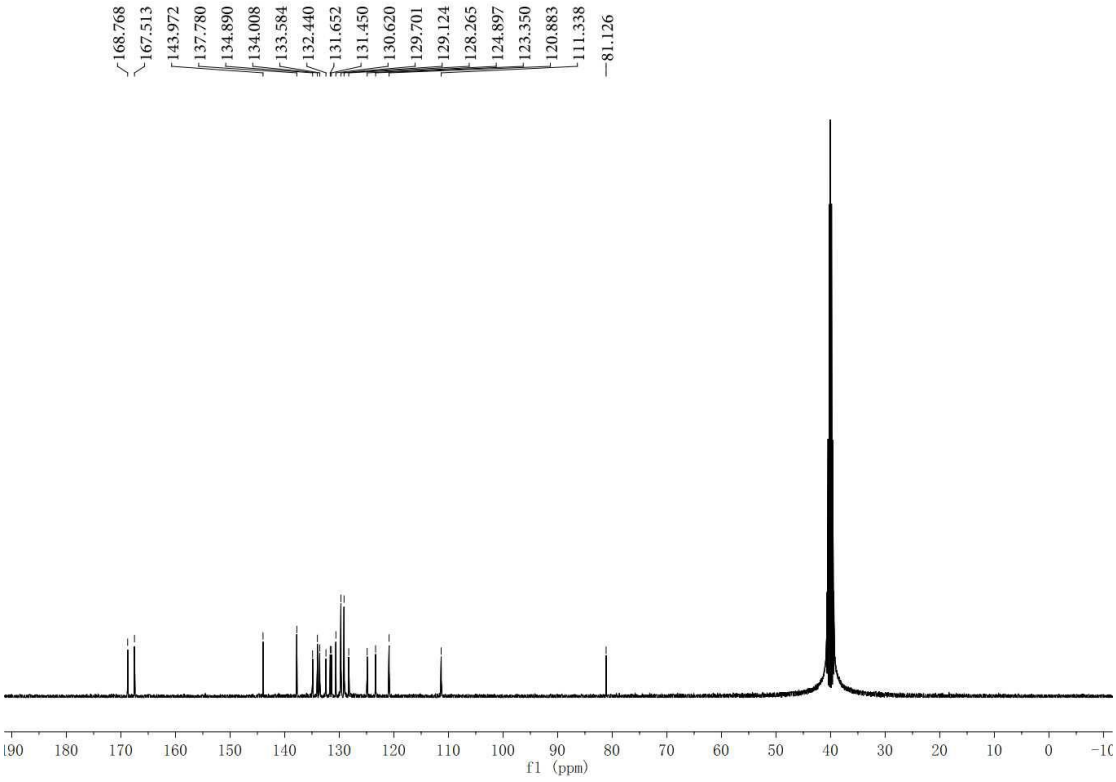
References

(1) T. Nishimura, A. Noishiki, G. Chit Tsui and T. Hayashi, *J. Am. Chem. Soc.*, 2012, **134**, 5056-5059.

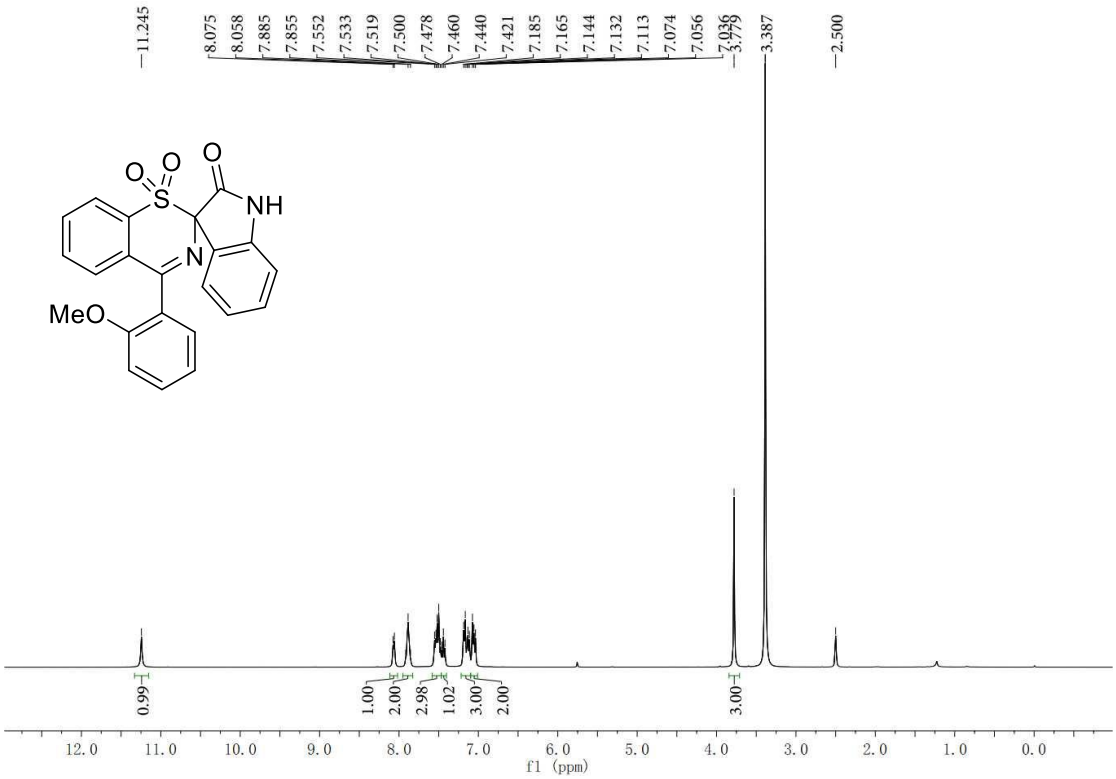
(2) V. Lakshmi Reddy, P. S. Prathima, V. J. Rao and R. Bikshapathi, *New J. Chem.*, 2018, **42**, 20152-20155.



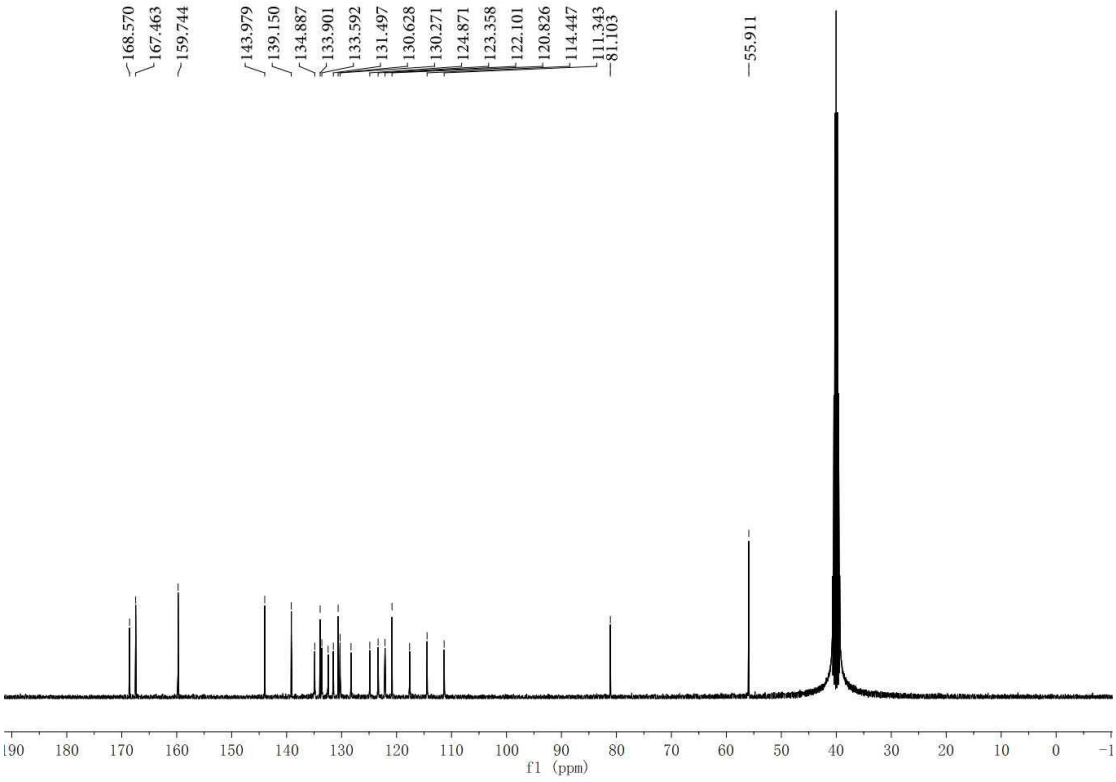
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound **3aa**



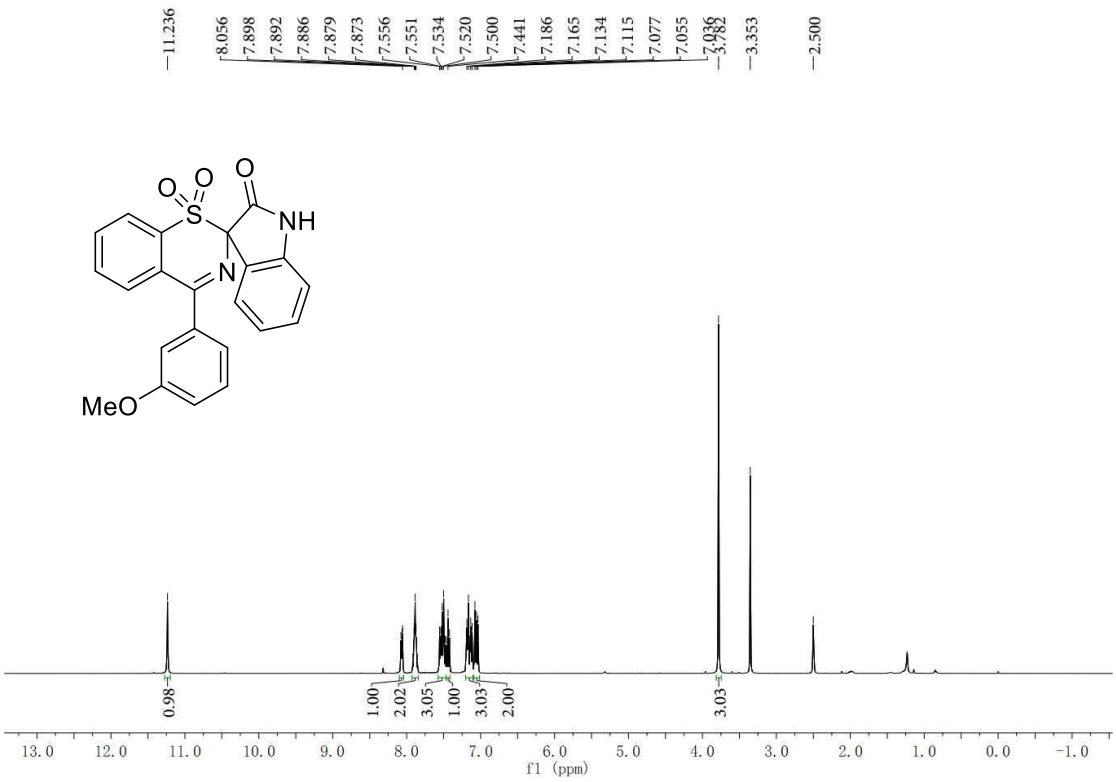
^{13}C NMR Spectrum (100 MHz, DMSO-d_6) of Compound **3aa**



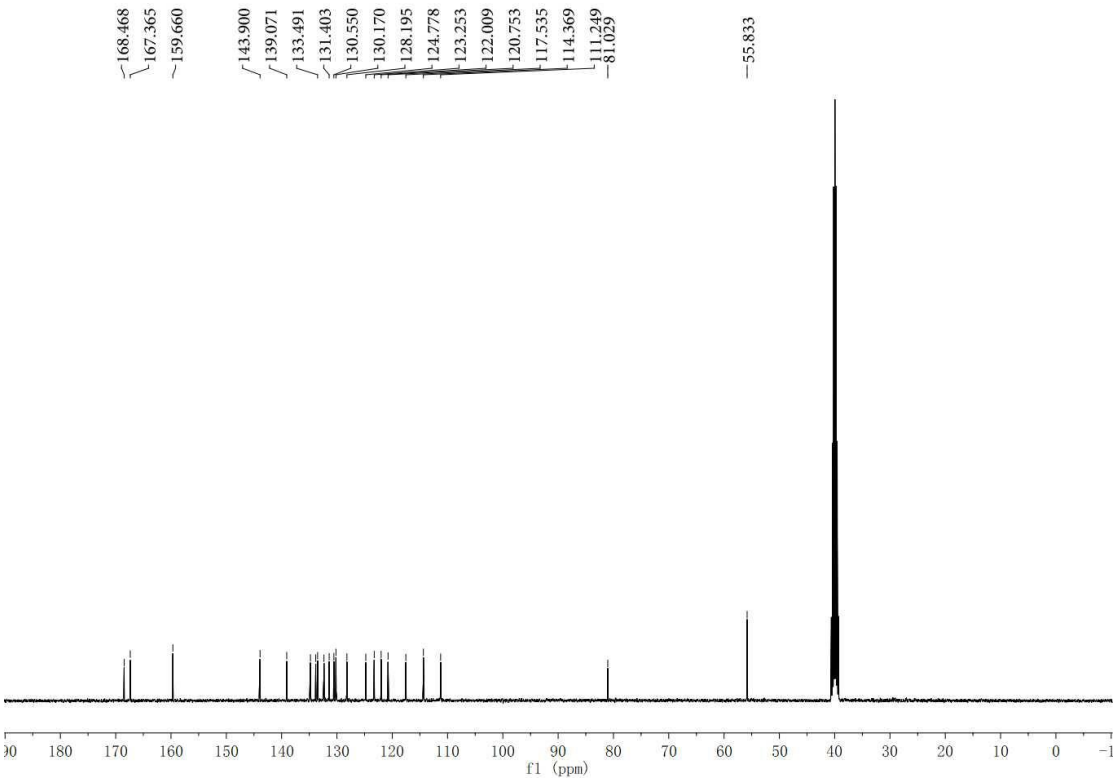
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound **3ba**



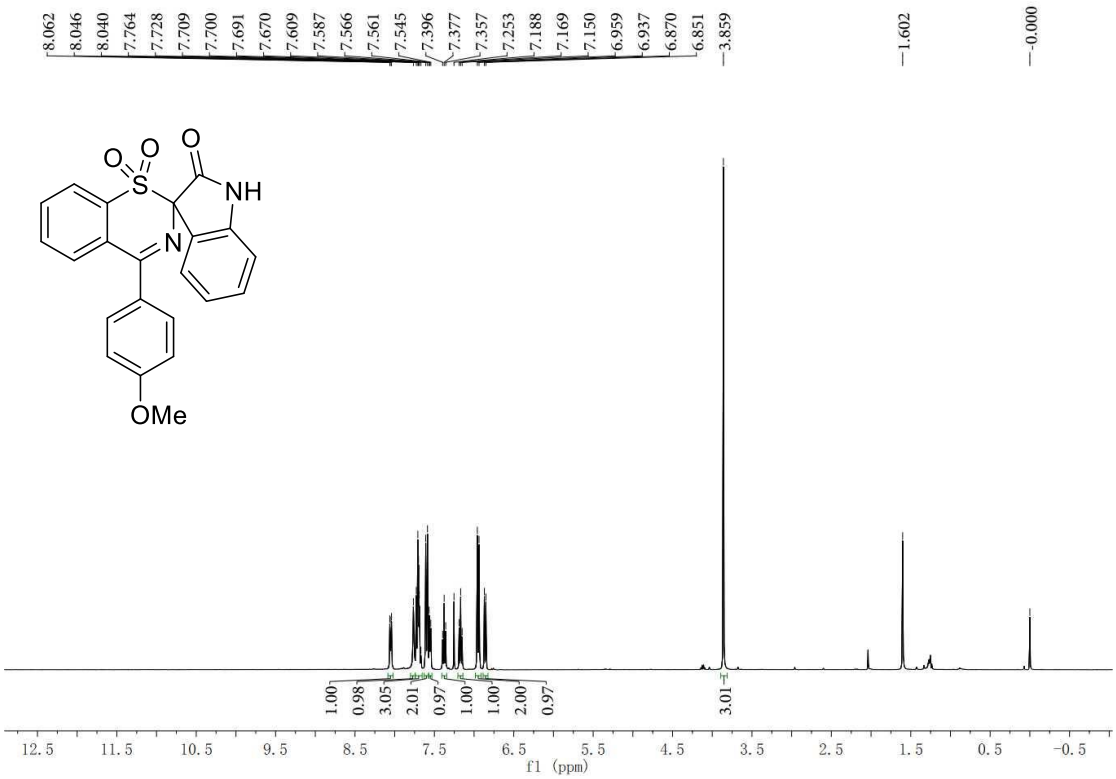
^{13}C NMR Spectrum (100 MHz, DMSO-d_6) of Compound **3ba**



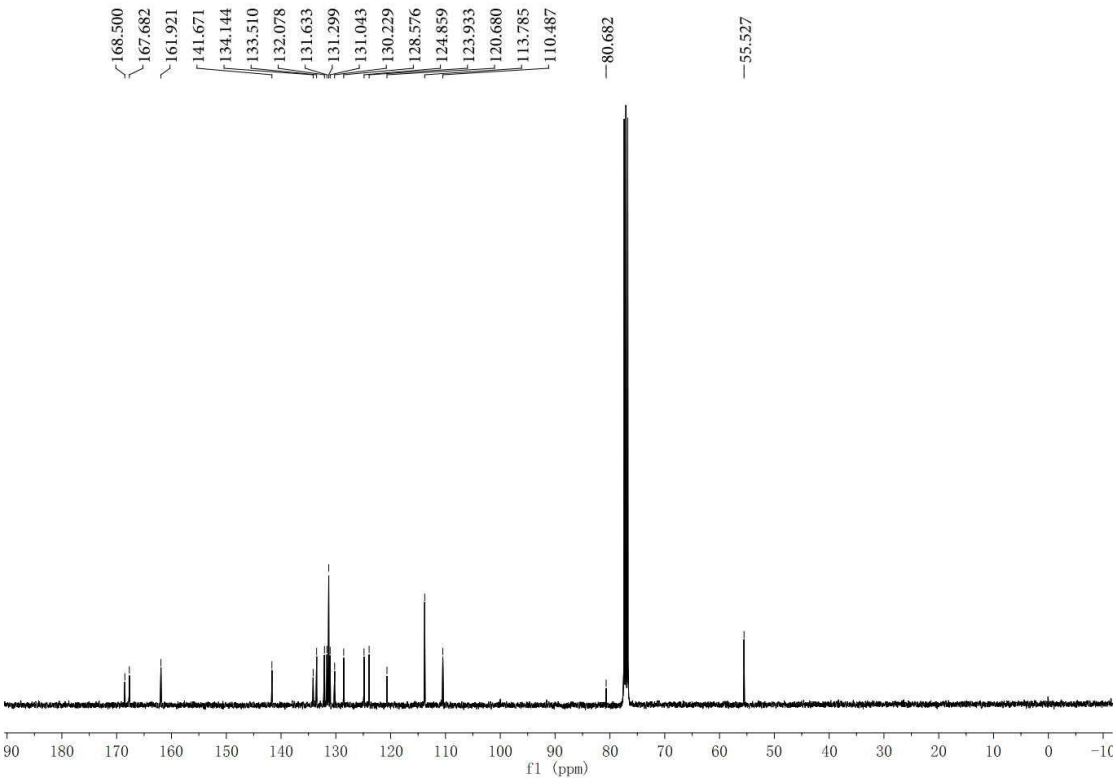
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound **3ca**



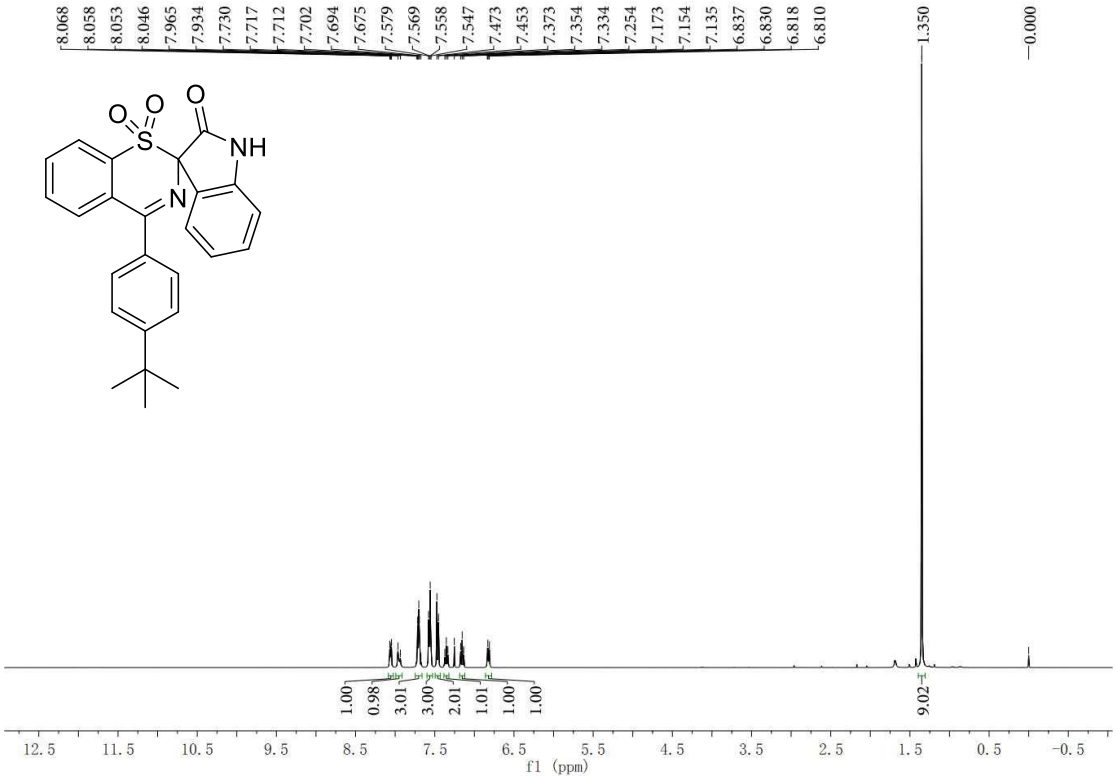
^{13}C NMR Spectrum (100 MHz, DMSO-d_6) of Compound **3ca**



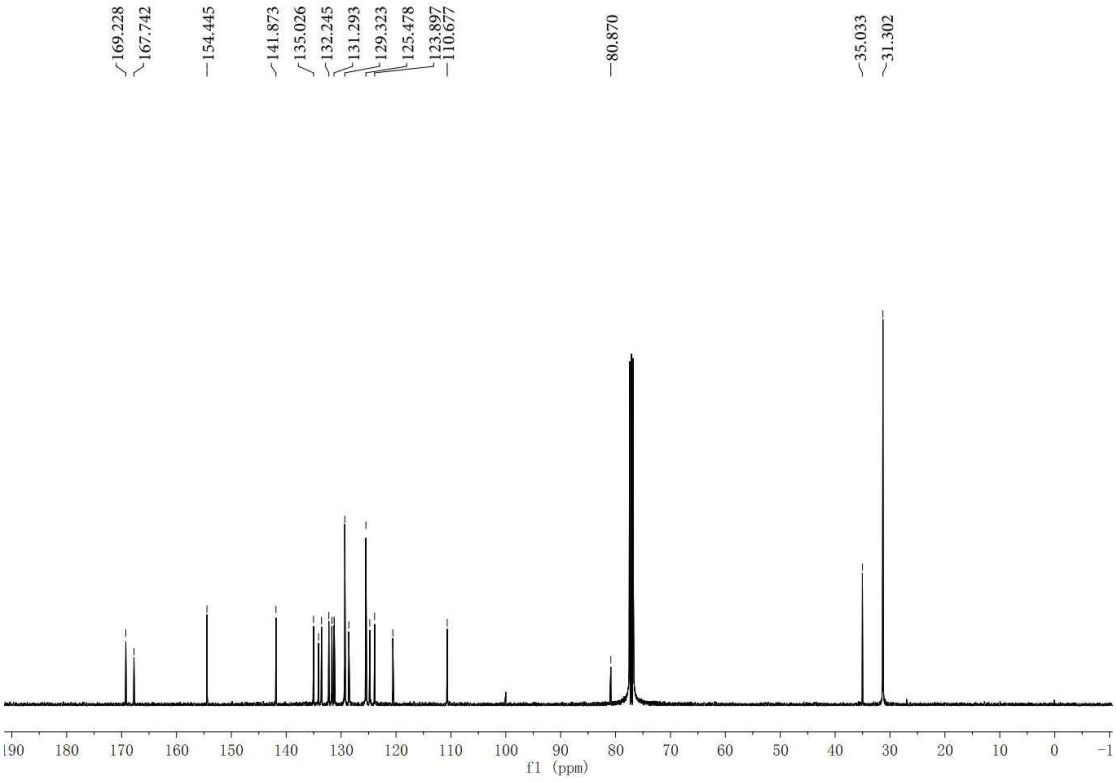
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3da**



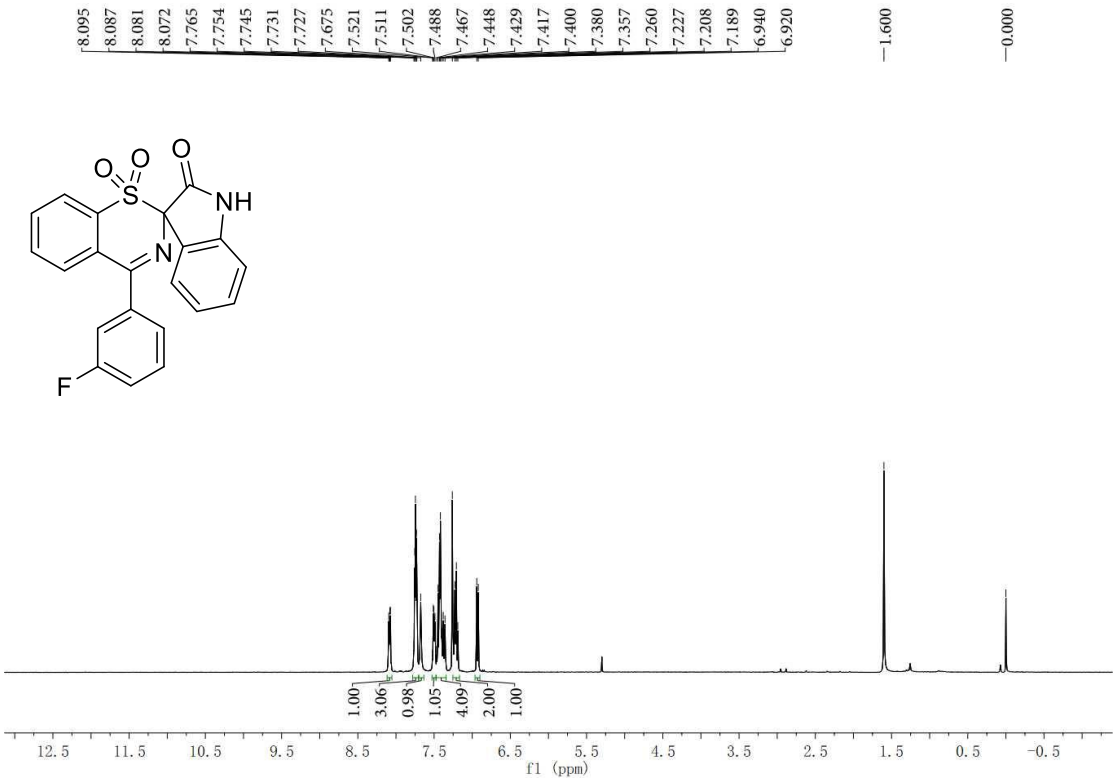
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3da**



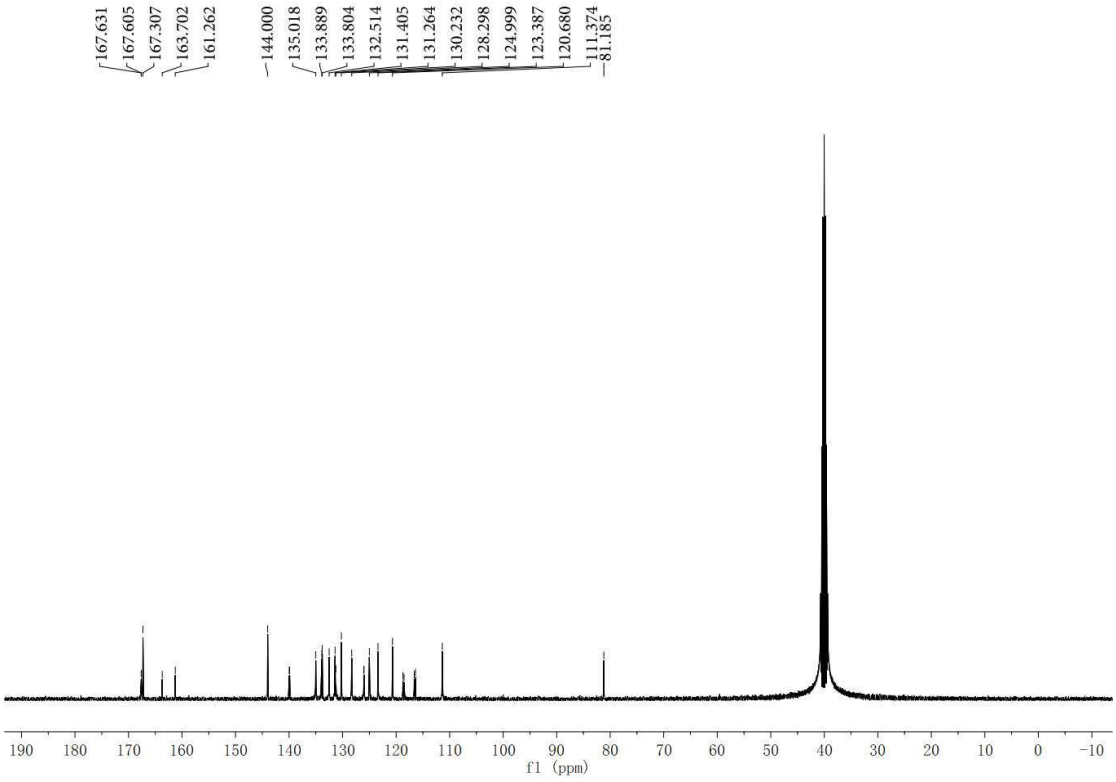
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ea**



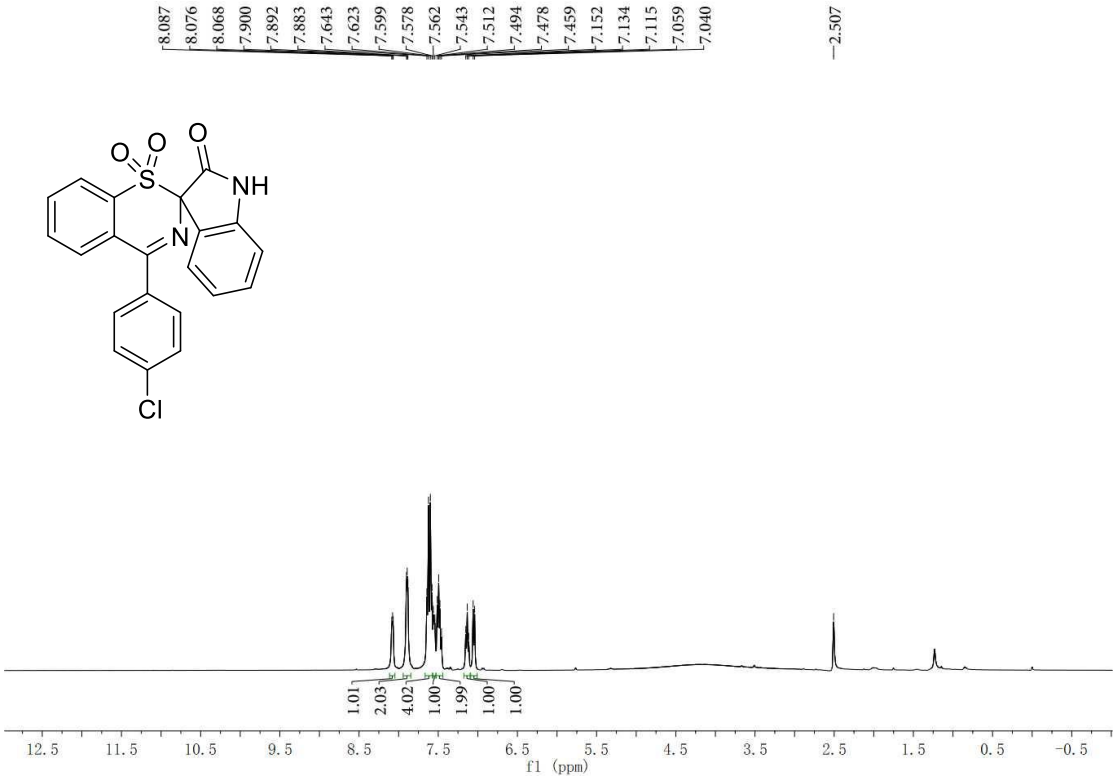
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3ea**



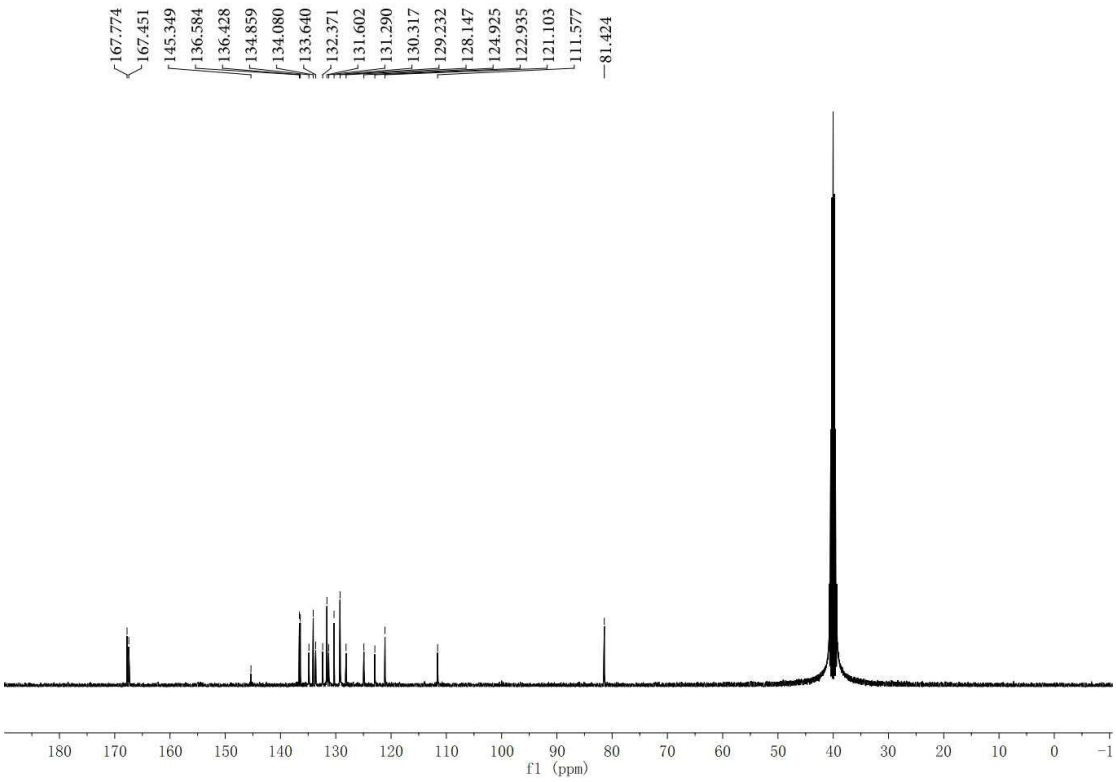
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3fa**



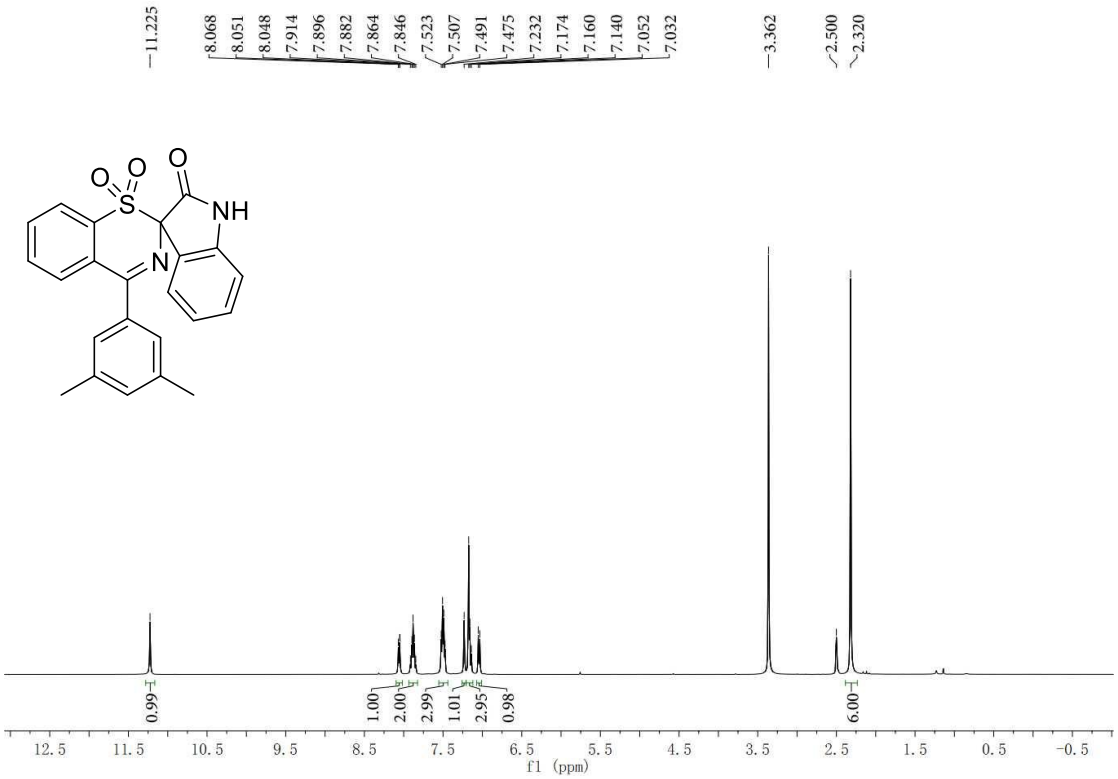
^{13}C NMR Spectrum (100 MHz, DMSO-d_6) of Compound **3fa**



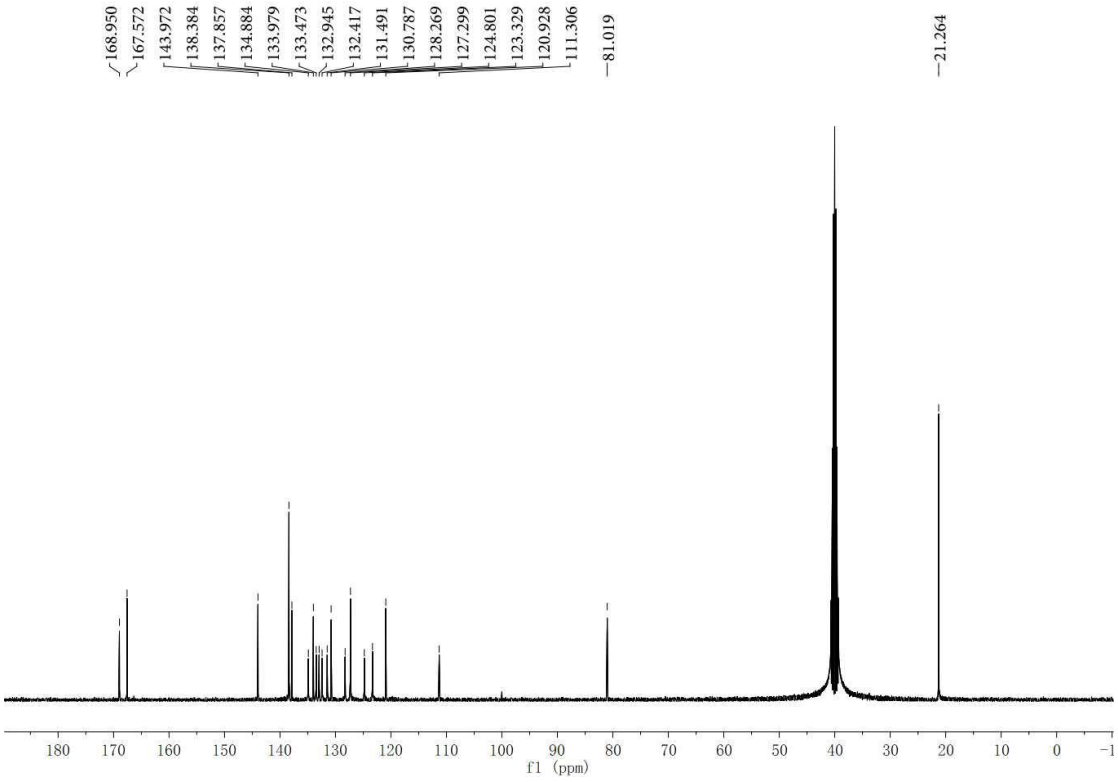
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound **3ga**



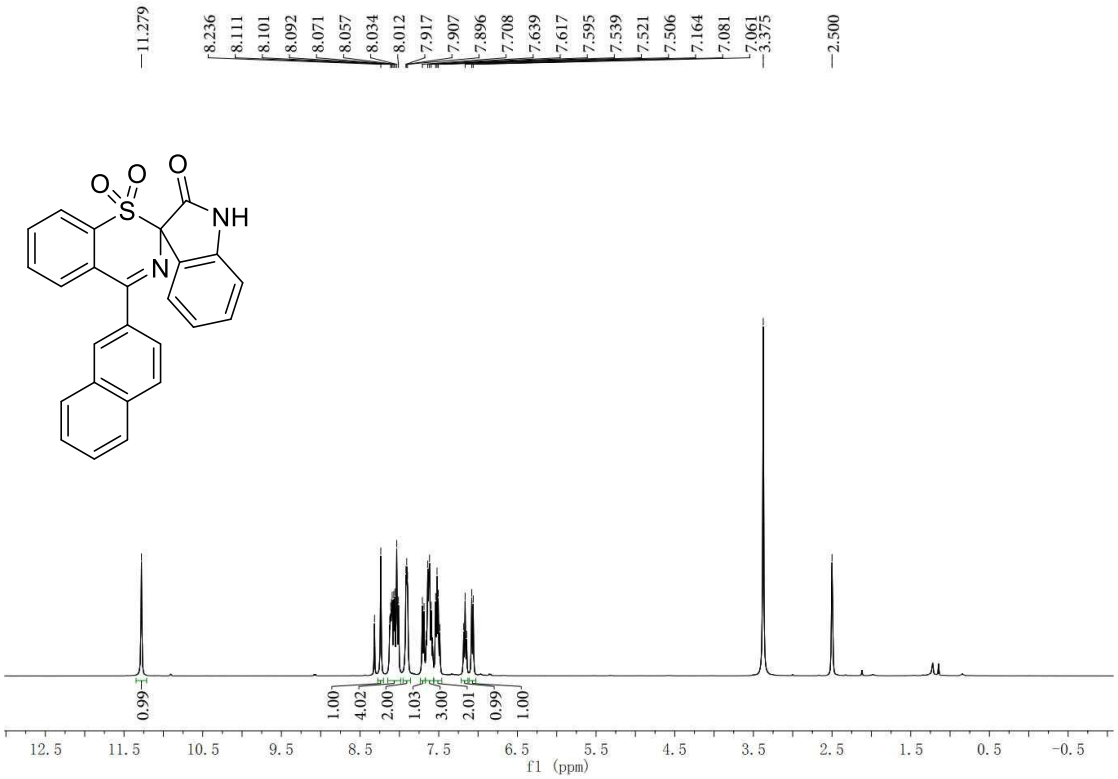
^{13}C NMR Spectrum (100 MHz, DMSO-d_6) of Compound **3ga**



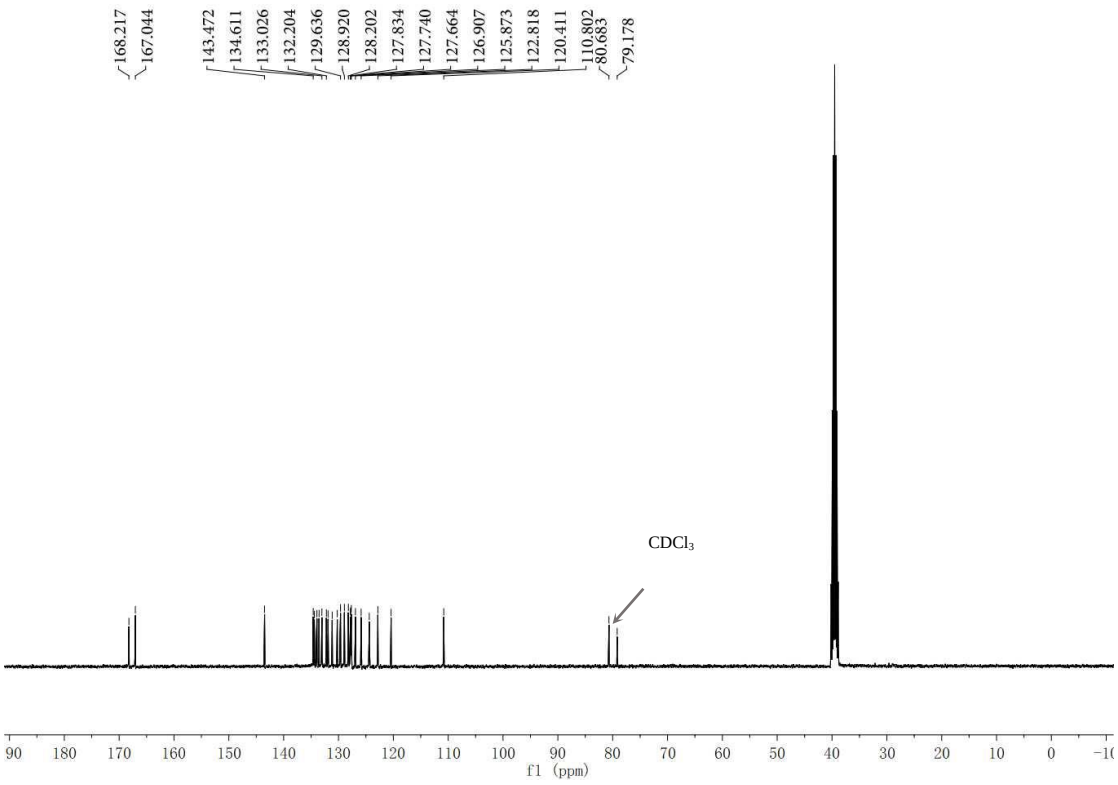
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound **3ha**



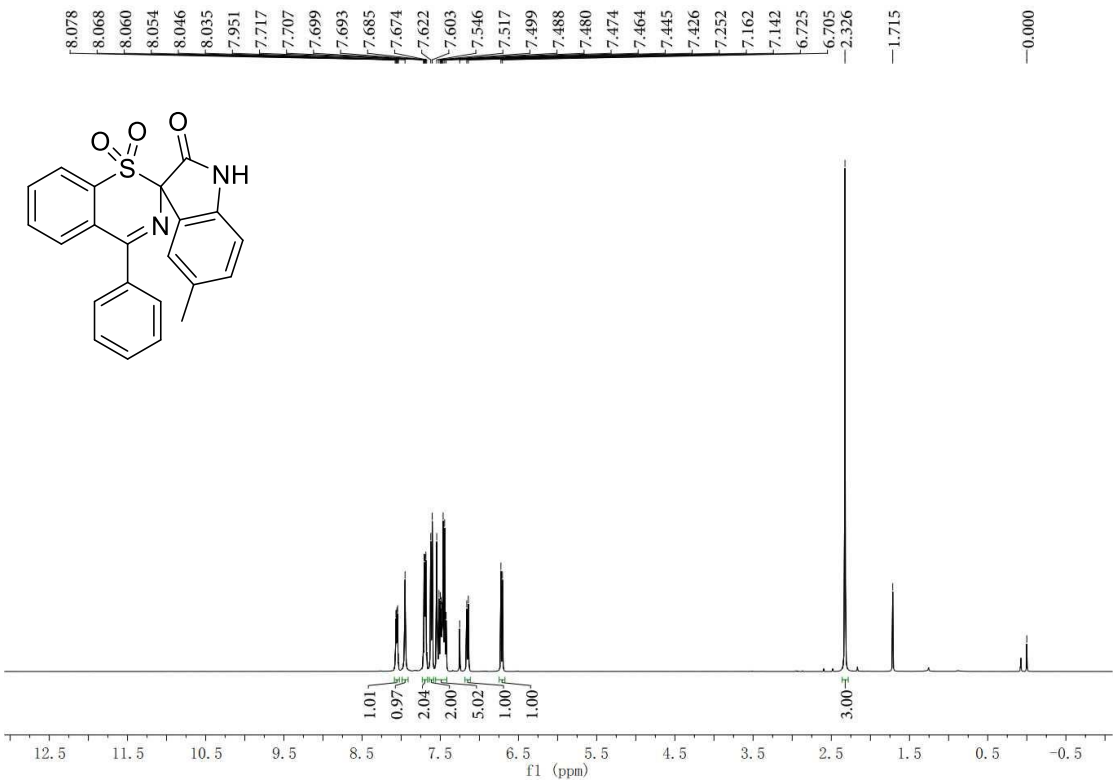
^{13}C NMR Spectrum (100 MHz, DMSO-d_6) of Compound **3ha**



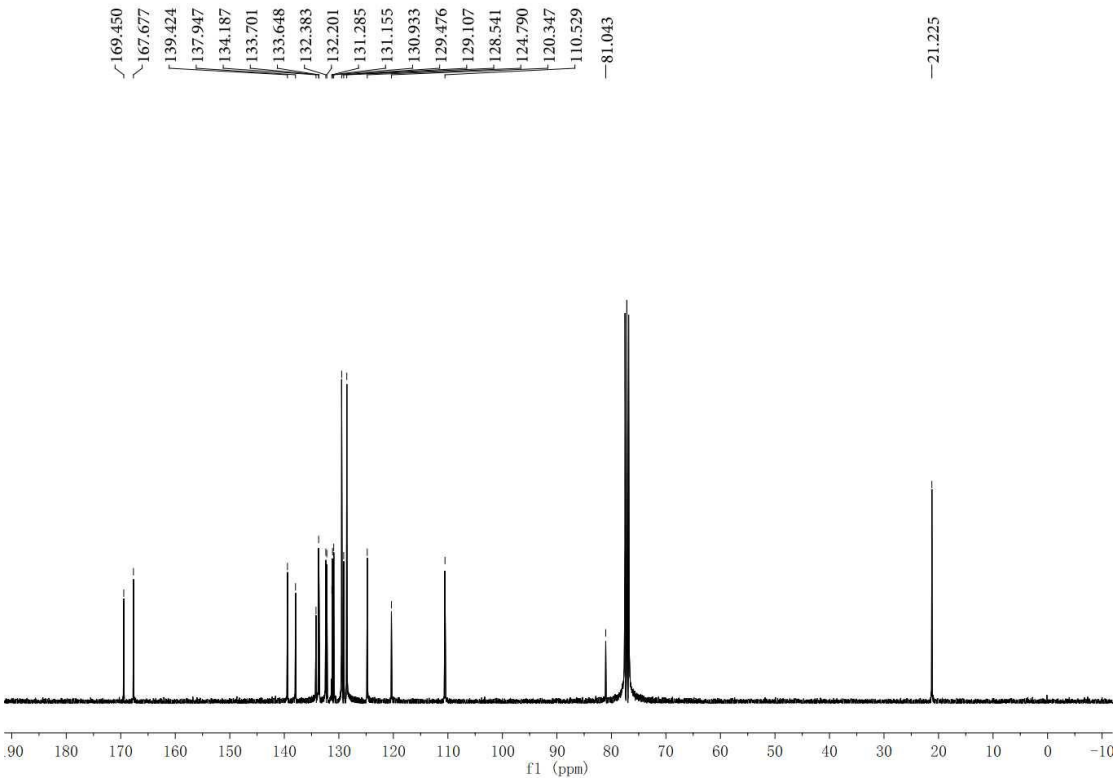
^{1}H NMR Spectrum (400 MHz, DMSO-d_6 & $CDCl_3$) of Compound **3ia**



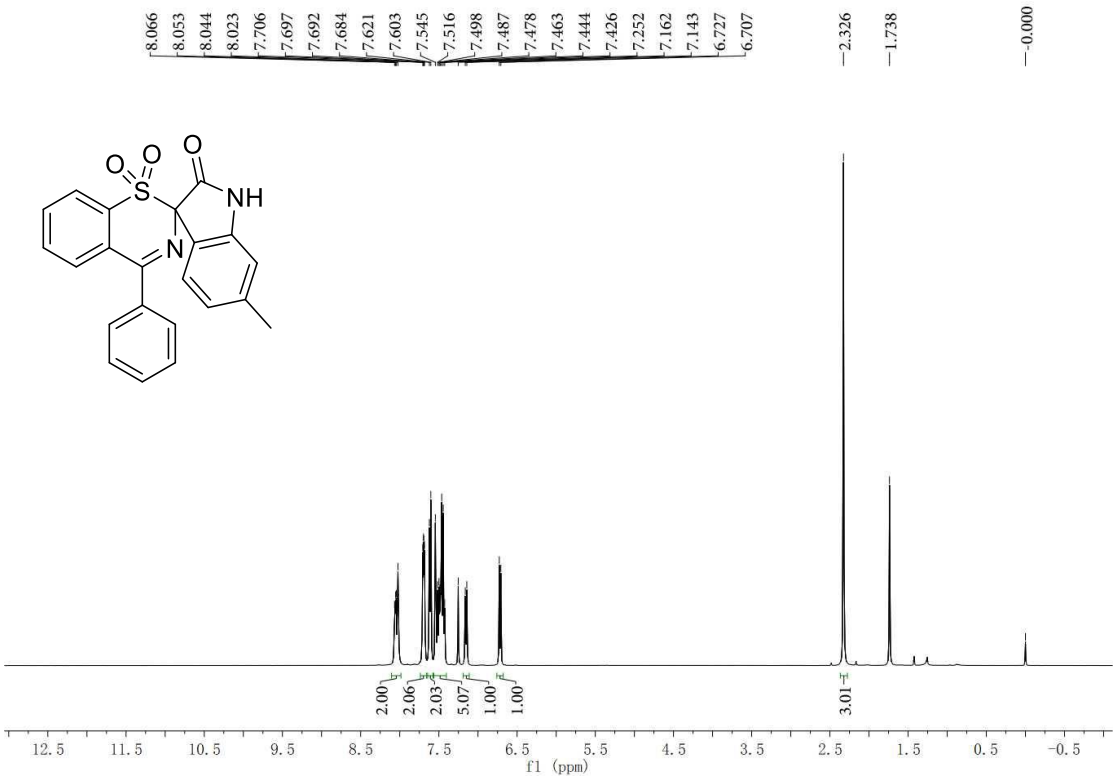
^{13}C NMR Spectrum (100 MHz, DMSO-d_6 & $CDCl_3$) of Compound **3ia**



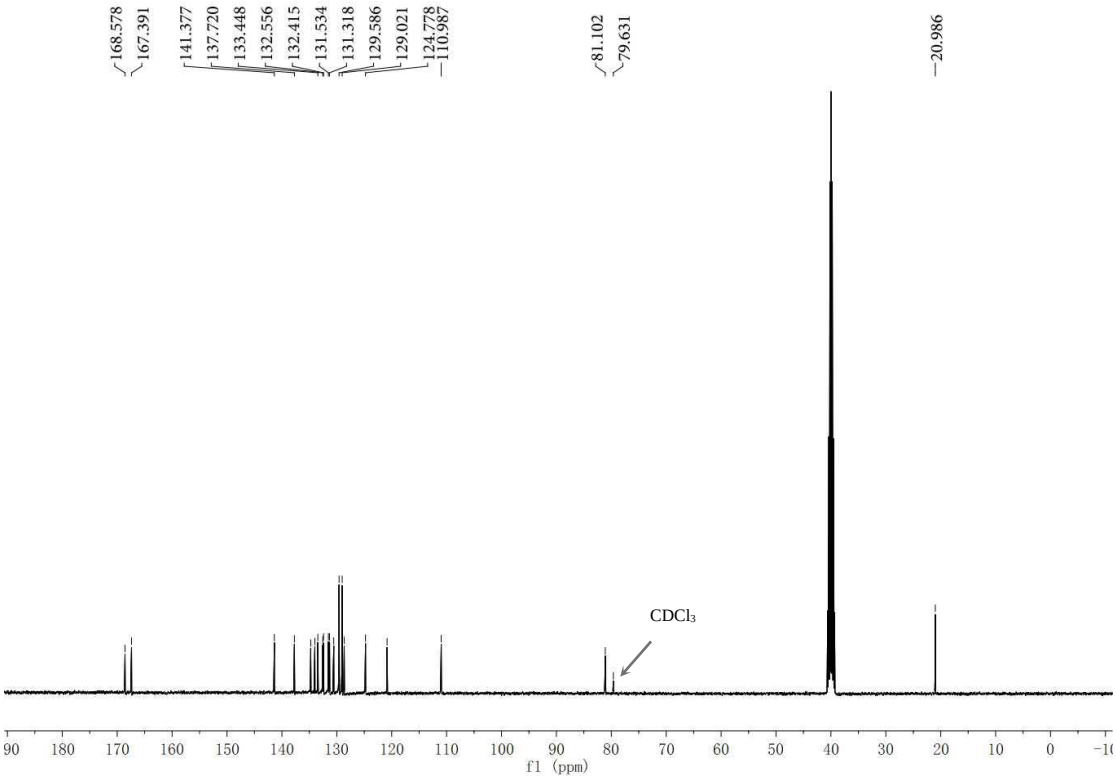
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ab**



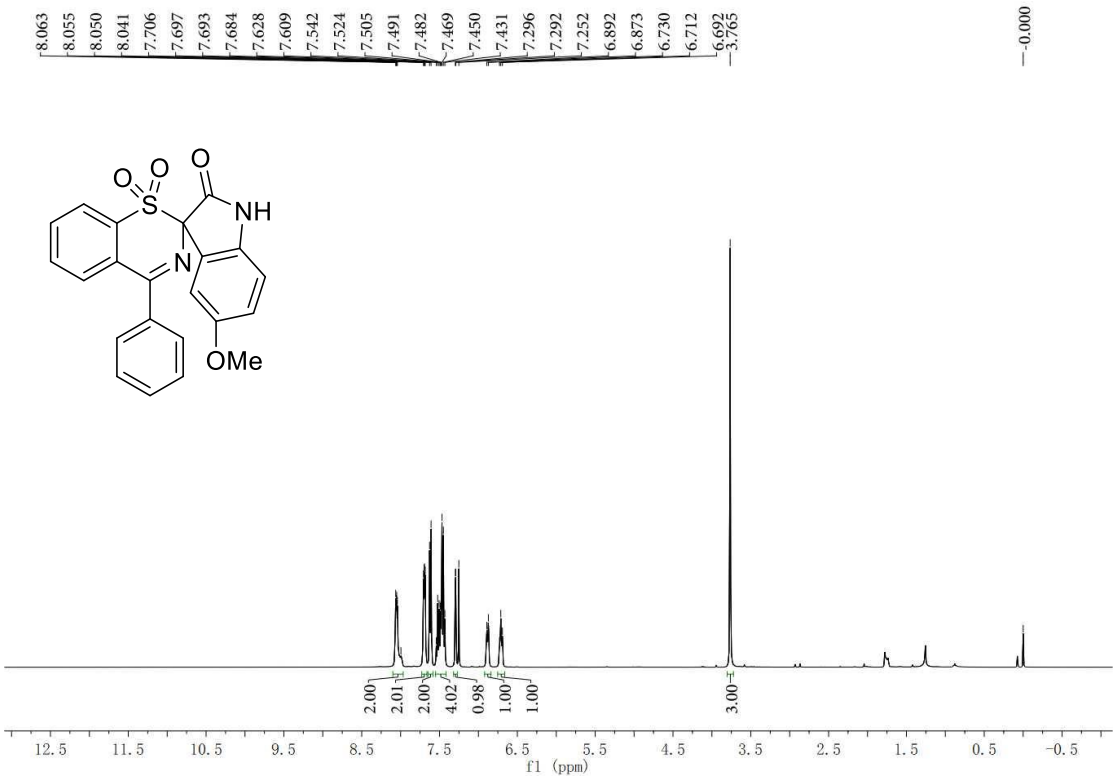
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3ab**



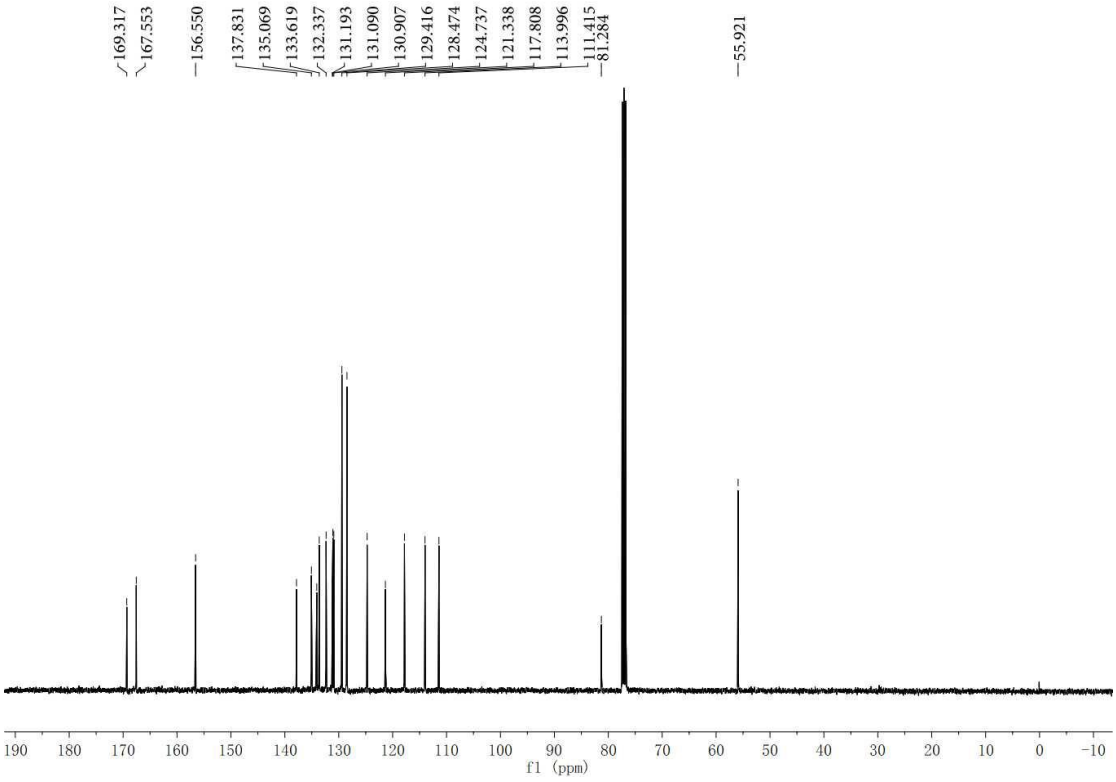
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ac**



^{13}C NMR Spectrum (100 MHz, DMSO-d_6 & $CDCl_3$) of Compound **3ac**



^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ad**



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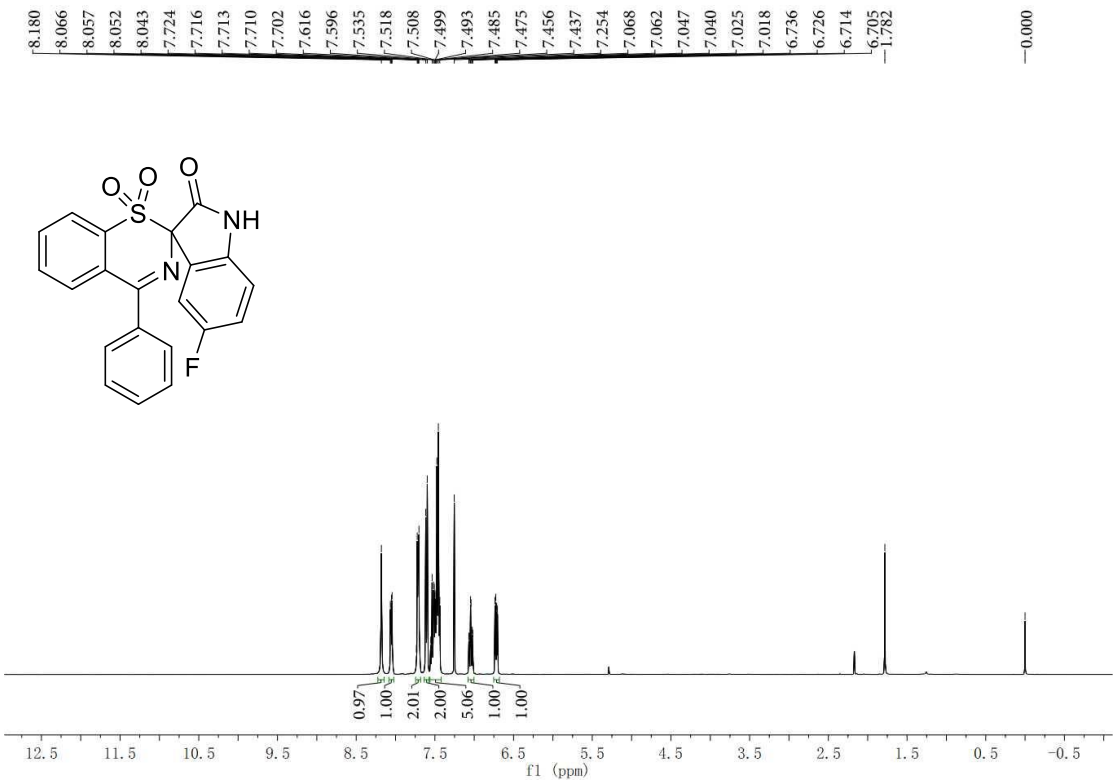
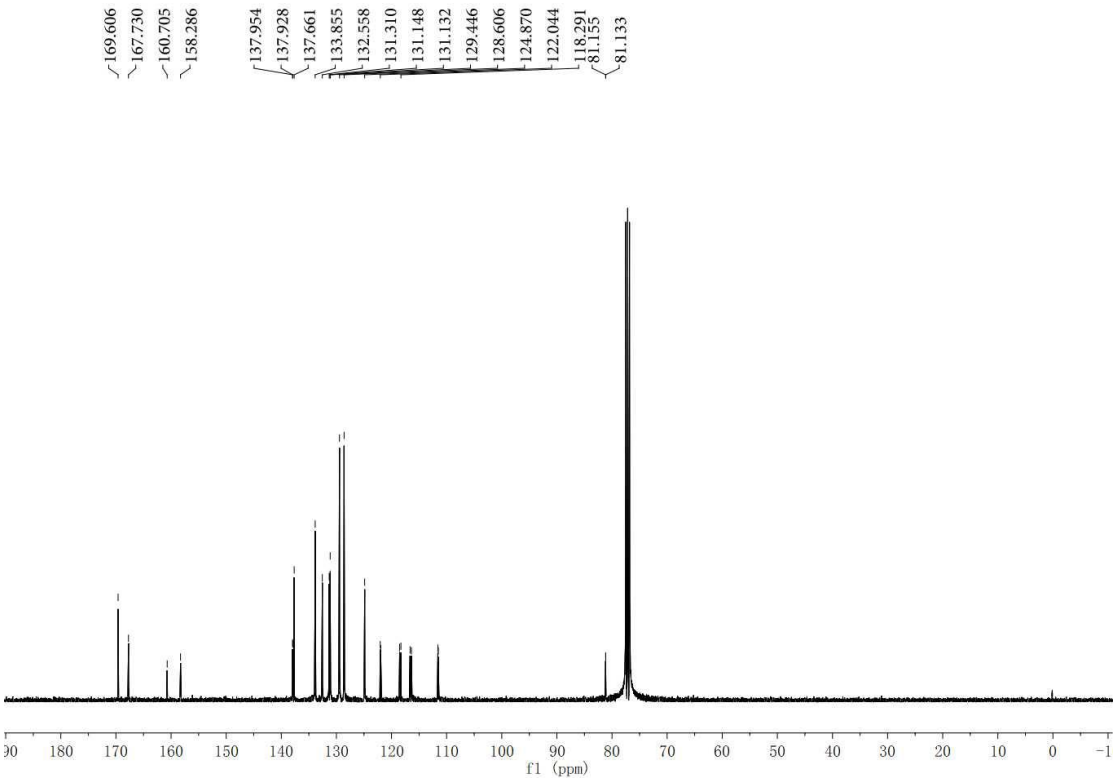


^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ae**



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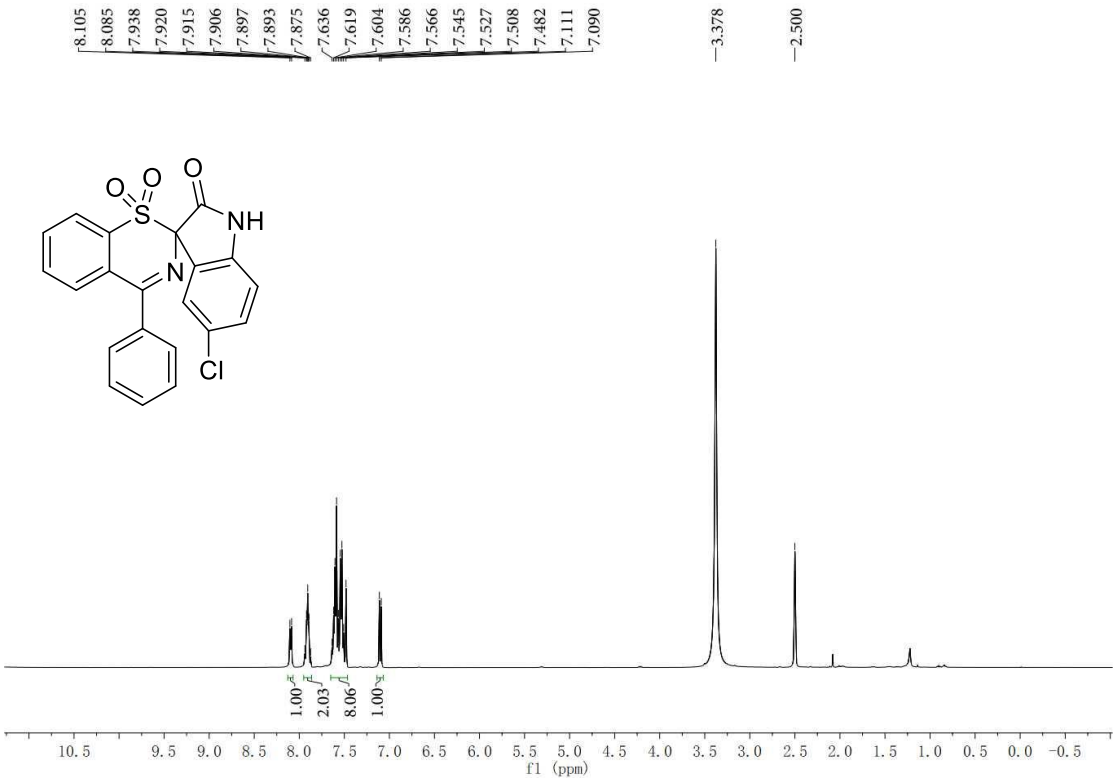

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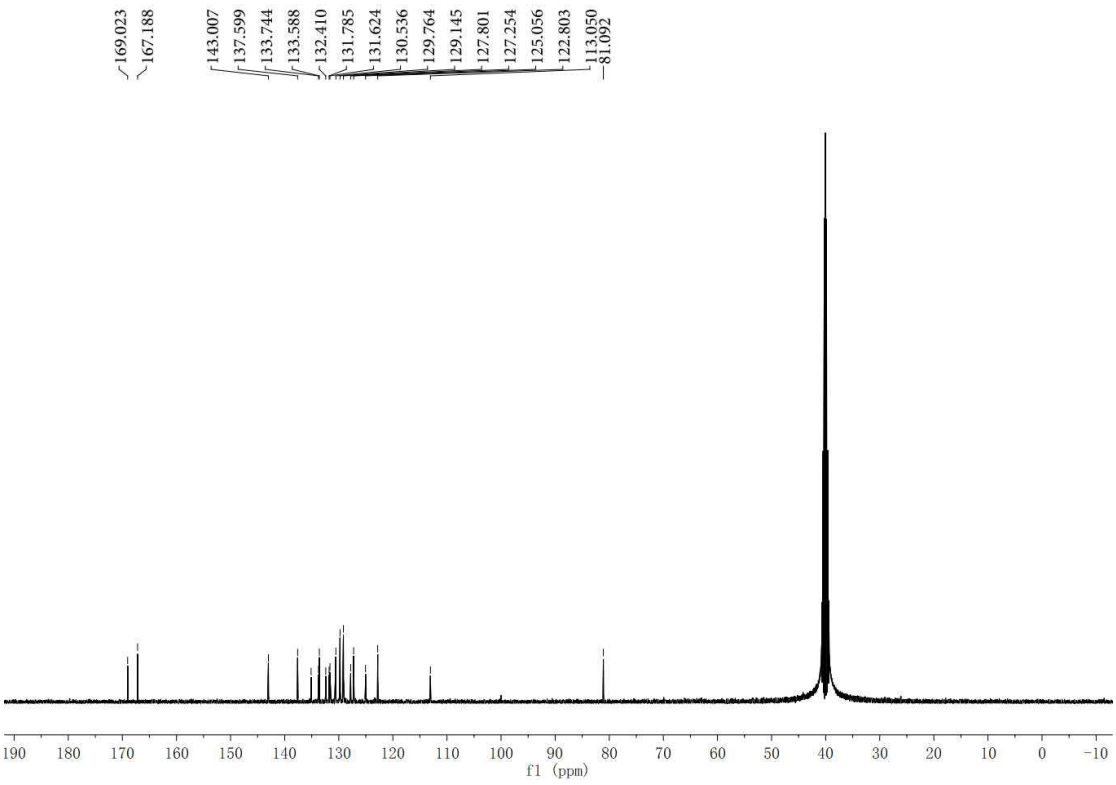

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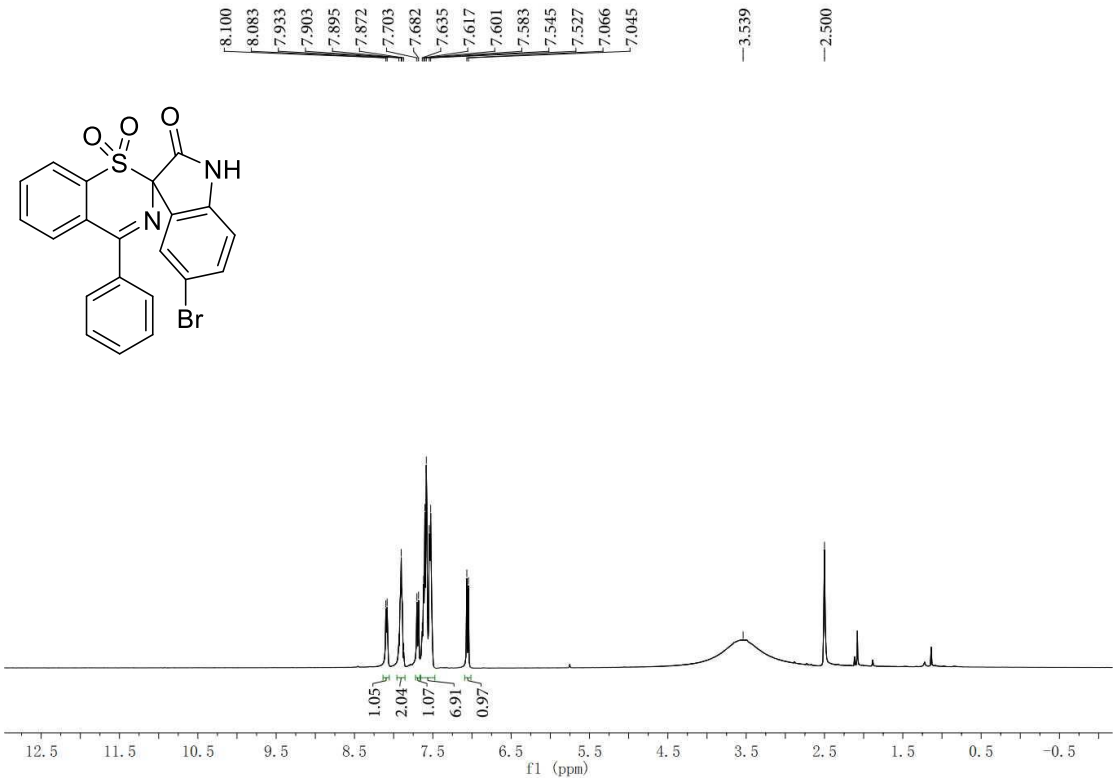
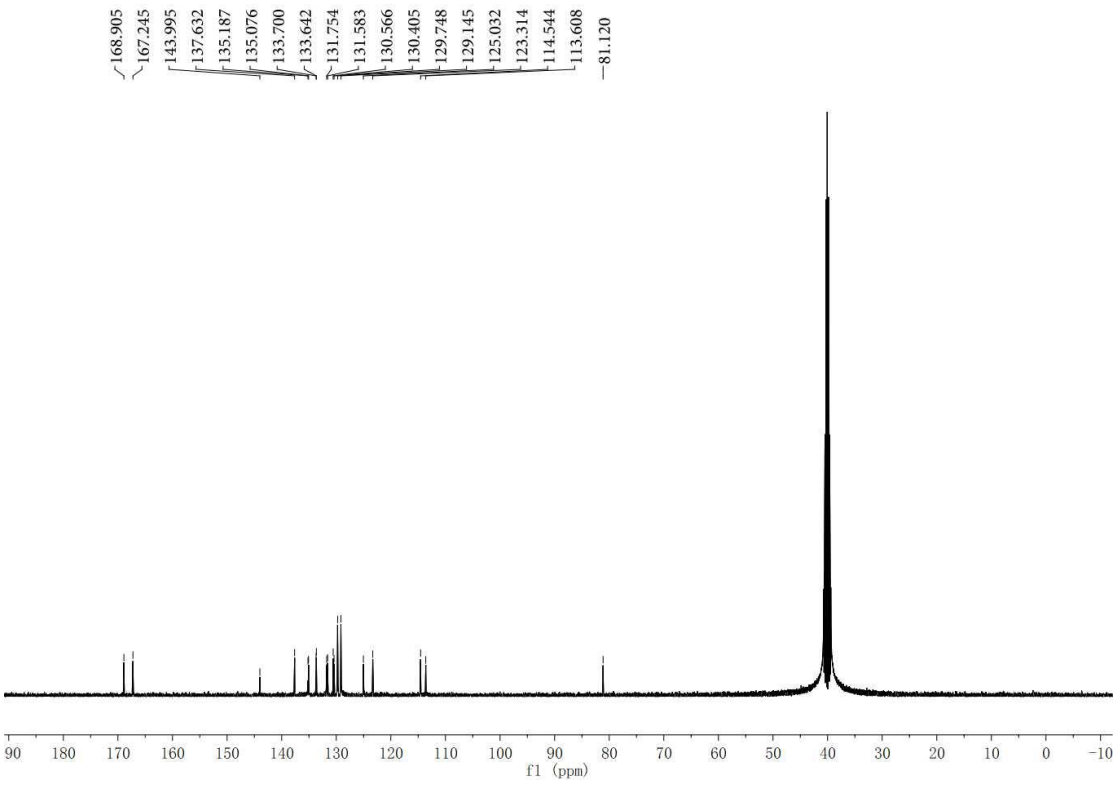
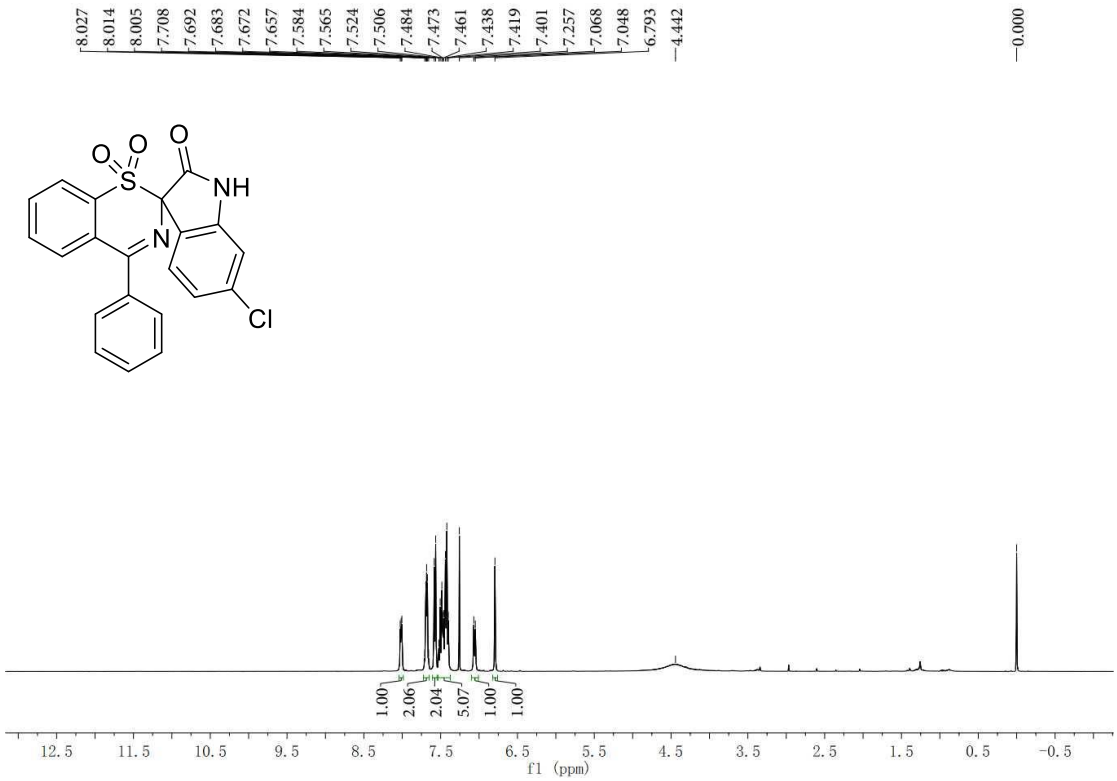


^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound **3ag**

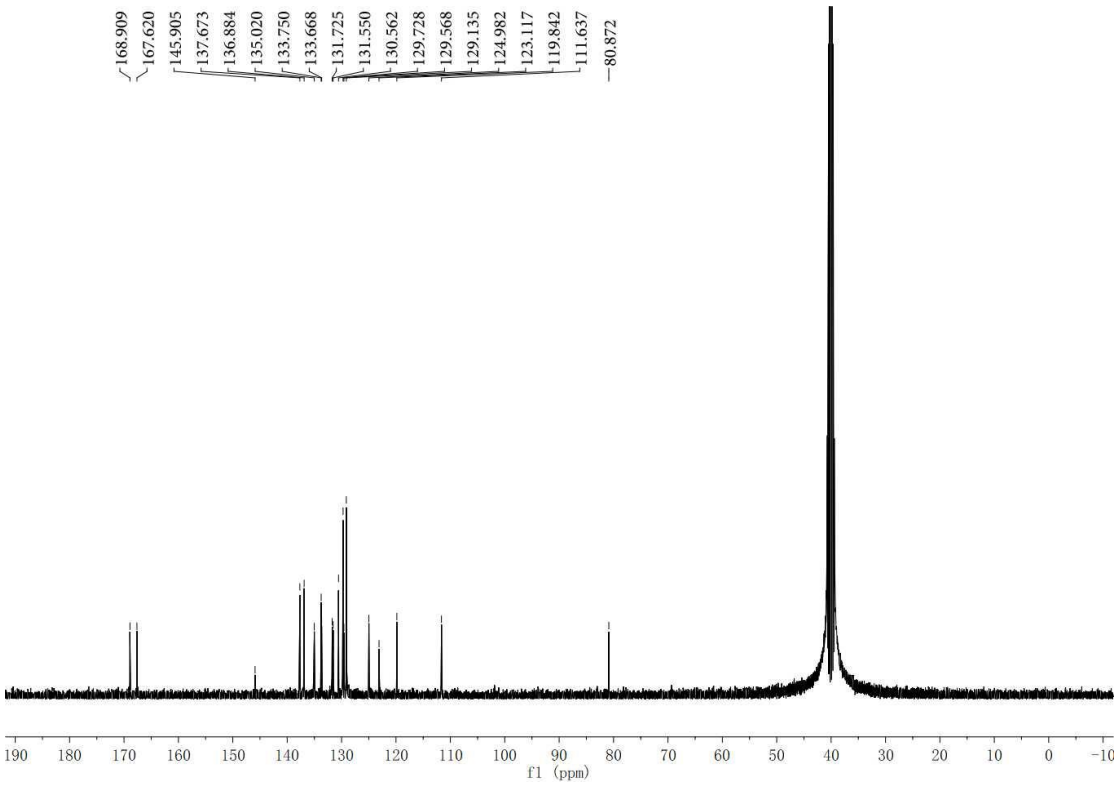


^{13}C NMR Spectrum (100 MHz, DMSO-d_6) of Compound **3ag**

3ag



^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ah**



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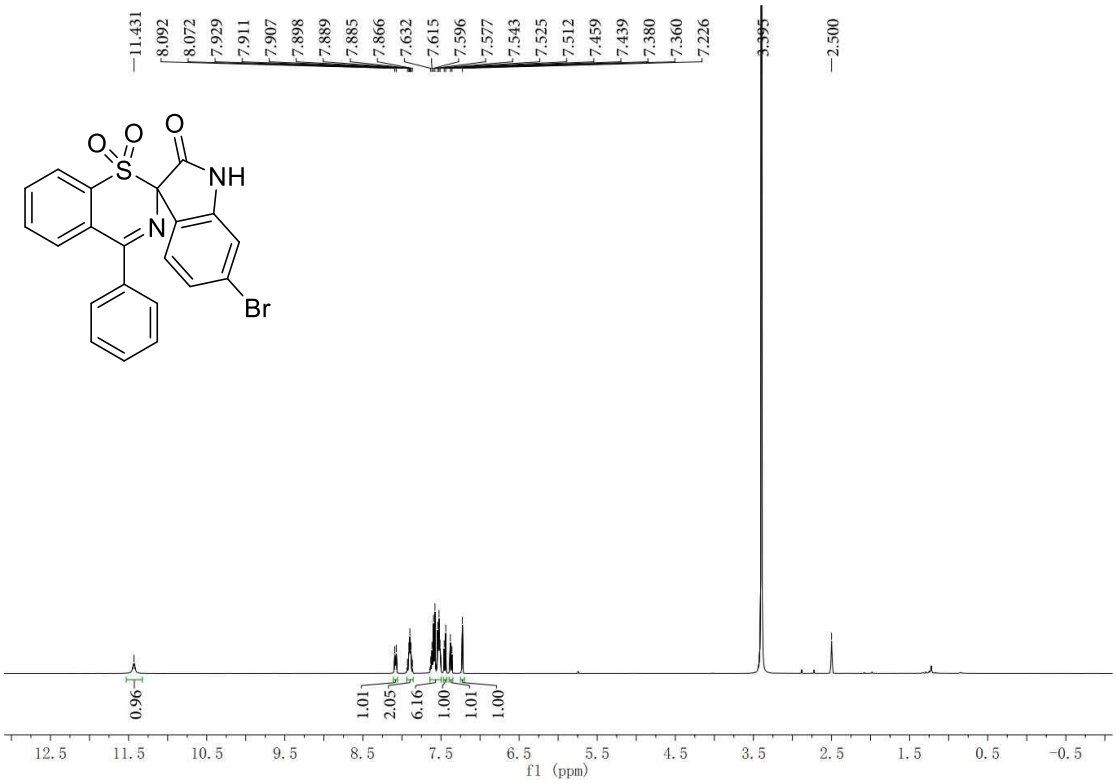
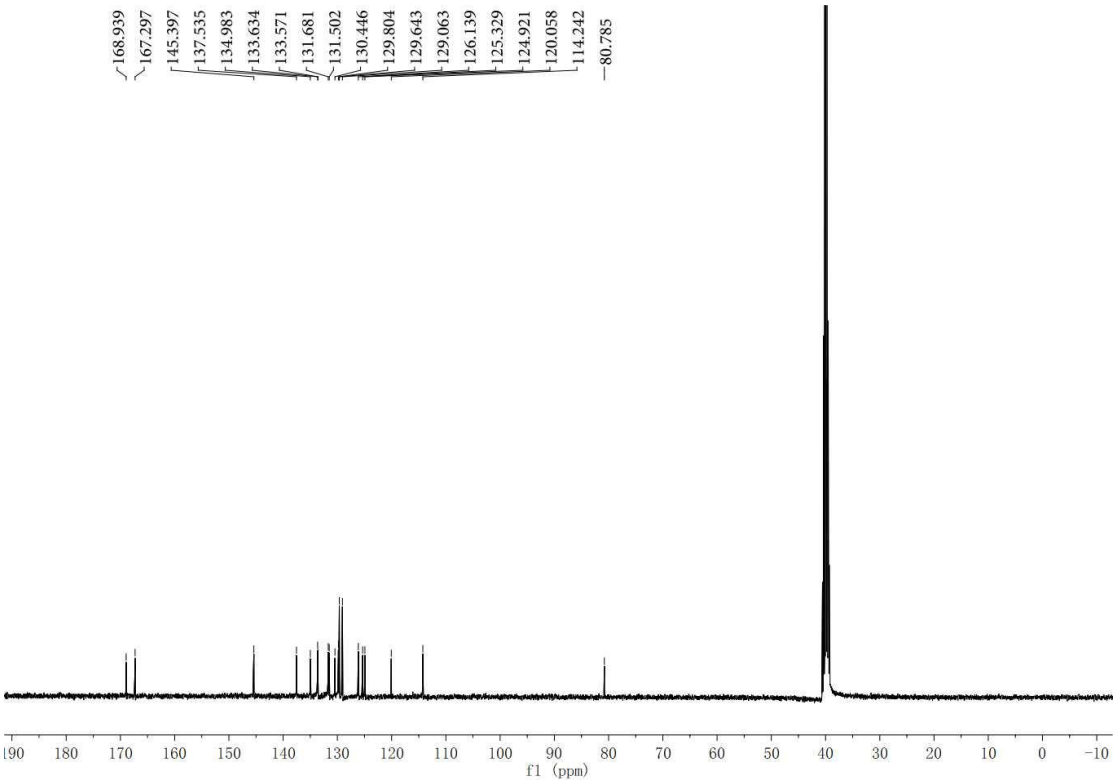


^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound **3ai**



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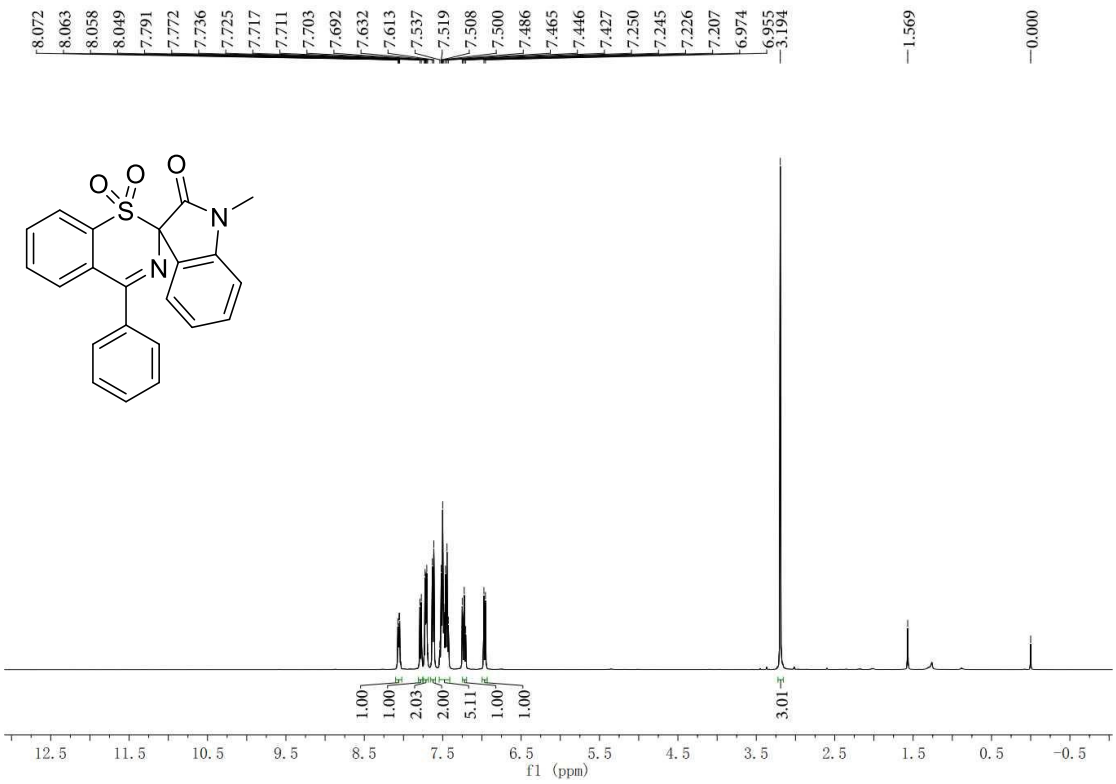
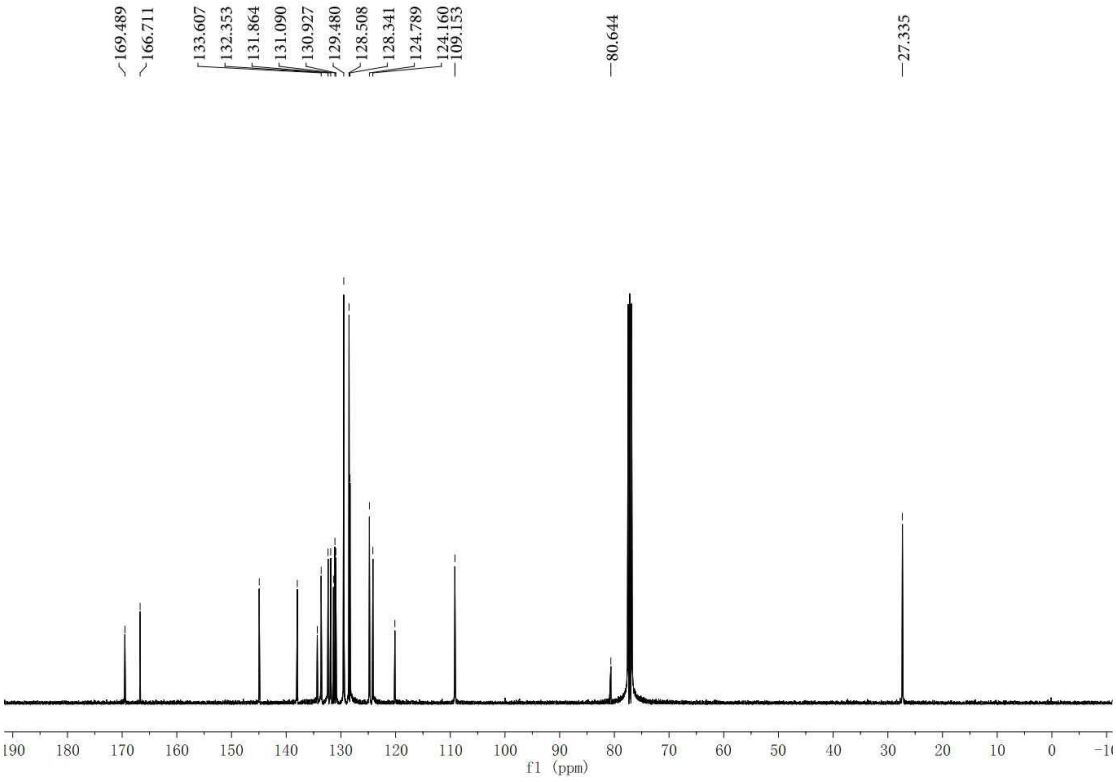


^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3aj**



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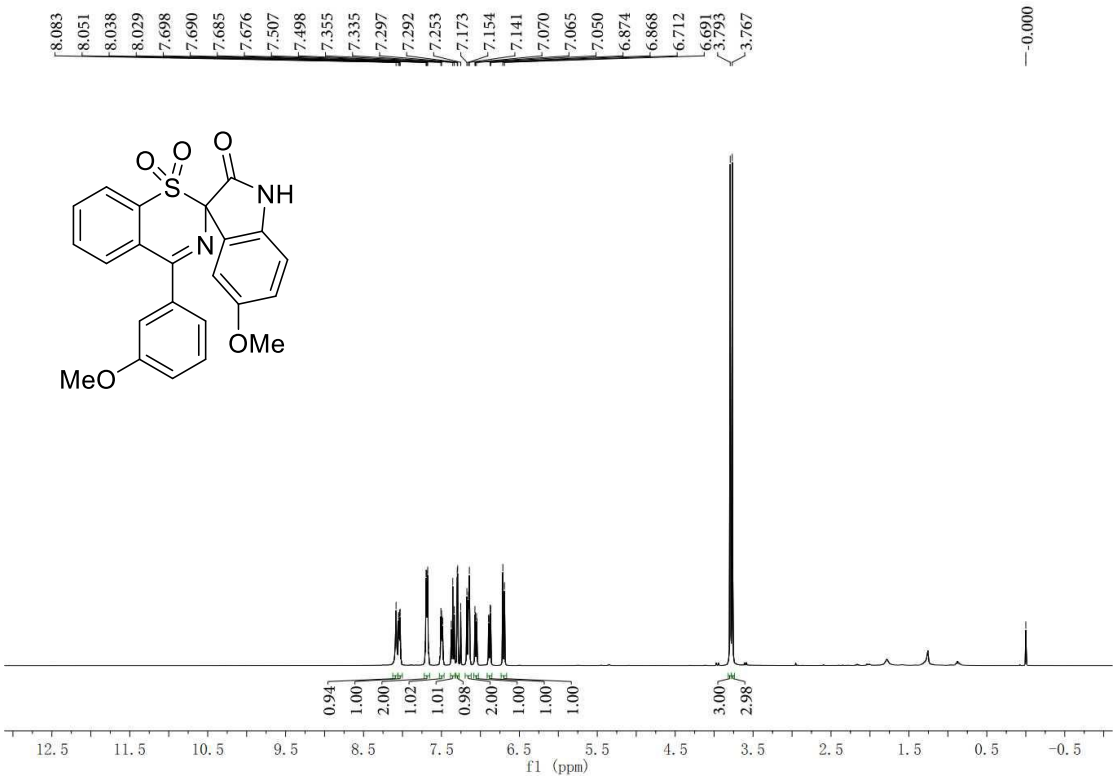

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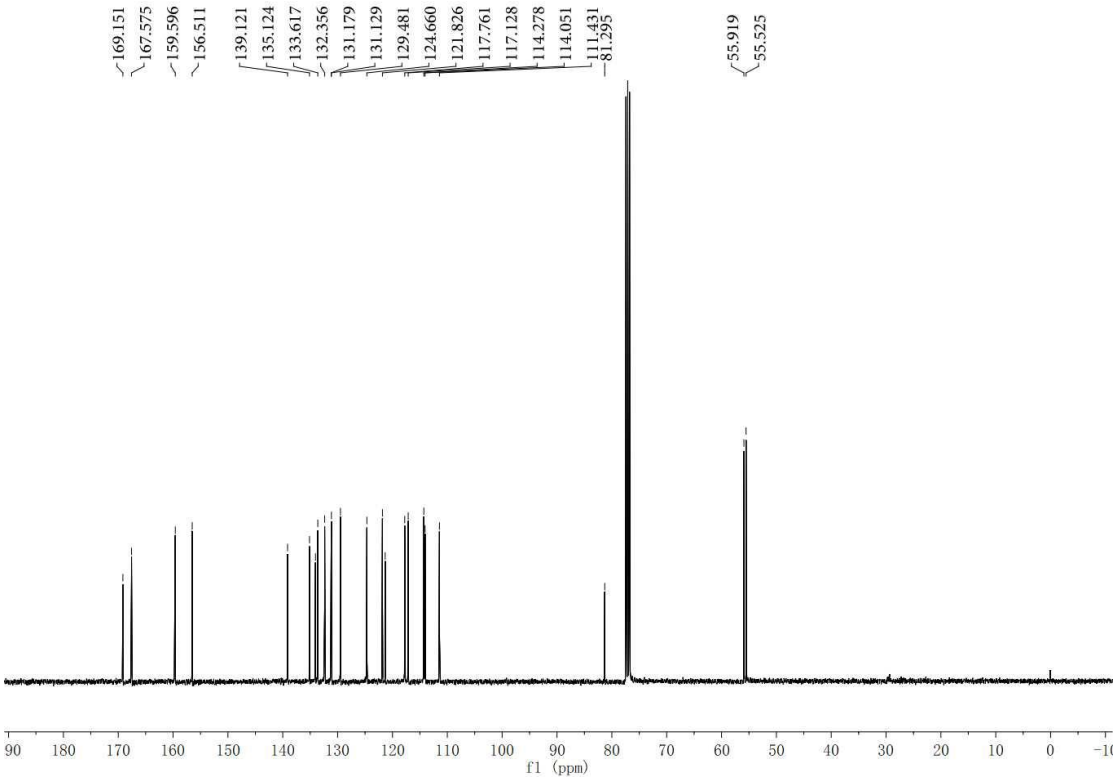

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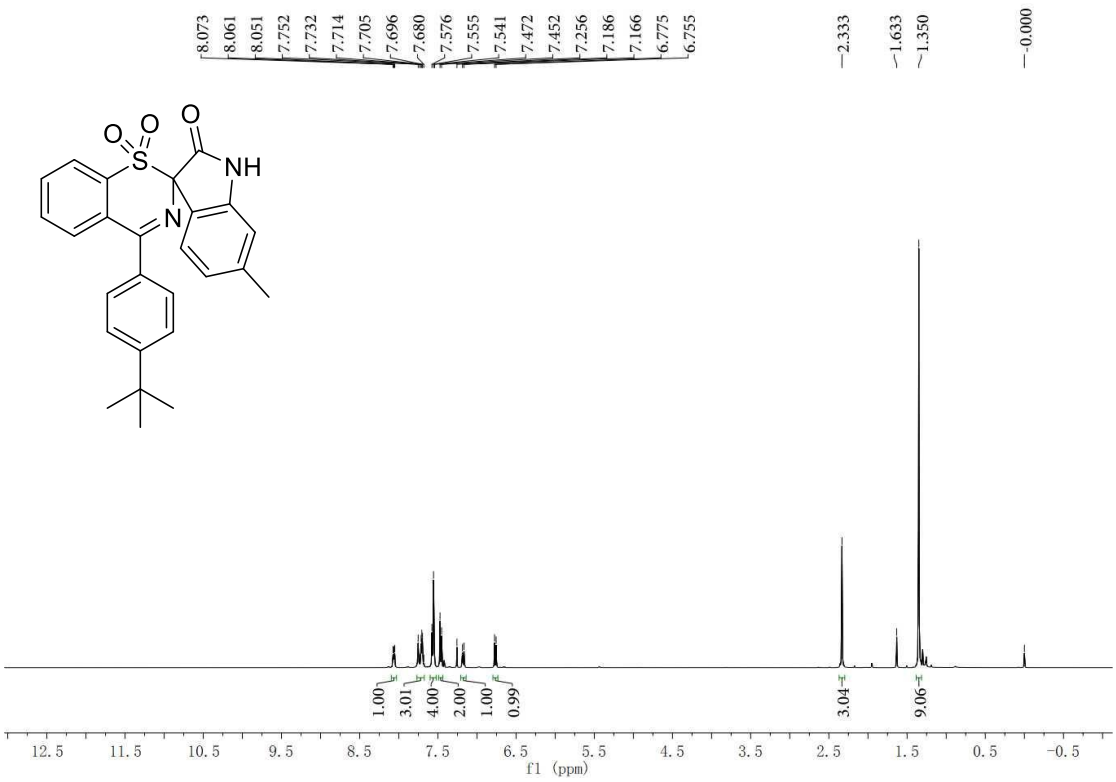
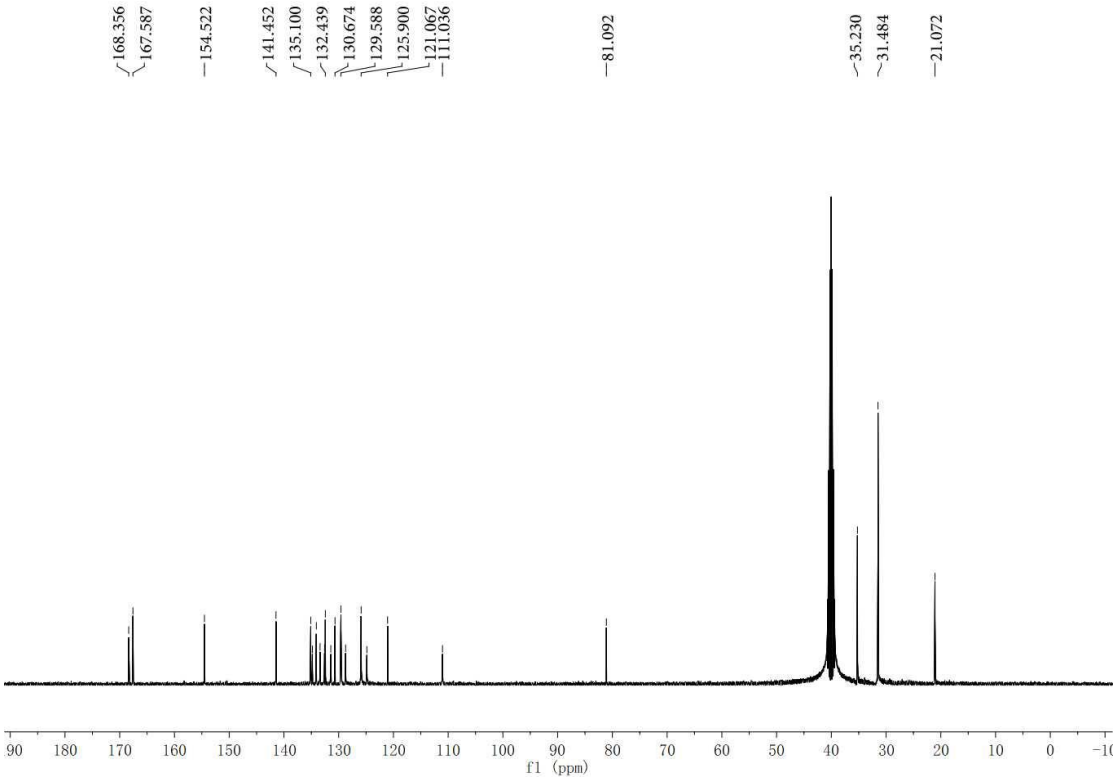
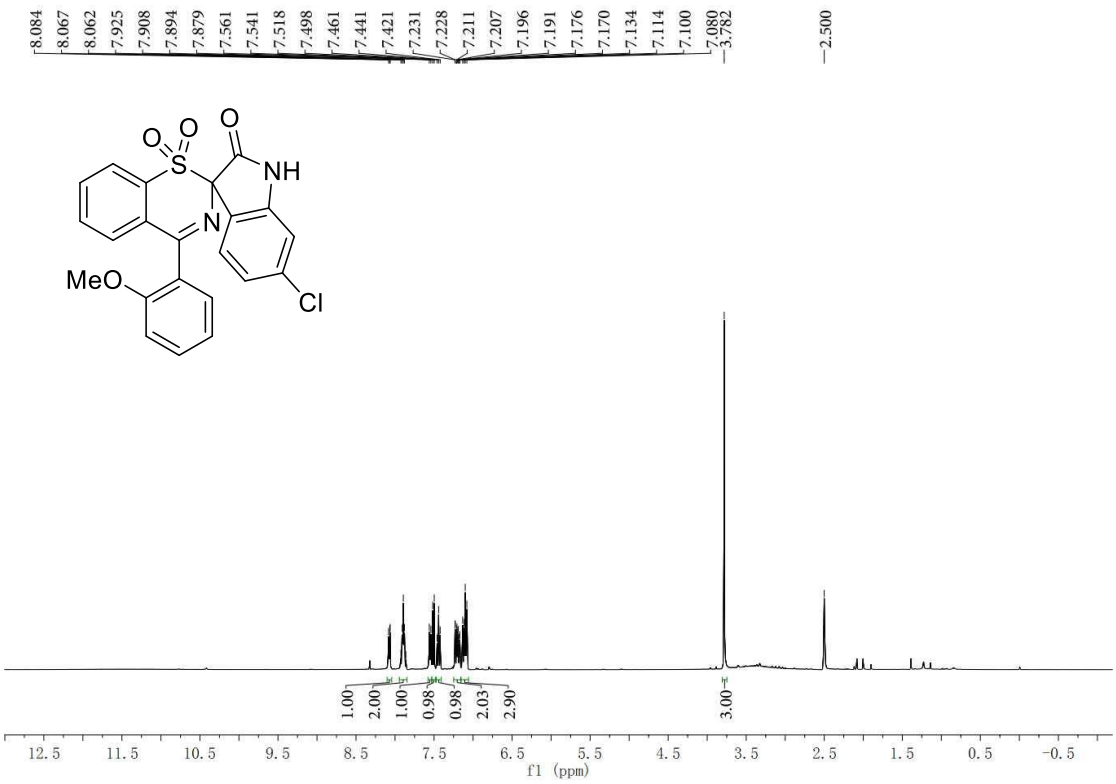


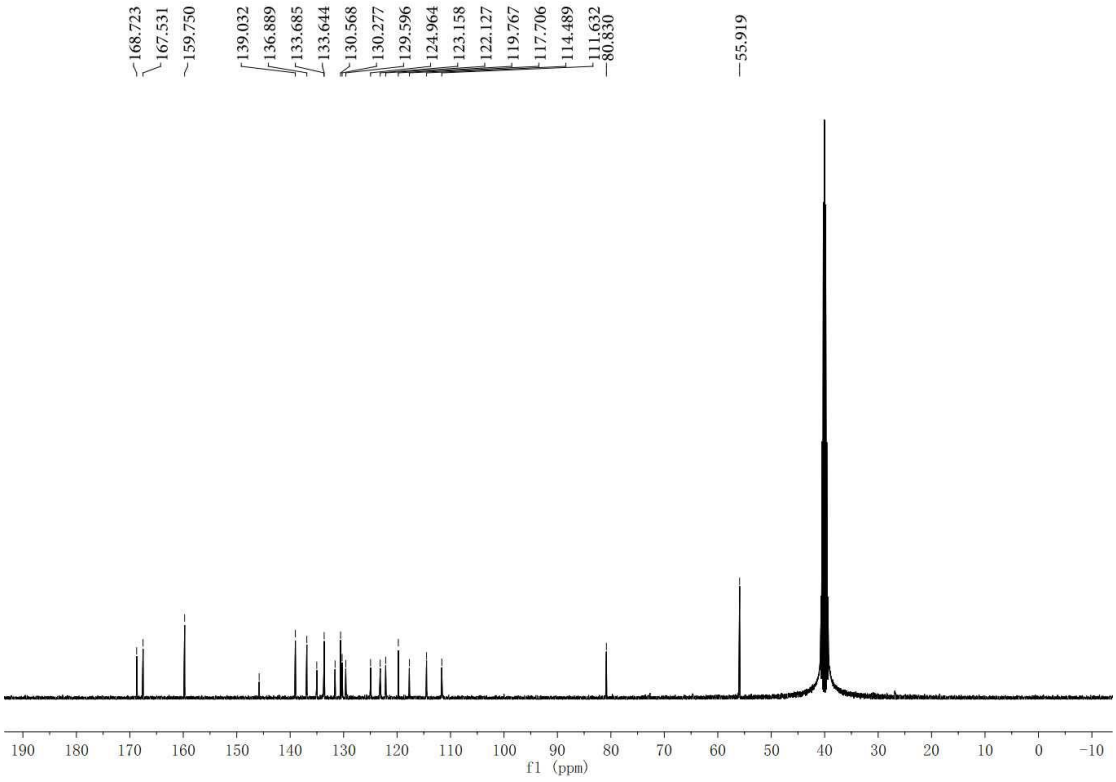
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ec**



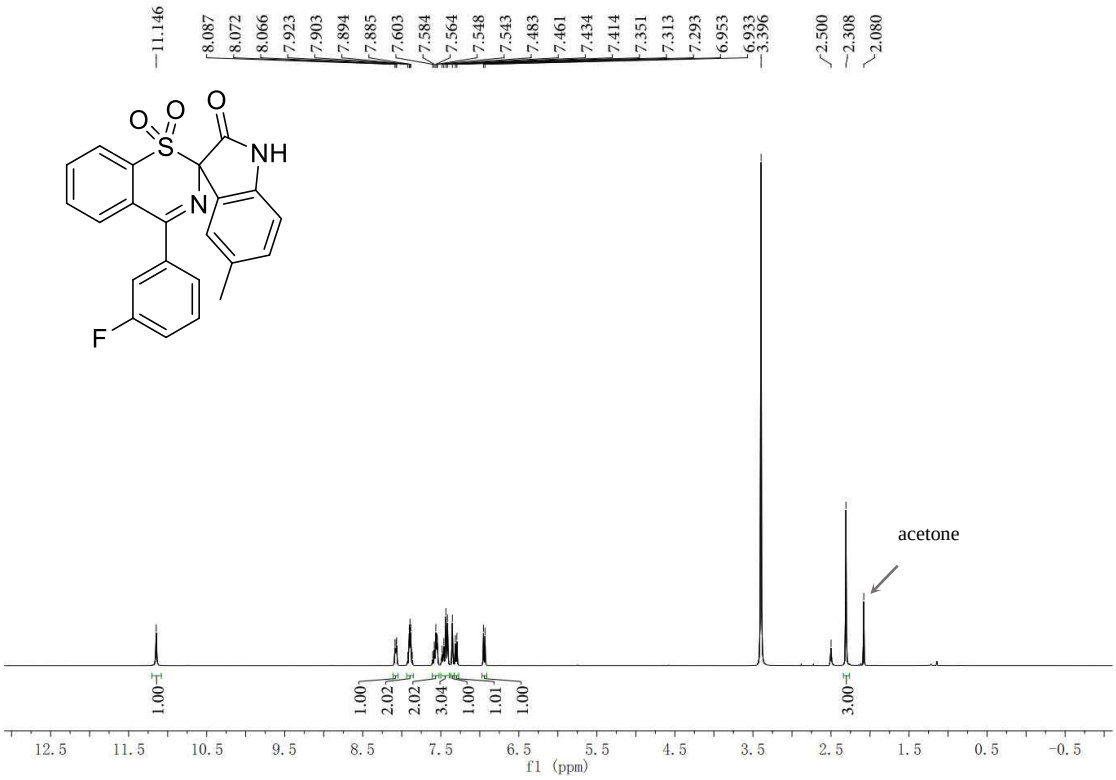
^{13}C NMR Spectrum (100 MHz, DMSO-d_6) of Compound **3ec**



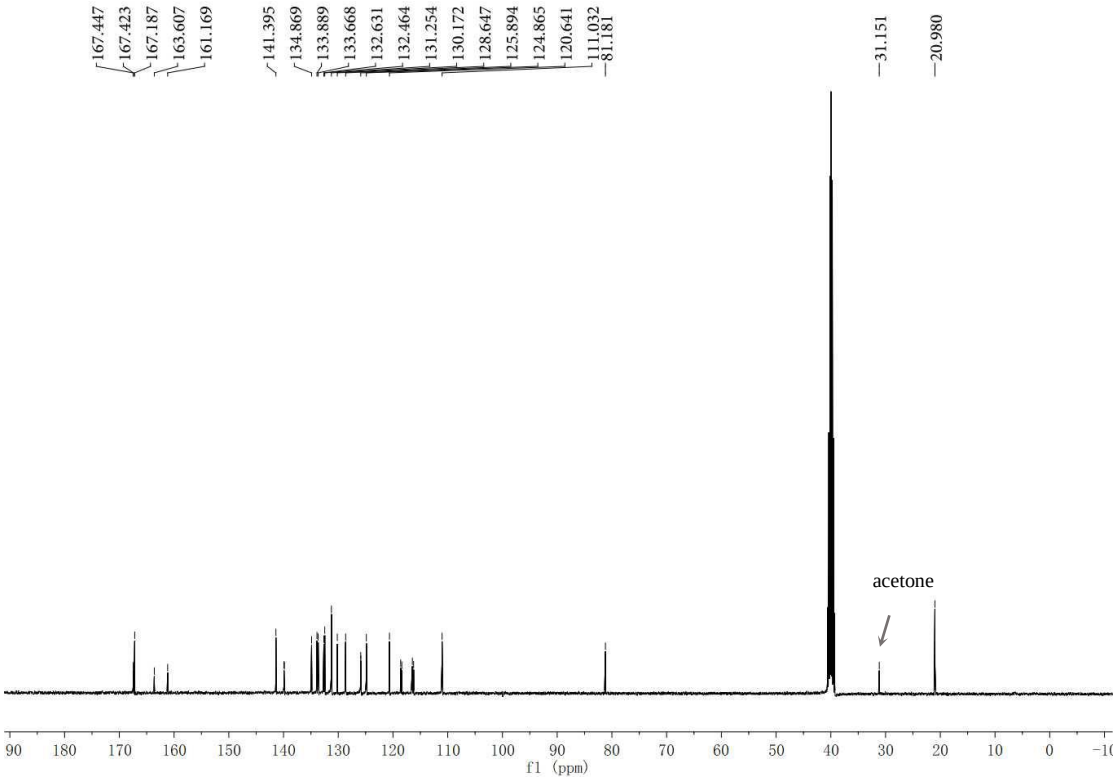
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound **3bh**



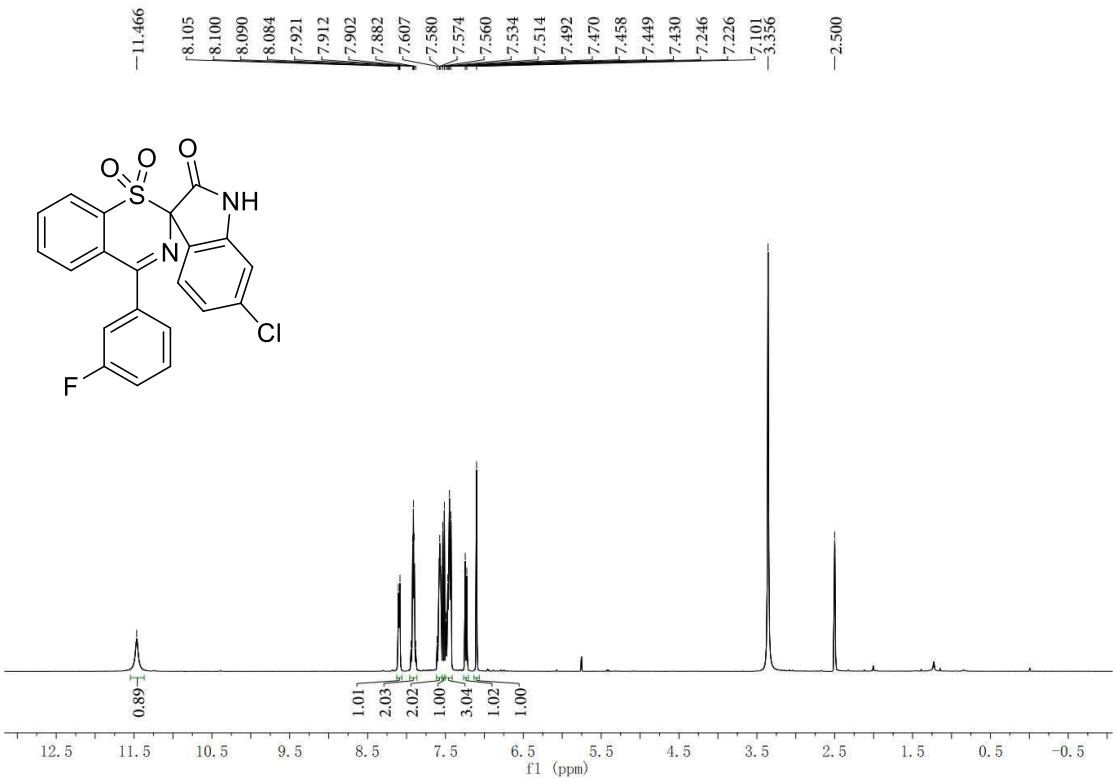
^{13}C NMR Spectrum (100 MHz, DMSO-d_6) of Compound **3bh**



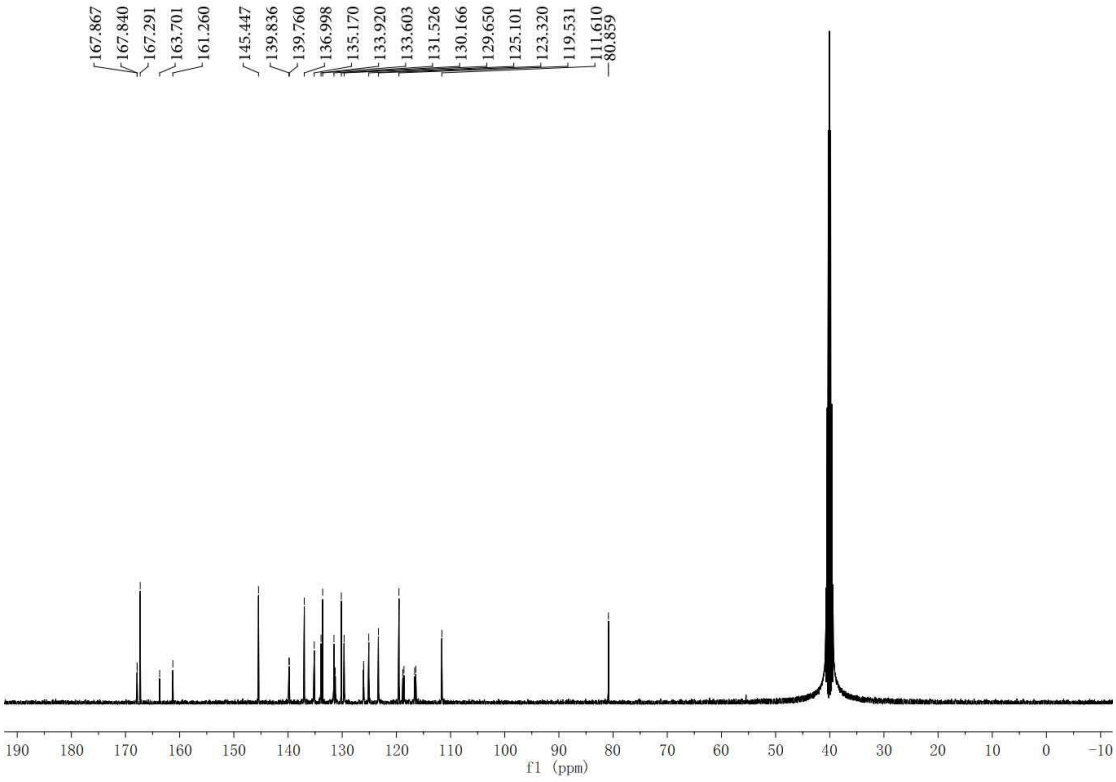
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound **3fb**



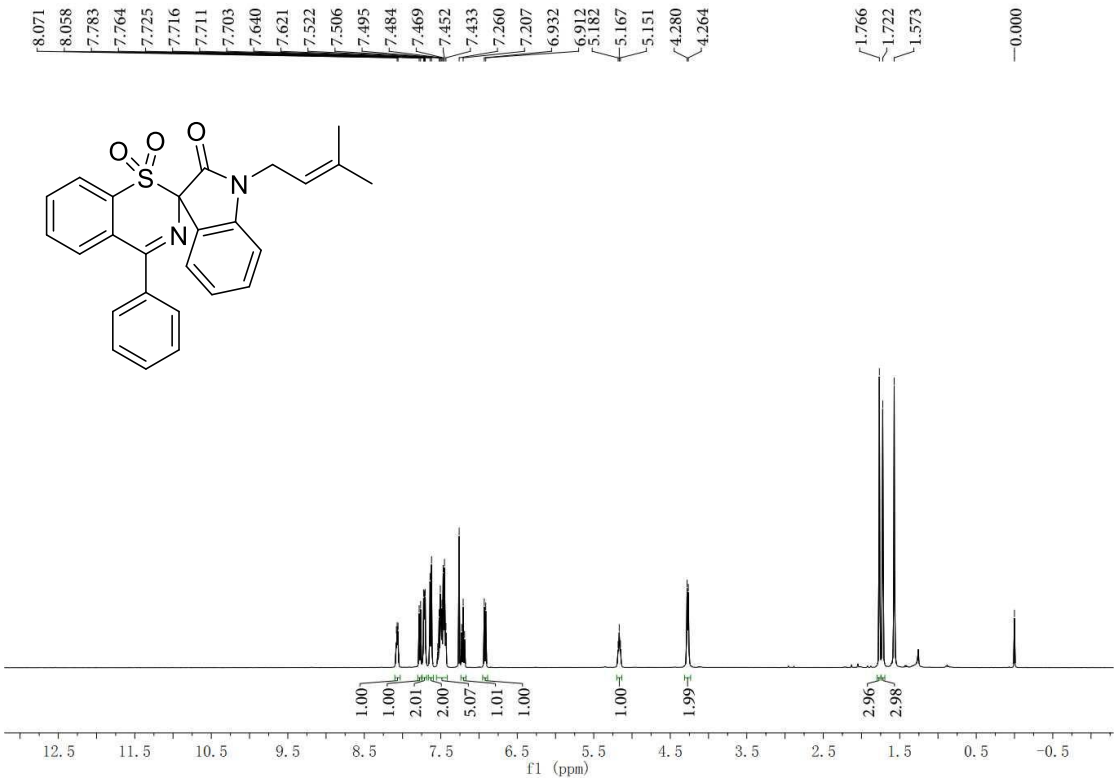
^{13}C NMR Spectrum (100 MHz, DMSO-d_6) of Compound **3fb**



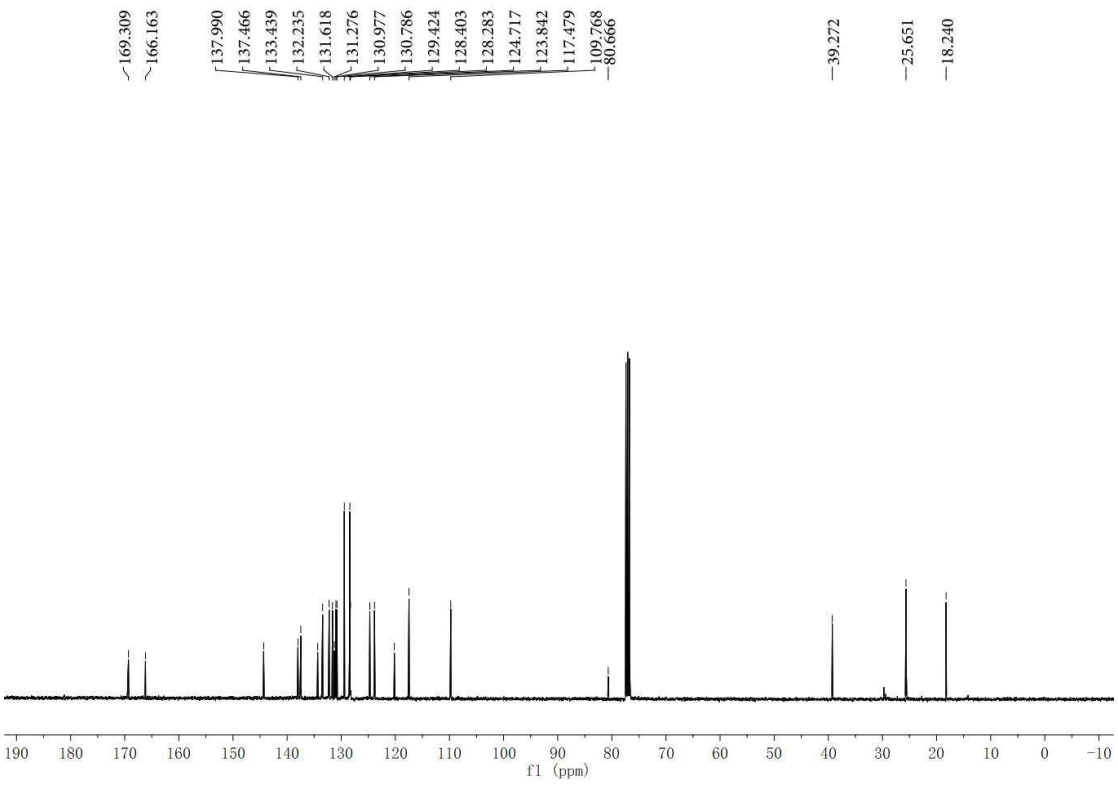
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound **3fh**



^{13}C NMR Spectrum (100 MHz, DMSO-d_6) of Compound **3fh**



^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **4**



^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **4**

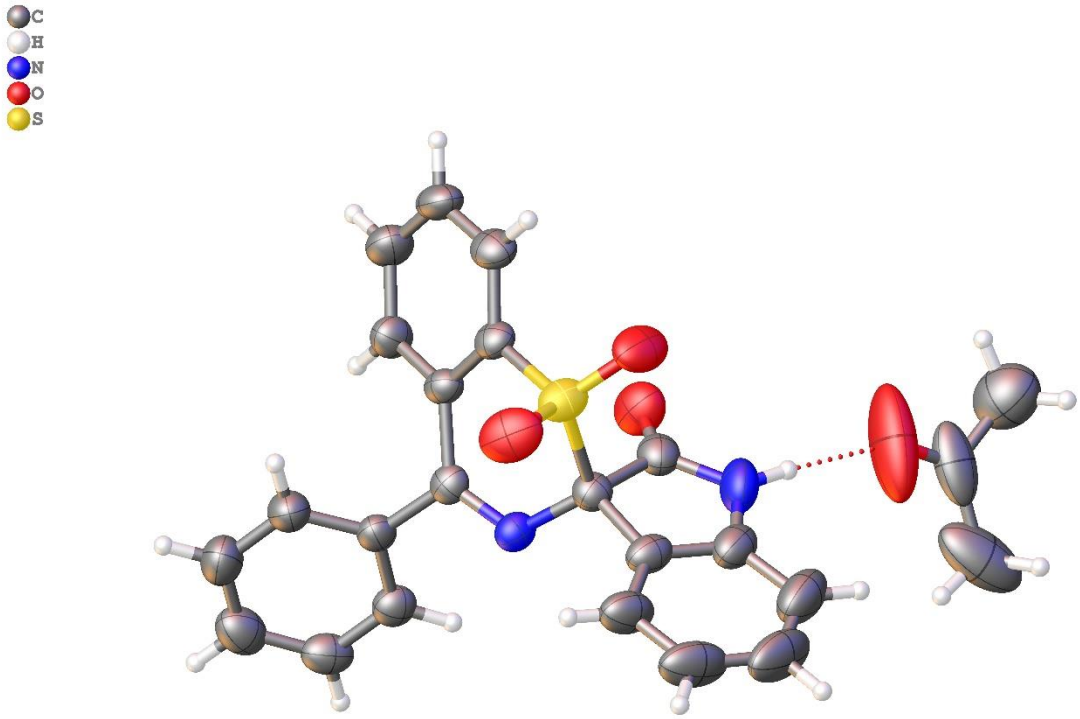


Figure S1. Crystal Structure of **3aa** (35% probability level for the thermal ellipsoids).

Table S1. Crystal Data for Compound **3aa**

Formula	$C_{24}H_{20}N_2O_4S$
Formula weight	432.48
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 8.7954(13) Å, α = 90 deg.
	b = 19.899(3) Å, β = 108.107(16) deg.
	c = 13.0118(18) Å, γ = 90 deg.
Volume	2164.5(6)
Z	4
Density (calculated)	1.327 g / cm^3
Absorption coefficient	0.183 mm^{-1}
F(000)	904.0
Crystal	0.2 × 0.18 × 0.15 mm
Theta range for data collection	3.878 to 48.988 deg
Limiting indices	$-10 \le h \le 9$, $-23 \le k \le 19$, $-15 \le l \le 14$
Reflections collected	10380
Independent reflections	3596 [Rint = 0.0598, Rsigma = 0.0940]
Data / restraints / parameters	3596/0/282
Goodness-of-fit on F^2	1.027
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0675, wR_2 = 0.1257
R indices (all data)	R_1 = 0.1297, wR_2 = 0.1544
Largest diff. peak and hole	0.47 and -0.32 e. $Å^{-3}$