

Fischer's bases-triggered formal (3+2) cycloadditions with 3-isothiocyanato oxindoles as acceptor-donor synthons

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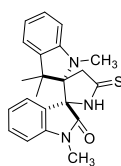
1. General information

Reactions were monitored by thin layer chromatography using UV light to visualize the course of reaction. Purification of reaction products was carried out by flash chromatography on silica gel or just by simple filtration and washing. ^1H and ^{13}C NMR spectra were obtained using a Bruker DPX-400 spectrometer. ^1H NMR chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in ppm (δ) from tetramethylsilane (TMS) with the solvent resonance as the internal standard. Melting points were measured on an electrothermal digital melting point apparatus.

2. Catalyst-free synthesis of bispiro[Fischer's base-oxindole] skeletons 3

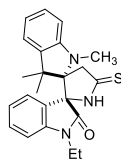
In a sealed tube equipped with a magnetic stirring bar, a mixture of 3-isothiocyanato oxindole **1** (0.2 mmol), Fischer's base **2** (0.3 mmol) in 1.0 mL of DCM was stirred at rt for 10 h, and then was directly loaded onto a silica gel and purified by flash chromatography to give the desired product **3**, using hexane/EtOAc (10/1, v/v) as the eluent. The lack of purity of the spectra is caused by the presence of a very small amount of diastereoisomers and impurities contained in the compounds (**3ae**, **3ai**, **3aj**, **3ak**, **3al**, **3bb**, **3bc**, **3be**, **3bf**, **3bh** and **3cb**). It is difficult to recrystallize them for purification.

3. Characterization data of compounds 3

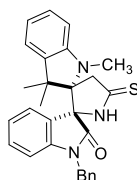


3aa: Light yellow solid, m.p. 220.5-221.2 °C; yield 80%, >20:1 dr; ^1H NMR (CDCl_3 , 400 MHz) δ : 0.73 (s, 3H), 1.31 (s, 3H), 2.84 (d, J = 17.6 Hz, 1H), 3.06 (s, 3H), 3.16 (s, 3H), 3.85 (d, J = 17.6 Hz, 1H), 6.41 (d, J = 7.6 Hz, 1H), 6.57-6.60 (m, 1H), 6.75 (d, J = 7.6 Hz, 2H), 6.93-7.02 (m, 2H), 7.26-7.32 (m, 2H), 8.22 (br s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 24.6, 25.6, 26.6, 32.8, 45.1, 49.3, 75.2, 86.7, 107.3, 108.8, 118.8, 120.8, 123.0, 123.5, 127.9, 128.1, 130.8, 137.6, 144.3, 148.1, 173.0, 206.3; HRMS (ESI-TOF) m/z : Calcd. for $\text{C}_{22}\text{H}_{23}\text{N}_3\text{NaOS}$ $[\text{M}+\text{Na}]^+$: 400.1454; Found:

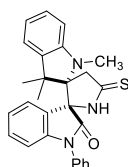
400.1457.



3ab: Light yellow solid, m.p. 166.8-167.3 °C; yield 77%, >20:1 dr; ^1H NMR (CDCl_3 , 400 MHz) δ : 0.83 (s, 3H), 1.31-1.35 (m, 3H), 1.42 (s, 3H), 2.90 (d, $J = 16.8$ Hz, 1H), 3.14 (s, 3H), 3.72-3.77 (m, 1H), 3.85-3.90 (m, 1H), 3.95 (d, $J = 16.8$ Hz, 1H), 6.52 (d, $J = 8.0$ Hz, 1H), 6.98-6.72 (m, 1H), 6.85-6.88 (m, 2H), 7.02-7.06 (m, 1H), 7.09-7.13 (m, 1H), 7.33-7.37 (m, 1H), 7.43 (d, $J = 7.6$ Hz, 1H), 8.51 (br s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 12.2, 24.8, 25.3, 32.9, 35.2, 45.1, 49.3, 75.1, 86.7, 107.4, 108.9, 118.8, 120.8, 123.1, 123.2, 127.9, 128.4, 130.8, 137.6, 143.5, 148.1, 172.5, 206.2; HRMS (ESI-TOF) m/z : Calcd. for $\text{C}_{23}\text{H}_{25}\text{N}_3\text{NaOS}$ $[\text{M}+\text{Na}]^+$: 414.1611; Found: 414.1617.

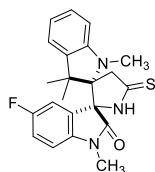


3ac: Light yellow solid, m.p. 170.9-171.2 °C; yield 75%, >20:1 dr; ^1H NMR (CDCl_3 , 400 MHz) δ : 0.75 (s, 3H), 1.43 (s, 3H), 2.95 (d, $J = 17.6$ Hz, 1H), 3.16 (s, 3H), 4.02 (d, $J = 17.6$ Hz, 1H), 4.87 (d, $J = 15.2$ Hz, 1H), 4.97 (d, $J = 15.2$ Hz, 1H), 6.52 (d, $J = 8.0$ Hz, 1H), 6.68-6.72 (m, 1H), 6.83-6.85 (m, 2H), 7.00-7.04 (m, 1H), 7.09-7.13 (m, 1H), 7.25-7.44 (m, 7H), 8.41 (br s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 24.9, 25.2, 32.9, 44.5, 45.1, 49.3, 75.1, 86.9, 107.4, 109.8, 118.9, 120.8, 123.0, 123.5, 127.9, 128.0 (2C), 128.1, 128.3, 129.0 (2C), 130.7, 134.9, 137.6, 143.7, 148.1, 173.1, 206.4; HRMS (ESI-TOF) m/z : Calcd. for $\text{C}_{28}\text{H}_{27}\text{N}_3\text{NaOS}$ $[\text{M}+\text{Na}]^+$: 476.1767; Found: 476.1762.

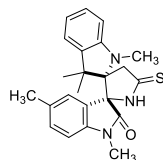


3ad: Light yellow solid, m.p. 236.4-237.1 °C; yield 63%, >20:1 dr; ^1H NMR (CDCl_3 , 400 MHz) δ : 1.05 (s, 3H), 1.44 (s, 3H), 2.97 (d, $J = 17.6$ Hz, 1H), 3.16 (s, 3H), 3.99 (d, $J = 17.6$ Hz, 1H), 6.53 (d, $J = 8.0$ Hz, 1H), 6.70-6.73 (m, 1H), 6.80 (d, $J = 8.0$ Hz, 1H), 6.89 (d, $J = 8.0$ Hz, 1H),

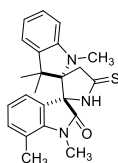
7.06-7.14 (m, 2H), 7.26-7.30 (m, 1H), 7.42-7.49 (m, 4H), 7.56-7.59 (m, 2H), 8.68 (br s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 25.0, 25.7, 32.9, 45.3, 49.3, 75.5, 87.0, 107.4, 110.2, 118.9, 120.8, 122.7, 123.9, 126.3 (2C), 128.0, 128.5, 128.7, 129.9 (2C), 130.7, 133.5, 137.6, 144.4, 148.2, 172.4, 206.4; HRMS (ESI-TOF) m/z : Calcd. for $\text{C}_{27}\text{H}_{25}\text{N}_3\text{NaOS}$ $[\text{M}+\text{Na}]^+$: 462.1611; Found: 462.1614.



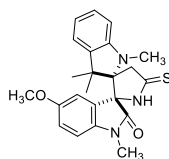
3ae: Light yellow solid, m.p. 173.2-174.0 °C; yield 60%, >20:1 dr; ^1H NMR ($\text{DMSO}-d_6$, 400 MHz) δ : 0.74 (s, 3H), 1.29 (s, 3H), 2.75 (d, $J = 17.2$ Hz, 1H), 3.03 (s, 3H), 3.18 (s, 3H), 3.73 (d, $J = 17.2$ Hz, 1H), 6.54-6.61 (m, 2H), 6.85-6.87 (m, 1H), 6.99-7.04 (m, 1H), 7.05-7.10 (m, 2H), 7.22-7.28 (m, 1H), 10.65 (br s, 1H); ^{13}C NMR ($\text{DMSO}-d_6$, 100 MHz) δ : 24.3, 26.0, 26.9, 32.7, 45.1, 49.6, 75.5, 86.2, 107.7, 110.6 (d, $J_{\text{CF}} = 8.1$ Hz), 115.8 (d, $J_{\text{CF}} = 26.1$ Hz), 117.1 (d, $J_{\text{CF}} = 23.4$ Hz), 118.9, 121.0, 125.6 (d, $J_{\text{CF}} = 8.3$ Hz), 128.2, 137.8, 141.1, 148.4, 158.8 (d, $J_{\text{CF}} = 236.2$ Hz), 173.3, 205.2; ^{19}F NMR (CDCl_3 , 470 MHz) δ : -120.20; HRMS (ESI-TOF) m/z : Calcd. for $\text{C}_{22}\text{H}_{22}\text{FN}_3\text{NaOS}$ $[\text{M}+\text{Na}]^+$: 418.1360; Found: 418.1358.



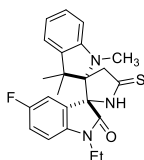
3af: Light yellow solid, m.p. 230.6-231.3 °C; yield 81%, >20:1 dr; ^1H NMR (CDCl_3 , 400 MHz) δ : 0.86 (s, 3H), 1.40 (s, 3H), 2.29 (s, 3H), 2.95 (d, $J = 17.6$ Hz, 1H), 3.17 (s, 3H), 3.23 (s, 3H), 3.99 (d, $J = 17.6$ Hz, 1H), 6.52 (d, $J = 7.6$ Hz, 1H), 6.66-6.73 (m, 2H), 6.84-6.85 (m, 1H), 7.08-7.17 (m, 3H), 8.01 (br s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 21.3, 24.2, 25.9, 26.6, 32.8, 45.1, 49.2, 75.4, 86.7, 107.1, 108.5, 118.7, 120.8, 122.9, 127.9, 129.0, 131.0, 132.9, 137.6, 141.8, 148.2, 173.0, 206.4; HRMS (ESI-TOF) m/z : Calcd. for $\text{C}_{23}\text{H}_{25}\text{N}_3\text{NaOS}$ $[\text{M}+\text{Na}]^+$: 414.1611; Found: 414.1615.



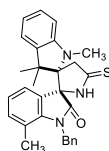
3ag: Light yellow solid, m.p. 167.6-168.6 °C; yield 67%, >20:1 dr; ¹H NMR (CDCl₃, 400 MHz) δ : 0.77 (s, 3H), 1.30 (s, 3H), 2.46 (s, 3H), 2.85 (d, J = 17.6 Hz, 1H), 3.05 (s, 3H), 3.43 (s, 3H), 3.93 (d, J = 17.6 Hz, 1H), 6.39 (d, J = 7.6 Hz, 1H), 6.56-6.60 (m, 1H), 6.74-6.76 (m, 1H), 6.79-6.83 (m, 1H), 6.96-7.01 (m, 2H), 7.16 (d, J = 7.2 Hz, 1H), 7.91 (br s, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ : 19.3, 24.5, 25.9, 30.2, 32.9, 45.2, 49.3, 74.5, 86.9, 107.2, 118.7, 120.2, 120.7, 123.2, 123.6, 126.0, 127.9, 134.6, 137.6, 142.1, 148.2, 173.9, 206.5; HRMS (ESI-TOF) m/z : Calcd. for C₂₃H₂₅N₃NaOS [M+Na]⁺: 414.1611; Found: 414.1607.



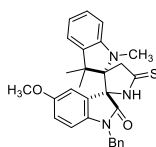
3ah: Light yellow solid, m.p. 172.3-173.1 °C; yield 64%, >20:1 dr; ¹H NMR (CDCl₃, 400 MHz) δ : 0.74 (s, 3H), 1.30 (s, 3H), 2.79 (d, J = 17.6 Hz, 1H), 3.05 (s, 3H), 3.12 (s, 3H), 3.65 (s, 3H), 3.84 (d, J = 17.6 Hz, 1H), 6.40 (d, J = 7.2 Hz, 1H), 6.57-6.60 (m, 1H), 6.64 (d, J = 8.4 Hz, 1H), 6.74-6.77 (m, 2H), 6.93 (d, J = 2.4 Hz, 1H), 6.97-7.01 (m, 1H), 8.46 (br s, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ : 24.6, 25.7, 26.7, 32.8, 45.1, 49.3, 55.8, 75.5, 86.6, 107.3, 109.1, 114.7, 116.0, 118.8, 120.8, 124.2, 127.9, 137.6, 137.7, 148.1, 156.1, 172.8, 206.2; HRMS (ESI-TOF) m/z : Calcd. for C₂₃H₂₅N₃NaO₂S [M+Na]⁺: 430.1560; Found: 430.1561.



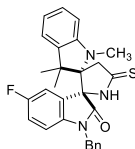
3ai: Light yellow solid, m.p. 207.3-208.5 °C; yield 65%, >20:1 dr; ¹H NMR (CDCl₃, 400 MHz) δ : 0.76 (s, 3H), 1.18-1.24 (m, 3H), 1.33 (s, 3H), 2.84 (d, J = 17.6 Hz, 1H), 3.04 (s, 3H), 3.63-3.66 (m, 1H), 3.73-3.84 (m, 1H), 3.86 (d, J = 17.6 Hz, 1H), 6.45 (d, J = 8.0 Hz, 1H), 6.60-6.64 (m, 1H), 6.69-6.72 (m, 1H), 6.76-6.78 (m, 1H), 6.95-7.10 (m, 3H), 8.35 (br s, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ : 12.1, 24.8, 25.4, 32.8, 35.3, 45.2, 49.2, 75.1, 86.7, 107.6, 109.3 (d, J_{CF} = 8.2 Hz), 116.8 (d, J_{CF} = 26.3 Hz), 117.1 (d, J_{CF} = 23.4 Hz), 119.1, 120.8, 124.7 (d, J_{CF} = 9.1 Hz), 128.1, 137.5, 139.5, 148.0, 158.9 (d, J_{CF} = 263.0 Hz), 172.4, 206.4; ¹⁹F NMR (CDCl₃, 470 MHz) δ : -118.94; HRMS (ESI-TOF) m/z : Calcd. for C₂₃H₂₄FN₃NaOS [M+Na]⁺: 432.1516; Found: 432.1516.



3aj: Light yellow solid, m.p. 191.2-192.2 °C; yield 60%, 19:1 dr; ^1H NMR (DMSO- d_6 , 400 MHz) δ : 0.83 (s, 3H), 1.31 (s, 3H), 2.17 (s, 3H), 2.74 (d, J = 17.6 Hz, 1H), 3.07 (s, 3H), 3.81 (d, J = 17.6 Hz, 1H), 5.06 (d, J = 17.2 Hz, 1H), 5.32 (d, J = 17.2 Hz, 1H), 6.54 (d, J = 7.6 Hz, 1H), 6.58-6.61 (m, 1H), 6.87 (d, J = 6.8 Hz, 1H), 6.93-7.06 (m, 3H), 7.25-7.31 (m, 4H), 7.35-7.39 (m, 2H), 10.96 (br s, 1H); ^{13}C NMR (DMSO- d_6 , 100 MHz) δ : 18.7, 24.7, 25.9, 33.0, 45.1, 45.3, 49.8, 74.8, 85.6, 107.7, 118.8, 120.4, 121.0, 123.4, 124.8, 126.2 (2C), 127.7, 128.1, 129.2 (2C), 134.6, 137.8, 137.9, 142.0, 148.5, 175.0, 205.4; HRMS (ESI-TOF) m/z : Calcd. for $\text{C}_{29}\text{H}_{29}\text{N}_3\text{NaOS}$ $[\text{M}+\text{Na}]^+$: 490.1924; Found: 490.1925.

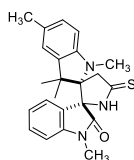


3ak: Light yellow solid, m.p. 182.1-182.9 °C; yield 66%, 12:1 dr; ^1H NMR (CDCl_3 , 400 MHz) δ : 0.70 (s, 3H), 1.33 (s, 3H), 2.85 (d, J = 17.6 Hz, 1H), 3.06 (s, 3H), 3.63 (s, 3H), 3.93 (d, J = 17.6 Hz, 1H), 4.74 (d, J = 15.2 Hz, 1H), 4.84 (d, J = 15.2 Hz, 1H), 6.41 (d, J = 7.6 Hz, 1H), 6.58-6.62 (m, 2H), 6.66-6.68 (m, 1H), 6.75 (d, J = 6.4 Hz, 1H), 6.94 (d, J = 2.4 Hz, 1H), 6.98-7.02 (m, 1H), 7.21-7.29 (m, 5H), 8.25 (br s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 24.8, 25.4, 32.9, 44.6, 45.2, 49.3, 55.8, 75.3, 86.9, 107.4, 110.0, 114.7, 116.0, 118.9, 120.8, 124.3, 127.9, 128.0 (2C), 128.1, 128.9 (2C), 135.0, 137.0, 137.6, 148.1, 156.1, 172.9, 206.5; HRMS (ESI-TOF) m/z : Calcd. for $\text{C}_{29}\text{H}_{29}\text{N}_3\text{NaO}_2\text{S}$ $[\text{M}+\text{Na}]^+$: 506.1873; Found: 506.1874.

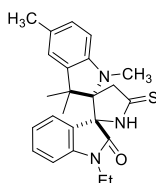


3al: Light yellow solid, m.p. 170.5-171.3 °C; yield 62%, 20:1 dr; ^1H NMR (CDCl_3 , 400 MHz) δ : 0.69 (s, 3H), 1.34 (s, 3H), 2.87 (d, J = 17.2 Hz, 1H), 3.04 (s, 3H), 3.91 (d, J = 17.2 Hz, 1H), 4.74 (d, J = 15.6 Hz, 1H), 4.87 (d, J = 15.6 Hz, 1H), 6.44 (d, J = 8.0 Hz, 1H), 6.60-6.66 (m, 2H), 6.76 (d, J = 6.8 Hz, 1H), 6.85-6.90 (m, 1H), 7.00-7.09 (m, 2H), 7.21-7.28 (m, 5H), 8.30 (br s, 1H); ^{13}C

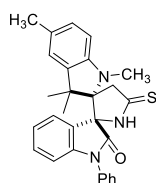
NMR (CDCl₃, 100 MHz) δ : 23.2, 23.6, 31.2, 43.0, 43.5, 47.5, 73.4, 85.2, 105.9, 108.6 (d, J_{CF} = 8.1 Hz), 114.8 (d, J_{CF} = 25.3 Hz), 115.4 (d, J_{CF} = 23.2 Hz), 117.5, 119.1, 122.9 (d, J_{CF} = 8.1 Hz), 126.2 (2C), 126.4, 126.5, 127.3 (2C), 132.9, 135.7, 137.9, 146.2, 157.2 (d, J_{CF} = 240.2 Hz), 171.3, 204.9; ¹⁹F NMR (CDCl₃, 470 MHz) δ : -118.55; HRMS (ESI-TOF) m/z: Calcd. for C₂₈H₂₆FN₃NaOS [M+Na]⁺: 494.1673; Found: 494.1676.



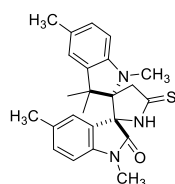
3ba: Light yellow solid, m.p. 254.1-255.0 °C; yield 70%, >20:1 dr; ¹H NMR (DMSO-*d*₆, 400 MHz) δ : 0.65 (s, 3H), 1.32 (s, 3H), 2.14 (s, 3H), 2.68 (d, J = 17.2 Hz, 1H), 2.99 (s, 3H), 3.20 (s, 3H), 3.70 (d, J = 17.2 Hz, 1H), 6.43 (d, J = 7.6 Hz, 1H), 6.69 (s, 1H), 6.81 (d, J = 8.0 Hz, 1H), 7.06-7.09 (m, 2H), 7.37-7.41 (m, 2H), 10.63 (br s, 1H); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ : 21.0, 24.8, 25.3, 26.8, 33.0, 44.9, 49.6, 75.3, 86.1, 107.7, 109.7, 121.8, 123.3, 127.5, 128.0, 128.3, 130.8, 138.0, 144.8, 146.3, 173.4, 205.1; HRMS (ESI-TOF) m/z: Calcd. for C₂₃H₂₅N₃NaOS [M+Na]⁺: 414.1611; Found: 414.1615.



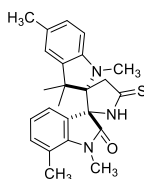
3bb: Light yellow solid, m.p. 154.3-155.2 °C; yield 63%, >20:1 dr; ¹H NMR (CDCl₃, 400 MHz) δ : 0.71 (s, 3H), 1.22-1.25 (m, 3H), 1.34 (s, 3H), 2.13 (s, 3H), 2.84 (d, J = 17.6 Hz, 1H), 3.02 (s, 3H), 3.62-3.68 (m, 1H), 3.75-3.80 (m, 1H), 3.87 (d, J = 17.6 Hz, 1H), 6.32 (d, J = 8.0 Hz, 1H), 6.59 (s, 1H), 6.77-6.82 (m, 2H), 6.93-6.97 (m, 1H), 7.24-7.29 (m, 1H), 7.36-7.38 (m, 1H), 7.90 (br s, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ : 11.0, 19.6, 23.8, 23.9, 31.9, 33.9, 43.9, 47.9, 73.8, 85.6, 106.2, 107.7, 120.4, 122.0, 122.2, 127.0, 127.1, 127.2, 127.4, 129.5, 136.6, 142.3, 144.7, 171.3, 205.3; HRMS (ESI-TOF) m/z: Calcd. for C₂₄H₂₇N₃NaOS [M+Na]⁺: 428.1767; Found: 428.1766.



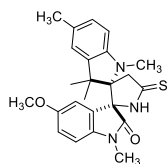
3bc: Light yellow solid, m.p. 186.5-187.2 °C; yield 70%, 20:1 dr; ^1H NMR (CDCl_3 , 400 MHz) δ : 0.91 (s, 3H), 1.35 (s, 3H), 2.14 (s, 3H), 2.87 (d, $J = 17.6$ Hz, 1H), 3.04 (s, 3H), 3.89 (d, $J = 17.6$ Hz, 1H), 6.34 (d, $J = 8.0$ Hz, 1H), 6.61 (s, 1H), 6.71 (d, $J = 7.6$ Hz, 1H), 6.82 (d, $J = 11.2$ Hz, 1H), 6.97-7.01 (m, 1H), 7.17-7.21 (m, 1H), 7.32-7.37 (m, 3H), 7.39-7.43 (m, 1H), 7.46-7.49 (m, 2H), 8.35 (br s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 19.8, 24.2, 24.4, 32.1, 44.3, 48.2, 74.3, 86.1, 106.4, 109.1, 120.7, 121.9, 122.8, 125.3 (2C), 127.2, 127.5, 127.6, 128.8 (2C), 129.6, 132.5, 136.7, 143.4, 144.9, 171.3, 205.5; HRMS (ESI-TOF) m/z : Calcd. for $\text{C}_{28}\text{H}_{27}\text{N}_3\text{NaOS}$ $[\text{M}+\text{Na}]^+$: 476.1767; Found: 476.1772.



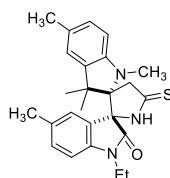
3bd: Light yellow solid, m.p. 163.3-164.0 °C; yield 62%, >20:1 dr; ^1H NMR (CDCl_3 , 400 MHz) δ : 0.78 (s, 3H), 1.39 (s, 3H), 2.20 (s, 3H), 2.27 (s, 3H), 2.92 (d, $J = 17.6$ Hz, 1H), 3.11 (s, 3H), 3.21 (s, 3H), 3.94 (d, $J = 17.6$ Hz, 1H), 6.40 (d, $J = 7.6$ Hz, 1H), 6.65 (s, 1H), 6.70 (d, $J = 8.0$ Hz, 1H), 6.88-6.90 (m, 1H), 7.12 (d, $J = 8.0$ Hz, 1H), 7.20 (s, 1H), 7.84 (br s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 20.8, 21.3, 24.7, 25.5, 26.5, 33.1, 45.1, 49.1, 75.3, 86.8, 107.2, 108.5, 121.7, 123.1, 128.1, 129.0, 130.9, 132.9, 137.8, 141.9, 146.0, 173.0, 206.5; HRMS (ESI-TOF) m/z : Calcd. for $\text{C}_{24}\text{H}_{27}\text{N}_3\text{NaOS}$ $[\text{M}+\text{Na}]^+$: 428.1767; Found: 428.1769.



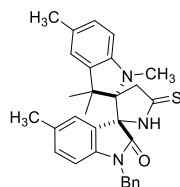
3be: Light yellow solid, m.p. 186.9-187.4 °C; yield 81%, >20:1 dr; ^1H NMR (CDCl_3 , 400 MHz) δ : 0.72 (s, 3H), 1.31 (s, 3H), 2.13 (s, 3H), 2.47 (s, 3H), 2.83 (d, $J = 17.6$ Hz, 1H), 3.01 (s, 3H), 3.43 (s, 3H), 3.89 (d, $J = 17.6$ Hz, 1H), 6.30 (d, $J = 8.0$ Hz, 1H), 6.58 (d, $J = 1.2$ Hz, 1H), 6.79-6.85 (m, 2H), 6.98 (d, $J = 7.6$ Hz, 1H), 7.19 (s, 1H), 7.85 (br s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 18.3, 19.7, 23.9, 24.5, 29.1, 32.1, 44.1, 48.2, 73.4, 86.0, 106.3, 119.2, 120.6, 122.2, 122.7, 125.0, 127.0, 127.1, 133.6, 136.7, 141.0, 145.0, 172.8, 205.6; HRMS (ESI-TOF) m/z : Calcd. for $\text{C}_{24}\text{H}_{27}\text{N}_3\text{NaOS}$ $[\text{M}+\text{Na}]^+$: 428.1767; Found: 428.1770.



3bf: Light yellow solid; yield 71%, >20:1 dr; ^1H NMR (CDCl_3 , 400 MHz) δ : 0.72 (s, 3H), 1.33 (s, 3H), 2.13 (s, 3H), 2.85 (d, $J = 17.6$ Hz, 1H), 3.03 (s, 3H), 3.13 (s, 3H), 3.68 (s, 3H), 3.88 (d, $J = 17.6$ Hz, 1H), 6.32 (d, $J = 7.6$ Hz, 1H), 6.59 (s, 1H), 6.65 (d, $J = 8.4$ Hz, 1H), 6.77-6.82 (m, 2H), 6.98 (d, $J = 2.8$ Hz, 1H), 7.75 (br s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 20.8, 24.8, 25.4, 26.6, 33.0, 45.2, 49.1, 55.8, 75.3, 86.8, 107.3, 109.0, 114.6, 116.1, 121.7, 124.4, 128.2, 137.7, 137.8, 145.9, 156.2, 172.7, 206.7; HRMS (ESI-TOF) m/z : Calcd. for $\text{C}_{24}\text{H}_{27}\text{N}_3\text{NaO}_2\text{S}$ $[\text{M}+\text{Na}]^+$: 444.1716; Found: 444.1712.

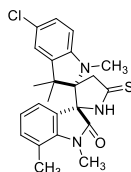


3bg: Light yellow solid, m.p. 176.8-177.2 $^\circ\text{C}$; yield 68%, >20:1 dr; ^1H NMR (CDCl_3 , 400 MHz) δ : 0.72 (s, 3H), 1.19-1.23 (m, 3H), 1.32 (s, 3H), 2.13 (s, 3H), 2.20 (s, 3H), 2.79 (d, $J = 17.6$ Hz, 1H), 3.02 (s, 3H), 3.61-3.64 (m, 1H), 3.71-3.77 (m, 1H), 3.84 (d, $J = 17.6$ Hz, 1H), 6.33 (d, $J = 8.0$ Hz, 1H), 6.58 (s, 1H), 6.65 (d, $J = 8.0$ Hz, 1H), 6.81 (d, $J = 8.0$ Hz, 1H), 7.04 (d, $J = 8.0$ Hz, 1H), 7.14 (s, 1H), 8.25 (br s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 10.7, 19.4, 19.9, 23.4, 23.7, 31.7, 33.7, 43.6, 47.7, 73.8, 85.3, 105.8, 107.1, 120.2, 121.9, 126.7, 126.8, 127.8, 129.4, 131.2, 136.4, 139.6, 144.6, 171.0, 204.9; HRMS (ESI-TOF) m/z : Calcd. for $\text{C}_{25}\text{H}_{29}\text{N}_3\text{NaOS}$ $[\text{M}+\text{Na}]^+$: 442.1924; Found: 442.1928.

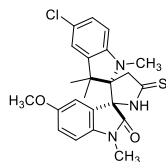


3bh: Light yellow solid, m.p. 175.2-176.0 $^\circ\text{C}$; yield 66%, 19:1 dr; ^1H NMR ($\text{DMSO}-d_6$, 400 MHz) δ : 0.63 (s, 3H), 1.30 (s, 3H), 2.12 (s, 3H), 2.23 (s, 3H), 2.68 (d, $J = 17.2$ Hz, 1H), 3.01 (s, 3H), 3.74 (d, $J = 17.2$ Hz, 1H), 4.84 (d, $J = 15.6$ Hz, 1H), 5.01 (d, $J = 15.6$ Hz, 1H), 6.43 (d, $J = 8.0$ Hz, 1H), 6.67 (s, 1H), 6.81 (d, $J = 8.0$ Hz, 1H), 6.89 (d, $J = 8.0$ Hz, 1H), 7.10 (d, $J = 8.0$ Hz,

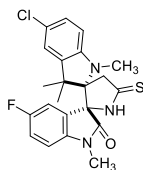
1H), 7.17 (s, 1H), 7.26-7.43 (m, 5H), 10.83 (br s, 1H); ^{13}C NMR (DMSO- d_6 , 100 MHz) δ : 25.7, 26.0, 29.4, 30.1, 37.9, 48.4, 49.7, 54.3, 80.3, 91.1, 112.4, 114.8, 126.5, 129.0, 132.2, 132.8, 133.0 (2C), 133.7, 133.8 (2C), 135.6, 136.9, 140.7, 142.8, 146.4, 151.1, 178.3, 209.9; HRMS (ESI-TOF) m/z : Calcd. for $\text{C}_{30}\text{H}_{31}\text{N}_3\text{NaOS}$ $[\text{M}+\text{Na}]^+$: 504.2080; Found: 504.2083.



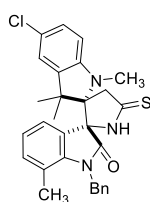
3ca: Light yellow solid, m.p. 183.2-184.1 °C; yield 65%, 20:1 dr; ^1H NMR (CDCl_3 , 400 MHz) δ : 0.80 (s, 3H), 1.27 (s, 3H), 2.47 (s, 3H), 2.85 (d, $J = 17.2$ Hz, 1H), 3.05 (s, 3H), 3.43 (s, 3H), 3.95 (d, $J = 17.2$ Hz, 1H), 6.28 (d, $J = 8.0$ Hz, 1H), 6.68 (d, $J = 2.0$ Hz, 1H), 6.79-6.83 (m, 1H), 6.91-6.94 (m, 1H), 6.99 (d, $J = 7.2$ Hz, 1H), 7.08 (d, $J = 7.2$ Hz, 1H), 7.64 (br s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 17.9, 22.6, 24.8, 28.3, 31.6, 44.0, 47.7, 73.1, 85.7, 106.5, 119.0, 119.8, 121.9, 122.0, 124.5, 126.2, 133.4, 138.0, 140.7, 145.5, 172.4, 205.0; HRMS (ESI-TOF) m/z : Calcd. for $\text{C}_{23}\text{H}_{24}\text{ClN}_3\text{NaOS}$ $[\text{M}+\text{Na}]^+$: 448.1221; Found: 448.1224.



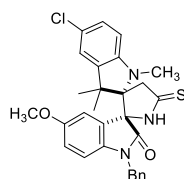
3cb: Light yellow solid, m.p. 191.3-192.2 °C; yield 60%, >20:1 dr; ^1H NMR (DMSO- d_6 , 400 MHz) δ : 0.77 (s, 3H), 1.28 (s, 3H), 2.77 (d, $J = 17.6$ Hz, 1H), 3.04 (s, 3H), 3.15 (s, 3H), 3.70 (s, 3H), 3.76 (d, $J = 17.6$ Hz, 1H), 6.54 (d, $J = 8.4$ Hz, 1H), 6.82 (d, $J = 2.4$ Hz, 1H), 6.90 (d, $J = 2.4$ Hz, 1H), 6.96-7.03 (m, 3H), 10.63 (br s, 1H); ^{13}C NMR (DMSO- d_6 , 100 MHz) δ : 28.5, 30.9, 31.6, 37.4, 50.0, 54.4, 60.8, 80.4, 91.0, 113.3, 114.9, 119.6, 120.1, 126.2, 126.7, 129.7, 132.5, 142.9, 144.9, 152.2, 160.6, 177.7, 209.7; HRMS (ESI-TOF) m/z : Calcd. for $\text{C}_{23}\text{H}_{24}\text{ClN}_3\text{NaO}_2\text{S}$ $[\text{M}+\text{Na}]^+$: 464.1170; Found: 464.1168.



3cc: Light yellow solid, m.p. 236.2-237.3 °C; yield 61%, >20:1 dr; ^1H NMR (DMSO- d_6 , 400 MHz) δ : 0.71 (s, 3H), 1.20 (s, 3H), 2.73 (d, J = 17.6 Hz, 1H), 2.96 (s, 3H), 3.11 (s, 3H), 3.67 (d, J = 17.6 Hz, 1H), 6.47 (d, J = 8.4 Hz, 1H), 6.85 (d, J = 2.4 Hz, 1H), 6.94-6.97 (m, 2H), 7.00-7.03 (m, 1H), 7.16-7.21 (m, 1H), 10.59 (br s, 1H); ^{13}C NMR (DMSO- d_6 , 100 MHz) δ : 23.7, 26.1, 26.9, 32.7, 45.3, 49.4, 75.5, 86.4, 108.8, 110.7 (d, J_{CF} = 8.1 Hz), 115.8 (d, J_{CF} = 26.1 Hz), 117.2 (d, J_{CF} = 23.1 Hz), 121.4, 122.1, 125.3 (d, J_{CF} = 8.1 Hz), 127.8, 140.0, 141.1, 147.4, 158.8 (d, J_{CF} = 237.0 Hz), 173.2, 205.1; ^{19}F NMR (CDCl_3 , 470 MHz) δ : -120.14; HRMS (ESI-TOF) m/z : Calcd. for $\text{C}_{22}\text{H}_{21}\text{ClFN}_3\text{NaOS}$ $[\text{M}+\text{Na}]^+$: 452.0970; Found: 452.0965.



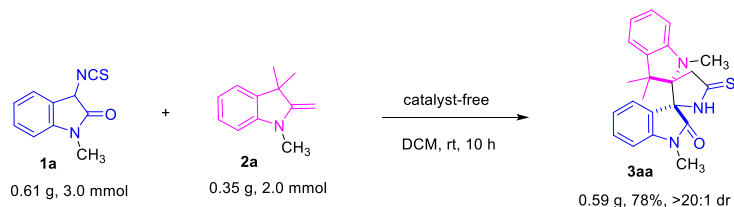
3cd: Light yellow solid, m.p. 168.9-169.5 °C; yield 64%, 17:1 dr; ^1H NMR (CDCl_3 , 400 MHz) δ : 0.83 (s, 3H), 1.27 (s, 3H), 2.22 (s, 3H), 2.84 (d, J = 17.6 Hz, 1H), 3.04 (s, 3H), 3.96 (d, J = 17.6 Hz, 1H), 4.91 (d, J = 16.4 Hz, 1H), 5.26 (d, J = 16.4 Hz, 1H), 6.29 (d, J = 8.4 Hz, 1H), 6.69 (d, J = 2.0 Hz, 1H), 6.81-6.85 (m, 1H), 6.92-6.95 (m, 2H), 7.10-7.20 (m, 4H), 7.23-7.27 (m, 2H), 8.29 (br s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 18.1, 23.4, 24.7, 32.0, 44.3, 44.9, 48.2, 73.4, 86.2, 107.0, 119.4, 120.1, 122.3, 122.4, 122.5, 125.0, 125.1 (2C), 126.6, 126.7, 128.0 (2C), 134.0, 135.7, 138.4, 140.7, 145.8, 173.4, 205.2; HRMS (ESI-TOF) m/z : Calcd. for $\text{C}_{29}\text{H}_{28}\text{ClN}_3\text{NaOS}$ $[\text{M}+\text{Na}]^+$: 524.1534; Found: 524.1537.



3ce: Light yellow solid, m.p. 158.0-158.9 °C; yield 82%, >20:1 dr; ^1H NMR (CDCl_3 , 400 MHz) δ : 0.70 (s, 3H), 1.29 (s, 3H), 2.85 (d, J = 17.6 Hz, 1H), 3.05 (s, 3H), 3.64 (s, 3H), 3.95 (d, J = 17.6 Hz, 1H), 4.72 (d, J = 15.2 Hz, 1H), 4.84 (d, J = 15.2 Hz, 1H), 6.31 (d, J = 8.0 Hz, 1H), 6.64 (d, J = 8.4 Hz, 1H), 6.68-6.69 (m, 2H), 6.69 (d, J = 2.4 Hz, 1H), 6.93-6.96 (m, 1H), 7.22-7.28 (m, 5H), 7.85 (br s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 23.4, 24.5, 31.9, 43.6, 44.2, 48.1, 54.8, 74.2, 86.0, 107.0, 109.1, 113.6, 115.0, 120.2, 122.4, 123.0, 126.6, 127.0 (2C), 127.1, 127.9 (2C), 133.8, 135.9,

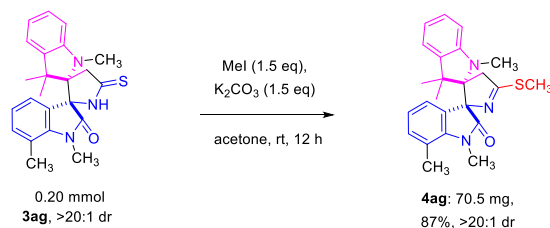
138.4, 145.7, 155.1, 171.7, 205.3; HRMS (ESI-TOF) m/z : Calcd. for $C_{29}H_{28}ClN_3NaO_2S$ $[M+Na]^+$: 540.1483; Found: 540.1487.

4. Preparative scale synthesis of the product 3aa



In a sealed tube equipped with a magnetic stirring bar, a mixture of 3-isothiocyanto oxindole **1a** (2.0 mmol), Fischer base **2a** (3.0 mmol) in 10.0 mL of DCM was stirred at rt for 10 h, and then was directly loaded onto a silica gel and purified by flash chromatography (hexane/EtOAc, 10/1, v/v) to give the desired product **3aa** (0.59 g, 78%, >20:1 dr).

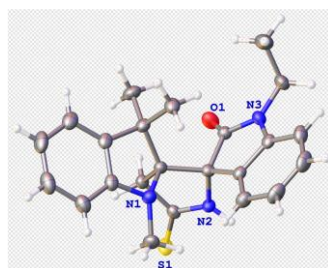
5. Further investigation of transformation of 3ag



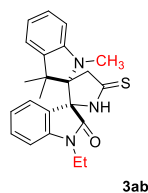
To a stirred solution of **3ag** (78.2 mg, 0.20 mmol) in acetone (1.0 mL) was added K_2CO_3 (41 mg, 0.30 mmol) at 0 °C. Then iodomethane (43 mg, 0.30 mmol) in 2.0 mL acetone was added dropwise into the stirred reaction mixture. The reaction mixture was allowed to stir at room temperature for another 12 h, and was directly loaded onto a silica gel and purified by flash chromatography (hexane/EtOAc, 10/1, v/v) to give the desired product **4ag**.

4ag: Light yellow solid, yield 87% (70.5 mg), >20:1 dr; 1H NMR ($CDCl_3$, 400 MHz) δ : 0.64 (s, 3H), 1.39 (s, 3H), 2.36 (s, 3H), 2.48 (s, 3H), 2.52 (d, $J = 16.0$ Hz, 1H), 2.84 (s, 3H), 3.44 (s, 3H), 3.78 (d, $J = 16.0$ Hz, 1H), 6.39 (d, $J = 7.6$ Hz, 1H), 6.58-6.62 (m, 1H), 6.79-6.83 (m, 2H), 6.94 (d, $J = 7.6$ Hz, 1H), 6.98-7.02 (m, 1H), 7.15 (d, $J = 7.6$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 12.1, 18.0, 23.6, 24.4, 28.6, 31.3, 43.1, 43.9, 82.0, 88.1, 105.8, 117.0, 118.3, 119.3, 121.4, 124.1, 126.2, 127.5, 131.7, 137.3, 140.8, 146.8, 173.2, 177.4; HRMS (ESI-TOF) m/z : Calcd. for $C_{24}H_{27}N_3NaOS$ $[M+Na]^+$: 428.1767; Found: 428.1767.

6. X-ray crystal data for compounds 3ab, 3ah and 3ba



CCDC 2232176 **3ab**

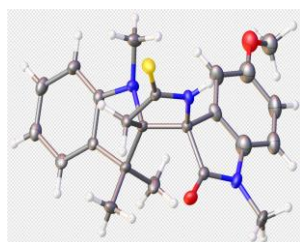


3ab

Table S1 Crystal data and structure refinement for 3ab

Identification code	3ab
Empirical formula	C ₂₃ H ₂₅ N ₃ OS
Formula weight	391.52
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	C2/c
a/Å, b/Å, c/Å	18.8625(12), 8.7470(7), 25.549(2)
$\alpha/^\circ$, $\beta/^\circ$, $\gamma/^\circ$,	90, 93.552(6), 90
Volume/Å ³	4207.3(5)
Z	8
$\rho_{\text{calc}}/\text{cm}^3$	1.236
μ/mm^{-1}	0.172
F(000)	1664.0
Radiation	Mo K α (λ = 0.71073)
Crystal size/mm ³	0.15 × 0.13 × 0.12
2 θ range for data collection/ $^\circ$	4.328 to 49.998
Index ranges	-22 ≤ h ≤ 19, -9 ≤ k ≤ 10, -30 ≤ l ≤ 29
Reflections collected	11218
Independent reflections	3688 [R_{int} = 0.0295, R_{sigma} = 0.0336]
Data/restraints/parameters	3688/0/257
Goodness-of-fit on F ²	1.033
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0399, wR_2 = 0.0919
Final R indexes [all data]	R_1 = 0.0486, wR_2 = 0.0971
Largest diff. peak/hole / e Å ⁻³	0.19/-0.23

Crystal Data for C₂₃H₂₅N₃OS (M = 391.52 g/mol): monoclinic, space group C2/c (no. 15), a = 18.8625(12) Å, b = 8.7470(7) Å, c = 25.549(2) Å, β = 93.552(6) $^\circ$, V = 4207.3(5) Å³, Z = 8, T = 149.99(10) K, $\mu(\text{Mo K}\alpha)$ = 0.172 mm⁻¹, D_{calc} = 1.236 g/cm³, 11218 reflections measured (4.328 $^\circ$ ≤ 2 θ ≤ 49.998 $^\circ$), 3688 unique (R_{int} = 0.0295, R_{sigma} = 0.0336) which were used in all calculations. The final R_1 was 0.0399 ($I > 2\sigma(I)$) and wR_2 was 0.0971 (all data).



CCDC 2232175 **3ah**

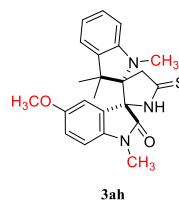
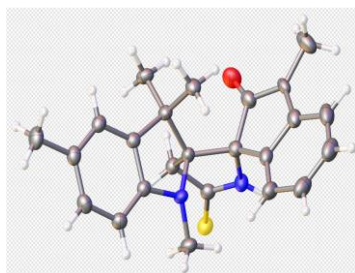


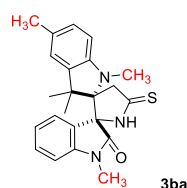
Table S2 Crystal data and structure refinement for 3ah

Identification code	3ah
Empirical formula	C ₂₃ H ₂₅ N ₃ O ₂ S
Formula weight	407.52
Temperature/K	150.00(10)
Crystal system	tetragonal
Space group	I-4
a/Å, b/Å, c/Å	20.8691(8), 20.8691(8), 10.3768(6)
α/°, β/°, γ/°	90, 90, 90
Volume/Å ³	4519.3(4)
Z	8
ρ _{calc} /cm ³	1.198
μ/mm ⁻¹	0.166
F(000)	1728.0
Radiation	Mo Kα (λ = 0.71073)
Crystal size/mm ³	0.16 × 0.13 × 0.12
2θ range for data collection/°	4.384 to 58.998
Index ranges	-28 ≤ h ≤ 18, -18 ≤ k ≤ 23, -13 ≤ l ≤ 10
Reflections collected	8173
Independent reflections	4774 [R _{int} = 0.0199, R _{sigma} = 0.0407]
Data/restraints/parameters	4774/77/257
Goodness-of-fit on F ²	1.080
Final R indexes [I > 2σ(I)]	R ₁ = 0.0649, wR ₂ = 0.1675
Final R indexes [all data]	R ₁ = 0.0759, wR ₂ = 0.1789
Largest diff. peak/hole / e Å ⁻³	0.71/-0.59
Flack parameter	-0.10(4)

Crystal Data for C₂₃H₂₅N₃O₂S (*M* = 407.52 g/mol): tetragonal, space group I-4 (no. 82), *a* = 20.8691(8) Å, *c* = 10.3768(6) Å, *V* = 4519.3(4) Å³, *Z* = 8, *T* = 150.00(10) K, μ(Mo Kα) = 0.166 mm⁻¹, *D*_{calc} = 1.198 g/cm³, 8173 reflections measured (4.384° ≤ 2θ ≤ 58.998°), 4774 unique (*R*_{int} = 0.0199, *R*_{sigma} = 0.0407) which were used in all calculations. The final *R*₁ was 0.0649 (*I* > 2σ(*I*)) and *wR*₂ was 0.1789 (all data).



CCDC 2232177 **3ba**



3ba

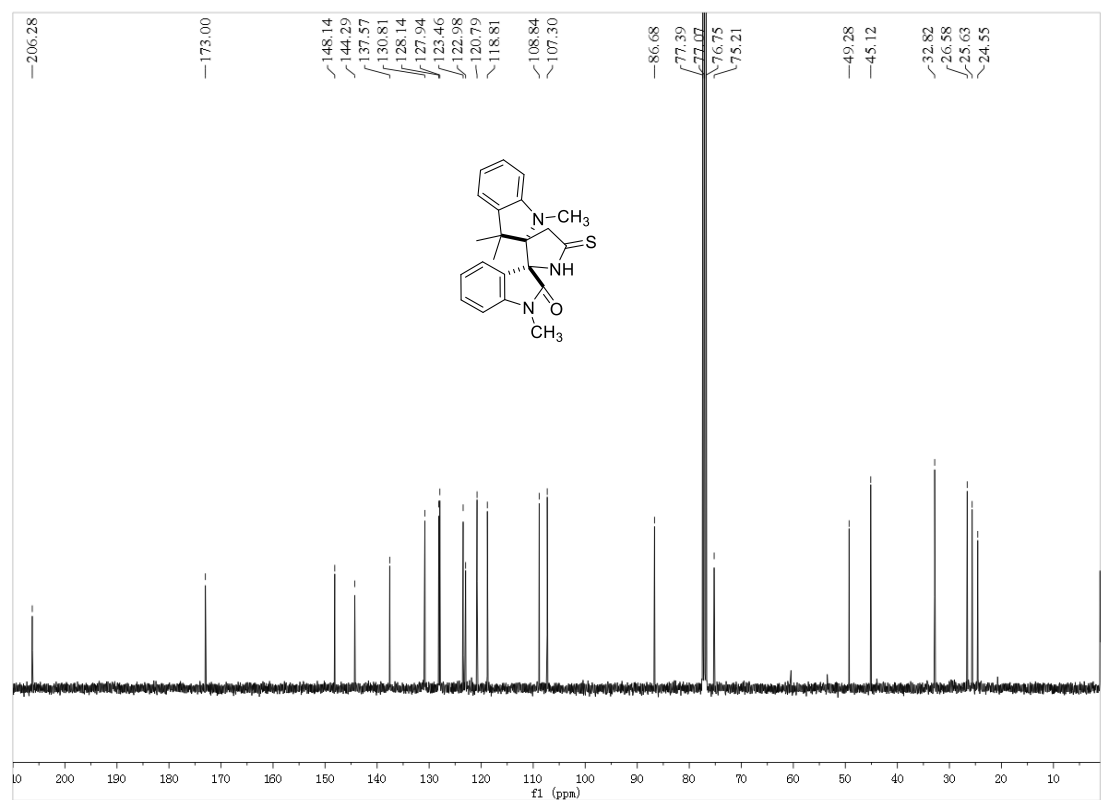
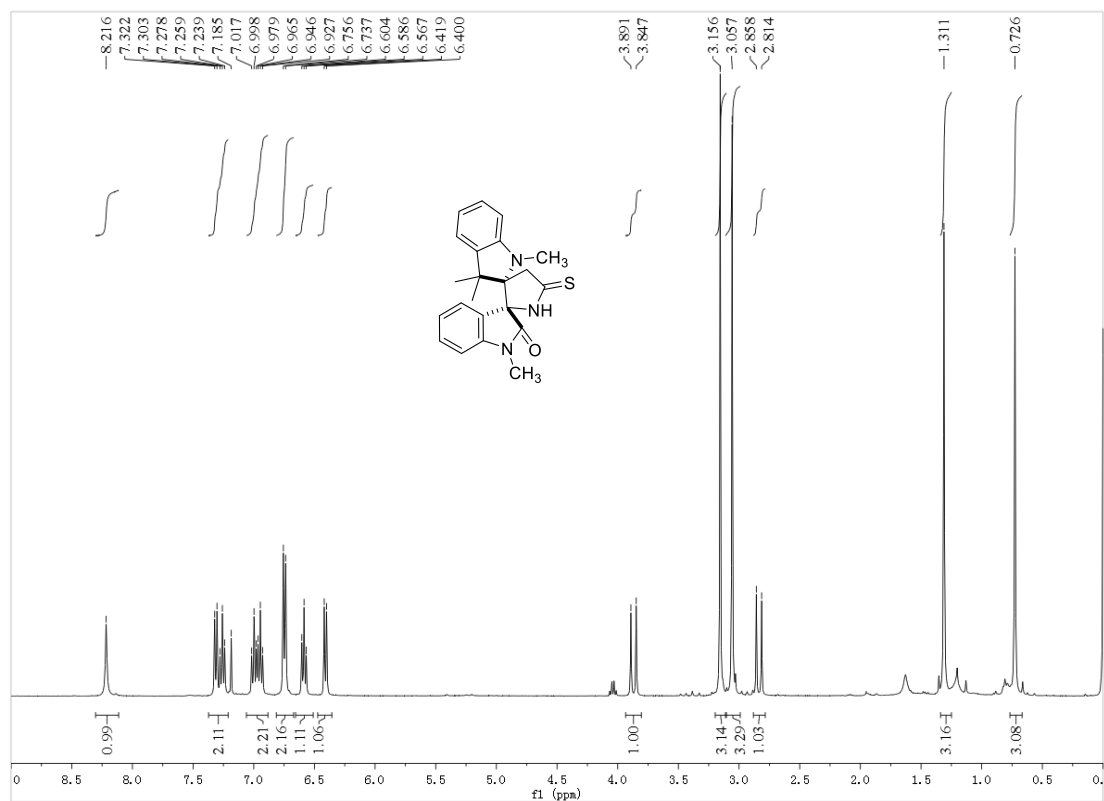
Table S3 Crystal data and structure refinement for 3ba

Identification code	3ba
Empirical formula	C ₂₄ H ₂₅ N ₂ OS
Formula weight	389.52
Temperature/K	150.00(10)
Crystal system	triclinic
Space group	P-1
a/Å, b/Å, c/Å	7.4539(5), 9.8480(6), 14.0220(9)
α/°, β/°, γ/°	78.299(5), 84.219(5), 85.023(5)
Volume/Å ³	1000.46(11)
Z	2
ρ _{calc} /g/cm ³	1.293
μ/mm ⁻¹	1.558
F(000)	414.0
Radiation	Cu Kα (λ = 1.54184)
Crystal size/mm ³	0.15 × 0.13 × 0.12
2θ range for data collection/°	6.46 to 147.314
Index ranges	-8 ≤ h ≤ 9, -10 ≤ k ≤ 12, -15 ≤ l ≤ 17
Reflections collected	6641
Independent reflections	3903 [R _{int} = 0.0329, R _{sigma} = 0.0392]
Data/restraints/parameters	3903/9/258
Goodness-of-fit on F ²	1.051
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0530, wR ₂ = 0.1462
Final R indexes [all data]	R ₁ = 0.0616, wR ₂ = 0.1523
Largest diff. peak/hole / e Å ⁻³	0.74/-0.39

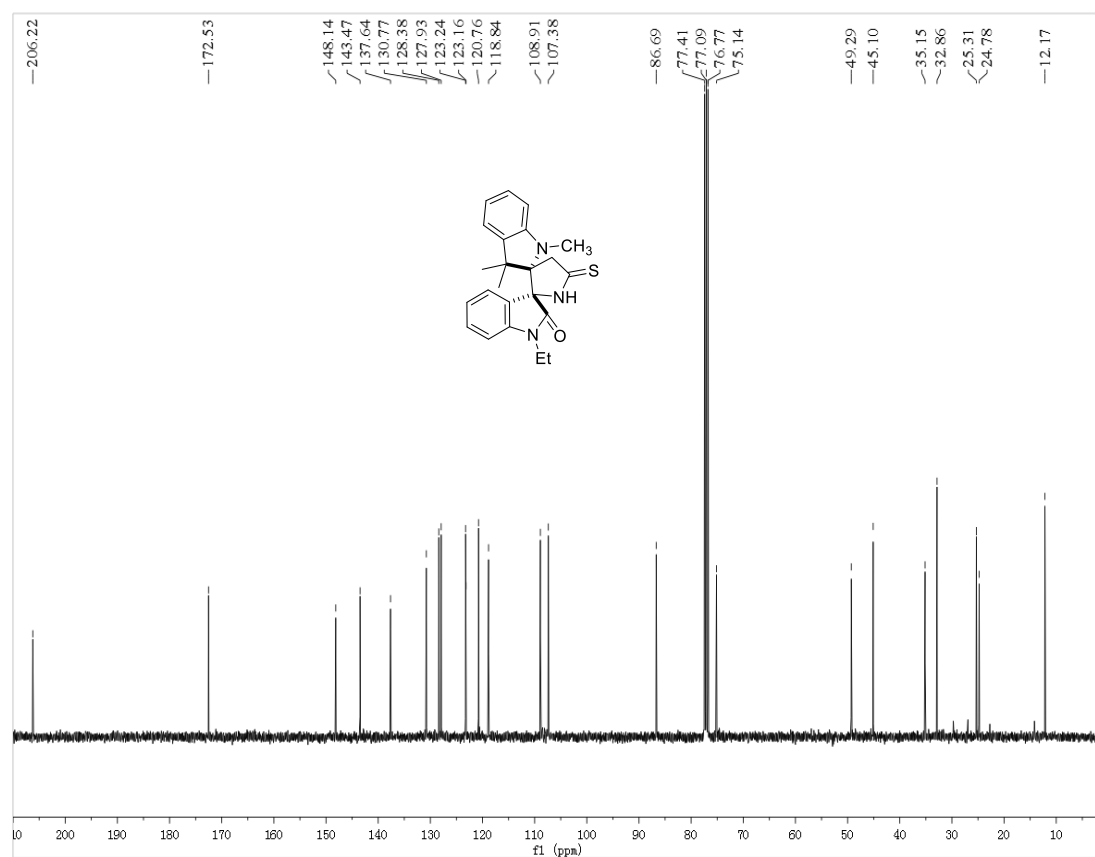
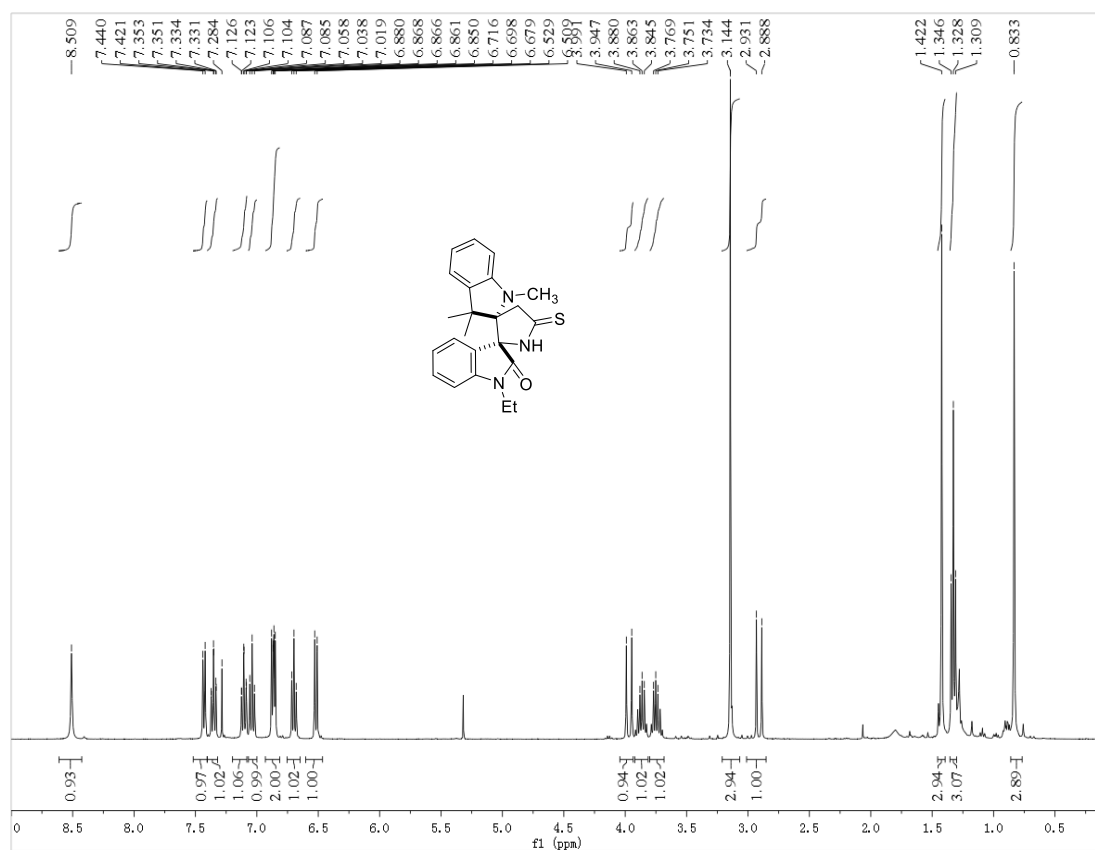
Crystal Data for C₂₄H₂₅N₂OS (*M* = 389.52 g/mol): triclinic, space group P-1 (no. 2), *a* = 7.4539(5) Å, *b* = 9.8480(6) Å, *c* = 14.0220(9) Å, α = 78.299(5)°, β = 84.219(5)°, γ = 85.023(5)°, *V* = 1000.46(11) Å³, *Z* = 2, *T* = 150.00(10) K, μ(Cu Kα) = 1.558 mm⁻¹, *D*_{calc} = 1.293 g/cm³, 6641 reflections measured (6.46° ≤ 2θ ≤ 147.314°), 3903 unique (*R*_{int} = 0.0329, *R*_{sigma} = 0.0392) which were used in all calculations. The final *R*₁ was 0.0530 (*I* > 2σ(*I*)) and *wR*₂ was 0.1523 (all data).

7. The copies of ^1H NMR and ^{13}C NMR spectra for compounds 3

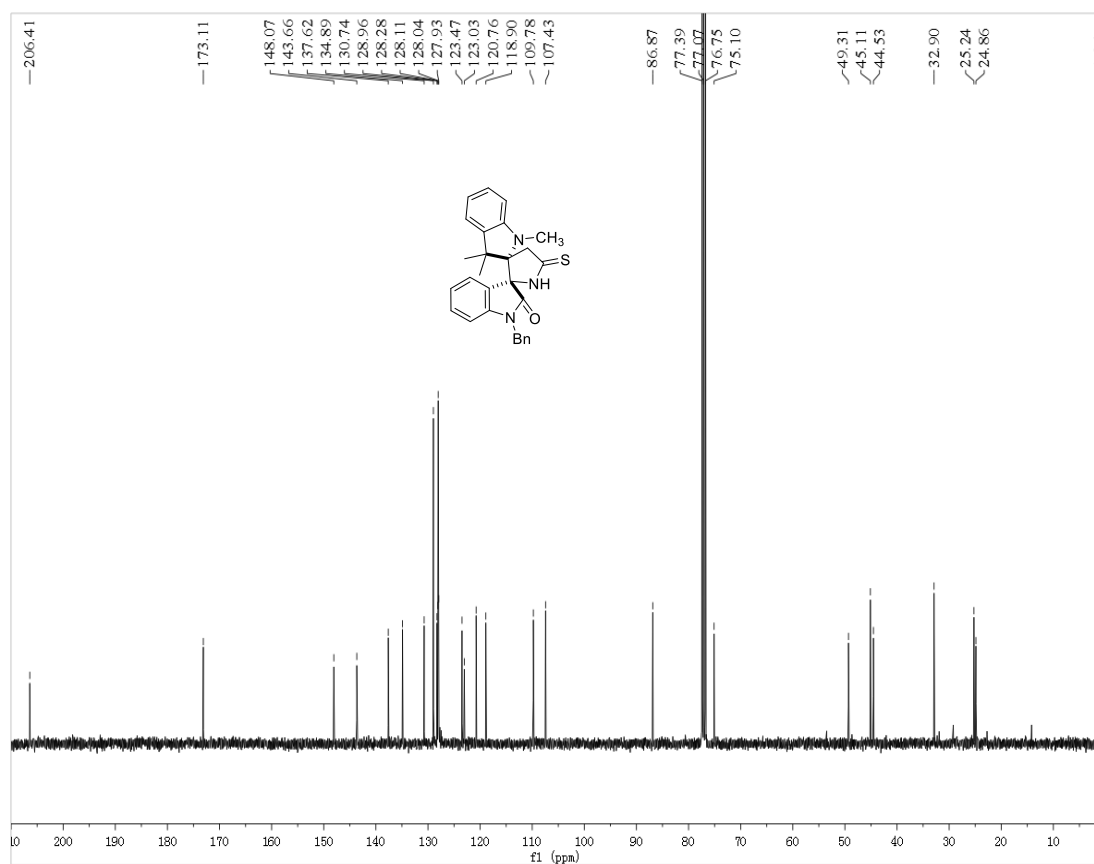
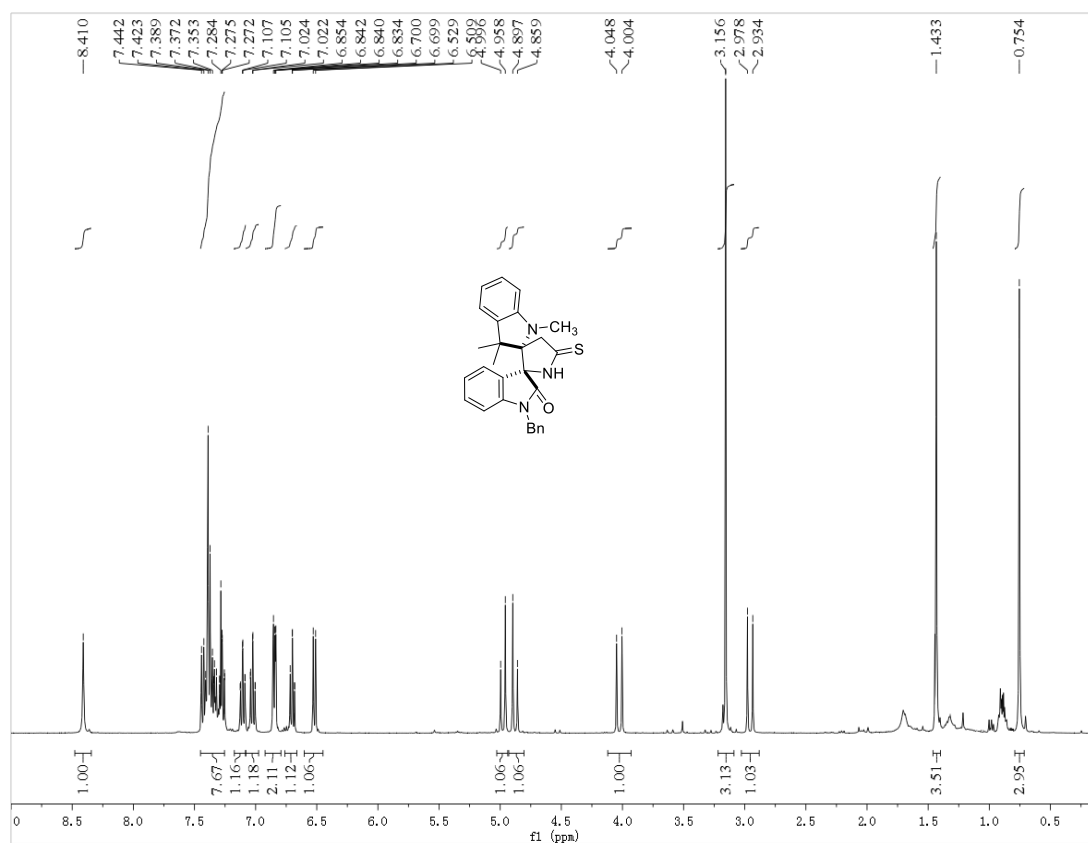
^1H and ^{13}C NMR of 3aa



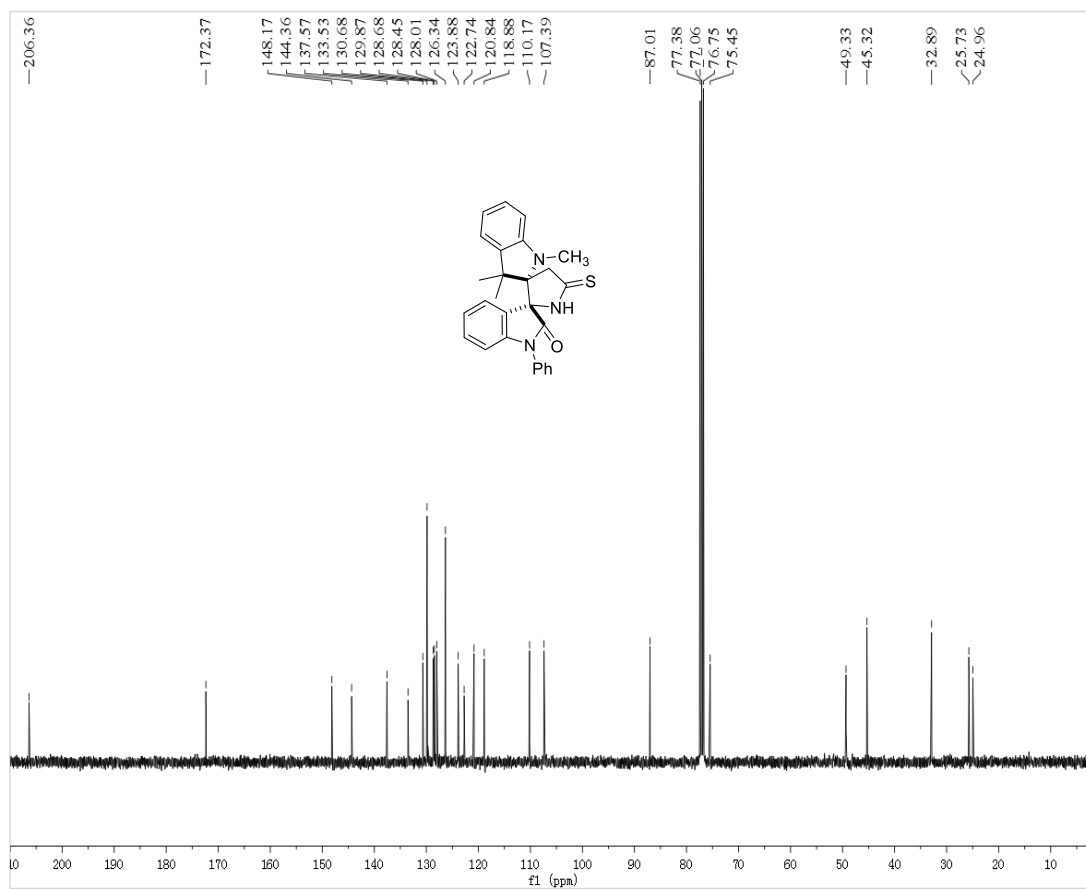
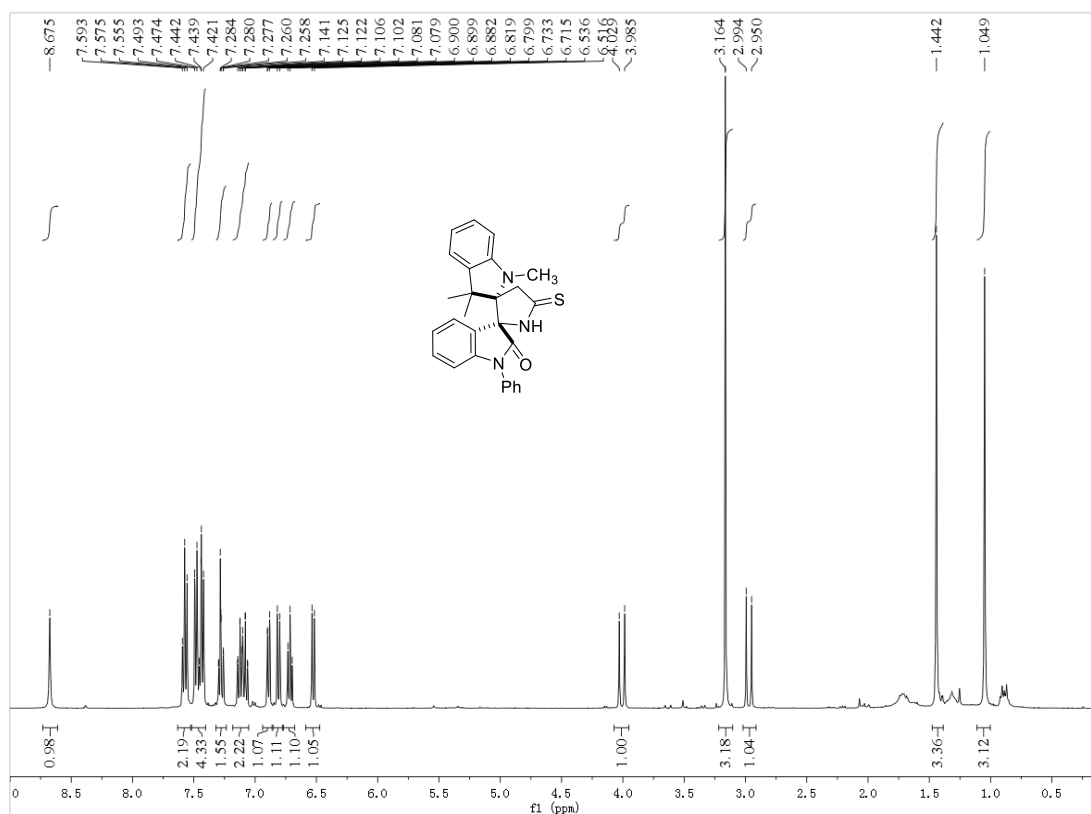
^1H and ^{13}C NMR of 3ab



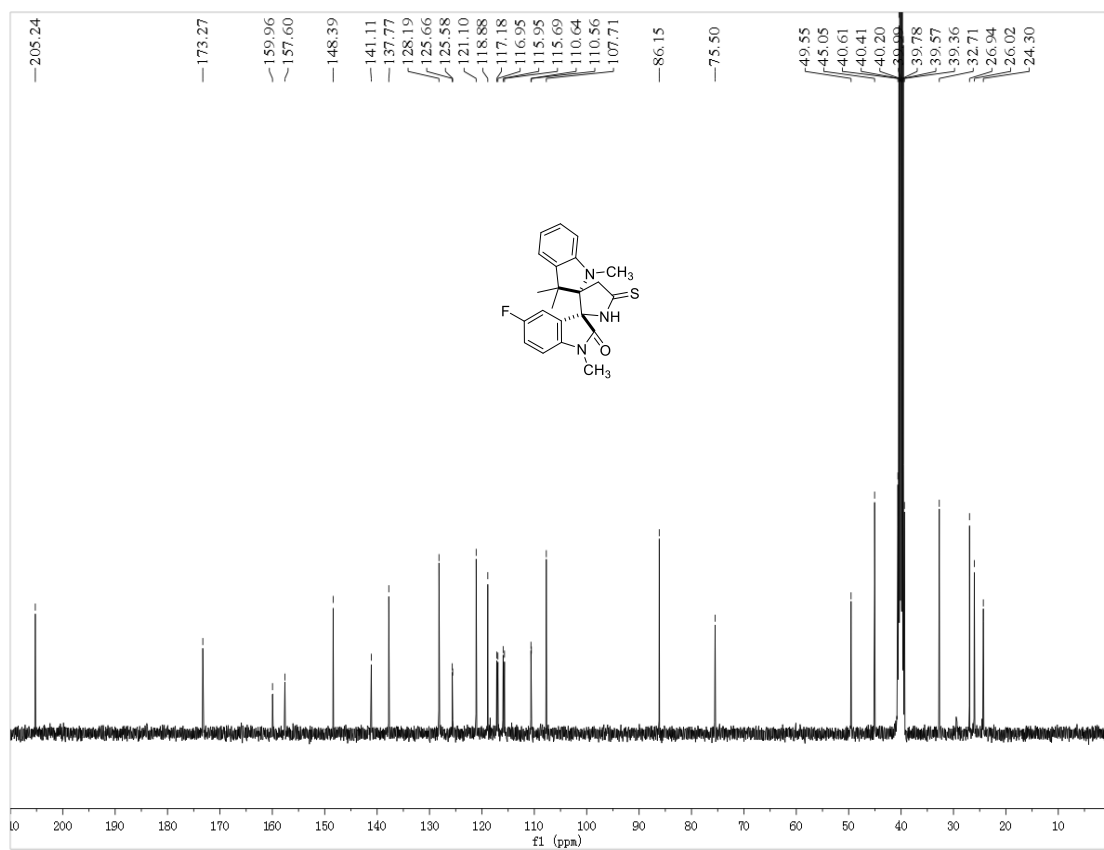
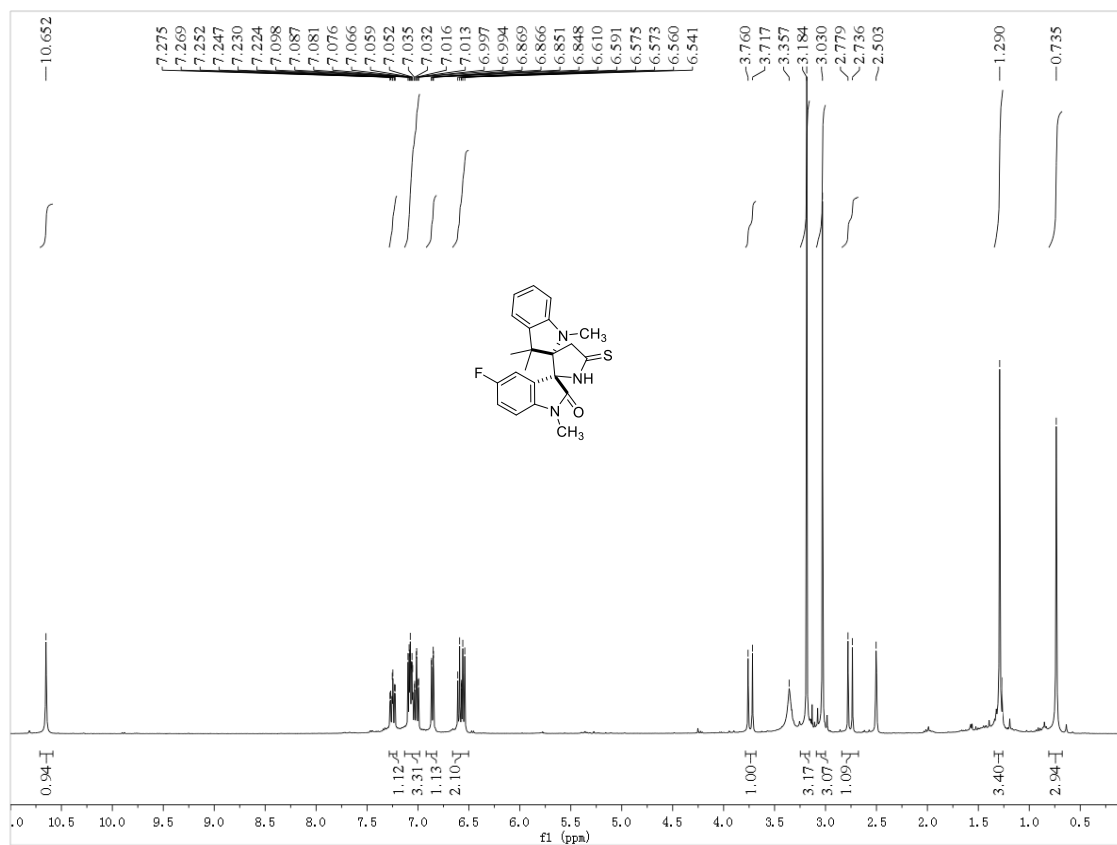
¹H and ¹³C NMR of 3ac



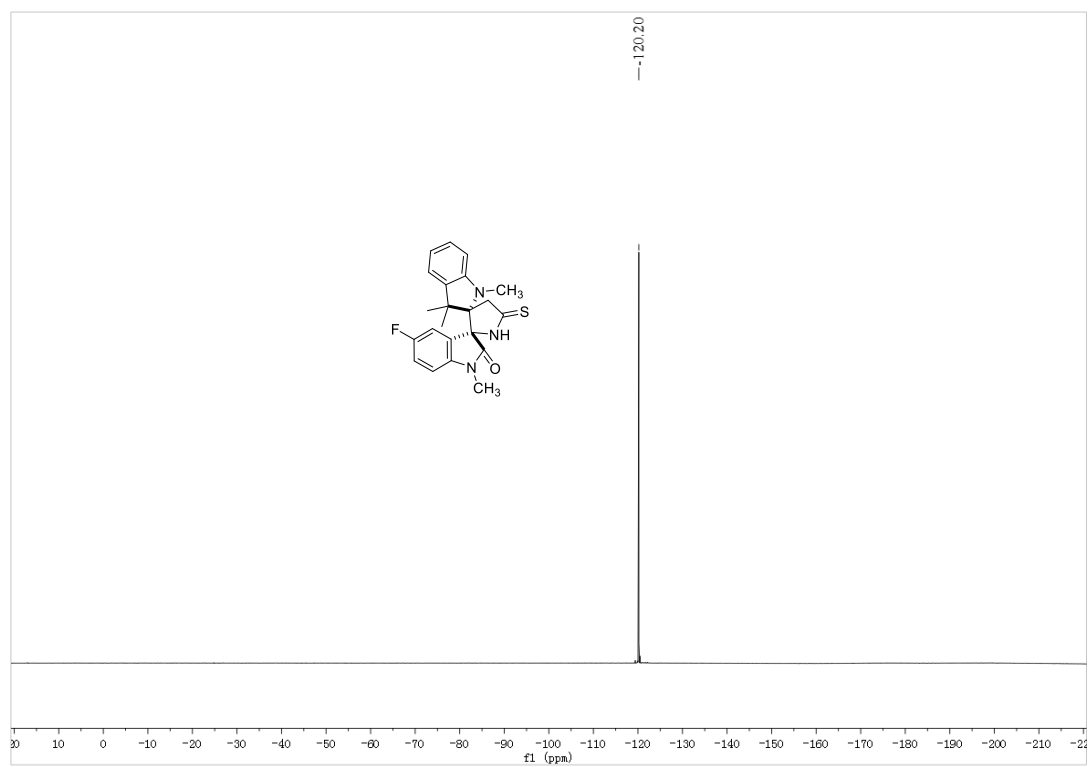
¹H and ¹³C NMR of 3ad



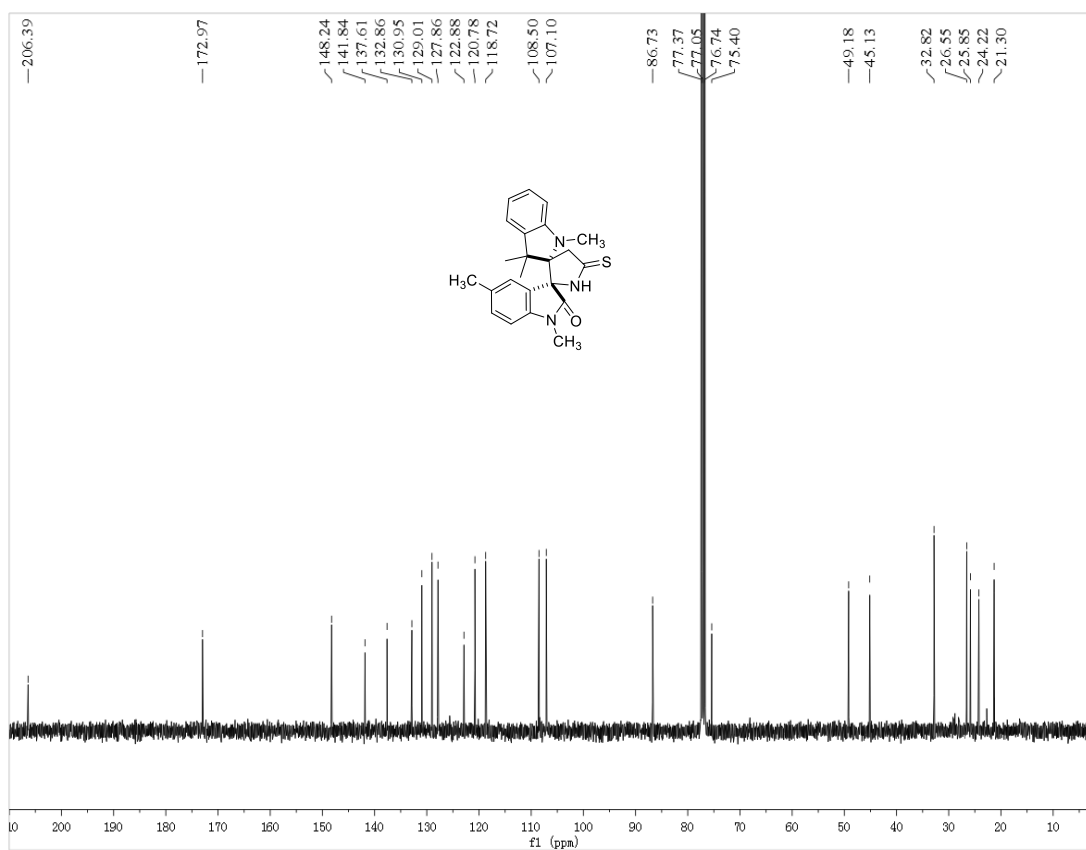
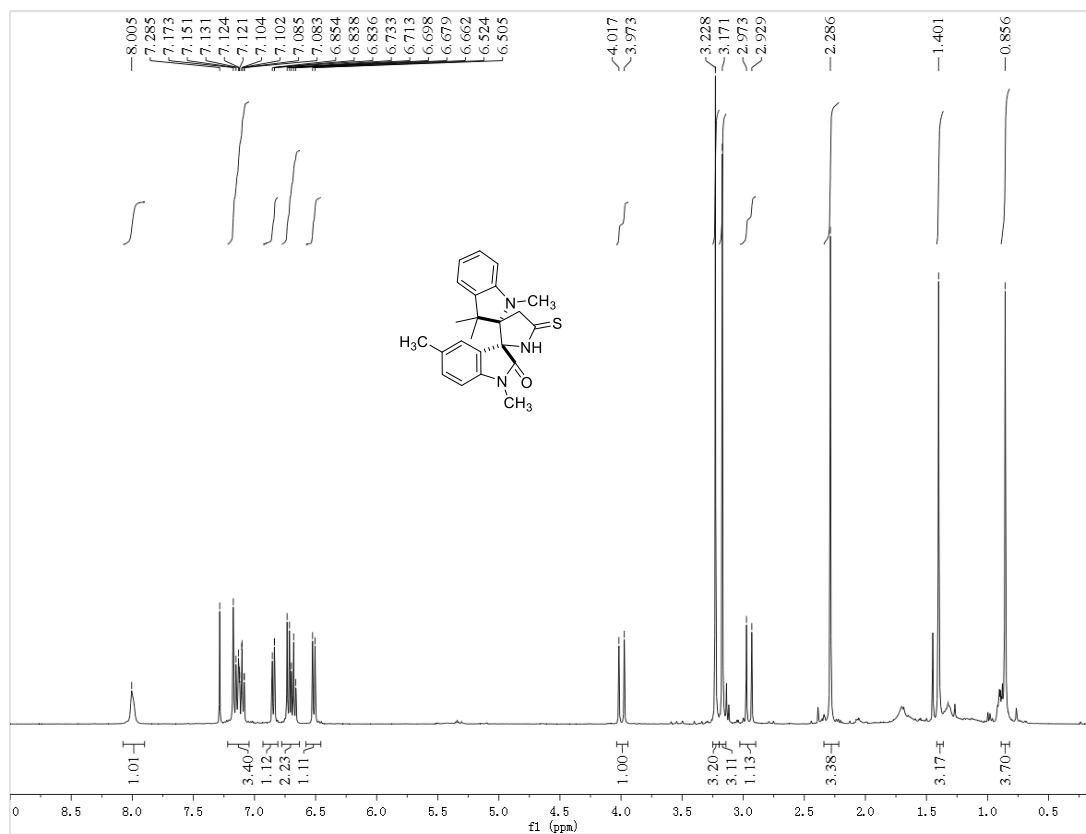
¹H and ¹³C NMR of 3ae



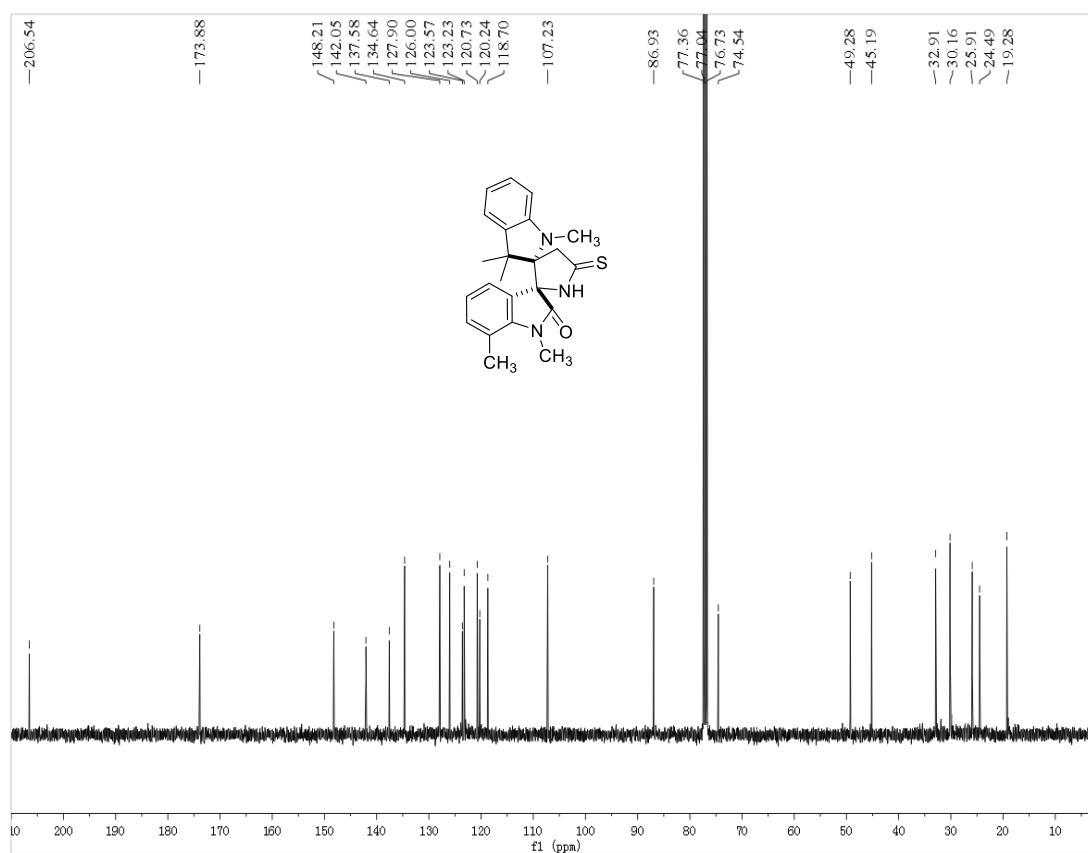
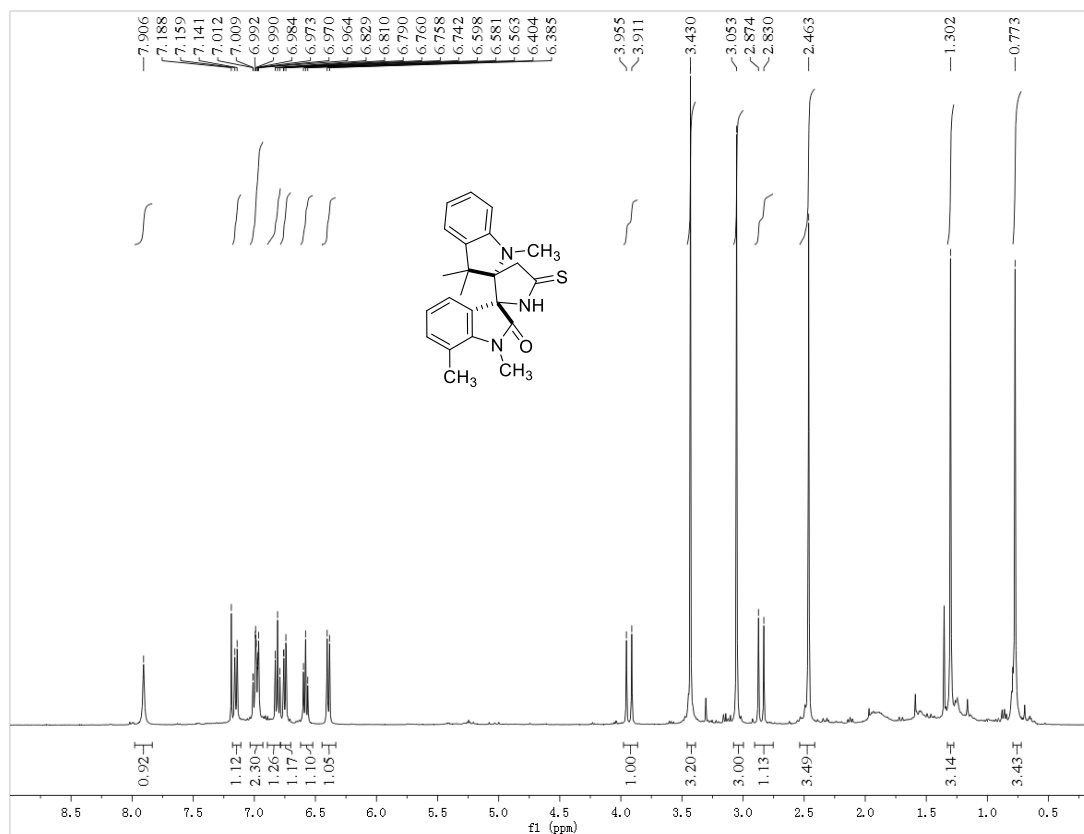
¹⁹F NMR of 3ae



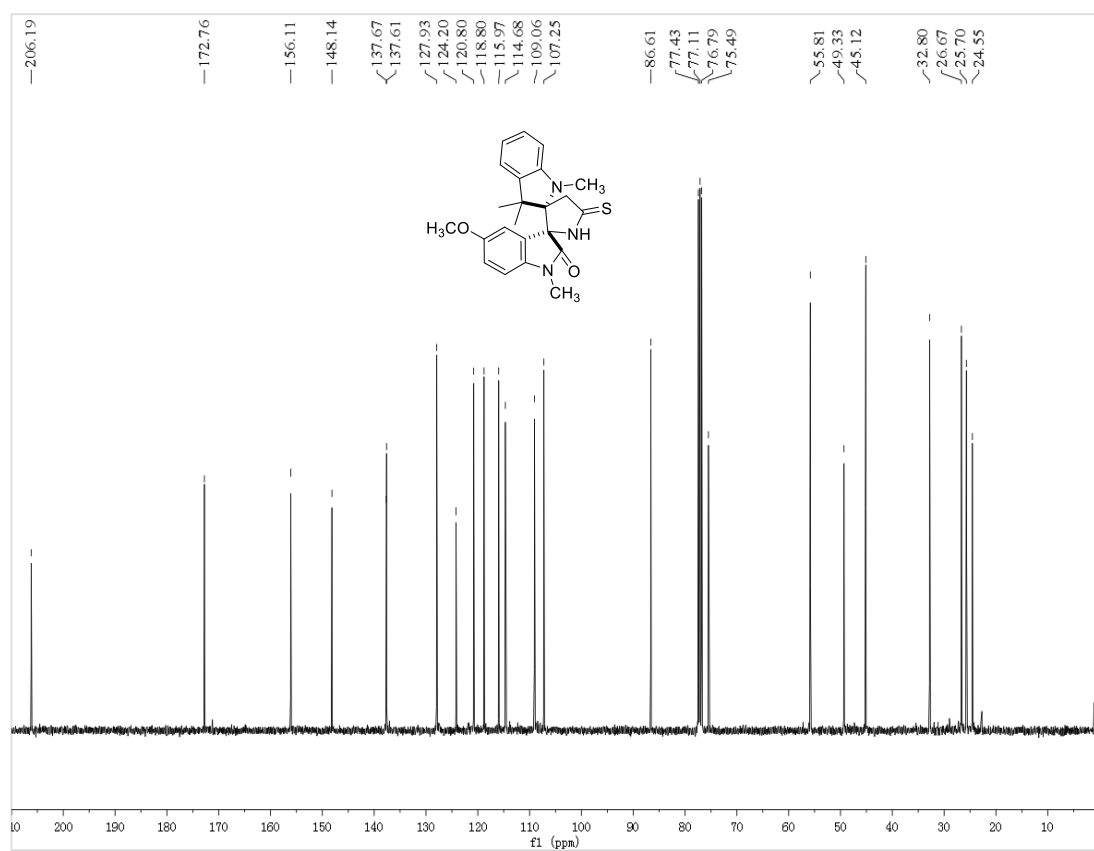
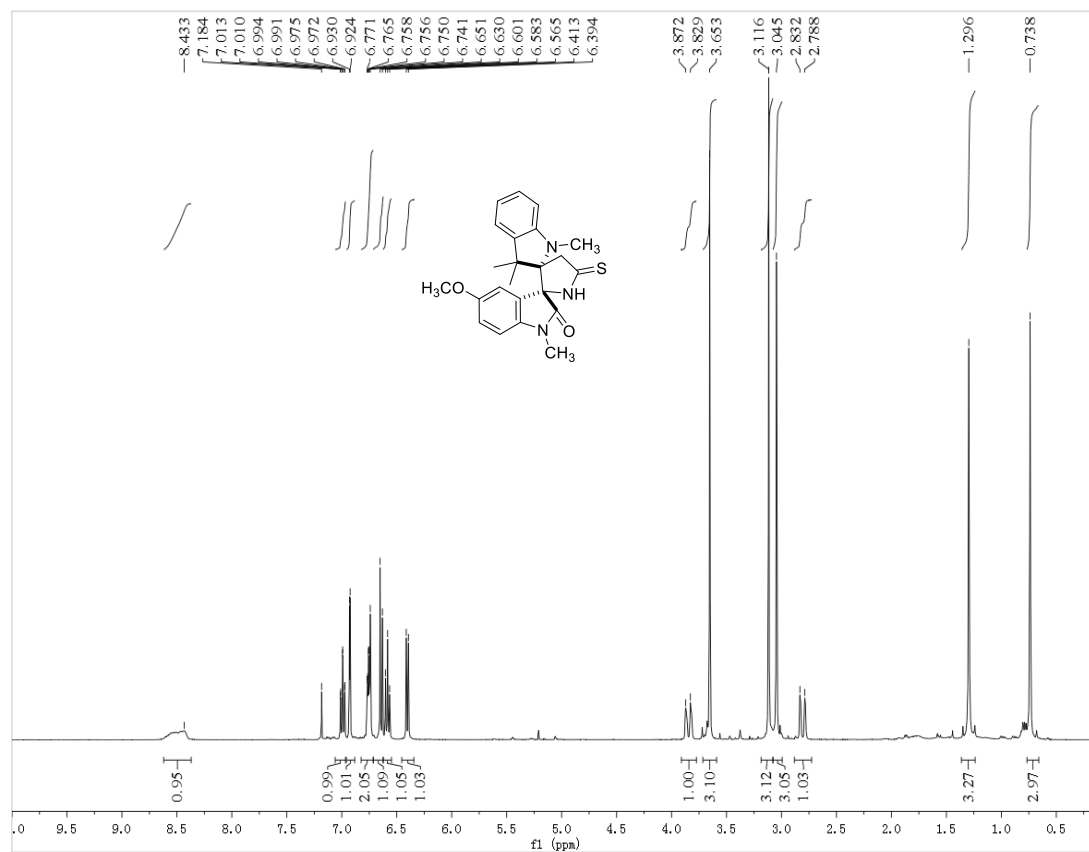
^1H and ^{13}C NMR of 3af



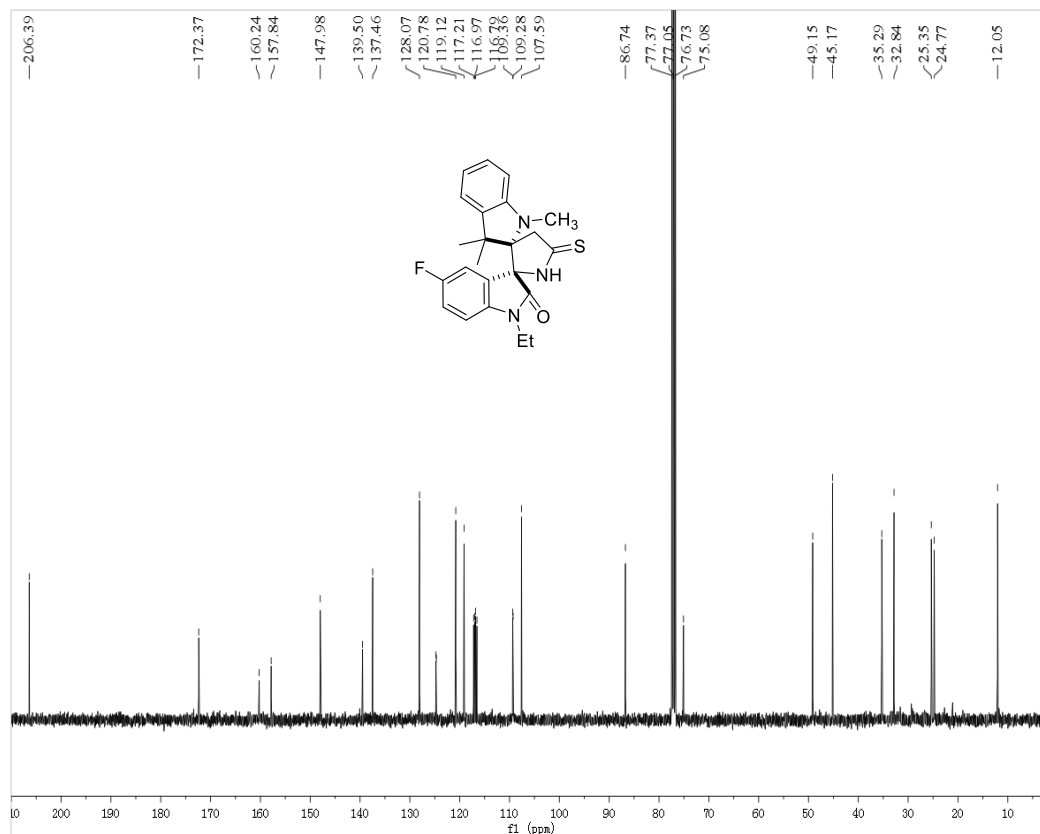
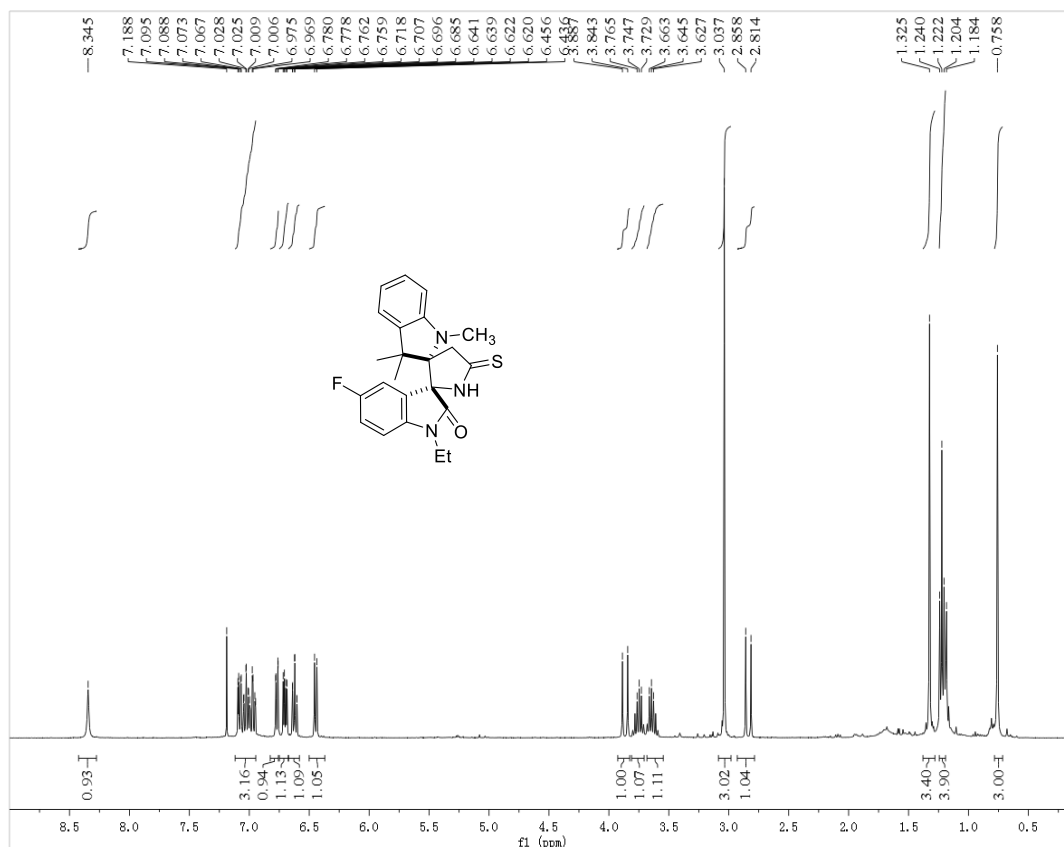
¹H and ¹³C NMR of 3ag



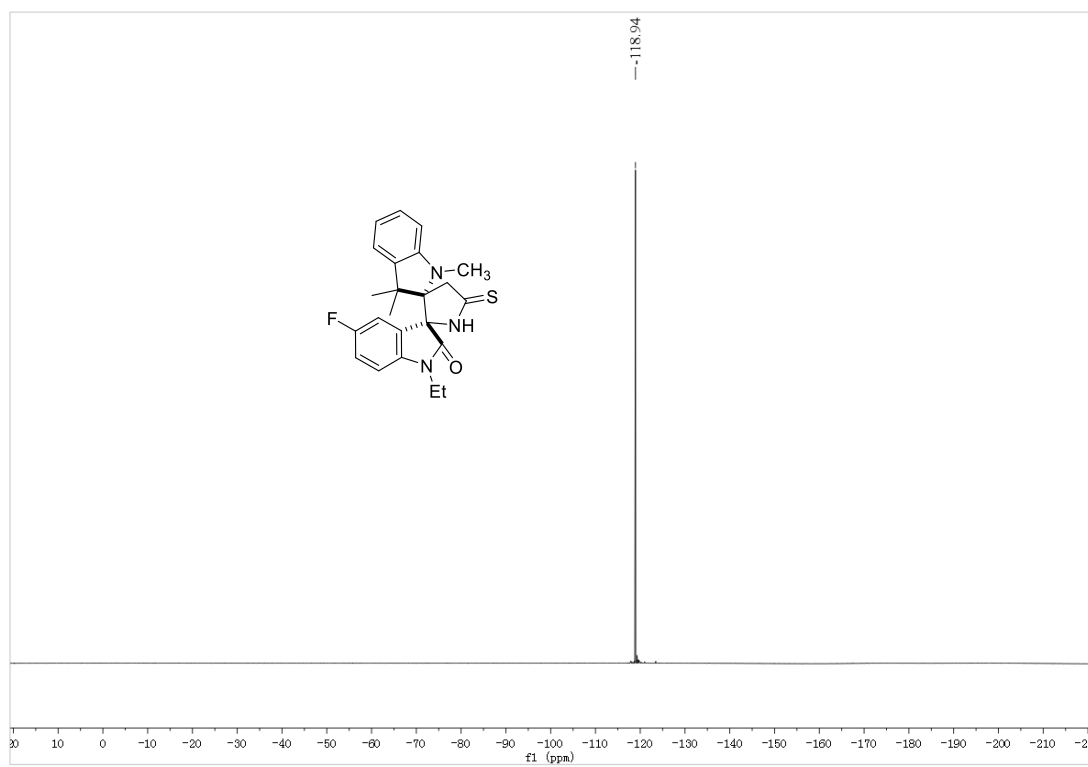
¹H and ¹³C NMR of 3ah



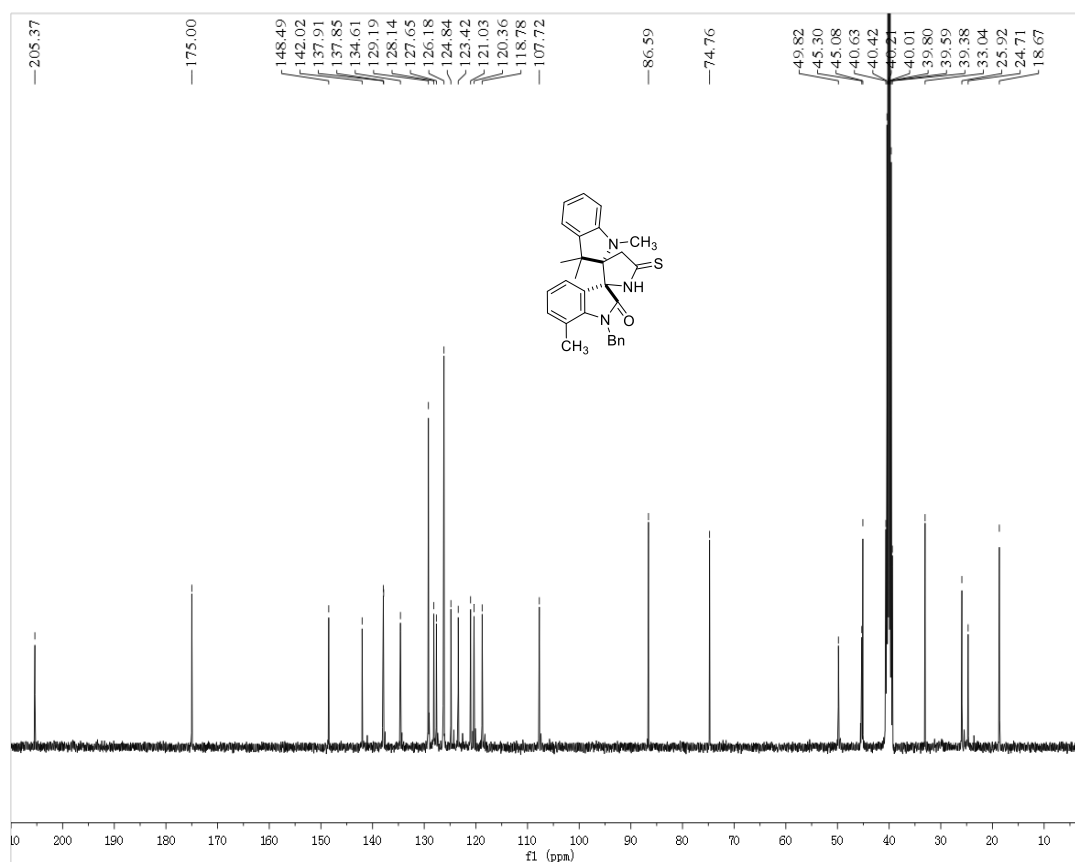
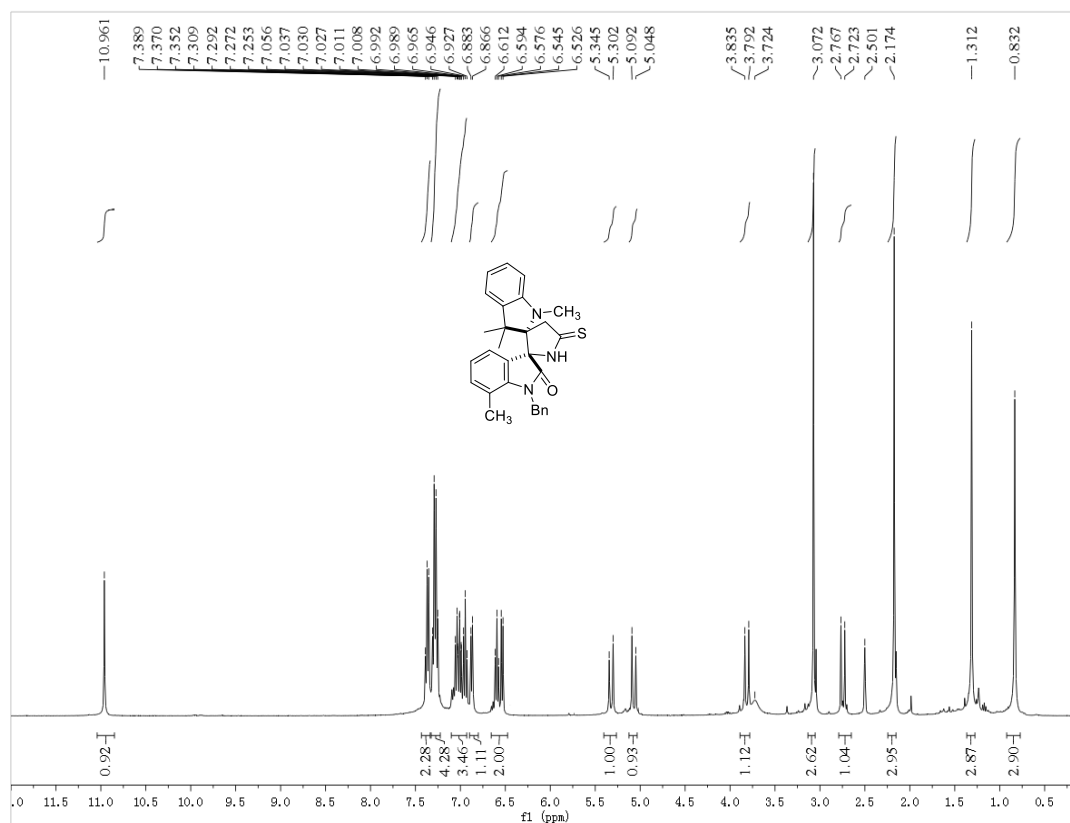
¹H and ¹³C NMR of 3ai



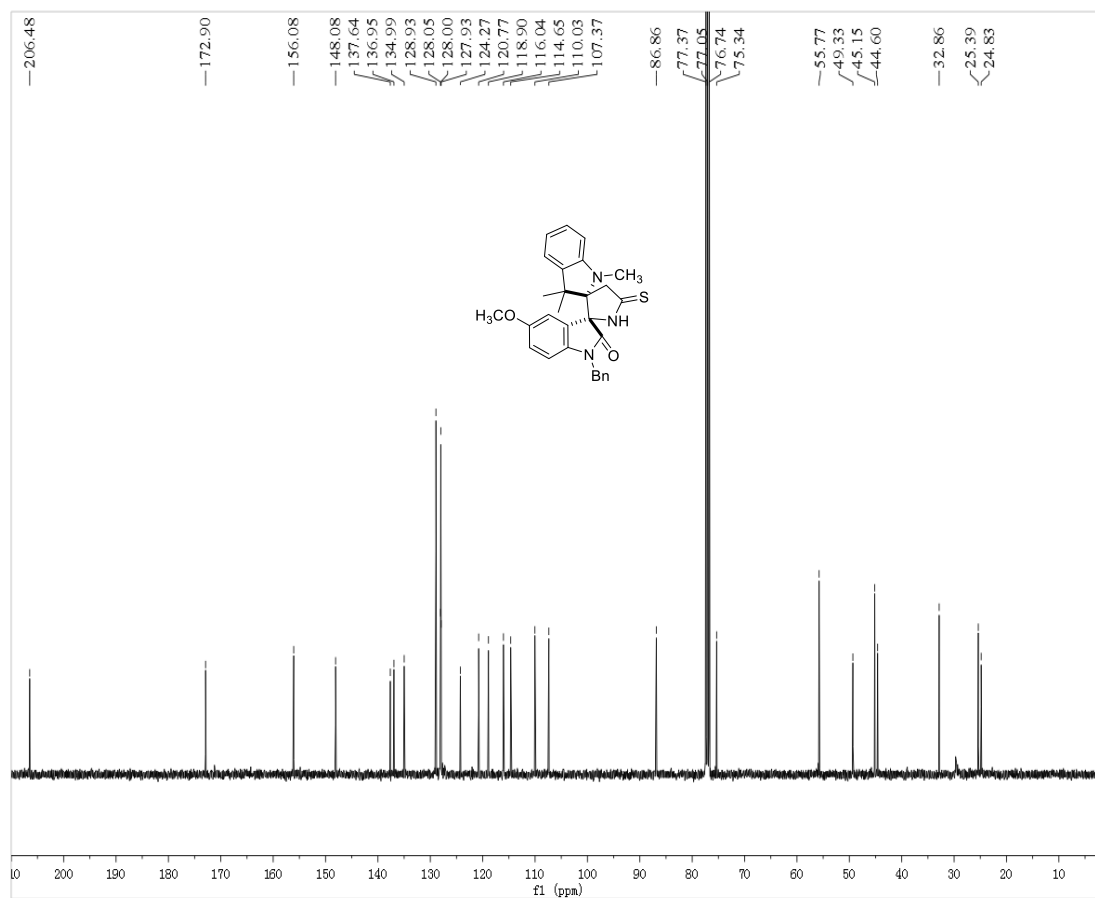
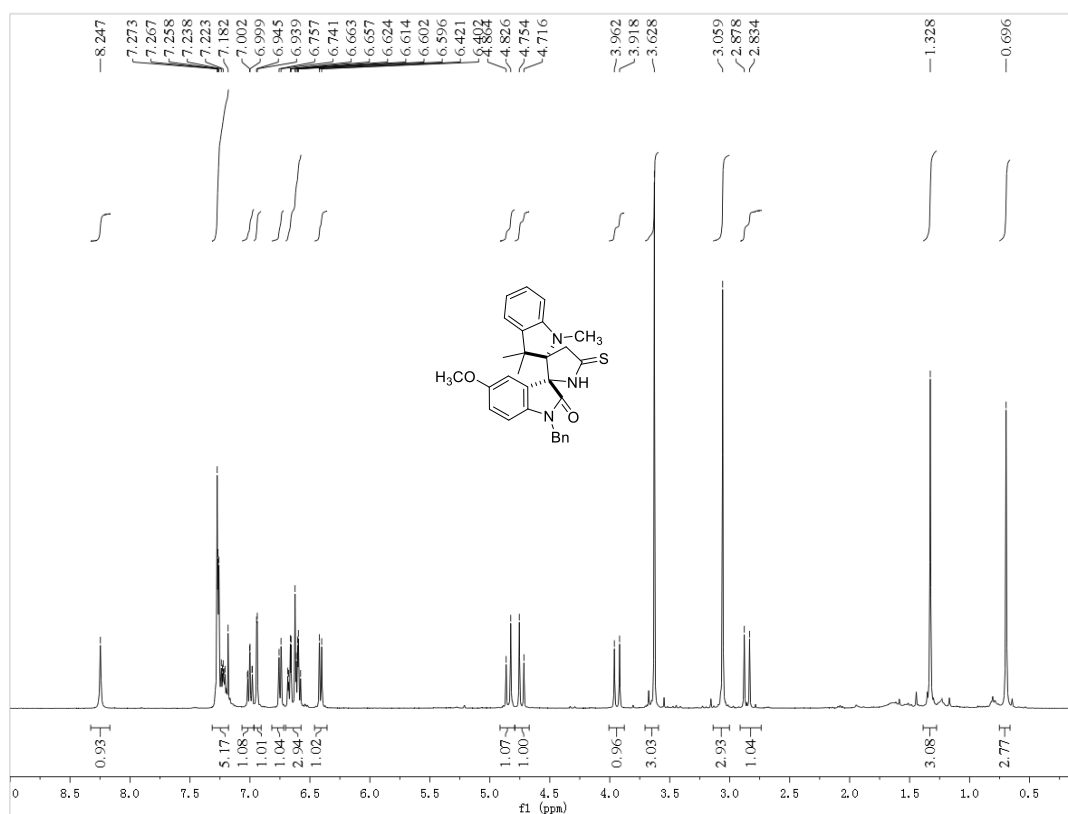
¹⁹F NMR of 3ai



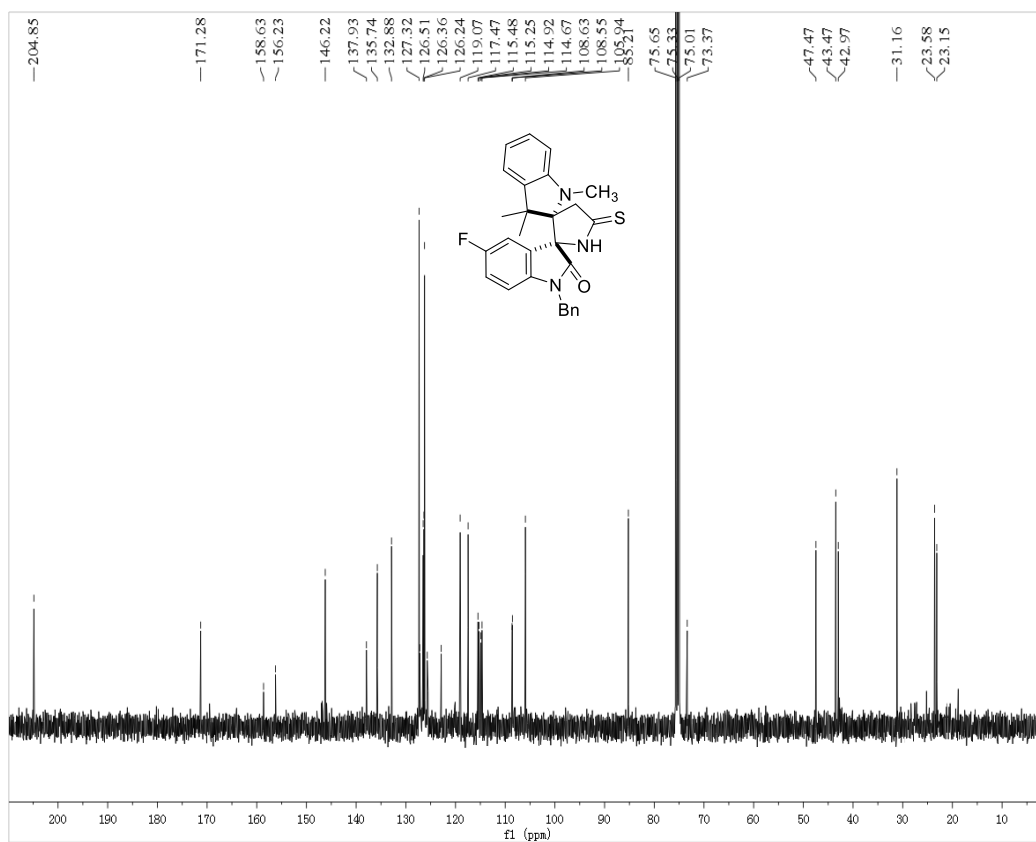
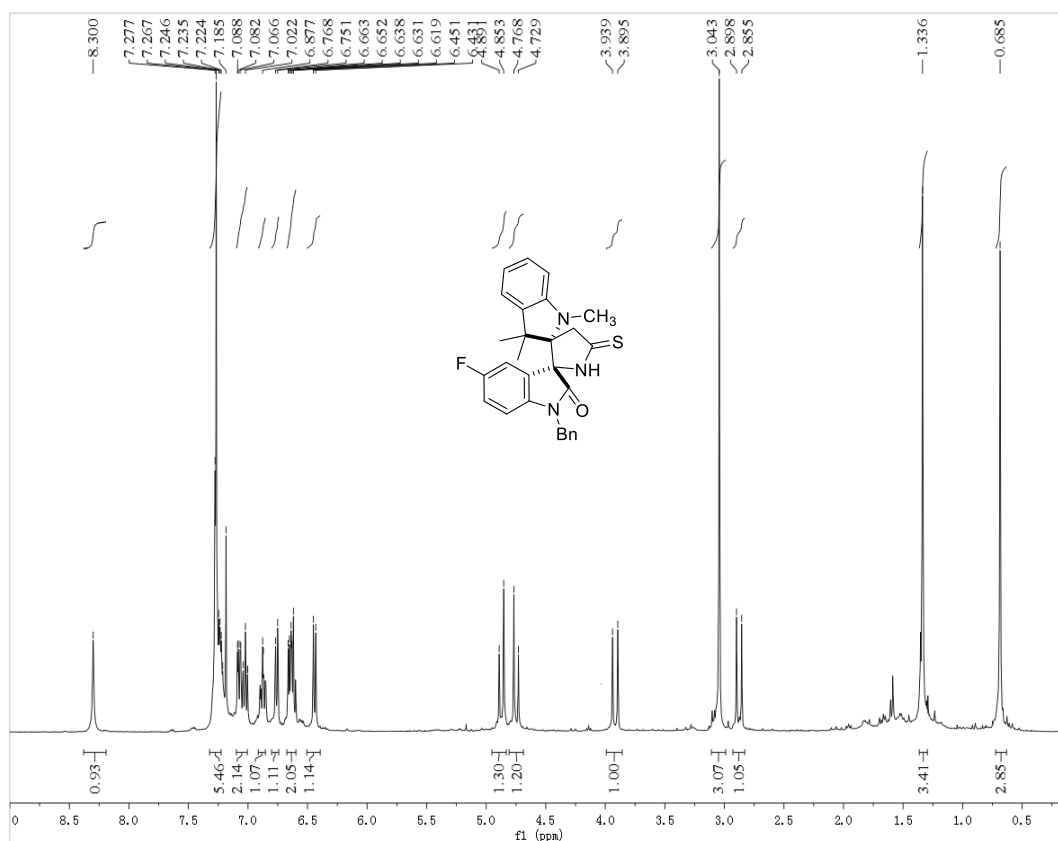
^1H and ^{13}C NMR of 3aj



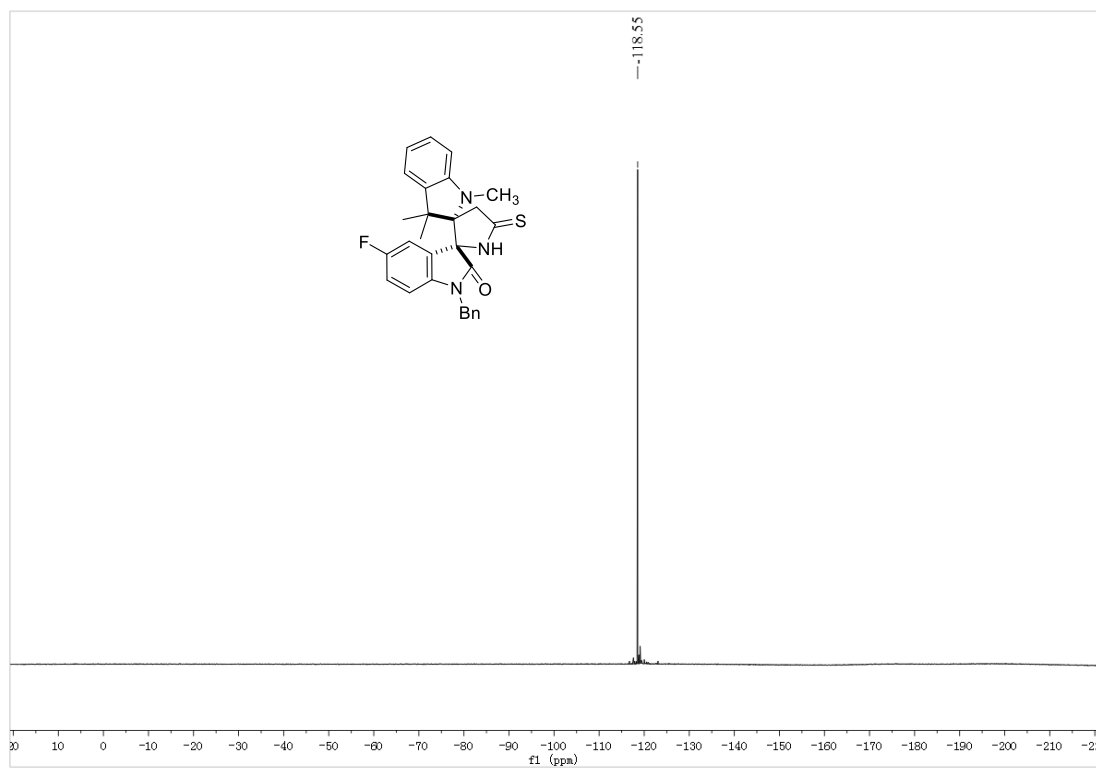
¹H and ¹³C NMR of 3ak



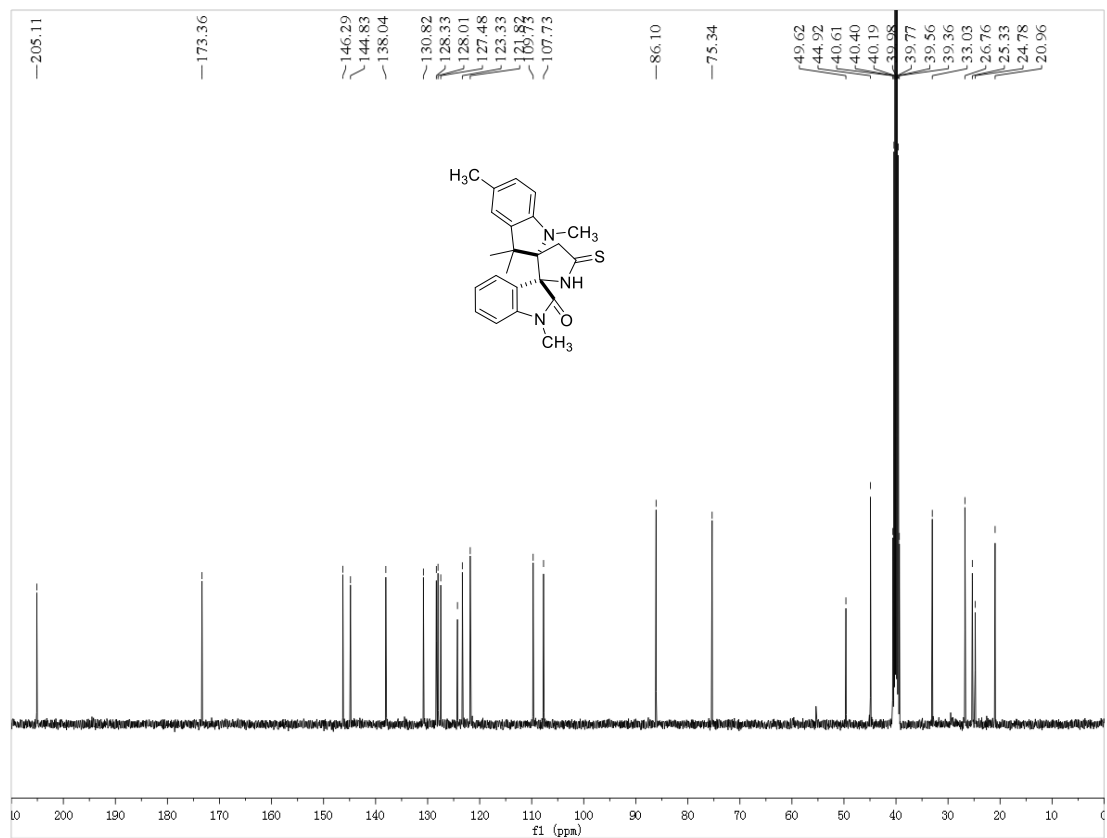
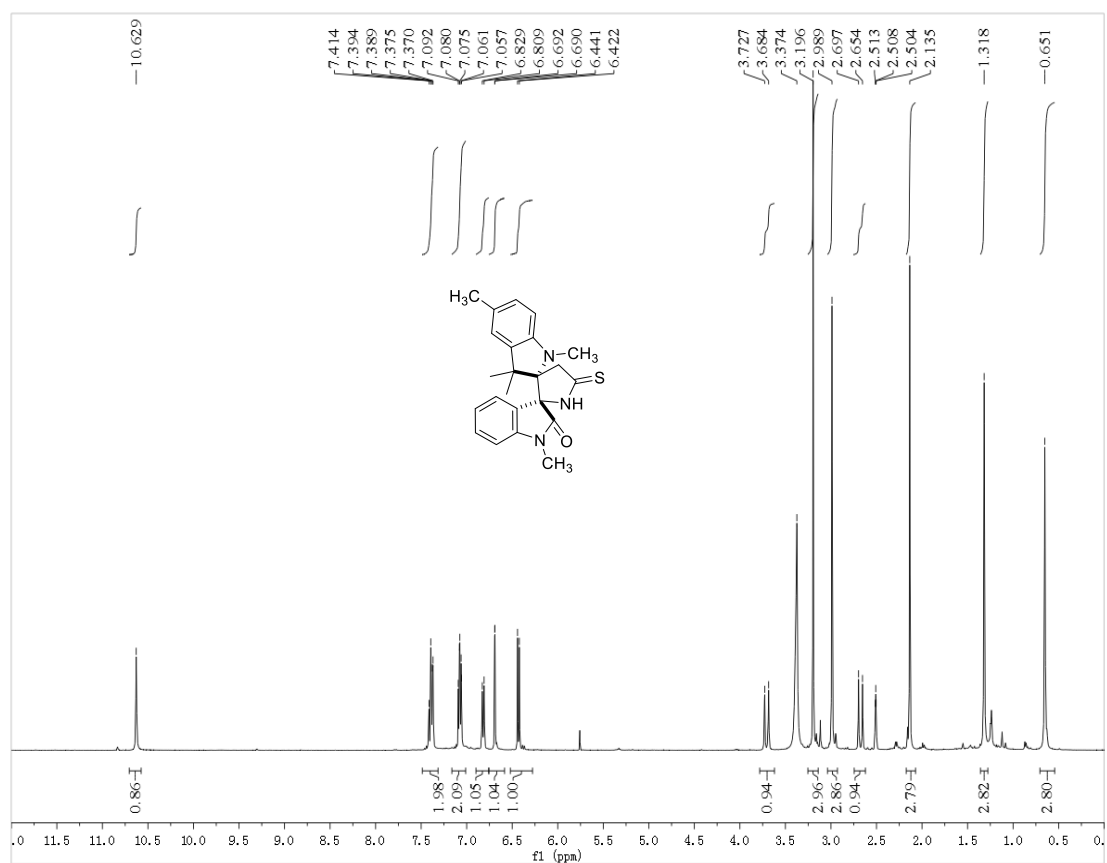
¹H and ¹³C NMR of 3al



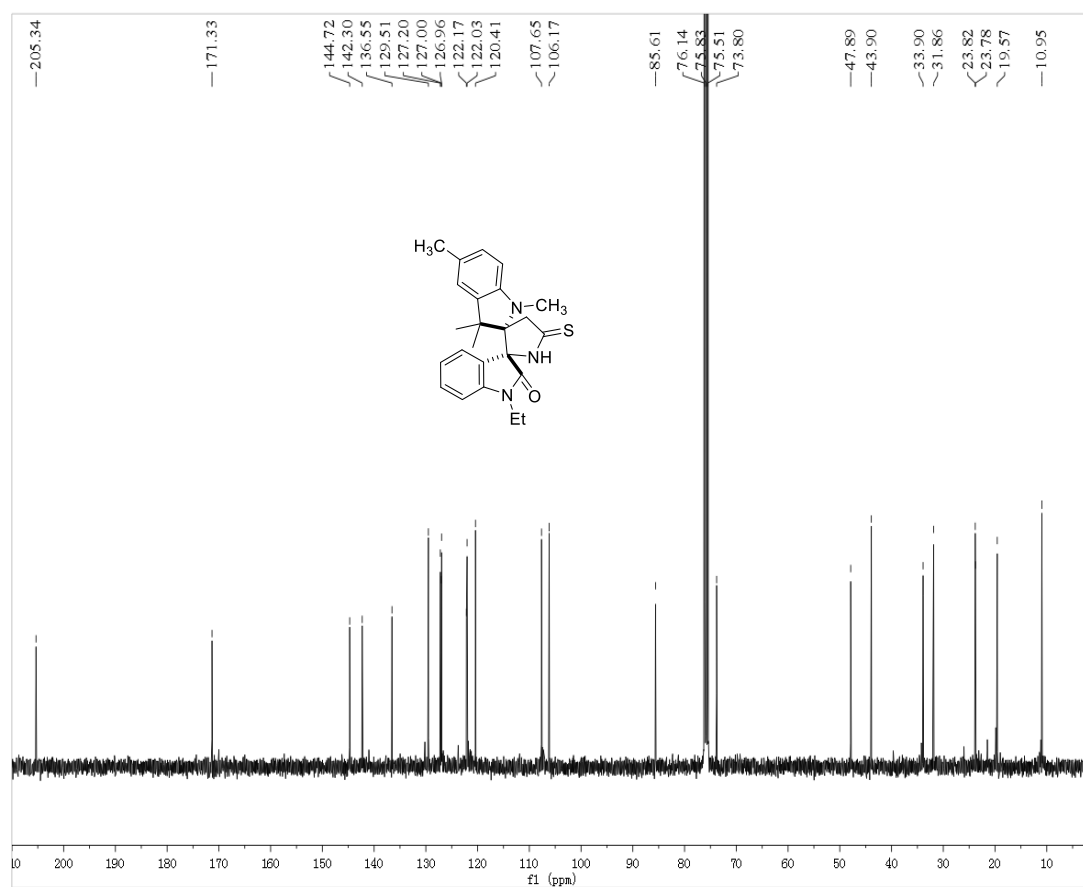
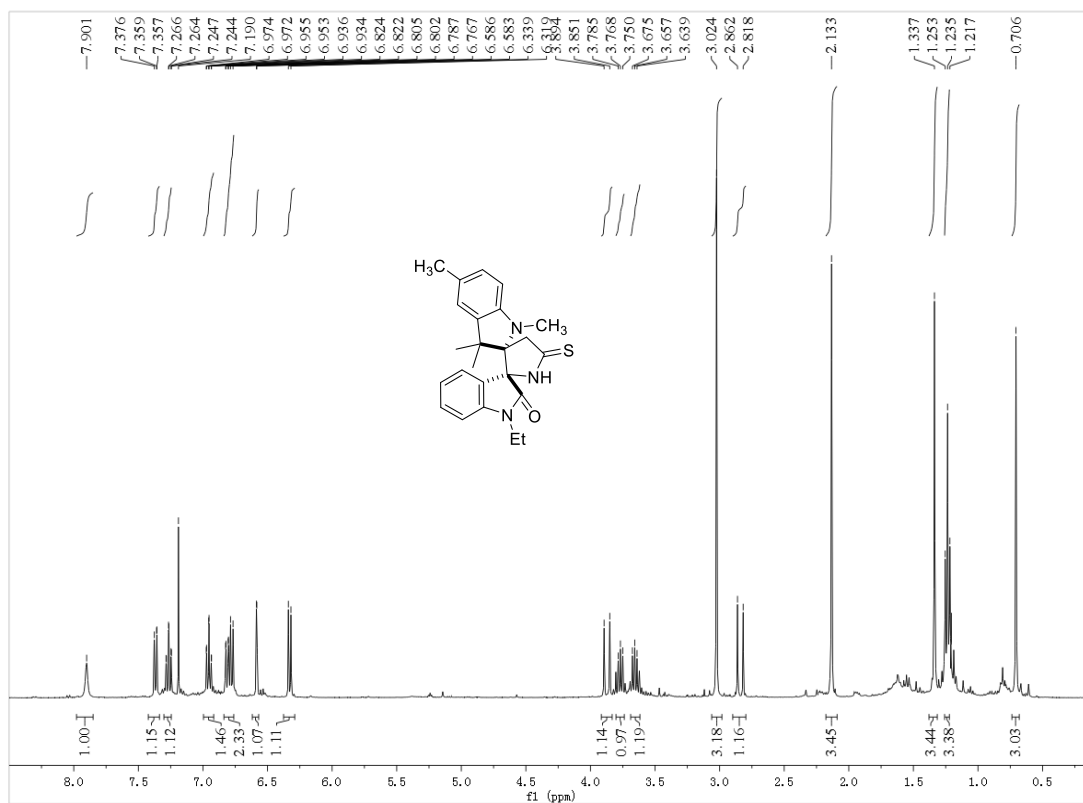
¹⁹F NMR of 3al



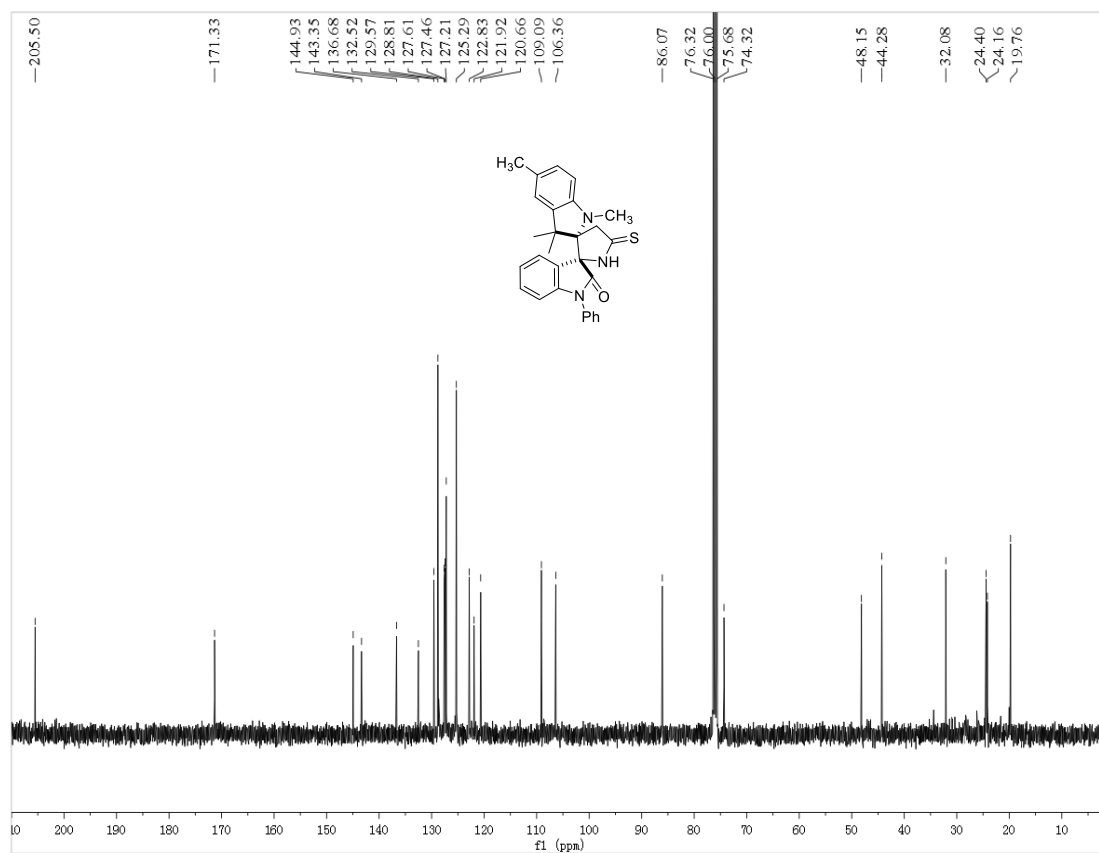
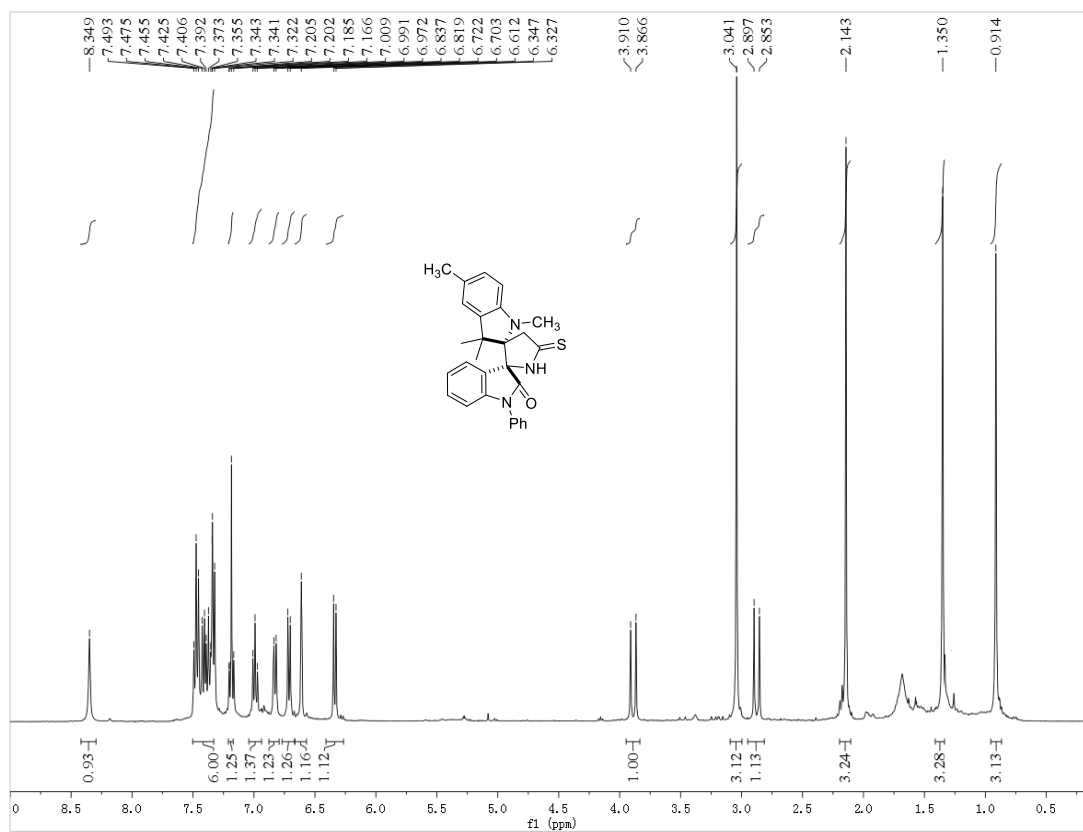
^1H and ^{13}C NMR of 3ba



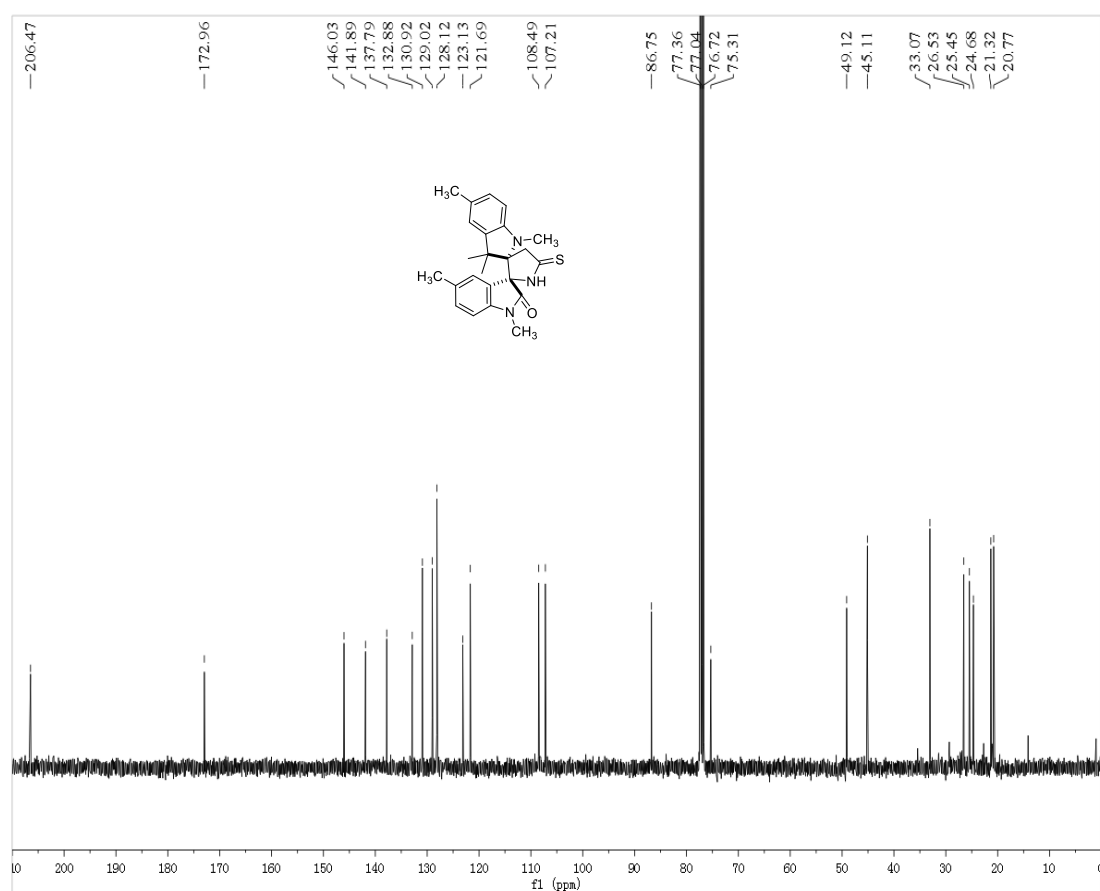
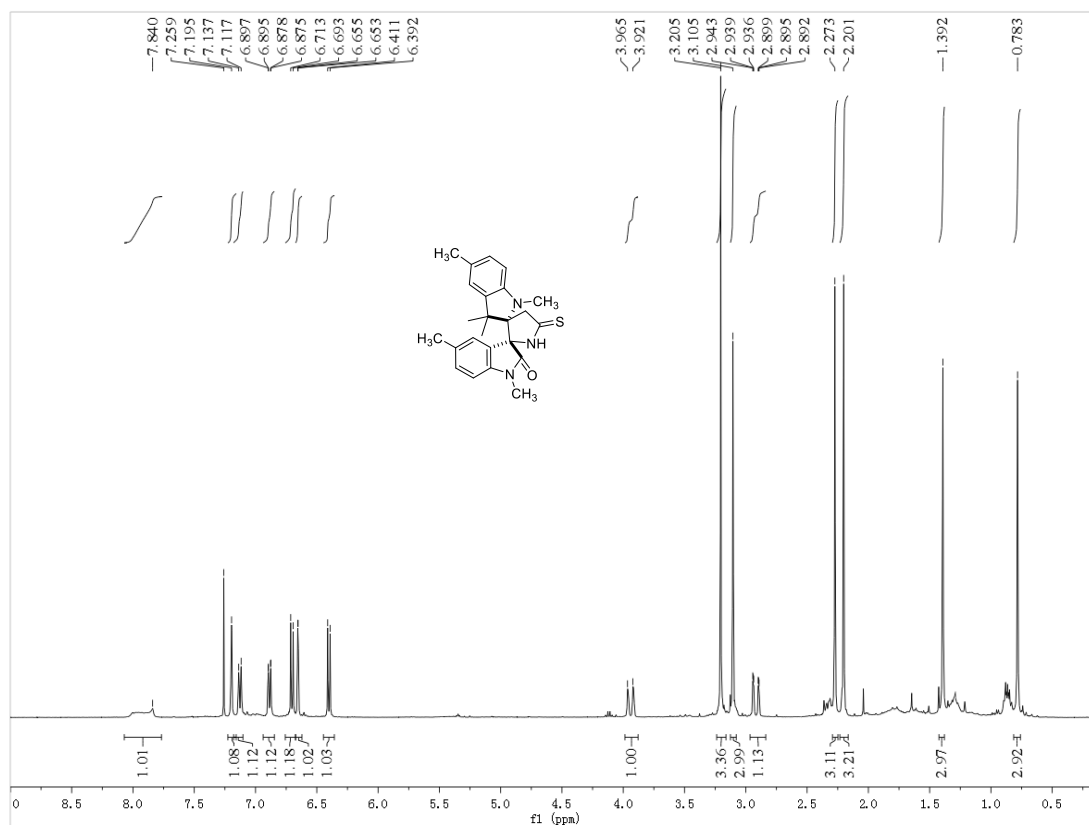
¹H and ¹³C NMR of 3bb



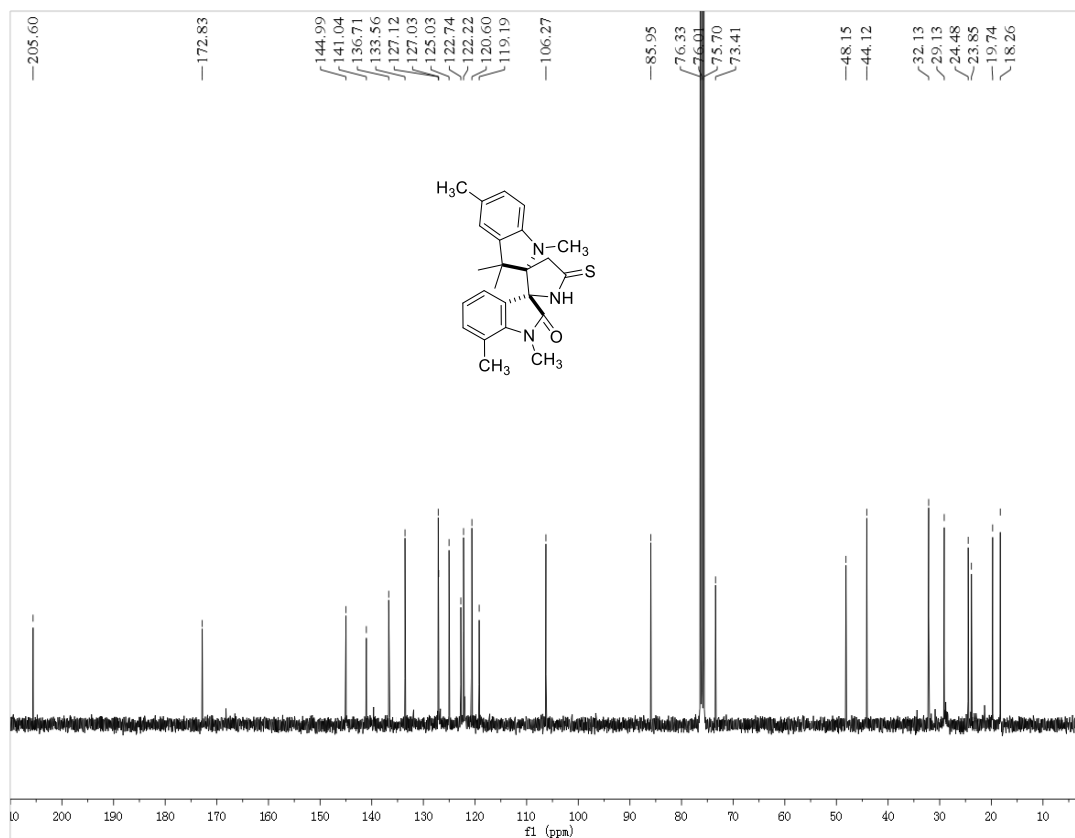
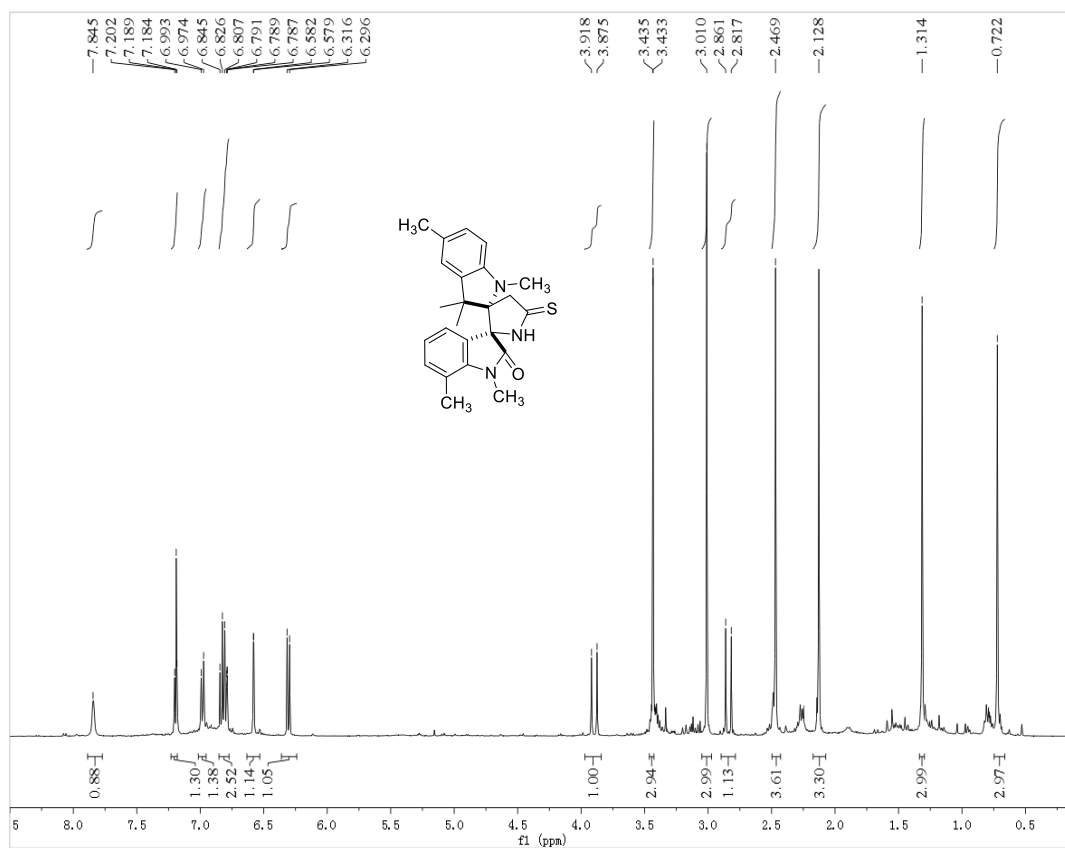
¹H and ¹³C NMR of 3bc



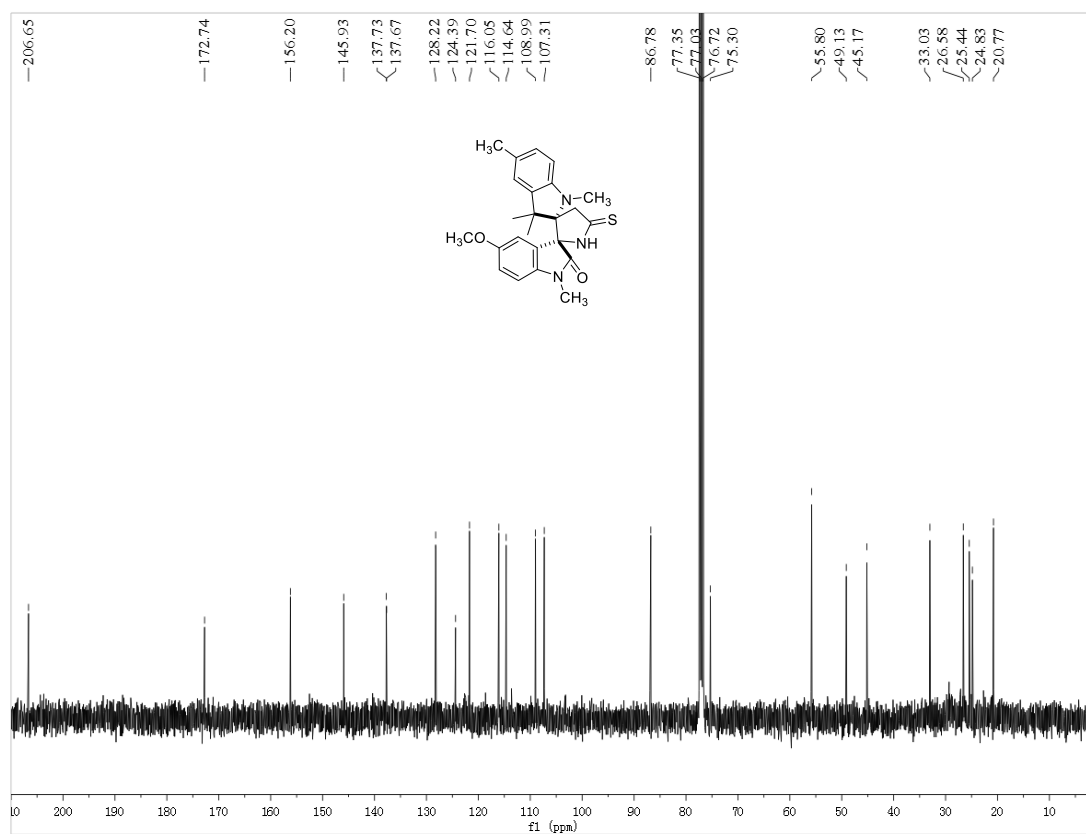
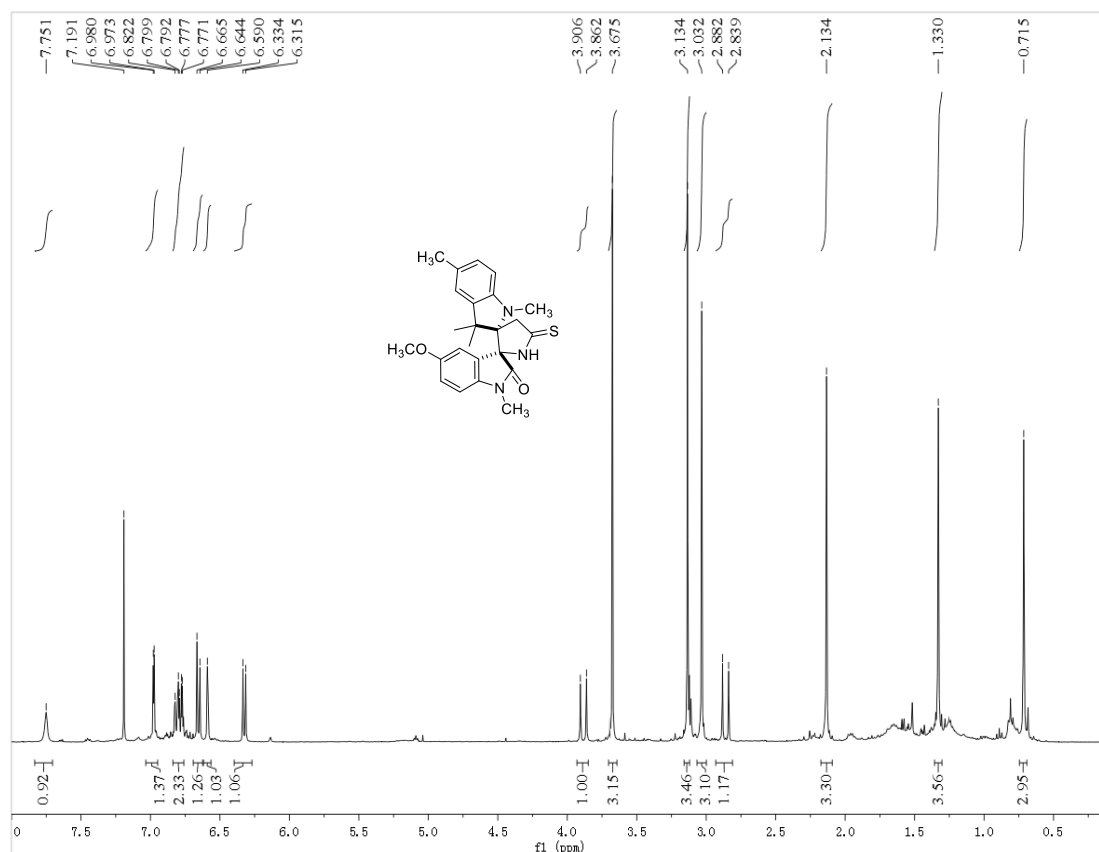
¹H and ¹³C NMR of 3bd



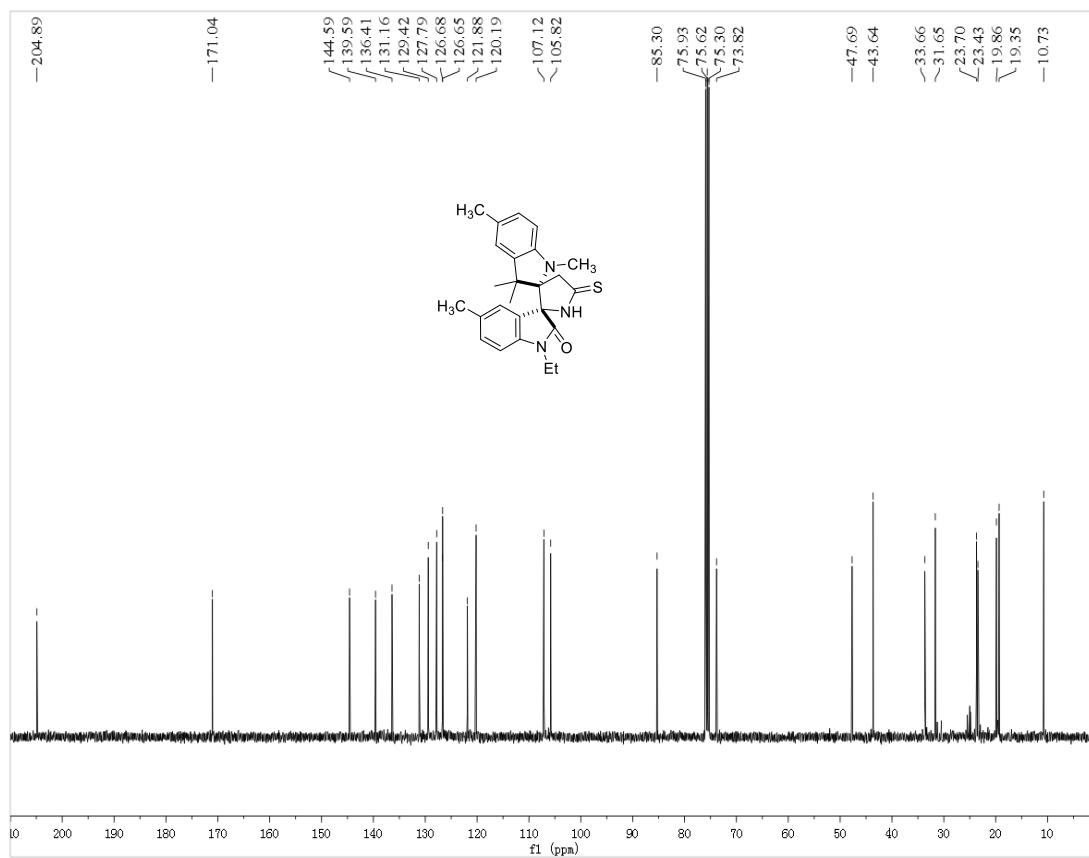
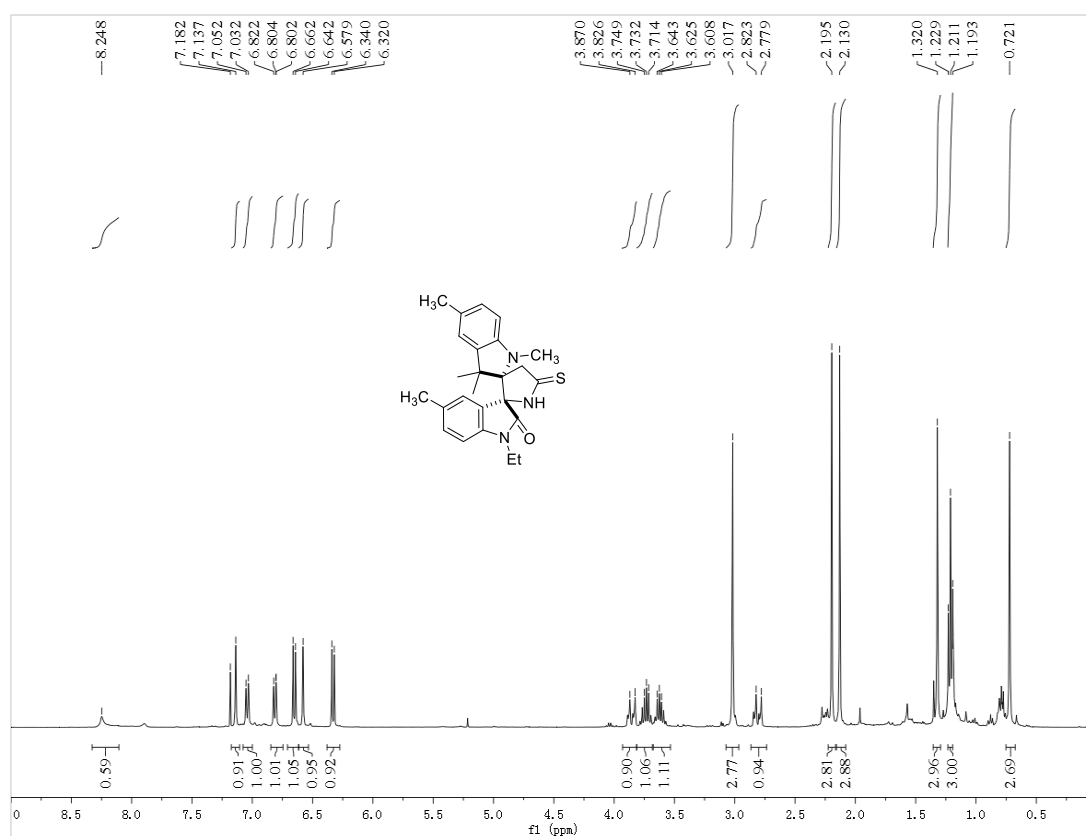
¹H and ¹³C NMR of 3be



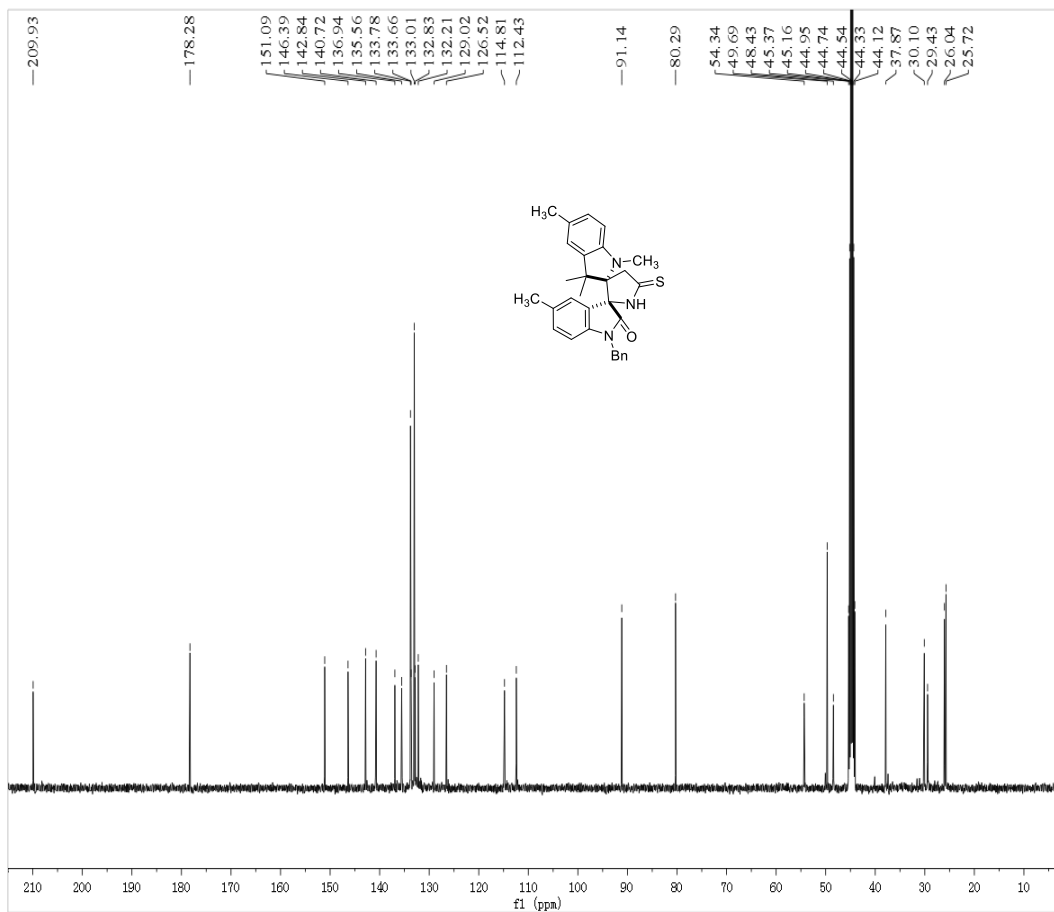
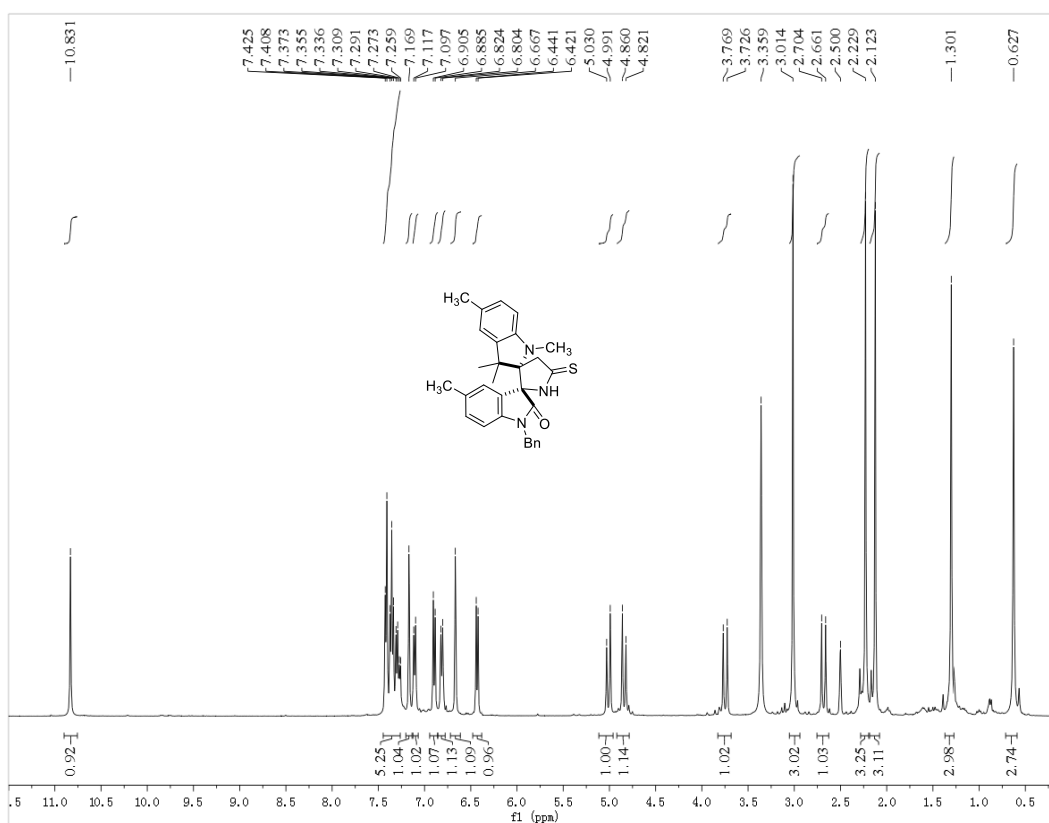
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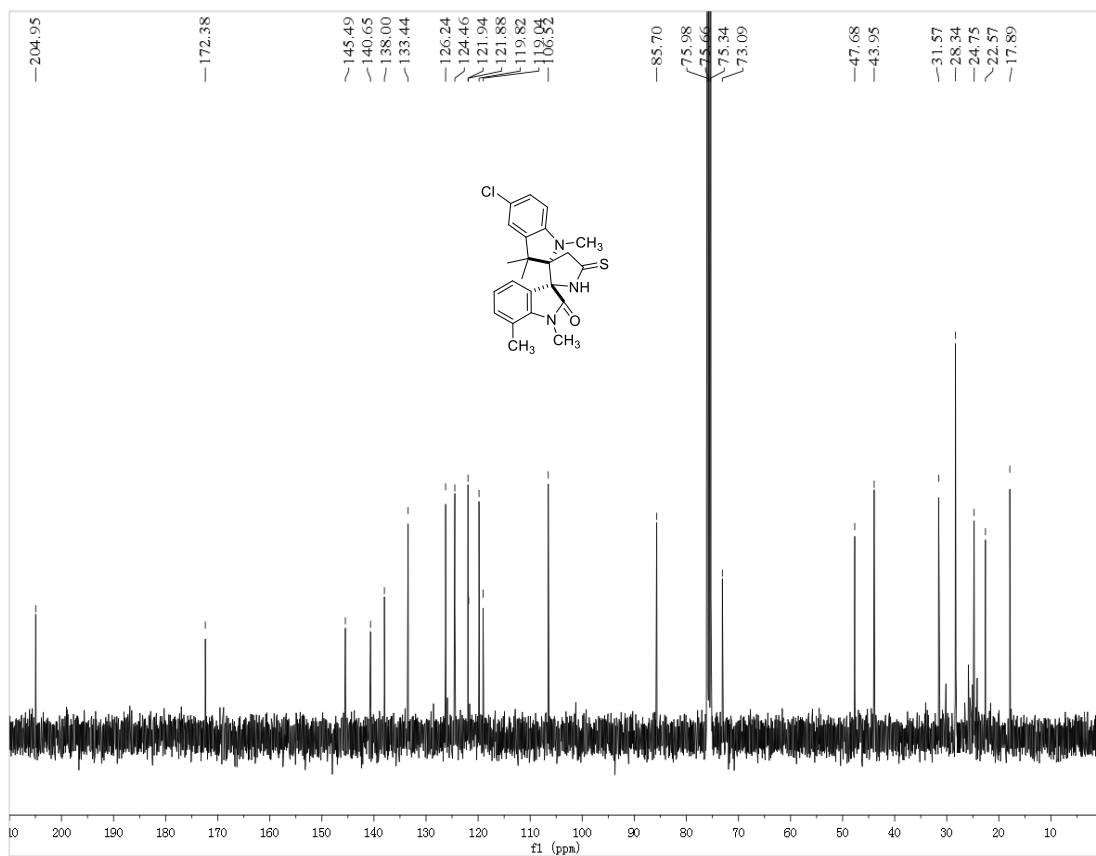
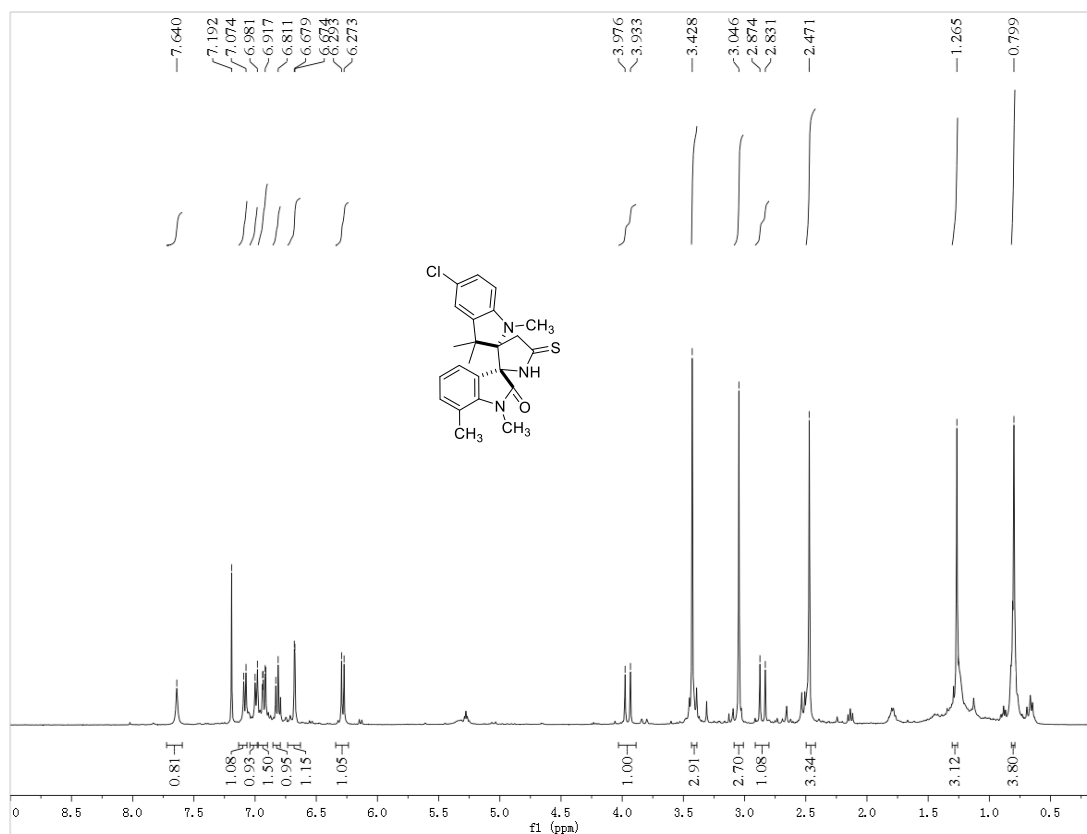


¹H and ¹³C NMR of 3bg

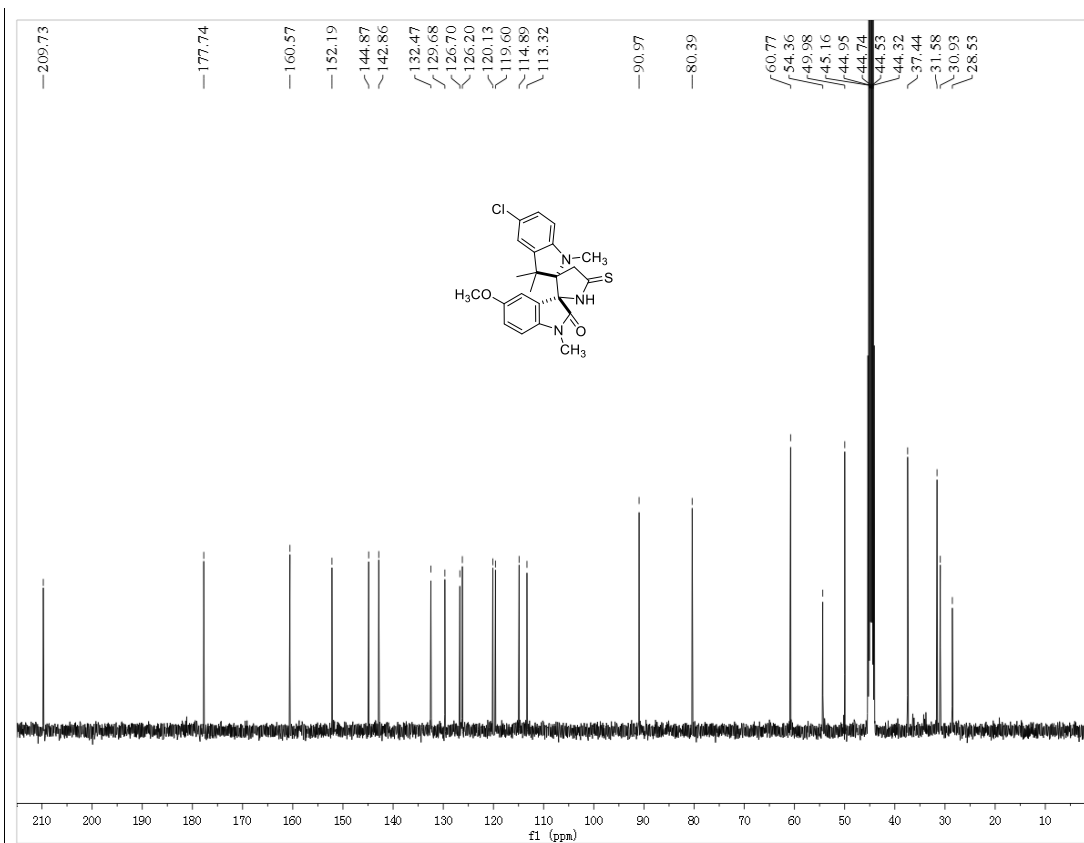
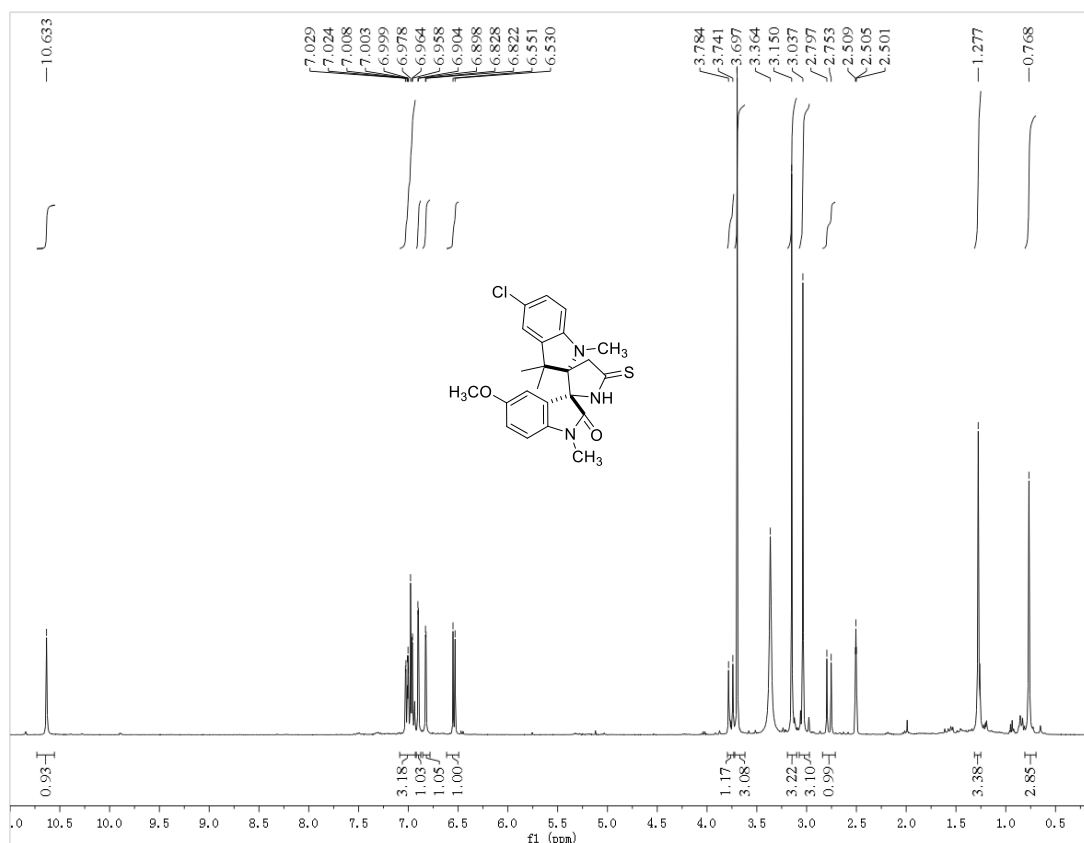


¹H and ¹³C NMR of 3bh

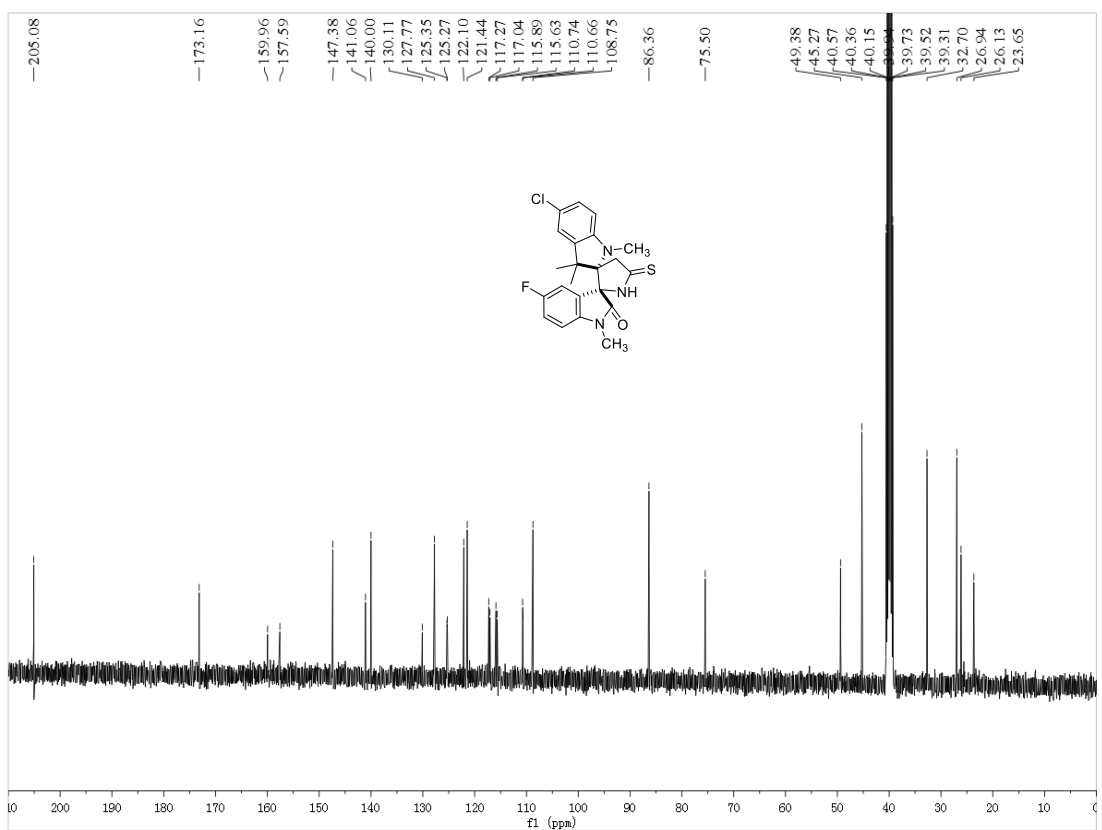
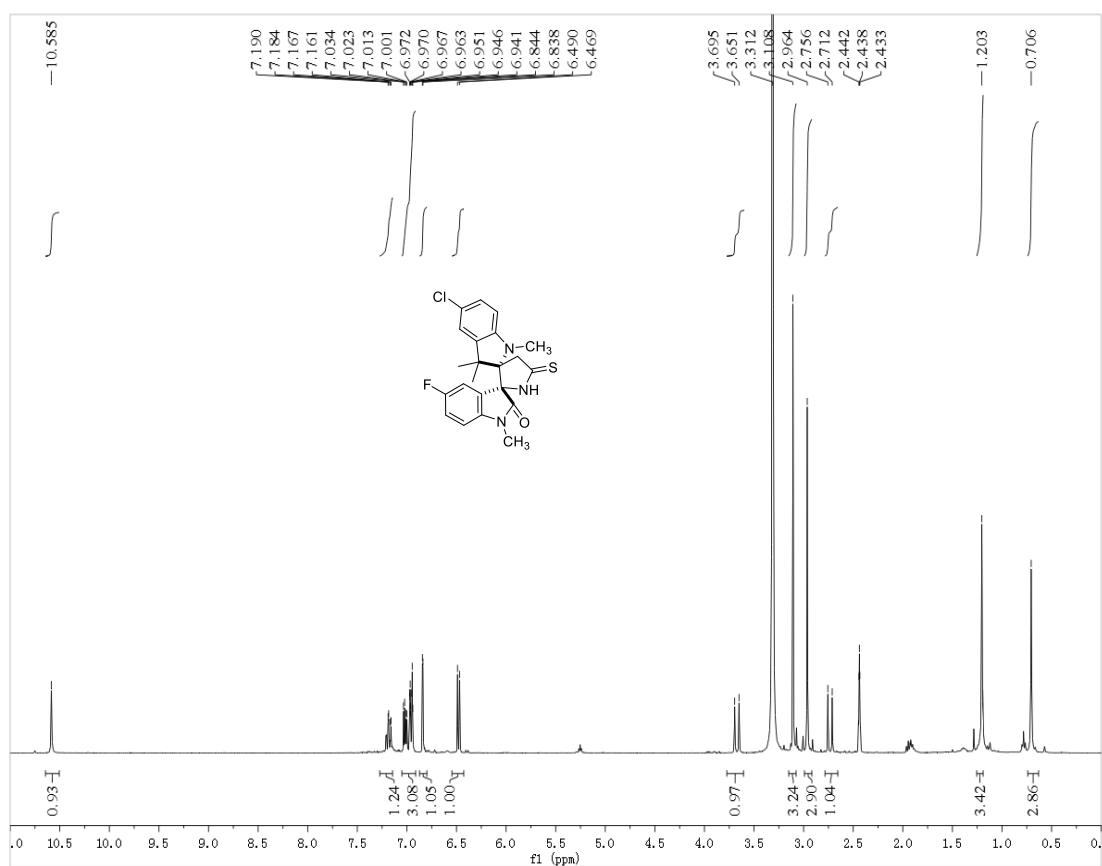


CN1C(=O)N2C(=O)N(C)C2C1C3=CC=C(C)C=C3C4=CC=C(C)C=C4

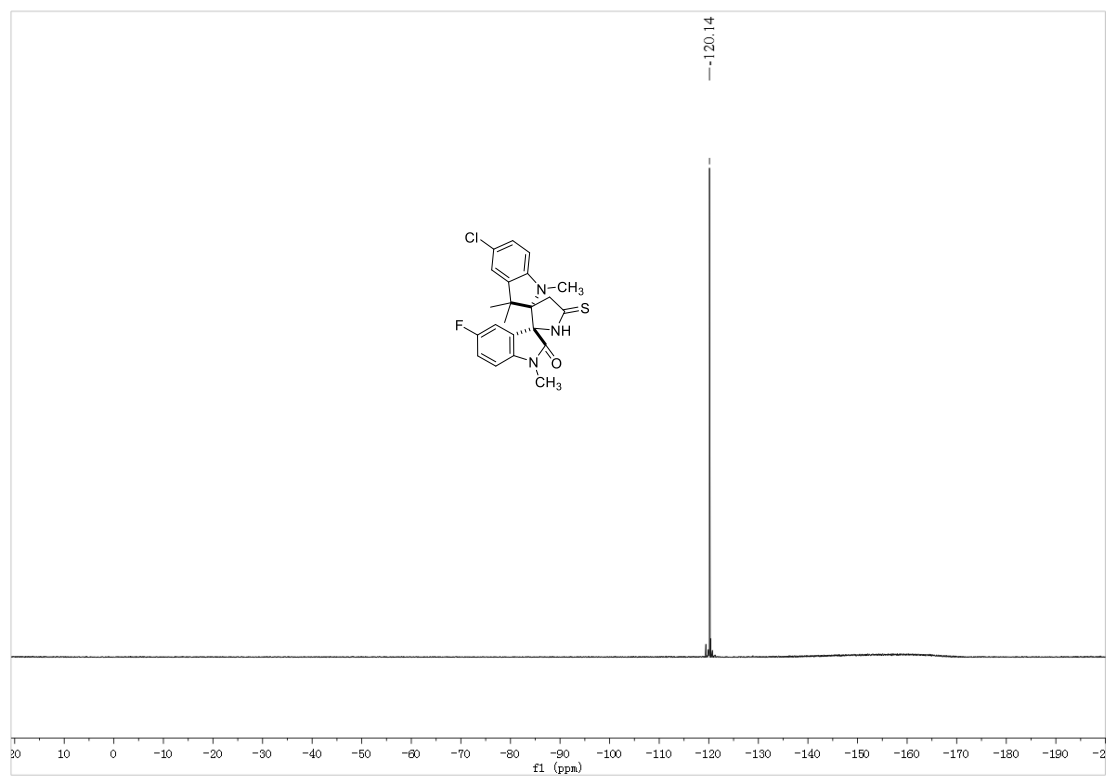
¹H and ¹³C NMR of 3cb



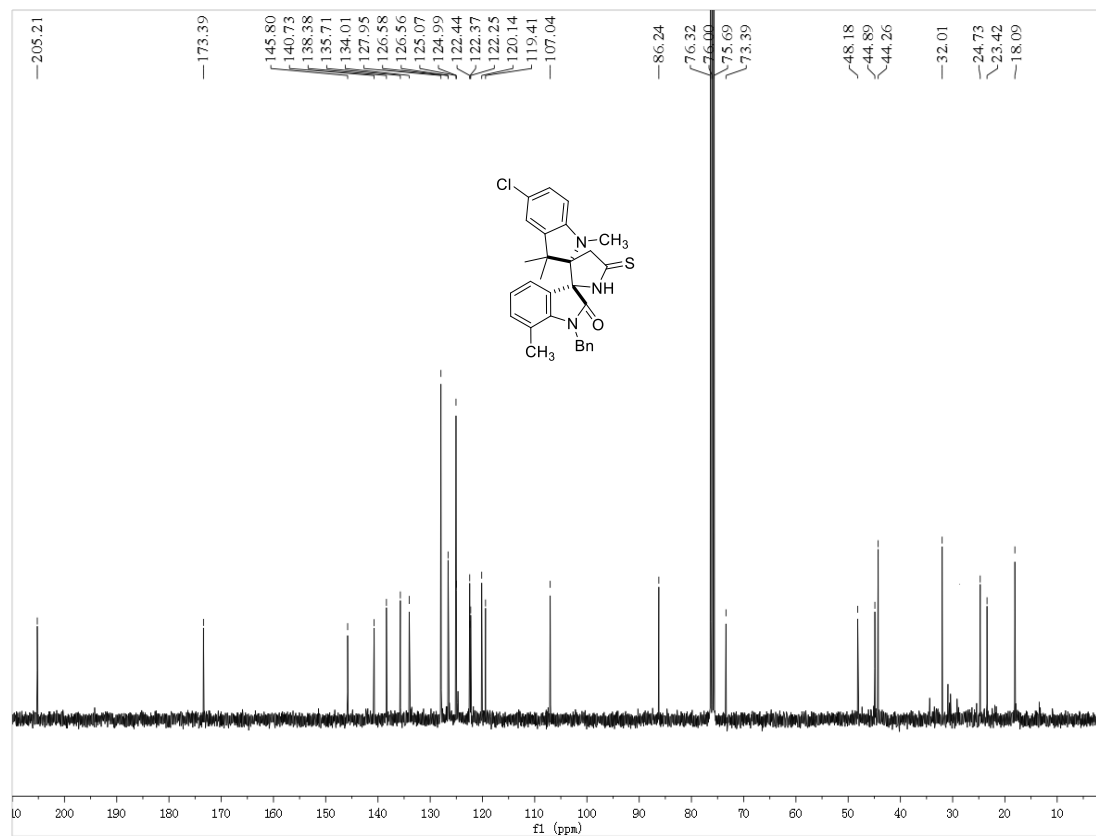
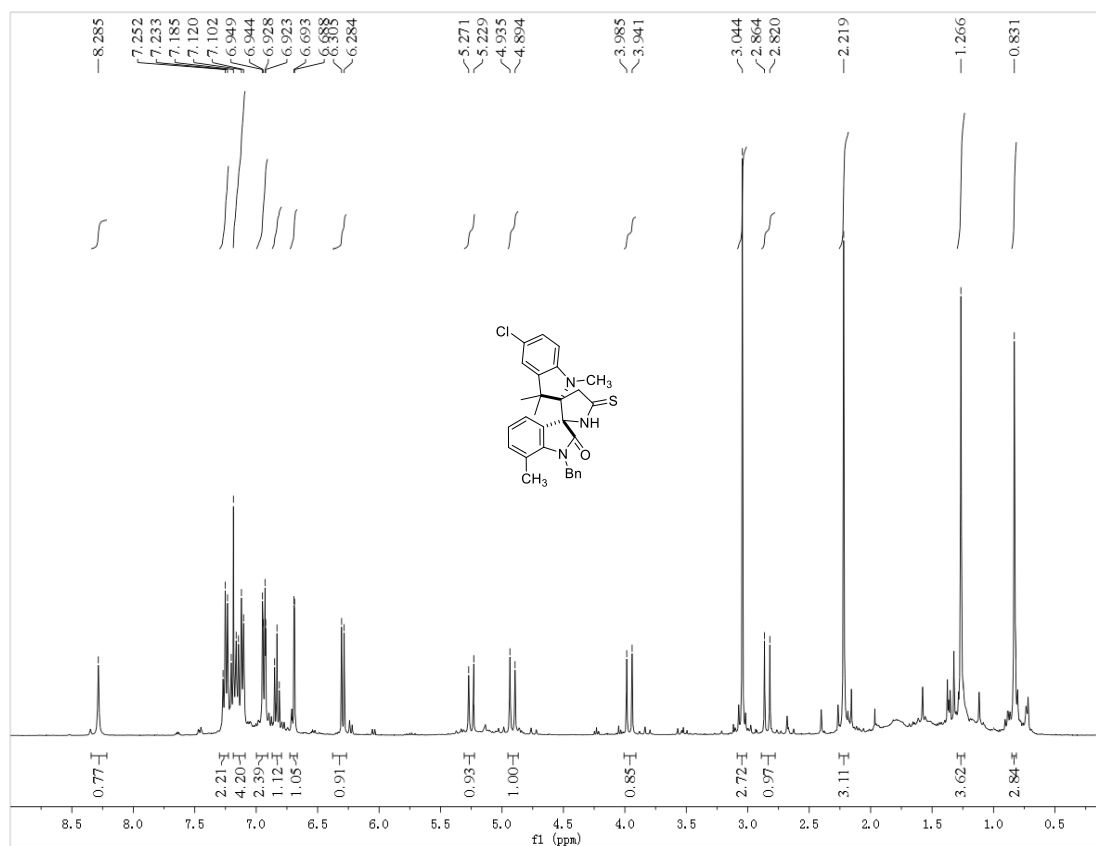
¹H and ¹³C NMR of 3cc



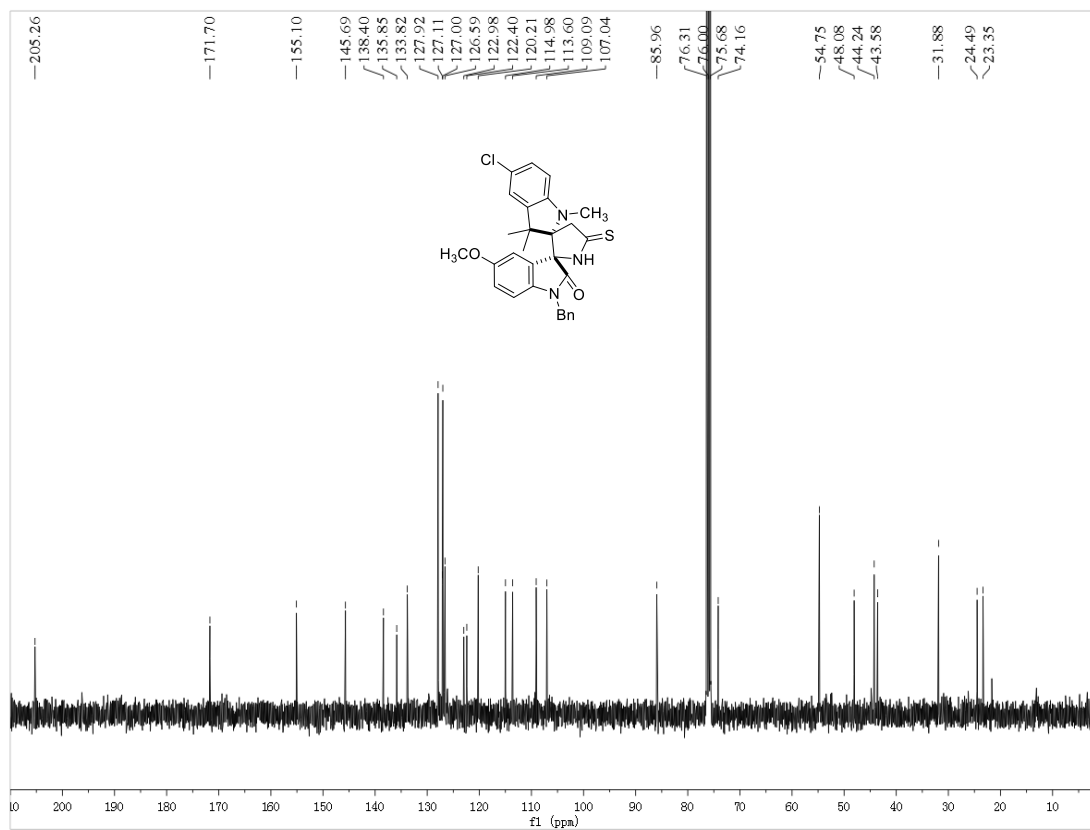
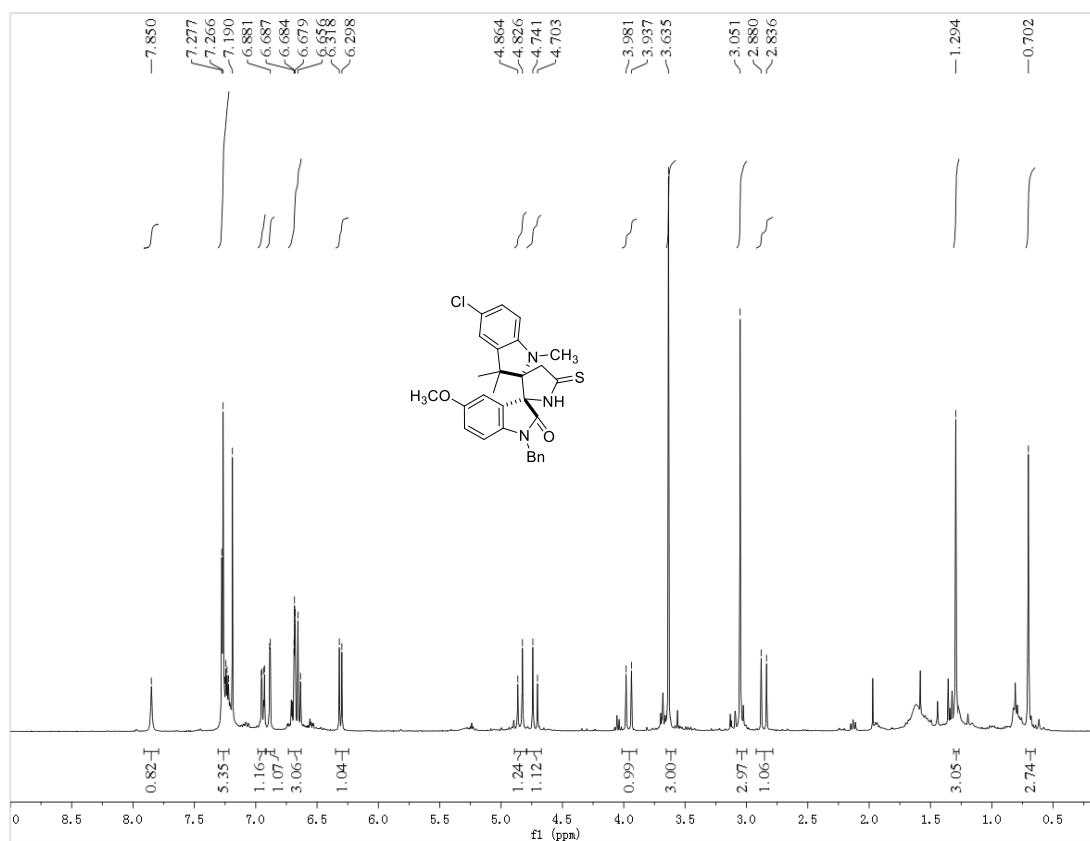
^{19}F NMR of 3cc



¹H and ¹³C NMR of 3cd



¹H and ¹³C NMR of 3ce



¹H and ¹³C NMR of 4ag

