

Supporting Information

for

Facile Synthesis of aza-Spirocyclopropanyl Oxindole by the Reaction of 3-(2-Bromoethyl)-Indole with 2,3-Dimethylimidazole-1-sulfonyl Azide Triflate

Mei-Hua Shen,* Ke Xu, Chu-Han Sun and Hua-Dong Xu *

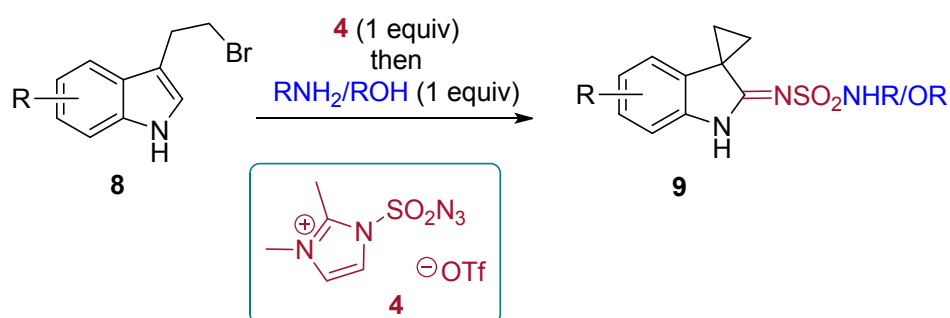
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I General Information and Materials

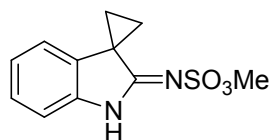
NMR spectra were recorded using Bruker AV-300 / AV-400 spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectra were acquired on an agilent 6230 spectrometer and were obtained by peak matching. Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator and/or by exposure to phosphormolybdic acid/cerium (IV) sulfate/ ninhydrine followed by brief heating with a heat gun. Liquid chromatography (flash chromatography) was performed on 200-300 Å mesh silica gel (SiO_2). All reactions were carried out under nitrogen or argon with anhydrous solvents in oven-dried glassware, unless otherwise noted. Commercially available reagents were used without further purification. Solvents were purified prior to use according to the standard methods.

II General Procedure for the Reaction of **8** with **4** and Alcohol/Amine



4 (0.5 mmol) was added to a mixture of **8** (0.5 mmol) in 1,2-DCE (8 mL) at 40 °C, and the reaction was stirred for 20 min at 40 °C. RNH_2 or ROH (0.5 mmol) was added, and the reaction was stirred for 30 min at 40 °C. The reaction was concentrated, the residue was purified by flash column chromatography eluting with hexanes/EtOAc to give **9**.

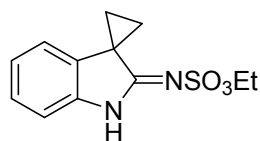
III Characterization of Compounds



9a

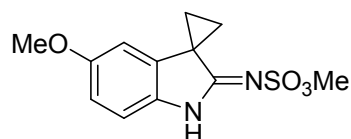
As the General Procedure, **8a** (70 mg, 0.31 mmol), **4** (110 mg, 0.31 mmol) and MeOH (10 mg, 0.31 mmol) were converted into **9a** (39 mg, 49%): White solid. m.p 166-167 °C. ^1H NMR (400 MHz, CDCl_3) δ 9.83 (s, 1H), 7.29 – 7.25 (m, 1H), 7.14-7.10 (m, 2H), 6.92 (d, $J = 7.5$ Hz, 1H), 3.87 (s, 3H), 1.96-1.93 (m, 2H), 1.80-1.77 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.6, 140.3, 131.3, 127.3, 123.8, 118.6, 111.3,

56.9, 30.8, 23.1; HRMS (ESI) m/z Calcd for $C_{11}H_{13}N_2O_3S^+$ $[M + H]^+$ 253.0631, found 253.0620.



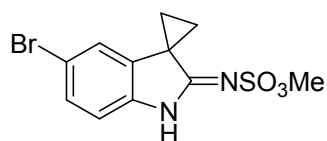
9b

As the General Procedure, **8a** (111 mg, 0.50 mmol), **4** (176 mg, 0.50 mmol) and EtOH (23 mg, 0.50 mmol) were converted into **9b** (68 mg, 51%): White solid. m.p 171-172 °C. 1H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.28 – 7.24 (m, 1H), 7.15 – 7.09 (m, 2H), 6.91 (d, $J = 7.5$ Hz, 1H), 4.25 (q, $J = 7.1$ Hz, 2H), 1.94 – 1.91 (m, 2H), 1.78 – 1.75 (m, 2H), 1.36 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 140.4, 131.3, 127.3, 123.7, 118.5, 111.3, 67.3, 30.7, 22.9, 14.8; HRMS (ESI) m/z Calcd for $C_{12}H_{15}N_2O_3S^+$ $[M + H]^+$ 267.0790, found 267.0779.



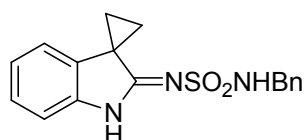
9c

As the General Procedure, **8b** (95 mg, 0.38 mmol), **4** (132 mg, 0.38 mmol) and MeOH (12 mg, 0.38 mmol) were converted into **9c** (46 mg, 43%): White solid. m.p 151-152 °C. 1H NMR (300 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.06 (d, $J = 8.6$ Hz, 1H), 6.80 (dd, $J = 8.6, 2.5$ Hz, 1H), 6.48 (d, $J = 2.4$ Hz, 1H), 3.86 (s, 3H), 3.79 (s, 3H), 1.97 – 1.93 (m, 2H), 1.77 – 1.73 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.4, 156.9, 133.8, 132.9, 112.0, 111.9, 105.4, 56.8, 55.8, 31.1, 23.1; HRMS (ESI) m/z Calcd for $C_{12}H_{14}N_2NaO_4S^+$ $[M + Na]^+$ 305.0566, found 305.0560.



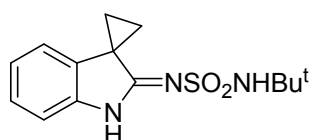
9d

As the General Procedure, **8c** (199 mg, 0.66 mmol), **4** (232 mg, 0.66 mmol) and MeOH (21 mg, 0.66 mmol) were converted into **9d** (80 mg, 37%): Yellow oil. 1H NMR (300 MHz, DMSO) δ 11.65 (s, 1H), 7.45 (d, $J = 9.5$ Hz, 2H), 7.28 (d, $J = 8.1$ Hz, 1H), 3.75 (s, 3H), 2.00 (d, $J = 4.0$ Hz, 2H), 1.74 (d, $J = 3.8$ Hz, 2H); ^{13}C NMR (75 MHz, DMSO) δ 171.7, 141.2, 134.6, 130.1, 122.9, 116.0, 114.5, 57.1, 31.3, 23.6; HRMS (ESI) m/z Calcd for $C_{11}H_{12}BrN_2O_3S^+$ $[M + H]^+$ 330.9752, found 330.9752.



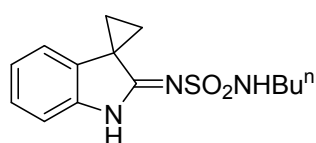
9e

As the General Procedure, **8a** (140 mg, 0.63 mmol), **4** (221 mg, 0.63 mmol) and BnNH₂ (12 mg, 0.63 mmol) were converted into **9e** (192 mg, 93%): White solid. m.p 146-147 °C. ¹H NMR (300 MHz, DMSO) δ 10.98 (s, 1H), 7.44 (t, *J* = 6.6 Hz, 1H), 7.33 – 7.30 (m, 3H), 7.27 – 7.18 (m, 4H), 7.04 – 7.01 (m, 2H), 4.09 (d, *J* = 6.5 Hz, 2H), 1.70 – 1.67 (m, 2H), 1.45 – 1.41 (m, 2H); ¹³C NMR (75 MHz, DMSO) δ 169.1, 142.4, 138.9, 131.5, 128.7, 128.3, 127.8, 127.5, 127.1, 123.1, 119.5, 112.2, 111.7, 46.9, 30.3, 22.2; HRMS (ESI) *m/z* Calcd for C₁₇H₁₈N₃O₂S⁺ [M + H]⁺ 328.1114, found 328.1113.



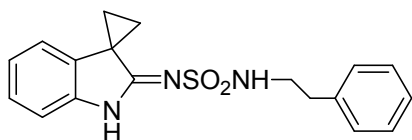
9f

As the General Procedure, **8a** (78 mg, 0.35 mmol), **4** (123 mg, 0.35 mmol) and ^tBuNH₂ (26 mg, 0.35 mmol) were converted into **9f** (90 mg, 88%): White solid. m.p 152-153 °C. ¹H NMR (300 MHz, CDCl₃) δ 9.97 (s, 1H), 7.23 (dd, *J* = 11.9, 4.5 Hz, 1H), 7.15 (d, *J* = 7.4 Hz, 1H), 7.06 (td, *J* = 7.4, 1.1 Hz, 1H), 6.88 (d, *J* = 7.3 Hz, 1H), 4.76 (s, 1H), 1.88 – 1.84 (m, 2H), 1.69 – 1.65 (m, 2H), 1.34 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 169.4, 141.1, 131.2, 127.1, 123.0, 118.3, 111.1, 53.9, 30.2, 30.0, 21.9; HRMS (ESI) *m/z* Calcd for C₁₄H₂₀N₃O₂S⁺ [M + H]⁺ 294.1271, found 294.1271.



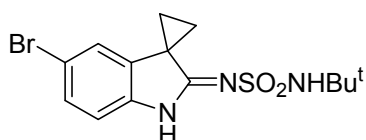
9g

As the General Procedure, **8a** (78 mg, 0.35 mmol), **4** (123 mg, 0.35 mmol) and ⁿBuNH₂ (26 mg, 0.35 mmol) were converted into **9g** (94 mg, 92%): White solid. m.p 159-160 °C. ¹H NMR (300 MHz, DMSO) δ 10.95 (s, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.24 – 7.17 (m, 1H), 7.09 – 6.98 (m, 2H), 6.79 (t, *J* = 6.1 Hz, 1H), 2.84 (dd, *J* = 13.3, 6.8 Hz, 2H), 1.78 (dd, *J* = 7.8, 3.8 Hz, 2H), 1.56 (dd, *J* = 7.7, 3.6 Hz, 2H), 1.46 – 1.36 (m, 2H), 1.31 – 1.23 (m, 2H), 0.82 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (75 MHz, DMSO) δ 169.0, 142.4, 131.4, 127.3, 122.9, 119.4, 111.9, 43.0, 31.4, 30.3, 22.1, 19.9, 14.1; HRMS (ESI) *m/z* Calcd for C₁₄H₂₀N₃O₂S⁺ [M + H]⁺ 294.1276, found 294.1277.



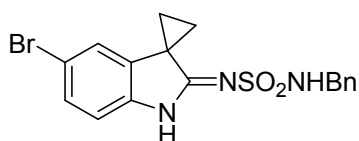
9h

As the General Procedure, **8a** (78 mg, 0.35 mmol), **4** (123 mg, 0.35 mmol) and Phenethylamine (43 mg, 0.35 mmol) were converted into **9h** (103 mg, 86%): White solid. m.p 175-176 °C. ¹H NMR (300 MHz, CDCl₃) δ 9.83 (s, 1H), 7.21 – 7.08 (m, 6H), 7.04 – 6.98 (m, 2H), 6.81 (d, *J* = 7.4 Hz, 1H), 4.46 (t, *J* = 6.4 Hz, 1H), 3.26 (q, *J* = 6.9 Hz, 2H), 2.80 (t, *J* = 7.0 Hz, 2H), 1.79 – 1.75 (m, 2H), 1.64 – 1.60 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 170.9, 140.8, 138.1, 131.2, 128.8, 128.7, 127.2, 126.7, 123.3, 118.4, 111.1, 44.8, 35.6, 30.3, 22.7; HRMS (ESI) *m/z* Calcd for C₁₈H₂₀N₃O₂S⁺ [M + H]⁺ 342.1276, found 342.1280.



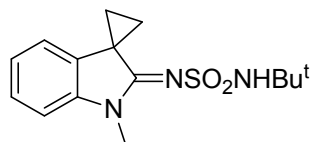
9i

As the General Procedure, **8c** (144 mg, 0.48 mmol), **4** (168 mg, 0.48 mmol) and ^tBuNH₂ (35 mg, 0.48 mmol) were converted into **9i** (135 mg, 76%): White solid. m.p 194-195 °C. ¹H NMR (400 MHz, DMSO) δ 10.92 (s, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.31 (s, 1H), 7.21 (d, *J* = 8.1 Hz, 1H), 6.70 (s, 1H), 1.84 (s, 2H), 1.56 (s, 2H), 1.19 (s, 9H); ¹³C NMR (100 MHz, DMSO) δ 167.4, 141.8, 134.2, 129.9, 122.7, 114.9, 113.5, 53.0, 30.3, 30.1, 22.2; HRMS (ESI) *m/z* Calcd for C₁₄H₁₉BrN₃O₂S⁺ [M + H]⁺ 372.0376, found 372.0368.



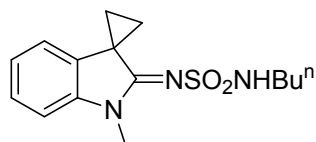
9j

As the General Procedure, **8c** (144 mg, 0.48 mmol), **4** (168 mg, 0.48 mmol) and BnNH₂ (52 mg, 0.48 mmol) were converted into **9j** (161 mg, 83%): White solid. m.p 188-189 °C. ¹H NMR (300 MHz, DMSO) δ 10.79 (s, 1H), 7.49 (s, 1H), 7.39 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.30 – 6.98 (m, 7H), 4.08 (s, 2H), 1.76 (d, *J* = 4.0 Hz, 2H), 1.42 (d, *J* = 3.9 Hz, 2H); ¹³C NMR (100 MHz, DMSO) δ 168.7, 141.9, 138.9, 134.3, 129.9, 128.5, 128.1, 127.4, 122.5, 115.0, 113.8, 46.9, 30.4, 22.8; HRMS (ESI) *m/z* Calcd for C₁₇H₁₇BrN₃O₂S⁺ [M + H]⁺ 406.0219, found 406.0208.



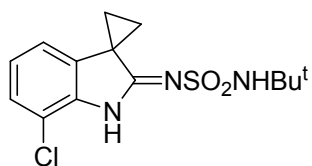
9k

As the General Procedure, **8d** (159 mg, 0.67 mmol), **4** (236 mg, 0.67 mmol) and ^tBuNH₂ (49 mg, 0.67 mmol) were converted into **9k** (146 mg, 71%): White solid. m.p 157-158 °C. ¹H NMR (400 MHz, DMSO) δ 7.27 (t, *J* = 6.9 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 7.08 – 6.98 (m, 2H), 6.67 (s, 1H), 3.41 (s, 3H), 2.59 (s, 2H), 1.71 (s, 2H), 1.28 (s, 9H); ¹³C NMR (100 MHz, DMSO) δ 167.5, 142.6, 133.0, 127.3, 123.2, 118.5, 109.6, 53.1, 30.2, 30.0, 29.8, 22.3; HRMS (ESI) *m/z* Calcd for C₁₅H₂₂N₃O₂S⁺ [M + H]⁺ 308.1427, found 308.1429.



9l

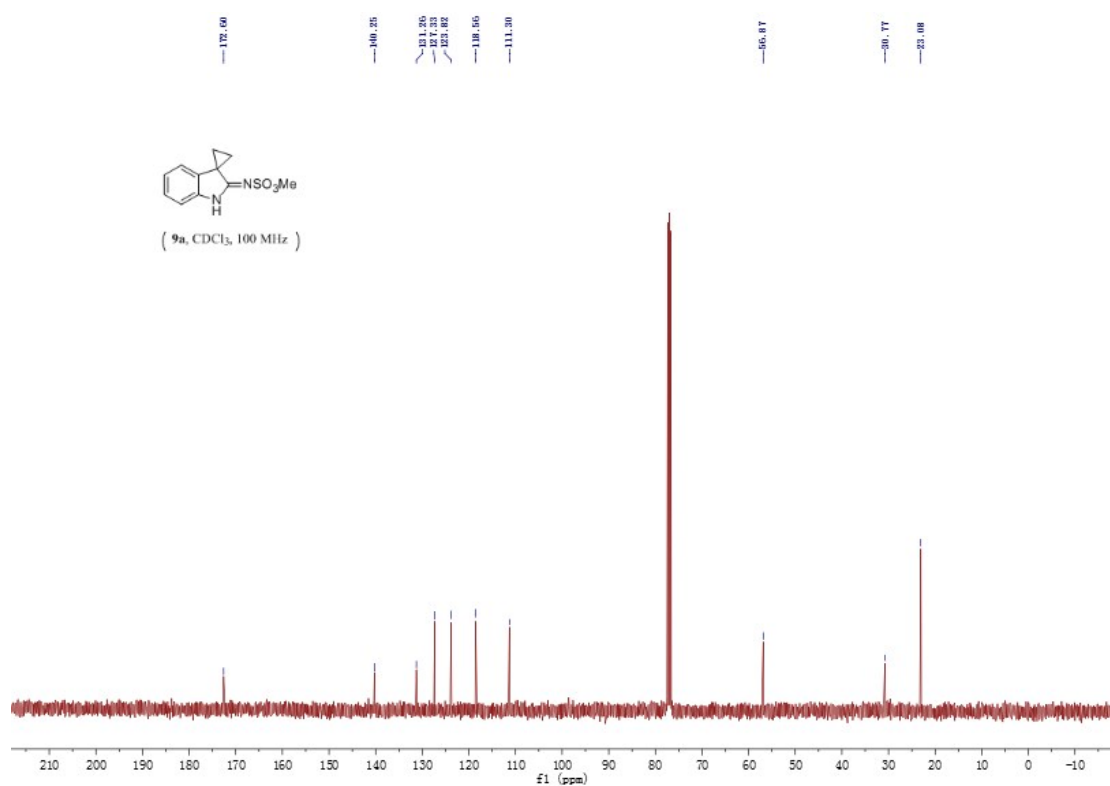
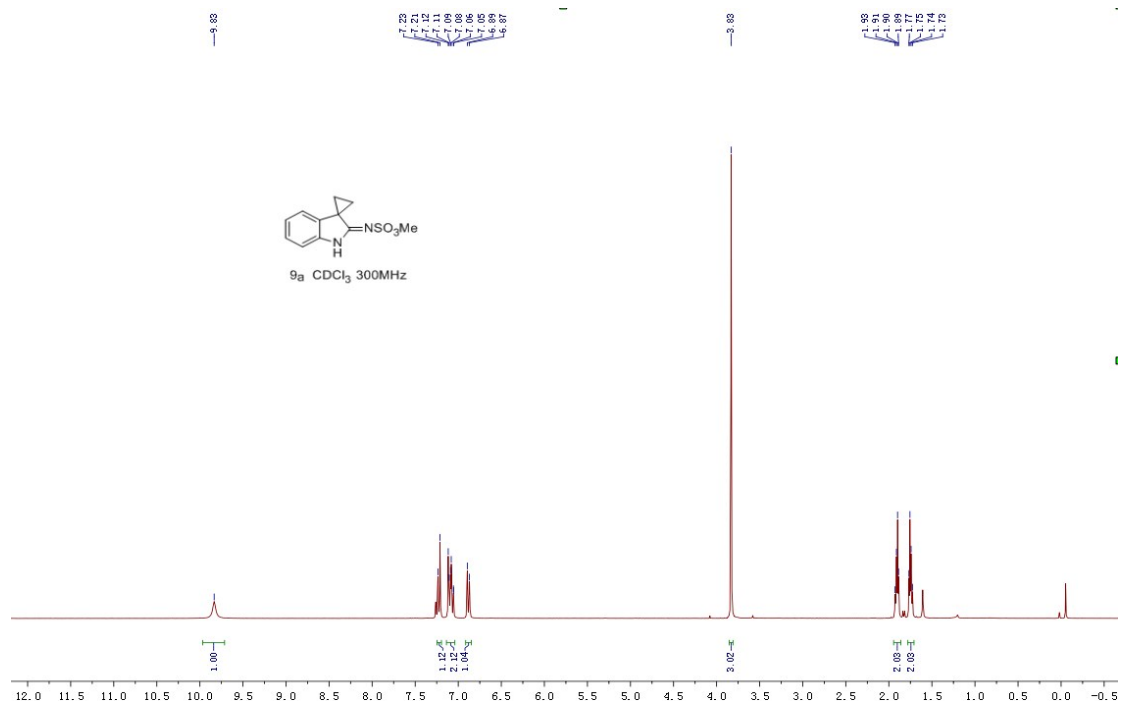
As the General Procedure, **8d** (154 mg, 0.65 mmol), **4** (228 mg, 0.65 mmol) and ⁿBuNH₂ (48 mg, 0.65 mmol) were converted into **9l** (126 mg, 63%): White solid. m.p 153-154 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.31 – 7.25 (m, 1H), 7.09 (td, *J* = 7.6, 0.8 Hz, 1H), 6.99 (d, *J* = 7.9 Hz, 1H), 6.83 (d, *J* = 7.0 Hz, 1H), 4.14 (t, *J* = 6.3 Hz, 1H), 3.51 (s, 3H), 3.19 (dd, *J* = 13.8, 6.8 Hz, 2H), 2.73 (q, *J* = 4.3 Hz, 2H), 1.70 (q, *J* = 4.4 Hz, 2H), 1.61 (t, *J* = 7.6 Hz, 2H), 1.48 – 1.36 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (75 MHz, DMSO) δ 168.3, 142.6, 132.90, 127.3, 123.4, 118.5, 109.8, 43.7, 42.3, 31.3, 29.9, 22.2, 20.0, 14.1; HRMS (ESI) *m/z* Calcd for C₁₅H₂₂N₃O₂S⁺ [M + H]⁺ 308.1433, found 308.1432.

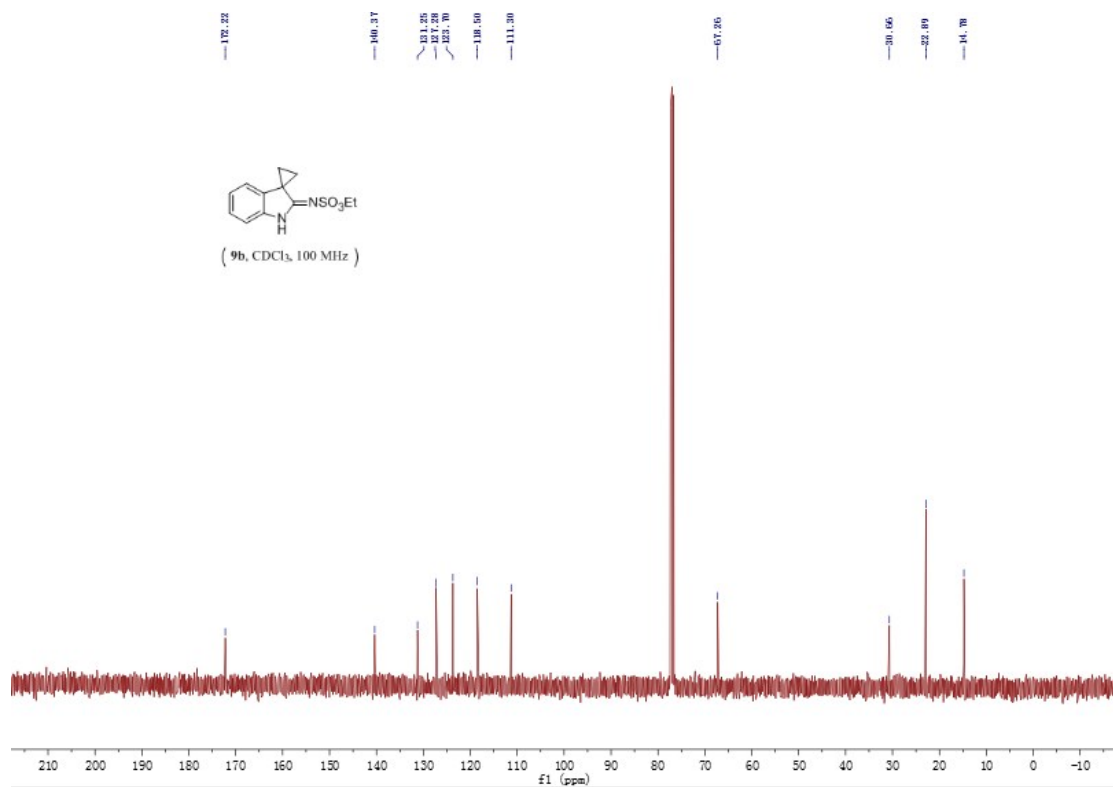
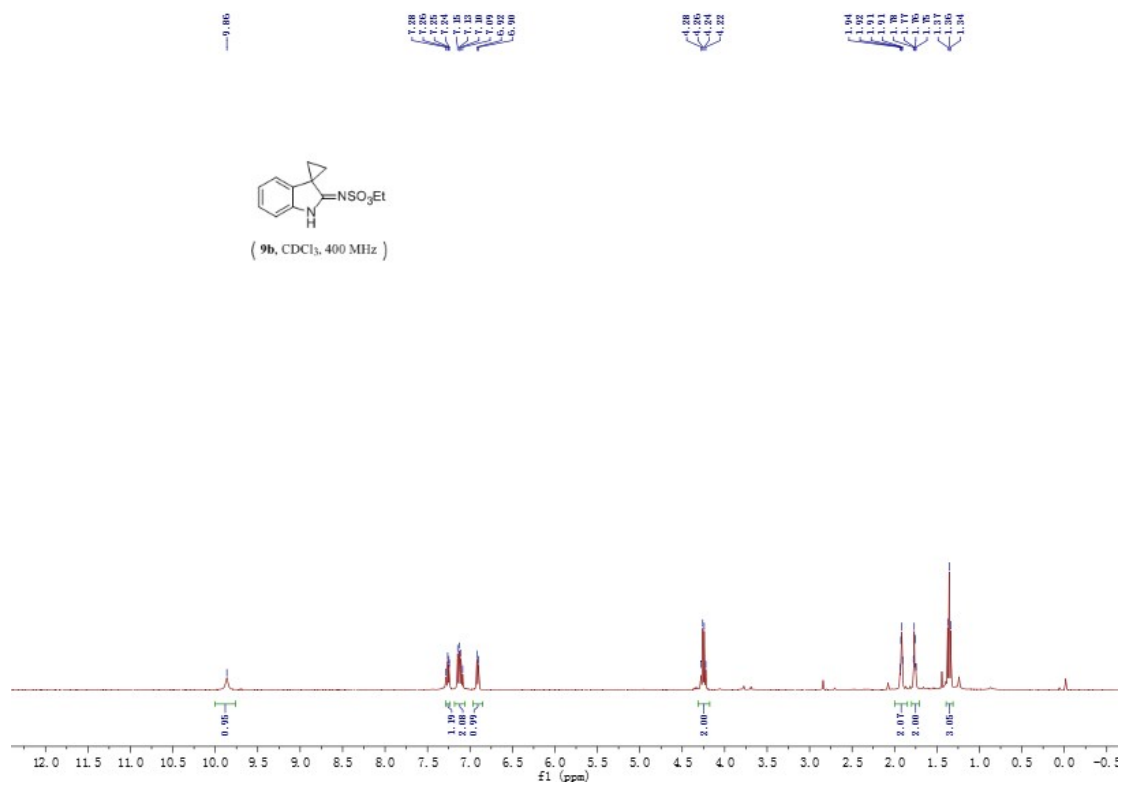


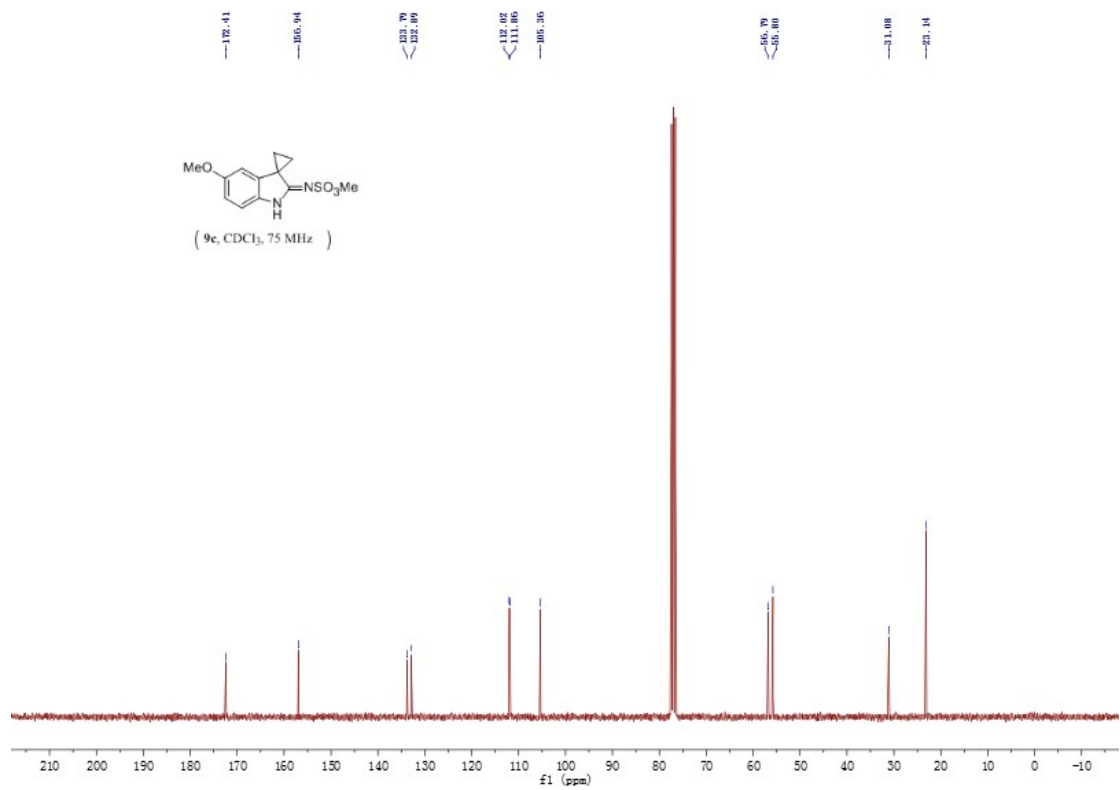
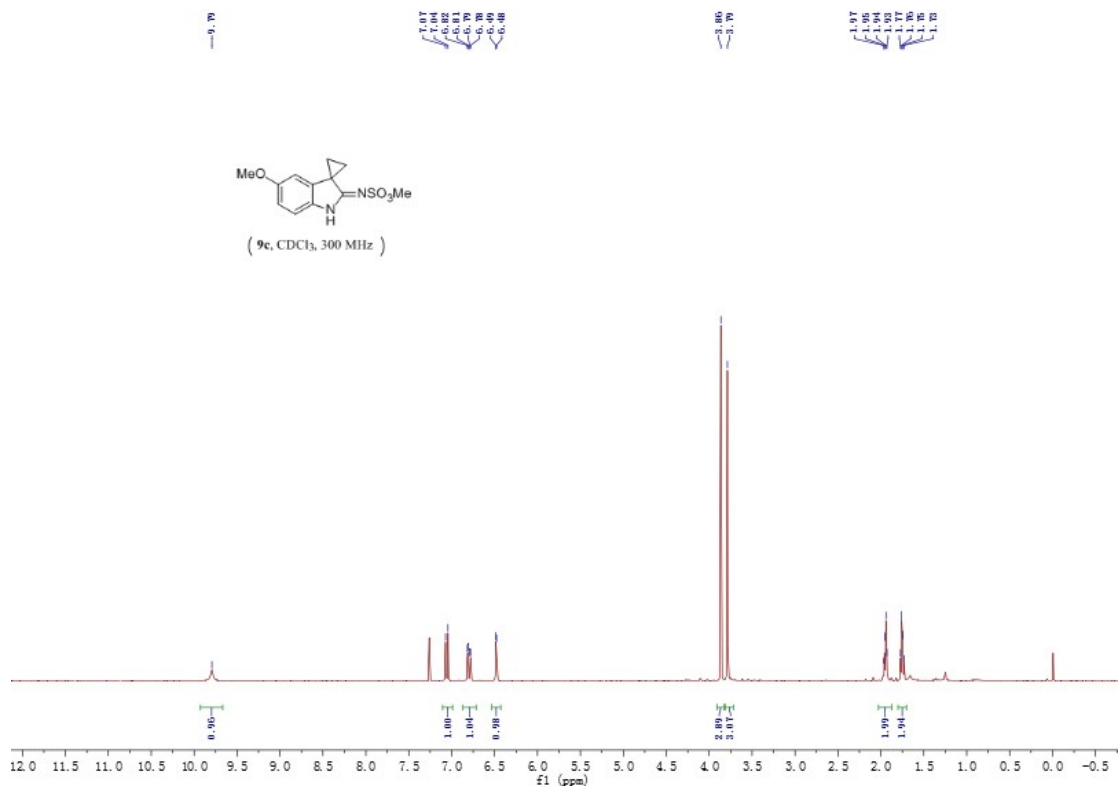
9m

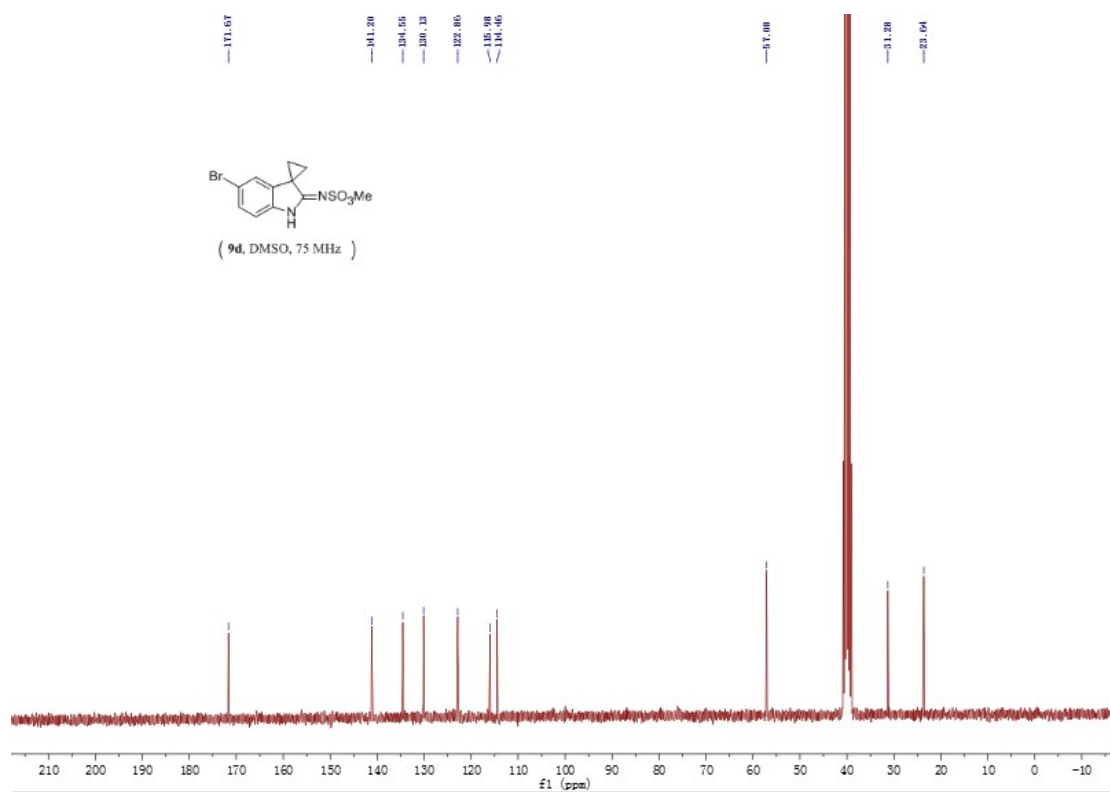
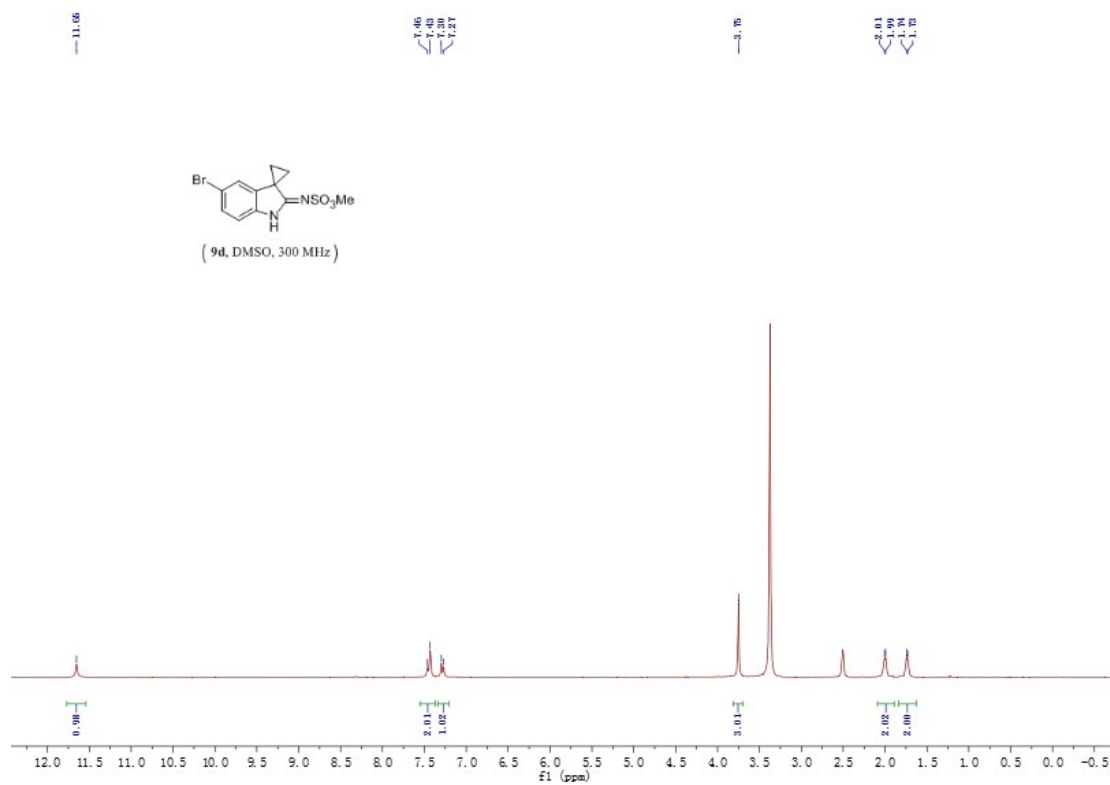
As the General Procedure, **8e** (230 mg, 0.89 mmol), **4** (314 mg, 0.89 mmol) and ^tBuNH₂ (66 mg, 0.89 mmol) were converted into **9m** (230 mg, 79%): White solid. m.p 197-198 °C. ¹H NMR (300 MHz, DMSO) δ 10.96 (s, 1H), 7.32 (s, 1H), 7.07 (s, 2H), 6.74 (s, 1H), 1.79 (s, 2H), 1.57 (s, 2H), 1.20 (s, 9H); ¹³C NMR (75 MHz, DMSO) δ 167.7, 143.8, 131.5, 130.4, 122.5, 120.9, 111.8, 53.0, 30.1, 30.0, 21.9; HRMS (ESI) *m/z* Calcd for C₁₄H₁₉ClN₃O₂S⁺ [M + H]⁺ 328.0881, found 328.0871.

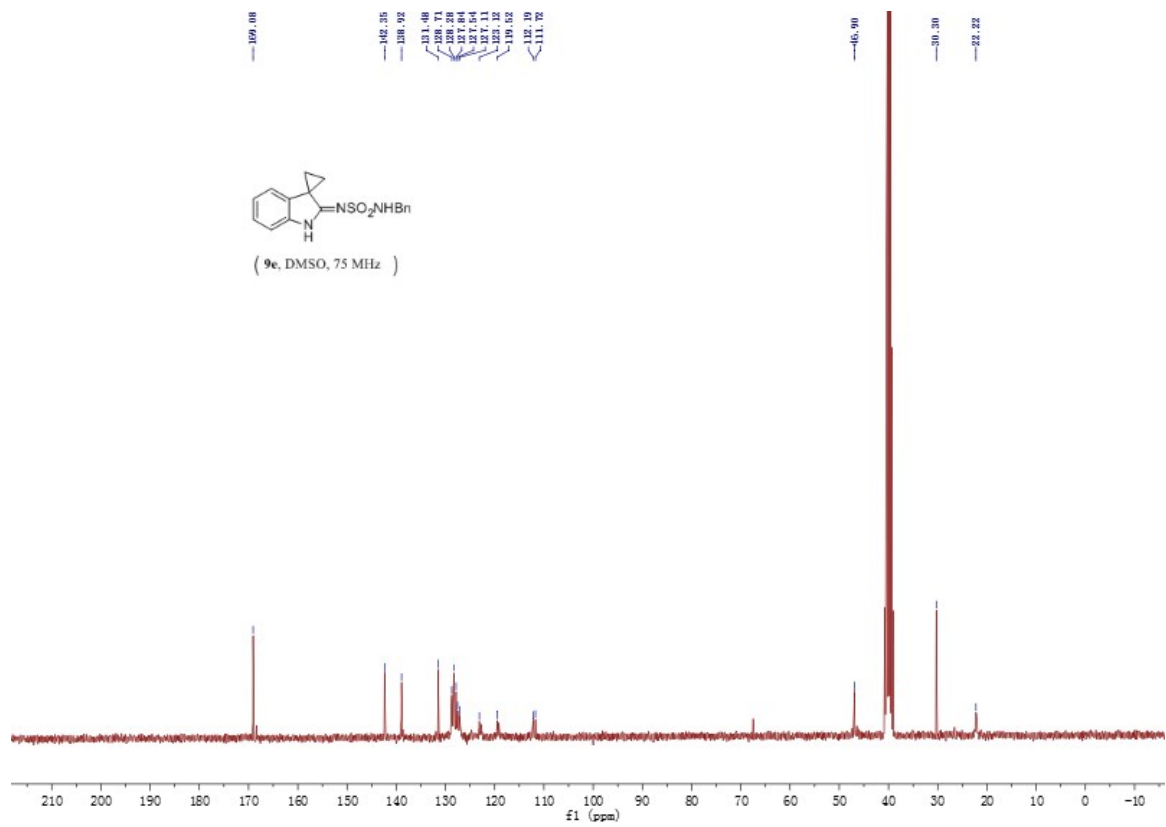
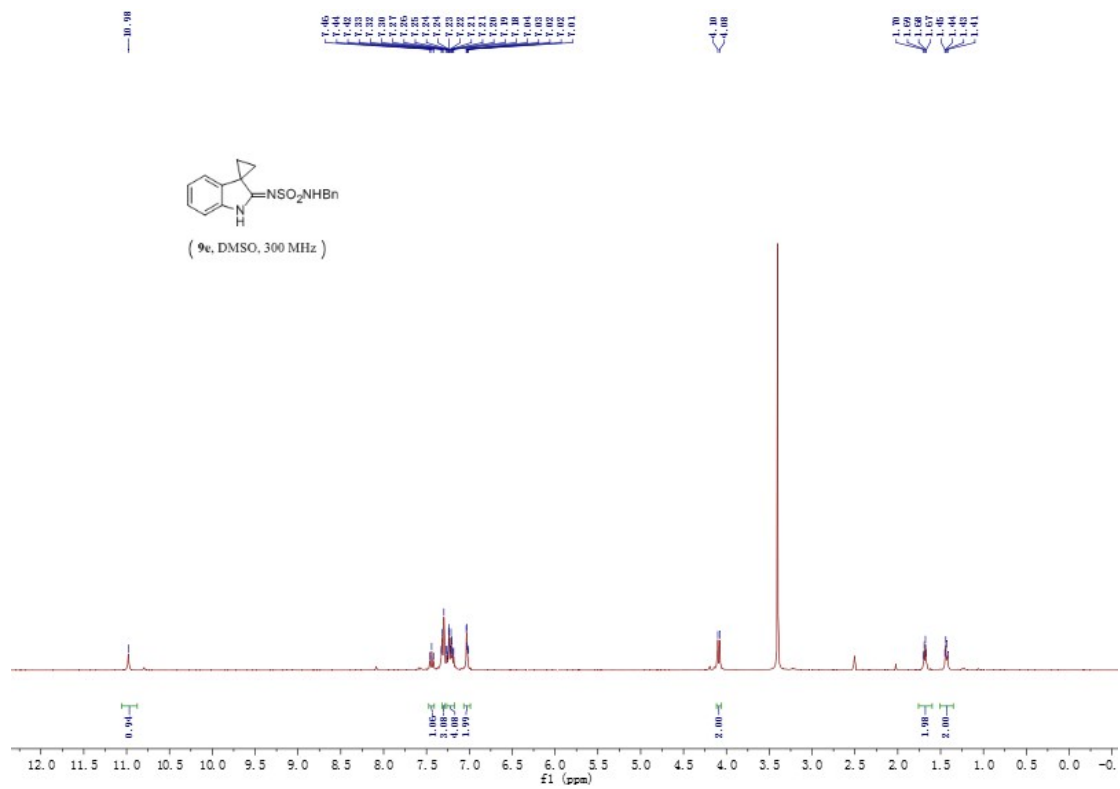
IV Copies of ^1H and ^{13}C NMR spectra of compounds

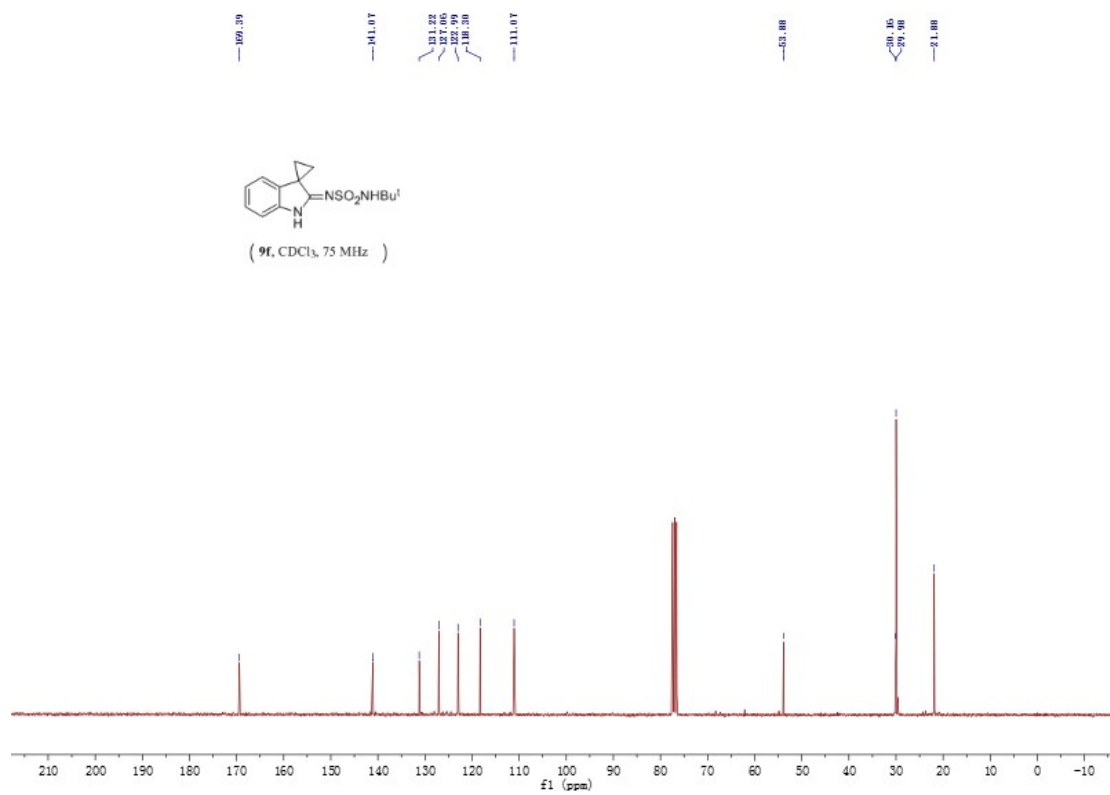
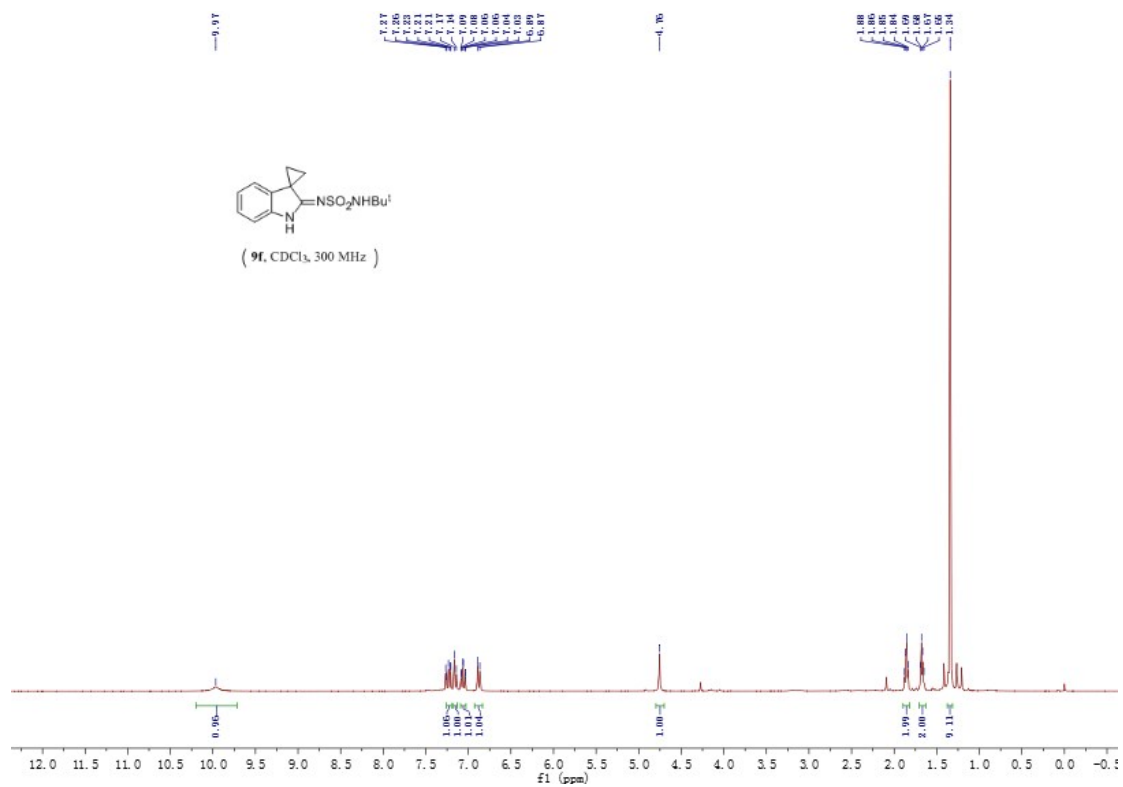


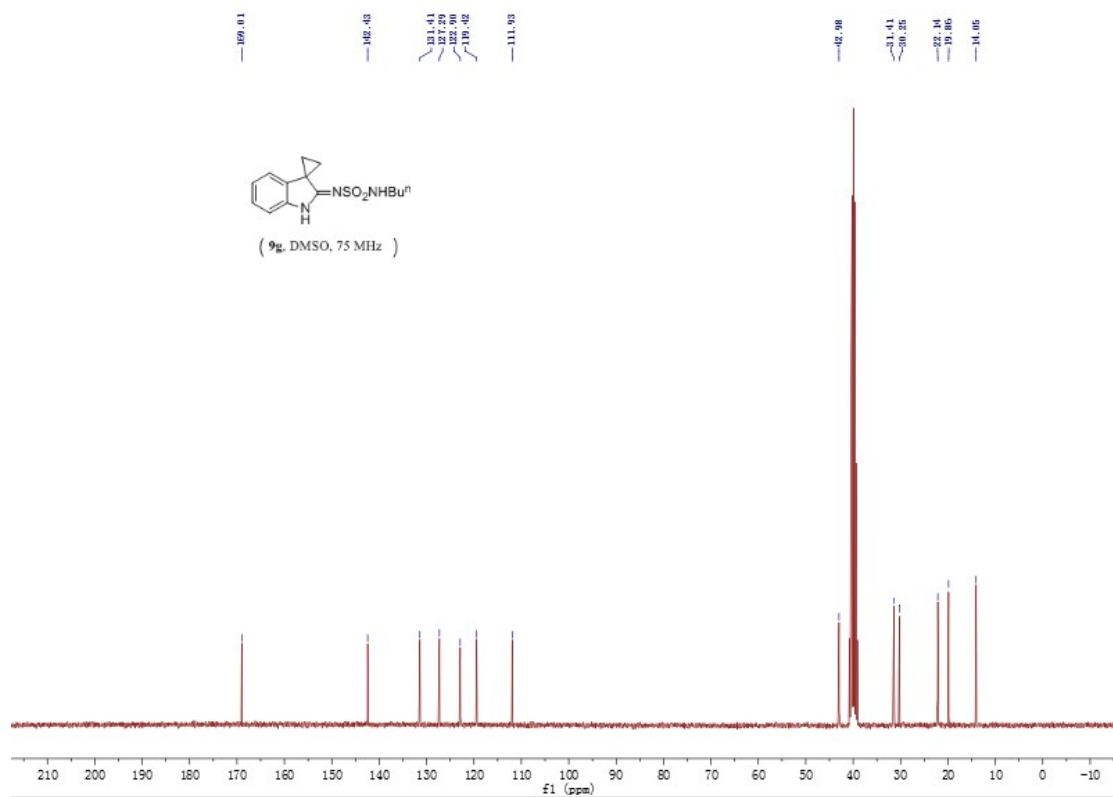
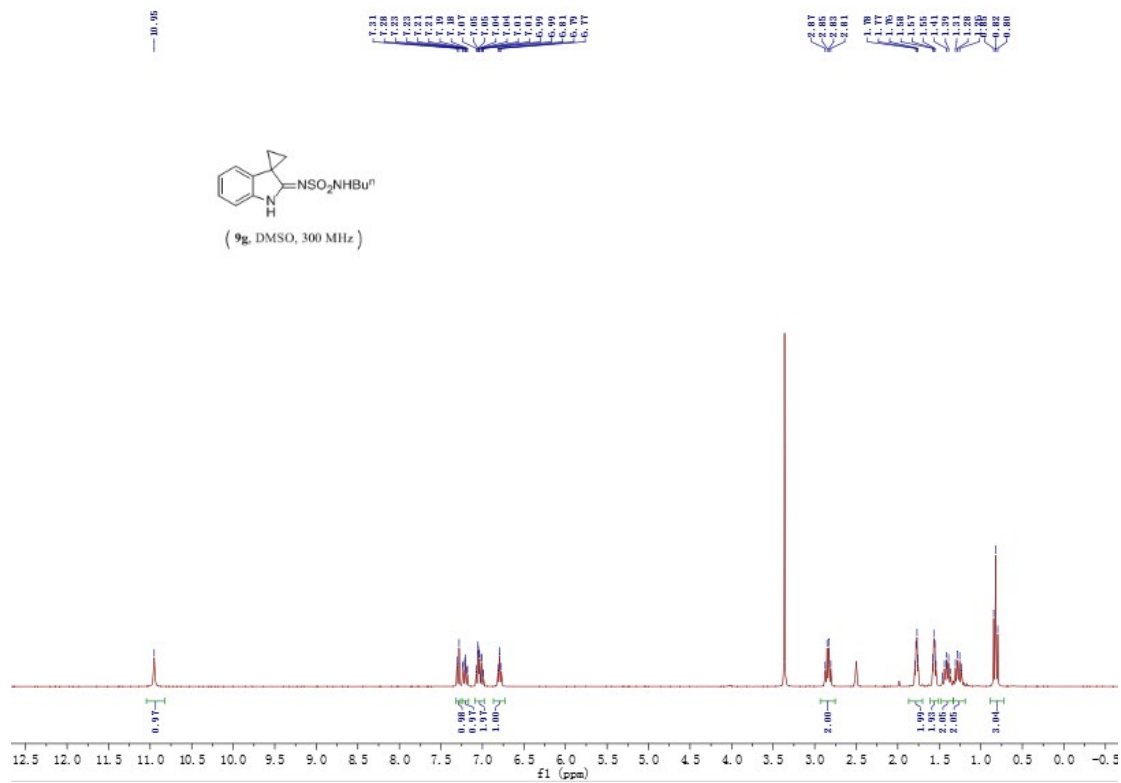


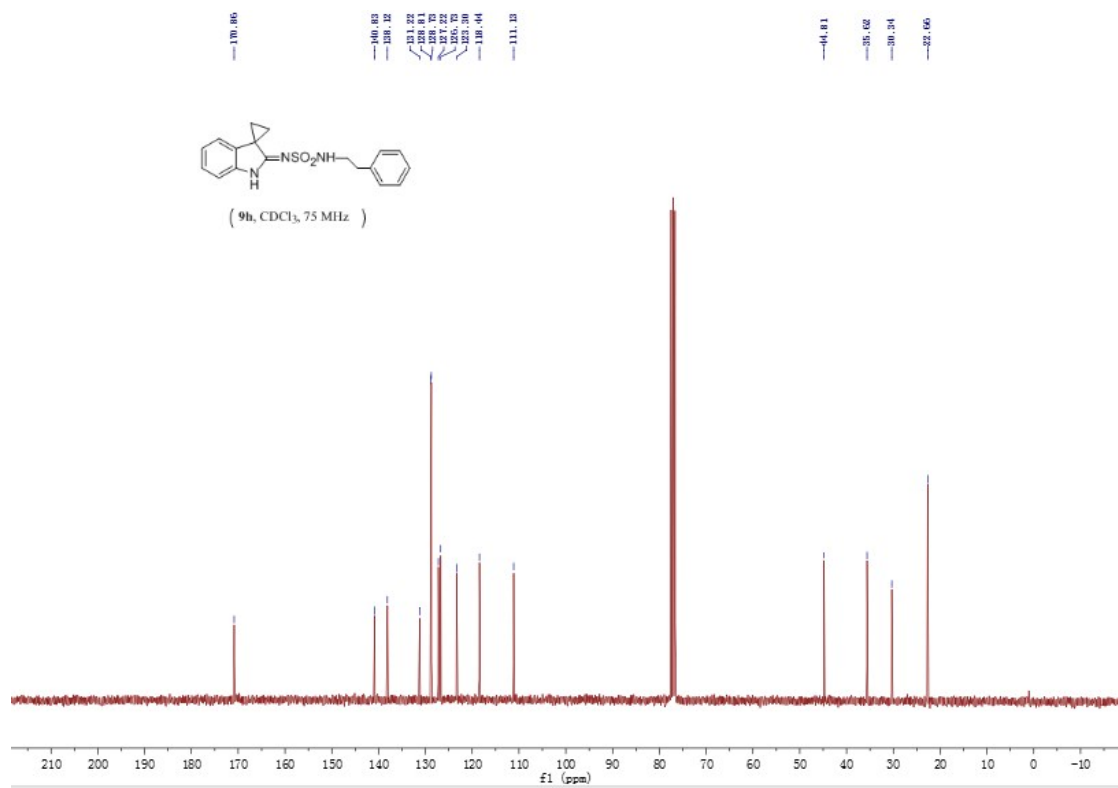
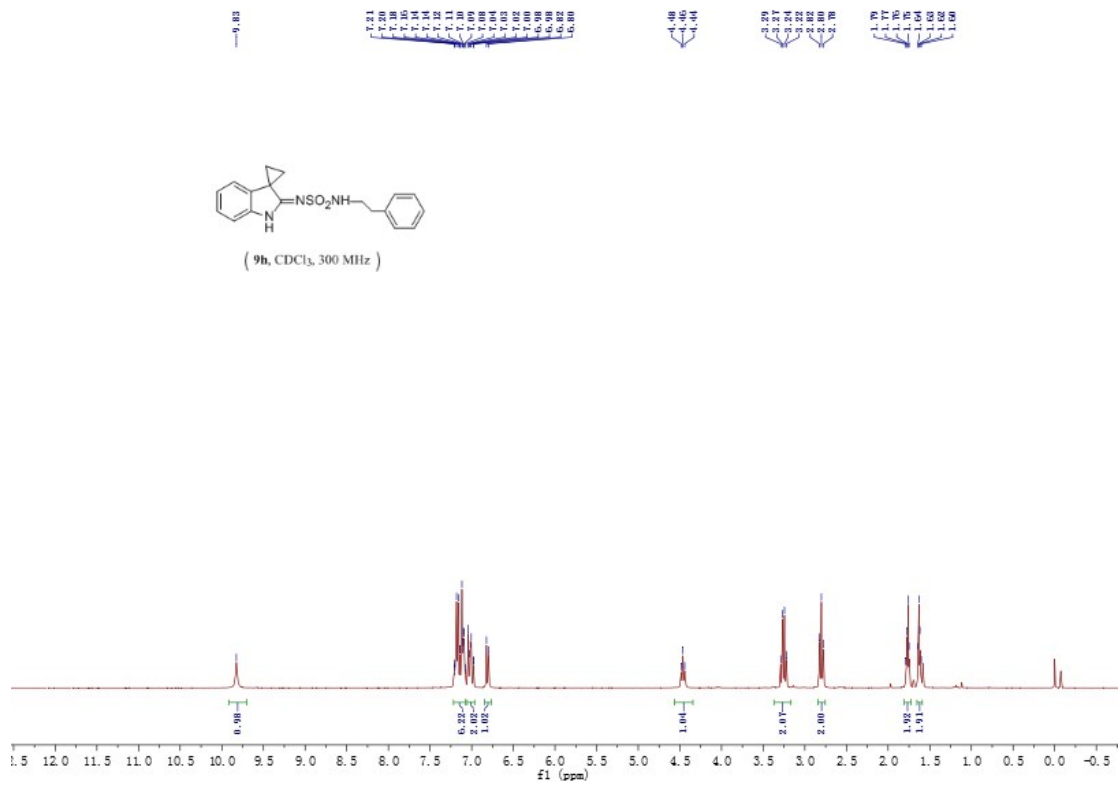


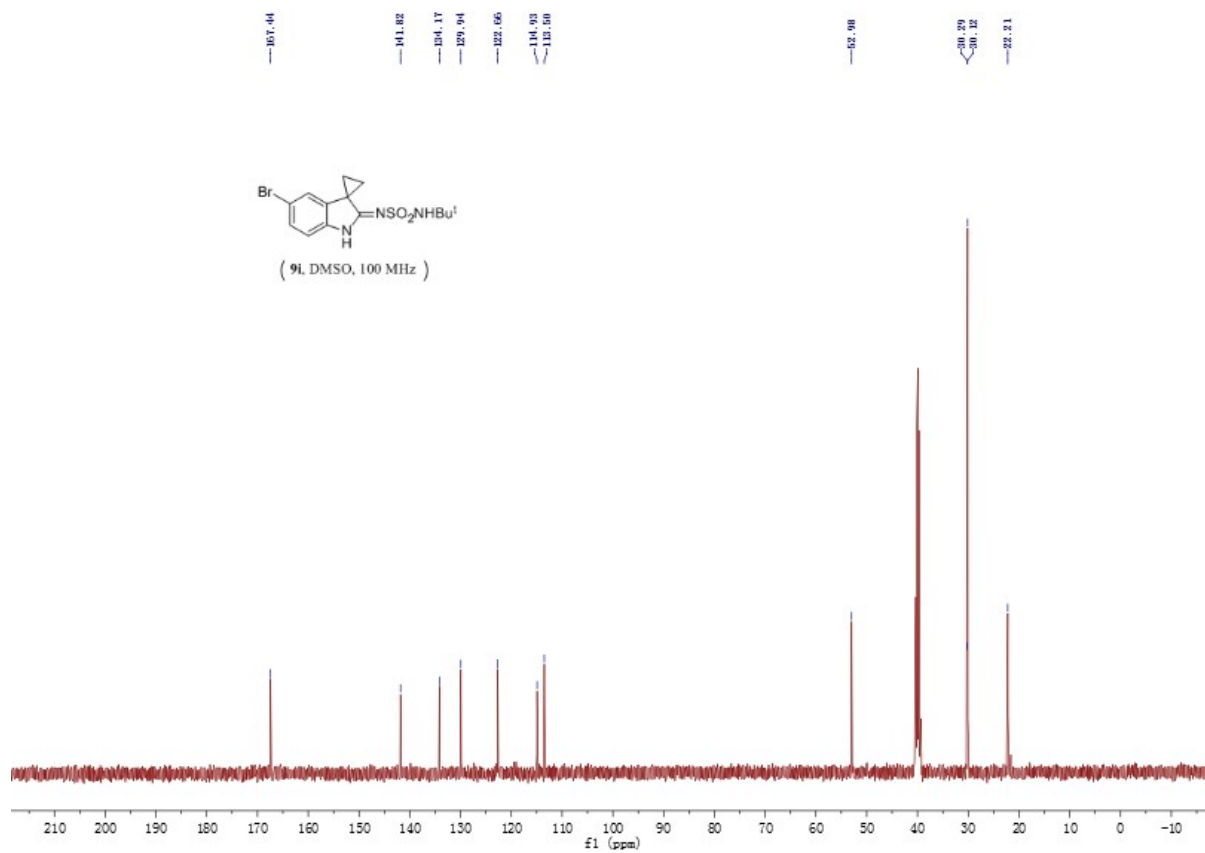
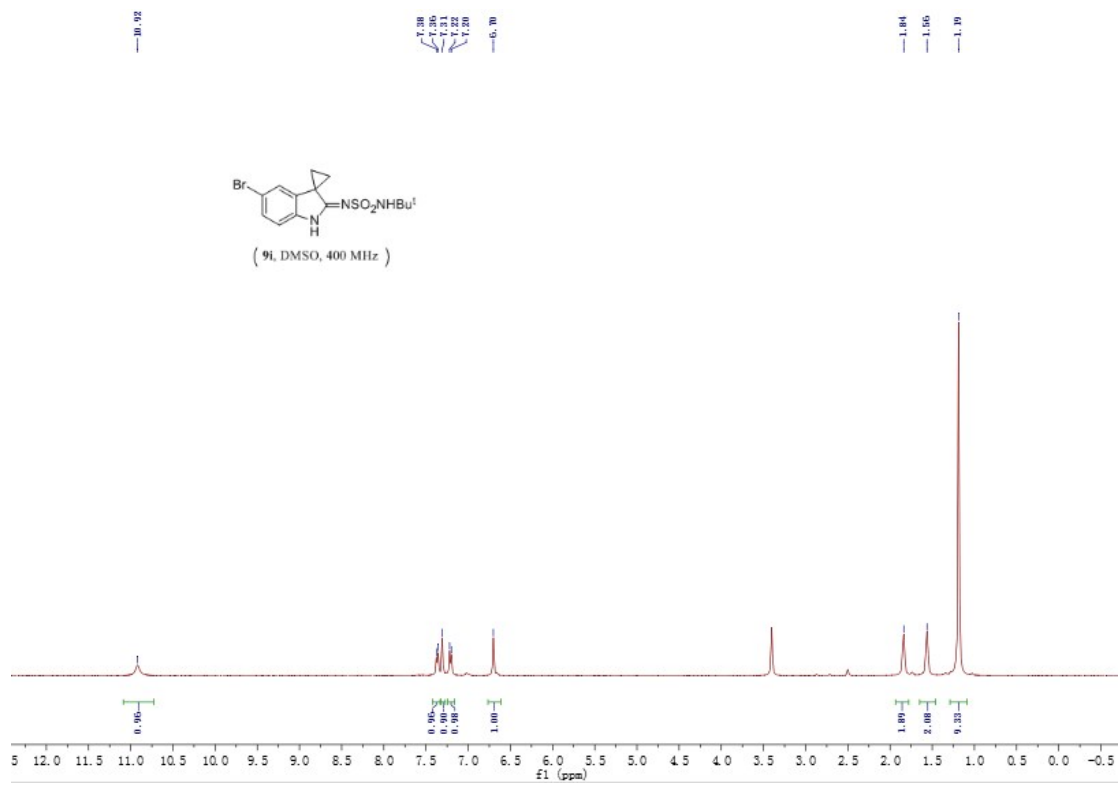


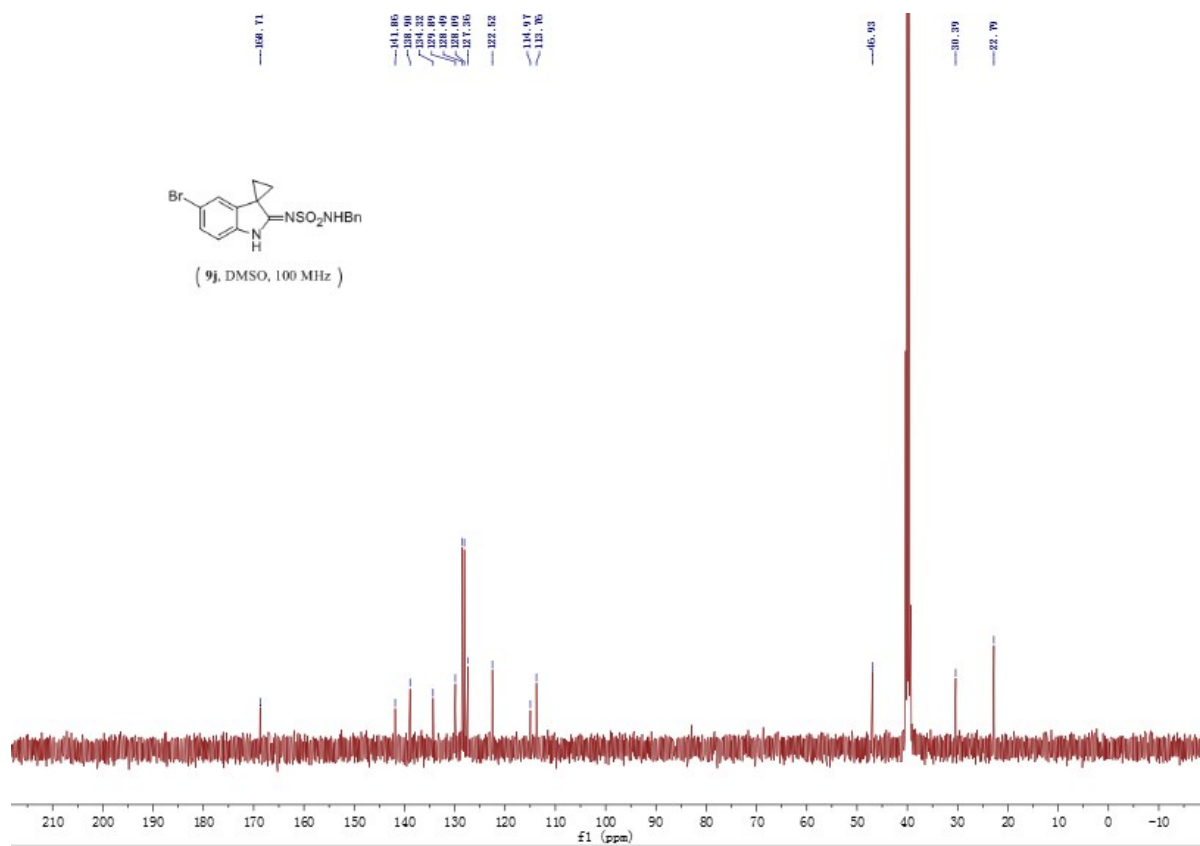
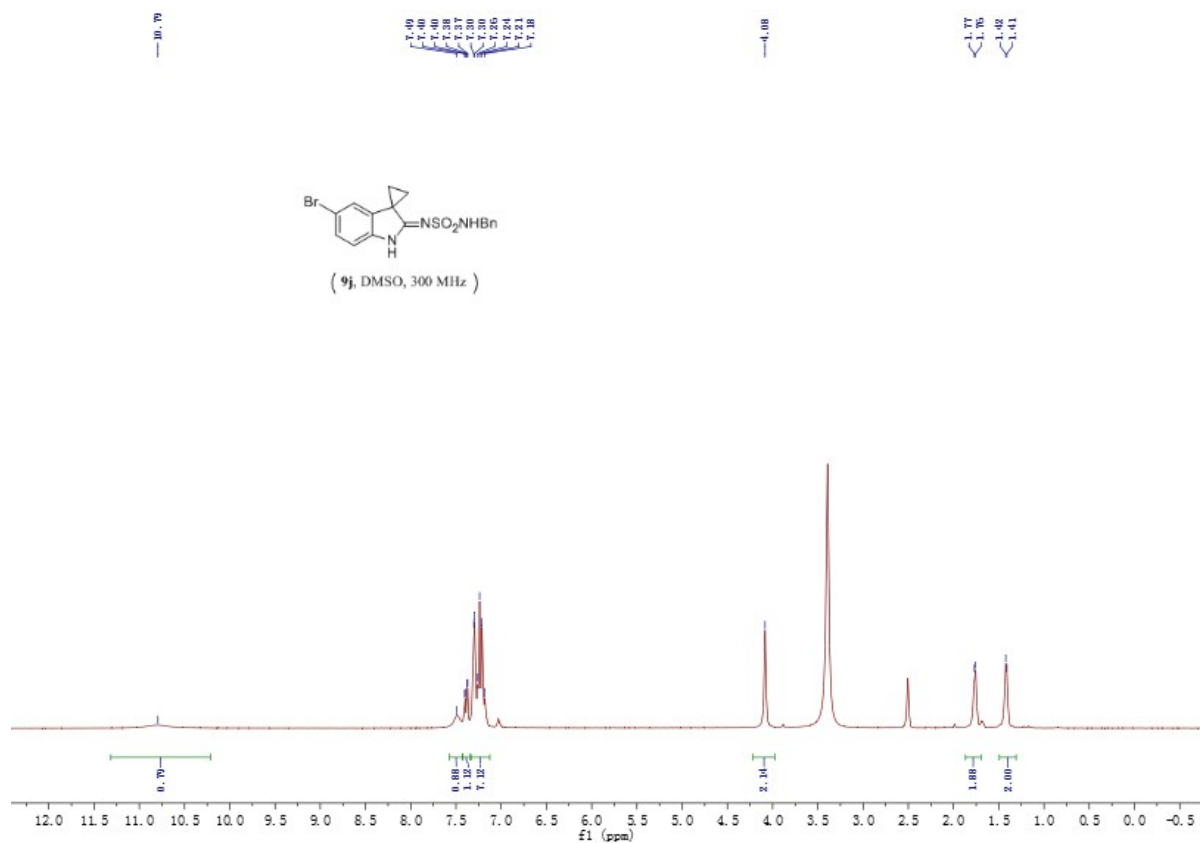


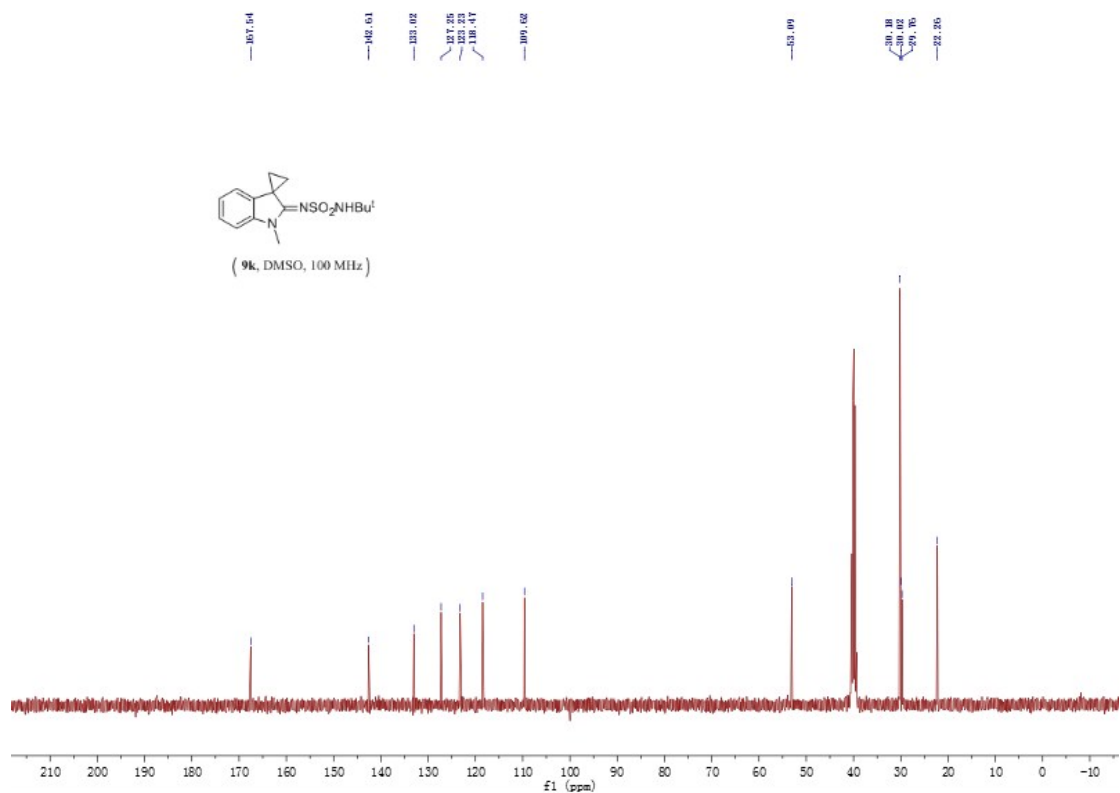
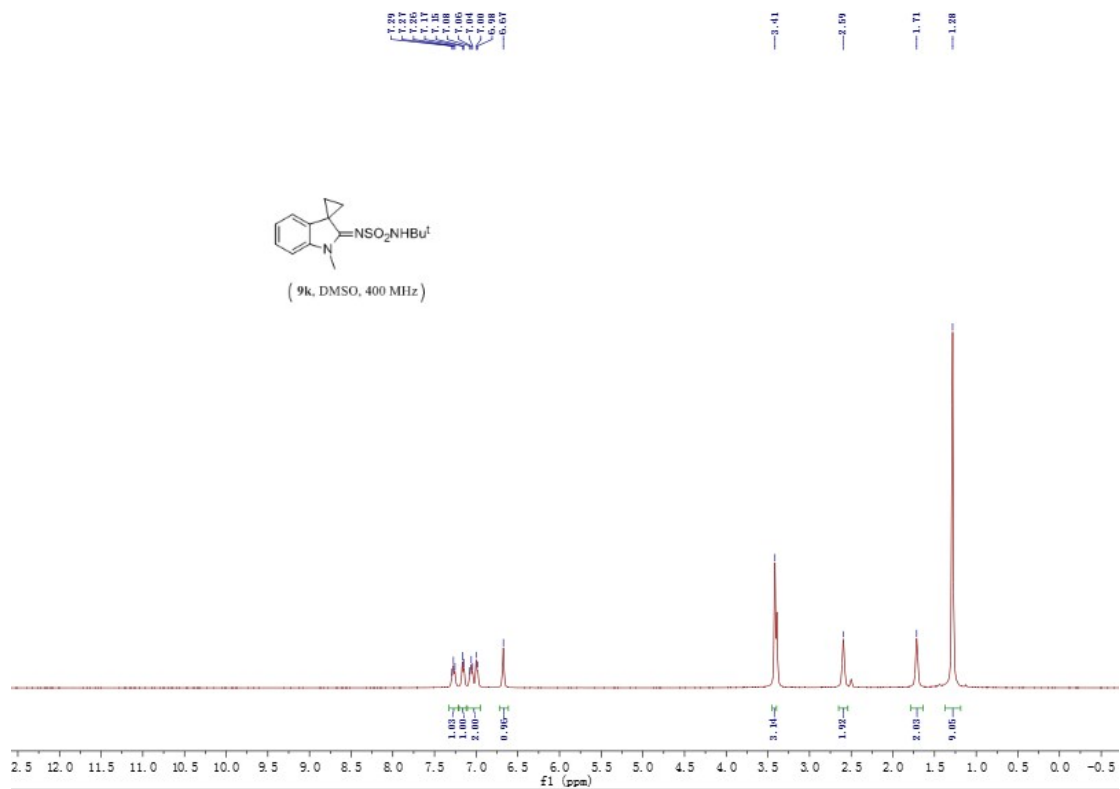


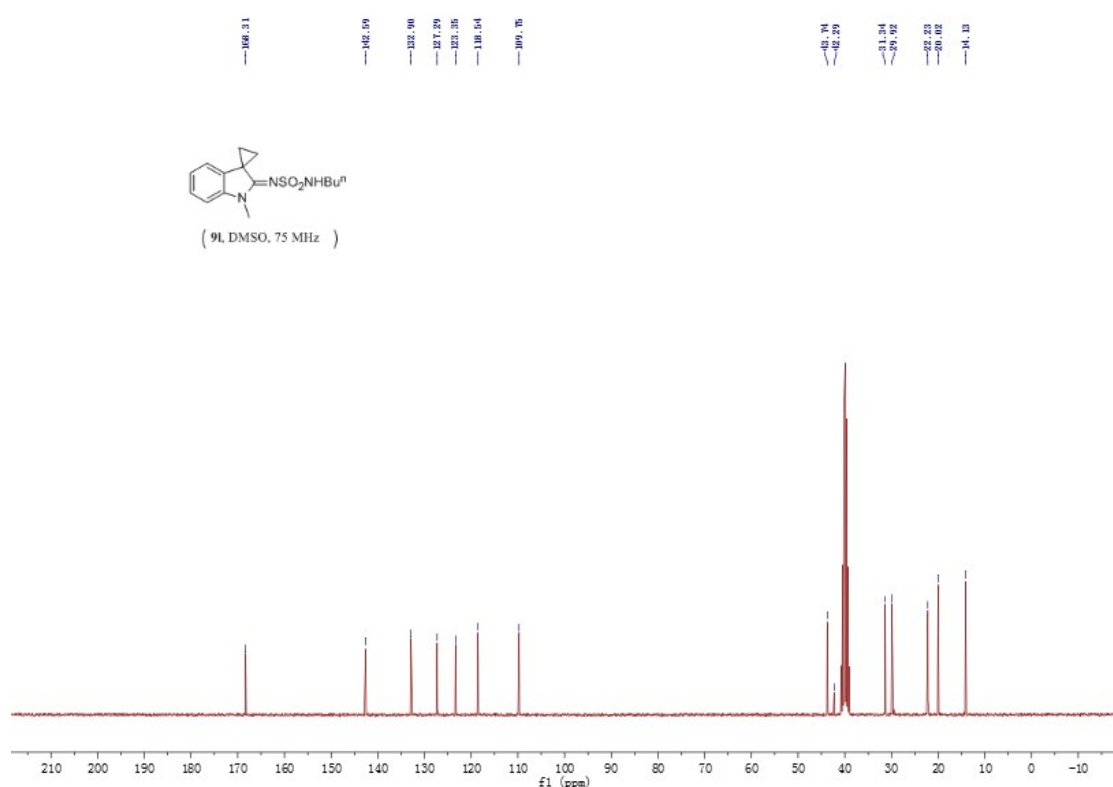
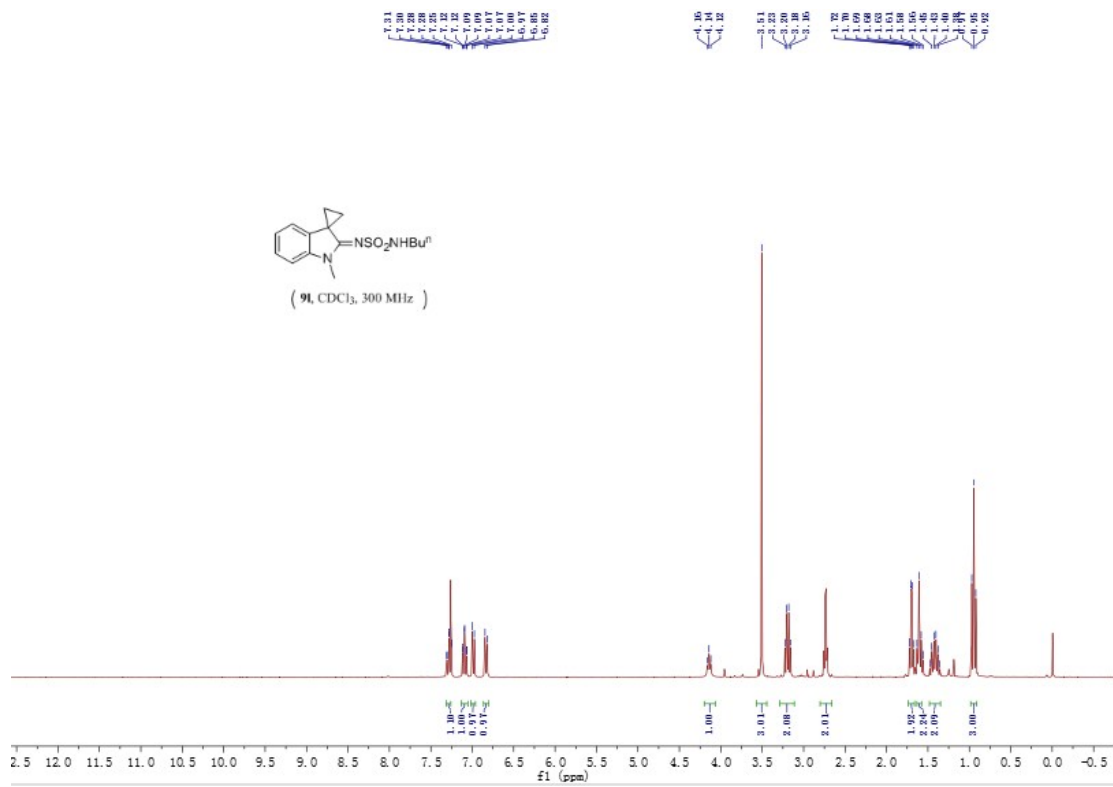


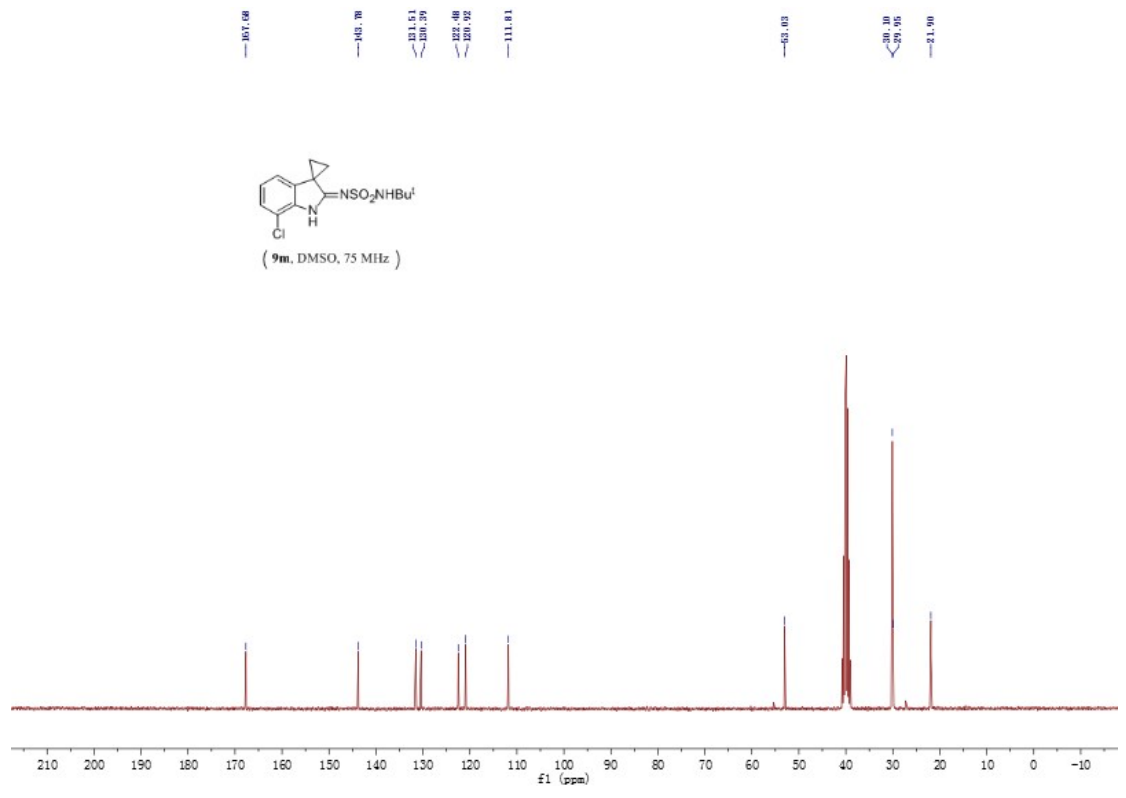
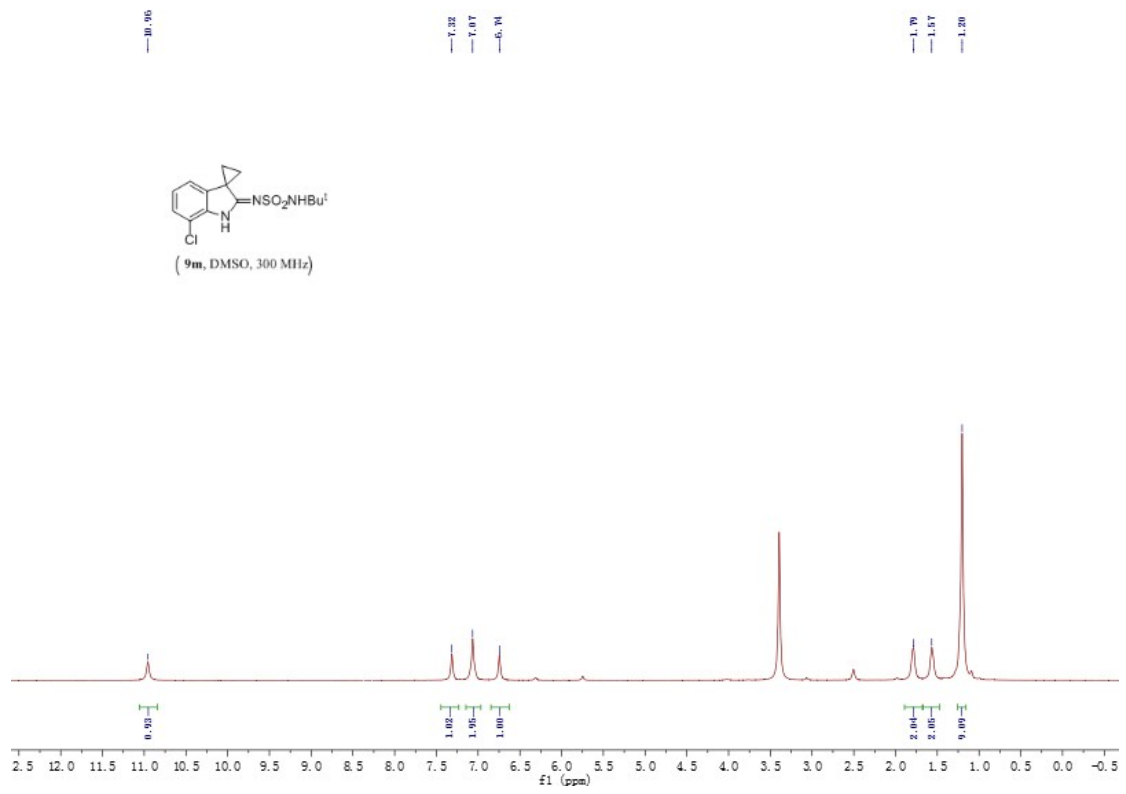












Crystal structure of **9b** (CCDC 1431979)

