Copper-catalyzed synthesis of benzo[4,5]thiazolo[3,2-*a*]indoles from element sulfur and 1-(2-iodophenyl)-1*H*-indoles

Supporting Information

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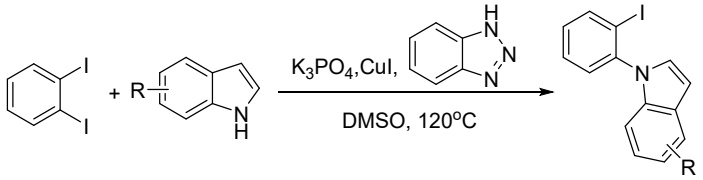
1. General methods

Unless noted, all reactions were carried out under air and all commercial reagents were without further purification. Reactions were monitored by thin layer chromatography. Purification of reaction products was carried out by flash chromatography on silica gel (200~300 mesh). ^{1}H NMR spectra were recorded at 500 MHz or 600 MHz, ^{13}C NMR spectra were recorded at 125 MHz or 150 MHz, and in $CDCl_3$ (containing 0.03% TMS) solutions. ^{1}H NMR spectra were recorded with tetramethylsilane (δ= 0.00 ppm) as internal reference; ^{13}C NMR spectra were recorded with $CDCl_3$ (δ= 77.00 ppm) as internal reference. High-resolution mass spectra were performed on a mass spectrometer with a TOF (for EI or ESI) or FT-ICR (for MALDI) analyzer. Single crystal X-ray diffraction data was collected in Bruker SMARTAPEX diffractiometers with molybdenum cathodes.

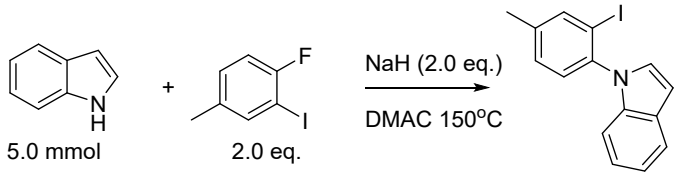
2. Synthesis of materials

The indole iodobenzenes **1a, 1b, 1c, 1d, 1e, 1f, 1g, 1h, 1j, 1k, 1m, 1n, 1o, 1p** were synthesized according to reference 1.

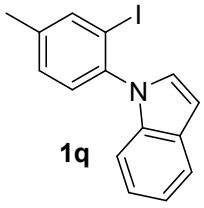


To a Schlenk tube was added indoles (11 mmol), 1,2-diiodobenzene (10 mmol), copper(I) iodide (1.0 mmol), benzotriazole (2.0 mmol) and tripotassium phosphate (20 mmol). Then, the flask was evacuated under reduced pressure and was charged with argon. 25 mL of DMSO was injected into the flask. The reaction mixture was stirred and then was heated at 120 °C for 24 to 48 h. The reaction mixture was cooled to room temperature, diluted with ethyl acetate, filtered on a Celite, washed by water and extracted with ethyl acetate. The residues concentrated in vacuo were purified by chromatography on silica gel using petroleum ether to give the corresponding aryl iodide.

1q was synthesized according to reference 2.

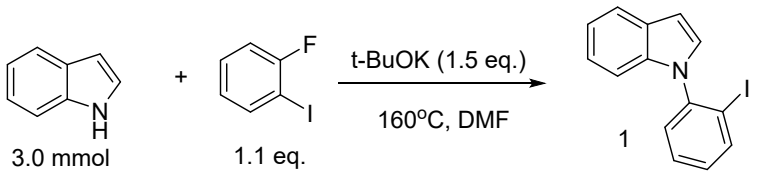


In a dried Schlenk tube, indole (5.0 mmol) and sodium hydride (10.0 mmol) were added at room temperature. Then a solution of 1-fluoro-2-iodo-4-methylbenzene (10.0 mmol) dissolved in 20 mL DMAC was introduced into the reaction mixture by a syringe. The resulting mixture was continually stirred at 150 °C in oil bath for 12 hours and indole was almost completely consumed determined by TLC analysis. Finally, saturated NH_4Cl was added to the mixture, and extracted with ethyl acetate. The combined organic phases were dried over anhydrous Na_2SO_4. After being filtrated through celite and concentrated, the residue was purified by column chromatography on silica gel eluting with PE.



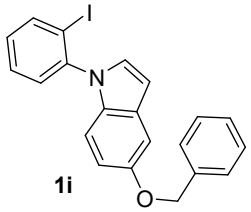
1-(2-iodo-4-methylphenyl)-1*H*-indole (1q) Yellow solid, isolated yield: 32%; mp: 77-79 °C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS) : δ 7.84 (s, 1H), 7.69 (d, J = 7.0 Hz, 1H), 7.29-7.23 (m, 2H), 7.20-7.13 (m, 3H), 7.03 (d, J = 7.0 Hz, 1H), 6.68 (d, J = 3.0 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 140.40, 140.22, 139.39, 136.75, 129.92, 128.84, 128.67, 128.27, 122.13, 120.88, 120.09, 110.66, 102.80, 97.49, 20.63; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{13}IN$ 334.0087, found 334.0085.

1i, 1l, 1r were synthesized by the follow method.



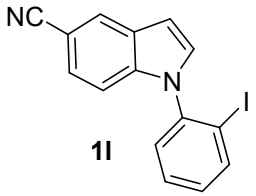
In a sealed tube, indoles (3.0 mmol), o-fluoroiodobenzenes (3.3 mmol), *t*-BuOK (4.5mmol, 504.9 mg) and DMF (10.0mL) were stirred at 160 °C (oil bath) under N_2. After the reaction was completed as monitored by thin-layer chromatography, the reaction mixture was then quenched by water, and the water layers were extracted with ethyl acetate. The combined organic layers were washed with brine, dried over

anhydrous Na_2SO_4. After removal of the EA, the residue was purified by chromatography on silica gel to afford **1**.



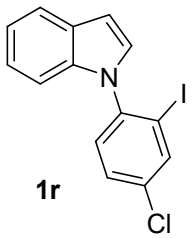
1i

5-(benzyloxy)-1-(2-iodophenyl)-1H-indole **(1i)** White solid, isolated yield: 76%; mp: 101-103 °C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS) : δ 8.01 (d, J = 8.5 Hz, 1H), 7.52-7.44 (m, 3H), 7.41-7.30 (m, 4H), 7.26-7.21 (m, 1H), 7.19-7.14 (m, 2H), 6.97-6.90 (m, 2H), 6.61 (d, J = 3.0 Hz, 1H), 5.12 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 153.75, 142.09, 140.14, 137.63, 132.09, 129.78, 129.30, 129.16, 129.12, 128.74, 128.51, 127.76, 127.54, 113.13, 111.45, 103.98, 102.75, 97.54, 70.74; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{16}INNaO$ 448.0169, found 448.0169.



1l

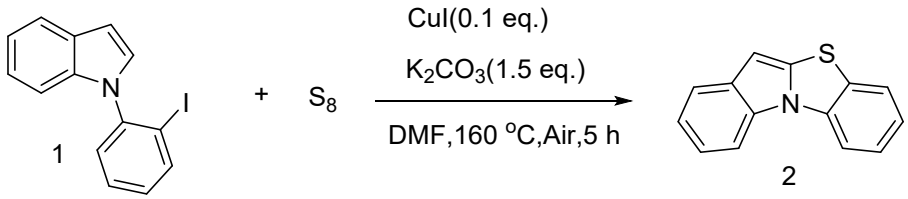
1-(2-iodophenyl)-1H-indole-5-carbonitrile **(1l)** White solid, isolated yield: 64%; mp: 132-134 °C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS) : δ 8.06-8.03 (m, 2H), 7.55-7.50 (m, 1H), 7.43-7.36 (m, 2H), 7.30 (d, J = 3.0 Hz, 1H), 7.25-7.22 (m, 1H), 7.07 (d, J = 7.0 Hz, 1H), 6.78-6.75 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 140.92, 140.35, 138.14, 130.84, 130.66, 129.47, 129.21, 128.11, 126.59, 125.32, 120.56, 111.59, 103.82, 103.54, 97.34; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{15}H_9IN_2Na$ 366.9703, found 366.9701.



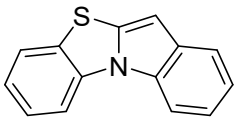
1r

1-(4-chloro-2-iodophenyl)-1H-indole **(1r)** Yellow oil, isolated yield: 23%; ^{1}H NMR (500 MHz, $CDCl_3$, TMS) : δ 8.05-7.98 (m, 1H), 7.70-7.66 (m, 1H), 7.46-7.42 (m, 1H), 7.30-7.11 (m, 4H), 7.05-7.00 (m, 1H), 6.69 (d, J = 3.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 140.81, 139.48, 136.57, 134.72, 129.80, 129.40, 128.41, 128.33, 122.47, 121.06, 120.43, 110.48, 103.50, 97.86; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{10}ClIN$ 353.9541, found 353.9537.

3. Synthesis of 2.



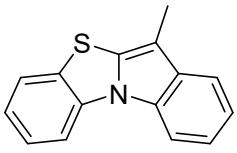
In a sealed tube, indole iodobenzenes **1** (0.4 mmol), S_8 (0.4 mmol, 102.6 mg), CuI (0.04 mmol, 7.6 mg), K_2CO_3 (0.6 mmol, 82.9 mg) and DMF (4.0 mL) were stirred at 160 °C (oil bath) under air. After the reaction was completed as monitored by thin-layer chromatography, the reaction mixture was then quenched by water, and the water layers were extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4. After removal of the EA, the residue was purified by chromatography on silica gel to afford **2**.



2a

benzo[4,5]thiazolo[3,2-a]indole (**2a)**. Yellow solid, obtained in 5 h and purified by chromatography on silica gel (petroleum ether); yield: 93%, 82.8 mg, m.p. 106-108 °C.

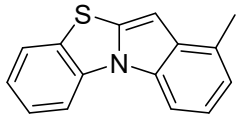
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01-7.96 (m, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.69-7.63 (m, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.45-7.40 (m, 1H), 7.30-7.25 (m, 2H), 7.24-7.19 (m, 1H), 6.57 (s, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 136.25, 135.86, 133.32, 131.12, 130.51, 126.00, 123.60, 122.95, 121.46, 120.41, 120.00, 111.96, 110.87, 93.08. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{10}NS$ 224.0529, found 224.0529.



2b

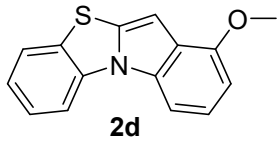
11-methylbenzo[4,5]thiazolo[3,2-a]indole (**2b)**. Yellow solid, obtained in 7 h (**1b** was consumed completely and polysulfide intermediates were observed) and purified by chromatography on silica gel (petroleum ether); yield: 45%, 42.4 mg, m.p. 67-69 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98-7.92 (m, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.64-7.57 (m, 2H), 7.45-7.39 (m, 1H), 7.33-7.27 (m, 2H), 7.22-7.17 (m, 1H), 2.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.19, 133.11, 132.92, 130.95, 130.35, 125.97, 123.70,

122.50, 120.84, 120.22, 117.88, 111.67, 110.75, 101.30, 9.38. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{12}NS$ 238.0685, found 238.0676.



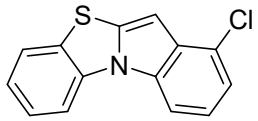
2c

1-methylbenzo[4,5]thiazolo[3,2-a]indole (**2c**). White solid, obtained in 5 h and purified by chromatography on silica gel (petroleum ether); yield: 89%, 84.9 mg, m.p. 129-131 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J*=8.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.46-7.40 (m, 1H), 7.25-7.18 (m, 2H), 7.09 (d, *J* = 6.5 Hz, 1H), 6.59 (s, 1H), 2.60 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.97, 135.59, 133.12, 130.82, 130.60, 129.35, 125.98, 123.59, 122.93, 121.73, 120.52, 111.99, 108.52, 91.60, 18.90. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{15}H_{11}NNaS$ 260.0504, found 260.0498.



2d

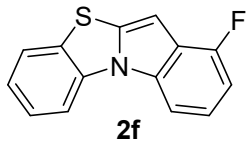
1-methoxybenzo[4,5]thiazolo[3,2-a]indole (**2d**). Yellow solid, obtained in 8 h and purified by chromatography on silica gel (petroleum ether); yield: 63%, 64.0 mg, m.p. 166-168 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.5 Hz, 1H), 7.62-7.55 (m, 2H), 7.43-7.37 (m, 1H), 7.24-7.17 (m, 2H),6.71 (d, *J* = 8.0 Hz, 1H), 6.67 (s, 1H), 3.98(s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.15, 135.81, 134.35, 132.17, 130.77, 125.88, 123.70, 123.56, 123.02, 121.28, 112.04, 104.38, 101.56, 90.32, 55.42. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{15}H_{11}NNaOS$ 276.0464, found 276.0447.



2e

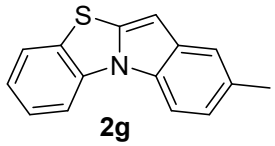
1-chlorobenzo[4,5]thiazolo[3,2-a]indole (**2e**). White solid, obtained in 7 h (**1e** was consumed completely and polysulfide intermediates were observed) and purified by chromatography on silica gel (petroleum ether); yield: 50%, 51.2 mg, m.p. 140-142 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90-7.80 (m, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.45-7.38 (m, 1H), 7.29-7.20 (m, 2H), 7.19-7.12 (m, 1H), 6.66 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.15, 135.46, 131.80, 131.54, 130.52, 126.11, 124.72, 123.70,

123.46, 121.20, 120.82, 112.11, 109.33, 91.66. HRMS (ESI) m/z: $[M+H]^+$calcd for $C_{14}H_9ClNS$ 258.0139, found 258.0140.



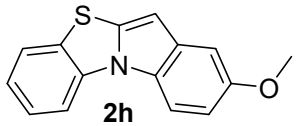
2f

1-fluorobenzo[4,5]thiazolo[3,2-a]indole (**2f**). Yellow solid, obtained in 8 h and purified by chromatography on silica gel (petroleum ether); yield: 64%, 61.9 mg, m.p. 106-108 °C. ^{1}H NMR (500MHz, $CDCl_3$) δ 7.85 (d, J = 8.5 Hz, 1H), 7.69 (d, J = 8.5 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.42-7.35 (m, 1H), 7.24-7.11 (m, 2H), 6.97-6.90 (m, 1H), 6.61 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.90 (d, J_{C-F} = 245.4 Hz), 136.34, 135.37, 133.16 (d, J_{C-F} = 11.3 Hz), 130.54, 126.04, 123.62, 123.38, 122.08 (d, J_{C-F} = 22.3 Hz), 120.81 (d, J_{C-F} = 7.6 Hz), 112.06, 106.99 (d, J_{C-F} = 3.6 Hz), 106.48 (d, J_{C-F} = 18.8 Hz), 88.91. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_9FNS$ 242.0434, found 242.0434.



2g

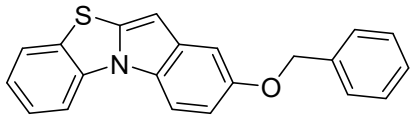
2-methylbenzo[4,5]thiazolo[3,2-a]indole (**2g**). Light yellow solid, obtained in 5 h and purified by chromatography on silica gel (petroleum ether); yield: 89%, 83.6 mg, m.p. 89-91 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.5 Hz, 1H), 7.57 (d, J = 7.0 Hz, 1H), 7.45-7.37 (m, 2H), 7.21-7.16 (m, 1H), 7.10-7.06 (m, 1H), 6.47 (s, 1H), 2.50 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.17, 135.89, 133.61, 130.87, 130.42, 129.45, 125.93, 123.53, 122.70, 121.85, 119.80, 111.76, 110.45, 92.64, 21.55. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{12}NS$ 238.0685, found 238.0686.



2h

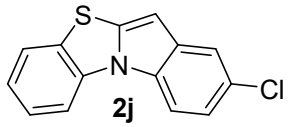
2-methoxybenzo[4,5]thiazolo[3,2-a]indole (**2h**). Yellow solid, obtained in 8 h and purified by chromatography on silica gel (petroleum ether); yield: 78%, 79.0 mg, m.p. 100-102 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87-7.80 (m, 2H), 7.56 (d, J = 7.5 Hz,

1H), 7.42-7.36 (m, 1H), 7.20-7.15 (m, 1H), 7.11 (d, J = 2.5 Hz, 1H), 6.92-6.87 (m, 1H), 6.47 (s, 1H), 3.88 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.13, 136.77, 135.76, 134.10, 130.22, 126.30, 125.95, 123.54, 122.61, 111.44, 111.40, 109.83, 102.14, 92.85, 55.70. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{12}NOS$ 254.0634, found 254.0634.



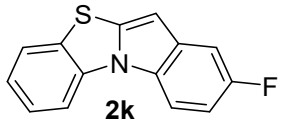
2i

2-(benzyloxy)benzo[4,5]thiazolo[3,2-a]indole (**2i)**. Yellow solid, obtained in 9 h and purified by chromatography on silica gel (PE:EA=20:1); yield: 92%, 120.9 mg, m.p. 120-122 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90-7.83 (m, 2H), 7.59 (d, J = 8.0 Hz, 1H), 7.52-7.47 (m, 2H), 7.44-7.37 (m, 3H), 7.36-7.30 (m, 1H), 7.23-7.18 (m, 2H), 7.02-6.97 (m, 1H), 6.49 (s, 1H), 5.15 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.31, 137.41, 136.84, 135.76, 134.05, 130.23, 128.54, 127.84, 127.53, 126.46, 125.98, 123.57, 122.67, 111.49, 111.44, 110.59, 103.63, 92.90, 70.65. HRMS (ESI) m/z: $[M+H]^+$calcd for $C_{21}H_{16}NOS$ 330.0947, found 330.0947.



2j

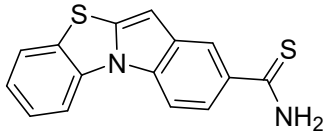
2-chlorobenzo[4,5]thiazolo[3,2-a]indole (**2j)**. White solid, obtained in 5 h and purified by chromatography on silica gel (petroleum ether); yield: 77%, 79.2 mg, m.p. 129-131 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86-7.78 (m, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.43-7.37 (m, 1H), 7.25-7.16 (m, 2H), 6.47 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.84, 135.42, 134.25, 130.36, 129.36, 127.12, 126.11, 123.69, 123.27, 120.44, 119.35, 111.90, 111.53, 92.70. HRMS (ESI) m/z: $[M+H]^+$calcd for $C_{14}H_9ClNS$ 258.0139, found 258.0141.



2k

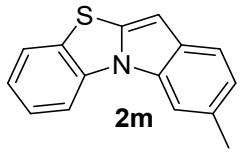
2-fluorobenzo[4,5]thiazolo[3,2-a]indole (**2k)**. White solid, obtained in 5 h and purified by chromatography on silica gel (petroleum ether); yield: 83%, 80.3 mg, m.p. 110-112 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89-7.82 (m, 2H), 7.59 (d, J = 7.5 Hz, 1H), 7.44-7.39 (m, 1H), 7.29 (dd, J_1 = 2.5 Hz, J_2 = 9.5 Hz, 1H), 7.25-7.19 (m, 1H), 7.03-6.96 (m, 1H), 6.51(s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.62 (d, $J_{C\text{-}F}$ = 235.6 Hz), 138.07, 135.56, 133.93 (d, $J_{C\text{-}F}$ = 10.4 Hz), 130.24, 127.74, 126.09, 123.68,

123.07, 111.62, 111.30 (d, $J_{C\text{-}F}$ = 9.9 Hz), 108.34 (d, $J_{C\text{-}F}$ = 26.0 Hz), 105.14 (d, $J_{C\text{-}F}$ = 23.9 Hz), 93.11 (d, $J_{C\text{-}F}$ = 4.3 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_9FNS$ 242.0434, found 242.0434.



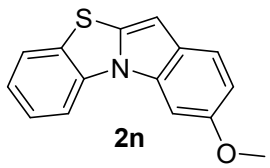
2l

benzo[4,5]thiazolo[3,2-a]indole-2-carbothioamide (**2l)**. Yellow solid, obtained in 12 h (**1l** was consumed completely and polysulfide intermediates were observed) and purified by chromatography on silica gel (PE:EA=2:1); yield:44%, 50.0 mg, m.p. 201-203 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.97 (d, J = 9.0 Hz, 2H), 7.89-7.84 (m, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.60 (s, 1H), 7.50-7.46 (m, 1H), 7.32-7.27 (m, 2H), 6.66 (s, 1H). ^{13}C NMR (125 MHz, DMSO) δ 200.84, 137.78, 135.03, 133.26, 132.39, 132.24, 130.38, 127.25, 124.87, 124.59, 121.13, 120.10, 113.30, 110.97, 95.05. HRMS (ESI) m/z: $[M+H]^+$calcd for Chemical Formula: $C_{15}H_{11}N_2S_2$ 283.0358, found 283.0352.



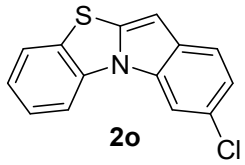
2m

3-methylbenzo[4,5]thiazolo[3,2-a]indole (**2m)**. Light yellow solid, obtained in 5 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 10:1); yield: 88%, 83.2 mg, m.p. 88-90 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 8.0 Hz, 1H), 7.74 (s, 1H), 7.53-7.50 (m, 2H), 7.39-7.35 (m, 1H), 7.20-7.07 (m, 2H), 6.47 (s, 1H), 2.55 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.86, 135.26, 131.45, 131.08, 130.51, 130.17, 125.83, 123.47, 123.01, 122.74, 119.54, 111.86, 111.04, 92.86, 21.90. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{12}NS$ 238.0685, found 238.0686.



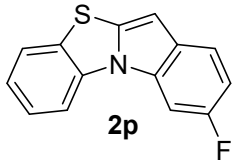
2n

3-methoxybenzo[4,5]thiazolo[3,2-a]indole (**2n**). Yellow solid, obtained in 5 h and purified by chromatography on silica gel (petroleum ether); yield: 88%, 89.6 mg, m.p. 94-96 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 9.0 Hz, 1H), 7.48 (d, *J* = 2.5 Hz, 1H), 7.44-7.39 (m, 1H), 7.23-7.18 (m, 1H), 6.98-6.92 (m, 1H), 6.48 (s, 1H), 3.95 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.09, 135.75, 134.46, 131.54, 130.70, 127.57, 125.84, 123.59, 122.92, 120.37, 111.76, 110.31, 96.05, 92.81, 56.03. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{12}NOS$ 254.0634, found 254.0634.



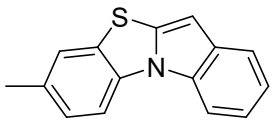
2o

3-chlorobenzo[4,5]thiazolo[3,2-a]indole (**2o**). Yellow solid, obtained in 5 h and purified by chromatography on silica gel (petroleum ether); yield: 68%, 70.3 mg, m.p. 150-152 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 6.5 Hz, 1H), 7.53 (d, *J* = 8.5 Hz, 1H), 7.46-7.40 (m, 1H), 7.27-7.20 (m, 2H), 6.52 (s, 1H) . ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.96, 135.31, 131.70, 131.05, 130.46, 126.18, 126.14, 123.70, 123.43, 122.01, 120.59, 112.03, 110.98, 93.10. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_9ClNS$ 258.0139, found 258.0145.



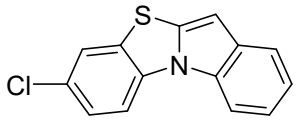
2p

3-fluorobenzo[4,5]thiazolo[3,2-a]indole (**2p**). Yellow solid, obtained in 5 h and purified by chromatography on silica gel (petroleum ether); yield: 76%, 73.2 mg, m.p. 129-131 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.67-7.62 (m, 1H), 7.59-7.51 (m, 2H), 7.44-7.38 (m, 1H), 7.25-7.19 (m, 1H), 7.07-7.00 (m, 1H), 6.51 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.43 (d, J_{C-F} = 236.3 Hz), 136.20 (d, J_{C-F} = 3.3 Hz), 135.34, 130.52, 130.34 (d, J_{C-F} = 12.0 Hz), 129.60, 126.02, 123.66, 123.30, 120.39 (d, J_{C-F} = 9.8 Hz), 111.82, 109.84 (d, J_{C-F} = 23.9 Hz), 97.97 (d, J_{C-F} = 27.4 Hz), 92.95. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_9FNS$ 242.0434, found 242.0438.



2q

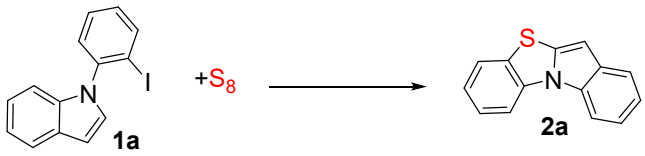
8-methylbenzo[4,5]thiazolo[3,2-a]indole (**2q)**. Yellow solid, obtained in 5 h and purified by chromatography on silica gel (petroleum ether); yield: 81%, 76.7 mg, m.p. 80-82 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94-7.90 (m, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.66-7.61 (m, 1H), 7.34 (s, 1H), 7.27-7.22 (m, 2H), 7.16 (d, *J* = 8.5 Hz, 1H), 6.52 (s, 1H), 2.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.28, 133.70, 133.13, 132.82, 130.98, 130.51, 126.68, 123.86, 121.19, 120.22, 119.91, 111.52, 110.73, 92.77, 21.05. HRMS (ESI) m/z: $[M+H]^+$calcd for $C_{15}H_{12}NS$ 238.0685, found 238.0687.



2r

8-chlorobenzo[4,5]thiazolo[3,2-a]indole (**2r)**. Yellow solid, obtained in 5 h (**1r** was consumed completely and polysulfide intermediates were observed) and purified by chromatography on silica gel (petroleum ether); yield: 50%, 50.9 mg, m.p. 118-120 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93-7.89 (m, 1H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.68-7.64 (m, 1H), 7.56 (d, *J* = 2.4 Hz, 1H), 7.40-7.37 (m, 1H), 7.30-7.27 (m, 2H), 6.57 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.83, 134.51, 133.23, 132.22, 130.97, 128.20, 126.10, 123.35, 121.71, 120.75, 120.22, 112.27, 110.68, 93.63. HRMS (ESI) m/z: $[M+H]^+$calcd for $C_{14}H_9ClNS$ 258.0137, found 258.0133.

4. Table S1. Optimization of the Reaction Conditions[a]

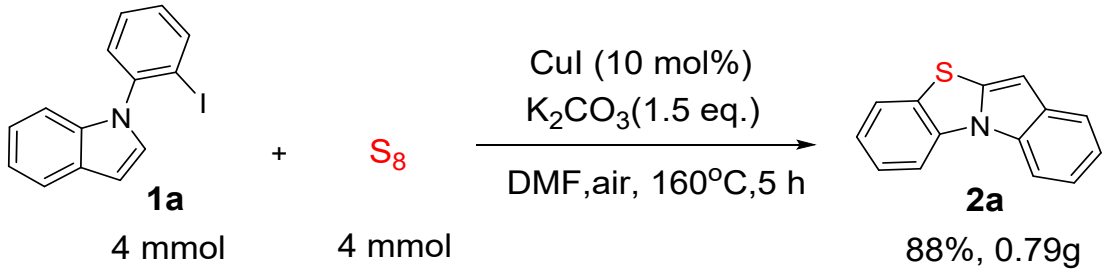


1a **2a**

entry	1a:S_8	base (equiv.)	[Cu]	solvent	*t* (h)	yield (%)
1	1:1.5	K_2CO_3(2)	-	DMF	3	19
2	1:1.5	K_2CO_3(2)	CuI	DMF	3	90
3	1:1.5	-	CuI	DMF	3	NP
4	1:1.5	K_2CO_3(2)	CuBr	DMF	3	89
5	1:1.5	K_2CO_3(2)	CuCl	DMF	3	85
6	1:1.5	K_2CO_3(2)	$CuCl_2$	DMF	3	81
7	1:1.5	Et_3N(2)	CuI	DMF	3	32
8	1:1.5	K_3PO_4(2)	CuI	DMF	3	9
9	1:1.5	K_2CO_3(2)	CuI	DMSO	3	trace
10	1:1.5	K_2CO_3(2)	CuI	toluene	3	NR
11	1:1.5	K_2CO_3(2)	CuI	1,4-dioxane	3	NR
12	1:1.3	K_2CO_3(2)	CuI	DMF	3	90
13	1:1	K_2CO_3(2)	CuI	DMF	3	89
14	1:1	K_2CO_3(1.5)	CuI	DMF	4	90
15	1:1	K_2CO_3(1)	CuI	DMF	7	86
16[b]	**1:1**	**K_2CO_3(1.5)**	**CuI**	**DMF**	**5**	**93**
17[c]	1:1	K_2CO_3(1.5)	CuI	DMF	10	85
18[b,d]	1:1	K_2CO_3(1.5)	CuI	DMF	9	55
19[b,e]	1:1	K_2CO_3(1.5)	CuI	DMF	5	83
20[b,f]	1:1	K_2CO_3(1.5)	CuI	DMF	5	NP

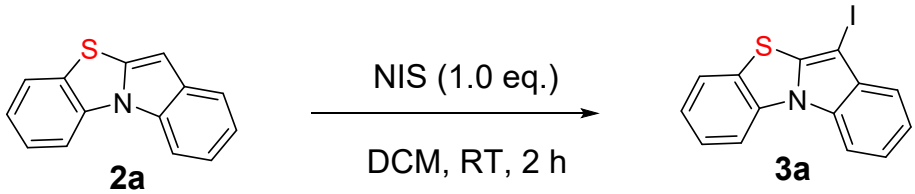
[a]Reaction conditions: **1a** (0.4 mmol), S_8 (0.4 mmol), [Cu] (20 mol%), base (0.6 mmol), solvent (4.0 mL), 160°C, air, isolated yields. [b][Cu] (10 mol%). [c][Cu] (5 mol%). [d]140°C. [e]N_2 balloon. [f]O_2 balloon. NR= no reaction. NP = no desired product.

5. Gram scales



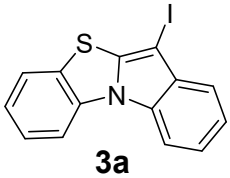
In a sealed tube, 1-(2-iodophenyl)-1H-indole **1a** (4.0 mmol, 1276.6 mg), S_8 (4.0 mmol, 1026.1 mg), K_2CO_3 (6.0 mmol, 829.3 mg), CuI (0.4 mmol, 76.2 mg) and DMF (40.0 mL) were stirred at 160 °C under air. After 5 h, the reaction mixture was cooled to room temperature and was treated with H_2O, then extracted with EA and washed the organic phase twice with saturated aqueous ammonium chloride solution. After the organic phase was dried with anhydrous Na_2SO_4 and concentrated, the residue was purified by chromatography on silica gel (PE) to afford **2a** (yellow-green solid, 785.9 mg, 88%).

6. Transformations of benzo[4,5]thiazolo[3,2-a]indole 2a



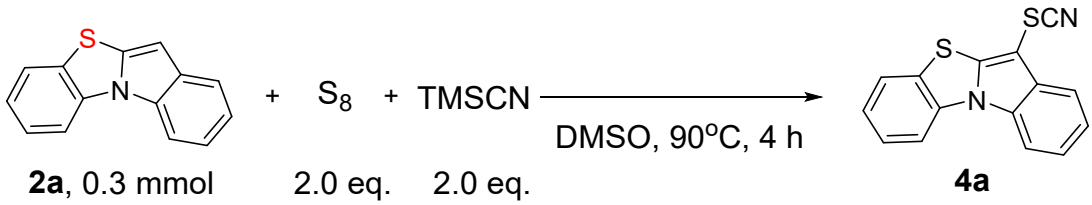
According to the method in reference 3, we synthesized **3a**. To a stirred solution of **2a** (67.0 mg, 0.3 mmol) in DCM (2.0 mL) at room temperature was added N-iodosuccinimide (NIS: 67.5 mg, 0.3 mmol). The reaction mixture was further stirred for 2 h at room temperature. After the reaction was completed as monitored by thin-layer chromatography, added 5 ml of DCM to the reaction system to dilute, and quench with saturated sodium bicarbonate solution. After the aqueous phase was

extracted with DCM, the organic phases were combined and dried over anhydrous Na_2SO_4. After removal of the DCM, the residue was purified by chromatography on silica gel (PE) to afford **3a** (white solid, 95.4 mg, 91%).



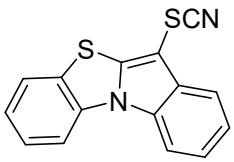
3a

11-iodobenzo[4,5]thiazolo[3,2-a]indole **(3a)**. White solid, purified by chromatography on silica gel (petroleum ether); yield: 91%, 95.4 mg, m.p. 165-167 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90-7.85 (m, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.47-7.38 (m, 2H), 7.35-7.27 (m, 2H), 7.25-7.19 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.20, 136.39, 134.47, 131.55, 129.18, 126.23, 123.90, 123.32, 122.12, 121.46, 120.01, 112.10, 110.91, 46.06. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_9INS$ 349.9495, found 349.9499.



2a, 0.3 mmol 2.0 eq. 2.0 eq. **4a**

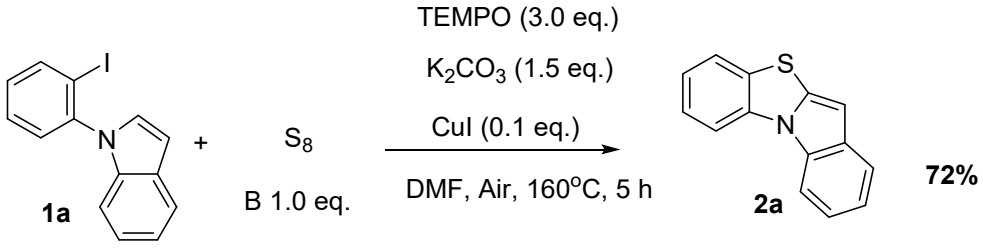
According to the method in reference 4, we synthesized **4a**. To the DMSO (3 ml) solvent containing 2a (67.0, 0.3 mmol) and sulfur (153.9 mg, 0.6 mmol), added TMSCN (75 μl, 0.6 mmol), and then stirred at 90 °C for 4 h. After the reaction was completed, diluted with EA, and added saturated ammonium chloride aqueous solution to quench. After the organic phase was washed twice with saturated ammonium chloride and dried with anhydrous Na_2SO_4, the organic phase was concentrated in vacuo. Then the residue was purified by chromatography on silica gel (PE:EA=50:1~PE:EA=10:1) to afford **4a** (yellow-green solid,57.7 mg, 69%).



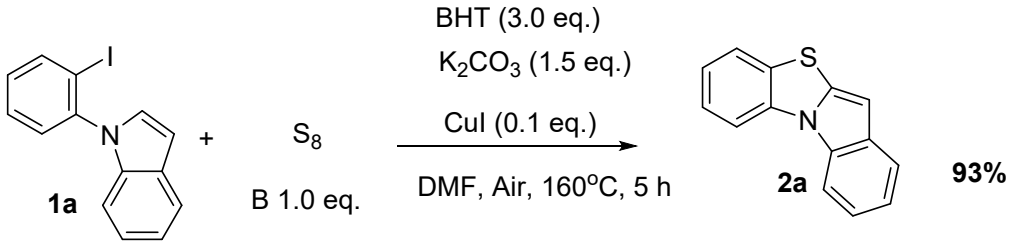
4a

11-thiocyanatobenzo[4,5]thiazolo[3,2-a]indole **(4a)**. Yellow solid, purified by chromatography on silica gel (PE:EA=50:1~PE:EA=10:1); yield: 69%, 57.7 mg, m.p. 170-172 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88-7.81 (m, 2H), 7.73 (d, *J* = 7.5 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.47-7.41 (m, 1H), 7.39-7.29 (m, 2H), 7.29-7.24 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.18, 135.51, 132.68, 131.67, 129.44, 126.71, 124.16, 123.94, 123.13, 122.20, 118.08, 112.80, 111.42, 110.28, 80.64. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_9N_2S_2$ 281.0202, found 281.0204.

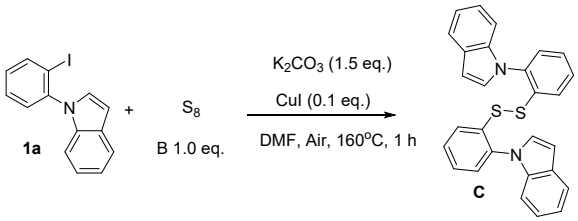
7. Control Experiment.



In a sealed tube, indole iodobenzenes **1a** (0.4 mmol), S_8 (0.4 mmol, 102.6 mg), CuI (0.04 mmol, 7.6 mg), K_2CO_3 (0.6 mmol, 82.9 mg), TEMPO (1.2 mmol, 187.5 mg) and DMF (4.0 mL) were stirred at 160 °C (oil bath) under air. After 5 hours of reaction, the reaction mixture was then quenched by water, and the water layers were extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4. After removal of the EA, the residue was purified by chromatography on silica gel (PE) to afford **2a** in 72%.



In a sealed tube, indole iodobenzenes **1a** (0.4 mmol), S_8 (0.4 mmol, 102.6 mg), CuI (0.04 mmol, 7.6 mg), K_2CO_3 (0.6 mmol, 82.9 mg), BHT (1.2 mmol, 187.5 mg) and DMF (4.0 mL) were stirred at 160 °C (oil bath) under air. After 5 hours of reaction, the reaction mixture was then quenched by water, and the water layers were extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4. After removal of the EA, the residue was purified by chromatography on silica gel (PE) to afford **2a** in 93%.



In a sealed tube, indole iodobenzenes **1a** (0.4 mmol), S_8 (0.4 mmol, 102.6 mg), CuI (0.04 mmol, 7.6 mg), K_2CO_3 (0.6 mmol, 82.9 mg) and DMF (4.0 mL) were stirred at 160 °C (oil bath) under air. After 1 hour of reaction, the reaction mixture was then quenched by water, and the water layers were extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4. After removal of the EA, a sample was extracted from the reaction mixture for ESI-MS analysis.

Mass Spectrum List Report

Analysis Info

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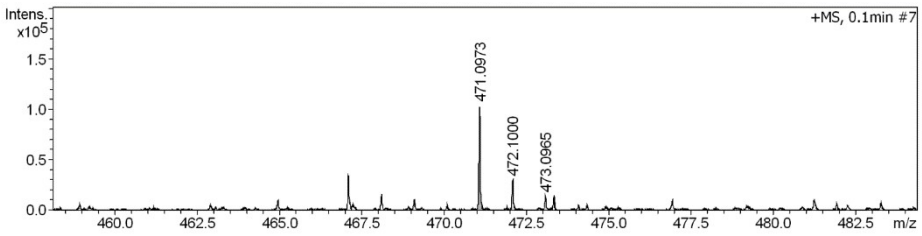
Sample Name	WZK-5-28	Instrument	maXis impact 282001.00122
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I %	FWHM
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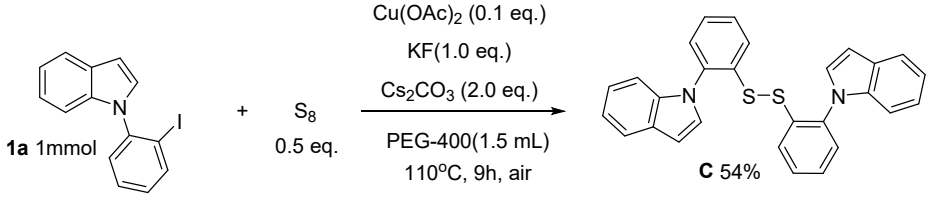
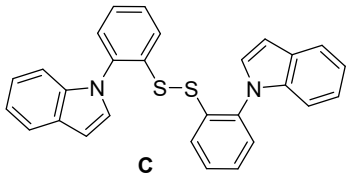
2	472.1000	13706	28.5	28920	28.2	0.0344
3	473.0965	10946	13.1	13332	13.0	0.0432

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma		Score	rdb	e⁻ Conf	N-Rule
471.0973	1	C28H20N2NaS2	471.0960	-2.7	22.1	3	100.00	19.5	even	ok

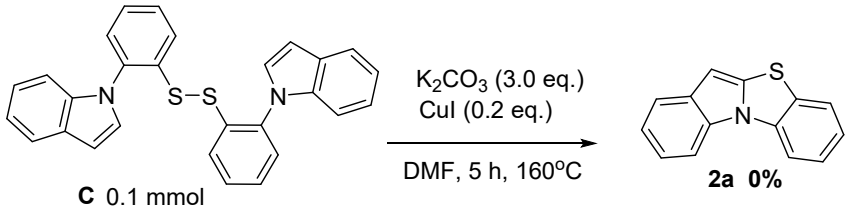


In a sealed tube, indole iodobenzenes **1a** (1.0 mmol), S_8 (0.5 mmol, 128.3 mg), $Cu(OAc)_2$ (0.1 mmol, 20.0 mg), Cs_2CO_3 (2.0 mmol, 651.6 mg), KF (1.0 mmol, 58.1 mg) and PEG-400 (1.5 mL) were stirred at 110 °C (oil bath) under air. After 8 hour of reaction, the reaction mixture was then quenched by water, and the water layers were extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4. After removal of the EA, the residue was purified by chromatography on silica gel (PE~PE:EA=100:1) to afford **C** in 54%.



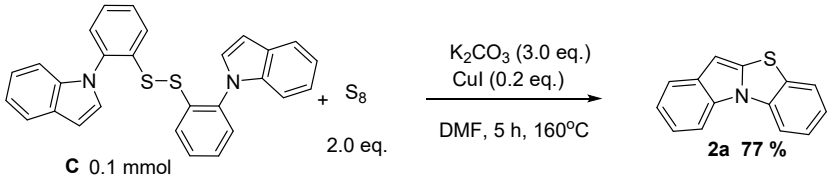
C

1,2-bis(2-(1H-indol-1-yl)phenyl)disulfane **(C)**. Yellow oil, purified by chromatography on silica gel (PE~PE:EA=100:1); yield: 54%, 120.8 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72-7.68 (m, 2H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.35-7.26 (m, 6H), 7.19-7.15 (m, 4H), 7.14-7.10 (m, 2H), 7.04-6.99 (m, 2H), 6.69 (d, *J* = 3.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.18, 137.03, 135.18, 129.05, 128.89, 128.62, 128.47, 128.43, 127.77, 122.34, 120.99, 120.38, 110.46, 103.40. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{28}H_{20}N_2NaS_2$ 471.0960, found 471.0973.



C 0.1 mmol **2a 0%**

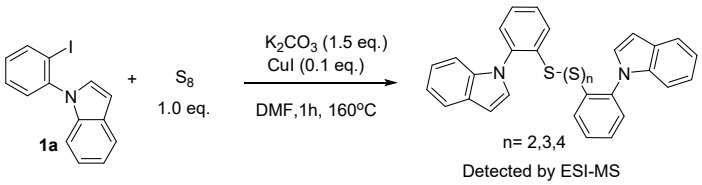
In a sealed tube, **C** (0.1 mmol, 44.9 mg), CuI (0.02 mmol, 3.8 mg), K_2CO_3 (0.3 mmol, 41.5 mg) and DMF (2.0 mL) were stirred at 160 °C (oil bath) under air. After 1 hour of reaction, the reaction mixture was then quenched by water.



C 0.1 mmol **2a 77 %**

In a sealed tube, **C** (0.1 mmol, 44.9 mg), CuI (0.02 mmol, 3.8 mg), K_2CO_3 (0.3 mmol, 41.5 mg) and DMF (2.0 mL) were stirred at 160 °C (oil bath) under air. After 5 hours of reaction, the reaction mixture was then quenched by water, and the water layers were extracted with ethyl acetate (15 mL × 3). The combined organic layers were

washed with brine, dried over anhydrous Na_2SO_4. After removal of the EA, the residue was purified by chromatography on silica gel (PE) to afford **2a** in 77% yield.



In a sealed tube, indole iodobenzenes **1a** (0.4 mmol), S_8 (0.4 mmol, 102.6 mg), CuI (0.04 mmol, 7.6 mg), K_2CO_3 (0.6 mmol, 82.9 mg) and DMF (4.0 mL) were stirred at 160 °C (oil bath) under air. After 1 hour of reaction, the reaction mixture was then quenched by water, and the water layers were extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4. After removal of the EA, a sample was extracted from the reaction mixture for ESI-MS analysis.

ESI-MS analysis result of trisulfide.

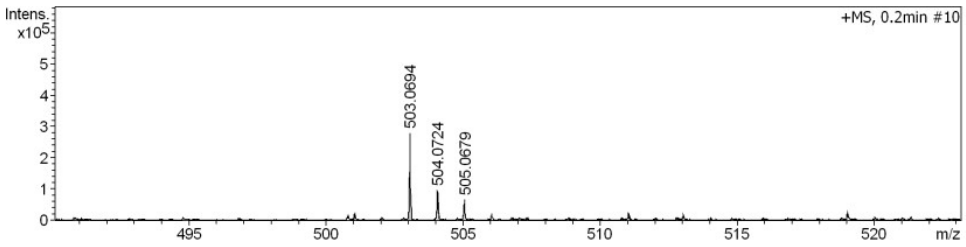
Mass Spectrum List Report

Analysis Info

Analysis Name	D:\Data\chem. dep\liyanzhong\WZK-DSZJT_P1-F-6_01_35224.d	Acquisition Date	10/28/2022 2:53:10 PM
Method	Tune_pos_low_LC with calibration_2min_20210727.m	Operator	ECNU-Chem
Sample Name	WZK-DSZJT	Instrument	maXis impact 282001.00122
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I %	FWHM
1	503.0694	16065	177.6	277608	100.0	0.0313
2	504.0724	13102	61.6	96156	34.6	0.0385
3	505.0679	13505	41.9	65392	23.6	0.0374

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma		Score	rdb	e¯ Conf	N-Rule
503.0694	1	C28H20N2NaS3	503.0681	-2.7	25.3	1	100.00	19.5	even	ok

ESI-MS analysis result of tetrasulfide.

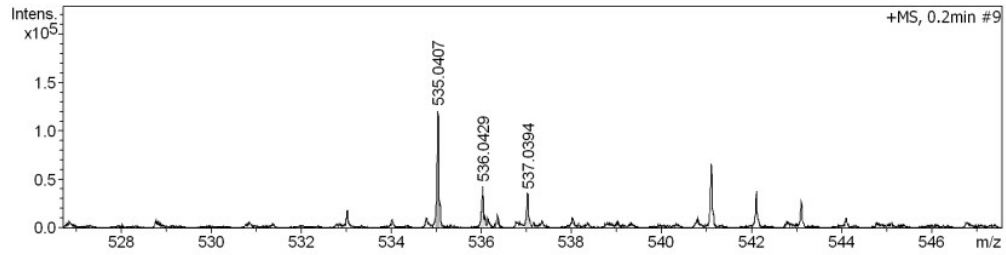
Mass Spectrum List Report

Analysis Info

Analysis Name	D:\Data\chem. dep\liyanzhong\WZK-DSZJT_P1-F-6_01_35224.d	Acquisition Date	10/28/2022 2:53:10 PM
Method	Tune_pos_low_LC with calibration_2min_20210727.m	Operator	ECNU-Chem
Sample Name	WZK-DSZJT	Instrument	maXis impact 282001.00122
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I %	FWHM
1	535.0407	13801	80.8	120804	100.0	0.0388
2	536.0429	13402	28.4	42336	35.0	0.0400
3	537.0394	11327	23.7	35236	29.2	0.0474

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma		Score	rdb	e¯ Conf	N-Rule
535.0407	1	C28H20N2NaS4	535.0402	-1.0	27.8	1	100.00	19.5	even	ok

ESI-MS analysis result of pentasulfide.

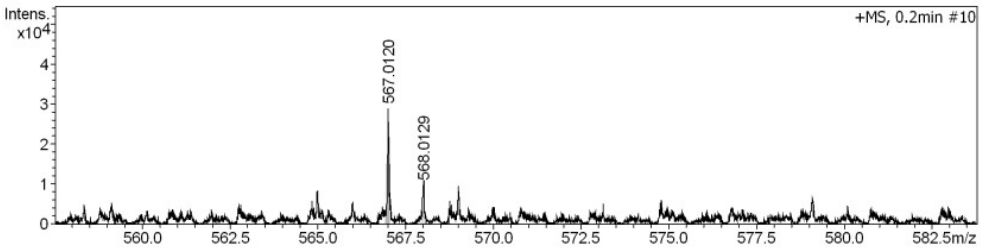
Mass Spectrum List Report

Analysis Info

Analysis Name	D:\Data\chem. dep\liyanzhong\WZK-DSZJT_P1-F-6_01_35224.d	Acquisition Date	10/28/2022 2:53:10 PM
Method	Tune_pos_low_LC with calibration_2min_20210727.m	Operator	ECNU-Chem
Sample Name	WZK-DSZJT	Instrument	maXis impact 282001.00122
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I %	FWHM
1	567.0120	14036	21.6	28812	100.0	0.0404
2	568.0129	12267	7.3	9752	33.8	0.0463

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma		Score	rdb	e¯ Conf	N-Rule
567.0120	1	C28H20N2NaS5	567.0122	0.5	35.1	1	100.00	19.5	even	ok

8. References

1. a) M. J. Sun, X. Y. Chen, Z. C. Feng, G. B. Deng, Y. Yang, Y. Liang, *Org. Chem. Front.*, **2021**, *8*, 6535; b) M. Elsherbini, W. J. Moran, *Org. Biomol. Chem.*, **2021**, *19*, 4706; c) R. X. Liu, Q. Wang, Y. Wei, M. Shi, *Chem. Commun.*, **2018**, *54*, 1225; d) H. H. Liu, T. T. Duan, Z. Y. Zhang, C. X. Xie, C. Ma, *Org. Lett.* **2015**, *17*, 2932; e) K. Naveen, S. A. Nikson, P. T. Perumal, *Adv. Synth. Catal.***2017**,*359*, 2407; f) A. K. Verma, J. Singh, R. C. Larock, *Tetrahedron.* **2009**, *65*, 8434

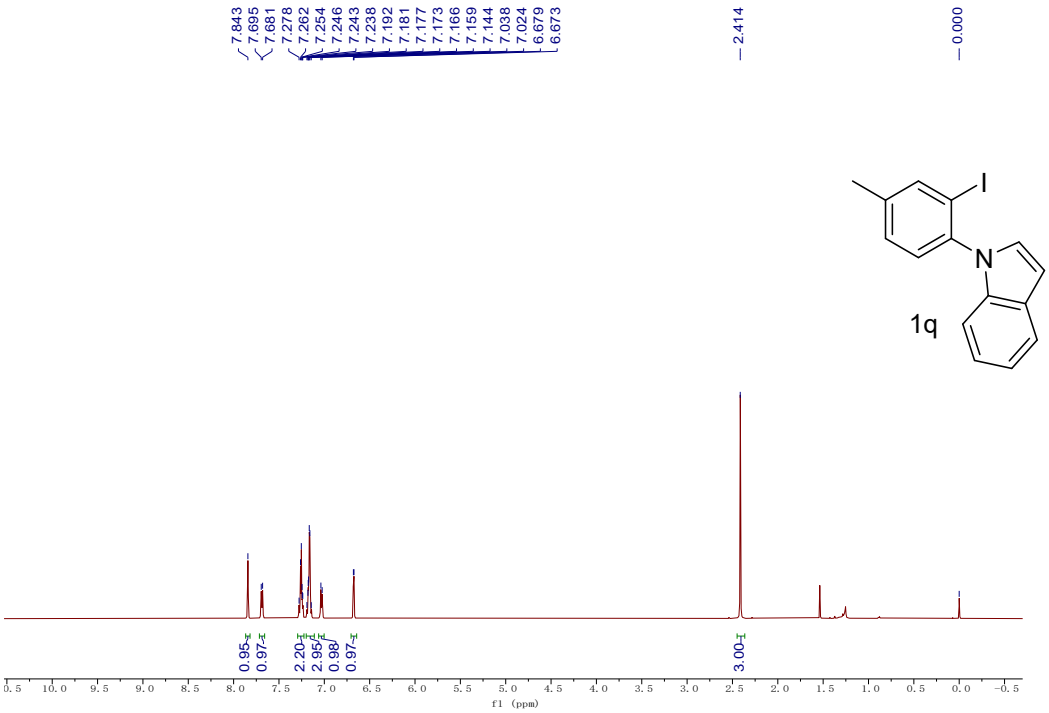
2. T. F. Yao, T. Xia, W. Yan, H. F. Xu, F. Zhang, Y. J. Xiao, J. L. Zhang, L. Liu, *Org. Lett.* **2020**, *22*, 4511.

3. U. K. Bandarage, C. M. Bligh, D. Boucher, M. J. Boyd, M. A. Brodney, M. P. Clark, V. Damagnez, L. T. D. Fanning, R. F. Fimognari, G. S. Fleming, CN 114096542.

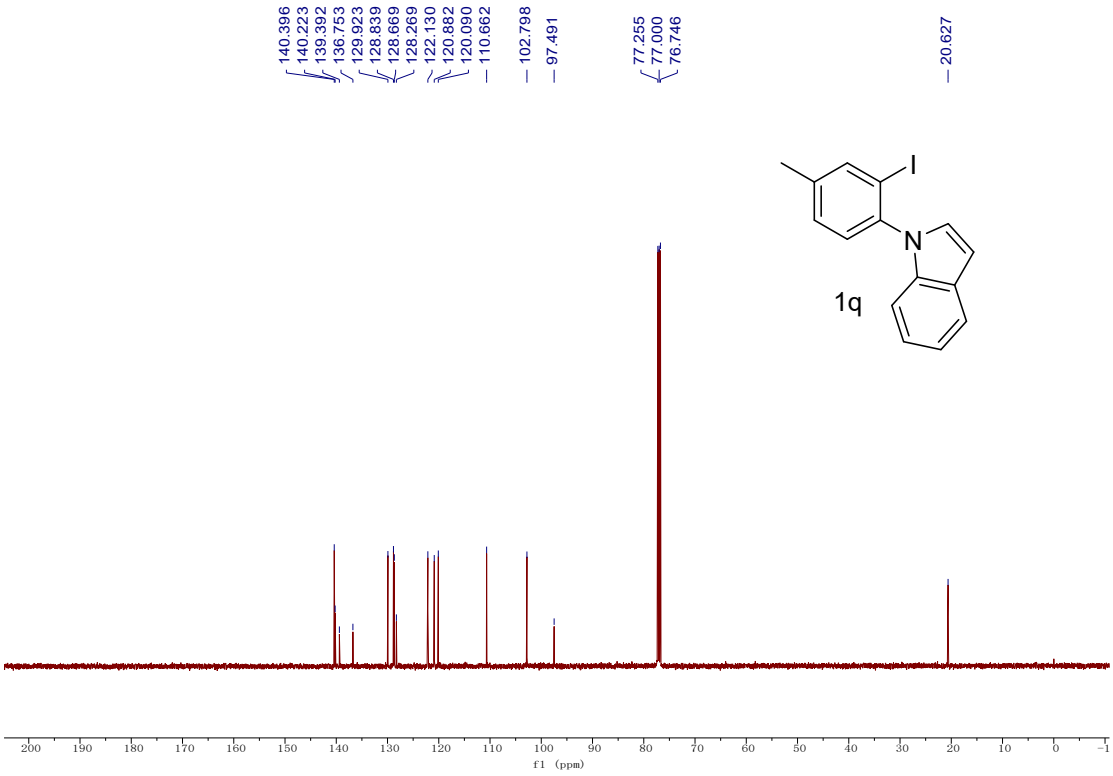
4. C. T. Feng, Y. Peng, G. R. Ding, X. X. Li, C. Cui and Y. Z. Yan, *Chem. Commun.* **2018**, *54*, 13367

9.Copies of spectra of products.

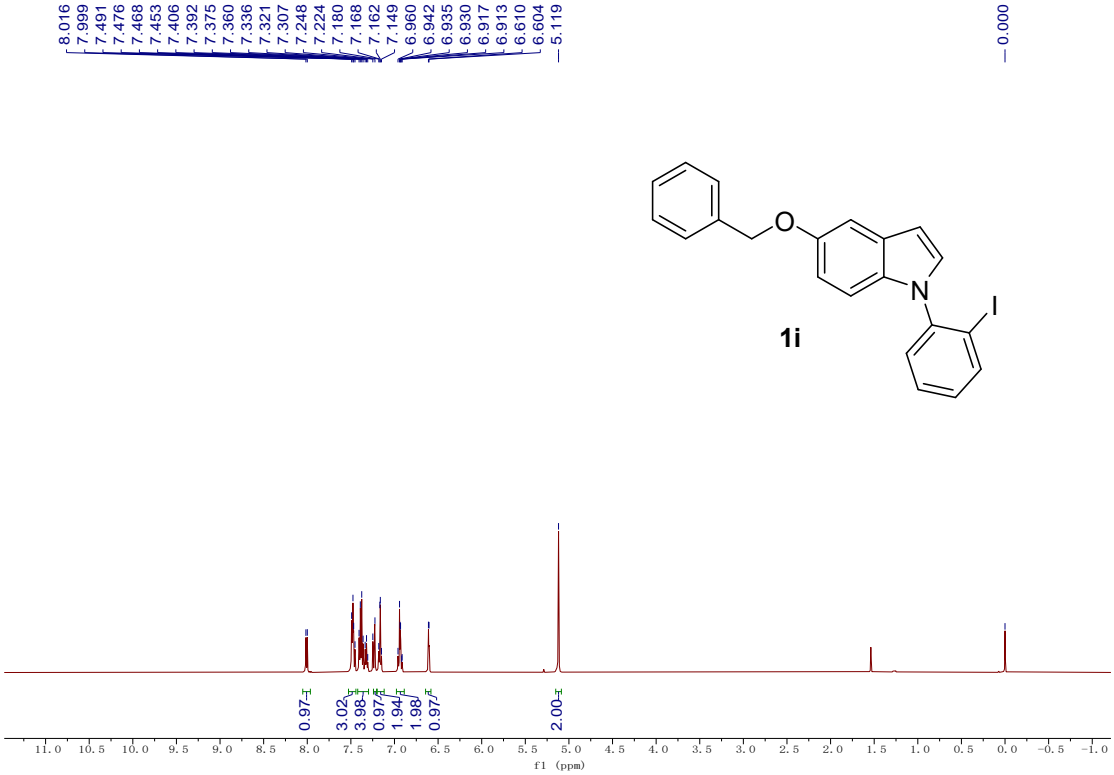
^{1}H NMR (500 MHz, $CDCl_3$)



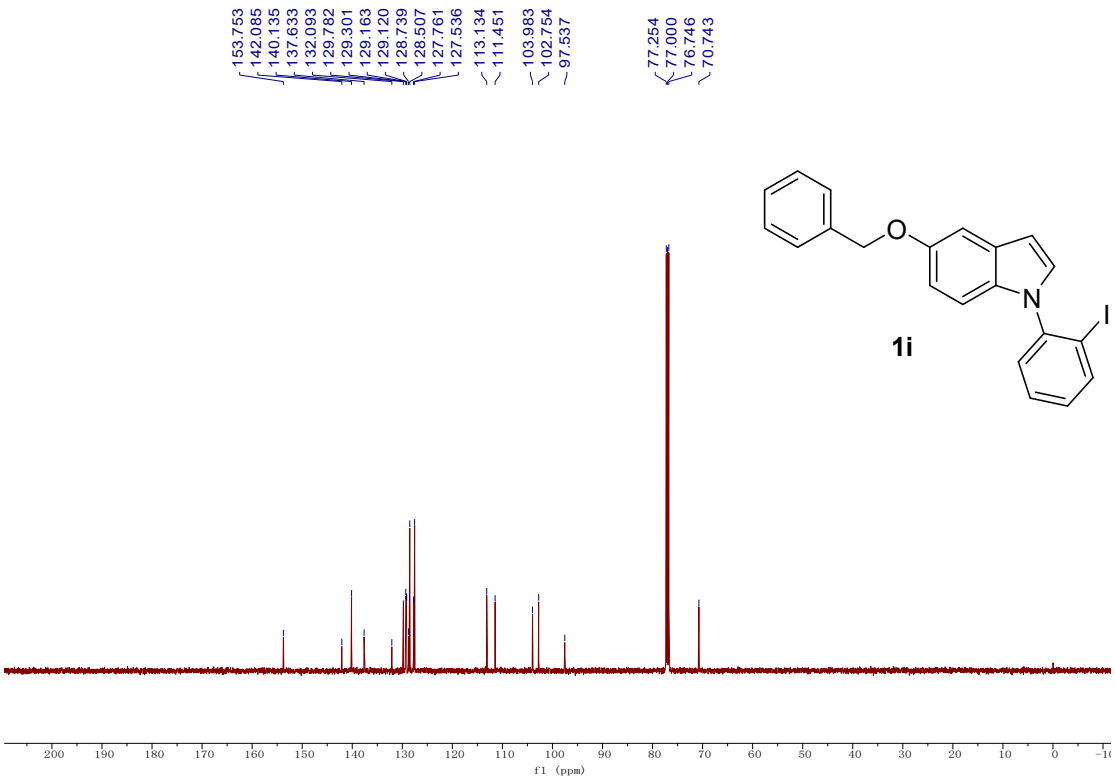
^{13}C NMR (125 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



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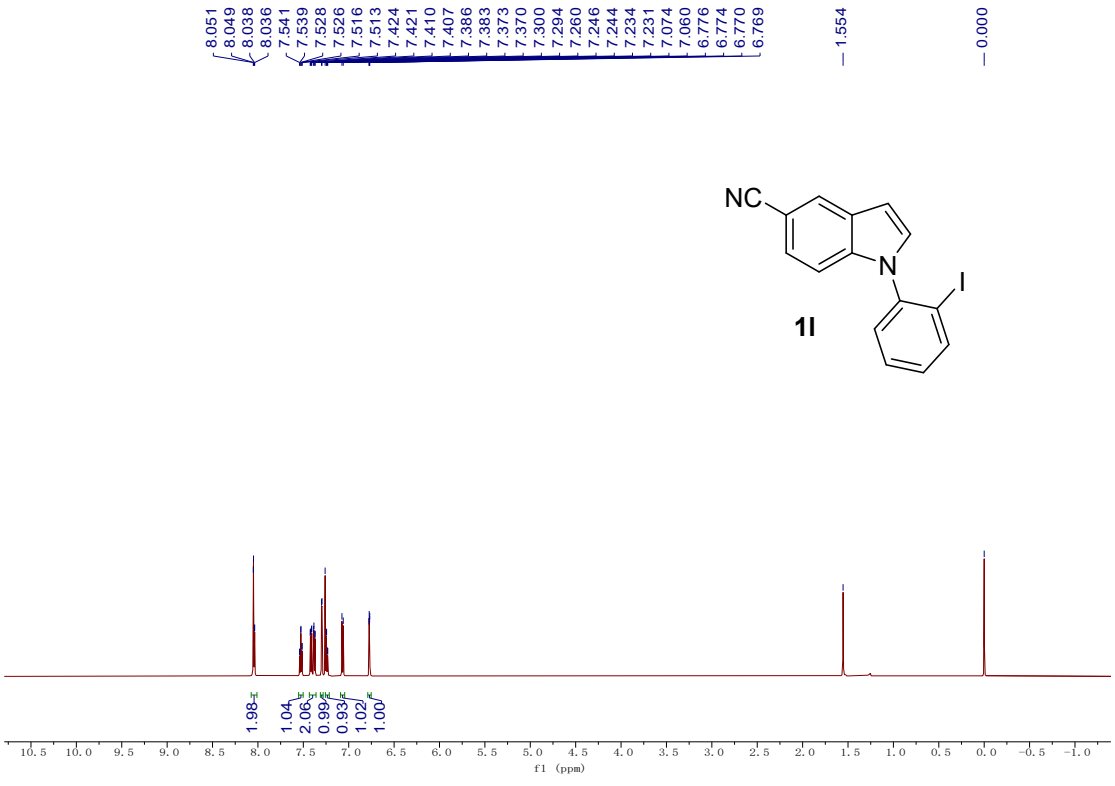

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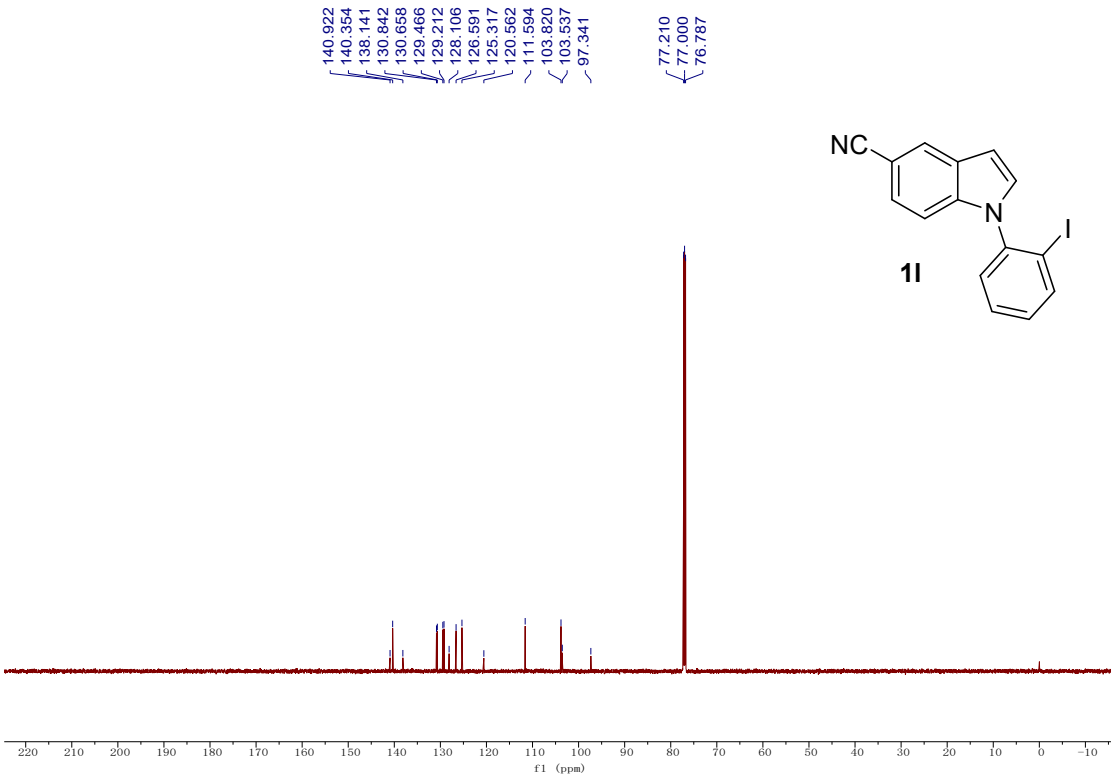

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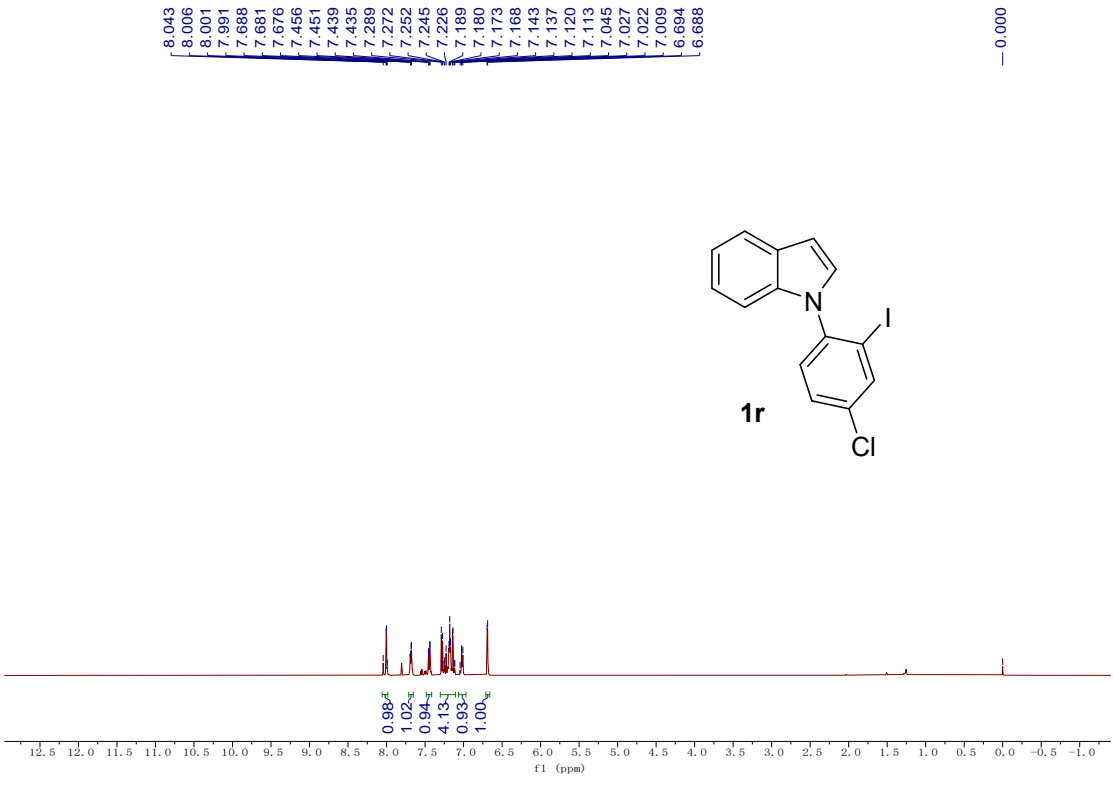

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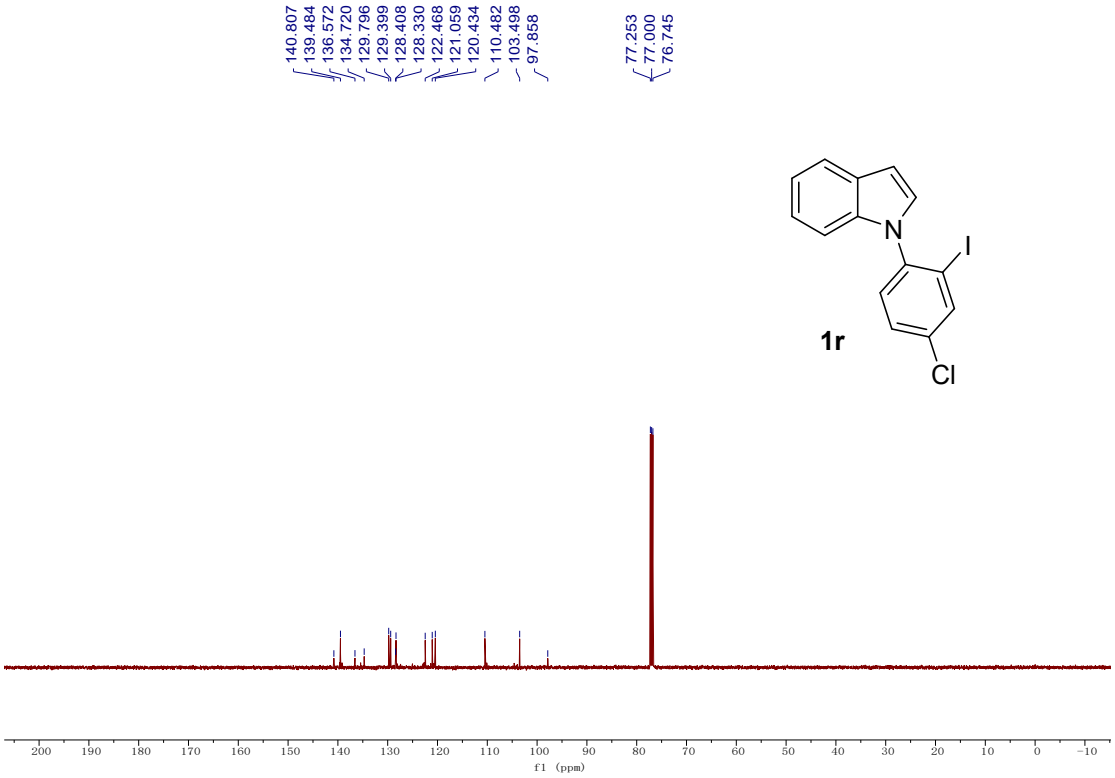

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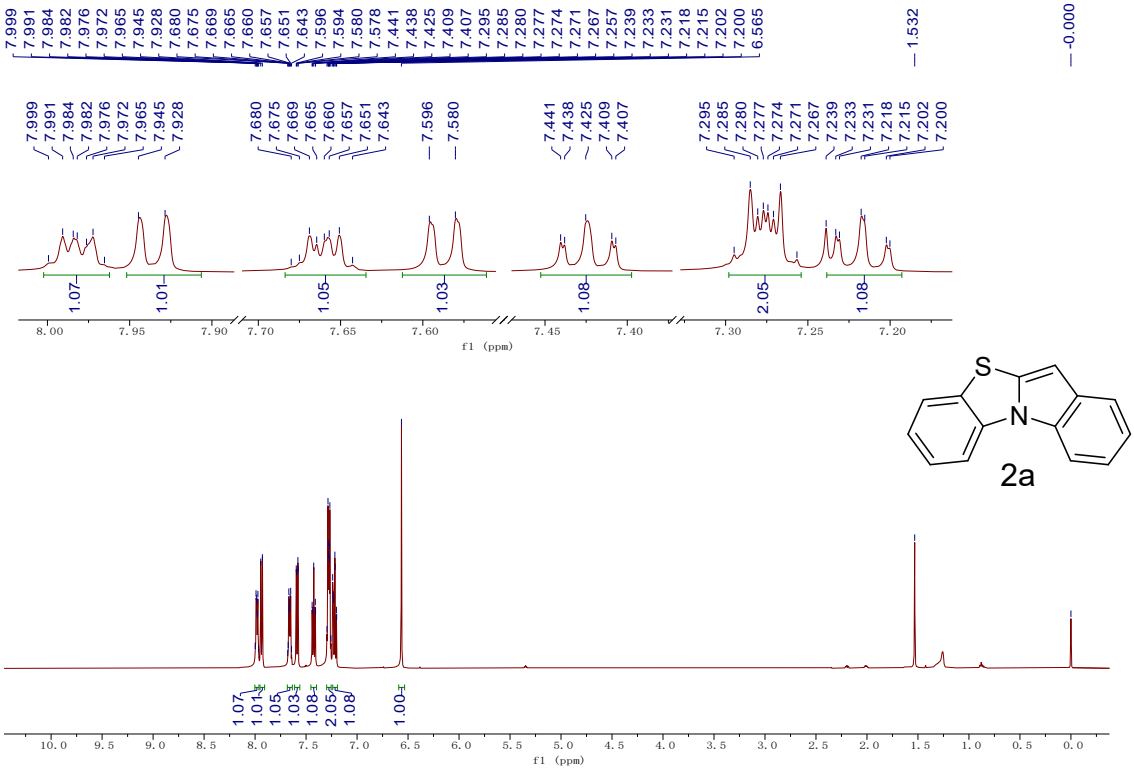

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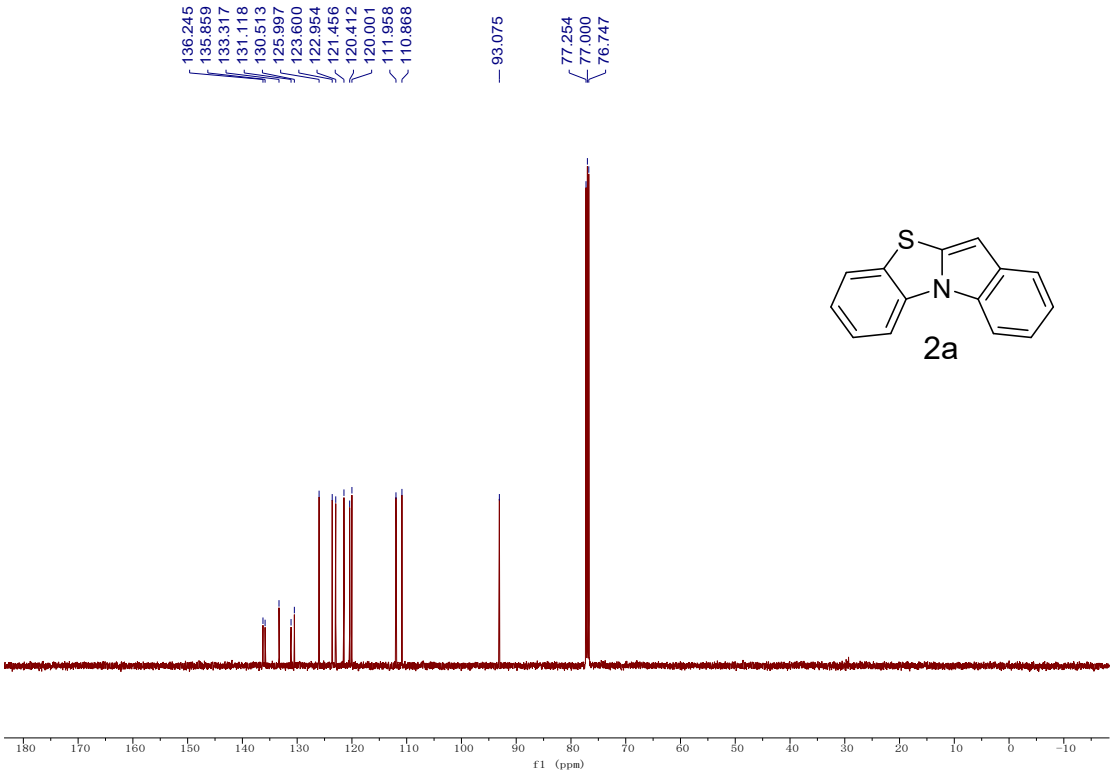

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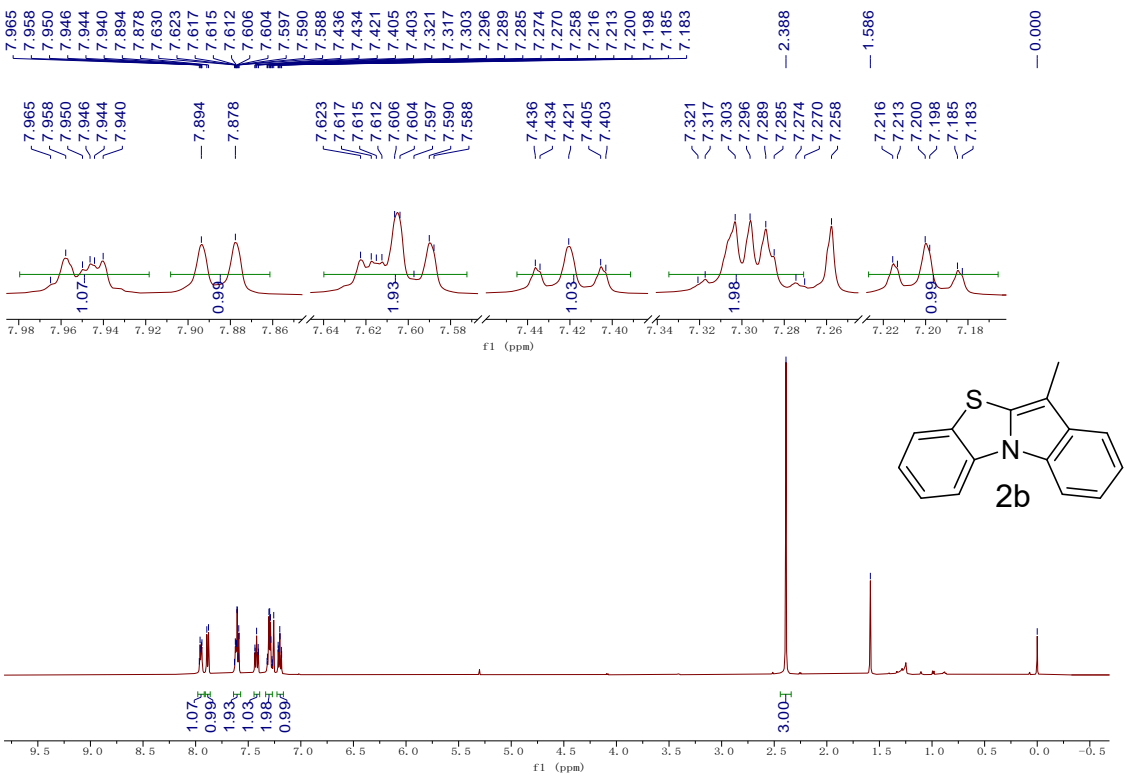

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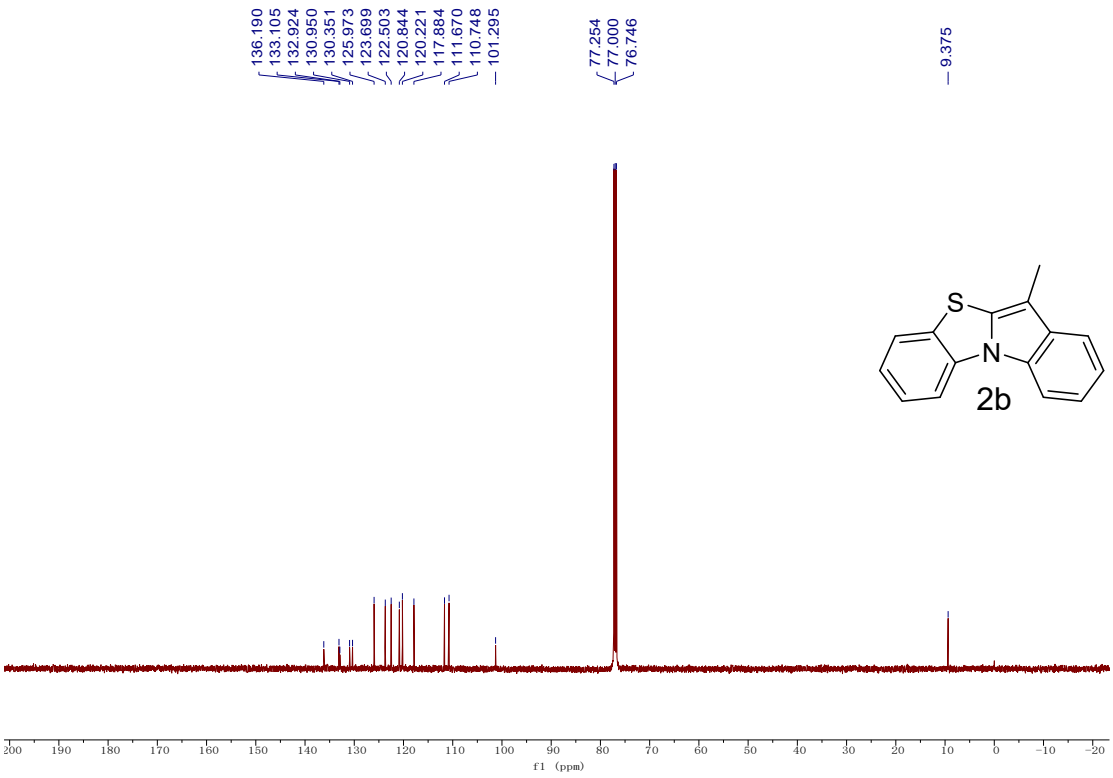

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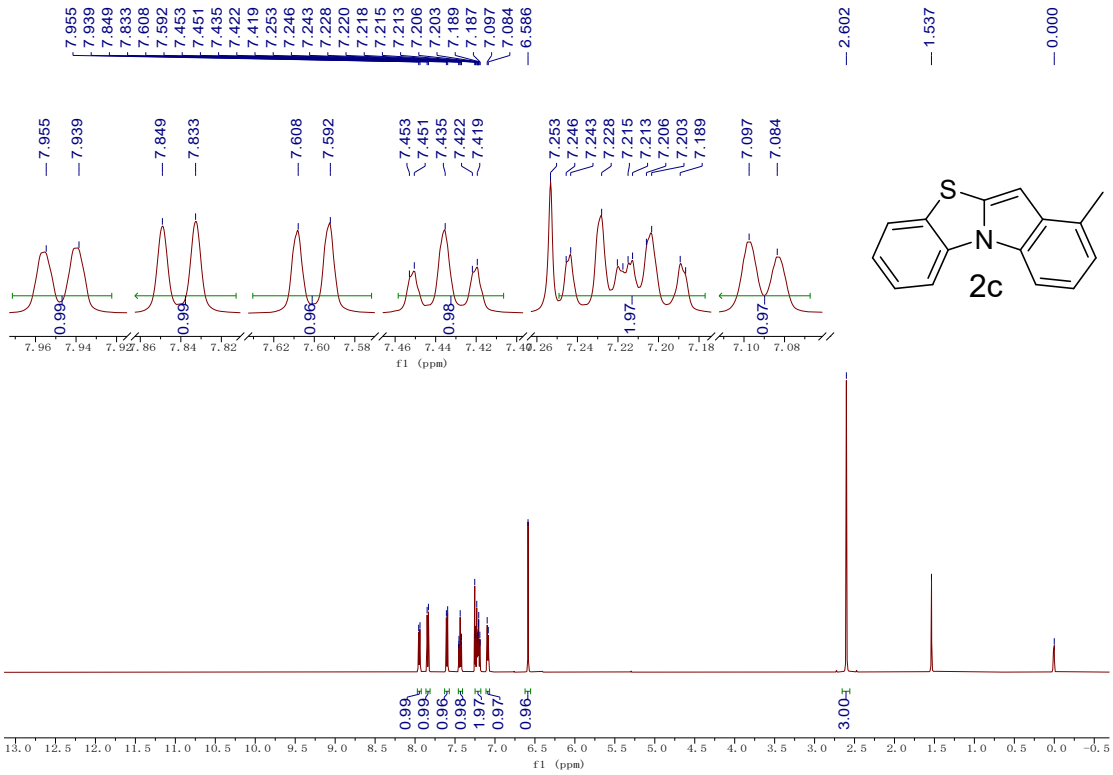

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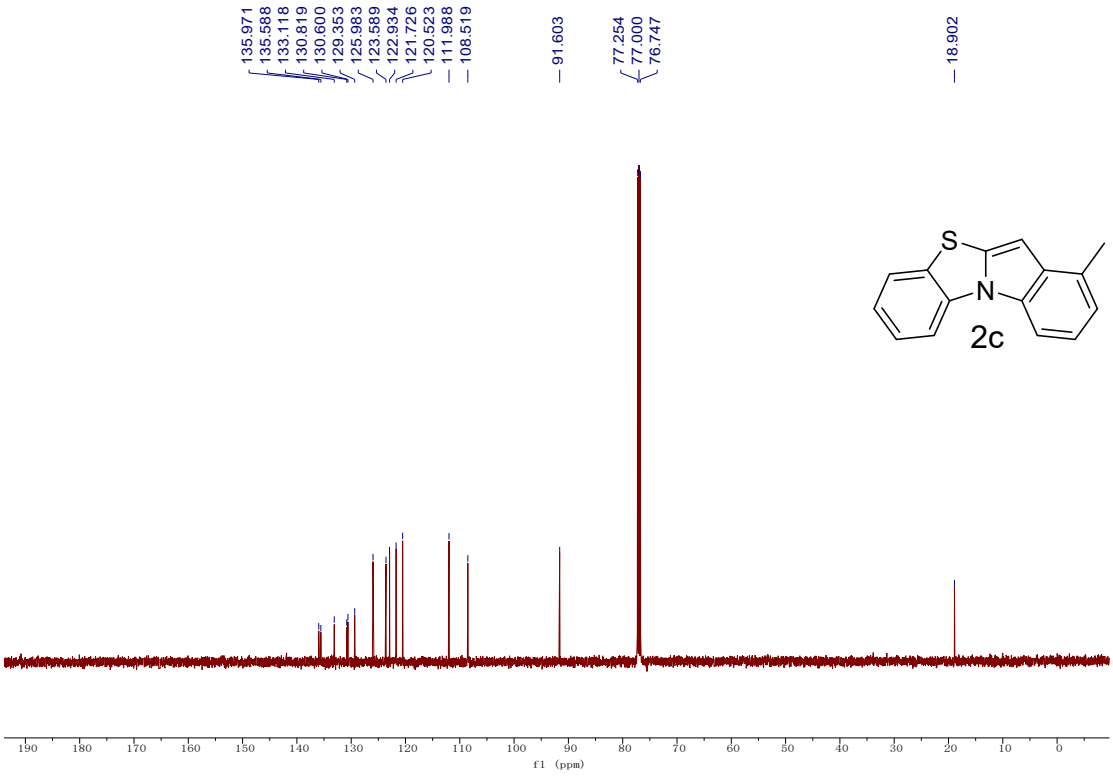

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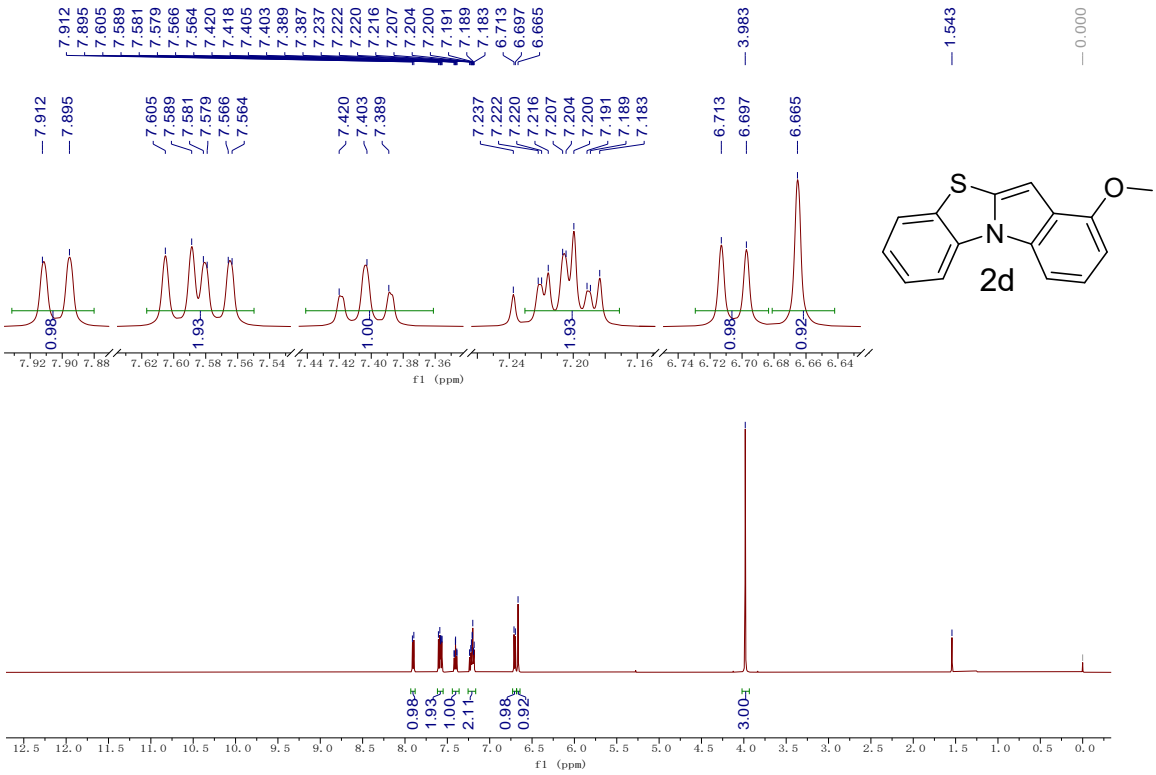

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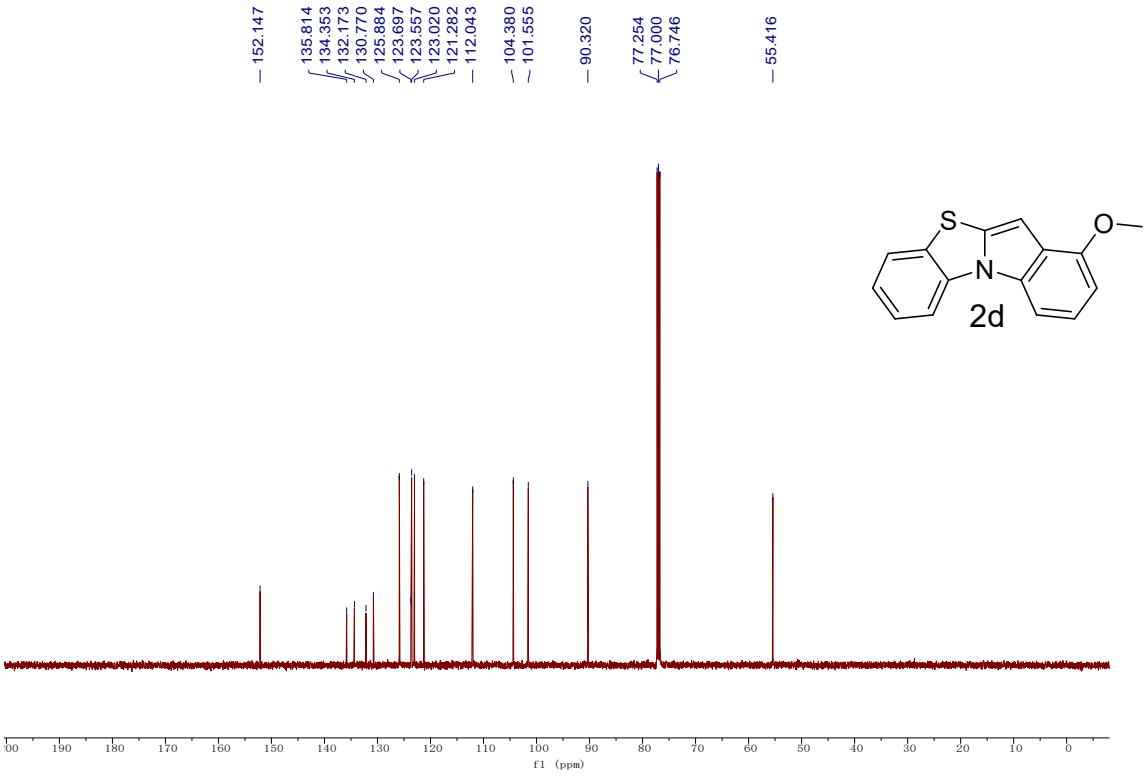

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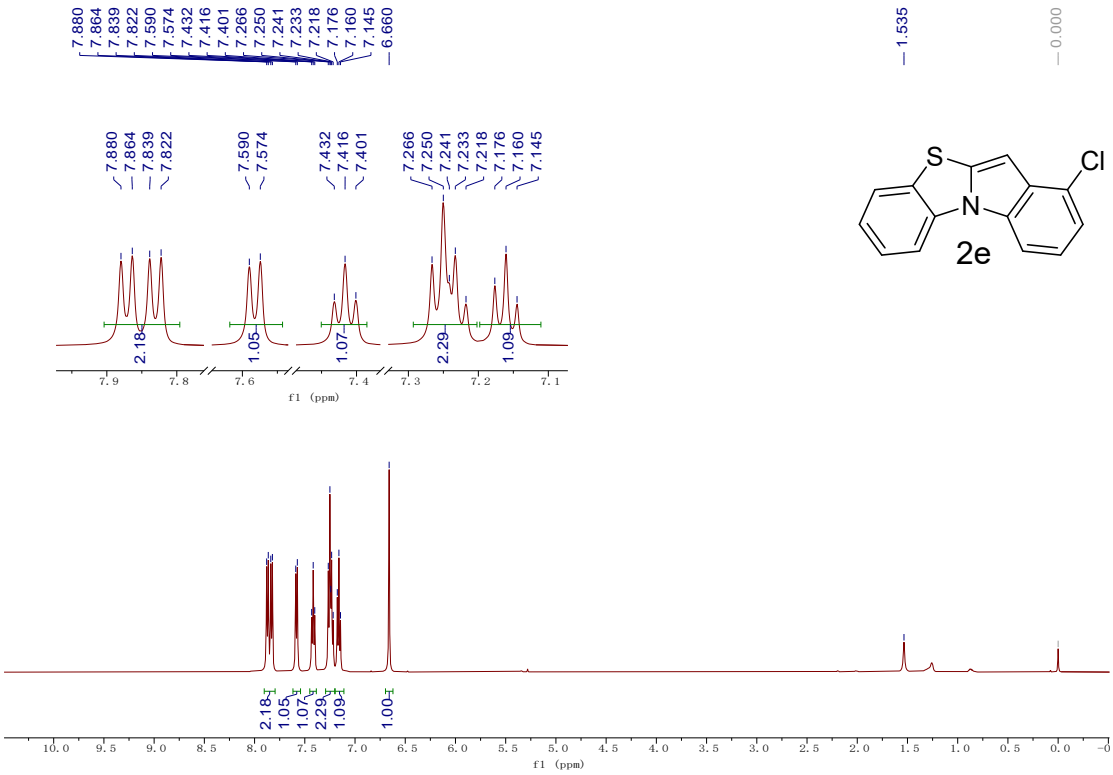

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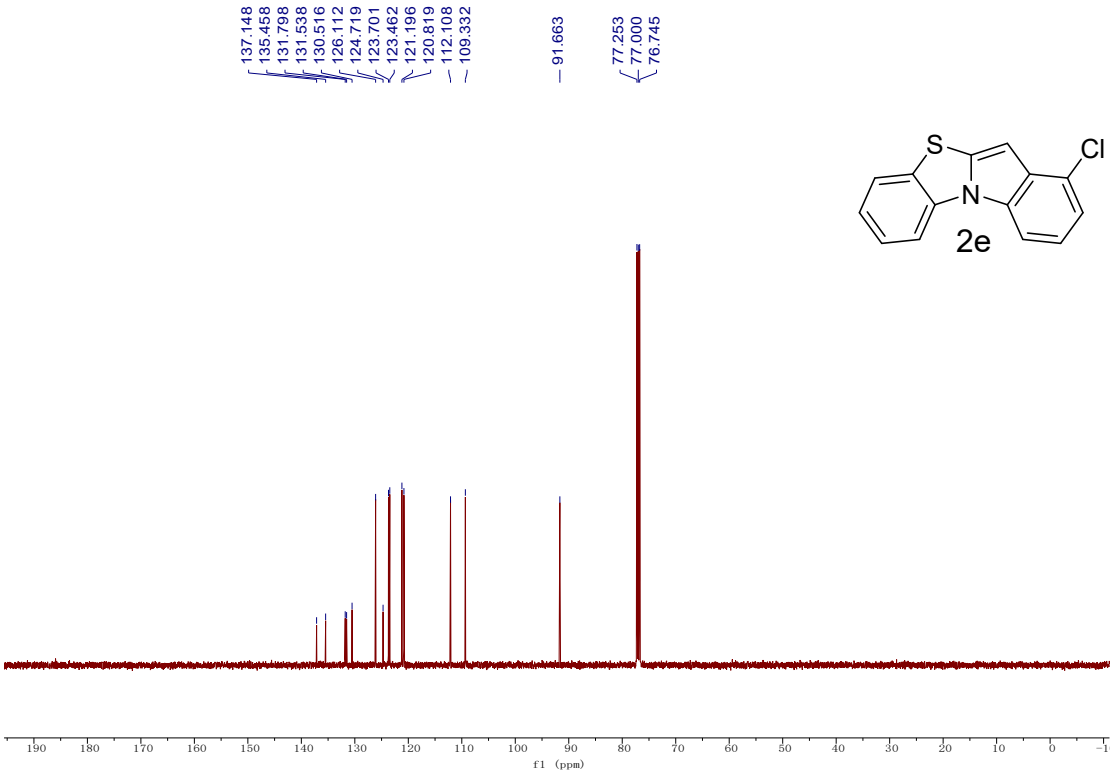

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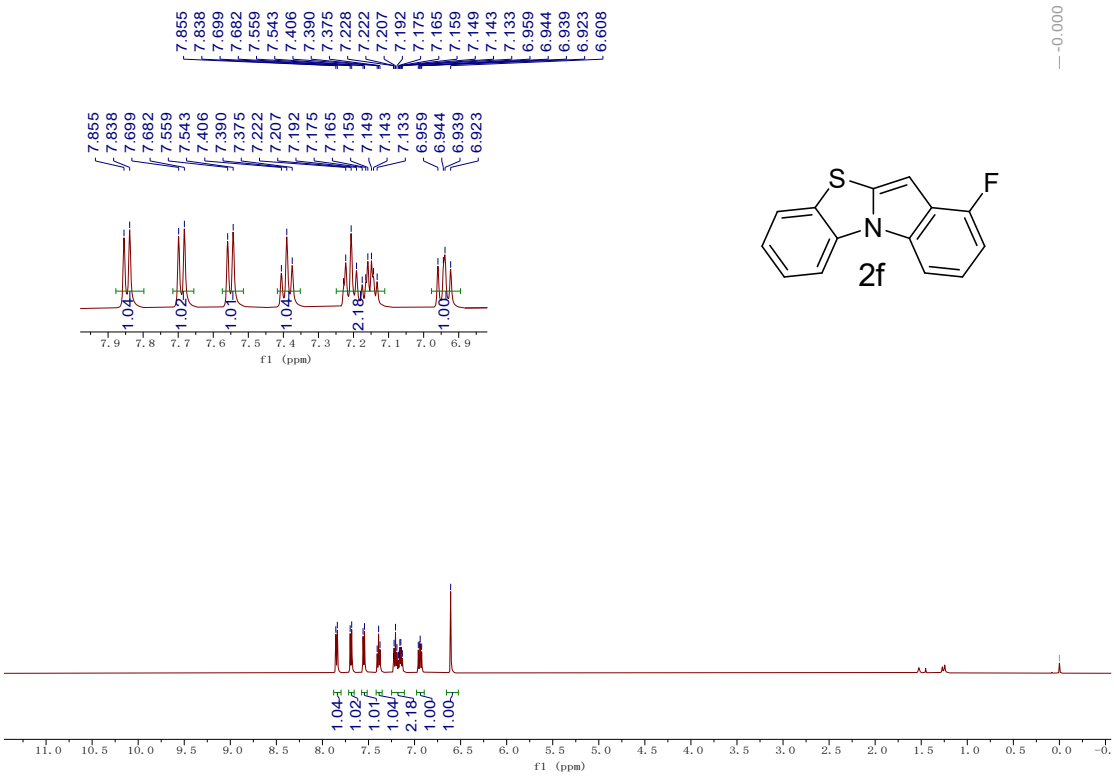

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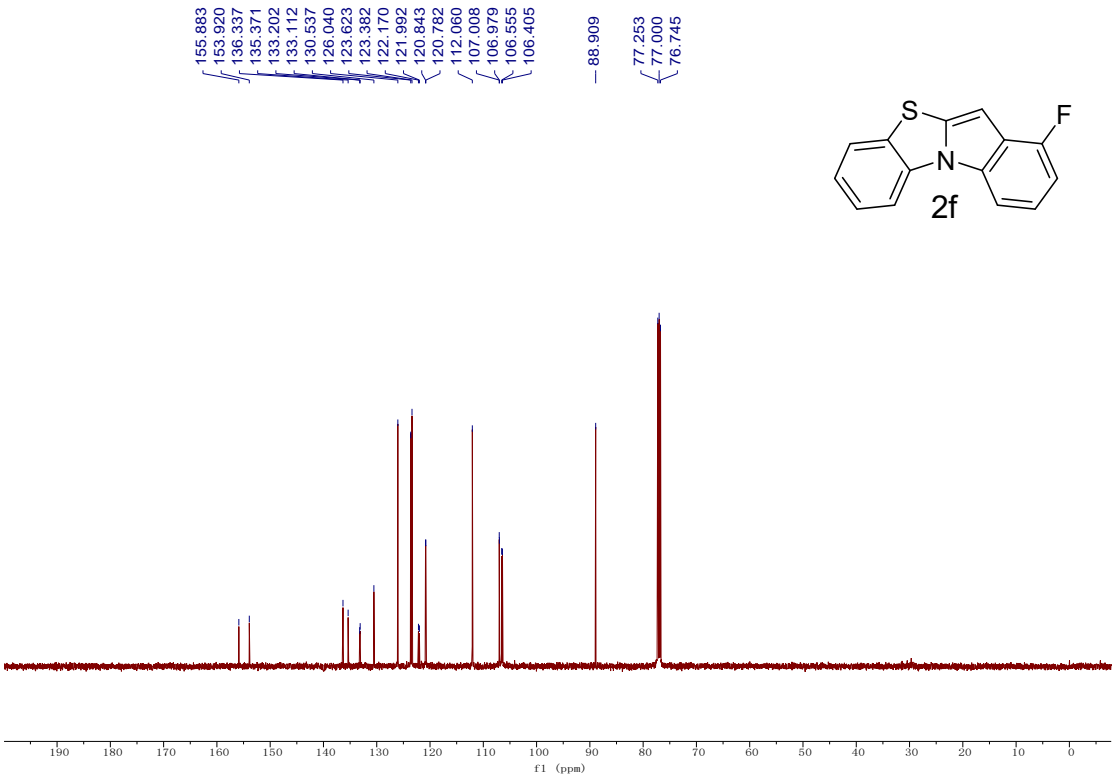

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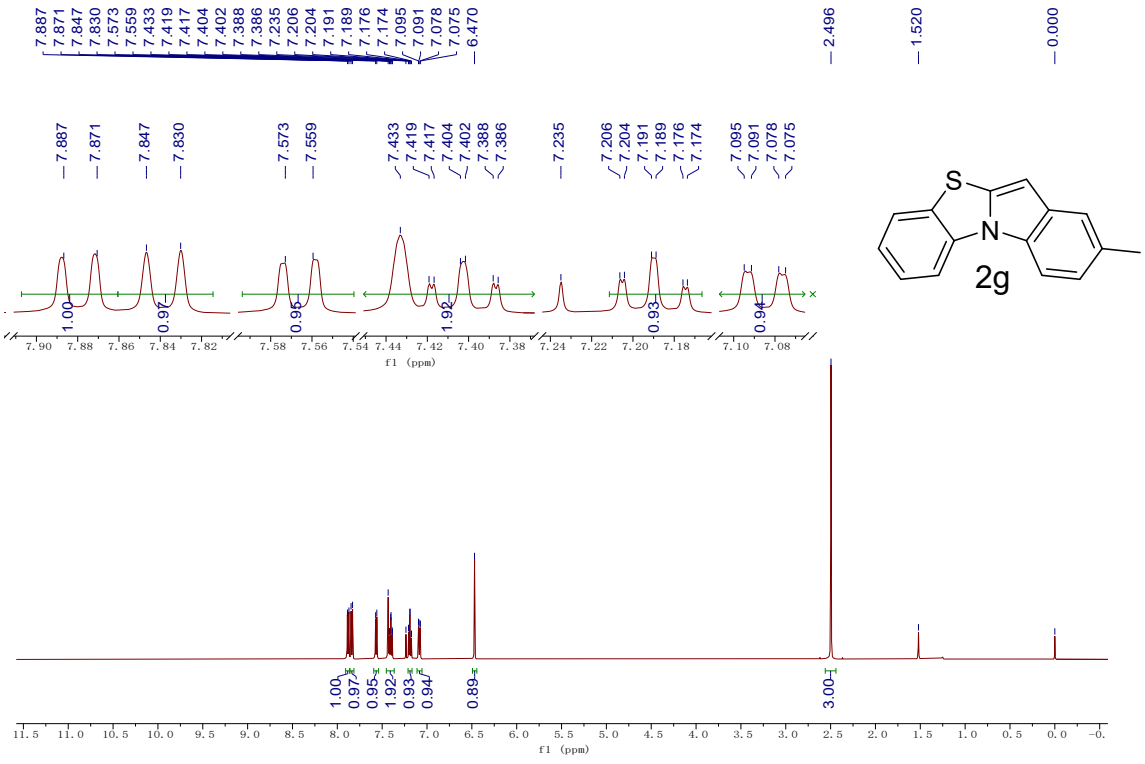

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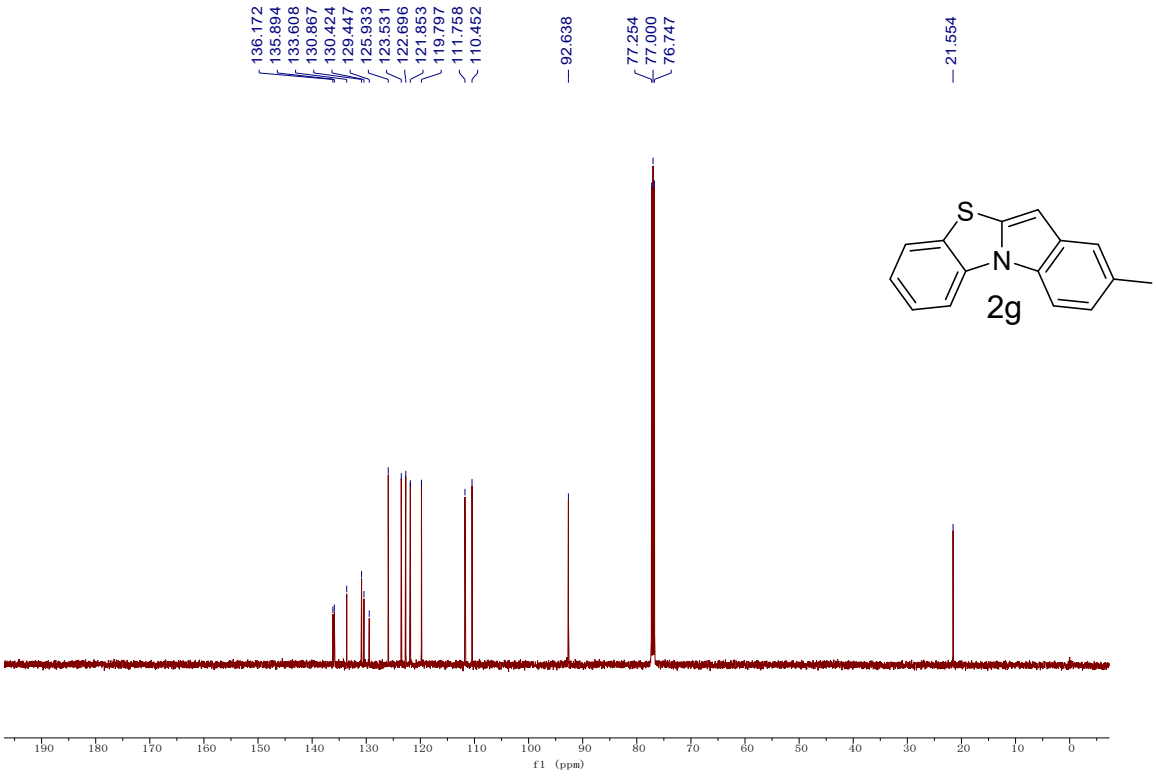

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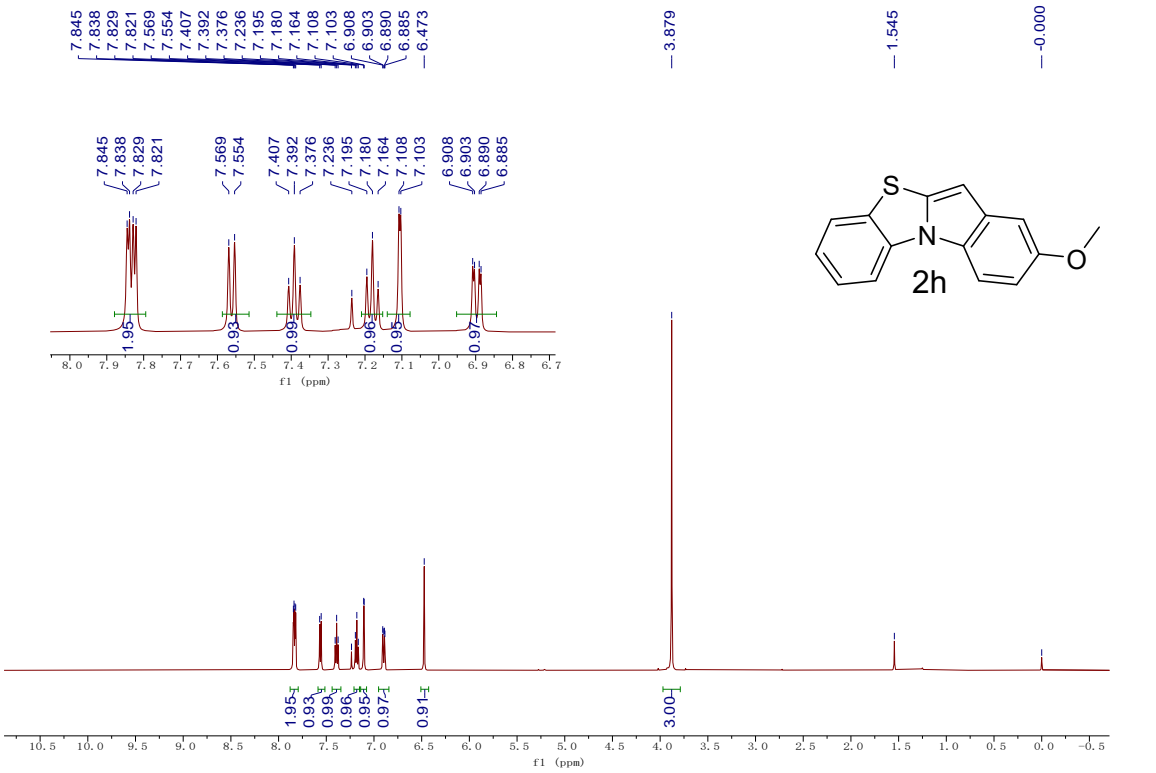

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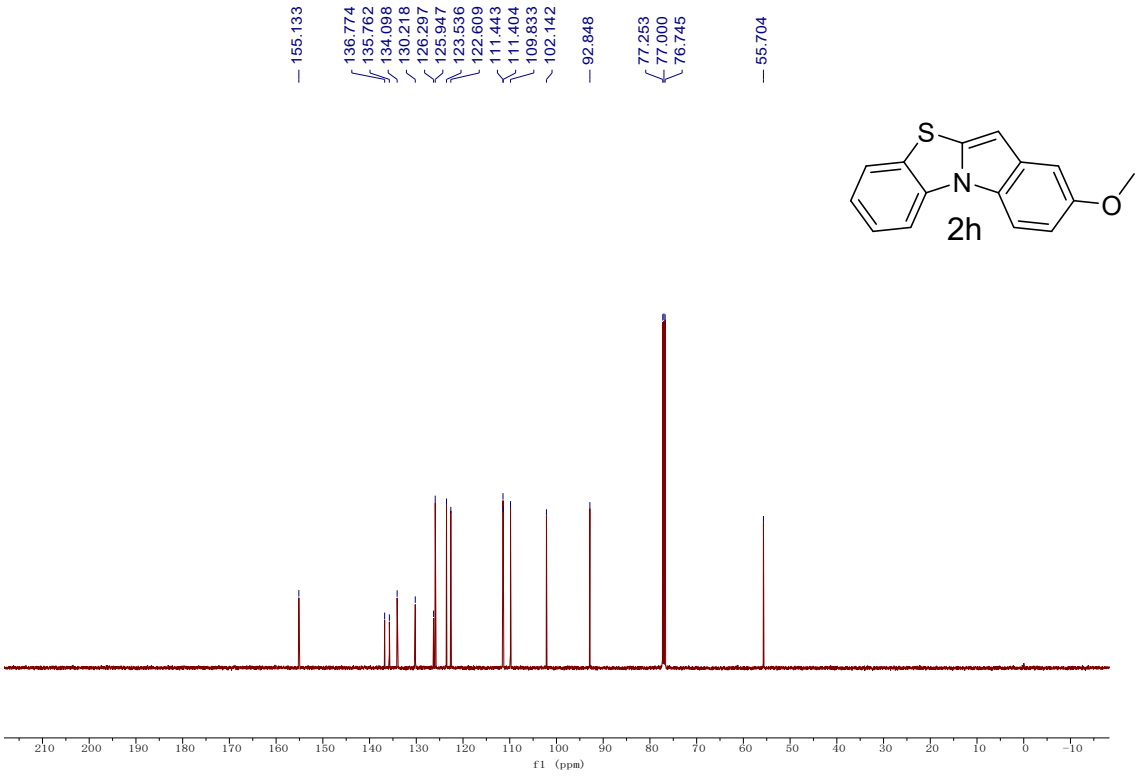

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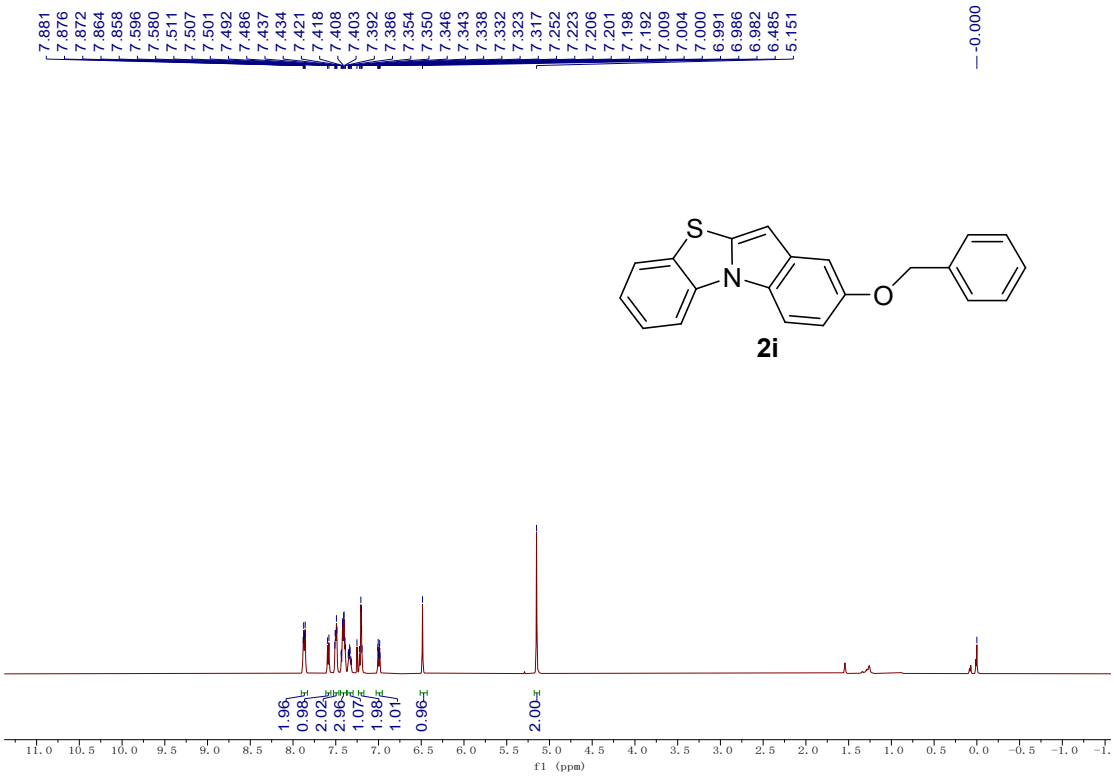

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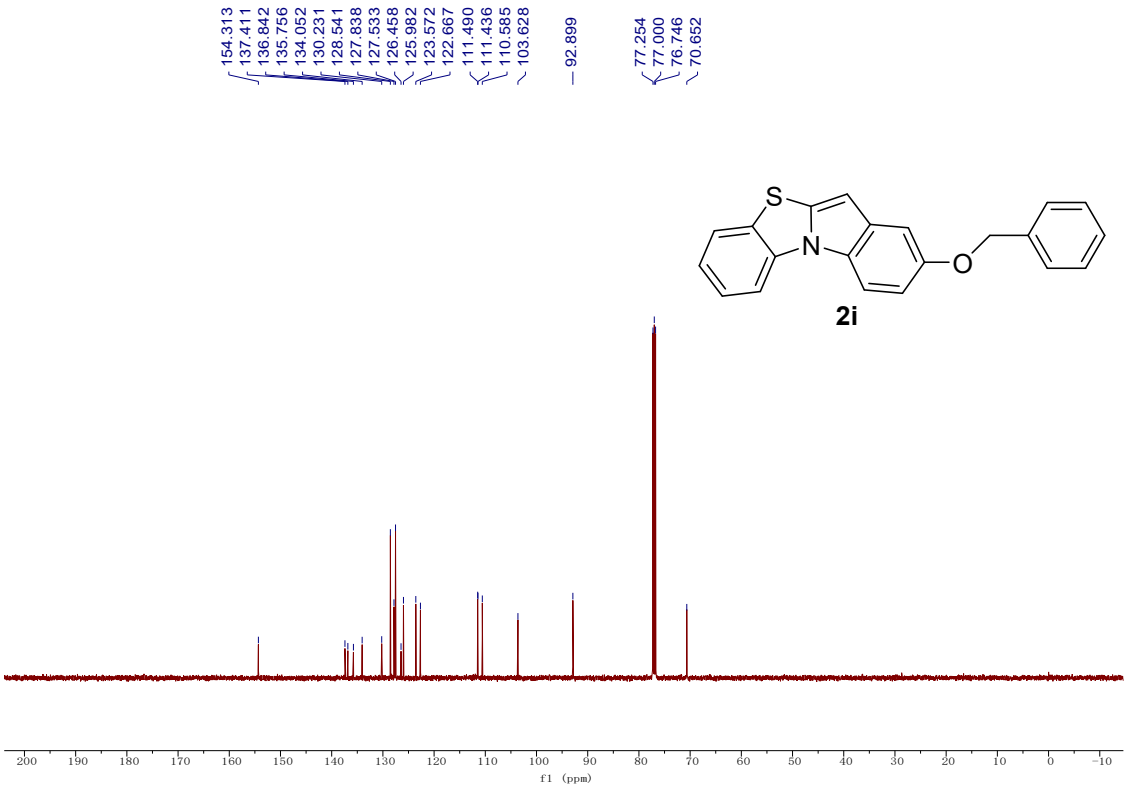

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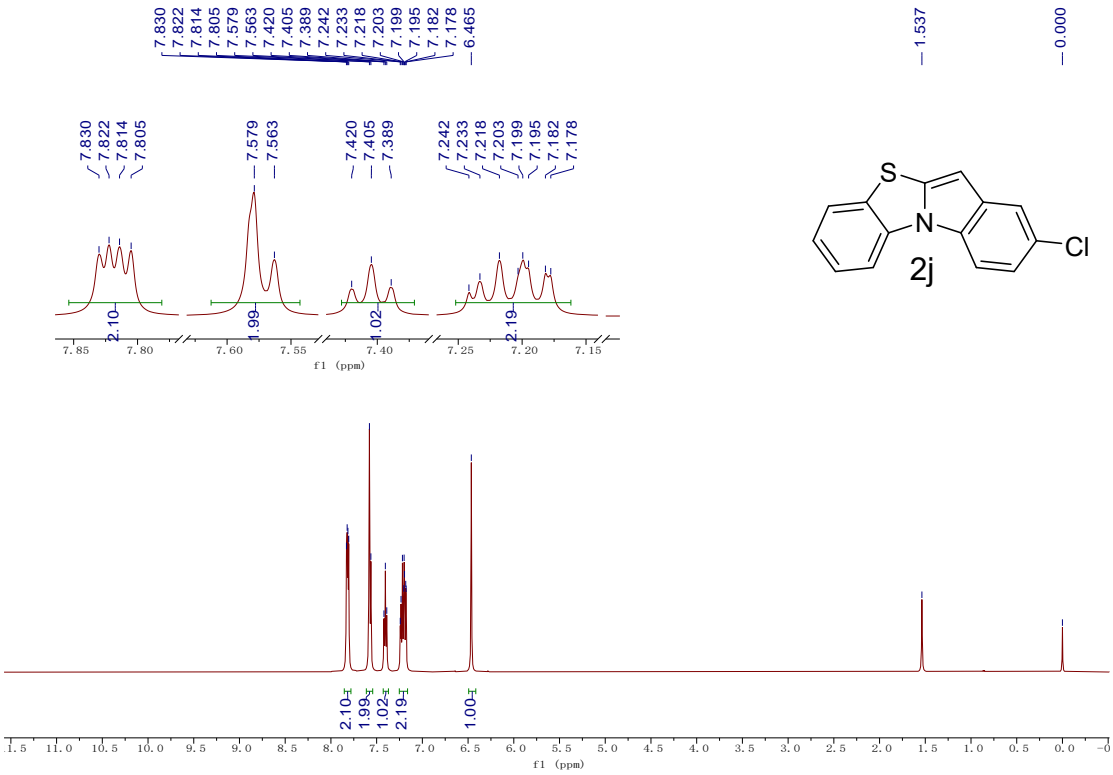
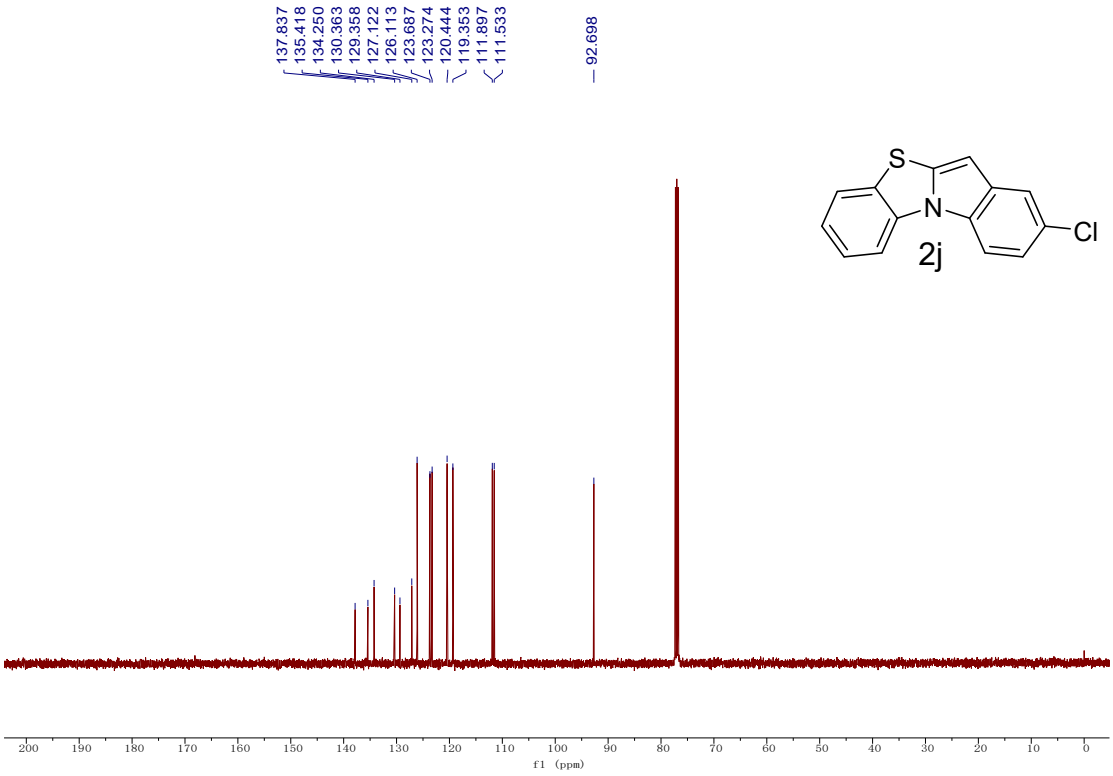


^{13}C NMR (125 MHz, $CDCl_3$)



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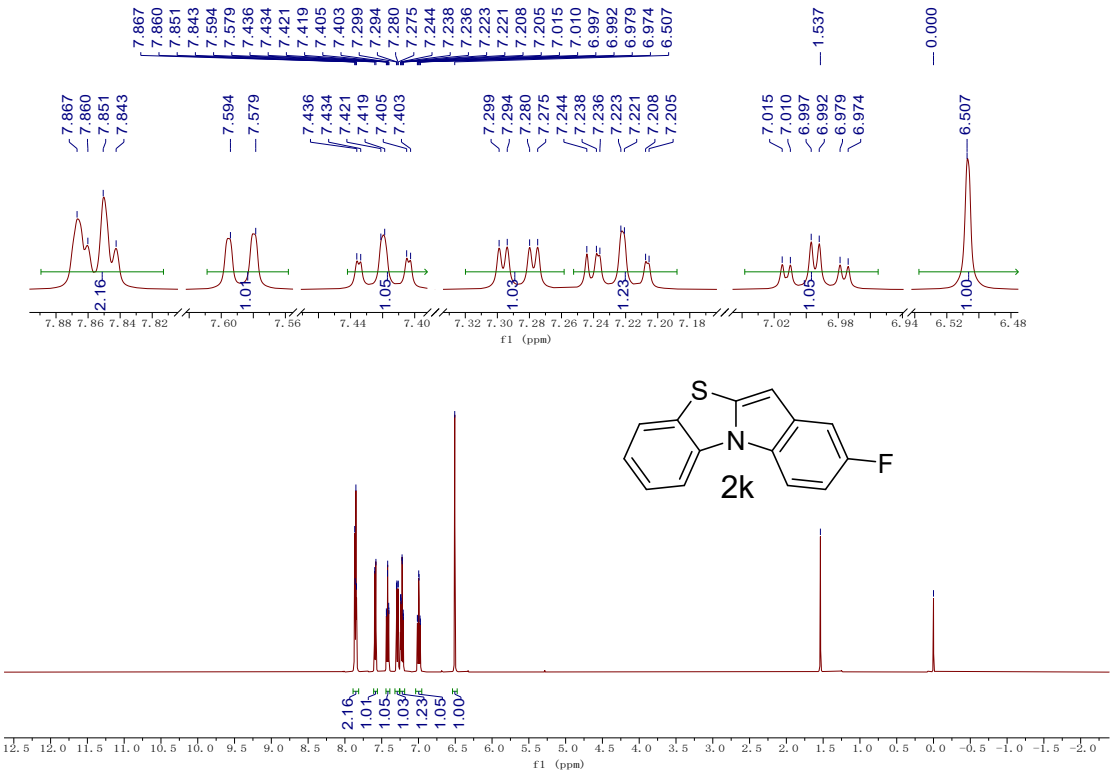
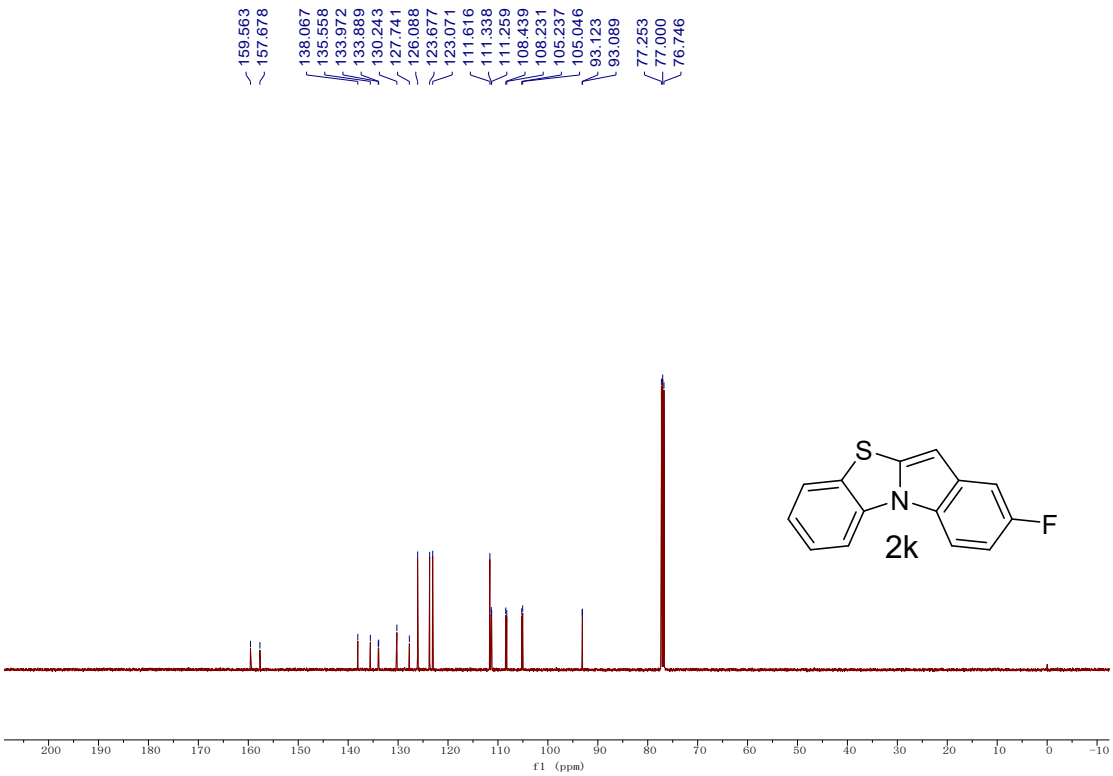
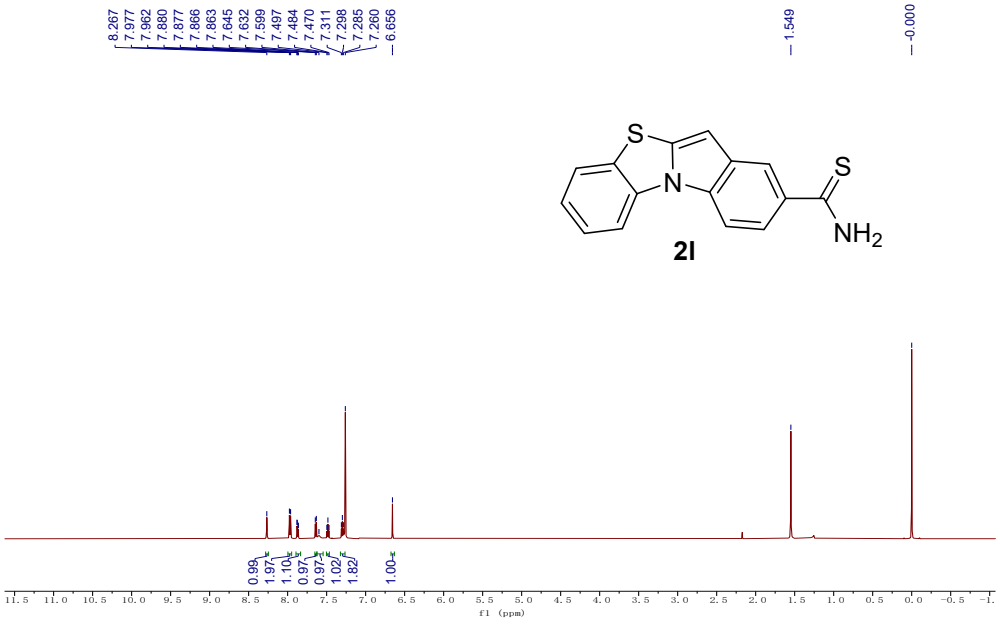


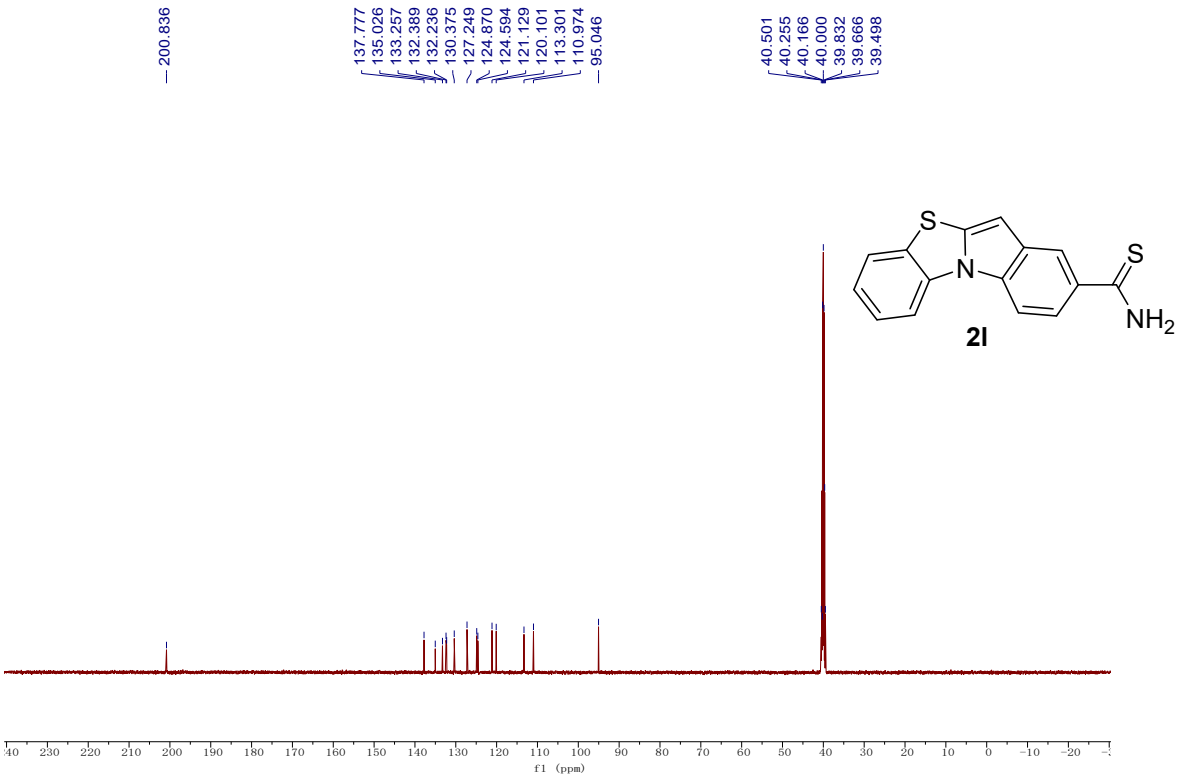
^{13}C NMR (125 MHz, $CDCl_3$)



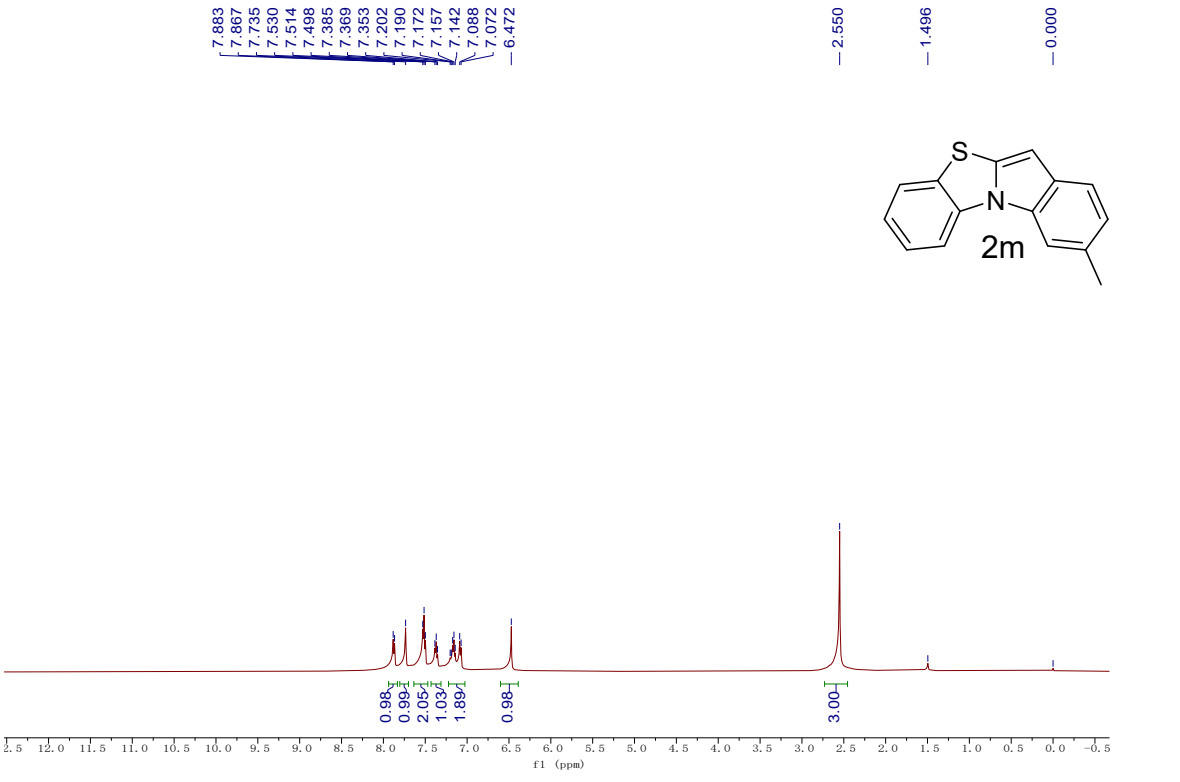
^{1}H NMR (600 MHz, $CDCl_3$)



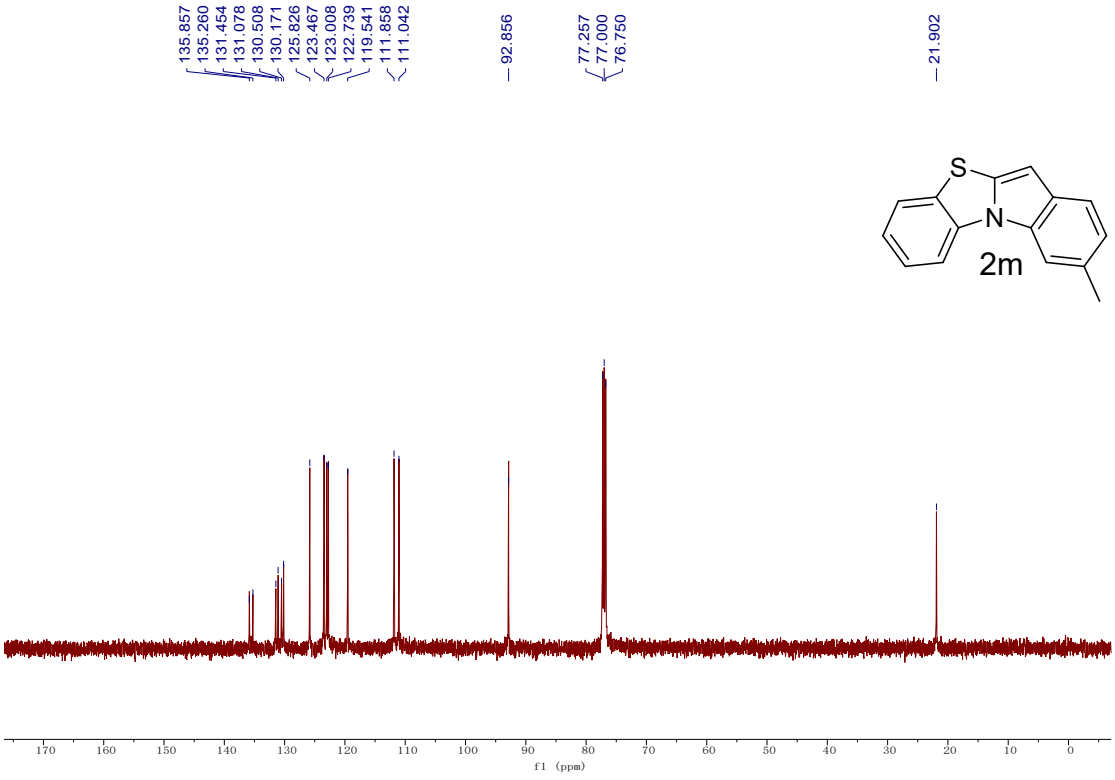
^{13}C NMR (125 MHz, DMSO)



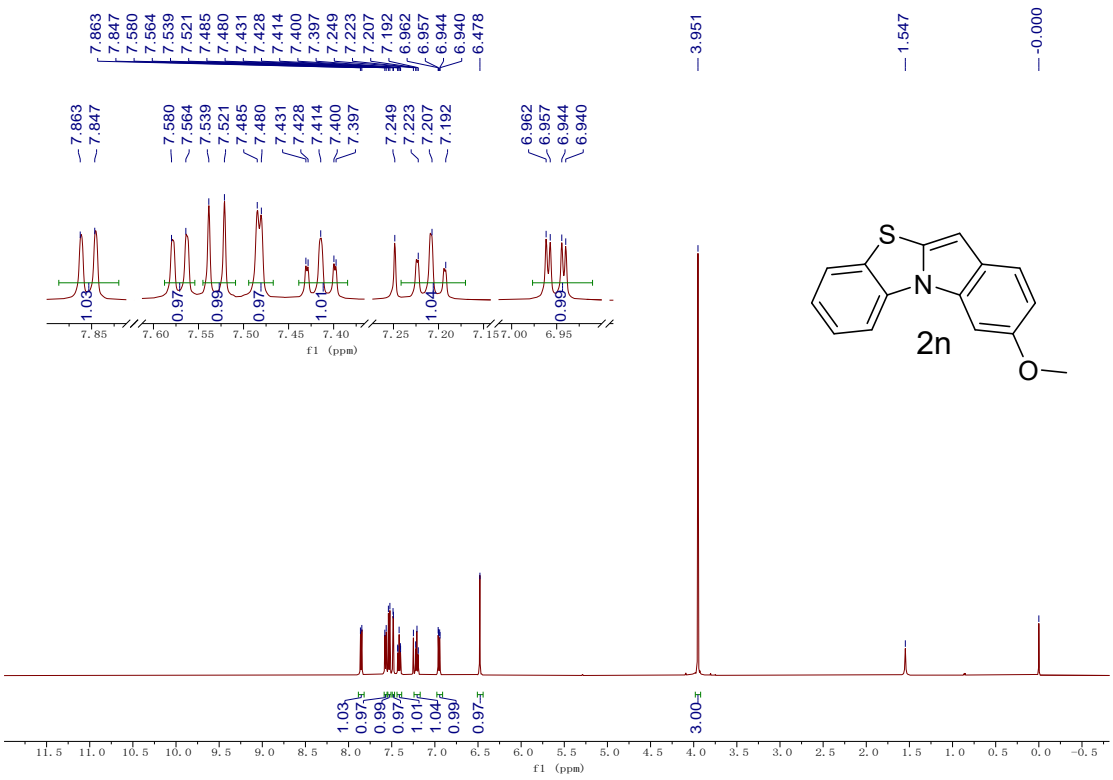
^{1}H NMR (500 MHz, $CDCl_3$)



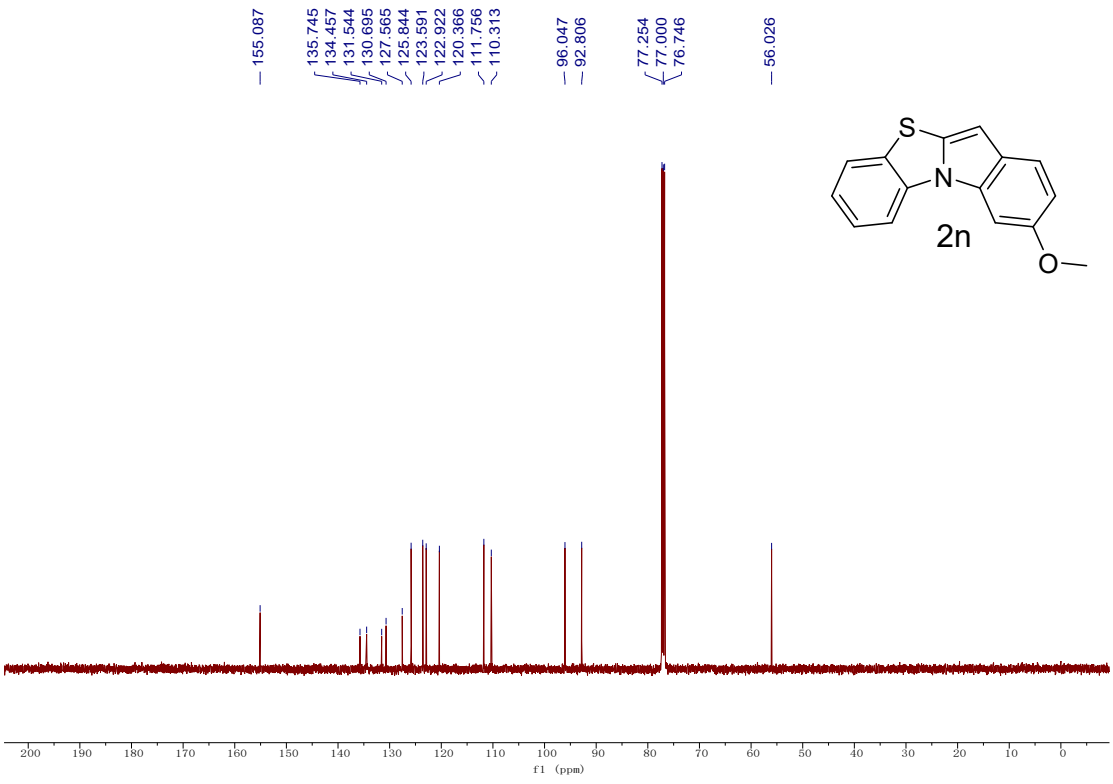
^{13}C NMR (125 MHz, $CDCl_3$)



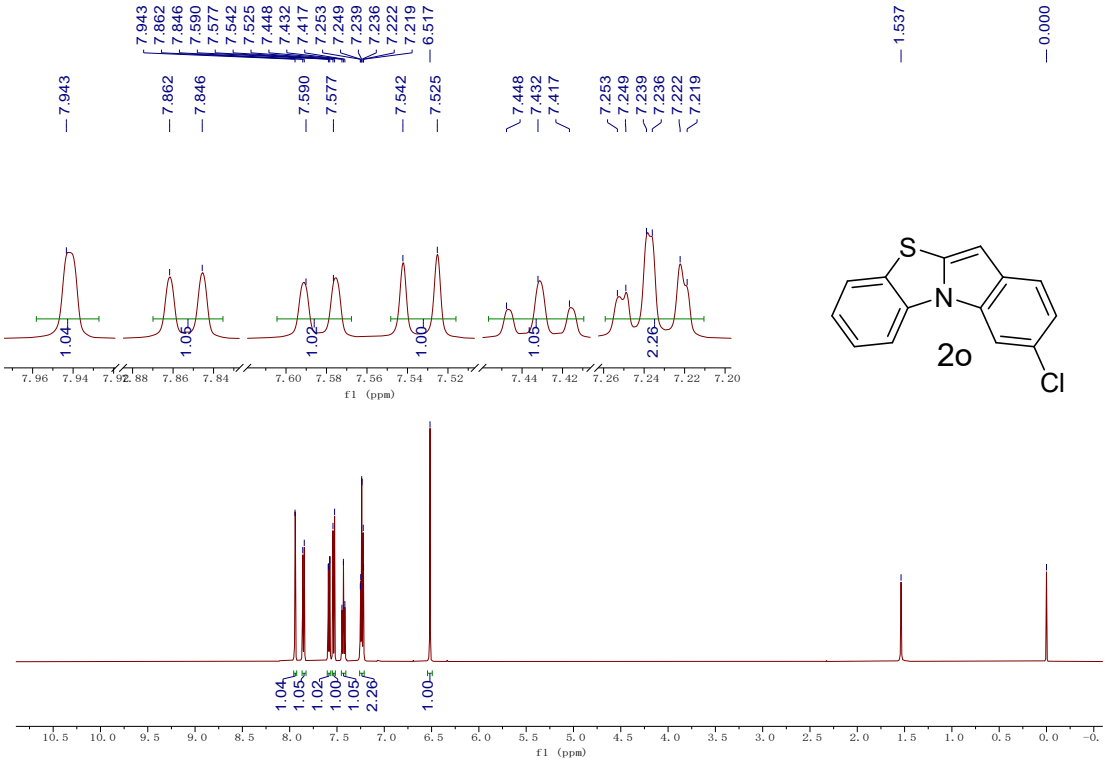
^{1}H NMR (500 MHz, $CDCl_3$)



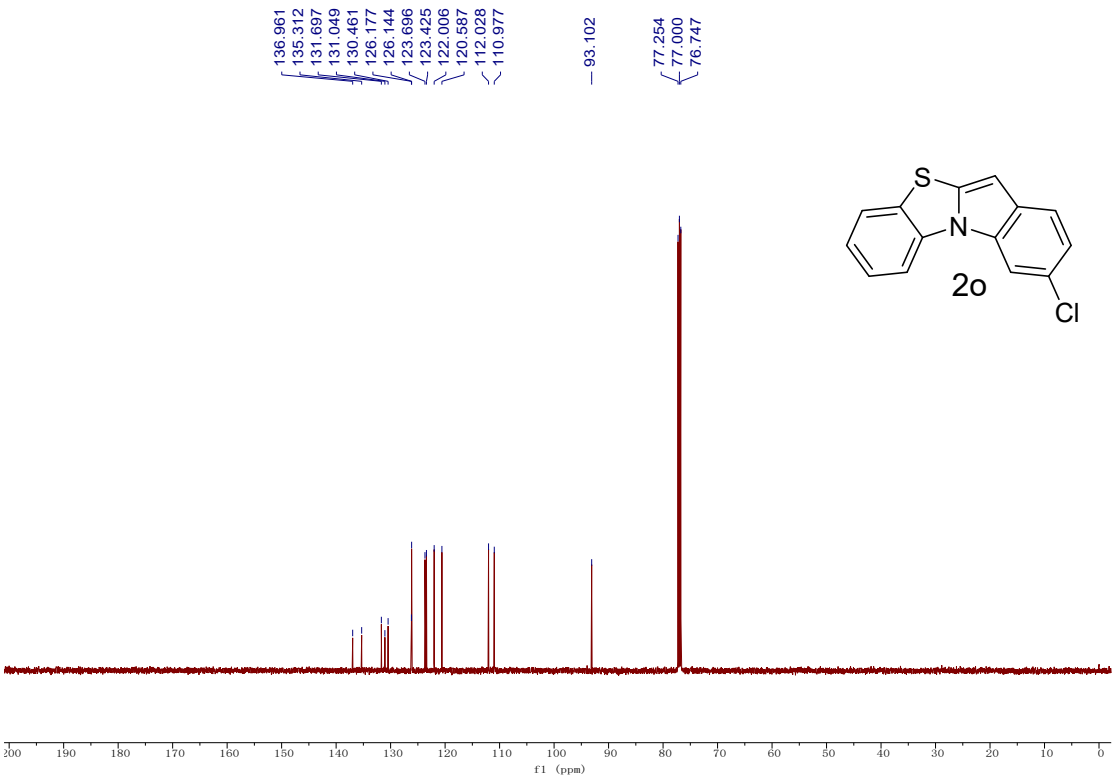
^{13}C NMR (125 MHz, $CDCl_3$)



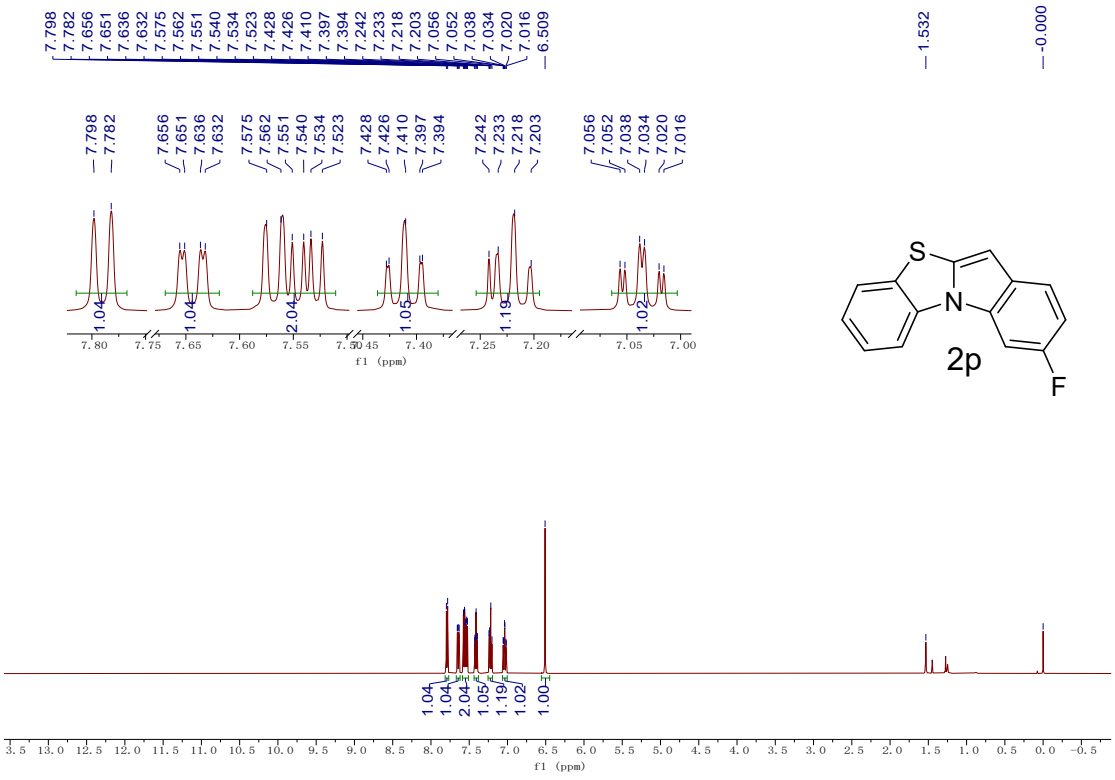
^{1}H NMR (500 MHz, $CDCl_3$)



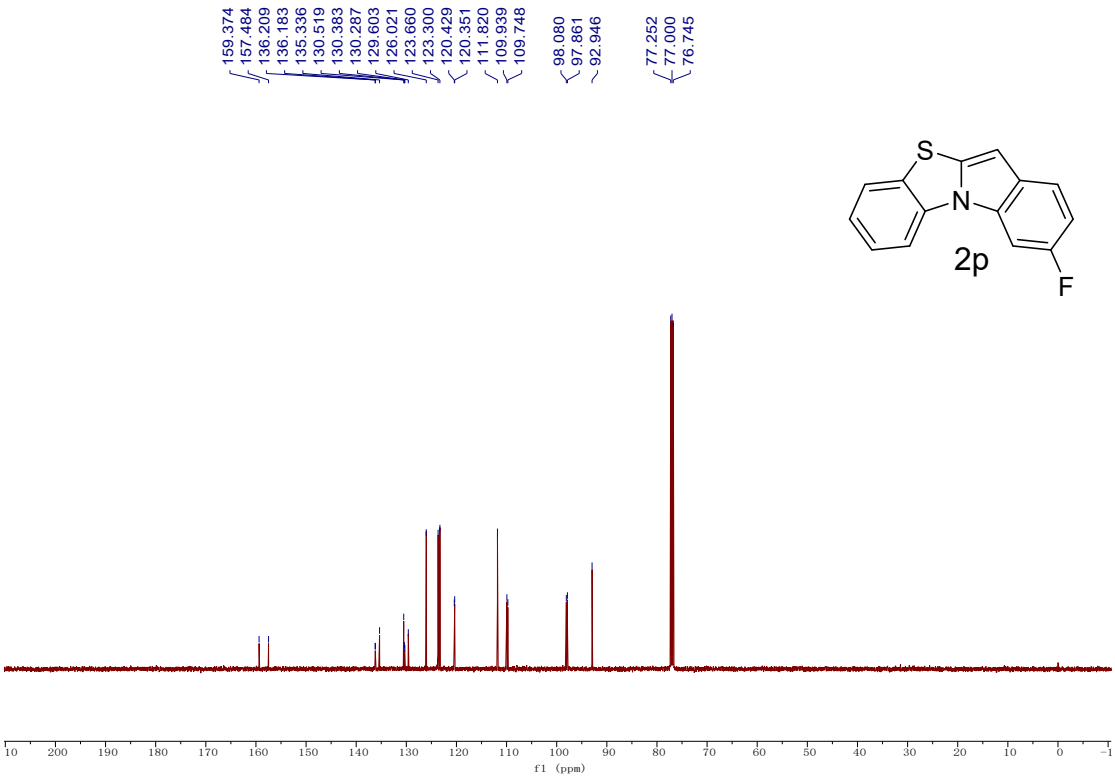
^{13}C NMR (125 MHz, $CDCl_3$)



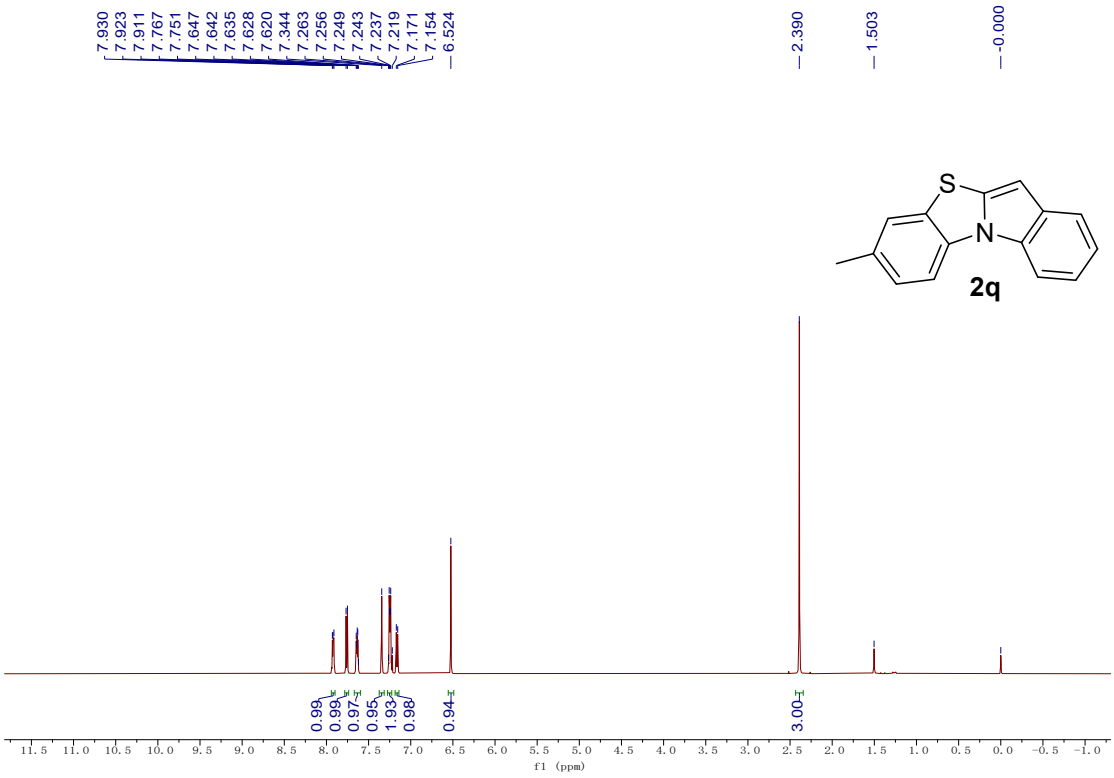
^{1}H NMR (500 MHz, $CDCl_3$)



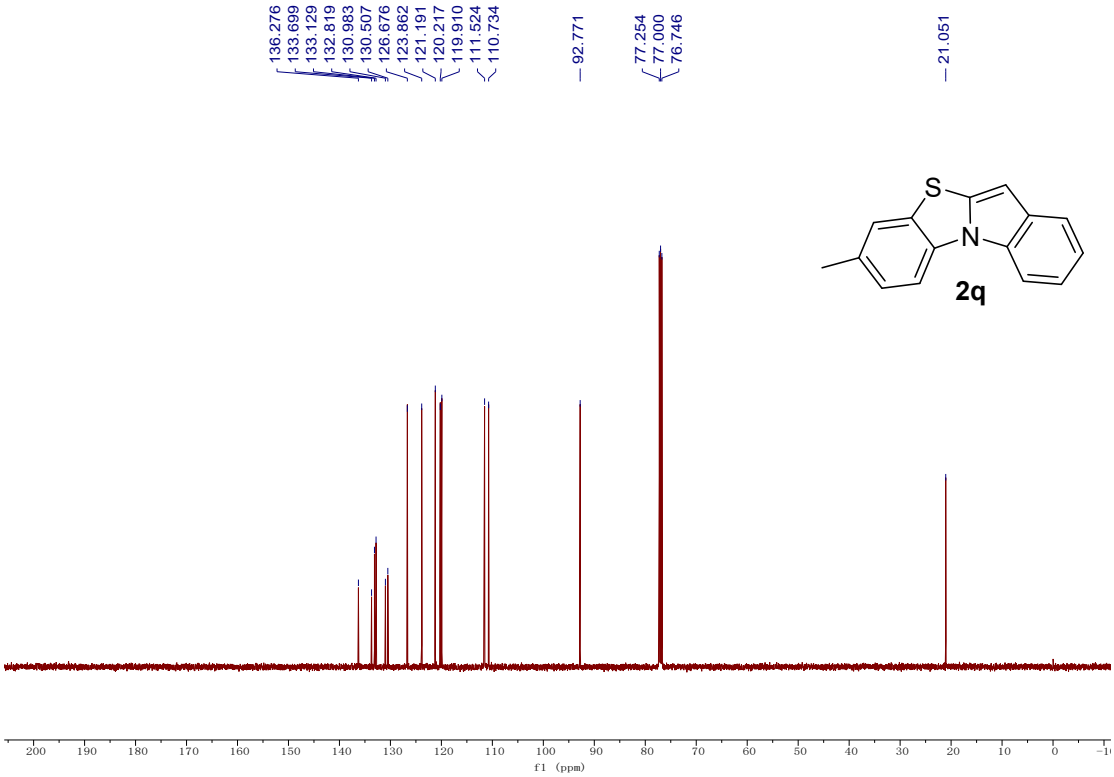
^{13}C NMR (125 MHz, $CDCl_3$)



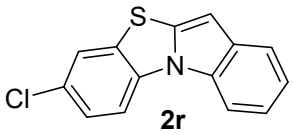
^{1}H NMR (500 MHz, $CDCl_3$)



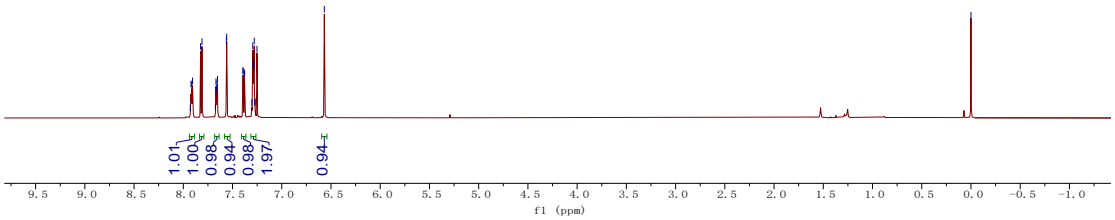
^{13}C NMR (125 MHz, $CDCl_3$)



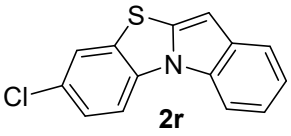
^{1}H NMR (600 MHz, $CDCl_3$)



2r

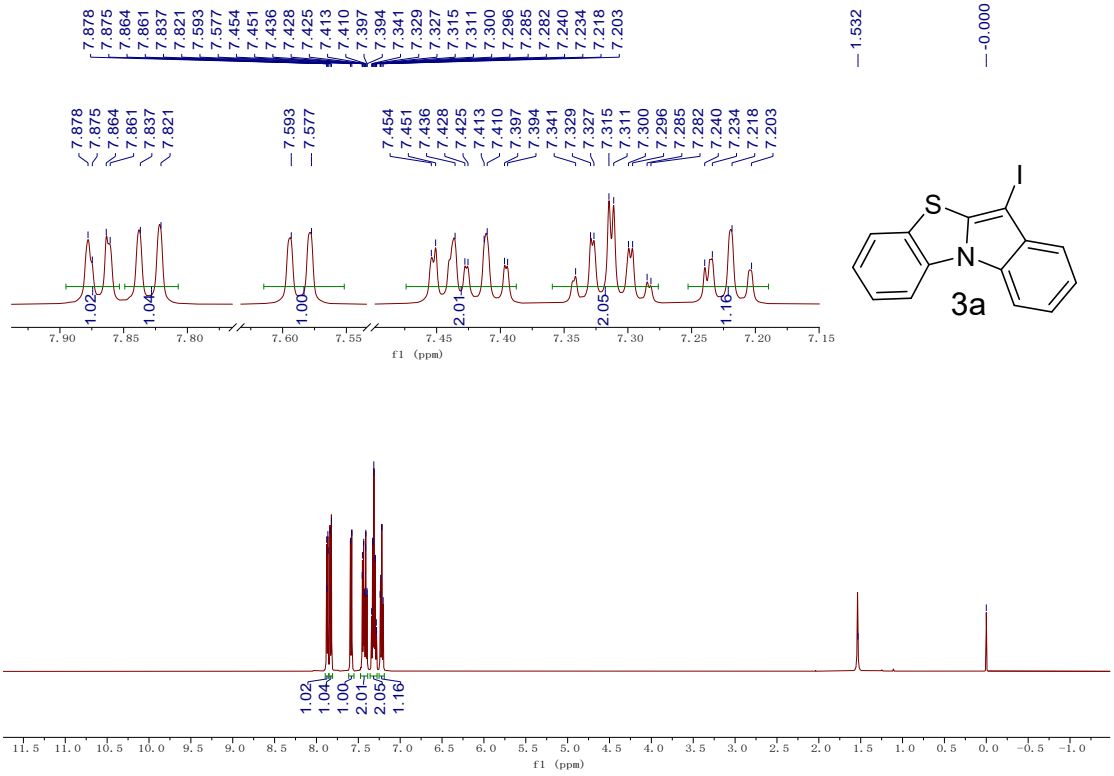


^{13}C NMR (150 MHz, $CDCl_3$)

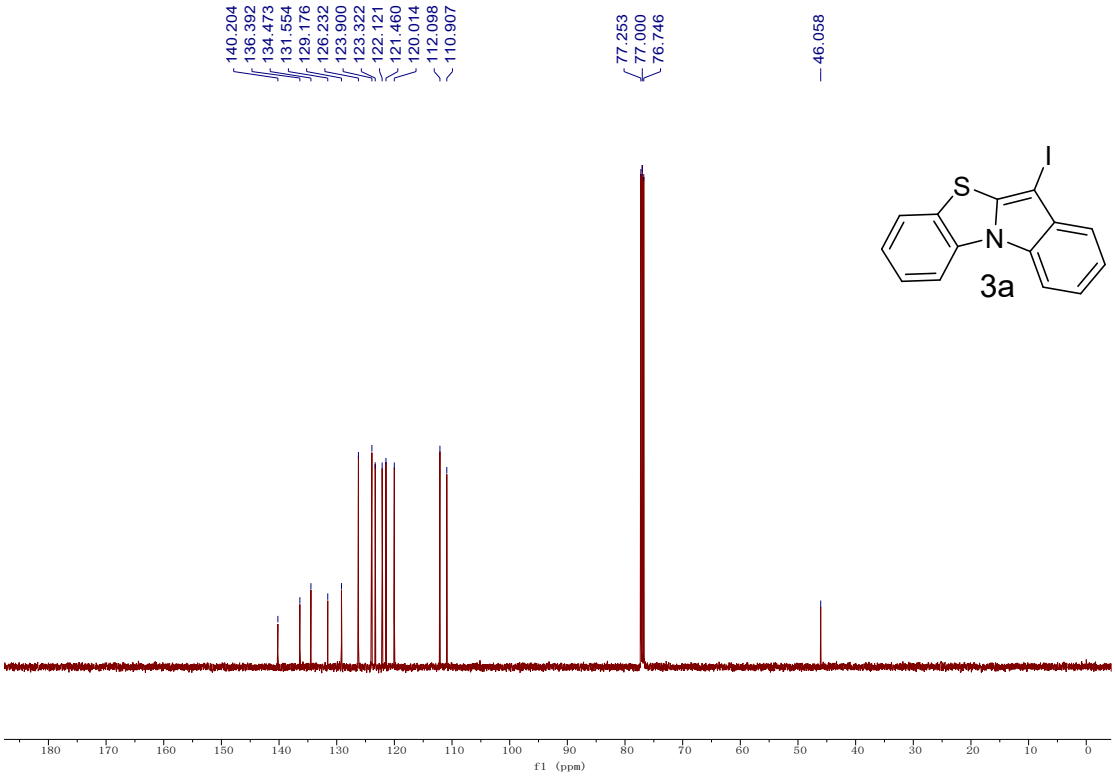


2r

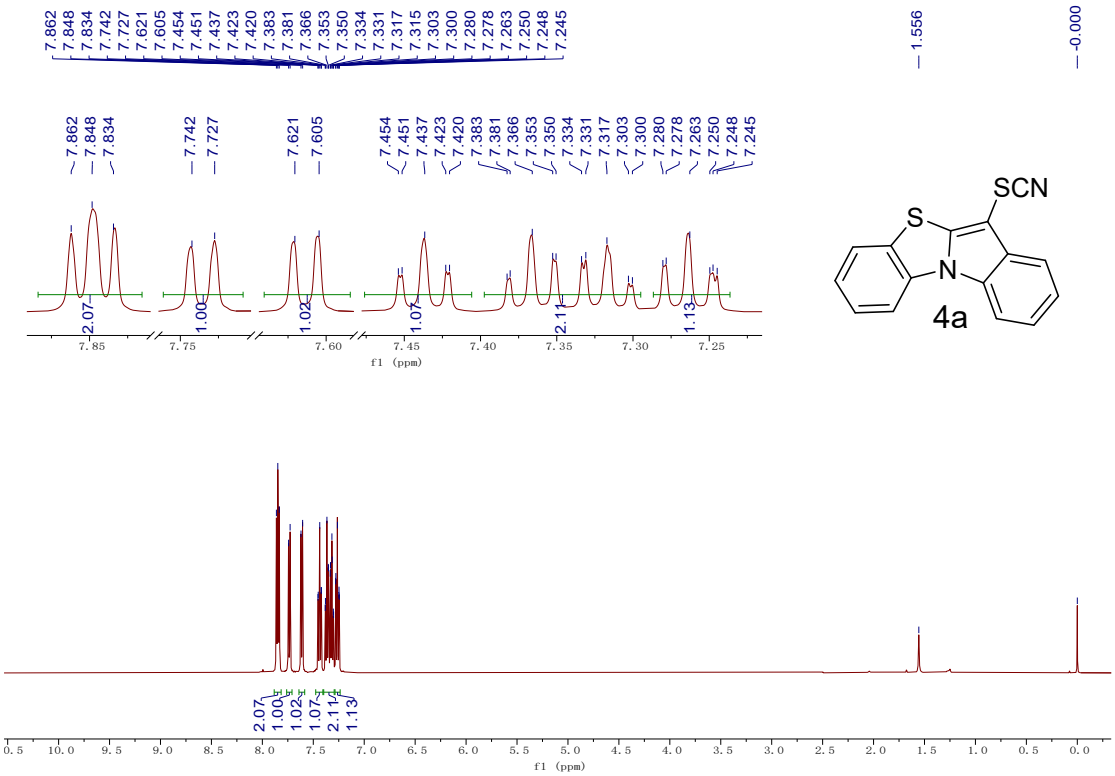
^{1}H NMR (500 MHz, $CDCl_3$)



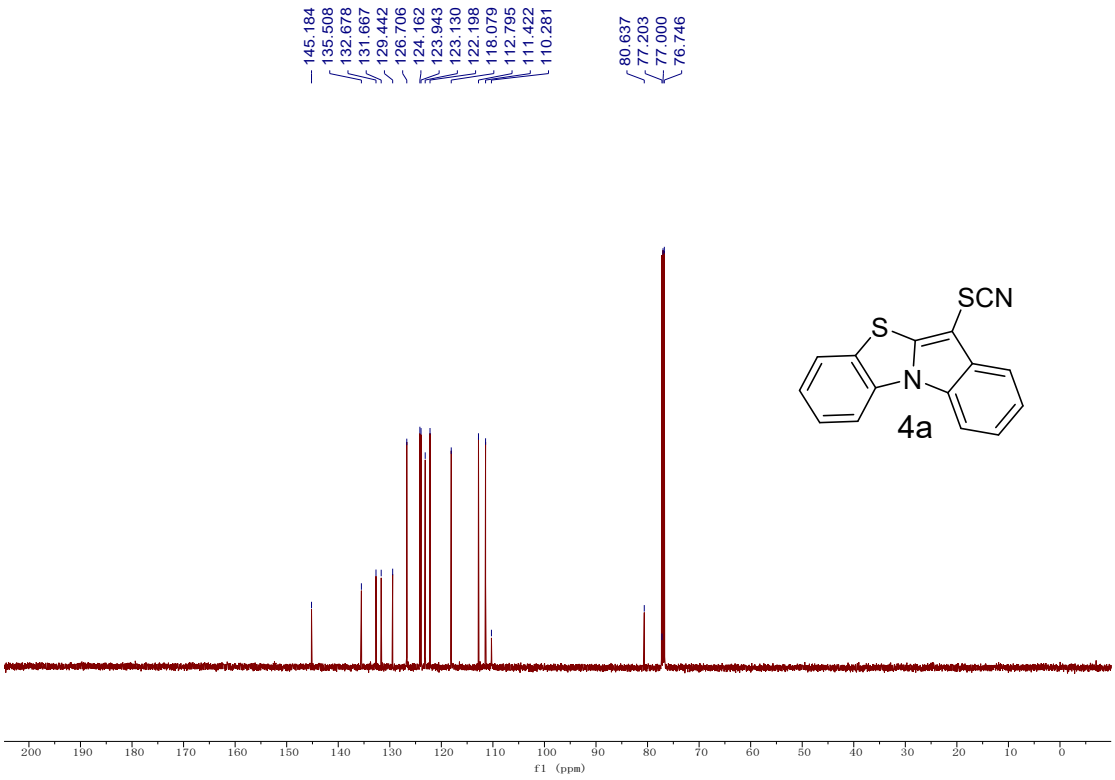
^{13}C NMR (125 MHz, $CDCl_3$)



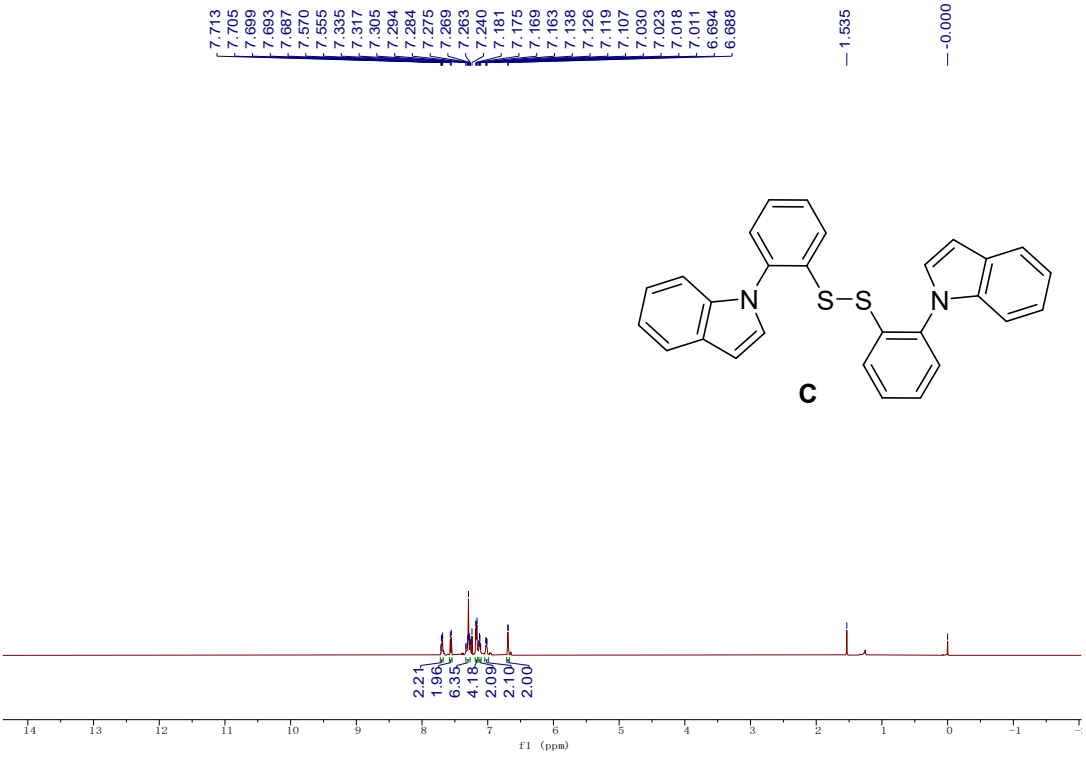
^{1}H NMR (500 MHz, $CDCl_3$)



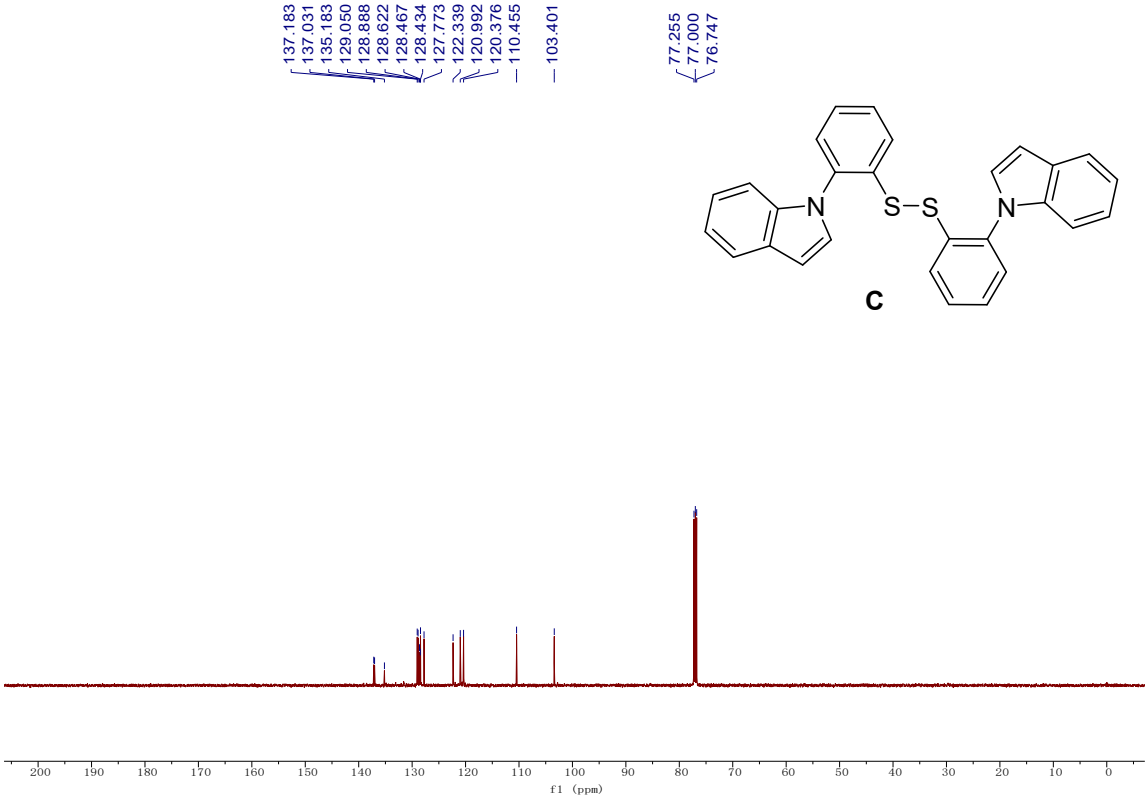
^{13}C NMR (125 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)



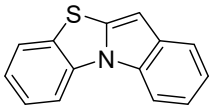
^{13}C NMR (125 MHz, $CDCl_3$)



10. X-ray crystallography of compound 2a.

benzo[4,5]thiazolo[3,2-a]indole **(2a, 2165685)**

(Ortep ellipsoids are depicted at the 50% level)



2a

Table S2. Crystal data and structure refinement for 2a.

Identification code	**2a**
Empirical formula	$C_{14.05}H_{10.1}NS_{0.95}$
Formula weight	223.39
Temperature	296.15 K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	P 2_1/c
Unit cell dimensions	a = 10.6100(7) Å, α= 90°. b = 8.4073(5) Å, β= 103.775(2)°. c = 12.0322(7) Å, γ = 90°.
Volume	1042.42(11) $Å^3$
Z	4
Density (calculated)	1.423 g/cm^3

Absorption coefficient	2.365 mm^{-1}
F(000)	466.0
Crystal size	0.32 x 0.18 x 0.15 mm^3
Radiation	CuKα (λ = 1.54178)
Theta range for data collection	8.58 to 144.912°.
Index ranges	-13<=h<=13, -10<=k<=10, -14<=l<=13
Reflections collected	25614
Independent reflections	2049 [R(int) = 0.0319, R(sigma) = 0.0162]
Completeness to theta = 26.000°	99.2 %
Absorption correction	MULTI-SCAN
Max. and min. transmission	0.754 and 0.616
Refinement method	Least Squares minimisation
Data / restraints / parameters	2049 / 64 / 166
Goodness-of-fit on F^2	1.087
Final R indices [I>2sigma(I)]	R1 = 0.0344, wR2 = 0.0966
R indices (all data)	R1 = 0.0352, wR2 = 0.0974
Largest diff. peak and hole	0.31 and -0.54 $e.Å^{-3}$