Supporting Information

Regioselective C-H Sulfonylation of *N*-Sulfonyl Protected 7-Azaindoles Promoted by TBAI: A Rapid Synthesis of 3-Thio-7-Azaindoles

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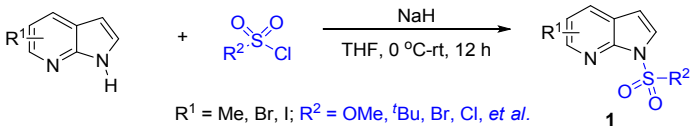
1. General information

All reactions were carried out under air atmosphere in a dried tube. All the reagents were obtained commercially and used without further purification. Silica gel was purchased from Qing Dao Hai Yang Chemical Industry Co. Analytical thin layer chromatography (TLC) was performed on precoated silica gel F_{254} plates. Compounds were visualized by irradiation with UV light (254 nm).

Analytical information: ^{1}H NMR and ^{13}C NMR spectra data were recorded by a BRUKER AVANCE III 400 MHz spectrometer (^{1}H 400 MHz, ^{13}C 100 MHz), using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. ^{1}H NMR spectral data are given as chemical shifts in ppm followed by multiplicity (s- singlet; d- doublet; t- triplet; q- quartet; m- multiplet), number of protons and coupling constants. ^{13}C NMR chemical shifts are expressed in ppm. Infrared spectra were recorded with a Thermo Scientific Nicolet 6700 FT-IR Spectrometer. HRMS data were obtained using AB SCIEX Triple TOF 5600+ high resolution mass spectrometer (USA). The products listed below were determined by ^{1}H and ^{13}C NMR spectra. Single crystal was detected on single crystal diffractometer of Agilent Gemini E with double light source X-ray. Melting points were measured on a microscopic apparatus and were uncorrected.

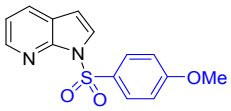
2. Synthesis of *N*-sulfonyl protected 7-azaindoles

2.1 General procedure for the synthesis of *N*-sulfonyl protected 7-azaindoles



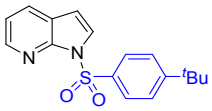
NaH (60% dispersion in mineral oil, 40 mmol) was added at 0 °C to a stirred solution of 7-azaindoles (16 mmol) in THF (25 ml). Then, sulfonyl chlorides (19.2 mmol) was added and the resulting mixture was stirred overnight at room temperature. The reaction mixture was extracted with EtOAc and washed with sat. NH_4Cl solution. The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting crude was purified by flash column chromatography on silica gel (eluent: PE/EA, 10/1), and the desired *N*-sulfonyl protected 7-azaindoles was identified by NMR, HRMS and IR.

2.2 Characterization of the *N*-sulfonyl protected 7-azaindoles 1b and 1d-f.



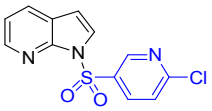
1b

Purification by column chromatography on silica gel (R_f = 0.48, petroleum ether/ethyl acetate = 3:1) yielded **1b** (81.8 mg, 50%) as a white solid; m. p. 154-158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: δ 8.44 – 8.40 (dd, J = 4.8, 1.6 Hz, 1H), 8.17-8.10 (m, 2H), 7.87-7.81 (dd, J = 7.9, 1.6 Hz, 1H), 7.74-7.69 (d, J = 4.0, 1H), 7.20-7.13 (dd, J =7.8, 4.8 Hz, 1H), 6.95-6.89 (m, 2H), 6.60-6.55 (d, J = 4.0 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 164.0, 147.2, 144.8, 130.4, 129.9, 129.5, 126.4, 122.8, 118.8, 114.2, 105.0, 55.6; IR(KBr): 3141, 3122, 3045, 2941, 1930, 1724, 1592, 1575, 1497, 1402, 1371, 1273, 1166, 1090, 993, 803, 715, 681, 577 cm^{-1}; HRMS (ESI) calcd. for $C_{14}H_{12}N_2O_3S$: $[M+H]^+$:289.0641, found: 289.0640.



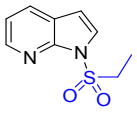
1d

Purification by column chromatography on silica gel (R_f = 0.48, petroleum ether/ethyl acetate = 5:1) yielded **1d** (39 mg, 24%) as a white solid; m. p. 147-151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: δ 8.56-8.40 (dd, J = 4.8, 1.6 Hz, 1H), 8.14-8.03 (m, 2H), 7.87-7.82 (dd, J = 7.9, 1.6 Hz, 1H), 7.74-7.71 (d, J = 4.0 Hz, 1H), 7.52-7.45 (m, 2H), 7.21-7.15 (dd, J = 7.9, 4.8 Hz, 1H), 6.60-6.56 (d, J =4.0 Hz, 1H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 158.0, 147.3, 144.9, 135.5, 129.5, 127.8, 126.5, 126.1, 122.8, 118.8, 105.1, 35.3, 31.0; IR(KBr): 3143, 2960, 1925, 1593, 1519, 1401, 1377, 1274, 1186, 1090, 995, 838, 741, 634, 580, 542 cm^{-1}; HRMS (ESI) calcd. for $C_{17}H_{18}N_2O_2S$: $[M+H]^+$: 315.1162, found: 315.1161.



1e

Purification by column chromatography on silica gel (R_f = 0.38, petroleum ether/ethyl acetate = 5:1) yielded **1e** (42.5 mg, 25%) as a white solid; m. p. 153-156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: δ 9.19-9.17 (d, J = 1.9 Hz, 1H), 8.54-8.49 (dd, J = 8.5, 2.6 Hz, 1H), 8.44-8.40 (dd, J = 4.9, 1.6 Hz, 1H), 7.90-7.86 (dd, J = 7.9, 1.6 Hz, 1H), 7.72-7.68 (d, J = 4.0 Hz, 1H), 7.47-7.43 (d, J = 8.4 Hz, 1H), 7.25-7.20 (dd, J = 7.9, 4.8 Hz, 1H), 6.67-6.63 (d, J = 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 156.9, 149.5, 147.1, 145.2, 138.5, 133.9, 130.0, 125.8, 124.6, 122.9, 119.5, 106.3; IR(KBr): 3103, 3044, 1560, 1450, 1385, 1361, 1269, 1181, 1017, 887, 783, 733,577 cm^{-1}; HRMS (ESI) calcd. for $C_{12}H_8ClN_3O_2S$: $[M+H]^+$: 294.0099, found: 294.0095.

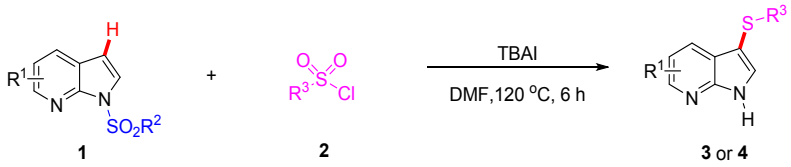


1f

Purification by column chromatography on silica gel (R_f = 0.40, petroleum ether/ethyl acetate = 3:1) yielded **1f** (196 mg, 66%) as a yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: δ 8.52-8.39 (dd, J = 4.8, 1.6 Hz, 1H), 8.01-7.93 (dd, J = 7.9, 1.6 Hz, 1H), 7.65-7.58 (d, J = 4.0 Hz, 1H), 7.29-7.22 (dd, J = 7.9, 4.8 Hz, 1H), 6.65-6.58 (d, J = 4.0 Hz, 1H), 3.87-3.75 (q, J = 7.4 Hz, 2H), 1.31-1.21 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 147.2, 144.8, 130.0, 126.6, 122.9, 119.0, 104.6, 48.7, 7.6; IR(KBr): 3144, 2942, 1740, 1519, 1363, 1273, 1161, 1049, 994, 892, 730, 598, 550 cm^{-1}; HRMS (ESI) calcd. for $C_9H_{10}N_2O_2S$: $[M+H]^+$: 211.0536, found: 211.0534.

3. General procedure for the preparation of products 3 and 4.

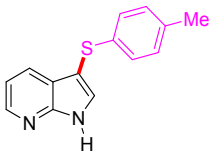
The preparation of product **3a** is representative for the synthesis of the 3-thio-7-azaindole products.



1 **2** **3** or **4**

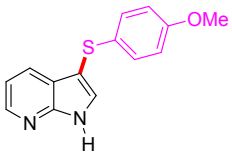
To a 10 mL tube, *N*-sulfonyl protected 7-azaindoles **1** (0.15 mmol), sulfonyl chlorides **2** (0.45 mmol), TBAI (0.45 mmol) and DMF (1.0 mL) were added under the air atmosphere. The resulting mixture was heated in a 120 °C oil bath with vigorous stirring for 6 h. Then, the reaction mixture was cooled to room temperature, quenched with a sat. NH_4Cl solution and subsequently extracted with ethyl acetate. The combined organic layers were dried over anhydrous $MgSO_4$, filtered and the solvent was evaporated under *vacuum*. The residue was purified by flash chromatography using dichloromethane/ethyl acetate (1:1) as eluent affording products **3** or **4** in 38-96% yields. In general, the identity and purity of the products were confirmed by ^{1}H and ^{13}C NMR spectroscopy, HRMS, IR and X-ray diffraction.

4. Characterization data of the products



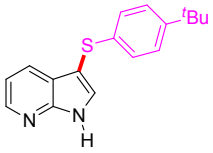
3a

Purification by column chromatography on silica gel (R_f = 0.29, petroleum ether/ethyl acetate = 3:1) yielded **3a**-1 (31.2 mg, 86%), **3a**-2 (21.6 mg, 60%), **3a**-3 (25.2 mg, 70%), **3a**-4 (24.9 mg, 69%), **3a**-5 (21.7 mg, 60%), **3a**-6 (19.5 mg, 54%) as a white solid; m. p. 133-136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 11.38 (s, 1H), 8.38 (s, 1H), 8.00-7.900 (dd, J = 7.8, 1.3 Hz, 1H), 7.67 (s, 1H), 7.17-7.11 (dd, J = 7.8, 4.8 Hz, 1H), 7.06-7.01 (dd, J = 6.3, 1.9 Hz, 2H), 7.01-6.96 (d, J = 8.3 Hz, 2H) 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 149.0 143.6 135.1 134.9 131.2 129.6 128.4 126.6, 121.9, 116.9, 102.5, 20.9;IR(KBr): 3130, 3018, 2918, 2854, 1894, 1605, 1588, 1489, 1283, 1112, 1083, 893, 803, 769, 614, 571 cm^{-1}; HRMS (ESI) calcd. for $C_{14}H_{12}N_2S$: $[M+H]^+$: 241.0794, found: 241.0791.



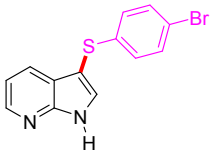
3b

Purification by column chromatography on silica gel (R_f = 0.48, petroleum ether/ethyl acetate = 1:1) yielded **3b** (34.9 mg, 91%) as a yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: δ 11.10 (s, 1H), 8.40-8.33 (d, J = 4.8 Hz, 1H), 7.98-7.91 (d, J = 7.9Hz, 1H), 7.64 (s, 1H), 7.19-7.09 (m, 3H), 6.81-6.71 (d, J = 8.8 Hz, 2H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 158.1, 149.1, 143.4, 130.8, 129.0, 128.9, 128.4, 121.9, 116.8, 114.6, 103.5, 55.3; IR(KBr): 3083, 2979, 2918, 2867, 1588, 1493, 1461, 1411, 1334, 1283, 1173, 1029, 893, 806, 765, 612, 571, 523, 504 cm^{-1}; HRMS (ESI) calcd. for $C_{14}H_{12}N_2OS$: $[M+H]^+$: 257.0743, found: 257.0742.



3c

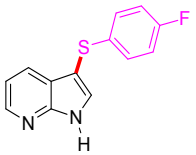
Purification by column chromatography on silica gel (R_f = 0.30, petroleum ether/ethyl acetate = 3:1) yielded **3c** (30.7 mg, 73%) as a white solid; m. p. 158-163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: δ 11.36 (s, 1H), 8.46-8.38 (dd, J =4.8, 1.6 Hz, 1H), 8.04-7.96 (dd, J =7.9, 1.5 Hz, 1H), 7.67 (s, 1H), 7.22-7.19 (m, 2H), 7.18-7.14 (dd, J=7.9, 4.8 Hz, 1H), 7.08-7.03 (m, 2H), 1.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 149.1, 148.3, 143.4, 135.2, 131.6, 128.5, 126.0, 125.9, 122.2, 116.8, 102.0, 34.3, 31.3; IR(KBr): 3135, 2954, 2860, 1677, 1587, 1497, 1415, 1312, 1283, 1116, 895, 839, 767, 618, 546, 504 cm^{-1}; HRMS (ESI) calcd. for $C_{17}H_{18}N_2S$: $[M+H]^+$:283.1263, found: 283.1260.



3d

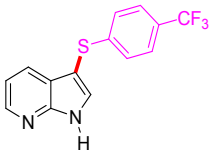
Purification by column chromatography on silica gel (R_f = 0.60, petroleum ether/ethyl acetate = 1:1) yielded **3d** (40.4 mg, 89%) as a white solid; m. p. 210-213 °C; ^{1}H NMR

(400 MHz, $CDCl_3$) ppm: δ 11.08 (s, 1H), 8.46-8.37 (dd, J=4.8, 1.6 Hz, 1H), 7.94-7.87 (dd, J=7.9, 1.6 Hz, 1H), 7.68 (s, 1H), 7.30-7.26 (m, 2H), 7.20-7.13 (dd, J =7.9, 4.8 Hz, 1H), 6.99-6.94 (m, 2H); ^{3}C NMR (100 MHz, $CDCl_3$) 149.1, 143.8, 138.0, 131.8, 131.8, 128.3, 127.6, 121.7, 118.7, 117.0, 101.0; IR(KBr): 3129, 3076, 2916, 1587, 1470, 1412, 1277, 1114, 1083, 1007, 893, 811, 773, 613, 570, 511 cm^{-1}; HRMS (ESI) calcd. for $C_{13}H_9BrN_2S$: $[M+H]^+$: 304.9743, found: 304.9740.



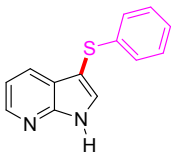
3e

Purification by column chromatography on silica gel (R_f = 0.50, petroleum ether/ethyl acetate = 1:1) yielded **3e** (35 mg, 96%) as a white solid; m. p. 176-179 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: δ 11.11 (s, 1H), 8.42-8.39 (dd, J = 4.8, 1.5 Hz, 1H), 7.94-7.90 (dd, J = 7.9, 1.6 Hz, 1H), 7.68 (s, 1H), 7.19-7.13 (dd, J=7.9, 4.8 Hz, 1H), 7.13-7.08 (m, 2H), 6.93-6.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 161.1 (d, J = 243.3 Hz), 149.1, 143.8, 133.51, 133.47, 131.4, 128.3, 128.2, 121.8, 117.0, 116.0, 115.8, 102.3; IR(KBr): 3128, 3073, 2916, 1589, 1487, 1410, 1308, 1281, 1212, 1112, 1081, 1011, 891, 821, 769, 616, 571, 502 cm^{-1}; HRMS (ESI) calcd. for $C_{13}H_9FN_2S$: $[M+H]^+$: 245.0543, found: 245.0539.



3f

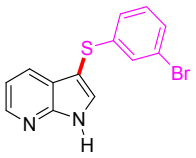
Purification by column chromatography on silica gel (R_f = 0.56, petroleum ether/ethyl acetate = 1:1) yielded **3f** (41.1 mg, 93%) as a white solid; m. p. 159-164 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: δ 10.99 (s, 1H), 8.46-8.40 (dd, J = 4.7, 1.6 Hz, 1H), 7.94-7.88 (dd, J = 7.9, 1.6 Hz, 1H), 7.71 (s, 1H), 7.45-7.37 (d, J =8.2 Hz, 2H), 7.21-7.16 (dd, J = 7.9, 4.8 Hz, 1H), 7.16 – 7.11 (d, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 149.2, 144.3, 143.7, 132.4, 128.4, 127.1 (q, J = 33 Hz), 125.64, 125.57, 125.4, 124.8 (q, J = 270 Hz), 121.9, 117.1, 99.8; IR(KBr): 3078, 2987, 2919, 1606, 1589, 1409, 1334, 1281, 1158, 1112, 1086, 961, 892, 825, 769, 615, 572, 507 cm^{-1}; HRMS (ESI) calcd. for $C_{14}H_9F_3N_2S$: $[M+H]^+$: 295.0511, found: 295.0510.



3g

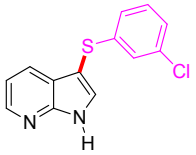
Purification by column chromatography on silica gel (R_f = 0.49, petroleum ether/ethyl acetate =1:1) yielded **3g** (30.2 mg, 89%) as a white solid; m. p. 175-178 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: δ 11.49 (s, 1H), 8.44-8.37 (dd, J = 4.8, 1.6 Hz, 1H), 8.00-7.90 (dd, J = 7.9, 1.6 Hz, 1H), 7.70 (s, 1H), 7.21-7.13 (m, 3H), 7.13-7.03 (dd, J = 16.0, 7.5

Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 149.2, 143.5, 138.8, 131.8, 128.8, 128.5, 126.0, 125.1, 122.1, 116.9, 101.5; IR(KBr): 3062, 2920, 1607, 1579, 1475, 1412, 1310, 1284, 1124, 1082, 1012, 964, 893, 794, 770, 736, 617, 572, 504 cm^{-1}; HRMS (ESI) calcd. for $C_{13}H_{10}N_2S$: $[M+H]^+$: 227.0637, found: 227.0633.



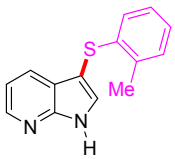
3h

Purification by column chromatography on silica gel (R_f = 0.56, petroleum ether/ethyl acetate = 1:1) yielded **3h** (36.6 mg, 80%) as a white solid; m. p. 116-118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: δ 10.62 (s, 1H), 8.46-8.37 (dd, J = 4.8, 1.6 Hz, 1H), 7.96-7.89 (dd, J =7.9, 1.5 Hz, 1H), 7.68 (s, 1H), 7.22-7.19 (dd, J = 6.3, 1.6 Hz, 2H), 7.19-7.16 (m, 1H), 7.08-6.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 149.1, 143.7, 141.4, 132.1, 130.1, 128.4, 128.3, 128.1, 124.4, 123.0, 121.9, 117.1, 100.5; IR(KBr): 3072, 2915, 1589, 1572, 1458, 1412, 1308, 1283, 1111, 1010, 894, 834, 768, 672, 571 cm^{-1}; HRMS (ESI) calcd. for $C_{13}H_9BrN_2S$: $[M+H]^+$: 304.9743, found: 304.9738.



3i

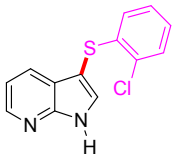
Purification by column chromatography on silica gel (R_f = 0.41, petroleum ether/ethyl acetate = 3:1) yielded **3i** (37.2 mg, 95%) as a yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: δ 11.92 (s, 1H), 8.45-8.42 (dd, J = 4.8, 1.6 Hz, 1H), 7.97-7.93 (dd, J=7.8, 1.6 Hz, 1H), 7.73 (s, 1H), 7.21-7.17 (dd, J = 7.9, 4.8 Hz, 1H), 7.13-7.07 (m, 1H), 7.06-7.02 (m, 2H), 7.00-6.96 (dt, J = 7.7, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 149.2, 143.6, 141.2, 134.8, 132.3, 129.8, 128.4, 125.5, 125.2, 123.9, 122.0, 117.0, 100.3; IR(KBr): 3132, 2976, 2870, 1574, 1498, 1409, 1337, 1282, 1109, 893, 795, 768, 677, 618, 570, 503 cm^{-1}; HRMS (ESI) calcd. for $C_{13}H_9ClN_2S$: $[M+H]^+$: 261.0248, found: 261.0247.



3j

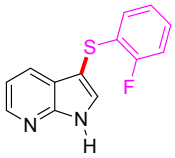
Purification by column chromatography on silica gel (R_f = 0.37, petroleum ether/ethyl acetate = 3:1) yielded **3j** (30.5 mg, 85%) as a white solid; m. p. 102-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: δ 11.31 (s, 1H), 8.48-8.35 (dd, J = 4.8, 1.6 Hz, 1H), 7.95-7.89 (dd, J = 7.9, 1.6 Hz, 1H), 7.67 (s, 1H), 7.20-7.10 (dd, J = 7.7, 4.9 Hz, 2H), 7.04-6.96 (td, J = 7.4, 1.4, 1H), 6.95-6.88 (m, 1H), 6.79-6.65 (d, J = 9.2, 1H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 149.2, 143.6, 137.8, 134.6, 131.8, 130.0, 128.5, 126.3, 125.4, 124.8, 122.2, 116.9, 101.1, 19.9; IR(KBr): 3067, 2922, 2561, 1587, 1466, 1410, 1336, 1313, 1283, 1124, 1044, 1013, 893, 792, 771, 749, 620, 572, 502 cm^{-1}; HRMS (ESI)

calcd. for $C_{14}H_{12}N_2S$: $[M+H]^+$: 241.0794, found: 241.0791.



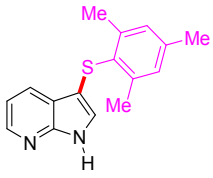
3k

Purification by column chromatography on silica gel (R_f = 0.60, petroleum ether/ethyl acetate = 1:1) yielded **3k** (34.5 mg, 88%) as a white solid; m. p. 167-171 °C; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: δ 11.70 (s, 1H), 8.50-8.37 (d, J =3.3 Hz, 1H), 8.00-7.91 (m, 1H), 7.73 (s, 1H), 7.40-7.30 (m, 1H), 7.22-7.15 (dd, J =7.9, 4.8 Hz, 1H), 7.05-6.98 (td, J = 7.5, 1.7 Hz, 1H), 7.00-6.91 (m, 1H), 6.70-6.60 (dd, J =7.9 Hz, 1.7, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 149.3, 143.7, 138.2, 132.6, 130.3, 129.4, 128.5, 127.0, 126.3, 125.7, 122.1, 117.1, 99.8; IR(KBr): 3131, 2919, 1589, 1572, 1489, 1447, 1431, 1412, 1313, 1281, 1121, 1029, 895, 823, 793, 771, 743, 614, 572, 514 cm^{-1}; HRMS (ESI) calcd. for $C_{13}H_9ClN_2S$: $[M+H]^+$: 261.0248, found: 261.0247.



3l

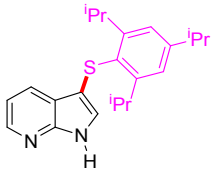
Purification by column chromatography on silica gel (R_f = 0.49, petroleum ether/ethyl acetate = 1:1) yielded **3l** (31.4 mg, 86%) as a white solid; m. p. 170-175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: δ 11.02 (s, 1H), 8.45-8.38 (dd, J = 4.8, 1.6 Hz, 1H), 7.99-7.92 (dd, J = 7.9, 1.6 Hz, 1H), 7.71 (s, 1H), 7.20-7.15 (dd, J = 7.9, 4.8 Hz, 1H), 7.11-7.00 (m, 2H), 6.91-6.85 (dt, J =8.0, 1.6 Hz, 1H), 6.84-6.77 (td, J =7.8, 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 160.5, 158.0, 149.1, 143.8, 132.1, 128.3, 126.8 (d, J = 7.4 Hz), 125.9 (d, J = 16.8 Hz), 124.4 (d, J = 3.5 Hz), 122.0, 117.1, 115.3 (d, J = 20.1), 99.8; IR(KBr): 3074, 2922, 1607, 1591, 1467, 1414, 1285, 1257, 1216, 1124, 1064, 894, 818, 745, 619, 572, 506 cm^{-1}; HRMS (ESI) calcd. for $C_{13}H_9FN_2S$: $[M+H]^+$: 245.0543, found: 245.0541.



3m

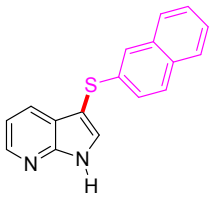
Purification by column chromatography on silica gel (R_f = 0.39, petroleum ether/ethyl acetate = 3:1) yielded **3m** (34.9 mg, 87%) as a yellow solid; m. p. 160-165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: δ 10.32 (s, 1H), 8.32-8.24 (dd, J = 4.8, 1.5 Hz, 1H), 7.82-7.73 (dd, J = 7.9, 1.5 Hz, 1H), 7.20 (s, 1H), 7.06-7.01 (dd, J = 7.9, 4.8 Hz, 1H), 6.91 (s, 2H), 2.51 (s, 6H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 148.6, 143.2, 142.2, 138.2, 129.3, 128.0, 126.5, 126.1, 121.0, 116.1, 106.6, 22.1, 21.0; IR(KBr): 3128, 2917, 1603, 1584, 1414, 1376, 1310, 1284, 1128, 1003, 893, 853, 798, 766, 609, 574, 511 cm^{-1};

HRMS (ESI) calcd. for $C_{16}H_{16}N_2S$: $[M+H]^+$: 269.1107, found: 269.1106.



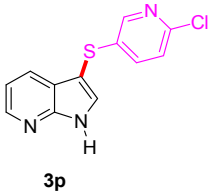
3n

Purification by column chromatography on silica gel (R_f = 0.49, petroleum ether/ethyl acetate = 3:1) yielded **3n** (34.3 mg, 65%) as a yellow solid; m. p. 213-215 °C; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: δ 10.28 (s, 1H), 8.31-8.25 (d, J = 3.2 Hz, 1H), 7.91-7.84 (dd, J = 7.9, 1.5 Hz, 1H), 7.09-7.05 (dd, J=7.9, 4.7 Hz, 1H), 7.04 (s, 2H), 6.95 (s, 1H), 4.10-3.99 (m, 2H), 2.94-2.83 (m, 1H), 1.27-1.25 (d, J = 6.9 Hz, 6H), 1.17-1.12 (d, J = 6.9 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) 152.7, 149.9, 148.5, 143.1, 127.9, 127.4, 124.5, 122.0, 120.3, 115.8, 109.2, 34.2, 31.6, 24.3, 23.9; IR(KBr): 3125, 3079, 2957, 2922, 1585, 1416, 1361, 1309, 1286, 1107, 894, 791, 769, 609, 576, 512 cm^{-1}; HRMS (ESI) calcd. for $C_{22}H_{28}N_2S$: $[M+H]^+$: 353.2046, found: 353.2043.



3o

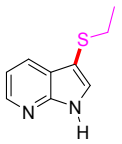
Purification by column chromatography on silica gel (R_f = 0.29, petroleum ether/ethyl acetate = 3:1) yielded **3o** (34.6 mg, 84%) as a yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: δ 12.33 (s, 1H), 8.35-8.31 (dd, J = 4.7, 1.6 Hz, 1H), 8.03 – 8.00 (d, J = 2.6 Hz, 1H), 7.85-7.76 (m, 3H), 7.71-7.66 (m, 1H), 7.56-7.52 (d, J = 1.9 Hz, 1H), 7.46 – 7.38 (tt, J=6.9, 5.2 Hz, 2H), 7.27-7.22 (dd, J=8.6, 1.9 Hz, 1H), 7.15-7.10 (dd, J=7.9, 4.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 149.0, 143.7, 136.1, 133.3, 133.2, 130.9, 128.5, 127.6, 126.74, 126.68, 126.66, 125.4, 124.4, 123.1, 120.9, 116.6, 98.5; IR(KBr): 3062, 2920, 2808, 1621, 1588, 1488, 1413, 1310, 1284, 1125, 1012, 894, 852, 809, 773, 619, 571, 504 cm^{-1}; HRMS (ESI) calcd. for $C_{17}H_{12}N_2S$: $[M+H]^+$: 277.0794, found: 277.0789.



3p

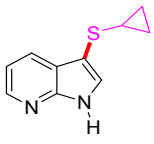
Purification by column chromatography on silica gel (R_f = 0.59, petroleum ether/ethyl acetate = 1:1) yielded **3p** (24.3 mg, 62%) as a white solid; m. p. 140-143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: δ 11.88 (s, 1H), 8.51-8.39 (dd, J = 4.8, 1.5 Hz, 1H), 8.21-8.13 (m, 1H), 7.97-7.90 (dd, J = 7.9, 1.5 Hz, 1H), 7.74 (s, 1H), 7.33-7.28 (dd, J = 8.4, 2.6 Hz, 1H), 7.23-7.17 (dd, J = 7.9, 4.8, 1H), 7.14-7.07 (dd, J = 8.4, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 149.2, 148.2, 146.9, 143.8, 136.4, 135.0, 132.2, 128.2, 124.2, 121.6,

117.2, 99.4; IR(KBr): 3073, 2841, 1582, 1547, 1443, 1409, 1352, 1276, 1112, 1011, 893, 821, 795, 722, 612, 568, 501 cm^{-1}; HRMS (ESI) calcd. for $C_{12}H_8ClN_3S$: $[M+H]^+$: 262.0200, found: 262.0196.



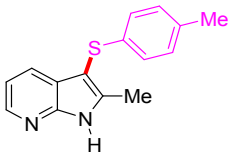
3q

Purification by column chromatography on silica gel (R_f = 0.29, petroleum ether/ethyl acetate = 3:1) yielded **3q** (13.8 mg, 52%) as a yellow liquid; ^1H NMR (400 MHz, $CDCl_3$) ppm: δ 11.50 (s, 1H), 8.39-8.36 (dd, J =4.8, 1.6 Hz, 1H), 8.14-8.08 (dd, J =7.9, 1.6 Hz, 1H), 7.53 (s, 1H), 7.21-7.16 (dd, J = 7.8, 4.8 Hz, 1H), 2.76-2.67 (q, J=7.3 Hz, 2H), 1.24-1.17 (t, J=7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 149.0, 143.0, 130.6, 128.1, 122.7, 116.3, 104.2, 30.6, 15.3; IR(KBr): 3070, 2916, 1585, 1444, 1410, 1334, 1284, 1110, 1006, 893, 789, 768, 614, 570, 503 cm^{-1}; HRMS (ESI) calcd. for $C_9H_{10}N_2S$: $[M+H]^+$: 179.0637, found: 179.0634.



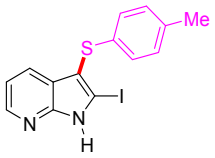
3r

Purification by column chromatography on silica gel (R_f = 0.30, petroleum ether/ethyl acetate = 3:1) yielded **3r** (13 mg, 46%) as a yellow solid; m. p. 103-106 °C; ^1H NMR (400 MHz, $CDCl_3$) ppm: δ 10.56 (s, 1H), 8.44-8.34 (dd, J = 4.8, 1.6 Hz, 1H), 8.14-8.03 (dd, J = 7.8, 1.5 Hz, 1H), 7.52-7.44 (d, J = 4.2 Hz, 1H), 7.22-7.13 (m, 1H), 2.21-2.12 (tt, J = 7.4, 4.3 Hz, 1H), 0.85-0.79 (td, J = 6.9, 4.6 Hz, 2H), 0.70-0.65 (dt, J = 6.8, 4.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 148.8, 143.3, 128.9, 128.1, 122.1, 116.5, 105.9, 16.8, 8.7; IR(KBr): 3084, 2920, 1586, 1487, 1441, 1409, 1282, 1114, 1006, 892, 872, 820, 767, 617, 502 cm^{-1}; HRMS (ESI) calcd. for $C_{10}H_{10}N_2S$: $[M+H]^+$: 191.0637, found: 191.0633.



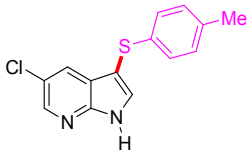
4a

Purification by column chromatography on silica gel (R_f = 0.30, petroleum ether/ethyl acetate = 3:1) yielded **4a** (26.6 mg, 70%) as a white solid; m. p. 154-157 °C; ^1H NMR (400 MHz, $CDCl_3$) ppm: δ 10.65 (s, 1H), 8.30-8.25 (dd, J = 4.9, 1.6 Hz, 1H), 7.87-7.81 (dd, J = 7.7, 1.6 Hz, 1H), 7.13-7.07 (dd, J = 7.8, 4.8 Hz, 1H), 7.01-6.97 (d, J = 8.4 Hz, 2H), 6.97-6.93 (d, J =8.4, 2H), 2.61 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 148.4, 142.3, 142.2, 135.2, 134.7, 129.6, 127.2, 125.9, 123.3, 116.8, 98.6, 20.8, 12.3; IR(KBr): 2916, 2847, 1589, 1531, 1490, 1410, 1280, 1116, 1016, 927, 802, 768, 661, 504 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{14}N_2S$: $[M+H]^+$: 255.0950, found: 255.0946.



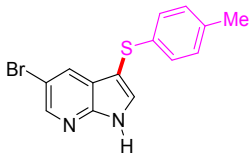
4b

Purification by column chromatography on silica gel (R_f = 0.40, petroleum ether/ethyl acetate = 3:1) yielded **4b** (29.2 mg, 53%) as a white solid; m. p. 168-171 °C; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: δ 13.92 (s, 1H), 8.41-8.38 (dd, J = 4.9, 1.6 Hz, 1H), 7.94-7.90 (dd, J = 7.9, 1.5 Hz, 1H), 7.20-7.16 (dd, J = 7.9, 4.8 Hz, 1H), 7.08-7.04 (d, J = 8.3 Hz, 2H), 7.03-6.99 (d, J = 8.2 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 147.2, 142.3, 135.5, 133.6, 132.3, 129.7, 128.2, 127.0, 123.3, 117.3, 99.8, 20.9; IR(KBr): 2970, 2659, 1584, 1493, 1411, 1343, 1280, 1085, 1016, 917, 806, 768, 630, 569 cm^{-1}; HRMS (ESI) calcd. for $C_{14}H_{11}IN_2S$: $[M+H]^+$: 366.9760, found: 366.9762.



4c

Purification by column chromatography on silica gel (R_f = 0.29, petroleum ether/ethyl acetate = 3:1) yielded **4c** (29.8 mg, 72%) as a white solid; m. p. 217-220 °C; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: δ 9.80 (s, 1H), 8.28-8.13 (d, J = 5.2 Hz, 1H), 7.65-7.55 (d, J = 2.4 Hz, 1H), 7.15-7.09 (d, J = 5.2 Hz, 1H), 7.08-7.03 (m, 2H), 7.03-6.98 (d, J =8.5 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 149.8, 144.2, 137.5, 136.0, 135.2, 132.4, 129.6, 126.7, 118.7, 118.4, 103.1, 20.9; IR(KBr): 3083, 2911, 1605, 1567, 1492, 1327, 1297, 1197, 1085, 951, 831, 802, 618, 600,544 cm^{-1}; HRMS (ESI) calcd. for $C_{14}H_{11}ClN_2S$: $[M+H]^+$: 275.0404, found: 275.0399.



4d

Purification by column chromatography on silica gel (R_f = 0.39, petroleum ether/ethyl acetate = 3:1) yielded **4d** (17.9 mg, 38%) as a white solid; m. p. 235-237 °C; ^{1}H NMR (400 MHz, $CDCl_3$) ppm: δ 9.85 (s, 1H), 8.41-8.38 (d, J = 2.1 Hz, 1H), 8.06-8.03 (d, J = 2.1 Hz, 1H), 7.63-7.61 (d, J = 2.5 Hz, 1H), 7.02 (s, 4H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 147.2, 144.7, 135.5, 134.2, 132.3, 130.4, 129.7, 126.7, 123.4, 113.0, 102.7, 20.9; IR(KBr): 3120, 2922, 1568, 1490, 1433, 1284, 1114, 1015, 902, 801, 627, 520 cm^{-1}; HRMS (ESI) calcd. for $C_{14}H_{11}BrN_2S$: $[M+H]^+$: 318.9899, found: 318.9902.

5. Single-crystal X-ray structure of 3b

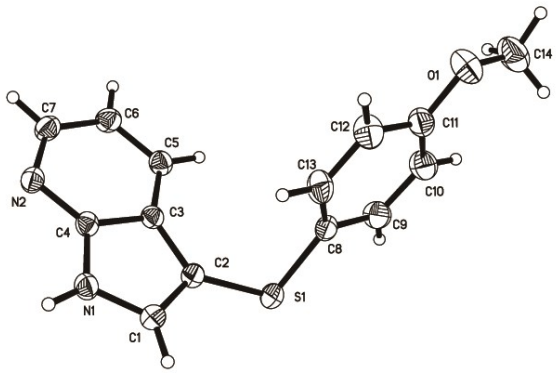


Figure S1. Single-crystal X-ray Structure of **3b**

The structure of **3b** was determined by the X-ray diffraction. Compound **3b** was recrystallized from Ethyl acetate. Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 2018442.

Table S1. Crystal data and structure refinement for 3b.

Identification code	20200771
Empirical formula	$C_{14}H_{12}N_2OS$
Formula weight	256.32
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.7203(9)
b/Å	5.3408(3)
c/Å	16.4985(9)
α/°	90
β/°	106.533(6)
γ/°	90
Volume/Å^3	1243.46(13)
Z	4
ρ_{calc}g/cm^3	1.369
μ/mm^{-1}	2.215
F(000)	536.0
Crystal size/mm^3	0.15 × 0.1 × 0.09

Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	11.162 to 134.134
Index ranges	$-17 \leq h \leq 17$, $-4 \leq k \leq 6$, $-17 \leq l \leq 19$
Reflections collected	4561
Independent reflections	2222 [R_{int} = 0.0263, R_{sigma} = 0.0425]
Data/restraints/parameters	2222/0/168
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0454, wR_2 = 0.1081
Final R indexes [all data]	R_1 = 0.0640, wR_2 = 0.1234
Largest diff. peak/hole / e Å^{-3}	0.18/-0.22

Table S2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3b. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	6710.6(5)	-280.9(14)	8079.3(4)	50.2(2)
O1	10898.8(14)	-8(4)	8850.1(15)	70.8(7)
N1	5464.8(15)	3927(4)	6121.8(13)	41.0(5)
N2	5787.0(14)	2245(4)	4880.6(12)	39.9(5)
C1	5723.2(17)	3337(5)	6964.7(15)	42.8(6)
C2	6284.4(17)	1258(5)	7108.4(15)	40.3(6)
C3	6397.8(16)	498(5)	6308.2(15)	35.9(5)
C4	5876.7(16)	2236(5)	5712.4(15)	36.0(5)
C5	6860.3(17)	-1404(5)	6013.3(16)	42.8(6)
C6	6768.2(19)	-1445(5)	5157.1(16)	45.9(6)
C7	6244.4(18)	369(5)	4629.9(16)	45.8(6)
C8	7962.1(18)	-177(5)	8279.8(15)	41.9(6)
C9	8485(2)	-2030(6)	8777.5(18)	55.1(8)
C10	9466(2)	-2020(6)	8993.3(19)	59.8(8)
C11	9934(2)	-174(6)	8691.7(18)	52.2(7)
C12	9416(2)	1683(6)	8179.2(19)	58.9(8)
C13	8437(2)	1691(5)	7982.0(18)	54.3(7)
C14	11451(2)	-1996(7)	9316(2)	78.1(11)

Table S3. Anisotropic Displacement Parameters (Å^2×10^3) for 3b. The Anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}

S1	47.7(4)	67.8(5)	35.9(4)	12.1(3)	13.3(3)	6.9(3)
O1	48.1(12)	73.6(16)	84.7(17)	4.7(12)	9.3(11)	3.7(11)
N1	40.8(11)	40.9(13)	38.7(12)	1.5(10)	7.1(9)	7.1(10)
N2	40.8(11)	43.3(12)	33.8(11)	1.5(9)	7.8(9)	-1.7(10)
C1	41.7(14)	50.0(16)	36.9(13)	-2.4(12)	11.5(11)	2.3(12)
C2	38.1(13)	48.2(15)	34.4(13)	2.6(11)	9.8(10)	0.1(12)
C3	32.0(12)	38.2(14)	36.9(13)	1.1(11)	8.9(10)	-1.1(10)
C4	32.5(12)	38.2(13)	35.1(13)	-1.4(10)	6.0(10)	-4.5(10)
C5	40.7(14)	42.5(15)	44.3(14)	5.0(12)	10.5(11)	4.9(12)
C6	50.9(15)	43.4(15)	45.9(15)	-2.6(13)	18.0(12)	6.0(13)
C7	49.2(15)	53.1(17)	36.1(14)	-3.8(12)	13.7(11)	-3.1(13)
C8	45.1(14)	47.3(15)	31.1(12)	0.4(11)	7.5(10)	4.9(12)
C9	57.6(17)	54.2(18)	55.9(18)	16.7(14)	19.8(14)	10.6(14)
C10	57.3(18)	60(2)	60.1(19)	16.0(15)	13.5(15)	19.8(16)
C11	45.7(15)	57.1(18)	50.1(16)	-6.6(14)	7.5(12)	2.7(14)
C12	57.3(18)	52.1(18)	62.4(19)	8.9(15)	9.3(15)	-8.4(15)
C13	53.9(17)	49.4(17)	52.4(17)	13.7(14)	3.4(13)	2.4(14)
C14	53.0(18)	79(3)	94(3)	-5(2)	8.0(18)	17.8(18)

Table S4 Bond Lengths for 3b.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C2	1.750(2)	C3	C4	1.410(3)
S1	C8	1.777(3)	C3	C5	1.386(3)
O1	C11	1.372(3)	C5	C6	1.380(3)
O1	C14	1.422(4)	C6	C7	1.381(4)
N1	C1	1.370(3)	C8	C9	1.373(3)
N1	C4	1.368(3)	C8	C13	1.386(4)
N2	C4	1.341(3)	C9	C10	1.385(4)
N2	C7	1.337(3)	C10	C11	1.374(4)
C1	C2	1.364(4)	C11	C12	1.383(4)
C2	C3	1.435(3)	C12	C13	1.384(4)

Table S5 Bond Angles for 3b.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	S1	C8	103.78(12)	C6	C5	C3	117.1(2)

C11	O1	C14	117.1(3)	C5	C6	C7	120.5(2)
C4	N1	C1	108.4(2)	N2	C7	C6	124.8(2)
C7	N2	C4	113.7(2)	C9	C8	S1	117.6(2)
C2	C1	N1	110.1(2)	C9	C8	C13	118.5(3)
C1	C2	S1	125.7(2)	C13	C8	S1	123.9(2)
C1	C2	C3	107.1(2)	C8	C9	C10	121.1(3)
C3	C2	S1	127.2(2)	C11	C10	C9	120.2(3)
C4	C3	C2	105.8(2)	O1	C11	C10	125.1(3)
C5	C3	C2	136.7(2)	O1	C11	C12	115.5(3)
C5	C3	C4	117.5(2)	C10	C11	C12	119.4(3)
N1	C4	C3	108.7(2)	C11	C12	C13	120.1(3)
N2	C4	N1	125.1(2)	C12	C13	C8	120.8(3)
N2	C4	C3	126.3(2)				

Table S6 Hydrogen Bonds for 3b.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/
N1	H1	N2[1]	0.86(3)	2.08(3)	2.928(3)	171(3)

Table S7 Torsion Angles for 3b.

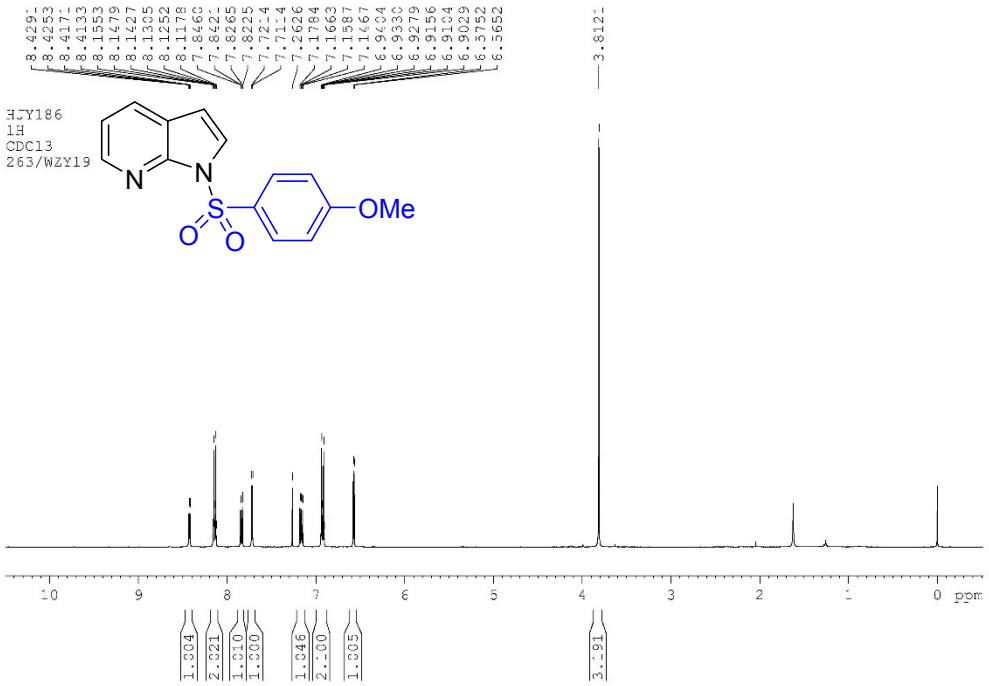
A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	C2	C3	C4	175.99(19)	C4	N2	C7	C6	0.0(4)
S1	C2	C3	C5	-3.6(4)	C4	C3	C5	C6	-0.3(3)
S1	C8	C9	C10	-177.2(2)	C5	C3	C4	N1	179.1(2)
S1	C8	C13	C12	178.5(2)	C5	C3	C4	N2	-0.4(4)
O1	C11	C12	C13	-179.9(3)	C5	C6	C7	N2	-0.7(4)
N1	C1	C2	S1	-175.43(18)	C7	N2	C4	N1	-178.8(2)
N1	C1	C2	C3	0.7(3)	C7	N2	C4	C3	0.6(3)
C1	N1	C4	N2	-179.4(2)	C8	S1	C2	C1	-121.5(2)
C1	N1	C4	C3	1.0(3)	C8	S1	C2	C3	63.2(2)
C1	C2	C3	C4	0.0(3)	C8	C9	C10	C11	-1.7(5)
C1	C2	C3	C5	-179.6(3)	C9	C8	C13	C12	0.2(4)
C2	S1	C8	C9	-153.3(2)	C9	C10	C11	O1	-178.6(3)
C2	S1	C8	C13	28.4(3)	C9	C10	C11	C12	0.7(5)
C2	C3	C4	N1	-0.6(3)	C10	C11	C12	C13	0.7(5)
C2	C3	C4	N2	179.9(2)	C11	C12	C13	C8	-1.2(5)

C2	C3	C5	C6	179.3(3)	C13	C8	C9	C10	1.2(4)
C3	C5	C6	C7	0.8(4)	C14	O1	C11	C10	4.5(4)
C4	N1	C1	C2	-1.1(3)	C14	O1	C11	C12	-174.9(3)

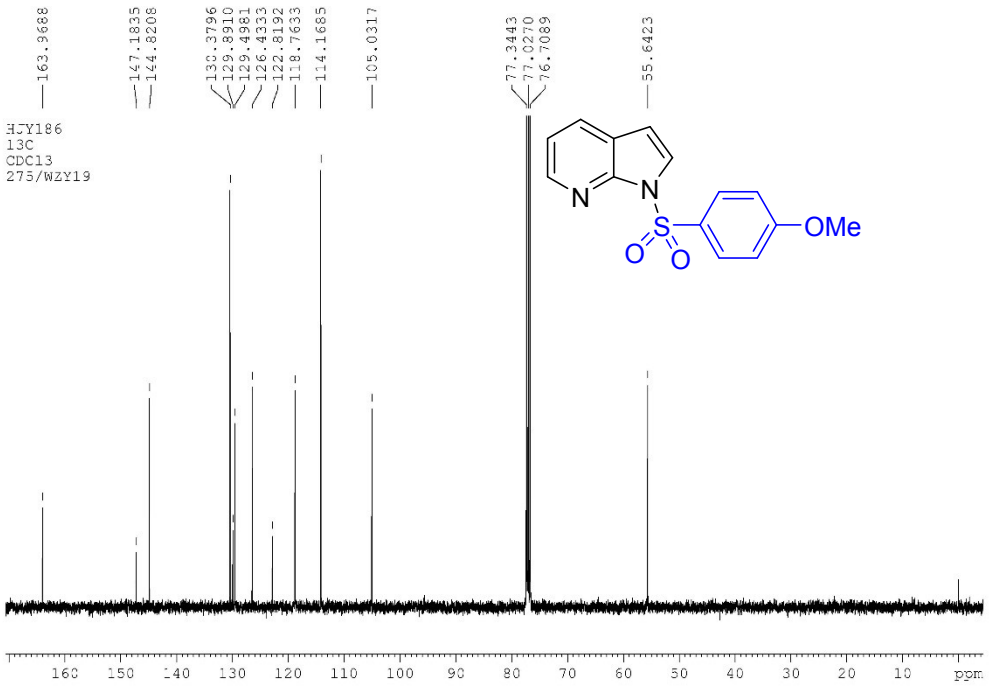
Table 8 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3b.

Atom	*x*	*y*	*z*	U(eq)
H1	5100(20)	5130(50)	5882(19)	61(10)
H1A	5542	4225	7378	51
H5	7217	-2601	6377	51
H6	7061	-2704	4933	55
H7	6207	278	4058	55
H9	8176	-3313	8973	66
H10	9809	-3266	9343	72
H12	9726	2929	7967	71
H13	8094	2963	7646	65
H14A	11249	-3555	9031	117
H14B	11370	-2055	9872	117
H14C	12107	-1722	9357	117

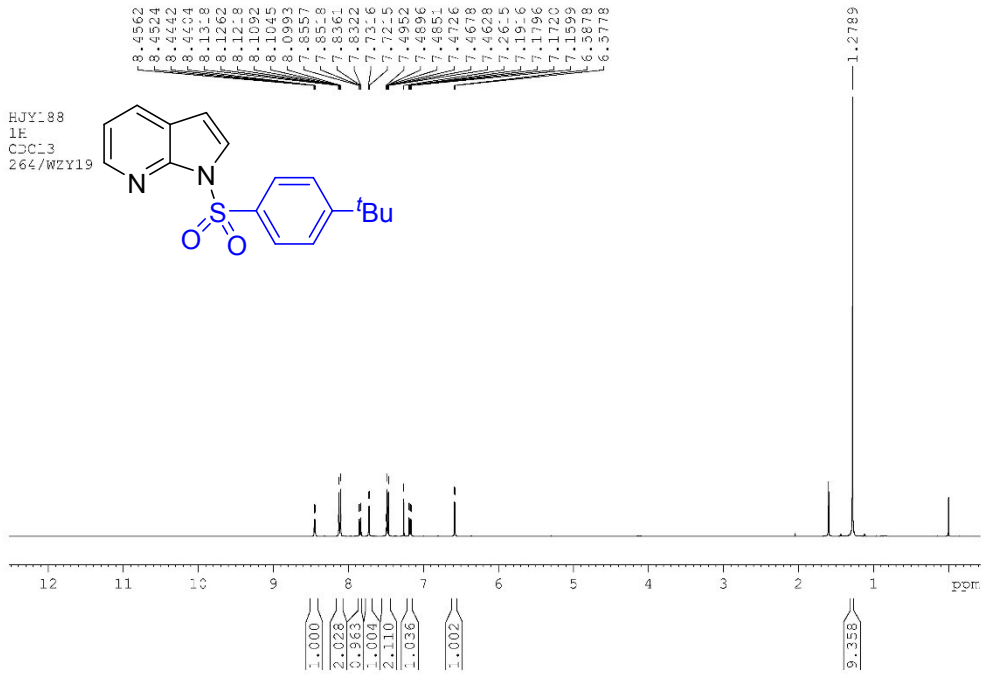
6. Copies of 1H NMR and 13C NMR spectra



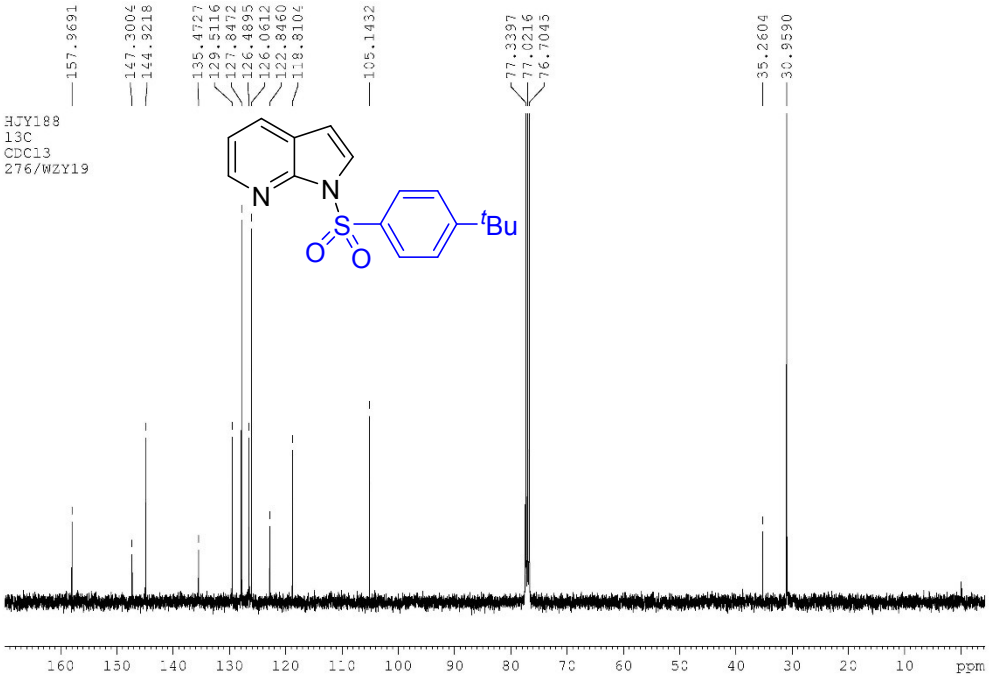
^{1}H NMR spectrum of compound **1b**



^{13}C NMR spectrum of compound **1b**



^{1}H NMR spectrum of compound **1d**



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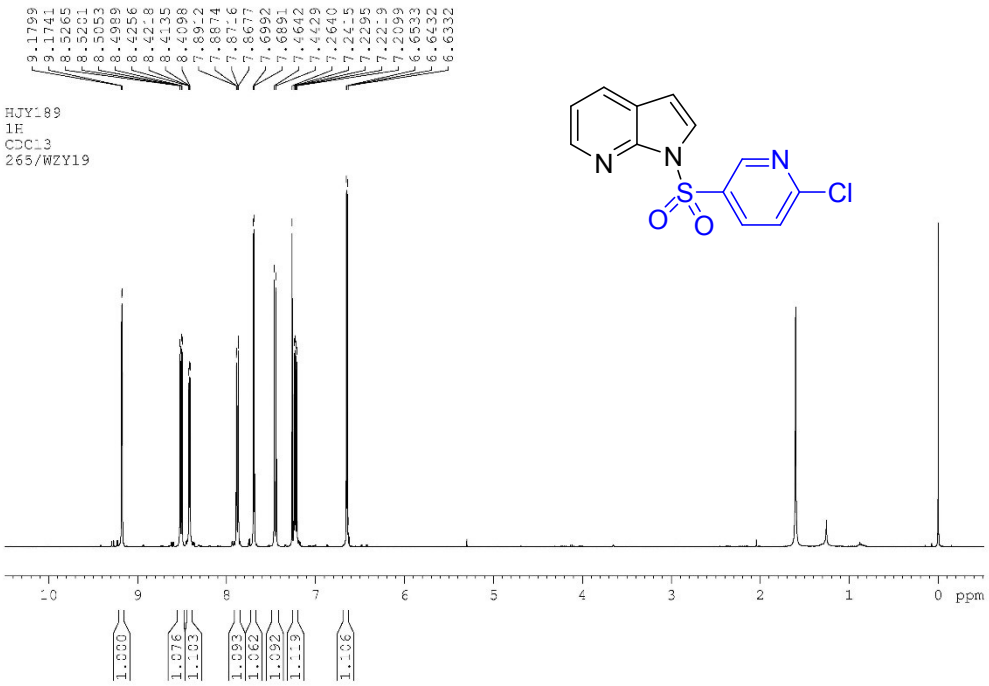
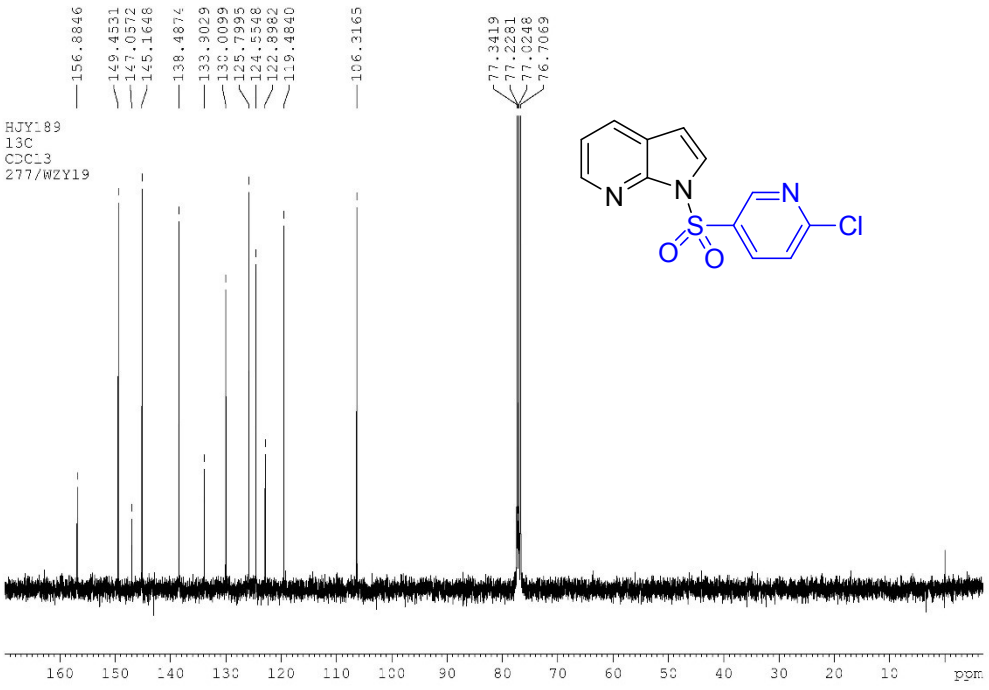
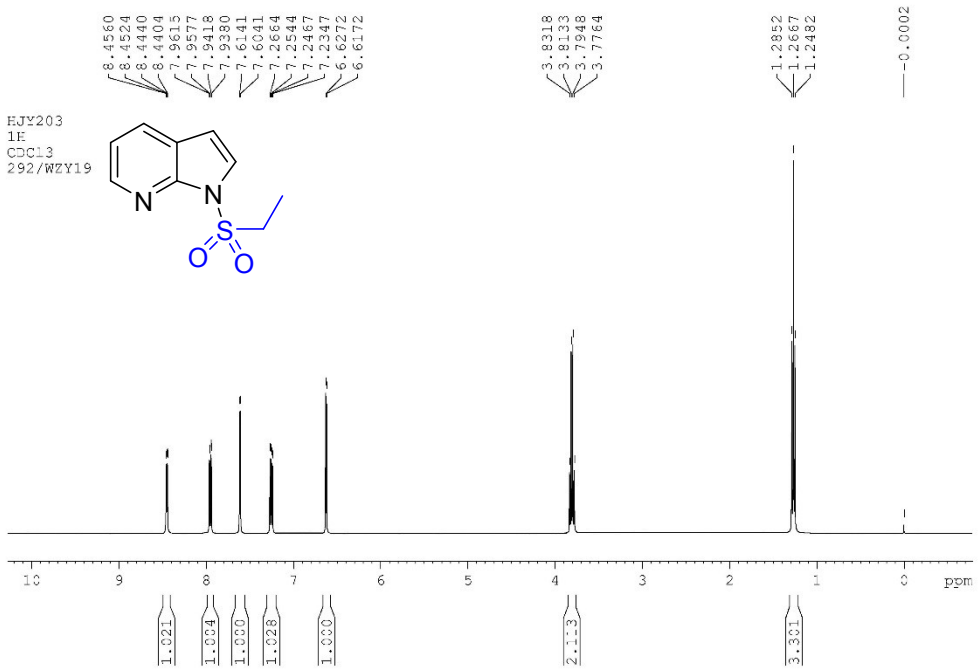


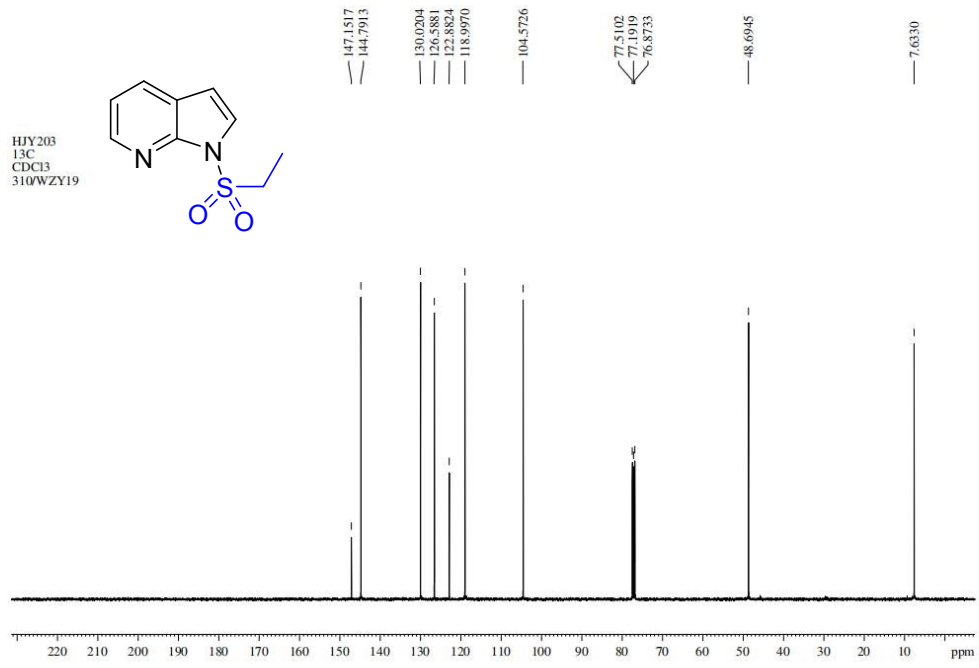
^{1}H NMR spectrum of compound **1e**



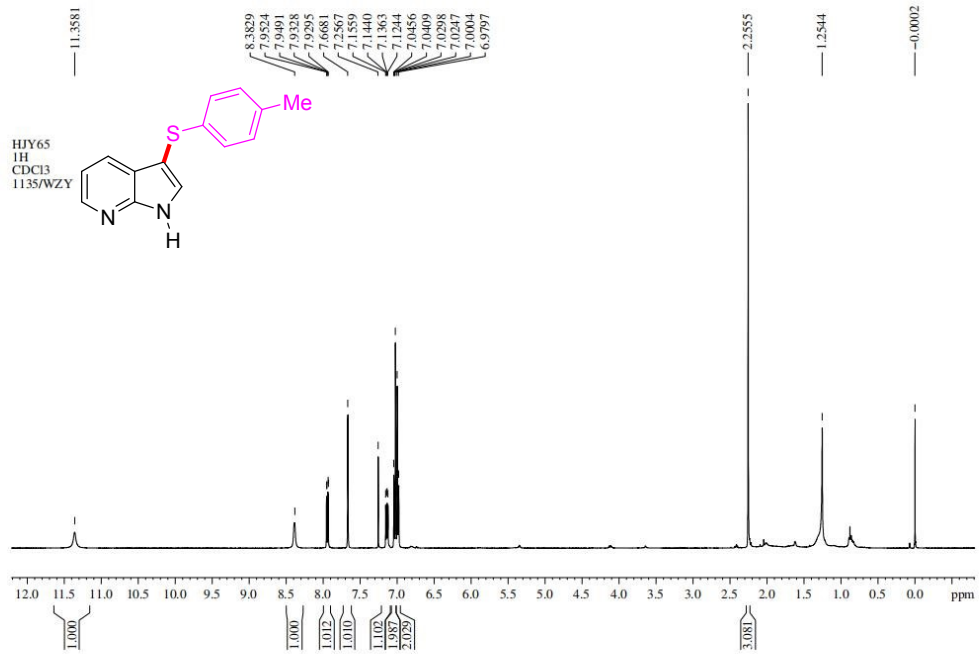
^{13}C NMR spectrum of compound **1e**



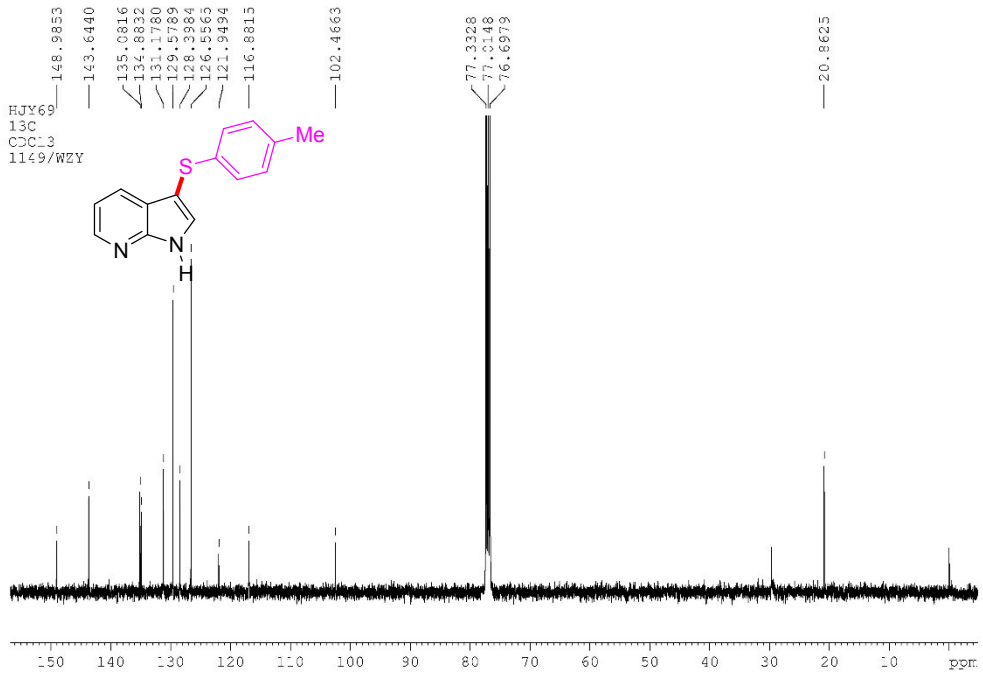
^{1}H NMR spectrum of compound **1f**



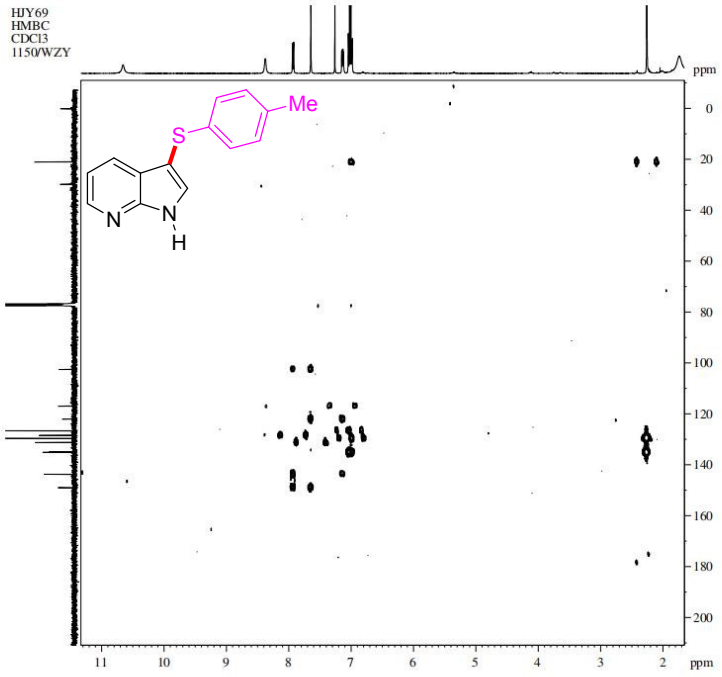
^{13}C NMR spectrum of compound **1f**



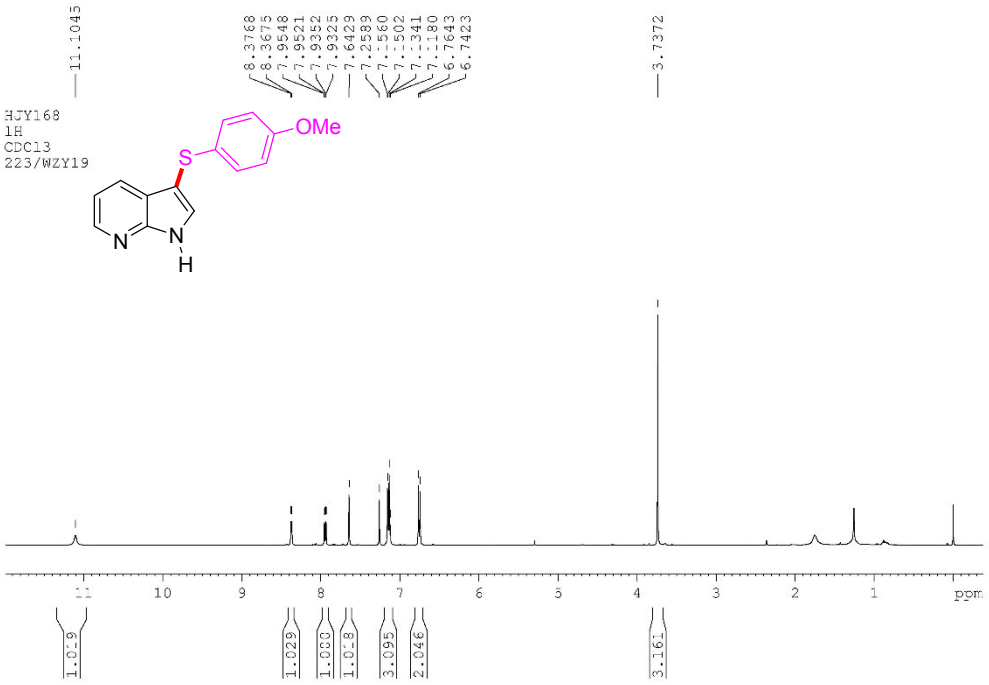
^{1}H NMR spectrum of compound **3a**



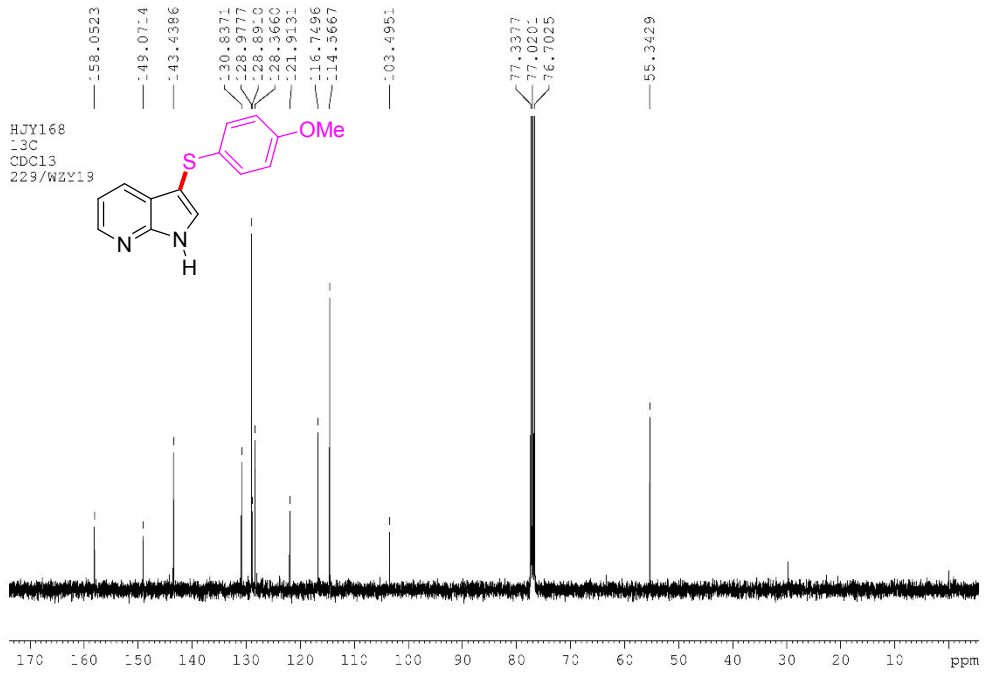
^{13}C NMR spectrum of compound **3a**



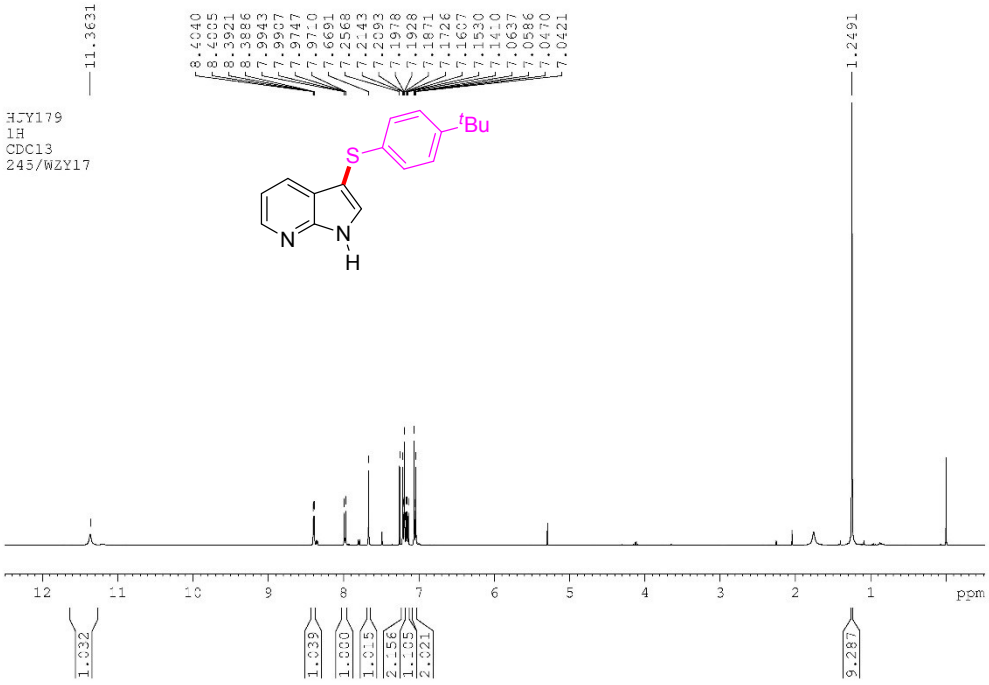
HMBC spectrum of compound **3a**



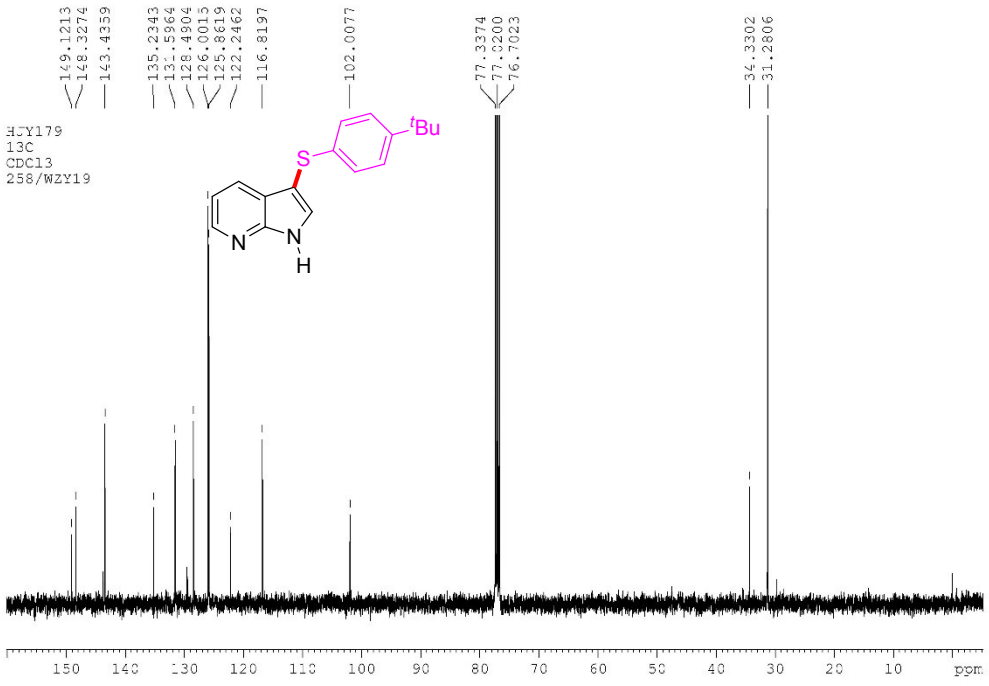
^{1}H NMR spectrum of compound **3b**



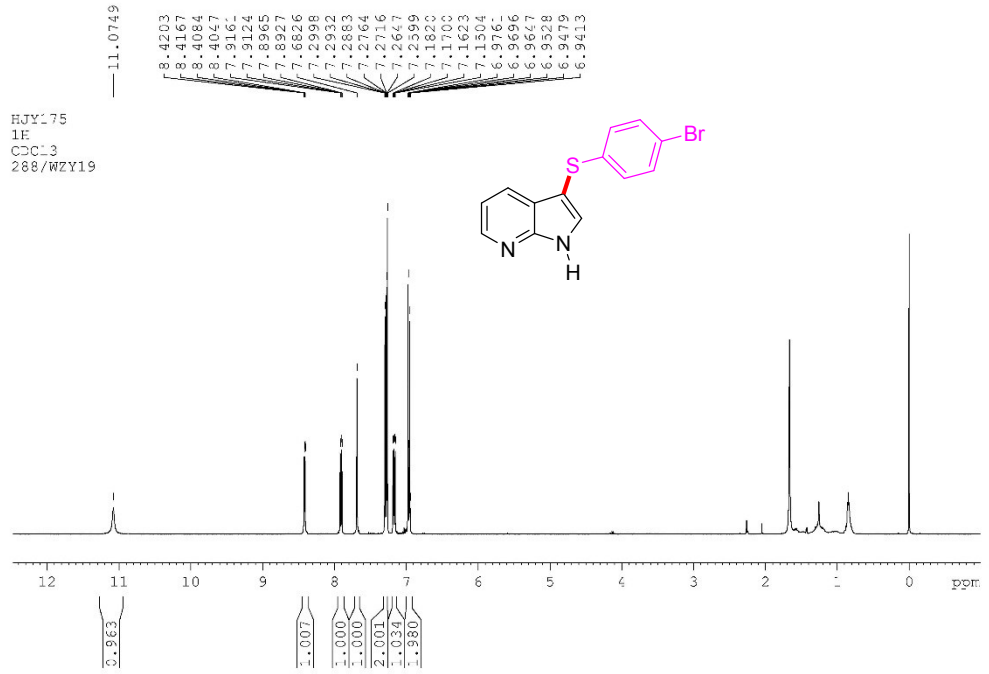
^{13}C NMR spectrum of compound **3b**



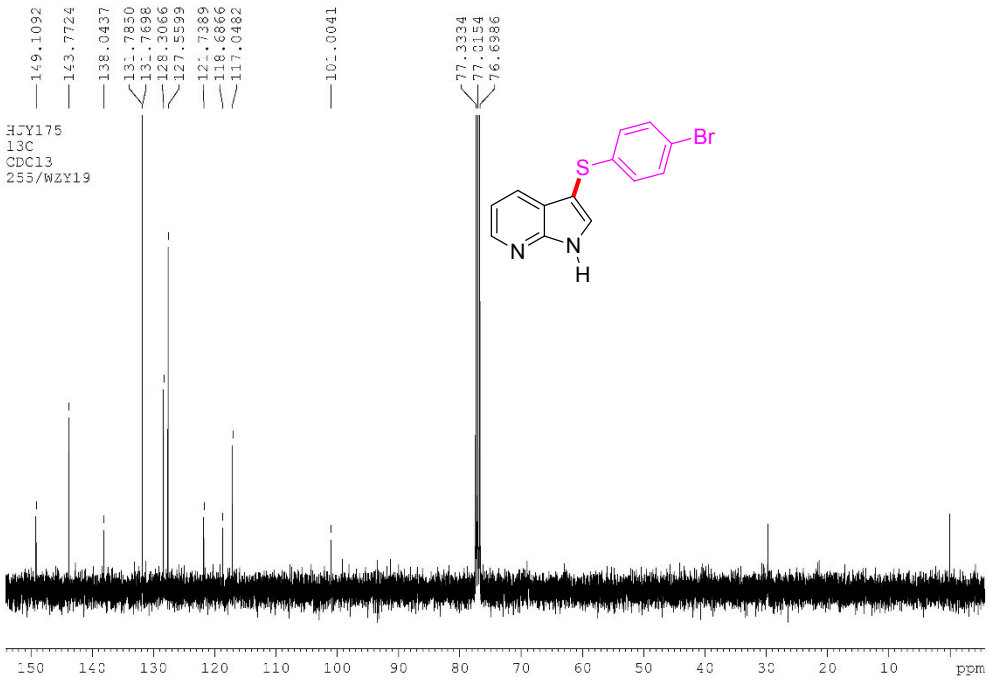
^{1}H NMR spectrum of compound **3c**



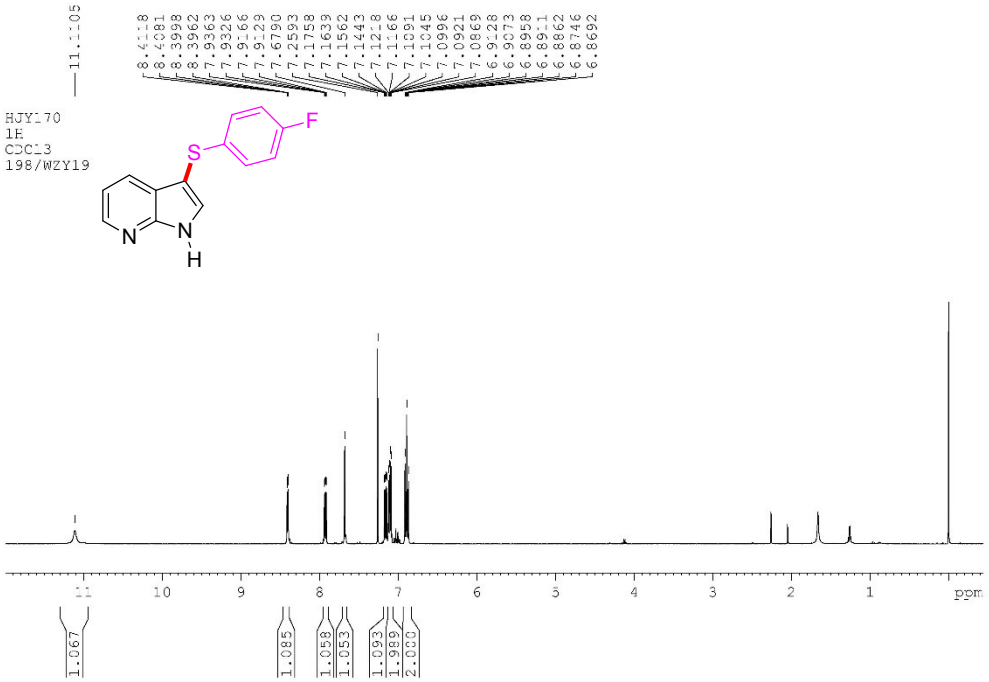
^{13}C NMR spectrum of compound **3c**



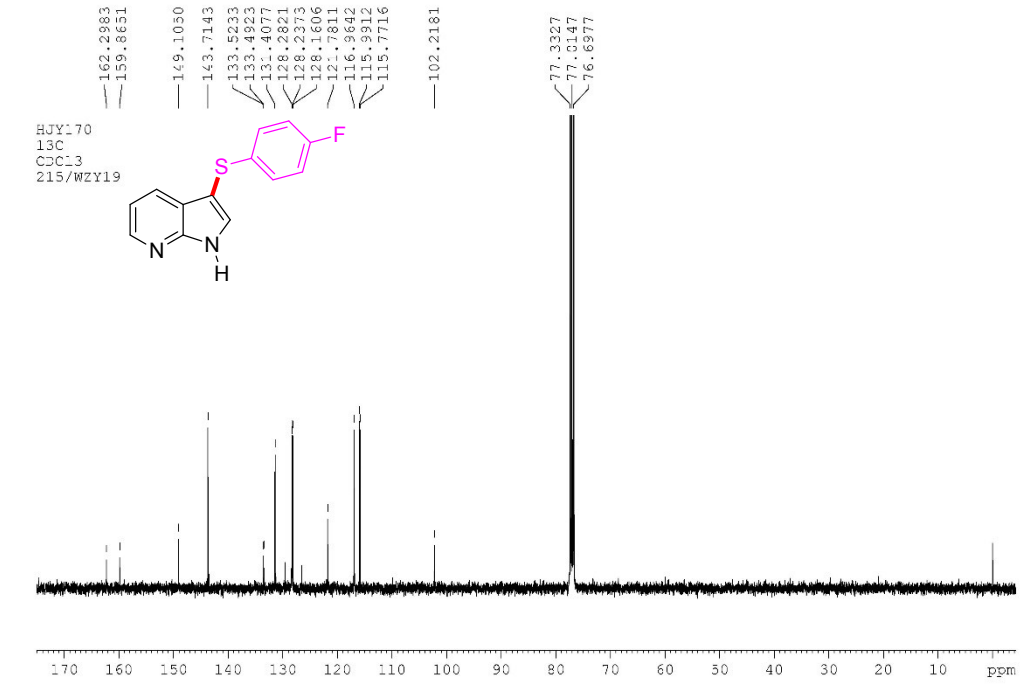
^{1}H NMR spectrum of compound **3d**



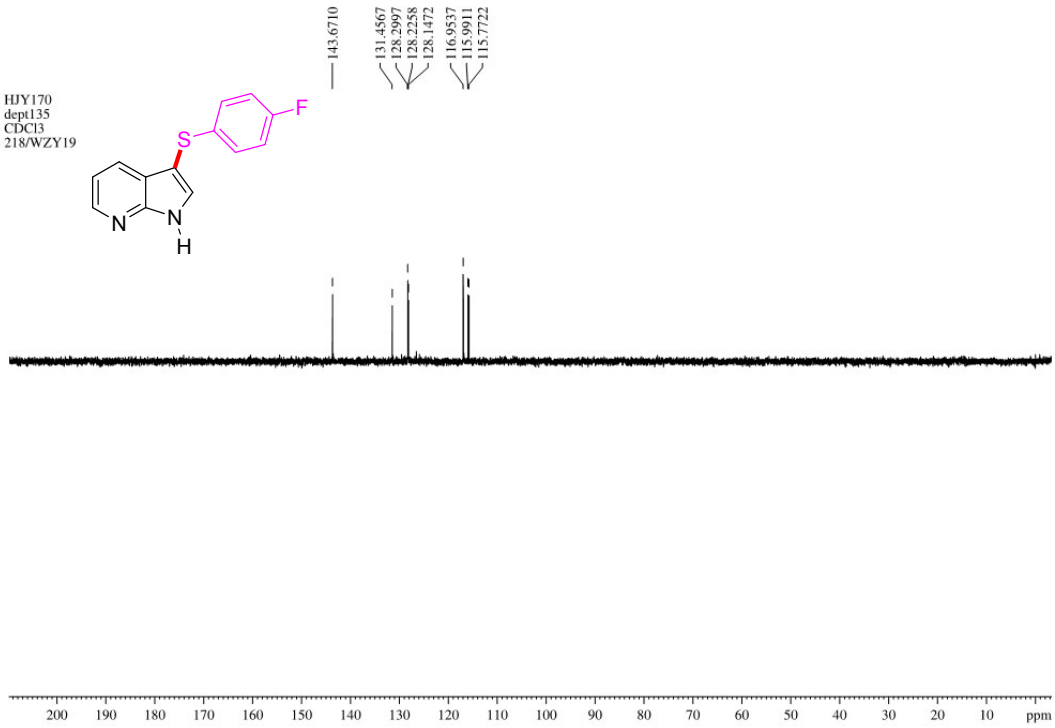
^{13}C NMR spectrum of compound **3d**



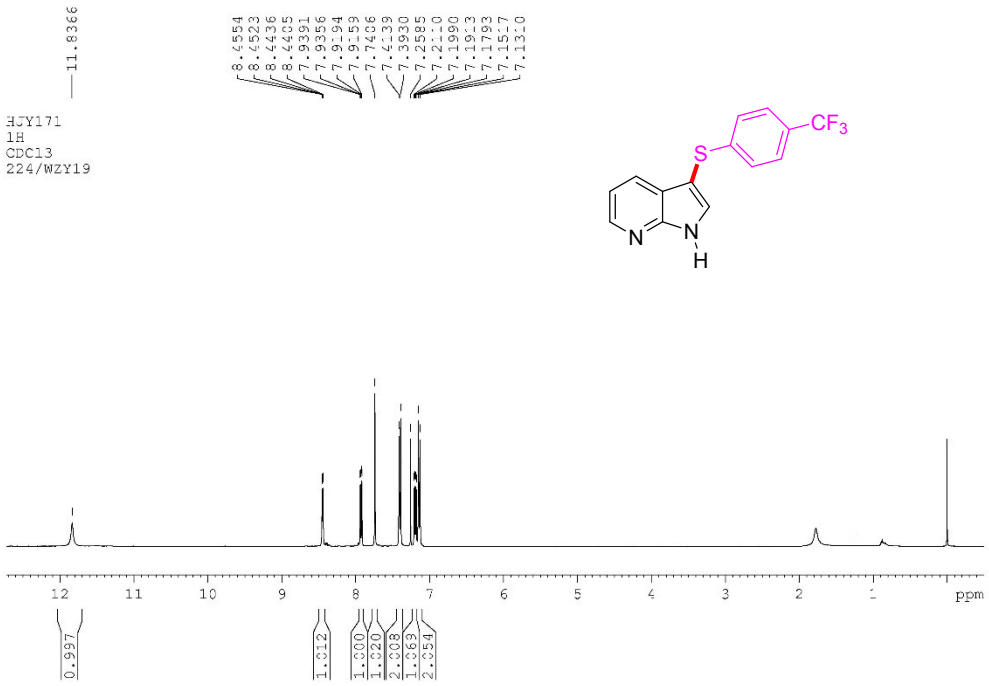
^{1}H NMR spectrum of compound **3e**



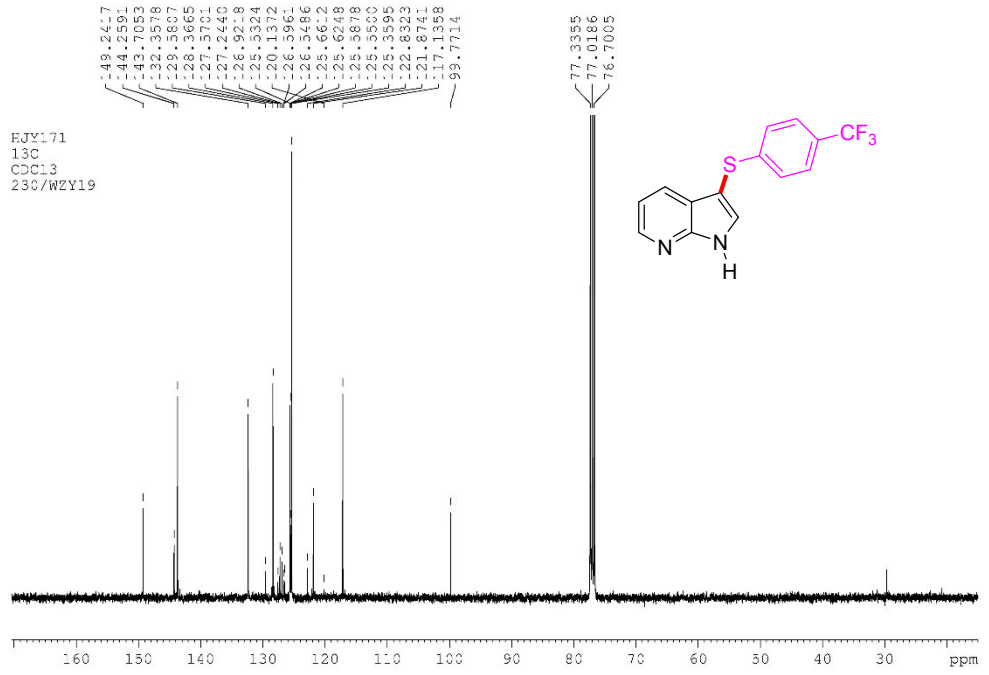
^{13}C NMR spectrum of compound **3e**



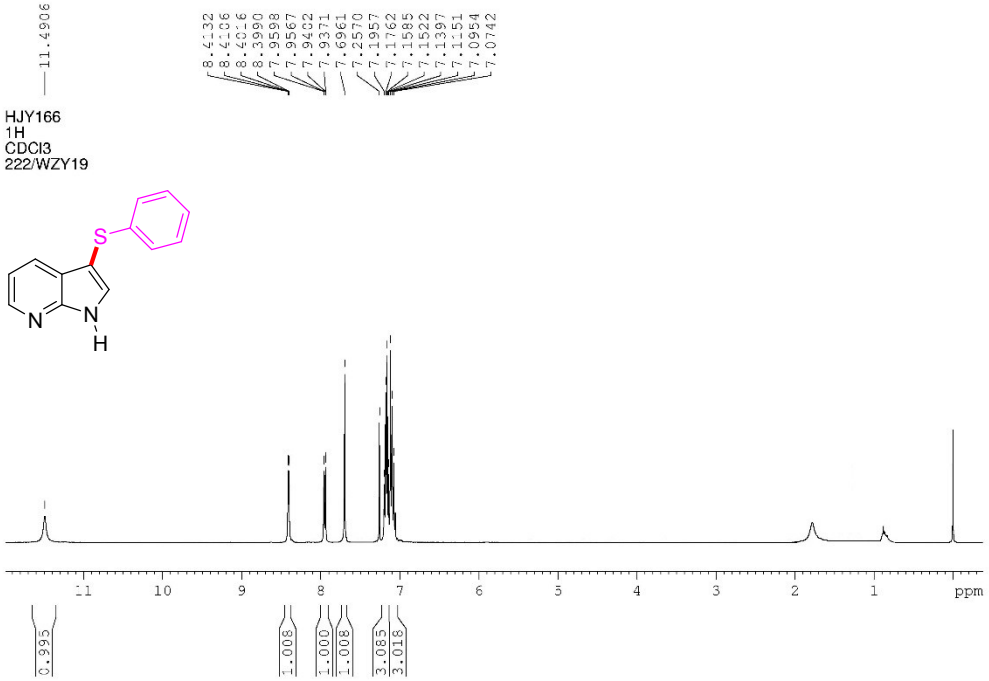
DEPT spectrum of compound **3e**



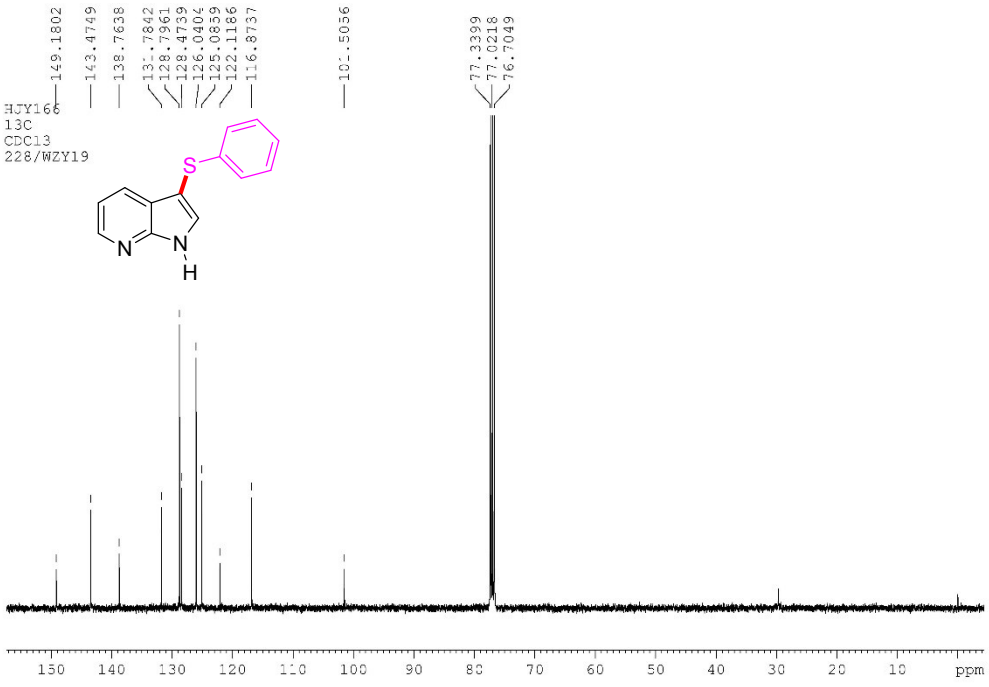
^{1}H NMR spectrum of compound **3f**



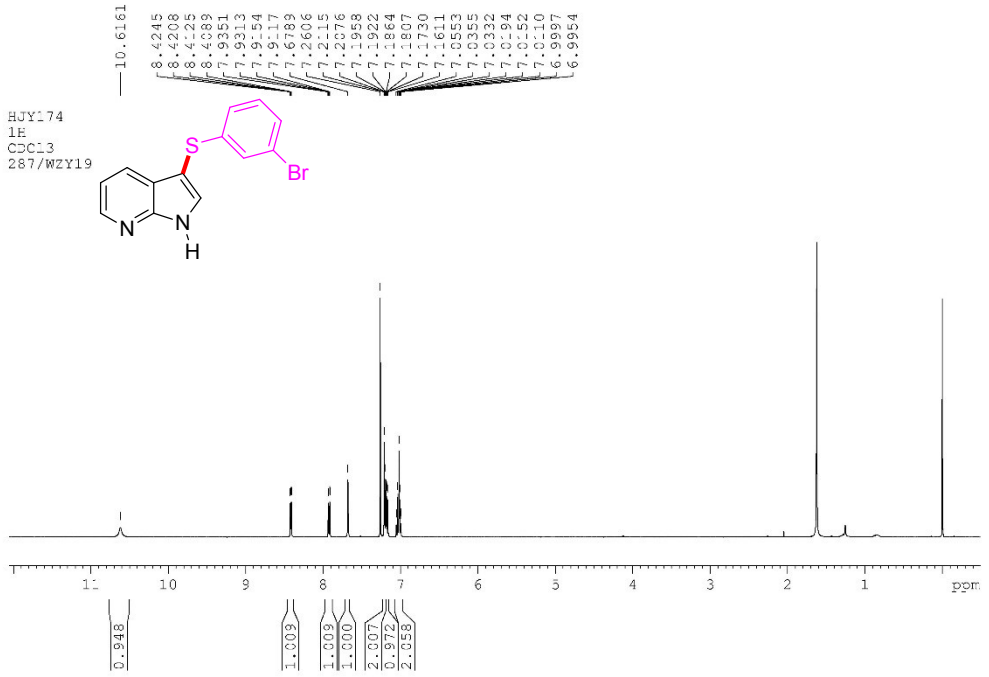
^{13}C NMR spectrum of compound **3f**



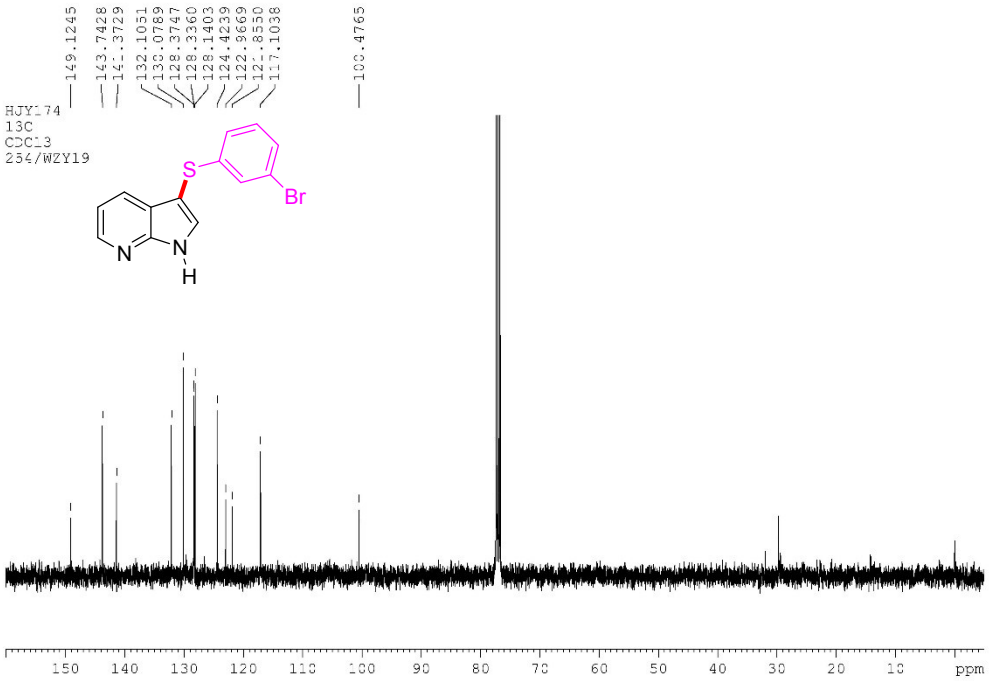
^{1}H NMR spectrum of compound **3g**



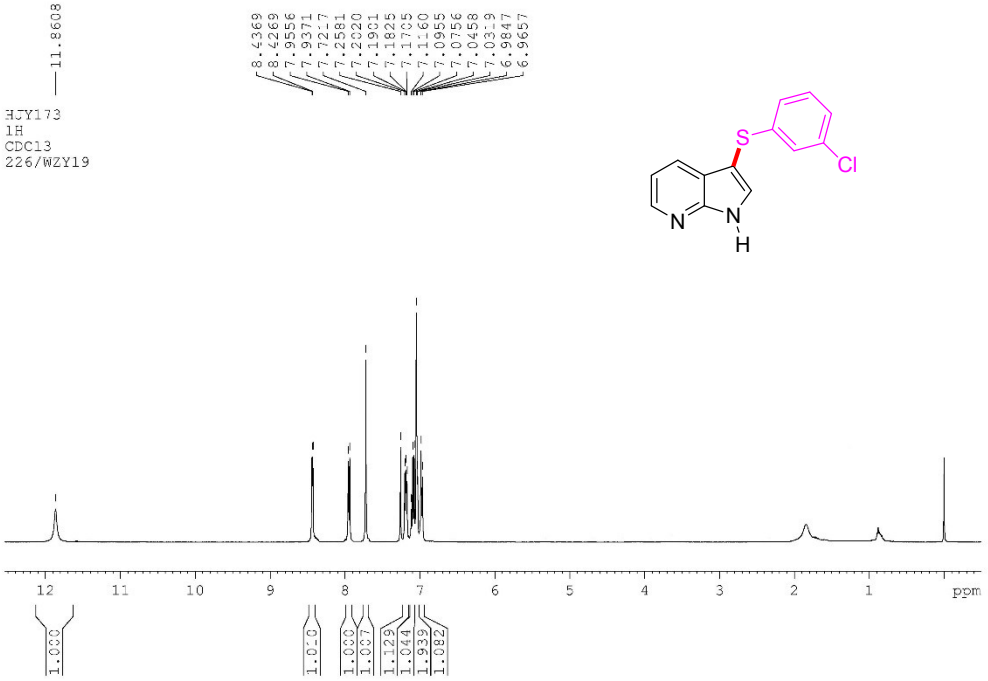
^{13}C NMR spectrum of compound **3g**



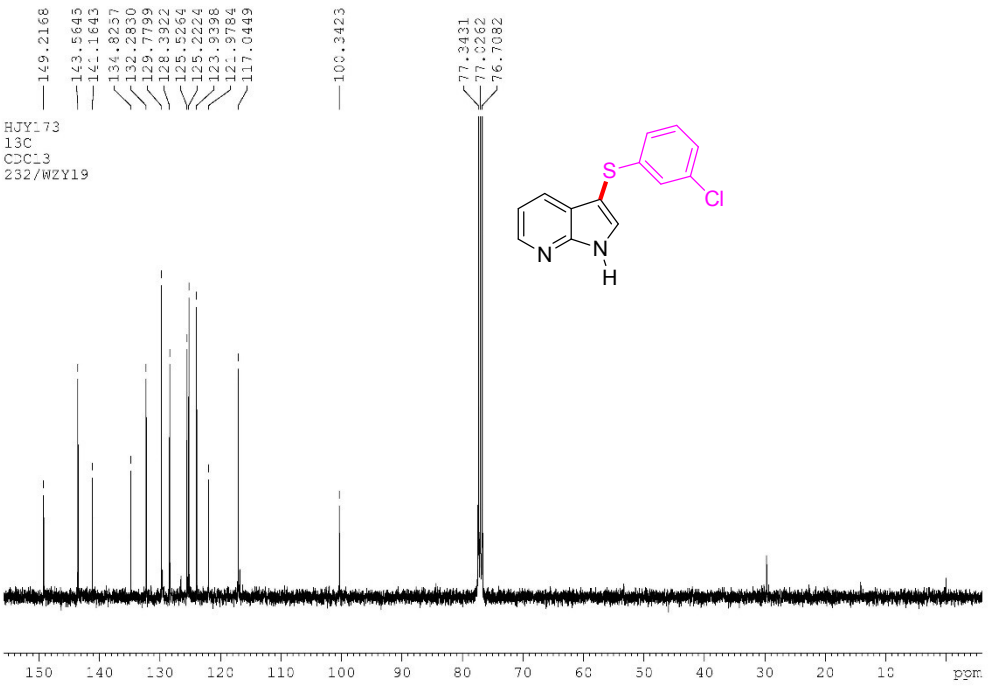
^{1}H NMR spectrum of compound **3h**



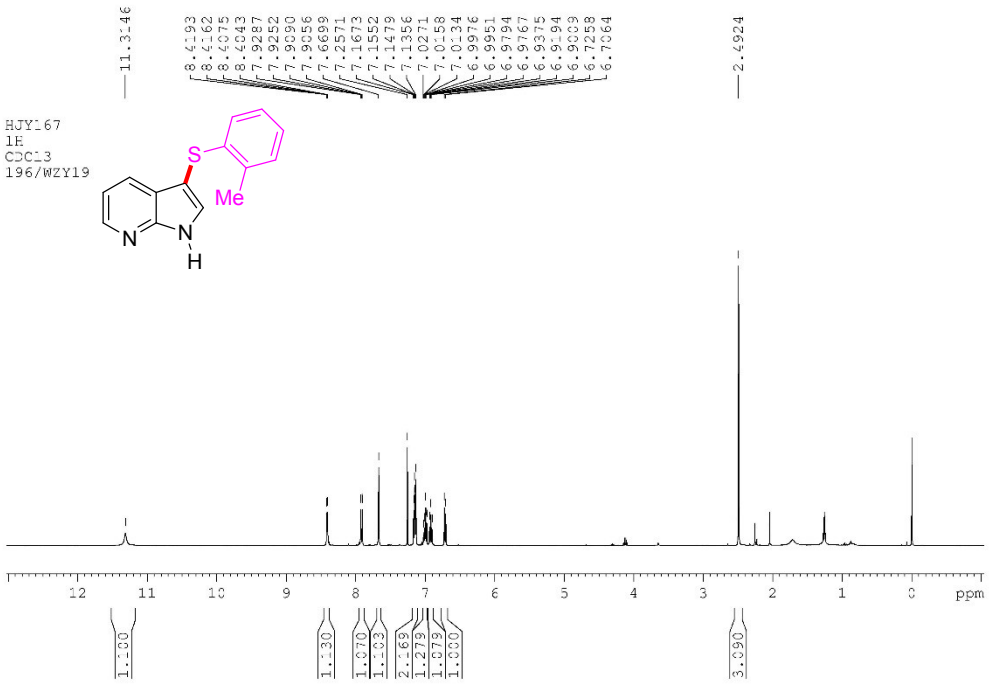
^{13}C NMR spectrum of compound **3h**



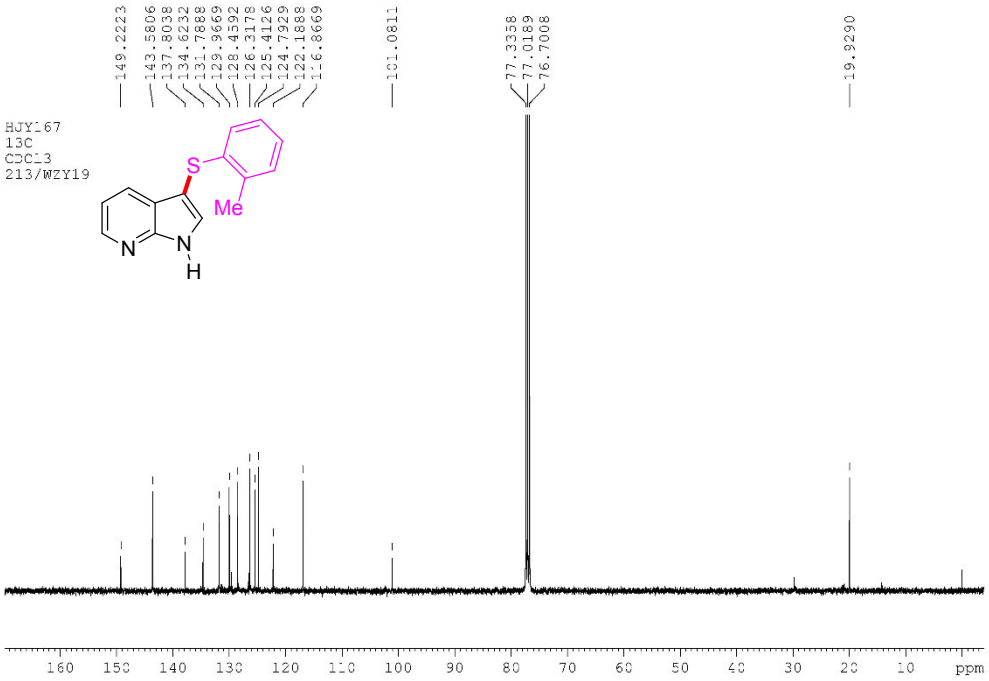
^{1}H NMR spectrum of compound **3i**



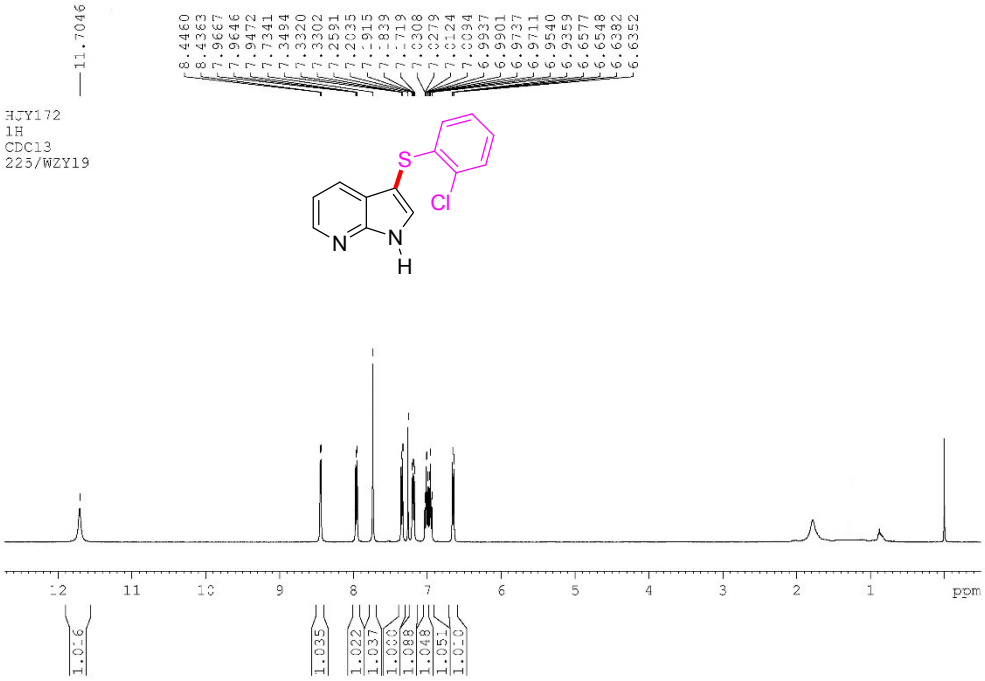
^{13}C NMR spectrum of compound **3i**



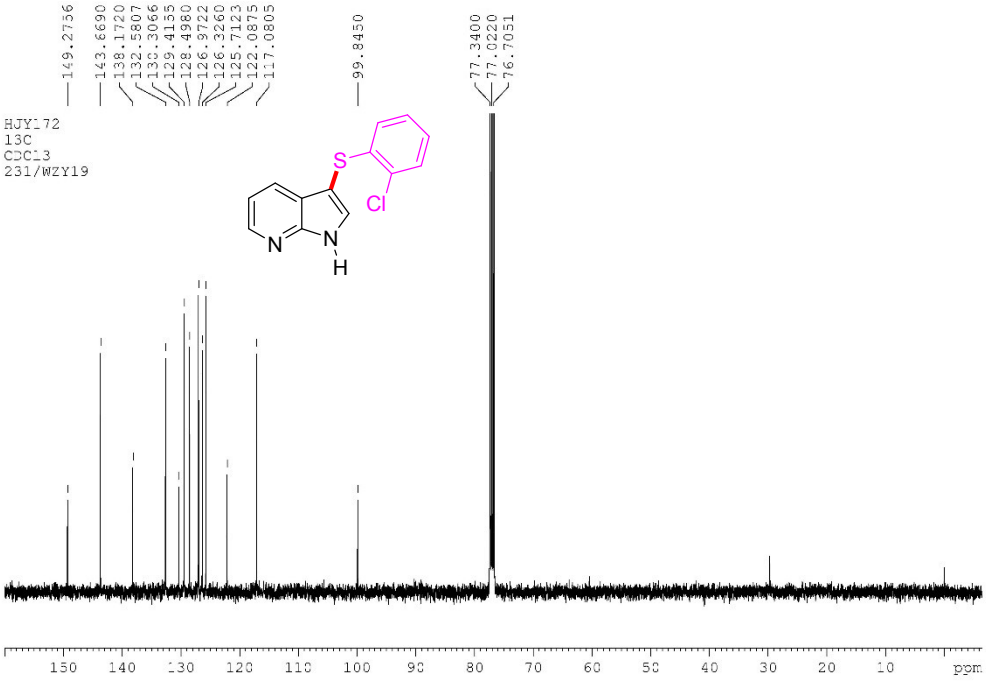
^{1}H NMR spectrum of compound **3j**



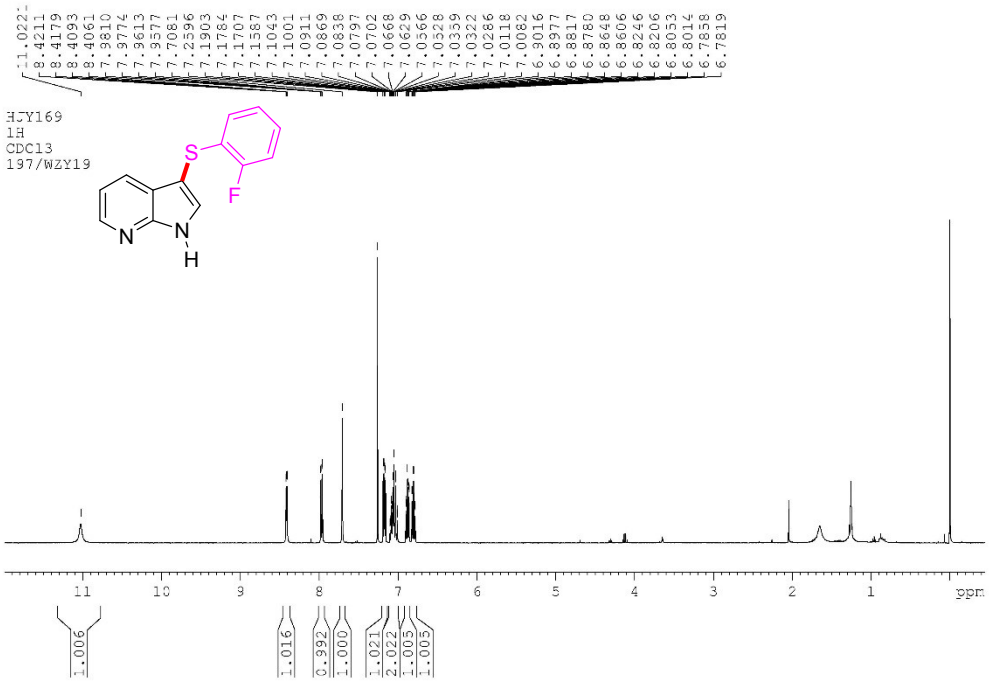
^{13}C NMR spectrum of compound **3j**



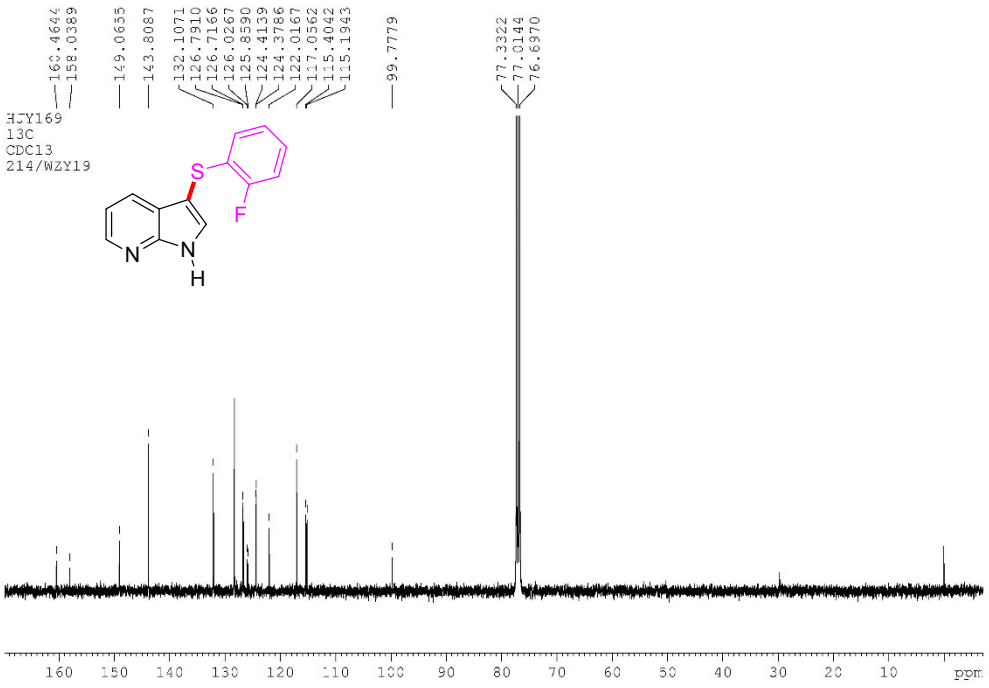
^{1}H NMR spectrum of compound **3k**



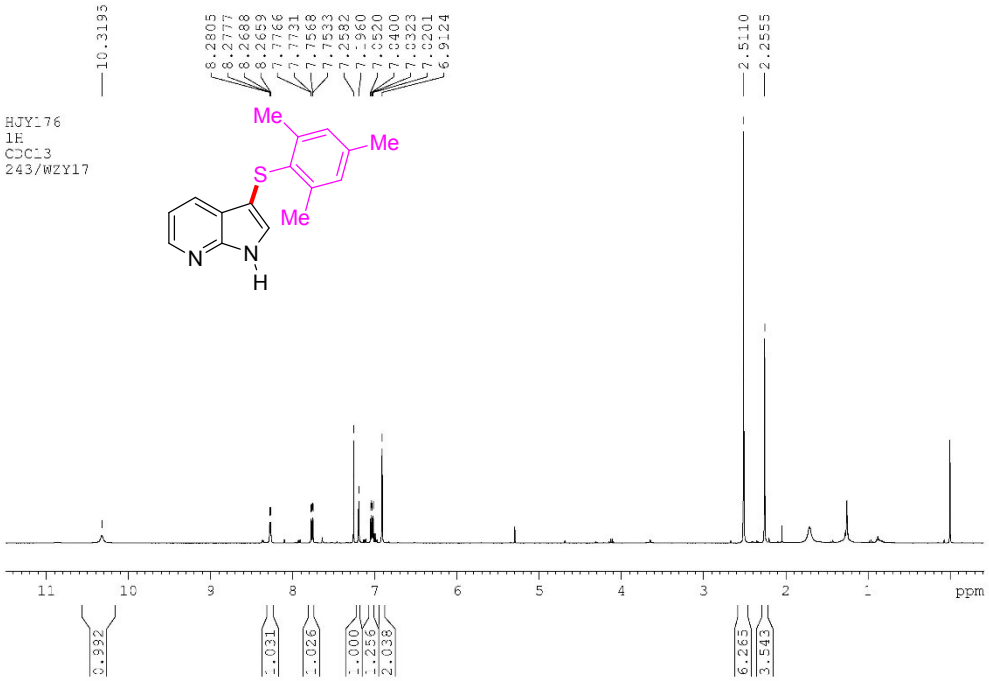
^{13}C NMR spectrum of compound **3k**



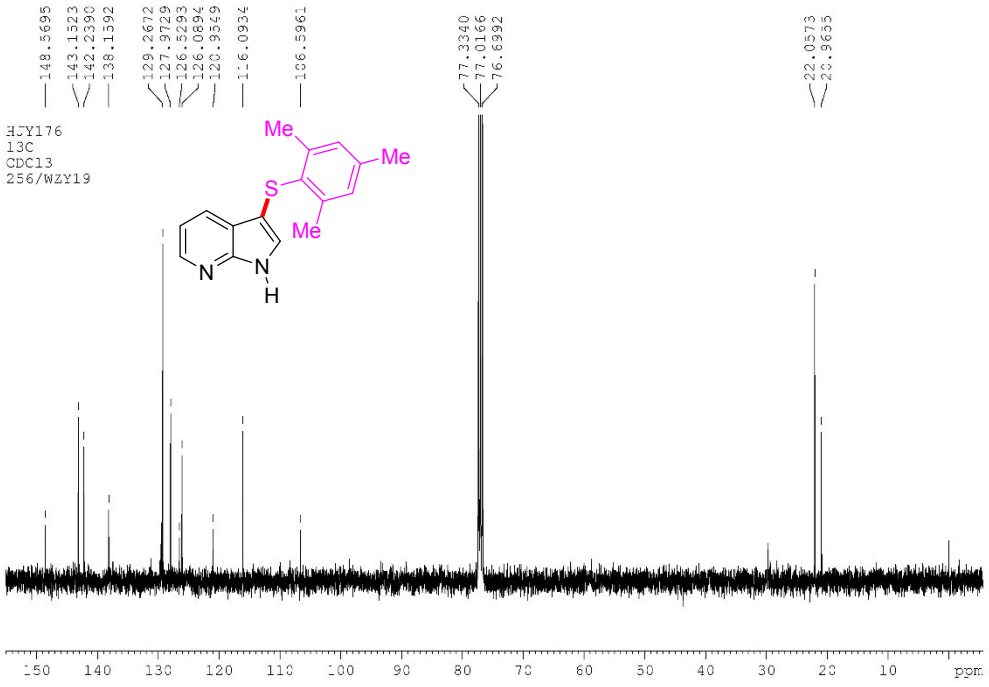
^{1}H NMR spectrum of compound **3l**



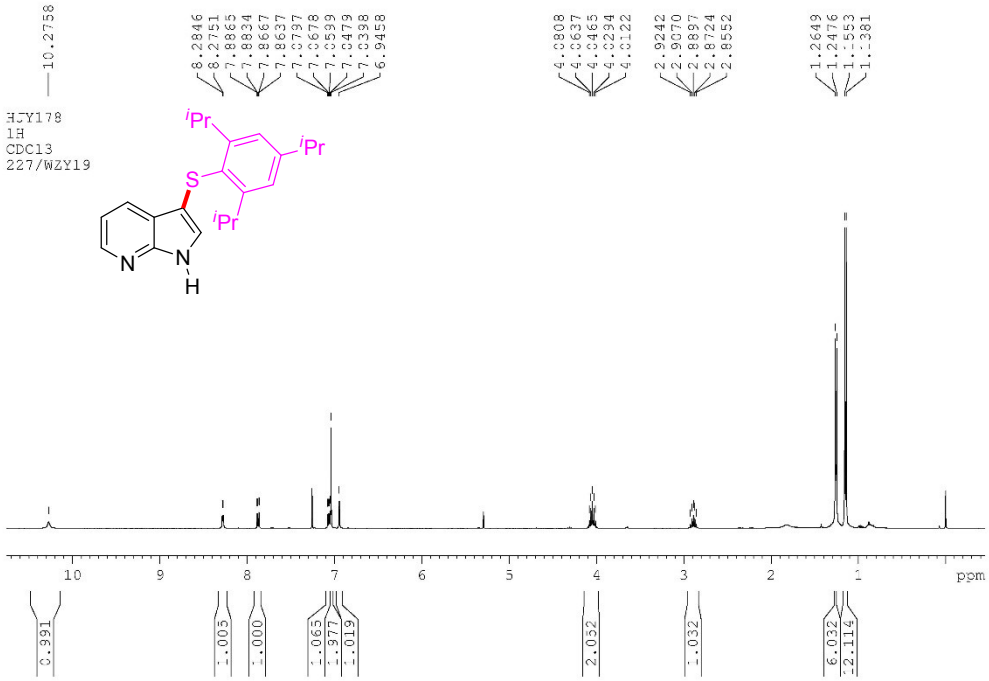
^{13}C NMR spectrum of compound **3l**



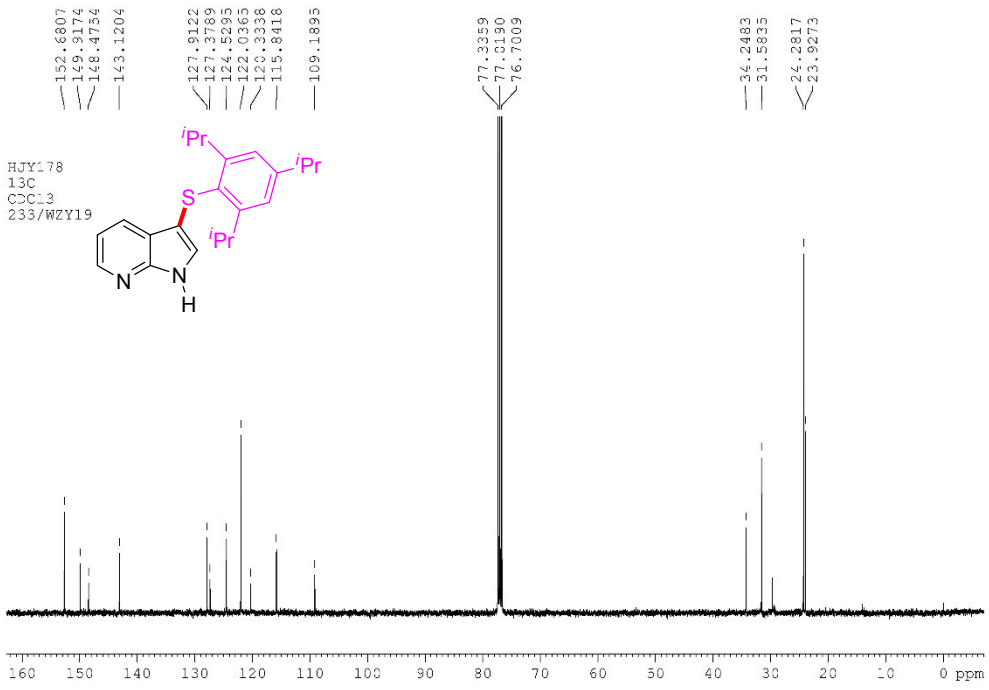
^{1}H NMR spectrum of compound **3m**



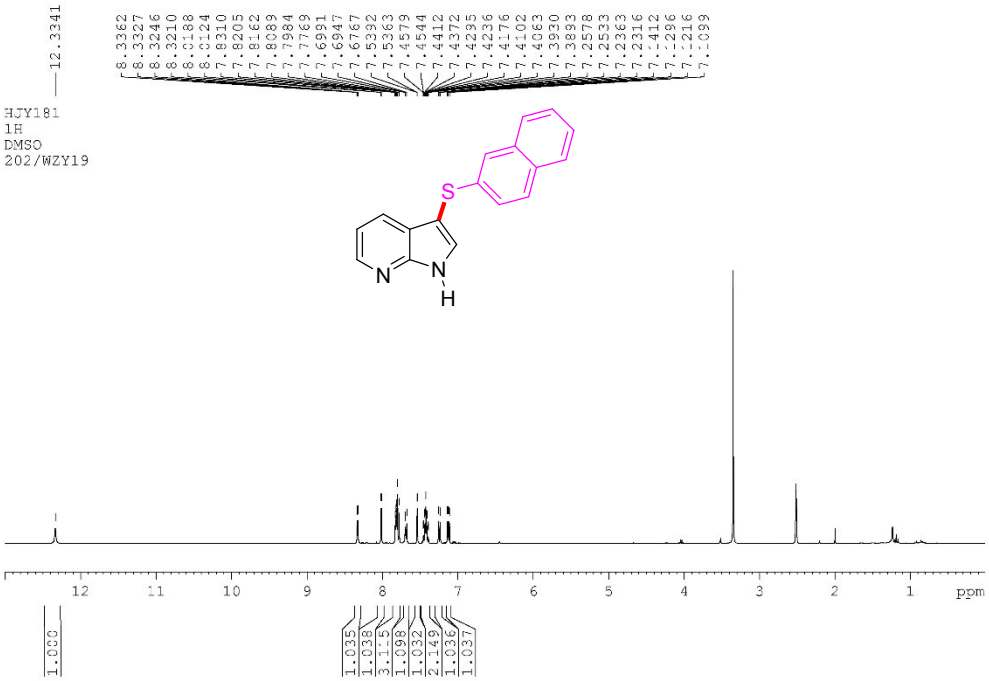
^{13}C NMR spectrum of compound **3m**



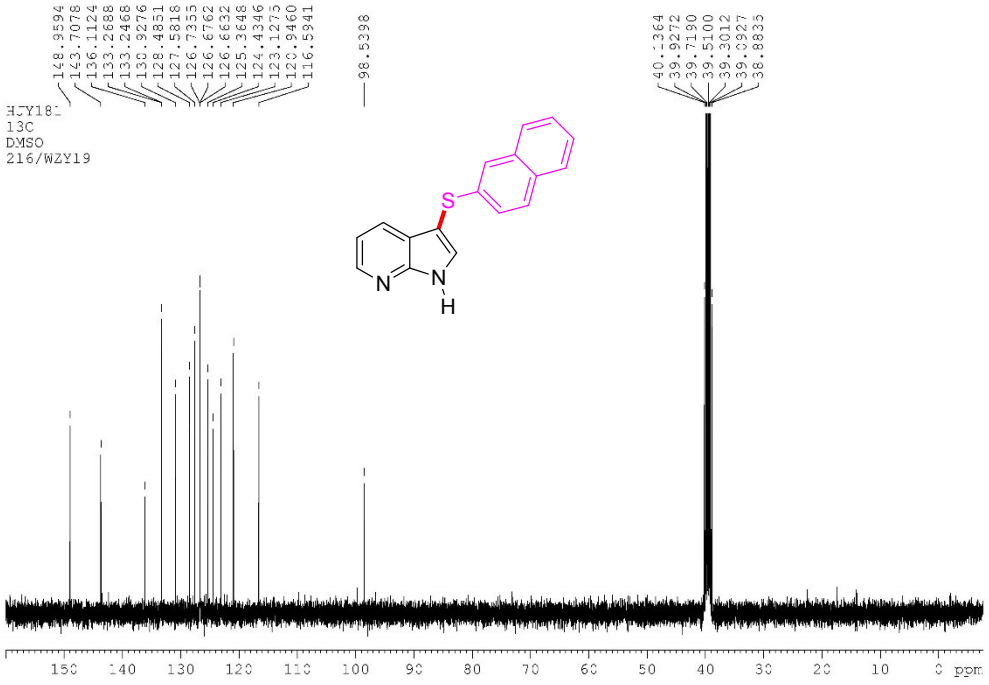
^{1}H NMR spectrum of compound **3n**



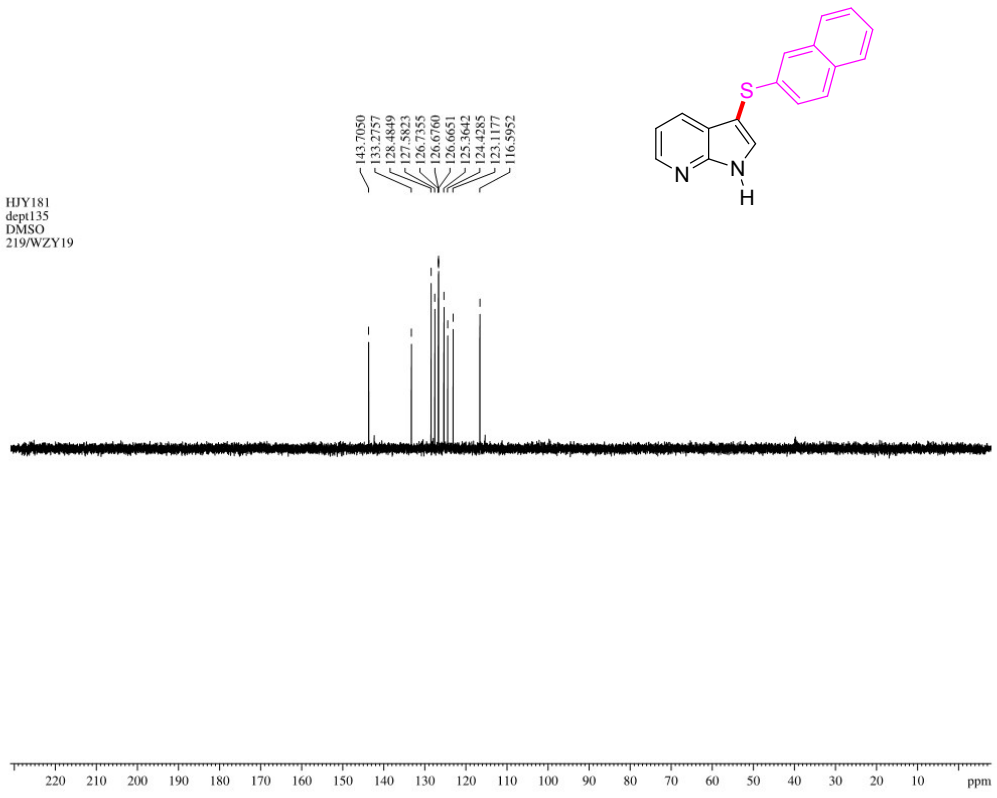
^{13}C NMR spectrum of compound **3n**



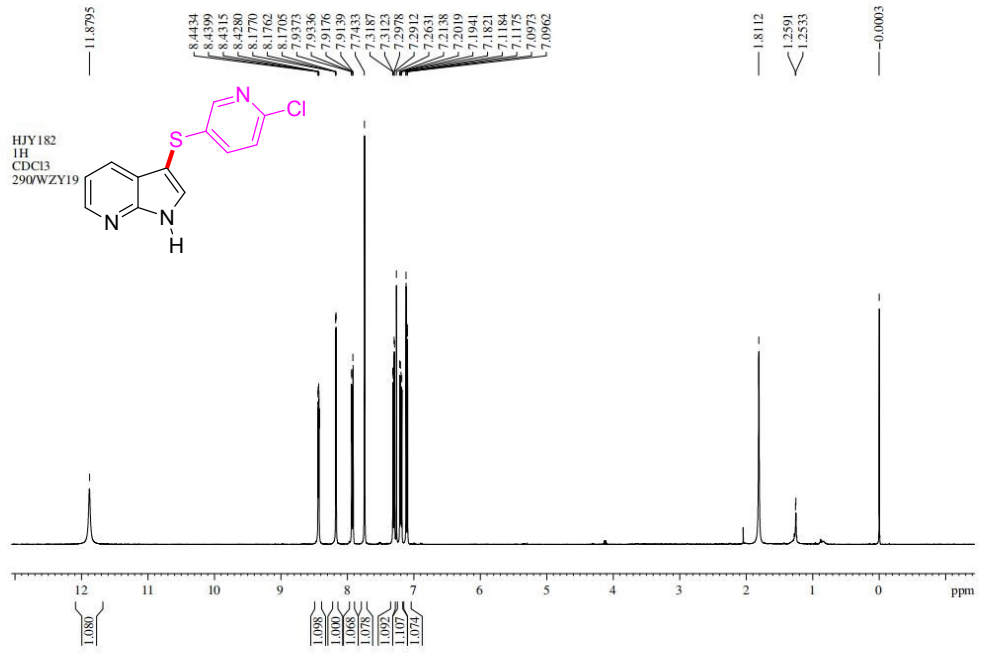
^{1}H NMR spectrum of compound **3o**



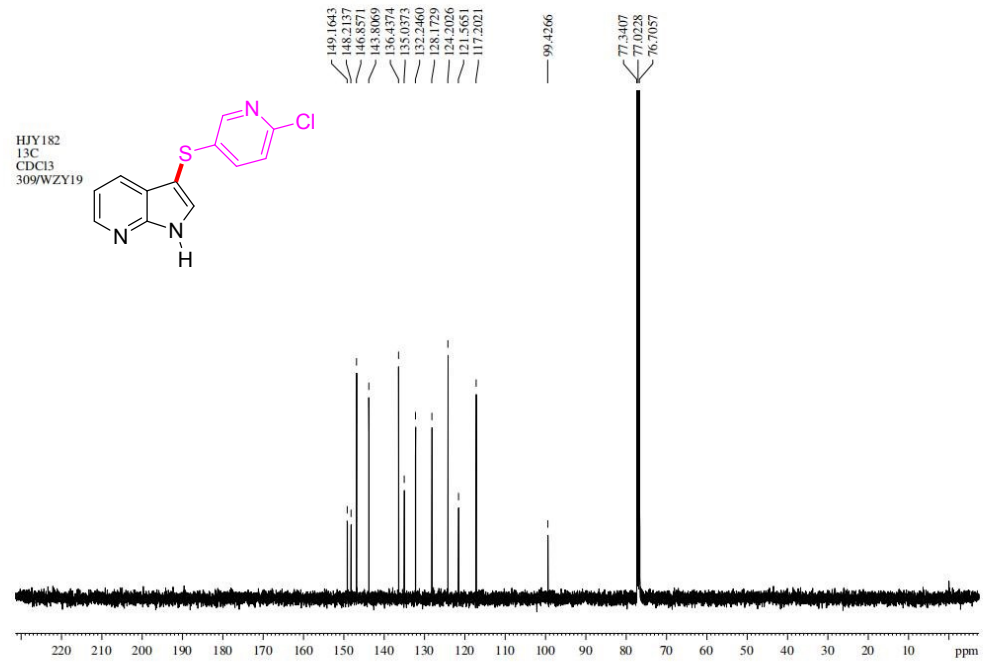
^{13}C NMR spectrum of compound **3o**



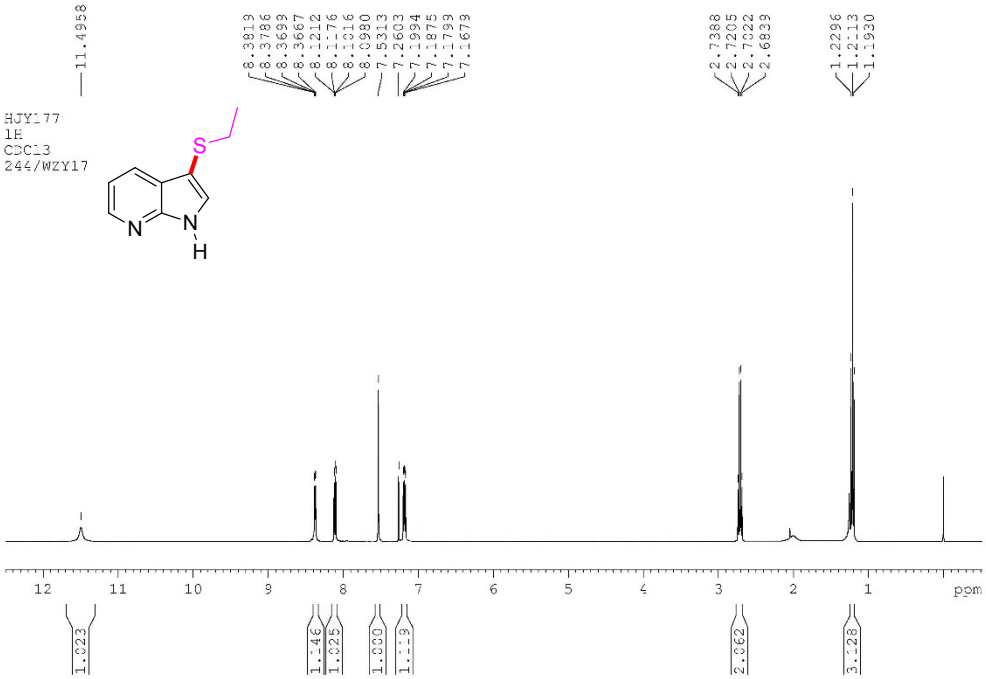
DEPT spectrum of compound **3o**



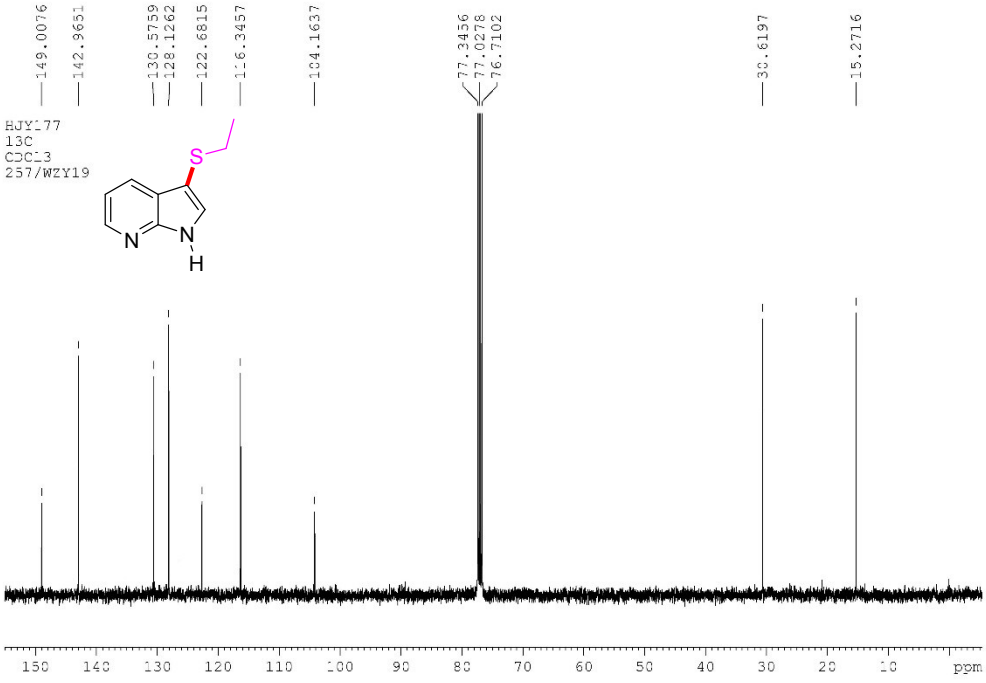
^{1}H NMR spectrum of compound **3p**



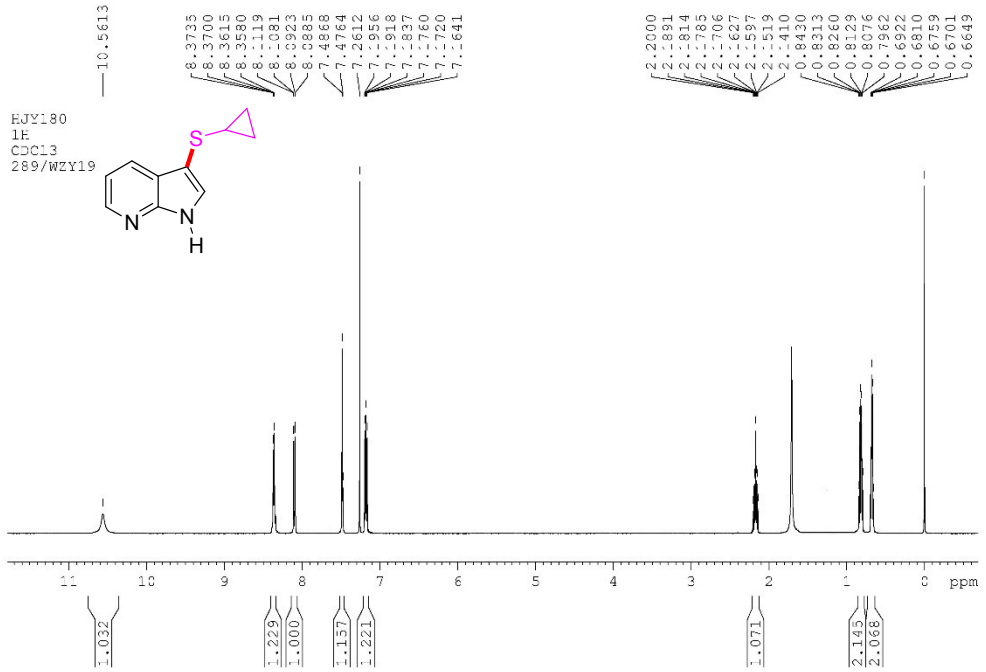
^{13}C NMR spectrum of compound **3p**



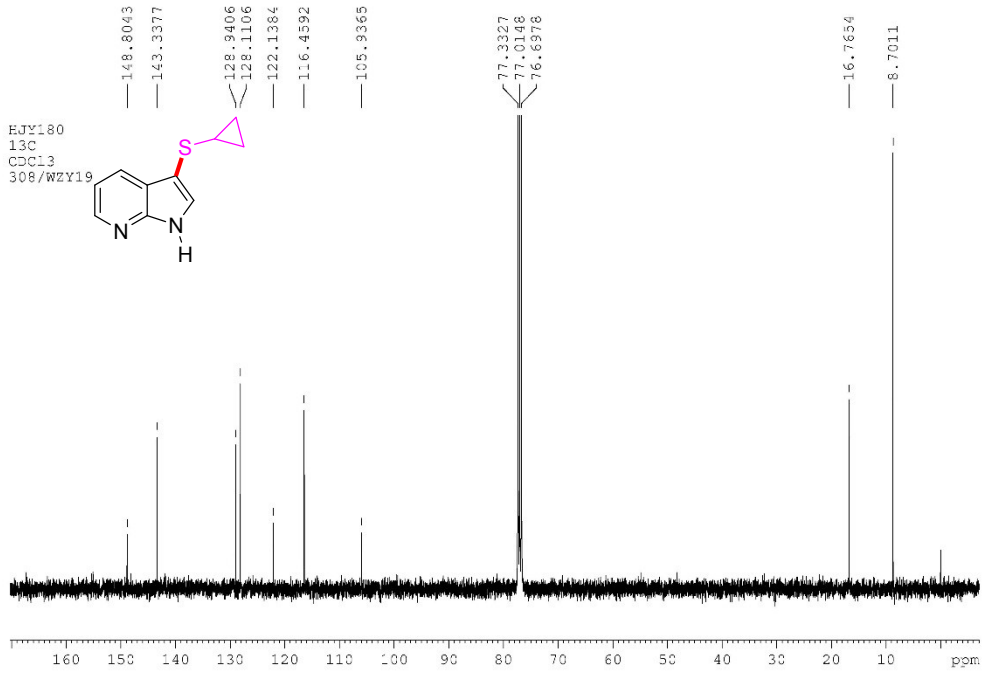
^{1}H NMR spectrum of compound **3q**



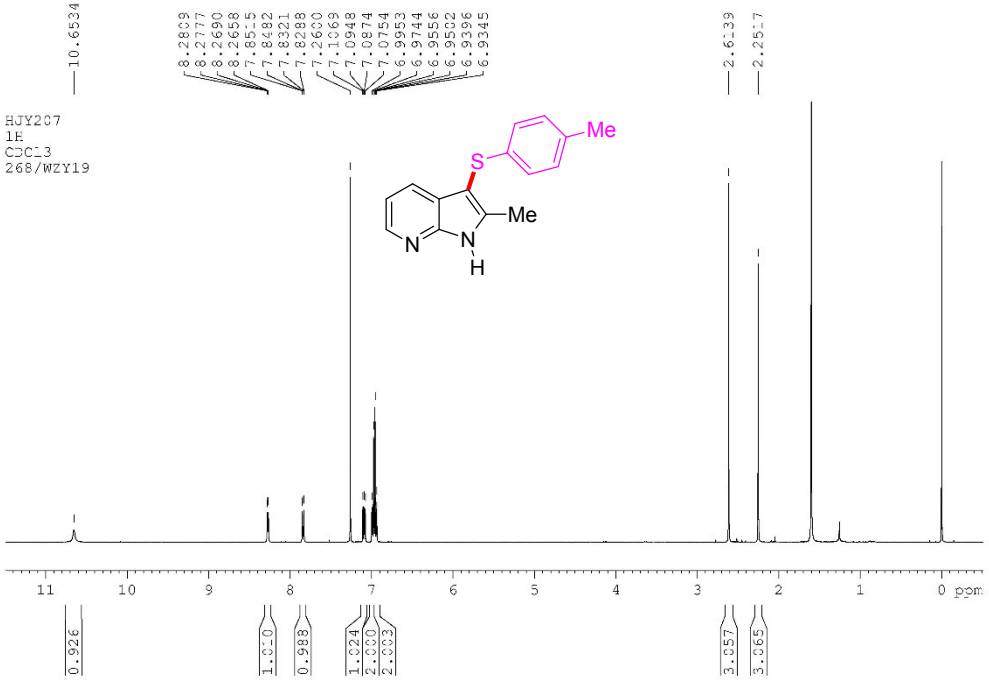
^{13}C NMR spectrum of compound **3q**



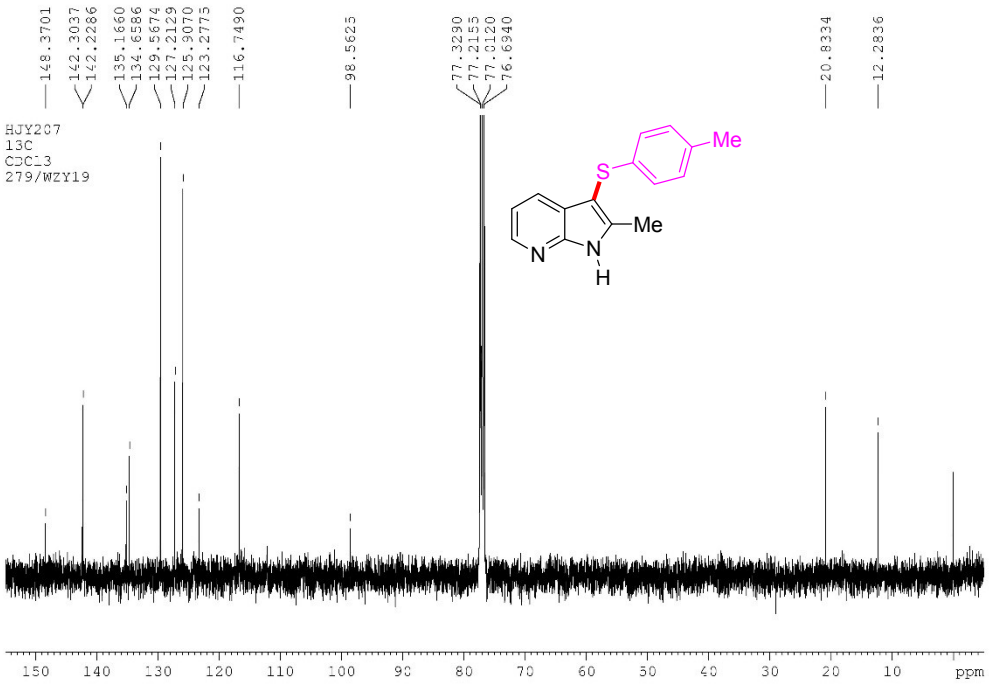
^{1}H NMR spectrum of compound **3r**



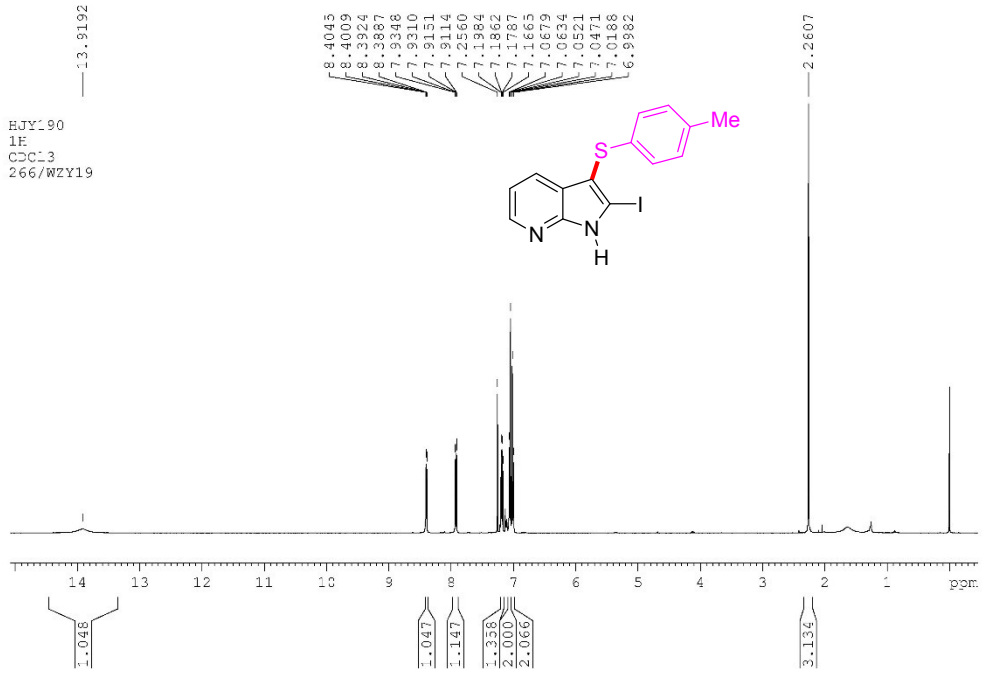
^{13}C NMR spectrum of compound **3r**



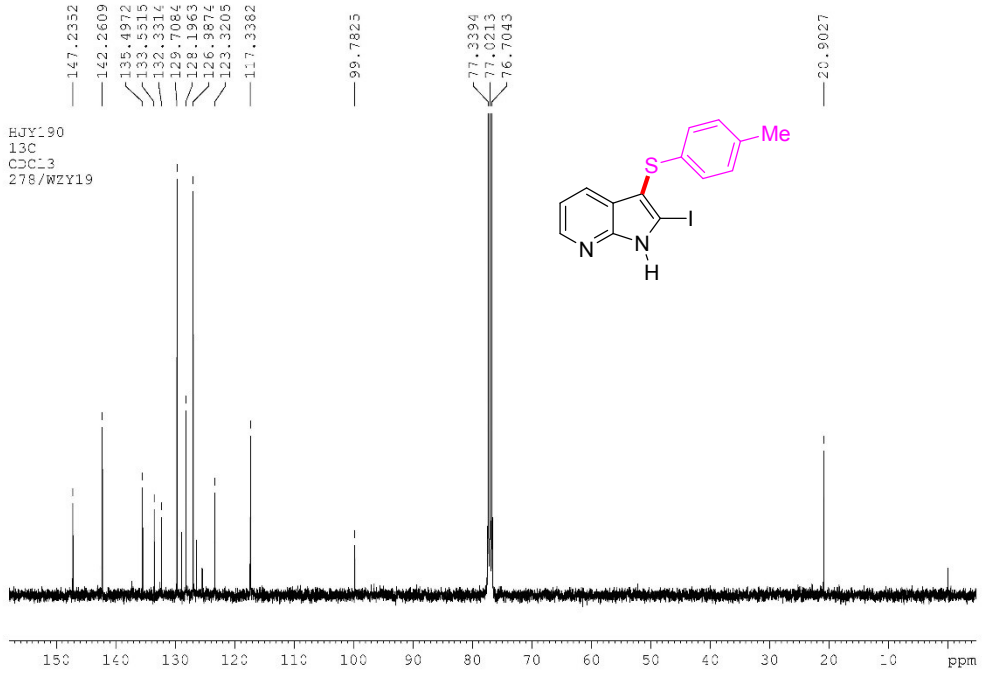
^{1}H NMR spectrum of compound **4a**



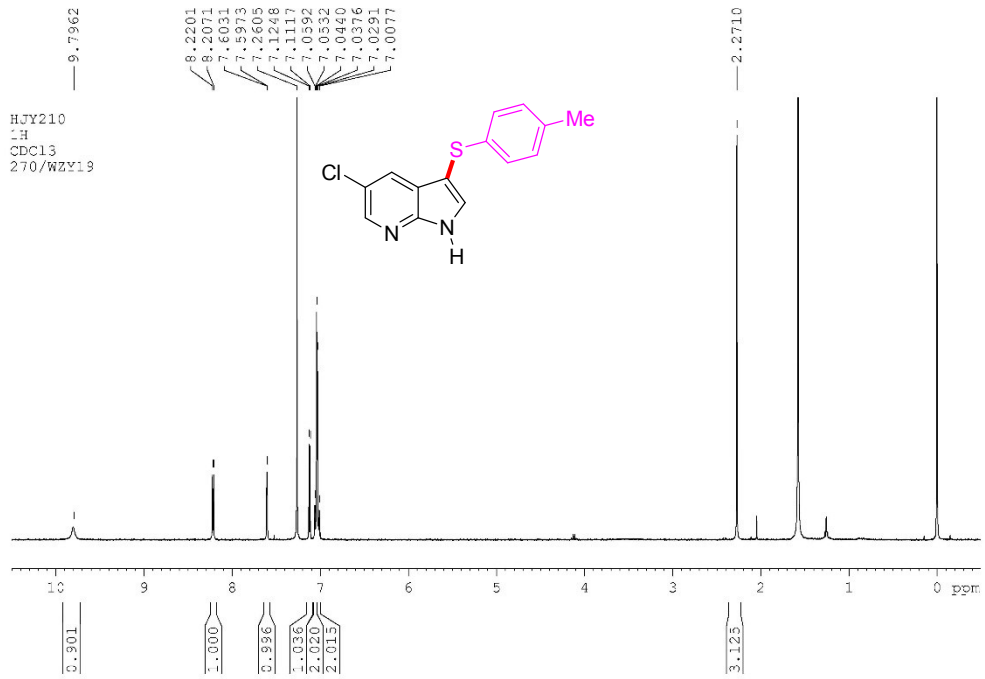
^{13}C NMR spectrum of compound **4a**



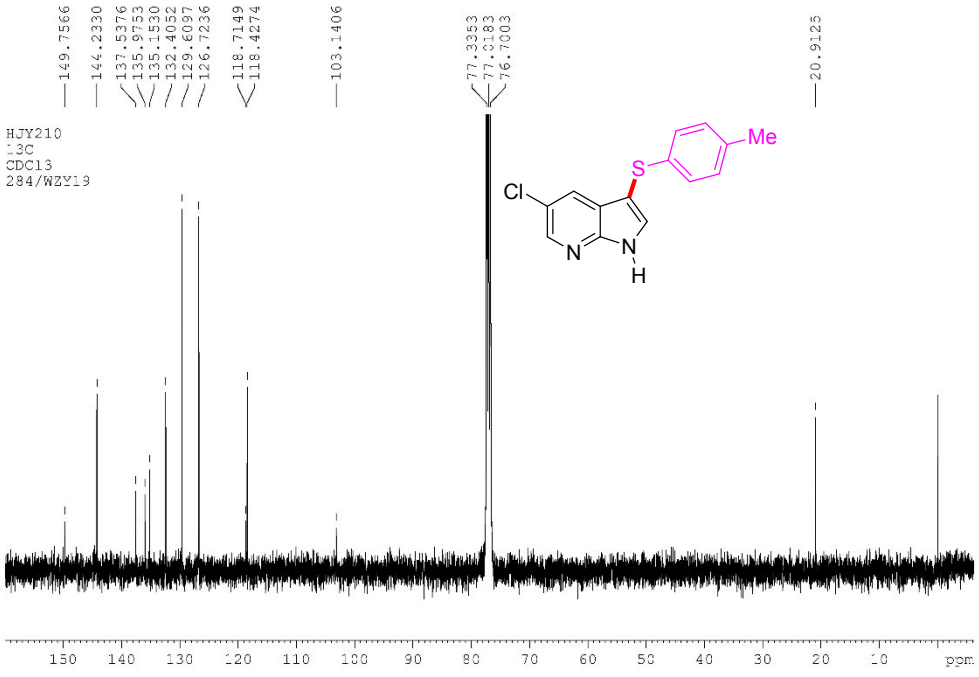
^{1}H NMR spectrum of compound **4b**



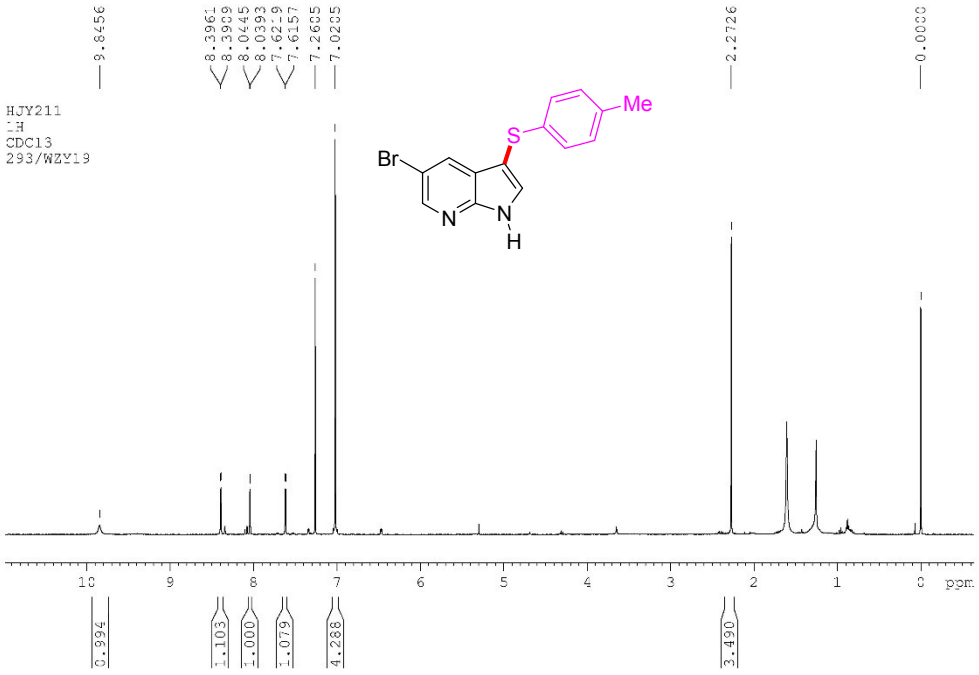
^{13}C NMR spectrum of compound **4b**



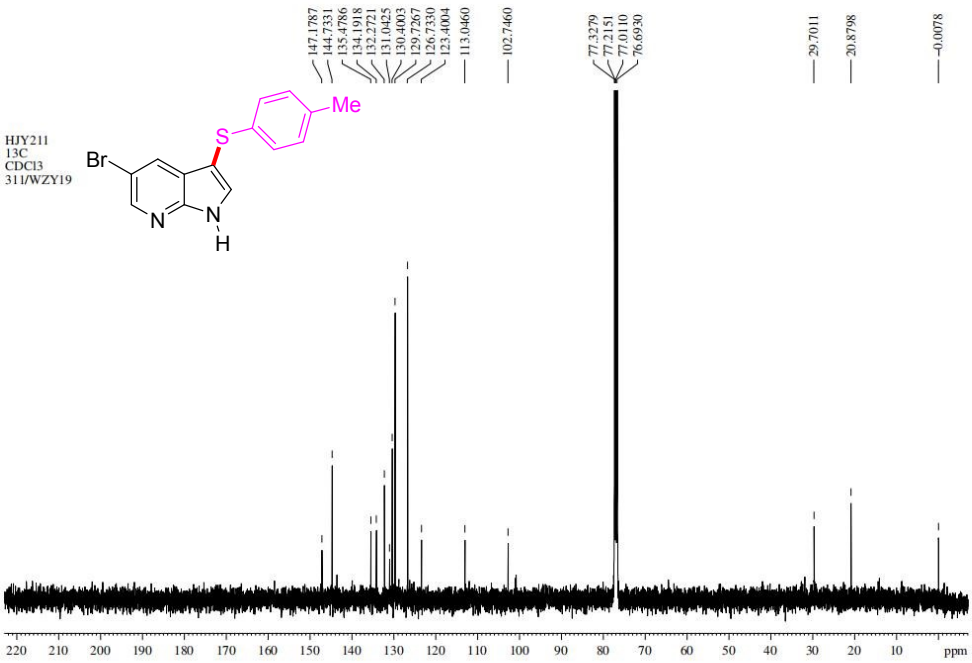
^{1}H NMR spectrum of compound **4c**



^{13}C NMR spectrum of compound **4c**



^{1}H NMR spectrum of compound **4d**



^{13}C NMR spectrum of compound **4d**