Supporting Information

Photocatalytic Direct C-S Bond Formation: Facile Access to 3- Sulfenylindoles via Metal-Free C-3 Sulfenylation of Indoles with Thiophenols

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A. General Methods

Melting points were measured using a melting point instrument and are uncorrected. ^{1}H and ^{13}CNMR spectra were recorded on a 400 MHz NMR spectrometer. IR spectra were obtained with an infrared spectrometer on either potassium bromide pellets or liquid films between two potassium bromide pellets. GC−MS data were obtained using electron ionization. HRMS was conducted on a high-resolution mass spectrometer. TLC was performed using commercially available 100−400 mesh silica gel plates (GF254). Unless otherwise noted, purchased chemicals were used without further purification.

B. General Procedure for the Preparation of 3

A mixture of indoles (0.10 mmol), benzenethiols (0.12 mmol), and Rose bengal (1 mol %) was stirred in CH_2Cl_2 (2.0 mL) under a 5 W 415 nm lamp at room temperature for 12 h. After completion of the reaction (monitored by TLC), water (10 mL) was added to the reaction mixture, and the resulting mixture was extracted with ethyl acetate. The combined organic layers were then dried over $MgSO_4$, filtered, and then concentrated in vacuum. The residue was purified by flash chromatography on silica gel to give the desired product (using the mixture of petroleum ether and ethyl acetate as eluents).

C. Analytical Data of 3

1-Methyl-3-(*p*-tolylthio)-1*H*-indole (3aa).[1] Yellow solid: 74% yield (18.7 mg); mp 111−113 ℃; IR (KBr) 3107, 2912, 1673, 1506, 1490, 1458, 1423, 1336, 799, 741 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.0 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.34-7.31 (m, 2H), 7.22-7.18 (m, 1H), 7.08-6.99 (m, 4H), 3.85 (s, 3H), 2.28 (s, 3H) ppm; ^{13}C NMR (100 MHz,

$CDCl_3$) δ 137.5, 136.0, 134.9, 134.5, 129.9, 129.5, 126.2, 122.5, 120.4, 119.8, 109.7, 101.2, 33.1, 20.9 ppm; MS (EI, 70 eV) *m/z* 253.2, 238.1, 221.2, 204.2, 178.2, 162.1, 146.1, 121.1, 103.1.

3-((4-Isopropylphenyl)thio)-1-methyl-1*H*-indole (3ab). Gray solid: 61% yield (17.1 mg); mp 119-120 ℃; IR (KBr) 2954, 2918, 2862, 1460, 1241, 1230, 826, 748, 537 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.30-7.26 (m, 2H), 7.19-7.14 (m, 1H), 7.05-6.99 (m, 4H), 3.81 (s, 3H), 2.81-2.76 (m, 1H), 1.16 (d, *J* = 6.8 Hz, 6H) ppm; ^{13}C NMR (100 MHz, CDCl3) δ 145.6, 137.5, 136.4, 135.0, 130.0, 126.9, 126.1, 122.5, 120.4, 119.8, 109.7, 101.1, 33.6, 33.1, 24.0 ppm; MS (EI, 70 eV) *m/z* 281.2, 266.2, 250.2, 239.2, 218.2, 204.2, 162.1, 131.2, 118.2, 103.2. HRMS (ESI) calcd $C_{18}H_{20}NS$ $[M + H]^+$ *m/z* 282.1311 found *m/z* 282.1308.

3-((4-Methoxyphenyl)thio)-1-methyl-1*H*-indole (3ac).[1] Red solid: 64% yield (17.2 mg); mp 68-70 ℃; IR (KBr) 2923, 1511, 1491, 1457, 1437, 823, 742 ppm; ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.17-7.10 (m, 3H), 6.73-6.71 (m, 2H), 3.81 (s, 3H), 3.71 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 137.5, 134.5, 130.0, 129.8, 128.4, 122.5, 120.4, 119.7, 114.5, 109.7, 102.3, 55.3, 33.1 ppm; MS (EI, 70 eV) *m/z* 269.2, 254.1, 237.2, 222.2, 210.1, 194.2, 172.1, 162.1, 152.1, 134.1, 120.1, 102.2.

3-((4-Fluorophenyl)thio)-1-methyl-1*H*-indole (3ad). [1] Orange oil: 30% yield (7.7 mg); IR (KBr) 3058, 2921, 1639, 1589, 1508, 1486, 1458, 820, 624 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58(d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.30-7.26 (m, 2H), 7.17-7.14 (m, 1H),

7.08-7.05 (m, 2H), 6.86-6.82 (m, 2H), 3.80 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8 (d, J = 243.0 Hz), 137.6, 134.9, 134.5 (d, J = 3.0 Hz), 129.6, 127.7 (d, J = 8.0 Hz), 122.6, 120.6, 119.6, 115.7 (d, J = 22.0 Hz), 109.8, 101.4, 33.1 ppm; MS (EI, 70 eV) *m/z* 257.2, 242.1, 225.2, 215.1, 196.2, 183.2, 162.1, 146.1, 121.1, 102.2.

3-((4-Chlorophenyl)thio)-1-methyl-1*H*-indole (3ae). [1] Yellow solid: 37% yield (10.1 mg); mp 122−124 ℃; IR (KBr) 2921, 1509, 1474, 1240, 1088, 1010, 808, 739, 543 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.0 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.31-7.27 (m, 2H), 7.17-7.14 (m, 1H), 7.08 (d, J = 8.0 Hz, 2H), 7.00-6.88 (d, J = 8.0 Hz, 2H), 3.81 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 137.6, 135.1, 130.4, 129.6, 128.7, 127.0, 122.8, 120.7,119.6, 109.9, 100.0, 33.2 ppm; MS (EI, 70 eV) *m/z* 273.1, 258.1 , 238.1, 223.1, 205.2, 162.1, 128.2, 118.4, 102.2.

3-((4-Bromophenyl)thio)-1-methyl-1*H*-indole (3af). [1] Orange solid: 67% yield (21.3 mg); mp 144−146 ℃; IR (KBr) 3108, 2926, 1505, 1474, 1084, 1006, 804, 742 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.23-7.19 (m, 2H), 7.16 (d, J = 8.0 Hz, 1H), 7.15 (d, J = 8.0 Hz, 1H), 7.09-7.06 (m, 1H), 6.65 (d, J = 8.0, 2H), 3.37 (s 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 137.6, 135.1, 131.6, 129.5, 127.3, 122.8, 120.7, 119.6, 118.2, 109.9, 99.9, 33.2 ppm; MS (EI, 70 eV) *m/z* 319.1, 254.1, 239.1, 221.1, 210.1, 165.1, 148.1, 134.6, 119.7, 104.1.

1-Methyl-3-(*m*-tolylthio)-1*H*-indole (3ag).[1] Yellow solid: 70% yield (17.7 mg); mp 76-78 ℃; IR (KBr) 3108, 2923, 1648, 1590, 1511, 1472, 765, 749, 690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.0 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 7.18-7.15 (m, 2H), 7.06-7.02

(m, 1H), 6.92-6.87 (m, 2H), 6.77-6.72 (m, 2H), 3.64 (s, 3H), 2.10 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 138.5, 137.6, 135.1, 130.0, 128.7, 126.4, 125.8, 123.0, 122.6, 120.5, 119.8, 109.8, 100.7, 33.2, 21.5 ppm; MS (EI, 70 eV) *m/z* 253.2, 238.2, 220.2, 204.2, 178.2, 162.1, 146.1, 121.1, 102.1.

3-((3-Fluorophenyl)thio)-1-methyl-1*H*-indole (3ah). Orange oil: 46% yield (11.8 mg); IR (KBr) 3058, 2923, 1597, 1577, 1510, 1469, 1422, 876, 773, 739 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 12.0 Hz, 1H), 7.31-7.27 (m, 2H), 7.18-7.15 (m, 1H), 7.12-7.06 (m, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.73-6.69 (m, 2H), 3.81 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4 (d, *J* = 245.0 Hz), 142.6 (d, *J* = 8.0 Hz), 137.6, 135.3, 129.9 (d, *J* = 9.0 Hz), 129.6, 122.8, 121.1 (d, *J* = 2.0 Hz), 120.7, 119.6, 112.5 (d, *J* = 24.0 Hz), 111.6 (d, *J* = 21.0 Hz), 109.9, 99.5, 33.2 ppm; MS (EI, 70 eV) *m/z* 257.2, 242.1, 225.2, 215.1, 183.2, 162.1, 146.1, 121.1, 102.2. HRMS (ESI) calcd $C_{15}H_{12}FNS$ $[M + H]^+$ *m/z* 258.0747 found *m/z* 258.0745.

3-((3-Chlorophenyl)thio)-1-methyl-1*H*-indole (3ai). Yellow oil: 45% yield (12.3 mg); IR (KBr) 3075, 3106, 3055, 2923, 1575, 1456, 1334, 1238, 868, 774, 740 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.31-7.27 (m, 2H), 7.18-7.15(m, 1H), 7.06-6.91 (m, 4H), 3.80 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 137.6, 135.4, 134.7, 129.7, 129.6, 125.3, 124.9, 123.8, 122.8, 120.8, 119.6, 109.9, 99.4, 33.2 ppm; MS (EI, 70 eV) *m/z* 273.1, 258.1, 238.1, 223.1, 205.2, 162.1, 128.1, 118.4, 102.2. HRMS (ESI) calcd $C_{15}H_{19}ClNS$ $[M + H]^+$ *m/z* 274.0452 found *m/z* 274.0448.

3-((2-Fluorophenyl)thio)-1-methyl-1*H*-indole (3aj). Yellow solid: 61% yield (15.7 mg); mp 73-75 ℃; IR (KBr) 3047, 2926, 1572, 1511, 1470, 1447, 809, 758, 740 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.37 (d, J = 8.0 Hz, 1H), 6.12 (d, J = 8.0 Hz, 1H), 6.05-6.02 (m, 2H), 5.93-5.89 (m, 1H), 5.75-5.73 (m, 2H), 5.55-5.49 (m, 2H), 2.52 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0 (d, J = 242.0 Hz), 137.7, 135.6, 129.9, 128.0 (d, J = 3.0 Hz), 127.0 (d, J = 17.0 Hz), 126.2 (d, J = 7.0 Hz), 124.4 (d, J = 4.0 Hz), 122.7, 120.7, 119.6, 115.1 (d, J = 21.0 Hz), 110.0, 98.2, 33.2 ppm; MS (EI, 70 eV) *m/z* 257.2, 242.1, 225.2, 215.1, 183.1, 162.1, 130.2, 121.1, 102.1. HRMS (ESI) calcd $C_{15}H_{13}FNS$ $[M + H]^+$ *m/z* 258.0747 found *m/z* 258.0744.

3-((3,4-Dimethylphenyl)thio)-1-methyl-1*H*-indole (3ak). Pink solid: 65% yield (17.4 mg); mp 119-121 ℃; IR (KBr) 3117, 2921, 2850, 1606, 1513, 1485, 1462, 1353, 1335, 1242, 882, 811, 739 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8 Hz, 1H), 7.29-7.20 (m, 3H), 7.13-7.09 (m, 1H), 6.95(s, 1H), 6.89-6.80 (m, 2H), 3.68 (s, 3H), 2.10-2.04 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 137.2, 136.3, 135.0, 133.5, 130.2, 130.1, 127.6, 123.9, 122.6, 120.5,119.9, 109.9, 101.4, 33.1, 19.9, 19.4 ppm ; MS (EI, 70 eV) *m/z* 267.2, 252.2, 234.2, 219.2, 204.2, 191.2, 178.2, 162.1, 146.1, 133.7, 118.5, 103.2. HRMS (ESI) calcd $C_{17}H_{18}NS$ $[M + H]^+$ *m/z* 268.1154 found *m/z* 268.1152.

3-((2-Chloro-4-fluorophenyl)thio)-1-methyl-1*H*-indole (3al). Yellow solid: 66% yield (19.2 mg); mp 132−133 ℃; IR (KBr) 2921, 1588, 1511, 1462, 893, 737, 629 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8 Hz, 1H), 7.38 (d, J = 8 Hz, 1H), 7.32-7.28 (m, 2H), 7.18-7.15 (m, 1H), 7.09-7.06 (m, 1H), 6.65-6.59 (m, 2H), 3.82 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1 (d, J = 245 Hz), 137.7, 135.6, 134.2, 130.4 (d, J = 10 Hz), 129.6, 127.6

(d, *J* = 8 Hz), 122.9, 120.8, 119.5, 116.7 (d, *J* = 25 Hz), 114.4 (d, *J* = 21 Hz), 110.0, 98.9, 33.3 ppm; MS (EI, 70 eV) *m/z* 291.1, 276.1, 256.1, 241.1, 223.2, 183.1, 162.1, 145.9, 128.0, 117.2, 104.2. HRMS (ESI) calcd $C_{15}H_{11}ClFNNaS$ $[M + Na]^+$ *m/z* 314.0177 found *m/z* 314.0185.

3-((2,5-Dichlorophenyl)thio)-1-methyl-1*H*-indole (3am). Yellow solid: 38% yield (11.7 mg); mp 95-97 ℃; IR (KBr) 3050, 2935, 1567, 1508, 1445, 1419, 797, 739, 573 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.33-7.29 (m, 2H), 7.22-7.17 (m, 2H), 6.93-6.90 (m, 1H), 6.77-6.72 (d, *J* = 2.4 Hz, 1H), 3.63 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 137.8, 135.8, 133.1, 130.2, 129.5, 128.2, 125.7, 125.5, 123.0, 121.0, 119.4, 110.1, 97.7, 33.3 ppm; MS (EI, 70 eV) *m/z* 307.0, 292.0, 272.1, 257.1, 237.1, 222.1, 195.1, 162.1, 136.0, 118.4, 109.1. HRMS (ESI) calcd $C_{15}H_{12}Cl_2NS$ $[M + H]^+$ *m/z* 308.0062 found *m/z* 308.0058.

3-((3,5-Bis(trifluoromethyl)phenyl)thio)-1-methyl-1*H*-indole (3an). Yellow solid: 34% yield (12.3 mg); mp 120−122 ℃; IR (KBr) 2921, 2850, 1600, 1516, 1177, 1126, 877, 748 ppm; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8 Hz, 2H), 7.47 (s, 2H), 7.42 (d, *J* = 8 Hz, 1H), 7.38 (s, 1H), 7.35-7.31 (m, 1H), 7.21-7.18 (m, 1H), 3.89 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 137.7, 135.5, 131.8 (dd, *J* = 33 Hz, *J* = 99 Hz), 129.1, 125.1 (d, *J* = 3 Hz), 123.1 (d, *J* = 271 Hz), 123.1, 121.1, 119.1, 118.3 (dd, *J* = 3 Hz, *J* = 11 Hz), 110.1, 97.6, 33.3 ppm; MS (EI, 70 eV) *m/z* 375.1, 360.0, 343.1, 305.1, 237.1, 187.6, 162.1, 143.1, 121.1, 102.1.

1-Methyl-3-((perfluorophenyl)thio)-1*H*-indole (3ao). Pale yellow solid (8.6 mg): 26% yield; mp 100-102 ℃; IR (KBr) 3108, 2921, 1634, 1514, 1486, 1460, 971, 855, 744 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8 Hz, 1H), 7.40 (s, 1H), 7.23 (d, *J* = 7.2 Hz, 1H),

7.24-7.18 (m, 2H), 3.75 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 146.0, 140.1, 138.8, 136.9, 135.7, 129.5, 122.7, 120.9, 119.2, 109.8, 99.8, 33.1 ppm; MS (EI, 70 eV) *m/z* 329.2, 314.1, 296.1, 255.1, 237.1, 162.1, 130.1, 117.1, 103.2. HRMS (ESI) calcd $C_{15}H_9F_5NS$ $[M + H]^+$ *m/z* 330.0370 found *m/z* 330.0363.

1-Methyl-3-(naphthalen-2-ylthio)-1*H*-indole (3ap).[1] Yellow solid: 38% yield (11.0 mg); mp 121-122 ℃; IR (KBr) 3114, 3047, 2926, 1617, 1507, 1457, 821, 739, 470 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.45 (m, 3H), 7.39-7.35 (m, 2H), 7.21-7.12 (m, 6H), 7.02-6.98 (m, 1H), 3.57 (d, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 137.4, 135.3, 133.9, 131.4, 130.0, 128.3, 127.8, 127.0, 126.5, 125.1, 124.8, 123.4, 122.7, 120.7, 119.8, 109.9, 100.5, 33.2 ppm; MS (EI, 70 eV) *m/z* 289.2, 274.1, 257.2, 241.2, 228.1, 215.2, 202.2, 162.1, 144.6, 128.1, 117.1, 101.2.

3-(p-Tolylthio)-1*H*-indole (3ba).[2] Red solid: 47% yield (11.2 mg); mp 102−104 ℃; IR (KBr) 3417, 3111, 2924, 1491, 1452, 1404, 807, 748, 532 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.61 (d, *J* = 8 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8 Hz, 1H), 7.25-7.22 (m, 1H), 7.17-7.13 (m, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 2.24 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 135.5, 134.7, 130.4, 129.5, 129.1, 126.3, 123.0, 120.8, 119.7, 111.6, 103.5, 20.9 ppm; MS (EI, 70 eV) *m/z* 239.1, 223.1, 207.1, 191.1, 179.1, 165.1, 148.1, 121.1, 104.1.

5-Fluoro-3-(p-tolylthio)-1*H*-indole (3ca). White solid: 54% yield (13.9 mg); mp 125-127 ℃; IR (KBr) 3415, 2926, 2856, 1583, 1485, 1453, 930, 857, 806 cm^{-1}; ^{1}H NMR (400 MHz, d^6-DMSO) δ 11.78 (s, 1H), 7.82 (s, 1H), 7.51-7.48 (m, 1H), 7.22 (s, 1H), 7.08-7.01 (m, 3H),

6.95 (d, *J* = 8 Hz, 2H), 2.19 (s, 3H) ppm; ^{13}C NMR (100 MHz, d^6-DMSO) δ 135.5, 134.8, 134.6, 133.8, 130.0, 126.4, 114.1, 110.9, 110.7, 103.5, 103.3, 100.8, 20.8 ppm; MS (EI, 70 eV) *m/z* 257.1, 241.1, 225.1, 209.1, 197.1, 183.1, 166.1, 139.0,127.6, 107.1. HRMS (ESI) calcd $C_{15}H_{13}FNS$ $[M + H]^+$ *m/z* 258.0747 found *m/z* 258.0744.

5-Chloro-3-(p-tolylthio)-1*H*-indole (3da).[3] Yellow oil: 38% yield (10.4 mg); IR (KBr) 3411, 3022, 2921, 2859, 1575, 1491, 1459, 1405, 891, 868, 802, 714 cm^{-1}; ^{1}H NMR (400 MHz, d^6-DMSO) δ 11.84 (s, 1H), 7.84 (d, *J* = 4.0 Hz, 1H), 7.51 (d, *J* =8.0 Hz, 1H), 7.33 (s, 1H), 7.19-7.17 (m, 1H), 7.03 (d, *J* =8 Hz, 2H), 6.95 (d, *J* =8 Hz, 2H) , 2.20 (s, 3H) ppm; ^{13}CNMR (100 MHz, d^6-DMSO) δ 135.7, 135.4, 134.9, 134.4, 130.4, 130.1, 126.4, 125.3, 122.6, 117.8, 114.5, 100.5, 20.8 ppm; MS (EI, 70 eV) *m/z* 273.1, 258.0, 238.1, 223.1, 205.1, 182.1, 155.0, 136.6, 123.0,111.5.

5-Bromo-3-(p-tolylthio)-1*H*-indole (3ea).[4] yellow oil: 31% yield (9.9 mg); IR (KBr) 3410, 3022 ,2918, 2848, 1491, 1454, 1401, 883, 753 cm^{-1}; ^{1}H NMR (400 MHz, d^6-DMSO) δ 11.87 (s, 1H), 7.81 (s, 1H), 7.46 (d, *J* =8.4 Hz, 1H), 7.29 (d, *J* =8.4 Hz, 1H), 7.22 (s, 1H), 7.02 (d, *J* =8 Hz, 2H), 6.94 (d, *J* =8 Hz, 2H), 2.19 (s, 3H) ppm; ^{13}CNMR (100 MHz, d^6-DMSO) δ 135.9, 134.9, 134.3, 130.6, 130.4, 130.1, 126.4, 125.2, 120.8, 114.9, 113.3, 100.4, 20.8 ppm; MS (EI, 70 eV) *m/z* 319.0, 304.0, 285.0, 238.1, 223.1, 205.1, 178.1, 165.1, 146.0, 111.6.

6-Fluoro-3-(p-tolylthio)-1*H*-indole (3fa).[3] Yellow solid: 54% yield (13.9 mg); mp 93-95 ℃; IR (KBr) 3397, 3125, 2921, 1624, 1508, 1491, 1449, 1394, 938, 829, 809 cm^{-1}; ^{1}H NMR (400 MHz, d^6-DMSO) δ 11.71 (m, 1H), 7.74 (d, *J* = 2.4 Hz, 1H), 7.35-7.32 (m, 1H), 7.27-7.24 (m, 1H), 7.22 (s, 1H), 7.02 (d, *J* =8 Hz, 2H), 6.94 (d, *J* =8.4 Hz, 2H), 2.19 (s, 3H) ppm; ^{13}CNMR

(100 MHz, d^6-DMSO) δ 135.5, 134.8, 133.2, 130.6, 130.4, 130.0, 126.4, 125.7, 120.0, 109.1 (d, J = 25 Hz), 101.0, 98.8 (d, J = 15 Hz), 20.8 ppm; MS (EI, 70 eV) *m/z* 257.1, 241.1, 225.1, 209.1, 166.0, 139.0, 120.9, 107.1.

7-Methyl-3-(p-tolylthio)-1*H*-indole (3ga).[5] Yellow solid: 62% yield (15.7 mg); mp 93-95 ℃; IR (KBr) 3416, 3108, 2921, 2850, 1490, 1454, 1421, 810, 785, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.36 (s, 1H), 7.05-7.00 (m, 4H), 6.94 (d, *J* = 8 Hz, 2H), 2.45 (s, 3H), 2.22 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 135.6, 134.6, 130.3, 129.5, 128.8, 126.3, 123.5, 121.0, 120.8, 117.4, 103.8, 20.9, 16.5 ppm; MS (EI, 70 eV) *m/z* 253.2, 237.1, 220.2, 205.1, 193.1, 178.1, 162.1, 134.1, 118.2, 102.2.

4-Methoxy-3-(p-tolylthio)-1*H*-indole (3ha). White solid: 58% yield (15.6 mg); mp 114-116 ℃; IR (KBr) 3407, 2918, 2848, 1584, 1506, 1492, 1456, 806, 779, 732 cm^{-1}; ^1H NMR (400 MHz, d^6-DMSO) δ 11.53 (s, 1H), 7.47 (s, 1H), 7.21-7.20 (m, 1H), 7.06-7.05 (m, 1H), 6.99-6.96 (m, 4H), 6.52-6.50 (m, 1H), 3.64 (s, 3H), 2.20 (s, 3H) ppm; ^{13}CNMR (100 MHz, d^6-DMSO) δ 154.4, 139.1, 137.9, 134.2, 131.4, 129.6, 126.6, 123.4, 118.6, 105.8, 101.3, 100.4, 55.7, 20.9 ppm; MS (EI, 70 eV) *m/z* 269.1, 254.1, 239.1, 221.1, 210.1, 165.1, 148.1, 134.6, 119.7, 104.1. HRMS (ESI) calcd $C_{16}H_{15}NNaOS$ $[M + Na]^+$ *m/z* 292.0767 found *m/z* 292.0766.

5-Bromo-1-methyl-3-(p-tolylthio)-1*H*-indole (3ja). Pale yellow solid: 22% yield (7.3 mg); mp 99-101 ℃; IR (KBr) 3097, 3016, 2918, 1509, 1489, 1466, 1422, 1373, 877, 799, 783, 745 cm^{-1}; ^1H NMR (400 MHz, d^6-DMSO) δ 7.81 (s, 1H), 7.54 (d, *J* = 8.8 Hz, 1H), 7.49 (s, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.03 (d, *J* = 8 Hz, 2H), 6.96 (d, *J* = 8 Hz, 2H), 3.85 (s, 3H), 2.20 (s, 3H) ppm; ^{13}CNMR (100 MHz, d^6-DMSO) δ 137.9, 136.5, 135.3, 135.0, 131.3, 130.1, 126.4, 125.2,

121.0, 113.6, 113.4, 99.4, 33.5, 20.9 ppm; MS (EI, 70 eV) *m/z* 333.0, 316.0, 301.0, 252.1, 237.1, 219.1, 204.1, 178.1, 160.1, 134.1, 118.6, 102.1.

1,2-dimethyl-3-(p-tolylthio)-1*H*-indole (3ka).[3] Silver grey solid: 71% yield (18.9 mg); mp 119−120 ℃; IR (KBr) 2915, 2856, 1869, 1488, 1471, 1395, 1079, 795, 739 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.57 (d, *J* = 8 Hz, 1H), 7.25 (d, *J* = 8 Hz, 1H), 7.20-7.16 (m, 1H), 7.11-7.08 (m, 1H), 6.92 (s, 4H), 3.62 (s, 3H), 2.44 (s, 3H), 2.20 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 142.8, 137.1, 136.3, 134.3, 129.9, 129.6, 125.8, 121.8, 120.5, 119.0, 109.1, 98.6, 30.3, 20.9, 10.9 ppm; MS (EI, 70 eV) *m/z* 267.2, 252.2, 235.2, 219.2, 204.1, 176.1, 144.2, 132.2, 118.6, 103.1.

1-Mthyl-2-phenyl-3-(p-tolylthio)-1*H*-indole (3la) Colorless solid: 52% yield (17.1 mg); mp 111-113 ℃; IR (KBr) 3072, 3019, 2940, 1594, 1491, 1464, 1441, 1374, 1334, 832, 802, 748, 702 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.64 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 6H), 7.30-7.26 (m, 1H), 7.18-7.14 (m, 1H), 6.96-6.90 (m, 4H), 3.67 (s, 3H), 2.20 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 145.8, 137.7, 136.4, 134.2, 130.7, 130.7, 129.9, 129.5, 128.8, 128.3, 125.9, 122.9, 121.0, 119.9, 109.8, 100.2, 31.8, 21.0 ppm; MS (EI, 70 eV) *m/z* 329.3, 314.2, 297.2, 281.2, 252.1, 237.1, 223.1, 204.2, 178.2, 165.0, 152.1, 139.2, 120.1, 103.1. HRMS (ESI) calcd $C_{22}H_{20}NS$ $[M + H]^+$ *m/z* 330.1311 found *m/z* 330.1310.

References:

[1] M. Chen, Z.-T. Huang, Q.-Y. Zheng, *Chem. Commun*., 2012, ***48***, 11686–11688.

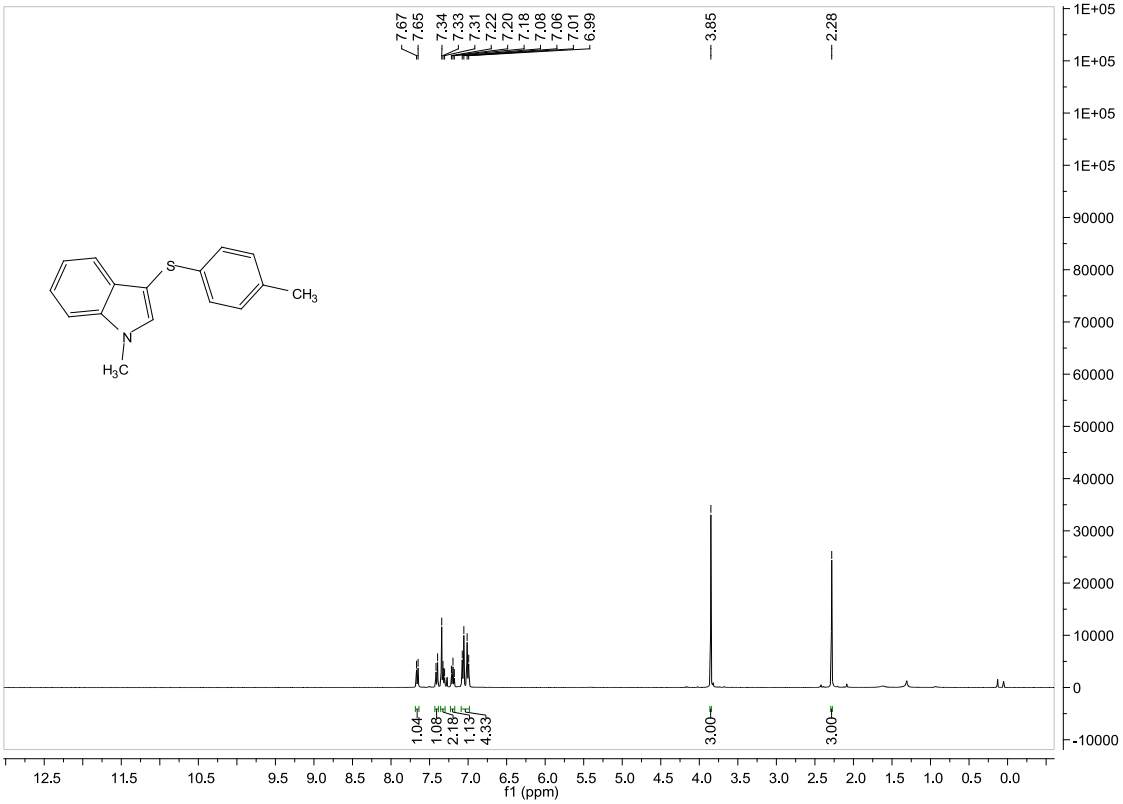
[2] H. Qi, T. Zhang, K. Wan, M. Luo, *J. Org. Chem*. 2016, ***81***, 4262-4268.

[3] H. Rao, P. Wang, J. Wang, Z. Li, X. Sun, S. Cao, *RSC. Adv*. 2014, ***4***, 49165-49169.

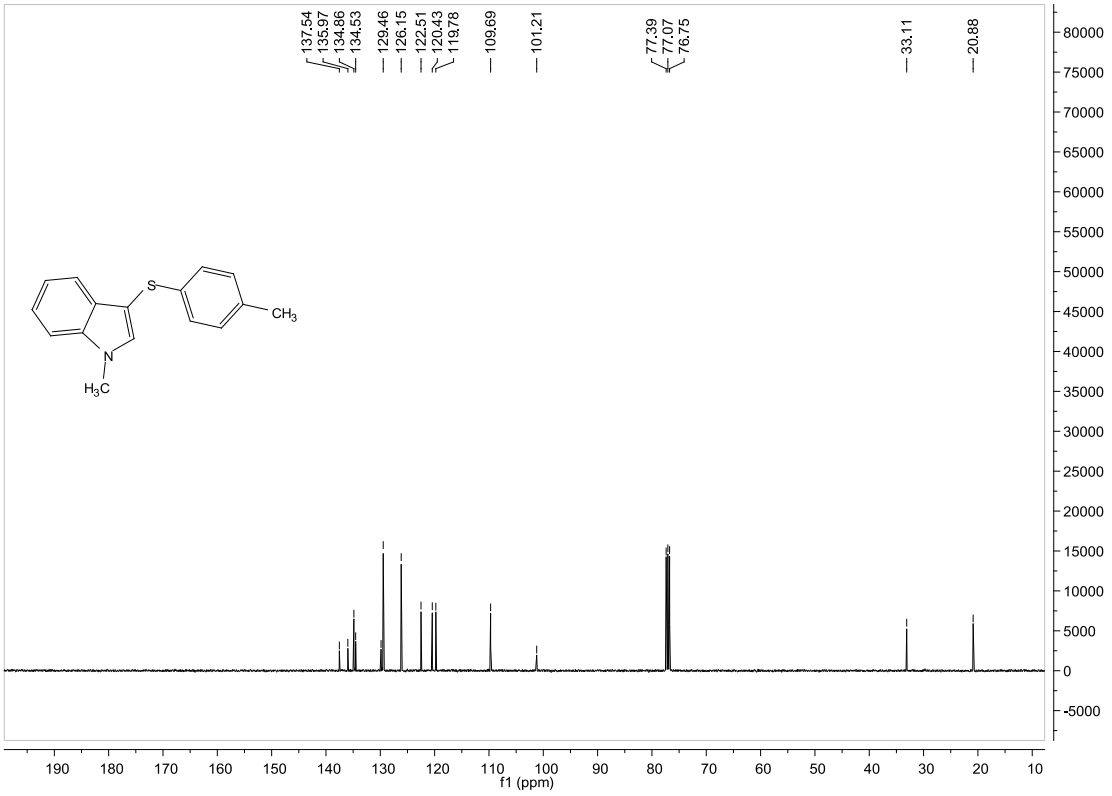
[4] (b) W. Ge, Y. Wei, *Green Chem*. 2012, ***14***, 2066-2070.

[5] X. Liu, H. Cui, D. Yang, Dai, S. Dai, G. Zhang, W. Wei, H. Wang, *Catal. Lett*. 2016, ***146***, 1743–1748.

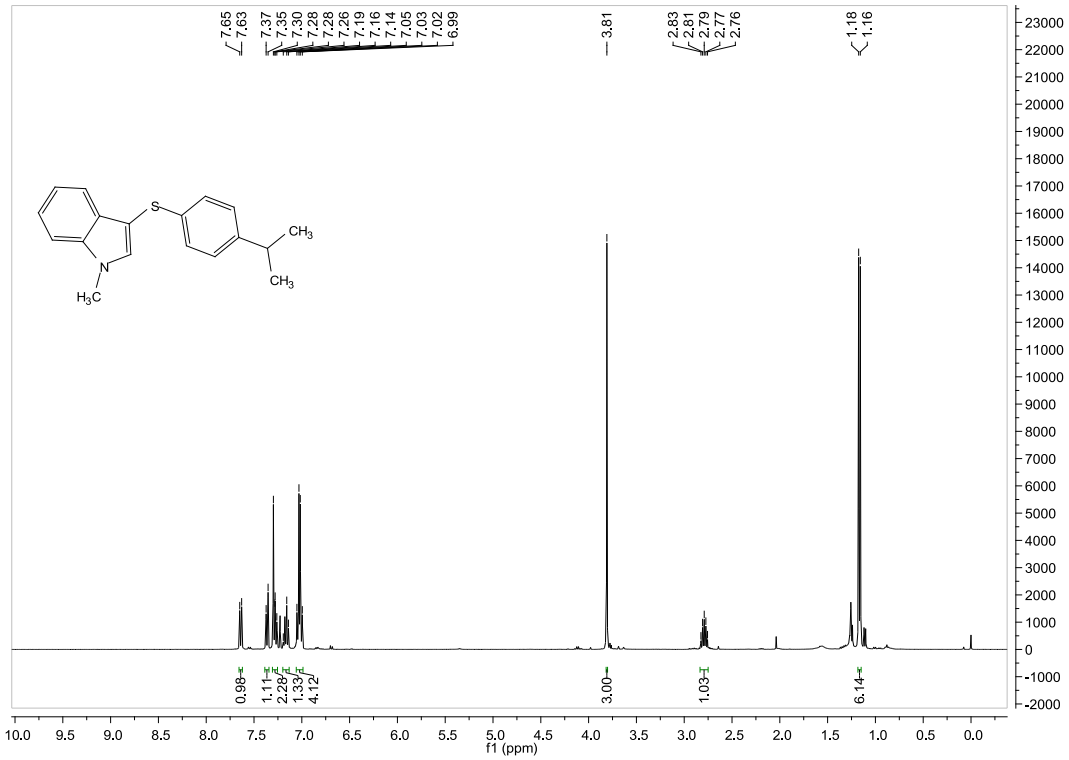
D. NMR Spectra



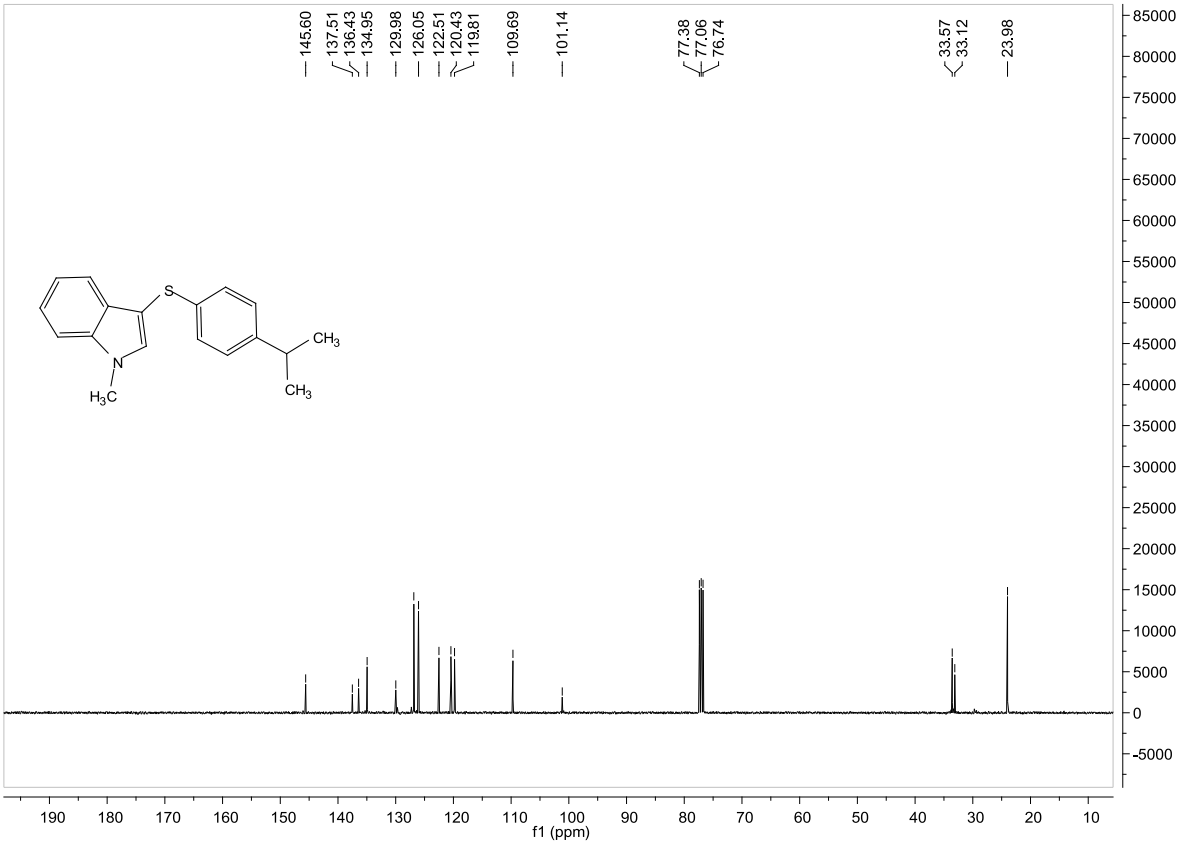
^{1}H NMR of **3aa**



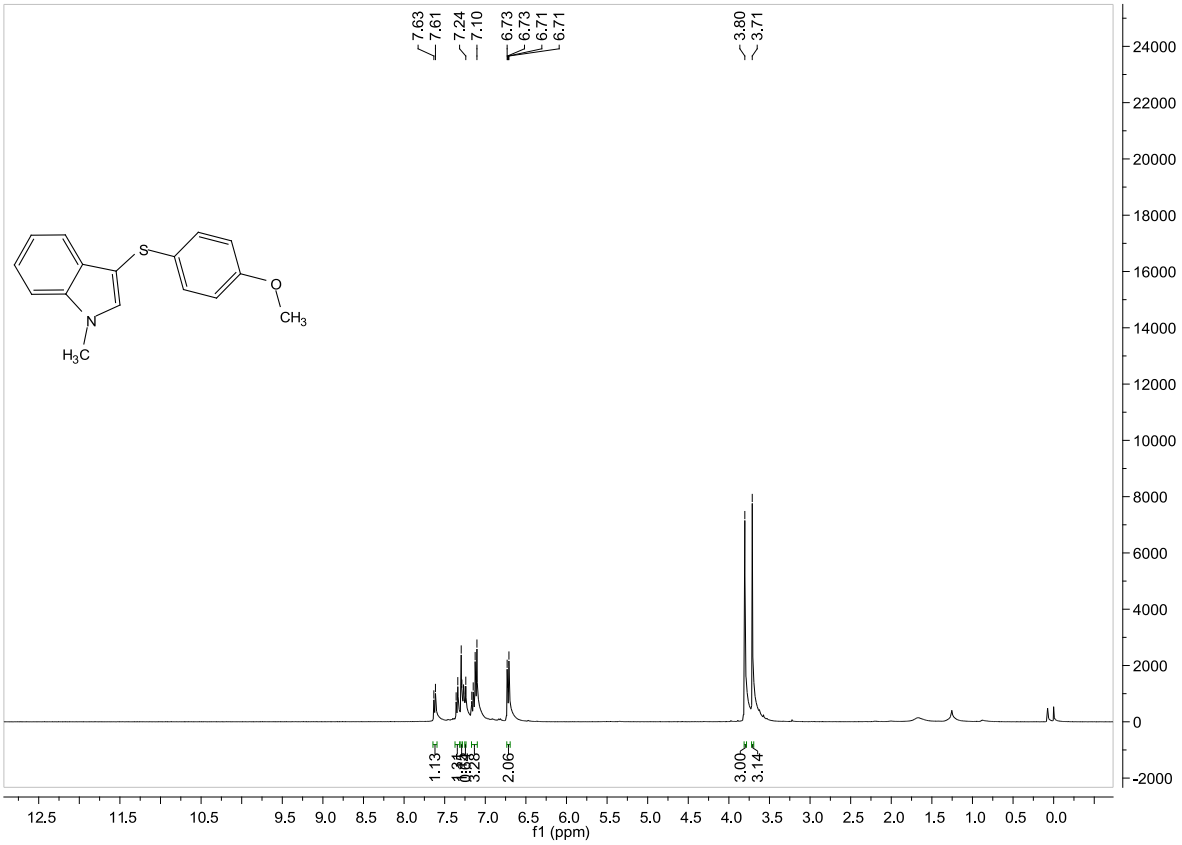
^{13}C NMR of **3aa**


7.65
7.63
7.37
7.35
7.30
7.28
7.28
7.26
7.19
7.16
7.14
7.05
7.03
7.02
6.99
3.81
2.83
2.81
2.79
2.77
2.76
1.18
1.16
S
N
H3C
CH3
CH3
0.98
1.11
2.28
1.33
4.12
3.00
1.03
6.14
f1 (ppm)

^{1}H NMR of **3ab**



^{13}C NMR of **3ab**


7.63
7.61
7.24
7.10
6.73
6.73
6.71
6.71
3.80
3.71
S
O
CH3
N
H3C
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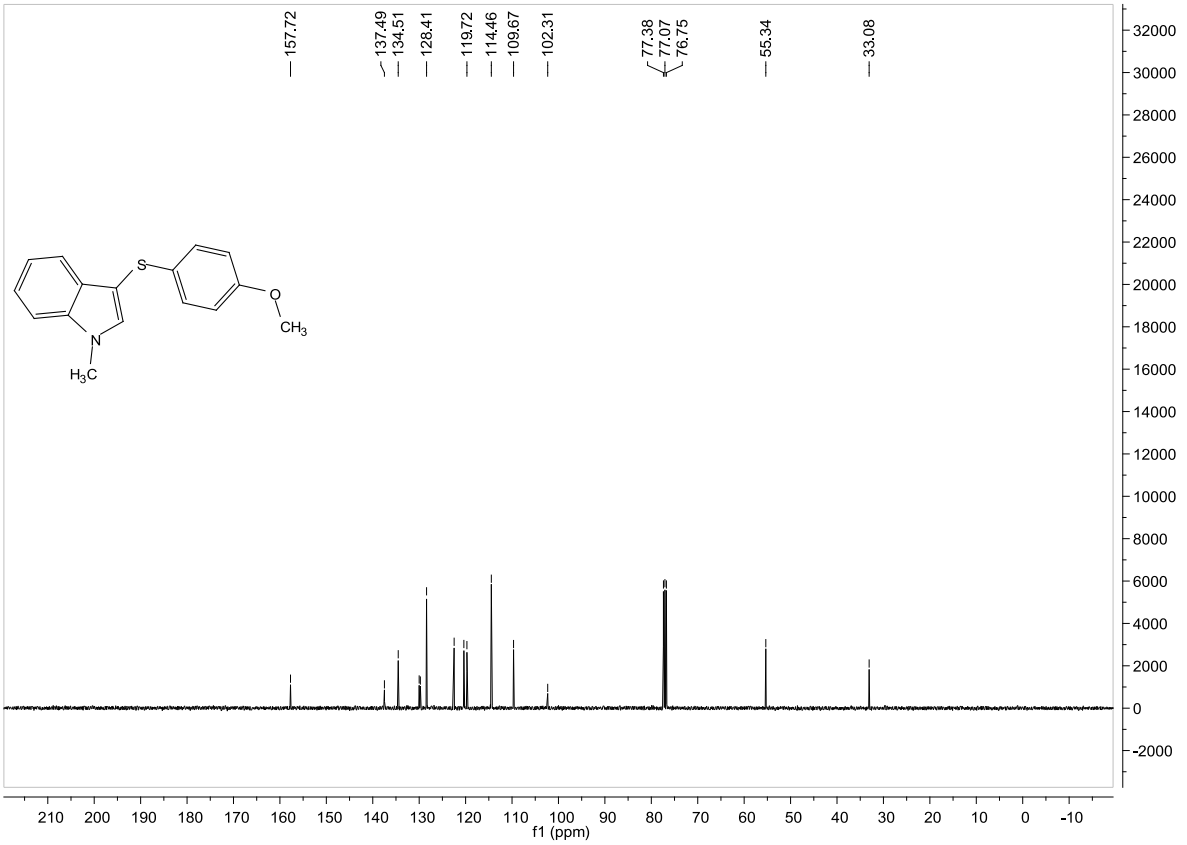
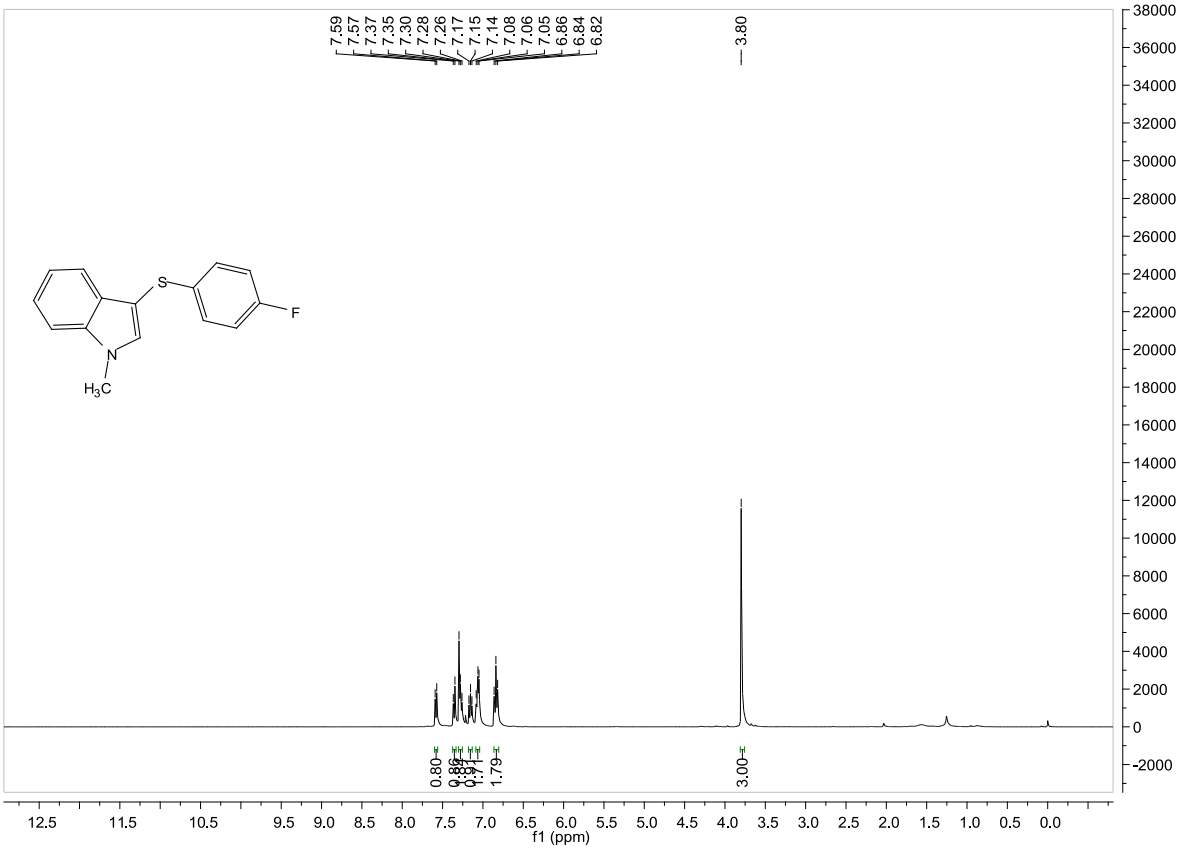
2.06
3.00
3.14
f1 (ppm)

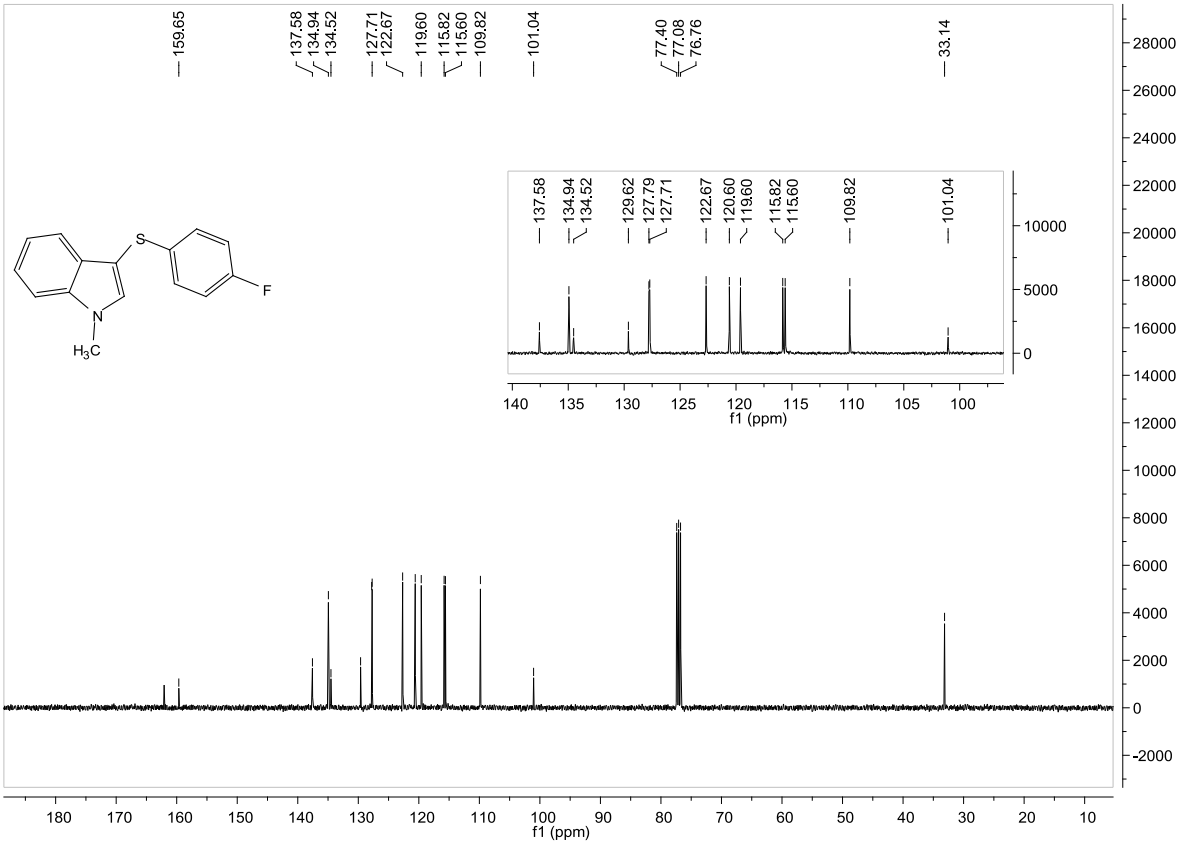
^{1}H NMR of **3ac**



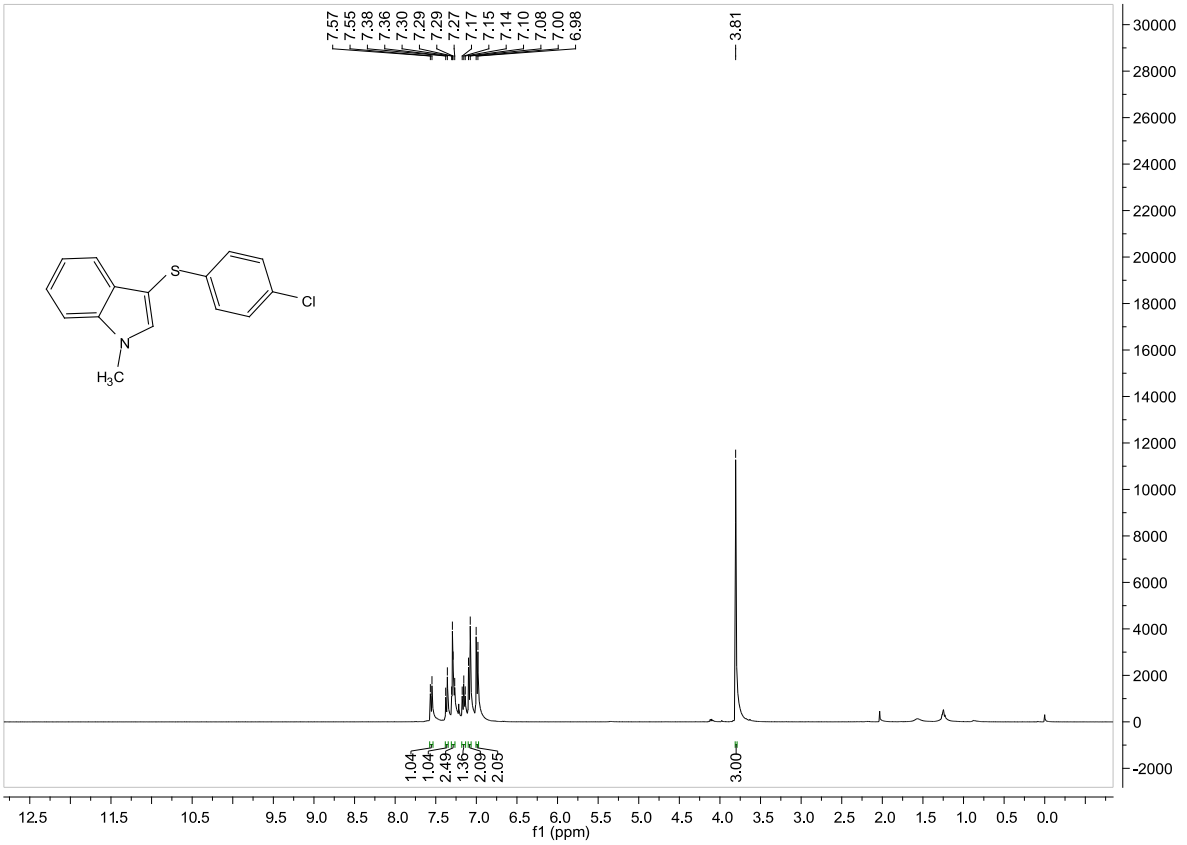
^{13}C NMR of **3ac**


7.59
7.57
7.37
7.35
7.30
7.28
7.26
7.17
7.15
7.14
7.08
7.06
7.05
6.86
6.84
6.82
3.80
S
F
N
H3C
0.80
0.86
0.89
0.91
1.79
3.00
f1 (ppm)

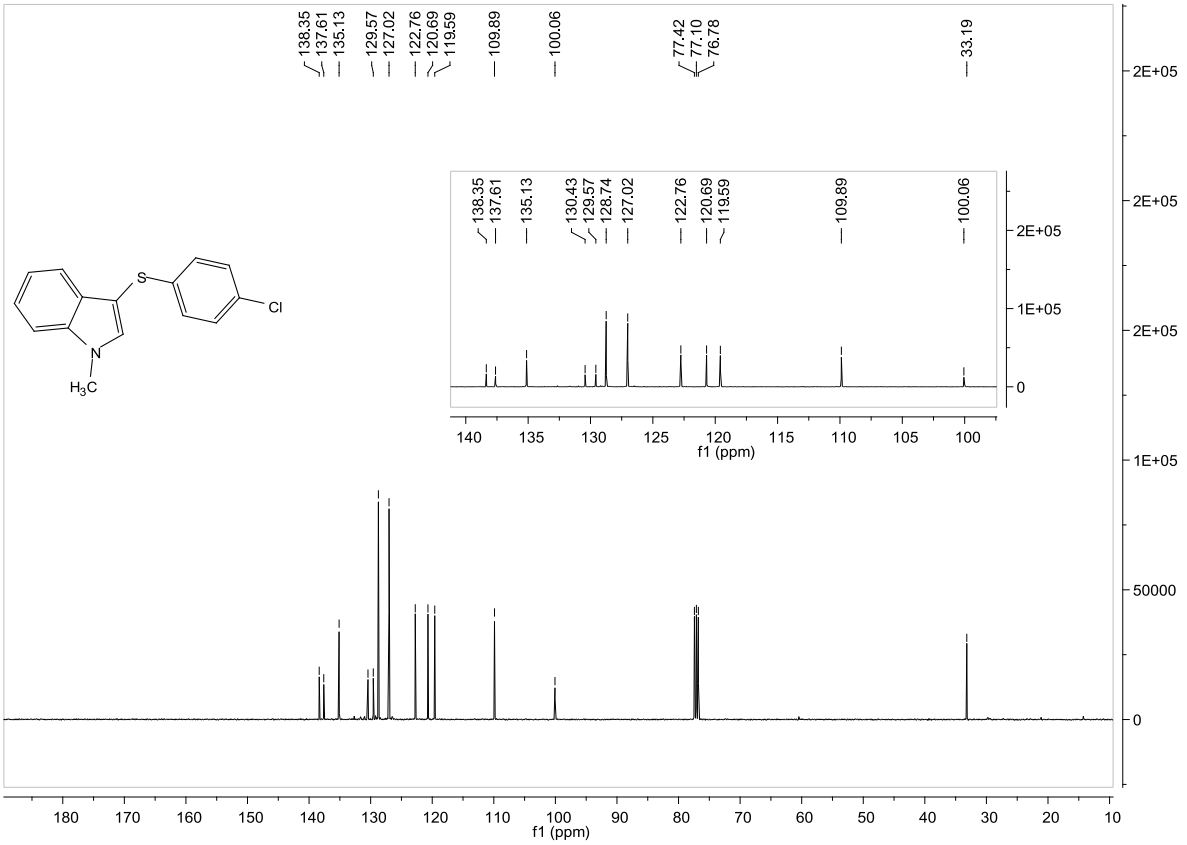
^{1}H NMR of **3ad**



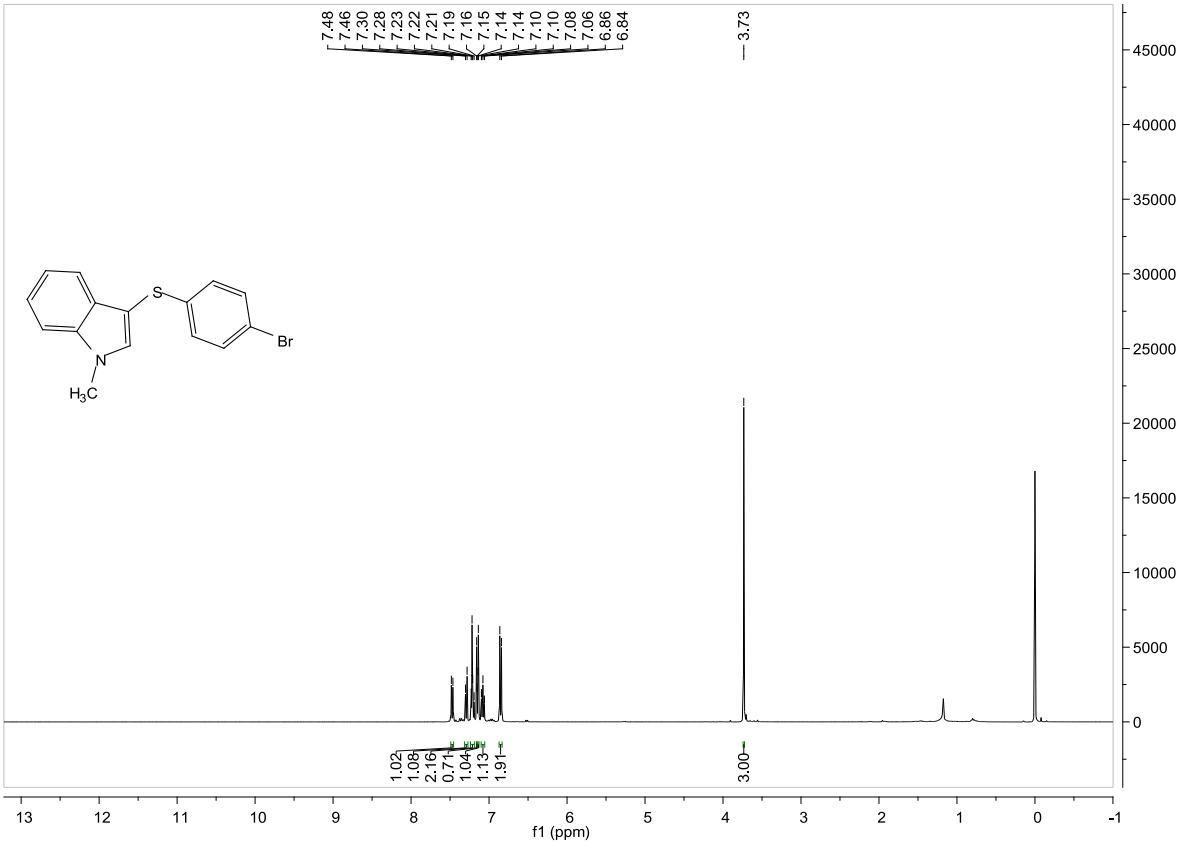
^{13}C NMR of **3ad**


7.57
7.55
7.38
7.36
7.30
7.29
7.29
7.27
7.17
7.15
7.14
7.10
7.08
7.00
6.98
3.81
S
Cl
N
H3C
1.04
1.04
2.49
1.36
2.09
2.05
3.00
f1 (ppm)

^{1}H NMR of **3ae**



^{13}C NMR of **3ae**


7.48
7.46
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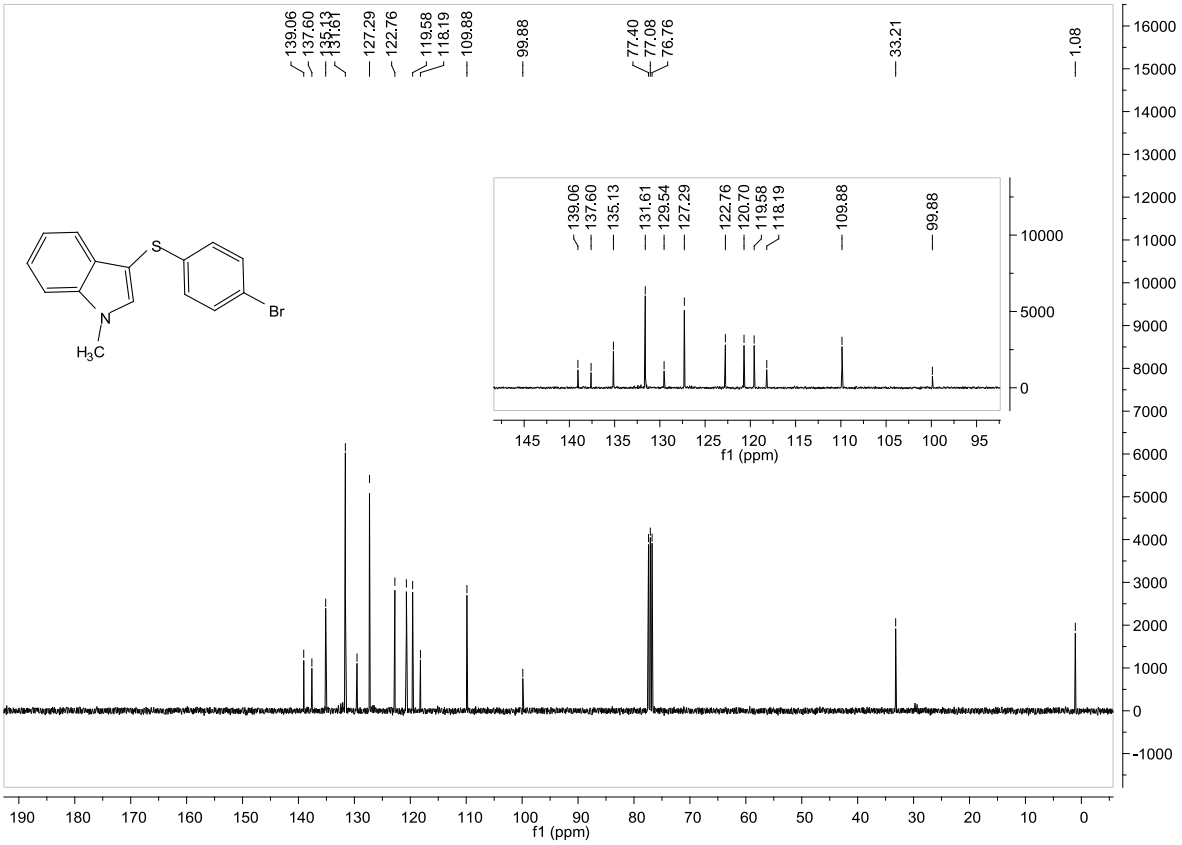
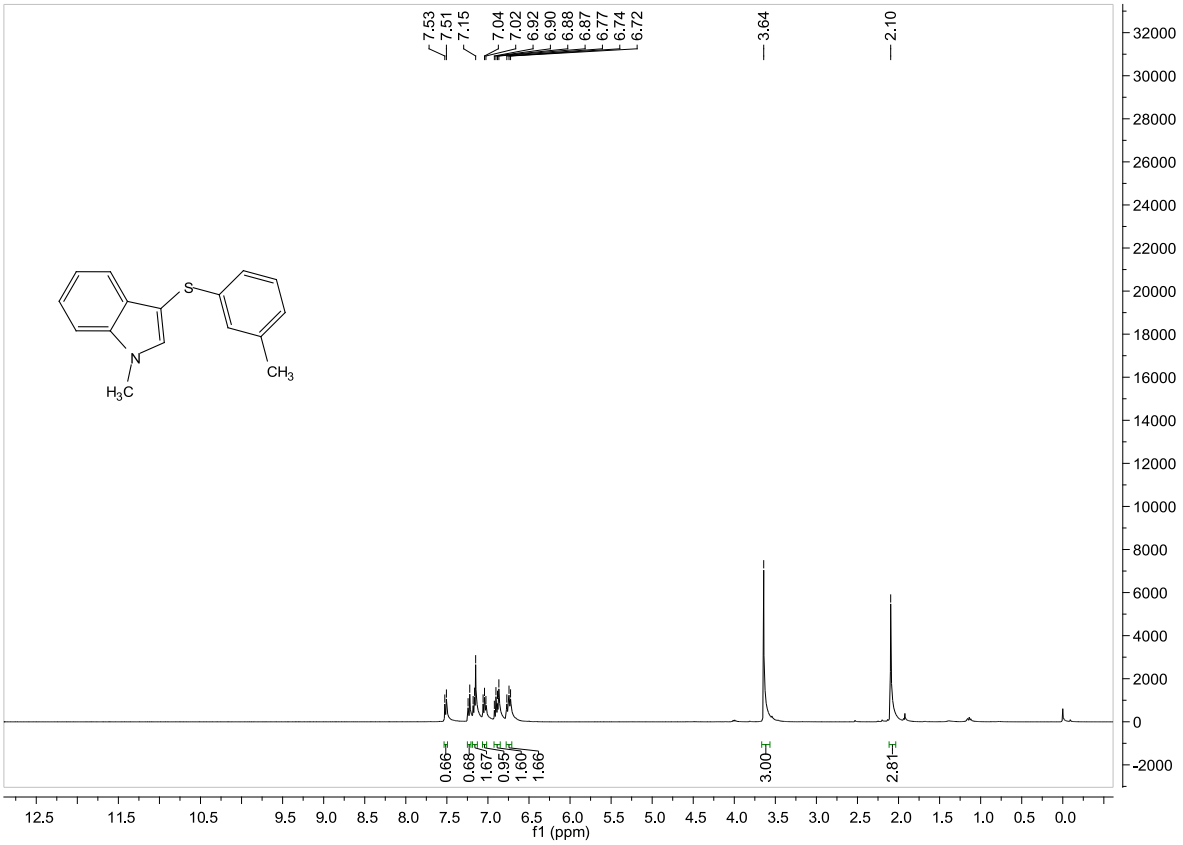
7.28
7.23
7.22
7.21
7.19
7.16
7.15
7.14
7.14
7.10
7.10
7.08
7.06
6.86
6.84
3.73
S
Br
N
H3C
1.02
1.08
2.16
0.71
1.04
1.13
1.91
3.00
f1 (ppm)

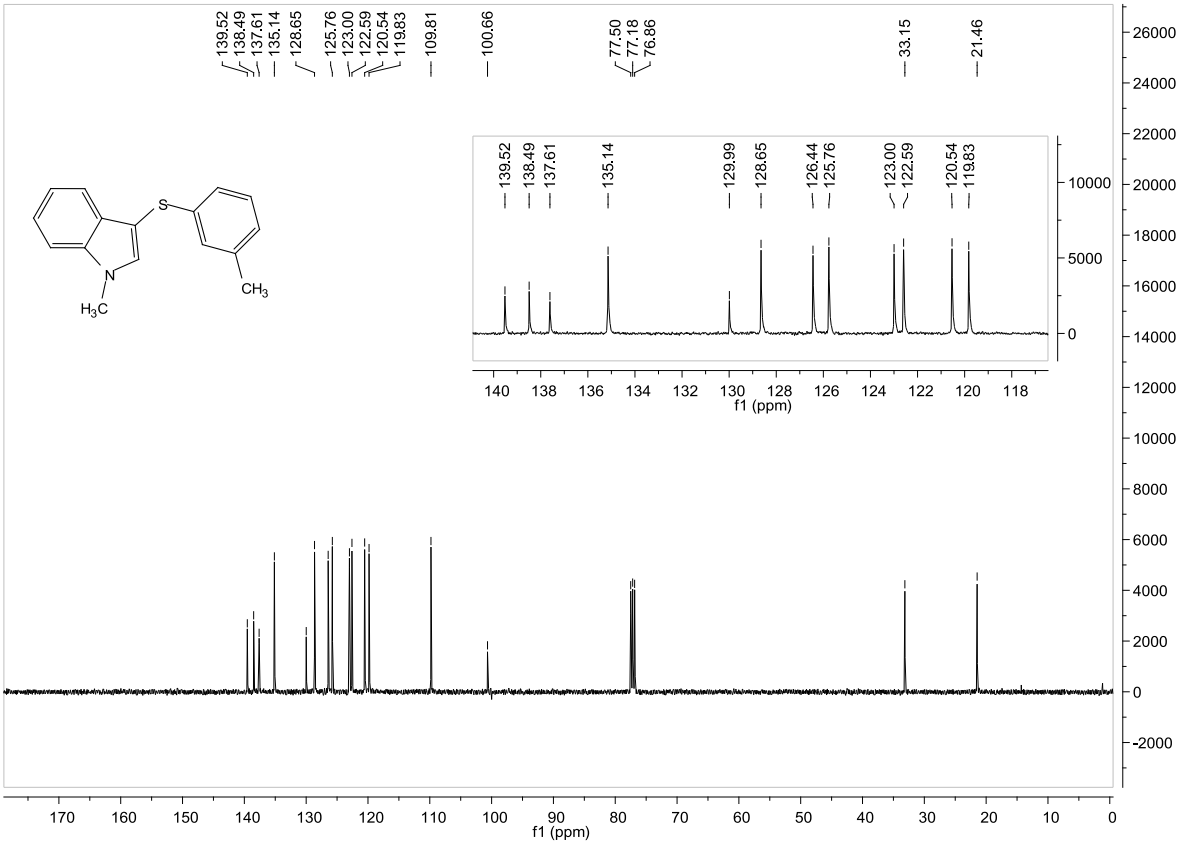
^{1}H NMR of **3af**



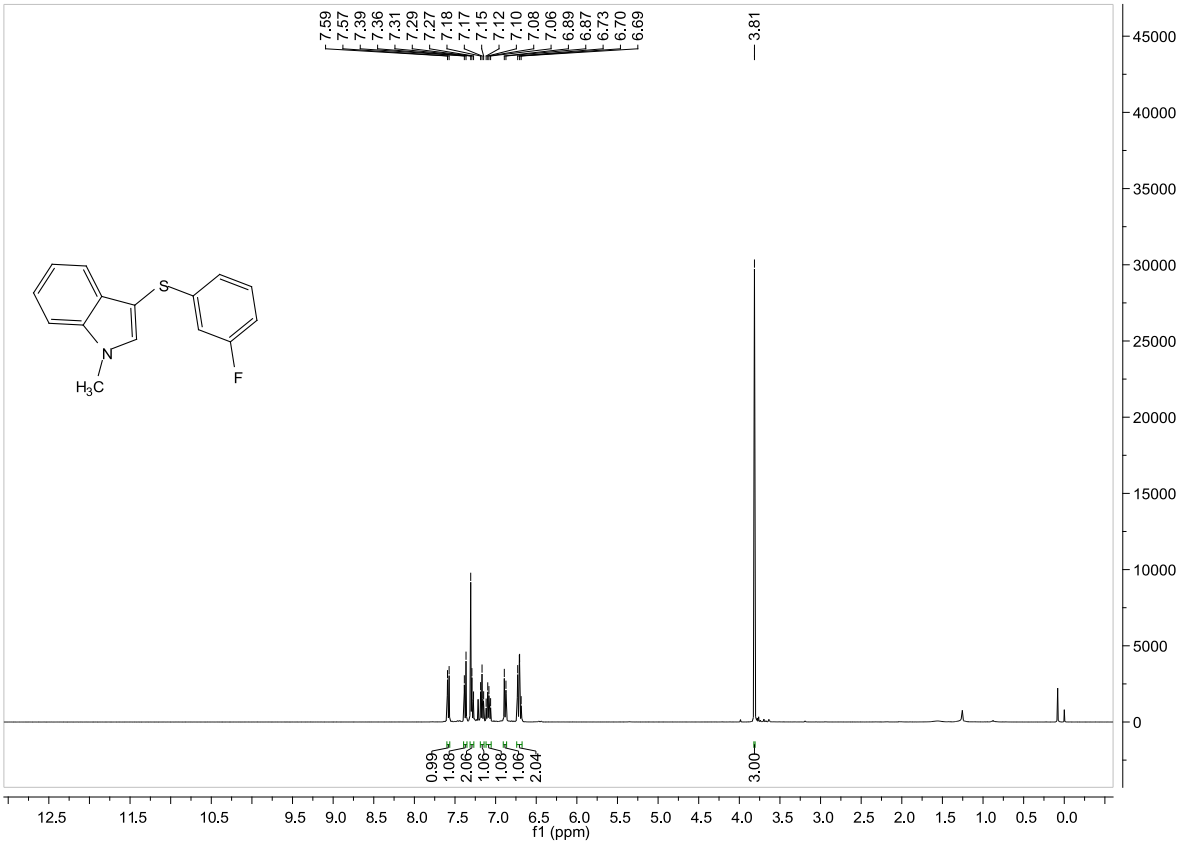
^{13}C NMR of **3af**


7.53
7.51
7.15
7.04
7.02
6.92
6.90
6.88
6.87
6.77
6.74
6.72
3.64
2.10
S
N
H3C
CH3
0.66
0.68
1.67
0.95
1.60
1.66
3.00
2.81
f1 (ppm)

^{1}H NMR of **3ag**



^{13}C NMR of **3ag**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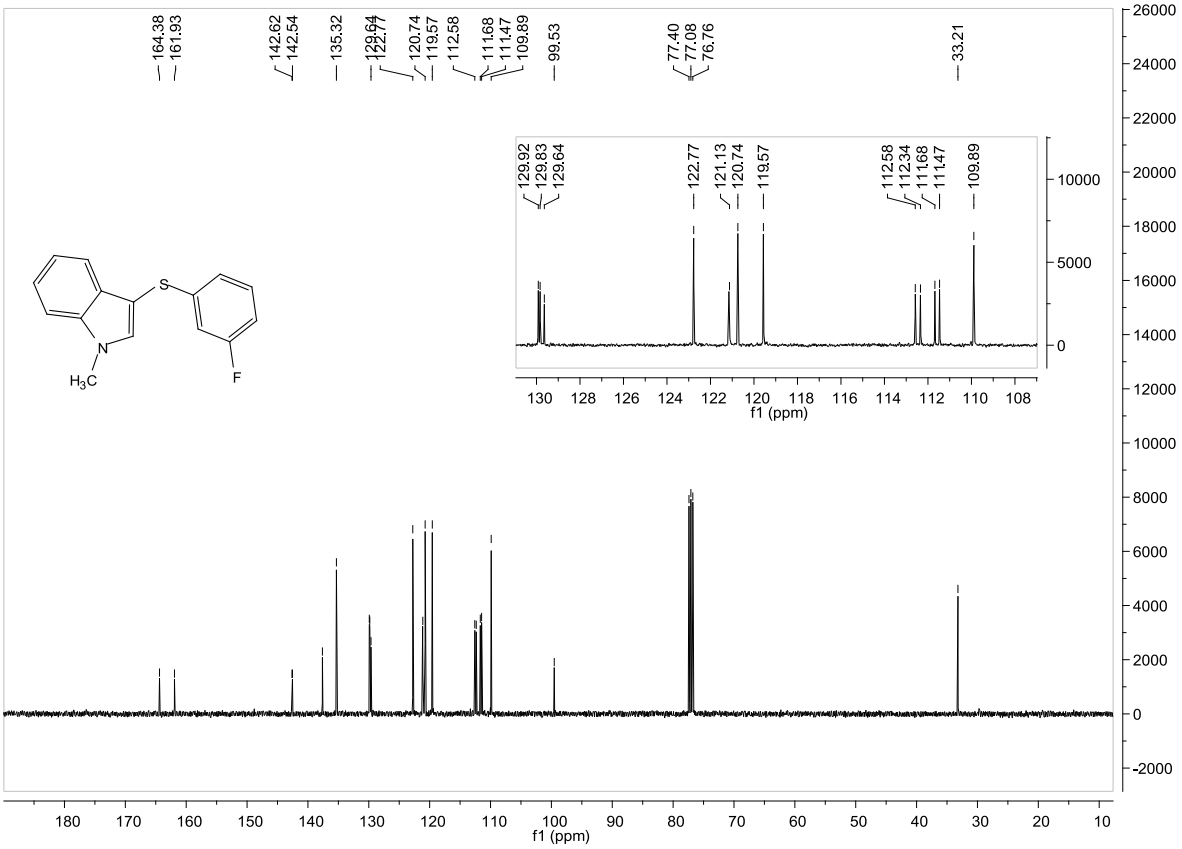
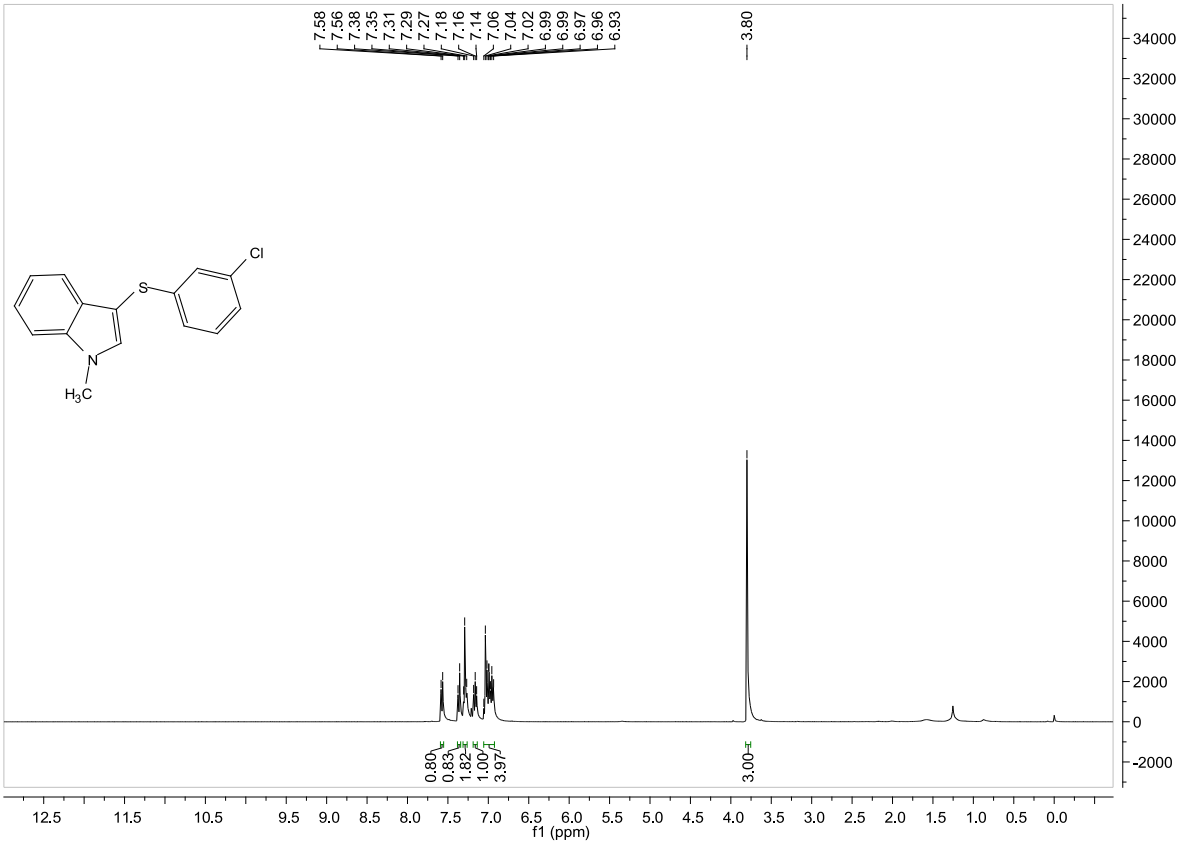
7.57
7.39
7.36
7.31
7.29
7.27
7.18
7.17
7.15
7.12
7.10
7.08
7.06
6.89
6.87
6.73
6.70
6.69
3.81
S
N
H3C
F
0.99
1.08
2.06
1.06
1.08
1.06
2.04
3.00
f1 (ppm)

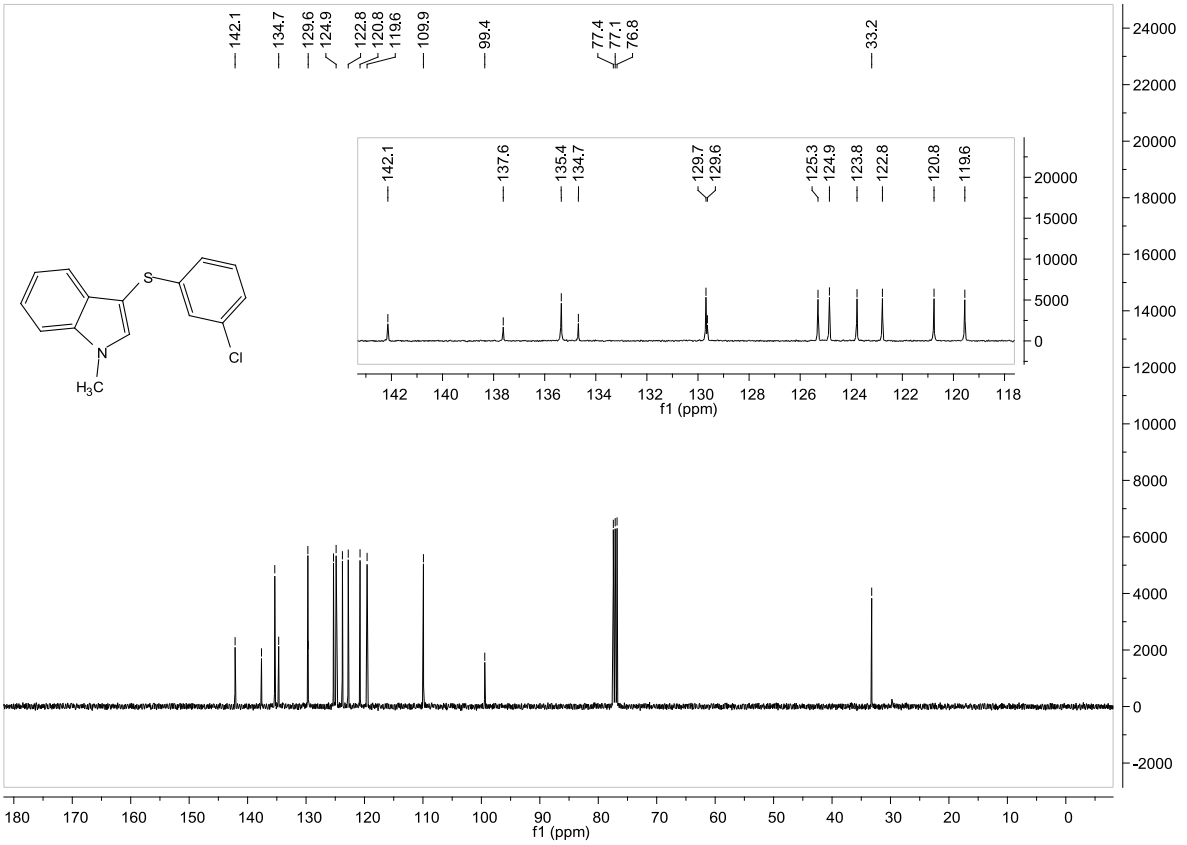
^{1}H NMR of **3ah**



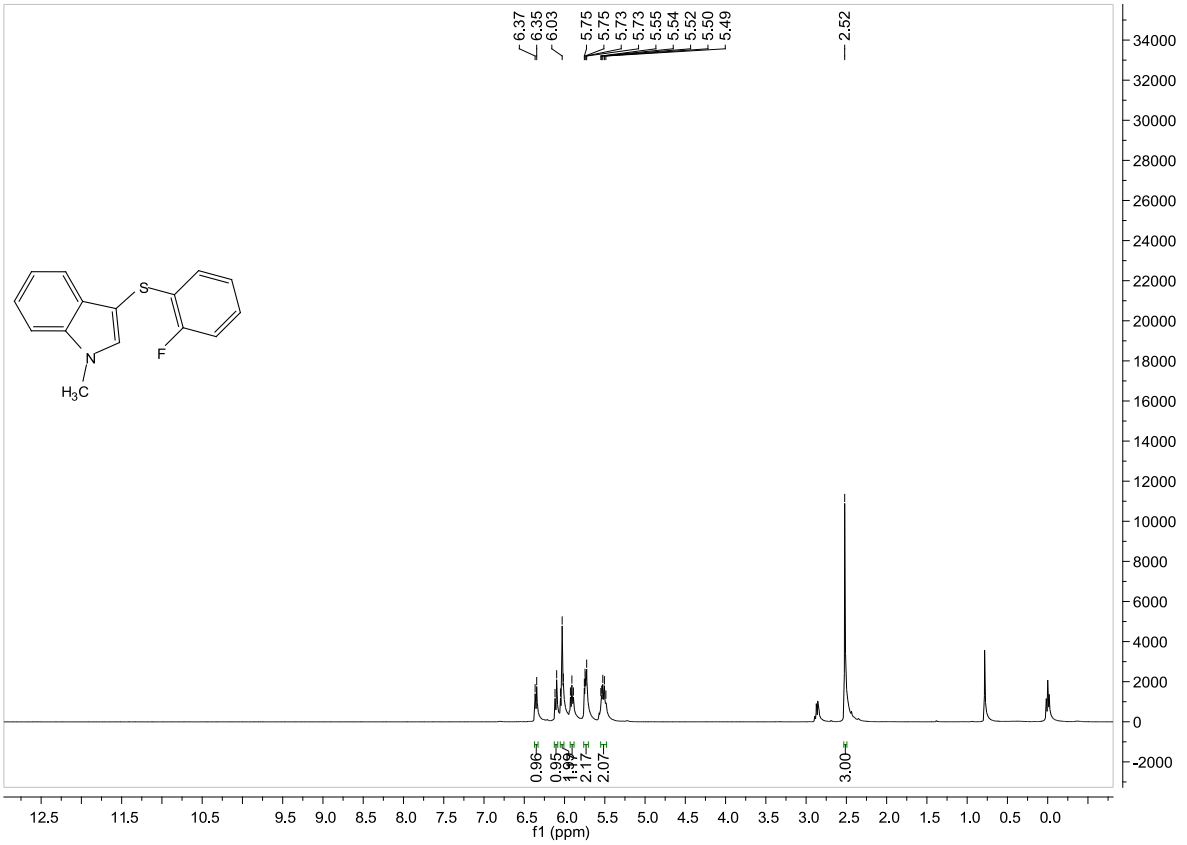
^{13}C NMR of **3ah**


7.58
7.56
7.38
7.35
7.31
7.29
7.27
7.18
7.16
7.14
7.06
7.04
7.02
6.99
6.99
6.97
6.96
6.93
3.80
Cl
S
N
H3C
0.80
0.83
1.82
1.00
3.97
3.00
f1 (ppm)

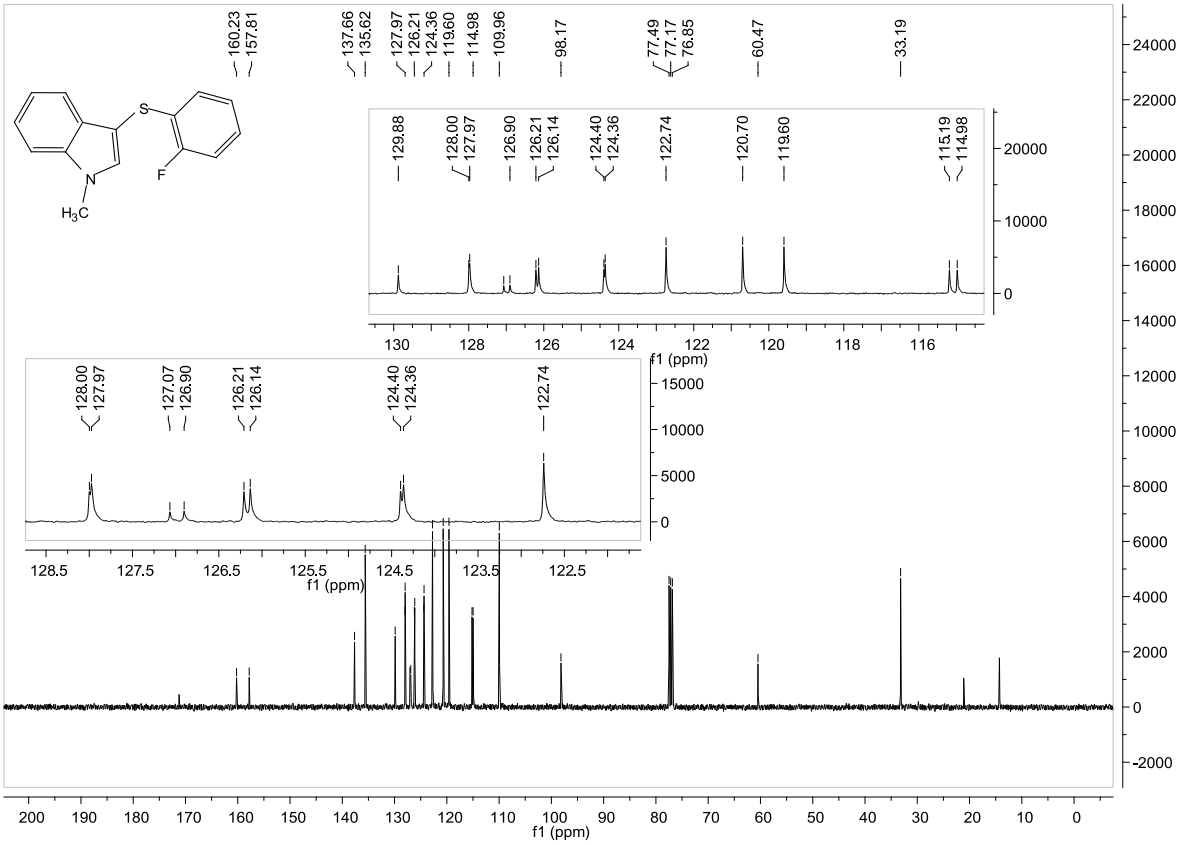
^{1}H NMR of **3ai**



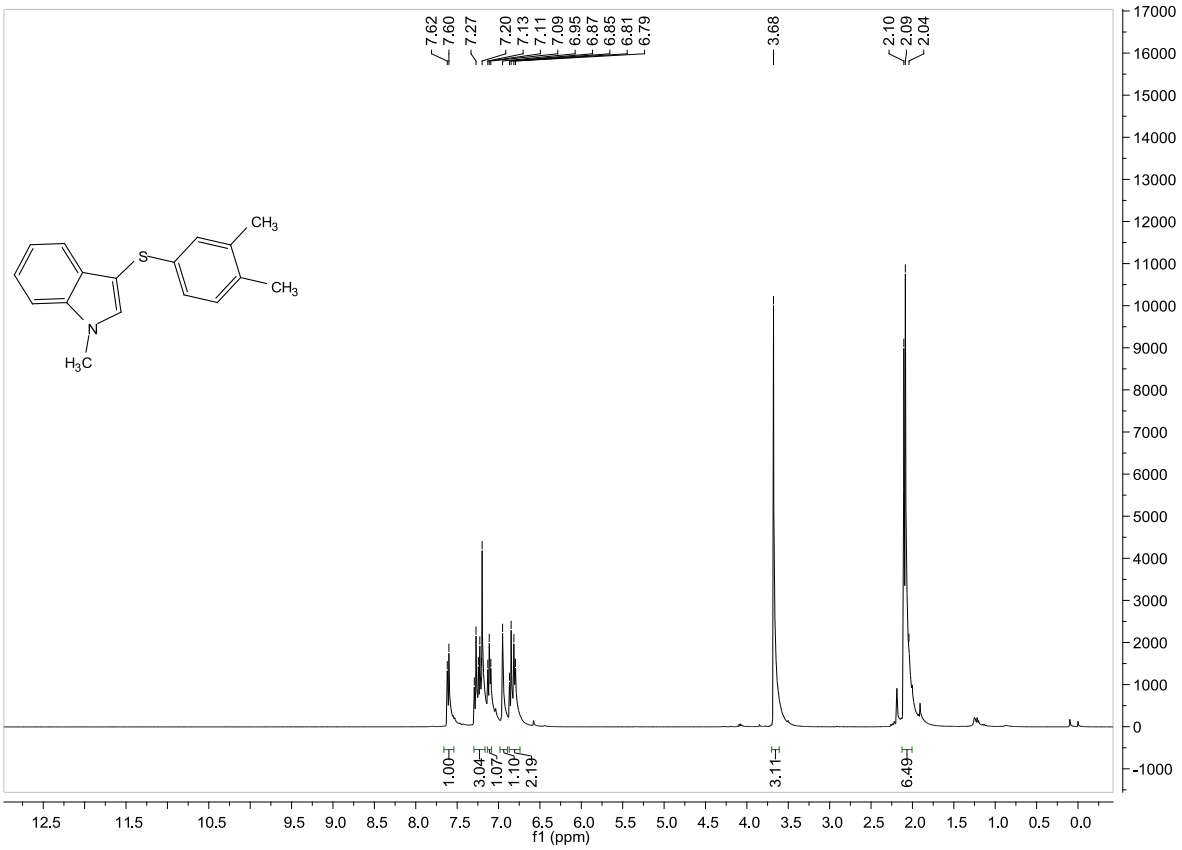
^{13}C NMR of **3ai**


6.37
6.35
6.03
5.75
5.75
5.73
5.55
5.54
5.52
5.50
5.49
2.52
S
F
N
H3C
0.96
0.95
1.94
2.17
2.07
3.00
f1 (ppm)

^{1}H NMR of **3aj**



^{13}C NMR of **3aj**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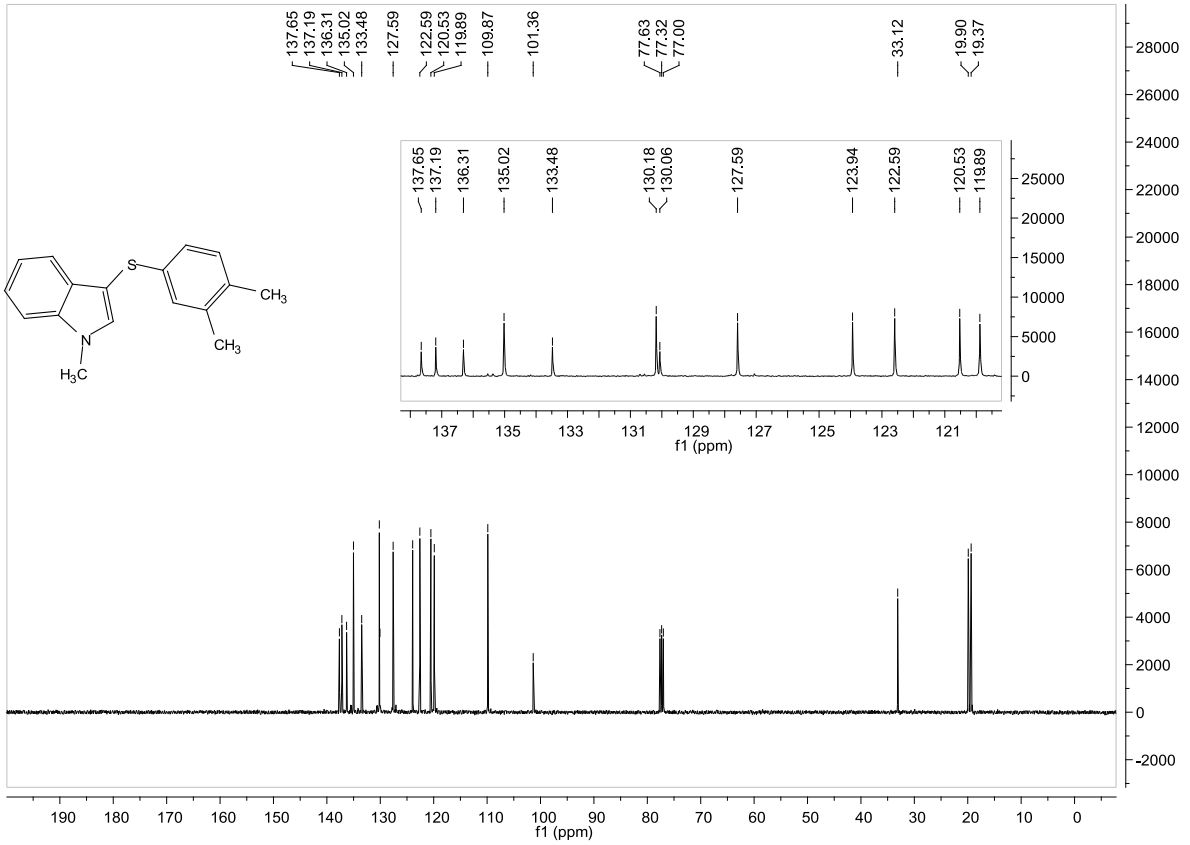
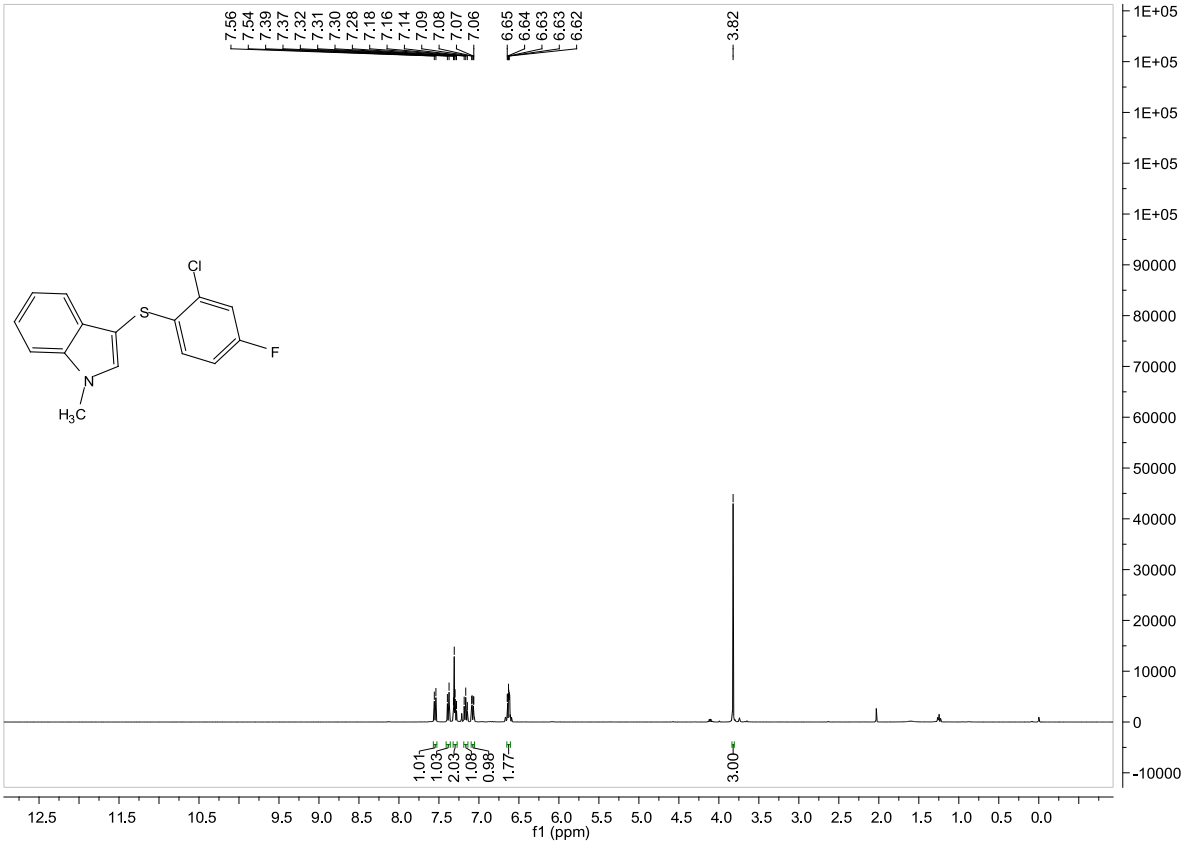
7.09
6.95
6.87
6.85
6.81
6.79
3.68
2.10
2.09
2.04
CH3
S
CH3
N
H3C
1.00
3.04
1.07
1.10
2.19
3.11
6.49
f1 (ppm)

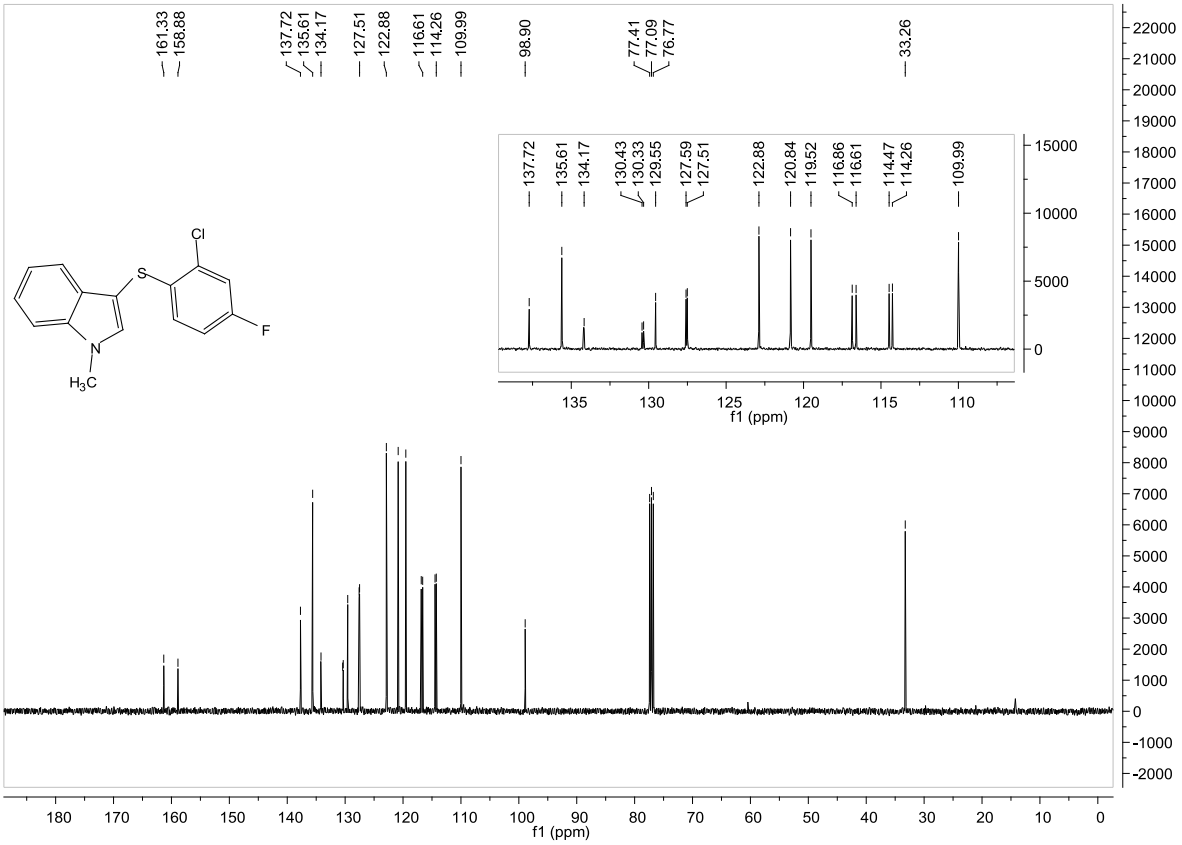
^{1}H NMR of **3ak**



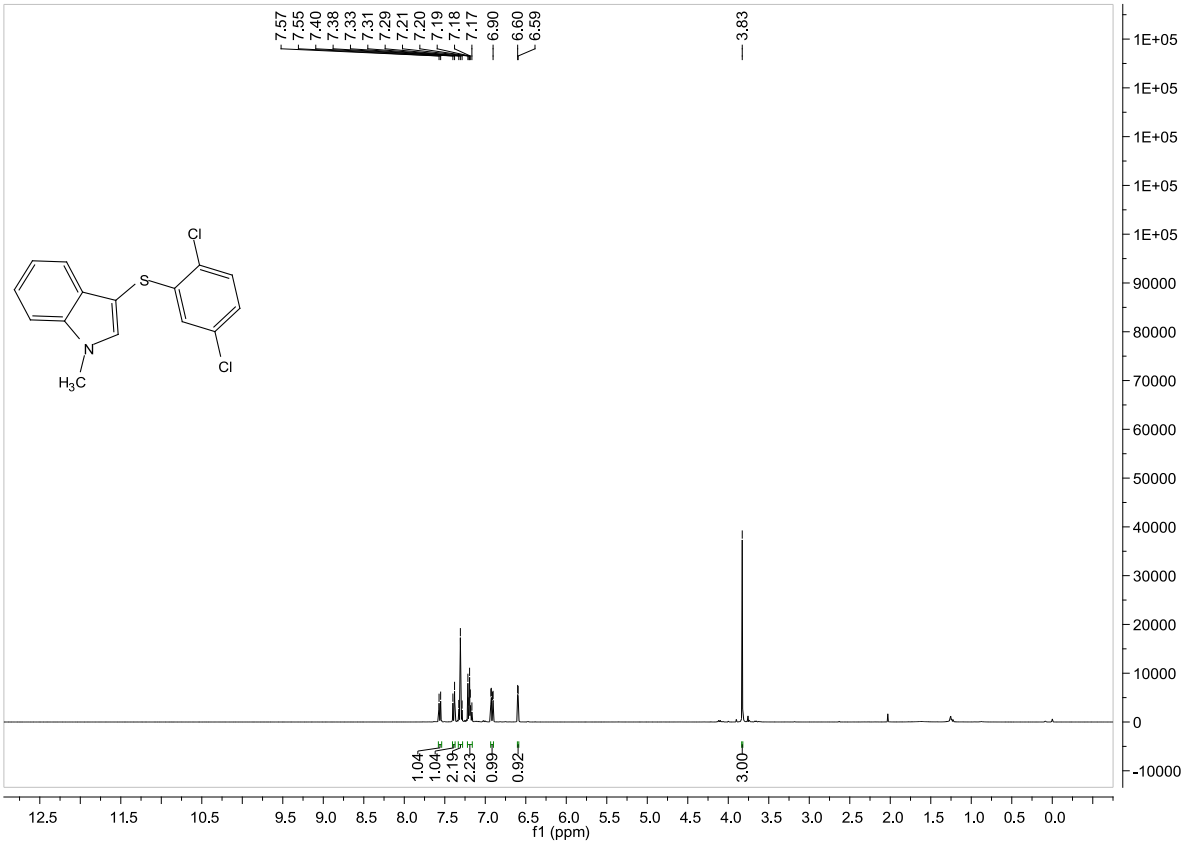
^{13}C NMR of **3ak**


7.56
7.54
7.39
7.37
7.32
7.31
7.30
7.28
7.18
7.16
7.14
7.09
7.08
7.07
7.06
6.65
6.64
6.63
6.63
6.62
3.82
Cl
S
F
N
H3C
1.01
1.03
2.03
1.08
0.98
1.77
3.00
f1 (ppm)

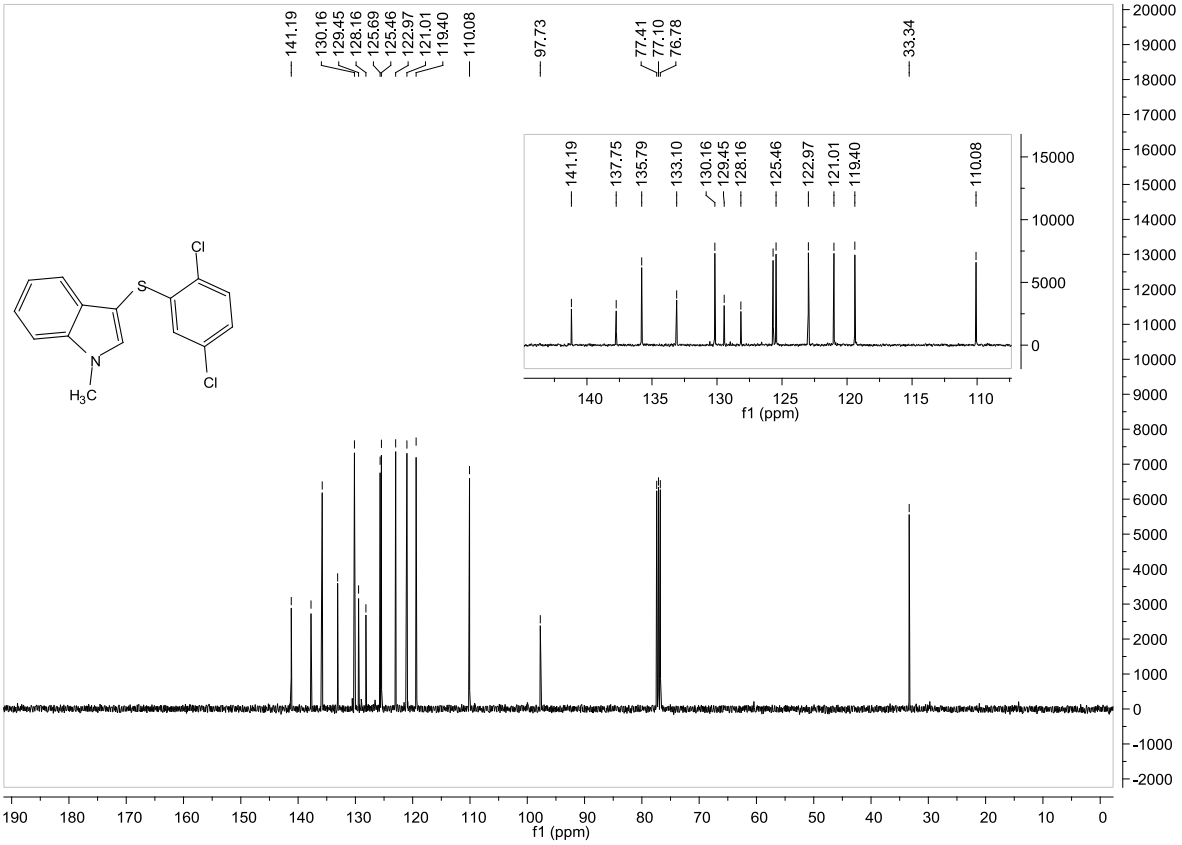
^{1}H NMR of **3al**



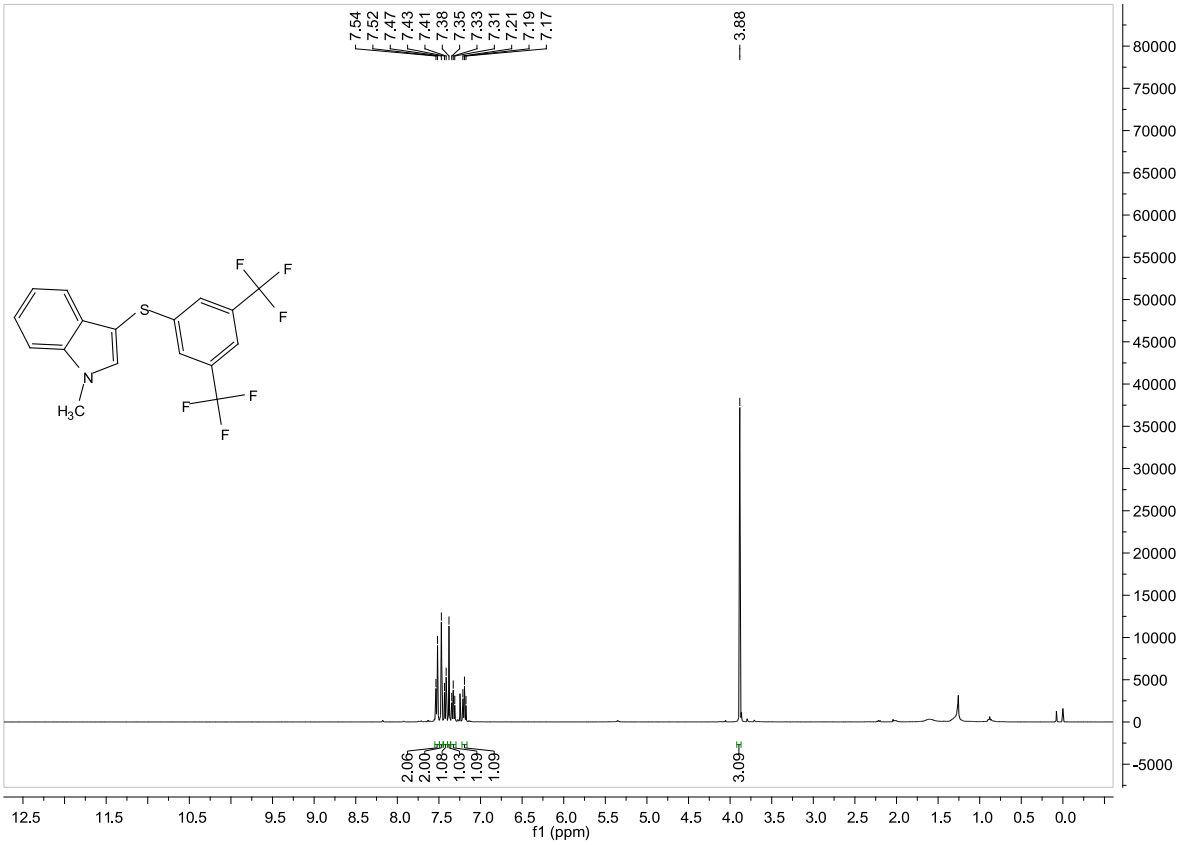
^{13}C NMR of **3al**


7.57
7.55
7.40
7.38
7.33
7.31
7.29
7.21
7.20
7.19
7.18
7.17
6.90
6.60
6.59
3.83
Cl
S
N
H3C
Cl
1.04
1.04
2.19
2.23
0.99
0.92
3.00
f1 (ppm)

^{1}H NMR of **3am**



^{13}C NMR of **3am**


7.54
7.52
7.47
7.43
7.41
7.38
7.35
7.33
7.31
7.21
7.19
7.17
3.88
F
F
F
S
N
H3C
F
F
F
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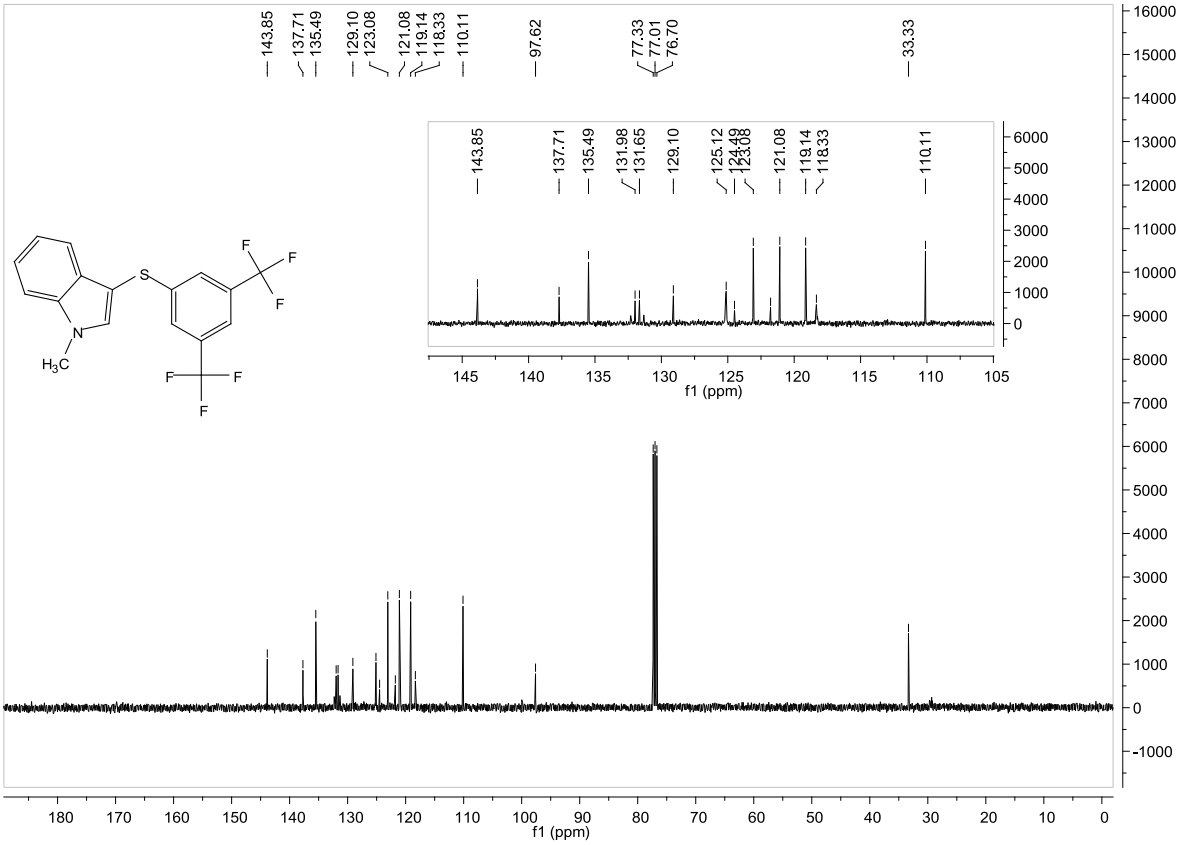
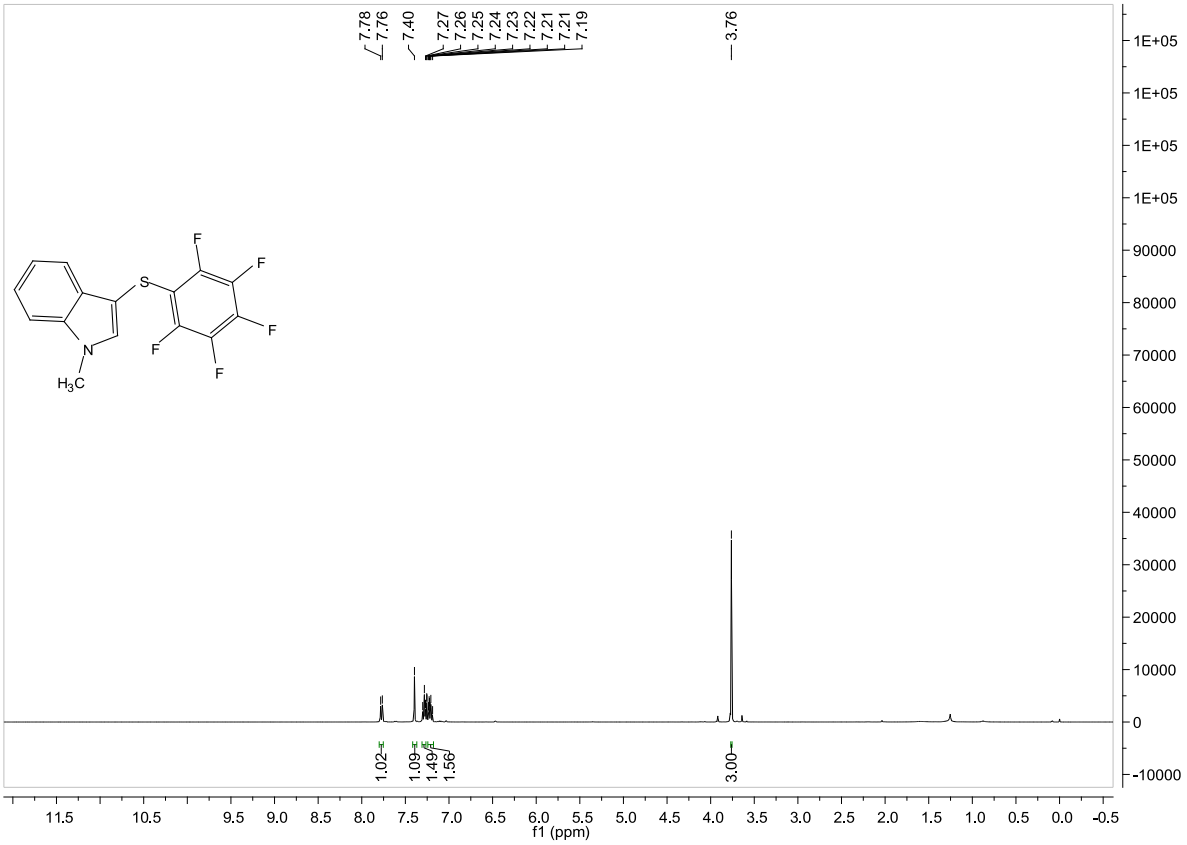
2.00
1.08
1.03
1.09
1.09
3.09
f1 (ppm)

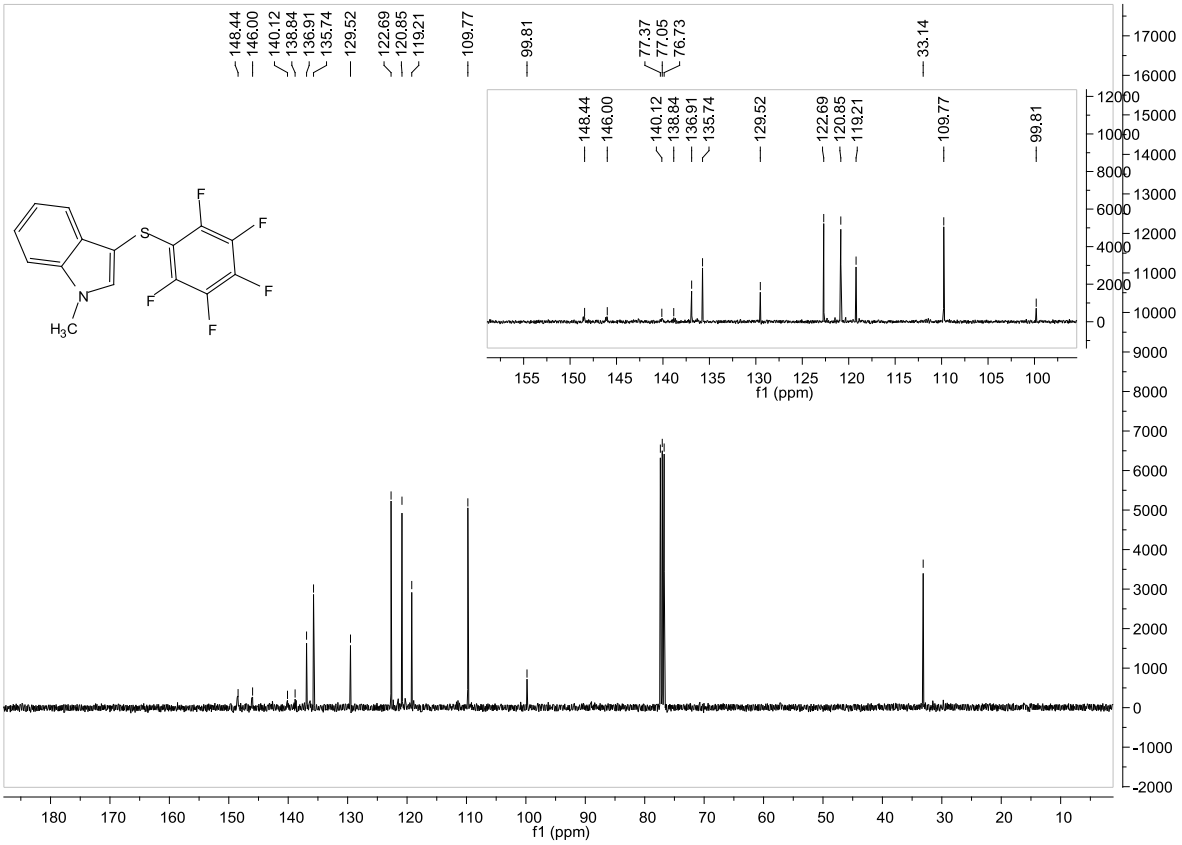
^{1}H NMR of **3an**



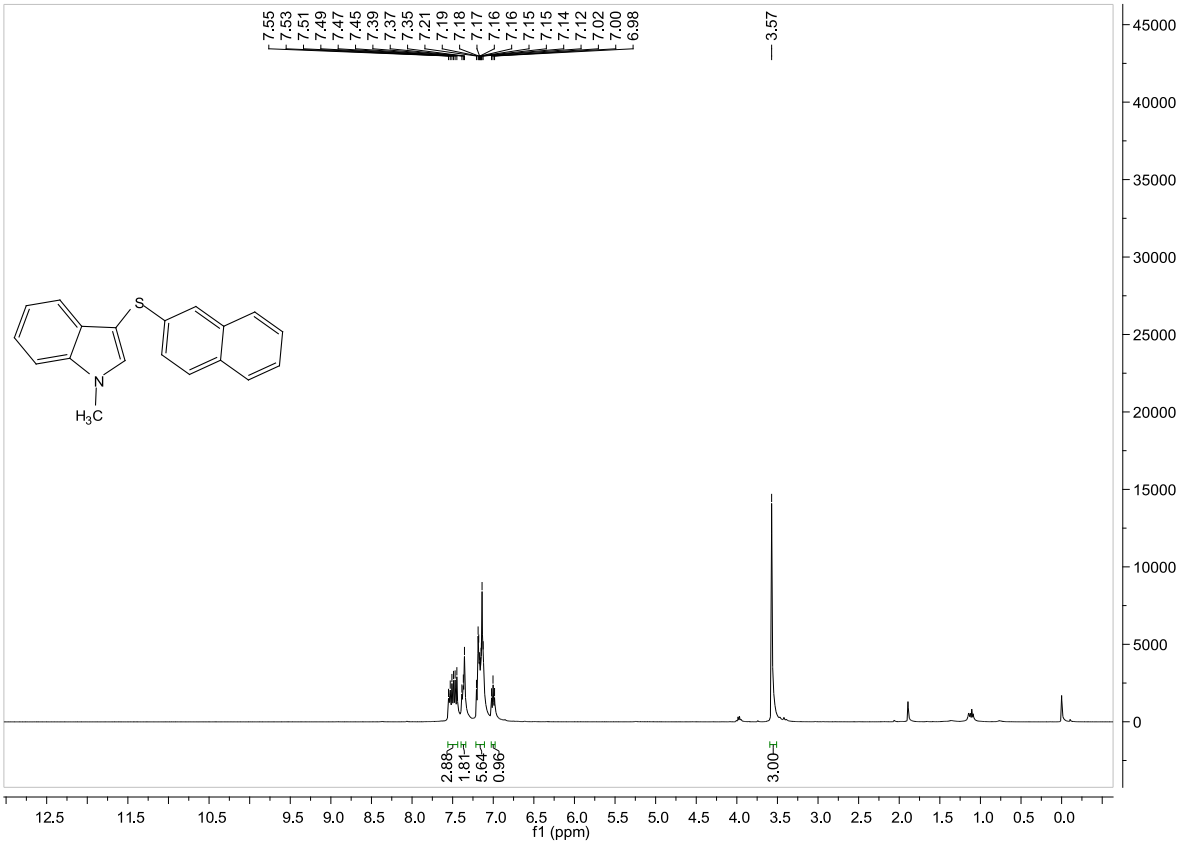
^{13}C NMR of **3an**


7.78
7.76
7.40
7.27
7.26
7.25
7.24
7.23
7.22
7.21
7.21
7.19
3.76
F
F
F
F
F
S
N
H3C
1E+05
1E+05
1E+05
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
1.02
1.09
1.49
1.56
3.00
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

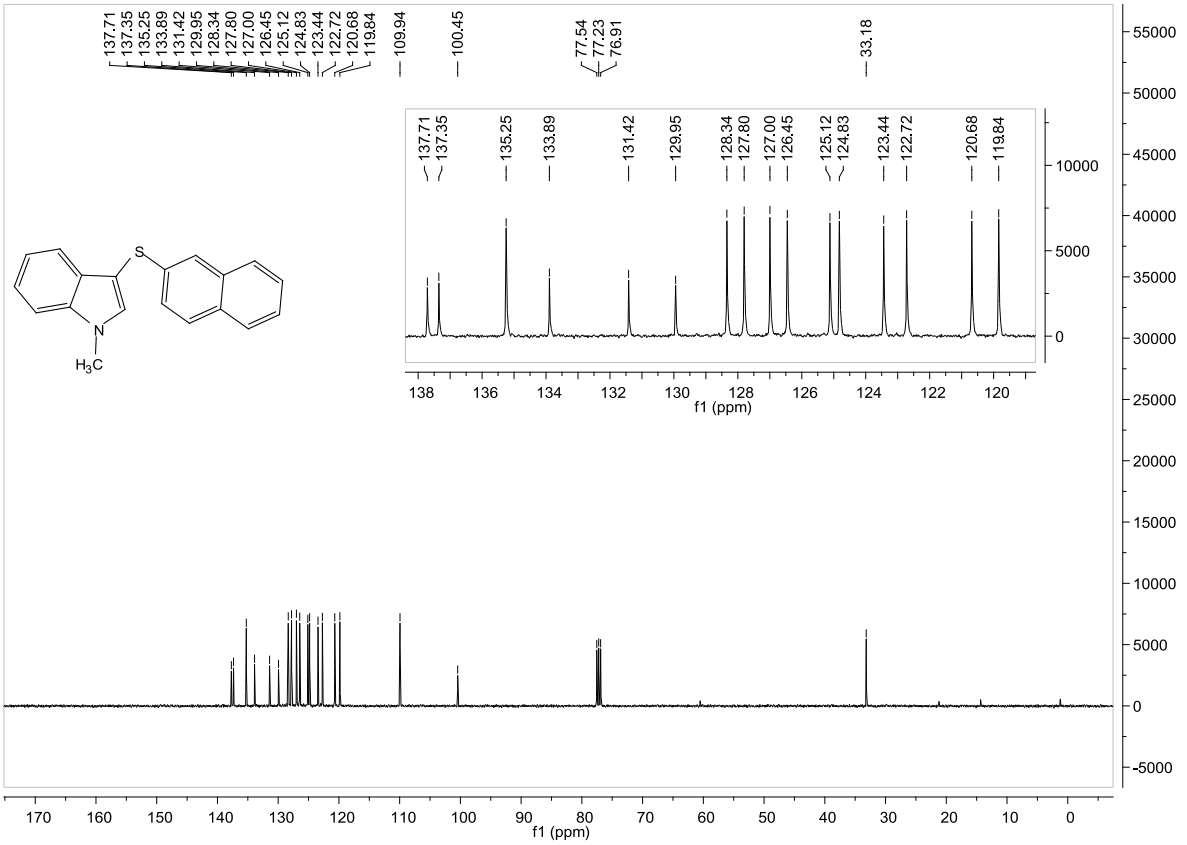
^{1}H NMR of **3ao**



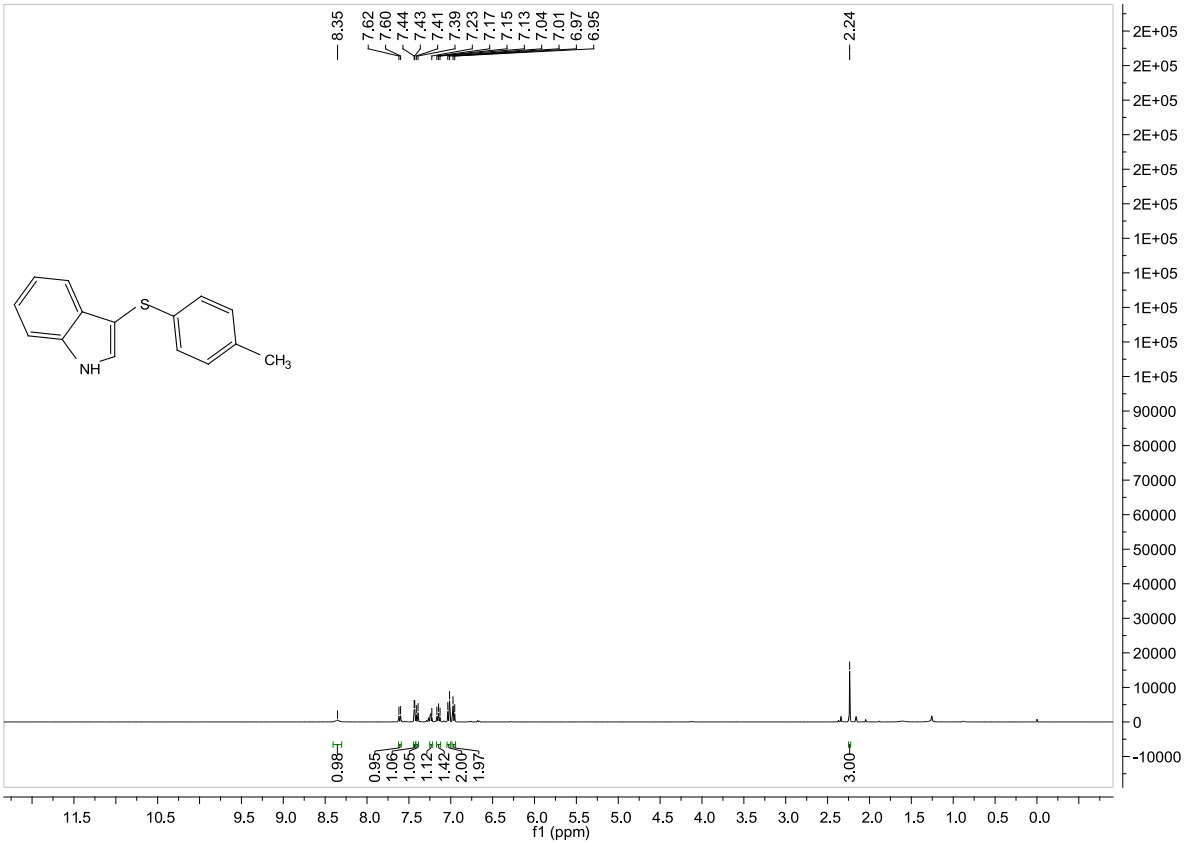
^{13}C NMR of **3ao**


7.55
7.53
7.51
7.49
7.47
7.45
7.39
7.37
7.35
7.21
7.19
7.18
7.17
7.16
7.16
7.15
7.15
7.14
7.12
7.02
7.00
6.98
3.57
S
N
H3C
2.88
1.81
5.64
0.96
3.00
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

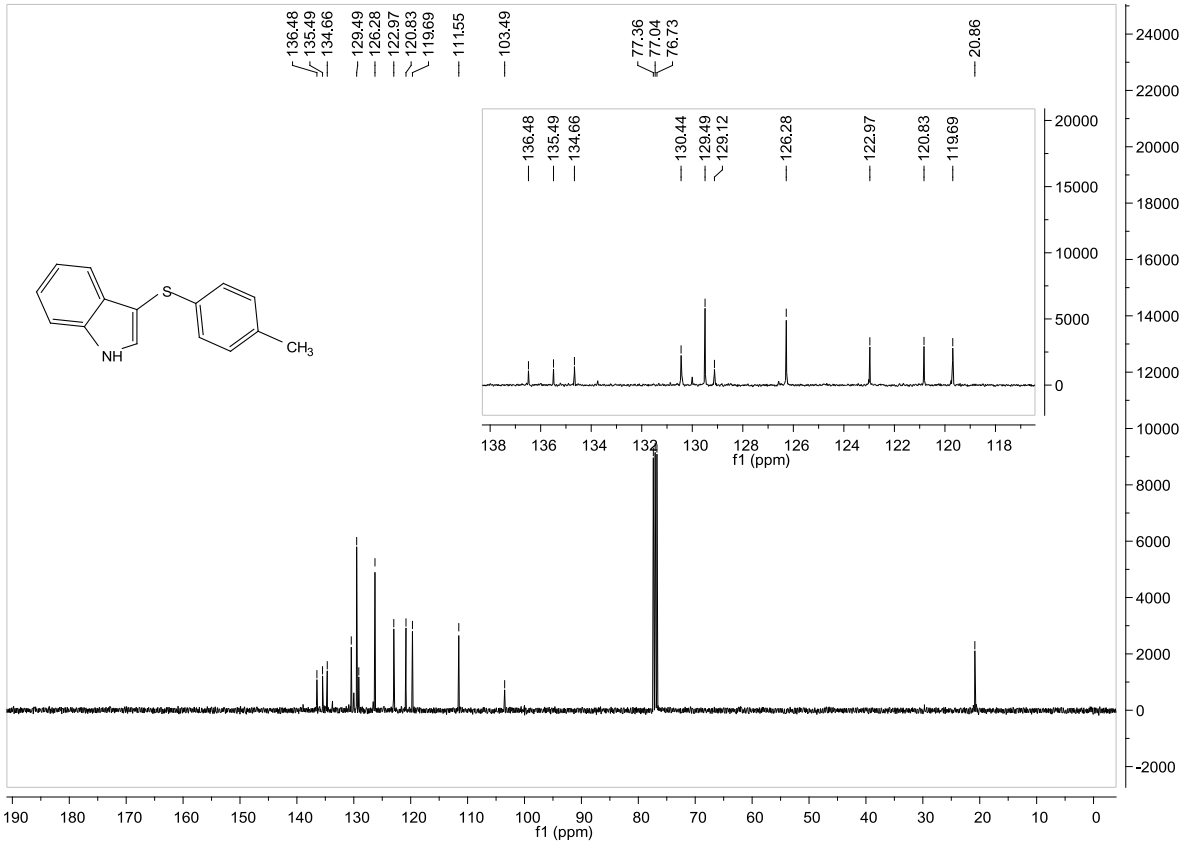
^{1}H NMR of **3ap**



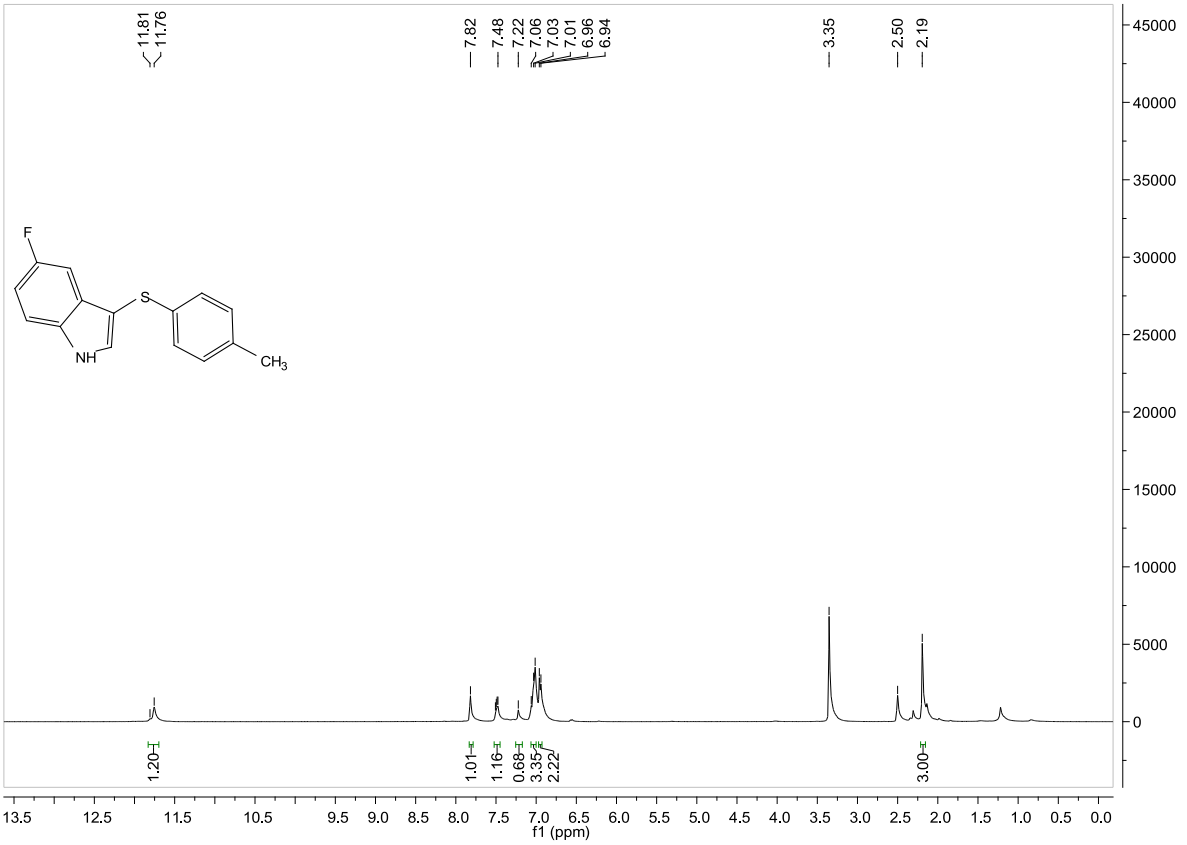
^{13}C NMR of **3ap**


8.35
7.62
7.60
7.44
7.43
7.41
7.39
7.23
7.17
7.15
7.13
7.04
7.01
6.97
6.95
2.24
S
NH
CH3
0.98
0.95
1.06
1.05
1.12
1.42
2.00
1.97
3.00
f1 (ppm)

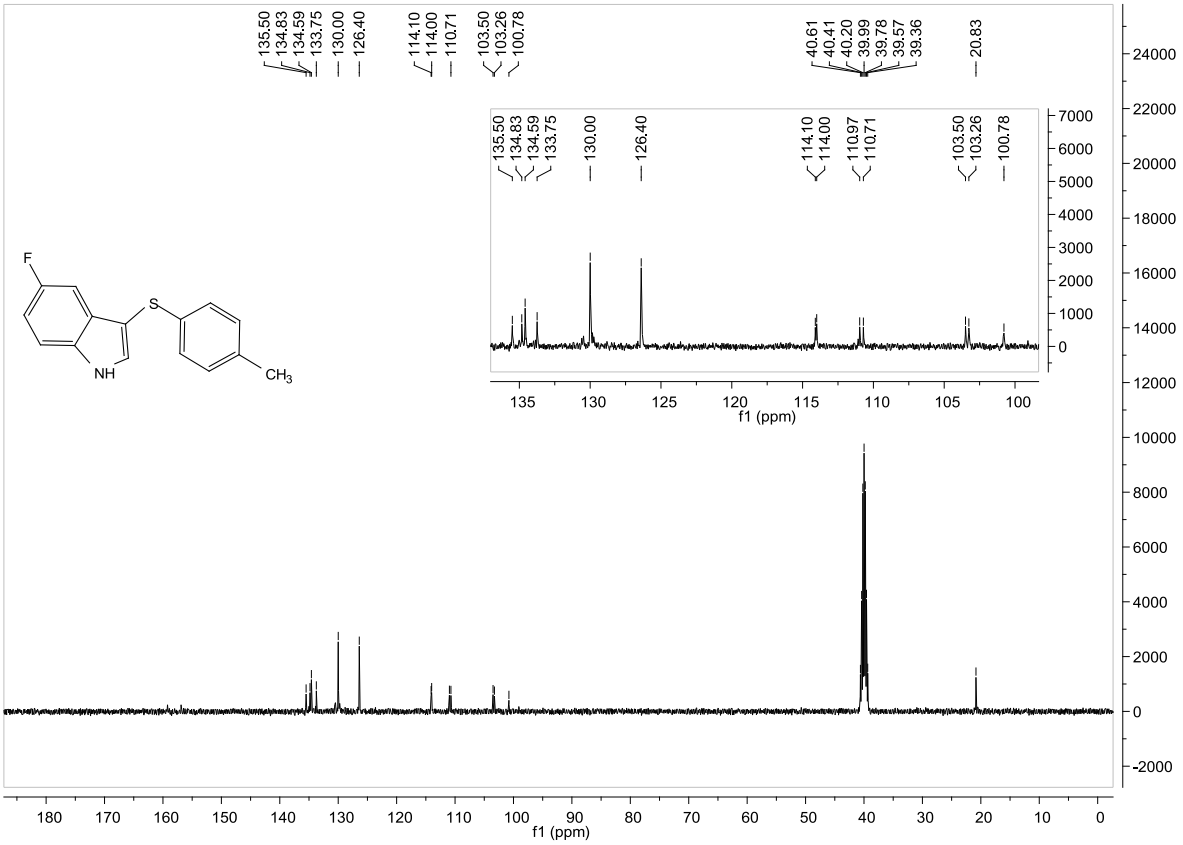
^{1}H NMR of **3ba**



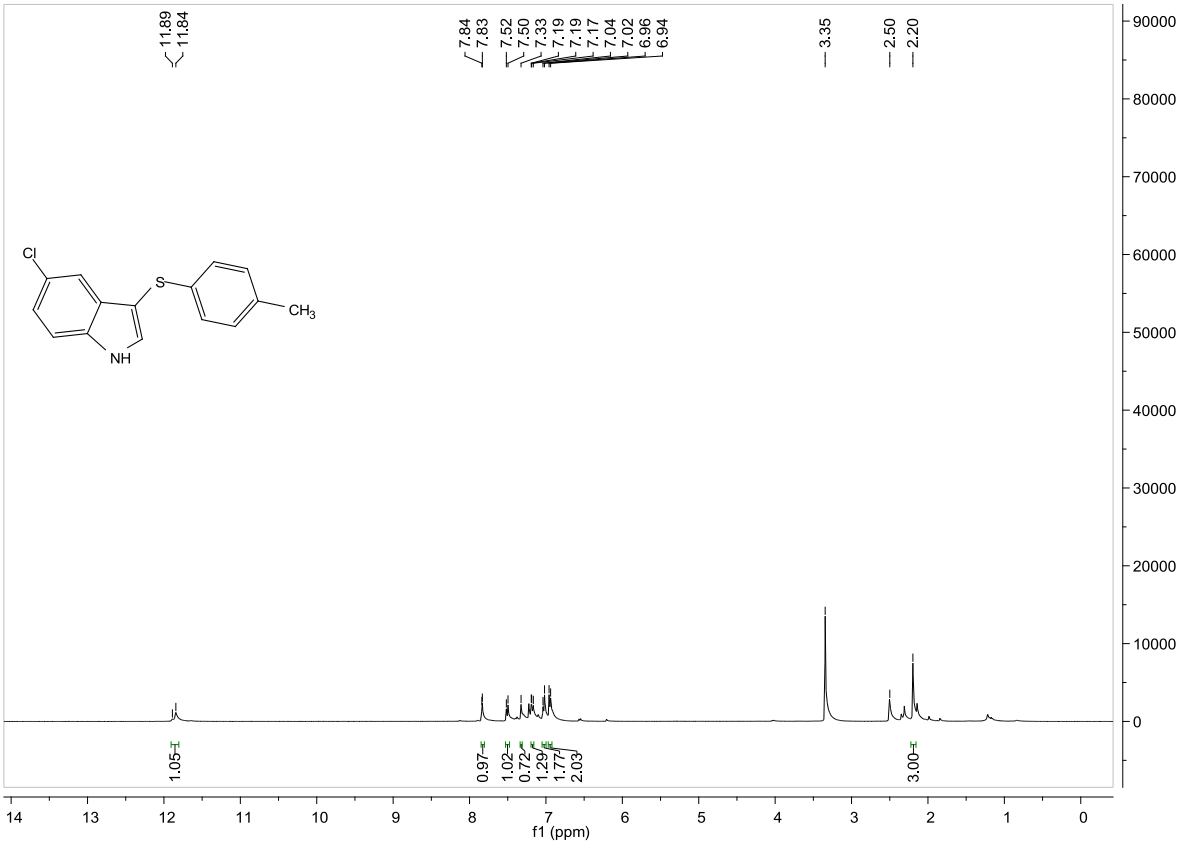
^{13}C NMR of **3ba**


11.81
11.76
7.82
7.48
7.22
7.06
7.03
7.01
6.96
6.94
3.35
2.50
2.19
F
S
NH
CH3
1.20
1.01
1.16
0.68
3.35
2.22
3.00
f1 (ppm)

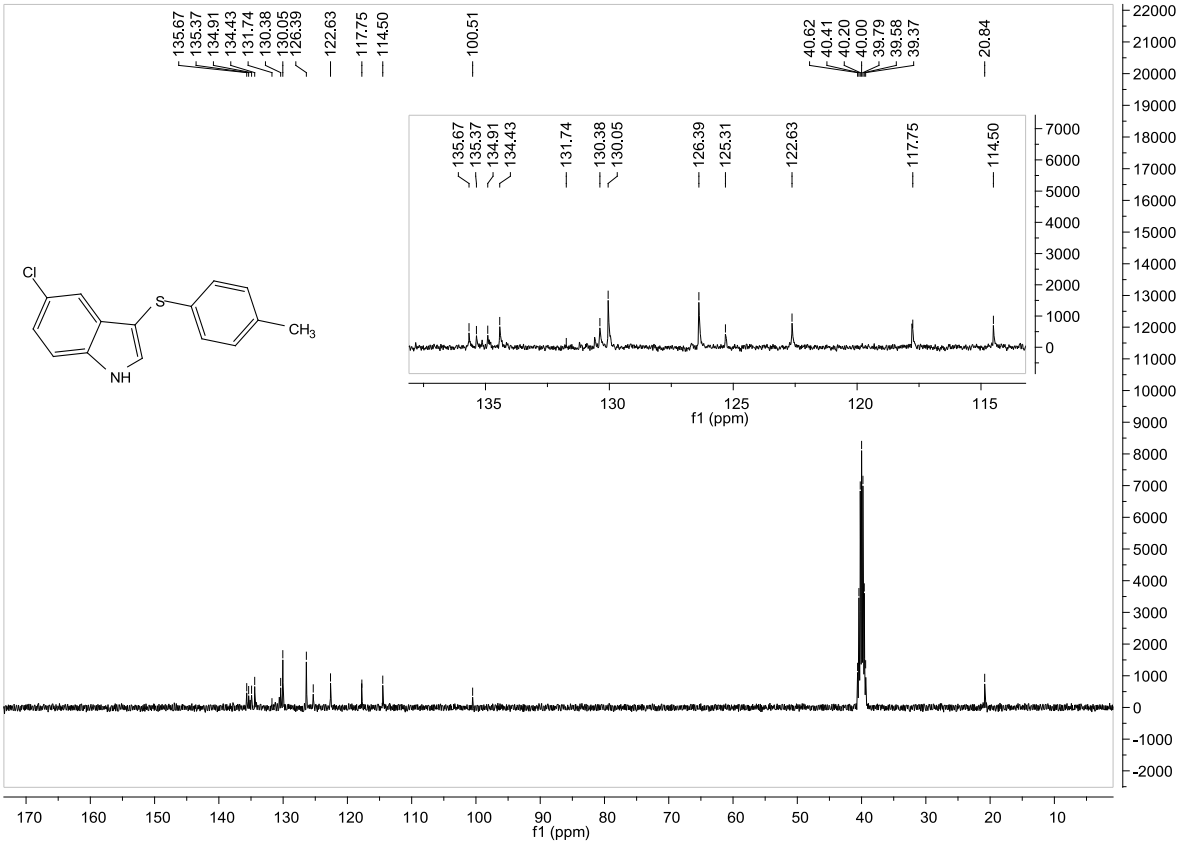
^{1}H NMR of **3ca**



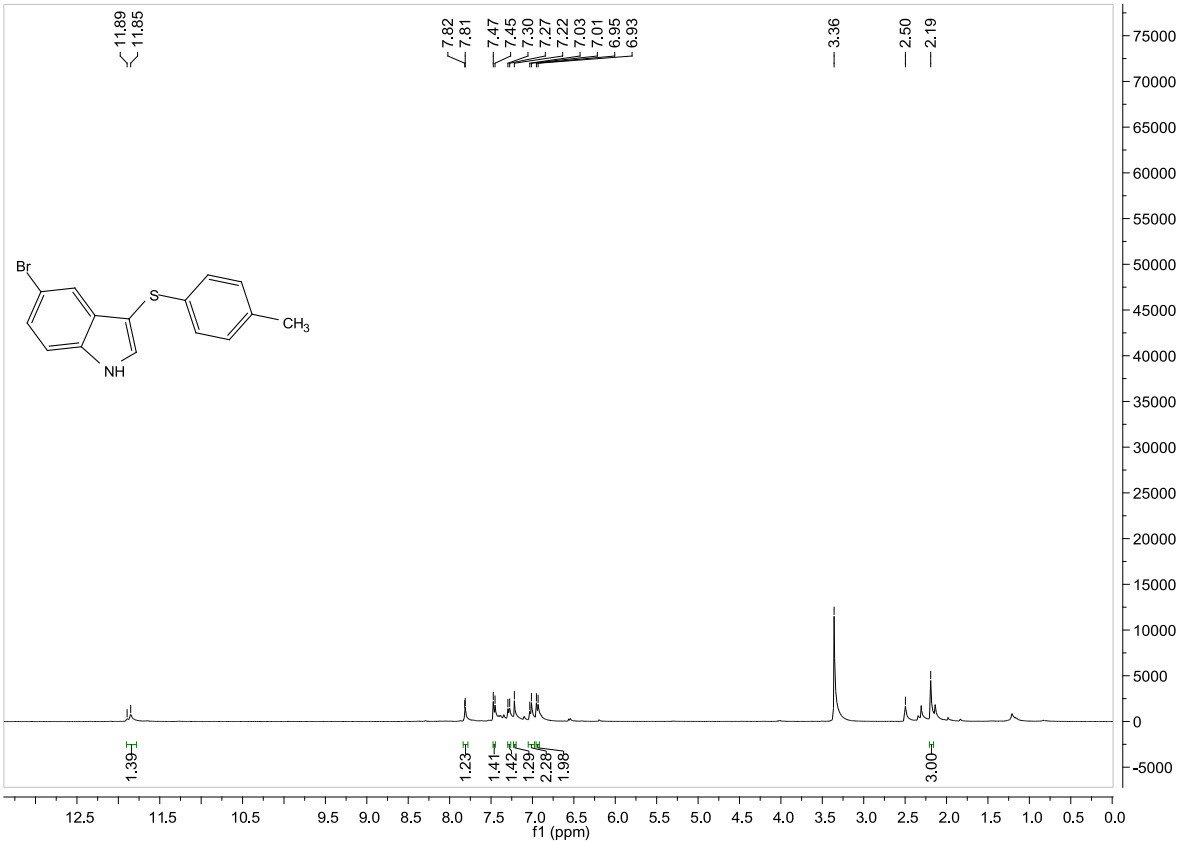
^{13}C NMR of **3ca**


11.89
11.84
7.84
7.83
7.52
7.50
7.33
7.19
7.19
7.17
7.04
7.02
6.96
6.94
3.35
2.50
2.20
Cl
S
CH3
NH
1.05
0.97
1.02
0.72
1.29
1.77
2.03
3.00
f1 (ppm)

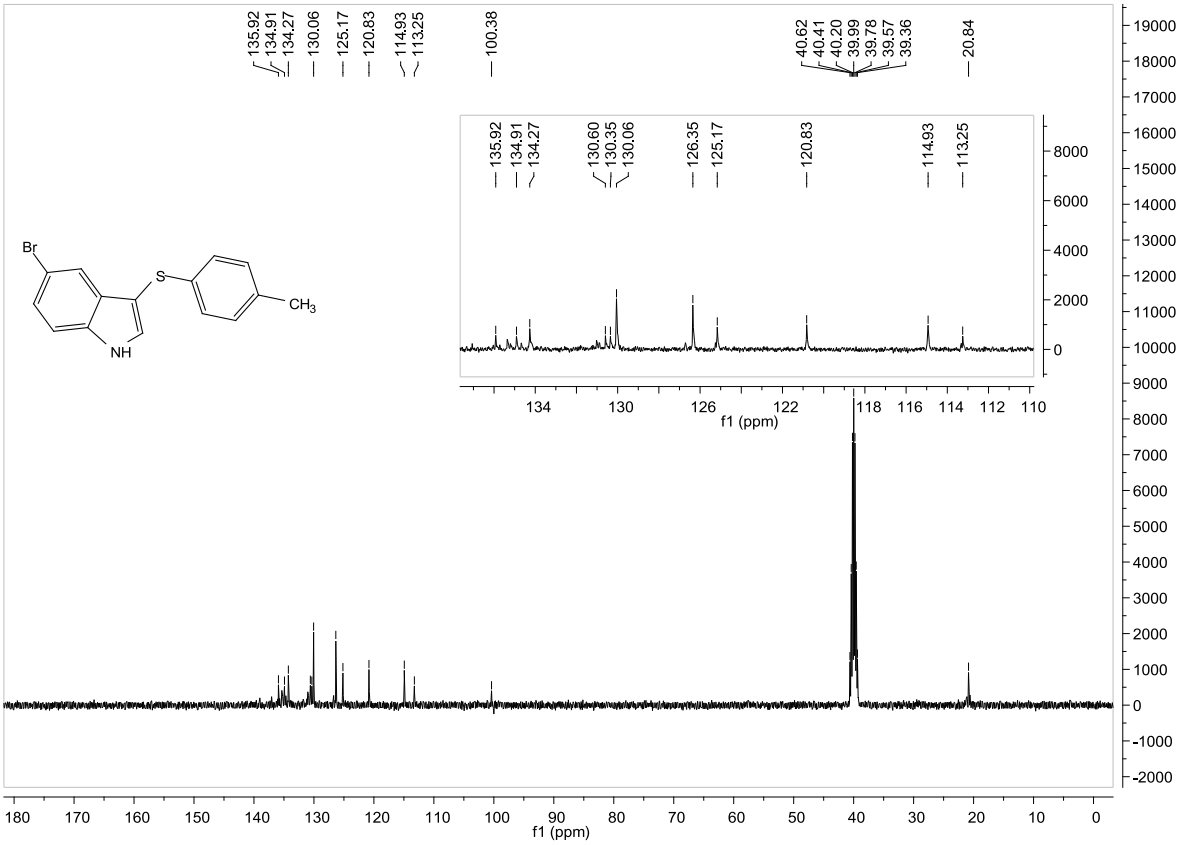
^{1}H NMR of **3da**



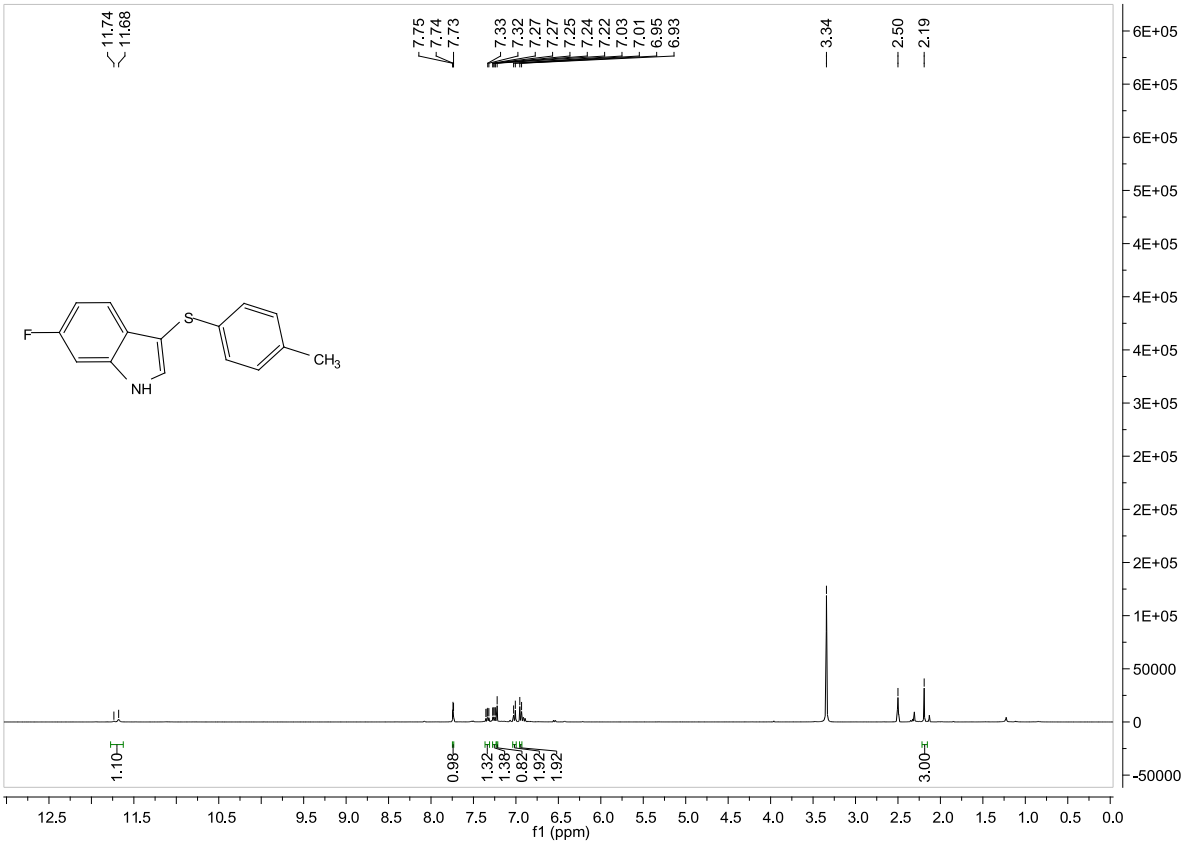
^{13}C NMR of **3da**


11.89
11.85
7.82
7.81
7.47
7.45
7.30
7.27
7.22
7.03
7.01
6.95
6.93
3.36
2.50
2.19
Br
S
CH3
NH
1.39
1.23
1.41
1.42
1.29
2.28
1.98
3.00
f1 (ppm)

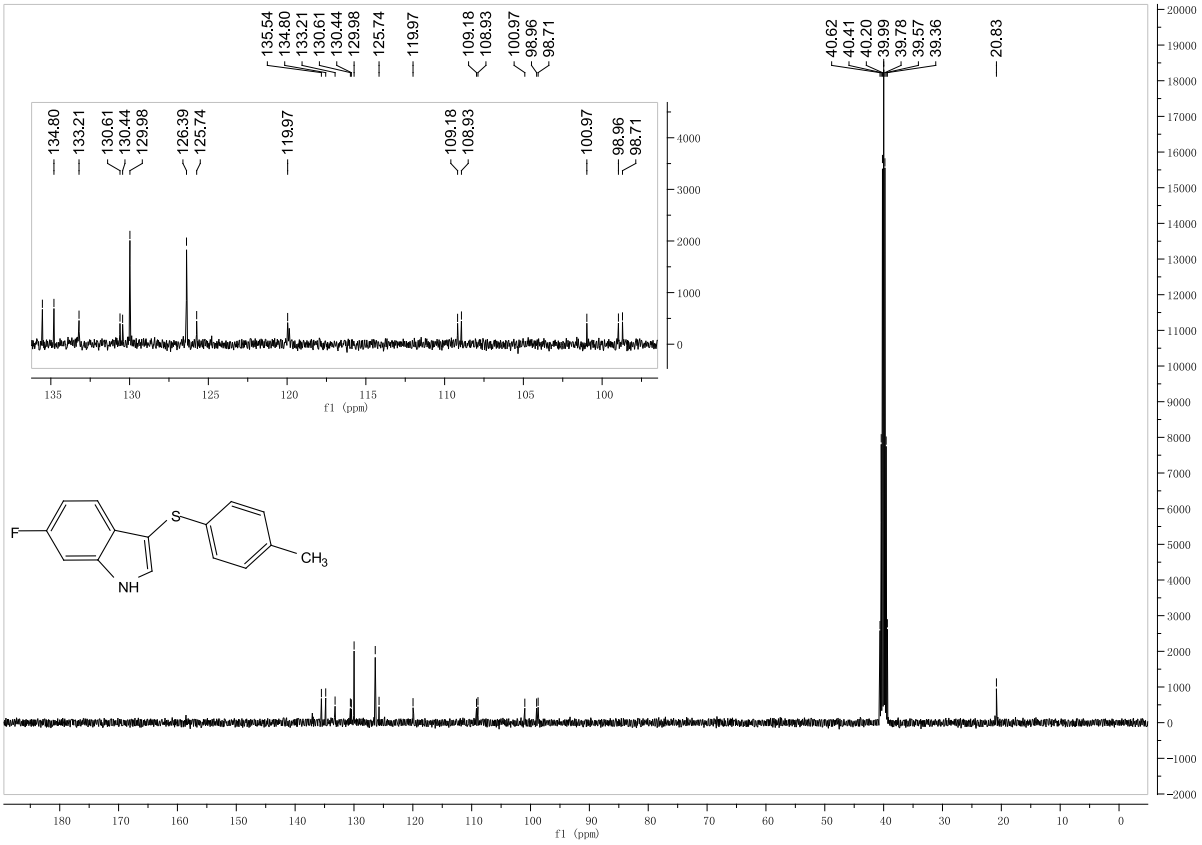
^{1}H NMR of **3ea**



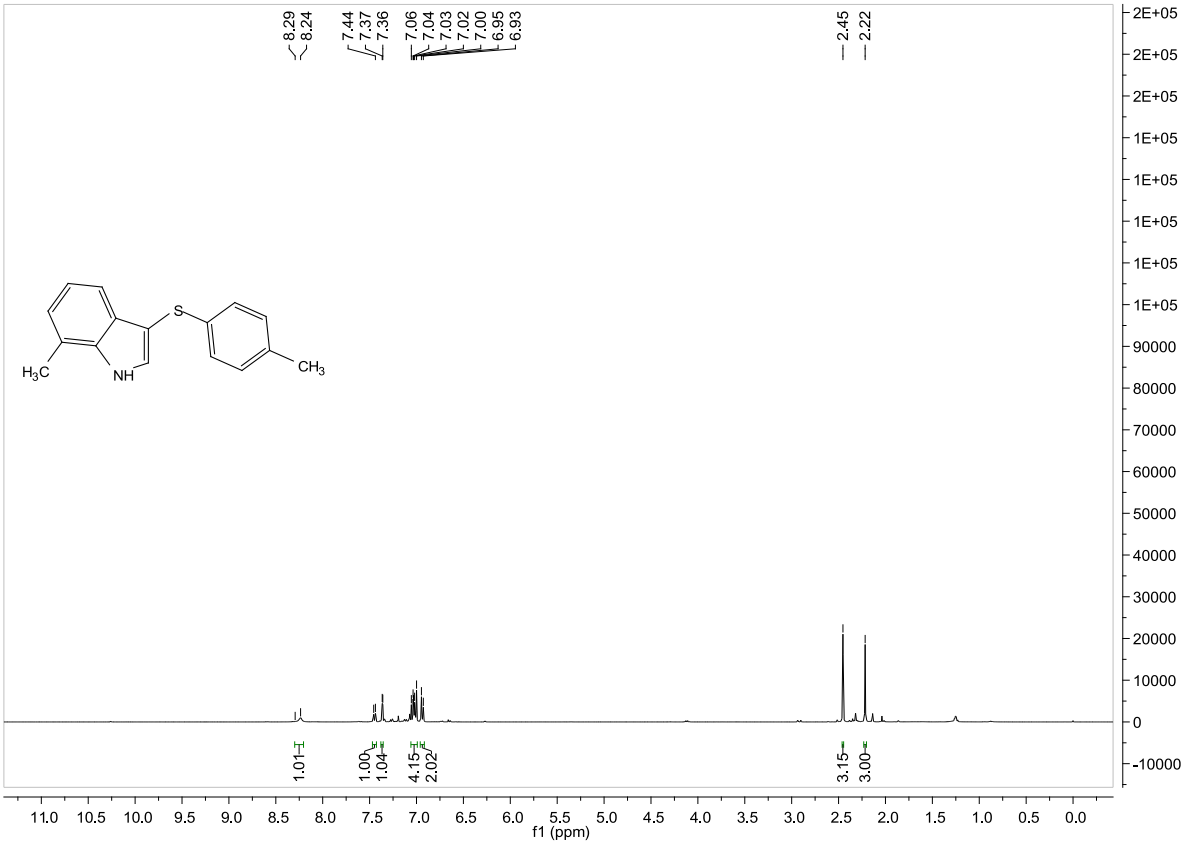
^{13}C NMR of **3ea**


11.74
11.68
7.75
7.74
7.73
7.33
7.32
7.27
7.27
7.25
7.24
7.22
7.03
7.01
6.95
6.93
3.34
2.50
2.19
F
S
CH3
NH
1.10
0.98
1.32
1.38
0.82
1.92
1.92
3.00
f1 (ppm)

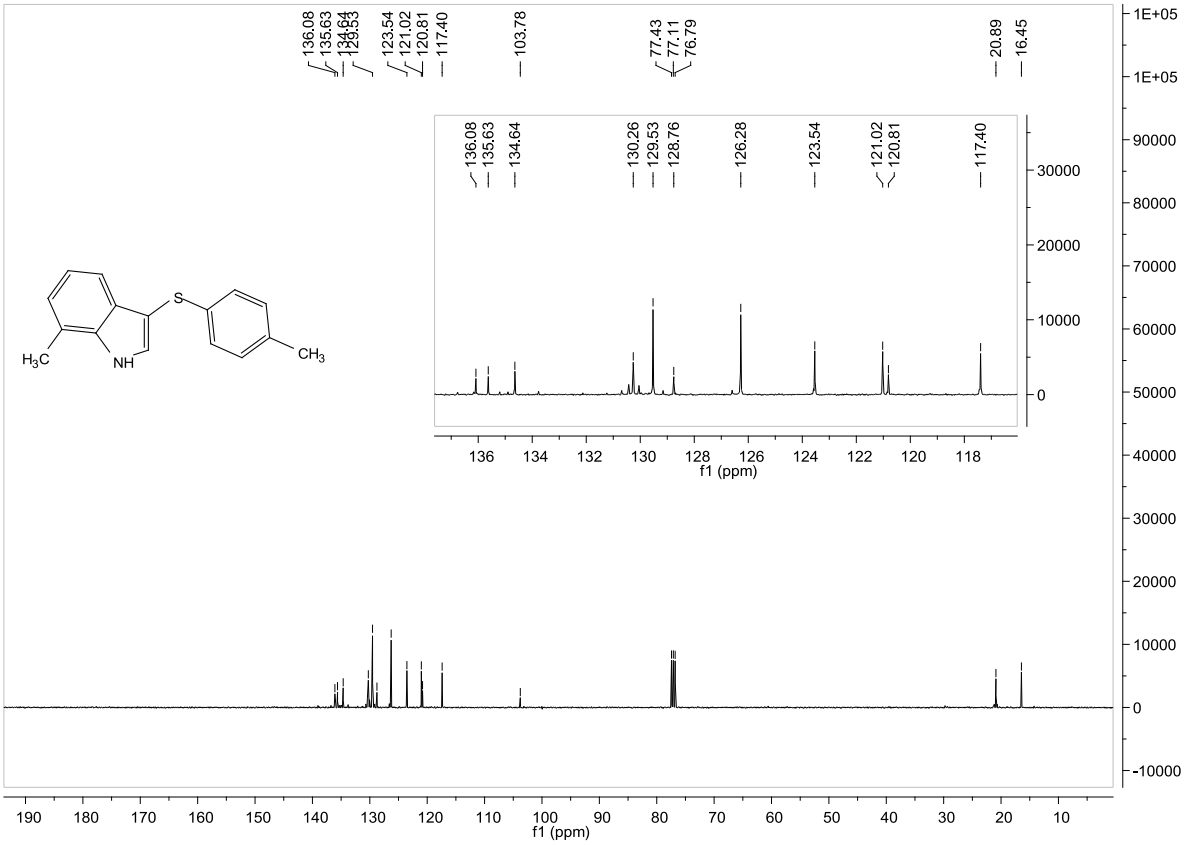
^{1}H NMR of **3fa**



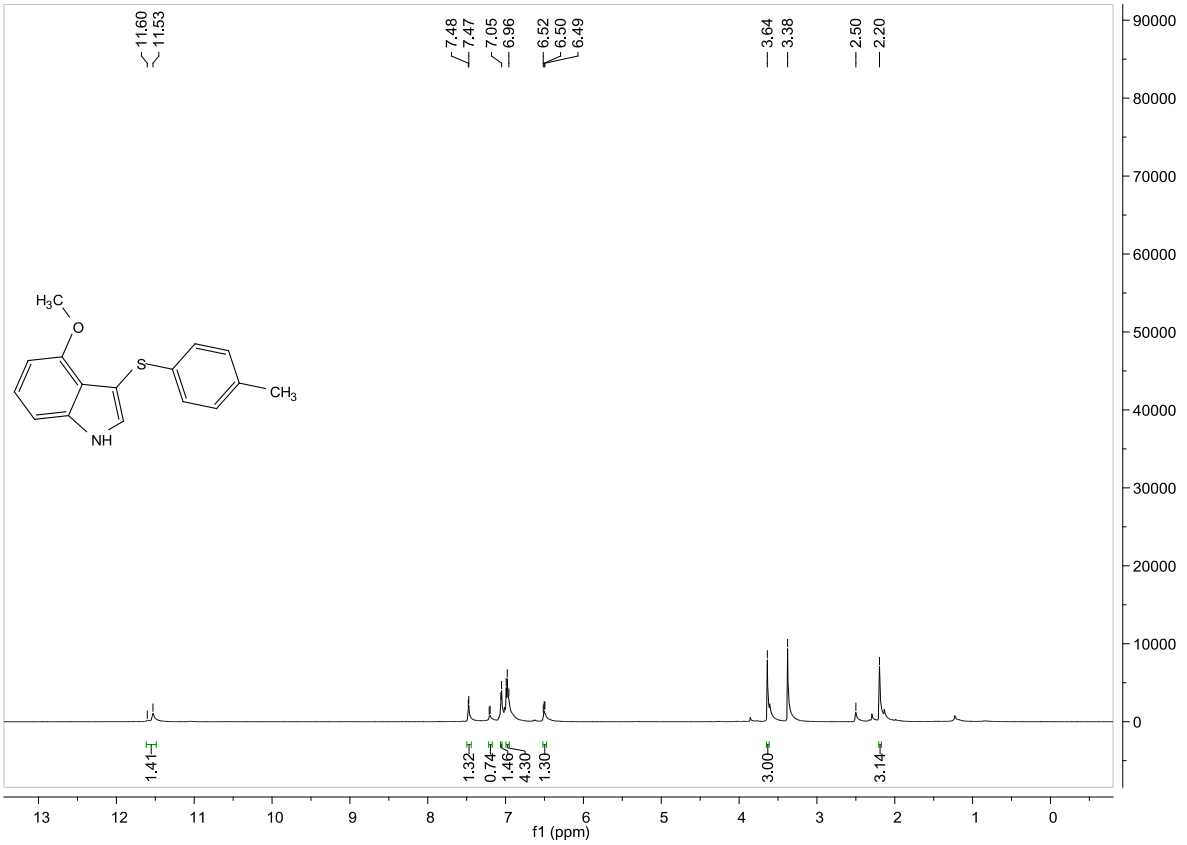
^{13}C NMR of **3fa**


8.29
8.24
7.44
7.37
7.36
7.06
7.04
7.03
7.02
7.00
6.95
6.93
2.45
2.22
S
NH
H3C
CH3
1.01
1.00
1.04
4.15
2.02
3.15
3.00
f1 (ppm)

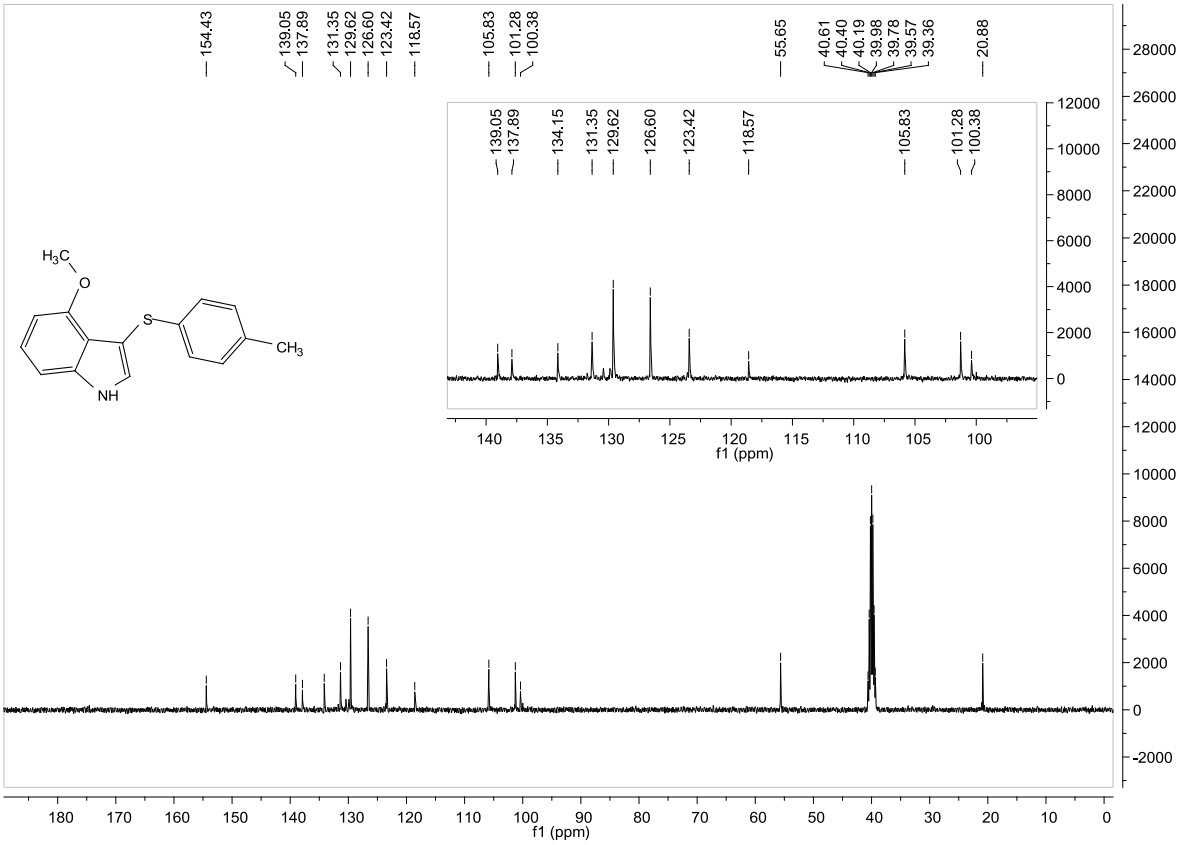
^{1}H NMR of **3ga**



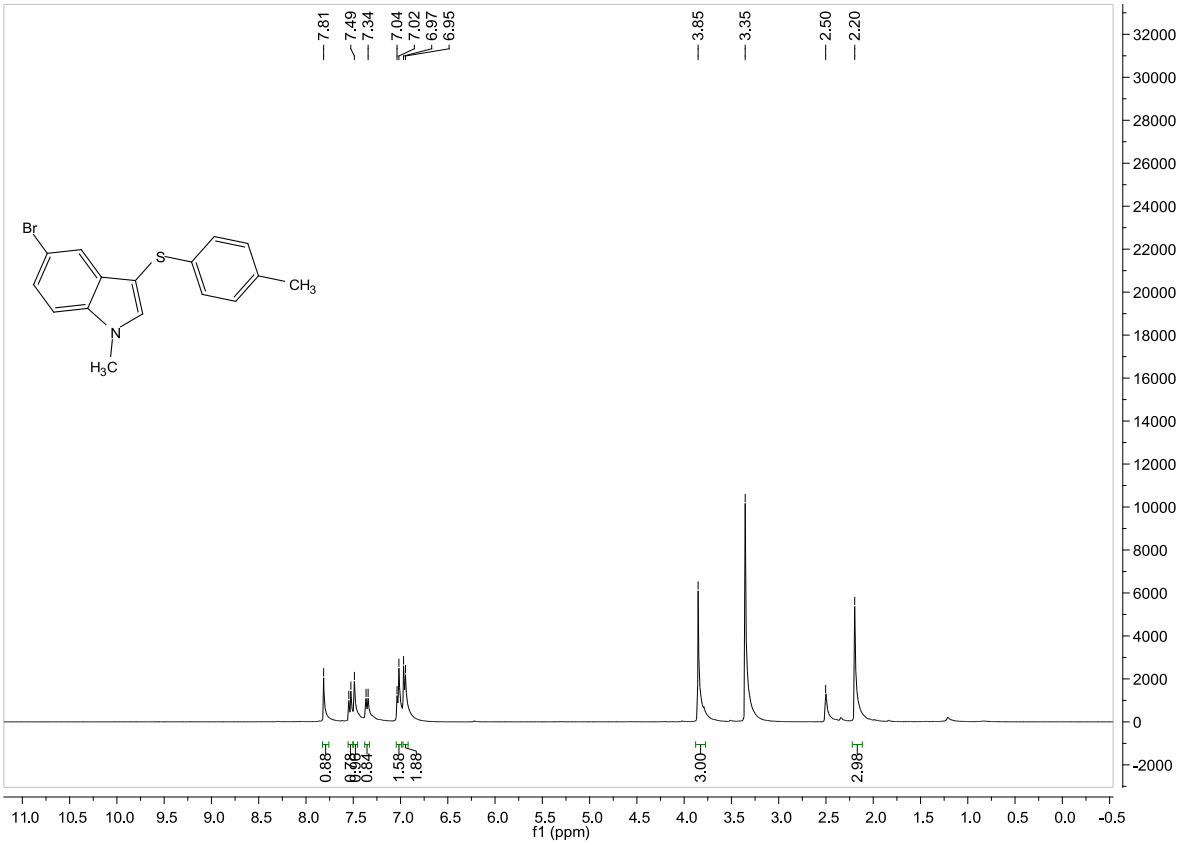
^{13}C NMR of **3ga**


11.60
11.53
7.48
7.47
7.05
6.96
6.52
6.50
6.49
3.64
3.38
2.50
2.20
H3C
O
S
CH3
NH
1.41
1.32
0.74
1.46
4.30
1.30
3.00
3.14
f1 (ppm)

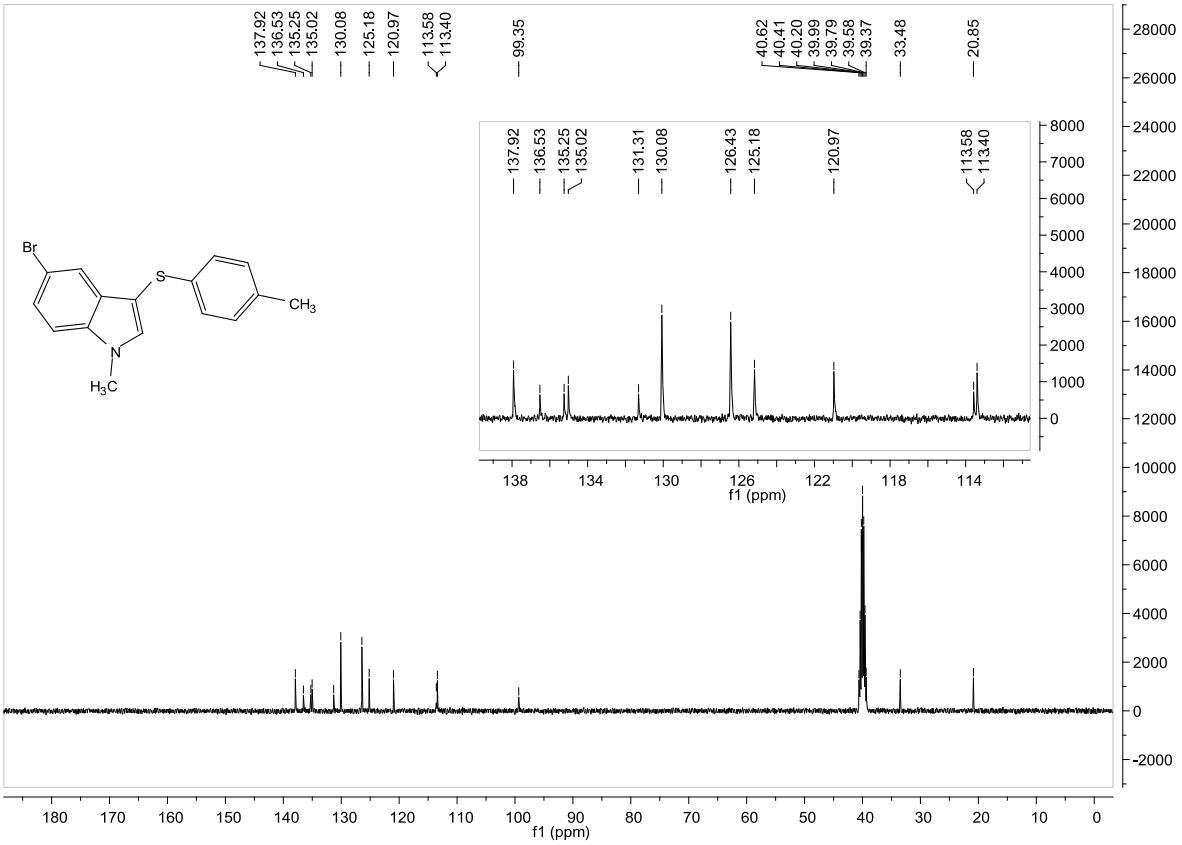
^{1}H NMR of **3ha**



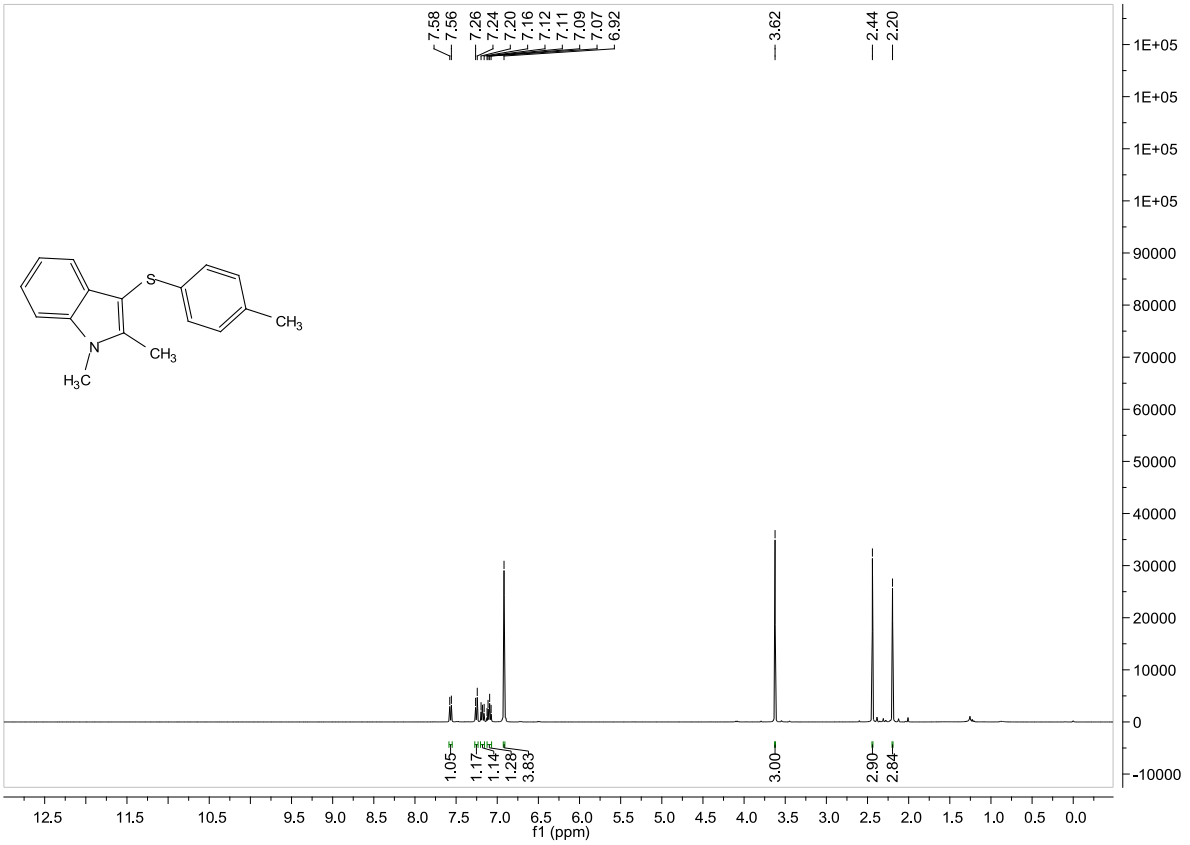
^{13}C NMR of **3ha**


7.81
7.49
7.34
7.04
7.02
6.97
6.95
3.85
3.35
2.50
2.20
Br
S
CH3
N
H3C
0.88
0.78
0.84
1.58
1.88
3.00
2.98
f1 (ppm)

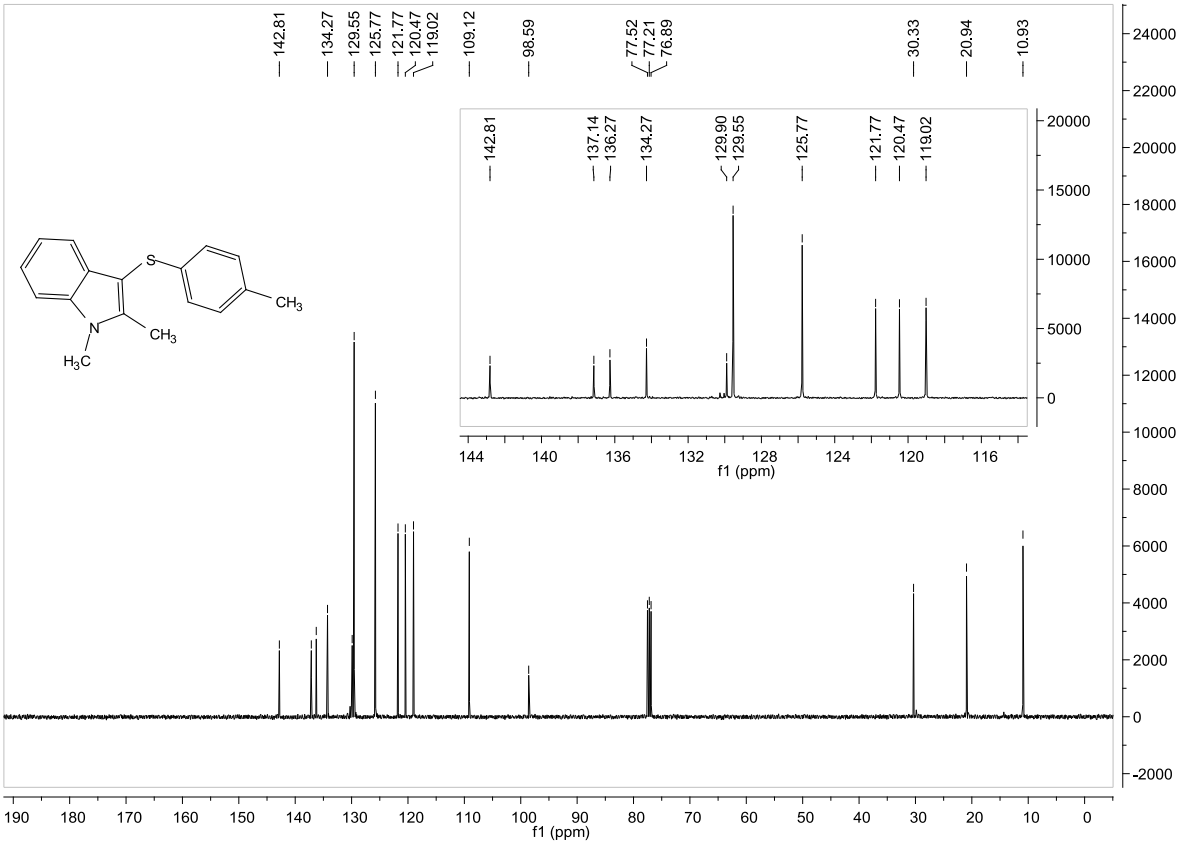
^{1}H NMR of **3ja**



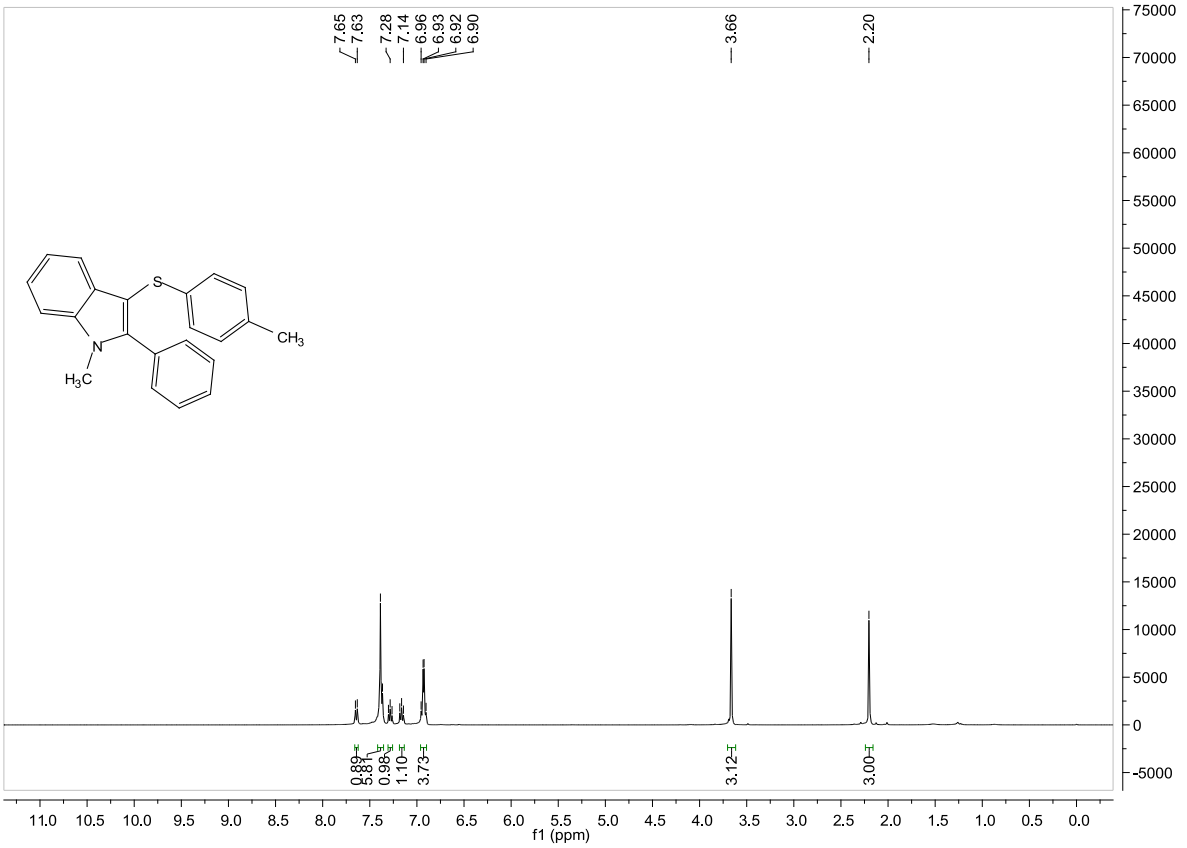
^{13}C NMR of **3ja**


7.58
7.56
7.26
7.24
7.20
7.16
7.12
7.11
7.09
7.07
6.92
3.62
2.44
2.20
S
CH3
N
CH3
H3C
1.05
1.17
1.14
1.28
3.83
3.00
2.90
2.84
f1 (ppm)

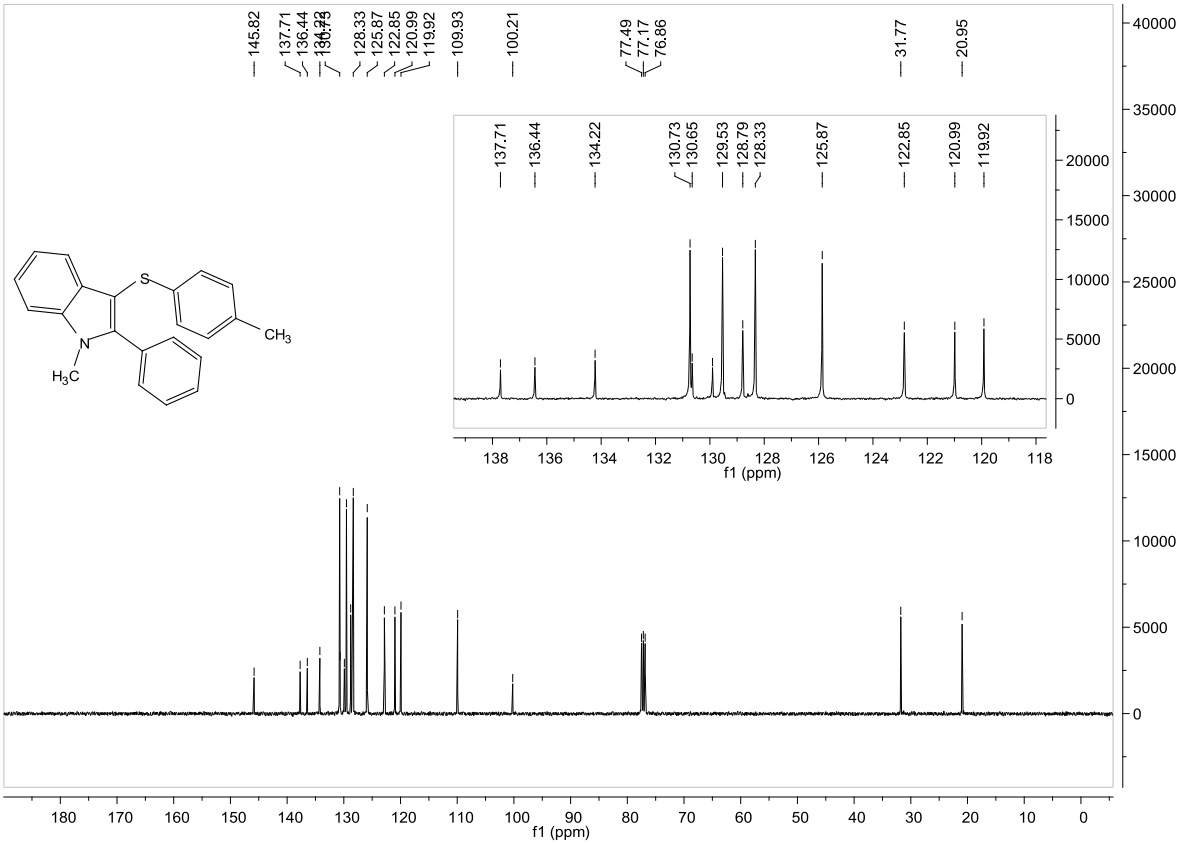
^{1}H NMR of **3ka**



^{13}C NMR of **3ka**


7.65
7.63
7.28
7.14
6.96
6.93
6.92
6.90
3.66
2.20
S
N
H3C
CH3
0.89
5.87
0.98
1.10
3.73
3.12
3.00
f1 (ppm)

^{1}H NMR of **3la**



^{13}C NMR of **3la**