

Supporting Information

**Metal- and base-free syntheses of aryl / alkylthioindoles by the iodine-induced reductive coupling of aryl / alkyl sulfonyl chlorides with indoles**

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## Experimental Section

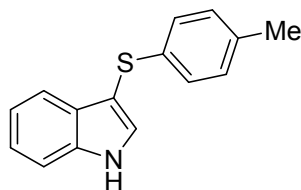
### General methods:

All reactions were conducted under open air atmosphere. Apparatus used for reactions are perfect oven dried. 1,4-Dioxane and other solvents were used as received. The  $^1\text{H}$  NMR spectra were recorded at 300 & 500 MHz, and  $^{13}\text{C}$  NMR 75 & 125 MHz in  $\text{CDCl}_3$ ,  $J$  values were recorded in hertz and abbreviations used were *s*-singlet, *d*-doublet, *t*-triplet, *m*-multiplet, br-broad, *dd*-doublet of doublet. Chemical shifts ( $\delta$ ) are reported relative to TMS ( $\delta = 0.0$ ) as an internal standard. IR (FT-IR) spectra were measured as KBr pellet or as film. Mass spectral data were compiled using MS (ESI), HRMS mass spectrometers. Column chromatography was carried out using Silica gel 100-200 mesh (commercial suppliers).

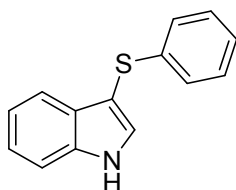
### The typical procedure for synthesis of 3-(*p*-Tolylthio)-1H-indole (**3a**):

To a stirred solution of indole **1a** (2 mmol) in 1,4-dioxane (3 mL) was added sulfonylchloride, **2a** (1.0 mmol) and CuI (10 mol%) successively. The resulting reaction mixture was heated at the 80 °C for 4h, in open air. Subsequently, the reaction mixture was allowed to reach ambient temperature, and the solvent was evaporated to result a residue which was purified by silica gel chromatography, eluting with hexane / ethyl acetate (10 : 0.5 to 10 : 1) furnished the thioindole, **3a** at an 86% yield.

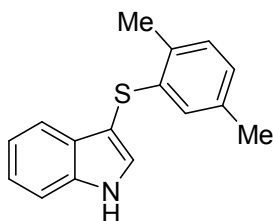
### Analytical Data of Indole Compounds:



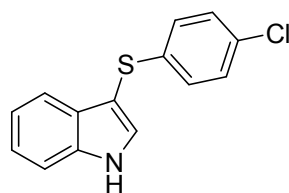
**3-(*p*-Tolylthio)-1H-indole (3a):** White solid, m.p. 124-126 °C; Yield - 206 mg (86%); **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>): δ 8.38 (s, br, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.27 – 7.24 (m, 1H), 7.17 – 7.14 (m, 1H), 7.04 – 6.96 (m, 4H), 2.25 (s, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ 136.4, 135.4, 134.6, 130.4, 129.4, 129.1, 126.2, 122.9, 120.8, 119.7, 111.5, 103.5, 20.8; **IR** (neat, cm<sup>-1</sup>): 3405, 2922, 2853, 1892, 1490, 1453, 1088, 772, 744; **HRMS** (m/z): Calculated for C<sub>15</sub> H<sub>13</sub> N S = 239.0768 found = 239.0775.



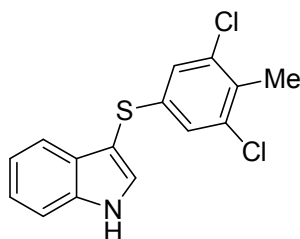
**3-(Phenylthio)-1H-indole (3b):** White solid, m.p. 150-152 °C; Yield - 191 mg (85%); **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>): δ 8.47 (s, br, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.28 – 7.25 (m, 1H), 7.18 – 7.03 (m, 6H); **<sup>13</sup>C-NMR** (125 MHz, CDCl<sub>3</sub>): δ 139.2, 136.5, 130.7, 129.1, 128.7, 125.8, 124.7, 123.0, 120.9, 119.7, 111.5, 102.8; **IR** (neat, cm<sup>-1</sup>): 3401, 3057, 2922, 2852, 1580, 1476, 1234, 1083, 770, 739; **HRMS** (m/z): Calculated for: C<sub>14</sub> H<sub>11</sub> N S (M+K) = 264.0249, found (M+K) = 264.0238.



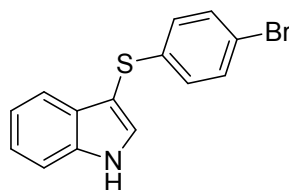
**3-((2,5-Dimethylphenyl)thio)-1H-indole (3c):** White solid, m.p. 125-127 °C; Yield - 215 mg (85%); **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>): δ 8.42 (s, br, 1H), 7.63 – 7.57 (m, 1H), 7.45 – 7.40 (m, 2H), 7.29 – 7.23 (m, 1H), 7.19 – 7.13 (m, 1H), 7.04 – 6.99 (m, 1H), 6.82 – 6.75 (m, 1H), 6.57 (s, 1H), 2.46 (s, 3H), 2.04 (s, 3H); **<sup>13</sup>C-NMR** (125 MHz, CDCl<sub>3</sub>): δ 137.7, 136.5, 135.8, 131.4, 130.7, 129.7, 129.2, 125.9, 125.4, 122.9, 120.7, 119.7, 111.5, 102.4, 21.0, 19.4; **IR** (neat, cm<sup>-1</sup>): 3412, 2926, 2857, 1896, 1520, 1456, 1075, 778, 734; **HRMS** (m/z): Calculated for C<sub>16</sub> H<sub>15</sub> N S (M-H) = 252.0842, found (M-H) = 252.0846.



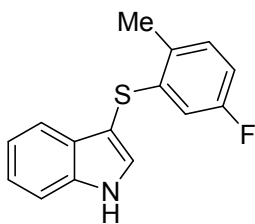
**3-(4-Chlorophenylthio)-1H-indole (3d):** White solid, m.p. 129-131 °C; Yield - 210 mg (81%); **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>): δ 8.42 (s, br, 1H), 7.56 (dd, *J* = 7.9 Hz, *J* = 0.8 Hz, 1H), 7.46 (d, *J* = 2.6 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.18 – 7.15 (m, 1H), 7.12 – 7.09 (m, 2H), 7.02 – 6.99 (m, 2H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ 137.8, 136.5, 130.7, 130.5, 128.7, 127.1, 123.2, 121.0, 119.5, 111.6, 102.4; **IR** (neat, cm<sup>-1</sup>): 3405, 2921, 2851, 1472, 1090, 1008, 812, 746; **HRMS** (m/z): Calculated for: C<sub>14</sub> H<sub>9</sub> N S Cl (M-H) = 258.0144, found (M-H) = 258.0150.



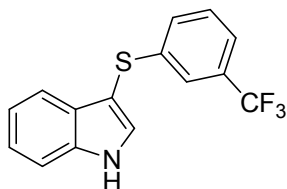
**3-((3,5-dichloro-4-methylphenyl)thio)-1H-indole (3e):** White solid, m.p. 142-145 °C; Yield - 239 mg (78%); **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>): δ 8.51 (s, br, 1H), 7.58 – 7.45 (m, 3H), 7.34 – 7.27 (m, 1H), 7.22 – 7.15 (m, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 6.41 (d, *J* = 8.7 Hz, 1H), 2.50 (s, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ 137.8, 136.6, 134.5, 131.3, 131.0, 130.7, 128.8, 127.3, 123.9, 123.3, 121.2, 119.5, 111.7, 101.3, 17.7; **IR** (neat, cm<sup>-1</sup>): 3405, 2923, 2863, 1894, 1488, 1463, 1091, 774; **HRMS** (m/z): Calculated for C<sub>15</sub> H<sub>10</sub> N Cl<sub>2</sub> S (M-H) = 305.9906, found (M-H) = 305.9921.



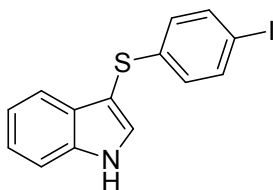
**3-(4-Bromophenylthio)-1H-indole (3f):** White solid, m.p. 141-143 °C; Yield - 242 mg (80%); **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>): δ 8.47 (s, br, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.30 – 7.15 (m, 4H), 6.97 – 6.93 (m, 2H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ 138.5, 136.5, 131.6, 130.7, 128.7, 127.3, 123.2, 121.0, 119.4, 118.2, 111.7, 102.1; **IR** (neat, cm<sup>-1</sup>): 3389, 3053, 2921, 2851, 1889, 1469, 1406, 1235, 1083, 1004, 808, 744; **HRMS** (m/z): Calculated for C<sub>14</sub> H<sub>9</sub> N S Br (M-H) = 301.9639, found (M-H) = 301.9645.



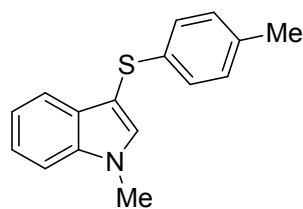
**3-((5-fluoro-2-methylphenyl)thio)-1H-indole (3g):** White solid, m.p. 136-138 °C; Yield - 198 mg (77%); **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>): δ 8.44 (s, br, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 2.6 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.30 – 7.24 (m, 2H), 7.20 – 7.16 (m, 1H), 6.85 – 6.79 (m, 1H), 6.64 – 6.59 (m, 1H), 2.06 (s, 3H); **<sup>13</sup>C-NMR** (125 MHz, CDCl<sub>3</sub>): δ 157.6 (d, *J*<sub>C-F</sub> = 241.6 Hz), 136.4, 133.8 (d, *J*<sub>C-F</sub> = 2.7 Hz), 131.0, 129.2, 128.5, 127.0 (d, *J*<sub>C-F</sub> = 7.3 Hz), 125.6 (d, *J*<sub>C-F</sub> = 16.4 Hz), 123.1, 120.9, 119.5, 114.8 (d, *J*<sub>C-F</sub> = 21.8 Hz), 111.6, 101.1, 20.7; **IR** (neat, cm<sup>-1</sup>): 3412, 2934, 2863, 1882, 1492, 1453, 1168, 764; **HRMS** (m/z): Calculated for C<sub>15</sub> H<sub>12</sub> F N S (M-H) = 256.0590, found (M-H) = 256.0592.



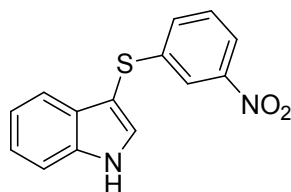
**3-((3-(trifluoromethyl)phenyl)thio)-1H-indole (3h):** White solid, m.p. 130-132 °C; Yield - 226 mg (77%); **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>): δ 8.47 (s, br, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.49 (d, *J* = 2.6 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.39 (s, 1H), 7.30 – 7.26 (m, 2H), 7.24 – 7.15 (m, 3H); **<sup>13</sup>C-NMR** (125 MHz, CDCl<sub>3</sub>): δ 140.9, 136.5, 131.0 (q, *J*<sub>C-F</sub> = 31.8 Hz), 130.9, 129.0, 128.7, 123.8 (q, *J*<sub>C-F</sub> = 272.5 Hz), 123.3, 122.3 (d, *J*<sub>C-F</sub> = 3.6 Hz), 121.4 (d, *J*<sub>C-F</sub> = 3.6 Hz), 121.1, 119.3, 111.7, 101.4; **IR** (neat, cm<sup>-1</sup>): 3445, 2932, 2865, 1922, 1495, 1454, 1378, 1088, 776, 754; **HRMS** (m/z): Calculated for C<sub>15</sub> H<sub>10</sub> F<sub>3</sub> N S (M-H) = 292.0402, found (M-H) = 292.0411.



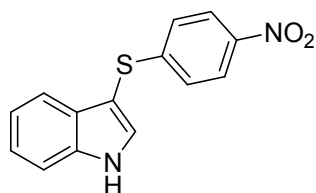
**3-((4-iodophenyl)thio)-1H-indole (3i):** White solid, m.p. 135-137 °C; Yield - 288 mg (82%); **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>): δ 8.44 (s, br, 1H), 7.58 – 7.54 (m, 1H), 7.48 – 7.41 (m, 4H), 7.30 – 7.25 (m, 1H), 7.20 – 7.14 (m, 1H), 6.84 – 6.80 (m, 2H); **<sup>13</sup>C-NMR** (125 MHz, CDCl<sub>3</sub>): δ 139.5, 137.5, 136.4, 130.7, 128.9, 127.6, 123.2, 121.0, 119.4, 111.6, 102.0, 88.9; **IR** (neat, cm<sup>-1</sup>): 3312, 2876, 2753, 1882, 1496, 1455, 1076, 994, 752; **HRMS** (m/z): Calculated for C<sub>14</sub> H<sub>10</sub> N I S (M-H) = 349.9495 found (M-H) = 349.9494.



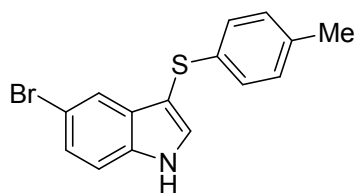
**1-Methyl-3-(p-tolylthio)-1H-indole (3j):** White solid, m.p. 86-88 °C; Yield - 190 mg (75%); **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.26 – 7.21 (m, 5H), 7.14 (d, *J* = 8.1 Hz, 2H), 2.42 (s, 3H), 2.38 (s, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ 144.5, 142.0, 140.4, 136.5, 130.2, 129.3, 127.6, 124.6, 29.7, 21.5; **IR** (neat, cm<sup>-1</sup>): 3412, 2946, 2845, 1894, 1490, 1463, 1088, 772; **HRMS** (m/z): Calculated for C<sub>11</sub> H<sub>18</sub> O<sub>3</sub> N S (M+H) = 253.0925, found (M+H) = 253.0931.



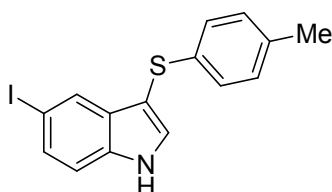
**3-((3-nitrophenyl)thio)-1H-indole (3k):** White solid, m.p. 135-137 °C; Yield - 205 mg (76%); **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>): δ 8.57 (s, br, 1H), 7.93 – 7.86 (m, 2H), 7.57 – 7.54 (m, 2H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.32 – 7.26 (m, 2H), 7.21 – 7.16 (m, 1H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ 136.4, 135.4, 134.6, 130.4, 129.4, 129.1, 126.2, 122.9, 120.8, 119.7, 111.5, 103.5, 20.8; **IR** (neat, cm<sup>-1</sup>): 3506, 2923, 2873, 1867, 1556, 1490, 1454, 1353, 1088, 782, 762; **HRMS** (m/z): Calculated for C<sub>14</sub> H<sub>9</sub> O<sub>2</sub> N<sub>2</sub> S (M-H) = 269.0379, found (M-H) = 269.0390.



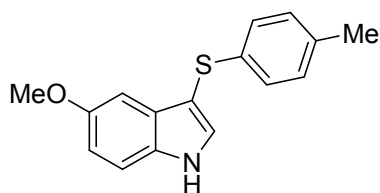
**3-((4-nitrophenyl)thio)-1H-indole (3l):** Yellow solid, m.p. 174-175 °C; Yield - 194 mg (72%); **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>): δ 8.92 (s, br, 1H), 7.95 (d, *J* = 9.0 Hz, 2H), 7.52 – 7.46 (m, 3H), 7.28 (t, *J* = 8.1 Hz, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 9.0 Hz, 2H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ 150.0, 144.6, 136.5, 131.3, 128.3, 124.9, 123.7, 123.3, 121.2, 118.9, 112.0, 99.6; **IR** (neat, cm<sup>-1</sup>): 3605, 3422, 2753, 1892, 1553, 1464, 1346, 1078, 784; **ESI-MS** (m/z): Calculated for C<sub>14</sub> H<sub>10</sub> O<sub>2</sub> N<sub>2</sub> S = 270, found (M-H) = 269.



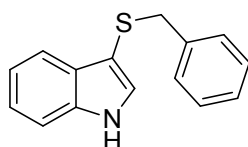
**5-bromo-3-(p-tolylthio)-1H-indole (3m):** White solid, m.p. 126-128 °C; Yield - 266 mg (84%); **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>+DMSO): δ 8.70 (s, br, 1H), 7.74 (d, *J* = 1.8 Hz, 1H), 7.42 (d, *J* = 2.6 Hz, 1H), 7.32 – 7.29 (m, 1H), 7.26 – 7.24 (m, 1H), 7.01 – 6.96 (m, 4H), 2.25 (s, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ 135.0, 134.8, 133.9, 132.1, 130.3, 128.8, 125.4, 124.4, 120.8, 113.1, 112.8, 100.5, 20.2; **IR** (neat, cm<sup>-1</sup>): 3744, 3611, 2922, 2852, 1696, 1509, 1454, 1219, 772, 657; **HRMS** (m/z): Calculated for C<sub>15</sub> H<sub>11</sub> N S Br (M-H) = 315.9795, found (M-H) = 315.9782.



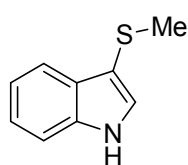
**5-iodo-3-(p-tolylthio)-1H-indole (3n):** White solid, m.p. 132-134 °C; Yield - 299 mg (82%); **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>): δ 8.46 (s, br, 1H), 7.97 – 7.95 (m, 1H), 7.51 (dd, *J* = 6.9 Hz, *J* = 1.7 Hz, 1H), 7.43 (d, *J* = 2.6 Hz, 1H), 7.20 (d, *J* = 8.5 Hz, 1H), 7.0 (s, 4H), 2.26 (s, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ 135.5, 134.9, 134.8, 131.6, 131.4, 131.2, 129.6, 128.4, 126.2, 113.5, 102.9, 84.7, 20.8; **IR** (neat, cm<sup>-1</sup>): 3645, 2924, 2853, 1692, 1512, 1453, 1098, 772, 646; **HRMS** (m/z): Calculated for C<sub>15</sub> H<sub>11</sub> N I S (M-H) = 363.9651, found (M-H) = 363.9665.



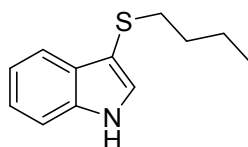
**5-methoxy-3-(p-tolylthio)-1H-indole (3o):** Brown oil; Yield - 234 mg (87%); **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>): δ 8.31 (s, br, 1H), 7.35 (d, *J* = 2.7 Hz, 1H), 7.24 (d, *J* = 8.9 Hz, 1H), 7.04 (d, *J* = 2.4 Hz, 1H), 7.03 – 6.99 (m, 2H), 6.98 – 6.95 (m, 2H), 3.76 (s, 3H), 2.23 (s, 3H); **<sup>13</sup>C-NMR** (125 MHz, CDCl<sub>3</sub>): δ 155.0, 135.6, 134.5, 131.3, 131.1, 129.9, 129.4, 125.9, 113.5, 112.3, 102.7, 100.8, 55.7, 20.8; **IR** (neat, cm<sup>-1</sup>): 3455, 2923, 2893, 1887, 1495, 1463, 1296, 1098, 772, 744; **HRMS** (m/z): Calculated for C<sub>15</sub> H<sub>13</sub> N S (M-H) = 253.0556, found (M-H) = 253.0561.



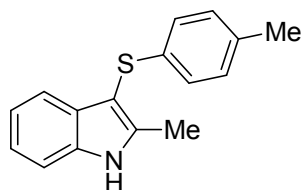
**3-(benzylthio)-1H-indole (3p):** Yellow solid, m.p. 81-82 °C; Yield - 182 mg (76%); **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>): δ 8.39 (s, br, 1H), 7.72-7.67 (m, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.14 (m, 5H), 7.10 – 7.04 (m, 2H), 6.95 (s, 1H), 3.85 (s, 2H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ 139.0, 136.2, 129.9, 129.2, 128.1, 126.7, 122.4, 120.3, 119.1, 111.5, 105.0, 40.9; **IR** (neat, cm<sup>-1</sup>): 3406, 2872, 1902, 1560, 1463, 1078, 736; **ESI-MS** (*m/z*): Calculated for C<sub>15</sub> H<sub>13</sub> N S = 239, found (*M-H*) = 238.



**3-(methylthio)-1H-indole (3q):** Colorless oil; Yield - 117 mg (72%); **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>): δ 8.21 (s, br, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.28 (d, *J* = 2.3 Hz, 1H), 7.26 – 7.18 (m, 2H), 2.37 (s, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ 134.2, 129.2, 127.8, 122.9, 121.0, 118.9, 110.7, 105.1, 19.0; **IR** (neat, cm<sup>-1</sup>): 3386, 2853, 1876, 1490, 1451, 1058, 776, 754; **ESI-MS** (*m/z*): Calculated for C<sub>9</sub> H<sub>9</sub> N S = 163, found (*M-H*) = 162.



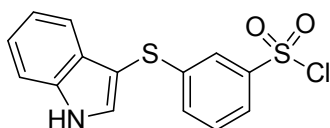
**3-(butylthio)-1H-indole (3r):** Yellow oil; Yield - 145 mg (71%); **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>): δ 8.26 (s, br, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.27 – 7.24 (m, 1H), 7.17 – 7.14 (m, 1H), 7.04 – 6.96 (m, 4H), 2.25 (s, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ **IR** (neat, cm<sup>-1</sup>): 3345, 2934, 2835, 1876, 1478, 1433, 1068, 762, 745; **HRMS** (*m/z*): Calculated for C<sub>12</sub> H<sub>15</sub> N S (*M-H*) = 204.0842, found (*M-H*) = 204.0844.



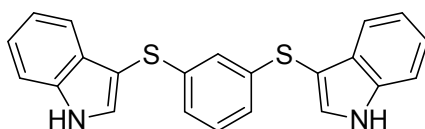
**2-methyl-3-(p-tolylthio)-1H-indole (5a):** White solid, m.p. 93-96 °C; Yield - 192 mg (76%); **<sup>1</sup>H-NMR** (500 MHz, CDCl<sub>3</sub>): δ 8.21 (s, br, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 7.9



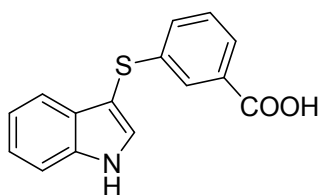
Hz, 1H), 7.19 – 7.15 (m, 1H), 7.13 – 7.09 (m, 1H), 6.95 (m, 4H), 2.49 (s, 3H), 2.23 (s, 3H);  $^{13}\text{C-NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  140.9, 135.6, 135.3, 134.2, 130.2, 129.4, 125.7, 122.0, 120.5, 118.9, 110.6, 99.6, 20.8, 12.0; **IR** (neat,  $\text{cm}^{-1}$ ): 3415, 2892, 2763, 1952, 1560, 1463, 1078, 784, 753; **HRMS** ( $m/z$ ): Calculated for  $\text{C}_{15}\text{H}_{13}\text{N}\text{S}$  = 239.0768 found = 239.0775.



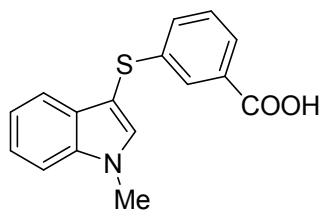
**3-((1H-indol-3-yl)thio)benzene-1-sulfonyl chloride (5b)**: White solid, m.p. 156-159 °C; Yield - 207 mg (64%);  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ +DMSO):  $\delta$  8.62 (s, br, 1H), 7.75 – 7.72 (m, 1H), 7.70 – 7.66 (m, 1H), 7.56 – 7.53 (m, 2H), 7.48 (d,  $J$  = 8.21 Hz, 1H), 7.36 – 7.28 (m, 3H), 7.21 – 7.17 (m, 1H);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  144.7, 143.3, 136.5, 131.7, 131.2, 129.7, 128.3, 123.5, 123.2, 122.7, 121.4, 119.1, 111.9, 100.3; **IR** (neat,  $\text{cm}^{-1}$ ): 3505, 3312, 2921, 2845, 1553, 1370, 1290, 1092, 776.



**1,3-bis((1H-indol-3-yl)thio)benzene (5c)**: White solid, m.p. 210-212 °C; Yield - 290 mg (78%);  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ +DMSO):  $\delta$  10.84 (s, br, 2H), 7.56 (s, 2H), 7.50 – 7.43 (m, 2H), 7.36 (d,  $J$  = 2.5 Hz, 2H), 7.24 – 7.16 (m, 2H), 7.11 – 7.03 (m, 2H), 6.89 (t,  $J$  = 7.7 Hz, 1H), 6.83 – 6.79 (m, 1H), 6.72 – 6.66 (m, 2H);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ +DMSO):  $\delta$  139.7, 136.1, 130.9, 128.2, 128.0, 121.7, 121.6, 121.3, 119.5, 118.2, 111.4, 99.5; **IR** (neat,  $\text{cm}^{-1}$ ): 3412, 2932, 2863, 1967, 1872, 1530, 1462, 1098, 792, 767; **HRMS** ( $m/z$ ): Calculated for  $\text{C}_{22}\text{H}_{16}\text{N}_2\text{S}_2$  ( $M+H$ ) = 373.0828, found ( $M+H$ ) = 373.0826.

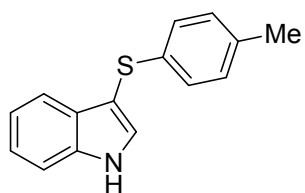


**3-((1H-indol-3-yl)thio)benzoic acid (5d)**: White solid, m.p. 183-186 °C; Yield - 218 mg (81%);  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$  + DMSO):  $\delta$  10.94 (s, br, 1H), 7.81 (s, 1H), 7.73 – 7.61 (m, 1H), 7.55 – 7.45 (m, 3H), 7.24 – 7.04 (m, 4H);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$  + DMSO):  $\delta$  167.3, 139.7, 136.3, 131.2, 130.8, 129.1, 128.2, 127.9, 126.2, 125.4, 121.7, 119.6, 118.2, 111.6, 99.4; **IR** (neat,  $\text{cm}^{-1}$ ): 3402, 2978, 2876, 1887, 1753, 1492, 1443, 1068, 768, 744; **HRMS** ( $m/z$ ): Calculated for  $\text{C}_{15}\text{H}_{11}\text{O}_2\text{N}\text{S}$  ( $M-H$ ) = 268.0426, found ( $M-H$ ) = 268.0427.

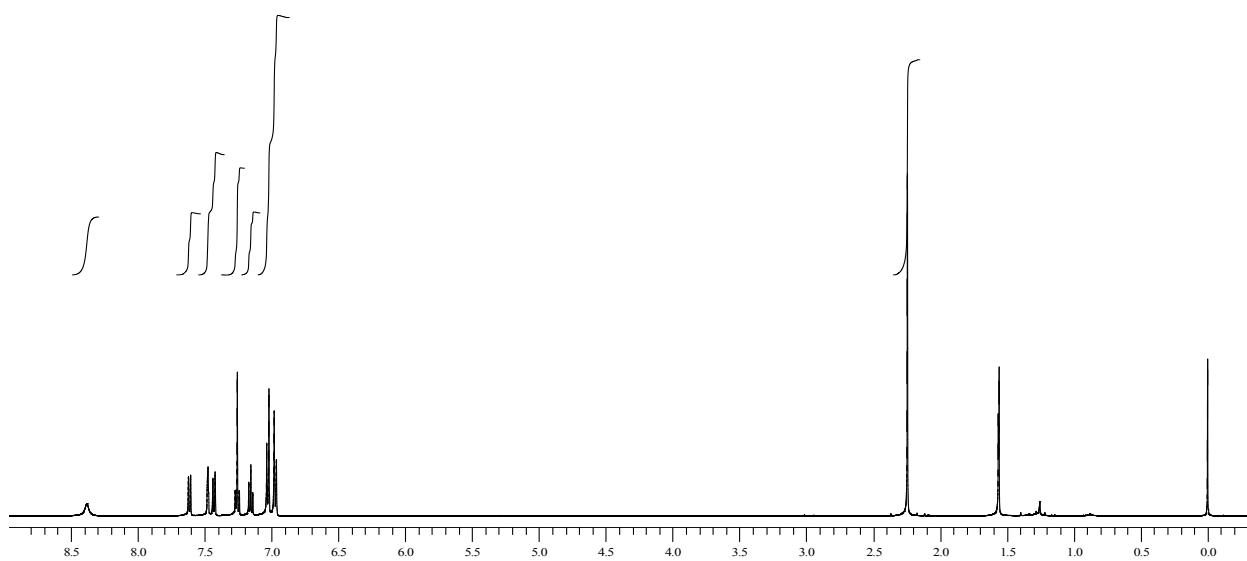


**3-((1-methyl-1H-indol-3-yl)thio)benzoic acid (5e):** White solid, m.p. 142-146 °C; Yield - 238 mg (84%); **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub> + DMSO): δ 7.84 – 7.59 (m, 2H), 7.56 – 7.38 (m, 3H), 7.33 – 7.08 (m, 4H), 3.88 (s, 3H); **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub> + DMSO): δ 167.2, 139.5, 136.9, 134.7, 130.8, 129.1, 128.8, 127.9, 126.2, 125.4, 121.9, 119.8, 118.5, 109.3, 98.8, 32.5; **IR** (neat, cm<sup>-1</sup>): 3305, 2972, 2845, 1892, 1745, 1490, 1453, 1413, 1294, 1076, 773; **ESI-MS** (m/z): Calculated for C<sub>16</sub> H<sub>13</sub> O<sub>2</sub> N S = 283, found (M-H) = 282.

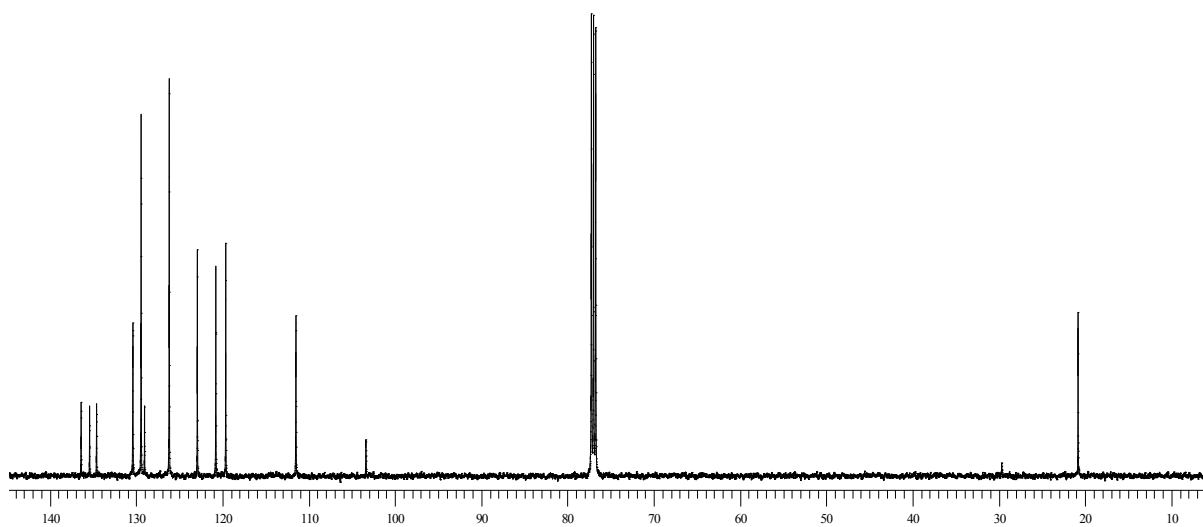
### Spectral data of Indole compounds:

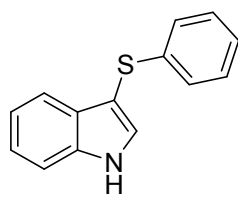


### <sup>1</sup>H-NMR:

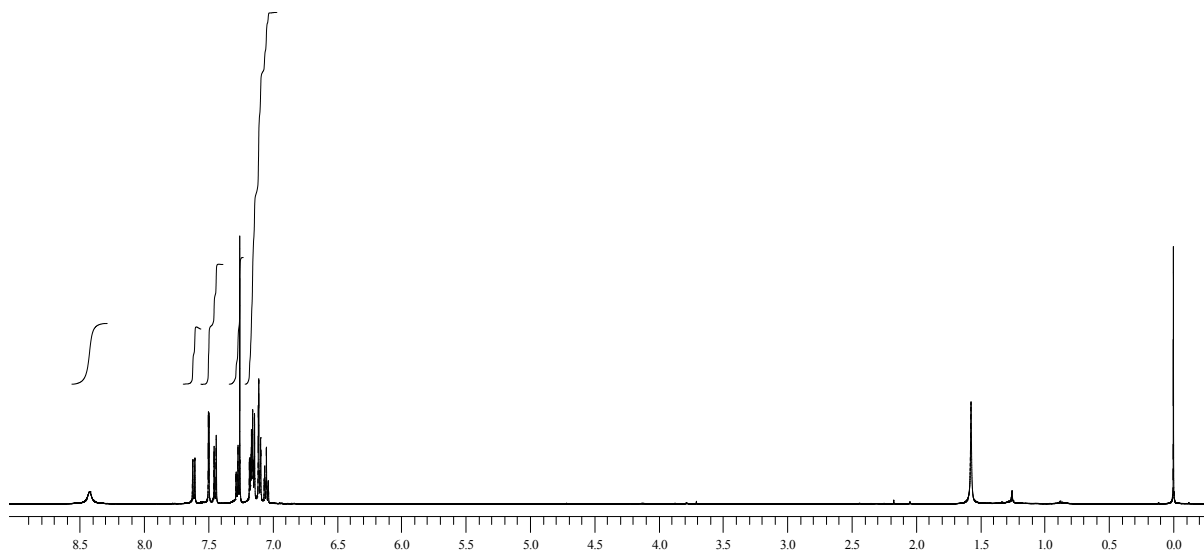


### <sup>13</sup>C-NMR:

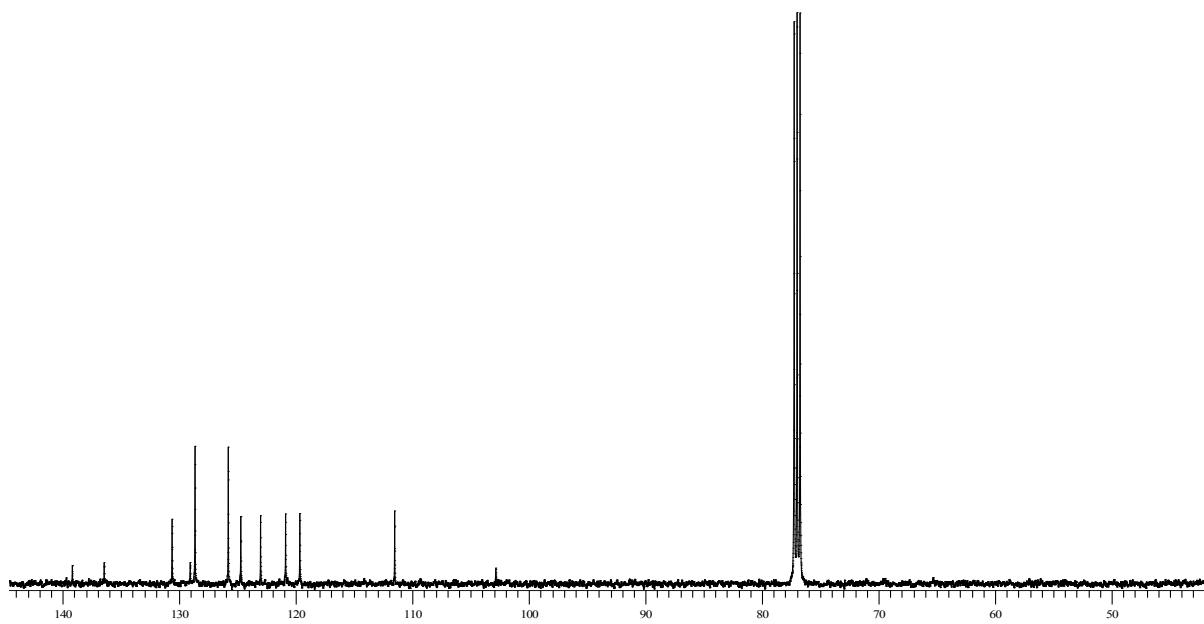


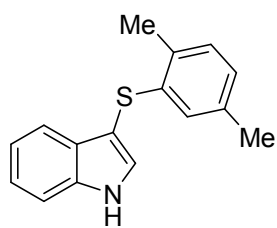


**<sup>1</sup>H-NMR:**

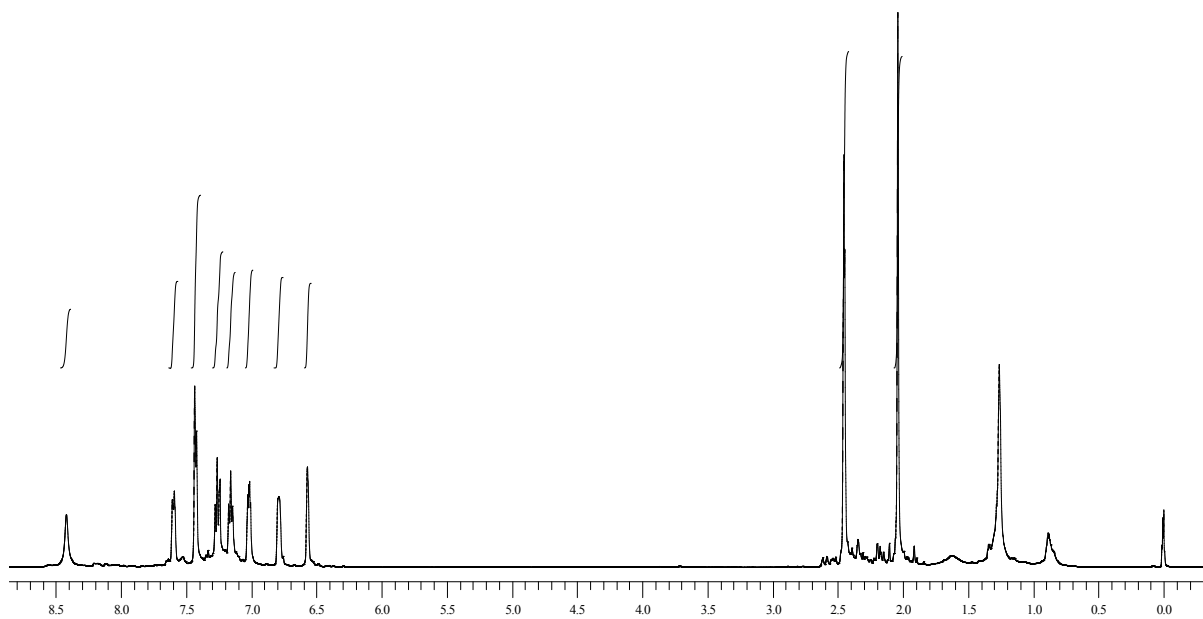


**<sup>13</sup>C-NMR:**

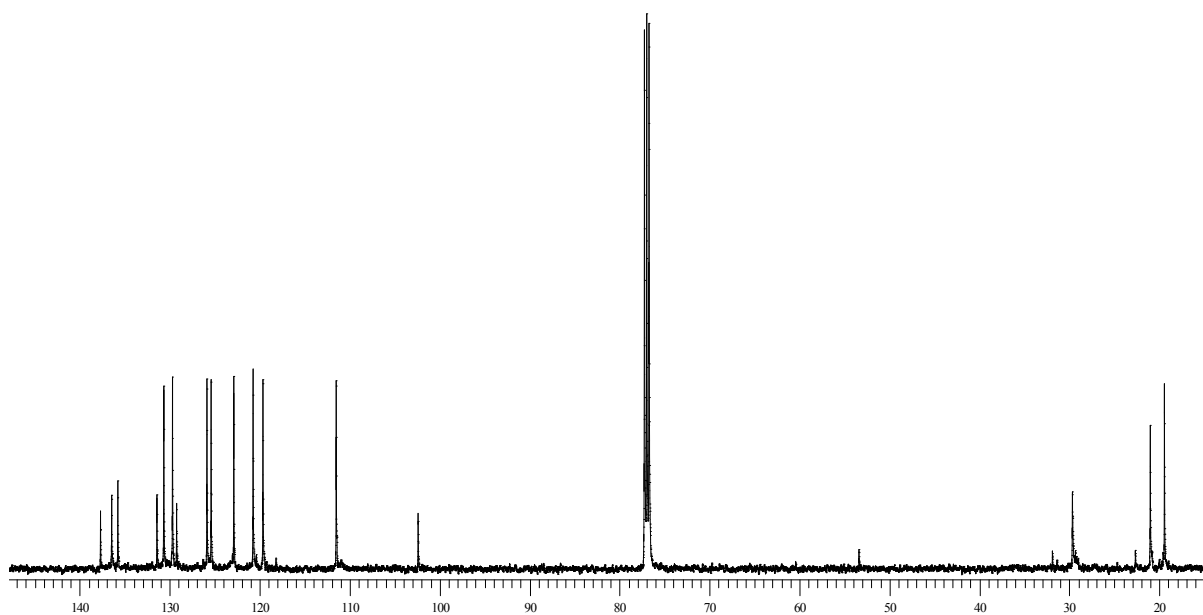


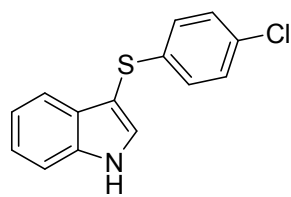


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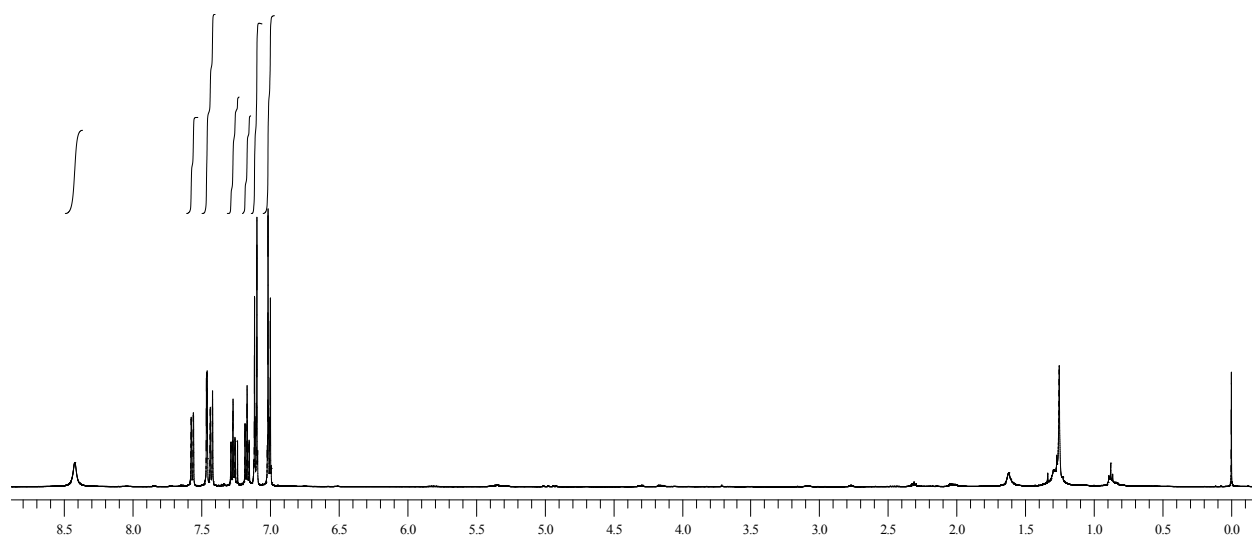


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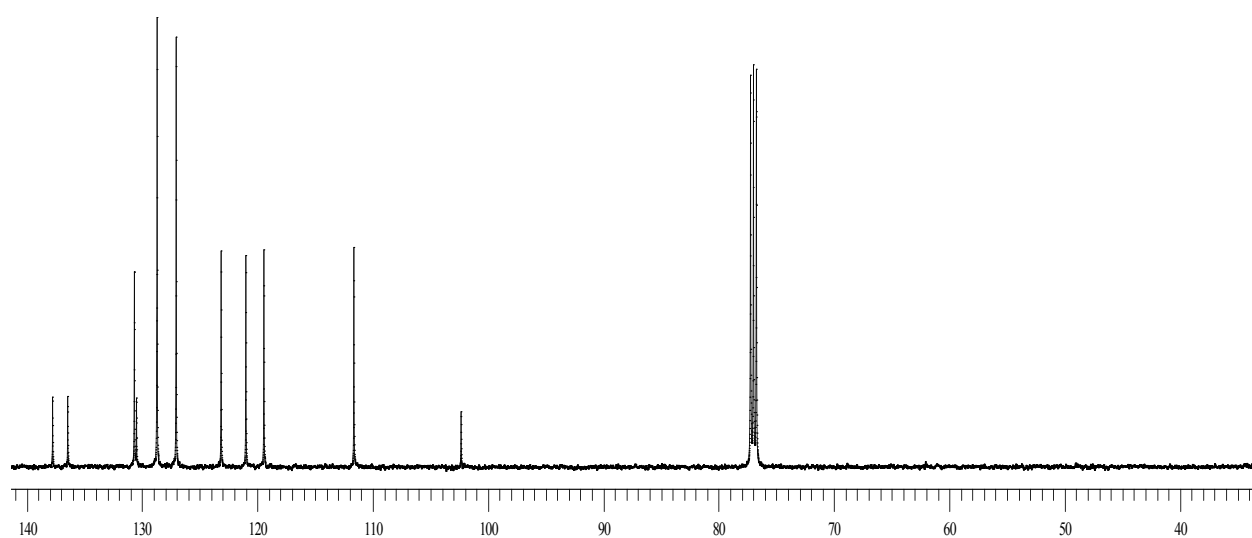


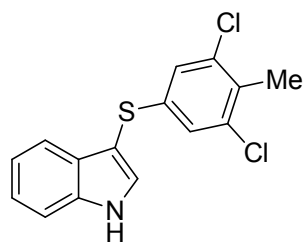


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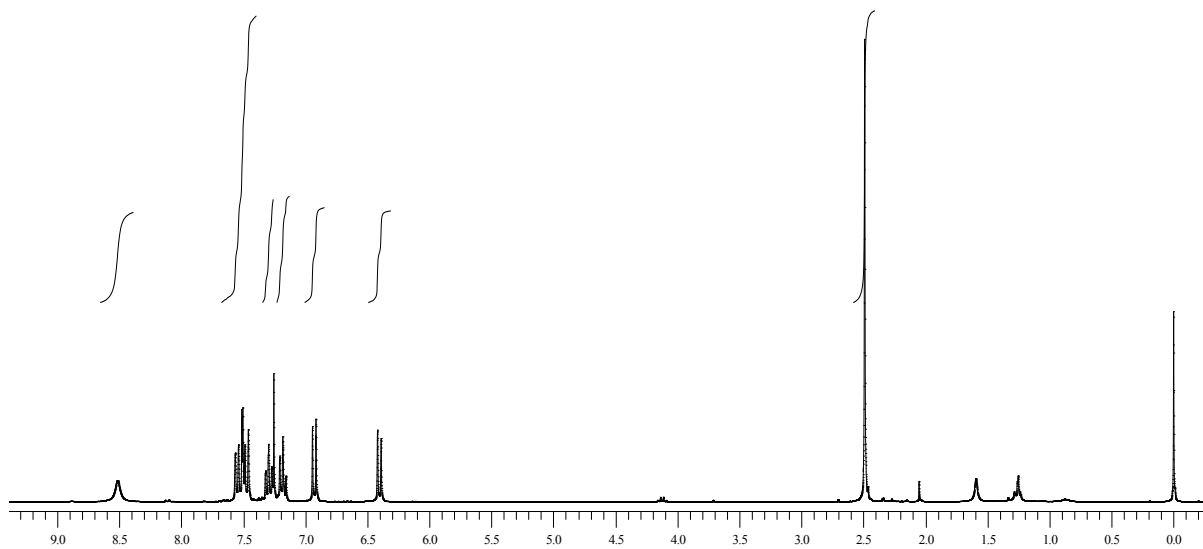


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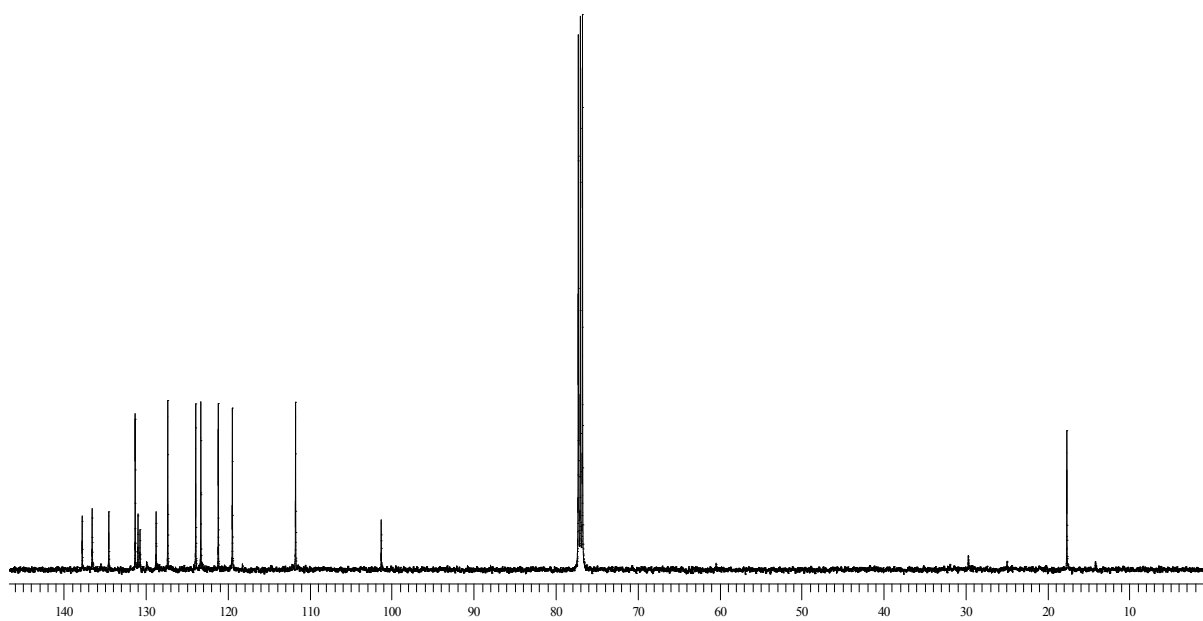


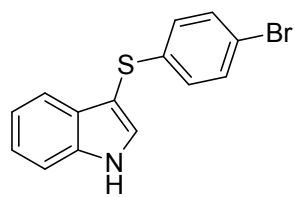


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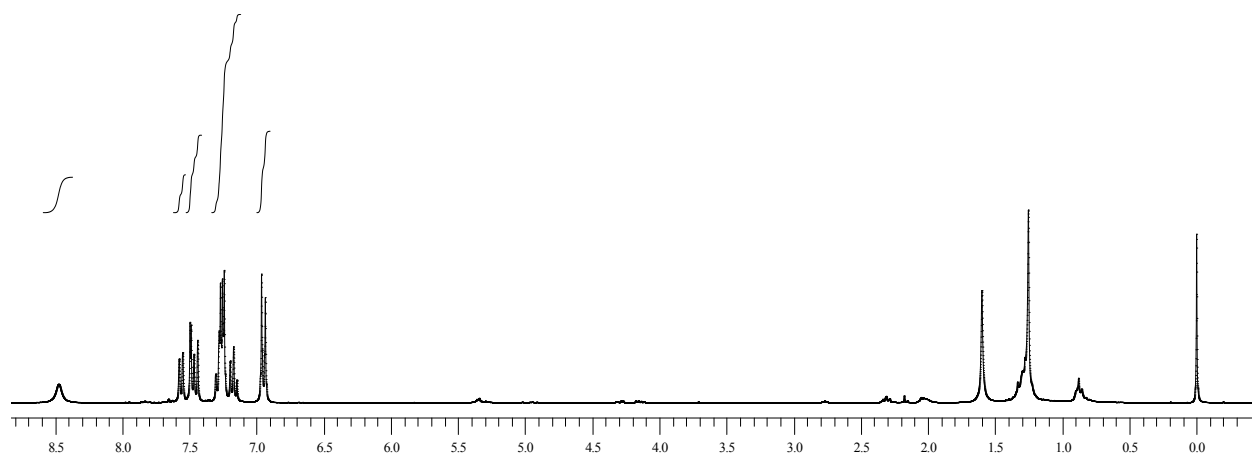


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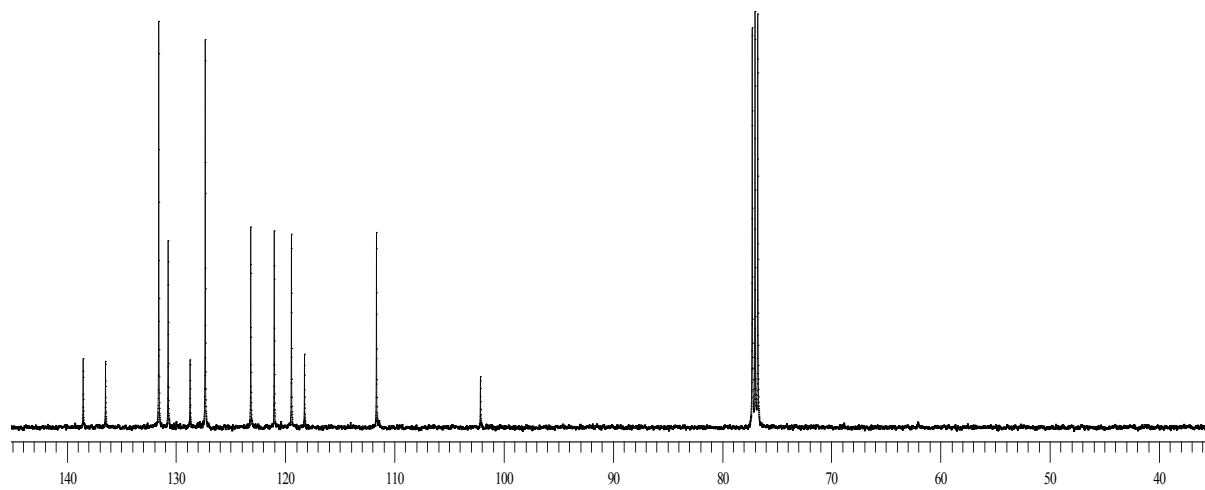




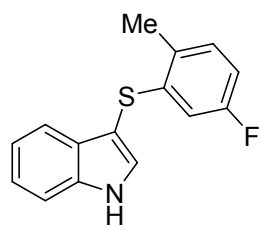
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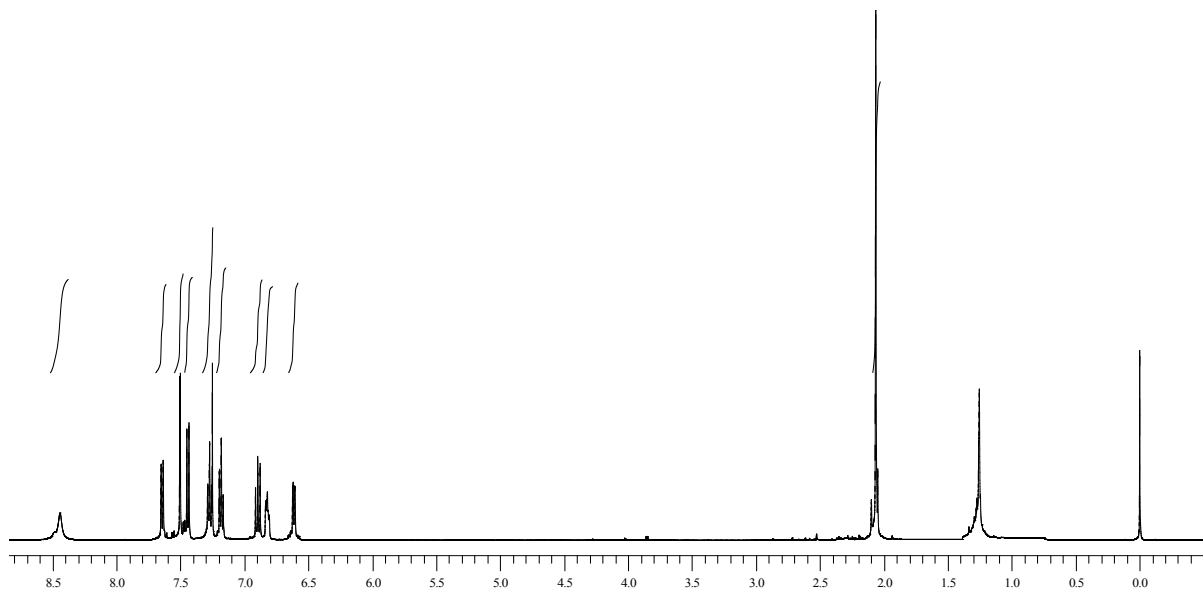
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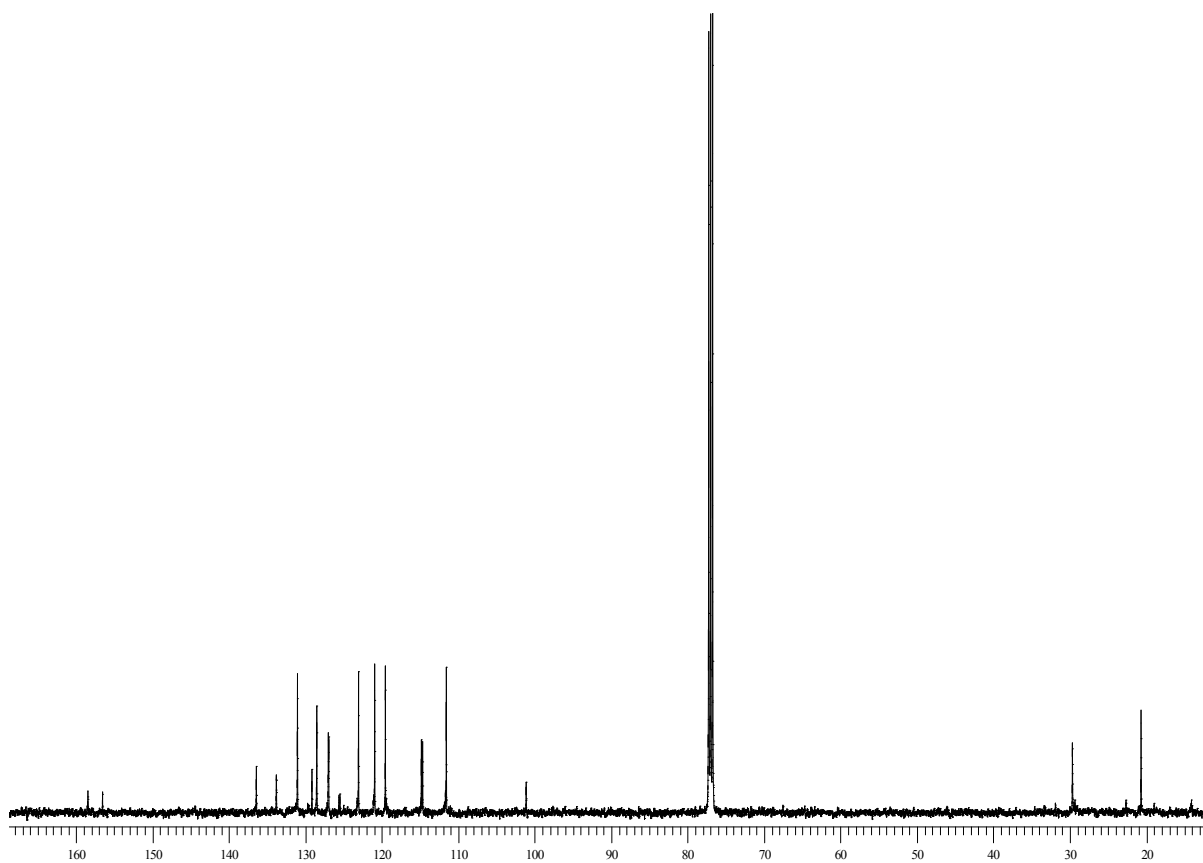


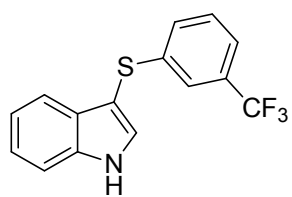


**<sup>1</sup>H-NMR:**

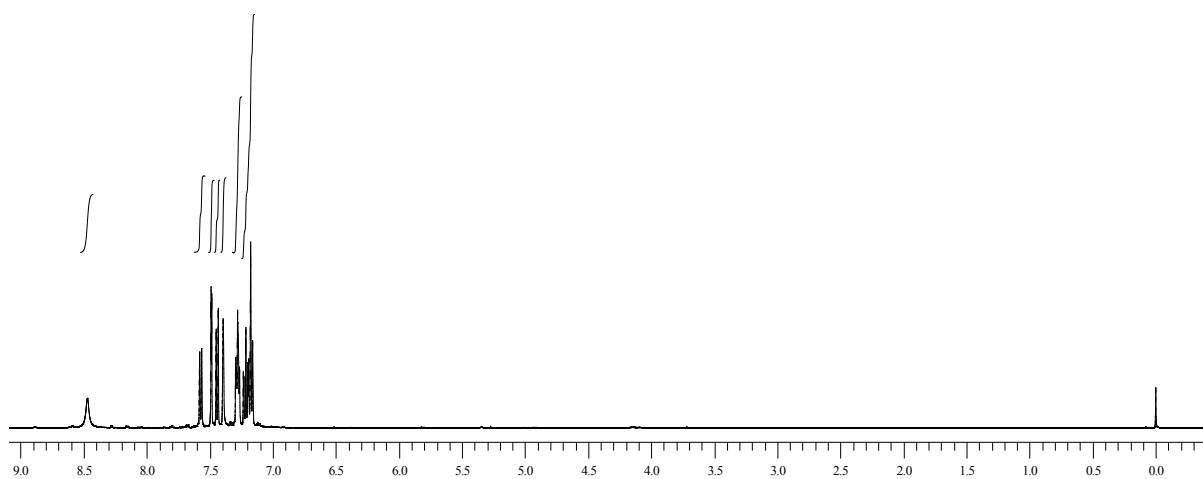


**<sup>13</sup>C-NMR:**

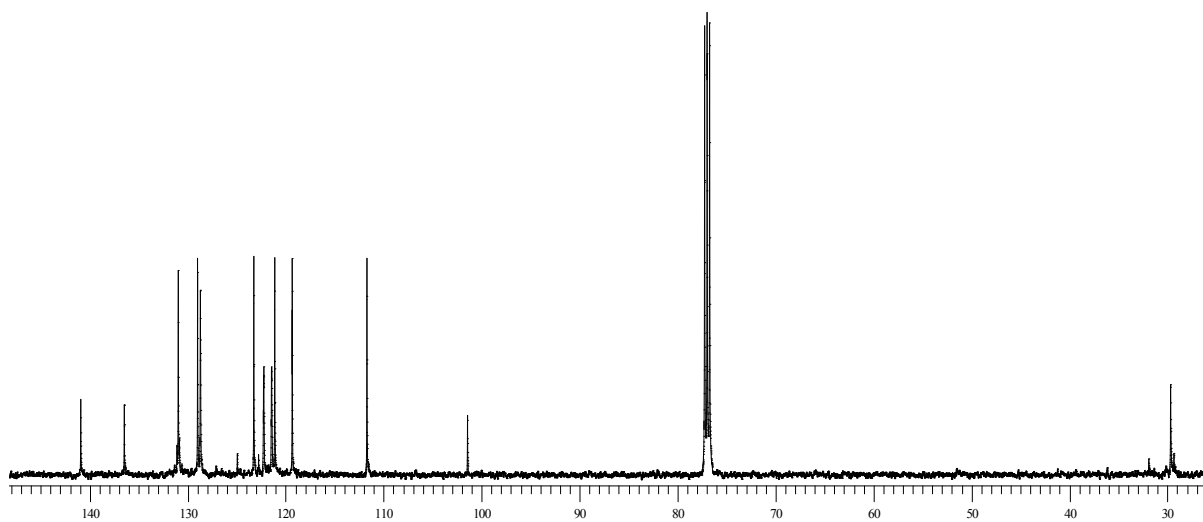




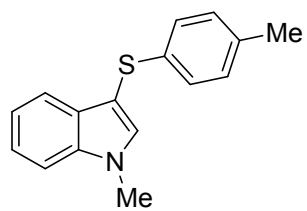
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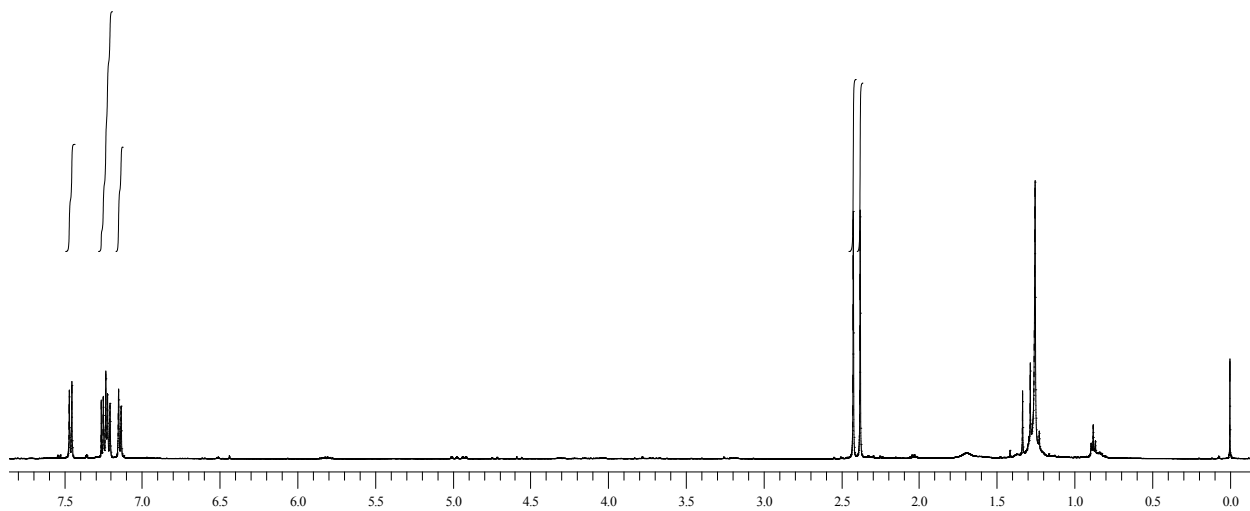
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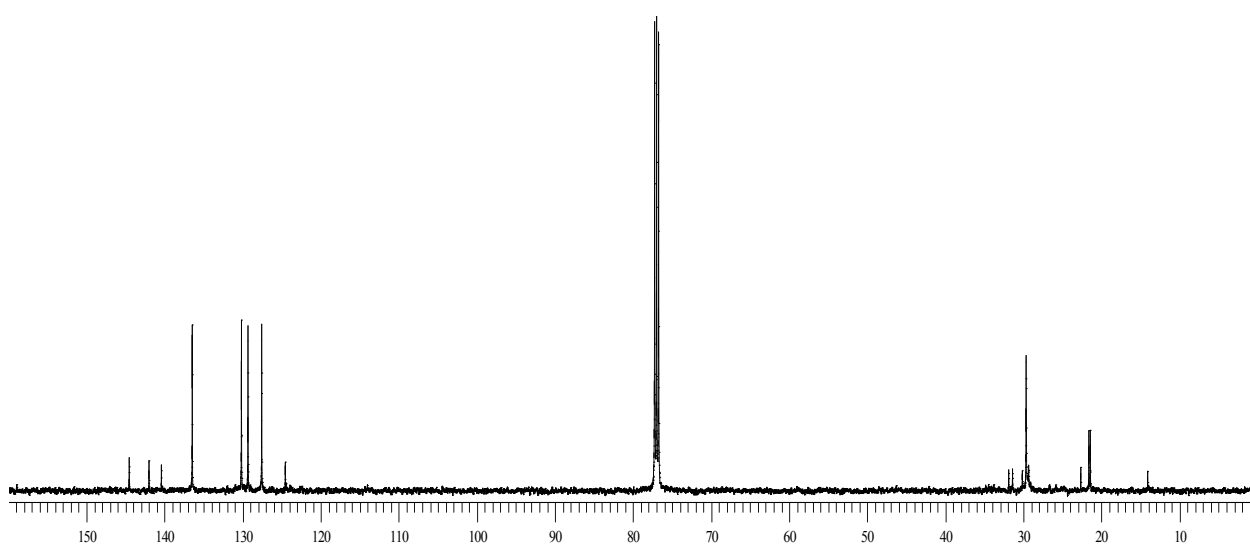


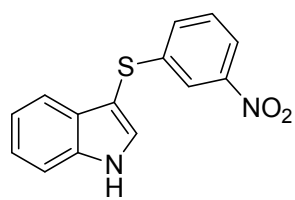


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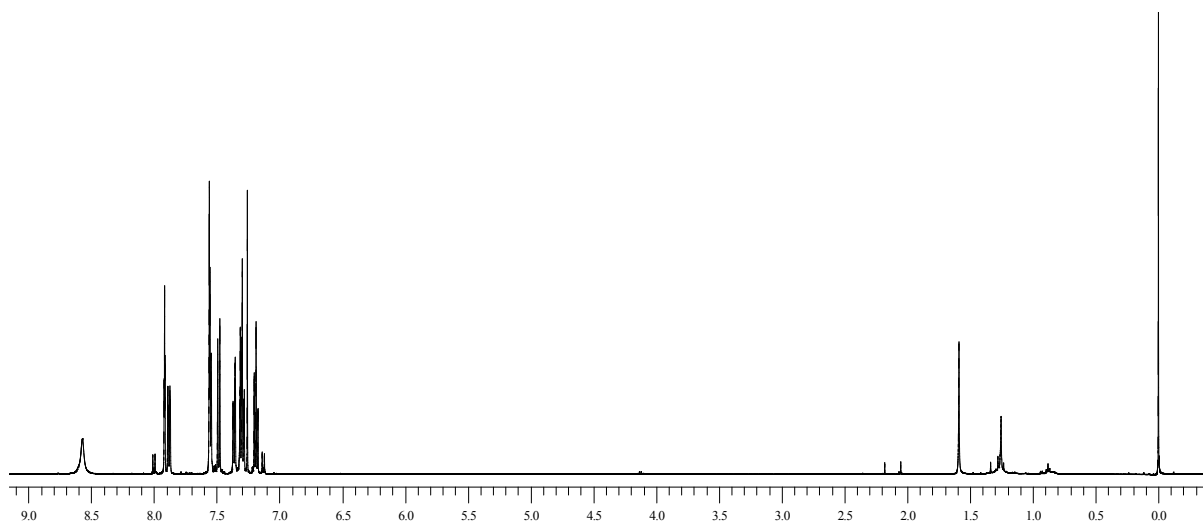


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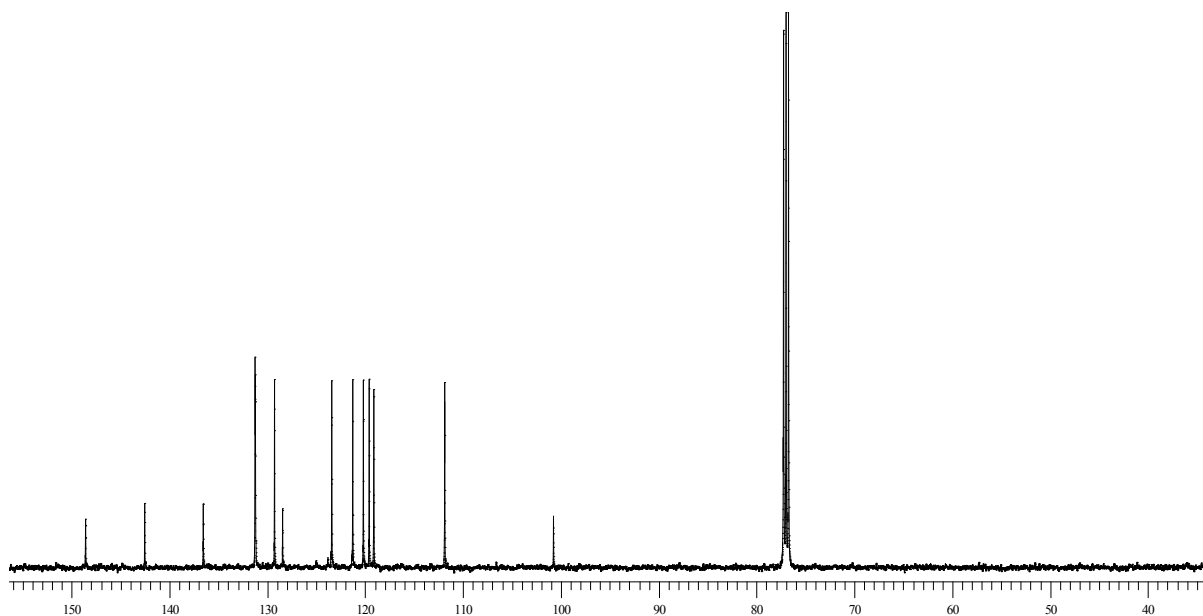


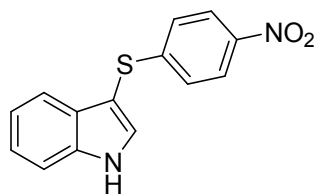


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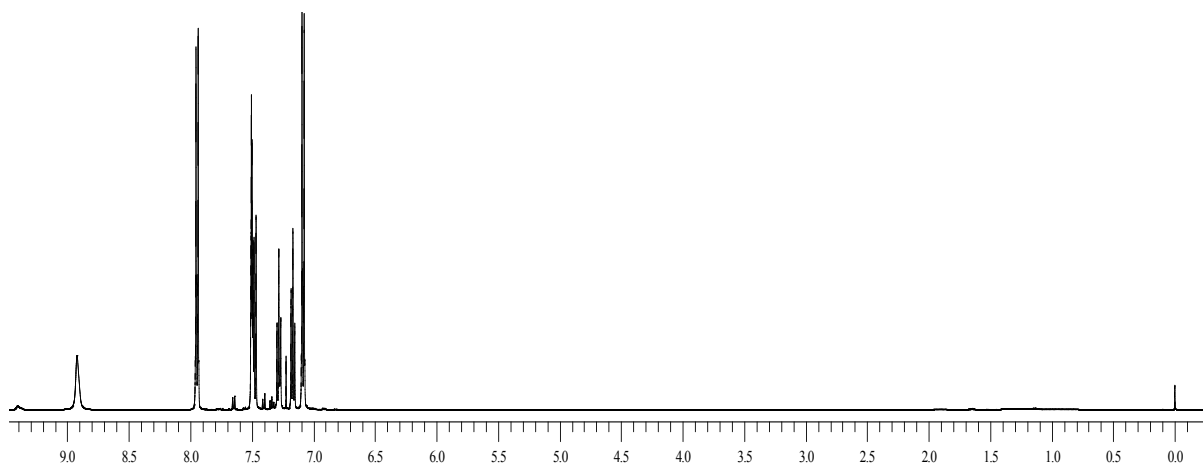


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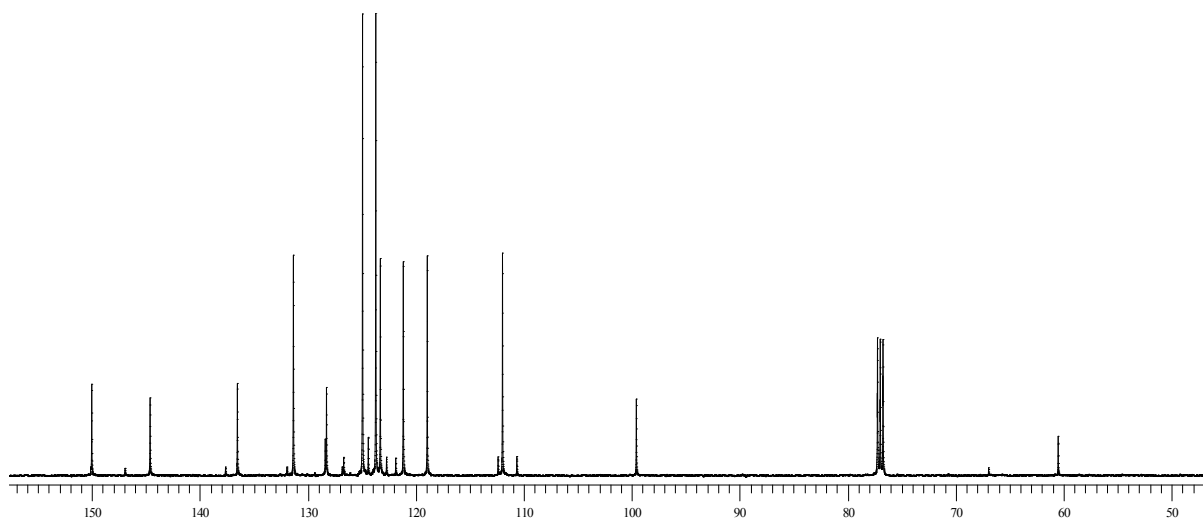


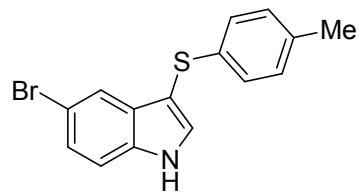


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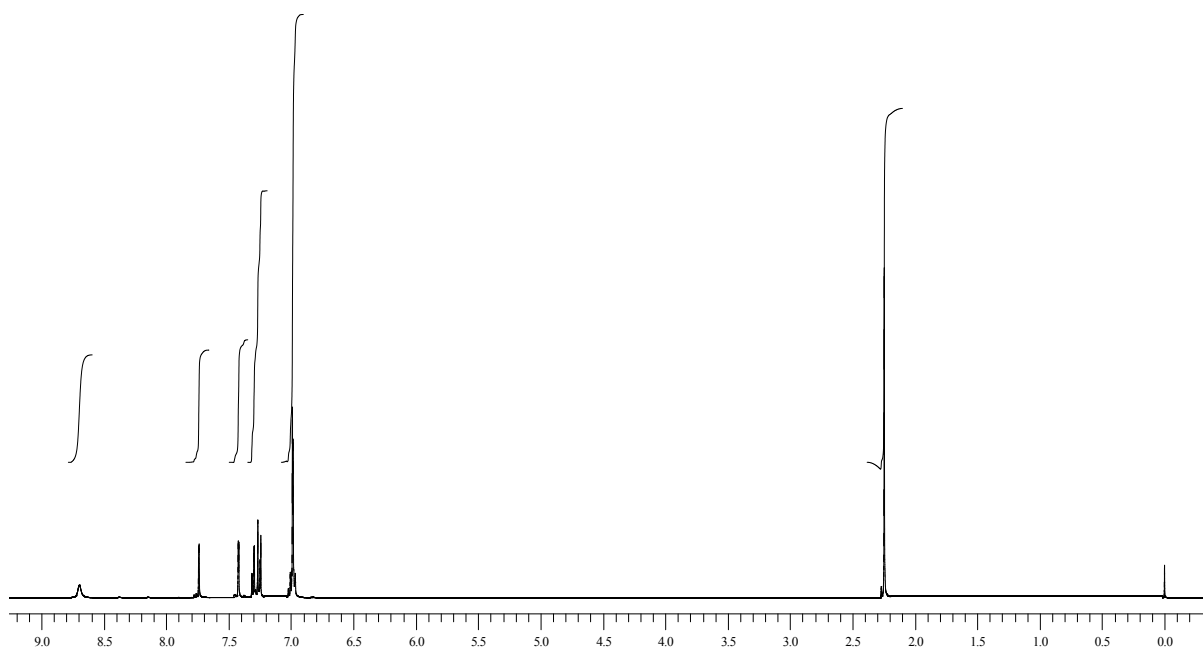


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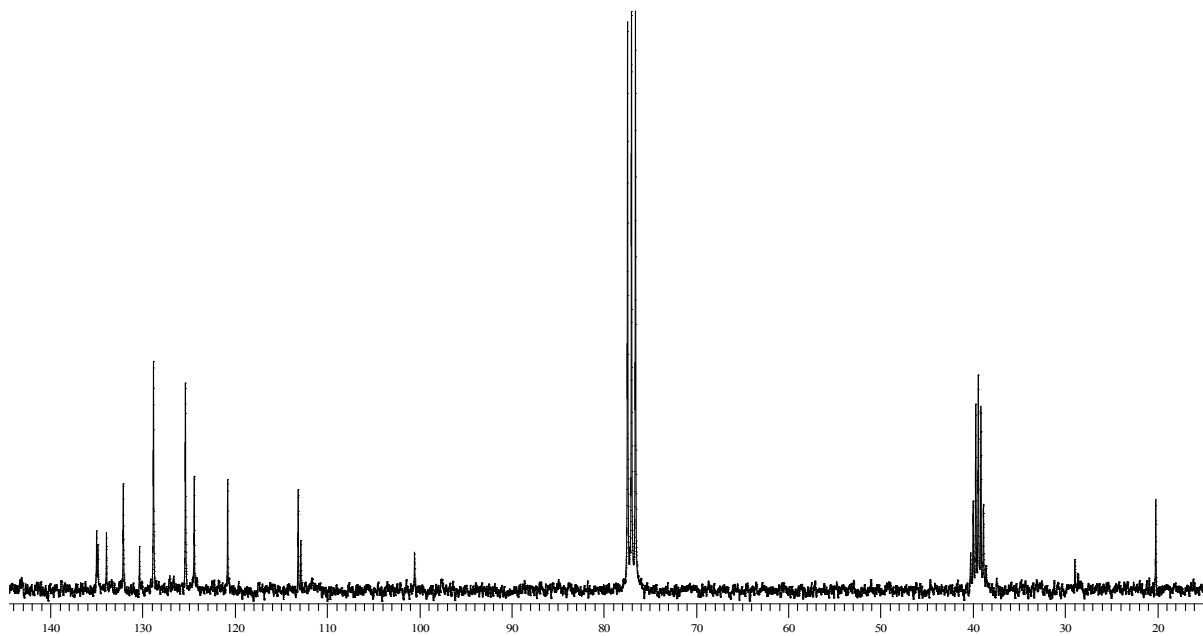


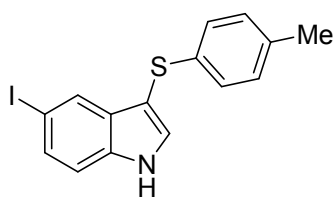


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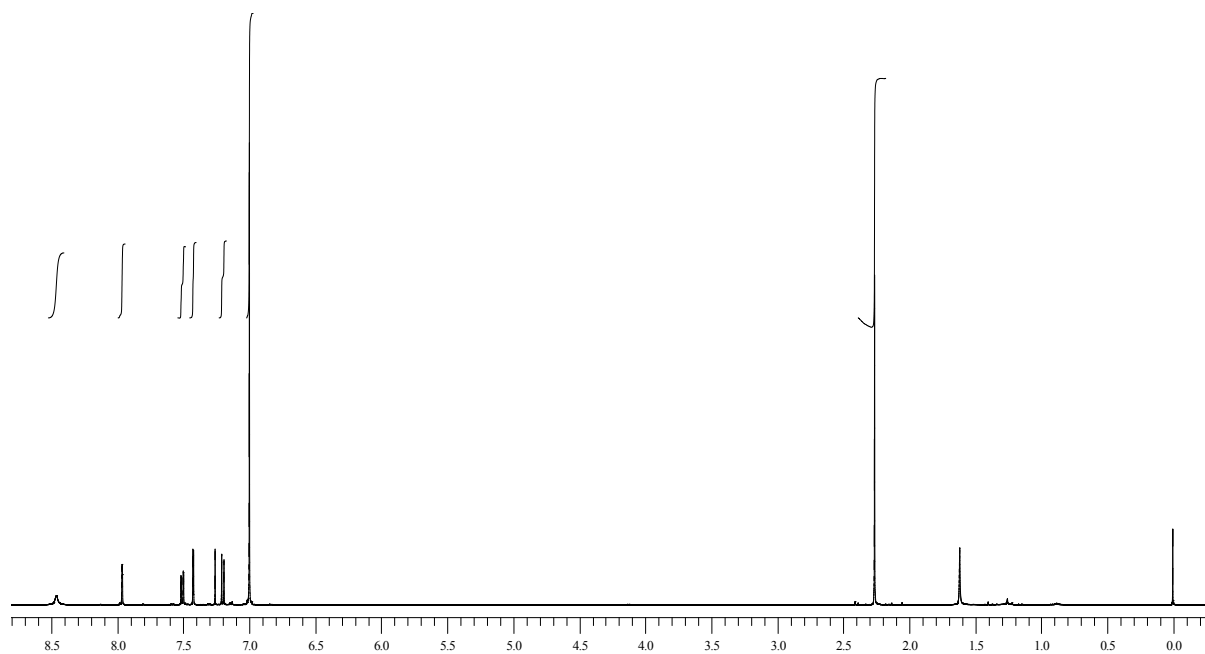


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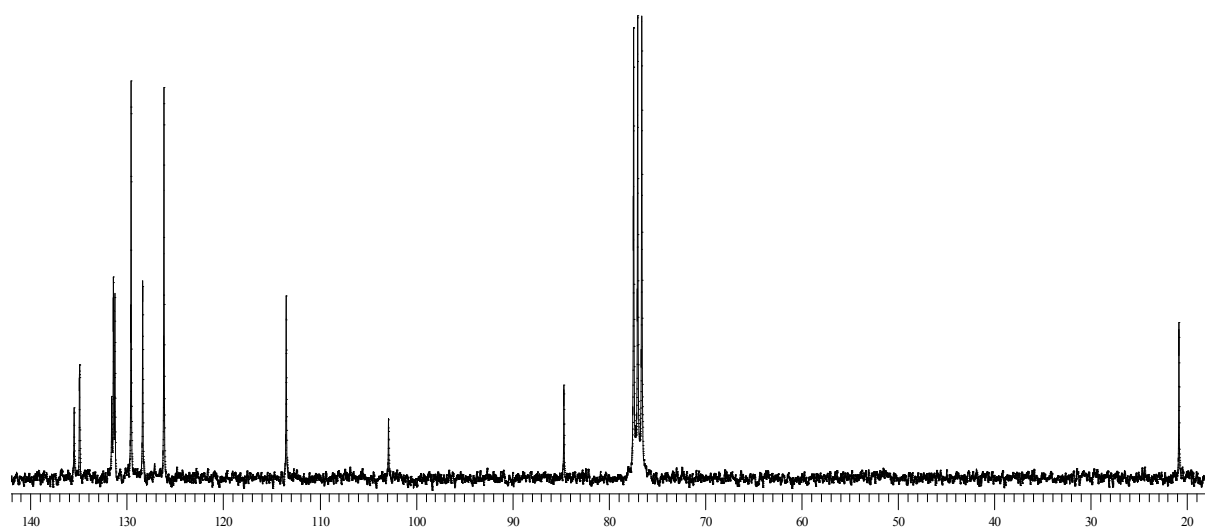




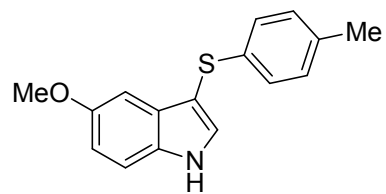
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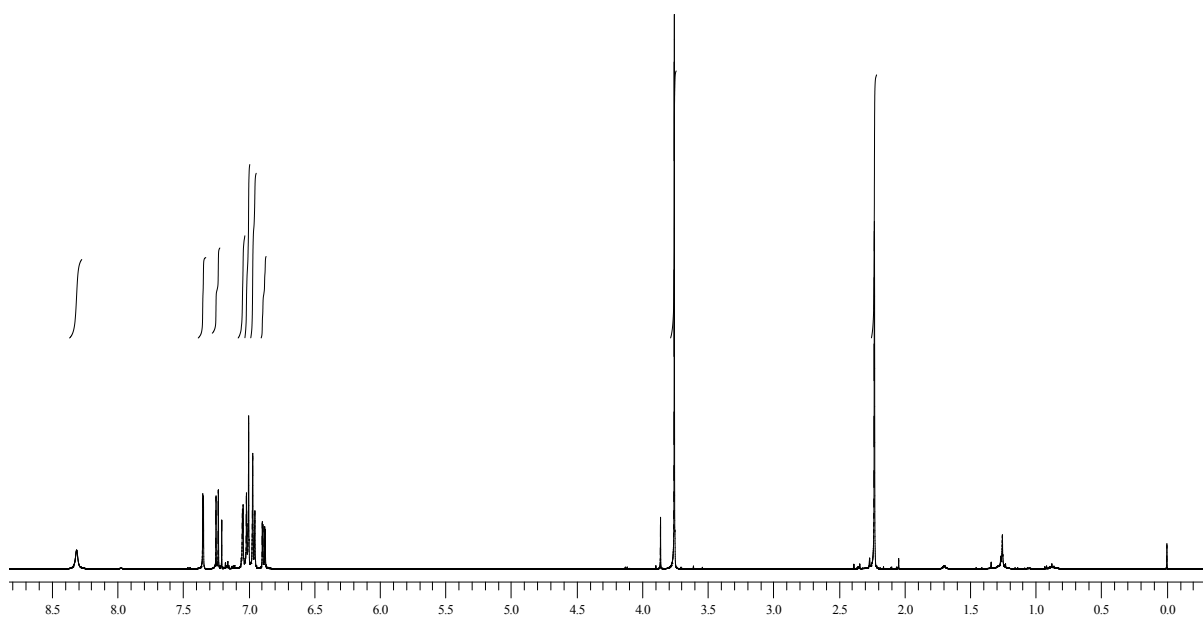
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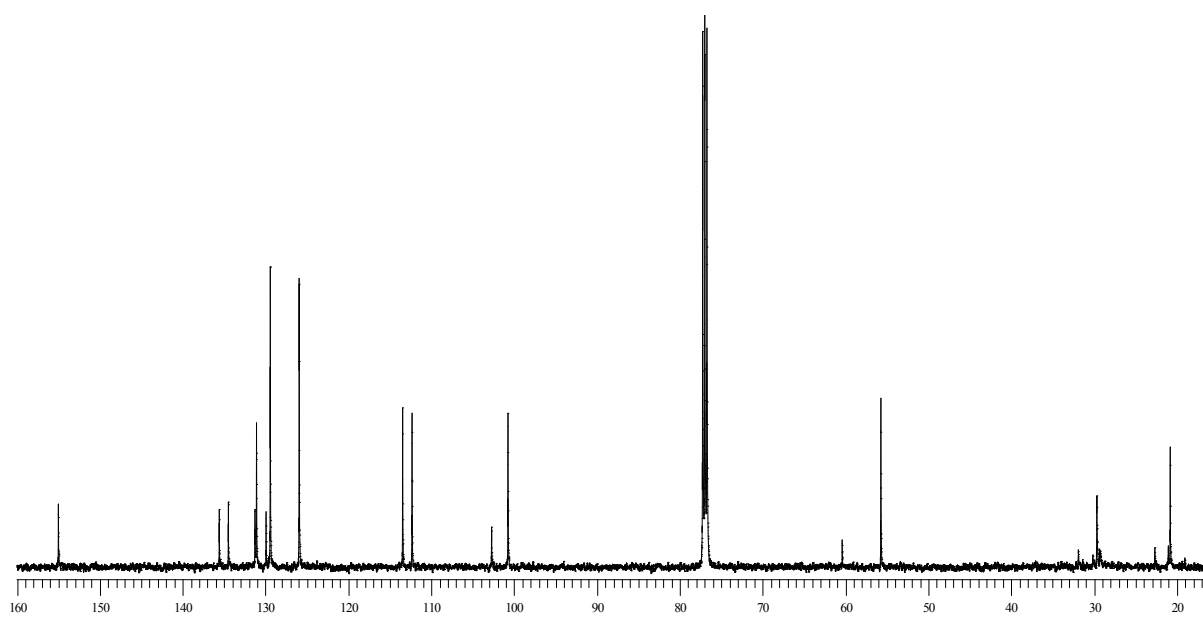


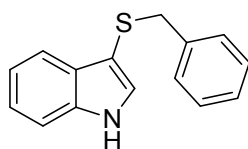


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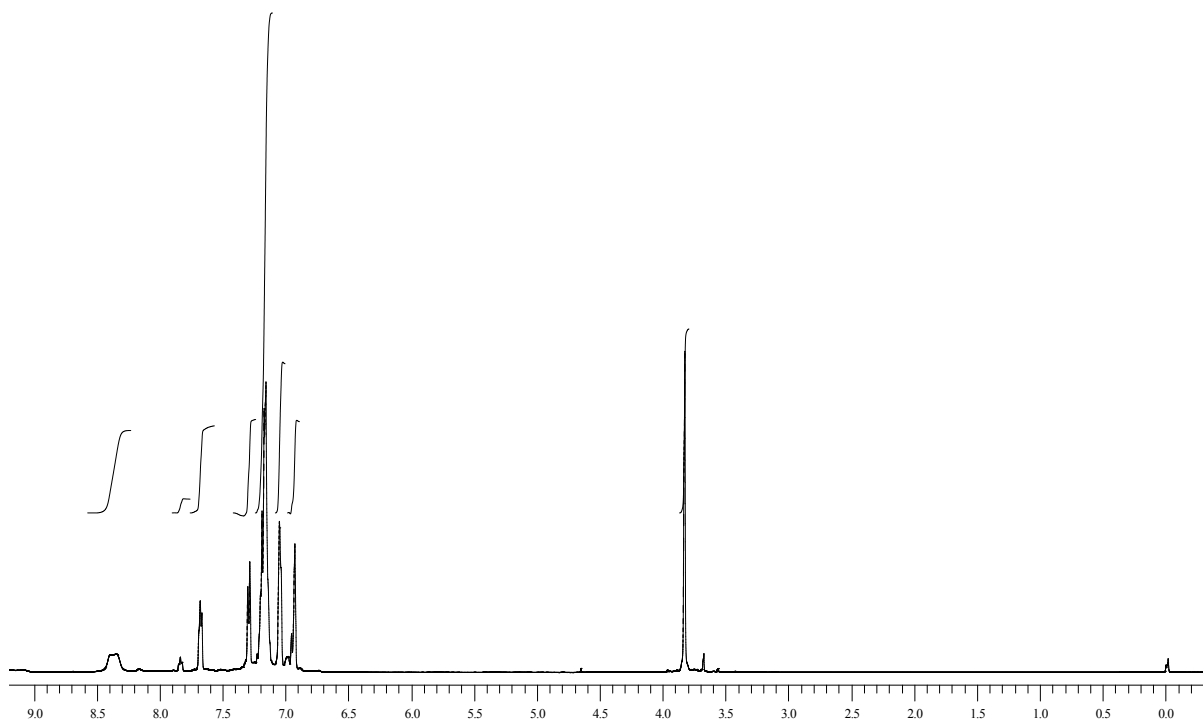


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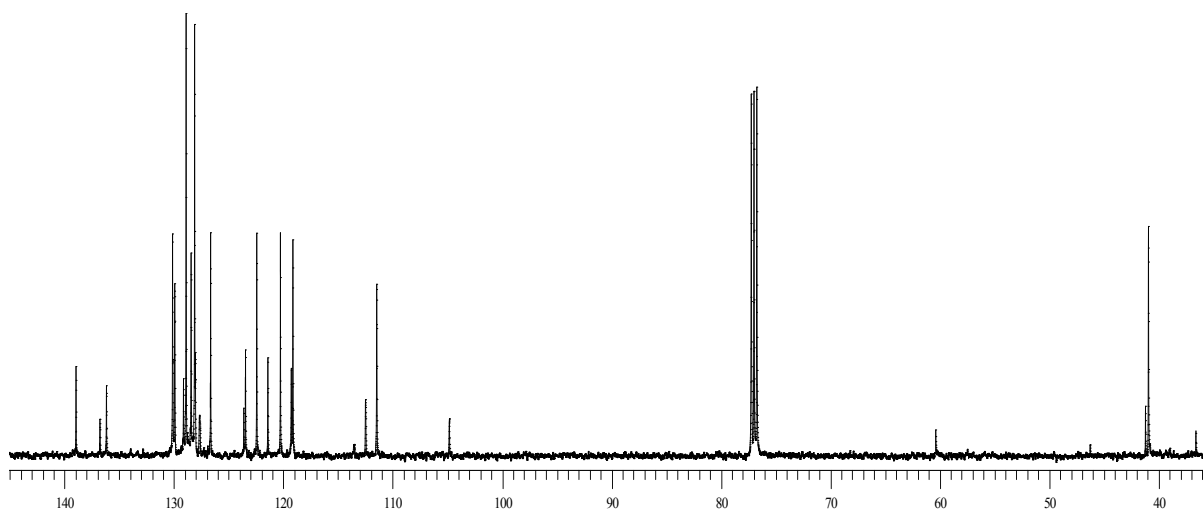


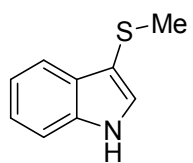


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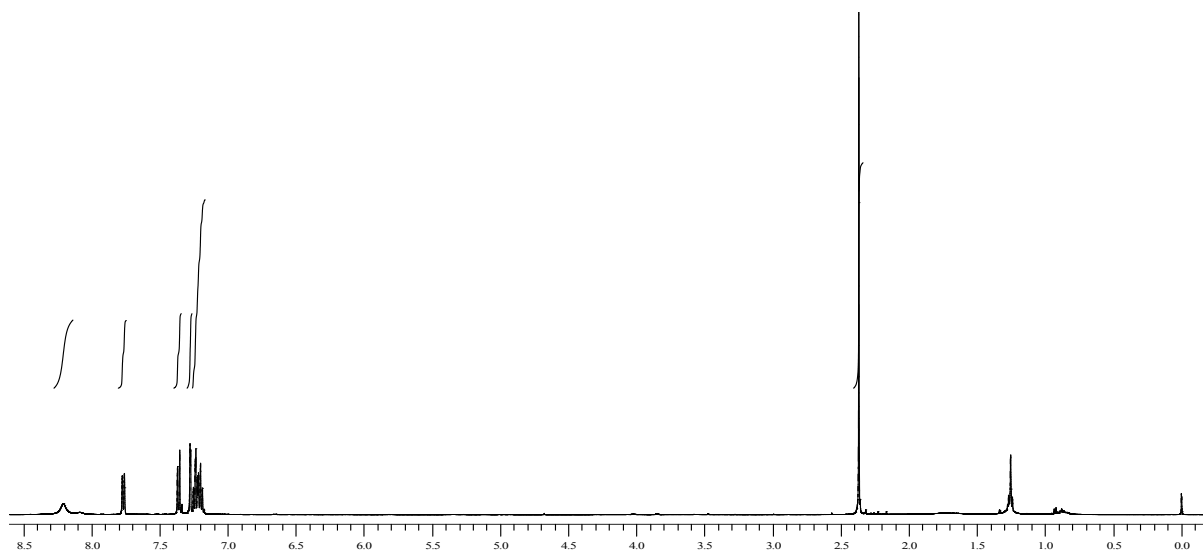


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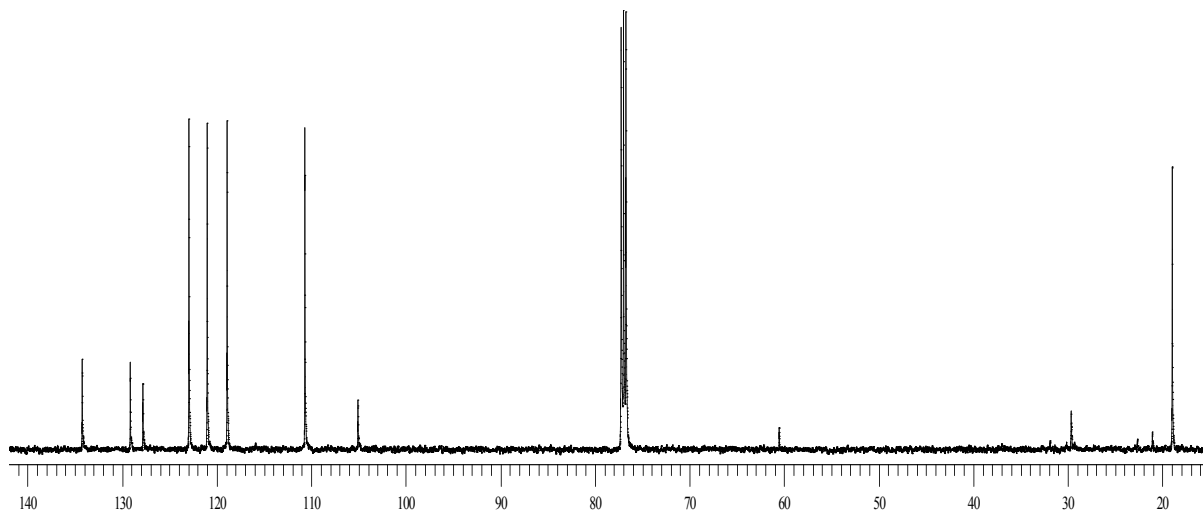


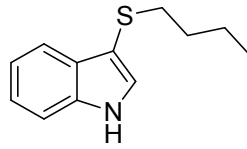


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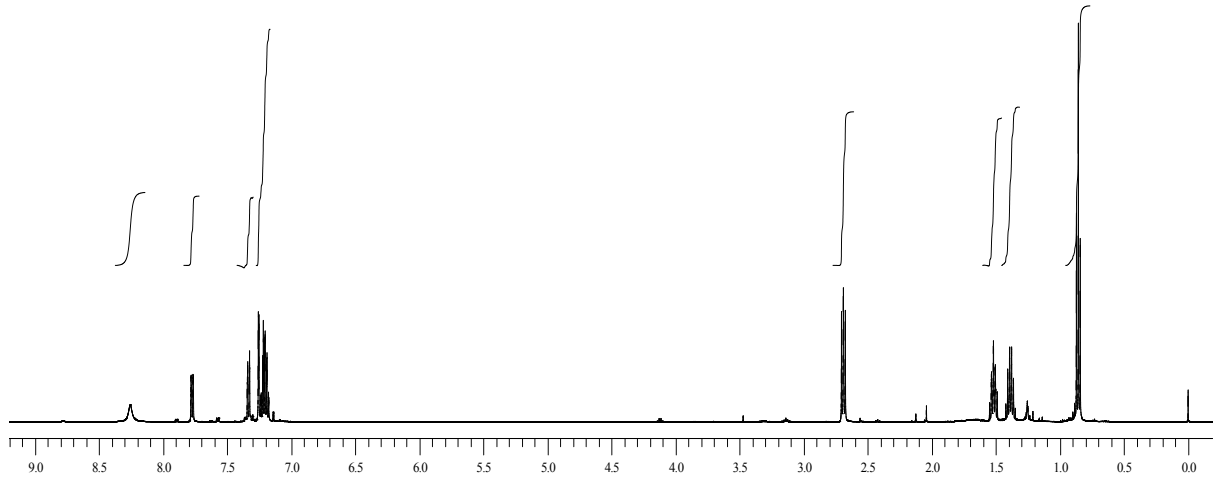


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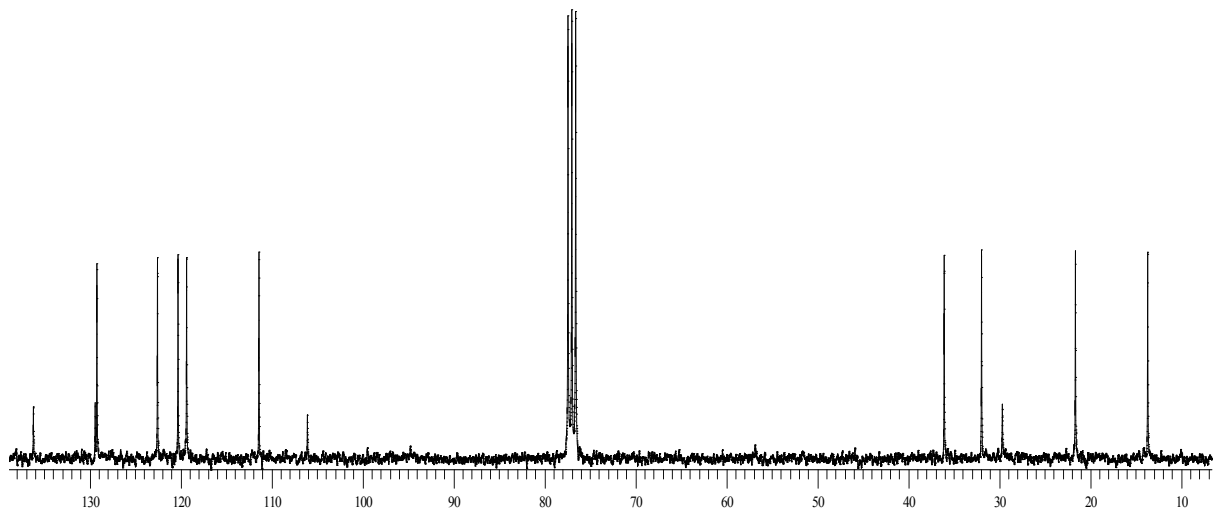


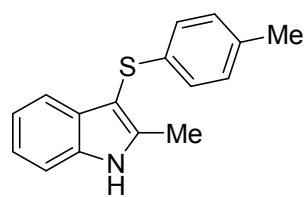


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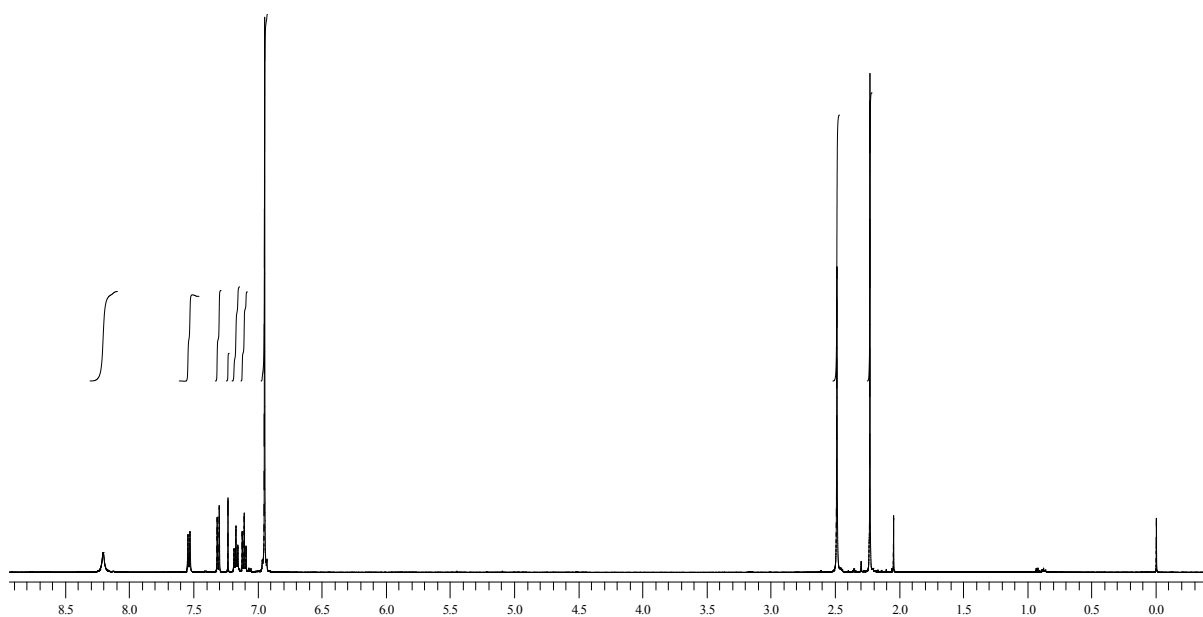


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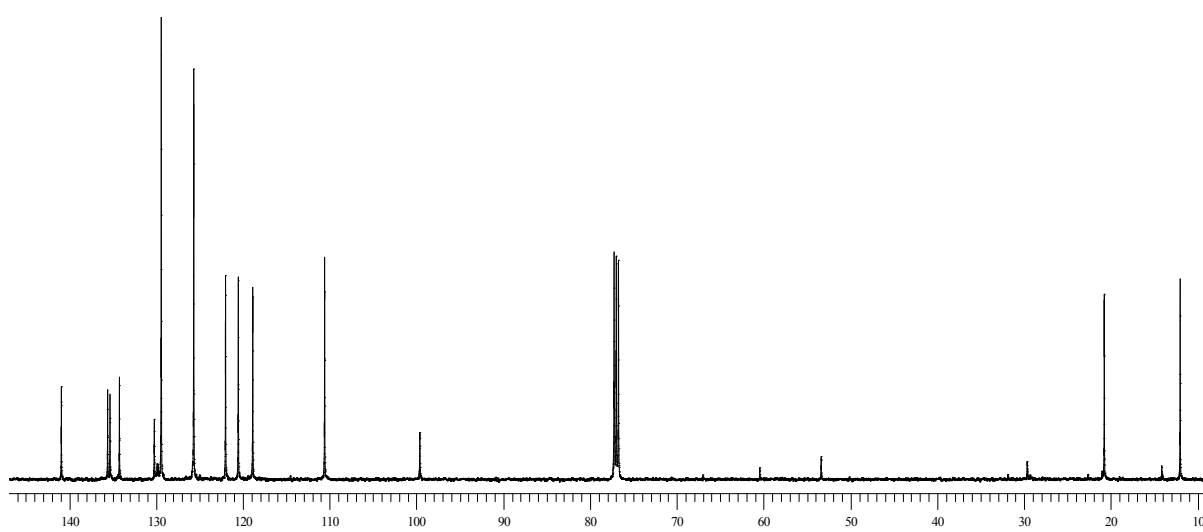


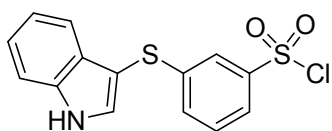


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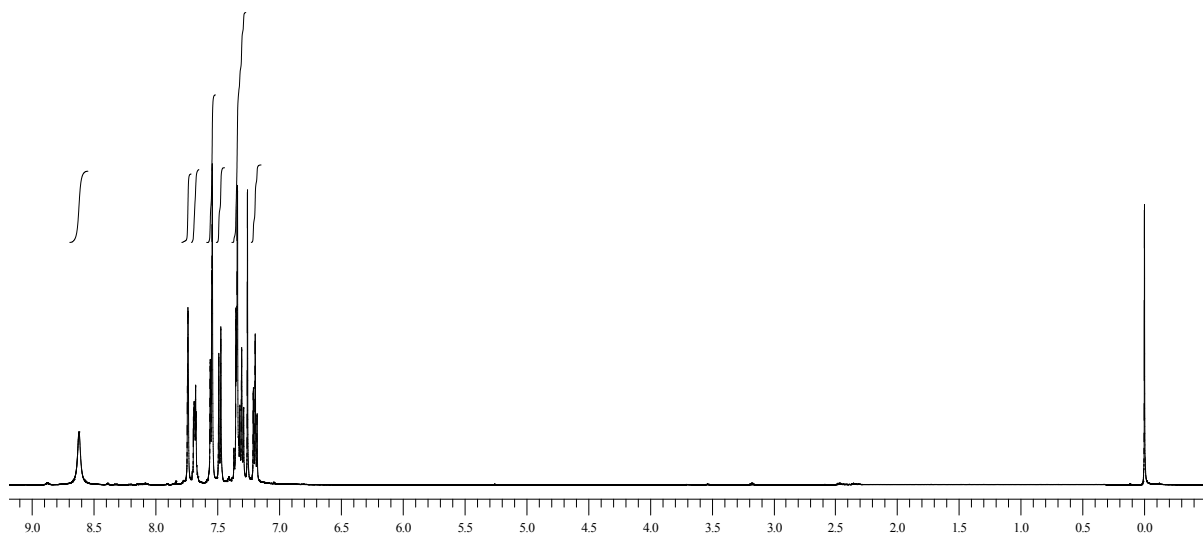


**<sup>13</sup>C-NMR:**

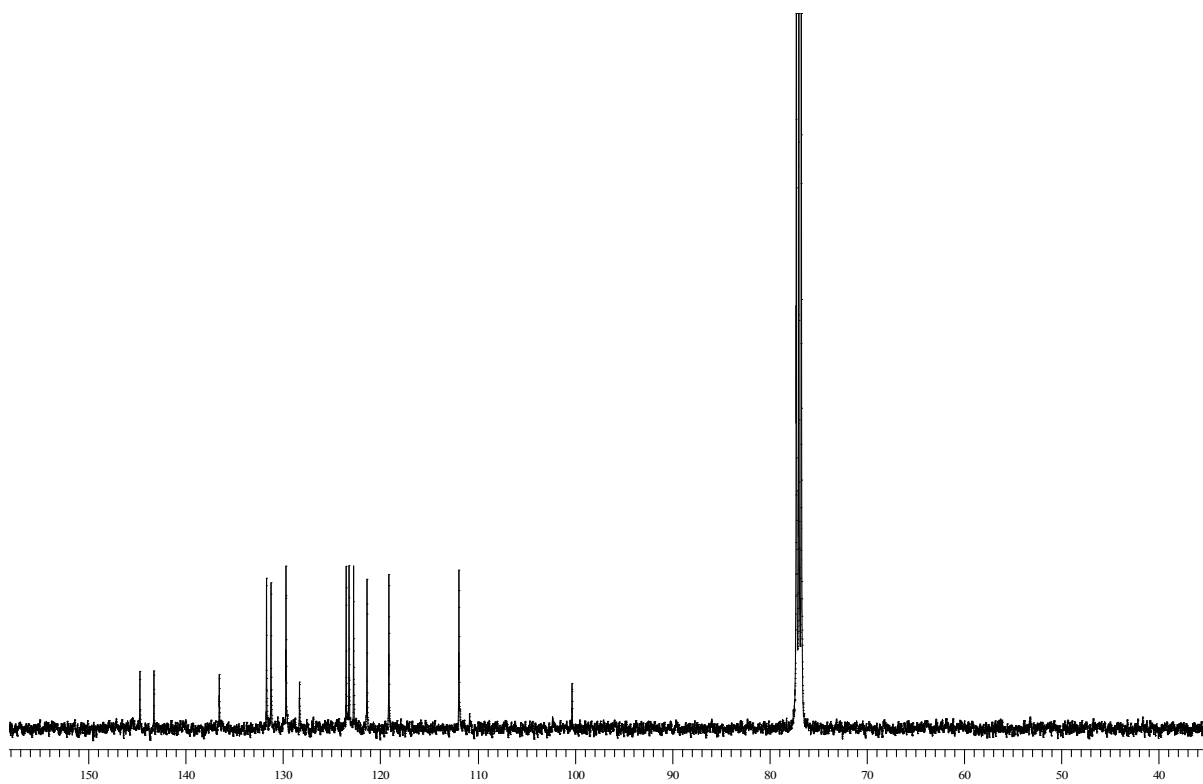


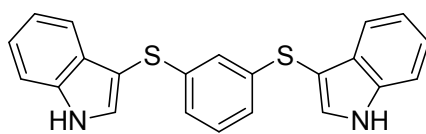


**<sup>1</sup>H-NMR:**

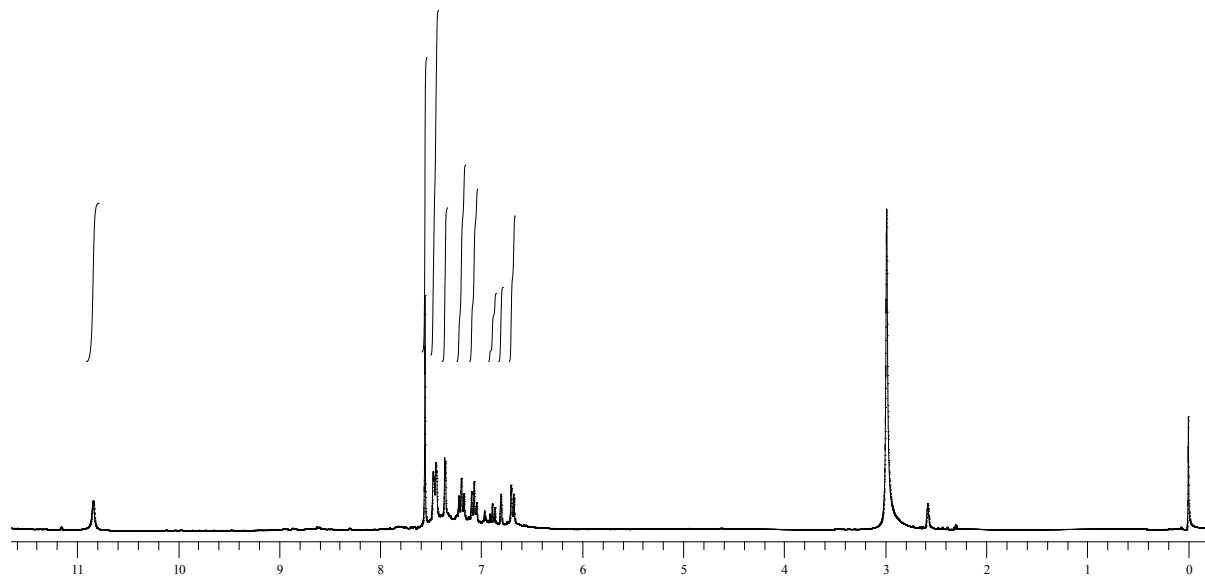


**<sup>13</sup>C-NMR:**

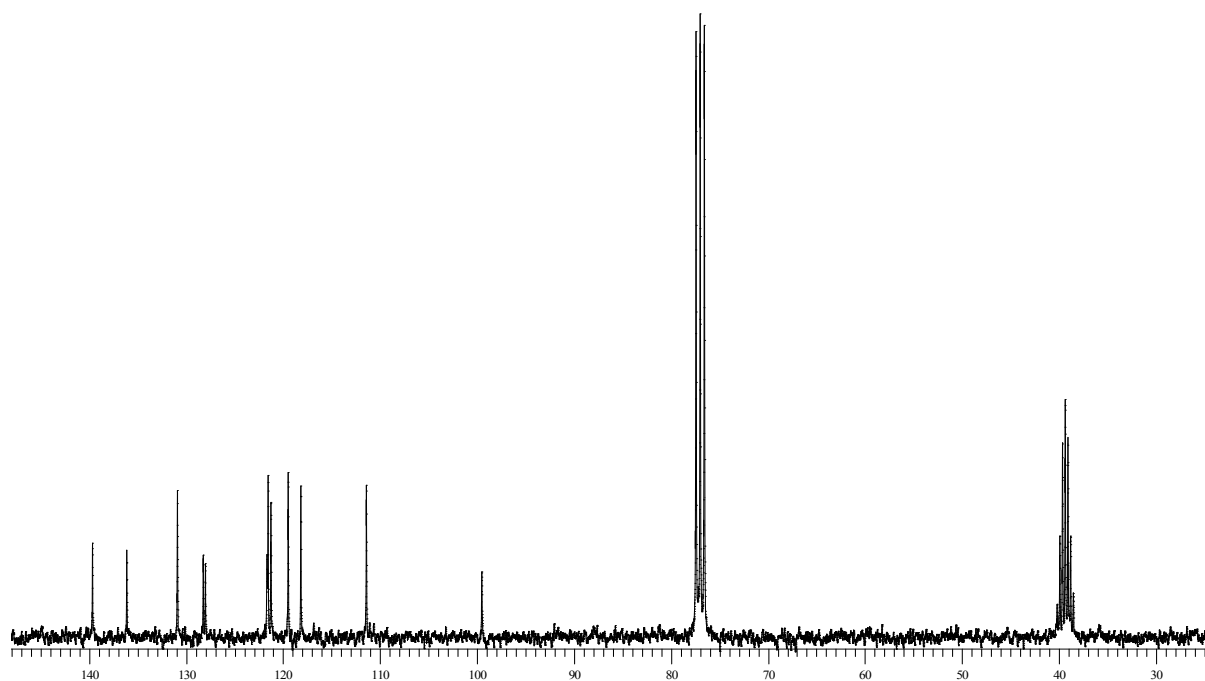


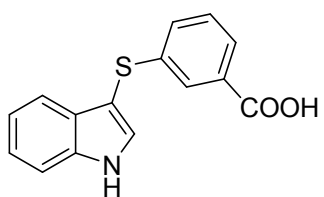


**<sup>1</sup>H-NMR:**

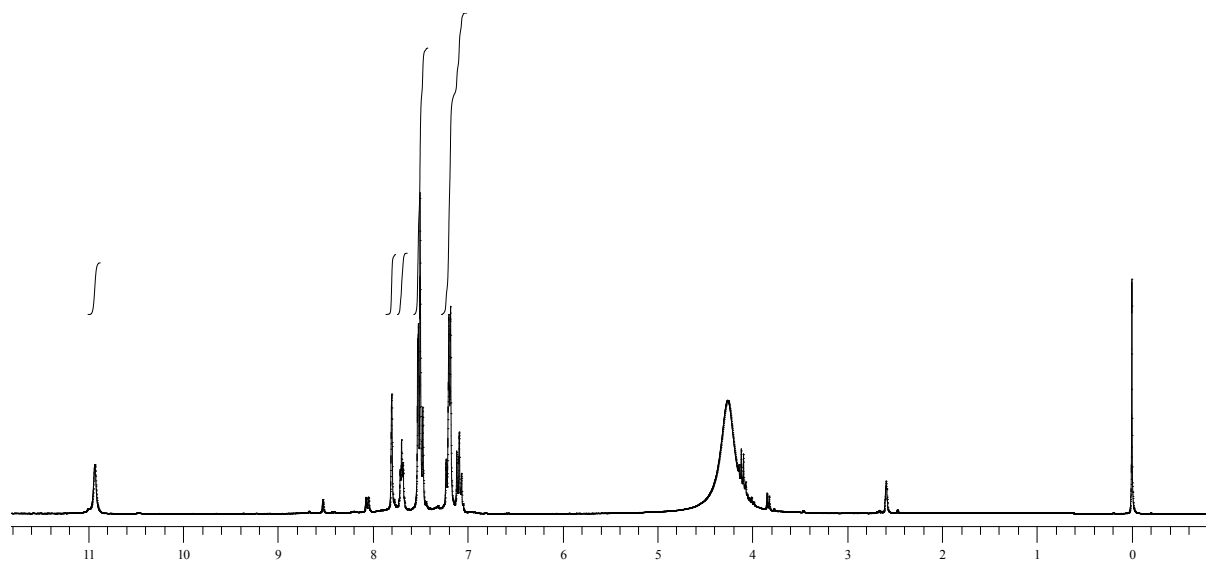


**<sup>13</sup>C-NMR:**

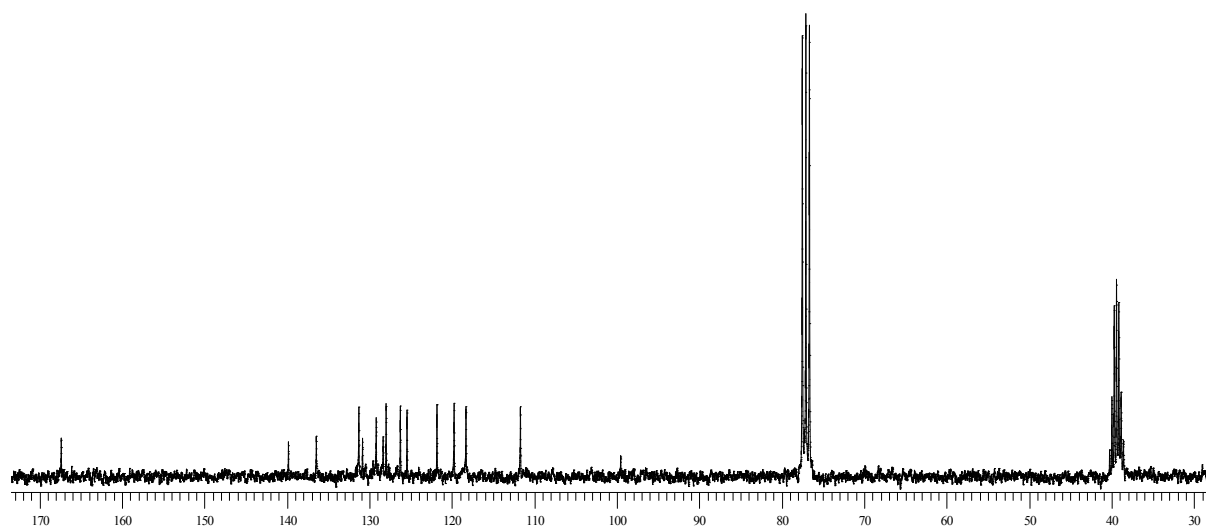




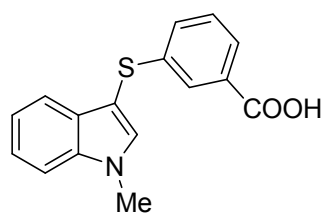
**<sup>1</sup>H-NMR:**



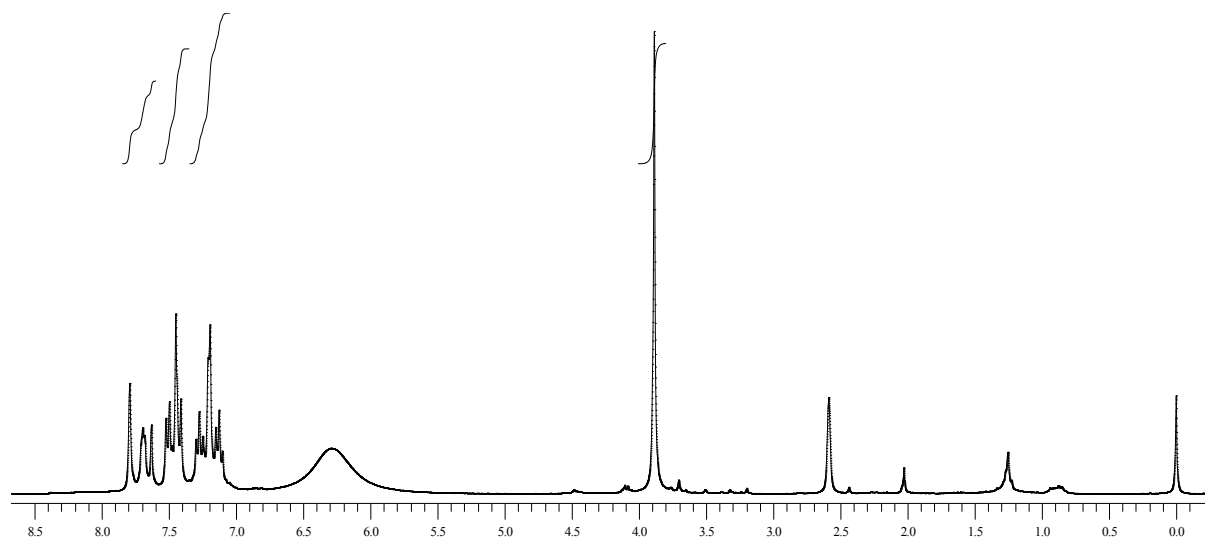
**<sup>13</sup>C-NMR:**







**<sup>1</sup>H-NMR:**



**<sup>13</sup>C-NMR:**

