Mild PIFA-Mediated Synthesis of Benzo[4,5]thiazolo[3,2-*a*]indoles via Oxidative Cyclization

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EXPERIMENTAL PROCEDURES

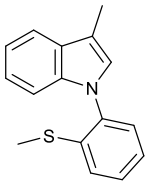
General. Solvent peaks were used as references: $CDCl_3$ at 7.26 ppm for ^1H NMR and 77.16 ppm for ^{13}C NMR. Chemical shifts δ are reported in ppm, and the following abbreviations are used: singlet (s), doublet (d), doublet of doublet (dd), triplet (t), multiplet (m), and broad singlet (bs). In the ^{13}C NMR spectra, signals corresponding to C, CH, CH_2, or CH_3 were assigned from the JMOD sequence. Reaction progress and product mixtures were routinely monitored by thin-layer chromatography (TLC) on silica gel, and compounds were visualized under a UVP Mineralight UVGL-58 lamp (254 nm). Flash chromatography was performed using silica gel 60 (40–63 mm, 230–400 mesh) at medium pressure (200 mbar). All solvents and reagents were used as obtained from suppliers, unless otherwise noted. Organic extracts were, in general, dried over $MgSO_4$ or Na_2SO_4. High-resolution mass spectra were recorded using a MicrOTOF-Q II. A positive ion mass spectrum for the known product was acquired on a Thermo LTQ-FT mass spectrometer with an electrospray ionization source. Specific rotations ($[\alpha]_D$) were measured with an Anton Paar polarimeter-MCP100. All reported compounds showed ^1H and ^{13}C NMR spectra in agreement with the assigned structures.

The 3-aryl-1*H*-indoles **1a**,[1] **1b**,[2] **1c**,[3] **1d**,[1] **1e**,[1] and **1f**[4] were prepared according to the procedures reported in the literature, with the corresponding references.

Preparation of 1-(2-(methylthio)phenyl)-1H-indole compounds (3)

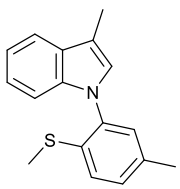
In a sealed tube under argon atmosphere, 1*H*-indole derivative **1** (1.0 equiv), copper powder (10 mol%), and K_2CO_3 (1.5 equiv) were solubilized in dry toluene (0.25 M). Then, *N,N'*-dimethylethylenediamine (DMEDA) (20 mol%), and (2-haloaryl)(methyl)sulfane **2** (1.0 equiv) were added. The sealed tube was stirred at 135 °C for 16 hours. After the reaction was completed, the mixture was concentrated under reduced pressure. The crude product was finally purified by silica gel chromatography using cyclohexane/ethyl acetate (0 to 15% of ethyl acetate) as eluent, resulting in the corresponding products.

*3-Methyl-1-(2-(methylthio)phenyl)-1H-indole (**3a**).*



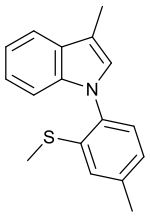
The reaction was carried out with 1.8 mmol of the corresponding 1*H*-indole derivative. White solid (310 mg, 70%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 99/1). mp: 76-77 ^{o}C; IR (film, cm^{-1}): 2918, 1678, 1612, 1585, 1479, 1456, 1436, 1384, 1384, 1369, 1305, 1259, 1228, 1161, 1122, 1085, 1060, 1039, 1012. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68-7.65 (m, 1H), 7.48 – 7.27 (m, 4H), 7.25 – 7.15 (m, 2H), 7.15 – 6.99 (m, 2H), 2.44 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.8, 136.9, 136.8, 128.8, 128.4 (2 C), 126.2, 126.0, 125.3, 122.0, 119.5, 119.0, 112.1, 110.5, 15.1 , 9.8. HRMS (ESI) m/z: $(M + H)^+$ $C_{16}H_{16}NS$ calcd. 254.0098, found 254.0093.

*3-Methyl-1-(5-methyl-2-(methylthio)phenyl)-1H-indole (**3b**).*



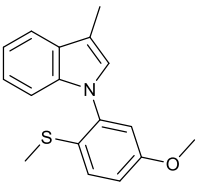
The reaction was carried out with 1.4 mmol of the corresponding 1*H*-indole derivative. Yellow liquid (148 mg, 40%); Rf = 0.5 (Cyclohexane/Ethyl acetate = 99/1). IR (film, cm^{-1}): 2916, 2856, 1598, 1560, 1481, 1458, 1355, 1305, 1267, 1221, 1188, 1157, 1122, 1087, 1056, 1010. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 – 7.62 (m, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.22 – 7.15 (m, 3H), 7.14 – 7.08 (m, 1H), 7.05 (q, *J* = 1.1 Hz, 1H), 2.44 (d, *J* = 1.1 Hz, 3H), 2.40 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.1, 137.0, 135.7, 133.8, 129.2 (2 C), 128.8, 126.8, 126.3, 121.9, 119.4, 118.9, 112.0, 110.6, 20.7, 15.6, 9.7. HRMS (ESI) m/z: $(M + H)^+$ $C_{17}H_{18}NS$ calcd. 268.1154, found 268.1149.

3-Methyl-1-(4-methyl-2-(methylthio)phenyl)-1H-indole (**3c**).



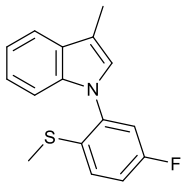
The reaction was carried out with 1.3 mmol of the corresponding 1*H*-indole derivative. White solid (175 mg, 50%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 99/1). mp: 96-97 °C; IR (film, cm^{-1}): 2616, 2858, 1680, 1610, 1490, 1456, 1398, 1365, 1305, 1263, 1228, 1161, 1122, 1085, 1058, 1037, 1010. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 – 7.65 (m, 1H), 7.26 – 7.18 (m, 4H), 7.14 – 7.07 (m, 2H), 7.05 (s, 1H), 2.50 (s, 3H), 2.46 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.4, 137.3, 137.2, 134.5, 128.8, 128.3, 126.8, 126.4, 126.2, 121.9, 119.4, 118.9, 111.9, 110.5, 21.4, 15.2, 9.7. HRMS (ESI) m/z: $(M + H)^+$ $C_{17}H_{18}NS$ calcd. 268.1154 found 268.1149.

*1-(5-Methoxy-2-(methylthio)phenyl)-3-methyl-1H-indole (**3d**).*



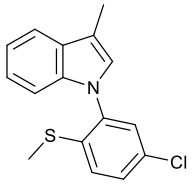
The reaction was carried out with 1.5 mmol of the corresponding 1*H*-indole derivative. Yellow solid (404 mg, 95%); Rf = 0.4 (Cyclohexane/Ethyl acetate = 99/1). mp: 69-70 ^{o}C; IR (film, cm^{-1}): 2916, 1676, 1597, 1566, 1479, 1460, 1384, 1359, 1307, 1284, 1265, 1226, 1201, 1176, 1159, 1124, 1089, 1060, 1028, 1012. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 – 7.59 (m, 1H), 7.45 – 7.34 (m, 1H), 7.20 (m, 3H), 7.10 (t, *J* = 1.2 Hz, 1H), 7.05 – 6.97 (m, 1H), 6.94 (m, 1H), 3.83 (d, *J* = 1.0 Hz, 3H), 2.45 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.4 , 138.9, 136.9, 129.9, 128.9, 127.5, 126.3, 122.1, 119.6, 119.0, 114.6, 113.9, 112.2, 110.5, 55.6, 16.8, 9.7. HRMS (ESI) m/z: $(M + H)^+$ $C_{17}H_{18}ONS$ calcd. 284.1104, found 284.1109.

*1-(5-Fluoro-2-(methylthio)phenyl)-3-methyl-1H-indole (**3e**).*



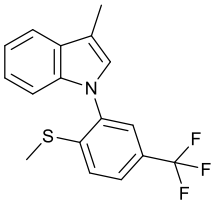
The reaction was carried out with 0.82 mmol of the corresponding 1*H*-indole derivative. White liquid (100 mg, 45%); Rf = 0.5 (Cyclohexane/Ethyl acetate = 99/1). IR (film, cm^{-1}): 2918, 1593,1475, 1458, 1431, 1354, 1303, 1263, 1222, 1180, 1120, 1087, 1055, 1012. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 – 7.59 (m, 1H), 7.40 (dd, *J* = 8.7, 5.8 Hz, 1H), 7.26 – 7.19 (m, 2H), 7.19 – 7.09 (m, 3H), 7.07 (q, *J* = 1.1 Hz, 1H), 2.43 (d, *J* = 1.1 Hz, 3H), 2.27 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.8 (d, *J* = 247.3 Hz), 138.7 (d, *J* = 9.8 Hz), 136.8, 132.5 (d, *J* = 3.8 Hz), 129.0, 128.8 (d, *J* = 7.5 Hz), 125.9, 122.3, 119.9, 119.1, 115.7 (d, *J* = 22.5 Hz), 115.3 (d, *J* = 22.5 Hz), 112.7, 110.4 , 16.1, 9.6. ^{19}F NMR (188 MHz, $CDCl_3$) δ -116.35. HRMS (ESI) m/z: $(M + H)^+$ $C_{16}H_{15}FNS$ calcd. 272.0904, found 272.0899.

*1-(5-Chloro-2-(methylthio)phenyl)-3-methyl-1H-indole. (**3f**).*



The reaction was carried out with 1.0 mmol of the corresponding 1*H*-indole derivative. Yellow liquid (236 mg, 82%); Rf = 0.5 (Cyclohexane/Ethyl acetate = 99/1). IR (film, cm^{-1}): 2916, 1610, 1577, 1556, 1471, 1452, 1411, 1352, 1301, 1224, 1161, 1099, 1056, 1012. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 – 7.58 (m, 1H), 7.40 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.34 – 7.26 (m, 2H), 7.22 – 7.18 (m, 2H), 7.13 – 7.06 (m, 1H), 7.01 (q, *J* = 1.2 Hz, 1H), 2.41 (d, *J* = 1.2 Hz, 3H), 2.30 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 136.8, 136.3, 130.8, 128.9, 128.5, 128.4, 127.4, 127.3, 125.8, 122.3, 119.8, 119.1, 112.8, 110.4, 15.4, 9.6. HRMS (ESI) m/z: $(M + H)^+$ $C_{16}H_{15}ClNS$ calcd. 288.0608, found 288.0604.

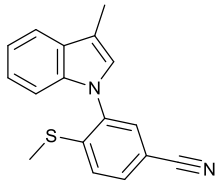
*3-Methyl-1-(2-(methylthio)-5-(trifluoromethyl)phenyl)-1H-indole (**3g**).*



The reaction was carried out with 1.3 mmol of the corresponding 1*H*-indole derivative. Yellow liquid (340 mg, 81%); Rf = 0.5 (Cyclohexane/Ethyl acetate = 99/1). IR (film, cm^{-1}): 2920, 1606, 1562, 1487, 1460, 1429, 1359, 1319, 1301, 1282, 1253, 1226, 1172, 1147, 1116, 1091, 1074, 1021. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 2H), 7.56 (d, *J* = 2.0 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.24 – 7.17 (m, 2H), 7.08 – 7.03 (m, 1H), 7.01 (q, *J* = 1.2 Hz, 1H), 2.42 (d, *J* = 1.1 Hz, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4 (C), 136.9 (C), 129.2 (2 C), 127.6 (q, *J* = 33.3 Hz, C), 125.8 (CH), 125.6 (CH), 125.3 (q, *J* = 4.0 Hz, CH), 125.2 (C), 125.1 (q, *J* = 4.0 Hz, CH), 124.0 (q, *J* = 283.1 Hz, C), 122.6 (CH), 120.1 (CH), 113.3 (C),

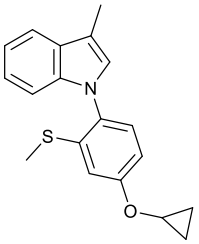
110.4 (CH), 14.9 (CH_3), 9.8 (CH_3). ^{19}F NMR (188 MHz, $CDCl_3$) δ -62.26. HRMS (ESI) m/z: $(M + H)^+$ $C_{17}H_{15}F_3NS$ calcd. 322.0872, found 322.0867.

*3-(3-Methyl-1H-indol-1-yl)-4-(methylthio)benzonitrile (**3h**).*



The reaction was carried out with 1.4 mmol of the corresponding 1*H*-indole derivative. Yellow solid (240 mg, 60%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 96/4). mp: 92-93 °C; IR (film, cm^{-1}): 2918, 2225, 1610, 1593, 1546, 1475, 1456, 1435, 1419, 1355, 1303, 1265, 1228, 1178, 1124, 1085, 1055, 1012. ^1H NMR (300 MHz, $CDCl_3$) δ 7.71 – 7.64 (m, 2H), 7.58 (d, *J* = 1.8 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.08 – 7.02 (m, 1H), 6.99 (s, 1H), 2.42 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.8, 137.0, 136.7, 131.5, 131.3, 129.1, 125.5, 125.4, 122.6, 120.2, 119.3, 118.1, 113.5, 110.2, 108.3, 14.6, 9.6. HRMS (ESI) m/z: $(M + H)^+$ $C_{17}H_{15}N_2S$ calcd. 279.0950, found 279.0946.

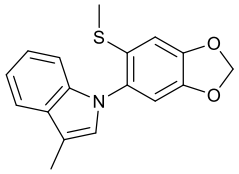
1-(4-Cyclopropoxy-2-(methylthio)phenyl)-3-methyl-1H-indole (**3i**).



The reaction was carried out with 1.5 mmol of the corresponding 1*H*-indole derivative. Yellow solid (240 mg, 52%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 98/2). mp: 83-84 °C; IR (film, cm^{-1}): 2918, 1595, 1566, 1489, 1456, 1354, 1305, 1284, 1263, 1240, 1224, 1215, 1197, 1122, 1080. ^1H NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.42 (m, 1H), 7.10 – 6.99 (m, 3H), 6.97 – 6.89 (m, 1H), 6.88 – 6.74 (m, 3H), 3.66 (m, 1H), 2.29 (s, 3H), 2.13 (s, 3H), 0.78 – 0.61 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 139.5, 137.5, 130.1, 129.4, 128.8, 126.6, 122.0,

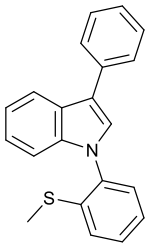
119.4, 118.9, 112.7, 111.8, 111.1, 110.5, 51.2, 15.0, 9.8, 6.4 (2 C). HRMS (ESI) m/z: (M + H)$^+$ $C_{19}H_{20}NOS$ calcd. 310.1260, found 310.1255.

*3-Methyl-1-(6-(methylthio)benzo[d][1,3]dioxol-5-yl)-1H-indole (**3j**).*



The reaction was carried out with 1.0 mmol of the corresponding 1*H*-indole derivative. White solid (204 mg, 69%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 98/2). mp: 113-114 ^oC; IR (film, cm^{-1}): 2916, 1676, 1610, 1500, 1475, 1462, 1352, 1321, 1298, 1226, 1195, 1116, 1072, 1033. ^1H NMR (300 MHz, $CDCl_3$) δ 7.73 – 7.57 (m, 1H), 7.24 – 7.16 (m, 2H), 7.11 – 7.04 (m, 1H), 6.98 (t, *J* = 1.2 Hz, 1H), 6.93 (s, 1H), 6.82 (s, 1H), 6.07 (s, 2H), 2.42 (d, *J* = 1.1 Hz, 3H), 2.23 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.0, 137.3, 131.1, 130.1 (2 C), 128.7, 126.5, 122.0, 119.4, 118.9, 111.9, 110.3, 109.4, 107.6, 101.9, 16.6, 9.6. HRMS (ESI) m/z: (M + H)$^+$ $C_{17}H_{16}NO_2S$ calcd. 298.0896, found 298.0892.

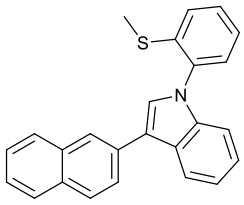
*1-(2-(Methylthio)phenyl)-3-phenyl-1H-indole (**3k**).*



The reaction was carried out with 0.63 mmol of the corresponding 1*H*-indole derivative. White oil (100 mg, 50%); Rf = 0.4 (Cyclohexane/Ethyl acetate = 98/2). IR (film, cm^{-1}): 2918, 1600, 1583, 1546, 1477, 1456, 1436, 1377, 1311, 1263, 1219, 1174, 1141, 1103, 1074, 1014. ^1H NMR (300 MHz, $CDCl_3$) δ 7.91 – 7.80 (m, 1H), 7.65 – 7.52 (m, 2H), 7.36 – 7.16 (m, 6H), 7.16 – 7.03 (m, 4H), 7.03 – 6.90 (m, 1H), 2.10 (d, *J* = 1.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.0 (C), 137.7 (C), 136.6 (C), 135.4 (C), 128.9 (CH), 128.8 (3 CH), 128.5

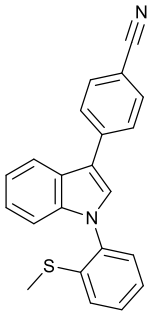
(CH), 127.6 (2 CH), 126.5 (2 CH), 126.4 (C), 126.1 (CH), 125.5 (CH), 122.6 (CH), 120.8 (CH), 120.0 (CH), 118.6 (C), 111.1 (CH), 15.2 (CH_3). HRMS (ESI) m/z: $(M + H)^+$ $C_{22}H_{18}NS$ calcd. 316.1154, found 316.1150.

*1-(2-(Methylthio)phenyl)-3-(naphthalen-2-yl)-1H-indole (**3l**).*



The reaction was carried out with 1.0 mmol of the corresponding 1*H*-indole derivative. Yellow liquid (297 mg, 81%); Rf = 0.5 (Cyclohexane/Ethyl acetate = 97/3). IR (film, cm^{-1}): 1583, 1541, 1481, 1456, 1435, 1311, 1263, 1217, 1143, 1074. ^1H NMR (300 MHz, $CDCl_3$) δ 8.12 (s, 1H), 8.08 – 7.99 (m, 1H), 7.87 – 7.72 (m, 4H), 7.46 (s, 1H), 7.44 – 7.29 (m, 5H), 7.22 – 7.14 (m, 3H), 7.11 – 7.05 (m, 1H), 2.23 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.9, 137.7, 136.5, 134.0, 132.9, 132.1, 128.9, 128.5, 128.3, 127.8, 127.7, 126.8, 126.5, 126.4, 126.4, 126.1, 125.5, 125.4, 125.2, 122.7, 120.9, 120.1, 118.5, 111.1, 15.2. HRMS (ESI) m/z: $(M + H)^+$ $C_{25}H_{20}NS$ calcd. 366.1311, found 366.1304.

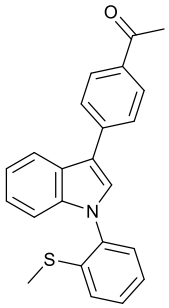
*4-(1-(2-(Methylthio)phenyl)-1H-indol-3-yl)benzonitrile (**3m**).*



The reaction was carried out with 1.1 mmol of the corresponding 1*H*-indole derivative. Yellow liquid (210 mg, 55%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 86/14). IR (film, cm^{-1}): 2222, 1604, 1583, 1541, 1477, 1456, 1436, 1379, 1313, 1278, 1255, 1219, 1174, 1143, 1074, 1039, 1016. ^1H NMR (300 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 1H), 7.68 – 7.59 (m, 2H),

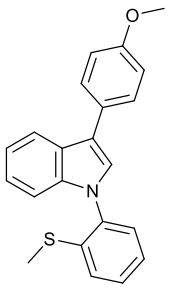
7.55 – 7.46 (m, 2H), 7.36 – 7.28 (m, 2H), 7.24 (m, 1H), 7.19 (m, 1H), 7.15 – 7.05 (m, 3H), 7.04 – 6.97 (m, 1H), 2.14 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4 , 137.9, 137.9, 135.9, 132.6 (2 C), 129.4, 128.4, 127.8, 127.4 (2 C), 126.4, 125.6, 123.2, 121.6, 121.5, 119.6, 119.4, 116.7, 111.4, 108.9, 15.1. HRMS (ESI) m/z: $(M + Na)^+$ $C_{22}H_{16}N_2SNa$ calcd. 363.0926, found 363.0924.

*1-(4-(1-(2-(Methylthio)phenyl)-1H-indol-3-yl)phenyl)ethan-1-one (**3n**).*



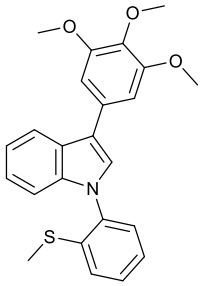
The reaction was carried out with 0.8 mmol of the corresponding 1*H*-indole derivative. Yellow solid (254 mg, 89%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 90/10). mp: 136-137 ^{o}C; IR (film, cm^{-1}): 3049, 2922, 1674, 1600, 1543, 1500, 1477, 1456, 1436, 1411, 1379, 1355, 1313, 1265, 1219, 1143, 1074, 1039, 1016. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 – 8.01 (m, 3H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.56 (s, 1H), 7.54 – 7.46 (m, 1H), 7.47 – 7.37 (m, 2H), 7.37 – 7.27 (m, 3H), 7.23 – 7.14 (m, 1H), 2.67 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.6, 140.5, 137.9, 137.8, 135.9, 134.5, 129.1 (2 C), 128.5, 127.5, 127.0 (3 C), 126.4, 125.8, 125.5, 122.9, 121.3, 119.9, 117.4, 111.2, 26.6, 15.1. HRMS (ESI) m/z: $(M + H)^+$ $C_{23}H_{20}NOS$ calcd. 358.1266, found 358.1265.

*3-(4-Methoxyphenyl)-1-(2-(methylthio)phenyl)-1H-indole (**3o**).*



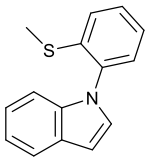
The reaction was carried out with 1.0 mmol of the corresponding 1*H*-indole derivative. Yellow liquid (229 mg, 66%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 96/4). IR (film, cm^{-1}): 2833, 1608, 1583, 1550, 1504, 1477, 1456, 1438, 1377, 1309, 1284, 1240, 1217, 1176, 1139, 1109, 1074, 1031. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 6.3, 2.9 Hz, 1H), 7.53 (d, *J* = 8.7 Hz, 2H), 7.30 – 7.18 (m, 4H), 7.16 – 7.06 (m, 3H), 7.04 – 6.97 (m, 1H), 6.88 (d, *J* = 8.7 Hz, 2H), 3.70 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.3, 137.9, 137.6, 136.7, 128.8, 128.7 (2 C), 128.6, 127.9, 126.5, 126.4, 125.8, 125.5, 122.5, 120.6, 119.9, 118.3, 114.4 (2 C), 111.0, 55.4, 15.2. HRMS (ESI) m/z: $(M + H)^+$ $C_{22}H_{20}NOS$ calcd. 346.1260, found 346.1253.

*1-(2-(Methylthio)phenyl)-3-(3,4,5-trimethoxyphenyl)-1H-indole (**3p**).*



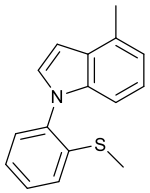
The reaction was carried out with 1.7 mmol of the corresponding 1*H*-indole derivative. Yellow solid (508 mg, 75%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 90/10). mp: 121-122 ^{o}C; IR (film, cm^{-1}): 1583, 1548, 1502, 1479, 1456, 1413, 1382, 1311, 1226, 1180, 1122, 1076, 1045, 1004. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 5.6, 3.6 Hz, 1H), 7.55 – 7.38 (m, 4H), 7.37 – 7.25 (m, 3H), 7.24 – 7.15 (m, 1H), 7.00 (s, 2H), 3.99 (s, 6H), 3.98 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6 (2 C), 138.0, 137.6, 136.8, 136.4, 131.0 (2 C), 128.9, 128.5, 126.3, 126.2, 125.5, 122.6, 120.8, 119.8, 118.7, 111.1, 104.9 (2 C), 61.0, 56.3 (2 C), 15.1. HRMS (ESI) m/z: $(M + H)^+$ $C_{24}H_{24}NO_3S$ calcd. 406.1471, found 406.1472.

1-(2-(Methylthio)phenyl)-1H-indole (**3q**).[5]



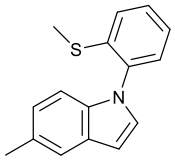
The reaction was carried out with 2.0 mmol of the corresponding 1*H*-indole derivative. White solid (350 mg, 73%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 99/1). mp: 76-77 ^{o}C; IR (film, cm^{-1}): 2920, 1583, 1510, 1479, 1456, 1435, 1328, 1305, 1255, 1228, 1211, 1136, 1111, 1080. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 – 7.67 (m, 1H), 7.47 (m, 1H), 7.44 – 7.35 (m, 2H), 7.32 (dd, *J* = 6.7, 1.6 Hz, 1H), 7.29 – 7.27 (m, 1H), 7.25 – 7.17 (m, 2H), 7.17 – 7.10 (m, 1H), 6.74 (d, *J* = 3.3 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.0, 136.8, 136.7, 128.7 (2 C), 128.5, 128.3, 126.2, 125.4, 122.1, 120.9, 120.2, 110.6, 102.9, 15.1. HRMS (ESI) m/z: $(M + H)^+$ $C_{15}H_{14}NS$ calcd. 240.0841, found 240.0837.

*4-Methyl-1-(2-(methylthio)phenyl)-1H-indole (**3r**).*



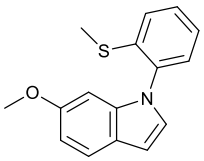
The reaction was carried out with 1.5 mmol of the corresponding 1*H*-indole derivative. Yellow solid (320 mg, 84%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 99/1). mp: 127-128 ^{o}C; IR (film, cm^{-1}): 2916, 1568, 1485, 1454, 1355, 1338, 1288, 1263, 1240, 1219, 1190, 1157, 1128, 1089, 1039, 1014. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 – 7.28 (m, 4H), 7.27 (d, *J* = 2.1 Hz, 1H), 7.18 – 7.07 (m, 1H), 7.04 – 6.92 (m, 2H), 6.75 (d, *J* = 3.3 Hz, 1H), 2.65 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.0, 136.9, 136.5, 130.3, 128.7, 128.5, 128.2, 128.1, 126.4, 125.4, 122.2, 120.4, 108.2, 101.3, 18.7, 15.2. HRMS (ESI) m/z: $(M + H)^+$ $C_{16}H_{16}NS$ calcd. 254.0998, found 254.0992.

*5-Methyl-1-(2-(methylthio)phenyl)-1H-indole (**3s**).*



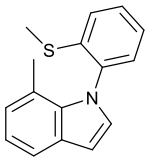
The reaction was carried out with 1.5 mmol of the corresponding 1*H*-indole derivative. White solid (333 mg, 88%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 99/1). mp: 82-83 °C; IR (film, cm^{-1}): 2918, 1585, 1514, 1483, 1436, 1367, 1330, 1294, 1259, 1240, 1222, 1159, 1112, 1080, 1058, 1039. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.51 – 7.36 (m, 3H), 7.36 – 7.25 (m, 2H), 7.06 (s, 2H), 6.67 (d, *J* = 3.2 Hz, 1H), 2.53 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.0, 137.0, 135.2, 129.4, 128.8, 128.7, 128.6, 128.5, 126.4, 125.4, 123.7, 120.6, 110.3, 102.5, 21.4, 15.2. HRMS (ESI) m/z: $(M + H)^+$ $C_{16}H_{16}NS$ calcd. 254.0998, found 254.0993.

*6-Methoxy-1-(2-(methylthio)phenyl)-1H-indole (**3t**).*



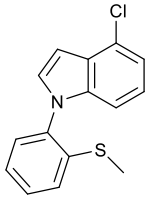
The reaction was carried out with 1.5 mmol of the corresponding 1*H*-indole derivative. Yellow liquid (256 mg, 65%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 98/2). IR (film, cm^{-1}): 2920, 1618, 1512, 1477, 1450, 1435, 1377, 1338, 1321, 1290, 1259, 1219, 1203, 1176, 1132, 1103, 1178, 1132, 1103, 1078, 1056, 1028. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.6 Hz, 1H), 7.40 – 7.28 (m, 2H), 7.25 – 7.15 (m, 2H), 7.04 (d, *J* = 4.3 Hz, 1H), 6.74 (dd, *J* = 9.1, 3.2 Hz, 1H), 6.54 (d, *J* = 3.2 Hz, 1H), 6.48 (d, *J* = 2.3 Hz, 1H), 3.68 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.6, 138.0, 137.6, 136.9, 128.6, 128.4, 127.7, 126.4, 125.4, 122.6, 121.4, 110.1, 102.8, 94.2 , 55.7, 15.1. HRMS (ESI) m/z: $(M + H)^+$ $C_{16}H_{16}NOS$ calcd. 270.0947, found 270.0941.

*7-Methyl-1-(2-(methylthio)phenyl)-1H-indole (**3u**).*



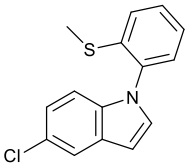
The reaction was carried out with 1.0 mmol of the corresponding 1*H*-indole derivative. White solid (100 mg, 40%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 99/1). mp: 128-129 °C; IR (film, cm^{-1}): 2922, 1583, 1519, 1483, 1475, 1454, 1332, 1282, 1244, 1220, 1163, 1138, 1058, 1037. ^1H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.9 Hz, 1H), 7.48 (m, 1H), 7.40 – 7.24 (m, 3H), 7.13 – 7.03 (m, 2H), 6.94 (d, *J* = 7.1 Hz, 1H), 6.70 (d, *J* = 3.2 Hz, 1H), 2.37 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.1, 138.6, 135.5, 129.5 (2 C), 129.1, 129.0, 124.4, 124.4, 124.3, 121.7, 120.3, 119.0, 103.0, 18.2, 14.4. HRMS (ESI) m/z: $(M + H)^+$ $C_{16}H_{16}NS$ calcd. 254.0998, found 254.0993.

*4-Chloro-1-(2-(methylthio)phenyl)-1H-indole (**3v**).*



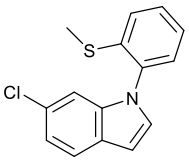
The reaction was carried out with 1.5 mmol of the corresponding 1*H*-indole derivative. Yellow liquid (245 mg, 60%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 99/1). IR (film, cm^{-1}): 2920, 1606, 1585, 1564, 1508, 1479, 1446, 1429, 1375, 1323, 1288, 1180, 1126, 1085, 1049, 1037. ^1H NMR (300 MHz, $CDCl_3$) δ 7.49 (m, 1H), 7.41 (m, 1H), 7.36 – 7.28 (m, 3H), 7.19 (m, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.83 (d, *J* = 3.2 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.1, 137.5, 136.3, 129.3, 129.1, 128.5, 127.2, 126.4, 126.2, 125.5, 122.7, 119.9, 109.3, 101.5, 15.1. HRMS (ESI) m/z: $(M + H)^+$ $C_{15}H_{13}ClNS$ calcd. 274.0452, found 274.0447.

*5-Chloro-1-(2-(methylthio)phenyl)-1H-indole (**3w**).*[5]



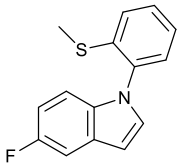
The reaction was carried out with 1.5 mmol of the corresponding 1*H*-indole derivative. Yellow liquid (308 mg, 75%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 99/1). IR (film, cm^{-1}): 2918, 1585, 1508, 1447, 1450, 1436, 1367, 1325, 1280, 1253, 1226, 1201, 1147, 1114, 1082, 1060, 1041. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.66 (d, *J* = 2.0 Hz, 1H), 7.53 – 7.37 (m, 2H), 7.35 – 7.31 (m, 1H), 7.31 – 7.24 (m, 2H), 7.14 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.01 (m, 1H), 6.65 (dd, *J* = 3.2, 0.9 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.0, 136.3, 135.2, 130.0, 129.4, 129.0, 128.4, 126.4, 125.9, 125.5, 122.4, 120.3, 111.6, 102.5, 15.1. HRMS (ESI) m/z: $(M + H)^+$ $C_{15}H_{13}ClNS$ calcd. 274.0452, found 274.0448.

*6-Chloro-1-(2-(methylthio)phenyl)-1H-indole (**3x**).*



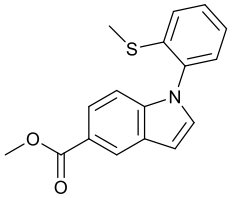
The reaction was carried out with 1.5 mmol of the corresponding 1*H*-indole derivative. White liquid (345 mg, 84%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 99/1). IR (film, cm^{-1}): 2920, 1697, 1606, 1585, 1506, 1477, 1460, 1436, 1334, 1319, 1271, 1228, 1207, 1139, 1116, 1082, 1055, 1037. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.4 Hz, 1H), 7.52 – 7.45 (m, 1H), 7.45 – 7.39 (m, 1H), 7.37 – 7.30 (m, 2H), 7.25 (d, *J* = 3.3 Hz, 1H), 7.18 – 7.09 (m, 2H), 6.69 (dd, *J* = 3.3, 0.9 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.1, 137.2, 136.1, 129.5, 129.1, 128.4, 128.2, 126.9, 126.4, 125.5, 121.7, 120.9, 110.6, 102.9, 15.1. HRMS (ESI) m/z: $(M + H)^+$ $C_{15}H_{13}ClNS$ calcd. 274.0452, found 274.0447.

*5-Fluoro-1-(2-(methylthio)phenyl)-1H-indole (**3y**).*[5]



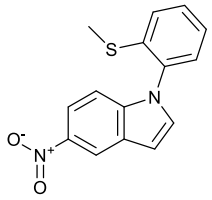
The reaction was carried out with 1.4 mmol of the corresponding 1*H*-indole derivative. Yellow solid (180 mg, 50%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 99/1). mp: 50-51 ^{o}C; IR (film, cm^{-1}): 2920, 1622, 1585, 1481, 1448, 1332, 1276, 1253, 1424, 1211, 1143, 1134, 1103, 1080, 1058, 1039. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.53 – 7.26 (m, 6H), 7.11 – 6.80 (m, 2H), 6.66 (d, *J* = 3.3 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.7 ((d, *J* = 233.2 Hz, C), 138.0, 136.5, 133.4, 130.3, 128.9, 128.7 (d, *J* = 10.5 Hz), 128.4, 126.3, 125.4, 111.3 (d, *J* = 9.7 Hz), 110.4 (d, *J* = 28.5 Hz), 105.6 (d, *J* = 22.5 Hz), 102.8 (d, *J* = 6 Hz), 15.1.^{19}F NMR (188 MHz, $CDCl_3$) δ -124.70. HRMS (ESI) m/z: $(M + H)^+$ $C_{15}H_{13}FNS$ calcd. 258.0747, found 258.0742.

*Methyl 1-(2-(methylthio)phenyl)-1H-indole-5-carboxylate (**3z**).*



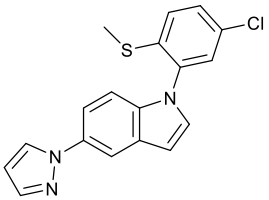
The reaction was carried out with 1.5 mmol of the corresponding 1*H*-indole derivative. Yellow liquid (351 mg, 79%); Rf = 0.4 (Cyclohexane/Ethyl acetate = 92/8). IR (film, cm^{-1}): 1705, 1610, 1514, 1483, 1433, 1330, 1298, 1271, 1251, 1224, 1114, 1082, 1037. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.80 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.43 – 7.34 (m, 1H), 7.30 (d, *J* = 6.6 Hz, 1H), 7.24 – 7.22 (m, 1H), 7.22 – 7.14 (m, 2H), 7.00 (d, *J* = 8.8 Hz, 1H), 6.70 (d, *J* = 3.2 Hz, 1H), 3.85 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.1, 139.2, 138.0, 136.2, 130.2, 129.2, 128.4, 127.9, 126.5, 125.5, 123.9, 123.5, 122.3, 110.3, 104.2, 51.8, 15.1. HRMS (ESI) m/z: $(M + H)^+$ $C_{17}H_{16}NO_2S$ calcd. 298.0896, found 298.0890.

*1-(2-(Methylthio)phenyl)-5-nitro-1H-indole (**3aa**).*



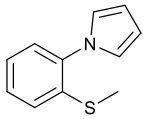
The reaction was carried out with 1.4 mmol of the corresponding 1*H*-indole derivative. Yellow solid (180 mg, 44%)*;* Rf = 0.3 (Cyclohexane/Ethyl acetate = 97/3). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.57 (d, *J* = 2.2 Hz, 1H), 8.00 (dd, *J* = 9.1, 2.2 Hz, 1H), 7.48 – 7.39 (m, 1H), 7.34 (s, 1H), 7.29 (d, *J* = 3.3 Hz, 1H), 7.28 – 7.21 (m, 2H), 7.01 (d, *J* = 9.0 Hz, 1H), 6.78 (d, *J* = 3.3 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.3, 139.6, 138.1, 135.4, 132.0, 129.7, 128.3, 127.6, 126.4, 125.6, 118.1, 117.8, 110.6, 105.1, 15.0. HRMS (ESI) m/z: $(M + H)^+$ $C_{15}H_{13}N_2O_2S$ calcd. 285.0692, found 285.0686.

*1-(5-Chloro-2-(methylthio)phenyl)-5-(1H-pyrazol-1-yl)-1H-indole (**3ab**).*



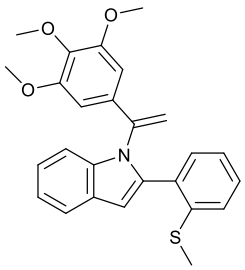
The reaction was carried out with 0.7 mmol of the corresponding 1*H*-indole derivative. White liquid (120 mg, 50%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 84/16). IR (film, cm^{-1}): 2922, 1571, 1556, 1514, 1481, 1452, 1433, 1394, 1338, 1315, 1290, 1263, 1220, 1188, 1151, 1120, 1101, 1045, 1026. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (m, 2H), 7.85 (dd, *J* = 1.9, 0.7 Hz, 1H), 7.67 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.54 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.49 (d, *J* = 2.2 Hz, 1H), 7.44 – 7.36 (m, 2H), 7.27 (m, 1H), 6.86 (m, 1H), 6.57 (m, 1H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.5, 137.3, 136.6, 135.3, 134.6, 130.9, 129.9, 129.0, 128.7, 128.5, 127.6, 127.3, 115.6, 112.1, 111.1, 106.9, 103.9, 15.3. HRMS (ESI) m/z: $(M + H)^+$ $C_{18}H_{15}N_3ClS$ calcd. 340.0670, found 340.0665.

*1-(2-(Methylthio)phenyl)-1H-pyrrole (**3ac**).*



The reaction was carried out with 1.7 mmol of the corresponding 1*H*-indole derivative. Yellow liquid (130 mg, 40%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 99/1). IR (film, cm^{-1}): 2918, 1720, 1585, 1490, 1438, 1325, 1247, 1116, 1076, 1066, 1041, 1014. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.32 (m, 2H), 7.31 – 7.23 (m, 2H), 6.90 (t, *J* = 2.1 Hz, 2H), 6.37 (t, *J* = 2.1 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.3, 135.9, 128.0, 126.9, 126.5, 125.4, 122.1 (2 C), 109.0 (2 C), 15.4. HRMS (ESI) m/z: $(M + H)^+$ $C_{11}H_{12}NS$ calcd. 190.0685, found 190.0682.

2-(2-(Methylthio)phenyl)-1-(1-(3,4,5-trimethoxyphenyl)vinyl)-1H-indole (**3ad**).

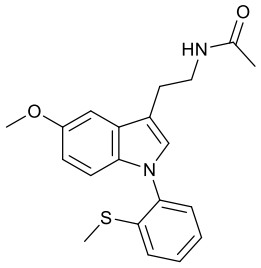


Under an argon atmosphere, a mixture of 2-(2-(methylthio)phenyl)-1*H*-indole (234 mg, 1.0 mmol, 1.0 equiv.), copper powder (6.3 mg, 0.1 mmol, 10 mol%), and potassium carbonate (208 mg, 1.5 mmol, 1.5 equiv.) in dry toluene (4 mL) was placed in a sealed reaction tube. This suspension was added *N,N'*-dimethylethylenediamine (DMEDA, 17.6 mg, 0.2 mmol, 20 mol%) followed by iodostyrene (481 mg, 1.5 mmol, 1.5 equiv.). The sealed tube was stirred at 135 °C for 16 hours. After cooling to room temperature, the crude mixture was concentrated under reduced pressure and purified by silica gel chromatography to afford product **3ad**.

Yellow solid (306 mg, 71%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 – 7.54 (m, 1H), 7.28 (d, *J* = 7.0 Hz, 1H), 7.15 – 7.06 (m, 4H), 7.02 – 6.87 (m, 2H), 6.67 (s, 1H), 6.16 (s, 2H), 5.55 (s, 1H),

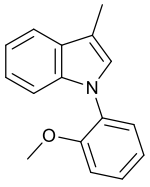
5.27 (s, 1H), 3.69 (s, 3H), 3.59 (s, 6H), 2.20 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.7 (2 C), 143.5, 139.4, 138.4, 138.0, 137.7, 133.5 , 131.2, 131.0 (CH), 128.5 (CH), 128.0 (C), 124.4 (CH), 123.5 (CH), 122.3 (CH), 120.7 (CH), 120.5 (CH), 111.8 (CH), 111.4 (2 CH), 106.0 (CH), 103.8 (2 CH), 60.8 (CH_3), 56.0 (2 CH_3), 15.7 (CH_3). HRMS (ESI) m/z: (M + H)+ $C_{26}H_{26}NO_3S$ calcd. 432.1628, found 432.1621.

*N-(2-(5-Methoxy-1-(2-(methylthio)phenyl)-1H-indol-3-yl)ethyl)acetamide (**3ae**).*



The reaction was carried out with 2.0 mmol of the corresponding 1*H*-indole derivative. Yellow liquid (527 mg, 75%); Rf = 0.3 (Ethyl acetate = 100%). IR (film, cm^{-1}): 2922, 1483, 1450, 1436, 1371, 1263, 1244, 1209, 1174, 1151, 1120, 1082, 1063, 1037. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (m, 1H), 7.29 – 7.24 (m, 1H), 7.23 – 7.15 (m, 2H), 7.03 (d, *J* = 2.4 Hz, 1H), 6.98 (s, 1H), 6.92 (d, *J* = 8.9 Hz, 1H), 6.76 (dd, *J* = 8.9, 2.4 Hz, 1H), 5.60 (s, 1H), 3.79 (s, 3H), 3.55 (s, 2H) 2.92 (t, *J* = 6.6 Hz, 2H), 2.22 (s, 3H), 1.86 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.9, 154.5, 137.6, 136.7, 132.5, 128.6, 128.2, 128.1, 127.3, 126.2, 125.4, 112.9, 112.5, 111.5, 100.7, 55.9, 39.4, 25.2, 23.4, 15.1. HRMS (ESI) m/z: $(M + H)^+$ $C_{20}H_{23}N_2O_2S$ calcd. 355.1475, found 355.1470.

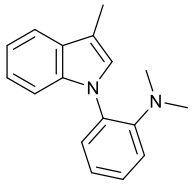
1-(2-Methoxyphenyl)-3-methyl-1H-indole (**3af**).



The reaction was carried out with 1.4 mmol of the corresponding 1H-indole derivative.

White oil (198 mg, 60%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 97/3). 1H NMR (300 MHz, $CDCl_3$) δ 7.58 – 7.47 (m, 1H), 7.34 – 7.20 (m, 2H), 7.12 – 7.03 (m, 3H), 7.02 – 6.94 (m, 3H), 3.69 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4, 137.0, 129.0, 128.5, 128.1, 127.8, 126.8, 121.8, 120.9, 119.3, 118.8, 112.5, 111.7, 110.8, 55.8, 9.7. HRMS (ESI) m/z: $(M + H)^+$ $C_{16}H_{16}NO$ calcd. 238.1226, found 238.1220.

N,N-Dimethyl-2-(3-methyl-1H-indol-1-yl)aniline (**3ag**).



The reaction was carried out with 3.1 mmol of the corresponding 1H-indole derivative. White oil (314 mg, 40%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 98/2). ^1H NMR (300 MHz, $CDCl_3$) δ 7.77 – 7.64 (m, 1H), 7.44 – 7.31 (m, 3H), 7.31 – 7.20 (m, 3H), 7.16 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.13 – 7.02 (m, 1H), 2.50 (d, *J* = 1.6 Hz, 6H), 1.54 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.9, 136.3, 130.5, 129.1, 128.7, 127.8, 126.1, 121.9, 120.8, 119.3, 118.7, 118.3, 112.1, 110.9, 41.9 (2 C), 9.8. HRMS (ESI) m/z: $(M + H)^+$ $C_{17}H_{19}N_2$ calcd. 251.1543, found 251.1538.

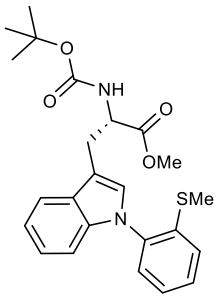
Preparation of compound (3ah).[6]

Preparation of tris(2-(methylthio)phenyl)bismuthane. A solution of (2-bromophenyl)(methyl)sulfane (1.26 g, 6.2 mmol, 3.1 equiv.) in 5 mL of THF was slowly added to a stirred suspension of magnesium (151 mg, 6.2 mmol, 3.1 equiv.) and iodine (406 mg, 1.6 mmol, 0.8 equiv.) in 15 mL of THF under Ar. The mixture was then heated for 3 h at 80 °C. $BiCl_3$ (631 mg, 2.0 mmol, 1.0 equiv.) dissolved in 10 mL of THF was slowly added in the reaction mixture at r.t. The reaction proceeded at 80 °C overnight. Then, the mixture was quenched with saturated ammonium chloride solution and extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in*

vacuo. The residue was purified by column chromatography to get crude product tris(2-(methylthio)phenyl)bismuthane. (Cyclohexane to Cyclohexane/Ethyl acetate = 8/2).

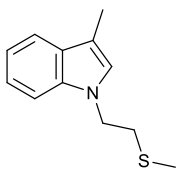
In a sealed tube under O_2, crude product tris(2-(methylthio)phenyl)bismuthane (405 mg, 0.7 mmol, 0.7 equiv.), Boc-Trp-OMe (318 mg, 1.0 mmol, 1.0 equiv.), copper (II) acetate (10 mol%), pyridine (1.0 equiv.) were solubilized in dry DCM (4 mL). The mixture was stirred at 50 °C overnight. The residue was purified by column chromatography (Cyclohexane to Cyclohexane/Ethyl acetate = 8/2) to afford the desired compound.

*Methyl N^{α}-(tert-butoxycarbonyl)-1-(2-(methylthio)phenyl)-L-tryptophanate (**3ah**)*.



Yellow liquid (120 mg, 30%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 88/12); $[\alpha]^{25}_{D}$ = + 0.016° (c =1, $CHCl_3$). IR (film, cm^{-1}): 2924, 1743, 1708, 1585, 1481, 1456, 1436, 1365, 1309, 1161, 1058, 1012. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.49 (m, 1H), 7.41 – 7.28 (m, 2H), 7.22 (ddd, *J* = 11.3, 7.3, 5.5 Hz, 2H), 7.15 – 7.05 (m, 2H), 7.01 (q, *J* = 3.0 Hz, 2H), 5.13 (d, *J* = 8.2 Hz, 1H), 4.86 – 4.39 (m, 1H), 3.62 (s, 3H), 3.30 (d, *J* = 5.3 Hz, 2H), 2.18 (s, 3H), 1.38 (s, 9H).^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6, 155.3, 137.8, 137.0, 136.7, 128.6, 128.4 (2 C), 128.2, 127.4, 126.7, 125.5, 122.4, 120.0, 118.9, 110.6, 79.7, 54.2, 52.2, 28.3 (3 C), 28.0, 15.2. HRMS (ESI) m/z: $(M + Na)^+$ $C_{24}H_{28}N_2O_4SNa$ calcd. 463.1662, found 463.1657.

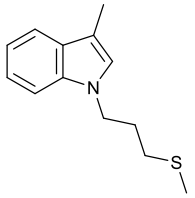
3-methyl-1-(2-(methylthio)ethyl)-1H-indole (**3ai**).



To a two-neck round-bottom flask were added indole (410 mg, 3.1 mmol, 1.0 equiv.), tetrabutylammonium hydrogen sulfate (42 mg, 0.12 mmol, 4 mol%), and sodium hydroxide (443 mg, 11.1 mmol, 3.6 equiv.). The flask was purged with nitrogen, followed by the addition of 2-chloroethyl methyl sulfide (340 µL, 3.3 mmol, 1.1 equiv.) and acetonitrile (7 mL). The reaction mixture was stirred at reflux for 16 h, then cooled to room temperature. The resulting precipitate was collected by vacuum filtration and washed with a small amount of acetonitrile. The crude product was purified by silica gel column chromatography (cyclohexane/EtOAc: 90/10) to afford the desired compound.

Yellow oil (100 mg, 16%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 97/3). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 – 7.63 (m, 1H), 7.46 – 7.38 (m, 1H), 7.38 – 7.27 (m, 1H), 7.27 – 7.17 (m, 1H), 6.99 (q, *J* = 1.1 Hz, 1H), 4.48 – 4.05 (m, 2H), 3.01 – 2.85 (m, 2H), 2.44 (d, *J* = 1.1 Hz, 3H), 2.13 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.1, 129.0, 125.4, 121.6, 119.2, 110.7, 118.8, 108.9, 46.0, 34.3, 15.8, 9.6. HRMS (ESI) m/z: $(M + H)^+$ $C_{12}H_{16}NS$ calcd. 206.0998, found 206.0995.

3-methyl-1-(3-(methylthio)propyl)-1H-indole (**3aj**).



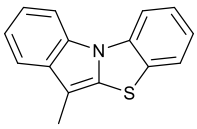
3-methyl-1*H*-indole (417 mg, 3.2 mmol, 1.0 equiv.) was solubilized in dry DMF (13 mL). NaH (60% dispersion in mineral oil, 115 mg, 3.2 mmol, 1.0 equiv.) was added to the reaction mixture at 0 °C, and the yellow solution was stirred at 0 °C under argon for 30 mins. A solution of (3-bromopropyl)(methyl)sulfane (531 mg, 3.2 mmol, 1.0 equiv.) in dry DMF (3 mL) and NaI (48 mg, 0.32 mmol, 0.1 equiv.) were incorporated. The solution was stirred at room temperature under argon for 48 h and quenched with water. The crude mixture was then extracted three times with ethyl acetate. The organic phase was washed

with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was then purified by chromatography on silica gel, with cyclohexane/EtOAc (0 to 80/20) as eluents. Pink oil (604 mg, 86%); Rf = 0.66 (Cyclohexane/Ethyl acetate = 9/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.40 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.31 – 7.23 (m, 1H), 7.17 (ddd, *J* = 7.9, 7.0, 1.0 Hz, 1H), 6.95 (q, *J* = 1.1 Hz, 1H), 4.26 (t, *J* = 6.7 Hz, 2H), 2.51 (t, *J* = 6.7 Hz, 2H), 2.40 (d, *J* = 1.1 Hz, 3H), 2.19 – 2.11 (m, 5H).^{13}C NMR (101 MHz, $CDCl_3$) δ 136.4, 128.9, 125.6, 121.5, 119.2, 118.7, 110.5, 109.2, 44.4, 31.4, 29.4, 15.6, 9.7.

Preparation of benzo[4,5]thiazolo[3,2-*a*]indole derivatives (4)

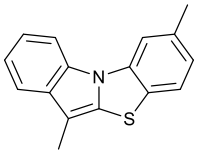
In a sealed tube under air, indole derivatives (0.2 mmol, 1.0 equiv.) were solubilized in dry acetonitrile (0.8 mL). PIFA (0.4 mmol, 2.0 equiv.) was added. The mixture was stirred at room temperature for 15 min. Then, the mixture was quenched with saturated sodium thiosulfate solution and extracted with EtOAc. The combined organic layers were dried with Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (Cyclohexane to Cyclohexane/Ethyl acetate = 8/2).

11-Methylbenzo[4,5]thiazolo[3,2-a]indole (**4a**).[7]



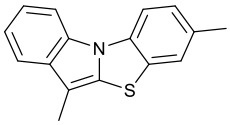
Yellow solid (36 mg, 74%); Rf = 0.5 (Cyclohexane/Ethyl acetate = 99/1). mp: 76-77 °C; IR (film, cm^{-1}): 2916, 2852, 1587, 1566, 1479, 1473, 1448, 1400, 1381, 1340, 1313, 1296, 1255, 1222, 1192, 1147, 1134, 1118, 1093, 1049, 1026, 1010. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 – 7.91 (m, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.68 – 7.53 (m, 2H), 7.42 (m, 1H), 7.36 – 7.26 (m, 2H), 7.20 (m, 1H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.3, 133.2, 132.9, 131.1, 130.5, 125.9, 123.7, 122.5, 120.9, 120.3, 117.9, 111.7, 110.8, 101.3, 9.3. HRMS (ESI) m/z: $(M + H)^+$ $C_{15}H_{12}NS$ calcd. 238.0685, found 238.0678.

*7,11-Dimethylbenzo[4,5]thiazolo[3,2-a]indole (**4b**).*



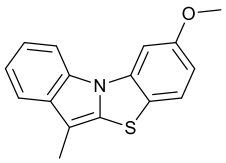
White solid (35 mg, 70%); Rf = 0.5 (Cyclohexane/Ethyl acetate = 99/1). mp: 126-127 °C; IR (film, cm^{-1}): 2912, 1600, 1585, 1483, 1471, 1448, 1406, 1375, 1338, 1298, 1232, 1213, 1193, 1163, 1141, 1130, 1097, 1047, 1014. ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.03 – 7.88 (m, 1H), 7.78 – 7.53 (m, 2H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.22 (m, 2H), 7.01 (d, *J* = 8.0 Hz, 1H), 2.53 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.4, 136.2, 133.5, 133.2, 131.1, 127.1, 123.4, 123.2, 120.8, 120.1, 117.8, 112.5, 110.8, 101.2, 21.7, 9.3. HRMS (ESI) m/z: $(M + H)^+$ $C_{16}H_{14}NS$ calcd. 252.0841, found 252.0833.

*8,11-Dimethylbenzo[4,5]thiazolo[3,2-a]indole (**4c**).*



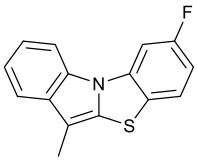
White solid (37 mg, 73%); Rf = 0.5 (Cyclohexane/Ethyl acetate = 99/1). mp: 109-110 °C; IR (film, cm^{-1}): 1570, 1490, 1450, 1383, 1338, 1317, 1288, 1261, 1228, 1195, 1093, 1045, 1012. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 – 7.88 (m, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.66 – 7.58 (m, 1H), 7.39 (s, 1H), 7.32 – 7.26 (m, 2H), 7.20 (d, *J* = 8.2 Hz, 1H), 2.45 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.2, 133.0, 132.3, 130.9 (2 C), 130.5, 126.7, 124.0, 120.6, 120.1 117.8, 111.3, 110.6, 101.1, 21.1, 9.3. HRMS (ESI) m/z: $(M + H)^+$ $C_{16}H_{14}NS$ calcd. 252.0841, found 252.0836.

*7-Methoxy-11-methylbenzo[4,5]thiazolo[3,2-a]indole (**4d**).*



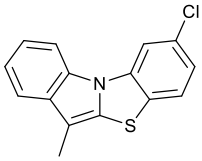
Yellow solid (38 mg, 72%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 98/2). mp: 62-63 °C; IR (film, cm^{-1}): 2854, 1597, 1585, 1568, 1477, 1442, 1377, 1334, 1311, 1301, 1263, 1234, 1190, 1165, 1147, 1130, 1095, 1056, 1028, 1012. ^1H NMR (300 MHz, $CDCl_3$) δ 7.95 – 7.58 (m, 1H), 7.59 – 7.43 (m, 1H), 7.43 – 7.30 (m, 2H), 7.30 – 7.07 (m, 2H), 6.68 (dd, *J* = 8.7, 2.4 Hz, 1H), 3.85 (s, 3H), 2.28 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 137.2, 134.2, 133.3 , 131.0, 123.8, 121.6, 121.0, 120.2, 117.8, 110.7, 108.1, 101.4, 99.1, 55.9, 9.3. HRMS (ESI) m/z: $(M + H)^+$ $C_{16}H_{14}NOS$ calcd. 268.0791, found 268.0782.

*7-Fluoro-11-methylbenzo[4,5]thiazolo[3,2-a]indole (**4e**).*



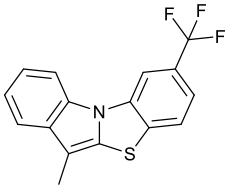
White solid (34 mg, 67%); Rf = 0.5 (Cyclohexane/Ethyl acetate = 99/1). mp: 135-136 °C; IR (film, cm^{-1}): 1608, 1593, 1440, 1375, 1309, 1251, 1230, 1207, 1161, 1145, 1120, 1091, 1061. ^1H NMR (300 MHz, $CDCl_3$) δ 7.71 – 7.62 (m, 1H), 7.50 – 7.40 (m, 1H), 7.37 (dd, *J* = 9.3, 2.4 Hz, 1H), 7.30 (dd, *J* = 8.6, 5.1 Hz, 1H), 7.20 – 7.12 (m, 2H), 6.76 (m, 1H), 2.22 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.6 (d, *J* = 242.2 Hz), 136.8 (d, *J* = 11.2 Hz), 133.7, 133.3, 130.9, 125.3 (d, *J* = 3.0 Hz), 123.9 (d, *J* = 9.8 Hz), 121.3, 120.5, 117.9, 110.6, 109.3 (d, *J* = 24.0 Hz), 101.9, 100.0 (d, *J* = 28.5 Hz), 9.2. ^{19}F NMR (188 MHz, $CDCl_3$) δ -115.15. HRMS (ESI) m/z: $(M + H)^+$ $C_{15}H_{11}NFS$ calcd. 256.0591, found 256.0582.

*7-Chloro-11-methylbenzo[4,5]thiazolo[3,2-a]indole (**4f**)*.



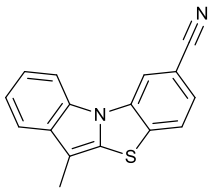
White solid (37 mg, 68%); Rf = 0.5 (Cyclohexane/Ethyl acetate = 99/1). mp: 160-161 ^{o}C; IR (film, cm^{-1}): 1587, 1483, 1294, 1220, 1080. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 – 7.78 (m, 1H), 7.75 (d, *J* = 1.9 Hz, 1H), 7.64 – 7.52 (m, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.34 – 7.25 (m, 2H), 7.13 (dd, *J* = 8.4, 1.9 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.9, 133.3, 133.0, 131.8, 130.9, 128.8, 123.9, 122.4, 121.3, 120.6, 118.0, 111.9, 110.7, 102.0, 9.2. HRMS (ESI) m/z: $(M + H)^+$ $C_{15}H_{11}NClS$ calcd. 272.0295, found 272.0290.

*11-Methyl-7-(trifluoromethyl)benzo[4,5]thiazolo[3,2-a]indole (**4g**).*



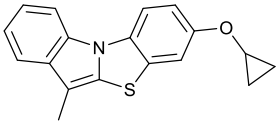
White solid (34 mg, 55%); Rf = 0.5 (Cyclohexane/Ethyl acetate = 99/1). mp: 133-134 ^{o}C; IR (film, cm^{-1}): 1600, 1585, 1477, 1323, 1313, 1259, 1222, 1165, 1139, 1111, 1070, 1012. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.93 – 7.83 (m, 1H), 7.68 – 7.55 (m, 2H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.38 – 7.30 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.3, 134.9, 133.3, 132.3, 130.9, 128.5 (q, *J* = 33 Hz), 124.1 (q, *J* = 271 Hz), 123.6, 121.5, 120.9, 119.2 (q, *J* = 4 Hz), 118.2, 110.7, 108.0 (q, *J* = 4 Hz), 102.4, 9.2. ^{19}F NMR (188 MHz, $CDCl_3$) δ -61.84. HRMS (ESI) m/z: $(M + H)^+$ $C_{16}H_{11}NF_3S$ calcd. 306.0559, found 306.0555.

*11-Methylbenzo[4,5]thiazolo[3,2-a]indole-7-carbonitrile (**4h**).*



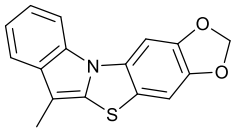
Yellow solid (31 mg, 58%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 94/6). mp: 202-203 °C; IR (film, cm^{-1}): 2227, 1712, 1581, 1486, 1469, 1456, 1438, 1381, 1371, 1332, 1300, 1267, 1230, 1205, 1165, 1141, 1093, 1047. ^1H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 1.5 Hz, 1H), 7.81 – 7.70 (m, 1H), 7.59 – 7.47 (m, 2H), 7.34 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.30 – 7.22 (m, 2H), 2.28 (3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.7, 136.4, 133.4 (2 C), 130.9, 126.0, 123.9, 121.8, 121.4, 118.7, 118.4, 113.8, 110.7, 109.4, 102.9, 9.2. HRMS (ESI) m/z: $(M + H)^+$ $C_{16}H_{11}N_2S$ calcd. 263.0637, found 263.0630.

*8-Cyclopropoxy-11-methylbenzo[4,5]thiazolo[3,2-a]indole (**4i**).*



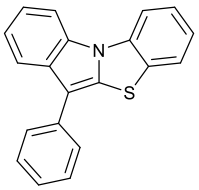
White solid (37 mg, 63%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 99/1). mp: 145-146 °C; IR (film, cm^{-1}): 1560, 1489, 1436, 1335, 1272, 1224, 1215, 1197, 1132, 1086. ^1H NMR (300 MHz, $CDCl_3$) δ 7.99 – 7.84 (m, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.70 – 7.57 (m, 1H), 7.39 – 7.22 (m, 3H), 7.10 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.82 (q, *J* = 4.5 Hz, 1H), 2.41 (d, *J* = 0.7 Hz, 3H), 1.03 – 0.55 (m, 4H).^{13}C NMR (75 MHz, $CDCl_3$) δ 154.9, 132.9, 132.7, 131.6, 130.8 (2 C), 120.5, 120.1, 117.9, 113.1, 111.8, 110.3 (2 C), 101.1, 51.4, 9.3, 6.3 (2 C). HRMS (ESI) m/z: $(M + H)^+$ $C_{18}H_{16}NOS$ calcd. 294.0953, found 294.0949.

*6-Methyl-[1,3]dioxolo[4'',5'':4',5']benzo[1',2':4,5]thiazolo[3,2-a]indole (**4j**).*



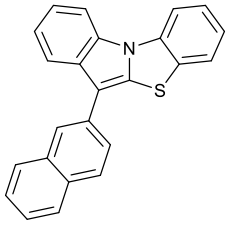
White solid (34 mg, 60%); Rf = 0.5 (Cyclohexane/Ethyl acetate = 96/4). mp: 187-188 ^{o}C; IR (film, cm^{-1}): 1500, 1458, 1247, 1215, 1176, 1120, 1085, 1039, 1001. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 – 7.70 (m, 1H), 7.58 – 7.44 (m, 1H), 7.36 (s, 1H), 7.23 – 7.18 (m, 1H), 7.18 – 7.13 (m, 1H), 6.95 (s, 1H), 5.96 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.8 , 143.6, 133.7, 132.7, 130.6, 121.4, 120.6, 119.9, 117.8, 110.3, 104.1, 101.8, 101.0, 97.4, 94.6, 9.2. HRMS (ESI) m/z: $(M + H)^+$ $C_{16}H_{12}NO_2S$ calcd. 282.0583, found 282.0581.

*11-Phenylbenzo[4,5]thiazolo[3,2-a]indole (**4k**).*



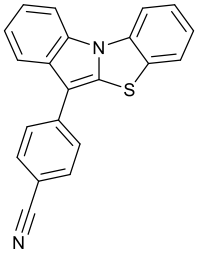
White solid (41 mg, 68%); Rf = 0.5 (Cyclohexane/Ethyl acetate = 99/1). mp: 163-164 ^{o}C; IR (film, cm^{-1}): 1585, 1541, 1479, 1446, 1384, 1300, 1242, 1174. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 – 8.03 (m, 2H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 2H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.52 (m, 3H), 7.42 – 7.30 (m, 3H), 7.26 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.8 , 134.6, 134.1, 131.8, 130.8, 129.9, 129.1 (2 C), 126.8 (2 C), 126.3, 125.8, 123.7 , 123.2, 121.9, 121.0, 119.1, 112.1 , 111.2, 107.6. HRMS (ESI) m/z: $(M + H)^+$ $C_{20}H_{14}NS$ calcd. 300.0841, found 300.0834.

*11-(Naphthalen-2-yl)benzo[4,5]thiazolo[3,2-a]indole (**4l**).*



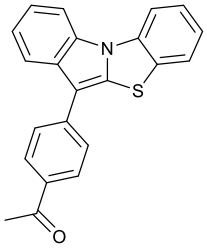
White solid (46 mg, 66%); Rf = 0.5 (Cyclohexane/Ethyl acetate = 99/1). mp: 129-130 ^{o}C; IR (film, cm^{-1}): 3051, 1627, 1587, 1535, 1475, 1446, 1300, 1234, 1193, 1166, 1031. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 – 7.98 (m, 2H), 7.97 – 7.89 (m, 1H), 7.90 – 7.74 (m, 5H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.46 – 7.32 (m, 3H), 7.31 – 7.21 (m, 2H), 7.13 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.9, 134.5, 134.1, 132.2 , 131.9, 131.9, 130.9, 129.9, 128.6, 127.8, 127.7, 126.3 (2 C), 125.5, 125.4, 124.9, 123.7, 123.3, 122.1, 121.1, 119.1, 112.2, 111.3, 107.7. HRMS (ESI) m/z: $(M + H)^+$ $C_{24}H_{16}NS$ calcd. 350.0998, found 350.0996.

*4-(Benzo[4,5]thiazolo[3,2-a]indol-11-yl)benzonitrile (**4m**).*



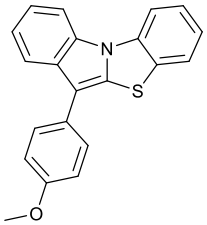
Yellow solid (42 mg, 65%); Rf = 0.4 (Cyclohexane/Ethyl acetate = 90/10). mp: 223-224 ^{o}C; IR (film, cm^{-1}): 1708, 1602, 1527, 1473, 1357, 1220. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 – 7.89 (m, 3H), 7.87 – 7.56 (m, 5H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.42 – 7.11 (m, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 139.7, 135.5, 132.8 (2 C), 132.1, 130.2, 129.5, 127.4, 126.7, 126.6 (2 C), 123.8 , 123.8, 122.6, 121.7, 119.4, 118.8, 112.5, 111.5, 108.2, 106.1. HRMS (ESI) m/z: $(M + H)^+$ $C_{21}H_{13}N_2S$ calcd. 325.0794, found 325.0792.

*1-(4-(Benzo[4,5]thiazolo[3,2-a]indol-11-yl)phenyl)ethan-1-one (**4n**).*



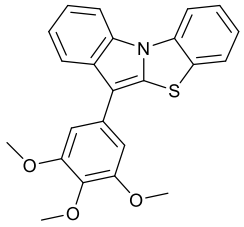
Yellow solid (42 mg, 61%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 88/12). mp: 213-214 °C; IR (film, cm^{-1}): 1672, 1598, 1537, 1494, 1479, 1448, 1271, 1172. ^1H NMR (300 MHz, $CDCl_3$) δ 8.18 – 7.96 (m, 5H), 7.91 – 7.79 (m, 2H), 7.71 – 7.62 (m, 1H), 7.57 – 7.44 (m, 1H), 7.43 – 7.35 (m, 2H), 7.34 – 7.27 (m, 1H), 2.66 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 197.3, 139.8, 135.6, 134.1 (2 C), 132.1, 130.5, 129.7, 129.3 (2 C), 126.5, 126.2 (2 C), 123.8, 123.6, 122.4, 121.5, 119.1, 112.4, 111.4, 106.8, 26.5. HRMS (ESI) m/z: $(M + H)^+$ $C_{22}H_{16}NOS$ calcd. 342.0947, found 342.0943.

*11-(4-Methoxyphenyl)benzo[4,5]thiazolo[3,2-a]indole (**4o**).*



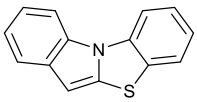
White solid (41 mg, 62%); Rf = 0.5 (Cyclohexane/Ethyl acetate = 96/4). mp: 135-136 °C; IR (film, cm^{-1}): 1585, 1546, 1504, 1479, 1471, 1446, 1384, 1300, 1284, 1238, 1199, 1180, 1029. ^1H NMR (300 MHz, $CDCl_3$) δ 7.96 – 7.81 (m, 3H), 7.64 – 7.55 (m, 2H), 7.52 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.40 – 7.31 (m, 1H), 7.29 – 7.21 (m, 2H), 7.16 – 7.10 (m, 1H), 7.02 – 6.94 (m, 2H), 3.80 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.8 , 135.9, 133.2, 131.7, 130.9, 129.9, 128.1 (2 C), 127.0, 126.2, 123.7, 123.1, 121.8, 120.8, 118.9, 114.6 (2 C), 112.0, 111.1, 107.4 , 55.4. HRMS (ESI) m/z: $(M + H)^+$ $C_{21}H_{16}NOS$ calcd. 330.0947, found 330.0952.

*11-(3,4,5-Trimethoxyphenyl)benzo[4,5]thiazolo[3,2-a]indole (**4p**).*



White solid (55 mg, 71%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 90/10). mp: 147-148 °C; IR (film, cm^{-1}): 1585, 1446, 1413, 1384, 1355, 1305, 1224, 1180, 1122, 1004. ^1H NMR (300 MHz, $CDCl_3$) δ 8.00 – 7.85 (m, 3H), 7.55 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.44 – 7.34 (m, 1H), 7.33 – 7.23 (m, 2H), 7.19 (dd, *J* = 7.7, 1.1 Hz, 1H), 6.90 (s, 2H), 3.89 (s, 6H), 3.86 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 153.8 (2 C), 136.4, 135.9, 133.9, 131.8, 130.7, 130.2, 129.8, 126.4, 123.7, 123.3, 122.0, 121.1, 118.9, 112.2, 111.3, 107.8, 104.1 (2 C), 61.0, 56.3 (2 C). HRMS (ESI) m/z: $(M + H)^+$ $C_{23}H_{20}NO_3S$ calcd. 390.1158, found 390.1150.

Benzo[4,5]thiazolo[3,2-a]indole (**4q**).[7]

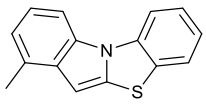


White solid (31 mg, 70%); Rf = 0.5 (Cyclohexane/Ethyl acetate = 99/1). mp: 116-117 °C; IR (film, cm^{-1}): 3064, 3047, 1585, 1544, 1514, 1481, 1469, 1442, 1404, 1379, 1359, 1338, 1311, 1298, 1257, 1222, 1192, 1153, 1134, 1120, 1068, 1026, 1012. ^1H NMR (300 MHz, $CDCl_3$) δ 8.11 – 7.90 (m, 2H), 7.78 – 7.57 (m, 2H), 7.47 (td, *J* = 7.8, 1.2 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.24 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.60 (s, 1H).^{13}C NMR (75 MHz, $CDCl_3$) δ 136.3 , 135.9, 133.4, 131.2, 130.5, 126.0, 123.6, 122.9, 121.5, 120.4, 120.0, 111.9, 110.9, 93.1. HRMS (ESI) m/z: $(M + H)^+$ $C_{14}H_{10}NS$ calcd. 224.0534, found 224.0525.

Gram-scale reaction of 4q: In a sealed tube under air, the corresponding indole derivative (1.2 g, 5 mmol, 1.0 equiv.) were solubilized in dry acetonitrile (18 mL). PIFA (2.0 equiv.) was added. The mixture was stirred at room temperature for 15 min. Then, the mixture was quenched with saturated sodium thiosulfate solution and extracted with EtOAc. The

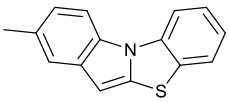
combined organic layers were dried with Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (Cyclohexane to Cyclohexane/Ethyl acetate = 8/2) to obtain the expected product as a white solid (792 mg, 71%).

1-Methylbenzo[4,5]thiazolo[3,2-a]indole (**4r**).[7]



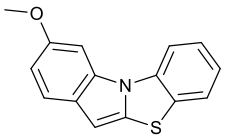
White solid (34 mg, 72%); Rf = 0.5 (Cyclohexane/Ethyl acetate = 99/1). mp: 126-127 °C; IR (film, cm^{-1}): 1514, 1490, 1469, 1286, 1247. ^1H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.35 – 7.19 (m, 2H), 7.13 (d, *J* = 7.3 Hz, 1H), 6.62 (s, 1H), 2.64 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.1, 135.7, 133.3, 131.0, 130.8, 129.5, 126.1, 123.7, 123.1, 121.9, 120.7, 112.1, 108.7, 91.8, 19.0. HRMS (ESI) m/z: $(M + H)^+$ $C_{15}H_{12}NS$ calcd. 238.0685, found 238.0680.

2-Methylbenzo[4,5]thiazolo[3,2-a]indole (**4s**).[7]



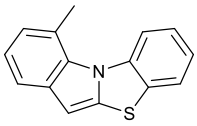
White solid (31 mg, 65%); Rf = 0.5 (Cyclohexane/Ethyl acetate = 99/1). mp: 94-95 °C; IR (film, cm^{-1}): 2920, 1581, 1519, 1508, 1481, 1458, 1381, 1336, 1292, 1263, 1234, 1192, 1161, 1124, 1066, 1039, 1022. ^1H NMR (300 MHz, $CDCl_3$) δ 7.99 – 7.77 (m, 2H), 7.59 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.49 – 7.36 (m, 2H), 7.21 (td, *J* = 7.7, 1.1 Hz, 1H), 7.11 (dd, *J* = 8.3, 1.7 Hz, 1H), 6.49 (d, *J* = 0.8 Hz, 1H), 2.52 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.2, 135.9, 133.7, 130.9, 130.5, 129.5, 125.9, 123.5, 122.7, 121.9, 119.8, 111.8, 110.5 , 92.7, 21.5. HRMS (ESI) m/z: $(M + H)^+$ $C_{15}H_{12}NS$ calcd. 238.0685, found 238.0680.

3-Methoxybenzo[4,5]thiazolo[3,2-a]indole (**4t**).[7]



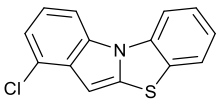
Yellow oil (35 mg, 69%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 99/1). IR (film, cm^{-1}): 1618, 1587, 1517, 1475, 1442, 1292, 1261, 1246, 1205, 1153, 1111, 1031. ^1H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 1H), 7.53 – 7.37 (m, 3H), 7.37 – 7.28 (m, 1H), 7.12 (t, *J* = 7.7 Hz, 1H), 6.87 (dd, *J* = 8.3, 2.6 Hz, 1H), 6.39 (s, 1H), 3.87 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.1 , 135.8, 134.5, 131.6, 130.7, 127.6, 125.8, 123.6, 122.9, 120.4, 111.8, 110.3, 96.1, 92.8, 56.0. HRMS (ESI) m/z: $(M + H)^+$ $C_{15}H_{12}NOS$ calcd. 254.0634, found 254.0629.

*4-Methylbenzo[4,5]thiazolo[3,2-a]indole (**4u**).*



White solid (24 mg, 50%); Rf = 0.5 (Cyclohexane/Ethyl acetate = 99/1). mp: 82-83 °C; IR (film, cm^{-1}): 1585, 1537, 1483, 1456, 1396, 1373, 1344, 1296, 1286, 1261, 1231, 1174, 1147, 1105, 1089, 1072, 1029. ^1H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.4 Hz, 1H), 7.56 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.34 (m, 1H), 7.22 – 7.14 (m, 2H), 7.05 – 6.99 (m, 1H), 6.59 (s, 1H), 3.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 137.1, 134.7, 132.3, 130.6, 125.6, 124.3, 123.9, 123.0, 122.2, 121.6, 117.8, 114.4, 94.5, 24.9. HRMS (ESI) m/z: $(M + H)^+$ $C_{15}H_{12}NS$ calcd. 238.0685, found 238.0680.

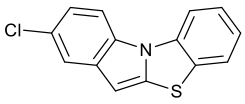
*1-Chlorobenzo[4,5]thiazolo[3,2-a]indole (**4v**).*[7]



White solid (39 mg, 75%); Rf = 0.5 (Cyclohexane/Ethyl acetate = 99/1). mp: 149-150 °C; IR (film, cm^{-1}): 1583, 1508, 1479, 1431, 1396, 1315, 1236, 1172. ^1H NMR (300 MHz, $CDCl_3$)

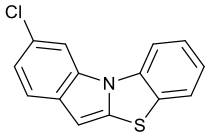
δ 8.00 – 7.80 (m, 2H), 7.61 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.53 – 7.38 (m, 1H), 7.36 – 7.06 (m, 3H), 6.68 (d, *J* = 0.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.2, 135.5, 131.8, 131.6, 130.6, 126.2, 124.7, 123.8, 123.5, 121.2, 120.9, 112.2, 109.4, 91.7. HRMS (ESI) m/z: $(M + H)^+$ $C_{14}H_9NClS$ calcd. 258.0139, found 258.0135.

*2-Chlorobenzo[4,5]thiazolo[3,2-a]indole (**4w**).*[7]



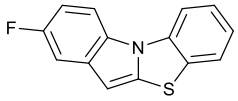
White solid (36 mg, 70%); Rf = 0.5 (Cyclohexane/Ethyl acetate = 99/1). mp: 132-133 °C; IR (film, cm^{-1}): 1581, 1516, 1477, 1458, 1444, 1219, 1190, 1064. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 8.9, 3.9 Hz, 2H), 7.58 – 7.46 (m, 2H), 7.42 – 7.28 (m, 1H), 7.18 – 7.11 (m, 2H), 6.42 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.9, 135.5, 134.3, 130.4, 129.4, 127.2, 126.1, 123.7, 123.3, 120.5, 119.4, 111.9, 111.5, 92.7. HRMS (ESI) m/z: $(M + H)^+$ $C_{14}H_9NClS$ calcd. 258.0139, found 258.0133.

3-Chlorobenzo[4,5]thiazolo[3,2-a]indole (**4x**).[7]



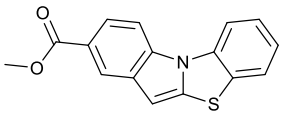
White solid (33 mg, 63%); Rf = 0.5 (Cyclohexane/Ethyl acetate = 99/1). mp: 161-162 °C; IR (film, cm^{-1}): 1583, 1510, 1479, 1465, 1286, 1220, 1112. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.58 (dd, *J* = 14.2, 8.1 Hz, 2H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.31 – 7.24 (m, 2H), 6.54 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.9, 135.3, 131.7, 131.1, 130.5, 126.2, 126.1, 123.7, 123.4, 122.0, 120.6, 112.0, 110.9, 93.1. HRMS (ESI) m/z: $(M + H)^+$ $C_{14}H_9NClS$ calcd. 258.0139, found 258.0133.

*2-Fluorobenzo[4,5]thiazolo[3,2-a]indole (**4y**).*[7]



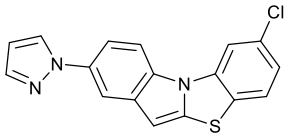
White solid (32 mg, 65%); Rf = 0.5 (Cyclohexane/Ethyl acetate = 99/1). mp: 116-117 ^{o}C; IR (film, cm^{-1}): 1583, 1479, 1454, 1249, 1190, 1155, 1097. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 – 7.83 (m, 2H), 7.64 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.47 (td, *J* = 7.9, 1.2 Hz, 1H), 7.40 – 7.20 (m, 2H), 7.04 (td, *J* = 9.0, 2.5 Hz, 1H), 6.56 (d, *J* = 0.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.2, 157.1, 136.8 (d, *J* = 186 Hz), 134.0 (d, *J* = 10.5 Hz), 130.3, 127.8, 126.1, 123.7, 123.1, 111.6, 111.3 (d, *J* = 9.7 Hz), 108.3 (d, *J* = 26.2 Hz), 105.2 (d, *J* = 24 Hz), 93.1 (d, *J* = 4.5 Hz). ^{19}F NMR (188 MHz, $CDCl_3$) δ -121.76. HRMS (ESI) m/z: $(M + H)^+$ $C_{14}H_9NFS$ calcd. 242.0434, found 242.0429.

*Methyl benzo[4,5]thiazolo[3,2-a]indole-2-carboxylate (**4z**).*



White solid (35 mg, 62%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 92/8). mp: 138-139 ^{o}C; IR (film, cm^{-1}): 1708, 1585, 1481, 1298, 1265, 1209, 1126, 1086. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.92 – 7.82 (m, 3H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 6.55 (s, 1H), 3.88 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.8, 137.7, 135.3, 133.2, 132.8, 130.7, 126.2, 123.8, 123.7, 123.3, 122.5, 121.7, 112.3, 110.4, 94.2, 51.9. HRMS (ESI) m/z: $(M + H)^+$ $C_{16}H_{12}NO_2S$ calcd. 282.0583, found 282.0585.

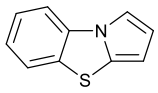
*7-Chloro-2-(1H-pyrazol-1-yl)benzo[4,5]thiazolo[3,2-a]indole (**4ab**).*



White solid (40 mg, 62%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 96/4). mp: 205-206 ^{o}C; IR (film, cm^{-1}): 1710, 1359, 1220. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 1.8 Hz, 1H), 7.96

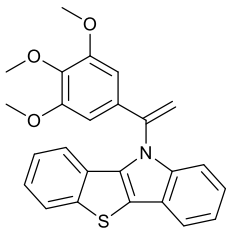
– 7.91 (m, 2H), 7.88 (d, *J* = 1.8 Hz, 1H), 7.76 (d, *J* = 1.1 Hz, 1H), 7.64 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.22 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.61 (s, 1H), 6.53 – 6.46 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9, 138.3, 136.4, 135.6, 133.9, 132.3, 129.6, 129.0, 127.4, 124.3, 123.4, 113.4, 112.4, 111.4, 111.0, 107.5, 94.3. HRMS (ESI) m/z: $(M + H)^+$ $C_{17}H_{11}N_3ClS$ calcd. 324.0357, found 324.0353.

*Benzo[d]pyrrolo[2,1-b]thiazole (**4ac**).*



Yellow liquid (22 mg, 64%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 99/1). mp: 54-55 °C; IR (film, cm^{-1}): 1481, 1460, 1375, 1323, 1300, 1251, 1134, 1018. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 6.4 Hz, 1H), 7.45 (dd, *J* = 2.9, 1.3 Hz, 1H), 7.35 (m, 1H), 7.22 (m, 1H), 6.64 – 6.57 (m, 1H), 6.24 (dd, *J* = 3.6, 1.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.7, 131.7, 127.8, 125.5, 123.9, 123.8, 114.9, 111.7, 110.4, 98.9. HRMS (ESI) m/z: $(M + H)^+$ $C_{10}H_8NS$ calcd. 174.0372, found 174.0370.

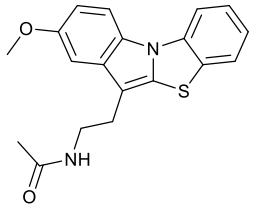
10-(1-(3,4,5-Trimethoxyphenyl)vinyl)-10H-benzo[4,5]thieno[3,2-b]indole (**4ad**).



White solid (59 mg, 71%); IR (film, cm-1): 2920, 1583, 1510, 1479, 1456, 1435, 1328, 1305, 1255, 1228, 1211, 1136, 1111, 1080, 1056, 1037, 1008, 883, 773, 742, 717, 665, 613. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 6.9, 1.5 Hz, 1H), 7.76 – 7.68 (m, 1H), 7.64 (dd, *J* = 7.2, 2.2 Hz, 1H), 7.22 – 7.11 (m, 5H), 6.51 (s, 2H), 6.01 (s, 1H), 5.48 (s, 1H), 3.76 (s, 3H), 3.59 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6 (2 C), 143.2, 143.0, 142.7, 139.4, 137.7, 132.0, 126.8, 124.2, 124.1, 124.0, 123.4, 122.3, 120.8, 120.5, 119.2, 117.2, 112.4, 112.1 (2

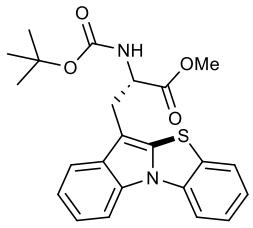
C), 103.6 (2 C), 60.9, 56.2 (2 C). HRMS (ESI) m/z: $(M + H)^+$ $C_{25}H_{22}NO_3S$ calcd. 416.1315, found 416.1310.

*N-(2-(2-Methoxybenzo[4,5]thiazolo[3,2-a]indol-11-yl)ethyl)acetamide (**4ae**).*



Yellow solid (47 mg, 70%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 20/80). mp: 138-139 °C; IR (film, cm^{-1}): 1710, 1361, 1267, 1222. ^1H NMR (300 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.9, 1.8 Hz, 2H), 7.64 – 7.51 (m, 1H), 7.49 – 7.35 (m, 1H), 7.21 (td, *J* = 7.6, 1.1 Hz, 1H), 7.07 (d, *J* = 2.5 Hz, 1H), 6.93 (dd, *J* = 8.9, 2.5 Hz, 1H), 5.64 (s, 1H), 3.92 (s, 3H), 3.63 (q, *J* = 6.3 Hz, 2H), 3.02 (t, *J* = 6.5 Hz, 2H), 1.94 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1, 155.2, 135.9, 134.5, 133.3, 129.8, 126.4, 126.2, 123.7, 122.6, 111.6, 111.4, 110.0, 102.6, 100.2, 55.8, 39.0, 25.0, 23.4. HRMS (ESI) m/z: $(M + H)^+$ $C_{19}H_{19}N_2O_2S$ calcd. 339.1162, found 339.1157.

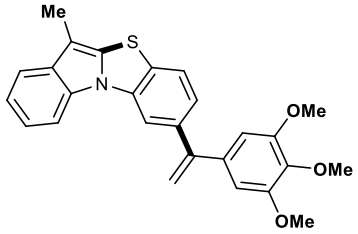
*Methyl (S)-3-(benzo[4,5]thiazolo[3,2-a]indol-11-yl)-2-((tert-butoxycarbonyl)amino)propanoate (**4ah**).*



White solid (51 mg, 60%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 88/12); $[\alpha]^{25}_D$ = + 0.009° (c =1, $CHCl_3$); mp: 120-121 °C; IR (film, cm^{-1}): 1710, 1481, 1363, 1265, 1222, 1166. ^1H NMR (300 MHz, $CDCl_3$) δ 7.89 – 7.78 (m, 2H), 7.55 – 7.46 (m, 2H), 7.34 (m, 1H), 7.21 – 7.17 (m, 2H), 7.13 (m, 1H), 5.11 (s, 1H), 4.66 (s, 1H), 3.61 (s, 3H), 3.32 (t, *J* = 4.4 Hz, 2H), 1.38 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.3, 155.1, 136.0, 132.9, 131.2, 130.2, 126.1 (2 C),

123.7, 122.9, 121.3, 120.6, 118.1, 111.9, 110.9, 100.4, 79.9, 54.1, 52.6, 29.7, 28.4 (3 C). HRMS (ESI) m/z: $(M + H)^+$ $C_{23}H_{25}N_2O_4S$ calcd. 425.1530, found 425.1524.

Preparation of 5a.



In a sealed tube under Ar, 2-dicyclohexylphosphino-2',4',6'- triisopropylbiphenyl (Xphos) (10 mol %), $Pd_2(dba)_3.CHCl_3$ (5 mol %), lithium *tert*-butoxide (26 mg, 0.33 mmol, 2.2 equiv.), 7-chloro-11-methylbenzo[4,5]thiazolo[3,2-a]indole (41 mg, 0.15 mmol, 1.0 equiv.), (*Z*)-4-methyl-*N'*-(1-(3,4,5-trimethoxyphenyl)ethylidene)benzenesulfonohydrazide (68 mg, 0.18 mmol, 1.2 equiv.) were solubilized in dioxane (1.5 mL). The system was heated at 110 ºC with stirring and reflux. The reaction was monitored by TLC. When the reaction was completed to reach room temperature, the crude mixture was taken up in dichloromethane and filtered through Celite©. The solvents were evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (Cyclohexane to Cyclohexane/Ethyl acetate = 8/2).

Yellow solid (61 mg, 94%); Rf = 0.3 (Cyclohexane/Ethyl acetate = 90/10). mp: 125-126 ºC; IR (film, cm^{-1}): 1579, 1504, 1485, 1459, 1411, 1342, 1222, 1126, 1006. ^1H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 1.6 Hz, 1H), 7.89 – 7.82 (m, 1H), 7.65 – 7.60 (m, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.21 (dd, *J* = 8.2, 1.6 Hz, 1H), 6.68 (s, 2H), 5.61 (d, *J* = 1.1 Hz, 1H), 5.58 (d, *J* = 1.1 Hz, 1H), 3.95 (s, 3H), 3.86 (s, 6H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.1 (2 C), 149.6, 139.7, 138.2, 136.8, 136.4, 133.2, 133.2, 131.1, 130.1, 123.2, 122.9,

121.0, 120.5, 117.9 114.4, 111.5, 110.7, 105.8 (2 C), 101.7, 60.9, 56.2 (2 C), 9.3. HRMS (ESI) m/z: $(M + H)^+$ $C_{26}H_{24}NO_3S$ calcd. 430.1471, found 430.1472.

Iodobenzene. ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 130.4, 127.6, 127.5, 94.5.

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Crystallographic data collection, structure determination and refinement

Elongated colourless crystals for compounds **4j**, **4y**, and **5a** were grown in saturated chloroform solutions after slow evaporation and were suitable for Single Crystal X-ray Diffraction (SCXRD) analysis on a RIGAKU XtaLABPro diffractometer at room temperature. This machine comprises a Mo $K\alpha$ microfocus sealed tube generator coupled to a double-bounce confocal Max-Flux® multilayer optic and a HPAD PILATUS3R 200K detector. The data processing was conducted using the *CrysAlisPro* software[1] in which a combination of an empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm, and a numerical one based on a Gaussian integration, was implemented. The structures were solved by intrinsic phasing methods (*SHELXT* program),[2] then refined by full-matrix least-squares methods on F^2 using *SHELX-L.*[3] Owing to crystal diffraction quality allowing the record of high resolution data in the *P* 2_1/n space group, the final structure of **4j** was achieved through Hirshfeld atom refinement (HAR)[4] using aspherical scattering factors via NoSpherA2[5, 6] partitioning in Olex2.[7] This was based on electron density obtained from iterative single-determinant SCF single-point DFT calculations using ORCA[8, 9] at the *R2SCAN*/def2-TZVP level of theory. The *NoSpherA2* software read any of these wavefunctions and the related electron-density was partitioned into Hirshfeld atoms. The Fourier transforms of these atoms are the non-spherical scattering factors, which were then tabulated in a .tsc file and provided to *olex2.refine*[10] for the L-M refinement. In this HAR approach, all hydrogen atoms were refined independently and anisotropically, providing better descriptions of their positions, and therefore more precise hydrogen-bond length (figure S1) and, in fine, better model statistics, as summarized in *Table S1*. The **4y** structure was solved in the polar orthorhombic space group, *P* na2_1, and was found to be disordered by a flip in the molecular plane around a pseudo-noncrystallographic twofold axis through the C1–N1 bond, with a refined occupancy ratio of 0.870(3):0.130(3) (figure S2). Some rigid-body, similar distance and anisotropic displacement restraints were applied to the minor conformer to make it behave like the major one. Eventually, the **5a** structure was solved in the monoclinic space group P 2_1/c, with two molecules of interest with different conformations in the asymmetric unit (asu) and one disordered chloroform solvent molecule pointing its hydrogen toward two methoxy oxygen atoms of one out of two molecules (Figure S3). With **4j** and **4y**, it constitutes the three new structures that document the indolo[2,1-b][1,3]benzothiazole[11] complex that was deposited with the CCDC[12] under the refcode number XIBVEN in 2023.

CCDC 2466374-2466376 for **4j**, **4y**, and **5a**, respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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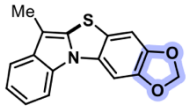
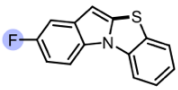
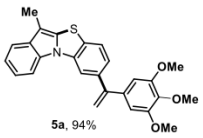
Table S1 Crystal data, data collection and structure refinement details for **4j**, **4y**, and **5a**.

Identification code		**4j**	**4y**	**5a**
				
Empirical formula		$C_{16}\ H_{11}\ N\ O_2\ S$	$C_{14}\ H_8\ F\ N\ S$	$2(C_{26}\ H_{23}\ N\ O_3\ S)$ $C\ H\ Cl_3$
Formula weight		281.337	241.27	978.40
Temperature	K	293(2)	293(2)	293(2)
Wavelength	Å	0.71073	0.71073	0.71073
Crystal system,		Monoclinic,	Orthorhombic,	Monoclinic,
space group		$P\ 2_1/n$	$P\ na2_1$	$P\ 2_1/c$
	Å	14.6282(7)	10.7774(8)	32.1651(13)
		5.1309(2)	24.6512(14)	7.2605(3)
Unit cell dimensions		17.2849(9)	4.0427(3)	21.6128(9)
	°	90	90	90
		106.392(5)	90	105.122(4)
		90	90	90

Volume	$Å^3$	1244.60(11)	1074.05(13)	4872.6(4)
Z,		4,	4,	4,
Calculated density	Mg/m^3	1.501	1.492	1.334
Absorption coefficient	mm^{-1}	0.260	0.286	0.326
F(000)		584	496	2040
Crystal size	mm	0.31 x 0.08 x 0.04	0.34 x 0.06 x 0.06	0.29 x 0.13 x 0.05
θ range for data collection	°	2.90 to 31.00	3.117 to 29.558	2.62 to 26.37
Limiting indices		$-21 \le h \le 20$,	$-14 \le h \le 14$,	$-40 \le h \le 40$,
		$-7 \le k \le 7$,	$-27 \le k \le 34$,	$-9 \le k \le 8$,
		$-25 \le l \le 24$	$-4 \le l \le 5$	$-27 \le l \le 27$
Reflections collected / unique		25386 / 3953	9408 / 2520	53071 / 9862
R(int)		0.0387	0.0337	0.044
Completeness to $\theta = 25.2°$	%	99.9	99.2	99.4
Absorption correction		Gaussian	Gaussian	Gaussian
Max. and min. transmission		1.000 and 0.777	1.000 and 0.713	1.000 and 0.424
Refinement method		Full-matrix least-squares on F^2		
		HAR	IAM	IAM
Data / restraints / parameters		3953 / 0 / 280	2515 / 203 / 284	9856 / 6 / 656
Goodness-of-fit on F^2		1.057	1.065	1.025
Final R indices	R1,	0.0258,	0.0414,	0.0492,
[I>2σ(I)]	wR2	0.0420	0.1045	0.1281
Final R indices	R1	0.0466,	0.0496,	0.0717,
(all data)	wR2	0.0480	0.1088	0.1403
Absolute structure parameter		-	-0.04(6)	-
Largest diff. peak and hole	$e.Å^{-3}$	0.305 and -0.251	0.287 and -0.198	0.300 and -0.352
CCDC deposit number		2466374	2466375	2466376

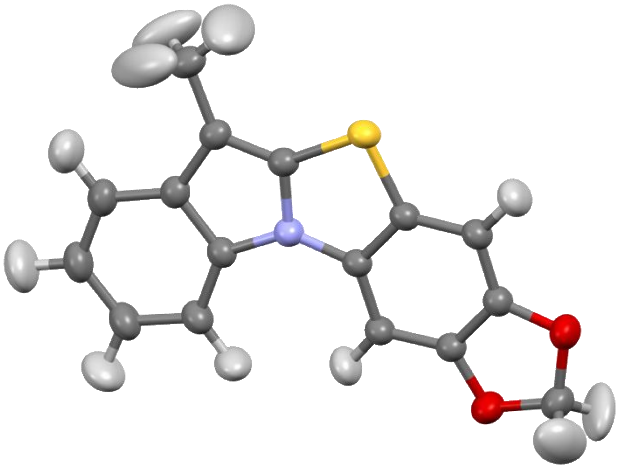


Figure S1 Ortep view of **4j**. Ellipsoids are drawn at 50% of probabilities.

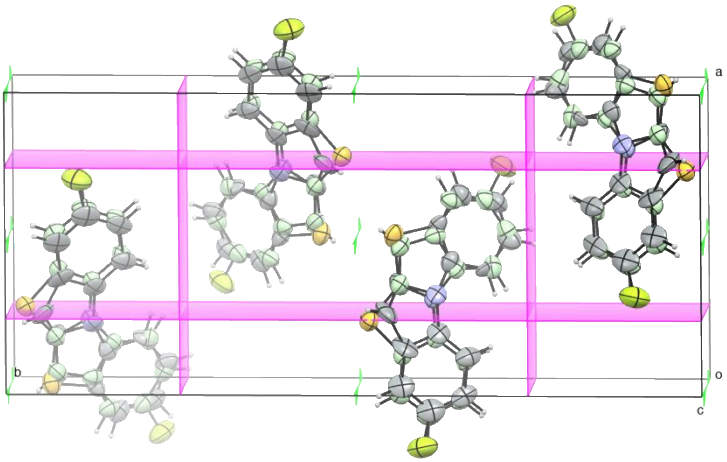


Figure S2 Partial view down the ***c*** axis of the **4y** crystal packing restricted to one unit cell. The crystallographic symmetry elements are shown (in green twofold screw axis with direction [010] at 0,y,1/4 with screw component [0,1/2,0] ; in gold, inversion centre at 0,0,0 ; in magenta, glide plane perpendicular to [010] with glide component [0,0,1/2]). Carbons in green belong to the minor conformer flipped over the major conformer (carbons in grey).

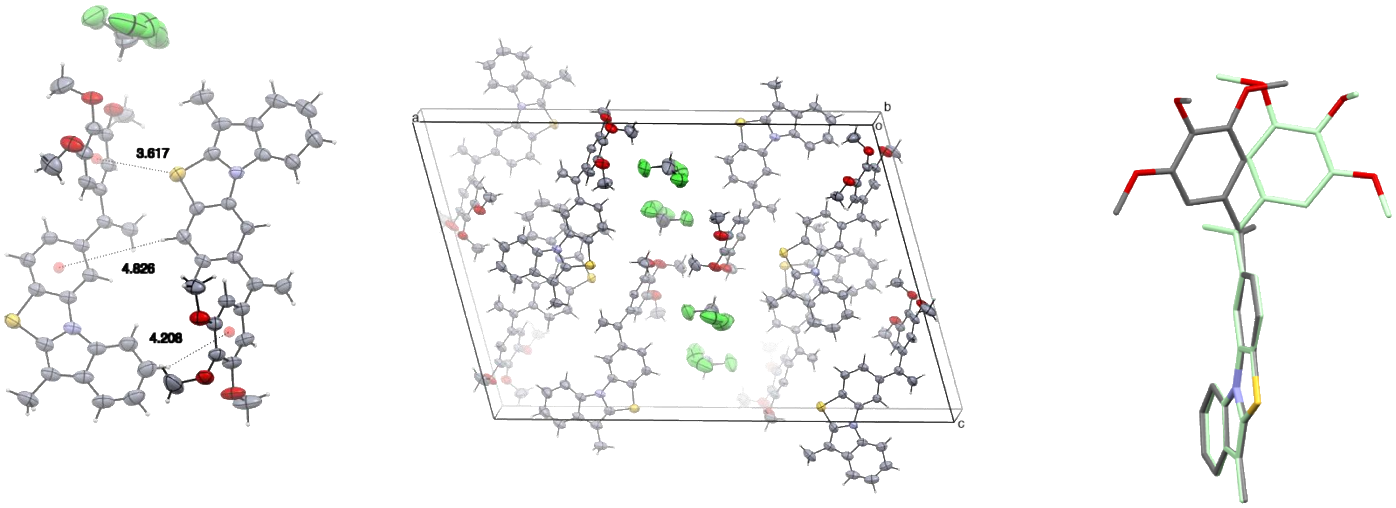
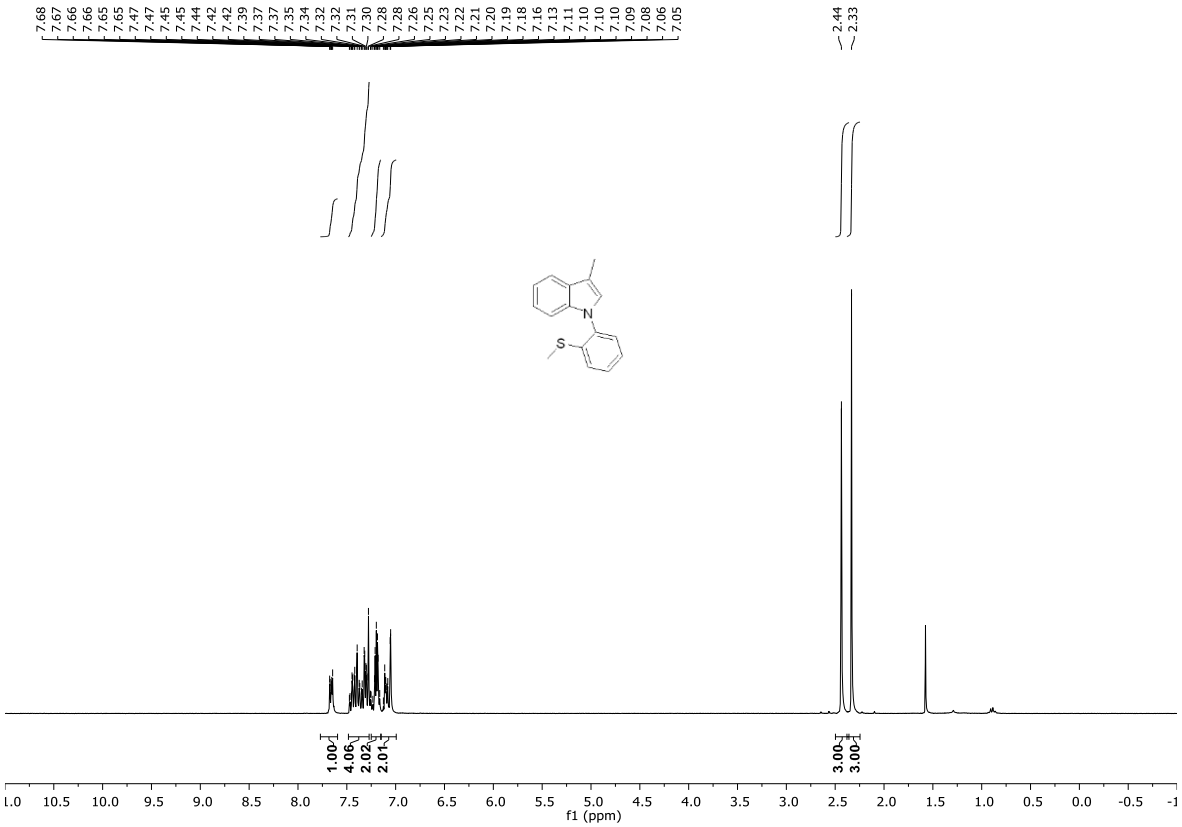


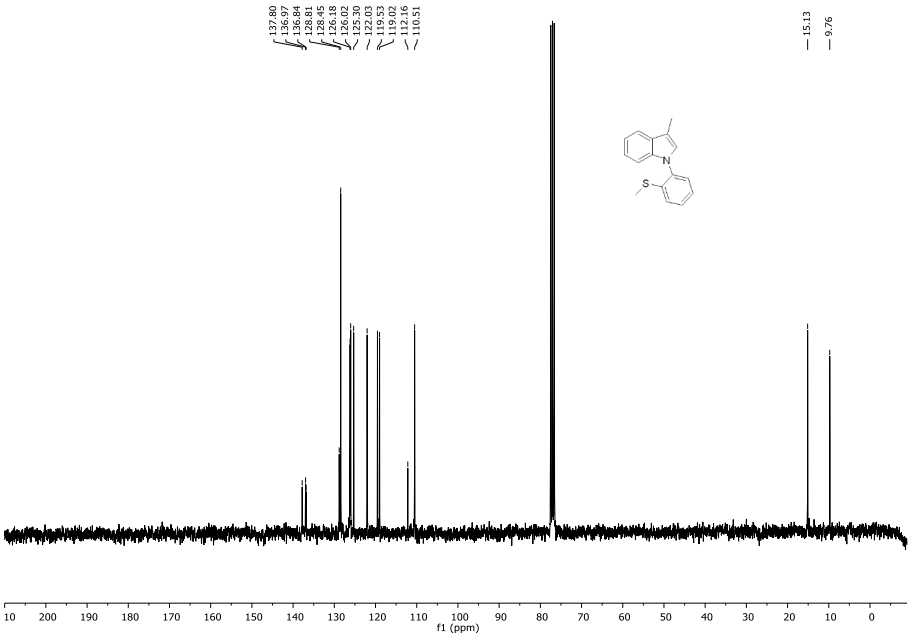
Figure S3 View of the asu of **5a** with short intermolecular distances (in Å) of S or C-H … π within the dimer (left). The right-hand image shows an overlay of the two conformers over the indolo[2,1-b][1,3]benzothiazole moiety. The conformer with green carbons corresponds to the one in which the chloroform pointing its hydrogen towards the methoxy groups. Partial view of the unit cell of **5a** down the ***b*** axis (middle).

Spectrum of 1-(2-(methylthio)phenyl)-1H-indole compounds (3)

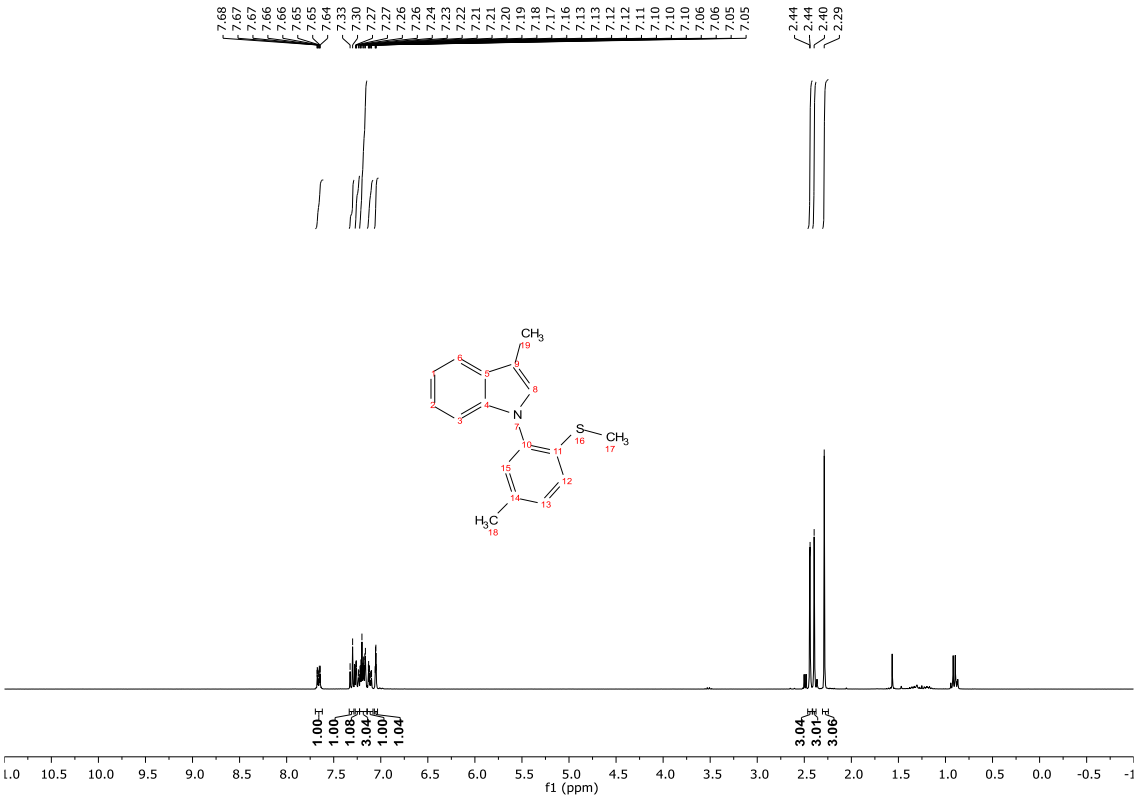
^{1}H NMR (300 MHz, $CDCl_3$) of 3a



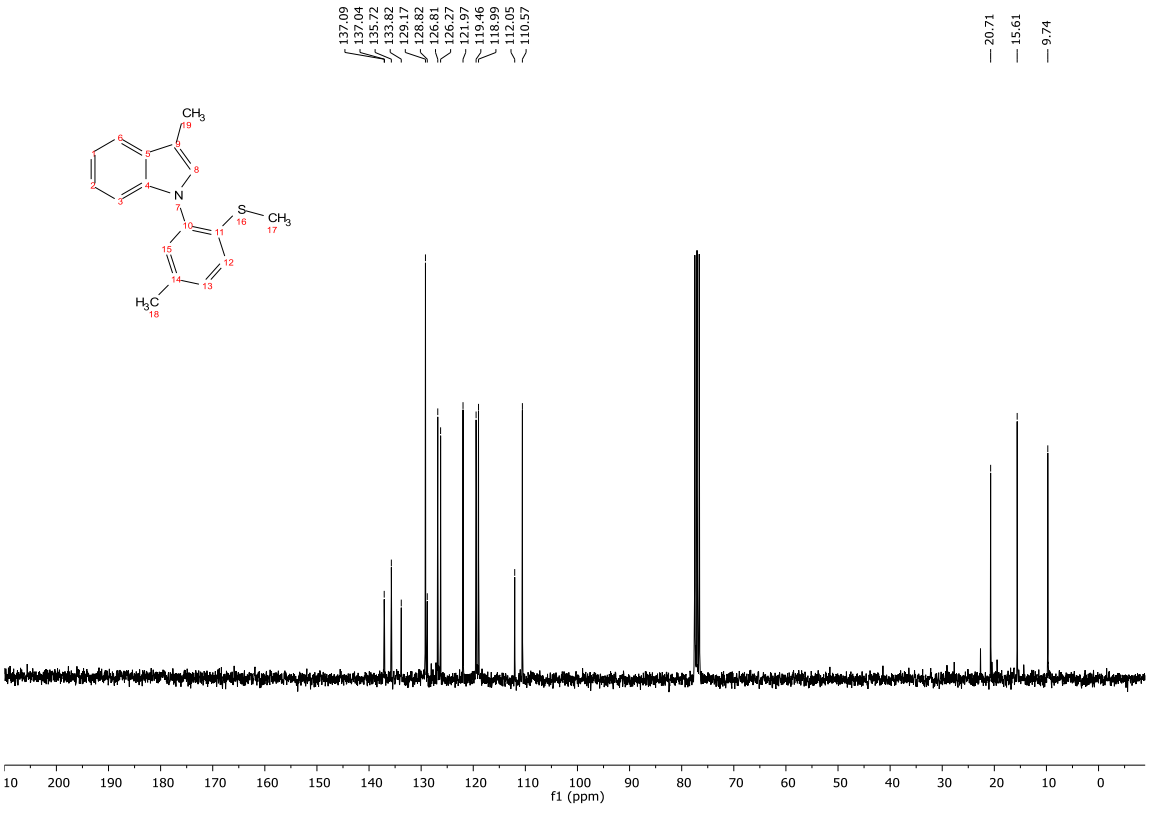
^{13}C NMR (75 MHz, $CDCl_3$) of 3a



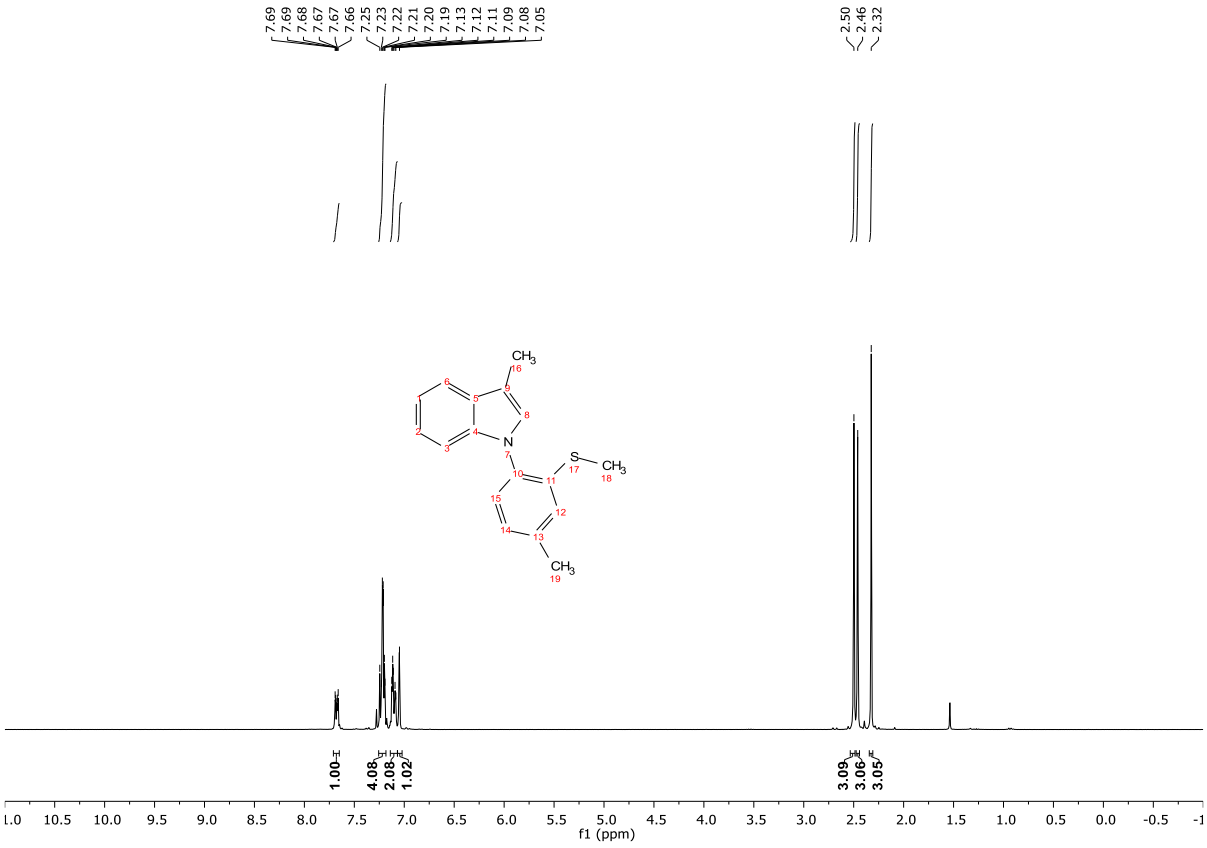
^{1}H NMR (300 MHz, $CDCl_3$) of 3b



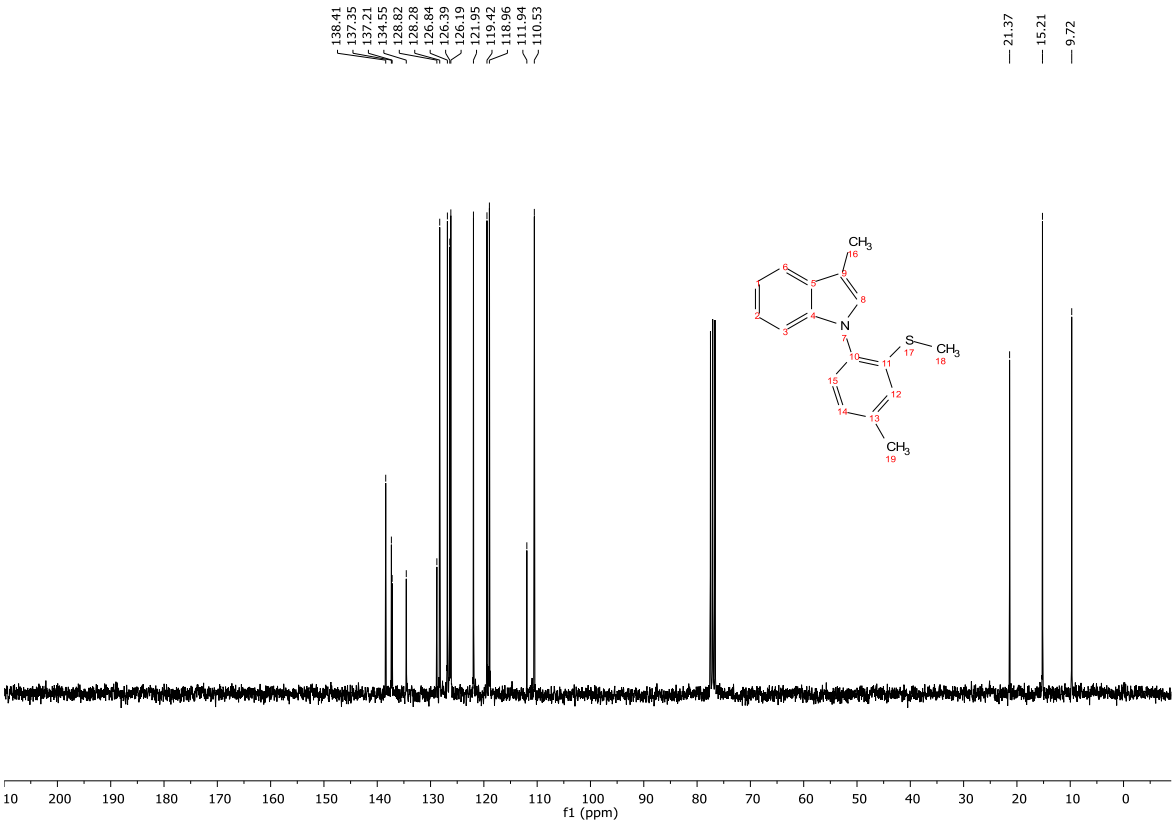
^{13}C NMR (75 MHz, $CDCl_3$) of 3b



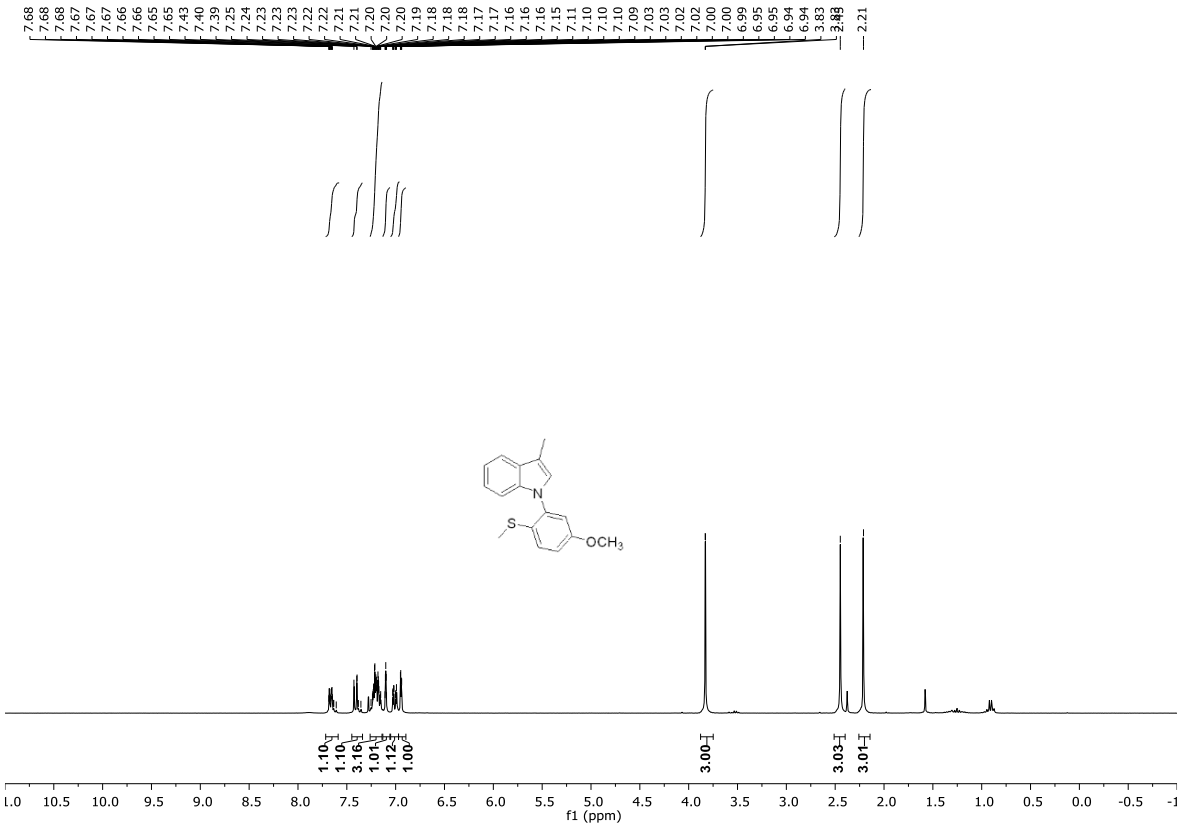
^{1}H NMR (300 MHz, $CDCl_3$) of 3c



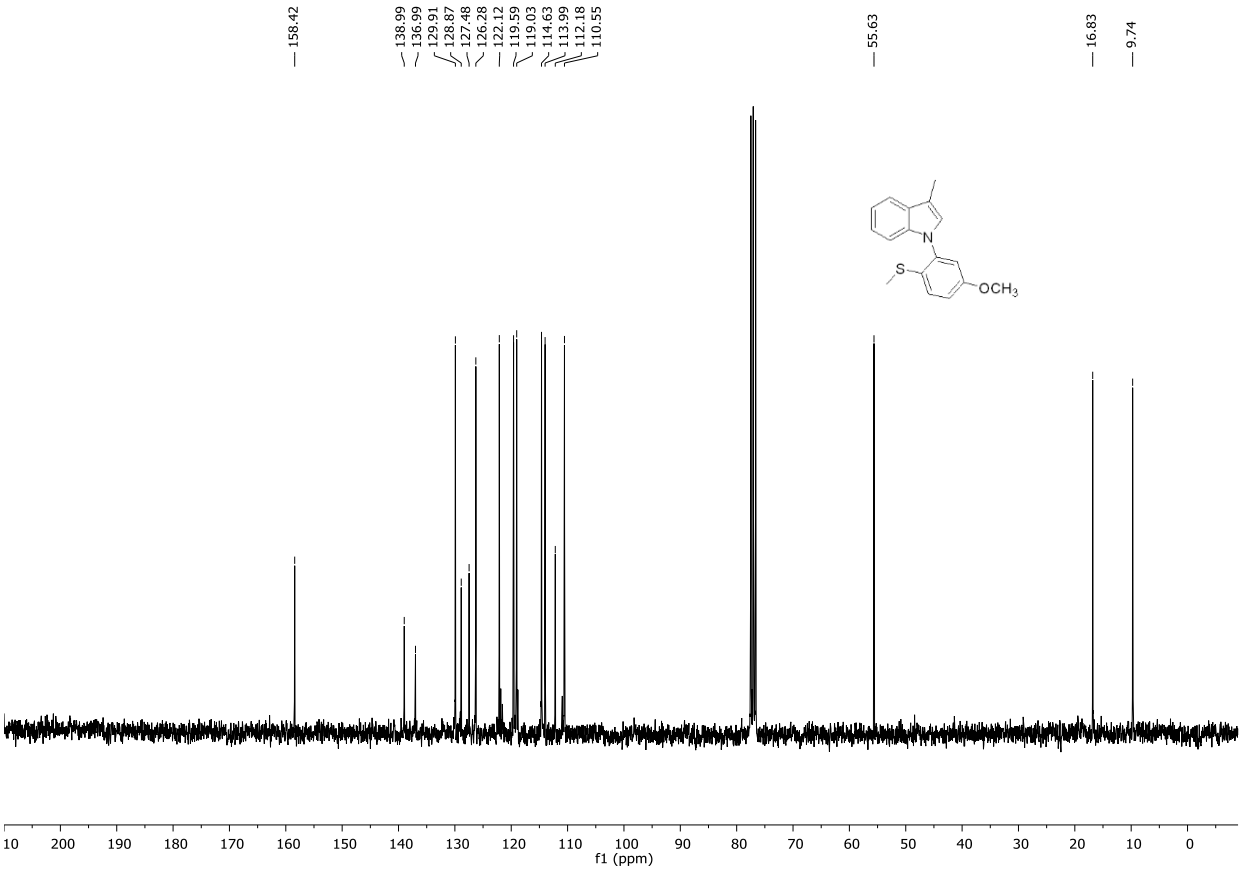
^{13}C NMR (75 MHz, $CDCl_3$) of 3c



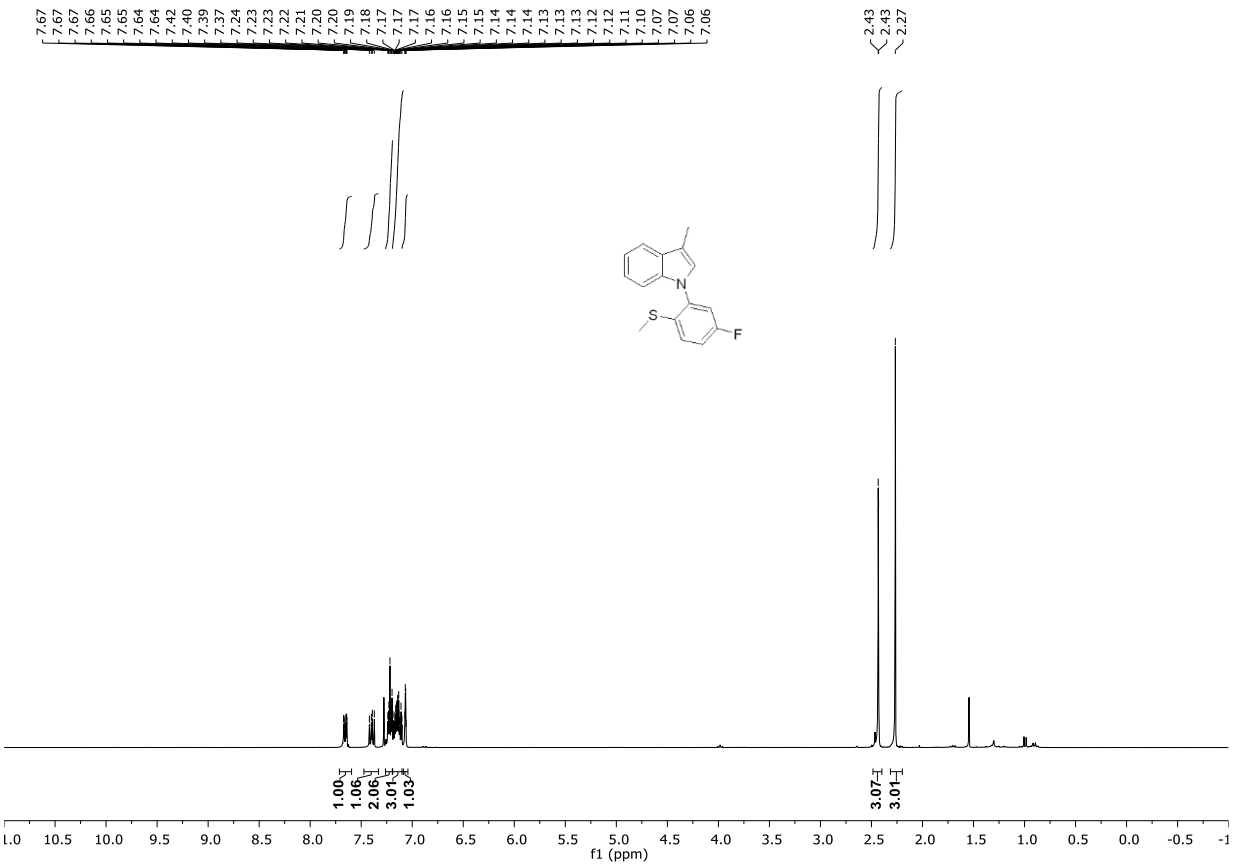
^{1}H NMR (300 MHz, $CDCl_3$) of 3d



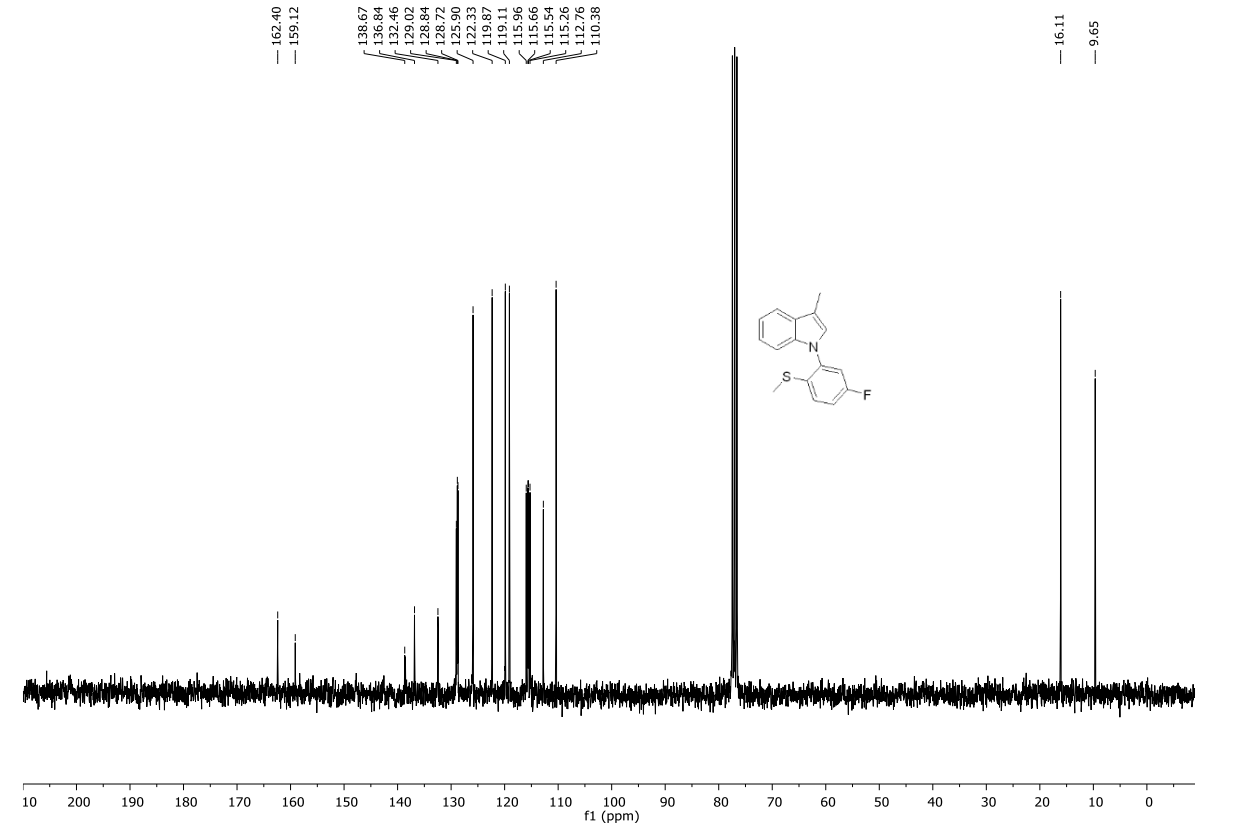
^{13}C NMR (75 MHz, $CDCl_3$) of 3d



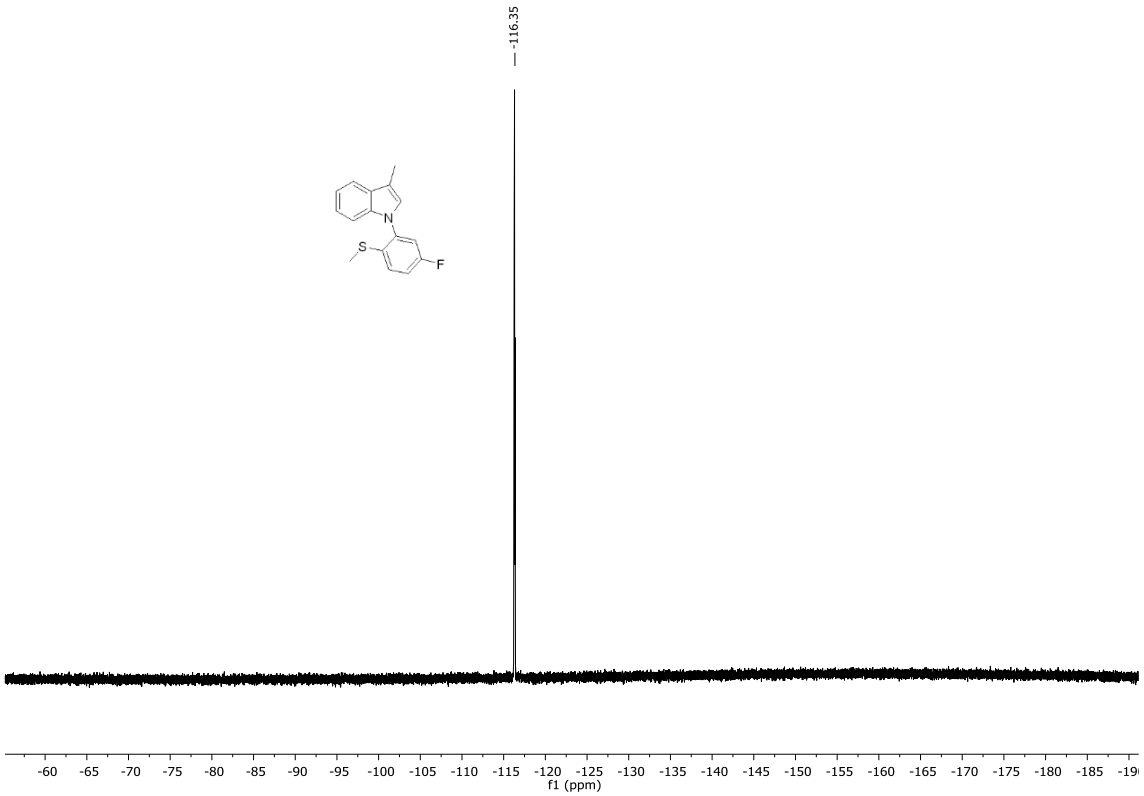
^{1}H NMR (300 MHz, $CDCl_3$) of 3e



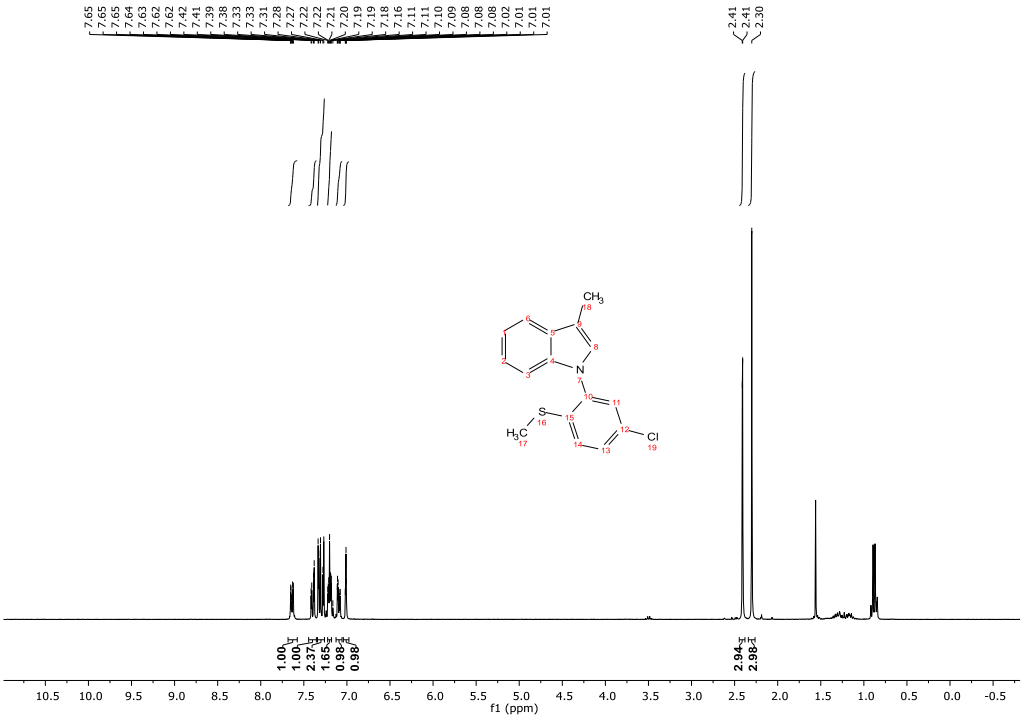
^{13}C NMR (75 MHz, $CDCl_3$) of 3e



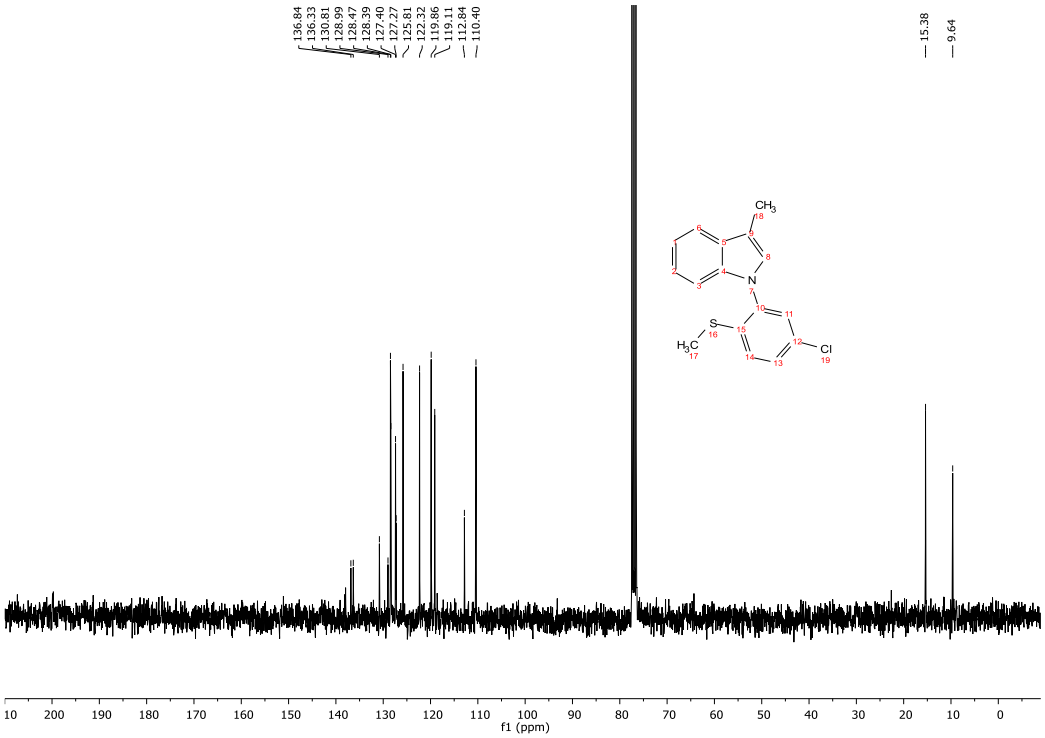
^{19}F NMR (188 MHz, $CDCl_3$) of 3e



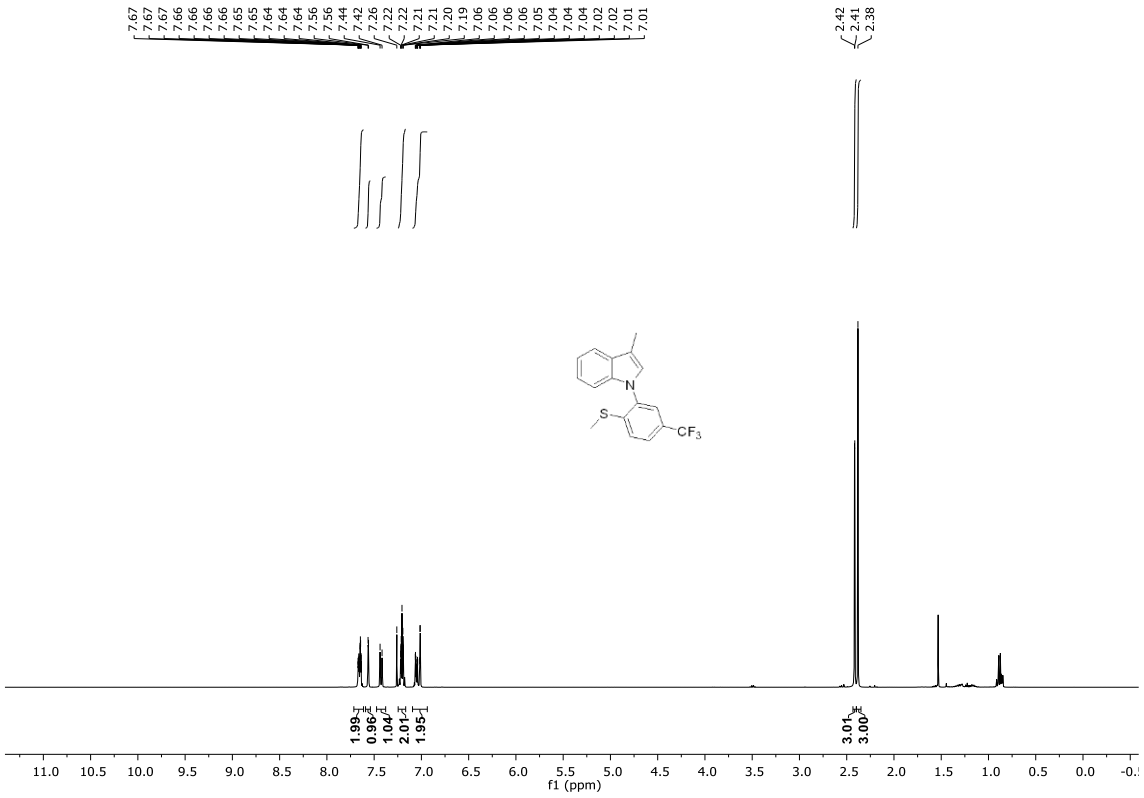
^{1}H NMR (300 MHz, $CDCl_3$) of 3f



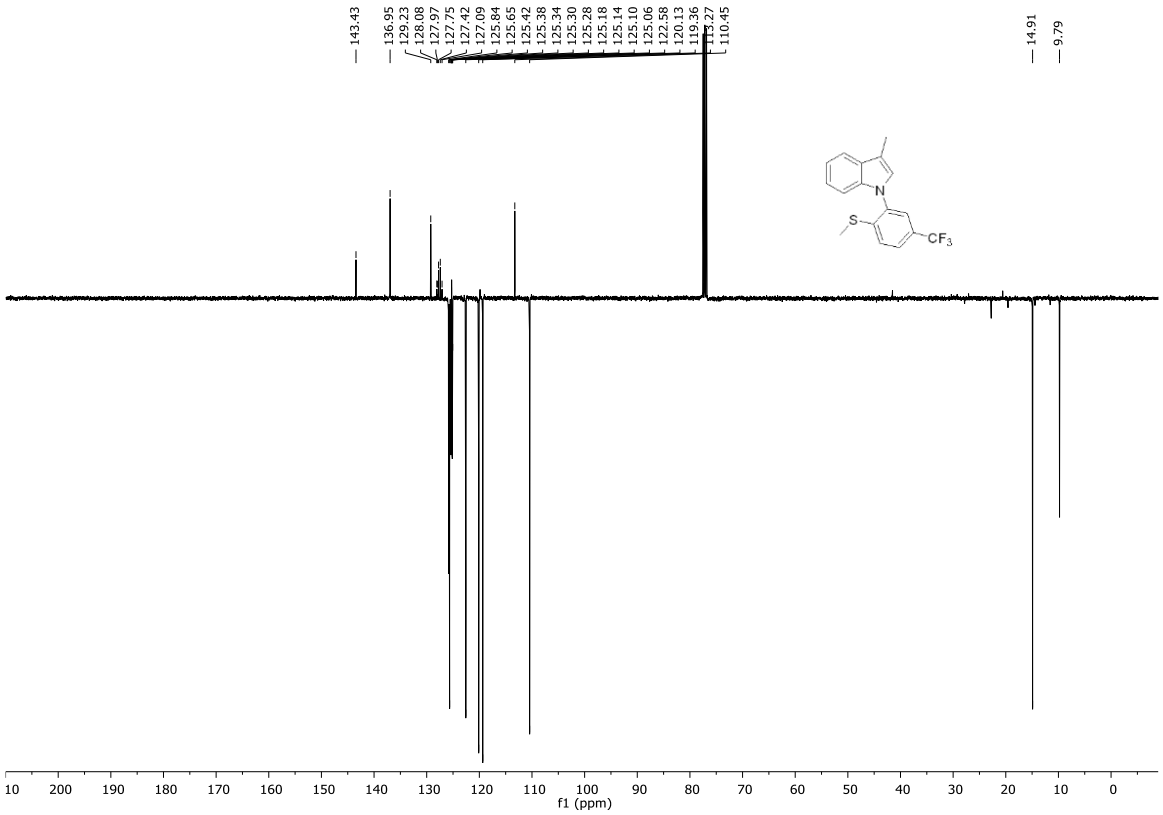
^{13}C NMR (75 MHz, $CDCl_3$) of 3f



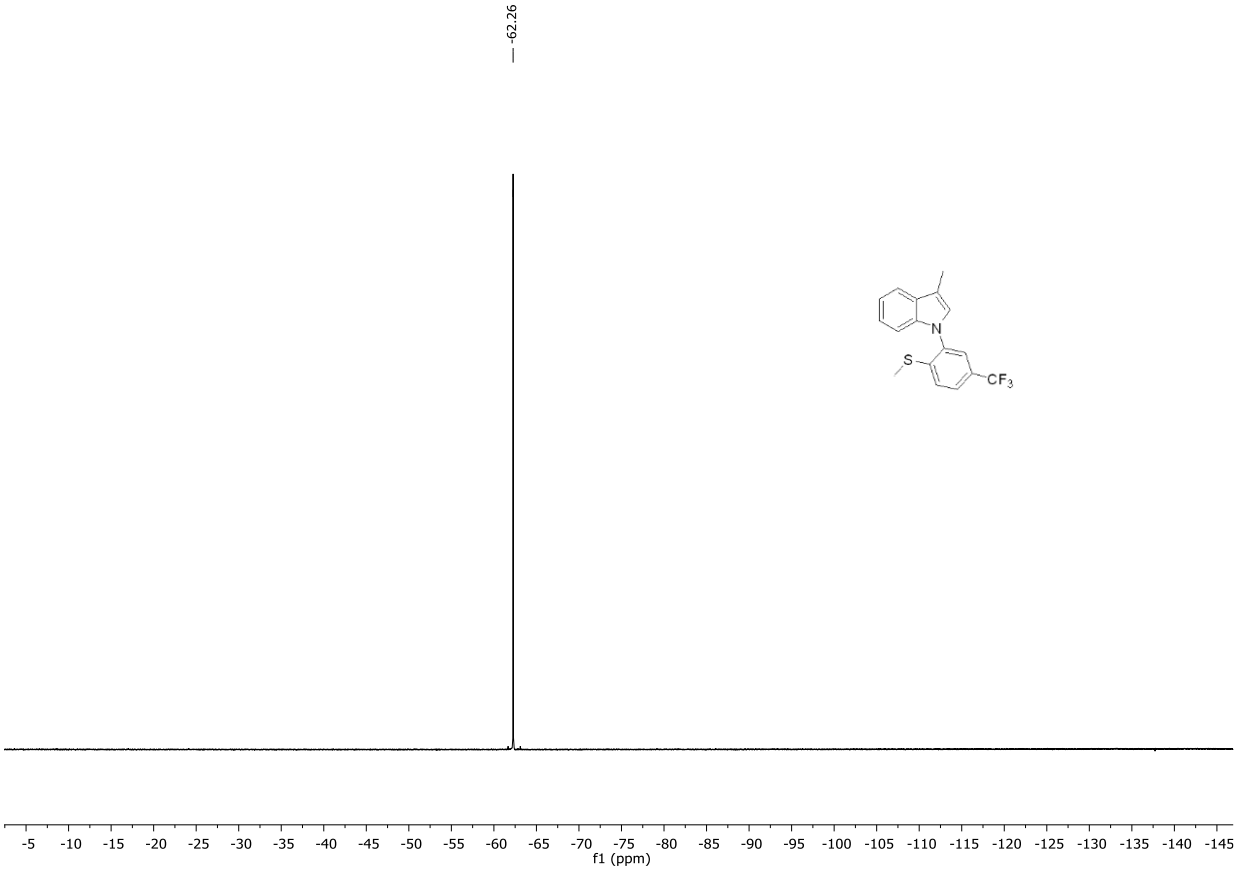
^{1}H NMR (400 MHz, $CDCl_3$) of 3g



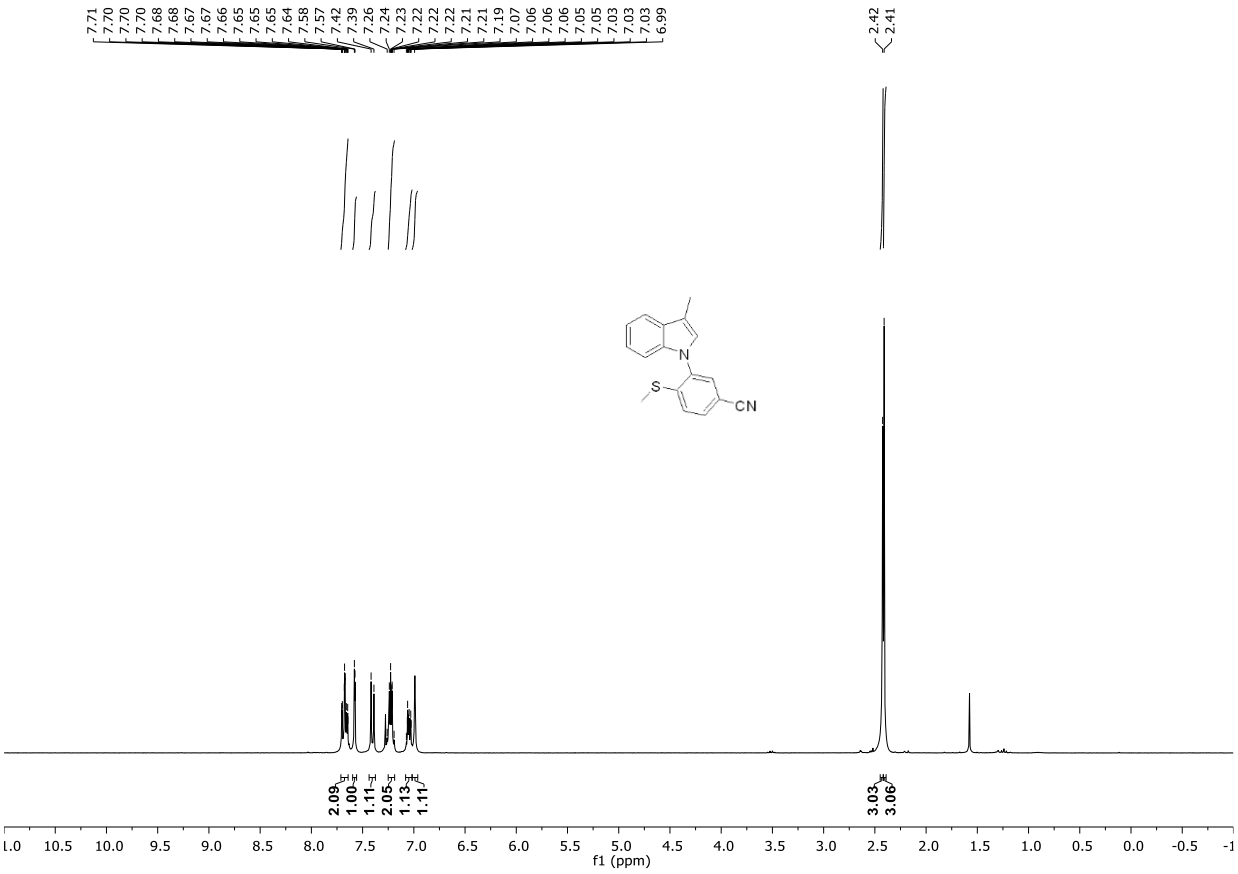
^{13}C JMOD NMR (101 MHz, $CDCl_3$) of 3g



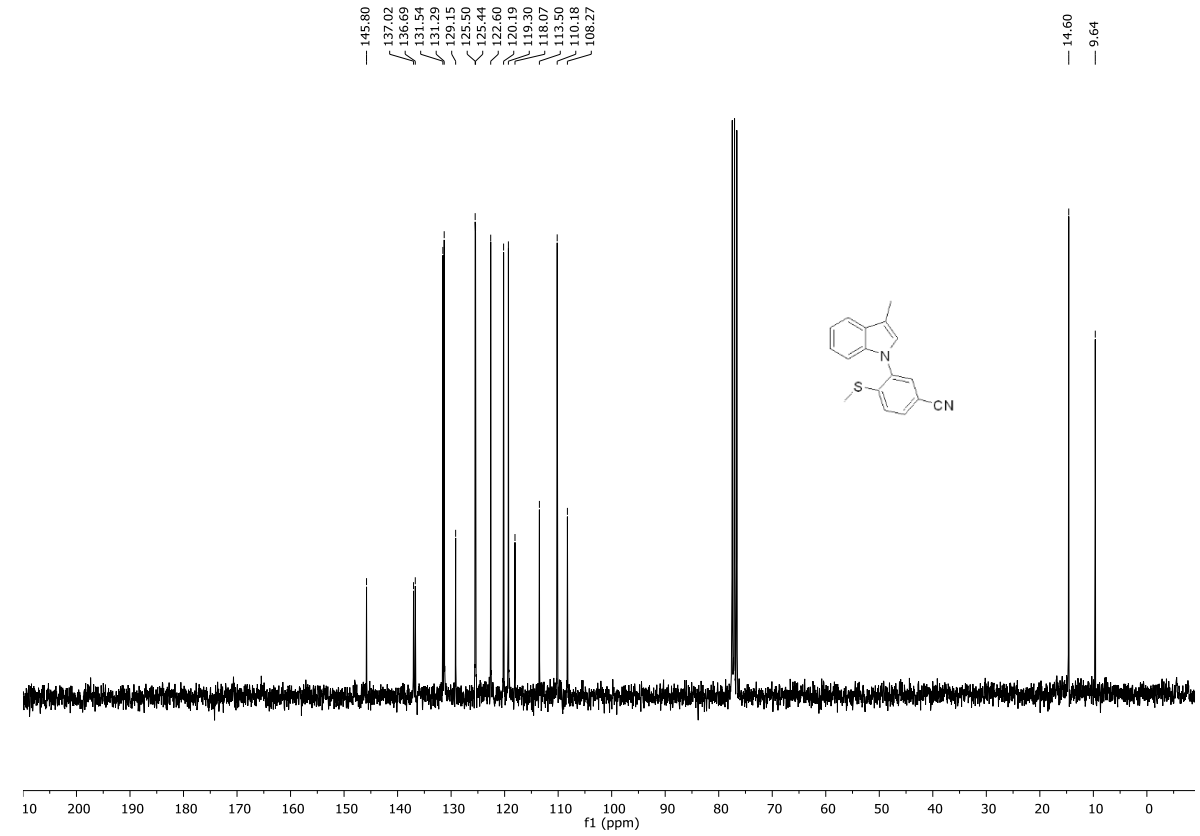
^{19}F NMR (188 MHz, $CDCl_3$) of 3g



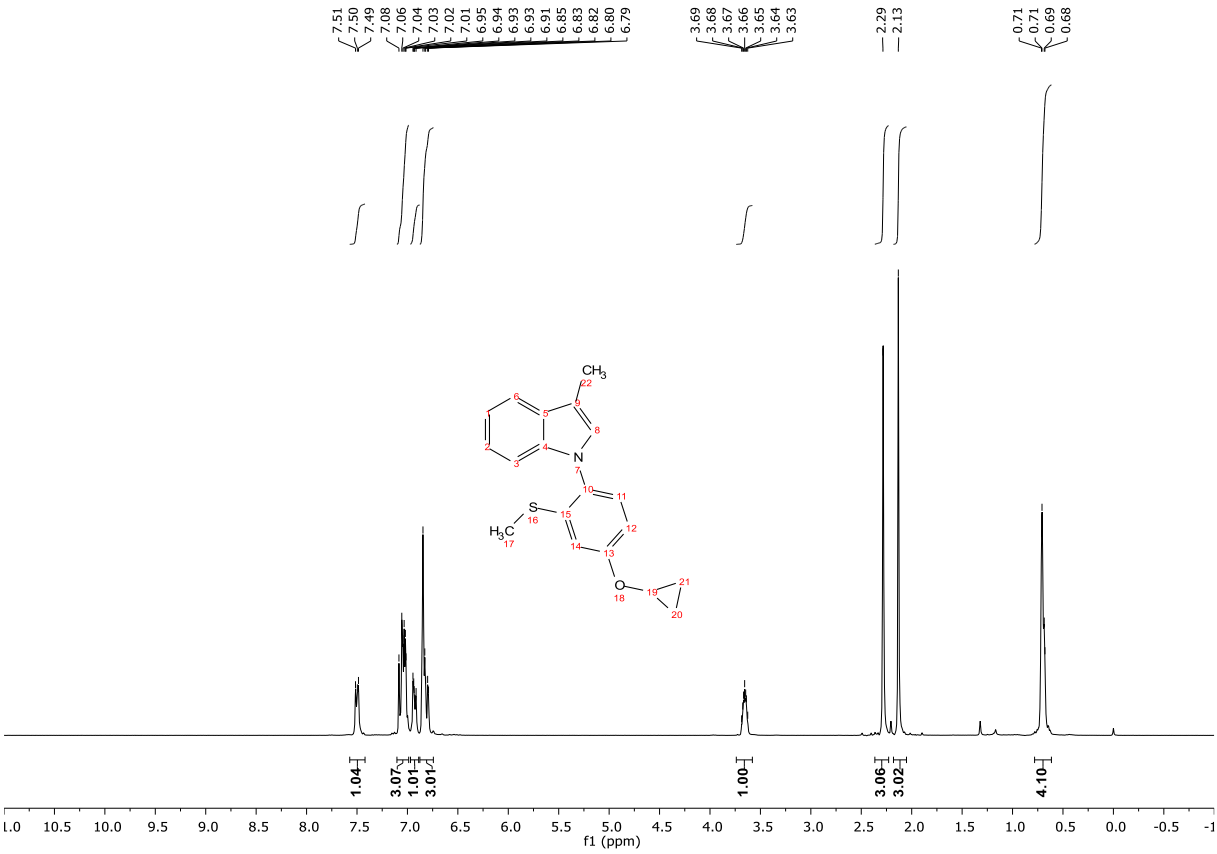
^{1}H NMR (300 MHz, $CDCl_3$) of 3h



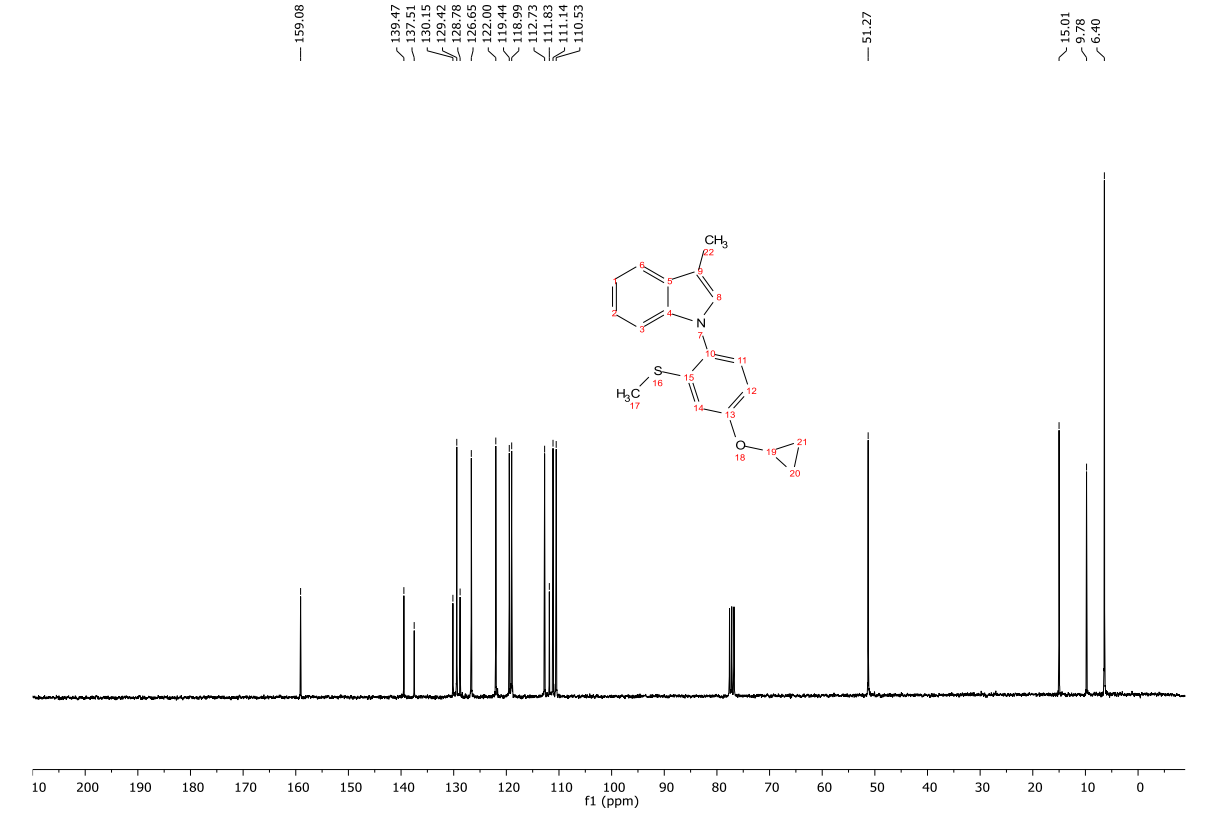
^{13}C NMR (75 MHz, $CDCl_3$) of 3h



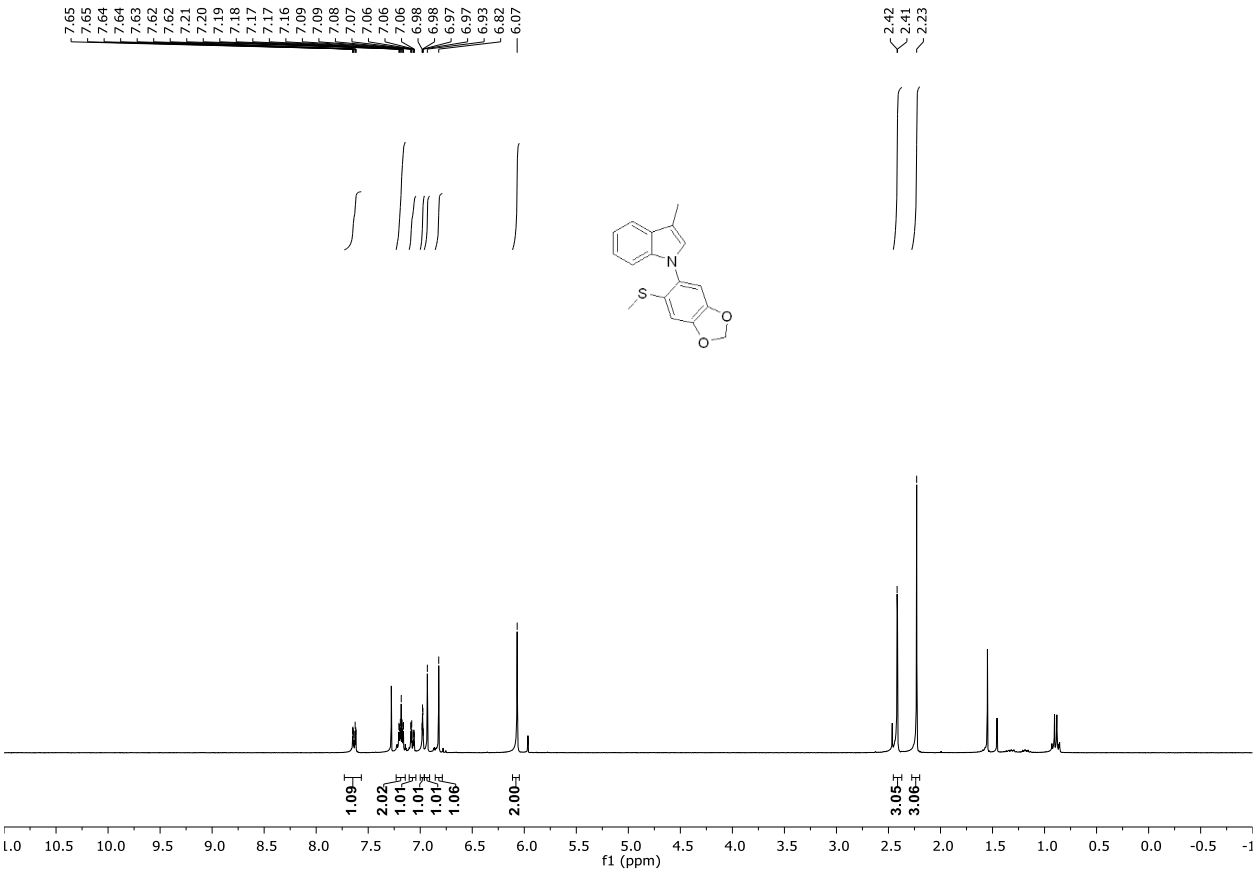
^{1}H NMR (300 MHz, $CDCl_3$) of 3i



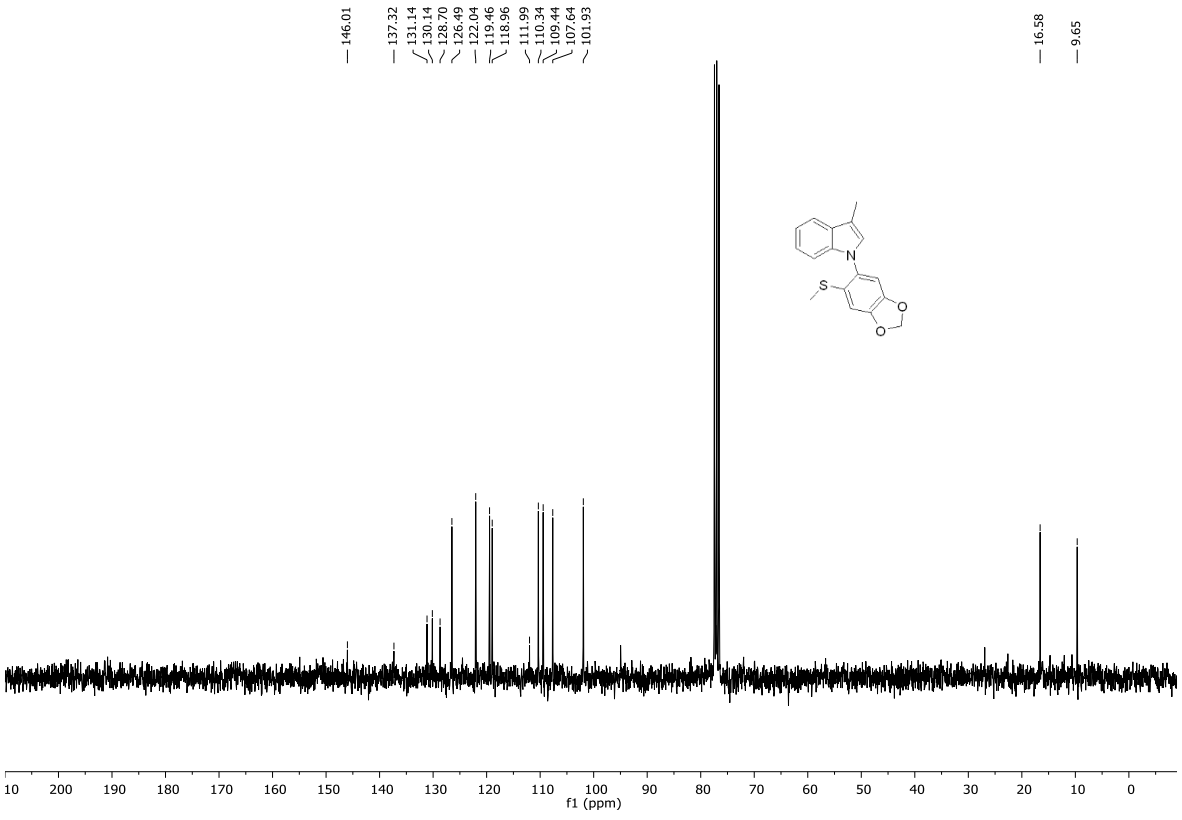
^{13}C NMR (75 MHz, $CDCl_3$) of 3i



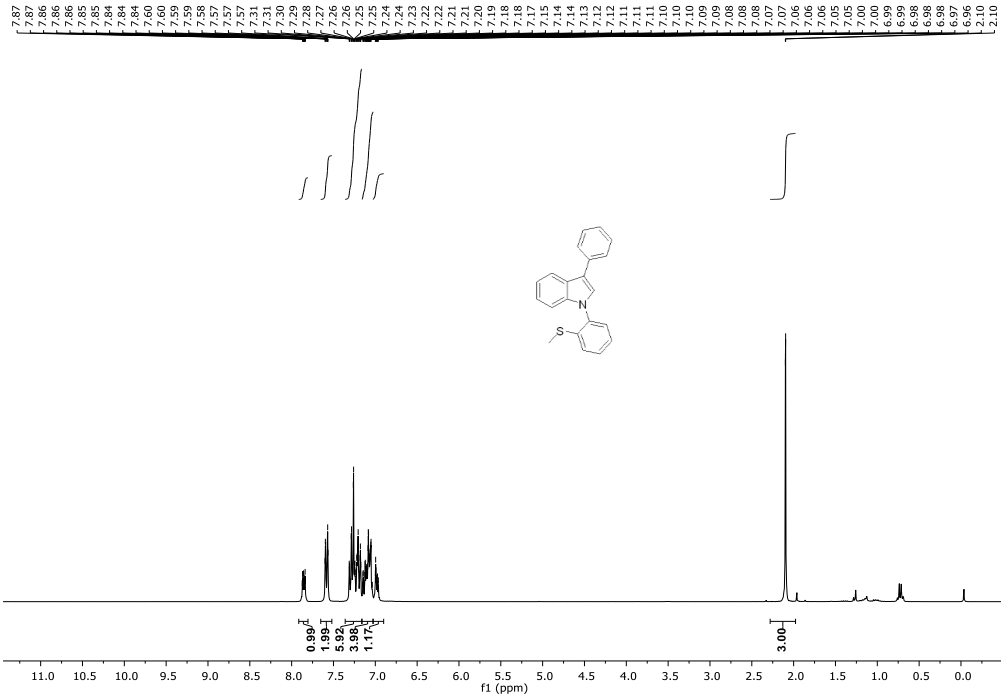
^{1}H NMR (300 MHz, $CDCl_3$) of 3j



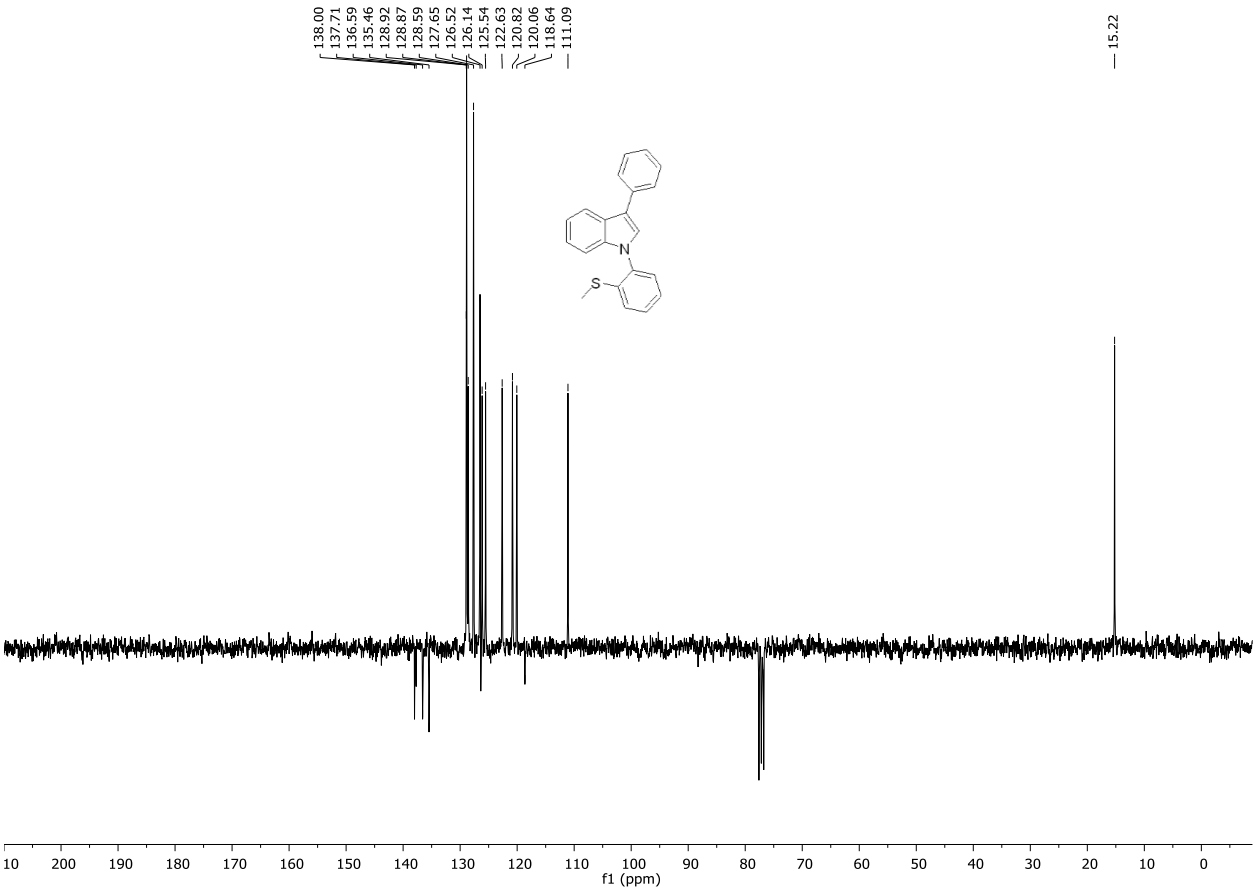
^{13}C NMR (75 MHz, $CDCl_3$) of 3j



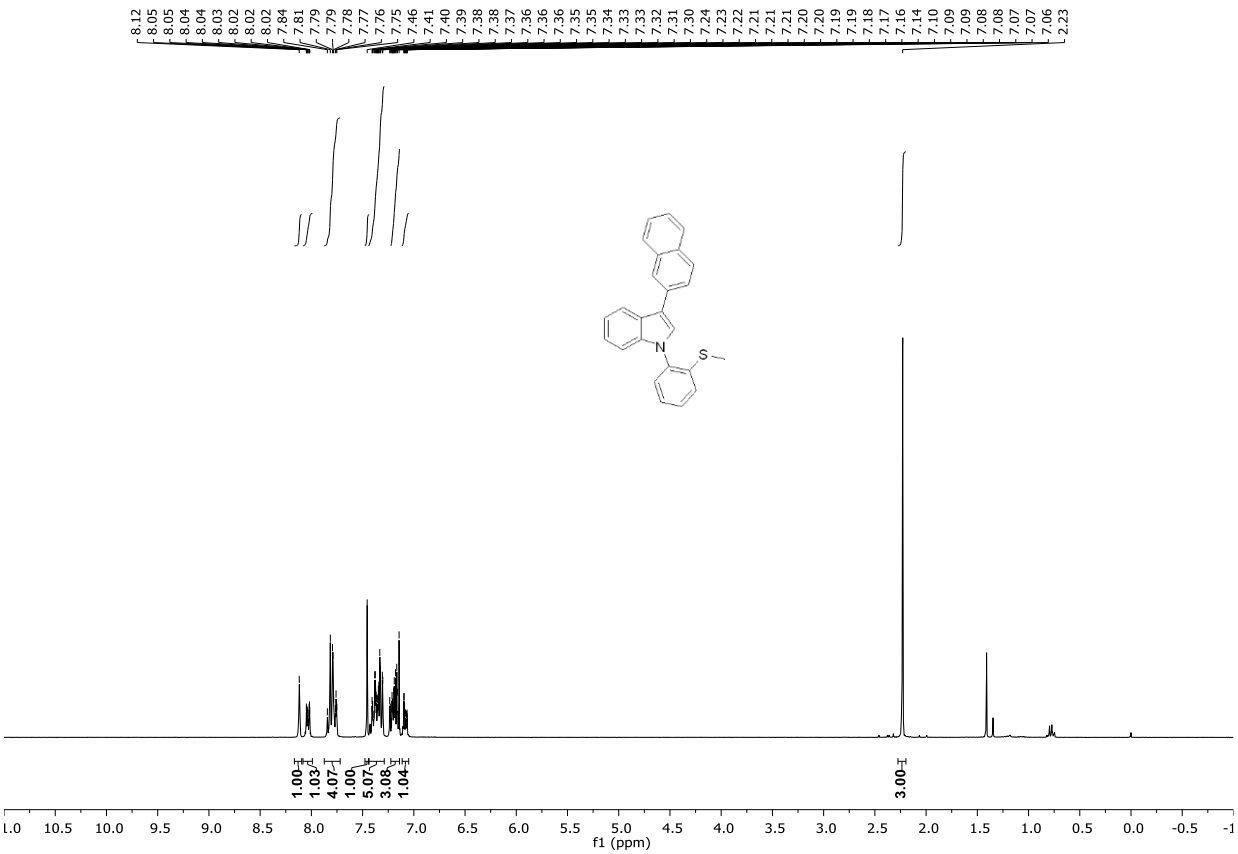
^{1}H NMR (300 MHz, $CDCl_3$) of 3k



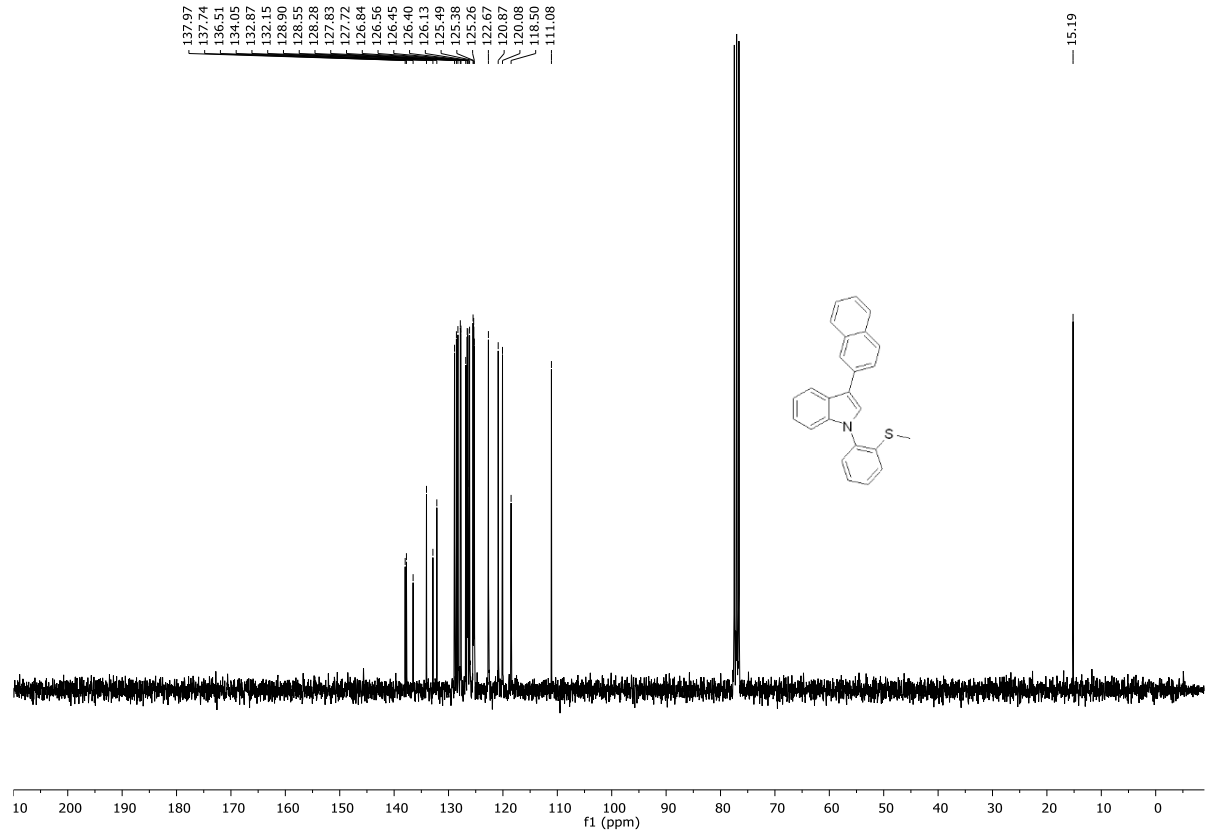
^{13}C JMOD NMR (75 MHz, $CDCl_3$) of 3k



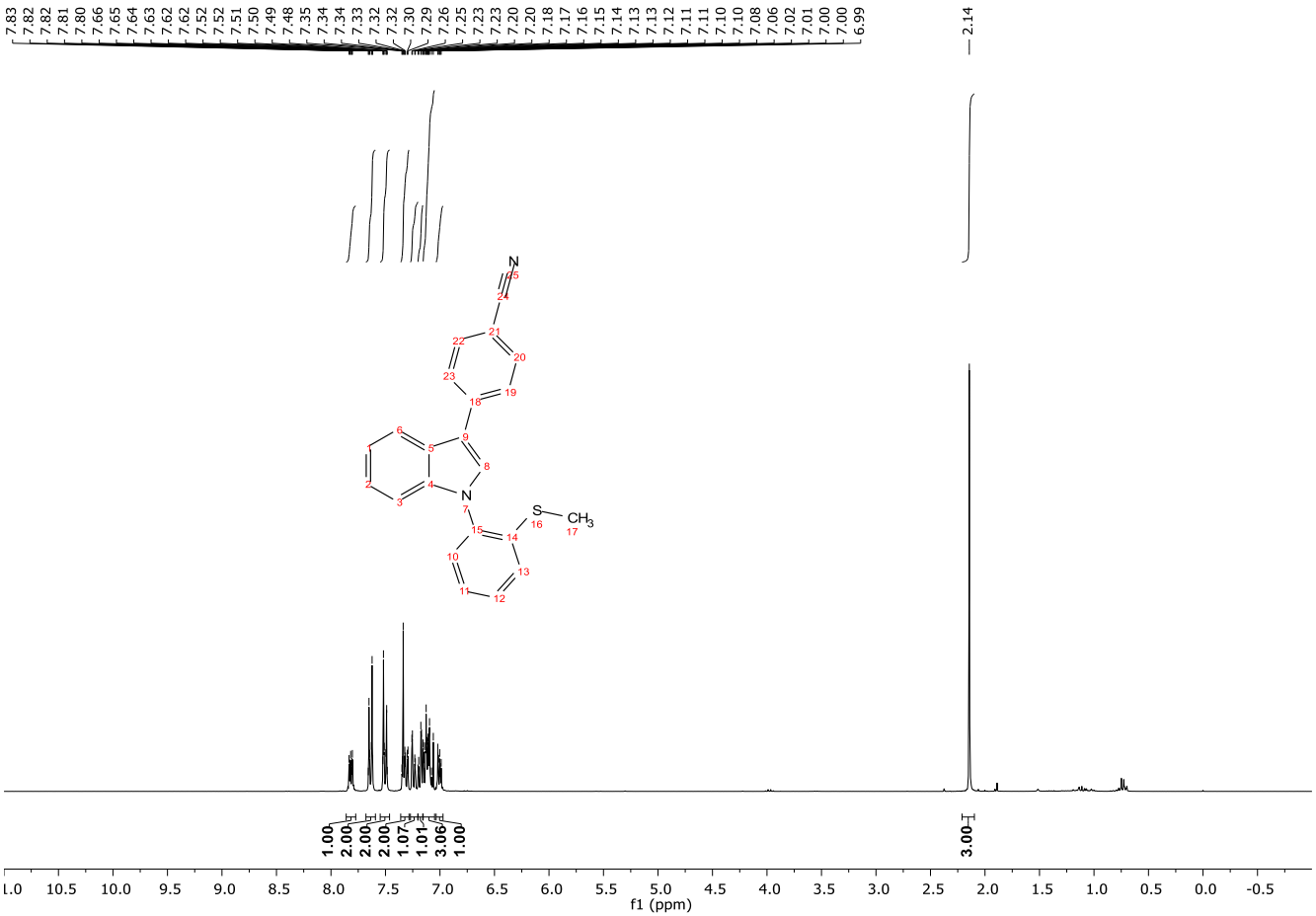
^{1}H NMR (300 MHz, $CDCl_3$) of 3l



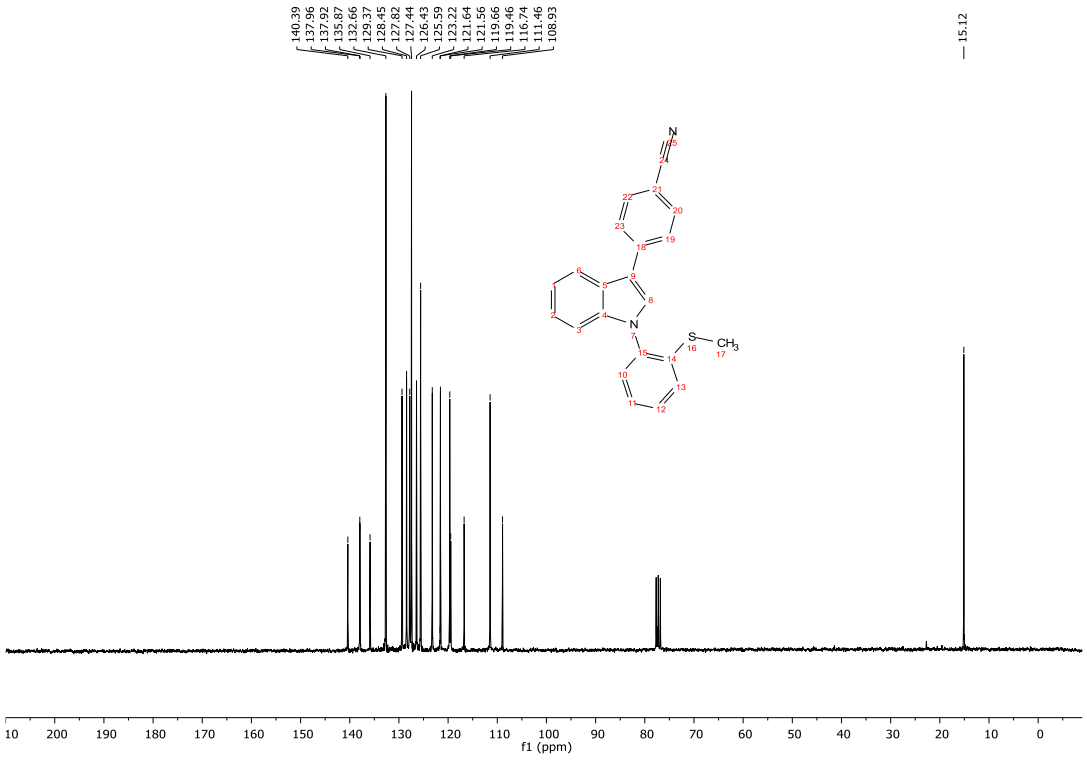
^{13}C NMR (75 MHz, $CDCl_3$) of 3l



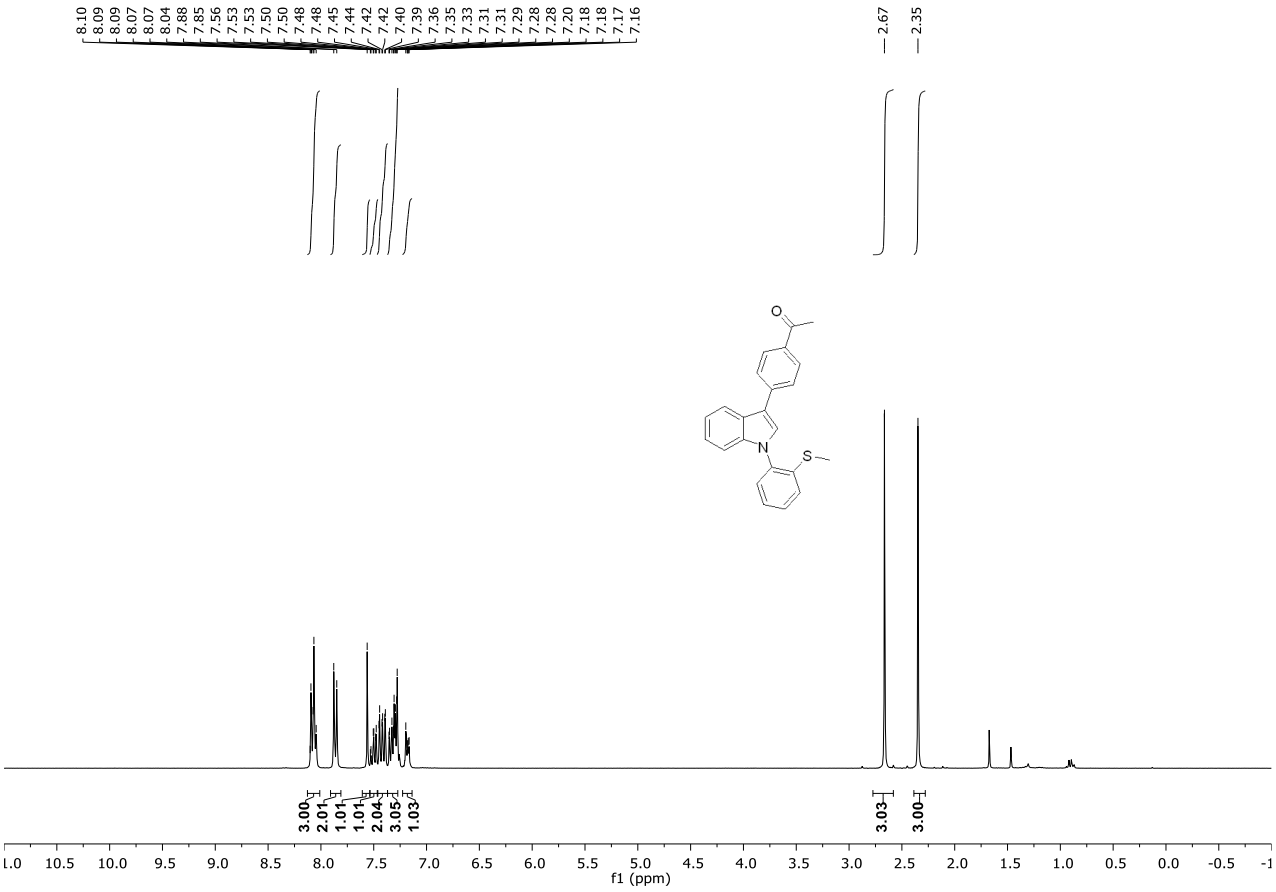
^{1}H NMR (300 MHz, $CDCl_3$) of 3m



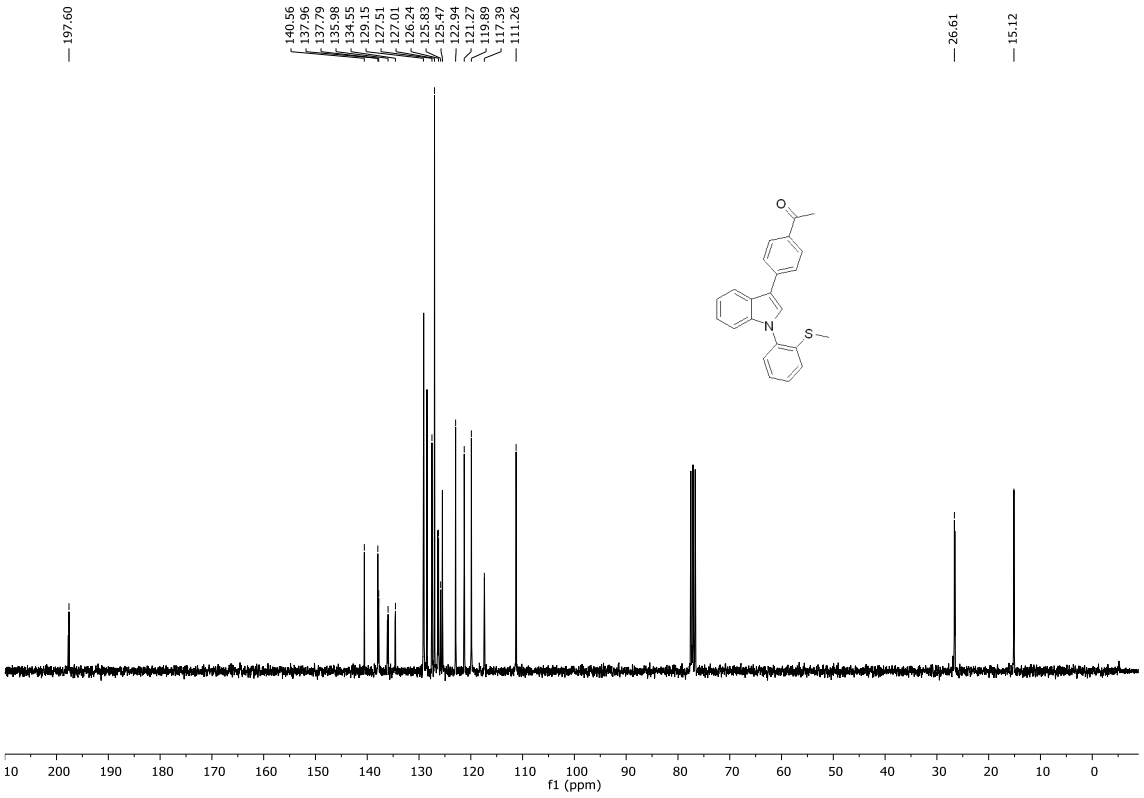
^{13}C NMR (75 MHz, $CDCl_3$) of 3m



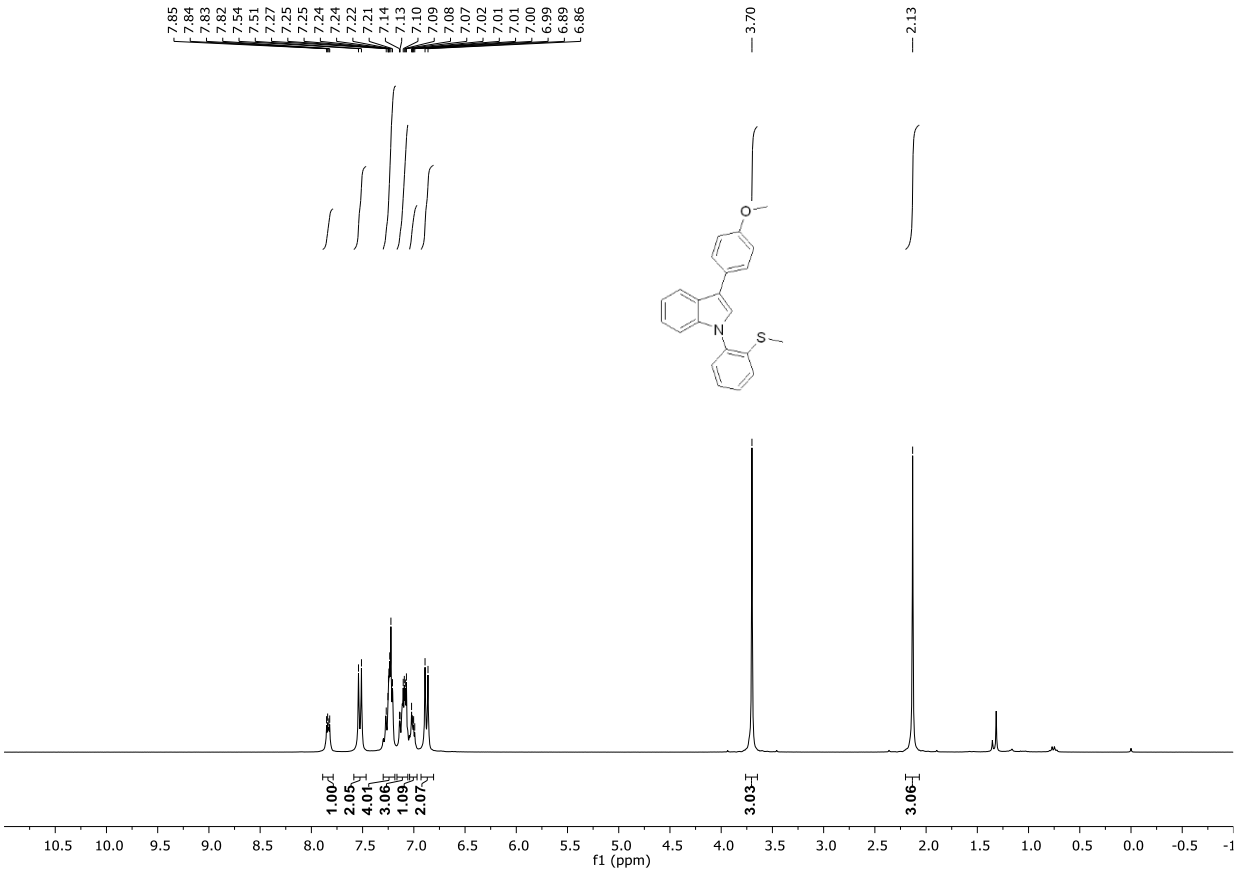
^{1}H NMR (300 MHz, $CDCl_3$) of 3n



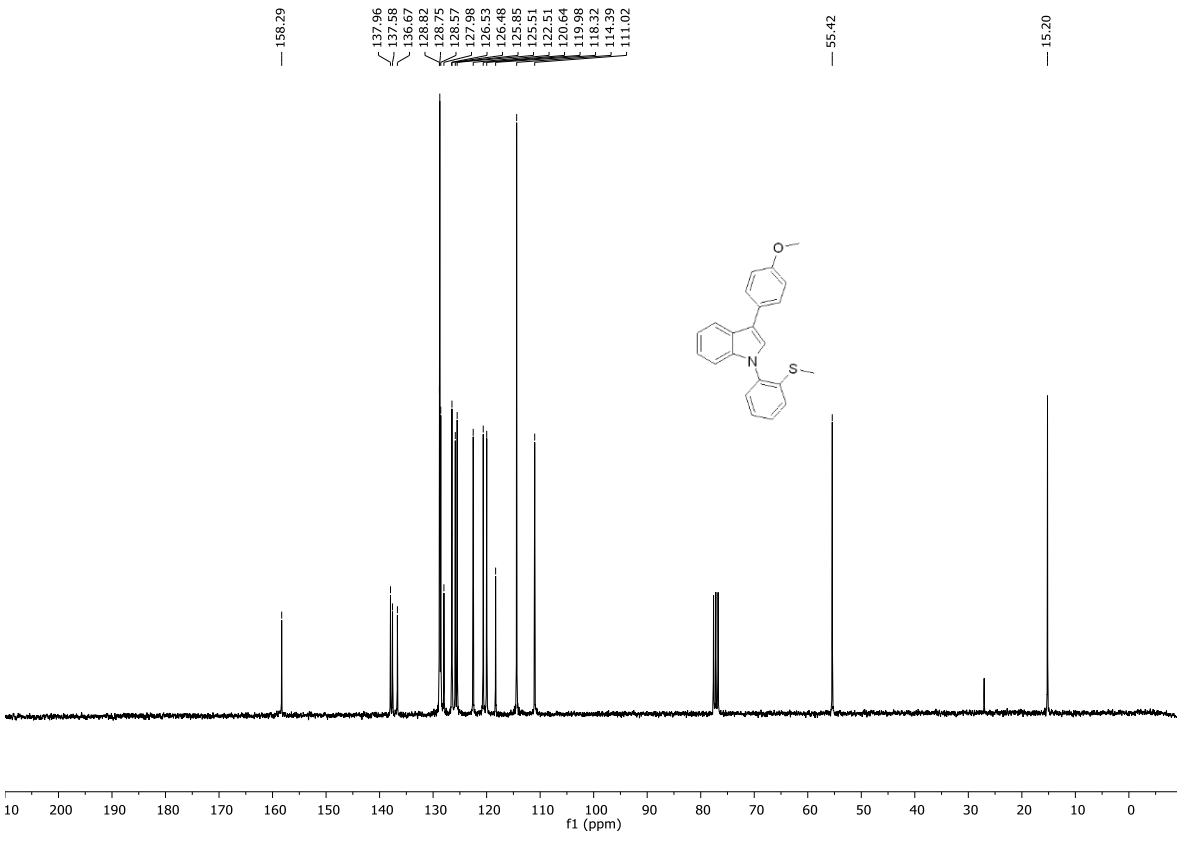
^{13}C NMR (75 MHz, $CDCl_3$) of 3n



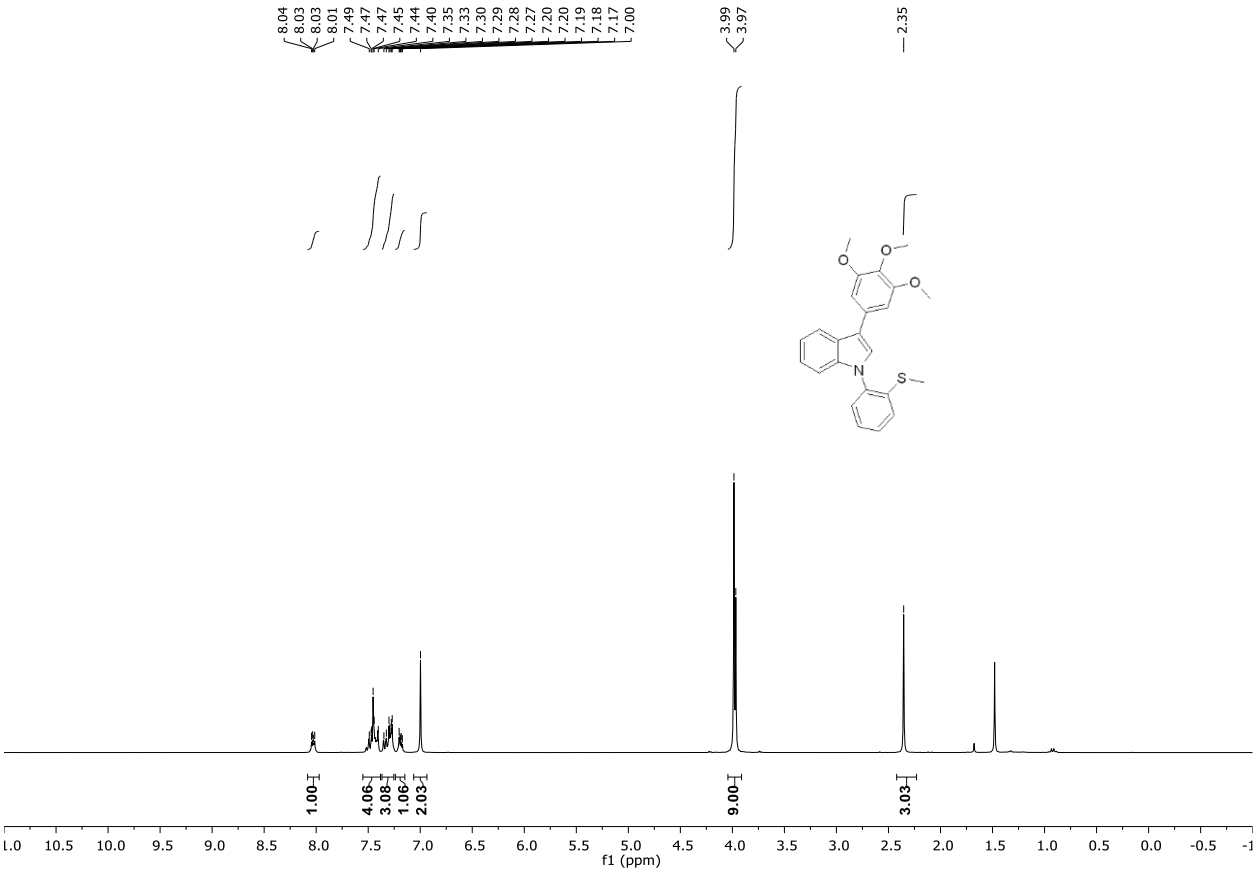
^{1}H NMR (300 MHz, $CDCl_3$) of 3o



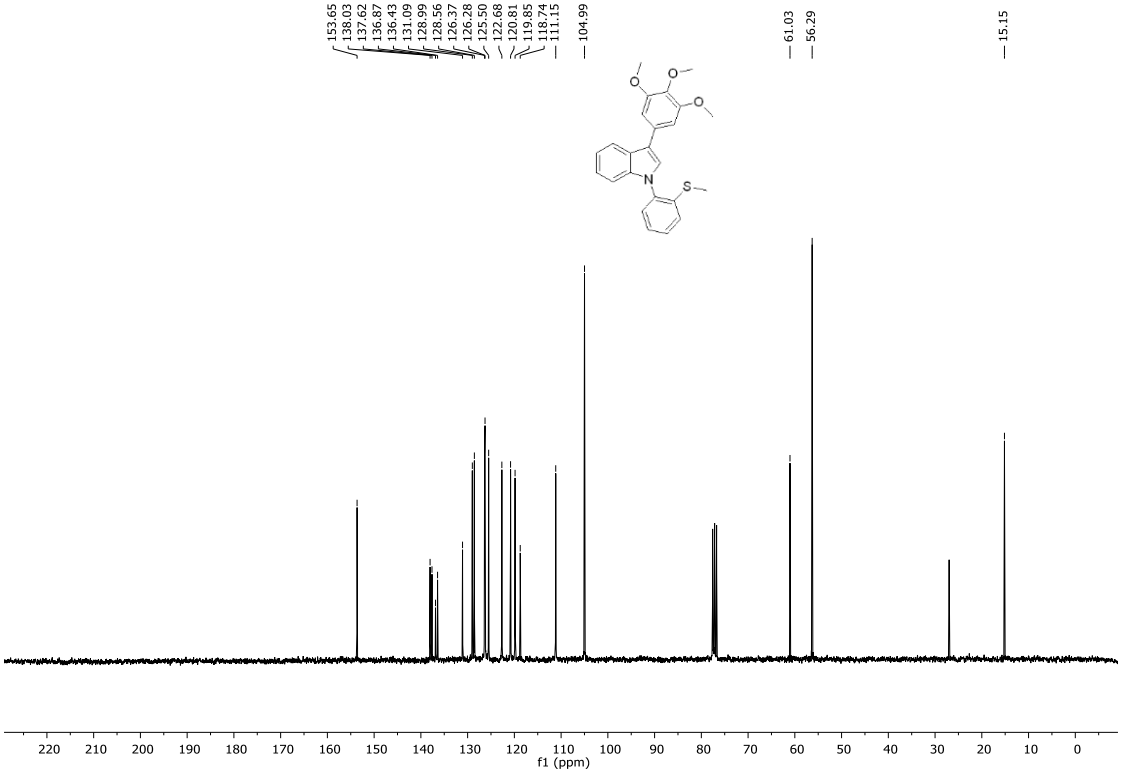
^{13}C NMR (75 MHz, $CDCl_3$) of 3o



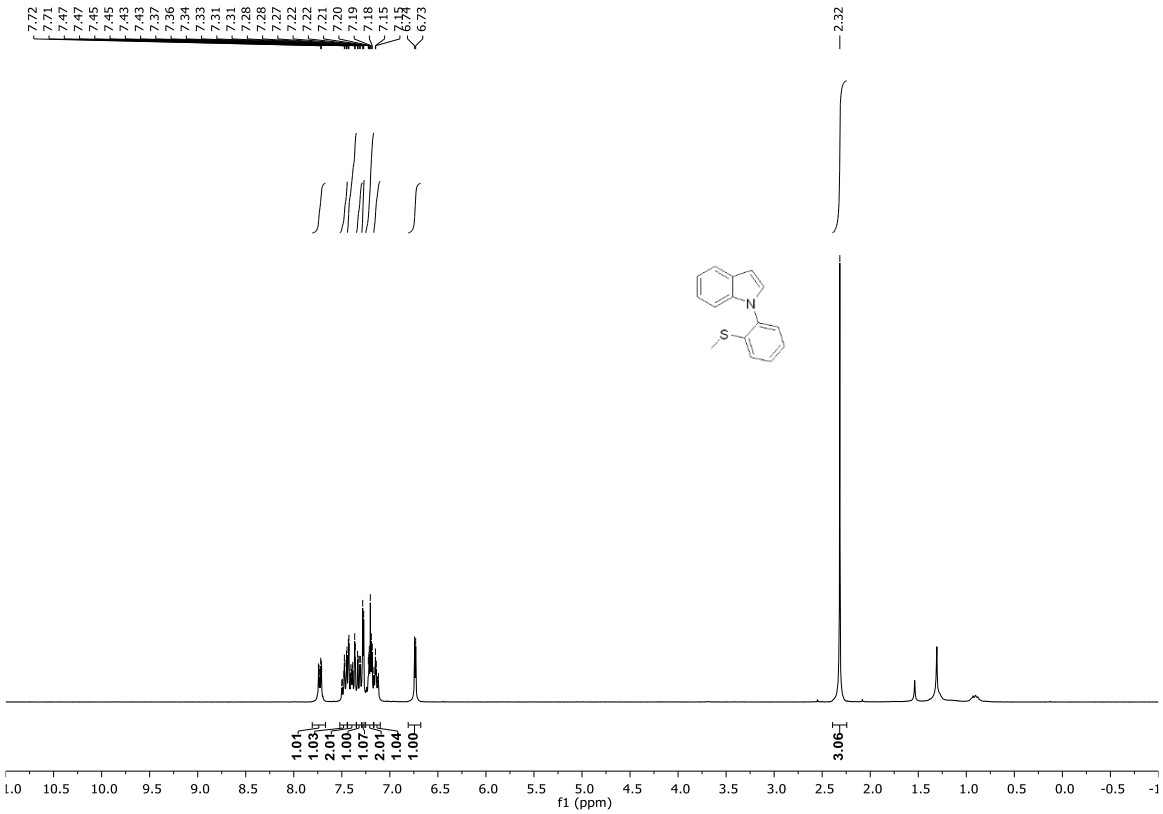
^{1}H NMR (300 MHz, $CDCl_3$) of 3p



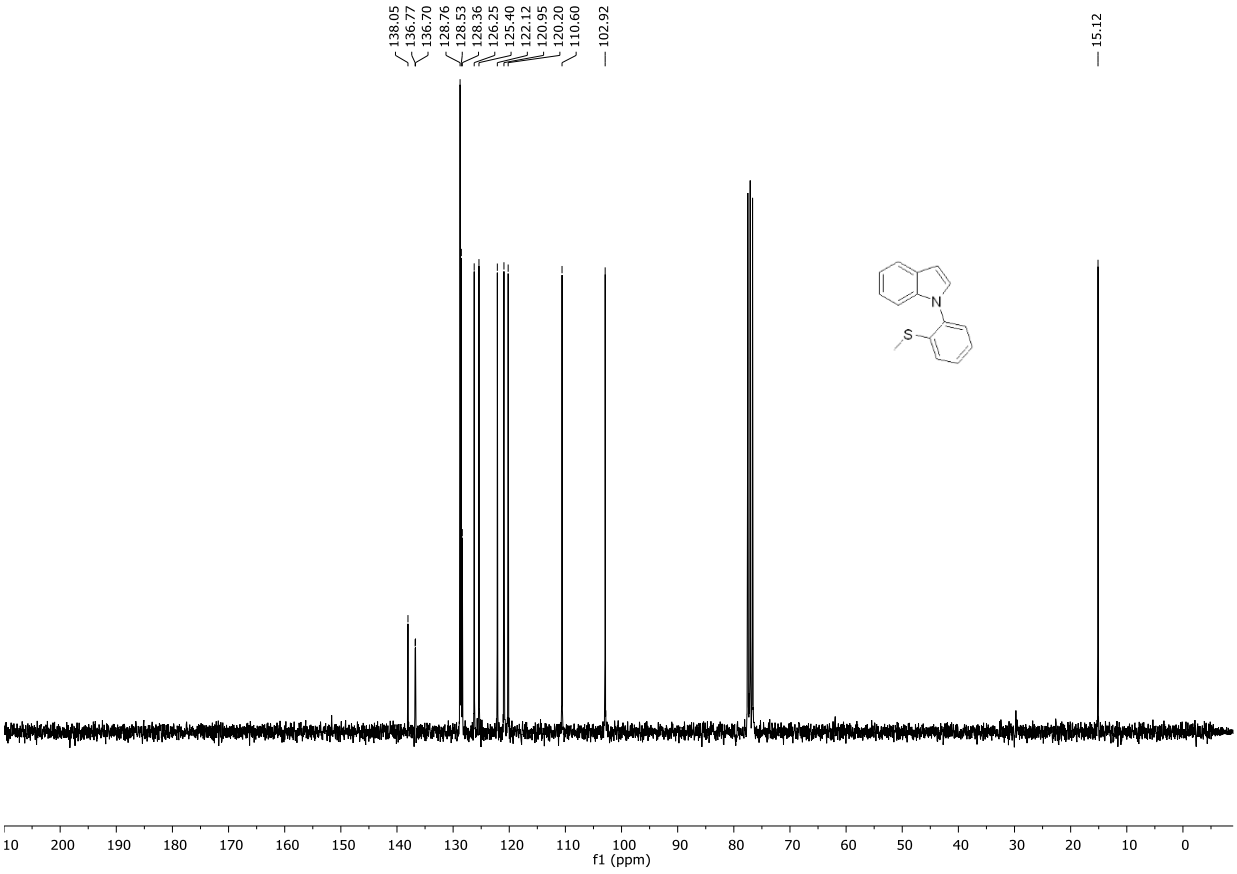
^{13}C NMR (75 MHz, $CDCl_3$) of 3p



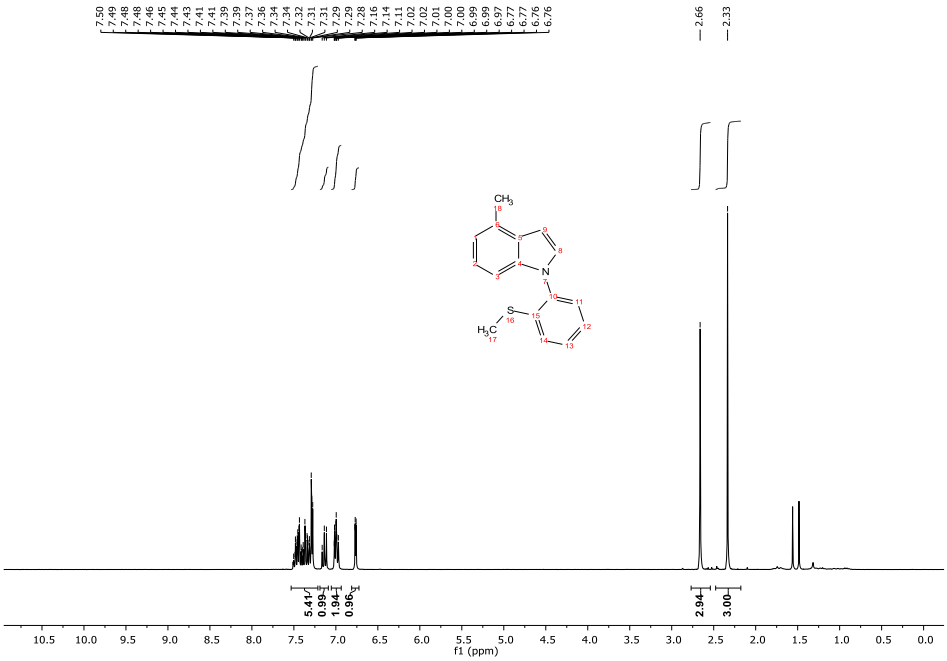
^{1}H NMR (300 MHz, $CDCl_3$) of 3q



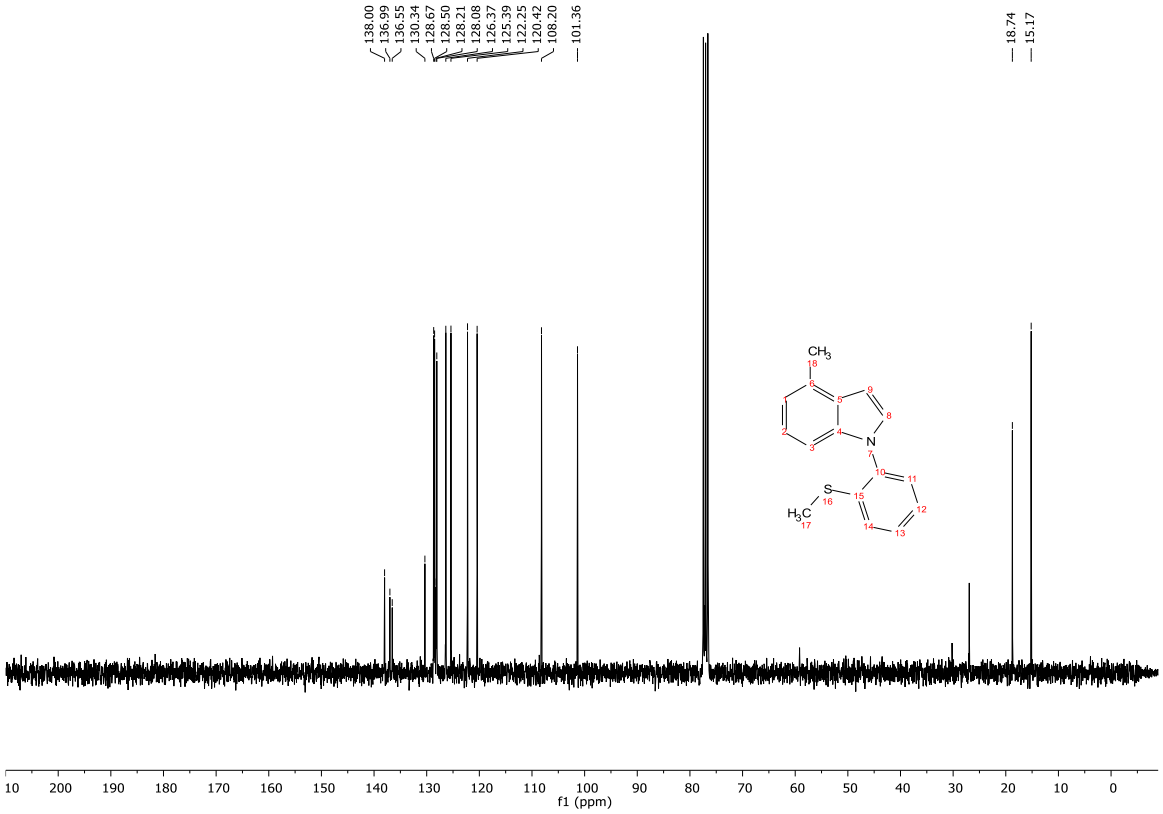
^{13}C NMR (75 MHz, $CDCl_3$) of 3q



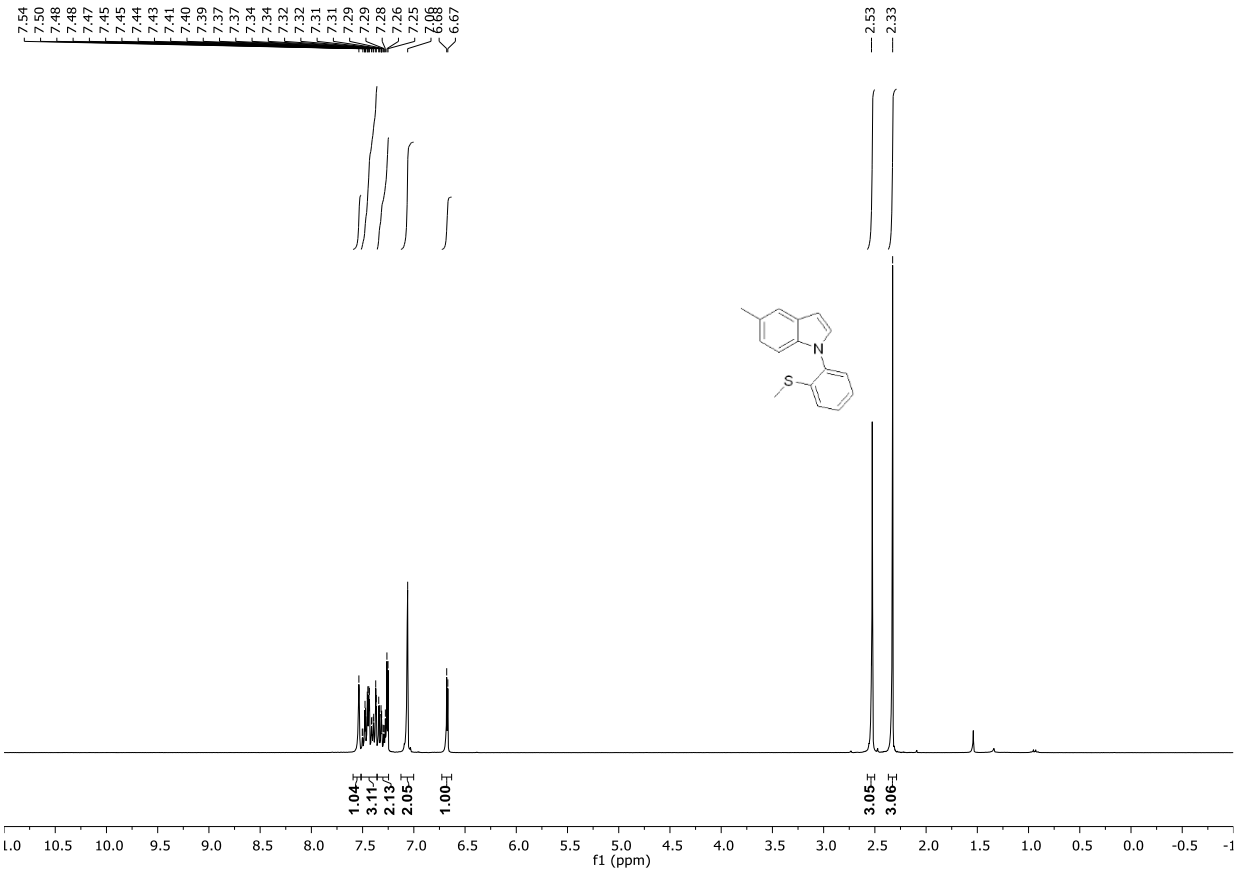
^{1}H NMR (300 MHz, $CDCl_3$) of 3r



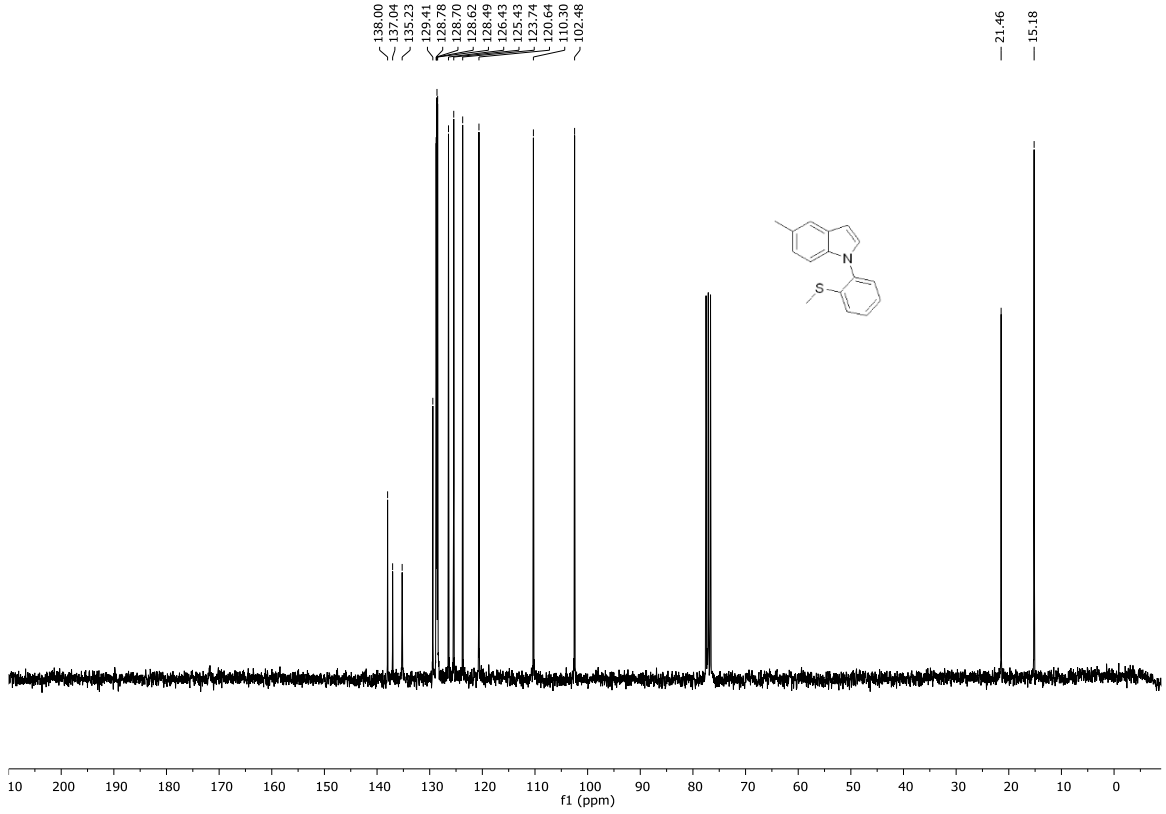
^{13}C NMR (75 MHz, $CDCl_3$) of 3r



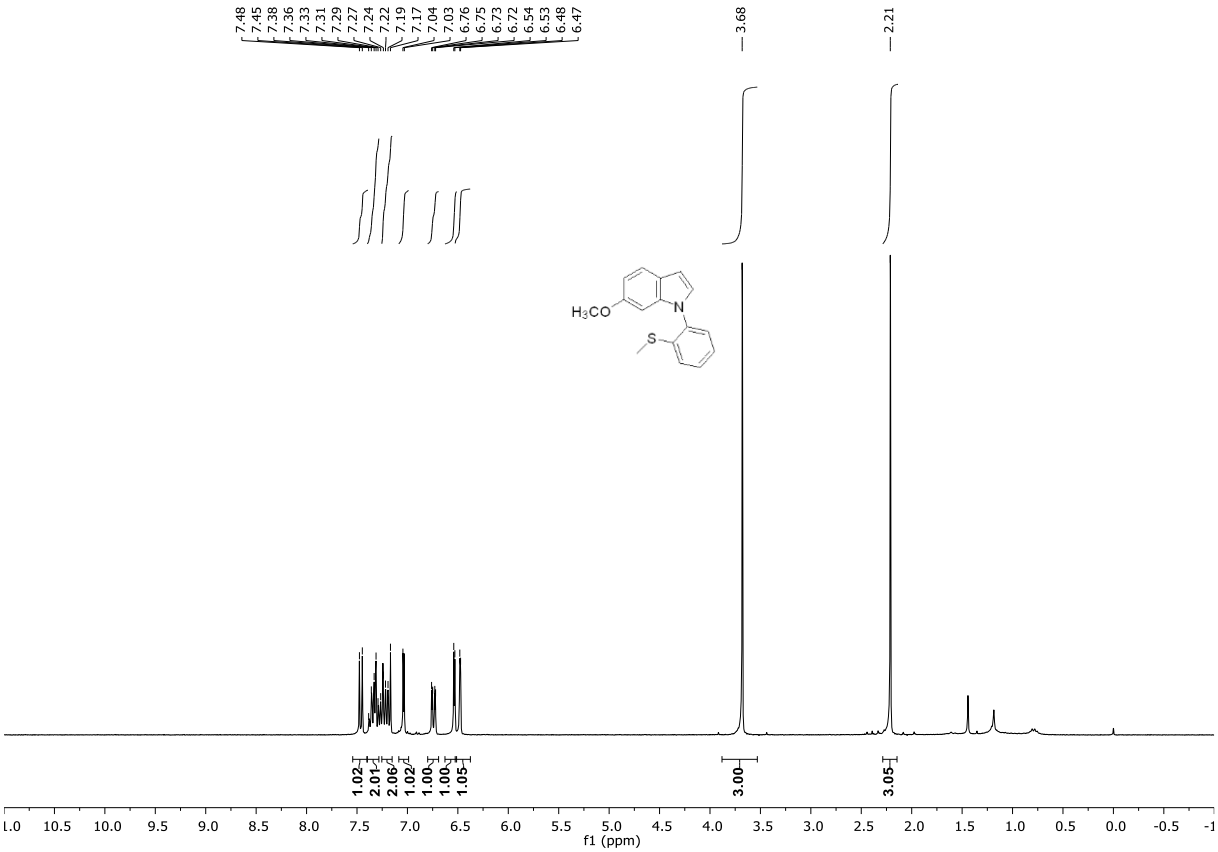
^{1}H NMR (300 MHz, $CDCl_3$) of 3s



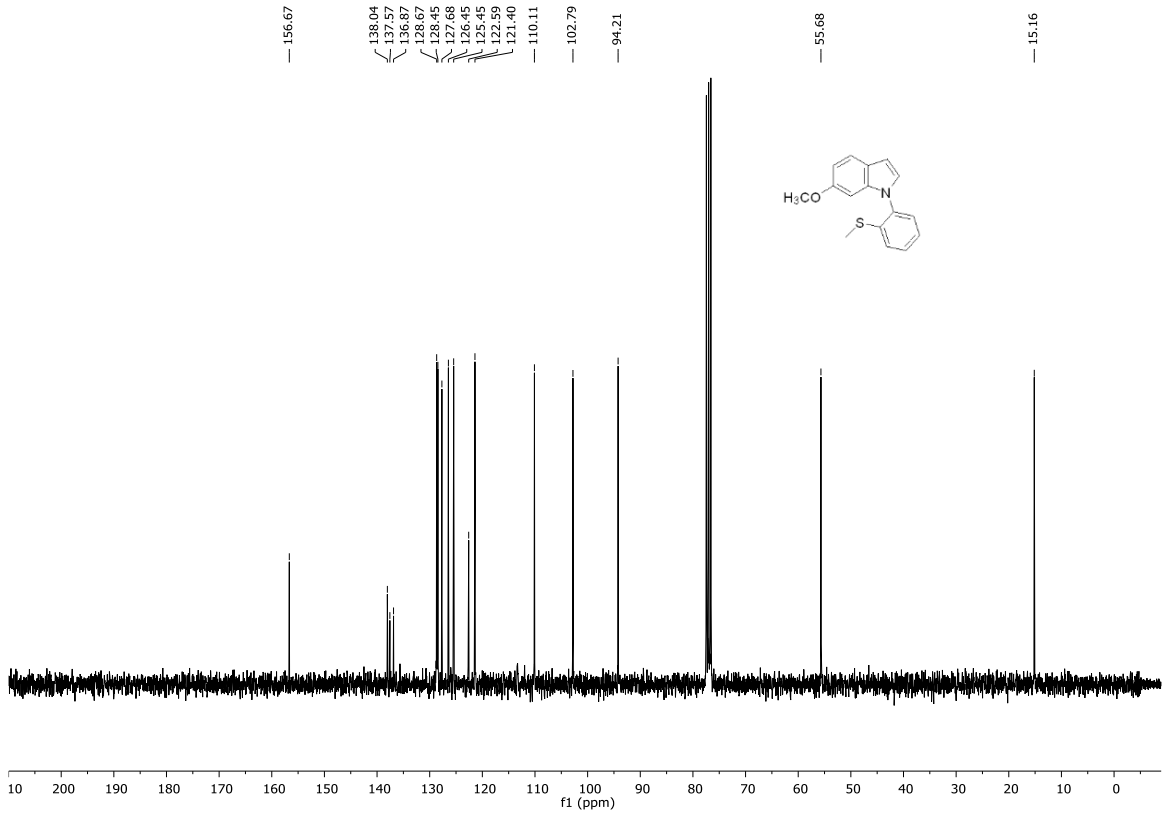
^{13}C NMR (75 MHz, $CDCl_3$) of 3s



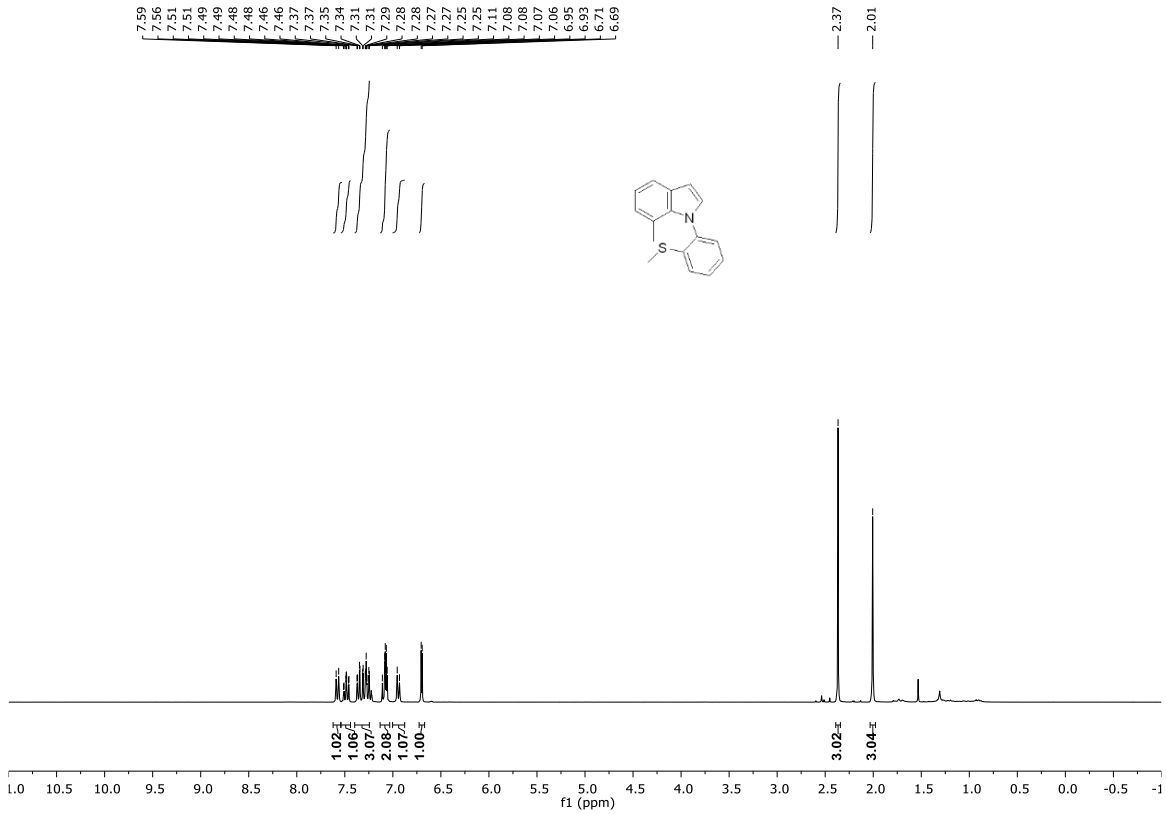
^{1}H NMR (300 MHz, $CDCl_3$) of 3t



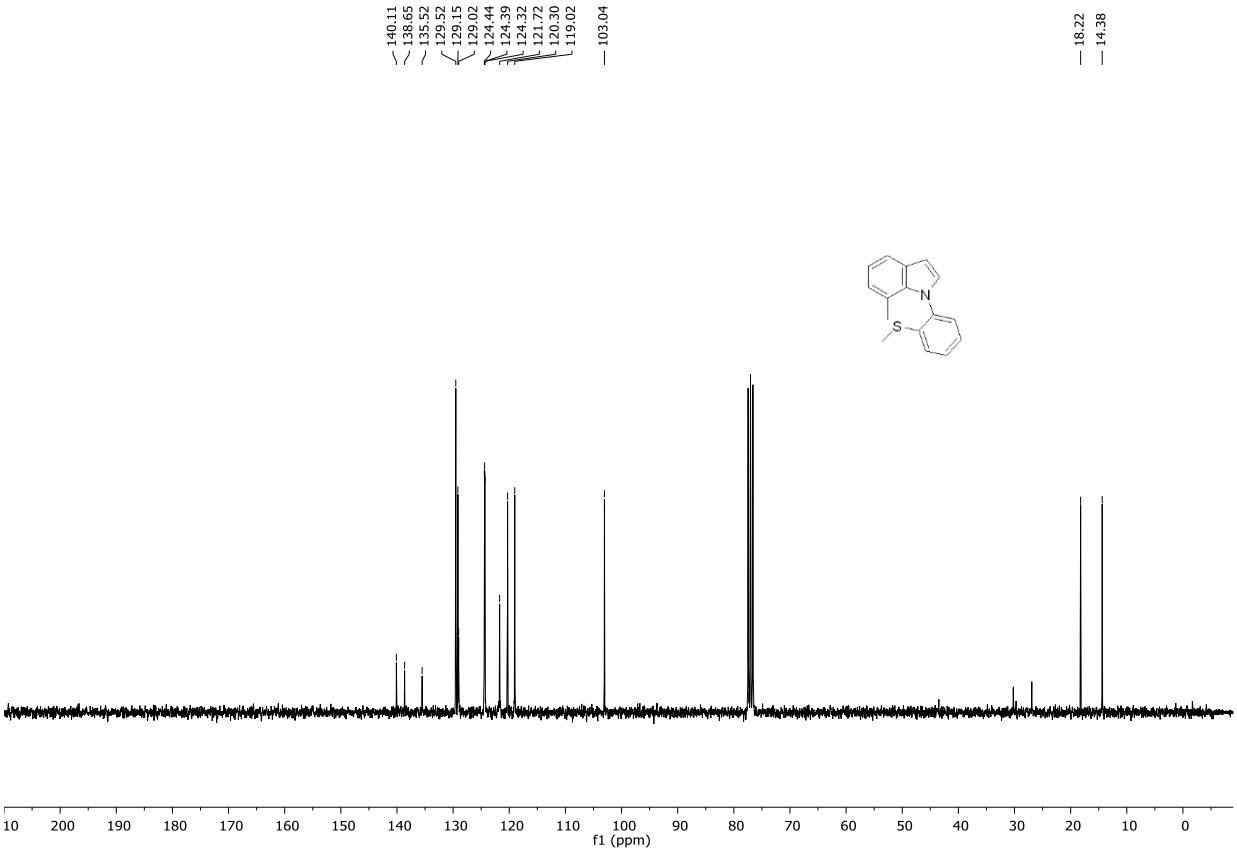
^{13}C NMR (75 MHz, $CDCl_3$) of 3t



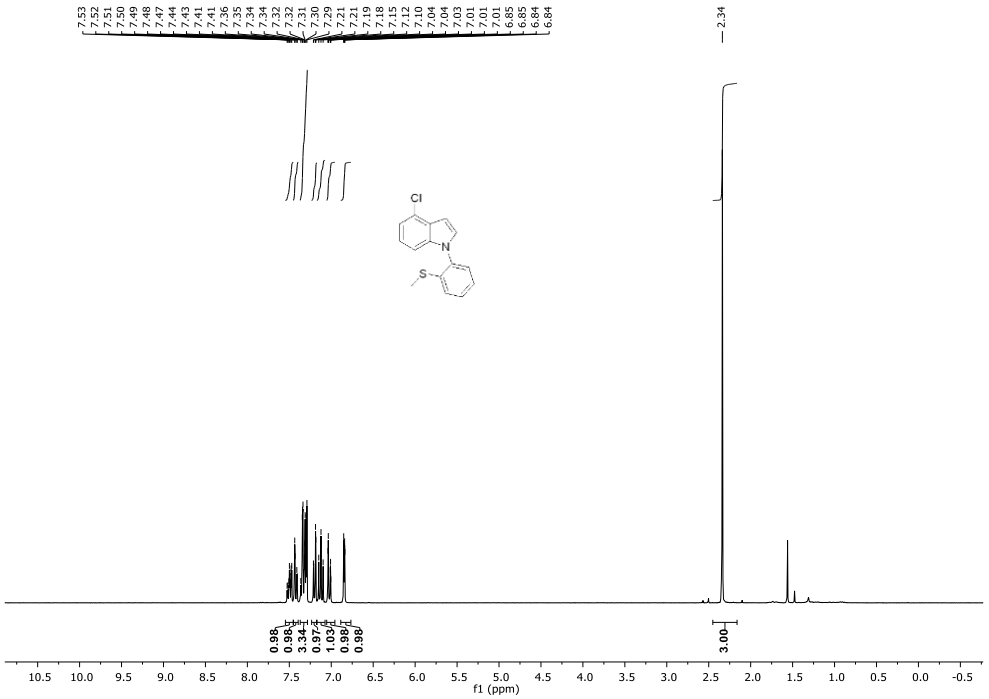
^{1}H NMR (300 MHz, $CDCl_3$) of 3u



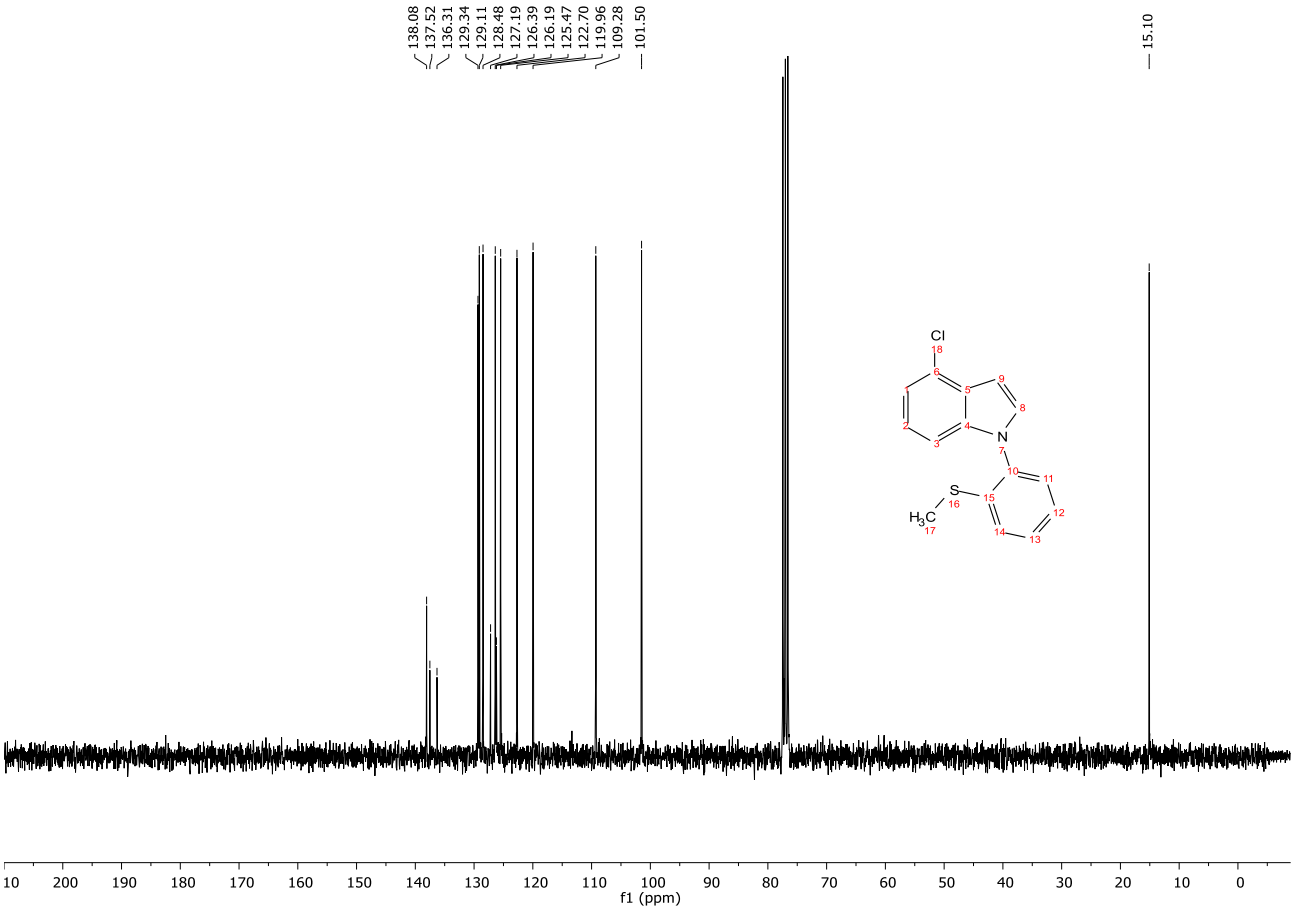
^{13}C NMR (75 MHz, $CDCl_3$) of 3u



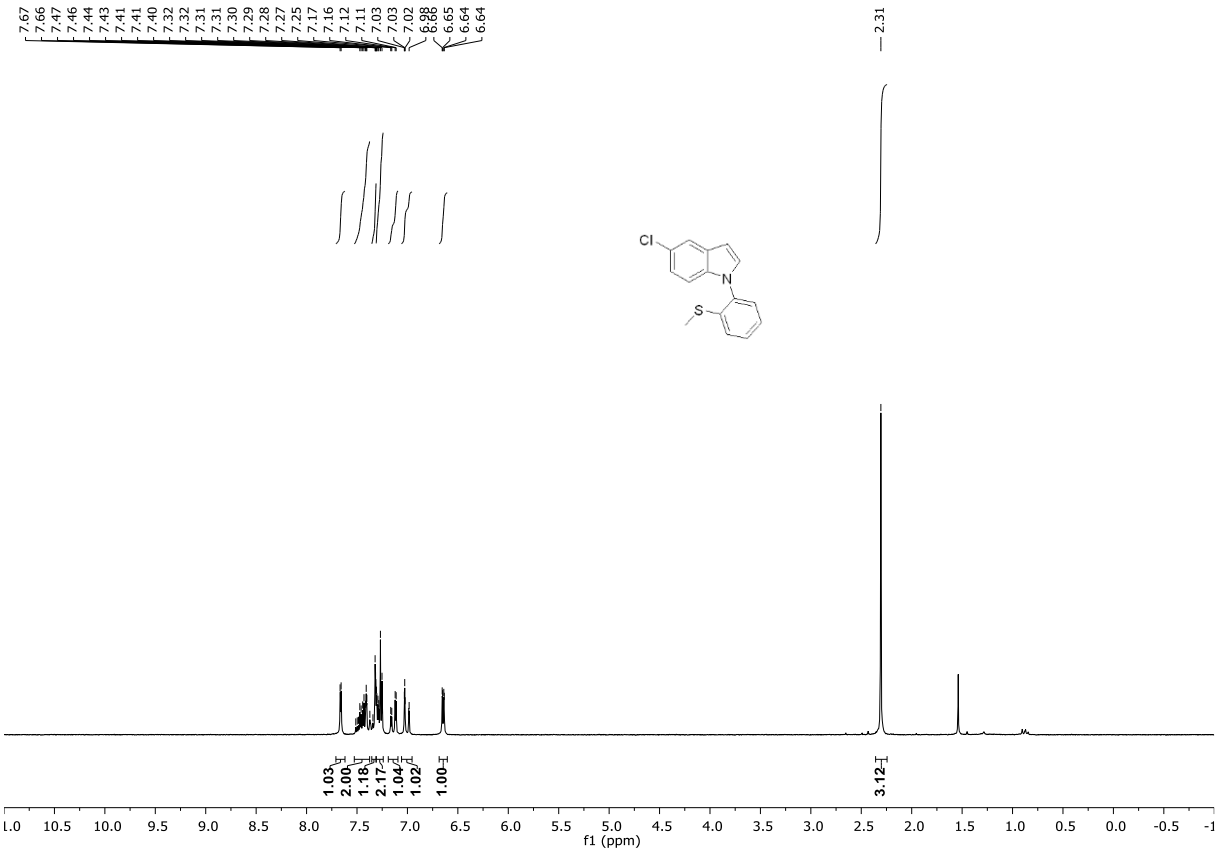
^{1}H NMR (300 MHz, $CDCl_3$) of 3v



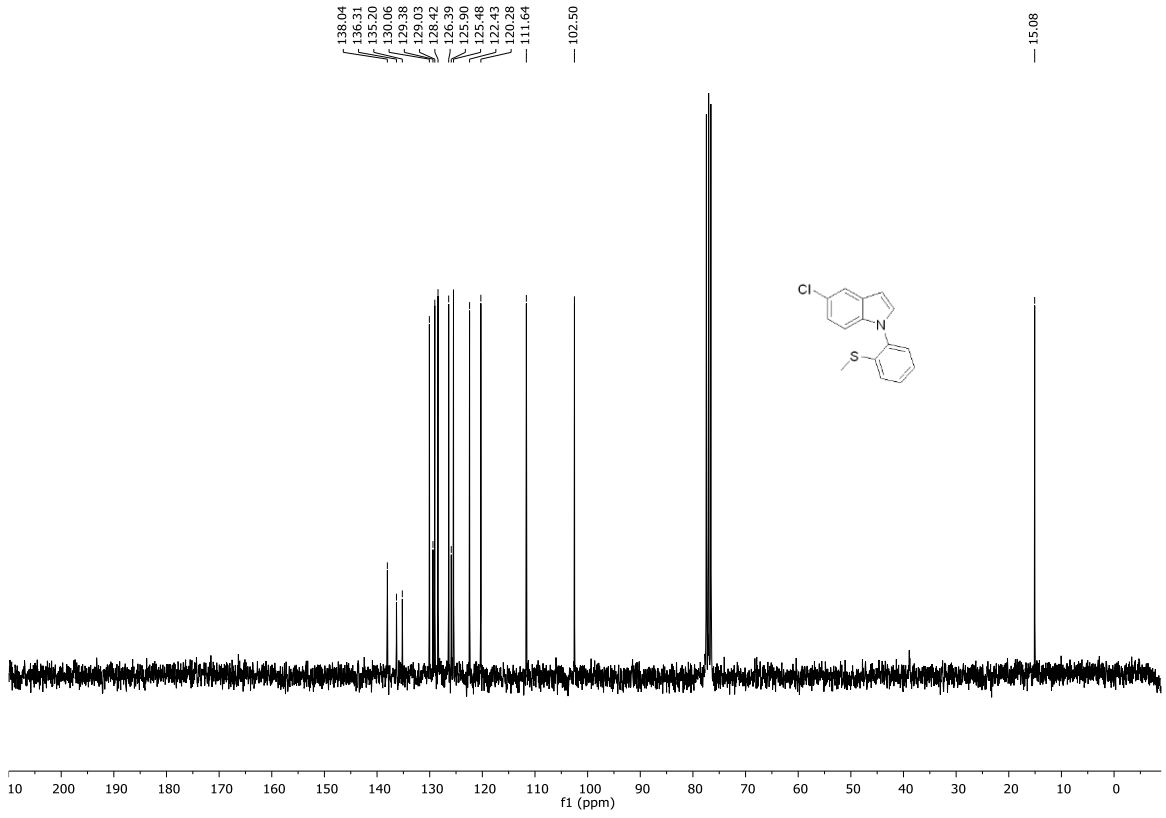
^{13}C NMR (75 MHz, $CDCl_3$) of 3v



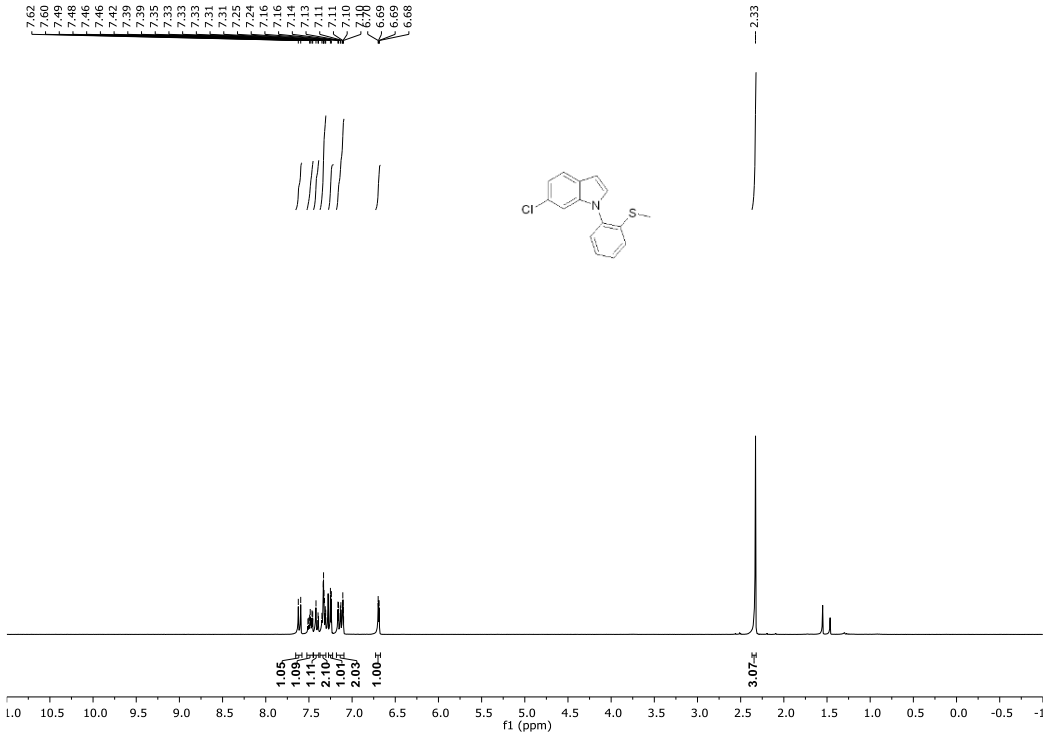
^{1}H NMR (200 MHz, $CDCl_3$) of 3w



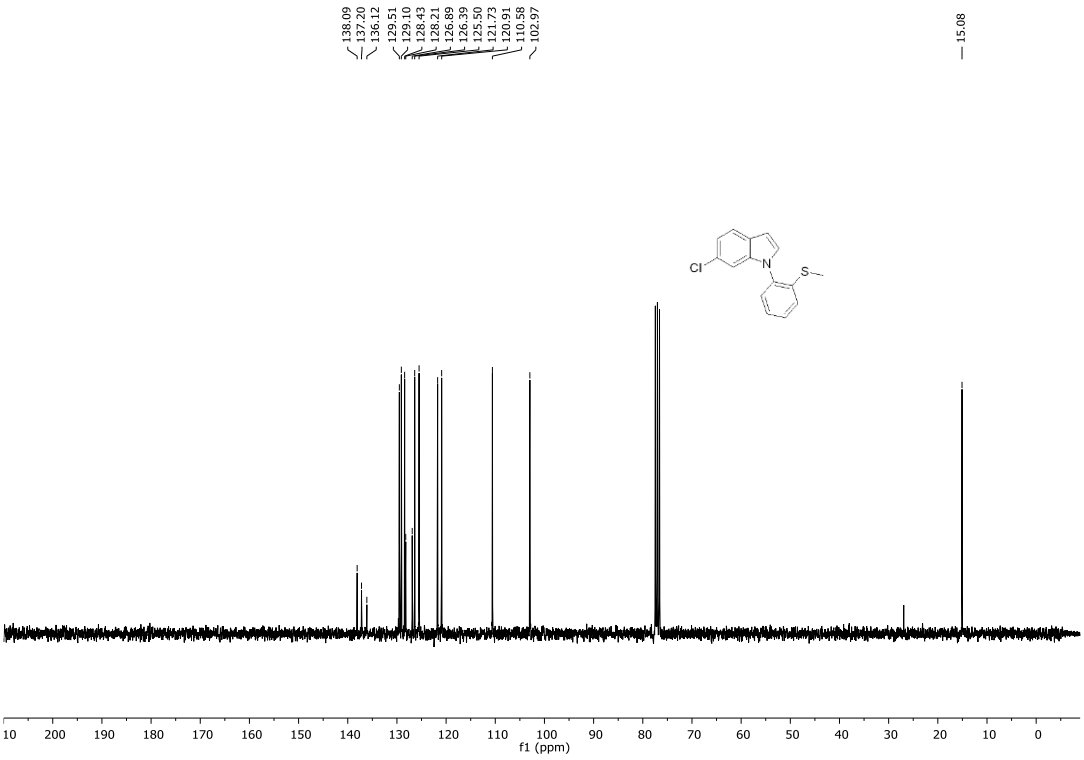
^{13}C NMR (75 MHz, $CDCl_3$) of 3w



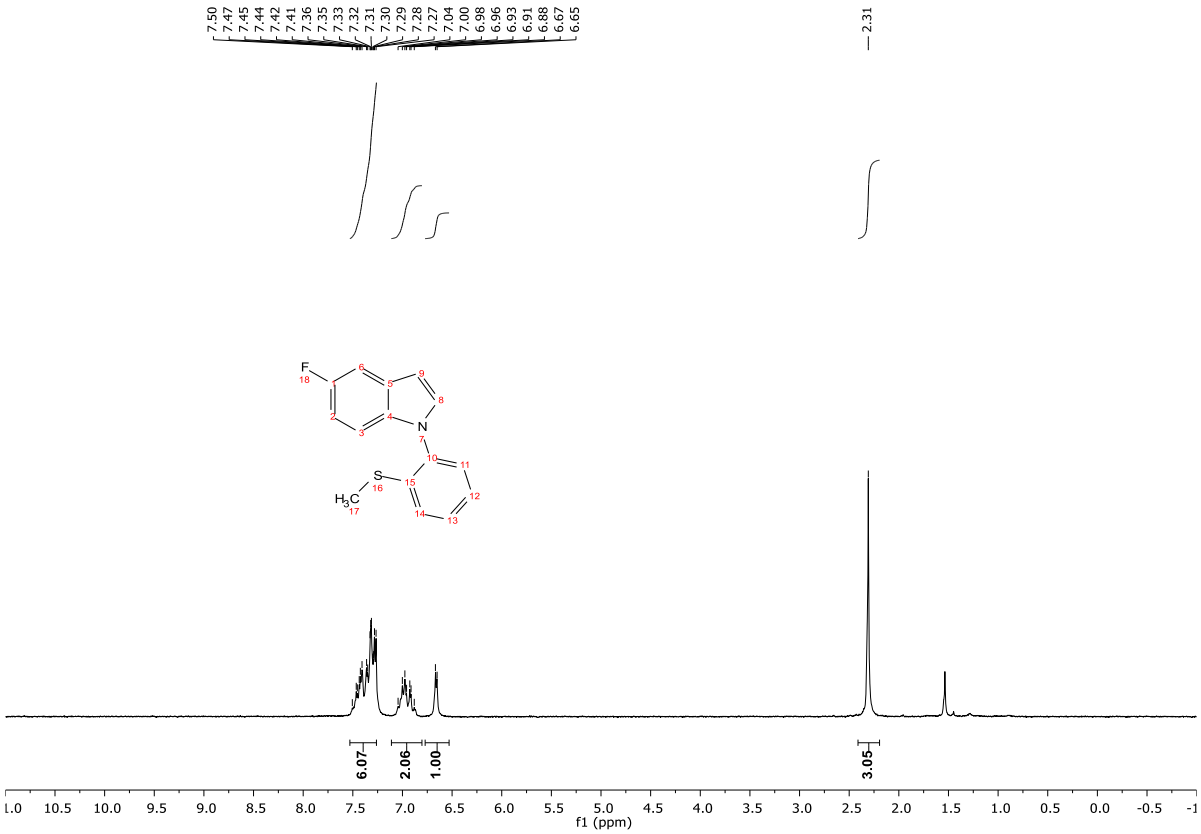
^{1}H NMR (300 MHz, $CDCl_3$) of 3x



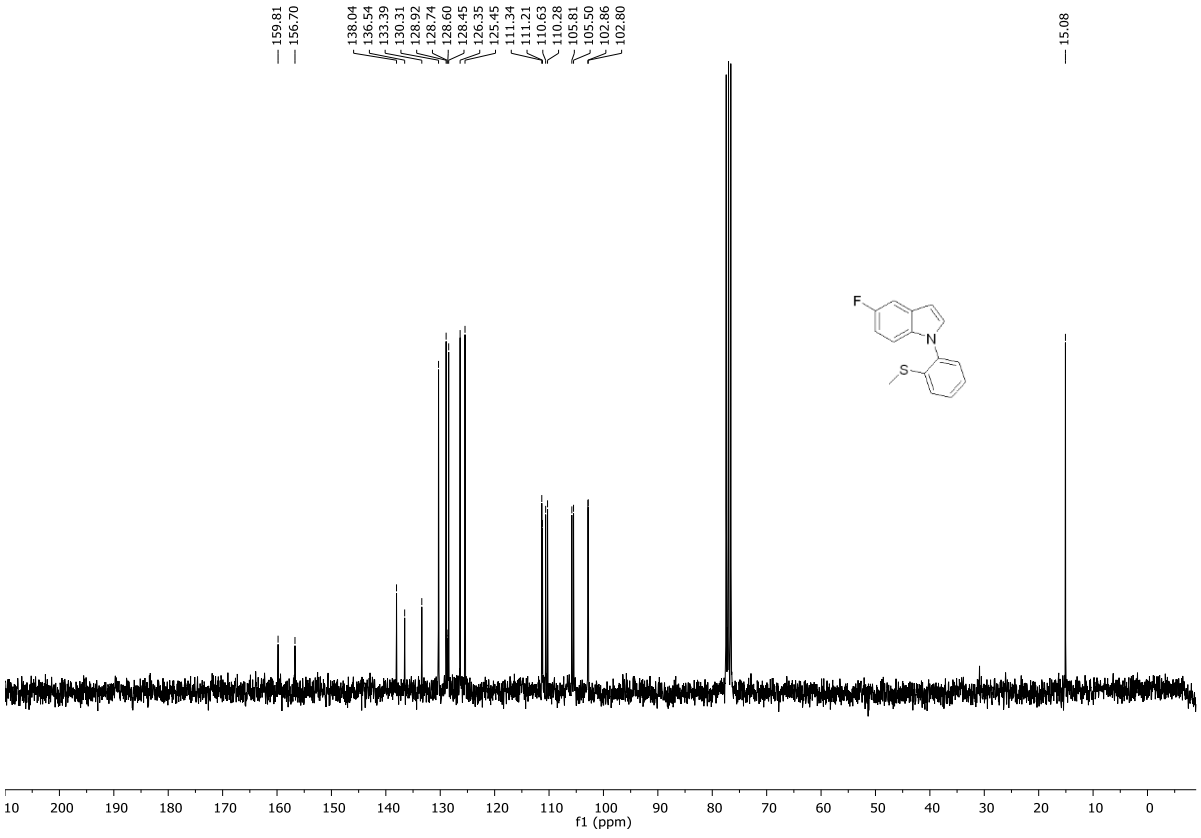
^{13}C NMR (75 MHz, $CDCl_3$) of 3x



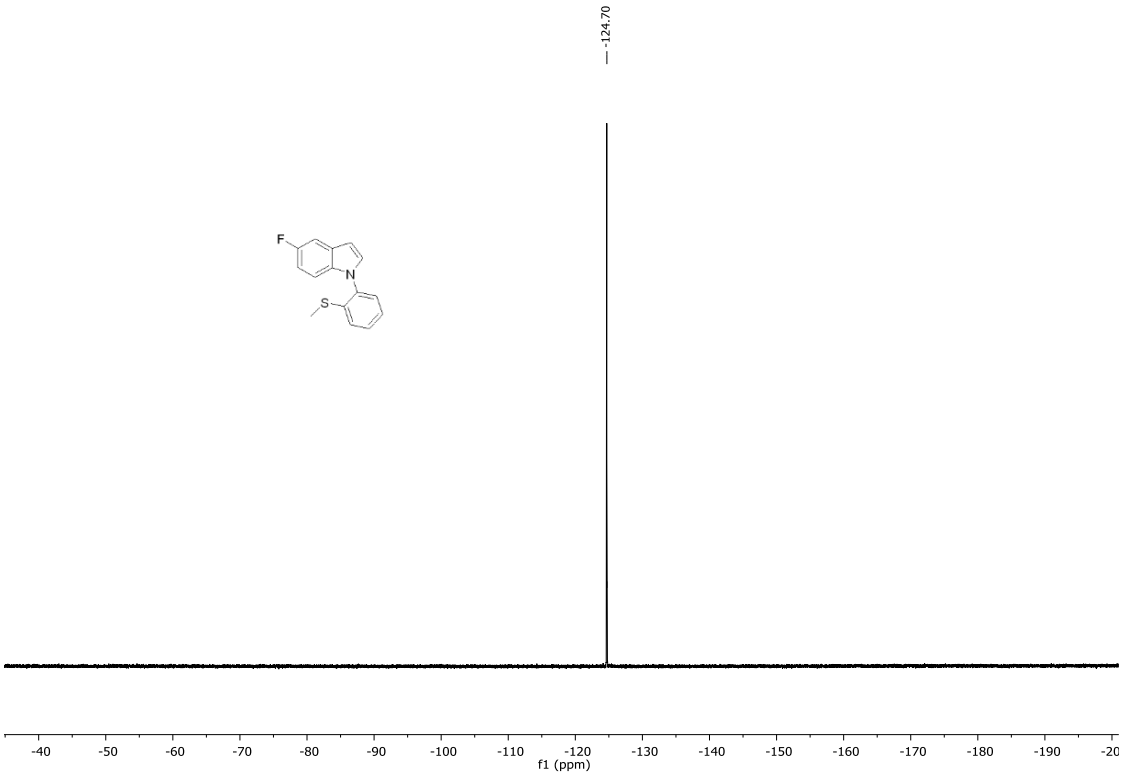
^{1}H NMR (200 MHz, $CDCl_3$) of 3y



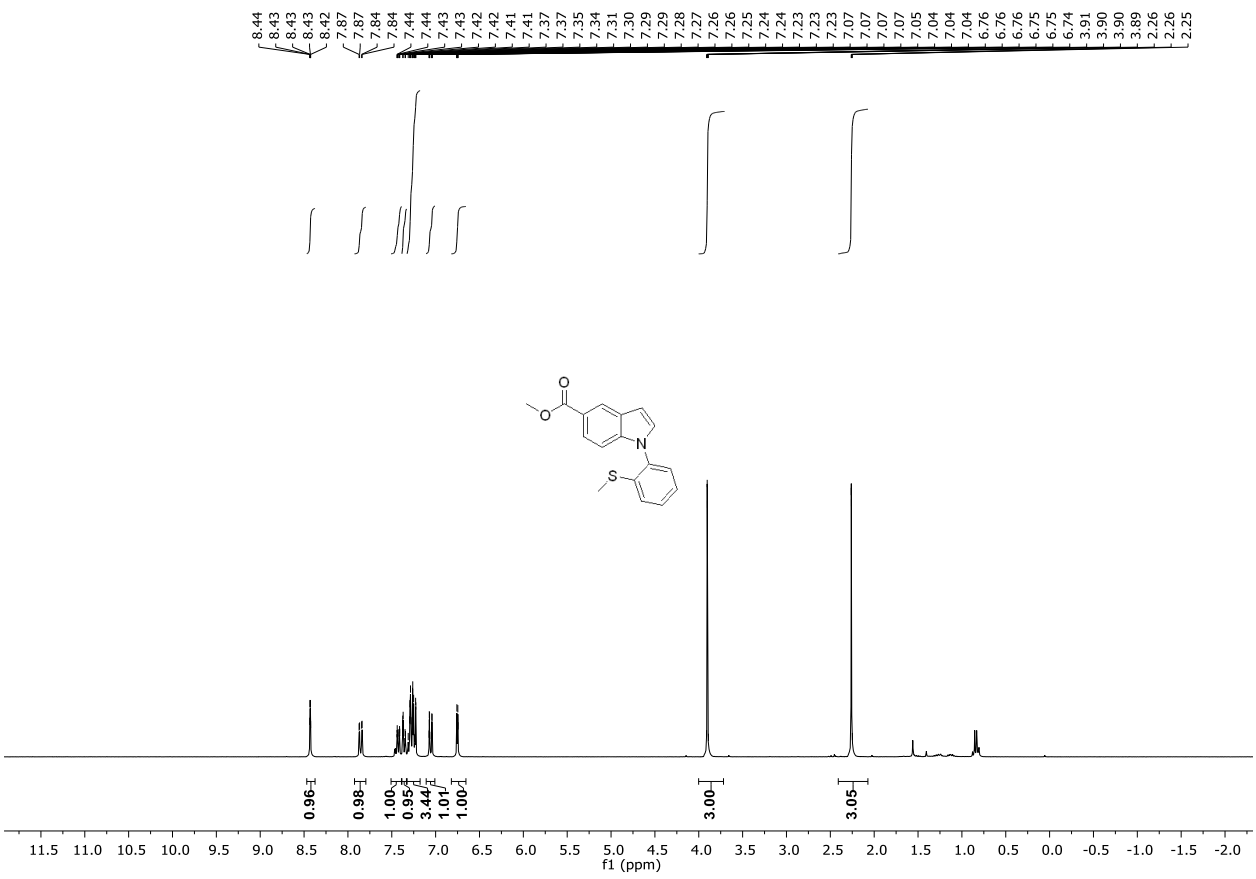
^{13}C NMR (75 MHz, $CDCl_3$) of 3y



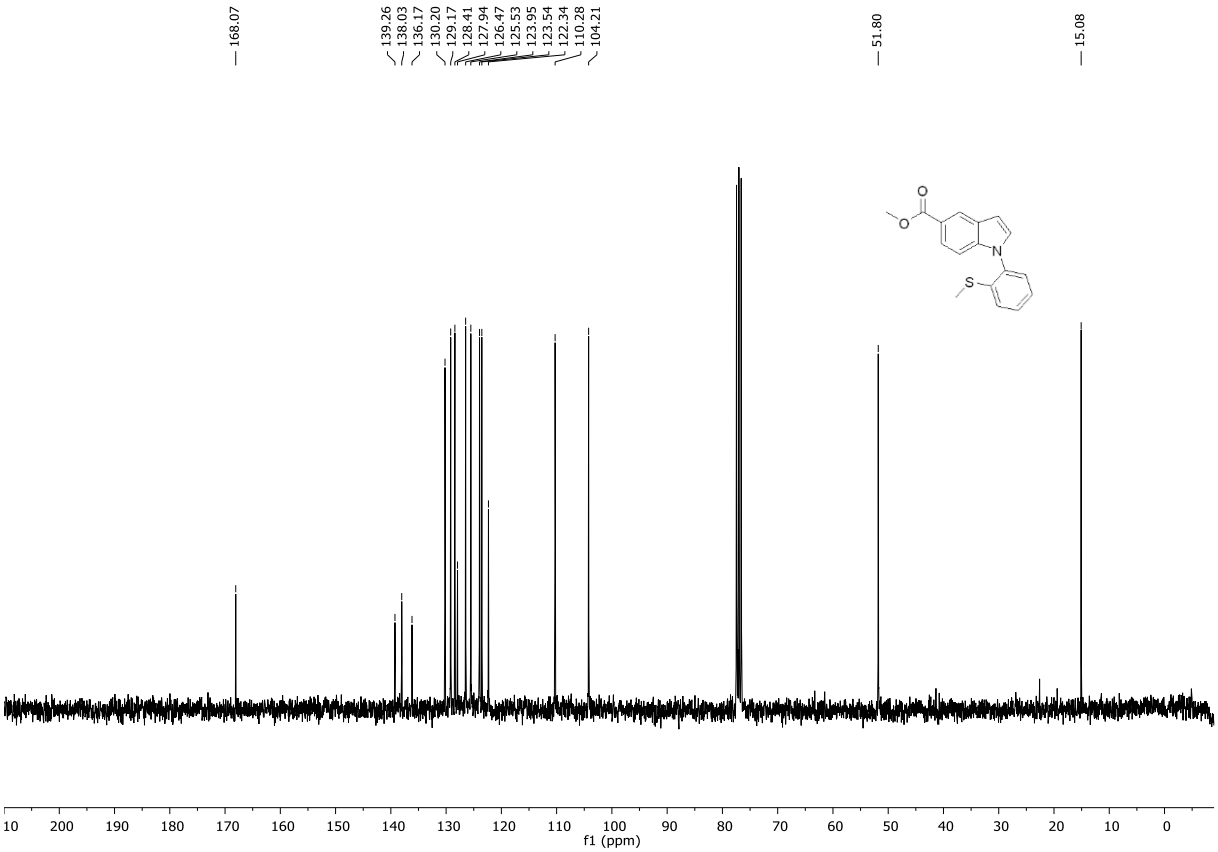
^{19}F NMR (188 MHz, $CDCl_3$) of 3y



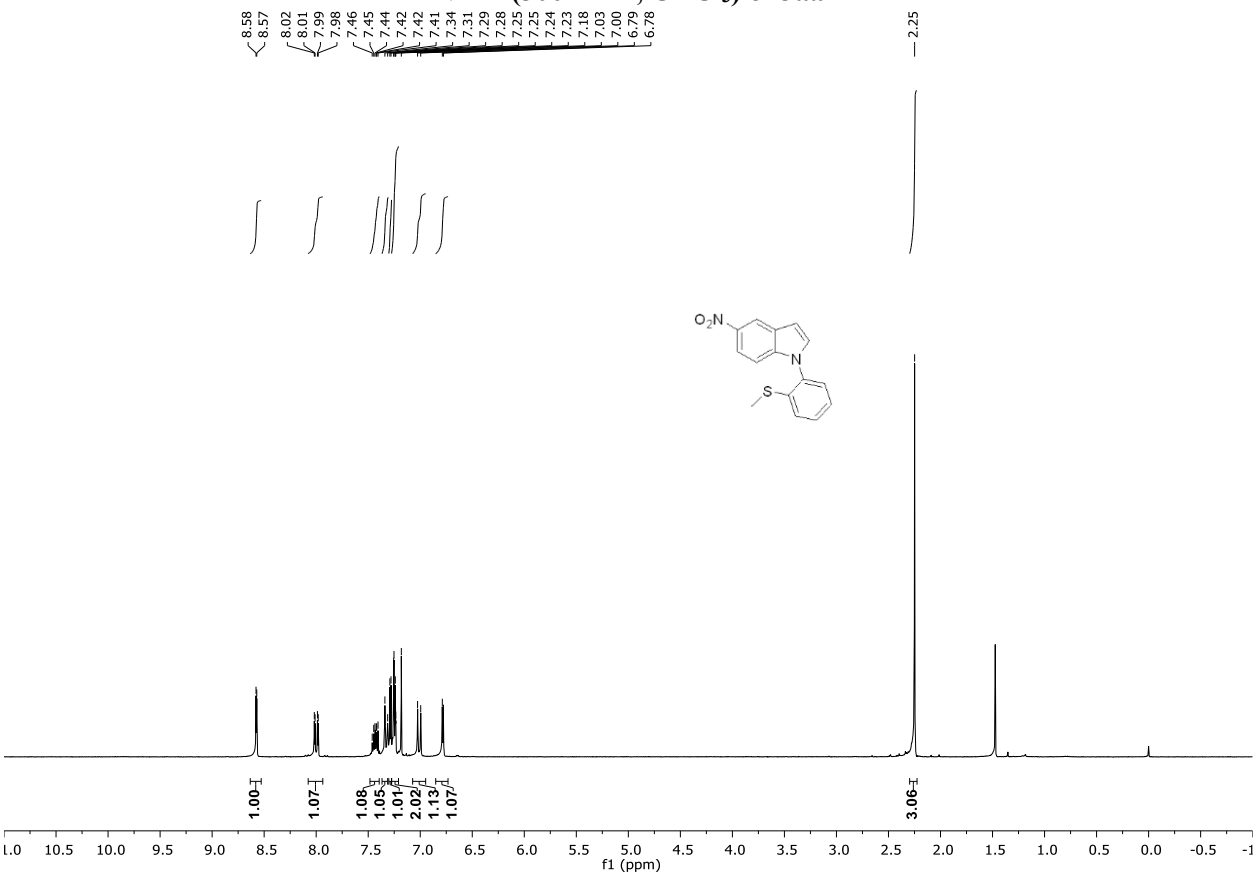
^{1}H NMR (300 MHz, $CDCl_3$) of 3z



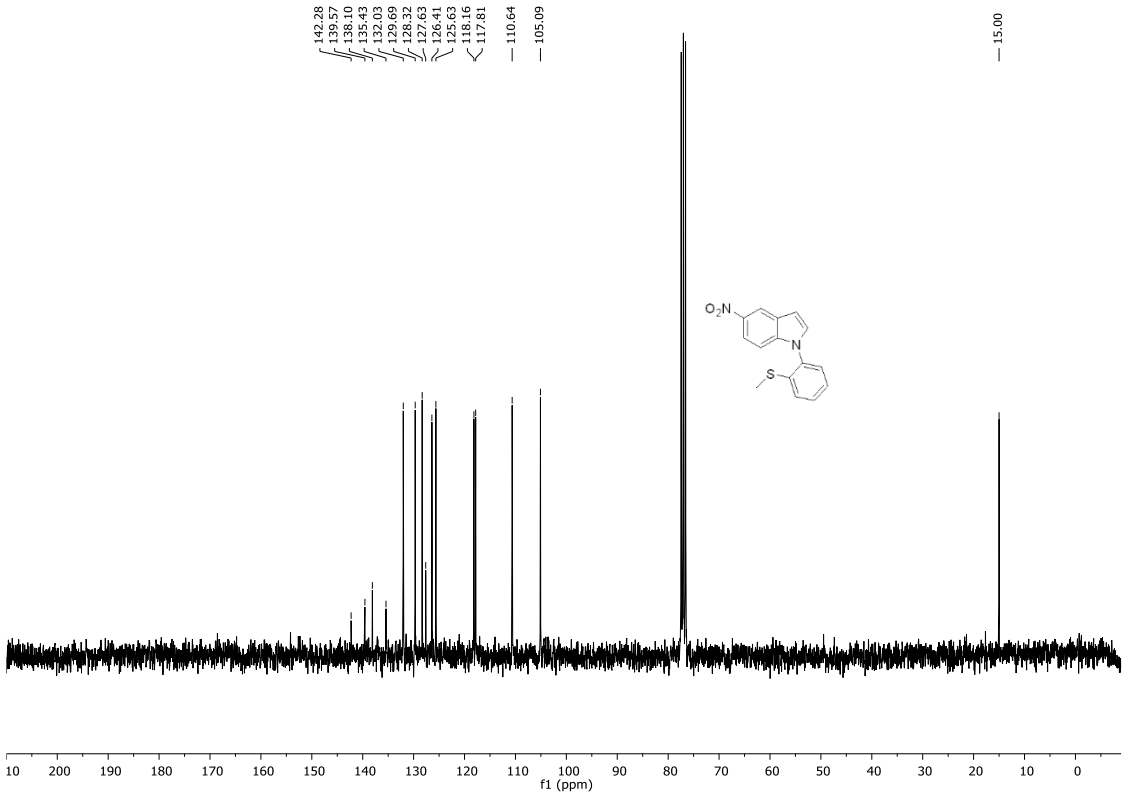
^{13}C NMR (75 MHz, $CDCl_3$) of 3z



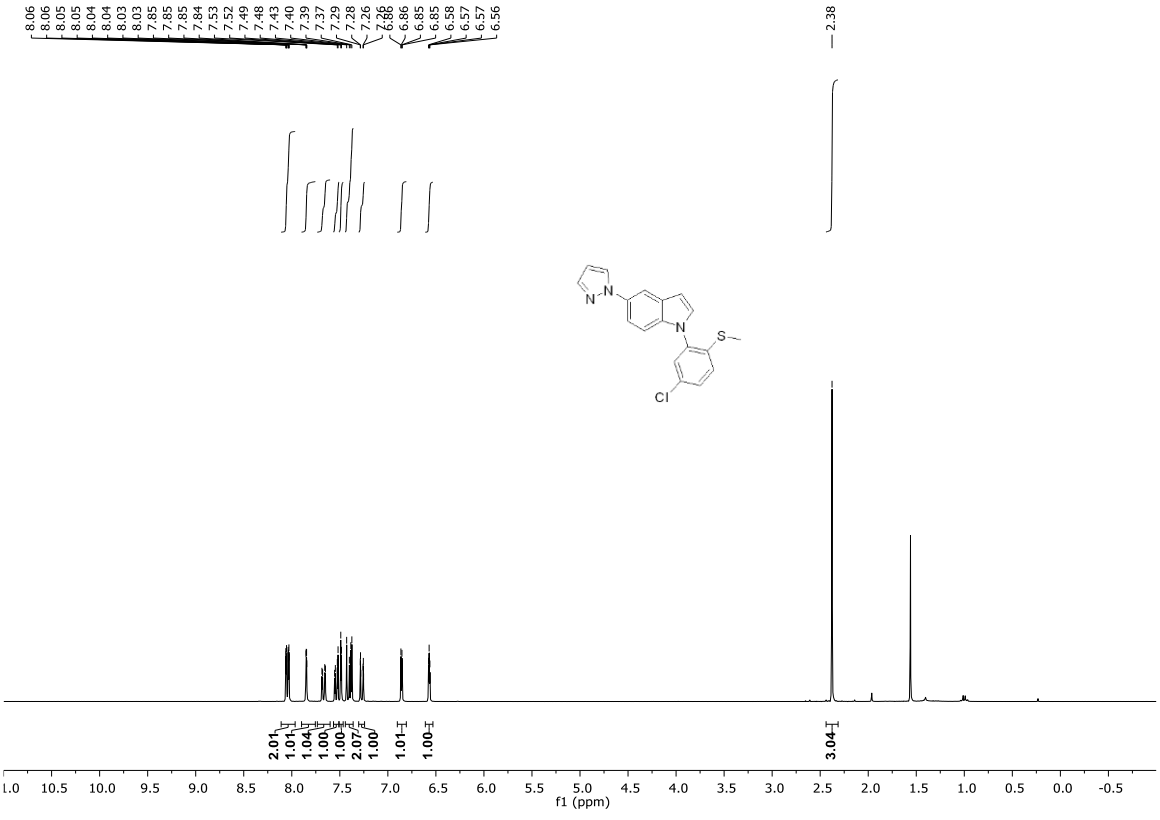
^{1}H NMR (300 MHz, $CDCl_3$) of 3aa



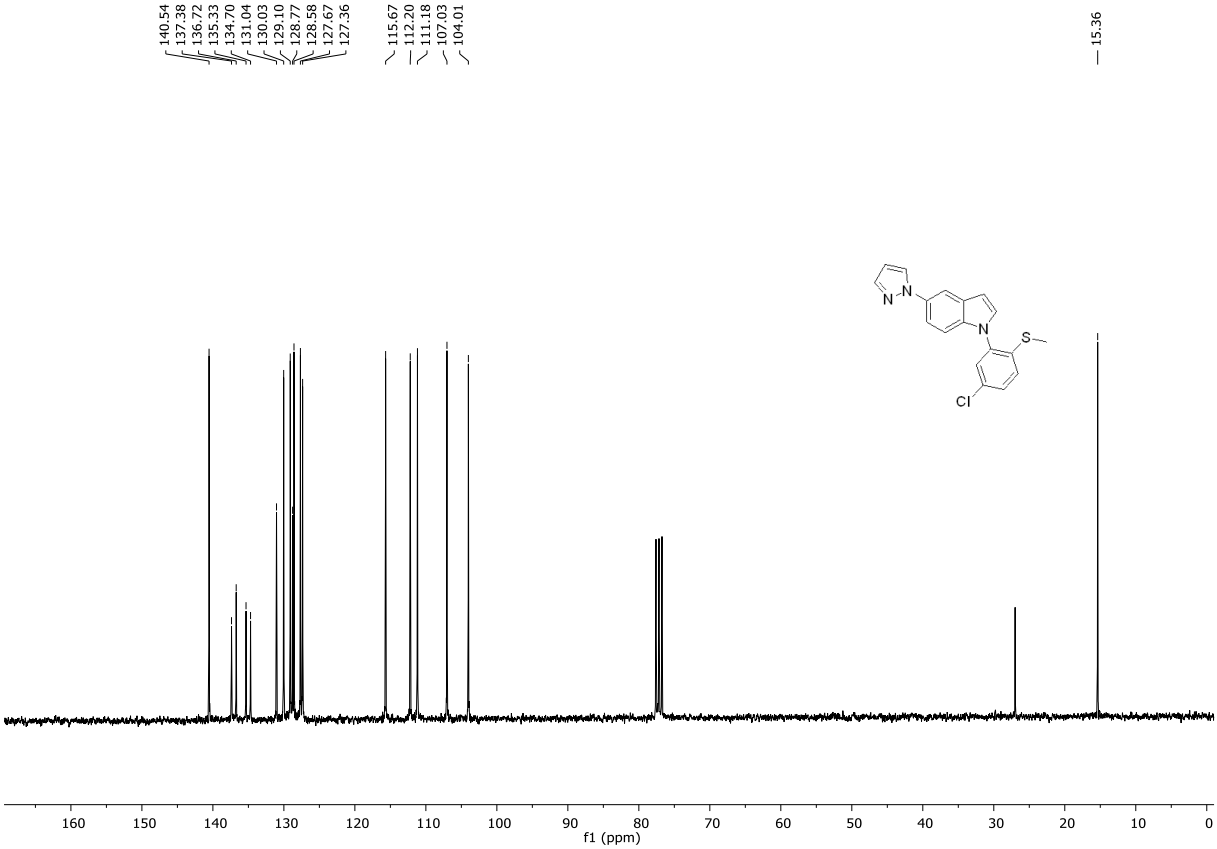
^{13}C NMR (75 MHz, $CDCl_3$) of 3aa



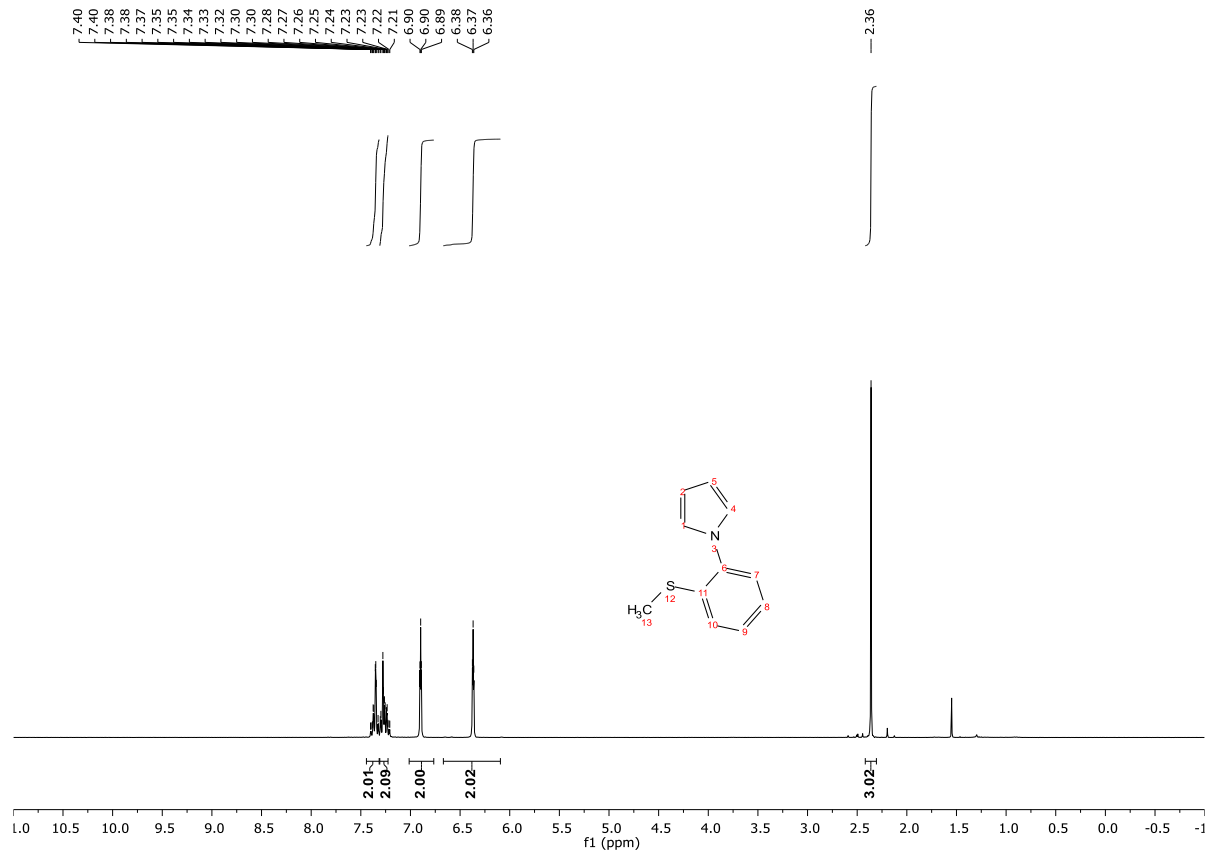
^{1}H NMR (300 MHz, $CDCl_3$) of 3ab



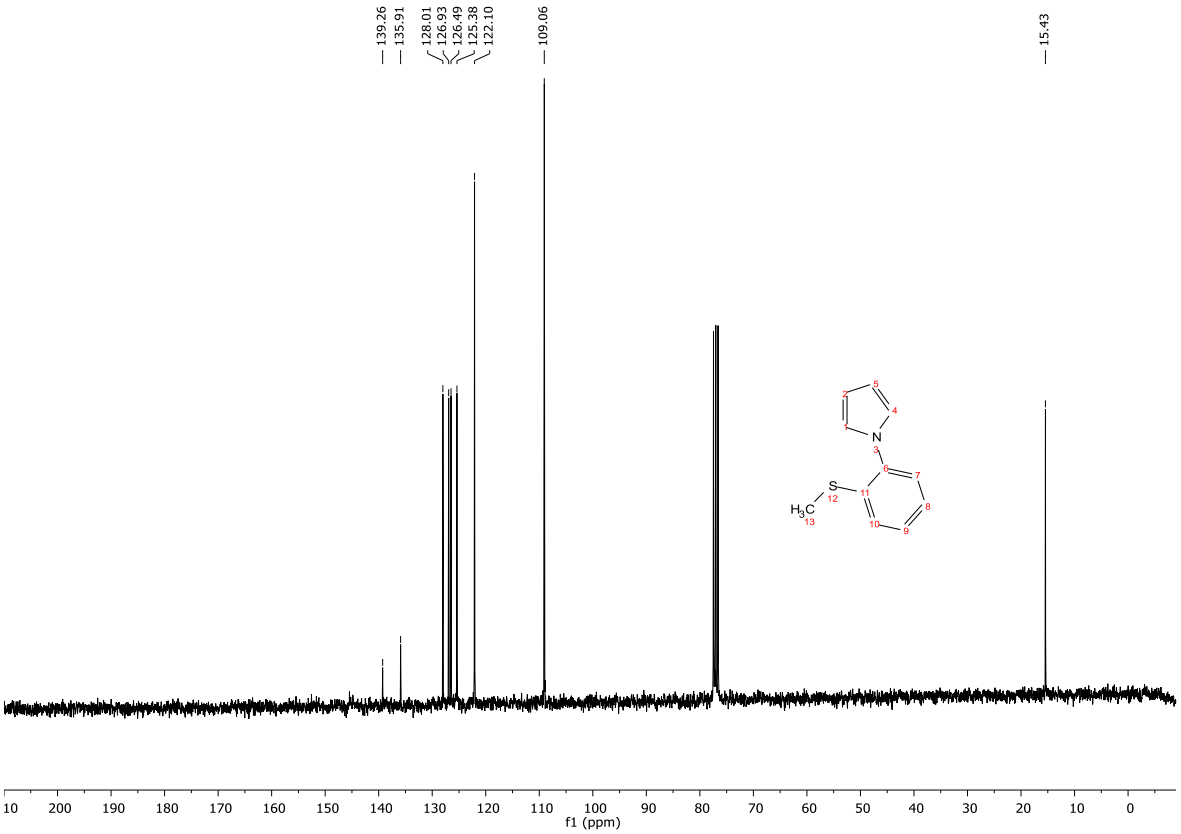
^{13}C NMR (75 MHz, $CDCl_3$) of 3ab



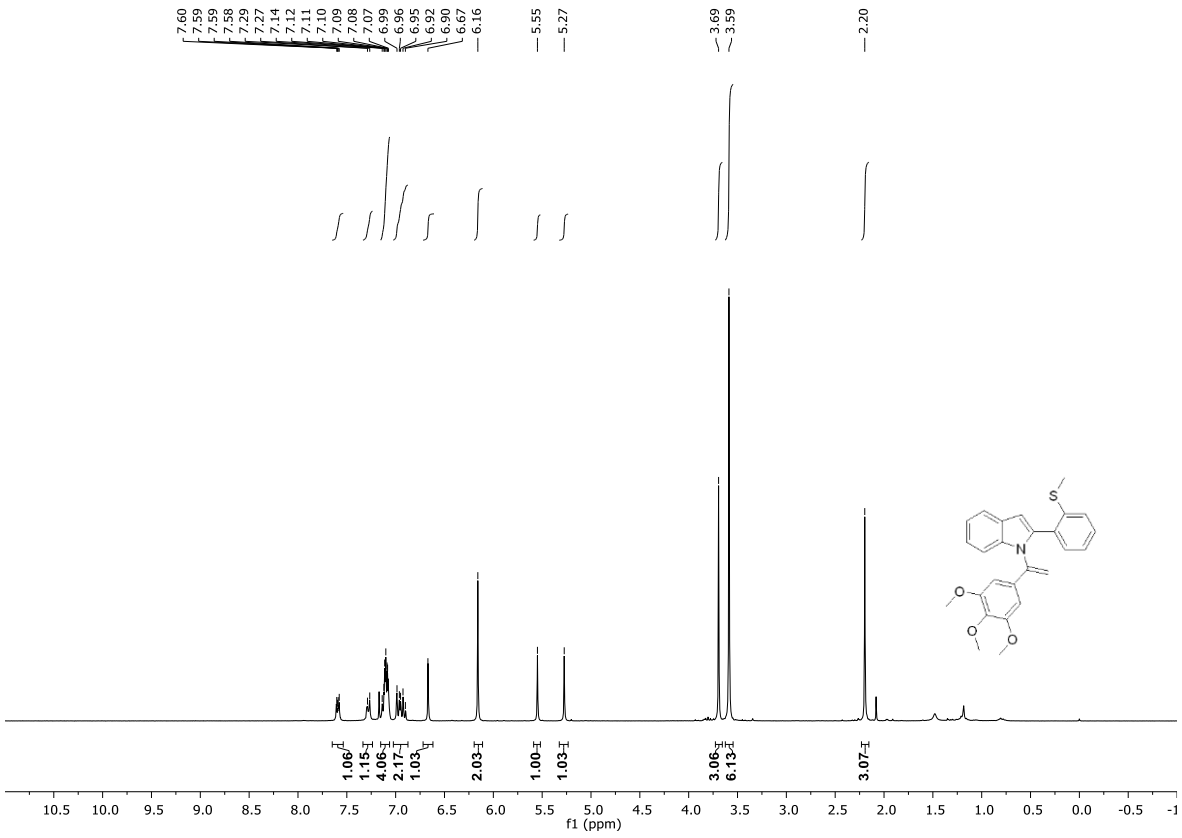
^{1}H NMR (300 MHz, $CDCl_3$) of 3ac



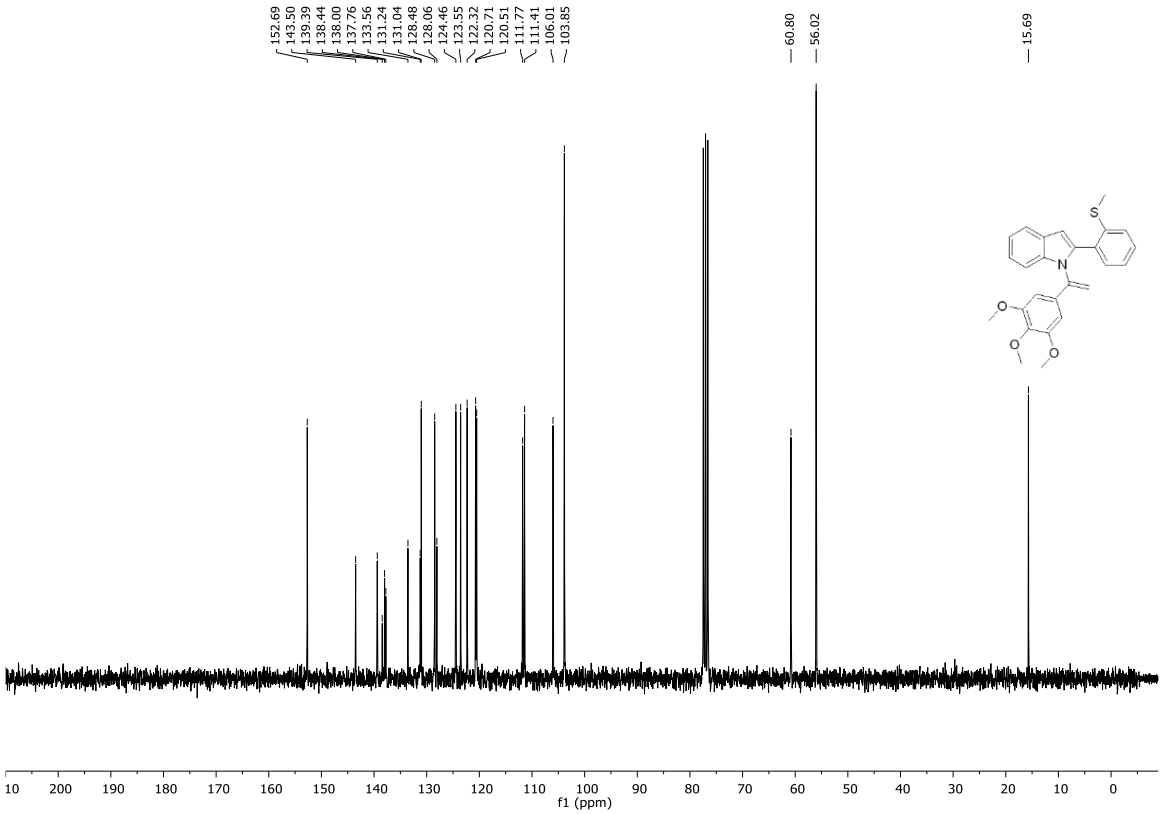
^{13}C NMR (75 MHz, $CDCl_3$) of 3ac



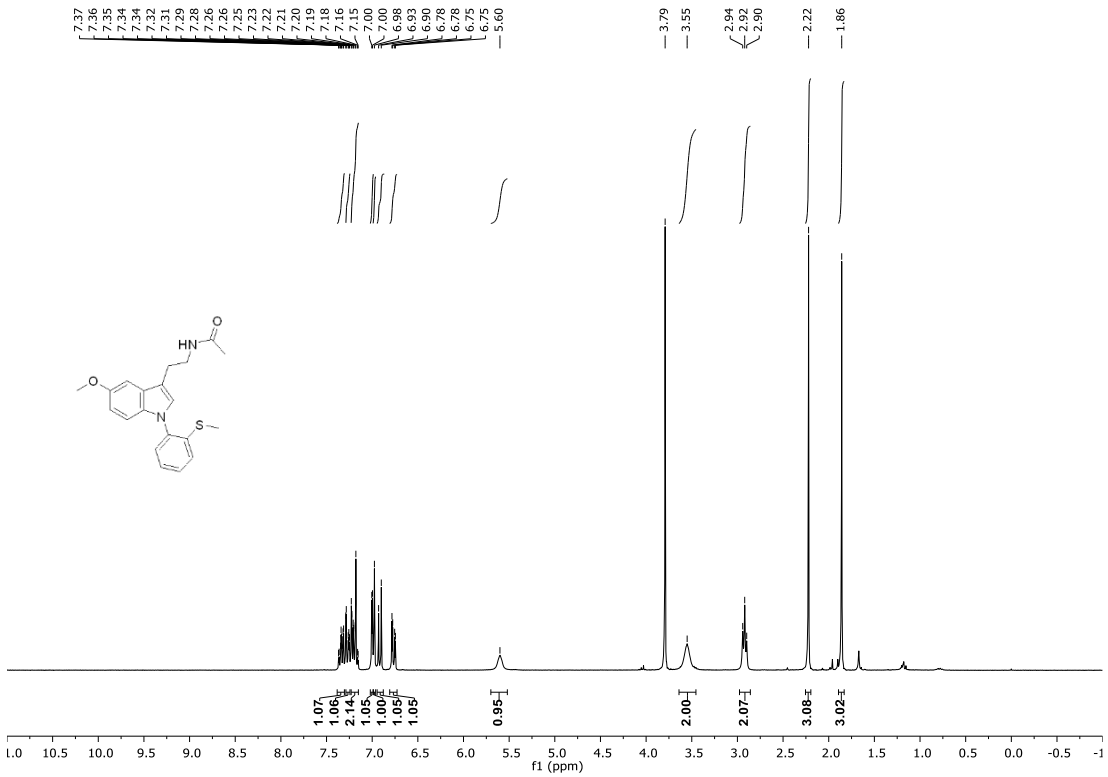
^{1}H NMR (300 MHz, $CDCl_3$) of 3ad



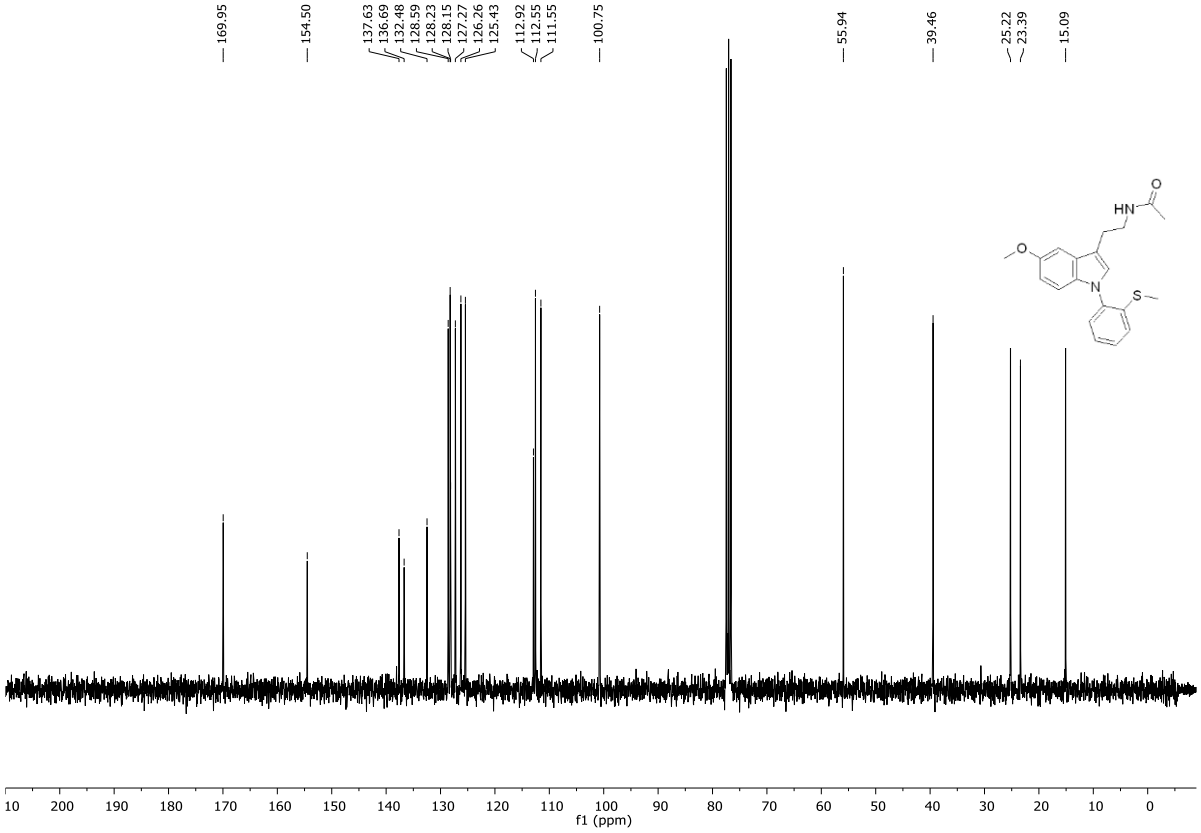
^{13}C NMR (75 MHz, $CDCl_3$) of 3ad



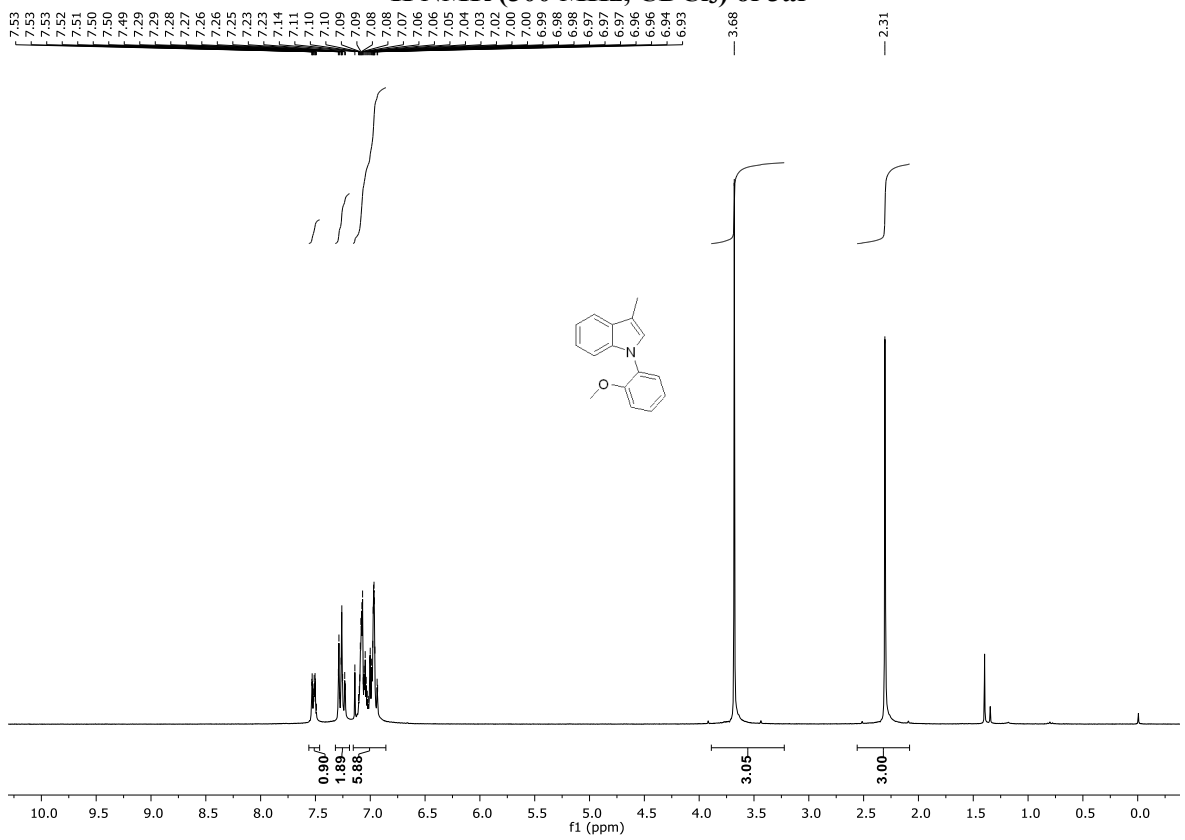
^{1}H NMR (300 MHz, $CDCl_3$) of 3ae



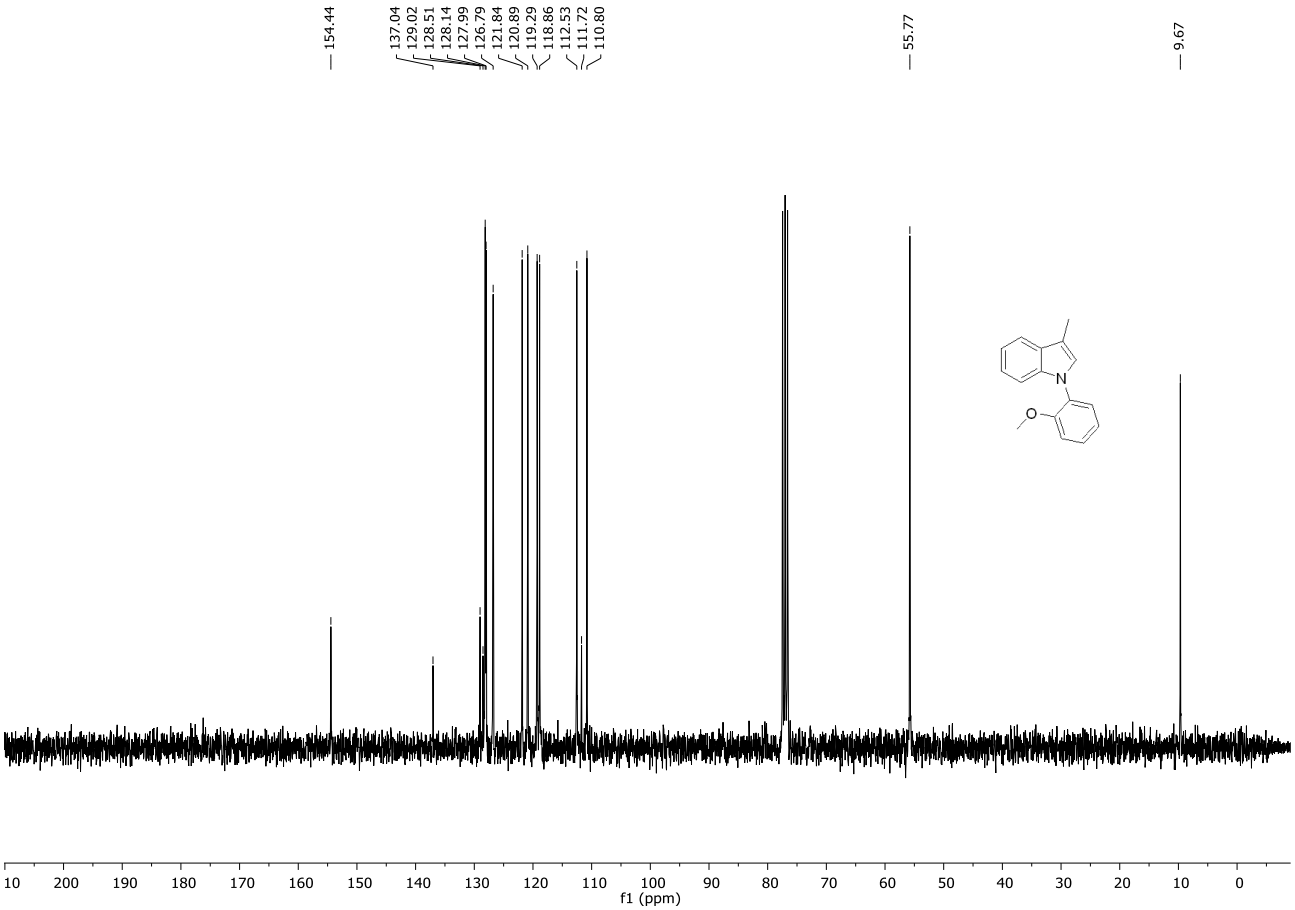
^{13}C NMR (75 MHz, $CDCl_3$) of 3ae



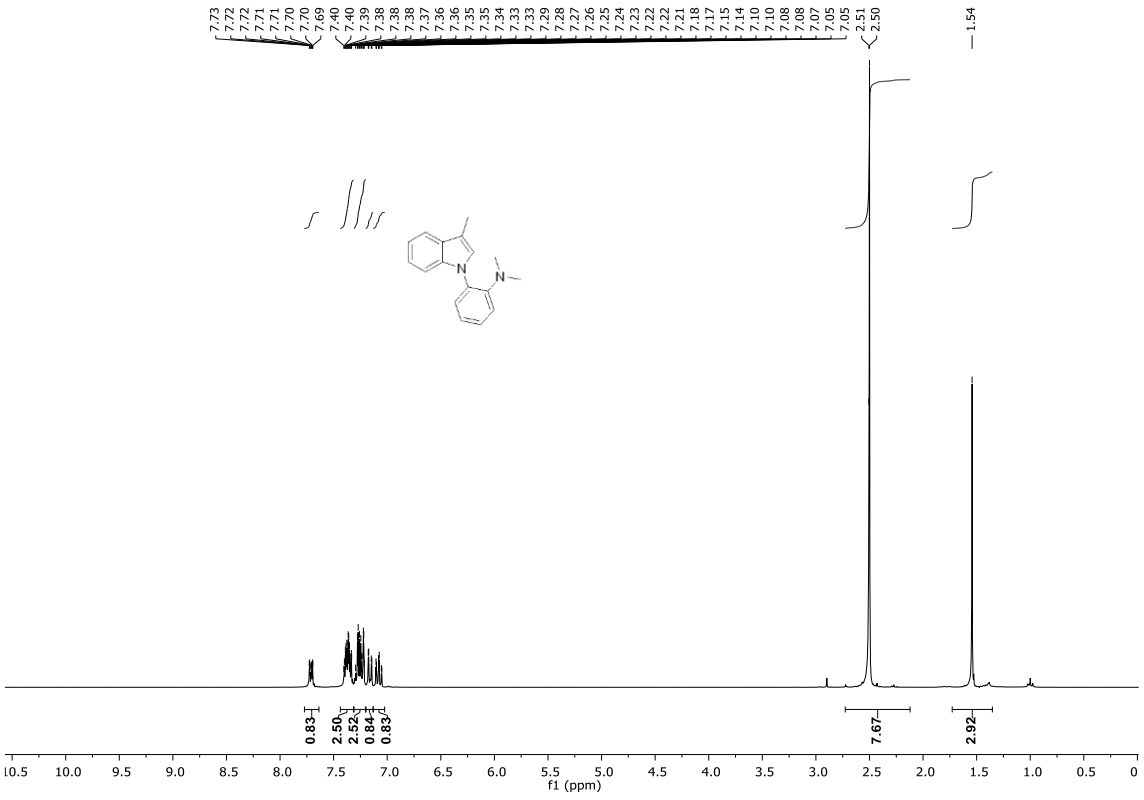
^{1}H NMR (300 MHz, $CDCl_3$) of 3af



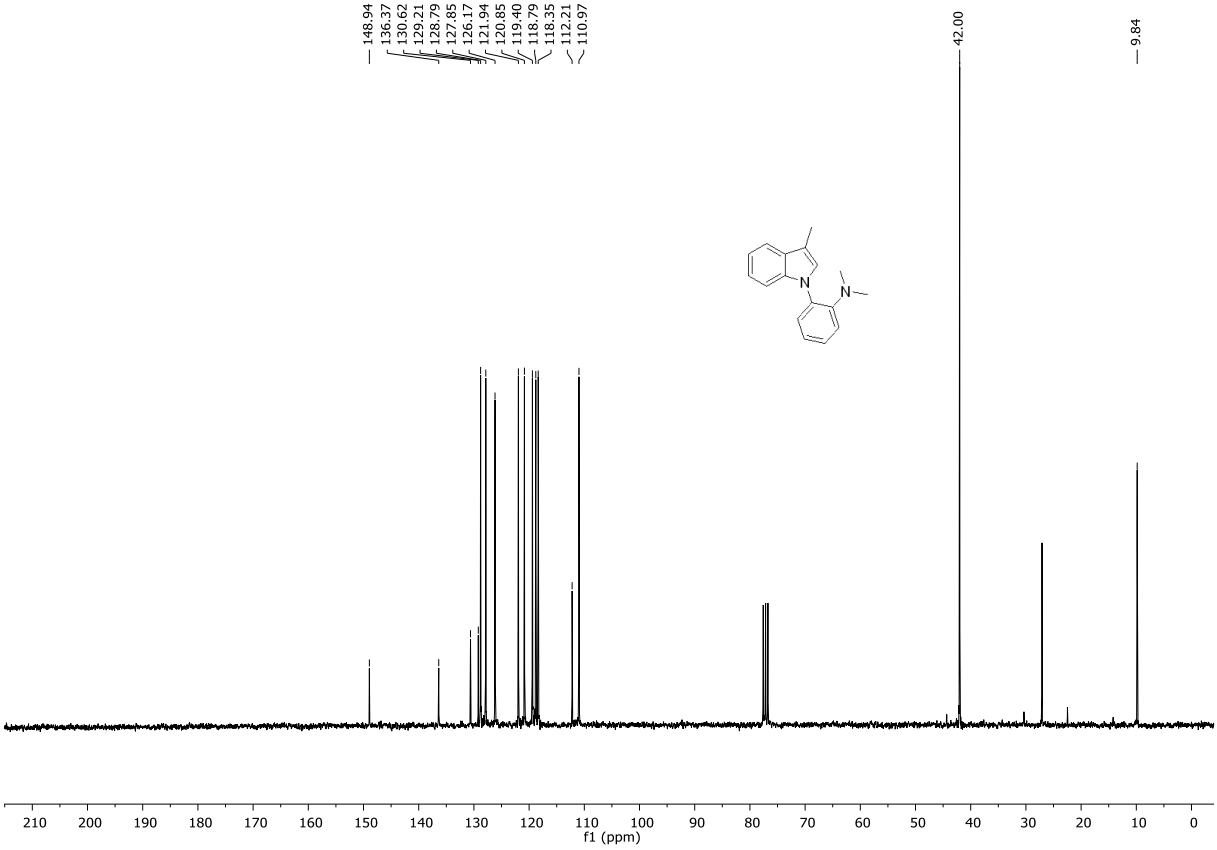
^{13}C NMR (75 MHz, $CDCl_3$) of 3af



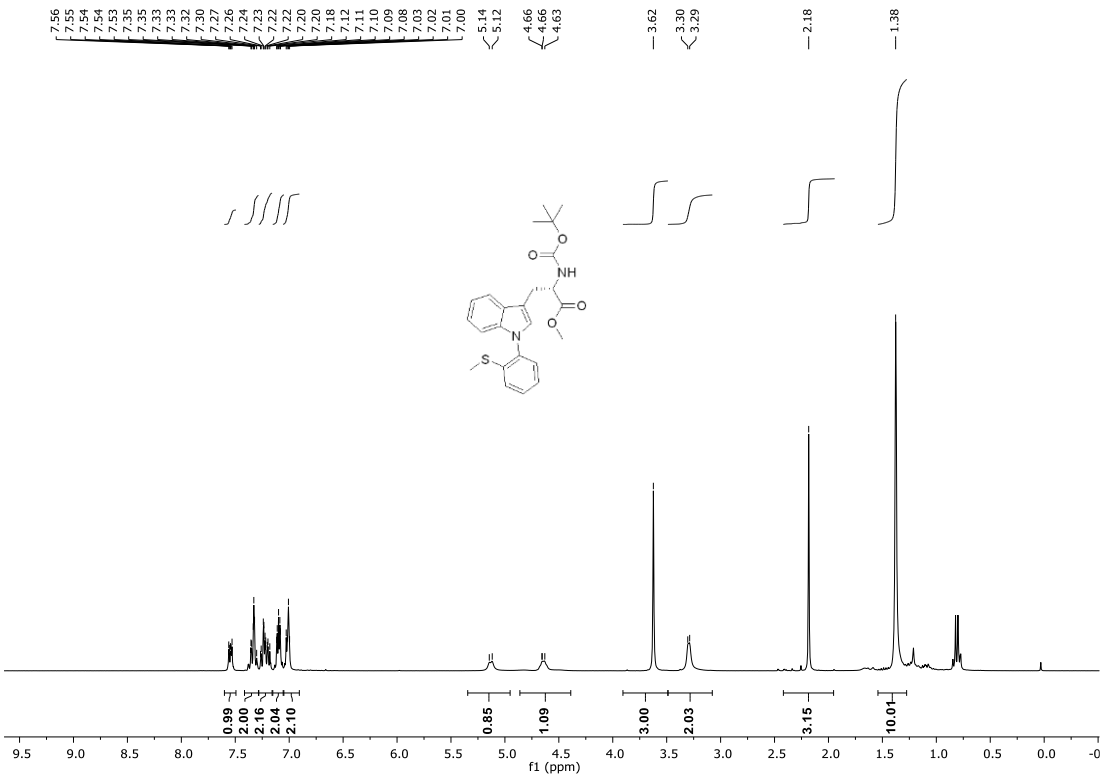
^{1}H NMR (300 MHz, $CDCl_3$) of 3ag



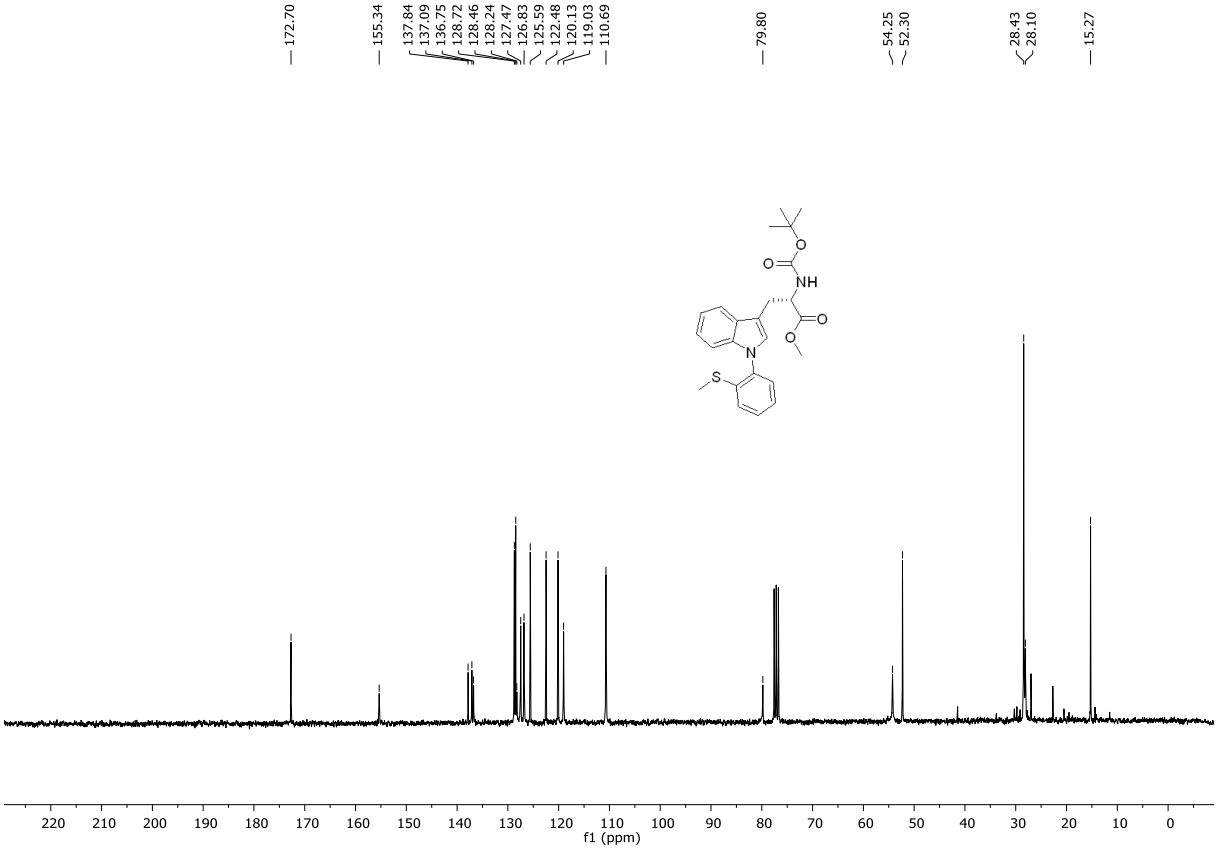
^{13}C NMR (75 MHz, $CDCl_3$) of 3ag



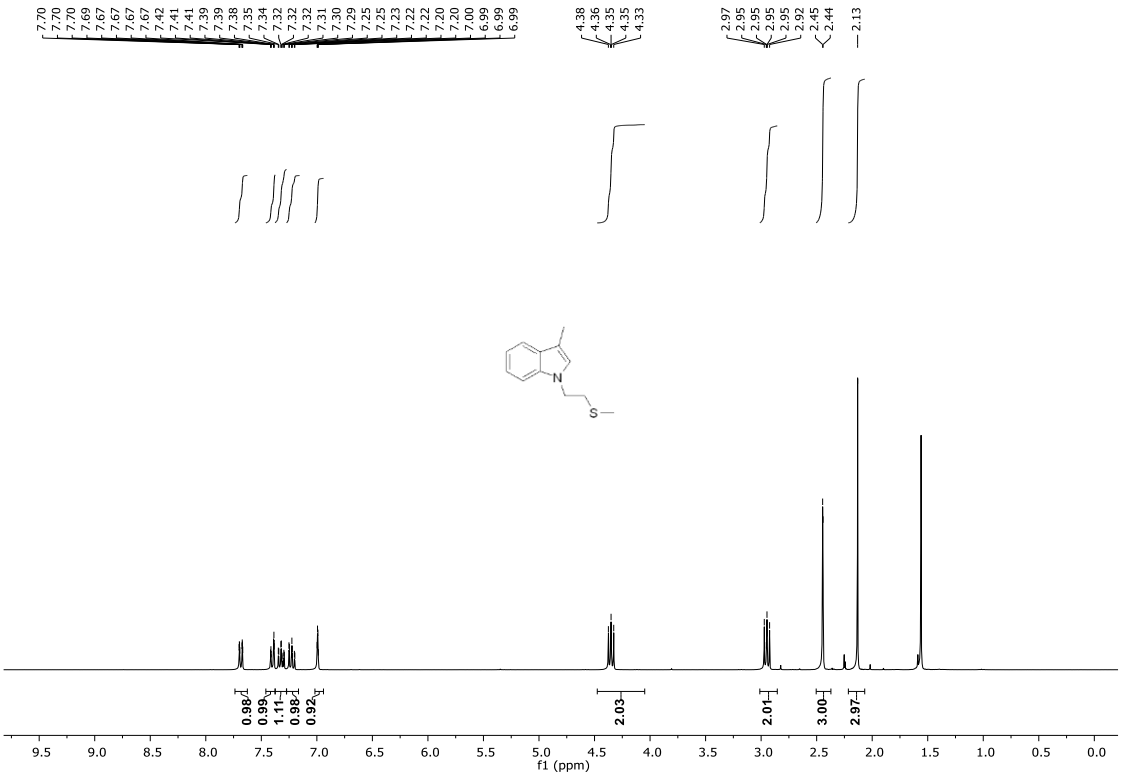
^{1}H NMR (300 MHz, $CDCl_3$) of 3ah



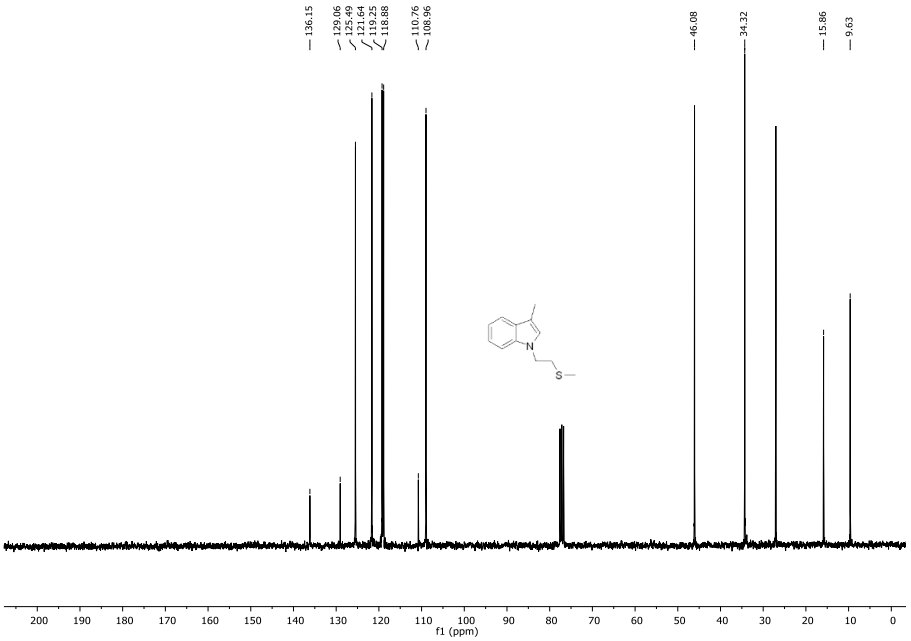
^{13}C NMR (75 MHz, $CDCl_3$) of 3ah



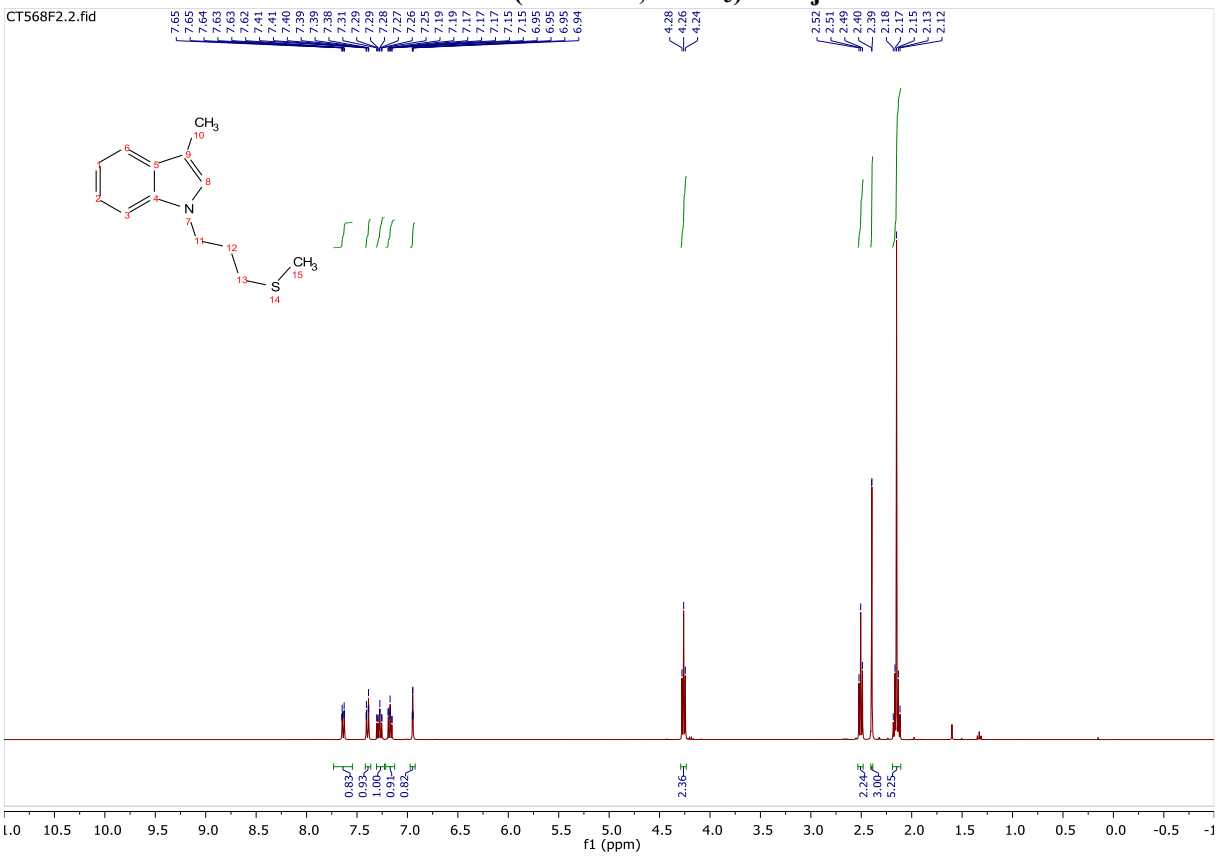
^{1}H NMR (300 MHz, $CDCl_3$) of 3ai



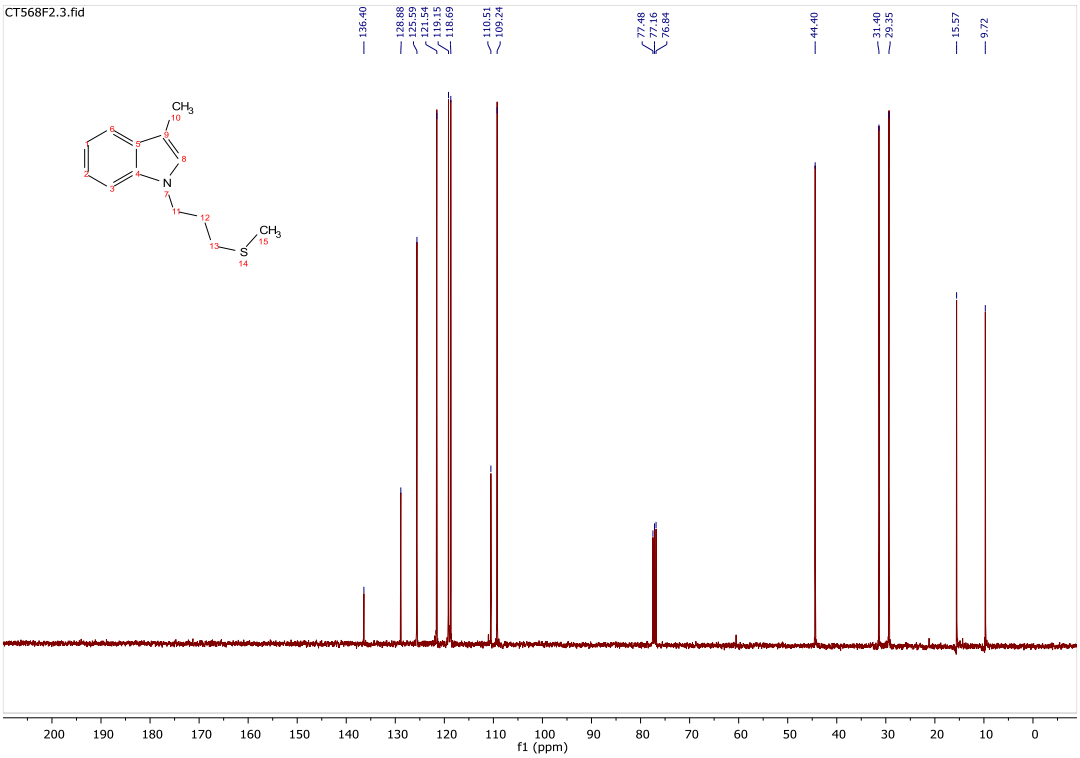
^{13}C NMR (75 MHz, $CDCl_3$) of 3ai



^{1}H NMR (400 MHz, $CDCl_3$) of 3aj

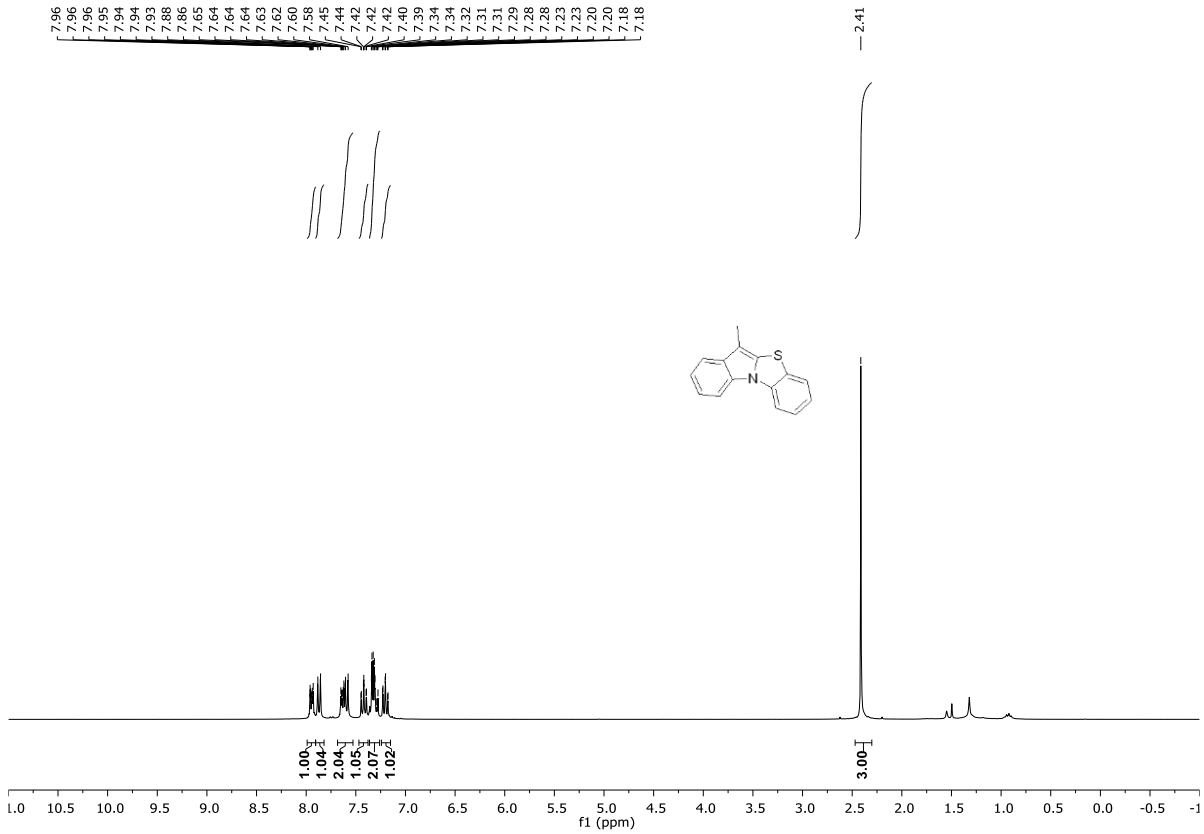


^{13}C NMR (101 MHz, $CDCl_3$) of 3aj

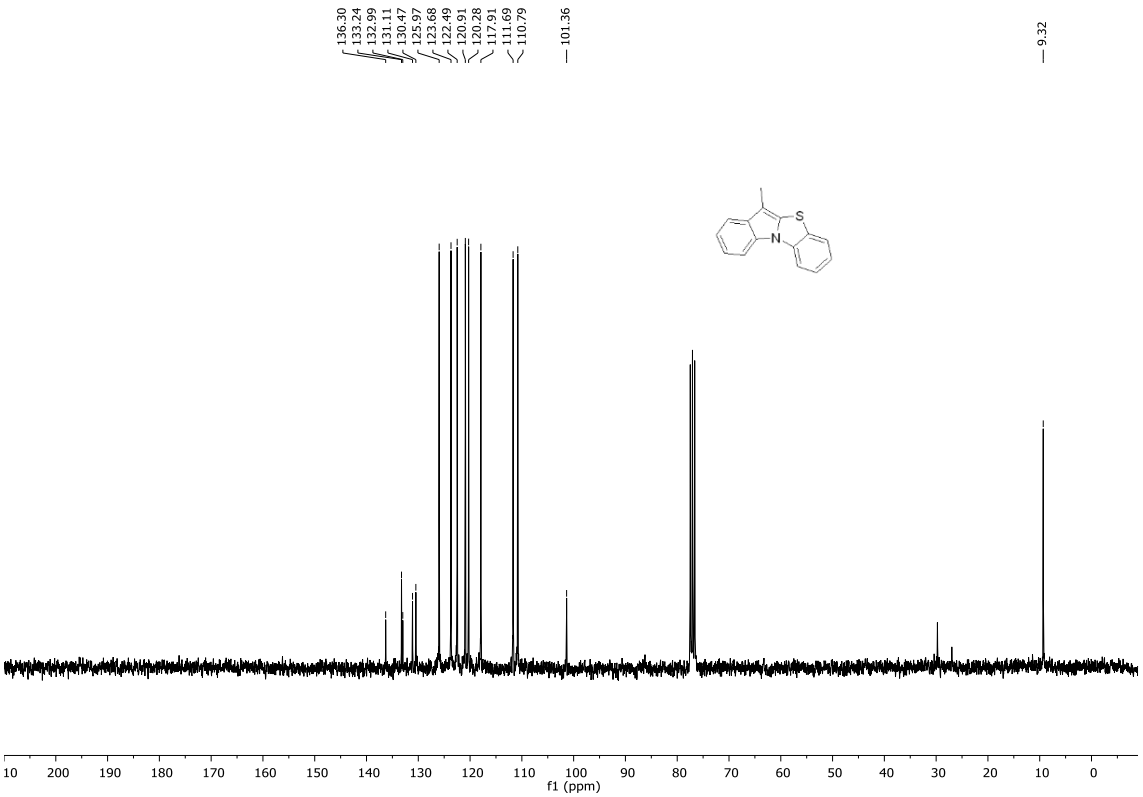


Spectrum of benzo[4,5]thiazolo[3,2-*a*]indole derivatives (4)

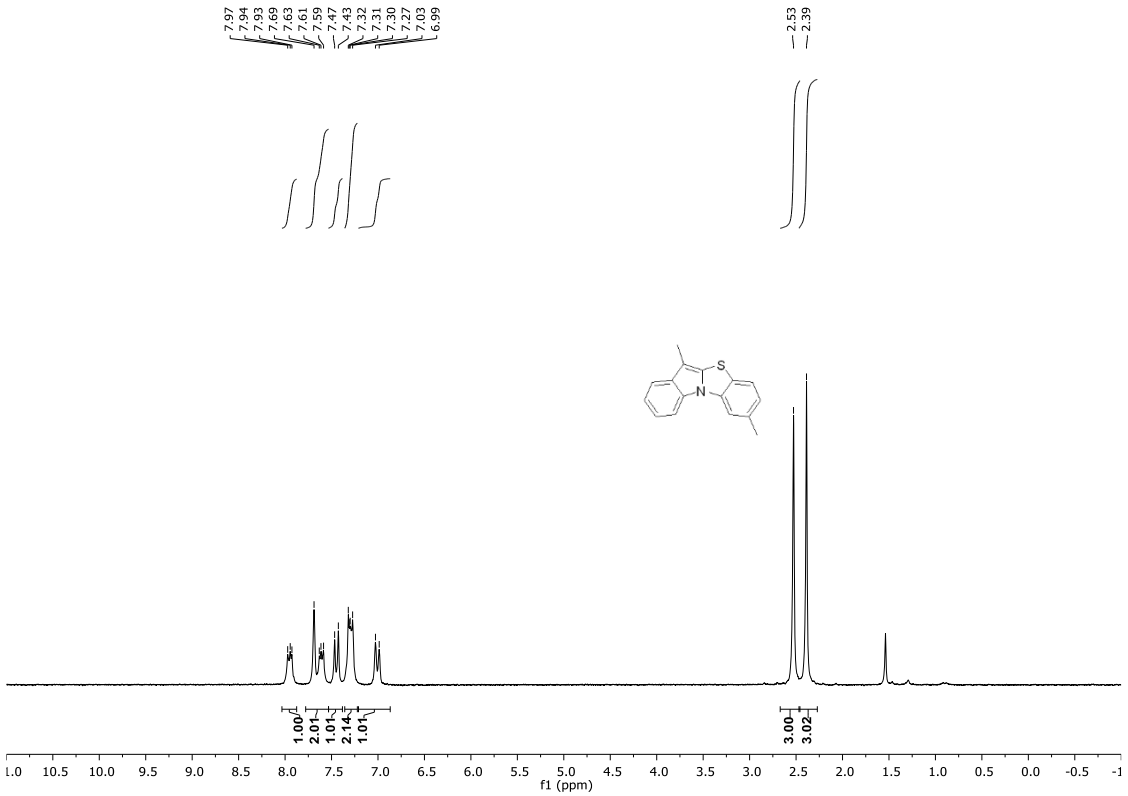
^{1}H NMR (300 MHz, $CDCl_3$) of 4a



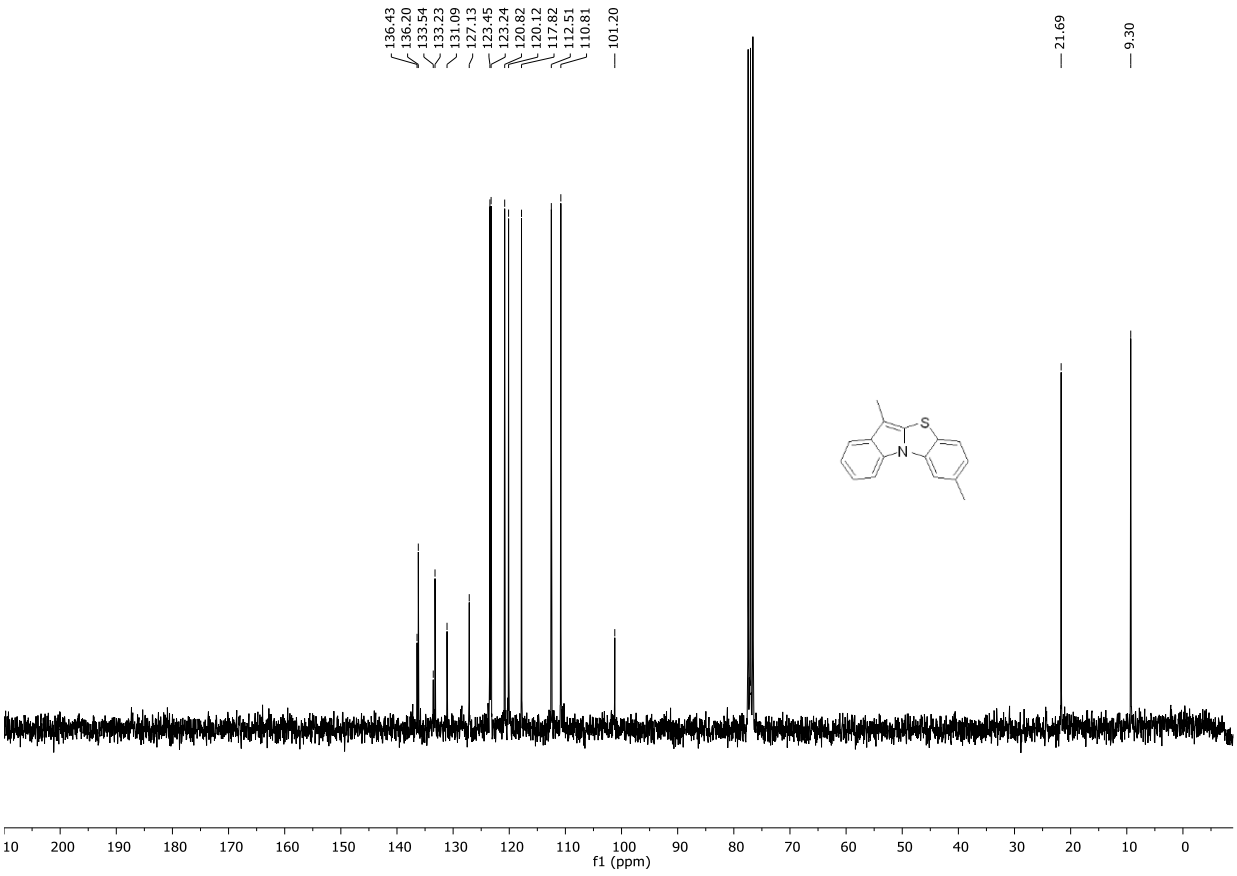
^{13}C NMR (75 MHz, $CDCl_3$) of 4a



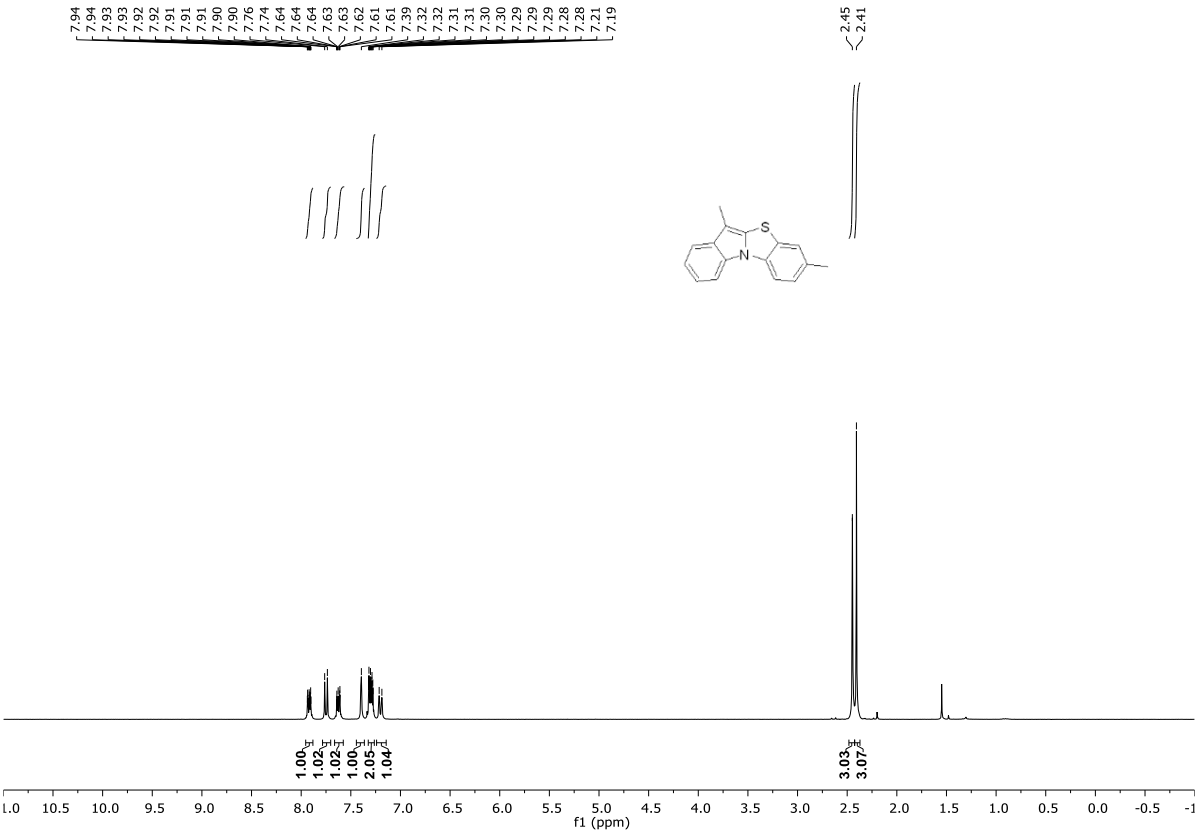
^{1}H NMR (300 MHz, $CDCl_3$) of 4b



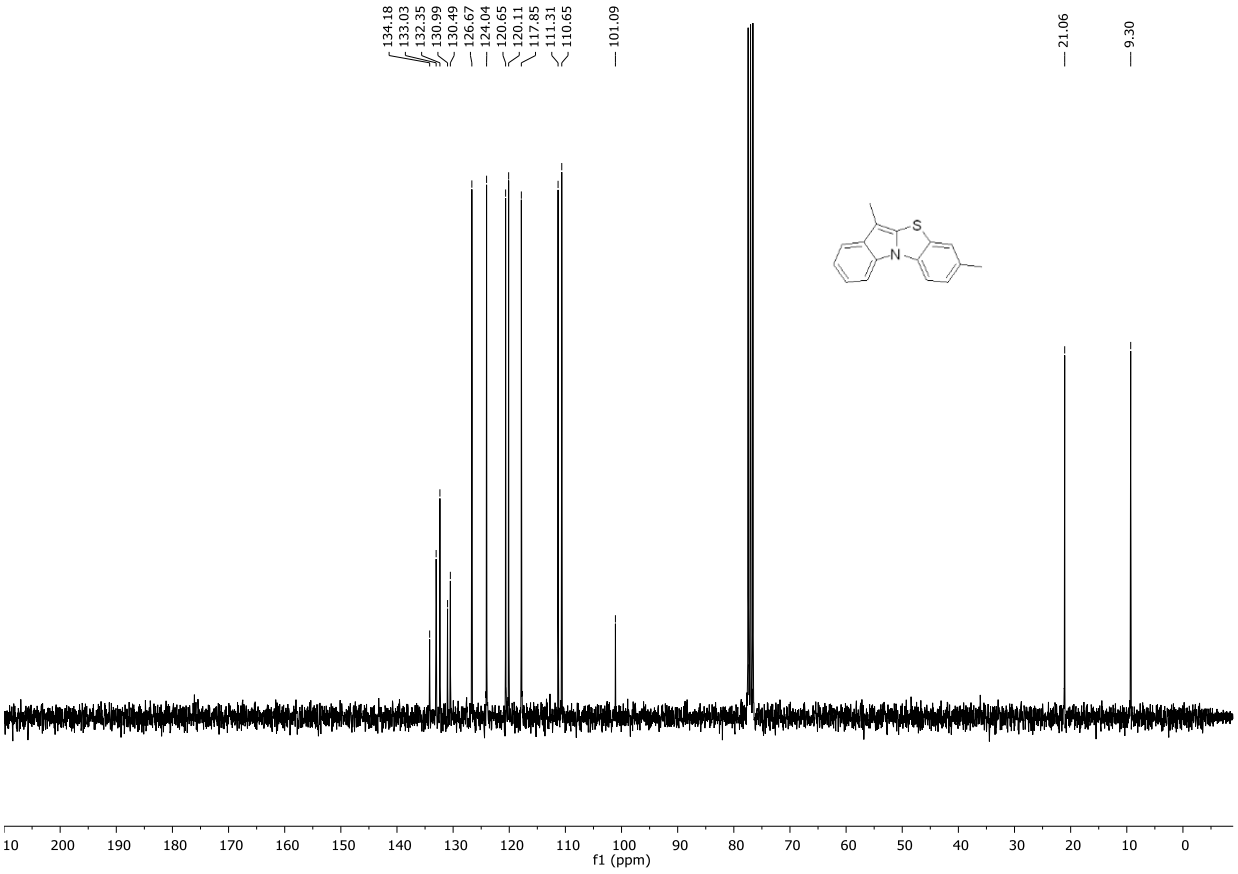
^{13}C NMR (75 MHz, $CDCl_3$) of 4b



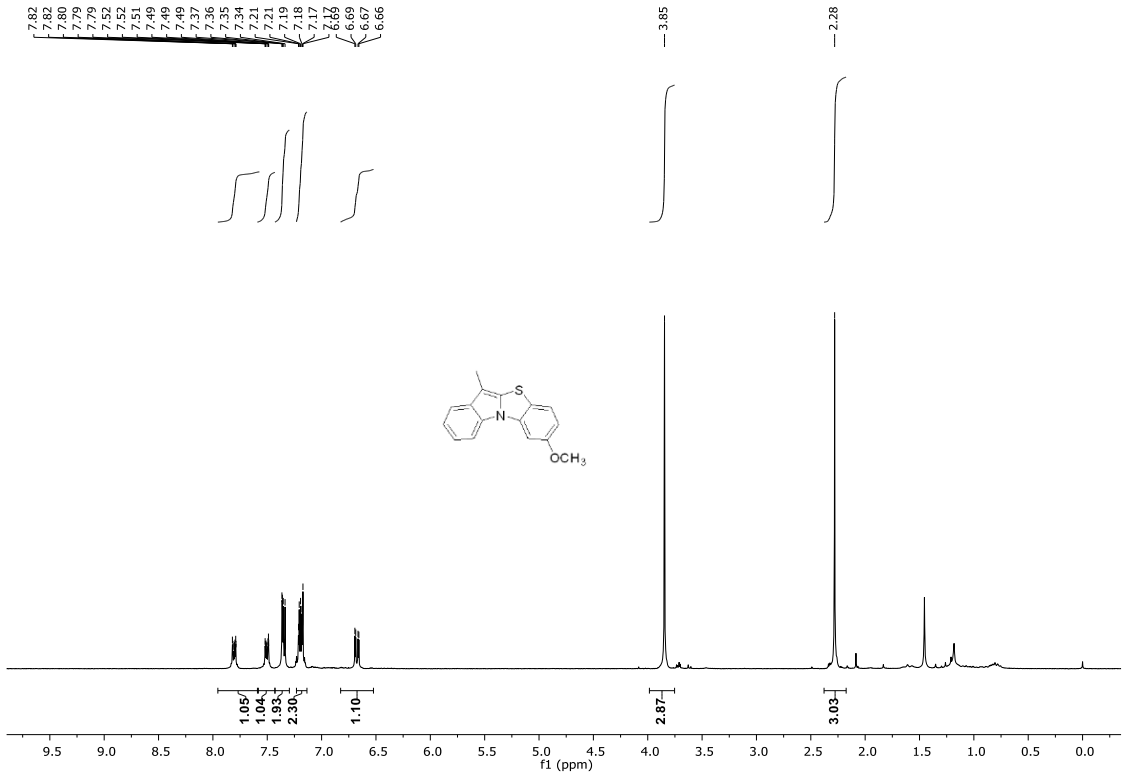
^{1}H NMR (300 MHz, $CDCl_3$) of 4c



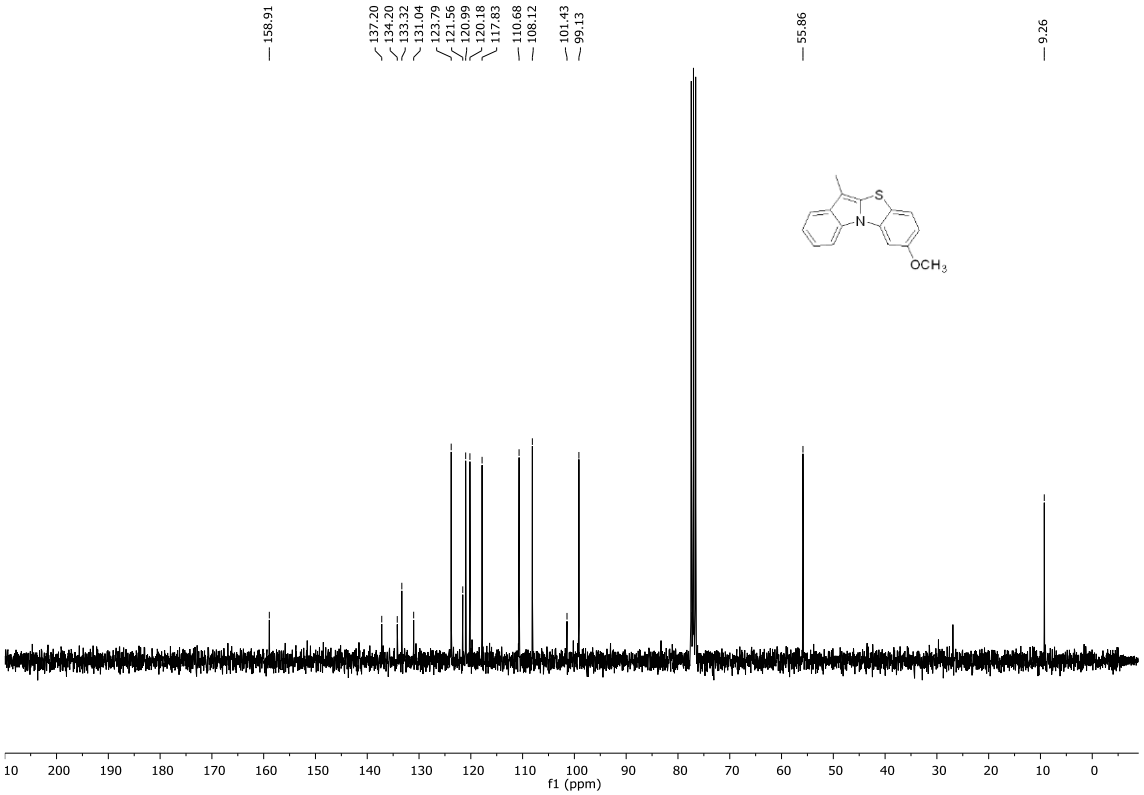
^{13}C NMR (75 MHz, $CDCl_3$) of 4c



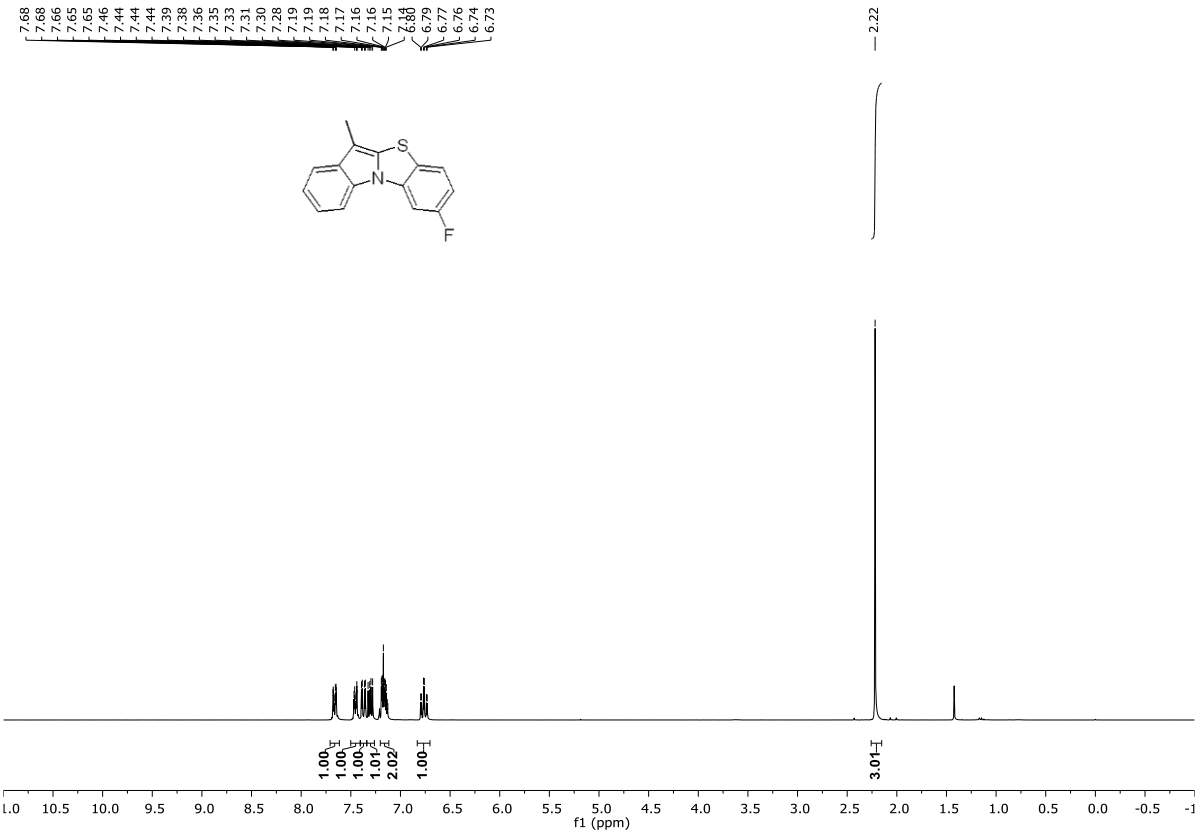
^{1}H NMR (300 MHz, $CDCl_3$) of 4d



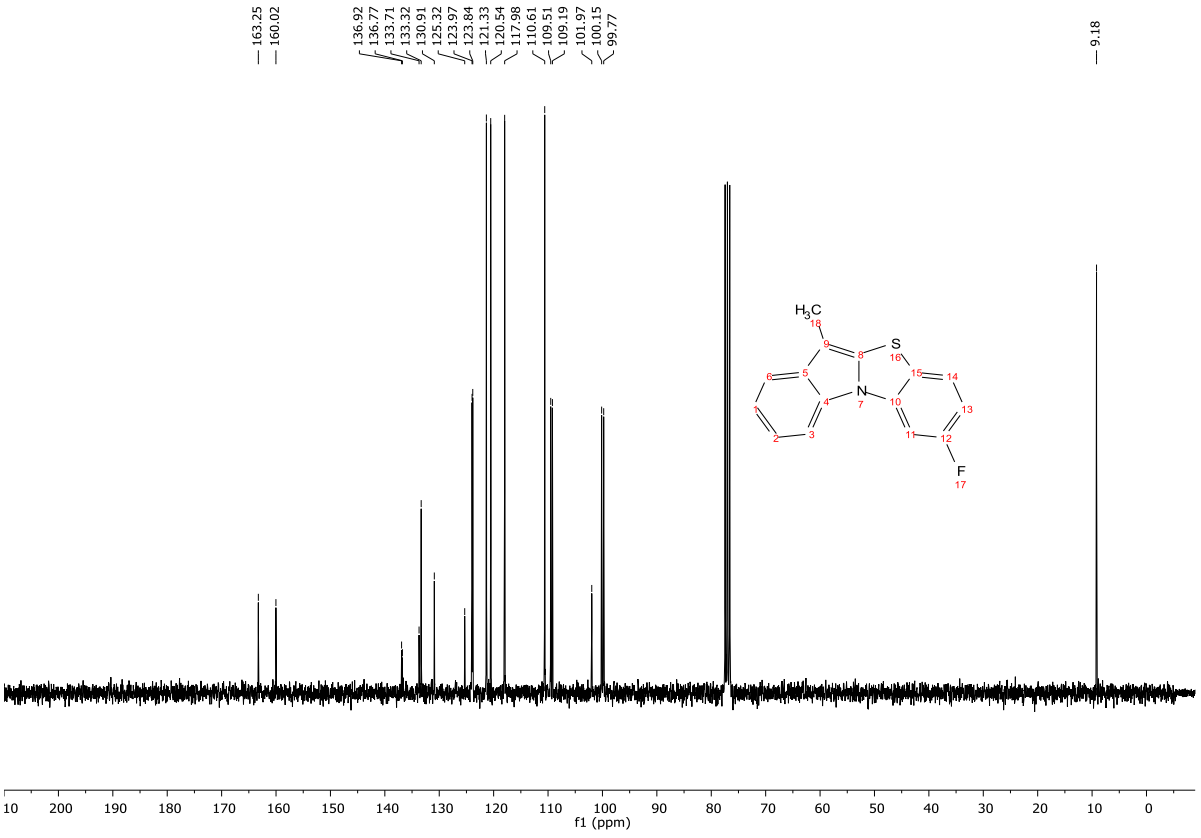
^{13}C NMR (75 MHz, $CDCl_3$) of 4d



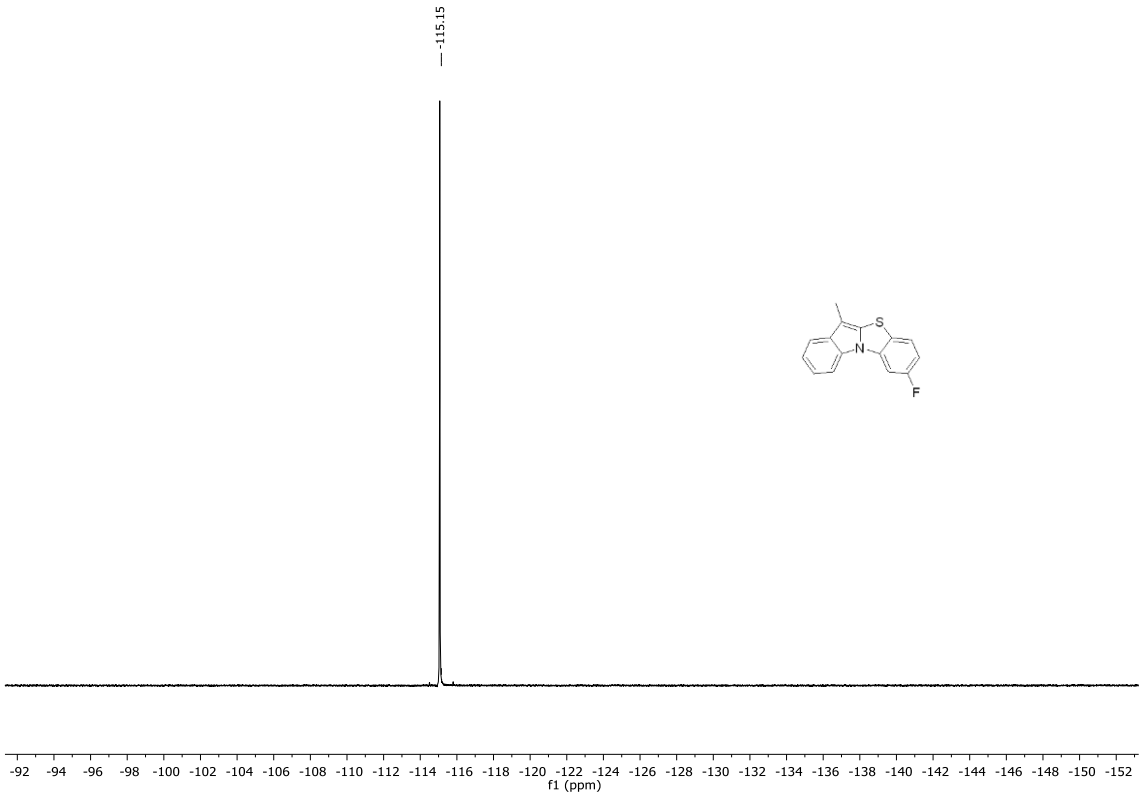
^{1}H NMR (300 MHz, $CDCl_3$) of 4e



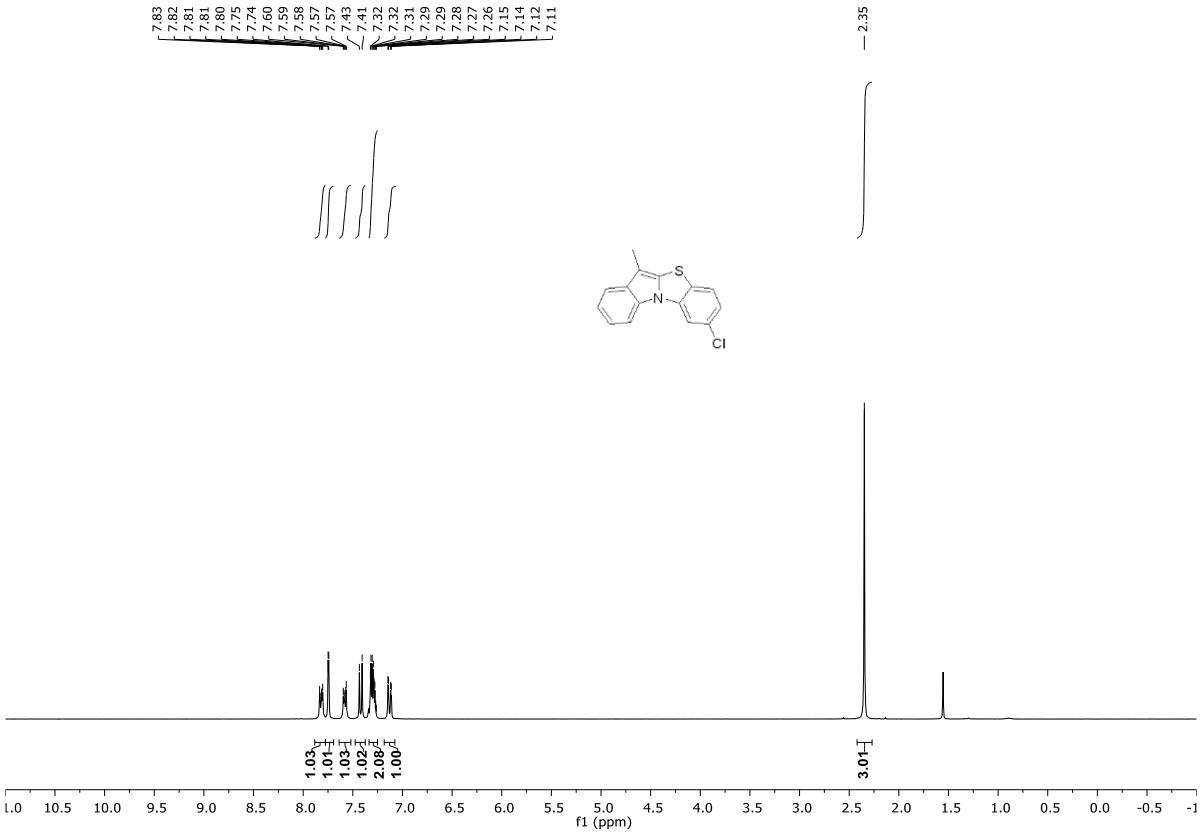
^{13}C NMR (75 MHz, $CDCl_3$) of 4e



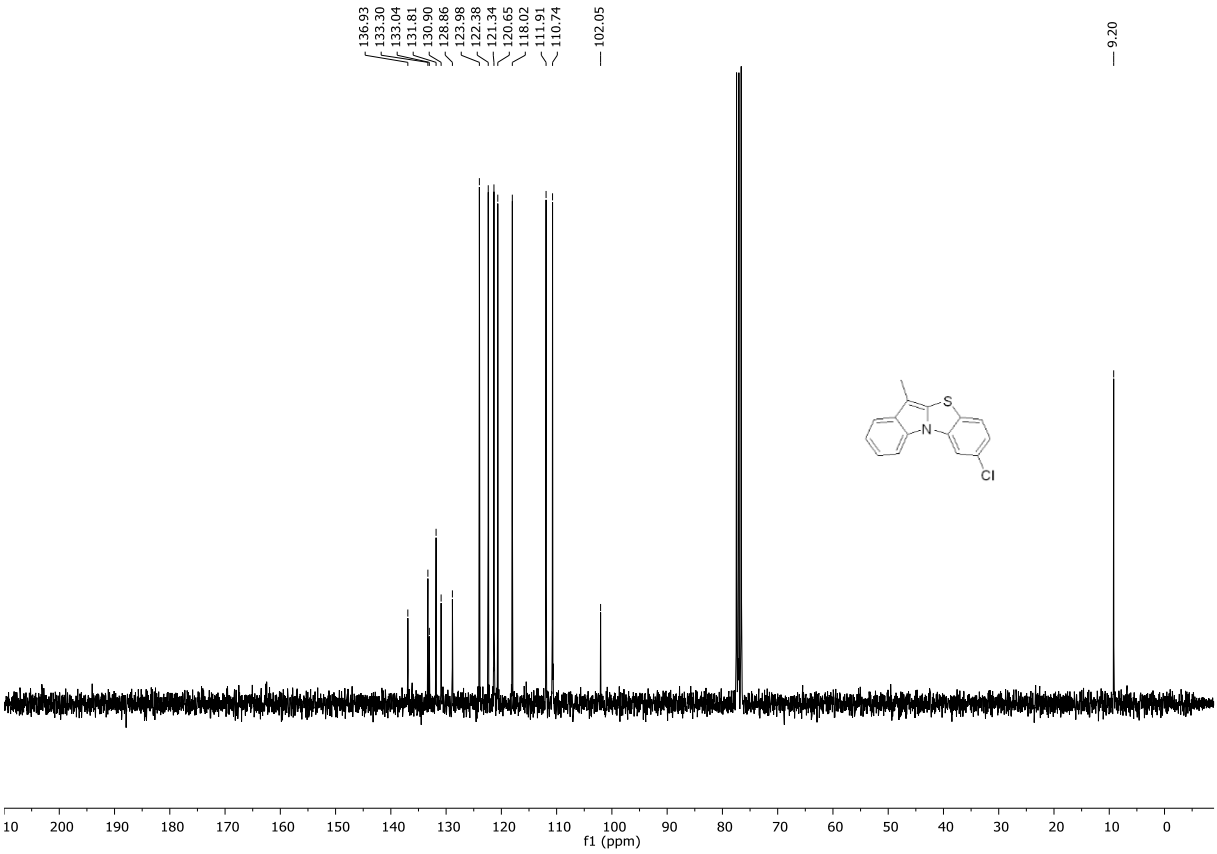
^{19}F NMR (188 MHz, $CDCl_3$) of 4e



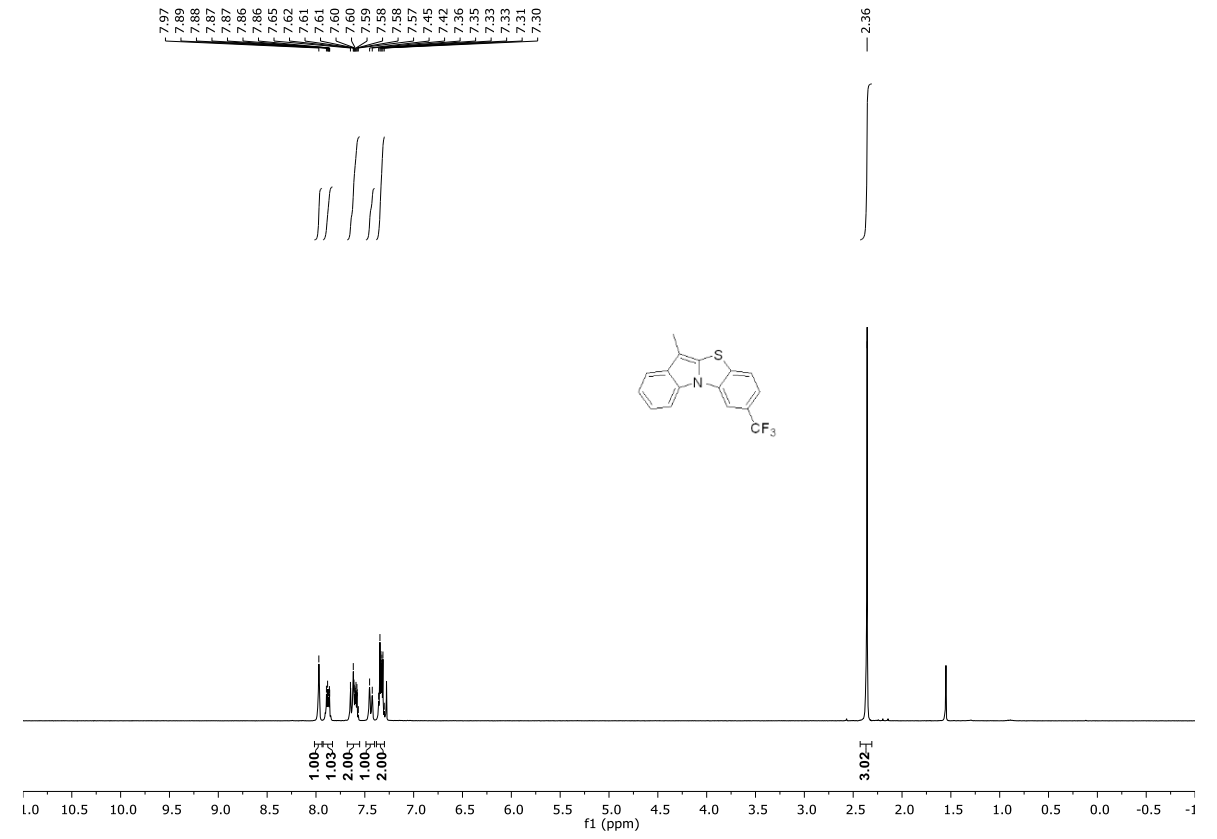
^{1}H NMR (300 MHz, $CDCl_3$) of 4f



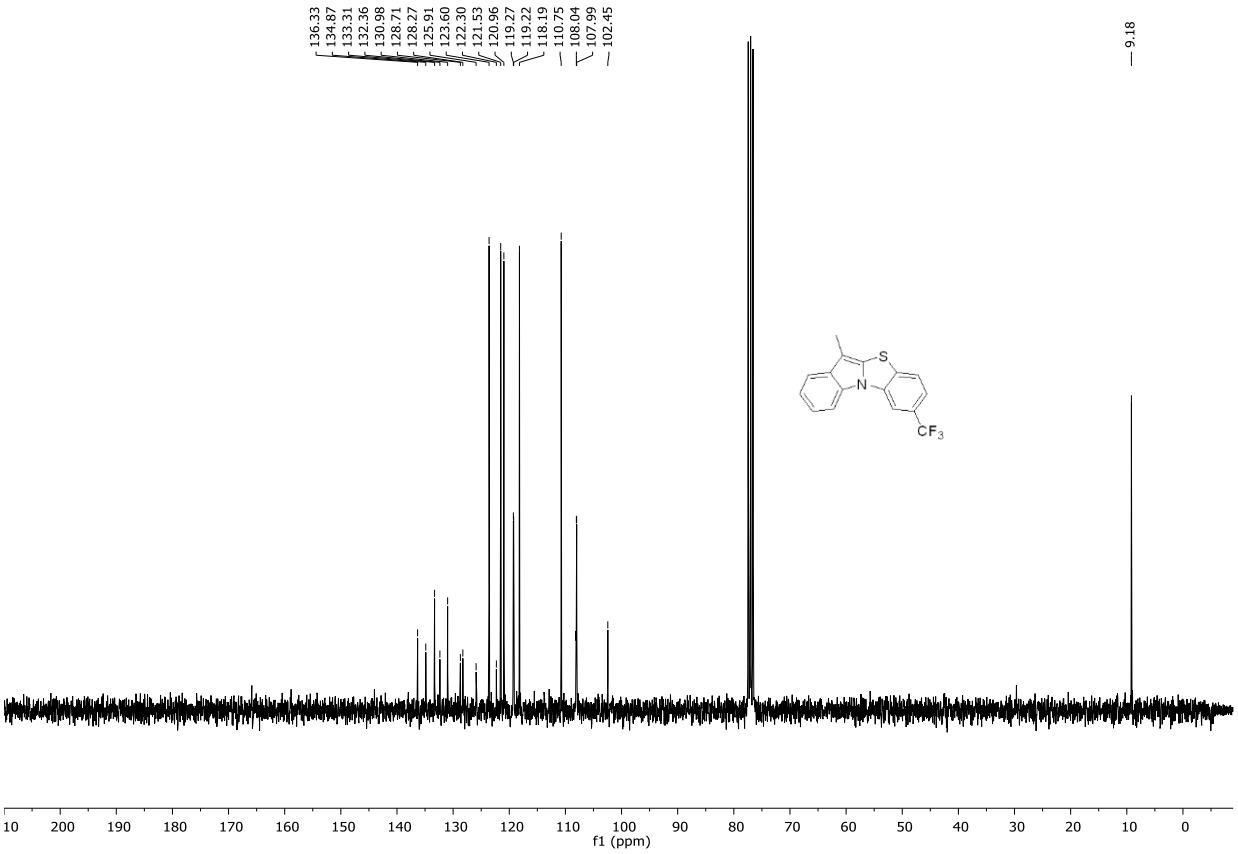
^{13}C NMR (75 MHz, $CDCl_3$) of 4f



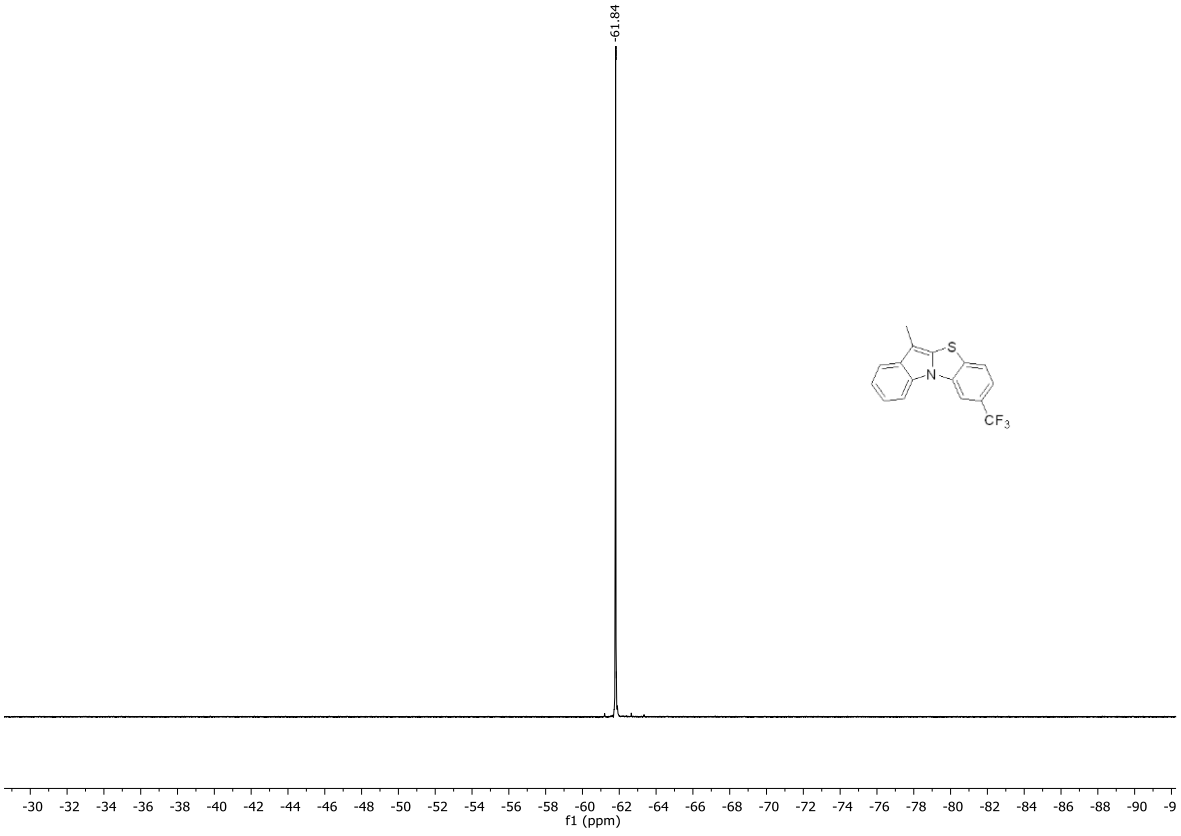
^{1}H NMR (300 MHz, $CDCl_3$) of 4g



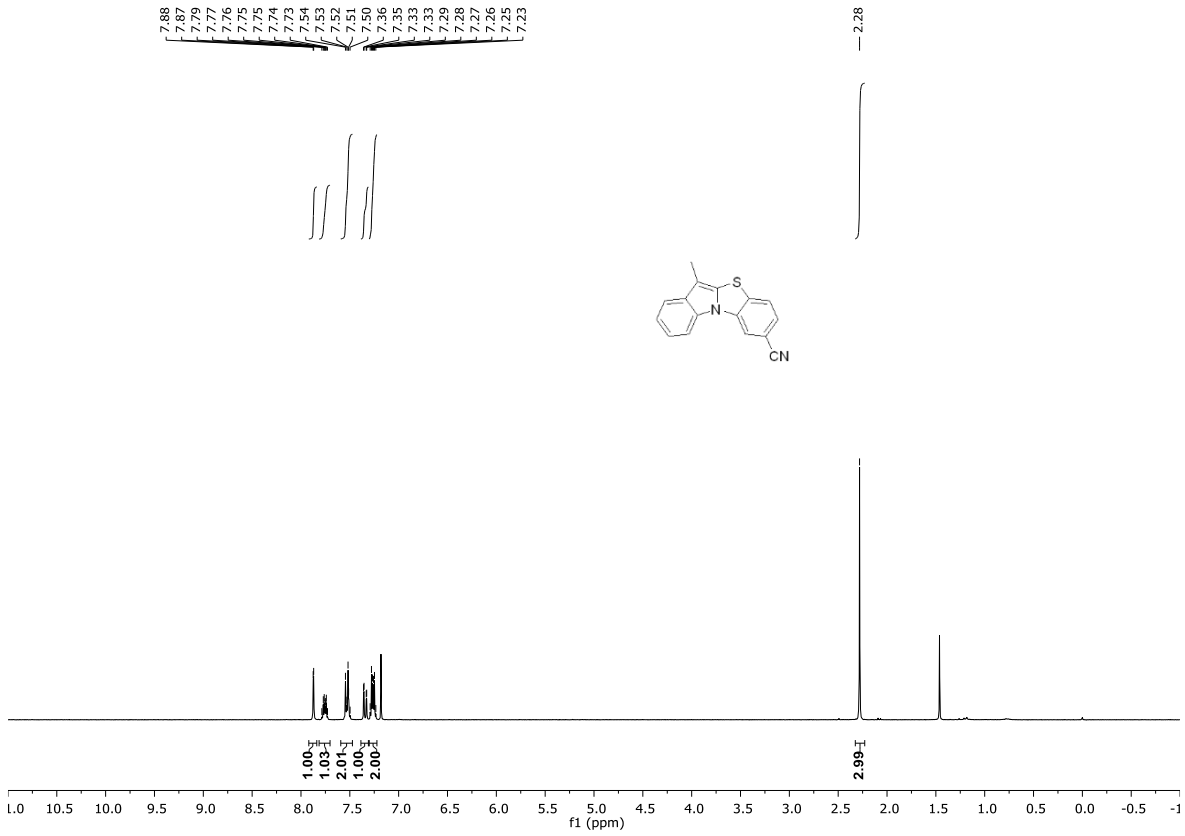
^{13}C NMR (75 MHz, $CDCl_3$) of 4g



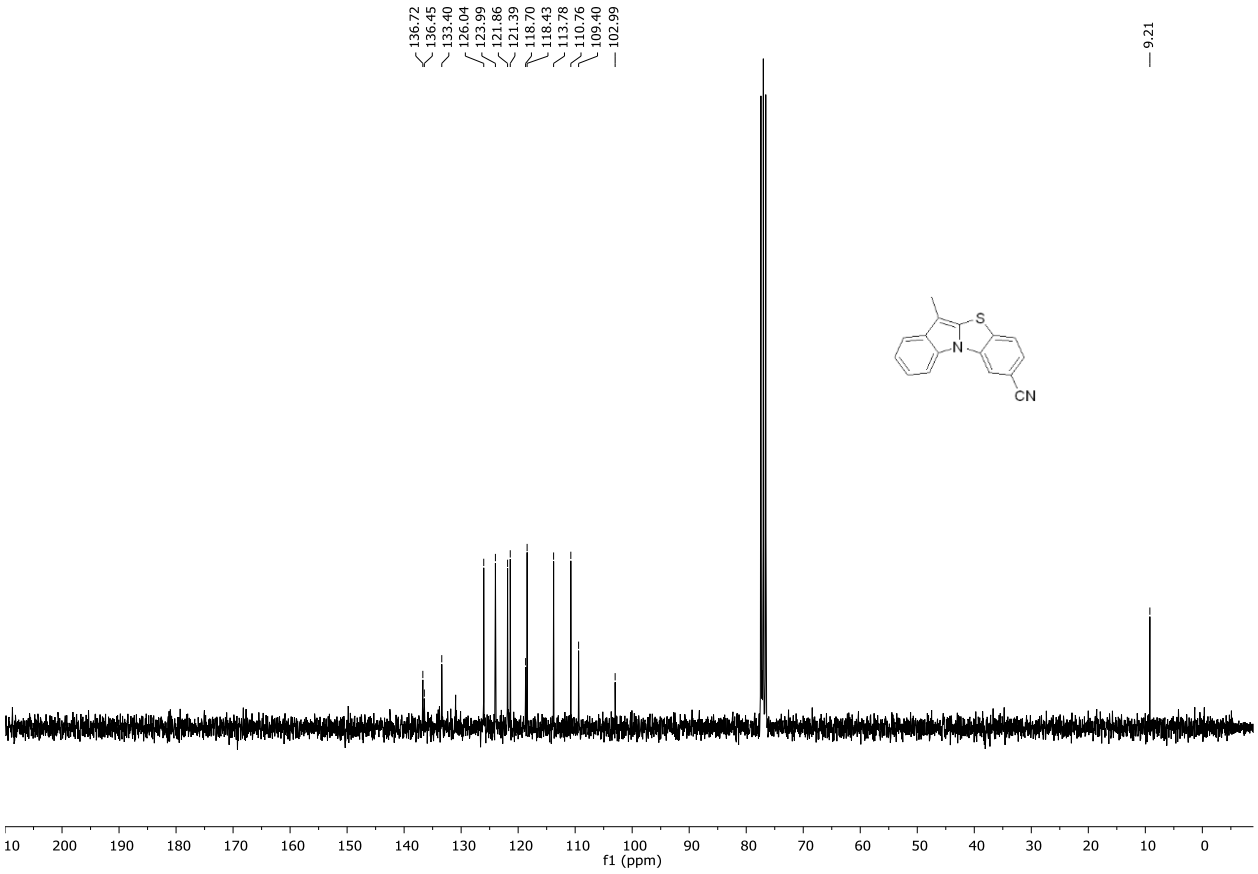
^{19}F NMR (188 MHz, $CDCl_3$) of 4g



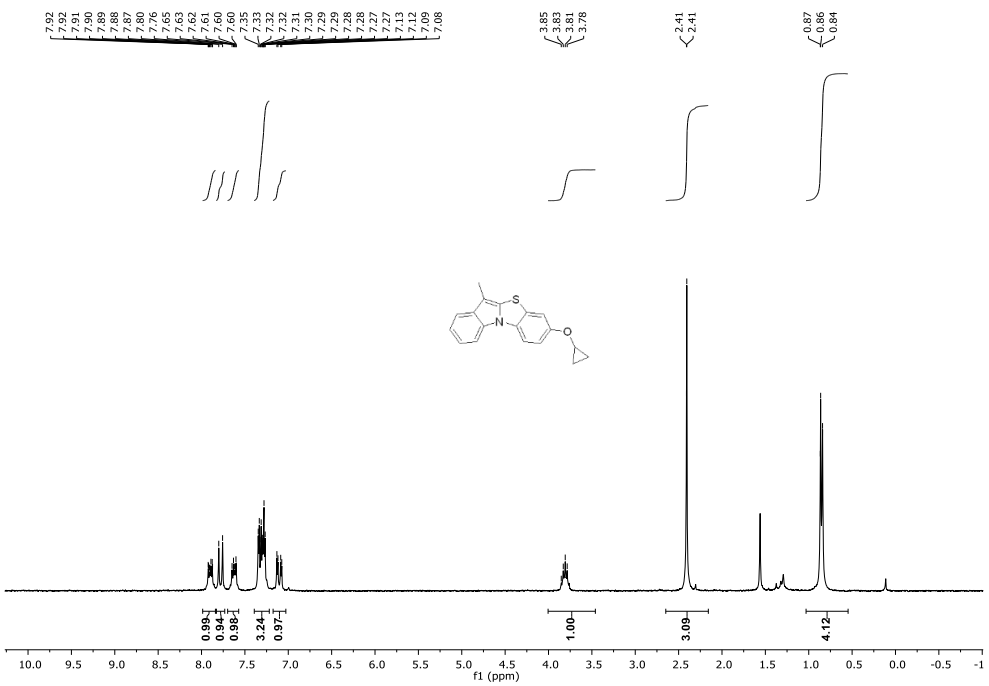
^{1}H NMR (300 MHz, $CDCl_3$) of 4h



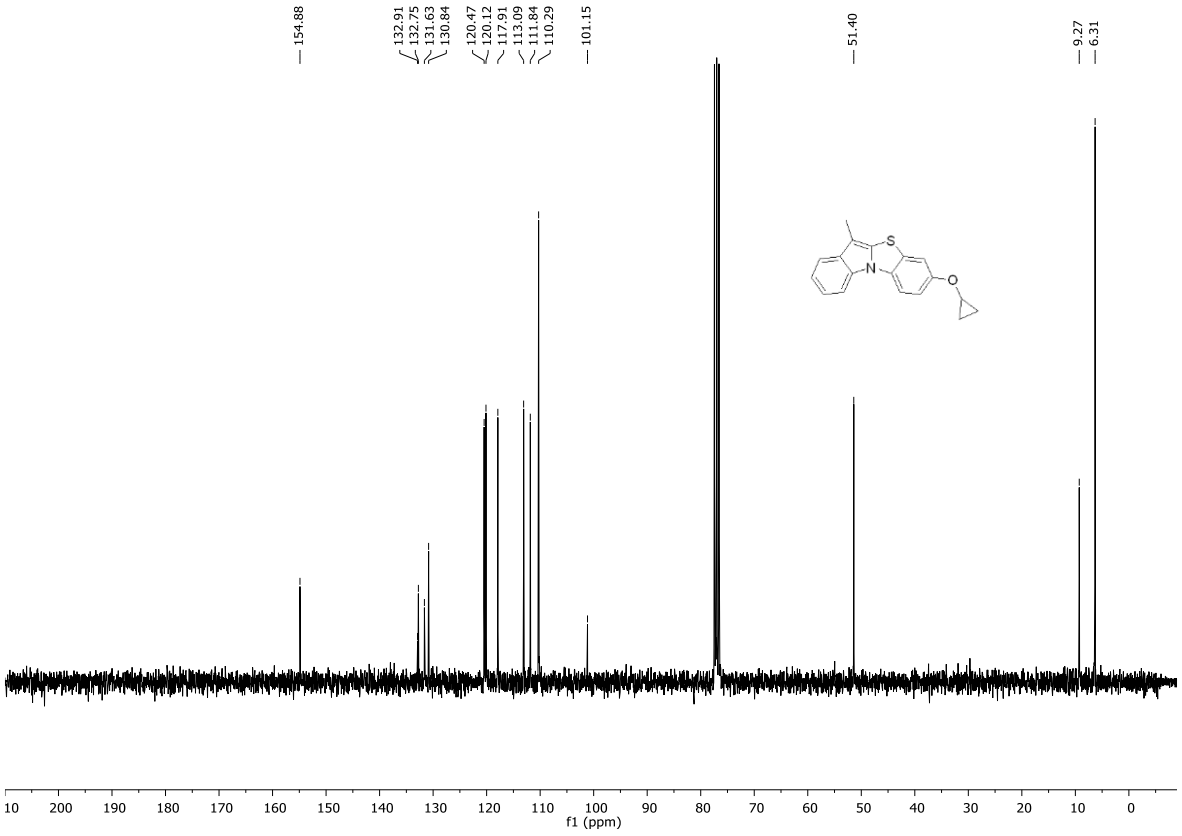
^{13}C NMR (75 MHz, $CDCl_3$) of 4h



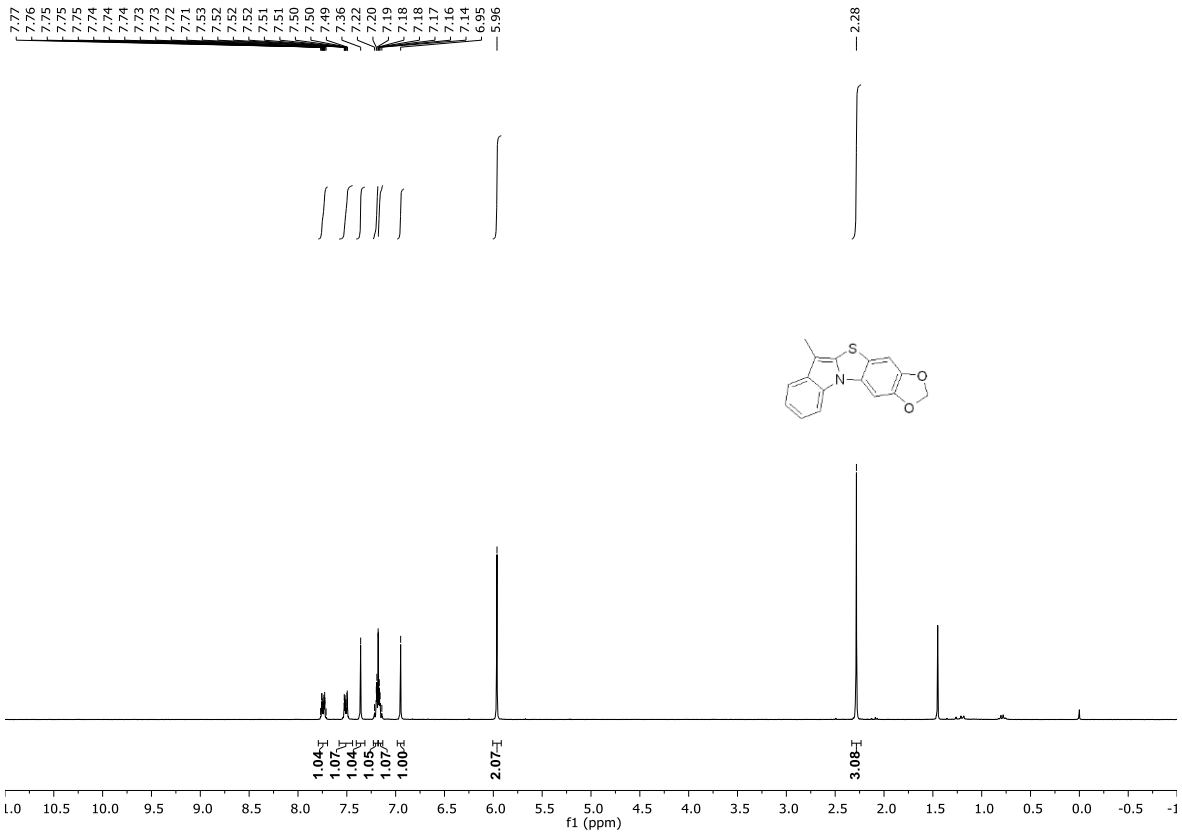
^{1}H NMR (300 MHz, $CDCl_3$) of 4i



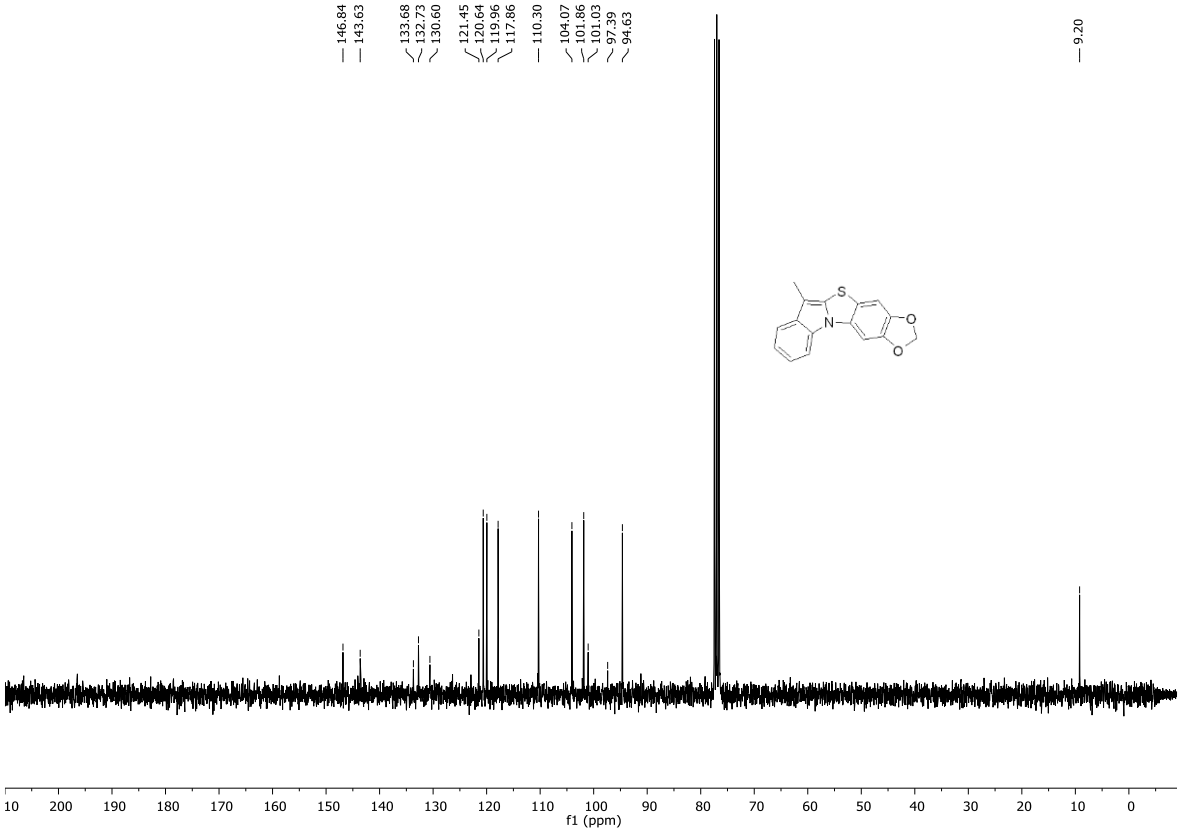
^{13}C NMR (75 MHz, $CDCl_3$) of 4i



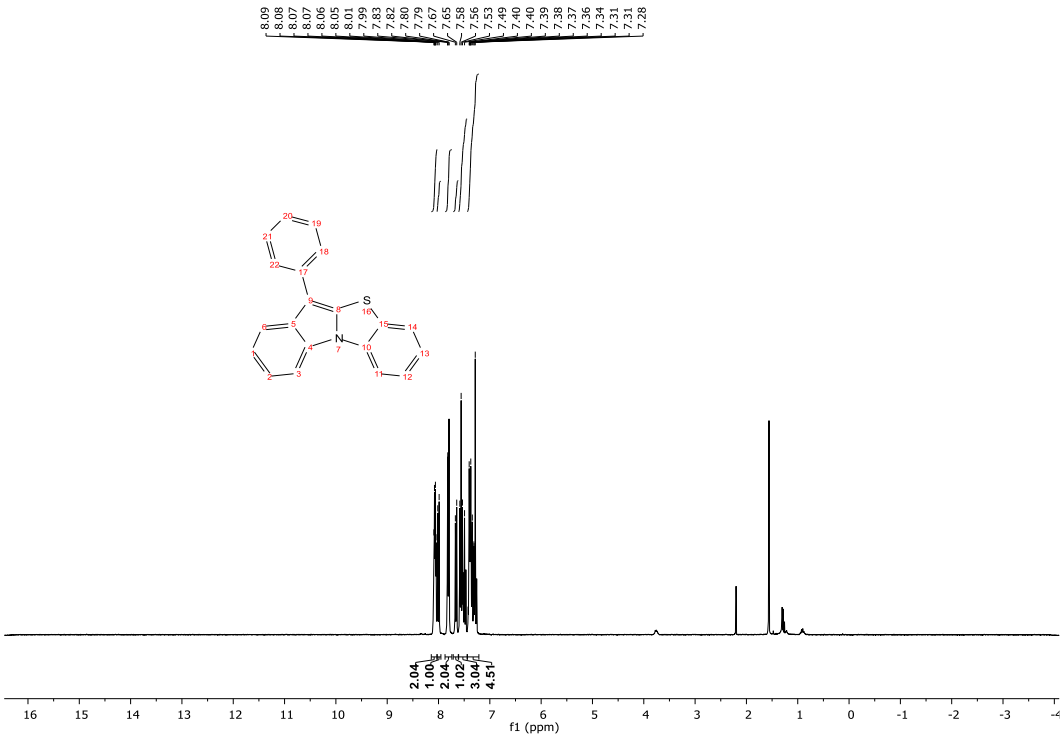
^{1}H NMR (300 MHz, $CDCl_3$) of 4j



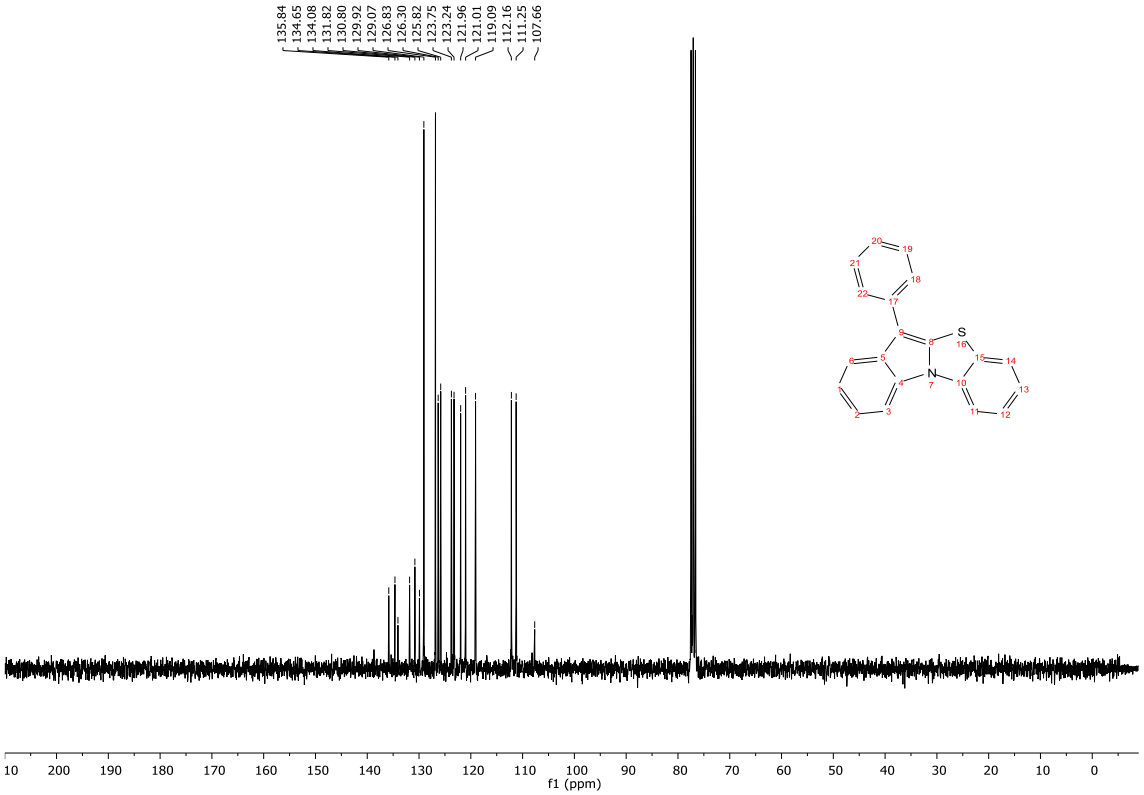
^{13}C NMR (75 MHz, $CDCl_3$) of 4j



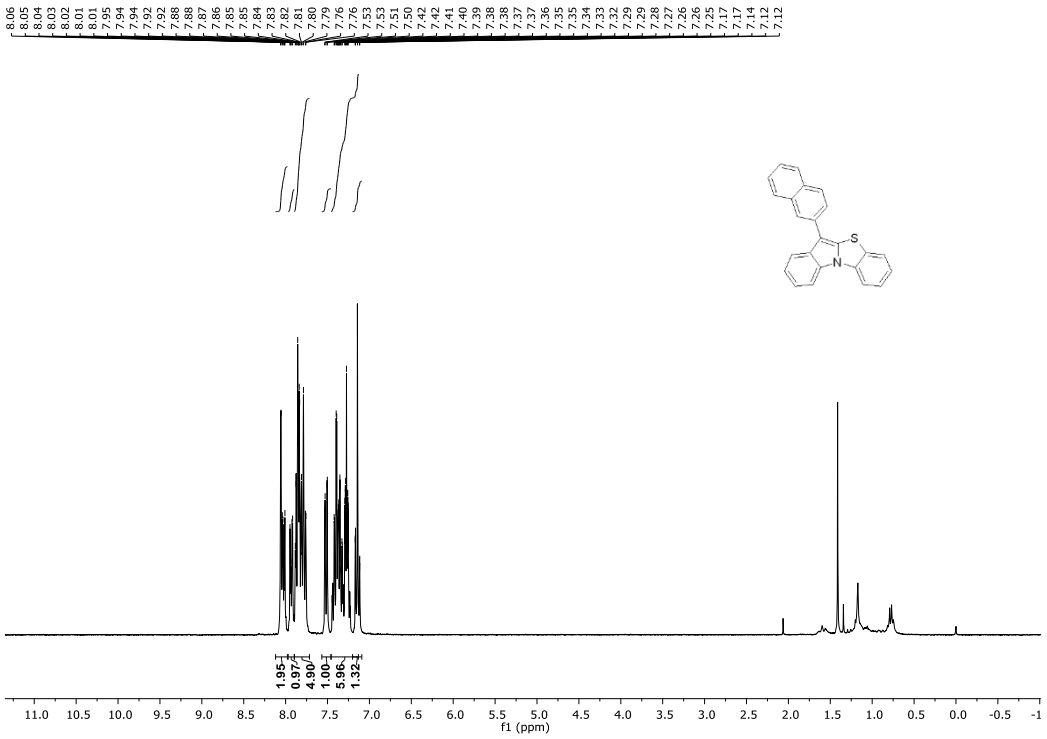
^{1}H NMR (300 MHz, $CDCl_3$) of 4k



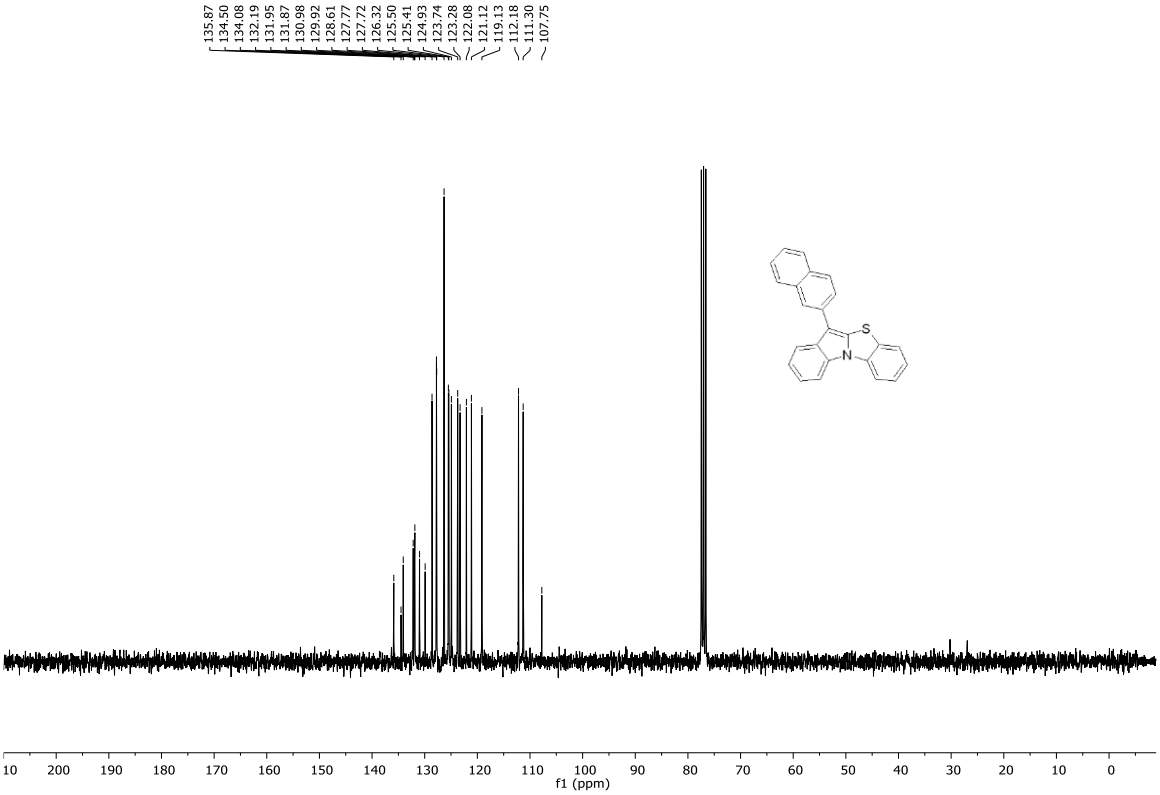
^{13}C NMR (75 MHz, $CDCl_3$) of 4k



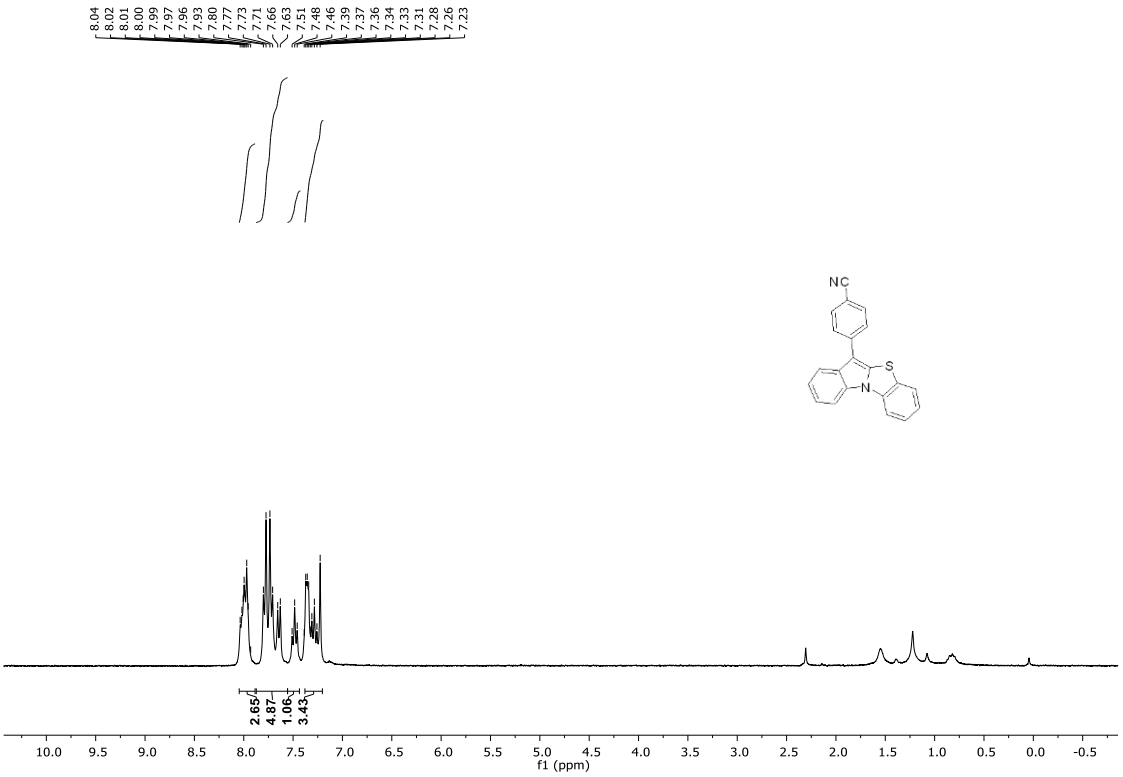
^{1}H NMR (300 MHz, $CDCl_3$) of 4l



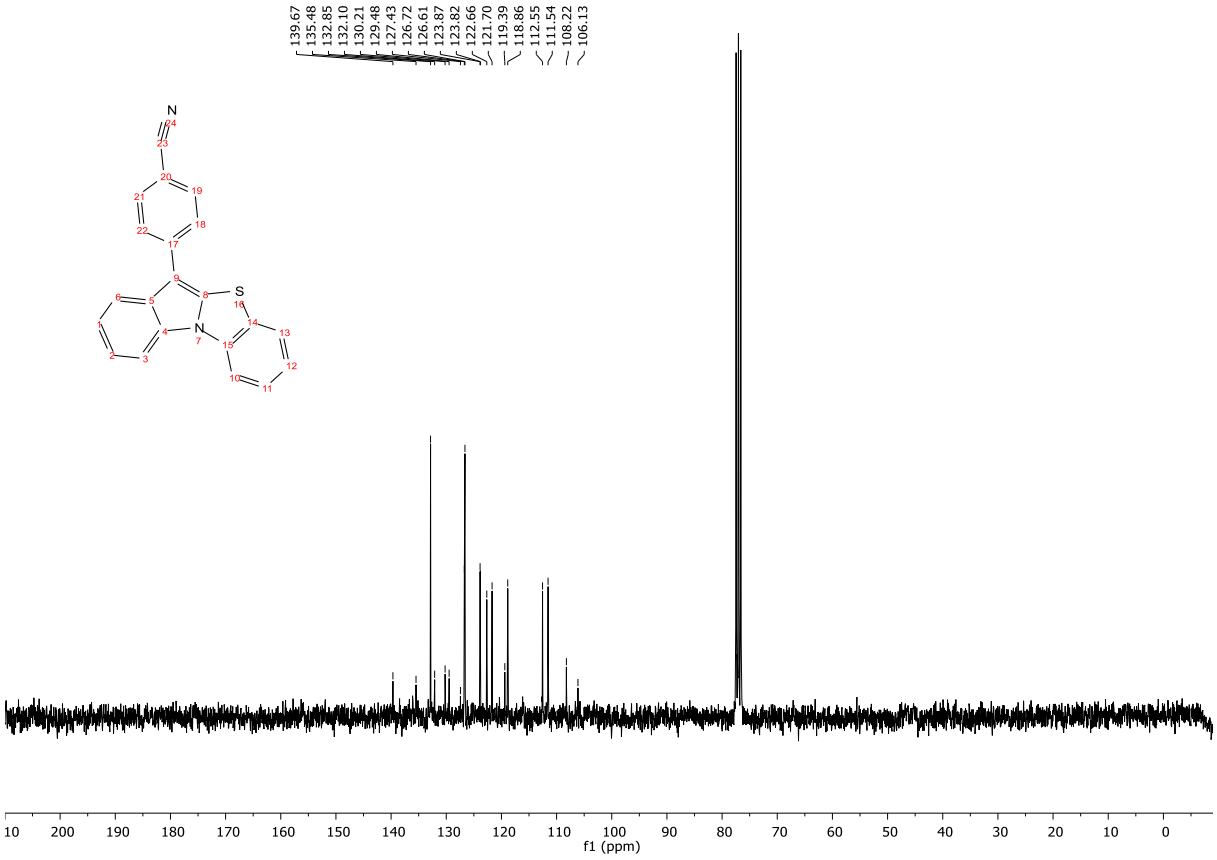
^{13}C NMR (75 MHz, $CDCl_3$) of 4l



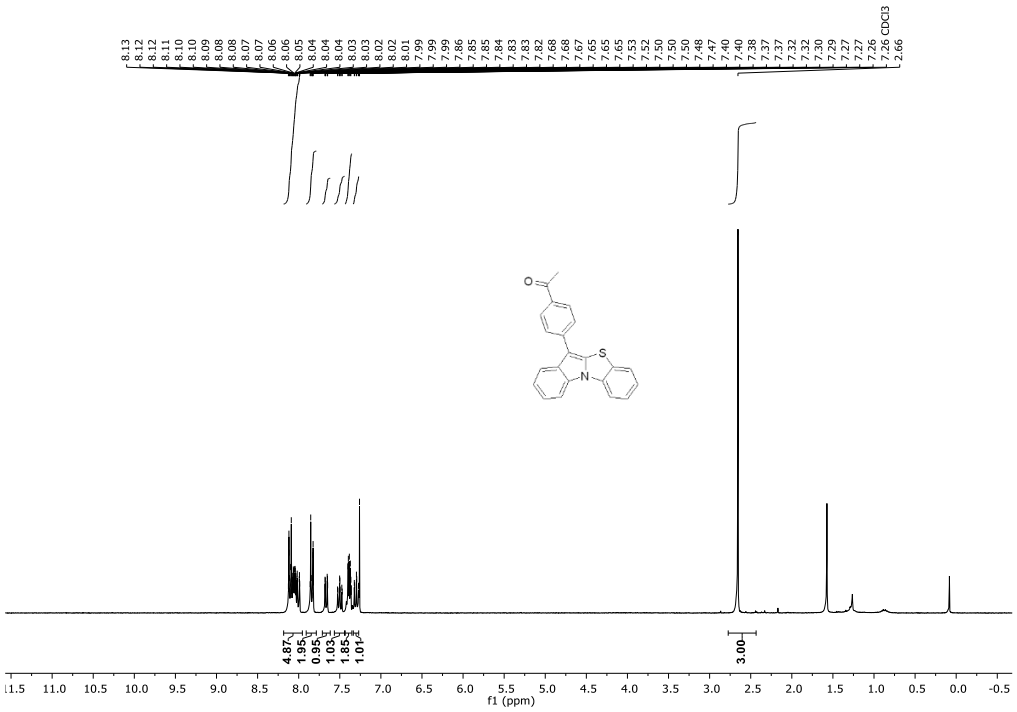
^{1}H NMR (300 MHz, $CDCl_3$) of 4m



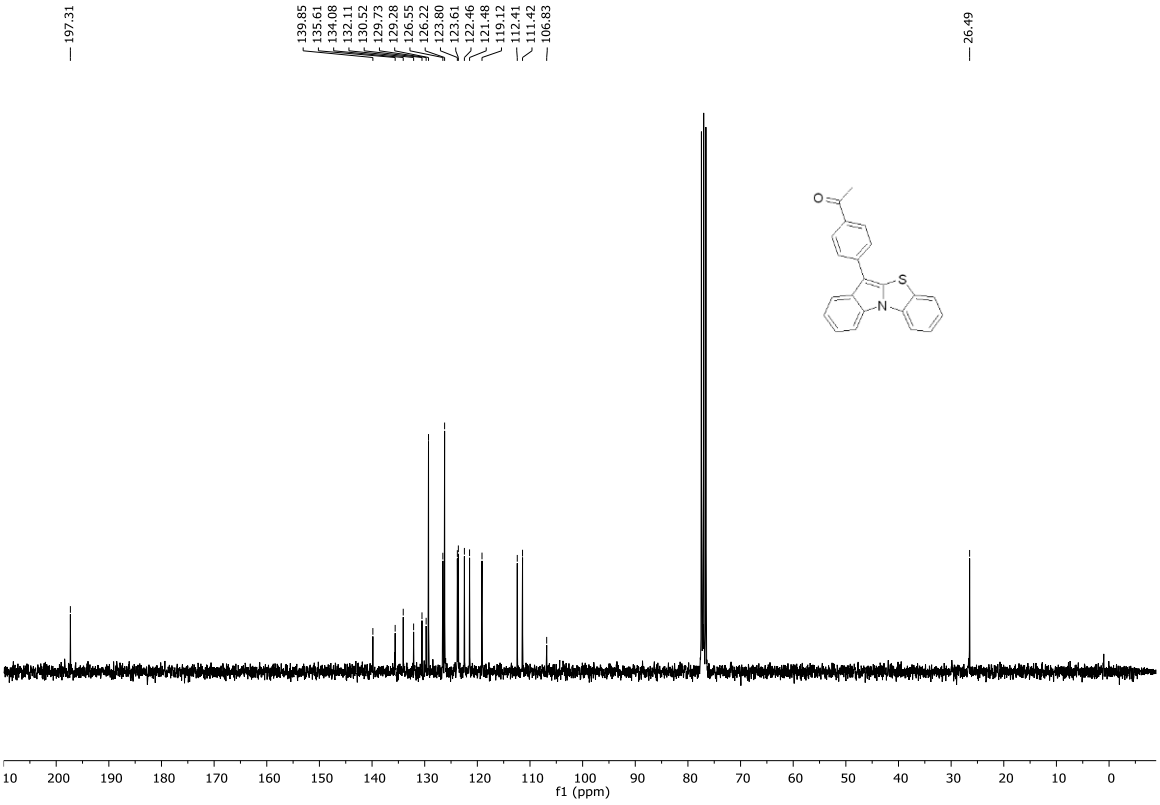
^{13}C NMR (75 MHz, $CDCl_3$) of 4m



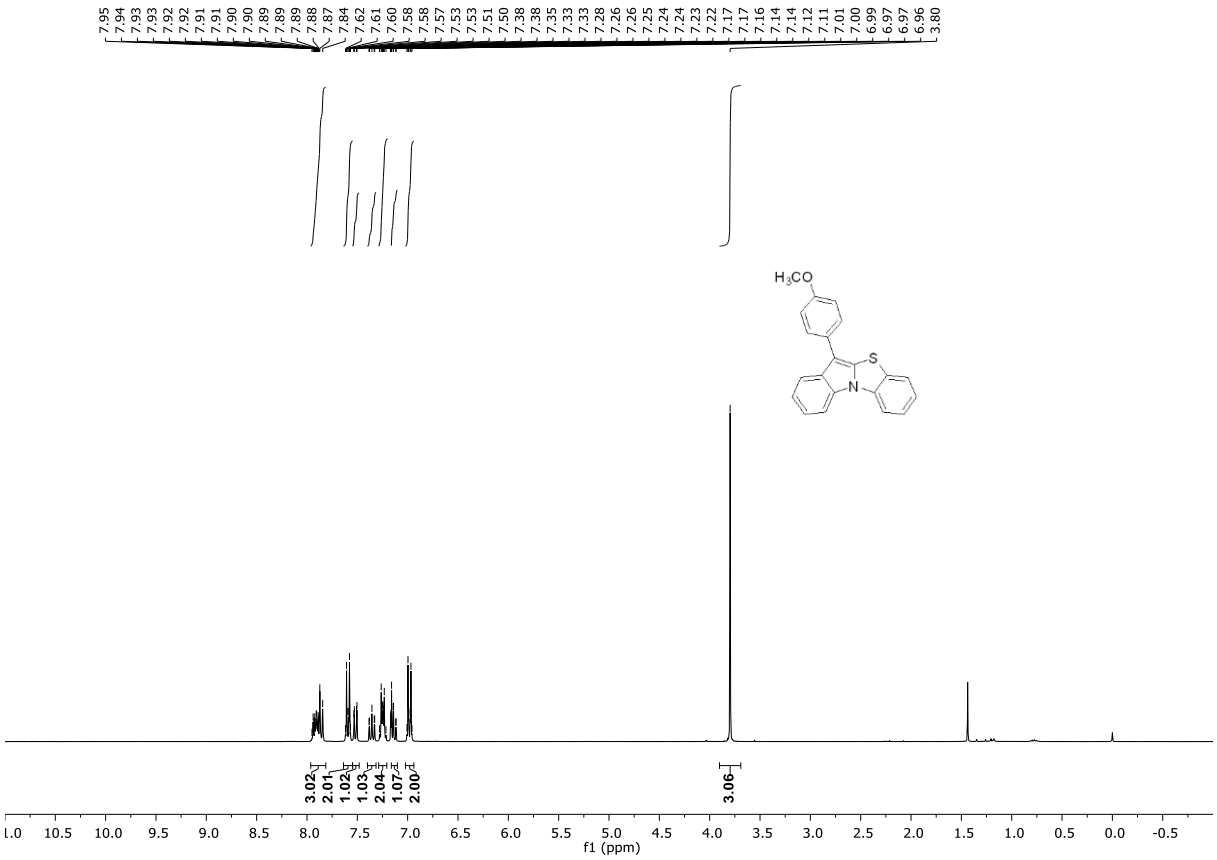
^{1}H NMR (300 MHz, $CDCl_3$) of 4n



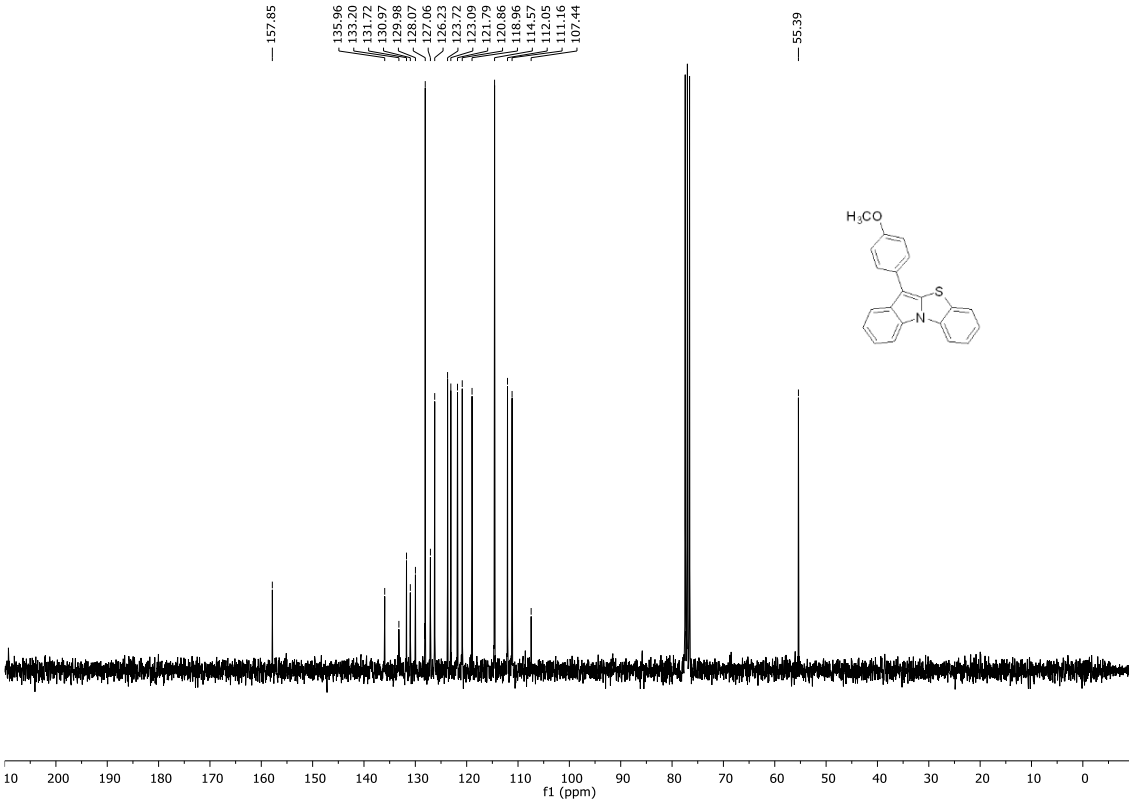
^{13}C NMR (75 MHz, $CDCl_3$) of 4n



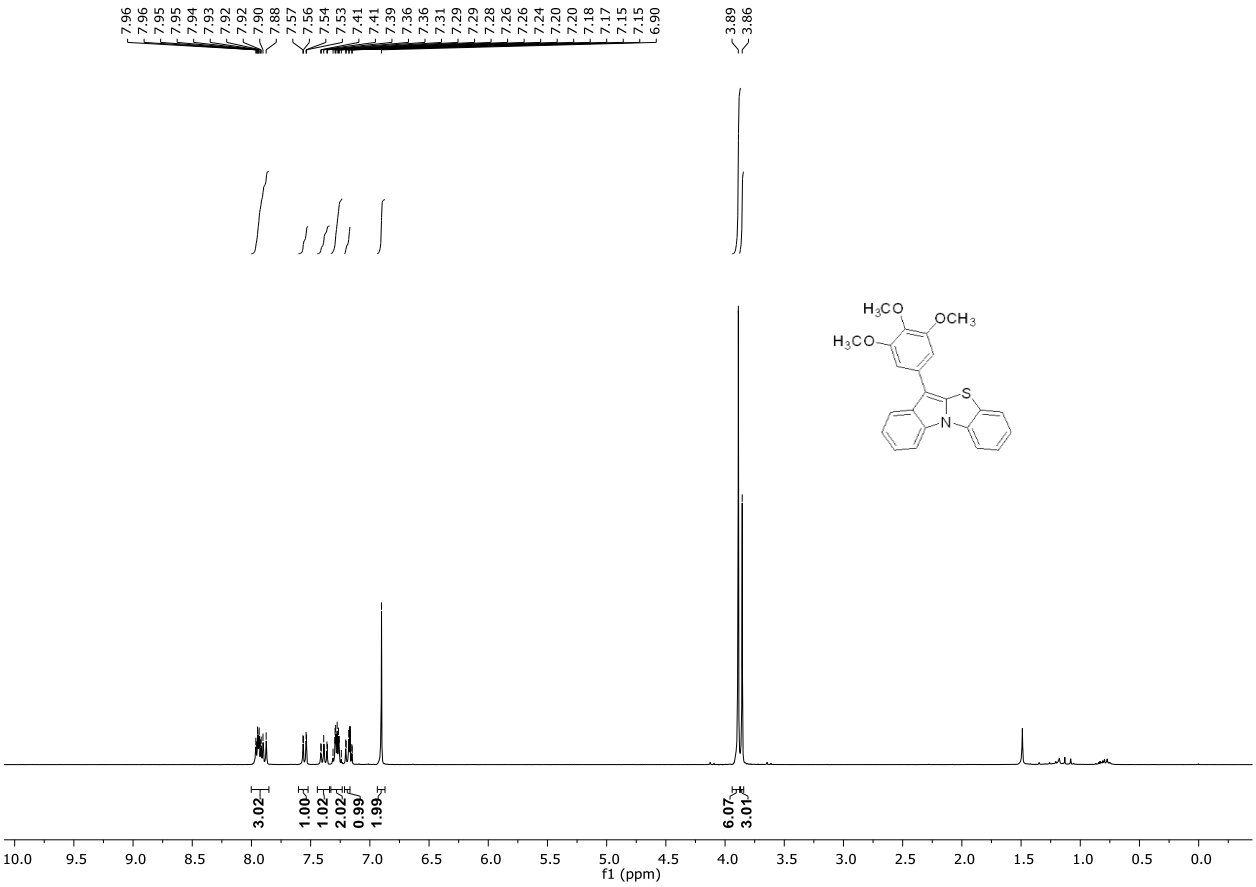
^{1}H NMR (300 MHz, $CDCl_3$) of 4o



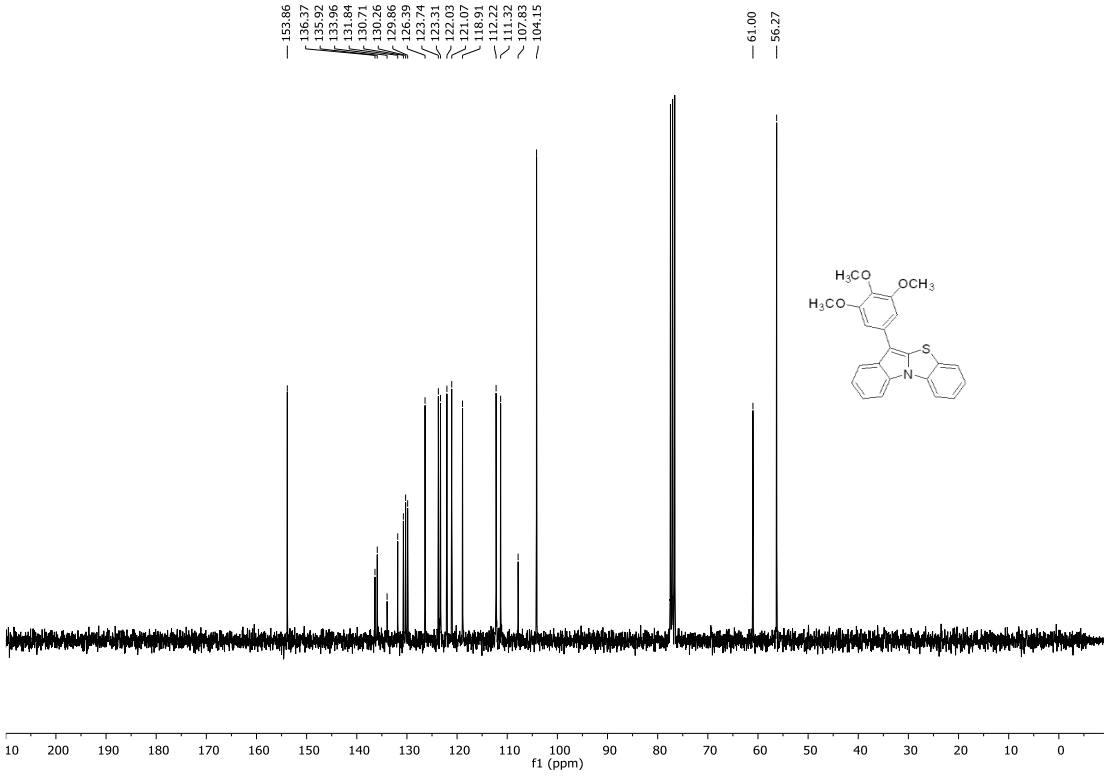
^{13}C NMR (75 MHz, $CDCl_3$) of 4o



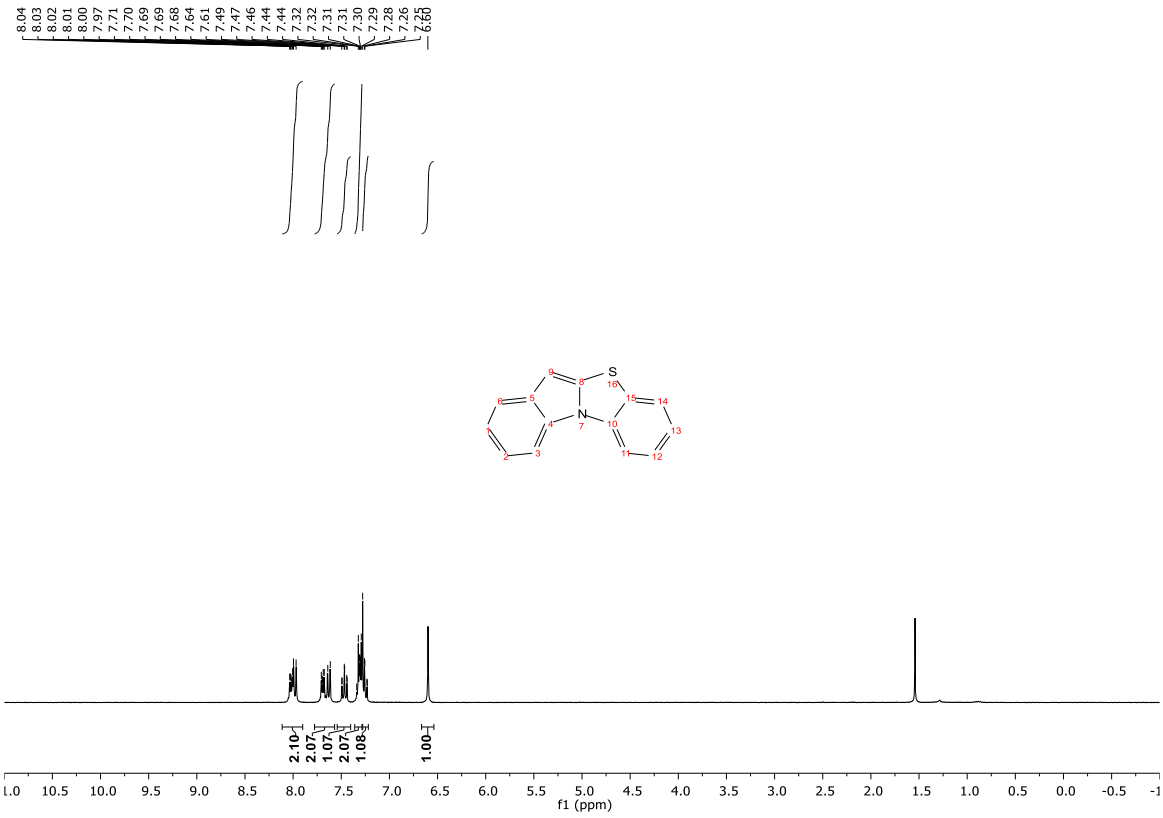
^{1}H NMR (300 MHz, $CDCl_3$) of 4p



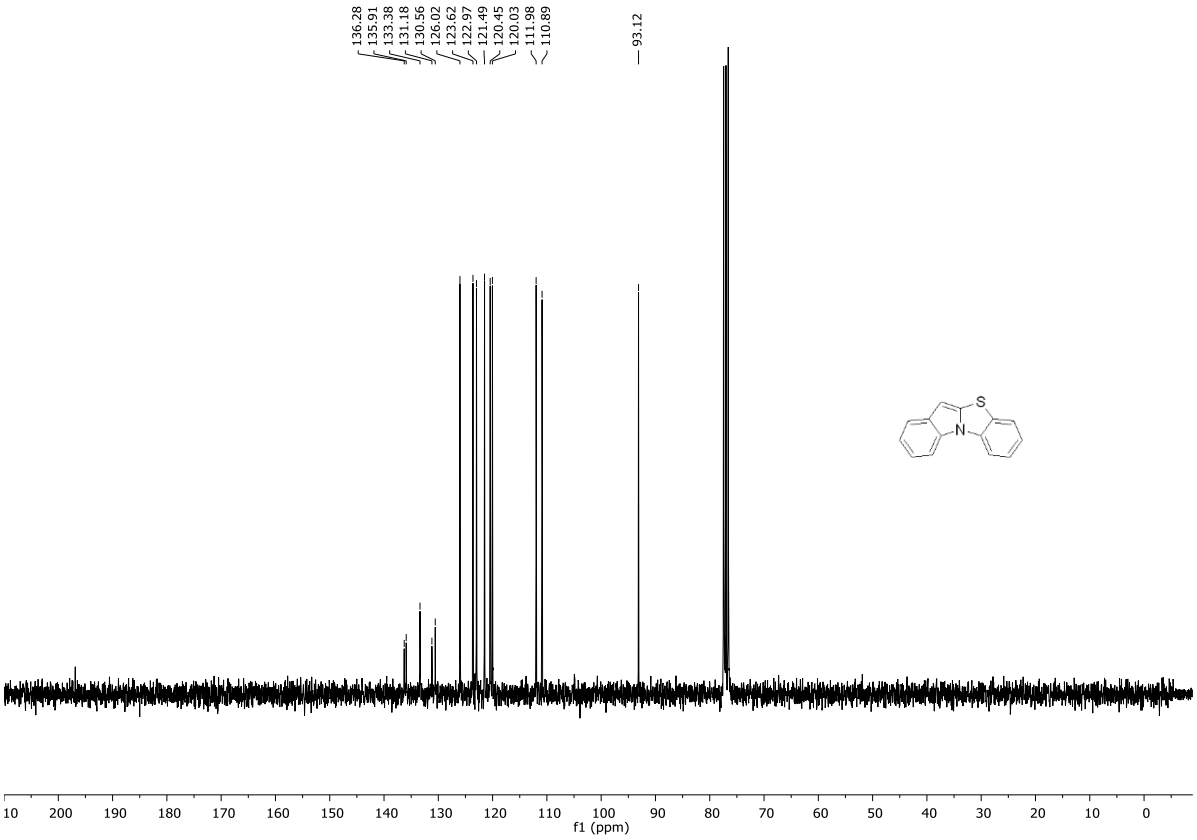
^{13}C NMR (75 MHz, $CDCl_3$) of 4p



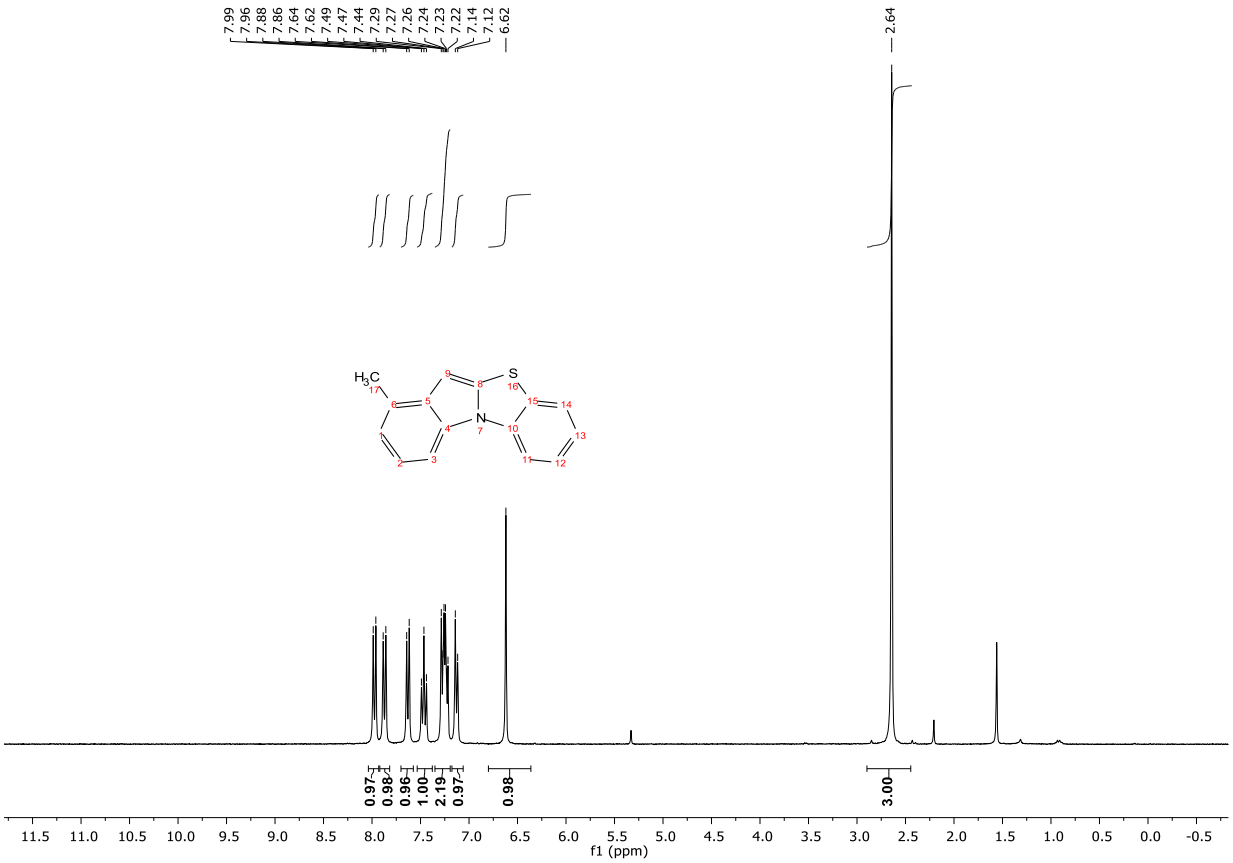
^{1}H NMR (300 MHz, $CDCl_3$) of 4q



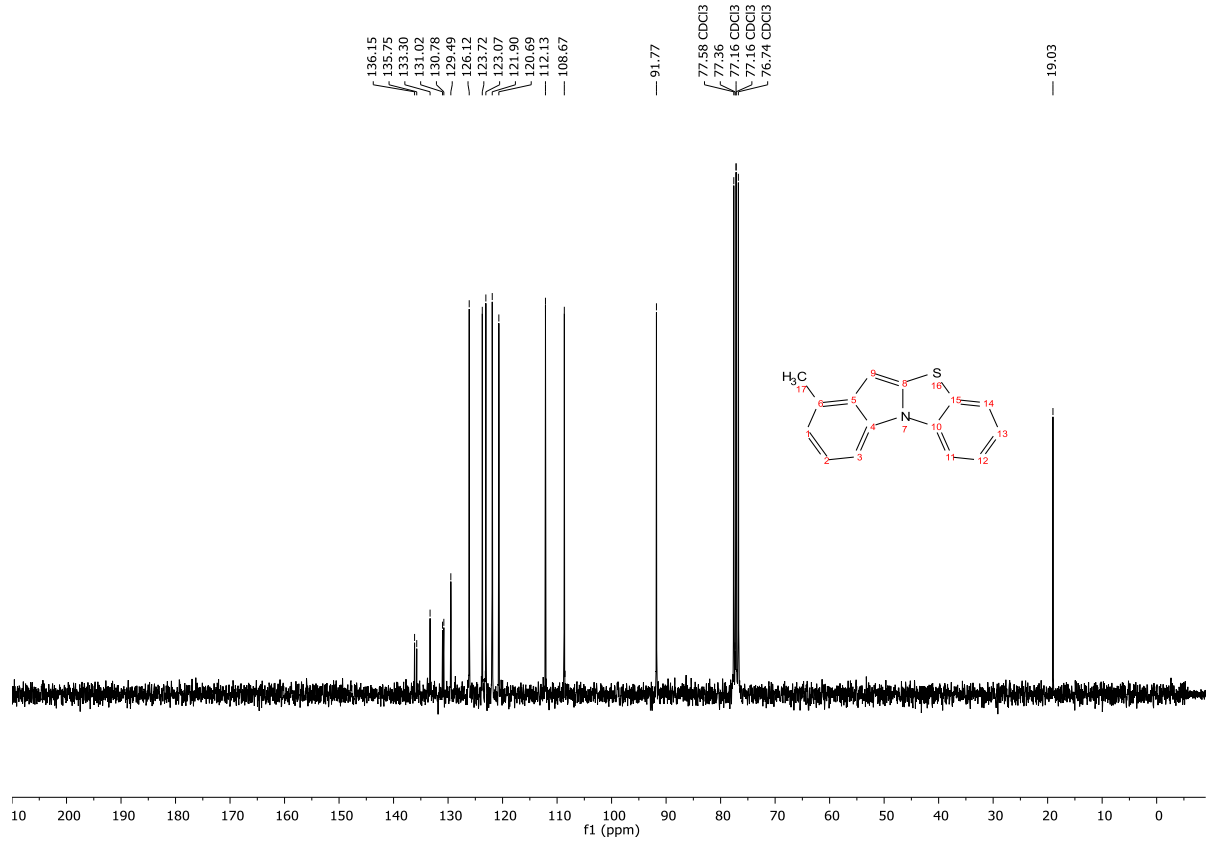
^{13}C NMR (75 MHz, $CDCl_3$) of 4q



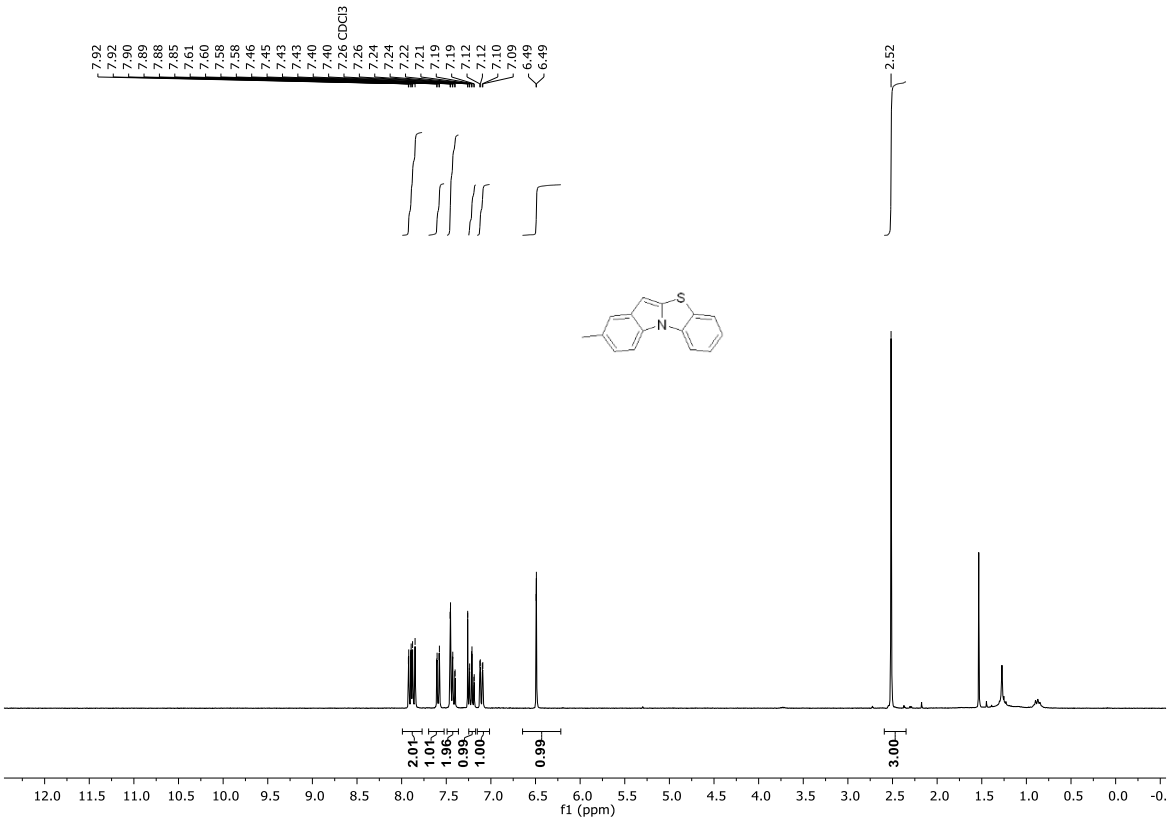
^{1}H NMR (300 MHz, $CDCl_3$) of 4r



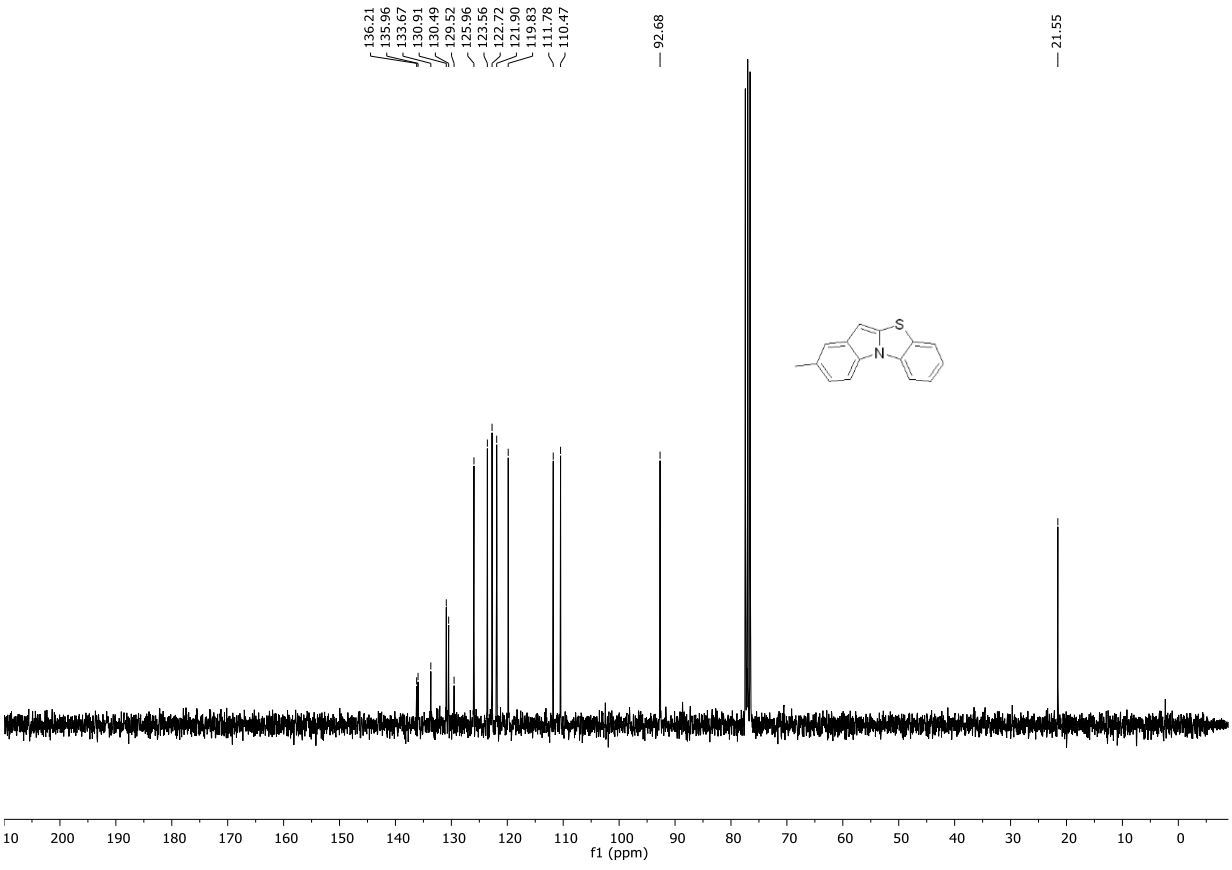
^{13}C NMR (75 MHz, $CDCl_3$) of 4r



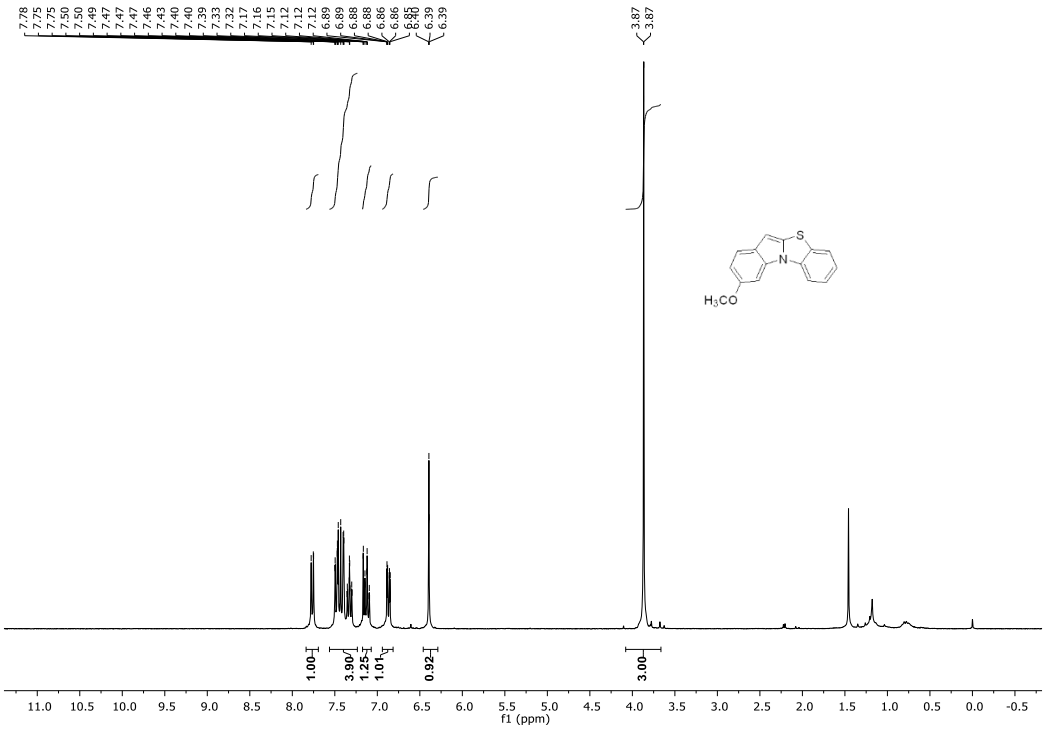
^{1}H NMR (300 MHz, $CDCl_3$) of 4s



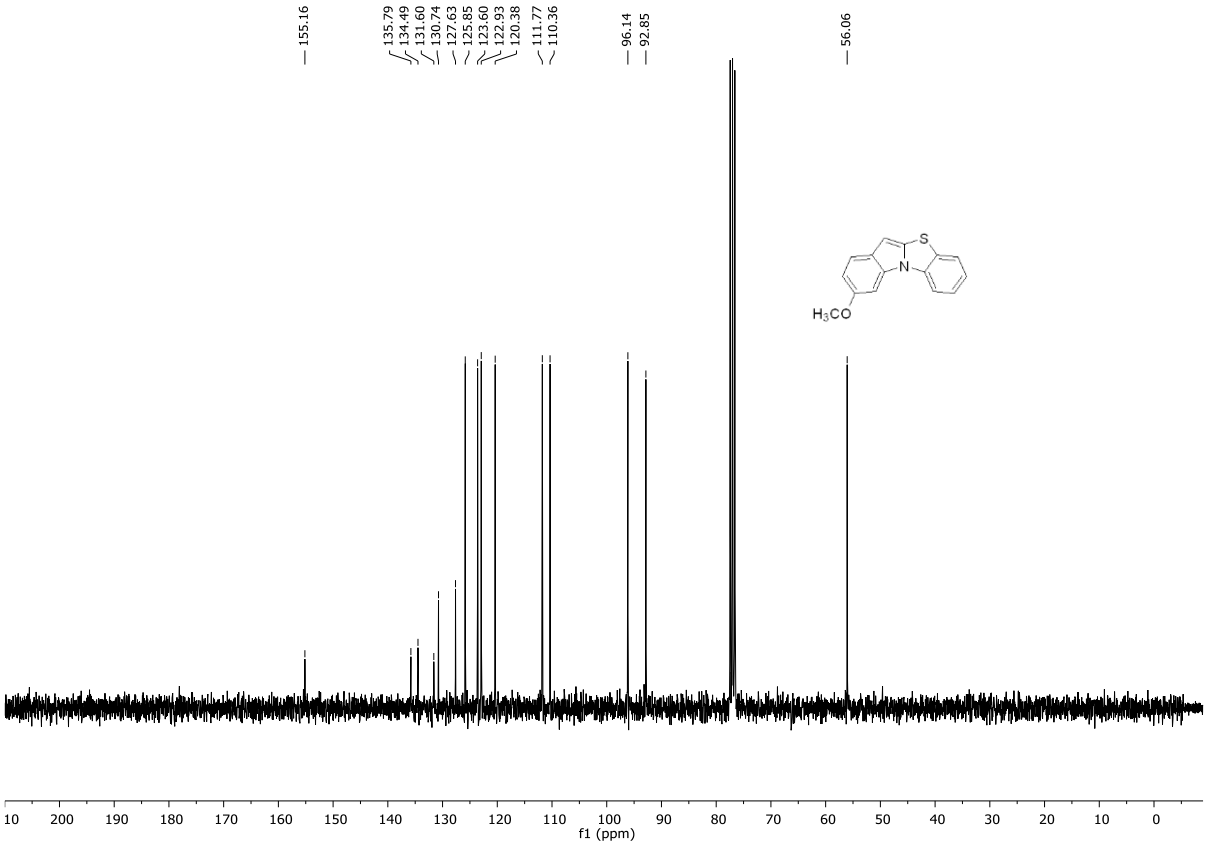
^{13}C NMR (75 MHz, $CDCl_3$) of 4s



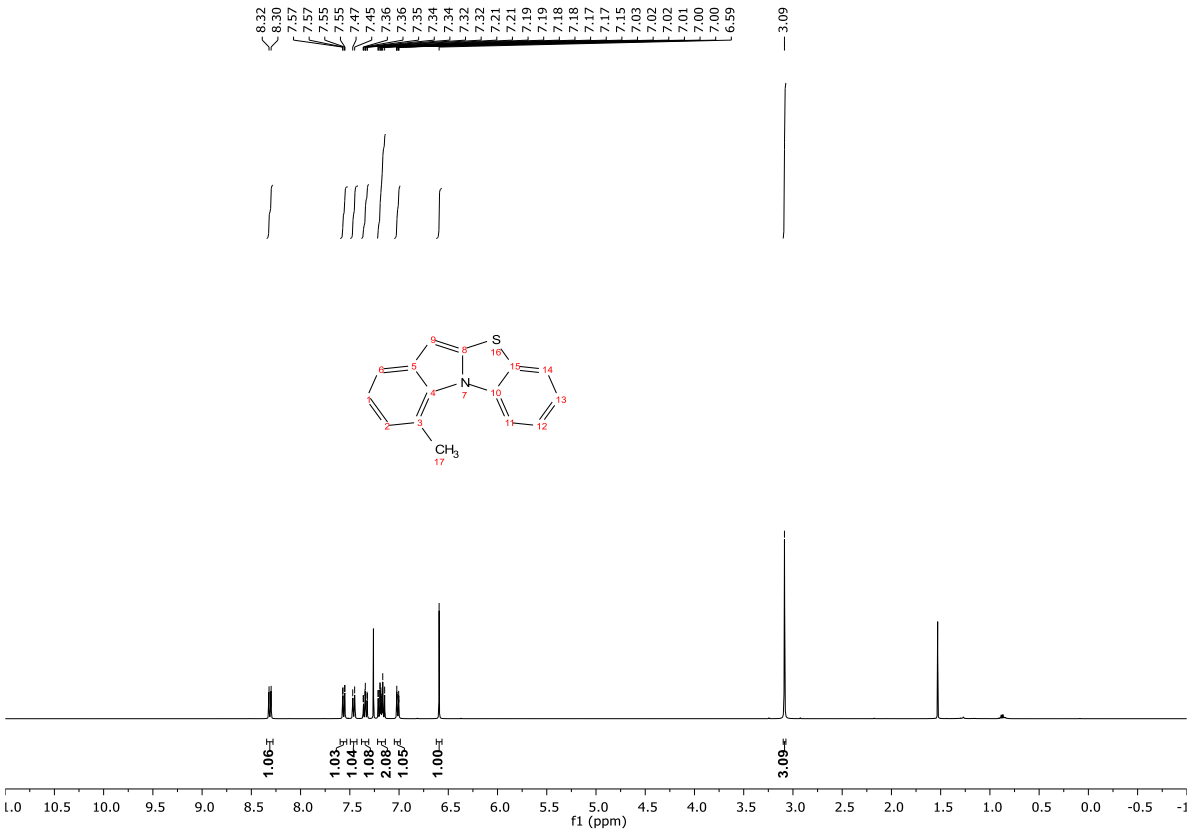
^{1}H NMR (300 MHz, $CDCl_3$) of 4t



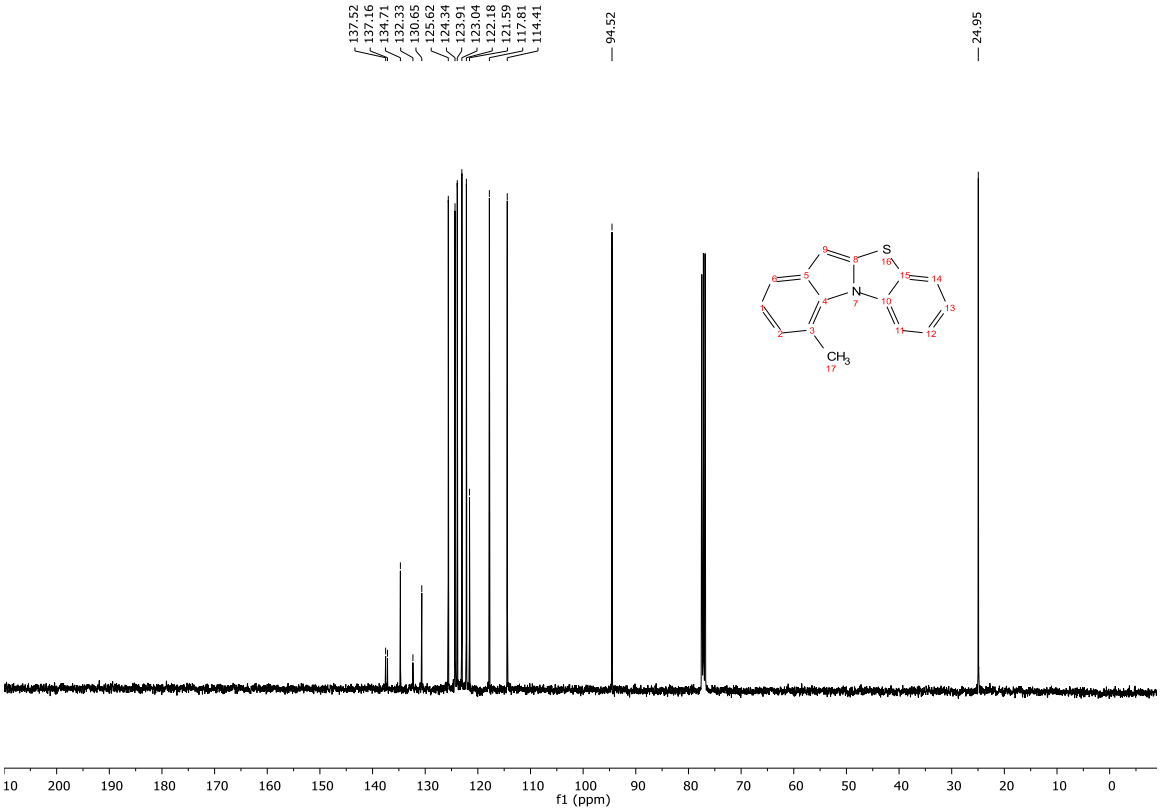
^{13}C NMR (75 MHz, $CDCl_3$) of 4t



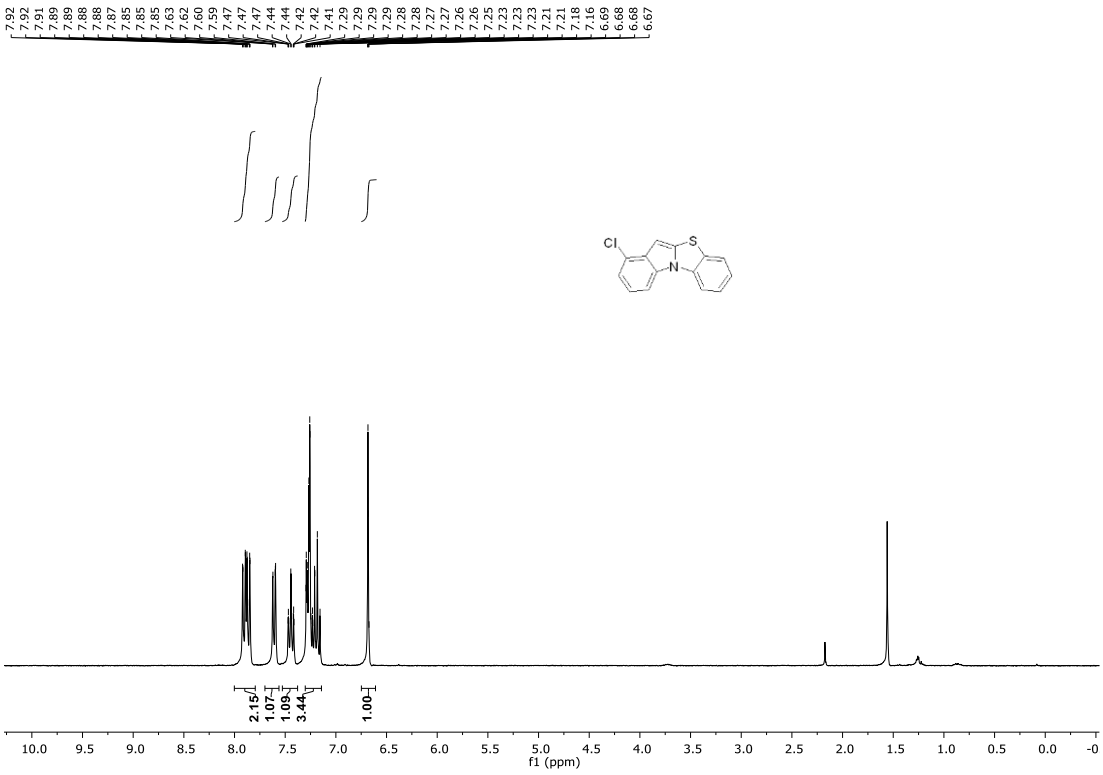
^{1}H NMR (300 MHz, $CDCl_3$) of 4u



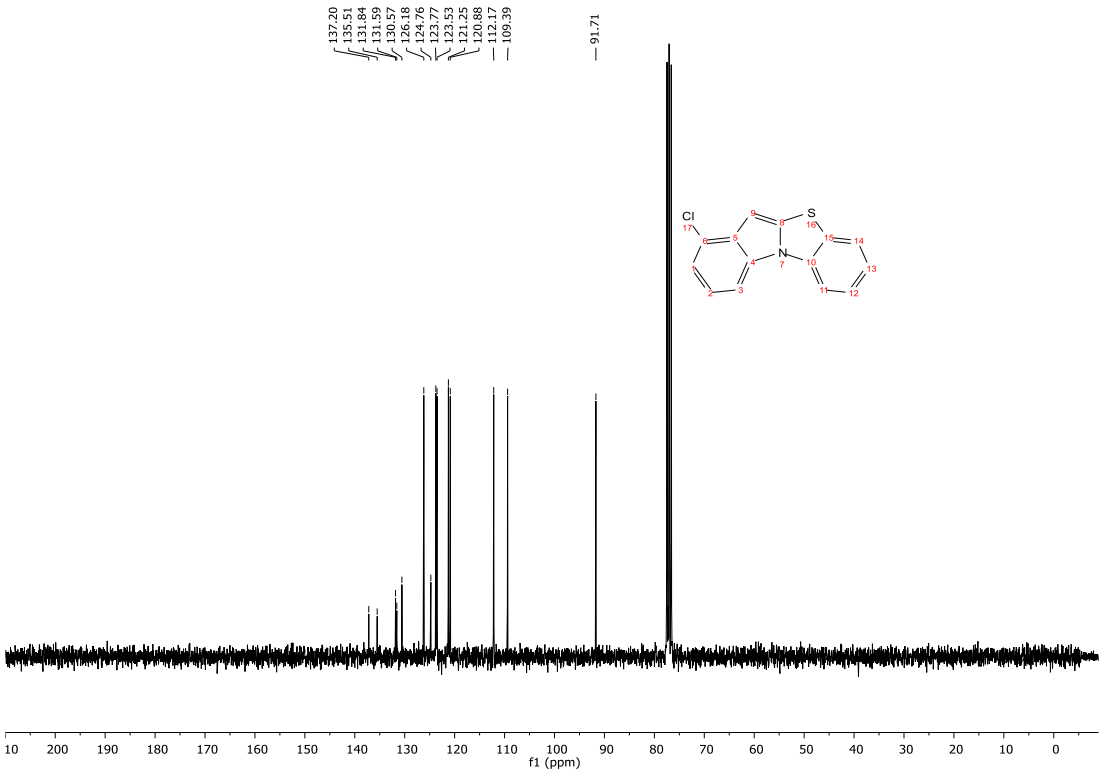
^{13}C NMR (75 MHz, $CDCl_3$) of 4u



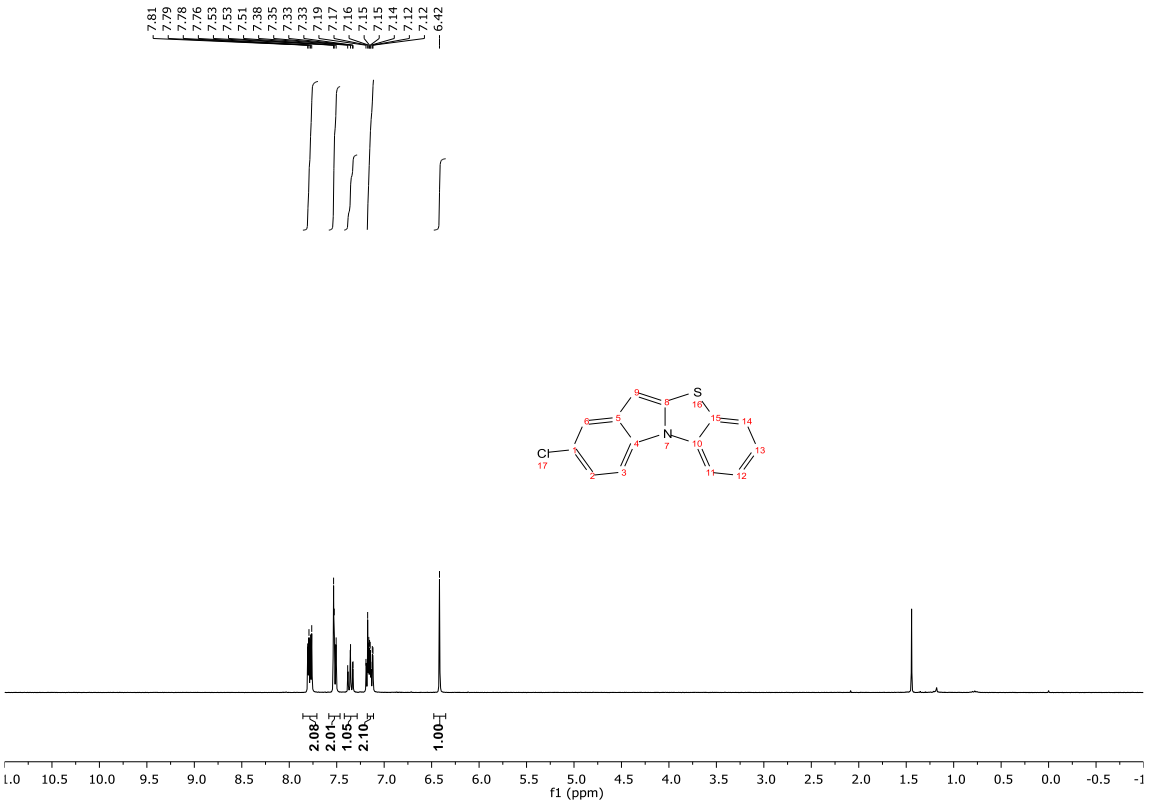
^{1}H NMR (300 MHz, $CDCl_3$) of 4v



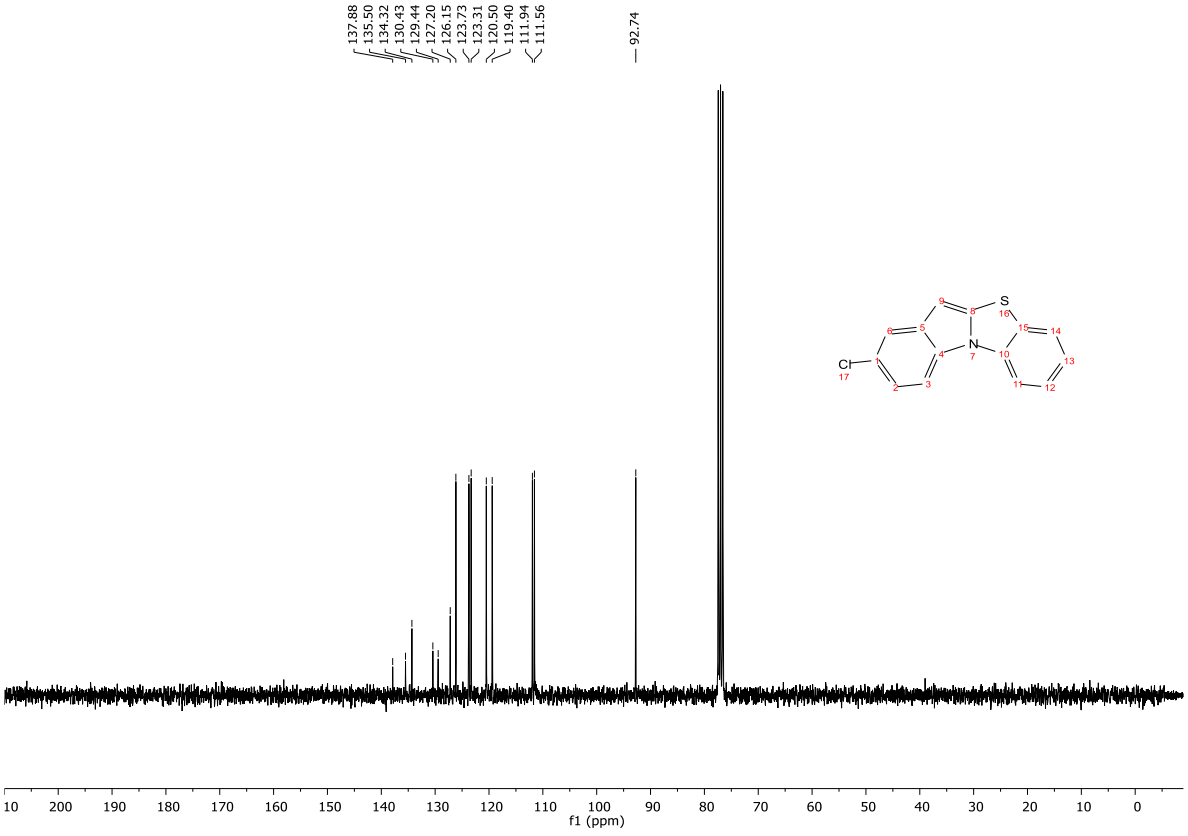
^{13}C NMR (75 MHz, $CDCl_3$) of 4v



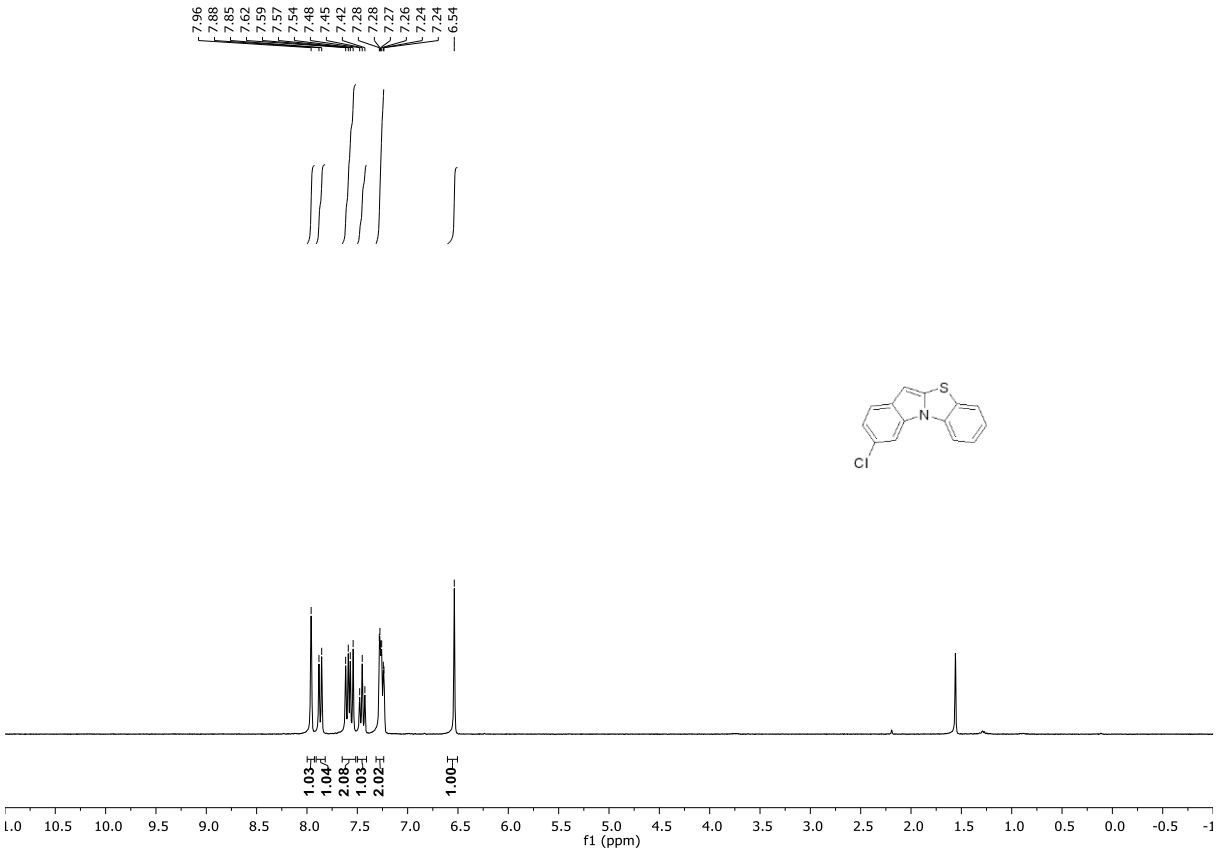
^{1}H NMR (300 MHz, $CDCl_3$) of 4w



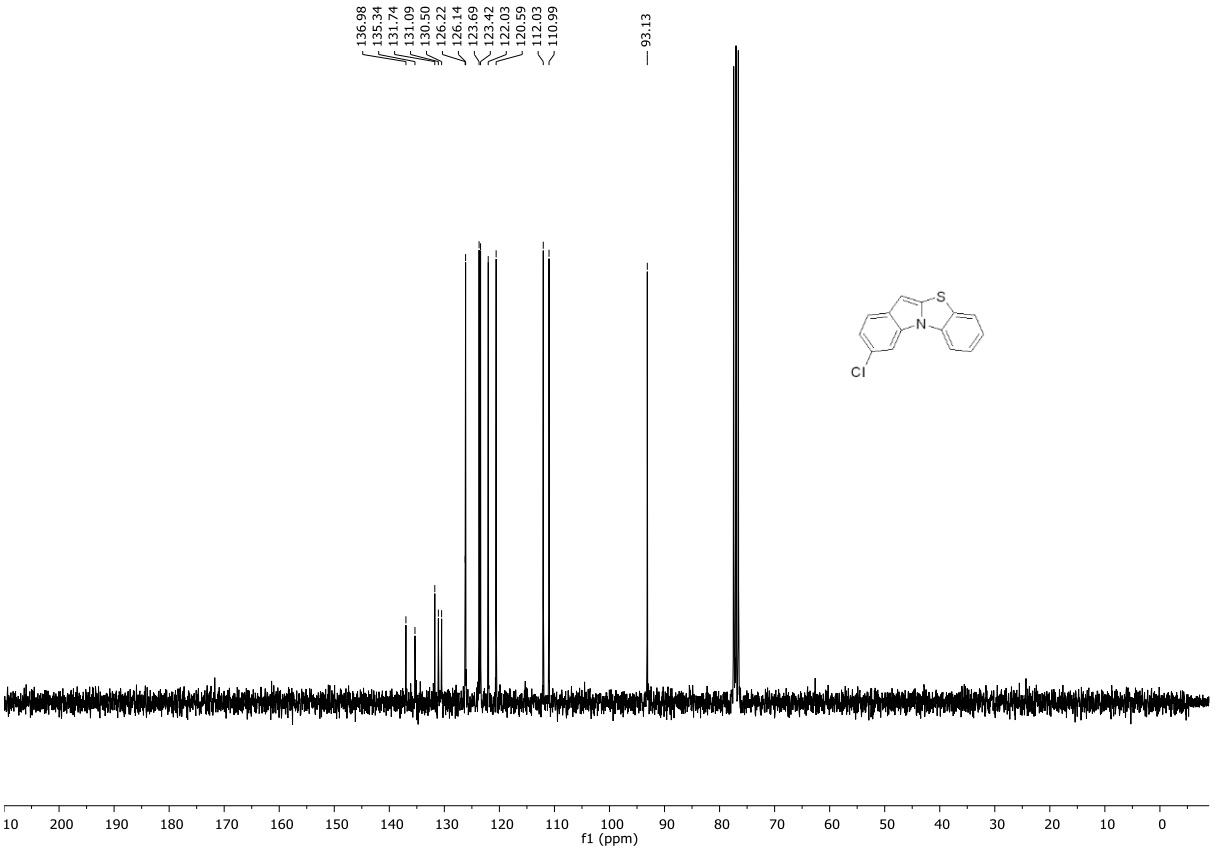
^{13}C NMR (75 MHz, $CDCl_3$) of 4w



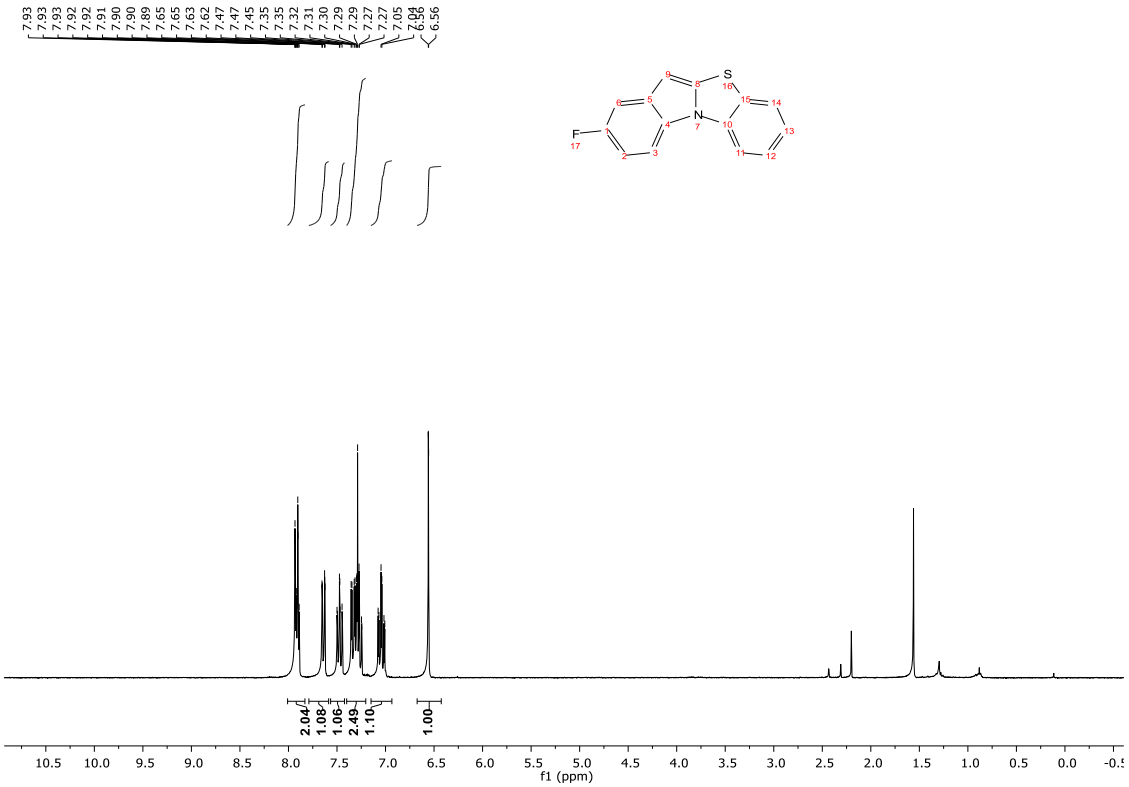
^{1}H NMR (300 MHz, $CDCl_3$) of 4x



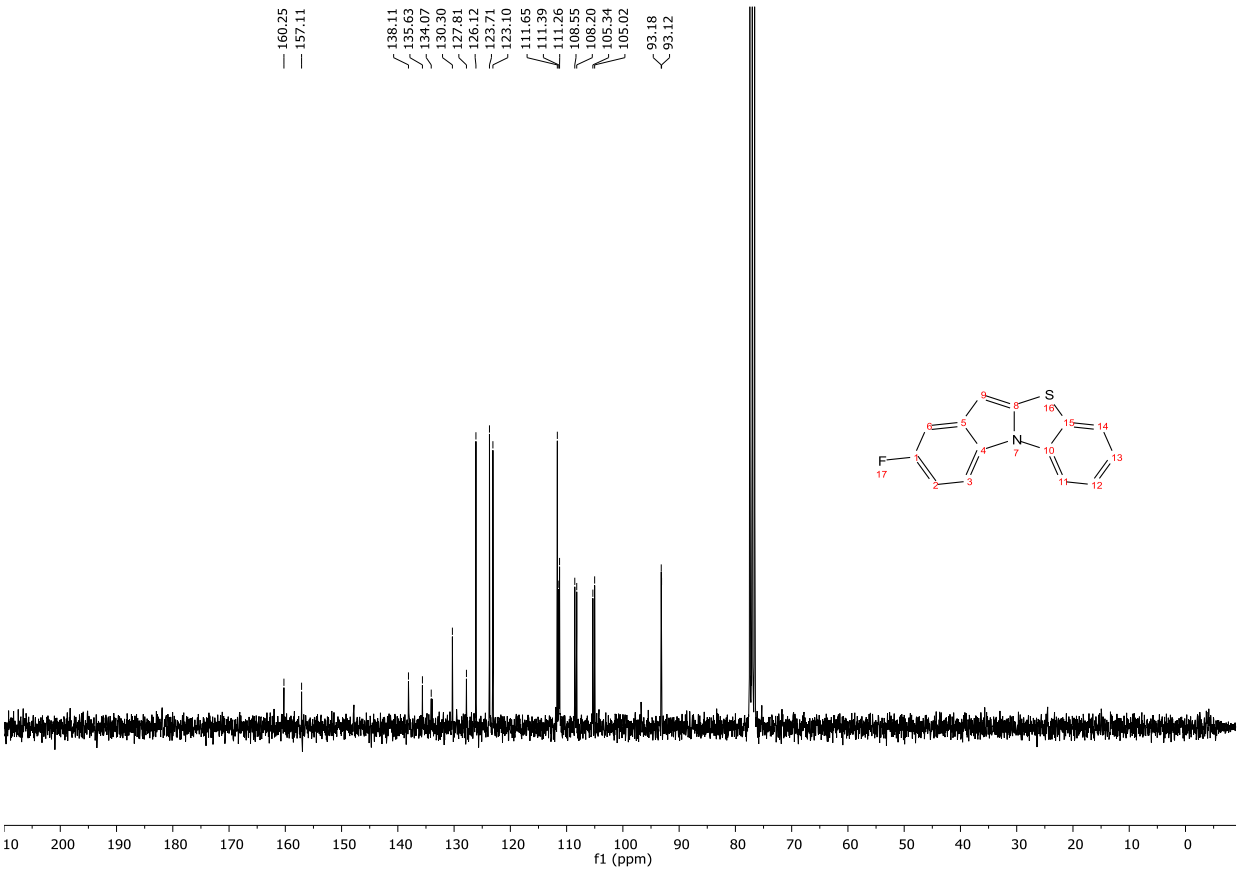
^{13}C NMR (75 MHz, $CDCl_3$) of 4x



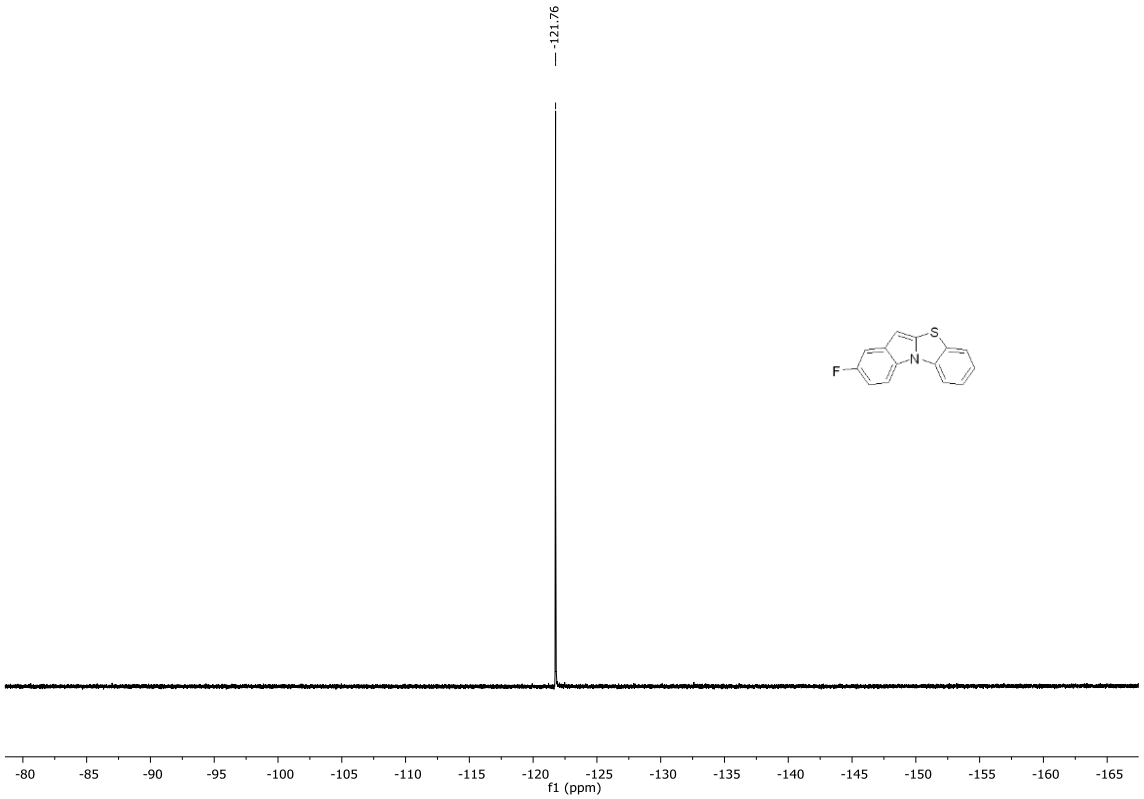
^{1}H NMR (300 MHz, $CDCl_3$) of 4y



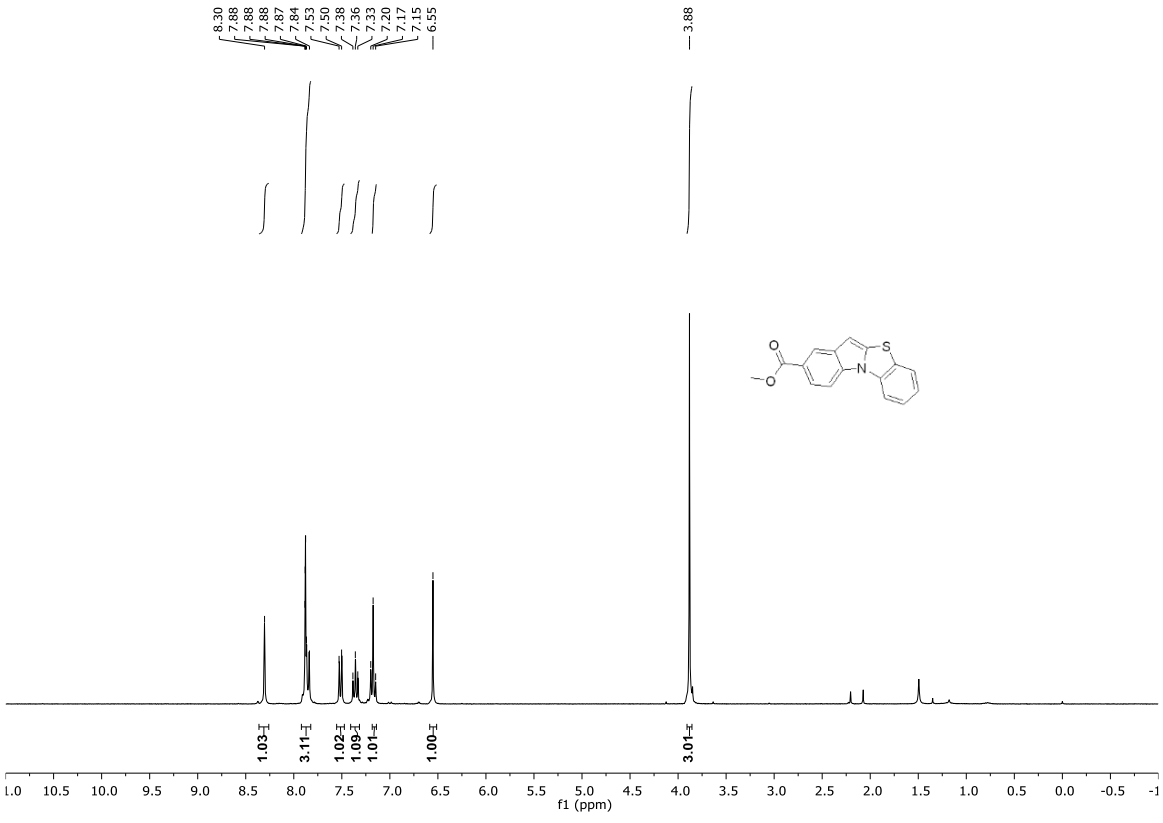
^{13}C NMR (75 MHz, $CDCl_3$) of 4y



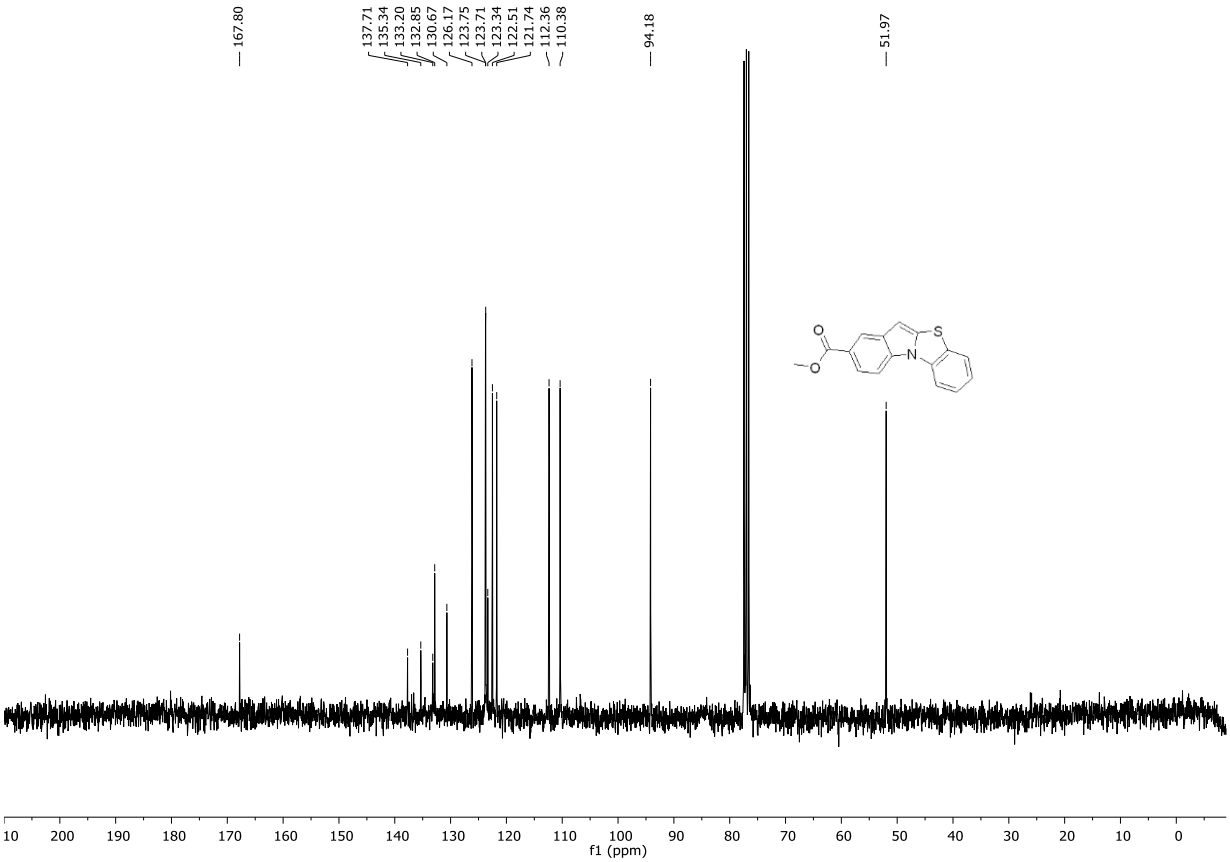
^{19}F NMR (188 MHz, $CDCl_3$) of 4y



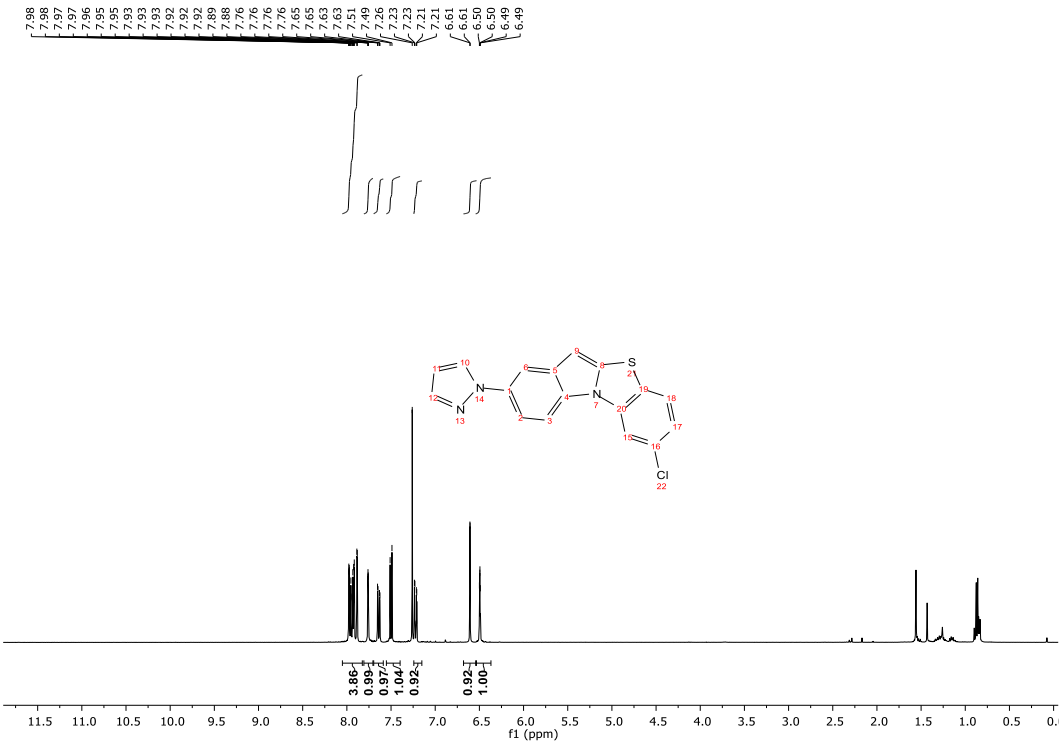
^{1}H NMR (300 MHz, $CDCl_3$) of 4z



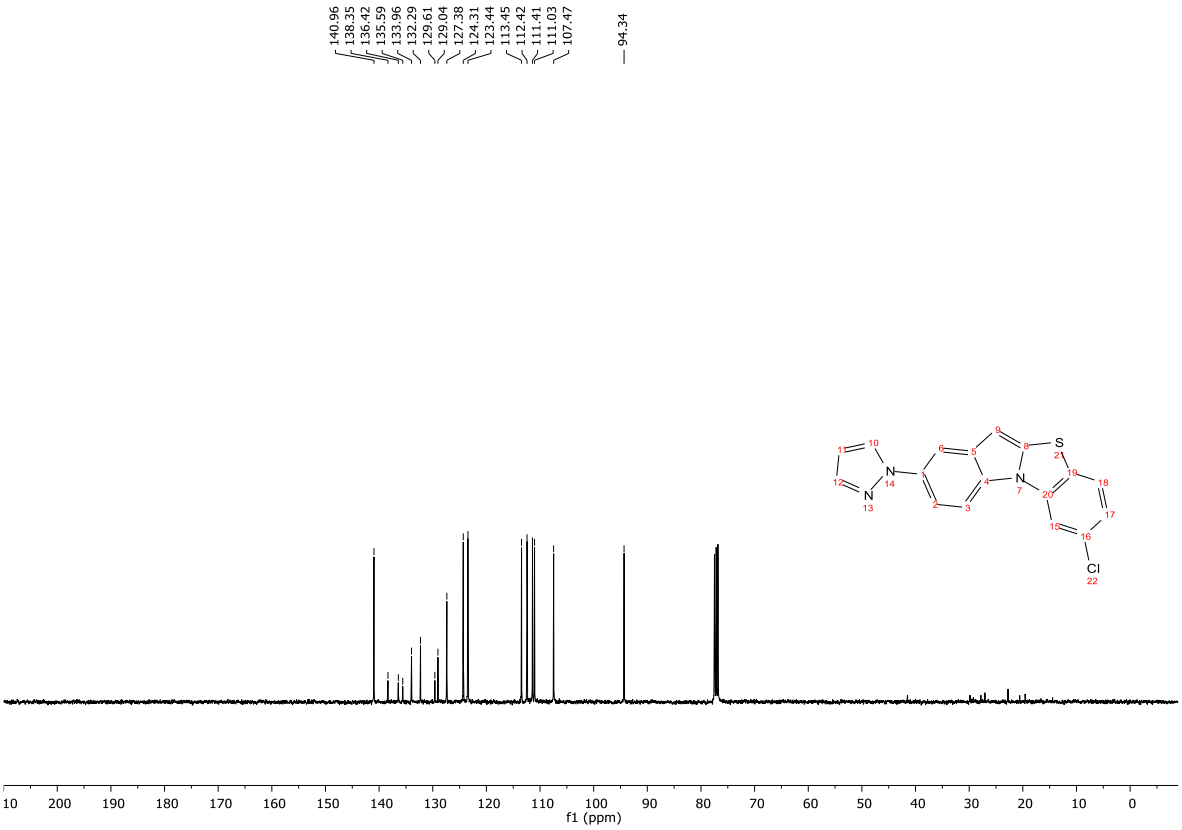
^{13}C NMR (75 MHz, $CDCl_3$) of 4z



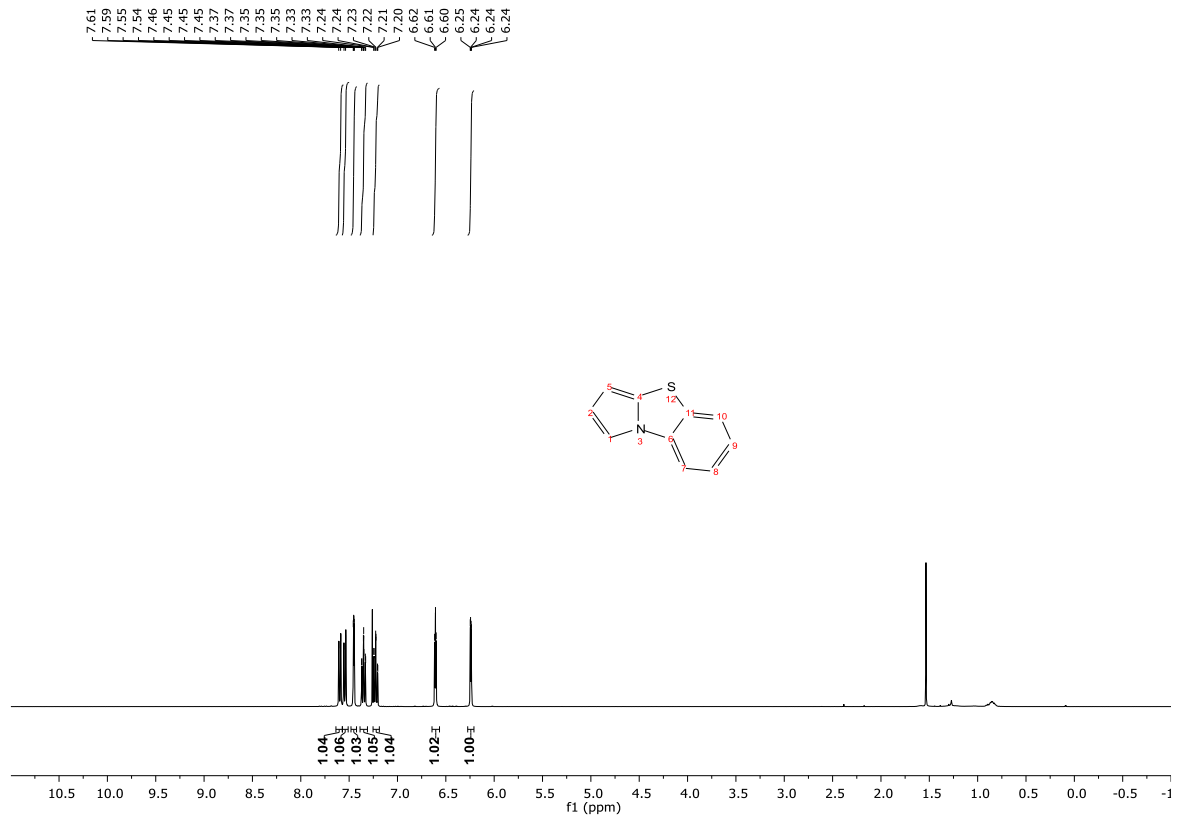
^{1}H NMR (400 MHz, $CDCl_3$) of 4ab



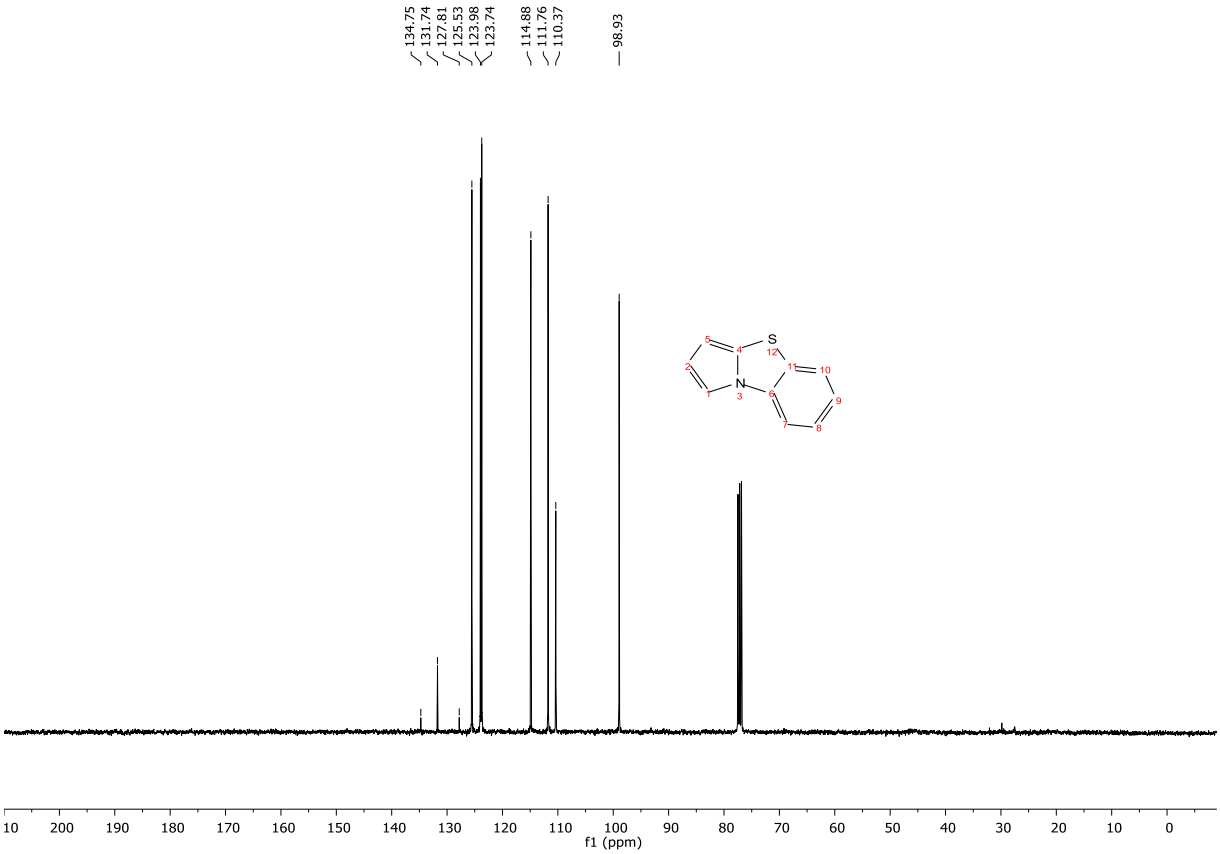
^{13}C NMR (101 MHz, $CDCl_3$) of 4ab



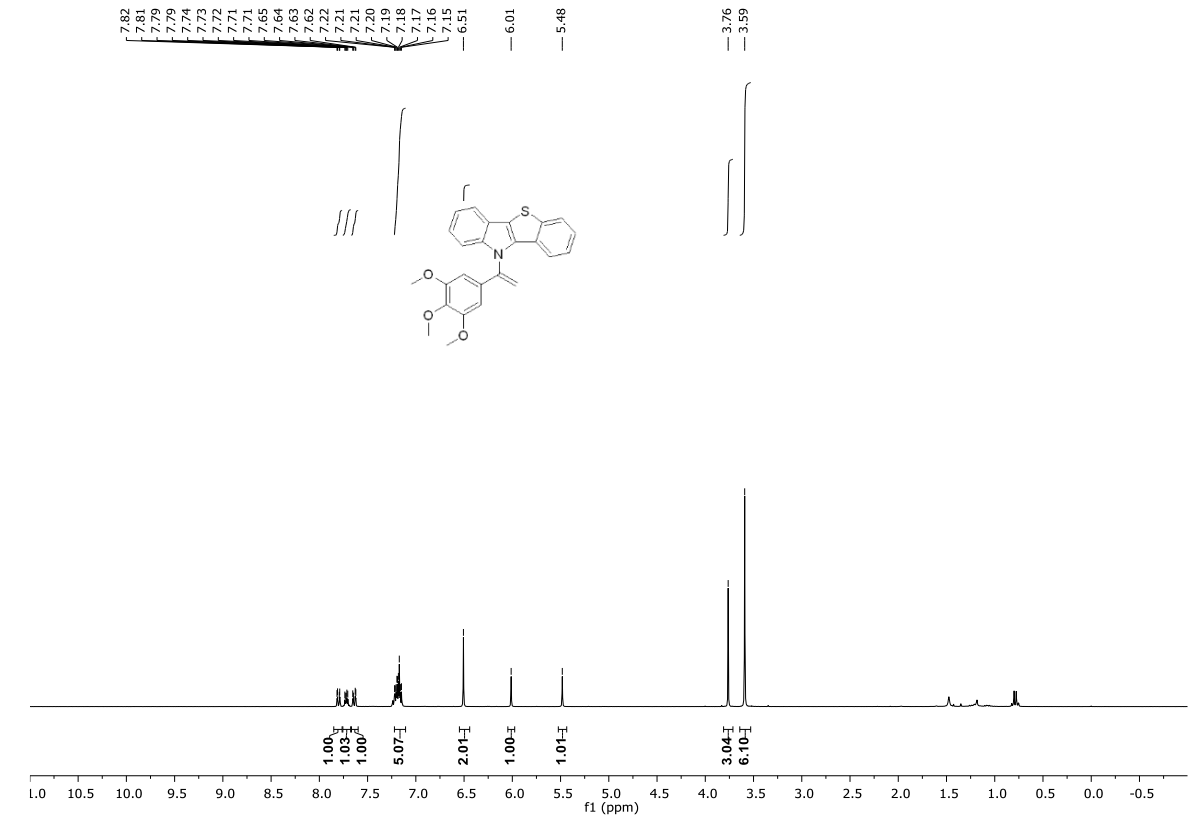
^{1}H NMR (400 MHz, $CDCl_3$) of 4ac



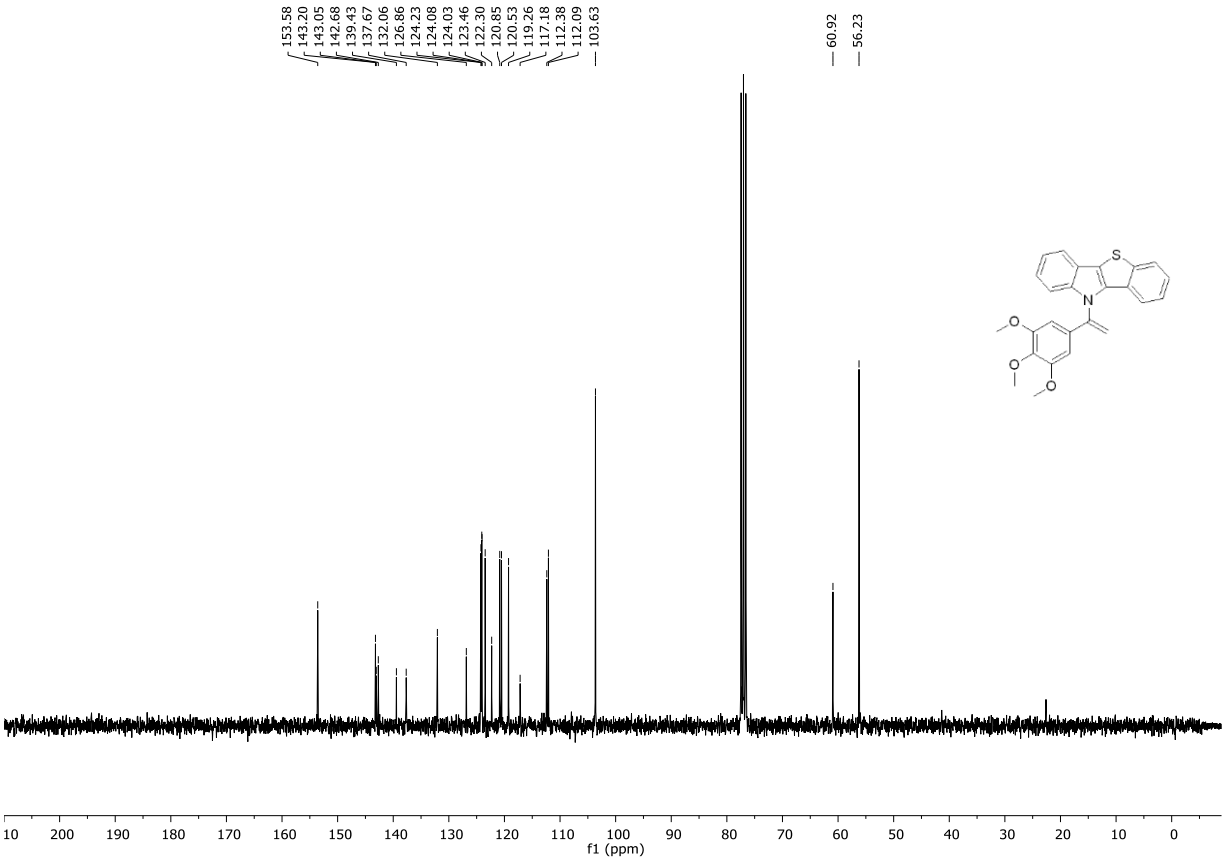
^{13}C NMR (101 MHz, $CDCl_3$) of 4ac



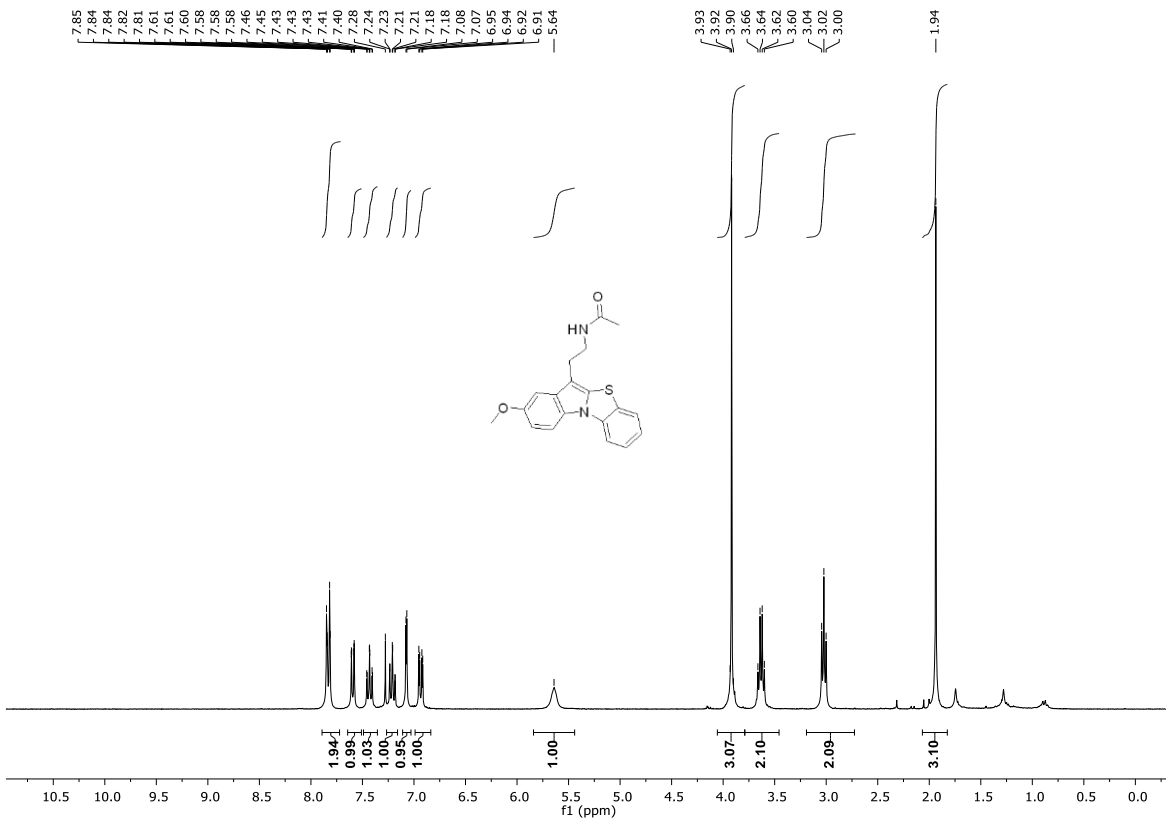
^{1}H NMR (300 MHz, $CDCl_3$) of 4ad



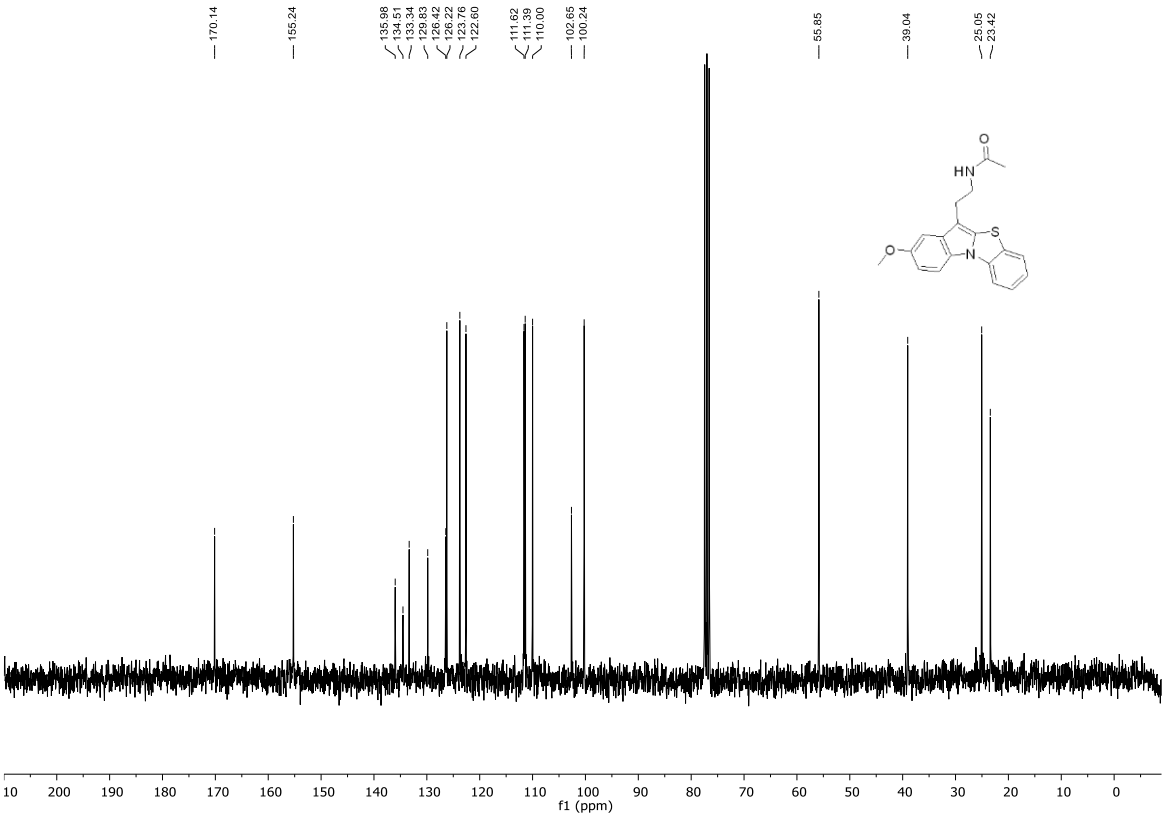
^{13}C NMR (101 MHz, $CDCl_3$) of 4ad



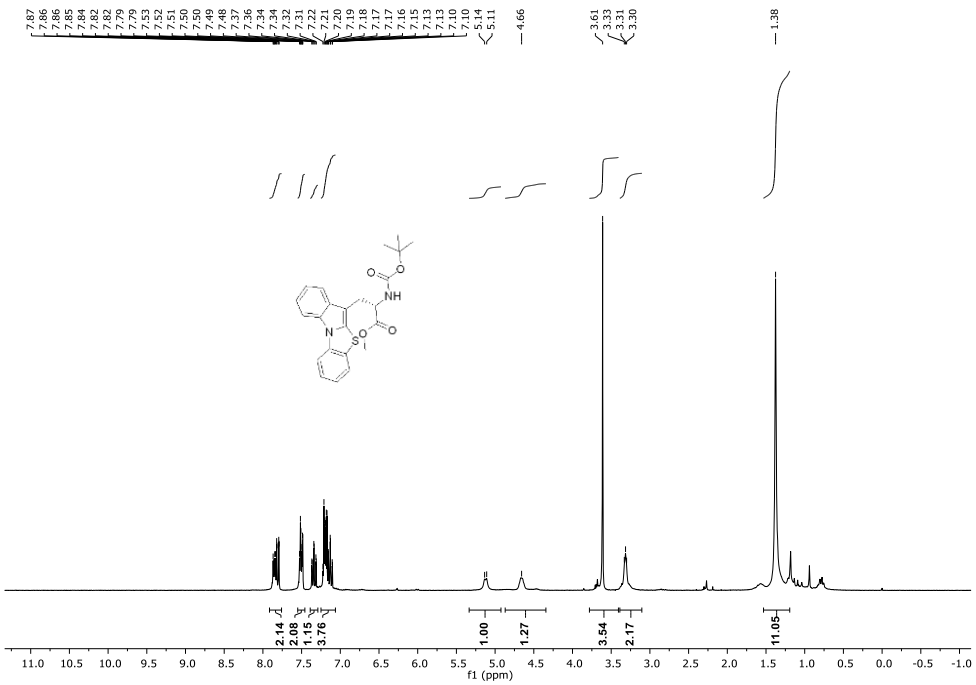
^{1}H NMR (300 MHz, $CDCl_3$) of 4ae



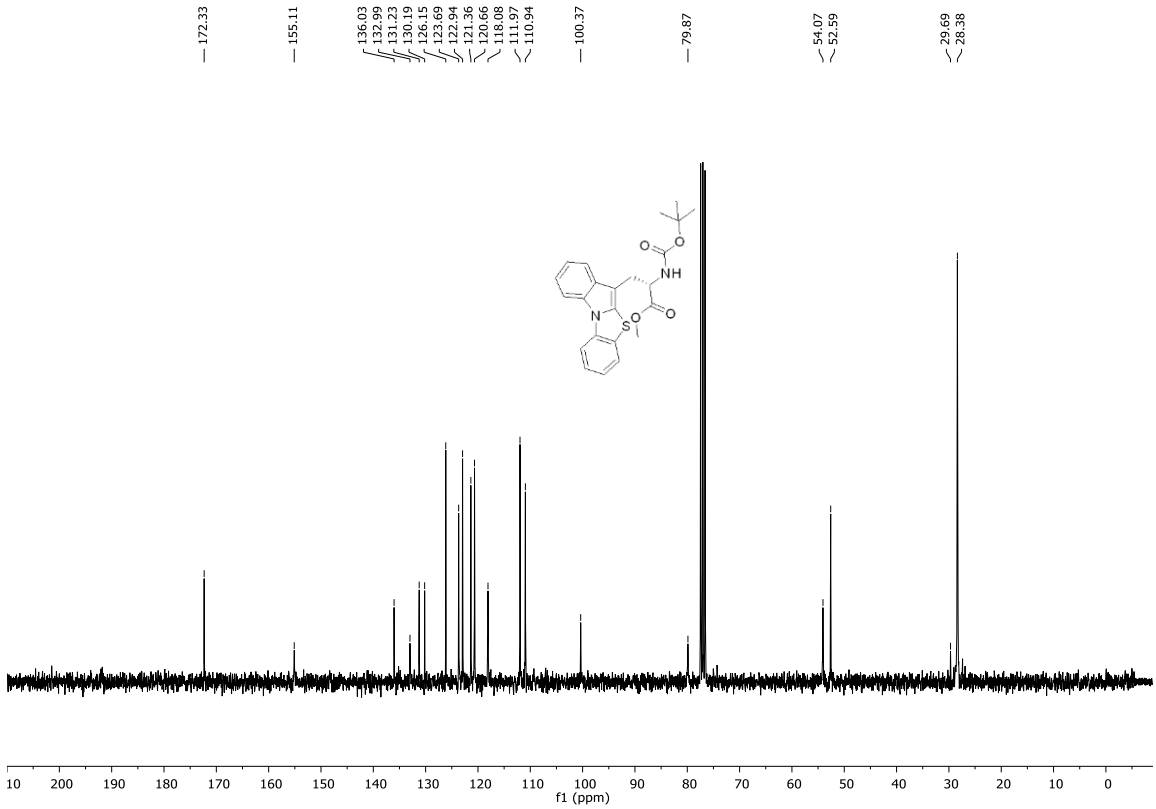
^{13}C NMR (75 MHz, $CDCl_3$) of 4ae



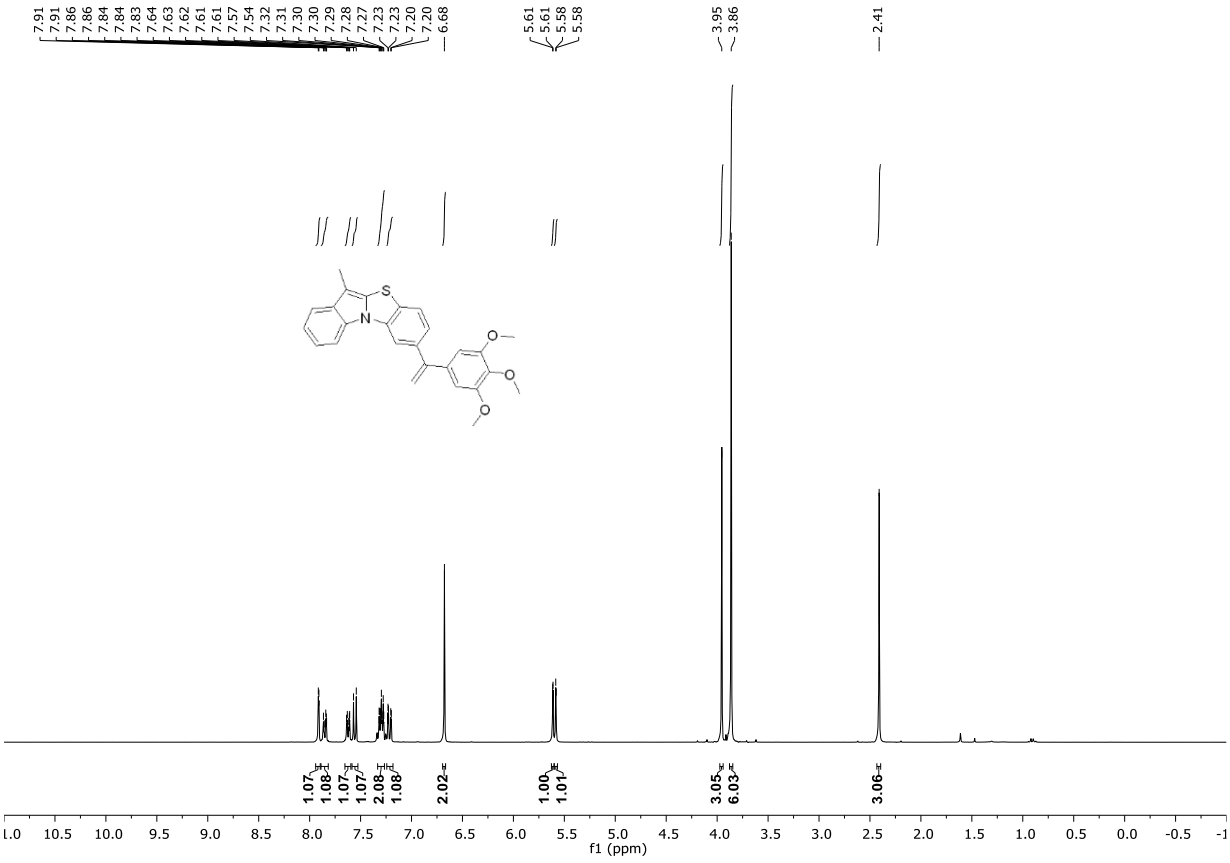
^{1}H NMR (300 MHz, $CDCl_3$) of 4ah



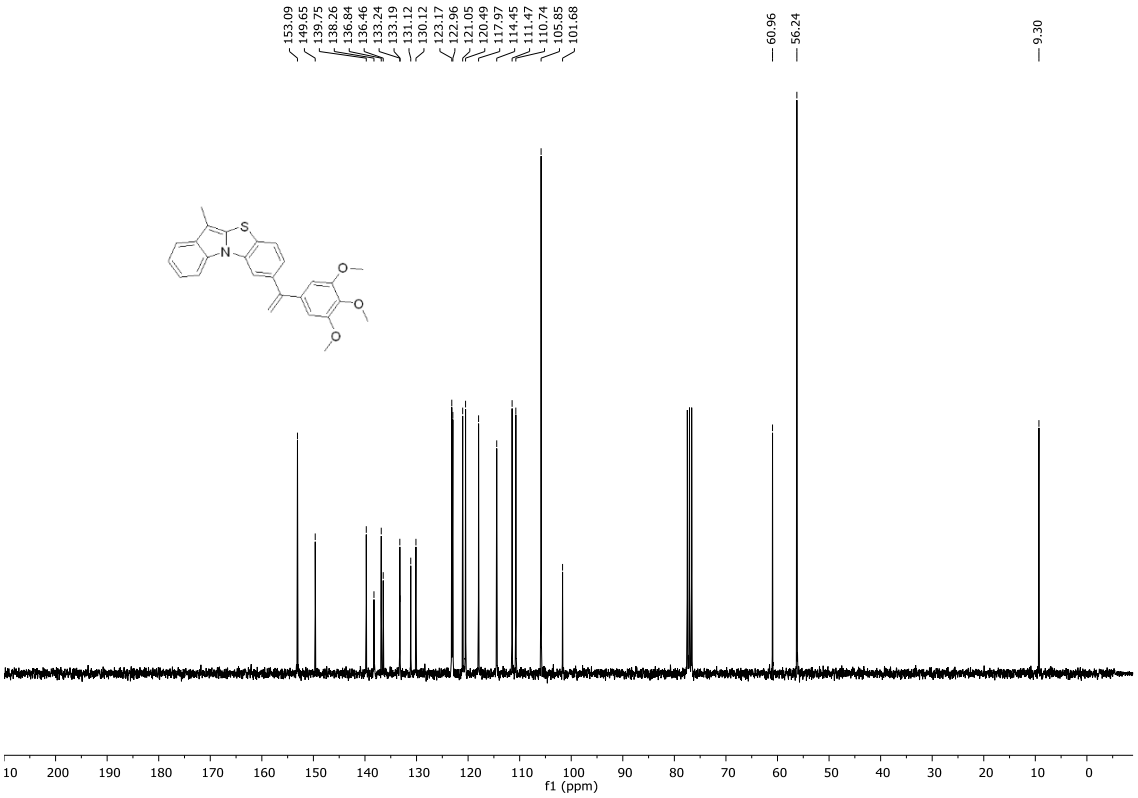
^{13}C NMR (75 MHz, $CDCl_3$) of 4ah



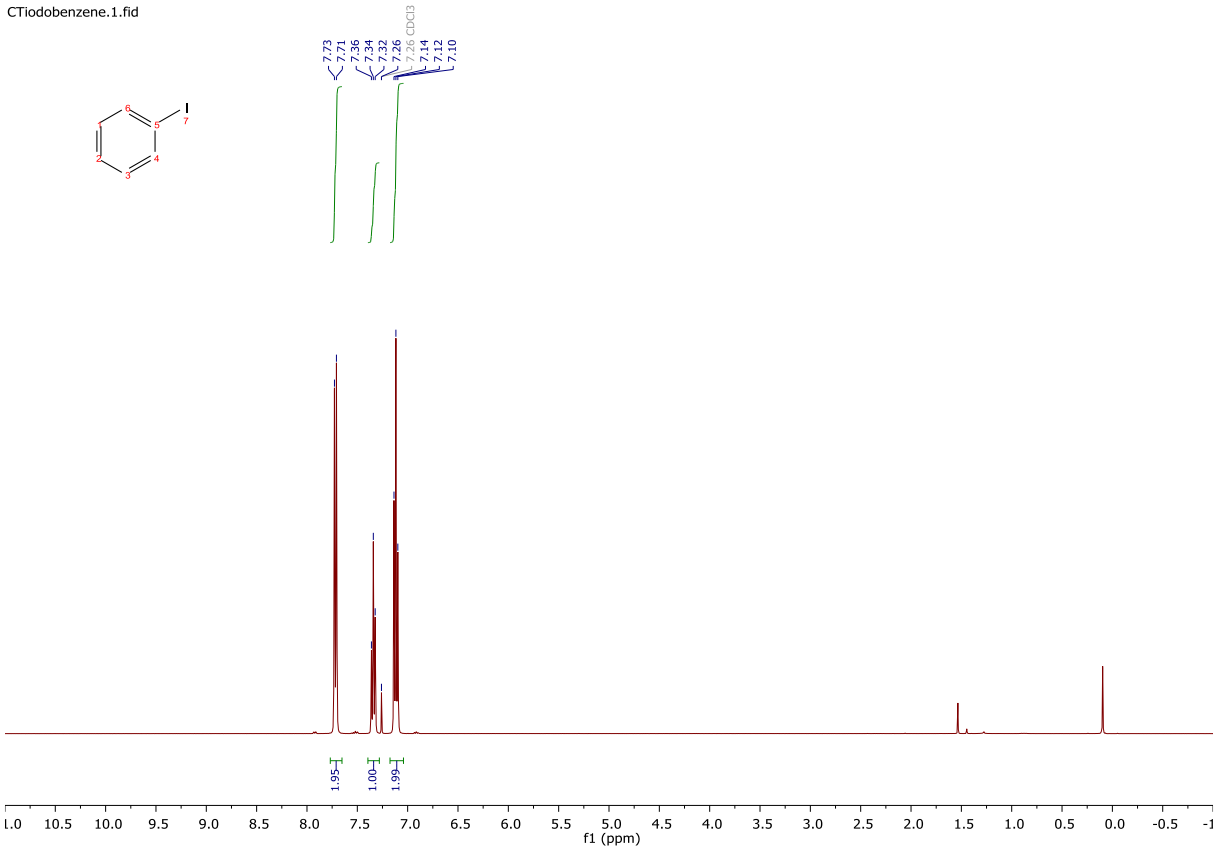
^{1}H NMR (300 MHz, $CDCl_3$) of 5a



^{13}C NMR (75 MHz, $CDCl_3$) of 5a



^{1}H NMR (400 MHz, $CDCl_3$) of iodobenzene



^{13}C NMR (101 MHz, $CDCl_3$) of iodobenzene