A convenient eco-friendly system for the synthesis of 5-sulfenyl tetrazole derivatives of indoles and pyrroles employing $CeCl_3.7H_2O$ in PEG-400

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Supplementary Information

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Synthetic Procedures

General procedure for the synthesis of 1-methyl-1*H*-indoles (1a-d)[1]

Indole (10 mmol) was transferred to a 100 mL round bottom flask and dissolved in DMF (30 mL). The solution was stirred and cooled to 0 ºC, powdered KOH (0.84 g, 15 mmol) was added during 15 min., followed by MeI (0.74 mL, 12 mmol). The solution was warmed to room temperature and stirring continued until complete consumption of the starting material was verified by TLC (3 h). Then, water was added (50 mL) and the product was extracted with EtOAc (3 × 30 mL). The combined organic phases were successively washed with water (2 × 30 mL) and brine (30 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography, eluting with hexanes.

1-Methyl-1*H*-indole (1a)[2]

Yellow oil; yield: 92%. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.62 (d, *J* = 8.0, 1H), 7.29 (d, *J* = 8.0, 1H), 7.24-7.05 (m, 2H), 7.0 (d, *J* = 3.1, 1H), 6.47 (d, *J* = 3.1, 1H) and 3.71 (s, 3H).

1-Methyl-5-bromo-1*H*-indole (1b)[3]

Beige solid, m.p.: 39-40 °C (Lit.:[4] 42-43 °C); yield: 90%. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.73 (d, *J* = 1.5, 1H), 7.28 (dd, *J* = 8.7 and 1.5, 1H), 7.15 (d, *J* = 8.7, 1H), 7.02 (d, *J* = 2.9, 1H), 6.40 (d, *J* = 2.9, 1H) and 3.74 (s, 3H).

1-Methyl-5-methoxy-1*H*-indole (1c)

White solid, m.p.: 83-85 °C (Lit.:[3] 84 °C); yield: 97%. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.21 (d, *J* = 8.9, 1H), 7.09 (d, *J* = 2.4, 1H), 7.01 (d, *J* = 2.4, 1H), 6.88 (dd, *J* = 8.8 and 2.4, 1H), 6.39 (d, *J* = 2.4, 1H), 3.84 (s, 3H) and 3.75 (s, 1H).

1-Methyl-5-(*p*-tolyl)1*H*-indole (1d)

White solid, m.p.:161-162 °C; yield: 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (s, 1H), 7.53 (d, *J* = 7.9, 2H), 7.44 (d, *J* = 8.5, 1H), 7.32 (d, *J* = 8.5, 1H), 7.22 (d, *J* = 7.9, 2H), 7.01 (d, *J* = 2.8, 1H), 6.50 (d, *J* = 2.8, 1H), 3.74 (s, 3H) and 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.8, 136.2, 135.8, 132.8, 129.3, 129.0, 127.2, 121.3, 119.1, 109.3, 101.3, 32.8 and 21.0. IR (KBr, ν): 3447, 3424, 3102, 3053, 3020, 2915, 2695, 2667, 2536, 1617, 1513, 1476, 1364, 1304, 1239, 1035 and 801 cm^{-1}. EI-MS (*m/z*, rel. int., %): 222 [$(M+1)^+$, 18], 221 (M^+, 100), 220 (34), 204 (11), 110 (10). Anal. Calc.: C, 86.84; H, 6.83. Found: C, 86.37; H, 6.97.

General procedure for the synthesis of 1-aryl-1*H*-indoles (1e-g)[5]

Indole (10 mmol), K_2CO_3 (1.93 g, 14 mmol), CuI (0.38 g, 2 mmol) and L-proline (0.23 g, 2 mmol) were transferred to a round bottom flask containing DMSO (10 mL). The mixture was stirred at ambient temperature for 20 minutes when iodobenzene (1.56 mL, 14 mmol) was added and the reaction was heated at 100 ºC for 24 h. Then, EtOAc (100 mL) was added, the mixture was filtered and the filtrate

was successively washed with water (2 × 100 mL) and brine (100 mL). The organic phase was dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified column chromatography eluting with hexanes.

1-Phenyl-1*H*-indole (1e)[6]

Yellow oil, yield: 70%. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.70-7.65 (m, 1H), 7.58-7.53 (m, 1H), 7.48-7.45 (m, 4H), 7.35-7.28 (m, 2H), 7.21-7.15 (m, 2H) and 6.66 (d, *J* = 3.3, 1H).

1-(*p*-Chlorophenyl)-1*H*-indole (1f)[7]

White solid, m.p.: 63.5-64.5 °C (Lit.:[8] 64-66 °C); yield: 65%. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.71-7.67 (m, 1H), 7.54-7.41 (m, 5H), 7.30-7.13 (m, 3H), 6.69 (dd, *J* = 3.3 and 0.7, 1H). EI-MS (*m/z*, rel. Int., %): 229 [$(M+2)^+$, 34], 228 [$(M+1)^+$, 17] and 227 (M^+, 100).

1-(*p*-Methoxyphenyl)-1*H*-indole (1g)[6]

White solid, m.p.: 56-57 °C (Lit.:[8] 57-58 °C), yield: 75%. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.70-7.66 (m, 1H), 7.48-7.37 (m, 3H), 7.28 (d, *J* = 3.2, 1H), 7.21-7.14 (m, 2H), 7.03 (d, *J* = 9.0, 2H), 6.65 (d, *J* = 3.2, 1H) and 3.88 (s, 3H). EI-MS (*m/z*, rel. Int., %): 224 [$(M+1)^+$, 17], 223 (M^+, 100), 208 (68), 180 (20) and 152 (14).

1-(n-Octyl)-1*H*-indole (1h)[2b,9]

A solution of indole (0.468 g, 4 mmol) in acetone (20 mL) was cooled to 0 ºC and then treated with powdered KOH (1.12 g, 20 mmol). After stirring 30 minutes at this temperature octyl bromide (1.39 mL, 8 mmol) was added dropwise. The mixture was allowed to attain room temperature and stirred for another 18 h. Then, water (30 mL) was added and the product extracted with EtOAc (50 mL). The organic phase was washed with brine (30 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography eluting with hexane, to afford **1h** (830 mg, 90%), as a yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.62 (d, *J* = 7.6, 1H), 7.34 (d, *J* = 8.1, 1H), 7.23-7.05 (m, 3H), 6.48 (d, *J* = 2.8, 1H), 4.09 (t, *J* = 7.1, 2H), 1.88-1.75 (m, 2H), 1.35-1.20 (m, 10H) and 0.87 (t, *J* = 6.4, 3H).

5-(*p*-Tolyl)-1*H*-indole (1l)[10]

5-Bromoindole (**1j**, 2.0 g, 10.2 mmol), $Pd(PPh_3)_4$ (1.17 g, 10 mol%) and toluene (20 mL) were successively added to a round bottom flask and the stirred mixture was treated with a solution of *p*-toluenеboronic acid (2.08 g, 15.2 mmol) in EtOH (10 mL) and saturated $NaHCO_3$ (6 mL) under argon. The reaction was heated to reflux for 24 h, when the system was cooled to room temperature, treated with brine (10 mL) and extracted with EtOAc (2 × 30 mL). The organic phase was washed with water (30 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography to give **1l** (1.56 g, 74%), as a beige solid, m.p.: 75.7-76.5 °C (Lit.:[11] 78-79 °C). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.97 (bs, 1H), 7.83 (s, 1H), 7.54 (d, *J* = 8.0, 2H), 7.43 (dd, *J* = 8.5 and 1.5, 1H), 7.34 (d, *J* = 8.5, 1H), 7.24 (d, *J* = 8.0, 2H), 7.14-7.11 (m, 1H), 6.57-7.55 (m, 1H) and

2.38 (s, 3H).

2-Methyl-1*H*-indole (1m)[12]

A mixture of phenyl hydrazine (2.16 g, 20 mmol), acetone (20 mL) and AcOH (6 drops) in EtOH (20 mL) was heated to reflux for 6 h. After cooling, the organic solvent was removed and the residue was partitioned between H_2O (50 mL) and EtOAc (2 × 50 mL). The combined organic phases were dried with $MgSO_4$ and concentrated under reduced pressure. The resulting hydrazone was treated dropwise with polyphosphoric acid until the color changed from red to black (10 mL). When the reaction began to give off gas, it was neutralized with 1M NaOH until a clear solution. The reaction was diluted with brine (50 mL) and the product was extracted with EtOAc (2 × 50 mL). The combined organic phases were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified chromatographically, affording **1m** (1.89 g, 72%), as a brown solid, m.p.: 51-53 °C (Lit.:[13] 52 °C). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.69 (bs, 1H), 7.52-7.48 (m, 1H), 7.23-7.01 (m, 3H), 6.18 (s, 1H), 2.36 (s, 3H).

1*H*-Indole-5-carbonitrile (1n)

A mixture of 5-bromoindole (**1b**, 980 mg, 5 mmol), CuCN (600 mg, 6.5 mmol) and NMP (5 mL) was submitted to microwave irradiation (200 °C, 100-180 W) during 15 min. After attaining room temperature, the reaction mixture was diluted with EtOAc (30 mL) and filtered under reduced pressure. The filtrate was washed with water (3 × 20 mL), dried (MgSO4) and concentrated under reduced pressure. The residue was chromatographed, affording **1n** (530 mg, 75%), as a beige solid, m.p.: 102.0-103.0°C (Lit.:[14] 102-104 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.90 (bs, 1H), 7.99 (s, 1H), 7.50-7.33 (m, 3H) and 6.62 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 137.5, 127.6, 126.6, 126.3, 124.7, 120.9, 112.0, 103.2 and 102.4. EI-MS (*m/z*, rel. int., %): 143 [$(M+1)^+$, 12], 142 (M^+, 100), 115 (51), 88 (14), 71 (8).

General procedure for the synthesis of 3-thiocyanato-1*H*-indoles (2a-n) and 3-thiocyanato-1-aryl-pyrroles (5a-c).[15]

A magnetically stirred mixture of indole (1 mmol) and ammonium thiocyanate (0.114 g, 15 mmol) in MeOH (10 mL) was treated with oxone (0.921 g, 1.5 mmol). The reaction was maintained at room temperature until complete consumption of the starting material (TLC). Water was added (30 mL) and the product was extracted with EtOAc (3 × 10 mL). The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. The product was purified by column chromatography eluting with hexane-EtOAc (90:10).

1-Methyl-3-thiocyanato-1*H*-indole (2a)

Reaction Time: 1 h. White solid, m.p.: 83.7-84.7°C (Lit.:[16] 83-84°C); yield: 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (d, *J* = 7.5, 1H), 7.33-7.25 (m, 4H) and 3.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.1, 134.9, 128.3, 123.3, 121.4, 118.7, 111.7, 110.1, 90.0 and 33.2. EI-MS (*m/z*, rel. int., %): 188 (M^+, 13), 187 (100), 172 (19), 154 (28), 130 (5), 93 (10) and 77 (17).

5-Bromo-1-methyl-3-thiocyanato-1*H*-indole (2b)

Reaction Time: 1 h. White solid, m.p.: 137.9-138.9°C; yield: 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87 (d, *J* = 1.6, 1H), 7.39-7.37 (m, 2H), 7.20 (d, *J* = 8.7, 1H) and 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.0, 135.8, 130.0, 126.4, 121.4, 115.2, 111.7, 111.3, 90.0 and 33.5. IR (KBr, ν): 3100, 2360, 2148, 1507, 1463, 1243, 1142, 880, 801, 791 and 611 cm^{-1}. EI-MS (*m/z*, rel. int., %): 267 [$(M+2)^+$, 45], 266 [$(M+1)^+$, 7], 250 (M^+, 42), 240 (9) and 187 (100). Anal. Calc.: C, 44.96; H, 2.64. Found: C, 44.97; H, 2.80.

5-Methoxy-1-methyl-3-thiocyanato-1*H*-indole (2c)

Reaction Time: 0.5 h. White solid, m.p.: 78.5-79.2 °C; yield: 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 (s, 1H), 7.23 (d, *J* = 8.9, 1H), 7.17 (d, *J* = 2.4, 1H), 6.96 (dd, *J* = 8.9 and 2.4, 1H), 3.90 (s, 3H) and 3.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.7, 135.2, 132.2, 129.2, 114.0, 111.8, 111.1, 100.1, 89.0, 55.8 and 33.5. IR (KBr, ν): 3444, 3109, 3003, 2949, 2936, 2829, 2147, 1621, 1509, 1488, 1449, 1289, 1246, 1036, 863, 823, 793, 673 and 626 cm^{-1}. EI-MS (*m/z*, rel. int., %): 220 [$(M+2)^+$, 6], 219 [$(M+1)^+$, 14], 218 (M^+, 100), 203 (74), 175 (41) and 160 (5). Anal. Calc.: C, 60.53; H, 4.62. Found: C, 60.18; H,4.52.

1-Methyl-3-thiocyanato-5-(*p*-tolyl)-1*H*-indole (2d)

Reaction Time: 1 h. White solid, m.p.: 130.0-131.8 °C; yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (d, *J* = 1.6, 1H), 7.57 (d, *J* = 8.1, 2H), 7.53 (dd, *J* = 8.6 and 1.6, 1H), 7.32 (d, *J* = 8.6, 1H), 7.29-7.25 (m, 3H), 3.68 (s, 3H) and 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.5, 136.6, 136.5, 135.4, 135.1, 129.5, 128.9, 127.2, 123.0, 116.8, 111.7, 110.4, 90.0, 33.3, 21.0. IR (KBr, ν): 3443, 3104, 2143, 1624, 1510, 1476, 1237, 1114, 798, 660 and 513 cm^{-1}. EI-MS (*m/z*, rel. int., %): 280 [$(M+2)^+$, 6], 279 [$(M+1)^+$, 20], 278 (M^+, 100), 263 (32) and 245 (14). Anal. Calc.: C, 73.35; H, 5.07 . Found: C, 73.05; H, 5.13.

1-Phenyl-3-thiocyanato-1*H*-indole (2e)

Reaction Time: 1.5 h. Pinkish solid, m.p.: 56.5-57.5°C; Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87-7.84 (m, 1H), 7.63 (s, 1H), 7.56-7.42 (m, 6H) and 7.37-7.30 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.2, 136.6, 133.9, 129.9, 128.7, 128.0, 124.7, 124.2, 122.3, 119.2, 111.4, 111.3 and 93.3. IR (KBr, ν): 3115, 2362, 2161, 1596, 1322, 1139, 774, 752, and 698 cm^{-1}. EI-MS (*m/z*, rel. int., %): 252 [$(M+2)^+$, 6], 251 [$(M+1)^+$, 21], 250 (M^+, 100), 249 (46), 223 (14), 190 (8), 145 (10), 121 (10) and 77 (29). Anal. Calc.: C, 71.97; H, 4.03. Found: C, 71.81; H, 3.95.

1-(4-Chlorophenyl)-3-thiocyanato-1*H*-indole (2f)

Reaction Time: 0.5 h. Beige solid, m.p.: 128.0-129.4 °C; yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86-7.84 (m, 1H), 7.59 (s, 1H), 7.51 (d, *J* = 8.6, 2H), 7.47-7.44 (m, 1H) and 7.40-7.31 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.7, 136.5, 133.8, 133.5, 130.1, 128.6, 125.9, 124.4, 122.5, 119.3, 111.1, 111.0 and 94.0. IR (KBr, ν): 3449, 3445, 3421, 3386, 3128, 3058, 2153, 1903, 1653, 1589, 1505,

1450, 1315, 1226, 1201, 1085, 1008 and 833 cm^{-1}. EI-MS (*m/z*, rel. int., %): 286 [$(M+2)^+$, 38], 285 [$(M+1)^+$, 25], 284 (M^+, 100), 258 (9) and 249 (22). Anal. Calc.: C, 63.27; H, 3.19. Found: C, 63.13; H, 3.21.

1-(4-Methoxyphenyl)-3-thiocyanato-1*H*-indole (2g)

Reaction Time: 1 h. White solid, m.p.: 95.5-96.0 °C; yield: 85%. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.84-7.82 (m, 1H), 7.54 (s, 1H), 7.41-7.38 (m, 1H), 7.34-7.26 (m, 4H), 7.02 (d, *J* = 8.99, 2H) and 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.2, 137.1, 134.2, 131.0, 128.4, 126.2, 123.9, 122.1, 119.0, 114.9, 111.3, 111.3, 92.4 and 55.6. IR (KBr, ν): 3445, 3132, 2949, 2925, 2900, 2829, 2153, 1657, 1608, 1590, 1519, 1511, 1509, 1451, 1291, 1248, 1231, 1177, 1165, 1032, 837 and 745 cm^{-1}. EI-MS (*m/z*, rel. int., %): 282 [$(M+2)^+$, 7], 281[$(M+1)^+$, 17], 280 (M^+, 100), 265 (25), 247 (14) and 222 (25). Anal. Calc.: C, 68.55; H, 4.31. Found: C, 68.43, H, 4.34.

1-Octyl-3-thiocyanato-1*H*-indole (2h)

Reaction Time: 2 h. Orange oil, yield: 95%. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.79-7.77 (m, 1H), 7.40 (s, 1H), 7.39-7.37 (m, 1H), 7.33-7.26 (m, 2H), 4.08 (t, *J* = 7.2, 2H), 1.84-1.81 (m, 2H), 1.30-1.25 (m, 10H) and 0.86 (t, *J* = 6.9, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.5, 133.9, 128.5, 123.2, 121.4, 119.0, 111.7, 110.3, 89.8, 47.0, 31.7, 29.9, 29.0, 29.0, 26.8, 22.5 and 14.0. IR (film, ν): 2927, 2360, 2155, 1508, 1458, 1165, 1013 and 742 cm^{-1}. EI-MS (*m/z*, rel. int., %): 288 [$(M+2)^+$, 7], 287 [$(M+1)^+$, 21], 286 (M^+, 100), 253 (33), 229 (19), 187 (85), 174 (20), 155 (40), 130 (38) and 77 (7). Anal. Calc.: C, 71.28; H, 7.74. Found: C, 71.46; H, 7.77.

3-Thiocyanato-1*H*-indole (2i)

Reaction Time: 1 h. Ligh brown solid, m.p.: 73-74°C (Lit.:[14] 72-73°C); yield: 93%. ^1H NMR (400 MHz, $CDCl_3$) δ: 8.69 (bs, 1H), 7.79-7.77 (m, 1H), 7.44 (d, *J* = 2.5, 1H), 7.40-7.38 (m, 1H) and 7.30-7.27 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.0, 131.0, 127.6, 123.7, 121.8, 118.5, 112.1 (2C) and 91.7. EI-MS (*m/z*, rel. int., %): 174 (M^+, 100), 148 (19), 142 (47), 120 (15), 116 (10) and 77 (18).

5-Bromo-3-thiocyanato-1*H*-indole (2j)

Reaction Time: 1 h. White solid, m.p.: 135-137 °C (Lit.:[15] 139-141 ºC); yield: 87%. ^1H NMR (400 MHz, DMSO-d_6) δ: 12.13 (s, 1H), 8.01 (d, *J* = 1.9, 1H), 7.80 (d, *J* = 1.8, 1H), 7.51 (d, *J* = 8.6, 1H) and 7.39 (dd, *J* = 8.6 and 1.9, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 134.9, 134.3, 129.0, 125.4, 120.0, 114.7, 113.6, 111.7 and 89.2. EI-MS (*m/z*, rel. int., %): 253 [$(M+2)^+$, 46], 252 [$(M+1)^+$, 5], 251 (M^+, 45), 172 (100), 145 (21), 129 (24), 86 (10) and 68 (15).

5-Methoxy-3-thiocyanato-1*H*-indole (2k)

Reaction Time: 0.5 h. Beige solid, m.p.: 117-119 °C (Lit.:[14] 113-115 ºC); yield: 83%. ^1H NMR (400 MHz, $CDCl_3$) δ: 8.69 (bs, 1H), 7.42 (d, *J* = 2.9, 1H), 7.27 (d, *J* = 8.9, 1H), 7.18 (d, *J* = 2.4, 1H), 6.93 (dd, *J* = 8.9 and 2.4, 1H) and 3.90 (s, 3H). ^{13}C (100 MHz, $CDCl_3$) δ: 155.8, 131.4, 130.9, 128.5, 114.5, 113.0, 112.0, 99.9, 91.5 and 55.8.

3-Thiocyanato-5(*p*-tolyl)-1*H*-indole (2l)

Reaction Time: 2 h. Brown solid, m.p.: 148.3-152.6°C; yield: 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.70 (bs, 1H), 7.94 (s, 1H), 7.56 (d, *J* = 7.9, 2H), 7.51 (d, *J* = 8.5, 1H), 7.45 (d, *J* = 2.6, 1H), 7.42 (d, *J* = 8.5, 1H), 7.26 (d, *J* = 7.9, 2H) and 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.6, 136.7, 135.5, 135.3, 131.5, 129.5, 128.2, 127.3, 123.6, 116.7, 112.3, 111.9, 92.5 and 21.0. IR (KBr, ν): 3369, 2360, 2333, 2151, 1472, 1101, 797 and 668 cm^{-1}. EI-MS (*m/z*, rel. int., %): 266 [$(M+2)^+$, 6], 265 [$(M+1)^+$, 19], 264 (100), 249 (28), 238 (10), 231 (12), 204 (14), and 102 (14). HRMS obsd. *m/z*: 265.0802; $C_{16}H_{13}N_2S$ [$(M+H)^+$] requires *m/z*: 265.0799.

2-Methyl-3-thiocyanto-1*H*-indole (2m)

Reaction Time: 0.5 h. Beige solid, m.p.: 99-101°C (Lit.:[15] 99-101°C); yield: 90%. ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ: 8.47 (bs, 1H), 7.71-7.67 (m, 1H), 7.37-7.21 (m, 3H) and 2.58 (s, 3H). EI-MS (*m/z*, rel. int., %): 190 [$(M+2)^+$, 5], 189 [$(M+1)^+$, 14], 188 (M^+, 100), 161 (21), 155 (30), 118 (18) and 77 (18).

3-Thiocyanato-1*H*-indole-5-carbonitrile (2n)[17]

Reaction Time: 2 h. Beige solid, m.p.: 202-204 °C; yield: 95%. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.46 (s, 1H), 8.19 (d, *J* = 2.7, 1H), 8.17 (s, 1H), 7.70 (d, *J* = 8.3, 1H) and 7.62 (dd, *J* = 8.3, 1.5, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 138.0, 135.6, 127.1, 125.5, 123.1, 119.6, 114.0, 111.7, 103.3 and 91.3. IR (KBr, ν): 3276, 3194, 3112, 2222, 2155, 1617, 1424, 1339, 1246, 1096, 888, 808 and 630 cm^{-1}. EI-MS (*m/z*, rel. int., %): 201 [$(M+2)^+$, 5], 200 [$(M+1)^+$, 13], 199 (M^+, 100), 173 (16), 172 (18), 167 (27), 145 (20). Anal. Calc.: C, 60.29; H, 2.53. Found: C, 60.29; H, 2.87.

1-Phenyl-2-thiocyanato-1*H*-pyrrole (5a)

Reaction Time: 2 h. Beige solid, m.p.: 92.8 °C (Lit.:[18] 92.8 ºC); yield: 89%. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.53-7.46 (m, 3H), 7.42-7.37 (m, 2H), 7.11 (dd, *J* = 3.0 and 1.9, 1H), 6.84 (dd, *J* = 3.8 and 1.9, 1H), 6.37 (dd, *J* = 3.8 and 3.0, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 138.3, 129.3, 128.9, 128.6, 126.6, 122.6, 110.7, 110.5 and 106.6. IR (KBr, ν): 3124, 2152, 1593, 1492, 1442, 1319, 1084, 771, 737 and 694 cm^{-1}. EI-MS (*m/z*, rel. int., %): 202 [$(M+2)^+$, 5], 201 [$(M+1)^+$, 15], 200 (M^+, 100), 173 (30) and 155 (8).

1-(4-Methoxyphenyl)-2-thiocyanato-1*H*-pyrrole (5b)

Reaction Time: 0.5 h. White solid, m.p.: 60-61 ºC (Lit.:[18] 60.3-60.9 ºC); yield: 92%. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.30 (d, *J* = 8.9, 2H), 7.06 (dd, *J* = 3.0 and 1.8, 1H), 7.01 (d, *J* = 8.9, 2H), 6.80 (dd, *J* = 3.8 and 1.8, 1H), 6.33 (dd, *J* = 3.8 and 3.0, 1H) and 3.87 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 159.6, 131.1, 129.1, 127.9, 122.0, 114.3, 110.8, 110.2, 106.9 and 55.5. IR (KBr, ν): 3120, 2152, 1609, 1516, 1524, 1026, 837 and 744 cm^{-1}. EI-MS (*m/z*, rel. Int., %): 232 [$(M+2)^+$, 6], 231 [$(M+1)^+$,15], 230 (M^+,100), 215 (18), 197 (14), 189 (8) and 172 (56).

1-(4-Chlorophenyl)-2-thiocyanato-1*H*-pyrrole (5c)

Reaction Time: 1.5 h. Beige solid, m.p.: 66 ºC (Lit.:[18] 67.4-68°C); yield: 92%. ^{1}H NMR (200 MHz,

$CDCl_3$) δ: 7.49 (d, *J* = 8.7, 2H), 7.34 (d, *J* = 8.7, 2H), 7.08 (dd, *J* = 3.1 and 1.8, 1H), 6.84 (dd, *J* = 3.8 and 1.8, 1H) and 6.37 (dd, *J* = 3.8 and 3.1, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 136.7, 134.6, 129.5, 128.8, 127.9, 122.9, 110.8, 110.5 and 107.0. IR (KBr, v): 3105, 2149, 1597, 1493, 1323, 1091, 833 and 737 cm^{-1}. EI-MS (*m/z*, rel. int., %): 236 [$(M+2)^+$, 34%], 235 [$(M+1)^+$, 19%], 234 (M^+, 100%), 199 (45%), 173 (36%), 111 (28%) and 75 (45%).

1,1'-Dimethyl-1*H*,1'*H*-2,2'-biindole (7a)[19]

A stirred solution of 1-methyl-1*H*-indole (1.31 g, 10 mmol) in Et_2O (30 mL) under argon was cooled to 0 ºC and treated dropwise with a solution of n-BuLi in hexane (2M, 14 mmol, 7 mL). The reaction was heated at reflux for 4 h, when it was allowed to come to room temperature. Anhydrous $CuCl_2$ (0.67 g, 5 mmol) was added in portions with vigorous stirring and the mixture was heated to reflux for 2 h. The reaction was cooled to room temperature, diluted with EtOAc (50 mL) and filtered through Celite. The filtrate was washed with H_2O (50 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Column chromatography of the residue, eluting with hexanes, afforded **7a** (585 mg, 45%), as a white solid, m.p.: 173.5-174.0 °C (Lit.:[19] 182-184 °C). ^1H NMR (200 MHz, $CDCl_3$) δ: 7.68 (d, *J* = 7.8, 2H), 7.39 (d, *J* = 8.0, 2H), 7.33-7.14 (m, 4H), 6.65 (s, 2H) and 3.69 (s, 6H). EI-MS (*m/z*, rel. Int., %): 261 [$(M+1)^+$, 20], 260 (M^+, 100), 245 (16) and 130 (23).

1*H*,1'*H*-2,2'-Biindole (7b)

A solution of indole (5.85 g, 50 mmol) in CH_2Cl_2 (100 mL) was treated successively pyridine (5.3 mL, 64.3 mmol), Boc_2O (14.5 g, 64.3 mmol) and DMAP (0.615 g, 5 mmol). The reaction mixture was stirred for 24 h at room temperature, when NH_4Cl (sat) (125 mL) and extracted with EtOAc (2 × 150 mL). The organic phase was dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography, eluting with mixtures of hexanes and EtOAc to give 1-Boc-1*H*-indole (8.69 g, 80%), as a colorless oil.[20] ^1H NMR (200 MHz, $CDCl_3$) δ: 1.67 (s, 9H), 6.56 (d, *J* = 3.5, 1H), 7.17-7.40 (m, 2H), 7.54- 7.56 (m, 1H), 7.60 (d, *J* = 3.5, 1H) and 8.19 (d, *J* = 8.1, 1H). A solution of diisopropylamine (3.53 g, 35 mmol) in THF (50 mL) was cooled to -30 ºC and treated dropwise with n-BuLi (2.5 M in hexane, 14.4 mL, 36 mmol). After 30 min., the temperature was lowered to -78 ºC and a solution of 1-Boc-1*H*-indole (7.595 g, 35 mmol) in THF (30 mL) was dripped into the system, which was stirred for 2 h at this temperature and then treated with CuCN (1.57 g, 17.5 mmol). The mixture was warmed to room temperature, stirred until all the solid had been dissolved, then treated with *p*- benzoquinone (5.67 g, 52.5 mmol) and stirred for another 4 h. The reaction was quenched with 2M HCl (10 mL) and the reaction mixture was extracted with EtOAc (2 × 100 mL). The combined organic phases were washed with brine (100 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Column chromatography of the residue afforded 1*H*,1'*H*-[2,2'-Biindole]-1,1'-di-*tert*-butyl dicarboxylate (5.82 g, 77%), as a white solid, m.p.: 151°C (Lit.:[21] 150-152°C). ^1H NMR (200 MHz, $CDCl_3$) δ: 1.23 (s, 18H), 6.64 (s, 2H), 7.24 (t, *J* = 7.4, 2H), 7.34 (t, *J* = 7.4, 2H), 7.56 (d, *J* = 7.4, 2H) and 8.31 (d, *J* = 7.4, 2H). F_3CCO_2H (10 mL) was added to a solution of 1*H*,1'*H*-[2,2'-Biindole]-1,1'-di-*tert*-butyl dicarboxylate (1.73 g, 4.0 mmol) in CH_2Cl_2 (60 mL) and the solution was heated under

reflux for 2 h. The system was then cooled to room temperature, treated with saturated $NaHCO_3$ (10 mL) and extracted with EtOAc (2 × 50 mL). The organic phase was washed with water (2 × 50 mL) and brine (50 mL), dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography, eluted with mixtures of hexane and ethyl acetate to give **7b** (752 mg, 81%) as a beige solid, m.p.: 290°C, dec.; (Lit.:[22] 292-294°C, dec.). ^{1}H NMR (200 MHz, DMSO-d_6) δ: 11.51 (br, s, 2H), 7.56 (d, *J* = 7.4, 2H), 7.40 (d, *J* = 7.7, 2H), 7.15-7.11 (m, 2H), 7.05-7.00 (m, 2H) and 6.95 (s, 2H).

1,1'-Diphenyl-1*H*,1'*H*-2,2'-biindole (7c)

A solution of diisopropylamine (1.01 g, 10 mmol) in THF (30 mL) was cooled to -30 ºC and treated dropwise with n-BuLi (2.5 M in hexane, 5.0 mL, 10 mmol). After 30 min., the temperature was lowered to -78 ºC and a solution of 1-phenyl-1*H*-indole (1.93 g, 10 mmol) in THF (10 mL) was dripped into the system. After stirring 2 h, CuCN (0.445 g, 5 mmol) was added, the mixture was warmed to room temperature, stirred until all the CuCN had dissolved, then treated with *p*-benzoquinone (1.62 g, 15 mmol) and stirred for another 4 h. The reaction was terminated by addition of a 2M HCl solution (10 mL) and the reaction mixture was extracted with EtOAc (2 × 30 mL). The organic phase was washed with brine (30 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography affording **7c** (481 mg, 25%), as a beige solid, m.p.: 135.5-136.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64-7.62 (m, 2H), 7.21-7.09 (m, 12H), 6.82-6.80 (m, 4H) and 6.77 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.0, 137.9, 131.8, 128.9, 128.0, 126.6, 126.4, 122.6, 120.7, 120.6, 110.5 and 107.0. IR (KBr, ν): 3441, 3430, 2361, 2338, 1595, 1497, 1451, 1374, 1320, 750, 740 and 695 cm^{-1}. EI-MS (*m/z*, rel. Int., %): 386 [$(M+2)^+$, 5], 385 [$(M+1)^+$, 28], 384 (M^+, 100) and 306 (22). Anal. Calc.: C, 87.47; H, 5.24. Found: C, 86.93; H, 4.99.

1,1'-Dibutyl-1*H*,1'*H*-2,2'-biindole (7d)[23]

NaOH (0.160 g, 4 mmol) and bromobutane (0.274 g, 2 mmol) were added to 1*H*,1'*H*-2,2'-biindole (**7b**, 0.232 g, 1 mmol), and the reaction was stirred at room temperature for 2 h. Water (20 mL) was added and the reaction products were extracted with EtOAc (3 × 20 mL). The organic extracts were washed with H_2O (3 × 20 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographically purified to afford **7d** (175 mg, 51%) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.68 (d, *J* = 7.7, 2H), 7.42 (d, *J* = 8.0, 2H), 7.31-7.23 (m, 2H), 7.20-7.12 (m, 2H), 6.62 (s, 2H), 4.08 (t, *J* = 7.4, 4H), 1.73-1.58 (m, 4H), 1.19 (sextet, *J* = 7.4, 4H) and 0.80 (t, *J* = 7.4, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.9, 131.2, 127.9, 121.9, 120.9, 119.7, 110.1, 104.6, 43.9, 32.2, 20.1 and 13.7. IR (film, ν): 3056, 2956, 2931, 2869, 1573, 1466, 1433, 1330, 1204, 1144, 749 and 728 cm^{-1}. EI-MS (*m/z*, rel. Int., %): 345 [$(M+1)^+$, 28], 344 (M^+, 100), 315 (10), 301 (33) and 184 (60). Anal. Calc.: C, 83.68; H, 8.19. Found: C, 83.38; H, 8.21.

Di(1*H*-indol-2-yl)sulfide (7e)

A solution of diisopropylamine (1.01 g, 10 mmol) in THF (30 mL) was cooled to -30 ºC and treated dropwiose with n-BuLi (2.5 M in hexane, 5.0 mL, 10 mmol). After 30 min., the temperature was

lowered to -78 ºC and a solution of *N*-Boc-indole (2.17 g , 10 mmol) in THF (10 mL) was dripped into the system, which was stirred for 2 h at this temperature and then treated portionwise with bis(phenylsulfonyl)sulfide (1.57 g, 5 mmol). The reaction was allowed to come to room temperature and stirring was continued for 24 h. AcOH (2.5 mL) and water (10 mL) were added, the system was stirred for 10 min. and extracted with EtOAc (50 mL). The organic phase was washed with saturated NH_4Cl solution (30 mL) and water (30 mL), dried ($MgSO_4$), and concentrated under reduced pressure. Chromatographic purification of the residue afforded the *N,N'*-bis-Boc derivative of **7e** (906 mg, 39%). 1M KOH (21 mL) was added to a solution of the *N,N'*-bis-Boc indole derivative of **7e** (464 mg, 1.0 mmol) in ethanol (35 mL) and the solution was heated at 90 °C for 3 h. The system was then cooled to room temperature, and extracted with EtOAc (2 × 20 mL). The combined organic phases were washed with water (2 × 20 mL) and brine (20 mL), dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography, eluted with mixtures of hexane and EtOAc to give **7e** (196 mg, 74%) as a brown solid, m.p.: 136.5-137.0 ºC (Lit.:[24] 144-146 ºC). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 11.47 (s, 2H), 7.49 (d, *J* = 7.8, 2H), 7.32 (d, *J* = 8.3, 2H), 7.14-7.06 (m, 2H), 7.03- 6.95 (m, 4H) and 6.64 (d, *J* = 1.3, 2H). EI-MS (*m/z*, rel. Int., %): 266 [$(M+2)^+$, 7], 265 [$(M+1)^+$, 21], 264 (M+, 100), 231 (29), 148 (21) and 117 (34).

General procedure for the synthesis of 3,3'-dithiocyanato-1*H*,1'*H*-2,2'-biindoles (8a-d)

A mixture of the 1*H*,1'*H*-2,2'-biindole (0.5 mmol), oxone (0.921 g, 1.5 mmol) and NH_4SCN (0.114 g, 1.5 mmol) in MeOH (5 mL) was heated to reflux until complete consumption of the starting material was assessed by TLC. Water was added (20 mL) and the reaction was extracted with EtOAc (20 mL). The organic layer was dried ($MgSO_4$), and the solvent was removed under reduced pressure. The products were purified by column chromatography.

1,1'-Dimethyl-3,3'-dithiocyanato-1*H*,1'*H*-2,2'-biindole (8a)

Reaction Time: 1 h. White solid, m.p.: 219-220.5°C; yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93 (d, *J* = 7.9, 2H), 7.55-7.49 (m, 4H), 7.46-7.43 (m, 2H) and 3.69 (s, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 137.8, 133.1, 127.9, 125.0, 122.7, 119.5, 110.8, 110.6, 95.6 and 31.8. IR (KBr, ν): 3061, 2962, 2152, 1465, 1390, 1336, 1261, 1239, 1158, 1111, 1009, 968, 795, 753 and 742 cm^{-1}. EI-MS (*m/z*, rel. Int., %): 376 [$(M+2)^+$, 5], 375 [$(M+1)^+$, 11], 374 (M^+, 47), 316 (30), 290 (28), 283 (100) and 257 (9). Anal. Calc.: C, 64.15; H, 3.77. Found: C, 63.97; H, 3.78.

3,3'-Dithiocyanato-1*H*,1'*H*-2,2'-biindole (8b)

Reaction Time: 0.5 h. Light brown solid, m.p.: 227 °C (dec.); yield: 87%. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.67 (s, 2H), 7.82 (d, *J* = 7.8, 2H), 7.64 (d, *J* = 7.9, 2H) and 7.45-7.37 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 136.4, 132.3, 127.9, 124.3, 121.8, 118.3, 112.8, 111.1 and 91.8. IR (KBr, ν): 3386, 2155, 1616, 1490, 1430, 1419, 1379, 1339, 1234, 1146, 1006, 765, 751, 746 and 636 cm^{-1}. EI-MS (*m/z*, rel. int., %): 348 [$(M+2)^+$, 11], 347 [$(M+1)^+$, 21], 346 (M^+, 85), 319 (39), 288 (30), 261 (100) and 229 (9). HRMS obsd. *m/z*: 369.0236; $C_{18}H_{10}N_4NaS_2$ [$(M+Na)^+$] requires *m/z*: 369.0245.

1,1'-Diphenyl-3,3'-dithiocyanato-1*H*,1'*H*-2,2'-biindole (8c)

Reaction Time: 1 h. Yellow solid, m.p.: 177.8-178.5 °C; yield: 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98 (d, *J* = 7.9, 2H), 7.44-7.40 (m, 2H), 7.35-7.31 (m, 2H), 7.29-7.19 (m, 8H) and 6.68 (bs, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.9, 136.0, 132.6, 129.5, 128.2, 127.9, 126.3, 125.5, 123.1, 119.6, 111.7, 109.9 and 98.6. IR (KBr, ν): 3444, 3423, 2154, 1593, 1496, 1449, 1378, 1217, 752 and 696 cm^{-1}. EI-MS (*m/z*, rel. Int., %): 500 [$(M+2)^+$, 7], 499 [$(M+1)^+$, 15], 498 (M^+, 42), 440 (30), 413 (89), 407 (15) and 380 (25). HRMS obsd. *m/z*: 521.0850; $C_{30}H_{18}N_4NaS_2$ [$(M+Na)^+$] requires *m/z*: 521.0865.

1,1'-Dibutyl-3,3'-dithiocyanato-1*H*,1'*H*-2,2'-biindole (8d)

Reaction Time: 0.75 h. White solid, m.p.: 92-92.7 °C; yield: 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, *J* = 7.8, 2H), 7.55 (d, *J* = 8.1, 2H), 7.51-7.47 (m, 2H), 7.45-7.41 (m, 2H), 4.20-4.13 (m, 2H), 3.89-3.82 (m, 2H), 1.74-1.62 (m, 4H), 1.18 (sextet, *J* = 7.2, 4H) and 0.80 (t, *J* = 7.2, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.0, 132.5, 128.1, 124.9, 122.4, 119.7, 111.3, 110.2, 95.9, 45.6, 31.8, 20.1 and 13.5. IR (KBr, ν): 3420, 2956, 2930, 2869, 2156 (SCN), 1457, 1437, 1387, 1362, 1339, 1176 and 747 cm^{-1}. EI-MS (*m/z*, rel. Int., %): 460 [$(M+2)^+$, 13], 459 [$(M+1)^+$, 31], 458 (M^+, 92), 400 (62), 373 (57), 367 (100) and 344 (12). Anal. Calc.: C, 68.09; H, 5.71. Found: C, 68.09; H, 5.89.

bis(3-Thiocyanato-1*H*-indol-2-yl)sulfide (8e)[25]

A solution of CAN (1.26 g, 2.3 mmol) in MeOH (5 mL) was added to a stirred mixture of di-(1*H*-indol-2-yl)sulfide (0.132 g, 0.5 mmol) and NH_4CN (0.228 g, 3 mmol) in MeOH (10 mL). Stirring continued for 0.5 h after formation of a light brown precipitate of the product. When complete consumption of the starting material was verified by TLC, water was added (20 mL) and the reaction was filtered under reduced pressure. The solid was washed with water (3 × 20 mL) and dried under vacuum to give **8e** (180 mg, 95%) as a light brown solid, m.p.: 234.5°C (dec.). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.38 (s, 2H), 7.67 (d, *J* = 7.6, 2H), 7.45 (d, *J* = 7.6, 2H) and 7.33-7.26 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 137.0, 132.0, 127.9, 123.9, 121.5, 117.8, 112.4, 110.9 and 95.5. IR (KBr, ν): 3278, 2923, 2160, 1579, 1402, 1346, 1231, 1152, 818, 744, 688 and 665 cm^{-1}. EI-MS (*m/z*, rel. int., %): 380 [$(M+2)^+$, 8], 379 [$(M+1)^+$, 11], 378 (M^+, 48), 320 (7), 293 (100) and 262 (61). HRMS obsd. *m/z*: 400.9923; $C_{18}H_{10}N_4NaS_3$ [$(M+Na)^+$] requires *m/z*: 400.9965.

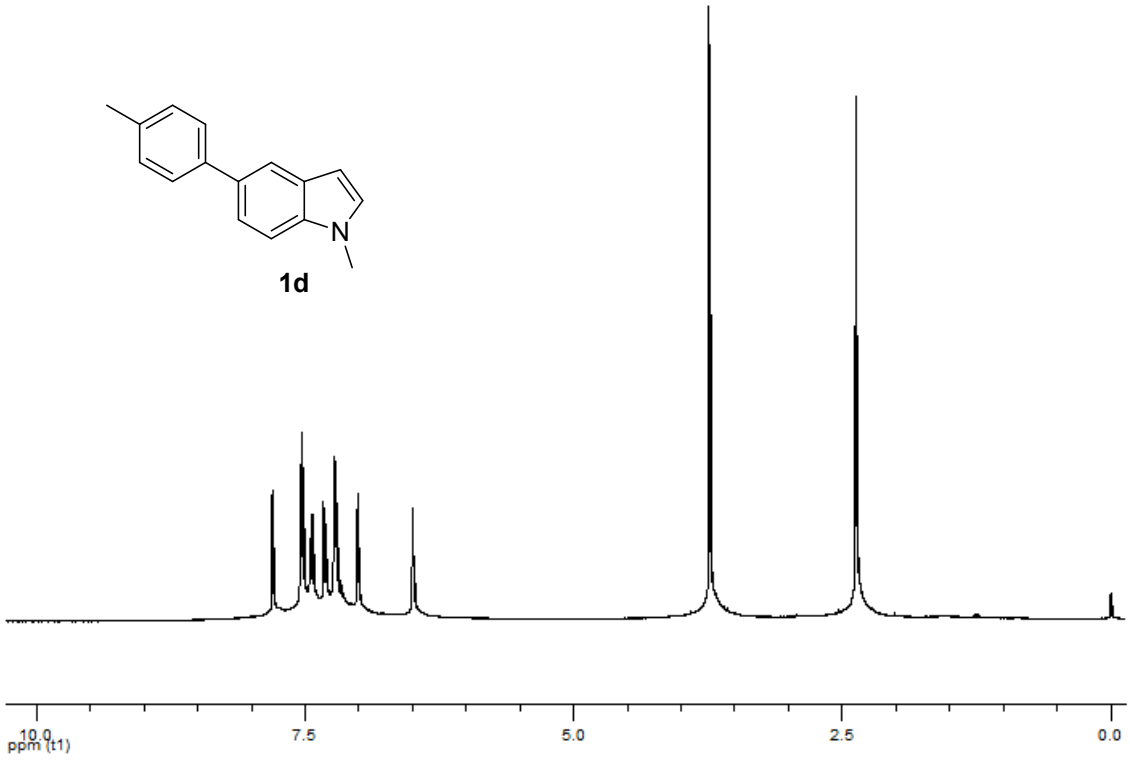

Figure S1. 400 MHz ^{1}H NMR spectrum of compound **1d** in $CDCl_3$.

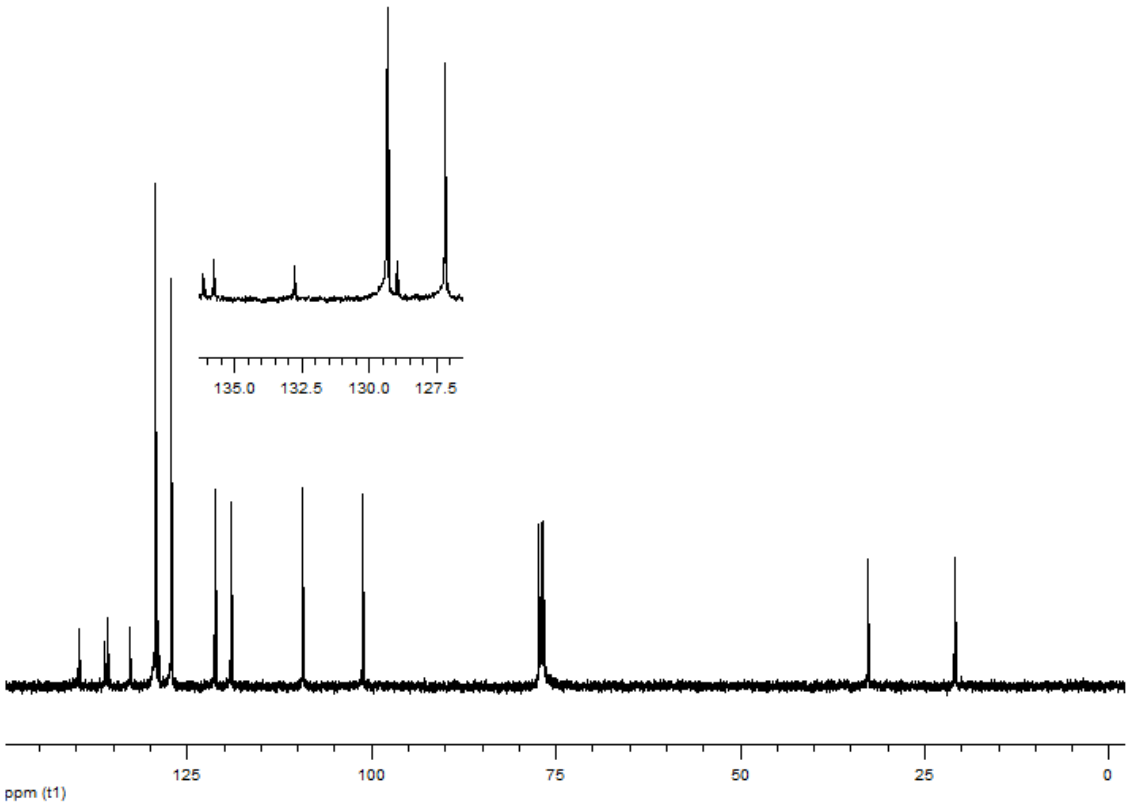

Figure S2. 100 MHz ^{13}C NMR spectrum of compound **1d** in $CDCl_3$.

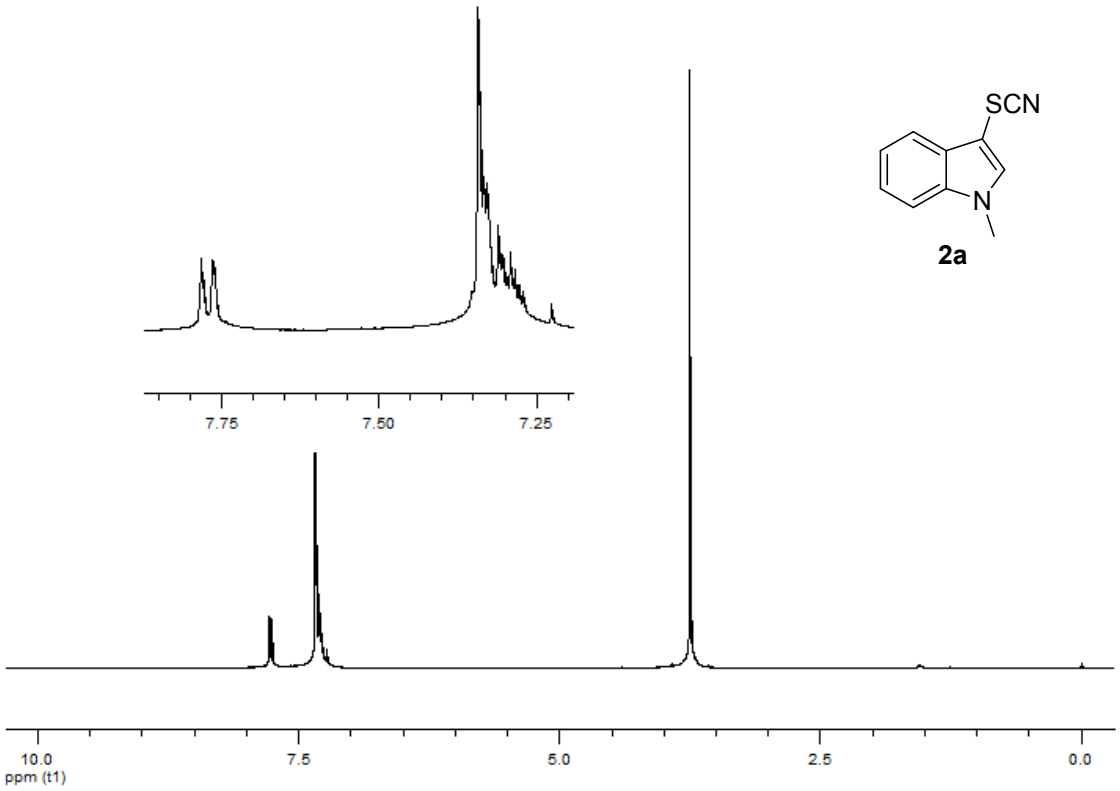

Figure S3. 400 MHz ^{1}H NMR spectrum of compound **2a** in $CDCl_3$.

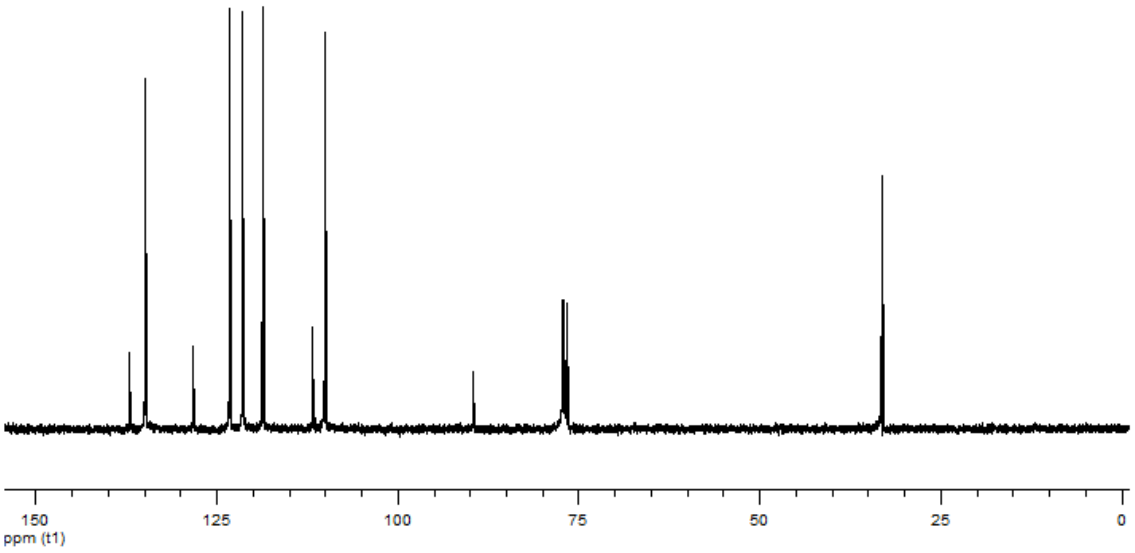

Figure S4. 100 MHz ^{13}C NMR spectrum of compound **2a** in $CDCl_3$.

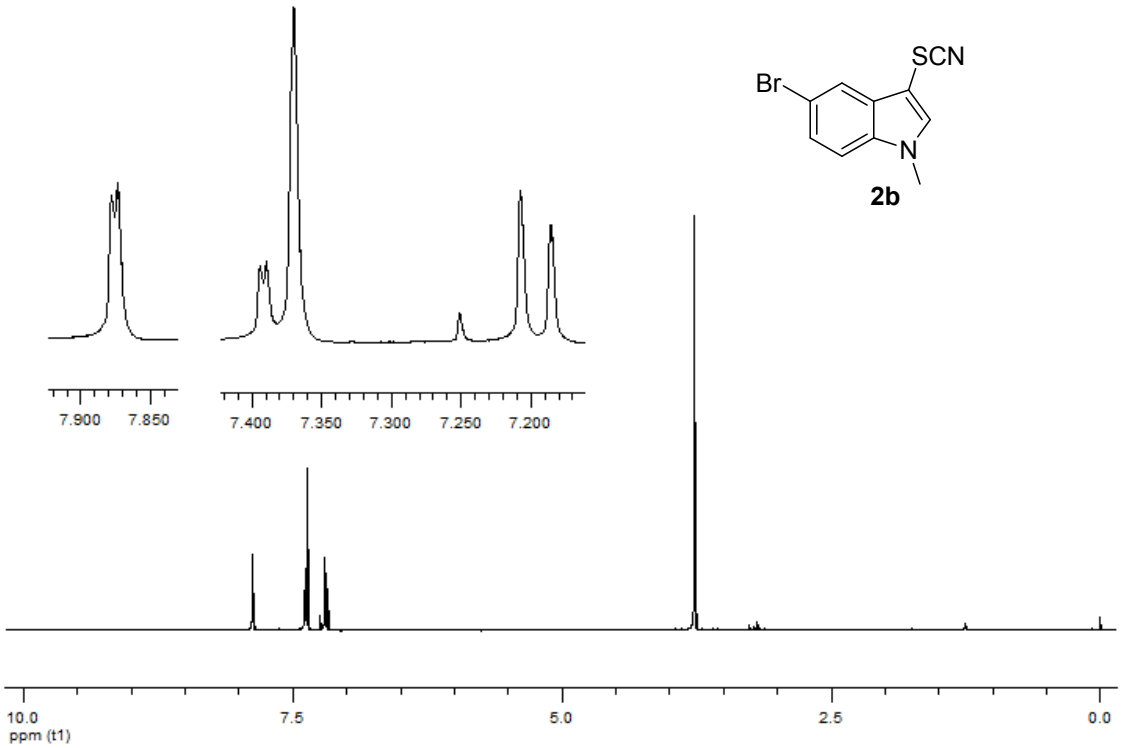

Figure S5. 400 MHz ^{1}H NMR spectrum of compound **2b** in $CDCl_3$.

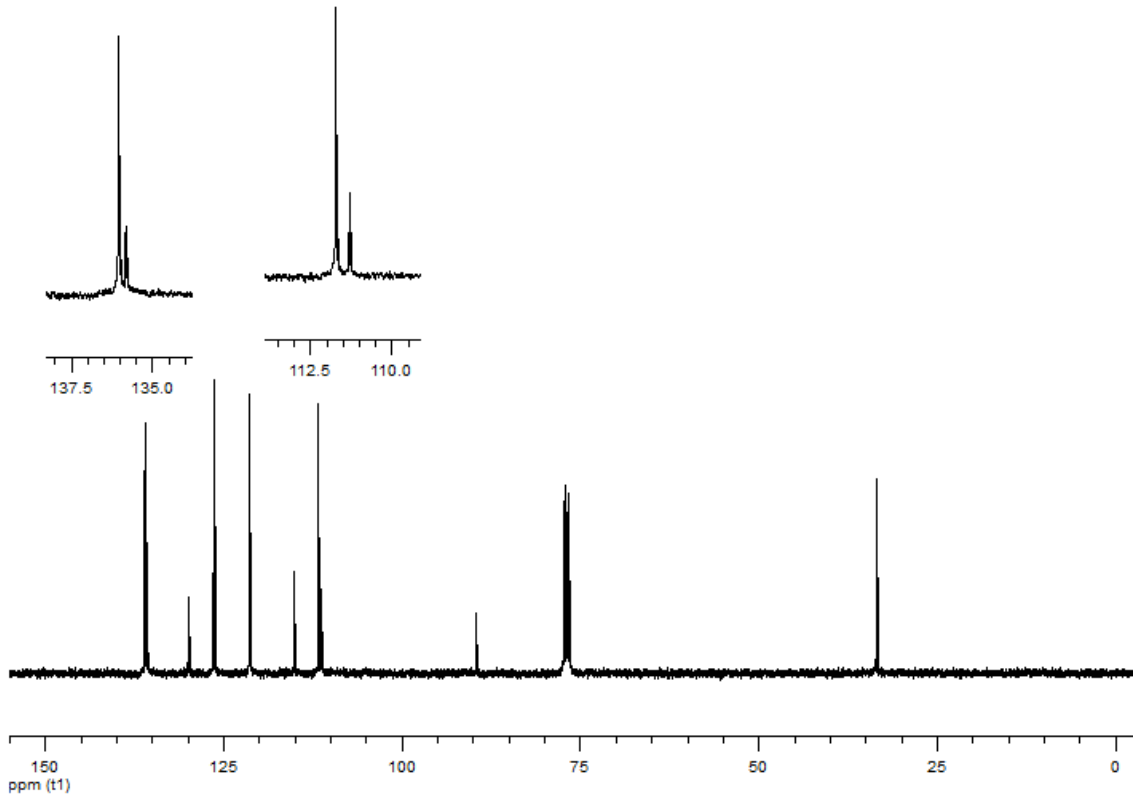

Figure S6. 100 MHz ^{13}C NMR spectrum of compound **2b** in $CDCl_3$.

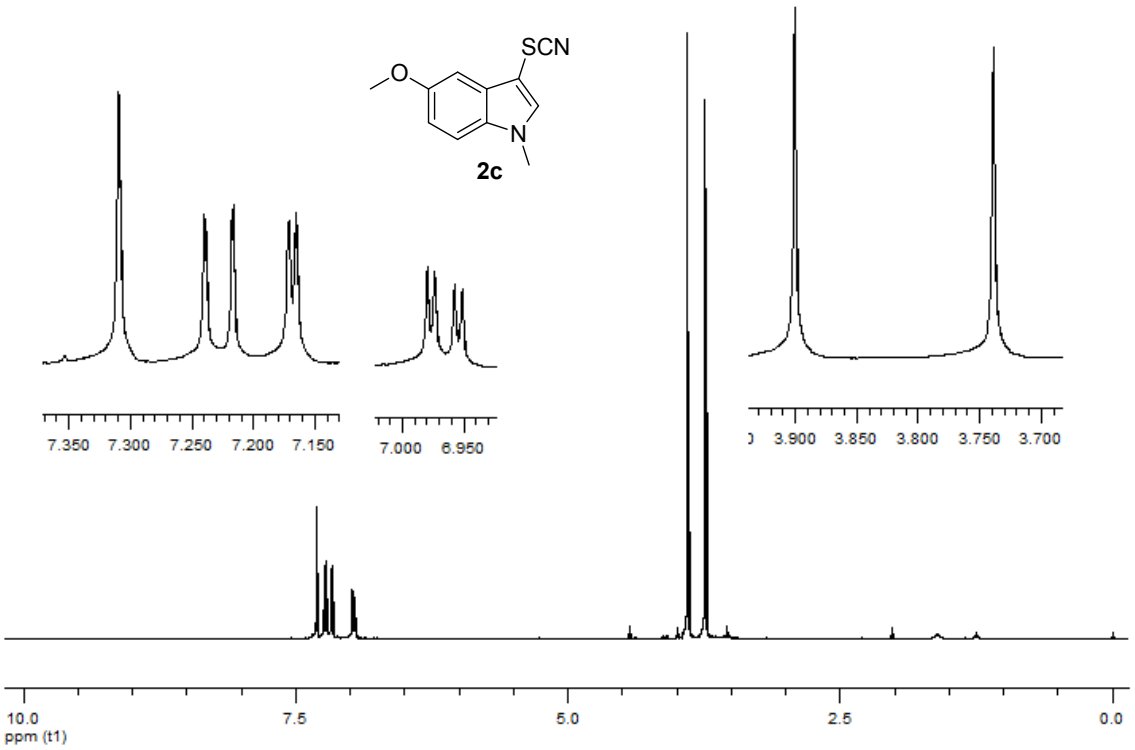

Figure S7. 400 MHz ^{1}H NMR spectrum of compound **2c** in $CDCl_3$.

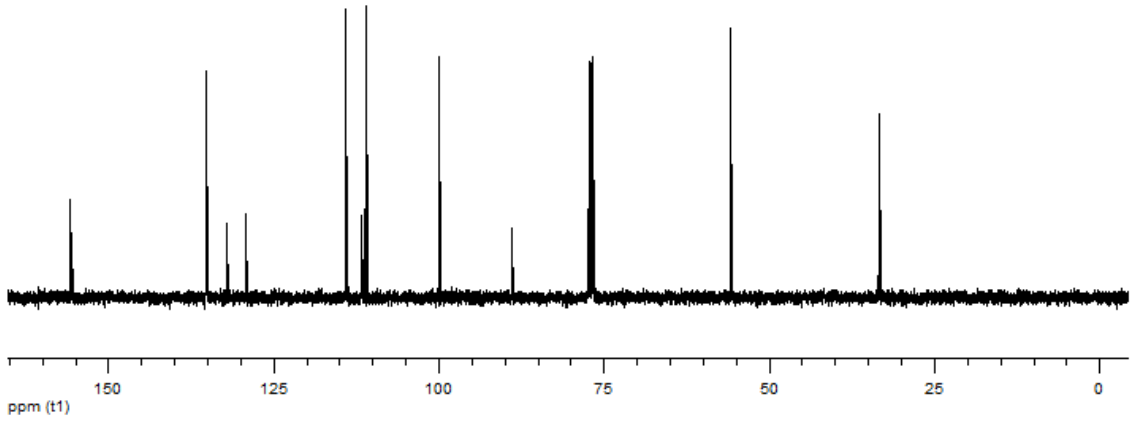

Figure S8. 100 MHz ^{13}C NMR spectrum of compound **2c** in $CDCl_3$.

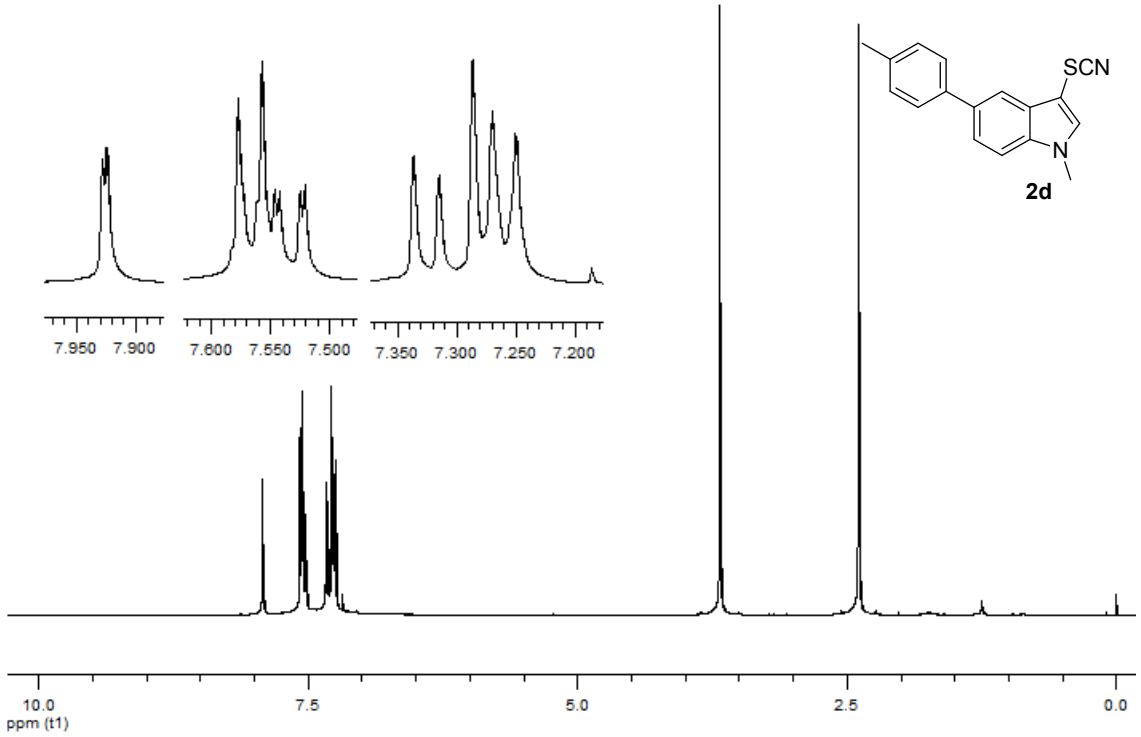

Figure S9. 400 MHz ^{1}H NMR spectrum of compound **2d** in $CDCl_3$.

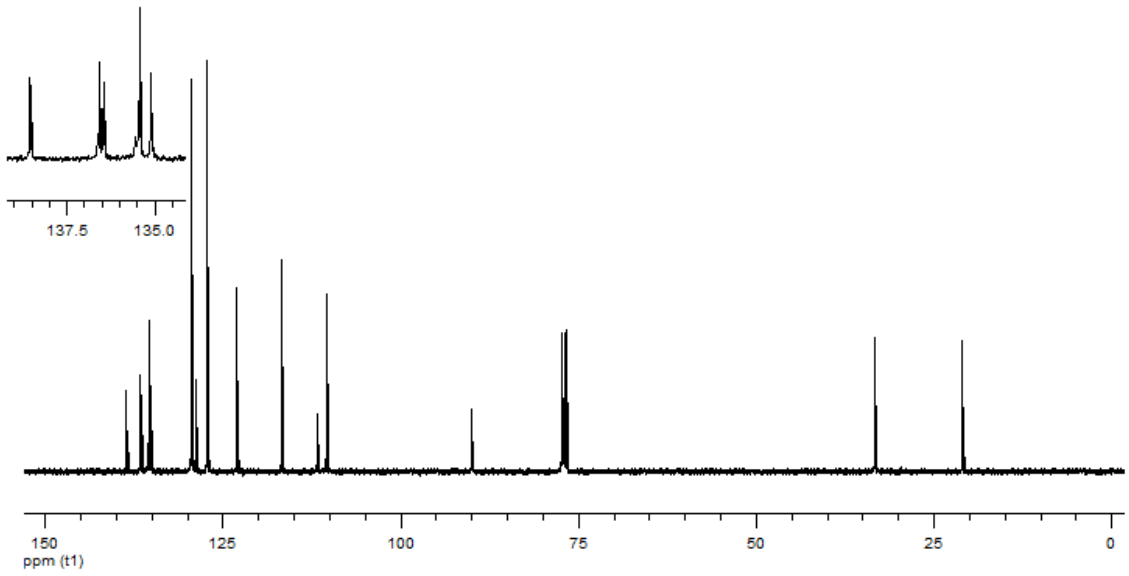

Figure S10. 100 MHz ^{13}C NMR spectrum of compound **2d** in $CDCl_3$.

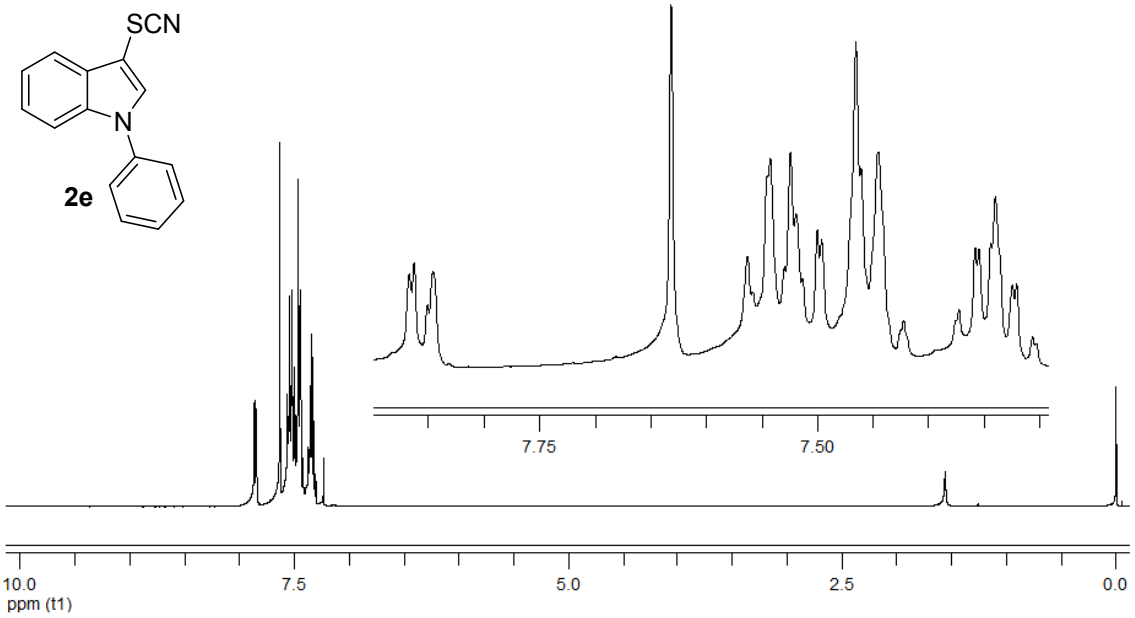

Figure S11. 400 MHz ^{1}H NMR spectrum of compound **2e** in $CDCl_3$

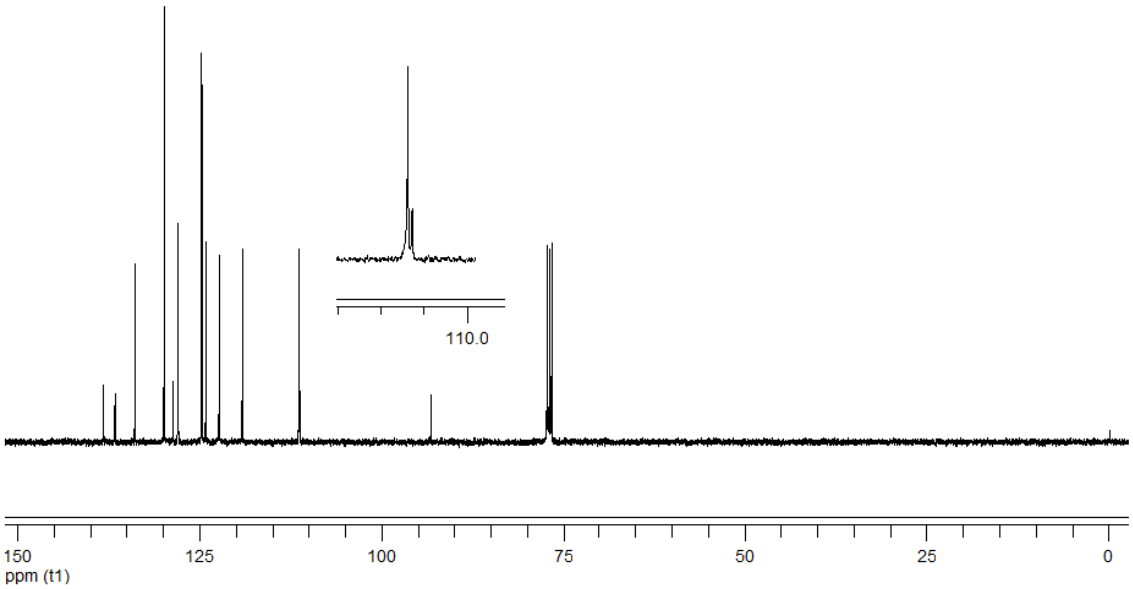

Figure S12. 100 MHz ^{13}C NMR spectrum of compound **2e** in $CDCl_3$.

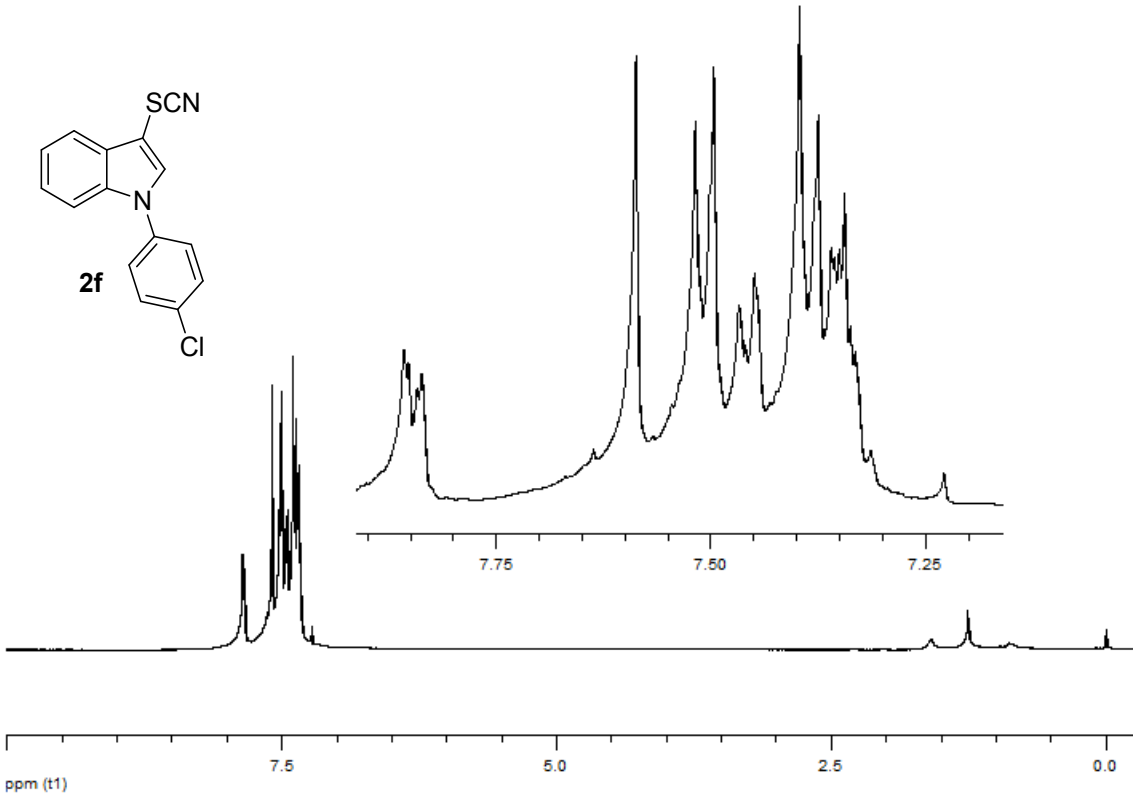

Figure S13. 400 MHz ^{1}H NMR spectrum of compound **2f** in $CDCl_3$.

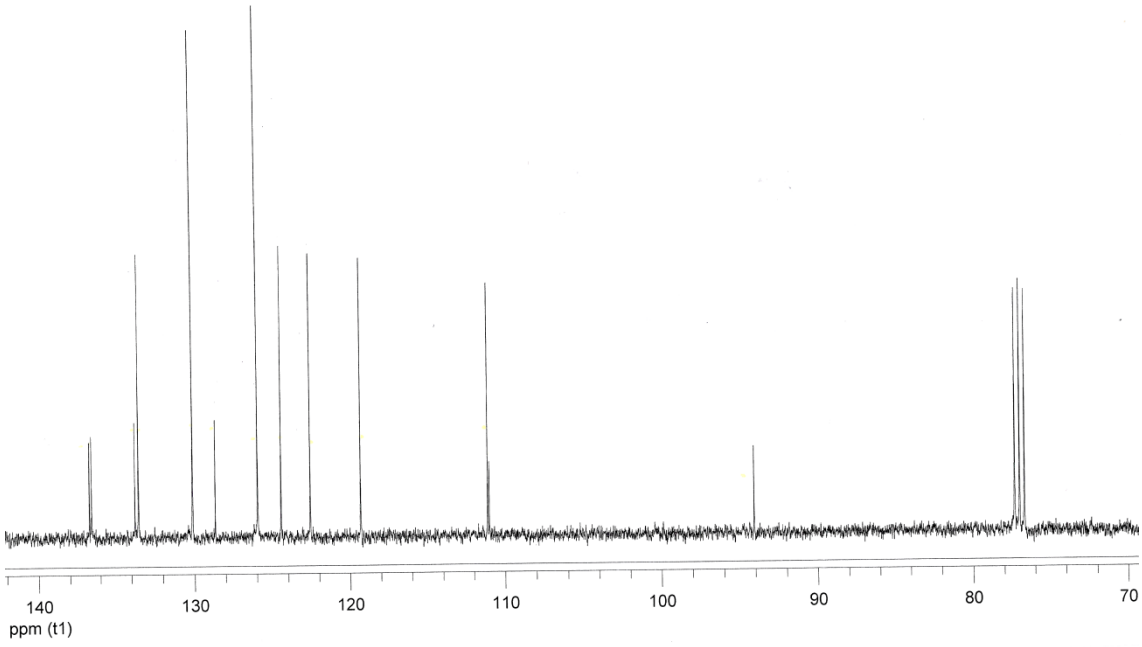

Figure S14. 100 MHz ^{13}C NMR spectrum of compound **2f** in $CDCl_3$.

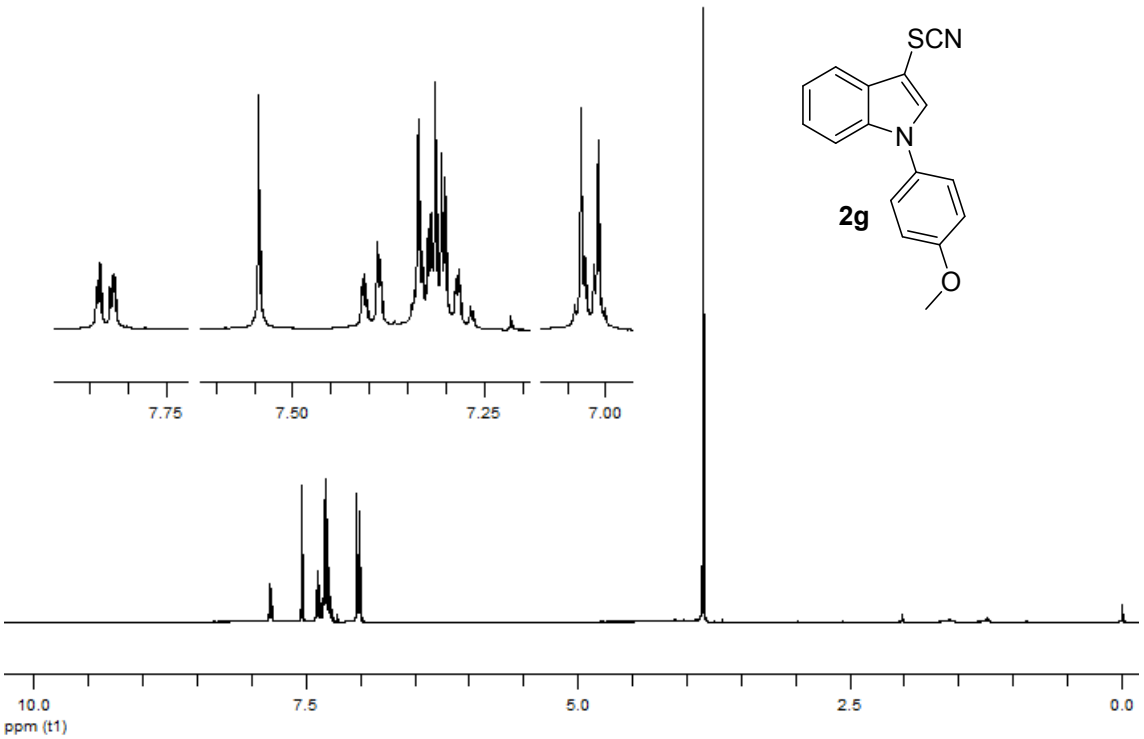

Figure S15. 400 MHz ^{1}H NMR spectrum of compound **2g** in $CDCl_3$

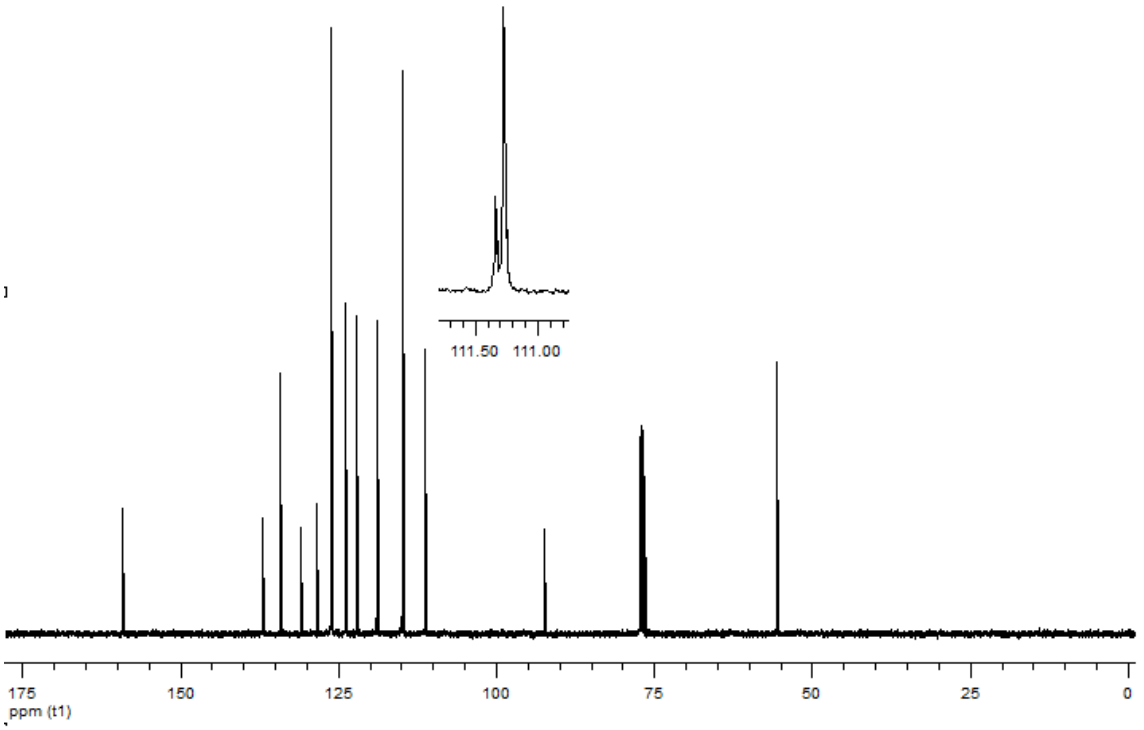

Figure S16. 100 MHz ^{13}C NMR spectrum of compound **2g** in $CDCl_3$.

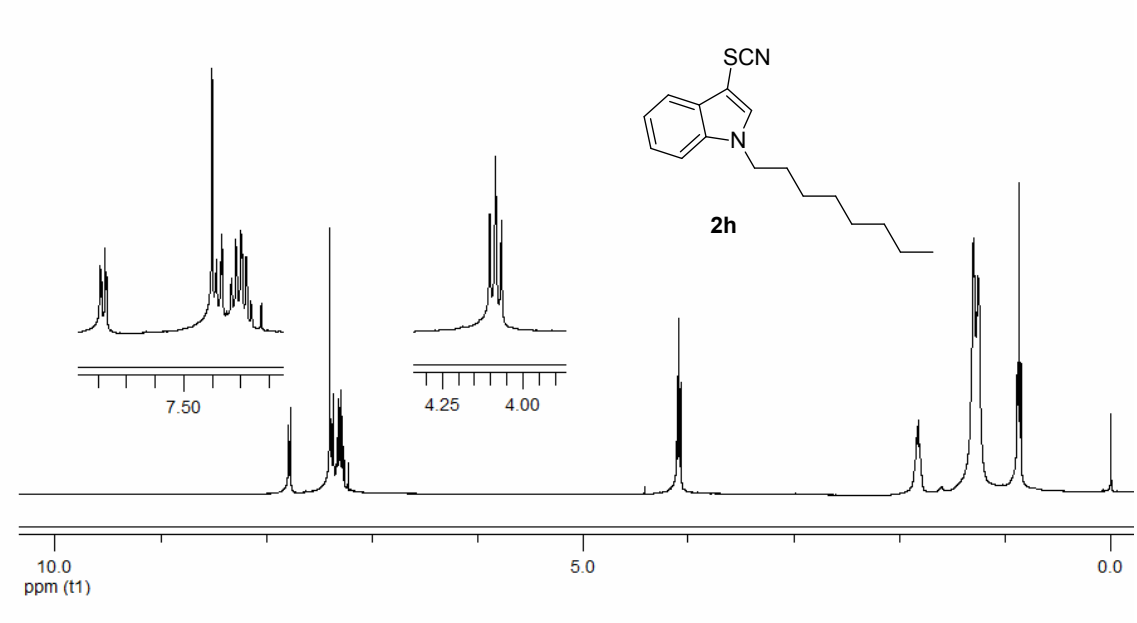

Figure S17. 400 MHz ^{1}H NMR spectrum of compound **2h** in $CDCl_3$.

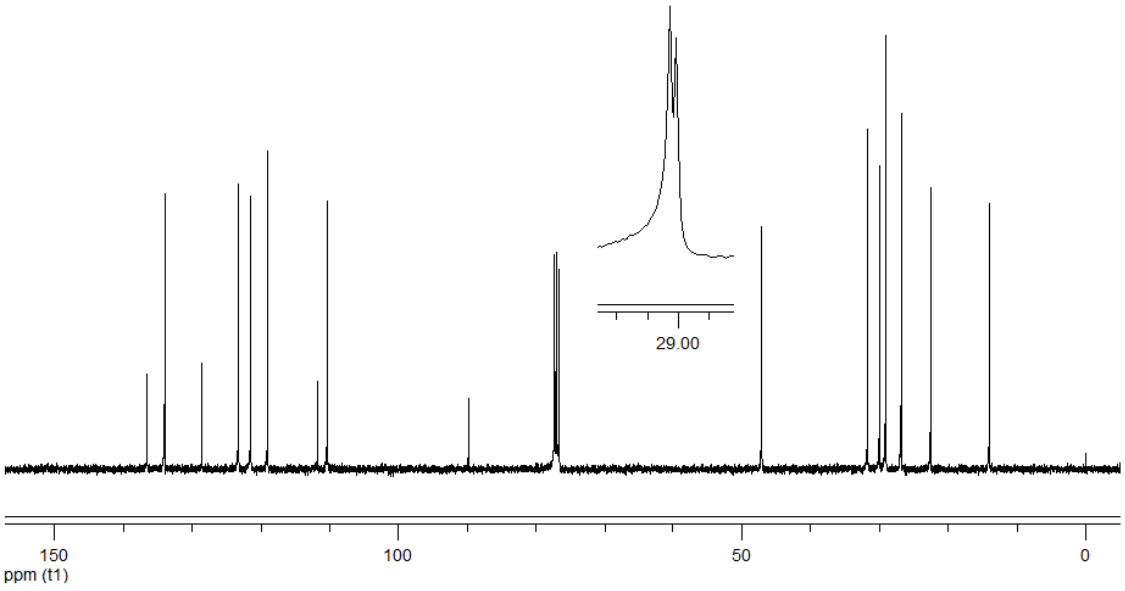

Figure S18. 100 MHz ^{13}C NMR spectrum of compound **2h** in $CDCl_3$.

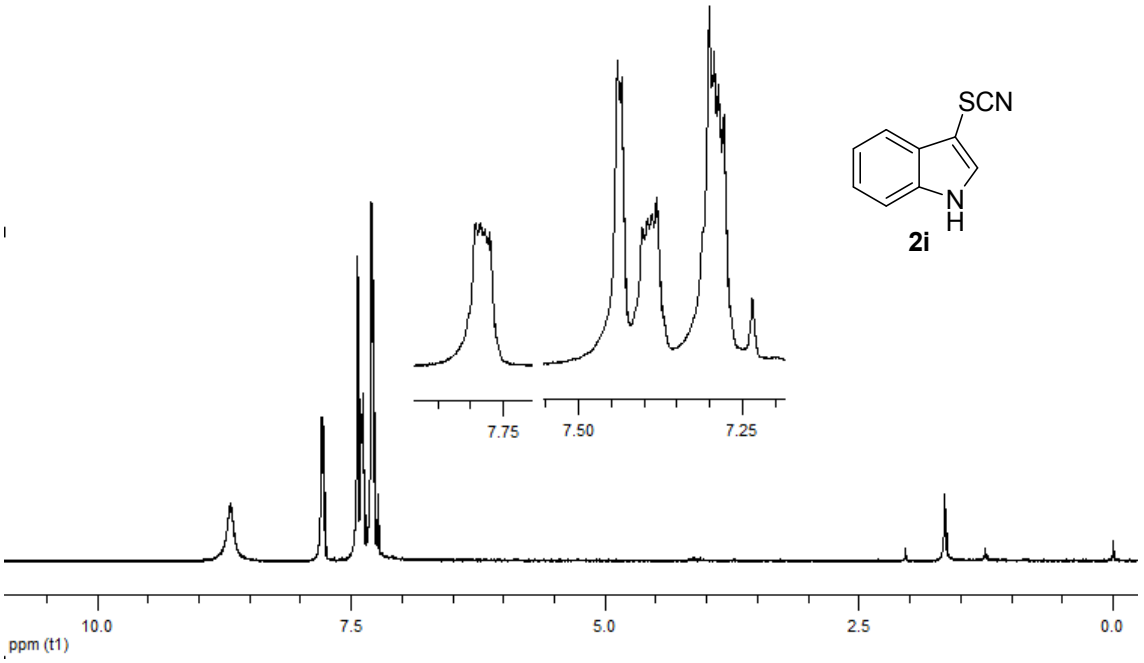

Figure S19. 400 MHz ^{1}H NMR spectrum of compound **2i** in $CDCl_3$.

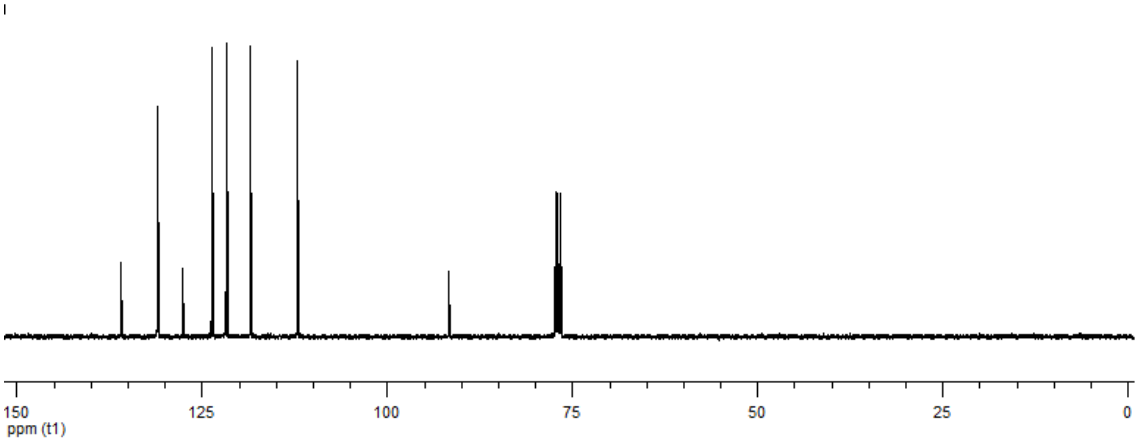

Figure S20. 100 MHz ^{13}C NMR spectrum of compound **2i** in $CDCl_3$.

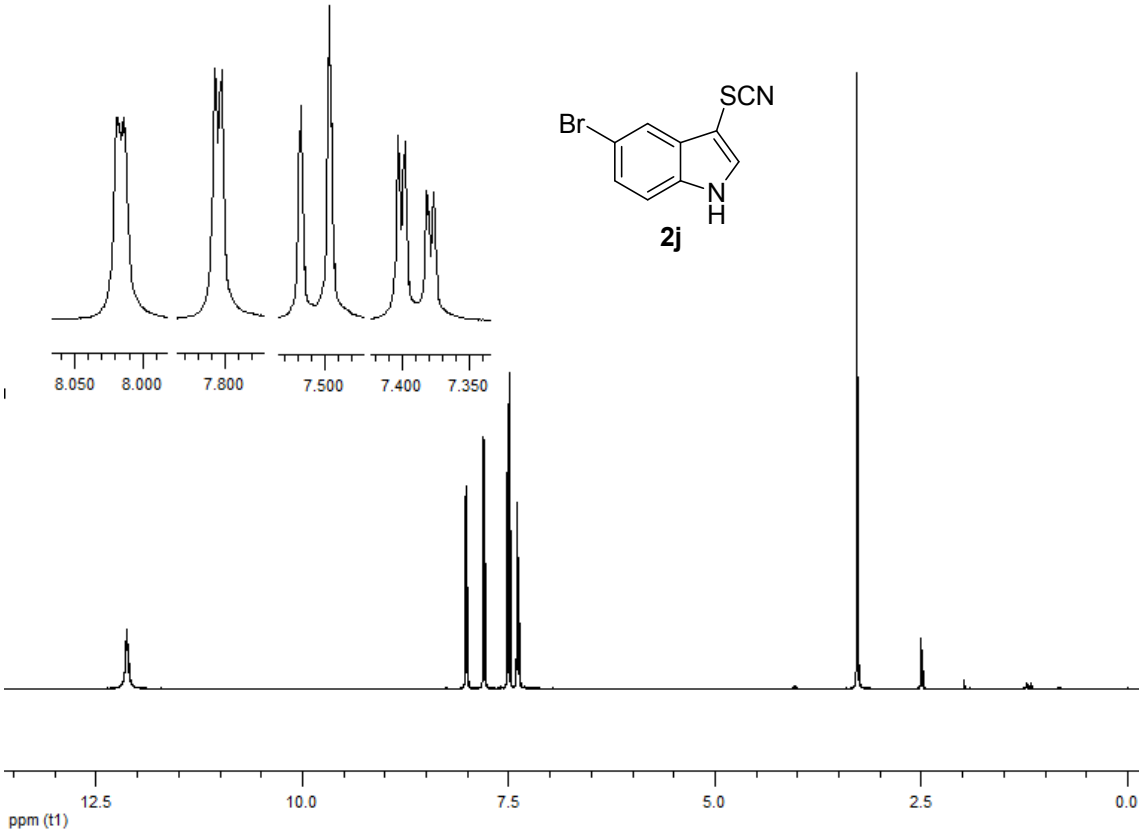

Figure S21. 400 MHz ^{1}H NMR spectrum of compound **2j** DMSO-d_6.

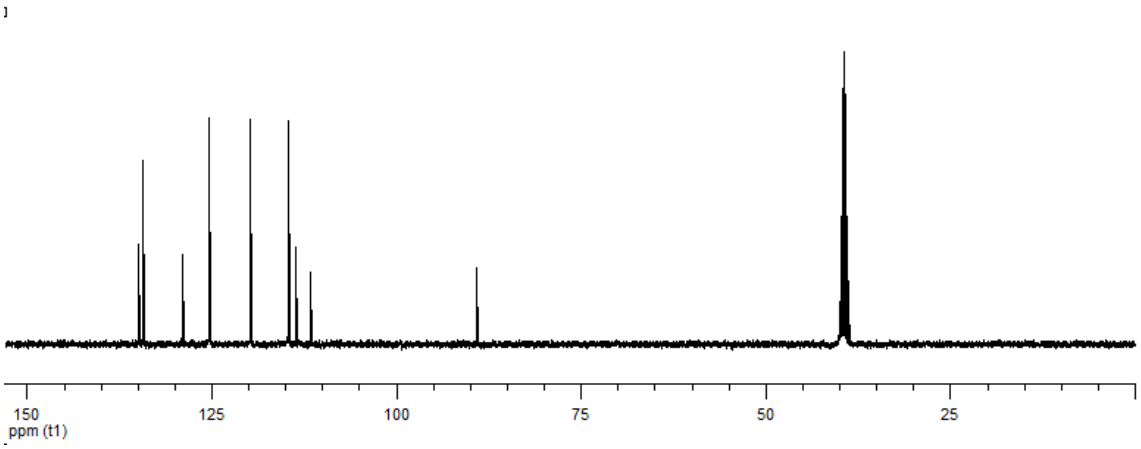

Figure S22. 100 MHz ^{13}C NMR spectrum of compound **2j** in DMSO-d_6.

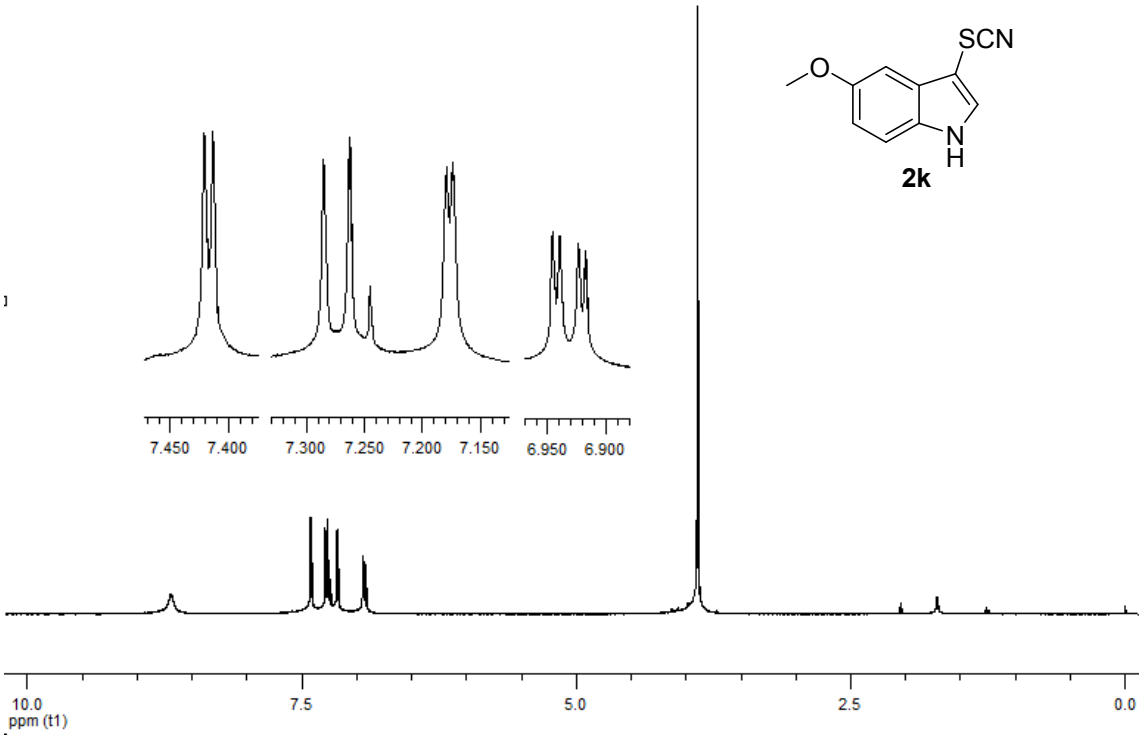

Figure S23. 400 MHz ^{1}H NMR spectrum of compound **2k** in $CDCl_3$.

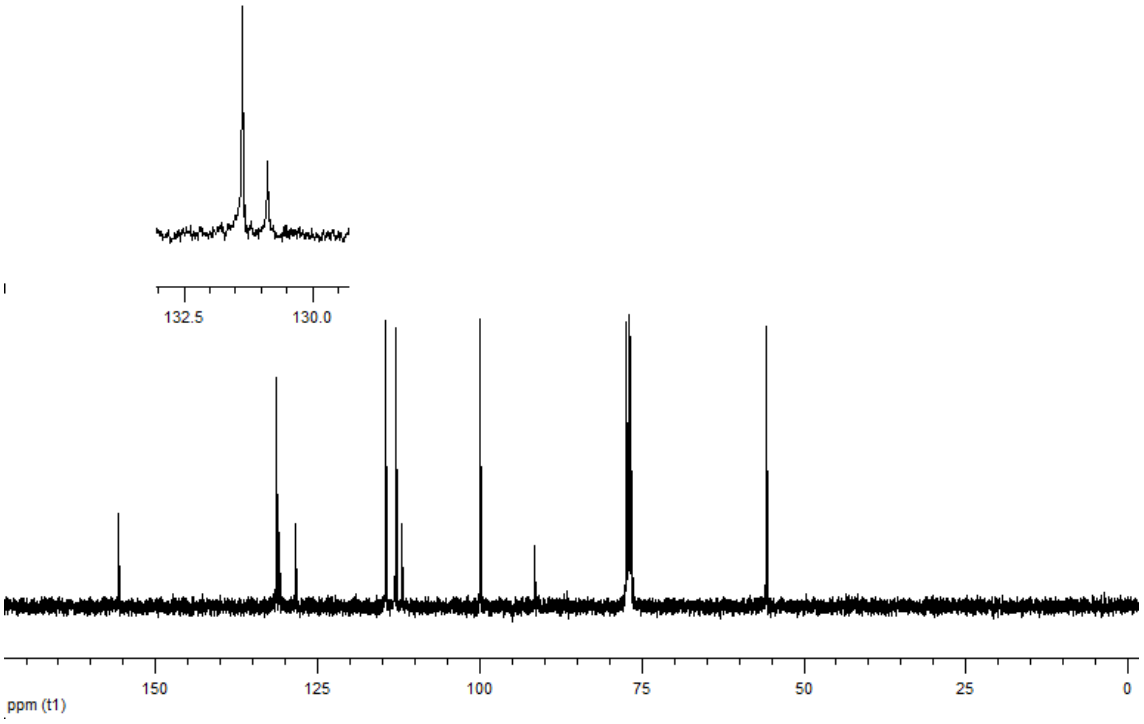

Figure S24. 100 MHz ^{13}C NMR spectrum of compound **2k** in $CDCl_3$.

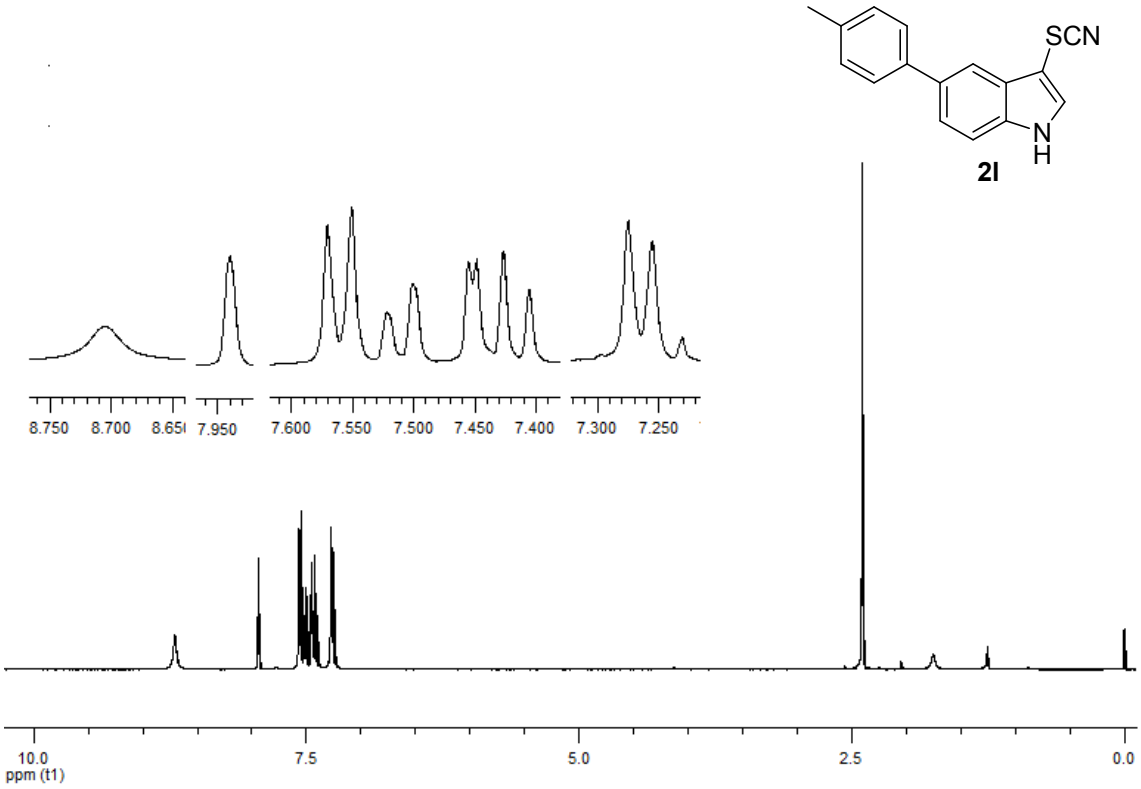

Figure S25. 400 MHz ^{1}H NMR spectrum of compound **2l** in $CDCl_3$.

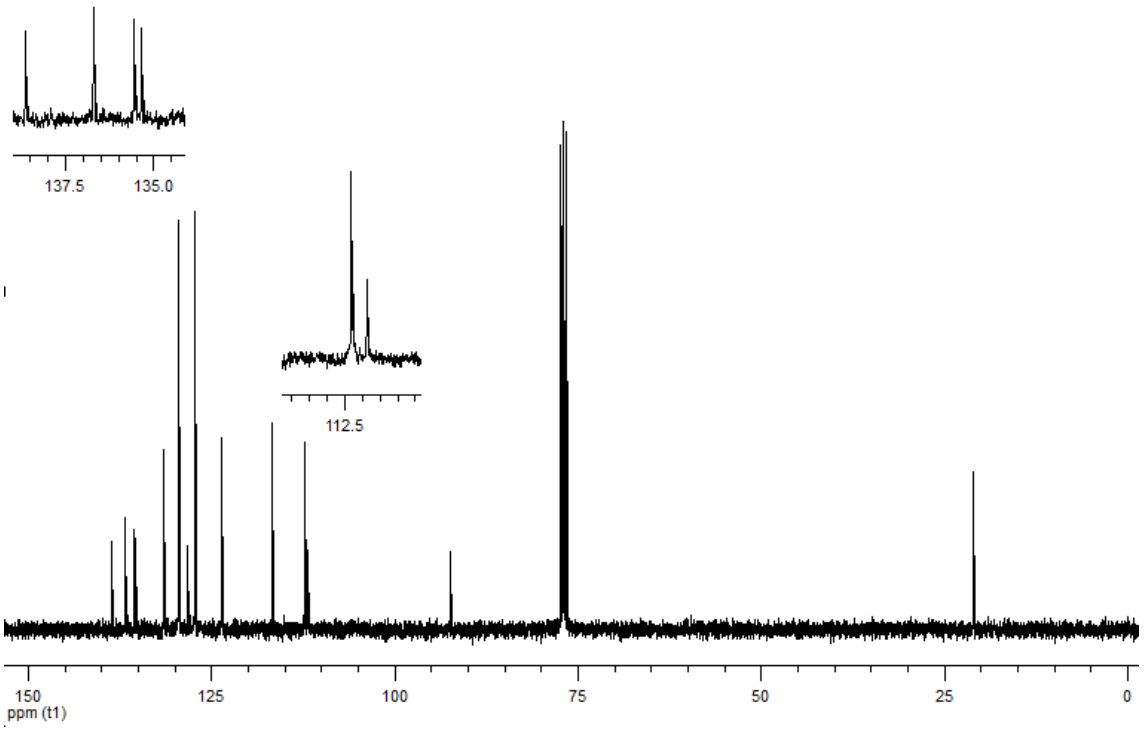

Figure S26. 100 MHz ^{13}C NMR spectrum of compound **2l** in $CDCl_3$.

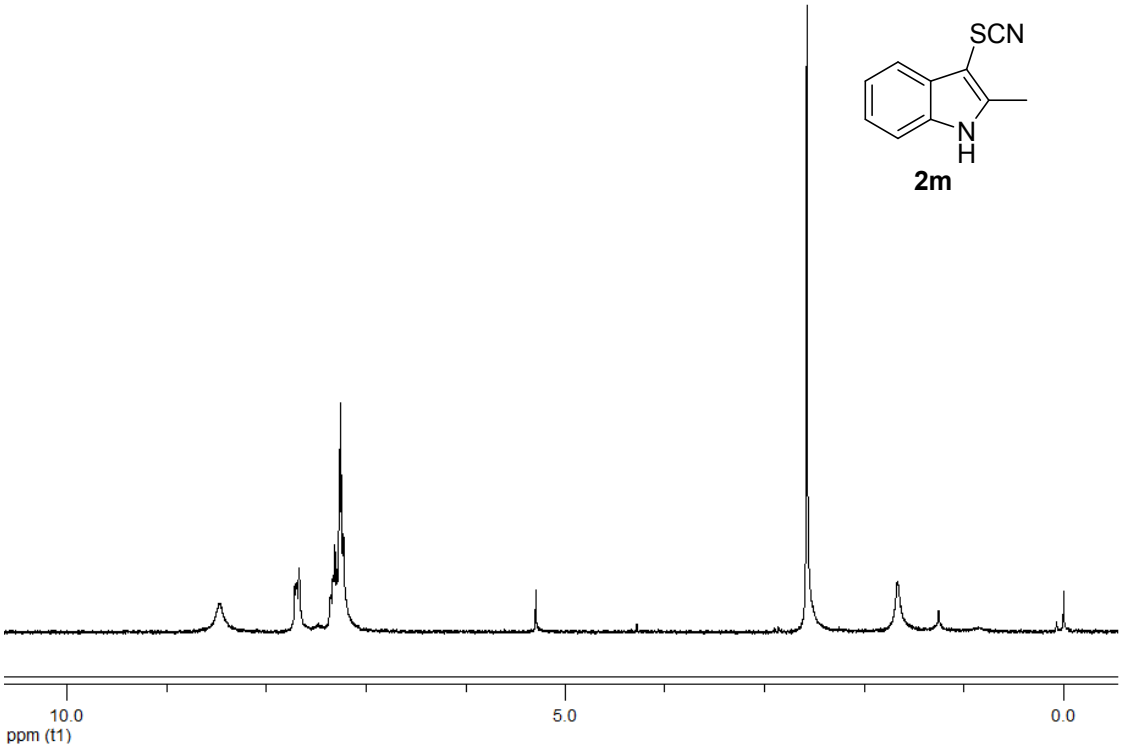

Figure S27. 200 MHz ^{1}H NMR spectrum of compound **2m** in $CDCl_3$.

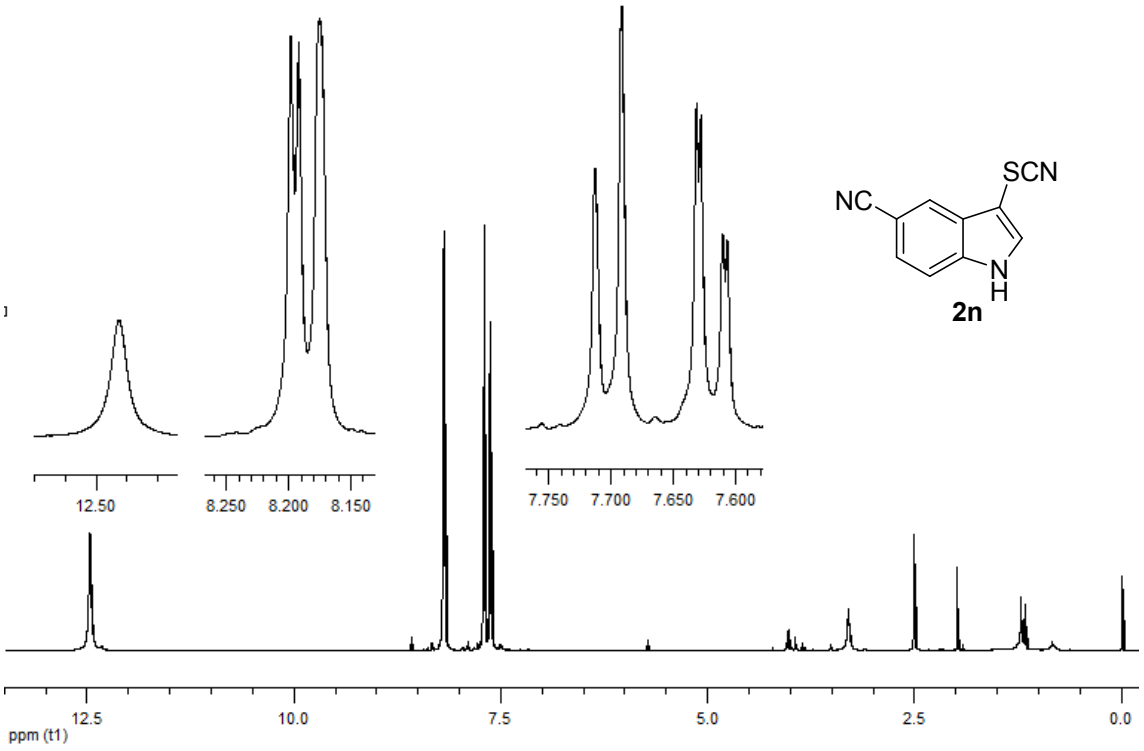

Figure S28. 400 MHz ^{1}H NMR spectrum of compound **2n** in DMSO-d_6.

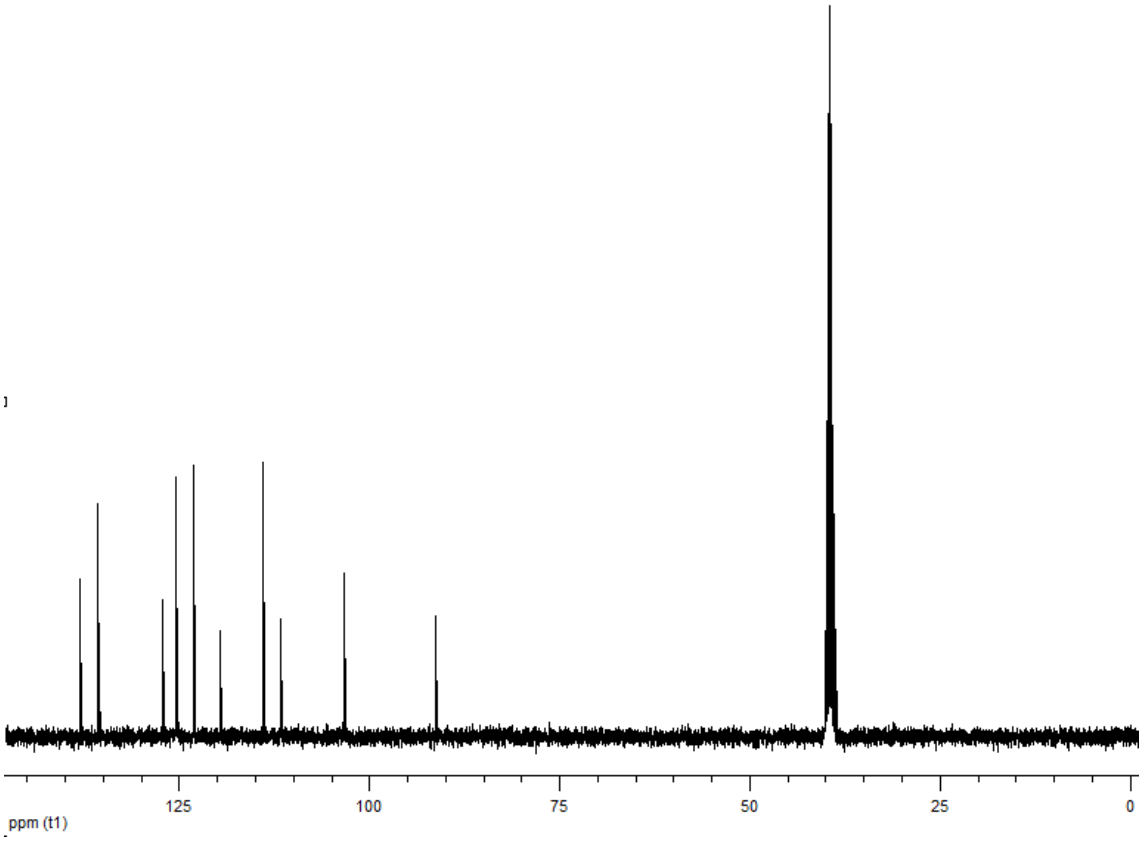

Figure S29. 100 MHz ^{13}C NMR spectrum of compound **2n** in DMSO-d_6.

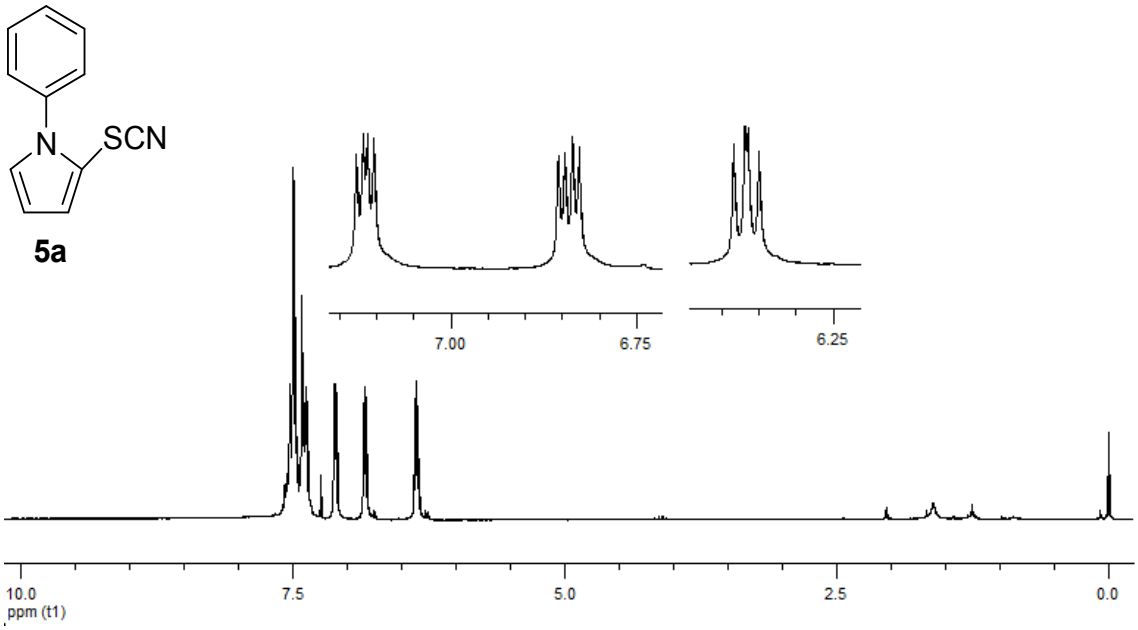

Figure S30. 200 MHz ^{1}H NMR spectrum of compound **5a** in $CDCl_3$.

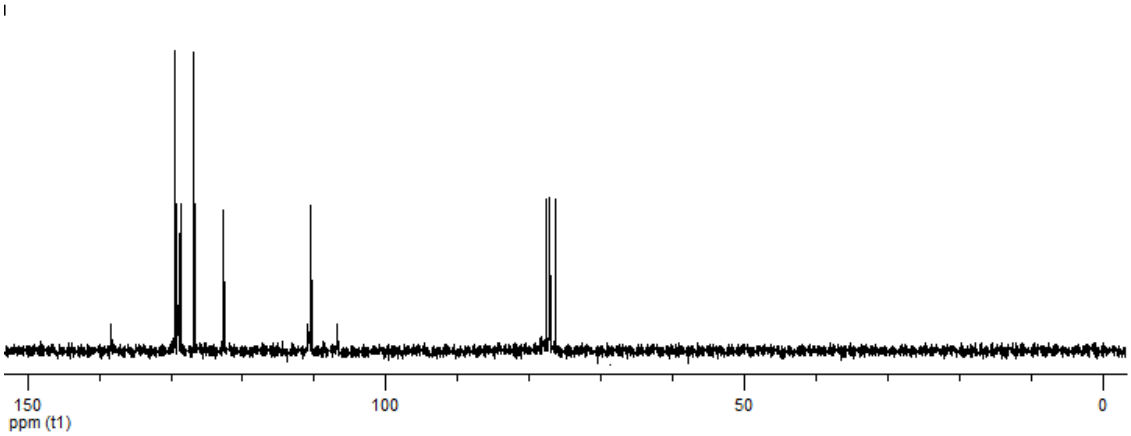

Figure S31. 50 MHz ^{13}C NMR spectrum of compound **5a** in $CDCl_3$ a 50 MHz.

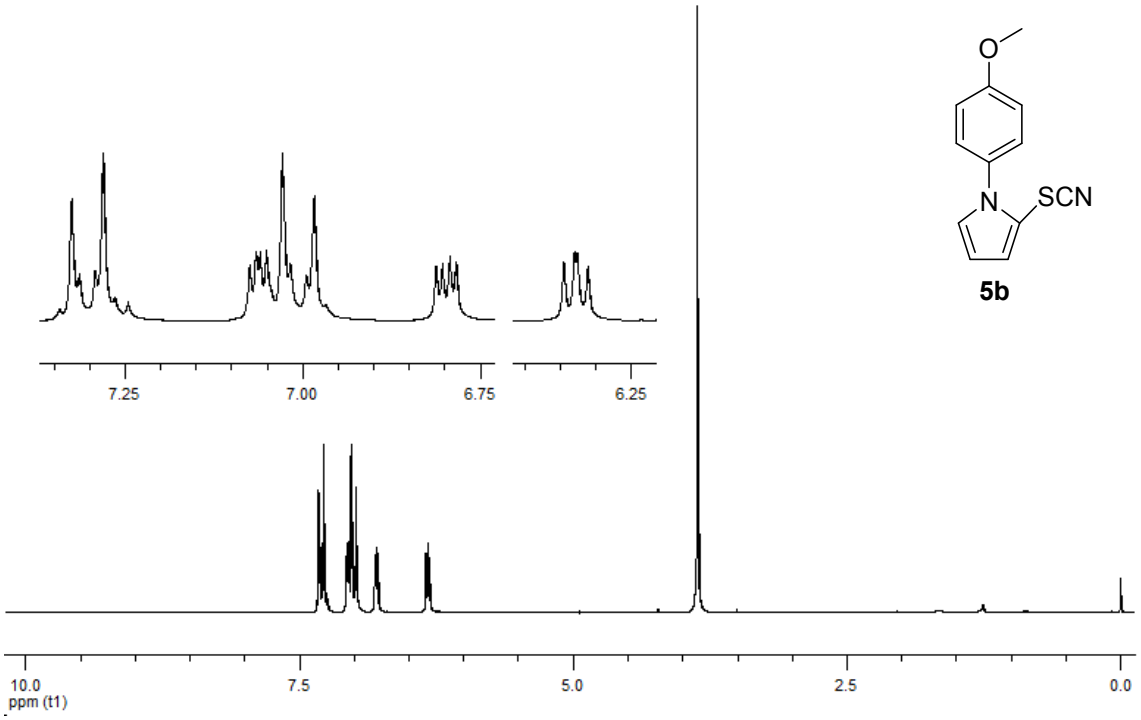

Figure S32. 200 MHz ^{1}H NMR spectrum of compound **5b** in $CDCl_3$.

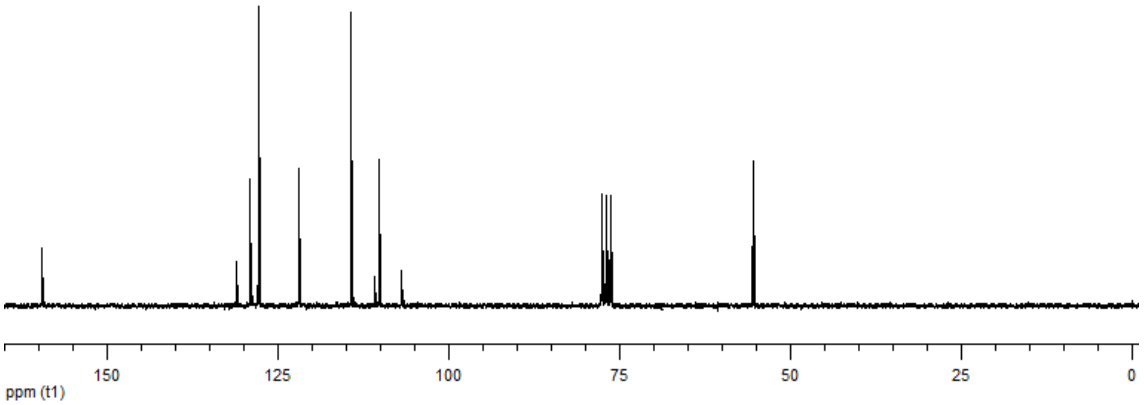

Figure S33. 50 MHz ^{13}C NMR spectrum of compound **5b** in $CDCl_3$.

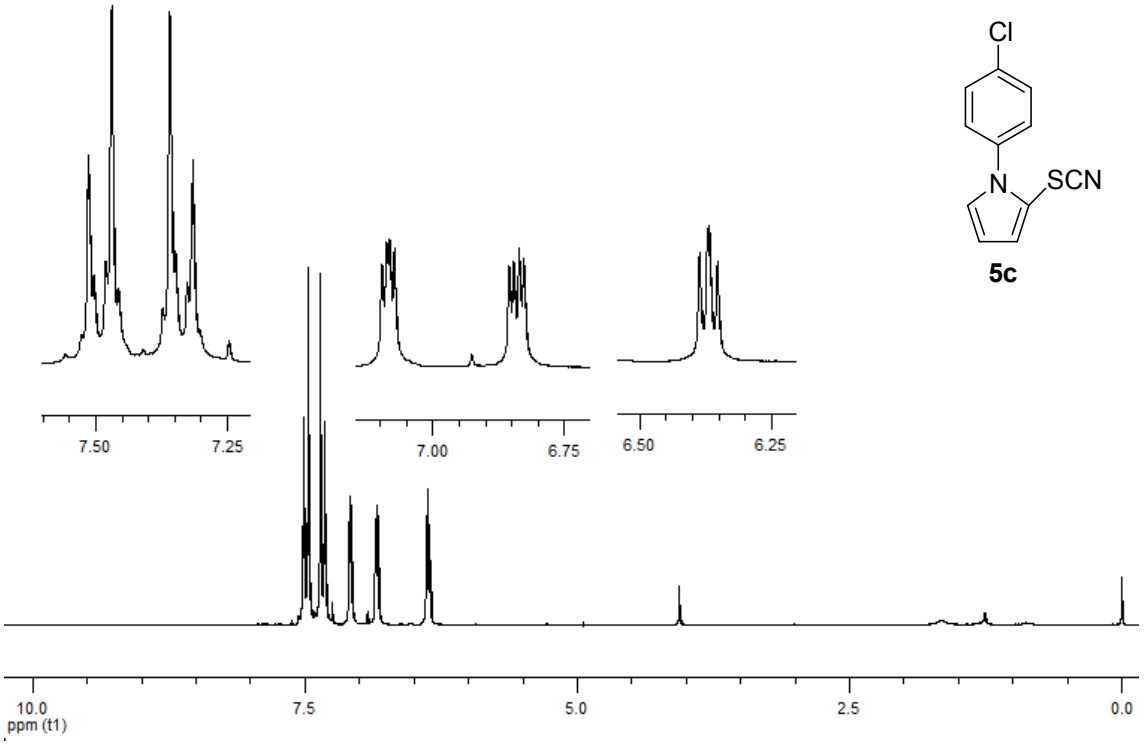

Figure S34. 200 MHz ^{1}H NMR spectrum of compound **5c** in $CDCl_3$.

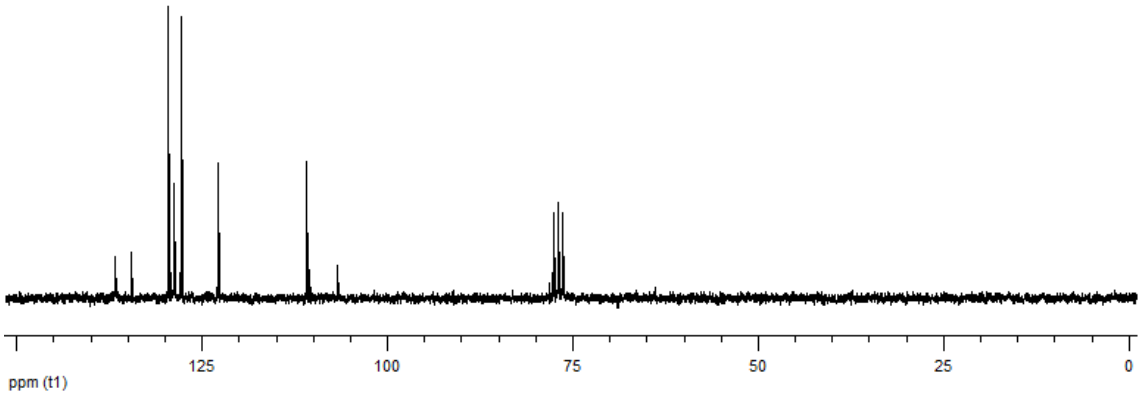

Figure S35. 50 MHz ^{13}C NMR spectrum of compound **5c** in $CDCl_3$.

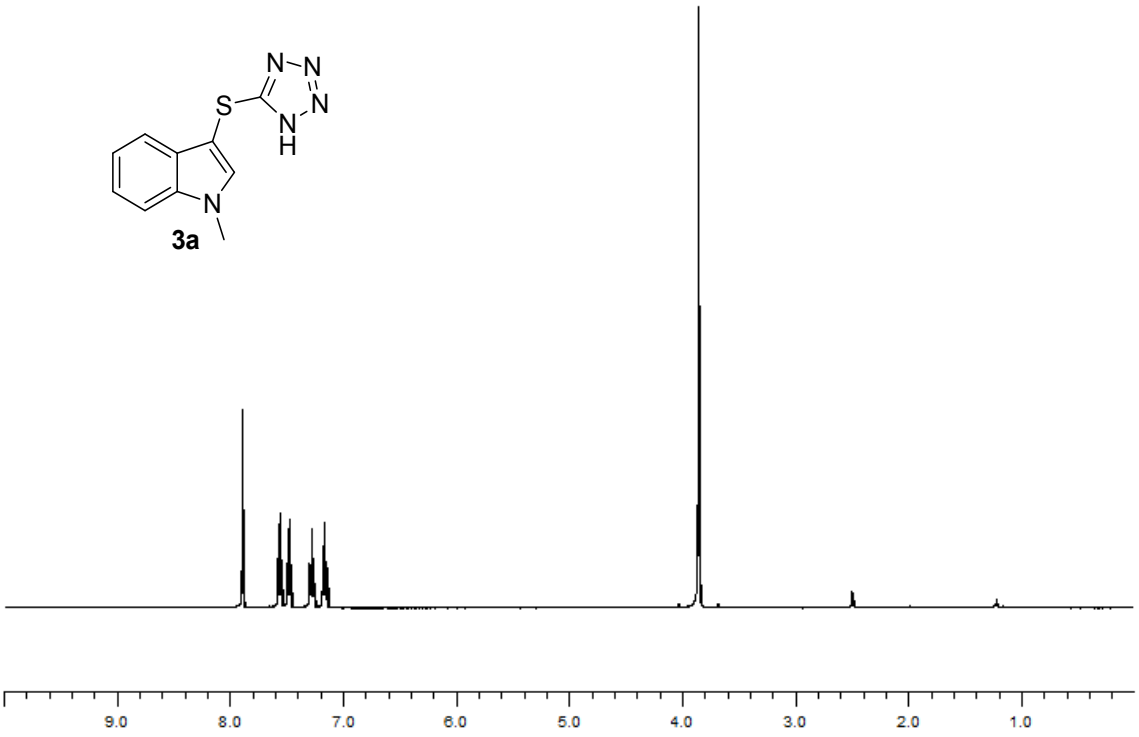

Figure S36. 400 MHz ^{1}H NMR spectrum of compound **3a** in DMSO-d_6.

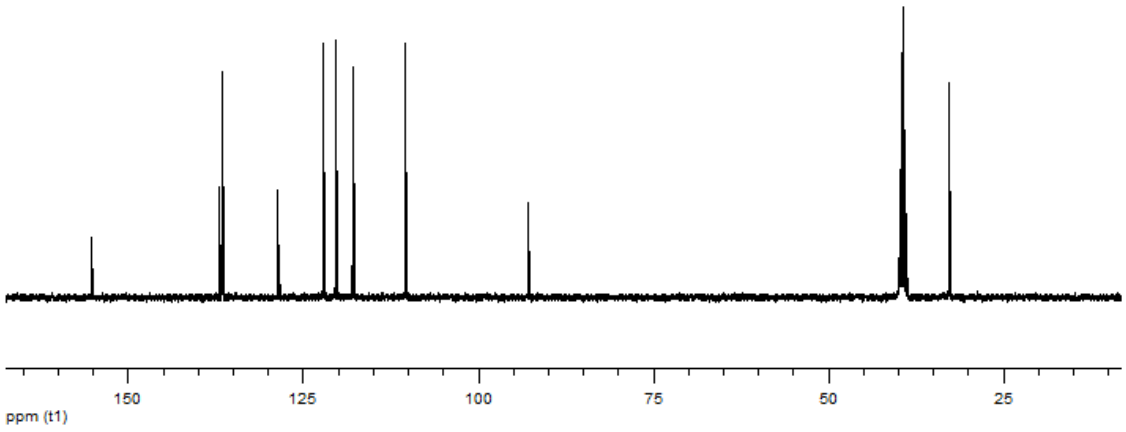

Figure S37. 100 MHz ^{13}C NMR spectrum of compound **3a** in DMSO-d_6.

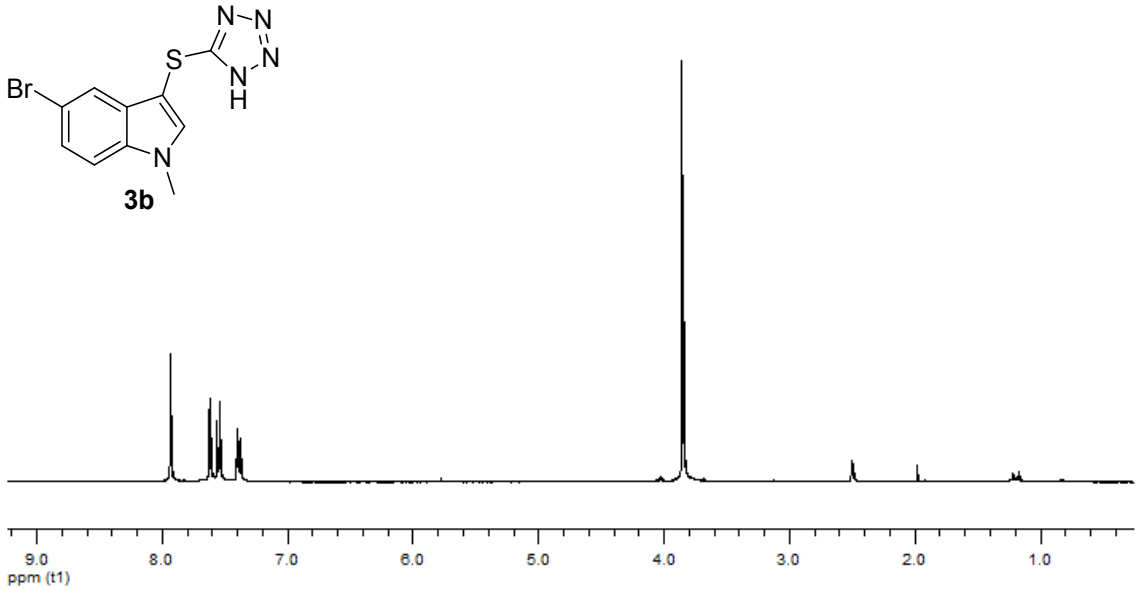

Figure S38. 400 MHz ^{1}H NMR spectrum of compound **3b** in DMSO-d_6.

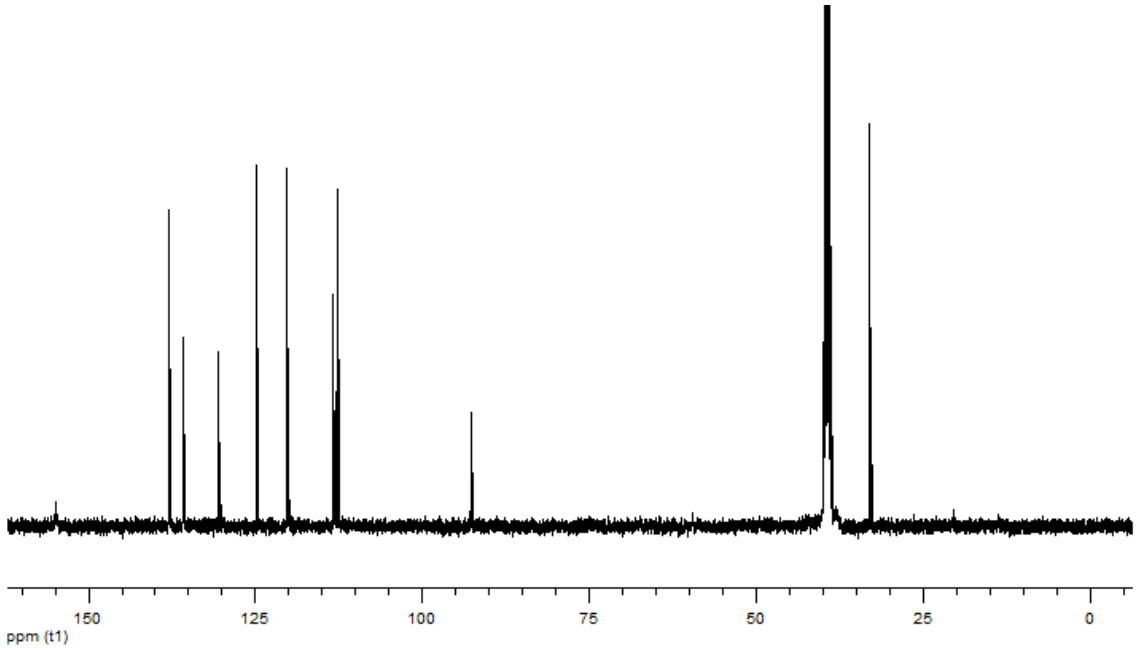

Figure S39. 100 MHz ^{13}C NMR spectrum of compound **3b** in DMSO-d_6.

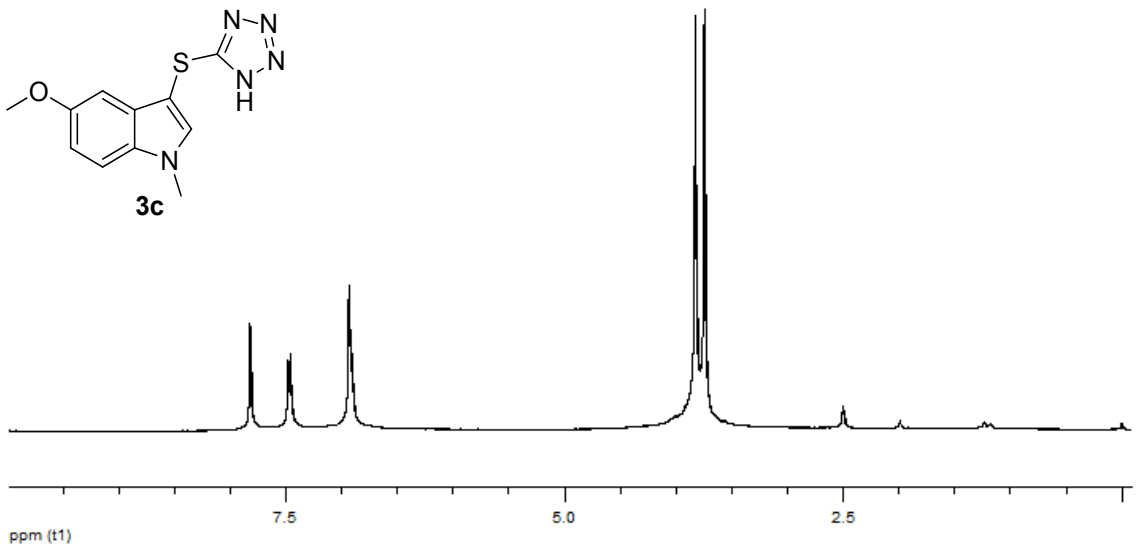

Figure S40. 400 MHz ^{1}H NMR spectrum of compound **3c** in DMSO-d_6.

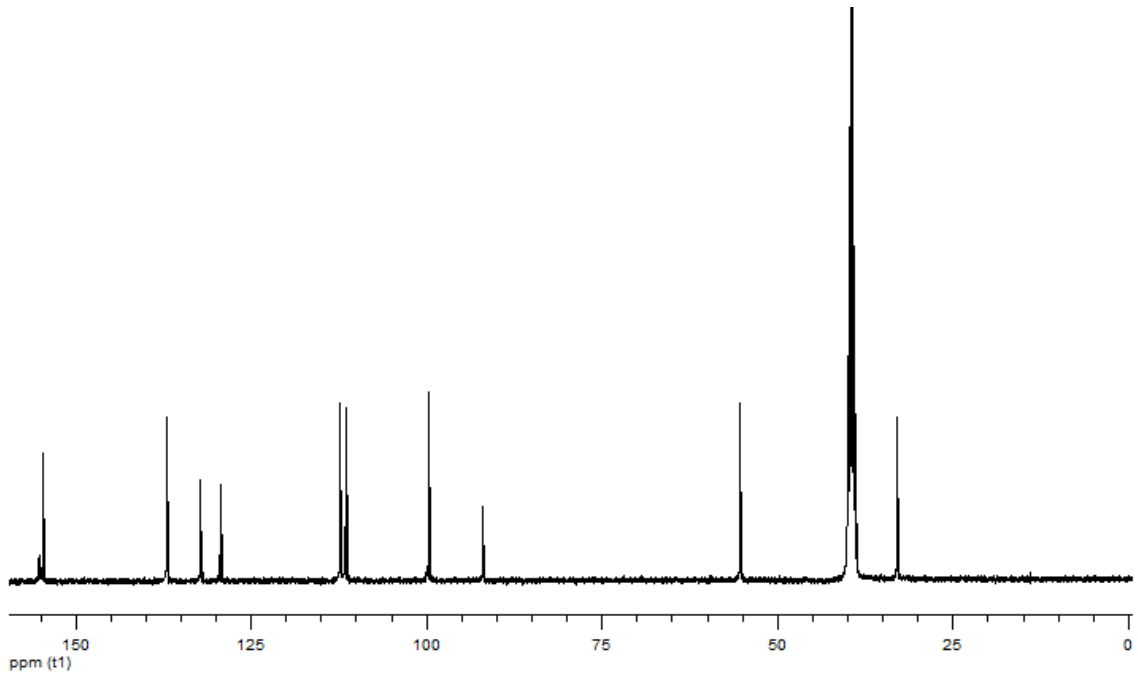

Figure S41. 100 MHz ^{13}C NMR spectrum of compound **3c** in DMSO-d_6.

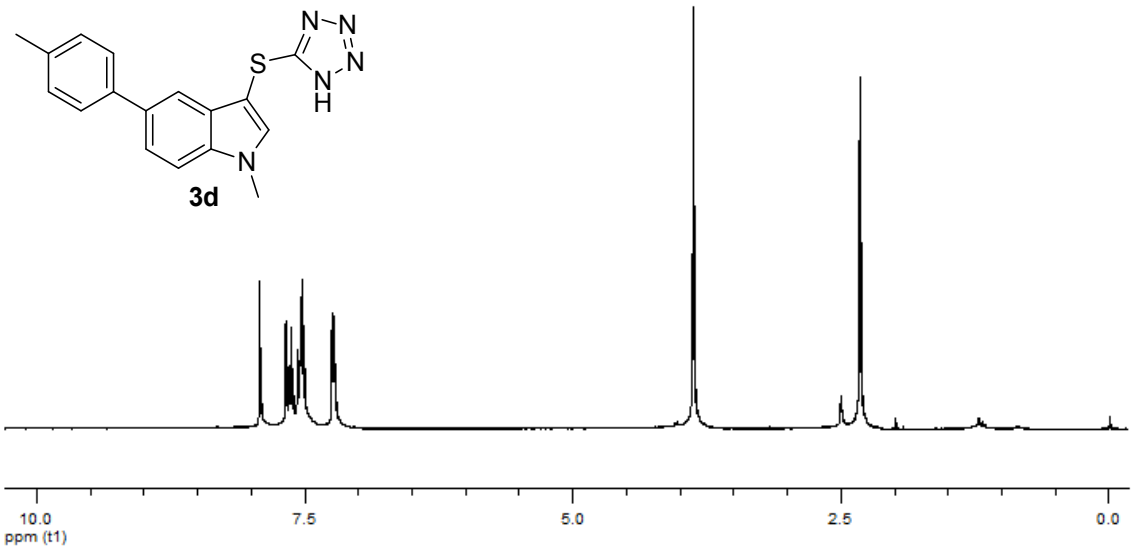

Figure S42. 400 MHz ^{1}H NMR spectrum of compound **3d** in DMSO-d_6.

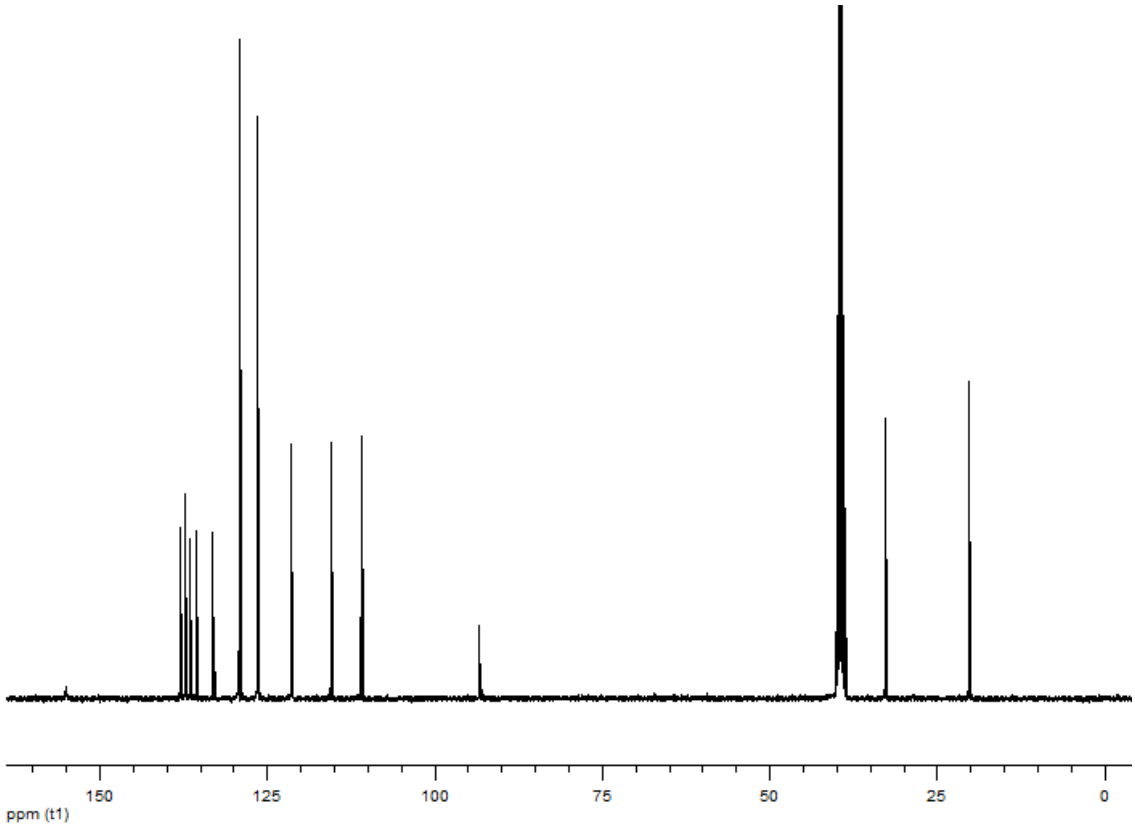

Figure S43. 100 MHz ^{13}C NMR spectrum of compound **3d** in DMSO-d_6.

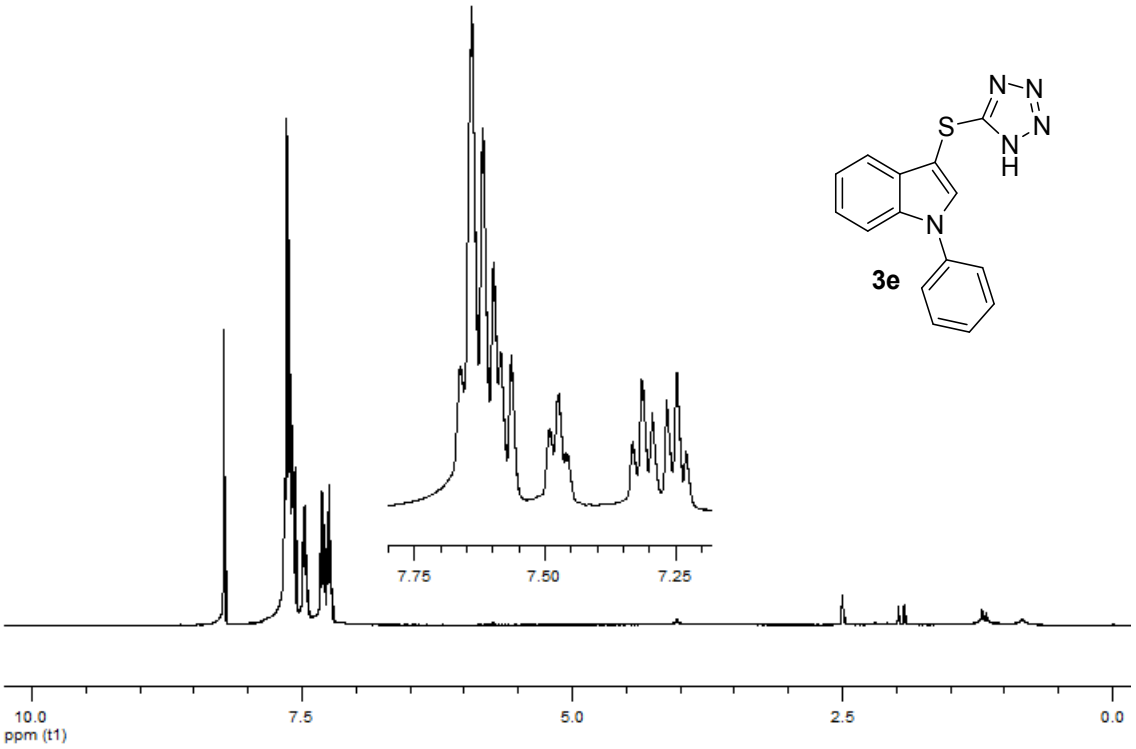

Figure S44. 400 MHz ^{1}H NMR spectrum of compound **3e** in DMSO-d_6.

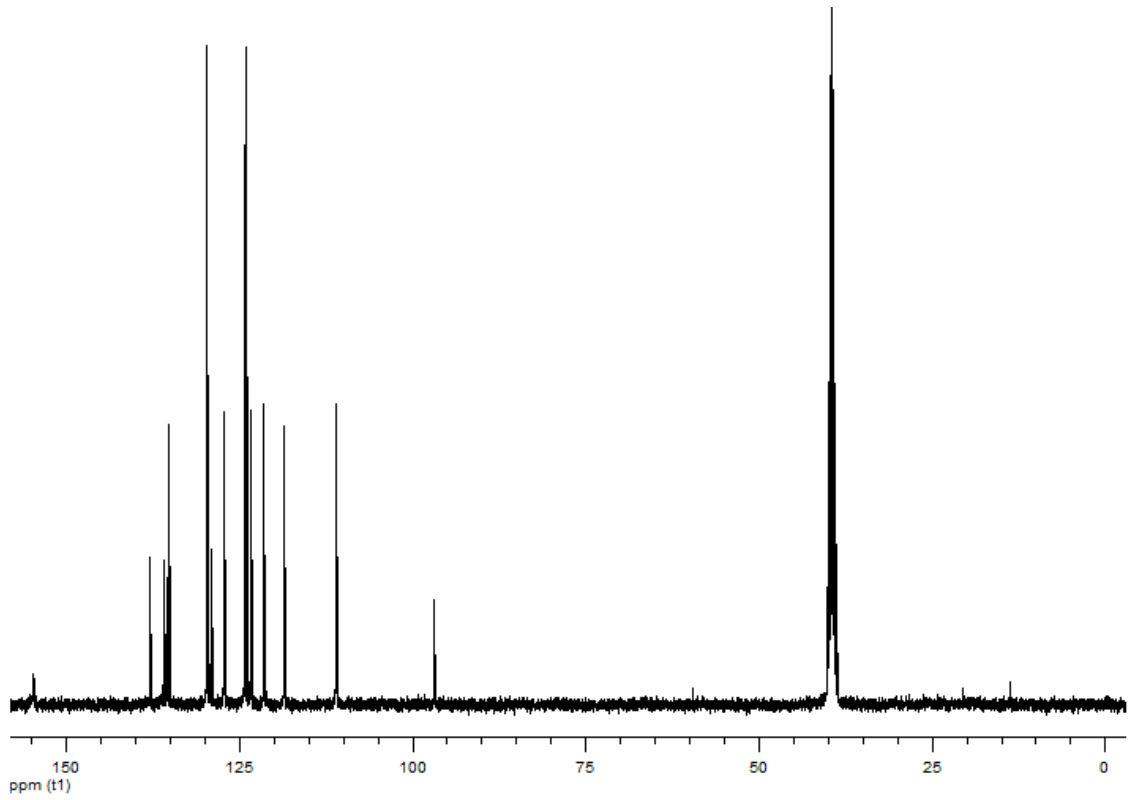

Figure S45. 100 MHz ^{13}C NMR spectrum of compound **3e** in DMSO-d_6.

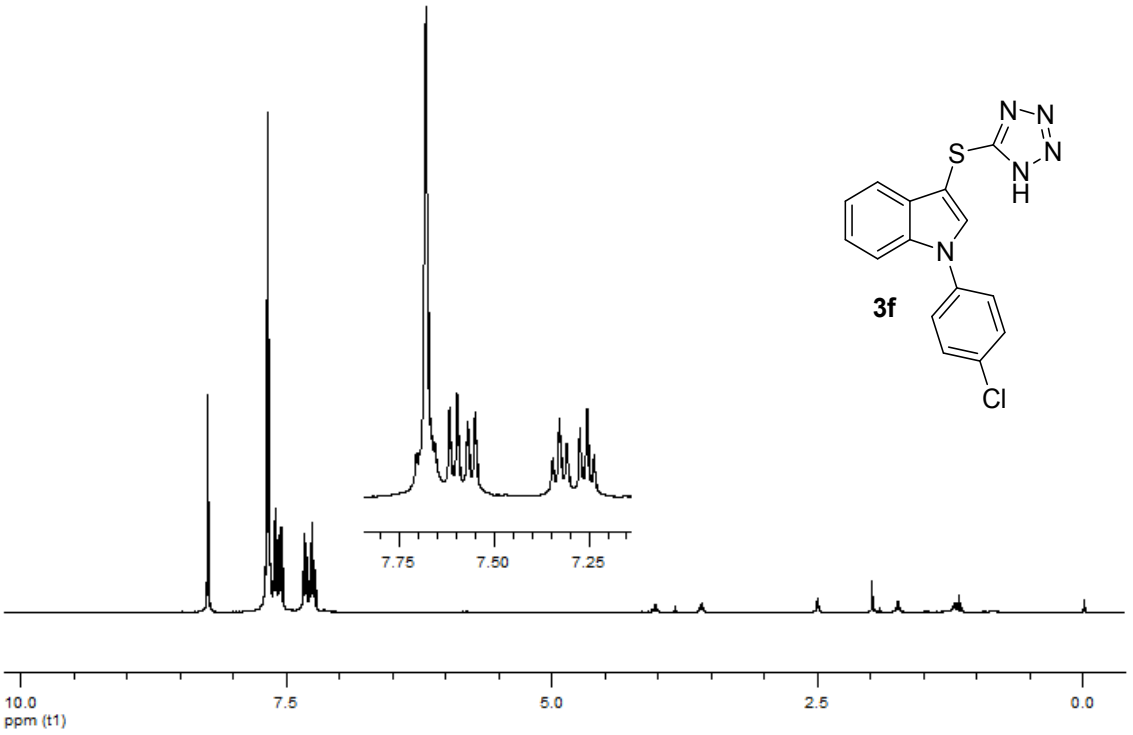

Figure S46. 400 MHz ^{1}H NMR spectrum of compound **3f** in DMSO-d_6.

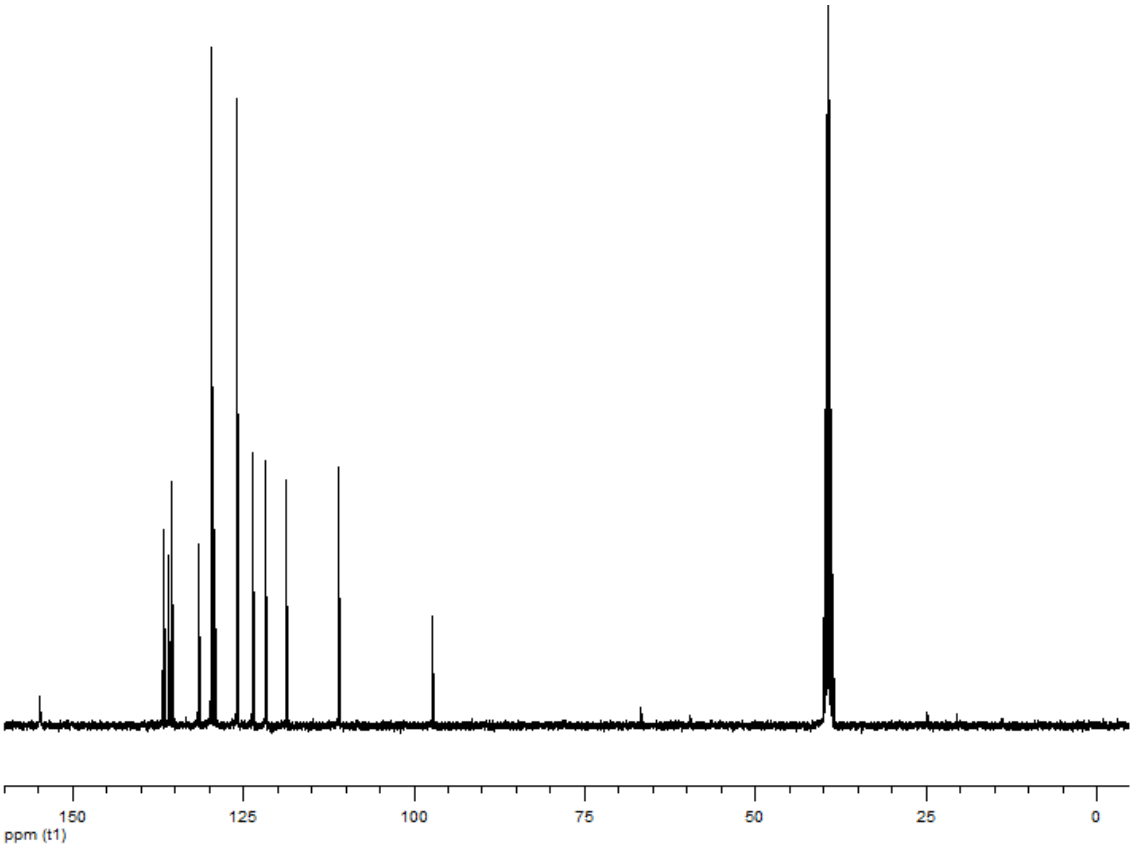

Figure S47. 100 MHz ^{13}C NMR spectrum of compound **3f** in DMSO-d_6.

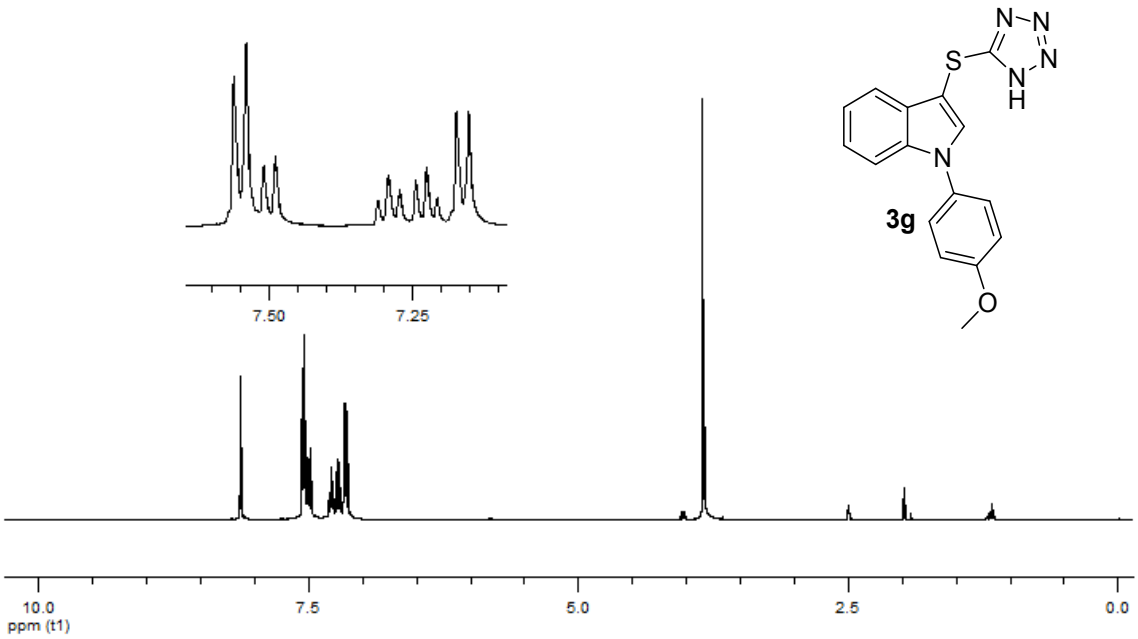

Figure S48. 400 MHz ^{1}H NMR spectrum of compound **3g** in DMSO-d_6.

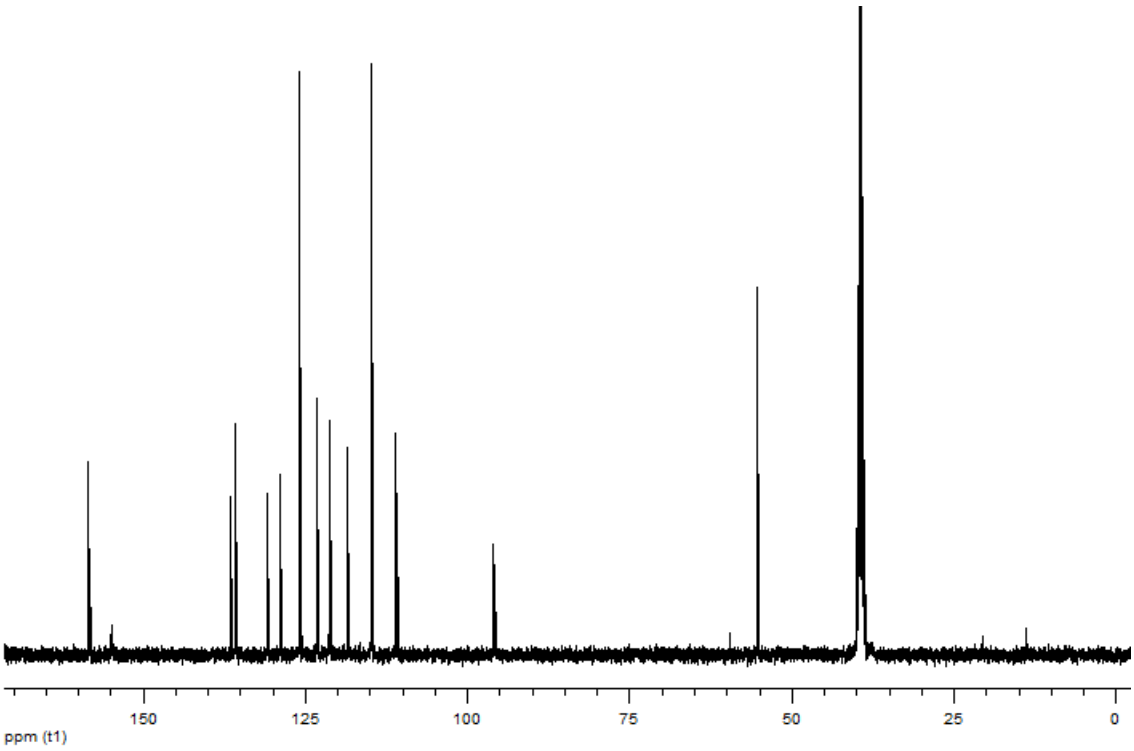

Figure S49. 100 MHz ^{13}C NMR spectrum of compound **3g** in DMSO-d_6.

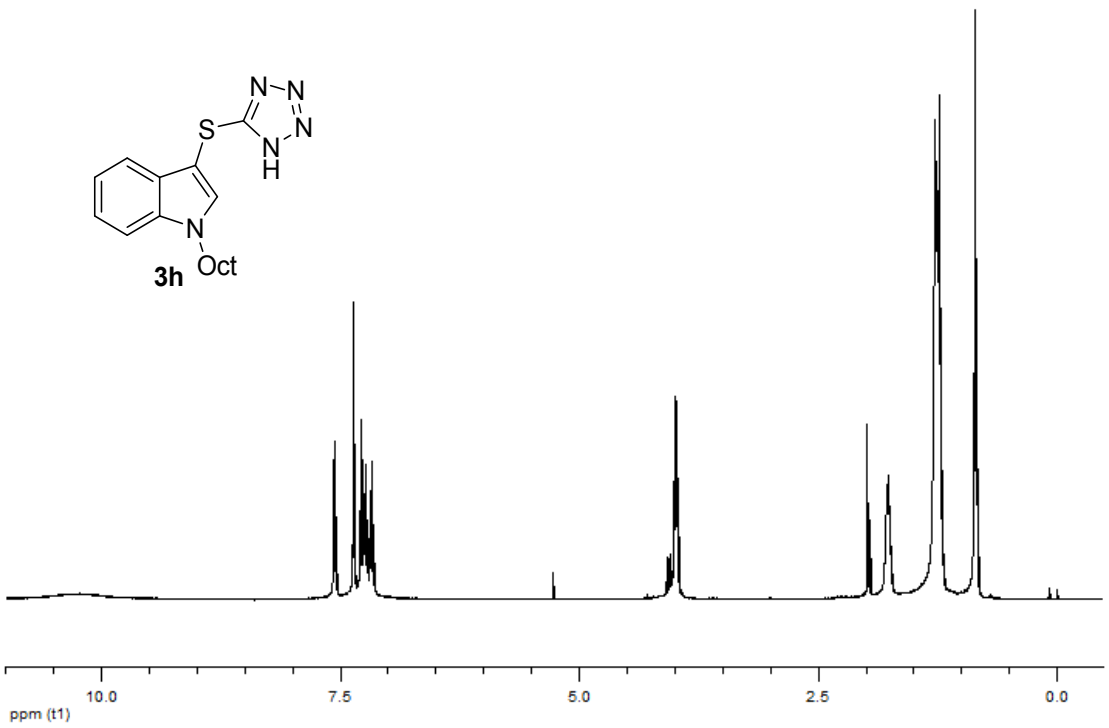

Figure S50. 400 MHz ^{1}H NMR spectrum of compound **3h** in DMSO-d_6.

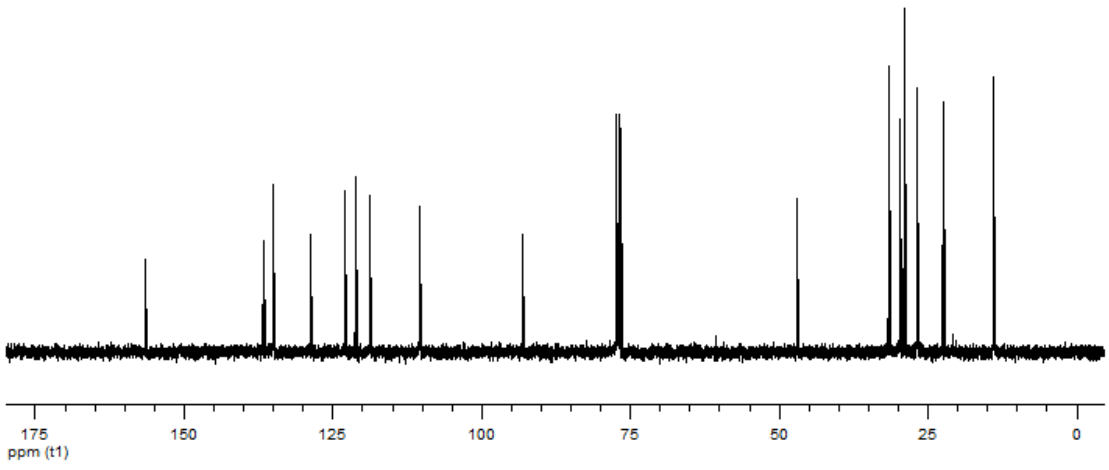

Figure S51. 100 MHz ^{13}C NMR spectrum of compound **3h** in DMSO-d_6.

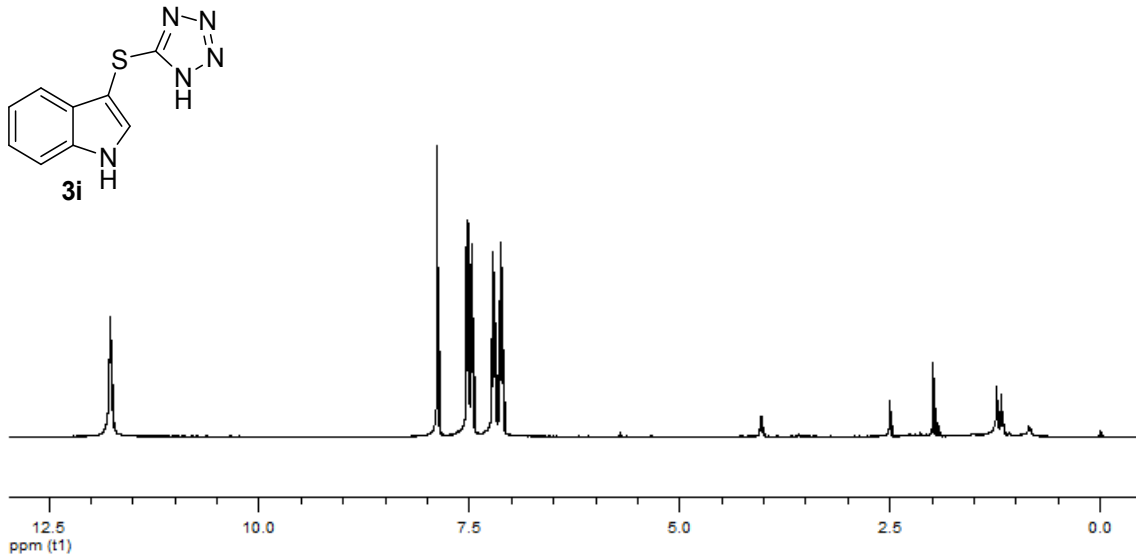

Figure S52. 400 MHz ^{1}H NMR spectrum of compound **3i** in DMSO-d_6.

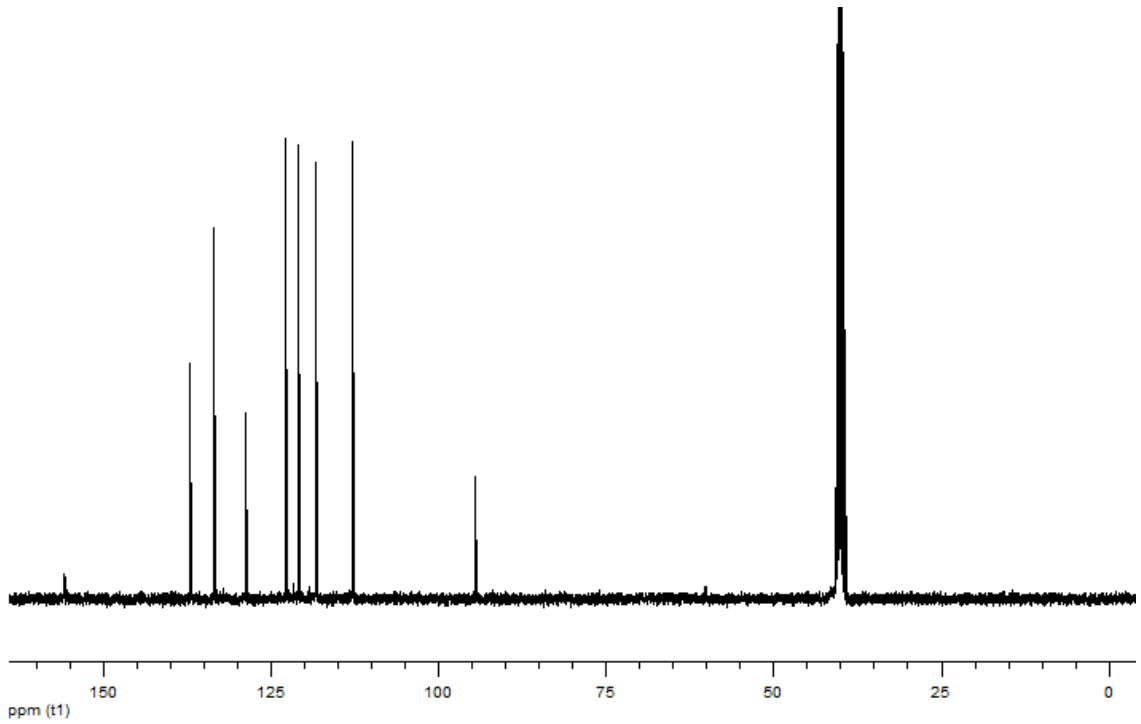

Figure S53. 100 MHz ^{13}C NMR spectrum of compound **3i** in DMSO-d_6.

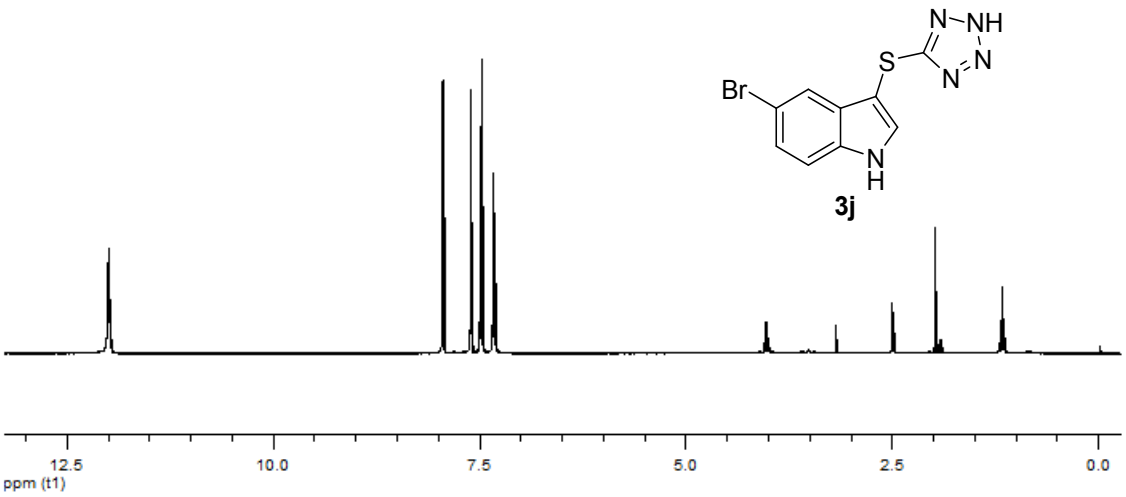

Figure S54. 400 MHz ^{1}H NMR spectrum of compound **3j** in DMSO-d_6.

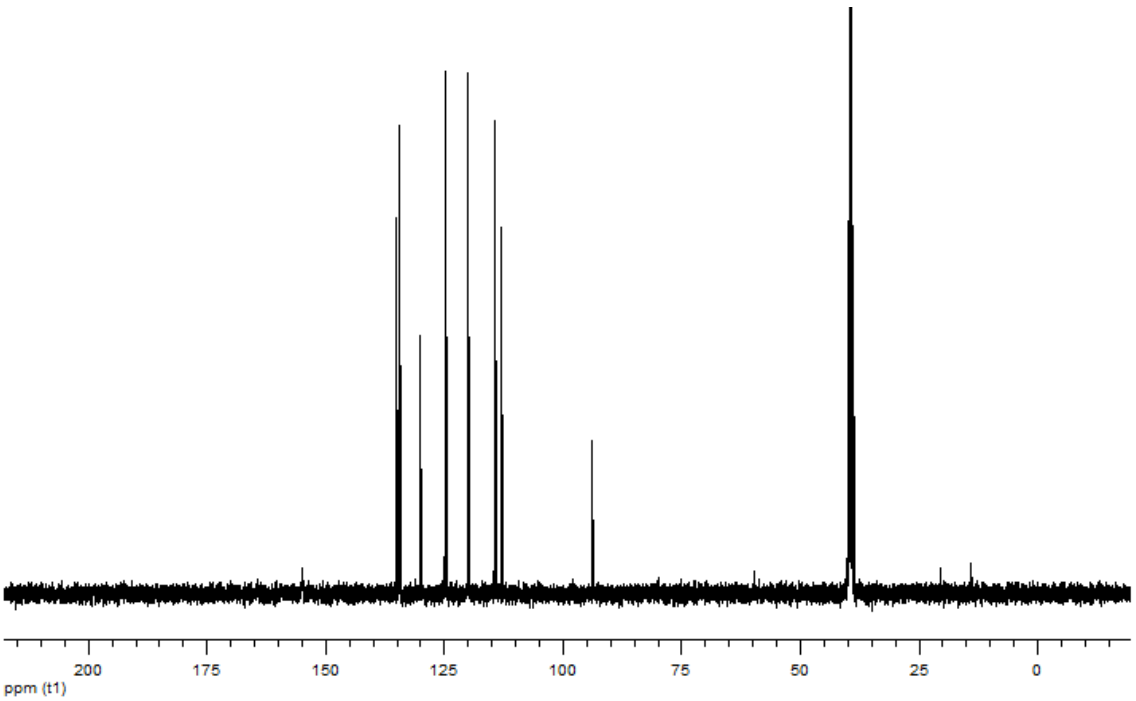

Figure S55. 100 MHz ^{13}C NMR spectrum of compound **3j** in DMSO-d_6.

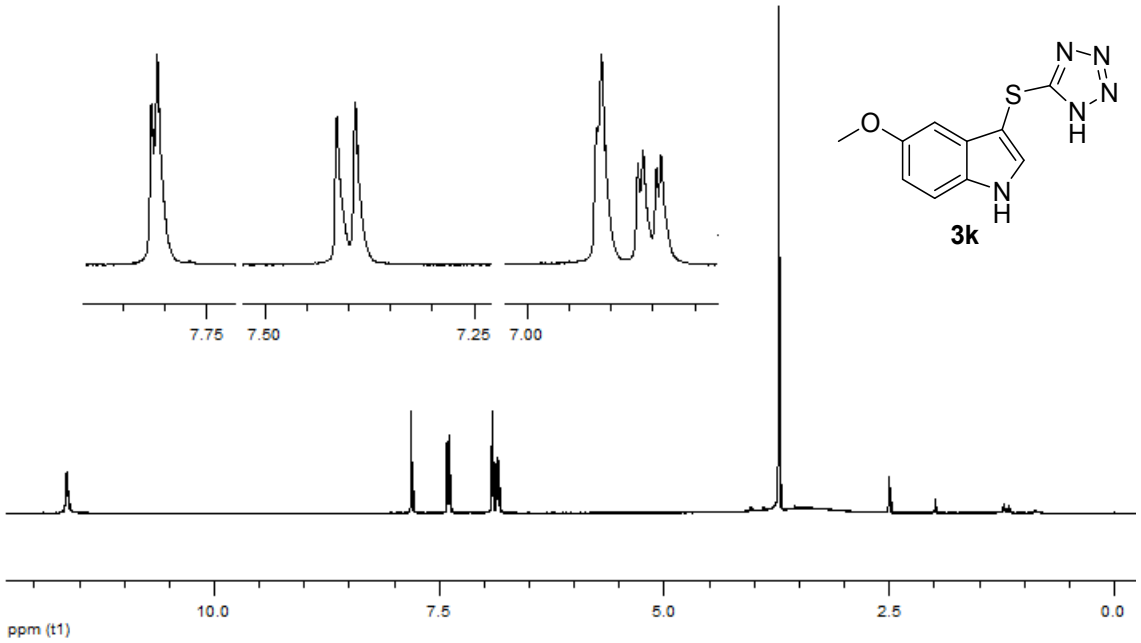

Figure S56. 400 MHz ^{1}H NMR spectrum of compound **3k** in DMSO-d_6.

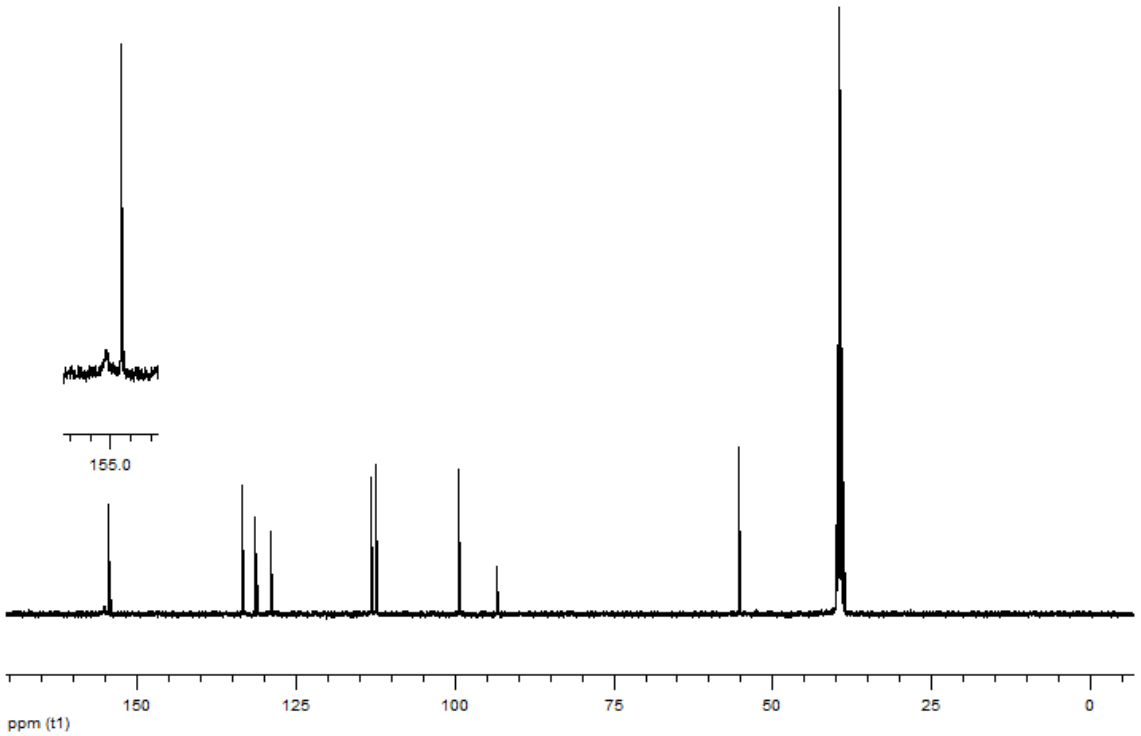

Figure S57. 100 MHz ^{13}C NMR spectrum of compound **3k** in DMSO-d_6.

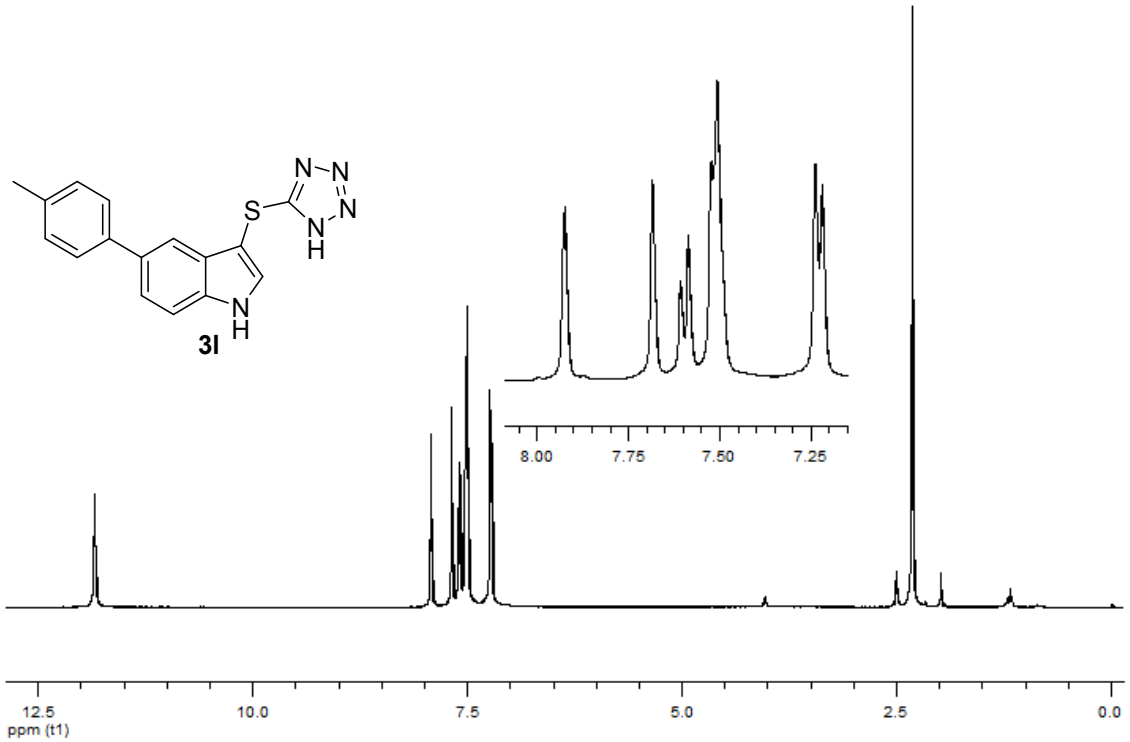

Figure S58. 400 MHz ^{1}H NMR spectrum of compound **3l** in DMSO-d_6.

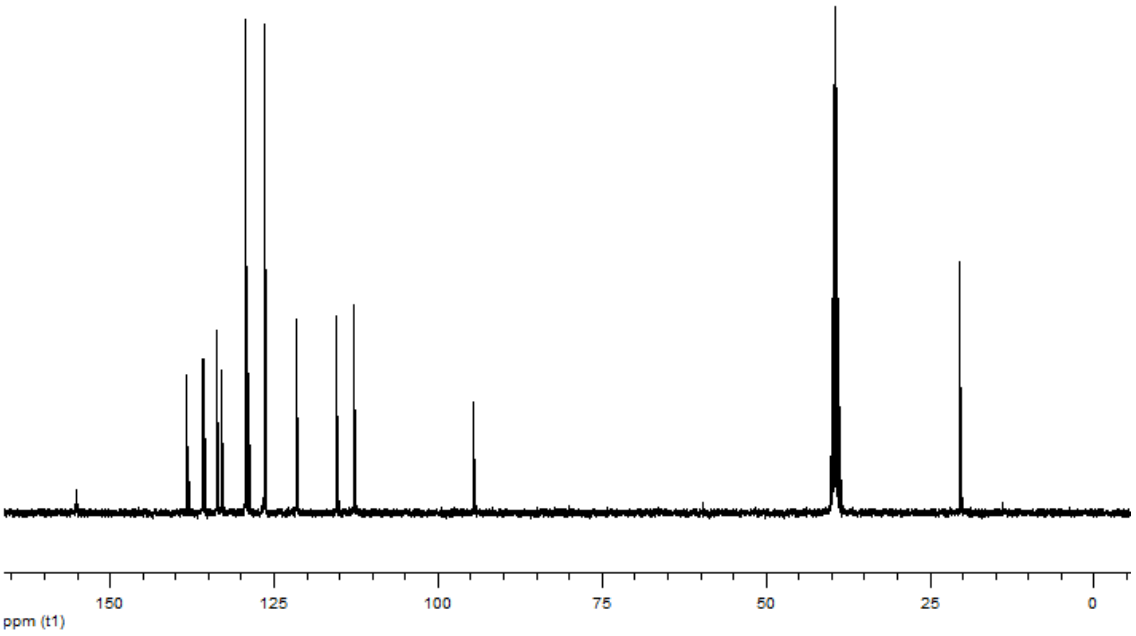

Figure S59. 100 MHz ^{13}C NMR spectrum of compound **3l** in DMSO-d_6.

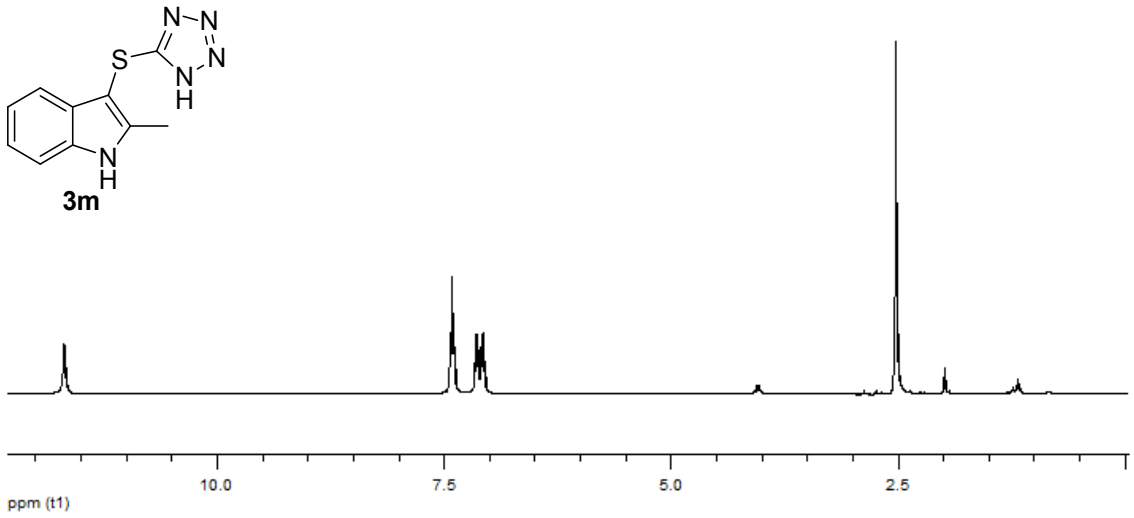

Figure S60. 400 MHz ^{1}H NMR spectrum of compound **3m** in DMSO-d_6.

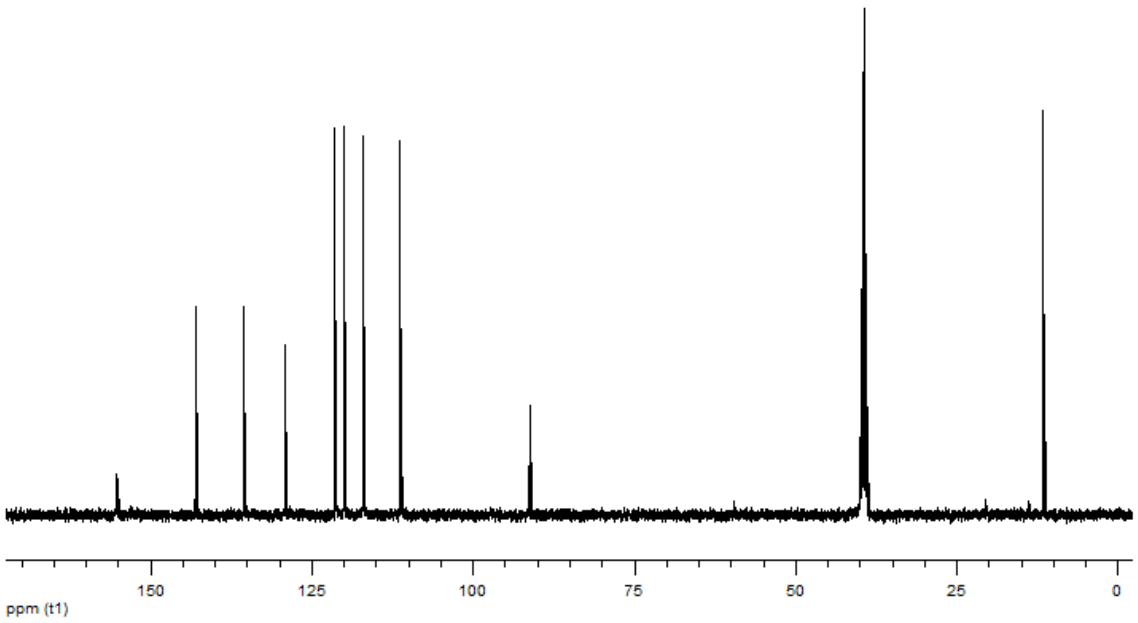

Figure S61. 100 MHz ^{13}C NMR spectrum of compound **3m** in DMSO-d_6.

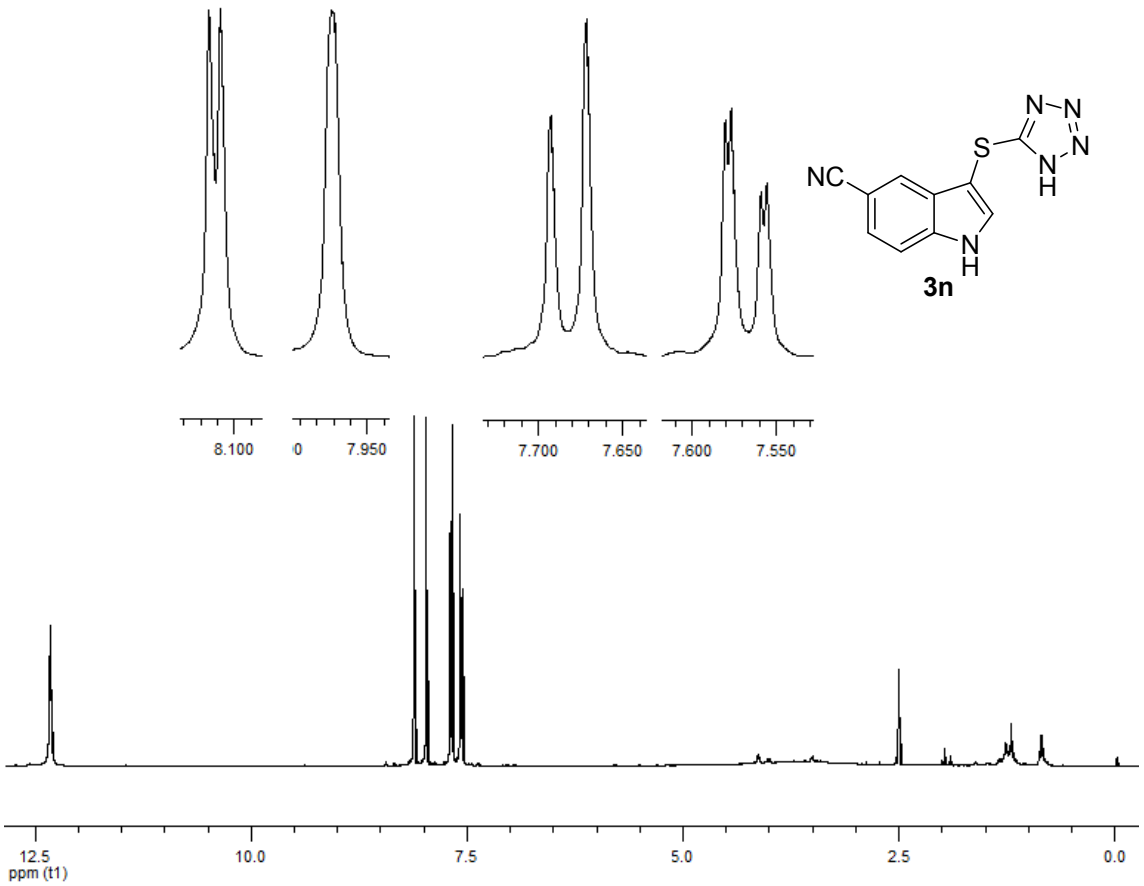

Figure S62. 400 MHz ^{1}H NMR spectrum of compound **3n** in DMSO-d_6.

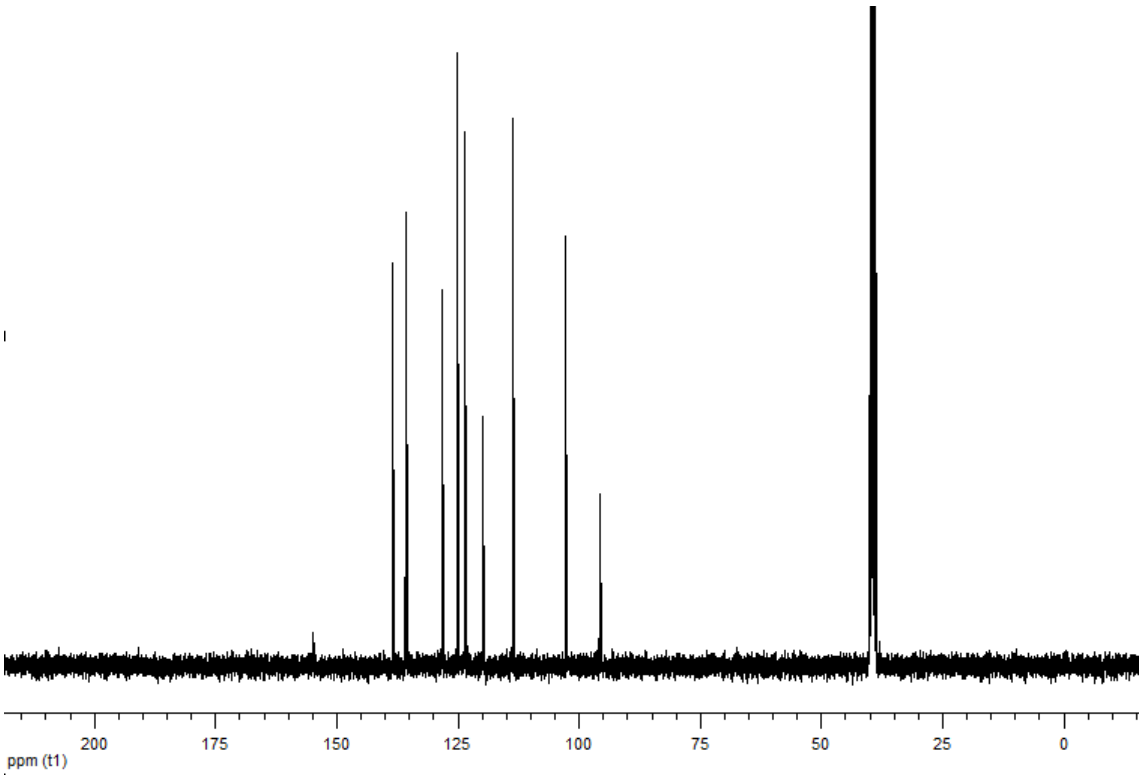

Figure S63. 100 MHz ^{13}C NMR spectrum of compound **3n** in DMSO-d_6.

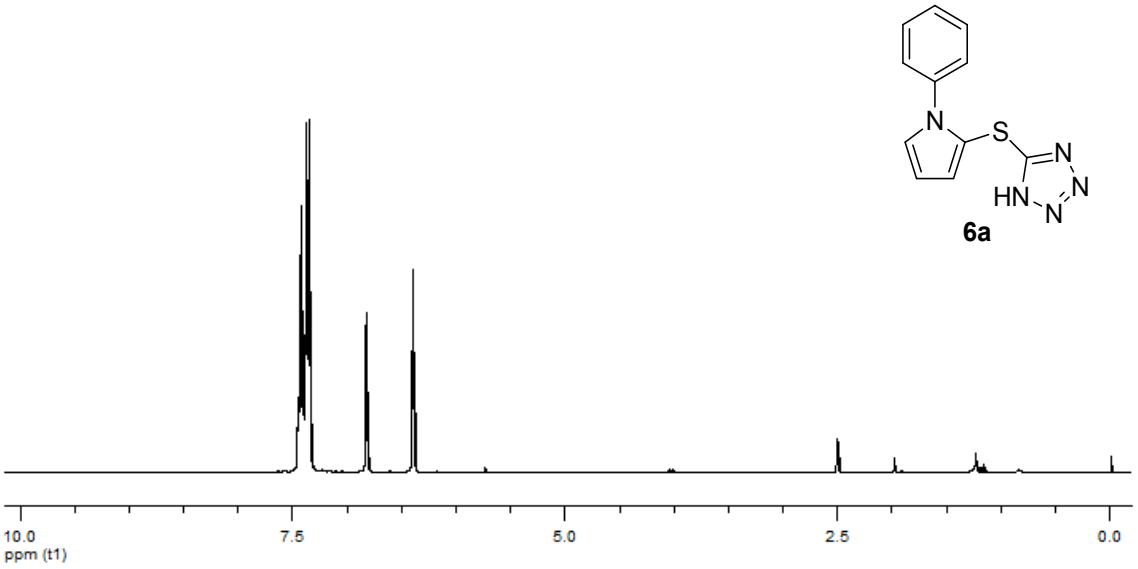

Figure S64. 400 MHz ^{1}H NMR spectrum of compound **6a** in DMSO-d_6.

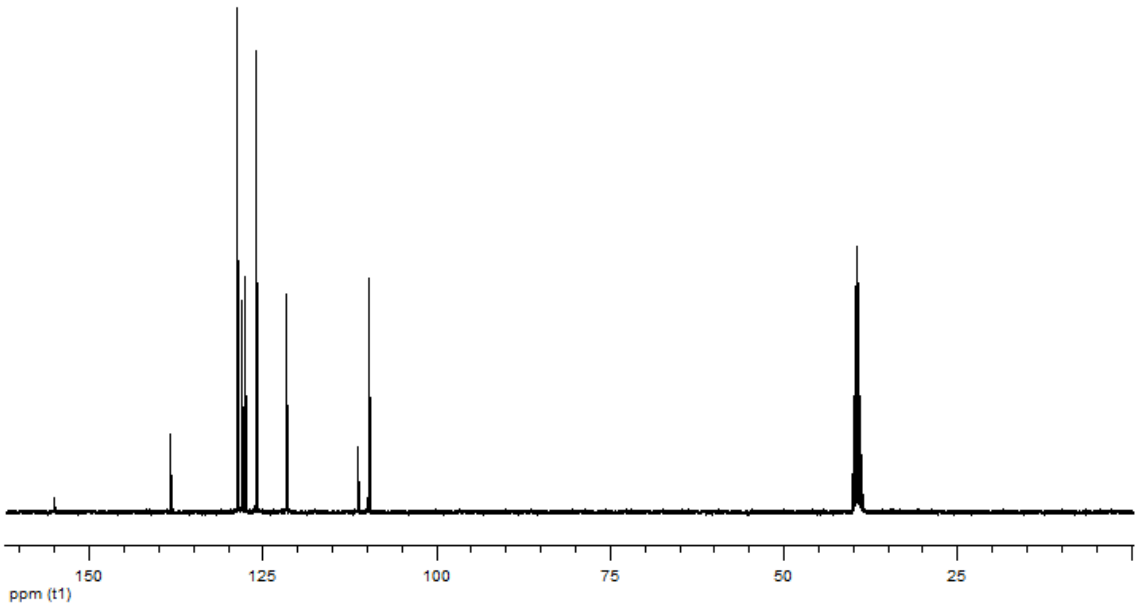

Figure S65. 100 MHz ^{13}C NMR spectrum of compound **6a** in DMSO-d_6.

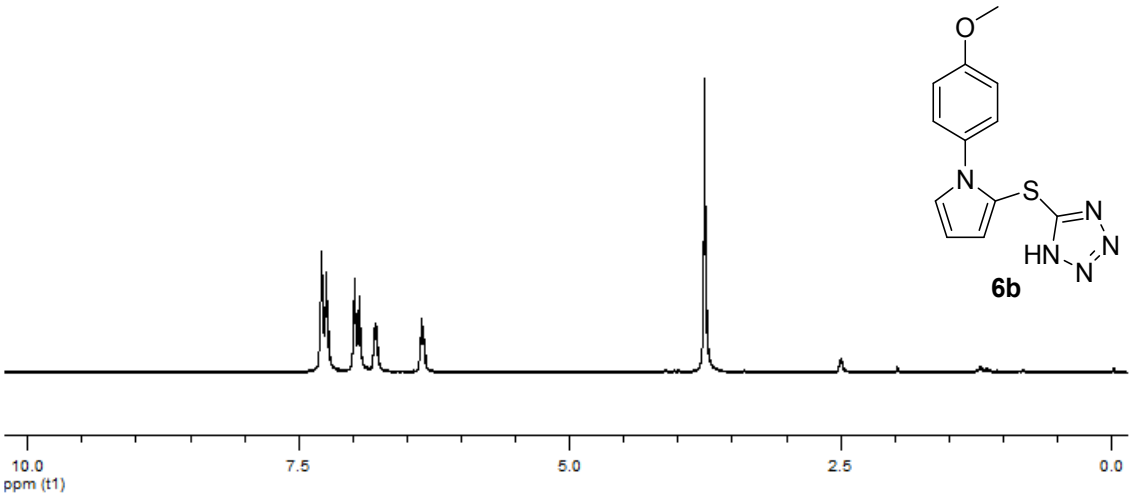

Figure S66. 200 MHz ^{1}H NMR spectrum of compound **6b** in DMSO-d_6.

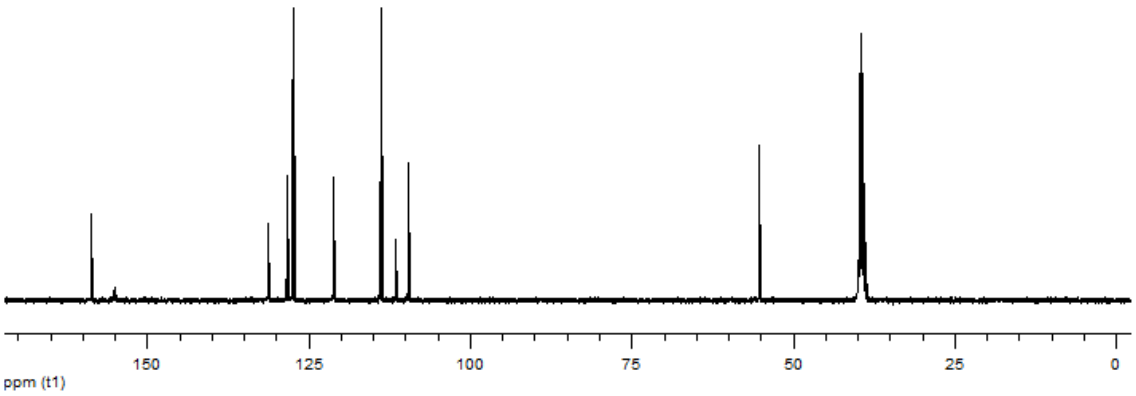

Figure S67. 100 MHz ^{13}C NMR spectrum of compound **6b** in DMSO-d_6.

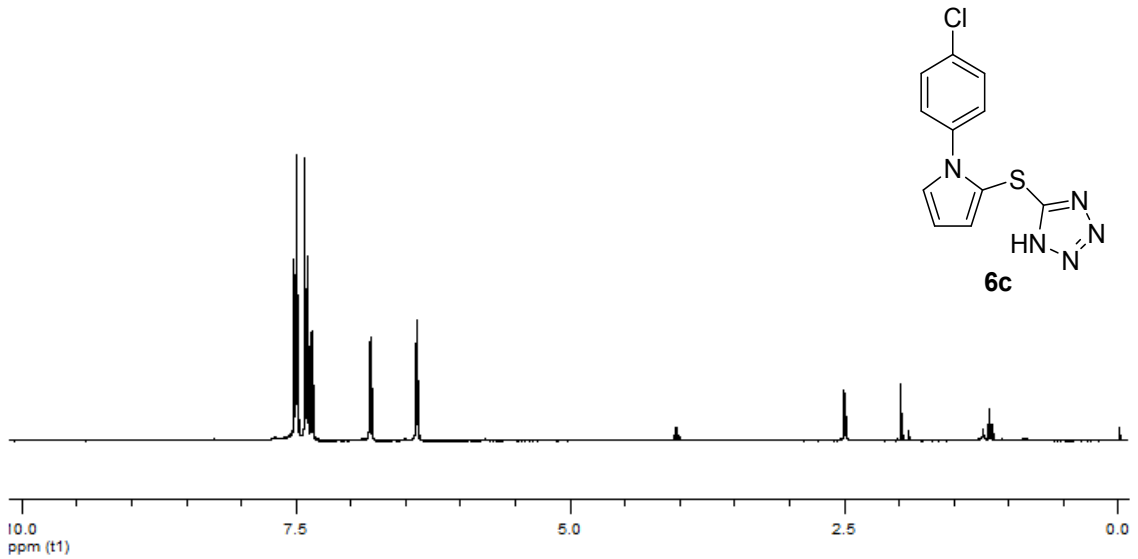

Figure S68. 400 MHz ^{1}H NMR spectrum of compound **6c** in DMSO-d_6.

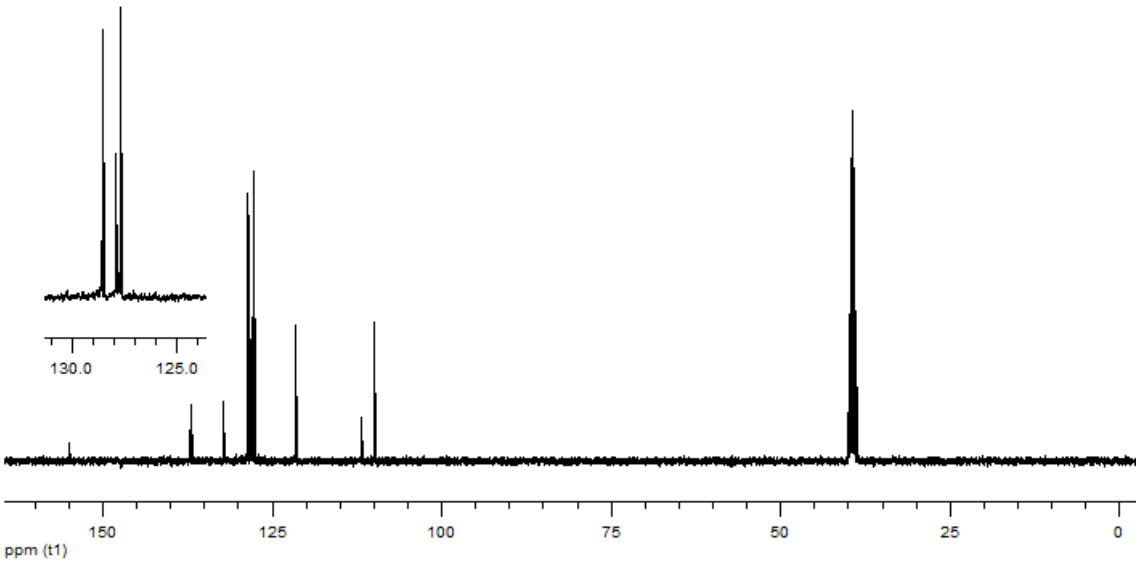

Figure S69. 100 MHz ^{13}C NMR spectrum of compound **6c** in DMSO-d_6.

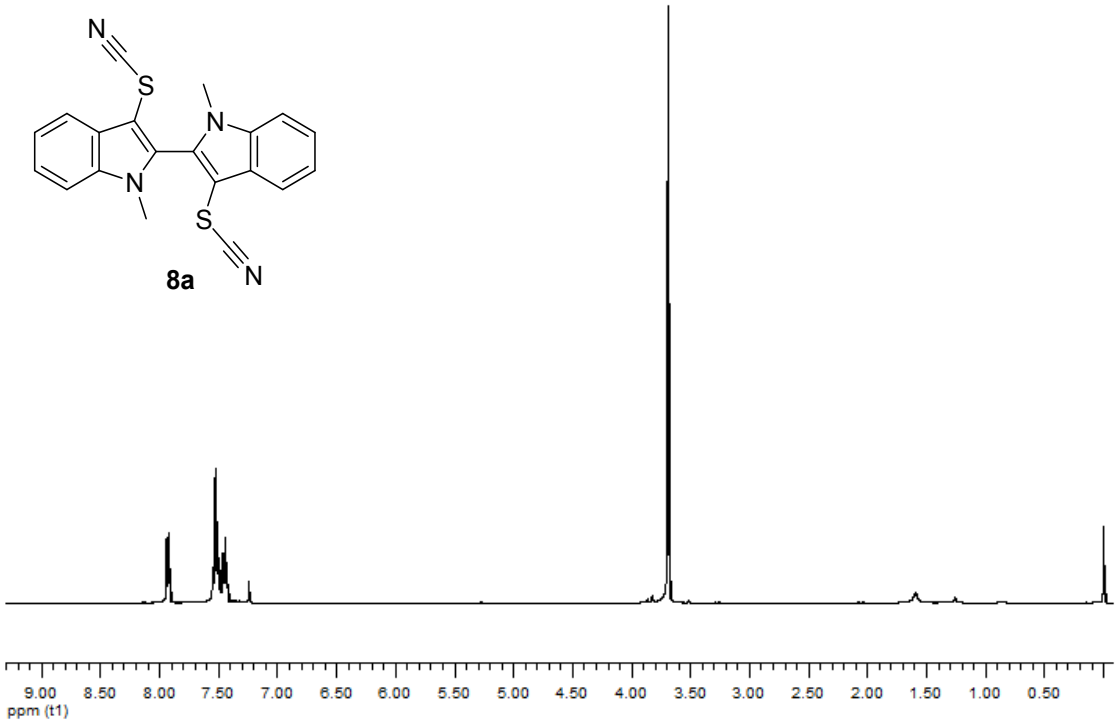

Figure S70. 400 MHz ^{1}H NMR spectrum of compound **8a** in DMSO-d_6.

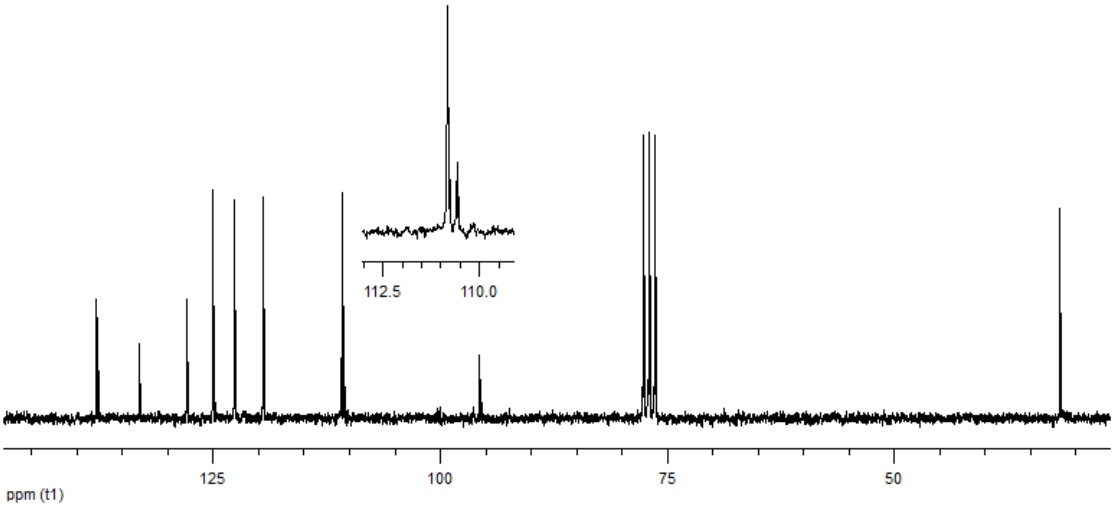

Figure S71. 50 MHz ^{13}C NMR spectrum of compound **8a** in DMSO-d_6.

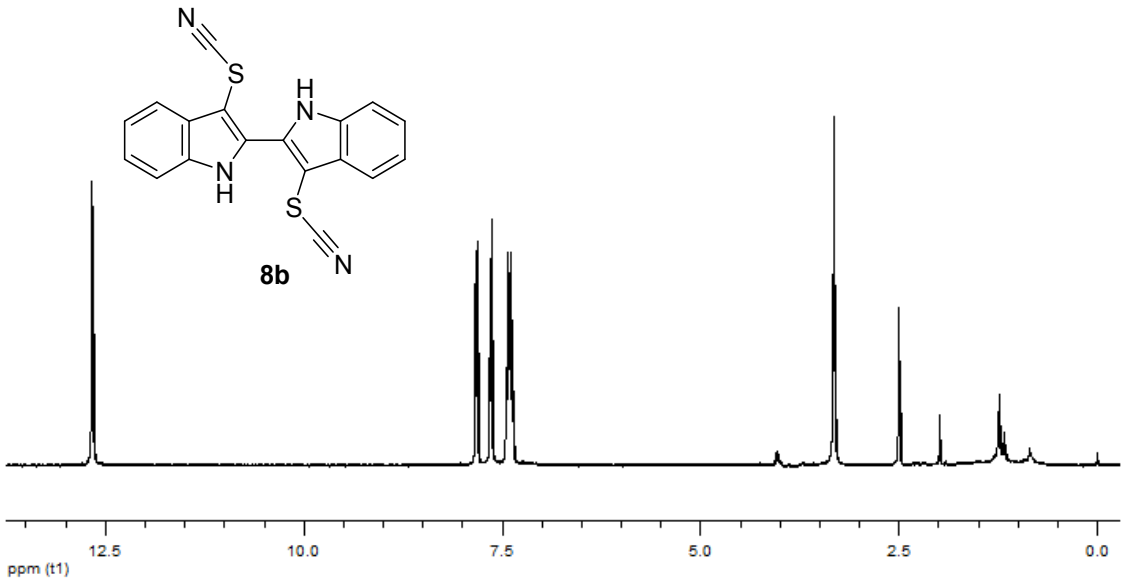

Figure S72. 400 MHz ^{1}H NMR spectrum of compound **8b** in DMSO-d_6.

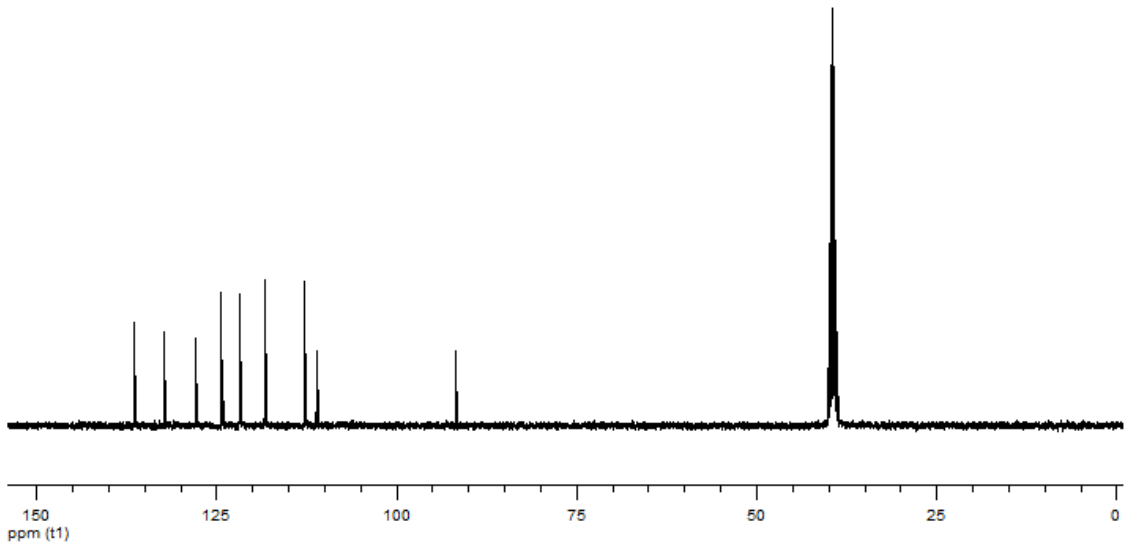

Figure S73. 100 MHz ^{13}C NMR spectrum of compound **8b** in DMSO-d_6.

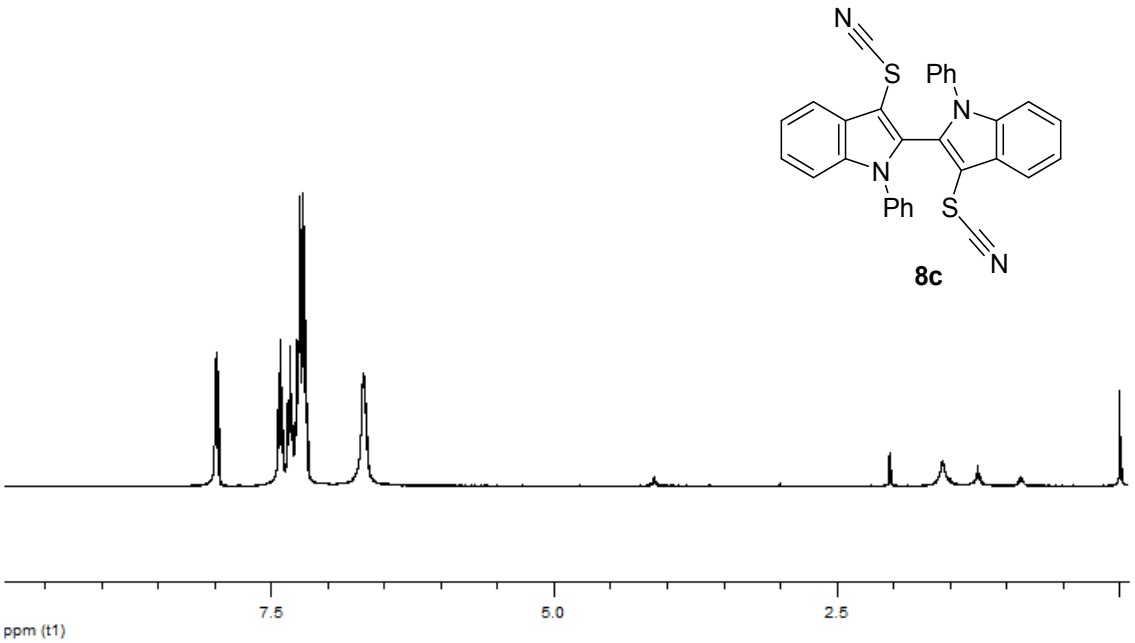

Figure S74. 400 MHz ^{1}H NMR spectrum of compound **8c** in DMSO-d_6.

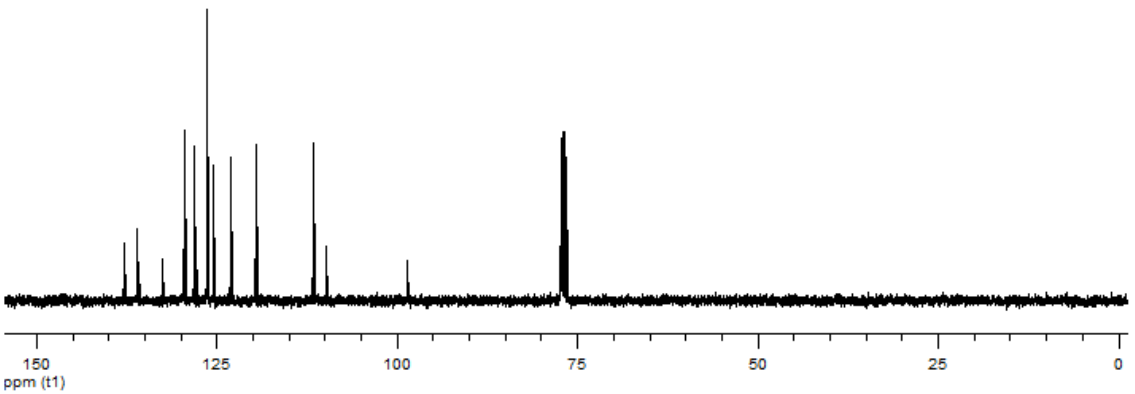

Figure S75. 100 MHz ^{13}C NMR spectrum of compound **8c** in DMSO-d_6.

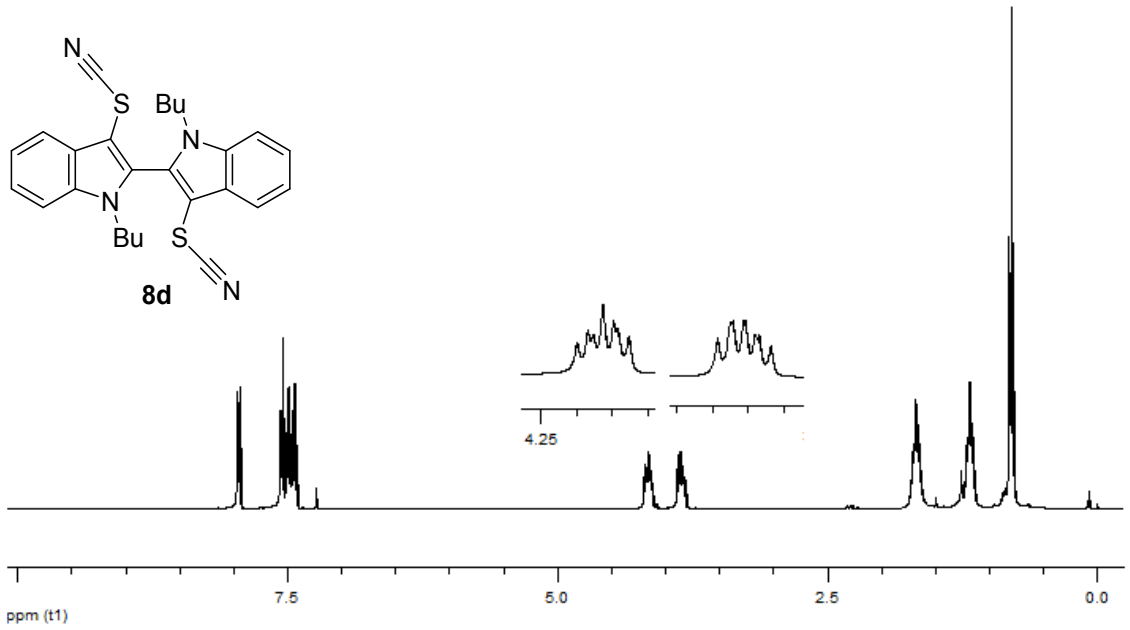

Figure S76. 400 MHz ^{1}H NMR spectrum of compound **8d** in DMSO-d_6.

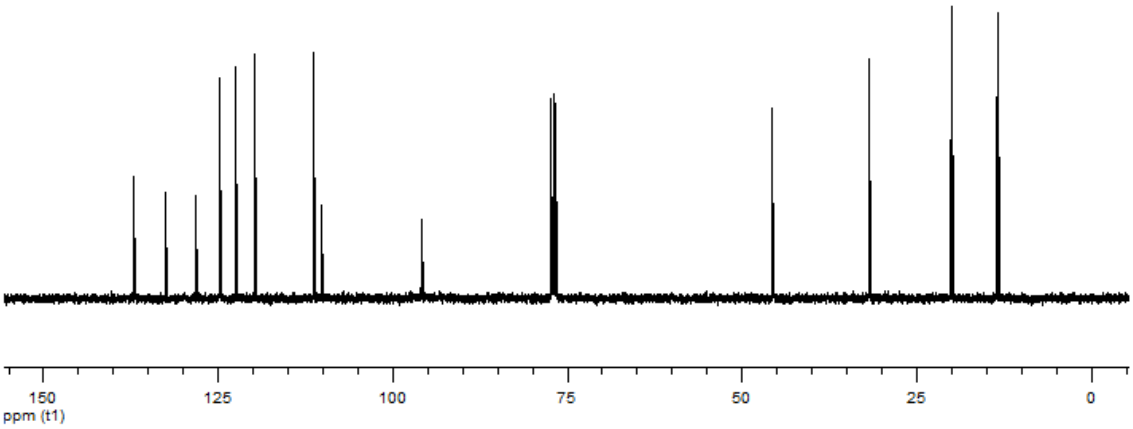

Figure S77. 100 MHz ^{13}C NMR spectrum of compound **8d** in DMSO-d_6.

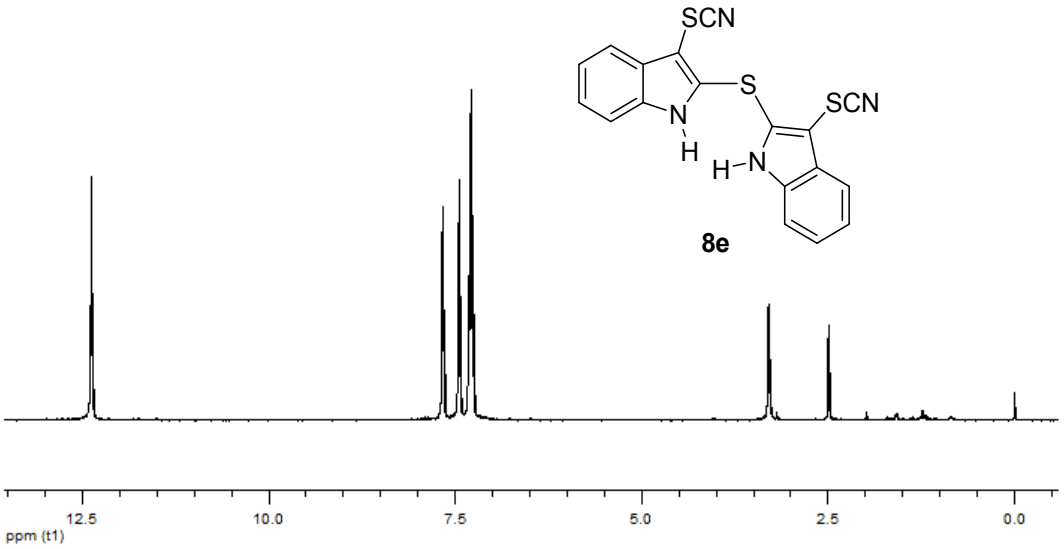

Figure S78. 400 MHz ^{1}H NMR spectrum of compound **8e** in DMSO-d_6.

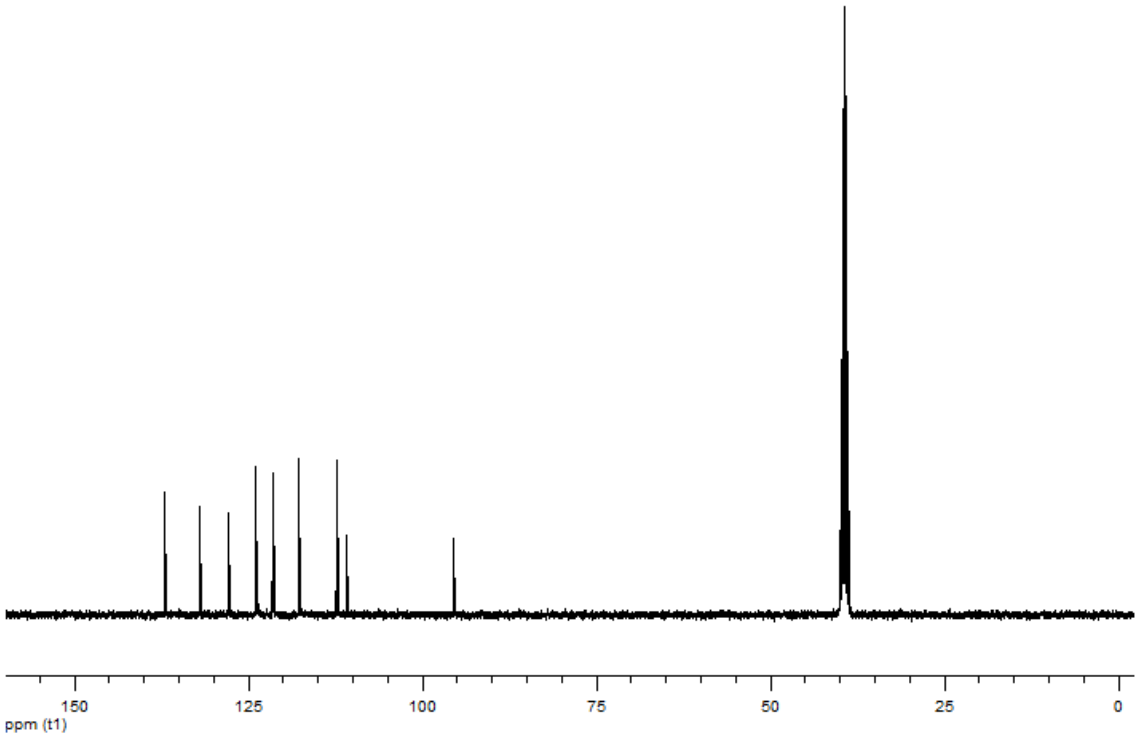

Figure S79. 100 MHz ^{13}C NMR spectrum of compound **8e** in DMSO-d_6.

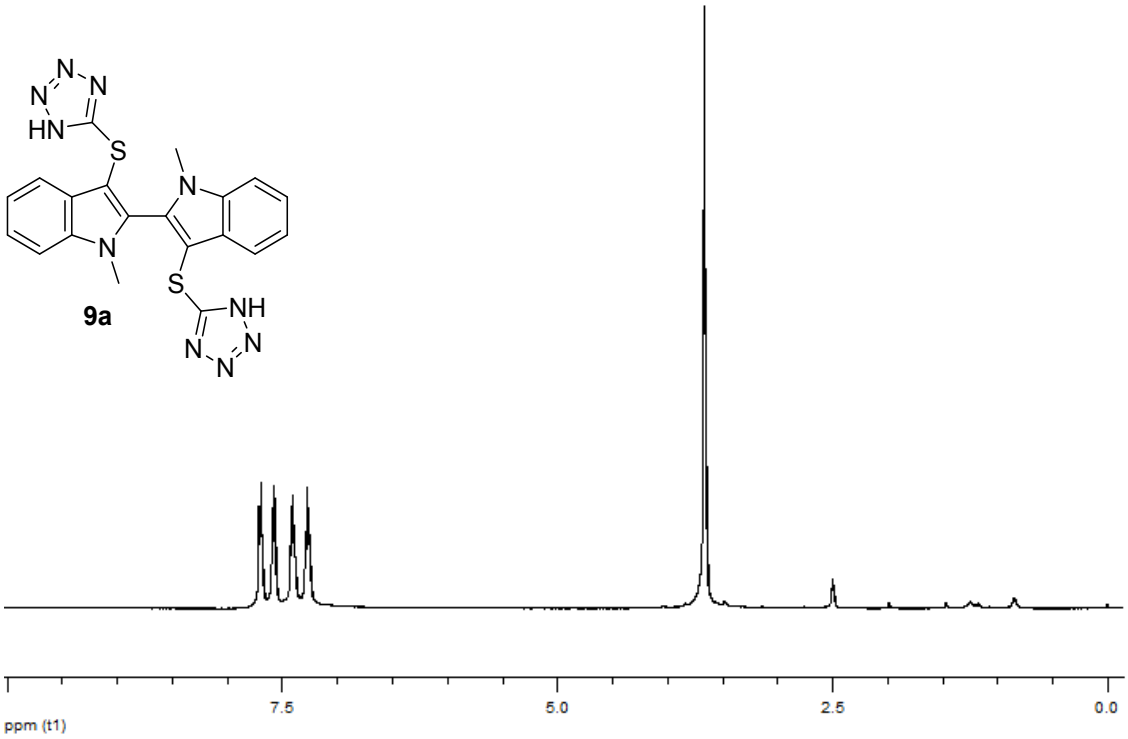

Figure S80. 400 MHz ^{1}H NMR spectrum of compound **9a** in DMSO-d_6.

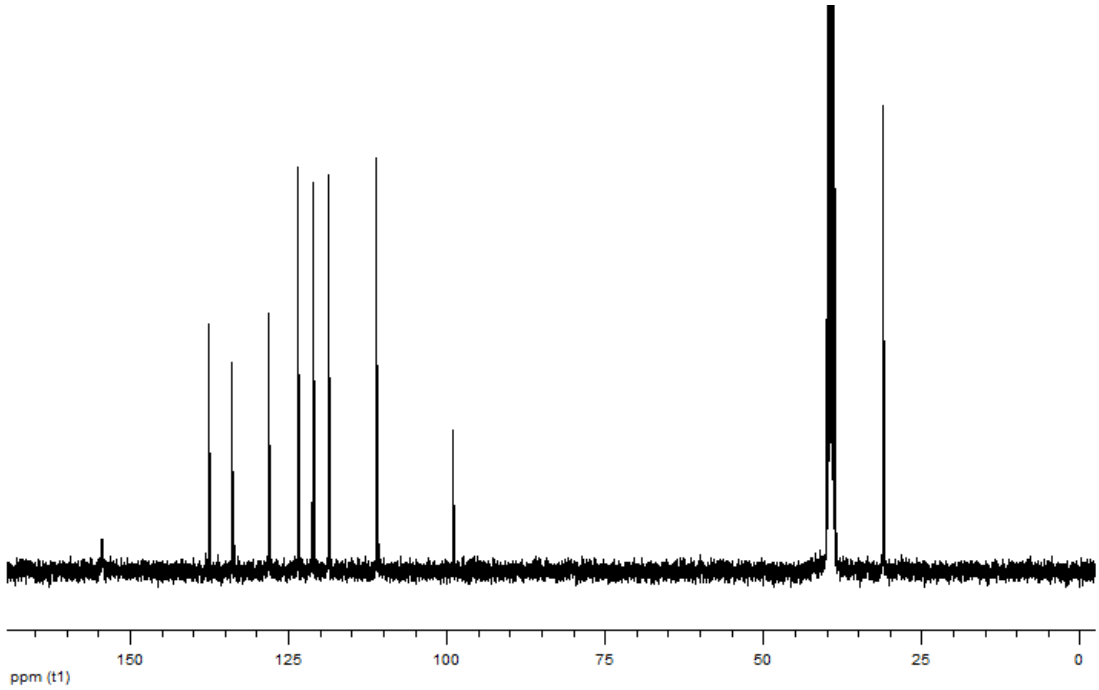

Figure S81. 100 MHz ^{13}C NMR spectrum of compound **9a** in DMSO-d_6.

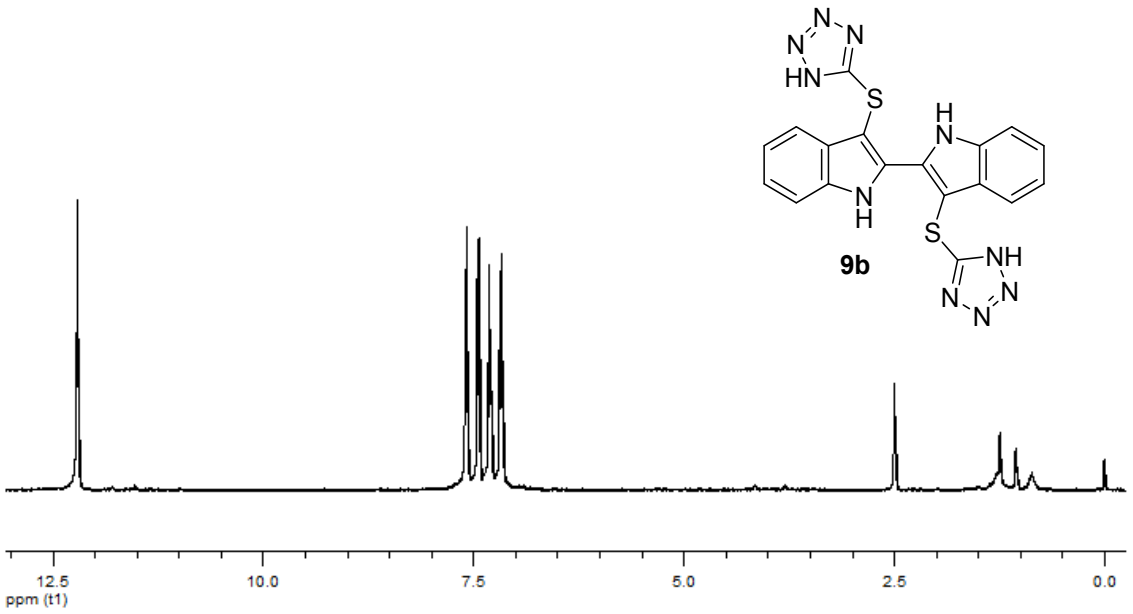

Figure S82. 400 MHz ^{1}H NMR spectrum of compound **9b** in DMSO-d_6.

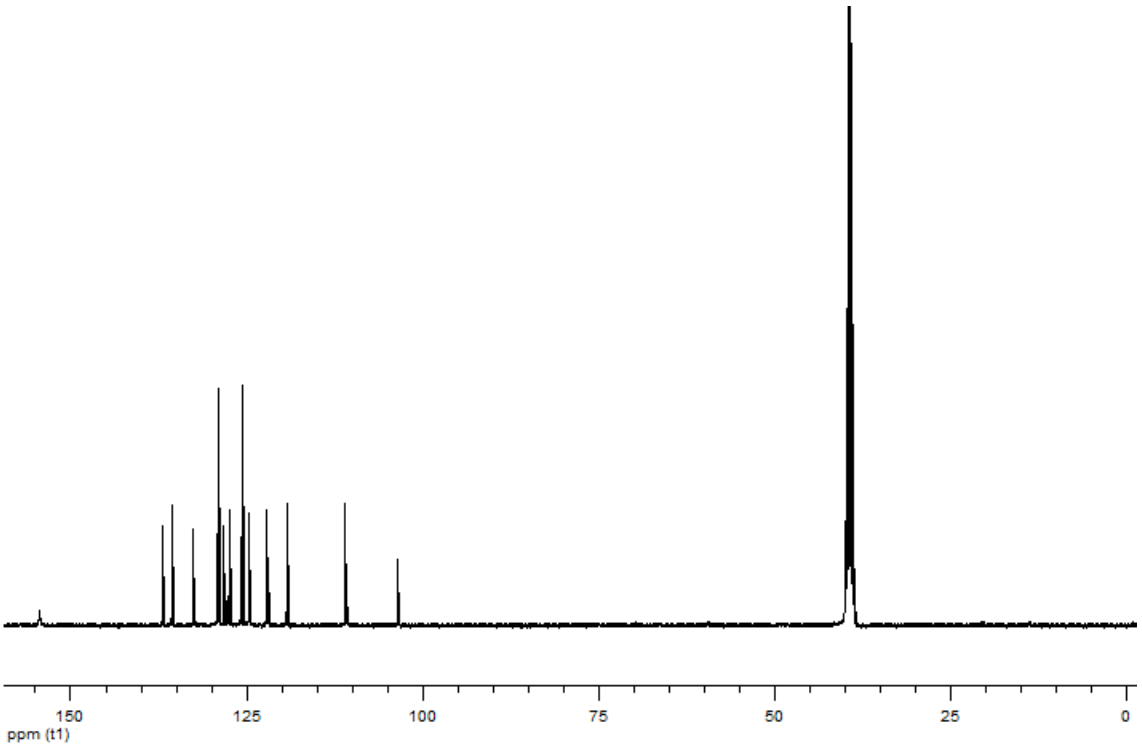

Figure S83. 100 MHz ^{13}C NMR spectrum of compound **9b** in DMSO-d_6.

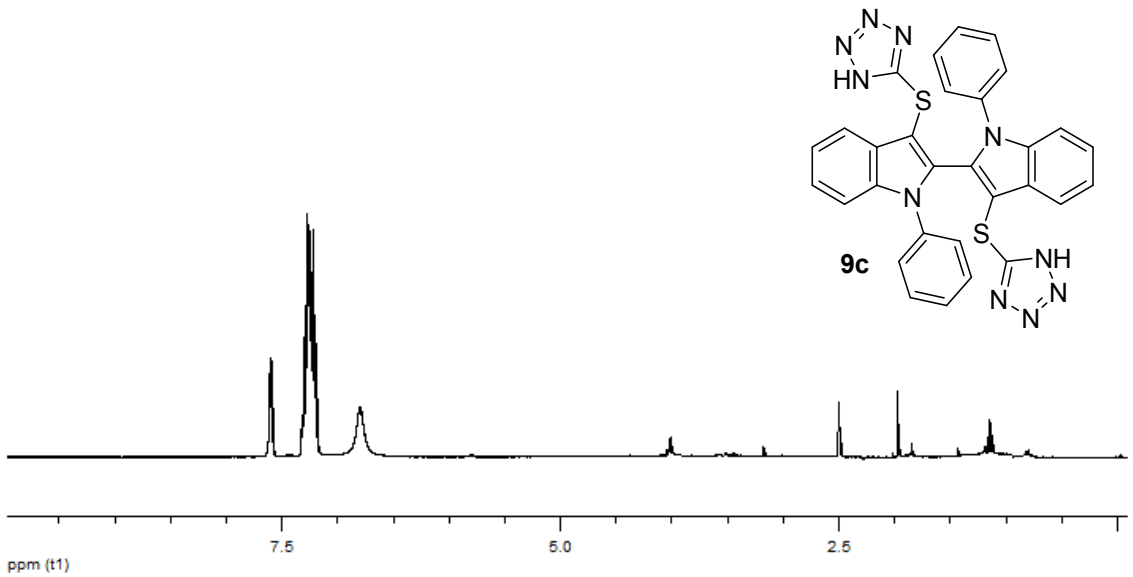

Figure S84. 400 MHz ^{1}H NMR spectrum of compound **9c** in DMSO-d_6.

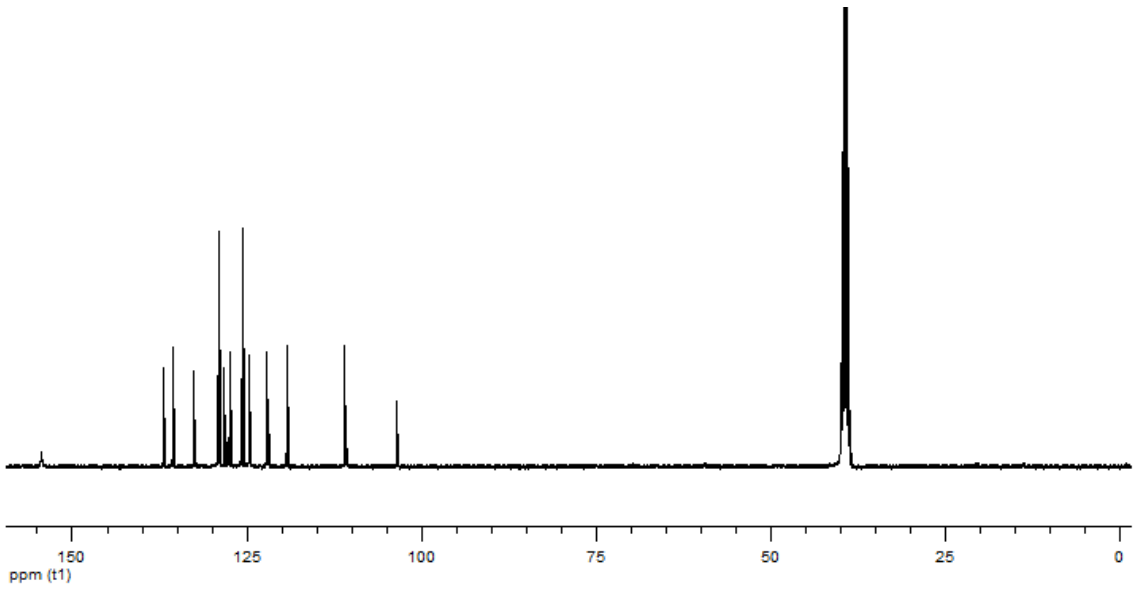

Figure S85. 100 MHz ^{13}C NMR spectrum of compound **9c** in DMSO-d_6.

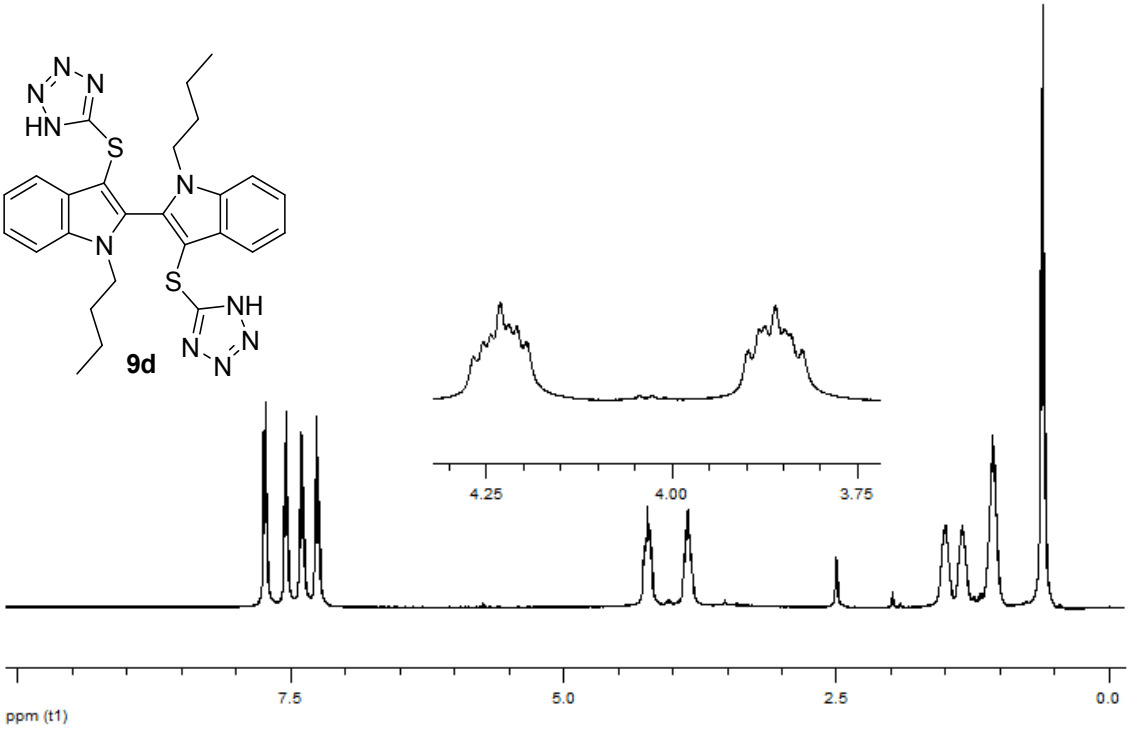

Figure S86. 400 MHz ^{1}H NMR spectrum of compound **9d** in DMSO-d_6.

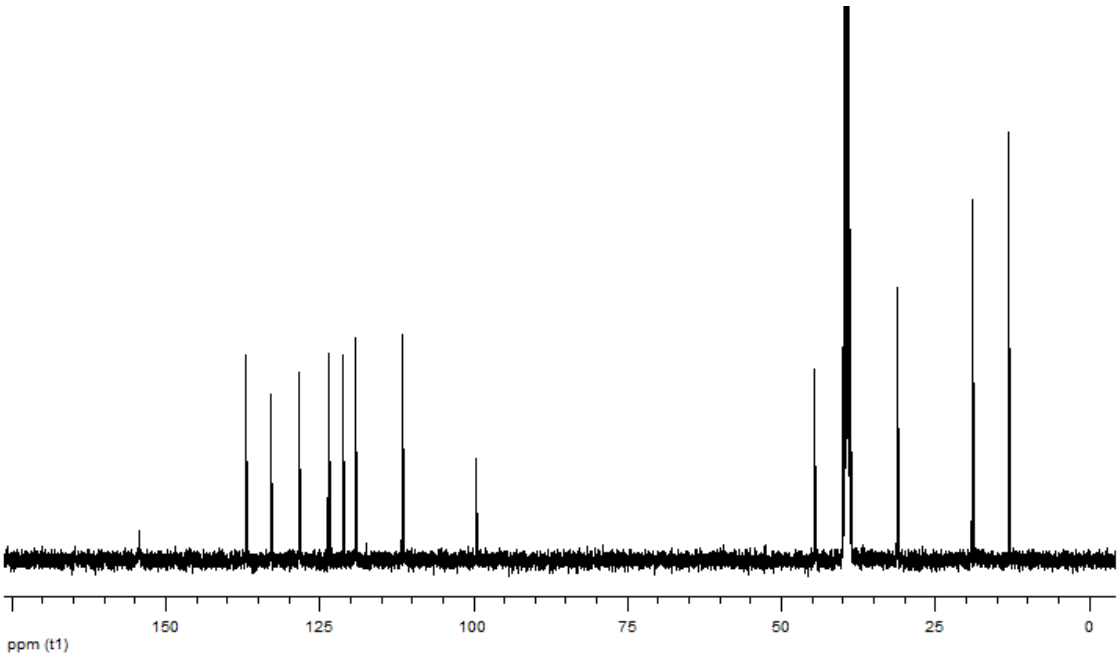

Figure S87. 100 MHz ^{13}C NMR spectrum of compound **9d** in DMSO-d_6.

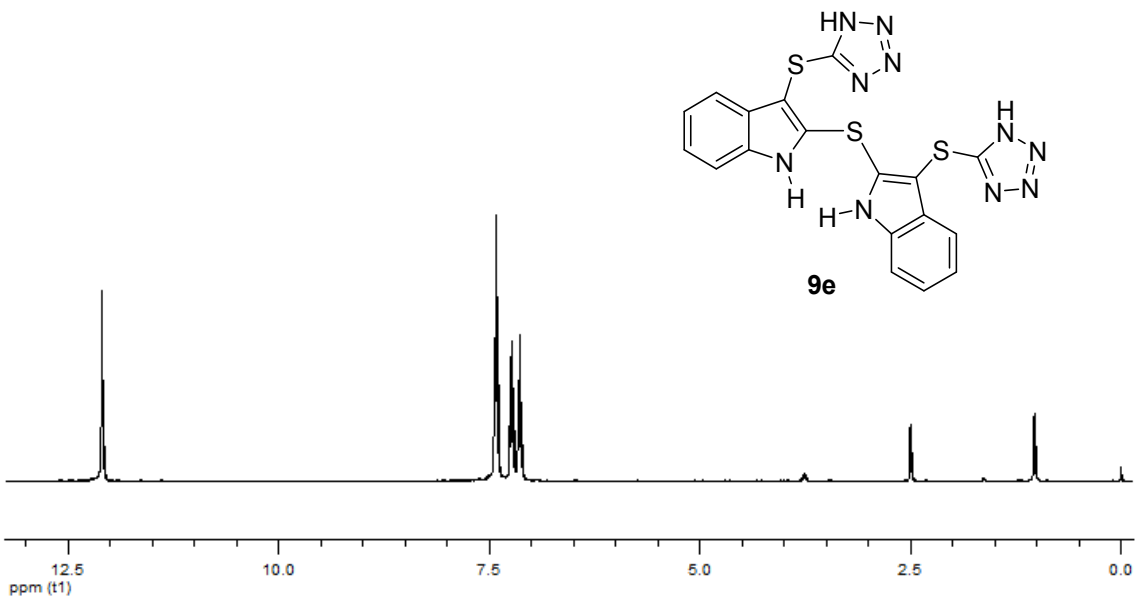

Figure S88. 400 MHz ^{1}H NMR spectrum of compound **9e** in DMSO-d_6.

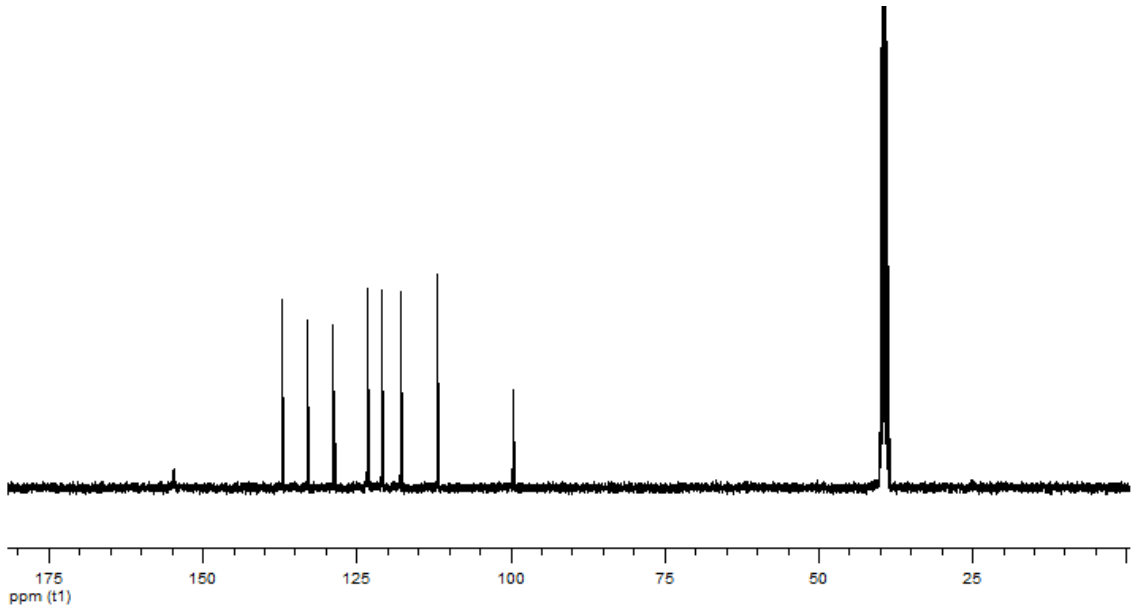

Figure S89. 100 MHz ^{13}C NMR spectrum of compound **9e** in DMSO-d_6.

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