Electronic Supplementary Information

A macrocycle based new organometallic nano-vessel towards sustainable C2-selective arylation of free indole in water

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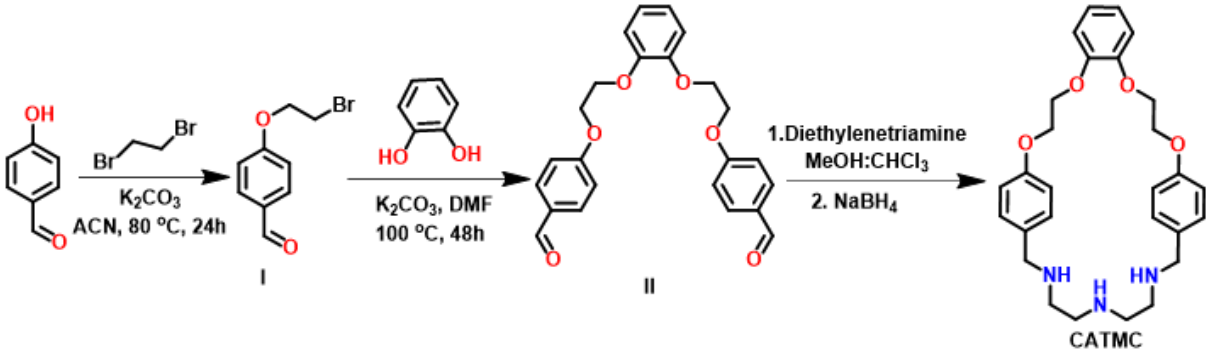
I. General Details

All the starting materials were purchased from commercial sources such as Sigma-Aldrich, Merck, Spectrochem and Alfa Aesar and were used as received without further purification. High resolution mass spectra were measured on Q-Tof micro-MS system by electron spray ionization (ESI) technique. All the NMR experiments were obtained on 300 MHz, 400 MHz and 600 MHz Bruker DPX. The Single Crystal XRD data were collected using Bruker SC-XRD. The absorption spectra were recorded with a Perkin Elmer Lambda 950 UV/VIS-NIR scanning spectrophotometer at 298 K.

II. Experimental procedures and data

1. Synthesis of macrocycle (**CATMC**)[S1]:

Initially, compound **I** was synthesised by using dibromoethane and 4-hydroxybenzaldehyde as starting materials in ACN solvent in presence of K_2CO_3 under reflux condition for 24h. Further dehydrobromination reaction occur with catechol in DMF solvent under similar basic condition to provide the corresponding compound **II**. Then macrocycle has been synthesised using high dilution principle as follows-



Scheme 1S. Synthesis of **CATMC**

In a 500ml two neck round bottom flask compound **II** (406 mg, 1mmol) was dissolved in CH_2Cl_2 in a pressure equalizer funnel and in another pressure-equalizing funnel Diethylenetriamine (108 µl, 1mmol) was dissolved in CH_3OH. The reactants were added dropwise to CH_2Cl_2-CH_3OH solvent mixture at stirring condition at room temperature under N_2 for 15h. After complete addition of above reactants, $NaBH_4$ (113 mg, 3mmol) was added and stirred another 4 hours at room temperature. Then, the reaction mixture was filtered and removed solvent in vacuo. The crude was extracted with $CHCl_3$ and water. After drying over sodium sulphate, the organic layer was completely evaporated and washed with diethyl ether to get the pure white solid product. Yield 83% (395mg). ^{1}H-NMR (400 MHz, DMSO-d_6) δ 7.15 (4H, d, J =11.2 Hz), 7.06 (2H, dd, J = 8.0 Hz, 4.8Hz), 6.94 (2H, dd, J = 8.0 Hz, 4.8 Hz), 6.80 (4H, d, J = 11.6 Hz), 4.27-4.23 (8H, m), 3.56 (4H, brs), 2.61 (8H, brs); ^{13}C-NMR (125 MHz, DMSO-d_6) δ 157.8, 149.0, 133.4, 129.6, 122.1, 115.2, 114.6, 68.3, 67.3, 52.7, 48.2, 48.0.

2. Synthesis of **CATMC-Pd**:

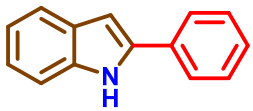
$PdCl_2$ (1 mmol) was added to the solution of **CATMC** (1mmol) in ACN and the mixture was stirred at 50-60 °C for 3-4 hours. Then solvent was evaporated and the solid residue was washed with diethyl-ether to get the pale yellowish crystalline **CATMC-Pd**. ^{1}H-NMR (600 MHz, DMSO-d_6) δ 7.74 (4H, d, J = 8.4 Hz), 7.15 (4H, d, J = 8.4 Hz), 7.08 (2H, dd, J = 6.0 Hz, 3.6 Hz), 6.94 (2H, dd, J = 6.0 Hz, 3.6 Hz,), 6.75 (2H, d, J = 7.8 Hz,), 6.34 (1H, t, J = 10.5 Hz), 4.43 (4H, t, J = 8.7 Hz), 4.22 (2H, t, J = 9.0 Hz), 4.16 (2H, t, J = 9.3 Hz), 4.05 (2H, dd, J = 12.6 Hz, 2.4 Hz), 3.07 (2H, dd, J = 12.3 Hz, 2.1 Hz), 2.72 (2H, dd, J = 24.7 Hz, 11.4 Hz), 2.61 (2H, d, J = 12.0 Hz), 2.41 – 2.33 (4H, m); ^{13}C-NMR (125 MHz, DMSO-d_6) δ 158.8, 148.6, 133.5, 127.2, 121.7, 115.1, 114.3, 67.3, 66.7, 53.4, 52.5, 52.2.

3. General procedure for synthesis of 2-arylindole compounds (3a-3ah):

In a 10mL round bottom flask corresponding indoles (1 mmol) and boronic acids (1.2 mmol) were taken in 2mL of water then **CATMC-Pd** complex (5 mol%) was added and overall reaction mixture was allowed to stir for another 12 h at 50 °C. Then the solvent was evaporated. All the crude products were extracted by chloroform and were purified by column chromatography.

4. Spectral Data of 2-arylindole derivatives:

2-phenyl-1H-indole (3a)[S2]**:** White solid (84%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.34 (1H, brs), 7.70 (3H, d, J = 7.6Hz), 7.49 (2H, t, J = 7.8Hz), 7.44 (1H, d, J = 8Hz), 7.38 (1H, t, J = 7.2 Hz), 7.26 (1H, t, J = 7.0 Hz), 7.19 (1H, t, J = 7.4 Hz), 6.89 (1H, s); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 137.9, 136.8, 132.4, 129.3, 129.0, 127.7, 125.2, 122.4, 120.7, 120.3, 110.9, 100.0; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{12}N$ 194.0965; Found 194.0969, m.p. 187-189 °C.



2-(p-tolyl)-1H-indole (3b)[S2]**:** White solid (86%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.31(1H, brs), 7.64 (1H, d, J = 7.5 Hz), 7.57 (2H, d, J = 8.1 Hz), 7.40 (1H, d, J = 8.1 Hz), 7.26 (2H, d, J = 7.8 Hz), 7.23-7.11(2H, m), 6.80 (1H, t, J =1.0 Hz), 2.41(3H, s); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 138.2, 137.8, 136.9, 129.9, 129.8, 129.5, 125.2, 122.3, 120.7, 120.4, 111.0, 99.6, 21.4; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{14}N$ 208.1121; Found 208.1128, m.p. 211-213 °C.

2-(4-ethylphenyl)-1H-indole (3c)[S3]**:** White solid (87%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.31(1H, brs), 7.65 (1H, d, J = 7.8 Hz), 7.60 (2H, d, J = 8.1 Hz), 7.40 (1H, d, J = 8.1 Hz), 7.30 (2H, d, J = 8.4 Hz), 7.21(1H, t, J = 6.9 Hz), 7.14 (1H, t, J = 7.2 Hz), 6.81(1H, d, J = 1.8 Hz), 2.71(2H, q, J = 7.6 Hz), 1.30 (3H, t, J = 7.6 HZ); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 144.2, 138.2, 136.9, 130.0, 129.5, 128.7, 125.3, 122.3, 120.7, 120.3, 111.0, 99.6, 28.8, 15.6; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{16}N$ 222.1278; Found 222.1284, m.p. 194-196 °C.

2-(4-propylphenyl)-1H-indole (3d)[S4]**:** White solid (87%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.31(1H, brs), 7.62 (1H, d, J = 7.6 Hz), 7.58 (2H, d, J = 8 Hz), 7.40 (1H, d, J = 8 Hz), 7.25 (2H, t, J = 4.0 Hz), 7.17 (1H, t, J=7.2 Hz), 7.11 (1H, t, J = 7.2 Hz), 6.78 (1H, s), 2.62(2H, t, J = 7.6 Hz), 1.72-1.63 (2H, m), 0.97 (3H, t, J = 7.4 Hz); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 142.5, 138.1, 136.7, 129.9, 129.4, 129.1, 125.1, 122.1, 120.5, 120.2, 110.8, 99.4, 37.8, 24.5, 13.8; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{18}N$ 236.1434; Found 236.1440, m.p. 197-199 °C.

2-(4-(tert-butyl)phenyl)-1H-indole (3e)[S5]**:** White solid (87%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.30 (1H, brs), 7.68(1H, d, J = 7.5 Hz), 7.61 (2H, d, J = 8.4 Hz), 7.50 (2H, d, J = 8.4 Hz), 7.41 (1H, d, J = 7.8 Hz), 7.26-7.16 (2H, m), 6.85 (1H, d, 1.5 Hz), 1.41 (9H, s); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 150.9, 138.0, 136.8, 129.6, 129.4, 126.0, 125.0, 122.2, 120.6, 120.2, 110.9, 99.6, 34.7, 31.4; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{20}N$ 250.1591; Found 250.1596, m.p. 186-189 °C.

2-(3,5-dimethylphenyl)-1H-indole (3f)[S6]**:** White solid (86%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.33 (1H, brs), 7.62 (1H, d, J=8 Hz), 7.39(1H, d, J=8 Hz), 7.30(2H, s), 7.18(1H, t, J=7.6 Hz), 7.11(1H, t, J=7.4 Hz), 6.98(1H, s), 6.80(1H, s), 2.39 (6H, s); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 138.6, 136.7,

132.2, 129.5, 129.3, 125.0, 123.1, 122.2, 120.6, 120.2, 110.8, 99.8, 21.4; HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{16}H_{16}N$ 222.1278; Found 222.1283, m.p. 116-118 °C.

2-(4-phenoxyphenyl)-1H-indole (3g)[S7]**:** White crystalline (88%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.29 (1H, brs), 7.63 (3H, d, J = 8.8 Hz), 7.38 (3H, dd, J = 13.6 Hz, J = 8 Hz), 7.21-7.06 (7H, m), 6.76 (1H, s); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 157.1, 156.9, 136.8, 129.9, 129.4, 127.6, 126.6, 123.6, 122.2, 120.5, 120.3, 119.2, 119.2, 110.8, 99.6; HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{20}H_{16}NO$ 286.1227; Found 286.1230, m.p. 168-170 °C.

2-(3,5-difluorophenyl)-1H-indole (3h)[S8]: White crystalline (82%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.32(1H, brs), 7.65 (1H, d, J = 8.1 Hz), 7.41 (1H, d, J = 8.4 Hz), 7.27-7.24 (1H, m), 7.22-7.14 (3H, m), 6.86 (1H, brs), 6.80-6.72 (1H, m); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 165.2, 137.2, 135.7, 129.0, 123.4, 121.2, 120.8, 111.2, 108.2, 107.8, 102.9, 101.9; HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{14}H_{20}F_2N$ 230.0776; Found 230.0782, m.p. 125-127 °C.

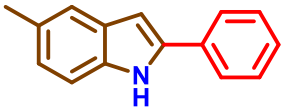
2-(4-(trifluoromethyl)phenyl)-1H-indole (3i)[S2]**:** White crystalline (85%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.36 (1H, brs), 7.76 (2H, d, J = 8.1 Hz), 7.70-7.64 (3H, m), 7.43 (1H, d, J = 8.1 Hz), 7.27-7.22 (1H, m), 7.15 (1H, t, J = 7.5 Hz), 6.93 (1H, d, J = 1.2 Hz); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 137.2, 136.1, 135.7, 129.0, 126.1, 126.0, 125.1, 123.2, 121.1, 120.7, 111.1, 101.7; HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{15}H_{11}F_3N$ 262.0838; Found 262.0835, m.p. 233-235 °C.

2-(3-nitrophenyl)-1H-indole (3j)[S9]**:** Yellowish crystalline (83%); ^{1}H-NMR (400 MHz, DMSO-d_6) δ 11.63 (1H, brs), 8.47 (1H, s), 8.17 (1H, d, J = 7.6 Hz), 8.06 (1H, d, J = 8.4 Hz), 7.97 (1H, d, J = 2.4 Hz), 7.92 (1H, d, J = 7.6 Hz), 7.71 (1H, t, J = 8 Hz), 7.50 (1H, d, J = 8 Hz), 7.23-7.16 (2H, m); ^{13}C-NMR (151 MHz, $CDCl_3$) δ 148.8, 137.4, 136.7, 133.0, 129.6, 125.2, 123.0, 122.7, 121.8, 121.0, 120.6, 119.3, 116.2, 111.7; HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{14}H_{11}N_2O_2$ 239.0815; Found 239.0819, m.p. 164-167 °C.

2-(naphthalen-2-yl)-1H-indole (3k)[S2]**:** White crystalline (86%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.49 (1H, brs), 8.05 (1H, s), 7.92-7.81 (4H, m), 7.68 (1H, d, J = 7.8 Hz), 7.55-7.42 (3H, m), 7.26-7.13 (2H, m), 6.97 (1H, d, J = 1.5 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 137.9, 137.1, 133.7, 132.9,

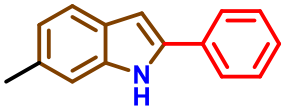
129.8, 129.4, 128.8, 128.1, 127.9, 126.8, 126.2, 123.9, 123.1, 122.6, 120.8, 120.4, 111.0, 100.8; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{14}N$ 244.1121; Found 244.1126, m.p. 194-196 °C.

5-methyl-2-phenyl-1H-indole (3l)[S2]**:** White solid (85%); ^{1}H-NMR (400 MHz, $CDCl_3$)



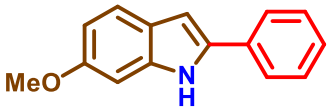
δ 8.27 (1H, brs), 7.68 (2H, d, *J* = 7.6 Hz), 7.49-7.47 (3H, m), 7.38-7.28 (2H, m), 7.07 (1H, d, *J* = 8.4 Hz), 6.80 (1H, s), 2.50 (3H, s); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 138.0, 135.2, 132.5, 129.6, 129.5, 129.0, 127.6, 125.1, 124.0, 120.3, 110.6, 99.6, 21.5; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{14}N$ 208.1121; Found 208.1124, m.p. 216-219 °C.

6-methyl-2-phenyl-1H-indole (3m)[S10]: White solid (84%); ^{1}H-NMR (300 MHz,



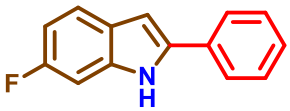
$CDCl_3$) δ 8.18 (1H, brs), 7.65 (2H, d, *J* =7.5 Hz), 7.52 (1H, d, *J* = 7.8 Hz), 7.44 (2H, t, *J* = 7.6 Hz), 7.31 (1H, t, *J* = 6.9 Hz), 7.19 (1H, s), 6.97 (1H, d, *J* = 8.1 Hz), 6.79 (1H, s), 2.48 (3H, s); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 137.4, 137.3, 132.6, 132.3, 129.1, 127.5, 127.2, 125.0, 122.1, 120.4, 110.9, 99.9, 21.9; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{14}N$ 208.1121; Found 208.1125, m.p. 193-195 °C.

6-methoxy-2-phenyl-1H-indole (3n)[S10]**:** White solid (83%); ^{1}H-NMR (400 MHz,



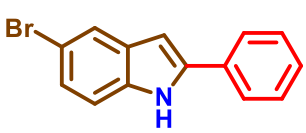
$CDCl_3$) δ 8.25(1H, brs), 7.65 (2H, d, *J* = 7.6 Hz), 7.52 (1H, d, *J* = 8.4 Hz), 7.45 (2H, t, *J* = 7.6 Hz), 7.32 (1H, t, *J* = 7.6 Hz), 6.93 (1H, s), 6.83 (1H, dd, *J* = 8.4 Hz, *J* = 2,4 Hz), 6.79 (1H, s), 3.89 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 137.7, 136.8, 132.6, 129.0, 127.3, 124.7, 123.6, 121.3, 110.2, 99.9, 94.5, 55.7; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{14}NO$ 224.1070; Found 224.1074, m.p. 162-164 °C.

6-fluoro-2-phenyl-1H-indole (3o)[S10]**:** White crystalline (88%); ^{1}H NMR (300 MHz,

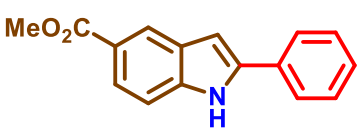


$CDCl_3$) δ 8.31 (1H, brs), 7.63 (2H, d, *J* = 7.2 Hz), 7.53 (1H, dd, *J* = 8.7 Hz, 5.4 Hz), 7.45 (2H, t, *J* = 7.5 Hz), 7.33 (1H, t, *J* = 7.4 Hz), 7.08 (1H, dd, *J* = 9.6 Hz, 2.2 Hz), 6.93-6.86 (1H, m), 6.79 (1H, dd, *J* = 2.2 Hz, 0.8 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 161.7, 158.6, 136.9, 136.7, 132.2, 129.1, 127.8, 125.9, 125.0, 121.5, 121.4, 109.3, 108.9, 99.9, 97.5, 97.2; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{11}FN$ 212.0870; Found 212.0866, m.p. 175-187 °C.

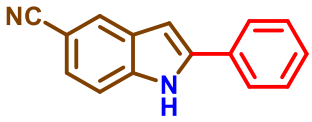
5-bromo-2-phenyl-1H-indole (3p)[S11]**:** White solid (86%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36 (1H, brs), 7.69-7.63 (2H, m), 7.44 (3H, dd, *J* = 15.6 Hz, 7.8 Hz), 7.33 (1H, dd, *J* = 8.4 Hz, 6.3 Hz), 7.19 (1H, dd, *J* = 8.1 Hz, 1.2 Hz), 7.15-7.10 (1H, m), 6.84 (1H, d, *J* = 1.8 Hz); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 137.9, 136.8, 132.4, 129.3, 129.0, 127.7, 125.2, 122.4, 120.7, 120.3, 110.9, 100.0; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{11}BrN$ 272.0069 (for ^{79}Br) and 274.0049 (for ^{81}Br); Found 272.0076 (for ^{79}Br) and 274.0056 (for ^{79}Br), m.p. 191-193 °C.



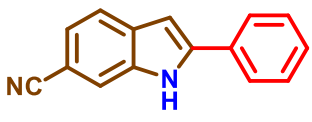
Methyl 2-phenyl-1H-indole-5-carboxylate (3q)[S2]**:** White solid (89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.40 (s, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 7.5 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 6.90 (s, 1H), 3.95 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 168.2, 139.4, 139.3, 131.8, 129.1, 128.8, 128.2, 125.3, 123.8, 123.6, 122.4, 110.6, 101.0, 51.9; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{14}NO_2$ 252.1019; Found 252.1026, m.p. 185-188 °C.



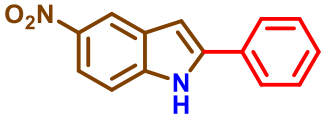
2-phenyl-1H-indole-5-carbonitrile (3r)[S11]**:** White solid (90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.97 (s, 1H), 7.68 (d, *J* = 7.5 Hz, 2H), 7.51 – 7.37 (m, 5H), 6.87 (s, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 140.4, 138.5, 131.3, 129.3, 129.1, 128.7, 126.1, 125.5, 125.3, 120.8, 111.8, 103.4, 100.3; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{11}N_2$ 219.0917; Found 219.0930, m.p. 194-196 °C.



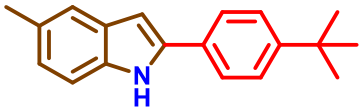
2-phenyl-1H-indole-6-carbonitrile (3s)[S12]**:** White solid (88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.74 (s, 1H), 7.69 (t, *J* = 8.7 Hz, 3H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 6.9 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 6.88 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 135.5, 132.5, 131.2, 129.3, 128.9, 125.6, 123.4, 121.3, 120.7, 115.6, 104.4, 100.5; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{11}N_2$ 219.0917; Found 219.0926, m.p. 232-234 °C.



5-nitro-2-phenyl-1H-indole (3t)[S11]**:** Yellowish crystalline (92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.59 (d, *J* = 2.0 Hz, 1H), 8.12 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.46 – 7.39 (m, 2H), 6.97 (d, *J* = 1.4 Hz, 1H); ^{13}C-NMR (101 MHz, CDCl3) δ 142.3, 141.2, 139.7, 131.1, 129.3, 128.8, 128.6, 125.4, 118.0, 117.7, 110.8, 101.7; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{11}N_2O_2$ 239.0815; Found 239.0826, m.p. 233-235°C.

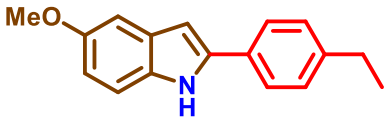


2-(4-(tert-butyl)phenyl)-5-methyl-1H-indole (3u)[S13]**:** White solid (86%); ^{1}H NMR



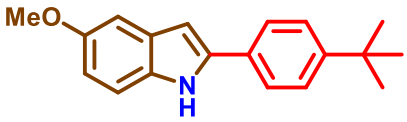
(400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.41 (s, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.72 (s, 1H), 2.46 (s, 3H), 1.37 (s, 9H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 150.8, 138.1, 135.1, 129.7, 129.4, 125.9, 124.8, 123.7, 120.2, 110.5, 99.1, 34.7, 31.3, 21.5; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{22}N$ 264.1747; Found 264.1741, m.p. 218-220 °C.

2-(4-ethylphenyl)-5-methoxy-1H-indole (3v): White solid (83%); ^{1}H NMR (300



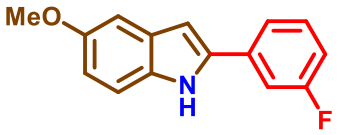
MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.57 – 7.49 (m, 2H), 7.24 (d, *J* = 7.9 Hz, 3H), 7.06 (d, *J* = 2.3 Hz, 1H), 6.82 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.70 (d, *J* = 1.4 Hz, 1H), 3.84 (s, 3H), 2.67 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 154.6, 144.1, 140.0, 132.1, 130.0, 128.6, 125.2, 112.4, 111.7, 102.4, 99.4, 56.0, 28.8, 15.6; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{18}NO$ 252.1383; Found 252.1391, m.p. 154-156 °C.

2-(4-(tert-butyl)phenyl)-5-methoxy-1H-indole (3w)[S14]**:** White solid (84%); ^{1}H NMR



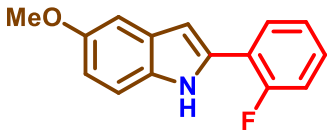
(400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.9 Hz, 1H), 7.11 (d, *J* = 1.9 Hz, 1H), 6.86 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.74 (s, 1H), 3.88 (s, 3H), 1.37 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 154.6, 151.0, 138.9, 132.1, 130.0, 129.8, 126.1, 125.0, 112.5, 111.7, 102.4, 99.5, 56.0, 34.8, 31.4; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{22}NO$ 280.1696; Found 280.1688, m.p. 248-250 °C.

2-(3-fluorophenyl)-5-methoxy-1H-indole (3x): White crystalline (82%); ^{1}H NMR



(300 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.39 (t, *J* = 5.3 Hz, 2H), 7.32 (dd, *J* = 17.1, 5.3 Hz, 2H), 7.09 (d, *J* = 2.3 Hz, 1H), 7.05 – 6.96 (m, 1H), 6.88 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.77 (d, *J* = 1.7 Hz, 1H), 3.87 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 161.9; 154.8, 137.4, 134.8, 132.2, 130.8, 129.7, 120.7, 114.6, 114.3, 113.4, 112.2, 111.9, 102.4, 100.8, 56.0; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{13}FNO$ 242.0976; Found 242.0981, m.p. 126-128 °C.

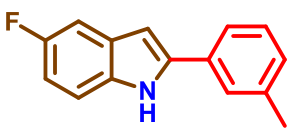
2-(2-fluorophenyl)-5-methoxy-1H-indole (3y): White crystalline (80%); ^{1}H NMR



(300 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.77 (td, *J* = 7.7, 1.9 Hz, 1H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.26 – 7.13 (m, 3H), 7.10 (d, *J* = 2.4 Hz, 1H), 6.92 – 6.86 (m, 2H), 3.87 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 154.6, 132.0, 128.9, 128.8, 128.0, 128.0, 124.9, 116.8, 116.5, 113.4, 111.9, 102.1, 101.5,

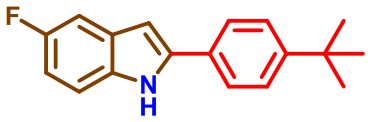
56.0; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{13}FNO$ 242.0976; Found 242.0979, m.p. 123-125 °C.

5-fluoro-2-(m-tolyl)-1H-indole (3z): White solid (88%); ^{1}H NMR (400 MHz, $CDCl_3$)



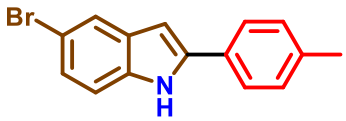
δ 8.32 (s, 1H), 7.46 (d, J = 11.2 Hz, 2H), 7.31 (ddd, J = 10.2, 9.4, 4.9 Hz, 3H), 7.16 (d, J = 7.5 Hz, 1H), 6.93 (td, J = 9.1, 2.4 Hz, 1H), 6.77 (s, 1H), 2.43 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 159.4, 157.0, 139.8, 138.8, 133.3, 132.0, 129.0, 128.9, 125.9, 122.4, 111.5, 110.6, 110.4, 105.5,105.3, 99.9, 21.5; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{13}FN$ 226.1027; Found 226.1033, m.p. 178-180 °C.

2-(4-(tert-butyl)phenyl)-5-fluoro-1H-indole (3aa): White crystalline (89%); ^{1}H



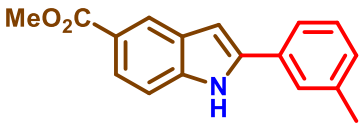
NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.61 (d, J = 8.3 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.30 (ddd, J = 9.6, 7.2, 3.3 Hz, 2H), 6.95 (td, J = 9.1, 2.4 Hz, 1H), 6.77 (s, 1H), 1.39 (s, 9H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 159.4, 157.0, 151.3, 139.8, 133.2, 129.8, 129.5, 129.2, 126.0, 125.0, 111.4, 110.5, 110.2, 105.4, 105.2, 99.6, 34.7, 31.3(; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{19}FN$ 268.1496; Found 268.1492, m.p. 212-214 °C.

5-bromo-2-(p-tolyl)-1H-indole (3ab)[S15]**:** White solid (87%); ^{1}H NMR (400 MHz,



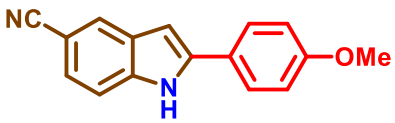
DMSO-d_6) δ 11.68 (s, 1H), 7.74 (d, J = 7.9 Hz, 2H), 7.68 (s, 1H), 7.34 (d, J = 8.5 Hz, 1H), 7.28 (d, J = 7.8 Hz, 2H), 7.18 (d, J = 8.5 Hz, 1H), 6.83 (s, 1H), 2.34 (s, 3H); ^{13}C-NMR (101 MHz, DMSO-d_6) δ 139.3, 137.3, 135.6, 130.6, 129.5, 128.9, 125.1, 123.7, 121.9, 113.1, 111.7, 97.6, 20.8; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{13}BrN$ 286.0226 (for ^{79}Br) and 288.0205 (for ^{81}Br); Found 286.0233 (for ^{79}Br) and 288.0212 (for ^{81}Br), m.p. 239-241 °C.

Methyl 2-(m-tolyl)-1H-indole-5-carboxylate (3ac): White solid (90%); ^{1}H NMR (300



MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.39 (s, 1H), 7.90 (dd, J = 8.4, 1.5 Hz, 1H), 7.48 (d, J = 8.8 Hz, 2H), 7.43 – 7.30 (m, 2H), 7.17 (d, J = 8.7 Hz, 1H), 6.88 (d, J = 1.5 Hz, 1H), 3.94 (s, 3H), 2.43 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 168.2, 139.5, 139.3, 138.8, 131.7, 129.0, 128.9, 126.0, 123.7, 123.5, 122.4, 122.3, 110.5, 100.8, 51.9, 21.5; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{16}NO_2$ 266.1176; Found 266.1187, m.p. 164-166 °C.

2-(4-methoxyphenyl)-1H-indole-5-carbonitrile (3ad)[S5]**:** White solid (90%); ^{1}H NMR



(300 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.93 (s, 1H), 7.60 (d, J = 8.9 Hz, 2H), 7.46 – 7.37 (m, 2H), 7.00 (d, J = 8.8 Hz, 2H), 6.76 (d, J = 1.7 Hz, 1H), 3.87 (s, 3H); ^{13}C-NMR (75 MHz,

$CDCl_3$) δ 160.2, 140.4, 138.4, 129.3, 127.0, 125.8, 125.0, 124.0, 120.9, 114.8, 111.6, 103.4, 99.2, 55.6; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{13}N_2O$ 249.1022; Found 249.1044, m.p. 210-212 °C.

2-(m-tolyl)-1H-indole-5-carbonitrile (3ae): White solid (91%); ^1H NMR (300 MHz, $CDCl_3$) δ 9.04 (s, 1H), 7.94 (s, 1H), 7.42 (ddd, *J* = 22.3, 17.5, 9.5 Hz, 5H), 7.20 (d, *J* = 8.2 Hz, 1H), 6.84 (d, *J* = 1.6 Hz, 1H), 2.43 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 140.7, 139.1, 138.7, 131.3, 129.6, 129.2, 129.1, 126.3, 126.1, 125.1, 122.7, 121.2, 112.0, 103.0, 100.0, 21.7; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{13}N_2$ 233.1073; Found 233.1092, m.p. 229-231 °C.

2-(p-tolyl)-1H-indole-5-carbonitrile (3af): White solid (91%); ^1H NMR (300 MHz, $CDCl_3$) δ 8.76 (s, 1H), 7.94 (s, 1H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.46 – 7.38 (m, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 6.82 (d, *J* = 1.8 Hz, 1H), 2.41 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 140.6, 138.9, 138.4, 130.0, 129.2, 125.9, 125.4, 125.1, 111.7, 103.3, 99.7, 21.4; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{13}N_2$ 233.1073; Found 233.1093, m.p. 207-209 °C.

5-nitro-2-(m-tolyl)-1H-indole (3ag): Yellowish solid (93%); ^1H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 1H), 8.58 (s, 1H), 8.10 (dd, *J* = 8.9, 1.8 Hz, 1H), 7.49 (d, *J* = 11.6 Hz, 2H), 7.41 (dd, *J* = 16.8, 8.3 Hz, 2H), 7.22 (d, *J* = 7.4 Hz, 1H), 6.95 (s, 1H), 2.45 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 142.2, 141.3, 139.6, 139.1, 131.0, 129.6, 129.2, 128.6, 126.1, 122.6, 117.9, 117.6, 110.7, 101.5, 21.5; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{13}N_2O_2$ 253.0972; Found 253.0991, m.p. 194-196 °C.

2-(4-(tert-butyl)phenyl)-5-nitro-1H-indole (3ah): Yellowish crystalline (93%); ^1H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.57 (s, 1H), 8.10 (dd, *J* = 8.9, 1.6 Hz, 1H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.9 Hz, 1H), 6.93 (s, 1H), 1.37 (s, 9H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 152.2, 142.2, 141.3, 139.7, 128.7, 128.2, 126.2, 125.2, 117.8, 117.5, 110.7, 101.2, 34.8, 31.2; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{19}N_2O_2$ 295.1441; Found 295.1463, m.p. 201-203 °C.

III. NMR spectra:

1. ^{1}H and ^{13}C spectra of **CATMC**:

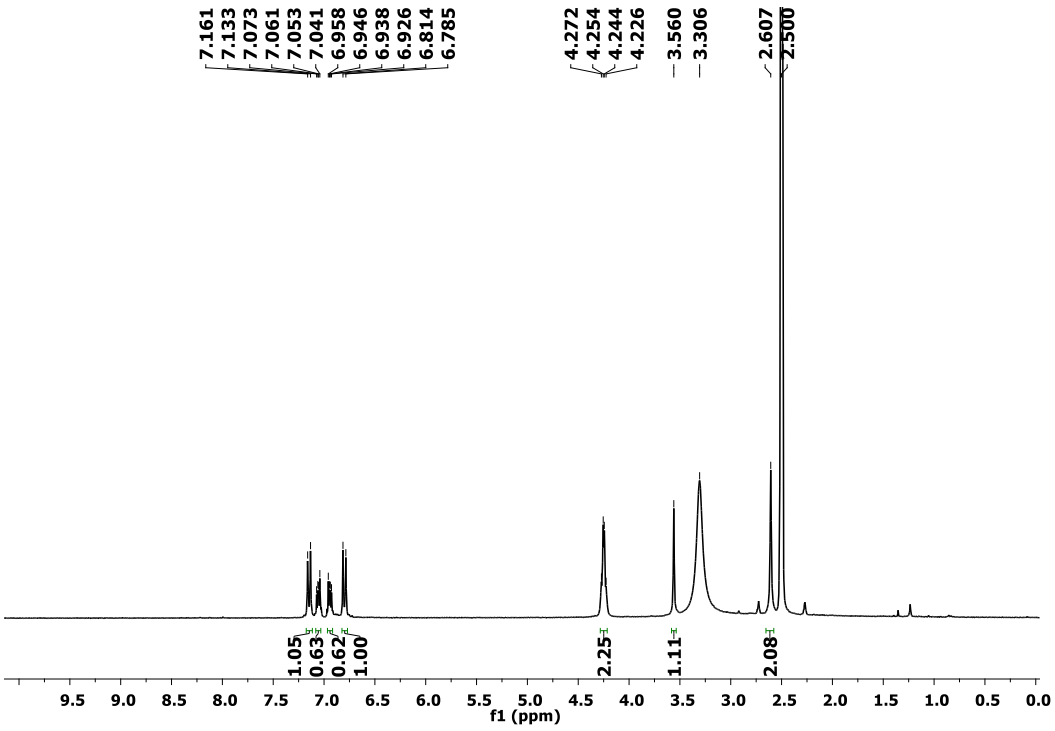


Figure 1S. 400 MHz ^{1}H-NMR spectrum of compound **CATMC** in DMSO-d_6

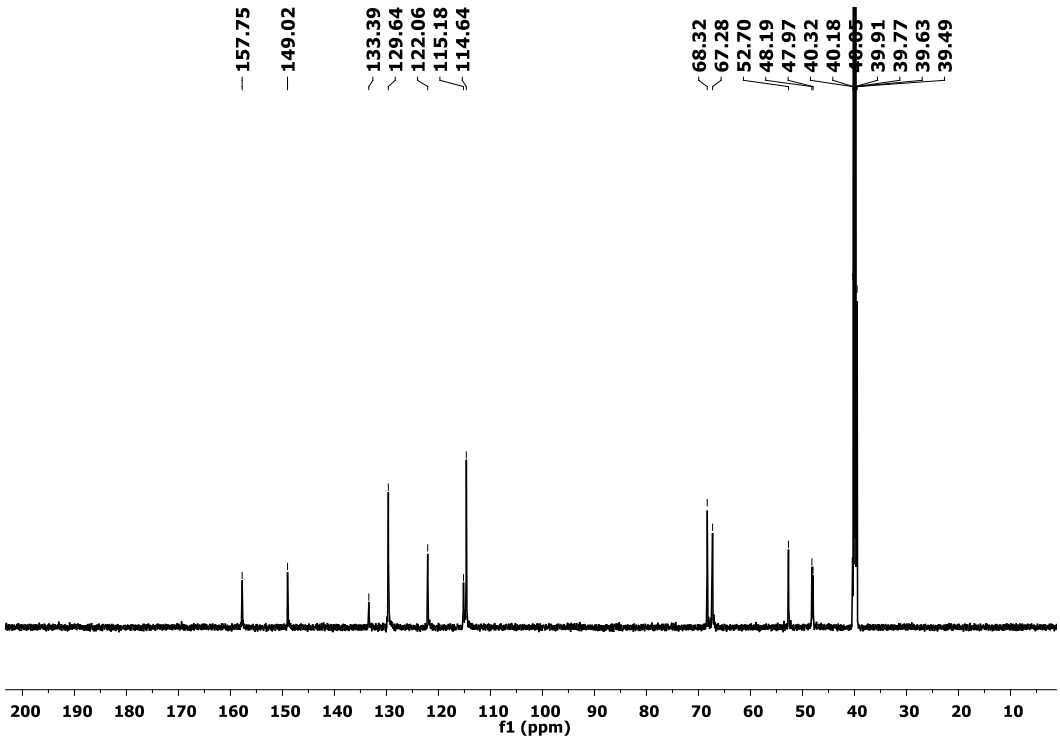


Figure 2S. 125 MHz ^{13}C-NMR spectrum of compound **CATMC** in DMSO-d_6

2. COSY spectrum of **CATMC**:

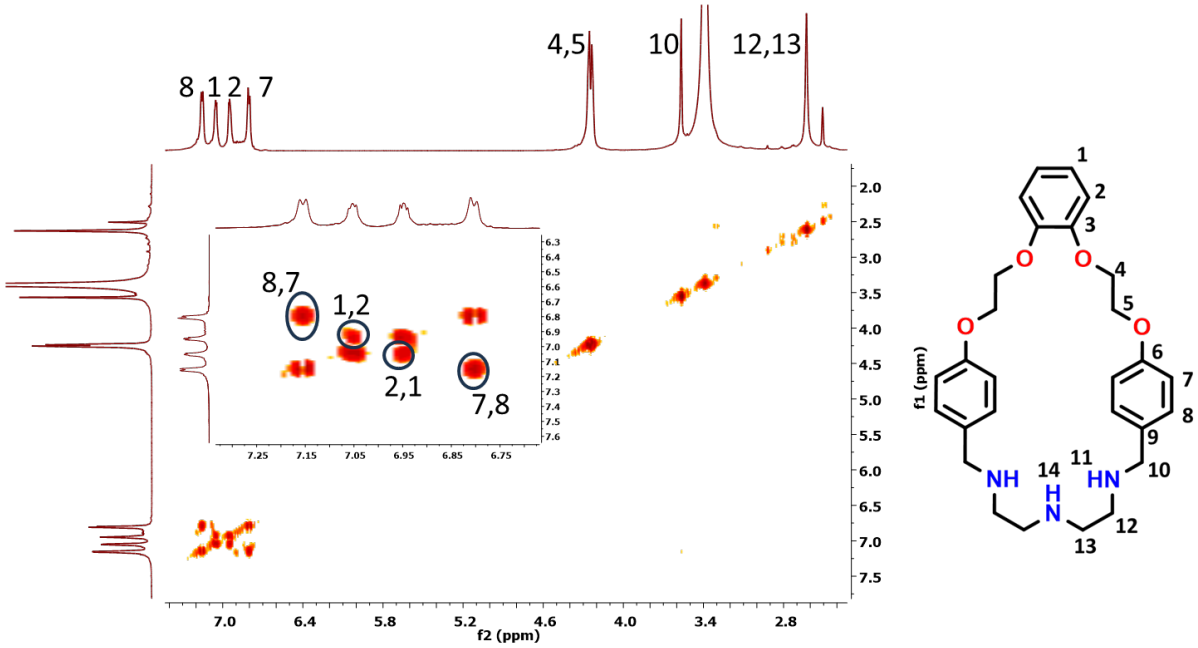


Figure 3S. 600 MHz COSY spectrum of **CATMC** in DMSO-d_6

3. ROESY spectrum of **CATMC**:

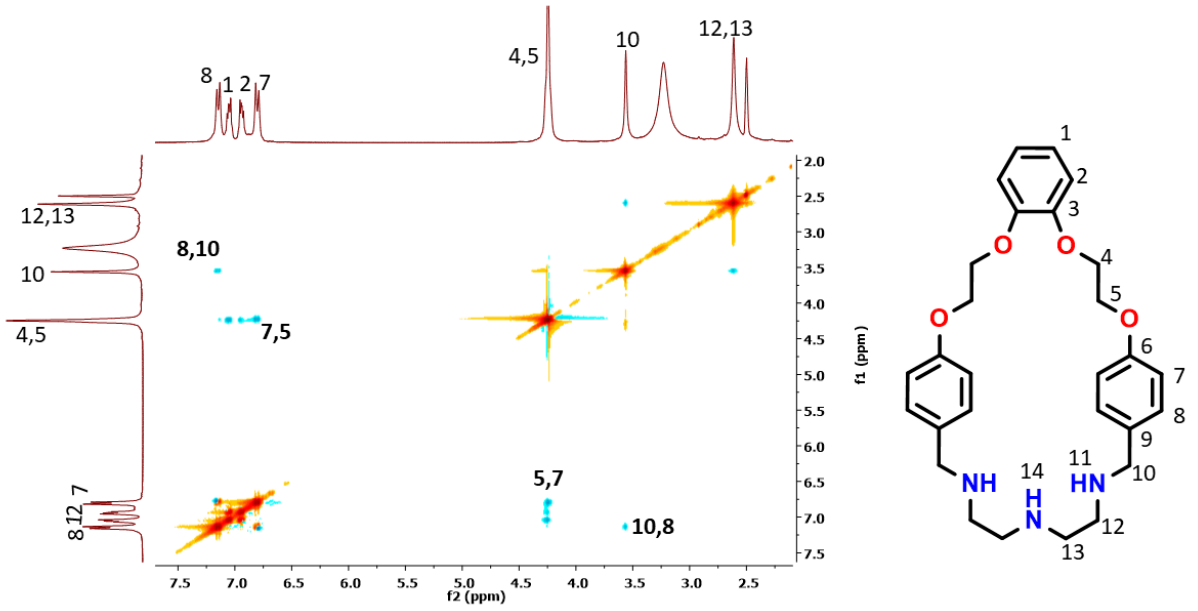


Figure 4S. 300 MHz ROESY spectrum of **CATMC** in DMSO-d_6

4. ^{1}H and ^{13}C spectra of compound **CATMC-Pd**:

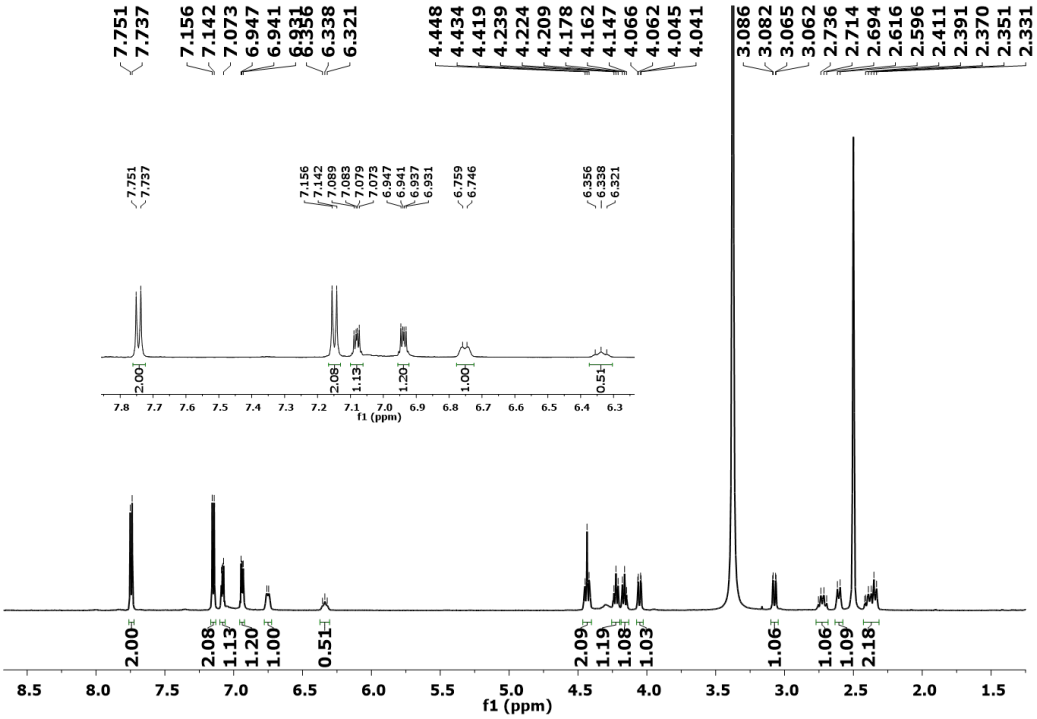


Figure 5S. 600 MHz ^{1}H-NMR spectrum of compound **CATMC-Pd** in DMSO-d_6

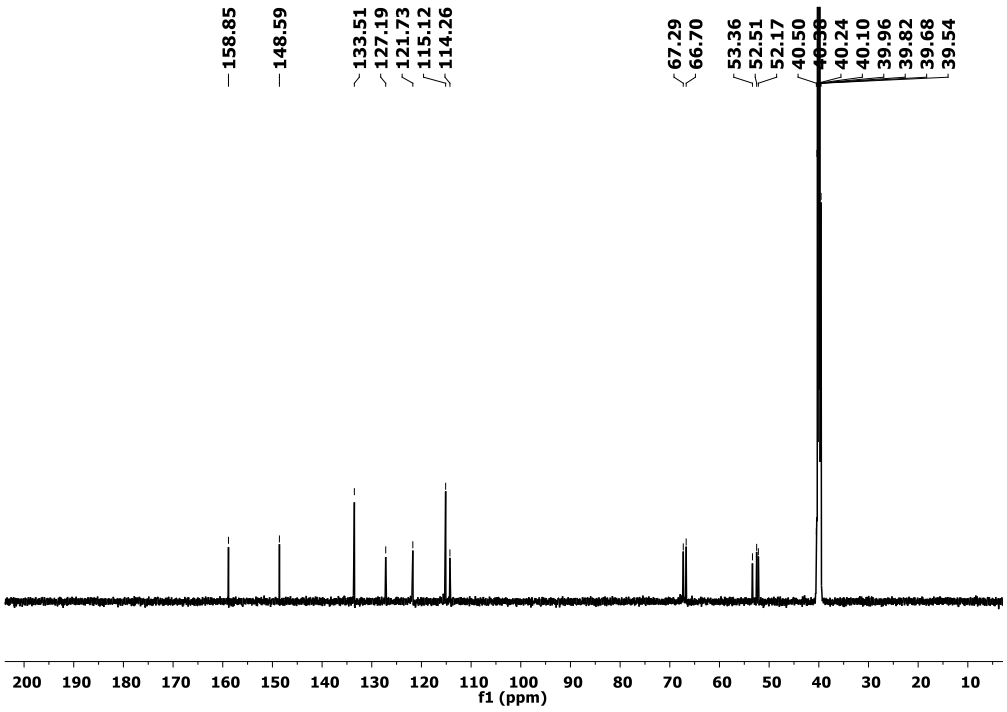


Figure 6S. 125 MHz ^{13}C-NMR spectrum of compound **CATMC-Pd** in DMSO-d_6

5. COSY spectrum of **CATMC-Pd**:

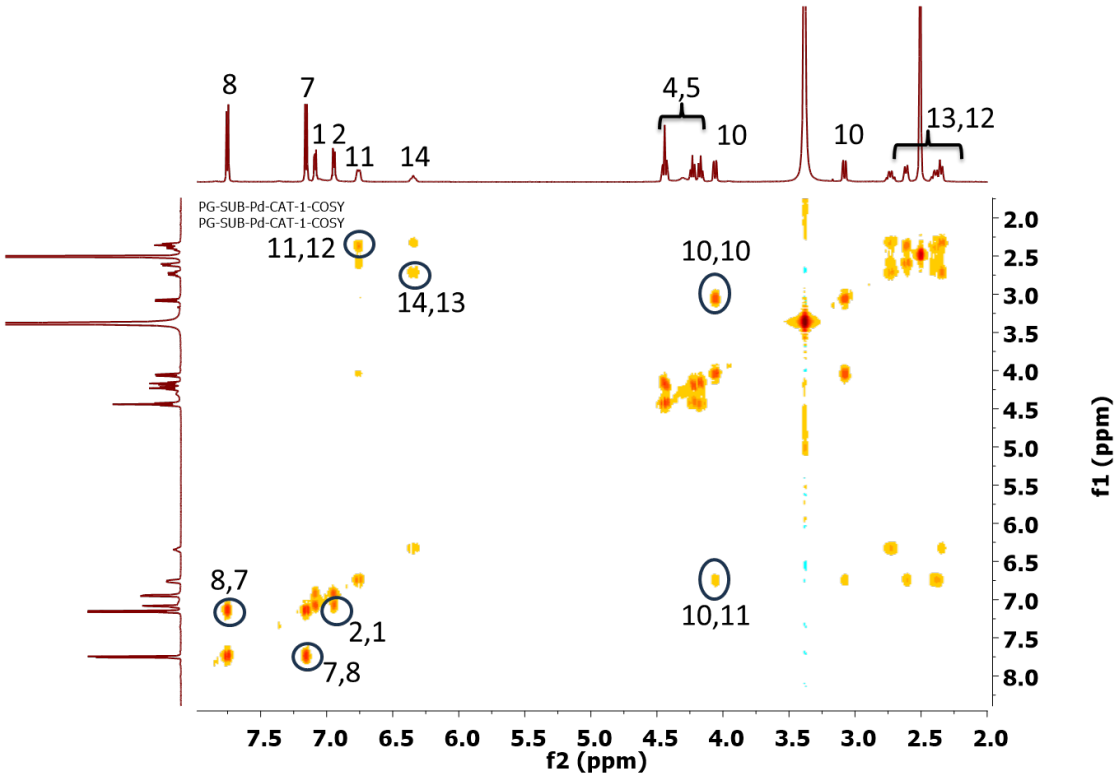


Figure 7S. 600 MHz COSY spectrum of **CATMC-Pd** in DMSO-d_6

6. ROESY spectrum of **CATMC-Pd**:

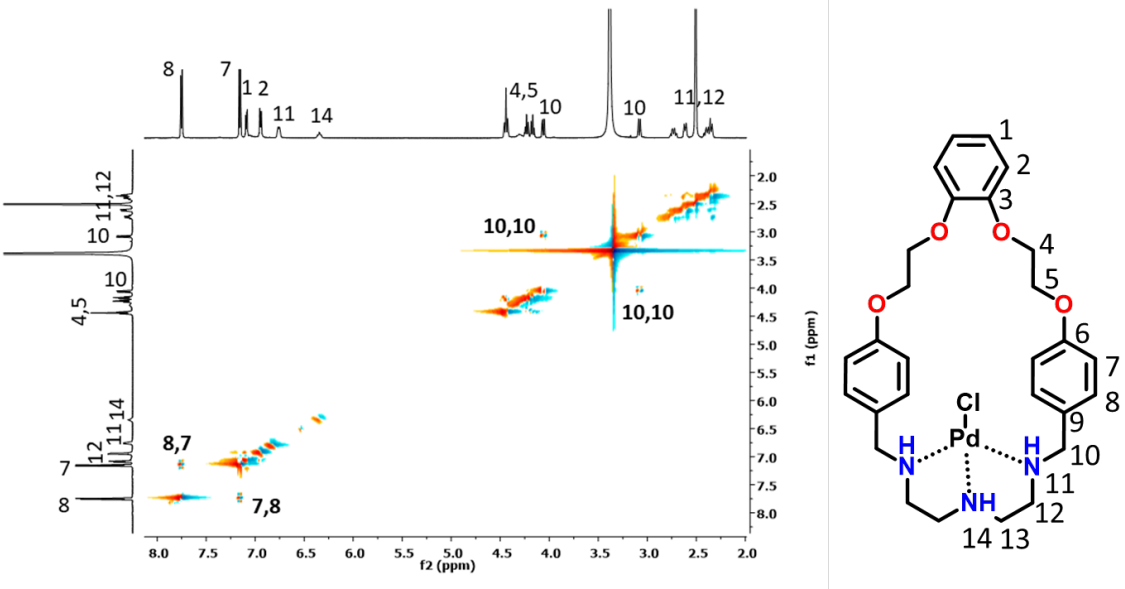


Figure 8S. 300 MHz ROESY spectrum of **CATMC-Pd** in DMSO-d_6

7. Reaction mixture only with $PdCl_2$:

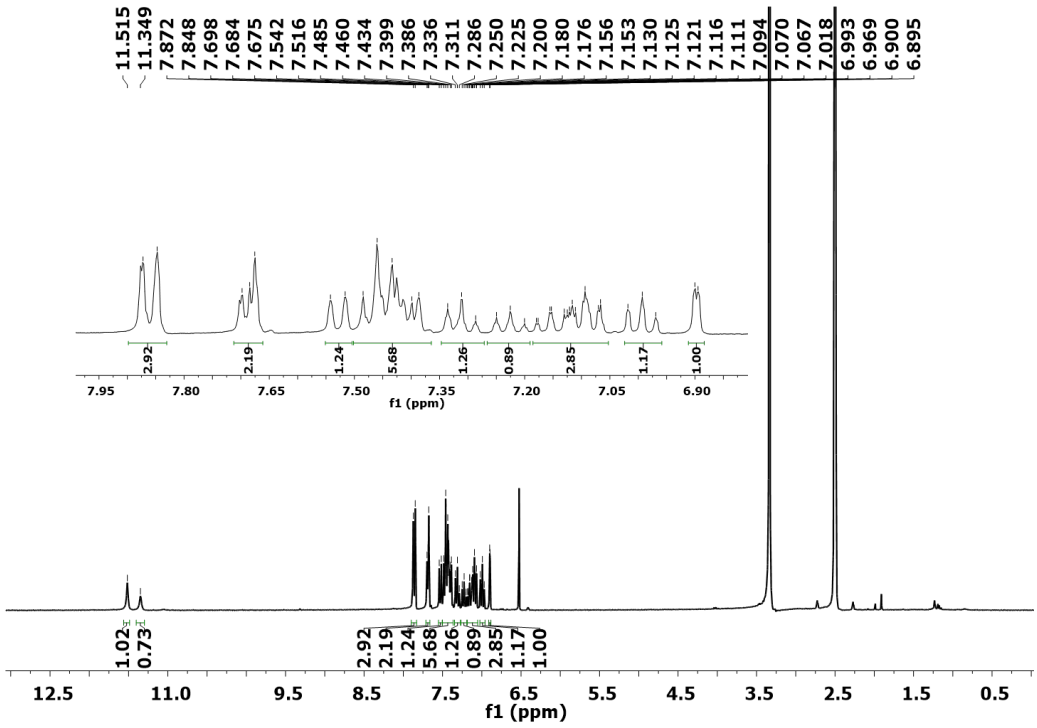


Figure 9S. 400 MHz ^{1}H-NMR spectrum of crude mixture reaction only with $PdCl_2$ in DMSO-d_6

8. Reaction mixture with **CATMC-Pd:**

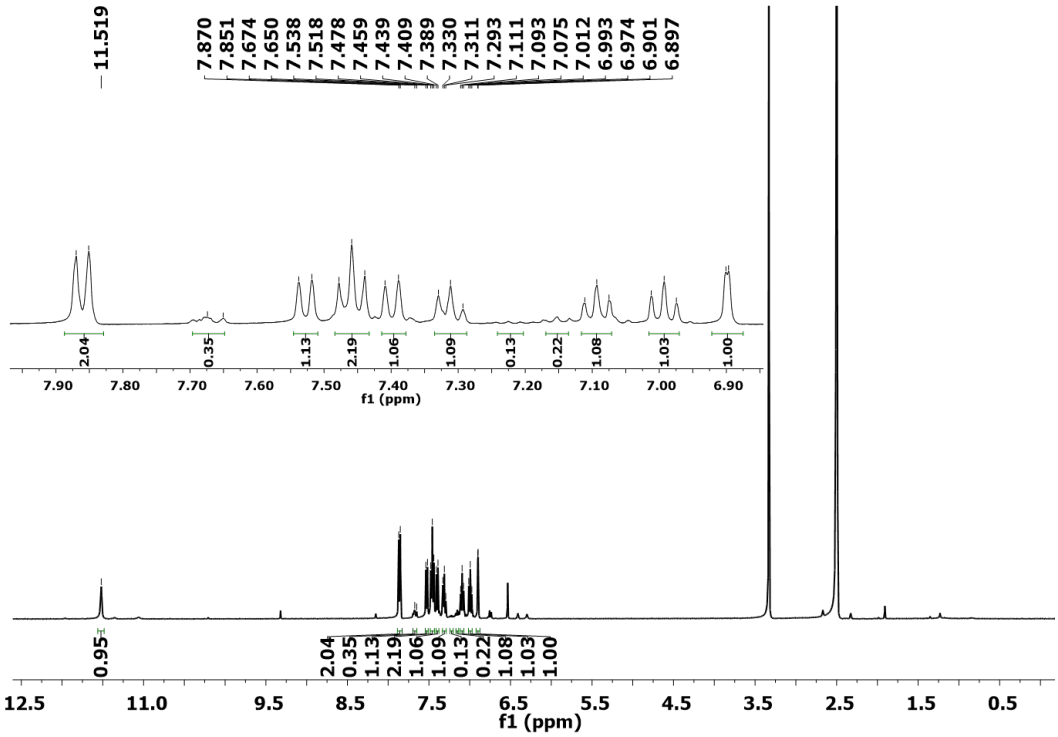


Figure 10S. 400 MHz ^{1}H-NMR spectrum of crude mixture reaction only with **CATMC-Pd** in DMSO-d_6

9. GC-MS chromatogram:

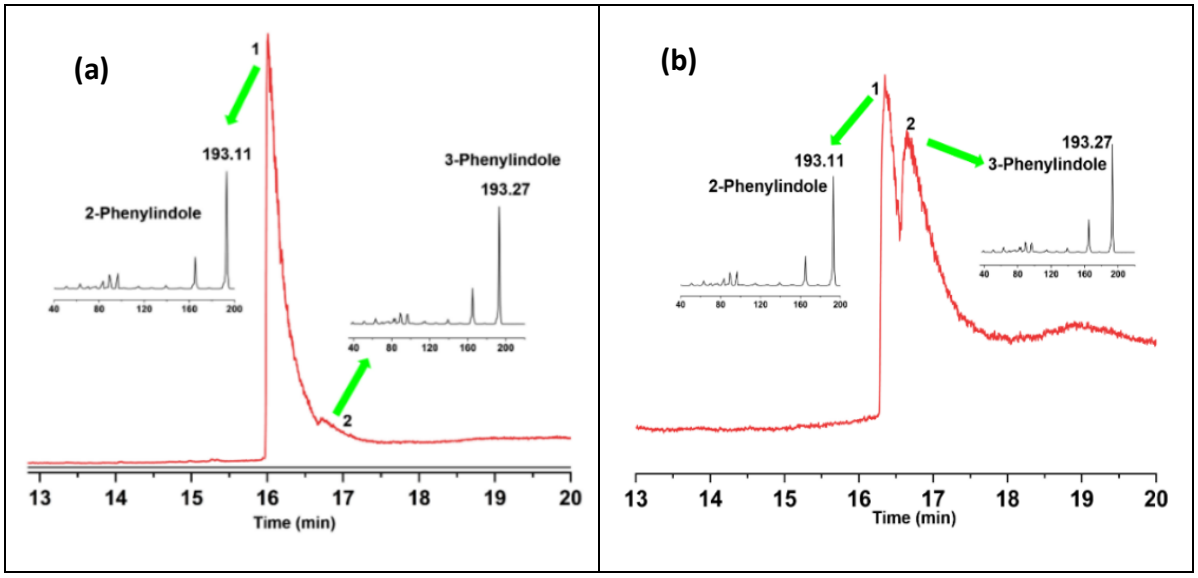


Figure 11S. GC-MS chromatogram for crude (a) with **CATMC-Pd** and (b) with $PdCl_2$

10. The equation for calculating the selectivity for C2-phenylindole (**3a**)

$$(\%\text{Selectivity})_{PdCl2} = \frac{I_{3a}}{I_{3a} + I_{4a}} \times 100$$

$$= \frac{1}{1+ 0.89} \times 100$$

$$= 52.91\%$$

$$(\%\text{Selectivity})_{CATMC\text{-}Pd} = \frac{I_{3a}}{I_{3a} + I_{4a}} \times 100$$

$$\approx \frac{1}{1+ (\text{trace amount})} \times 100$$

$$> 90\%$$

Where $\mathbf{I}_{3a}$ and $\mathbf{I}_{4a}$ are the peak intensities corresponding products **3a** and **4a** respectively as determined from the crude ^{1}H-NMR (Figure 9S-10S, ESI).

11. Leaching test:

a. Characterization of **CATMC-Pd** bound with 4-Methylpyridine

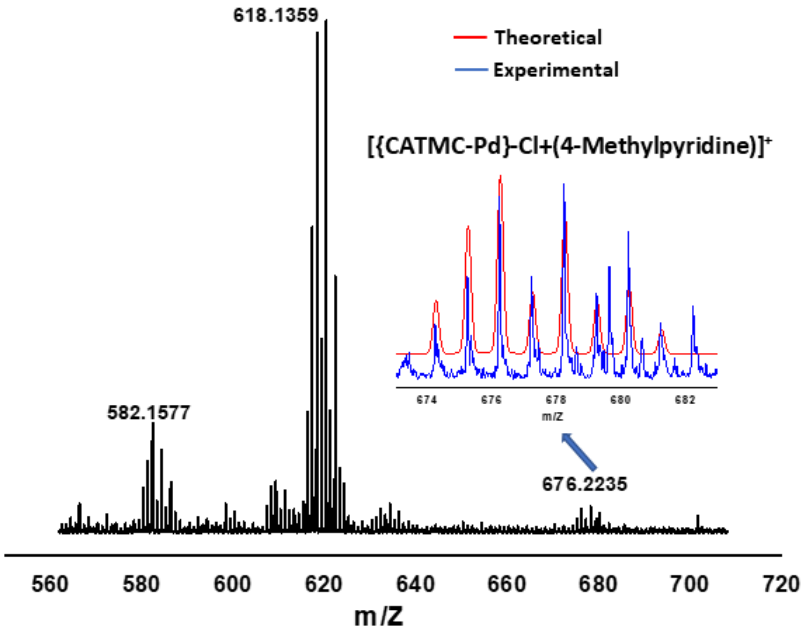
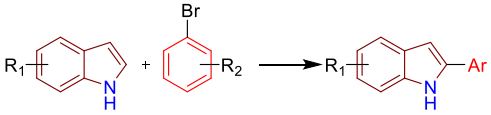


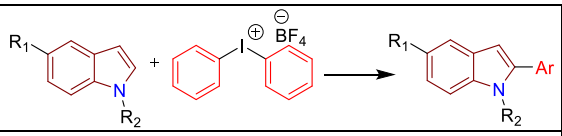
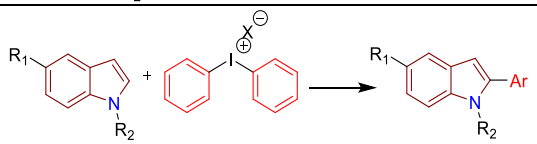
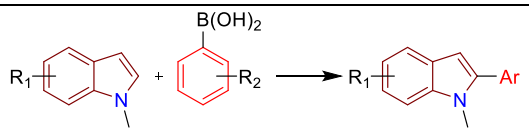
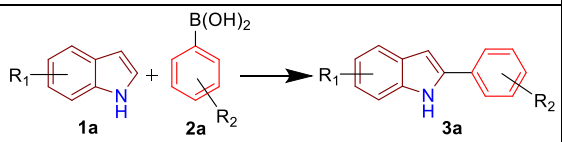
Figure 12S. HRMS data of [{**CATMC-Pd**}-Cl+(4-Methylpyridine)]$^+$

b. ICP-MS data

SampleID	Analyte	Mean
Calib Blank 1		
	Pd 340.458	
0.1		
	Pd 340.458	[0.1] mg/L
0.5		
	Pd 340.458	[0.5] mg/L
1		
	Pd 340.458	[1] mg/L
rev-Pd		
	Pd 340.458	18.95 mg/L

12. Table 1S: Comparative table of direct C2-arylation with previous reported catalysts vs. our catalyst

Ref.	Reactions	Catalyst (mol %)	Additives	Temp (°C).	Time	Solvent	Yields (%)
S16		Na_2PdCl_4 (5)	KOAc	100 (**High temp.**)	4h	DCE	85

S17		Pd@MOF (1)	___	80	5h	GVL	80
S18		Pd/C (10)	___	70	4h	PC/H_2O	93
S19		Pd-NPs (10)	AgTFA (**Stoichiometric additional additive**)	50	5h	MeOH/ H_2O	82
Our Work		**CATMC-Pd (5)** (**lower catalyst loading**)	___ (additive free)	**50** (**ambient temp.**)	**12h**	**H_2O**	**93**

IV. References:

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S18. F. Campana, B. M. Massaccesi, S. Santoro, O. Piermatti and L. Vaccaro, *ACS Sustainable Chem. Eng.*, 2020, **8**, 16441-16450.

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13. ^{1}H and ^{13}C Spectra of Synthesized 2-arylindole derivatives:

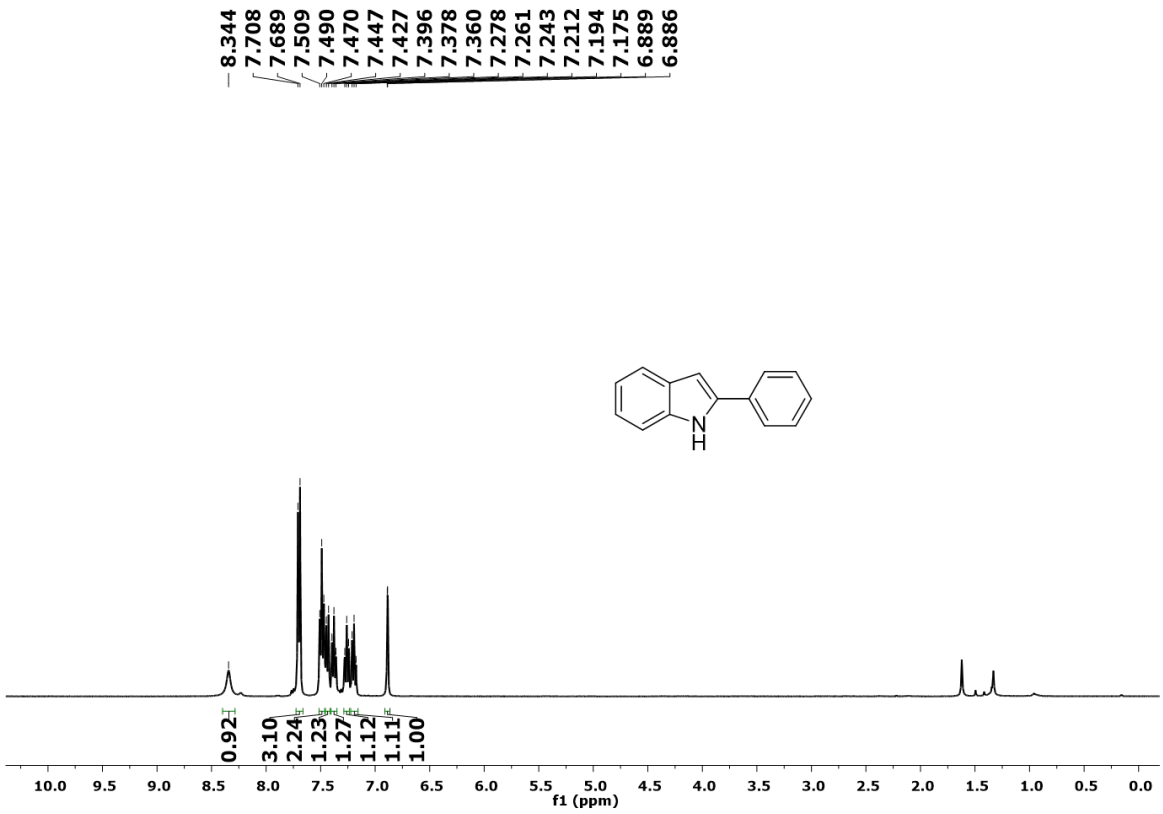

Figure 13S. 400 MHz ^{1}H-NMR spectrum of compound **3a** in $CDCl_3$

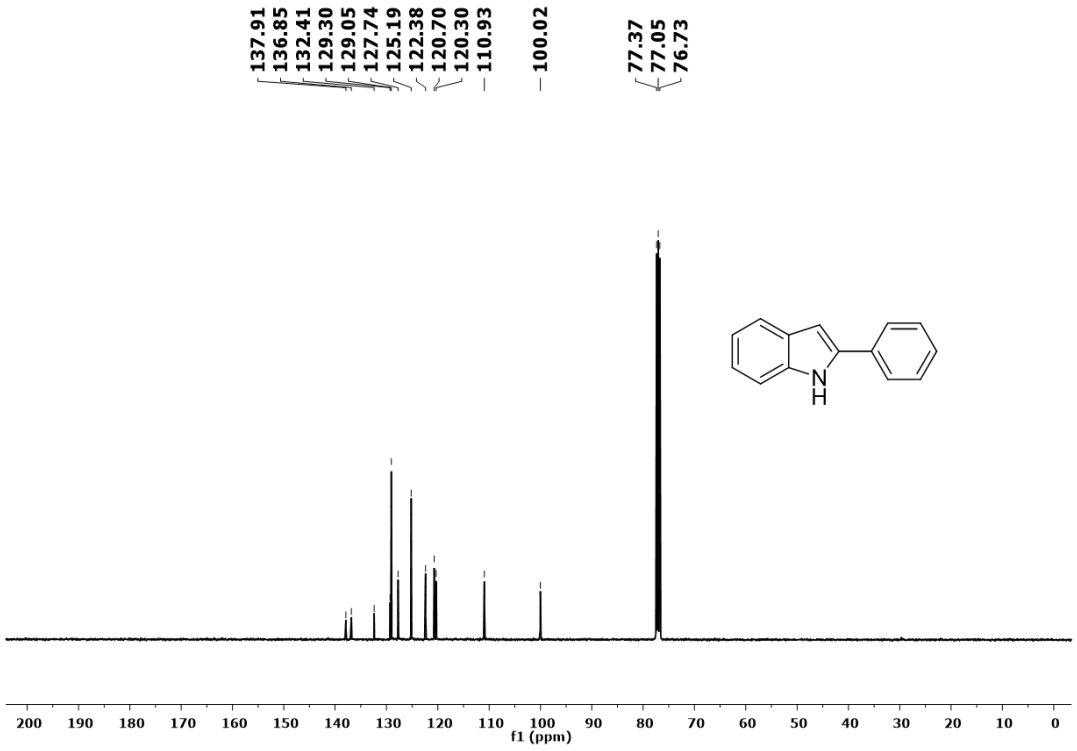

Figure 14S. 101 MHz ^{13}C-NMR spectrum of compound **3a** in $CDCl_3$

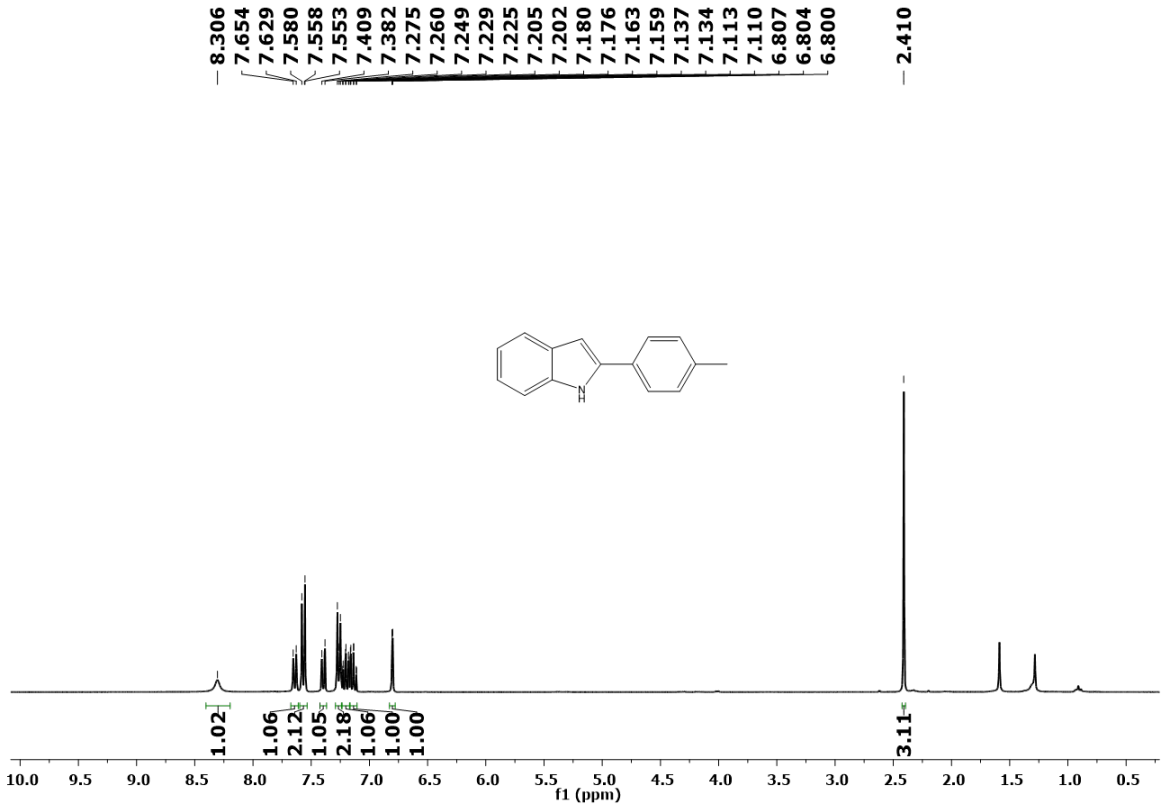

Figure 15S. 300 MHz ^{1}H-NMR spectrum of compound **3b** in $CDCl_3$

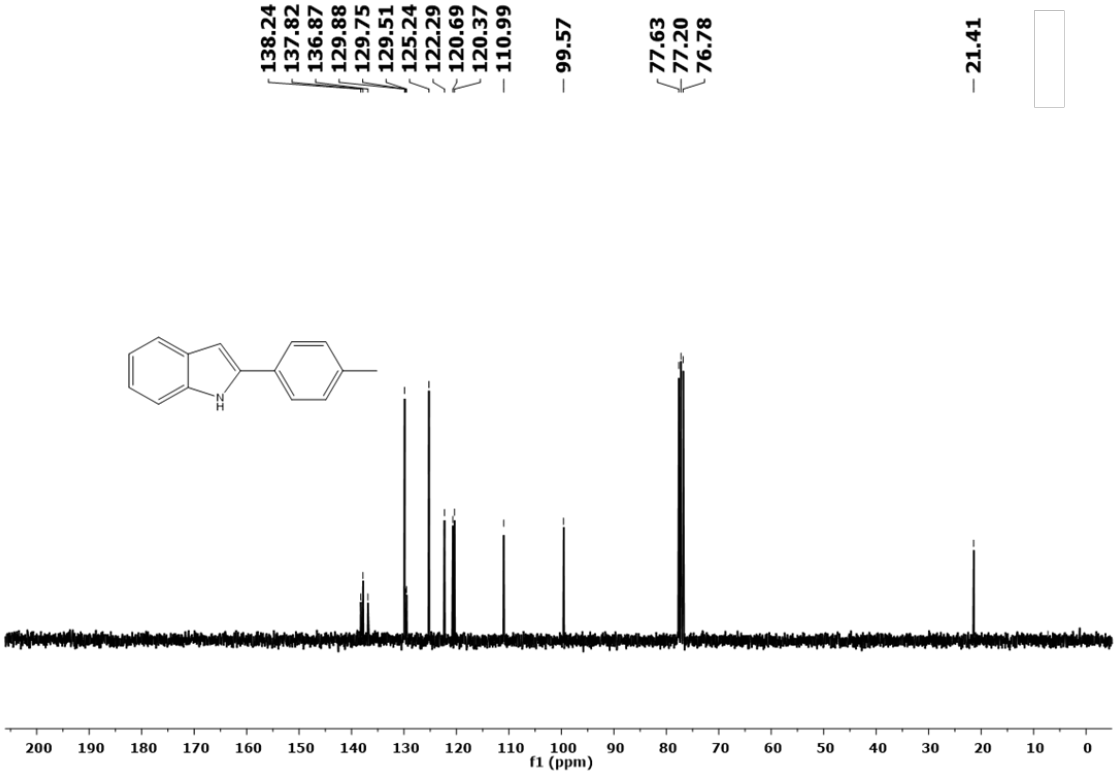

Figure 16S. 75 MHz ^{13}C-NMR spectrum of compound **3b** in $CDCl_3$

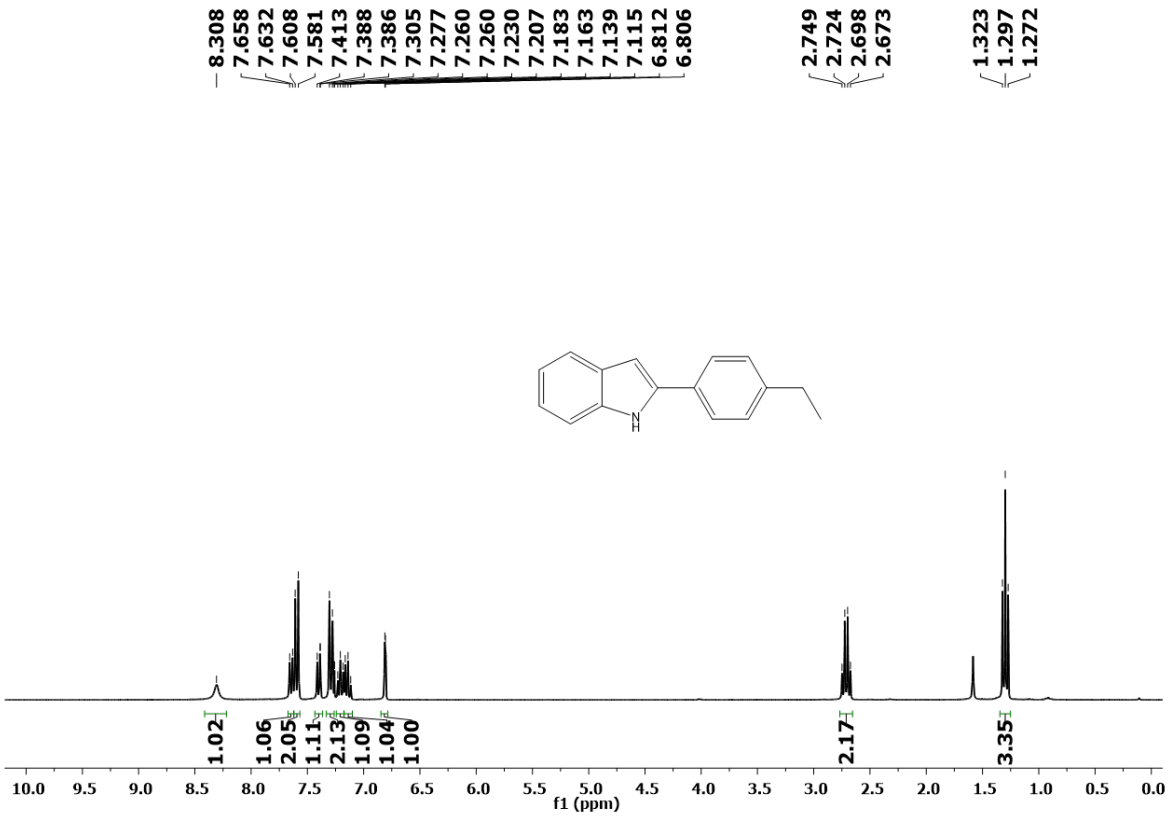

Figure 17S. 300 MHz ^{1}H-NMR spectrum of compound **3c** in $CDCl_3$

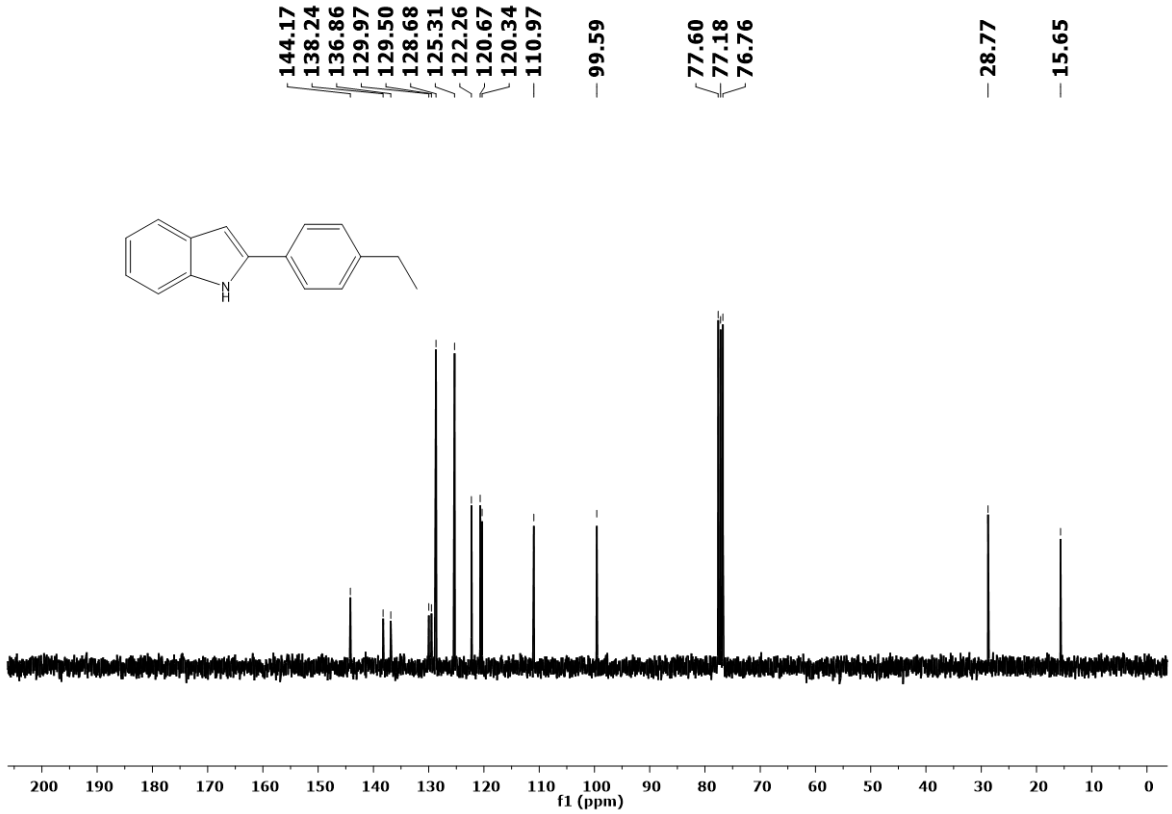

Figure 18S. 75 MHz ^{13}C-NMR spectrum of compound **3c** in $CDCl_3$

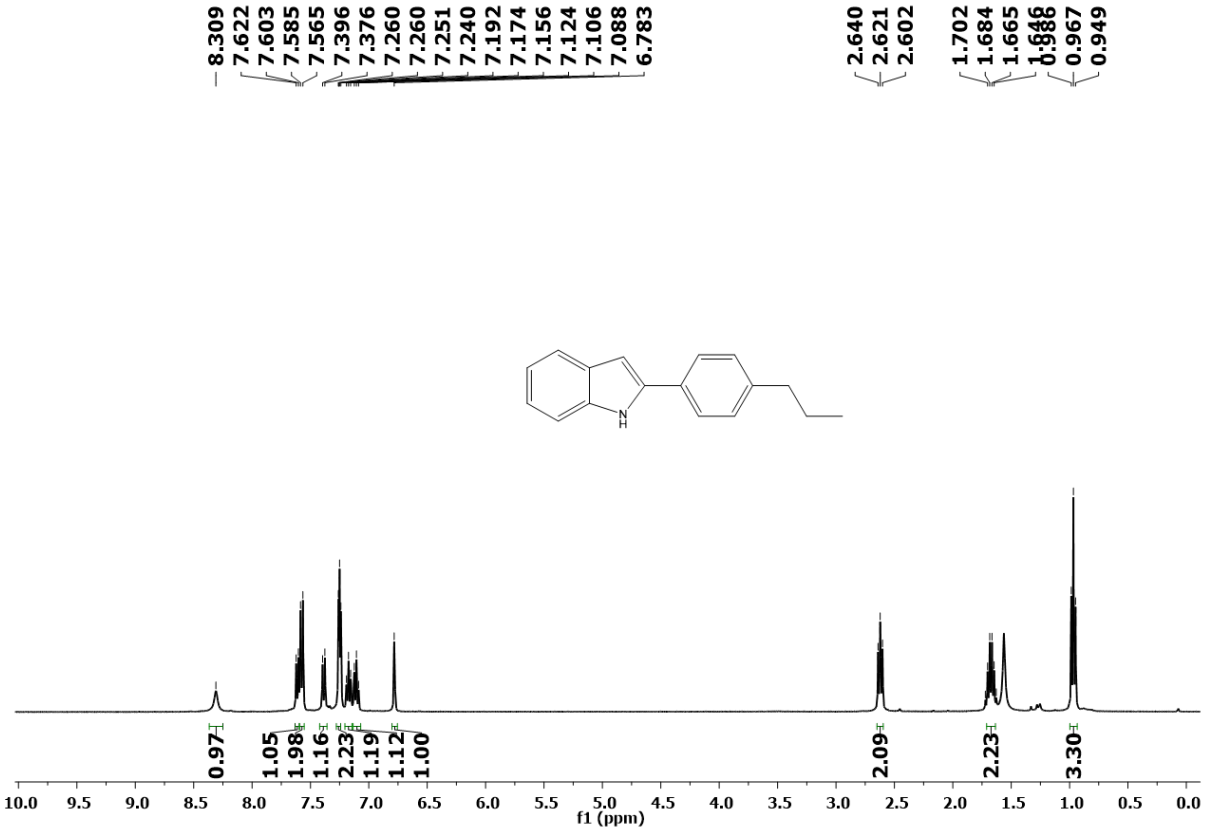

Figure 19S. 400 MHz ^{1}H-NMR spectrum of compound **3d** in $CDCl_3$

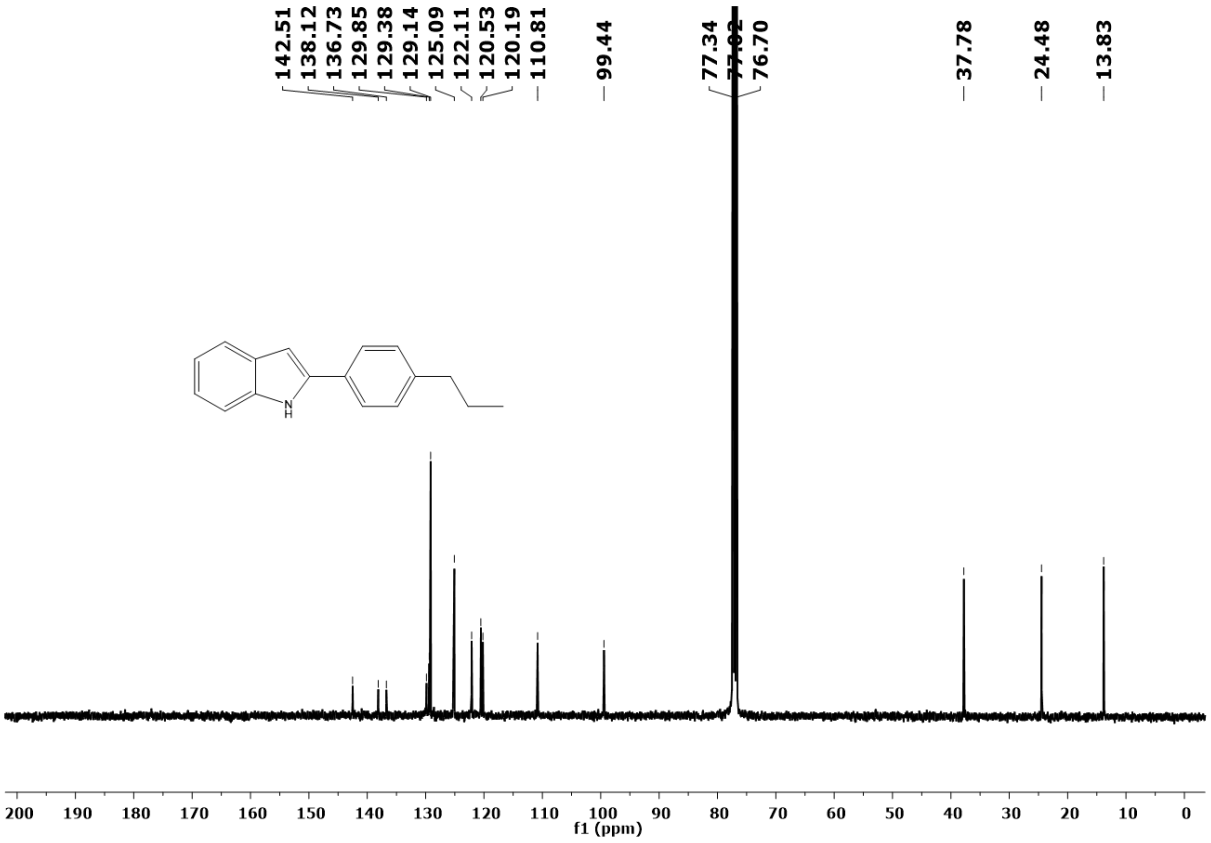

Figure 20S. 101 MHz ^{13}C-NMR spectrum of compound **3d** in $CDCl_3$

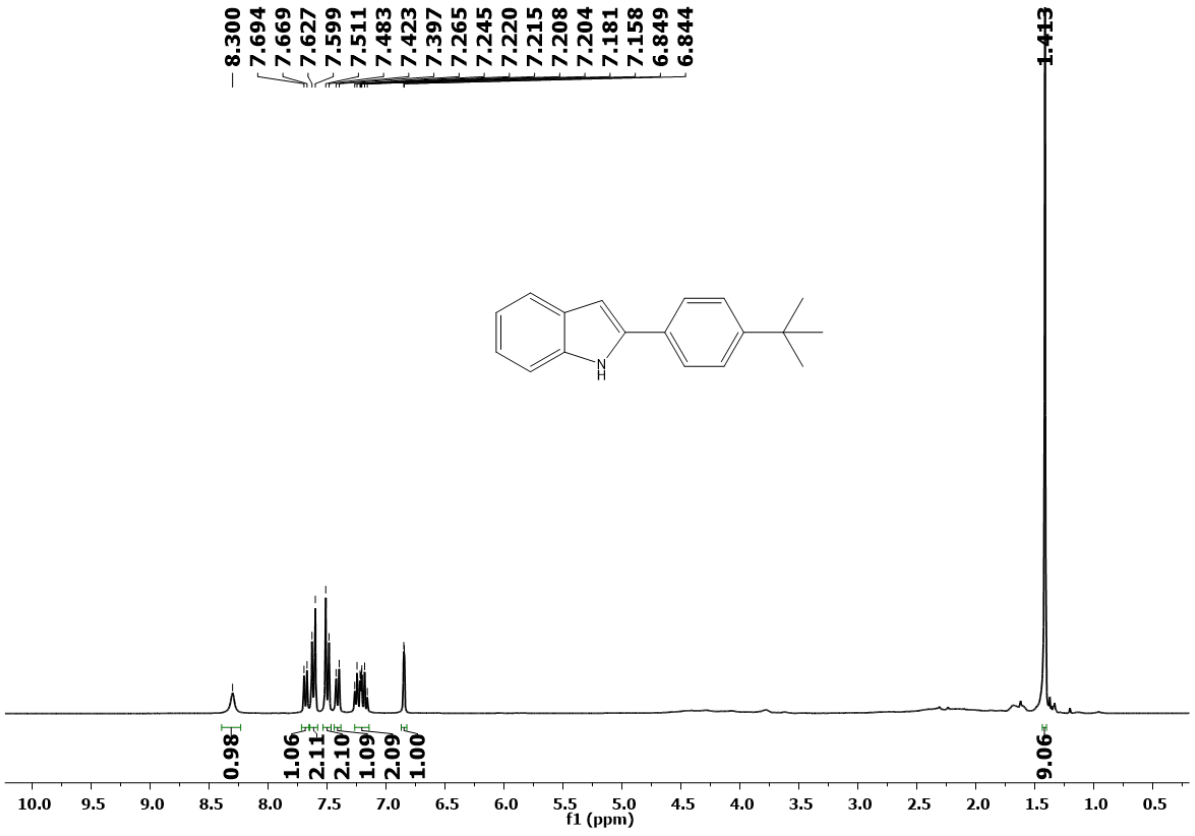

Figure 21S. 300 MHz ^{1}H-NMR spectrum of compound **3e** in $CDCl_3$

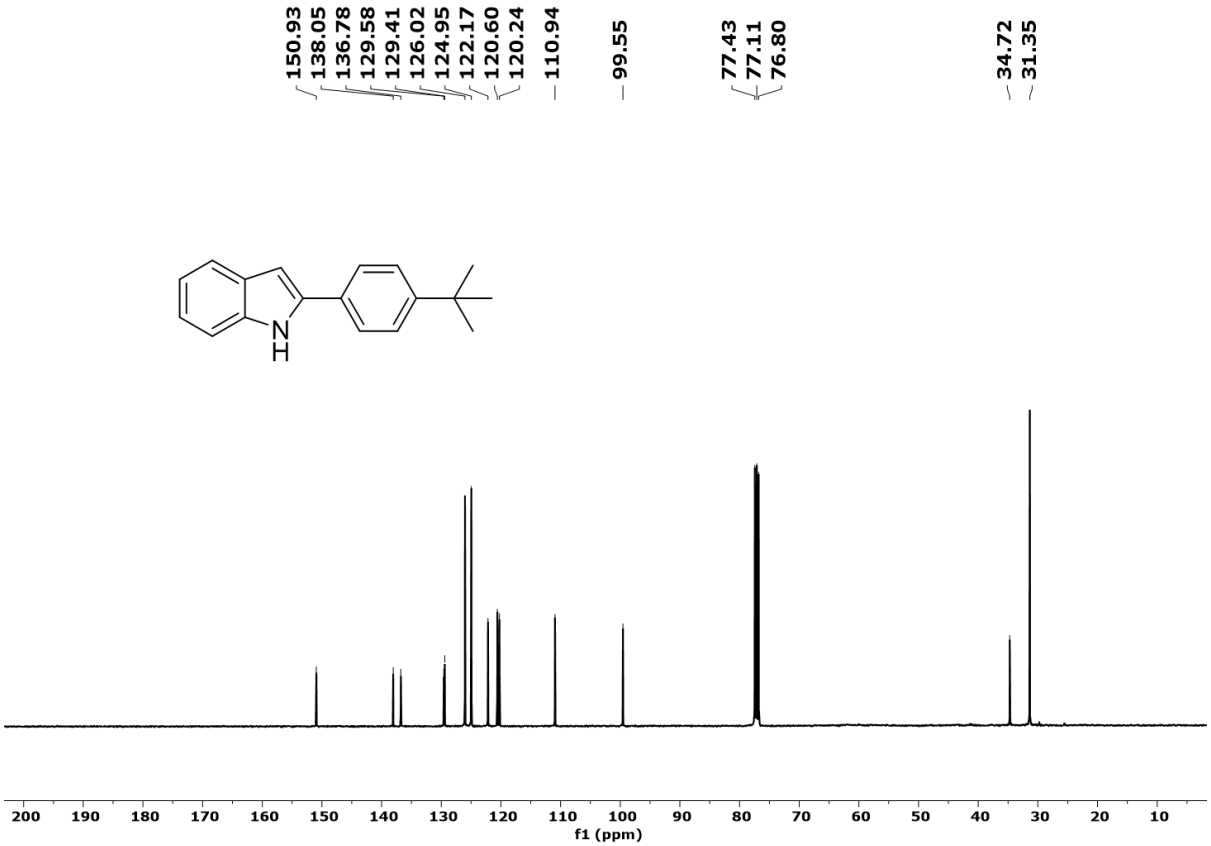

Figure 22S. 101 MHz ^{13}C-NMR spectrum of compound **3e** in $CDCl_3$

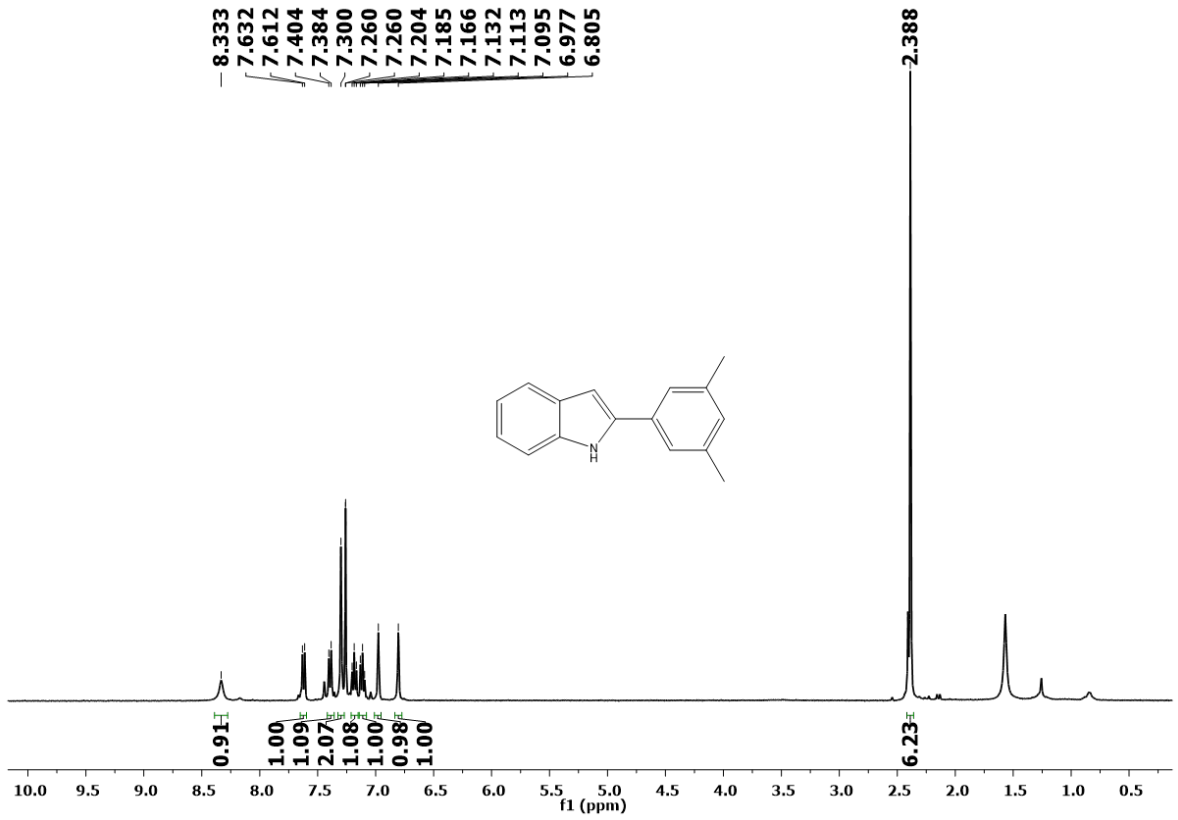

Figure 23S. 400 MHz ^{1}H-NMR spectrum of compound **3f** in $CDCl_3$

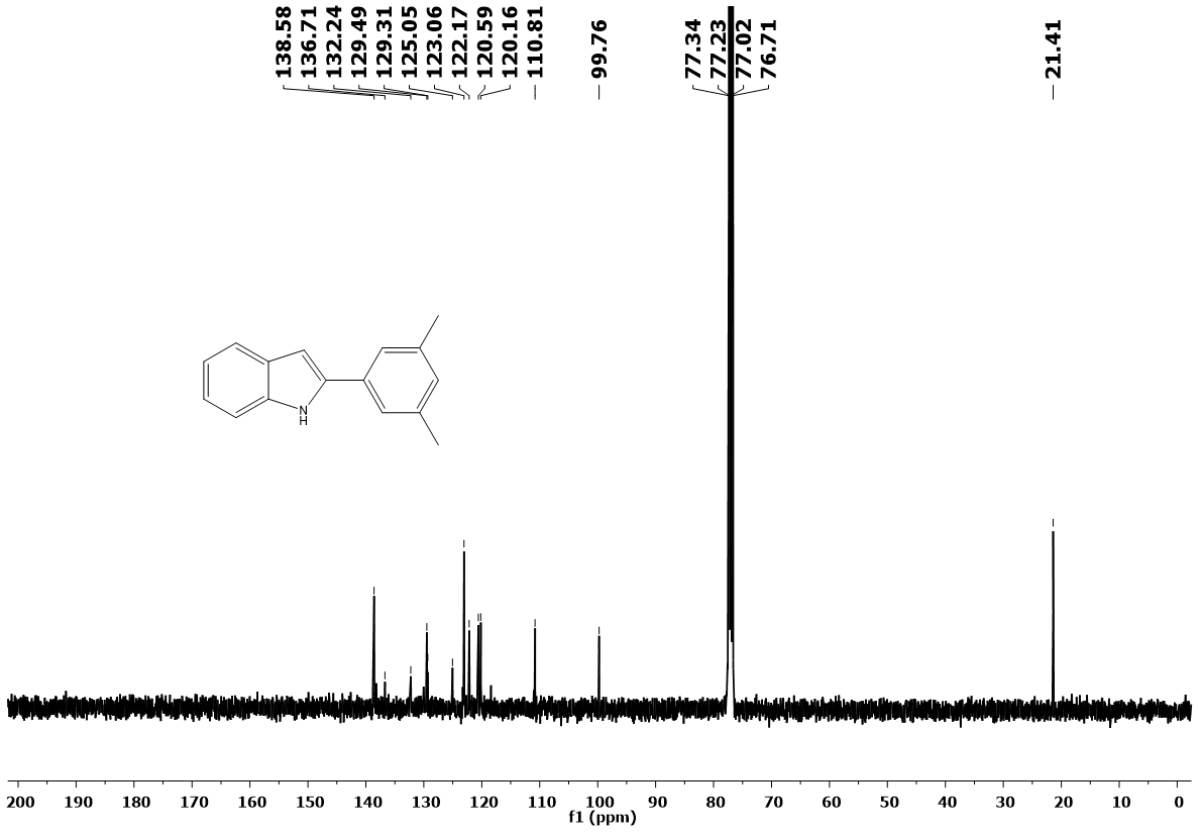

Figure 24S. 101 MHz ^{13}C-NMR spectrum of compound **3f** in $CDCl_3$

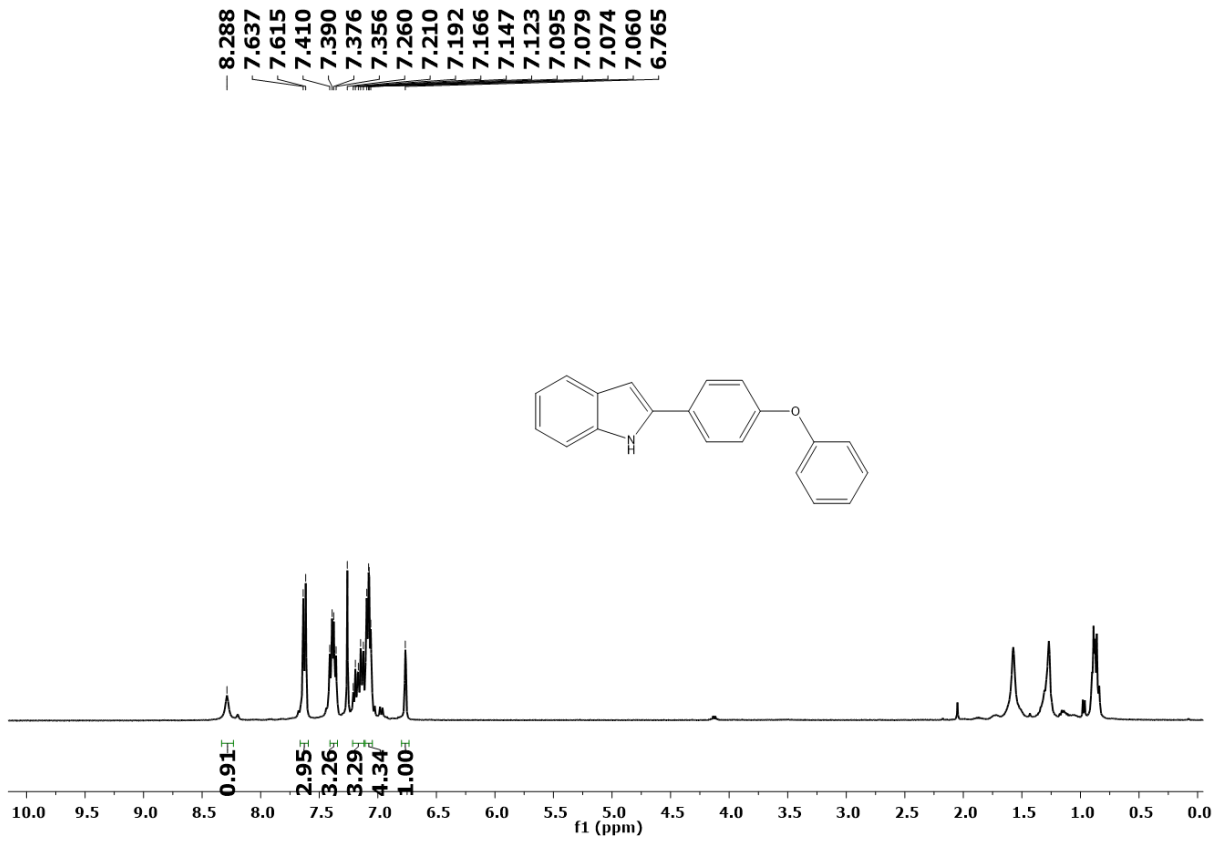

Figure 25S. 400 MHz ^{1}H-NMR spectrum of compound **3g** in $CDCl_3$

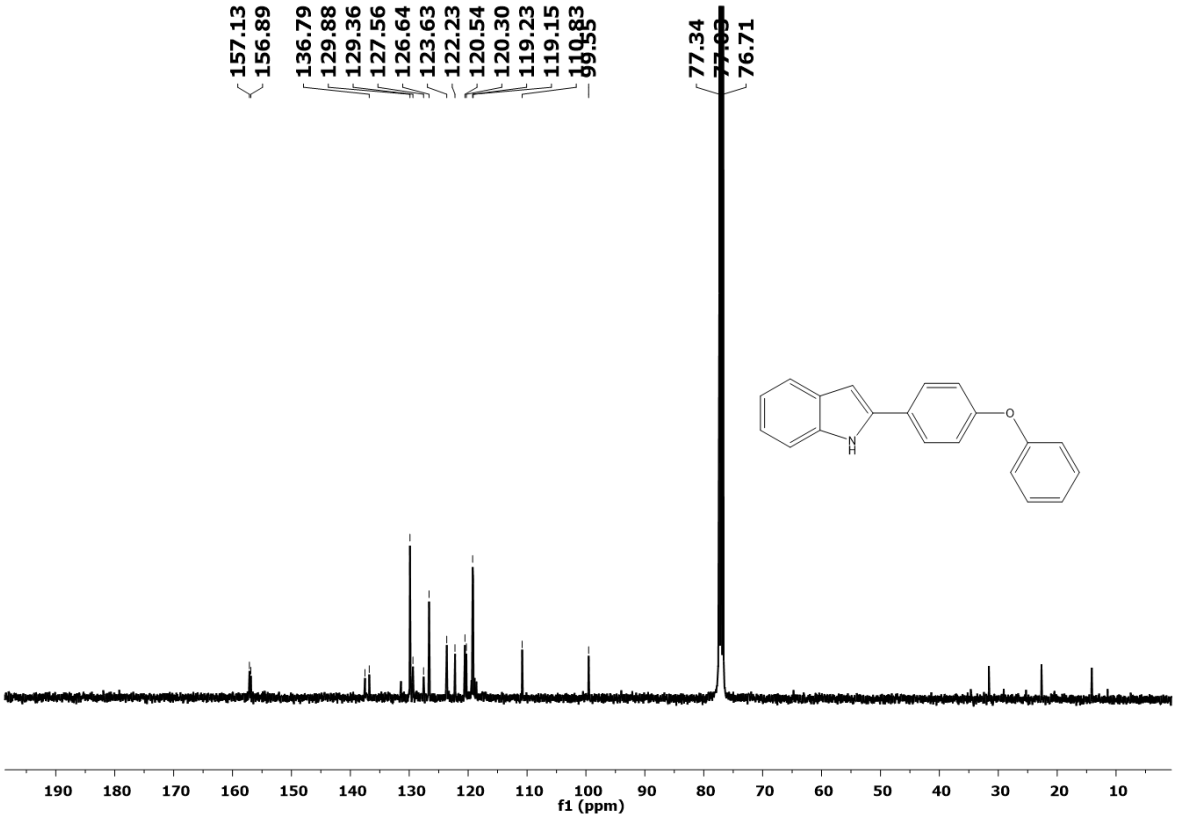

Figure 26S. 101 MHz ^{13}C-NMR spectrum of compound **3g** in $CDCl_3$

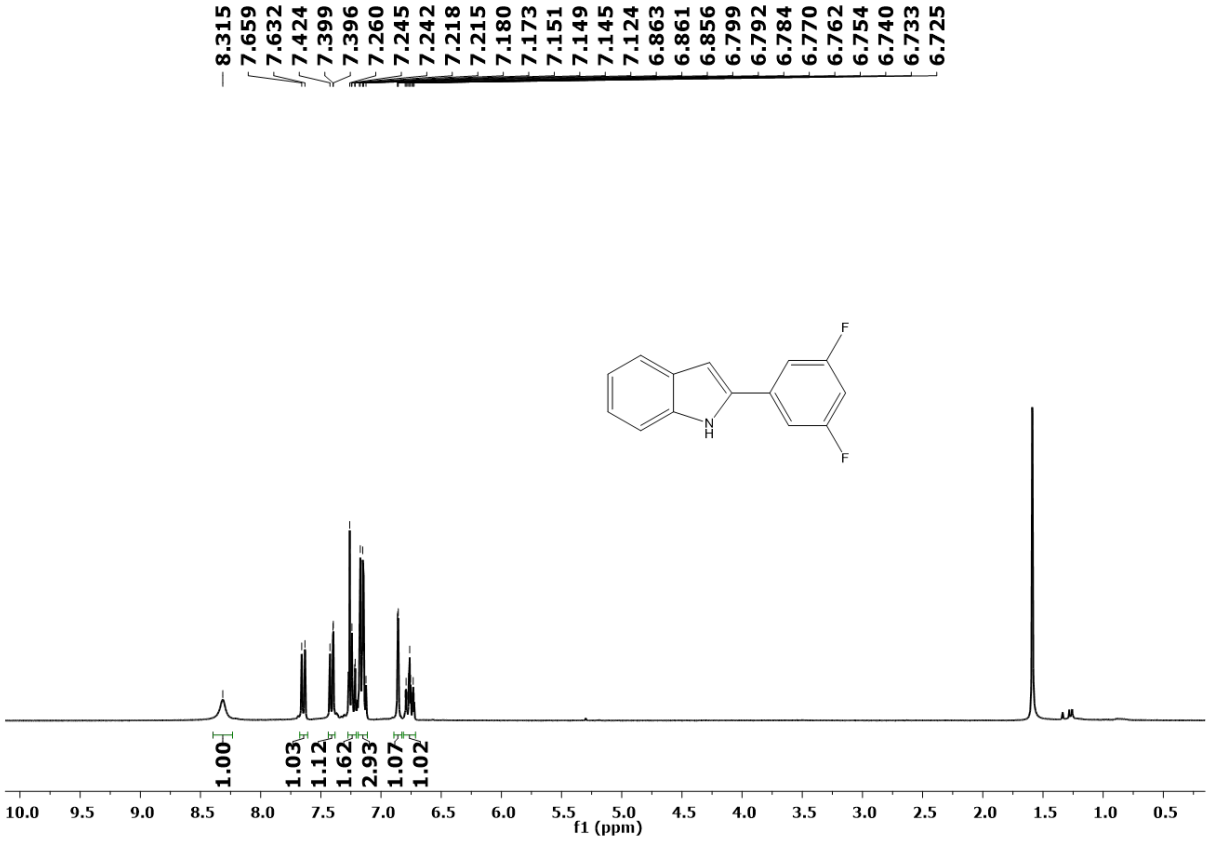

Figure 27S. 300 MHz ^{1}H-NMR spectrum of compound **3h** in $CDCl_3$

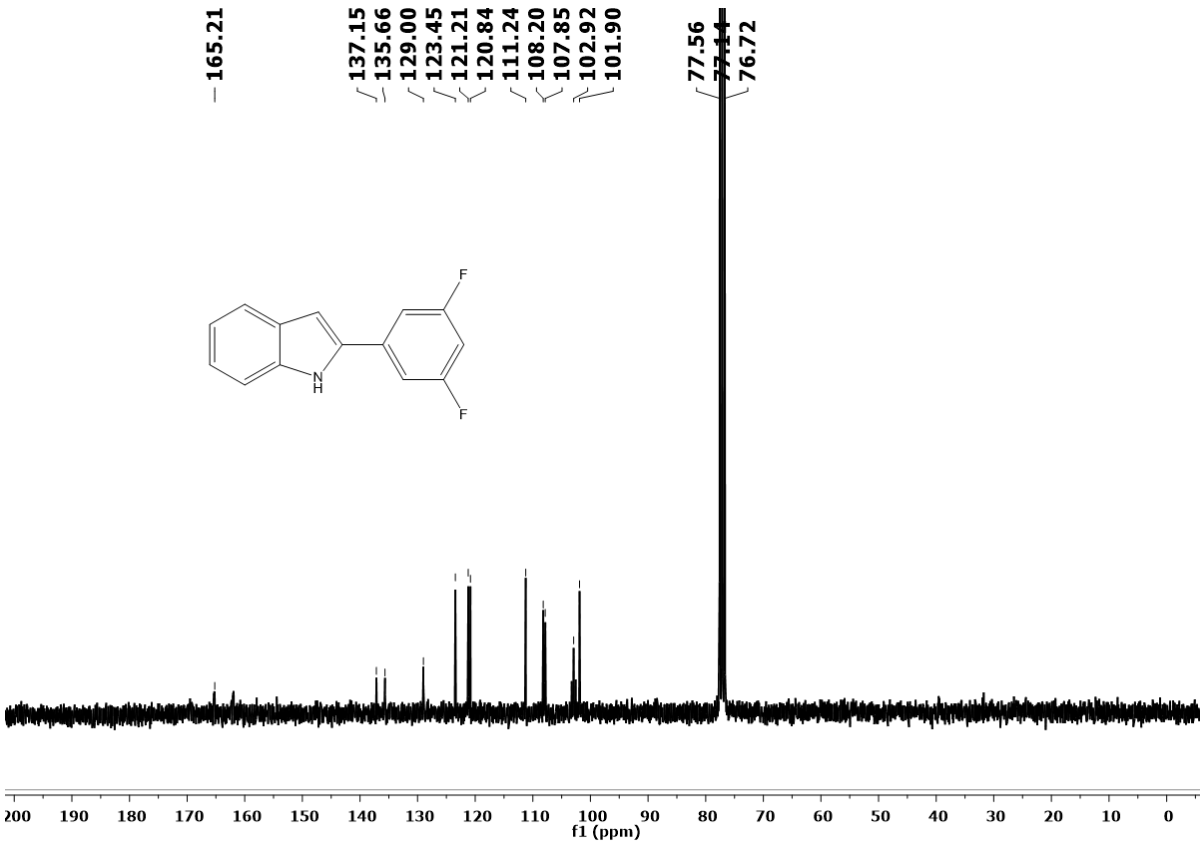

Figure 28S. 75 MHz ^{13}C-NMR spectrum of compound **3h** in $CDCl_3$

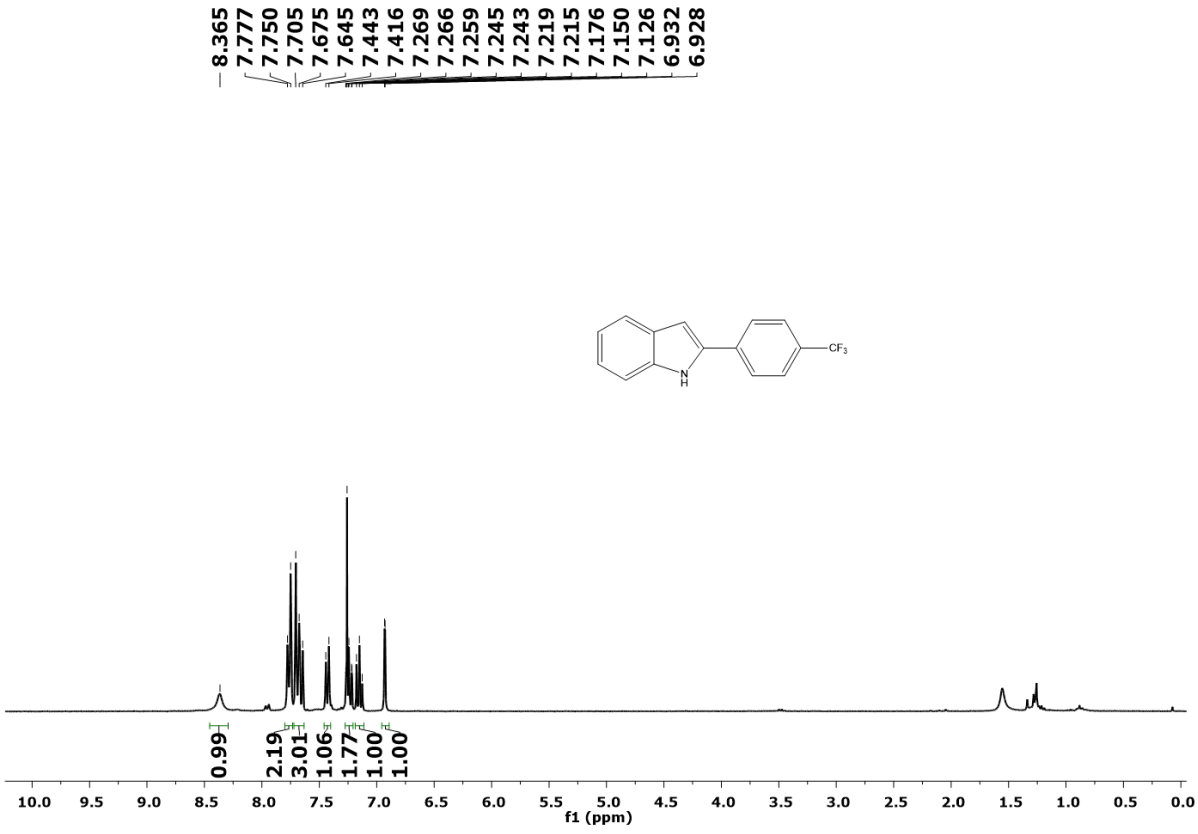

Figure 29S. 300 MHz ^{1}H-NMR spectrum of compound **3i** in $CDCl_3$

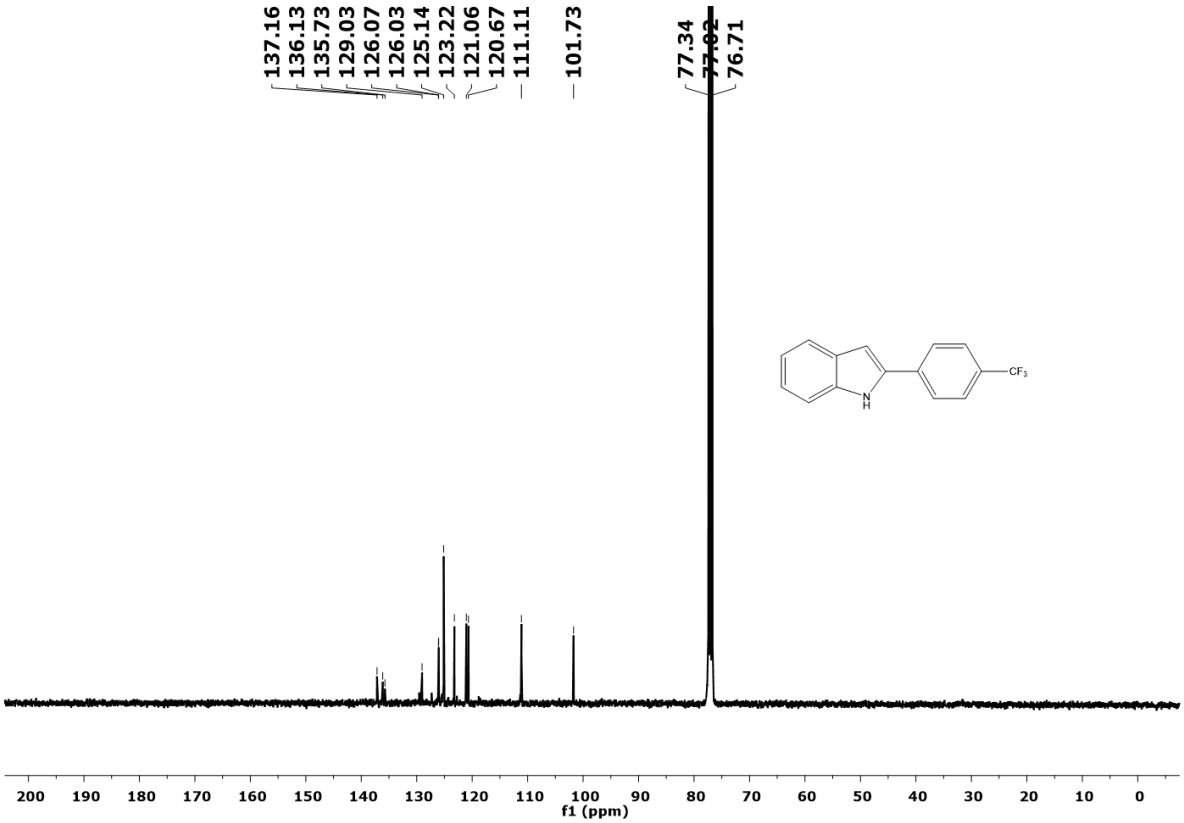

Figure 30S. 101 MHz ^{13}C-NMR spectrum of compound **3i** in $CDCl_3$

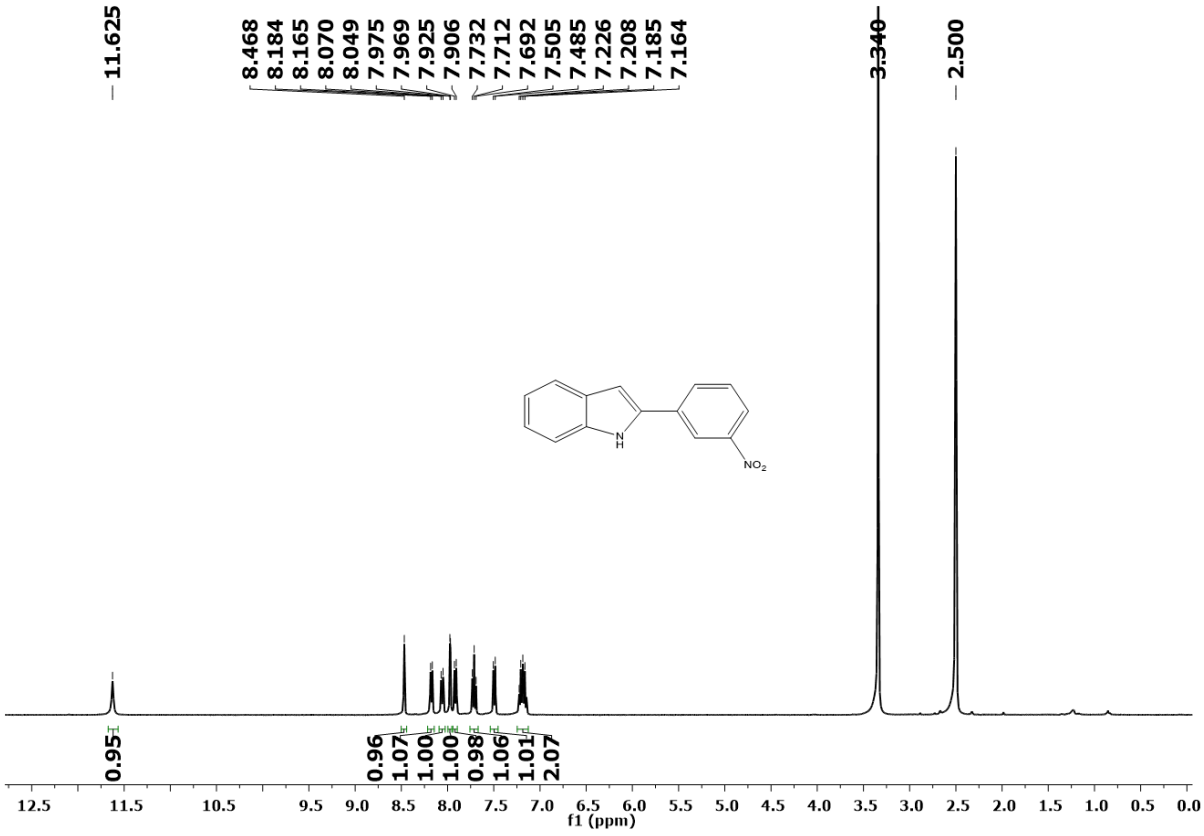

Figure 31S. 400 MHz ^{1}H-NMR spectrum of compound **3j** in DMSO-d_6

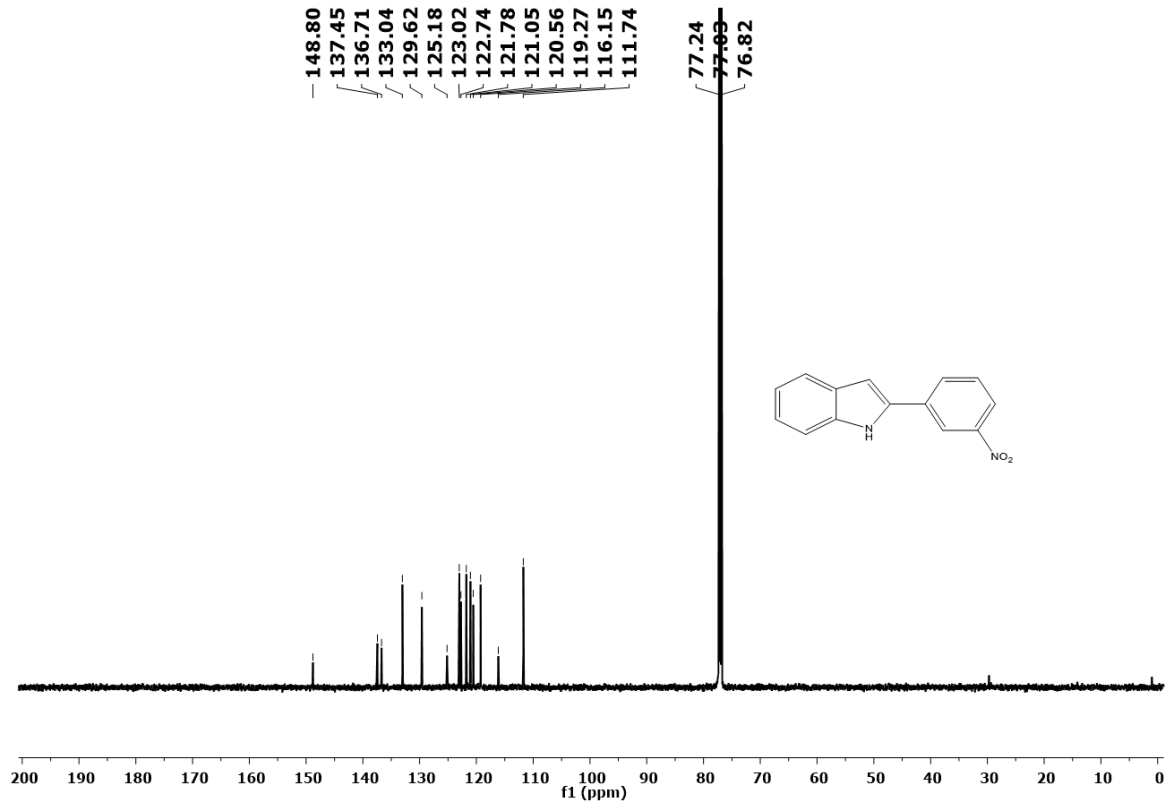

Figure 32S. 151 MHz ^{13}C-NMR spectrum of compound **3j** in $CDCl_3$

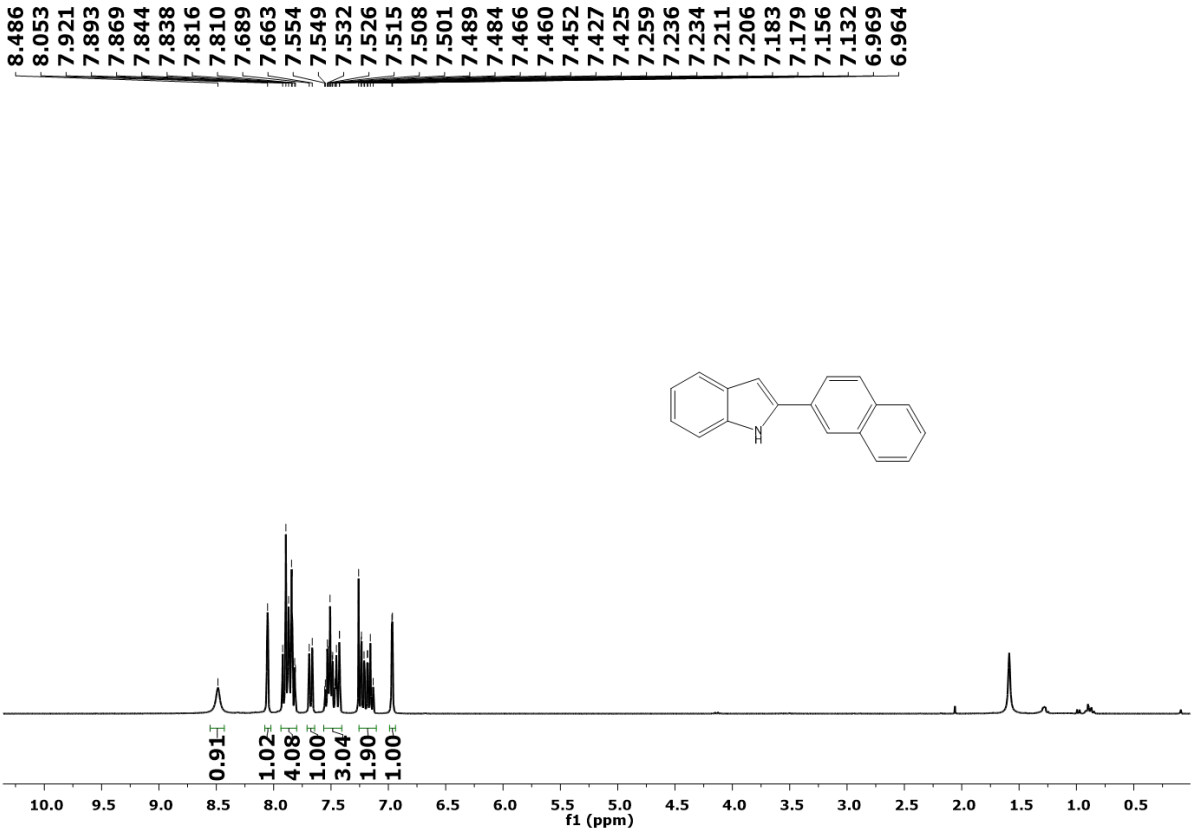

Figure 33S. 300 MHz ^{1}H-NMR spectrum of compound **3k** in $CDCl_3$

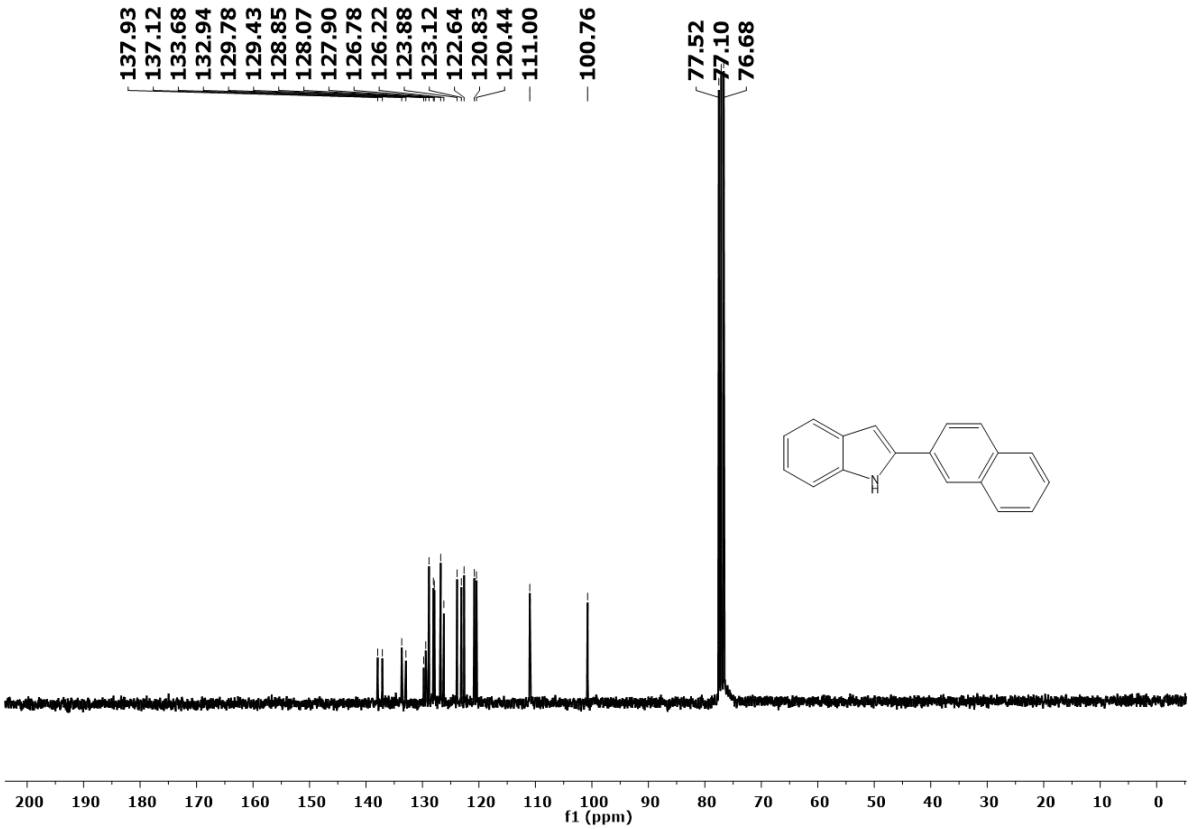

Figure 34S. 75 MHz ^{13}C-NMR spectrum of compound **3k** in $CDCl_3$

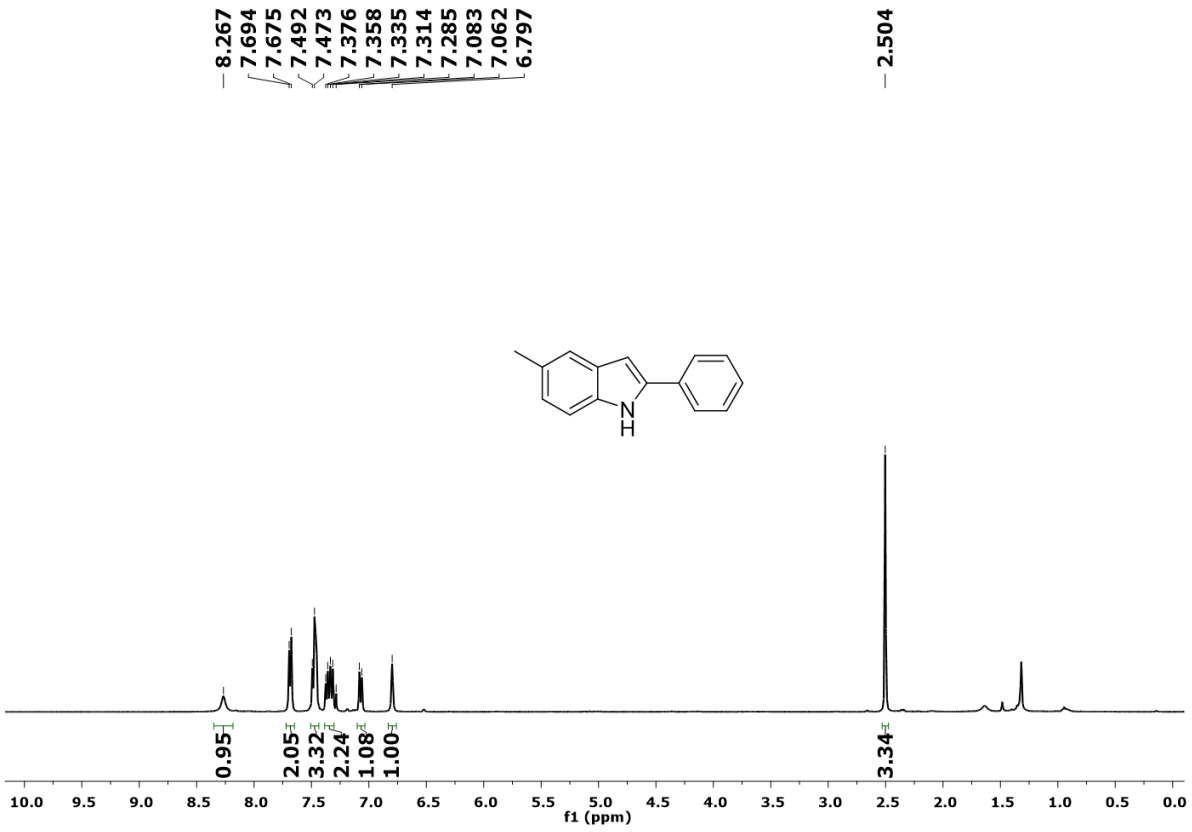

Figure 35S. 400 MHz ^{1}H-NMR spectrum of compound **3l** in $CDCl_3$

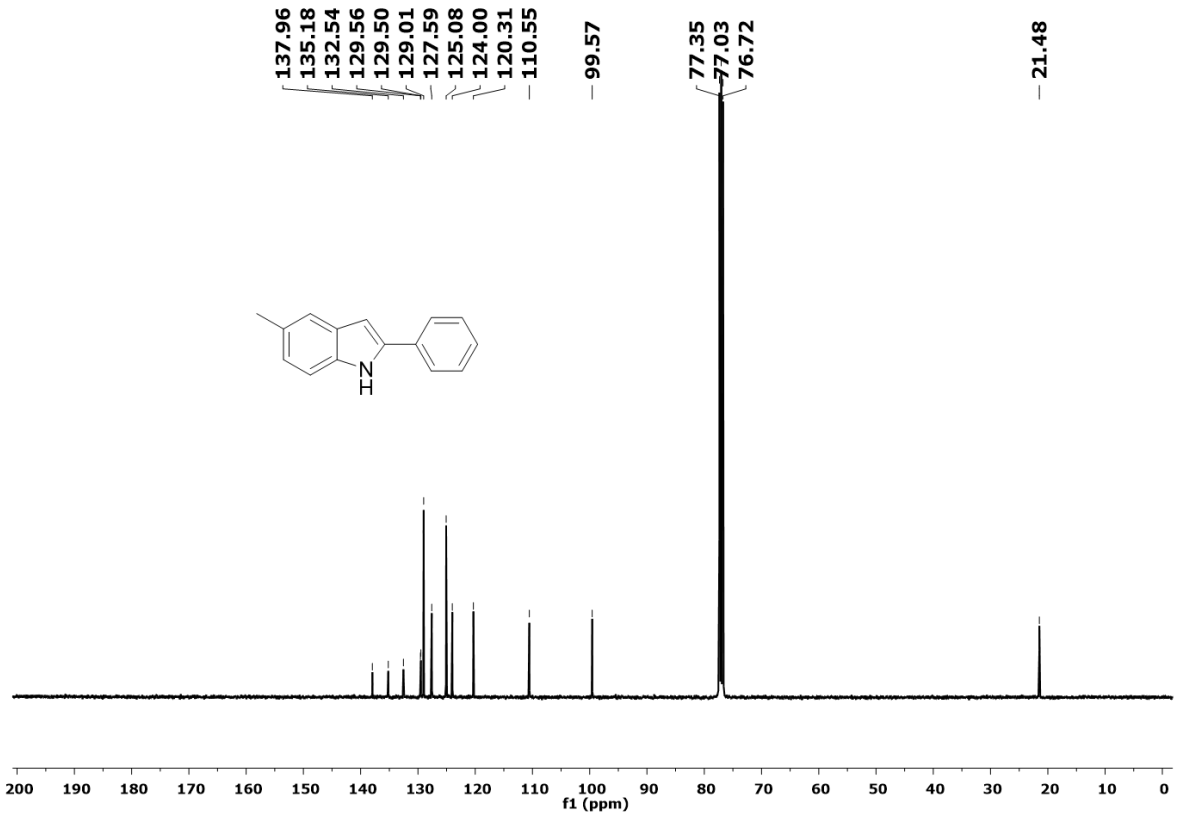

Figure 36S. 101 MHz ^{13}C-NMR spectrum of compound **3l** in $CDCl_3$

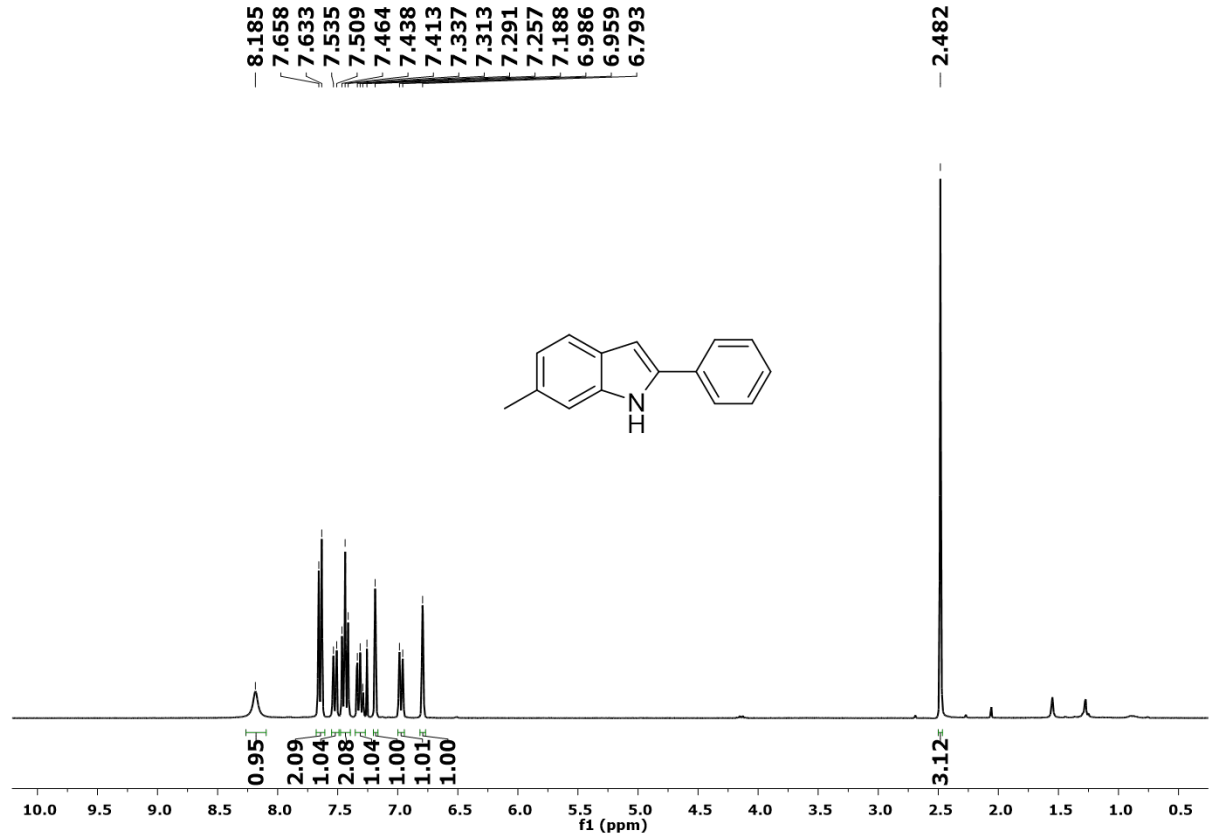

Figure 37S. 300 MHz ^{1}H-NMR spectrum of compound **3m** in $CDCl_3$

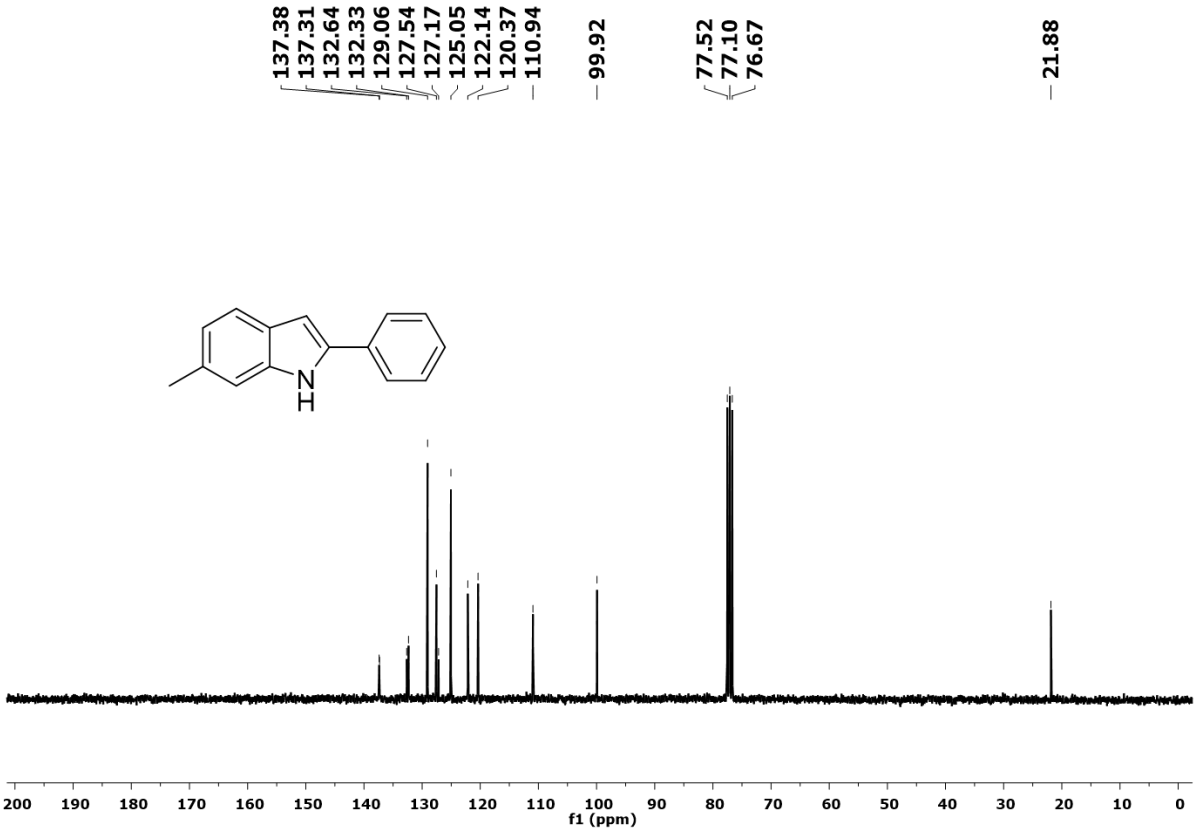

Figure 38S. 75 MHz ^{13}C-NMR spectrum of compound **3m** in $CDCl_3$

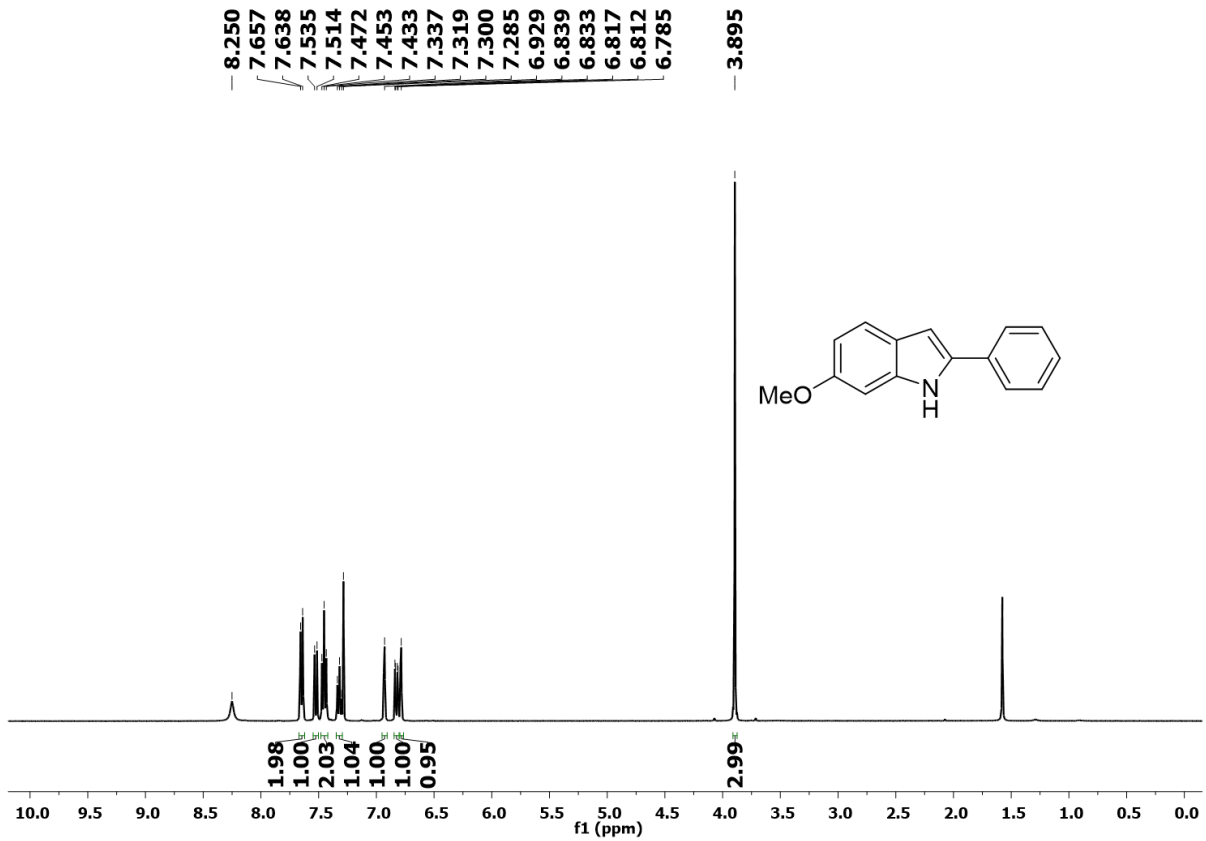

Figure 39S. 400 MHz ^{1}H-NMR spectrum of compound **3n** in $CDCl_3$

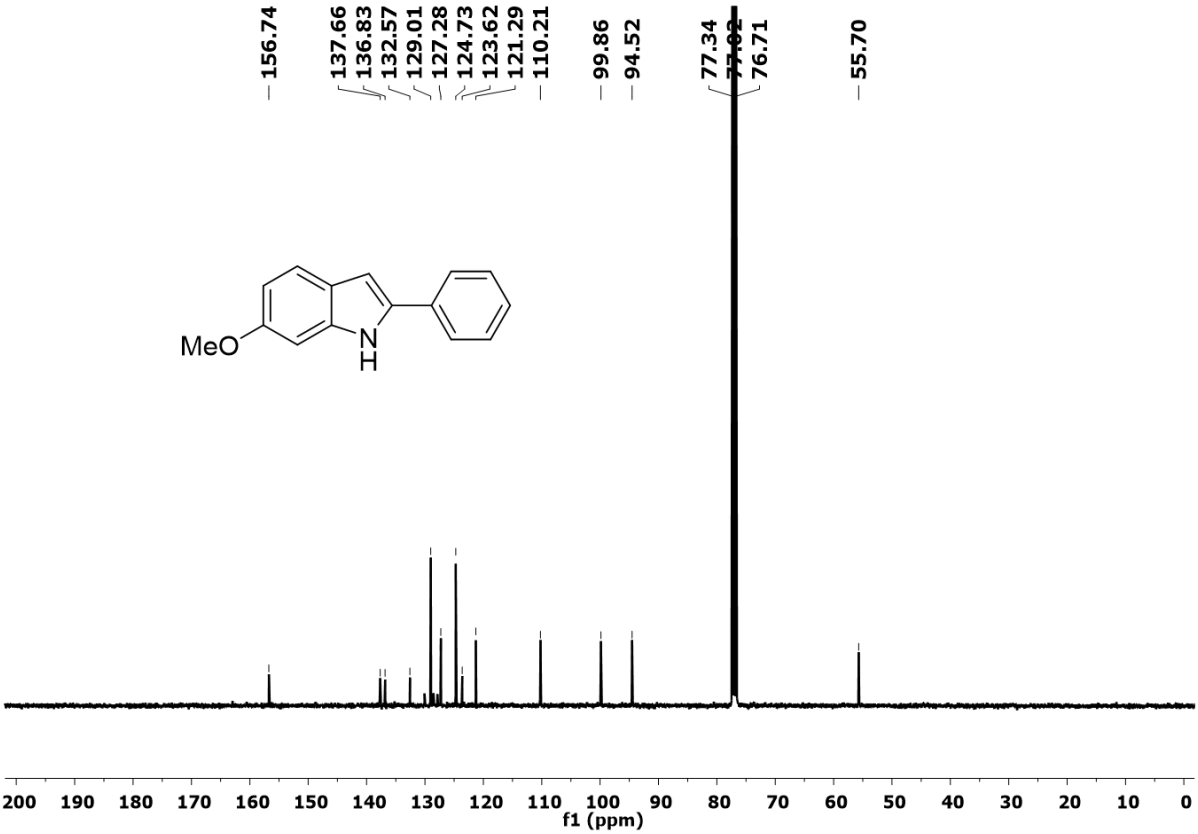

Figure 40S. 101 MHz ^{13}C-NMR spectrum of compound **3n** in $CDCl_3$

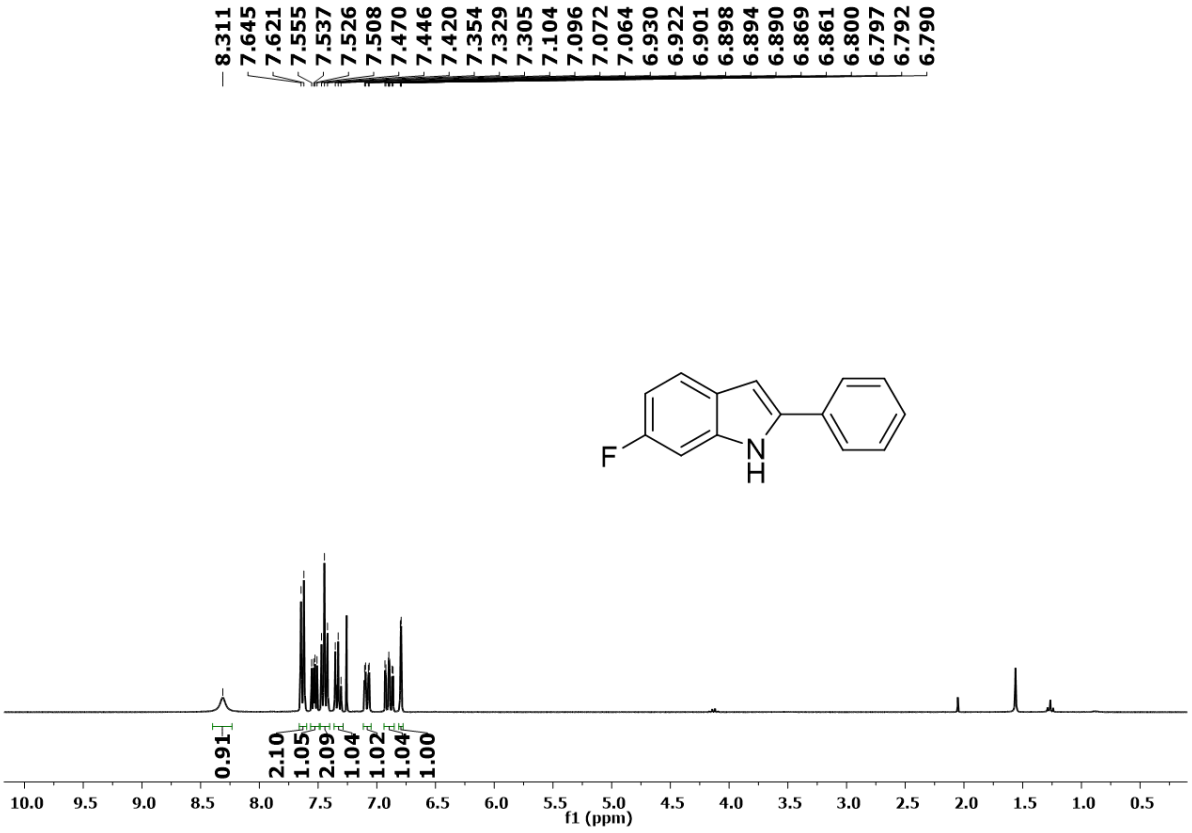

Figure 41S. 300 MHz ^{1}H-NMR spectrum of compound **3o** in $CDCl_3$

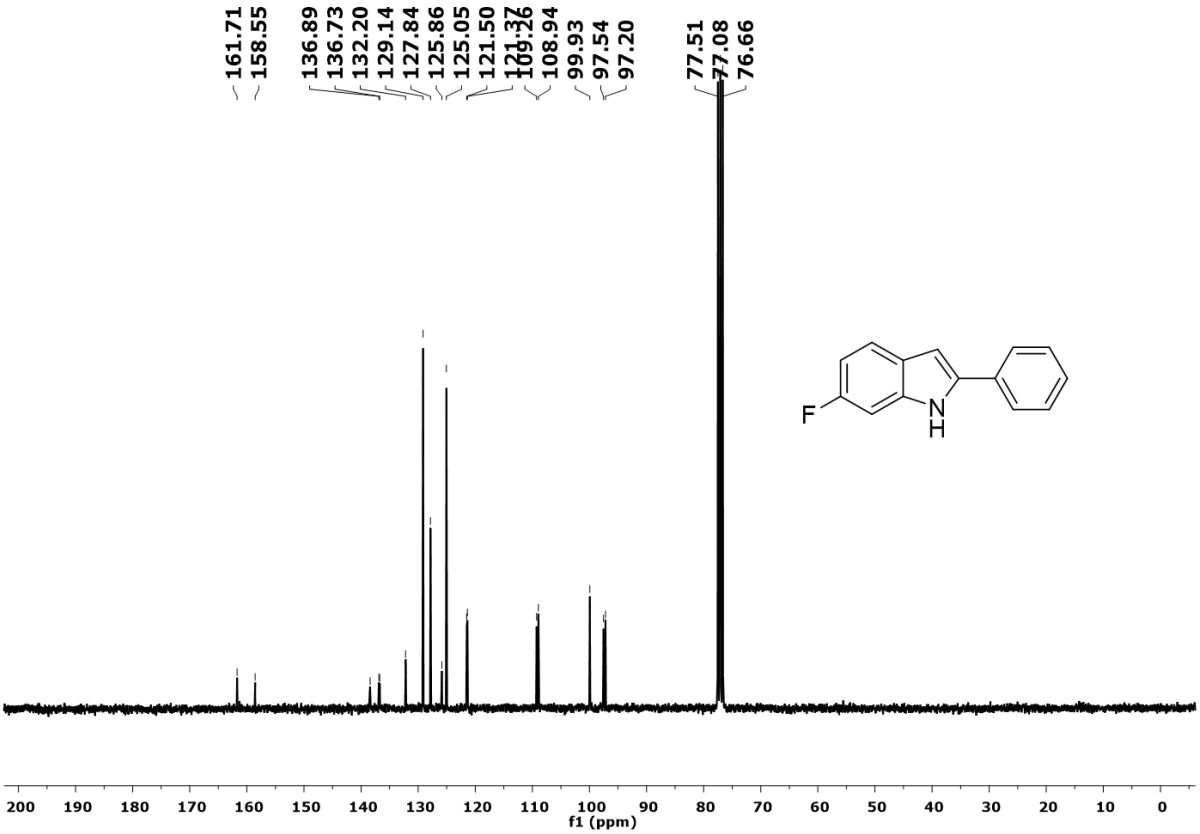

Figure 42S. 75 MHz ^{13}C-NMR spectrum of compound **3o** in $CDCl_3$

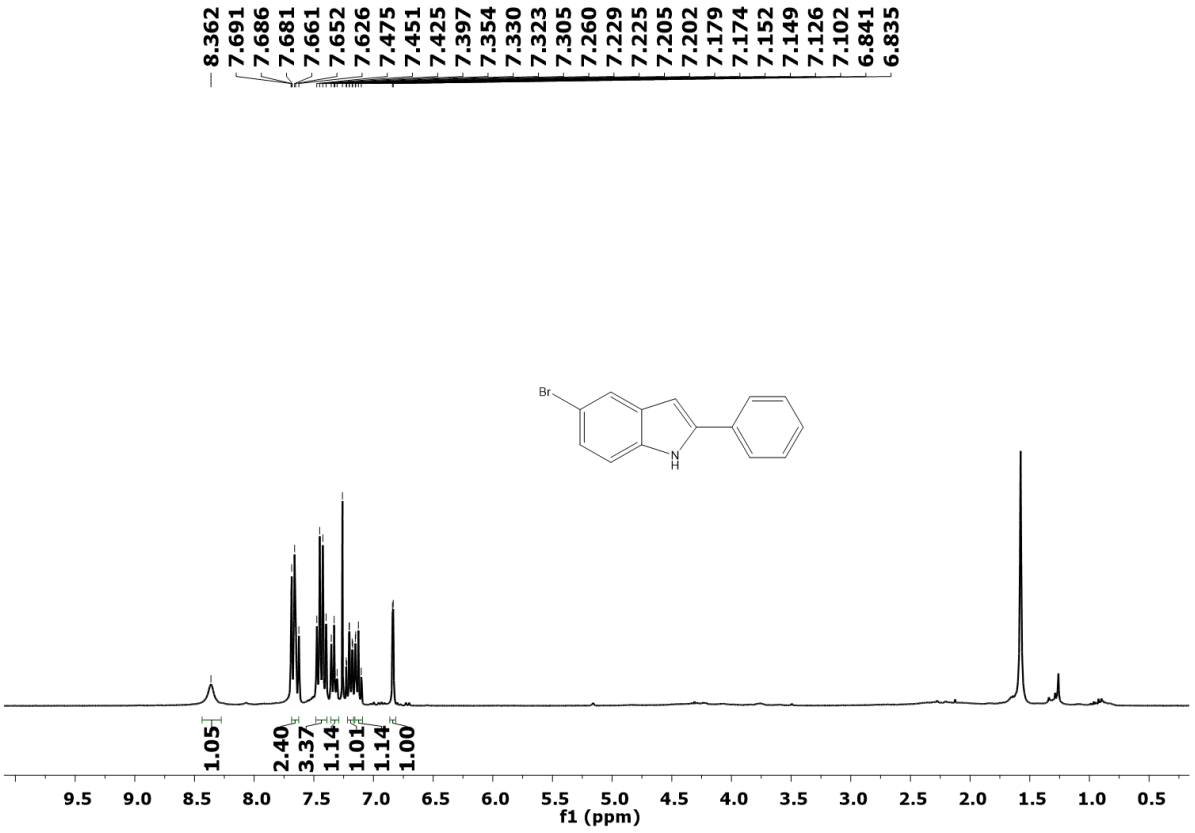

Figure 43S. 300 MHz ^{1}H-NMR spectrum of compound **3p** in $CDCl_3$

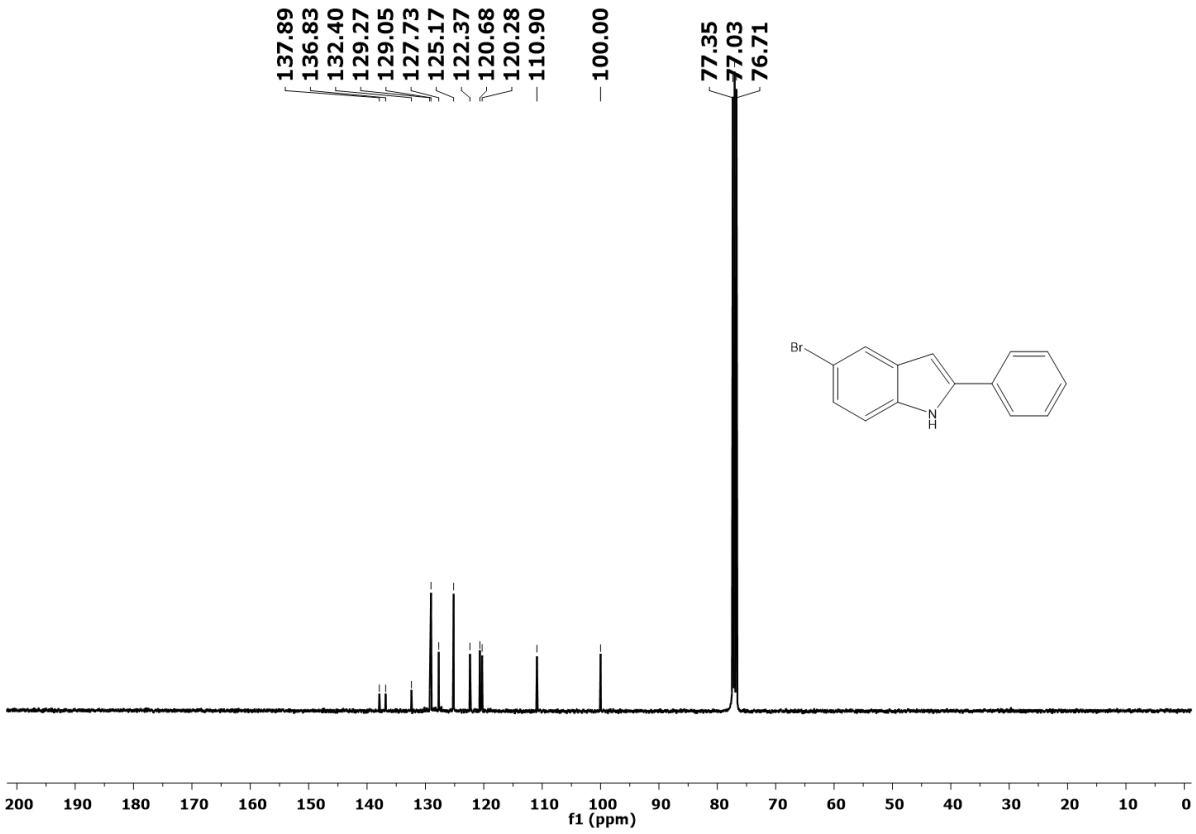

Figure 44S. 101 MHz ^{13}C-NMR spectrum of compound **3p** in $CDCl_3$

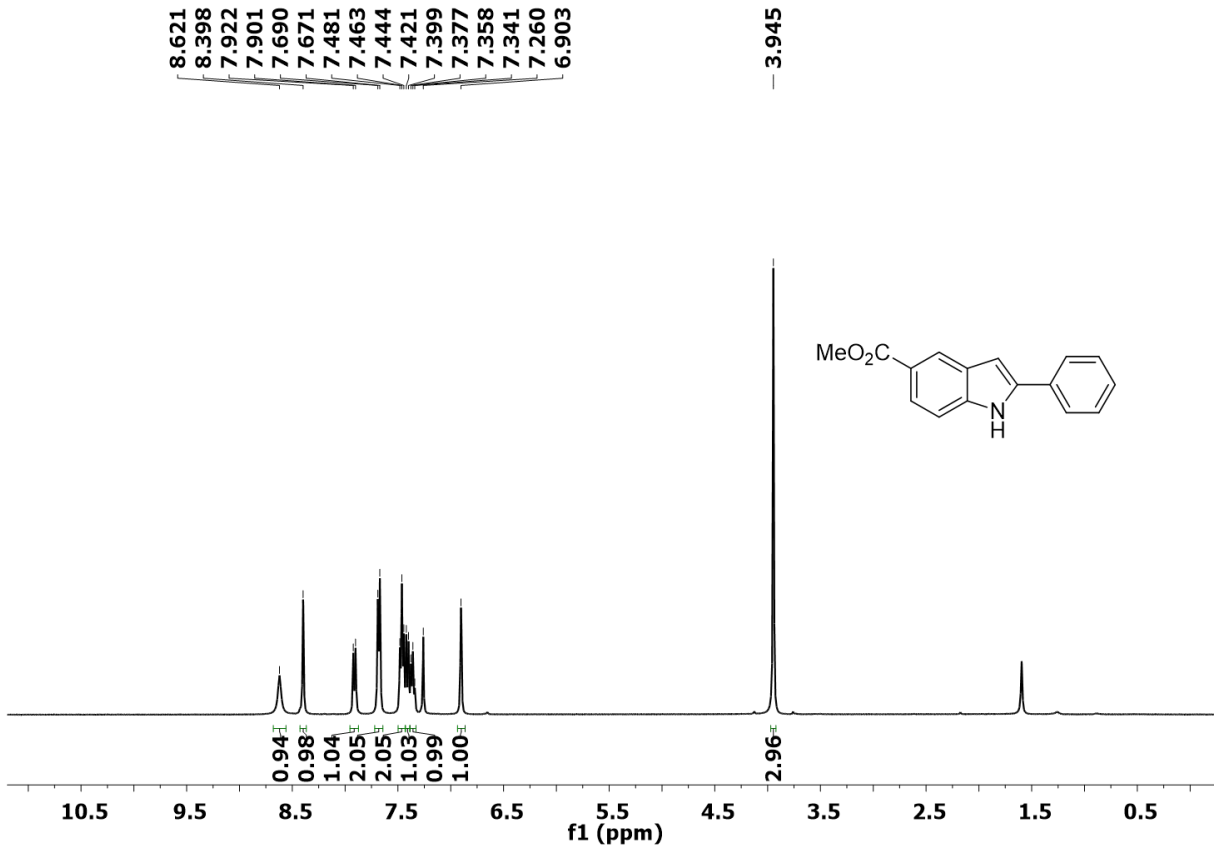

Figure 45S. 400 MHz ^{1}H-NMR spectrum of compound **3q** in $CDCl_3$

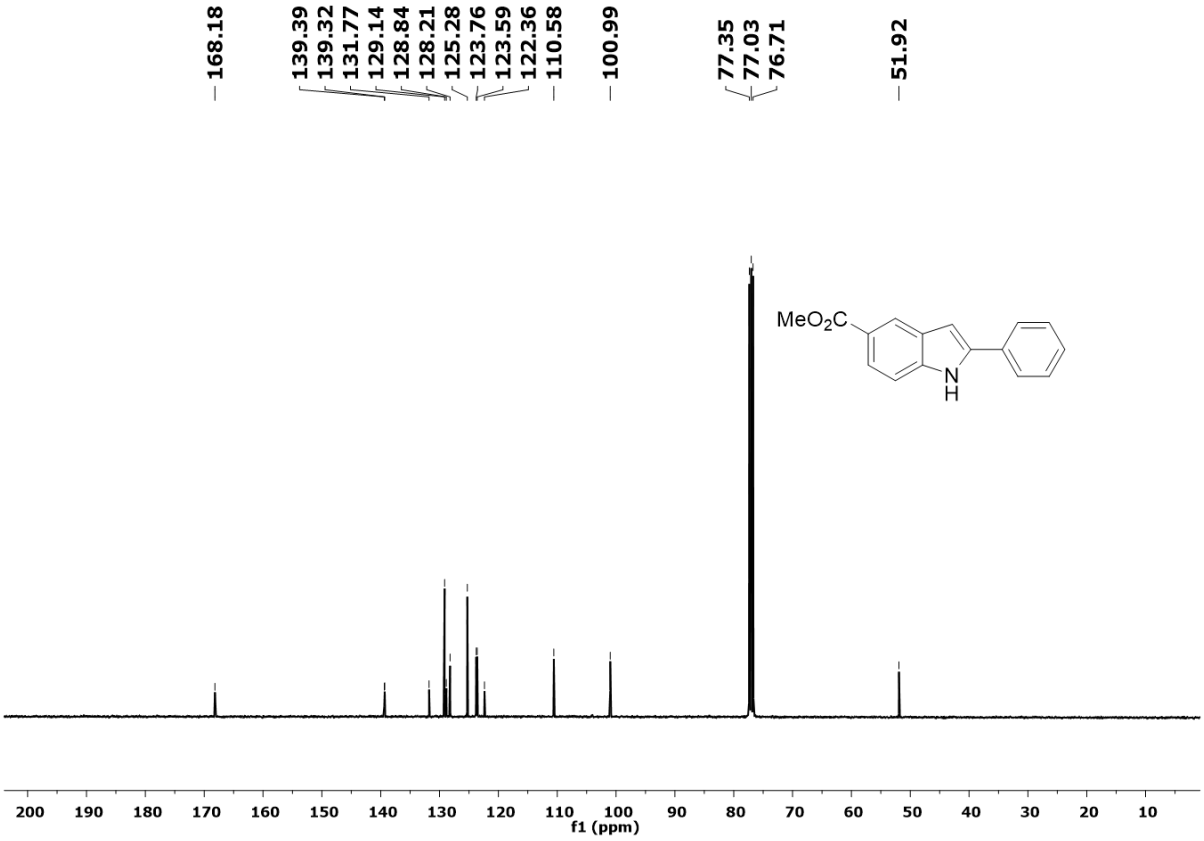

Figure 46S. 101 MHz ^{13}C-NMR spectrum of compound **3q** in $CDCl_3$

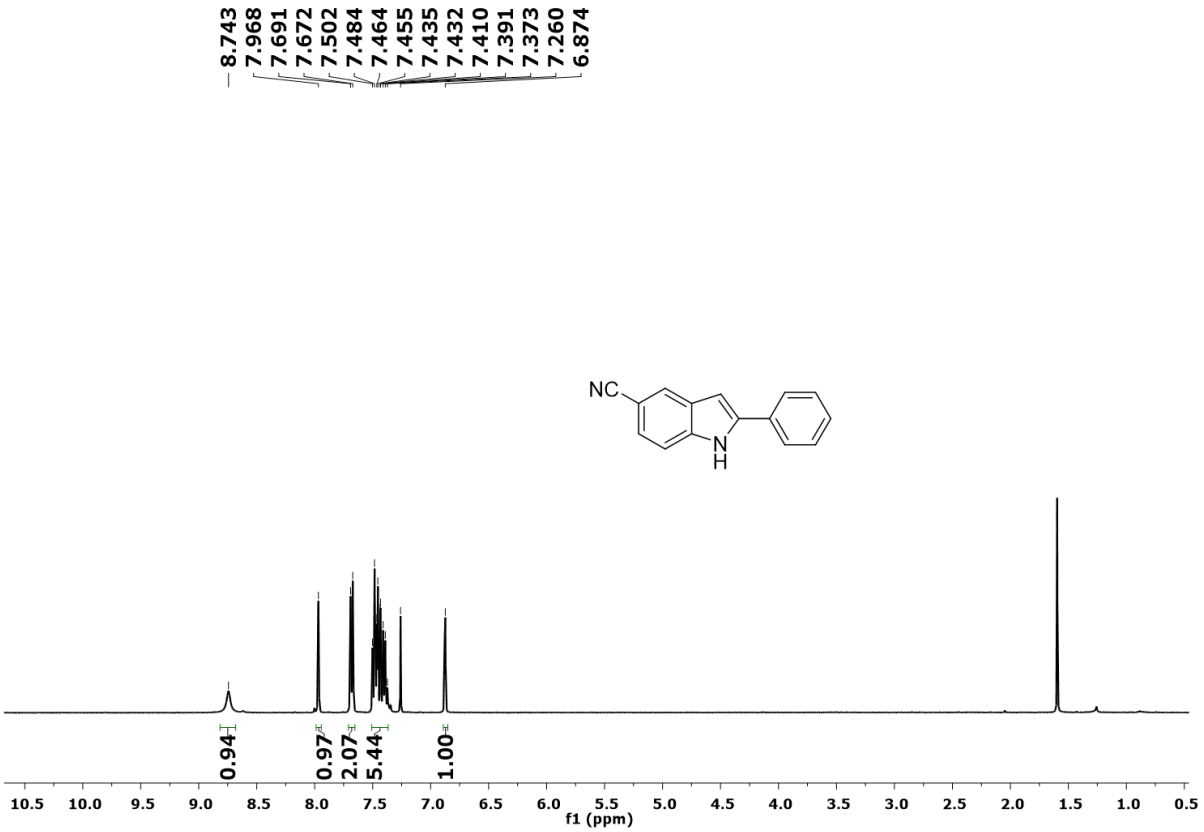

Figure 47S. 400 MHz ^{1}H-NMR spectrum of compound **3r** in $CDCl_3$

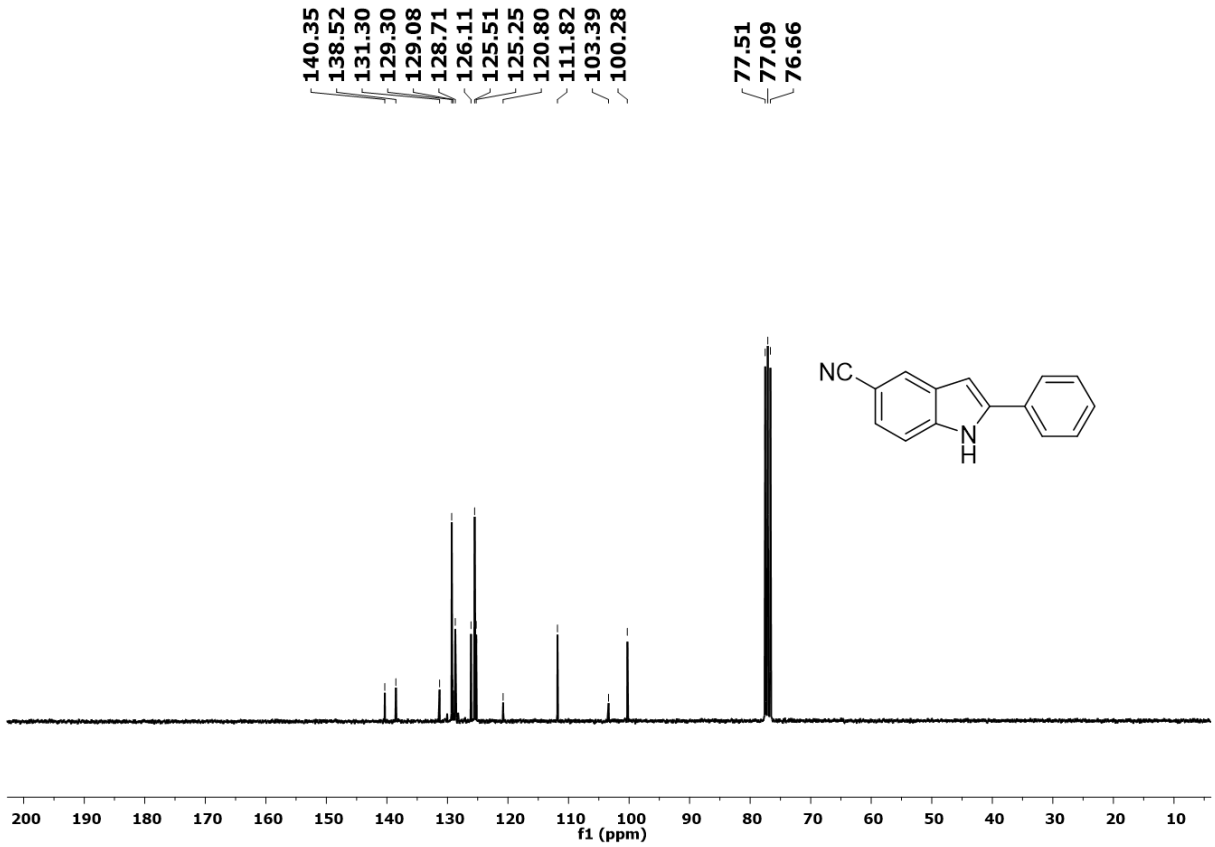

Figure 48S. 75 MHz ^{13}C-NMR spectrum of compound **3r** in $CDCl_3$

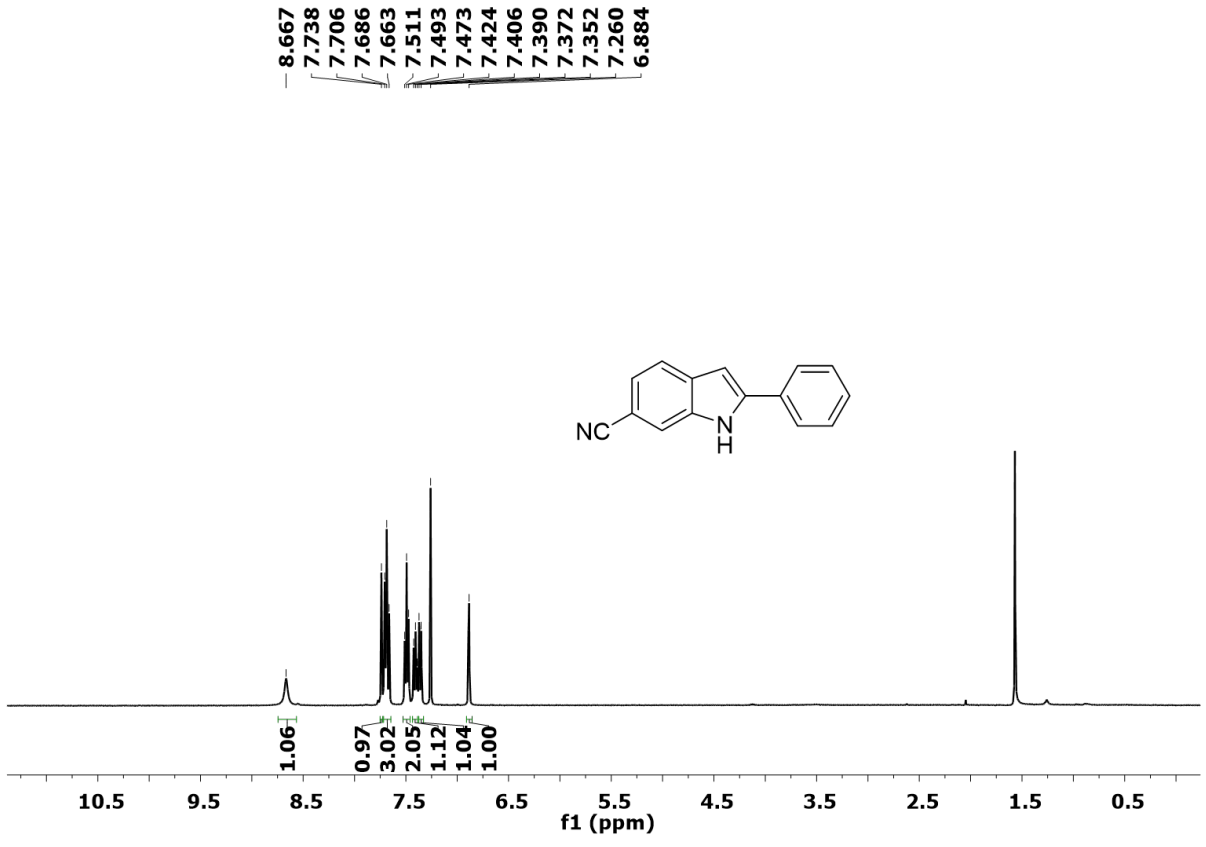

Figure 49S. 400 MHz ^{1}H-NMR spectrum of compound **3s** in $CDCl_3$

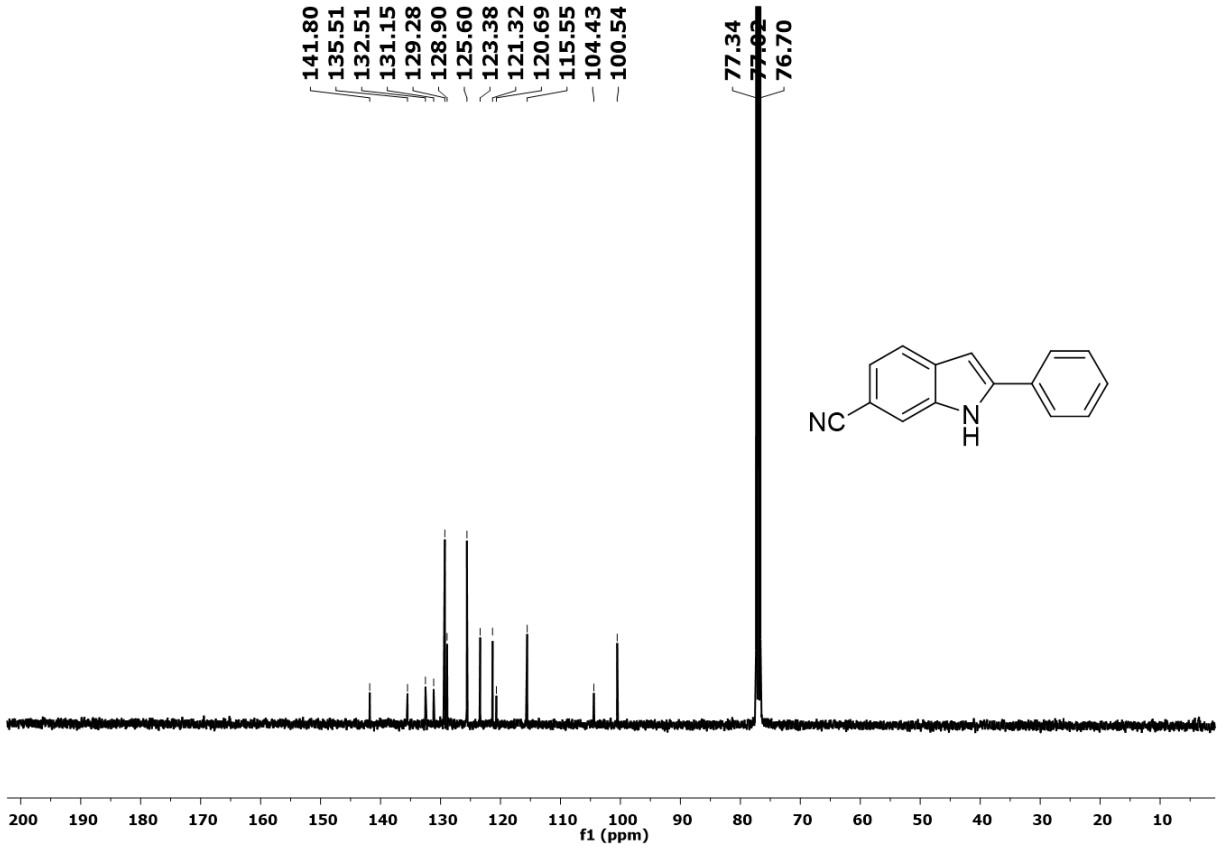

Figure 50S. 101 MHz ^{13}C-NMR spectrum of compound **3s** in $CDCl_3$

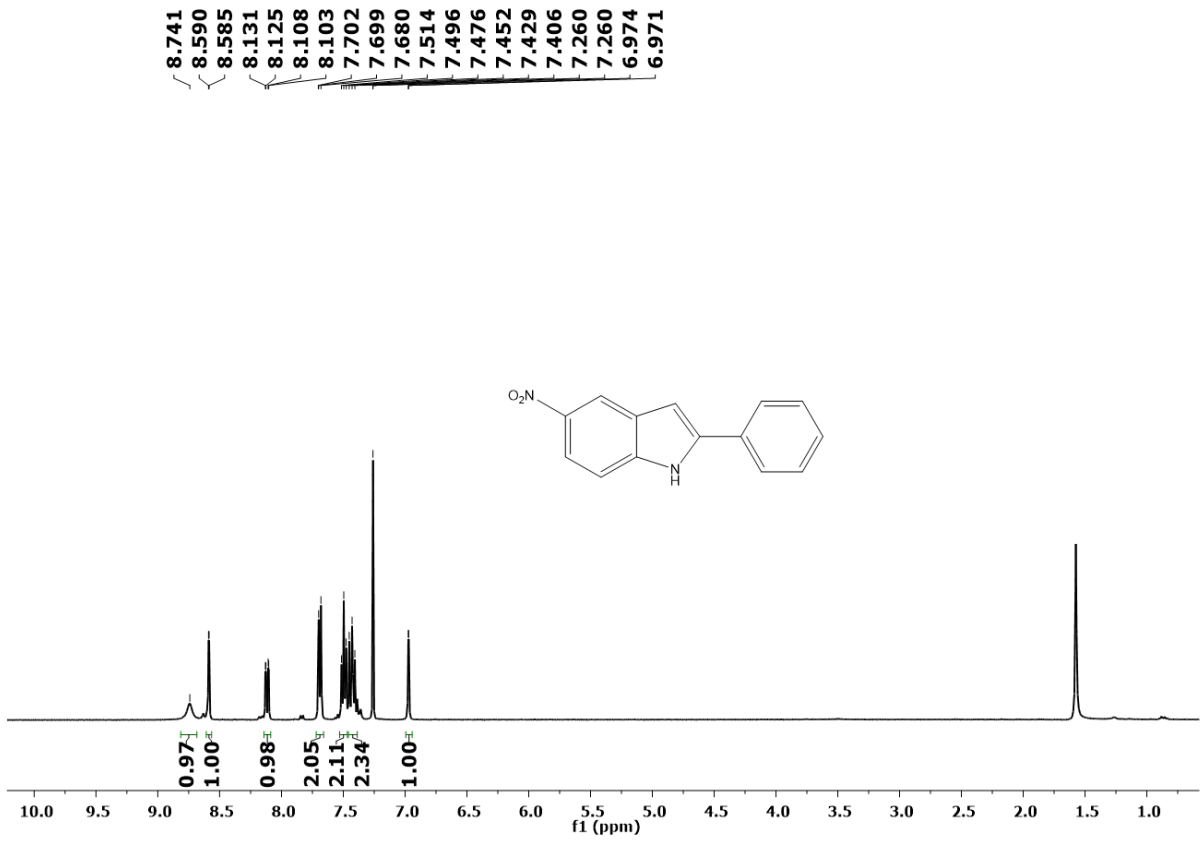

Figure 51S. 400 MHz ^{1}H-NMR spectrum of compound **3t** in $CDCl_3$

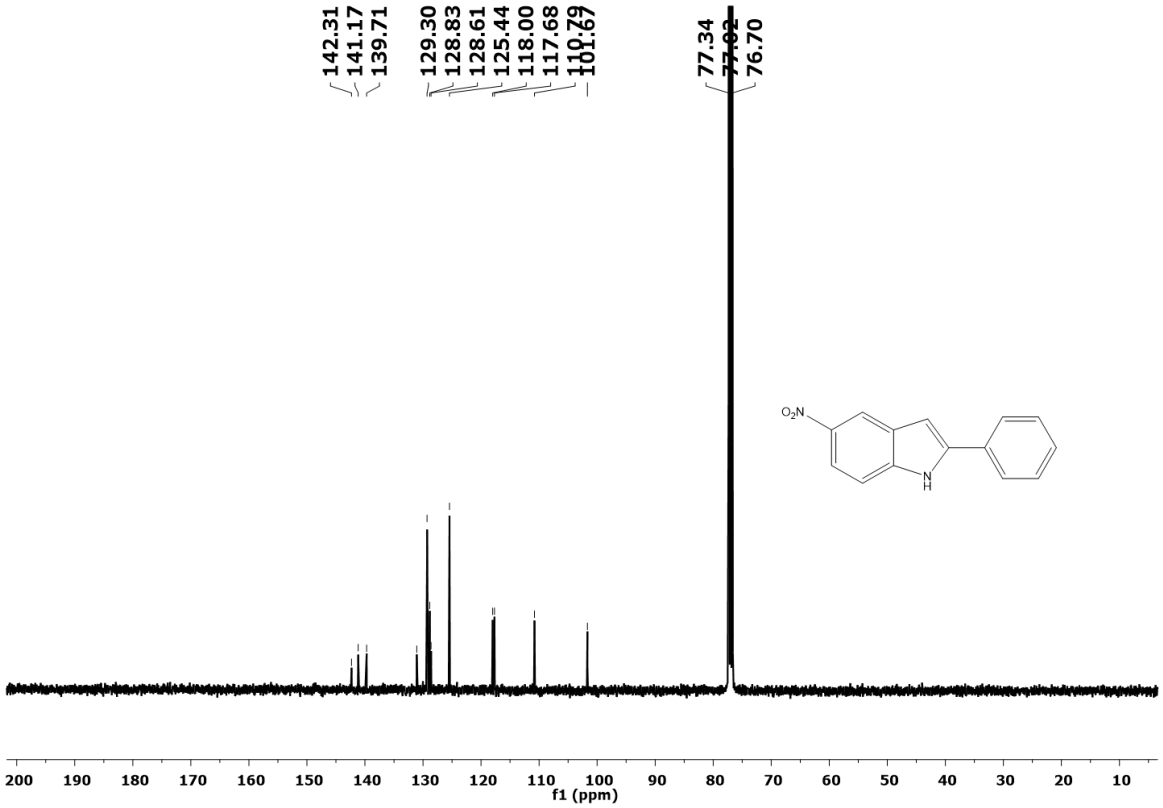

Figure 52S. 101 MHz ^{13}C-NMR spectrum of compound **3t** in $CDCl_3$

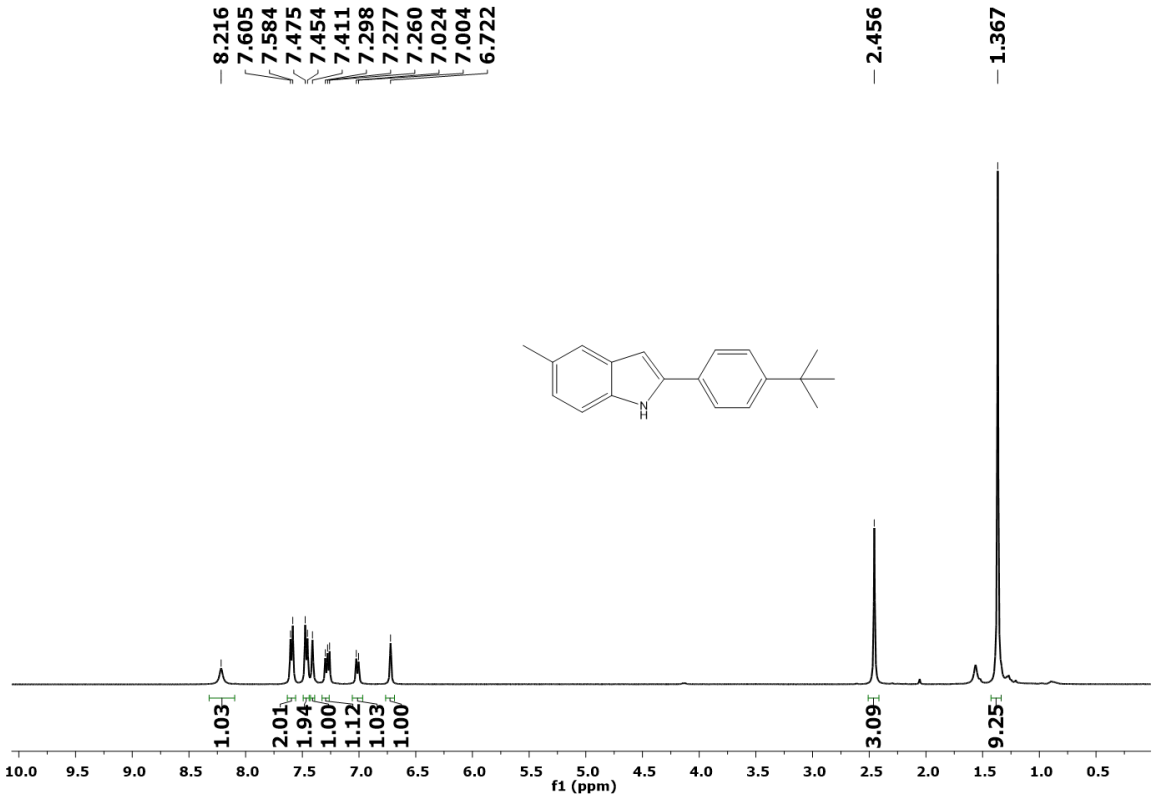

Figure 53S. 400 MHz ^{1}H-NMR spectrum of compound **3u** in $CDCl_3$

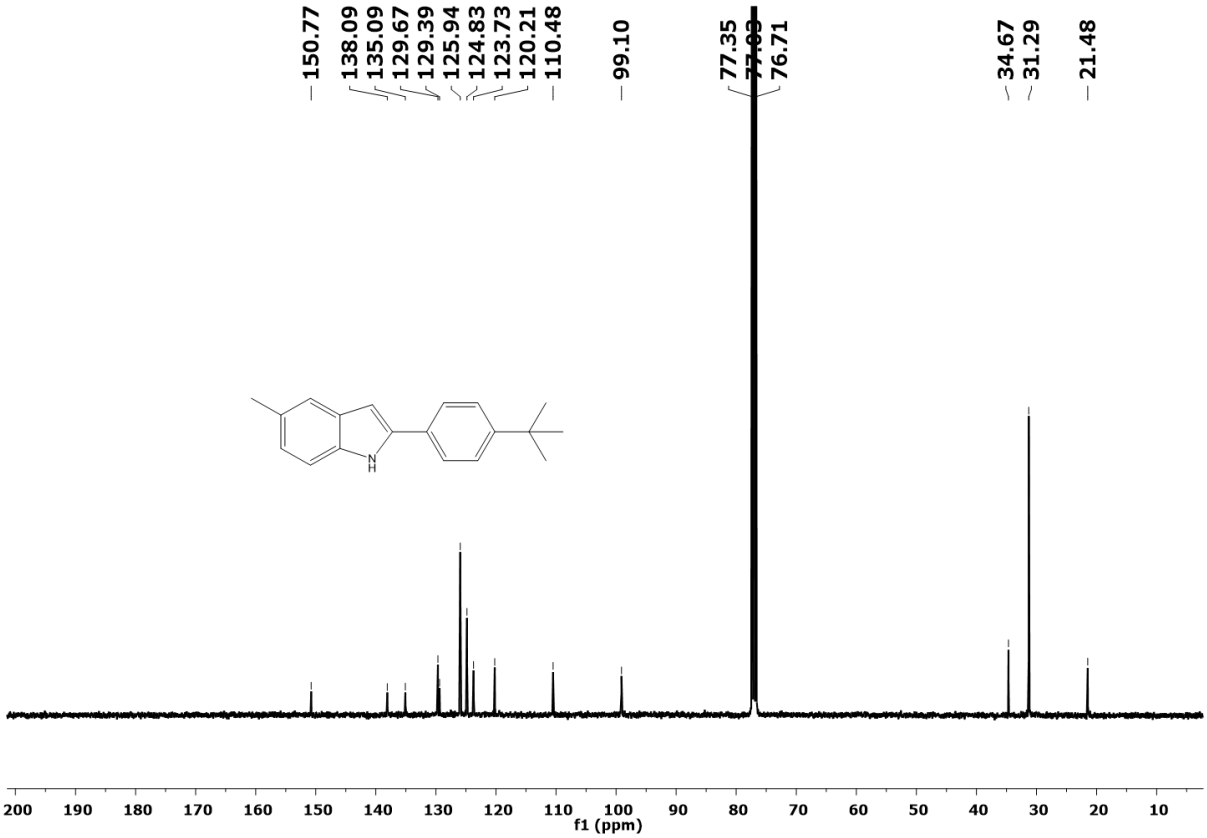

Figure 54S. 101 MHz ^{13}C-NMR spectrum of compound **3u** in $CDCl_3$

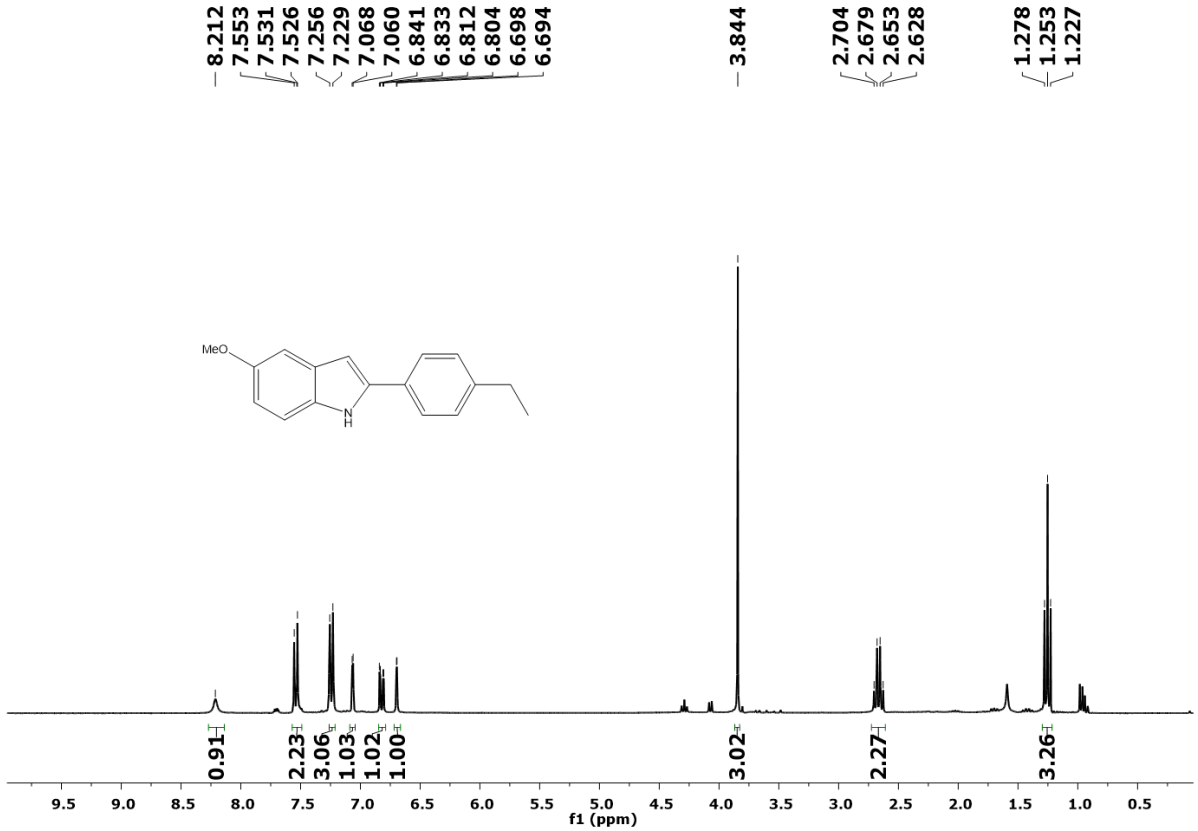

Figure 55S. 300 MHz ^{1}H-NMR spectrum of compound **3v** in $CDCl_3$

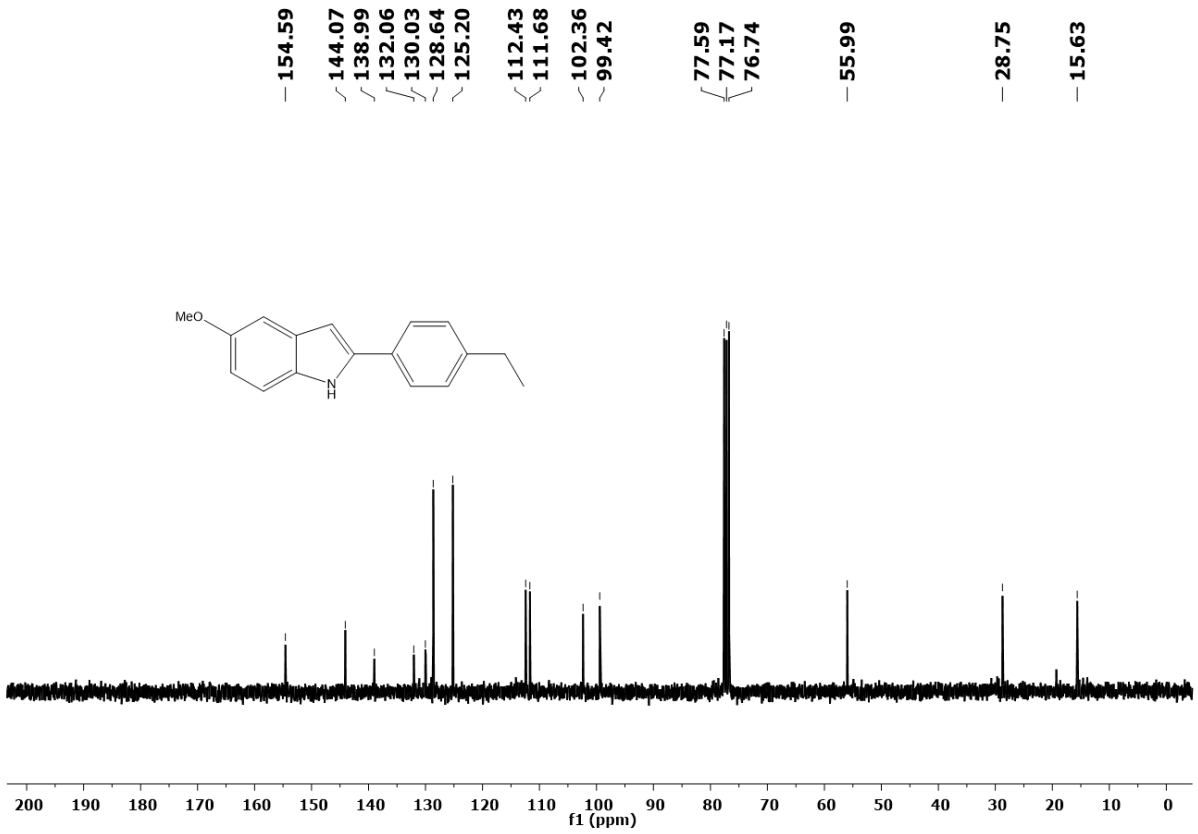

Figure 56S. 75 MHz ^{13}C-NMR spectrum of compound **3v** in $CDCl_3$

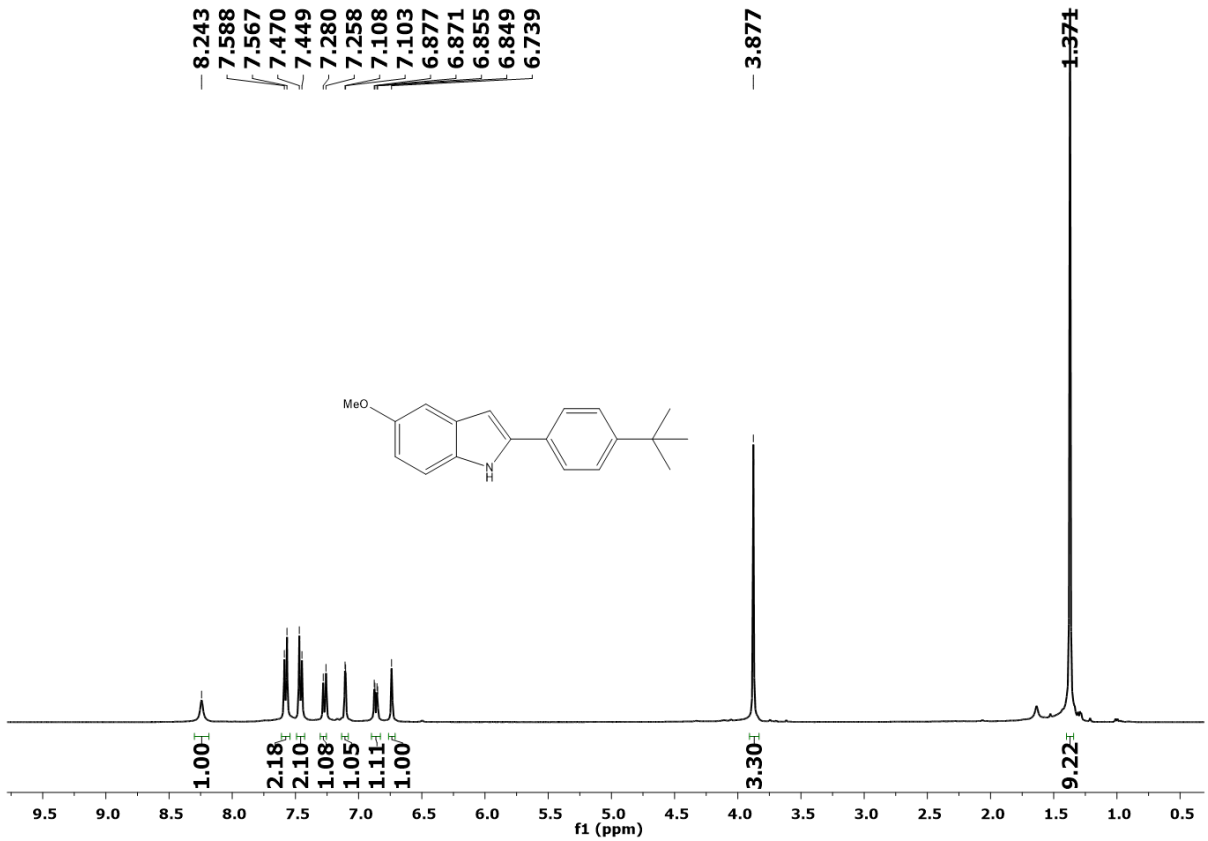

Figure 57S. 400 MHz ^{1}H-NMR spectrum of compound **3w** in $CDCl_3$

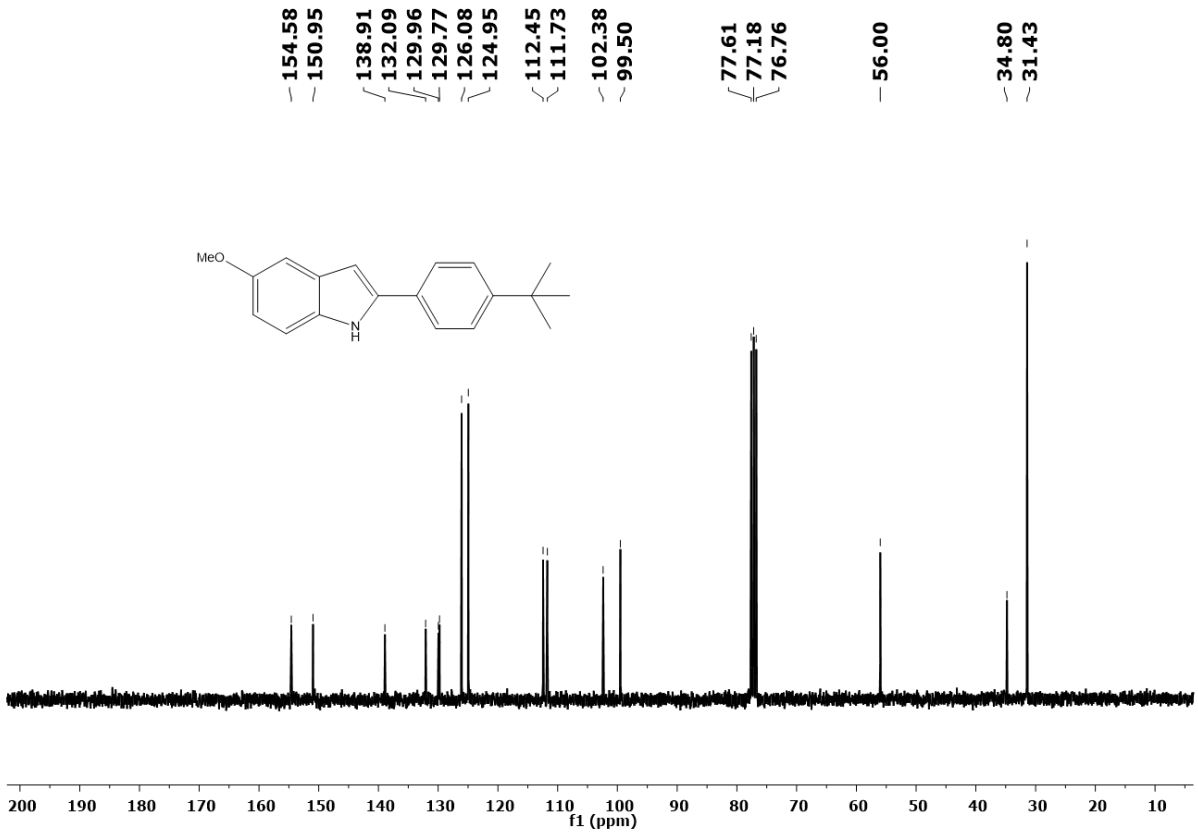

Figure 58S. 75 MHz ^{13}C-NMR spectrum of compound **3w** in $CDCl_3$

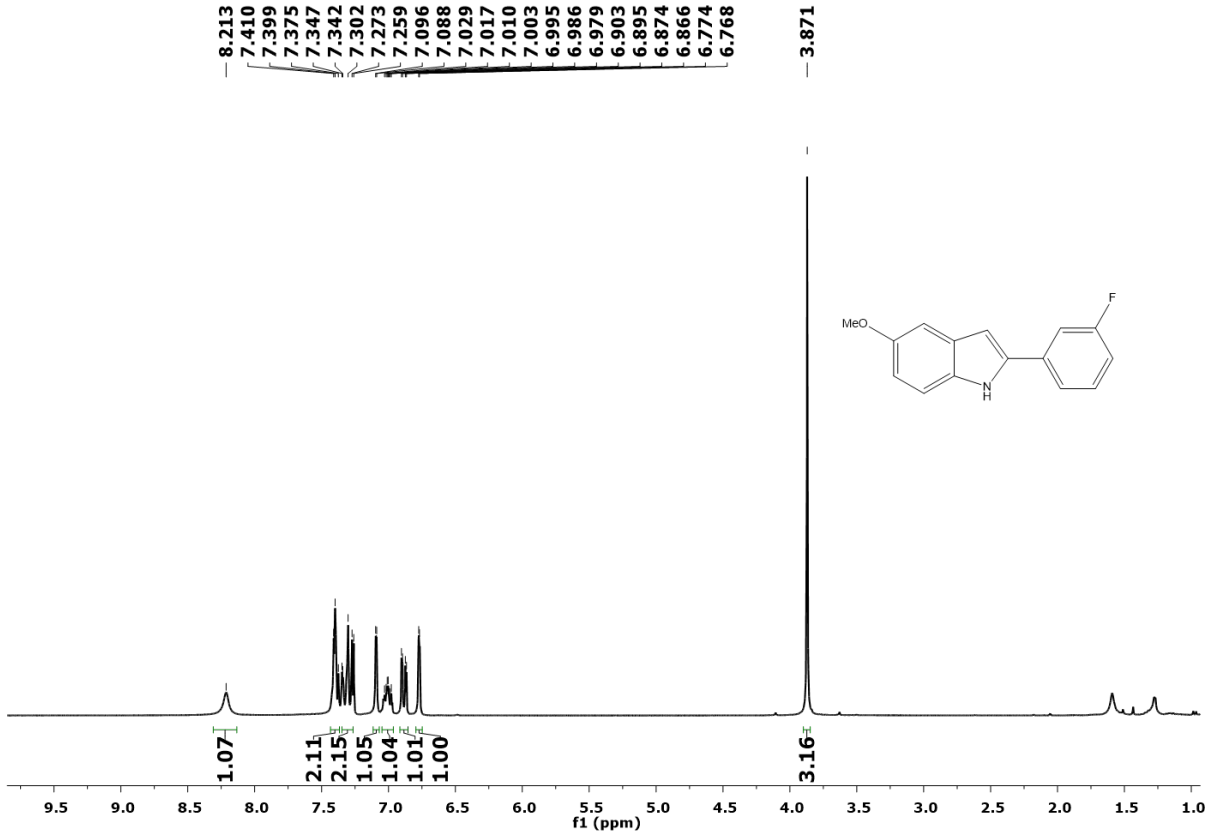

Figure 59S. 300 MHz ^{1}H-NMR spectrum of compound **3x** in $CDCl_3$

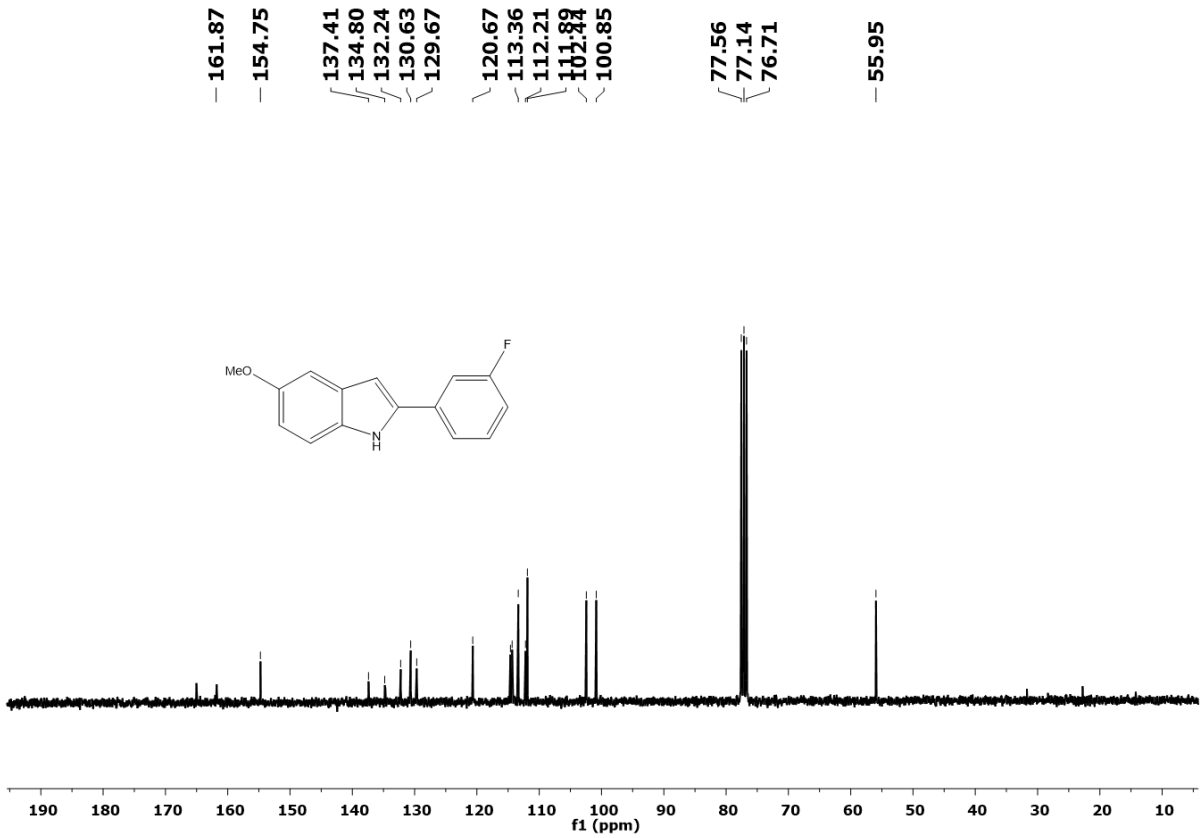

Figure 60S. 75 MHz ^{13}C-NMR spectrum of compound **3x** in $CDCl_3$

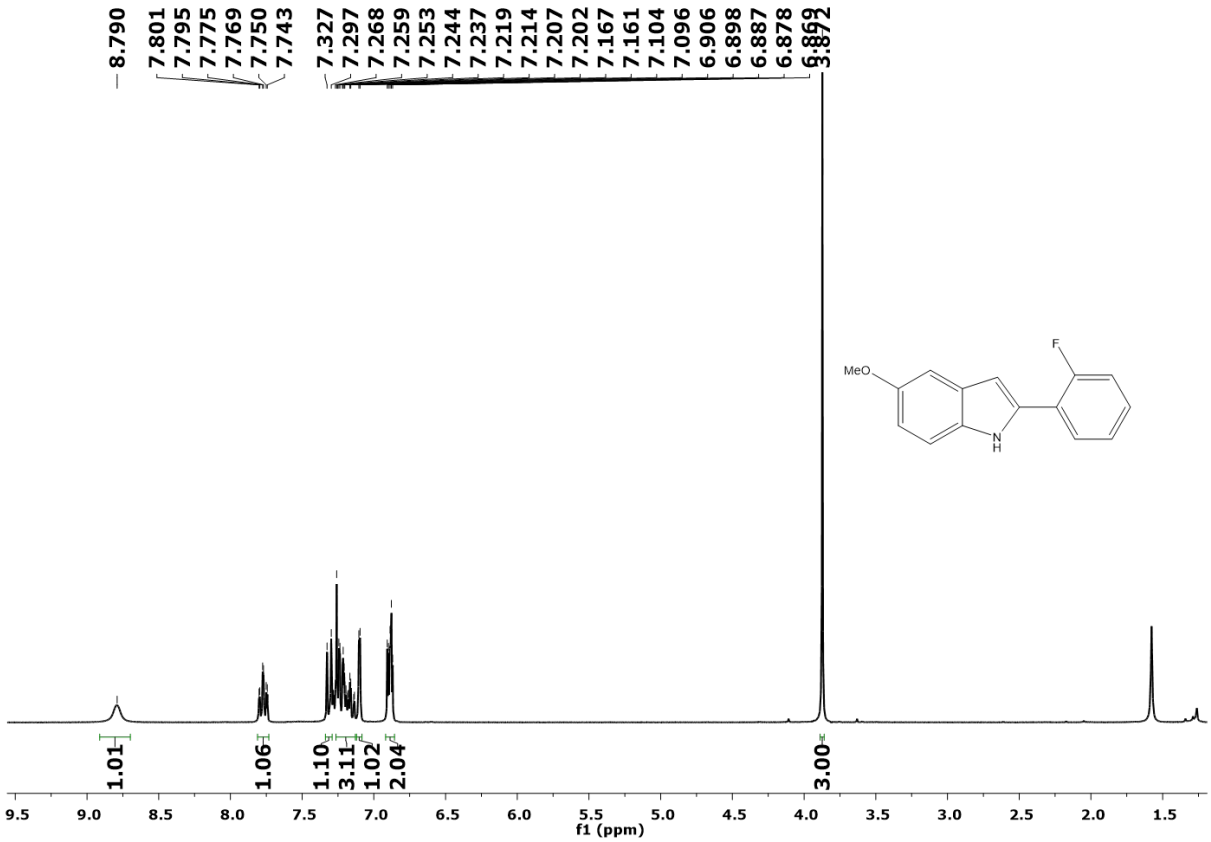

Figure 61S. 300 MHz ^{1}H-NMR spectrum of compound **3y** in $CDCl_3$

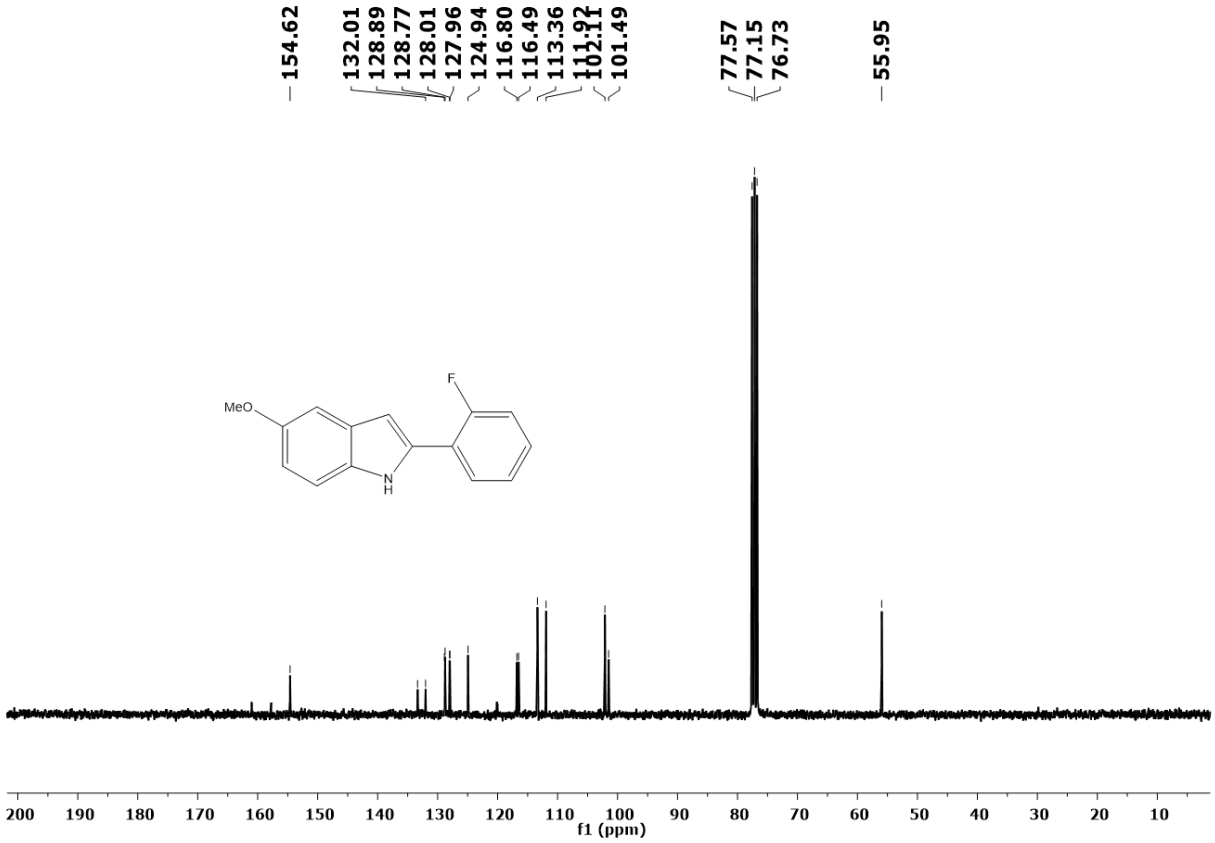

Figure 62S. 75 MHz ^{13}C-NMR spectrum of compound **3y** in $CDCl_3$

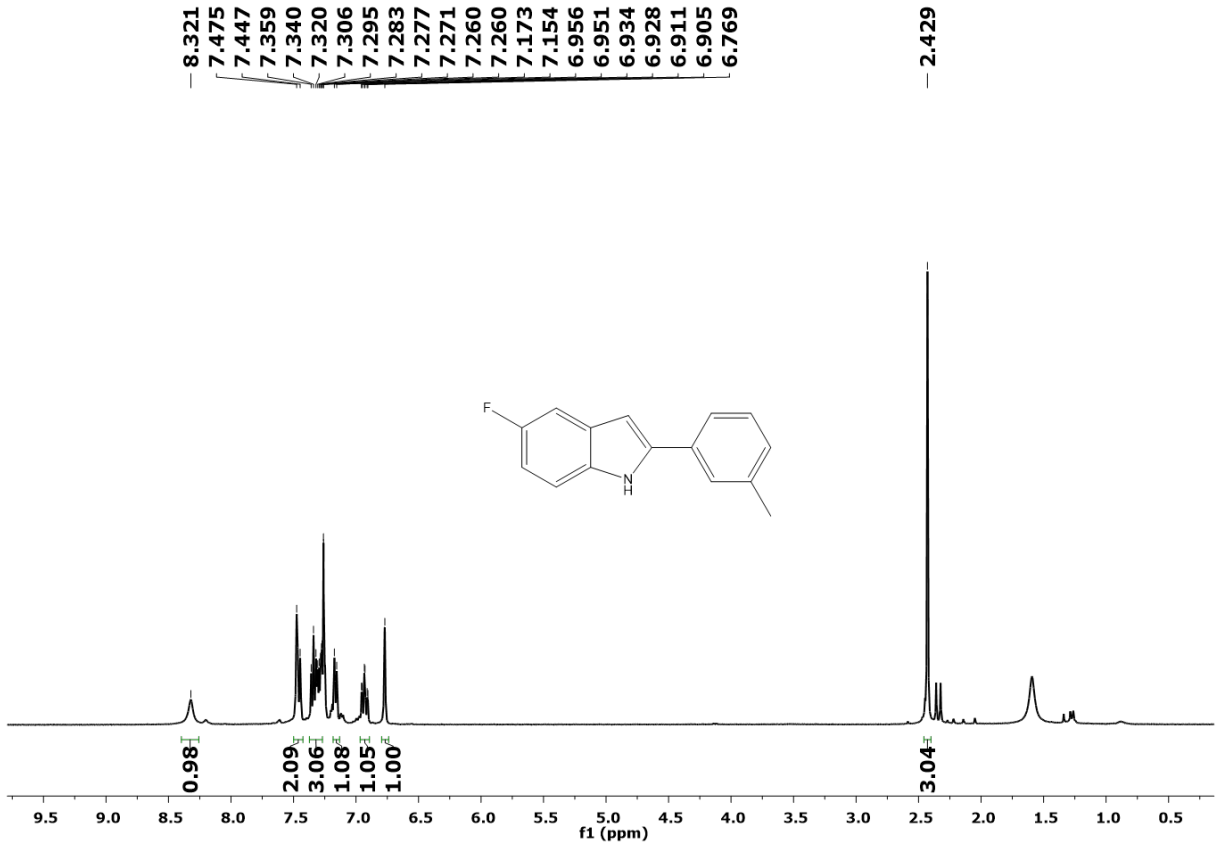

Figure 63S. 400 MHz ^{1}H-NMR spectrum of compound **3z** in $CDCl_3$

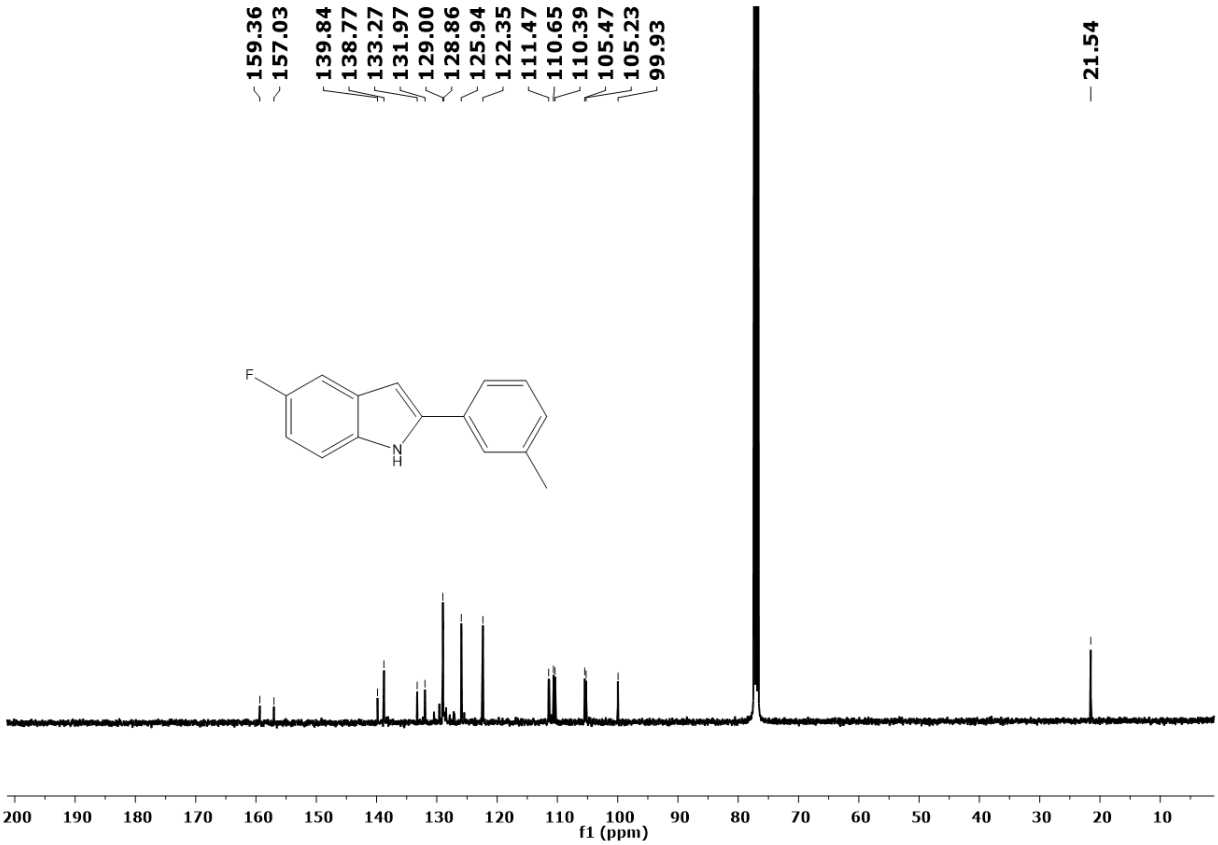

Figure 64S. 101 MHz ^{13}C-NMR spectrum of compound **3z** in $CDCl_3$

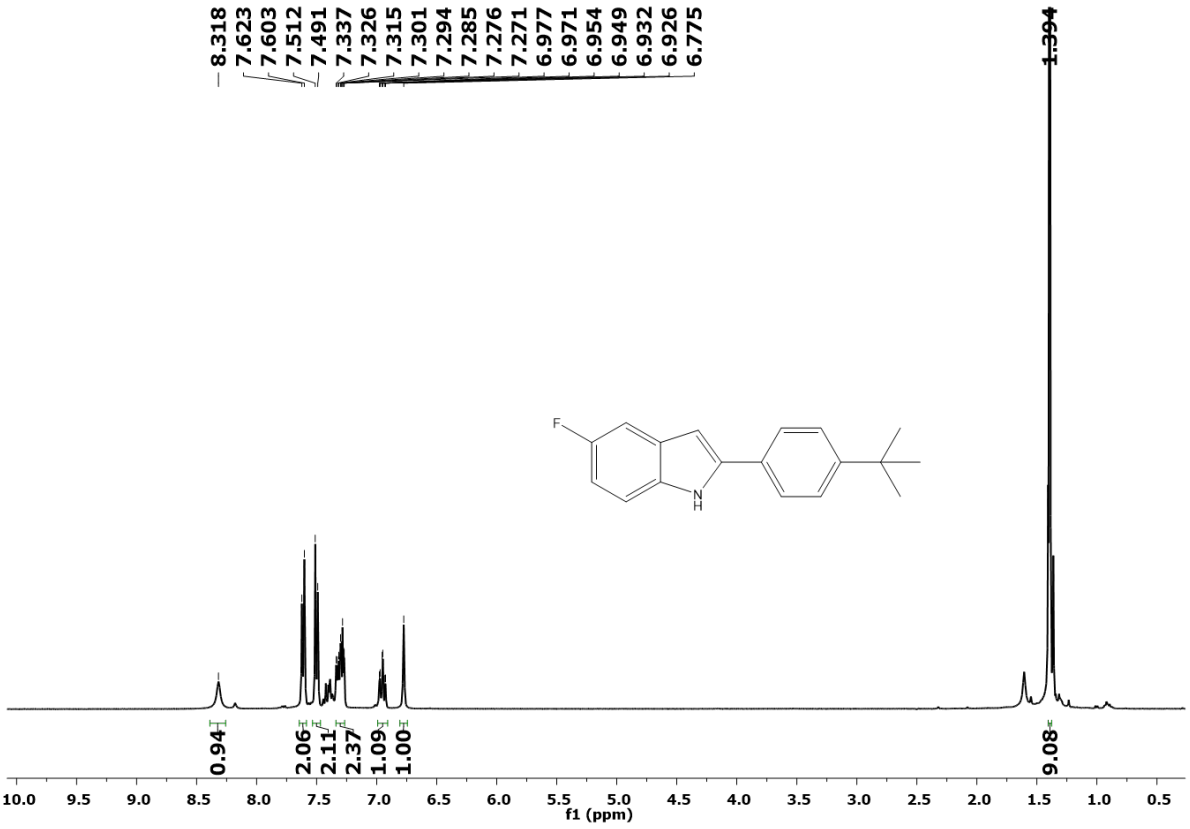

Figure 65S. 400 MHz ^{1}H-NMR spectrum of compound **3aa** in $CDCl_3$

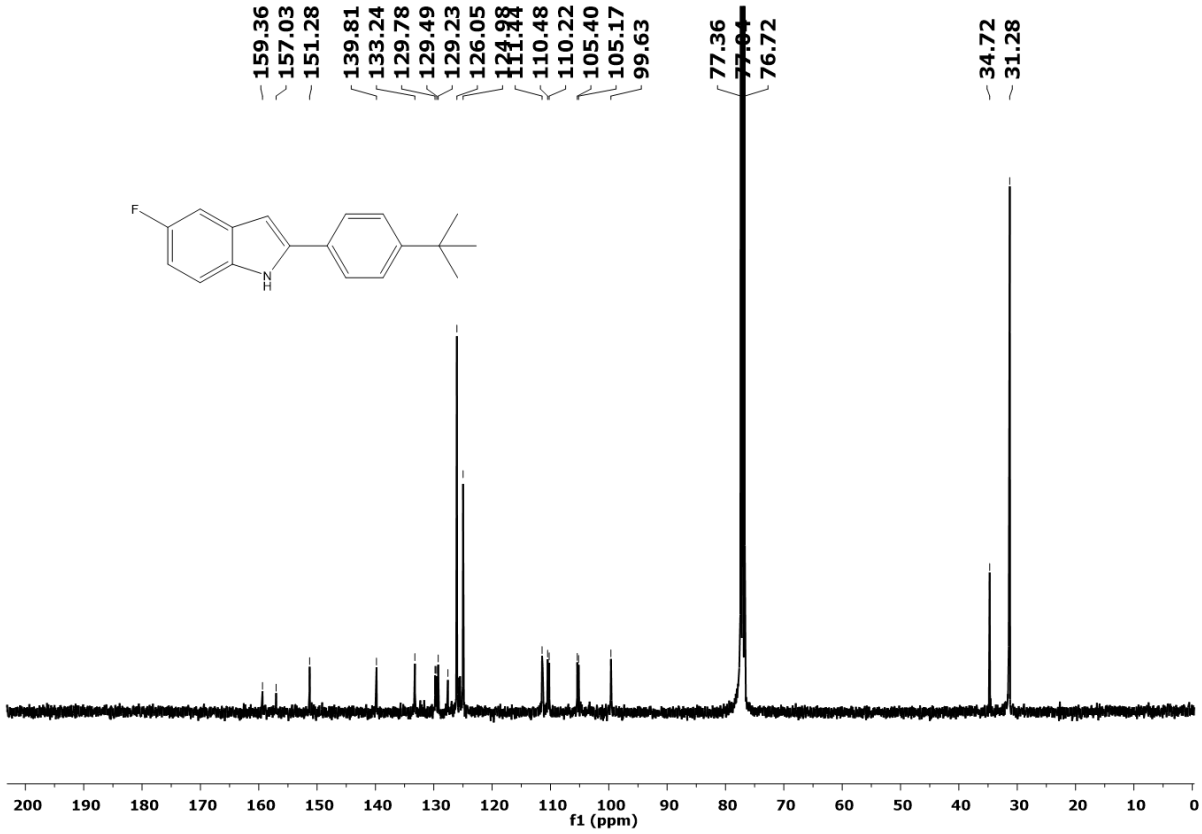

Figure 66S. 101 MHz ^{13}C-NMR spectrum of compound **3aa** in $CDCl_3$

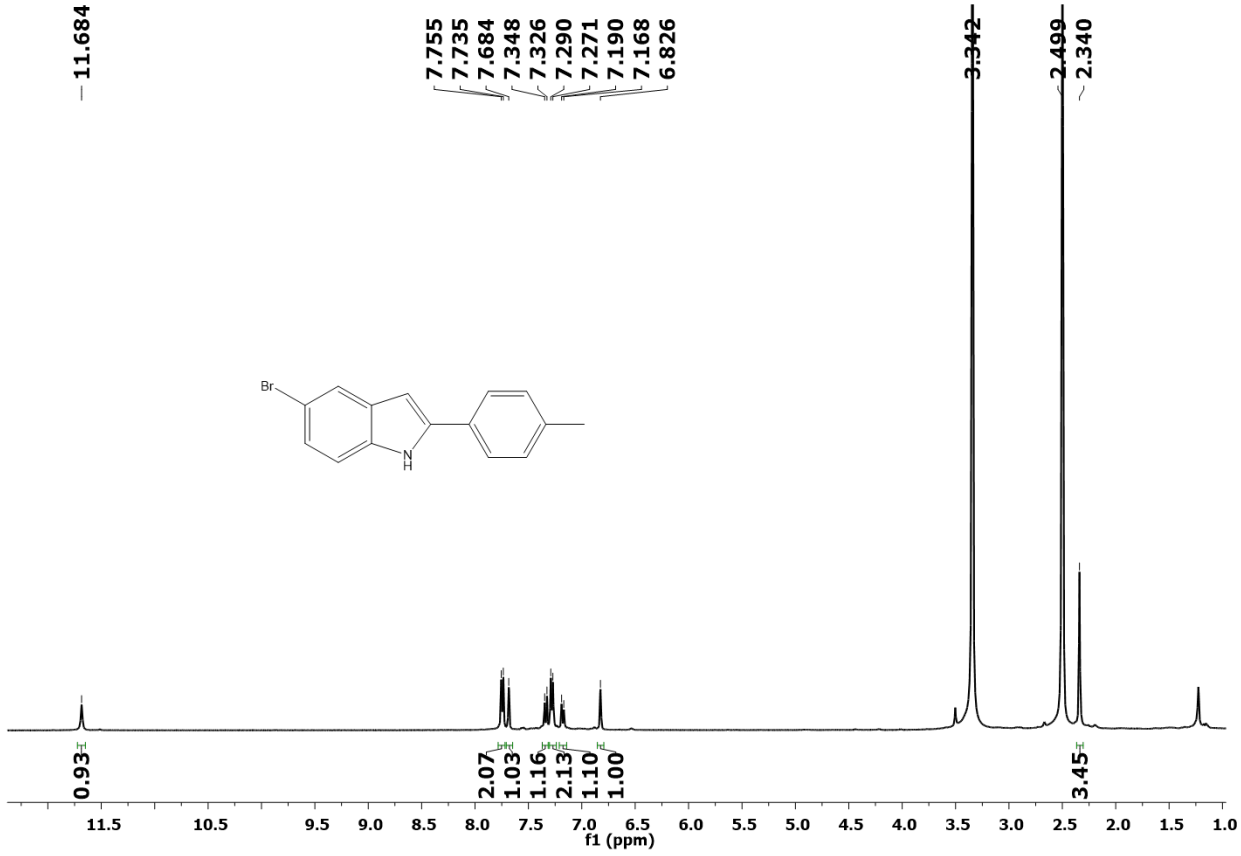

Figure 67S. 400 MHz ^{1}H-NMR spectrum of compound **3ab** in DMSO-d_6

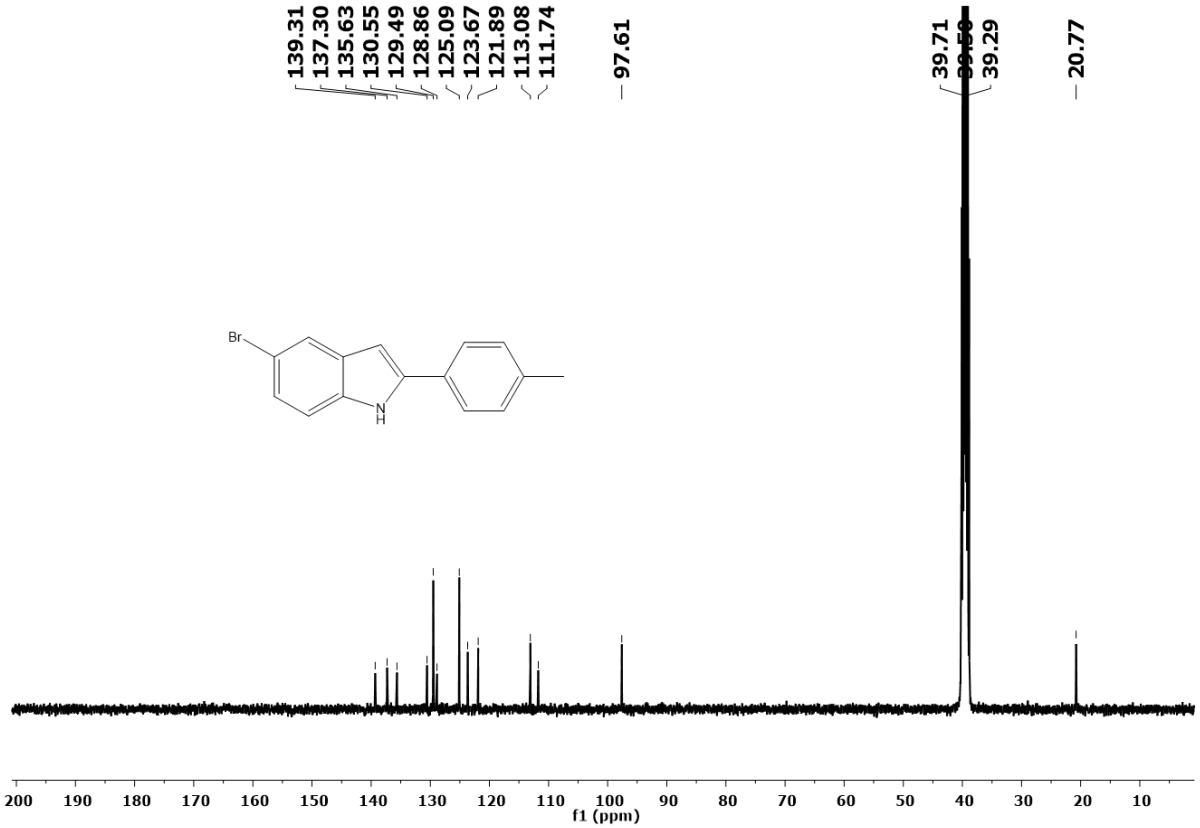

Figure 68S. 101 MHz ^{13}C-NMR spectrum of compound **3ab** in DMSO-d_6

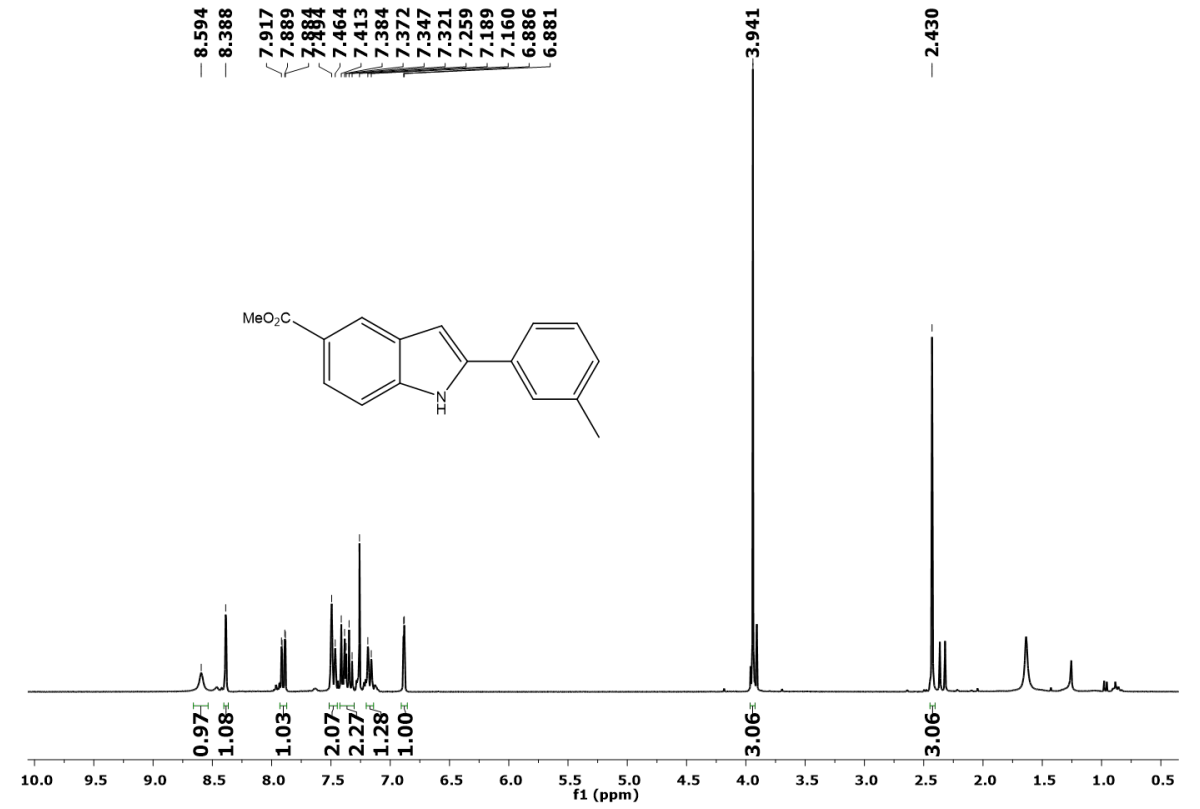

Figure 69S. 300 MHz ^{1}H-NMR spectrum of compound **3ac** in $CDCl_3$

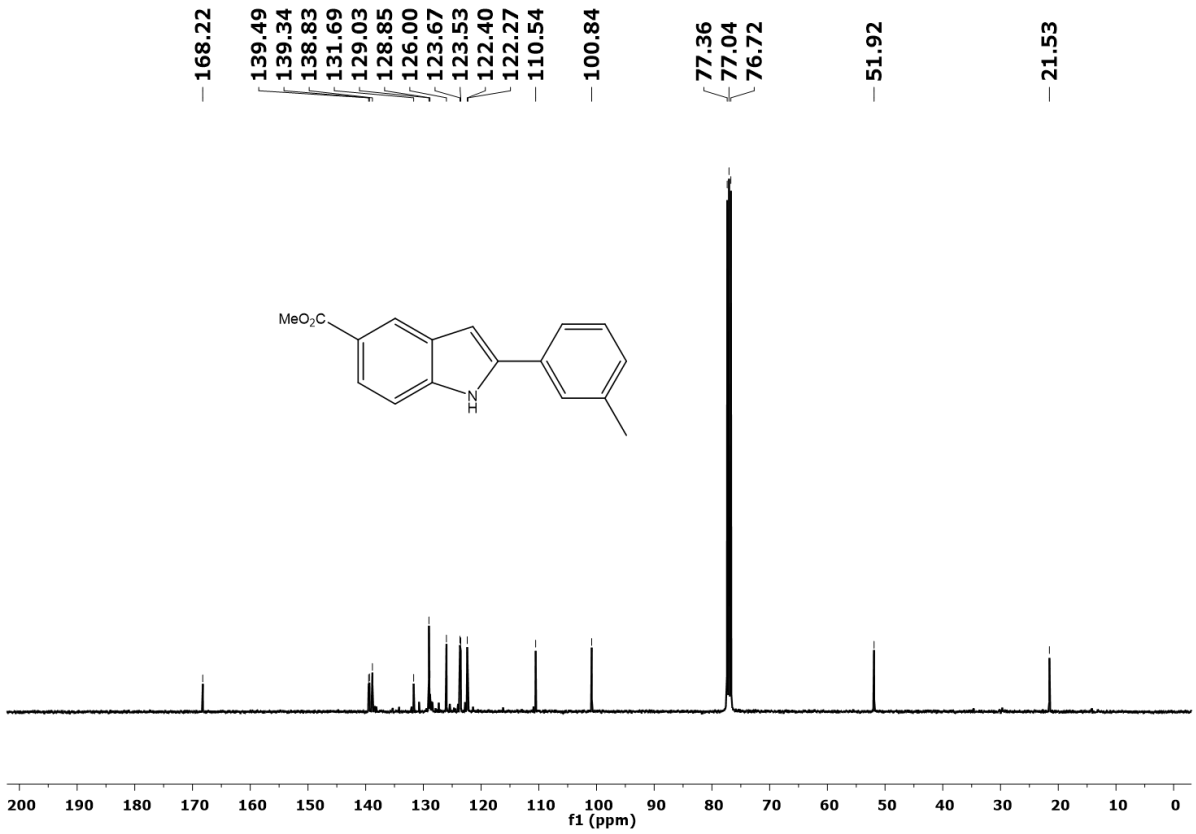

Figure 70S. 101 MHz ^{13}C-NMR spectrum of compound **3ac** in $CDCl_3$

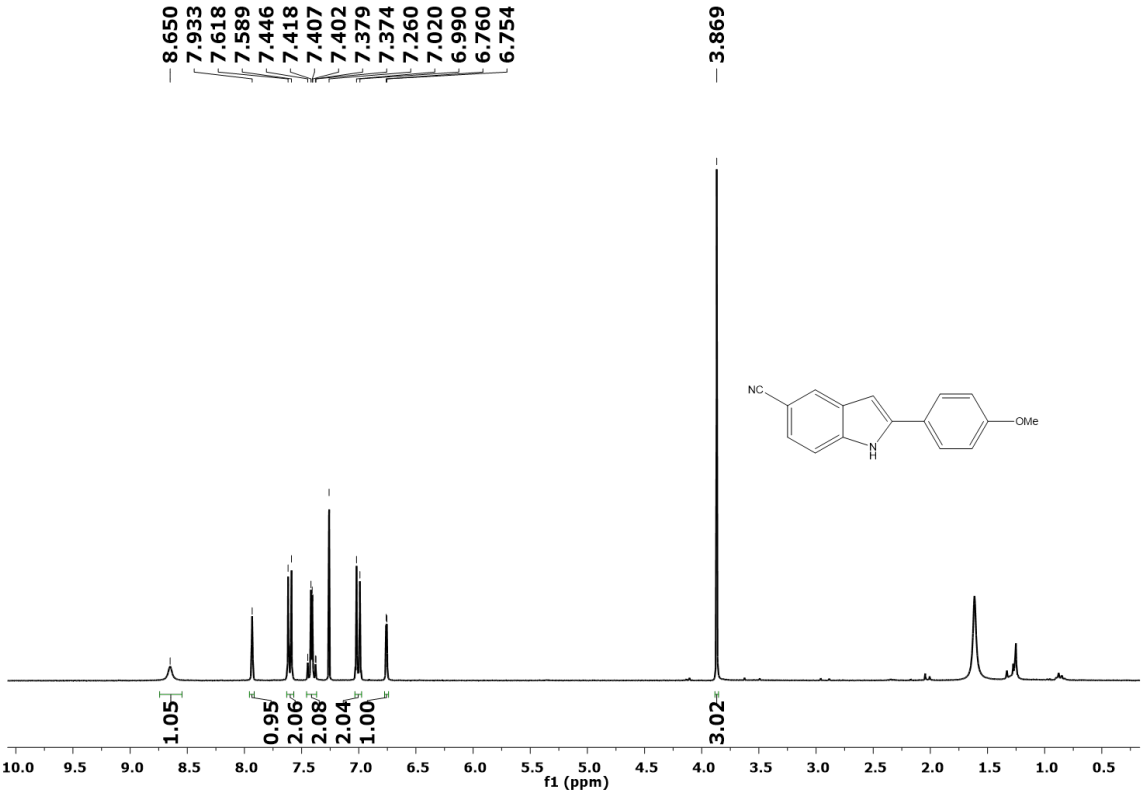

Figure 71S. 300 MHz ^{1}H-NMR spectrum of compound **3ad** in $CDCl_3$

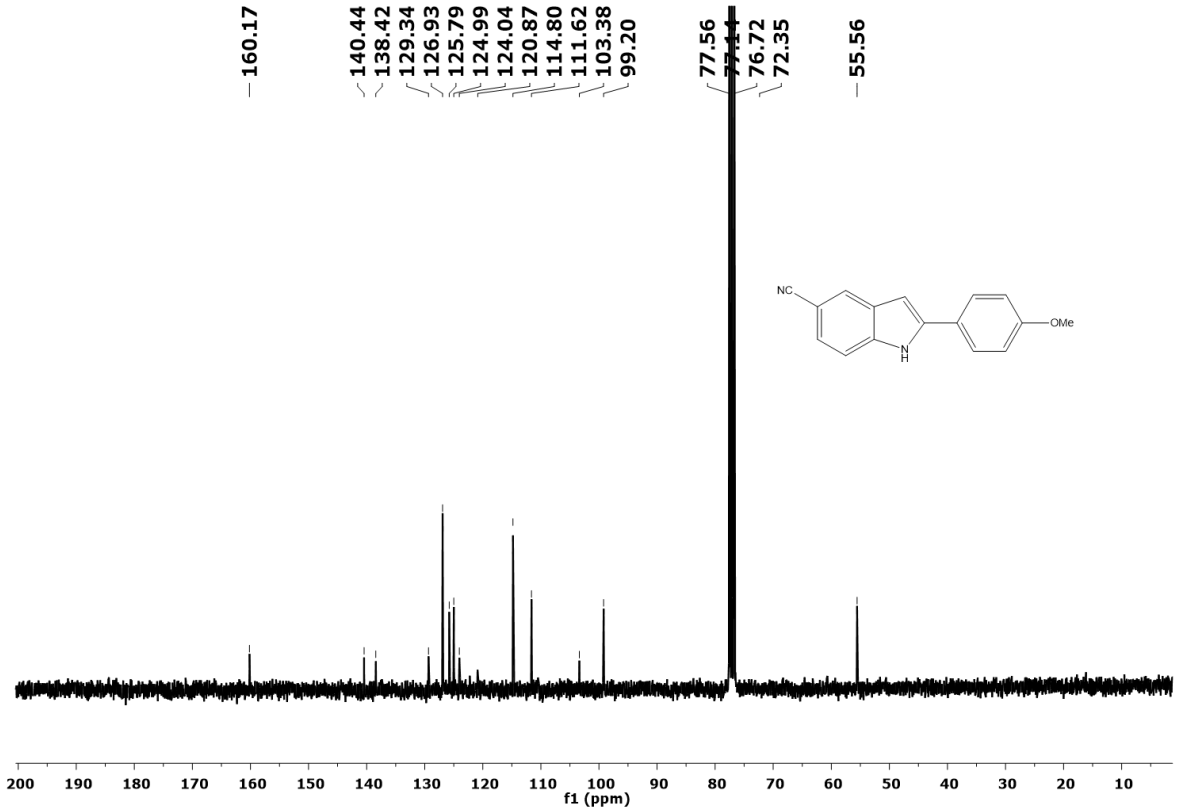

Figure 72S. 75 MHz ^{13}C-NMR spectrum of compound **3ad** in $CDCl_3$

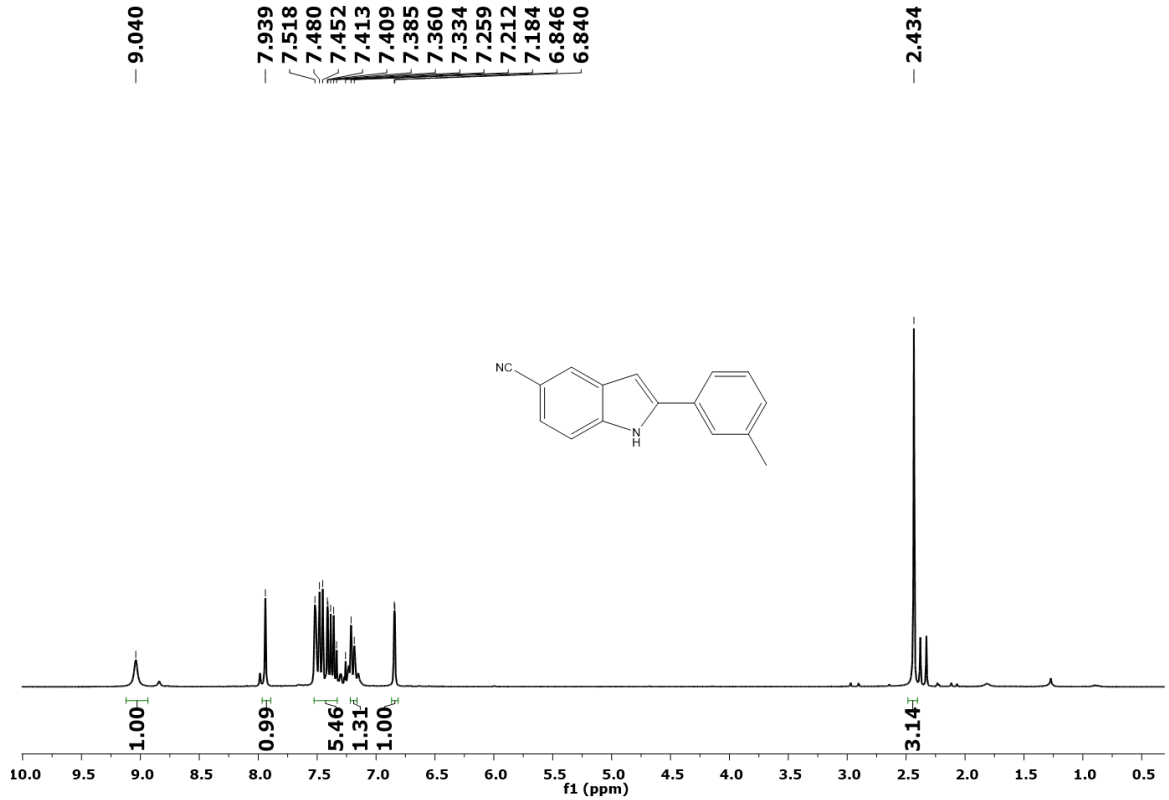

Figure 73S. 300 MHz ^{1}H-NMR spectrum of compound **3ae** in $CDCl_3$

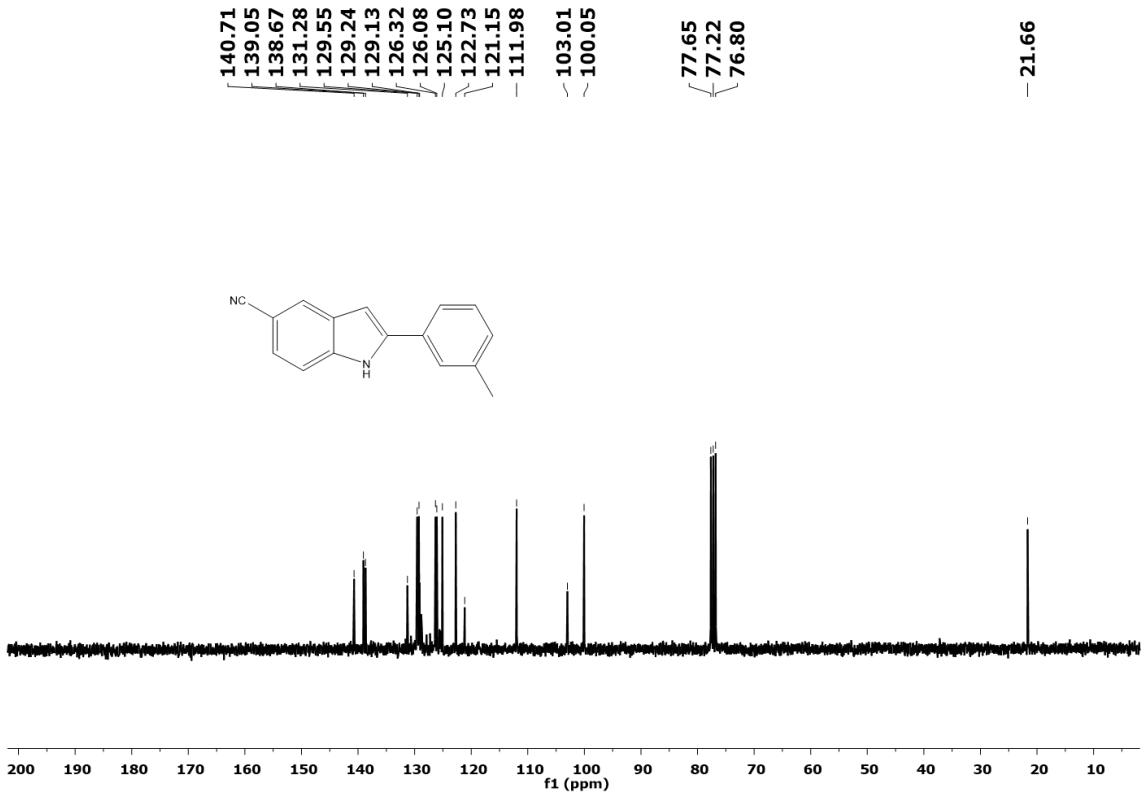

Figure 74S. 75 MHz ^{13}C-NMR spectrum of compound **3ae** in $CDCl_3$

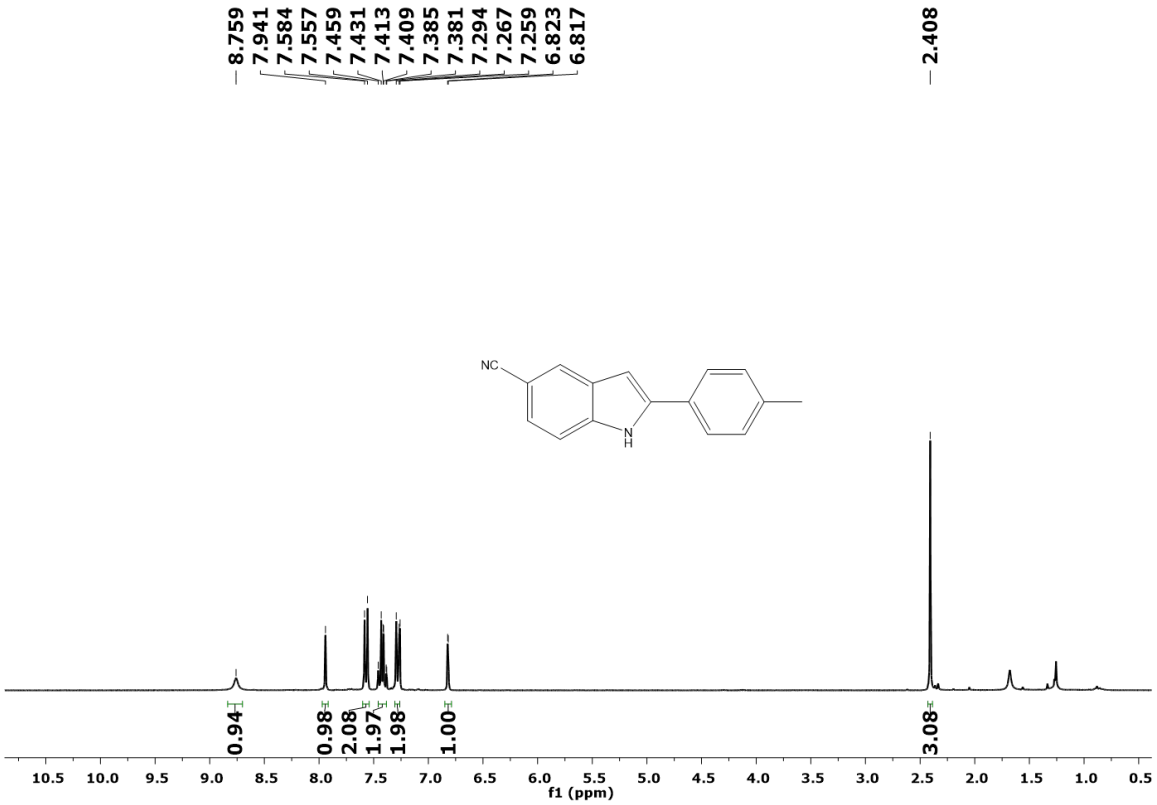

Figure 75S. 300 MHz ^{1}H-NMR spectrum of compound **3af** in $CDCl_3$

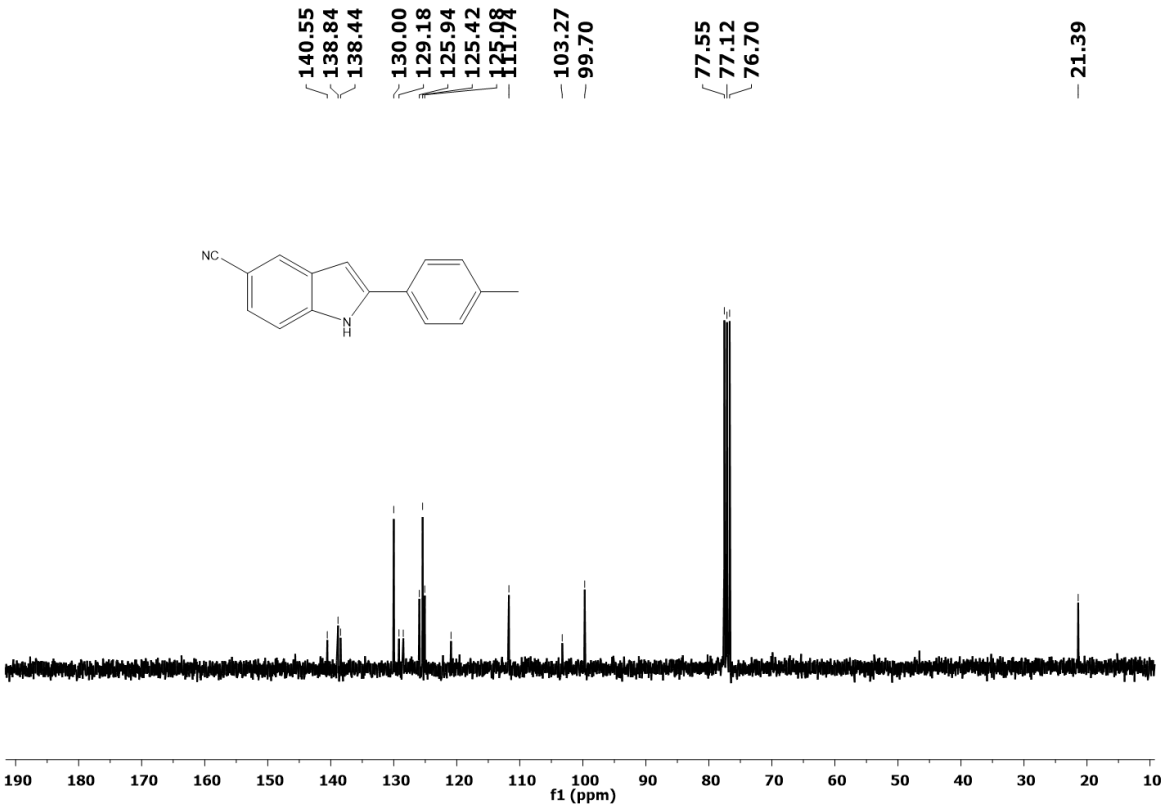

Figure 76S. 75 MHz ^{13}C-NMR spectrum of compound **3af** in $CDCl_3$

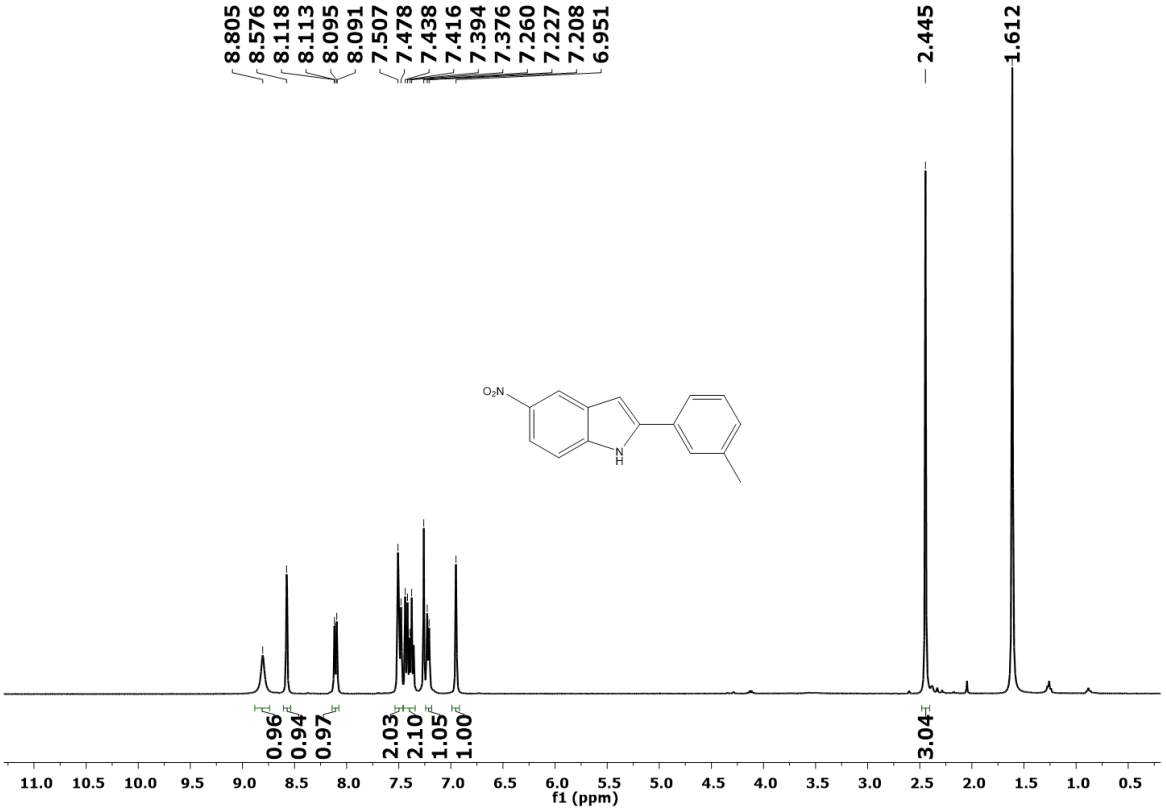

Figure 77S. 400 MHz ^{1}H-NMR spectrum of compound **3ag** in $CDCl_3$

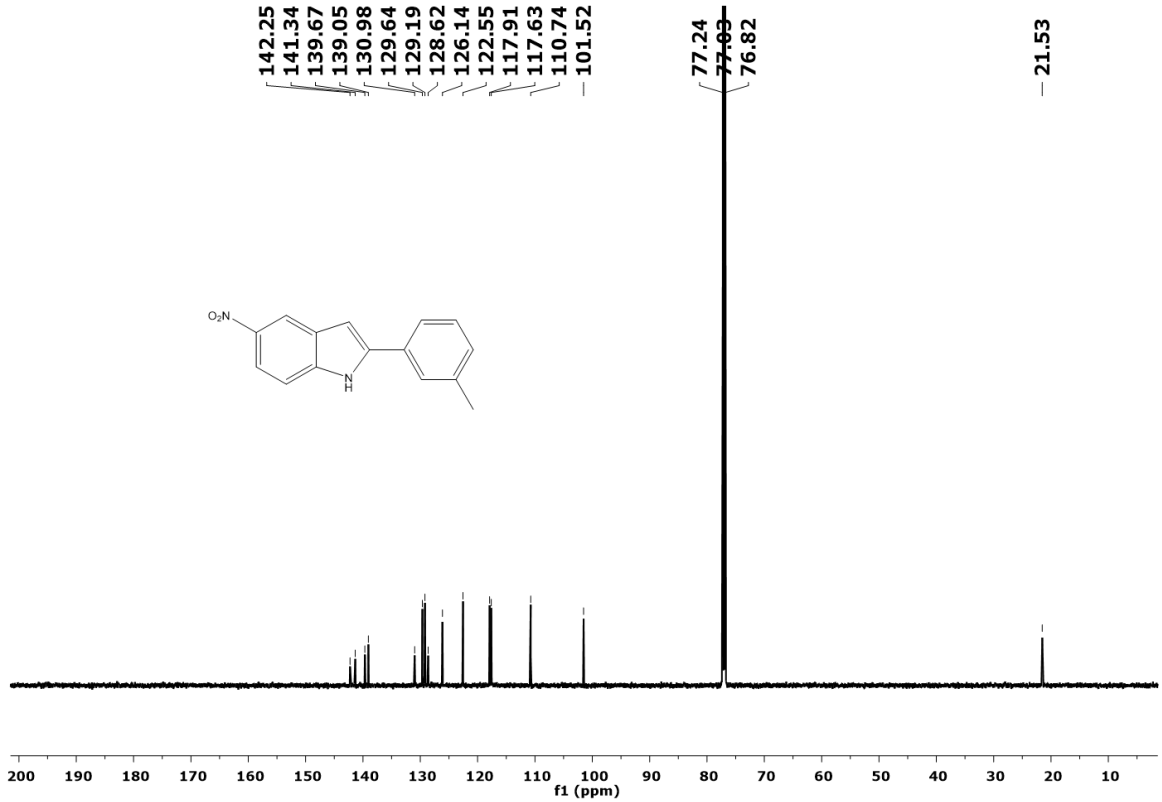

Figure 78S. 151 MHz ^{13}C-NMR spectrum of compound **3ag** in $CDCl_3$

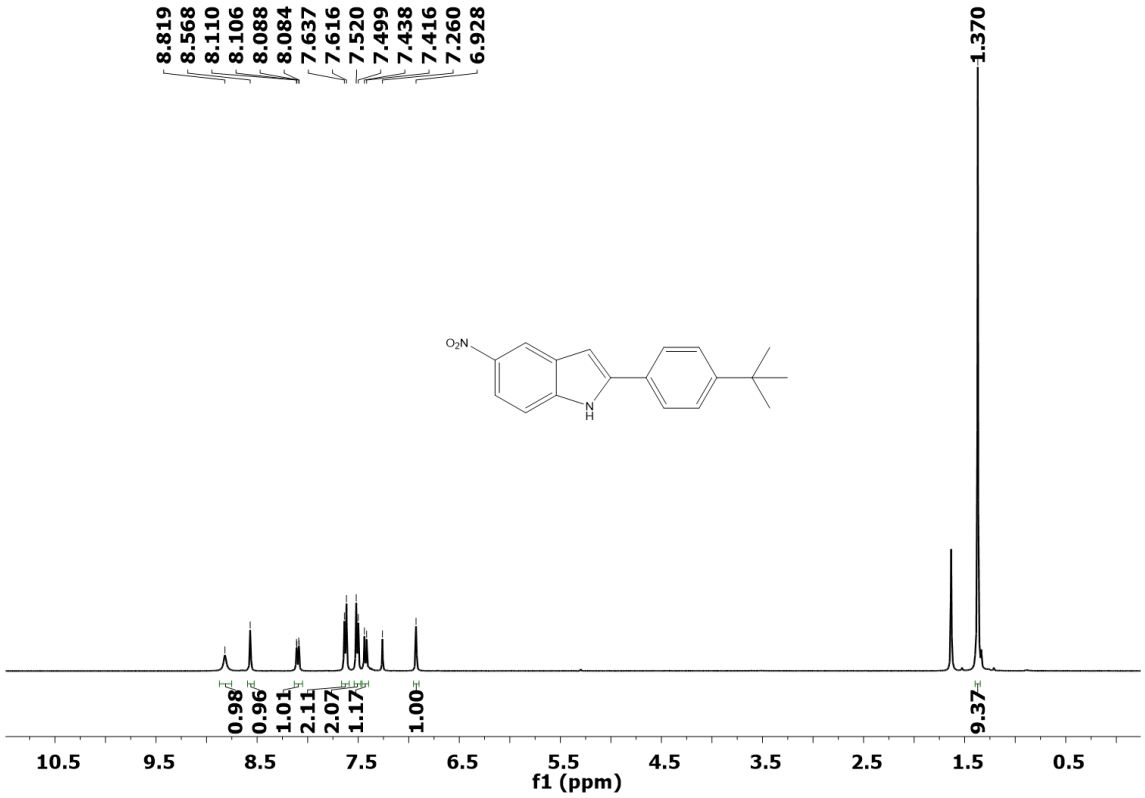

Figure 79S. 400 MHz ^{1}H-NMR spectrum of compound **3ah** in $CDCl_3$

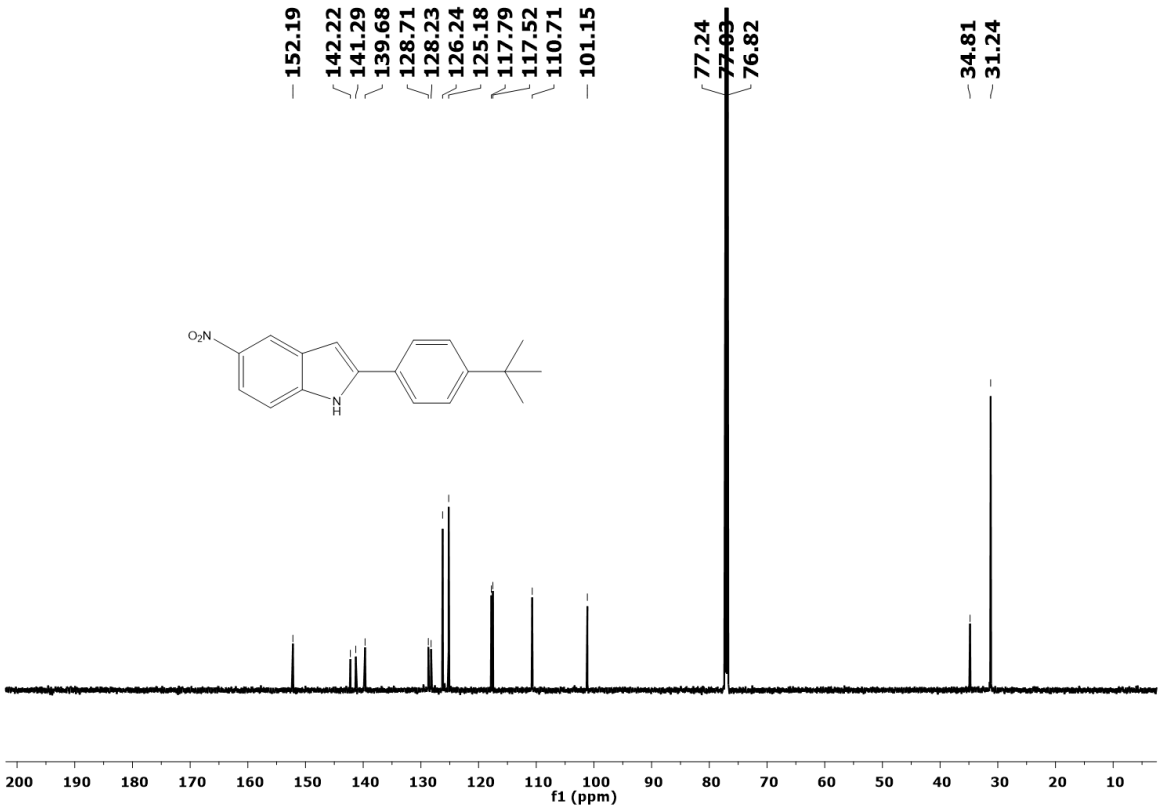

Figure 80S. 151 MHz ^{13}C-NMR spectrum of compound **3ah** in $CDCl_3$

V. Crystal Information and Structure:

X-ray quality single crystals of **CATMC-Pd** was obtained by diffusion of diethyl-ether into the DMSO. Single crystal X-ray diffraction data were collected using Bruker APEX III D8 Venture, PHOTON II detector (Mo Kα, λ=0.7107 Å). Data collection, data reduction, structure solution and refinement were carried out using the software package of the corresponding diffractometer. All the structures were solved by direct methods and refined in a routine manner. Hydrogen atoms were geometrically fixed. All the non-hydrogen atoms were treated anisotropically. CCDC-numbers **2272228** contain the crystallographic data for **CATMC-Pd**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

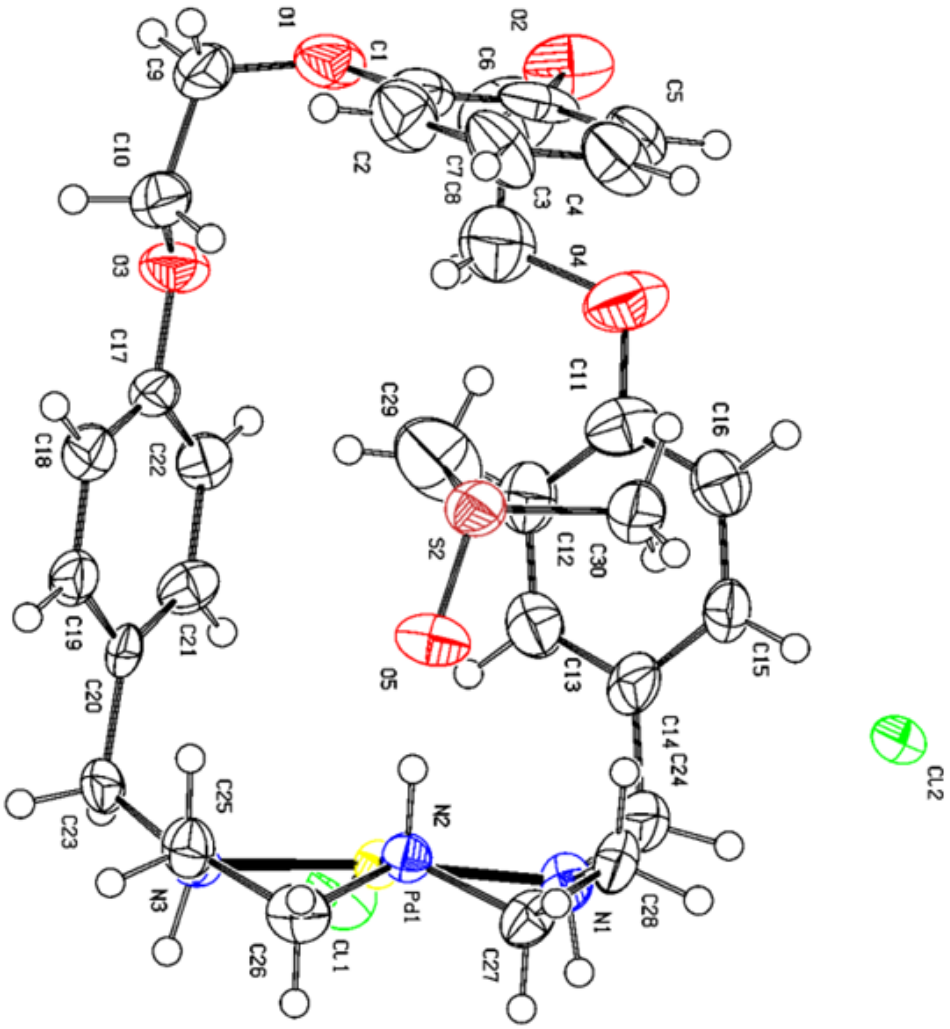

Figure 81S. ORTEP diagram of **CATMC-Pd**. Thermal ellipsoids are shown at 50% probability.

Table 2S. Crystallographic details of the **CATMC-Pd** crystal, related to Figure 3a

Identification code	**CATMC-Pd**
CCDC No.	**2272228**
Empirical formula	$C_{30}H_{41}Cl_2N_3O_5PdS$
Formula weight	733.02
Temperature/K	140.02
Crystal system	monoclinic
Space group	$P2_1/n$

a/Å	8.576(3)
b/Å	38.304(13)
c/Å	10.469(4)
α/°	90
β/°	109.747(10)
γ/°	90
Volume/Å^3	3236.7(19)
Z	4
ρ_{calc}g/cm^3	1.504
μ/mm^{-1}	0.845
F(000)	1512.0
Crystal size/mm^3	0.6 × 0.5 × 0.4
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.648 to 50.052
Index ranges	$-10 \leq h \leq 10$, $-44 \leq k \leq 45$, $-12 \leq l \leq 12$
Reflections collected	23410
Independent reflections	5684 [R_{int} = 0.1073, R_{sigma} = 0.0932]
Data/restraints/parameters	5684/22/381
Goodness-of-fit on F^2	1.070
Final R indexes [I>=2σ (I)]	R_1 = 0.0933, wR_2 = 0.2378
Final R indexes [all data]	R_1 = 0.1076, wR_2 = 0.2494
Largest diff. peak/hole / e Å^{-3}	1.27/-1.14