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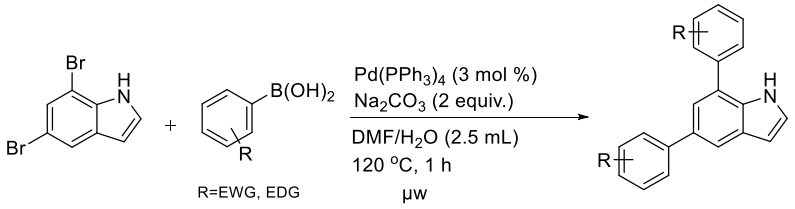
[I] General methods

All reagents and solvents were purchased commercially and used directly without any further purification. TLC was performed on Merck silica gel 60 F254 plates, using UV light at 254 nm for a detection. ^{1}H and ^{13}C-NMR (proton-decoupled) spectra were recorded at ambient temperature at a frequency of 400 and 101 MHz, respectively. The chemical shifts are reported in ppm relative to residual $CHCl_3$ for proton (δ = 7.26 ppm) and $CDCl_3$ for carbon (δ = 77.0 ppm) and with DMSO-d_6 for proton (δ = 2.50 ppm) and for carbon (δ = 39.0 ppm) and CD_3OD for proton (δ = 3.31 ppm) and for carbon (δ= 41.0 ppm) with tetramethylsilane as an external reference. The splitting patterns were recorded as a singlet (s); doublet (d), triplet (t), quartet (q), doublet of doublet (dd), doublet of triplet (dt), doublet of doublet of doublets (ddd), multiplet (m). NMR collection parameters [for ^{1}H-NMR: Sweep width (20.0229 ppm), number of scans (16), temperature (298K)] and [for ^{13}C-NMR: Sweep width (20.0229 ppm), number of scans (2048), temperature (298K)]. Flash column chromatography was performed by using the indicated solvent system and silicagel (40–63 mm). GC-MS chromatograms were recorded on a Thermo Scientific Trace GC Ultra with a Thermo Scientific ITQ 1100 detector. IR spectra were obtained on a Agilent Technologies Cary 630 FTIR spectrometer. High-resolution mass spectra (HRMS) were recorded using MeOH solution on LTQ Orbitrap XL in a positive or negative electrospray ionization (ESI) method. The microwave reactions were performed in a 10 mL vials with caps using Discover SP from CEM using the monowave instrument.

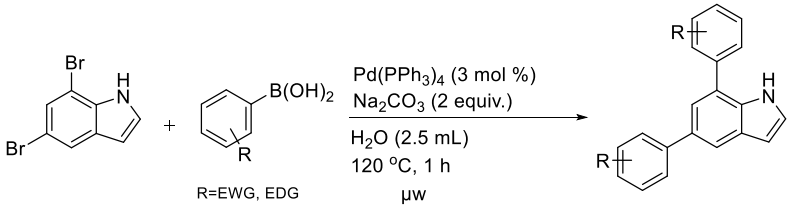
[II] Experimental Section

(a) General Procedure for the synthesis of 5,7-diarylindoles in DMF/H_2O



In a microwave vial (10 mL), 5,7-dibromoindole (1 mmol), Phenylboronic acid (3 mmol), Na_2CO_3 (2 mmol), tetrabutylammonium iodide (TBAI; 0.1 mmol), and $Pd(PPh_3)_4$ (0.03 mmol, 3 mol-%) were added. The vial was sealed and flushed with N_2 and then a mixture of solvent DMF (2.0 mL) and water (0.5 mL) was added into the tube. The solution was stirred for 10 s under ultra-sonication before being subjected into microwave heating for 60 min at 120 °C. After the reaction time, the solvent DMF was removed using the rotavapor. The reaction crude was diluted with ethyl acetate (40 mL) and washed with water (30 mL). The water layer was extracted with ethyl acetate (2 × 30 mL). The organic layers were combined and dried over anhydrous Na_2SO_4. The drying agent was filtered off and the crude product was purified by silica-gel flash column chromatography using the ethyl acetate/pentane or methanol/dichloromethane eluent system to obtain the 5,7-diarylindoles.

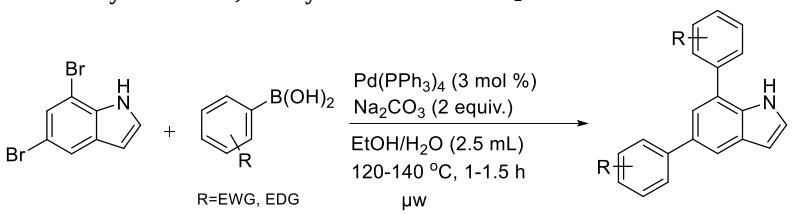
(b) General Procedure for the synthesis of 5,7-diarylindoles in H_2O



In a microwave vial (10 mL), 5,7-dibromoindole (1 mmol), Phenylboronic acid (3 mmol), Na_2CO_3 (2 mmol) and $Pd(PPh_3)_4$ (0.03 mmol, 3 mol-%) were added. The vial was sealed and flushed with N_2 and then water (2.5 mL) was added. The solution

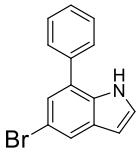
was stirred for 10 s under ultra-sonication before being subjected into microwave heating for 60 min at 120 °C. After the reaction time, the reaction crude was diluted with ethyl acetate (40 mL) and washed with water (30 mL). The water layer was extracted with ethyl acetate (2 × 30 mL). The organic layers were combined and dried over anhydrous Na_2SO_4. The drying agent was filtered off and the crude product was purified by silica-gel flash column chromatography using the ethyl acetate/hexane or ethyl acetate/pentane eluent system to obtain the 5,7-diarylindoles.

(c) General Procedure for the synthesis of 5,7-diarylindoles in EtOH/H_2O



In a microwave vial (10 mL), 5,7-dibromoindole (1 mmol), Phenylboronic acid (3 mmol), Na_2CO_3 (2 mmol), tetrabutylammonium iodide (TBAI; 0.1 mmol), and $Pd(PPh_3)_4$ (0.03 mmol, 3 mol-%) were added. The vial was sealed and flushed with N_2 and then a mixture of solvent EtOH (2.0 mL) and water (0.5 mL) was added into the vial. The solution was sonicated for 10 s before being subjected into microwave heating for 60 min/90 min at 120 °C/140 °C. After the reaction time, the solvent ethanol was removed under reduced pressure. The reaction crude was diluted with ethyl acetate (40 mL) and washed with water (30 mL). The water layer was extracted with ethyl acetate (2 × 30 mL). The organic layers were combined and dried over anhydrous Na_2SO_4. The drying agent was filtered off and the crude product was purified by silica-gel flash column chromatography [ethyl acetate/hexane or ethyl acetate/pentane] to obtain the 5,7-diarylindoles.

(d)Procedure for the synthesis of 5-bromo-7-phenyl-1*H*-indole (4)

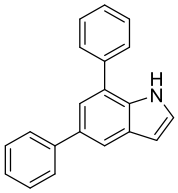


4

In a microwave vial (10 mL), 5,7-dibromoindole **(1)** (0.10 g, 0.364 mmol), phenylboronic acid (0.067 g, 0.546 mmol), Na_2CO_3 (0.077 g, 0.726 mmol), and $Pd(PPh_3)_4$ (0.013 g, 0.018 mmol) were added. The vial was sealed and flushed with N_2 and then acetonitrile (2.5 mL) was added. The solution was stirred for 10 s under ultra-sonication before being subjected into microwave heating for 90 min at 120 °C. After the reaction time, the reaction crude was diluted with ethyl acetate (30 mL) and washed with water (25 mL). The water layer was extracted with ethyl acetate (2 × 25 mL). The organic layers were combined and dried over anhydrous Na_2SO_4. The drying agent was filtered off and the crude product was purified by silica-gel flash column chromatography using [(EtOAc: Pentane, 5:95)] eluent to obtain the desired title compound **4** as a pale-yellow liquid (0.030 g, 31 %). R_f = 0.50 [(EtOAc:Pentane, 10:90)]. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.40 (s, 1H), 7.77 (d, *J* = 2.1 Hz, 1H), 7.62 – 7.58 (m, 2H), 7.55 – 7.50 (m, 2H), 7.47 – 7.42 (m, 1H), 7.34 (d, *J* = 1.8 Hz, 1H), 7.22 (t, *J* = 2.8 Hz, 1H), 6.57 (dd, *J* = 3.2, 2.1 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 137.88, 132.52, 129.91, 129.32, 128.17, 128.01, 127.16, 125.52, 124.50, 122.35, 113.46, 102.75.**MS (EI)**: m/z (%). 274 (15), 273 (88), 272 (17), 271 (100, M^+), 193 (13), 192 (71), 191 (87), 165 (33), 164 (25), 163 (31), 96 (24), 81 (12). **HR-MS** Calcd $(M-H)^-$ for $C_{14}H_9BrN^-$ 269.9924; Found 269.9924.

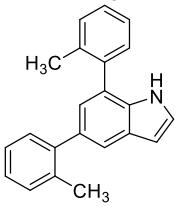
5,7-diarylindole derivatives:

5,7-diphenyl-1*H*-indole (3a) [NEW].



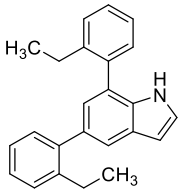
Following the general procedure (b), 5,7-dibromoindole **(1)** (0.10 g, 0.364 mmol), phenylboronic acid (0.133 g, 1.091 mmol), Na_2CO_3 (0.077 g, 0.726 mmol) and $Pd(PPh_3)_4$ (0.013 g, 0.018 mmol). The product was isolated using [(EtOAc: Pentane, 10:90)] eluent and obtained as a pale-yellow liquid (0.081 g, 83 %). R_f = 0.48 [(EtOAc:Pentane, 20:80)]. **^{1}H NMR (400 MHz, Chloroform-*d*) δ** 8.42 (s, 1H), 7.89 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.76 – 7.68 (m, 4H), 7.59 – 7.44 (m, 6H), 7.39 – 7.32 (m, 1H), 7.28 – 7.25 (m, 1H), 6.70 (dd, *J* = 3.2, 2.1 Hz, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*) δ** 142.56, 139.27, 134.14, 133.43, 129.35, 129.00, 128.80, 128.41, 127.71, 127.59, 126.57, 125.92, 125.18, 122.00, 118.68, 103.61. MS (EI): m/z (%). 270 (22), 269 (100, M^+), 268 (22), 267 (17), 239 (5), 191 (3), 167 (4), 133 (2), 119 (2). **HR-MS** Calcd $(M+H)^+$ for $C_{20}H_{16}N^+$ 270.1277; Found 270.1279. **IR (neat)**. 3428.6, 3059.7, 3029.6, 1707.5, 1473.4, 1421.4, 1350.5, 877.4, 732.3, 702.9.

5,7-di-*o*-tolyl-1*H*-indole (3b) [NEW].



Following the general procedure (b), 5,7-dibromoindole **(1)** (0.10 g, 0.364 mmol), *o*-tolylboronic acid (0.148 g, 1.090 mmol), Na_2CO_3 (0.077 g, 0.726 mmol) and $Pd(PPh_3)_4$ (0.013 g, 0.018 mmol). The product was isolated using [(EtOAc:pentane, 10:90)] eluent and obtained as a pale-brown liquid (0.076 g, 70 %). R_f = 0.65 [(EtOAc:Hx, 20:80)]. **^{1}H NMR (400 MHz, Chloroform-*d*) δ** 7.96 (s, 1H), 7.61 (dd, *J* = 1.5, 0.7 Hz, 1H), 7.46 – 7.25 (m, 8H), 7.21 (t, *J* = 2.8 Hz, 1H), 7.09 (d, *J* = 1.6 Hz, 1H), 6.66 (dd, *J* = 3.2, 2.1 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*) δ** 143.14, 138.10, 136.75, 135.86, 133.98, 133.59, 130.77, 130.54, 130.32, 130.10, 127.94, 127.85, 126.83, 126.16, 125.75, 124.79, 124.71, 124.52, 120.23, 103.11, 20.91, 20.20. **MS (EI):** m/z (%). 298 (23), 297 (100, M^+), 296 (36), 282 (13), 281 (11), 265 (7), 252 (6), 206 (26), 179 (5), 139 (2). **HR-MS** Calcd $(M+H)^+$ for $C_{22}H_{20}N^+$ 298.1590; Found 298.1595. **IR (neat)**. 3417.7, 3018.7, 2951.7, 2925.7, 1462.5, 1417.5, 1313.5, 911.5, 762.2, 728.1.

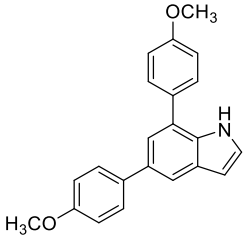
5,7-bis(2-ethylphenyl)-1*H*-indole (3c) [NEW].



Following the general procedure (b), 5,7-dibromoindole **(1)** (0.10 g, 0.364 mmol), 4-ethylphenylboronic acid (0.164 g, 1.093 mmol), Na_2CO_3 (0.077 g, 0.726 mmol) and $Pd(PPh_3)_4$ (0.013 g, 0.018 mmol). The product was isolated using [(EtOAc:Pentane, 10:90)] eluent and obtained as a brown liquid (0.071 g, 62 %). R_f = 0.60 [(EtOAc:Pentane, 20:80)]. **^{1}H NMR (400 MHz, Chloroform-*d*) δ** 8.33 (s, 1H), 7.79 (d, *J* = 1.7 Hz, 1H), 7.62 – 7.50 (m, 4H), 7.43 (d, *J* = 1.7 Hz, 1H), 7.35 – 7.26 (m, 2H), 7.30 – 7.21 (m, 2H), 7.17 (dd, *J* = 5.9, 3.1 Hz, 1H), 6.61 (dd, *J* = 3.2, 2.0 Hz, 1H), 2.68 (dq, *J* = 14.9, 7.6 Hz, 4H), 1.27 (dt, *J* = 9.2, 7.6 Hz, 6H). **^{13}C NMR (101 MHz, Chloroform-*d*) δ** 143.78, 142.55, 140.02, 136.63, 134.10, 133.38, 128.93, 128.83, 128.32 (d, *J* = 1.4 Hz), 127.50, 125.86, 125.01, 121.86, 118.22, 103.51, 28.78, 28.63, 15.76. **MS (EI):** m/z (%). 326 (27), 325

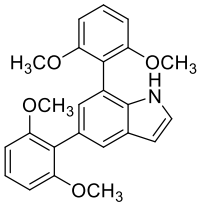
(100, M^+), 311 (18), 310 (69), 296 (6), 295 (18), 280 (8), 204 (2), 148 (4), 140 (3). **HR-MS** Calcd $(M+H)^+$ for $C_{24}H_{24}N^+$ 326.1903; Found 326.1909. **IR (neat).** 3424.6, 2962.6, 2929.6, 2873.6, 1469.5, 1413.4, 1313.5, 832.2, 728.2.

5,7-bis(4-methoxyphenyl)-1*H*-indole (3d) [1351557-38-4].



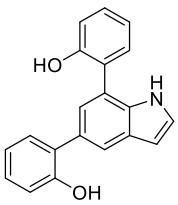
Following the general procedure (b), 5,7-dibromoindole **(1)** (0.10 g, 0.364 mmol), 4-methoxyhenylboronic acid (0.166 g, 1.092 mmol), Na_2CO_3 (0.077 g, 0.726 mmol) and $Pd(PPh_3)_4$ (0.013 g, 0.012 mmol). The product was isolated using [(EtOAc:Pentane, 15:85)] eluent and obtained as a white solid (0.091 g, 76 %). R_f = 0.38 [(EtOAc:Pentane, 20:80)]. **^{1}H NMR (400 MHz, Chloroform-*d*) δ** 8.37 (s, 1H), 7.78 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.68 – 7.57 (m, 4H), 7.40 (d, *J* = 1.7 Hz, 1H), 7.30 – 7.22 (m, 2H), 7.14 – 7.05 (m, 2H), 7.04 – 6.96 (m, 2H), 6.66 (dd, *J* = 3.2, 2.1 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*) δ** 159.30, 158.70, 135.31, 133.83, 133.27, 131.72, 129.48, 128.95, 128.54, 125.59, 125.03, 121.62, 117.77, 114.78, 114.26, 103.51, 55.56, 55.51. **MS (EI)**: m/z (%). 330 (24), 329 (100, M^+), 315 (13), 314 (58), 299 (4), 286 (14), 271 (7), 242 (9), 207 (6), 165 (5), 143 (3), 121 (4). **HR-MS** Calcd $(M+H)^+$ for $C_{22}H_{20}NO_2^+$ 330.1489; Found 330.1493. **IR (neat)**. 3383.7, 1611.7, 1521.6, 1506.6, 1473.6, 1413.7, 1242.5, 1179.6, 1030.6, 829.5, 747.5.

5,7-bis(2,6-dimethoxyphenyl)-1H-indole (3e) [NEW].



Following the general procedure (b), 5,7-dibromoindole **(1)** (0.10 g, 0.364 mmol), 2,6-dimethoxyphenylboronic acid (0.199 g, 1.094 mmol), Na_2CO_3 (0.077 g, 0.726 mmol) and $Pd(PPh_3)_4$ (0.013 g, 0.012 mmol). The product was isolated using [(EtOAc:hexane, 20:80)] eluent and obtained as a brown solid (0.072 g, 51 %). R_f = 0.35 [(EtOAc:Hexane, 40:60)]. **^{1}H NMR (400 MHz, Chloroform-*d*) δ** 7.91 (s, 1H), 7.63 (dd, *J* = 1.5, 0.7 Hz, 1H), 7.40 – 7.18 (m, 3H), 7.12 (t, *J* = 2.8 Hz, 1H), 6.70 (dd, *J* = 12.6, 8.3 Hz, 4H), 6.57 (dd, *J* = 3.2, 2.0 Hz, 1H), 3.73 (d, *J* = 9.4 Hz, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*) δ** 158.46, 158.23, 134.26, 128.94, 128.00, 127.75, 127.46, 124.44, 123.52, 122.19, 121.36, 116.27, 116.23, 104.64, 104.58, 102.88, 56.04. **MS (EI):** m/z (%). 390 (29), 389 (100, M^+), 375 (11), 374 (37), 360 (7), 359 (18), 344 (9), 434 (11), 328 (6), 253 (9), 238 (15), 187 (4), 151 (6), 121 (5). **HR-MS** Calcd $(M+H)^+$ for $C_{24}H_{24}NO_4^+$ 390.1700; Found 390.1697. **IR (neat)**. 3420.9, 2936.8, 2836.8, 1581.6, 1469.7, 1432.7, 1242.6, 1104.6, 728.6.

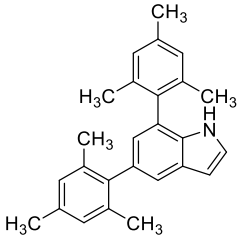
2,2'-(1*H*-indole-5,7-diyl)diphenol (3f) [NEW].



Following the general procedure (b), 5,7-dibromoindole **(1)** (0.10 g, 0.364 mmol), 2-hydroxyphenylboronic acid (0.151 g, 1.095 mmol), Na_2CO_3 (0.077 g, 0.726 mmol) and $Pd(PPh_3)_4$ (0.013 g, 0.012 mmol). The product was isolated using [(EtOAc: Hexane, 20:80)] eluent and obtained as a pale-yellow liquid (0.089 g, 82 %). R_f = 0.39 [(EtOAc:Hexane, 40:60)]. **^{1}H NMR (400 MHz, Chloroform-*d*) δ** 8.32 (s, 1H), 7.78 (d, *J* = 1.6 Hz, 1H), 7.44 – 7.38 (m, 1H), 7.37 – 7.25 (m, 5H), 7.03 (dddd, *J* = 23.7, 7.4, 6.3, 1.2 Hz, 4H), 6.67 (dd, *J* = 3.2, 2.0 Hz, 1H), 5.35 (d, br, *J* = 76.2 Hz, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*) δ** 152.91, 152.79, 133.80, 130.75, 129.98, 129.37, 129.34, 128.90, 128.85, 125.94, 124.31, 124.26, 121.42, 121.28, 121.18,

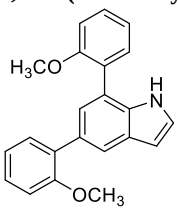
120.88, 116.48, 115.75, 103.57. **HR-MS** Calcd (M-H)$^-$ for $C_{20}H_{14}NO_2^-$ 300.1030; Found 300.1023. **IR (neat)**. 3402.6, 1700.4, 1581.6, 1451.4, 1421.5, 1205.4, 1179.4, 754.2, 732.2.

5,7-dimesityl-1H-indole (3g) [NEW].



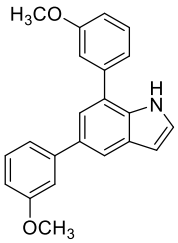
Following the general procedure (b), 5,7-dibromoindole **(1)** (0.10 g, 0.364 mmol), 2,4,6-tri-methylphenylboronic acid (0.179 g, 1.091 mmol), Na_2CO_3 (0.077 g, 0.726 mmol) and $Pd(PPh_3)_4$ (0.013 g, 0.012 mmol). The reaction gave only 2% yield based on GC. The product was not isolated from the crude mixture. **MS (EI):** m/z (%). 354 (25), 353 (100, M$^+$), 352 (21), 339 (10), 338 (29), 337 (15), 323 (12), 308 (8), 281 (14), 267 (5), 234 (8), 207 (28), 193 (6), 133 (2), 73 (5).

5,7-bis(2-methoxyphenyl)-1*H*-indole (3h) [NEW].



Following the general procedure (b), 5,7-dibromoindole **(1)** (0.10 g, 0.364 mmol), 2-methoxyphenylboronic acid (0.166 g, 1.092 mmol), Na_2CO_3 (0.077 g, 0.726 mmol) and $Pd(PPh_3)_4$ (0.013 g, 0.012 mmol). The product was isolated using [(EtOAc:pentane, 15:85)] eluent and obtained as a white solid (0.105 g, 85 %). R_f = 0.41 [(EtOAc:Pentane, 20:80)]. **^{1}H NMR (400 MHz, Chloroform-*d*) δ** 8.28 (s, 1H), 7.83 (dd, *J* = 1.6, 0.7 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.50 – 7.36 (m, 3H), 7.31 (ddd, *J* = 8.3, 7.5, 1.8 Hz, 1H), 7.22 (dd, *J* = 3.2, 2.4 Hz, 1H), 7.14 – 6.99 (m, 4H), 6.63 (dd, *J* = 3.2, 2.0 Hz, 1H), 3.84 (s, 6H). **^{13}C NMR (101 MHz, Chloroform-*d*) δ** 156.84, 156.78, 133.85, 132.22, 132.17, 131.60, 130.38, 129.01, 128.36, 128.08, 127.90, 125.67, 124.55, 122.00, 121.49, 121.18, 120.88, 111.85, 111.36, 103.04, 56.07, 55.77. **MS (EI):** m/z (%). 330 (24), 329 (100, M$^+$), 315 (6), 314 (27), 299 (19), 298 (10), 270 (10), 254 (6), 223 (10), 208 (8). **HR-MS** Calcd (M+H)$^+$ for $C_{22}H_{20}NO_2^+$ 330.1489; Found 330.1495. **IR (neat)**. 3432.9, 2929.9, 2836.9, 1495.8, 1462.8, 1439.8, 1417.8, 1242.7, 1026.7, 754.7, 732.7.

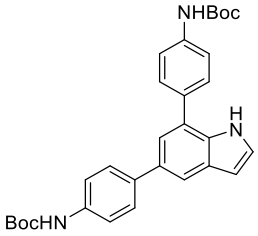
5,7-bis(3-methoxyphenyl)-1*H*-indole (3i) [NEW].



Following the general procedure (b), 5,7-dibromoindole **(1)** (0.10 g, 0.364 mmol), 3-methoxyphenylboronic acid (0.166 g, 1.092 mmol), Na_2CO_3 (0.077 g, 0.726 mmol) and $Pd(PPh_3)_4$ (0.013 g, 0.012 mmol). The product was isolated using [(EtOAc:Hexane, 10:90)] eluent and obtained as a brown solid (0.084 g, 70 %). R_f = 0.56 [(EtOAc:Hexane, 40:60)]. **^{1}H NMR (400 MHz, Chloroform-*d*) δ** 8.32 (s, 1H), 7.73 (d, *J* = 1.6 Hz, 1H), 7.37 (d, *J* = 1.7 Hz, 1H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.26 – 7.11 (m, 3H), 7.11 (dd, *J* = 3.4, 2.2 Hz, 2H), 7.09 (dd, *J* = 2.6, 1.6 Hz, 1H), 6.84 (ddd, *J* = 8.3, 2.7, 1.0 Hz, 1H), 6.76 (ddd, *J* = 8.1, 2.6, 1.0 Hz, 1H), 6.54 (dd, *J* = 3.2, 2.0 Hz, 1H), 3.75 (d, *J* = 4.1 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.29, 159.93, 143.99, 140.54, 133.84, 133.35, 130.26, 129.65, 128.84, 125.64, 125.11, 121.73, 120.59, 120.04, 118.69, 113.98, 113.11, 113.08, 112.02, 103.49, 55.41, 55. 34. **MS (EI):** m/z (%). 330 (19), 329 (100, M$^+$), 286 (15), 271 (4), 243 (3), 121 (2). **HR-**

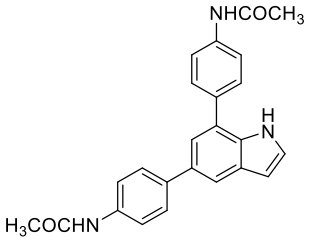
MS Calcd (M-H)$^-$ for $C_{22}H_{18}NO_2^-$ 328.1343; Found 328.1340. **IR (neat)**. 3335.8, 3018.8, 2981.8, 2948.8, 1581.7, 1465.7, 1432.7, 1287.7, 1231.7, 1037.7, 862.7, 780.6, 706.6.

Di-tert-butyl ((1*H*-indole-5,7-diyl)bis(4,1-phenylene))dicarbamate (3j) [NEW].



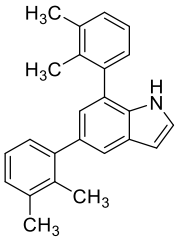
Following the general procedure (b), 5,7-dibromoindole **(1)** (0.100 g, 0.364 mmol), 4-(*N*-Boc-amino) phenylboronic acid (0.259 g, 1.092 mmol), Na_2CO_3 (0.077 g, 0.726 mmol) and $Pd(PPh_3)_4$ (0.013 g, 0.012 mmol). The product was isolated using [(EtOAc:Hexane, 15:85)] eluent and obtained as a white solid (0.083 g, 46 %). R_f = 0.48 [(EtOAc:Hexane, 40:60)]. **^{1}H NMR (400 MHz, Chloroform-*d*) δ** 8.39 (s, 1H), 7.79 (d, *J* = 1.6 Hz, 1H), 7.65 – 7.57 (m, 4H), 7.56 – 7.48 (m, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 1.7 Hz, 1H), 7.24 (t, *J* = 2.8 Hz, 1H), 6.65 (dd, *J* = 3.3, 2.0 Hz, 1H), 6.56 (d, *J* = 31.7 Hz, 2H), 1.55 (d, *J* = 5.4 Hz, 18H). **^{13}C NMR (101 MHz, Chloroform-*d*) δ** 152.84, 137.79, 137.34, 136.89, 133.87, 133.46, 133.20, 128.87, 128.82, 127.86, 125.33, 125.03, 121.34, 119.36, 117.93, 103.40, 80.82, 80.53, 28.39, 28.38. **HR-MS** Calcd (M-H)$^-$ for $C_{30}H_{32}N_3O_4^-$ 498.2398; Found 498.2394. **IR (neat)**. 3409.9, 3361.9, 3294.9, 2981.9, 2929.9, 1719.8, 1700.7, 1529.7, 1320.8, 1160.7, 1063.8, 739.7.

***N*,*N*'-((1*H*-indole-5,7-diyl)bis(4,1-phenylene))diacetamide (3k) [NEW].**



Following the general procedure (b), 5,7-dibromoindole **(1)** (0.10 g, 0.364 mmol), 4-acetamidophenylboronic acid (0.195 g, 1.090 mmol), Na_2CO_3 (0.077 g, 0.726 mmol) and $Pd(PPh_3)_4$ (0.013 g, 0.012 mmol). The product was isolated using [(EtOAc: Pentane, 90:10)] eluent and obtained as a white solid (0.059 g, 42 %). R_f = 0.20 [(EtOAc, 100)]. **^{1}H NMR (400 MHz, Acetone-d_6) δ** 10.29 (s, 1H), 9.29 (s, 1H), 9.18 (s, 1H), 7.83 – 7.74 (m, 3H), 7.77 – 7.69 (m, 2H), 7.72 – 7.63 (m, 4H), 7.43 (d, *J* = 1.7 Hz, 1H), 7.38 (t, *J* = 2.9 Hz, 1H), 6.61 (dd, *J* = 3.2, 1.9 Hz, 1H), 2.11 (d, *J* = 8.8 Hz, 6H). **^{13}C NMR (101 MHz, Acetone-d_6) δ** 206.15, 206.12, 168.96, 139.80, 139.07, 138.25, 133.65, 130.58, 129.52, 128.02, 126.84, 126.51, 121.41, 120.45, 120.27, 118.21, 103.36, 24.31. **HR-MS** Calcd (M-H)$^-$ for $C_{24}H_{20}N_3O_2^-$ 382.1561; Found 382.1556. **IR (neat)**. 3294.9, 1666.8, 1596.8, 1521.8, 13116.8, 825.8, 728.8.

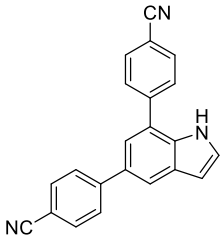
5,7-bis(2,6-dimethylphenyl)-1*H*-indole (3l) [NEW].



Following the general procedure (b), 5,7-dibromoindole **(1)** (0.10 g, 0.364 mmol), 2,3-dimethylphenylboronic acid (0.164 g, 1.093 mmol), Na_2CO_3 (0.077 g, 0.726 mmol) and $Pd(PPh_3)_4$ (0.013 g, 0.012 mmol). The product was isolated using [(EtOAc: Hexane, 5:95)] eluent and obtained as a brown solid (0.072 g, 61%). R_f = 0.56 [(EtOAc: Hexane, 40:60)]. **^{1}H NMR (400 MHz,**

Chloroform-*d*) δ 7.97 (s, 1H), 7.59 (s, 1H), 7.33 – 7.14 (m, 7H), 7.07 (s, 1H), 6.66 (t, *J* = 2.7 Hz, 1H), 2.40 (d, *J* = 8.1 Hz, 6H), 2.28 (s, 3H), 2.17 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*) δ** 143.48, 138.28, 137.76, 137.14, 135.26, 134.55, 133.70, 129.45, 128.45, 127.97, 127.68, 125.77, 125.23, 125.18, 125.01, 124.71, 120.22, 103.03, 20.92, 20.83, 17.38, 16.93. **MS (EI):** m/z (%). 326 (24), 325 (100, M^+), 324 (28), 311 (5), 310 (21), 309 (13), 294 (10), 278 (4), 221 (7), 220 (26), 205 (6), 204 (6). **HR-MS** Calcd $(M+H)^+$ for $C_{24}H_{24}N^+$ 326.1903; Found 326.1907. **IR (neat)**. 3376.9, 2962.9, 2921.9, 2854.9, 1458.9, 1417.9, 1313.9, 1264.9, 1022.8, 788.8, 739.8, 724.8.

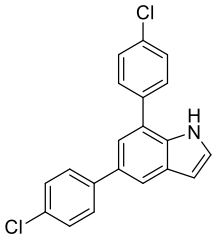
4,4'-(1*H*-indole-5,7-diyl)dibenzonitrile (3m) [NEW].



Following the general procedure (b), 5,7-dibromoindole **(1)** (0.10 g, 0.364 mmol), 4-cyanophenylboronic acid (0.160 g, 1.093 mmol), Na_2CO_3 (0.077 g, 0.726 mmol) and $Pd(PPh_3)_4$ (0.013 g, 0.012 mmol). The reaction gave desired coupled product 3m in 32% conversion and mono coupled product (5 or 7 substituted) in 51% conversion based on GC. The desired product was not isolated from the crude mixture. **MS (EI):** m/z (%). 320 (26), 319 (100, M^+), 291 (5), 281 (10), 264 (4), 207 (22), 192 (4), 73 (4).

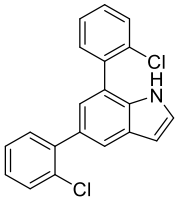
Following the general procedure b) **using microwave temperature 140 °C for 90 minutes**, 5,7-dibromoindole **(1)** (0.10 g, 0.364 mmol), 4-cyanophenylboronic acid (0.160 g, 1.093 mmol), Na_2CO_3 (0.077 g, 0.726 mmol) and $Pd(PPh_3)_4$ (0.013 g, 0.012 mmol). The product was isolated using [(EtOAc: Hexane, 20:80)] eluent and obtained as a brown solid (0.083 g, 72%). R_f = 0.48 [(EtOAc: Hexane, 40:60)]. **^{1}H NMR (400 MHz, DMSO-d_6) δ** 11.33 (s, 1H), 8.08 – 7.88 (m, 9H), 7.56 (d, *J* = 1.8 Hz, 1H), 7.45 (t, *J* = 2.8 Hz, 1H), 6.66 (dd, *J* = 3.2, 1.7 Hz, 1H). **^{13}C NMR (101 MHz, DMSO-d_6) δ** 145.88, 143.15, 133.08, 132.78, 132.68, 130.07, 129.65, 129.46, 127.64, 127.56, 124.12, 120.92, 119.56, 119.10, 118.92, 109.99, 108.87, 102.71. **HR-MS** Calcd $(M-H)^-$ for $C_{22}H_{12}N_3^-$ 318.1037; Found 318.1031. **IR (neat).** 3335.8, 1607.8, 1097.8, 836.7, 732.7.

5,7-bis(4-chlorophenyl)-1*H*-indole (3n) [NEW].



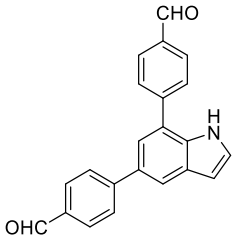
Following the general procedure (b), 5,7-dibromoindole **(1)** (0.10 g, 0.364 mmol), 4-chlorophenylboronic acid (0.171 g, 1.094 mmol), Na_2CO_3 (0.077 g, 0.726 mmol), $Pd(PPh_3)_4$ (0.013 g, 0.012 mmol). The product was isolated using [(EtOAc: Hexane, 10:90)] eluent and obtained as a grey solid (0.065 g, 53 %). R_f = 0.47 [(EtOAc:Hexane, 20:80)] **^{1}H NMR (400 MHz, Chloroform-*d*) δ** 8.08 (s, 1H), 7.58 (d, *J* = 1.6 Hz, 1H), 7.54 – 7.28 (m, 4H), 7.32 – 7.14 (m, 2H), 7.15 (d, *J* = 2.0 Hz, 1H), 7.13 (d, *J* = 1.7 Hz, 1H), 7.00 (dd, *J* = 3.7, 2.1 Hz, 1H), 6.43 (dd, *J* = 3.2, 2.0 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 140.69, 137.39, 133.67, 133.25, 132.83, 132.59, 129.54, 129.46, 129.04, 128.83, 128.63, 125.41, 124.73, 121.51, 118.80, 103.69. **MS (EI):** m/z (%). 340 (16), 339 (65), 338 (25), 337 (100, M^+), 304 (4), 303 (8), 302 (12), 301 (19), 268 (5), 267 (25), 266 (15), 264 (4), 239 (8), 134 (4), 133 (9), 119 (7). **HR-MS** Calcd $(M-H)^-$ for $C_{20}H_{12}Cl_2N^-$ 336.0352; Found 336.0349. **IR (neat).** 3365.6, 1491.3, 1469.5, 1402.6, 1093.5, 821.4, 743.4, 724.5.

5,7-bis(2-chlorophenyl)-1*H*-indole (3o) [NEW].



Following the general procedure (b), 5,7-dibromoindole **(1)** (0.10 g, 0.364 mmol), 2-chlorophenylboronic acid (0.171 g, 1.094 mmol), Na_2CO_3 (0.077 g, 0.726 mmol), $Pd(PPh_3)_4$ (0.013 g, 0.012 mmol). The product was isolated using [(EtOAc: Hexane, 10:90)] eluent and obtained as a pale-brown liquid (0.073 g, 60 %). R_f = 0.43 [(EtOAc:Hexane, 20:80)]. **^{1}H NMR (400 MHz, Chloroform-*d*) δ** 7.93 (s, 1H), 7.63 (d, *J* = 1.5 Hz, 1H), 7.45 – 7.32 (m, 4H), 7.25 – 7.22 (m, 2H), 7.17 – 7.08 (m, 4H), 6.53 (dd, *J* = 3.2, 2.0 Hz, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*) δ** 141.38, 137.34, 133.41, 133.36, 132.93, 132.06, 132.04, 131.26, 130.18, 129.90, 129.18, 127.98, 127.83, 127.15, 126.72, 125.12, 124.95, 122.43, 121.52, 103.34. **MS (EI)**: m/z (%). 340 (15), 339 (69), 338 (24), 337 (100, M^+), 304 (6), 303 (7), 302 (18), 301 (9), 268 (13), 267 (58), 266 (19), 264 (10), 239 (10), 134 (5), 133 (12), 119 (10). **HR-MS** Calcd $(M+H)^+$ for $C_{20}H_{14}Cl_2N^+$ 338.0498; Found 338.0504. **IR (neat).** 3435.6, 3056.7, 1707.6, 1458.4, 1421.4, 1041.38, 758.2, 728.1.

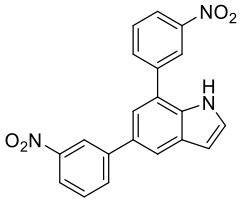
4,4'-(1*H*-indole-5,7-diyl)dibenzaldehyde (3p) [NEW].



Following the general procedure (b), 5,7-dibromoindole **(1)** (0.10 g, 0.364 mmol), 4-formylphenylboronic acid (0.164 g, 1.094 mmol), Na_2CO_3 (0.077 g, 0.726 mmol), $Pd(PPh_3)_4$ (0.013 g, 0.012 mmol). The reaction gave desired coupled product in 12% yield based on GC. The desired product was not isolated from the crude mixture. **MS (EI):** m/z (%). 326 (24), 325 (100, M^+), 324 (32), 297 (8), 296 (19), 269 (5), 268 (11), 267 (16), 266 (11), 239 (6), 207 (5), 134 (3), 133 (6).

Following the general procedure (c), 5,7-dibromoindole **(1)** (0.10 g, 0.364 mmol), 4-formylphenylboronic acid (0.164 g, 1.094 mmol), Na_2CO_3 (0.077 g, 0.726 mmol), TBAB (0.013 g, 0.035 mmol), $Pd(PPh_3)_4$ (0.013 g, 0.012 mmol) at 120 °C for 1 hour. The product was isolated using [(EtOAc: Hexane, 50:50)] eluent and obtained as a pale-brown solid (0.065 g, 53 %). R_f = 0.60 [(EtOAc:Hexane, 60:40)]. **^{1}H NMR (400 MHz, DMSO-d_6) δ** 11.32 (s, 1H), 10.13 (s, 1H), 10.04 (s, 1H), 8.12 – 7.95 (m, 9H), 7.61 (s, 1H), 7.44 (t, *J* = 2.7 Hz, 1H), 6.67 (d, *J* = 3.1 Hz, 1H). **^{13}C NMR (101 MHz, DMSO-d_6) δ** 192.82, 192.63, 147.25, 144.48, 135.14, 134.31, 133.16, 130.58, 130.12, 130.10, 129.66, 129.17, 127.54, 127.31, 124.59, 121.00, 119.48, 102.67. **HR-MS** Calcd $(M-H)^-$ for $C_{22}H_{14}NO_2^-$ 324.1030; Found 324.1023.

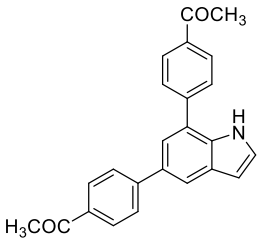
5,7-bis(3-nitrophenyl)-1H-indole (3q) [NEW].



Following the general procedure (b), 5,7-dibromoindole **(1)** (0.10 g, 0.364 mmol), 3-nitrophenylboronic acid (0.182 g, 1.091 mmol), Na_2CO_3 (0.077 g, 0.726 mmol), $Pd(PPh_3)_4$ (0.013 g, 0.012 mmol) at 140 °C for 90 minutes. The product was isolated using [(EtOAc: Hexane, 20:80)] eluent and obtained as a yellow solid (0.060 g, 46 %). R_f = 0.25 [(EtOAc:Hexane, 20:80)]. **^{1}H**

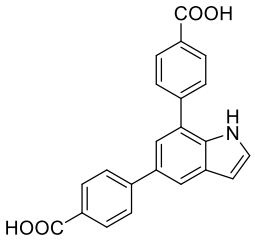
NMR (400 MHz, Chloroform-*d*) δ 8.54 (dt, *J* = 10.5, 2.1 Hz, 3H), 8.29 (ddd, *J* = 8.3, 2.3, 1.1 Hz, 1H), 8.18 (ddd, *J* = 8.2, 2.3, 1.0 Hz, 1H), 8.07 – 7.98 (m, 2H), 7.96 (d, *J* = 1.6 Hz, 1H), 7.74 (t, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 1.7 Hz, 1H), 7.36 (t, *J* = 2.8 Hz, 1H), 6.75 (dd, *J* = 3.3, 2.0 Hz, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*) δ** 148.98, 148.83, 143.70, 140.55, 134.46, 133.51, 133.37, 131.65, 130.50, 129.77, 129.62, 126.24, 123.81, 123.05, 122.76, 122.13, 121.71, 121.53, 120.14, 104.20. **HR-MS** Calcd (M-H)$^-$ for $C_{20}H_{12}N_3O_4^-$ 358.0833; Found 358.0824. **IR (neat)**. 3409.9, 1525.8, 1350.8, 743.8, 687.8.

1,1'-((1H-indole-5,7-diyl)bis(4,1-phenylene))bis(ethan-1-one) (3r) [NEW].



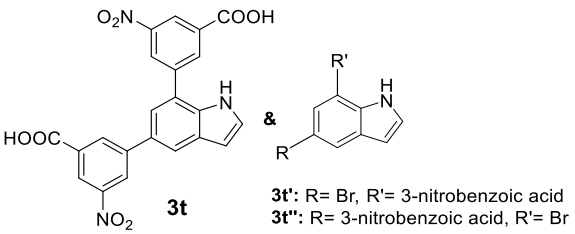
Following the general procedure (b), 5,7-dibromoindole **(1)** (0.10 g, 0.364 mmol), 4-acetylphenylboronic acid (0.179 g, 1.092 mmol), Na_2CO_3 (0.077 g, 0.726 mmol), $Pd(PPh_3)_4$ (0.013 g, 0.012 mmol) at 140 ºC for 90 minutes. The product was isolated using [(EtOAc: Hexane, 50:50)] eluent obtained as a white solid (0.040 g, 33 %). R_f = 0.45 [(EtOAc:Hexane, 60:40)]. **^{1}H NMR (400 MHz, Chloroform-*d*) δ** 8.58 (s, 1H), 8.12 (d, *J* = 7.8 Hz, 2H), 8.05 (d, *J* = 7.9 Hz, 2H), 7.96 (s, 1H), 7.83 – 7.75 (m, 4H), 7.53 (s, 1H), 7.32 (s, 1H), 6.73 (s, 1H), 2.66 (d, *J* = 8.0 Hz, 6H). **^{13}C NMR (101 MHz, Chloroform-*d*) δ** 197.99, 197.73, 146.95, 143.91, 136.40, 135.41, 133.68, 132.79, 129.49, 129.40, 129.09, 128.55, 127.47, 125.83, 124.98, 121.88, 119.93, 104.01, 26.83, 26.79. **HR-MS** Calcd (M-H)$^-$ for $C_{24}H_{18}NO^-$ 352.1343; Found 352.1336. **IR (neat).** 3260.7, 1678.6, 1663.5, 1603.6, 1428.7, 1272.5, 1249.6, 832.5, 747.5.

4,4'-(1H-indole-5,7-diyl)dibenzoic acid (3s) [NEW].



Following the general procedure (b), 5,7-dibromoindole **(1)** (0.10 g, 0.364 mmol), 4-carboxyphenylboronic acid (0.181 g, 1.091 mmol), Na_2CO_3 (0.077 g, 0.726 mmol), $Pd(PPh_3)_4$ (0.013 g, 0.012 mmol) at 140 ºC for 90 minutes. The product was isolated using [(MeOH: DCM, 90:10)] eluent and finally the product was washed with DCM (10 mL) to remove the traces of impurities and obtained as a pale-yellow solid (0.045 g, 35 %). **^{1}H NMR (400 MHz, DMSO-d_6) δ** 11.23 (s, 1H), 8.16 – 8.09 (m, 2H), 8.05 – 7.96 (m, 3H), 7.88 (t, *J* = 8.1 Hz, 4H), 7.54 (d, *J* = 1.7 Hz, 1H), 7.41 (t, *J* = 2.8 Hz, 1H), 6.64 (dd, *J* = 3.1, 1.7 Hz, 1H). **^{13}C NMR (101 MHz, DMSO-d_6) δ** 168.02, 145.83, 142.81, 133.51, 131.42, 130.36, 130.01, 128.87, 127.78, 127.14, 125.38, 121.17, 119.22, 102.97. **HR-MS** Calcd (M-H)$^-$ for $C_{22}H_{14}NO_4^-$ 356.0928; Found 356.0923. **IR (neat).** 2971.7, 1685.8, 1607.8, 1421.9, 1294.8, 1253.8, 847.8.

5,5'-(1*H*-indole-5,7-diyl)bis(3-nitrobenzoic acid) (3t) [NEW].

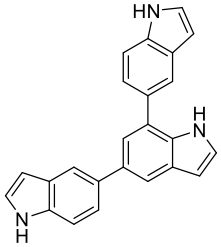


3t

3t': R= Br, R'= 3-nitrobenzoic acid
3t'': R= 3-nitrobenzoic acid, R'= Br

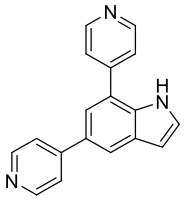
Following the general procedure (c), 5,7-dibromoindole **(1)** (0.10 g, 0.364 mmol), 3-nitrophenylboronic acid (0.230 g, 1.091 mmol), Na_2CO_3 (0.077 g, 0.726 mmol), $Pd(PPh_3)_4$ (0.013 g, 0.012 mmol) at 140 °C for 90 minutes. The crude product was purified by using [(MeOH: DCM, 90:10)] eluent and obtained a mixture of both the desired bis-coupled product (**3t**) and 5 or 7 substituted mono coupled product (**3t'&3t''**) as a yellow solid (0.055 g, 34 %). **^{1}H NMR (400 MHz, DMSO-d_6) δ** 11.51 (d, *J* = 32.9 Hz, 2H), 8.68 – 8.45 (m, 6H), 8.04 (d, *J* = 1.6 Hz, 1H), 7.89 – 7.75 (m, 2H), 7.59 – 7.45 (m, 3H), 7.37 (d, *J* = 1.9 Hz, 1H), 6.69 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.58 (dd, *J* = 3.1, 1.7 Hz, 1H). **^{13}C NMR (101 MHz, DMSO-d_6) δ** 166.05, 149.08, 148.83, 139.58, 135.55, 132.42, 131.16, 129.83, 128.57, 127.65, 127.27, 124.70, 123.96, 123.46, 123.14, 112.35, 102.26. **HR-MS** Calcd $(M-H)^-$ for $C_{15}H_8BrN_2O_4^-$ 358.9673; Found 358.9670 (mono coupled product).

1*H*,1'*H*,1''*H*-5,5':7',5''-terindole (5a) [NEW].



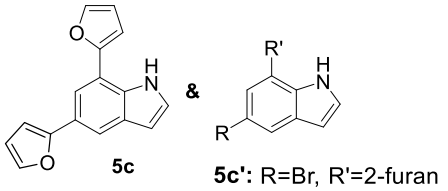
Following the general procedure (c), 5,7-dibromoindole **(1)** (0.10 g, 0.364 mmol), 5-indolylboronic acid (0.176 g, 1.093 mmol), Na_2CO_3 (0.077 g, 0.726 mmol), $Pd(PPh_3)_4$ (0.013 g, 0.012 mmol) at 120 °C for 60 minutes. The product was isolated using [(EtOAc: Hexane, 30:70)] eluent and obtained as a pale-yellow solid (0.066 g, 52 %). R_f = 0.30 [(EtOAc:Hexane, 60:40)]. **^{1}H NMR (400 MHz, Chloroform-*d*) δ** 8.48 (s, 1H), 8.22 (s, 1H), 8.13 (s, 1H), 7.98 (td, *J* = 2.2, 0.9 Hz, 2H), 7.89 (d, *J* = 1.6 Hz, 1H), 7.72 – 7.36 (m, 5H), 7.36 – 7.09 (m, 3H), 6.69 (dd, *J* = 3.2, 2.0 Hz, 1H), 6.68 – 6.59 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*) δ** 135.46, 135.41, 135.07, 133.51, 131.26, 128.86, 128.66, 128.58, 127.00, 125.17, 124.81, 124.70, 123.01, 122.78, 122.72, 120.38, 119.53, 117.97, 111.83, 111.17, 103.38, 103.11, 103.09. **HR-MS** Calcd $(M-H)^-$ for $C_{24}H_{16}N_3^-$ 346.1350; Found 346.1348. **IR (neat).** 3394.7, 1722.8, 1458.8, 1417.7, 873.7, 728.6.

5,7-di(pyridin-4-yl)-1*H*-indole (5b) [NEW].



Following the general procedure (c), 5,7-dibromoindole **(1)** (0.10 g, 0.364 mmol), 4-pyridinylboronic acid (0.134 g, 1.090 mmol), Na_2CO_3 (0.077 g, 0.726 mmol), TBAB (0.013 g, 0.035 mmol) and $Pd(PPh_3)_4$ (0.013 g, 0.012 mmol). The product was isolated using [(MeOH:DCM, 5:95)] eluent and obtained as a pale-yellow solid (0.080 g, 81 %). R_f = 0.75 [(MeOH:DCM, 10:90)]. **^{1}H NMR (400 MHz, DMSO-d_6) δ** 11.39 (s, 1H), 8.76 – 8.70 (m, 4H), 8.63 – 8.57 (m, 4H), 8.12 (d, *J* = 1.7 Hz, 2H), 7.80 (ddd, *J* = 15.2, 4.5, 1.7 Hz, 9H), 7.65 (d, *J* = 1.7 Hz, 2H), 7.46 (d, *J* = 3.1 Hz, 2H), 6.67 (d, *J* = 3.1 Hz, 2H). **^{13}C NMR (101 MHz, DMSO-d_6) δ** 150.13, 150.01, 148.06, 145.64, 129.67, 129.64, 128.81, 127.70, 127.54, 123.29, 123.28, 123.07, 121.27, 120.31, 119.57, 102.73, 102.69. **MS (EI):** m/z (%). 272 (19), 271 (100, M^+), 270 (22), 243 (7), 207 (6), 193 (4), 168 (3), 108 (2). **HR-MS** Calcd $(M-H)^-$ for $C_{18}H_{12}N_3^-$ 270.1037; Found 270.1031. **IR (neat).** 3037.9, 2367.9, 2333.9, 2307.9, 2247.9, 1599.8, 1406.8, 1302.8, 996.8, 825.8, 717.8.

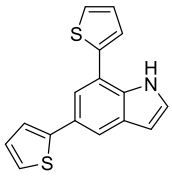
5,7-di(furan-2-yl)-1H-indole (5c) [NEW].



5c **5c':** R=Br, R'=2-furan
5c'': R=2-furan, R'=Br

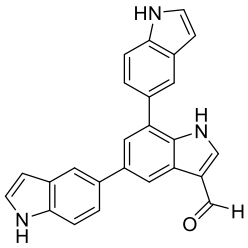
Following the general procedure (c), 5,7-dibromoindole **(1)** (0.10 g, 0.364 mmol), 2-furanylboronic acid (0.122 g, 1.090 mmol), Na_2CO_3 (0.077 g, 0.726 mmol), TBAB (0.013 g, 0.035 mmol) and $Pd(PPh_3)_4$ (0.013 g, 0.012 mmol). The reaction gave only trace amount of desired product (**5c**) based on GC and 8% of mono coupled product (5 or 7 substituted) (**5c'**) was observed. **MS (EI) (5c'):** m/z (%). 264 (14), 263 (100), 262 (15), 261 (99, M^+), 234 (30), 232 (32), 209 (7), 207 (30), 154 (79), 153 (45), 127 (16), 126 (21), 77 (7).

5,7-di(thiophen-2-yl)-1*H*-indole (5d) [2096983-67-2].



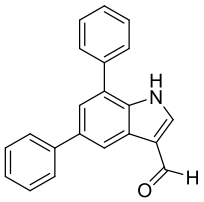
Following the general procedure (c), 5,7-dibromoindole **(1)** (0.10 g, 0.364 mmol), 2-thienylboronic acid (0.140 g, 1.094 mmol), Na_2CO_3 (0.077 g, 0.726 mmol), TBAB (0.013 g, 0.035 mmol) and $Pd(PPh_3)_4$ (0.013 g, 0.012 mmol). The product was isolated using [(EtOAc: Hexane, 10:90)] eluent and obtained as a brown liquid (0.093 g, 91 %). R_f = 0.40 [(EtOAc:Hexane, 20:80)]. **^{1}H NMR (400 MHz, Chloroform-*d*) δ** 8.59 (s, 1H), 7.83 (d, *J* = 1.6 Hz, 1H), 7.59 (d, *J* = 1.6 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.28 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.17 (dd, *J* = 5.1, 3.6 Hz, 1H), 7.05 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.60 (dd, *J* = 3.2, 2.1 Hz, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*) δ** 145.75, 140.85, 133.07, 129.19, 128.16, 128.04, 127.32, 125.55, 125.30, 125.00, 124.01, 122.54, 120.87, 118.87, 118.28, 103.85. **MS (EI):** m/z (%). 282 (21), 281 (100, M^+), 280 (6), 247 (9), 237 (9), 236 (43), 204 (4), 191 (3). **HR-MS** Calcd $(M-H)^-$ for $C_{16}H_{10}NS_2^-$ 280.0260; Found 280.0260. **IR (neat).** 3428.6, 3104.6, 3070.6, 1410.5, 1309.4, 825.4, 691.3.

1*H*,1'*H*,1''*H*-[5,5':7',5''-terindole]-3'-carbaldehyde (6a) [NEW].



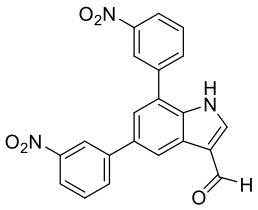
Following the general procedure (c), 5,7-dibromoindole-3-carbaxaldehyde **(1a)** (0.10 g, 0.330 mmol), 5-indolylboronic acid (0.159 g, 0.988 mmol), Na_2CO_3 (0.070 g, 0.660 mmol), TBAB (0.012 g, 0.032mmol) and $Pd(PPh_3)_4$ (0.011 g, 0.010 mmol). The product was isolated using [(EtOAc: 100)] eluent and obtained as a pale-yellow solid (0.096 g, 77 %). R_f = 0.23 [(EtOAc: 100)]. **^{1}H NMR (400 MHz, DMSO-d_6) δ** 10.02 (s, 1H), 8.40 – 8.20 (m, 2H), 7.90 (d, *J* = 1.6 Hz, 2H), 7.59 (d, *J* = 7.9 Hz, 2H), 7.50 (d, *J* = 1.6 Hz, 2H), 7.47 – 7.42 (m, 2H), 7.38 (d, *J* = 3.1 Hz, 1H), 6.62 – 6.46 (m, 2H). **^{13}C NMR (101 MHz, DMSO-d_6) δ** 185.17, 139.16, 137.14, 135.44, 135.09, 133.49, 132.39, 128.59, 128.32, 128.22, 128.15, 125.99, 125.74, 125.67, 123.34, 121.93, 120.84, 120.06, 118.57, 118.29, 116.98, 111.95, 111.70, 101.58, 101.44. **HR-MS** Calcd $(M-H)^-$ for $C_{25}H_{16}N_3O^-$ 374.1299; Found 374.1295. IR (cm^{-1}). **IR (neat).** 3243.6, 1626.8, 1607.8, 1354.8, 814.8, 773.8, 728.8.

5,7-diphenyl-1H-indole-3-carbaldehyde (6b) [NEW].



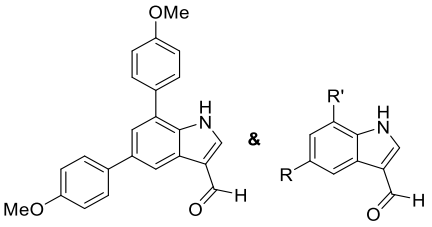
Following the general procedure (c), 5,7-dibromoindole-3-carbaxaldehyde **(1a)** (0.10 g, 0.330 mmol), phenylboronic acid (0.121 g, 0.990 mmol), Na_2CO_3 (0.070 g, 0.660 mmol), TBAB (0.012 g, 0.032mmol) and $Pd(PPh_3)_4$ (0.011 g, 0.010 mmol). The product was isolated using [(EtOAc:Pentane, 50:50)] eluent and obtained as a white solid (0.071 g,72 %). R_f = 0.29 [(EtOAc:Pentane, 60:40)]. **^{1}H NMR (400 MHz, DMSO-d_6) δ** 12.10 (s, 1H), 10.03 (s, 1H), 8.38 (d, *J* = 1.8 Hz, 1H), 8.31 (d, *J* = 2.8 Hz, 1H), 7.74 (ddt, *J* = 7.0, 5.9, 1.2 Hz, 4H), 7.67 – 7.53 (m, 3H), 7.49 (t, *J* = 7.6 Hz, 3H), 7.41 – 7.32 (m, 1H). **^{13}C NMR (101 MHz, DMSO-d_6) δ** 185.27, 140.96, 139.73, 137.57, 135.40, 133.81, 129.06, 128.92, 128.62, 127.82, 127.02, 126.95, 126.81, 125.80, 122.92, 118.60, 118.09. **MS (EI):** m/z (%). 298 (23), 297 (100, M^+), 296 (64), 269 (7), 268 (12), 267 (23), 266 (11), 239 (5), 191 (3), 148 (2), 133 (3), 119 (2). **HR-MS** Calcd (M-H)$^-$ for $C_{21}H_{14}NO^-$ 296.1081; Found 296.1076. **IR (neat).** 3245.8, 2799.8, 2434.8, 1640.5, 1532.7, 1443.7, 1123.7, 754.5, 702.5.

5,7-bis(3-nitrophenyl)-1H-indole-3-carbaldehyde (6c) [NEW].



Following the general procedure (c), 5,7-dibromoindole-3-carbaxaldehyde **(1a)** (0.10 g, 0.330 mmol), 3-nitrophenylboronic acid (0.165 g, 0.988 mmol), Na_2CO_3 (0.070 g, 0.660 mmol), TBAB (0.012 g, 0.032mmol) and $Pd(PPh_3)_4$ (0.011 g, 0.010 mmol). The product was isolated using [(EtOAc:Pentane, 60:40)] eluent and obtained as a brown solid (0.020 g, 16 %). The product contains 10% impurities of monocoupled product. R_f = 0.45 [(EtOAc:Pentane, 80:20)]. **^{1}H NMR (400 MHz, DMSO-d_6) δ** 12.29 (s, 1H), 10.00 (s, 1H), 8.57 – 8.49 (m, 1H), 8.45 – 8.40 (m, 2H), 8.38 (d, *J* = 3.1 Hz, 1H), 8.26 – 8.12 (m, 3H), 7.77 (t, *J* = 7.9 Hz, 2H), 7.67 (dd, *J* = 2.9, 1.3 Hz, 2H). **^{13}C NMR (101 MHz, DMSO-d_6) δ** 185.69, 148.94, 143.25, 139.86, 137.62, 133.90, 132.77, 131.01, 125.39, 123.36, 122.02, 121.56, 119.69, 118.89, 113.78. **HR-MS** Calcd (M-H)$^-$ for $C_{21}H_{12}N_3O_5^-$ 386.0782; Found 386.0778. **IR (neat).** 3201.9, 1640.9, 1525.9, 1424.9, 1350.9, 1100.9, 877.9, 736.9.

5,7-bis(4-methoxyphenyl)-1H-indole-3-carbaldehyde (6d) [NEW].



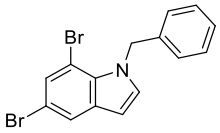
6d

6d': R= Br, R'= 4-OMePh
6d'': R=4-OMePh, R'=Br

Following the general procedure (c), 5,7-dibromoindole-3-carbaxaldehyde **(1a)** (0.05 g, 0.165 mmol), 4-methoxyphenylboronic acid (0.75 g, 0.493 mmol), Na_2CO_3 (0.035g, 0.330 mmol), TBAB (0.006 g, 0.016 mmol) and $Pd(PPh_3)_4$ (0.006 g, 0.005 mmol). The product was isolated using [(EtOAc:Pentane, 60:40)] eluent and obtained as a pale-white solid (0.025 g). The product contains 10% of 5 or 7 substituted mono-coupled product (**6d &6d**). R_f = 0.33 [(EtOAc:Pentane, 80:20)]. **^{1}H NMR (400 MHz, DMSO-d_6) δ** 11.99 (s, 1H), 10.00 (s, 1H), 8.27 (d, *J* = 5.6 Hz, 2H), 7.73 – 7.61 (m, 4H), 7.45 (s, 1H), 7.17 – 7.02 (m, 4H). **^{13}C NMR (101 MHz, DMSO-d_6) δ** 185.20, 159.03, 158.55, 139.55, 135.14, 133.52, 129.96, 129.81, 129.78, 128.05, 126.50, 125.74, 122.39, 118.56, 117.03, 114.50, 114.36, 55.28, 55.16. MS (EI): m/z (%). 358 (19), 357 (100, M^+), 342 (65), 341 (9),

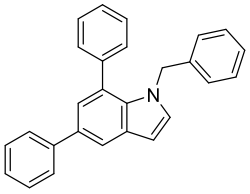
314 (16), 281 (18), 267 (7), 242 (5), 207 (53), 193 (4), 73 (5). **HR-MS** Calcd (M-H)$^-$ for $C_{23}H_{18}NO_3^-$ 356.1292; Found 356.1285. **IR (neat).** 3037.7, 2959.7, 2895.7, 2843.7, 1629.6, 1611.6, 1518.6, 1454.6, 1249.6, 1033.4, 836.5, 784.4.

1-benzyl-5,7-dibromo-1*H*-indole (7) [NEW].



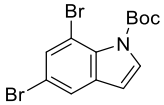
To a stirred solution of 5,7-dibromoindole **(1)** (0.10 g, 0.364 mmol) in THF (10 mL), KOH (0.082 g, 1.461 mmol) and benzyl bromide (0.09 mL, 0.731 mmol) were added at 0 ◦C. The reaction mixture was stirred at room temperature for overnight. After 24 hours, the mixture was poured into saturated aqueous $NaHCO_3$ solution (20 mL) and extracted with ether (2x40 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concerntrated in vacuo. The product was isolated using [(Pentane, 100%)] eluent and obtained as a white solid (0.125 g, 94 %). R_f = 0.89 [(EtOAc:Pentane, 20:80)]. **^{1}H NMR (400 MHz, Chloroform-*d*) δ** 7.64 (d, *J* = 1.8 Hz, 1H), 7.39 (d, *J* = 1.8 Hz, 1H), 7.27 – 7.13 (m, 3H), 7.04 (d, *J* = 3.2 Hz, 1H), 6.95 – 6.86 (m, 2H), 6.43 (d, *J* = 3.2 Hz, 1H), 5.71 (s, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*) δ** 138.74, 133.11, 132.60, 131.78, 129.18, 128.88, 127.62, 126.20, 123.04, 112.71, 104.45, 102.16, 51.60. **MS (EI):** m/z (%). 367 (27), 366 (10), 365 (52, M^+), 364 (6), 363 (28), 284 (6), 205 (31), 204 (23), 203 (11), 176 (3), 114 (5), 102 (4), 92(7), 91(100), 65 (19). **IR (neat).** 3078.7, 3029.7, 2925.7, 1547.5, 1469.5, 1290.5, 1167.5, 1045.5, 736.4, 721.3.

1-benzyl-5,7-diphenyl-1*H*-indole (8) [NEW].



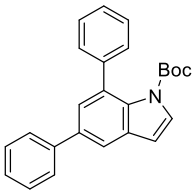
Following the general procedure (c), 1-benzyl-5,7-dibromo-1*H*-indole **(7)** (0.10 g, 0.274 mmol), phenylboronic acid (0.100 g, 0.820 mmol), Na_2CO_3 (0.058 g, 0.547 mmol), TBAB (0.010 g, 0.024 mmol) and $Pd(PPh_3)_4$ (0.009 g, 0.009 mmol). The product was isolated using [(EtOAc:Pentane, 5:95)] eluent and obtained as a pale-yellow solid (0.069 g,70 %). R_f = 0.77 [(EtOAc:Pentane, 20:80)]. **^{1}H NMR (400 MHz, Chloroform-*d*) δ** 7.92 (d, *J* = 1.8 Hz, 1H), 7.74 – 7.62 (m, 2H), 7.44 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.43 – 7.29 (m, 2H), 7.33 – 7.23 (m, 5H), 7.23 – 7.09 (m, 4H), 6.73 (d, *J* = 3.2 Hz, 1H), 6.57 (dd, *J* = 7.4, 2.1 Hz, 2H), 4.97 (s, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*) δ** 142.10, 140.21, 138.52, 132.85, 131.29, 130.83, 129.97, 128.76, 128.40, 127.80, 127.44, 127.34, 127.32, 127.14, 126.50, 126.16, 124.54, 118.67, 102.71, 51.95. MS (EI): m/z (%). 360 (27), 359 (100, M^+), 358 (20), 283 (7), 282 (29), 268 (20), 239 (3), 91 (15). **HR-MS** Calcd (M+H)$^+$ for $C_{27}H_{22}N^+$ 360.1747; Found 360.1753. **IR (neat).** 3059.6, 3029.6, 2914.6, 1451.5, 1328.4, 1030.4, 762.3, 721.2, 702.2.

tert-butyl 5,7-dibromo-1H-indole-1-carboxylate (9) [NEW].



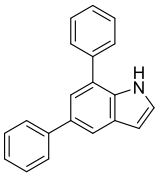
5,7-dibromoindole **(1)** (0.10 g, 0.364 mmol) was dissolved in DCM (10 mL). To the stirred solution, Boc anhydride (0.119 g, 0.545 mmol) and DMAP (0.004 g, 0.033 mmol) were added under N_2. The reaction mixture was stirred at room temperature for overnight. After the completion of the reaction by TLC, the mixture was concentrated to remove the DCM and the residue was purified by silica-gel column chromatography. The product was isolated using [(EtOAc:Pentane, 10:90)] eluent and obtained as a pale-yellow liquid (0.071 g,72 %). R_f = 0.84 [(EtOAc:Pentane, 20:80)]. **^{1}H NMR (400 MHz, Chloroform-*d*) δ** 7.65 (q, *J* = 1.8 Hz, 2H), 7.52 (d, *J* = 3.6 Hz, 1H), 6.50 (d, *J* = 3.7 Hz, 1H), 1.65 (s, 9H). **^{13}C NMR (101 MHz, Chloroform-*d*) δ** 148.31, 135.32, 133.02, 131.85, 130.70, 122.93, 116.28, 108.58, 106.32, 84.96, 28.10. **HR-MS** Calcd (M+Na)$^+$ for $C_{13}H_{13}{}^{79}Br^{81}BrNO_2Na^+$ 397.9185; Found 397.9189. **IR (neat).** 2981.8, 1756.4, 1741.3, 1443.4, 1313.1, 1246.2, 1146.7, 721.2.

tert-butyl 5,7-diphenyl-1H-indole-1-carboxylate (10) [NEW].



Following the general procedure (c), tert-butyl 5,7-dibromo-1H-indole-1-carboxylate **(9)** (0.10 g, 0.270 mmol), phenylboronic acid (0.099 g, 0.812 mmol), Na_2CO_3 (0.057 g, 0.538 mmol), TBAB (0.010 g, 0.027 mmol) and $Pd(PPh_3)_4$ (0.009 g, 0.008 mmol). The product was isolated using [(EtOAc:Pentane, 5:95)] eluent and obtained as a pale-white solid (0.019 g,19 %). R_f = 0.68 [(EtOAc:Pentane, 20:80)]. **^{1}H NMR (400 MHz, Chloroform-*d*) δ** 7.67 (d, *J* = 1.8 Hz, 1H), 7.61 – 7.57 (m, 2H), 7.52 (d, *J* = 3.6 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.43 (d, *J* = 1.8 Hz, 1H), 7.39 – 7.34 (m, 4H), 7.28 – 7.23 (m, 2H), 6.60 (d, *J* = 3.6 Hz, 1H), 1.20 (s, 9H). **^{13}C NMR (101 MHz, Chloroform-*d*) δ** 142.25, 141.57, 136.81, 133.34, 130.20, 129.51, 128.89, 128.86, 128.58, 127.73, 127.54, 127.30, 127.08, 126.96, 126.75, 118.48, 107.50, 83.88, 27.72. **HR-MS** Calcd $(M+Na)^+$ for $C_{25}H_{23}NO_2Na^+$ 392.1621; Found 392.1627. **IR (neat).** 3059.8, 3033.8, 2977.8, 2929.8, 1756.5, 1730.4, 1331.3, 1130.2, 762.3, 702.1.

In addition to the reaction yield of (**10**), 63% of Boc-deprotected compound (3a) was observed under the experimental conditions)

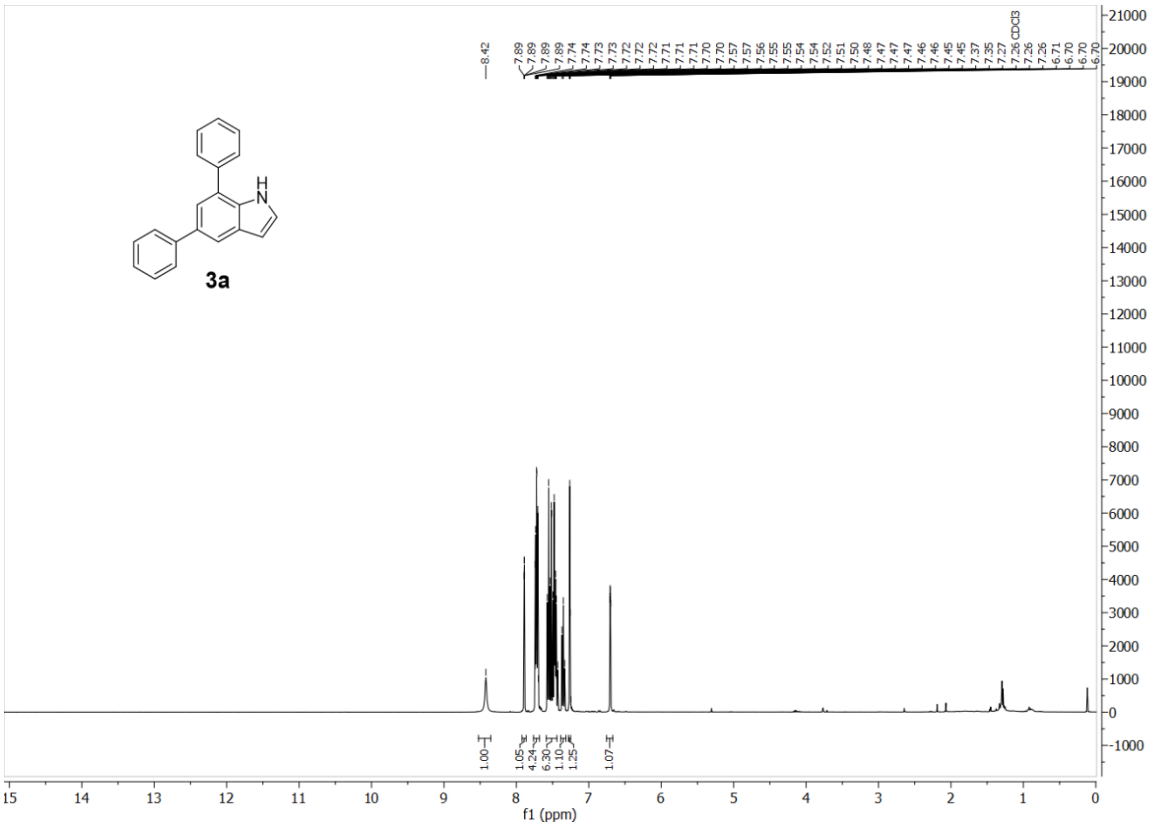


5,7-diphenyl-1H-indole (3a) [NEW]

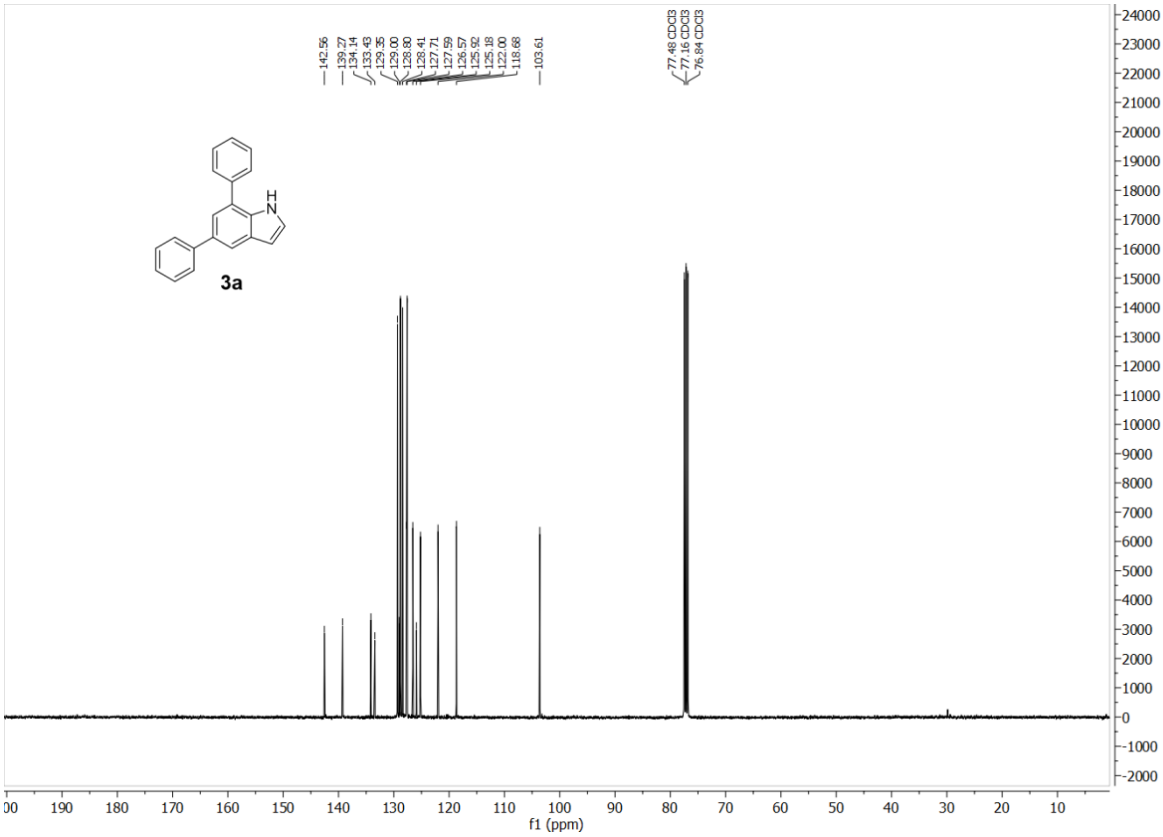
Following the general procedure (c), tert-butyl 5,7-dibromo-1*H*-indole-1-carboxylate **(9)** (0.10 g, 0.270 mmol), phenylboronic acid (0.099 g, 0.812 mmol), Na_2CO_3 (0.057 g, 0.538 mmol), TBAB (0.010 g, 0.027 mmol) and $Pd(PPh_3)_4$ (0.009 g, 0.008 mmol). The product was isolated using [(EtOAc:Pentane, 10:90)] eluent and obtained (**3a**) as a pale-white solid (0.045 g, 63 %). R_f = 0.50 [(EtOAc:Pentane, 20:80)]. **^{1}H NMR (400 MHz, Chloroform-*d*) δ** 8.42 (s, 1H), 7.88 (d, *J* = 1.6 Hz, 1H), 7.75 – 7.67 (m, 4H), 7.59 – 7.38 (m, 6H), 7.38 – 7.31 (m, 1H), 7.26 (d, *J* = 5.6 Hz, 0H), 6.70 (dd, *J* = 3.2, 2.0 Hz, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*) δ** 142.57, 139.29, 134.16, 133.45, 129.35, 129.01, 128.81, 128.41, 127.72, 127.60, 126.57, 125.93, 125.17, 122.01, 118.69, 103.62. **HR-MS** Calcd $(M+H)^+$ for $C_{20}H_{16}N^+$ 270.1277; Found 270.1283. **IR (neat).** 3428.6, 3059.7, 3029.6, 1707.5, 1473.4, 1421.4, 1350.5, 877.4, 732.3, 702.9.

[III] ^{1}H-NMR and ^{13}C-NMR spectra

^{1}H-NMR



^{13}C-NMR



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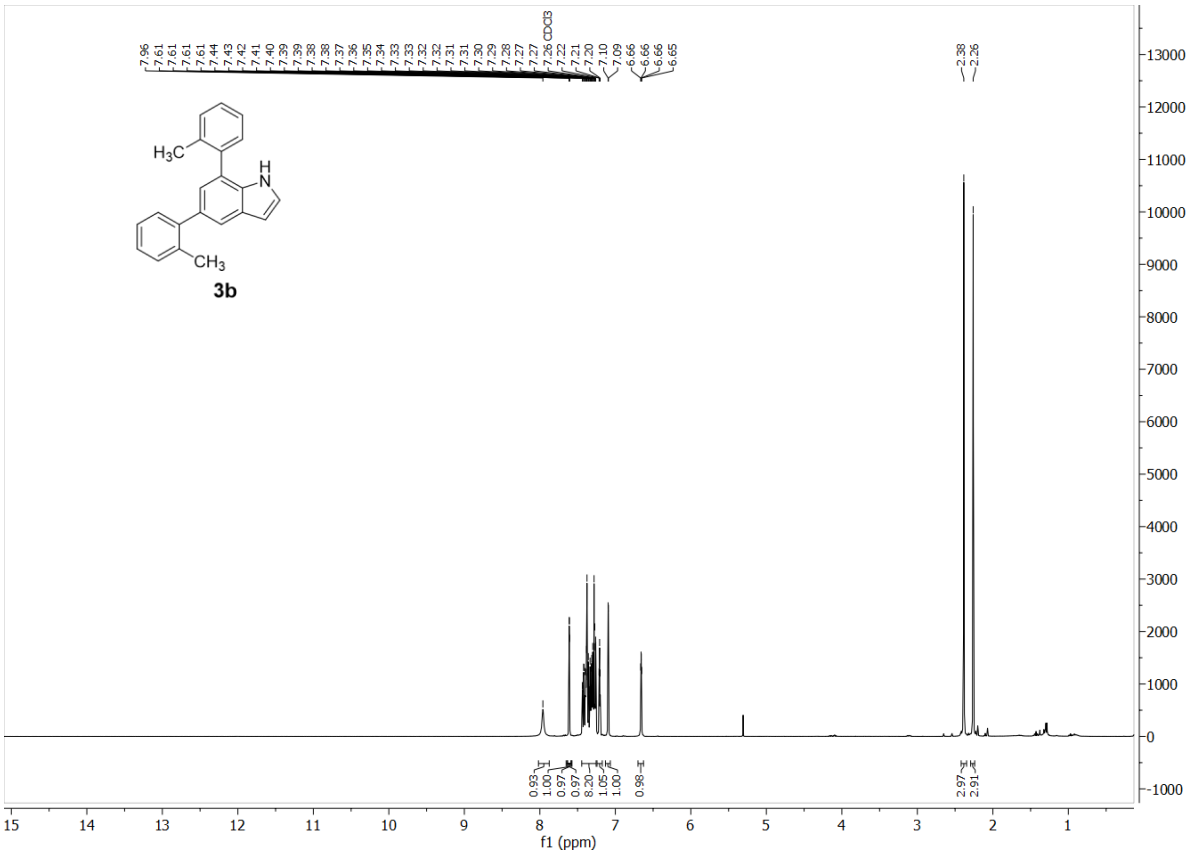

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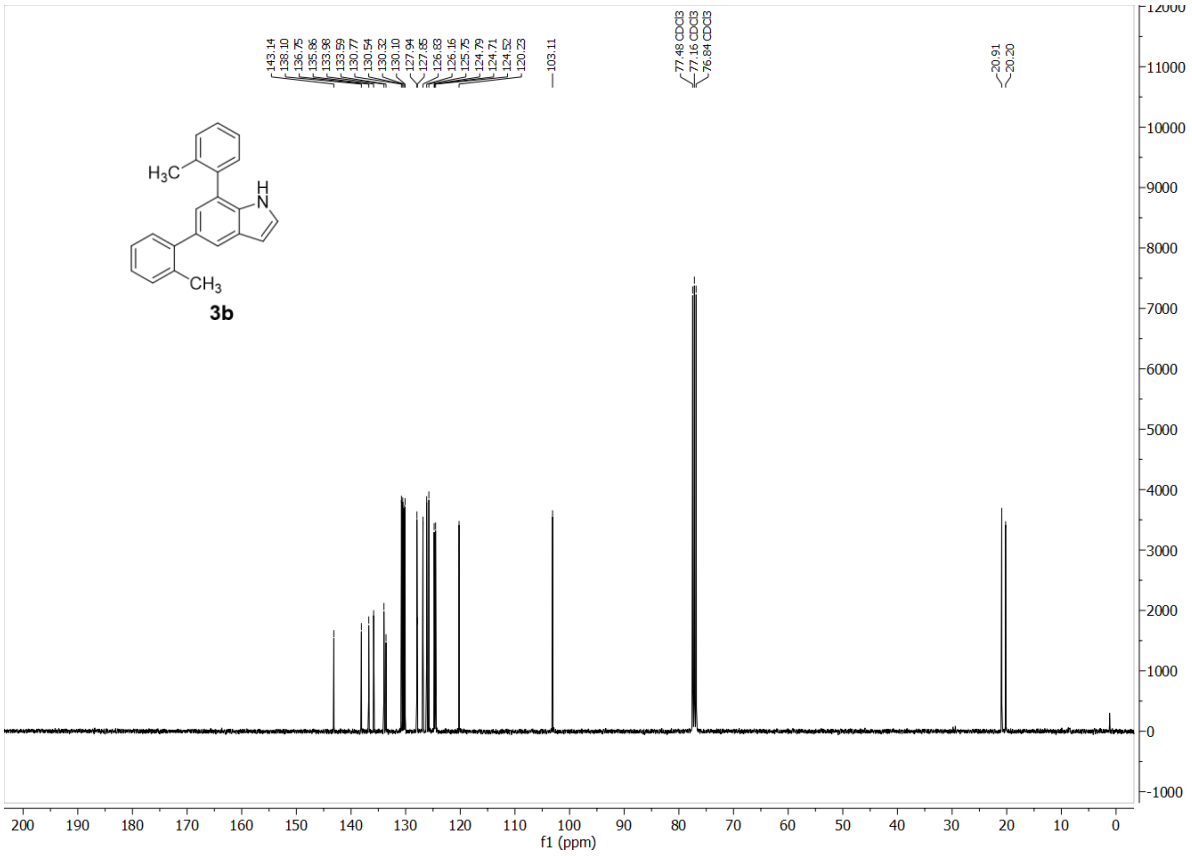

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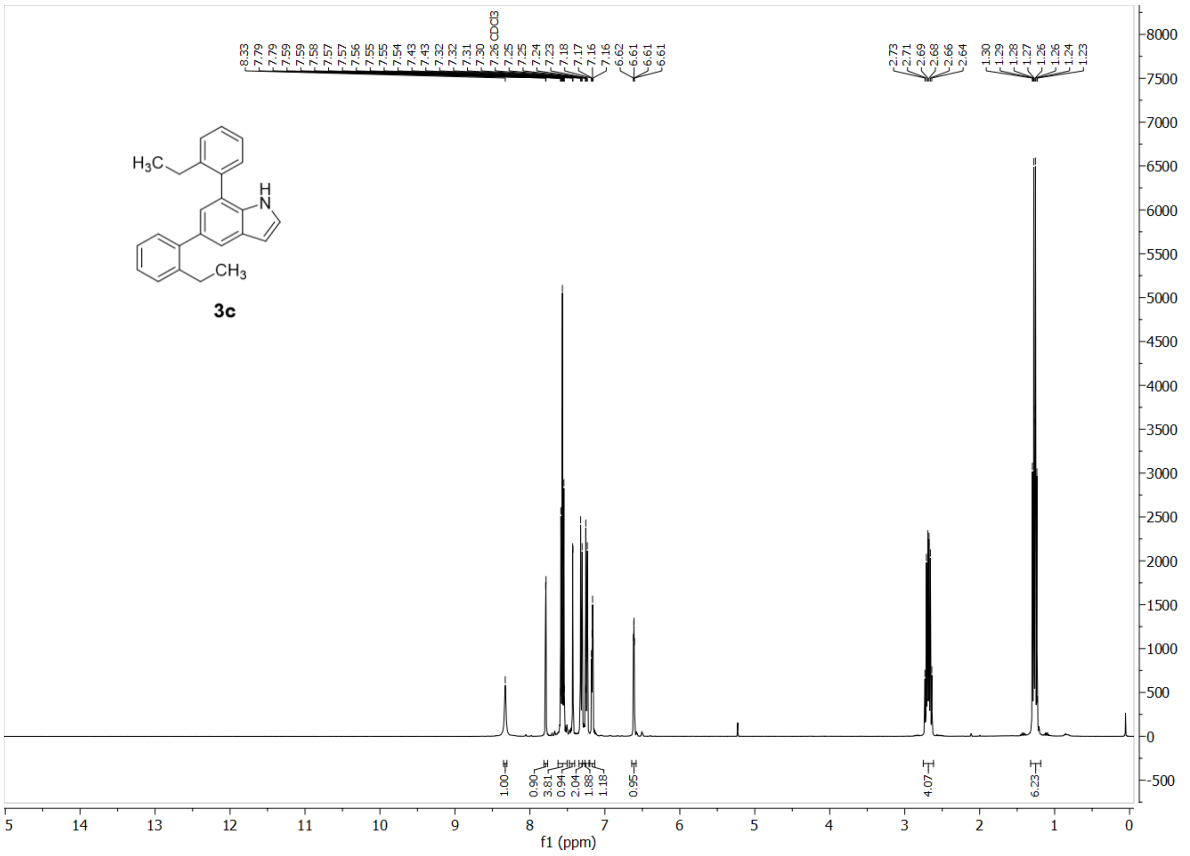

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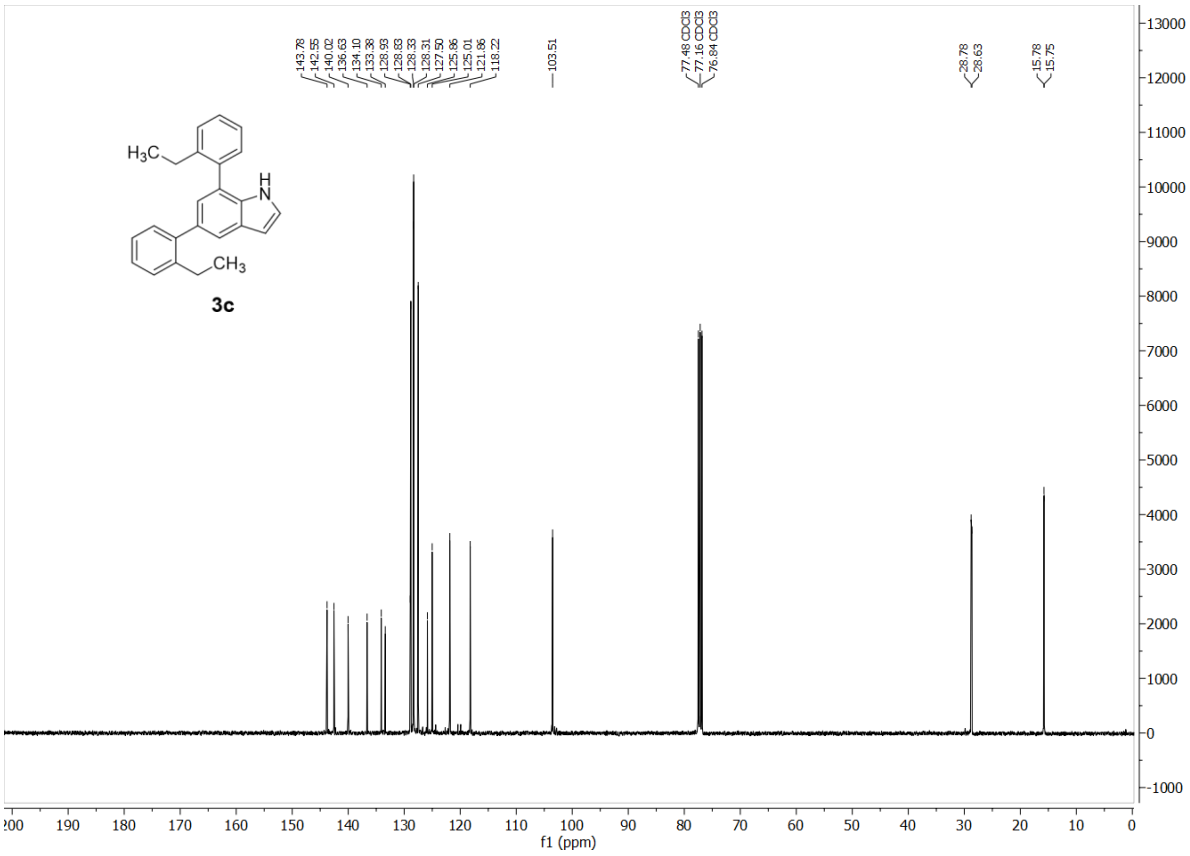

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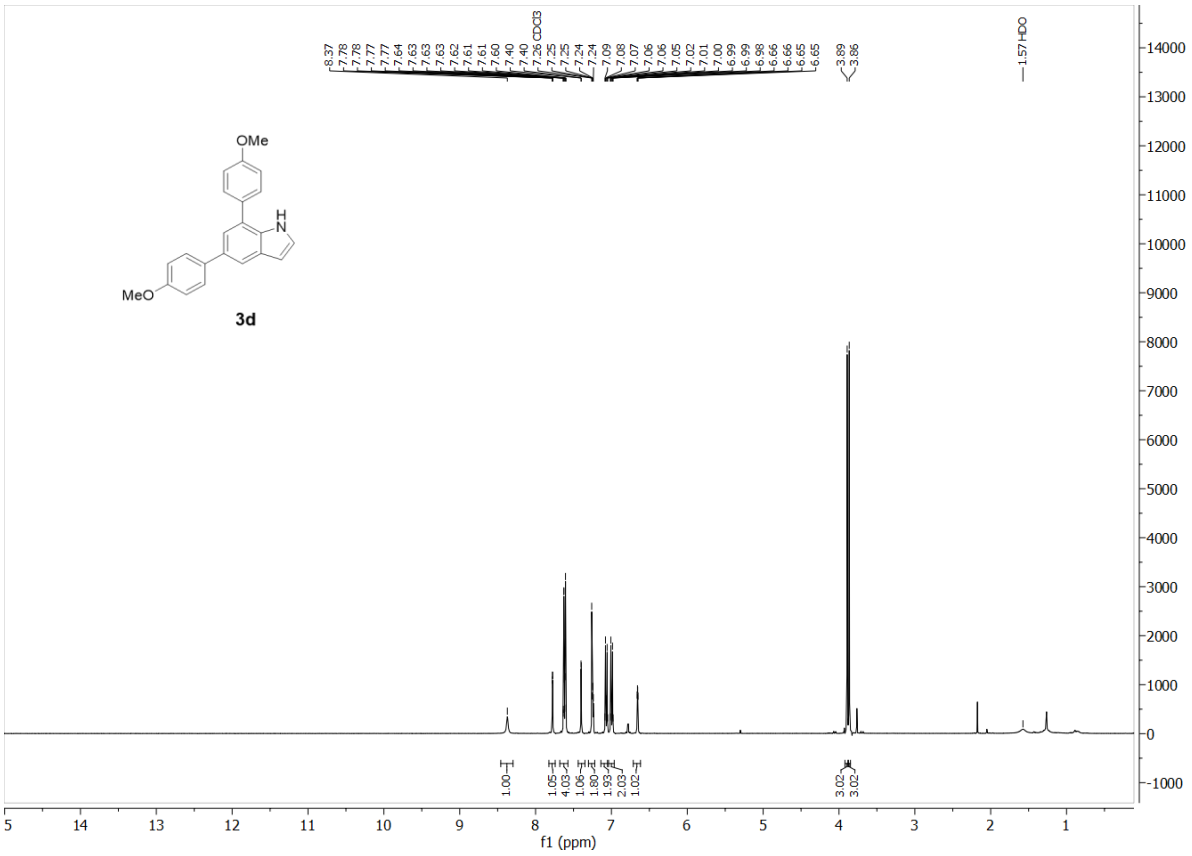

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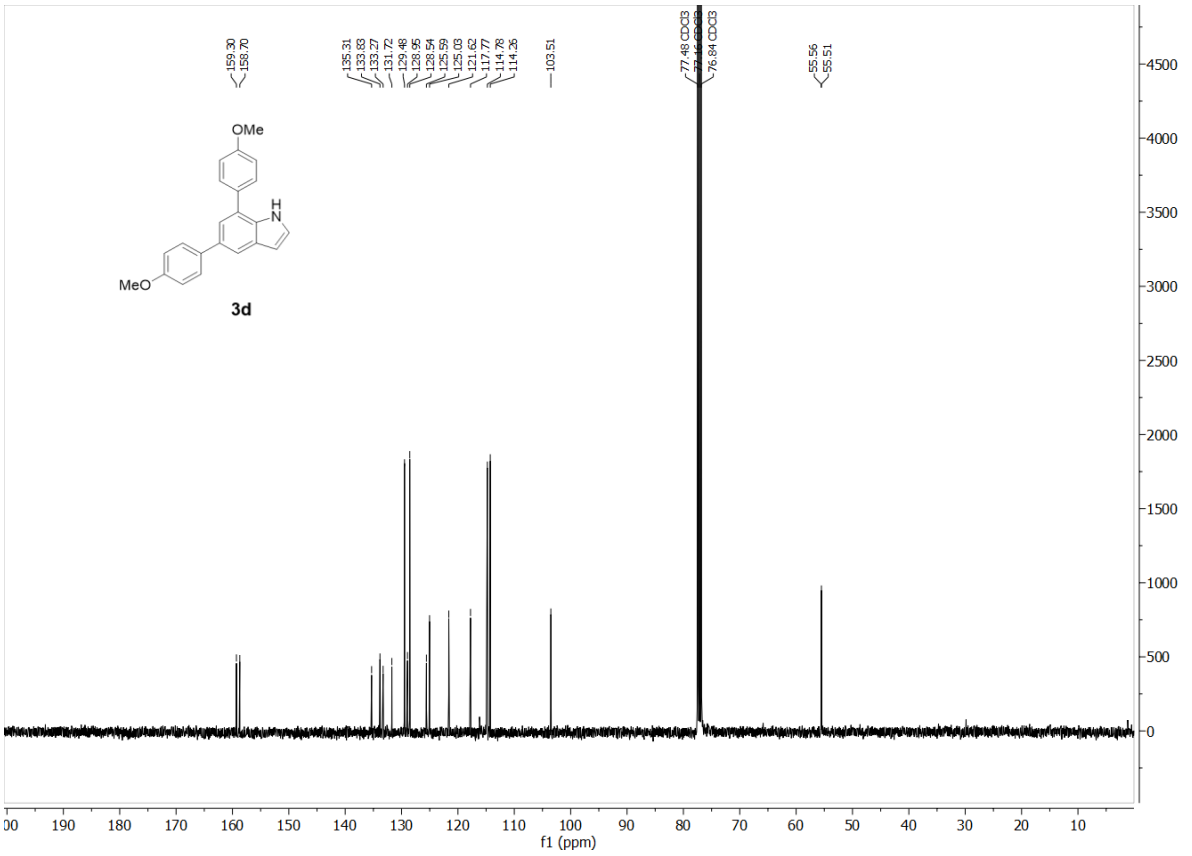

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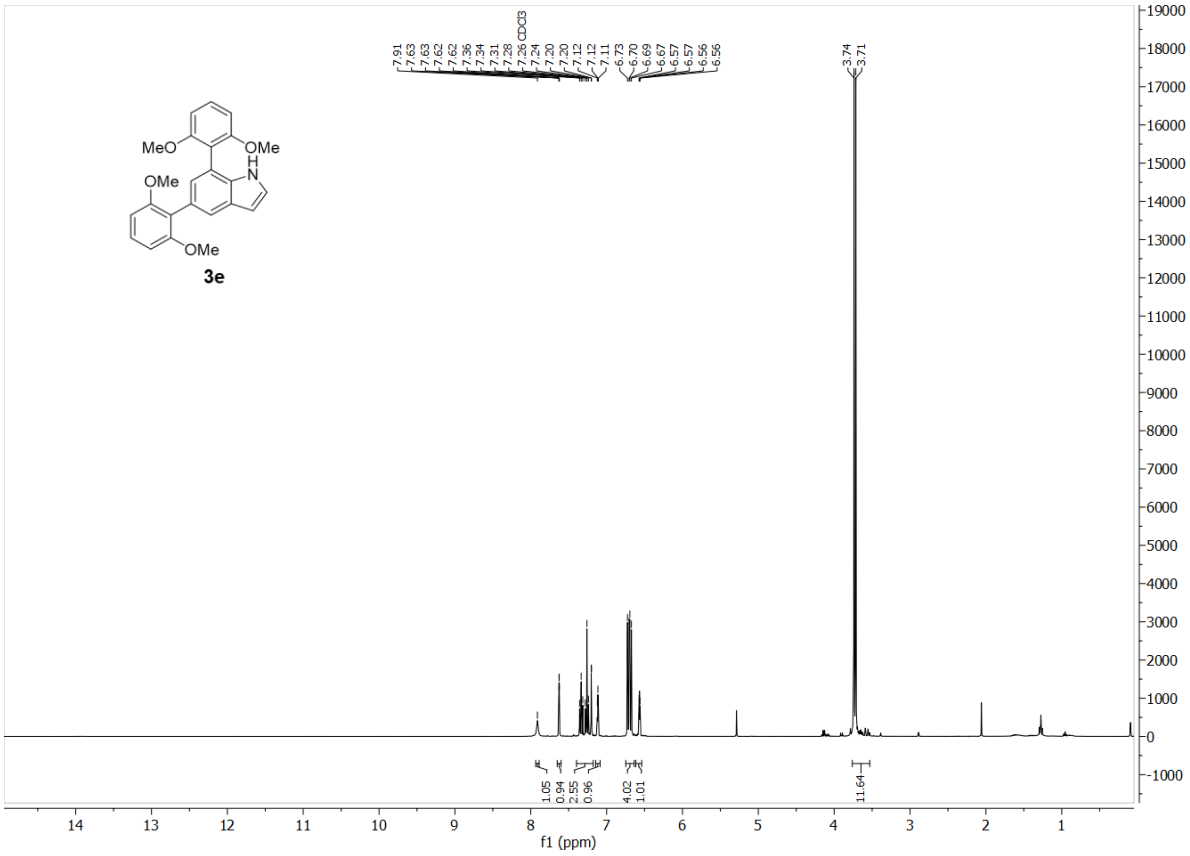

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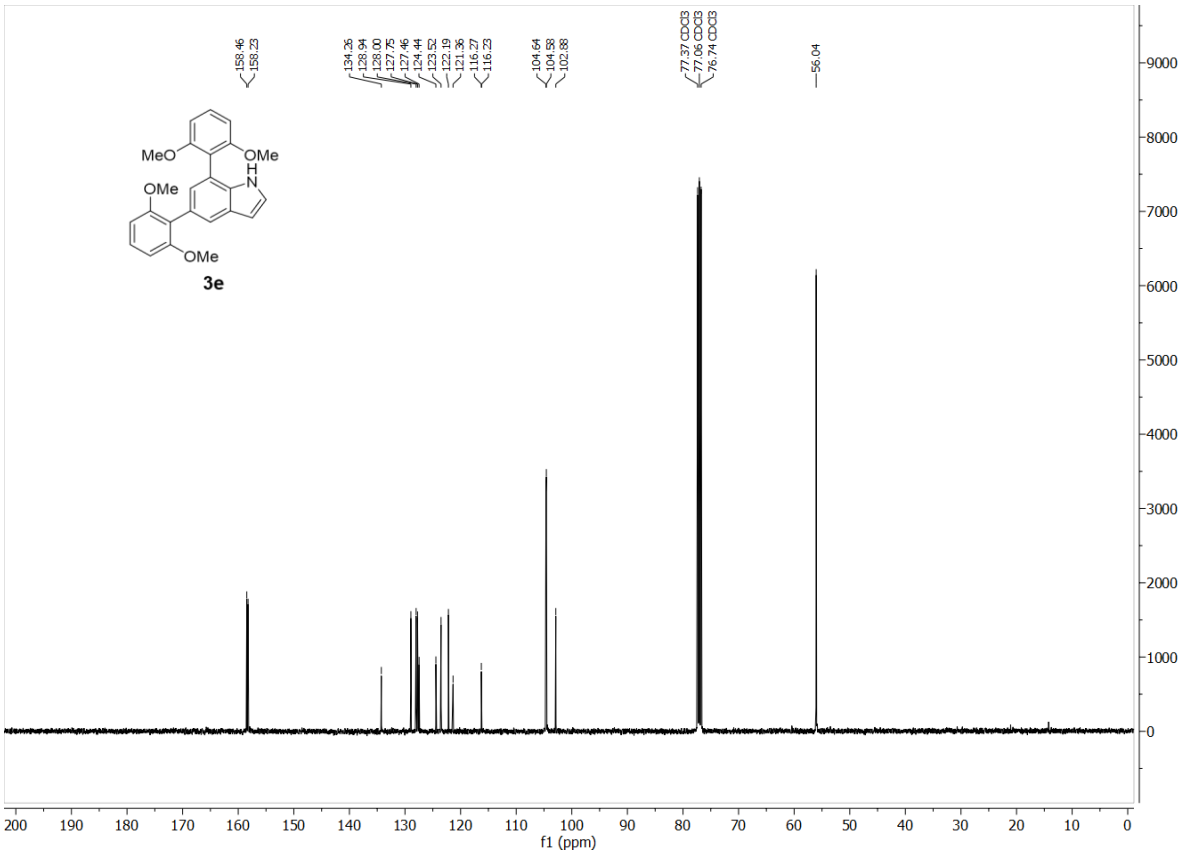

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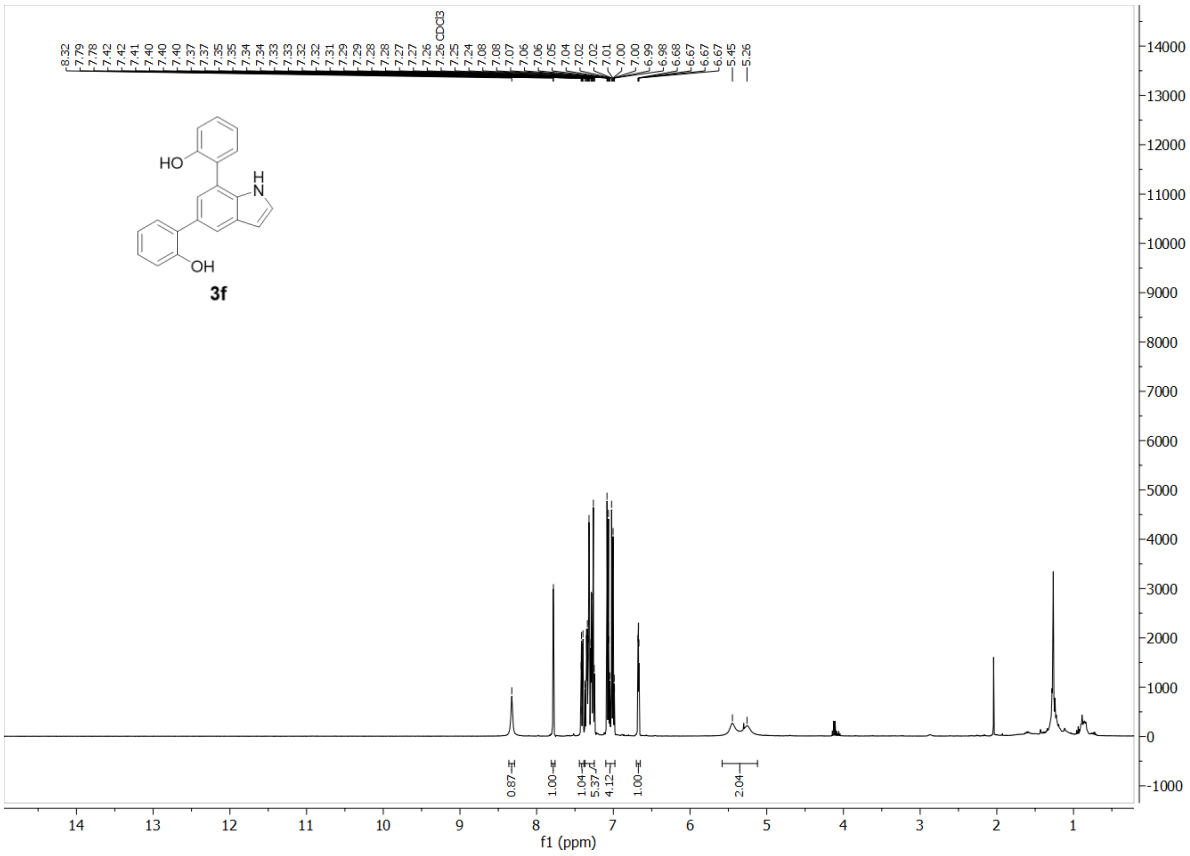

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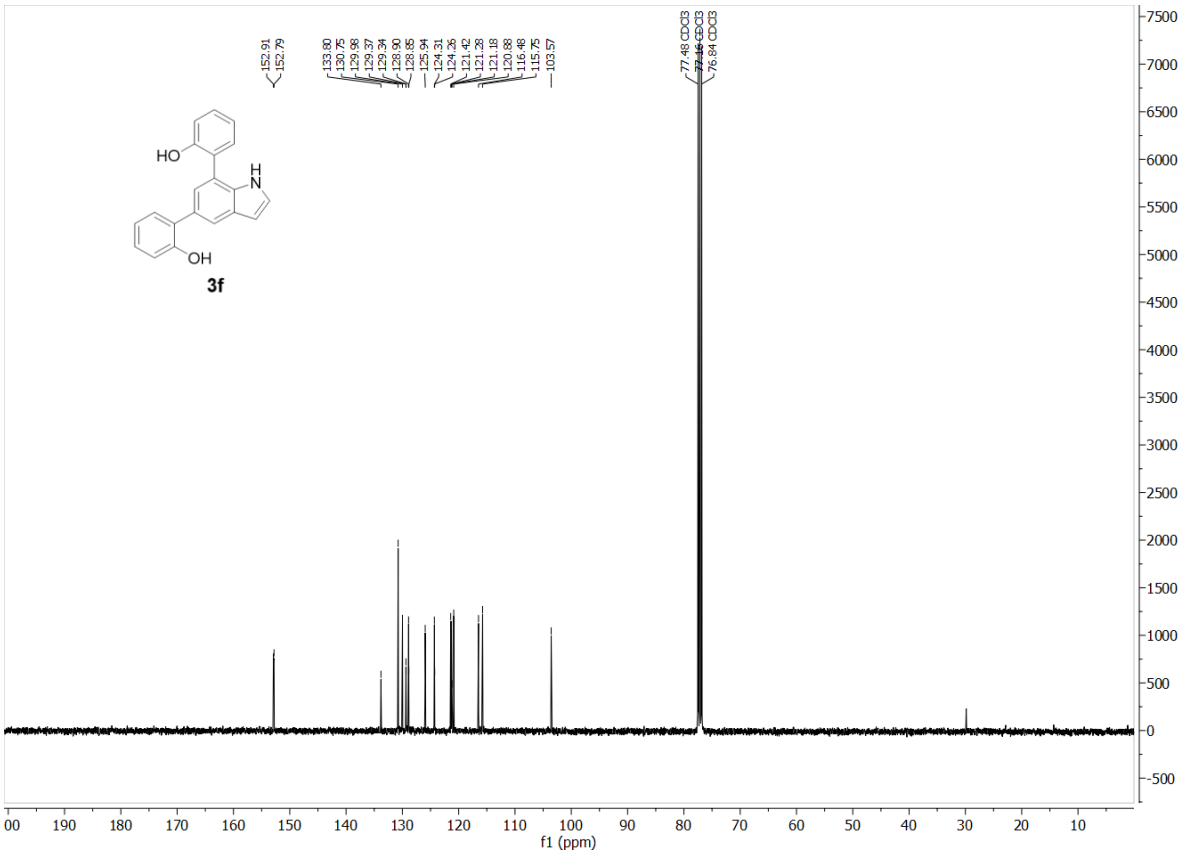

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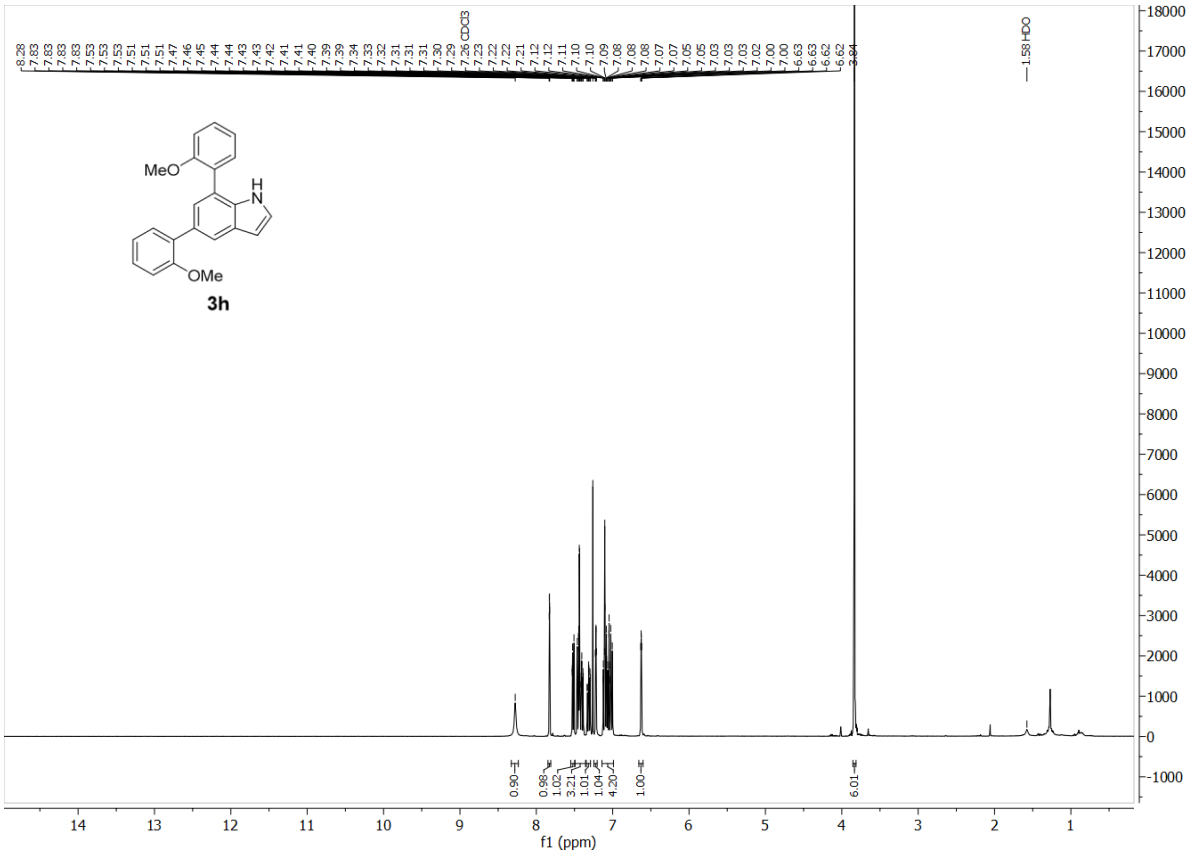

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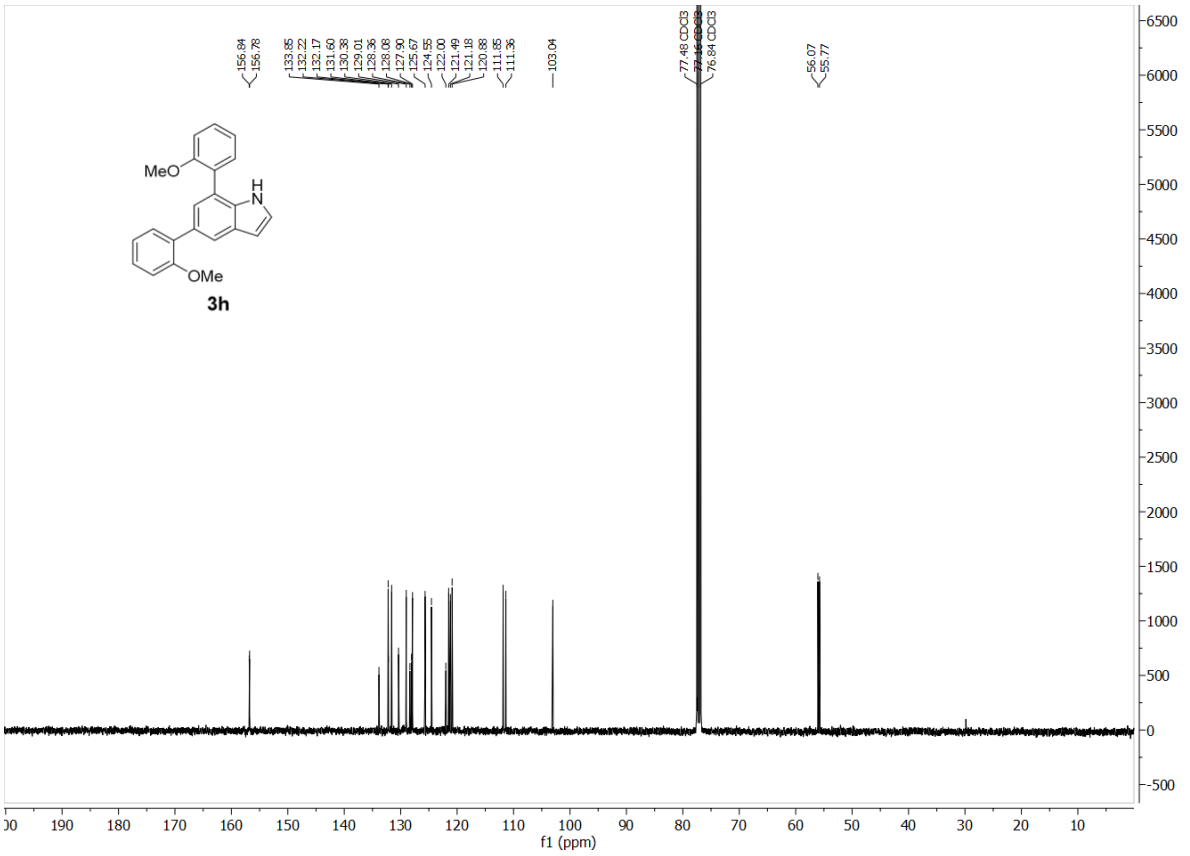

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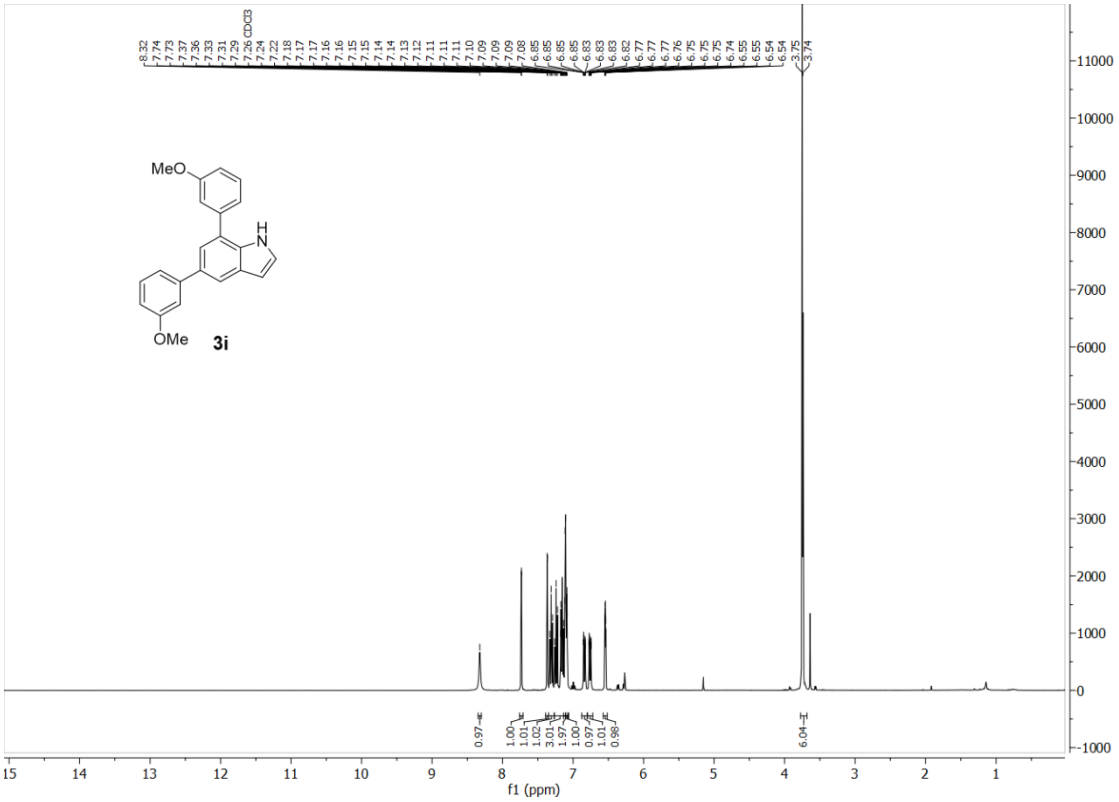

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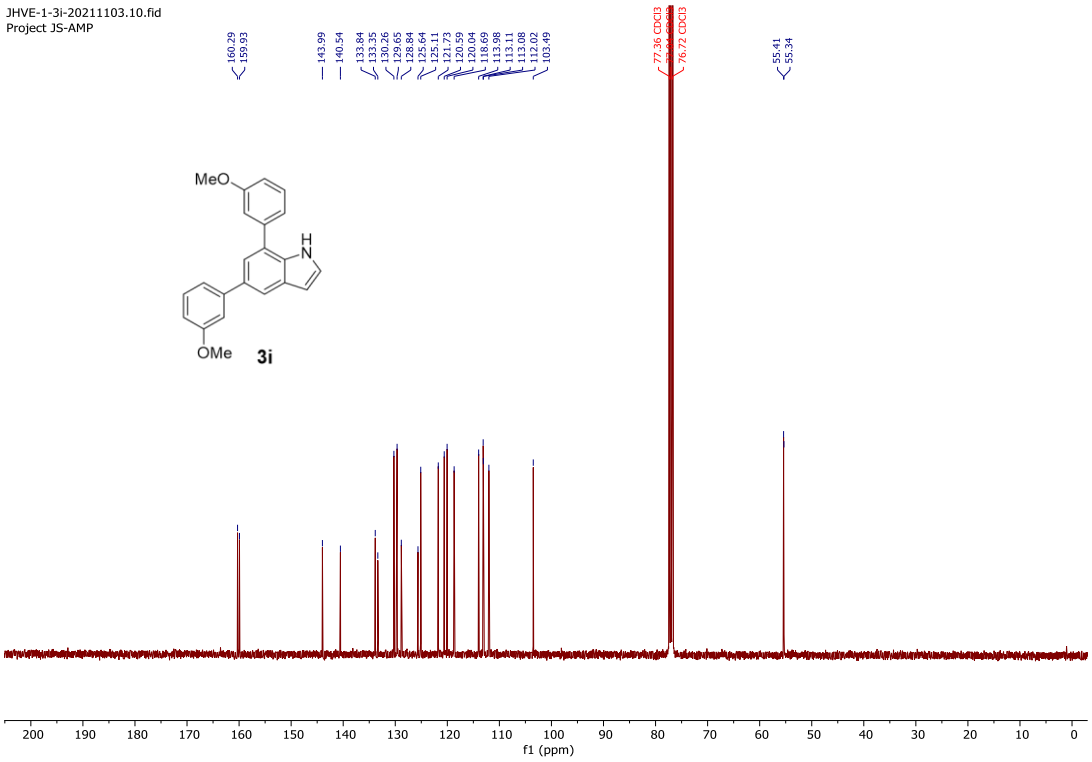

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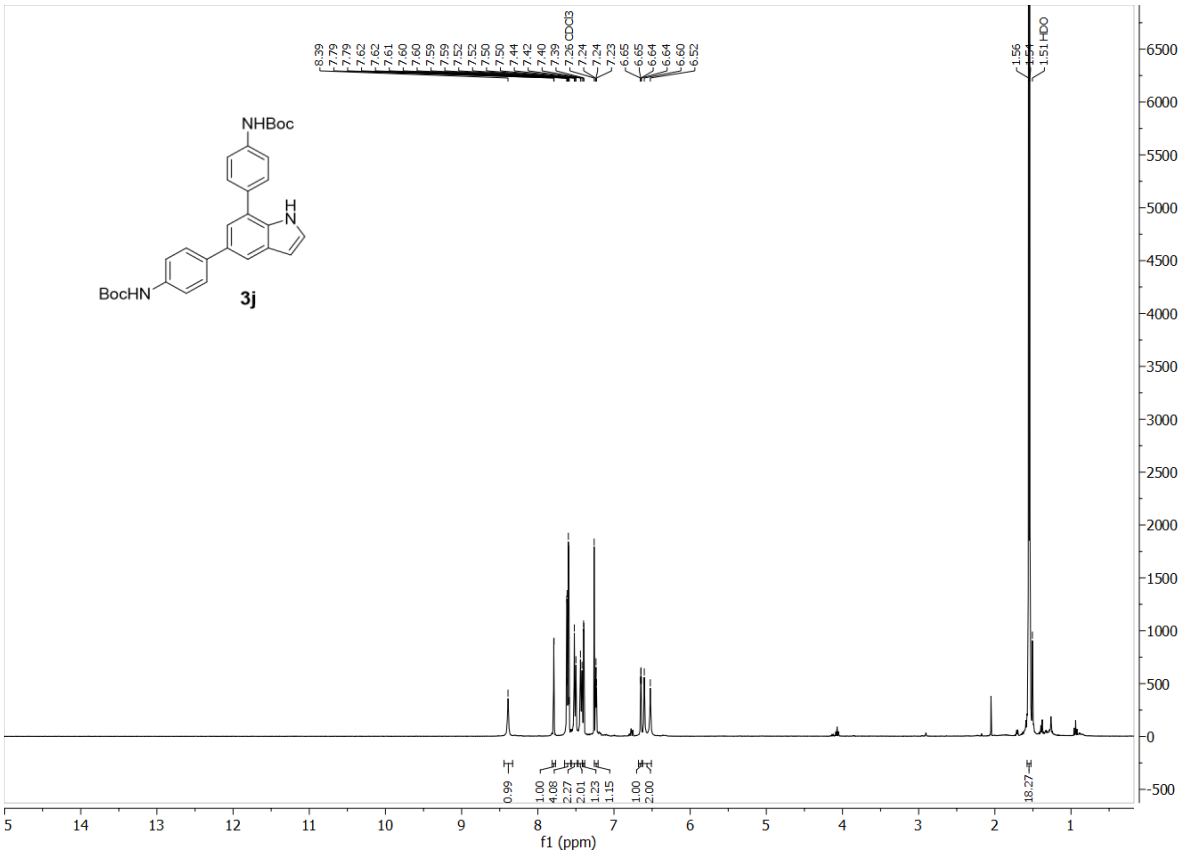

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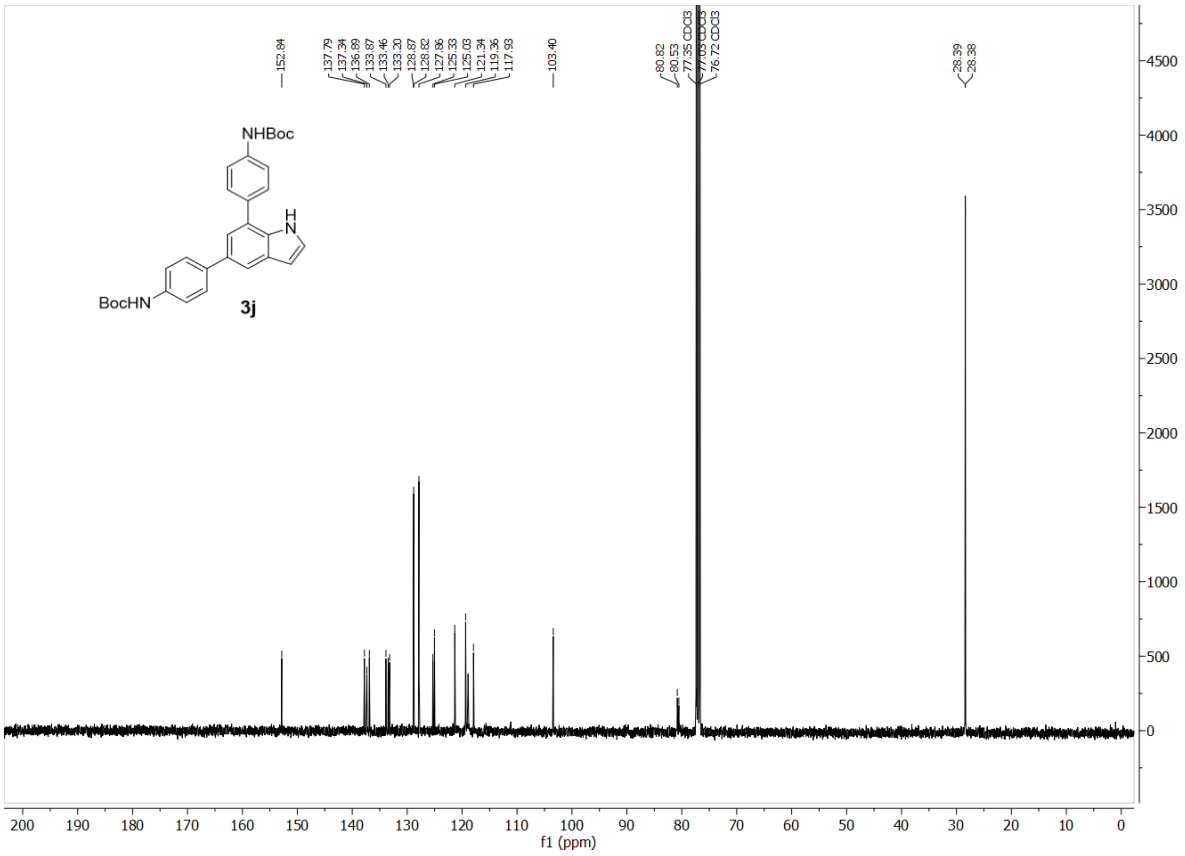

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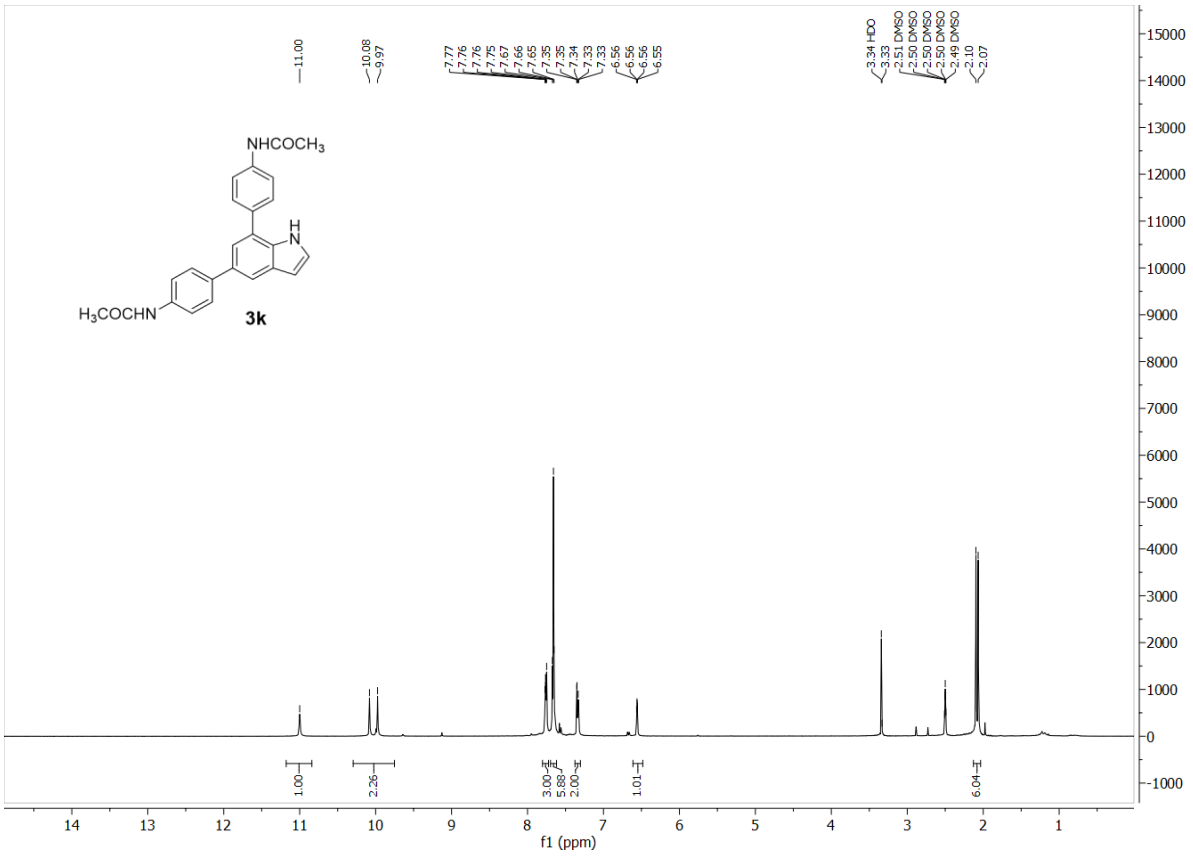

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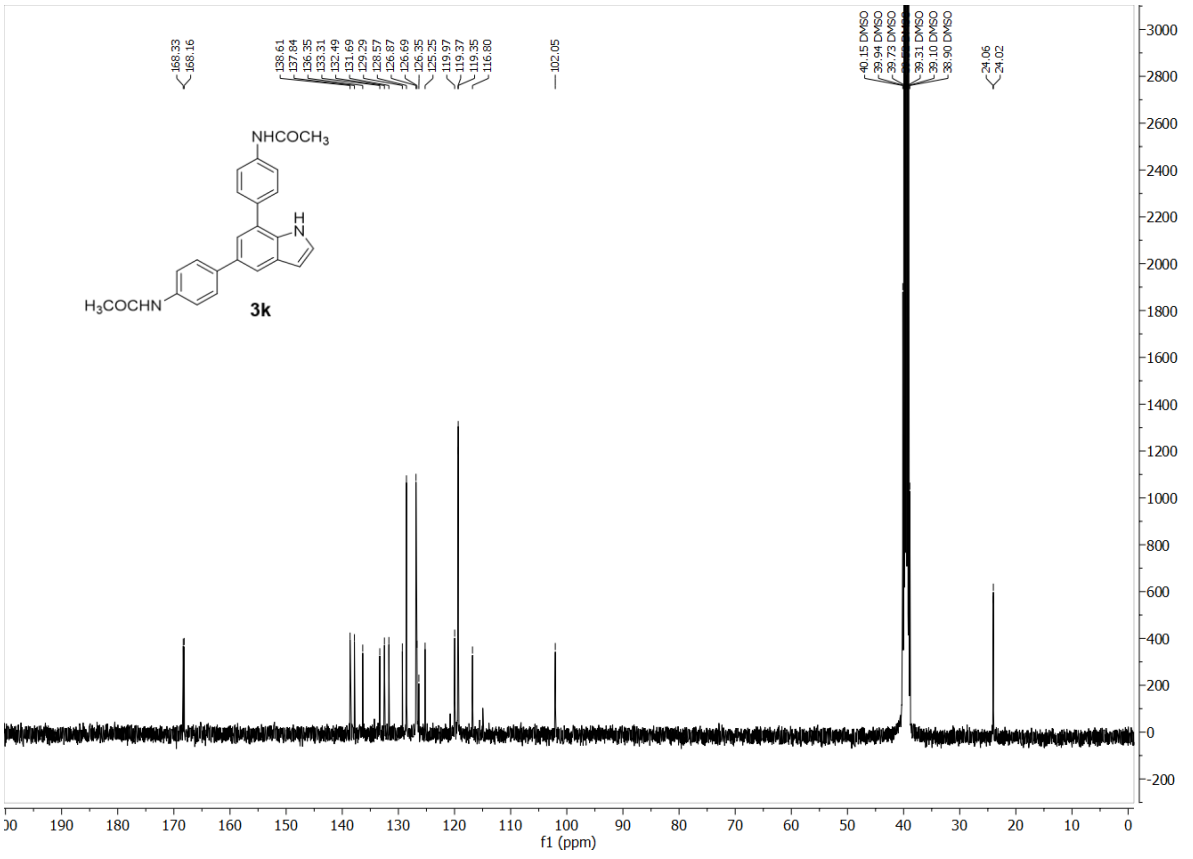

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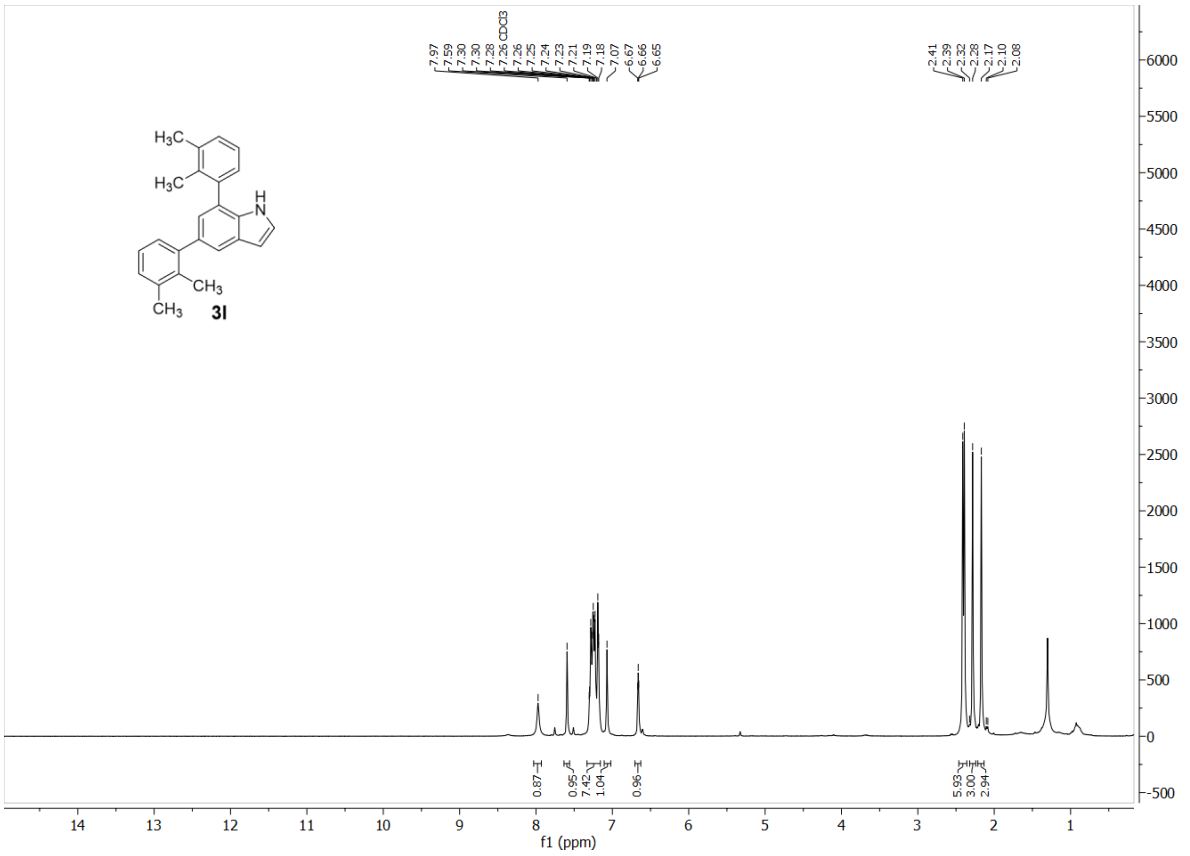

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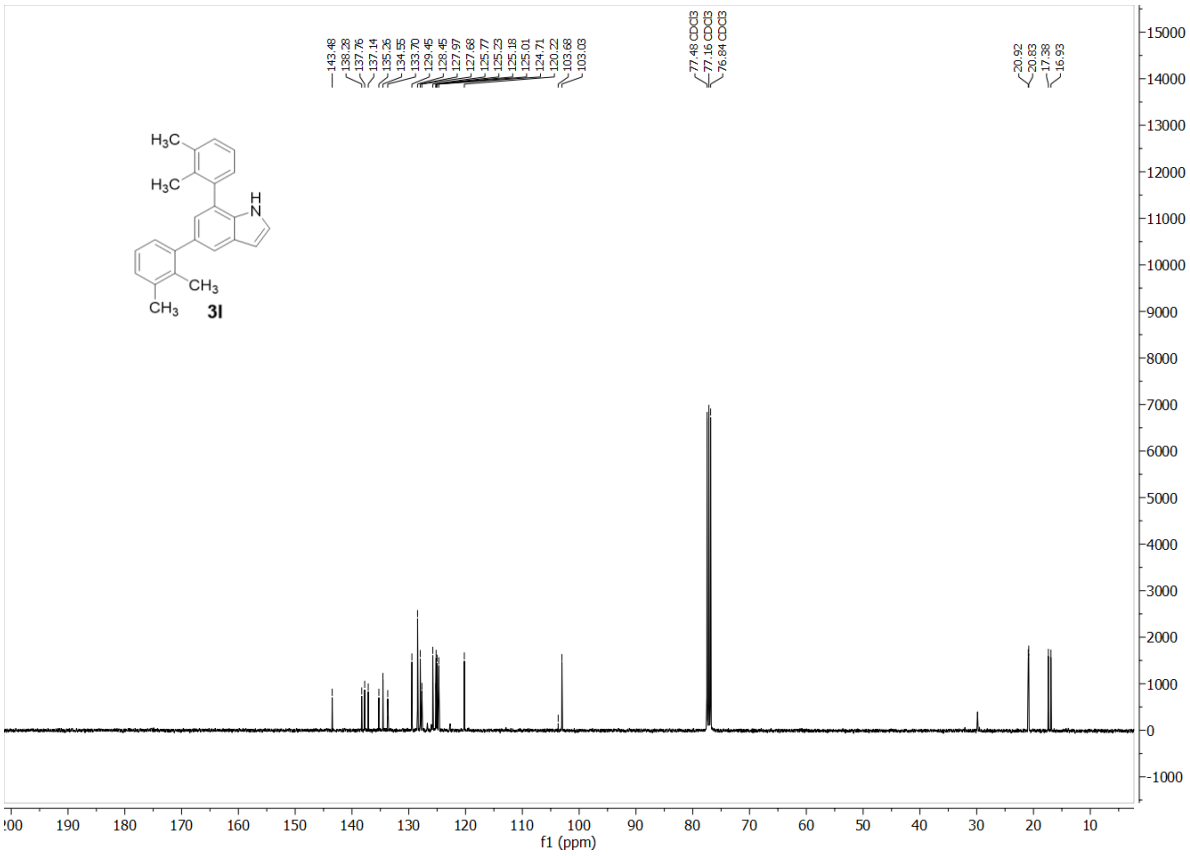

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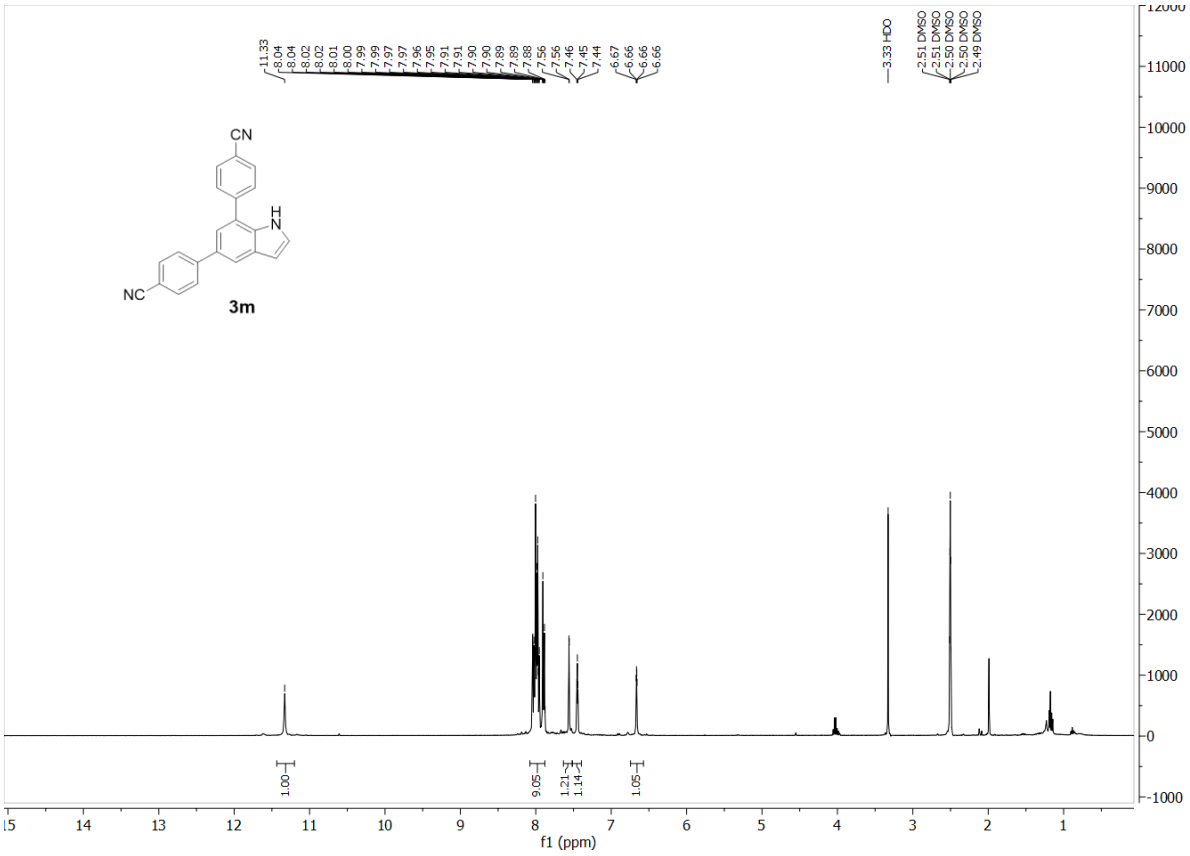

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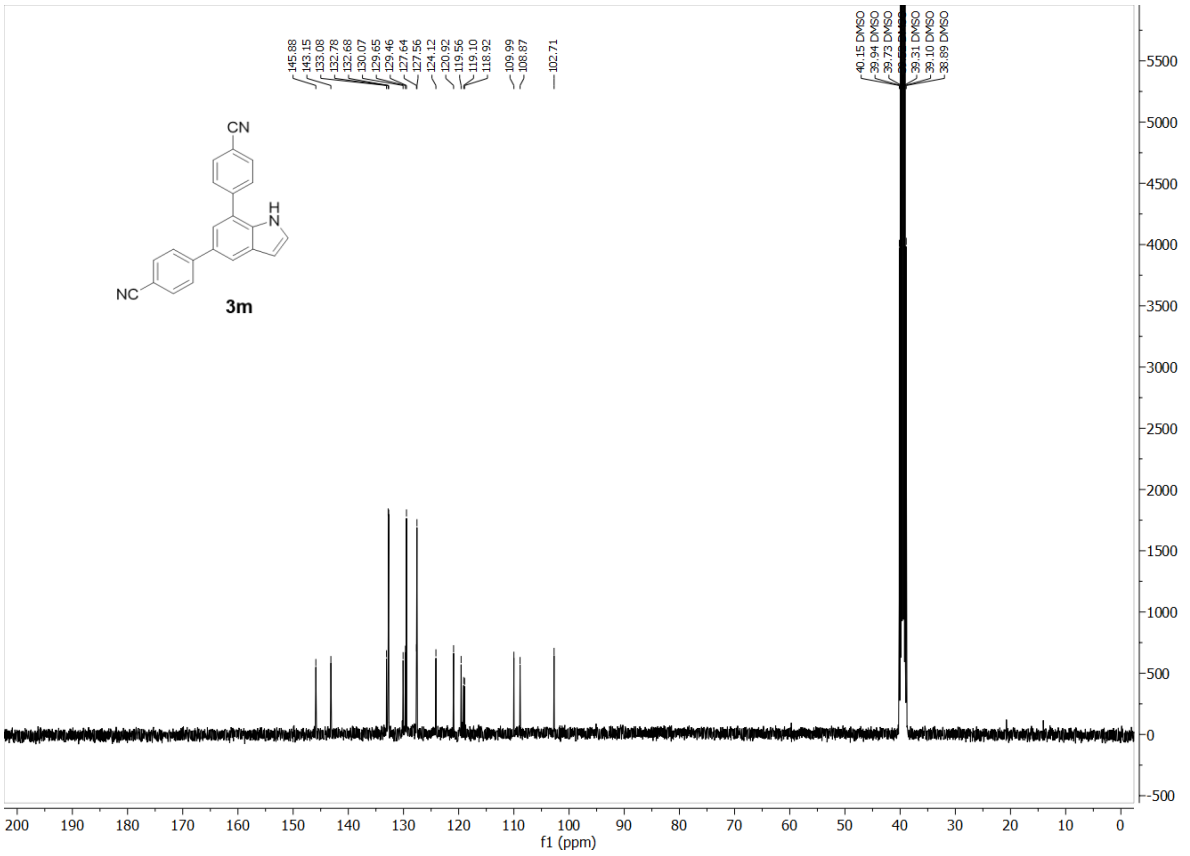

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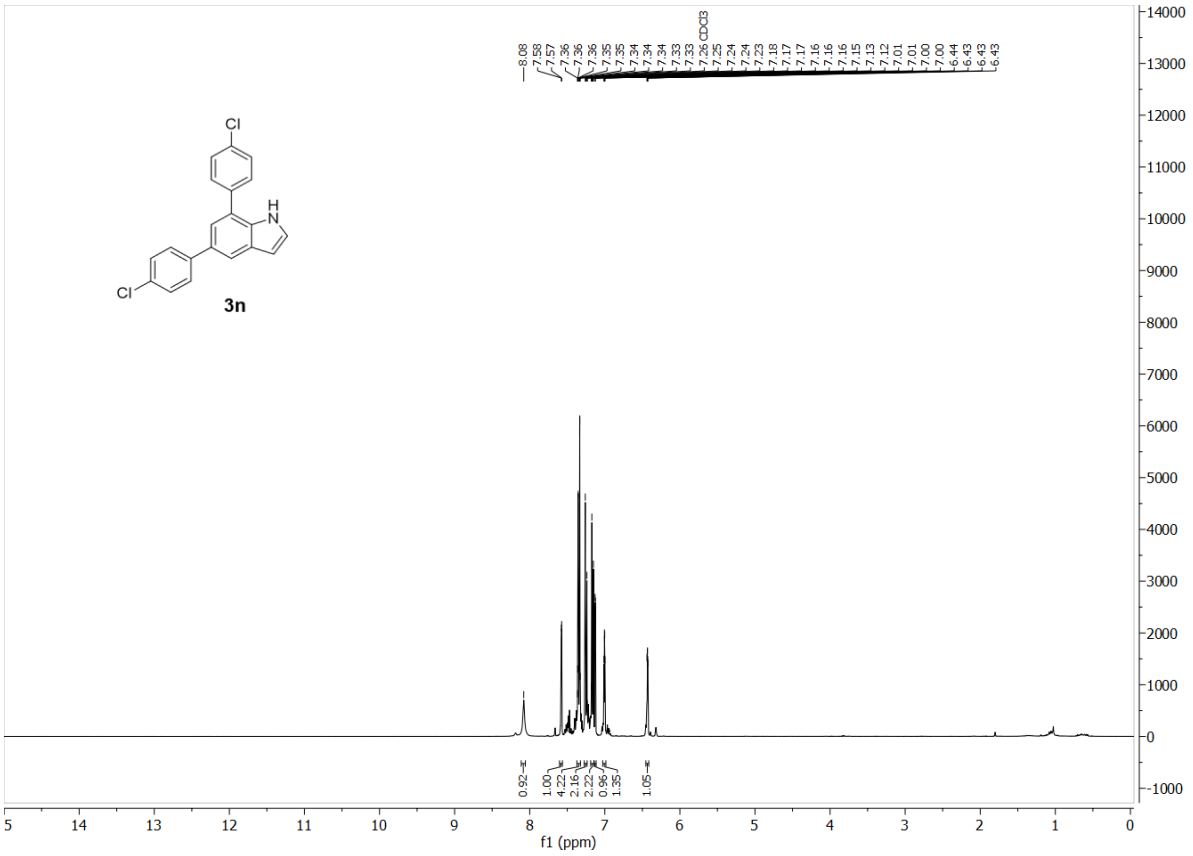

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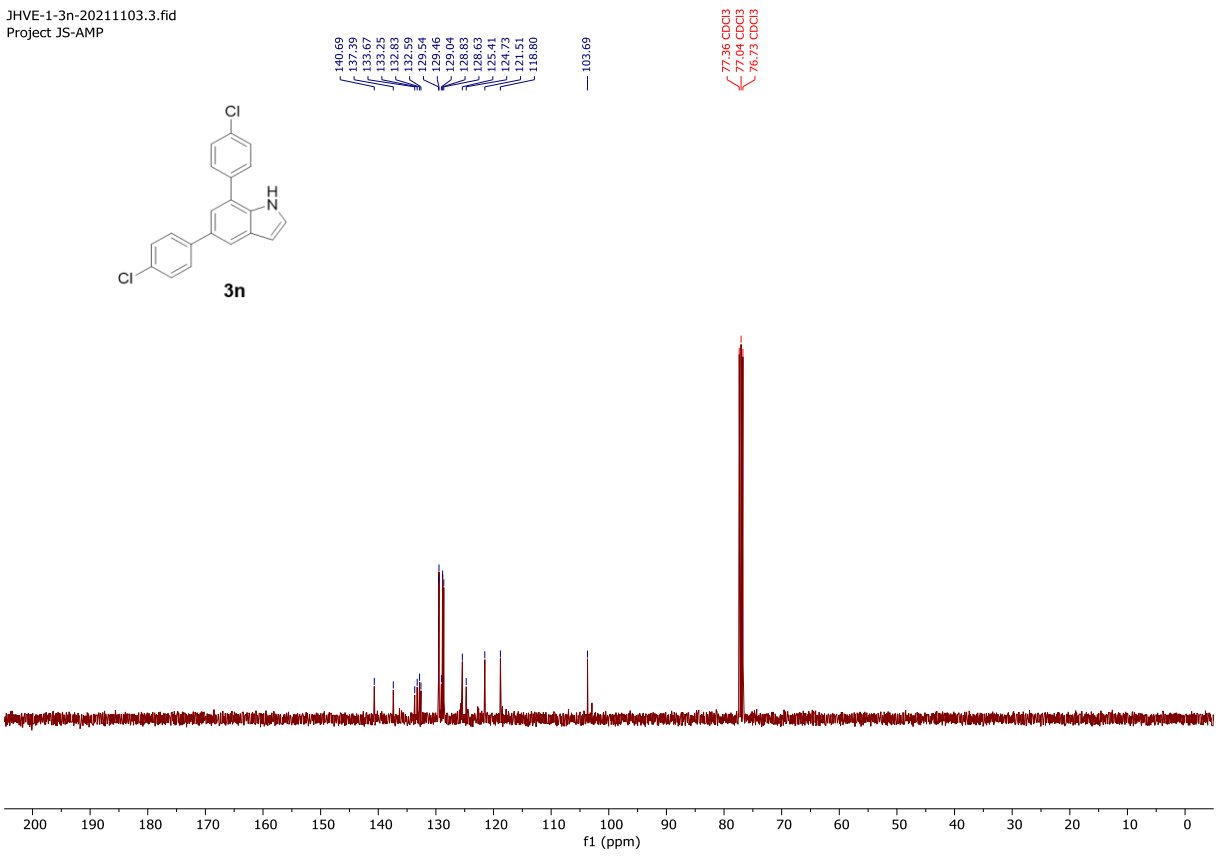

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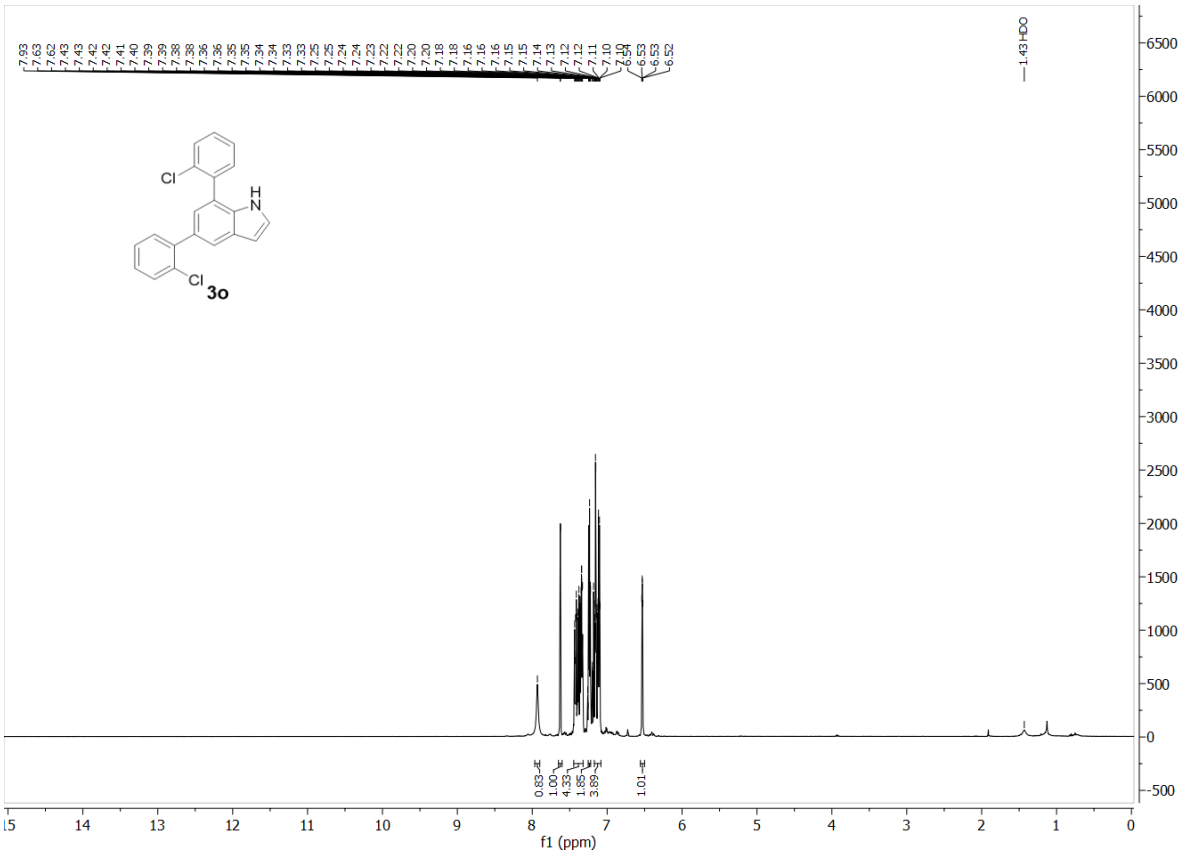

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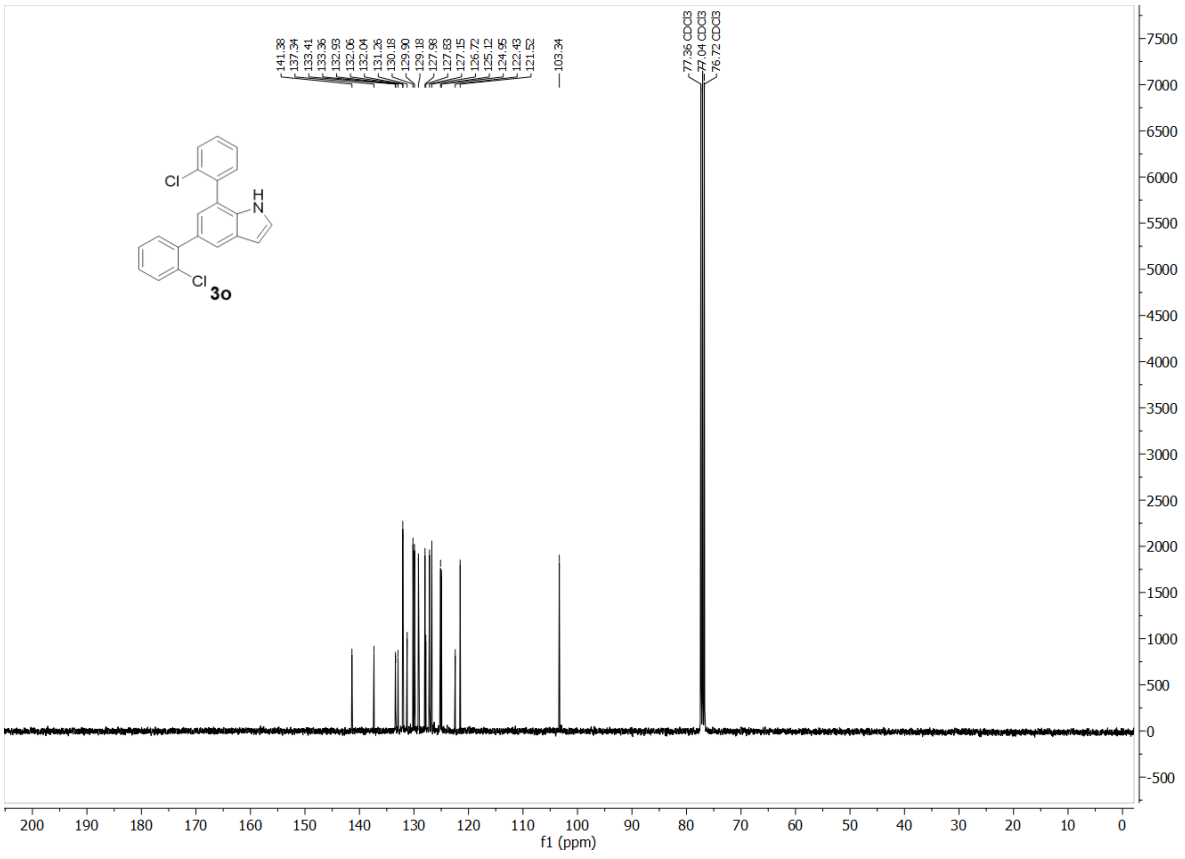

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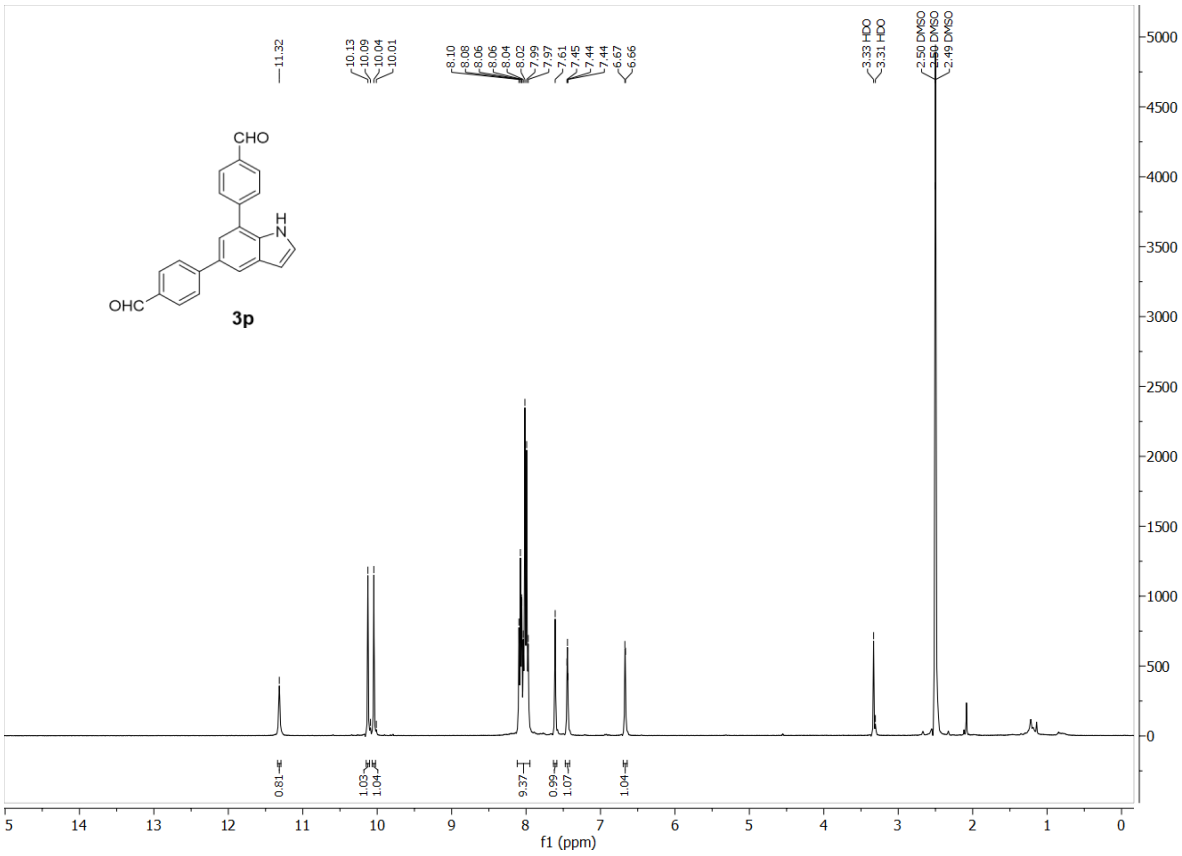

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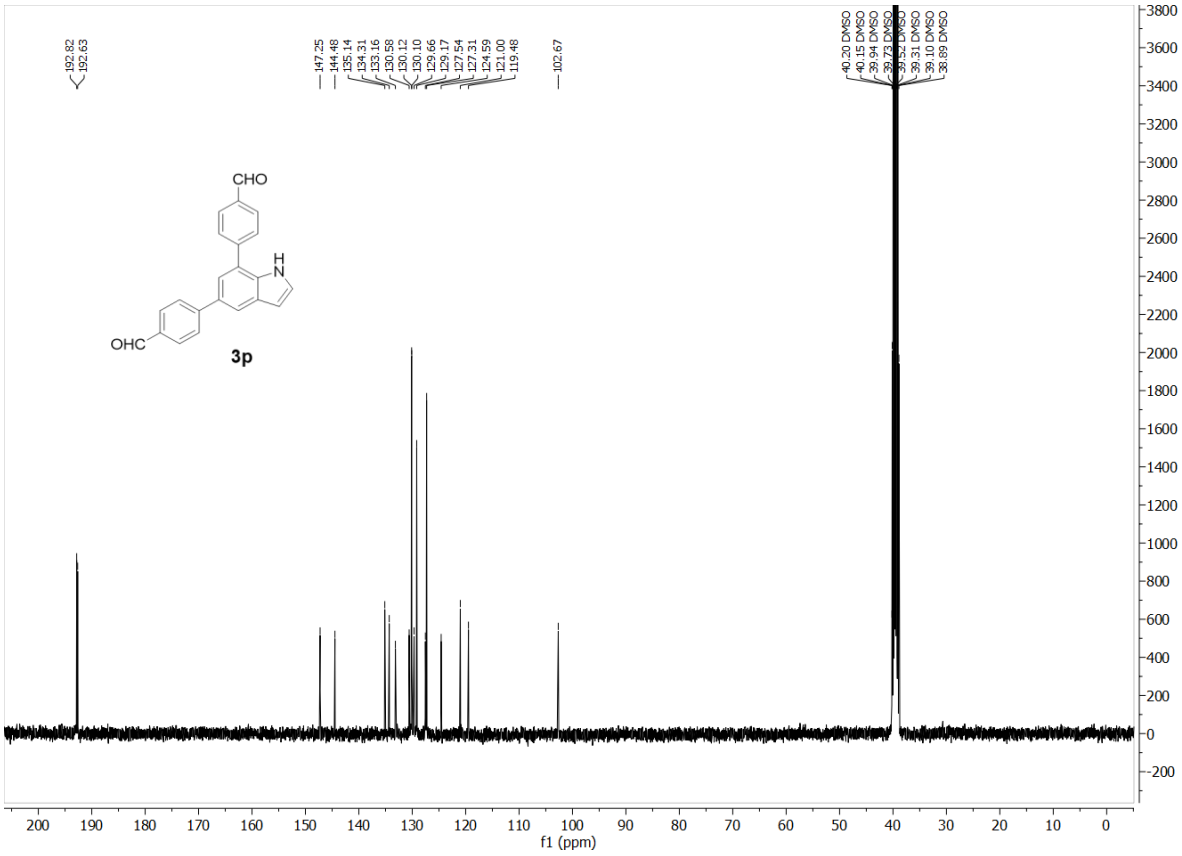

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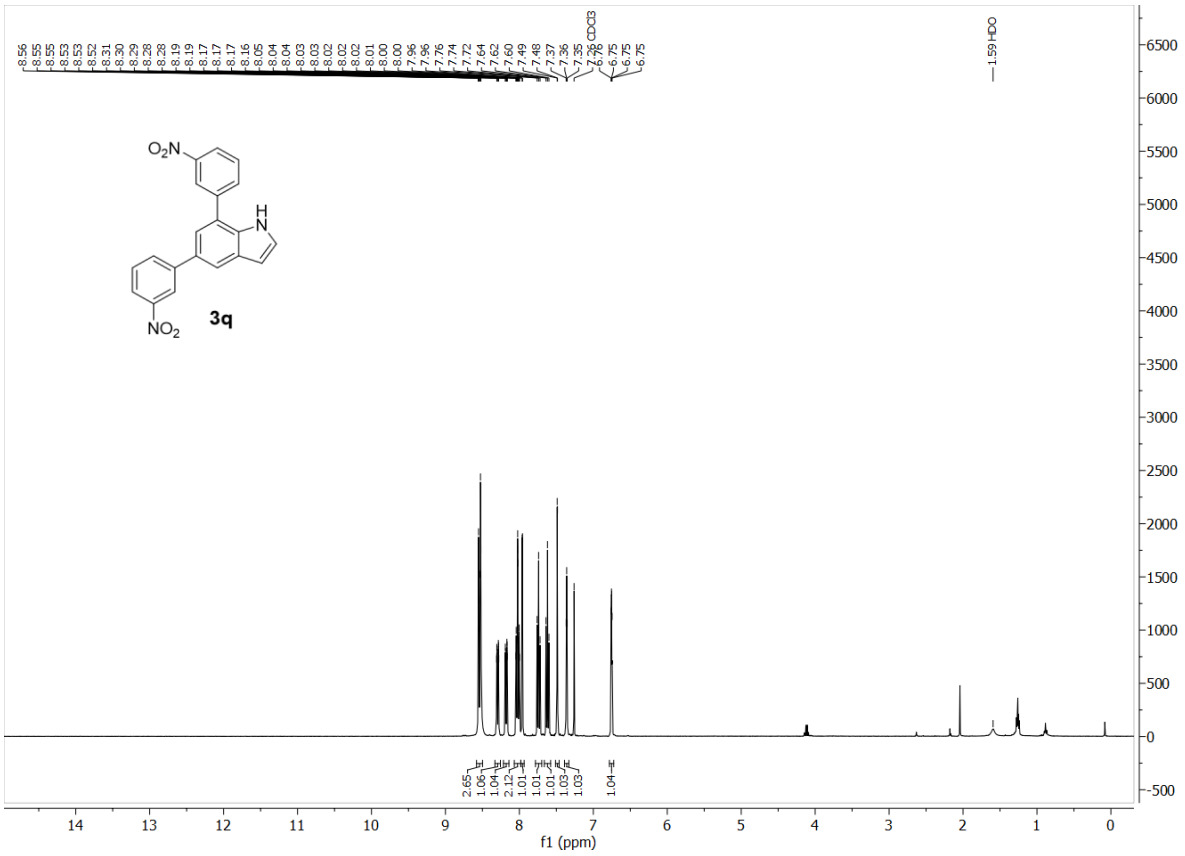

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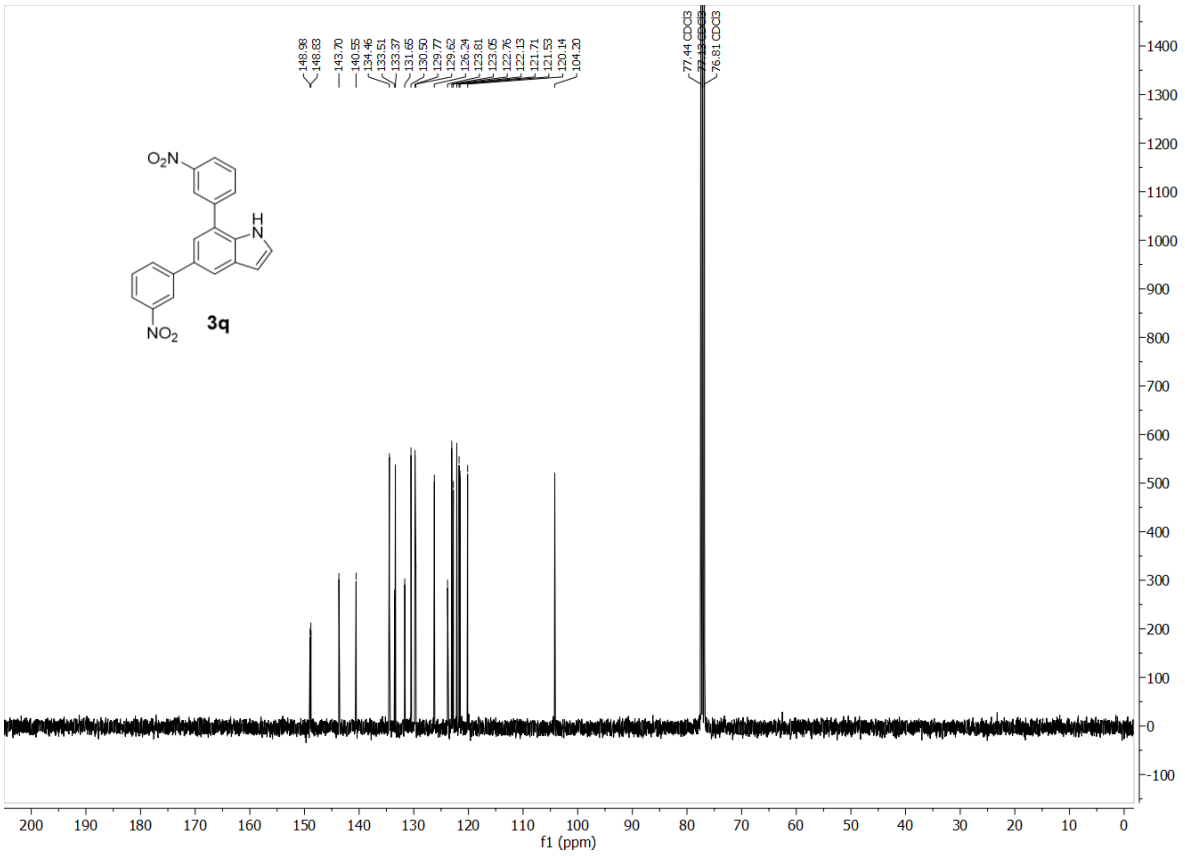

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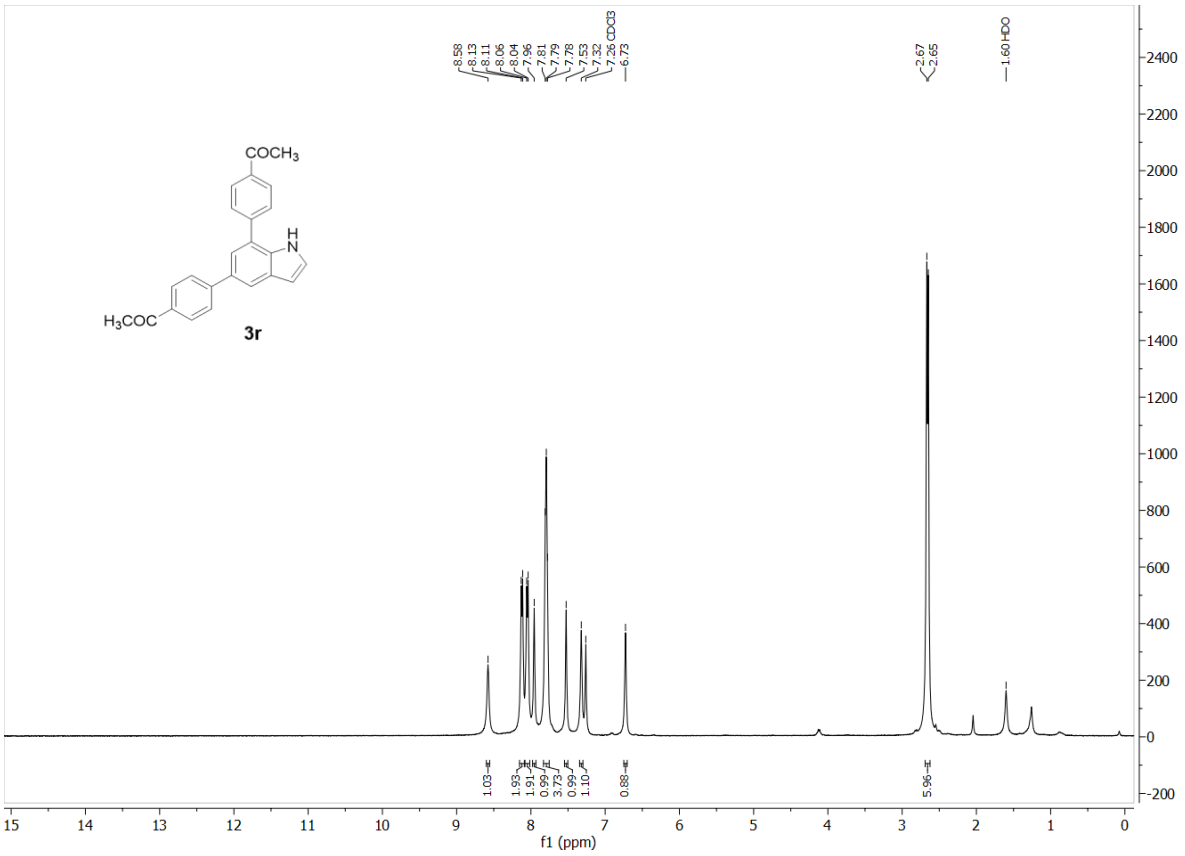

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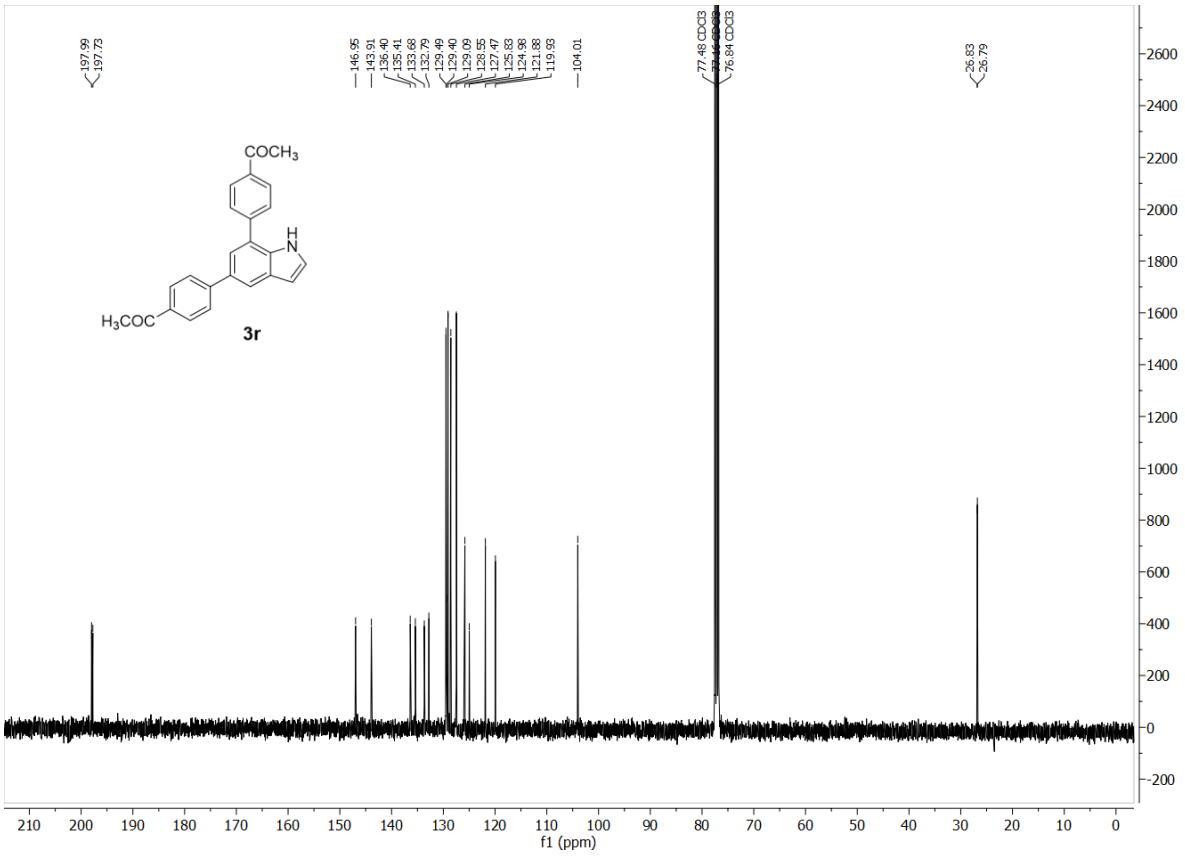

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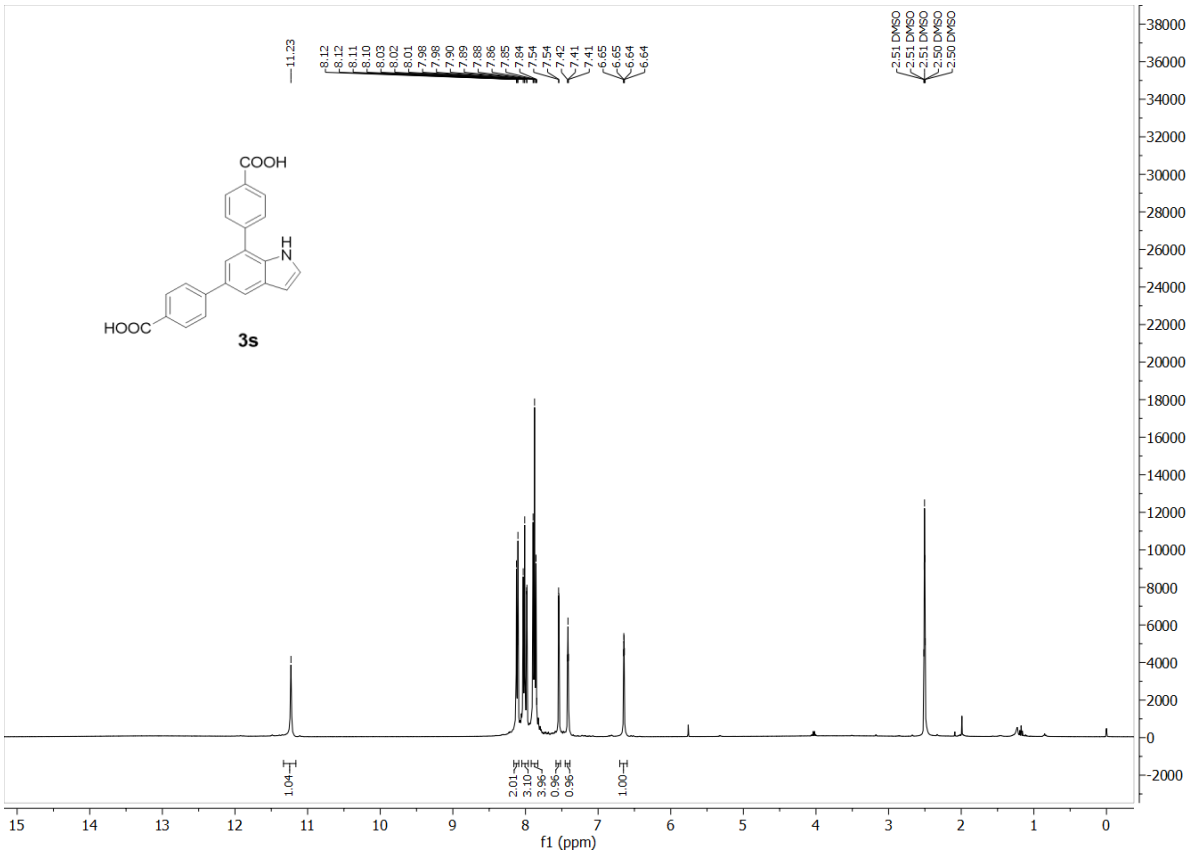

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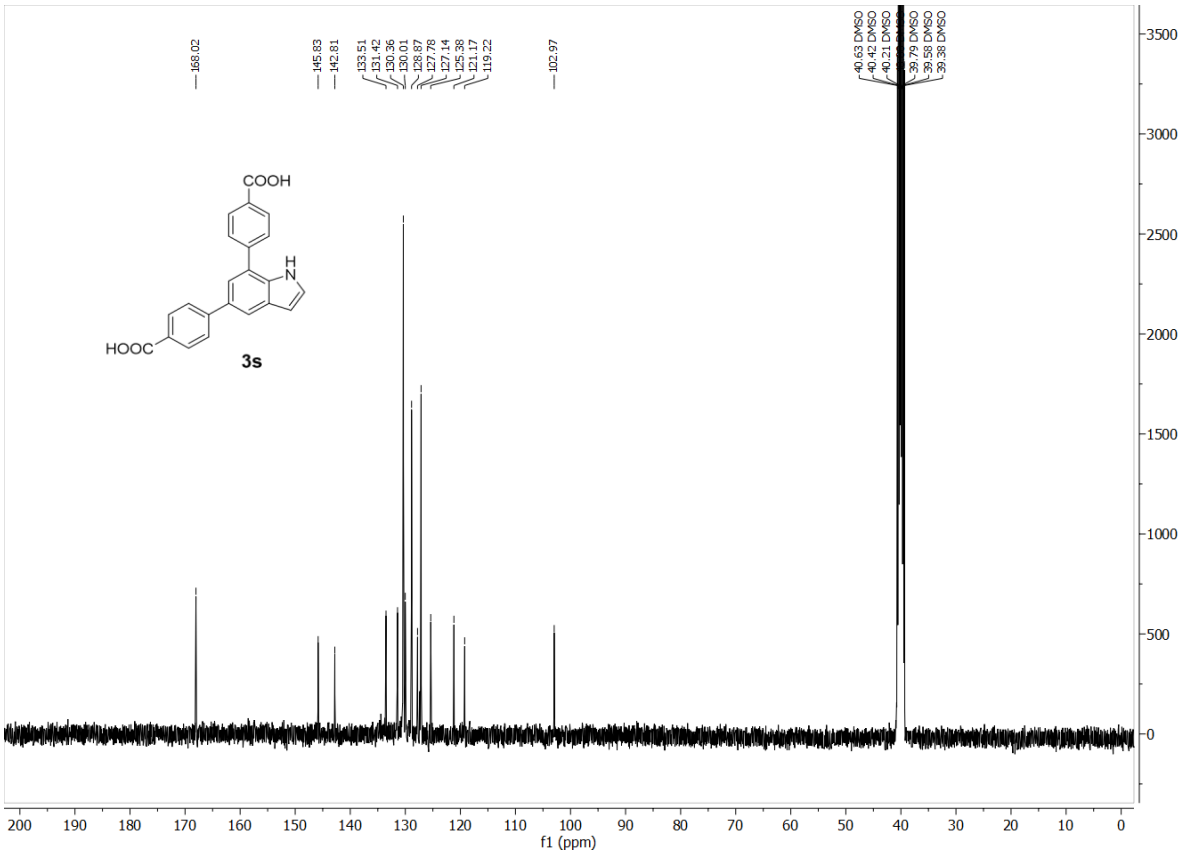

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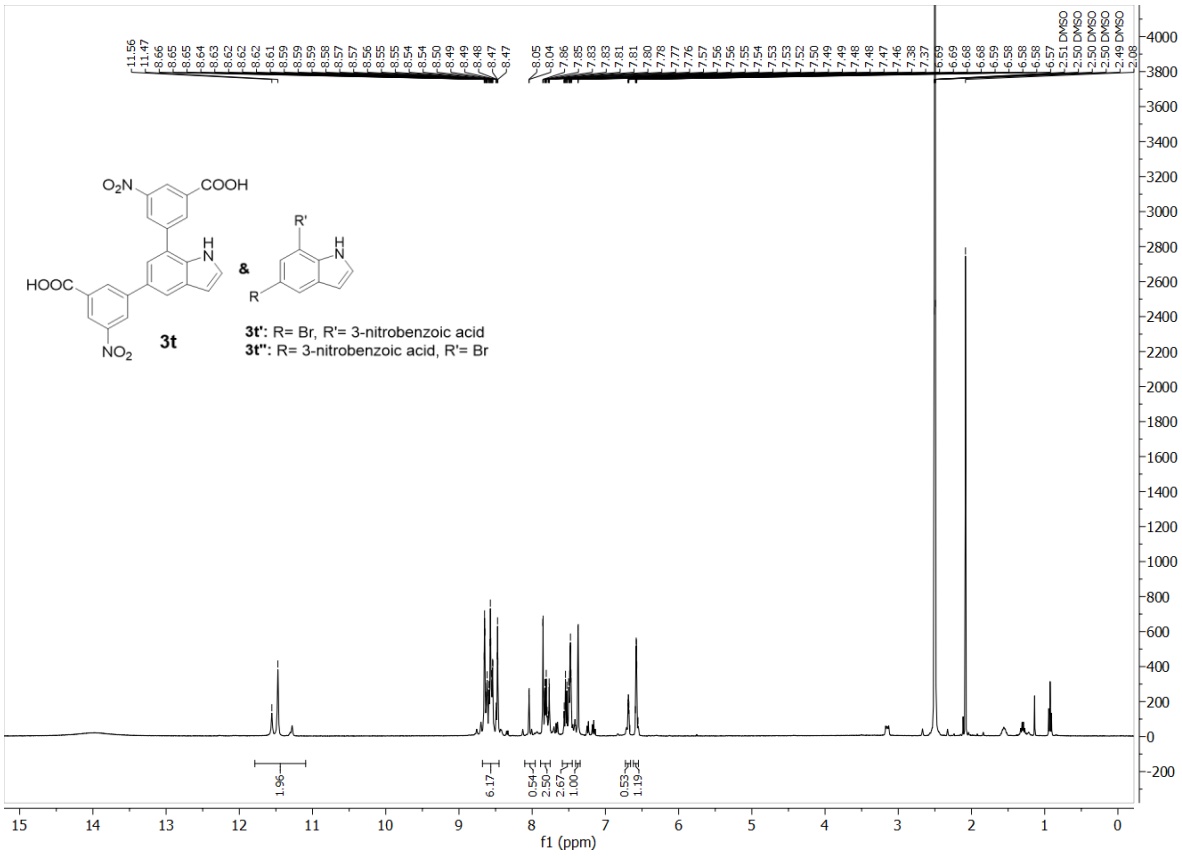

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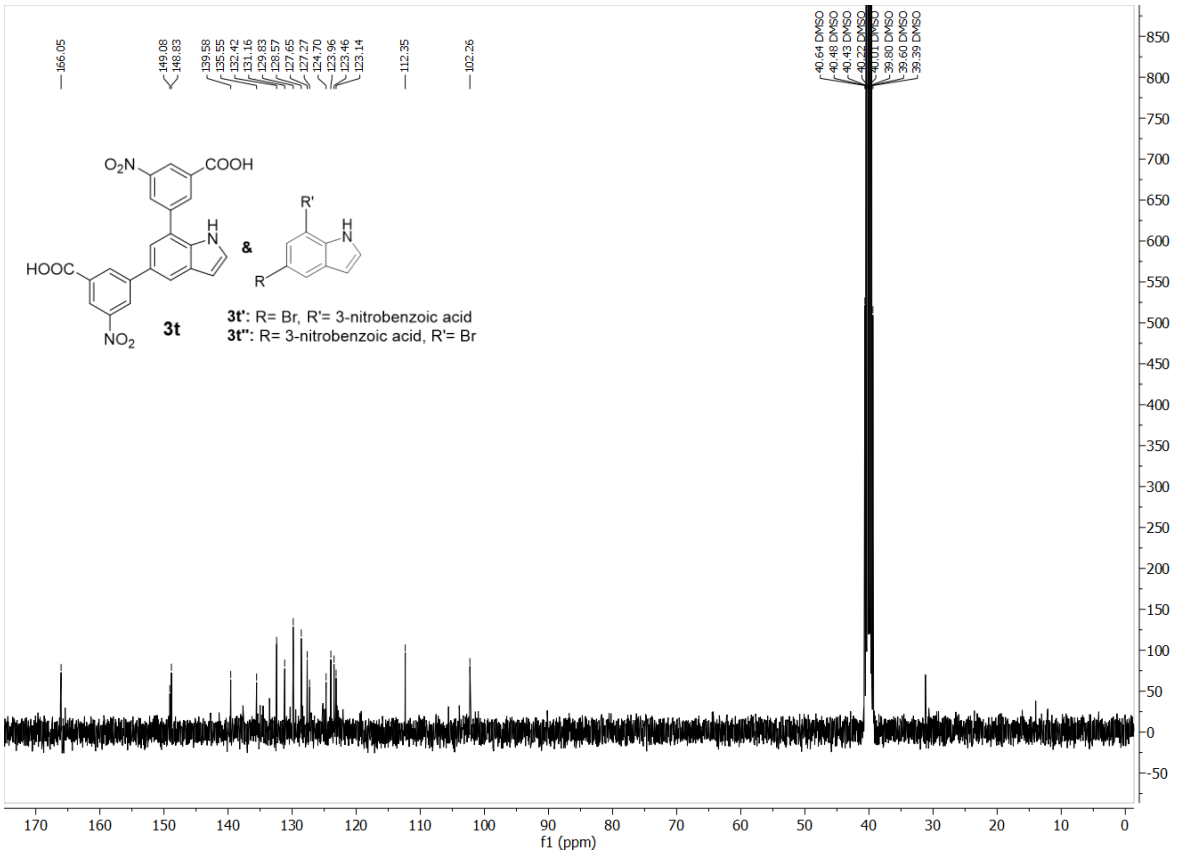

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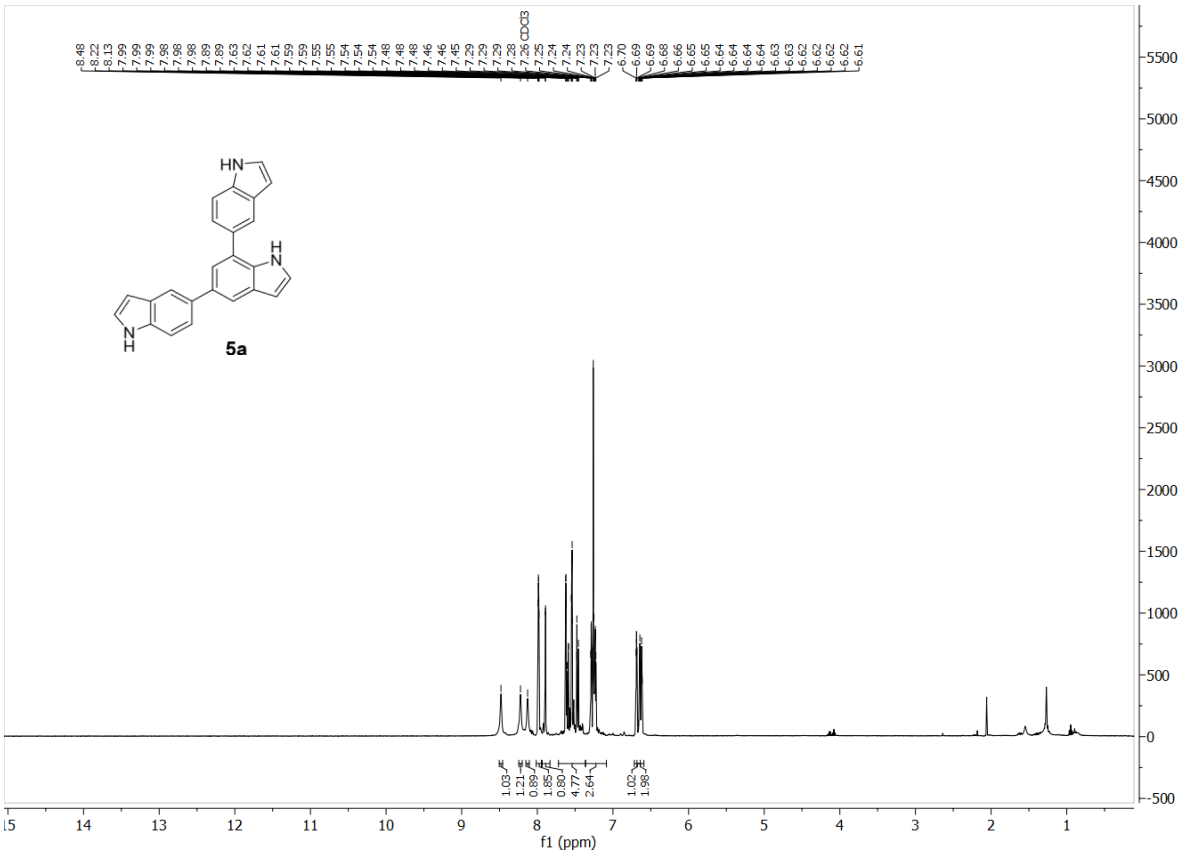

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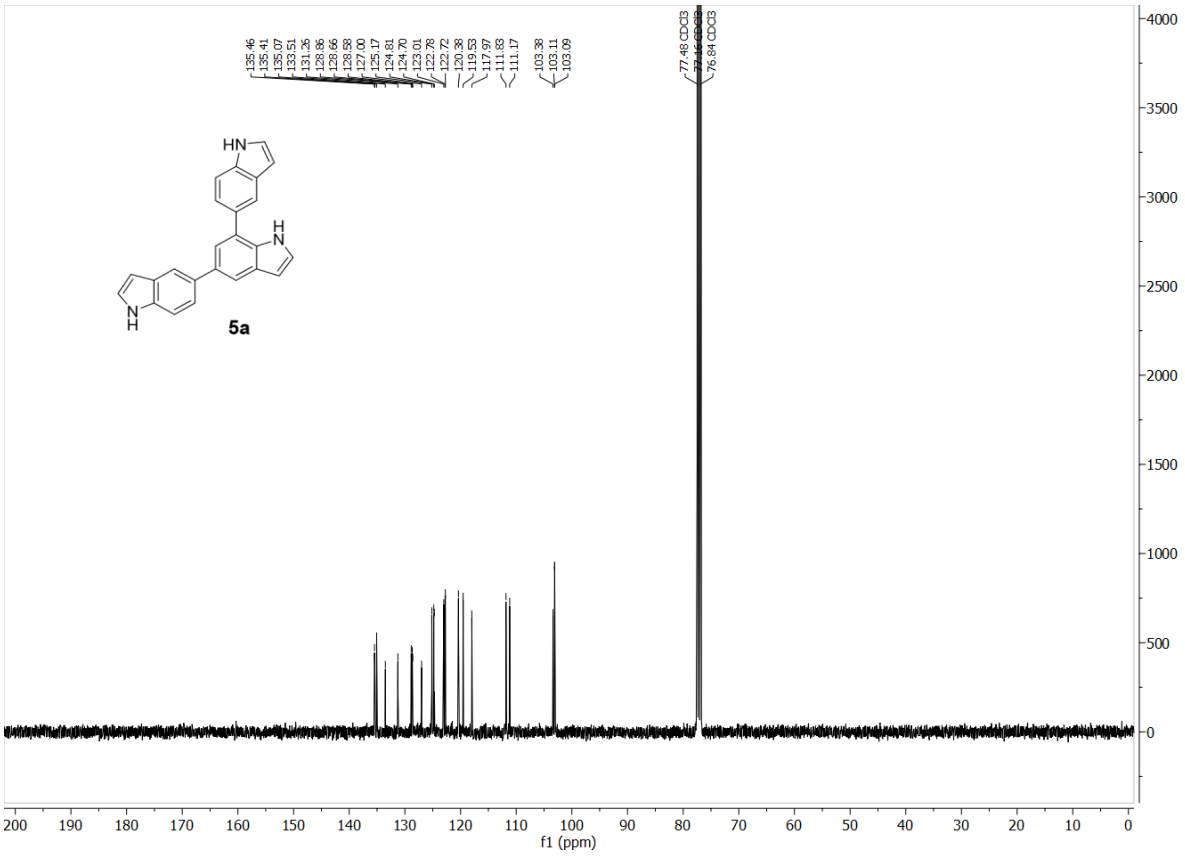

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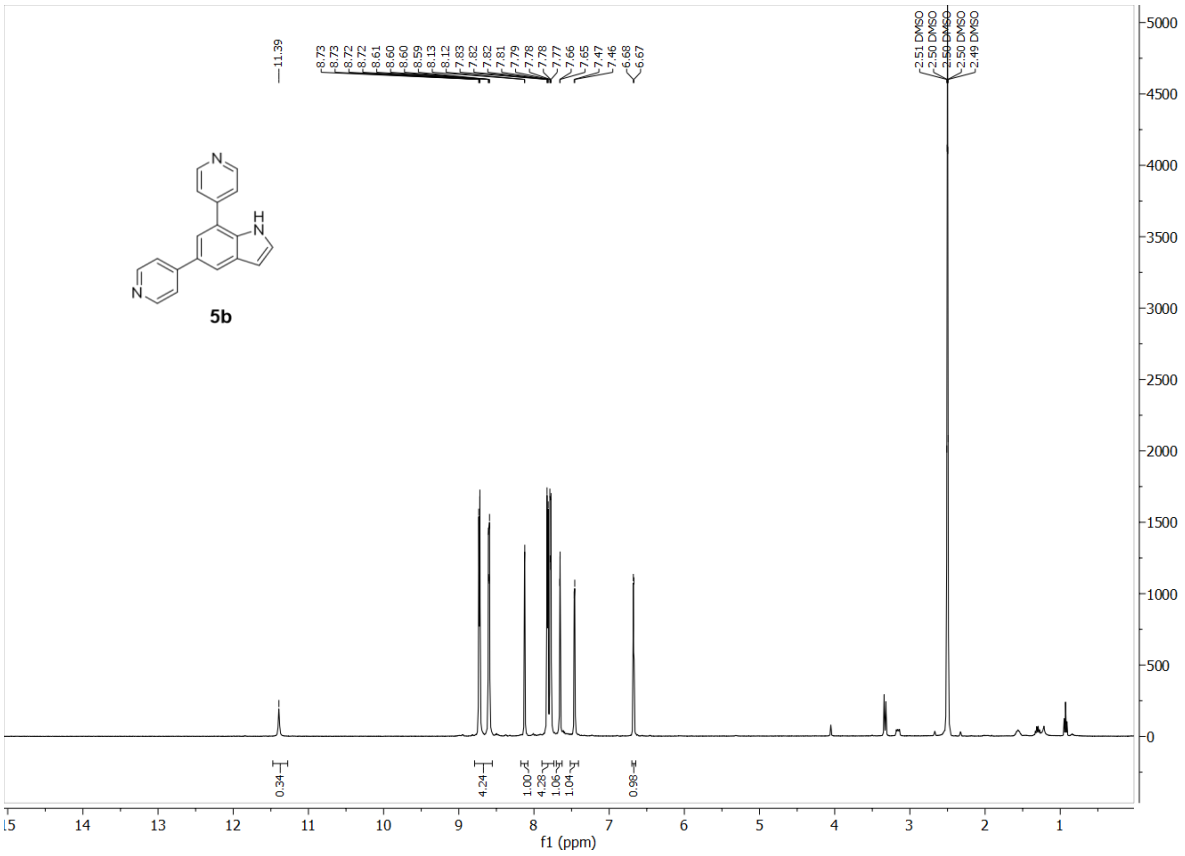
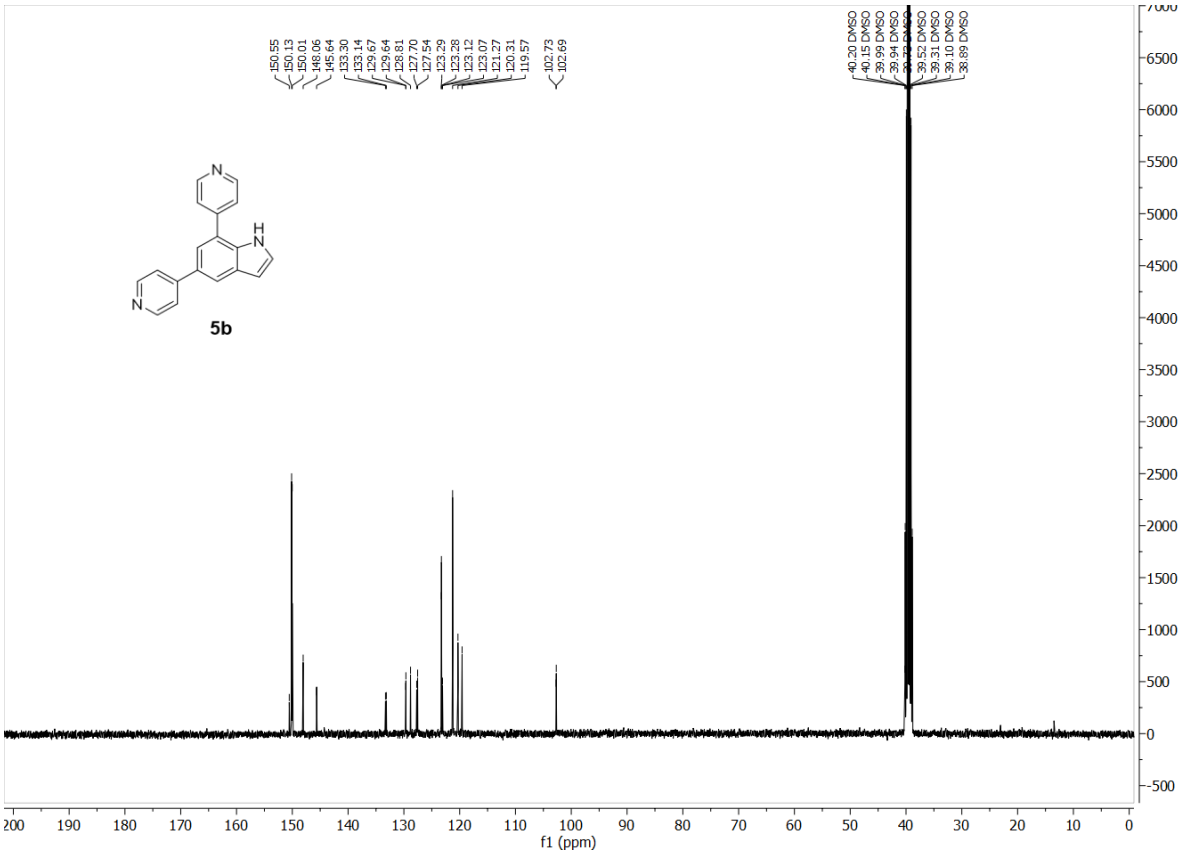


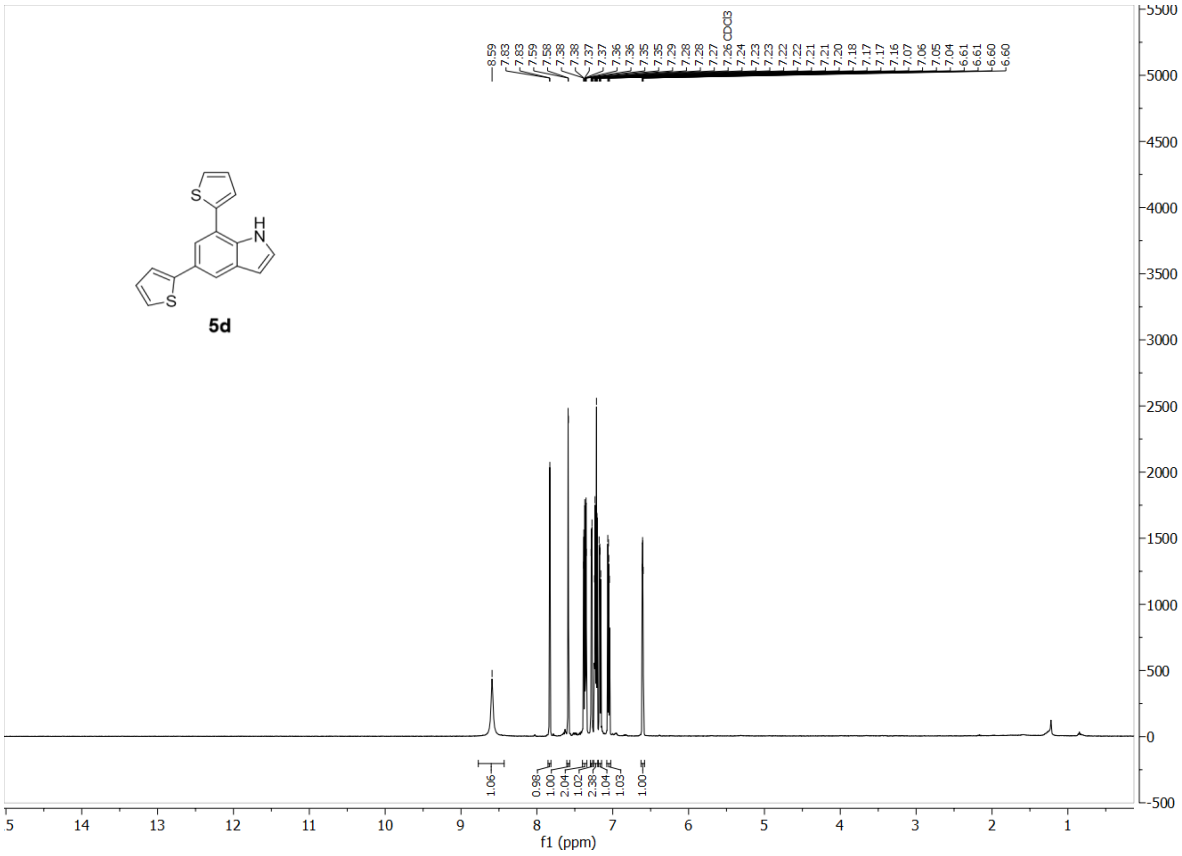
5b

^{13}C-NMR



5b

^{1}H-NMR



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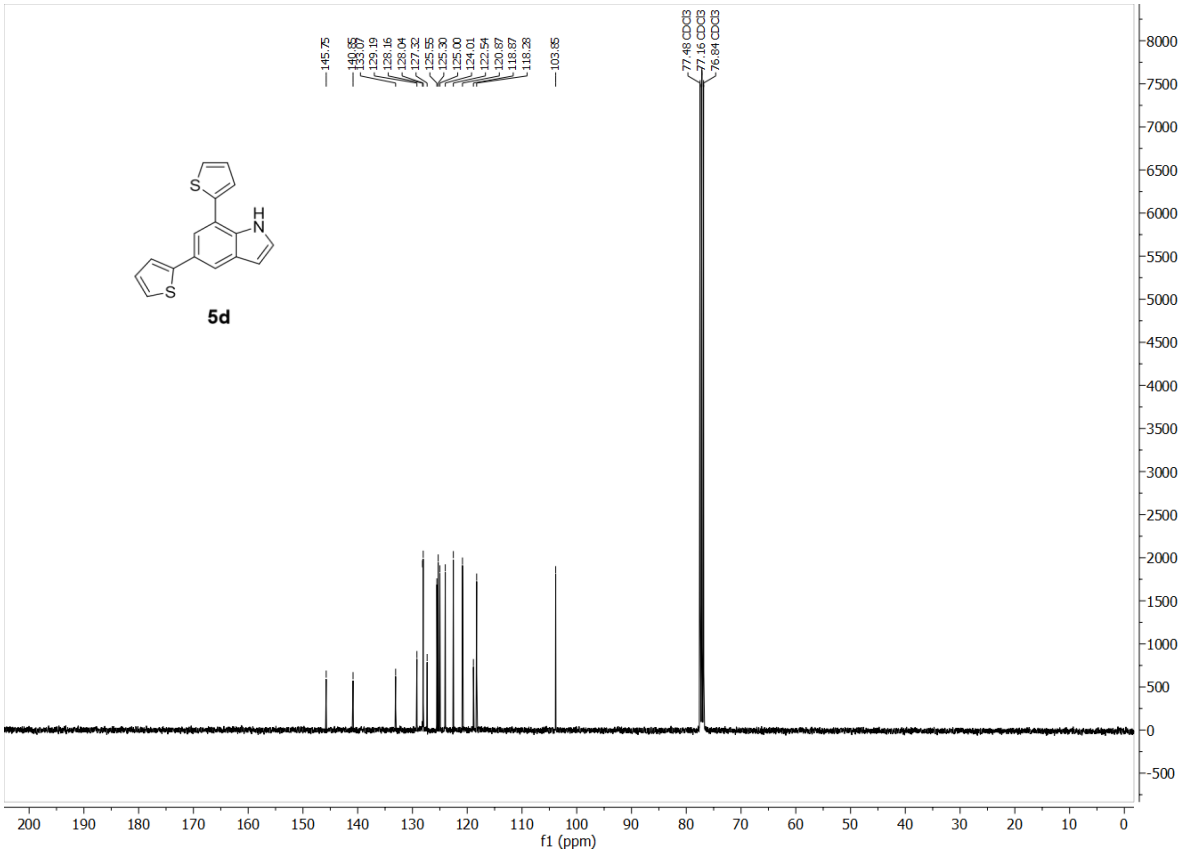
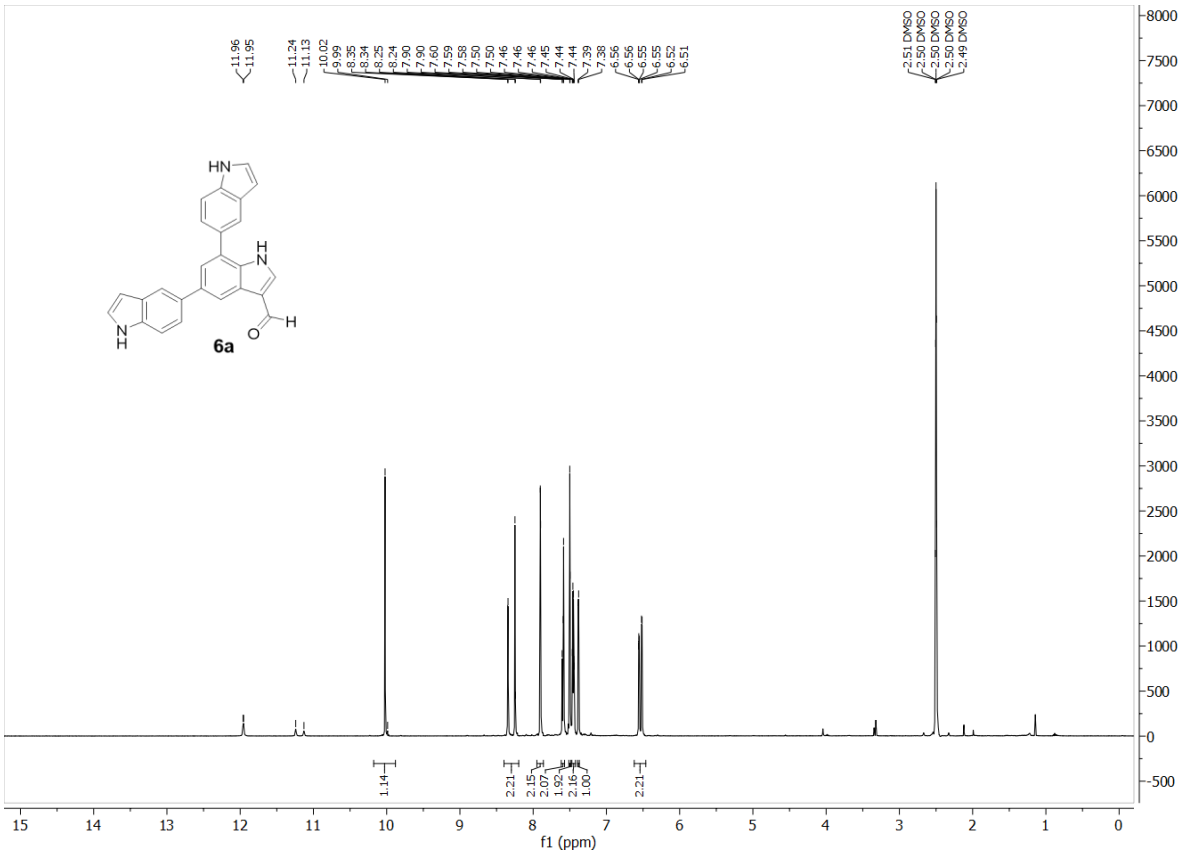


^{1}H-NMR



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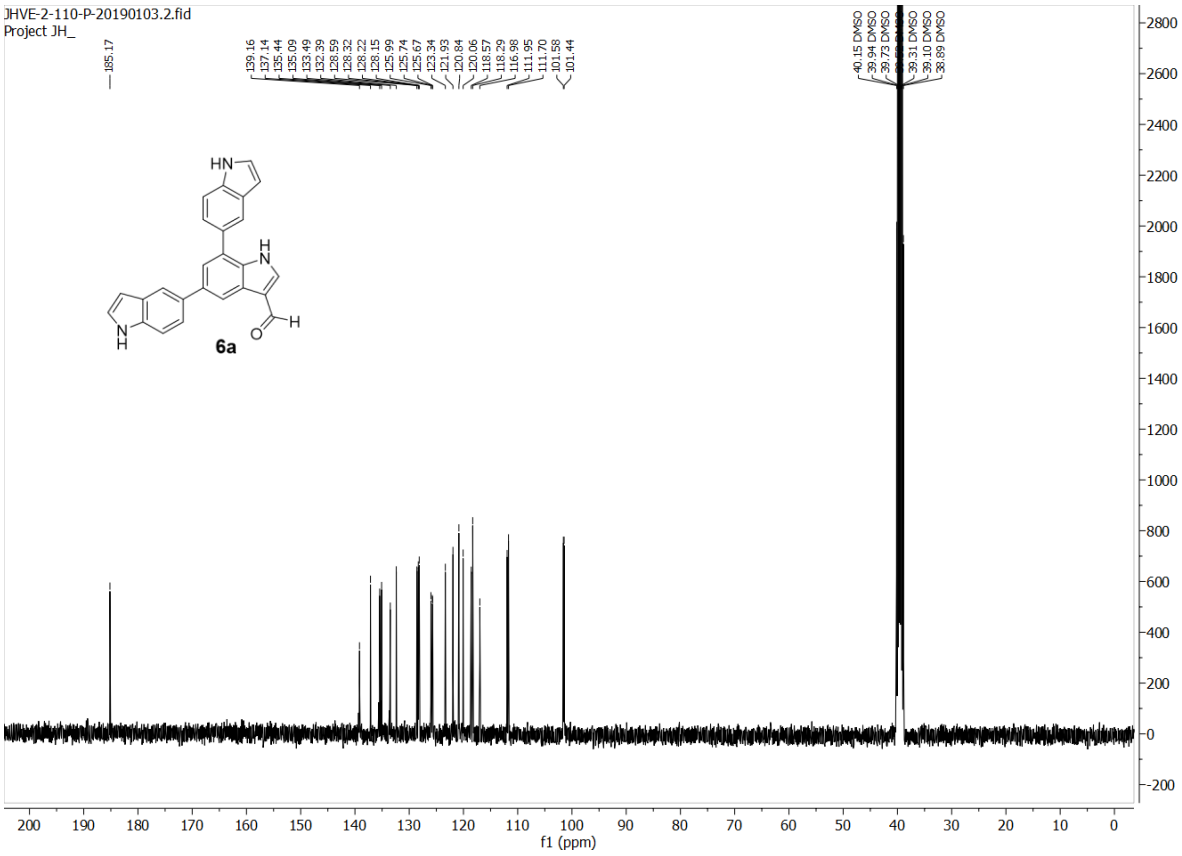

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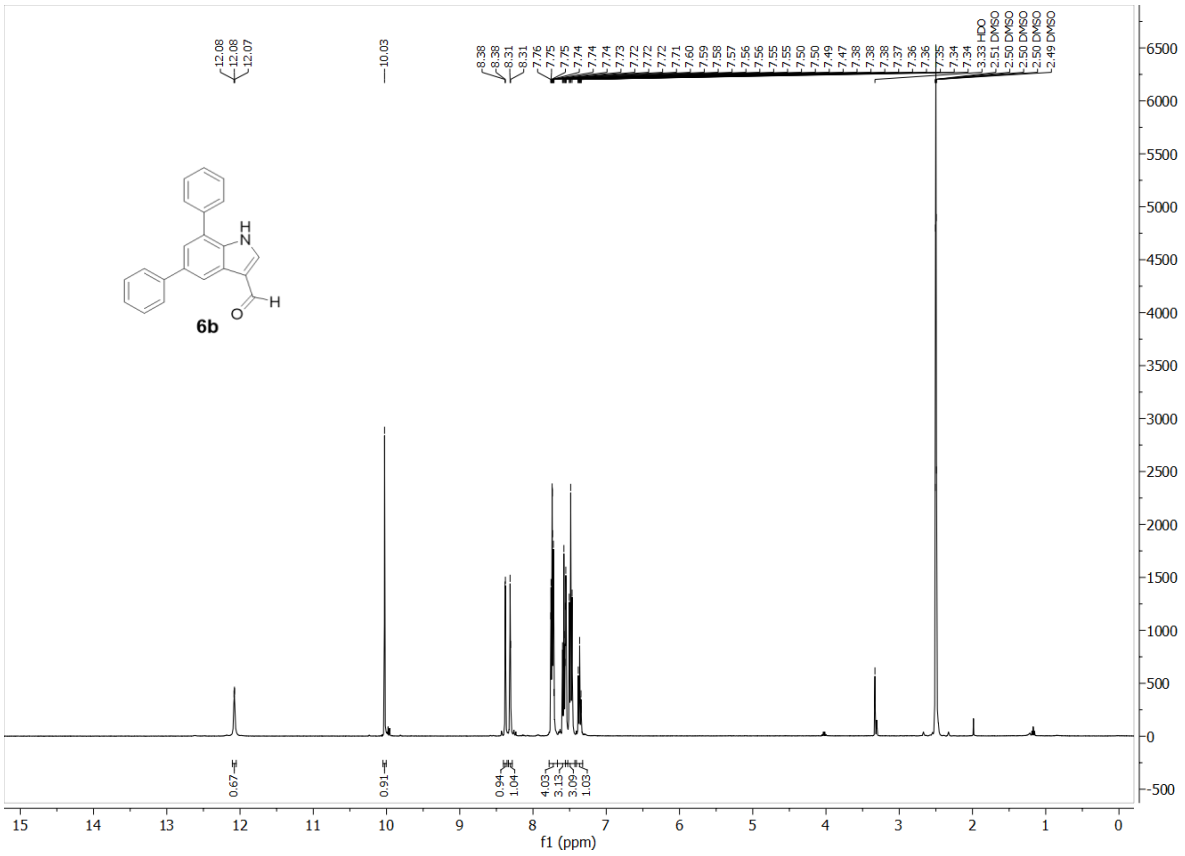

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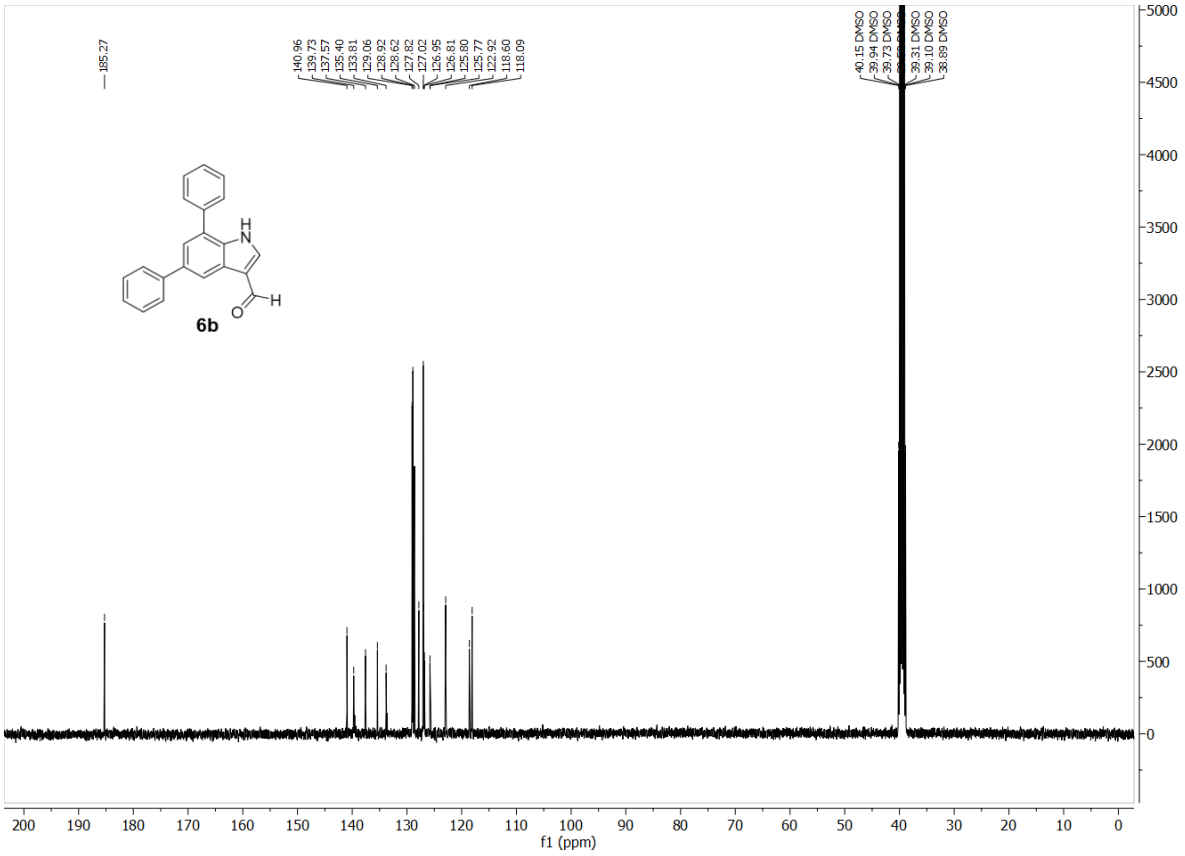
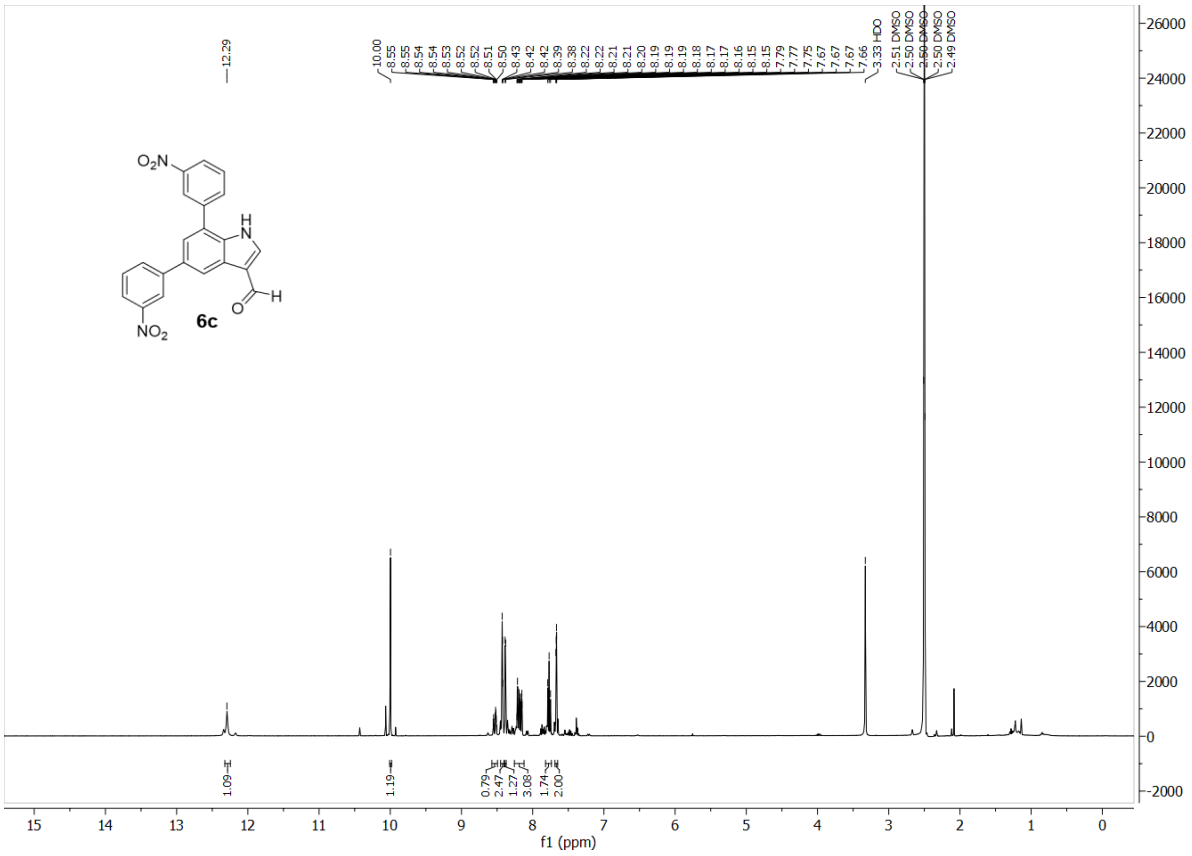
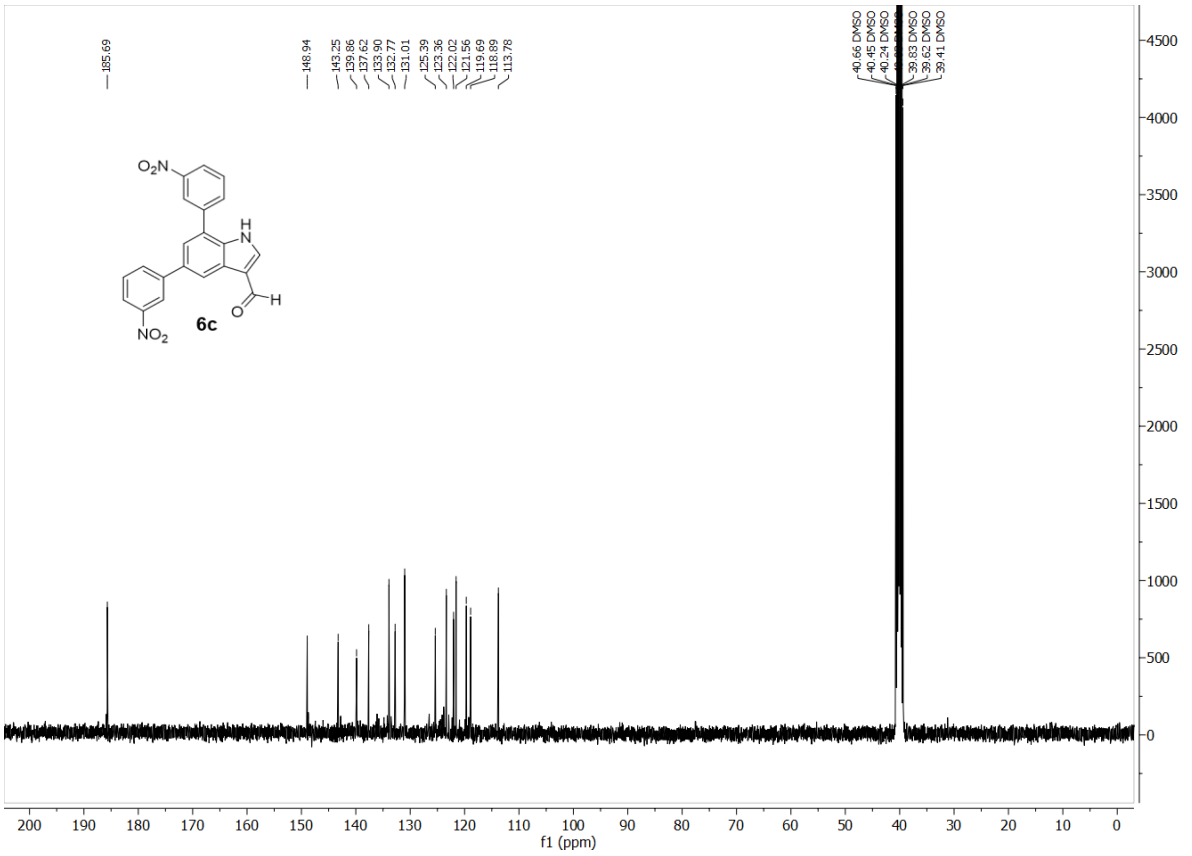


^{1}H-NMR



^{13}C-NMR



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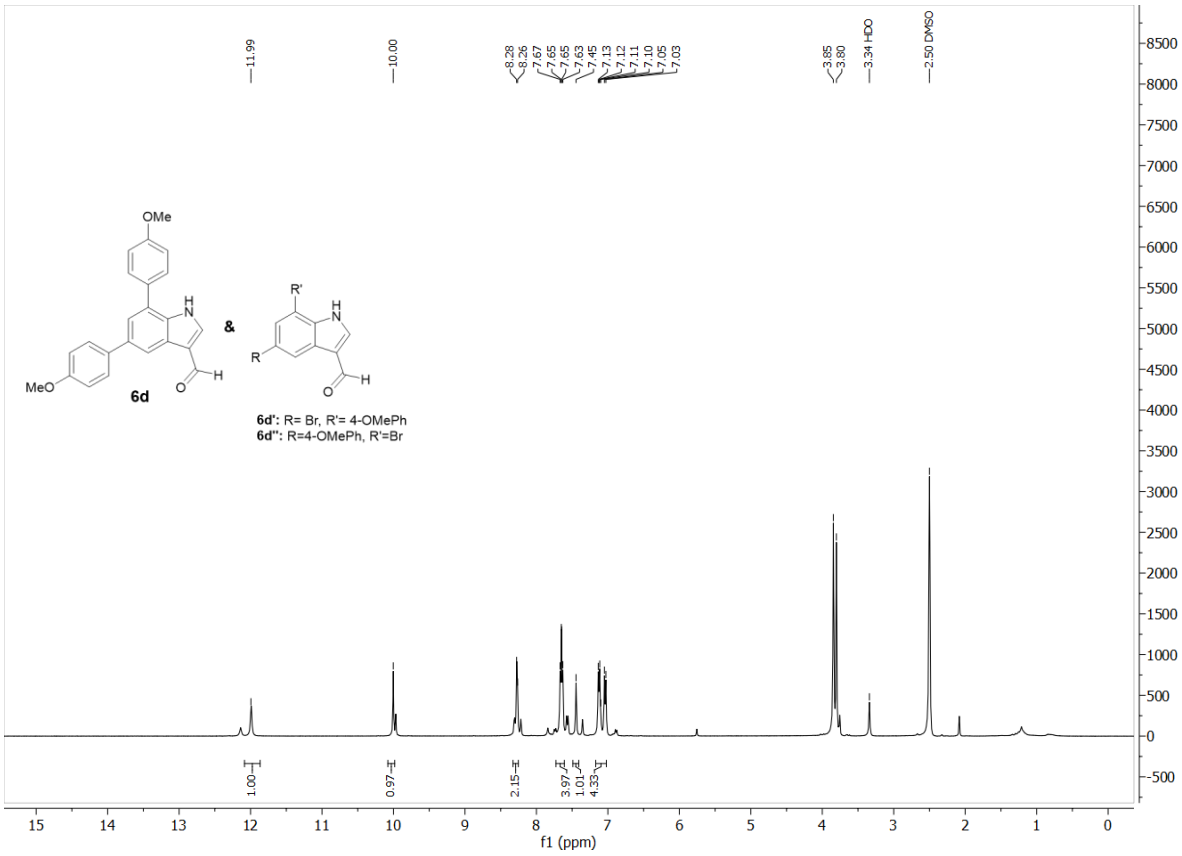

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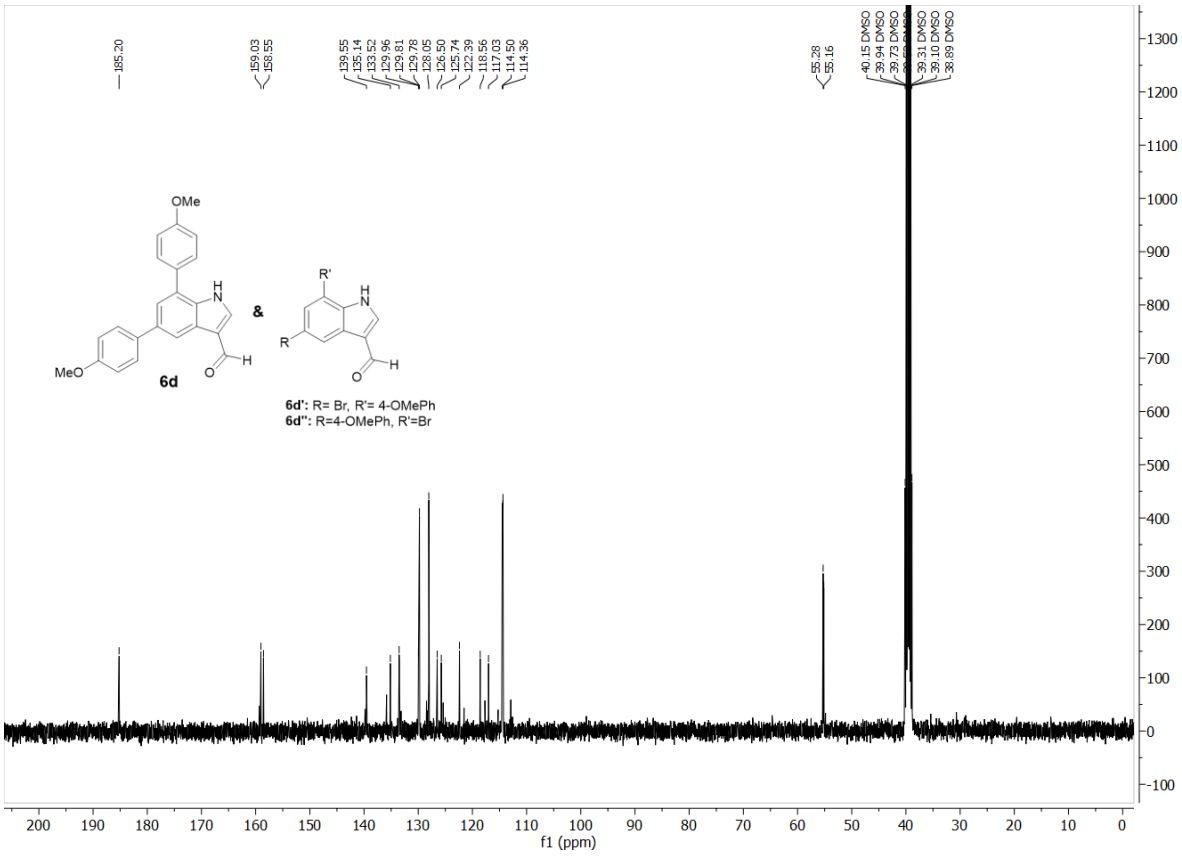

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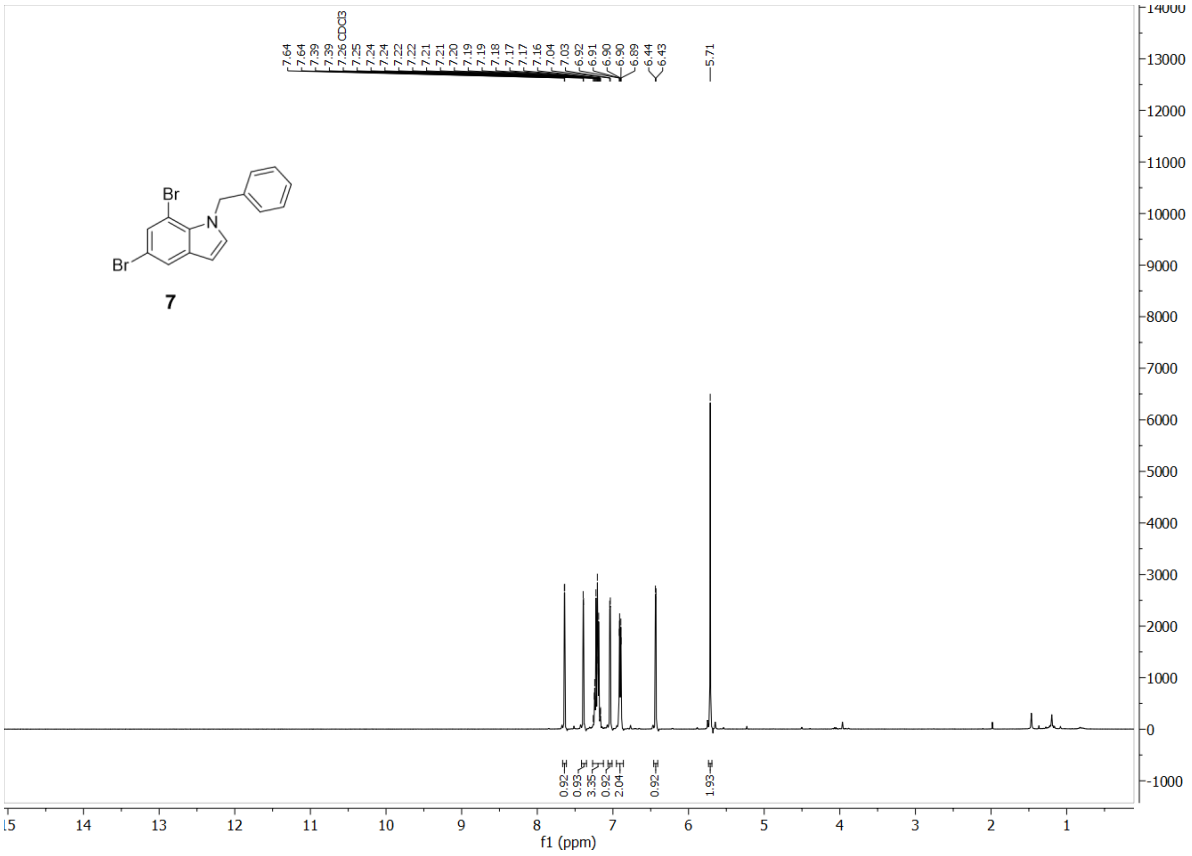

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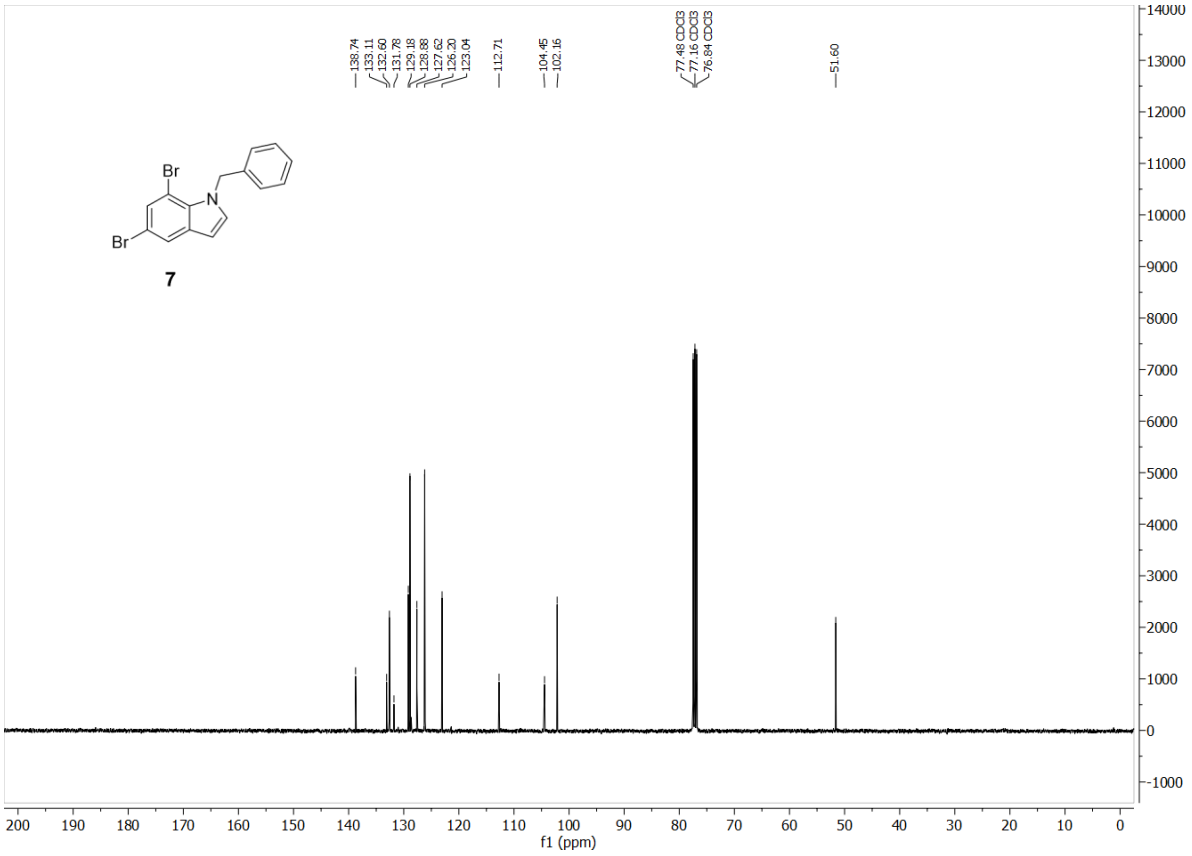

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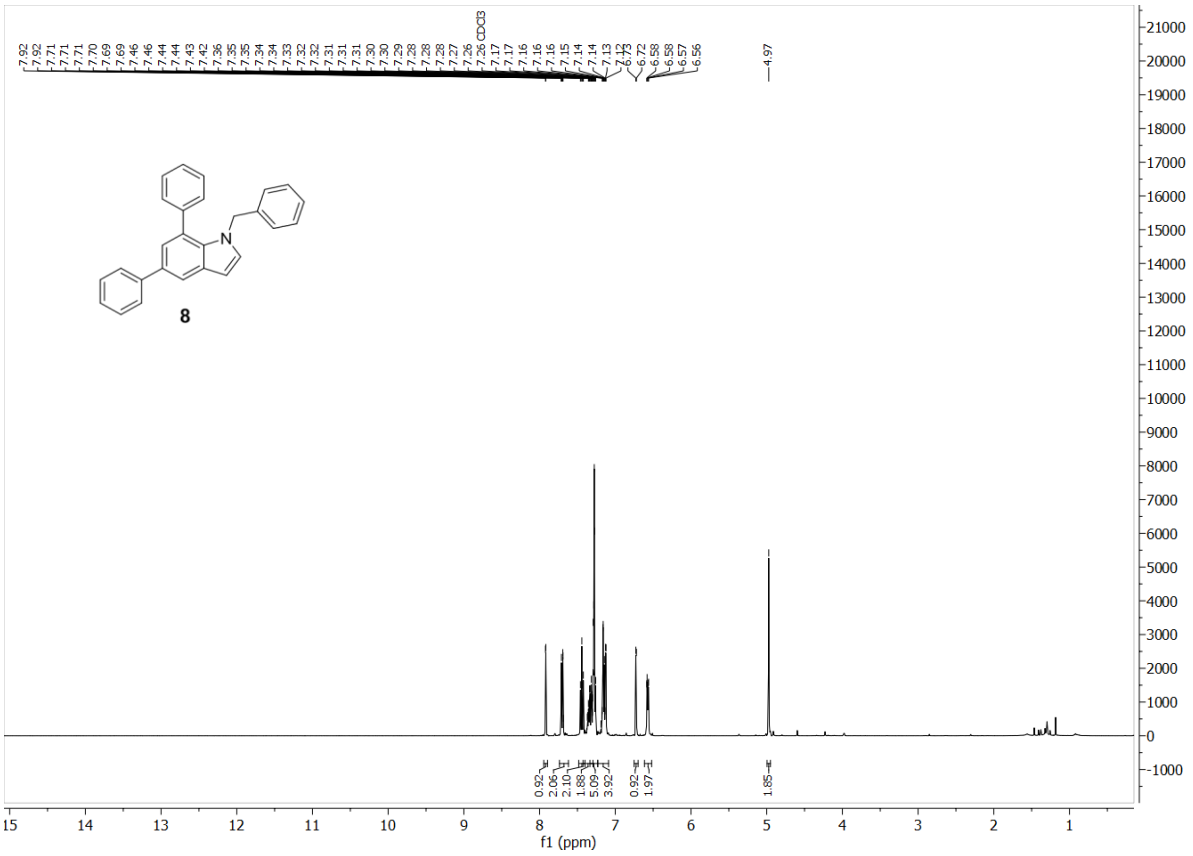

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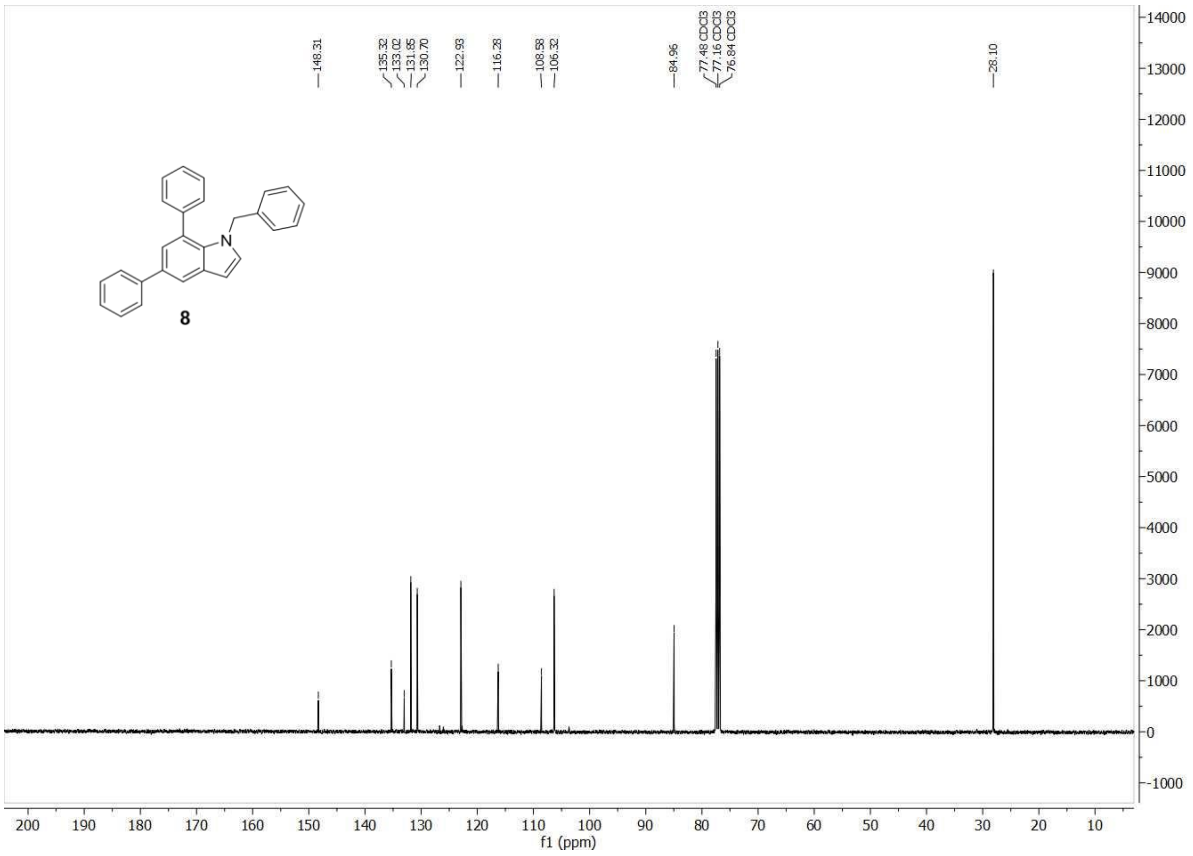

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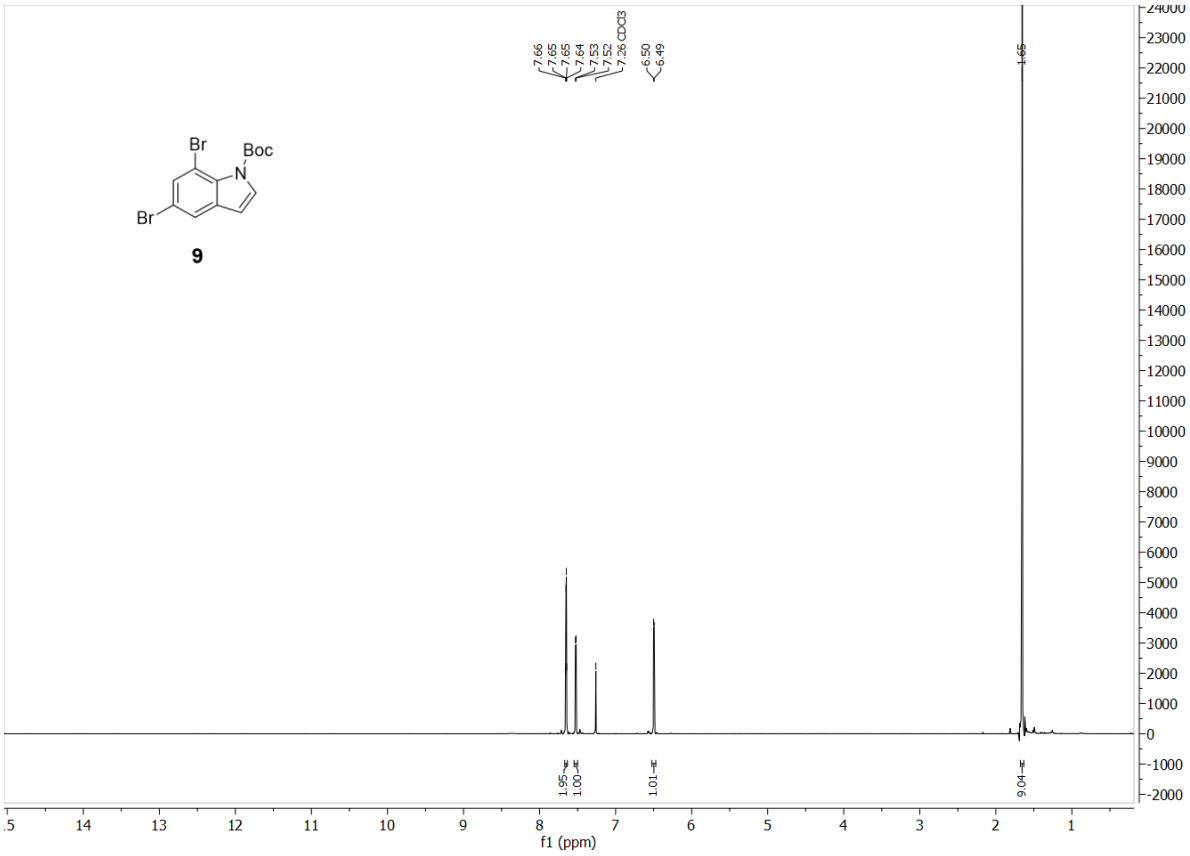

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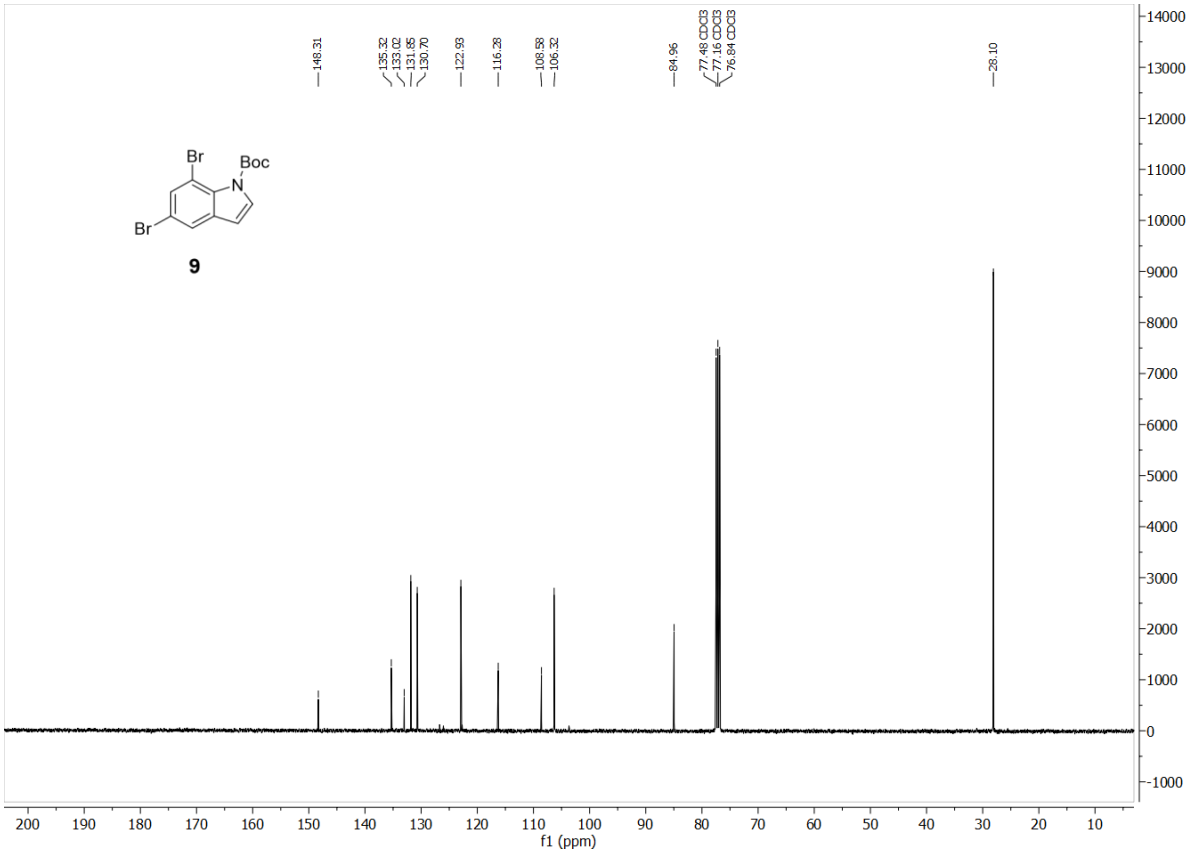

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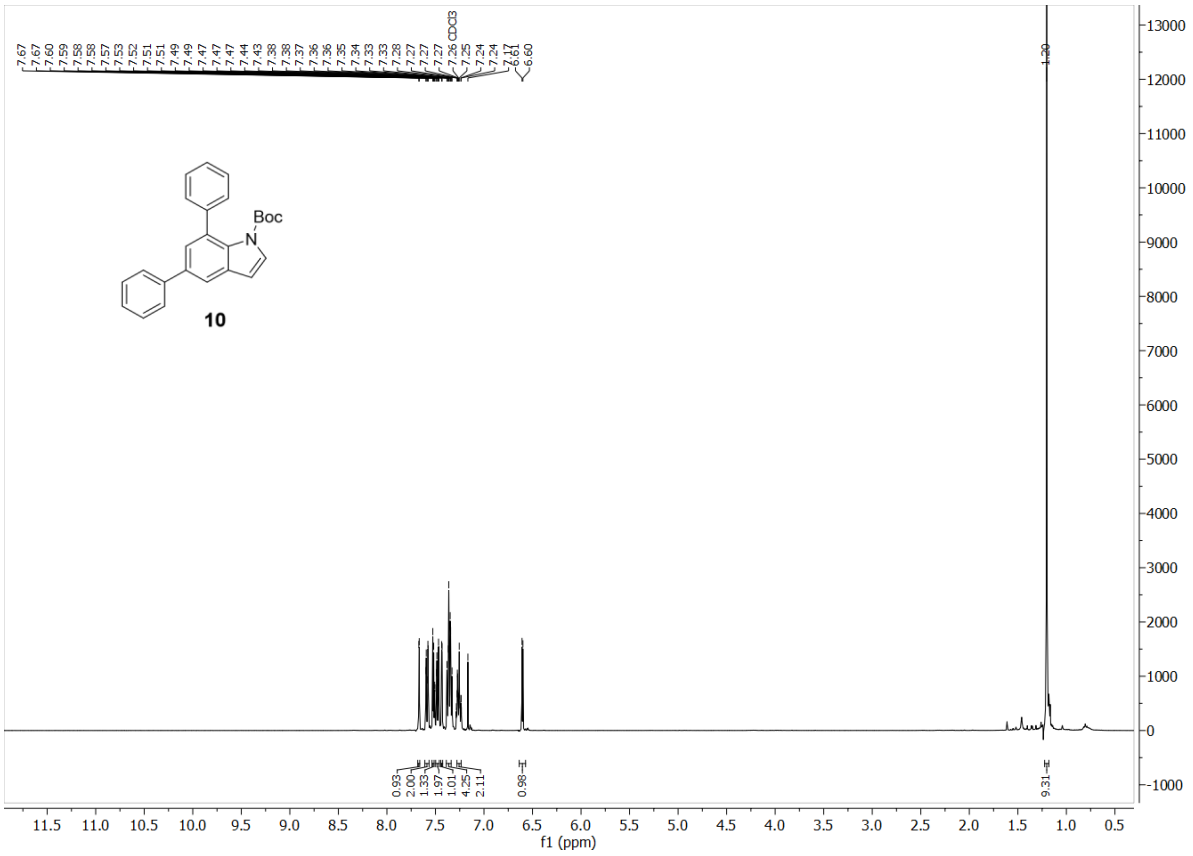
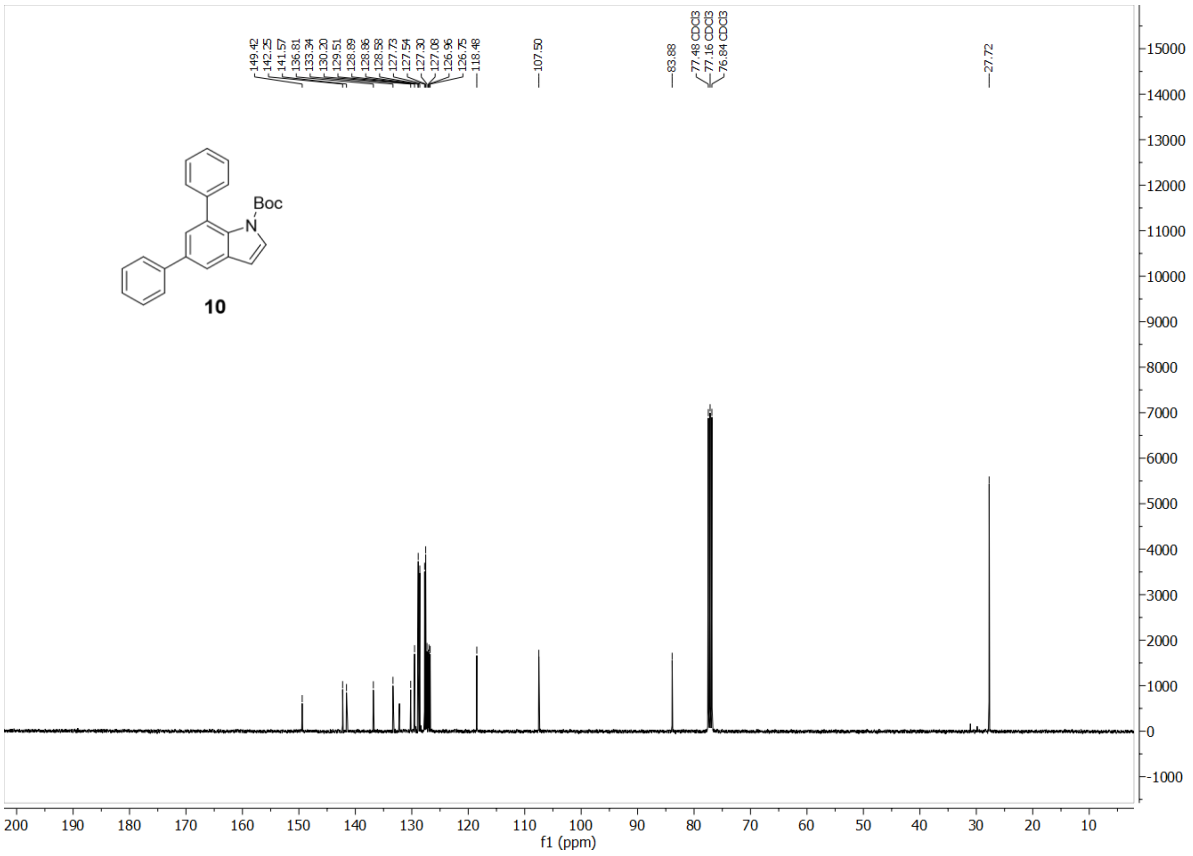
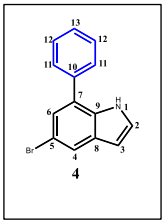
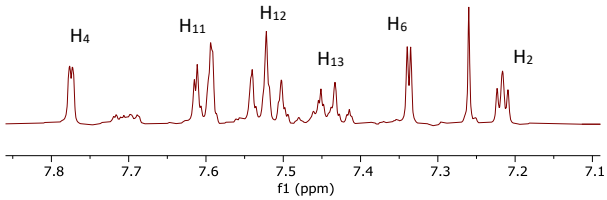


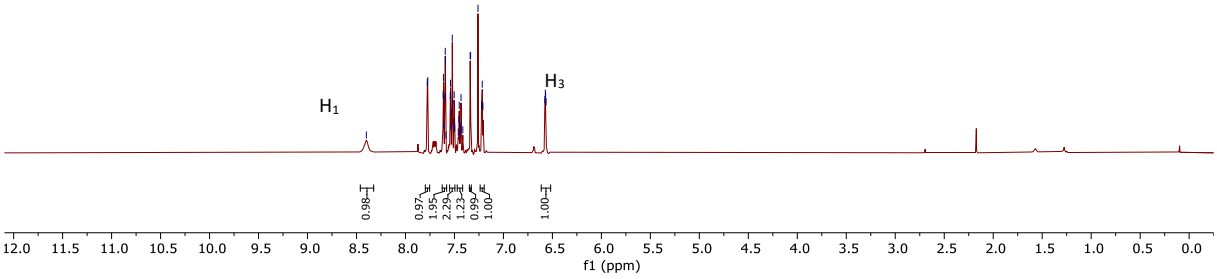
^{13}C-NMR



^{1}H-NMR of 5-bromo-7-phenyl-1*H*-indole 4







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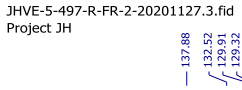
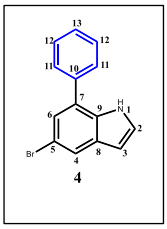
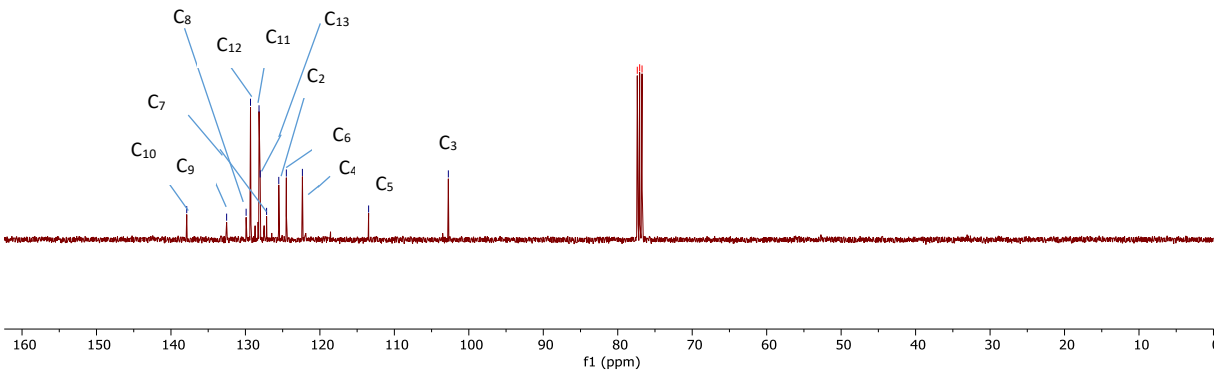
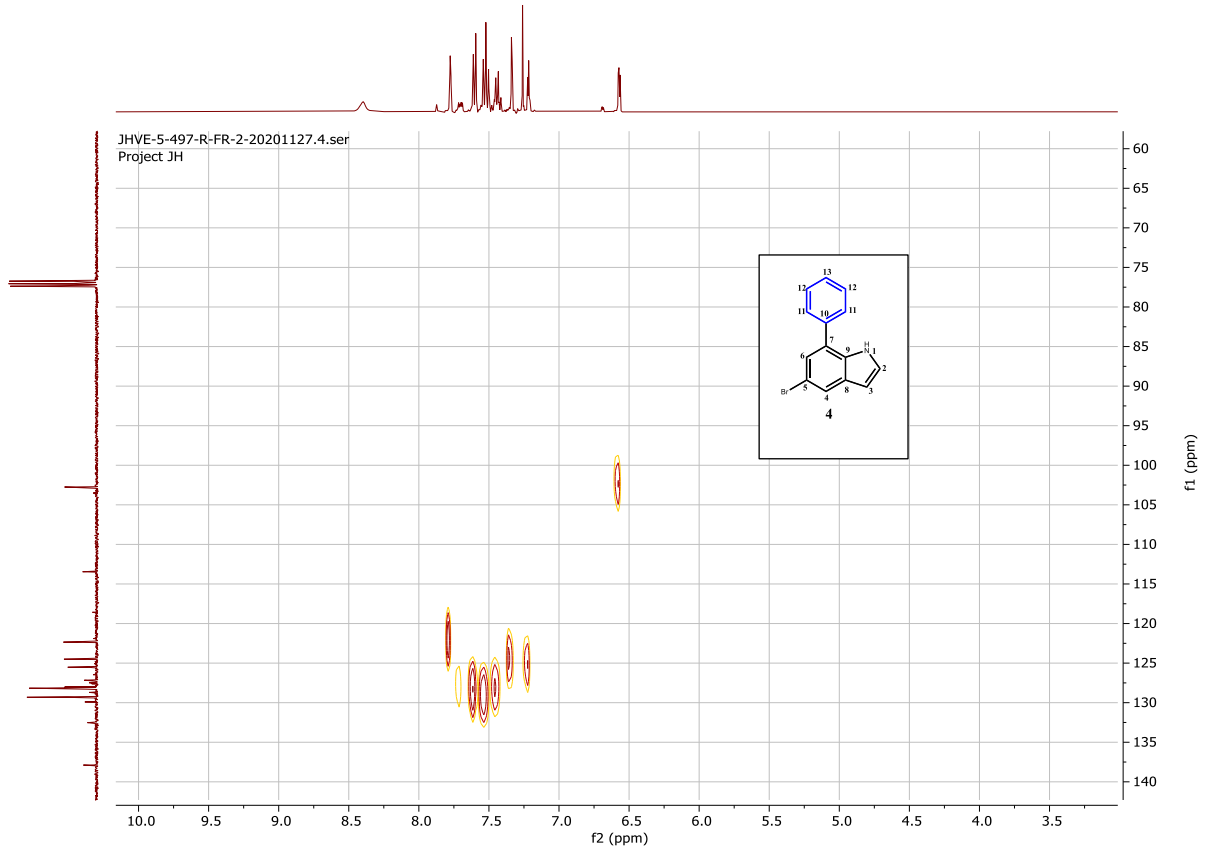






HSQC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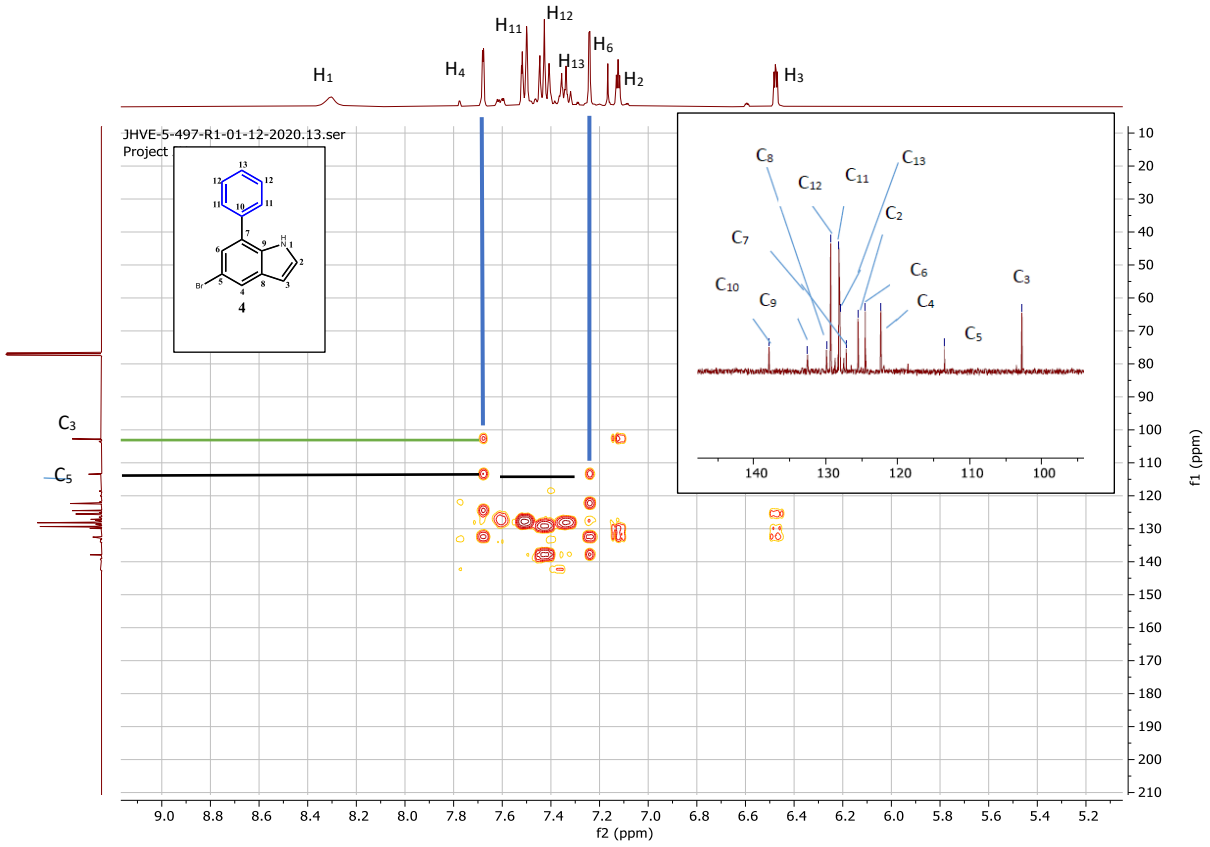
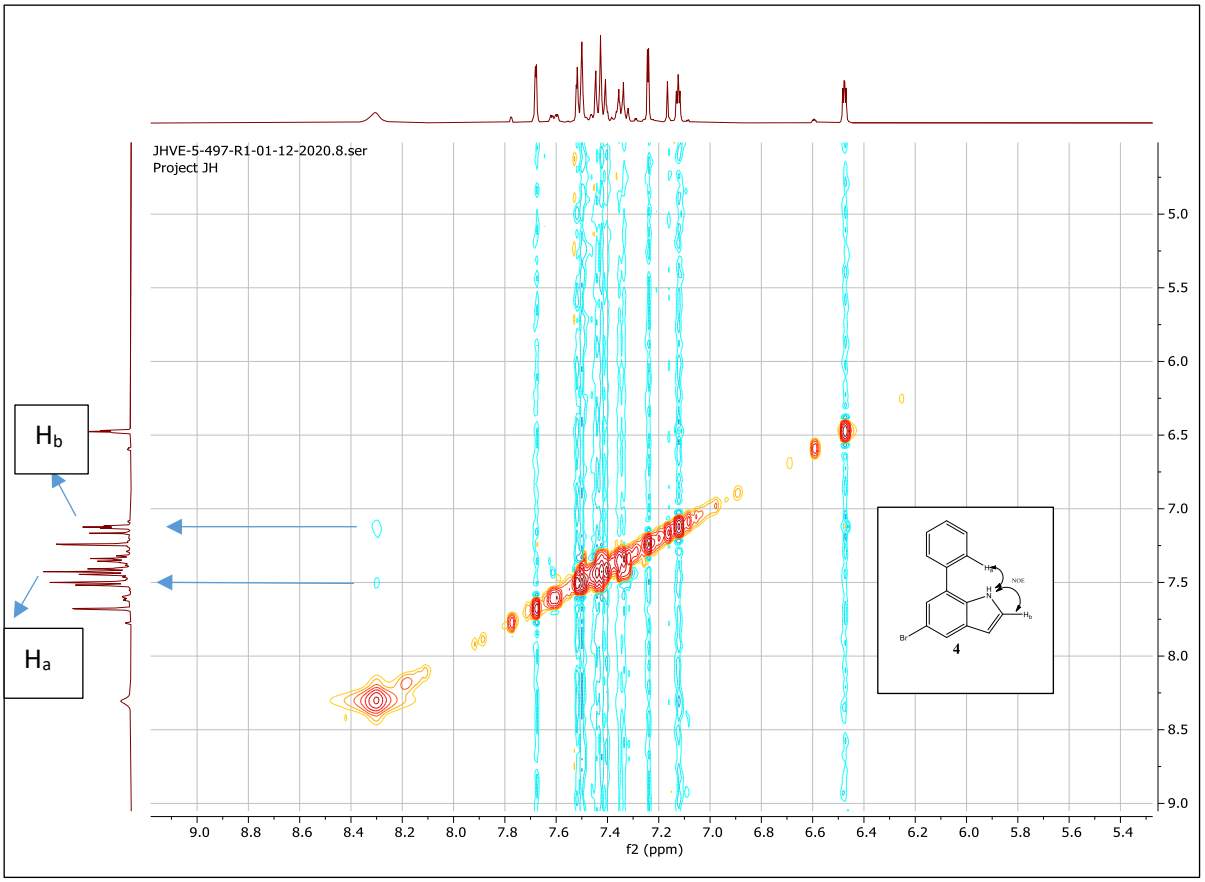
Project JH
f2 (ppm)
f1 (ppm)

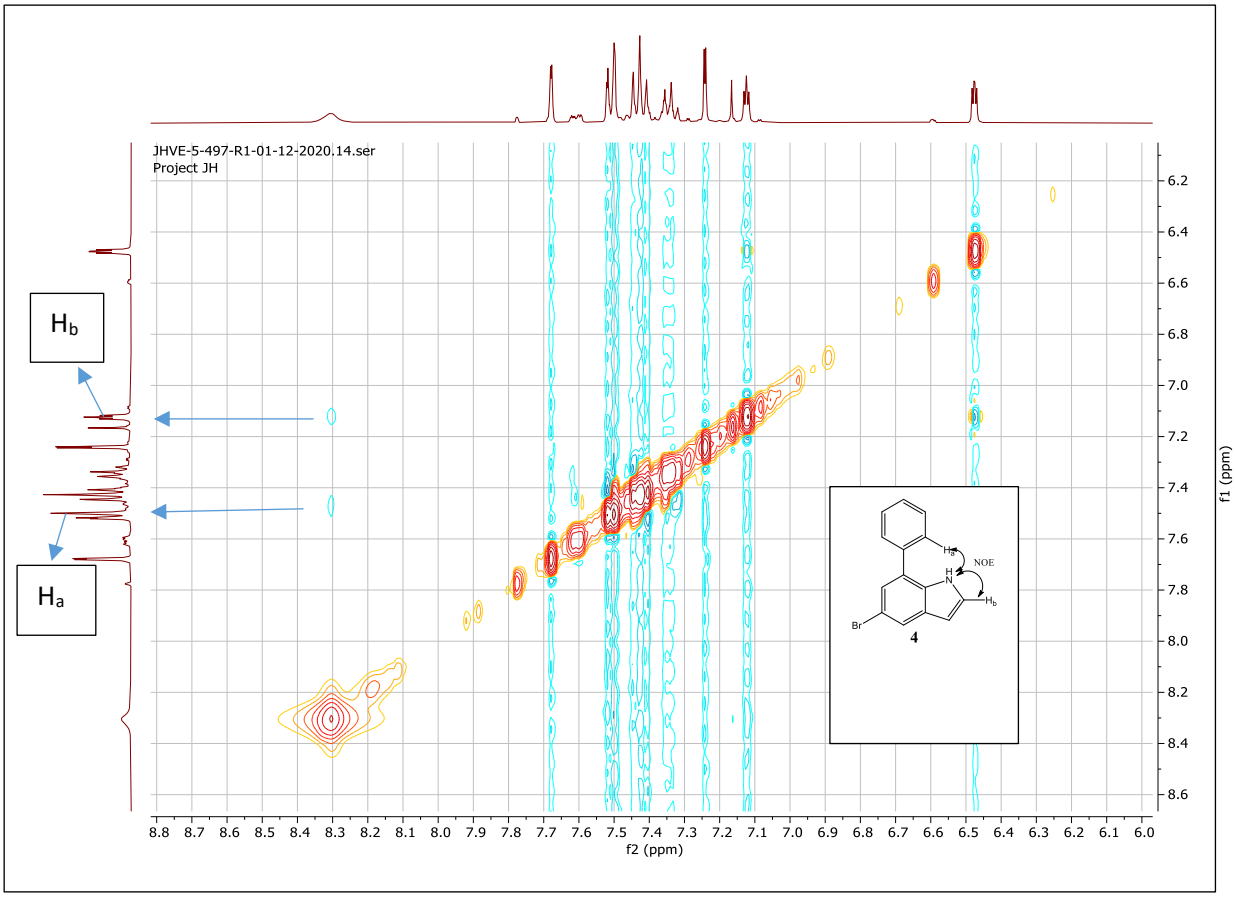
HMBC


H1
H4
H11
H12
H13
H6
H2
H3
JHVE-5-497-R1-01-12-2020.13.ser
Project
C3
C5
C8
C12
C11
C13
C2
C7
C6
C3
C10
C9
C4
C5
f2 (ppm)
f1 (ppm)

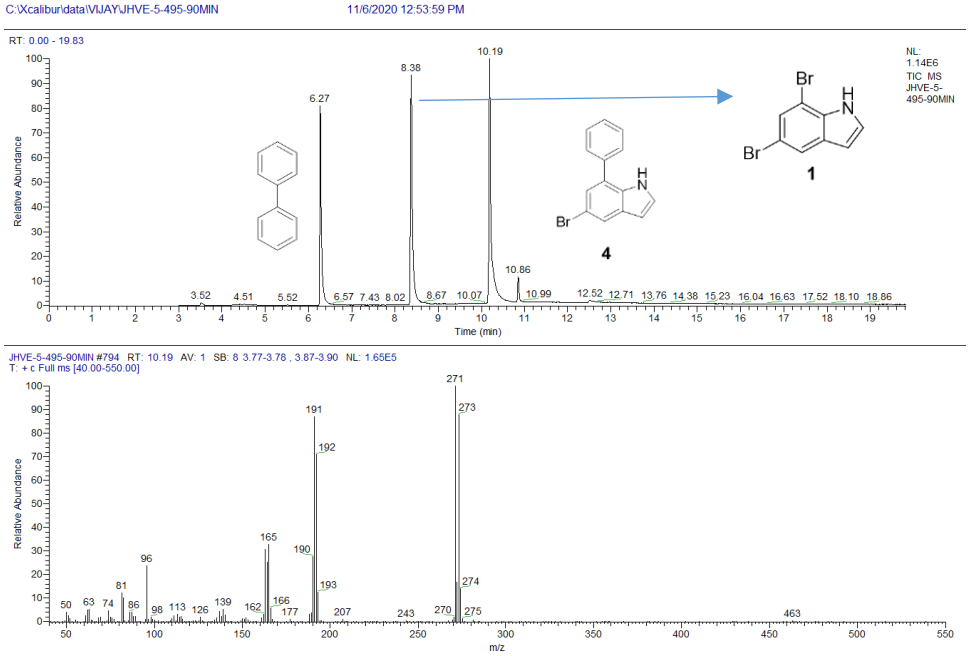
NOESY



ROESY



GC-MS of 5-bromo-7-phenyl-1*H*-indole 4 (unpurified, 54% conversion (GC))



GC-MS of 5-bromo-7-phenyl-1*H*-indole 4 (purified, 30 % yield, 98% purity)