Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Synthesis of 1*H*-Indazoles from *N*-Tosylhydrazones and Nitroaromatic Compounds

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Contents

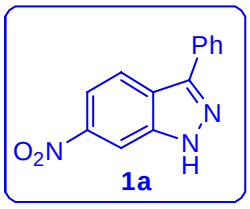
1. General. All reactions were performed under nitrogen atmosphere in an oven-dried reaction flask. 1,4-Dioxane, toluene and THF were distilled over Na with benzophenone-ketyl intermediate as indicator. 200-300 Mesh silica gels for the chromatography (Qingdao, China) were used. Melting points were measured on a SGW X-4 microscopic melting point instrument and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz with Bruker ARX 400 spectrometer. Chemical shifts are reported in ppm using tetramethylsilane as internal standard and $CDCl_3$ as solvent. IR spectra were recorded with a Nicolet 5MX-S infrared spectrometer. HRMS were obtained on a Bruker Apex IV FTMS. PE: petroleum ether; EA: ethyl acetate. All the starting materials (nitroaromatic compounds and aldehydes) were purchased and used without further purification.

2. General Procedure for the Synthesis of 1*H*-Indazoles from *N*-Tosylhydrazones and Nitroaromatic Compounds

To a mixture of nitroaromatic compound (0.3 mmol), *N*-tosylhydrazone (0.36 mmol)[1] and base (Cs_2CO_3 or NaH, 1.08 mmol) in 10 ml Schlenk tube was added dry DMF (2.0 ml) under N_2 atmosphere. The solution was stirred for indicated time at 80 ^{o}C or 60 ^{o}C. The crude mixture was purified by silica-gel column chromatography to give the 1*H*-indazole product.

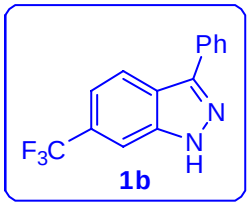
3. Characterization Data for Products

6-Nitro-3-phenyl-1*H*-indazole[2]



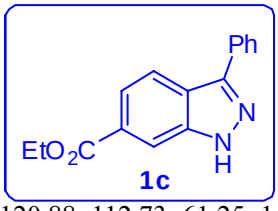
Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.63 (br, 1H), 8.26 (s, 1H), 8.14-8.07 (m, 2H), 7.98-7.96 (m, 2H), 7.61-7.51 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 146.99, 146.56, 140.32, 132.02, 129.27, 129.17, 127.72, 124.13, 122.07, 116.19, 106.96.

3-Phenyl-6-(trifluoromethyl)-1*H*-indazole



Pale yellow solid; m.p. 149-151 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.09 (br, 1H), 8.11 (d, J = 8.5 Hz, 1H), 7.98 (d, J = 7.2 Hz, 2H), 7.60-7.49 (m, 3H), 7.46-7.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 146.42, 136.97, 132.54, 128.94, 128.64, 127.73, 125.51, 124.57 (q, J = 4.4 Hz), 124.27 (q, J = 271.4 Hz), 122.63, 120.80, 113.00 (q, J = 34.4 Hz); HRMS (ESI, *m/z*): calcd for $C_{14}H_{10}F_3N_2$ $[M+H]^+$ 263.0791, found 263.0792; LRMS (EI, *m/z*): 262 (M^+, 100), 243 (6), 235 (8), 77 (17), 51 (8); IR (film): 1055, 1124, 1169, 1238, 1340 cm^{-1}.

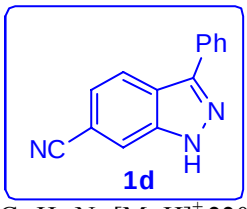
Ethyl 3-phenyl-1*H*-indazole-6-carboxylate



1c

White solid; m.p. 103-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.16 (br, 1H), 8.06-7.98 (m, 4H), 7.88-7.86 (m, 1H), 7.56-7.52 (m, 2H), 7.47-7.43 (m, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.75, 145.71, 141.13, 132.86, 129.02, 128.84, 128.45, 127.59, 123.32, 121.80, 120.88, 112.73, 61.25, 14.33; HRMS (ESI, *m*/*z*): calcd for $C_{16}H_{15}N_2O_2$ $[M+H]^+$ 267.1128, found 267.1134; LRMS (EI, *m*/*z*): 266 (M^+, 100), 238 (34), 221 (48), 193 (16), 166 (11); IR (film): 697, 743, 1221, 1313, 1714 cm^{-1}.

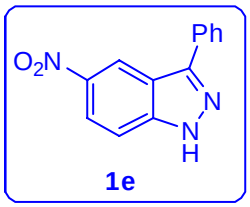
3-Phenyl-1*H*-indazole-6-carbonitrile



1d

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.20 (br, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 7.2 Hz, 2H), 7.70 (s, 1H), 7.59-7.49 (m, 3H), 7.45 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 146.51, 140.26, 132.22, 129.17, 128.97, 127.72, 123.57, 123.07, 122.53, 119.08, 115.50, 110.18; HRMS (ESI, *m*/*z*): calcd for $C_{14}H_{10}N_3$ $[M+H]^+$ 220.0869, found 220.0872; LRMS (EI, *m*/*z*): 219 (M^+, 100), 192 (19), 164 (13), 77 (19), 51 (15); IR (film): 697, 748, 816, 987, 1472, 1705 cm^{-1}.

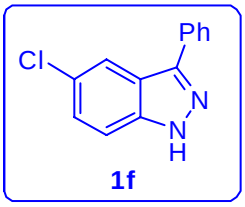
5-Nitro-3-phenyl-1*H*-indazole[3]



1e

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.84 (br, 1H), 8.98 (s, 1H), 8.26 (d, *J* = 9.2 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 2H), 7.62-7.53 (m, 3H), 7.29 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 148.67, 143.39, 142.96, 131.72, 129.35, 127.81, 122.14, 120.37, 119.18, 110.60.

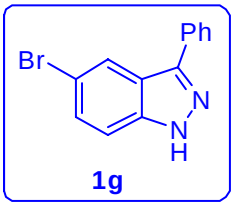
5-Chloro-3-phenyl-1*H*-indazole[4]



1f

Pale yellow solid; m.p. 109-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.55 (br, 1H), 7.98-7.93 (m, 3H), 7.56-7.45 (m, 3H), 7.32-7.29 (m, 1H), 7.17-7.14 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 145.36, 140.04, 132.78, 129.07, 128.53, 127.63, 127.11, 121.80, 120.35, 111.35.

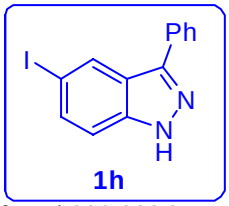
5-Bromo-3-phenyl-1*H*-indazole



1g

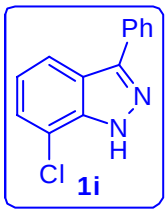
White solid; m.p. 127-130 °C. ^{1}H NMR (400 MHz, CD_3COCD_3) δ 12.57 (br, 1H), 8.27 (d, *J* = 1.0 Hz, 1H), 8.04 (d, *J* = 7.4 Hz, 2H), 7.63-7.61 (m, 1H), 7.56-7.51 (m, 3H), 7.44-7.42 (m, 1H); ^{13}C NMR (100 MHz, CD_3COCD_3) 144.35, 141.29, 134.06, 129.63, 129.32, 128.45, 127.63, 123.60, 122.74, 114.26, 112.88; HRMS (ESI, *m*/*z*): calcd for $C_{13}H_{10}{}^{79}BrN_2$ $[M+H]^+$ 273.0022, found 273.0027; LRMS (EI, *m*/*z*): 272 (M^+, 100), 192 (13), 166 (20), 139 (6), 77 (17); IR (film): 698, 774, 787, 912, 1478 cm^{-1}.

5-Iodo-3-phenyl-1*H*-indazole



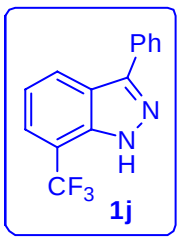
Yellow solid; m.p. 159-162 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.74 (br, 1H), 8.30 (s, 1H), 7.92-7.91 (m, 2H), 7.53-7.48 (m, 4H), 6.70 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 144.75, 140.51, 135.08, 132.69, 129.80, 129.15, 128.58, 127.83, 123.26, 112.22, 84.70; HRMS (ESI, *m/z*): calcd for $C_{13}H_{10}IN_2$ $[M+H]^+$ 320.9883, found 320.9886; LRMS (EI, *m/z*): 320 (M^+, 100), 192 (12), 166 (28), 77 (28), 63 (20); IR (film): 696, 774, 906, 1476 cm^{-1}.

7-Chloro-3-phenyl-1*H*-indazole



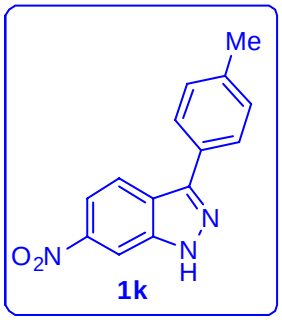
Yellow solid; m.p. 154-157 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.35 (br, 1H), 7.98-7.93 (m, 3H), 7.55-7.51 (m, 2H), 7.46-7.41 (m, 2H), 7.20-7.17 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 146.93, 139.50, 133.01, 128.90, 128.47, 127.58, 126.01, 122.59, 122.25, 119.85, 115.83; HRMS (ESI, *m/z*): calcd for $C_{13}H_{10}{}^{35}ClN_2$ $[M+H]^+$ 229.0527, found 229.0525; LRMS (EI, *m/z*): 228 (M^+, 100), 192 (12), 166 (9), 77 (11), 51 (7); IR (film): 652, 694, 734, 791,1333 cm^{-1}.

3-Phenyl-7-(trifluoromethyl)-1*H*-indazole[5]



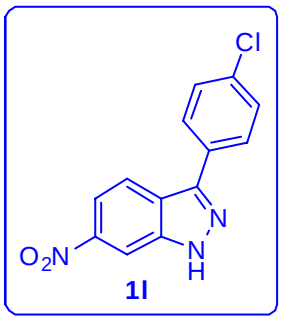
White solid; m.p. 139-141 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.82 (br, 1H), 8.22 (d, *J* = 8.2 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 2H), 7.70 (d, *J* = 7.2 Hz, 1H), 7.56-7.44 (m, 3H), 7.31 (t, *J* = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 146.42, 136.97, 132.54, 128.94, 128.64, 127.73, 125.51, 124.57 (q, *J* = 4.4 Hz), 124.27 (q, *J* = 271.4 Hz), 122.63, 120.80, 113.00 (q, *J* = 34.4 Hz).

6-Nitro-3-*p*-tolyl-1*H*-indazole



Yellow solid; m.p. 179-182 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.60 (br, 1H), 8.09-8.03 (m, 2H), 8.00 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 146.98, 146.62, 140.24, 139.64, 130.14, 128.99, 127.72, 124.03, 122.02, 115.99, 107.20, 21.40; HRMS (ESI, *m/z*): calcd for $C_{14}H_{12}N_3O_2$ $[M+H]^+$ 254.0924, found 254.0927; LRMS (EI, *m/z*): 253 (M^+, 100), 207 (31), 178 (14), 91 (18), 63 (17); IR (film): 782, 792, 827, 1347, 1522 cm^{-1}.

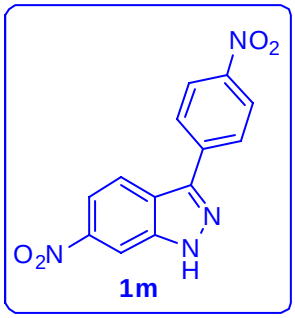
3-(4-Chlorophenyl)-6-nitro-1*H*-indazole



Yellow solid; m.p. 193-196 °C. ^{1}H NMR (400 MHz, CD_3COCD_3) δ 13.05 (br, 1H), 8.56-8.53 (m, 1H), 8.26-8.20 (m, 1H), 8.06-8.01 (m, 3H), 7.57-7.53 (m, 2H); ^{13}C NMR (100 MHz, CD_3COCD_3) 146.95, 144.14, 141.21, 134.18, 132.18, 129.46, 129.12, 123.86, 122.15, 116.04, 107.79; HRMS (ESI, *m/z*): calcd for $C_{13}H_9{}^{35}ClN_3O_2$ $[M+H]^+$ 274.0378, found 274.0380; LRMS (EI, *m/z*): 273 (M^+,

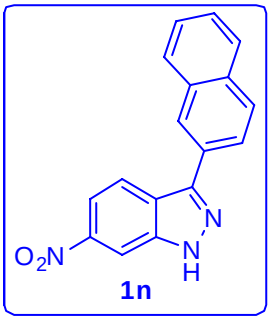
100), 228 (34), 208 (61), 164 (49), 75(28); IR (film): 733, 792, 836, 1094, 1347, 1519 cm^{-1}.

6-Nitro-3-(4-nitrophenyl)-1*H*-indazole[6]



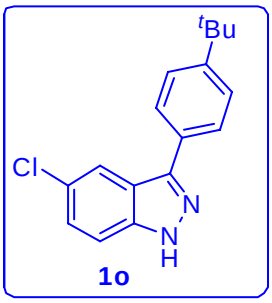
Yellow solid; m.p. 259-261 °C. ^{1}H NMR (400 MHz, CD_3COCD_3) δ 13.33 (br, 1H), 8.59 (s, 1H), 8.37-8.29 (m, 5H), 8.08-8.06 (m, 1H); ^{13}C NMR (100 MHz, CD_3COCD_3) 147.93, 147.10, 143.11, 141.40, 139.67, 128.22, 124.55, 124.05, 122.17, 116.70, 108.12.

3-(Naphthalen-2-yl)-6-nitro-1*H*-indazole



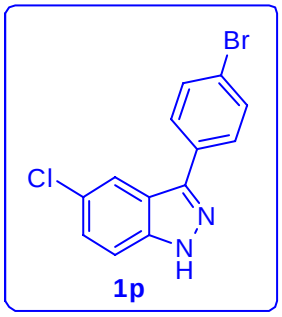
Yellow solid; m.p. 220-224 °C. ^{1}H NMR (400 MHz, CD_3COCD_3) δ 13.08 (br, 1H), 8.60 (s, 2H), 8.48 (d, *J* = 8.1 Hz, 1H), 8.22 (d, *J* = 8.1 Hz, 1H), 8.10-8.05 (m, 3H), 7.97 (d, *J* = 6.0 Hz, 1H), 7.58 (d, *J* = 3.3 Hz, 2H); ^{13}C NMR (100 MHz, CD_3COCD_3) 147.15, 145.44, 141.49, 134.30, 133.91, 131.07, 129.17, 128.95, 128.30, 127.09, 127.03, 126.69, 125.70, 124.40, 122.76, 116.11, 107.88; HRMS (ESI, *m/z*): calcd for $C_{17}H_{12}N_3O_2$ $[M+H]^+$ 290.0924, found 290.0928; LRMS (EI, *m/z*): 289 (M^+, 100), 243 (53), 216 (17), 189 (10), 127 (24); IR (film): 733, 744, 792, 1346, 1522 cm^{-1}.

3-(4-(*tert*-Butyl)phenyl)-5-chloro-1*H*-indazole



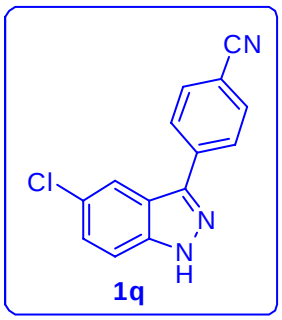
Pale yellow solid; 205-207 °C. ^{1}H NMR (400 MHz, CD_3COCD_3) δ 12.50 (br, 1H), 8.10 (d, *J* = 1.1 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.40 (dd, *J* = 1.7, 8.8 Hz, 1H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, CD_3COCD_3) 151.39, 144.54, 141.18, 131.40, 127.44, 127.17, 126.71, 126.25, 122.18, 120.57, 112.59, 34.90, 31.32; HRMS (ESI, *m/z*): calcd for $C_{17}H_{18}{}^{35}ClN_2$ $[M+H]^+$ 285.1153, found 285.1152; LRMS (EI, *m/z*): 284 (M^+, 36), 269 (100), 241 (9), 120 (9), 77 (3); IR (film): 657, 792, 841, 919, 1479 cm^{-1}.

3-(4-Bromophenyl)-5-chloro-1*H*-indazole



Pale yellow solid; m.p. 166-168 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.62 (br, 1H), 7.95 (s, 1H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 1.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 144.37, 140.05, 132.14, 131.81, 128.91, 127.76, 127.43, 122.57, 121.69, 120.20, 111.19; HRMS (ESI, *m/z*): calcd for $C_{13}H_9{}^{35}Cl^{79}BrN_2$ $[M+H]^+$ 306.9632, found 306.9636; LRMS (EI, *m/z*): 308 (M^+, 100), 192 (18), 163 (11), 75 (7), 63 (6); IR (film): 667, 793, 922, 1477, 2924 cm^{-1}.

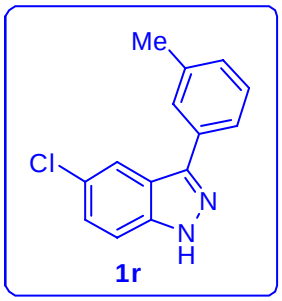
4-(5-Chloro-1*H*-indazol-3-yl)benzonitrile



1q

Yellow solid; m.p. 245-246 °C. ^{1}H NMR (400 MHz, CD_3COCD_3) δ 12.82 (br, 1H), 8.27 (d, *J* = 8.2 Hz, 2H), 8.18 (s, 1H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.9 Hz, 1H), 7.45 (d, *J* = 8.9 Hz, 1H); ^{13}C NMR (100 MHz, CD_3COCD_3) 142.60, 141.26, 138.54, 133.21, 128.05, 127.63, 127.59, 121.97, 120.29, 119.08, 112.93, 111.66; HRMS (ESI, *m/z*): calcd for $C_{14}H_9{}^{35}ClN_3$ $[M+H]^+$ 254.0480, found 254.0486; LRMS (EI, *m/z*): 253 (M^+, 100), 226 (7), 191 (6), 102 (12), 63 (13); IR (film): 843, 920, 1317, 1477, 1609, 2228 cm^{-1}.

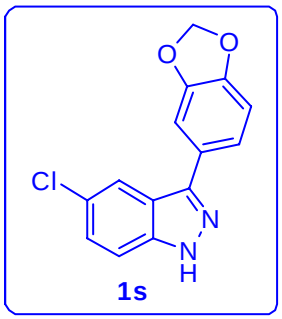
5-Chloro-3-*m*-tolyl-1*H*-indazole



1r

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.63 (br, 1H), 7.93 (s, 1H), 7.74-7.71 (m, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 8.9 Hz, 1H), 6.93-6.88 (m, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 145.27, 140.00, 138.86, 132.67, 129.32, 129.04, 128.37, 127.47, 126.87, 124.92, 121.68, 120.19, 111.57, 21.52; HRMS (ESI, *m/z*): calcd for $C_{14}H_{12}{}^{35}ClN_2$ $[M+H]^+$ 243.0684, found 243.0690; LRMS (EI, *m/z*): 242 (M^+, 100), 206 (6), 178 (4), 91 (10), 65 (5); IR (film): 702, 734, 792, 922, 1484 cm^{-1}.

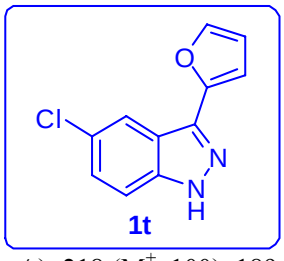
3-(Benzo[*d*][1,3]dioxol-5-yl)-5-chloro-1*H*-indazole



1s

White solid; m.p. 138-141 °C. ^{1}H NMR (400 MHz, CD_3COCD_3) δ 12.45 (br, 1H), 8.05 (s, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.54-7.49 (m, 2H), 7.38 (q, *J* = 1.8, 8.8 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.07 (s, 2H); ^{13}C NMR (100 MHz, CD_3COCD_3) 148.73, 148.13, 144.24, 141.05, 128.15, 127.07, 126.58, 121.78, 121.36, 120.38, 112.42, 108.91, 107.73, 101.80; HRMS (ESI, *m/z*): calcd for $C_{14}H_{10}{}^{35}ClN_2O_2$ $[M+H]^+$ 273.0425, found 273.0433; LRMS (EI, *m/z*): 272 (M^+, 100), 179 (15), 150 (8), 136 (10), 63 (5); IR (film): 922, 1039, 1237, 1465, 1479 cm^{-1}.

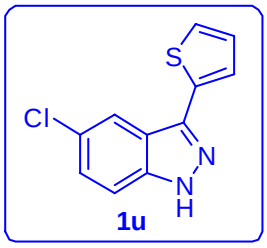
5-Chloro-3-(furan-2-yl)-1*H*-indazole



1t

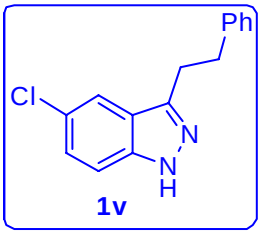
Pale yellow soild; m.p. 170-172 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.75 (br, 1H), 8.07 (s, 1H), 7.59 (s, 1H), 7.38-7.33 (m, 2H), 6.92 (d, *J* = 3.1 Hz, 1H), 6.58 (d, *J* = 1.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 148.21, 142.61, 139.60, 137.27, 128.02, 127.28, 120.93, 120.71, 111.62, 111.32, 107.51; HRMS (ESI, *m/z*): calcd for $C_{11}H_8{}^{35}ClN_2O$ $[M+H]^+$ 219.0320, found 219.0324; LRMS (EI, *m/z*): 218 (M^+, 100), 189 (18), 155 (29), 126 (17), 109 (8); IR (film): 734, 790, 923, 994, 1308 cm^{-1}.

5-Chloro-3-(thiophen-2-yl)-1*H*-indazole



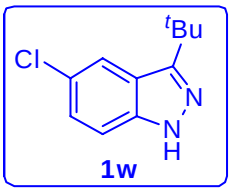
Pale yellow soild; m.p. 179-181 °C. ^{1}H NMR (400 MHz, CD_3COCD_3) δ 12.50 (br, 1H), 8.13 (d, *J* = 1.3 Hz, 1H), 7.80-7.79 (m, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.52 (d, *J* = 5.1 Hz, 1H), 7.43 (q, J_1 = 8.9 Hz, J_2 = 1.8 Hz, 1H), 7.22 (q, J_1 = 5.0 Hz, J_2 = 3.7 Hz, 1H); ^{13}C NMR (100 MHz, CD_3COCD_3) 141.01, 140.00, 136.45, 128.34, 127.63, 127.06, 125.72, 125.26, 121.47, 120.24, 112.72; HRMS (ESI, *m/z*): calcd for $C_{11}H_8{}^{35}ClN_2S$ $[M+H]^+$ 235.0091, found 235.0094; LRMS (EI, *m/z*): 234 (M^+, 100), 205 (5), 171 (12), 117 (6), 63 (5); IR (film): 700, 789, 802, 919, 1479 cm^{-1}.

5-Chloro-3-phenethyl-1*H*-indazole



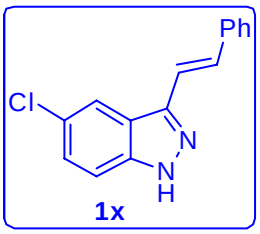
Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.60 (br, 1H), 7.45 (s, 1H), 7.24-7.10 (m, 7H), 3.18 (t, *J* = 7.9 Hz, 2H), 3.03 (t, *J* = 7.9 Hz, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) 146.11, 141.28, 139.49, 128.42, 128.39, 127.39, 126.15, 125.88, 123.04, 119.47, 110.91, 35.16, 29.00; HRMS (ESI, *m/z*): calcd for $C_{15}H_{14}{}^{35}ClN_2$ $[M+H]^+$ 257.0840, found 257.0835; LRMS (EI, *m/z*): 256 (M^+, 71), 165 (100), 138 (7), 91 (24), 65 (8); IR (film): 701, 799, 918, 1047, 1497 cm^{-1}.

3-(*tert*-Butyl)-5-chloro-1*H*-indazole



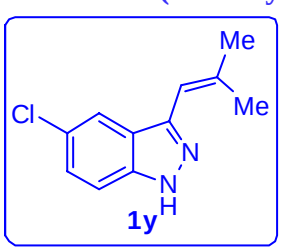
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.07 (br, 1H), 7.84 (d, *J* = 1.3 Hz, 1H), 7.34 (d, J = 8.8 Hz, 1H), 7.28 (dd, *J* = 1.6, 8.8 Hz, 1H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 153.98, 140.29, 126.85, 125.28, 121.28, 111.09, 33.65, 29.88; HRMS (ESI, *m/z*): calcd for $C_{11}H_{14}{}^{35}ClN_2$ $[M+H]^+$ 209.0840, found 209.0835; LRMS (EI, *m/z*): 208 (M^+, 22), 193 (100), 165 (6), 153 (16), 128 (4); IR (film): 734, 800, 926, 1206, 1476 cm^{-1}.

(*E*)-5-chloro-3-styryl-1*H*-indazole



Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.40 (br, 1H), 7.86 (s, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.38-7.27 (m, 5H), 7.22-7.20 (m, 2H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.07 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 143.43, 139.93, 136.76, 131.78, 128.77, 128.16, 127.71, 127.05, 126.55, 121.96, 120.16, 119.10, 111.33; HRMS (ESI, *m/z*): calcd for $C_{15}H_{12}{}^{35}ClN_2$ $[M+H]^+$ 255.0684, found 255.0683; LRMS (EI, *m/z*): 254 (M^+, 52), 253 (100), 218 (40), 189 (9), 109 (5); IR (film): 694, 740, 924, 1316, 1475 cm^{-1}.

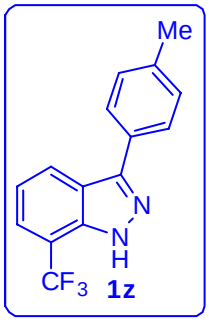
5-Chloro-3-(2-methylprop-1-en-1-yl)-1*H*-indazole



Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.59 (br, 1H), 7.69 (s, 1H), 7.38-7.30 (m, 2H), 6.40 (s, 1H), 2.12 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 143.79, 140.84, 138.97, 127.36, 126.12, 123.70, 119.77, 113.44, 110.72, 26.85, 20.74; HRMS (ESI, *m/z*): calcd for $C_{11}H_{12}{}^{35}ClN_2$ $[M+H]^+$ 207.0684, found 207.0679; LRMS (EI, *m/z*): 206 (M^+, 100), 189 (19), 155 (23), 128 (7),

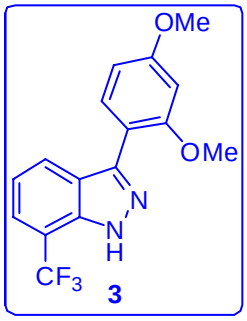
85 (9); IR (film): 772, 797, 922, 1307, 1486 cm^{-1}.

3-*p*-Tolyl-7-(trifluoromethyl)-1*H*-indazole



Yellow solid; m.p. 150-154 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.69 (br, 1H), 8.21 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 7.2 Hz, 1H), 7.36-7.29 (m, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.49, 138.59, 136.97, 129.69, 129.65, 127.60, 126.38 (q, *J* = 271.1 Hz), 125.57, 124.50 (q, *J* = 4.4 Hz), 122.66, 120.66, 112.91 (q, *J* = 34.1 Hz), 21.34; HRMS (ESI, *m/z*): calcd for $C_{15}H_{12}F_3N_2$ $[M+H]^+$ 277.0947, found 277.0955; LRMS (EI, *m/z*): 276 (M^+, 100), 256 (17), 241 (6), 227 (6), 128 (5); IR (film): 1095, 1110, 1164, 1320, 1713 cm^{-1}.

3-(2,4-Dimethoxyphenyl)-7-(trifluoromethyl)-1*H*-indazole[7]



Yellow solid; m.p. 147-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.59 (br, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.57 (d, *J* = 9.0 Hz, 1H), 7.26-7.21 (m, 1H), 6.66-6.64 (m, 2H), 3.89 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.63, 158.32, 144.26, 136.83, 131.97, 126.73, 124.39 (q, *J* = 271.0 Hz), 124.30 (q, *J* = 4.4 Hz), 123.87, 119.93, 113.98, 112.90 (q, *J* = 34.1 Hz), 104.98, 99.03, 55.49.

4. References

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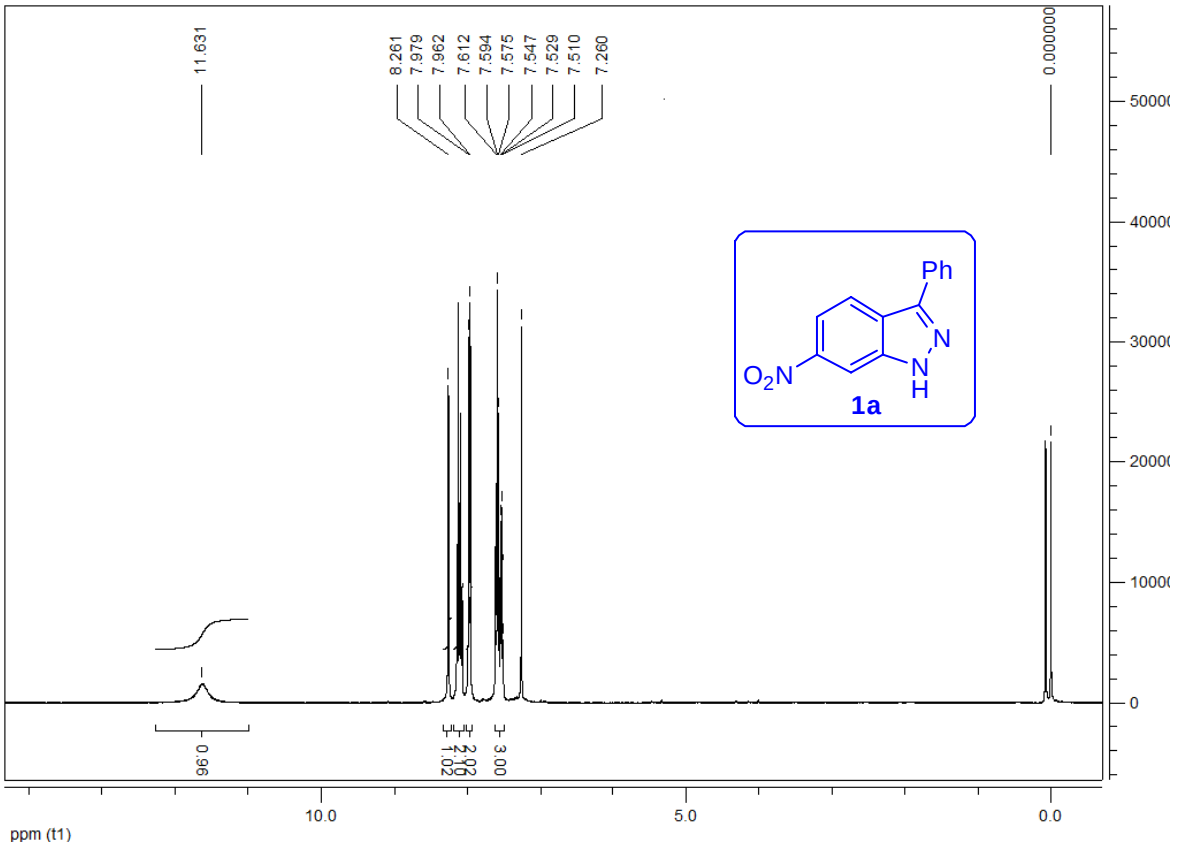
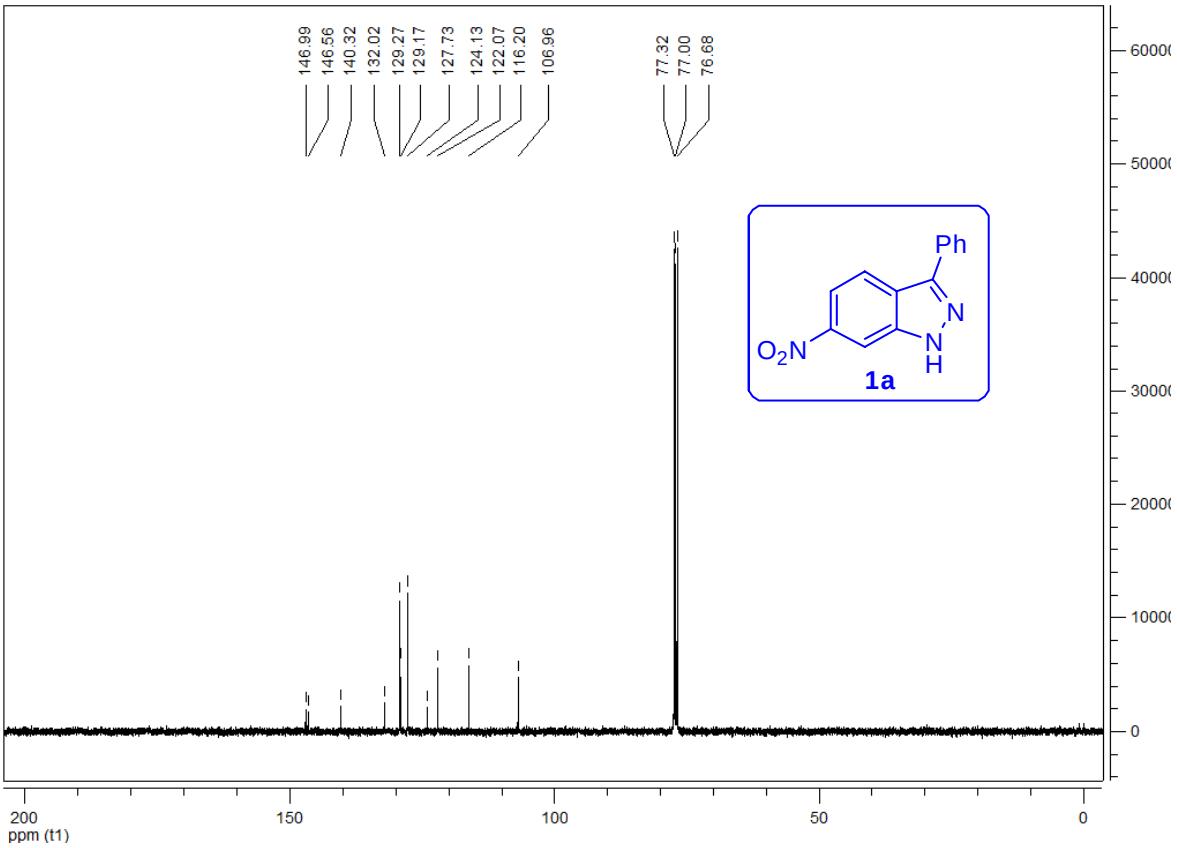
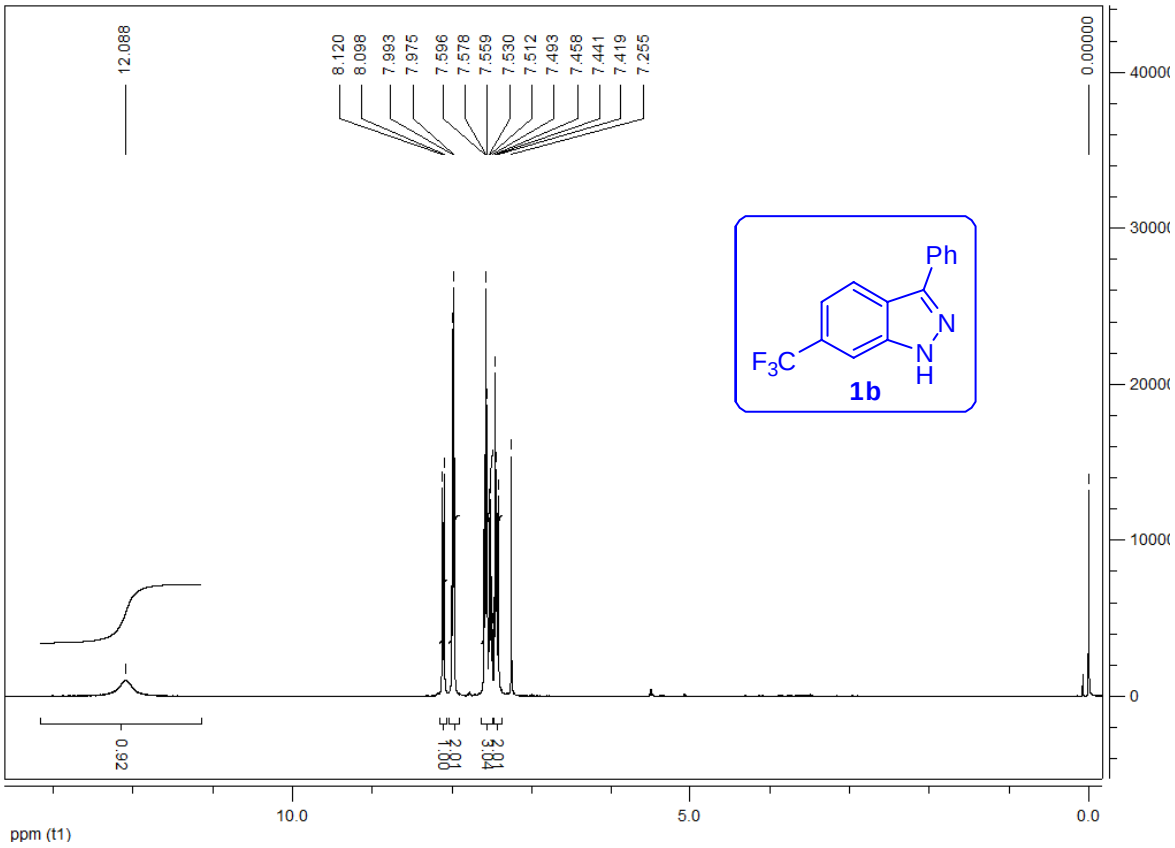
7 I. A. Murray, G. Krishnegowda, B. C. DiNatale, C. Flaveny, C. Chiaro, J. -M. Lin, A. K. Sharma, S. Amin and G. H. Perdew, *Chem. Res. Toxicol*. 2010, **23**, 955.

5. ^{1}H NMR and ^{13}C NMR Spectra



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7.578
7.559
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7.441
7.419
7.255
0.00000
Ph
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N
H
F3C
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10.0
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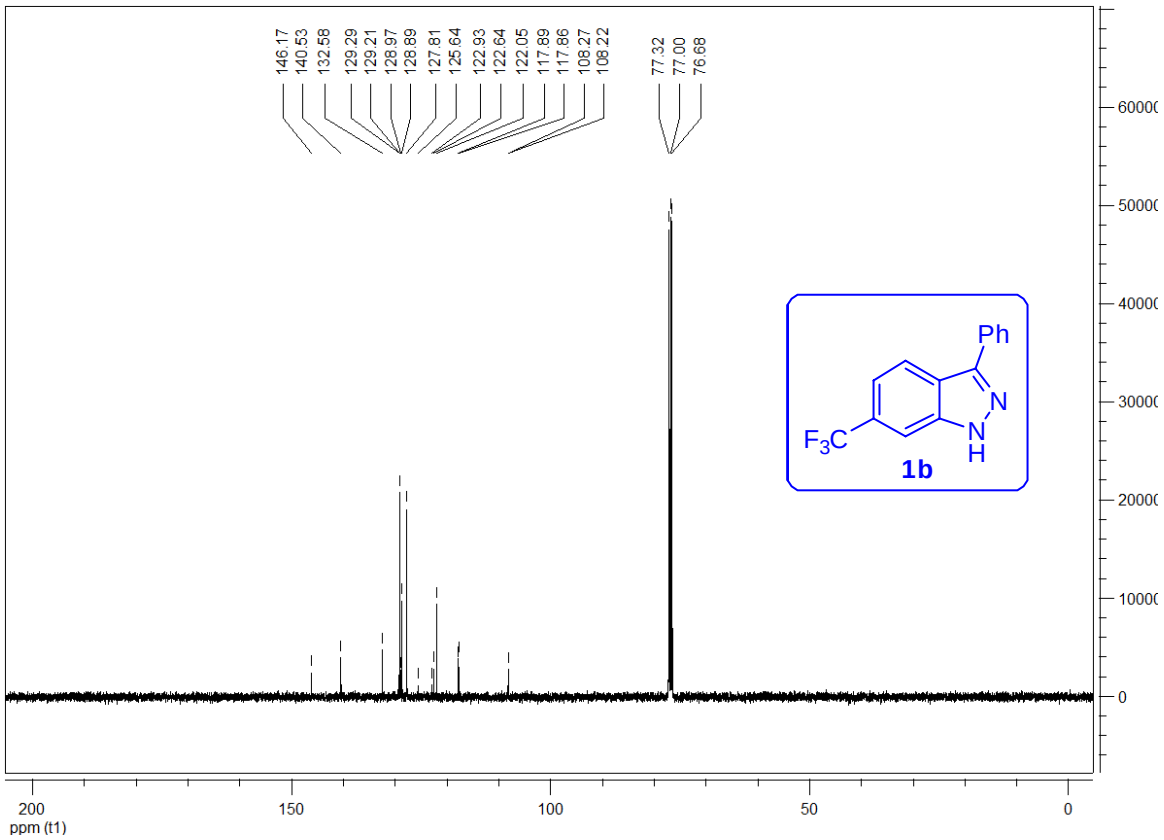
0.0
ppm (t1)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128.97
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122.93
122.64
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108.27
108.22
77.32
77.00
76.68
Ph
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N
H
F3C
1b
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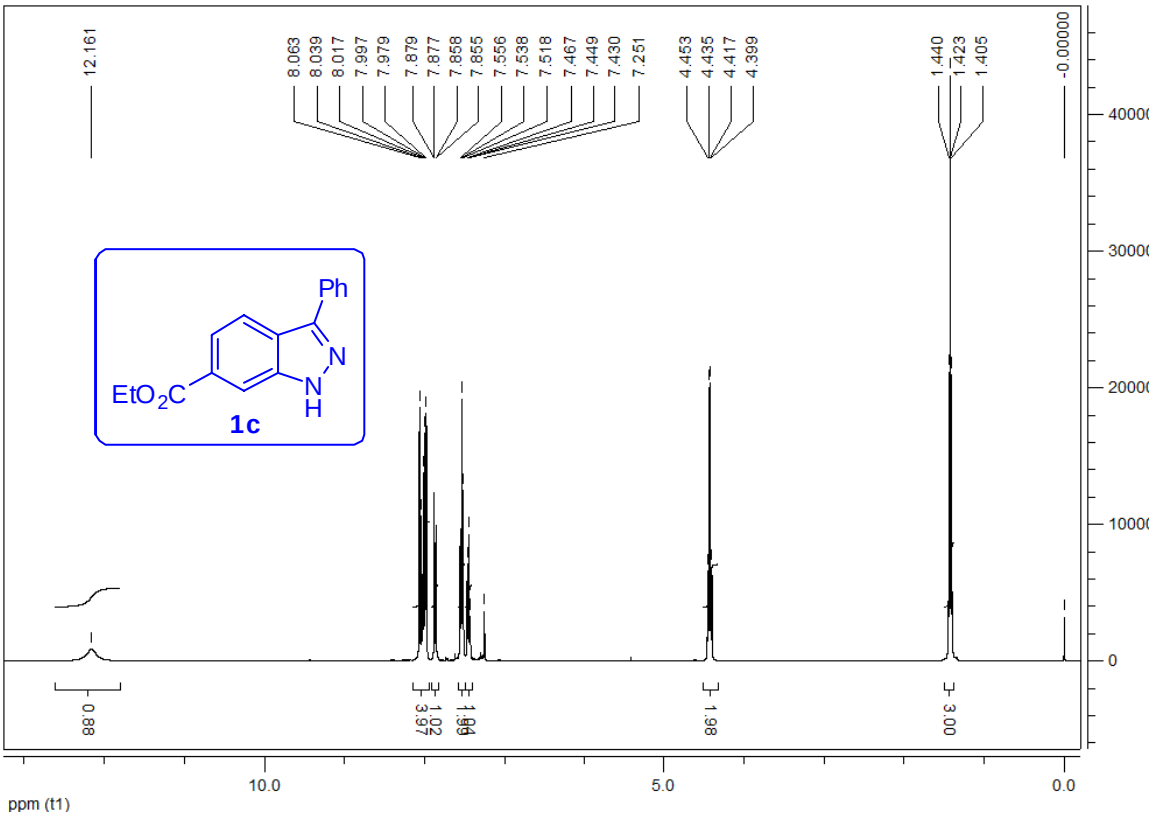
150
100
50
0
ppm (t1)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7.518
7.467
7.449
7.430
7.251
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1.405
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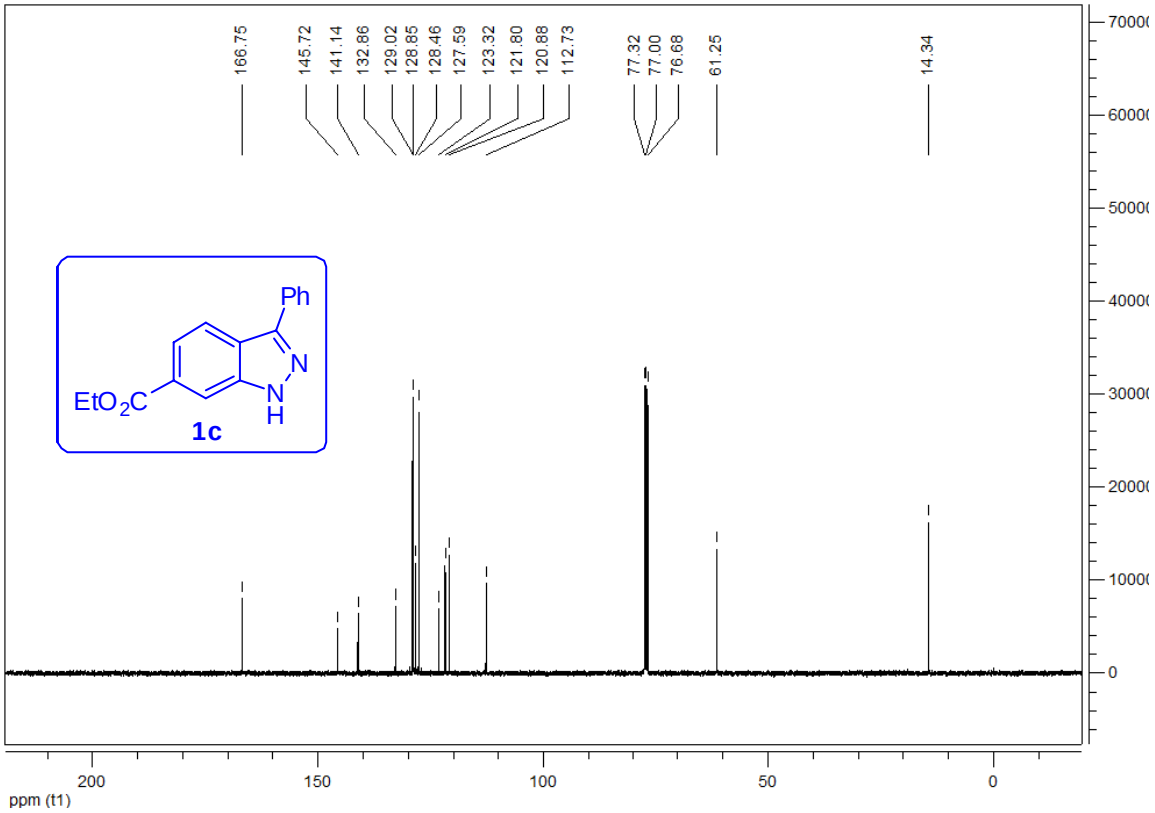
ppm (t1)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128.46
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121.80
120.88
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77.32
77.00
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14.34
Ph
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N
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EtO2C
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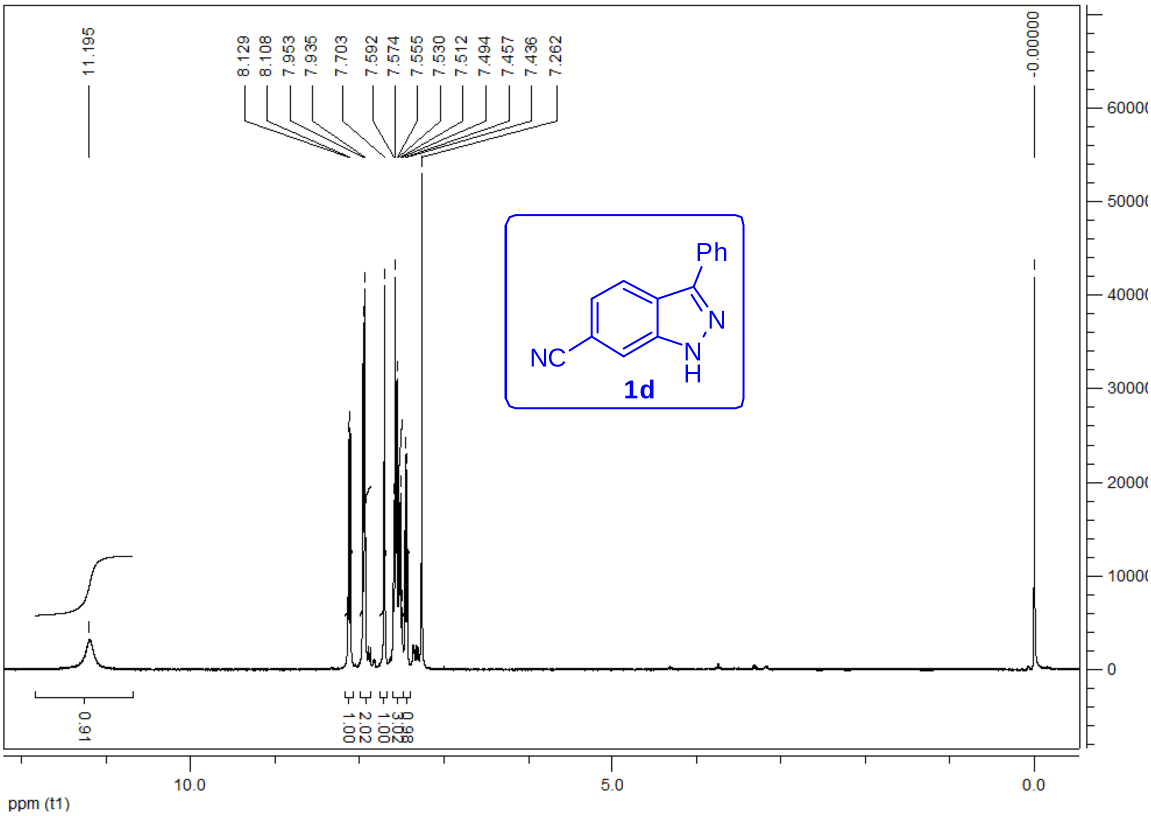
50
0
ppm (t1)



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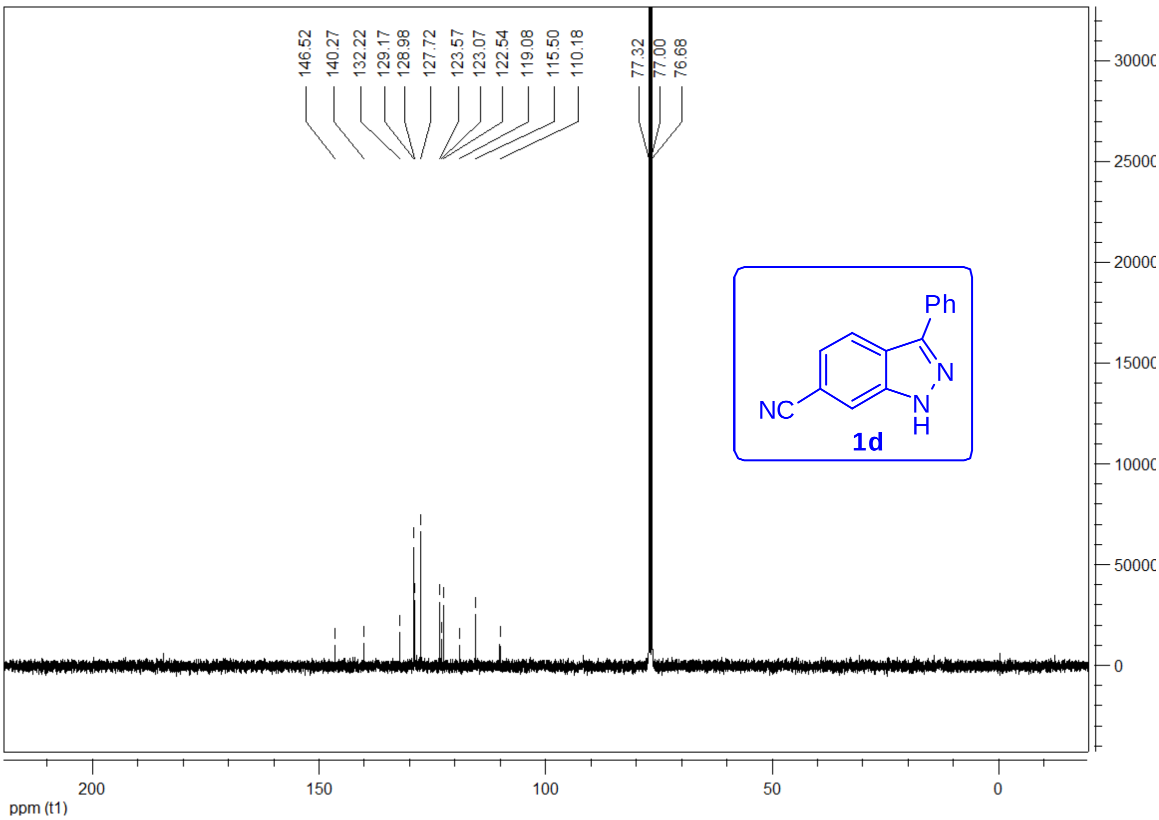
ppm (t1)



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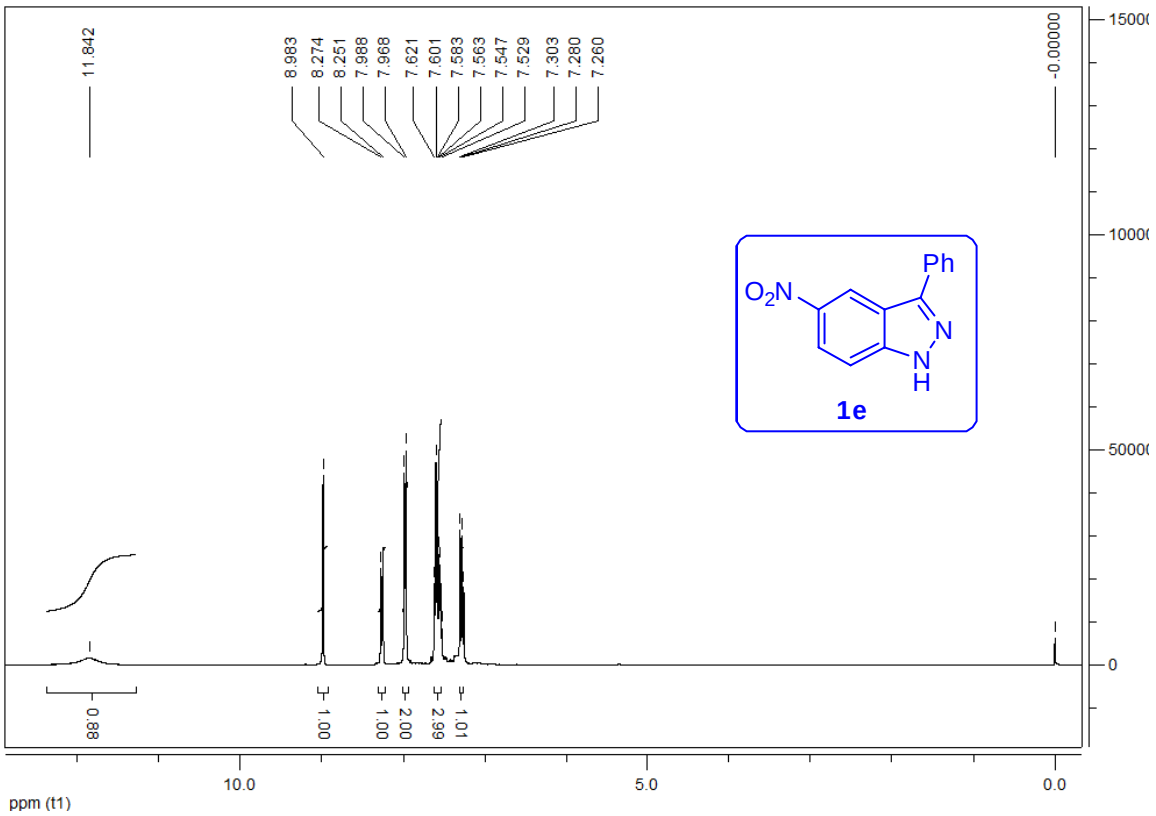
ppm (t1)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7.260
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N
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H
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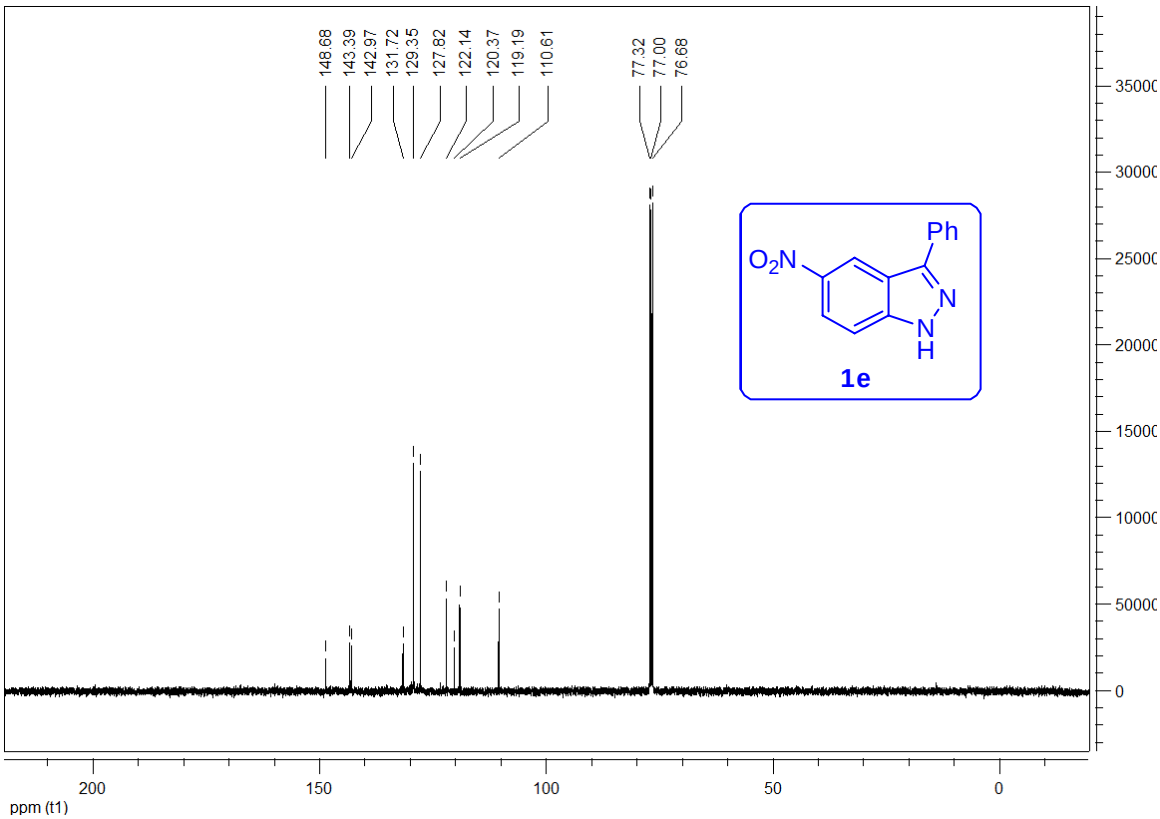
ppm (t1)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120.37
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110.61
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Ph
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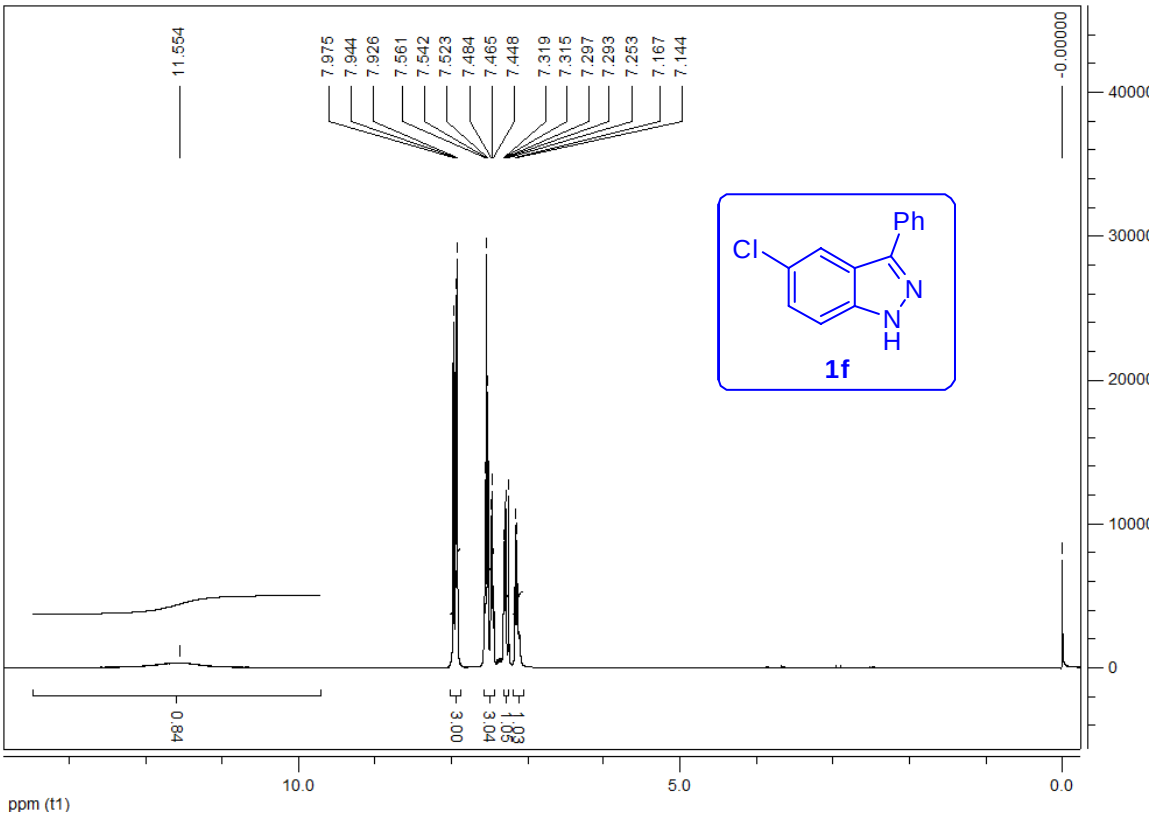
N
N
H
1e
200
150
100
50
0
ppm (t1)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7.167
7.144
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Ph
Cl
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N
H
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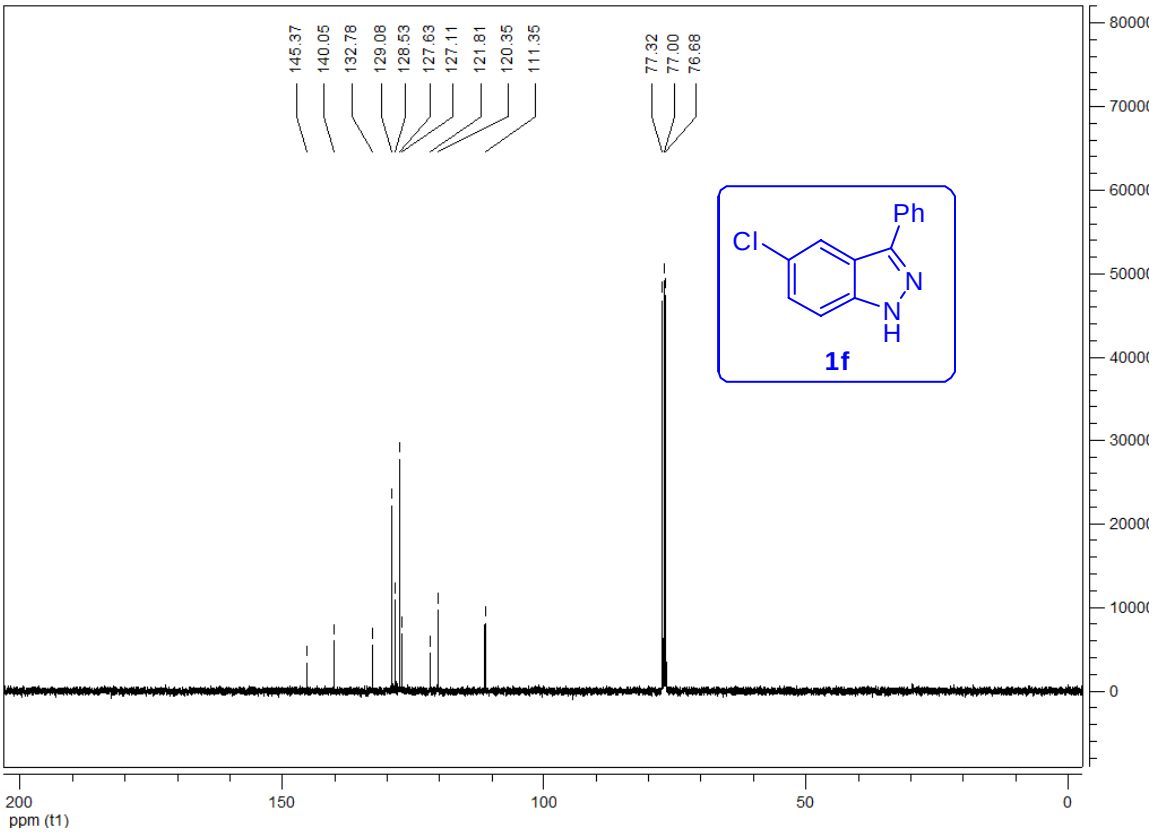
1.08
2.03
10.0
5.0
0.0
ppm (t1)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140.05
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127.11
121.81
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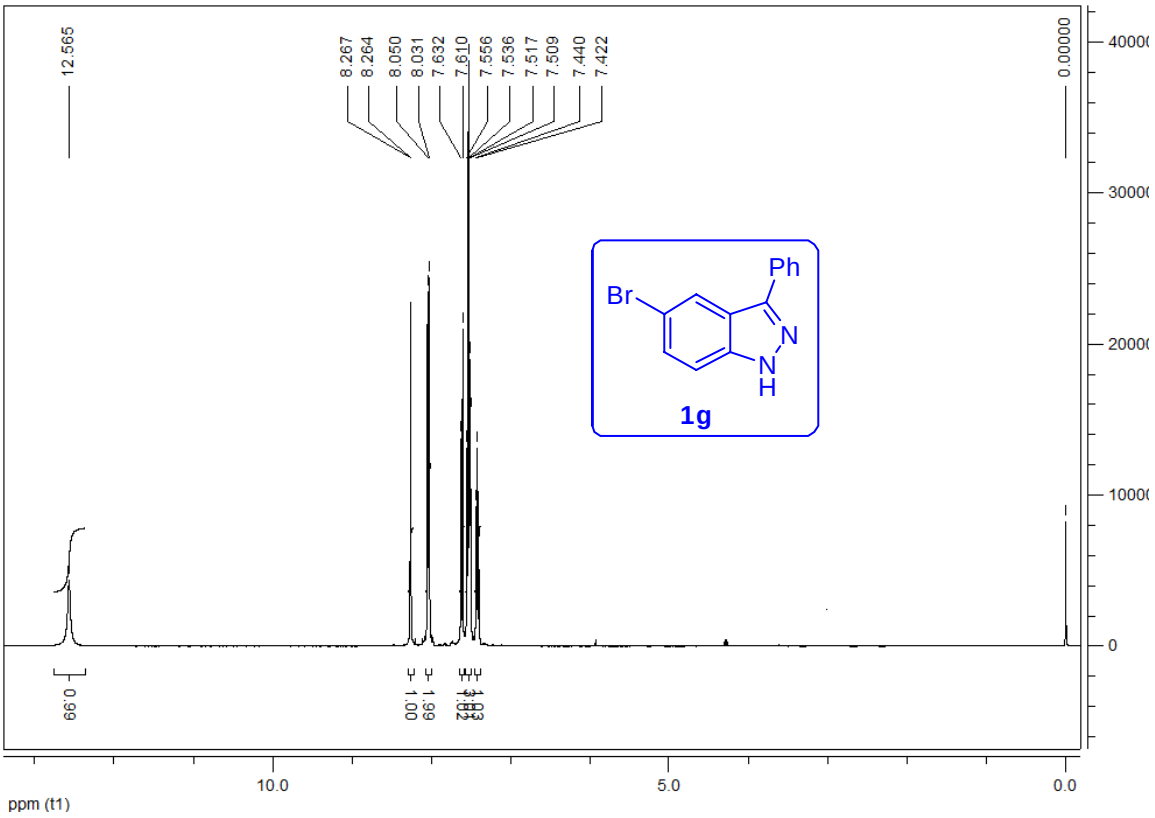
111.35
77.32
77.00
76.68
Ph
Cl
N
N
H
1f
200
150
100
50
0
ppm (t1)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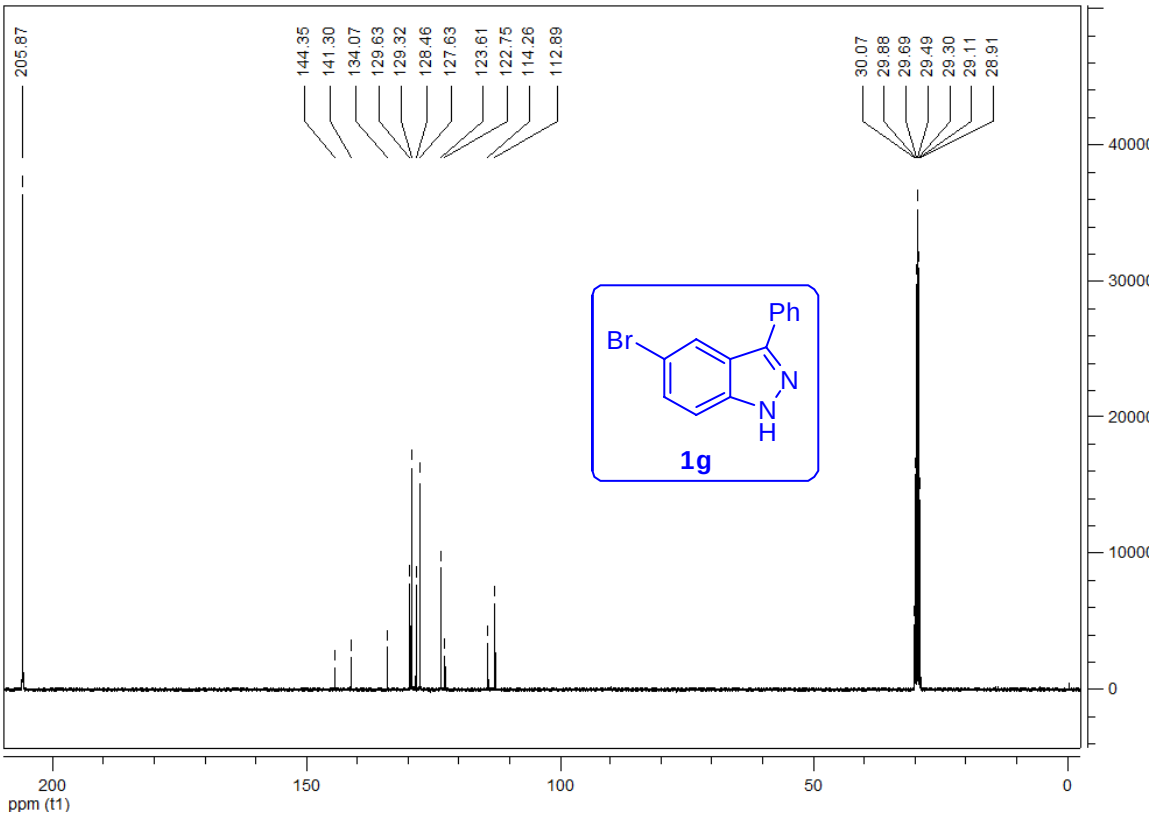
ppm (t1)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29.69
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Ph
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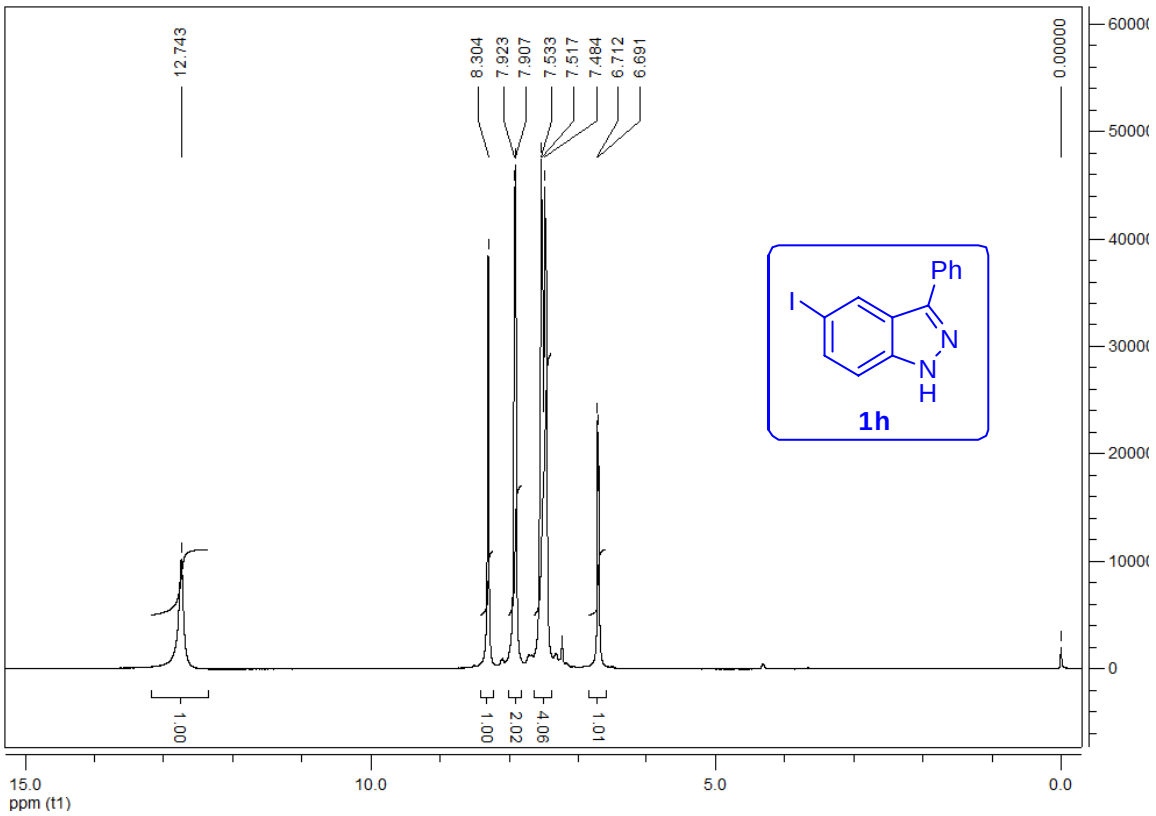
ppm (t1)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I
N
N
H
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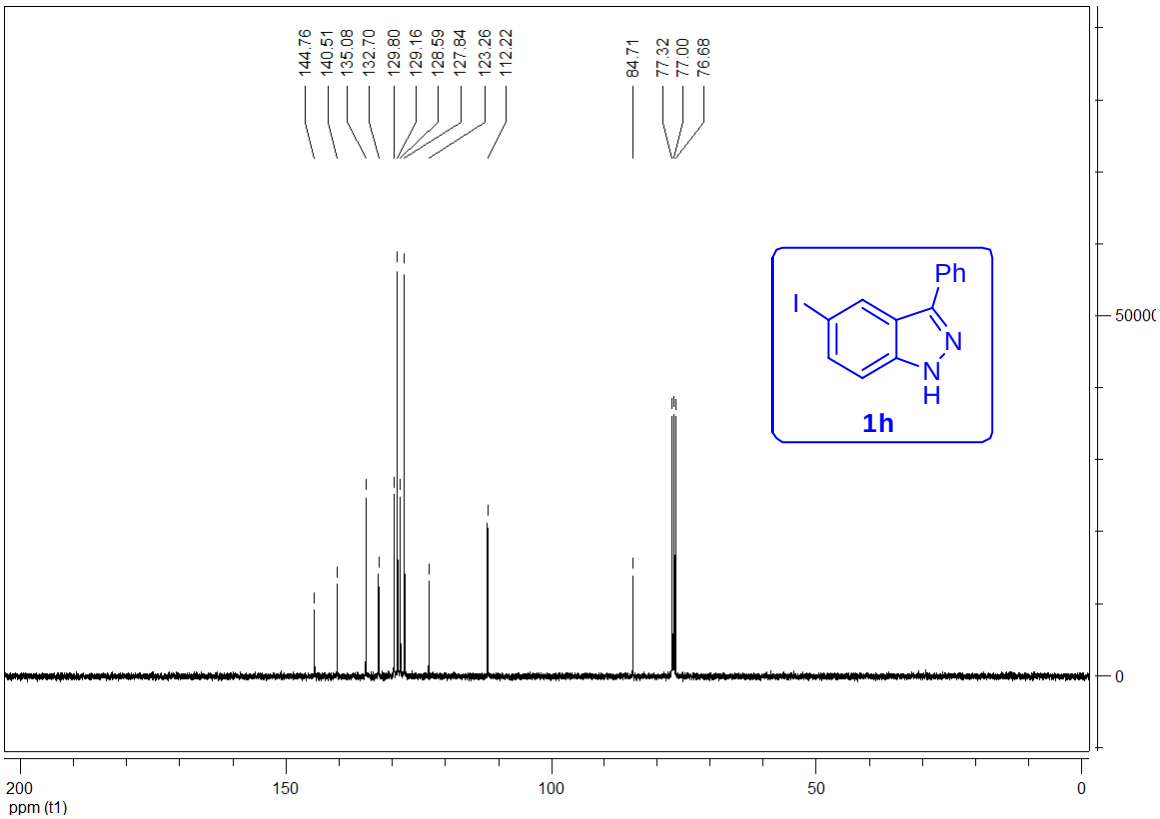
15.0
10.0
5.0
0.0
ppm (t1)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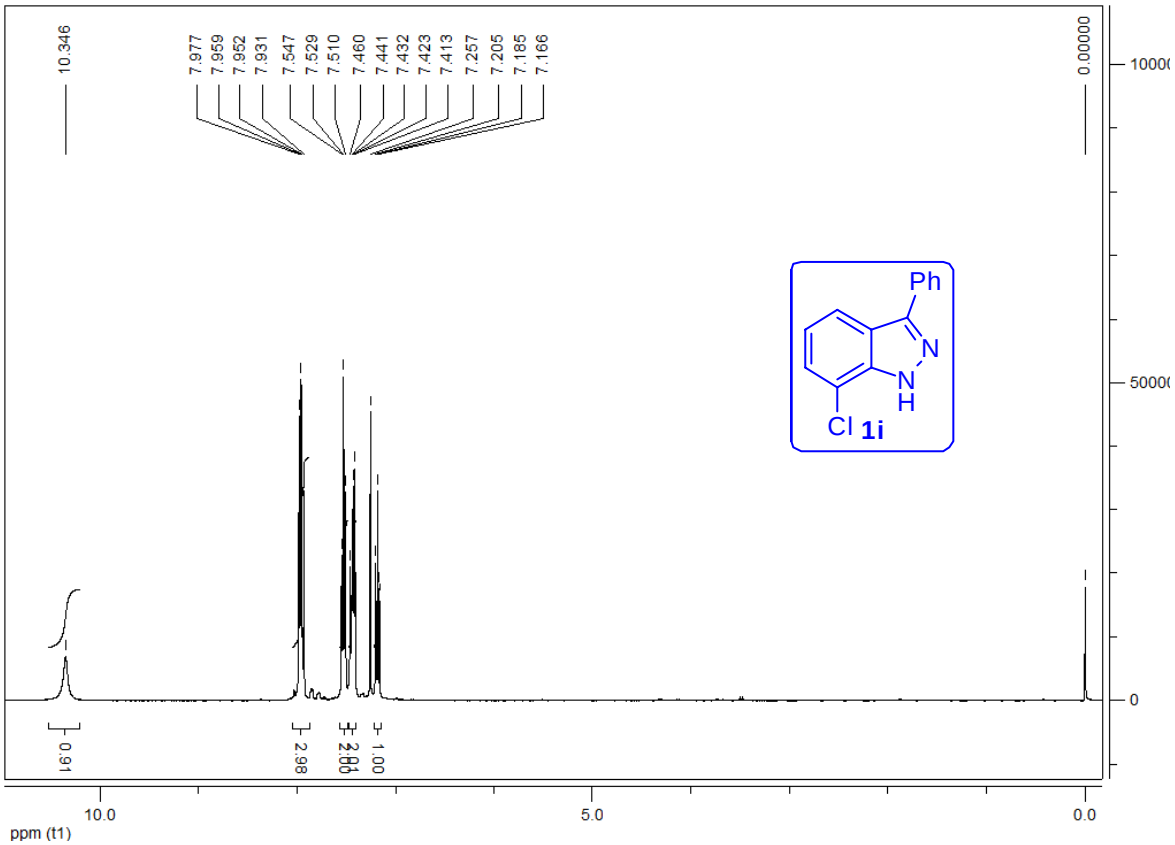
140.51
135.08
132.70
129.80
129.16
128.59
127.84
123.26
112.22
84.71
77.32
77.00
76.68
Ph
I
N
N
H
1h
200
150
100
50
0
ppm (t1)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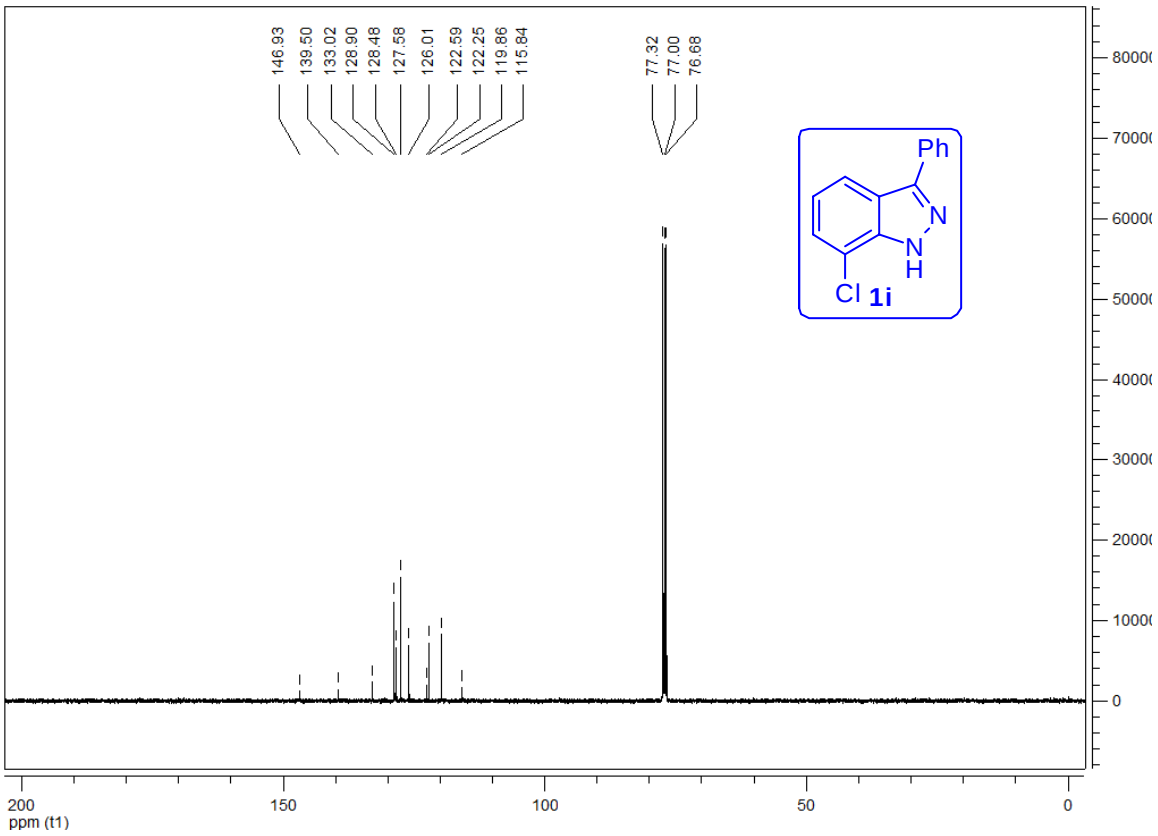
7.959
7.952
7.931
7.547
7.529
7.510
7.460
7.441
7.432
7.423
7.413
7.257
7.205
7.185
7.166
0.00000
0.91
2.98
2.00
1.00
10.0
5.0
0.0
ppm (t1)
Ph
N
N
H
Cl
1i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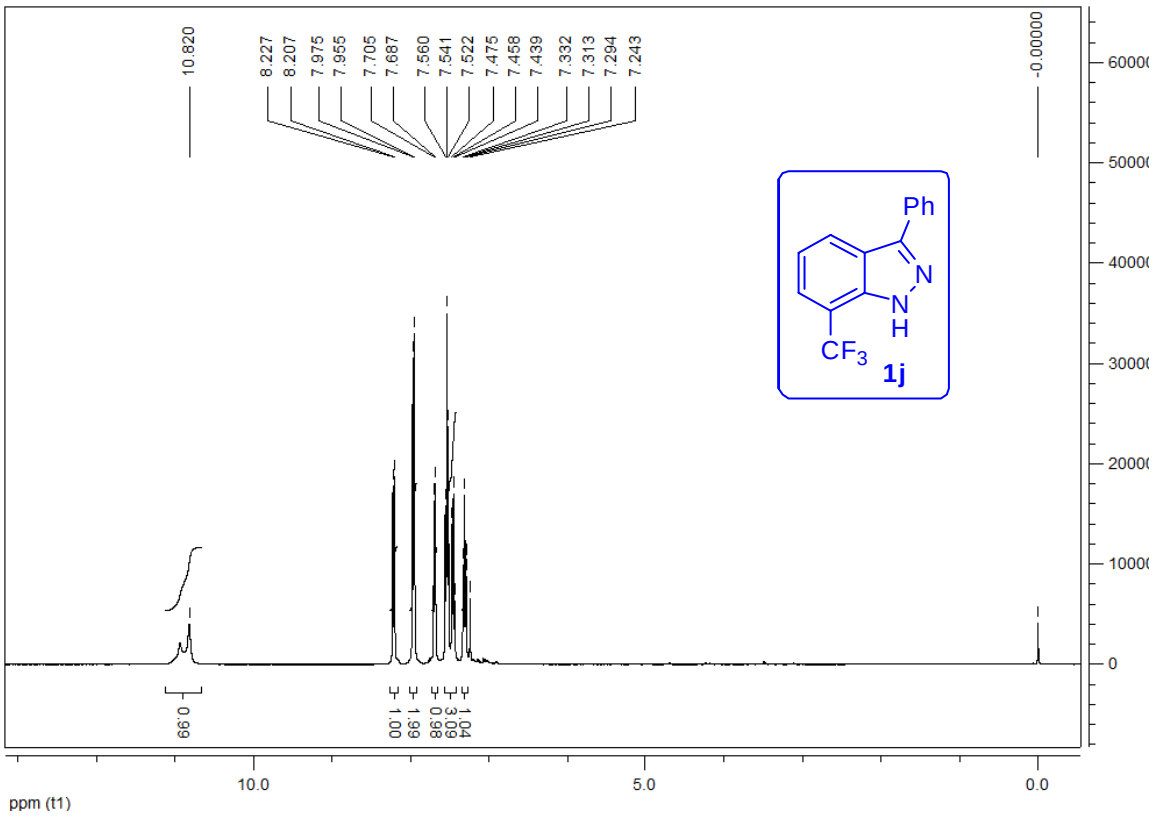
139.50
133.02
128.90
128.48
127.58
126.01
122.59
122.25
119.86
115.84
77.32
77.00
76.68
200
150
100
50
0
ppm (t1)
Ph
N
N
H
Cl
1i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8.227
8.207
7.975
7.955
7.705
7.687
7.560
7.541
7.522
7.475
7.458
7.439
7.332
7.313
7.294
7.243
-0.00000
Ph
N
N
H
CF3
1j
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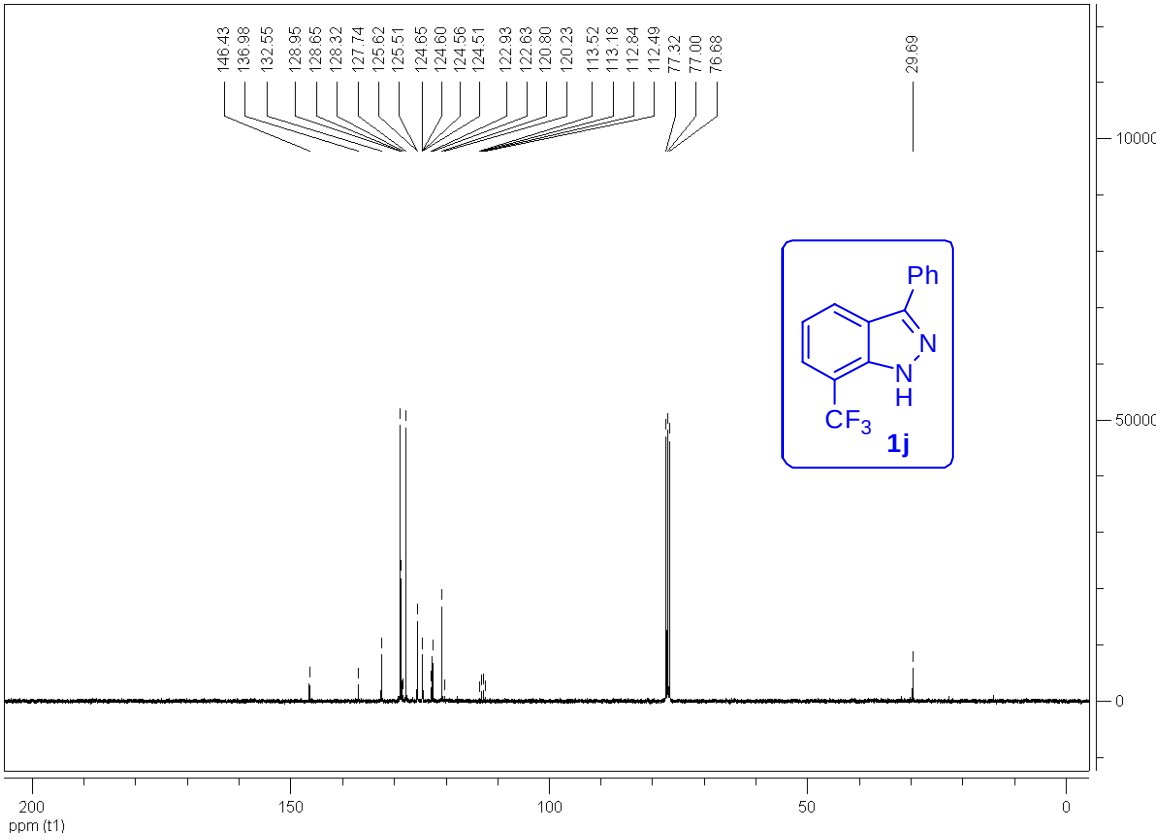
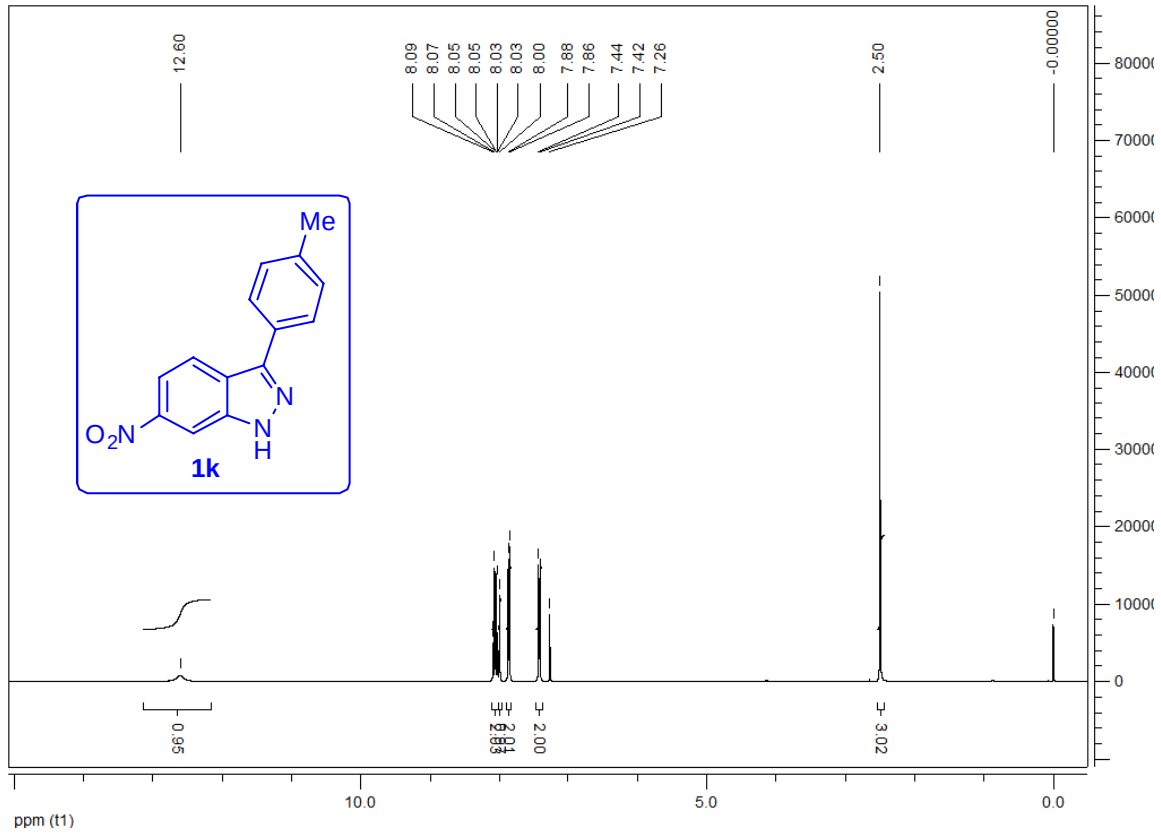
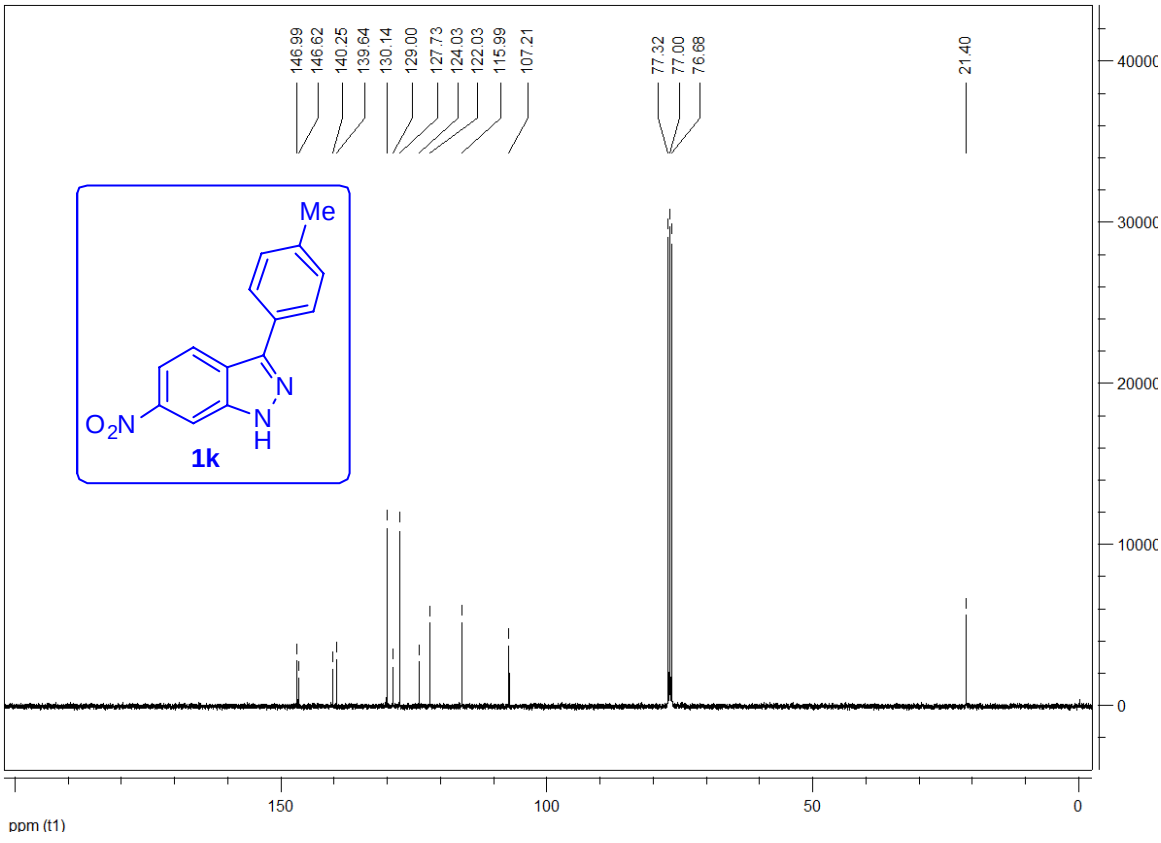
1.00
1.99
0.98
3.09
1.04
10.0
5.0
0.0
ppm (t1)


146.43
136.98
132.55
128.95
128.65
128.32
127.74
125.62
125.51
124.65
124.60
124.56
124.51
122.93
122.63
120.80
120.23
113.52
113.18
112.84
112.49
77.32
77.00
76.68
29.69
Ph
N
N
H
CF3
1j
200
150
100
50
0
ppm (t1)


12.60
8.09
8.07
8.05
8.05
8.03
8.03
8.00
7.88
7.86
7.44
7.42
7.26
2.50
-0.00000
Me
N
N
H
O2N
1k
0.96
2.00
3.02
10.0
5.0
0.0
ppm (t1)


146.99
146.62
140.25
139.64
130.14
129.00
127.73
124.03
122.03
115.99
107.21
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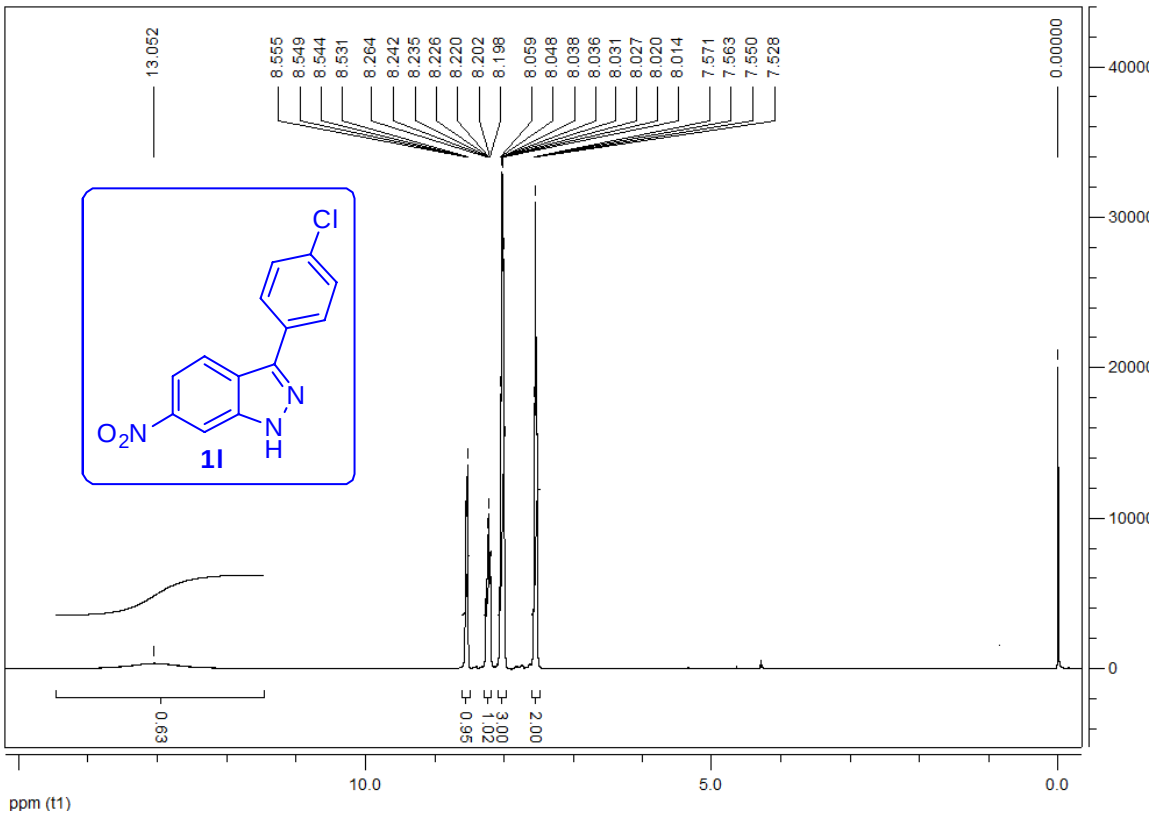
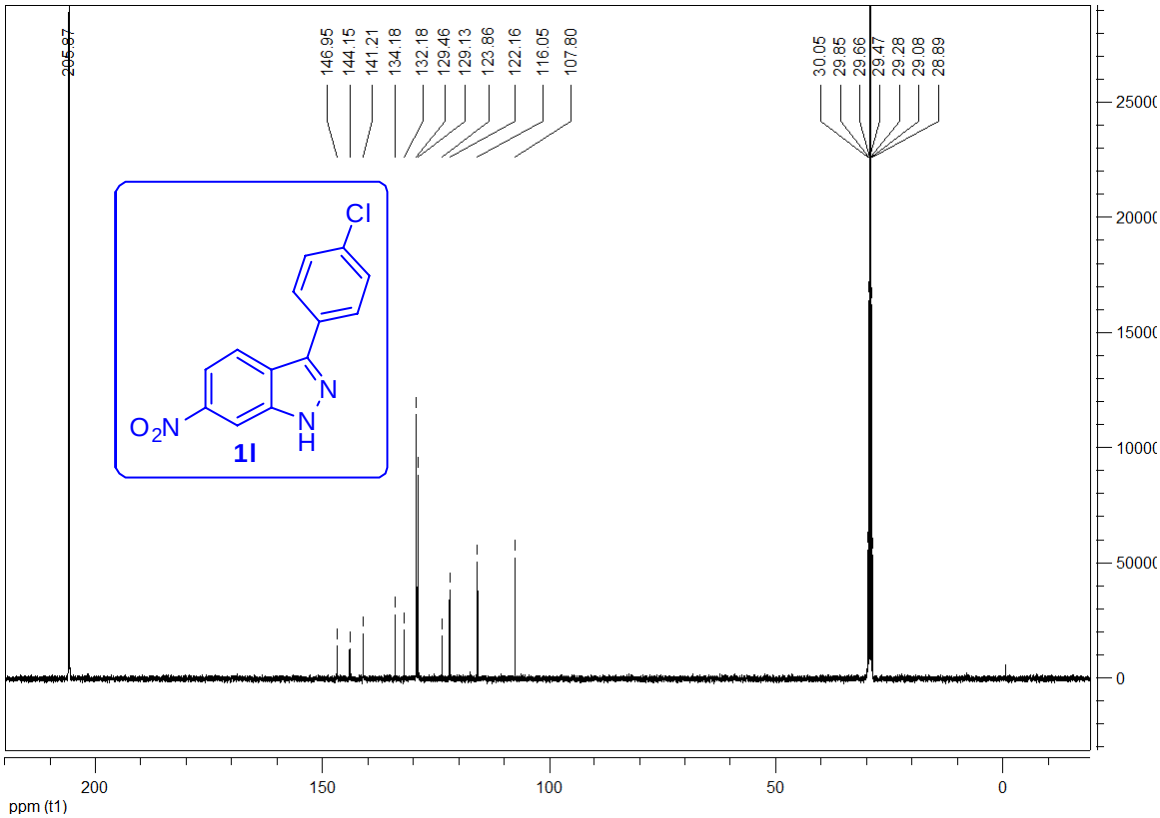
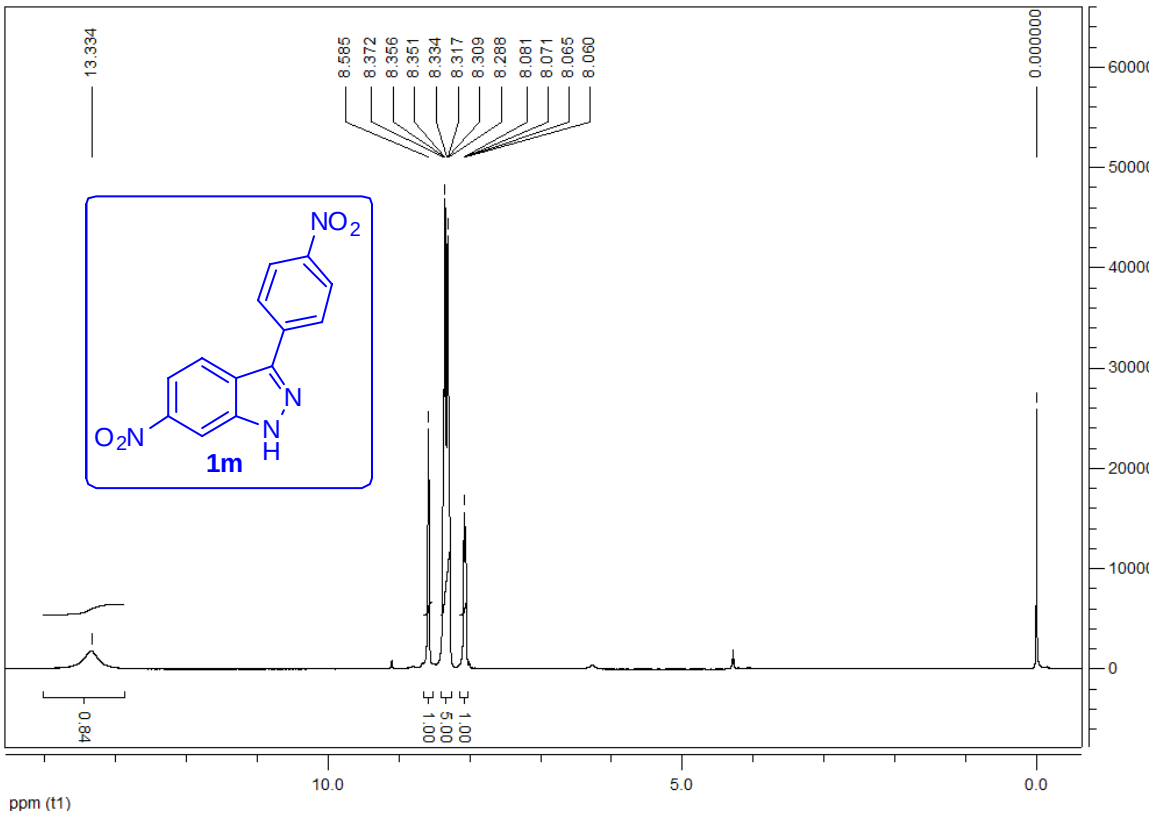
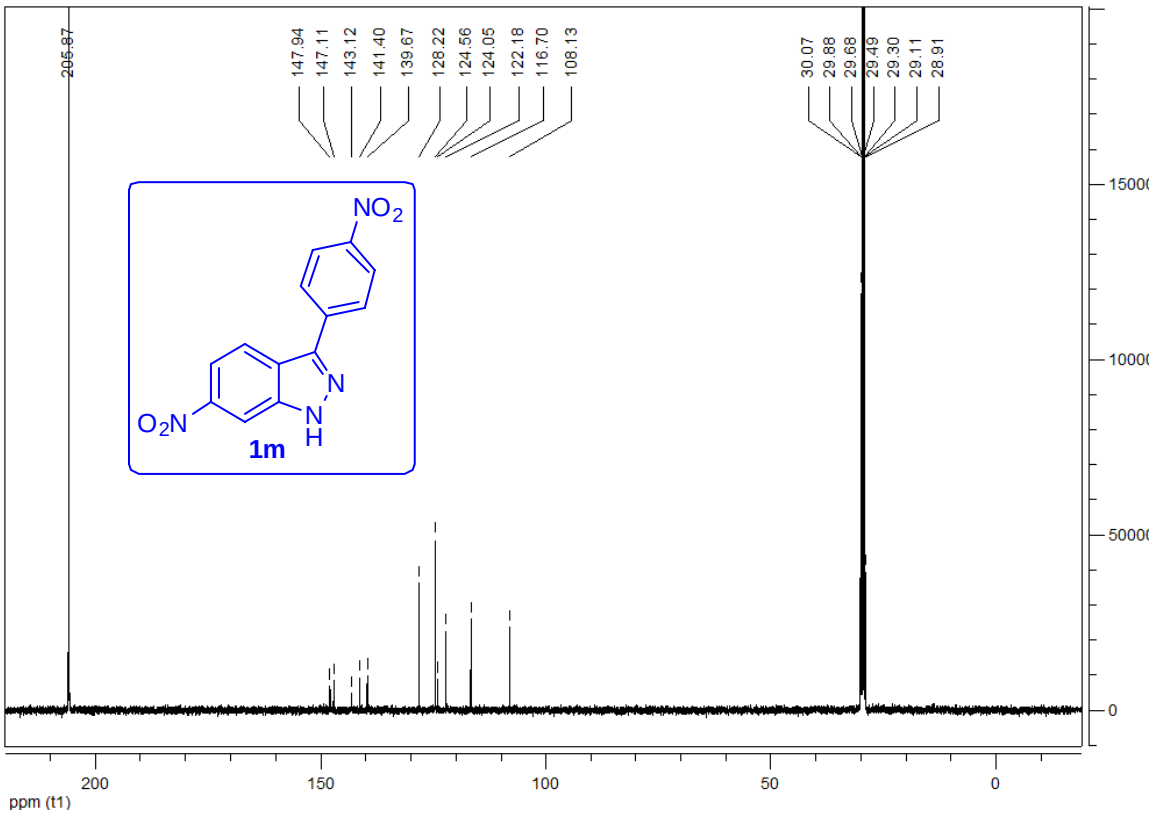
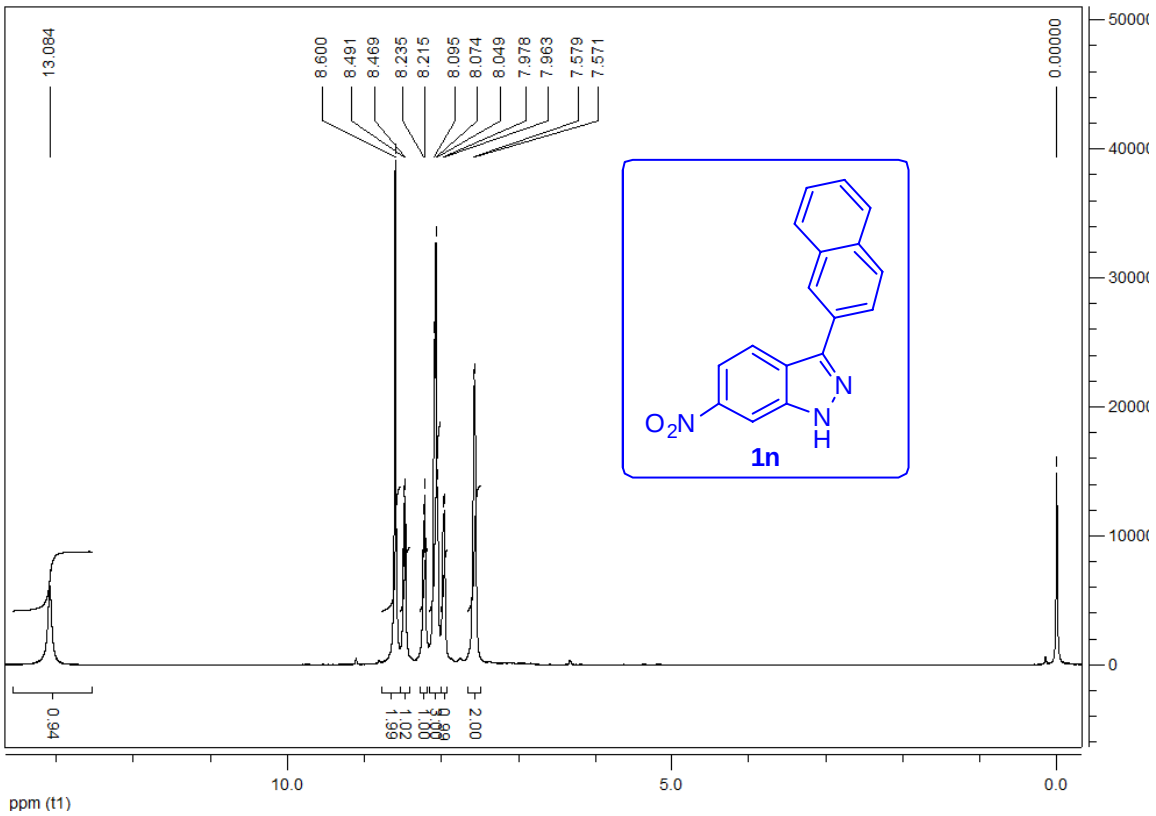
77.00
76.68
21.40
Me
N
N
H
O2N
1k
150
100
50
0
ppm (t1)

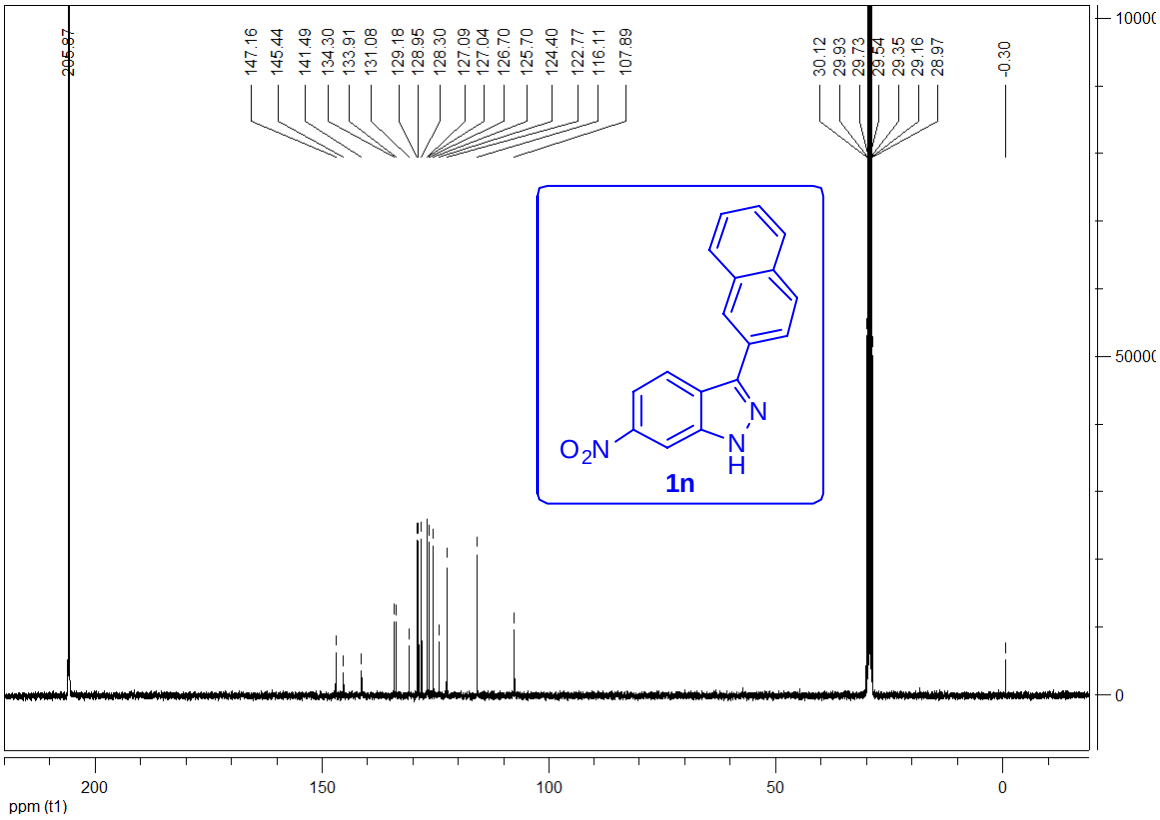

13.052
8.555
8.549
8.544
8.531
8.264
8.242
8.235
8.226
8.220
8.202
8.198
8.059
8.048
8.038
8.036
8.031
8.027
8.020
8.014
7.571
7.563
7.550
7.528
0.00000
Cl
O2N
N
N
H
1l
0.63
0.95
1.02
3.00
2.00
10.0
5.0
0.0
ppm (t1)

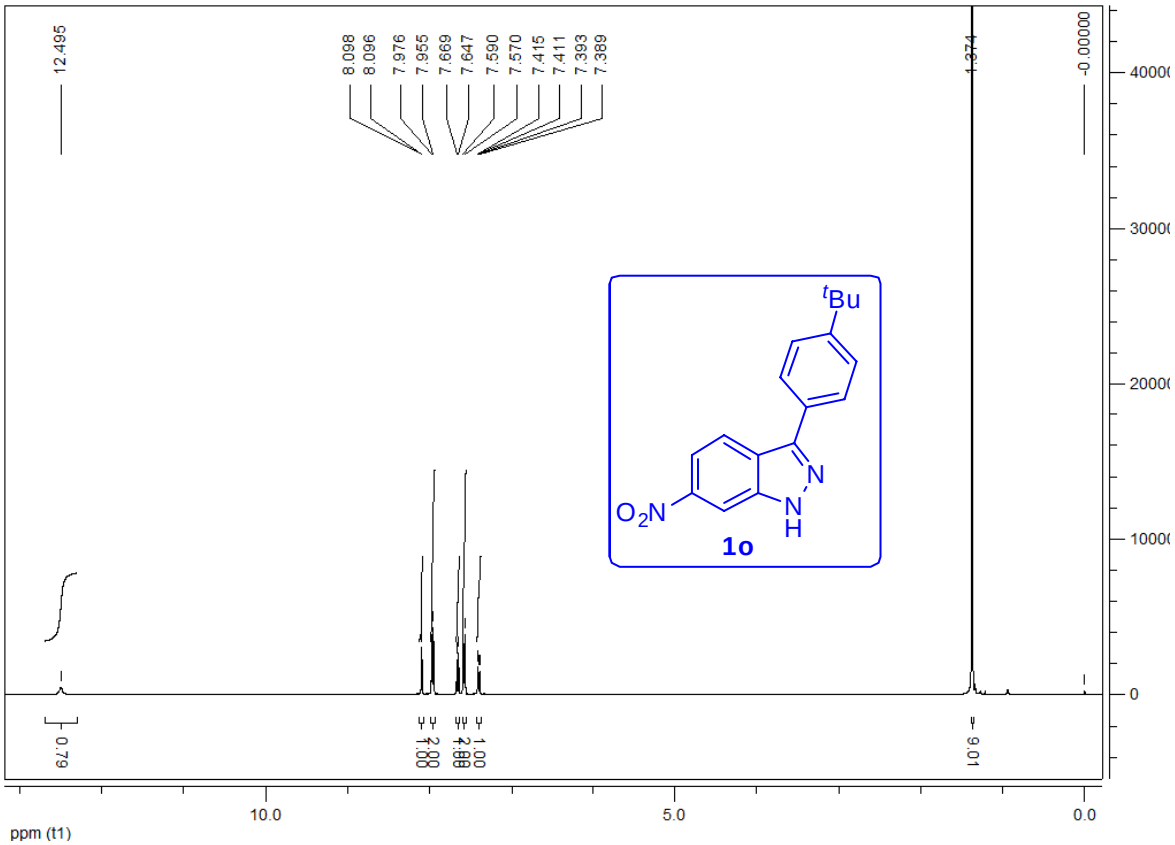

206.87
146.95
144.15
141.21
134.18
132.18
129.46
129.13
123.86
122.16
116.05
107.80
30.05
29.85
29.66
29.47
29.28
29.08
28.89
Cl
O2N
N
N
H
1l
200
150
100
50
0
ppm (t1)


13.334
8.585
8.372
8.356
8.351
8.334
8.317
8.309
8.288
8.081
8.071
8.065
8.060
0.000000
NO2
O2N
N
N
H
1m
0.84
1.00
5.00
1.00
10.0
5.0
0.0
ppm (t1)


205.87
147.94
147.11
143.12
141.40
139.67
128.22
124.56
124.05
122.18
116.70
108.13
30.07
29.88
29.68
29.49
29.30
29.11
28.91
NO2
O2N
N
N
H
1m
200
150
100
50
0
ppm (t1)


13.084
8.600
8.491
8.469
8.235
8.215
8.095
8.074
8.049
7.978
7.963
7.579
7.571
0.00000
0.94
1.99
1.02
1.00
2.00
O_2N
N
N
H
1n
10.0
5.0
0.0
ppm (t1)


206.87
147.16
145.44
141.49
134.30
133.91
131.08
129.18
128.95
128.30
127.09
127.04
126.70
125.70
124.40
122.77
116.11
107.89
30.12
29.93
29.73
29.54
29.35
29.16
28.97
-0.30
O_2N
N
N
H
1n
200
150
100
50
0
ppm (t1)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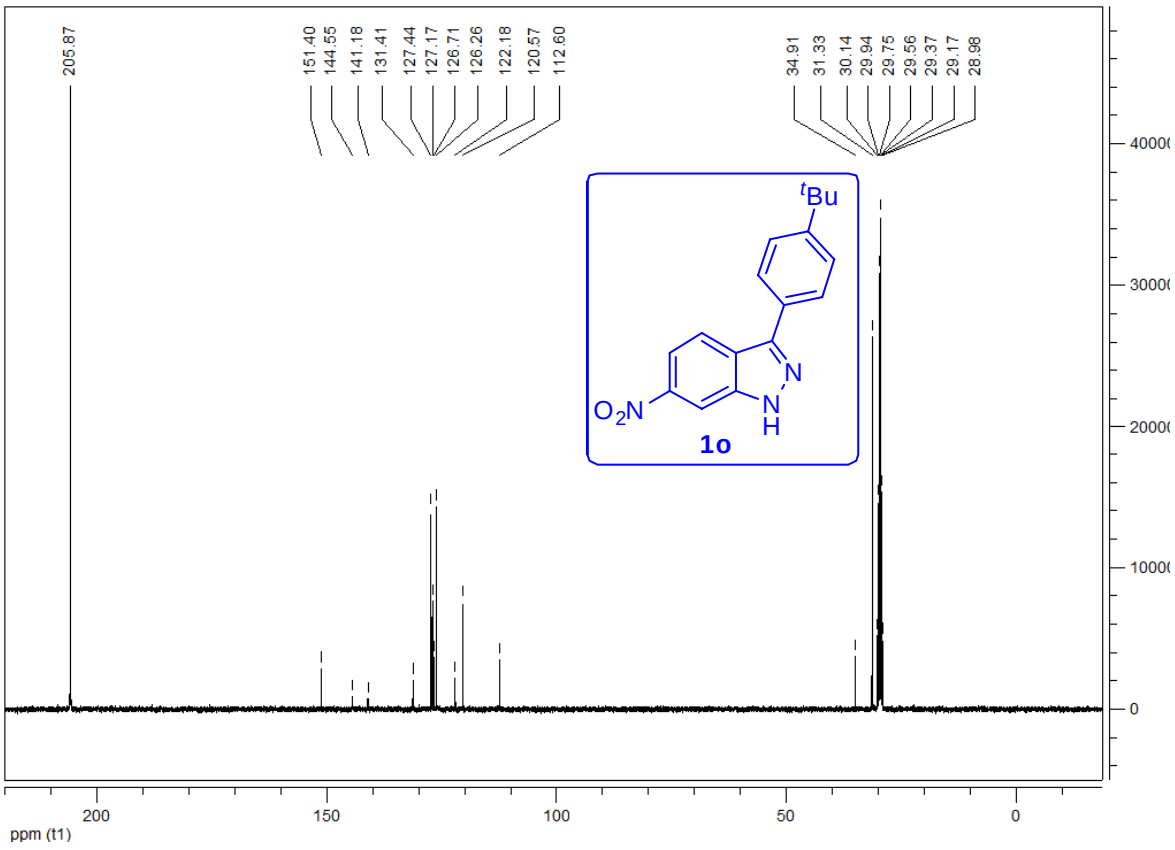
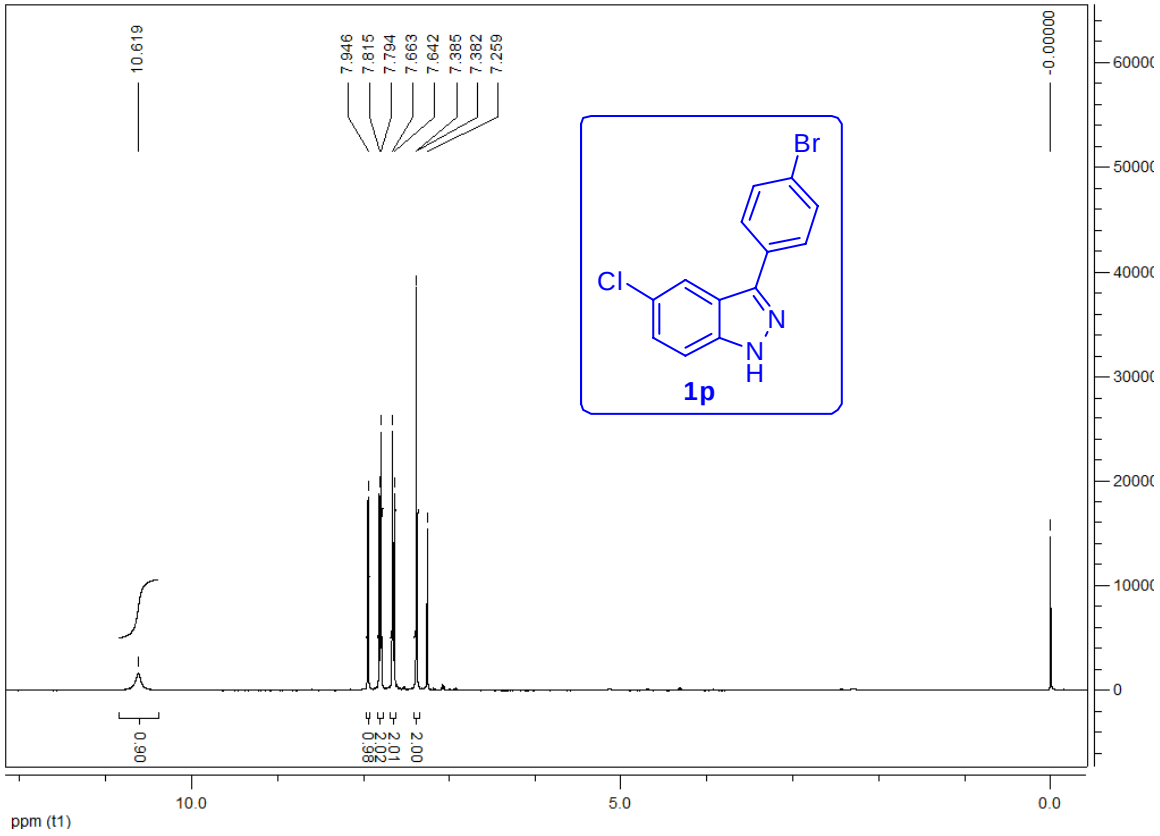
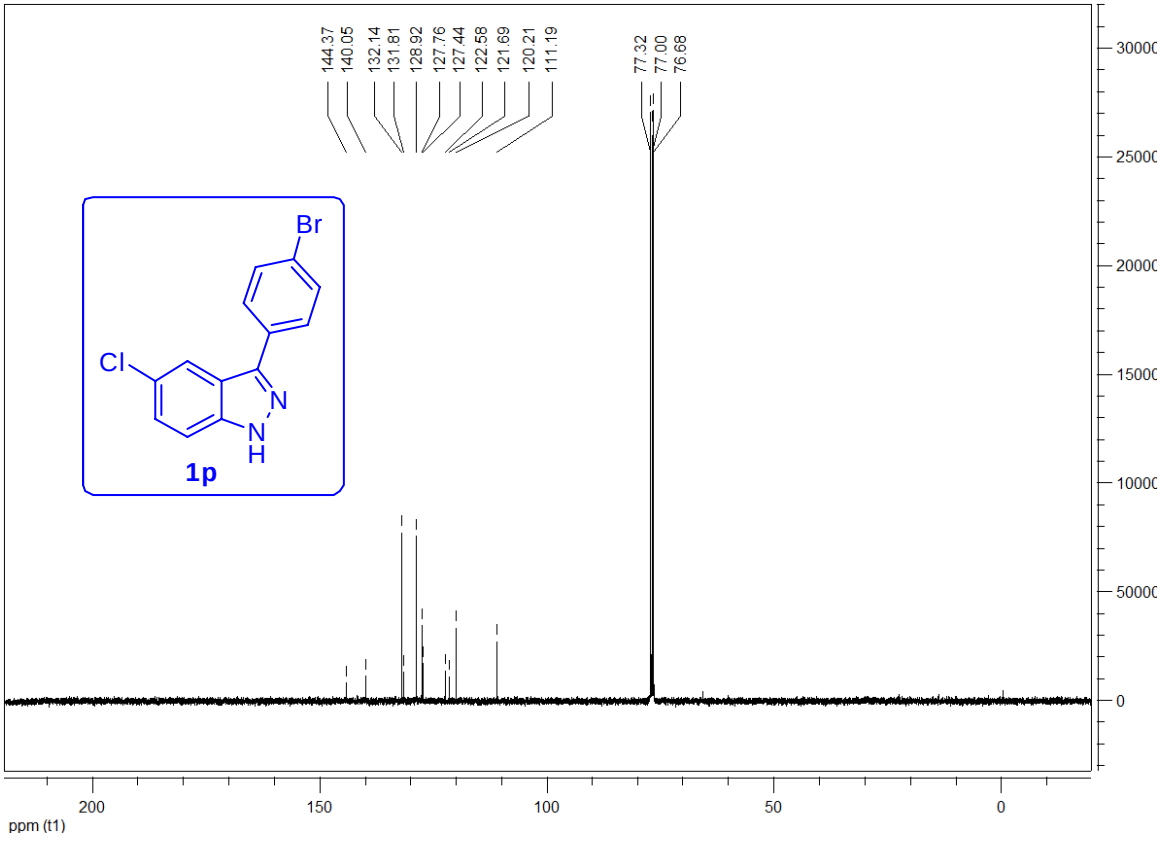
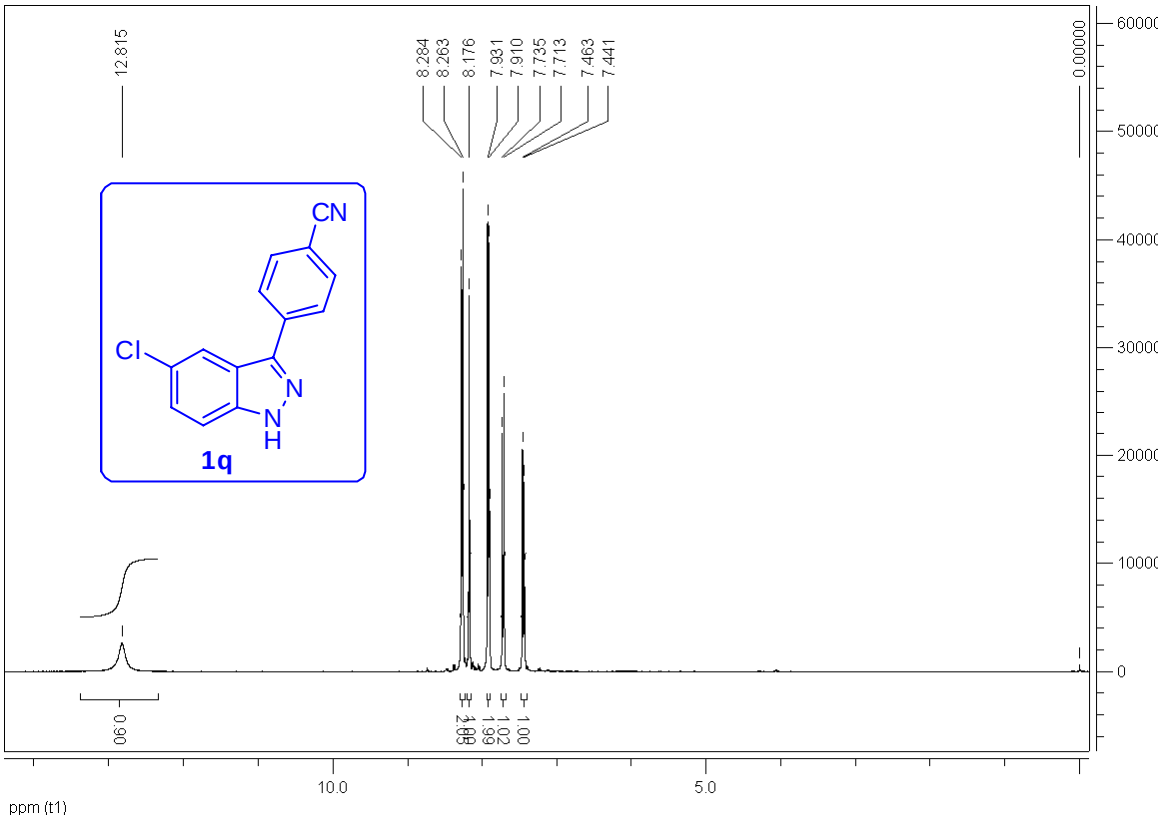
8.098
8.096
7.976
7.955
7.669
7.647
7.590
7.570
7.415
7.411
7.393
7.389
1.374
-0.00000
0.79
2.00
2.00
2.00
1.00
9.01
tBu
O2N
N
N
H
1o
10.0
5.0
0.0
ppm (t1)


205.87
151.40
144.55
141.18
131.41
127.44
127.17
126.71
126.26
122.18
120.57
112.60
34.91
31.33
30.14
29.94
29.75
29.56
29.37
29.17
28.98
tBu
O2N
N
N
H
1o
200
150
100
50
0
ppm (t1)


10.619
7.946
7.815
7.794
7.663
7.642
7.385
7.382
7.259
-0.00000
Br
Cl
N
N
H
1p
0.90
2.02
2.01
2.00
10.0
5.0
0.0
ppm (t1)


144.37
140.05
132.14
131.81
128.92
127.76
127.44
122.58
121.69
120.21
111.19
77.32
77.00
76.68
Br
Cl
N
N
H
1p
200
150
100
50
0
ppm (t1)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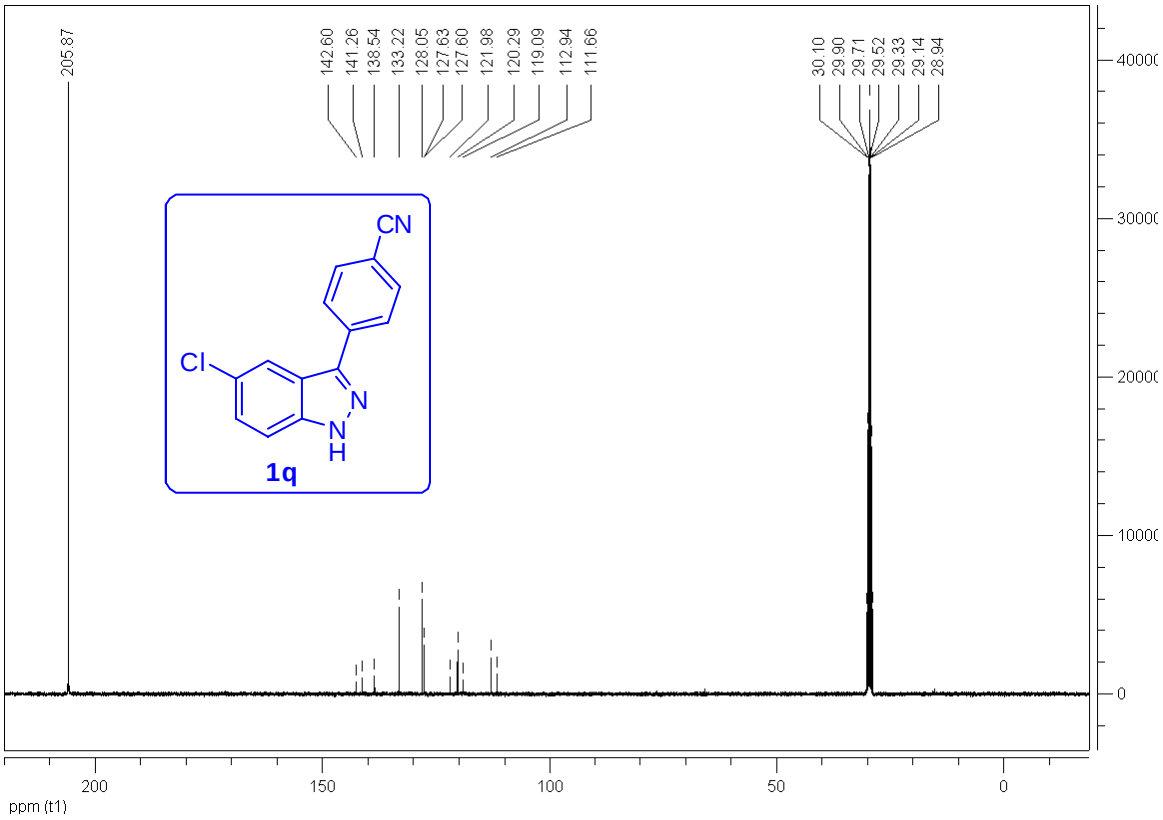
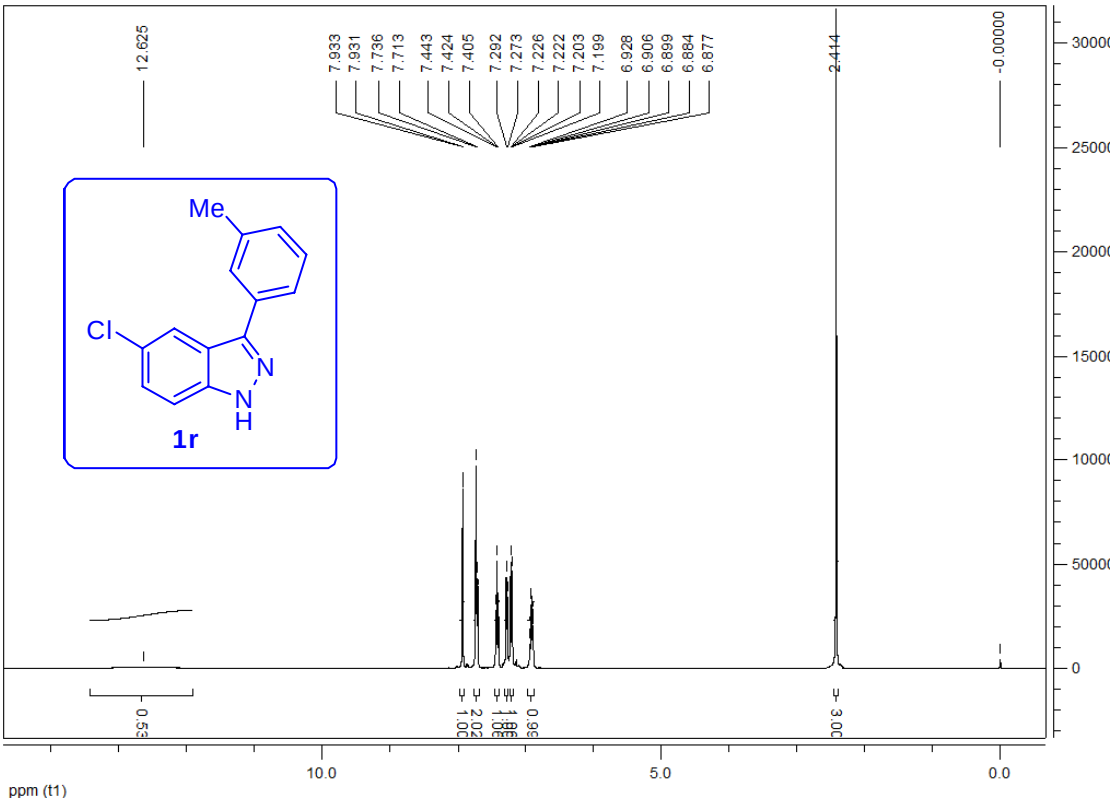
8.284
8.263
8.176
7.931
7.910
7.735
7.713
7.463
7.441
0.00000
CN
Cl
N
N
H
1q
0.90
2.08
1.99
1.02
1.00
10.0
5.0
ppm (t1)


205.87
142.60
141.26
138.54
133.22
128.05
127.63
127.60
121.98
120.29
119.09
112.94
111.66
30.10
29.90
29.71
29.52
29.33
29.14
28.94
CN
Cl
N
N
H
1q
200
150
100
50
0
ppm (t1)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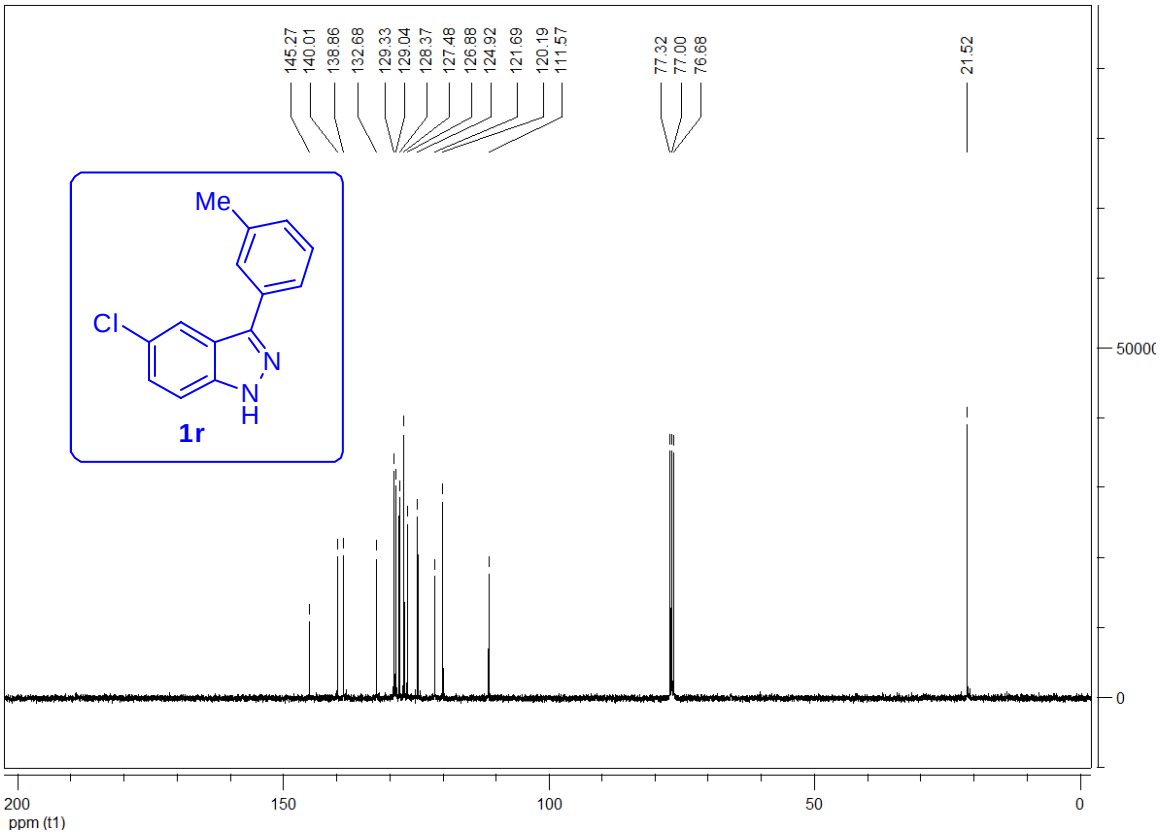
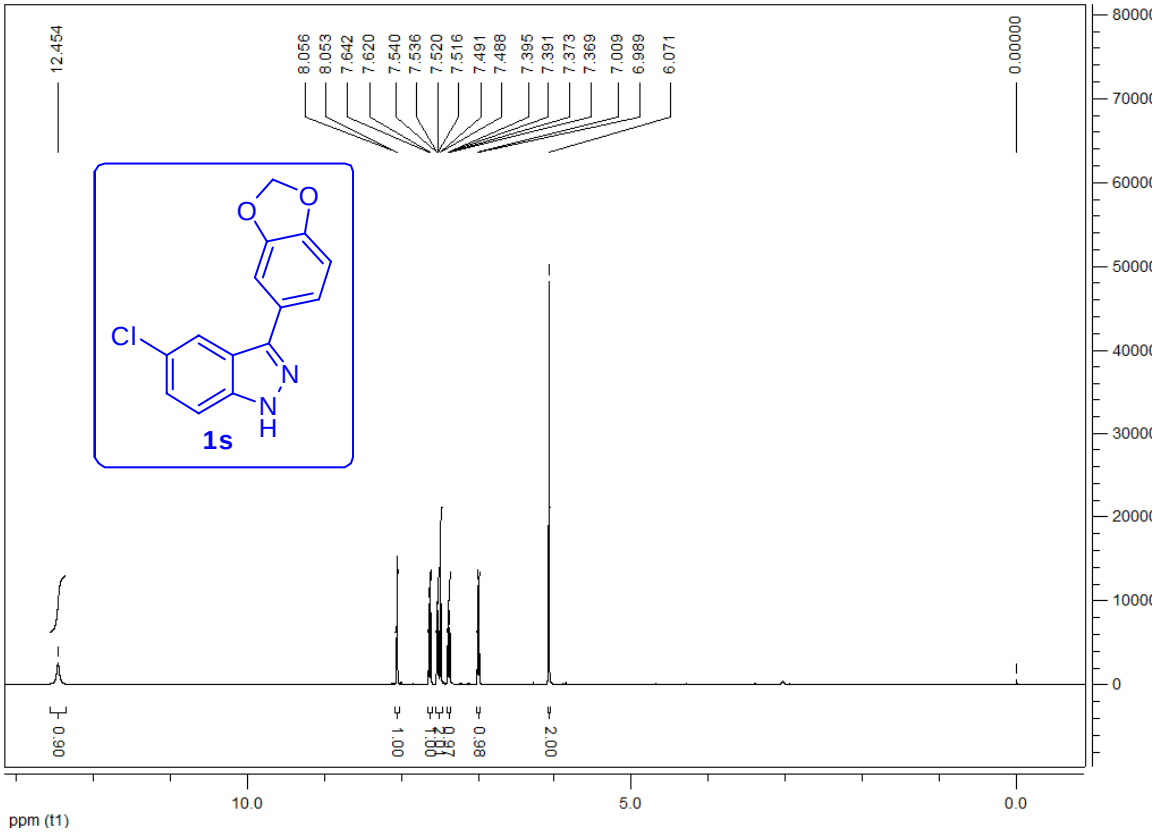
7.931
7.736
7.713
7.443
7.424
7.405
7.292
7.273
7.226
7.222
7.203
7.199
6.928
6.906
6.899
6.884
6.877
2.414
-0.00000
Me
Cl
N
N
H
1r
ppm (t1)


145.27
140.01
138.86
132.68
129.33
129.04
128.37
127.48
126.88
124.92
121.69
120.19
111.57
77.32
77.00
76.68
21.52
Me
Cl
N
N
H
1r
ppm (t1)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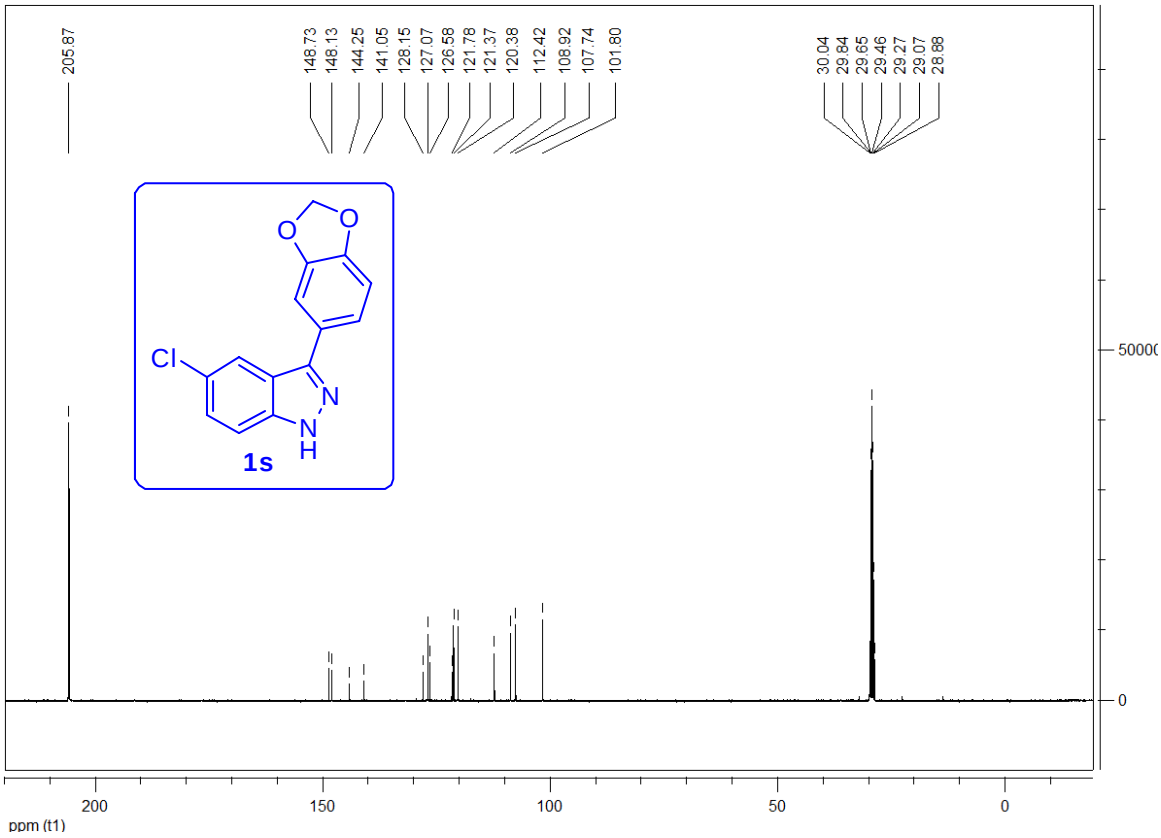
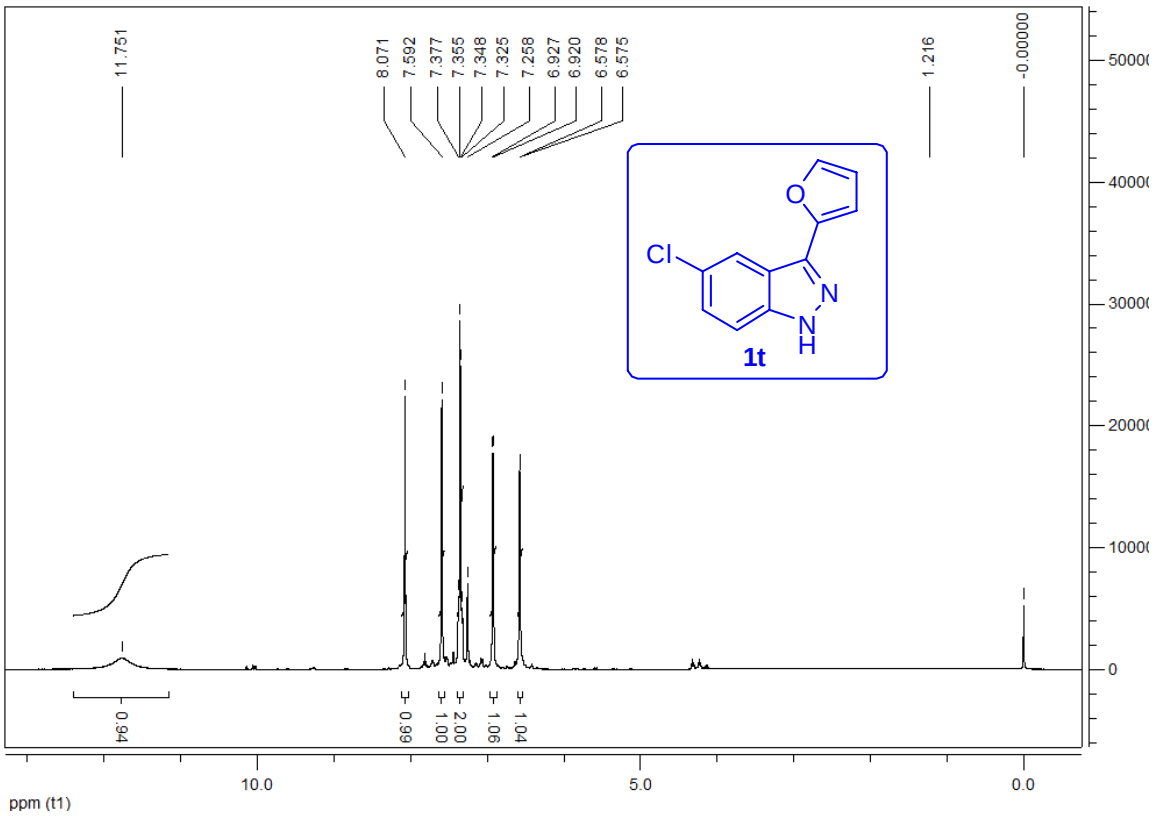
8.053
7.642
7.620
7.540
7.536
7.520
7.516
7.491
7.488
7.395
7.391
7.373
7.369
7.009
6.989
6.071
0.00000
1s
0.90
1.00
0.98
2.00
ppm (t1)


205.87
148.73
148.13
144.25
141.05
128.15
127.07
126.58
121.78
121.37
120.38
112.42
108.92
107.74
101.80
30.04
29.84
29.65
29.46
29.27
29.07
28.88
1s
ppm (t1)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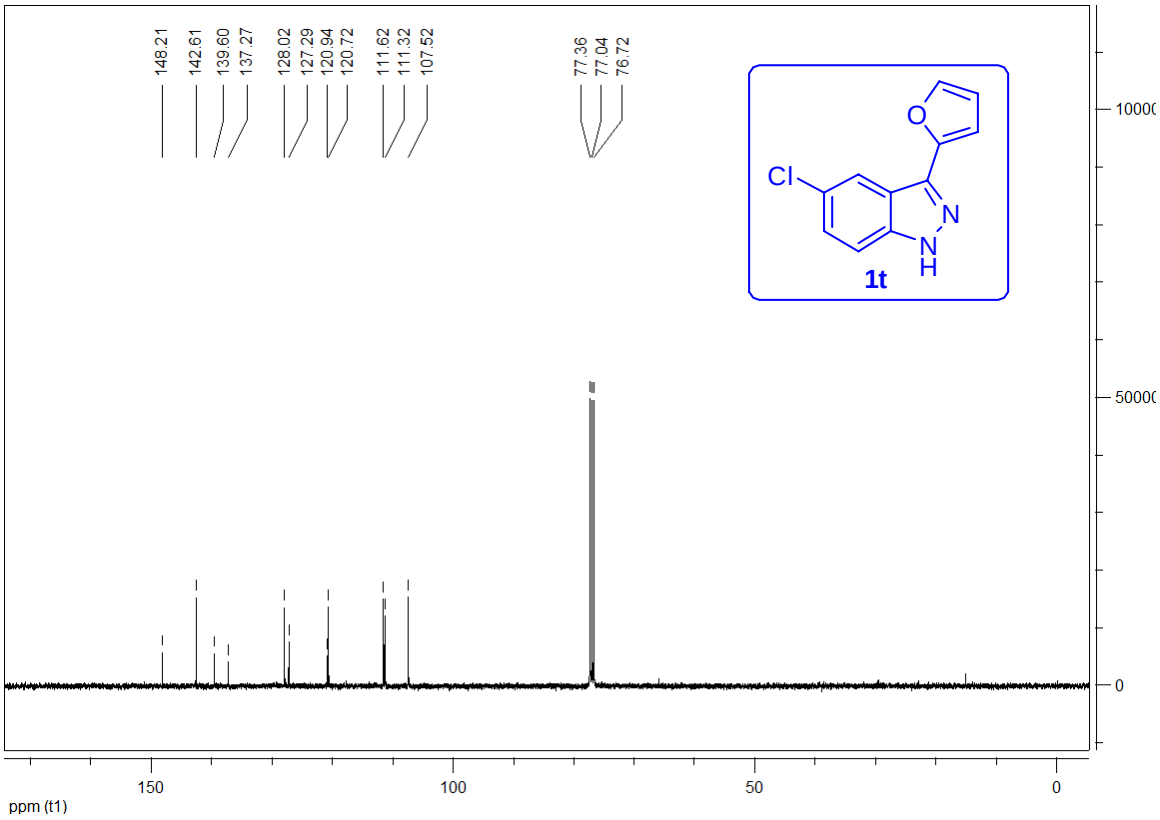
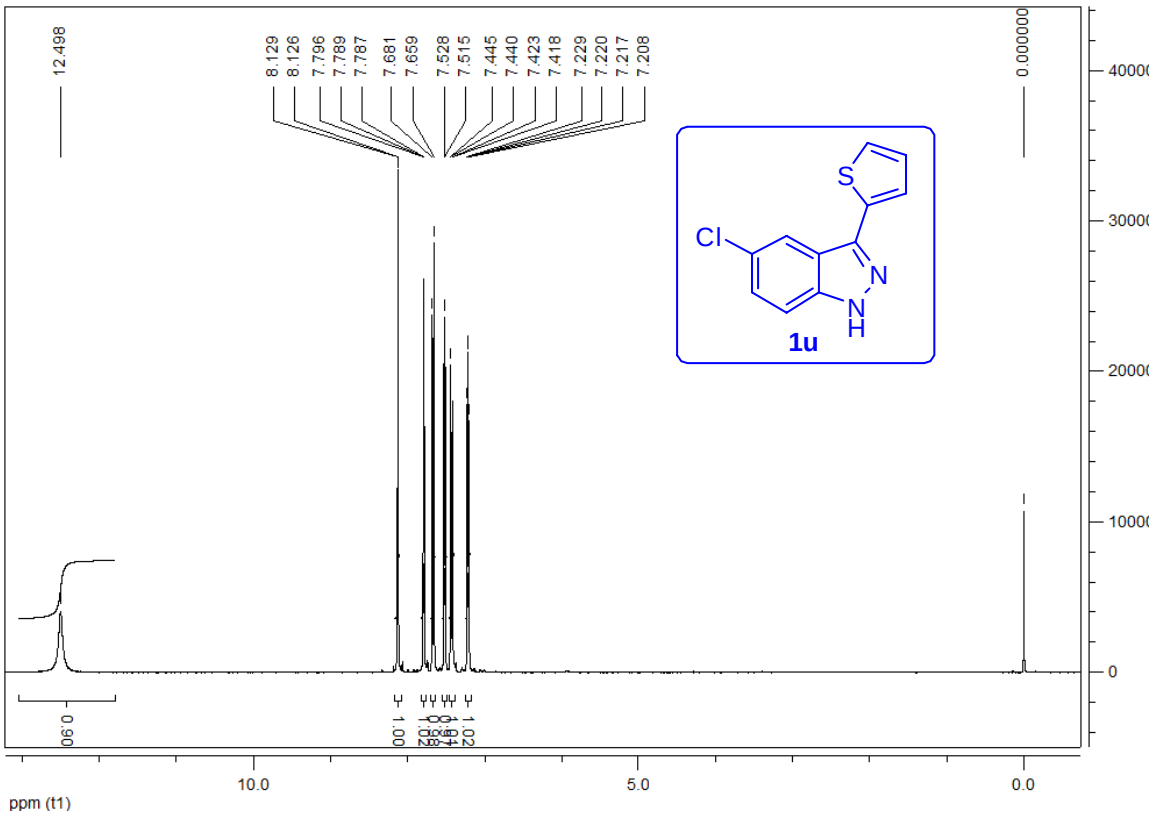
7.377
7.355
7.348
7.325
7.258
6.927
6.920
6.578
6.575
1.216
-0.00000
Cl
O
N
N
H
1t
0.94
0.99
1.00
2.00
1.06
1.04
10.0
5.0
0.0
ppm (t1)


148.21
142.61
139.60
137.27
128.02
127.29
120.94
120.72
111.62
111.32
107.52
77.36
77.04
76.72
Cl
O
N
N
H
1t
150
100
50
0
ppm (t1)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8.126
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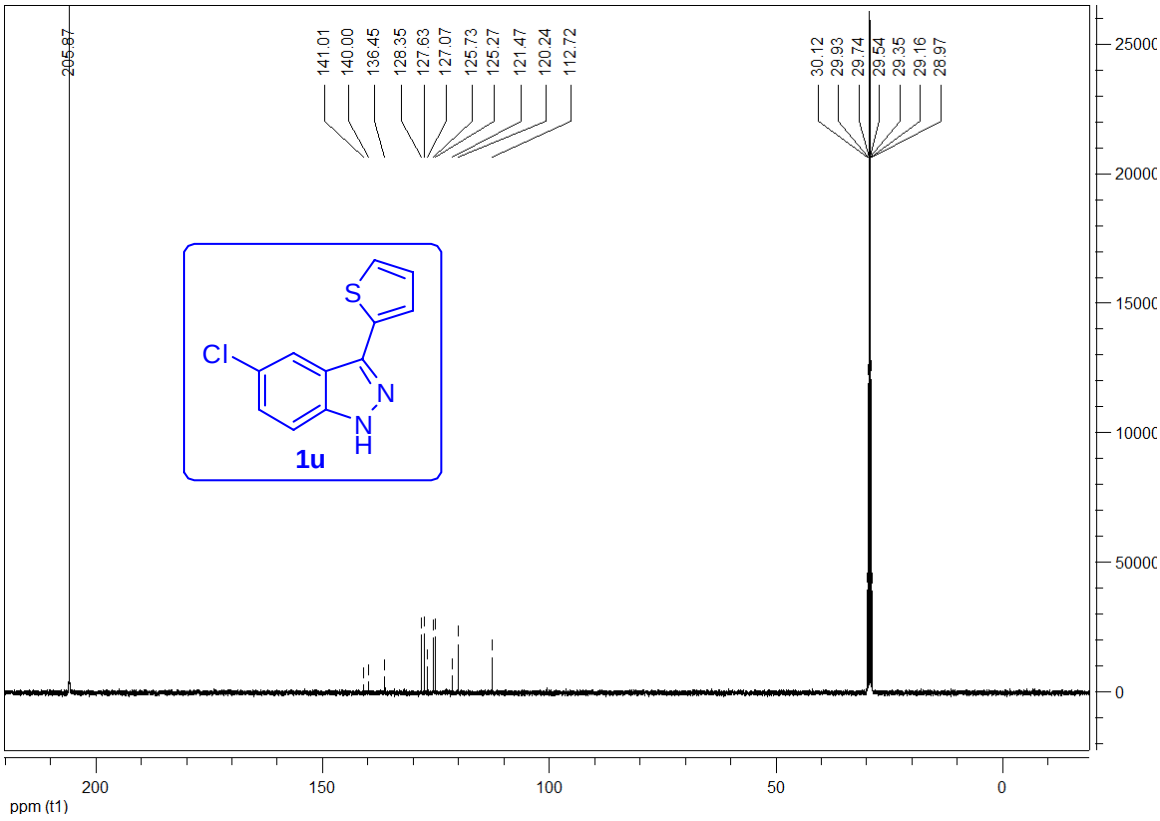
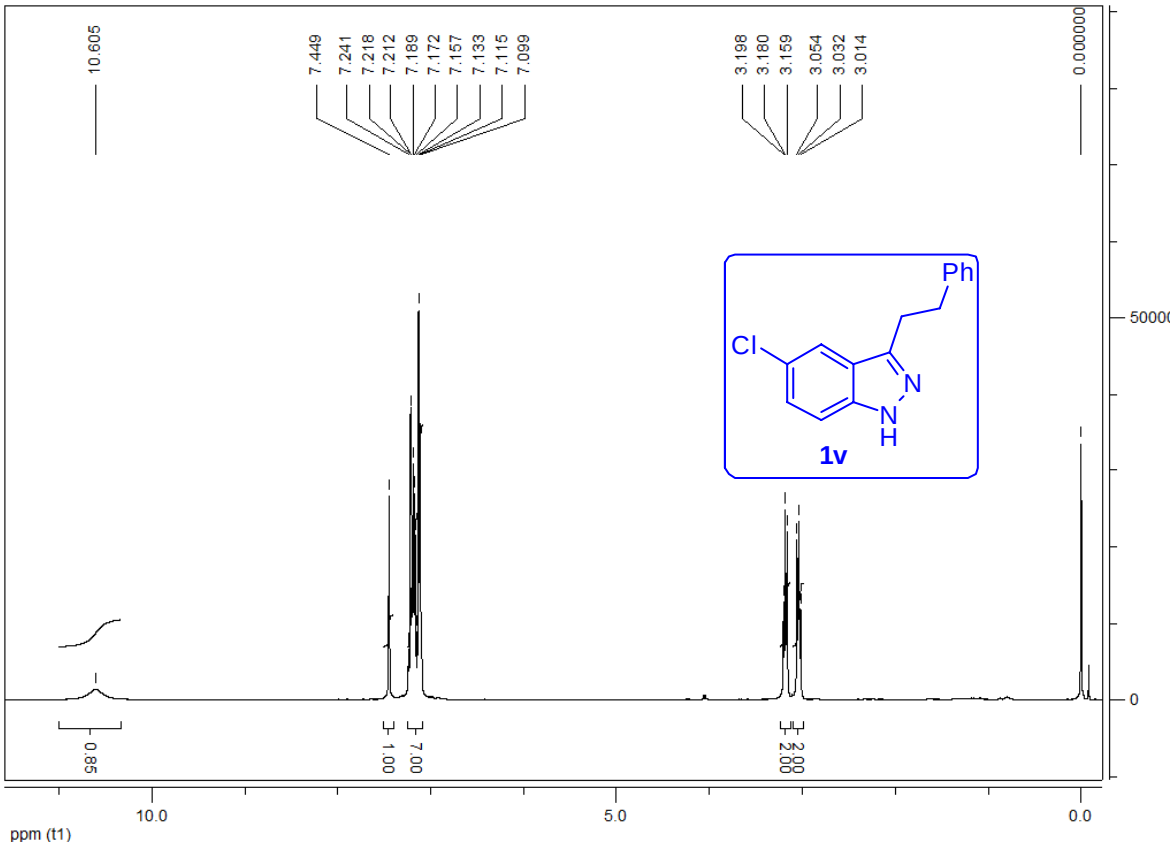
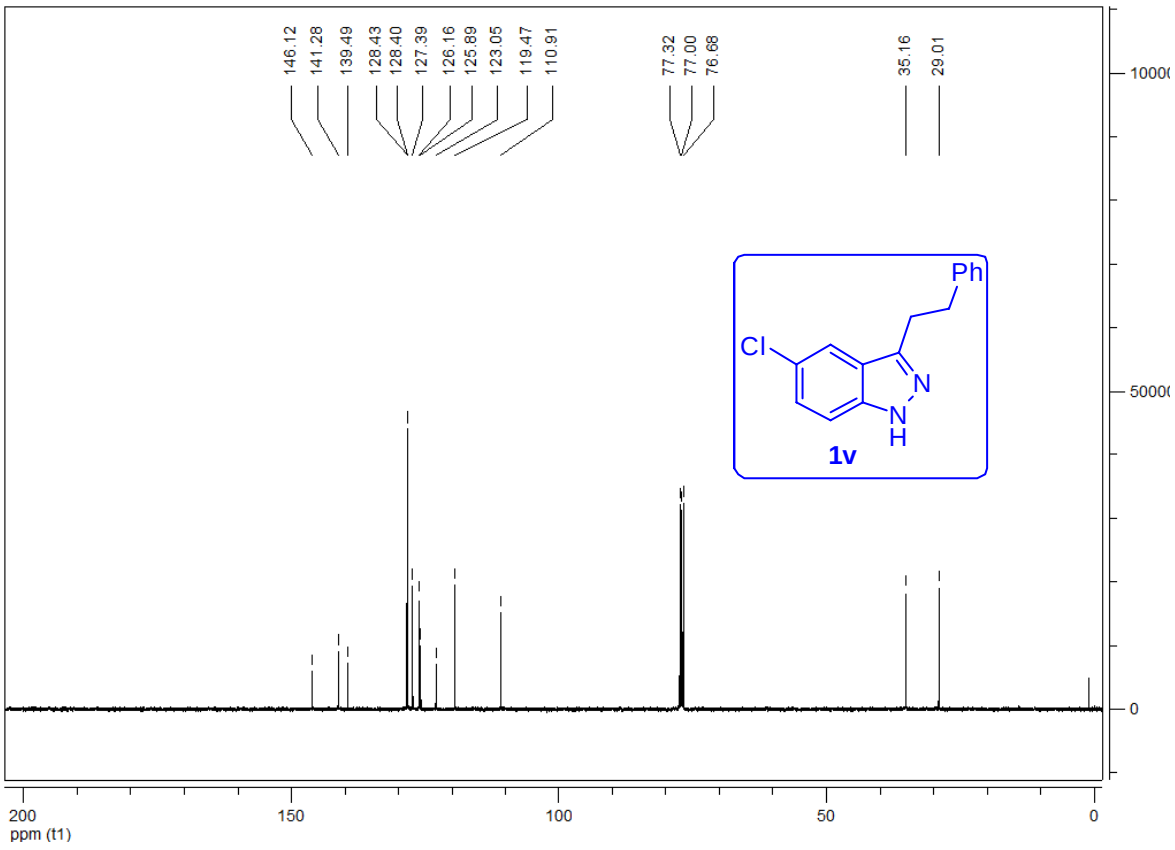
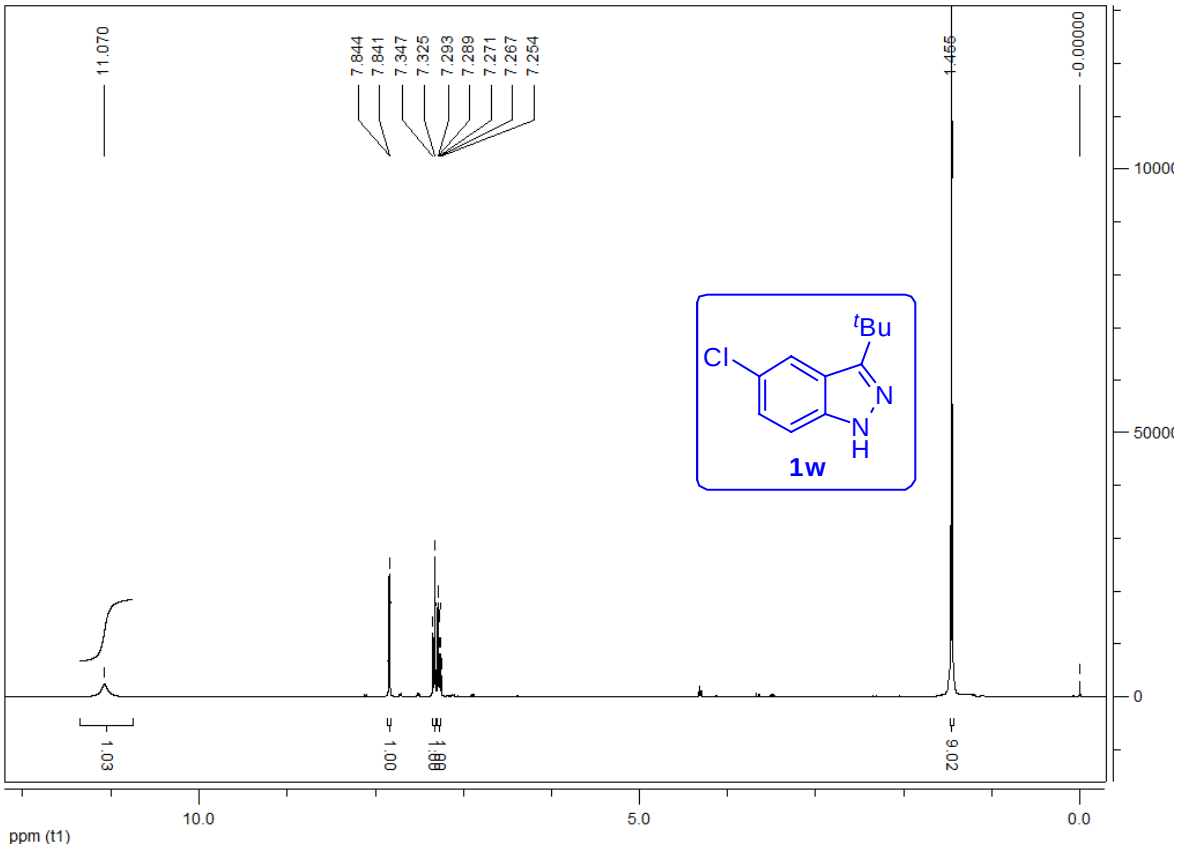
7.789
7.787
7.681
7.659
7.528
7.515
7.445
7.440
7.423
7.418
7.229
7.220
7.217
7.208
0.000000
1.00
1.02
0.90
1u
ppm (t1)


205.87
141.01
140.00
136.45
128.35
127.63
127.07
125.73
125.27
121.47
120.24
112.72
30.12
29.93
29.74
29.54
29.35
29.16
28.97
1u
ppm (t1)


10.605
7.449
7.241
7.218
7.212
7.189
7.172
7.157
7.133
7.115
7.099
3.198
3.180
3.159
3.054
3.032
3.014
0.000000
Ph
Cl
N
N
H
1v
0.85
1.00
7.00
2.00
10.0
5.0
0.0
ppm (t1)


146.12
141.28
139.49
128.43
128.40
127.39
126.16
125.89
123.05
119.47
110.91
77.32
77.00
76.68
35.16
29.01
Ph
Cl
N
N
H
1v
200
150
100
50
0
ppm (t1)


11.070
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7.325
7.293
7.289
7.271
7.267
7.254
1.455
-0.00000
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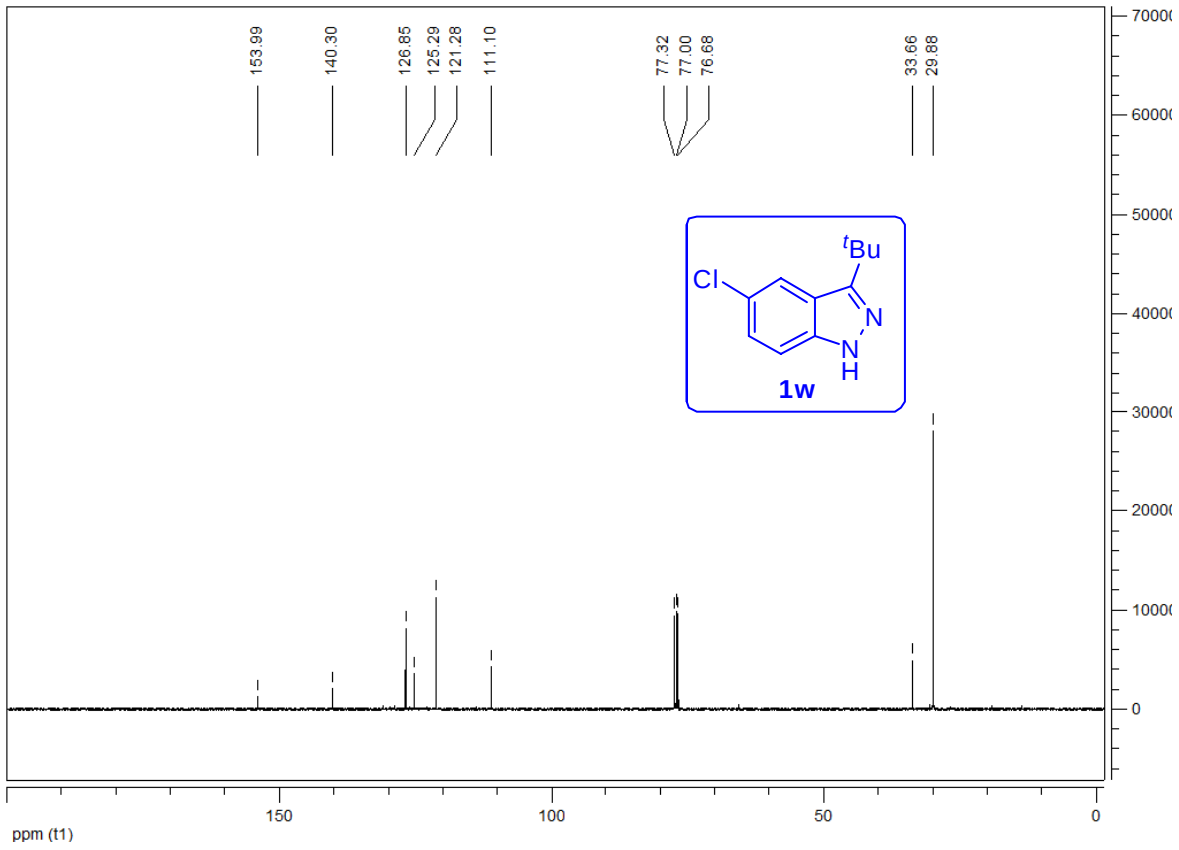
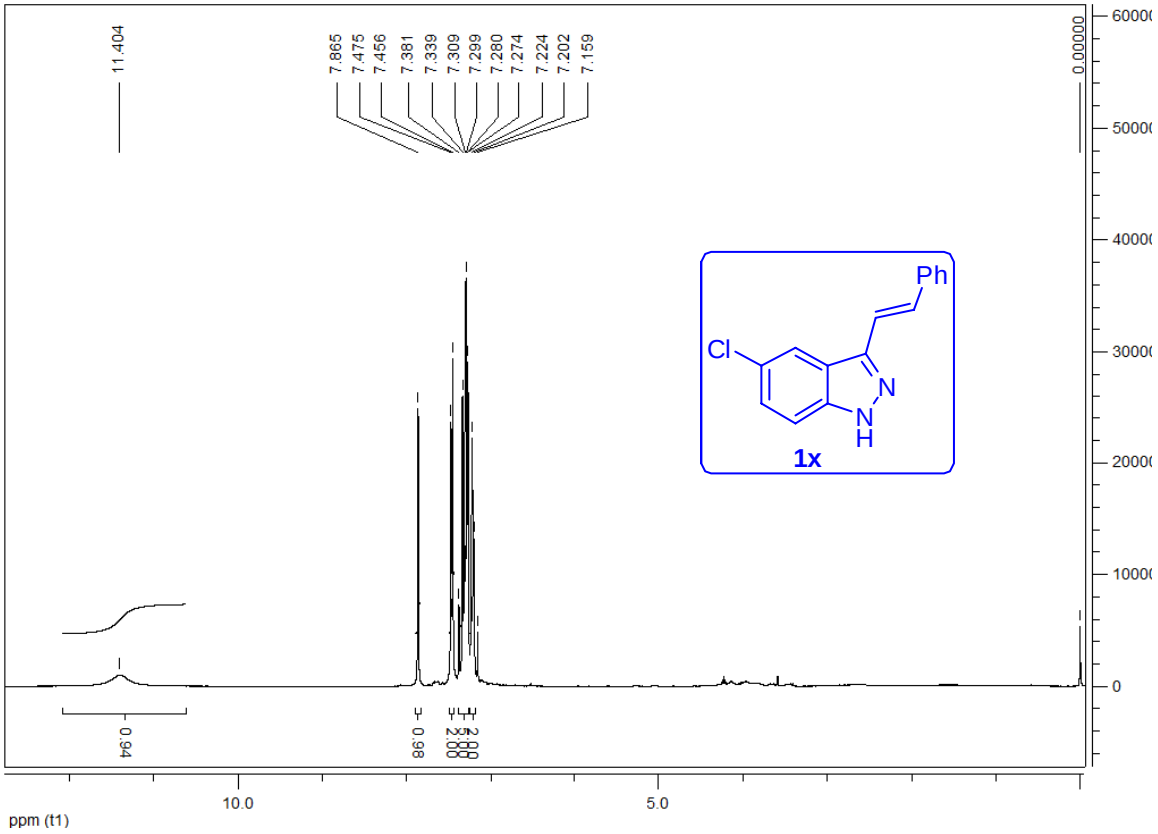
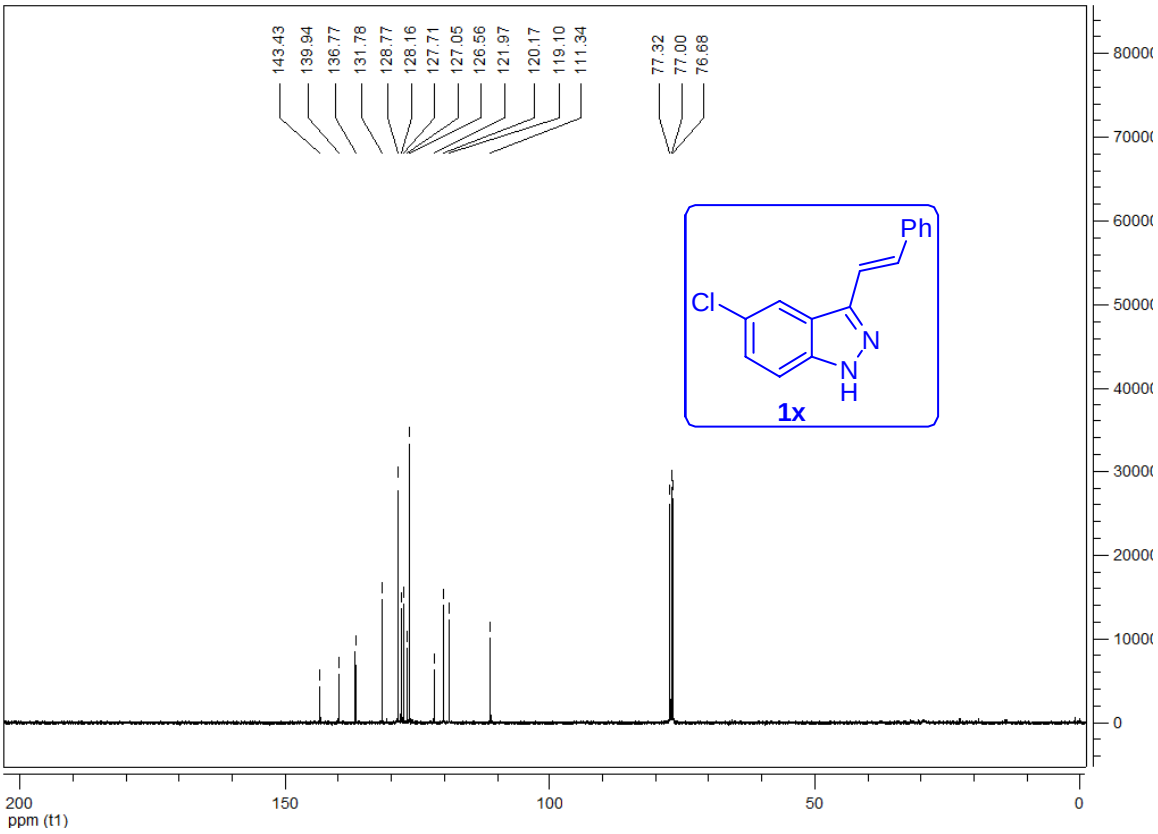
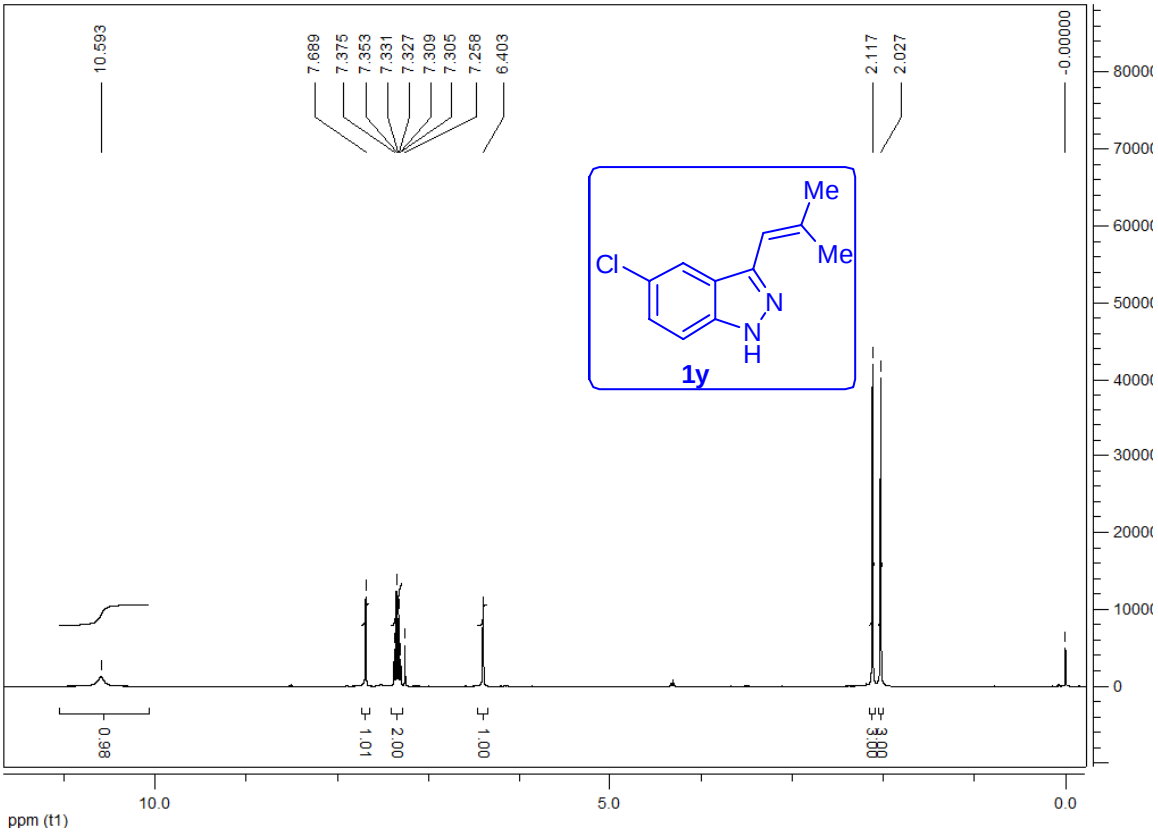
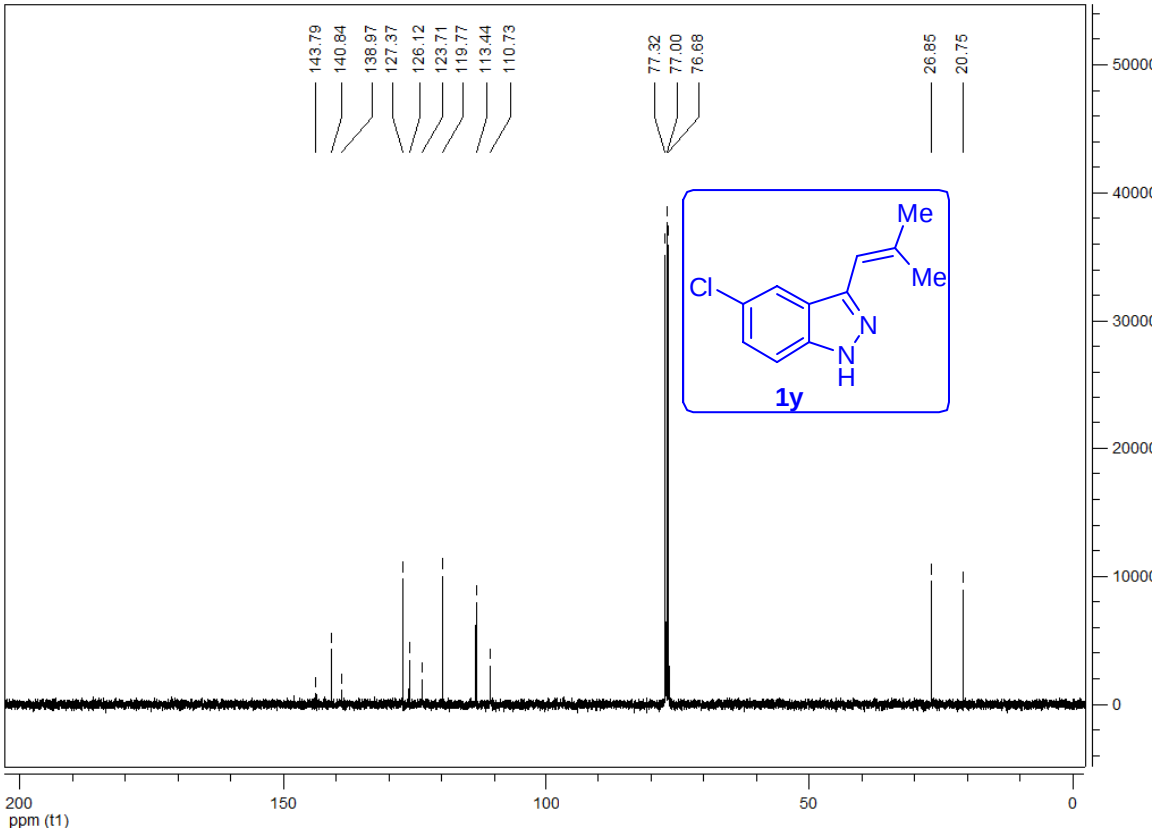
1.00
1.88
9.02
tBu
Cl
N
N
H
1w
10.0
5.0
0.0
ppm (t1)

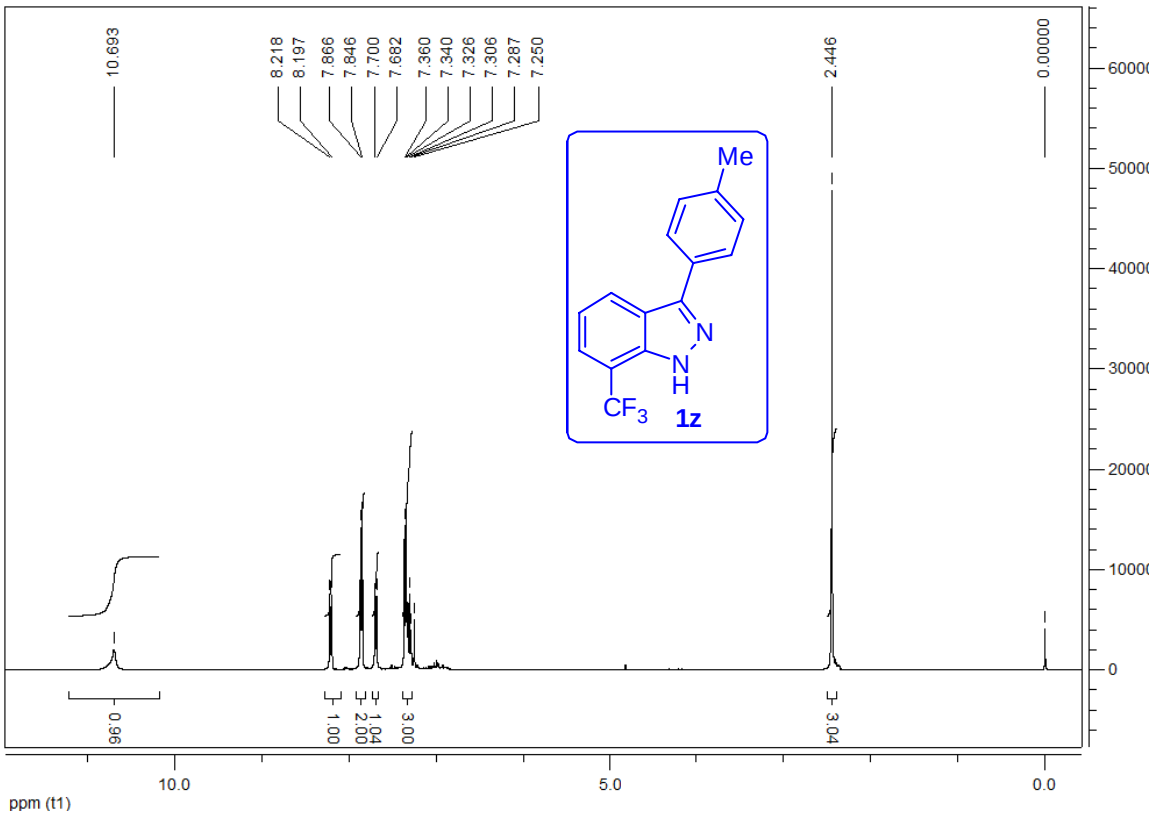

153.99
140.30
126.85
125.29
121.28
111.10
77.32
77.00
76.68
33.66
29.88
tBu
Cl
N
N
H
1w
150
100
50
0
ppm (t1)

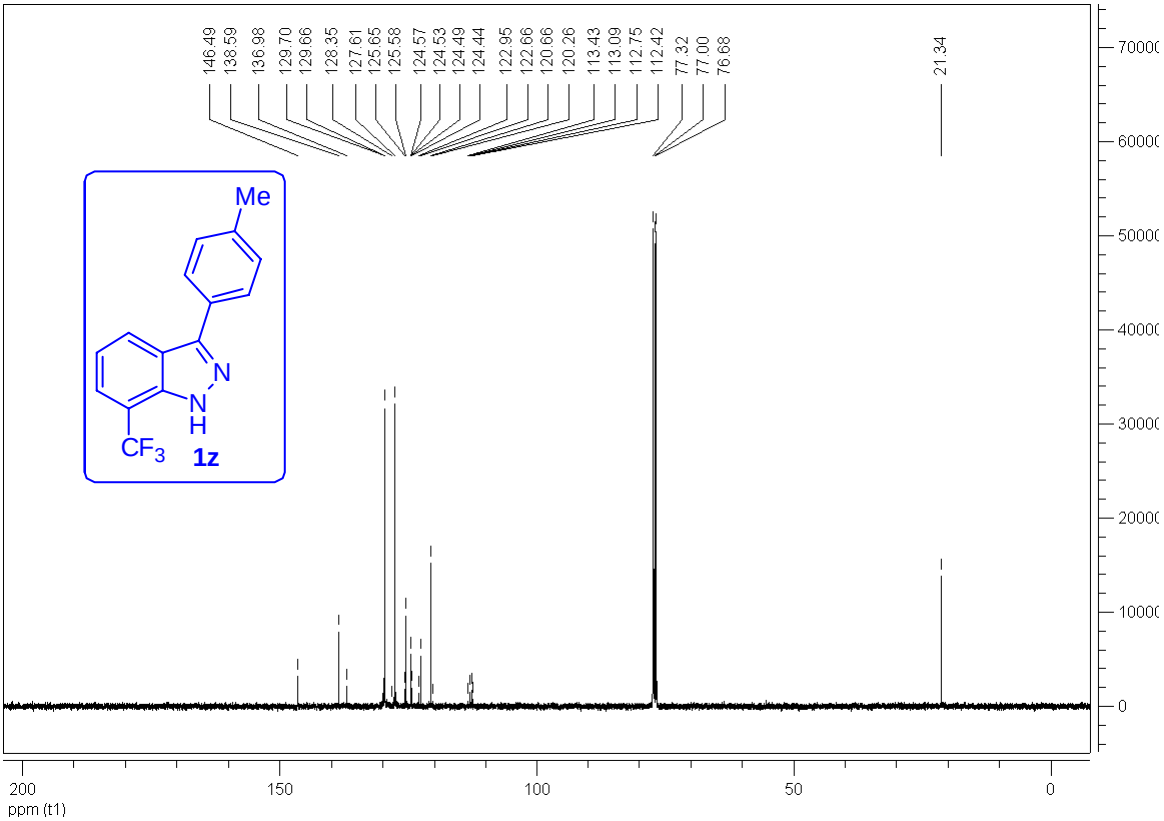

11.404
7.865
7.475
7.456
7.381
7.339
7.309
7.299
7.280
7.274
7.224
7.202
7.159
0.00000
Ph
Cl
N
N
H
1x
0.94
0.98
2.00
2.14
2.88
10.0
5.0
ppm (t1)

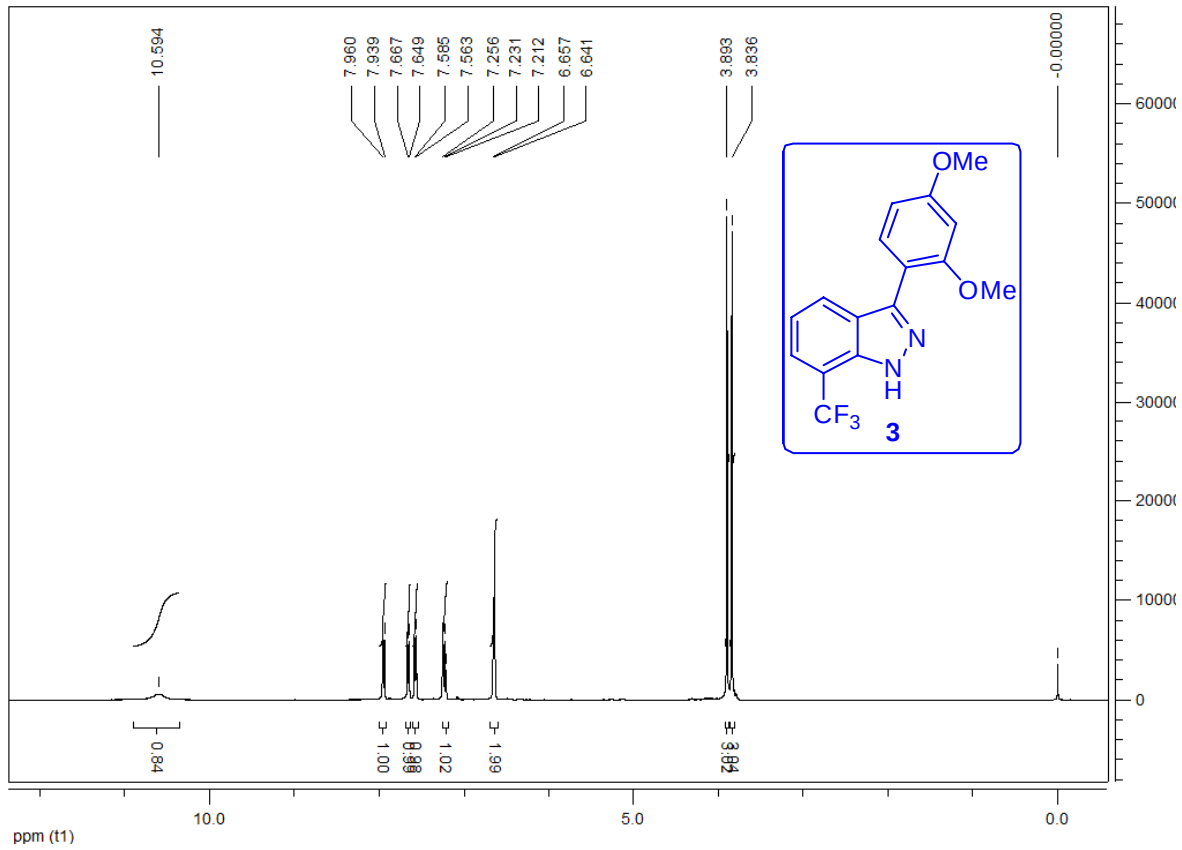

143.43
139.94
136.77
131.78
128.77
128.16
127.71
127.05
126.56
121.97
120.17
119.10
111.34
77.32
77.00
76.68
Ph
Cl
N
N
H
1x
200
150
100
50
0
ppm (t1)

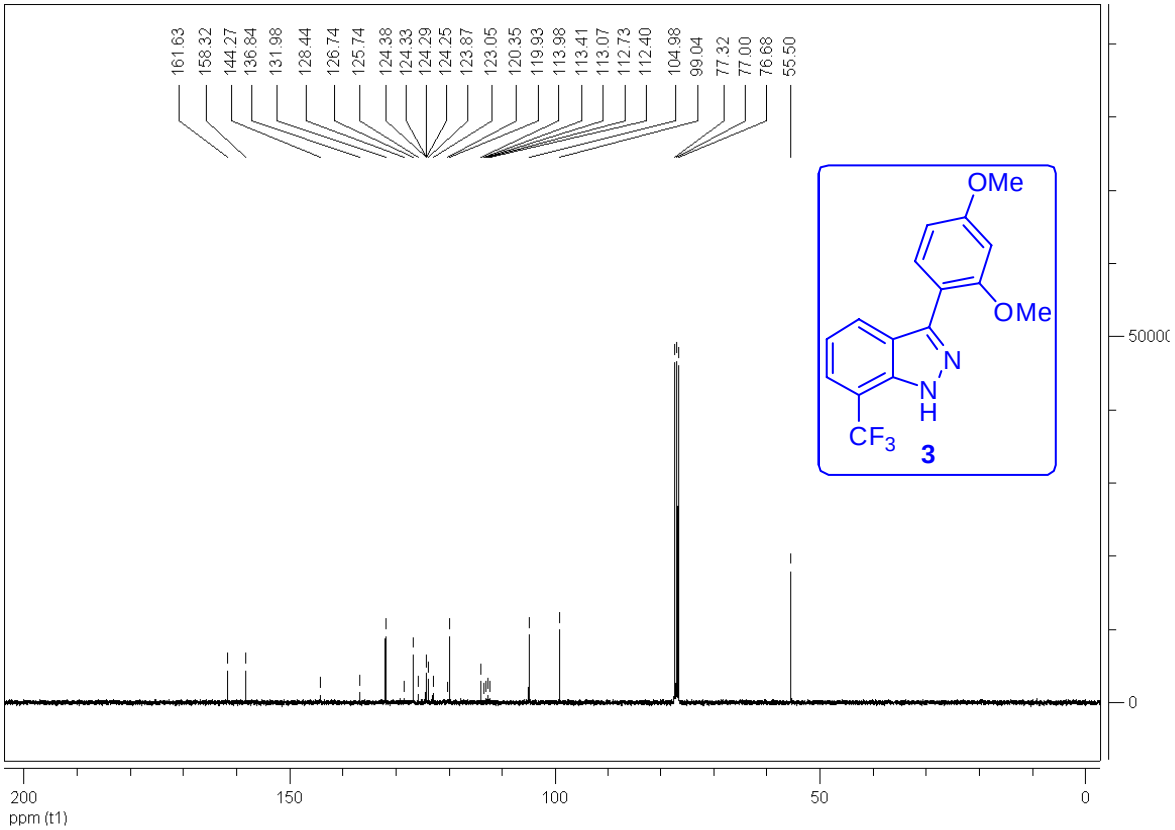

10.593
7.689
7.375
7.353
7.331
7.327
7.309
7.305
7.258
6.403
2.117
2.027
-0.00000
Me
Me
Cl
N
N
H
1y
0.98
1.01
2.00
1.00
3.88
10.0
5.0
0.0
ppm (t1)


143.79
140.84
138.97
127.37
126.12
123.71
119.77
113.44
110.73
77.32
77.00
76.68
26.85
20.75
Me
Me
Cl
N
N
H
1y
200
150
100
50
0
ppm (t1)


10.693
8.218
8.197
7.866
7.846
7.700
7.682
7.360
7.340
7.326
7.306
7.287
7.250
2.446
0.00000
Me
N
N
H
CF3
1z
0.96
1.00
2.00
1.14
3.00
3.04
10.0
5.0
0.0
ppm (t1)


146.49
138.59
136.98
129.70
129.66
128.35
127.61
125.65
125.58
124.57
124.53
124.49
124.44
122.95
122.66
120.66
120.26
113.43
113.09
112.75
112.42
77.32
77.00
76.68
21.34
Me
N
N
H
CF3
1z
200
150
100
50
0
ppm (t1)


10.594
7.960
7.939
7.667
7.649
7.585
7.563
7.256
7.231
7.212
6.657
6.641
3.893
3.836
-0.00000
OMe
OMe
N
N
H
CF3
3
0.84
1.00
1.02
1.99
3.84
10.0
5.0
0.0
ppm (t1)


161.63
158.32
144.27
136.84
131.98
128.44
126.74
125.74
124.38
124.33
124.29
124.25
123.87
123.05
120.35
119.93
113.98
113.41
113.07
112.73
112.40
104.98
99.04
77.32
77.00
76.68
55.50
OMe
OMe
N
N
H
CF3
3
200
150
100
50
0
ppm (t1)