From Biomass to Medicines. A Simple Synthesis of Indolo[3,2-c]quinolines, Antimalarial Alkaloid Isocrylptolepine, and its Derivatives

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Experimental

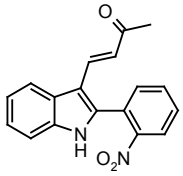
General

Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a "Bruker DPX 300" spectrometer at room temperature; the chemical shifts δ were measured in ppm with respect to the solvent ($CDCl_3$, ^{1}H: δ = 7.26 ppm, ^{13}C: δ = 77.2 ppm; DMSO-d_6, ^{1}H: δ = 2.50 ppm, ^{13}C: δ = 39.5 ppm). Coupling constants (*J*) are in Hz. Splitting patterns of an apparent multiplet associated with an averaged coupling constant were designed as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets) and br (broadened). IR spectra were measured as KBr plates on Specord M-80-2 and Bruker Alpha FT-IR instruments. Mass spectra were recorded on a Kratos MS-30 instrument with 70 eV electron impact ionization at 200 ºC. Column chromatography was performed on silica gel KSK (50-160 μm, LTD Sorbpolymer). 2-(5-Alkylfuran-2-yl)anilines **3** were prepared by published procedure[1]. All the reactions were carried out using freshly distilled and dry solvents from solvent stills.

General Procedure for the Synthesis of Indoles 4:

2-Furylaniline **3** (3 mmol) and aldehyde **6** (3 mmol) were added to solution of conc. HCl (0.01 mL) in acetic acid (5 mL). The resulting mixture was stirred at 40 °C for 3h, poured into H_2O (200 mL) and neutralized with $NaHCO_3$. The formed precipitate was filtered off and air-dried. Product was purified by column chromatography on silica gel. Non-polar admixtures were firstly removed by using a CH_2Cl_2/hexane (1:4) mixture; then product was isolated using acetone as an eluent. Indoles **4** were recrystallized using the specified solvents.

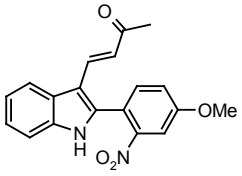
(3*E*)-4-[2-(2-Nitrophenyl)-1*H*-indol-3-yl]but-3-en-2-one (4a)[2]



4a

Yield 58 %. Red solid. R_f = 0.48 (acetone-hexane 1:1). Mp 251–252 °C (EtOH–acetone).

(3*E*)-4-[2-(4-Methoxy-2-nitrophenyl)-1*H*-indol-3-yl]but-3-en-2-one (4b)



4b

Yield: 56 %. Dark yellow solid. R_f = 0.48 (acetone-hexane 1:1). Mp 255–256 °C (EtOH).

^{1}H NMR (DMSO-d_6): 2.20 (s, 3H, Me), 3.94 (s, 3H, OMe), 6.78 (d, ^3J = 16.2 Hz, 1H, =CH), 7.19 (d, ^4J = 2.7 Hz, 1H, H_{Ar}), 7.22–7.32 (m, 2H, H_{Ar}), 7.34 (dd, J = 2.7, 9.0 Hz, 1H, H_{Ar}), 7.38 (d, ^3J = 16.2 Hz, 1H, =CH), 7.46–7.49 (m, 1H, H_{Ar}), 8.02–8.04 (m, 1H, H_{Ar}), 8.30 (d, ^3J = 9.0 Hz, 1H, H_{Ar}), 12.23 (s, 1H, NH).

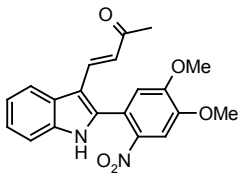
^{13}C NMR (DMSO-d_6): 27.9, 56.5, 109.4, 112.2, 115.4, 118.7, 120.6, 121.4, 122.2, 123.2, 125.2, 127.8, 128.2, 135.1, 136.8, 139.6, 141.8, 162.6, 197.0.

IR: 3212, 1612, 1576, 1508, 1460, 1436, 1344, 1272, 1236, 752 cm^{-1}.

MS (EI, 70 eV): *m/z* (%) = 336 (M^+, 100), 275 (22), 262 (19), 248 (49), 247 (56), 232 (16), 204 (46), 191 (18), 172 (16), 139 (13), 106 (20), 43 (27).

Anal. Calcd for $C_{19}H_{16}N_2O_4$: C, 67.85; H, 4.79; N, 8.33. Found: C, 67.60; H, 4.93; N, 8.13.

(3*E*)-4-[2-(4,5-Dimethoxy-2-nitrophenyl)-1*H*-indol-3-yl]but-3-en-2-one (4c)



4c

Yield 59 %. Orange solid. R_f = 0.45 (acetone–hexane 1:1). Mp 265–266 °C (dioxane–EtOH).

^{1}H NMR (DMSO-d$_6$): 2.20 (s, 3H, Me), 3.92 (s, 3H, OMe), 3.99 (s, 3H, OMe), 6.73 (d, ^3J = 16.2 Hz, 1H, =CH), 7.21 (s, 1H, H$_{Ar}$), 7.21–7.32 (m, 2H, H$_{Ar}$), 7.40 (d, ^3J = 16.2 Hz, 1H, =CH), 7.47–7.50 (m, 1H, H$_{Ar}$), 7.83 (s, 1H, H$_{Ar}$), 7.99–8.01 (m, 1H, H$_{Ar}$), 12.14 (s, 1H, NH).

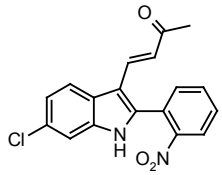
^{13}C NMR (DMSO-d$_6$): 27.6, 56.3, 56.6, 108.2, 109.4, 112.1, 115.0, 119.4, 120.4, 121.2, 122.0, 123.0, 125.2, 135.4, 136.7, 139.9, 141.6, 149.2, 152.3, 196.9.

IR: 3210, 1661, 1561, 1519, 1459, 1335, 1274, 1221, 1189, 1160, 1095, 1051, 971, 753 cm^{-1}.

MS (EI, 70 eV): *m/z* (%) = 366 (M$^+$, 100), 334 (27), 323 (35), 292 (49), 279 (35), 247 (19), 220 (16), 190 (24), 172 (15), 144 (18), 94 (18), 69 (24), 43 (50).

Anal. Calcd for $C_{20}H_{18}N_2O_5$: C, 65.57; H, 4.95; N, 7.65. Found: C, 65.61; H, 4.83; N, 7.40.

(3*E*)-4-[6-Chloro-2-(2-nitrophenyl)-1*H*-indol-3-yl]but-3-en-2-one (4d)



4d

Yield 67 %. Dark yellow solid. R_f = 0.50 (acetone–hexane 1:1). Mp 327–328 °C (dioxane–EtOH).

^{1}H NMR (DMSO-d$_6$): 2.20 (s, 3H, Me), 6.75 (d. ^3J = 16.2 Hz, 1H, =CH), 7.25 (dd, J = 2.1, 8.7 Hz, 1H, H$_{Ar}$), 7.33 (d, ^3J = 16.2 Hz, 1H, =CH), 7.52 (d, ^4J = 2.1 Hz, 1H, H$_{Ar}$), 7.71–7.74 (m, 1H, H$_{Ar}$), 7.83–7.89 (m, 1H, H$_{Ar}$), 7.91–7.97 (m, 1H, H$_{Ar}$), 8.05 (d, ^3J = 8.7 Hz, 1H, H$_{Ar}$), 8.24–8.28 (m, 1H, H$_{Ar}$), 12.36 (s, 1H, NH).

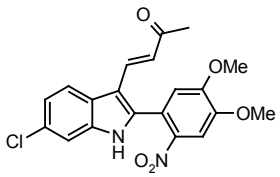
^{13}C NMR (DMSO-d$_6$): 27.8, 109.7, 111.7, 121.5, 121.9, 123.0, 123.9, 124.9, 125.0, 127.8, 131.1, 133.5, 133.6, 134.2, 137.3, 139.8, 148.9, 196.9.

IR: 3168, 1644, 1612, 1568, 1524, 1476, 1452, 1436, 1420, 1348, 1276, 1256, 1240, 1168, 1064, 924, 848, 808, 748 cm^{-1}.

MS (EI, 70 eV): *m/z* (%) = 342/340 (M$^+$, 33/100), 327 (24), 325 (32), 310/308 (20/60), 299/297 (21/63), 269 (75), 251 (86), 232 (54), 217 (56), 203 (44), 171 (30), 120 (33), 95 (57), 83 (66), 73 (58), 55 (60), 43 (71).

Anal. Calcd for $C_{18}H_{13}ClN_2O_3$: C, 63.44; H, 3.85; N, 8.22. Found: C, 63.56; H, 3.92; N, 8.22.

(3*E*)-4-[6-Chloro-2-(4,5-dimethoxy-2-nitrophenyl)-1*H*-indol-3-yl]but-3-en-2-one (4e)



4e

Yield 58 %. Orange solid. R_f = 0.49 (acetone–hexane 1:1). Mp 310–311 °C (dioxane–EtOH).

^{1}H NMR (DMSO-d_6): 2.20 (s, 3H, Me), 3.91 (s, 3H, OMe), 3.98 (s, 3H, OMe), 6.71 (d, ^3J = 16.2 Hz, 1H, =CH), 7.20 (s, 1H, H_{Ar}), 7.24 (dd, J = 2.1, 8.4 Hz, 1H, H_{Ar}), 7.36 (d, ^3J = 16.2 Hz, 1H, =CH), 7.51 (d, ^4J = 2.1 Hz, 1H, H_{Ar}), 7.84 (s, 1H, H_{Ar}), 8.02 (d, ^3J = 8.4 Hz, 1H, H_{Ar}), 12.28 (s, 1H, NH).

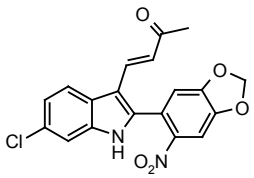
^{13}C NMR (DMSO-d_6): 27.7, 56.3, 56.6, 108.3, 109.4, 111.6, 115.0, 119.0, 121.4, 121.7, 122.6, 124.0, 127.5, 134.7, 137.2, 140.6, 141.5, 149.3, 152.4, 197.0.

IR: 3124, 1636, 1616, 1568, 1512, 1456, 1440, 1428, 1352, 1344, 1280, 1264, 1236, 1220, 1164, 1052, 1012, 868 cm^{-1}.

MS (EI, 70 eV): *m/z* (%) = 402/400 (M^+, 33/100), 371/369 (20/60), 340 (33), 326 (35), 312 (53), 301 (30), 269 (23), 120 (28), 101 (37), 82 (57), 59 (38), 43 (63).

Anal. Calcd for $C_{20}H_{17}ClN_2O_5$: C, 59.93; H, 4.28; N, 6.99. Found: C, 59.77; H, 4.36; N, 7.09.

(3*E*)-4-[6-Chloro-2-(6-nitro-1,3-benzodioxol-5-yl)-1*H*-indol-3-yl]but-3-en-2-one (4f)



4f

Yield 59 %. Red solid. R_f = 0.48 (acetone–hexane 1:1). Mp 323–324 °C (dioxane–EtOH).

^{1}H NMR (DMSO-d_6): 2.21 (s, 3H, Me), 6.37 (s, 2H, CH_2), 6.75 (d, ^3J = 15.9 Hz, 1H, =CH), 7.24 (dd, J = 2.1, 8.7 Hz, 1H, H_{Ar}), 7.27 (s, 1H, H_{Ar}), 7.34 (d, ^3J = 15.9 Hz, 1H, =CH), 7.50 (d, ^4J = 2.1 Hz, 1H, H_{Ar}), 7.88 (s, 1H, H_{Ar}), 8.03 (d, ^3J = 8.7 Hz, 1H, H_{Ar}), 12.31 (s, 1H, NH).

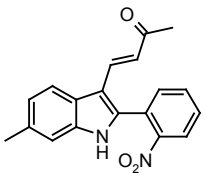
^{13}C NMR (DMSO-d_6): 27.9, 104.0, 105.6, 109.5, 111.6 (2C), 121.1, 121.4, 121.8, 122.7, 123.9, 127.6, 134.3, 137.1, 140.2, 143.3, 148.9, 151.4, 197.0.

IR: 3164, 1612, 1524, 1504, 1480, 1456, 1332, 1268, 1252, 1236, 1116, 1036, 924, 800 cm^{-1}.

MS (EI, 70 eV): *m/z* (%) = 386/384 (M^+, 33/100), 341 (26), 310 (53), 295 (71), 284 (25), 237 (35), 201 (43), 178 (30), 163 (27), 97 (31), 88 (29), 73 (29), 43 (53).

Anal. Calcd for $C_{19}H_{13}ClN_2O_5$: C, 59.31; H, 3.41; N, 7.28. Found: C, 59.37; H, 3.59; N, 7.13.

(3*E*)-4-[6-Methyl-2-(2-nitrophenyl)-1*H*-indol-3-yl]but-3-en-2-one (4g)



4g

Yield 65 %. Red solid. R_f = 0.45 (acetone–hexane 1:1). Mp 270–271 °C (dioxane–EtOH).

^{1}H NMR (DMSO-d_6): 2.19 (s, 3H, Me), 2.44 (s, 3H, Me), 6.75 (d, ^3J = 15.9 Hz, 1H, =CH), 7.08 (d, ^3J = 8.1 Hz, 1H, H_{Ar}), 7.26 (s, 1H, H_{Ar}), 7.32 (d, ^3J = 15.9 Hz, 1H, =CH), 7.69–7.72 (m, 1H, H_{Ar}), 7.81–7.86 (m, 1H, H_{Ar}), 7.88–7.95 (m, 2H, H_{Ar}), 8.23 (d, ^3J = 8.1 Hz, 1H, H_{Ar}), 12.10 (s, 1H, NH).

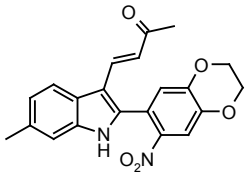
^{13}C NMR (DMSO-d_6): 21.2, 27.7, 109.7, 112.0, 120.2, 122.1, 123.0, 123.1, 124.9, 125.5, 130.8, 132.7, 133.4, 133.5, 135.1, 137.3, 138.6, 149.1, 196.8.

IR: 3188, 1612, 1572, 1524, 1452, 1348, 1276, 1252, 1236, 752 cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 320 (M^+, 100), 305 (15), 260 (17), 245 (47), 230 (80), 220 (27), 120 (17), 95 (62), 83 (19), 55 (30), 43 (71).

Anal. Calcd for $C_{19}H_{16}N_2O_3$: C, 71.24; H, 5.03; N, 8.74. Found: C, 71.40; H, 5.21; N, 8.64.

(3*E*)-4-[6-Methyl-2-(7-nitro-2,3-dihydro-1,4-benzodioxin-6-yl)-1*H*-indol-3-yl]but-3-en-2-one (4h)



4h

Yield 56 %. Orange solid. R_f = 0.44 (acetone–hexane 1:1). Mp 296–297 °C (dioxane–EtOH).

^{1}H NMR (DMSO-d_6): 2.20 (s, 3H, Me), 2.44 (s, 3H, Me), 4.45 (br. s, 4H, CH_2CH_2), 6.74 (d, ^3J = 16.2 Hz, 1H, =CH), 7.06 (dd, J = 1.2, 8.1 Hz, 1H, H_{Ar}), 7.14 (s, 1H, H_{Ar}), 7.23 (d, ^4J = 1.2, Hz, 1H, H_{Ar}), 7.34 (d, ^3J = 16.2 Hz, 1H, =CH), 7.83 (s, 1H, H_{Ar}), 7.87 (d, ^3J = 8.1 Hz, 1H, H_{Ar}), 11.96 (s, 1H, NH).

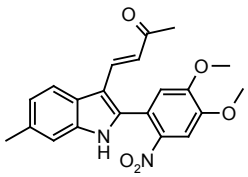
^{13}C NMR (DMSO-d_6): 21.2, 28.0, 64.4, 64.8, 109.4, 111.9, 114.5, 119.6, 120.2, 121.2, 121.6, 122.9, 123.1, 132.5, 135.3, 137.2, 139.1, 141.9, 144.0, 147.5, 196.9.

IR: 3200, 1600, 1576, 1520, 1480, 1456, 1340, 1324, 1292, 1268, 1252, 1236, 1188, 1060, 976, 908, 872 cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 378 (M^+, 100), 346 (42), 335 (37), 303 (27), 289 (42), 205 (34), 162 (25), 143 (36), 134 (57), 43 (30).

Anal. Calcd for $C_{21}H_{18}N_2O_5$: C, 66.66; H, 4.79; N, 7.40. Found: C, 66.48; H, 4.79; N, 7.30.

(3*E*)-4-[2-(4,5-Dimethoxy-2-nitrophenyl)-6-methyl-1*H*-indol-3-yl]-3-buten-2-one (4i)



4i

Yield 57 %. Red solid. R_f = 0.45 (acetone–hexane 1:1). Mp 265–266 °C (dioxane–DMF–EtOH).

^{1}H NMR (DMSO-d_6): 2.20 (s, 3H, Me), 2.45 (s, 3H, Me), 3.92 (s, 3H, OMe), 3.98 (s, 3H, OMe), 6.72 (d, ^3J = 16.2 Hz, 1H, =CH), 7.07 (dd, J = 1.2, 8.1 Hz, 1H, H_{Ar}), 7.19 (s, 1H, H_{Ar}), 7.27 (d, ^4J = 1.2 Hz, 1H, H_{Ar}), 7.39 (d, ^3J = 16.2 Hz, 1H, =CH), 7.83 (s, 1H, H_{Ar}), 7.88 (d, ^3J = 8.1 Hz, 1H, H_{Ar}), 12.02 (s, 1H, NH).

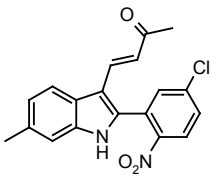
^{13}C NMR (DMSO-d_6): 21.3, 27.6, 56.3, 56.6, 108.3, 109.4, 111.9, 115.0, 119.6, 120.2, 121.8, 122.9, 123.2, 132.4, 135.6, 137.3, 139.5, 141.6, 149.2, 152.3, 196.9.

IR: 3164, 1632, 1612, 1573, 1515, 1497, 1454, 1354, 1343, 1280, 1264, 1239, 1222, 1052, 1010 cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 380 (M^+, 58), 348 (35), 338 (33), 321 (42), 309 (44), 292 (100), 277 (38), 261 (28), 247 (31), 233 (54), 205 (54), 186 (32), 165 (40), 59 (19), 43 (47).

Anal. Calcd for $C_{21}H_{20}N_2O_5$: C, 66.31; H, 5.30; N, 7.36. Found: C, 66.52; H, 5.46; N, 7.36.

(3*E*)-4-[2-(5-Chloro-2-nitrophenyl)-6-methyl-1*H*-indol-3-yl]but-3-en-2-one (4j)



4j

Yield 54 %. Pale brown solid. R_f = 0.55 (acetone–hexane 1:1). Mp 261–262 °C (dioxane–EtOH).

^{1}H NMR (DMSO-d_6): 2.21 (s, 3H, Me), 2.45 (s, 3H, Me), 6.75 (d, ^3J = 15.9 Hz, 1H, =CH), 7.09 (dd, J = 1.2, 8.1 Hz, 1H, H_{Ar}), 7.29 (d, ^4J = 1.2 Hz, 1H, H_{Ar}), 7.35 (d, ^3J = 15.9 Hz, 1H, =CH), 7.84 (d, ^4J = 2.1 Hz, 1H, H_{Ar}), 7.89 (dd, J = 2.1, 8.7 Hz, 1H, H_{Ar}), 8.25 (d, ^3J = 8.7 Hz, 1H, H_{Ar}), 12.10 (s, 1H, NH).

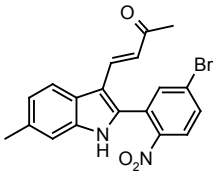
^{13}C NMR (DMSO-d_6): 21.1, 27.6, 110.1, 112.0, 120.2, 122.7, 123.0, 123.1, 126.7, 127.4, 130.6, 132.8, 132.9, 134.6, 136.6, 137.4, 137.9, 147.7, 196.8.

IR: 3248, 1605, 1568, 1526, 1456, 1340, 1266, 1233, 1172, 1153, 1098, 1000, 972, 850 cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 356/354 (M^+, 33/100), 322 (30), 311 (56), 307 (24), 294 (63), 280 (69), 266 (92), 242 (35), 229 (58), 217 (26), 202 (20), 186 (27), 101 (33), 88 (32), 59 (61), 43 (66).

Anal. Calcd for $C_{19}H_{15}ClN_2O_3$: C, 64.32; H, 4.26; N, 7.90. Found: C, 64.19; H, 4.37; N, 7.83.

(3*E*)-4-[2-(5-Bromo-2-nitrophenyl)-6-methyl-1*H*-indol-3-yl]but-3-en-2-one (4k)



4k

Yield 55 %. Orange solid. R_f = 0.55 (acetone–hexane 1:1). Mp 275–276 °C (dioxane–EtOH).

^{1}H NMR (DMSO-d_6): 2.21 (s, 3H, Me), 2.45 (s, 3H, Me), 6.74 (d, ^3J = 15.9 Hz, 1H, =CH), 7.09 (dd, J = 1.2, 8.4 Hz, 1H, H_{Ar}), 7.29 (d, ^4J = 1.2 Hz, 1H, H_{Ar}), 7.34 (d, ^3J = 15.9 Hz, 1H, =CH), 7.88 (d, ^3J = 8.4 Hz, 1H, H_{Ar}), 7.96 (d, ^4J = 2.1 Hz, 1H, H_{Ar}), 8.02 (dd, J = 2.1, 8.7 Hz, 1H, H_{Ar}), 8.16 (d, ^3J = 8.7 Hz, 1H, H_{Ar}), 12.10 (s, 1H, NH).

^{13}C NMR (DMSO-d_6): 21.1, 27.6, 110.1, 112.0, 120.2, 122.7, 122.9, 123.1, 126.6, 126.7, 127.4, 132.9, 133.6, 134.6, 135.6, 136.5, 137.4, 148.1, 196.8.

IR: 3250, 1603, 1561, 1525, 1455, 1341, 1266, 1232, 1152, 998, 972, 848 cm^{-1}.

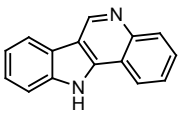
MS (EI, 70 eV): *m*/*z* (%) = 400/398 (M^+, 54/54), 373/371 (20/20), 357/355 (38/38), 339 (36), 326/324 (36/36), 311 (47), 276 (25), 248 (21), 229 (100), 217 (35), 186 (32), 158 (23), 115 (22), 101 (23), 59 (52), 57 (61), 43 (39).

Anal. Calcd for $C_{19}H_{15}BrN_2O_3$: C, 57.16; H, 3.79; N, 7.02. Found: C, 57.18; H, 3.96; N, 6.88.

General Procedure for the Synthesis of Indolo[3,2-*c*]quinolines 5:

Mixture of 3-(2-acylvinyl)-2-(2-nitroaryl)indole **4** (1,6 mmol), iron powder (32 mmol) and acetic acid (25 mL) was refluxed for 5 min after full dissolution of solid. Reaction mixture was poured into water and neutralized with $NaHCO_3$. The formed residue was filtered off. Aqueous solution was extracted with ethyl acetate (3 × 50 mL); solid residue was extracted with 1,4-dioxane (4 × 50 mL). The combined extracts were dried with Na_2SO_4, treated with activated charcoal, and evaporated to dryness under reduced pressure. Indolo[3,2-*c*]quinolines **5a-k** were purified by recrystallization using the specified solvents.

11*H*-Indolo[3,2-*c*]quinoline (5a)



5a

Yield 86 %. White solid. R_f = 0.61 (acetone/benzene/ammonia 8:8:1). Mp 320 °C with sublimation (dioxane); lit.:[3] 342 °C with sublimation (aq. methanol).

^{1}H NMR (DMSO-d_6): 7.32–7.37 (m, 1H, H_{Ar}), 7.48–7.53 (m, 1H, H_{Ar}), 7.67–7.78 (m, 3H, H_{Ar}), 8.13–8.16 (m, 1H, H_{Ar}), 8.31–8.34 (m, 1H, H_{Ar}), 8.52–8.55 (m, 1H, H_{Ar}), 9.61 (s, 1H, H_{Py}), 12.75 (br. s, 1H, NH).

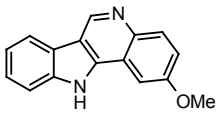
^{13}C NMR (DMSO-d_6): 111.9, 114.3, 117.0, 120.1, 120.6, 121.9, 122.1, 125.6, 125.7, 128.1, 129.2, 138.8, 139.9, 144.6, 145.1.

IR: 3116, 1628, 1596, 1572, 1512, 1504, 1456, 1364, 1336, 1284, 1264, 1236, 1216, 1156, 932, 764, 744, 732 cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 218 (M^+, 100), 190 (18), 108 (21), 101 (19), 90 (11), 59 (15), 43 (68).

Anal. Calcd for $C_{15}H_{10}N_2$: C, 82.55; H, 4.62; N, 12.83. Found: C, 82.60; H, 4.70; N, 12.80.

2-Methoxy-11*H*-indolo[3,2-*c*]quinoline (5b)



5b

Yield 74 %. White solid. R_f = 0.60 (acetone/benzene/ammonia 8:8:1) Mp 300 °C with sublimation (dioxane); lit.:[4] 312–314 °C (ethanol).

^{1}H NMR (DMSO-d_6): 3.98 (s, 3H, OMe), 7.30–7.35 (m, 1H, H_{Ar}), 7.37 (dd, J = 3.0, 9.0 Hz, 1H, H_{Ar}), 7.46–7.52 (m, 1H, H_{Ar}), 7.70–7.73 (m, 1H, H_{Ar}), 7.97 (d, ^4J = 3.0 Hz, 1H, H_{Ar}), 8.04 (d, ^3J = 9.0 Hz, 1H, H_{Ar}), 8.28–8.31 (m, 1H, H_{Ar}), 9.45 (s, 1H, H_{Py}), 12.57 (br. s, 1H, NH).

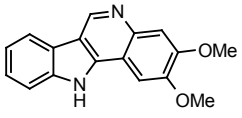
^{13}C NMR (DMSO-d_6): 55.5, 101.3, 111.8, 114.3, 117.7, 119.4, 120.1, 120.4, 121.9, 125.5, 131.0, 138.8, 139.5, 141.0, 142.2, 156.9.

IR: 3121, 1632, 1600, 1572, 1520, 1468, 1368, 1336, 1280, 1240, 1204, 1172, 1132, 1028, 948, 856, 816, 744 cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 248 (M^+, 96), 233 (49), 217 (15), 205 (100), 177 (34), 128 (30), 101 (42), 76 (33), 43 (21).

Anal. Calcd for $C_{16}H_{12}N_2O$: C, 77.40; H, 4.87; N, 11.28. Found: C, 77.20; H, 4.72; N, 11.14.

2,3-Dimethoxy-11*H*-indolo[3,2-*c*]quinoline (5c)



5c

Yield 79 %. White solid. R_f = 0.48 (acetone/benzene/ammonia 8:8:1). Mp 320–321 °C (dioxane–EtOH).

^{1}H NMR (DMSO-d_6): 3.95 (s, 3H, OMe), 4.00 (s, 3H, OMe), 7.27–7.32 (m, 1H, H_{Ar}), 7.42–7.48 (m, 1H, H_{Ar}), 7.54 (s, 1H, H_{Ar}), 7.66–7.69 (m, 1H, H_{Ar}), 7.93 (s, 1H, H_{Ar}), 8.23–8.25 (m, 1H, H_{Ar}), 9.39 (s, 1H, H_{Py}), 12.36 (br. s, 1H, NH).

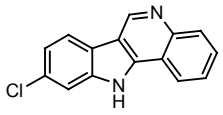
^{13}C NMR (DMSO-d_6): 55.5, 55.7, 101.2, 109.2, 111.0, 111.5, 113.5, 119.8, 120.2, 122.0, 125.1, 138.7, 139.7, 142.0, 142.1, 148.7, 150.6.

IR: 3119, 1628, 1511, 1491, 1466, 1423, 1339, 1303, 1263, 1238, 1218, 1195, 1181, 1110, 835, 743 cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 278 (M^+, 100), 235 (38), 220 (22), 205 (47), 192 (26), 164 (21), 139 (25), 59 (17), 43 (24).

Anal. Calcd for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.07; N, 10.07. Found: C, 73.54; H, 5.22; N, 10.05.

9-Chloro-11*H*-indolo[3,2-*c*]quinoline (5d)



5d

Yield 75 %. White solid. R_f = 0.58 (acetone/benzene/ammonia 8:8:1). Mp 325 °C with sublimation (dioxane).

^{1}H NMR (DMSO-d_6): 7.37 (dd, *J* = 1.8, 8.4 Hz, 1H, H_{Ar}), 7.69–7.80 (m, 2H, H_{Ar}), 7.74 (d, ^4J = 1.8 Hz, 1H, H_{Ar}), 8.13–8.16 (m, 1H, H_{Ar}), 8.35 (d, ^3J = 8.4 Hz, 1H, H_{Ar}), 8.50–8.53 (m, 1H, H_{Ar}), 9.60 (s, 1H, H_{Py}), 12.82 (br. s, 1H, NH).

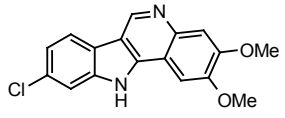
^{13}C NMR (DMSO-d_6): 111.4, 113.8, 116.9, 120.7, 120.8, 121.4, 122.0, 125.8, 128.2, 129.5, 129.8, 139.3, 140.3, 144.7, 145.5.

IR: 3180, 1592, 1568, 1512, 1436, 1332, 1236, 1216, 936, 804, 756 cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 254/252 (M^+, 33/100), 217 (42), 190 (26), 163 (16), 126 (69), 59 (27), 43 (40).

Anal. Calcd for $C_{15}H_9ClN_2$: C, 71.30; H, 3.59; N, 11.09. Found: C, 71.48; H, 3.71; N, 11.08.

9-Chloro-2,3-dimethoxy-11*H*-indolo[3,2-*c*]quinoline (5e)



5e

Yield 77 %. Beige solid. R_f = 0.55 (acetone/benzene/ammonia 8:8:1). Mp 309–310 °C (acetone–hexane) lit.[5] 260–261 °C.

^{1}H NMR (DMSO-d_6): 3.95 (s, 3H, OMe), 3.99 (s, 3H, OMe), 7.31 (dd, J = 2.1, 8.4 Hz, 1H, H_{Ar}), 7.53 (s, 1H, H_{Ar}), 7.70 (d, ^4J = 2.1 Hz, 1H, H_{Ar}), 7.91 (s, 1H, H_{Ar}), 8.26 (d, ^3J = 8.4 Hz, 1H, H_{Ar}), 9.40 (s, 1H, H_{Py}), 12.54 (br. s, 1H, NH).

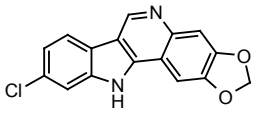
^{13}C NMR (DMSO-d_6): 55.5, 55.7, 101.1, 109.1, 110.9, 111.2, 113.0, 120.4, 121.0, 121.1, 129.5, 139.3, 140.3, 142.1(2C), 148.8, 150.8.

IR: 3170, 1636, 1568, 1508, 1484, 1424, 1356, 1292, 1264, 1244, 1184, 1124, 1064, 1056, 940, 872, 824, 804 cm^{-1}.

MS (EI, 70 eV): m/z (%) = 314/312 (M^+, 33/100), 271/269 (10/30), 239 (16), 226 (36), 59 (16), 43 (37).

Anal. Calcd for $C_{17}H_{13}ClN_2O_2$: C, 65.29; H, 4.19; N, 8.96. Found: C, 65.26; H, 4.32; N, 8.98.

9-Chloro-11*H*-[1,3]dioxolo[4,5-*g*]indolo[3,2-*c*]quinoline (5f)



5f

Yield 72 %. Beige solid. R_f = 0.63 (acetone/benzene/ammonia 8:8:1). Decomp. 375 °C (DMF–EtOH).

^{1}H NMR (DMSO-d_6): 6.22 (s, 2H, OCH_2O), 7.34 (dd, J = 2.1, 8.4 Hz, 1H, H_{Ar}), 7.50 (s, 1H, H_{Ar}), 7.69 (d, ^4J = 2.1 Hz, 1H, H_{Ar}), 7.86 (s, 1H, H_{Ar}), 8.27 (d, ^3J = 8.4 Hz, 1H, H_{Ar}), 9.42 (s, 1H, H_{Py}), 12.59 (br. s, 1H, NH).

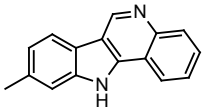
^{13}C NMR (DMSO-d_6): 98.0, 102.0, 106.1, 111.3, 112.1, 113.3, 120.7 (3C), 121.4, 129.9, 139.3, 140.9, 141.8, 146.9, 148.3.

IR: 3116, 1608, 1524, 1468, 1372, 1256, 1244, 1180, 1036, 936, 844 cm^{-1}.

MS (EI, 70 eV): m/z (%) = 298/296 (M^+, 33/100), 205/203 (12/36), 176 (13), 101 (17), 88 (33), 59 (39), 43 (52).

Anal. Calcd for $C_{16}H_9ClN_2O_2$: C, 64.77; H, 3.06; N, 9.44. Found: C, 64.82; H, 3.03; N, 9.32.

9-Methyl-11*H*-indolo[3,2-*c*]quinoline (5g)



5g

Yield 73 %. Beige solid. R_f = 0.63 (acetone/benzene/ammonia 8:8:1). Mp 310 °C with sublimation (dioxane).

^{1}H NMR (DMSO-d$_6$): 2.53 (s, 3H, Me), 7.17 (dd, J = 1.2, 8.1 Hz, 1H, H$_{Ar}$), 7.50 (d, ^4J = 1.2 Hz, 1H, H$_{Ar}$), 7.65–7.76 (m, 2H, H$_{Ar}$), 8.11–8.14 (m, 1H, H$_{Ar}$), 8.18 (d, ^3J = 8.1 Hz, 1H, H$_{Ar}$), 8.49–8.52 (m, 1H, H$_{Ar}$), 9.55 (s, 1H, H$_{Py}$), 12.62 (br. s, 1H, NH).

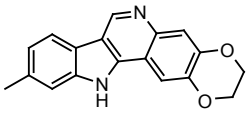
^{13}C NMR (DMSO-d$_6$): 21.6, 111.7, 114.3, 117.1, 119.7, 121.9, 122.1, 125.5, 127.7, 129.4, 135.1, 139.2, 139.6, 144.4 (2C), 145.1.

IR: 3048, 1628, 1592, 1568, 1508, 1456, 1364, 1336, 1240, 1216, 804, 756 cm^{-1}.

MS (EI, 70 eV): m/z (%) = 232 (M$^+$, 100), 116 (13), 59 (17), 43 (18).

Anal. Calcd for C$_{16}$H$_{12}$N$_2$: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.98; H, 5.38; N, 11.87.

10-Methyl-2,3-dihydro-12*H*-[1,4]dioxino[2,3-*g*]indolo[3,2-*c*]quinoline (5h)



5h

Yield 70 %. White solid. R$_f$ = 0.60 (acetone/benzene/ammonia 8:8:1). Decomp. 380 °C (DMF–dioxane).

^{1}H NMR (DMSO-d$_6$): 2.51 (s, 3H, Me), 4.40 (br. s, 4H, OCH$_2$CH$_2$O), 7.12 (dd, J = 1.2, 8.1 Hz, 1H, H$_{Ar}$), 7.42 (d, ^4J = 1.2 Hz, 1H, H$_{Ar}$), 7.49 (s, 1H, H$_{Ar}$), 7.89 (s, 1H, H$_{Ar}$), 8.09 (d, ^3J = 8.1 Hz, 1H, H$_{Ar}$), 9.31 (s, 1H, H$_{Py}$), 12.22 (br. s, 1H, NH).

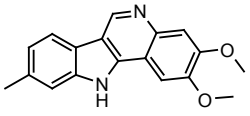
^{13}C NMR (DMSO-d$_6$): 21.6, 64.2, 64.3, 106.7, 111.5, 112.2, 113.1, 114.5, 119.4, 119.8, 121.8, 134.6, 138.9, 139.1, 141.5, 142.9, 143.3, 145.0.

IR: 3128, 1633, 1598, 1570, 1510, 1474, 1365, 1342, 1288, 1253, 1187, 1139, 1068, 931, 913, 900, 869, 807 cm^{-1}.

MS (EI, 70 eV): m/z (%) = 290 (M$^+$, 70), 234 (15), 206 (100), 152 (21), 145 (22), 138 (33), 59 (83) 55 (84), 43 (54).

Anal. Calcd for C$_{18}$H$_{14}$N$_2$O$_2$: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.36; H, 5.01; N, 9.50.

2,3-Dimethoxy-9-methyl-11*H*-indolo[3,2-*c*]quinoline (5i)



5i

Yield 78 %. White solid. R$_f$ = 0.48 (acetone/benzene/ammonia 8:8:1). Mp 161–162 °C (DMF–EtOH).

^{1}H NMR (DMSO-d$_6$): 2.50 (s, 3H, Me), 3.93 (s, 3H, OMe), 3.99 (s, 3H, OMe), 7.09 (d, ^4J = 7.8 Hz, 1H, H$_{Ar}$), 7.45 (s, 1H, H$_{Ar}$), 7.52 (s, 1H, H$_{Ar}$), 7.90 (s, 1H, H$_{Ar}$), 8.08 (d, ^3J = 7.8 Hz, 1H, H$_{Ar}$), 9.33 (s, 1H, H$_{Py}$), 12.24 (br. s, 1H, NH).

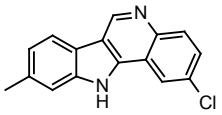
^{13}C NMR (DMSO-d_6): 21.6, 55.5, 55.7, 101.1, 109.2, 111.2, 111.5, 113.7, 119.5, 119.8, 121.8, 134.7, 139.2, 139.7, 141.8, 141.9, 148.6, 150.5.

IR: 3157, 1632, 1576, 1513, 1493, 1462, 1435, 1366, 1302, 1262, 1243, 1215, 1196, 1185, 1121, 993, 849, 804.

MS (EI, 70 eV): *m*/*z* (%) = 292 (M^+, 100), 277 (21), 249 (31), 235 (21), 231 (20), 219 (20), 206 (63), 146 (21), 59 (28), 43 (32).

Anal. Calcd for $C_{18}H_{16}N_2O_2$: C, 73.96; H, 5.52; N, 9.58. Found: C, 73.85; H, 5.72; N, 9.88.

2-Chloro-9-methyl-11*H*-indolo[3,2-*c*]quinoline (5j)



5j

Yield 79 %. Beige solid. R_f = 0.63 (acetone/benzene/ammonia 8:8:1). Mp 330 °C with sublimation (DMF–EtOH).

^{1}H NMR (DMSO-d_6): 2.53 (s, 3H, Me), 7.18 (dd, J = 1.5, 8.1 Hz, 1H, H_{Ar}), 7.51 (d, ^4J = 1.5 Hz, 1H, H_{Ar}), 7.71 (dd, J = 2.4, 9.0 Hz, 1H, H_{Ar}), 8.13 (d, ^3J = 9.0 Hz, 1H, H_{Ar}), 8.19 (d, ^3J = 8.1 Hz, 1H, H_{Ar}), 8.61 (d, ^4J = 2.4 Hz, 1H, H_{Ar}), 9.56 (s, 1H, H_{Py}), 12.60 (br. s, 1H, NH).

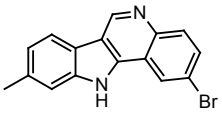
^{13}C NMR (DMSO-d_6): 21.6, 111.8, 114.9, 117.9, 119.3, 120.0, 121.1, 122.4, 128.0, 129.8, 131.6, 135.7, 138.6, 139.3, 143.6, 145.0.

IR: 3120, 1629, 1618, 1592, 1566, 1506, 1466, 1453, 1361, 1335, 1284, 1260, 1237, 1209, 1139, 1084, 867, 822, 805.

MS (EI, 70 eV): *m*/*z* (%) = 268/266 (M^+, 33/100), 203 (13), 134 (11), 115 (12), 43 (27).

Anal. Calcd for $C_{16}H_{11}ClN_2$: C, 72.05; H, 4.16; N, 10.50. Found: C, 72.26; H, 4.36; N, 10.30.

2-Bromo-9-methyl-11*H*-indolo[3,2-*c*]quinoline (5k)



5k

Yield 76%. Beige solid. R_f = 0.63 (acetone/benzene/ammonia 8:8:1). Mp 292–293 °C (DMF–EtOH).

^{1}H NMR (DMSO-d_6): 2.54 (s, 3H, Me), 7.20 (dd, J = 2.1, 8.1 Hz, 1H, H_{Ar}), 7.51 (d, ^4J = 2.1 Hz, 1H. H_{Ar}), 7.82 (dd, J = 2.4, 9.0 Hz, 1H, H_{Ar}), 8.06 (d, ^3J = 9.0 Hz, 1H, H_{Ar}), 8.19 (d, ^3J = 8.1 Hz, 1H, H_{Ar}), 8.78 (d, ^4J = 2.4 Hz, 1H, H_{Ar}), 9.58 (s, 1H, H_{Py}), 12.59 (br.s, 1H, NH).

^{13}C NMR (DMSO-d_6): 21.6, 111.7, 114.9, 118.2, 118.4, 119.3, 119.9, 122.4, 124.3, 130.5, 131.7, 135.6, 138.4, 139.3, 143.7, 145.1.

IR: 3084, 1613, 1590, 1567, 1504, 1465, 1361, 1334, 1208, 1140, 1066, 865, 819, 804 cm^{-1}.

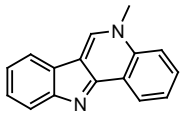
MS (EI, 70 eV): *m*/*z* (%) = 312/310 (M^+, 98/100), 229 (21), 204 (14), 155 (17), 116 (13), 102 (13), 88 (14), 59 (44), 55 (32), 43 (18).

Anal. Calcd for $C_{16}H_{11}BrN_2$: C, 61.76; H, 3.56; N, 9.00. Found: C, 61.96; H, 3.64; N, 8.92.

General Procedure for the Synthesis of 5-methyl-5*H*-indolo[3,2-*c*]quinolines 7:

5-Methyl-5H-indolo[3,2-c]quinolines **7** were synthesized according to the published procedure.[3] Methyl iodide (10 mL) was added to solution of compound **6a** (0.8 g, 3.7 mmol) in nitrobenzene (30 mL). Reaction mixture was stirred at 80 °C for 2 h and cooled to room temperature. The formed precipitate was filtered, washed on filter with Et_2O and dissolved in hot water (40 mL). Aqueous ammonia (30 mL) was added to boiling solution; mixture was refluxed for 10 min and cooled to room temperature. Precipitate was filtered and recrystallized from benzene. Compounds **7b**–**m** were prepared by analogous procedure using 500 mL of water for transformation of salts into the corresponding bases. 5-Methyl-5*H*-indolo[3,2-*c*]quinolines **7** were purified by recrystallization using the specified solvents.

5-Methyl-5*H*-indolo[3,2-*c*]quinoline (7a)



7a

Yield 86 %. Yellow solid. R_f = 0.48 (acetone/benzene/ammonia 8:8:1). Mp 201–202 °C (benzene); lit.[3] 195 °C (benzene).

^{1}H NMR ($CDCl_3$): 3.78 (s, 3H, Me), 7.13–7.19 (m, 1H, H_{Ar}), 7.36–7.52 (m, 4H, H_{Ar}), 7.70–7.73 (m, 1H, H_{Ar}), 7.87–7.90 (m, 1H, H_{Ar}), 7.92 (s, 1H, H_{Py}), 8.73–8.76 (m, 1H, H_{Ar}).

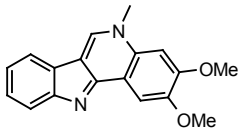
^{13}C NMR ($CDCl_3$): 42.5, 116.1, 117.5, 119.2, 119.3, 120.7, 121.4, 125.1, 125.2, 125.5, 126.5, 129.4, 135.4, 135.6, 153.9, 155.1.

IR: 3406, 1636, 1596, 1453, 1443, 1351, 1315, 1222, 1118, 743 cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 232 (M^+, 100), 217 (32), 204 (12), 190 (22), 116 (35), 101 (43), 59 (68), 43 (40).

Anal. Calcd for $C_{16}H_{12}N_2 \cdot 2H_2O$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.96; H, 6.00; N, 10.41.

2,3-Dimethoxy-5-methyl-5*H*-indolo[3,2-*c*]quinoline (7b)



7b

Yield 75 %. Yellow solid. R_f = 0.18 (acetone/benzene/ammonia 8:8:1). Mp 279–280 °C (DMF–EtOH).

^{1}H NMR (DMSO-d_6): 4.00 (s, 3H, OMe), 4.01 (s, 3H, OMe), 4.22 (s, 3H, Me), 7.15–7.20 (m, 1H, H_{Ar}), 7.34 (s, 1H, H_{Ar}), 7.35–7.41 (m, 1H, H_{Ar}), 7.70–7.73 (m, 1H, H_{Ar}), 8.03–8.06 (m, 1H, H_{Ar}), 8.08 (s, 1H, H_{Ar}), 9.14 (s, 1H, H_{Py}).

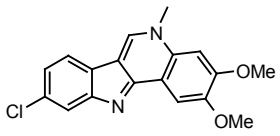
^{13}C NMR (DMSO-d_6): 42.2, 55.7, 56.0, 99.5, 103.5, 114.9, 115.6, 117.8, 118.9, 119.4, 125.2, 125.4, 130.9, 136.2, 147.8, 151.0, 152.3, 154.4.

IR: 3442, 1639, 1598, 1509, 1475, 1461, 1440, 1426, 1354, 1275, 1227, 1060, 734 cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 292 (M^+, 100), 265 (10), 250 (10), 146 (23), 115 (26), 57 (12), 43 (25).

Anal. Calcd for $C_{18}H_{16}N_2O_2 \cdot 2H_2O$: C, 65.84; H, 6.14; N, 8.53. Found: C, 65.80; H, 5.87; N, 8.40.

9-Chloro-2,3-dimethoxy-5-methyl-5*H*-indolo[3,2-*c*]quinoline (7c)



7c

Yield 74 %. Yellow solid. R_f = 0.39 (acetone/benzene/ammonia 8:8:1). Mp 270–271 °C (dioxane–EtOH).

^{1}H NMR (DMSO-d_6): 4.00 (s, 3H, OMe), 4.01 (s, 3H, OMe), 4.23 (s, 3H, Me), 7.16 (dd, J = 2.1, 8.1 Hz, 1H, H_{Ar}), 7.36 (s, 1H, H_{Ar}), 7.70 (d, ^4J = 2.1 Hz, 1H, H_{Ar}), 8.03 (d, ^3J = 8.1 Hz, 1H, H_{Ar}), 8.05 (s, 1H, H_{Ar}), 9.19 (s, 1H, H_{Py}).

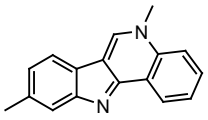
^{13}C NMR (DMSO-d_6): 42.4, 55.7, 56.0, 99.5, 103.4, 114.9, 115.0, 117.2, 118.6, 120.5, 124.2, 129.4, 130.9, 136.7, 148.0, 151.2, 153.6, 155.5.

IR: 3384, 1641, 1594, 1509, 1460, 1413, 1351, 1276, 1226, 1056, 855 cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 328/326 (M^+, 33/100), 283 (16), 268 (10), 240 (10), 43 (26).

Anal. Calcd for $C_{18}H_{15}ClN_2O_2 \cdot 2H_2O$: C, 59.59; H, 5.28; N, 7.72. Found: C, 59.43; H, 4.98; N, 7.60.

5,9-Dimethyl-5*H*-indolo[3,2-*c*]quinoline (7d)



7d

Yield 85 %. Yellow solid. R_f = 0.49 (acetone/benzene/ammonia 8:8:1). Mp 272–273 °C (CH_2Cl_2–benzene–hexane).

^{1}H NMR (DMSO-d_6): 2.51 (s, 3H, Me), 4.25 (s, 3H, Me), 7.09 (dd, J = 1.2, 7.8 Hz, 1H, H_{Ar}), 7.59 (d, ^4J = 1.2 Hz, 1H, H_{Ar}), 7.67-7.72 (m, 1H, H_{Ar}), 7.80–7.86 (m, 1H, H_{Ar}), 7.99 (d, ^3J = 7.8 Hz, 1H, H_{Ar}), 8.03–8.06 (m, 1H, H_{Ar}), 8.73–8.77 (m, 1H, H_{Ar}), 9.28 (s, 1H, H_{Py}).

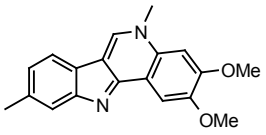
^{13}C NMR (DMSO-d_6): 21.9, 42.2, 116.2, 117.5, 118.3, 119.2, 120.7, 121.5, 123.0, 123.9, 125.1, 129.3, 134.9, 135.4, 137.7, 152.3, 154.3.

IR: 3442, 1641, 1601, 1484, 1451, 1423, 1396, 1367, 1351, 1312, 1241, 1228, 1126, 1067, 806, 752 cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 246 (M^+, 100), 231 (13), 43 (18).

Anal. Calcd for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.37. Found: C, 82.85; H, 5.92; N, 11.21.

2,3-Dimethoxy-5,9-dimethyl-5*H*-indolo[3,2-*c*]quinoline (7e)



7e

Yield 82 %. Yellow solid. R_f = 0.20 (acetone/benzene/ammonia 8:8:1). Mp 252–253 °C (CH_2Cl_2–benzene–hexane).

^{1}H NMR (DMSO-d_6): 2.51 (s, 3H, Me), 4.01 (s, 3H, OMe), 4.04 (s, 3H, OMe), 4.30 (s, 3H, Me), 7.10 (dd, J = 1.2, 7.8 Hz, 1H, H_{Ar}), 7.43 (s, 1H, H_{Ar}), 7.54 (d, ^4J = 1.2 Hz, 1H, H_{Ar}), 7.98 (d, ^3J = 7.8 Hz, 1H, H_{Ar}), 8.09 (s, 1H, H_{Ar}), 9.30 (s, 1H, H_{Py}).

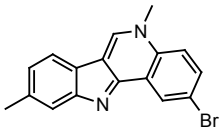
^{13}C NMR (DMSO-d_6): 21.8, 42.8, 55.9, 56.2, 99.6, 103.2, 113.6, 114.9, 116.4, 119.4 (2C), 121.6, 121.8, 131.3 (2C), 135.5, 136.8, 148.4, 151.7.

IR: 3443, 1639, 1605, 1512, 1463, 1432, 1350, 1286, 1240, 1211, 1129, 1060, 810 cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 306 (M^+, 100), 264 (12), 178 (22), 142 (18), 115 (12), 64 (13), 57 (18), 43 (36).

Anal. Calcd for $C_{19}H_{18}N_2O_2 \cdot 2H_2O$: C, 66.65; H, 6.48; N, 8.18. Found: C, 66.78; H, 6.26; N, 8.42.

2-Bromo-5,9-dimethyl-5*H*-indolo[3,2-*c*]quinoline (7f)



7f

Yield 77 %. Yellow solid. R_f = 0.58 (acetone/benzene/ammonia 8:8:1). Mp 292–293 °C (acetone).

^{1}H NMR (DMSO-d_6): 2.51 (s, 3H, Me), 4.22 (s, 3H, Me), 7.09 (dd, J = 1.2, 8.1 Hz, 1H, H_{Ar}), 7.59 (d, ^4J = 1.2 Hz, 1H, H_{Ar}), 7.93 (dd, J = 2.4, 9.0 Hz, 1H, H_{Ar}), 7.97 (d, ^3J = 8.1 Hz, 1H, H_{Ar}), 7.99 (d, ^3J = 9.0 Hz, 1H, H_{Ar}), 8.81 (d, ^4J = 2.4 Hz, 1H, H_{Ar}), 9.24 (s, 1H, H_{Py}).

^{13}C NMR (DMSO-d_6): 21.9, 42.1, 116.8, 117.7, 118.8, 119.3, 120.1, 121.7, 122.3, 123.1, 125.7, 131.5, 134.2, 135.1, 137.7, 151.5, 155.1.

IR: 3269, 1639, 1613, 1597, 1484, 1446, 1430, 1411, 1363, 1348, 1310, 1241, 1223, 1161, 1120, 1083, 1066, 805, 786 cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 326/324 (M^+, 100/100), 309 (12), 245 (15), 229 (23), 163 (13), 43 (23).

Anal. Calcd for $C_{17}H_{13}BrN_2$: C, 62.79; H, 4.03; N, 8.61. Found: C, 62.62; H, 4.20; N, 8.47.

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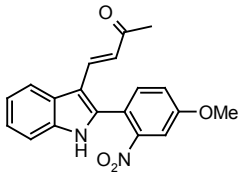
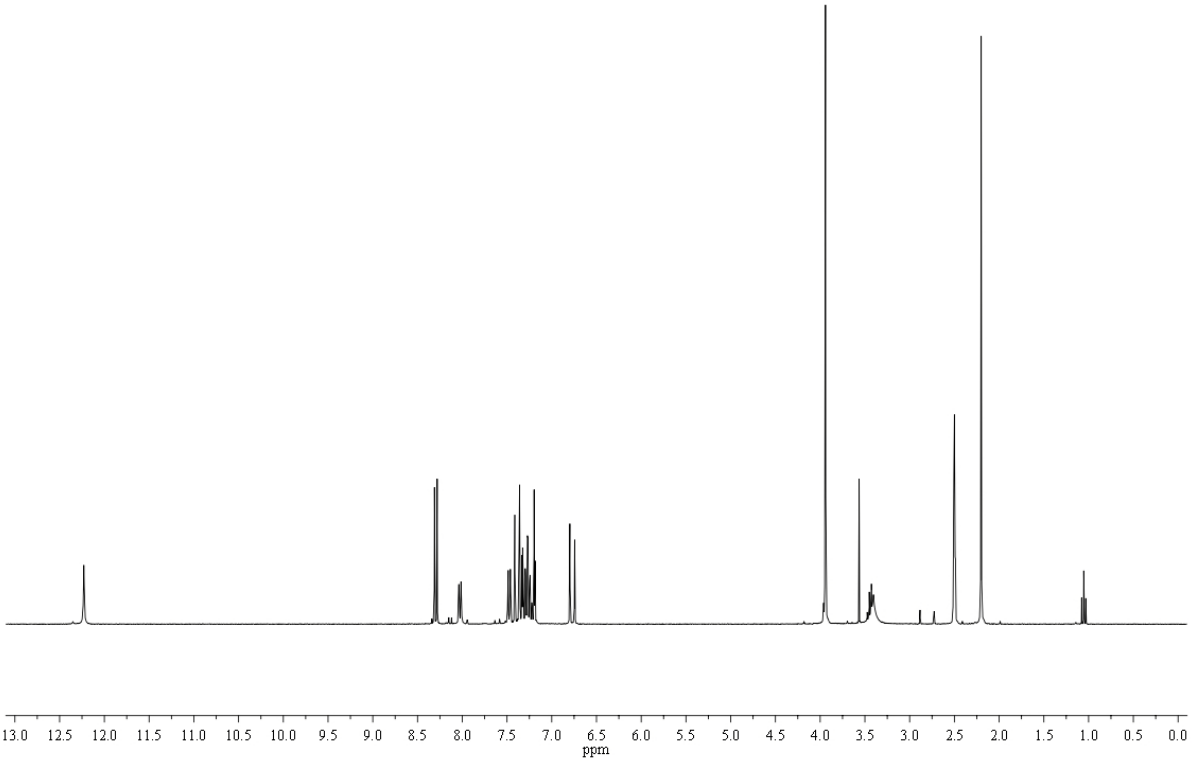
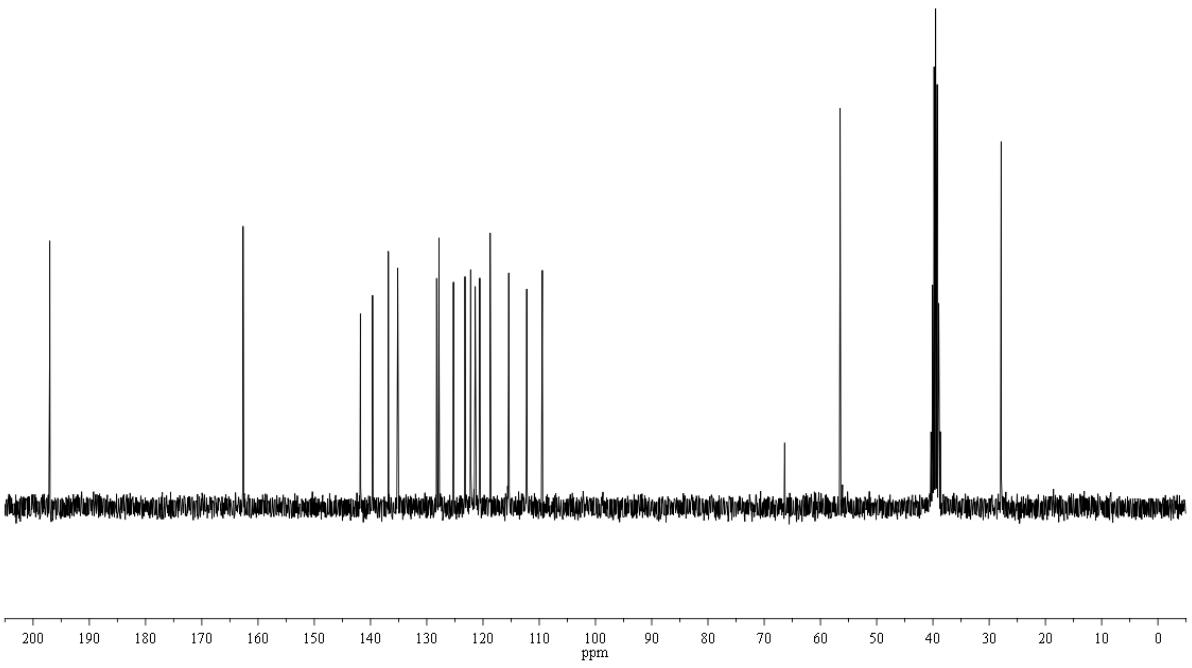
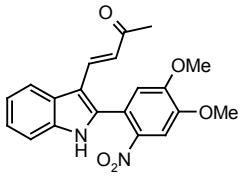


4b







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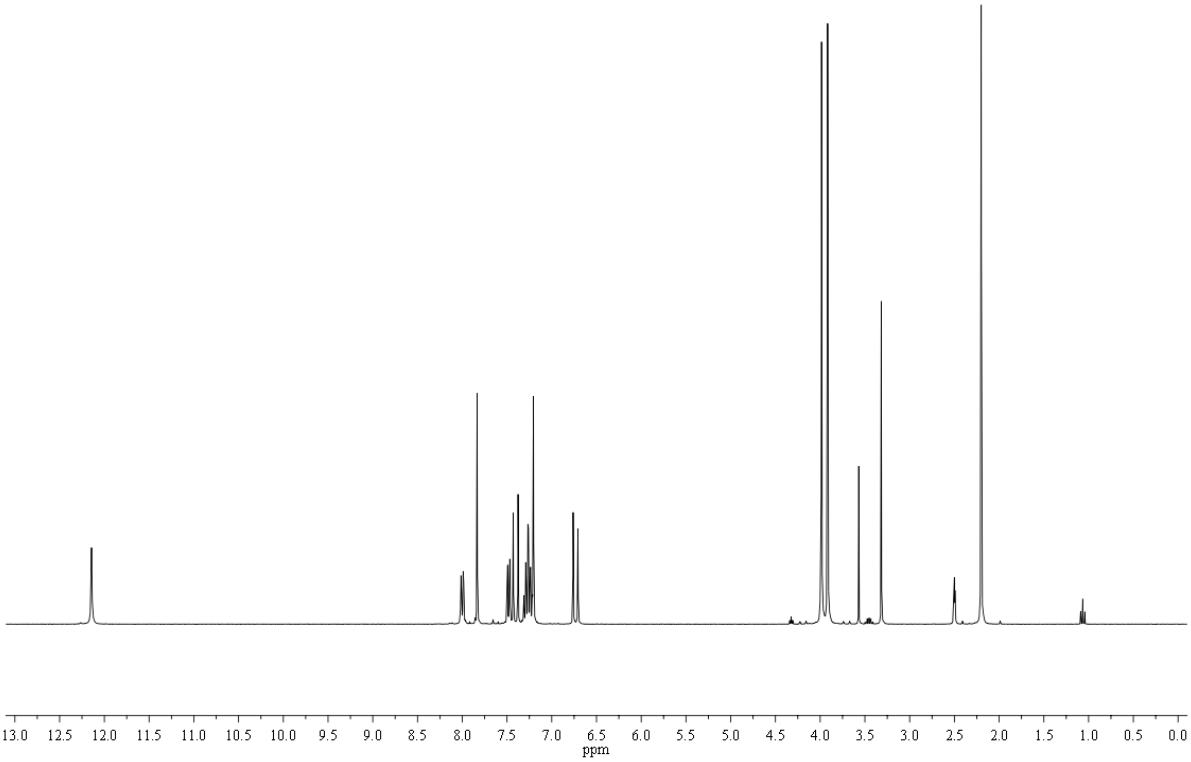

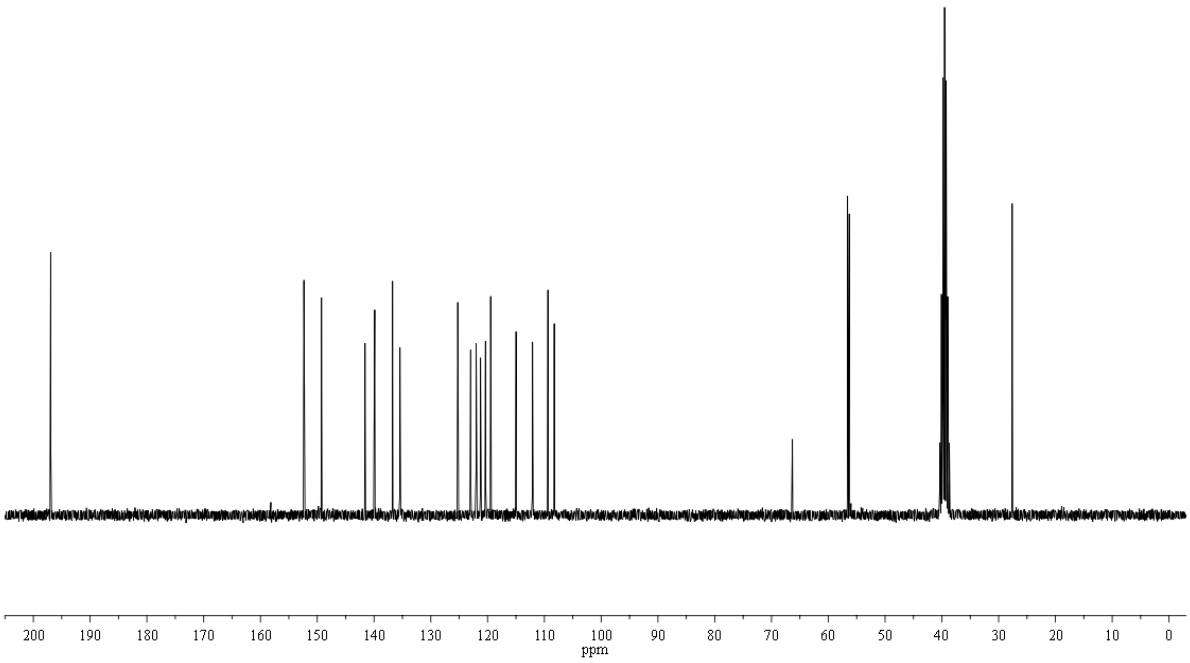

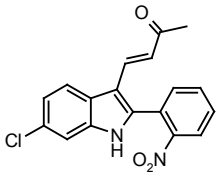

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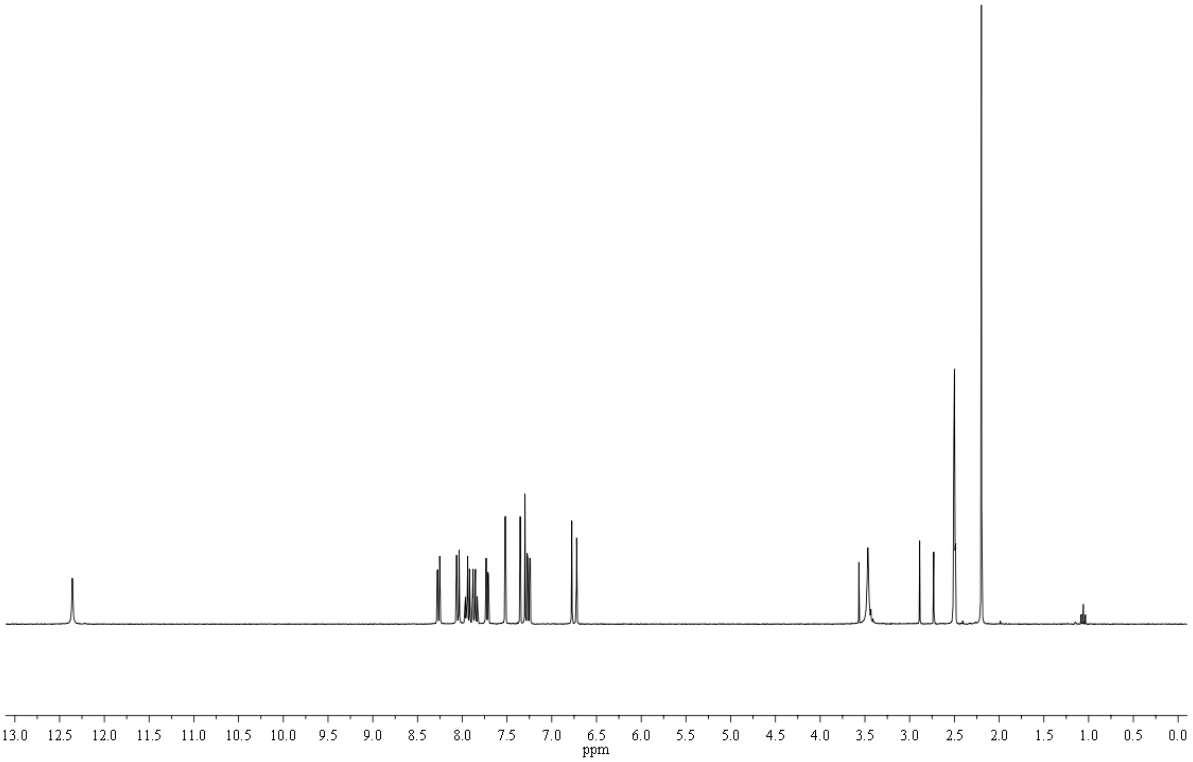

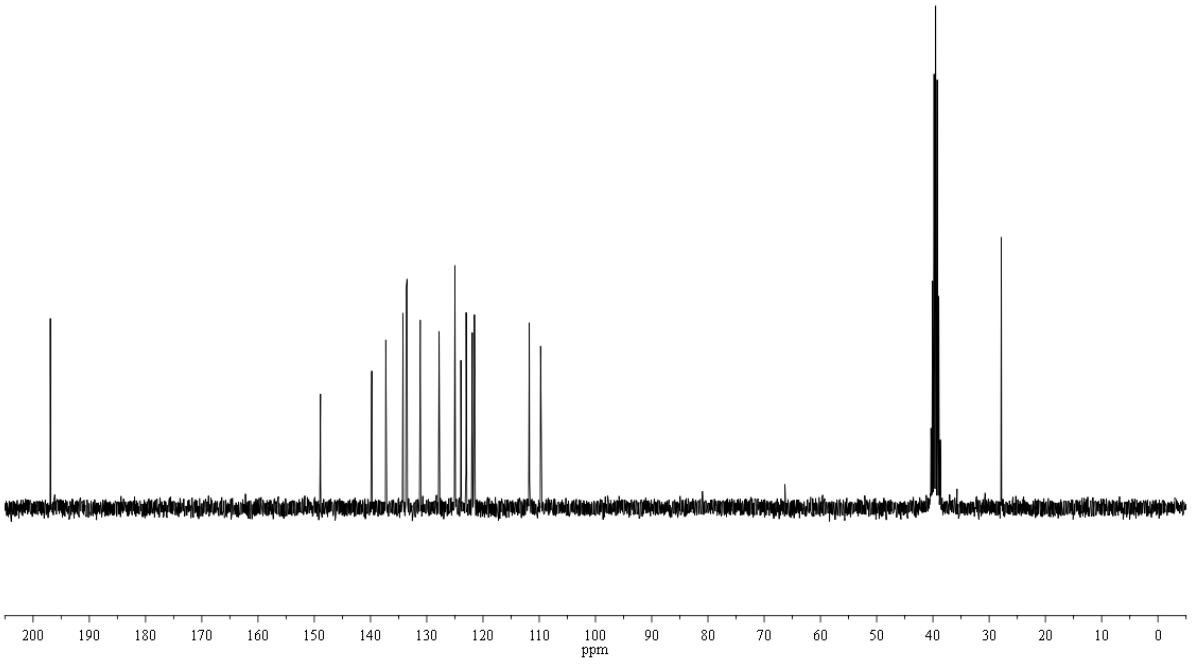

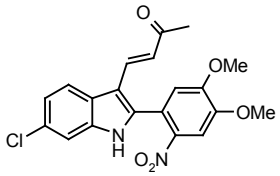

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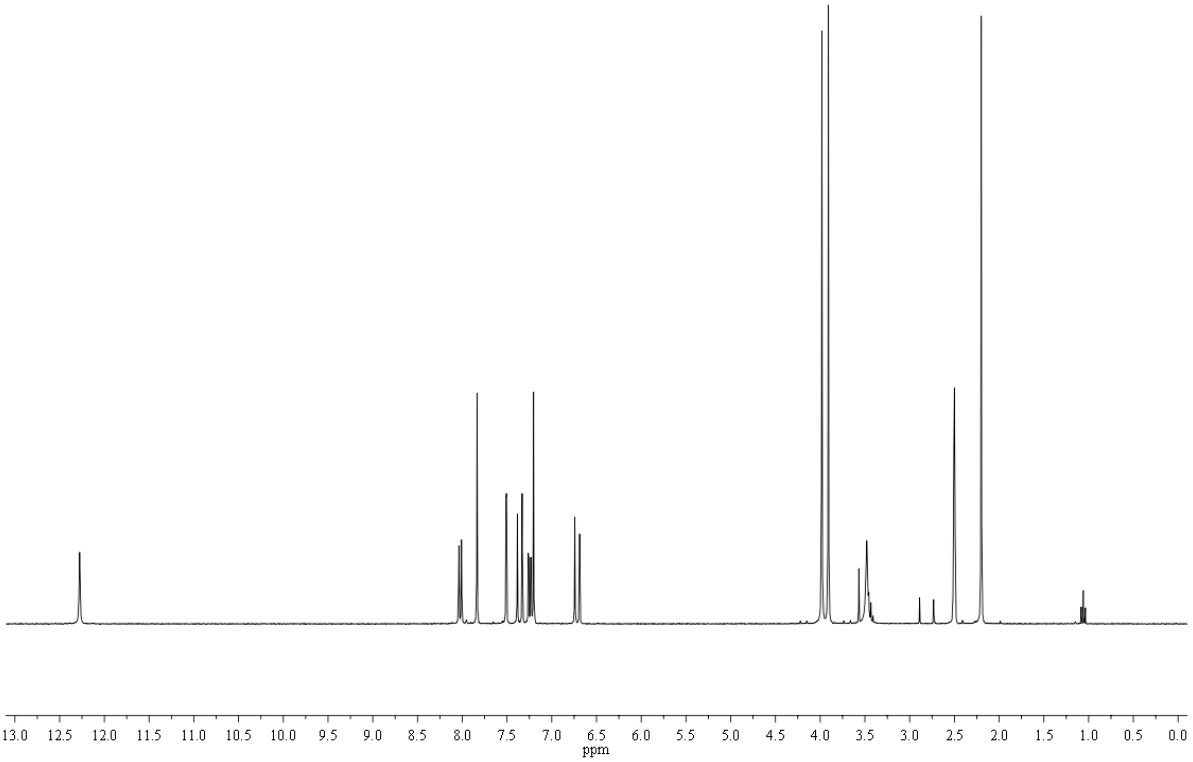

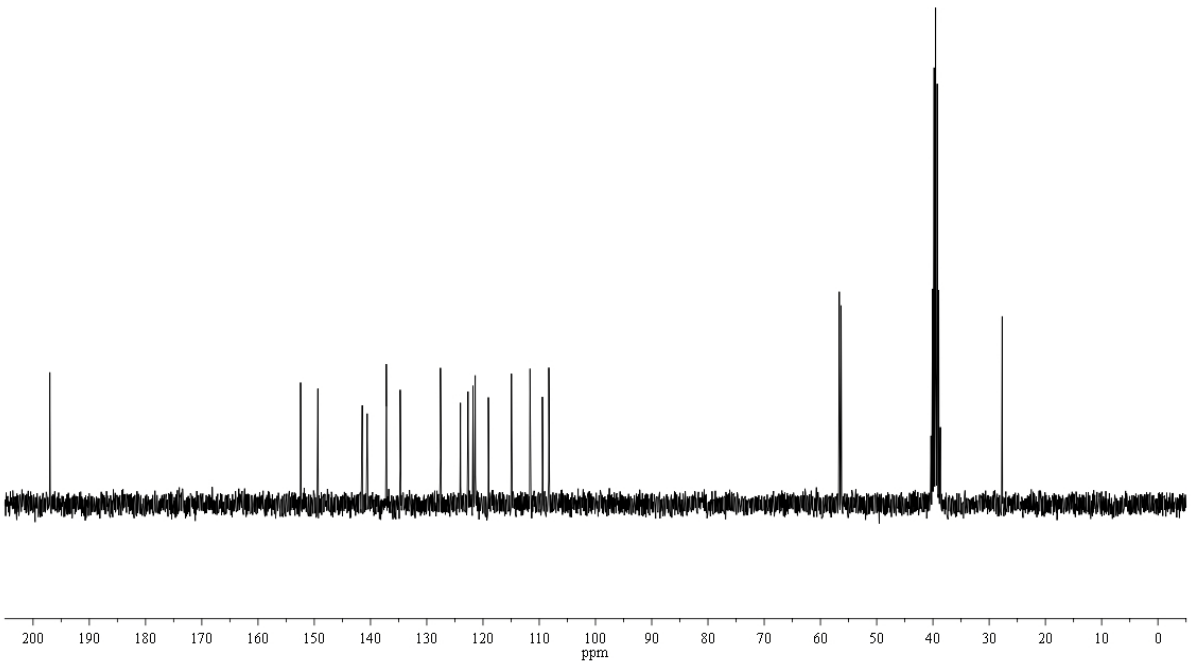

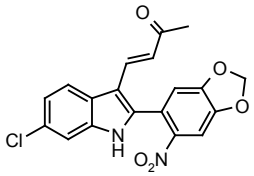

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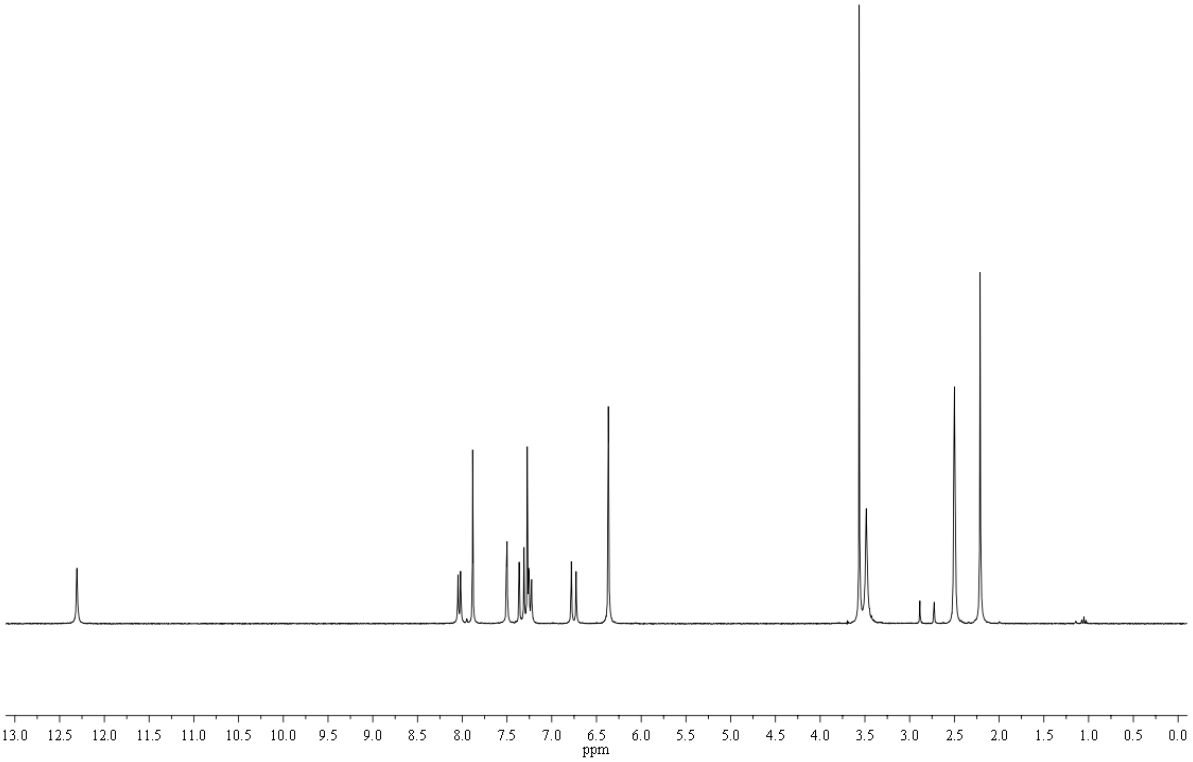

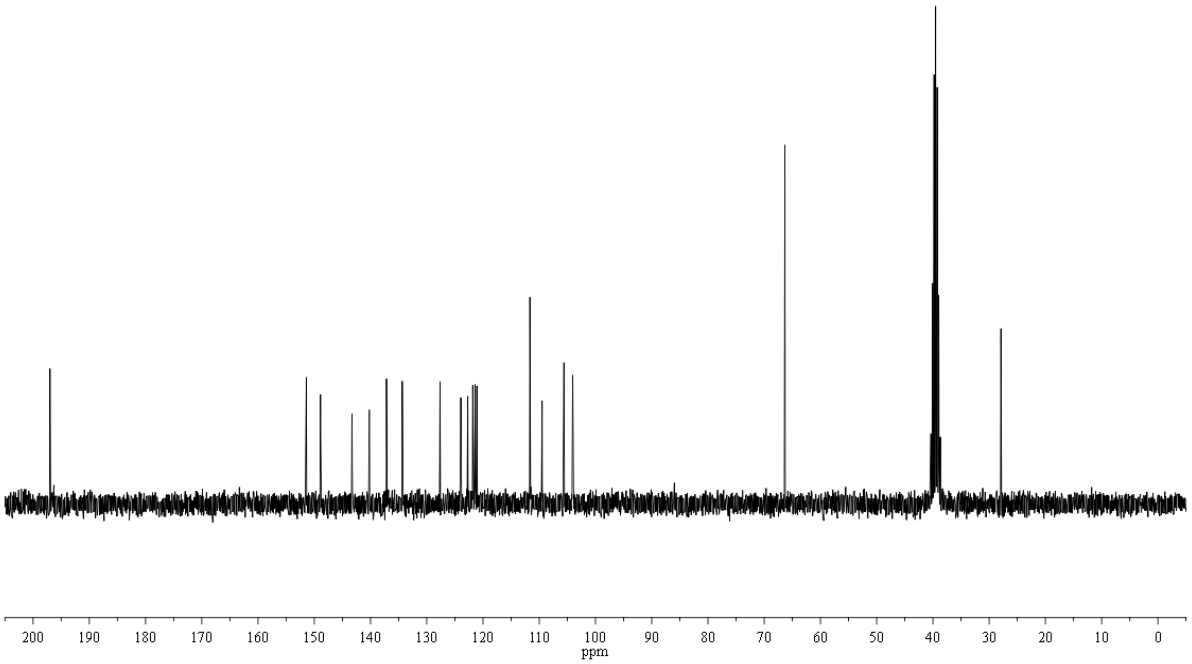

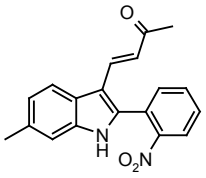

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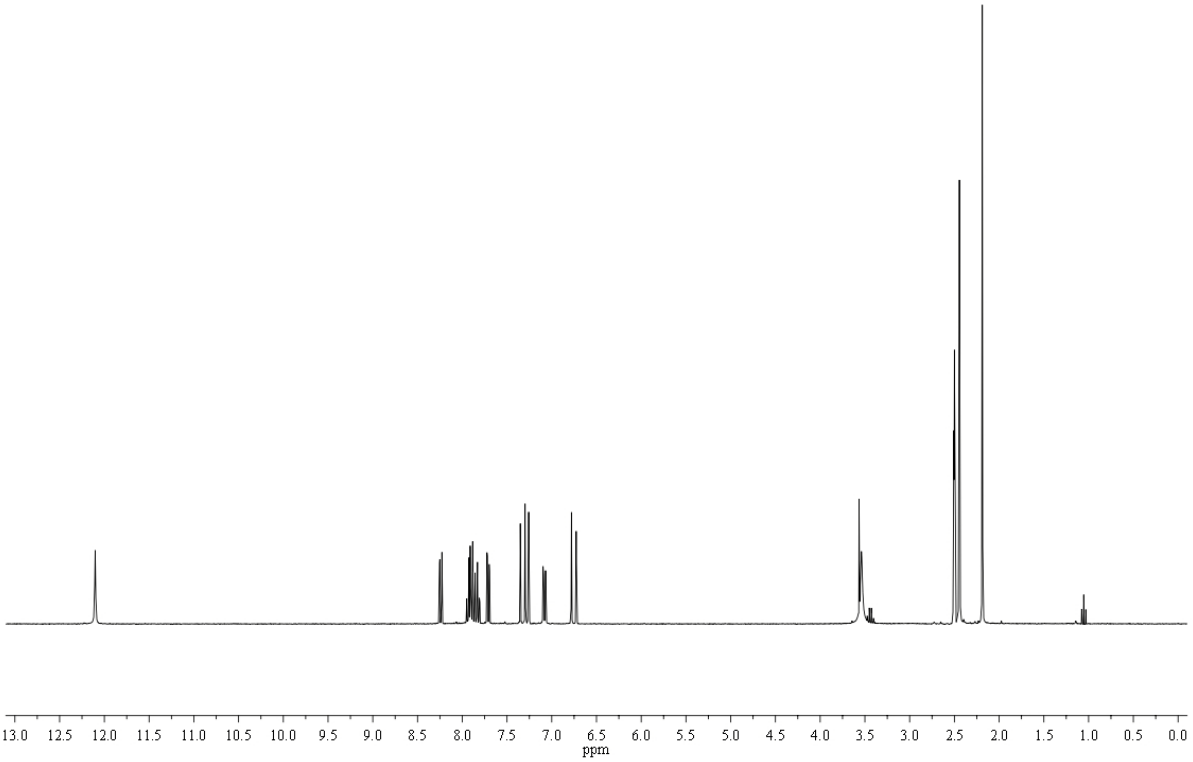

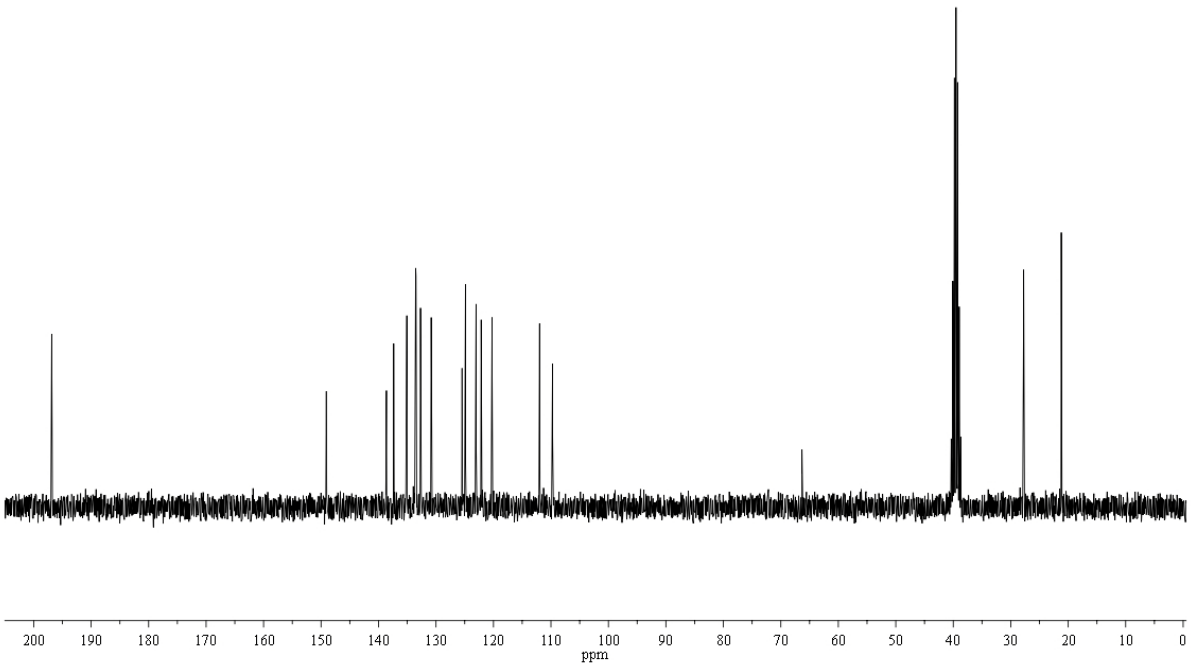

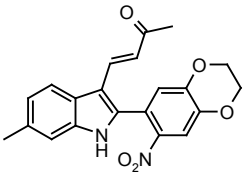

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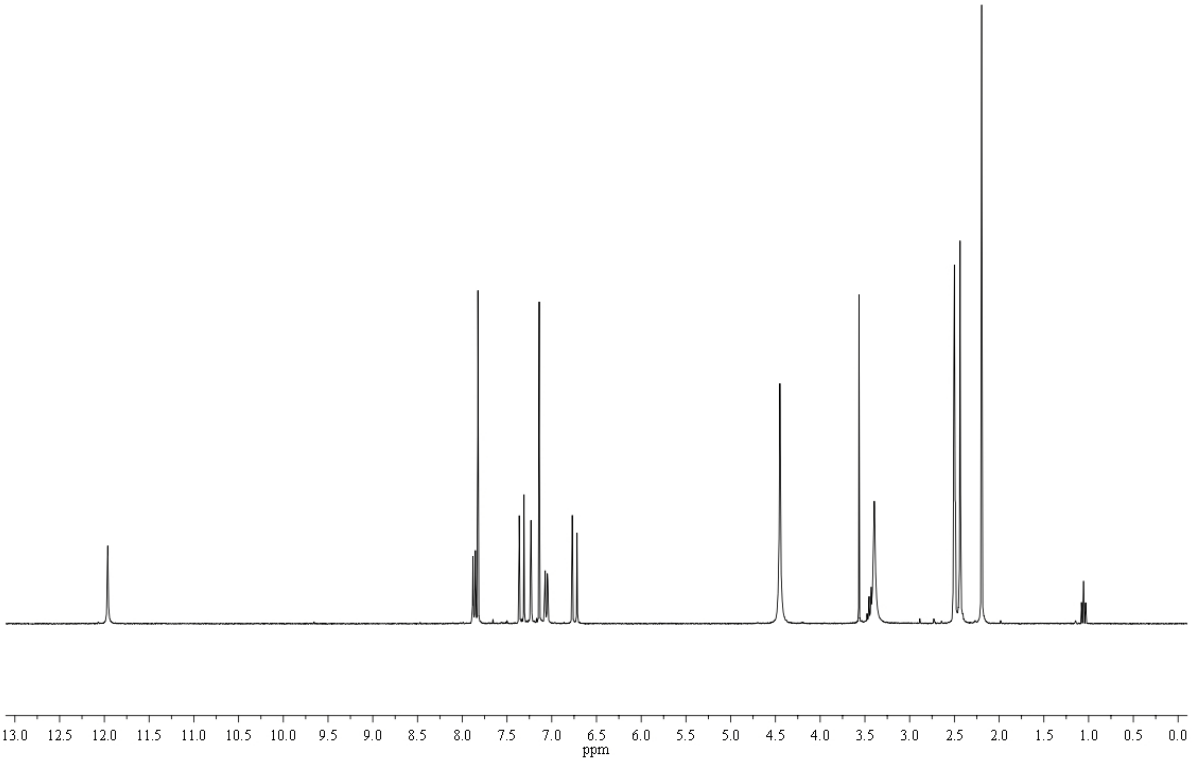

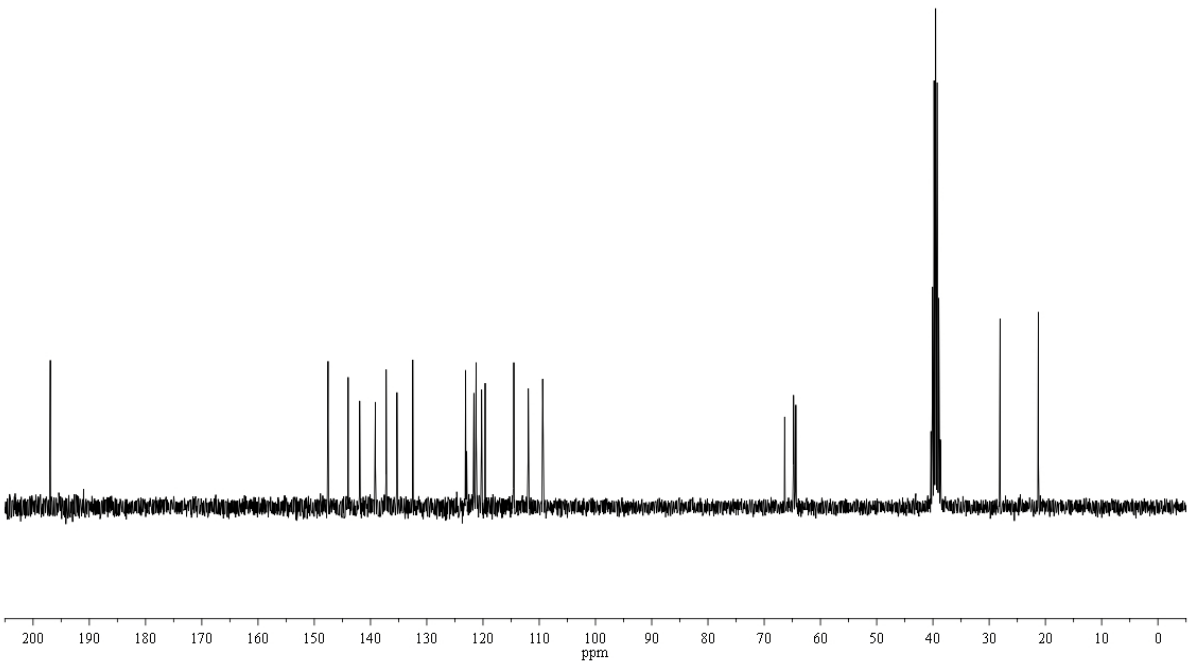

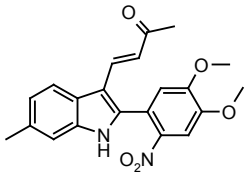

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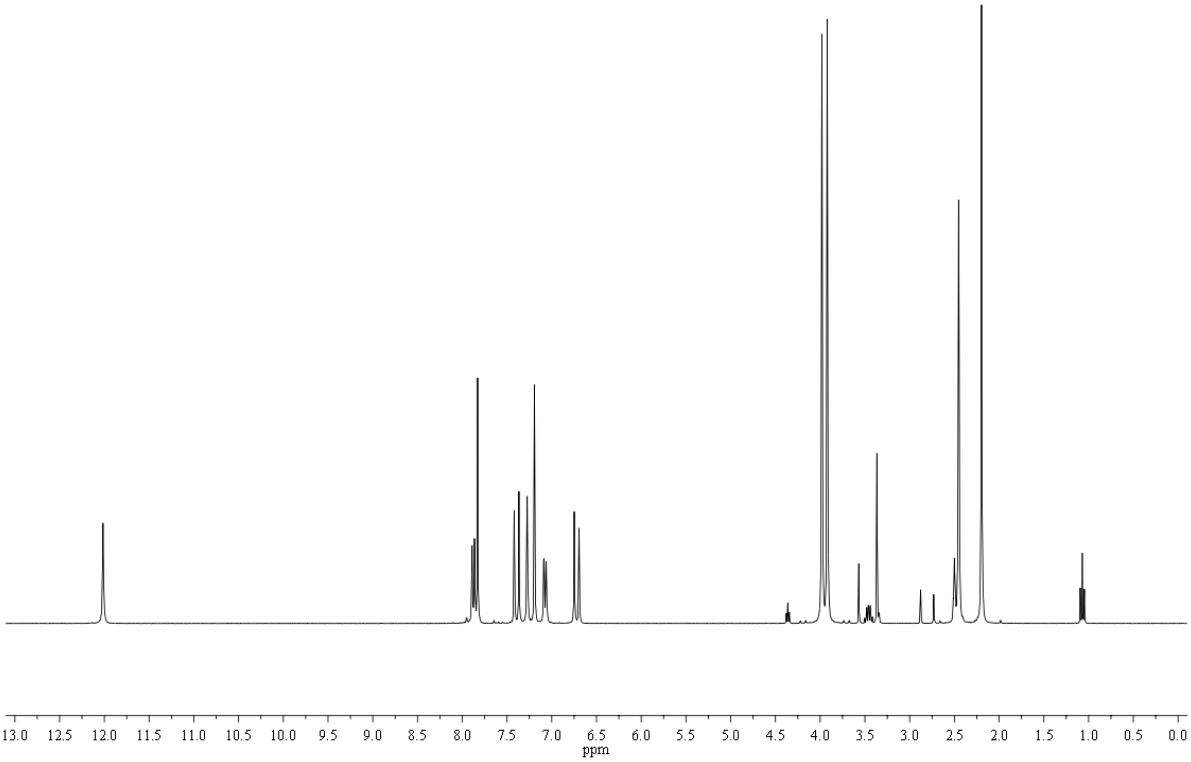

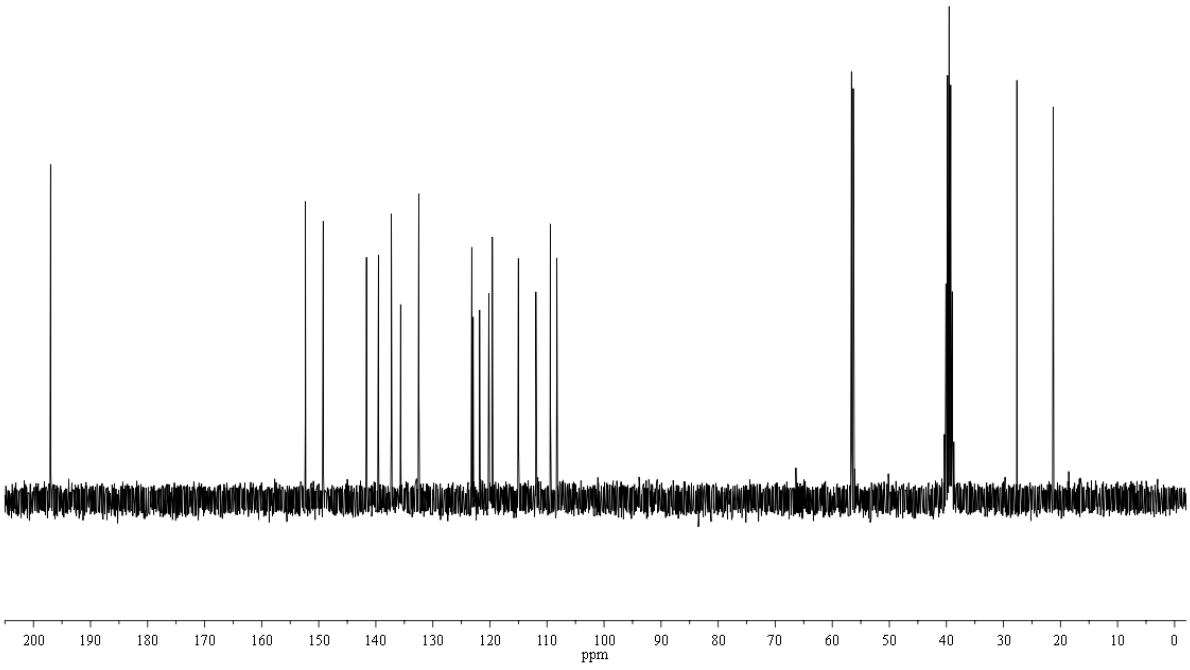

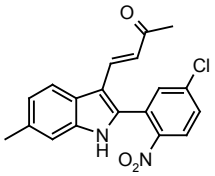

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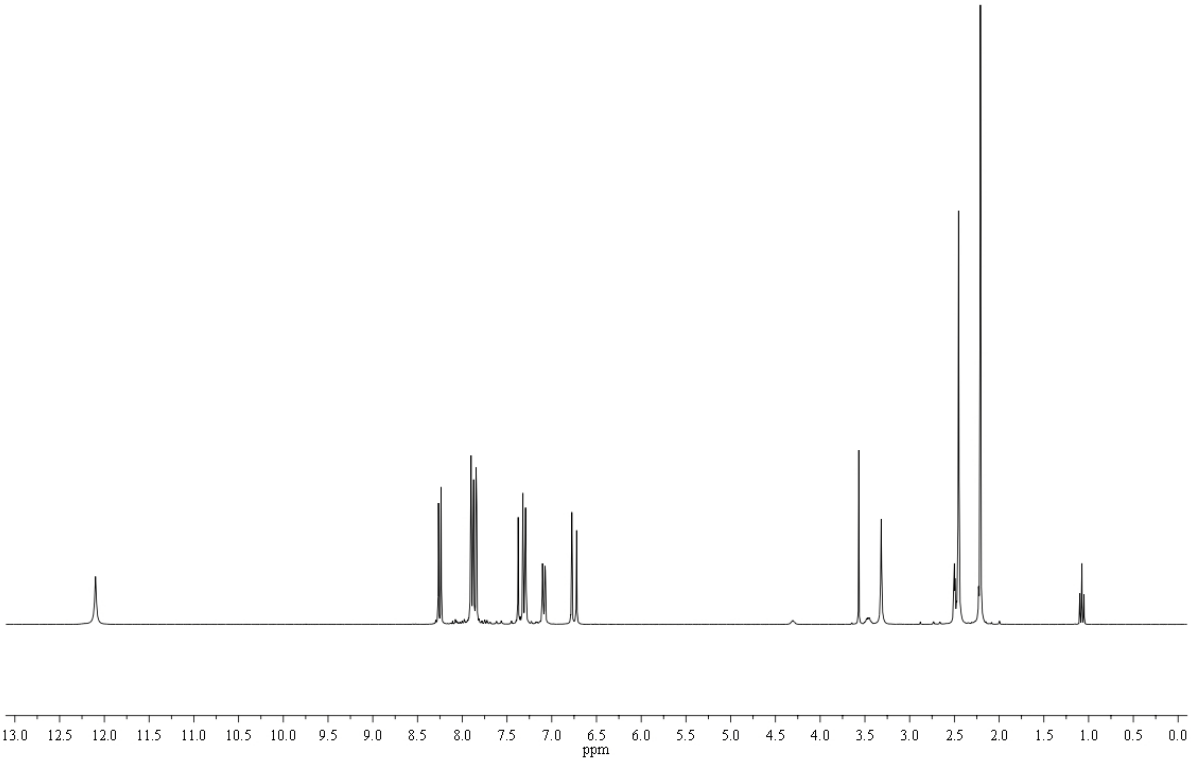

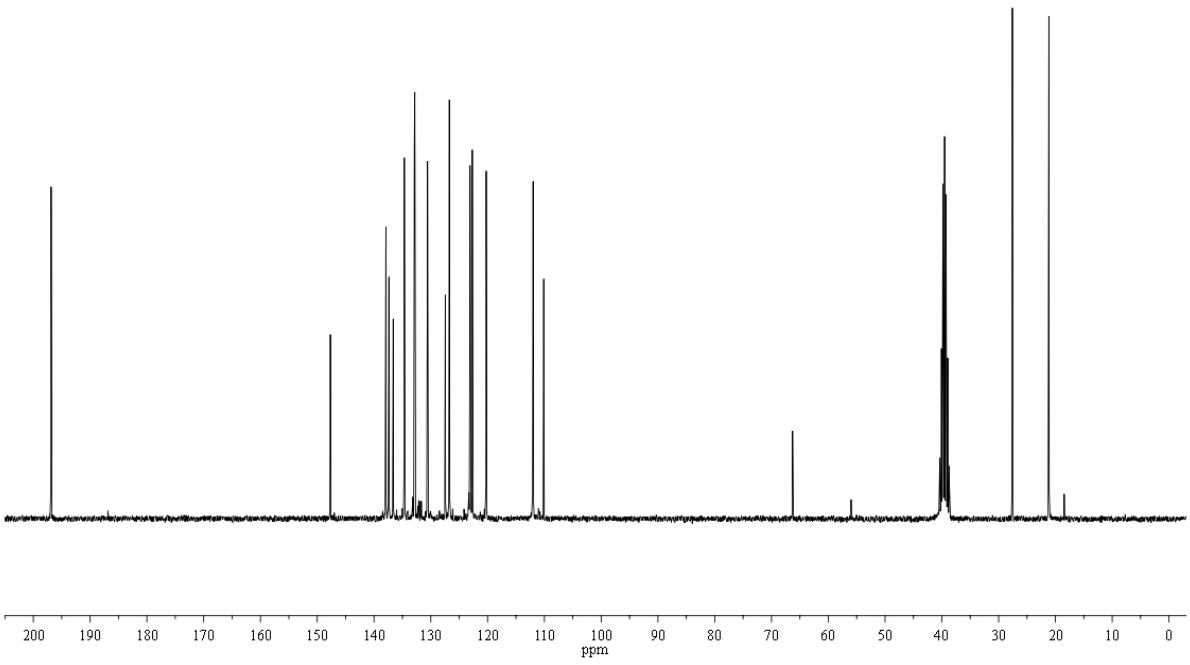

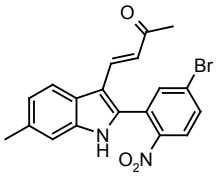

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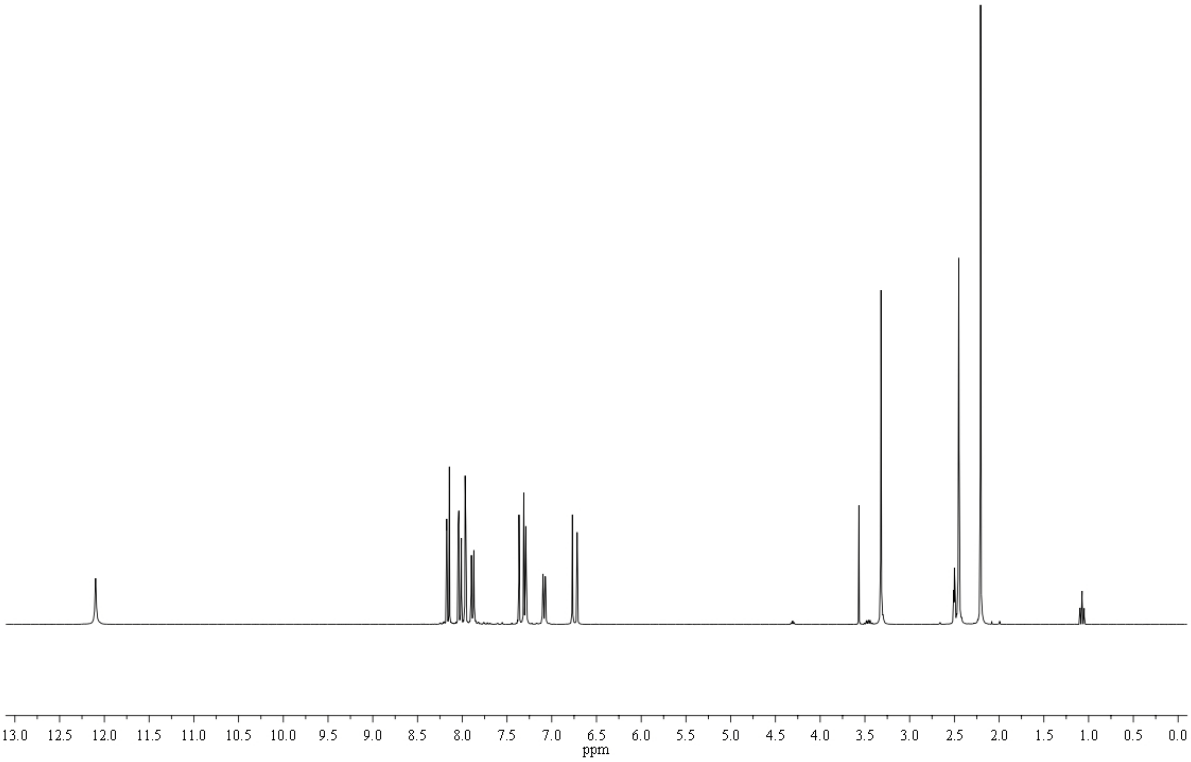

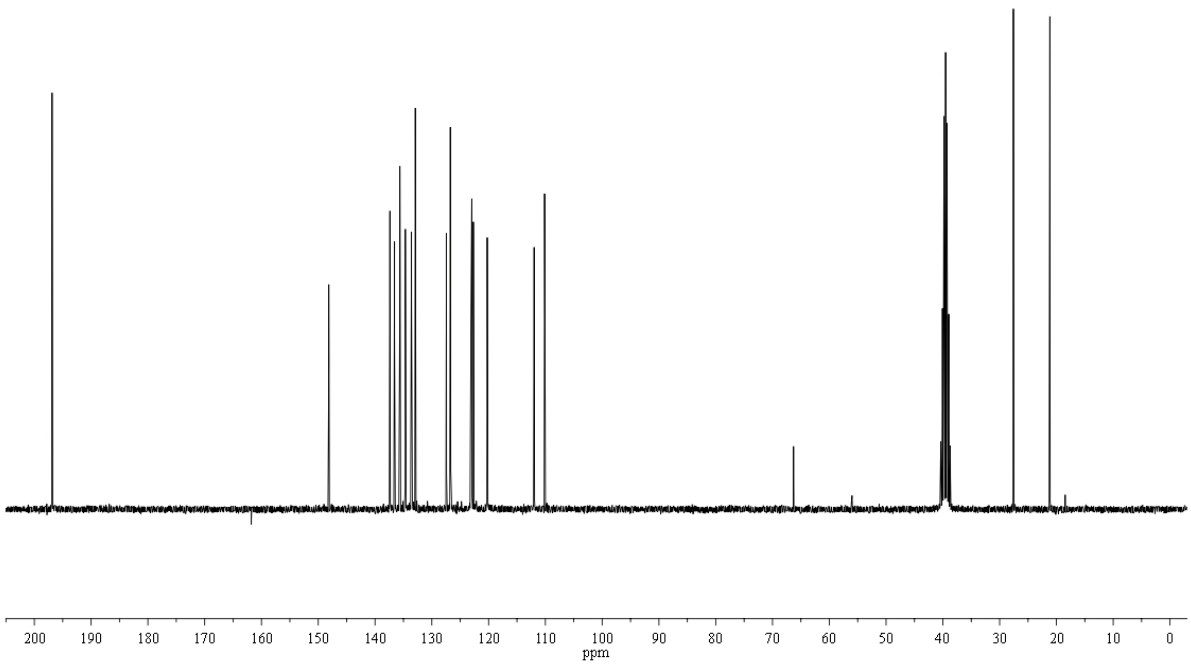

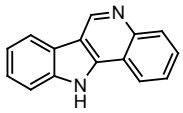

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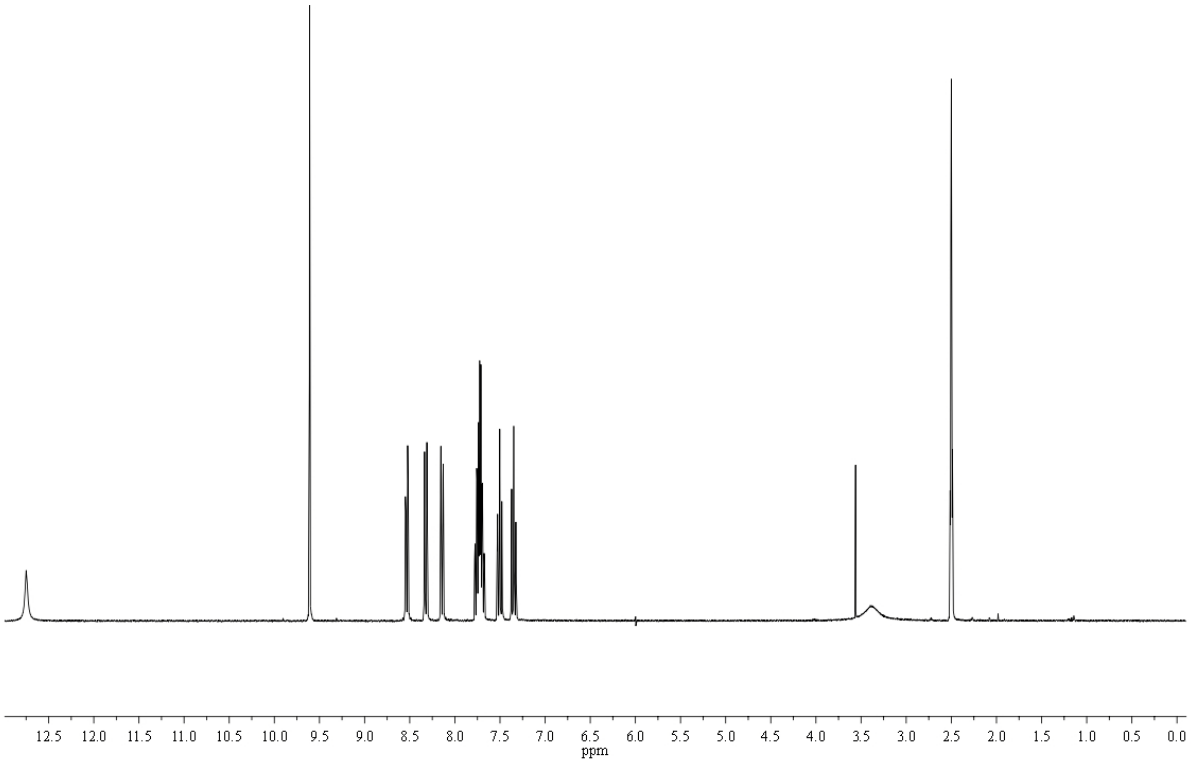

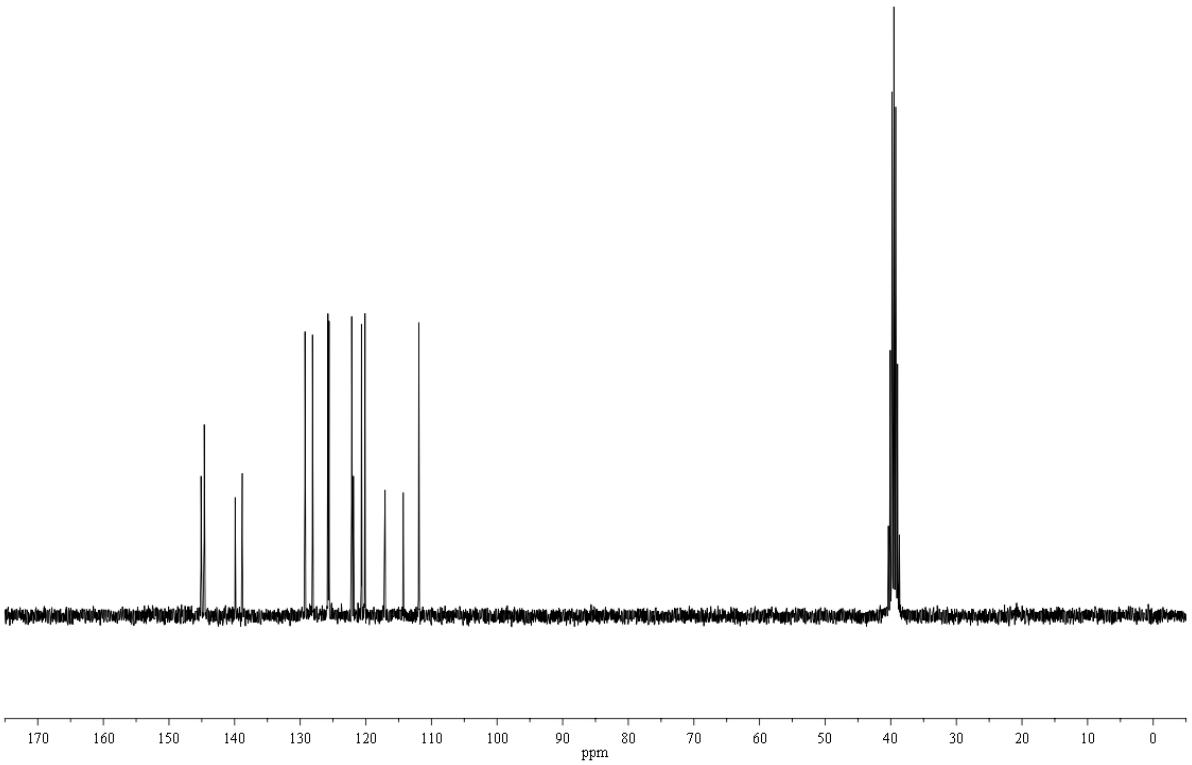

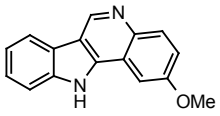

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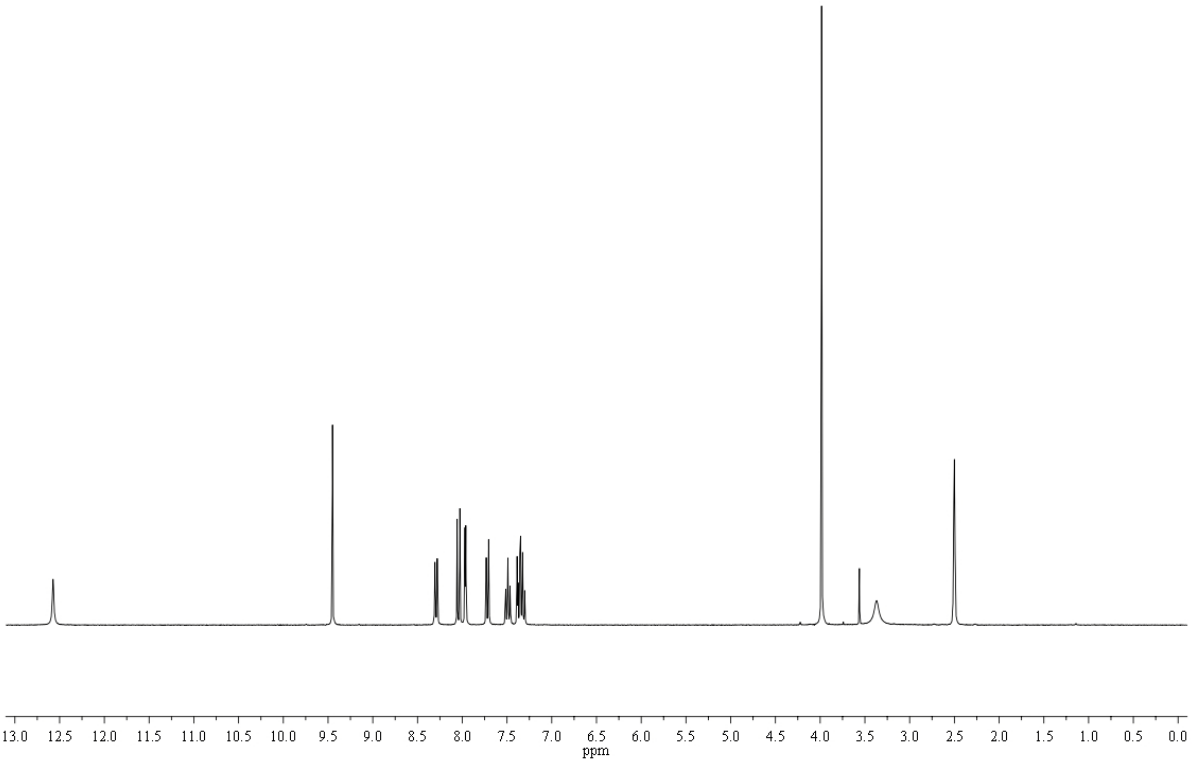

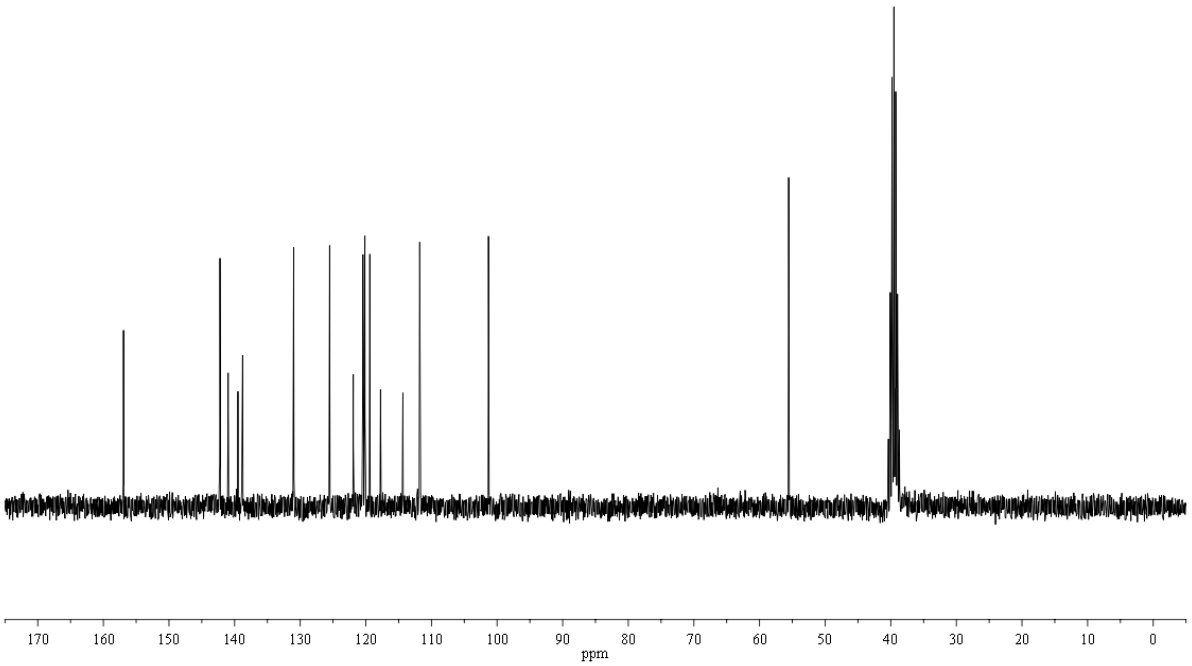

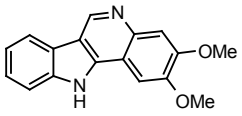

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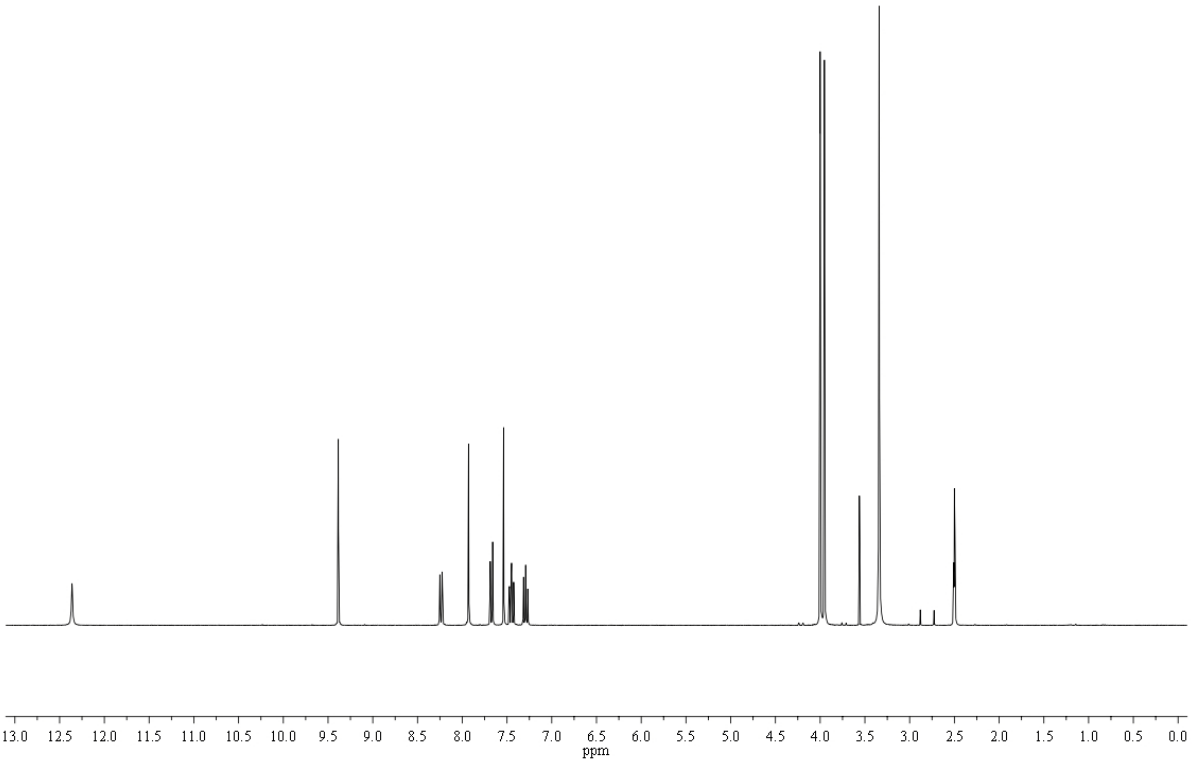

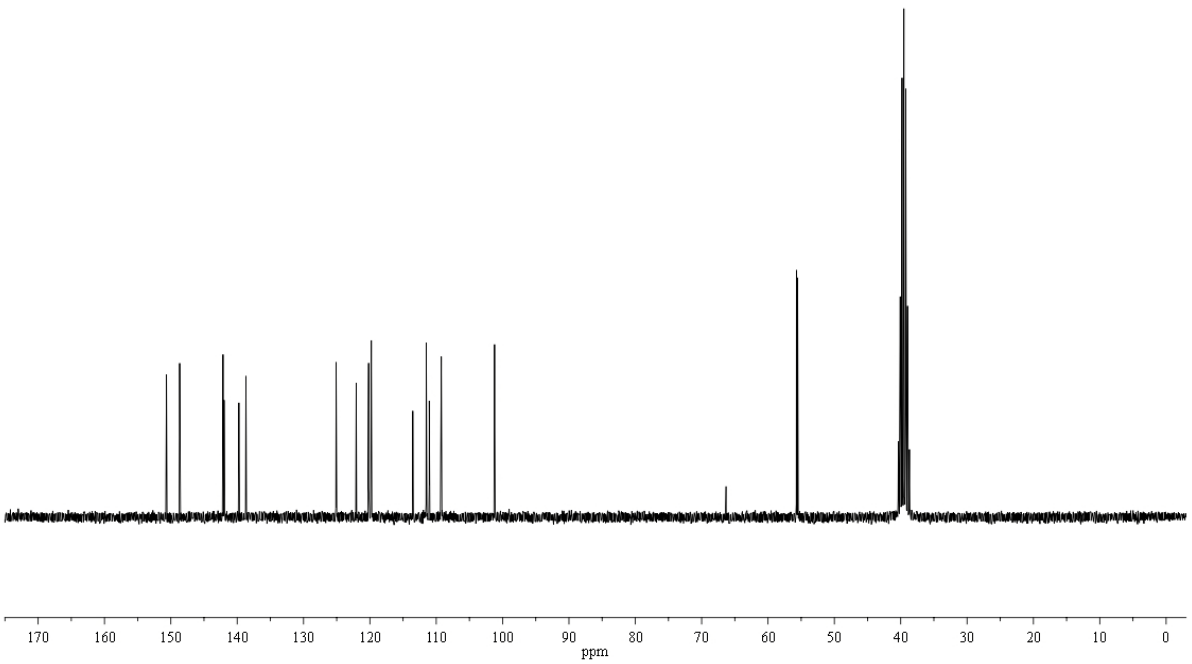

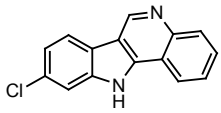

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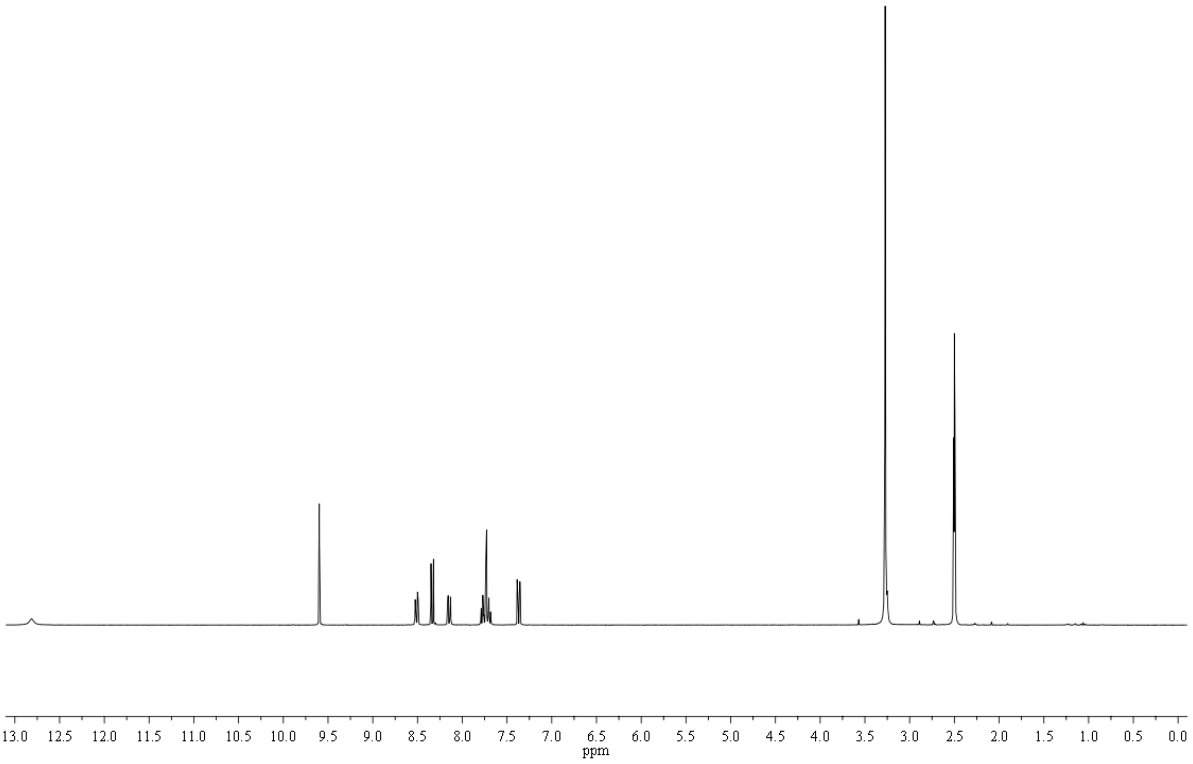

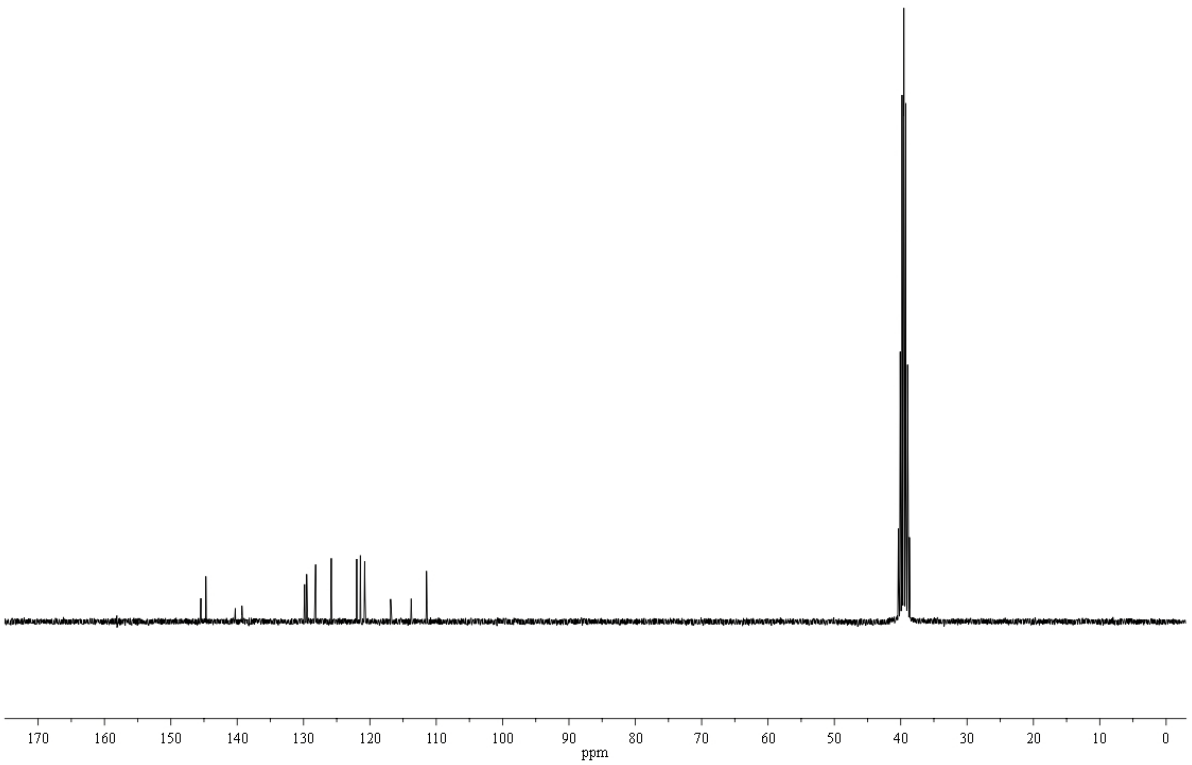

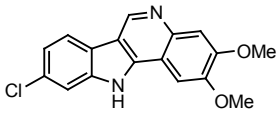

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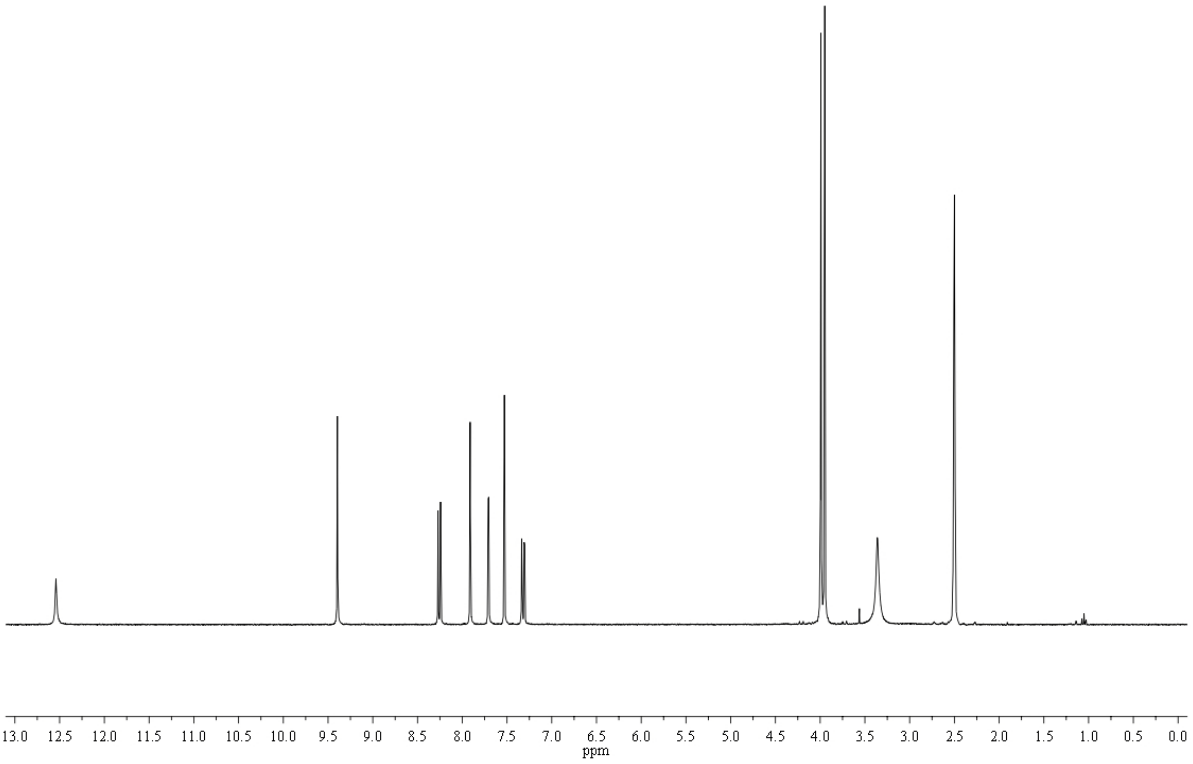

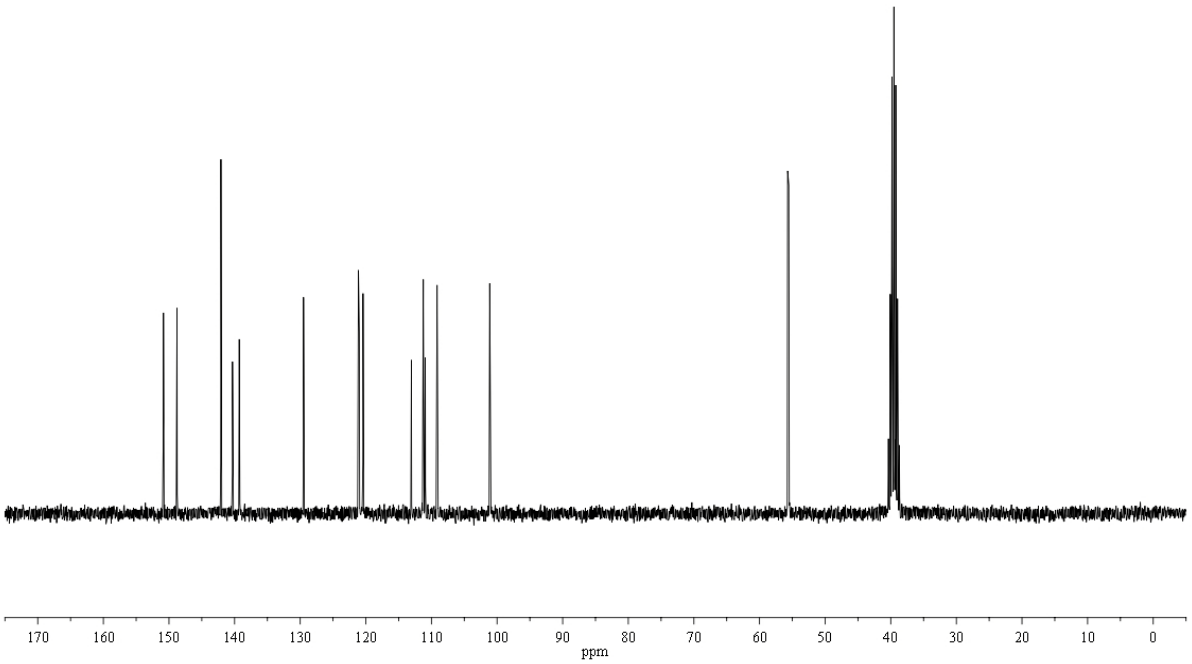

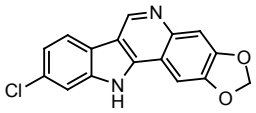

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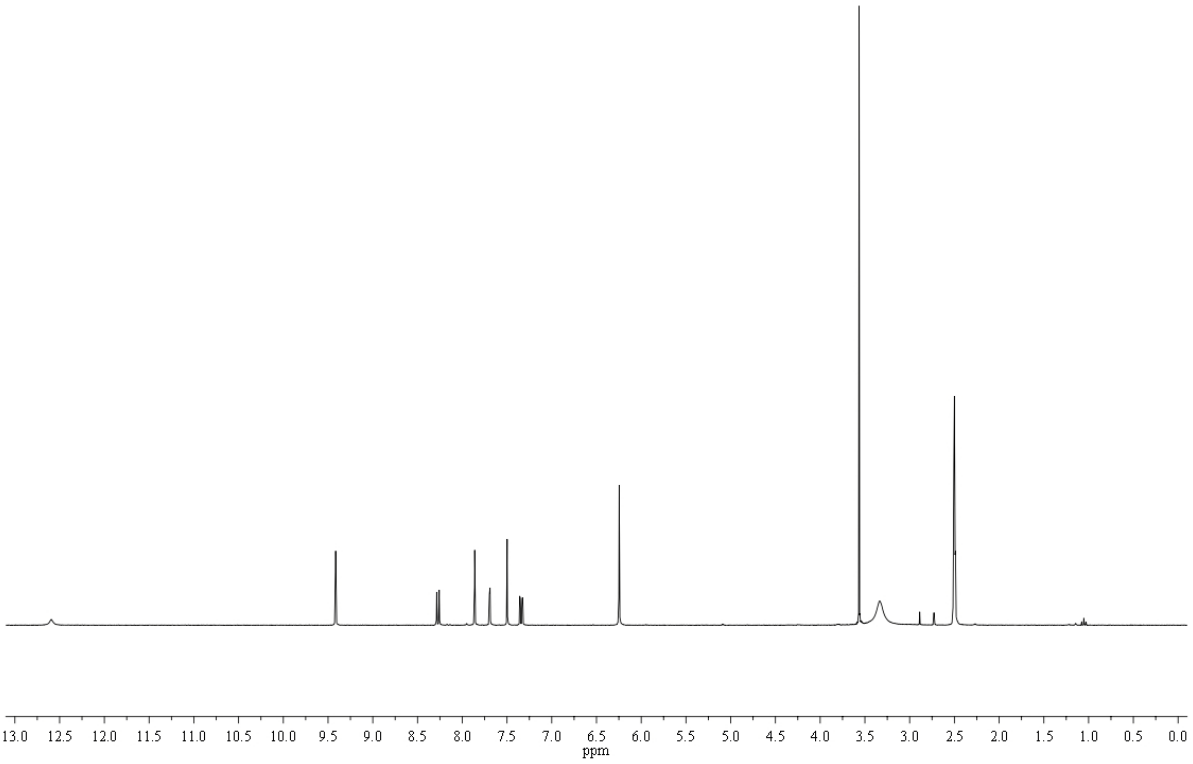

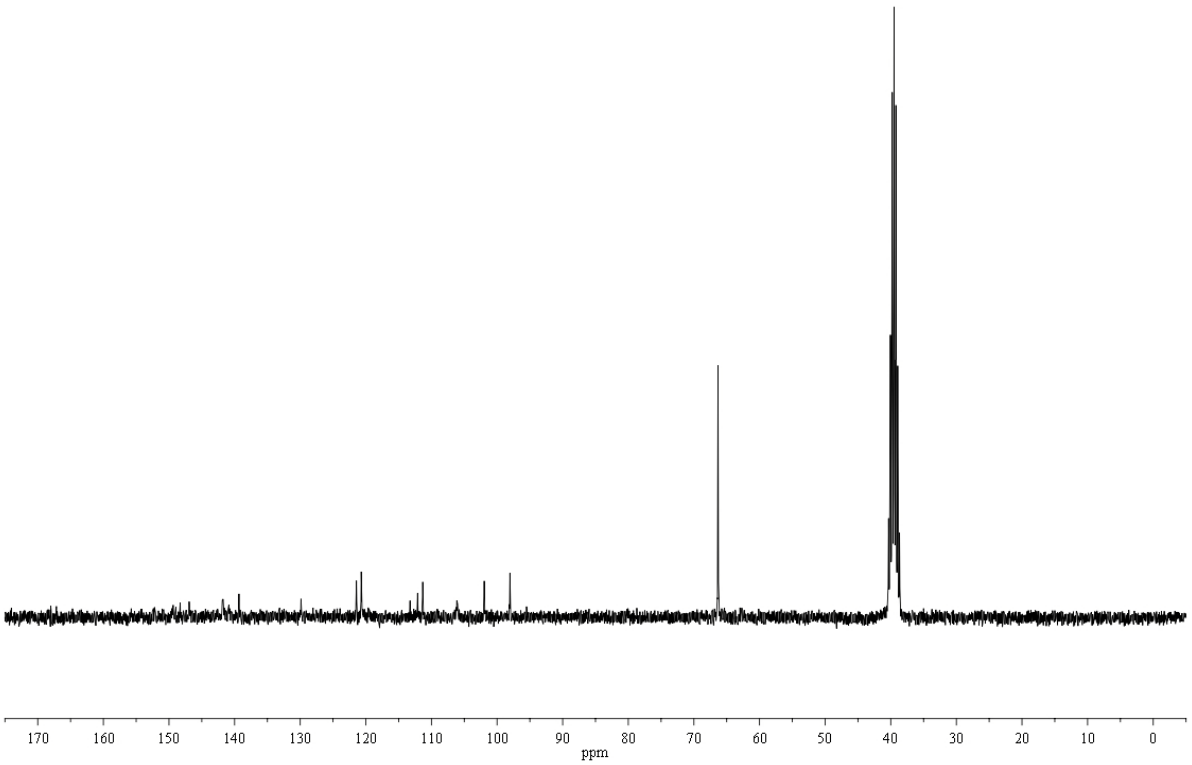

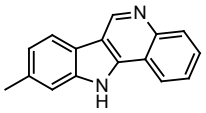

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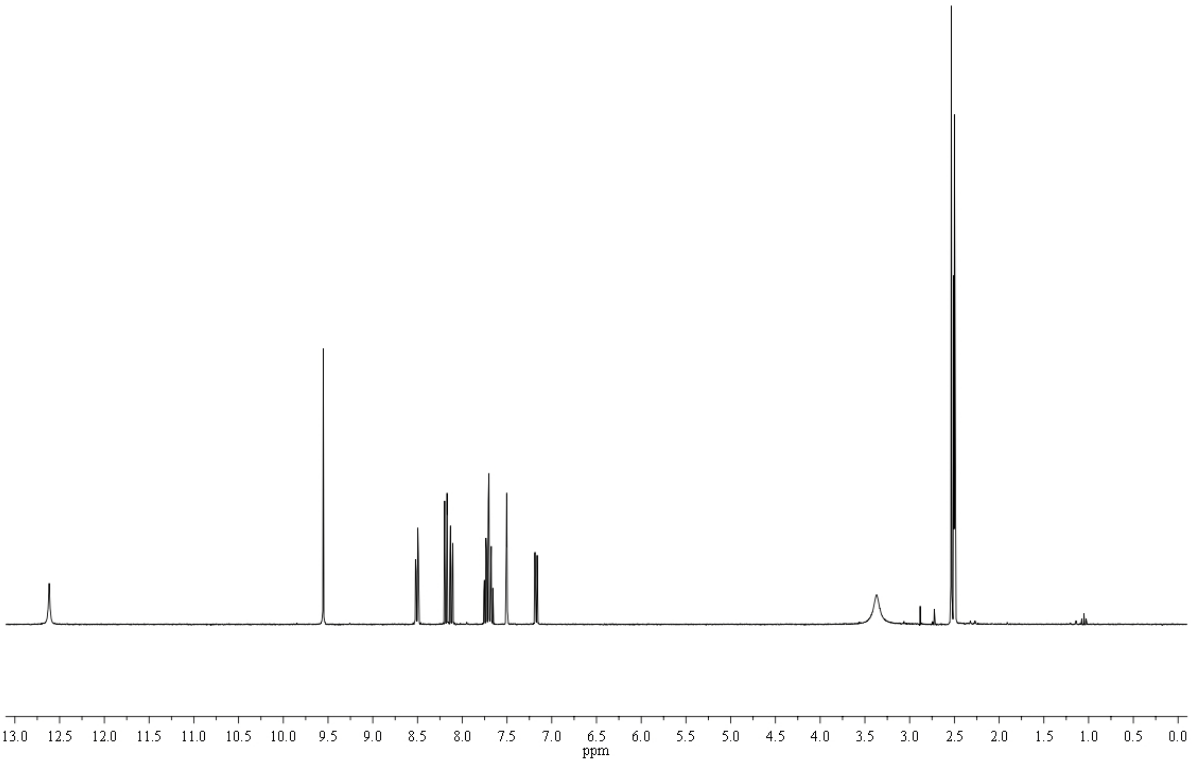

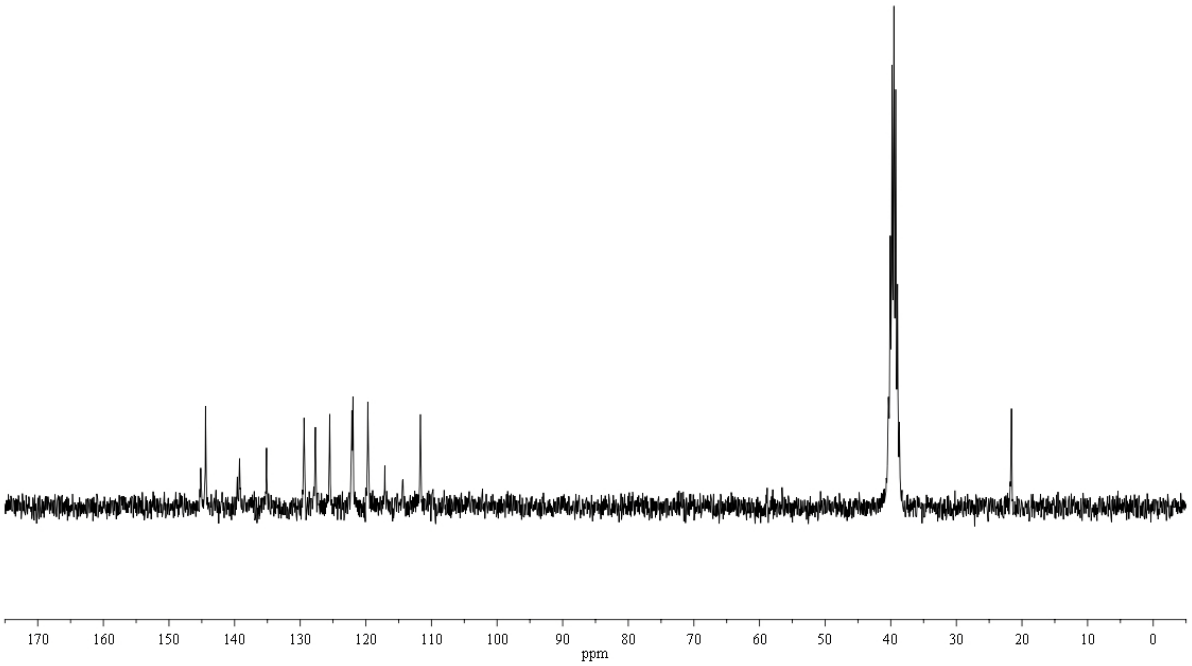

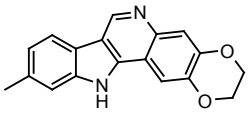

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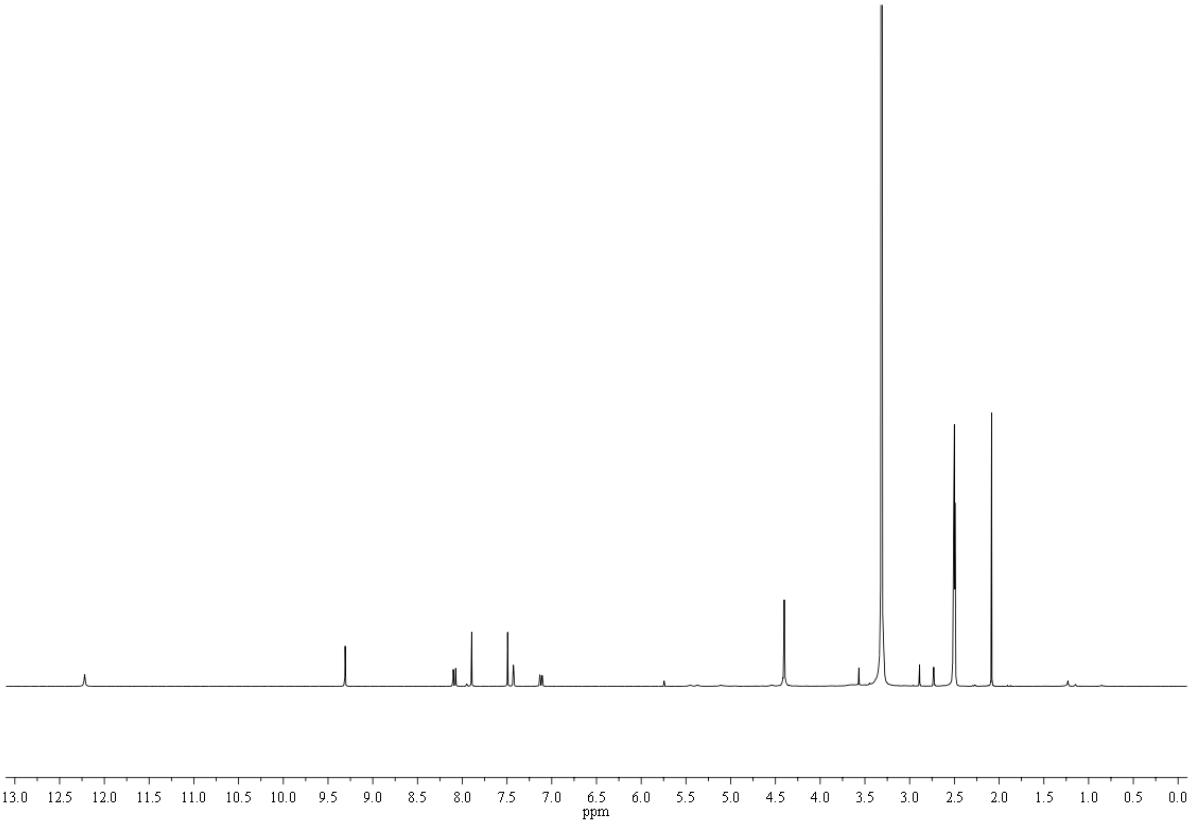

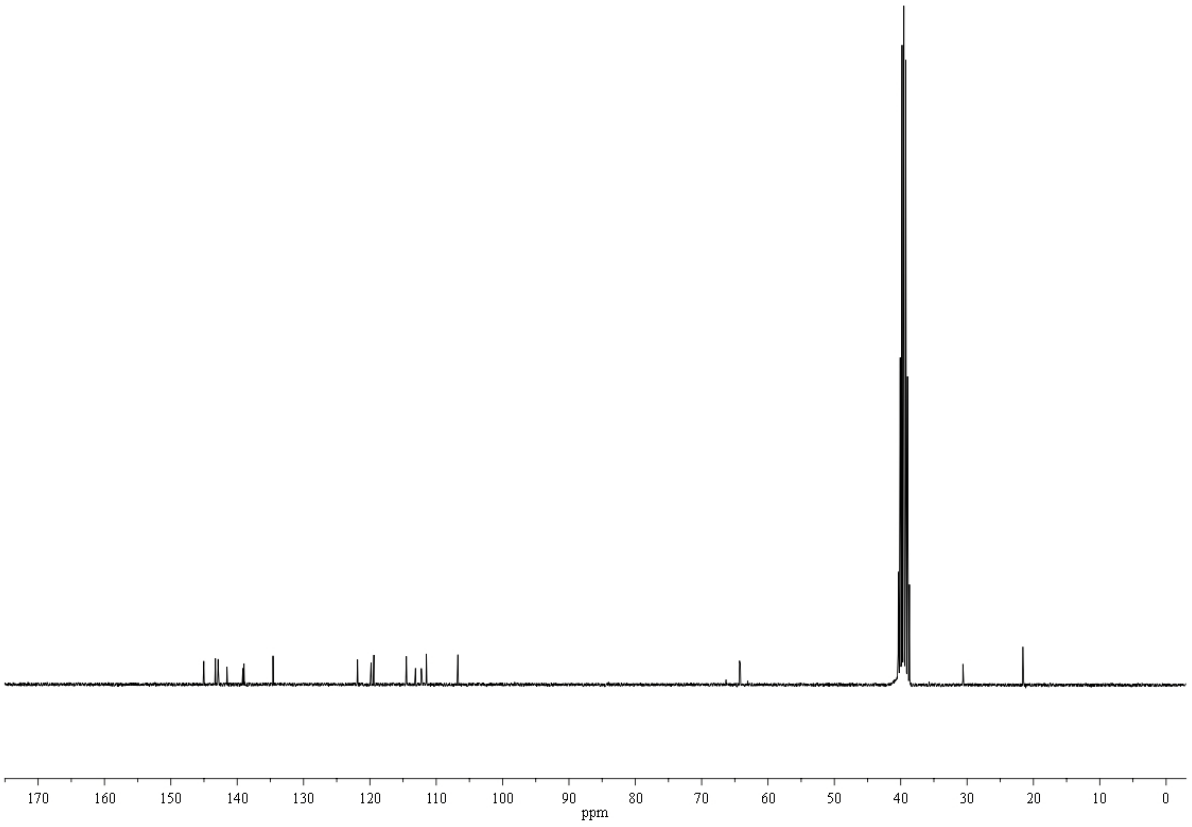

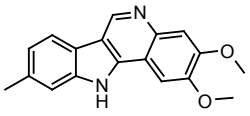

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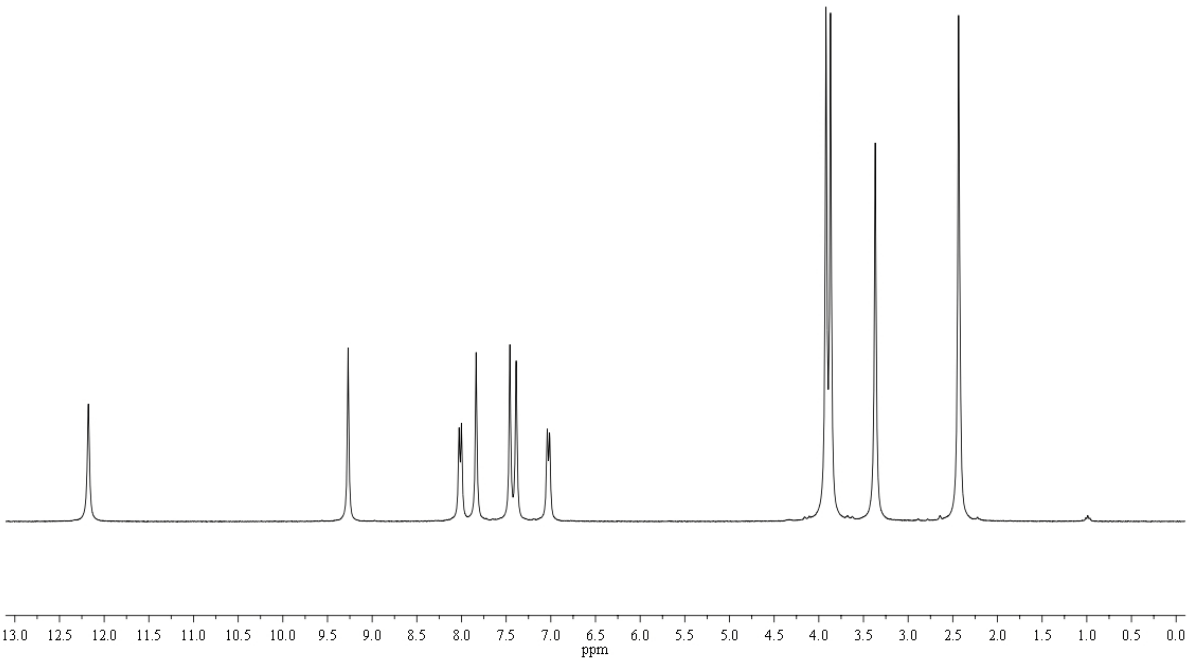

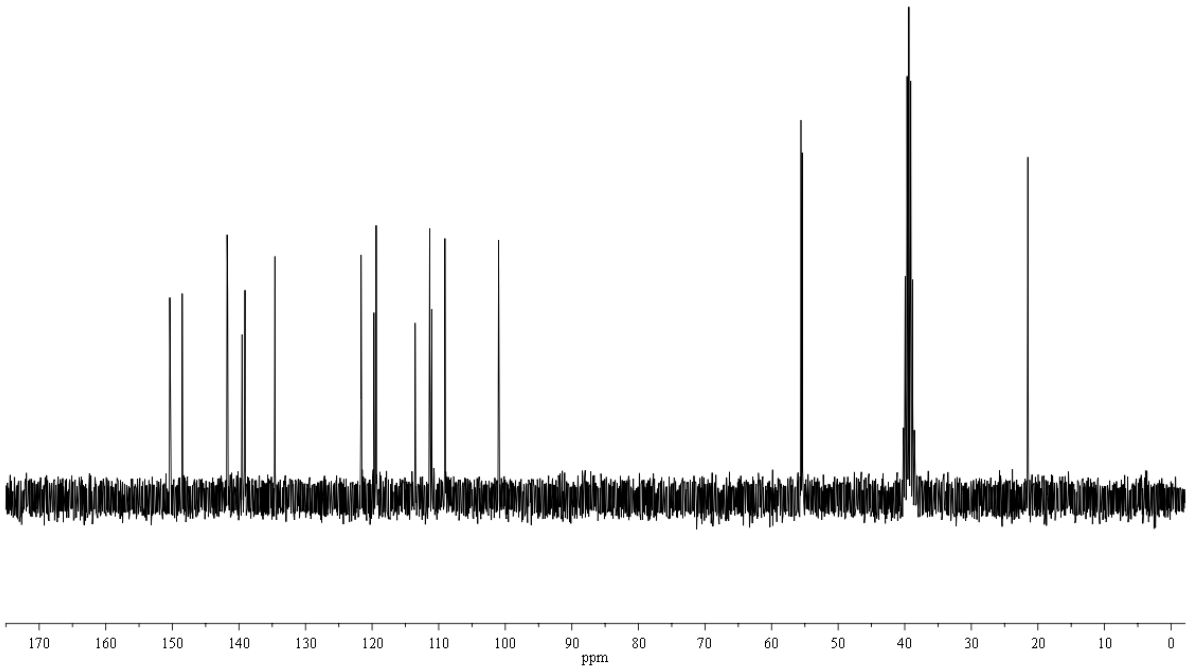

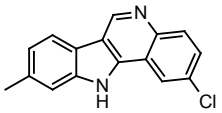

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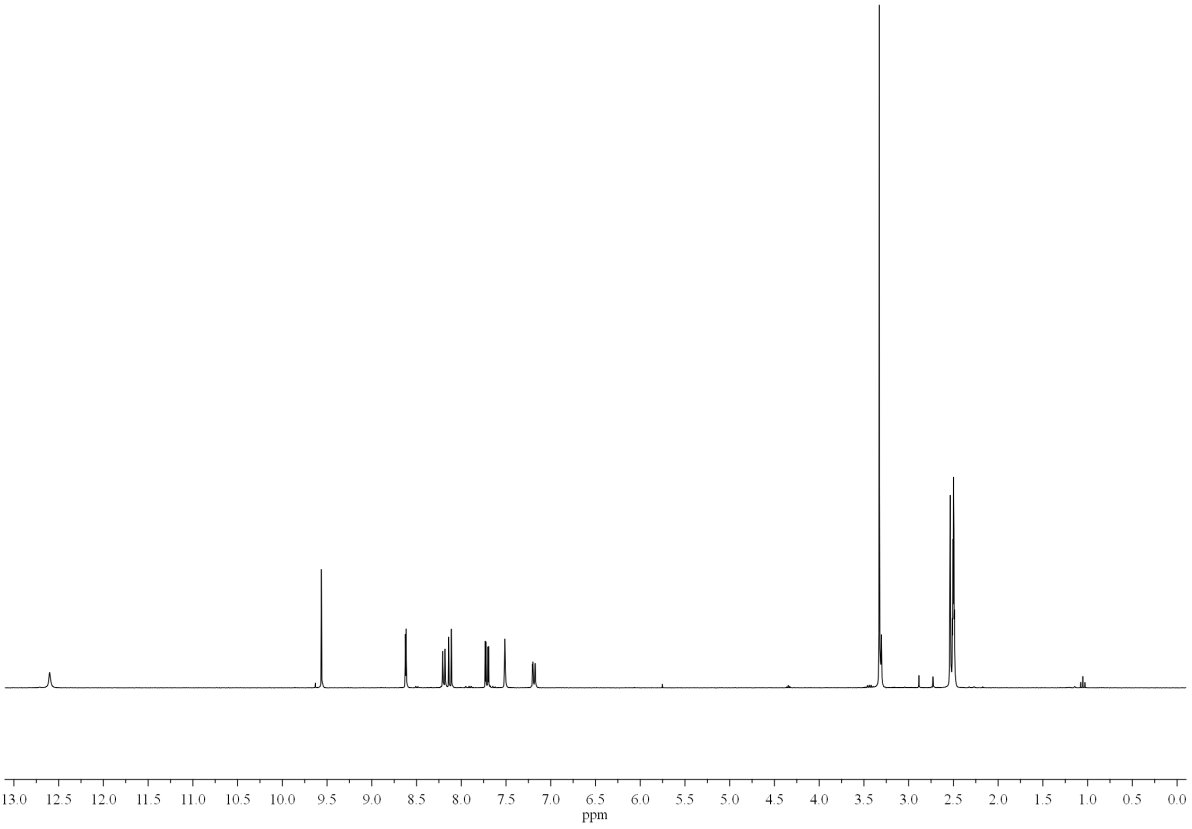

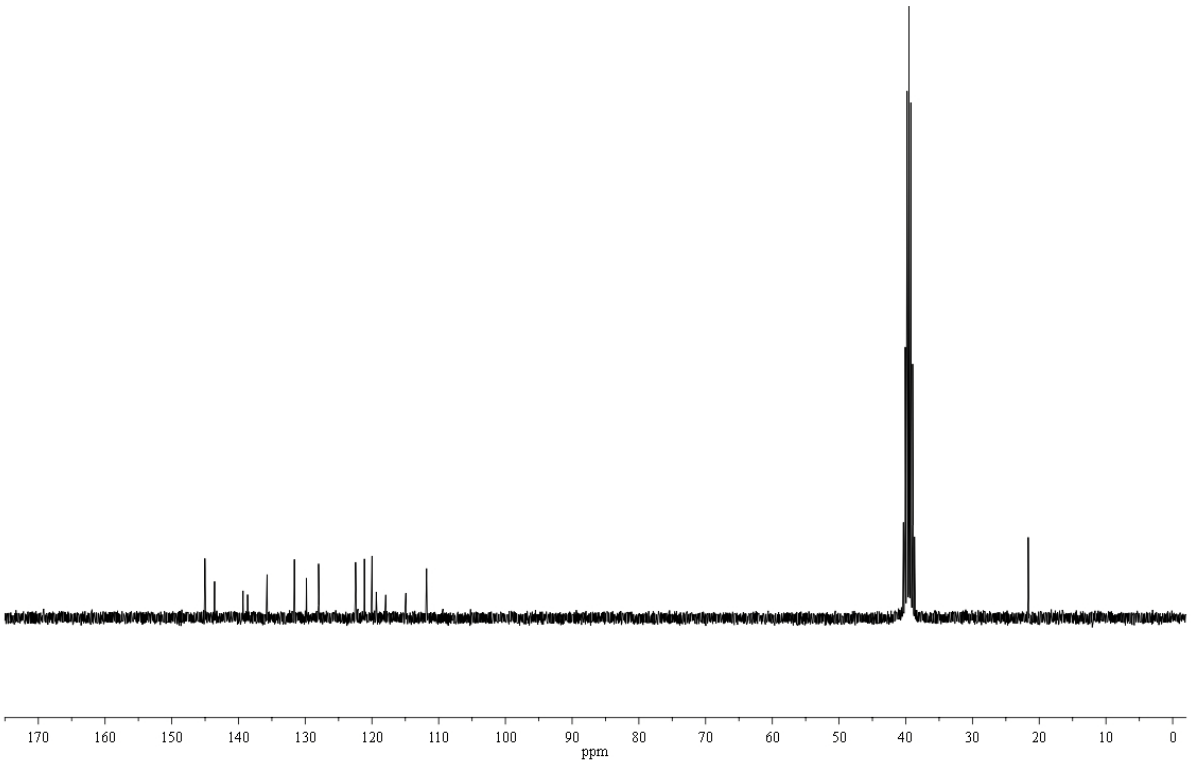

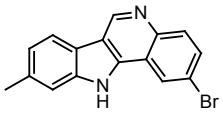

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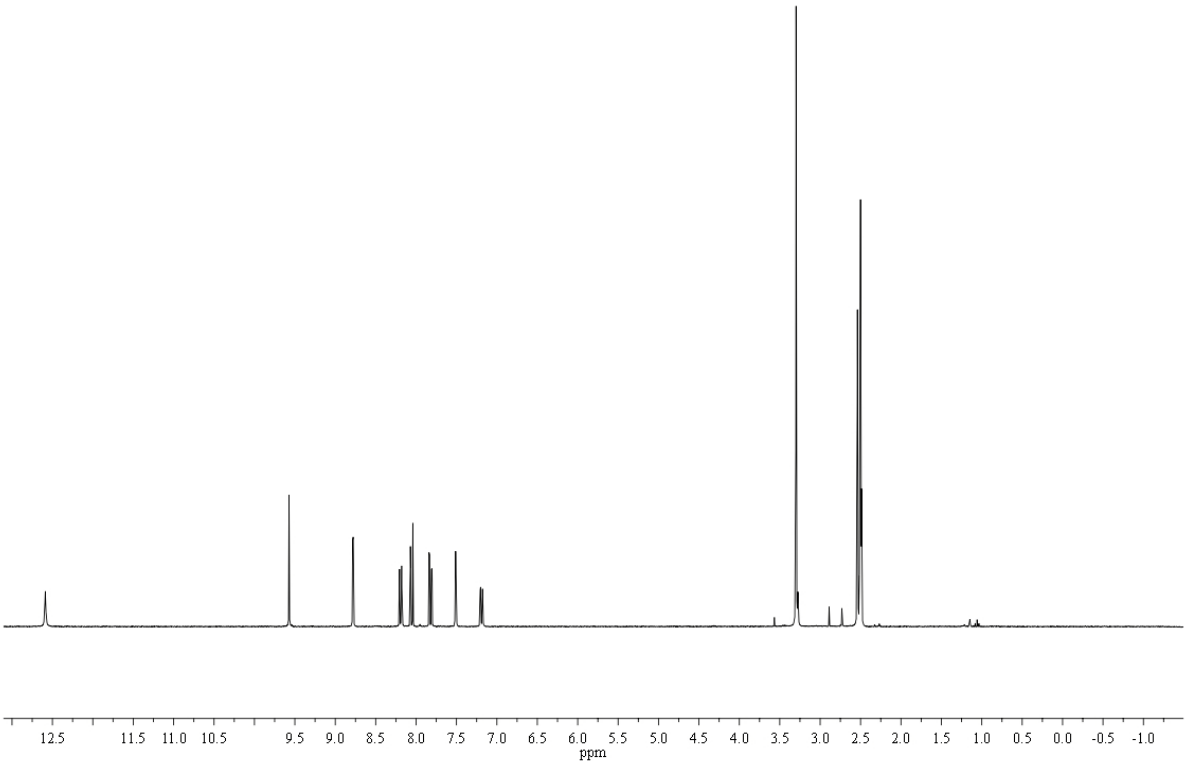

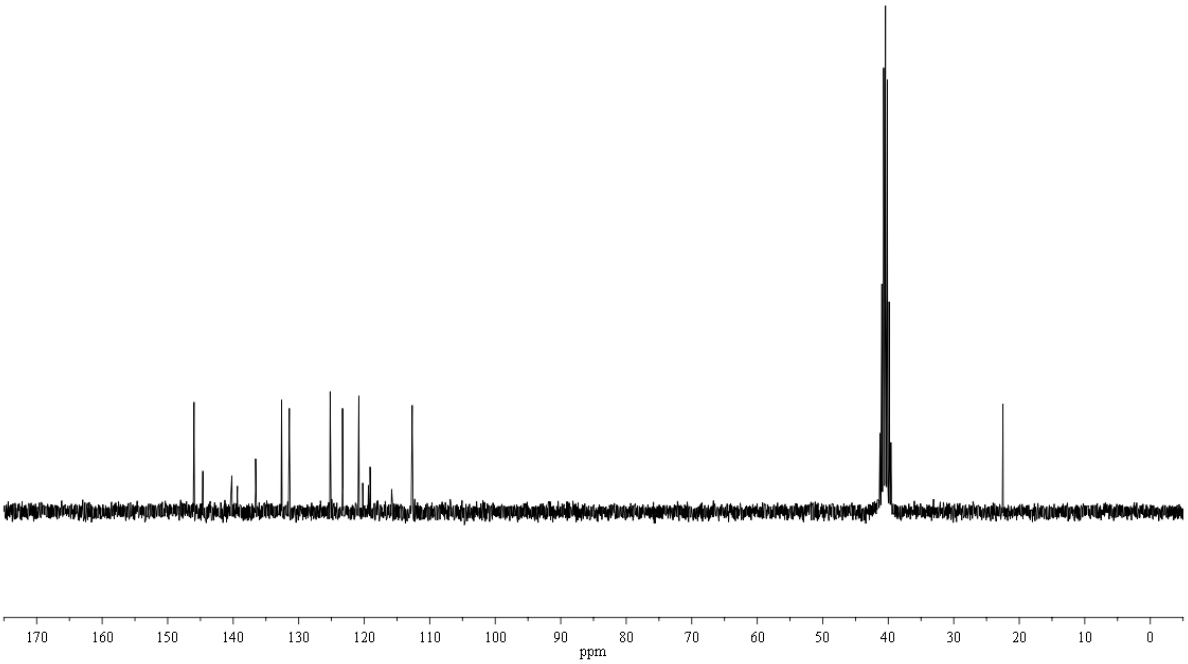

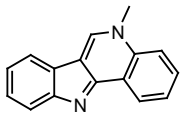

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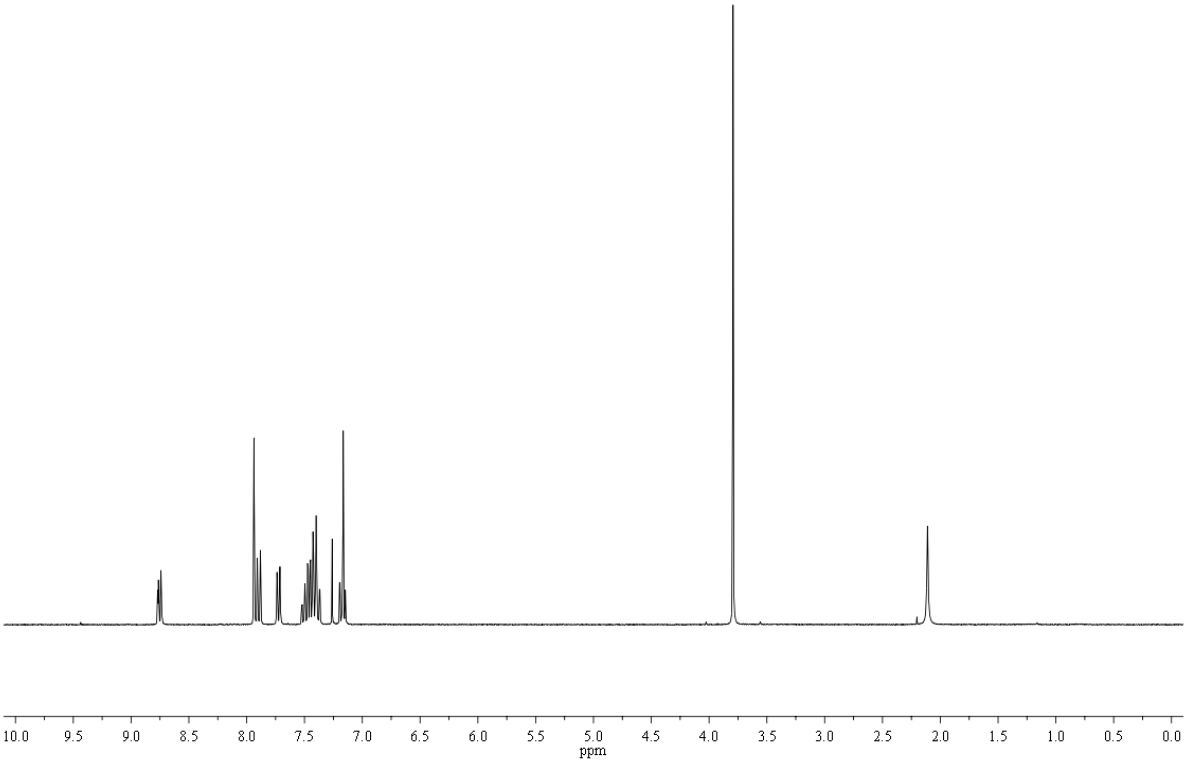

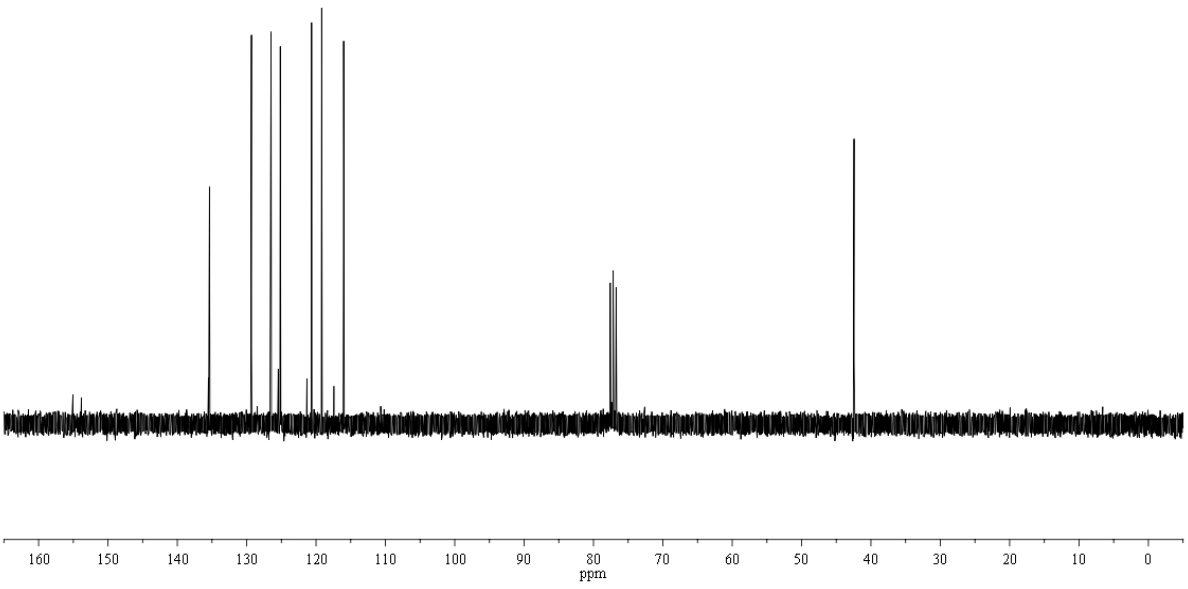

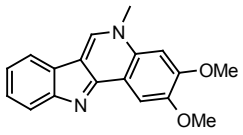

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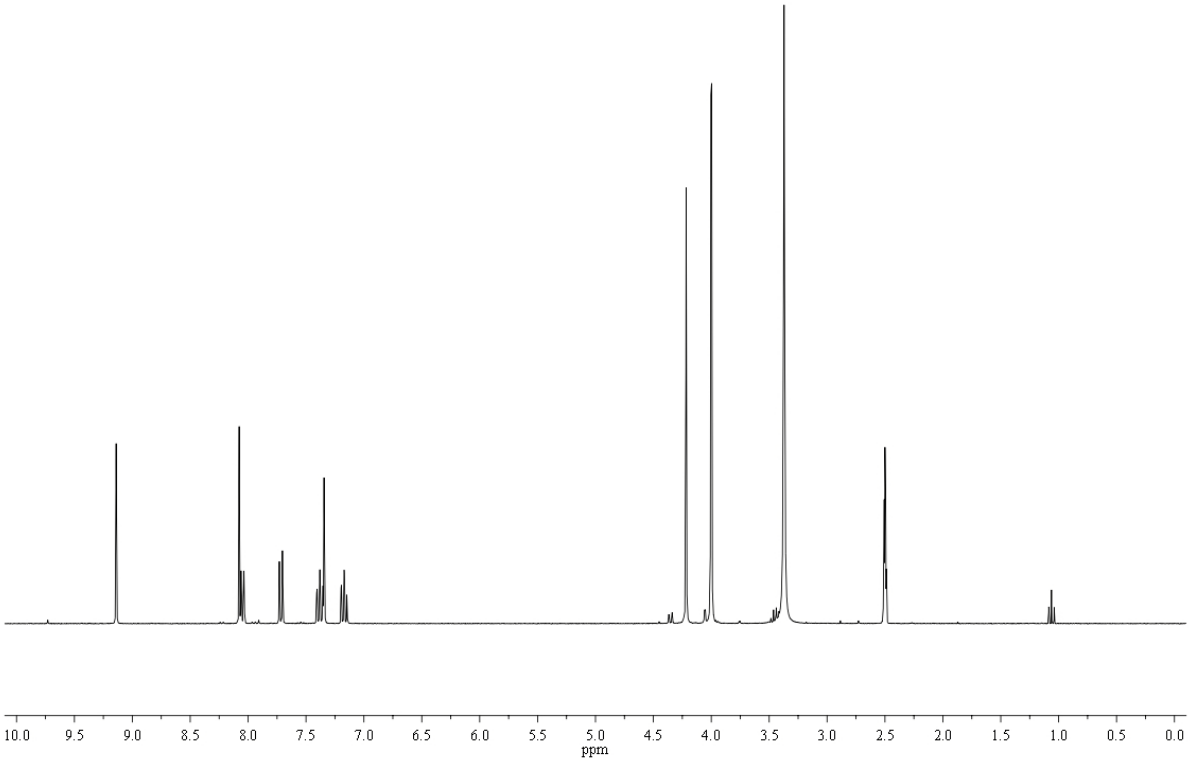

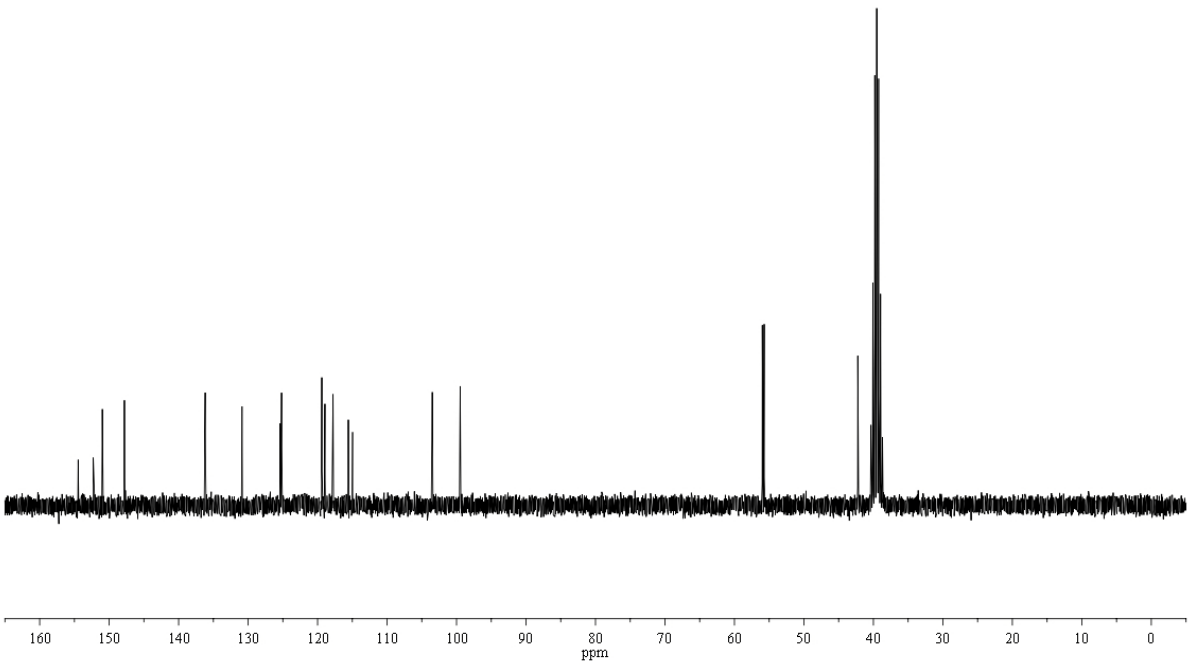

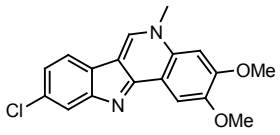

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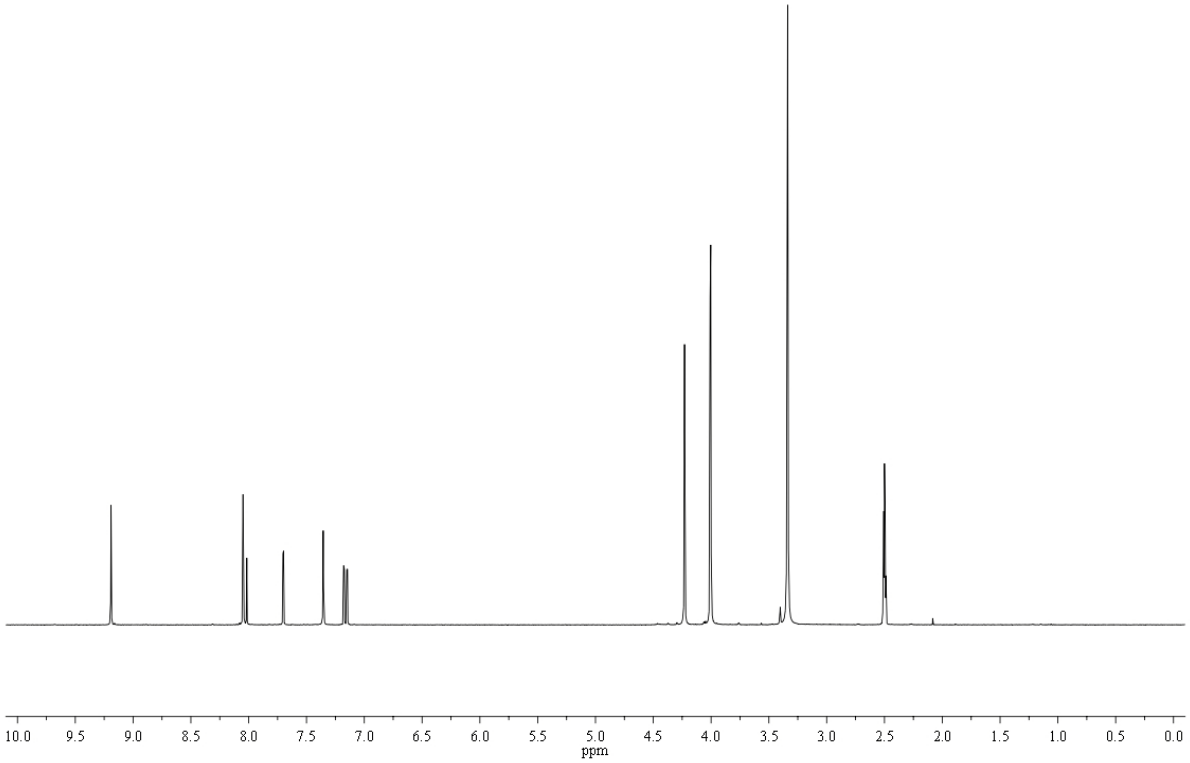

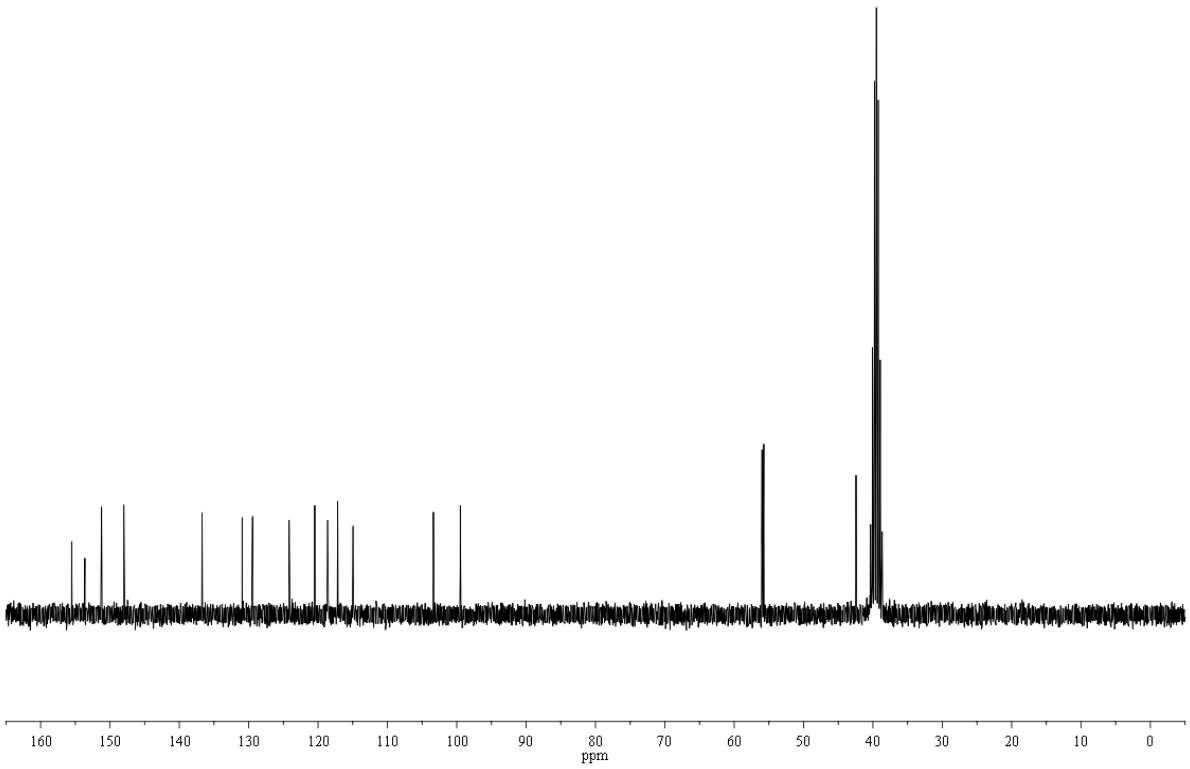

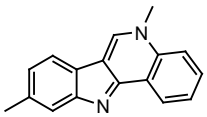

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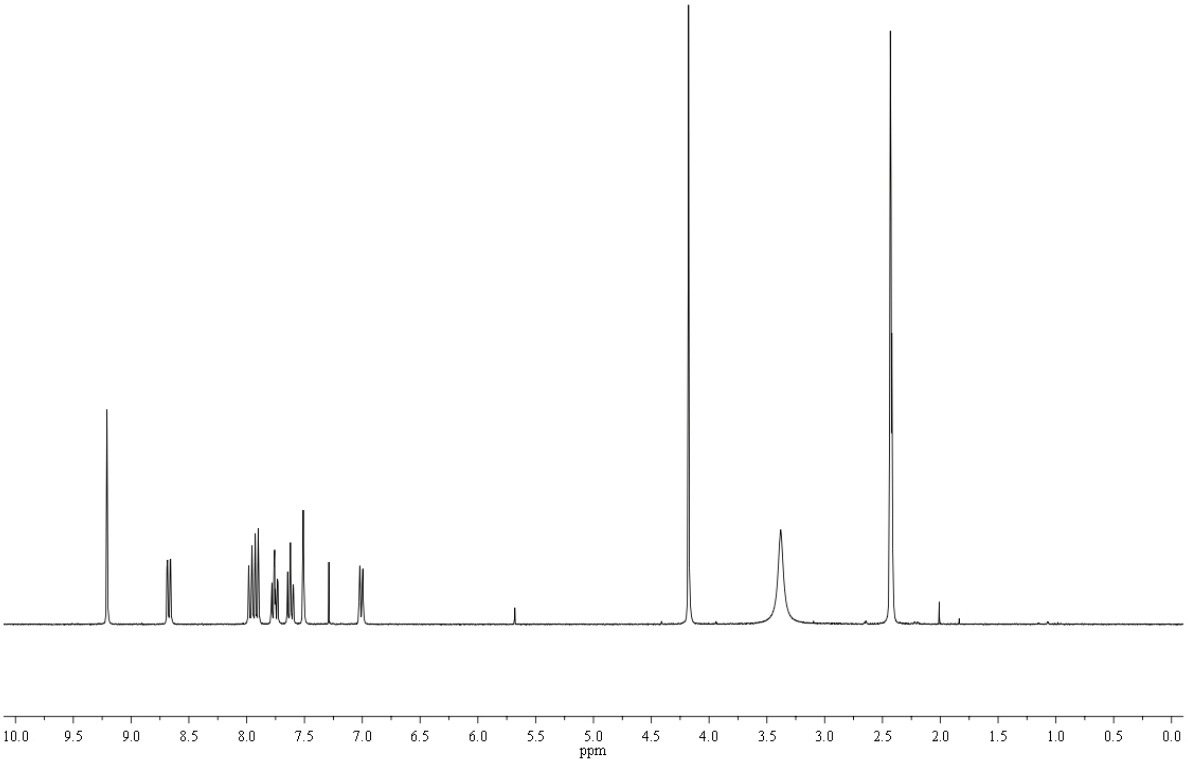

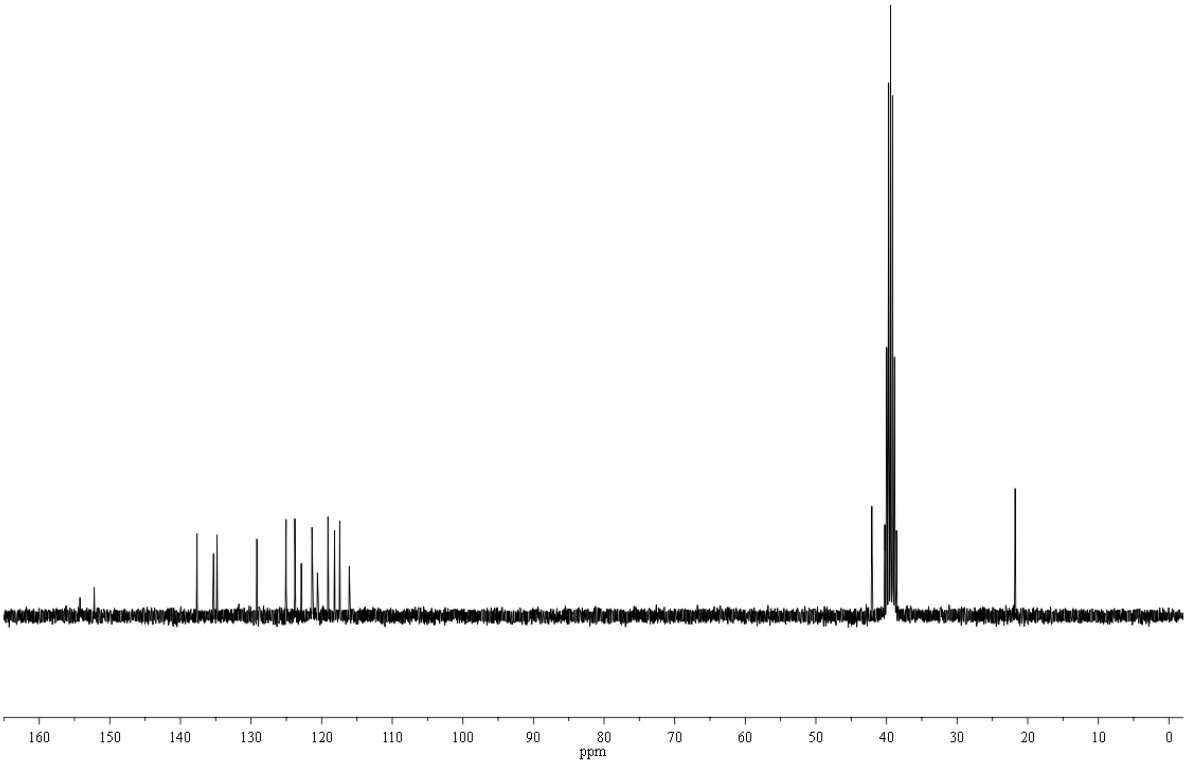

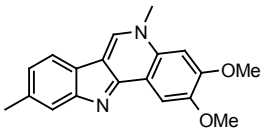

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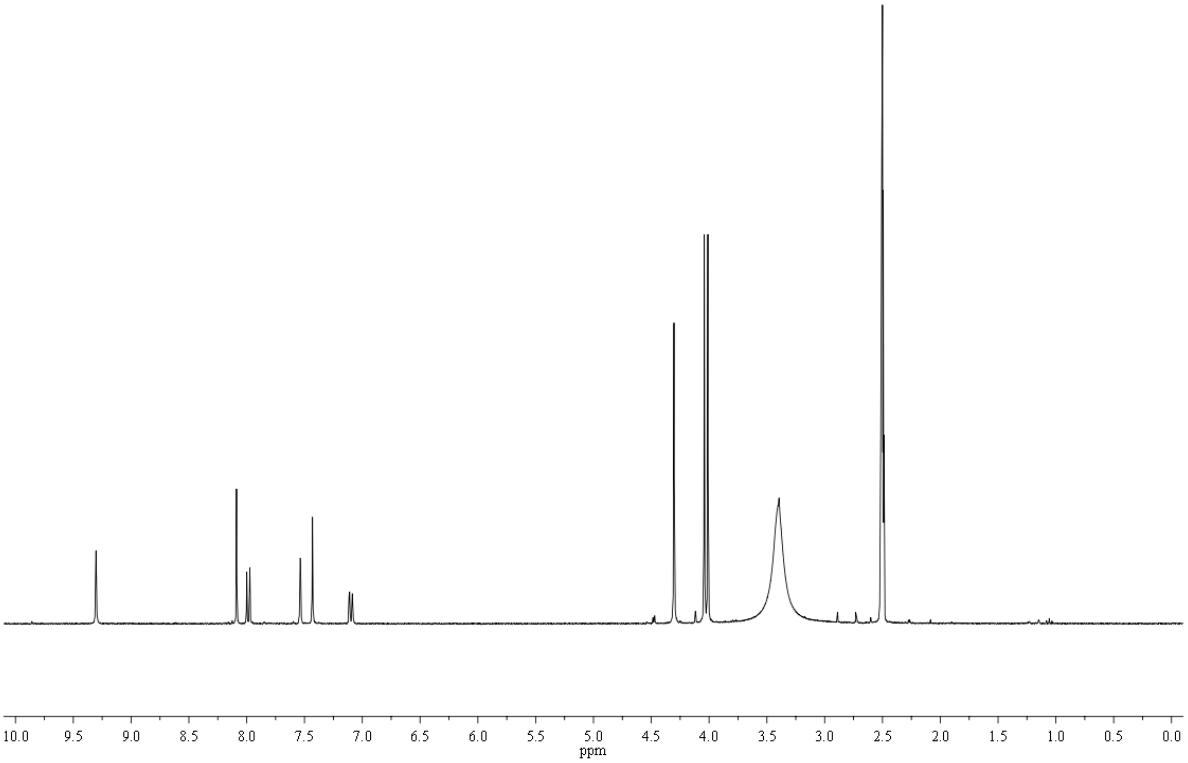

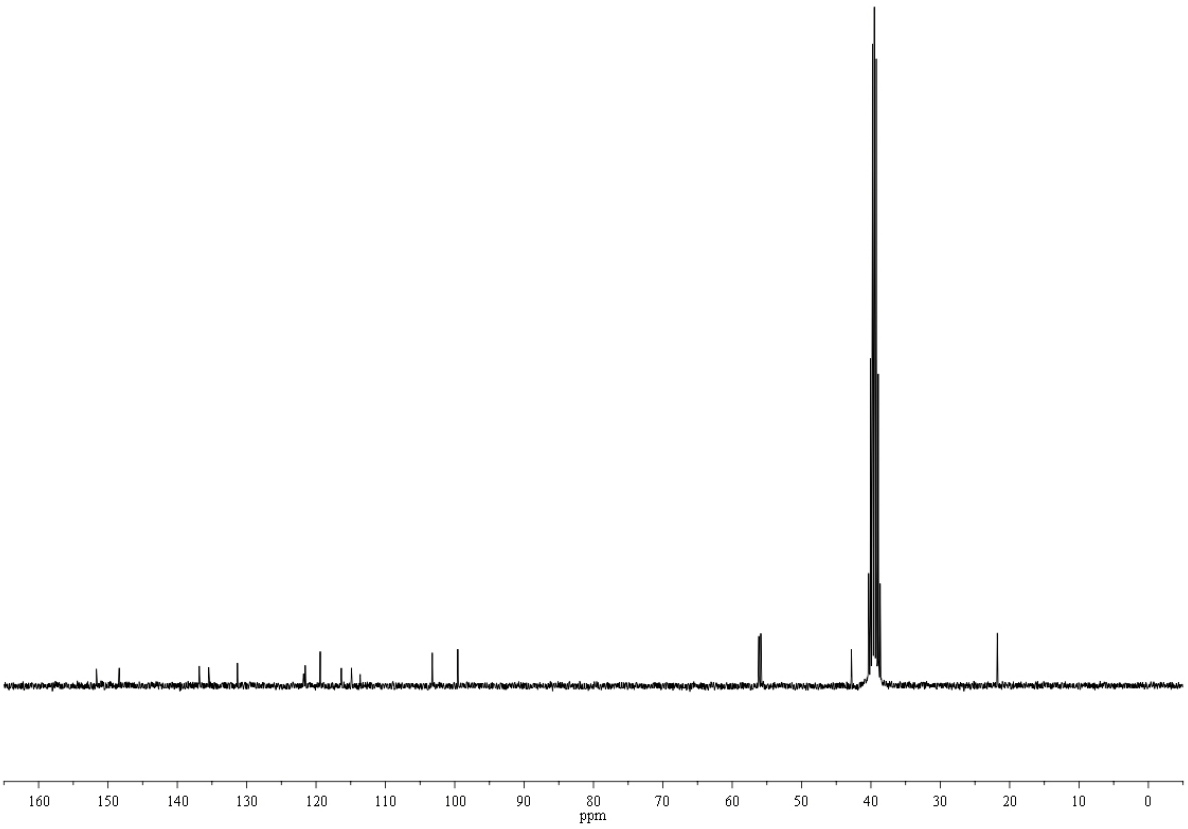

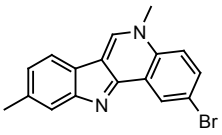

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