Indium-Catalyzed Denitrogenative Transannulation Of Pyridotriazoles: Synthesis of Pyrido[1,2-a]indoles

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1. Experimental Section

General: All commercially available chemicals and reagents were used without any further purification unless otherwise indicated. ^{1}H and ^{13}C NMR spectra were recorded at 600, and 150 MHz, respectively. The spectra were recorded in $CDCl_3$ as solvent. Multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); m (multiplet); dd (doublet of doublets), etc. and coupling constants (J) were given in Hz. Chemical shifts are reported in ppm relative to TMS as an internal standard. The peaks around delta values of ^{1}H NMR (7.26), and ^{13}C NMR (77.00) are correspond to deuterated solvent chloroform respectively,[δ value around (1.5) in ^{1}H NMR is of water]. Mass spectra were obtained using electron impact (EI) ionization method. Progress of the reactions was monitored by thin layer chromatography (TLC). All products were purified through column chromatography using silica gel 100-200 mesh size using hexane/ethyl acetate as eluent, unless otherwise indicated.

Note: As we observed the during the study, when we rerecorded NMR spectra of one of the compound **3t** (see Figure S3) immediately the spectra appeared good, the same spectra recorded after 4 days and we observed some impurities in aliphatic region of ^{1}H NMR, however ^{13}C NMR was clear, which shows that compound is not stable under normal conditions. Such pattern was observed with other products also.

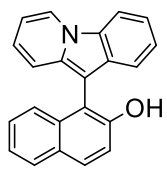
General procedure:

(a) Synthesis of triazolopyridine derivatives: Hydrazine monohydrate (0.30 mmol) and acetic acid (0.02 mmol) were added to a solution of 2-acylpyridine (0.20 mmol) in ethanol (1.0 mL), at room temperature. The reaction mixture was heated at reflux for 6 h, and then EtOAc (5.0 mL) and $Cu(OAc)_2$ (0.01 mmol) were added. After stirring at the indicated temperature for the indicated time, the resulting mixture was cooled to room temperature and then diluted with EtOAc (20 mL). The organic phase was washed with water (10 mL) and then dried over Na_2SO_4. Concentration under reduced pressure and successive purification by column chromatography gave the desired triazolopyridine derivatives.

(b) Synthesis of 1-(pyrido[1,2-a]indol-10-yl)naphthalene-2-ol (3a) : To a reaction tube equipped with a magnetic stir bar, added 3-phenyl-[1,2,3]triazolo[1,5-a]pyridine (**1a**) (39.0 mg, 0.2 mmol), naphthalene-2-ol (**2a**) (43.2 mg, 0.3 mmol), trifluoroacetic acid (56.4mg, 0.4 mmol), indium triflate {0.04 mmol (20 mol%)} and 1.0 mL of 1,2-dichlorobenzene. The mixture was heated in an oil bath at 130 °C in a closed tube for 6h. Reaction was monitored by TLC, after completion of the reaction it was allowed to attain room temperature. Then the mixture was poured into 30 mL of sodium chloride solution. The product was extracted with EtOAc (15 mL X 3) and dried with anhydrous Na_2SO_4. Removal of the solvent under reduced pressure the left-out residue was purified by column chromatography using silica gel (5% EtOAc/hexane) to afford **3a** (58.0 mg; 93% yield).

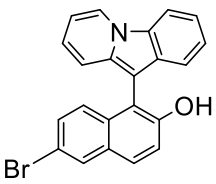
2. Characterization data :

1-(pyrido[1,2-a]indol-10-yl)naphthalene-2-ol (3a) :



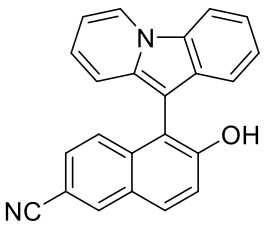
(Eluent: 5% EtOAc/hexane); 93% yield (58.0 mg); yellow semi solid; ^{1}H NMR (600 MHz, $CDCl_3$), δ 8.39 (d, J = 7.3 Hz, 1H), 7.96 – 7.92 (m, 1H), 7.80 (dd, J = 10.8, 9.0 Hz, 2H), 7.39 – 7.35 (m, 1H), 7.35 – 7.27 (m, 4H), 7.24 (t, J = 7.3 Hz, 1H), 7.18 (dd, J = 14.0, 6.7 Hz, 1H), 7.02 (d, J = 9.2 Hz, 1H), 6.84 (dd, J = 9.1, 6.5 Hz, 1H), 6.54 (t, J = 6.8 Hz, 1H), 5.34 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.31, 135.06, 134.22, 129.95, 129.56, 129.24, 128.72, 128.22, 126.32, 125.30, 124.58, 123.63, 123.40, 123.11, 120.54, 119.86, 118.18, 117.17, 112.15, 110.50, 108.63, 95.04; HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{22}H_{16}NO$, 310.1232; found 310.1254.

6- bromo1-(pyrido[1,2-a]indol-10-yl)naphthalene-2-ol (3b) :



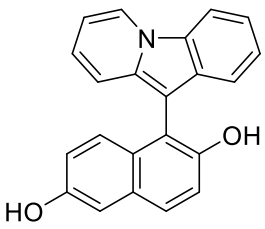
(Eluent: 5% EtOAc/hexane); 79% yield (61.0 mg); yellow semi solid; ^{1}H NMR (600 MHz, $CDCl_3$), δ 8.49 (d, J = 7.3 Hz, 1H), 8.03 (d, J = 8.9 Hz, 2H), 7.81 (d, J = 8.7 Hz, 1H), 7.49 – 7.43 (m, 1H), 7.43 – 7.37 (m, 3H), 7.34 (d, J = 9.3 Hz, 1H), 7.29 (d, J = 9.0 Hz, 1H), 7.09 (d, J = 9.2 Hz, 1H), 6.96 (dd, J = 9.0, 6.4 Hz, 1H), 6.65 (t, J = 6.7 Hz, 1H), 5.46 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.57, 135.04, 132.71, 130.37, 130.08, 129.94, 129.48, 128.54, 127.21, 124.64, 124.56, 123.76, 120.66, 119.61, 118.32, 117.96, 116.89, 112.53, 110.56, 108.75, 94.33; HRMS-ESI (m/z) $[M-H]^+$calcd. For $C_{22}H_{13}BrNO$, 386.0181; found 386.0183.

6-hydroxy-5(pyrido[1,2-a]indol-10-yl)-2-naphthonitrile (3c) :



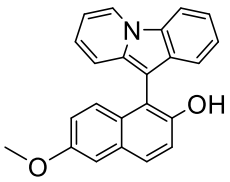
(Eluent: 5% EtOAc/hexane); 84% yield (56.0 mg); yellow semi solid ;^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 (d, J = 7.1 Hz, 1H), 8.25 (s, 1H), 8.05 (d, J = 7.4 Hz, 1H), 7.94 (d, J = 9.0 Hz, 1H), 7.49 (d, J = 8.9 Hz, 1H), 7.47 – 7.38 (m, 5H), 7.06 (d, J = 9.2 Hz, 1H), 7.01 – 6.96 (m, 1H), 6.68 (t, J = 6.6 Hz, 1H), 5.68 (s, 1H) ;^{13}C NMR (150 MHz, $CDCl_3$ δ 154.99, 135.96, 135.19, 134.37, 130.11, 128.46, 128.15, 126.96, 126.52, 124.74, 124.07, 124.02, 120.90, 119.68, 119.41, 119.11, 117.68, 113.01, 110.71, 108.97, 106.39, 93.47; HRMS-ESI (m/z) $[M-H]^+$calcd. For $C_{23}H_{13}N_2O$, 333.1028; found 333.1035.

1-(pyrido[1,2-a]indol-10-yl)naphthalene-2,6-diol (3d) :



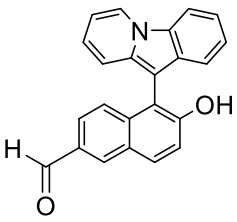
(Eluent: 10% EtOAc/hexane); 60% yield (39.0 mg); yellow semi solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (d, J = 7.1 Hz, 1H), 8.03 (d, J = 7.9 Hz, 1H), 7.72 (d, J = 8.9 Hz, 1H), 7.47 (d, J = 7.2 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.35 (d, J = 8.5 Hz, 1H), 7.30 (d, J = 9.1 Hz, 1H), 7.21 (d, J = 1.4 Hz, 1H), 7.11 (d, J = 9.2 Hz, 1H), 6.94 (dd, J = 9.1, 6.2 Hz, 1H), 6.90 (d, J = 9.1 Hz, 1H), 6.63 (t, J = 6.6 Hz, 1H), 5.25 (s, 1H), 4.91 (s, 1H).; ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.45, 150.68, 135.01, 130.17, 129.93, 129.47, 128.70, 127.82, 127.26, 124.57, 123.65, 123.43, 120.55, 119.85, 118.18, 117.91, 112.41, 110.50, 110.15, 108.64, 95.23; HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{22}H_{16}NO_2$, 326.1176; found 326.1163.

6-methoxy-1-(pyrido[1,2-a]indol-10-yl)naphthalen-2-ol (3e) :



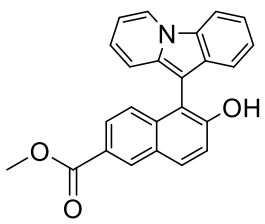
(Eluent: 5% EtOAc/hexane); 68% yield (46.0 mg); yellow semi solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (d, J = 7.2 Hz, 1H), 8.03 (dd, J = 6.4, 2.5 Hz, 1H), 7.79 (d, J = 8.8 Hz, 1H), 7.47 (dd, J = 6.2, 2.5 Hz, 1H), 7.40 – 7.37 (m, 2H), 7.36 (d, J = 9.0 Hz, 1H), 7.31 (d, J = 9.2 Hz, 1H), 7.21 (d, J = 2.3 Hz, 1H), 7.11 (d, J = 9.2 Hz, 1H), 6.98 – 6.92 (m, 2H), 6.63 (t, J = 6.7 Hz, 1H), 5.25 (s, 1H), 3.92 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.78, 150.74, 135.01, 129.99 (d, J = 19.6 Hz), 129.48, 128.72, 128.17, 126.91, 124.56, 123.64, 123.40, 120.54, 119.85, 118.71, 118.19, 117.57, 112.46, 110.49, 108.63, 106.60, 95.30, 55.33; HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{23}H_{18}NO_2$, 340.1338; found 340.1337.

6- hydroxy 5-(pyrido[1,2-a]indol-10-yl)-2-naphthaldehyde (3f) :



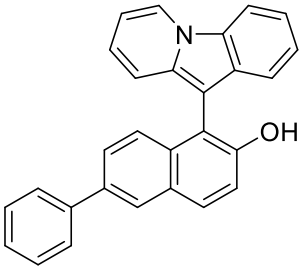
(Eluent: 10% EtOAc/hexane); 68% yield (46.0 mg); Red solid (melting point 201-203 °C); ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.11 (s, 1H), 8.52 (d, J = 6.9 Hz, 1H), 8.37 (d, J = 1.4 Hz, 1H), 8.05 (d, J = 8.9 Hz, 2H), 7.74 (d, J = 9.6 Hz, 1H), 7.48 (dd, J = 8.9, 2.7 Hz, 2H), 7.41 (dd, J = 8.5, 4.2 Hz, 3H), 7.10 – 7.04 (m, 1H), 6.98 (dd, J = 9.2, 6.3 Hz, 1H), 6.68 (t, J = 6.8 Hz, 1H), 5.71 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.09, 155.24, 137.76, 135.18, 134.93, 131.89, 131.33, 130.03, 128.50, 128.32, 126.38, 123.93, 123.48, 120.81, 119.50, 118.44, 117.80, 113.16, 110.67, 108.90, 93.91; HRMS-ESI (m/z) $[M-H]^+$calcd. For $C_{23}H_{14}NO_2$, 336.1025; found 336.1029.

methyl 6-hydroxy 5-(pyrido[-10-yl)-2-naphthoate (3g):



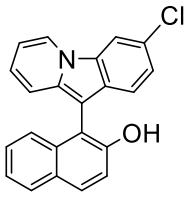
(Eluent: 20% EtOAc/hexane); 41% yield (30.8 mg); yellow semi solid ; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.50 (d, J = 7.2 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 8.9 Hz, 1H), 7.84 (d, J = 8.8 Hz, 1H), 7.45 – 7.37 (m, 5H), 7.08 (d, J = 9.2 Hz, 1H), 6.99 – 6.93 (m, 1H), 6.65 (t, J = 6.3 Hz, 1H), 5.61 (s, 1H), 3.94 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.45, 154.40, 136.68, 135.14, 131.49, 131.07, 130.02, 128.56, 128.27, 125.77, 125.51, 124.66, 123.83, 123.74, 120.73, 119.64, 118.11, 117.95, 112.58, 110.61, 108.81, 94.28, 52.05; HRMS-ESI (m/z) $[M+Na]^+$calcd. For $C_{24}H_{17}NO_3Na$, 390.1106; found 390.1087.

6-phenyl-1-(pyrido[1,2-a]indol-10-yl)naphthalene-2-ol (3h) :



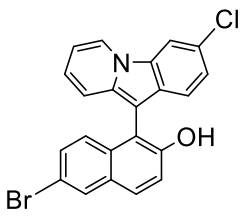
(Eluent: 5% EtOAc/hexane); 75% yield (58.0 mg); yellow semi solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.51 (d, J = 7.2 Hz, 1H), 8.09 (s, 1H), 8.05 (d, J = 7.9 Hz, 1H), 7.96 (d, J = 8.9 Hz, 1H), 7.70 (d, J = 7.6 Hz, 2H), 7.55 (d, J = 8.7 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.47 (t, J = 8.0 Hz, 3H), 7.44 – 7.39 (m, 3H), 7.35 (t, J = 7.3 Hz, 1H), 7.15 (d, J = 9.2 Hz, 1H), 6.99 – 6.94 (m, 1H), 6.65 (t, J = 6.7 Hz, 1H), 5.45 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.45, 141.18, 135.89, 135.10, 133.42, 129.98, 129.87, 129.49, 128.77, 127.20, 127.00, 126.18, 125.96, 124.64, 124.56, 123.68, 123.51, 120.60, 119.85, 118.22, 117.63, 112.15, 110.54, 108.69, 94.96; HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{28}H_{20}NO$, 386.1545; found 386.1575.

1-(3-chloropyrido[1,2-a]indol-10-yl)naphthalene-2-ol (3i):



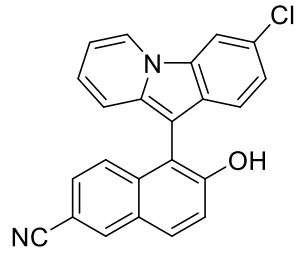
(Eluent: 5% EtOAc/hexane); 84% yield (58.0 mg); yellow semi solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (d, J = 7.4 Hz, 1H), 8.02 (s, 1H), 7.90 (dd, J = 12.6, 8.5 Hz, 2H), 7.44 – 7.32 (m, 5H), 7.31 (dd, J = 18.2, 11.0 Hz, 1H), 7.11 (d, J = 9.2 Hz, 1H), 6.99 – 6.91 (m, 1H), 6.64 (t, J = 6.6 Hz, 1H), 5.35 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.30, 135.56, 134.12, 130.05, 129.80, 129.23, 128.27, 127.13, 126.44, 126.39, 125.03, 124.38, 124.36, 123.66, 123.22, 120.80, 118.36, 117.20, 111.51, 110.59, 109.25, 95.39; HRMS-ESI (m/z)$[M+H]^+$ calcd. For $C_{22}H_{13}ClNO$, 344.0842; found 344.0829.

6-bromo-1-(3-chloropyrido[1,2-a]indol-10-yl)naphthalene-2-ol (3j):



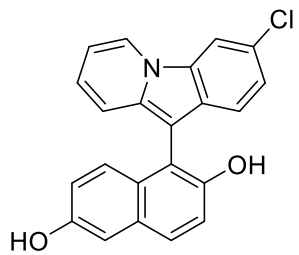
(Eluent: 5% EtOAc/hexane); 62% yield (53.0 mg); yellow semi solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (d, J = 7.1 Hz, 1H), 8.01 (s, 2H), 7.79 (d, J = 9.0 Hz, 1H), 7.37 (d, J = 9.2 Hz, 1H), 7.35 – 7.29 (m, 3H), 7.19 (t, J = 4.6 Hz, 1H), 7.06 (d, J = 9.2 Hz, 1H), 6.97-6.94 (m, 1H), 6.66 (t, J = 6.6 Hz, 1H), 5.35 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.59, 135.59, 132.64, 130.51, 130.38, 130.15, 129.64, 128.82, 127.69, 126.97, 126.58, 124.58, 124.44, 123.98, 120.59, 118.37, 118.15, 117.00, 111.90, 110.69, 109.41, 94.70; HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{22}H_{14}BrClNO$, 421. 9947; found 421.9997.

5-(3-chloropyrido[1,2-a]indol-10-yl)-6-hydroxy-2-naphthonitrile (3k):



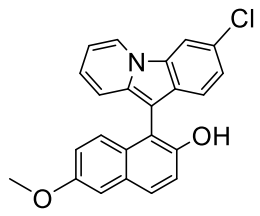
(Eluent: 5% EtOAc/hexane); 73% yield (54.2 mg); yellow semi solid; ^{1}H NMR (600 MHz, $CDCl_3$), δ 8.41 (d, J = 6.8 Hz, 1H), 8.24 (s, 1H), 8.03 (s, 1H), 7.94 (d, J = 8.5 Hz, 1H), 7.47 (t, J = 11.4 Hz, 1H), 7.40 (d, J = 11.3 Hz, 2H), 7.32 (dd, J = 23.6, 8.2 Hz, 2H), 7.05 (d, J = 9.1 Hz, 1H), 7.02 – 6.96 (m, 1H), 6.70 (t, J = 6.2 Hz, 1H), 5.65 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$), δ 155.00, 135.86, 135.70, 134.38, 130.33, 130.17, 128.12, 127.07, 126.86, 126.76, 126.25, 124.77, 124.55, 124.32, 120.34, 119.54, 119.16, 117.89, 112.36, 110.81, 109.57, 106.46, 93.84 HRMS-ESI (m/z) $[M+H]^+$ calcd. For $C_{23}H_{14}ClN_2O$, 369.0795; found 369.0786.

1-(3-chloropyrido[1,2-a]indol-10-yl)naphthalene-2,6-diol (3l):



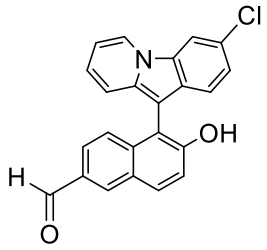
(Eluent: 10% EtOAc/hexane); 55% yield (44.0 mg); yellow semi solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (d, J = 7.0 Hz, 1H), 8.01 (s, 1H), 7.72 (d, J = 9.0 Hz, 1H), 7.37 (d, J = 9.0 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.24 (d, J = 9.1 Hz, 1H), 7.21 (d, J = 2.3 Hz, 1H), 7.10 (d, J = 9.2 Hz, 1H), 6.95 (dd, J = 9.2, 6.4 Hz, 1H), 6.91 (dd, J = 9.0, 2.8 Hz, 1H), 6.65 (t, J = 6.8 Hz, 1H), 5.17 (s, 1H), 5.13 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.59, 150.66, 135.51, 130.19, 129.32, 128.07, 127.12, 126.97, 126.42, 124.42, 123.69, 120.82, 118.40, 118.06, 117.91, 110.60, 110.20, 109.28, 95.60; HRMS-ESI (m/z) $[M-Cl]^+$calcd. For $C_{22}H_{15}NO_2$, 360.0791; found 360.0793.

1-**(3-chloropyrido[1,2-a]indol-10-yl)-6-methoxynaphthalen-2-ol (3m):**



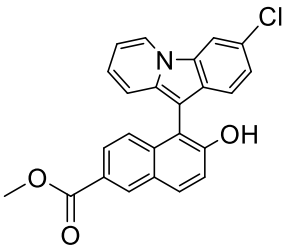
(Eluent: 5% EtOAc/hexane); 55% yield (41.0 mg); yellow semi solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32 (d, J = 7.3 Hz, 1H), 7.96 (s, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.30 (dd, J = 17.2, 9.0 Hz, 3H), 7.20 (d, J = 4.2 Hz, 1H), 7.15 (d, J = 1.8 Hz, 1H), 7.04 (d, J = 9.2 Hz, 1H), 6.93 – 6.86 (m, 2H), 6.59 (t, J = 6.7 Hz, 1H), 5.10 (s, 1H), 3.86 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.83, 150.73, 135.52, 130.04, 129.36, 128.42, 127.13, 126.67, 126.42, 124.39, 123.68, 120.82, 118.87, 118.46, 117.58, 111.82, 110.59, 109.27, 106.67, 55.34; HRMS-ESI (m/z) $[M-H]^+$calcd. For $C_{23}H_{15}ClNO_2$, 372.0792; found 372.0784.

5-(3-chloropyrido[1,2-a]indol-10-yl)-6-hydroxy-2-naphthaldehyde (3n):



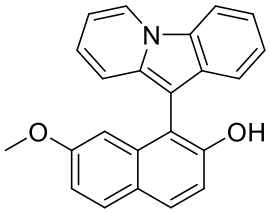
(Eluent: 5% EtOAc/hexane); 72% yield (54.0 mg); Red solid (melting point 229-231 °C); ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.11 (s, 1H), 8.41 (d, J = 7.1 Hz, 1H), 8.37 (s, 1H), 8.10 – 8.02 (m, 2H), 7.75 (d, J = 9.0 Hz, 1H), 7.47 (d, J = 9.1 Hz, 1H), 7.43 (d, J = 8.7 Hz, 1H), 7.33 (d, J = 9.2 Hz, 2H), 7.07 (d, J = 9.2 Hz, 1H), 7.03 – 6.97 (m, 1H), 6.69 (t, J = 6.6 Hz, 1H), 5.63 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.14, 155.34, 137.78, 135.81, 135.02, 132.06, 131.67, 130.27, 128.44, 127.02, 126.82, 126.21, 124.65, 124.30, 123.75, 120.56, 118.56, 118.16, 112.62, 110.88, 109.64, 94.36; HRMS-ESI (m/z)$[M-H]^+$calcd. For $C_{23}H_{13}ClNO_2$, 370.0635; found 370.0645.

Methyl 5-(3-chloropyrido[1,2-a]indol-10-yl)-6-hydroxy-2-naphthoate (3o):



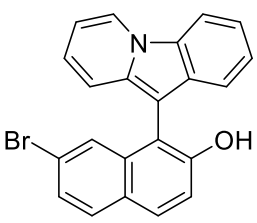
(Eluent: 5% EtOAc/hexane); 40% yield (33.4 mg); yellow semi solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.40 (d, J = 6.9 Hz, 1H), 8.03 (s, 1H), 8.00 (d, J = 9.0 Hz, 1H), 7.87 – 7.83 (m, 1H), 7.43 (d, J = 8.8 Hz, 1H), 7.39 – 7.32 (m, 3H), 7.08 (d, J = 9.2 Hz, 1H), 6.97 (dd, J = 9.2, 6.4 Hz, 1H), 6.67 (t, J = 6.8 Hz, 1H), 5.53 (s, 1H), 3.95 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.45, 154.40, 136.68, 135.14, 131.49, 131.07, 130.02, 128.56, 128.27, 125.77, 125.51, 124.76, 124.66, 123.84, 123.75, 120.73, 119.64, 118.11, 117.95, 112.58, 110.61, 108.81, 94.28, 52.05; HRMS-ESI (m/z)$[M-H]^+$calcd. For $C_{24}H_{15}ClNO_3$, 400.0741; found 400.0737.

7-methoxy-1-(pyrido[1,2-a]indol-10-yl)naphthalene-2-ol (3p):



(Eluent: 5% EtOAc/hexane); 60% yield (39.0 mg); yellow semi solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.48 (d, J = 7.1 Hz, 1H), 8.04 – 8.00 (m, 1H), 7.80 (d, J = 8.8 Hz, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.50 (dd, J = 7.5, 4.1 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.26 – 7.19 (m, 1H), 7.13 (d, J = 9.2 Hz, 1H), 7.02 – 6.91 (m, 2H), 6.73 (s, 1H), 6.63 (t, J = 6.6 Hz, 1H), 5.38 (s, 1H), 3.50 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.26, 152.80, 135.46, 134.79, 130.97, 130.00, 129.77, 129.25, 128.39, 124.61, 123.56, 123.32, 120.55, 120.02, 118.33, 115.34, 114.66, 111.36, 110.52, 108.62, 104.32, 95.29, 55.04; HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{23}H_{18}NO_2$, 340.1338; found 340.1368.

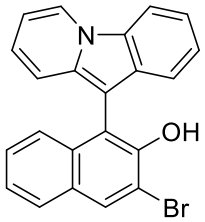
7-bromo-1-(pyrido[1,2-a]indol-10-yl)naphthalene-2 ol (3q):



(Eluent: 5% EtOAc/hexane); 87% yield (68.0 mg); yellow semi solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (d, J = 7.0 Hz, 1H), 7.94 – 7.88 (m, 1H), 7.74 (d, J = 8.9 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.45 (s, 1H), 7.34 (dt, J = 6.6, 3.4 Hz, 1H), 7.32 – 7.25 (m, 4H), 6.97 (d, J = 9.2 Hz, 1H), 6.84 (dd, J = 8.9, 6.5 Hz, 1H), 6.52 (t, J = 6.6 Hz, 1H), 5.37 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.16, 135.57, 135.14, 129.99, 129.90, 129.47, 128.51, 127.67, 127.32, 126.50, 124.66, 124.59, 123.83, 121.00, 120.67, 119.47, 117.85, 117.60, 111.69, 110.60, 108.79, 94.02; HRMS-ESI (m/z) $[M+Cl]^-$ calcd. For $C_{22}H_{14}BrNOCl$, 421.9947; found 421.9940.

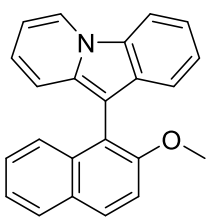
3-bromo-1-(pyrido[1,2-a]indol-10-yl)naphthalene-2-ol (3r):

(Eluent: 5% EtOAc/hexane); 72% yield (56.0 mg); yellow semi solid; ^{1}H NMR (600 MHz, $CDCl_3$)



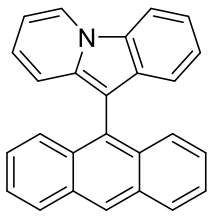
δ 8.49 (d, J = 7.1 Hz, 1H), 8.18 (s, 1H), 8.03-8.02 (m, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.44–7.42 (m, 1H), 7.40-7.33 (m, 4H), 7.28-7.24 (m, 1H), 7.09 (d, J= 6.48 Hz, 1H), 6.96-6.93 (m, 1H), 6.64 (t, J = 6.7 Hz, 1H), 5.77 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.30, 148.70, 135.04, 133.33, 131.81, 129.87, 129.67, 128.84, 127.69, 127.26, 125.62, 124.61, 124.53, 123.72, 120.60, 119.69, 118.06, 114.24, 111.36, 110.54, 108.74, 95.00, HRMS-ESI (m/z) $[M+Na]^+$calcd. For $C_{22}H_{14}BrNO$, 410.0156; found 410.0200.

10-(2-methoxynaphthalen-1-yl)pyrido[1,2-a]indole (3s):



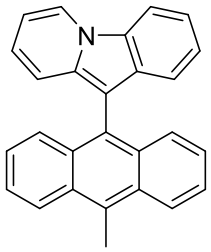
(Eluent: 5% EtOAc/hexane); 80% yield (54.8 mg); yellow solid (melting point 251-253 °C); ^{1}H NMR (600 MHz, $CDCl_3$ δ 8.43 (d, J = 7.2 Hz, 1H), 8.04 – 7.91 (m, 2H), 7.88 (d, J = 8.1 Hz, 1H), 7.53 (d, J = 8.6 Hz, 1H), 7.47 (d, J = 8.9 Hz, 1H), 7.43 – 7.38 (m, 1H), 7.37 – 7.30 (m, 3H), 7.29 – 7.26 (m, 1H), 7.05 (d, J = 9.2 Hz, 1H), 6.84 (dd, J = 9.2, 6.1 Hz, 1H), 6.53 (t, J = 6.8 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.58, 134.42, 134.29, 129.41, 129.13, 128.90, 128.00, 127.9, 126.21, 126.09, 124.34, 123.43, 122.72, 121.98, 120.42, 119.60, 119.14, 117.01, 113.98, 110.20, 107.81, 98.97, 56.64; HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{23}H_{18}NO$, 324.1388; found 324.1340.

10-(anthracen-9-yl)pyrido[1,2-a]indole (3t):



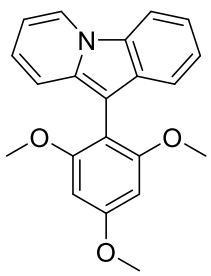
(Eluent: 2% EtOAc/hexane); 55% yield (38.0 mg); yellow solid (melting point 264-266 °C); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.41 (d, J = 7.0 Hz, 1H), 8.02 (d, J = 8.6 Hz, 2H), 7.97 (d, J = 8.5 Hz, 1H), 7.62 (d, J = 8.9 Hz, 2H), 7.40 – 7.35 (m, 2H), 7.31 – 7.27 (m, 1H), 7.21 (d, J = 3.8 Hz, 2H), 7.17 (dd, J = 13.5, 5.6 Hz, 2H), 6.80 (d, J = 9.5 Hz, 1H), 6.72 (dd, J = 9.2, 6.5 Hz, 1H), 6.48 (t, J = 6.9 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.03, 131.81, 131.71, 130.01, 129.35, 128.95, 128.59, 127.37, 126.66, 125.23, 125.09, 124.44, 123.09, 122.51, 120.13, 119.98, 118.57, 110.28, 108.08, 101.25; HRMS-ESI (m/z)$[M]^+$calcd. For $C_{26}H_{17}N$, 343.1361; found 343.1357.

10-(10-methylanthracen-9-yl)pyrido[1,2-a]indole (3u):



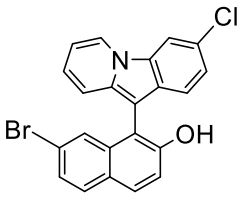
(Eluent: 2% EtOAc/hexane); 55% yield (39.0 mg); yellow solid (melting point 226-228 °C); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.48 (d, J = 7.2 Hz, 1H), 8.41 (d, J = 9.0 Hz, 2H), 8.04 (d, J = 8.3 Hz, 1H), 7.72 (d, J = 8.9 Hz, 2H), 7.53 – 7.47 (m, 2H), 7.36 (t, J = 7.3 Hz, 1H), 7.31 – 7.24 (m, 4H), 6.85 (d, J = 9.2 Hz, 1H), 6.80 – 6.75 (m, 1H), 6.55 (t, J = 6.6 Hz, 1H), 3.23 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.14, 131.59, 130.24, 129.30, 128.09, 127.43, 125.02, 124.89, 124.71, 124.42, 123.04, 122.39, 120.12, 119.93 , 118.57, 110.25, 108.01, 101.70, 14.29; HRMS-ESI (m/z)$[M+H]^+$calcd. For $C_{27}H_{20}N$, 358.1596; found 358.1561.

10-(2,4,6-trimethoxyphenyl)pyrido[1,2-a]indole (3v):



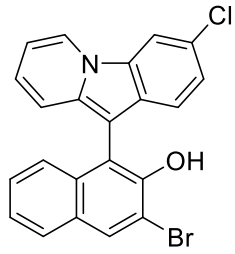
(Eluent: 5% EtOAc/hexane); 80% yield (44.8 mg); yellow semi solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.88 (d, J = 7.9 Hz, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.32 (s, 2H), 7.16 (s, 1H), 6.82 (s, 1H), 6.46 (s, 1H), 6.34 (s, 2H), 3.92 (s, 3H), 3.72 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.44, 159.43, 133.99, 129.28, 128.89, 126.20, 125.73, 124.16, 122.26, 121.28, 120.74, 119.71, 119.22, 110.05, 107.48, 91.04, 55.77, 55.41, 30.92; HRMS-ESI (m/z) $[M+H]^+$calcd. For $C_{21}H_{20}NO_3$, 334.1438; found 334.1409.

7-bromo-1-(3-chloropyrido[1,2-a]indol-10-yl)naphthalene-2-ol (3w):



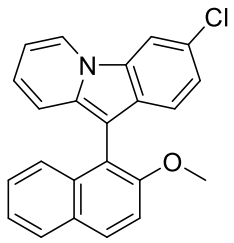
(Eluent: 5% EtOAc/hexane); 67% yield (57.0 mg); yellow semi solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (d, J = 6.9 Hz, 1H), 8.02 (s, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.74 (d, J = 9.0 Hz, 1H), 7.50 (s, 1H), 7.44 – 7.40 (m, 1H), 7.40 – 7.34 (m, 3H), 7.08 (d, J = 9.2 Hz, 1H), 6.97 (dd, J = 9.2, 6.3 Hz, 1H), 6.66 (t, J = 6.8 Hz, 1H), 5.39 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.16, 135.64, 135.47, 130.12, 129.95, 129.73, 127.66, 127.09, 126.95, 126.56, 124.59, 124.07, 121.14, 120.46, 118.07, 117.98, 117.68, 117.62, 111.02, 110.73, 109.42, 94.39; HRMS-ESI (m/z)$[M-H]^+$calcd. For $C_{22}H_{12}BrClNO$, 419.9791; found 419.9832.

3-bromo-1-(3- chloropyrido[1,2-a]indol-10-yl)naphthalene-2-ol (3x):



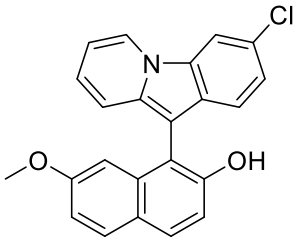
(Eluent: 5% EtOAc/hexane); 65% yield (56.0 mg); yellow semi solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 (d, J = 7.1 Hz, 1H), 8.19 (s, 1H), 8.02 (s, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.37 – 7.33 (m, 3H), 7.32 – 7.27 (m, 2H), 7.09 (d, J = 9.2 Hz, 1H), 6.96 (dd, J = 9.2, 6.3 Hz, 1H), 6.66 (t, J = 6.8 Hz, 1H), 5.71 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.65, 135.55, 133.31, 131.97, 130.00, 129.69, 127.34, 126.94, 126.75, 126.46, 125.42, 124.45 (d, J = 9.7 Hz), 124.26, 123.87, 120.76, 118.37, 113.68, 111.51, 110.66, 109.36, 95.64; HRMS-ESI (m/z)$[M+H]^+$calcd For $C_{22}H_{14}BrClNO$, 421.9947; found 421.9832.

3-chloro-10-(2-methoxynaphthalen-1-yl)pyrido[1,2-a]indole (3y):



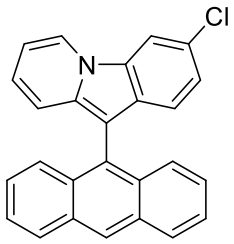
(Eluent: 5% EtOAc/hexane); 61% yield (43.0 mg); yellow solid (melting point 235-237 °C); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (d, J = 7.3 Hz, 1H), 7.90 (d, J = 8.7 Hz, 2H), 7.82 (d, J = 8.1 Hz, 1H), 7.41 (dd, J = 13.7, 8.9 Hz, 2H), 7.28 (dd, J = 16.7, 8.1 Hz, 2H), 7.21 (dt, J = 8.5, 6.9 Hz, 2H), 6.98 (d, J = 9.2 Hz, 1H), 6.77 (dd, J = 9.2, 6.1 Hz, 1H), 6.47 (t, J = 6.9 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.54, 134.95, 134.16, 129.51, 129.36, 129.18, 128.09, 127.50, 126.23, 125.90, 125.38, 124.21, 123.53, 122.26, 121.36, 119.39, 119.32, 116.24, 113.76, 110.28, 108.48, 99.26, 56.53; HRMS-ESI (m/z)$[M]^+$calcd. For $C_{23}H_1ClNO$, 357.0920; found 357.0922.

1-(3-chloropyrido[1,2-a]indol-10-yl)-7-methoxynaphthalen-2-ol (3z):



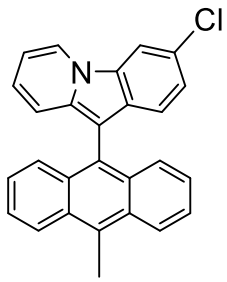
(Eluent: 5% EtOAc/hexane);40% yield (39.0 mg);yellow semi solid;^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (d, J = 7.1 Hz, 1H), 8.02 (s, 1H), 7.81 (d, J = 8.9 Hz, 1H), 7.77 (d, J = 9.0 Hz, 1H), 7.41 (d, J = 8.8 Hz, 1H), 7.34 (d, J = 9.9 Hz, 1H), 7.22 (d, J = 9.0 Hz, 1H), 7.14 (d, J = 9.2 Hz, 1H), 7.01 (dd, J = 9.0, 1.8 Hz, 1H), 6.99 – 6.94 (m, 1H), 6.70 – 6.63 (m, 2H), 5.31 (s, 1H), 3.52 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.36, 152.81, 135.39, 135.30, 130.11, 129.84, 129.51, 126.83, 126.41, 124.56, 124.33, 123.63, 120.98, 118.57, 115.43, 115.31, 114.72, 110.67, 109.26, 104.13, 95.65, 55.08; HRMS-ESI (m/z) $[M-H]^+$calcd. For $C_{23}H_{15}ClNO_2$, 372.0792; found 372.0791.

10-(anthracen-9-yl)-3-chloropyrido[1,2-a]indole (3aa):



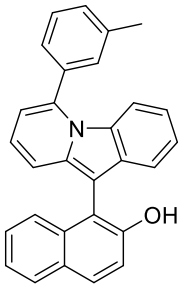
(Eluent: 2% EtOAc/hexane); 45% yield (34.0 mg); yellow solid (melting point 243-245 °C); ^{1}H NMR (600 MHz,) δ 8.56 (s, 1H), 8.39 (d, J = 7.4 Hz, 1H), 8.10 (d, J = 8.5 Hz, 2H), 8.04 (d, J = 1.6 Hz, 1H), 7.64 (d, J = 8.8 Hz, 2H), 7.48 – 7.43 (m, 2H), 7.27 (dd, J = 15.0, 7.2 Hz, 3H), 7.18 (d, J = 8.6 Hz, 1H), 6.87 (d, J = 9.2 Hz, 1H), 6.81 (dd, J = 9.2, 6.2 Hz, 1H), 6.59 (t, J = 6.7 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.55, 131.78, 131.68, 129.48, 128.66, 128.36, 128.13, 127.05, 126.94, 125.83, 125.43, 125.15, 124.23, 123.90, 122.79, 121.05, 118.81, 110.39, 108.77, 101.51; CHNS data calcd. For $C_{26}H_{16}ClN$ (C= 82.64%, H=4.27%, N=3.71%) found (C=82.55%, H=4.489%, N=3.94%).

3-chloro-10-(10-methylanthracen-9-yl)pyrido[1,2-a]indole (3ab):



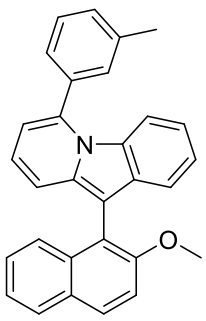
(Eluent: 2% EtOAc/hexane); 40% yield (38.0 mg); yellow solid (melting point 218-220 °C); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (dd, J = 8.8 Hz, 7.3 Hz,3H), 8.04 (s, 1H), 7.66 (d, J = 8.8 Hz, 2H), 7.52 – 7.49 (m, 2H), 7.27 – 7.21 (m, 3H), 7.16 (d, J = 9.0 Hz, 1H), 6.84 (d, J = 9.4 Hz, 1H), 6.79-6.77 (m, 1H), 6.58 (t, J = 6.2 Hz, 1H), 3.23 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.82, 131.69, 130.67, 130.37, 129.57, 128.73, 127.94, 127.21, 126.75, 125.92, 125.23, 125.13, 125.06, 124.38, 124.00, 122.83, 121.18, 118.97, 110.52, 108.86, 101.94 14.47; HRMS-ESI (m/z) $[M]^+$calcd. For $C_{27}H_{18}ClN$, 391.1128; found 391.1121.

1-(6-(m-tolyl)pyrido[1,2-a]indol-10-yl)naphthalen-2-ol (3ac):



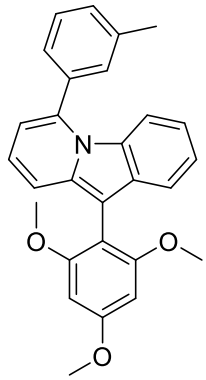
(Eluent: 1% EtOAc/hexane); 74% yield (59.0 mg); yellow semi solid ; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (dd, J = 14.6, 8.5 Hz, 2H), 7.52 – 7.42 (m, 4H), 7.40 (t, J = 7.6 Hz, 3H), 7.33 (t, J = 7.3 Hz, 1H), 7.27 (t, J = 7.5 Hz, 1H), 7.24 – 7.22 (m, 1H), 7.10 (d, J = 9.2 Hz, 1H), 6.98 – 6.92 (m, 2H), 6.70 (d, J = 8.8 Hz, 1H), 6.42 (d, J = 6.8 Hz, 1H), 5.43 (d, J = 2.0 Hz, 1H), 2.48 (d, J = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.39, 140.91, 138.98, 136.75, 136.14, 134.28, 130.89, 130.33, 129.61, 129.24, 129.00, 128.20, 126.30, 126.18, 125.37, 123.11, 122.99, 119.78, 119.32, 117.19, 116.98, 115.39, 112.22, 111.09, 96.13, 21.52; HRMS-ESI (m/z)$[M+Na]^+$ calcd. For $C_{29}H_{21}NONa$, 422.1521; found 422.1523.

10-(2-methoxynaphthalen-1-yl)-6-(m-tolyl)pyrido[1,2-a]indole (3ad):



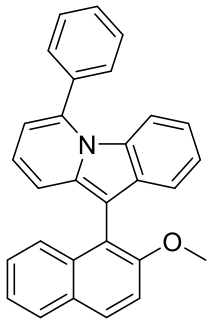
(Eluent: 1% EtOAc/hexane); 85% yield (71.0 mg); yellow semi solid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, J = 9.1 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.52 (t, J = 8.0 Hz, 1H), 7.47 (ddd, J = 22.1, 12.1, 5.6 Hz, 5H), 7.38 – 7.32 (m, 2H), 7.28 (t, J = 7.4 Hz, 1H), 7.18 (t, J = 7.4 Hz, 1H), 7.07 (d, J = 9.1 Hz, 1H), 6.92 – 6.84 (m, 2H), 6.69 (d, J = 8.8 Hz, 1H), 6.34 (d, J = 6.4 Hz, 1H), 3.84 (s, 3H), 2.49 (d, J = 4.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.80, 140.60, 138.87, 136.74, 136.17, 134.51, 130.43, 130.04, 129.88, 129.49, 129.11, 128.94, 128.08, 126.37, 123.56, 121.78, 119.96, 118.95, 118.05, 117.13, 115.25, 114.12, 110.53, 100.24, 56.80, 29.80; HRMS-ESI (m/z)$[M+Na]^+$ calcd. For$C_{30}H_{23}NONa$, 436.1677; found 436.1668.

6-**(m-tolyl)-10-(2,4,6-trimethoxyphenyl)pyrido[1,2-a]indole. (3ae):**



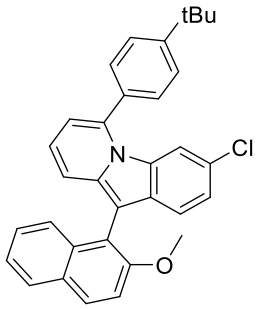
(Eluent: 1% EtOAc/hexane); 80% yield (67.0 mg); yellow semi solid: ^{1}H NMR (600 MHz, $CDCl_3$)) δ 7.44 (t, J = 6.7 Hz, 2H), 7.38 (d, J = 9.6 Hz, 3H), 7.18 (t, J = 8.1 Hz, 2H), 6.89 – 6.84 (m, 1H), 6.82 (t, J = 7.5 Hz, 1H), 6.60 (d, J = 8.6 Hz, 1H), 6.35 (s, 2H), 6.25 (d, J = 6.0 Hz, 1H), 3.93 (s, 3H), 3.73 (s, 6H), 2.45 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.50, 148.08, 145.67, 139.18, 138.60, 136.33, 135.24, 134.55, 131.11, 130.18, 129.86, 128.75, 127.57, 126.72, 125.84, 120.58, 117.28, 117.04, 110.83, 106.30, 105.19, 93.92, 61.46, 61.06, 55.29, 21.45; HRMS-ESI (m/z)$[M+Na]^+$ calcd. For $C_{28}H_{25}NNaO_3$, 446.1732; found 446.1715.

10-(2-methoxynaphthalen-1-yl)-7-phenylpyrido[1,2-a]indole (3af):



(Eluent: 1% EtOAc/hexane); 85% yield (71.0 mg); yellow semi solid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, J = 9.0 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.67 (dd, J = 11.4, 5.2 Hz, 2H), 7.65 – 7.58 (m, 3H), 7.55 (d, J = 8.7 Hz, 1H), 7.50 (d, J = 8.8 Hz, 1H), 7.37 (t, J = 6.8 Hz, 2H), 7.32 – 7.28 (m, 1H), 7.20 (t, J = 7.4 Hz, 1H), 7.10 (d, J = 9.2 Hz, 1H), 6.94 – 6.86 (m, 2H), 6.68 (d, J = 8.9 Hz, 1H), 6.36 (d, J = 5.8 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.82, 140.41, 136.87, 136.17, 134.52, 130.44, 130.09, 129.51, 129.44, 129.37, 129.16, 129.09, 128.11, 126.36, 123.58, 122.22, 121.79, 120.04, 119.04, 118.27, 117.10, 115.17, 114.08, 110.73, 100.37, 56.79; HRMS-ESI (m/z)$[M+H]^+$ calcd. For $C_{29}H_{22}NO$, 400.1701; found 400.1692.

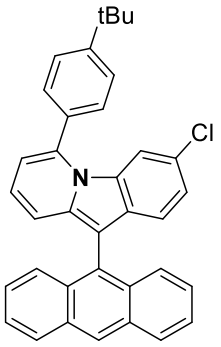
6-(4-tert-butyl)phenyl)-3-chloro-10-(2-methoxynaphthalen-1-yl)pyrido[1,2-a]indole (3ag):



(Eluent: hexane); 67% yield (65.0 mg); yellow semi solid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, J = 9.1 Hz, 1H), 7.89 (d, J = 8.1 Hz, 1H), 7.68 – 7.64 (m, 2H), 7.58 – 7.51 (m, 2H), 7.48 (d, J = 8.9 Hz, 2H), 7.36 (t, J = 7.4 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.23 (d, J = 8.8 Hz, 1H), 7.12 (d, J = 9.5 Hz, 1H), 7.04 (d, J = 9.2 Hz, 1H), 6.88 (dd, J = 9.2, 6.8 Hz, 1H), 6.39 (d, J = 5.4 Hz, 2H), 3.84 (s, 3H), 1.49 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.64, 140.32, 133.11, 130.71, 130.44, 129.53, 129.41, 129.03, 128.41, 128.22, 128.04, 126.67, 126.42, 126.27, 126.15, 125.71, 124.50, 123.67, 122.90, 122.19, 120.65, 118.23, 116.51, 115.29, 113.98,

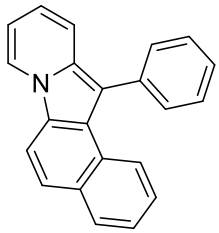
110.69, 100.40, 56.61, 34.99, 31.41; HRMS-ESI (m/z)$[M+H]^+$ calcd. For $C_{33}H_{29}ClNO$, 490.1938; found 490.1925.

10-(Anthracen-9-yl)-6-(4-(*tert*-butyl)phenyl)-3-chloropyrido[1,2-a]indole (3ah):



(Eluent: Hexane); 59% yield (61.0 mg); yellow solid (melting point 240-242 °C): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.12 (d, J = 8.5 Hz, 2H), 7.71 – 7.65 (m, 4H), 7.60 (d, J = 8.0 Hz, 2H), 7.50 – 7.45 (m, 2H), 7.32 – 7.27 (m, 2H), 7.09 (s, 2H), 6.90 – 6.84 (m, 2H), 6.44 (d, J = 8.3 Hz, 2H), 1.51 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.47, 140.47, 137.20, 132.97, 131.78 (d, J = 5.2 Hz), 130.21, 129.14, 128.89, 128.65, 128.34, 127.15, 126.96, 126.23, 125.42, 125.16, 123.14, 122.56, 120.26, 117.58, 115.21, 110.71, 102.46, 35.04, 31.43; HRMS-ESI (m/z) $[M]^+$ calcd. For $C_{36}H_{28}ClN$, 509.1910; found 509.1948.

12-Phenylbenzo[e]pyrido[1,2-a]indole (3ai):[1]



(Eluent:1% EtOAc/hexane); 60% yield (35.0 mg); green semi solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.44 (d, J = 7.0 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H), 7.98 (dd, J = 12.4, 8.5 Hz, 2H), 7.67 (d, J = 9.0 Hz, 1H), 7.64 (d, J = 7.7 Hz, 2H), 7.58 – 7.54 (m, 2H), 7.49 – 7.42 (m, 3H), 7.34 (t, J = 7.6 Hz, 1H), 6.87 (dd, J = 9.0, 6.5 Hz, 1H), 6.65 (t, J = 6.7 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 136.21, 133.47, 131.39, 131.34, 128.73, 128.63, 128.33, 126.85, 125.28, 125.17, 124.54, 122.94, 122.87, 122.41, 121.49, 120.58, 118.11, 118.06, 110.76, 109.53.

3. Crystal structure of 3f (CCDC-1842992)

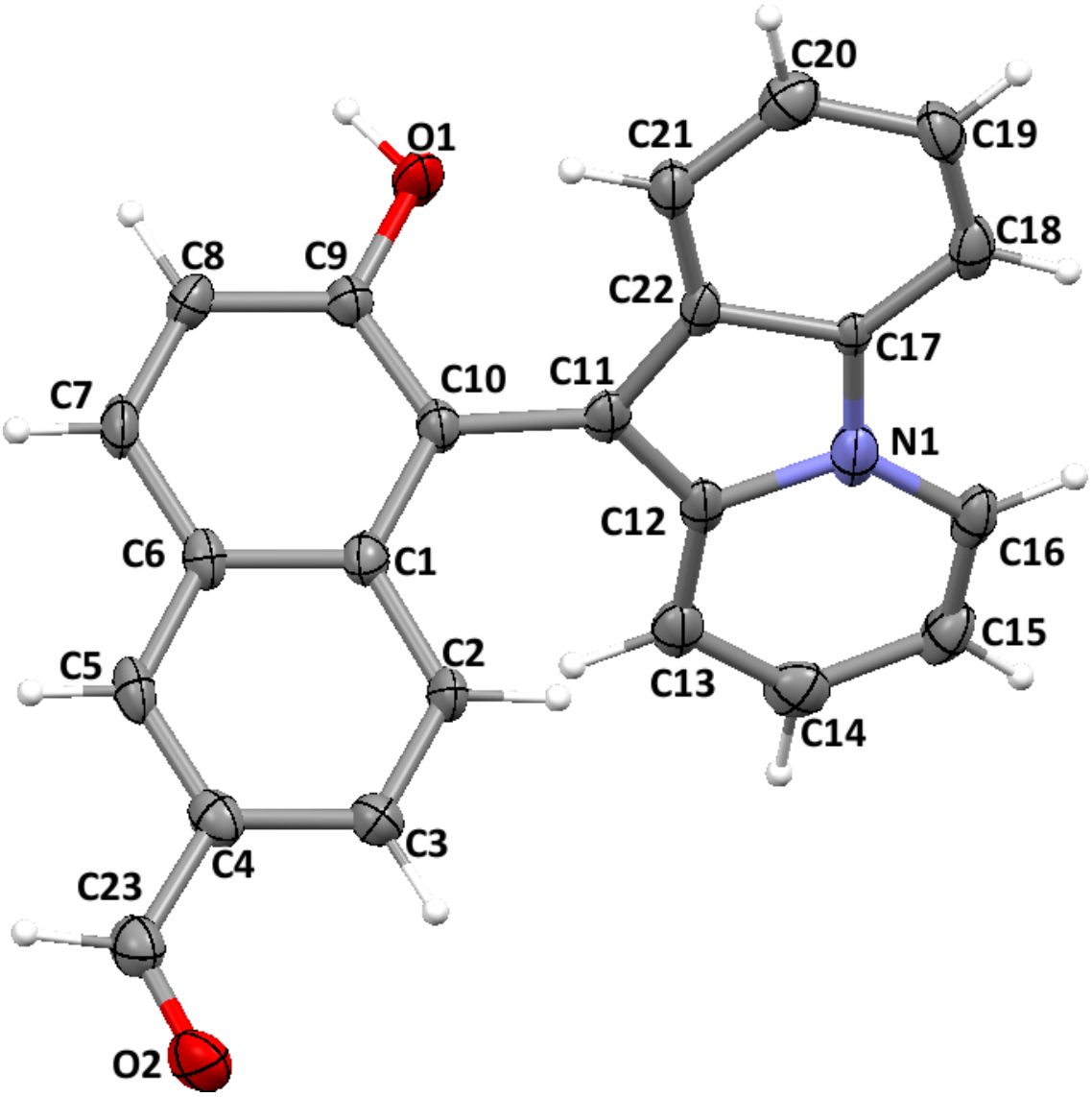


Figure S1. Crystal structure of 3f

4. Computational Methods:

We have carried out all the geometry optimization with B3LYP DFT functional along with LANL2DZ basis set, which includes a double-ζ quality basis set with the Los Alamos effective core potential, for In and Ag and 6-31G(d) basis set for C, N, O, F, H and S in the gas phase.[2-6] We have further calculated harmonic frequencies for all stationary points to examine the minima with no imaginary frequency. On the other hand, transition structures are located on the potential energy surface with only one imaginary frequency. The B3LYP DFT functional has been considered as one of the best functional and widely applied to explore the transition metal chemistry. The transition state structures were further confirmed by intrinsic reaction coordinated (IRC) calculations.[7] Furthermore, we have performed single point energy calculations at SMD_{DCB}-M06/6-31++G(d,p)/LANL2DZ level of theory in o-dichlorobenzene phase (ε=10.0) using B3LYP/6-31G(d)/LANL2DZ level of theory optimized geometries. The solvent medium calculations have been carried out with Self Consistent Reaction Field (SCRF) method using SMD solvation model.[8,9] The solvent phase free energy have been calculated using the following equation:

$$G_{DCB} = E_{DCB} + G_{correction,gas} \ldots\ldots\ldots 2$$

where, G_{DCB} is the o-dichlorobenzene solvent phase free energy, E_{DCB} is the o-dichlorobenzene solvent phase energy, and $G_{correction,gas}$ is the free energy correction value of the gas phase. The o-dichlorobenzene phase free energy differences have been calculated as:

$$\Delta G = G_X - G_N \ldots\ldots\ldots\ldots 1$$

where G_X is the free energy of the intermediate or transition state and G_N is the free energy of initial molecules, and ΔG is the difference in the free energies.

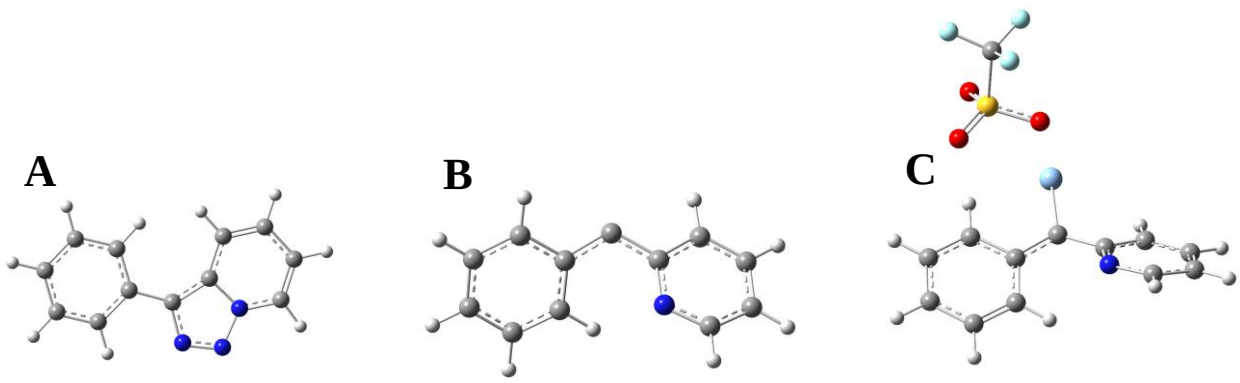


Figure S2: A) optimized geometry of 1a, B) optimized geometry of 1a′, C) optimized geometry of A′.

Coordinates:

1a				**1a′**			
C	-3.46840000	0.55411600	0.00003200	C	2.61273400	-1.19685300	0.77356300
C	-1.14390600	-0.18637800	-0.00001700	C	1.25567200	0.54851200	0.10212800
C	-1.59060900	-1.53312600	-0.00014400	C	2.34327000	1.15703000	-0.57308200
C	-2.93785500	-1.80255200	-0.00017500	C	3.56516000	0.49998000	-0.63458600
C	-3.89241200	-0.74265700	-0.00008200	C	3.71484800	-0.69848600	0.06849600
H	-4.10294300	1.43127900	0.00010200	H	2.70983600	-2.11282500	1.35650000
H	-0.87068300	-2.34136500	-0.00022700	H	2.19254700	2.12945800	-1.03026300
H	-3.28349900	-2.83137700	-0.00027400	H	4.40038500	0.93228200	-1.17945700
H	-4.95564800	-0.95474100	-0.00010700	H	4.66258300	-1.22836500	0.08796700
C	1.46670700	0.13820900	0.00002900	C	-1.22656000	0.53530500	0.01668100
C	2.46806400	1.12843200	-0.00022600	C	-1.36230300	-0.76618500	-0.54360800
C	3.81540300	0.77998900	-0.00025900	C	-2.61121200	-1.36261000	-0.66061700
C	4.20038900	-0.56357600	-0.00003800	C	-3.74947100	-0.70023700	-0.18263300
C	3.21812200	-1.55427500	0.00022200	C	-3.64705100	0.57476800	0.38765500
C	1.86694100	-1.20864800	0.00025700	C	-2.40649300	1.19547300	0.45473700
H	2.16789500	2.17042000	-0.00039800	H	-0.47428100	-1.28415400	-0.88765400
H	4.56974200	1.56248900	-0.00045900	H	-2.70741300	-2.34882100	-1.10696900
H	5.25270900	-0.83430900	-0.00006400	H	-4.72321200	-1.17691100	-0.26514000
H	3.50105000	-2.60376300	0.00040500	H	-4.53743600	1.08243200	0.74794200
H	1.12859000	-2.00246200	0.00048400	H	-2.29595500	2.19851600	0.85517300
C	0.05680700	0.55199300	0.00005400	C	0.00336300	1.25855400	0.13431500
N	-0.27498600	1.87120200	0.00015300	N	1.40303000	-0.63759000	0.76622900
N	-1.56940200	2.04456600	0.00016000				
N	-2.12171600	0.80347000	0.00006000				
OTf				**TfOH**			
O	-1.84991700	-0.45924800	0.00000000	O	1.26284700	0.18221600	1.43335100
S	-0.41545600	-0.82609700	0.00000000	S	0.85165400	-0.14843200	0.07660300
C	0.42184000	0.83894800	0.00000000	C	-1.00621700	0.00910100	-0.00101100
O	0.08791100	-1.43431200	1.25244000	O	1.24788100	1.09409000	-0.90476300
O	0.08791100	-1.43431200	-1.25244000	O	1.21396000	-1.37515400	-0.60043100
F	0.08791100	1.57086200	1.08645200	F	-1.35809200	1.22096400	0.43290200
F	1.76962500	0.72570400	0.00000000	F	-1.42202300	-0.15929000	-1.25122700
F	0.08791100	1.57086200	-1.08645200	F	-1.54027300	-0.92192900	0.78467500
				H	1.49681500	1.85338200	-0.34199900
2				**2-OTf**			
C	-2.91068200	0.36188400	-0.00002700	C	-5.76847000	-1.31522500	-0.15309500
C	-1.84946300	1.24206900	0.00000500	C	-5.49616500	0.03581200	-0.12695400
C	-0.50273500	0.78220000	0.00003400	C	-4.16198900	0.51461400	-0.07309200

C	-0.22500400	-0.64548900	-0.00004200
C	-1.36722700	-1.50816200	-0.00002400
C	-2.66303800	-1.03720300	-0.00003000
H	0.41949300	2.74848700	-0.00011100
H	-3.93471400	0.73497200	-0.00004500
H	-2.03387300	2.31861400	0.00000100
C	0.59919800	1.67262900	0.00000200
C	1.09318200	-1.20344200	0.00008400
H	-1.15905400	-2.57704200	-0.00002200
H	-3.50302300	-1.73226400	-0.00004800
C	2.08576700	-0.23059900	0.00028600
C	1.88878300	1.17049000	0.00003800
H	2.74650300	1.84573100	-0.00010900
O	3.41448100	-0.66633000	-0.00028900
H	3.25615400	-1.63411300	0.00069100

C	-3.07777600	-0.42684800	-0.04539800
C	-3.39532400	-1.81510700	-0.07313900
C	-4.70191300	-2.24775200	-0.12560000
H	-4.65709600	2.62465300	-0.06456600
H	-6.79646000	-1.66791400	-0.19418900
H	-6.30831600	0.76124000	-0.14718400
C	-3.84432200	1.90029700	-0.04502800
C	-1.74011300	0.03587100	0.00753600
H	-2.57798300	-2.53236300	-0.05108300
H	-4.91928200	-3.31355900	-0.14566800
C	-1.46278900	1.39633900	0.03283500
C	-2.54184300	2.32966200	0.00627400
H	-2.29384400	3.38718900	0.02865200
O	-0.22598600	1.91630300	0.07987400
H	0.46359000	1.19347200	0.09544600
H	-0.91726500	-0.67310800	0.02731500
O	1.48664600	-0.14689200	-0.03119500
S	2.77250200	-0.33401500	0.72194300
C	4.02949900	-0.14572100	-0.64023500
O	3.10003000	0.76374800	1.64918200
O	2.99133000	-1.70895100	1.20327100
F	3.95132900	1.06800400	-1.21869700
F	5.28248400	-0.28839900	-0.16399000
F	3.85481900	-1.06856900	-1.60547900

In(OTf)3

In	0.00000000	0.00000000	0.27356500
O	0.56330800	1.78653200	1.33025800
O	-1.82883600	-0.40542700	1.33025800
O	1.26552800	-1.38110500	1.33025800
S	0.00000000	2.76486000	0.29432900
S	-2.39443900	-1.38243000	0.29432900
S	2.39443900	-1.38243000	0.29432900
C	2.36258200	-3.09765400	-0.45104600
C	-3.86393900	-0.49722900	-0.45104600
C	1.50135600	3.59488400	-0.45104600
O	1.80454400	-0.47367500	-0.79133100
O	3.74165700	-1.11257300	0.74900100
O	-2.83434400	-2.68408300	0.74900100
O	-1.31248700	-1.32594300	-0.79133100
O	-0.90731200	3.79665600	0.74900100
O	-0.49205700	1.79961800	-0.79133100
F	2.33983100	2.66128300	-0.88836300
F	2.08497800	4.33378600	0.48426600
F	1.10132500	4.36003100	-1.45975300
F	-3.47465400	0.69571100	-0.88836300
F	-4.32656000	-1.22624000	-1.45975300
F	-4.79565800	-0.36124900	0.48426600
F	1.13482300	-3.35699400	-0.88836300
F	3.22523500	-3.13379100	-1.45975300
F	2.71067900	-3.97253700	0.48426600

AgOTf

O	-0.13249100	0.48095500	1.22761200
S	0.69671200	0.79738800	0.00002700
C	1.97834700	-0.55155200	0.00003400
O	-0.13249700	0.48056200	-1.22755600
O	1.42014700	2.06283600	-0.00016100
F	1.36614900	-1.74707500	0.00018900
F	2.74334300	-0.45802800	-1.08816300
F	2.74366900	-0.45796500	1.08799000
Ag	-1.99866400	-0.20587400	0.00000100

A

C	3.51300000	-0.61159700	4.12738400
C	2.48178200	-0.14716600	2.11617300
C	2.30037900	1.20394500	2.48539200
C	2.79429800	1.64319400	3.71139100
C	3.39795400	0.71944400	4.55914600
C	1.98536800	-0.63795800	0.83636600
C	2.04699300	-2.37122200	-0.91329400
C	2.69664300	-1.64557500	0.13385000
C	4.07390800	-1.94825300	0.39778300

A′

O	-2.24333900	-1.09795900	0.90884500
S	-3.14154200	0.10385000	0.62354300
C	-3.83988900	-0.36736300	-1.03386300
O	-4.28344600	0.21636300	1.52750200
O	-2.33767100	1.31815300	0.34632400
F	-4.51522500	-1.51792400	-0.95537900
F	-4.66233400	0.58833800	-1.48033500
F	-2.83984200	-0.51862200	-1.92233200
Ag	-0.18735800	-0.57514000	0.54091100

H	4.60854100	-1.37625000	1.14303300
C	4.73316000	-2.92463000	-0.32489700
C	4.04897300	-3.64681300	-1.31607100
C	2.70685300	-3.37293600	-1.60422100
H	3.96363100	-1.36148200	4.77517400
H	2.68583800	2.68343600	4.00218800
H	3.76762300	1.00831600	5.53822600
H	5.78212400	-3.12788200	-0.13301100
H	4.57407400	-4.41551200	-1.87704700
H	2.17739500	-3.92711600	-2.37204800
In	0.07357900	0.24099500	0.00413800
H	1.81870700	1.89767500	1.80904700
H	1.01014600	-2.18324600	-1.15577700
N	3.09815200	-1.03965600	2.94081500
C	-3.36721300	1.20847900	1.87415000
C	0.54461400	3.02743100	-2.96074900
C	-2.85631600	-3.30525100	-0.24674000
O	-1.66016500	1.62404700	-0.17796700
O	-1.06145200	-1.43805400	-0.13370800
O	0.63312400	0.47879500	-2.07881500
S	-1.75369100	1.94979100	1.29916800
S	-1.83451200	-2.14563300	-1.28420100
S	1.47347300	1.75151200	-1.96338600
O	-0.93120300	-2.99434300	-2.06713300
O	-2.76100200	-1.24985800	-1.96634800
O	1.30477300	2.15241200	-0.51314800
O	2.82360200	1.69414700	-2.49940900
O	-0.67662700	1.04719700	1.90657500
O	-1.75669800	3.34348400	1.70599300
F	-3.66378500	-2.61859200	0.56401200
F	-3.59280900	-4.06716300	-1.05903400
F	-2.06045200	-4.08865900	0.48750500
F	0.60152800	2.68563800	-4.24571600
F	-0.71857500	3.08807600	-2.56194500
F	1.13515800	4.20876200	-2.78153700
F	-4.36926300	1.83569300	1.26608600
F	-3.46403500	1.37381900	3.19316900
F	-3.39688000	-0.08745800	1.58125200

C	4.76415800	-1.65104600	-1.12631500
C	2.82914400	-0.96889900	-0.06873500
C	2.71239400	-2.22070800	0.57385700
C	3.70033700	-3.18373800	0.38669400
C	4.74369500	-2.90192800	-0.49184500
H	5.55249000	-1.41130400	-1.83787900
H	1.85609000	-2.41442700	1.21161400
H	3.63866700	-4.14274700	0.89236200
H	5.52016100	-3.63172500	-0.69974700
C	2.07692600	1.43494100	0.04177300
C	3.39666000	1.98215400	0.07705300
C	3.59813400	3.34974400	-0.00555400
C	2.50254800	4.21402200	-0.14593400
C	1.19670300	3.71154700	-0.17628300
C	0.98110300	2.34654100	-0.05786400
H	4.24239000	1.31793100	0.18766900
H	4.60492300	3.75409300	0.04022300
H	2.66944300	5.28588900	-0.21465300
H	0.35124500	4.38559100	-0.27053100
H	-0.03638900	1.96362900	-0.05324600
C	1.79115700	0.03772800	0.14308500
N	3.86076200	-0.69907300	-0.91295500

TS1

C	4.22191500	-3.42469500	-1.22759100
C	2.53296600	-1.85784400	-1.35225300
C	1.64066300	-2.82545100	-1.84750600
C	2.09029100	-4.13041000	-2.05278800
C	3.40493600	-4.44657900	-1.72989200
C	2.03580500	-0.46257700	-1.25262500
C	2.33493600	1.70319800	-2.36392400
C	2.92330600	0.64349300	-1.63422600
C	4.32127400	0.69680200	-1.40399500
H	4.78627500	-0.10325800	-0.84506800
C	5.07937600	1.75895000	-1.88438500
C	4.47670000	2.78789100	-2.61719300
C	3.10324600	2.75372800	-2.86121500
H	5.25725800	-3.63509500	-0.95802600
H	1.40847900	-4.87902100	-2.44670000
H	3.79967200	-5.45071500	-1.85897700
H	6.14780000	1.78867500	-1.68429900
H	5.07684300	3.61477200	-2.99019000
H	2.61764400	3.54768900	-3.42082400
In	0.10572900	0.00920800	-0.26987000
H	0.61630200	-2.56508900	-2.08514800
H	1.27007600	1.69505600	-2.56480400
N	3.81768200	-2.17076200	-1.05471600

B

C	3.42748600	-2.95599100	2.36711200
C	2.28661900	-1.22912400	1.34428000
C	1.78499200	-0.80475900	2.59027300
C	2.13060100	-1.50295400	3.74056800
C	2.97075000	-2.61333100	3.63566600
C	1.95966800	-0.43129700	0.07425500
C	2.42612200	-0.38439600	-2.43171200
C	2.16171100	-1.13487800	-1.27015100
C	1.94505000	-2.51671900	-1.42925500
H	1.71715800	-3.12968300	-0.56718300
C	2.01201800	-3.11613000	-2.68606600
C	2.29498600	-2.35977800	-3.82409800
C	2.49518400	-0.98683700	-3.68786200
H	4.08888900	-3.81150100	2.22973000
H	1.73513500	-1.18697600	4.70225000
H	3.25821300	-3.19681800	4.50567800
H	1.82190600	-4.18289600	-2.76941200
H	2.33815800	-2.82965100	-4.80345300
H	2.69358800	-0.37125100	-4.56168000
In	-0.22934900	-0.04531800	-0.03373600
H	1.12566100	0.05474500	2.66828700
H	2.57173100	0.68889800	-2.35697200
N	3.10844200	-2.28536400	1.25328100

C	-3.61775500	-0.27685800	2.64482200
C	-2.43149900	3.13729900	-0.34541800
C	-3.56061700	-1.79626100	-1.40393400
O	-1.49413000	-0.00700800	1.15783200
O	-1.33826100	-0.43770600	-1.70033400
O	-0.71230400	3.15715000	-2.38273400
S	-1.78076900	-0.55346400	2.54562700
S	-2.13340500	-1.43525600	-2.53772100
S	-0.66637600	3.28649000	-0.92202600
O	-1.44523000	-2.72739100	-2.68311400
O	-2.71393000	-0.81480600	-3.72532700
O	-0.01903900	2.07024600	-0.24640400
O	-0.17095500	4.53242900	-0.33743100
O	-1.60704500	-2.02998400	2.59457300
O	-1.21048400	0.22492400	3.64246400
F	-4.19530900	-0.67349600	-1.05942600
F	-4.43079100	-2.60806800	-2.02555200
F	-3.12411500	-2.41284200	-0.29749600
F	-2.98074200	2.00218100	-0.78361600
F	-2.49254600	3.16469700	0.98951800
F	-3.13889200	4.17134400	-0.82874500
F	-4.04180700	-0.63345600	3.86723400
F	-4.27305400	-1.00456800	1.73835600
F	-3.89592200	1.01463700	2.45230000
C	4.29854100	2.18162000	2.36198300
C	3.29802100	1.57958800	1.62631300
C	2.89192200	0.24684100	1.90168500
C	3.52307600	-0.44768000	2.99147300
C	4.55320300	0.19840300	3.72346900
C	4.94038900	1.48419800	3.41182500
H	4.58698400	3.20606200	2.14121800
H	2.78514700	2.12689400	0.84278300
C	1.85489700	-0.40196600	1.16963800
C	3.07154700	-1.75393400	3.33148800
H	5.02152100	-0.33424900	4.54919000
H	5.72589000	1.97179100	3.98415000
C	2.03972900	-2.35923800	2.64943700
C	1.45713100	-1.66632000	1.56559900
H	3.54687800	-2.26810900	4.16422700
H	1.67263600	-3.34220400	2.93058200
O	0.41867200	-2.22724600	0.82560700
H	-0.33886100	-2.43528600	1.43551700

C	-3.28421900	1.50168300	-2.38530100
C	-3.18938100	-3.03710600	0.36187000
C	-2.70861500	2.57277900	2.08274100
O	-0.87588700	1.38782600	-1.36744500
O	-1.65811300	0.27596000	1.41900800
O	-0.62049800	-2.89959500	1.11880700
S	-1.46821600	1.61121600	-2.77430800
S	-1.95501300	0.99941900	2.73507400
S	-1.39548800	-2.96439900	-0.13224000
O	-0.74327800	1.42295700	3.44515400
O	-3.02845700	0.35036500	3.48038200
O	-1.33576500	-1.59938100	-0.84755600
O	-1.20916700	-4.09528600	-1.03690700
O	-1.24613900	2.99451400	-3.19656100
O	-1.18284300	0.51715800	-3.69860100
F	-3.78183200	2.31778700	1.33529100
F	-3.06626100	3.36094400	3.10422100
F	-1.81953900	3.25731300	1.32561800
F	-3.50663600	-2.03852700	1.18249800
F	-3.96745100	-2.97632300	-0.72510300
F	-3.41660800	-4.20274800	0.98724300
F	-3.99297300	1.69684600	-3.50693600
F	-3.62703900	2.44244800	-1.49455600
F	-3.59254200	0.30273000	-1.88517200
C	6.31669900	0.05023500	-0.44278700
C	4.95763800	-0.09421400	-0.26235500
C	4.12384000	1.03290800	-0.01090000
C	4.75333200	2.32300400	0.05672000
C	6.15553300	2.43554200	-0.14176300
C	6.92758700	1.32430300	-0.38952100
H	6.92582200	-0.83091900	-0.62804200
H	4.51726100	-1.08273100	-0.29151000
C	2.69652400	0.91617200	0.17128000
C	3.96578000	3.47180800	0.33114700
H	6.60696000	3.42428100	-0.08962000
H	8.00010900	1.42168100	-0.53865400
C	2.61862100	3.35387700	0.55120500
C	2.01026300	2.08025700	0.47391200
H	4.44733900	4.44536500	0.37960800
H	2.00831700	4.22066600	0.79190000
O	0.65861400	1.97755800	0.76071600
H	0.15972300	2.77395000	0.51329000

C			
C	1.38561500	3.59184600	-0.24825300
C	0.58858200	1.50666400	0.30853500
C	-0.28708900	2.05147500	1.26866100
C	-0.29654200	3.43054400	1.46245600
C	0.54811900	4.22089100	0.68528800
C	0.66688400	0.04843100	0.11494800
C	1.95023800	-1.75362700	-0.98367700
C	1.92800200	-0.55213800	-0.22208500
C	3.16693700	0.04156100	0.14385500
H	3.17337900	0.93576500	0.75335900
C	4.36515600	-0.54931300	-0.22657700
C	4.36122800	-1.72424600	-0.98863900
C	3.15137100	-2.32181500	-1.37121600
H	2.05200100	4.18010400	-0.87528200
H	-0.94930300	3.87703600	2.20618100
H	0.56661400	5.30072000	0.79335300
H	5.30602500	-0.10112400	0.07620800
H	5.30289500	-2.17492500	-1.28883500
H	3.15695100	-3.22145200	-1.97840000

TS2			
C	-2.86476500	2.52768000	-0.20320600
C	-0.96953400	1.15634900	-0.44265900
C	-0.25209800	2.20757400	-1.03861000
C	-0.86716200	3.44557100	-1.17504300
C	-2.19061500	3.61758700	-0.74433000
C	-0.52071000	-0.22840900	-0.28916200
C	-1.44634500	-2.27155900	0.78714900
C	-1.59006300	-1.06677900	0.02341600
C	-2.92738800	-0.49339600	-0.15000900
H	-3.20792300	-0.18509300	-1.15573200
C	-3.99403400	-0.98574100	0.66759500
C	-3.77822600	-2.08637600	1.45623300
C	-2.50881600	-2.75194900	1.50119000
H	-3.89223400	2.59383200	0.14320000
H	-0.33012900	4.27264000	-1.62889600
H	-2.68383400	4.58154000	-0.80940700
H	-4.98906300	-0.56568500	0.56151400
H	-4.60587200	-2.50506400	2.02240600
H	-2.39021900	-3.62143800	2.13941500

H	-0.92076000	1.40194900	1.86171700	H	0.75045900	2.02815000	-1.40913000
H	1.01162000	-2.19297300	-1.30439100	H	-0.45976200	-2.71125100	0.88337300
N	1.42101400	2.27435300	-0.43211800	N	-2.24356100	1.35641500	-0.02297400
C	-3.14502900	0.93755100	-1.86532600	C	2.74378300	1.53273300	2.04927900
C	-1.91693900	0.62677900	-1.30655600	C	1.69872600	0.94428300	1.36381000
C	-1.80197000	-0.37010100	-0.30896900	C	1.93988100	0.01363400	0.32019000
C	-2.98433600	-1.09424900	0.04462900	C	3.30042200	-0.33689000	0.03970800
C	-4.23008000	-0.75336400	-0.53933300	C	4.35282000	0.28775600	0.75714500
C	-4.31540900	0.25702500	-1.47412400	C	4.08425000	1.21507400	1.73998100
H	-3.20174900	1.70933800	-2.62725000	H	2.52992800	2.23866800	2.84663100
H	-1.03336400	1.14533800	-1.66082200	H	0.67955300	1.17980700	1.65124800
C	-0.52549500	-0.75032400	0.28431200	C	0.87786300	-0.63150300	-0.41826600
C	-2.88215100	-2.18429900	0.94952000	C	3.56893200	-1.33317800	-0.93682300
H	-5.11338700	-1.31663300	-0.25102800	H	5.37753300	0.00985000	0.52522000
H	-5.26987900	0.51213200	-1.92325800	H	4.89433200	1.68545900	2.28830700
C	-1.67380000	-2.58160800	1.46848200	C	2.55425200	-1.97973400	-1.59780300
C	-0.48831200	-1.89299400	1.12911100	C	1.20504300	-1.64457700	-1.33374200
H	-3.78529000	-2.72357500	1.22272800	H	4.60224400	-1.59339100	-1.14977700
H	-1.62002700	-3.42108400	2.15743600	H	2.77748200	-2.74734000	-2.33518000
O	0.68055400	-2.24451200	1.69957300	O	0.19836500	-2.26114900	-2.00365100
H	0.54287100	-2.98311000	2.31627500	H	0.56821700	-2.89530500	-2.63939800

D				**TS3**			
C	-3.81541800	-0.83943600	0.73010500	C	-1.45889700	-1.42140600	1.90652400
C	-1.46464900	-0.98847900	0.27972800	C	0.69409500	-1.23530000	0.84192600
C	-1.41266200	-2.23772100	0.91117200	C	0.97057100	-2.57859900	1.17083700
C	-2.57247900	-2.76226600	1.46082500	C	0.04106600	-3.30615500	1.88162100
C	-3.79005900	-2.05812500	1.37493700	C	-1.19482000	-2.72342900	2.25298400
C	-0.42897800	-0.18047400	-0.33643000	C	1.43878600	-0.25965900	0.11915500
C	-0.48190200	2.20283200	-1.28461800	C	0.94191500	2.22038100	-0.36259200
C	-1.02488900	0.97379700	-0.77635200	C	0.65981900	0.89331600	0.07630600
C	-2.51636800	0.90379600	-0.57663000	C	-0.65558900	0.62915300	0.68355000
H	-2.96752400	0.66703800	-1.55868300	H	-1.43794600	0.37952700	-0.22600900
C	-3.14009800	2.19309500	-0.11773600	C	-1.34385700	1.75622900	1.33181700
C	-2.52354100	3.33501800	-0.48229000	C	-0.98606800	3.00991300	0.95088800
C	-1.22303700	3.33678100	-1.14721300	C	0.13106300	3.23635700	0.06909100
H	-4.71114300	-0.24109500	0.61242700	H	-2.39944600	-0.92507200	2.10317200
H	-2.54483200	-3.72521900	1.96112900	H	0.24663300	-4.33954300	2.14366600
H	-4.70203000	-2.45452600	1.80512100	H	-1.94420800	-3.29200900	2.79063000
H	-4.12077400	2.18978700	0.34833000	H	-2.23088600	1.57924900	1.92990100
H	-2.99304100	4.29176700	-0.27396100	H	-1.56122900	3.86270400	1.29627600
H	-0.81657200	4.28999600	-1.47104600	H	0.35380800	4.25797200	-0.22616400
H	-0.46674100	-2.76275300	0.95778900	H	1.91016500	-3.00886600	0.84574400
H	0.53545500	2.22894700	-1.65985100	H	1.83350200	2.41965500	-0.94783100
N	-2.67116300	-0.33810700	0.21306000	N	-0.51320400	-0.69688400	1.25371700
C	2.80837000	1.87730300	1.78021000	C	5.05372000	1.70478700	1.56868400
C	1.77633700	1.22566200	1.13896600	C	3.91360400	1.06776200	1.12980900
C	2.03117400	0.13324500	0.26566500	C	3.94458300	0.19721400	0.00420400
C	3.39257600	-0.28409400	0.08867400	C	5.20528100	-0.00933100	-0.65021100
C	4.43177000	0.41319300	0.75995300	C	6.36032900	0.66703000	-0.17475500
C	4.15080000	1.47616900	1.58752700	C	6.29143400	1.51049100	0.91034800
H	2.58739900	2.70686000	2.44592300	H	5.00272700	2.36213600	2.43259400
H	0.75376900	1.54433500	1.31191700	H	2.97410500	1.22209200	1.64939800
C	0.99206500	-0.58101700	-0.42232000	C	2.77620000	-0.47941400	-0.47987100
C	3.67234200	-1.39606800	-0.74845900	C	5.26816000	-0.89515400	-1.75694900
H	5.45744800	0.08618800	0.61033600	H	7.30561300	0.50163100	-0.68648800
H	4.95187100	2.00197300	2.09773400	H	7.18118700	2.02200700	1.26614200
C	2.66621400	-2.08326000	-1.38212400	C	4.14818800	-1.55585900	-2.19795100
C	1.32181400	-1.67505100	-1.21580300	C	2.90042300	-1.34920400	-1.55857300
H	4.70525400	-1.70606200	-0.88118700	H	6.22225100	-1.05051800	-2.25419400
H	2.89335000	-2.93532200	-2.01908800	H	4.20623300	-2.23706300	-3.04486500
O	0.29754100	-2.33486300	-1.83909100	O	1.77757800	-1.99919100	-1.98424500
H	0.65963900	-3.04566000	-2.39230100	H	1.97904600	-2.50331100	-2.78792200

O	-2.47079300	-0.28664300	-1.05321600
S	-3.74711300	0.51149100	-1.29943300
C	-4.83917700	-0.14986000	0.05466200
O	-3.60182400	1.93490500	-0.96290900
O	-4.42541600	0.13667800	-2.53936500
F	-4.28438600	0.10896700	1.27551800
F	-6.04044700	0.43081100	0.03077700
F	-4.99701800	-1.47509200	-0.03743900

3

C	3.81686000	-0.82848000	-0.81277700
C	1.42937100	-0.99522600	-0.32658600
C	1.45891700	-2.33690800	-0.79970100
C	2.62643300	-2.88445000	-1.25707900
C	3.83360900	-2.11361700	-1.26328500
C	0.41979900	-0.17576700	0.17292200
C	0.54536000	2.29470200	1.01782600
C	1.03206800	1.08660400	0.47360000
C	2.41263300	1.00594700	0.13924100
C	3.29720600	2.07530400	0.31899600
C	2.78514200	3.25169000	0.84981600
C	1.41890200	3.35545800	1.19723700
H	4.69001900	-0.18766100	-0.79091300
H	2.64518200	-3.90813500	-1.61855100
H	4.76365400	-2.53884900	-1.62320600
H	4.34873300	1.99594100	0.05733900
H	3.44373200	4.10194700	1.00205200
H	1.04927400	4.28812000	1.61528700
H	0.53355300	-2.90143800	-0.78457700
H	-0.50194900	2.38541000	1.28952700
N	2.64747700	-0.27261000	-0.35200300
C	-2.87805200	1.74083600	-1.91299900
C	-1.83325700	1.11204300	-1.27187800
C	-2.06660300	0.10575400	-0.29189500
C	-3.42899400	-0.25057500	-0.01197700
C	-4.48331000	0.42092300	-0.68740600
C	-4.21981100	1.40060400	-1.61685000
H	-2.66946100	2.50377500	-2.65858500
H	-0.81021300	1.37654100	-1.51410500
C	-0.99129000	-0.55937300	0.39128700
C	-3.68971100	-1.27936400	0.92849700
H	-5.50860200	0.13992000	-0.45640100
H	-5.03417100	1.90676600	-2.12800200
C	-2.65719100	-1.92865300	1.55914100
C	-1.31213000	-1.56891700	1.29508900
H	-4.71985000	-1.55357000	1.14219800
H	-2.86355400	-2.71964600	2.27894600
O	-0.29030200	-2.21262700	1.94261200
H	-0.67198000	-2.85103200	2.56479800

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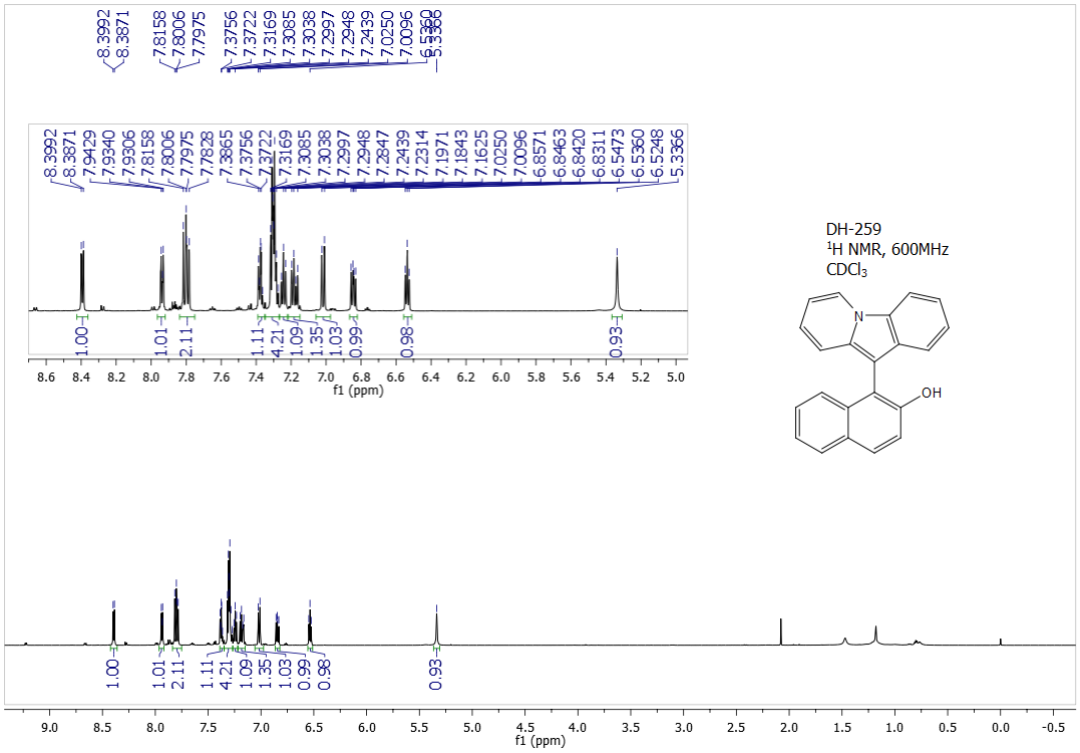
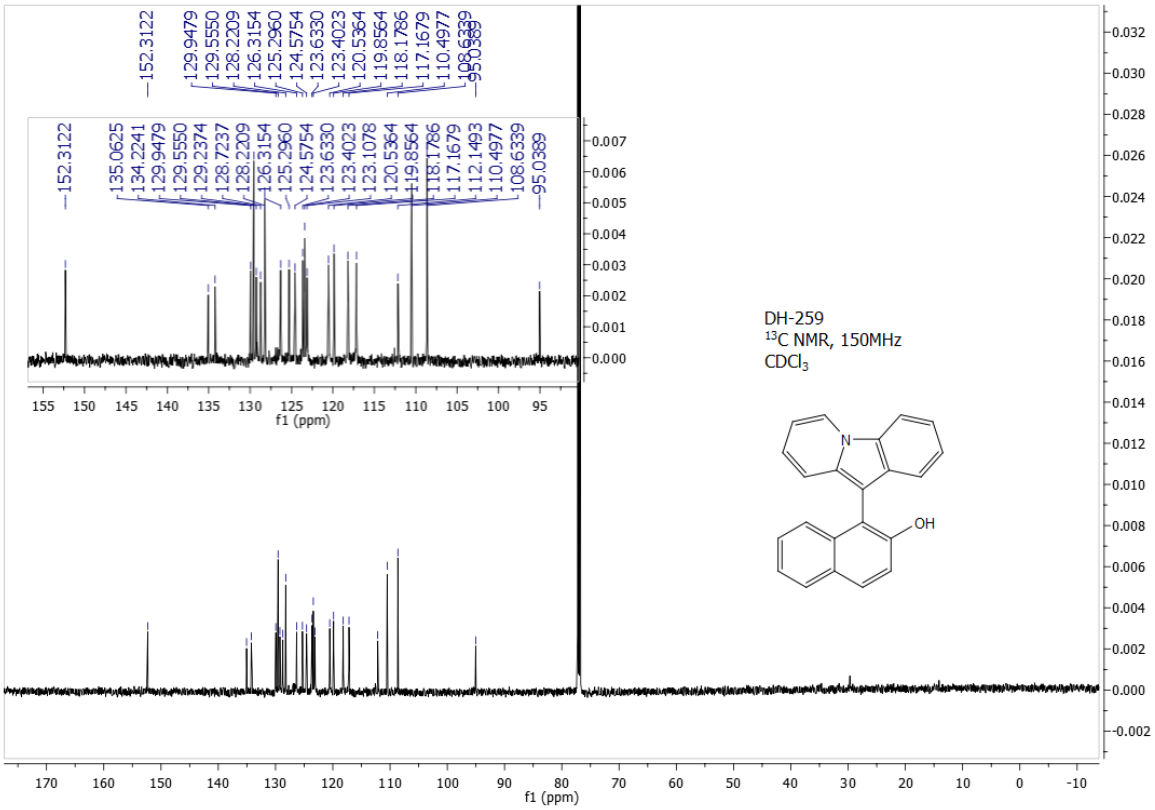
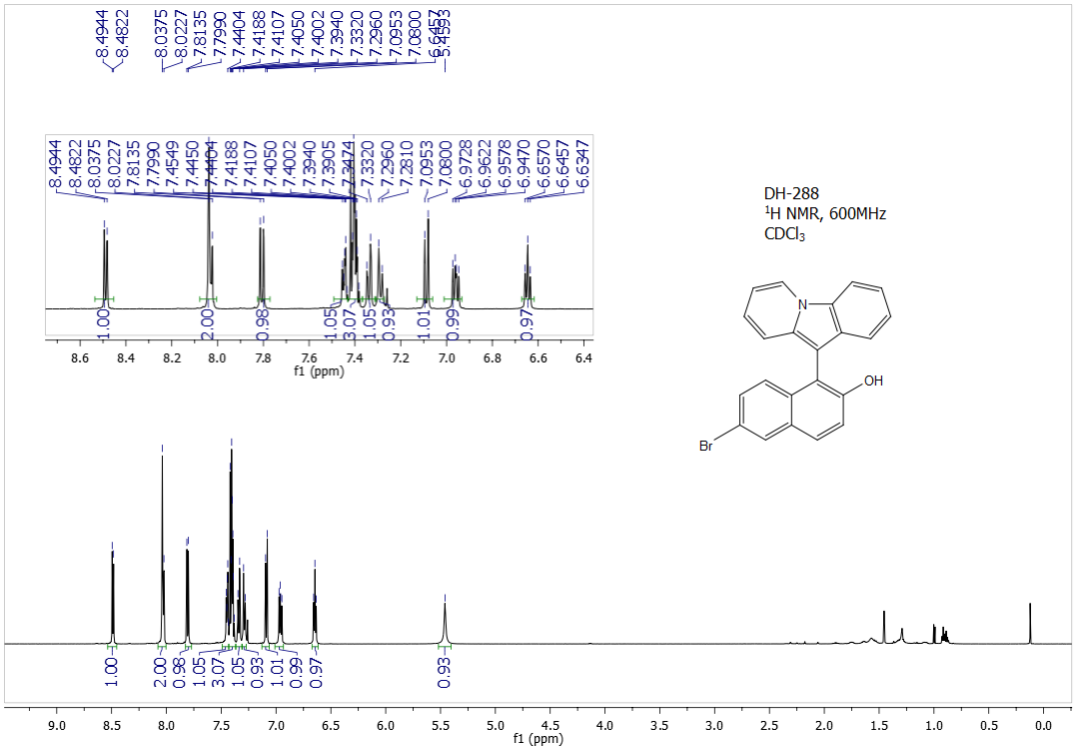
5. ^{1}H &^{13}C- NMR Spectra

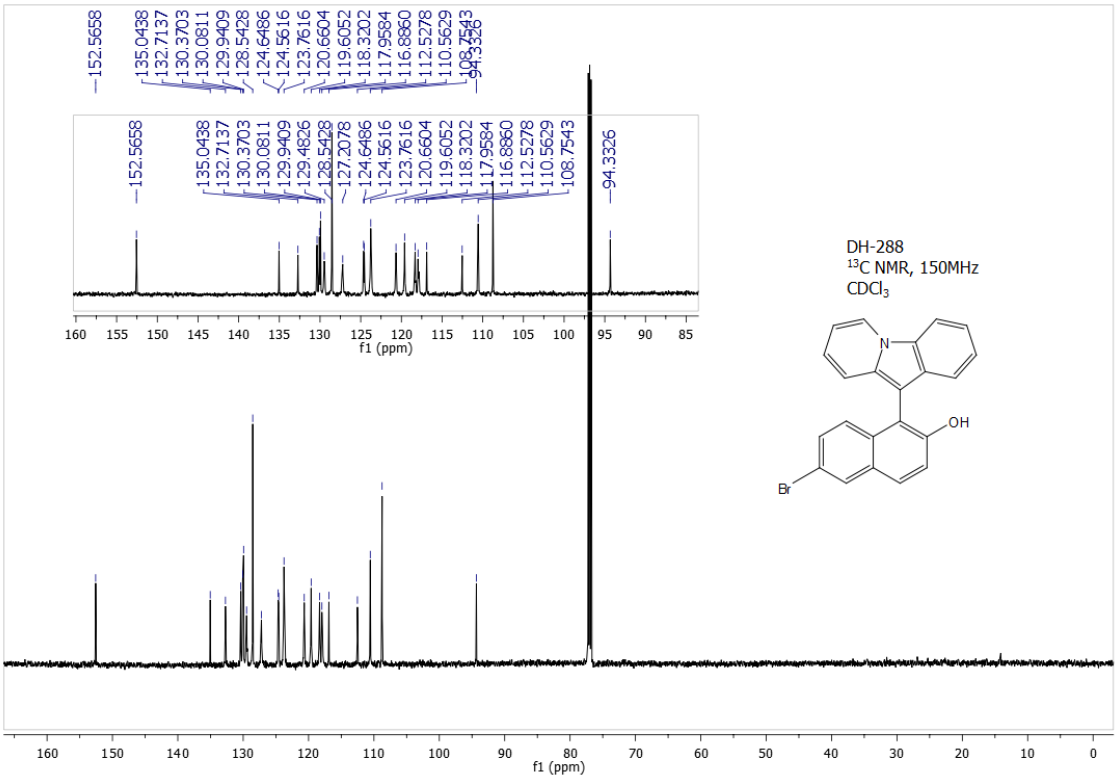
1-(pyrido[1,2-a]indol-10-yl)naphthalene-2-ol (3a) :



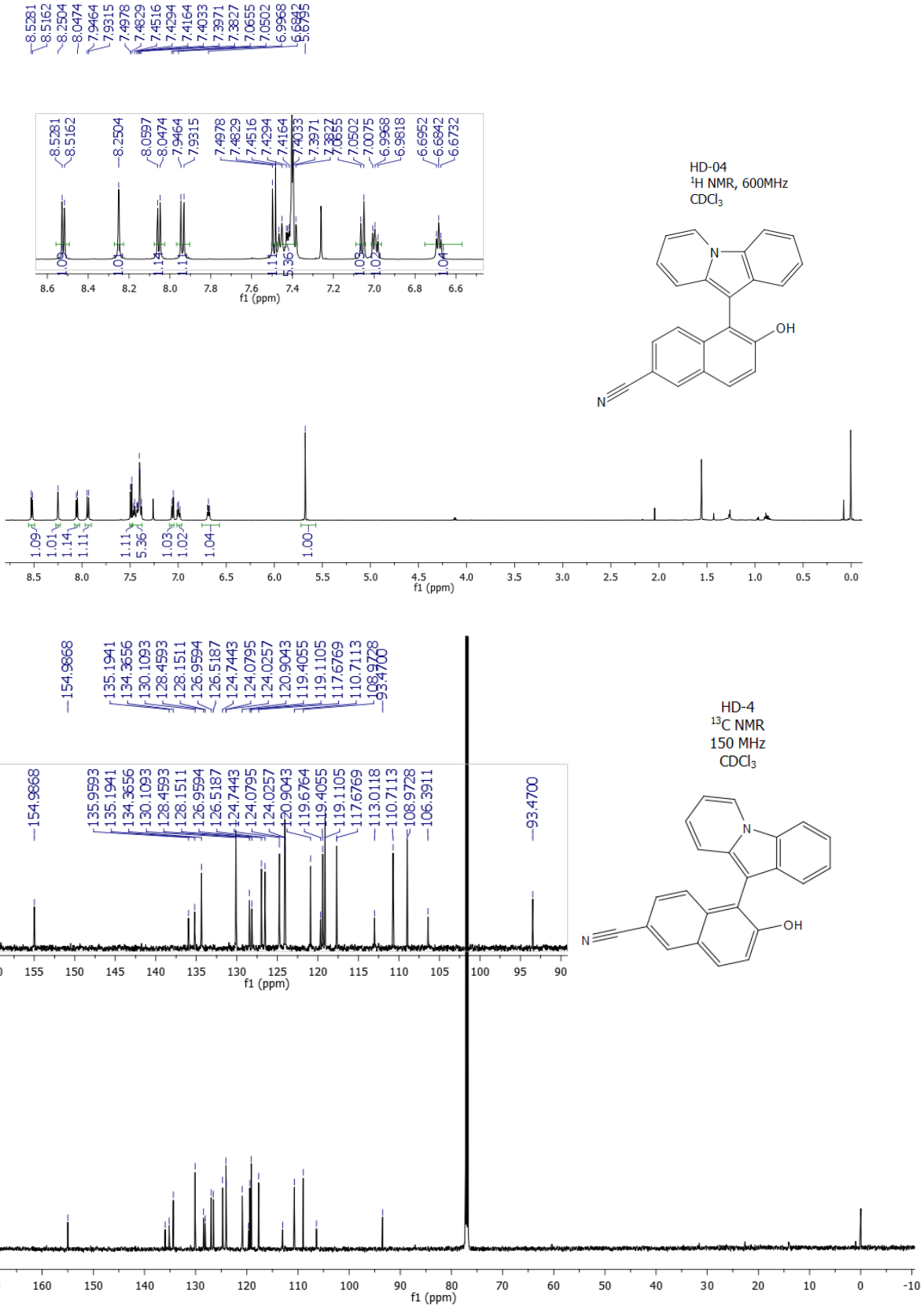


6- bromo1-(pyrido[1,2-a]indol-10-yl)naphthalene-2-ol (3b) :

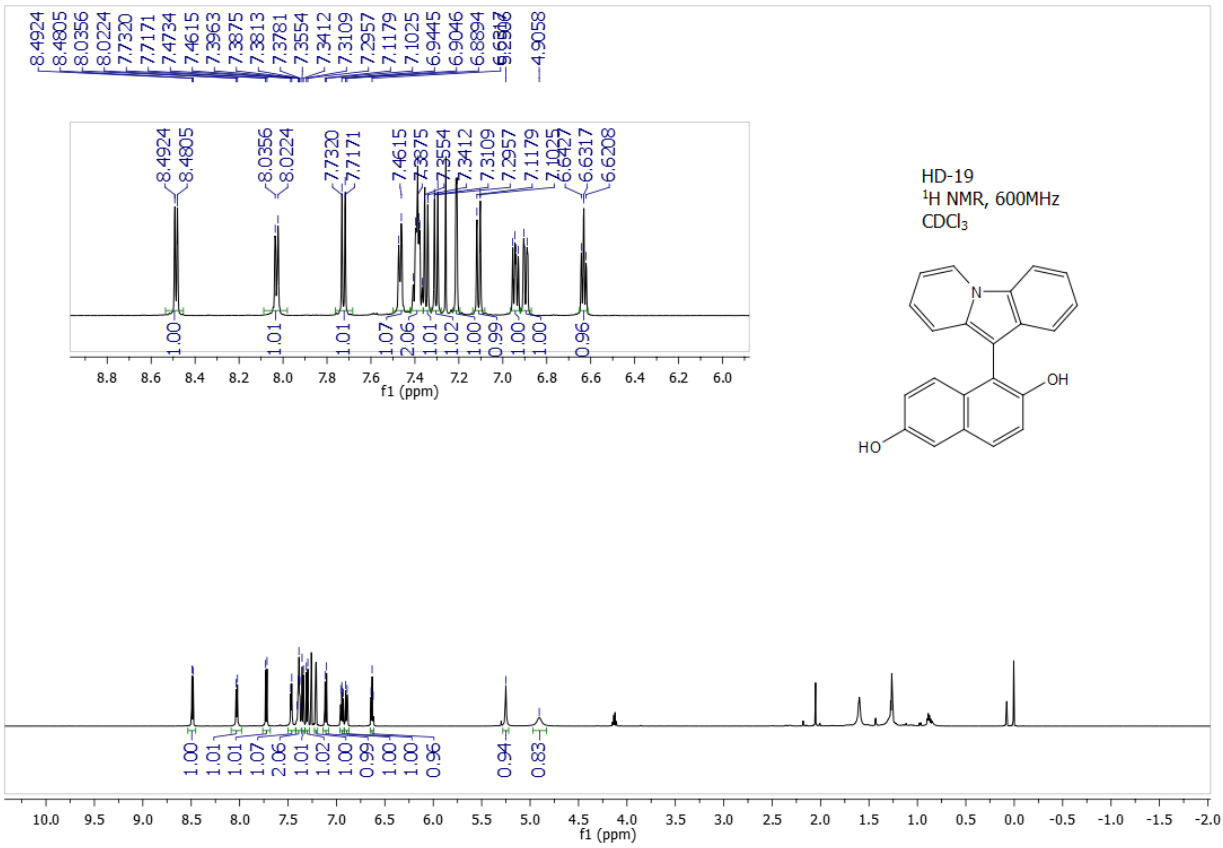


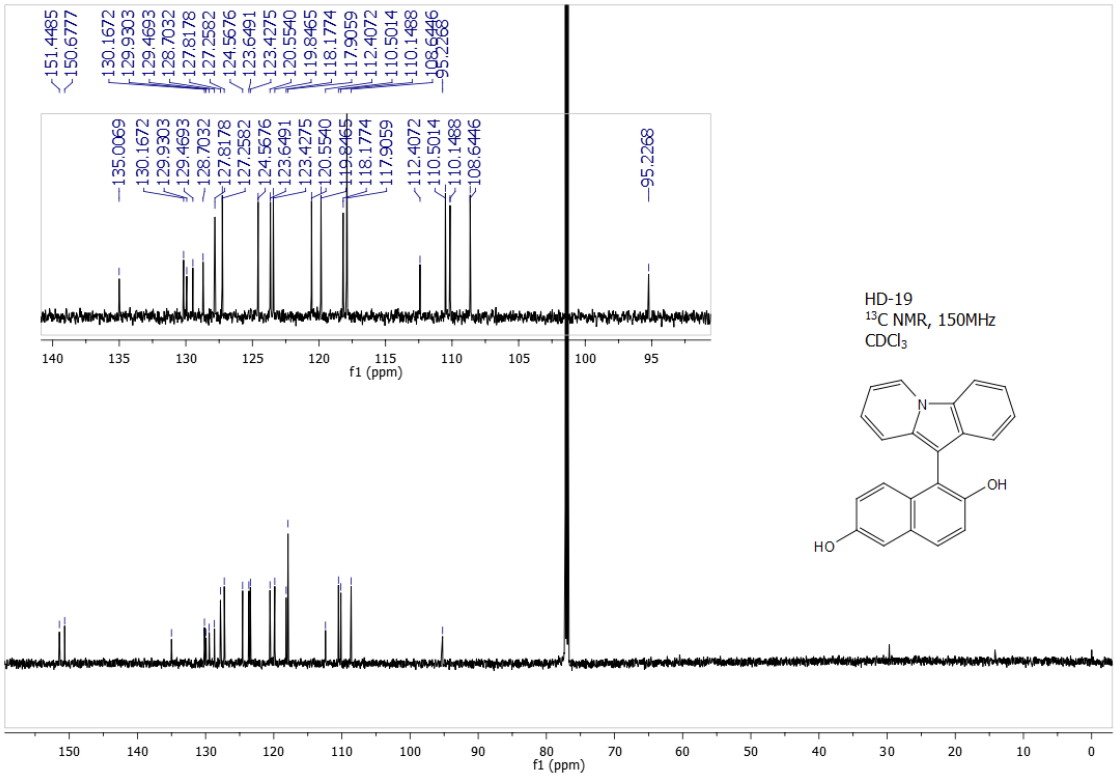


6-hydroxy-5(pyrido[1,2-a]indol-10-yl)-2-naphthonitrile (3c)



1-(pyrido[1,2-a]indol-10-yl)naphthalene-2,6-diol (3d) :





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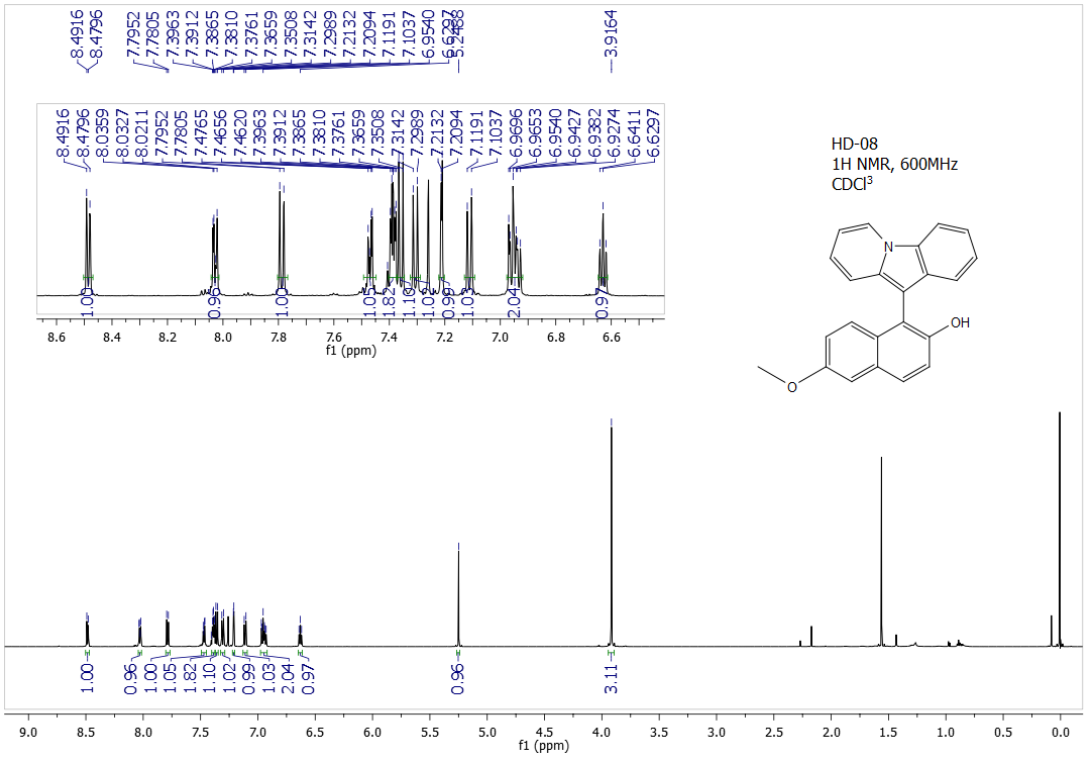
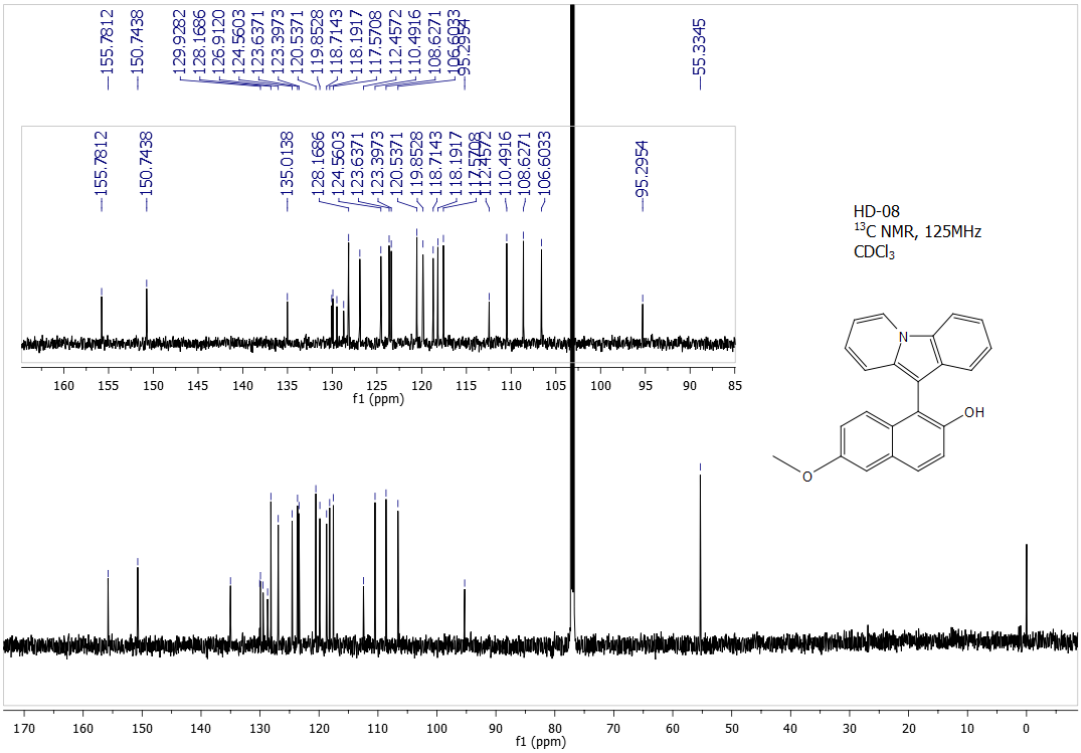
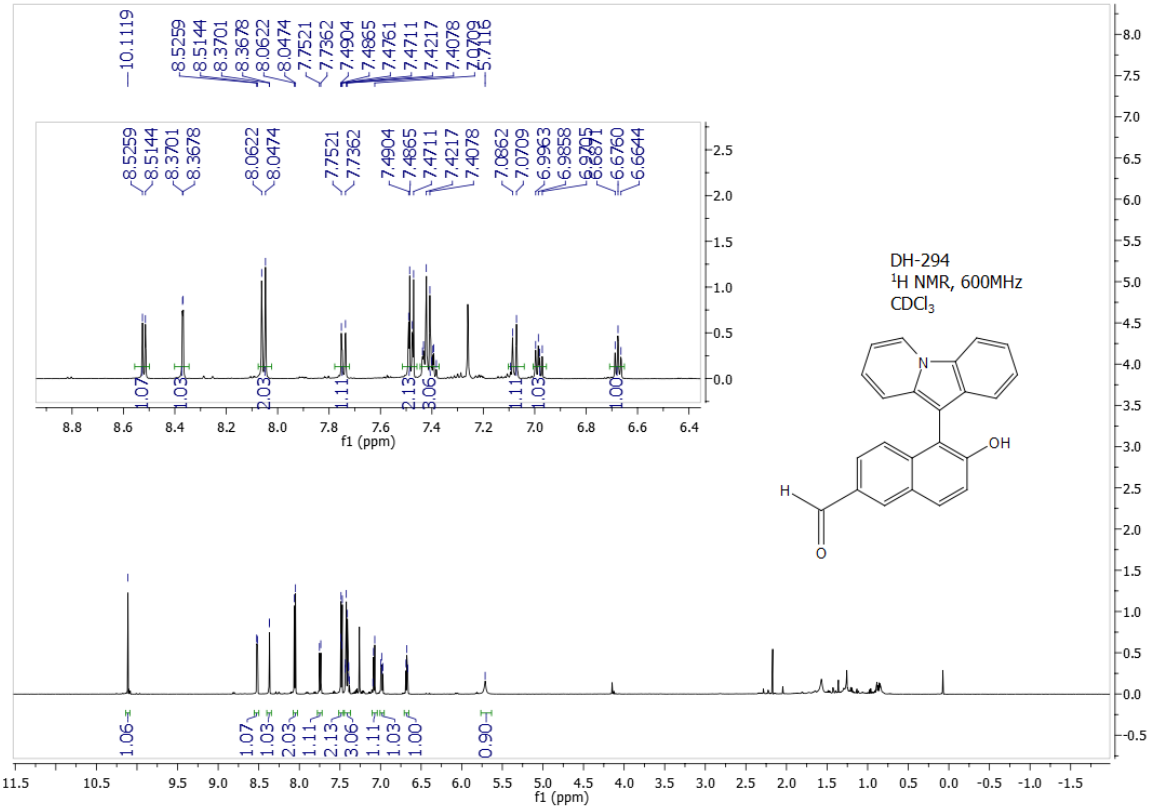
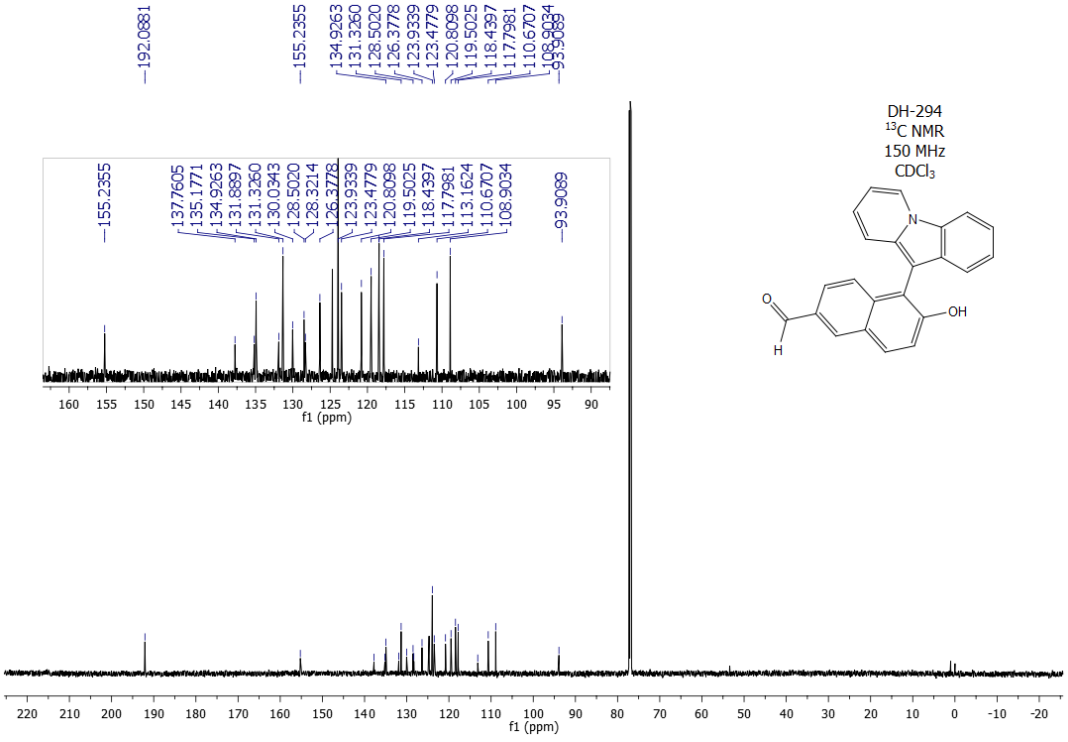


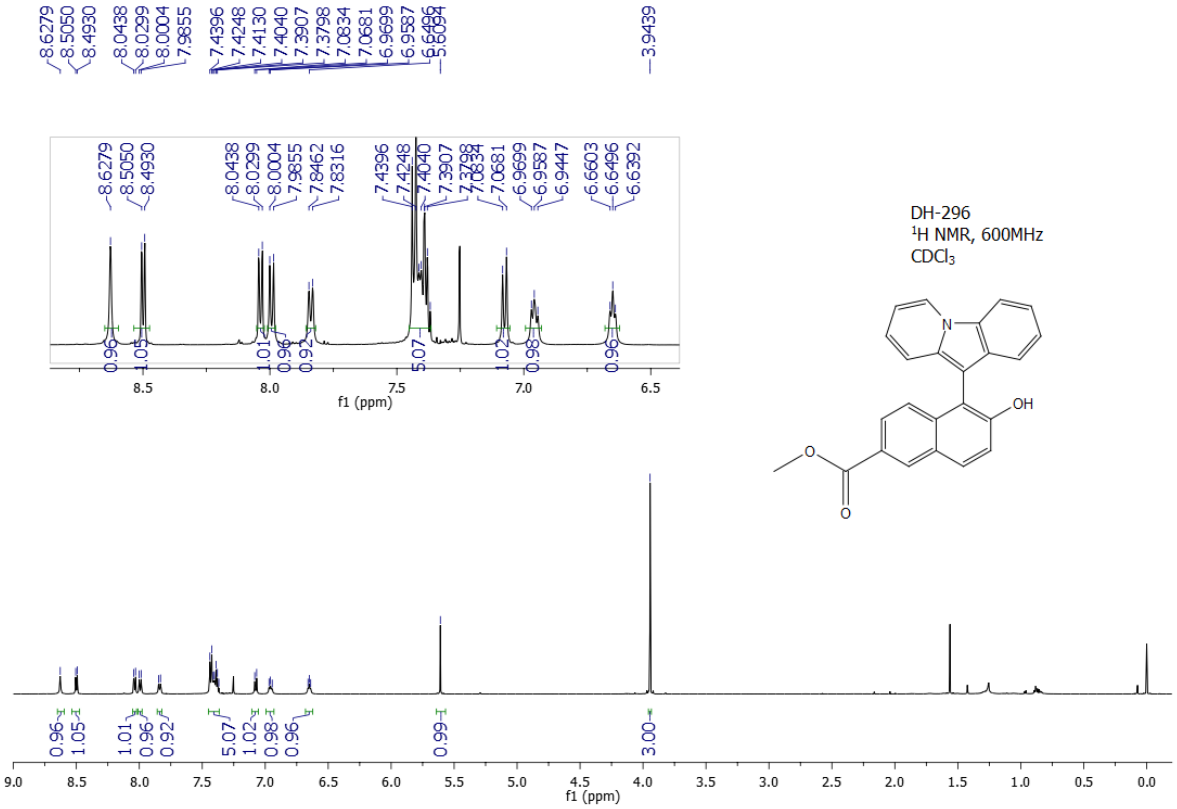


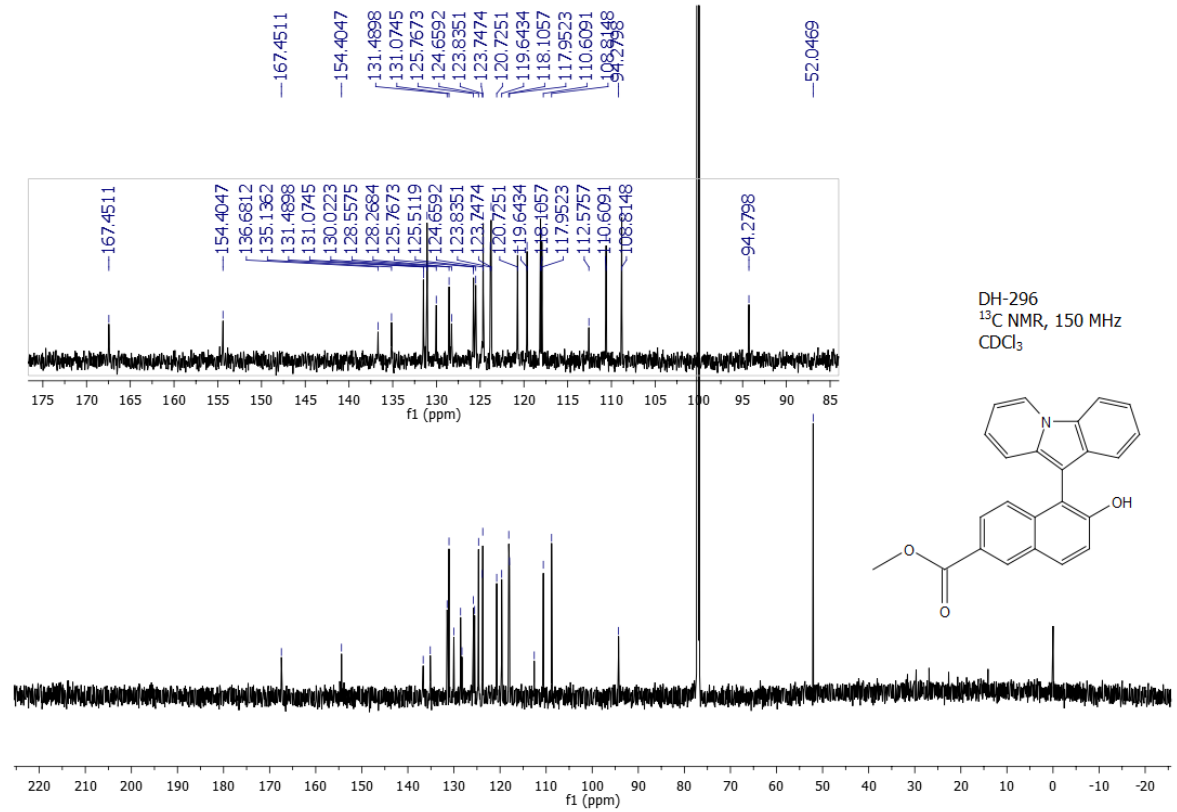
6- hydroxy 5-(pyrido[1,2-a]indol-10-yl)-2-naphthaldehyde (3f) :



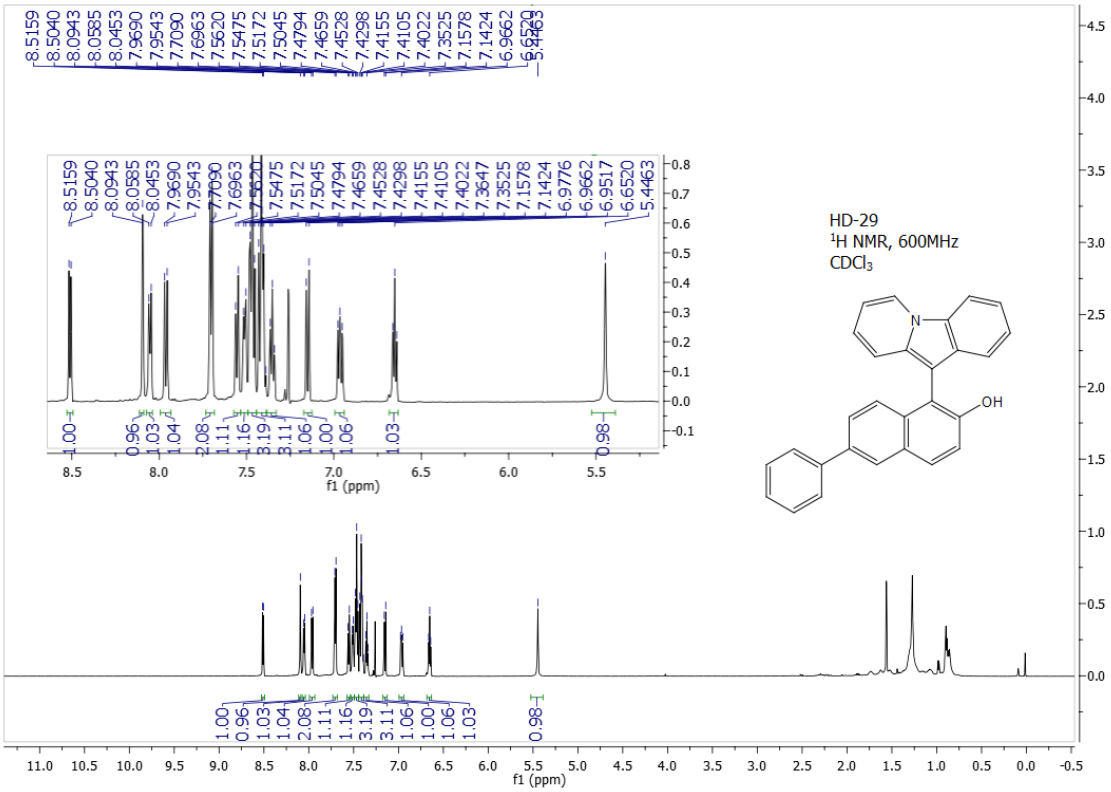


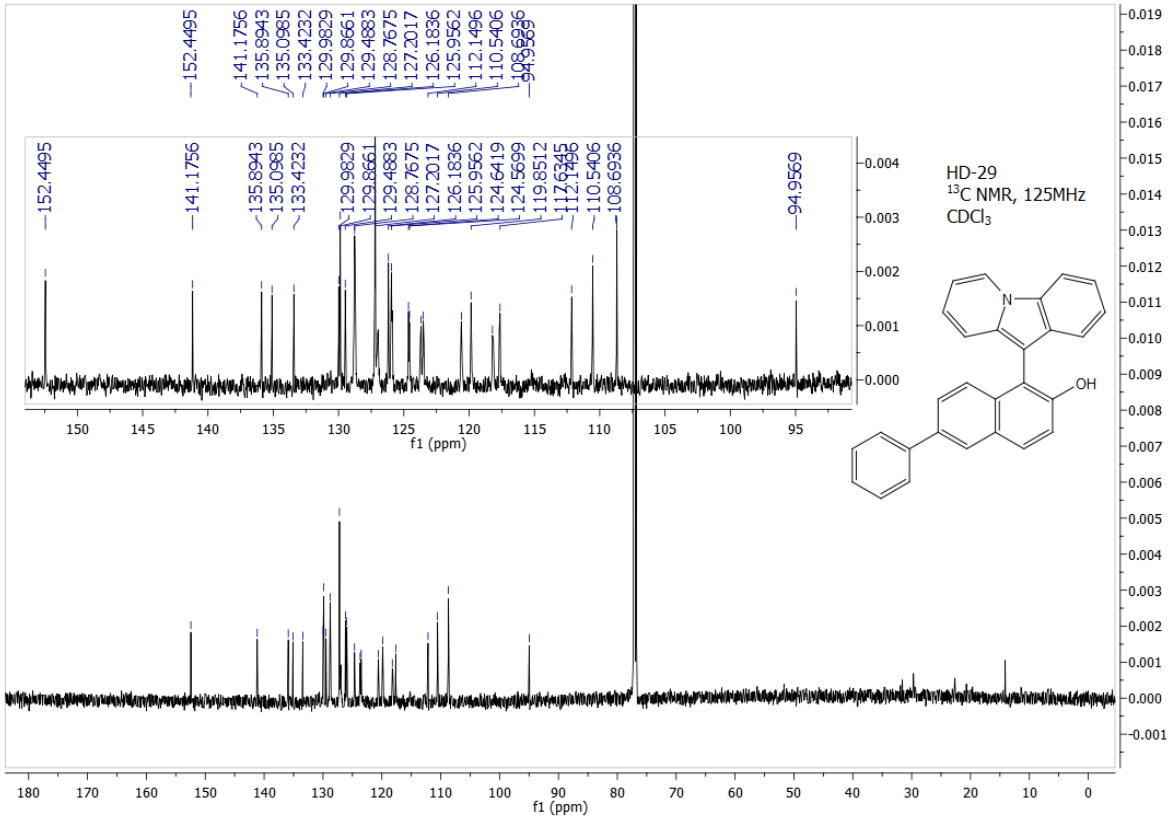
Methyl 6- hydroxy 5-(pyrido[-10-yl)-2-naphthoate (3g):



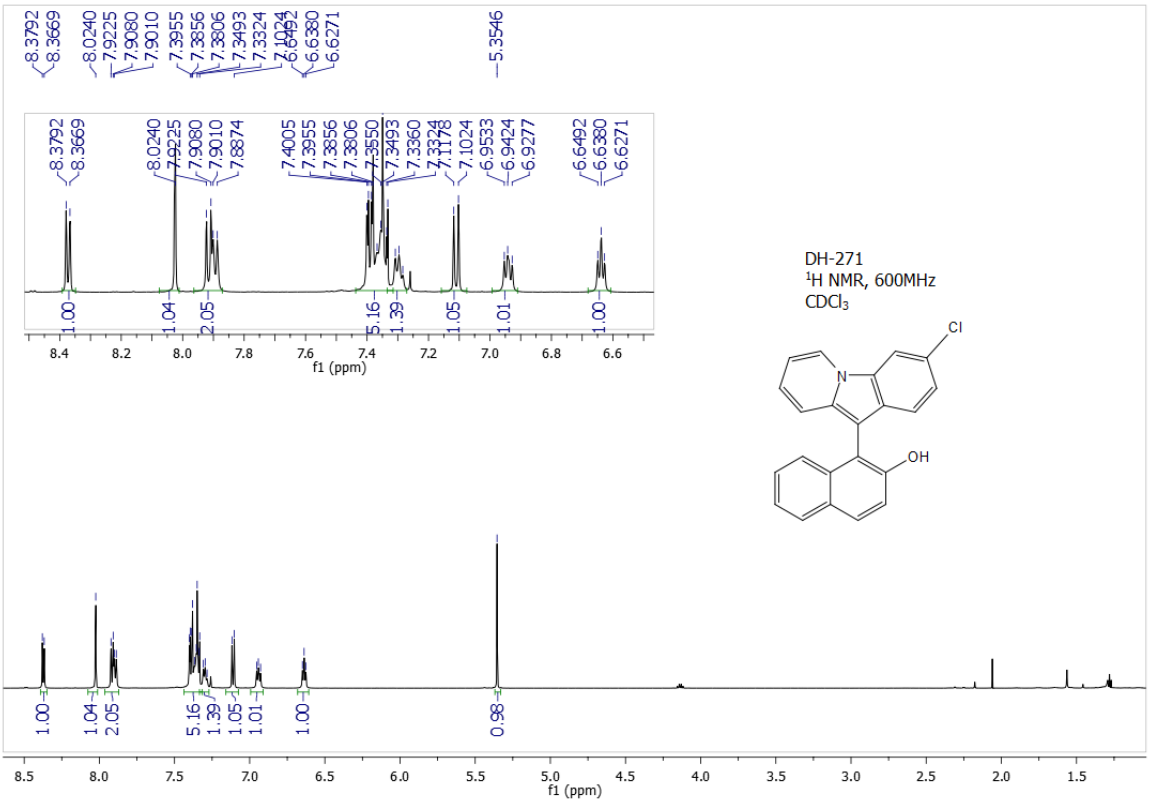


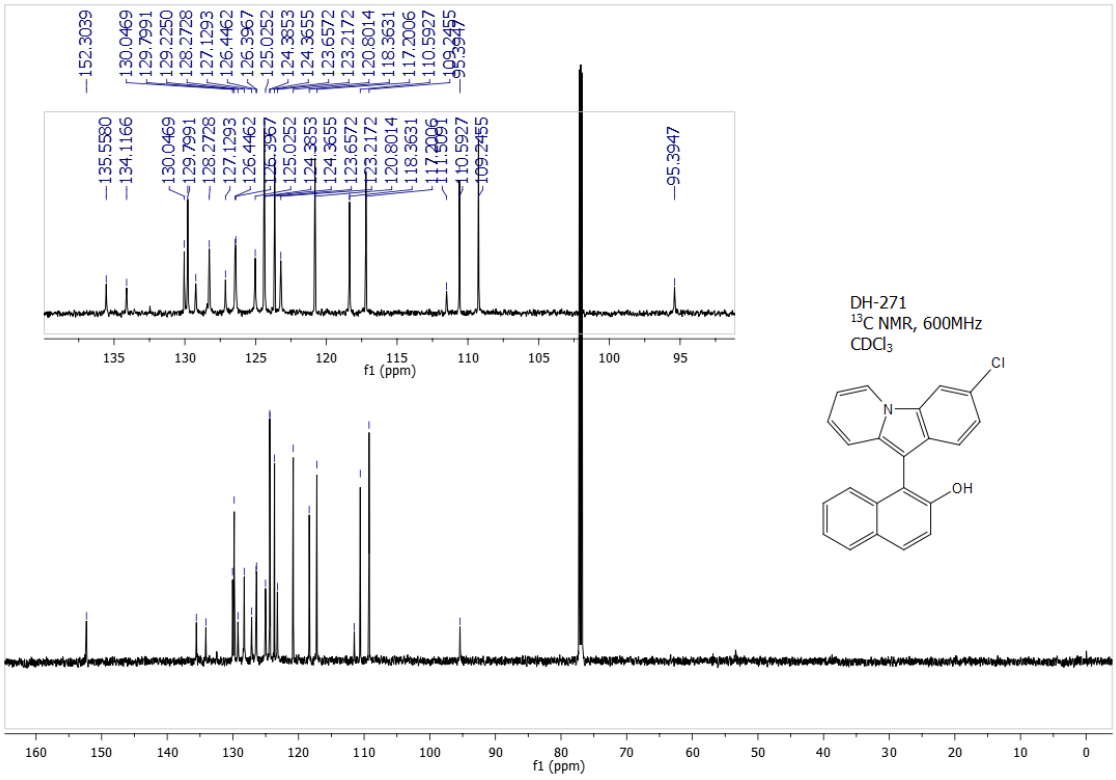
6-phenyl-1-(pyrido[1,2-a]indol-10-yl)naphthalene-2-ol (3h) :



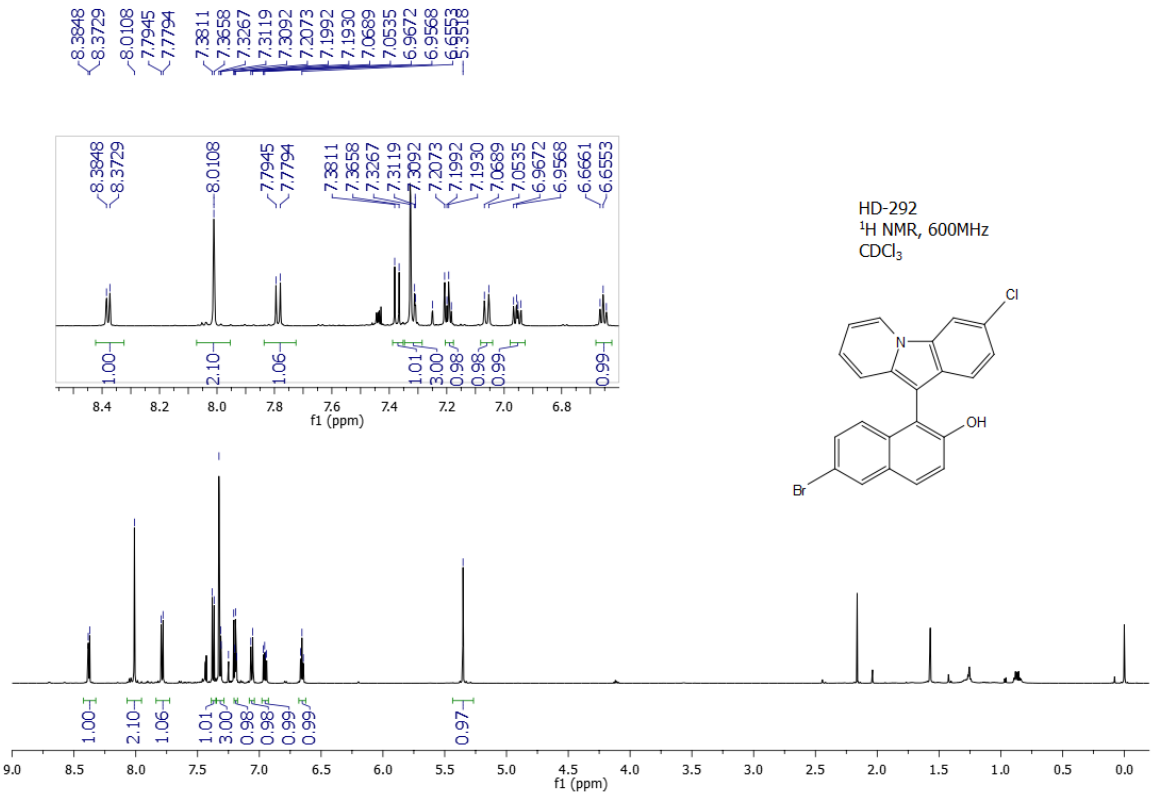


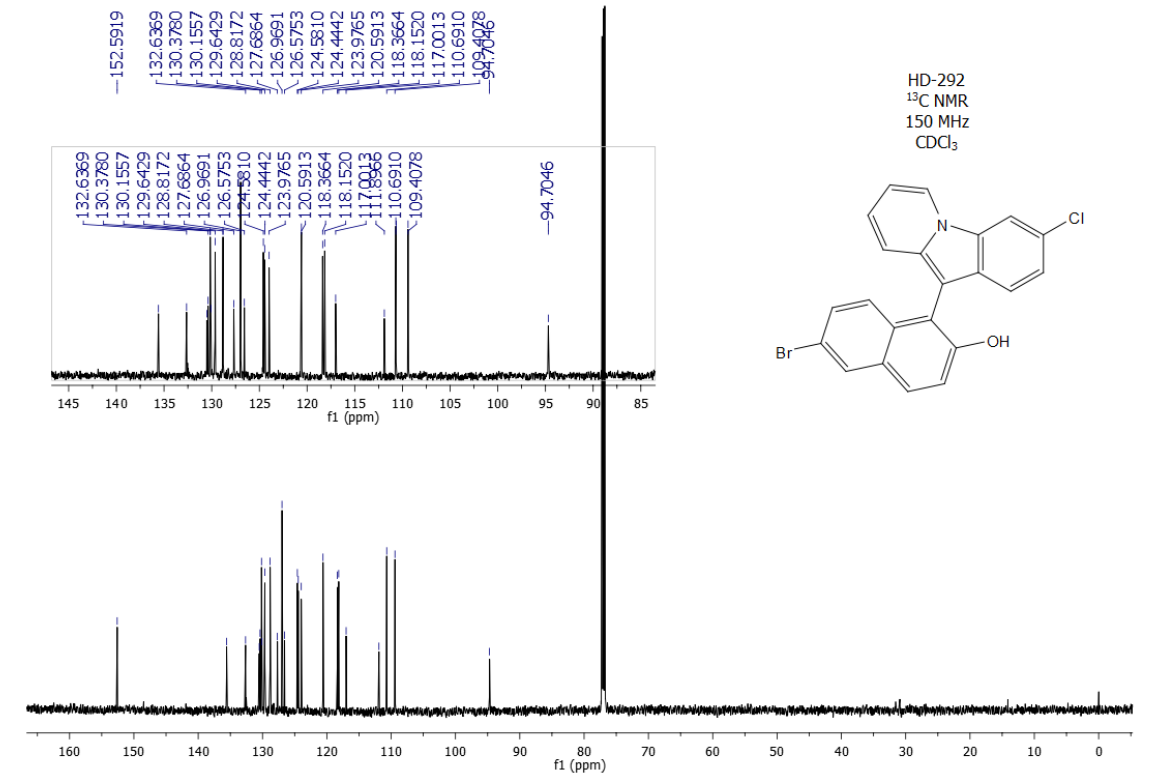
1-(3-chloropyrido[1,2-a]indol-10-yl)naphthalene-2-ol (3i):



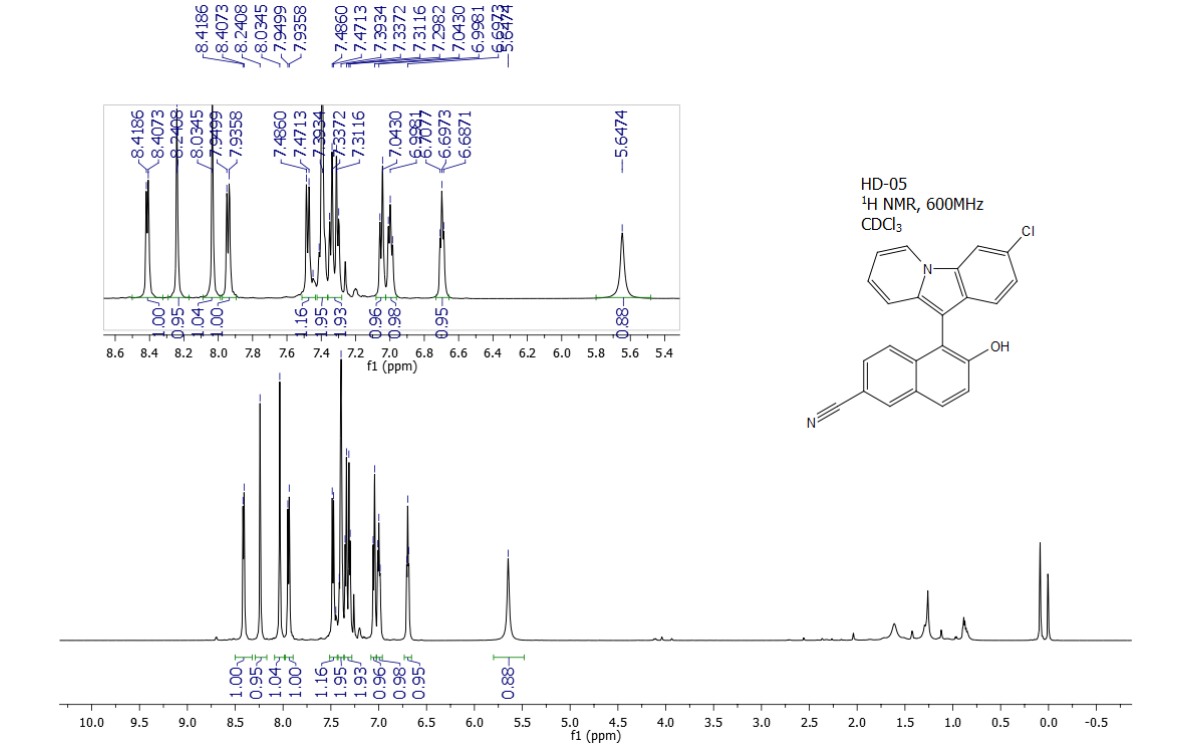


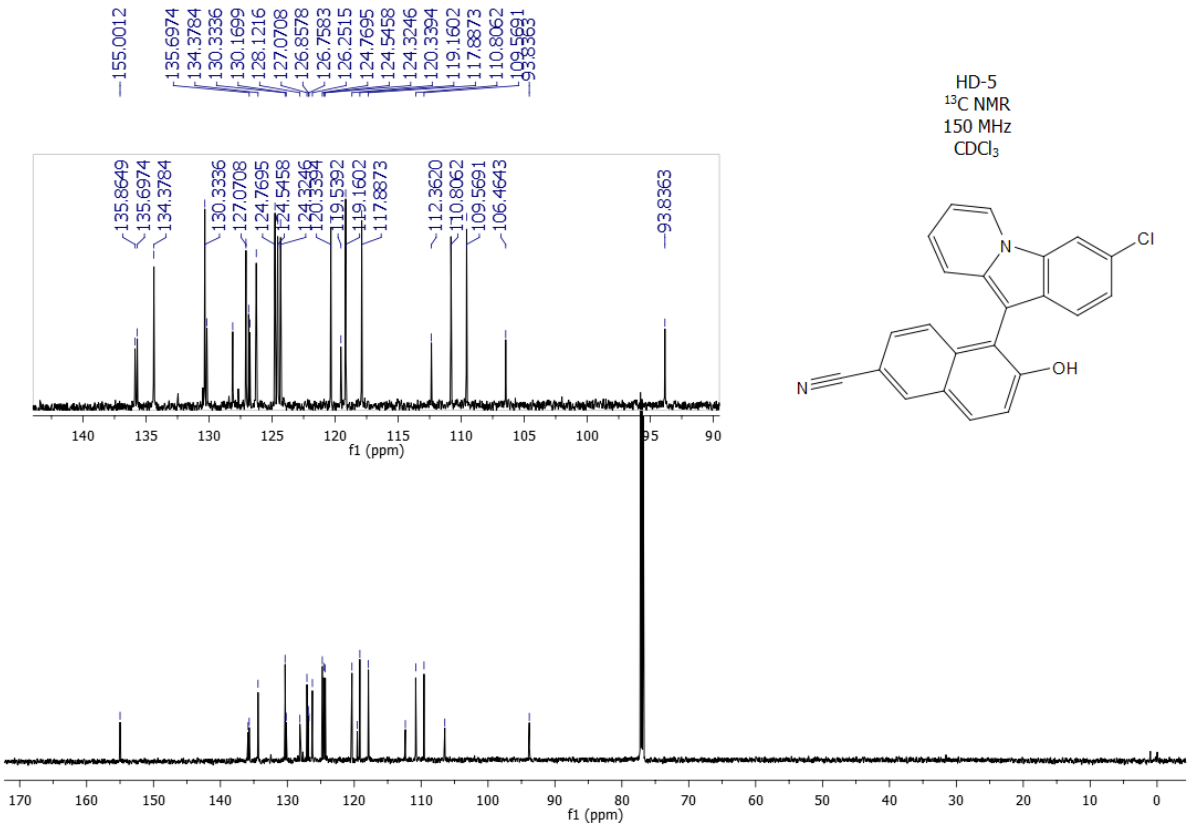
6-bromo-1-(3-chloropyrido[1,2-a]indol-10-yl)naphthalene-2-ol (3j):



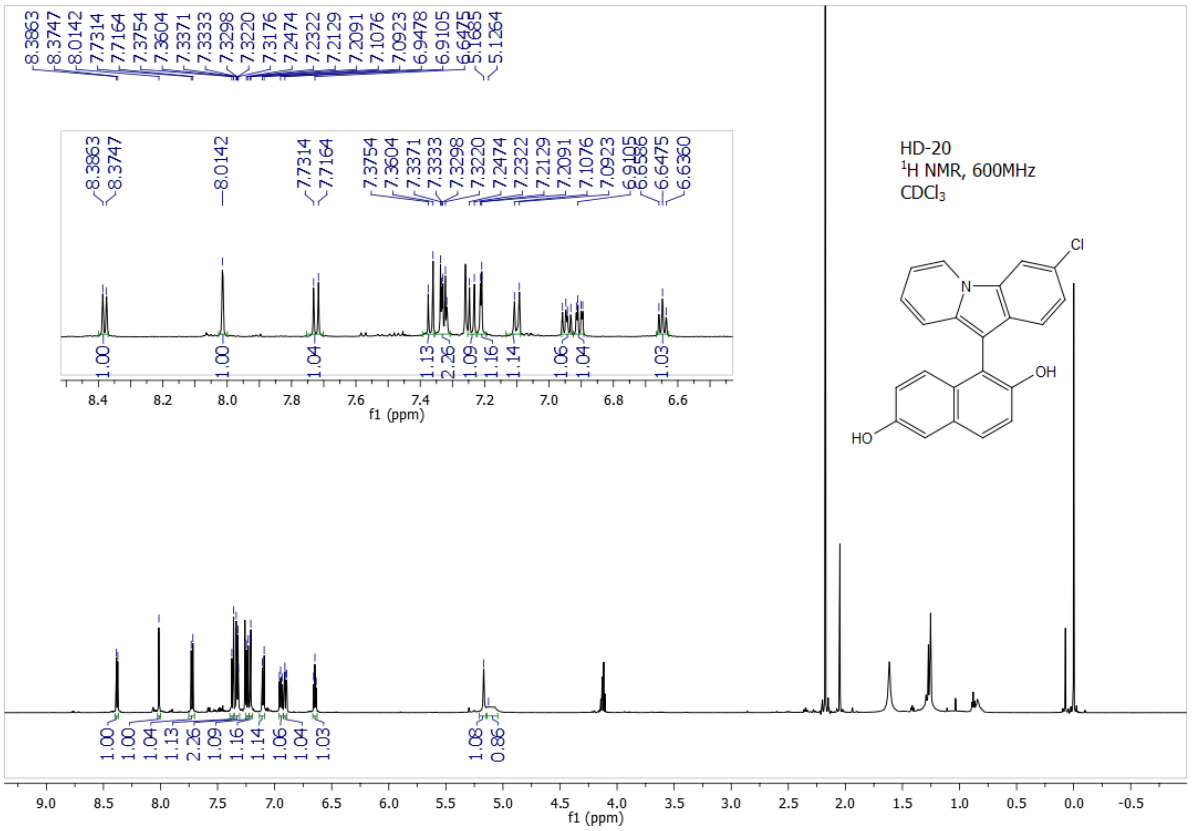


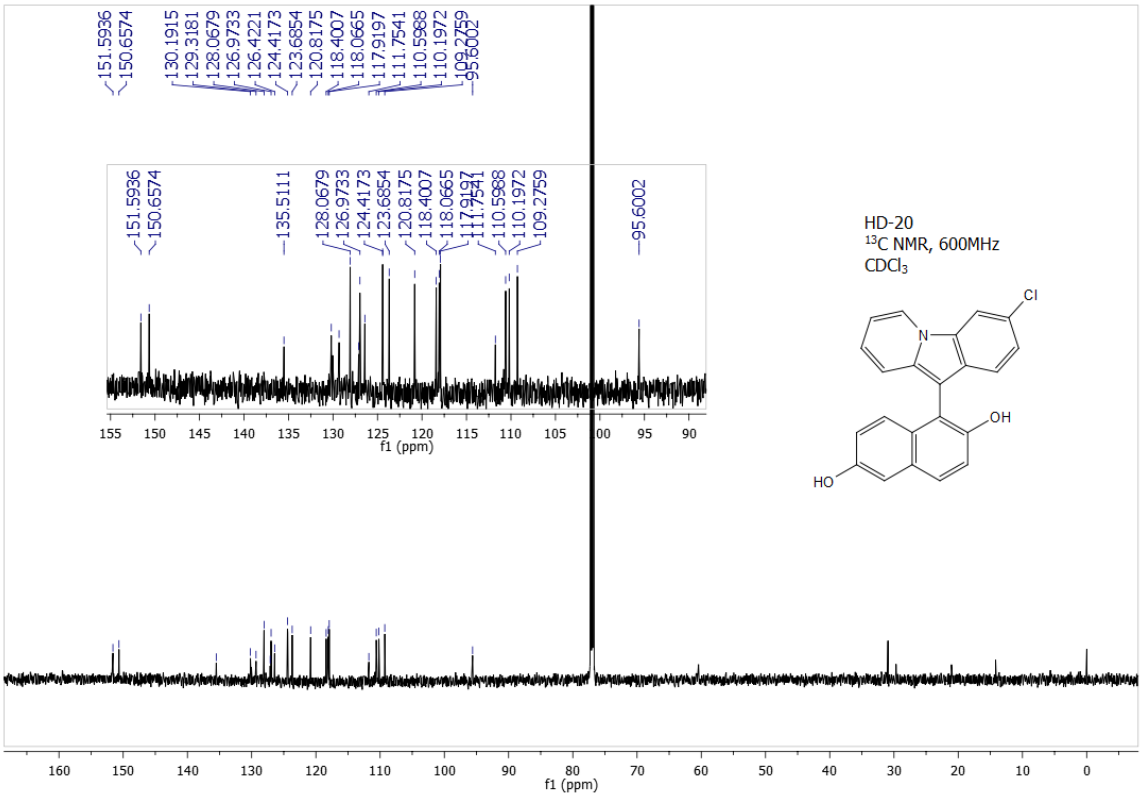
5-(3-chloropyrido[1,2-a]indol-10-yl)-6-hydroxy-2-naphthonitrile (3k):



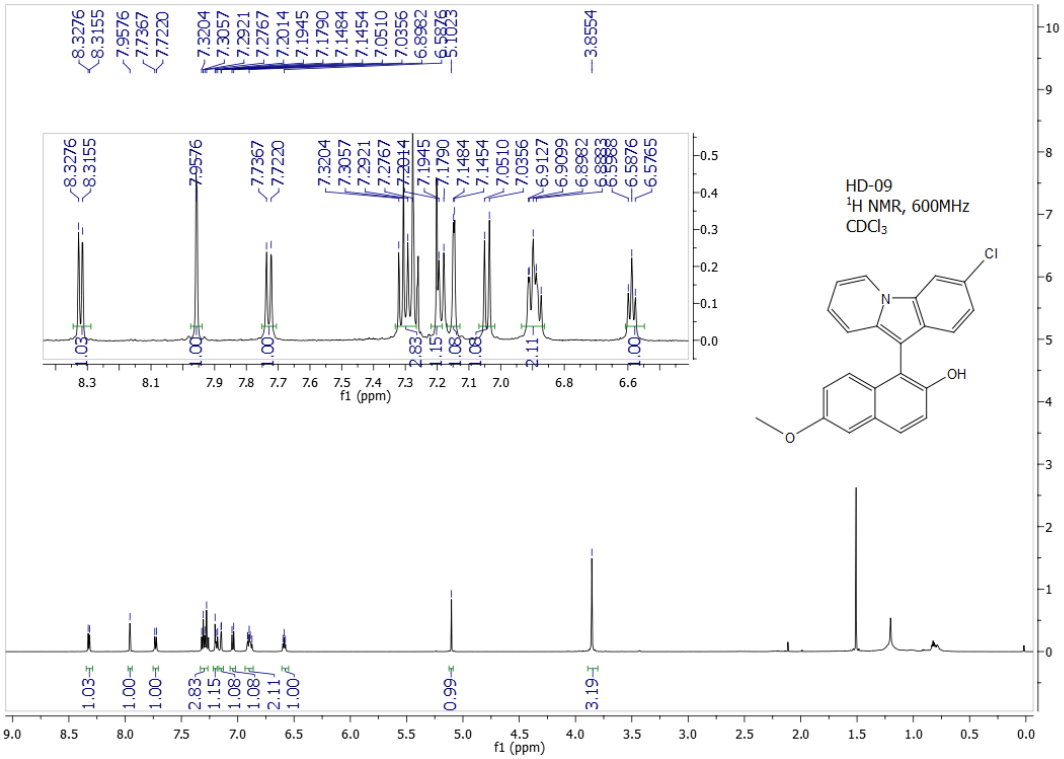


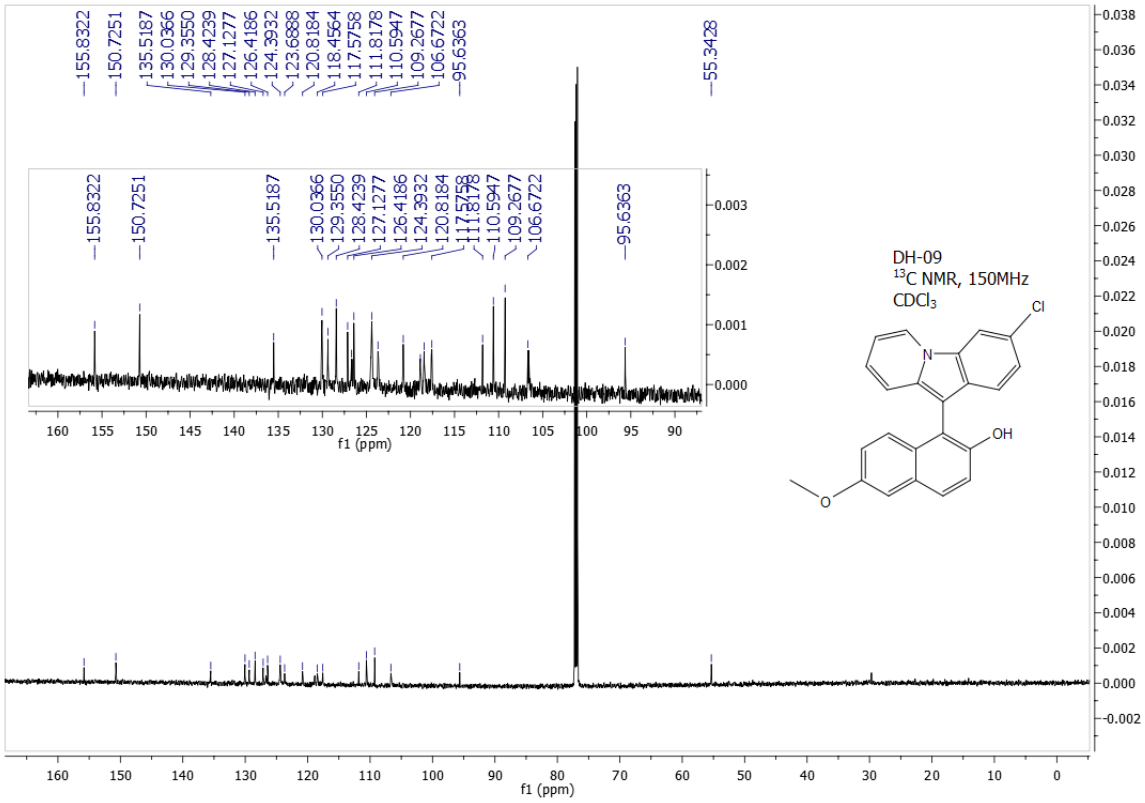
1-(3-chloropyrido[1,2-a]indol-10-yl)naphthalene-2,6-diol (3l):



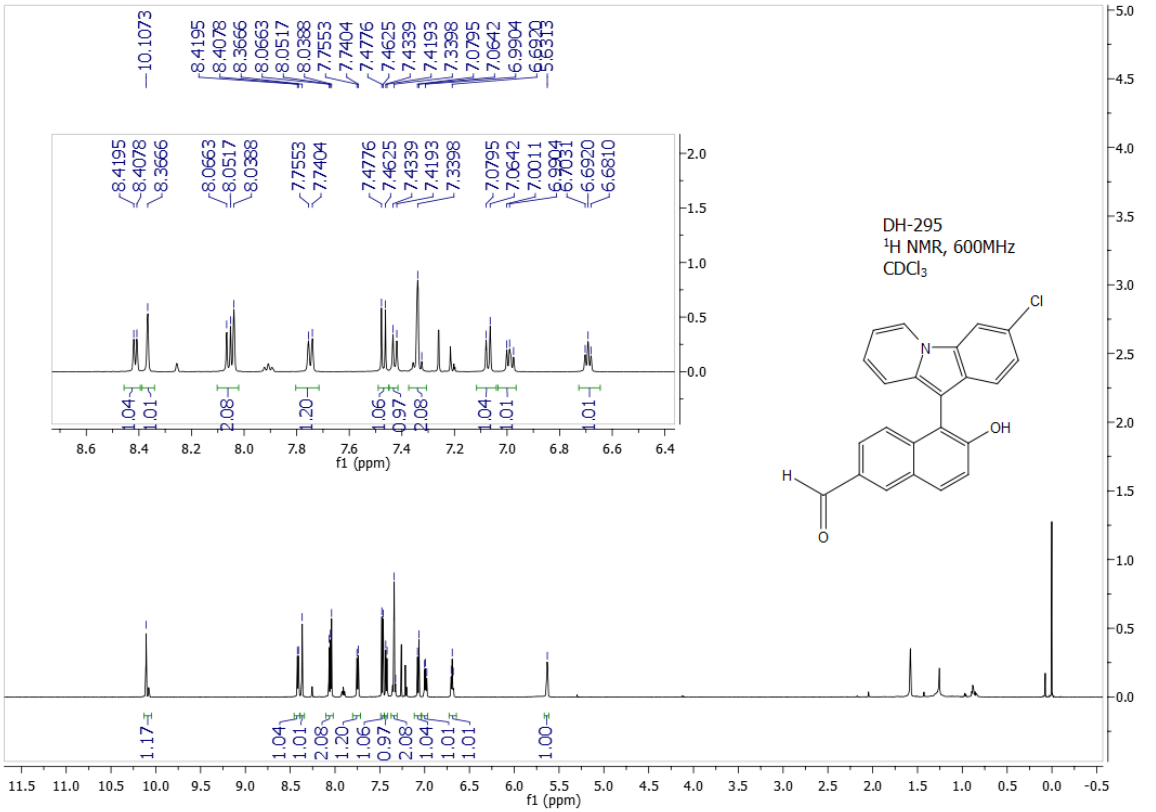


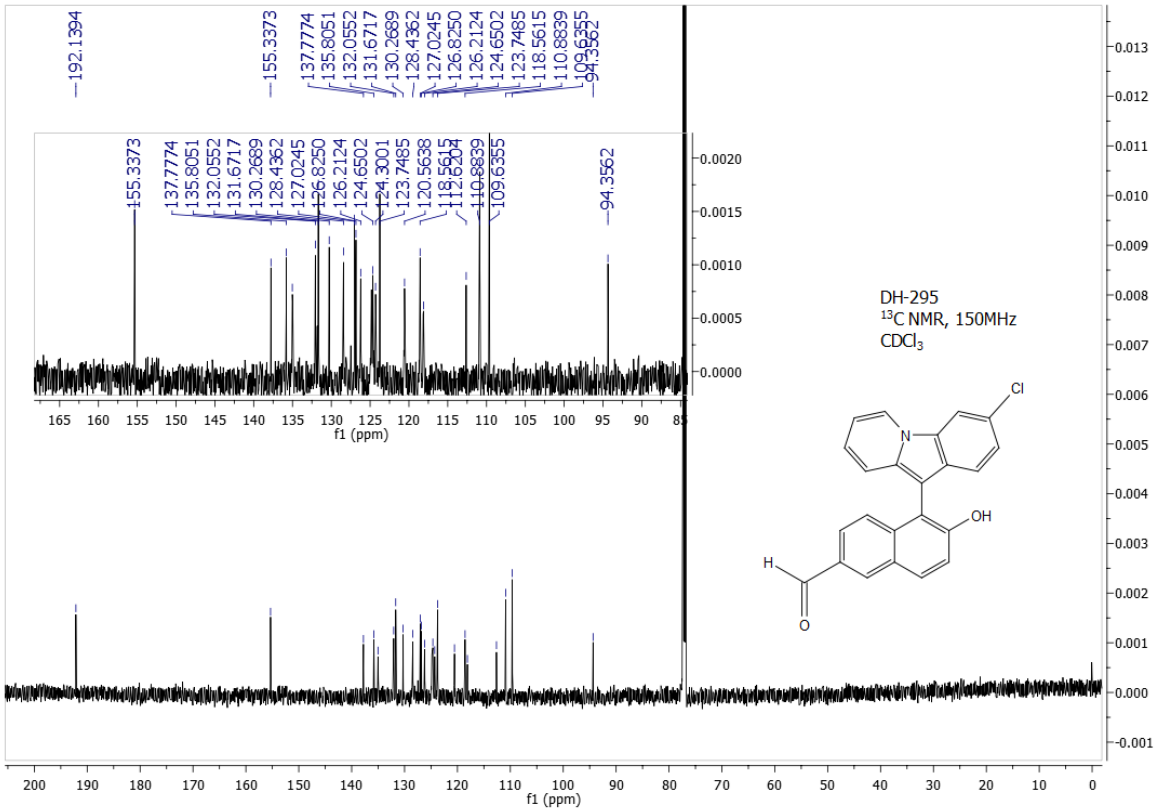
1-**(3-chloropyrido[1,2-a]indol-10-yl)-6-methoxynaphthalen-2-ol (3m):**



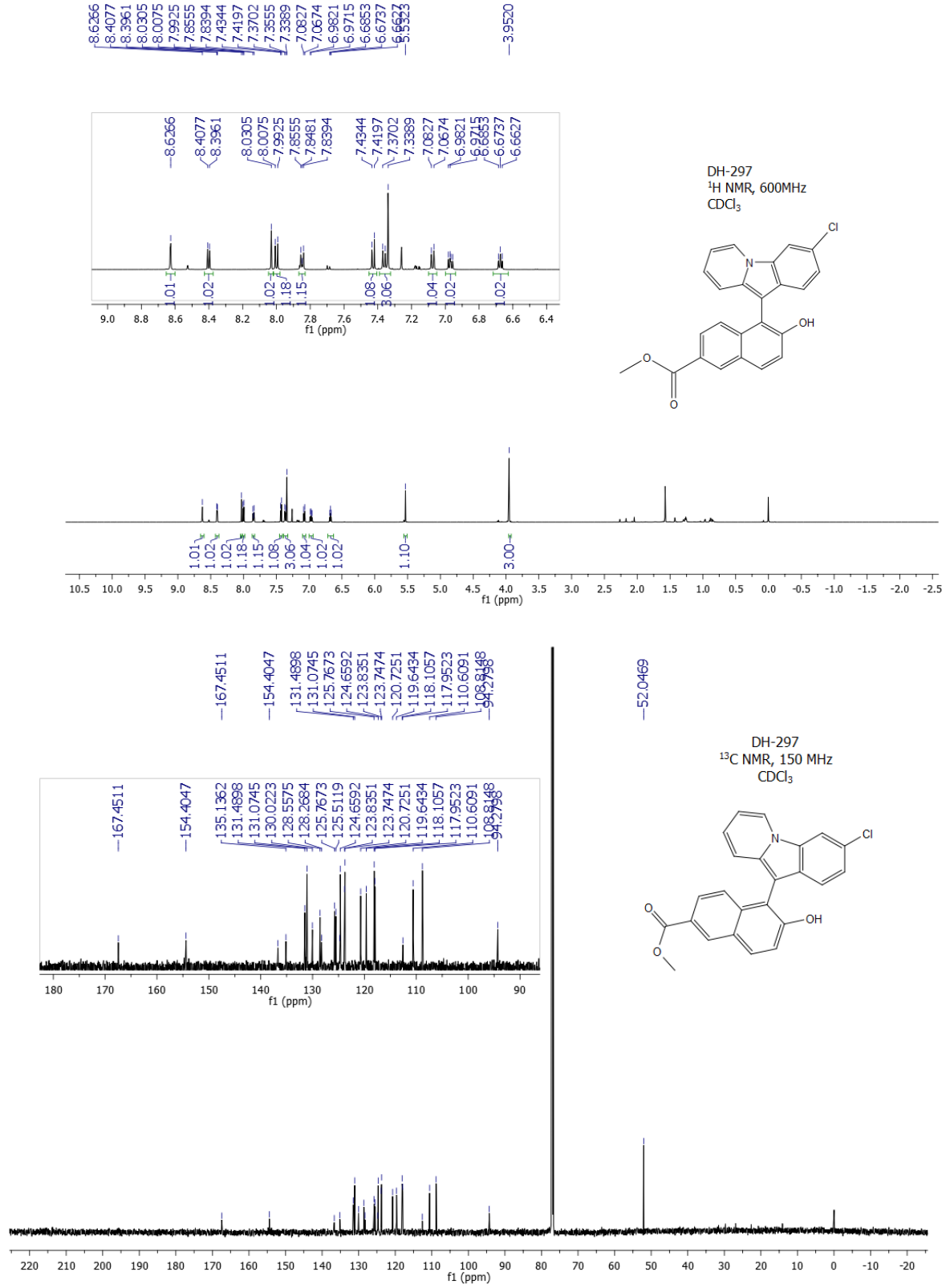


5-(3-chloropyrido[1,2-a]indol-10-yl)-6-hydroxy-2-naphthaldehyde (3n):

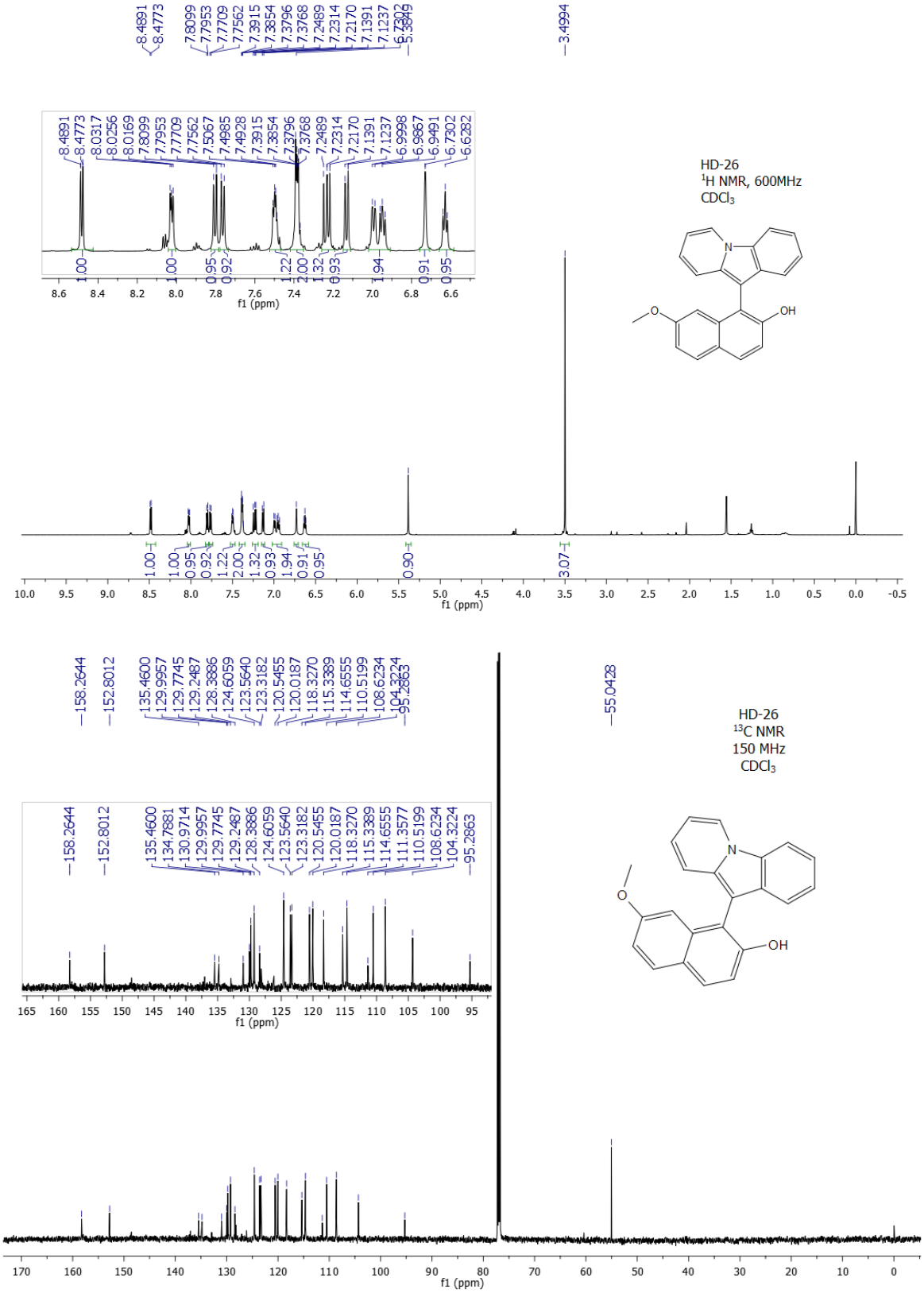




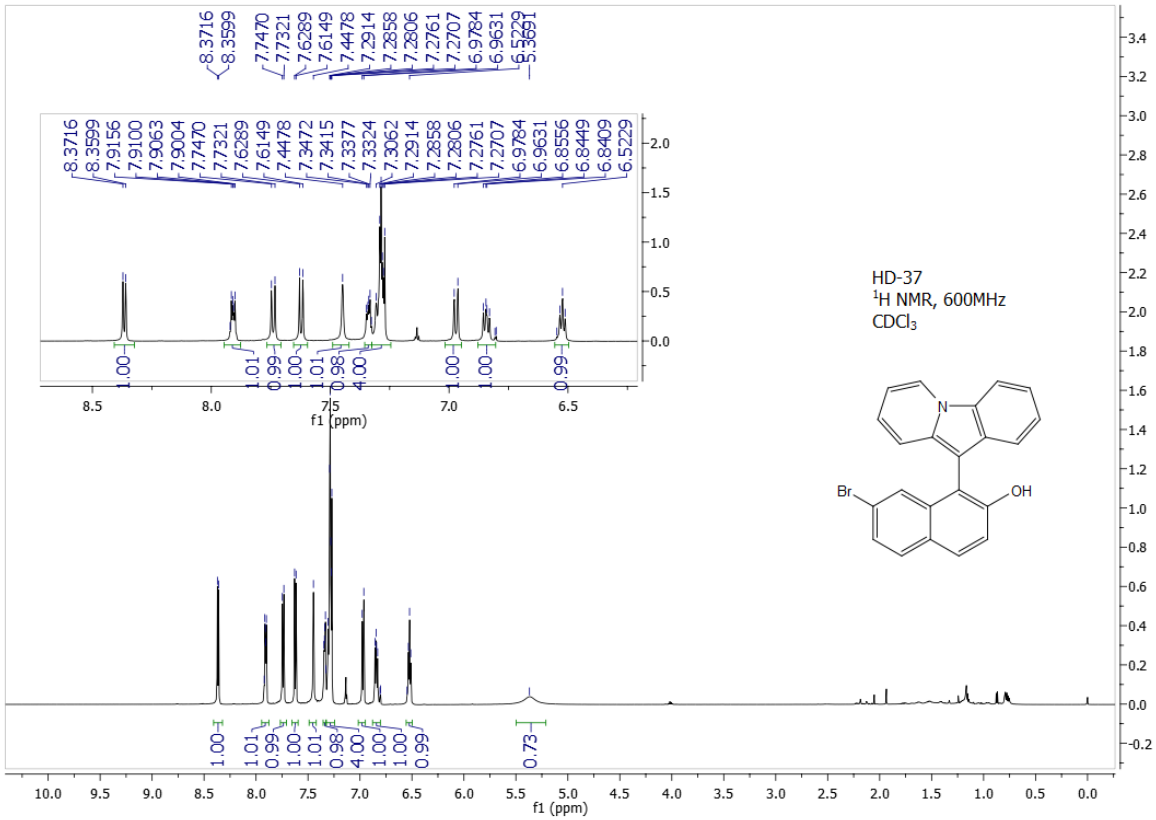
Methyl 5-(3-chloropyrido[1,2-a]indol-10-yl)-6-hydroxy-2-naphthoate (3o):

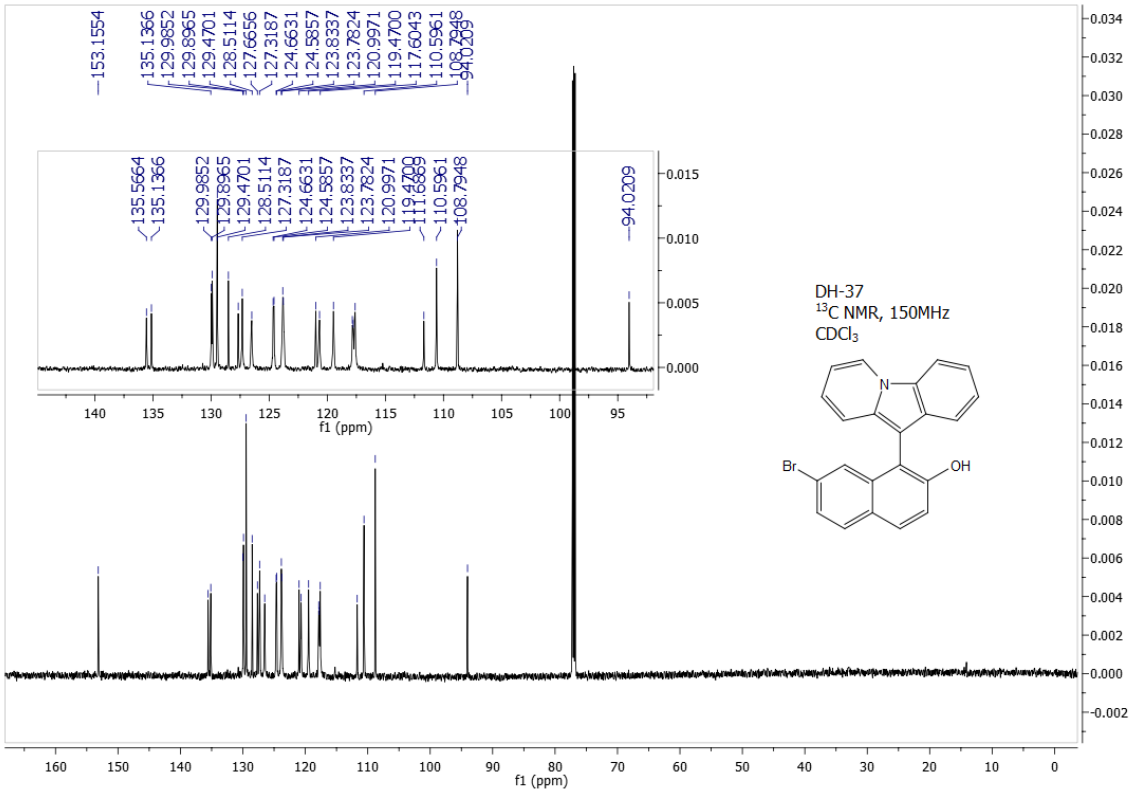


7-methoxy-1-(pyrido[1,2-a]indol-10-yl)naphthalene-2-ol (3p):

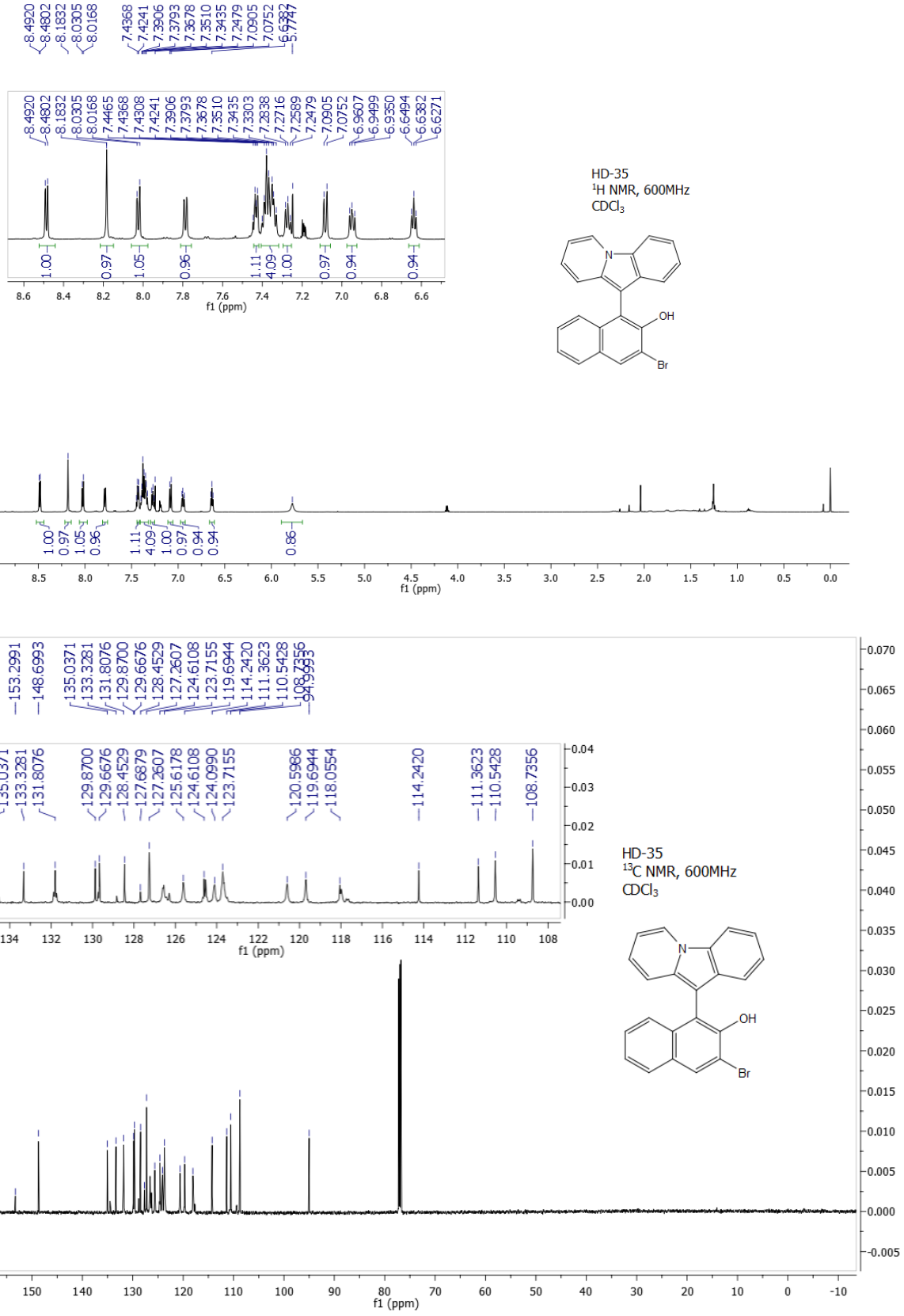


7-bromo-1-(pyrido[1,2-a]indol-10-yl)naphthalene-2 ol (3q):

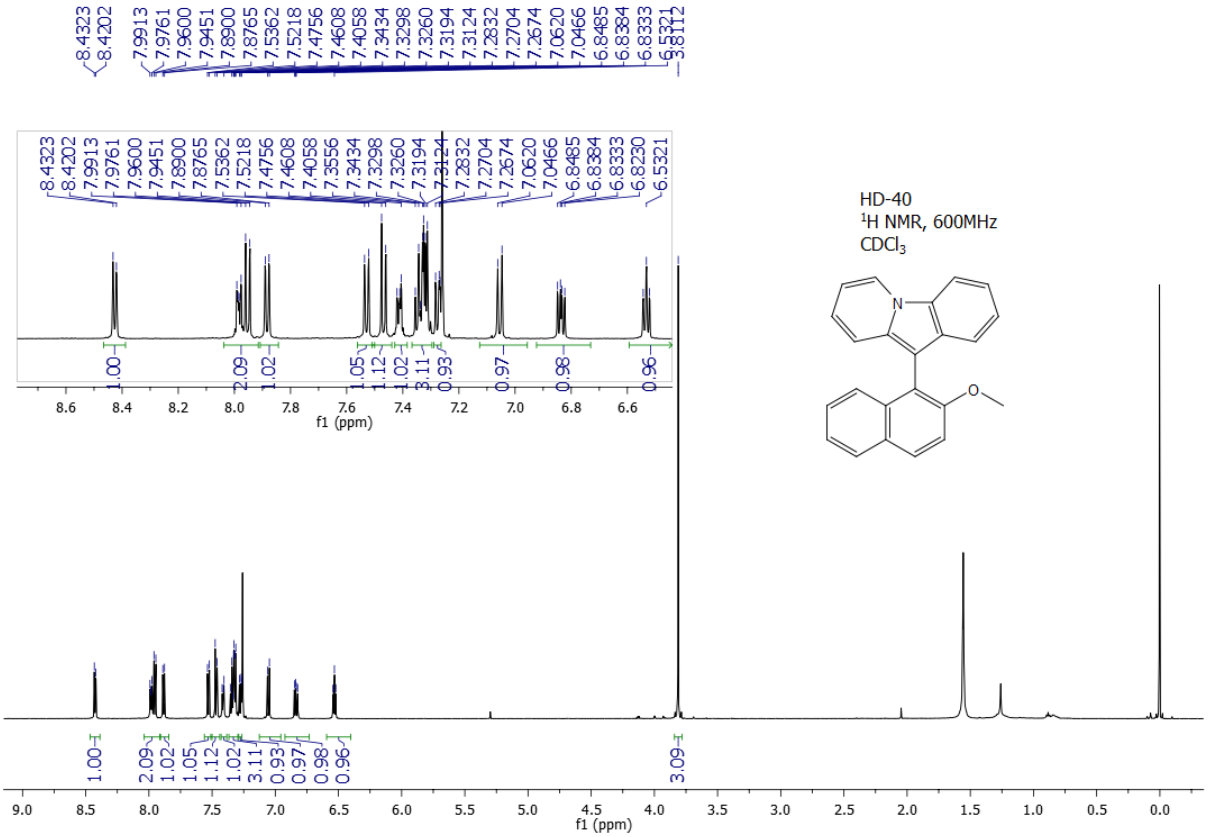


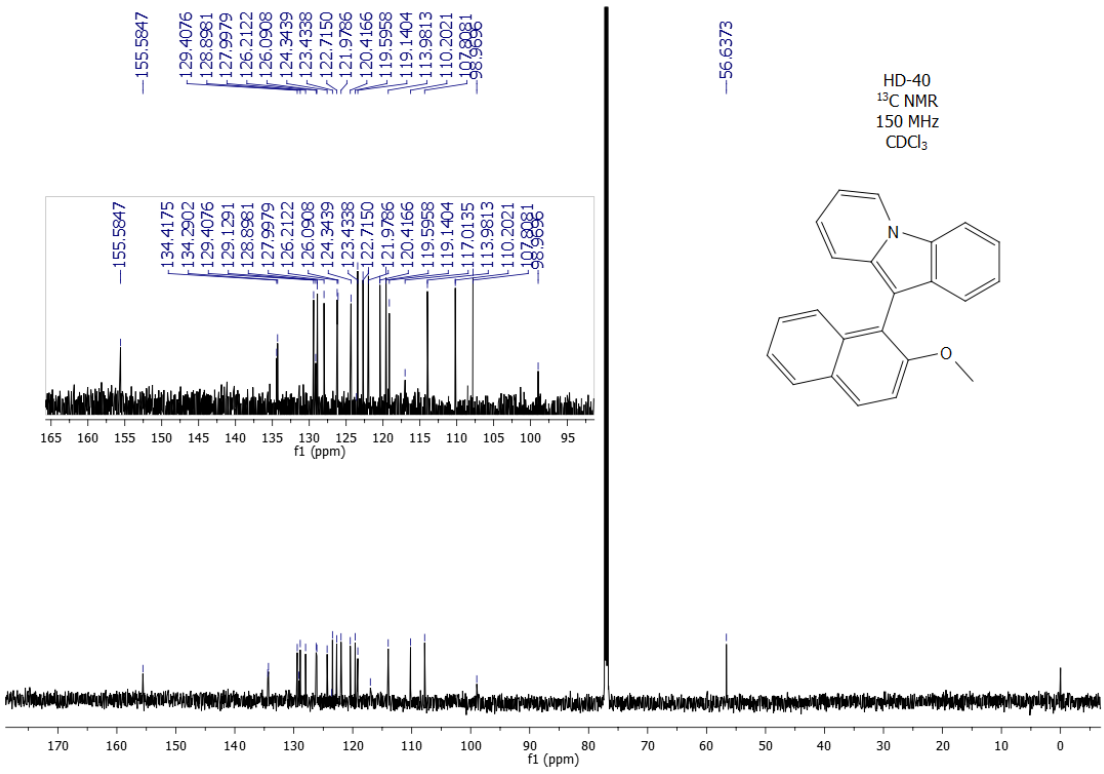


3-bromo-1-(pyrido[1,2-a]indol-10-yl)naphthalene-2-ol (3r):

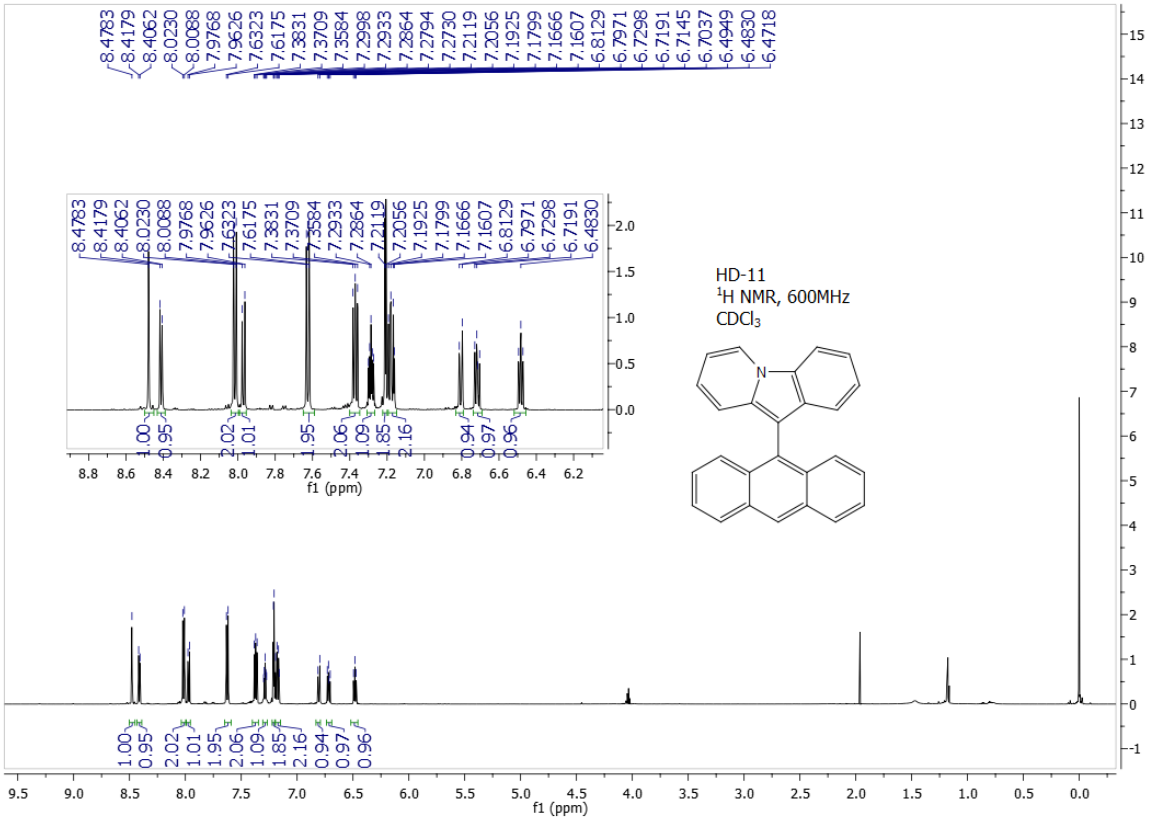


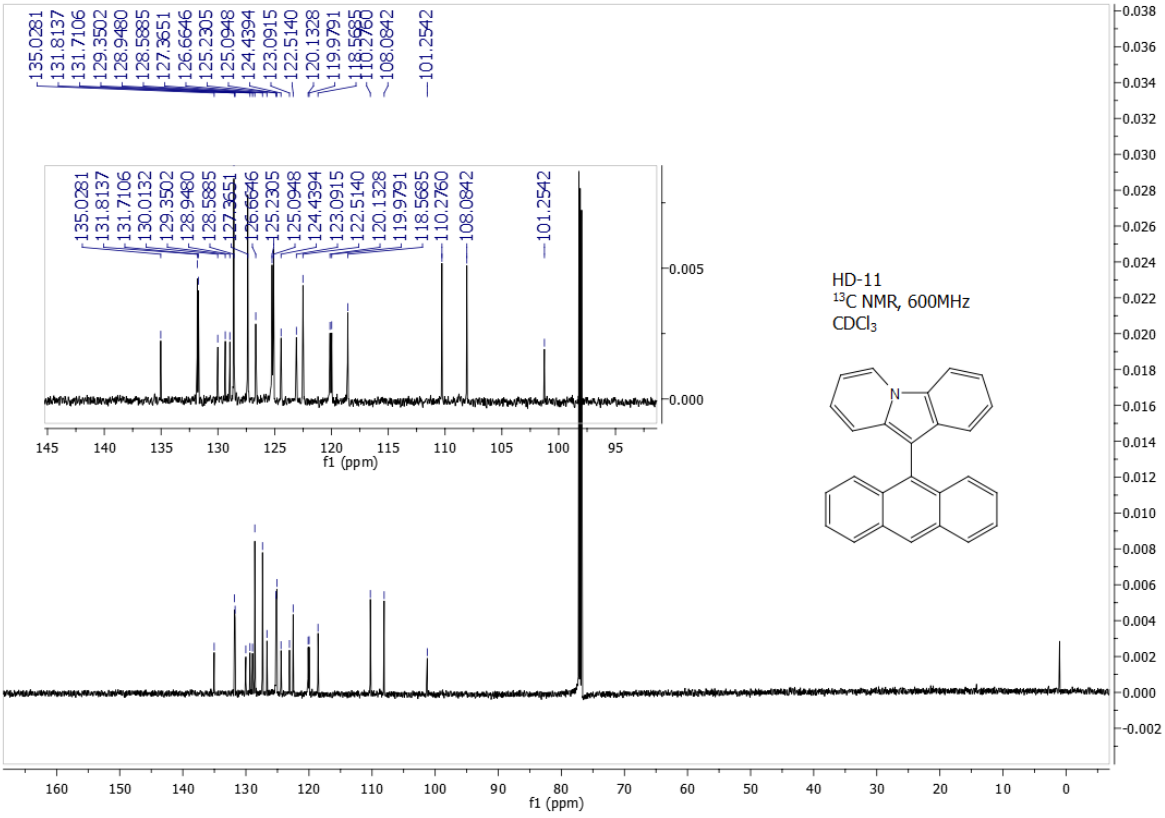
10-(2-methoxynaphthalen-1-yl)pyrido[1,2-a]indole (3s):





10-(anthracen-9-yl)pyrido[1,2-a]indole (3t):





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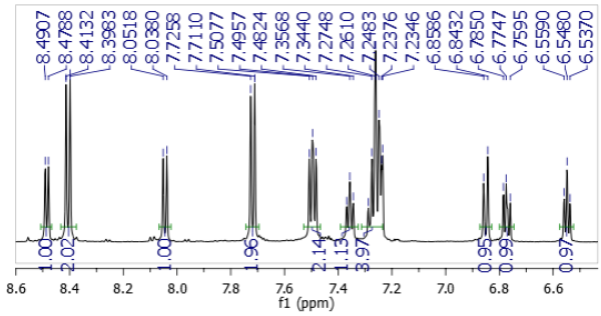
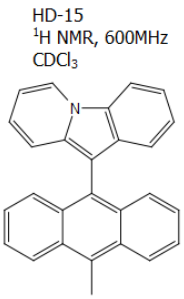
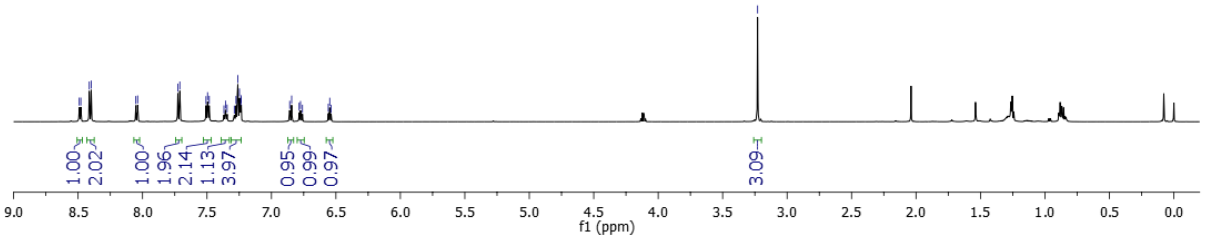
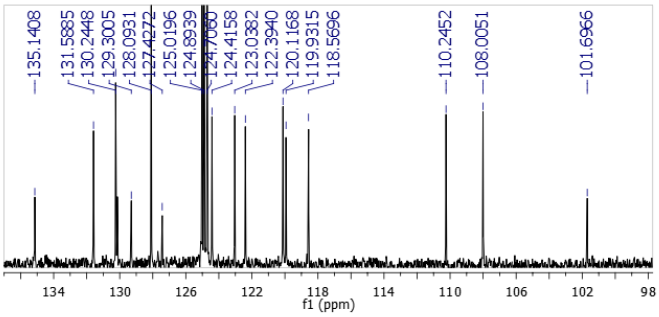
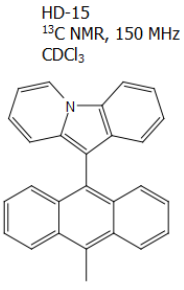
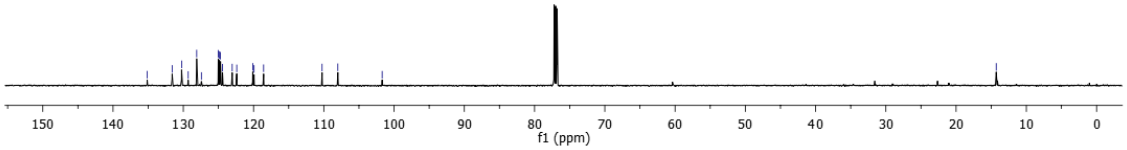




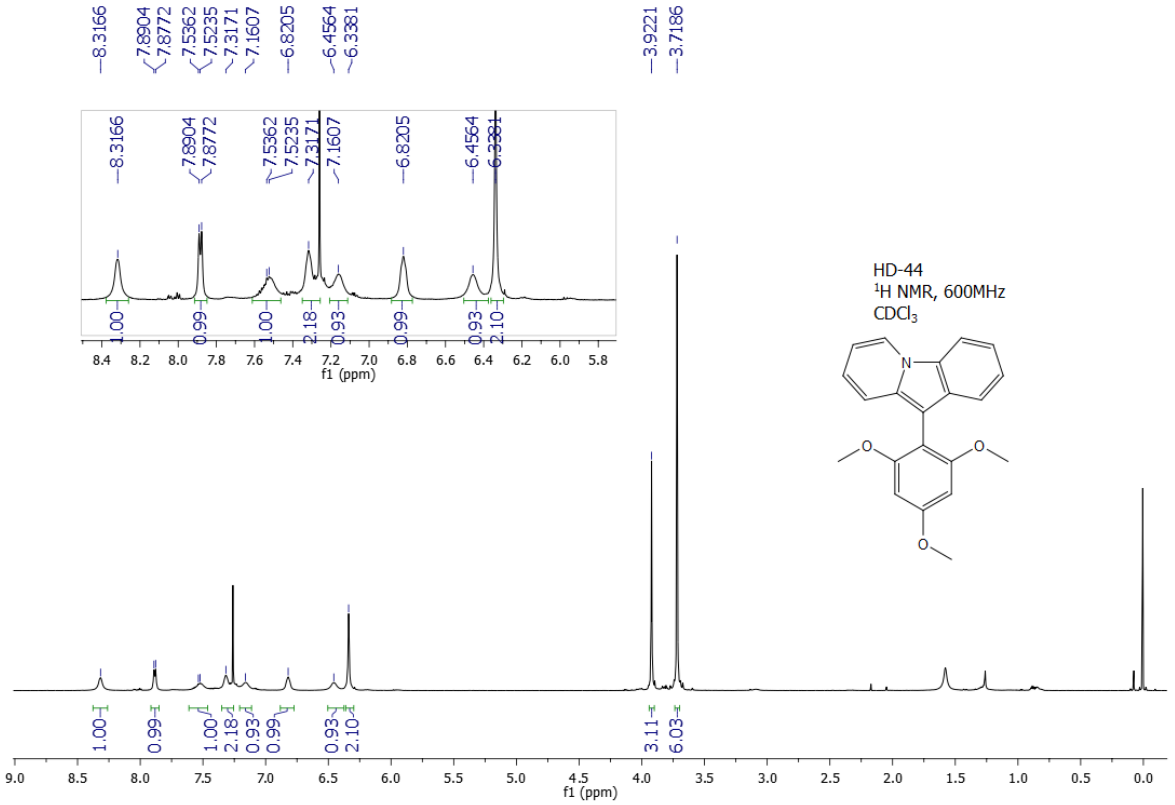


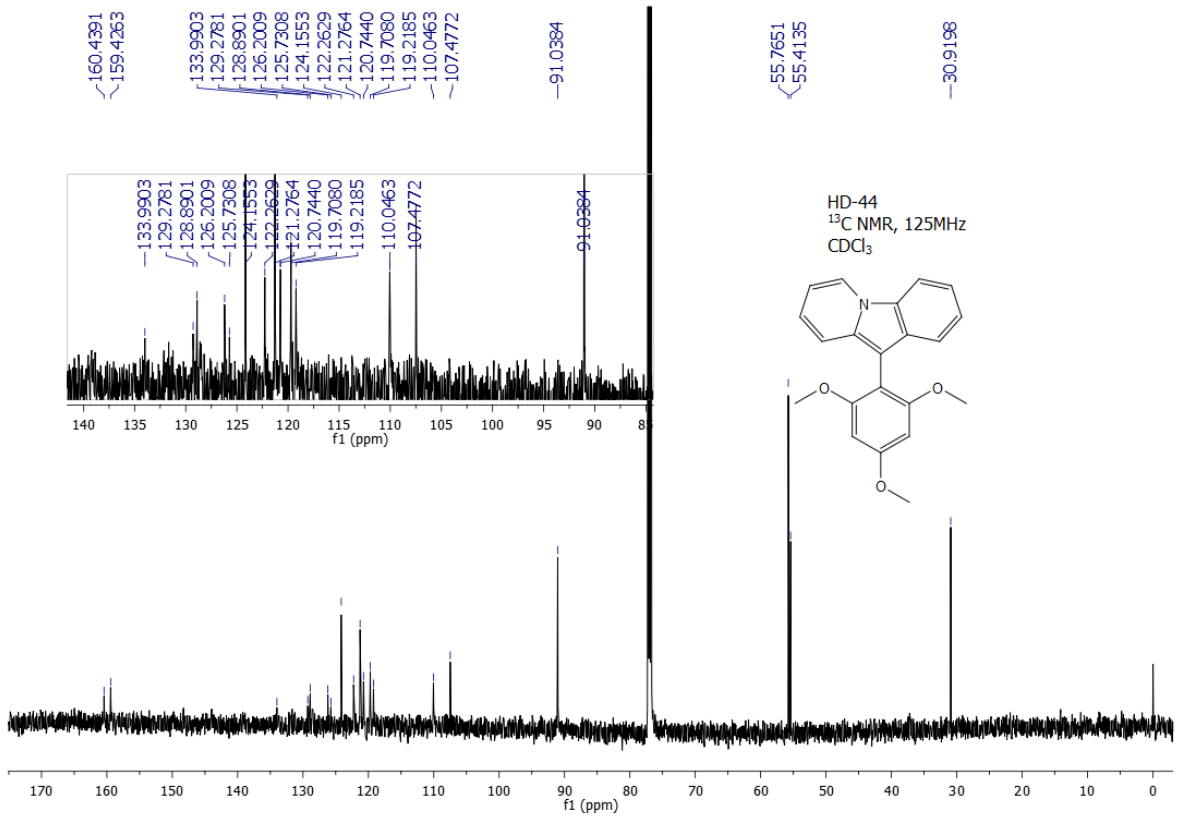




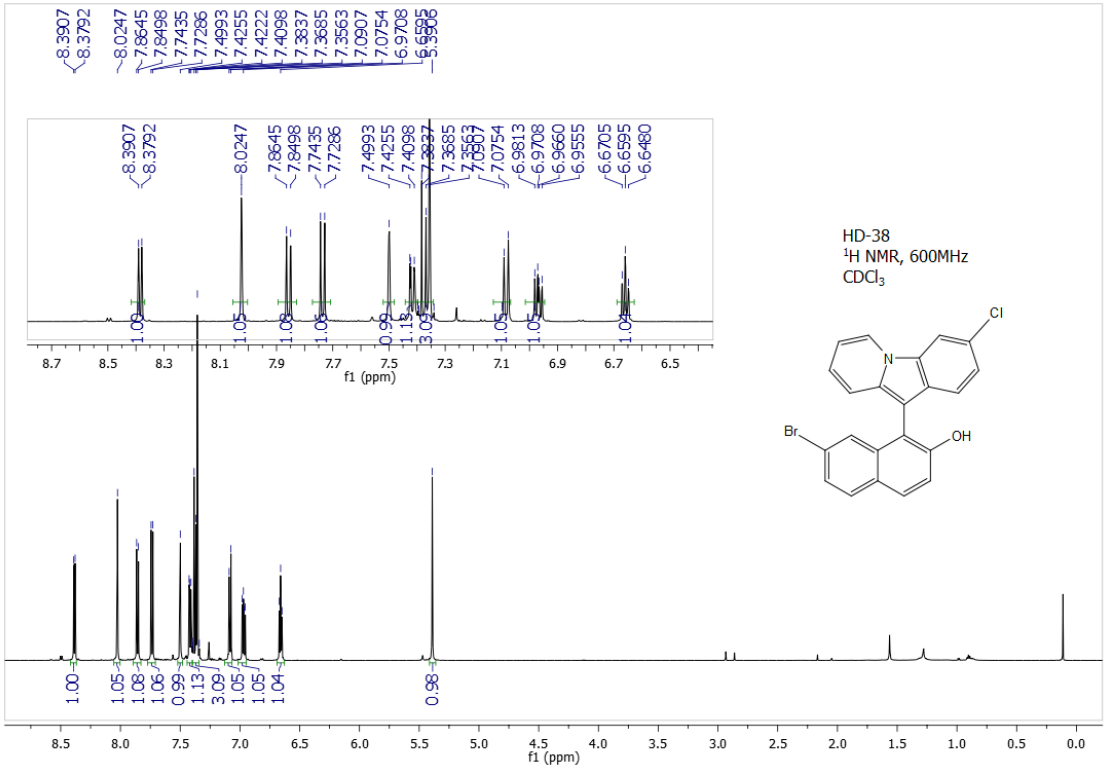


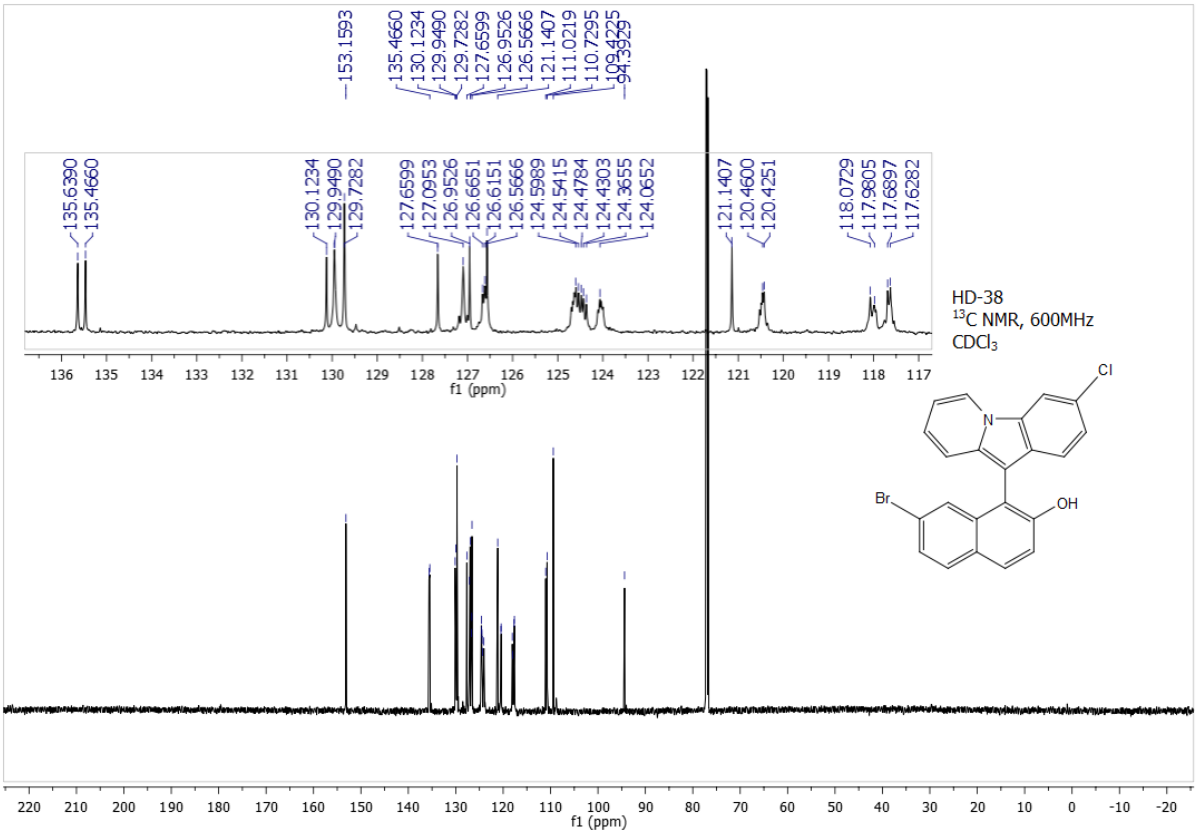
10-(2,4,6-trimethoxyphenyl)pyrido[1,2-a]indole (3v):



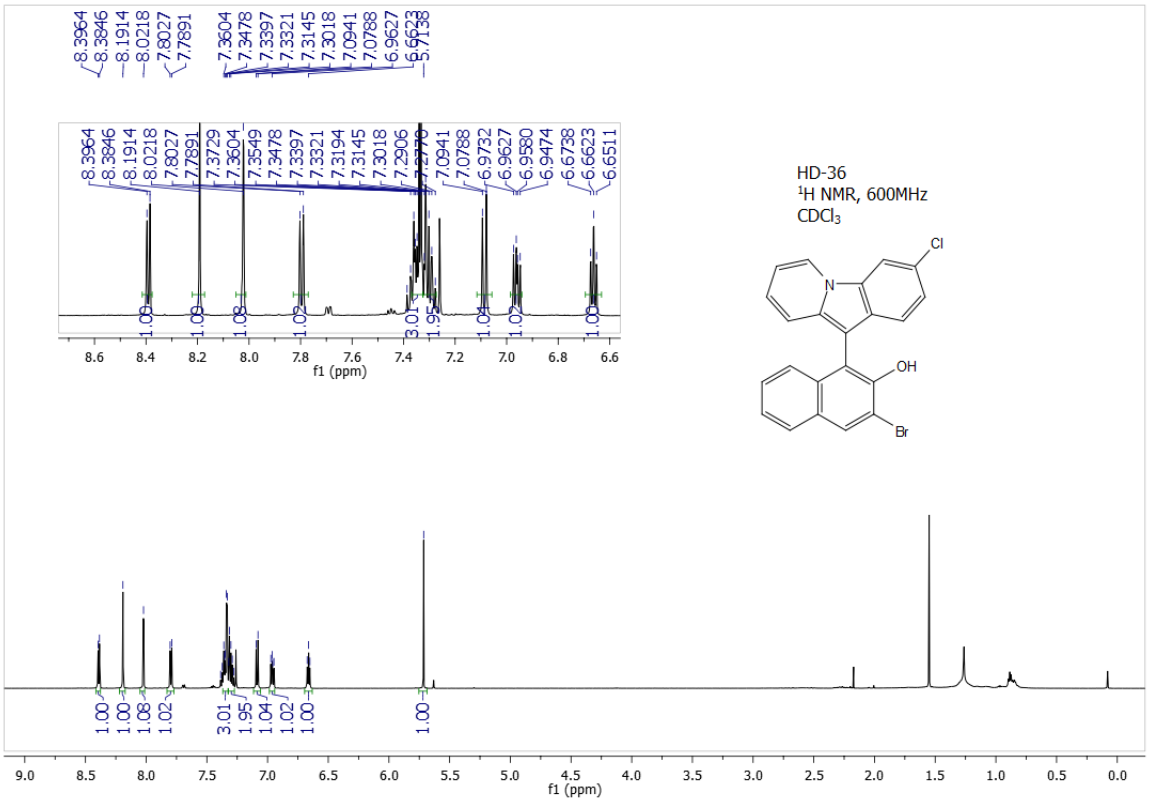


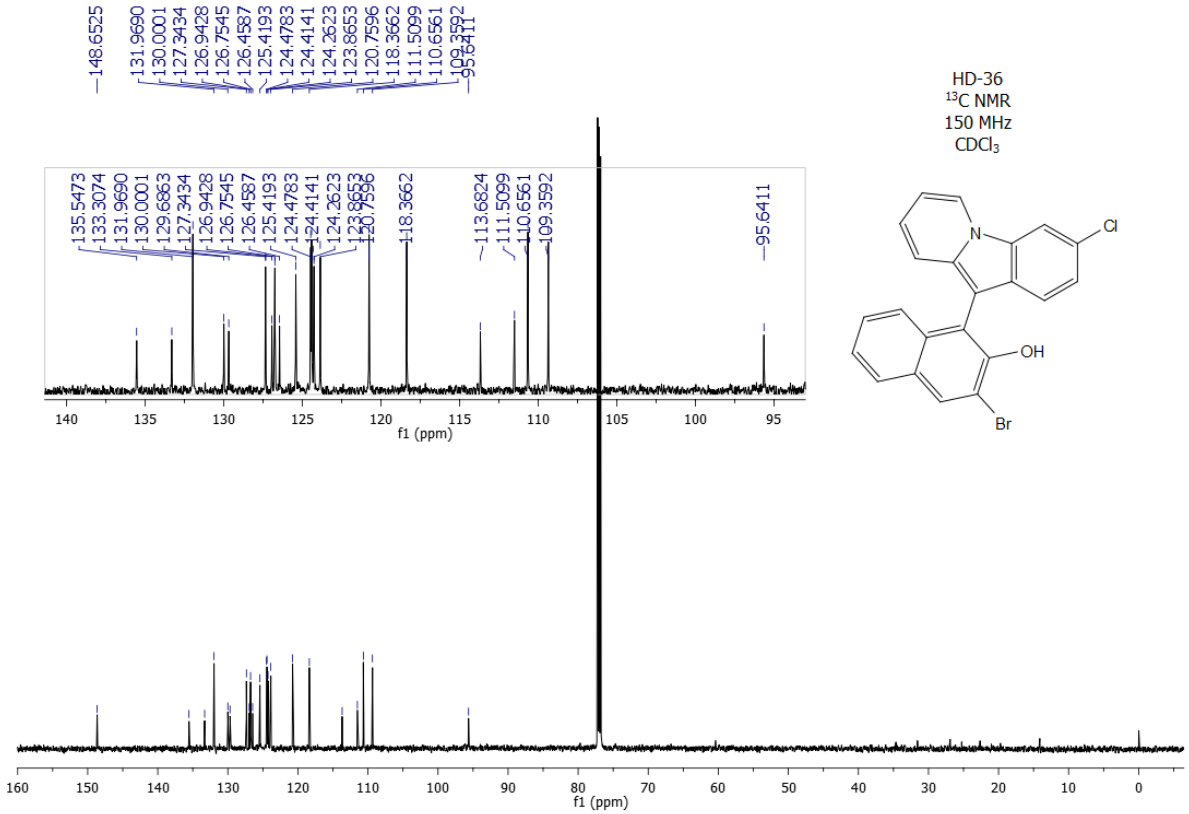
7-bromo-1-(3-chloropyrido[1,2-a]indol-10-yl)naphthalen-2-ol (3w):



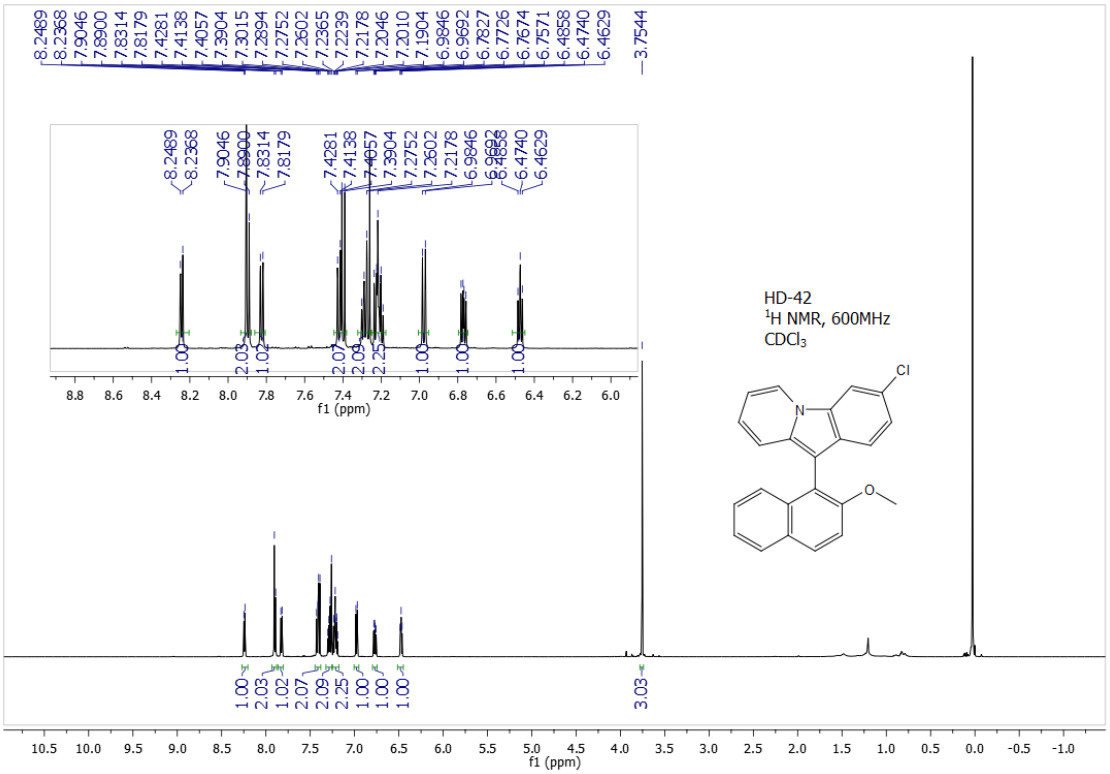


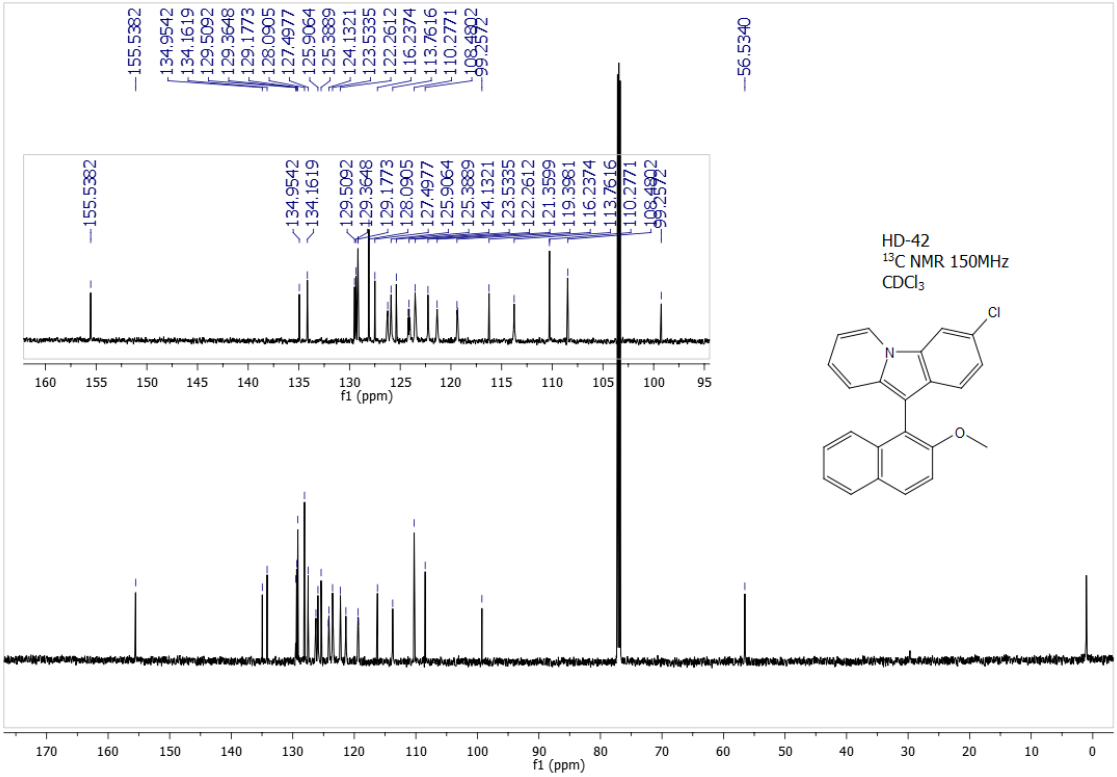
3-bromo-1-(3- chloropyrido[1,2-a]indol-10-yl)naphthalene-2-ol (3x):



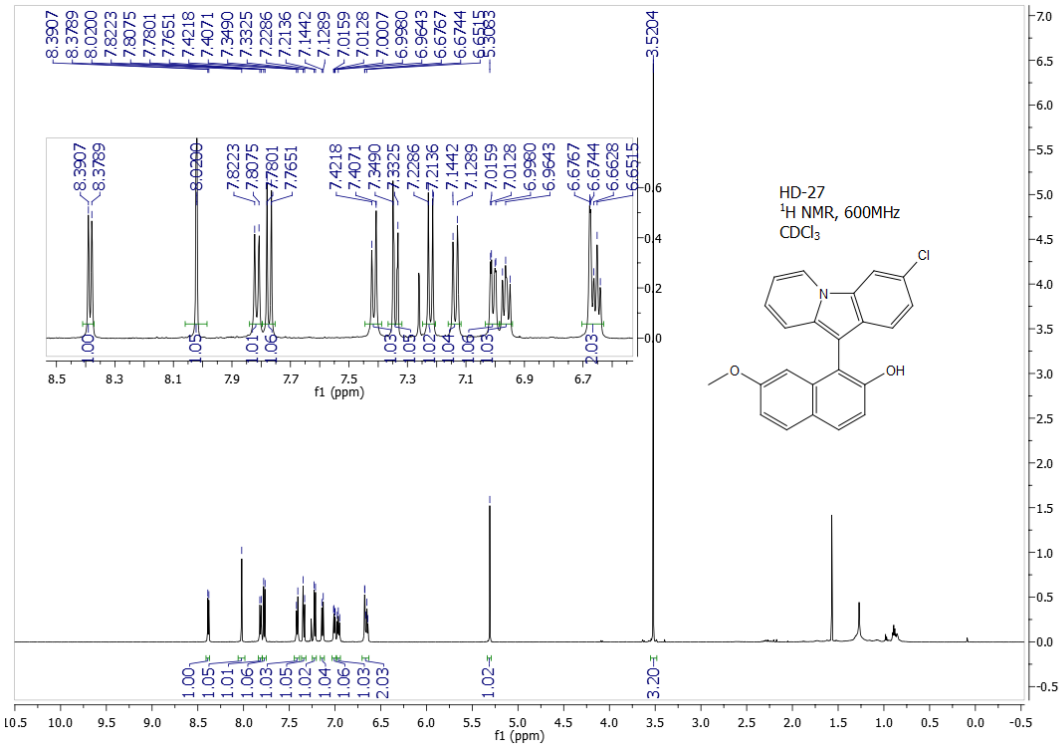


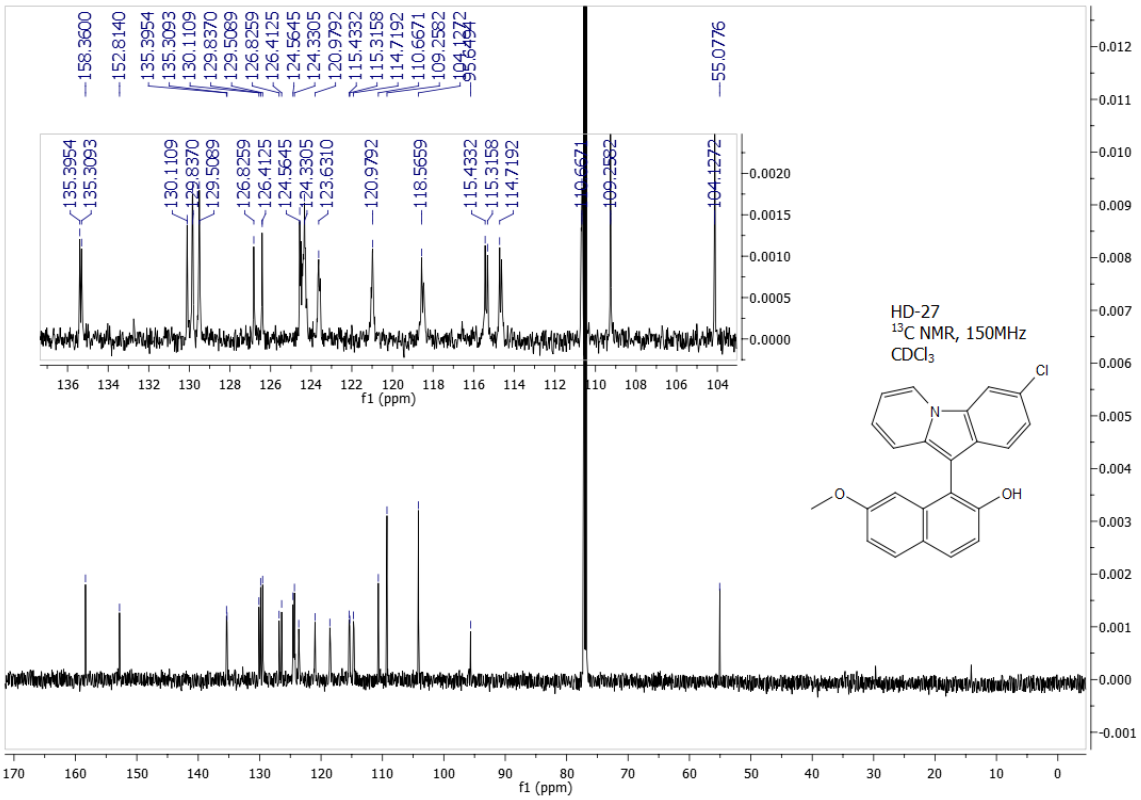
3-chloro-10-(2-methoxynaphthalen-1-yl)pyrido[1,2-a]indole (3y):



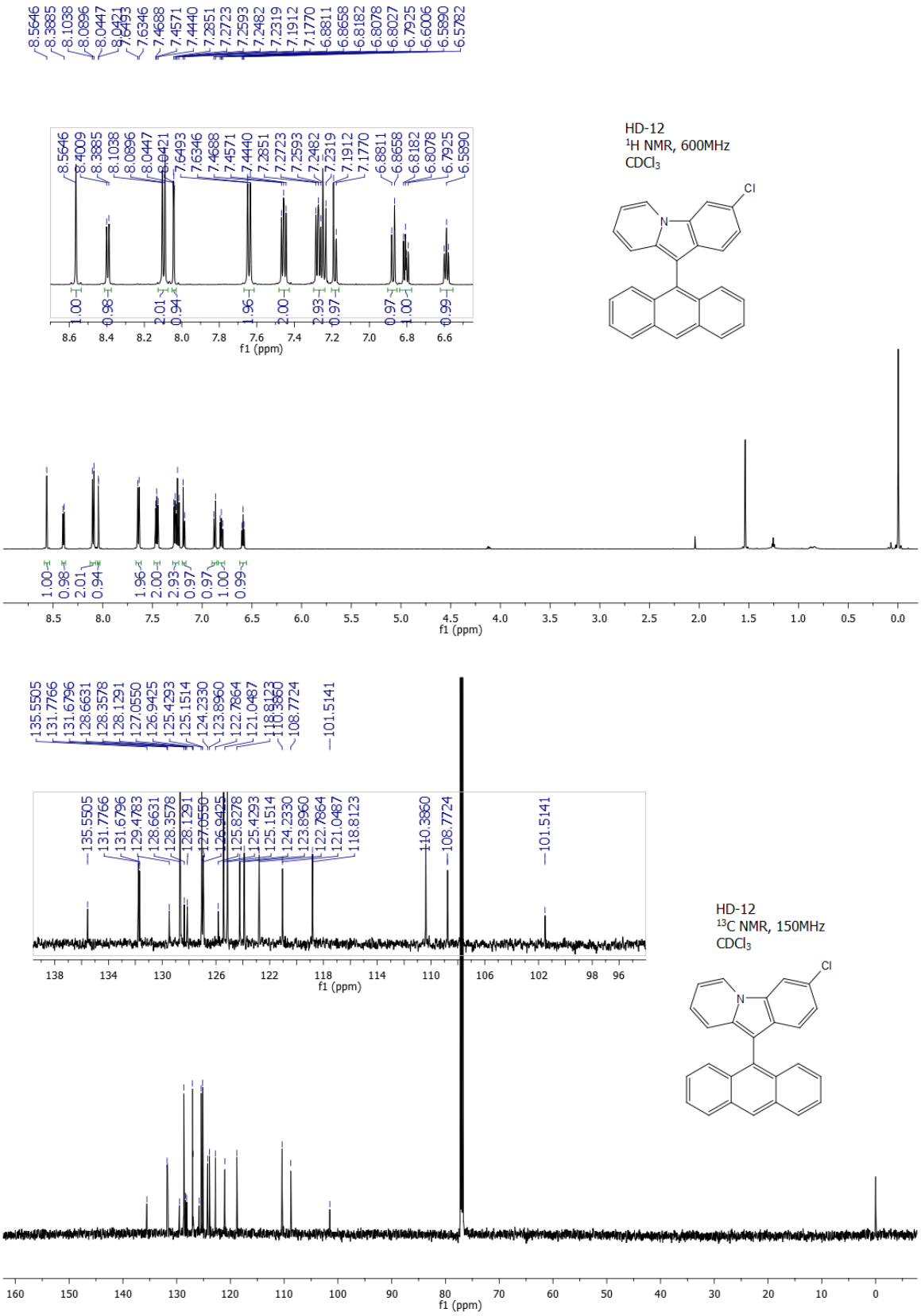


1-(3-chloropyrido[1,2-a]indol-10-yl)-7-methoxynaphthalen-2-ol (3z):

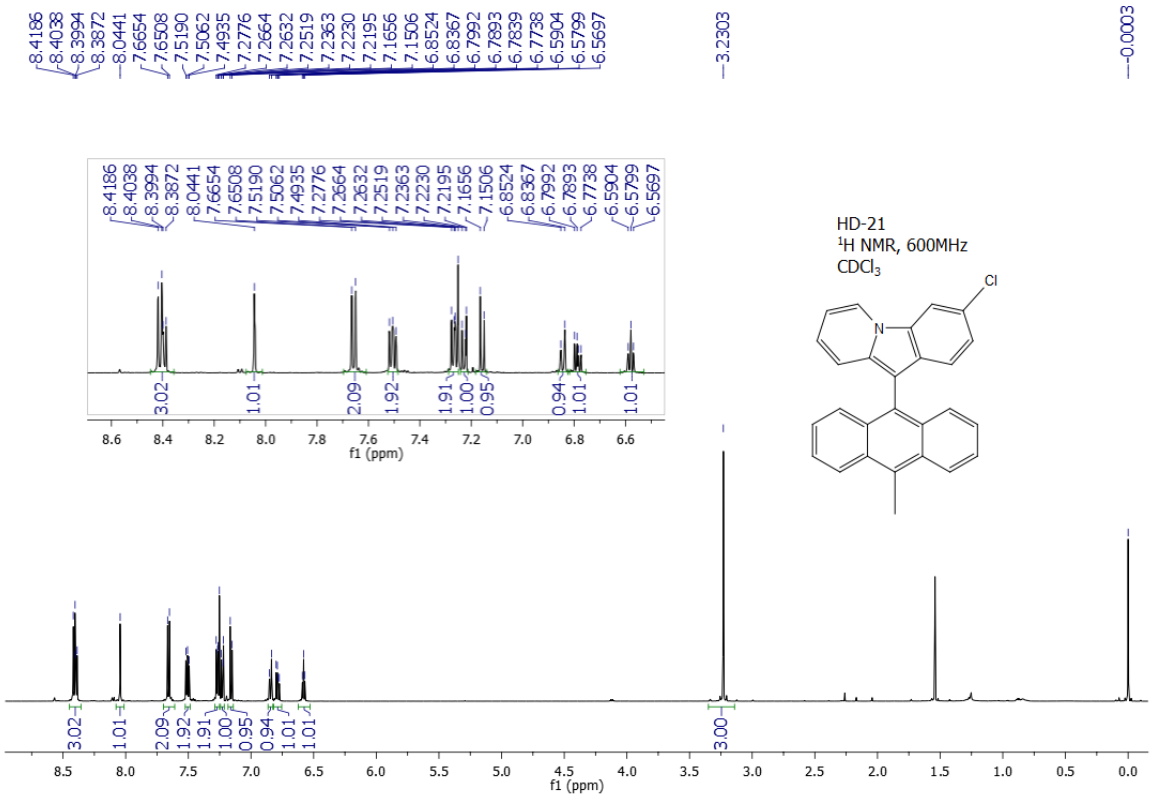


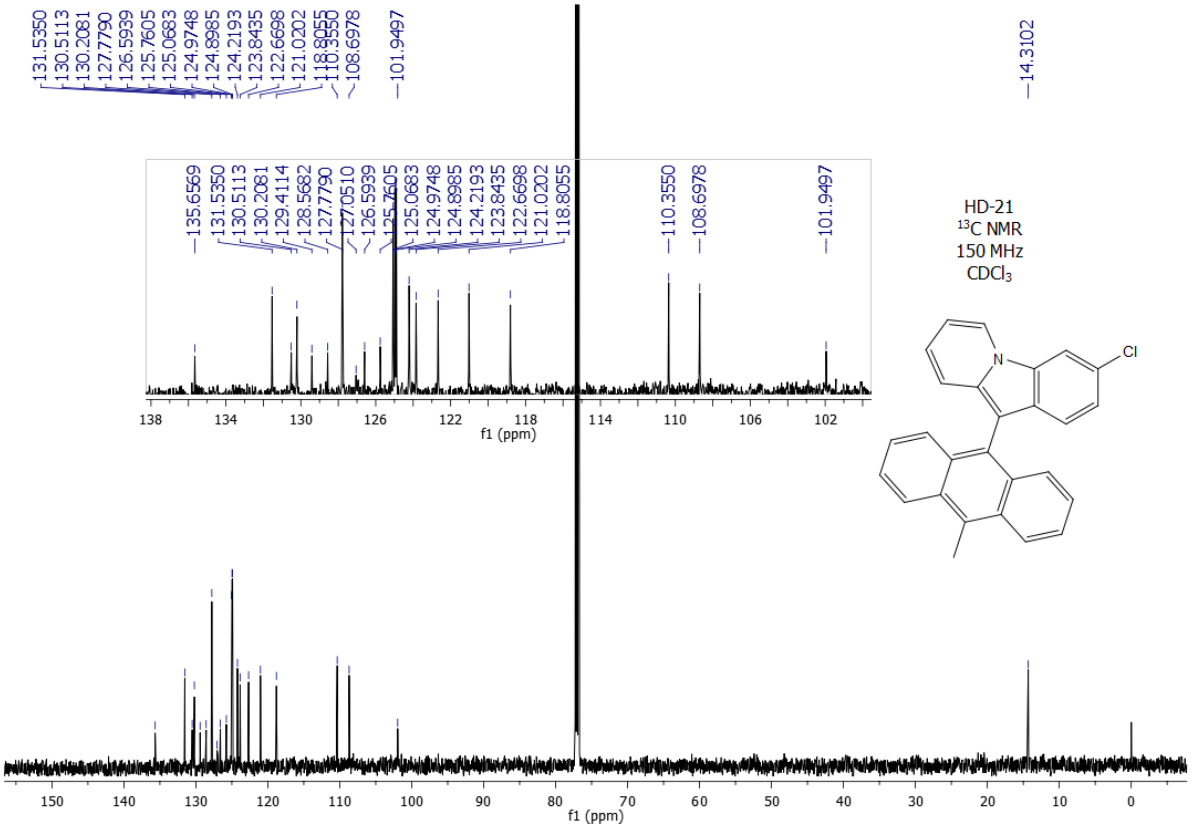


10-(anthracen-9-yl)-3-chloropyrido[1,2-a]indole (3aa):

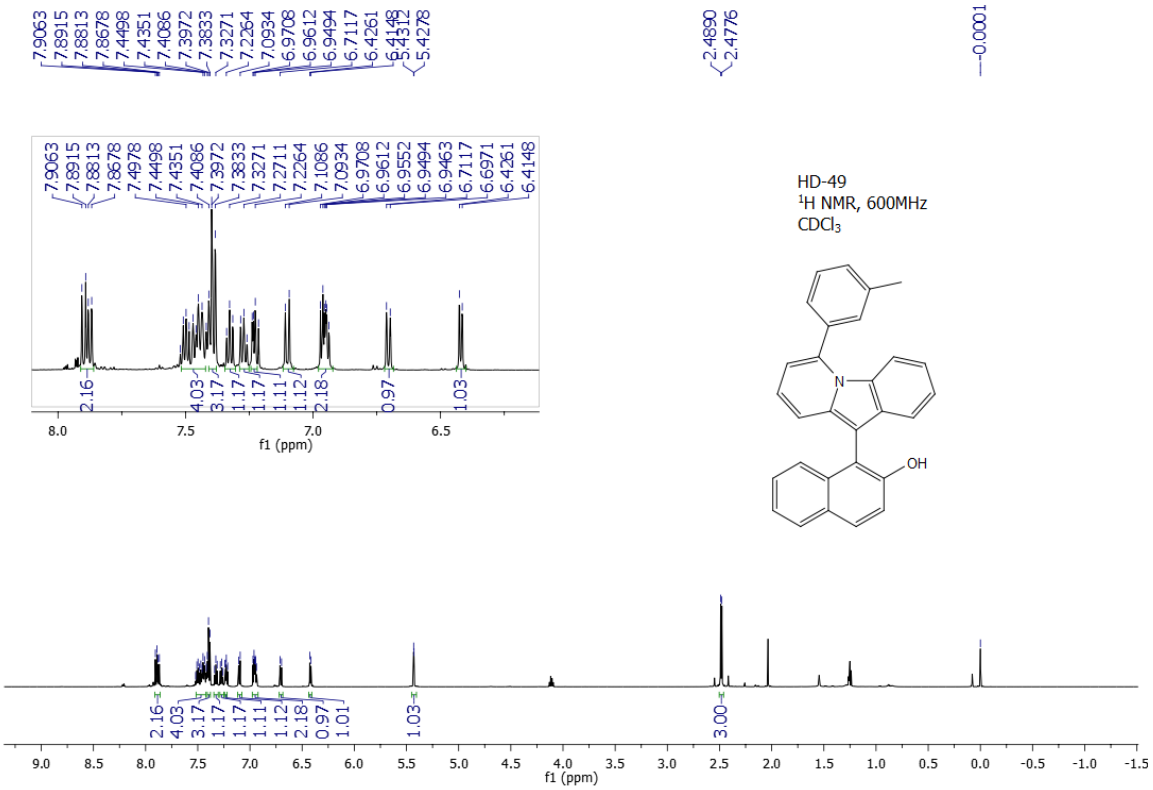


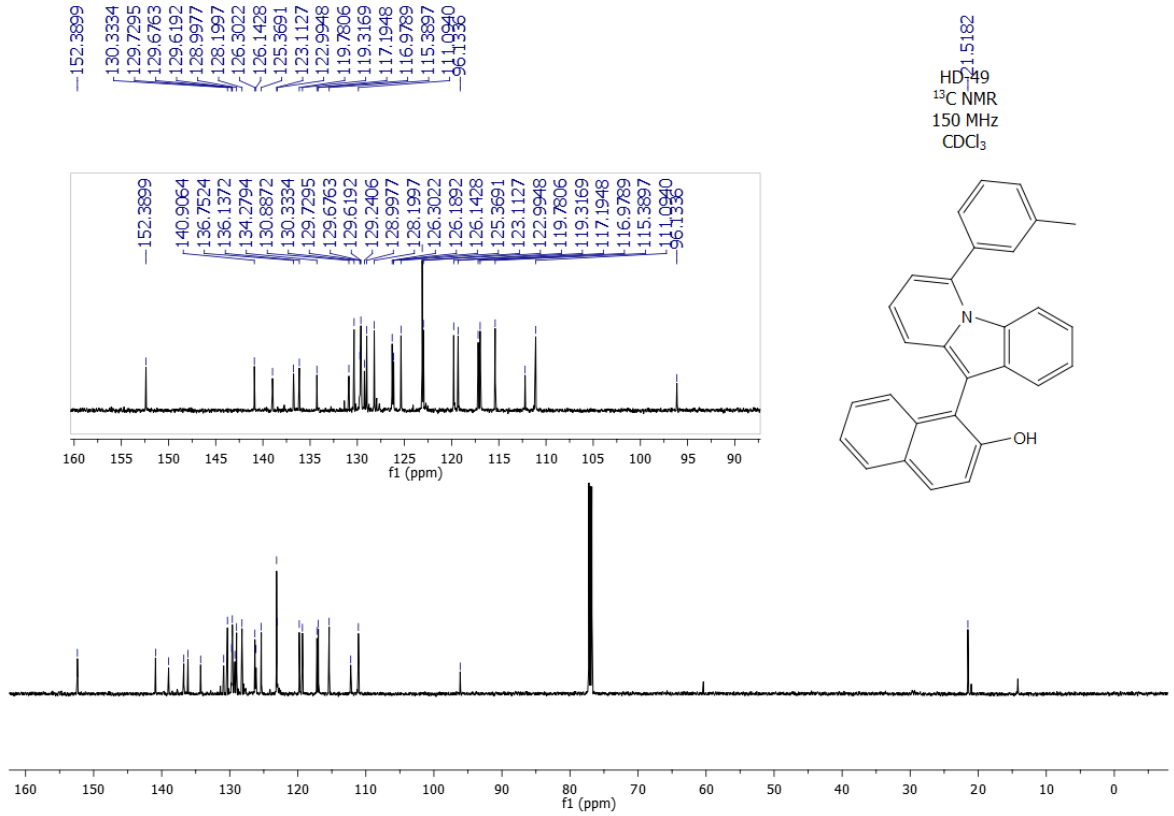
3-chloro-10-(10-methylanthracen-9-yl)pyrido[1,2-a]indole (3ab):



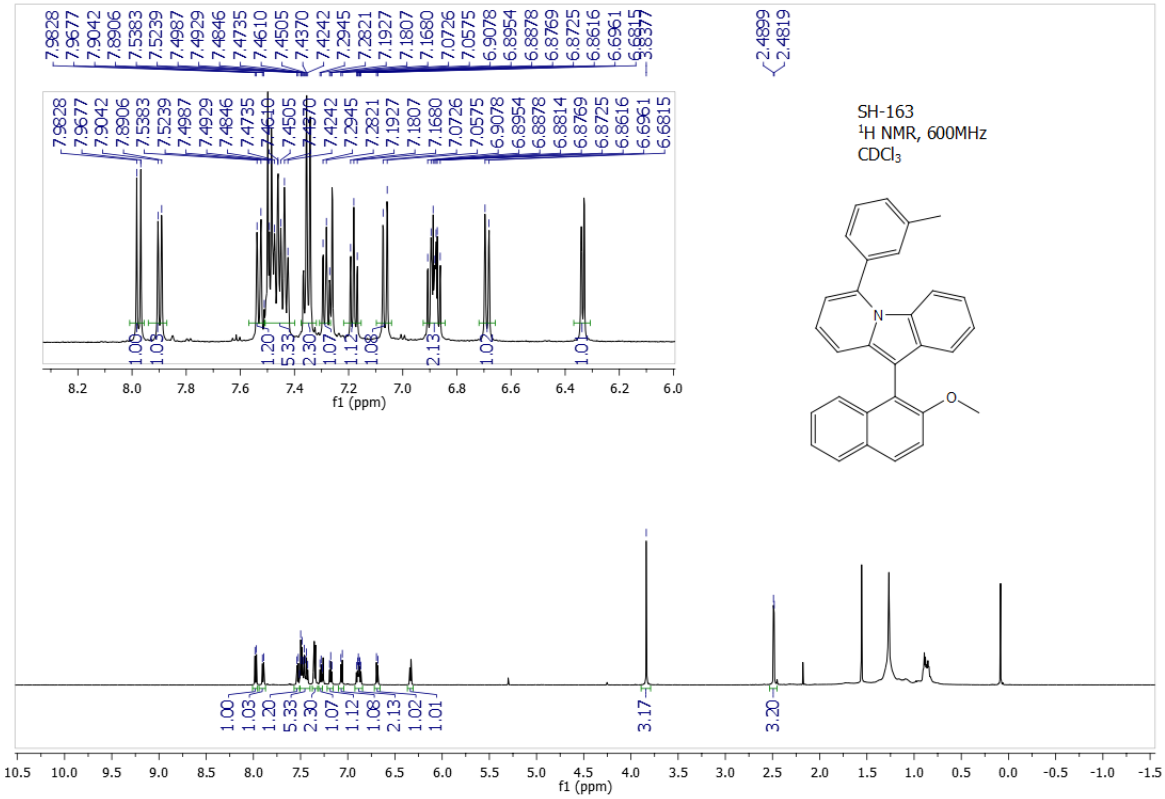


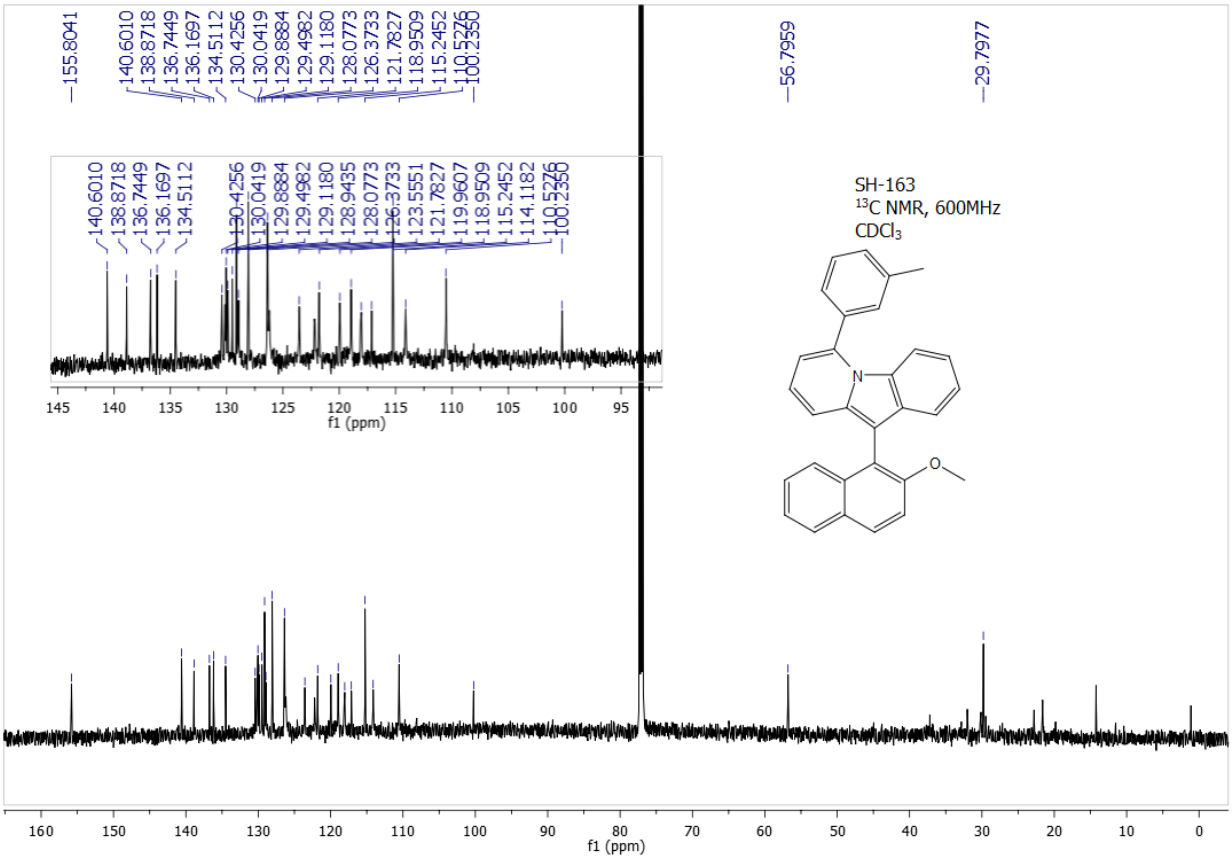
1-(6-(m-tolyl)pyrido[1,2-a]indol-10-yl)naphthalen-2-ol (3ac):



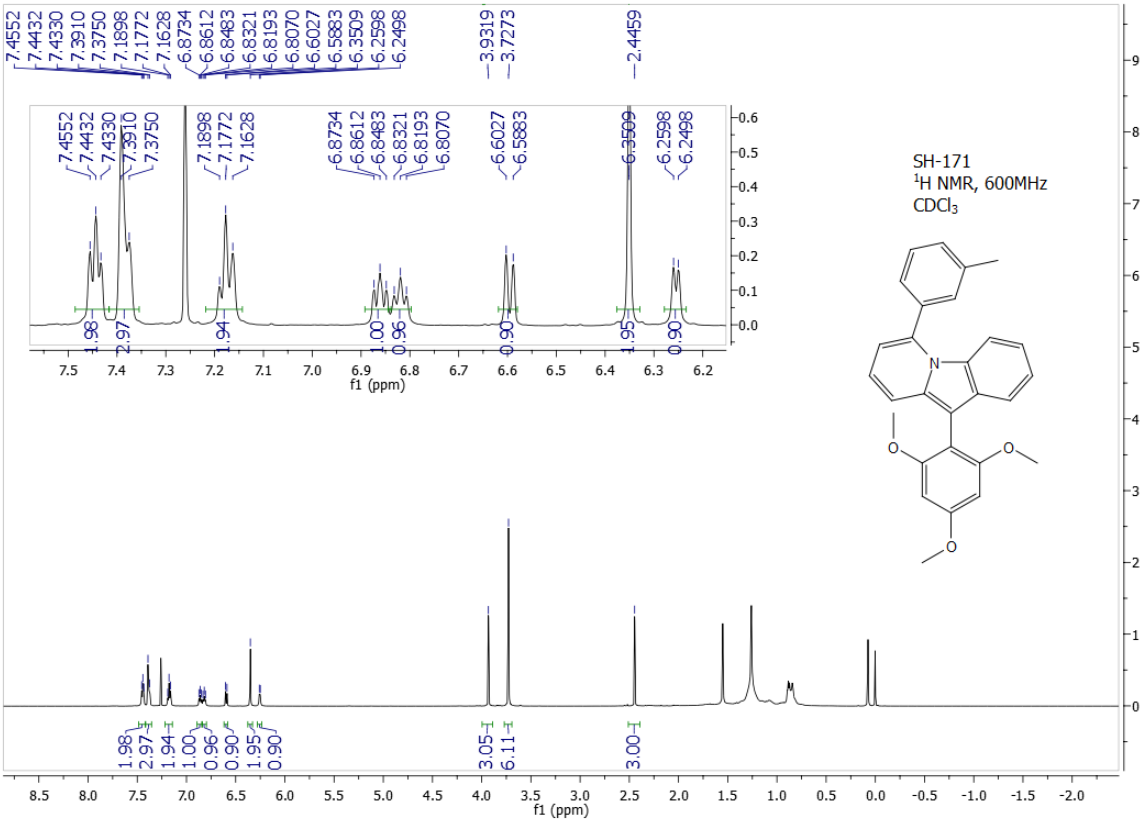


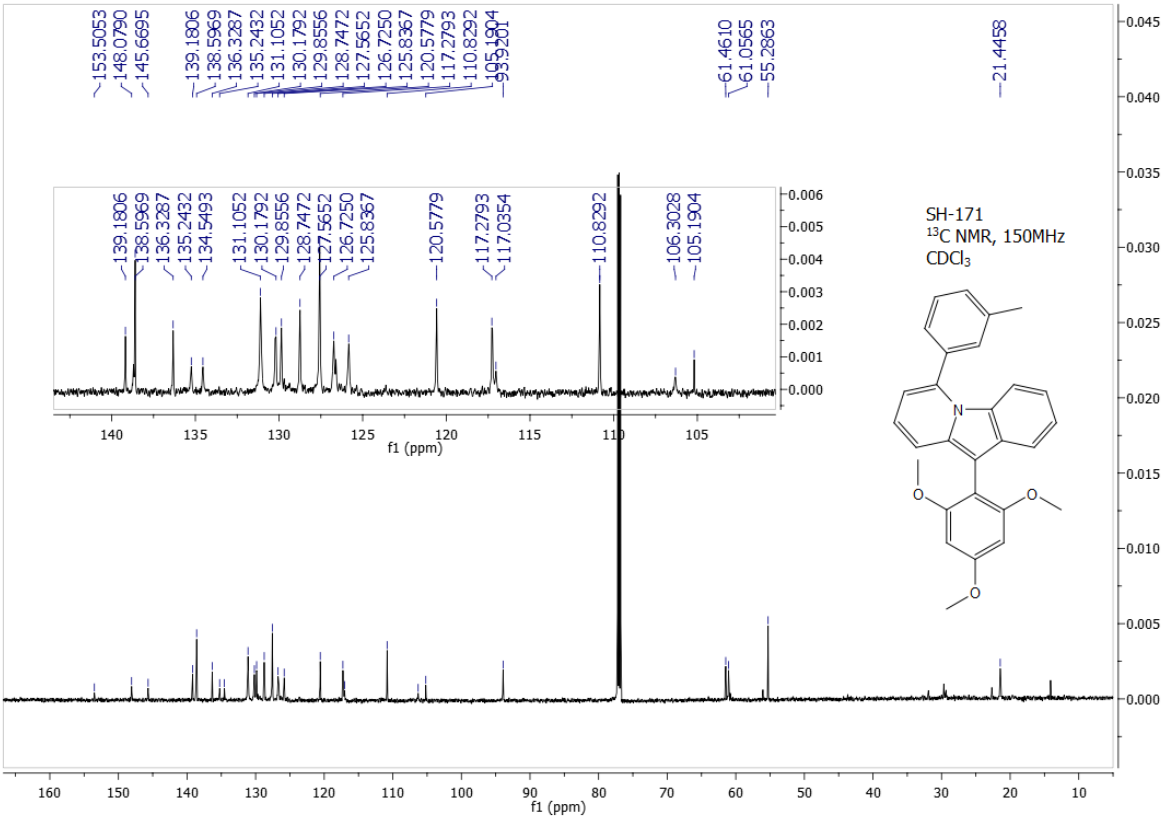
10-(2-methoxynaphthalen-1-yl)-6-(m-tolyl)pyrido[1,2-a]indole (3ad):



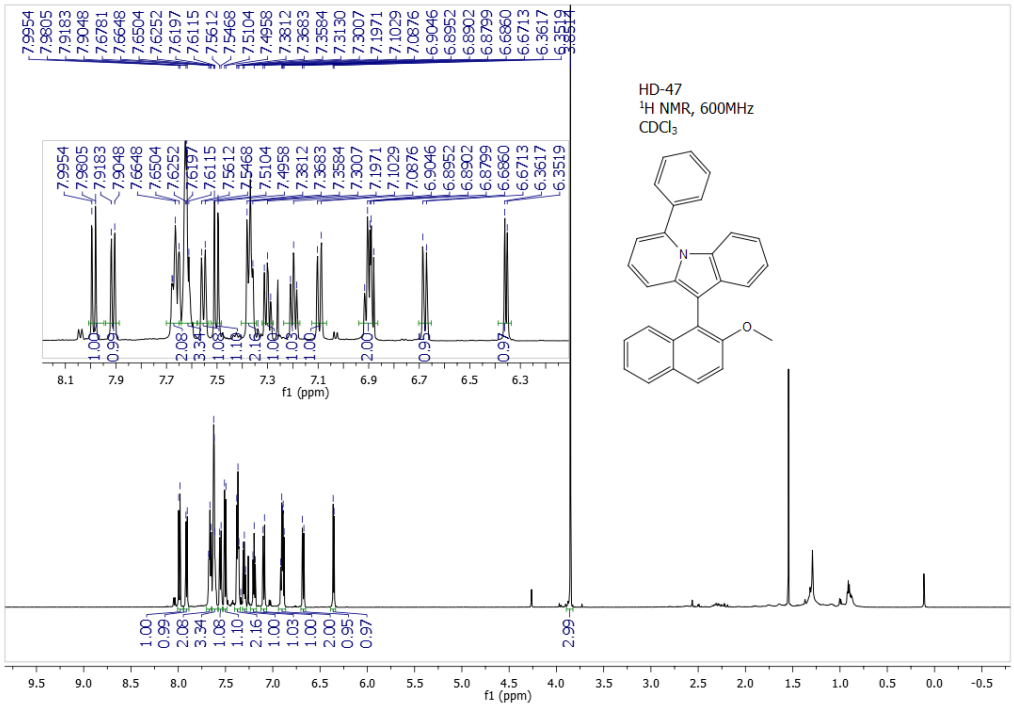


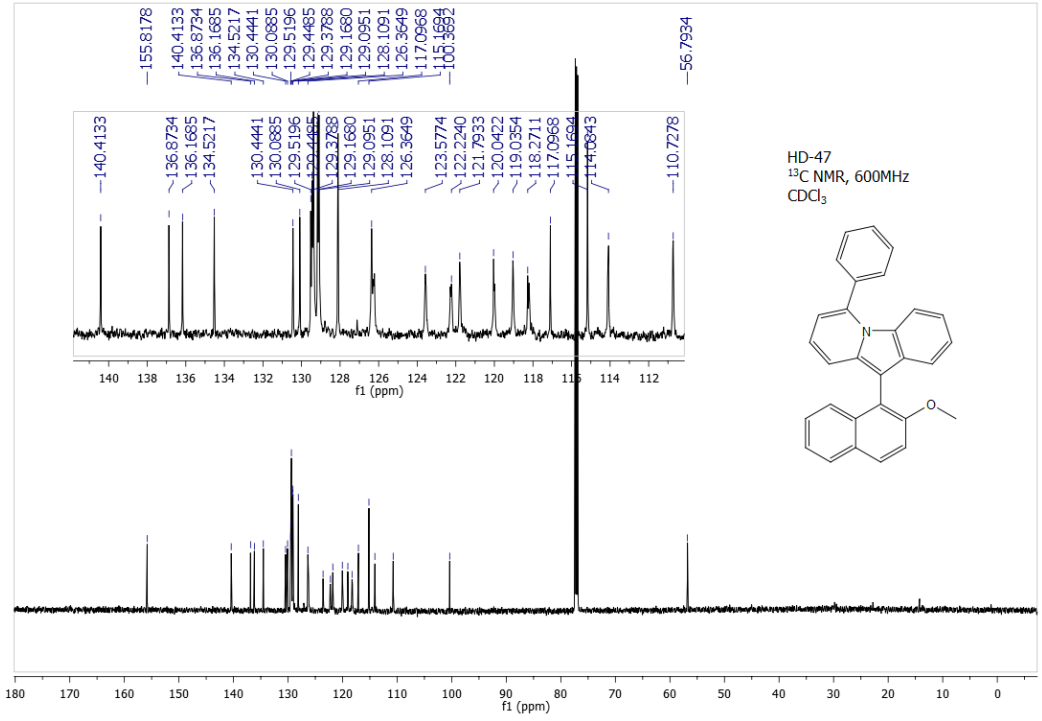
6-(m-tolyl)-10-(2,4,6-trimethoxyphenyl)pyrido[1,2-a]indole (3ae):



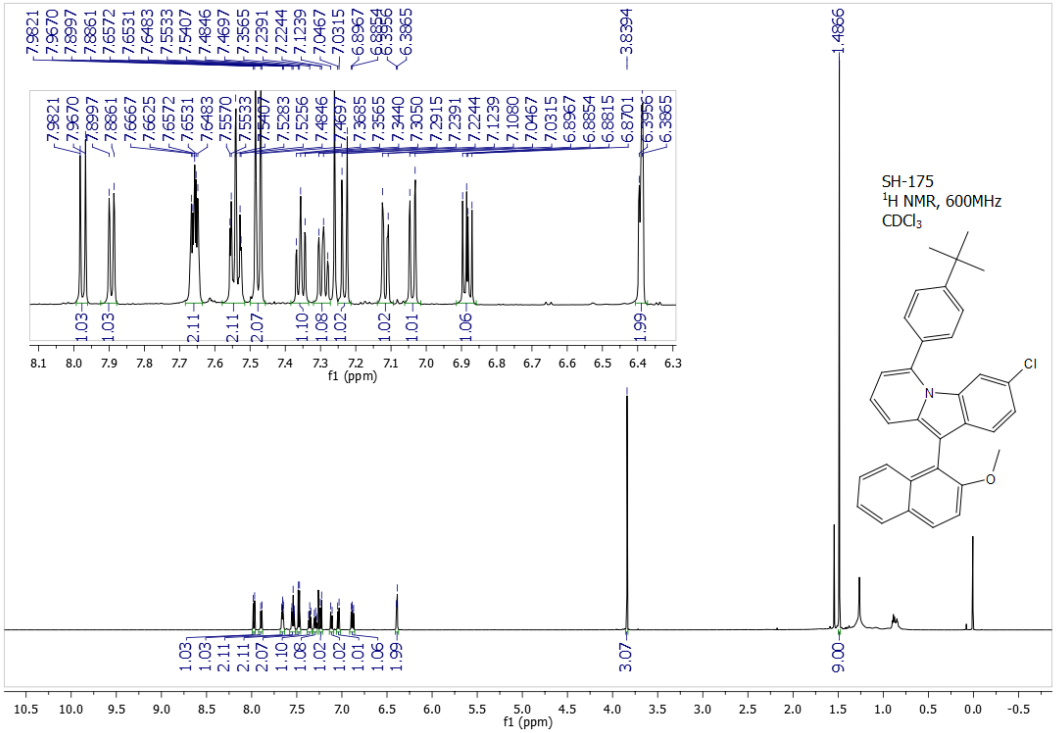


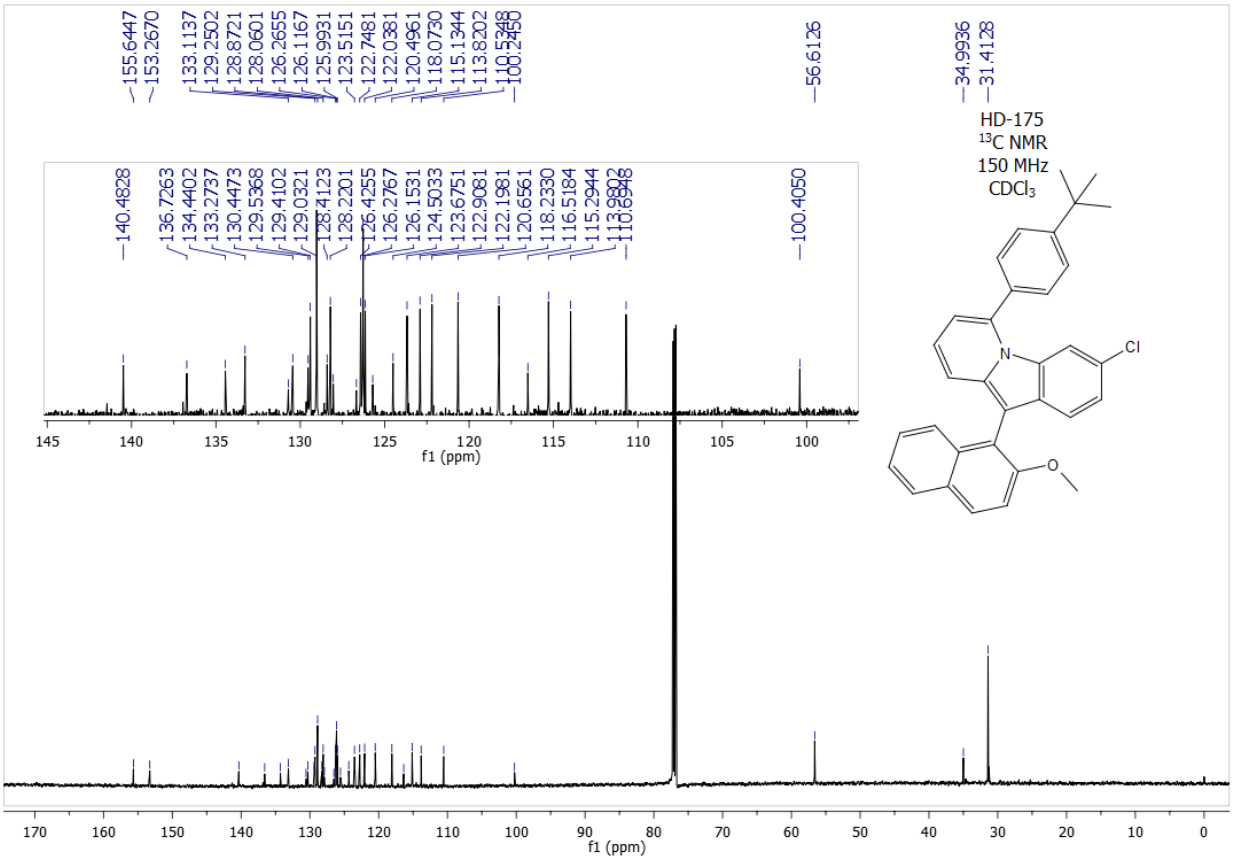
10-(2-methoxynaphthalen-1-yl)-7-phenylpyrido[1,2-a]indole (3af):



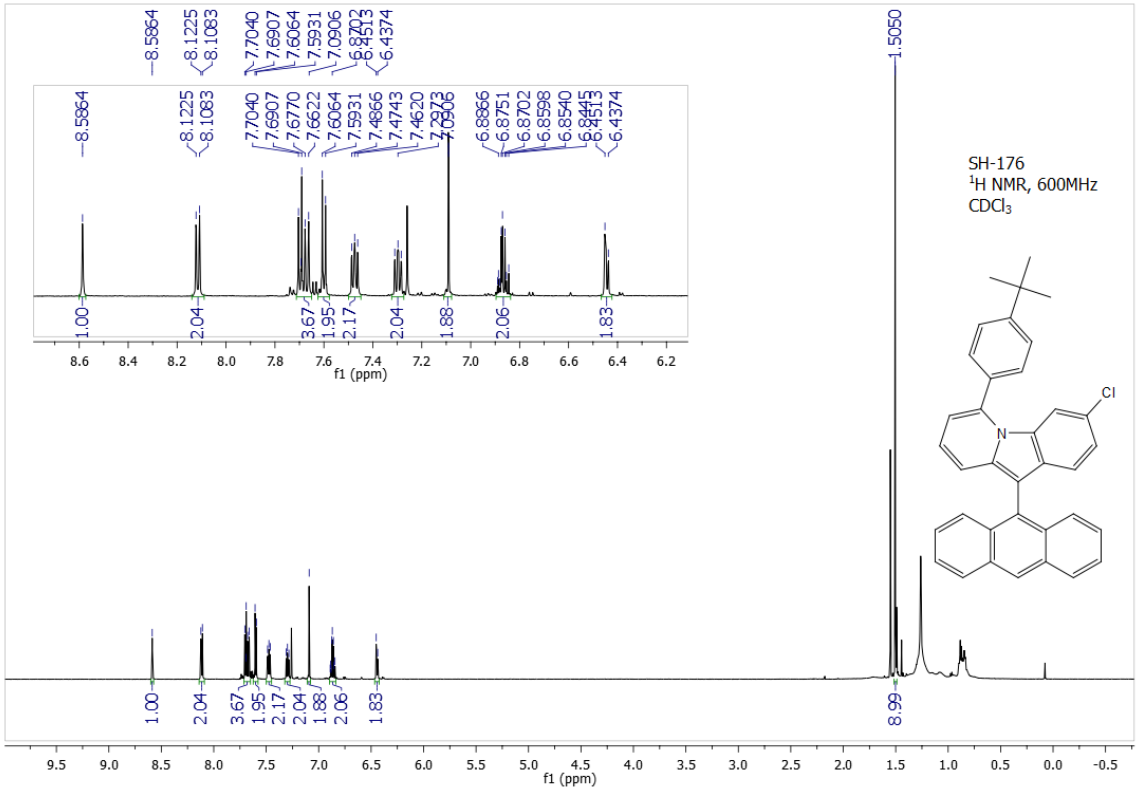


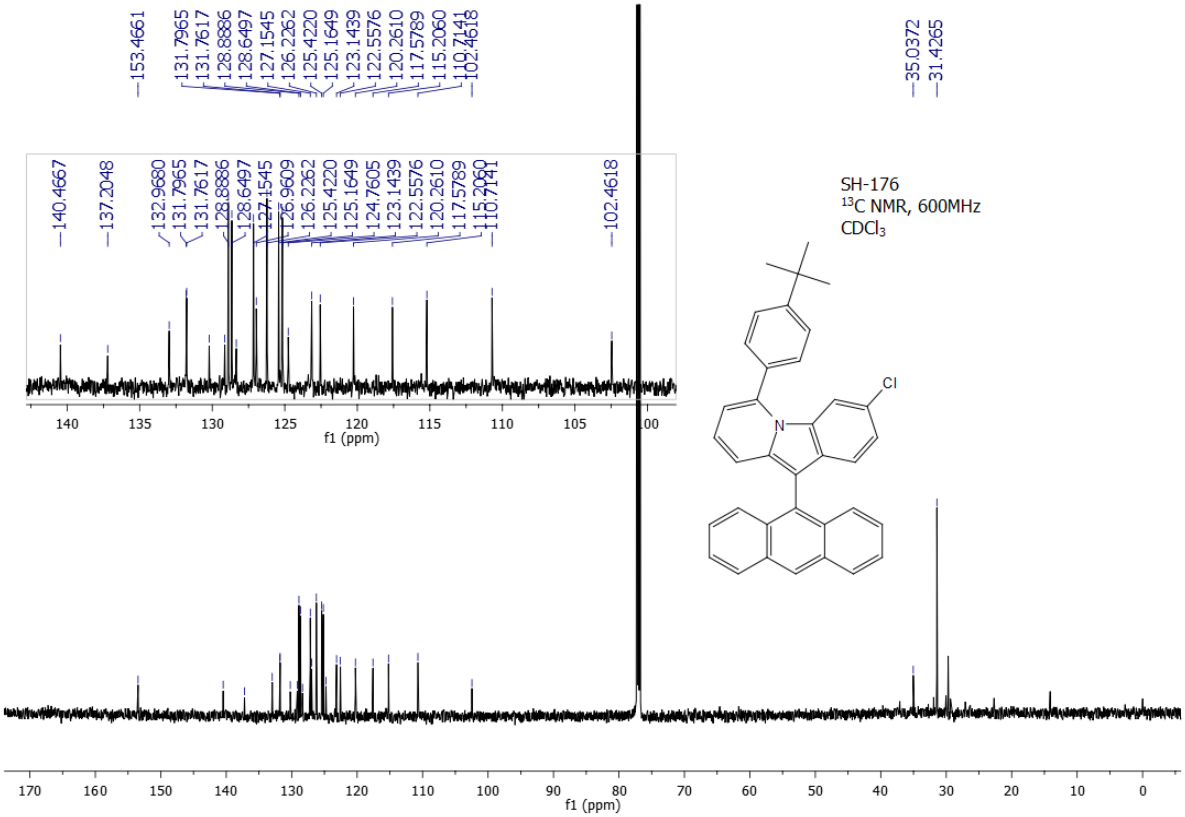
6-(4-tert-butyl)phenyl)-3-chloro-10-(2-methoxynaphthalen-1-yl)pyrido[1,2-a]indole (3ag):



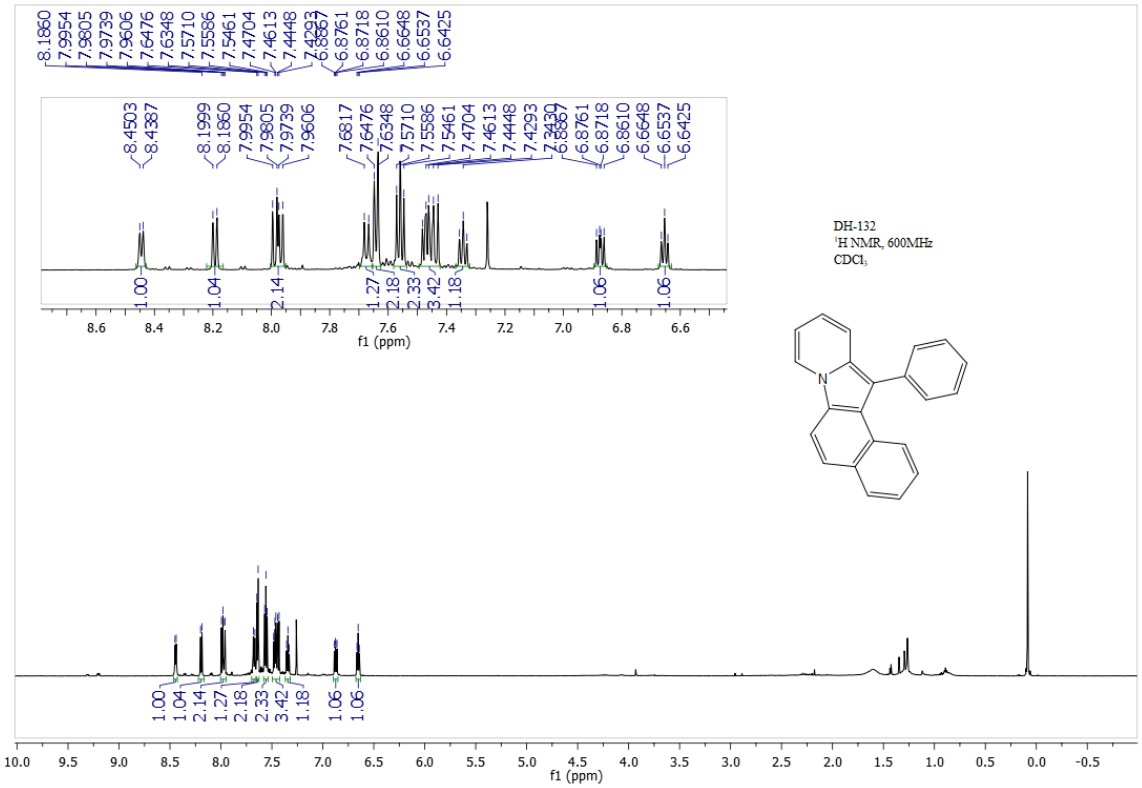


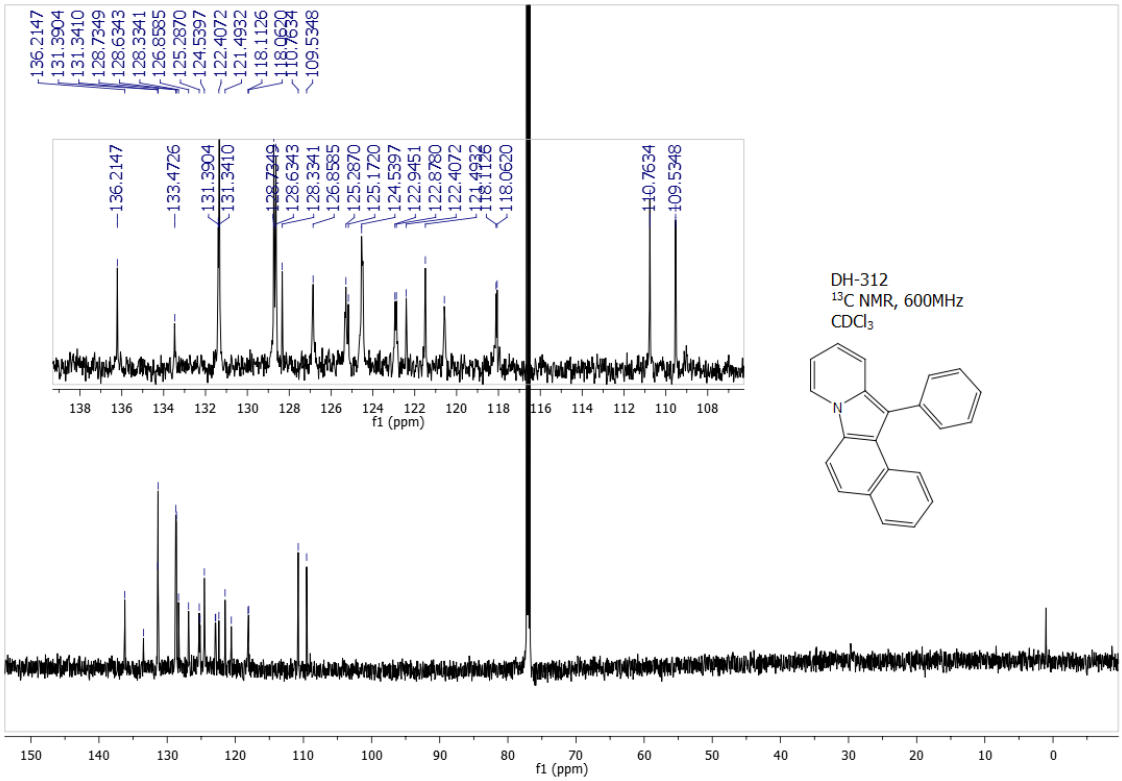
10-(Anthracen-9-yl)-6-(4-(*tert*-butyl)phenyl)-3-chloropyrido[1,2-a]indole (3ah):





12-Phenylbenzo[e]pyrido[1,2-a]indole (3ai):





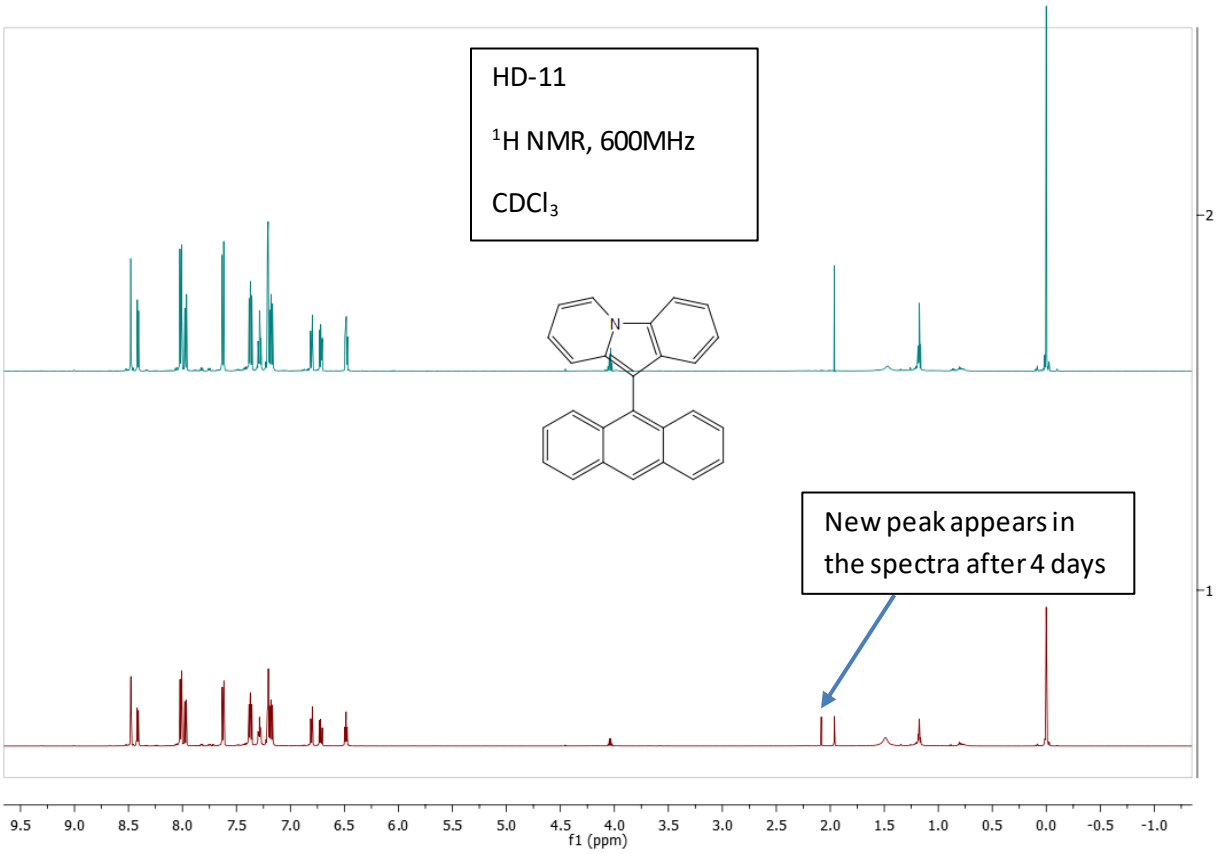


Figure S3. Comparative study of ^{1}H NMR of 3t, immediately and after 4 days