Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Rh/Cu-Catalyzed Multiple C-H, C-C and C-N Bonds Cleavage: Facile Synthesis of Pyrido[2,1-a]indoles from 1-(Pyridin-2-yl)-1*H*-indoles and *γ*-Substituted *tert*-Propargyl Alcohols

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1. General

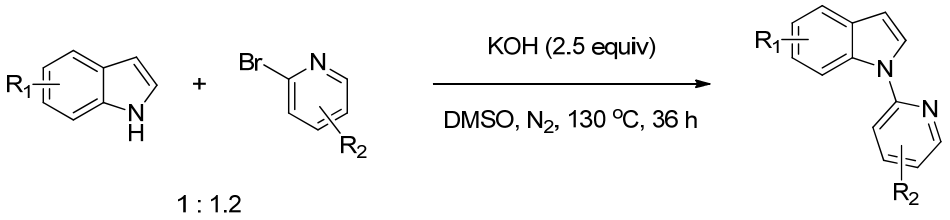
Unless otherwise noted, all reagents and solvents were obtained from commercial suppliers and used without further purification. All glassware was dried overnight at 110 °C prior to use. Chromatography was performed on 300-400 mesh silica gel. Melting points were determined on a Mel-Temp apparatus and are reported uncorrected. Mass spectra (HRMS) were obtained on Bruker En Apex ultra 7.0T FT-MS by the Public Instrument Platform of College of Chemistry and Chemical Engineering at Xiamen University.

^{1}H NMR spectra were recorded on a Bruker AV-400 spectrometer and a Bruker AV-500 spectrometer in chloroform-d_3. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data is being reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, brs = broad singlet, coupling constant (s) in Hz, integration).

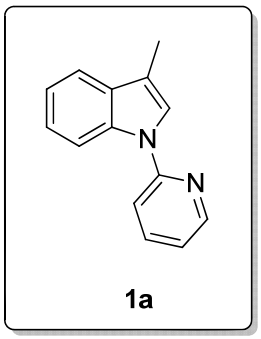
^{13}C NMR spectra were recorded on on a Bruker AV-400 spectrometer and a Bruker AV-500 spectrometer in chloroform-d_3. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard.

2. Preparation of Starting Materials

Compounds **1a-1o** were prepared according to the known procedures.[1]

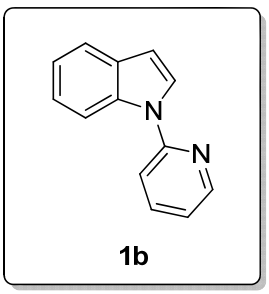


3-methyl-1-(pyridin-2-yl)-1*H*-indole (1a)



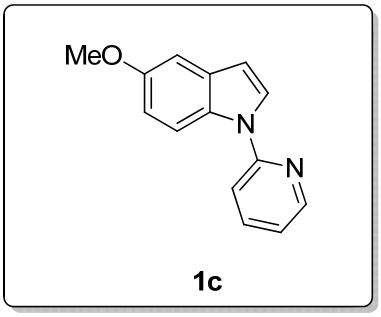
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.40 (m, 1H), 8.12 (d, *J* = 8.2 Hz, 1H), 7.60 (dt, *J* = 2.2 Hz, *J* = 8.6 Hz, 1H), 7.48 (m, 1H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.32 (m, 1H), 7.24 (m, 1H), 7.11 (dt, *J* =1.1 Hz, *J* = 7.4 Hz, 1H), 6.94 (m, 1H), 2.26 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 152.5, 148.7, 138.2, 135.3, 131.0, 123.2, 123.1, 120.8, 119.3, 119.0, 114.7, 113.8, 113.1, 9.6 ppm. This compound is known and the spectroscopic date match those reported.[1]

1-(pyridin-2-yl)-1*H*-indole (1b)



^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.61 (d, *J* = 4.0 Hz, 1H), 8.27 (d, *J* = 8.2 Hz, 1H), 7.83 (t, *J* = 6.5 Hz, 1H), 7.77 (d, *J* = 3.4 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.36 (t, *J* =7.7 Hz, 1H), 7.27 (t, *J* = 7.3 Hz, 1H), 7.19 (m, 1H), 6.77 (d, *J* =3.4 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 152.5, 148.9, 138.3, 135.1, 130.4, 126.0, 123.1, 121.2, 121.0, 120.0, 114.5, 113.0, 105.5 ppm. This compound is known and the spectroscopic date match those reported.[1]

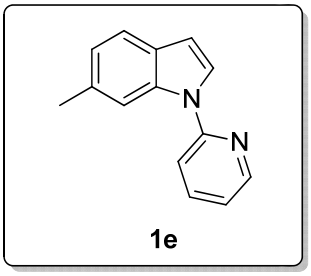
5-methoxy-1-(pyridin-2-yl)-1*H*-indole (1c)



1c

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.55 (d, *J* = 4.1 Hz, 1H), 8. 18 (d, *J* = 8.8 Hz, 1H), 7.80 (m, 1H), 7.70 (d, *J* = 3.4 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.14 (m, 2H), 6.95 (dd, *J* =1.9 Hz, *J* = 8.8 Hz, 1H), 6.67 (d, *J* = 3.9 Hz, 1H), 3.37 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 155.0, 152.6, 148.9, 138.4, 131.2, 130.2, 126.3, 119.7, 114.2, 113.9, 112.7, 105.4, 103.0, 55.8 ppm; This compound is known and the spectroscopic date match those reported.[1]

6-methyl-1-(pyridin-2-yl)-1*H*-indole (1e)

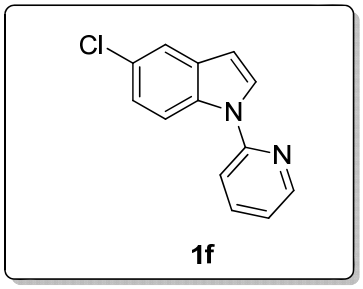


1e

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.60 = (dd, *J* = 1.0 Hz, *J* = 4.8 Hz, 1H), 8.17(d, *J* = 8.6 Hz, 1H), 7.81(m, 1H), 7.75(d, *J* = 3.4 Hz, 1H), 7.50 (br, 2H), 7.17(m, 2H), 6.69 (d, *J* = 3.4 Hz, 1H), 2.54 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 152.5, 148.8, 138.2, 133.3,

130.7, 130.5, 125.8, 124.5, 120.8, 120.0, 114.1, 112.7, 105.1, 21.3 ppm; HRMS m/z (ESI) Calcd for $C_{14}H_{12}N_2Na$ $(M+Na)^+$ 231.0893, found 231.0898.

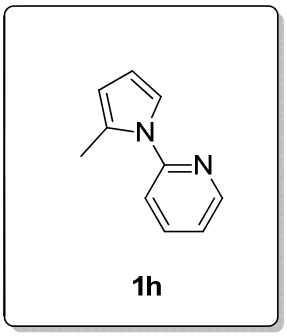
5-chloro-1-(pyridin-2-yl)-1*H*-indole (1f)



1f

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.59 (m, 1H), 8.23 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 1.5 Hz, *J* = 6.8 Hz, 1H), 7.73(d, *J* = 3.4 Hz, 1H), 7.64(d, *J* = 2.0 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.27 (dd, *J* =1.9 Hz, *J* =8.8 Hz, 1H), 7.20 (dd, *J* = 4.5 Hz, *J* = 7.1 Hz, 1H), 6.67 (d, *J* =3.9 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 152.3, 149.0, 138.5, 133.6, 131.5, 127.0, 126.8, 123.3, 120.4, 120.3, 114.4, 114.3, 105.0 ppm; This compound is known and the spectroscopic date match those reported.[1]

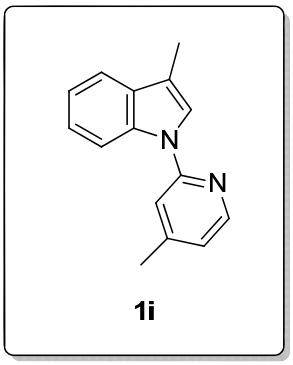
2-(2-methyl-1*H*-pyrrol-1-yl)pyridine (1h)



1h

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.53 (m 1H), 7.79 (m, 1H), 7.31 (dt, *J* = 0.9, 8.2 Hz, 1H), 7.20 (m, 1H), 7.09 (dd, *J* = 1.9, 3.0 Hz, 1H), 6.23 (t, *J* = 3.2 Hz, 1H), 6.07 (m, 1H), 2.45 (s, 3H), 2.25 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 153.0, 148.8, 138.2, 129.2, 120.9, 120.3, 117.0, 110.2, 109.1, 14.2 ppm; This compound is known and the spectroscopic date match those reported.[1]

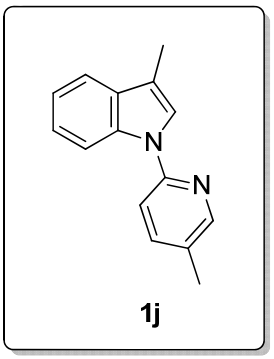
3-methyl-1-(4-methylpyridin-2-yl)-1*H*-indole (1i)



1i

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (s, 1H), 8.25 (d, *J* = 8.3 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.57 (d, *J* = 6.3 Hz, 1H), 7.54 (s, 1H), 7.33 (m, 3H), 2.46 (s, 3H), 2.39 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 150.5, 148.9, 139.0, 135.4, 130.9, 129.0, 123.5, 123.1, 120.6, 119.1, 114.2, 113.8, 112.9, 17.8, 9.8 ppm; HRMS m/z (ESI) Calcd for $C_{15}H_{14}N_2Na$ $(M+Na)^+$, 245.1049, found 245.1042.

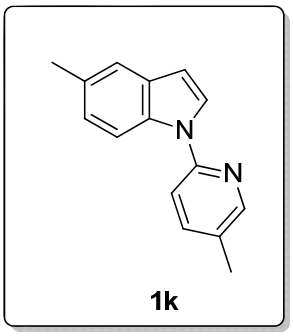
3-methyl-1-(5-methylpyridin-2-yl)-1*H*-indole (1j)



1j

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (dd, *J* = 6.4, 11.8 Hz, 1H), 8.27 (dd, *J* = 7.0, 11.8 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.54 (s, 1H), 7.35 (m, 1H), 7.28 (m, 3H), 6.96 (d, *J* = 8.2 Hz, 1H), 2.43 (s, 3H), 2.42 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 152.8, 149.6, 148.5, 135.4, 131.0, 123.4, 123.1, 120.8, 120.7, 119.1, 114.7, 114.5, 113.1, 21.3, 9.7 ppm; HRMS m/z (ESI) Calcd for $C_{15}H_{14}N_2Na$ $(M+Na)^+$, 245.1049, found 245.1042.

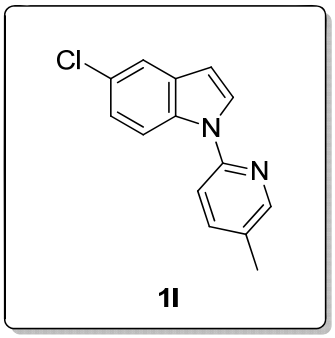
5-methyl-1-(5-methylpyridin-2-yl)-1*H*-indole (1k)



1k

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.26 (d, *J* = 1.7 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 3.4 Hz, 1H), 7.47 (dd, *J* = 1.9, 8.3 Hz, 1H), 7.34 (s, 1H), 7.25 (d, *J* = 8.3 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 1H), 6.51 (d, *J* = 3.5 Hz, 1H), 2.37 (s, 3H), 2.25 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 150.5, 149.0, 138.9, 133.4, 130.6, 130.3, 129.3, 126.1, 124.5, 120.8, 114.0, 112.4, 104.7, 21.4, 17.8 ppm; HRMS m/z (ESI) Calcd for $C_{15}H_{14}N_2Na$ $(M+Na)^+$, 245.1049, found 245.1042.

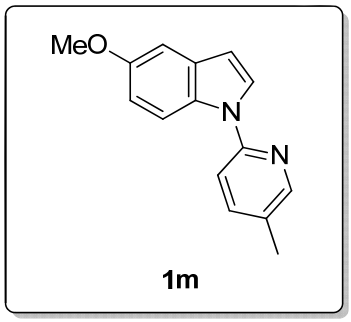
5-chloro-1-(5-methylpyridin-2-yl)-1*H*-indole (1l)



1l

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.31 (dd, *J* = 0.6, 1.6 Hz, 1H), 8.02 (d, *J* = 8.9 Hz, 1H), 7.60 (d, *J* = 3.5 Hz, 1H), 7.56 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.54 (d, *J* = 2.1 Hz, 1H), 7.27 (d, *J* = 8.3 Hz, 1H), 7.15 (dd, *J* = 2.3, 8.9 Hz, 1H), 6.56 (dd, *J* = 0.6, 3.4 Hz, 1H), 2.32 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 150.1, 149.0, 139.1, 133.5, 131.2, 130.0, 127.2, 126.6, 123.1, 120.4, 114.1, 114.0, 104.5, 17.8 ppm; HRMS m/z (ESI) Calcd for $C_{14}H_{11}N_2ClNa$ $(M+Na)^+$, 265.0503, found 265.0505.

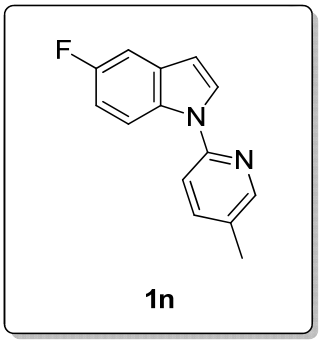
5-methoxy-1-(5-methylpyridin-2-yl)-1*H*-indole (1m)



1m

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.29 (dd, *J* = 0.5, 1.5 Hz, 1H), 8.00 (d, *J* = 9.1 Hz, 1H), 7.58 (d, *J* = 3.4 Hz, 1H), 7.53 (dd, *J* = 2.3, 8.4 Hz, 1H), 7.04 (d, *J* = 2.5 Hz, 1H), 6.85 (dd, *J* = 2.5, 9.1 Hz, 1H), 6.54 (d, *J* = 3.2 Hz, 1H), 3.80 (s, 3H), 2.30 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 154.9, 150.4, 148.9, 138.9, 130.9, 130.2, 129.3, 126.4, 113.8, 112.6, 104.8, 102.9, 55.8, 17.8 ppm; HRMS m/z (ESI) Calcd for $C_{15}H_{14}N_2ONa$ $(M+Na)^+$, 261.0998, found 261.0991.

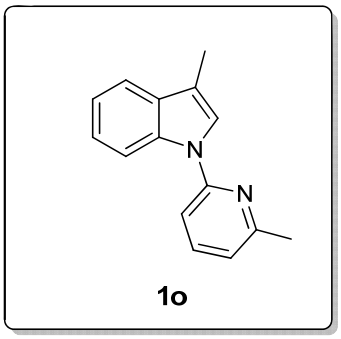
5-fluoro-1-(5-methylpyridin-2-yl)-1*H*-indole (1n)



1n

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.27 (s, 1H), 8.04 (dd, *J* = 4.6, 9.1 Hz, 1H), 7.58 (t, *J* = 3.1 Hz, 1H), 7.50 (t, *J* = 5.7 Hz, 1H), 7.22 (m, 2H), 6.92 (t, *J* = 9.5 Hz, 1H), 6.55 (m, 1H), 2.27 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 158.4 (J_{CF} = 235.6 MHz), 150.3, 148.9, 139.1, 131.7, 130.8 (J_{CF} = 10.1 MHz), 129.8, 127.4, 114.0, 113.9, 111.0 (J_{CF} = 25.6 MHz), 105.8 (J_{CF} = 23.1 MHz), 104.8 (J_{CF} = 4.1 MHz), 17.8 ppm; HRMS m/z (ESI) Calcd for $C_{14}H_{11}N_2FNa$ $(M+Na)^+$, 249.0798, found 249.0799.

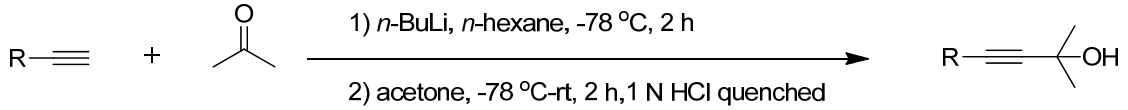
3-methyl-1-(6-methylpyridin-2-yl)-1*H*-indole (1o)



1o

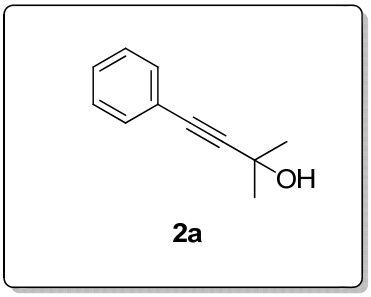
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 8.4 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 1.1 Hz, 1H), 7.23 (t, *J* = 9.0 Hz, 1H), 7.16 (m, 2H), 6.90 (d, *J* = 7.5 Hz, 1H), 2.55 (s, 3H), 2.31 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 158.1, 152.0, 138.4, 135.4, 131.0, 123.3, 123.0, 120.6, 119.0, 118.8, 114.4, 113.2, 110.8, 24.4, 9.6 ppm. HRMS m/z (ESI) Calcd for $C_{15}H_{14}N_2Na$ $(M+Na)^+$, 245.1049, found 245.1042.

Compounds **2a-2l** were prepared according to the known procedures.[2-3]



R = Ar, Alkanyl

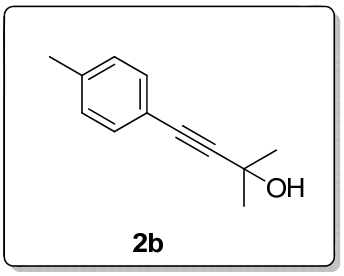
2-methyl-4-phenylbut-3-yn-2-ol (2a)



2a

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34 (m, 2H), 7.21 (m, 3H), 2.16 (br, 1H), 1.54 (s, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 159.5, 133.0, 114.8, 113.8, 92.5, 81.9, 65.5, 55.2, 31.5 ppm. This compound is known and the spectroscopic date match those reported.[2]

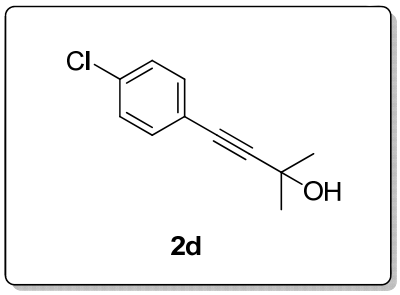
2-methyl-4-(p-tolyl)but-3-yn-2-ol (2b)



2b

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.19 (d, *J* = 8.1 Hz, 2H), 6.97 (d, *J* = 8.1 Hz, 2H), 2.21 (br, 1H), 1.49 (s, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ =138.3, 131.5, 129.0, 119.7, 93.2, 82.2, 65.6, 31.5, 21.4 ppm. This compound is known and the spectroscopic date match those reported.[2]

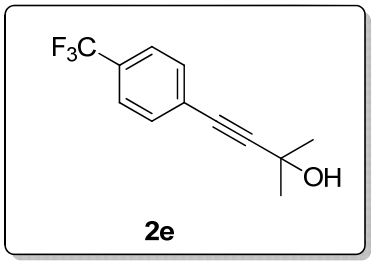
4-(4-chlorophenyl)-2-methylbut-3-yn-2-ol (2d)



2d

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 2.20 (br, 1H), 1.53 (s, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 134.2, 132.8, 128.5, 121.2, 94.7, 81.0, 65.5, 31.4. This compound is known and the spectroscopic date match those reported.[2]

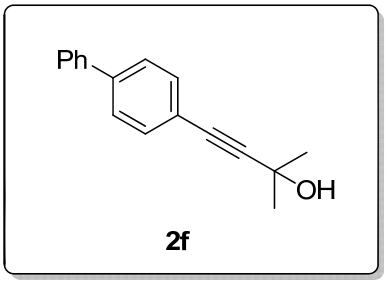
2-methyl-4-(4-(trifluoromethyl)phenyl)but-3-yn-2-ol (2e)



2e

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (m, 4H), 2.34 (br, 1H), 1.65 (s, 6H) ppm. This compound is known and the spectroscopic date match those reported.[2]

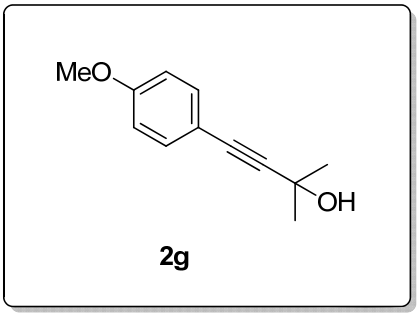
4-([1,1'-biphenyl]-4-yl)-2-methylbut-3-yn-2-ol (2f)



2f

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 7.9 Hz, 2H), 7.46 (d, *J* = 7.9 Hz, 2H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 8.2 Hz, 3H), 1.99 (br, 1H), 1.56 (s, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 141.0, 140.3, 132.0, 128.8, 127.6, 127.0, 126.9, 121.6, 94.4, 82.0, 65.7, 31.5 ppm. This compound is known and the spectroscopic date match those reported.[2]

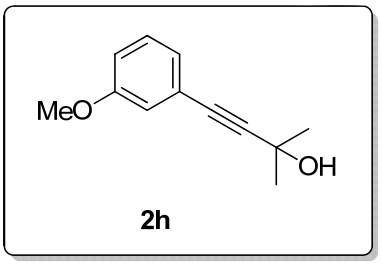
4-(4-methoxyphenyl)-2-methylbut-3-yn-2-ol (2g)



2g

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.26 (d, *J* = 7.7 Hz, 2H), 6.73 (d, *J* = 7.7 Hz, 2H), 3.71 (s, 3H), 2.32 (br, 1H), 1.55 (s, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 159.5, 133.0, 114.8, 113.8, 92.5, 81.9, 65.5, 55.2, 31.5 ppm. This compound is known and the spectroscopic date match those reported.[2]

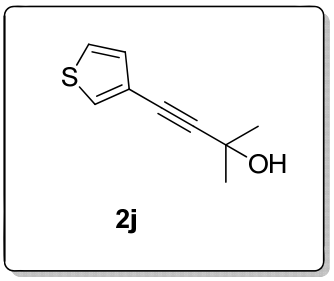
4-(3-methoxyphenyl)-2-methylbut-3-yn-2-ol (2h)



2h

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (m, 1H), 7.02 (m, 1H), 6.96 (m, 1H), 6.87 (m, 1H), 3.81 (s, 3H), 2.21 (br, 1H), 1.64 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 159.3, 129.3, 124.2, 123.8, 116.5, 114.9, 93.7, 82.1, 65.6, 55.3, 31.5 ppm. This compound is known and the spectroscopic date match those reported.[2]

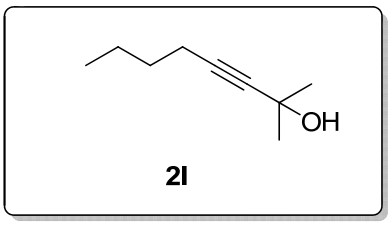
2-methyl-4-(thiophen-3-yl)but-3-yn-2-ol (2j)



2j

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.27 (m, 1H), 7.10 (m, 1H), 6.95 (m, 1H), 2.38 (br, 1H), 1.5347 (s, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 129.9, 128.6, 125.3, 121.8, 93.5, 77.3, 65.6, 41.5 ppm. This compound is known and the spectroscopic date match those reported.[2]

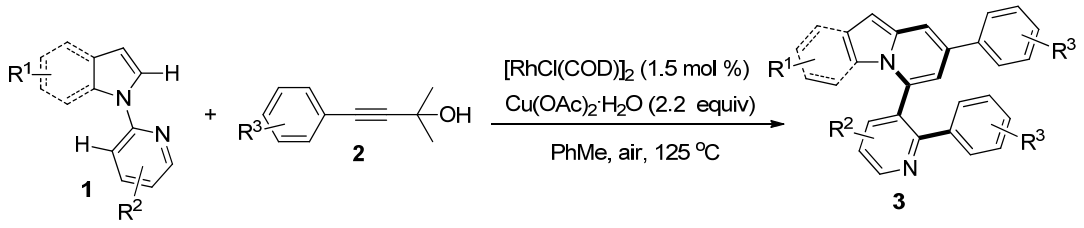
2-methyloct-3-yn-2-ol (2l)



2l

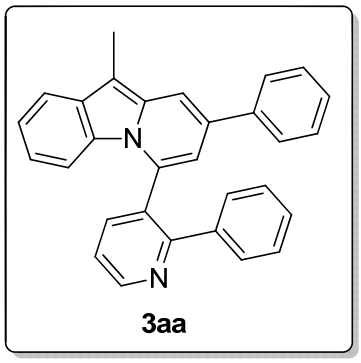
^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.20 (m, 3H), 1.51 (s, 6H), 1.43 (m, 3H), 1.23 (br, 1H), 1.05 (br, 1H), 0.93 (m, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 85.07, 82.58, 65.30, 31.77, 21.90, 18.25, 13.58 ppm. This compound is known and the spectroscopic date match those reported.[2]

3. General Procedure



A mixture of 1-(pyridin-2-yl)-1*H*-indole derivatives **1** (0.20 mmol), *γ*-substituted *tert*-propargyl alcohols **2** (0.80 mmol), $[RhCl(COD)]_2$ (1.5 mol %), $Cu(OAc)_2{\cdot}H_2O$ (88 mg, 0.44 mmol) and toluene (2 mL) were added to a Schlenk tube under an air atmosphere. Then the mixture was stirred at 125 °C (bath temperature, pre-heated) under air for desired time (usually 6 h) until complete consumption of starting materials judged by TLC. Then the reaction mixture was filtered through a short plug of silica gel, washed with ethyl acetate and concentrated, the residue was purified by chromatography (ethyl acetate/ hexane = 1/100 to 1/20) to afford the desired products **3**.

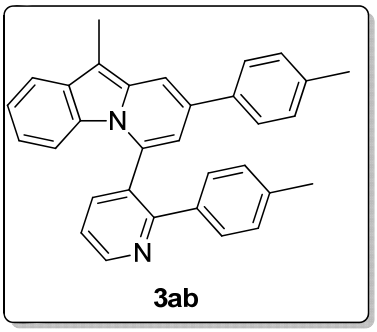
10-methyl-8-phenyl-6-(2-phenylpyridin-3-yl)pyrido[1,2-a]indole (3aa)



3aa: Yield: 78%; yellow solid, 64 mg; m.p: 152-154 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 7.6 Hz, 2H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.68-7.60 (m, 4H), 7.55 (s, 1H), 7.44 (t, *J* = 7.0 Hz, 2H), 7.37-7.30 (m, 2H), 7.21-7.19 (m, 2H), 7.03-6.97 (m, 4H), 6.52 (d, *J* = 8.5 Hz, 1H), 2.48 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 150.0, 141.7, 141.4, 139.5, 138.3, 134.9, 133.7, 131.5, 130.7, 130.4, 129.2, 128.9, 128.5, 128.4, 128.2, 128.1, 127.8, 127.2, 126.1, 123.3, 120.6, 117.9, 114.4, 104.8, 101.8, 7.9 ppm; HRMS m/z (ESI) Calcd for $C_{30}H_{23}N_2$ $(M+H)^+$, 411.1856, found 411.1859.

10-methyl-8-(p-tolyl)-6-(2-(p-tolyl)pyridin-3-yl)pyrido[1,2-a]indole (3ab)

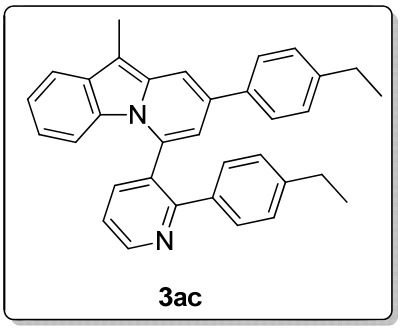


3ab

3ab: Yield: 66%; yellow solid, 58 mg; m.p: 207-209 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 8.3 Hz, 2H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.62-7.56 (m, 4H), 7.51 (s, 1H), 7.30 (t, *J* = 7.1 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.1 (d, *J* = 8.4 Hz, 2H), 6.95 (t, *J* = 7.3 Hz, 1H), 6.81 (d, *J* = 7.7 Hz, 2H), 6.45 (d, *J* = 8.7 Hz, 1H), 2.47 (s, 3H), 2.40 (s, 3H), 2.12 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 150.0, 141.7, 141.3, 138.0, 136.8, 136.7, 135.5, 134.9, 133.8, 131.5, 130.7, 130.3, 129.3, 129.1, 128.9, 128.6, 128.3, 127.9, 126.0, 123.2, 120.4, 117.8, 114.5, 104.1, 101.4, 21.2, 20.9, 7.9 ppm; HRMS m/z (ESI) Calcd for $C_{32}H_{27}N_2$ $(M+H)^+$, 439.2169, found 439.2172.

8-(4-ethylphenyl)-6-(2-(4-ethylphenyl)pyridin-3-yl)-10-methylpyrido[1,2-a]indole (3ac)



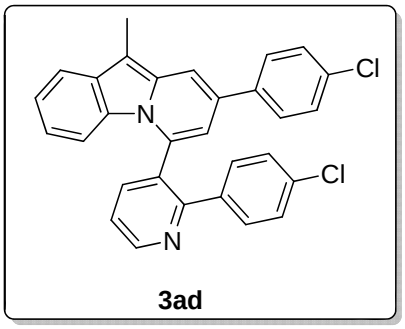
3ac

3ac: Yield: 76%; yellow solid, 71 mg; m.p: 220-222 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.2 Hz, 2H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.55-7.44 (m, 4H), 7.41 (s, 1H), 7.17 (m, 3H), 7.00 (d, *J* = 8.1 Hz, 2H), 6.85 (t, *J* = 8.1 Hz, 1H), 6.73 (d, *J* = 8.1 Hz, 2H), 6.37 (d, *J* = 8.5 Hz, 1H), 2.60 (q, *J* = 7.6 Hz, 2H), 2.36 (s, 3H), 2.32 (q, *J* = 7.8 Hz, 2H), 1.18 (q, *J* = 7.6 Hz, 3H), 0.95 (q, *J* = 7.8 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 150.1, 144.4, 143.1, 141.8, 141.3, 136.8, 135.8, 134.8,

133.8, 131.5, 130.6, 130.3, 129.2, 128.9, 128.3, 129.1, 127.9, 127.3, 126.1, 123.2, 120.3, 117.7, 114.5, 104.2, 101.3, 28.7, 28.3, 15.6, 15.2, 7.9 ppm; HRMS m/z (ESI) Calcd for $C_{34}H_{31}N_2$ $(M+H)^+$, 467.2482, found 467.2484.

8-(4-chlorophenyl)-6-(2-(4-chlorophenyl)pyridin-3-yl)-10-methylpyrido[1,2-a]indole (3ad)

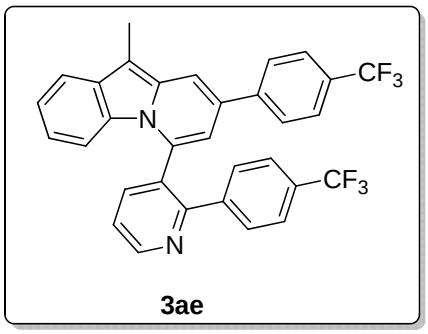


3ad

3ad: Yield: 67%; yellow solid, 64 mg; m.p: 202-204 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 8.9 Hz, 2H), 7.73 (t, *J* = 7.1 Hz, 1H), 7.68-7.62 (m, 3H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.53 (s, 1H), 7.40 (d, *J* = 8.7 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.1 Hz, 2H), 7.00-6.96 (m, 3H), 6.41 (d, *J* = 8.6 Hz, 2H), 2.48 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 149.8, 140.3, 140.0, 137.9, 136.6, 134.7, 134.1, 133.4, 133.3, 131.5, 130.6, 130.5, 129.6, 129.2, 128.8, 128.7, 128.6, 128.0, 127.2, 123.4, 120.9, 118.2, 114.2, 105.0, 102.5, 7.9 ppm; HRMS m/z (ESI) Calcd for $C_{30}H_{21}Cl_2N_2$ $(M+H)^+$, 479.1076, found 479.1077.

10-methyl-8-(4-(trifluoromethyl)phenyl)-6-(2-(4-(trifluoromethyl)phenyl)pyridin-3-yl)pyrido[1,2-a]indole (3ae)

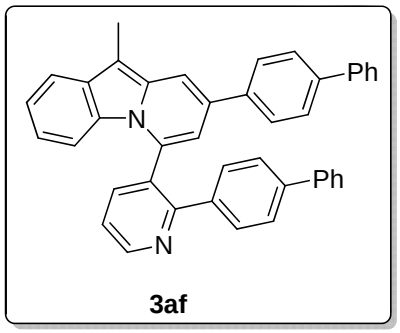


3ae

3ae: Yield: 41%; yellow solid, 45 mg; m.p: 192-194 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 6.9 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.62 (m, 2H), 7.60 (m, 1H), 7.54 (m, 3H), 7.25 (t, *J* = 7.2 Hz, 1H), 7.17 (m, 4H), 6.91 (t, *J* = 5.7 Hz, 1H), 6.38 (d, *J* = 8.6 Hz, 1H), 2.40 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 149.8, 143.0, 141.3, 139.8, 134.6, 133.1, 132.8, 131.5, 130.8, 130.6, 129.3, 129.1, 128.9, 128.7, 126.1, 125.6, 125.5, 124.7, 123.7, 121.3, 118.5, 114.2, 106.3, 103.5, 7.9 ppm; HRMS m/z (ESI) Calcd for $C_{32}H_{20}F_6N_2$ $(M+H)^+$, 547.1603, found 547.1603.

8-([1,1'-biphenyl]-4-yl)-6-(2-([1,1'-biphenyl]-4-yl)pyridin-3-yl)-10-methylpyrido[1,2-a]indole (3af)

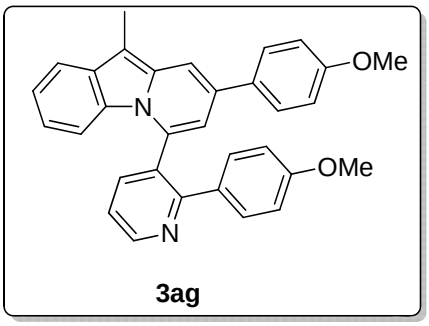


3af

3af: Yield: 76%; yellow solid, 85 mg; m.p: 215-217 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.4 Hz, 2H), 7.73 (t, *J* = 8.0 Hz, 1H), 7.68-7.62 (m, 4H), 7.62-7.55 (m, 5H), 7.44 (t, *J* = 7.6 Hz, 3H), 7.37 (t, *J* = 6.3 Hz, 3H), 7.32-7.27 (m, 3H), 7.24-7.20 (m, 3H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.48 (d, *J* = 8.0 Hz, 1H), 2.45 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 150.1, 142.0, 141.2, 140.9, 140.9, 140.8, 140.4, 140.1, 139.8, 138.5, 137.2, 134.9, 133.7, 132.9, 131.5, 130.6, 130.5, 129.3, 129.0, 128.9, 128.8, 128.6, 128.3, 127.9, 127.4, 127.3, 127.2, 127.1, 127.0, 126.8, 126.5, 126.4, 123.3, 120.7, 118.0, 114.4, 104.8, 102.1, 8.0 ppm; HRMS m/z (ESI) Calcd for $C_{42}H_{31}N_2$ $(M+H)^+$, 563.2482, found 563.2476.

8-(4-methoxyphenyl)-6-(2-(4-methoxyphenyl)pyridin-3-yl)-10-methylpyrido[1,2-a]indole (3ag)

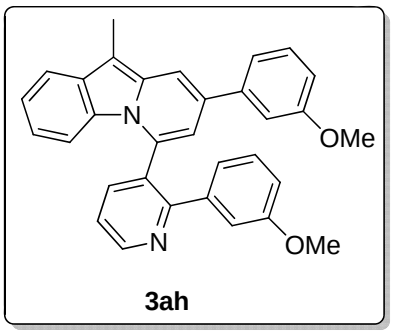


3ag

3ag: Yield: 74%; yellow solid, 70 mg; m.p: 165-167 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 8.6 Hz, 2H), 7.72 (t, *J* = 7.2 Hz, 1H), 7.65-7.57 (m, 4H), 7.48 (s, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 8.3 Hz, 2H), 7.00-6.95 (m, 3H), 6.55 (d, *J* = 8.4 Hz, 2H), 6.46 (d, *J* = 8.4 Hz, 1H), 3.87 (s, 3H), 3.60 (s, 3H), 2.48 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 159.8, 158.7, 150.1, 141.4, 140.9, 134.8, 133.9, 132.0, 131.5, 131.0, 130.5, 130.3, 129.5, 129.2, 128.8, 127.8, 127.4, 123.2, 120.3, 117.7, 114.3, 114.0, 113.3, 103.3, 101.1, 55.3, 54.9, 7.9 ppm; HRMS m/z (ESI) Calcd for $C_{32}H_{27}N_2O_2$ $(M+H)^+$, 471.2067, found 471.2064.

8-(4-methoxyphenyl)-6-(2-(4-methoxyphenyl)pyridin-3-yl)-10-methylpyrido[1,2-a]indole (3ah)



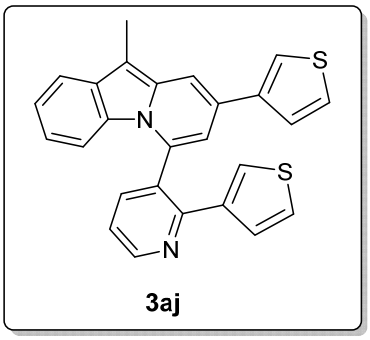
3ah

3ah: Yield: 41%; yellow solid, 39 mg; m.p: 168-170 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.74 (t, *J* = 6.1 Hz, 1 H), 7.67-7.60 (m, 4 H), 7.65 (d, *J* = 7.7 Hz, 1 H), 7.51 (s, 2 H), 7.33 (dd, *J* = 16.0, 8.1 Hz, 2 H), 6.99 (t, *J* = 8.3 Hz, 1 H), 6.91 (t, *J* = 7.6 Hz, 2 H), 6.80 (s, 1 H), 6.75 (t, *J* = 7.3 Hz, 1 H), 6.57 (dd, *J* = 8.1, 2.2 Hz, 1 H), 6.48 (d, *J* = 8.6 Hz, 1 H), 3.87 (s, 3 H), 3.37 (s, 3 H), 2.47 (s, 3 H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 160.0, 159.0, 150.7, 141.4, 140.8, 138.8, 133.1, 131.8, 130.8, 130.6, 129.6, 129.1, 128.9, 128.3, 123.8, 121.1, 120.9, 118.6, 118.2, 114.6, 114.4, 114.3, 113.0,

111.7, 105.5, 55.4, 54.9, 8.0 ppm; HRMS m/z (ESI) Calcd for $C_{32}H_{27}N_2O_2$ $(M+H)^+$, 471.2067, found 471.2064.

10-methyl-8-(thiophen-3-yl)-6-(2-(thiophen-3-yl)pyridin-3-yl)pyrido[1,2-a]indole (3aj)

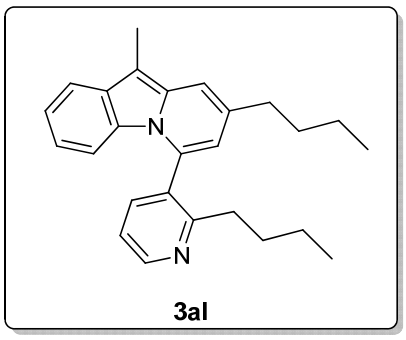


3aj

3aj: Yield: 76%; yellow solid, 64 mg; m.p: 184-186 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 1.9 Hz, 2H), 7.62-7.56 (m, 2H), 7.54-7.45 (m, 4H), 7.35 (s, 1H), 7.29 (dd, *J* = 5.0, 3.1 Hz, 1H), 7.18 (t, *J* = 8.0 Hz, 1H), 6.88 (dd, *J* = 3.0, 1.3 Hz, 1H), 6.84-6.80 (m, 2H), 6.76 (dd, *J* = 5.0, 1.3 Hz, 1H), 6.26 (d, *J* = 8.9 Hz, 1H), 2.37(s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 150.4, 140.8, 139.6, 138.1, 135.9, 134.3, 133.3, 131.6, 130.5, 130.0, 129.3, 129.1, 128.2, 127.6, 126.3, 125.3, 125.1, 123.4, 123.2, 122.9, 120.7, 117.9, 114.3, 104.4, 102.0, 8.0 ppm; HRMS m/z (ESI) Calcd for $C_{26}H_{19}N_2S_2$ $(M+H)^+$, 423.0984, found 423.0988.

8-butyl-6-(2-butylpyridin-3-yl)-10-methylpyrido[1,2-a]indole (3al)



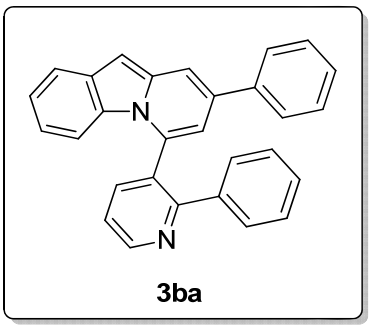
3al

3al: Yield: 41%; yellow solid, 30 mg; m.p: 135-137 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.0 Hz, 1H), 7.57 (dt, *J* = 8.4, 1.5 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.46-7.40 (m, 2H), 7.35 (t, *J* = 7,6 Hz, 1H), 7.05 (s, 1H), 6.92 (t,

J = 8.5 Hz, 1H), 6.28 (d, *J* = 8.6 Hz, 1H), 2.85-2.70 (m, 2H), 2.55-2.47 (m, 4H), 2.36-2.28 (m, 1H), 1.85-1.75 (m, 1H), 1.22-1.12 (m, 1H), 1.01 (t, *J* = 7.1 Hz, 3H), 0.73 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 150.4, 140.8, 139.6, 138.1, 135.9, 134.3, 133.3, 131.6, 130.5, 130.0, 129.3, 129.1, 128.2, 127.6, 126.3, 125.3, 125.1, 123.4, 123.2, 122.9, 120.7, 117.9, 114.3, 104.4, 102.0, 8.0 ppm; HRMS m/z (ESI) Calcd for $C_{26}H_{31}N_2$ $(M+H)^+$, 371.2482, found 371.2477.

8-phenyl-6-(2-phenylpyridin-3-yl)pyrido[1,2-a]indole (3ba)

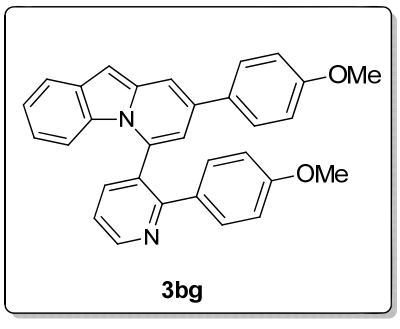


3ba

3ba: Yield: 61%; yellow solid, 48 mg; m.p: 144-147 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 7.8 Hz, 2H), 7.77-7.70 (m, 2H), 7.66-7.61 (m, 3H), 7.60 (s, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 7.0 Hz, 1H), 7.15 (dd, *J* = 5.6, 1.7 Hz, 2H), 7.02-6.95 (m, 4H), 6.65 (s, 1H), 6.53 (d, *J* = 8.4 Hz, 1H); **^{13}C NMR (125MHz, $CDCl_3$)**: δ = 150.0, 142.7, 141.3, 139.3, 137.9, 137.0, 134.7, 131.0, 130.6, 130.5, 129.2, 129.1, 128.5, 128.3, 128.2, 127.7, 127.2, 126.1, 123.7, 120.5, 119.9, 114.6, 106.4, 94.3 ppm; HRMS m/z (ESI) Calcd for $C_{29}H_{21}N_2$ $(M+H)^+$, 397.1699, found 397.1701.

8-(4-methoxyphenyl)-6-(2-(4-methoxyphenyl)pyridin-3-yl)pyrido[1,2-a]indole (3bg)

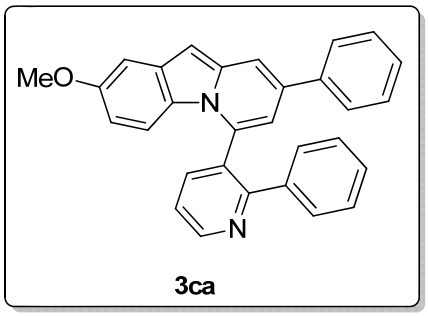


3bg

3bg: Yield: 66%; yellow solid, 60 mg; m.p: 153-155 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.79-7.71 (m, 2H), 7.70-7.64 (m, 3H), 7.63-7.56 (m, 3H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.00 (t, *J* = 8.5 Hz, 1H), 6.96-6.91 (m, 2H), 6.76-6.75 (m, 2H), 6.69 (s, 1H), 6.60 (dd, *J* = 8.3, 1.6 Hz, 1H), 6.54 (d, *J* = 8.5 Hz, 1H), 3.90 (s, 3H), 3.38 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 160.1, 158.9, 150.1, 142.6, 141.3, 140.8, 139.5, 137.0, 134.8, 131.1, 130.5, 129.6, 129.3, 129.2, 128.8, 128.3, 123.8, 120.9, 120.7, 120.1, 118.6, 114.7, 114.3, 114.2, 112.9, 111.7, 94.5, 55.4, 54.9 ppm; HRMS m/z (ESI) Calcd for $C_{31}H_{25}N_2O_2$ $(M+H)^+$, 457.1911, found 457.1919.

2-methoxy-8-phenyl-6-(2-phenylpyridin-3-yl)pyrido[1,2-a]indole (3ca)

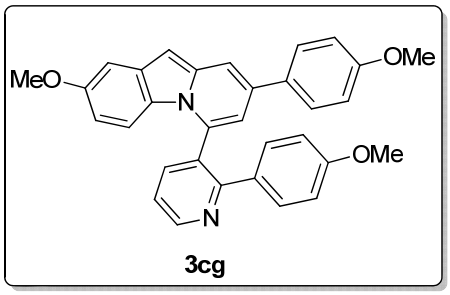


3ca

3ca: Yield: 68%; yellow solid, 58 mg; m.p: 159-161 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 7.2 Hz, 2H), 7.79-7.72 (m, 2H), 7.66 (d, *J* = 7.4 Hz, 2H), 7.58 (s, 1H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.40 (t, *J* = 6.8 Hz, 1H), 7.20 (dd, *J* = 5.0, 2.0 Hz, 2H), 7.04 (dd, *J* = 5.0, 2.0 Hz, 4H), 6.65 (dd, *J* = 9.3, 2.5 Hz, 1H), 6.58 (s, 1H), 6.42 (d, *J* = 9.2 Hz, 1H), 3.86 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 156.7, 149.5, 142.7, 141.3, 139.3, 138.0, 137.8, 134.6, 132.2, 130.6, 130.5, 129.2, 128.5, 128.4, 128.3, 128.2, 127.7, 127.2, 126.1, 124.2, 115.4, 111.1, 106.1, 100.4, 94.0, 55.3; HRMS (ESI) m/z Calcd for $C_{30}H_{23}N_2O$ $(M+H)^+$, 427.1805, found 427.1802.

2-methoxy-8-(4-methoxyphenyl)-6-(2-(4-methoxyphenyl)pyridin-3-yl)pyrido[1,2-a]indole (3cg)

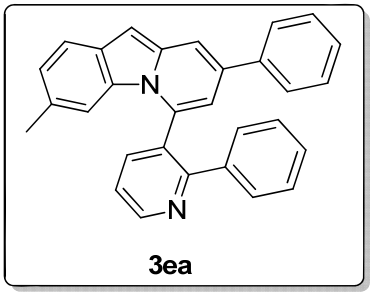


3cg

3cg: Yield: 78%; yellow solid, 76 mg; m.p: 159-161 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.9 Hz, 2H), 7.72 (dt, *J* = 8.1, 1.7 Hz, 1H), 7.67 (d, *J* = 1.7 Hz, 1H), 7.61 (m, 2H), 7.49 (s, 1H), 7.09 (d, *J* = 8.8 Hz, 2H), 6.99 (m, 3H), 6.54 (m, 4H), 6.31 (d, *J* = 9.2 Hz, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 3.63 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 160.0, 158.8, 156.7, 149.7, 142.6, 141.0, 138.1, 134.7, 132.3, 131.9, 130.8, 130.6, 130.5, 129.5, 129.3, 127.9, 127.5, 124.3, 115.4, 114.0, 113.3, 110.8, 104.7, 100.4, 93.4, 55.4, 55.3, 55.0 ppm; HRMS (ESI) m/z Calcd for $C_{32}H_{27}N_2O_3$ $(M+H)^+$, 487.2016, found 487.2013.

3-methyl-8-phenyl-6-(2-phenylpyridin-3-yl)pyrido[1,2-a]indole (3ea)

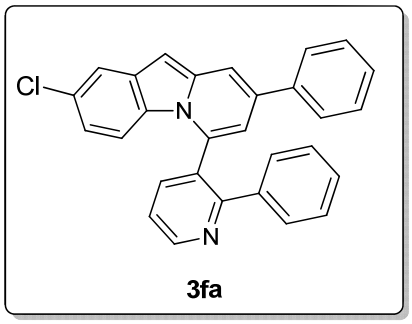


3ea

3ea: Yield: 74%; yellow solid, 61 mg; m.p: 192-194 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 7.4 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.46 (s, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 7.9 Hz, 2H), 7.25 (t, *J* = 7.9 Hz, 2H), 7.03 (m, 3H), 6.90 (m, 3H), 6.50 (s, 1H), 6.16 (s, 1H), 2.18 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 150.0, 142.1, 141.4, 139.5, 138.0, 136.6, 134.8, 130.5, 130.4, 130.2, 129.5, 129.3, 128.9, 128.6, 128.3, 128.2, 128.1, 127.7, 127.2, 126.1, 125.5, 119.5, 114.7, 106.6, 94.2, 22.0 ppm; HRMS m/z (ESI) Calcd for $C_{30}H_{23}N_2$ $(M+H)^+$, 411.1856, found 411.1859.

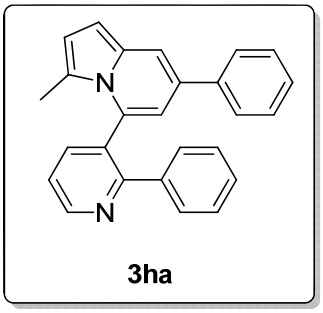
2-chloro-8-phenyl-6-(2-phenylpyridin-3-yl)pyrido[1,2-a]indole (3fa)



3fa: Yield: 61%; yellow solid, 53 mg; m.p: 159-161 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 7.4 Hz, 2H), 7.77 (t, *J* = 7.4 Hz, 1H), 7.73 (d, *J* = 7.4 Hz, 2H), 7.65 (m, 2H), 7.60 (s, 1H), 7.57 (d, *J* = 1.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.1 Hz, 1H), 7.11 (m, 2H), 7.01 (m, 3H), 6.91 (dd, *J* = 1.8, 9.1 Hz, 1H), 6.56 (s, 1H), 6.38 (d, *J* = 9.0 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 150.0, 143.4, 141.3, 139.1, 138.3, 137.7, 134.4, 132.0, 130.8, 130.7, 129.6, 129.2, 128.7, 128.6, 128.4, 128.3, 127.8, 127.6, 127.4, 126.3, 120.8, 119.1, 115.5, 106.3, 93.7 ppm; HRMS m/z (ESI) Calcd for $C_{29}H_{20}ClN_2$ $(M+H)^+$, 431.1310, found 431.1316.

3-methyl-7-phenyl-5-(2-phenylpyridin-3-yl)indolizine (3ha)

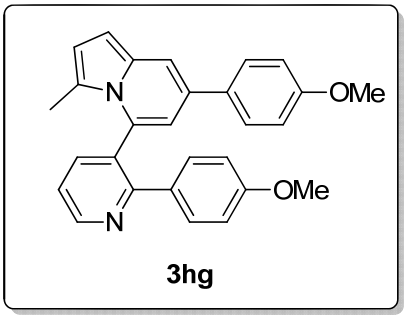


3ha: Yield: 61%; yellow solid, 44 mg; m.p: 135-137 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84 (dd, *J* = 1.3, 8.4 Hz, 2H), 7.56 (dd, *J* = 1.0, 7.5 Hz, 1H), 7.52 (dt, *J* = 1.4, 7.6 Hz, 1H), 7.47 (s, 1H), 7.44 (dd, *J* = 1.0, 7.5 Hz, 1H), 7.41 (dt, *J* = 1.4, 7.4 Hz, 1H), 7.32 (t, *J* =7.4 Hz, 2H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.15 (dd, *J* = 1.8, 8.2 Hz, 2H), 7.03 (m, 3H), 6.30 (d, *J* = 3.7 Hz, 1H), 6.27 (t, *J* = 3.7 Hz, 1H), 1.77 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 146.9, 141.5, 139.8, 138.5, 137.7, 135.0, 134.3, 130.3,

129.9, 129.7, 128.5, 128.4, 128.1, 127.4, 127.2, 126.8, 125.6, 121.5, 117.4, 107.4, 99.8, 14.9 ppm; HRMS m/z (ESI) Calcd for $C_{26}H_{21}N_2$ $(M+H)^+$, 361.1699, found 360.1692.

7-(4-methoxyphenyl)-5-(2-(4-methoxyphenyl)pyridin-3-yl)-3-methylindolizine (3hg)

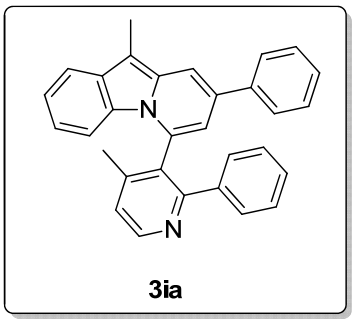


3hg

3hg: Yield: 66%; yellow solid, 56 mg; m.p: 154-156 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.38 (m, 3H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2), 6.57 (d, *J* = 8.8 Hz, 2H), 6.28 (d, *J* = 3.4 Hz, 1H), 6.23 (d, *J* = 3.4 Hz, 1H), 3.76 (s, 3H), 3.59 (s, 3H), 1.73 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 159.4, 158.8, 147.1, 141.1, 137.6, 134.9, 134.4, 132.3, 131.2, 130.4, 129.8, 129.6, 129.5, 126.9, 126.3, 121.3, 117.3, 114.0, 113.6, 106.3, 99.2, 55.3, 55.1, 14.8 ppm; HRMS m/z (ESI) Calcd for $C_{28}H_{25}O_2N_2$ $(M+H)^+$, 421.1911, found 421.1917.

10-methyl-6-(4-methyl-2-phenylpyridin-3-yl)-8-phenylpyrido[1,2-a]indole (3ia)



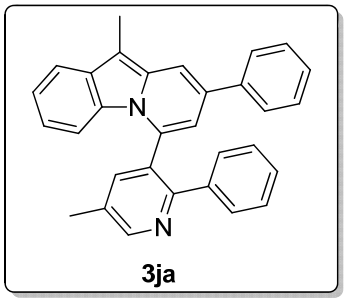
3ia

3ia: Yield: 31%; yellow solid, 26 mg; m.p: 174-176 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.88 (dd, *J* = 1.9, 8.1 Hz, 2H), 7.43 (m, 3H), 7.33 (m, 3H), 7.26 (t, *J* = 8.1 Hz, 1H), 7.06 (m, 2H), 6.89 (m, 3H), 6.70 (dd, *J* = 1.5, 8.7 Hz, 1H), 6.47 (s, 1H), 6.31 (d, *J* = 8.7 Hz, 1H), 2.41 (s, 3H), 2.34 (s, 3H); **^{13}C NMR (125 MHz,**

$CDCl_3$): δ = 149.4, 141.7, 141.6, 140.1, 138.4, 136.9, 134.5, 133.3, 131.8, 131.5, 130.0, 129.8, 128.5, 128.4, 128.3, 128.0, 127.7, 127.0, 126.1, 123.4, 121.0, 118.0, 113.7, 104.7, 101.8, 31.4, 19.2, 7.9 ppm; HRMS m/z (ESI) Calcd for $C_{31}H_{25}N_2$ $(M+H)^+$, 425.2012, found 425.2008.

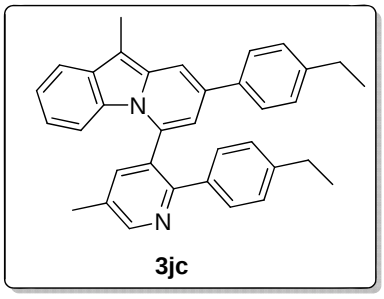
10-methyl-6-(5-methyl-2-phenylpyridin-3-yl)-8-phenylpyrido[1,2-a]indole (3ja)



3ja: Yield: 84%; yellow solid, 71 mg; m.p: 167-169 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 7.6 Hz, 2H), 7.51 (d, *J* =7.9 Hz, 1H), 7.45-7.41 (m, 3H), 7.38 (s, 1H), 7.34 (t, *J* =7.6 Hz, 2H), 7.28-7.17 (m, 2H), 7.08 (dd, *J* = 6.0, 2.5 Hz, 2H), 6.95-6.81 (m, 4H), 6.43 (d, *J* = 8.3 Hz, 1H), 2.40 (s, 3H), 2.36 (s, 3H); **^{13}C NMR (125MHz, $CDCl_3$)**: δ = 150.4, 141.5, 139.4, 138.5, 138.2, 138.1, 134.4, 133.6, 131.5, 131.3, 130.6, 129.6, 128.9, 128.6, 128.4, 128.1, 127.7, 127.0, 126.2, 123.3, 120.6, 117.9, 114.6, 104.9, 101.9, 21.1, 7.9 ppm; HRMS m/z (ESI) Calcd for $C_{31}H_{25}N_2$ $(M+H)^+$, 425.2012, found 425.2008.

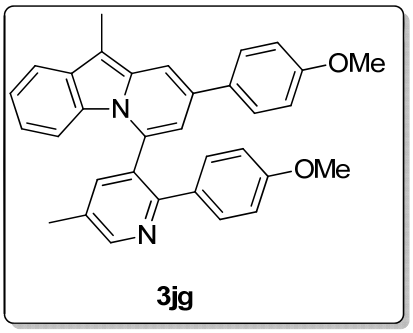
8-(4-ethylphenyl)-6-(2-(4-ethylphenyl)-5-methylpyridin-3-yl)-10-methylpyrido[1,2-a]indole (3jc)



3jc: Yield: 91%; yellow solid, 87 mg; m.p: 184-186 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.42 (s, 3H), 7.35 (s, 1H), 7.18 (dd, *J* = 4, 9.7 Hz, 3H), 6.99 (d, *J* = 7.59 Hz, 2H), 6.87 (t, *J* = 7.7 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 2H), 6.40 (d, *J* = 8.5 Hz, 1H), 2.61 (q, *J* = 7.6 Hz, 2H), 2.39 (s, 3H) , 2.37 (s, 3H), 2.32 (q, *J* = 7.8 Hz, 2H) , 1.19 (t, *J* = 7.6 Hz, 3H), 0.95 (q, *J* = 7.8 Hz, 3H); **^{13}C NMR (125MHz, $CDCl_3$)**: δ = 150.3, 144.4, 142.8, 141.8, 138.4, 137.8, 136.8, 135.8, 134.6, 133.8, 131.5, 131.1, 130.5, 129.6, 128.9, 128.3, 128.1, 127.2, 126.1, 123.2, 120.3, 117.7, 114.6, 104.2, 101.3, 28.7, 28.2, 21.1, 15.6, 15.2, 7.9; HRMS m/z (ESI) Calcd for $C_{35}H_{33}N_2$ $(M+H)^+$, 481.2638, found 481.2671.

8-(4-methoxyphenyl)-6-(2-(4-methoxyphenyl)-5-methylpyridin-3-yl)-10-methylpyrido[1,2-a]indole (3jg)

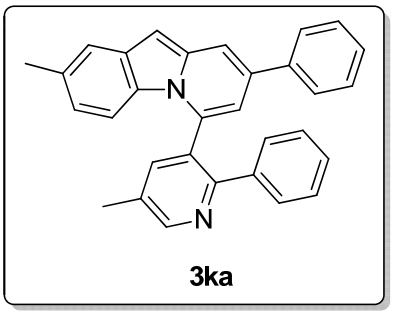


3jg

3jg: Yield: 86%; red solid, 83 mg; m.p: 222-225 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 7.9 Hz, 2H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.39 (dd, *J* = 7.9, 9.4 Hz, 2H), 7.34 (d, *J* = 9.4 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 8.9 Hz, 2H), 6.87 (m, 3H), 6.42 (d, *J* = 8.7 Hz, 2H), 6.35 (d, *J* = 8.9 Hz, 1H), 3.77 (s, 3H), 3.50 (s, 3H), 2.38 (s, 3H), 2.36 (s, 3H); **^{13}C NMR (125MHz, $CDCl_3$)**: δ = 159.9, 158.6, 150.4, 141.5, 138.0, 137.7, 134.6, 133.9, 132.0, 131.6, 131.2, 131.1, 130.5, 129.6, 129.5, 128.9, 127.5, 123.2, 120.3, 117.7, 114.5, 114.0, 113.3, 103.4, 101.1, 55.5, 55.0, 21.1, 8.0 ppm; HRMS m/z (ESI) Calcd for $C_{33}H_{29}N_2O_2$ $(M+H)^+$, 485.2224, found 485.2221.

2-methyl-6-(5-methyl-2-phenylpyridin-3-yl)-8-phenylpyrido[1,2-a]indole (3ka)

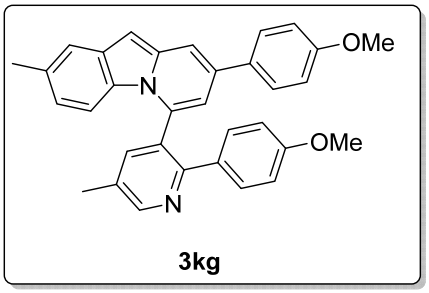


3ka

3ka: Yield: 88%; yellow solid, 75 mg; m.p: 161-163 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00 (dd, *J* = 2.0, 8.2 Hz, 2H), 7.59(s, 1H), 7.55 (s, 2H), 7.52 (s, 1H), 7.45 (m, 3H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.18 (m, 2H), 7.02 (m, 3H), 6.83 (dd, *J* = 1.5, 8.7 Hz, 1H), 6.59 (s, 1H), 6.43 (d, *J* = 8.7 Hz, 1H), 2.52 (s, 3H), 2.46 (s, 3H); **^{13}C NMR (125MHz, $CDCl_3$)**: δ 150.1, 142.6, 139.4, 138.5, 138.1, 138.0, 137.2, 134.5, 133.4, 131.4, 131.2, 130.5, 129.6, 128.6, 128.4, 128.2, 127.7, 127.6, 127.0, 126.2, 122.4, 119.5, 114.3, 106.4, 93.8, 21.5, 21.1 ppm; HRMS m/z (ESI) Calcd for $C_{31}H_{25}N_2$ $(M+H)^+$, 425.2012, found 425.2008.

8-(4-methoxyphenyl)-6-(2-(4-methoxyphenyl)-5-methylpyridin-3-yl)-2-methylpyrido[1,2-a]indole (3kg)

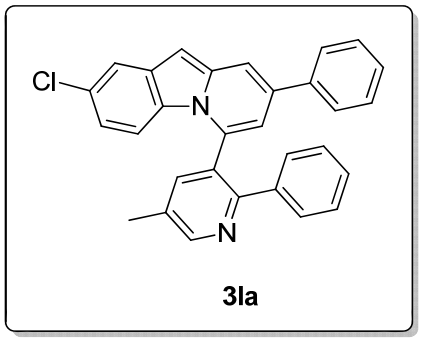


3kg

3kg: Yield: 84%; yellow solid, 81 mg; m.p: 187-189 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 = (d, *J* = 8.8 Hz, 2H), 7.38 (m, 3H), 7.33 (s, 1H), 7.29 (s, 1H), 6.98 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.66 (dd, *J* = 1.2, 8.8 Hz, 1H), 6.41 (m, 3H), 6.23 (d, *J* = 8.6 Hz, 1H), 3.76 (s, 3H), 3.50 (s, 3H), 2.38 (s, 3H), 2.32 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 159.0, 157.6, 149.3, 141.3, 137.0, 136.7, 136.4, 133.3, 132.3, 130.9, 130.5, 130.2, 129.7, 129.5, 128.5, 128.4, 126.6, 126.5, 121.2, 118.3, 113.3, 113.0, 112.3, 104.0, 92.3, 54.4, 54.0, 20.5, 20.1 ppm; HRMS m/z (ESI) Calcd for $C_{33}H_{29}N_2O_2$ $(M+H)^+$, 485.2224, found 484.2226.

2-chloro-6-(5-methyl-2-phenylpyridin-3-yl)-8-phenylpyrido[1,2-a]indole (3la)

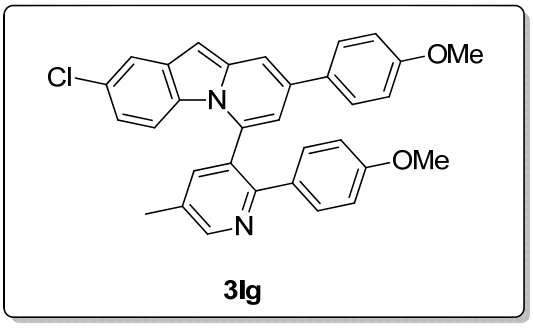


3la

3la: Yield: 74%; yellow solid, 66 mg; m.p: 171-173 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 = (d, *J* = 7.5 Hz, 2H), 7.47 (s, 1H), 7.44 (m, 4H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 1H), 6.99 (m, 2H), 6.87 (m, 3H), 6.80 (dd, *J* = 2.0, 9.0 Hz, 1H), 6.43 (s, 1H), 6.28 (d, *J* = 9.0 Hz, 1H), 2.42 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 150.2, 143.4, 139.0, 138.4, 138.3, 138.2, 137.7, 134.0, 132.0, 131.5, 130.5, 129.6, 128.7, 128.6, 128.2, 127.8, 127.5, 127.2, 126.3, 120.7, 119.0, 115.6, 106.3, 93.7, 21.1 ppm; HRMS m/z (ESI) Calcd for $C_{30}H_{22}ClN_2$ $(M+H)^+$, 445.1466, found 445.1472.

2-chloro-8-(4-methoxyphenyl)-6-(2-(4-methoxyphenyl)-5-methylpyridin-3-yl)pyrido[1,2-a]indole (3lg)



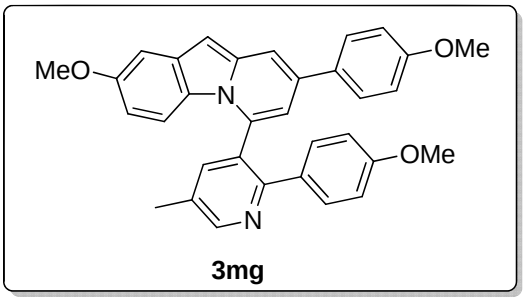
3lg

3lg: Yield: 84%; yellow solid, 85 mg; m.p: 187-189 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 9.0 Hz, 2H), 7.44 (d, *J* = 1.5 Hz, 1H), 7.43 (d, *J* = 1.5 Hz, 1H), 7.39 (t, *J* = 5.5 Hz, 3H), 6.92 (m, 4H), 6.78 (dd, *J* = 2.0, 9.0 Hz, 1H), 6.41 (m, 3H), 6.23 (d, *J* = 8.9 Hz, 1H), 3.78 (s, 3H), 3.51 (s, 3H), 2.42 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 160.3, 158.7, 150.3, 143.2, 138.4, 137.9, 134.0, 132.1, 131.5,

131.4, 130.5, 130.4, 129.6, 127.7, 127.5, 120.5, 118.9, 115.6, 114.1, 114.0, 113.3, 104.8, 93.1, 55.4, 55.0, 21.1 ppm; HRMS m/z (ESI) Calcd for $C_{32}H_{27}ClN_2O_2$ $(M+H)^+$, 505.1677, found 505.1674.

2-methoxy-8-(4-methoxyphenyl)-6-(2-(4-methoxyphenyl)-5-methylpyridin-3-yl)pyrido[1,2-a]indole (3mg)

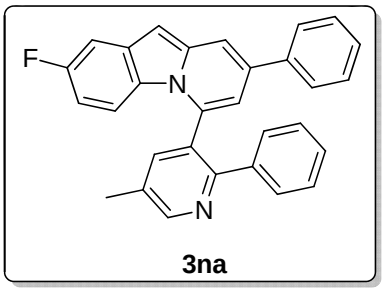


3mg

3mg: Yield: 79%; yellow solid, 79 mg; m.p: 188-190 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 8.8 Hz, 2H), 7.43 (dd, *J* = 1.2, 7.9 Hz, 1H), 7.38 (m, 3H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.3 Hz, 2H), 6.48 (dd, *J* = 2.4, 9.1 Hz, 1H), 6.43 (m, 3H), 6.23 (d, *J* = 9.1 Hz, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.52 (s, 3H), 2.41 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 160.0, 158.6, 156.6, 149.9, 142.5, 138.0, 137.9, 137.8, 134.3, 132.3, 131.8, 131.3, 130.7, 130.4, 129.6, 129.4, 127.6, 124.3, 115.5, 114.0, 113.3, 110.8, 104.7, 100.3, 93.4, 55.4, 55.3, 55.0, 21.1 ppm; HRMS m/z (ESI) Calcd for $C_{33}H_{29}N_2O_3$ $(M+H)^+$, 501.2173, found: 501.2171.

2-fluoro-6-(5-methyl-2-phenylpyridin-3-yl)-8-phenylpyrido[1,2-a]indole (3na)



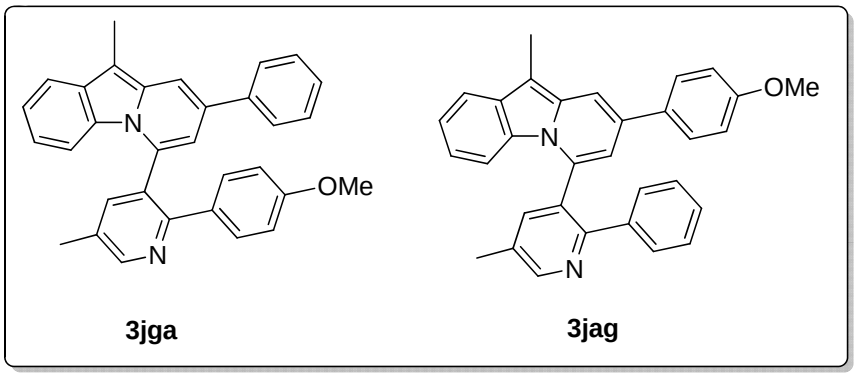
3na

3na: Yield: 74%; yellow solid, 63 mg; m.p: 186-189 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 7.3 Hz, 2H), 7.48 (s, 1H), 7.44 (m, 3H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.11 (dd, *J* = 2.1, 9.2 Hz, 1H), 6.99 (m,

2H), 6.87 (m, 3H), 6.60 (dt, *J* = 2.4, 9.0 Hz, 1H), 6.47 (s, 1H), 6.33 (dd, *J* = 4.4, 9.3 Hz, 1H), 2.44 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 159.8 (*J* = 240.8 MHz), 150.2, 143.3, 139.0, 138.5, 138.4, 138.3, 137.7, 134.1, 131.9 (*J* = 11.0 MHz), 131.5, 130.5, 129.6, 128.6, 128.5, 128.2, 127.7, 127.1, 126.3, 125.8, 115.7 (*J* = 9.6 MHz), 109.0 (*J* = 25.4 MHz), 106.1, 104.2 (*J* = 23.5 MHz), 94.2 (*J* = 4.5 MHz), 21.2 ppm; HRMS m/z (ESI) Calcd for $C_{30}H_{22}FN_2$ $(M+H)^+$, 429.1762, found 429.1766.

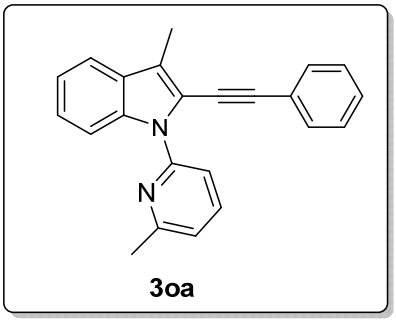
6-(2-(4-methoxyphenyl)-5-methylpyridin-3-yl)-10-methyl-8-phenylpyrido[1,2-a]indole (3jga) and 8-(4-methoxyphenyl)-10-methyl-6-(5-methyl-2-phenylpyridin-3-yl)pyrido[1,2-a]indole (3jag)



3jga and 3jag: 1 : 1.1, Yield: 36%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 7.6 Hz, 2.2H), 7.84 (d, *J* = 8.7 Hz, 2H), 3.75 (s, 3H), 3.49 (s, 3.3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 159.8, 158.6, 150.4, 150.1, 141.6, 141.5, 139.5, 138.4, 138.3, 138.1, 138.0, 137.7, 134.7, 134.5, 133.9, 133.6, 131.9, 131.5, 131.4, 131.2, 131.0, 130.5, 130.4, 129.6, 129.5, 128.9, 128.8, 128.6, 128.4, 128.1, 127.7, 127.4, 126.9, 126.1, 123.2, 123.1, 120.5, 120.2, 117.8, 117.7, 114.5, 114.4, 114.0, 113.3, 104.8, 103.3, 101.7, 101.0, 55.3, 55.0, 21.1, 21.0, 7.9, 7.8 ppm; HRMS m/z (ESI) Calcd for $C_{32}H_{27}ON_2$ $(M+H)^+$, 455.2118, found 455.2119.

3-methyl-1-(6-methylpyridin-2-yl)-2-(phenylethynyl)-1*H*-indole (3oa)



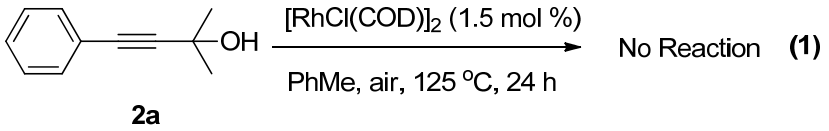
3oa

3oa: Yield: 61%; colorless solid, 39 mg; m.p: 150-152 °C.

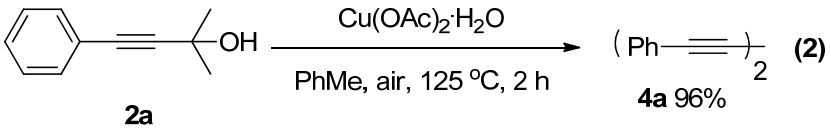
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 = (d, *J* = 8.3 Hz, 1H), 7.76 (t, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.44-7.42 (m, 2H), 7.34-7.30 (m, 3H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 2.66 (s, 3H), 2.53 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ = 158.0, 150.9, 137.9, 136.6, 131.0, 128.6, 128.3, 128.2, 124.4, 123.2, 121.2, 121.0, 120.8, 119.1, 118.5, 116.6, 112.1, 98.2, 81.5, 24.3, 9.9; HRMS m/z (ESI) Calcd for $C_{23}H_{18}N_2Na$ $(M+Na)^+$, 345.1362, found 345.1367.

4. Mechanism Studies

4.1 Stoichiometric reactions of 2a with $[RhCl(COD)]_2$ and $Cu(OAc)_2{\cdot}H_2O$

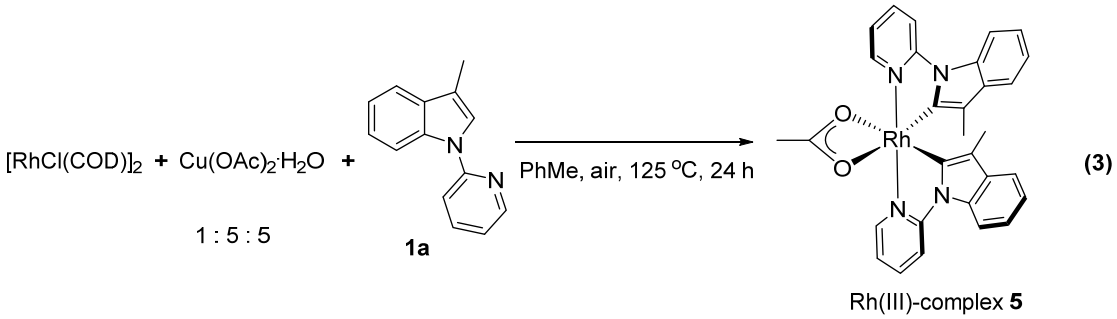


A mixture of 2-methyl-4-phenyl-3-butyn-2-ol **2a** (0.80 mmol), $[RhCl(COD)]_2$ (1.5 mol %, 0.024 mmol) and toluene (2 ml) were added to a Schlenk tube under an air atmosphere. Then the mixture was stirred at 125 °C (bath temperature, pre-heated) under air for 24 h. Only trace amount of **4a** was detected by TLC.



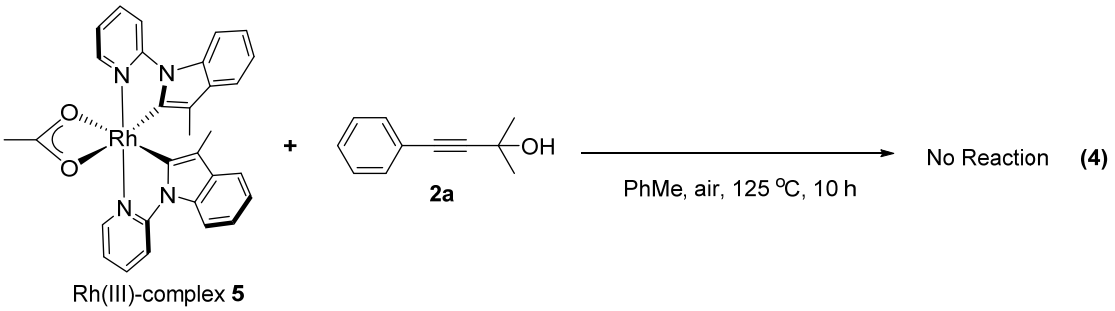
A mixture of 2-methyl-4-phenyl-3-butyn-2-ol **2a** (0.80 mmol), $Cu(OAc)_2{\cdot}H_2O$ (80 mg, 0.40 mmol) and toluene (2 mL) were added to a Schlenk tube under an air atmosphere. The mixture was stirred at 125 °C (bath temperature, pre-heated) under air for 2 h, which was then filtered through a short plug of silica gel, washed with ethyl acetate and concentrated. The residue was purified by chromatography (hexane) to afford the desired products **4a** in 96% isolated yield.

4.2 Stoichiometric reactions of 1a with $[RhCl(COD)]_2$ in the presence of $Cu(OAc)_2{\cdot}H_2O$

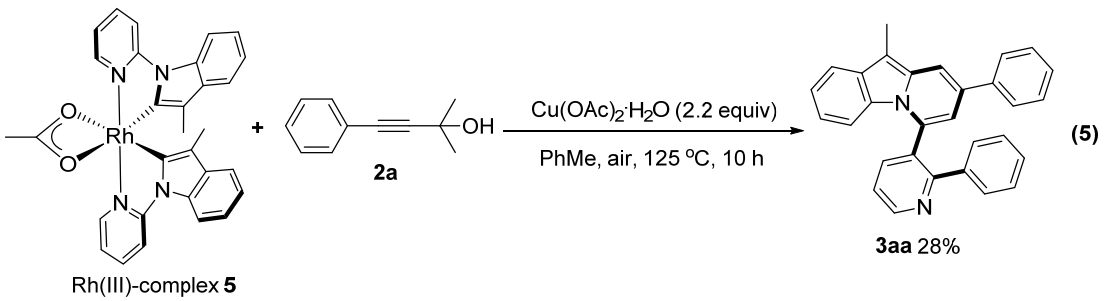


A mixture of $[RhCl(COD)]_2$ (0.2 mmol), $Cu(OAc)_2{\cdot}H_2O$ (200 mg, 1 mmol), 1-(pyridin-2-yl)-1*H*-indole **1a** (208 mg, 1 mmol) and toluene (2 mL) were added to a Schlenk tube under an air atmosphere. The mixture was stirred at 125 ^oC (bath temperature, pre-heated) under air for 24 h, which was then concentrated. The residue was purified by chromatography (methanol/ethyl acetate/hexane = 1/20/100) to afford the desired product **5** in 85% isolated yield. **5**: Yield: 85%. **^{1}H NMR (500 MHz, $CDCl_3$)**: δ = 8.72 (d, *J* = 5.5 Hz, 2H), 7.87 (m, 2H), 7.79 (m, 2H), 7.59 (d, *J* = 7.9 Hz, 2H), 7.06 (d, *J* = 7.7 Hz, 2H), 6.96 (m, 6H), 1.98 (s, 3H) , 1.26 (s, 3H) ppm; The poor solubility of complex **5** prevented $^{13}C\{^1H\}$ NMR characterization.

4.3 Stoichiometric reactions of complex 6 with 2a and copper phenylacetylide 6

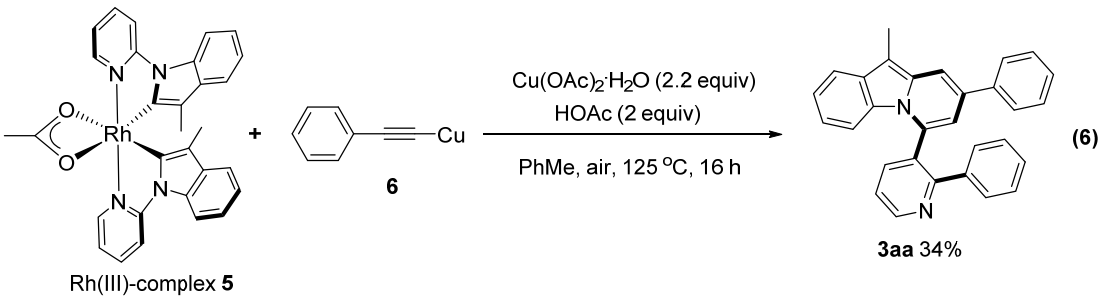


A mixture of **5** (0.2 mmol), 2-methyl-4-phenyl-3-butyn-2-ol **2a** (0.22 mmol) and toluene (2 mL) were added to a Schlenk tube under an air atmosphere. Then the mixture was stirred at 125 ^oC (bath temperature, pre-heated) under air for 10 h. No reaction took place as detected by TLC.



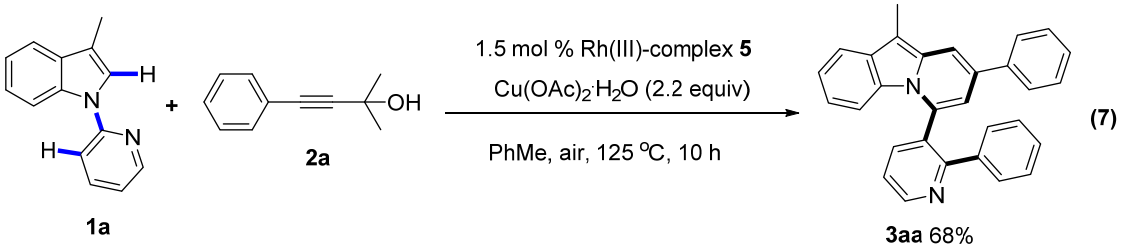
A mixture of **5** (0.2 mmol), 2-methyl-4-phenyl-3-butyn-2-ol **2a** (0.22 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.44 mmol) and toluene (2 mL) were added to a Schlenk tube under an

air atmosphere. Then the mixture was stirred at 125 °C (bath temperature, pre-heated) under air for for 10 h until complete consumption of **2a** judged by TLC. Then the reaction mixture was filtered through a short plug of silica gel, washed with ethyl acetate and concentrated. The residue was purified by chromatography (ethyl acetate/hexane = 1/50) to afford the desired products **3aa** in 28% isolated yield based on comlex **5**.



A mixture of **5** (0.2 mmol), PhC≡CCu **6** (1.0 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.44 mmol), HOAc (0.44 mmol) and toluene (2 mL) were added to a Schlenk tube under an air atmosphere. The mixture was stirred at 125 °C (bath temperature, pre-heated) under air for for 16 h, which was then filtered through a short plug of silica gel, washed with ethyl acetate and concentrated. The residue was purified by chromatography (ethyl acetate/hexane = 1/50) to afford the desired products **3aa** in 34% isolated yield.

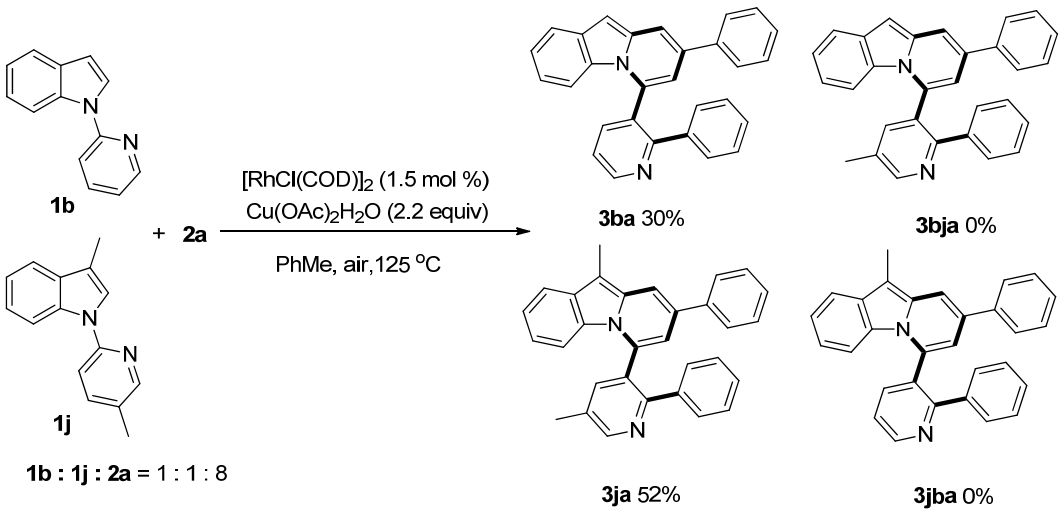
4.4 catalytic activity of complex 5



A mixture of 1-(pyridin-2-yl)-1*H*-indole **1a** (0.20 mmol), 2-methyl-4-phenyl-3-butyn-2-ol **2a** (0.80 mmol), **5** (1.5 mol %), $Cu(OAc)_2 \cdot H_2O$ (88 mg, 0.44 mmol) and toluene (2 mL) was added to a Schlenk tube under an air atmosphere. Then the mixture was stirred at 125 °C (bath temperature, pre-heated) under air for about 10 h until complete consumption of **1a** judged by TLC. Then the reaction mixture was filtered through a short plug of silica

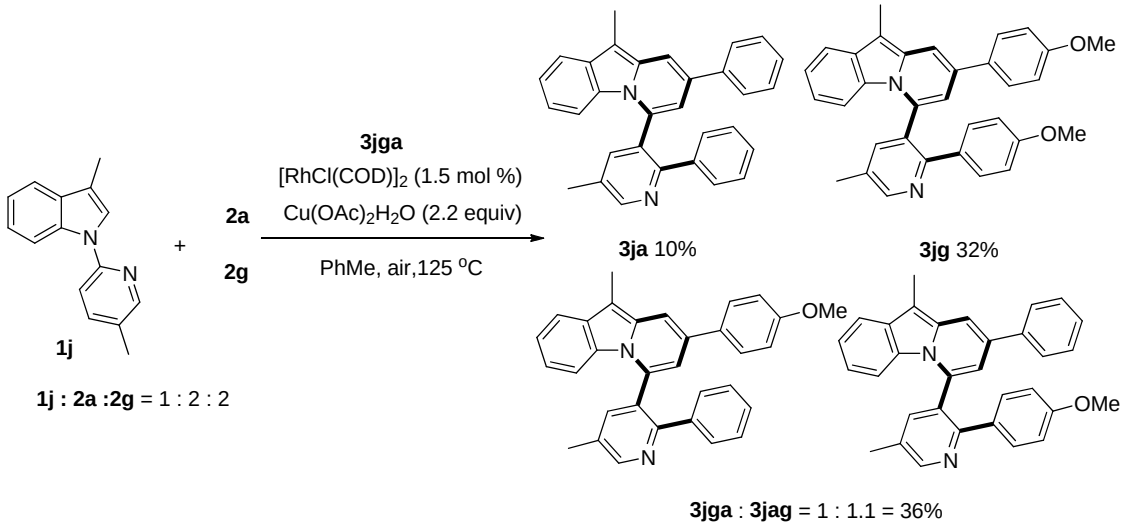
gel, washed with ethyl acetate and concentrated, the residue was purified by chromatography (ethyl acetate/hexane = 1/50) to afford the desired products **3aa** in 68% isolated yield.

4.5 Cross Reactions between 1b, 1j, and 2a



A mixture of 1-(pyridin-2-yl)-1*H*-indole **1b** (0.10 mmol), 3-methyl-1-(5-methylpyridin-2-yl)-1*H*-indole **1j** (0.10 mmol), 2-methyl-4-phenyl-3-butyn-2-ol **2a** (0.80 mmol), $[RhCl(COD)]_2$ (1.5 mol %), $Cu(OAc)_2 \cdot H_2O$ (88 mg, 0.44 mmol) and toluene (2 mL) was added to a Schlenk tube. Then the mixture was stirred at 125 °C (bath temperature, pre-heated) under air for 8 h until complete consumption of **1b** and **1j** judged by TLC. The reaction mixture was filtered through a short plug of silica gel, washed with ethyl acetate and concentrated. The resulting residue was purified by chromatography to afford **3ba** in 30% isolated yield (ethyl acetate/hexane = 1/150) and **3ja** in 52% isolated yield (ethyl acetate/hexane = 1/30).

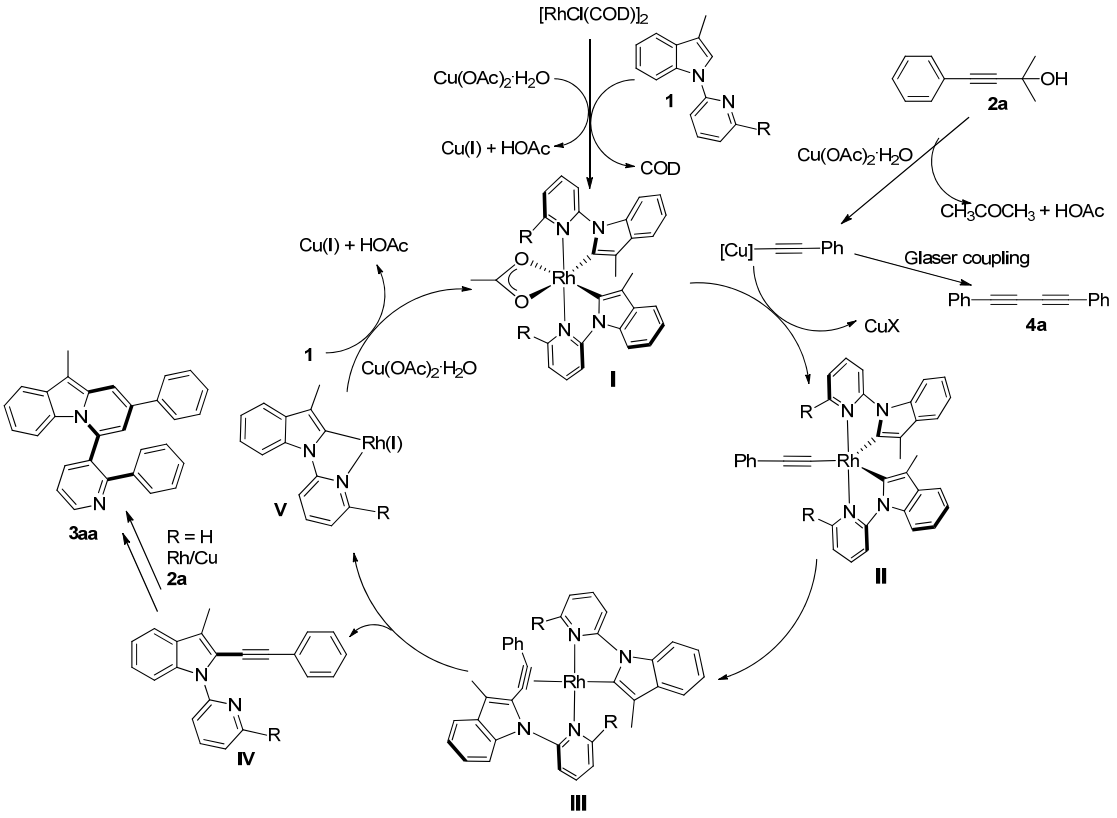
4.6 Cross Reactions between 1j, 2a, and 2g



A mixture of 3-methyl-1-(5-methylpyridin-2-yl)-1*H*-indole **1j** (0.20 mmol), 2-methyl-4-phenyl-3-butyn-2-ol **2a** (0.40 mmol), 4-(4-methoxyphenyl)-2-methylbut-3-yn-2-ol **2g** (0.40 mmol), $[RhCl(COD)]_2$ (1.5 mol %), $Cu(OAc)_2 \cdot H_2O$ (88 mg, 0.44 mmol) and toluene (2 mL) were added to a Schlenk tube. The mixture was stirred at 125 ^oC (bath temperature, pre-heated) under air for 8 h until complete consumption of **1j** judged by TLC. Then the reaction mixture was filtered through a short plug of silica gel, washed with ethyl acetate and concentrated. The residue was purified by chromatography to afford **3ja** in 10% isolated yield (ethyl acetate/hexane = 1/200), **3jga** and **3jag** as a mixture in 36% isolated yield (ethyl acetate/hexane = 1/50), and **3jg** in 32% isolated yield (ethyl acetate/hexane = 1/20).

5. Proposed mechanism for C-H alkynylation

It is worthy to note that blocking the C-6 position of the pyridine directing group with a Me group (substrate **1o**) suppressed formation of the corresponding pyrido[2,1-a]indole product and only the the alkynylation product **3oa** was isolated. Probably, the steric hindrance of the Me group at the C-6 position prevented the further transformation of **3oa**. Isolation of **3oa** indicated that the alkynylation step was possibly involved in the catalytic cycle for the formation of pyrido[2,1-a]indoles **3**. Thus it is reasonable to believe that the catalytic reactions start with the direct C-H alkynylation of substrates **1**, which then proceed to undergo a series of transformations to afford the target products finally.



Scheme S1. Proposed mechanism for the C-H alkynylation.

A proposed mechanism for the C-H alkynylation is shown in Scheme S1. Initially, the reaction of $[RhCl(COD)]_2$ with $Cu(OAc)_2 \cdot H_2O$ leads to formation of active metalating agent **I.** Then, substrate **1a** could react with complex **I** to generate intermediate **II** through chelation with pyridyl nitrogen and subsequent C-H activation of the alkene. Meanwhile, copper phenylacetylide was generated from the reactionn of **2a** with $Cu(OAc)_2 \cdot H_2O$ via *β*-carbon elimination. Transmetalation of the alkynl group from Cu to Rh generated the

Rh(III) species **III**. Intermediate **III** could undergo a reductive elimination to yield the desired alkynylation product and extruded Rh(I), which could be reoxidized by Cu(II) to the catalytically active species **I** to complete the catalytic cycle. Cu(II) might also regenerate from Cu(I) with O_2 in the air. Meanwhile, copper phenylacetylide generated in situ could undergo Glaser coupling to afford conjugate diyne **4a** as a byproduct. The alkynylation product **3aa** could react with another **2a** to yield pyrido[2,1-a]indole skeleton.

Unfortunately, our further attempt to detect or isolate other intermediates from the reaction mixtures failed. The mechanistic details for the further transformation of the alkynylation product to give the pyrido[2,1-a]indole skeleton are unclear yet.

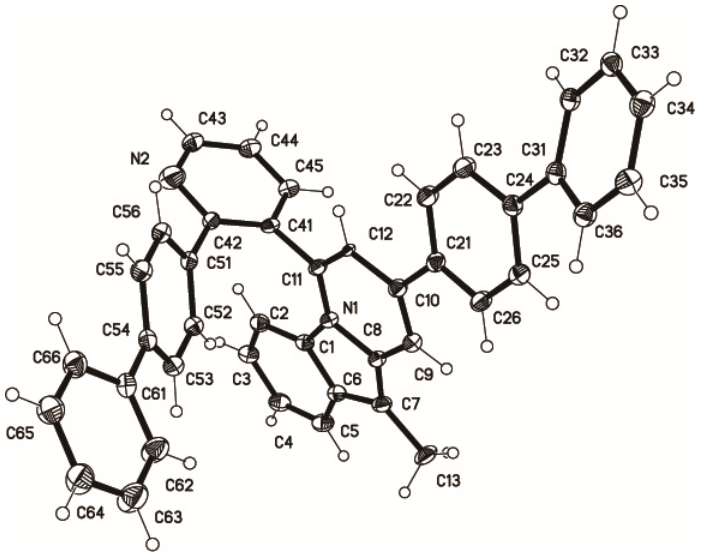
6. References

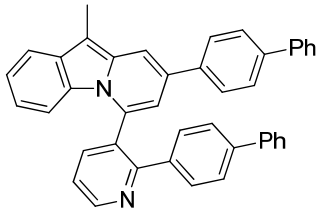
1. S. Xu, X. Huang, X. Hong, B. Xu, *Org. Lett.* **2012**, *14*, 4614.
2. S. Ma, B. Wu, X. Jiang, S. Zhao, *J. Org. Chem.* **2005**, *70*, 2568-2575.
3. Y. Yu, W. Yang, F. Rominger, A.-S.-K. Hashmi, *Angew. Chem.*, *Int. Ed.* **2013**, *52*, 7586.

7. X-ray studies

7.1 X-ray Crystal Structures of 3af

The data (CCDC1032403) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.





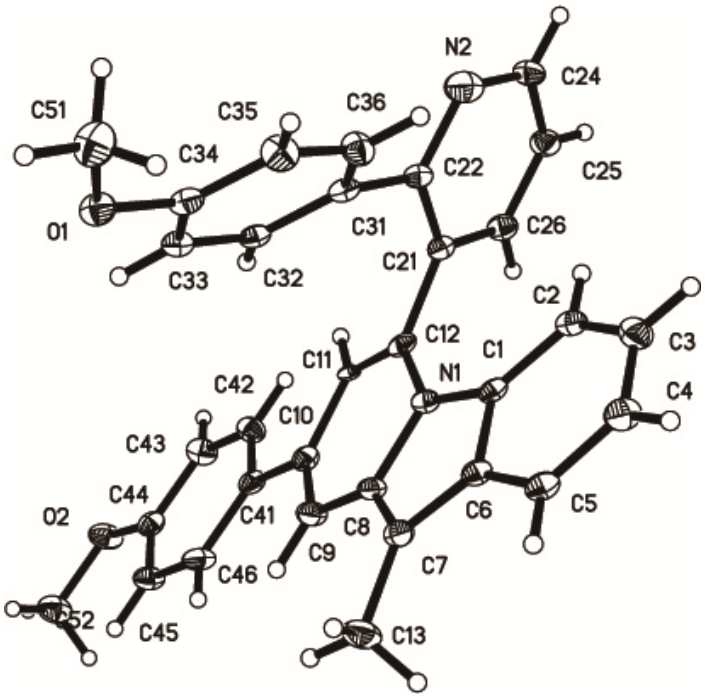
3af

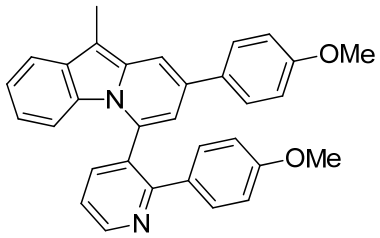
Table S1: Crystallographic Details for **3af**

Complex NO.	**3af**
empirical formula	C_{42} H_{30} N_2
formula weight	562.68
temperature, K	173(2)
radiation (Mo Kα), Å	0.71073
crystal system	Triclinic
space group	P-1
a, Å	11.0719(10)
b, Å	11.9763(11)
c, Å	12.7664(9)
α, °	95.060(7)
β, °	92.632(6)
γ, °	117.362(9)
V, Å^3	1490.4(2)
Z	2
d_{calcd}, g cm^{-3}	1.254
abs coeff, mm^{-1}	0.073
F(000)	592
crystal size, mm	0.15 x 0.13 x 0.11
θ range, °	3.22 to 26.00
indep reflns	10217 / 5857 [R(int) = 0.0266]
data-restraints-params	5857 / 0 / 397
GOF on F^2	1.134
final *R* ($I > 2\sigma(I)$)	R_1 = 0.0681, wR_2 = 0.1520
R indices (all data)	R_1 = 0.0915, wR_2 = 0.1634
peak and hole, e.Å^{-3}	0.571 and -0.696

7.2 X-ray Crystal Structures of 3ag

The data (CCDC1032402) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.





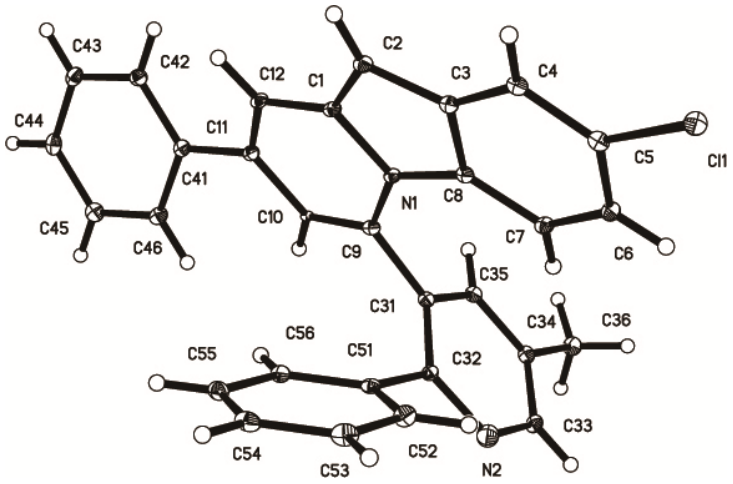
3ag

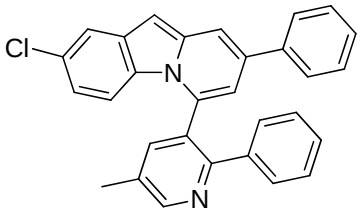
Table S2: Crystallographic Details for **3ag**

Complex NO.	**3ag**
empirical formula	$C_{32}\ H_{26}\ N_2\ O_2$
formula weight	470.55
temperature, K	173(2)
radiation (Mo Kα), Å	0.71073
crystal system	Monoclinic
space group	P2(1)/c
a, Å	18.889(2)
b, Å	7.1199(8)
c, Å	18.6541(19)
α, °	90
β, °	104.646(11)
γ, °	90
V, Å^3	2427.3(5)
Z	4
d_{calcd}, g cm^{-3}	1.288
abs coeff, mm^{-1}	0.080
F(000)	992
crystal size, mm	0.15 x 0.13 x 0.12
θ range, °	3.07 to 25.99
indep reflns	10153 / 4763 [R(int) = 0.0611]
data-restraints-params	4763 / 2 / 325
GOF on F^2	1.059
final R ($I > 2\sigma(I)$)	R_1 = 0.0791, wR_2 = 0.1860
R indices (all data)	R_1 = 0.1145, wR_2 = 0.2093
peak and hole, e.Å^{-3}	0.685 and -0.615

7.3 X-ray Crystal Structures of 3ia

The data (CCDC1032405) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.





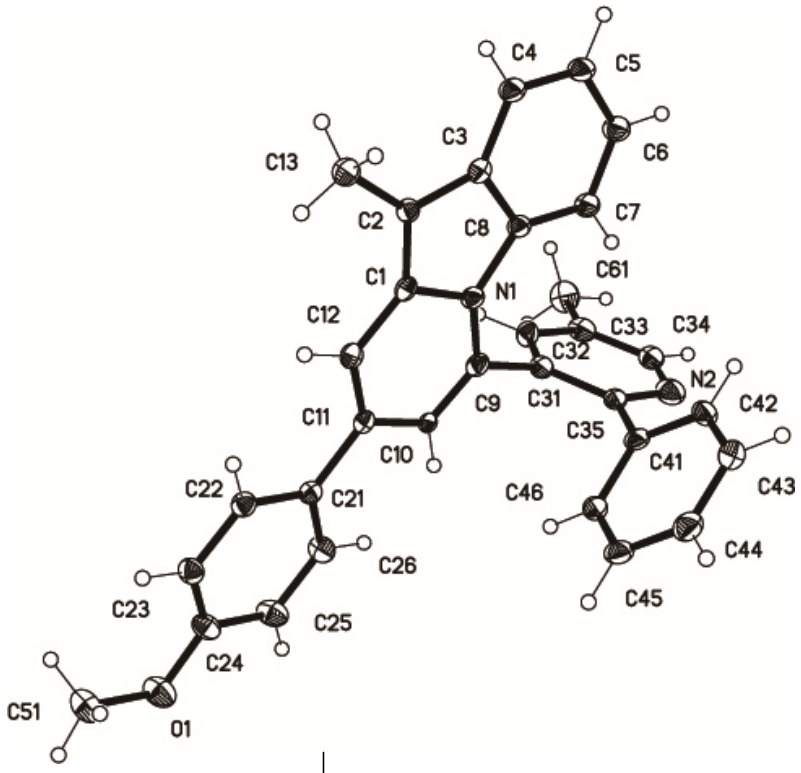
3la

Table S3: Crystallographic Details for **3la**

Complex NO.	**3la**
empirical formula	$C_{30}\ H_{21}\ Cl\ N_2$
formula weight	444.94
temperature, K	173(2)
radiation (Mo Kα), Å	0.71073
crystal system	Triclinic
space group	P-1
a, Å	8.8053(4)
b, Å	11.2771(10)
c, Å	12.0975(13)
α, °	67.401(9)
β, °	89.113(7)
γ, °	83.151(6)
V, Å^3	1100.51(16)
Z	2
d_{calcd}, g cm^{-3}	1.343
abs coeff, mm^{-1}	0.195
F(000)	464
crystal size, mm	0.15 x 0.12 x 0.10
θ range, °	3.42 to 26.00
indep reflns	8275 / 4304 [R(int) = 0.0340]
data-restraints-params	4304 / 0 / 298
GOF on F^2	1.061
final *R* ($I > 2\sigma(I)$)	R_1 = 0.0630, wR_2 = 0.1664
R indices (all data)	R_1 = 0.0764, wR_2 = 0.1778
peak and hole, e.Å^{-3}	0.758 and -0.815

7.4 X-ray Crystal Structures of 3jga

The data (CCDC1032406) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



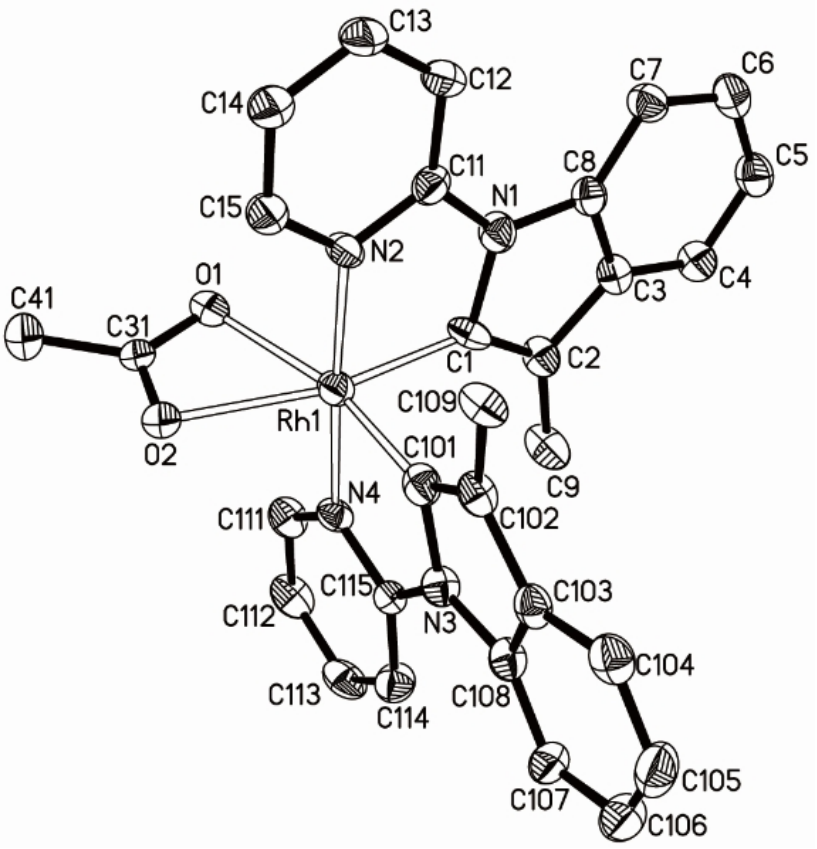
3jga

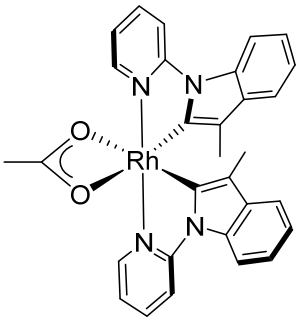
Table S4: Crystallographic Details for **3iga**

Complex NO.	**3iga**
empirical formula	C_{32} H_{26} N_2 O
formula weight	454.55
temperature, K	173(2)
radiation (Mo Kα), Å	0.71073
crystal system	Monoclinic
space group	$P2_1/c$
a, Å	9.9489(5)
b, Å	17.1959(6)
c, Å	14.4905(8)
α, °	90
β, °	109.121(6)
γ, °	90
V, Å^3	2342.26(19)
Z	2
d_{calcd}, g cm^{-3}	1.343
abs coeff, mm^{-1}	0.195
F(000)	960
crystal size, mm	0.15 x 0.14 x 0.11
θ range, °	3.42 to 26.00
indep reflns	8275 / 4304 [R(int) = 0.0340]
data-restraints-params	4304 / 0 / 298
GOF on F^2	1.061
final R ($I > 2\sigma(I)$)	R_1 = 0.0630, wR_2 = 0.1664
R indices (all data)	R_1 = 0.0764, wR_2 = 0.1778
peak and hole, e.Å^{-3}	0.758 and -0.815

7.6 X-ray Crystal Structures of complex 5

The data (CCDC1032404) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.





Rh(III)-complex **5**

Table S5: Crystallographic Details for **5**

Complex NO.	**5**
empirical formula	$C_{30}\ H_{25}\ N_4\ O_2\ Rh \cdot 0.3\ CH_2Cl_2$
formula weight	601.93
temperature, K	173(2)
radiation (Mo Kα), Å	0.71073
crystal system	Triclinic
space group	P-1
a, Å	9.6401(19)
b, Å	11.069(2)
c, Å	12.562(3)
α, °	82.69(3)
β, °	77.98(3)
γ, °	83.72(3)
V, Å^3	1295.6(4)
Z	2
d_{calcd}, g cm^{-3}	1.543
abs coeff, mm^{-1}	0.757
F(000)	613
crystal size, mm	0.14 x 0.14 x 0.12
θ range, °	3.30 to 26.00
indep reflns	16782 / 4565 [R(int) = 0.0616]
data-restraints-params	4565 / 0 / 362
GOF on F^2	1.051
final R ($I > 2\sigma(I)$)	R_1 = 0.0505, wR_2 = 0.1225
R indices (all data)	R_1 = 0.0727, wR_2 = 0.1693
peak and hole, e.Å^{-3}	0.901 and -0.964

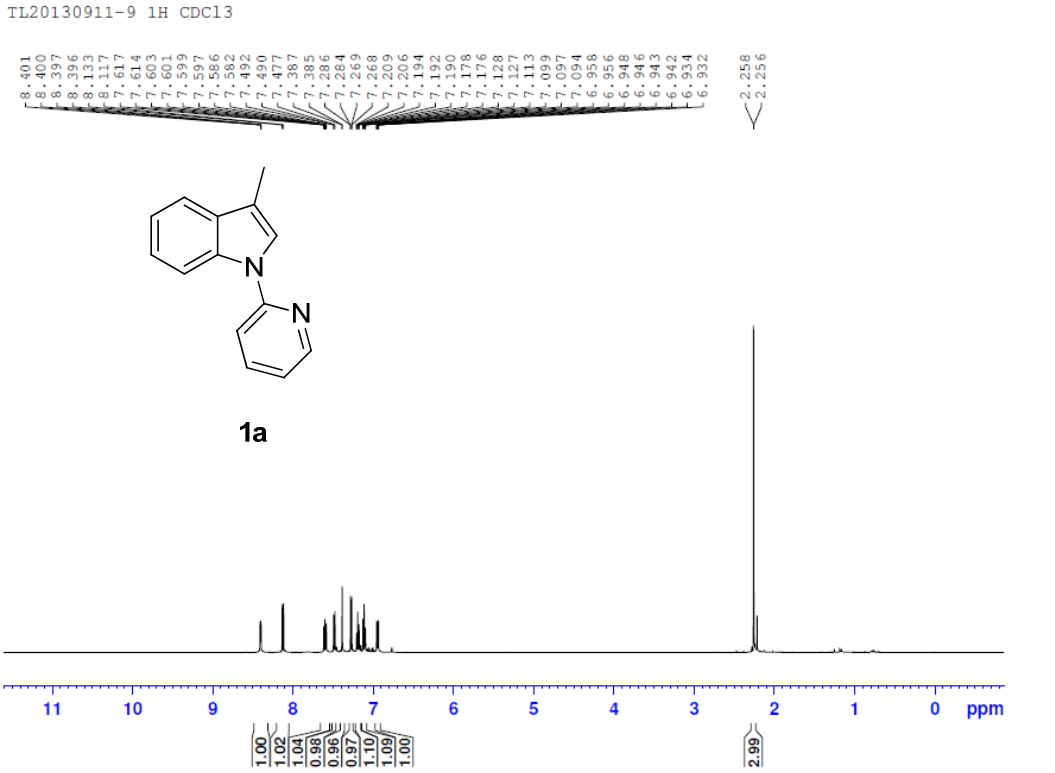
Table S6: Bond lengths [A] and angles [deg] for **5**.

Bond lengths [A]			
Rh(1)-C(1)	1.967(7)	Rh(1)-N(4)	2.035(5)
Rh(1)-C(101)	1.927(7)	Rh(1)-N(2)	2.037(5)
Rh(1)-O(1)	2.241(5)	Rh(1)-O(2)	2.246(5)
O(1)-C(31)	1.305(8)	O(2)-C(31)	1.283(8)
N(1)-C(11)	1.379(8)	N(2)-C(15)	1.334(8)
N(1)-C(8)	1.416(8)	N(2)-C(11)	1.349(8)
N(1)-C(1)	1.438(8)	C(2)-C(3)	1.450(9)
C(1)-C(2)	1.351(9)	C(2)-C(9)	1.503(9)
N(3)-C(115)	1.373(8)	N(4)-C(111)	1.340(8)
N(3)-C(108)	1.414(8)	N(4)-C(115)	1.340(8)
N(3)-C(101)	1.456(8)	C(4)-C(5)	1.379(10)
C(3)-C(4)	1.382(9)	C(5)-C(6)	1.393(10)
C(3)-C(8)	1.403(9)	C(6)-C(7)	1.385(9)
C(7)-C(8)	1.395(9)	C(102)-C(109)	1.507(9)
C(11)-C(12)	1.390(9)	C(104)-C(105)	1.376(11)
C(12)-C(13)	1.380(10)	C(105)-C(106)	1.385(12)
C(103)-C(104)	1.384(9)	C(106)-C(107)	1.383(10)
C(103)-C(108)	1.406(9)	C(107)-C(108)	1.386(9)
C(103)-C(102)	1.447(9)	C(111)-C(112)	1.378(10)
C(13)-C(14)	1.376(10)	C(112)-C(113)	1.392(11)
C(14)-C(15)	1.356(9)	C(113)-C(114)	1.366(10)
C(31)-C(41)	1.508(10)	C(114)-C(115)	1.397(9)
C(101)-C(102)	1.380(9)		

Bond angles [deg]			
C(101)-Rh(1)-C(1)	86.4(3)	C(101)-Rh(1)-O(1)	165.7(2)
C(101)-Rh(1)-N(4)	81.0(2)	C(1)-Rh(1)-O(1)	107.7(2)
C(1)-Rh(1)-N(4)	95.9(2)	N(4)-Rh(1)-O(1)	94.53(18)
C(101)-Rh(1)-N(2)	98.2(2)	N(2)-Rh(1)-O(1)	86.98(19)
C(1)-Rh(1)-N(2)	81.2(2)	C(101)-Rh(1)-O(2)	106.0(2)
N(4)-Rh(1)-N(2)	177.05(19)	C(1)-Rh(1)-O(2)	167.2(2)
N(4)-Rh(1)-O(2)	89.30(18)	N(4)-Rh(1)-C(31)	92.2(2)
N(2)-Rh(1)-O(2)	93.65(18)	N(2)-Rh(1)-C(31)	90.4(2)
O(1)-Rh(1)-O(2)	60.14(17)	O(1)-Rh(1)-C(31)	30.3(2)
C(101)-Rh(1)-C(31)	135.7(2)	O(2)-Rh(1)-C(31)	29.8(2)
C(1)-Rh(1)-C(31)	137.9(3)	C(31)-O(1)-Rh(1)	89.4(4)
C(11)-N(1)-C(8)	131.9(5)	N(1)-C(1)-Rh(1)	111.1(4)
C(11)-N(1)-C(1)	119.0(5)	C(31)-O(2)-Rh(1)	89.8(4)
C(8)-N(1)-C(1)	109.1(5)	C(15)-N(2)-C(11)	119.1(5)
C(2)-C(1)-N(1)	107.7(5)	C(15)-N(2)-Rh(1)	125.3(4)
C(2)-C(1)-Rh(1)	141.1(5)	C(11)-N(2)-Rh(1)	115.4(4)
C(1)-C(2)-C(3)	108.7(6)	C(4)-C(3)-C(8)	119.3(6)
C(1)-C(2)-C(9)	128.5(6)	C(4)-C(3)-C(2)	132.4(6)
C(3)-C(2)-C(9)	122.9(6)	C(8)-C(3)-C(2)	108.3(5)
C(115)-N(3)-C(108)	132.1(5)	C(111)-N(4)-C(115)	119.5(5)
C(115)-N(3)-C(101)	117.9(5)	C(111)-N(4)-Rh(1)	124.5(4)
C(108)-N(3)-C(101)	109.8(5)	C(115)-N(4)-Rh(1)	116.0(4)
C(5)-C(4)-C(3)	120.0(6)	N(2)-C(11)-N(1)	113.1(5)
C(4)-C(5)-C(6)	120.0(6)	N(2)-C(11)-C(12)	120.8(6)
C(7)-C(6)-C(5)	121.7(6)	N(1)-C(11)-C(12)	126.2(6)
C(6)-C(7)-C(8)	117.3(6)	C(13)-C(12)-C(11)	118.5(6)

C(7)-C(8)-C(3)	121.7(6)	C(104)-C(103)-C(108)	119.5(6)
C(7)-C(8)-N(1)	132.2(6)	C(104)-C(103)-C(102)	131.8(6)
C(3)-C(8)-N(1)	106.2(5)	C(108)-C(103)-C(102)	108.5(5)
C(14)-C(13)-C(12)	120.2(6)	C(105)-C(104)-C(103)	119.4(7)
C(15)-C(14)-C(13)	118.2(7)	C(104)-C(105)-C(106)	120.5(7)
N(2)-C(15)-C(14)	123.2(6)	C(107)-C(106)-C(105)	121.6(7)
O(2)-C(31)-O(1)	120.7(6)	C(106)-C(107)-C(108)	117.7(7)
O(2)-C(31)-C(41)	121.1(7)	C(107)-C(108)-C(103)	121.2(6)
O(1)-C(31)-C(41)	118.2(7)	C(107)-C(108)-N(3)	132.4(6)
O(2)-C(31)-Rh(1)	60.5(3)	C(103)-C(108)-N(3)	106.4(6)
O(1)-C(31)-Rh(1)	60.2(3)	N(4)-C(111)-C(112)	122.6(7)
C(41)-C(31)-Rh(1)	177.8(6)	C(111)-C(112)-C(113)	117.8(6)
C(102)-C(101)-N(3)	106.0(6)	C(114)-C(113)-C(112)	120.0(6)
C(102)-C(101)-Rh(1)	141.8(5)	C(113)-C(114)-C(115)	119.1(7)
N(3)-C(101)-Rh(1)	112.2(4)	N(4)-C(115)-N(3)	112.8(5)
C(101)-C(102)-C(103)	109.2(6)	N(4)-C(115)-C(114)	120.9(6)
C(101)-C(102)-C(109)	127.7(6)	N(3)-C(115)-C(114)	126.3(6)
C(103)-C(102)-C(109)	123.1(5)		

8. NMR Spectra



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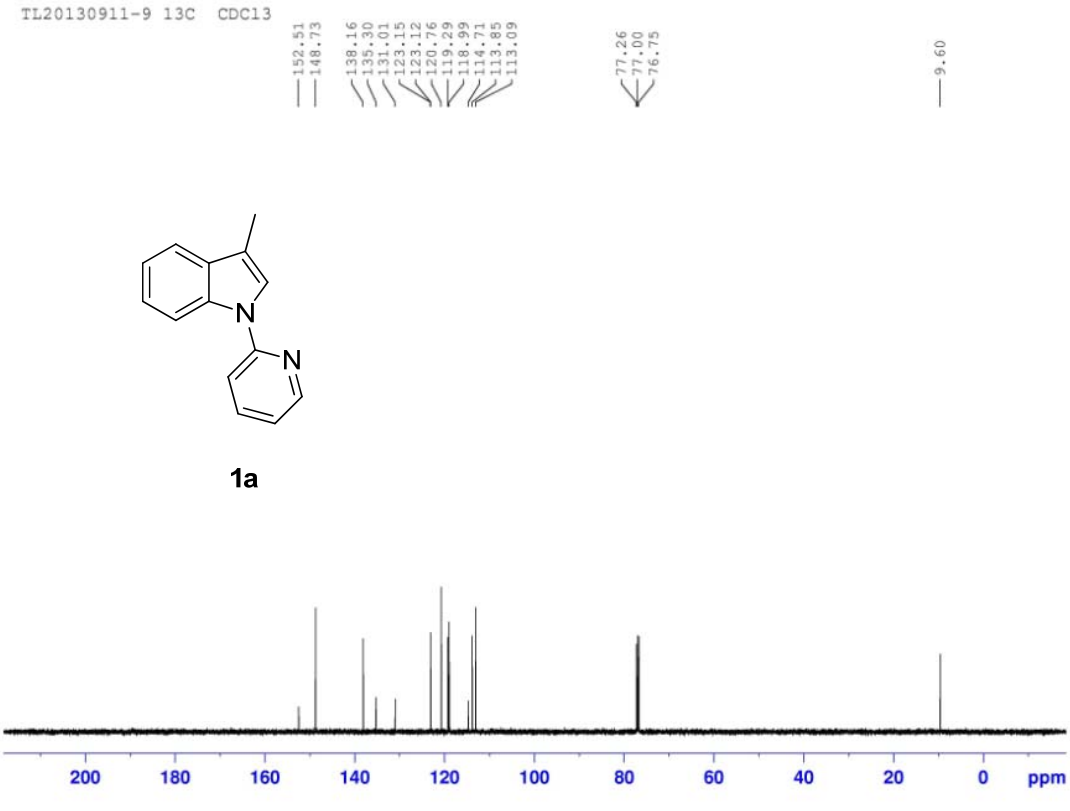

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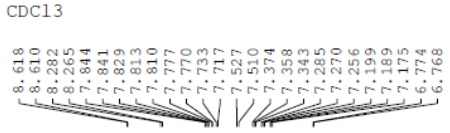
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7.829
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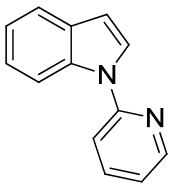
7.810
7.777
7.770
7.733
7.717
7.527
7.510
7.374
7.358
7.343
7.285
7.270
7.256
7.199
7.189
7.175
6.774
6.768



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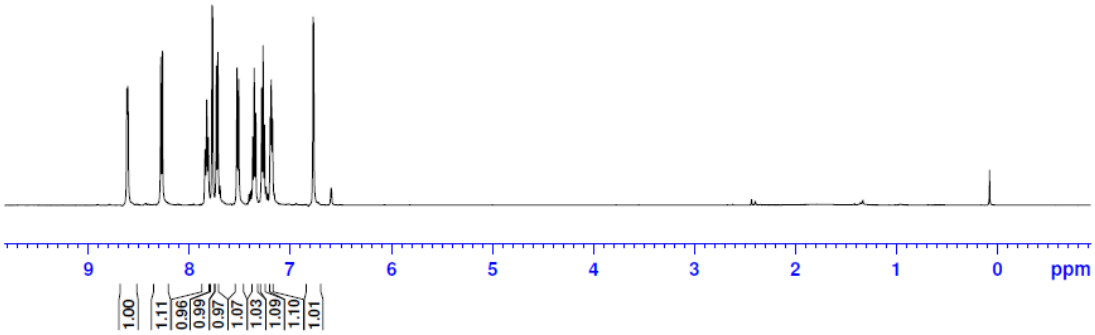
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8
7
6
5
4
3
2
1
0
ppm
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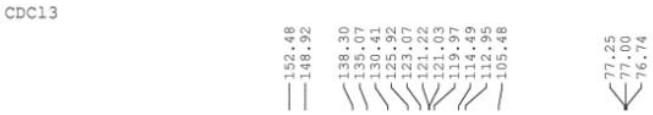
1.11
0.96
0.99
0.97
1.07
1.03
1.09
1.10
1.01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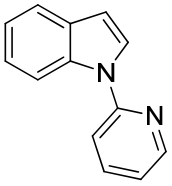
135.07
130.41
125.92
123.07
121.22
121.03
119.97
114.49
112.95
105.48
77.25
77.00
76.74



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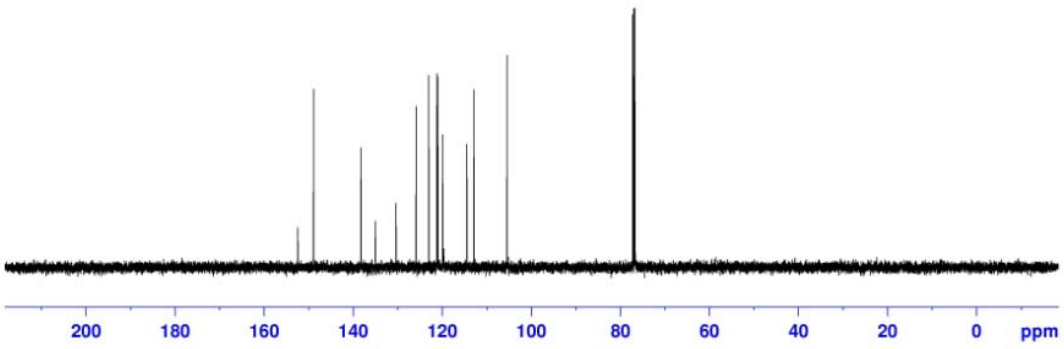
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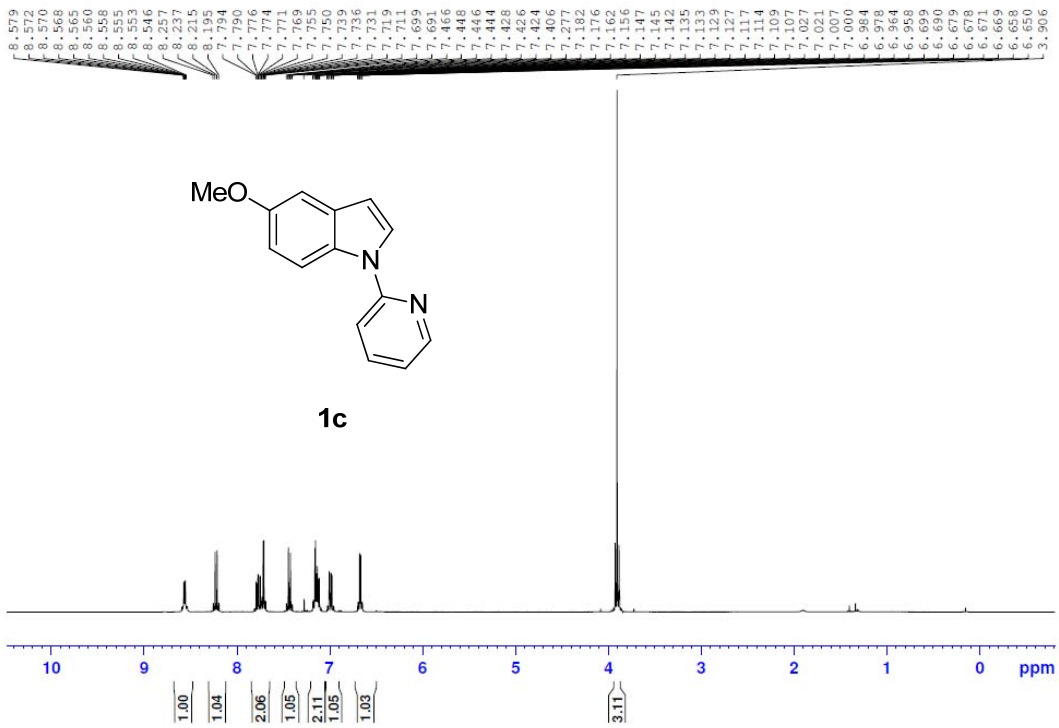
100
80
60
40
20
0
ppm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8.568
8.565
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8.257
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8.195
7.794
7.790
7.776
7.774
7.771
7.769
7.755
7.750
7.739
7.736
7.731
7.719
7.711
7.699
7.691
7.466
7.448
7.446
7.444
7.428
7.426
7.424
7.406
7.277
7.182
7.176
7.162
7.156
7.147
7.145
7.142
7.135
7.133
7.129
7.127
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7.114
7.109
7.107
7.027
7.021
7.007
7.000
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6.978
6.964
6.958
6.699
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6.658
6.650
3.906
MeO
N
N
1c
10
9
8
7
6
5
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ppm
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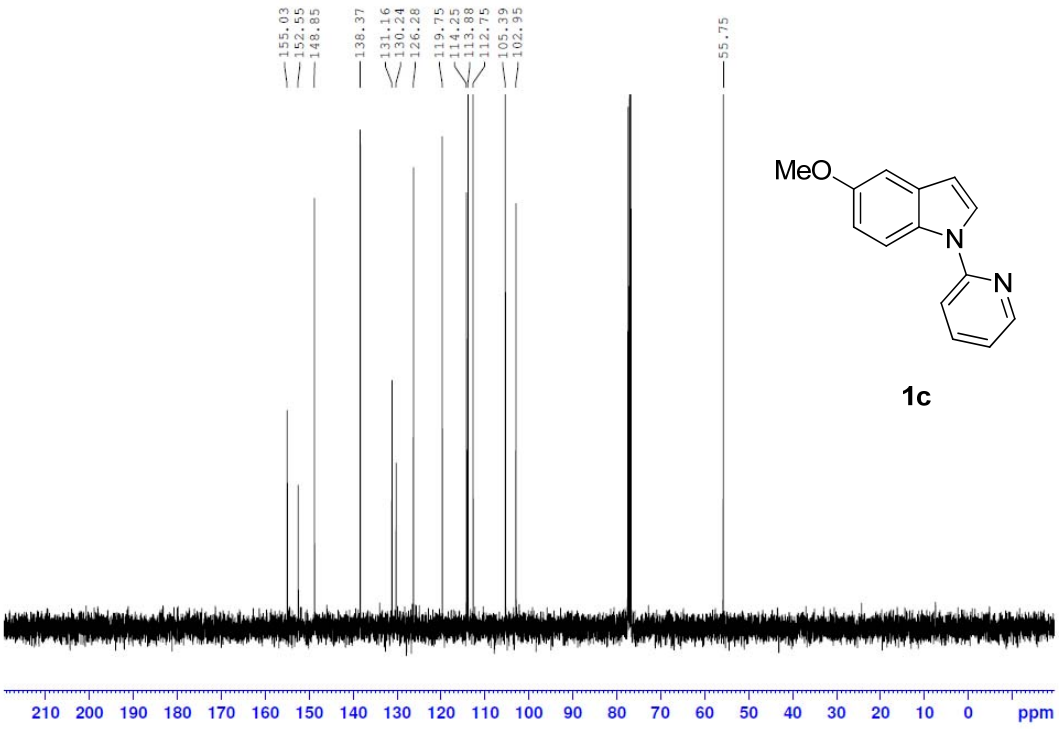
2.06
1.05
2.11
1.05
1.03
3.11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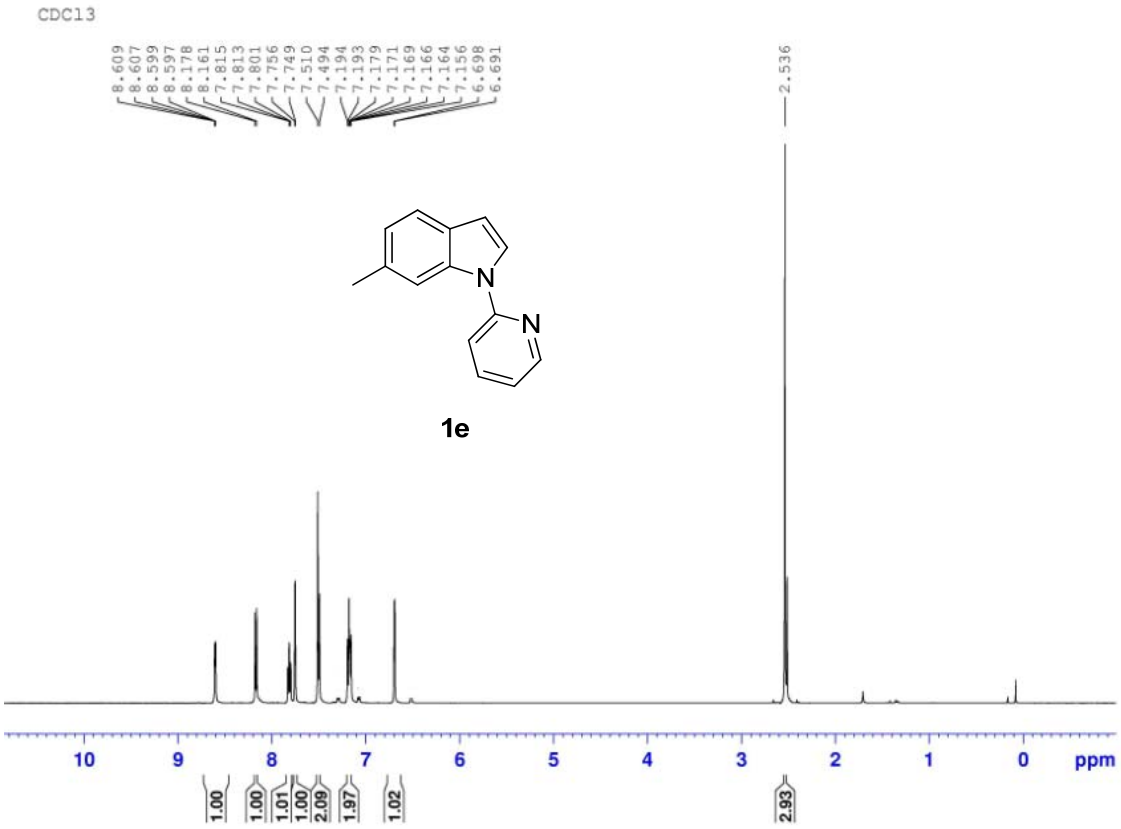
138.37
131.16
130.24
126.28
119.75
114.25
113.88
112.75
105.39
102.95
55.75
MeO
N
N
1c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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8.597
8.178
8.161
7.815
7.813
7.801
7.756
7.749
7.510
7.494
7.194
7.193
7.179
7.171
7.169
7.166
7.164
7.156
6.698
6.691
2.536
N
N
1e
10
9
8
7
6
5
4
3
2
1
0
ppm
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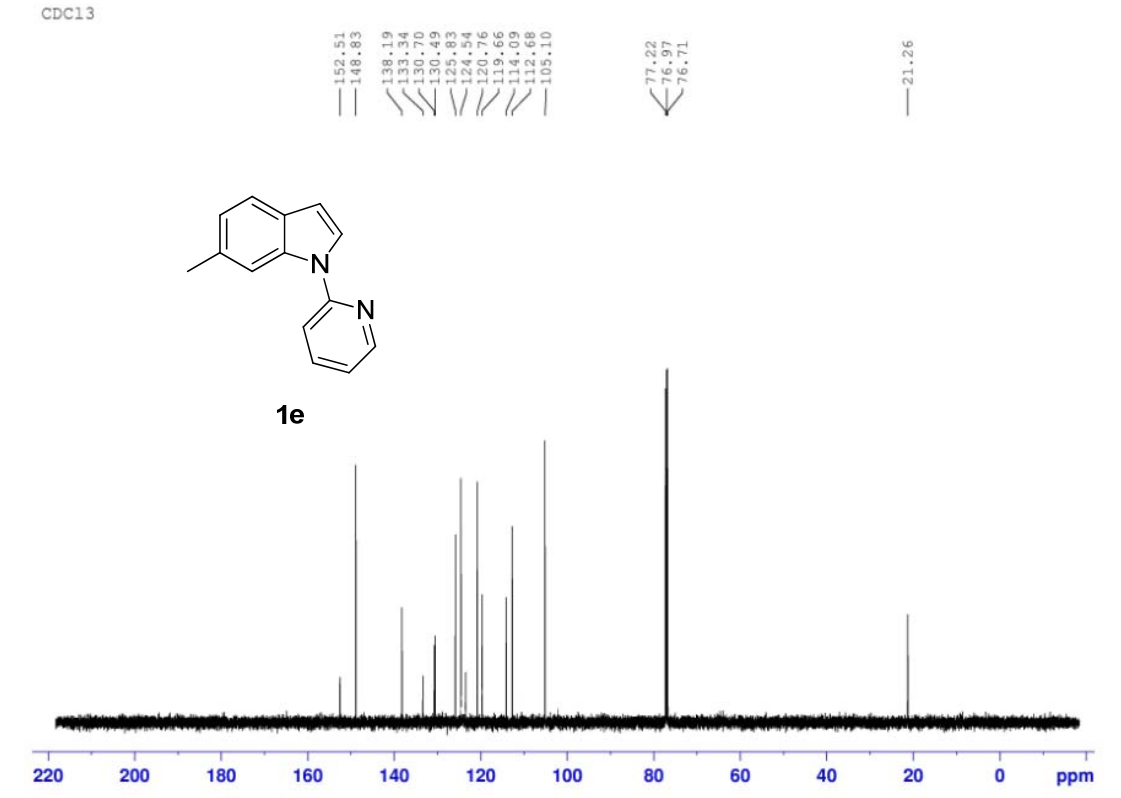
1.00
1.01
1.00
2.09
1.97
1.02
2.93


CDC13
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138.19
133.34
130.70
130.49
125.83
124.54
120.76
119.66
114.09
112.68
105.10
77.22
76.97
76.71
21.26
N
N
1e
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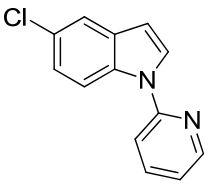
200
180
160
140
120
100
80
60
40
20
0
ppm

TL20131204-9 1H CDCl3



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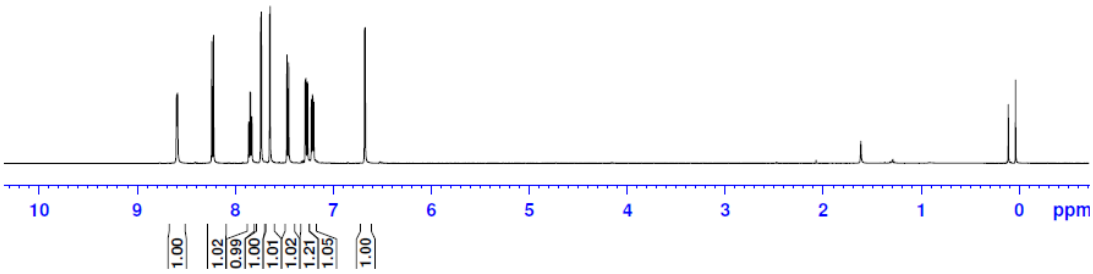
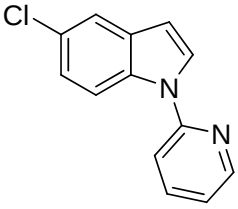


TL20131204-9 13C CDCl3



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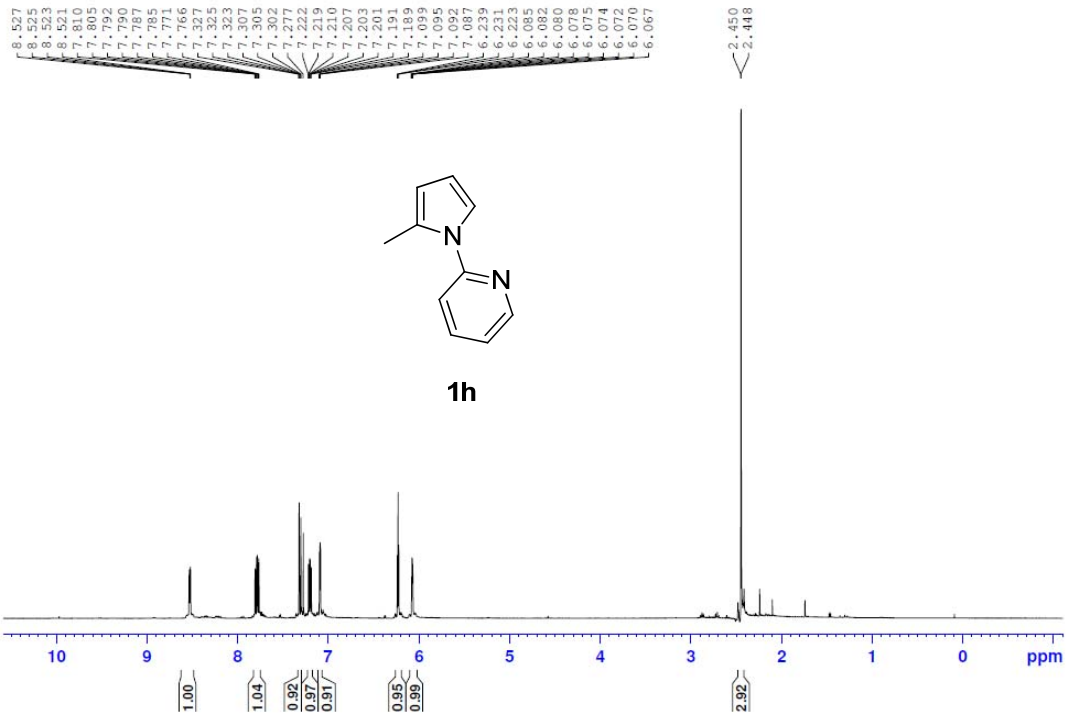
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7.323
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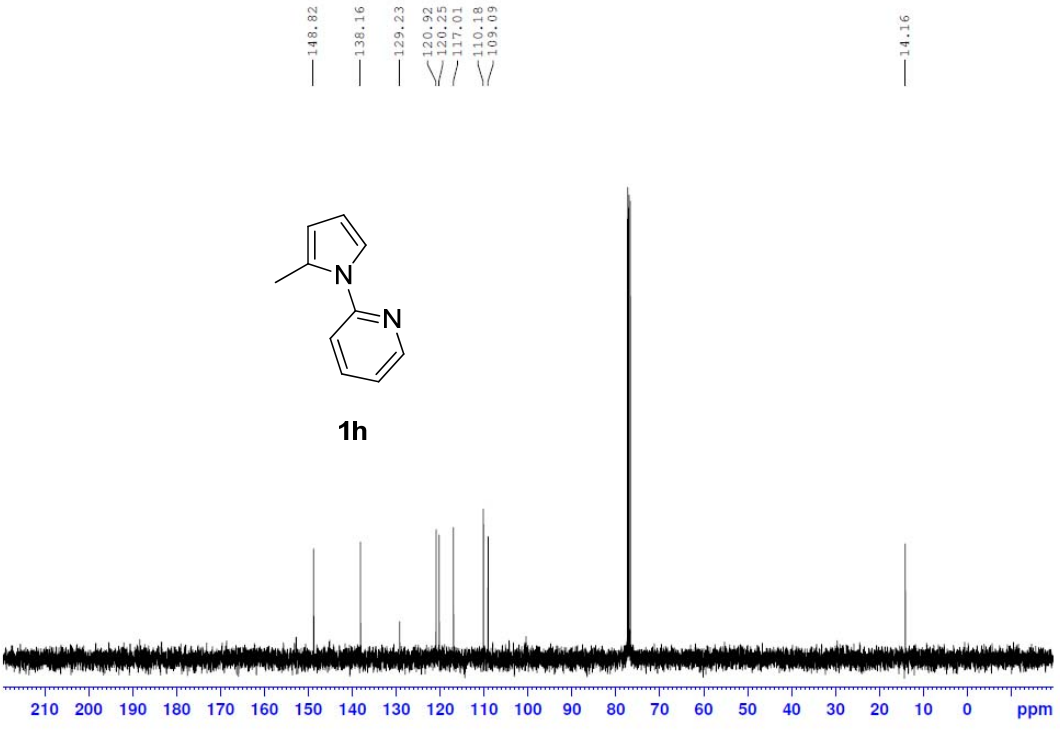
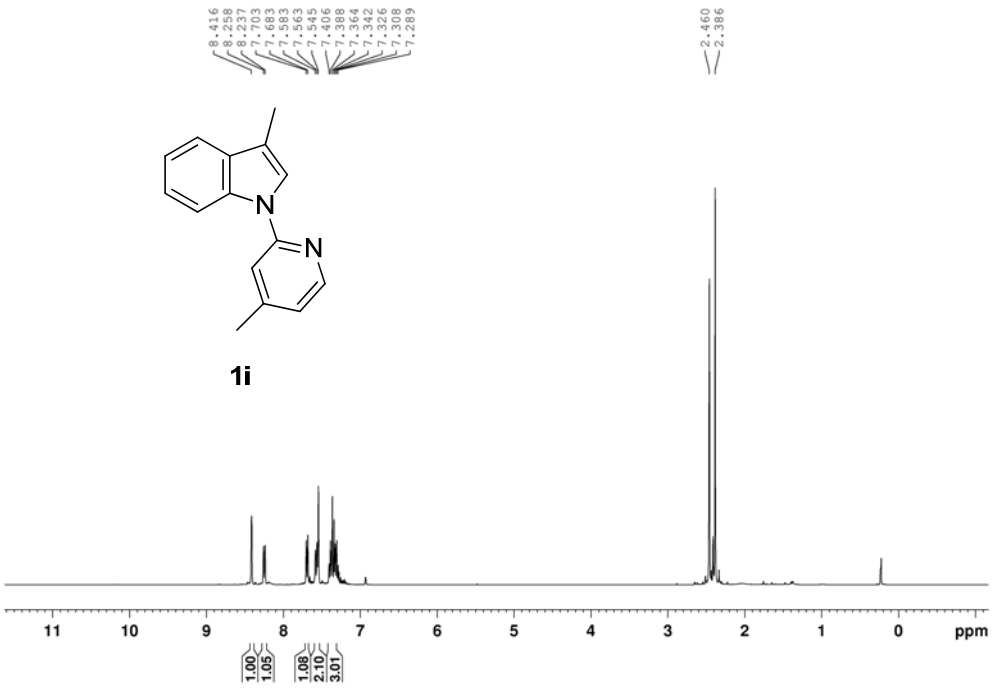
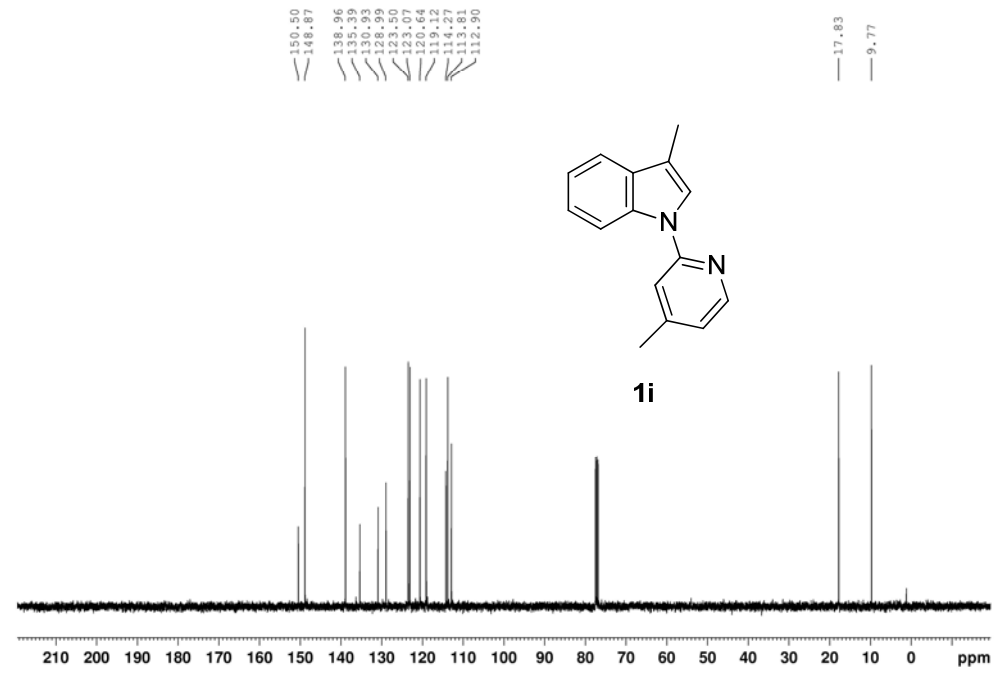
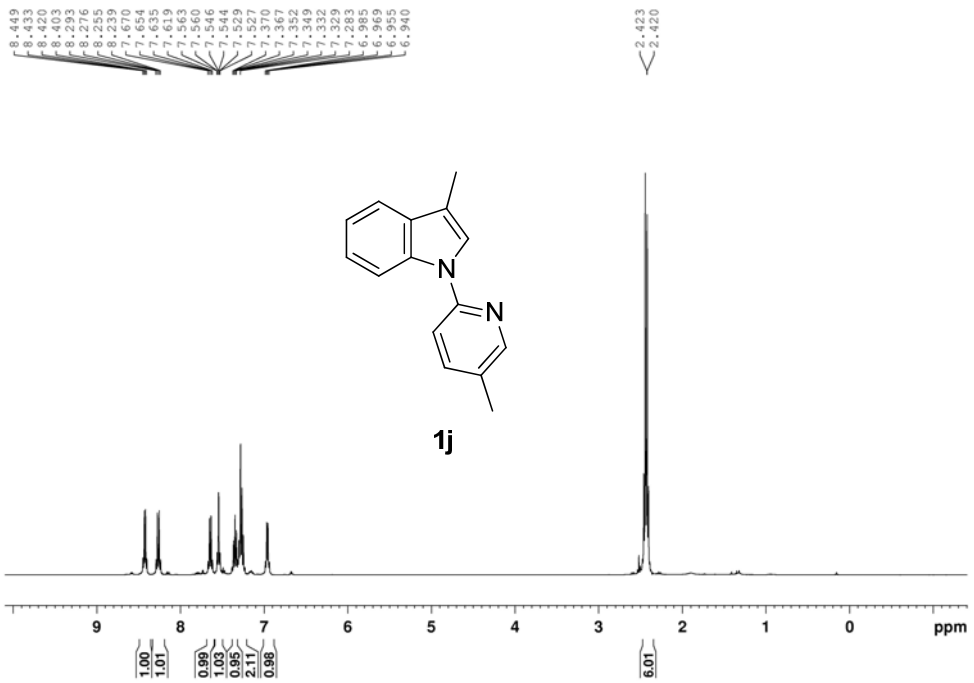
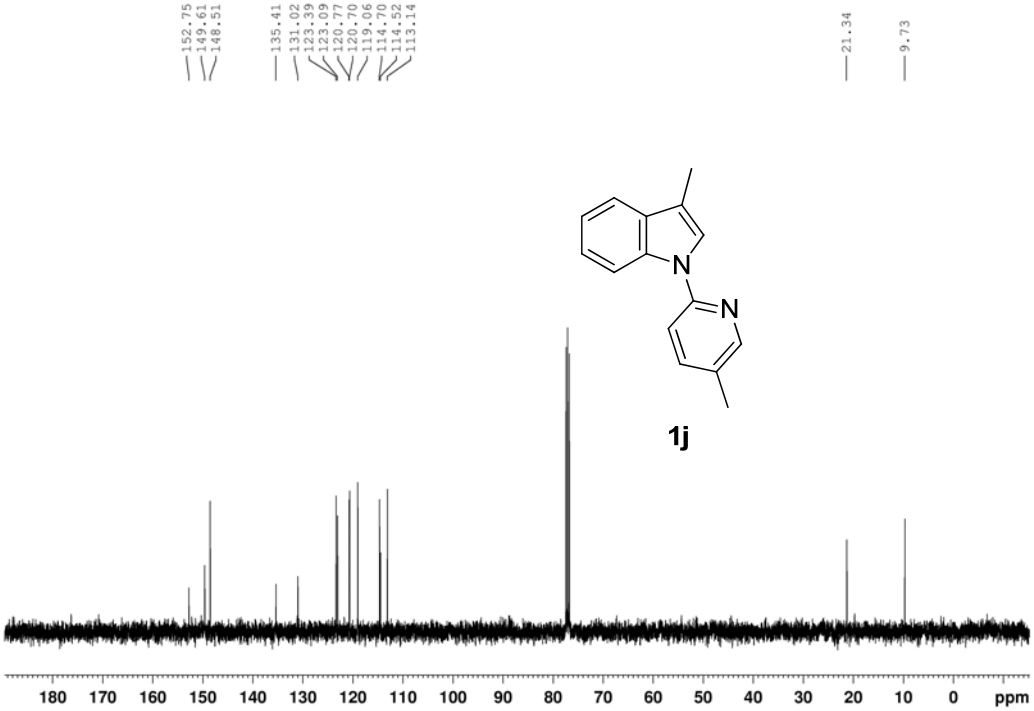
7.189
7.099
7.095
7.092
7.087
6.239
6.231
6.223
6.085
6.082
6.080
6.078
6.075
6.074
6.072
6.070
6.067
2.450
2.448
N
N
1h
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.04
0.92
0.97
0.91
0.95
0.99
2.92

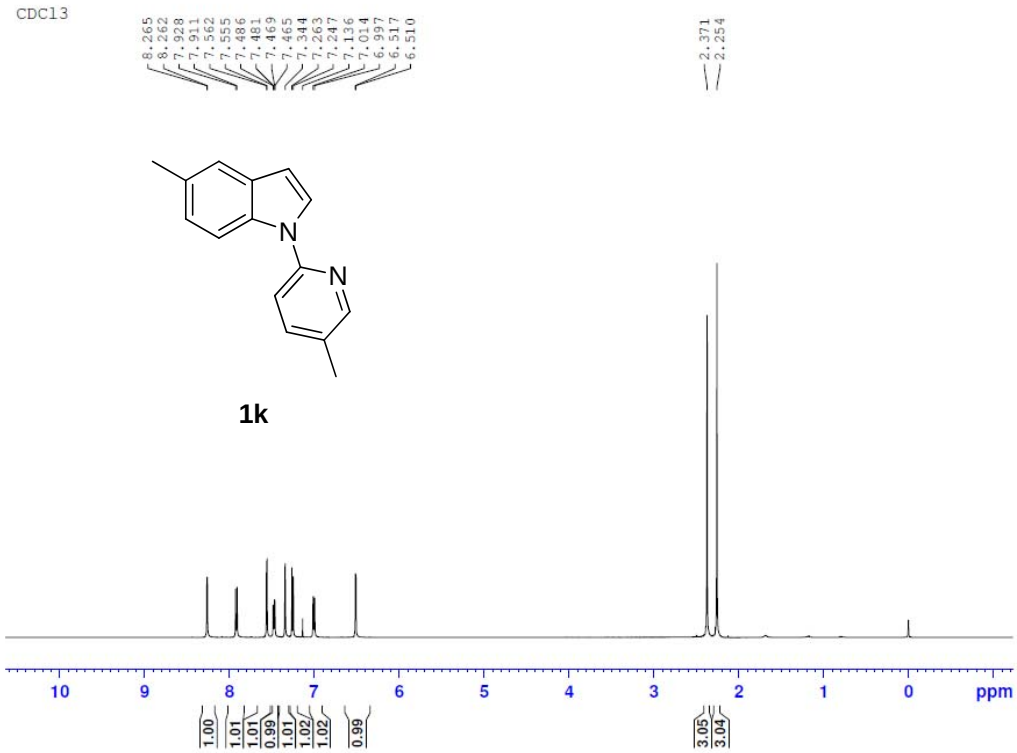

148.82
138.16
129.23
120.92
120.25
117.01
110.18
109.09
14.16
N
N
1h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

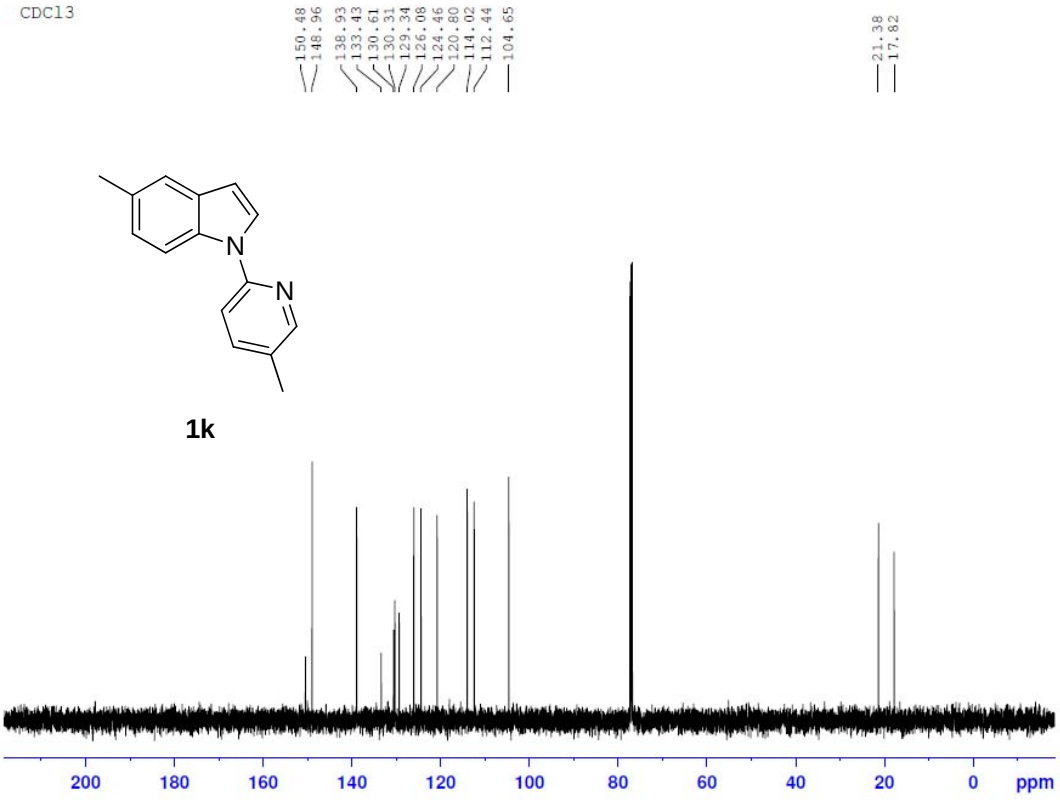

8.416
8.258
8.237
7.703
7.683
7.583
7.563
7.545
7.406
7.388
7.364
7.342
7.326
7.308
7.289
2.460
2.386
N
N
1i
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.05
1.08
2.10
3.01

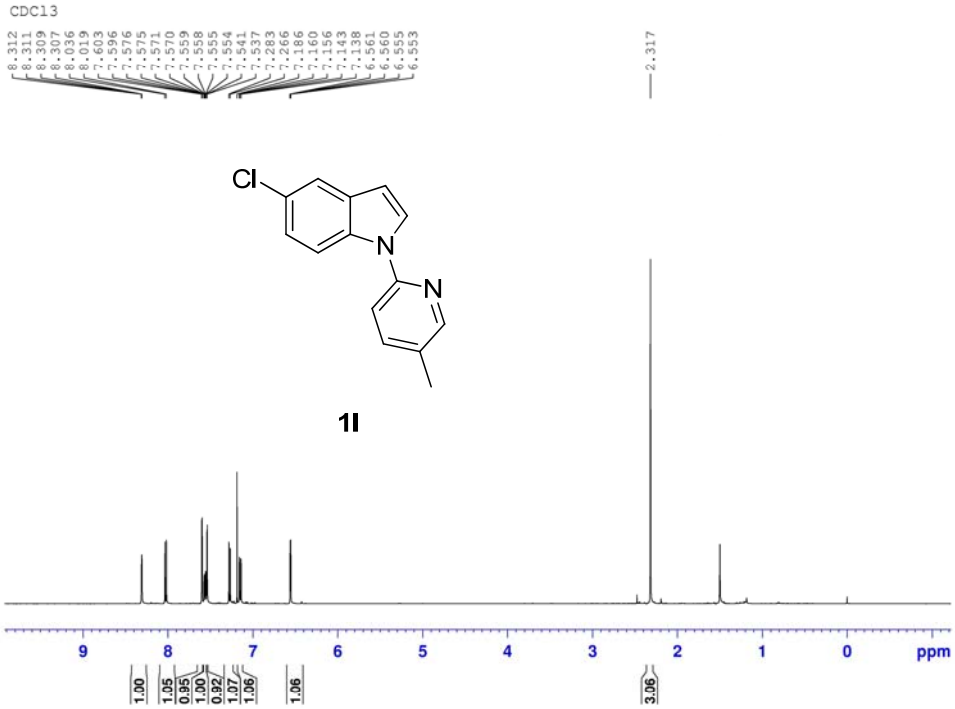

150.50
148.87
138.96
135.39
130.93
128.99
123.50
123.07
120.64
119.12
114.27
113.81
112.90
17.83
9.77
N
N
1i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

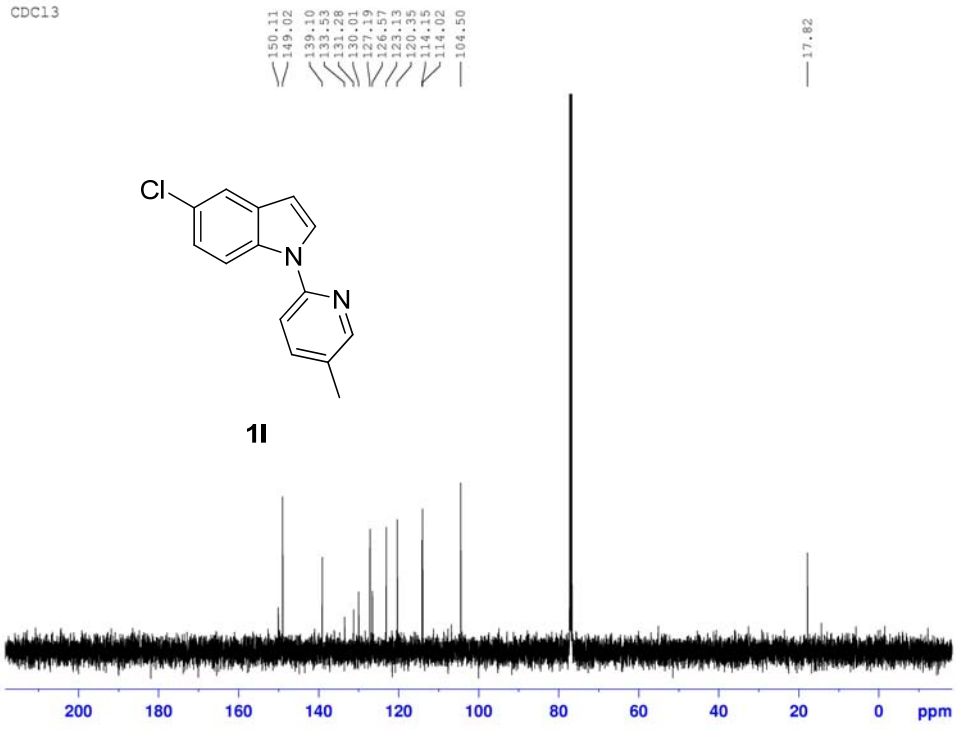

8.449
8.433
8.420
8.403
8.293
8.276
8.255
8.239
7.670
7.654
7.635
7.619
7.563
7.560
7.546
7.544
7.529
7.527
7.370
7.367
7.352
7.349
7.332
7.329
7.283
6.985
6.969
6.955
6.940
2.423
2.420
1j
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
0.99
1.03
0.95
2.11
0.98
6.01

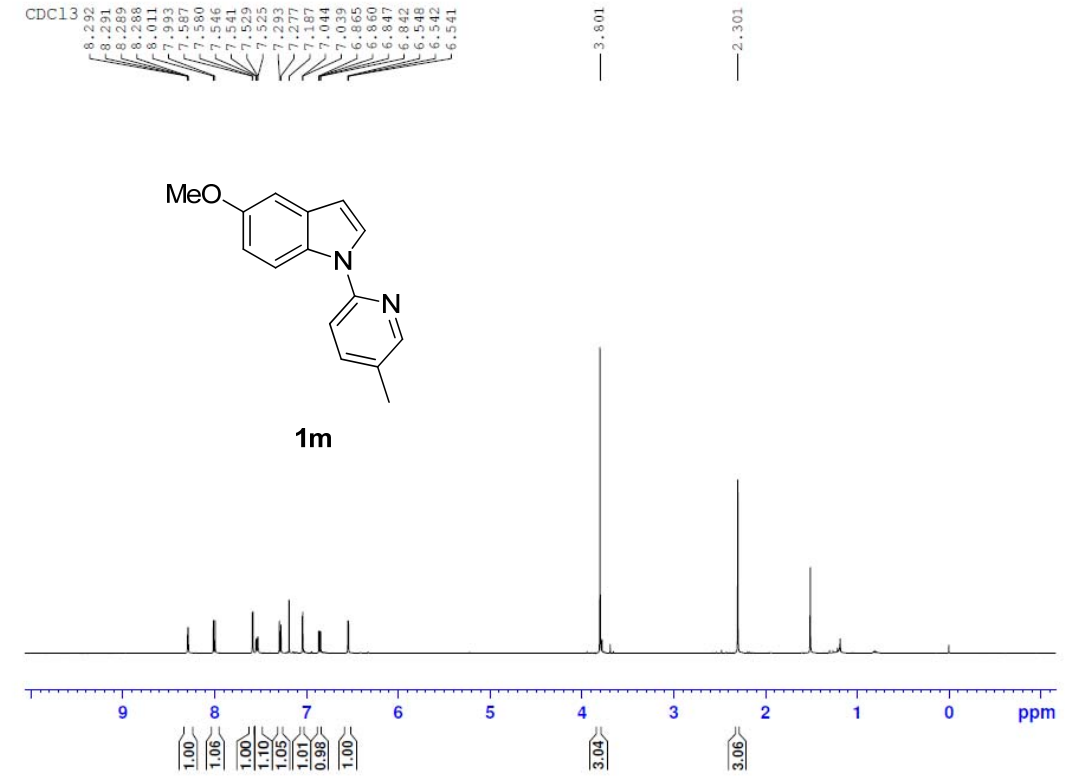

152.75
149.61
148.51
135.41
131.02
123.39
123.09
120.77
120.70
119.06
114.70
114.52
113.14
21.34
9.73
1j
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

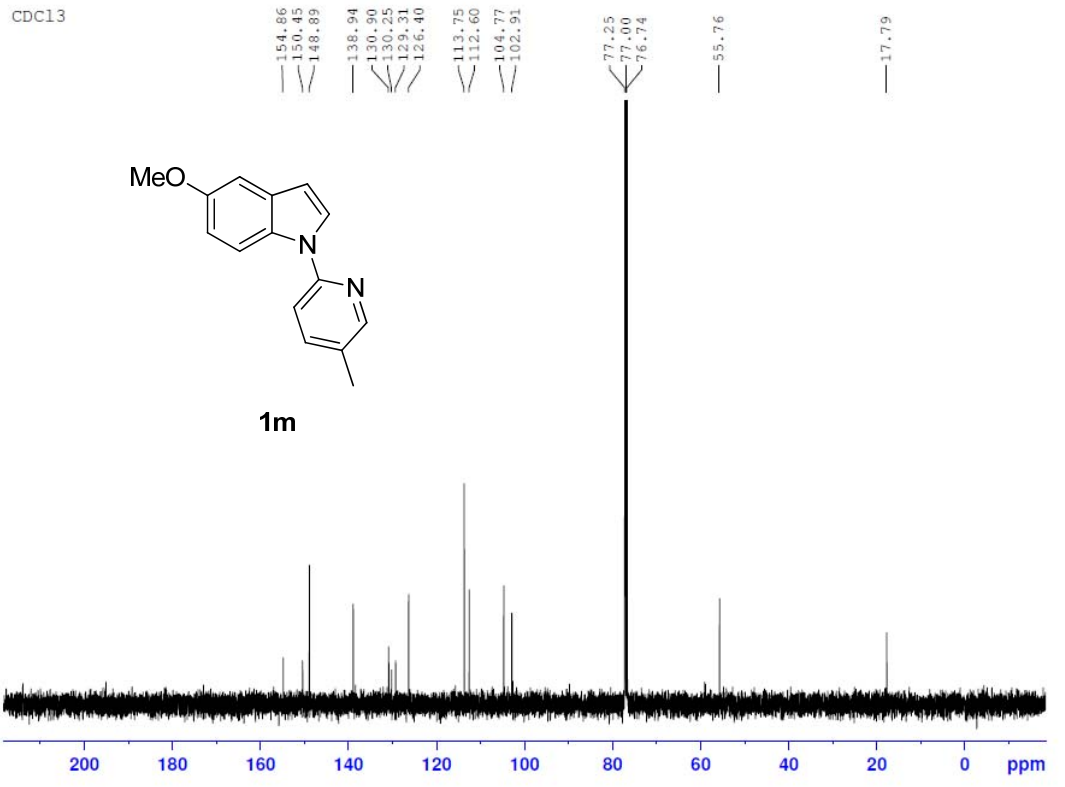

CDCl3
8.265
8.262
7.928
7.911
7.562
7.555
7.486
7.481
7.469
7.465
7.344
7.263
7.247
7.136
7.014
6.997
6.517
6.510
2.371
2.254
N
N
1k
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
1.01
0.99
1.01
1.02
1.02
0.99
3.05
3.04

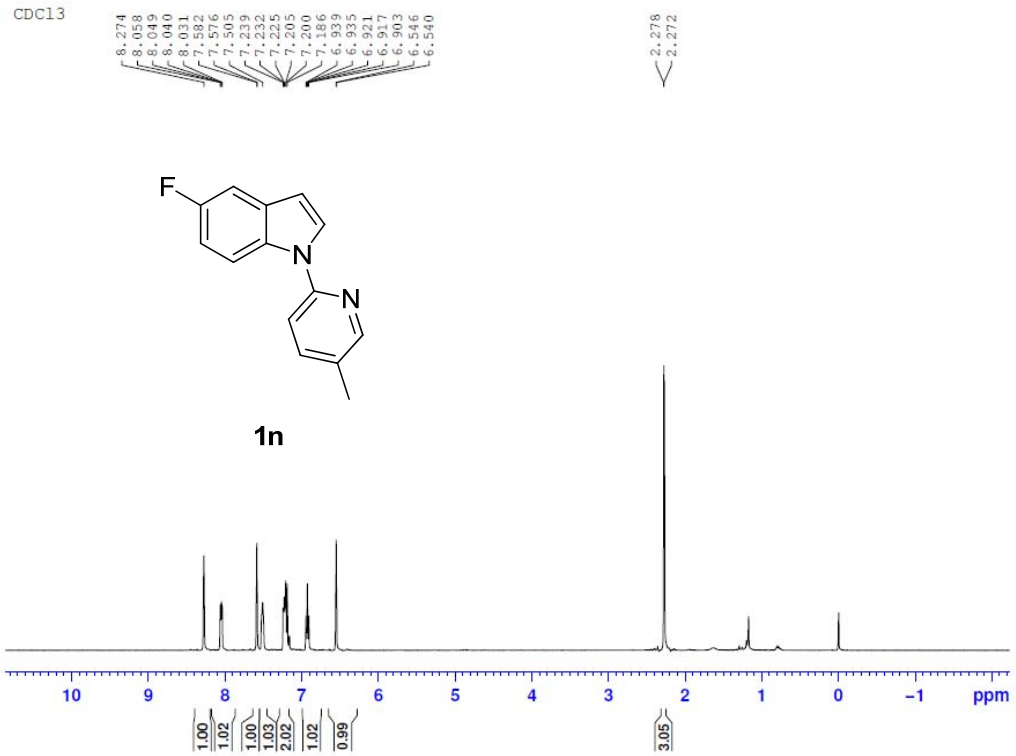

CDCl3
150.48
148.96
138.93
133.43
130.61
130.31
129.34
126.08
124.46
120.80
114.02
112.44
104.65
21.38
17.82
N
N
1k
200
180
160
140
120
100
80
60
40
20
0
ppm

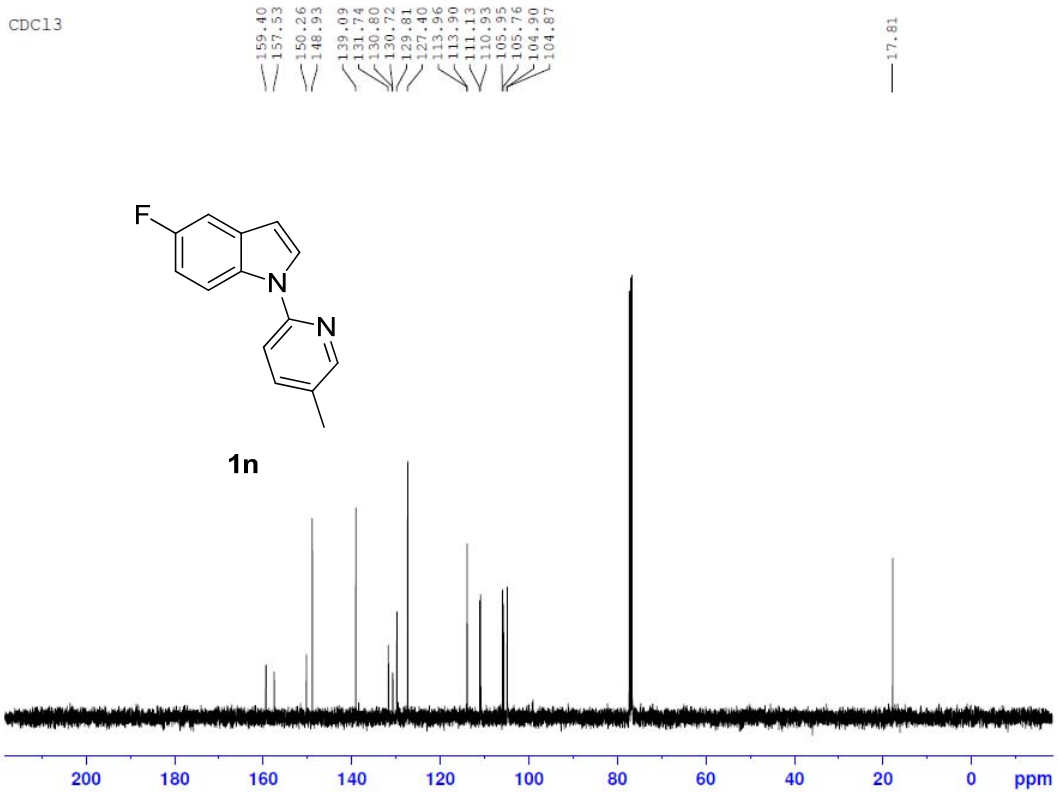

CDCl3
8.312
8.311
8.309
8.307
8.036
8.019
7.603
7.596
7.576
7.575
7.571
7.570
7.559
7.558
7.555
7.554
7.541
7.537
7.283
7.266
7.186
7.160
7.156
7.143
7.138
6.561
6.560
6.555
6.553
2.317
Cl
N
N
1l
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.05
0.95
1.00
0.92
1.07
1.06
1.06
3.06

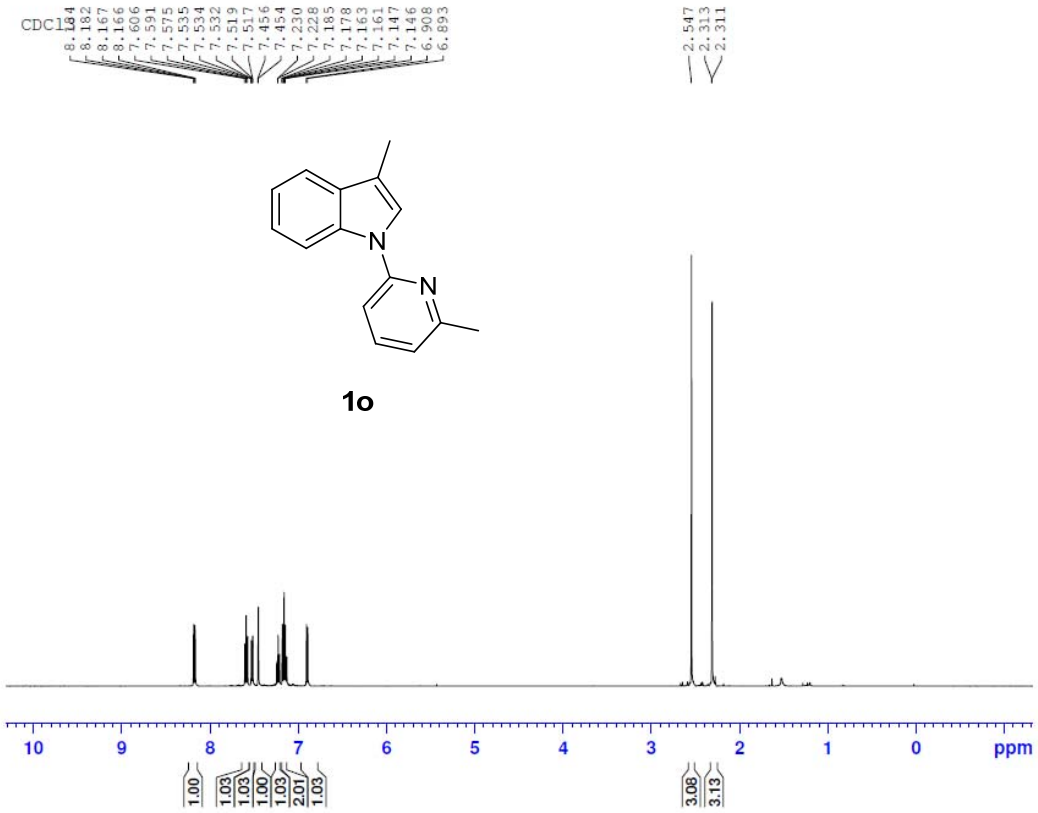

CDCl3
150.11
149.02
139.10
133.53
131.28
130.01
127.49
126.57
123.13
120.35
114.15
114.02
104.50
17.82
Cl
N
N
1l
200
180
160
140
120
100
80
60
40
20
0
ppm

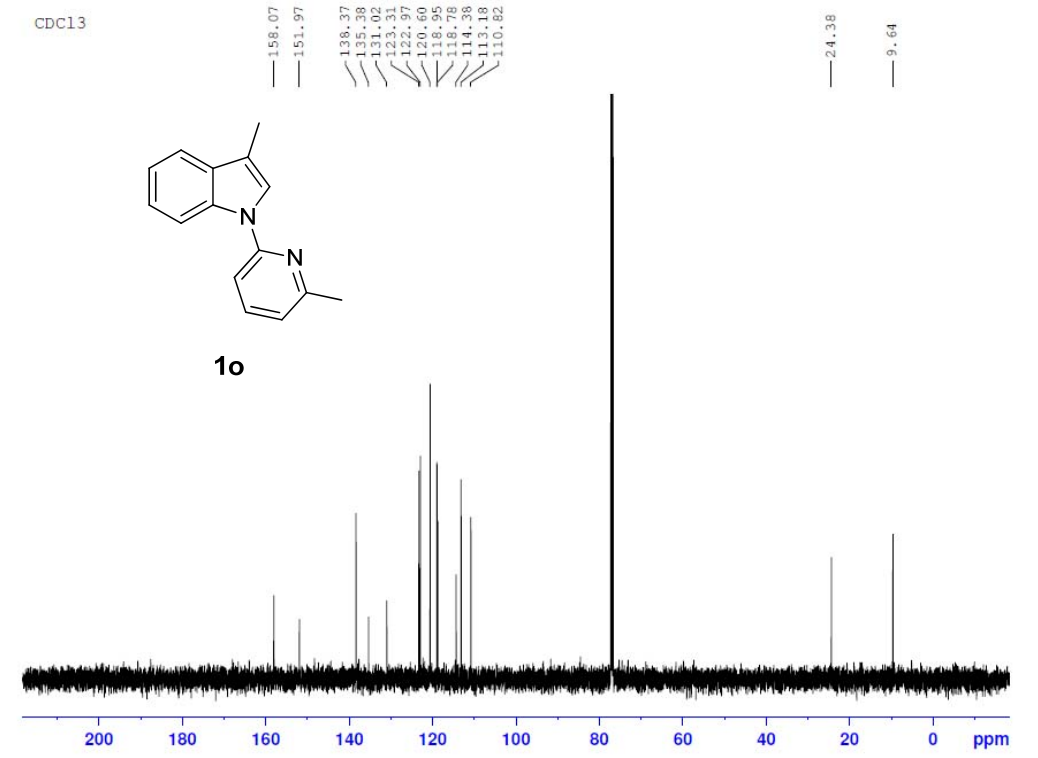

CDCl3
8.292
8.291
8.289
8.288
8.011
7.993
7.587
7.580
7.546
7.541
7.529
7.525
7.293
7.277
7.187
7.044
7.039
6.865
6.860
6.847
6.842
6.548
6.542
6.541
3.801
2.301
MeO
N
N
1m
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.06
1.00
1.10
1.05
1.01
0.98
1.00
3.04
3.06

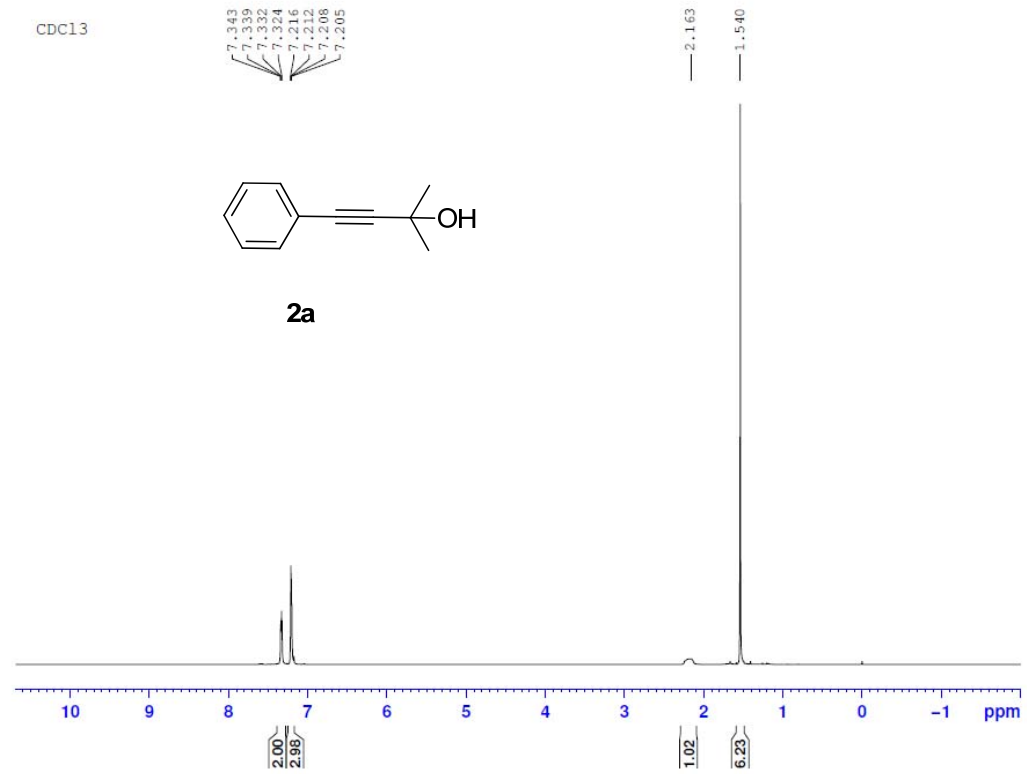

CDCl3
154.86
150.45
148.89
138.94
130.90
130.25
129.31
126.40
113.75
112.60
104.77
102.91
77.25
77.00
76.74
55.76
17.79
MeO
N
N
1m
200
180
160
140
120
100
80
60
40
20
0
ppm

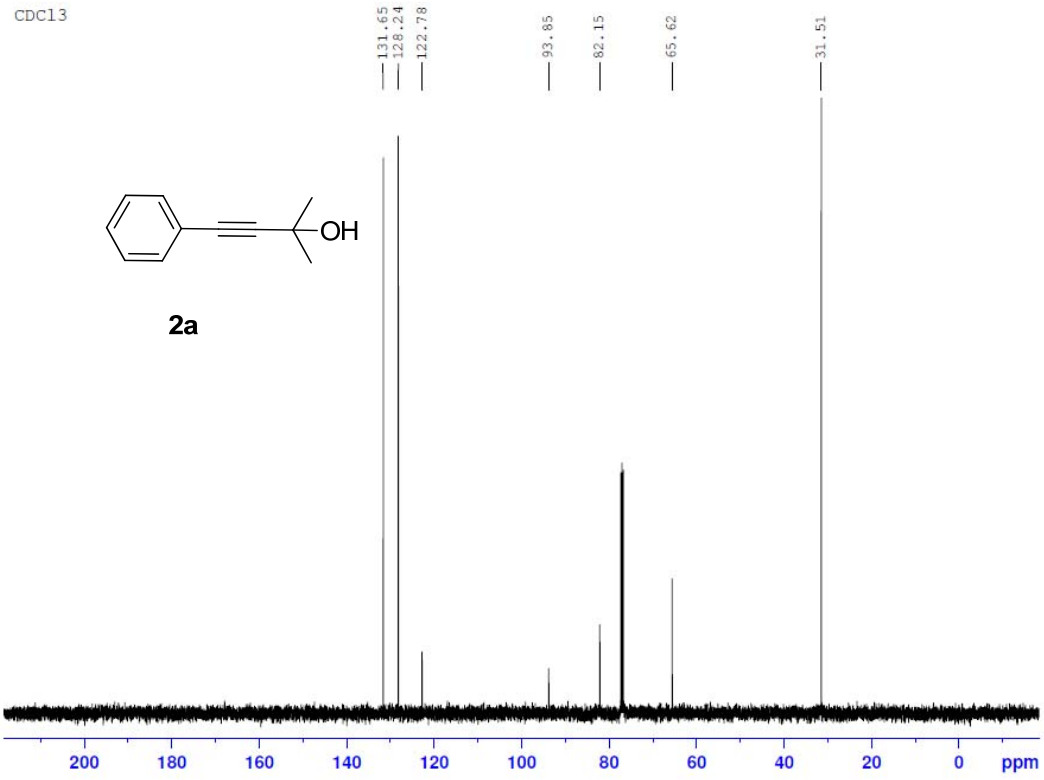

CDCl3
8.274
8.058
8.049
8.040
8.031
7.582
7.576
7.505
7.239
7.232
7.225
7.205
7.200
7.186
6.939
6.935
6.921
6.917
6.903
6.546
6.540
2.278
2.272
F
N
N
1n
10
9
8
7
6
5
4
3
2
1
0
−1
ppm
1.00
1.02
1.00
1.03
2.02
1.02
0.99
3.05

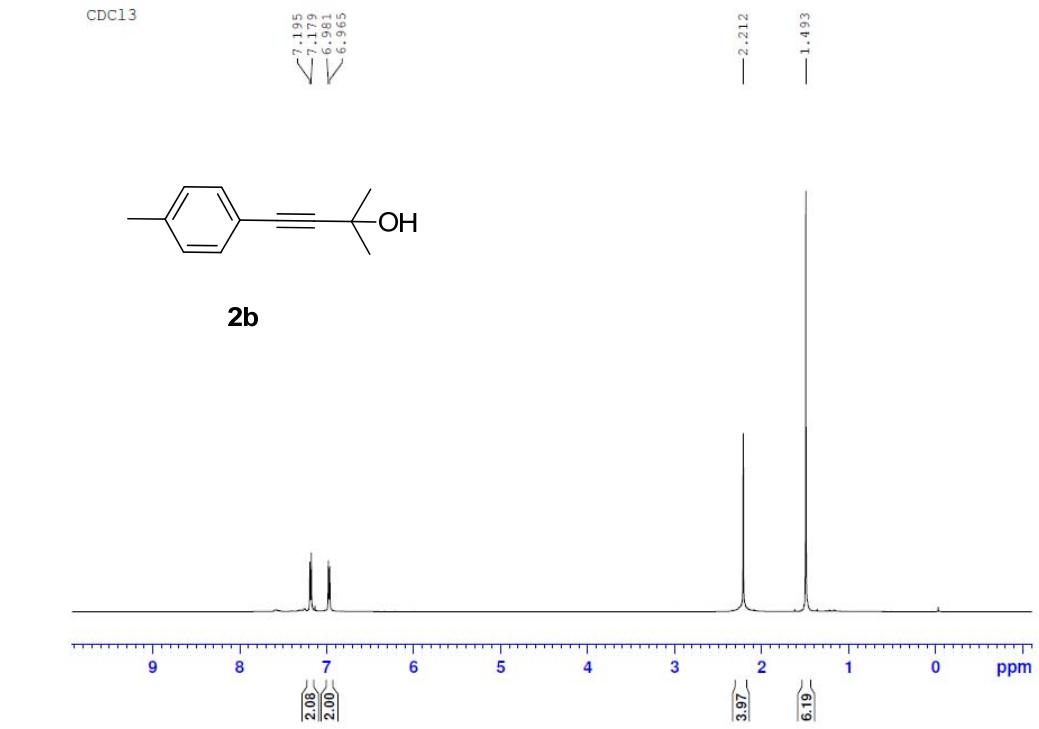

CDCl3
159.40
157.53
150.26
148.93
139.09
131.74
130.80
130.72
129.81
127.40
113.96
113.90
111.13
110.93
105.95
105.76
104.90
104.87
17.81
F
N
N
1n
200
180
160
140
120
100
80
60
40
20
0
ppm

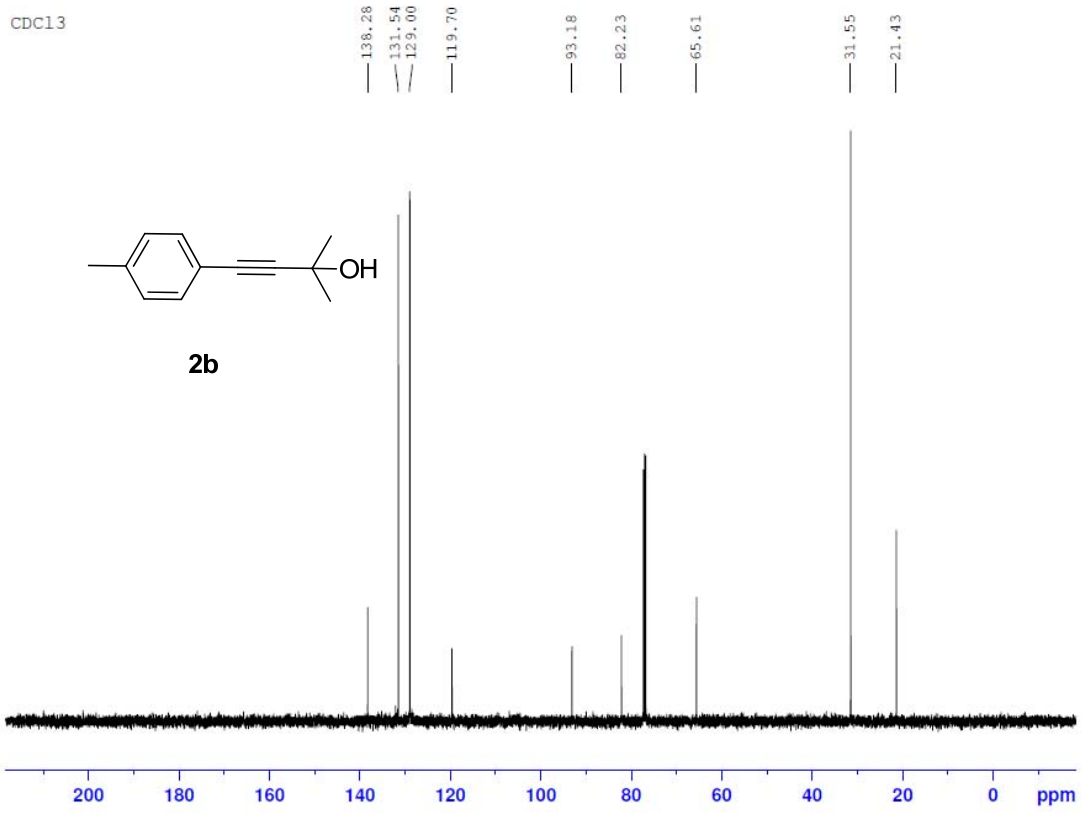

CDCl3
8.184
8.182
8.167
8.166
7.606
7.591
7.575
7.535
7.534
7.532
7.519
7.517
7.456
7.454
7.230
7.228
7.185
7.178
7.163
7.161
7.147
7.146
6.908
6.893
2.547
2.313
2.311
1o
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.03
1.03
1.00
1.03
2.01
1.03
3.08
3.13


CDCl3
158.07
151.97
138.37
135.38
131.02
123.31
122.97
120.60
118.95
118.78
114.38
113.18
110.82
24.38
9.64
1o
200
180
160
140
120
100
80
60
40
20
0
ppm


CDCl3
7.343
7.339
7.332
7.324
7.216
7.212
7.208
7.205
2.163
1.540
OH
2a
10
9
8
7
6
5
4
3
2
1
0
−1
ppm
2.00
2.98
1.02
6.23


CDCl3
131.65
128.24
122.78
93.85
82.15
65.62
31.51
OH
2a
200
180
160
140
120
100
80
60
40
20
0
ppm


CDCl3
7.195
7.179
6.981
6.965
2.212
1.493
OH
2b
9
8
7
6
5
4
3
2
1
0
ppm
2.08
2.00
3.97
6.19


CDCl3
138.28
131.54
129.00
119.70
93.18
82.23
65.61
31.55
21.43
OH
2b
200
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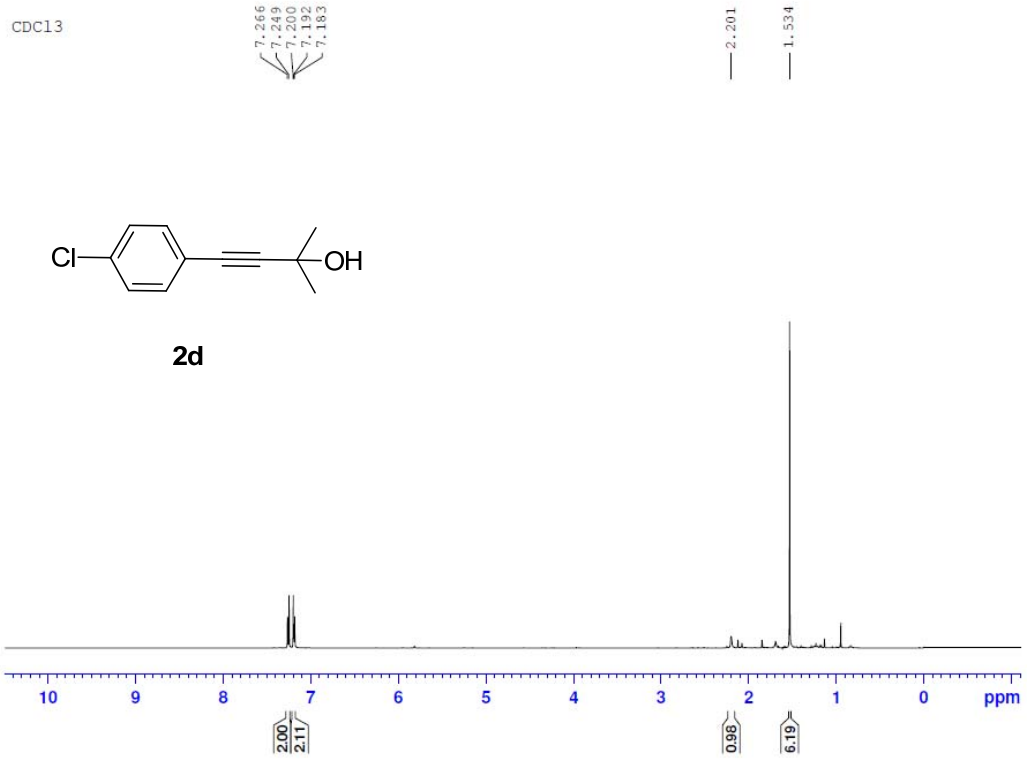
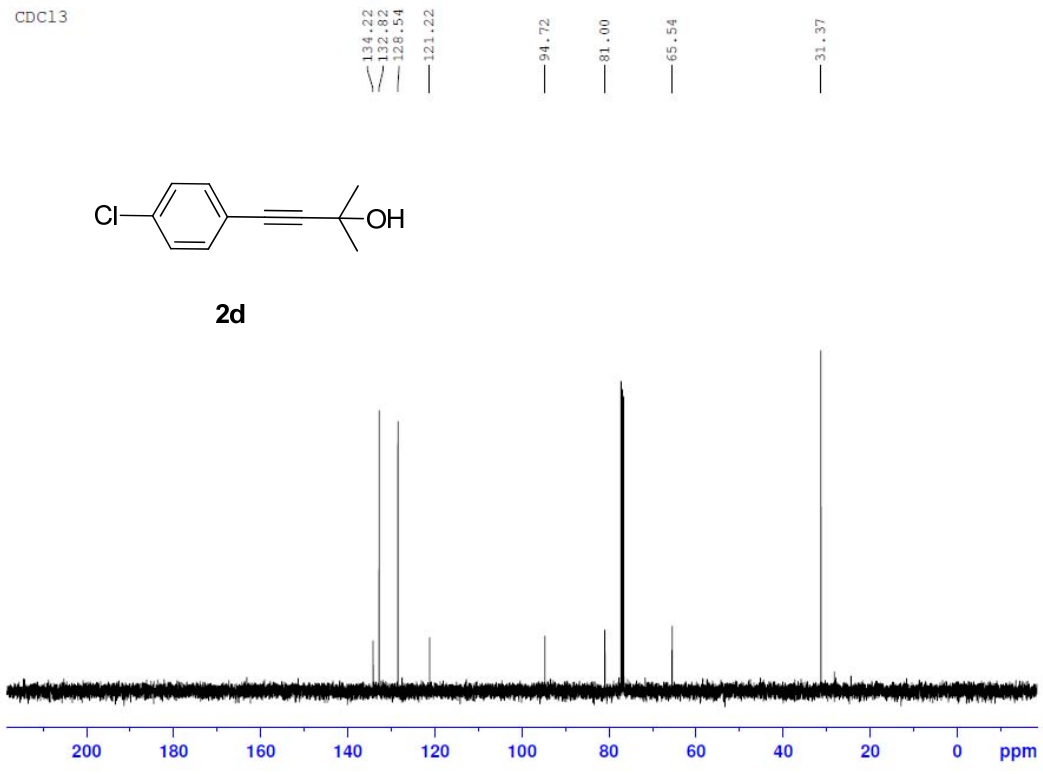
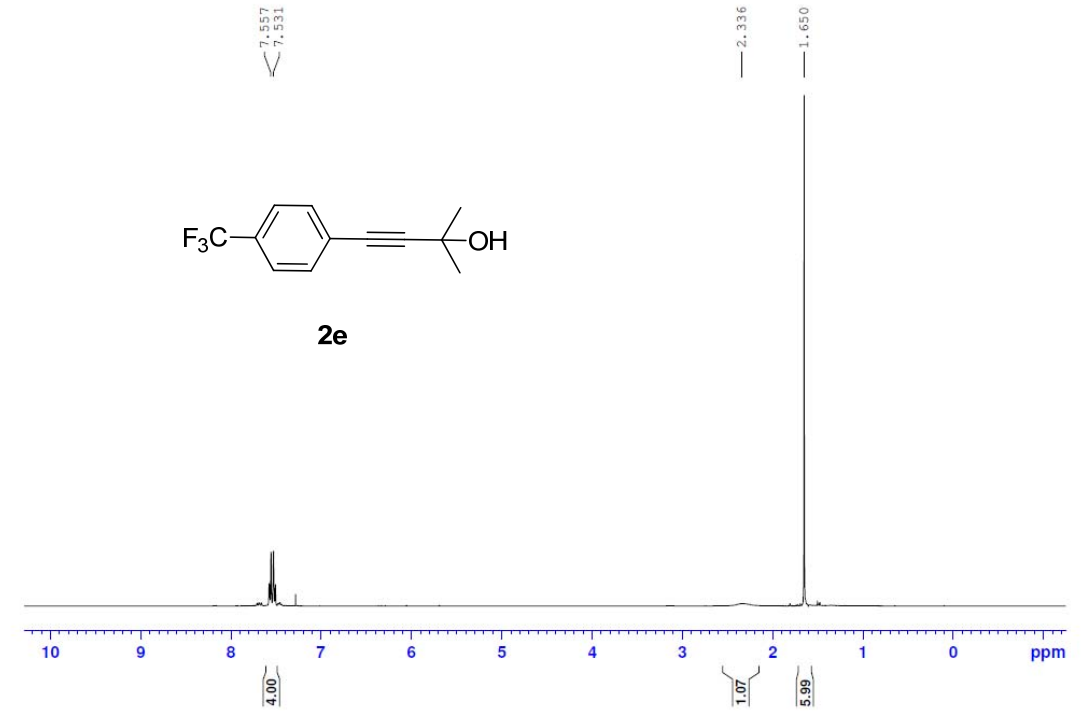
160
140
120
100
80
60
40
20
0
ppm

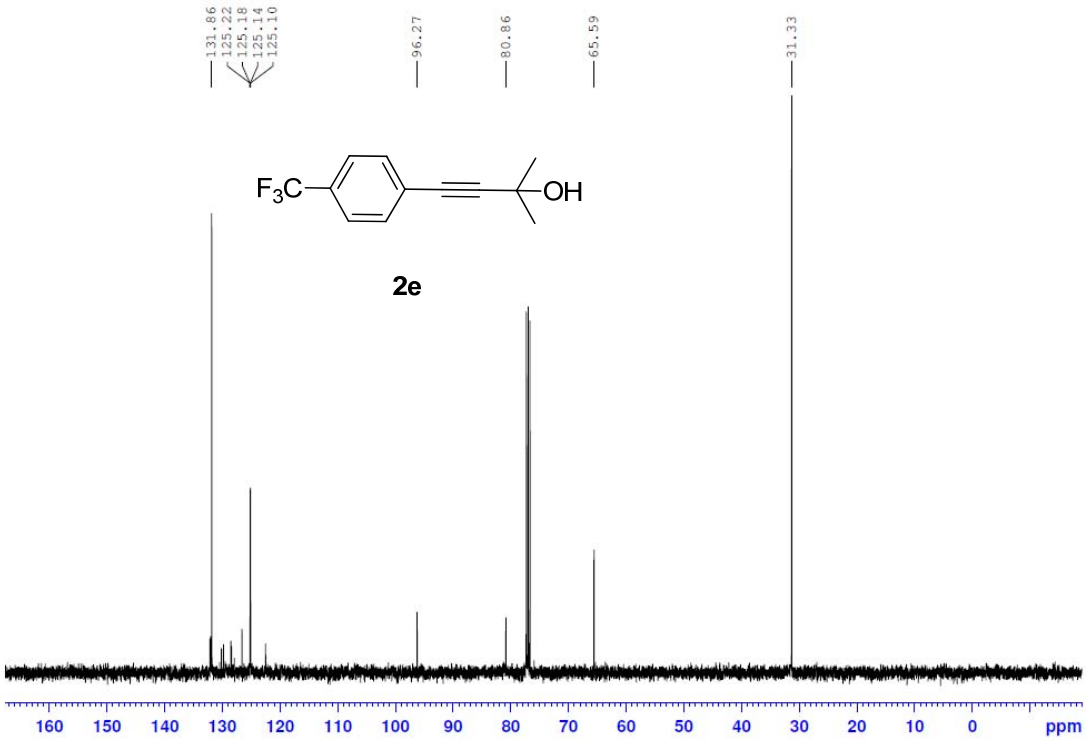

CDCl3
7.266
7.249
7.200
7.192
7.183
2.201
1.534
Cl
OH
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.11
0.98
6.19

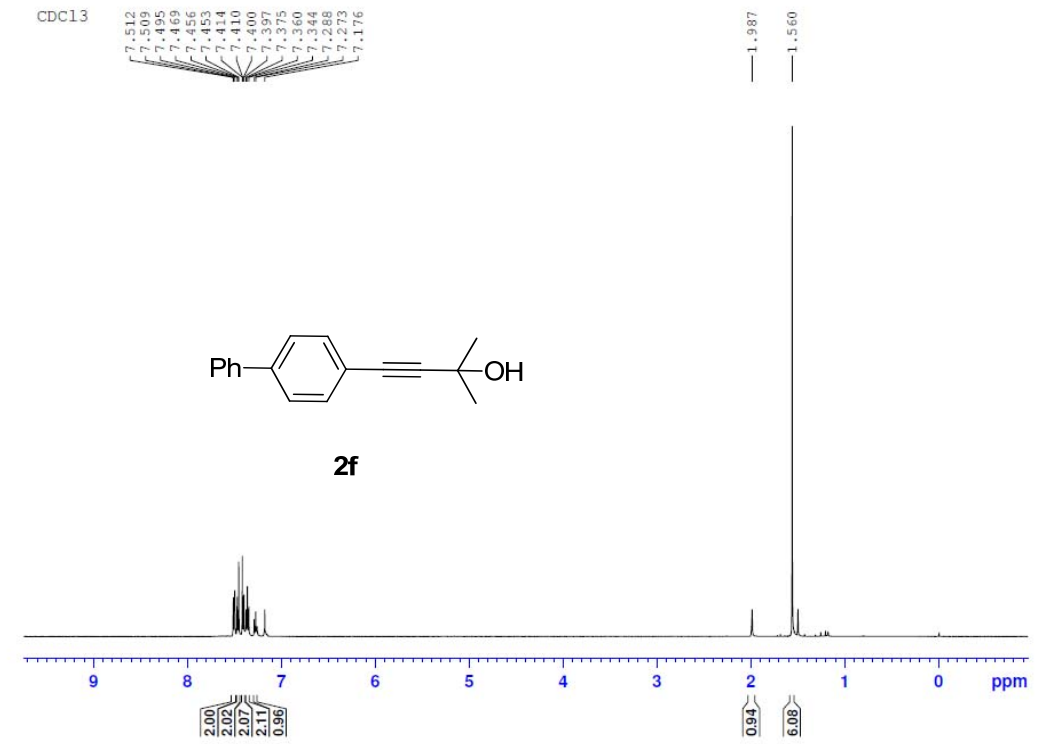
2d


CDCl3
134.22
132.82
128.54
121.22
94.72
81.00
65.54
31.37
Cl
OH
200
180
160
140
120
100
80
60
40
20
0
ppm

2d


7.557
7.531
2.336
1.650
F3C
OH
2e
10
9
8
7
6
5
4
3
2
1
0
ppm
4.00
1.07
5.99


131.86
125.22
125.18
125.14
125.10
96.27
80.86
65.59
31.33
F3C
OH
2e
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


CDCl3
7.512
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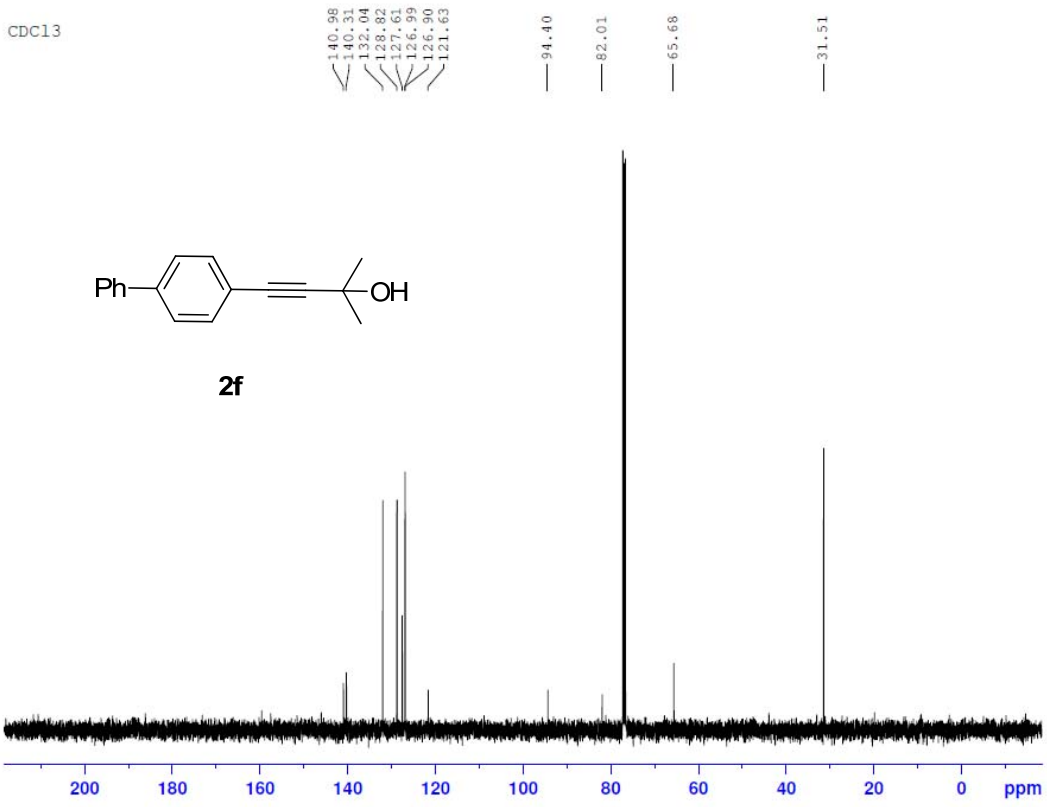
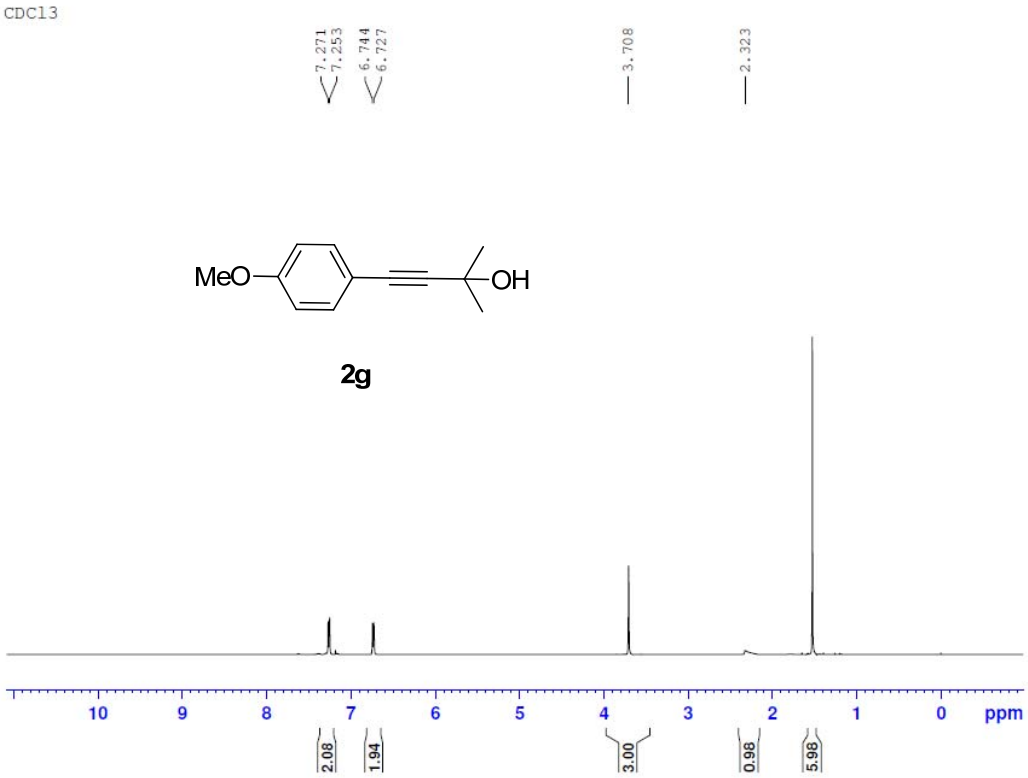
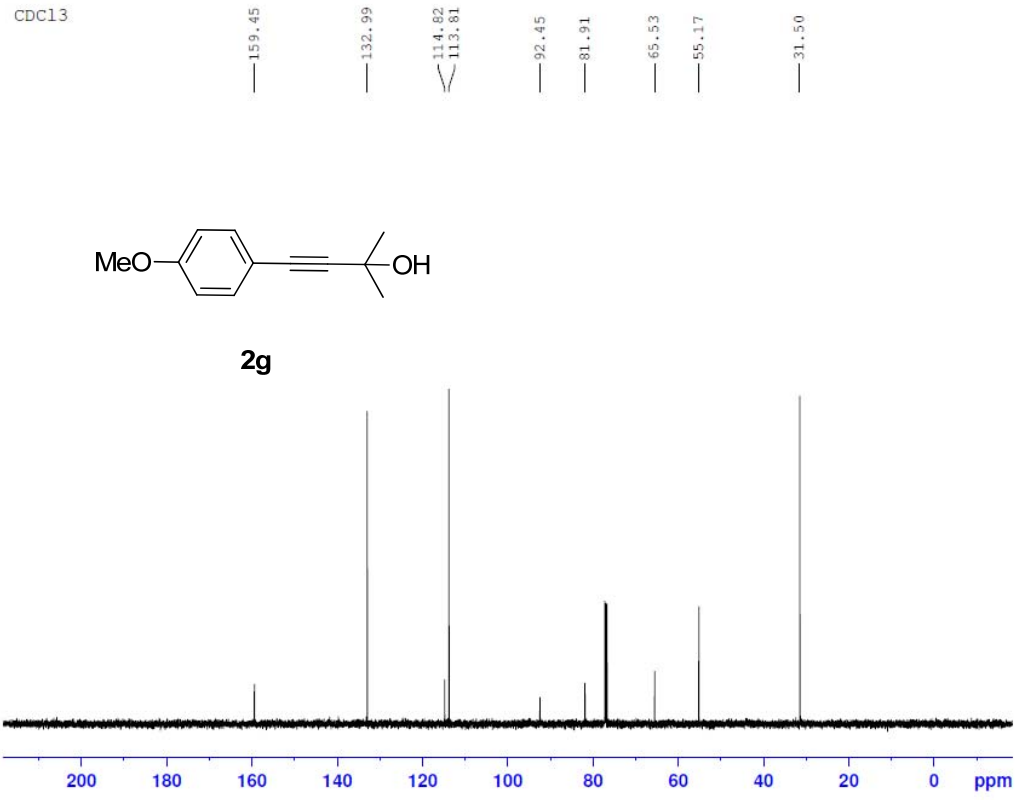
7.495
7.469
7.456
7.453
7.414
7.410
7.400
7.397
7.375
7.360
7.344
7.288
7.273
7.176
1.987
1.560
Ph
OH
2f
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.02
2.07
2.11
0.96
0.94
6.08

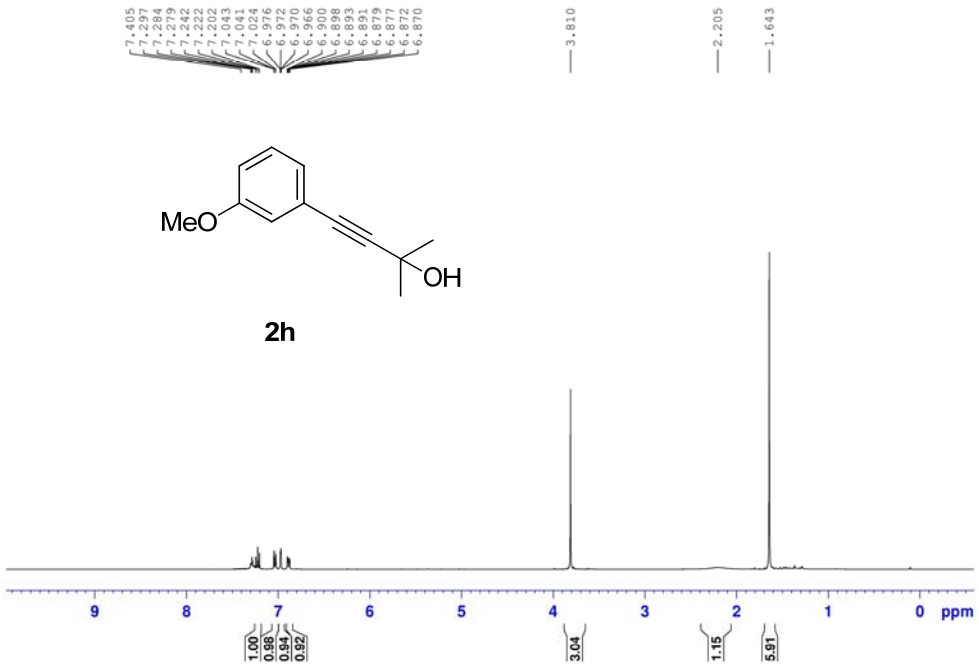

CDCl3
140.98
140.31
132.04
128.82
127.61
126.99
126.90
121.63
94.40
82.01
65.68
31.51
Ph
OH
2f
200
180
160
140
120
100
80
60
40
20
0
ppm

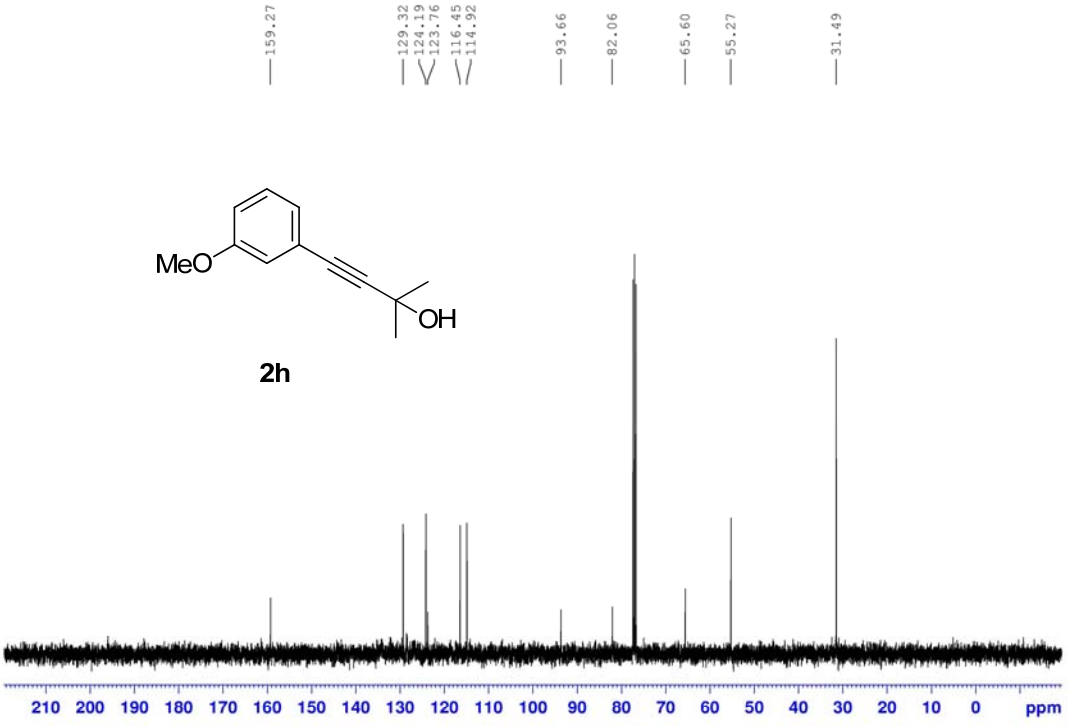

CDCl3
7.271
7.253
6.744
6.727
3.708
2.323
MeO
OH
10
9
8
7
6
5
4
3
2
1
0
ppm
2.08
1.94
3.00
0.98
5.98

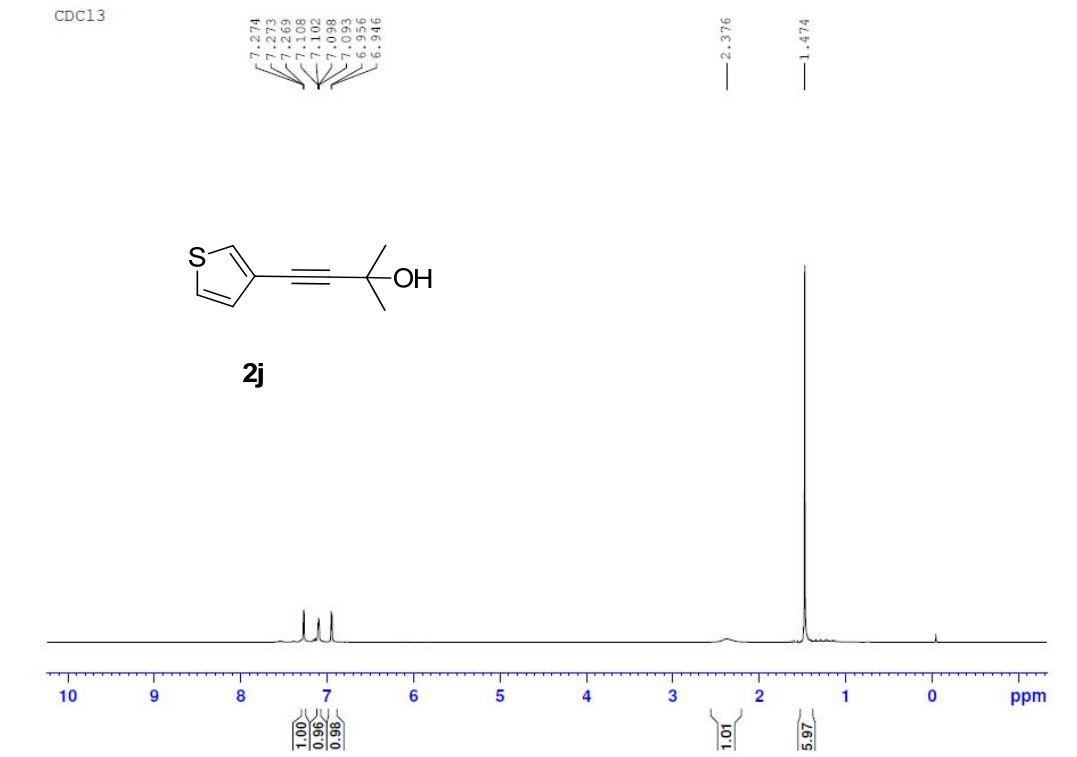
2g


CDCl3
159.45
132.99
114.82
113.81
92.45
81.91
65.53
55.17
31.50
MeO
OH
200
180
160
140
120
100
80
60
40
20
0
ppm

2g


7.405
7.297
7.284
7.279
7.242
7.222
7.202
7.043
7.041
7.024
6.976
6.972
6.970
6.966
6.900
6.898
6.893
6.891
6.879
6.877
6.872
6.870
3.810
2.205
1.643
MeO
OH
2h
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.98
0.94
0.92
3.04
1.15
5.91


159.27
129.32
124.19
123.76
116.45
114.92
93.66
82.06
65.60
55.27
31.49
MeO
OH
2h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


CDCl3
7.274
7.273
7.269
7.108
7.102
7.098
7.093
6.956
6.946
2.376
1.474
S
OH
2j
10
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8
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6
5
4
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2
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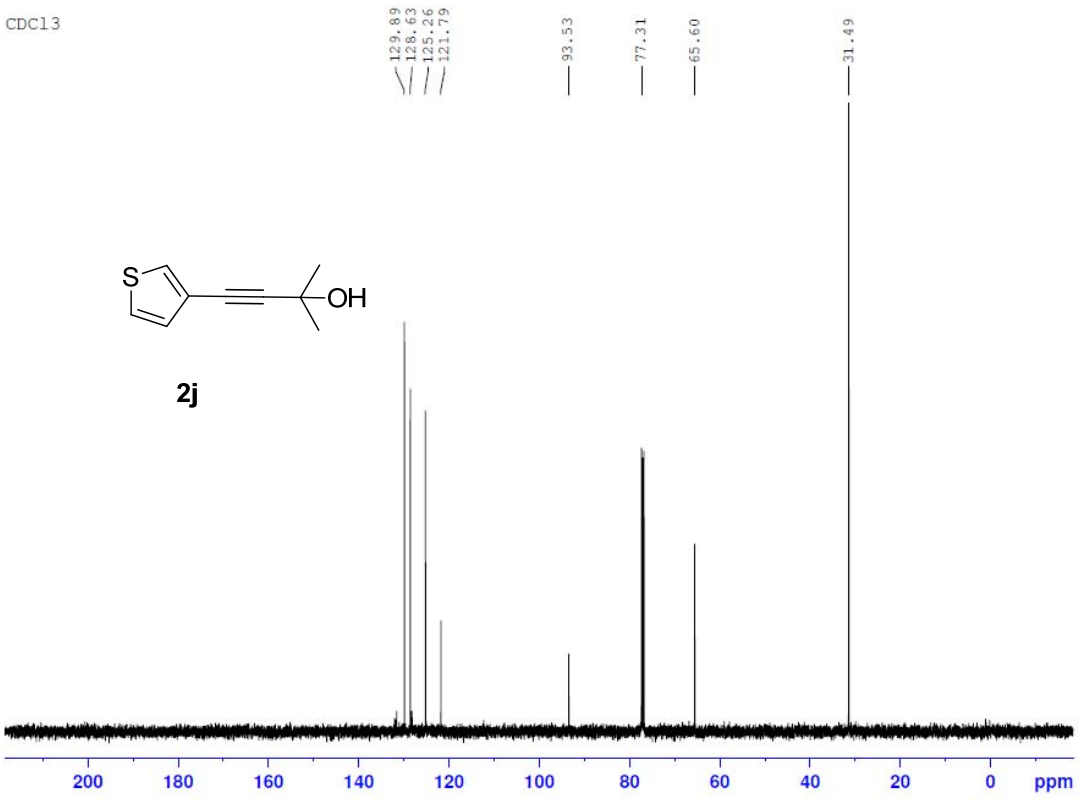
0.98
1.01
5.97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S
OH
2j
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120
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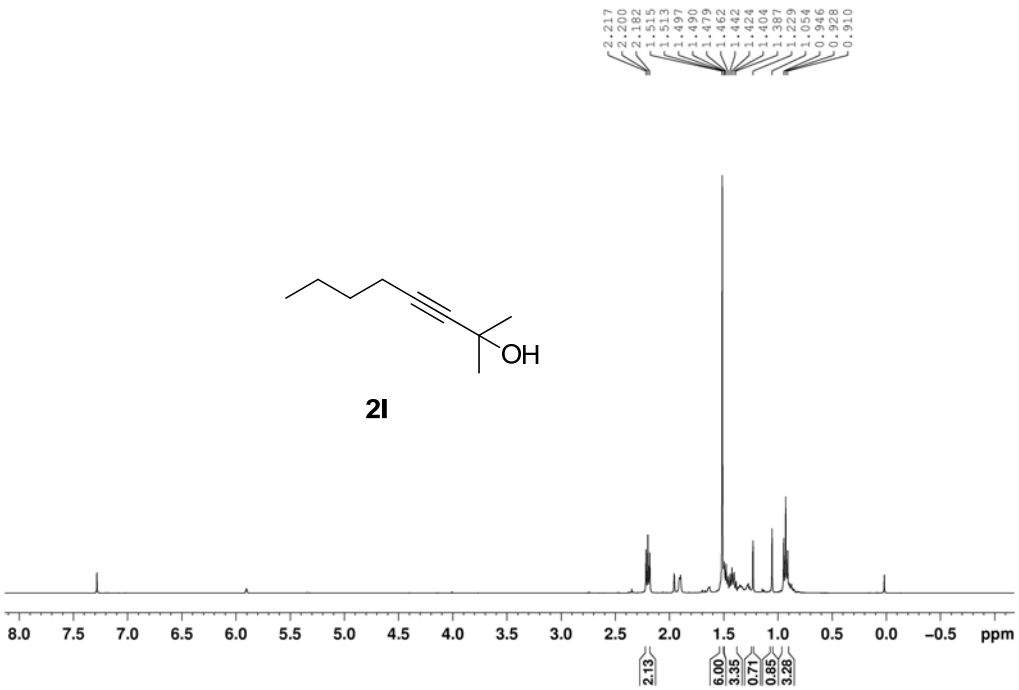
40
20
0
ppm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2.200
2.182
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1.513
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1.490
1.479
1.462
1.442
1.424
1.404
1.387
1.229
1.054
0.946
0.928
0.910
OH
2I
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm
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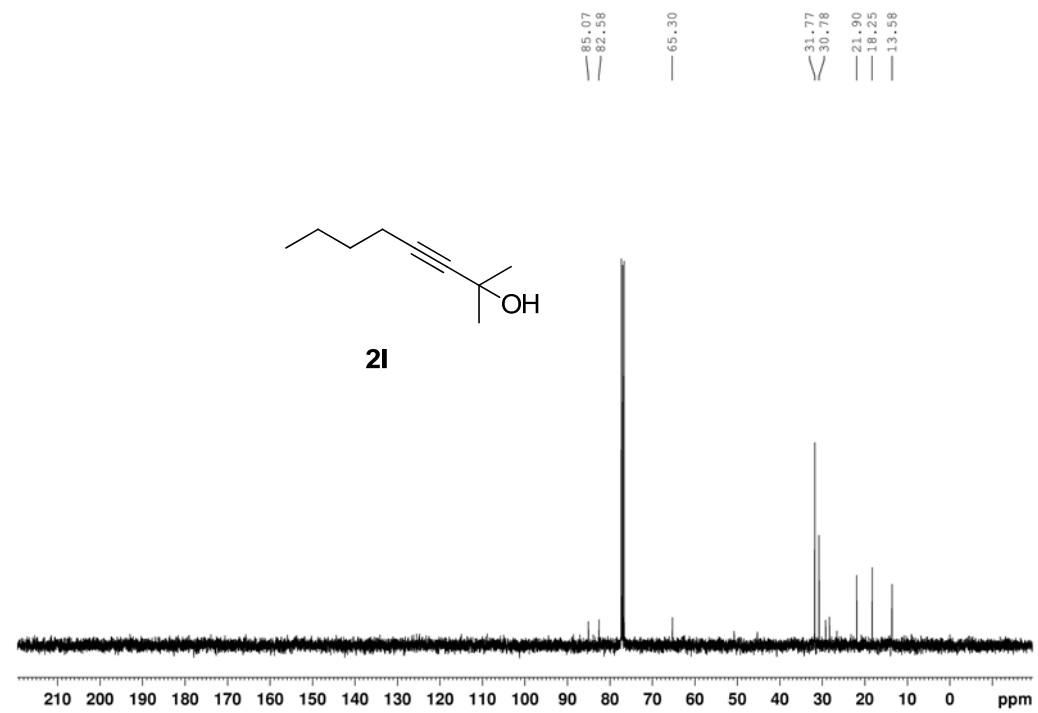
0.85
3.28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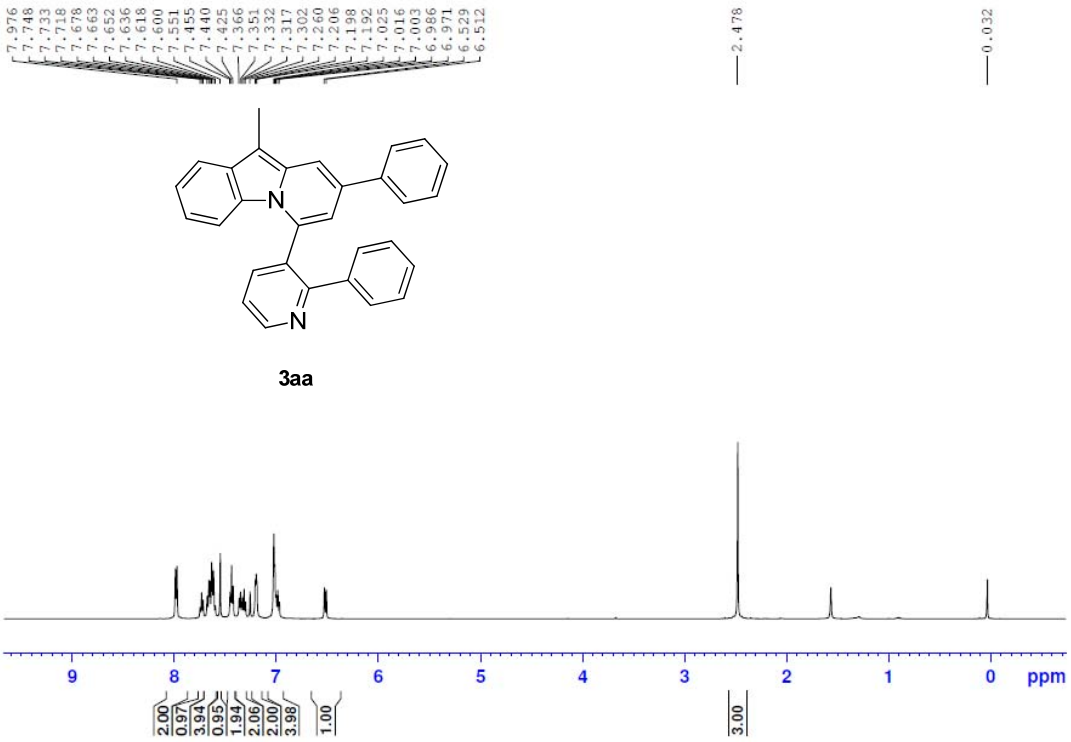
82.58
65.30
31.77
30.78
21.90
18.25
13.58
OH
2I
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.678
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7.600
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7.455
7.440
7.425
7.366
7.351
7.332
7.317
7.302
7.260
7.206
7.198
7.192
7.025
7.016
7.003
6.986
6.971
6.529
6.512
2.478
0.032
N
N
3aa
9
8
7
6
5
4
3
2
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ppm
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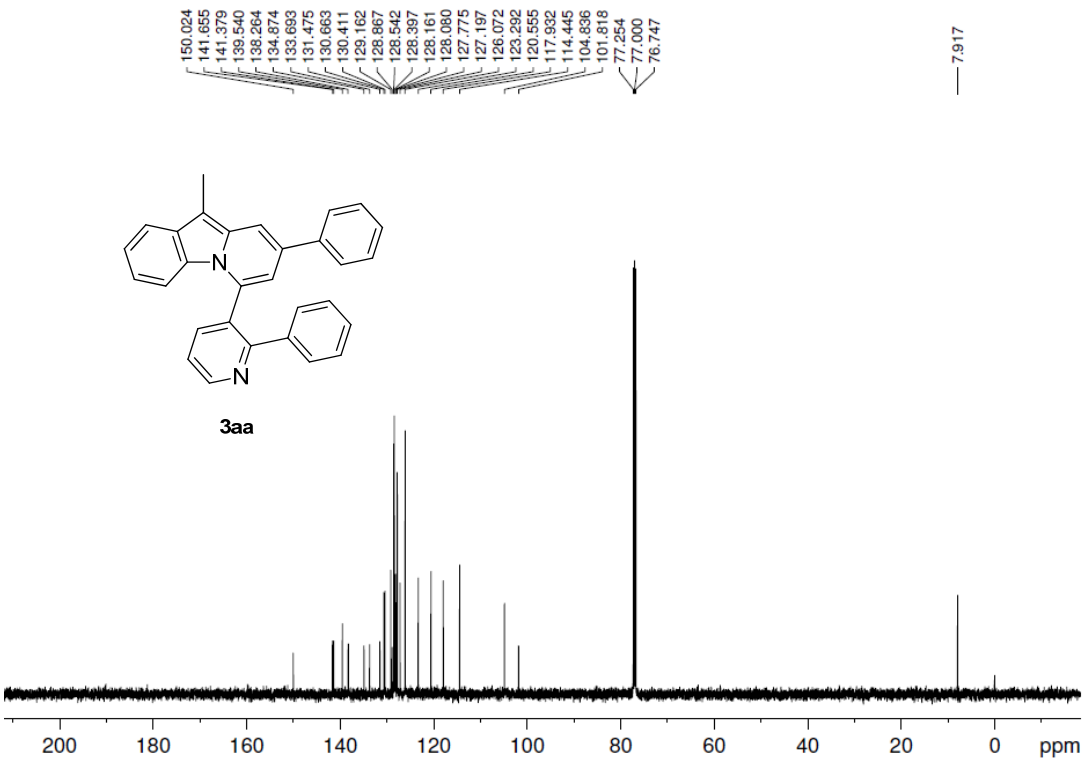
0.95
1.94
2.06
2.00
3.98
1.00
3.00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131.475
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130.411
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128.867
128.542
128.397
128.161
128.080
127.775
127.197
126.072
123.292
120.555
117.932
114.445
104.836
101.818
77.254
77.000
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7.917
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N
3aa
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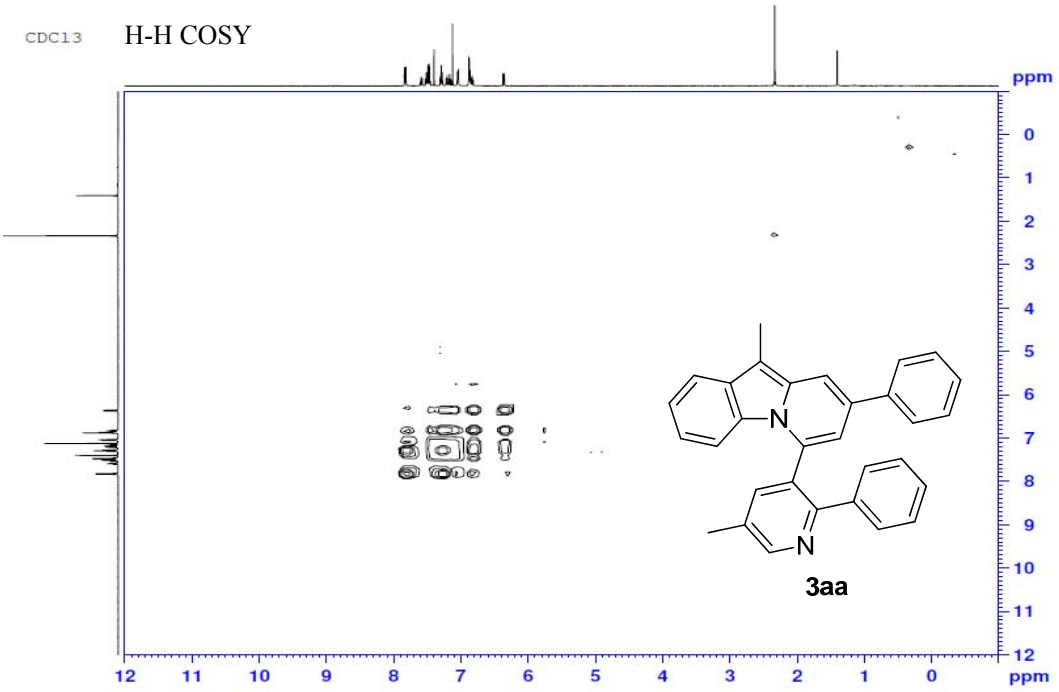
180
160
140
120
100
80
60
40
20
0
ppm


CDC13
H-H COSY
ppm
0
1
2
3
4
5
6
7
8
9
10
11
12
N
N
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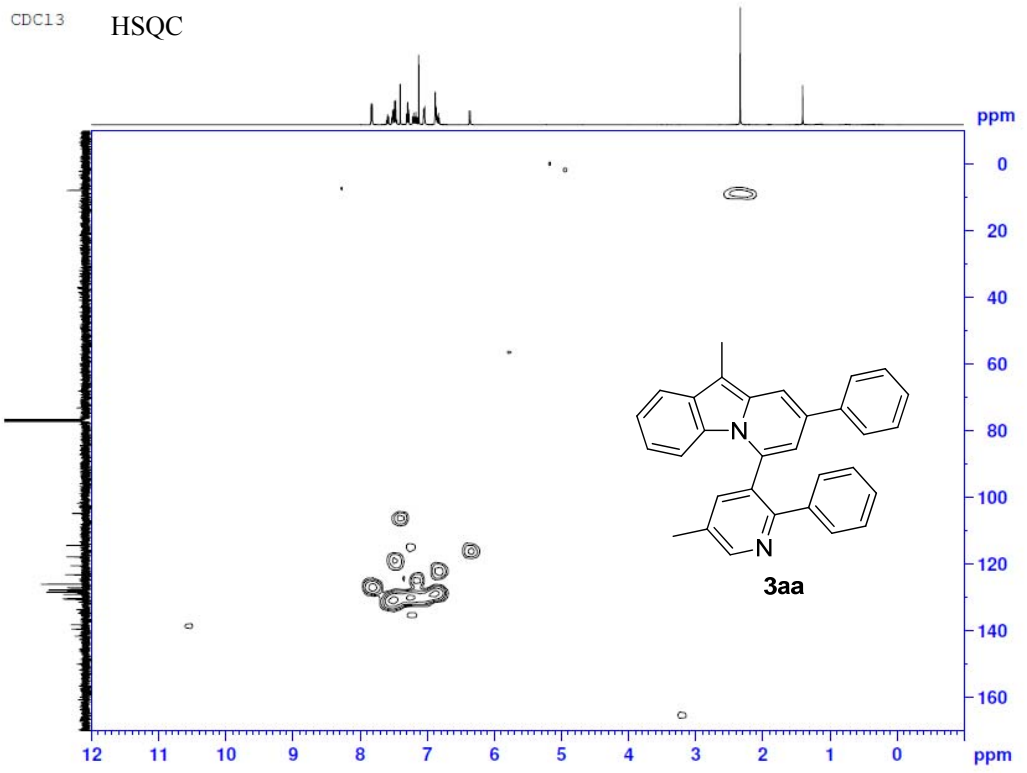
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm


CDC13
HSQC
ppm
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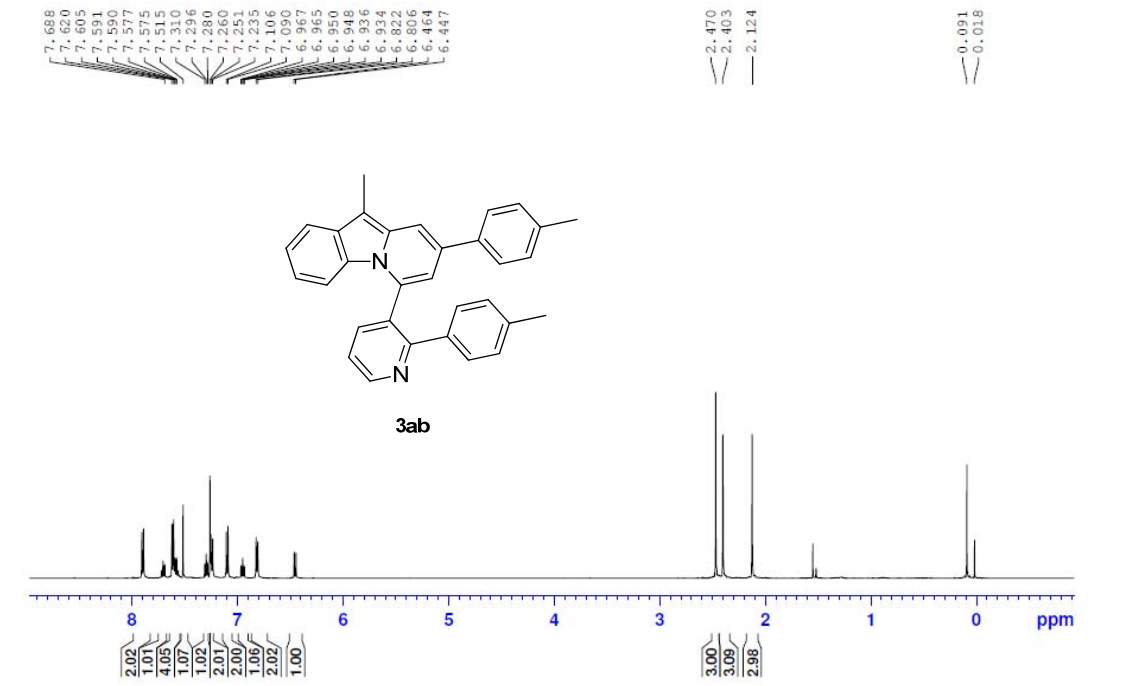
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7.260
7.251
7.235
7.106
7.090
6.967
6.965
6.950
6.948
6.936
6.934
6.822
6.806
6.464
6.447
2.470
2.403
2.124
0.091
0.018
N
N
3ab
8
7
6
5
4
3
2
1
0
ppm
2.02
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1.07
1.02
2.01
2.00
1.06
2.02
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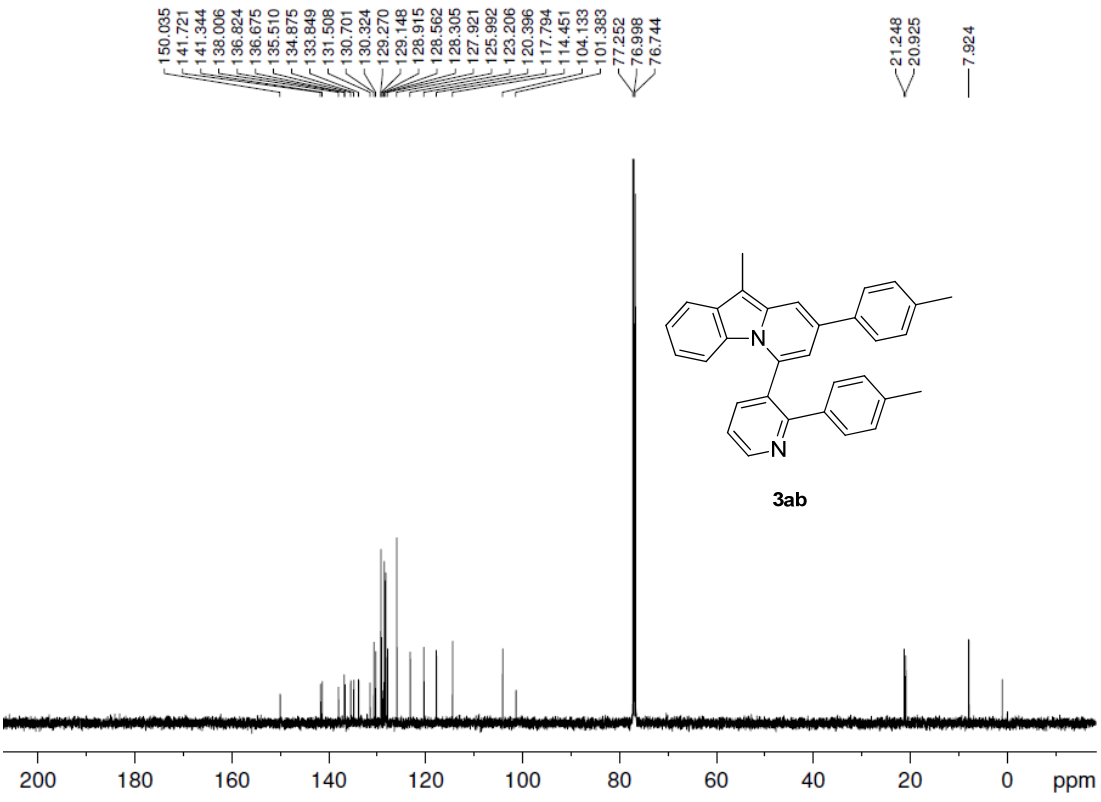
3.00
3.09
2.98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141.344
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134.875
133.849
131.508
130.701
130.324
129.270
129.148
128.915
128.562
128.305
127.921
125.992
123.206
120.396
117.794
114.451
104.133
101.383
77.252
76.998
76.744
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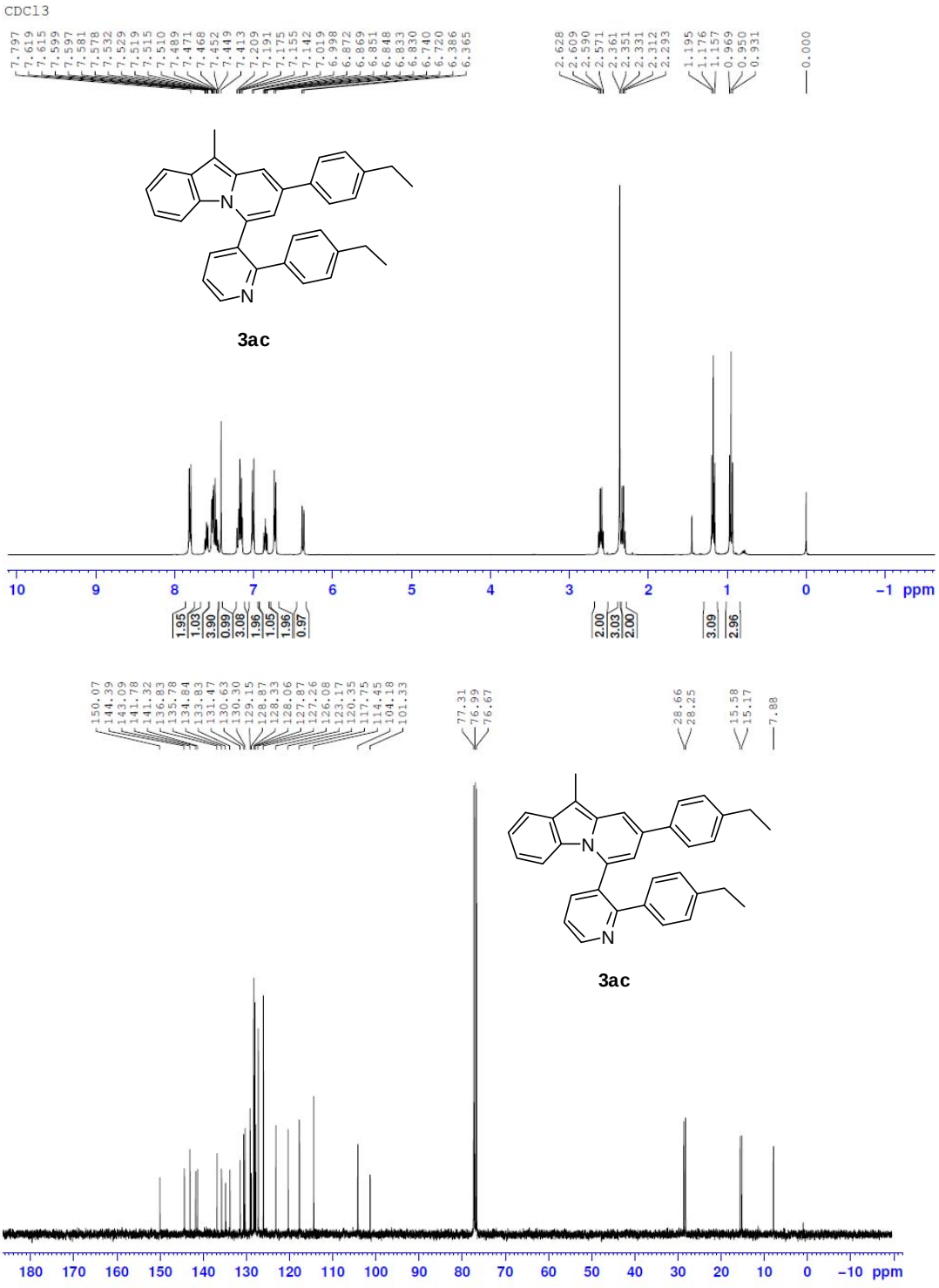
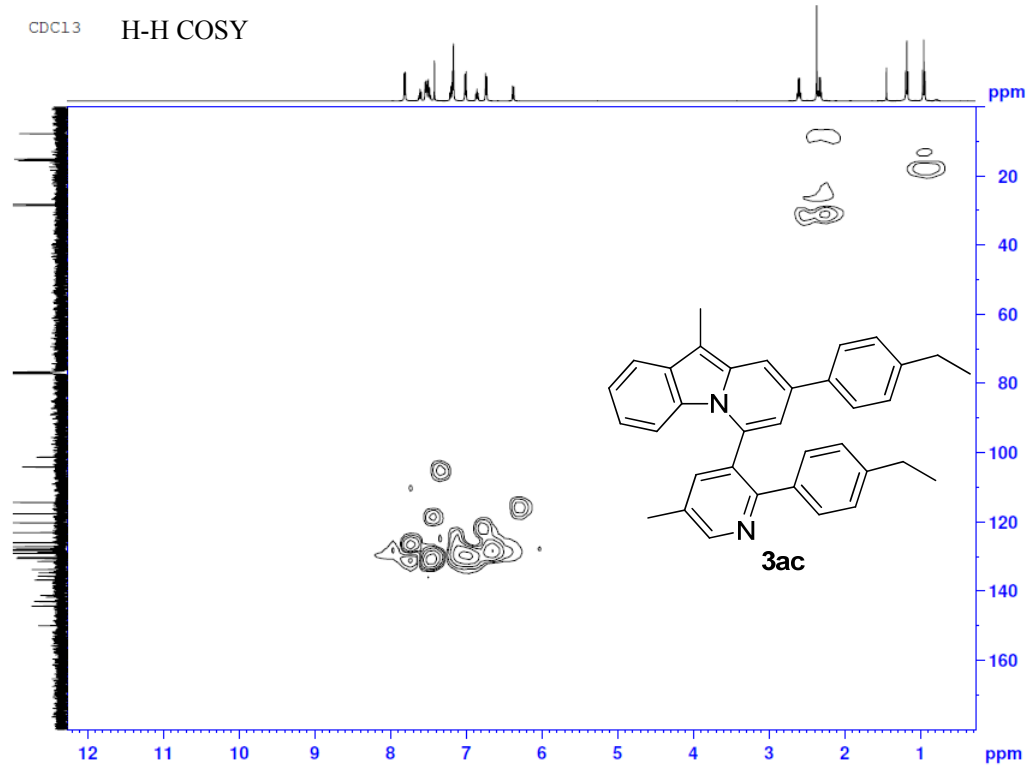
7.924
N
N
3ab
200
180
160
140
120
100
80
60
40
20
0
ppm


CDCl3
3ac
3ac


CDC13
H-H COSY
ppm
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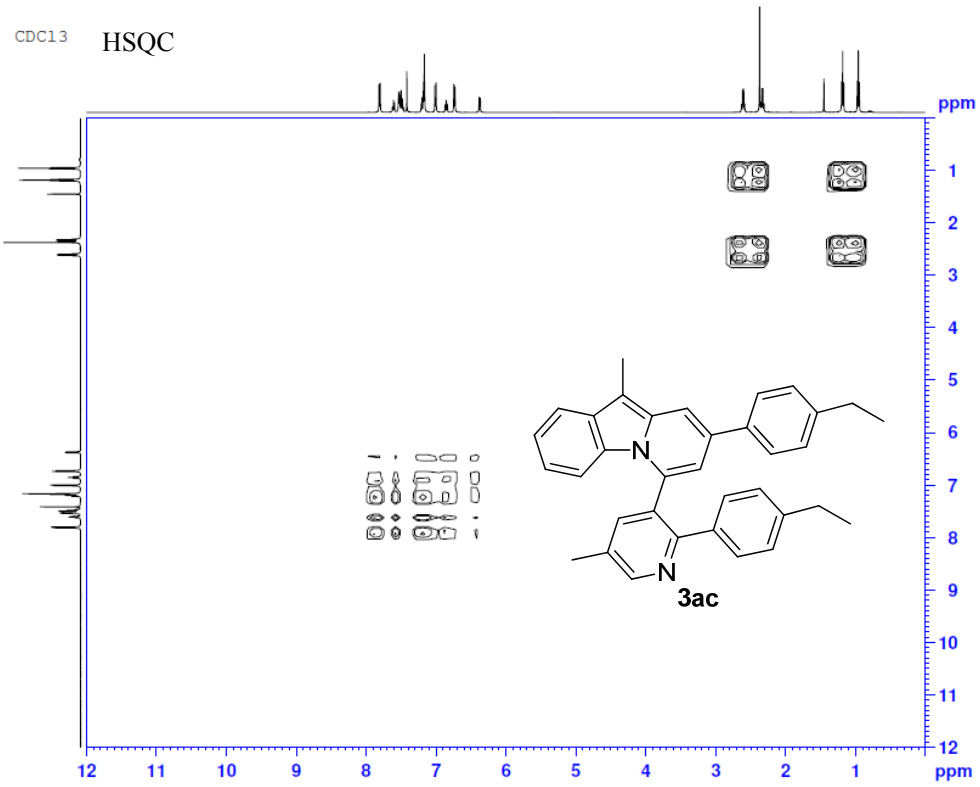
40
60
80
100
120
140
160
12
11
10
9
8
7
6
5
4
3
2
1
ppm
N
N
3ac


CDC13
HSQC
ppm
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2
3
4
5
6
7
8
9
10
11
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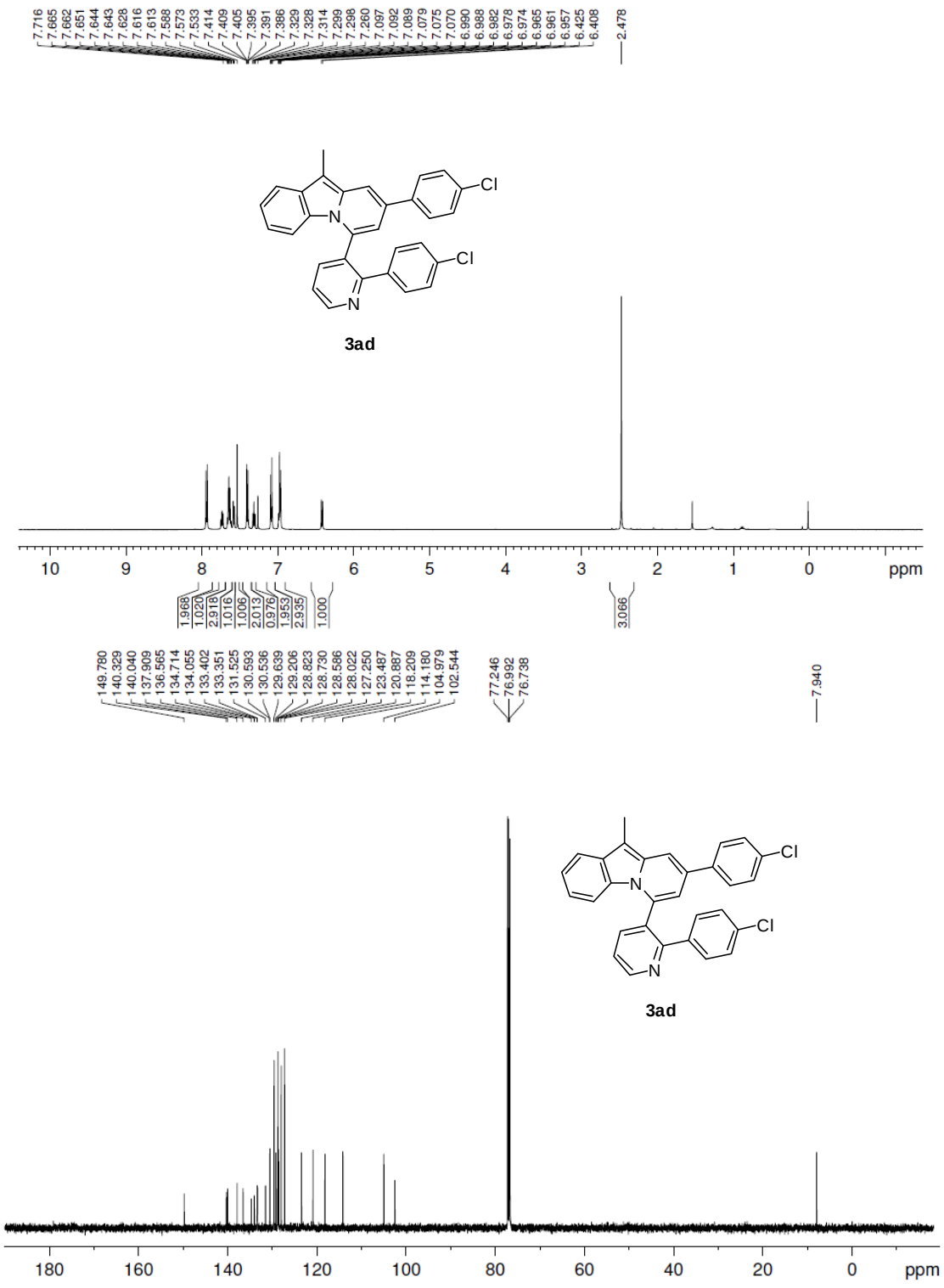
12
11
10
9
8
7
6
5
4
3
2
1
ppm
N
N
3ac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7.628
7.616
7.613
7.588
7.573
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7.409
7.405
7.395
7.391
7.386
7.329
7.328
7.314
7.299
7.298
7.260
7.097
7.092
7.089
7.079
7.075
7.070
6.990
6.988
6.982
6.978
6.974
6.965
6.961
6.957
6.425
6.408
2.478
Cl
Cl
N
N
3ad
10
9
8
7
6
5
4
3
2
1
0
ppm
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1.020
2.918
1.016
1.006
2.013
0.976
1.953
2.935
1.000
3.066
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140.040
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136.565
134.714
134.055
133.402
133.351
131.525
130.593
130.536
129.639
129.206
128.823
128.730
128.586
128.022
127.250
123.487
120.887
118.209
114.180
104.979
102.544
77.246
76.992
76.738
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Cl
Cl
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N
3ad
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140
120
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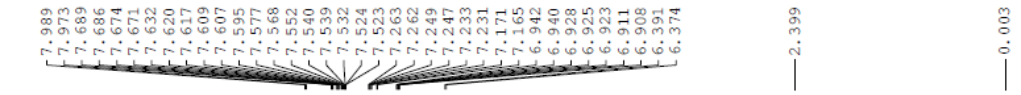
0
ppm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7.671
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7.620
7.617
7.609
7.607
7.595
7.577
7.568
7.552
7.540
7.539
7.532
7.524
7.523
7.263
7.262
7.249
7.247
7.233
7.231
7.171
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6.928
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6.923
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6.908
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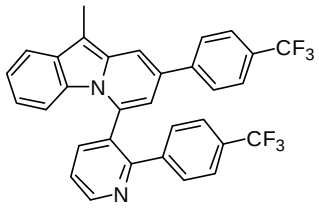
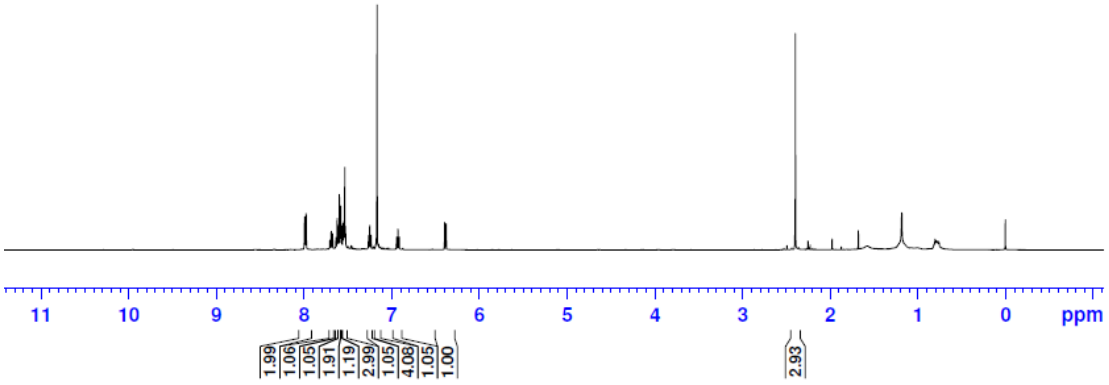

CF3
CF3
N
N

3ae


11
10
9
8
7
6
5
4
3
2
1
0
ppm
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1.06
1.05
1.91
1.19
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1.05
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1.05
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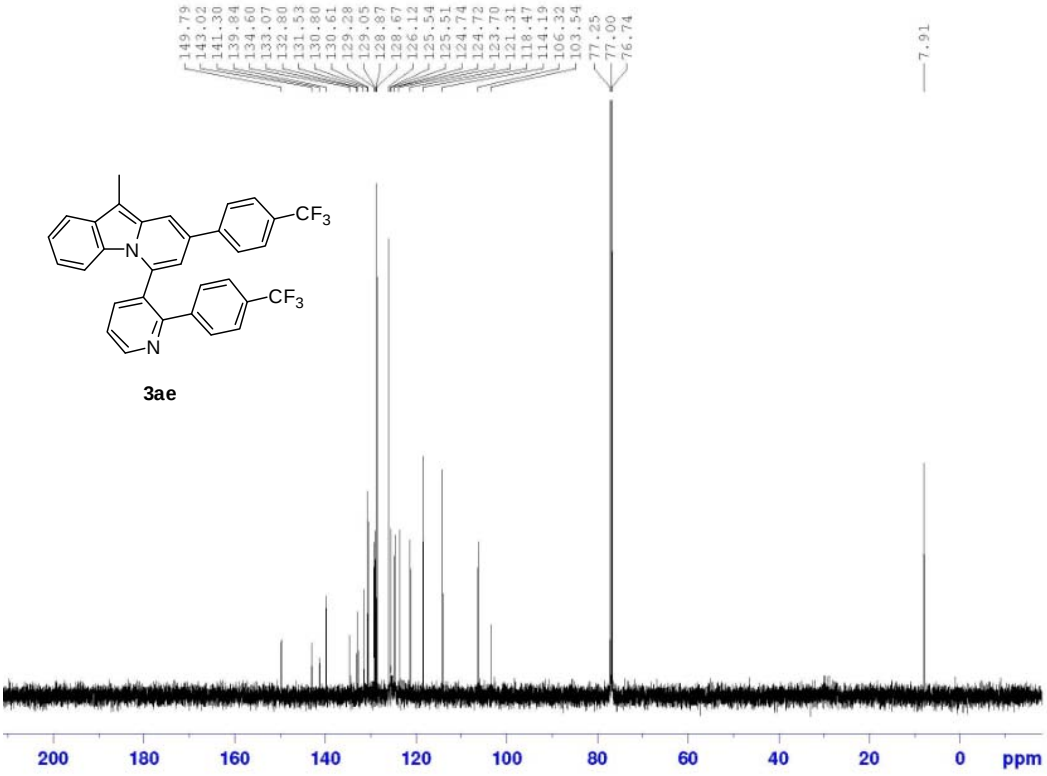
2.93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128.87
128.67
126.12
125.54
125.51
124.74
124.72
123.70
121.31
118.47
114.19
106.32
103.54
77.25
77.00
76.74
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140
120
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0
ppm

CF3
CF3
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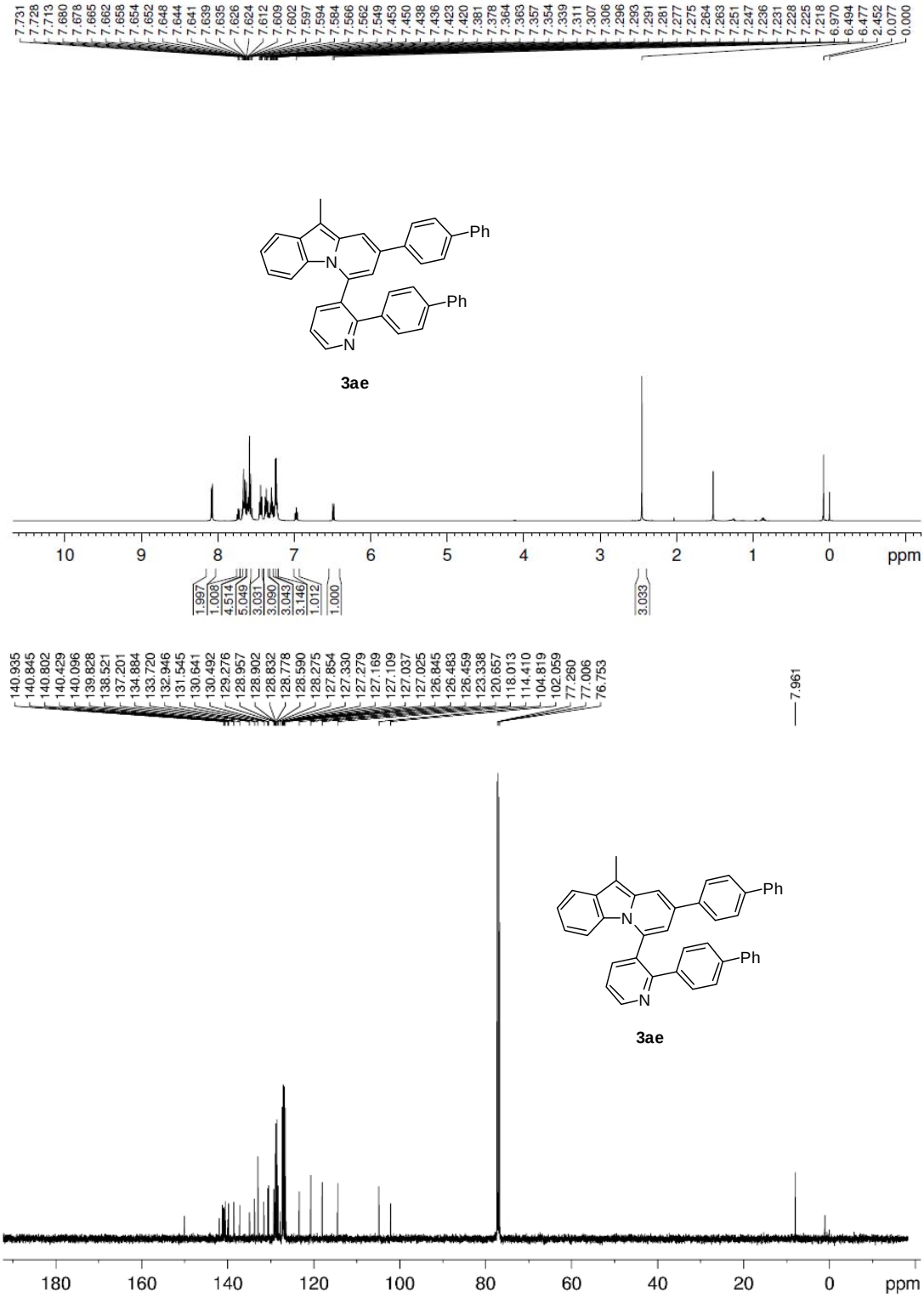
N

3ae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7.641
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7.635
7.626
7.624
7.612
7.609
7.602
7.597
7.594
7.584
7.566
7.562
7.549
7.453
7.450
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7.363
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7.354
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7.291
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7.264
7.263
7.251
7.247
7.236
7.231
7.228
7.225
7.218
6.970
6.494
6.477
2.452
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0.000
Ph
Ph
N
N
3ae
10
9
8
7
6
5
4
3
2
1
0
ppm
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5.049
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3.043
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1.012
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140.802
140.429
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77.006
76.753
7.961
Ph
Ph
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3ae
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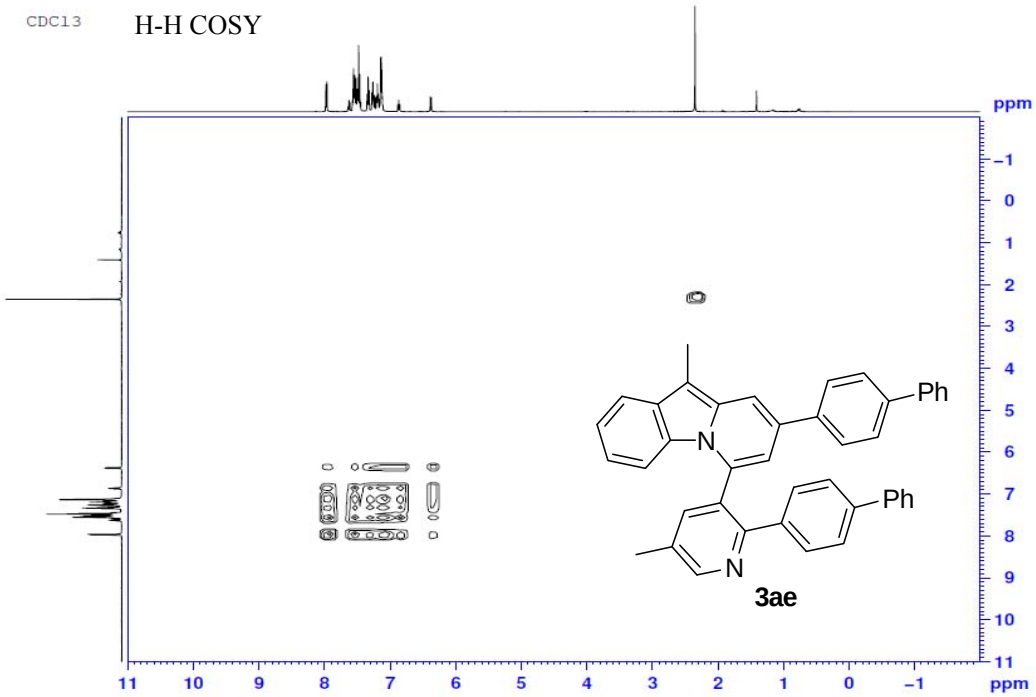
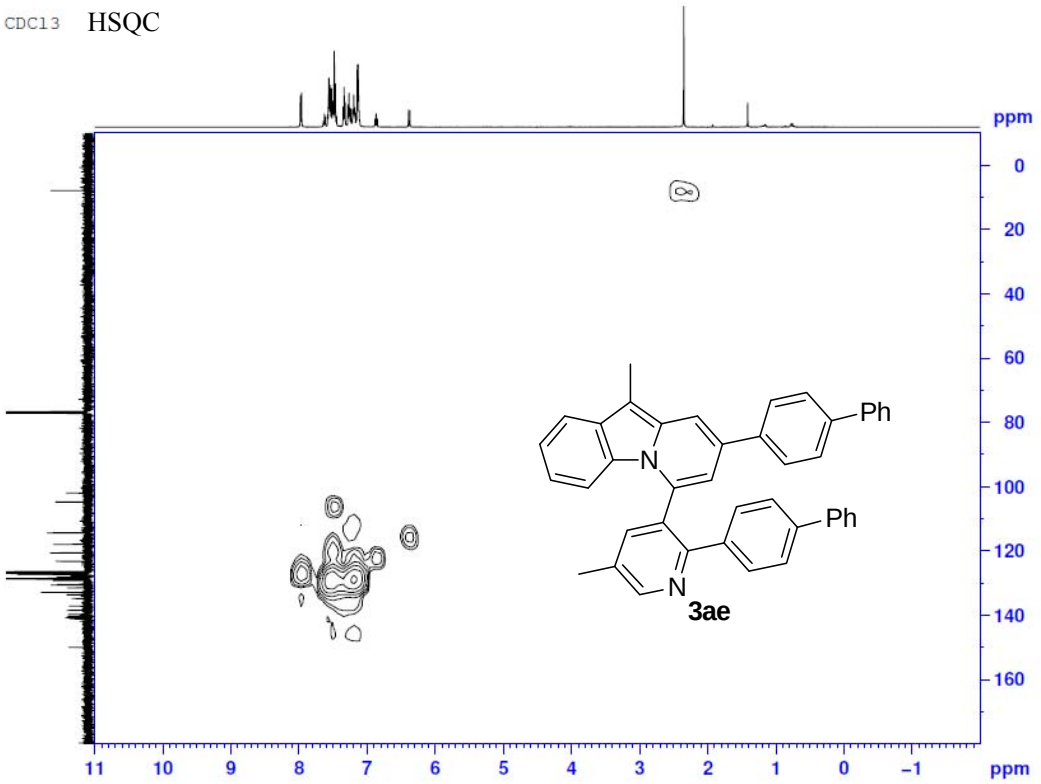
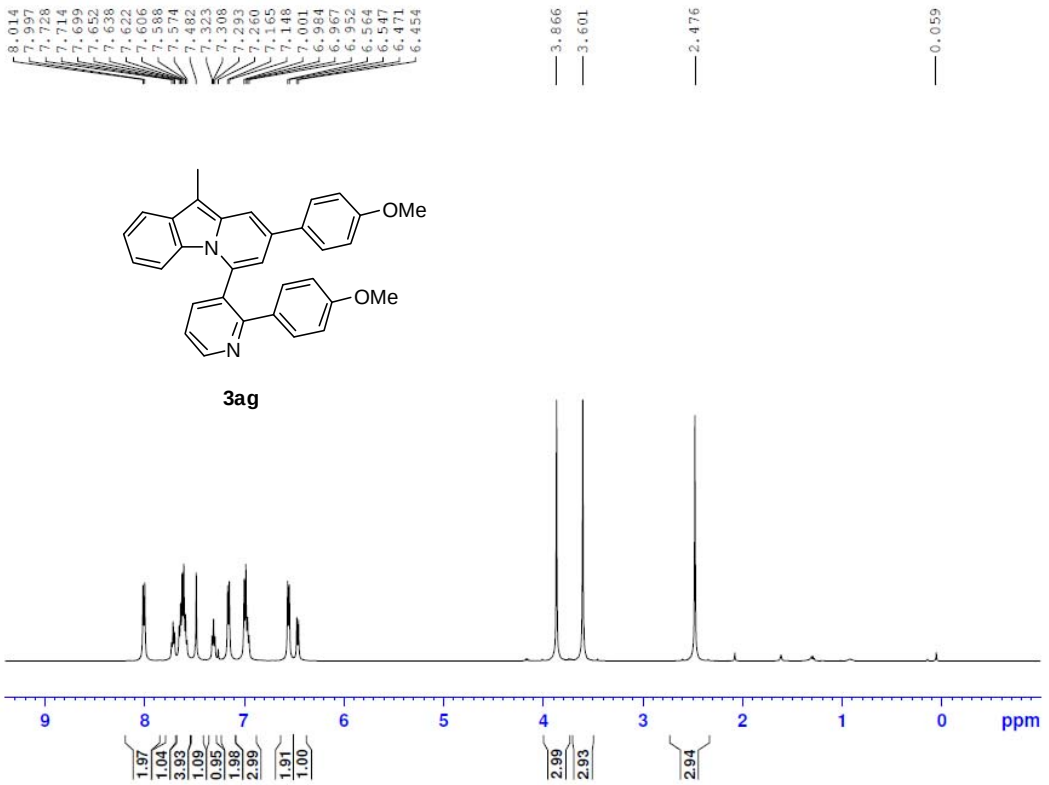
ppm

CDC13 H-H COSY



CDC13 HSQC

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7.622
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7.482
7.323
7.308
7.293
7.260
7.165
7.148
7.001
6.984
6.967
6.952
6.564
6.547
6.471
6.454
3.866
3.601
2.476
0.059
OMe
OMe
N
N
3ag
9
8
7
6
5
4
3
2
1
0
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1.91
1.00
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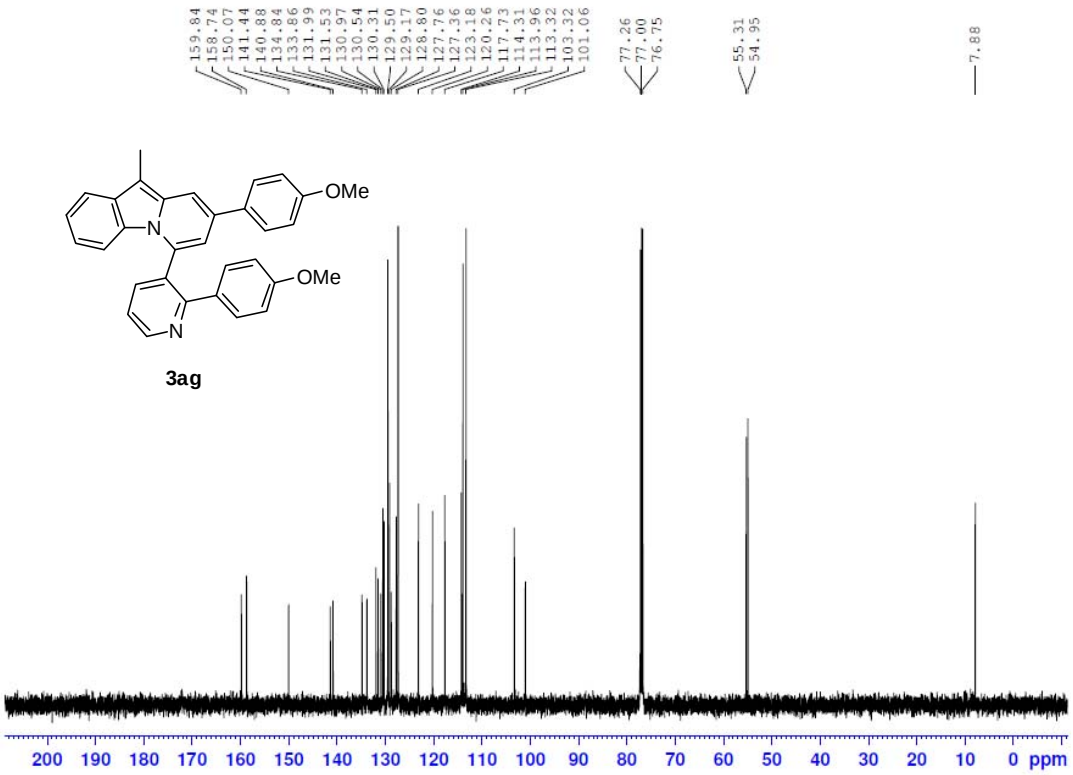
2.93
2.94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130.97
130.54
130.31
129.50
129.17
128.80
127.76
127.36
123.18
120.26
117.73
114.31
113.96
113.32
103.32
101.06
77.26
77.00
76.75
55.31
54.95
7.88
OMe
OMe
N
N
3ag
200
190
180
170
160
150
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50
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30
20
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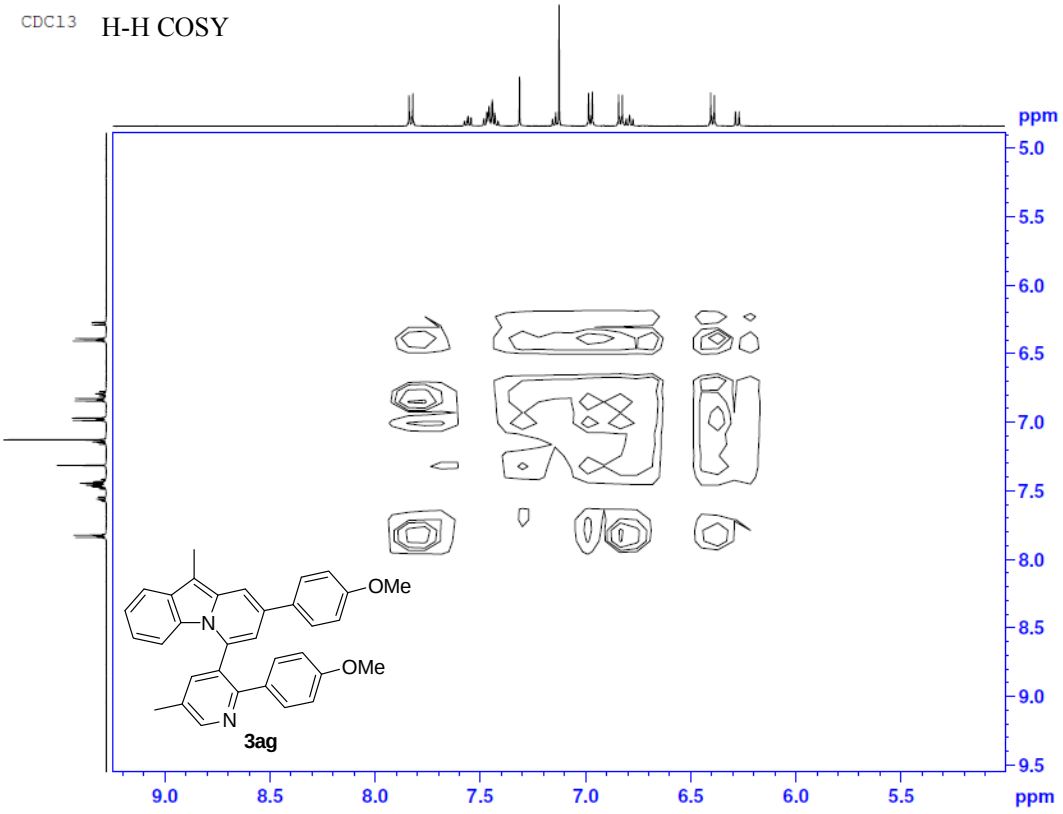
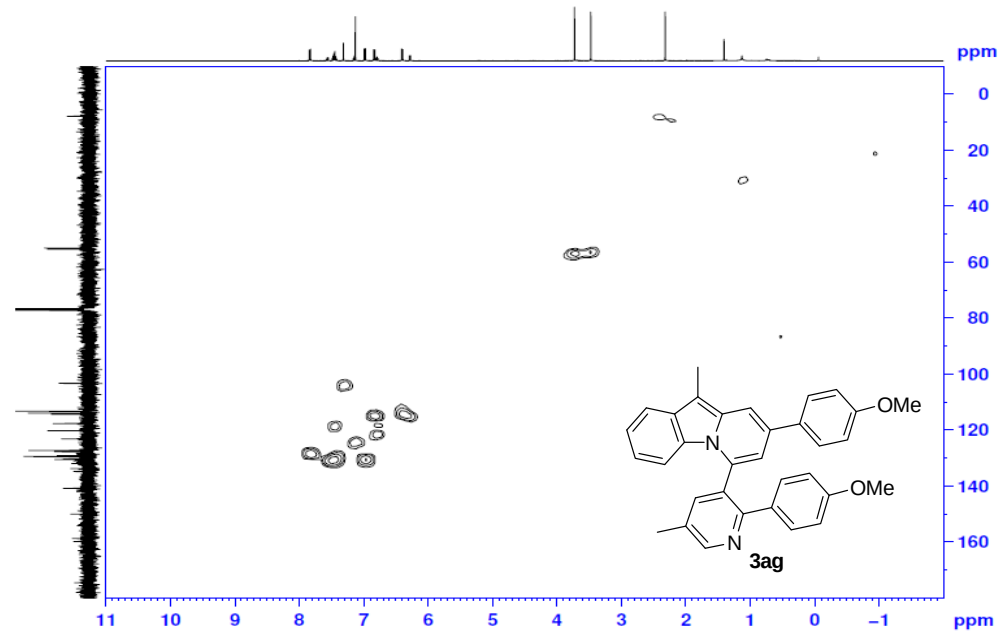
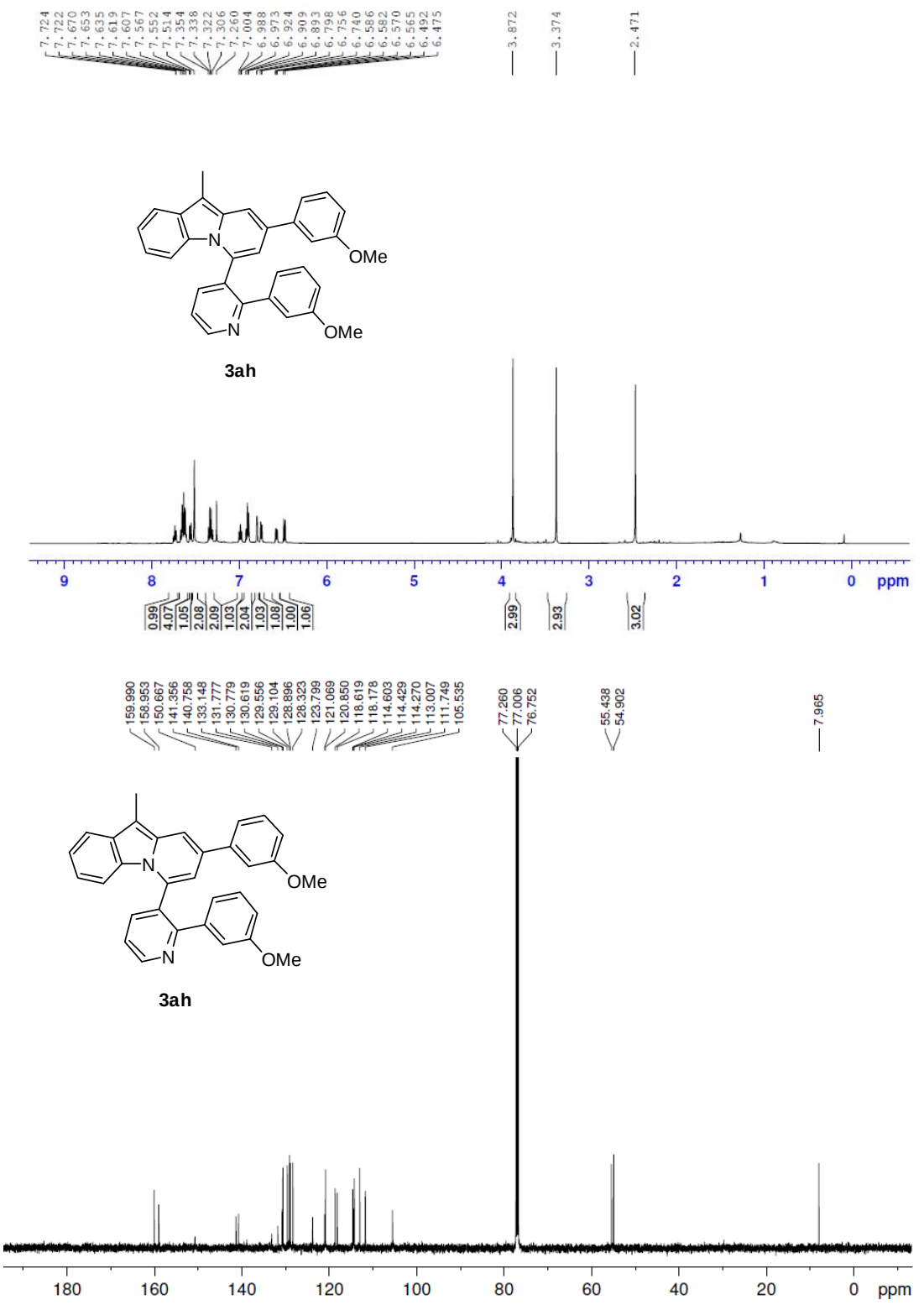
0
ppm

CDCl3 H-H COSY



CDCl3 HSQC

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7.322
7.306
7.260
7.004
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6.973
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6.909
6.893
6.798
6.756
6.740
6.586
6.582
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6.565
6.492
6.475
3.872
3.374
2.471
OMe
OMe
N
N
3ah
9
8
7
6
5
4
3
2
1
0
ppm
0.99
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1.05
2.08
2.09
1.03
2.04
1.03
1.08
1.00
1.06
2.99
2.93
3.02
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OMe
N
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3ah
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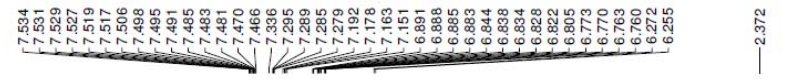
ppm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7.481
7.470
7.466
7.336
7.295
7.289
7.285
7.279
7.192
7.178
7.163
7.151
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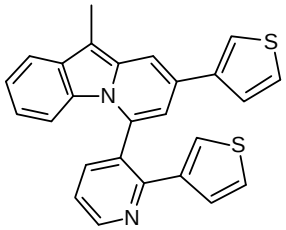
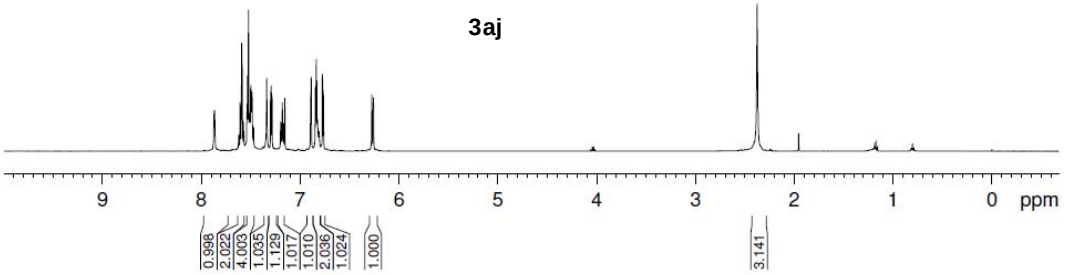

S
N
S
N

3aj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8
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6
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4
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1
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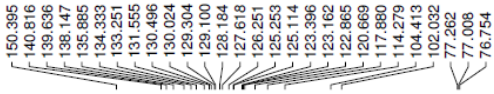
1.129
1.017
1.010
2.036
1.024
1.000
3.141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139.636
138.147
135.885
134.333
133.251
131.555
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130.024
129.304
129.100
128.184
127.618
126.251
125.253
125.114
123.396
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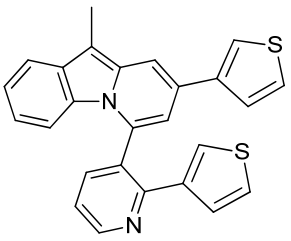
120.669
117.880
114.279
104.413
102.032
77.262
77.008
76.754
7.953


S
N
S
N

3aj

200
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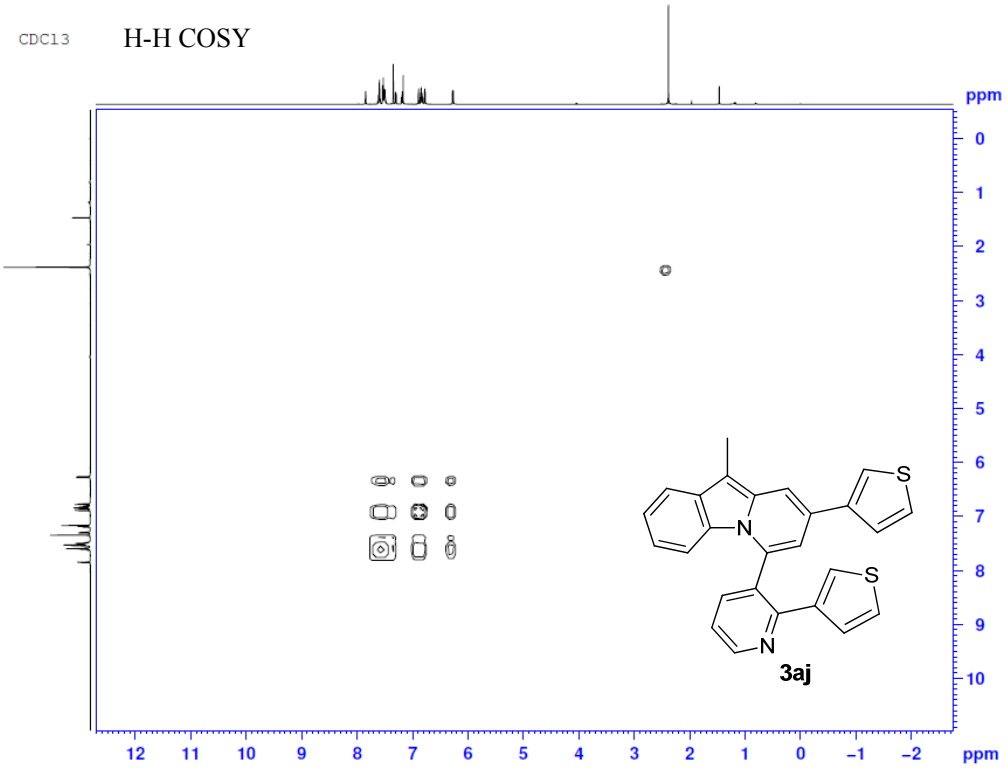
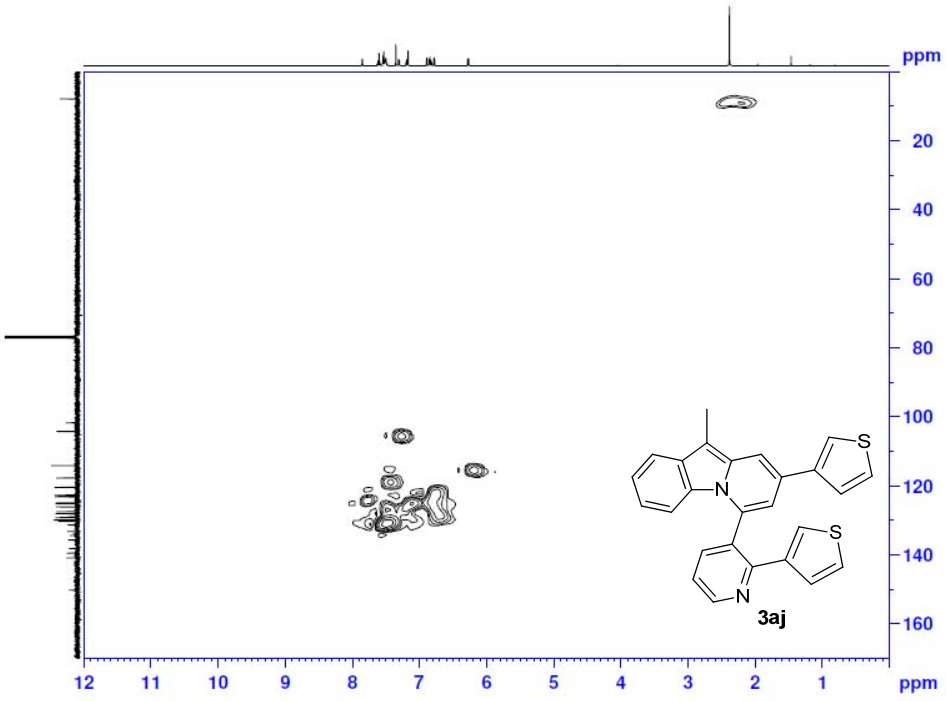
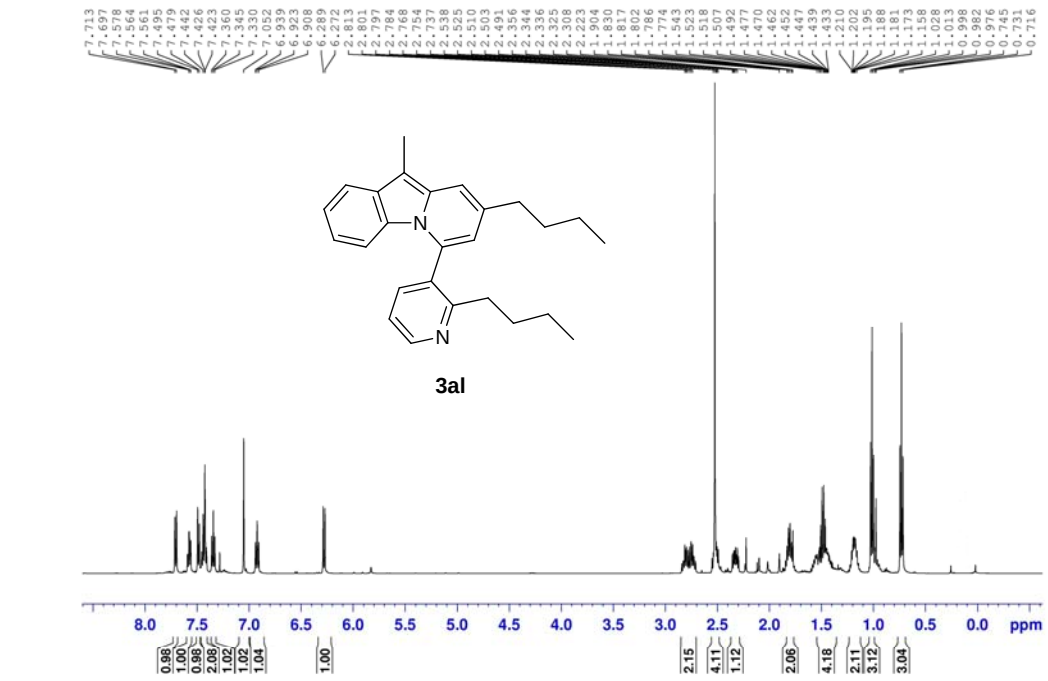
160
140
120
100
80
60
40
20
0
ppm

CDCl3 H-H COSY

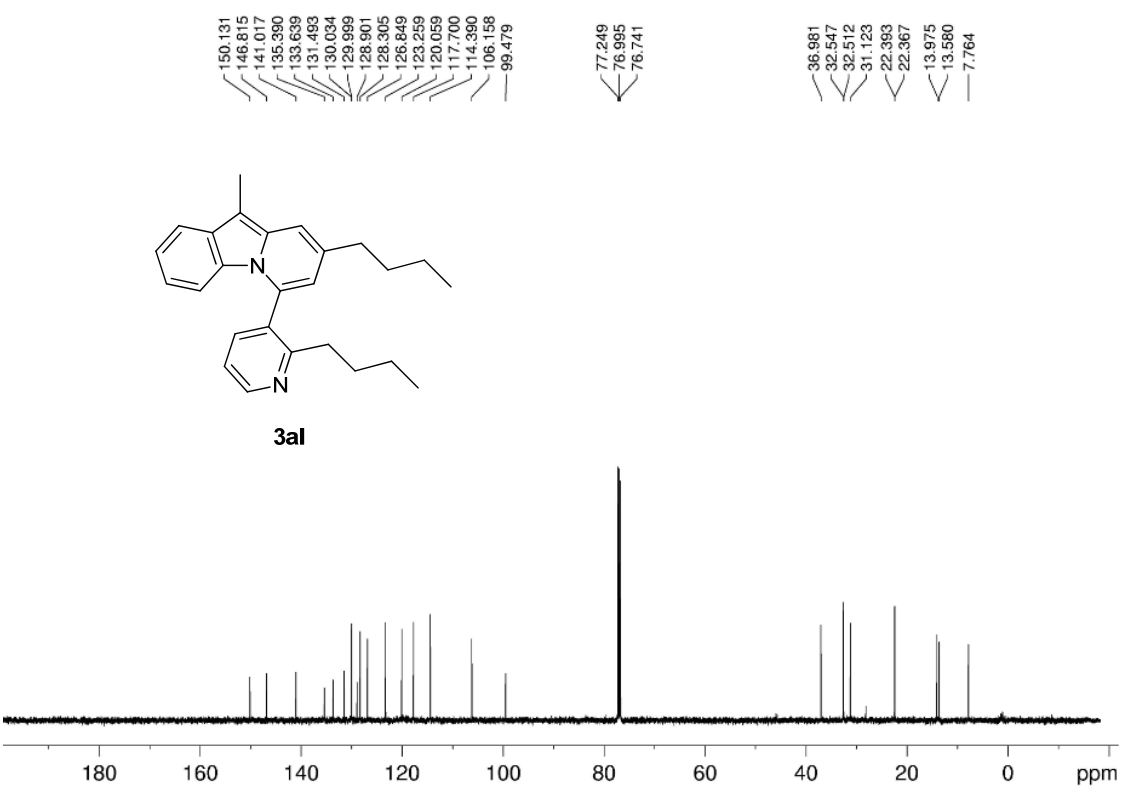


CDCl3 HSQC





3al



3al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7.635
7.626
7.624
7.602
7.465
7.462
7.450
7.435
7.385
7.371
7.356
7.297
7.296
7.282
7.267
7.260
7.165
7.162
7.158
7.154
7.150
7.146
7.016
7.007
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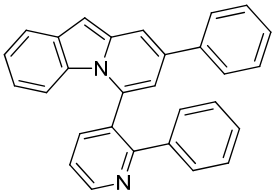
6.959
6.957
6.650
6.536
6.519


0.114
0.036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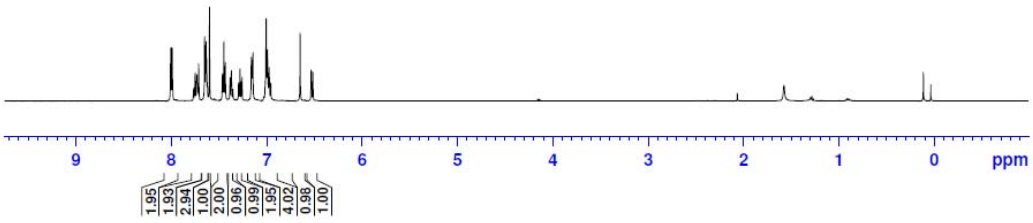
3ba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1
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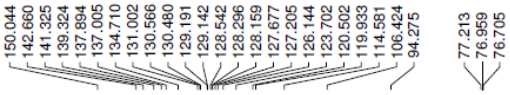
1.93
2.94
1.00
2.00
0.96
0.99
1.95
4.02
0.98
1.00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142.660
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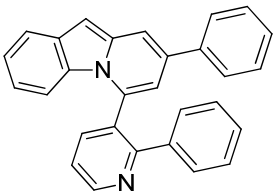
139.324
137.894
137.005
134.710
131.002
130.566
130.480
129.191
129.142
128.542
128.296
128.159
127.677
127.205
126.144
123.702
120.502
119.933
114.581
106.424
94.275
77.213
76.959
76.705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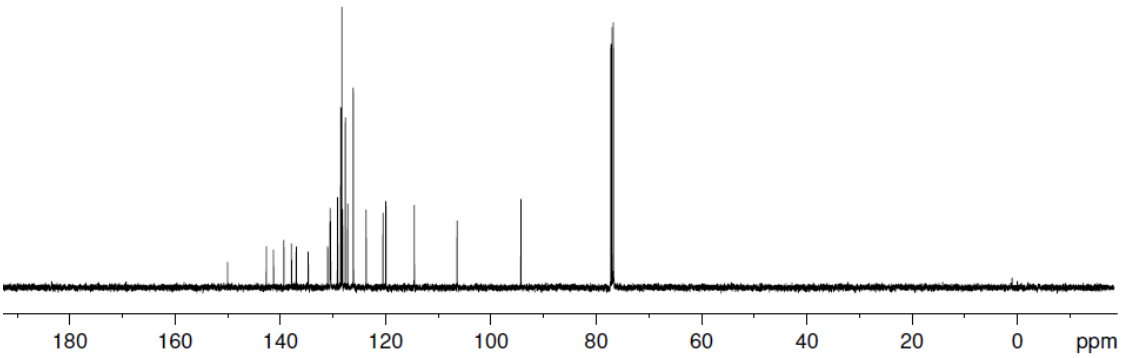
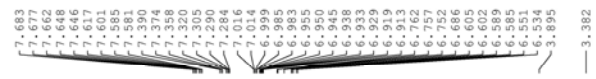
N

3ba


180
160
140
120
100
80
60
40
20
0
ppm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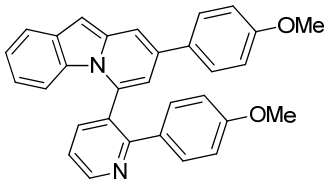
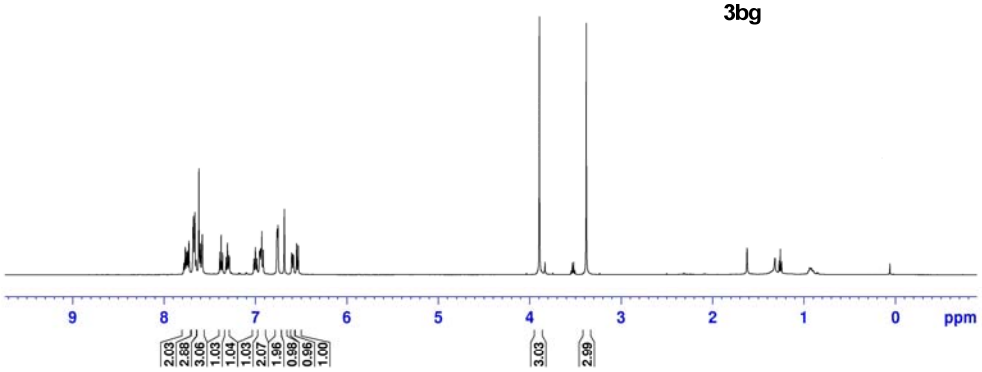
7.677
7.662
7.648
7.646
7.617
7.601
7.585
7.581
7.390
7.374
7.358
7.320
7.305
7.290
7.284
7.016
7.014
6.999
6.985
6.983
6.955
6.950
6.945
6.938
6.933
6.929
6.919
6.913
6.762
6.757
6.752
6.686
6.605
6.602
6.589
6.585
6.551
6.534
3.895
3.382


OMe
OMe
N
N

3bg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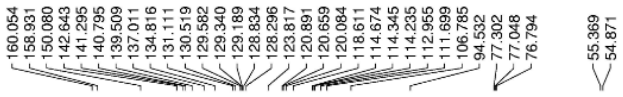
8
7
6
5
4
3
2
1
0
ppm
2.03
2.88
3.06
1.03
1.04
1.09
2.07
1.96
0.98
0.96
1.00
3.03
2.99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158.931
150.080
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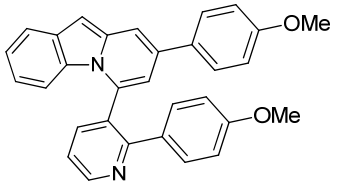
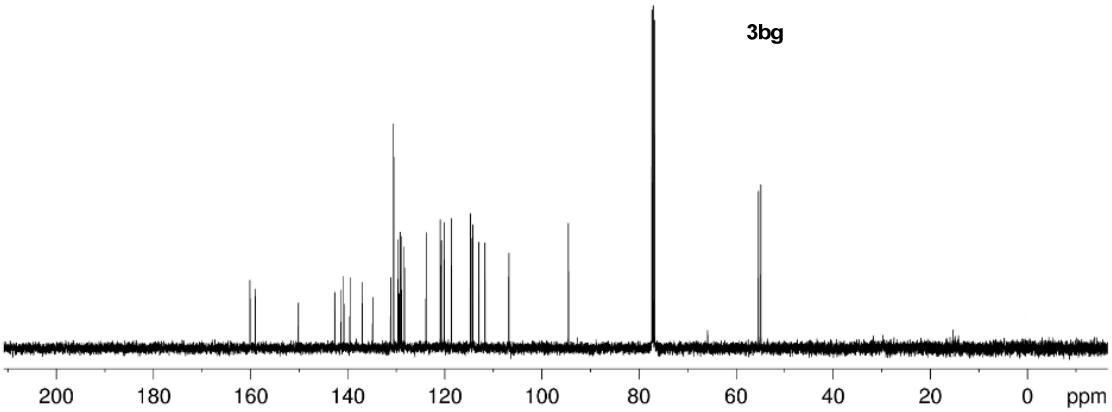
140.795
139.509
137.011
134.816
131.111
130.519
129.582
129.340
129.189
128.834
128.296
123.817
120.891
120.659
120.084
118.611
114.674
114.345
114.235
112.955
111.699
106.785
94.532
77.302
77.048
76.794
55.369
54.871


OMe
OMe
N
N

3bg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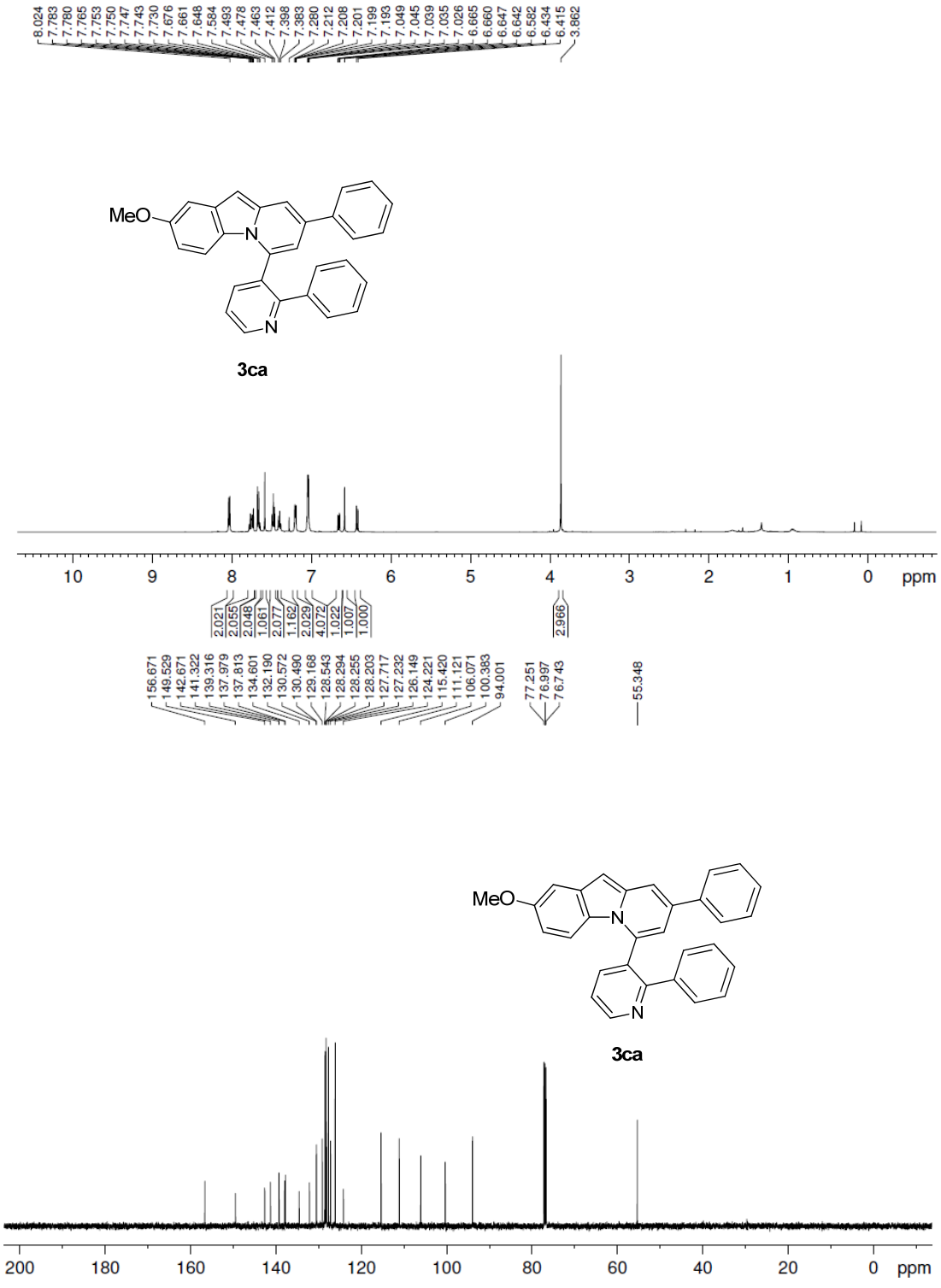
160
140
120
100
80
60
40
20
0
ppm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7.780
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7.753
7.750
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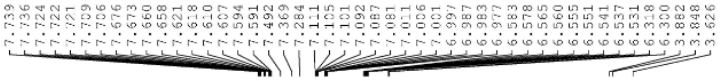
7.743
7.730
7.676
7.661
7.648
7.584
7.493
7.478
7.463
7.412
7.398
7.383
7.280
7.212
7.206
7.201
7.199
7.193
7.049
7.045
7.039
7.035
7.026
6.665
6.660
6.647
6.642
6.582
6.434
6.415
3.862
MeO
N
N
3ca
10
9
8
7
6
5
4
3
2
1
0
ppm
2.021
2.055
2.048
1.061
2.077
1.162
2.029
4.072
1.022
1.007
1.000
2.966
156.671
149.529
142.671
141.322
139.316
137.979
137.813
134.601
132.190
130.572
130.490
129.168
128.543
128.294
128.255
128.203
127.717
127.232
126.149
124.221
115.420
111.121
106.071
100.383
94.001
77.251
76.997
76.743
55.348
MeO
N
N
3ca
200
180
160
140
120
100
80
60
40
20
0
ppm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7.724
7.722
7.721
7.709
7.706
7.676
7.673
7.660
7.658
7.621
7.618
7.610
7.607
7.594
7.591
7.492
7.369
7.284
7.111
7.105
7.101
7.092
7.087
7.081
7.011
7.006
7.001
6.997
6.987
6.983
6.977
6.583
6.578
6.565
6.560
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6.551
6.541
6.537
6.531
6.318
6.300
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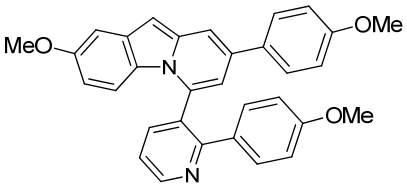
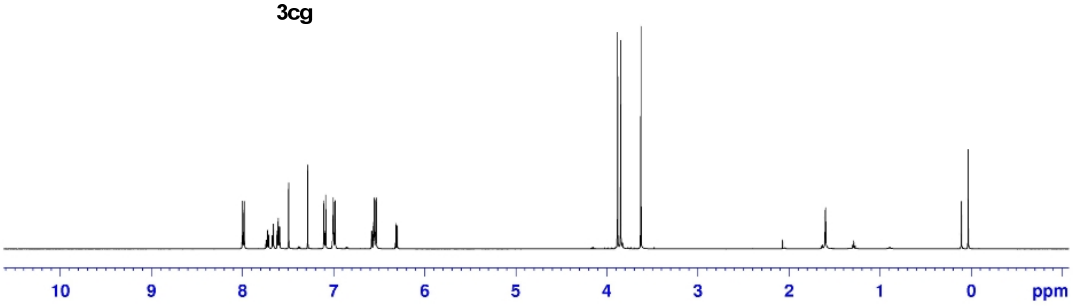
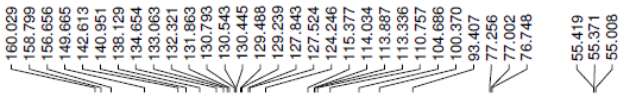
3.848
3.626


MeO
OMe
OMe
N
N

3cg


10
9
8
7
6
5
4
3
2
1
0
ppm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134.654
133.063
132.321
131.863
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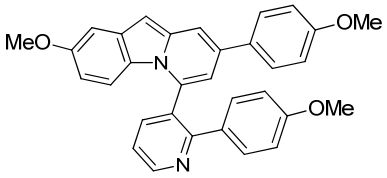
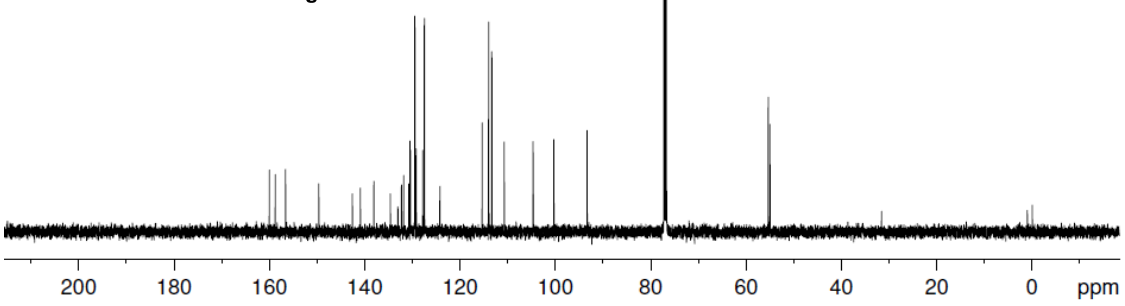
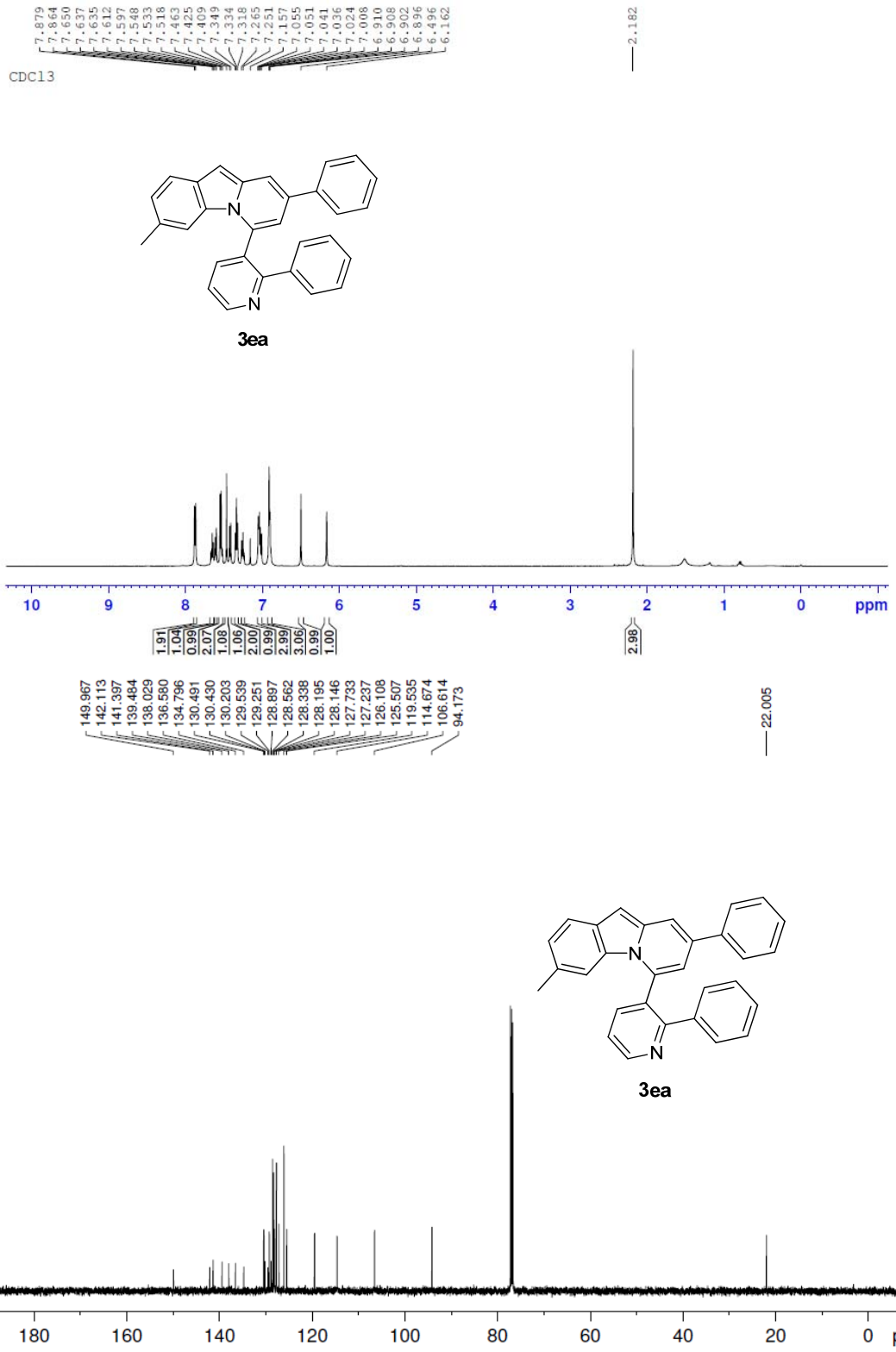
130.543
130.445
129.488
129.239
127.843
127.524
124.246
115.377
114.034
113.887
113.336
110.757
104.686
100.370
93.407
77.256
77.002
76.748
55.419
55.371
55.008


MeO
OMe
OMe
N
N

3cg


200
180
160
140
120
100
80
60
40
20
0
ppm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7.864
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7.635
7.612
7.597
7.548
7.533
7.518
7.463
7.425
7.409
7.349
7.334
7.318
7.265
7.251
7.157
7.055
7.051
7.041
7.036
7.024
7.008
6.910
6.908
6.902
6.896
6.496
6.162
CDCl3
2.182
3ea
10
9
8
7
6
5
4
3
2
1
0
ppm
1.91
1.04
0.99
2.07
1.08
1.06
2.00
0.99
2.99
3.06
0.99
1.00
2.98
149.967
142.113
141.397
139.484
138.029
136.580
134.796
130.491
130.430
130.203
129.539
129.251
128.897
128.562
128.338
128.195
128.146
127.733
127.237
126.108
125.507
119.535
114.674
106.614
94.173
22.005
3ea
180
160
140
120
100
80
60
40
20
0
ppm


8.034
8.019
7.768
7.753
7.734
7.720
7.677
7.682
7.648
7.633
7.597
7.579
7.576
7.486
7.471
7.455
7.412
7.398
7.279
7.126
7.113
7.111
7.026
7.013
6.999
6.919
6.915
6.901
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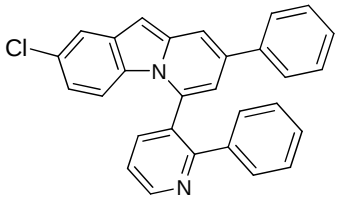
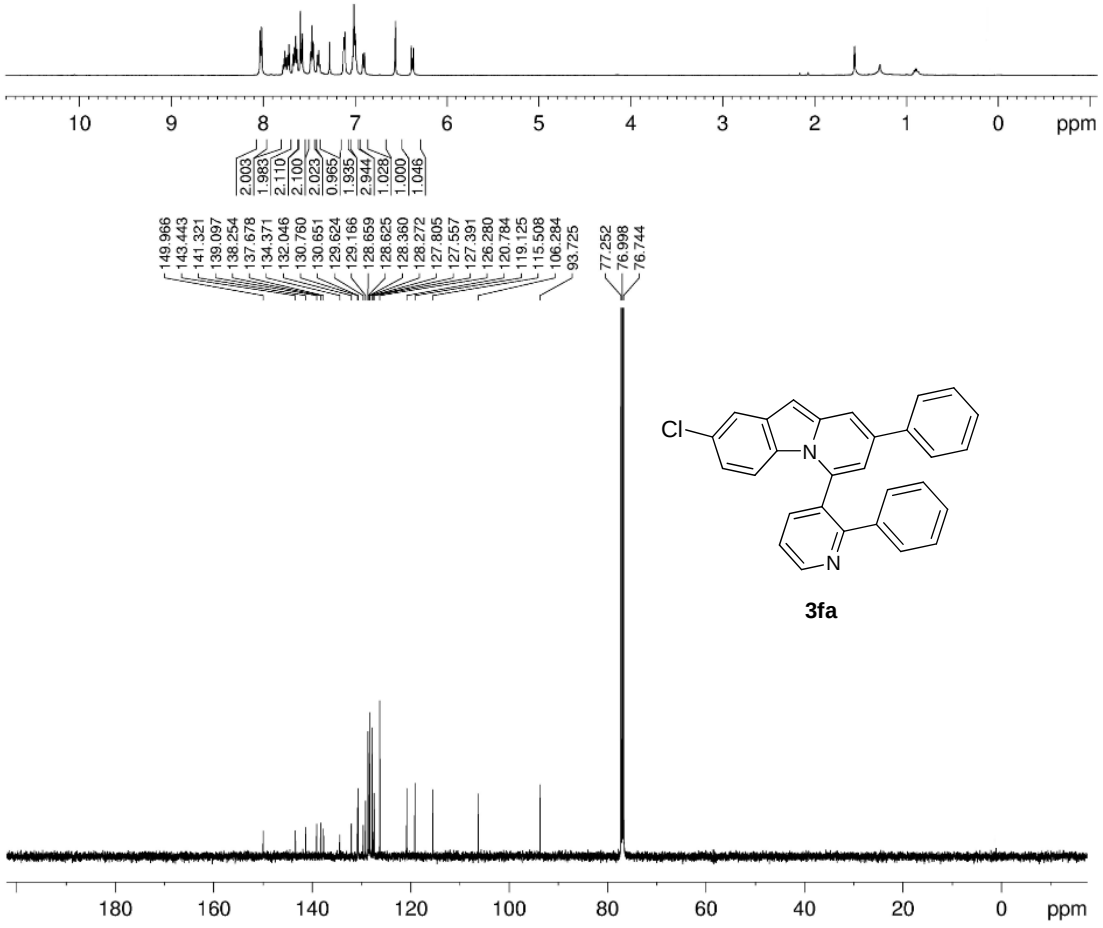
6.387
6.369


Cl
N
N

3fa


10
9
8
7
6
5
4
3
2
1
0
ppm
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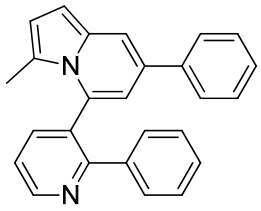
2.100
2.023
0.965
1.935
2.944
1.028
1.000
1.046
149.966
143.443
141.321
139.097
138.254
137.678
134.371
132.046
130.760
130.651
129.624
129.166
128.659
128.625
128.360
128.272
127.805
127.557
127.391
126.280
120.784
119.125
115.508
106.284
93.725
77.252
76.998
76.744
180
160
140
120
100
80
60
40
20
0
ppm

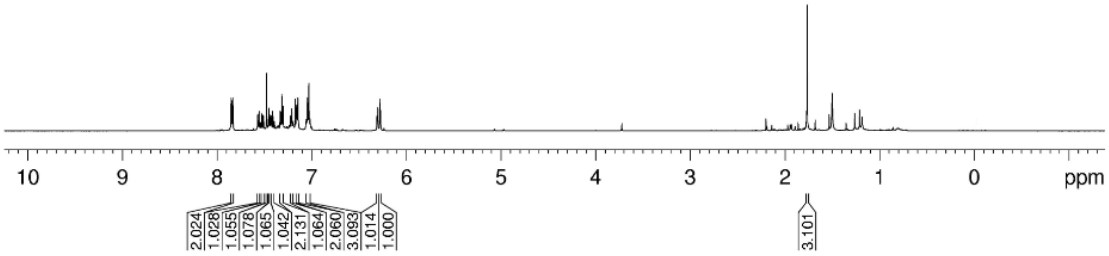
Cl
N
N

3fa


7.522
7.510
7.507
7.474
7.449
7.435
7.433
7.425
7.423
7.410
7.408
7.395
7.331
7.328
7.316
7.300
7.223
7.208
7.194
7.173
7.161
7.158
7.154
7.145
7.142
7.055
7.052
7.043
7.037
7.032
7.028
7.024
7.016
7.014
6.308
6.301
6.300
6.279
6.271
1.765


N
N

3ha


10
9
8
7
6
5
4
3
2
1
0
ppm
2.024
1.028
1.055
1.078
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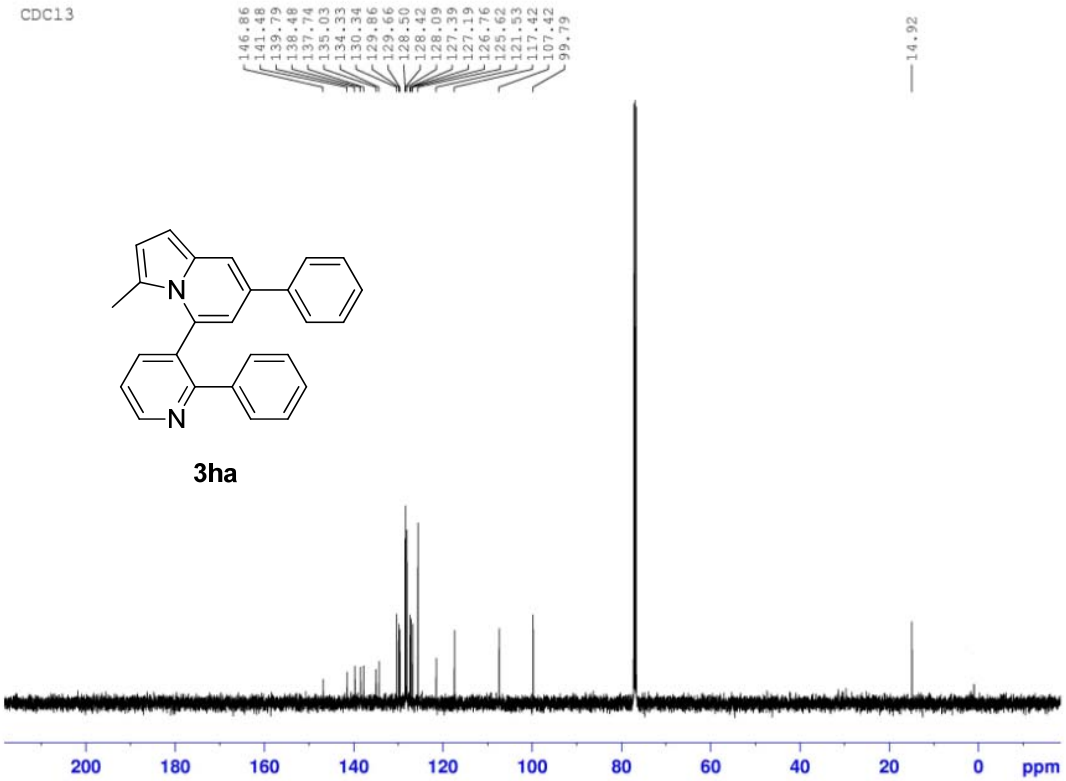
1.064
2.060
3.093
1.014
1.000
3.101


CDC13
146.86
141.48
139.79
138.48
137.74
135.03
134.33
130.34
129.86
129.66
128.50
128.42
128.09
127.39
127.19
126.76
125.62
121.53
117.42
107.42
99.79
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N
N
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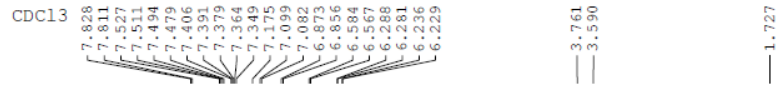
140
120
100
80
60
40
20
0
ppm

3ha


CDCl3
7.828
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7.494
7.479
7.406
7.391
7.379
7.364
7.349
7.175
7.099
7.082
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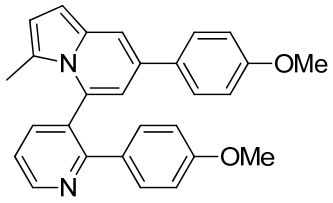
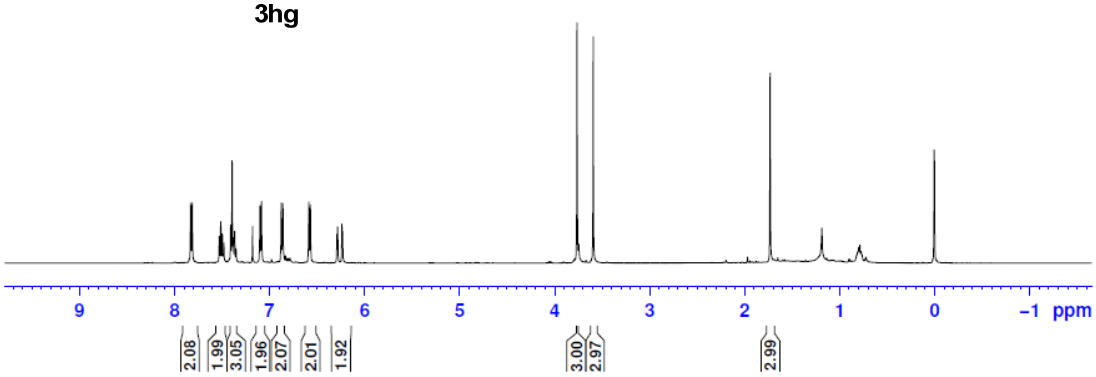
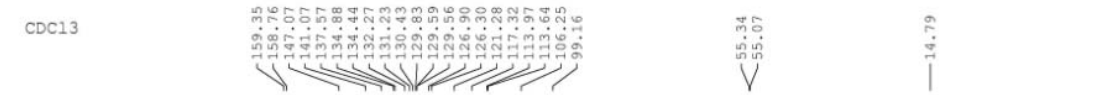
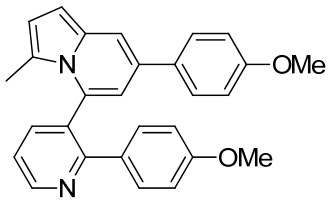
6.584
6.567
6.288
6.281
6.236
6.229
3.761
3.590
1.727


N
OMe
OMe
N

3hg


9
8
7
6
5
4
3
2
1
0
−1 ppm
2.08
1.99
3.05
1.96
2.07
2.01
1.92
3.00
2.97
2.99


CDCl3
159.35
158.76
147.07
141.07
137.57
134.88
134.44
132.27
131.23
130.43
129.83
129.59
129.56
126.90
126.30
121.28
117.32
113.97
113.64
106.25
99.16
55.34
55.07
14.79


N
OMe
OMe
N

3hg

200
180
160
140
120
100
80
60
40
20
0
ppm


7.887
7.876
7.465
7.434
7.418
7.396
7.353
7.350
7.338
7.323
7.314
7.273
7.271
7.269
7.260
7.257
7.253
7.244
7.242
7.163
7.066
7.062
7.056
7.054
7.047
6.902
6.898
6.892
6.888
6.880
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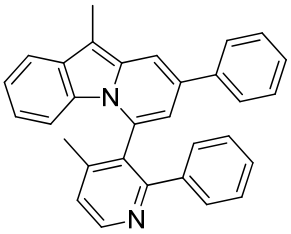
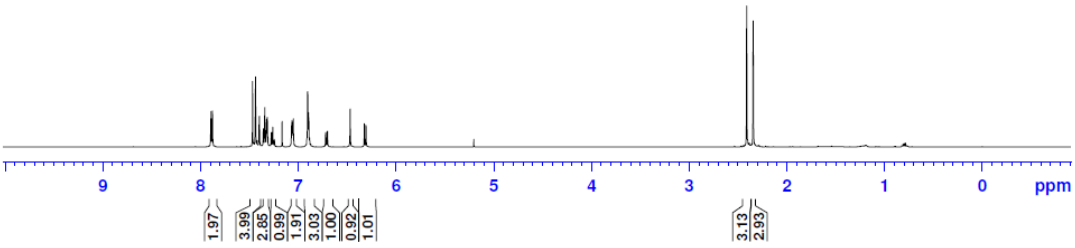
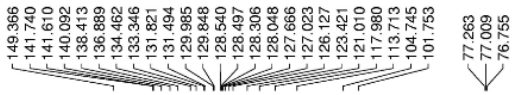
6.697
6.465
6.320
6.303
2.406
2.341



3ia


9
8
7
6
5
4
3
2
1
0
ppm
1.97
3.99
2.85
0.99
1.91
3.03
1.00
0.92
1.01
3.13
2.93


149.366
141.740
141.610
140.092
138.413
136.889
134.462
133.346
131.821
131.494
129.985
129.848
128.540
128.497
128.306
128.048
127.666
127.023
126.127
123.421
121.010
117.980
113.713
104.745
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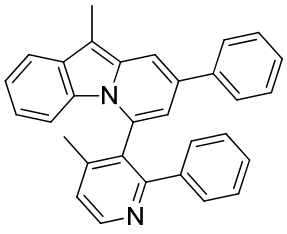
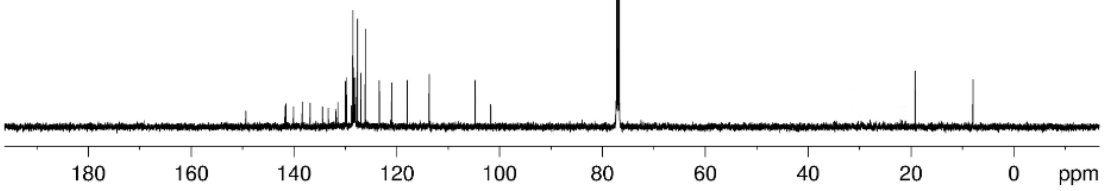
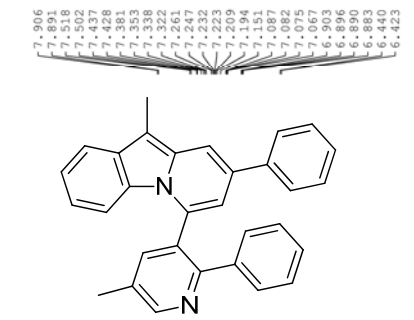
77.263
77.009
76.755
19.188
7.945

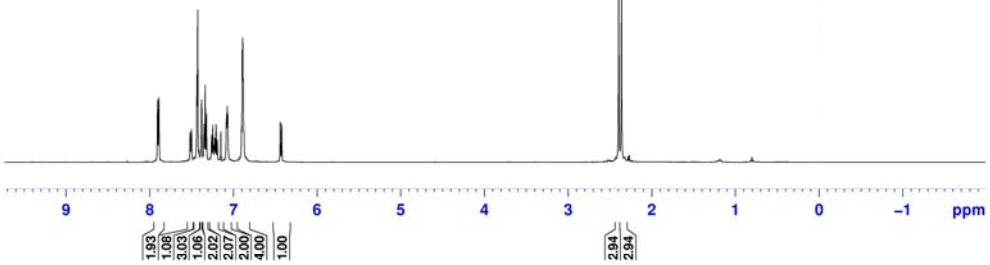


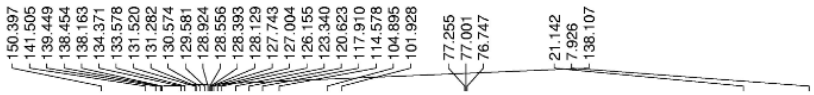
3ia

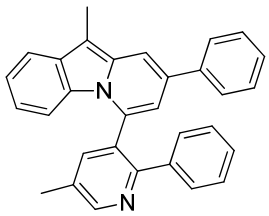

180
160
140
120
100
80
60
40
20
0
ppm



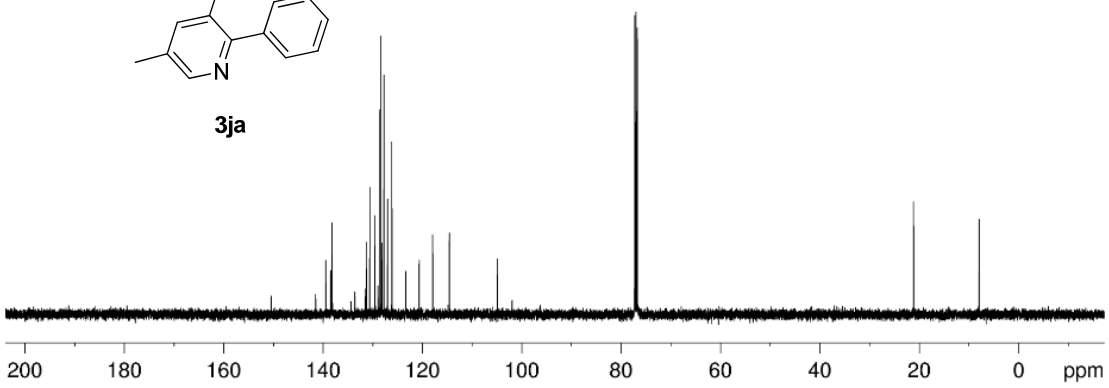
3ja

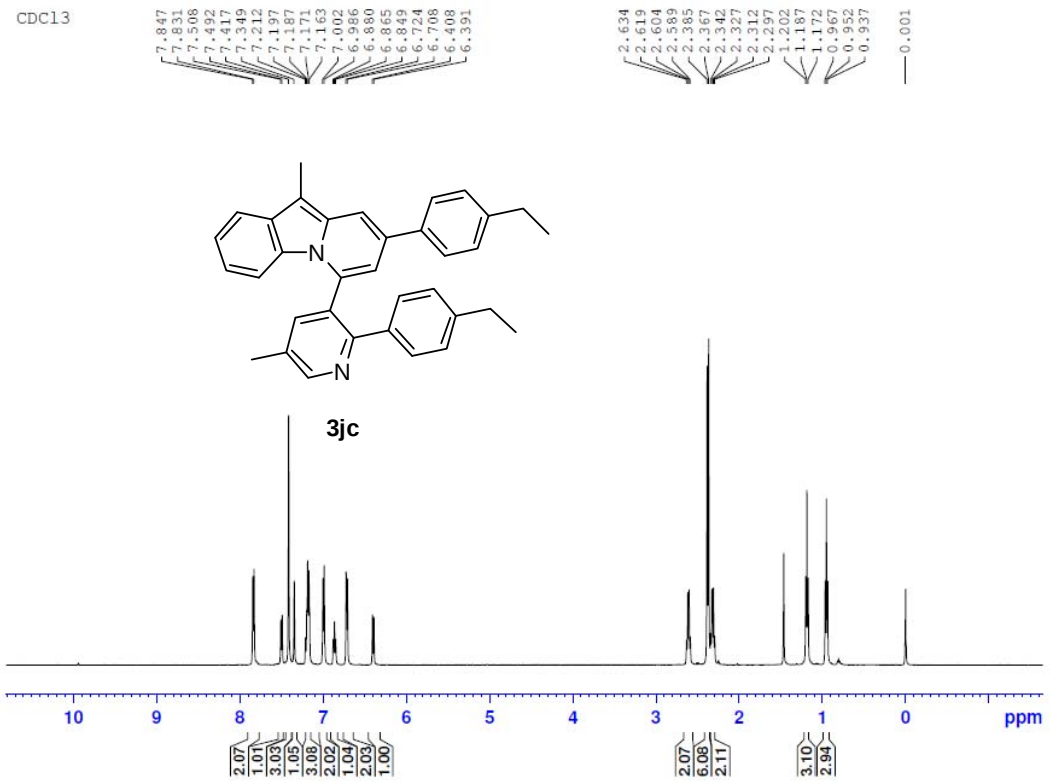


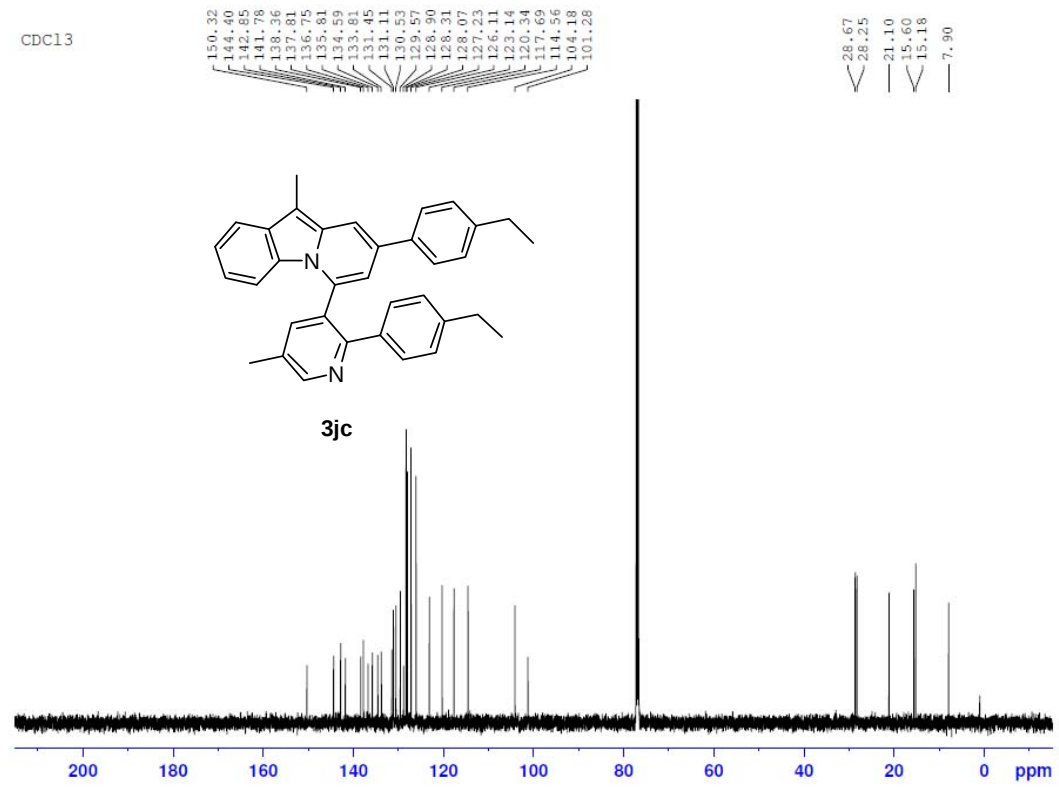




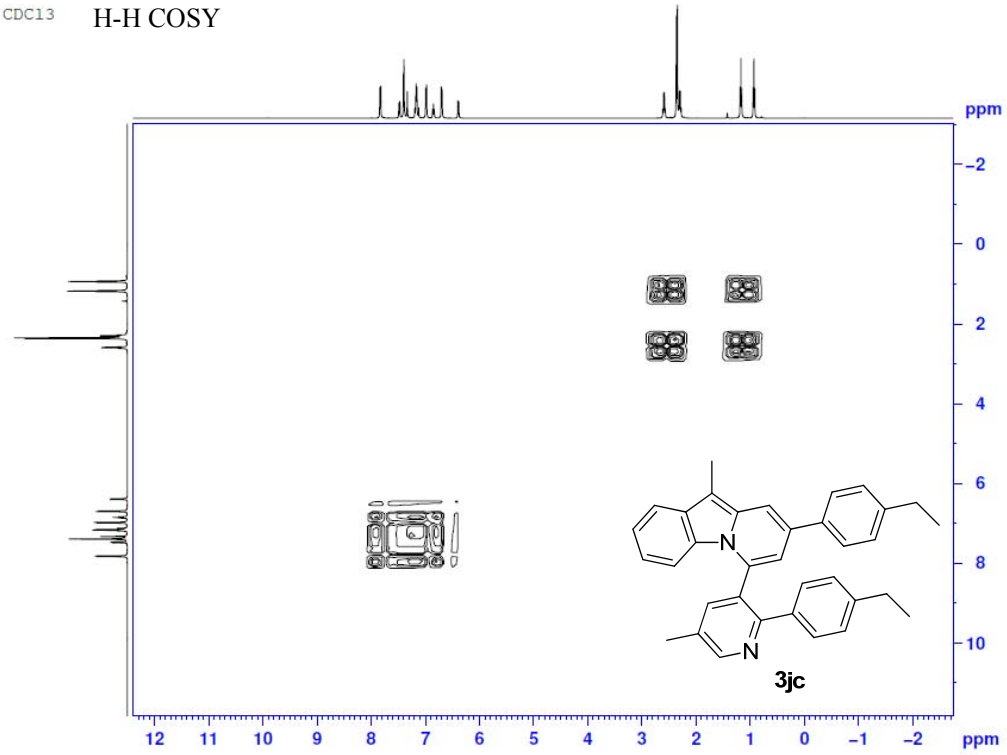
3ja



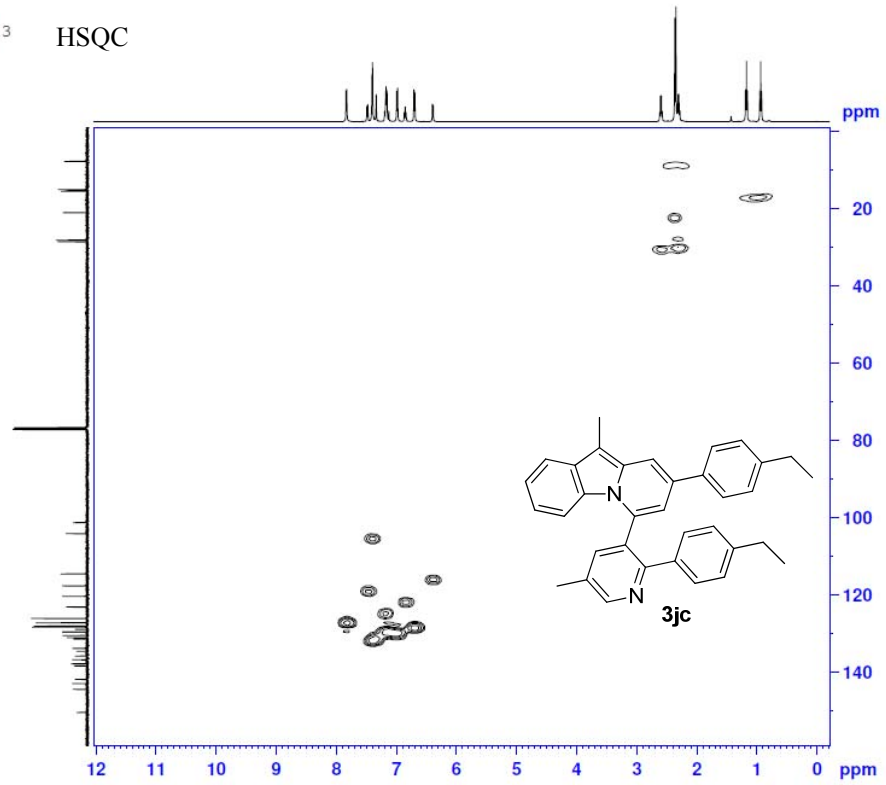

CDCl3
7.847
7.831
7.508
7.492
7.417
7.349
7.212
7.197
7.187
7.171
7.163
7.002
6.986
6.880
6.865
6.849
6.724
6.708
6.408
6.391
2.634
2.619
2.604
2.589
2.385
2.367
2.342
2.327
2.312
2.297
1.202
1.187
1.172
0.967
0.952
0.937
0.001
N
N
3jc
10
9
8
7
6
5
4
3
2
1
0
ppm
2.07
1.01
3.03
1.05
3.08
2.02
1.04
2.03
1.00
2.07
6.08
2.11
3.10
2.94

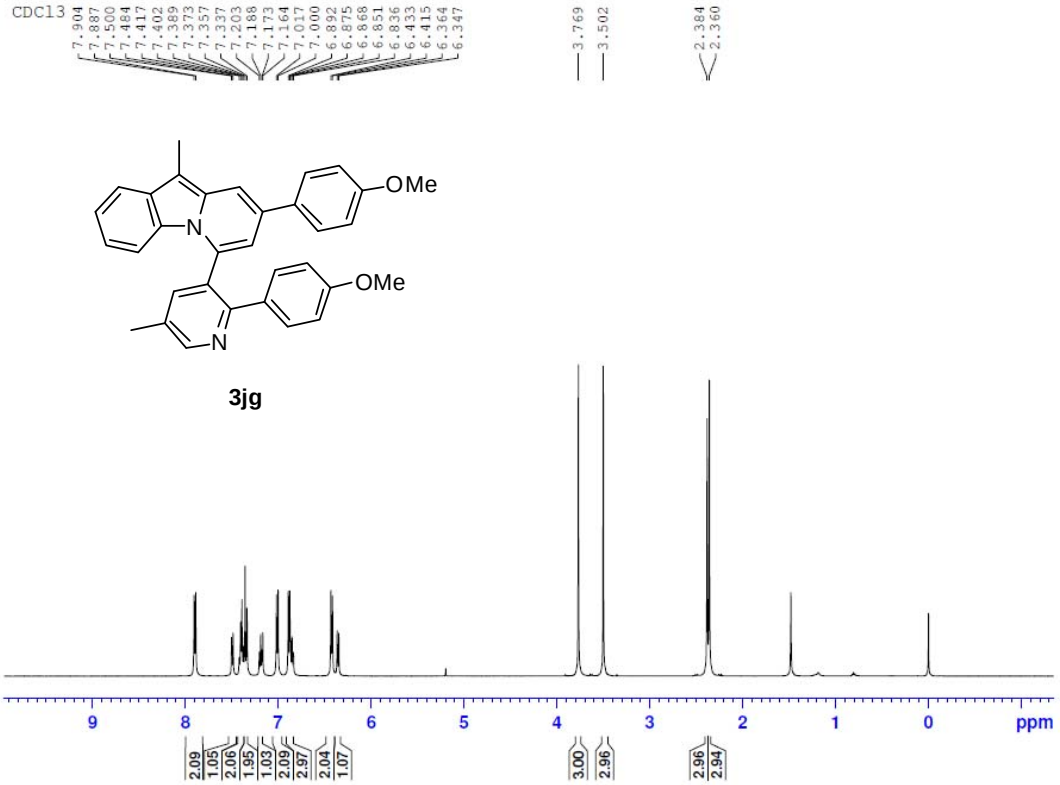

CDCl3
150.32
144.40
142.85
141.78
138.36
137.81
136.75
135.81
134.59
133.81
131.45
131.11
130.53
129.57
128.90
128.31
128.07
127.23
126.11
123.14
120.34
117.69
114.56
104.18
101.28
28.67
28.25
21.10
15.60
15.18
7.90
N
N
3jc
200
180
160
140
120
100
80
60
40
20
0
ppm

CDC13 H-H COSY

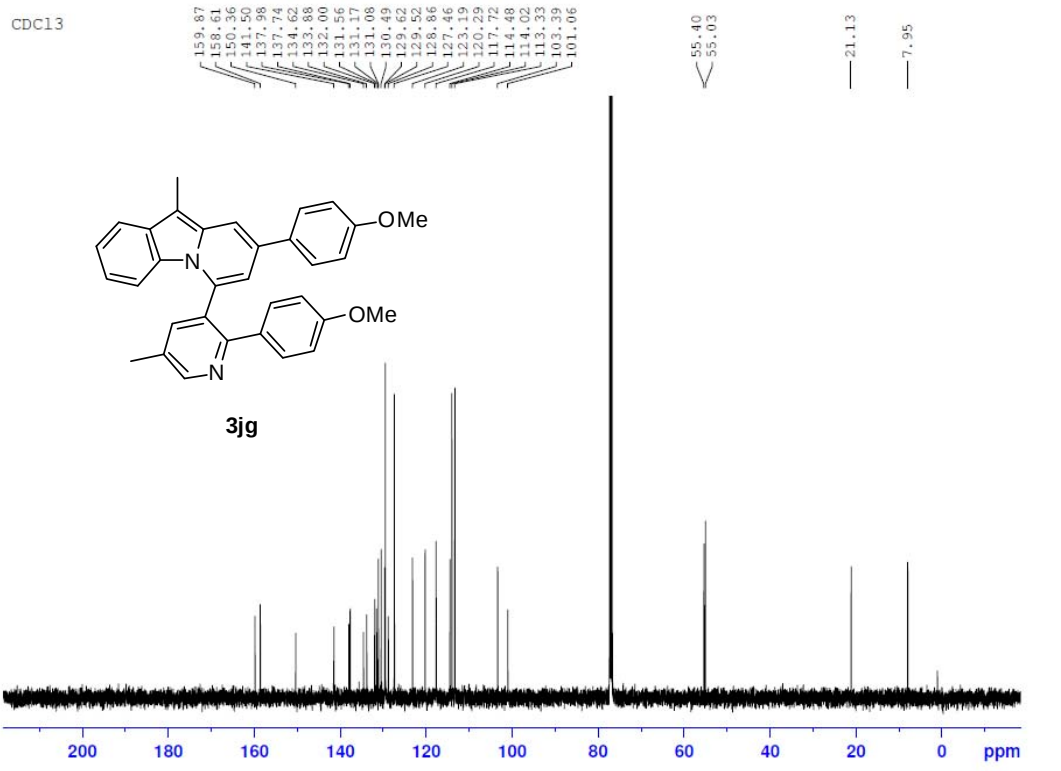


CDC13 HSQC

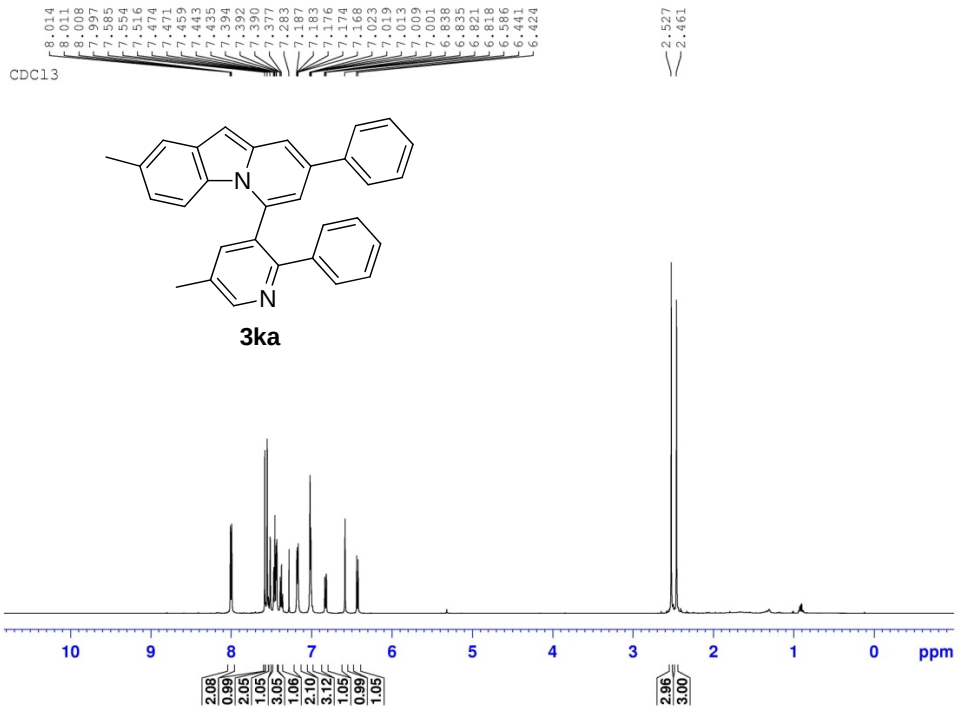


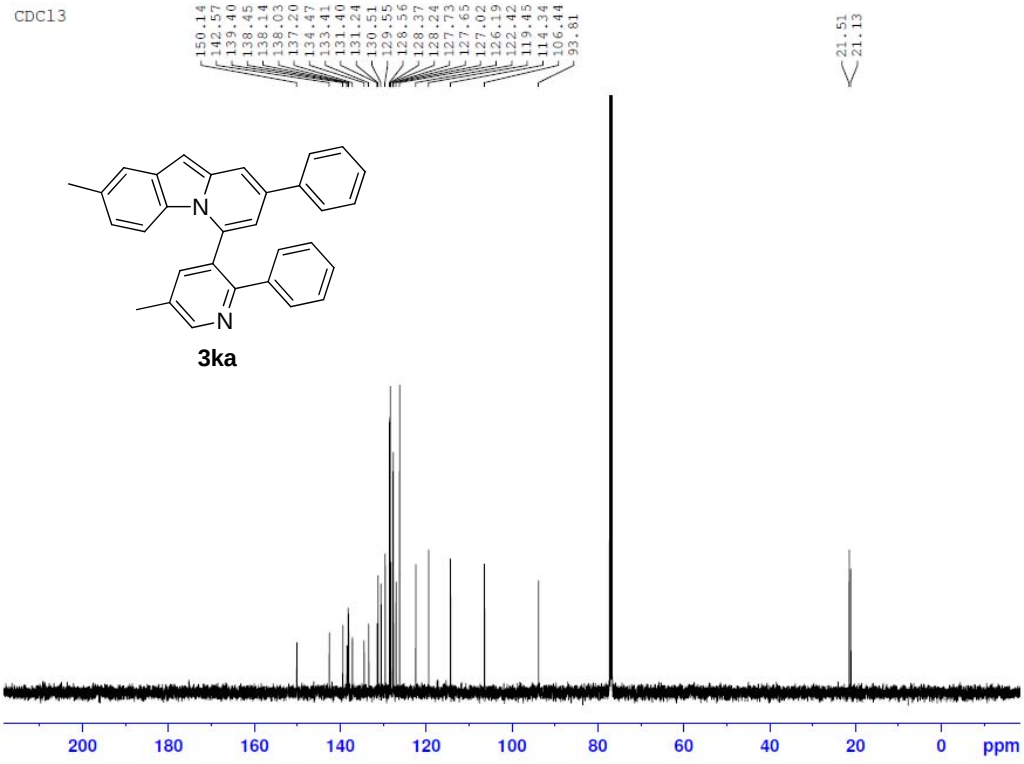

CDCl3
7.904
7.887
7.500
7.484
7.417
7.402
7.389
7.373
7.357
7.337
7.203
7.188
7.173
7.164
7.017
7.000
6.892
6.875
6.868
6.851
6.836
6.433
6.415
6.364
6.347
3.769
3.502
2.384
2.360
OMe
OMe
N
N
9
8
7
6
5
4
3
2
1
0
ppm
2.09
1.05
2.06
1.95
1.03
2.09
2.97
2.04
1.07
3.00
2.96
2.96
2.94

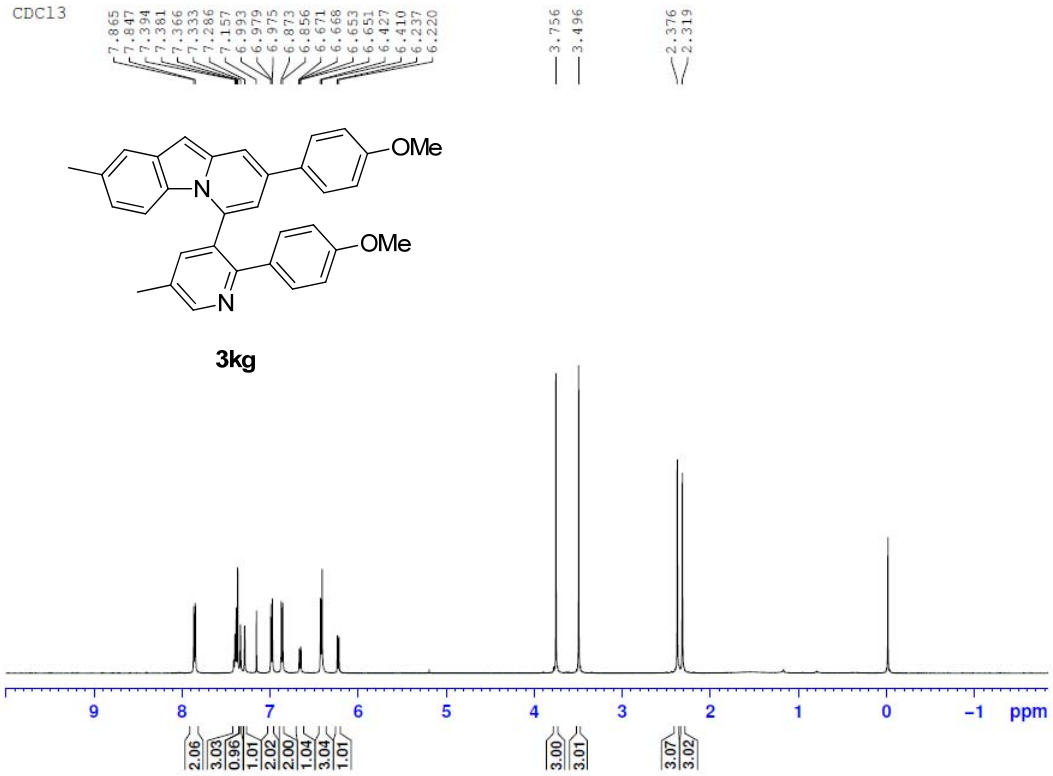
3jg

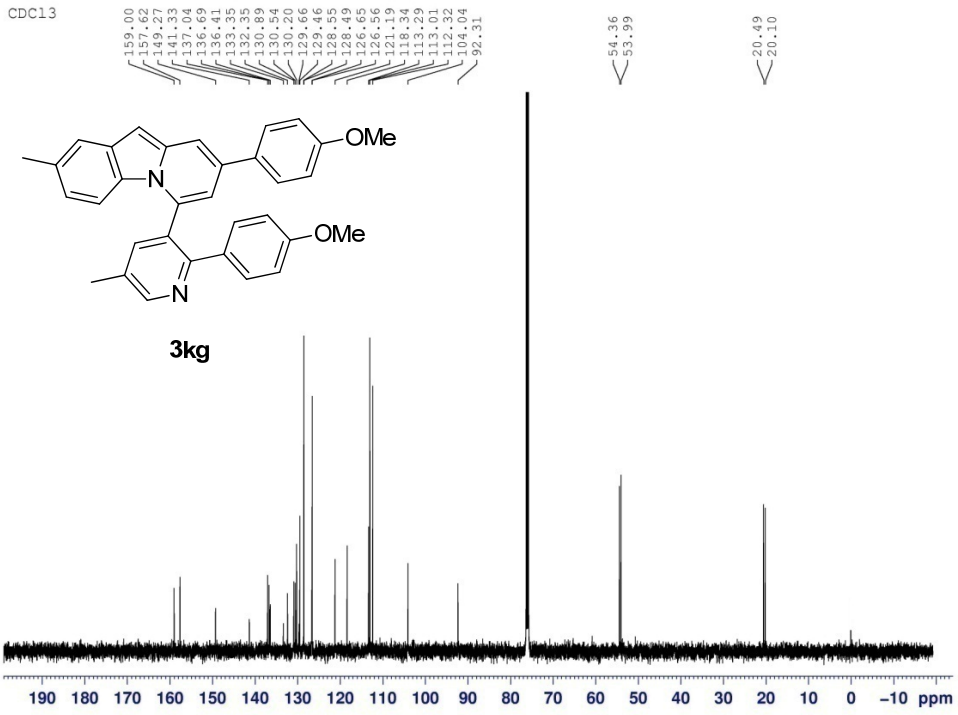

CDCl3
159.87
158.61
150.36
141.50
137.98
137.74
134.62
133.88
132.00
131.56
131.17
131.08
130.49
129.62
129.52
128.86
127.46
123.19
120.29
117.72
114.48
114.02
113.33
103.39
101.06
55.40
55.03
21.13
7.95
OMe
OMe
N
N
200
180
160
140
120
100
80
60
40
20
0
ppm

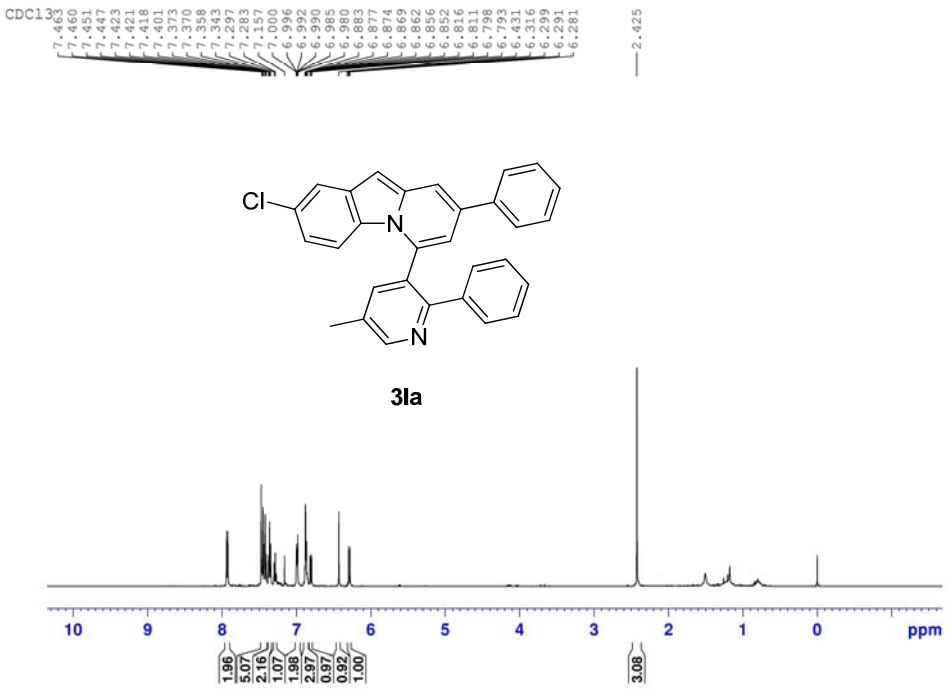
3jg


8.014
8.011
8.008
7.997
7.585
7.554
7.516
7.474
7.471
7.459
7.443
7.435
7.394
7.392
7.390
7.377
7.283
7.187
7.183
7.176
7.174
7.168
7.023
7.019
7.013
7.009
7.001
6.838
6.835
6.821
6.818
6.586
6.441
6.424
2.527
2.461
CDCl3
N
N
3ka
10
9
8
7
6
5
4
3
2
1
0
ppm
2.08
0.99
2.05
1.05
3.05
1.06
2.10
3.12
1.05
0.99
1.05
2.96
3.00


CDCl3
150.14
142.57
139.40
138.45
138.14
138.03
137.20
134.47
133.41
131.40
131.24
130.51
129.55
128.56
128.37
128.24
127.73
127.65
127.02
126.19
122.42
119.45
114.34
106.44
93.81
21.51
21.13
N
N
3ka
200
180
160
140
120
100
80
60
40
20
0
ppm


CDCl3
7.865
7.847
7.394
7.381
7.366
7.333
7.286
7.157
6.993
6.979
6.975
6.873
6.856
6.671
6.668
6.653
6.651
6.427
6.410
6.237
6.220
3.756
3.496
2.376
2.319
OMe
OMe
N
N
3kg
9
8
7
6
5
4
3
2
1
0
−1
ppm
2.06
3.03
0.96
1.01
2.02
2.00
1.04
3.04
1.01
3.00
3.01
3.07
3.02


CDCl3
159.00
157.62
149.27
141.33
137.04
136.69
136.41
133.35
133.35
132.89
130.54
130.20
129.66
129.46
128.55
128.49
126.65
126.56
121.19
118.34
113.29
113.01
112.32
104.04
92.31
54.36
53.99
20.49
20.10
OMe
OMe
N
N
3kg
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
ppm


CDCl3
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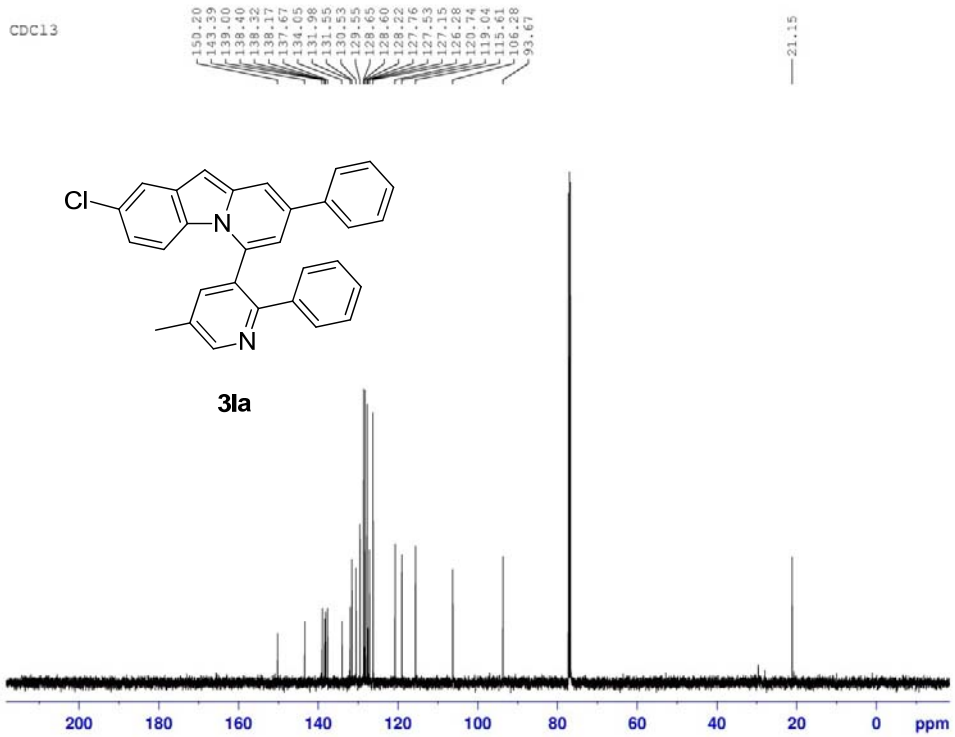
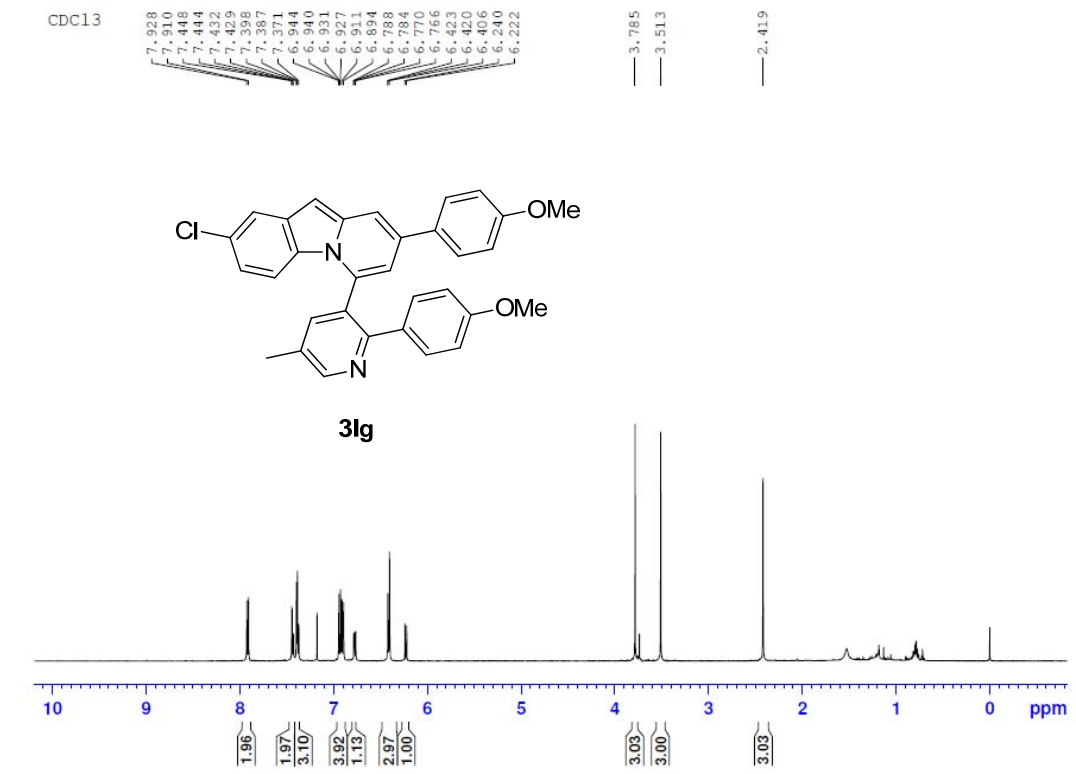
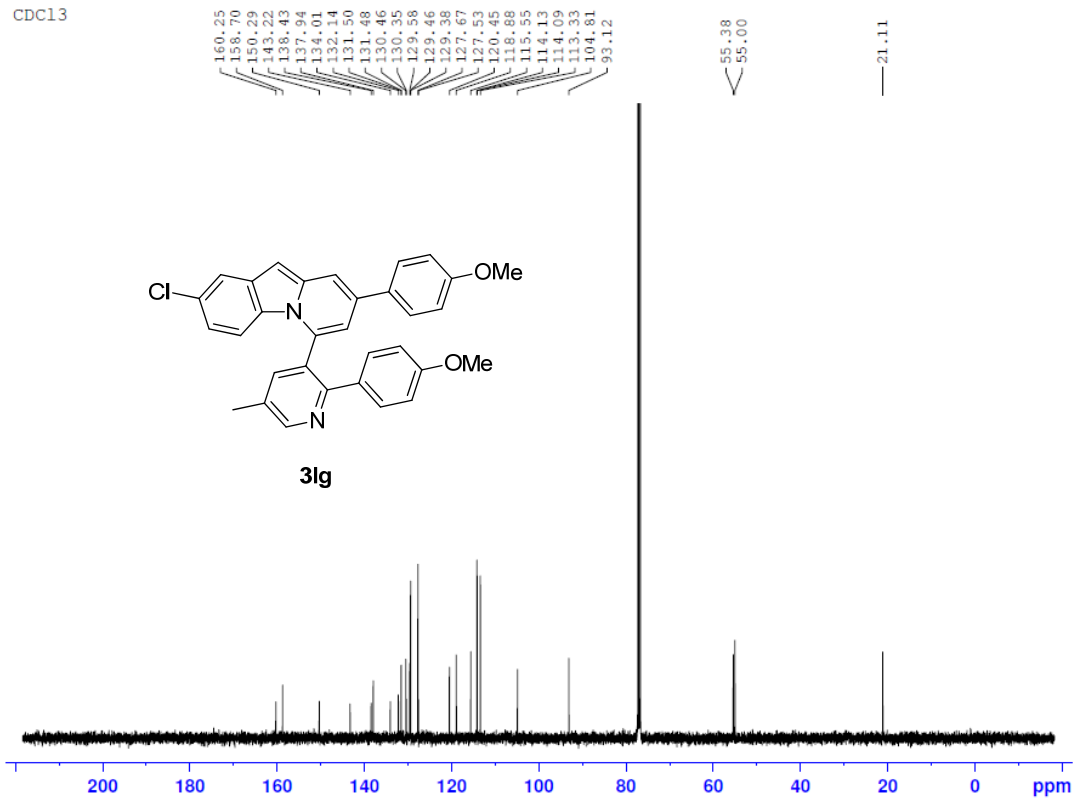
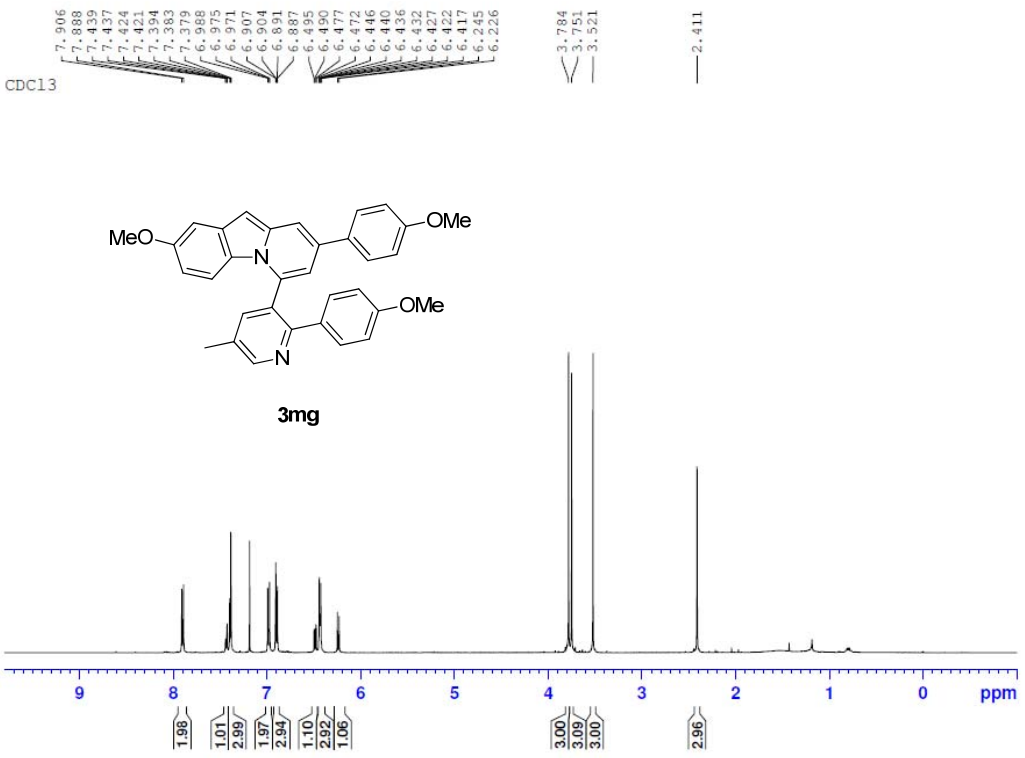
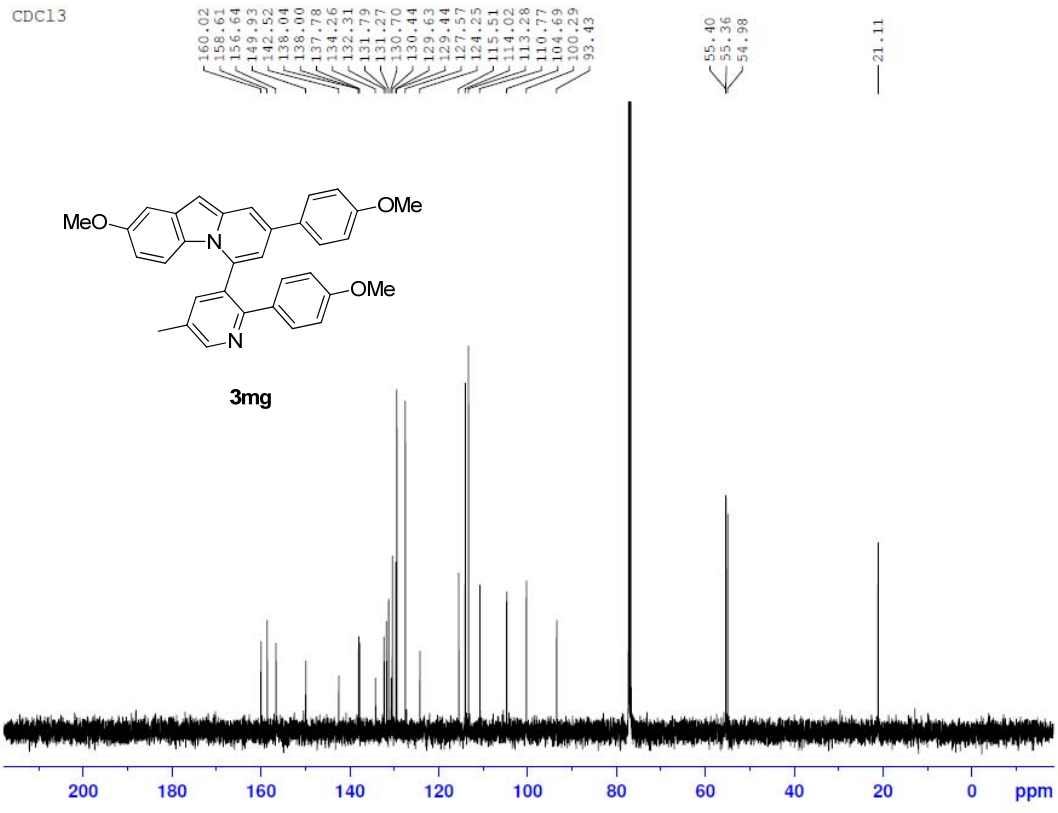
7.447
7.423
7.421
7.418
7.401
7.373
7.370
7.358
7.343
7.297
7.283
7.157
7.000
6.996
6.992
6.990
6.985
6.980
6.883
6.877
6.874
6.869
6.862
6.856
6.852
6.816
6.811
6.798
6.793
6.431
6.316
6.299
6.291
6.281
2.425
Cl
N
N
3la
10
9
8
7
6
5
4
3
2
1
0
ppm
1.96
5.07
2.16
1.07
1.98
2.97
0.97
0.92
1.00
3.08

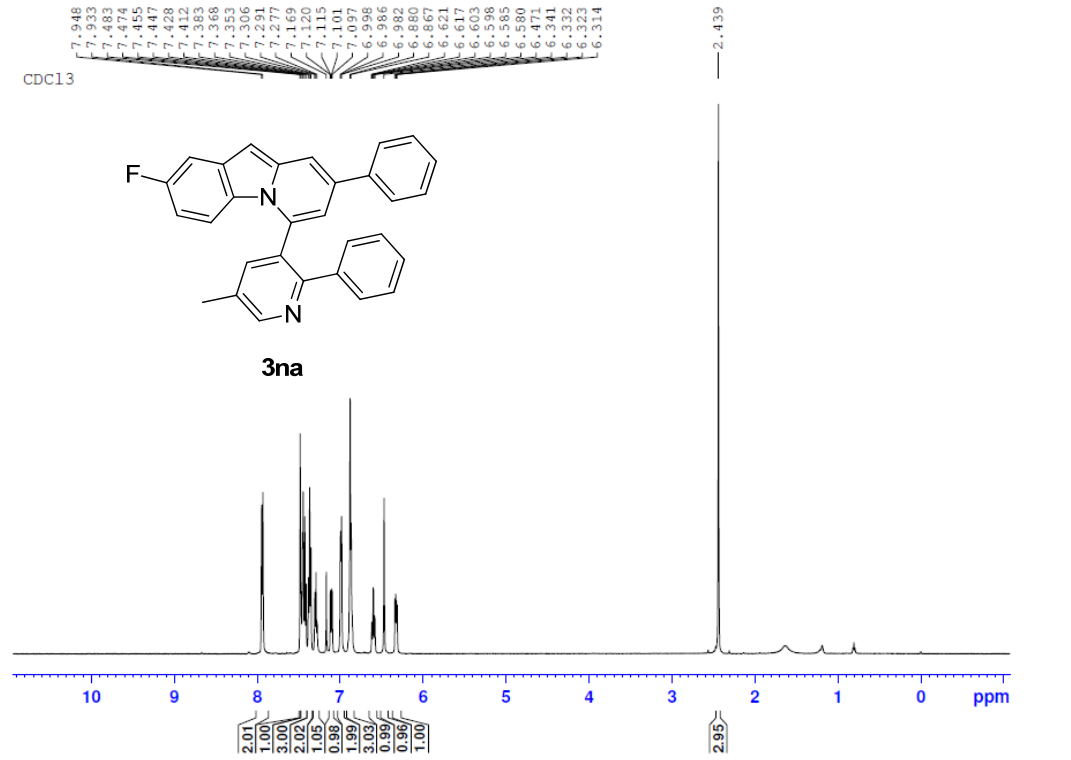

CDCl3
150.20
143.39
139.00
138.40
138.32
138.17
137.67
134.05
131.98
131.55
130.53
129.55
128.65
128.60
128.22
127.76
127.53
127.15
126.28
120.74
119.04
115.61
106.28
93.67
21.15
Cl
N
N
3la
200
180
160
140
120
100
80
60
40
20
0
ppm


CDCl3
7.928
7.910
7.448
7.444
7.432
7.429
7.398
7.387
7.371
6.944
6.940
6.931
6.927
6.911
6.894
6.788
6.784
6.770
6.766
6.423
6.420
6.406
6.240
6.222
3.785
3.513
2.419
Cl
N
OMe
OMe
N
3Ig
10
9
8
7
6
5
4
3
2
1
0
ppm
1.96
1.97
3.10
3.92
1.13
2.97
1.00
3.03
3.00
3.03


CDCl3
160.25
158.70
150.29
143.22
138.43
137.94
134.01
132.14
131.50
131.48
130.46
130.35
129.58
129.46
129.38
127.67
127.53
120.45
118.88
115.55
114.13
114.09
113.33
104.81
93.12
55.38
55.00
21.11
Cl
N
OMe
OMe
N
3Ig
200
180
160
140
120
100
80
60
40
20
0
ppm


7.906
7.888
7.439
7.437
7.424
7.421
7.394
7.383
7.379
6.988
6.975
6.971
6.907
6.904
6.891
6.887
6.495
6.490
6.477
6.472
6.446
6.440
6.436
6.432
6.427
6.422
6.417
6.245
6.226
3.784
3.751
3.521
2.411
CDCl3
MeO
OMe
OMe
N
N
3mg
9
8
7
6
5
4
3
2
1
0
ppm
1.98
1.01
2.99
1.97
2.94
1.10
2.92
1.06
3.00
3.09
3.00
2.96


CDCl3
160.02
158.61
156.64
149.93
142.52
138.04
138.00
137.78
134.26
132.31
131.79
131.27
130.70
130.44
129.63
129.44
127.57
124.25
115.51
114.02
113.28
110.77
104.69
100.29
93.43
55.40
55.36
54.98
21.11
MeO
OMe
OMe
N
N
3mg
200
180
160
140
120
100
80
60
40
20
0
ppm


7.948
7.933
7.483
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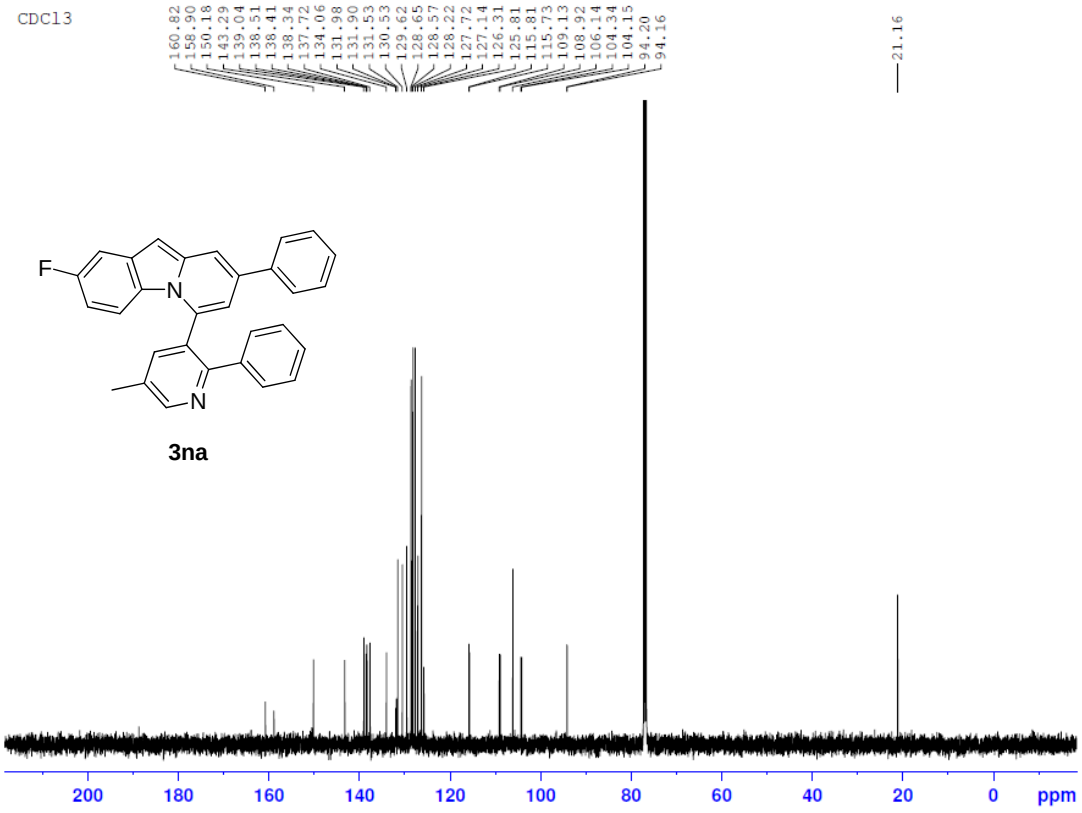
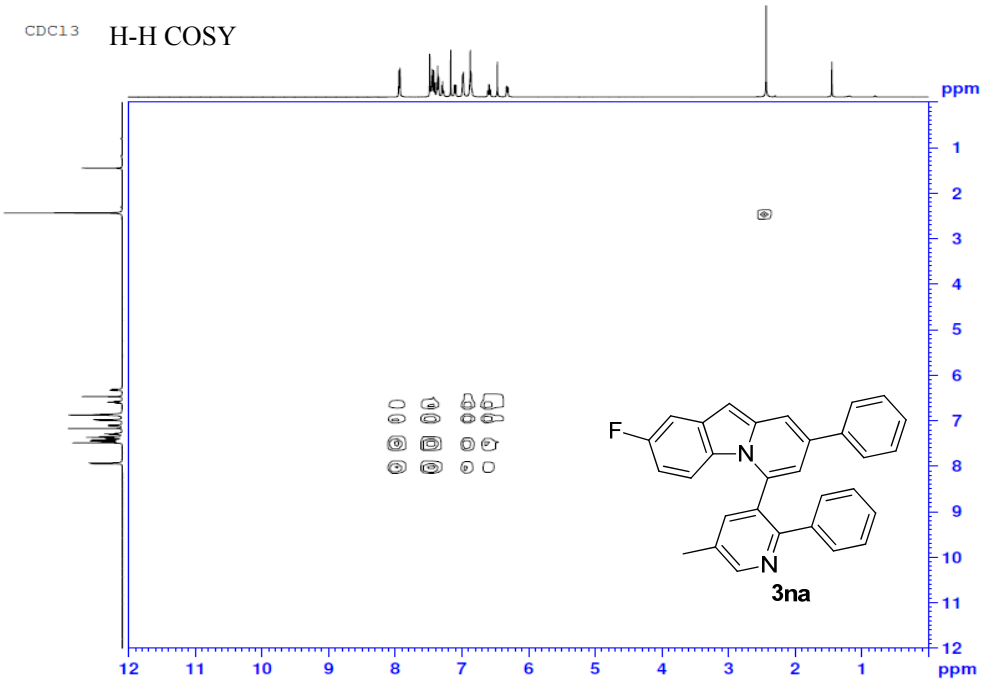
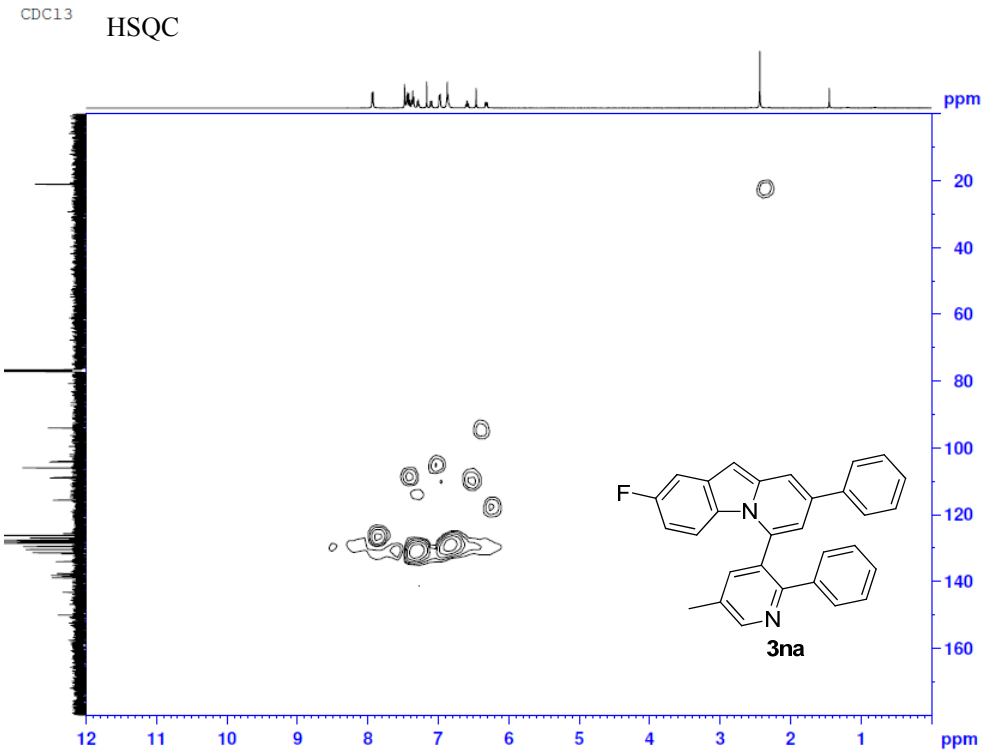
7.447
7.428
7.412
7.383
7.368
7.353
7.306
7.291
7.277
7.169
7.120
7.115
7.101
7.097
6.998
6.986
6.982
6.880
6.867
6.621
6.617
6.603
6.598
6.585
6.580
6.471
6.341
6.332
6.323
6.314
CDCl3
2.439
F
N
N
10
9
8
7
6
5
4
3
2
1
0
ppm
2.01
1.00
3.00
2.02
1.05
0.98
1.99
3.03
0.99
0.96
1.00
2.95

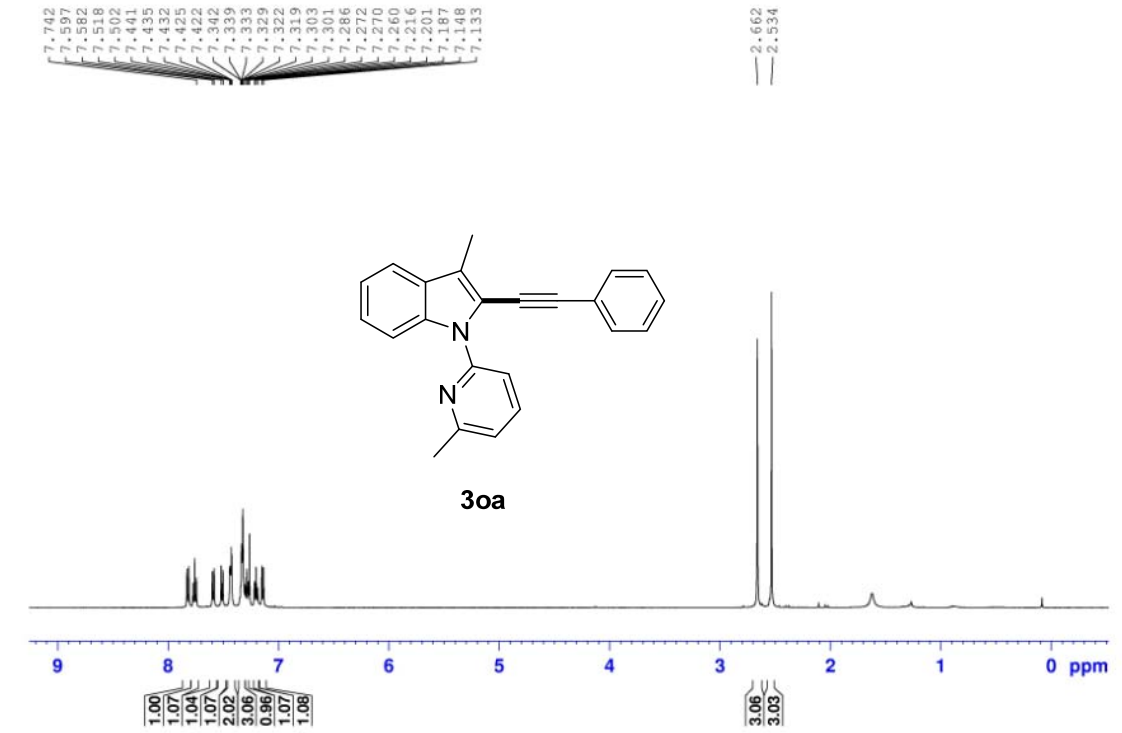
3na

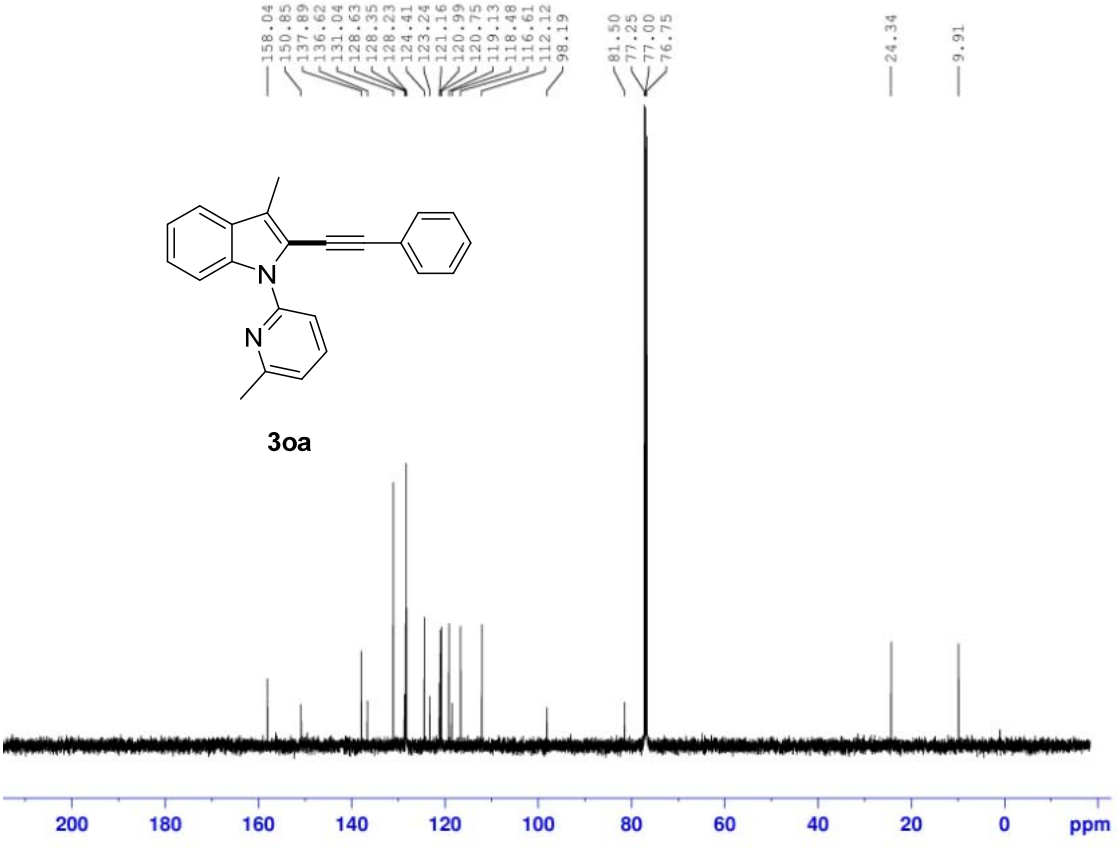

CDCl3
160.82
158.90
150.18
143.29
139.04
138.51
138.41
138.34
137.72
134.06
131.98
131.90
131.53
130.53
129.62
128.65
128.57
128.22
127.72
127.14
126.31
125.81
115.81
115.73
109.13
108.92
106.14
104.34
104.15
94.20
94.16
21.16
F
N
N
200
180
160
140
120
100
80
60
40
20
0
ppm

3na

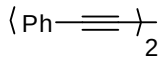

CDCl3
H-H COSY
ppm
1
2
3
4
5
6
7
8
9
10
11
12
12 11 10 9 8 7 6 5 4 3 2 1 ppm
F
N
N
3na


CDCl3
HSQC
ppm
20
40
60
80
100
120
140
160
12 11 10 9 8 7 6 5 4 3 2 1 ppm
F
N
N
3na

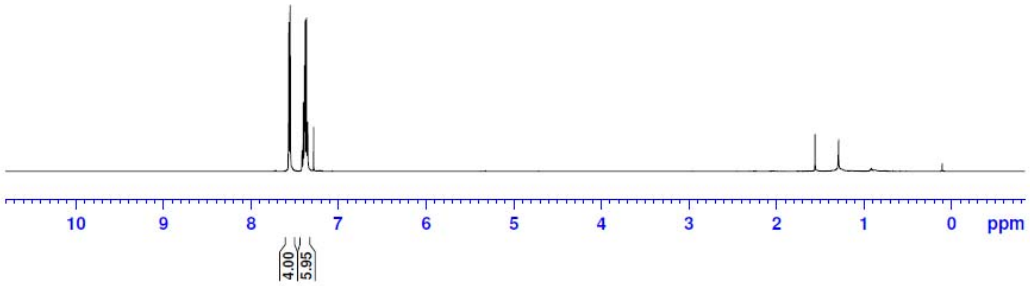

7.742
7.597
7.582
7.518
7.502
7.441
7.435
7.432
7.425
7.422
7.342
7.339
7.333
7.329
7.322
7.319
7.303
7.301
7.286
7.272
7.270
7.260
7.216
7.201
7.187
7.148
7.133
2.662
2.534
N
N
3oa
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.07
1.04
1.07
2.02
3.06
0.96
1.07
1.08
3.06
3.03

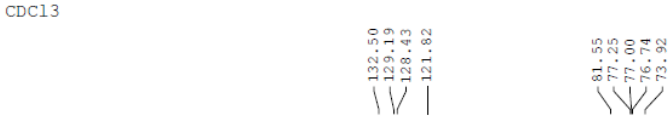

158.04
150.85
137.89
136.62
131.04
128.63
128.35
128.23
124.41
123.24
121.16
120.99
120.75
119.13
118.48
116.61
112.12
98.19
81.50
77.25
77.00
76.75
24.34
9.91
N
N
3oa
200
180
160
140
120
100
80
60
40
20
0
ppm

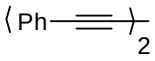

CDCl3
7.571
7.568
7.565
7.559
7.555
7.552
7.418
7.403
7.397
7.392
7.389
7.385
7.380
7.378
7.369
7.366
7.362
7.356
7.353
7.348
7.284


Ph
2

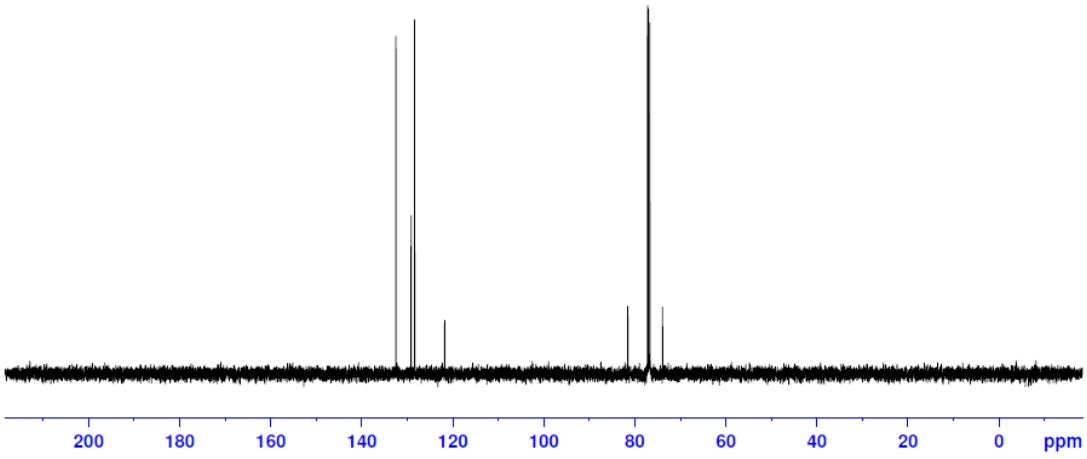
4a

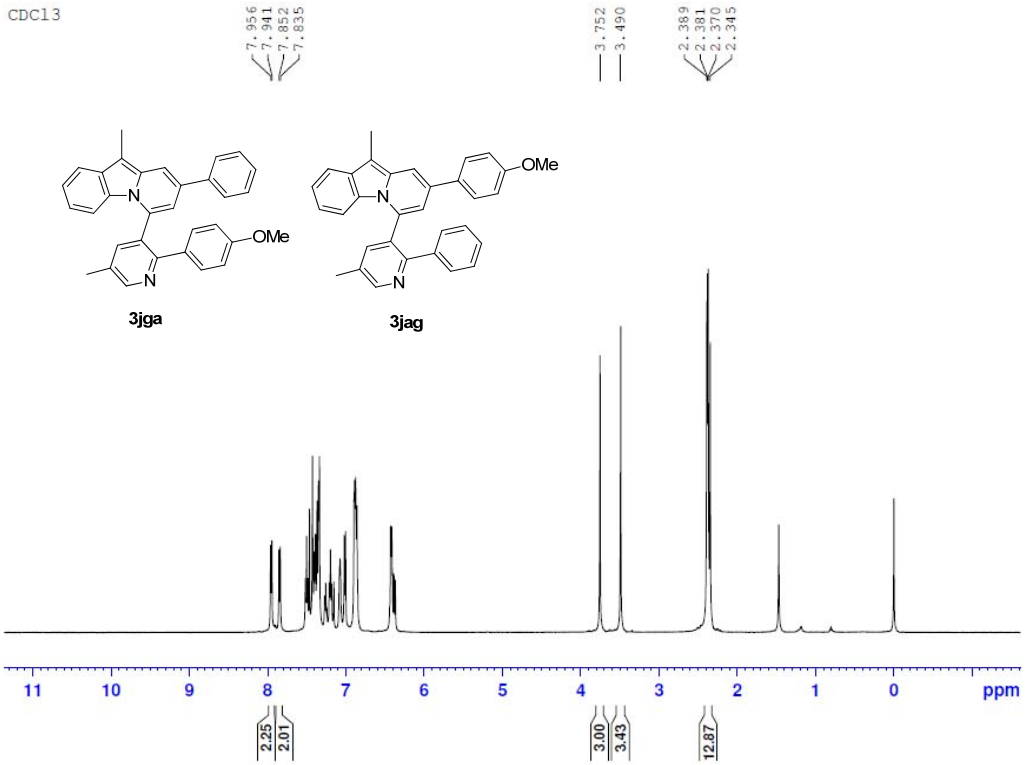

10
9
8
7
6
5
4
3
2
1
0
ppm
4.00
5.95

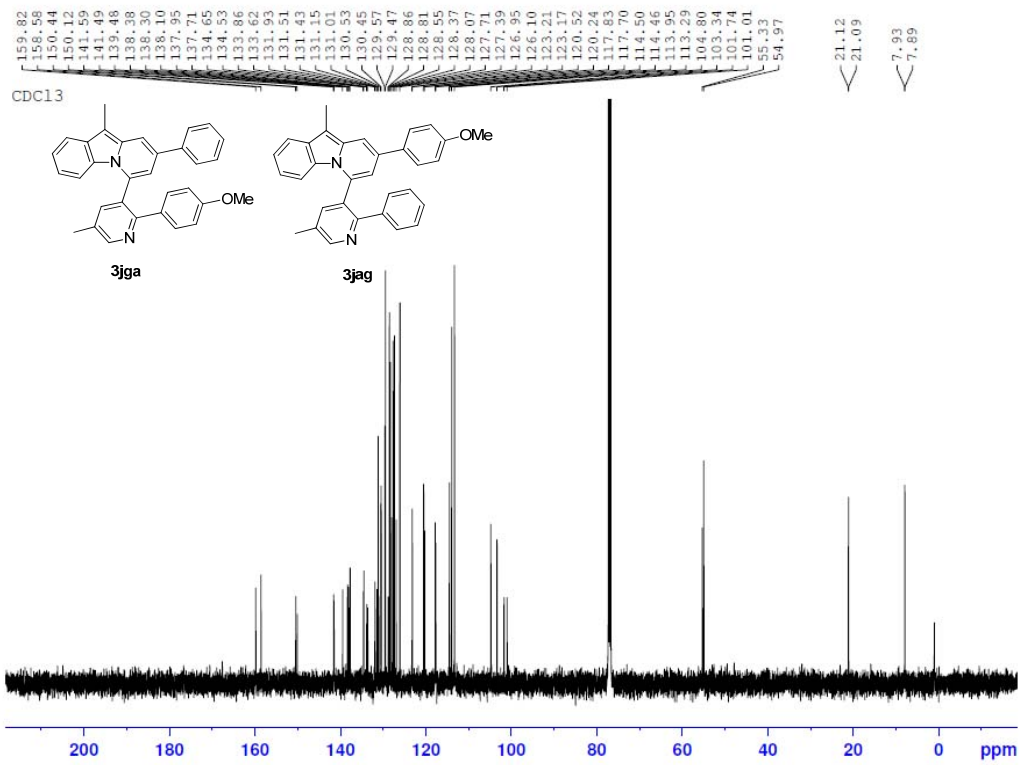

CDCl3
132.50
129.19
128.43
121.82
81.55
77.25
77.00
76.74
73.92

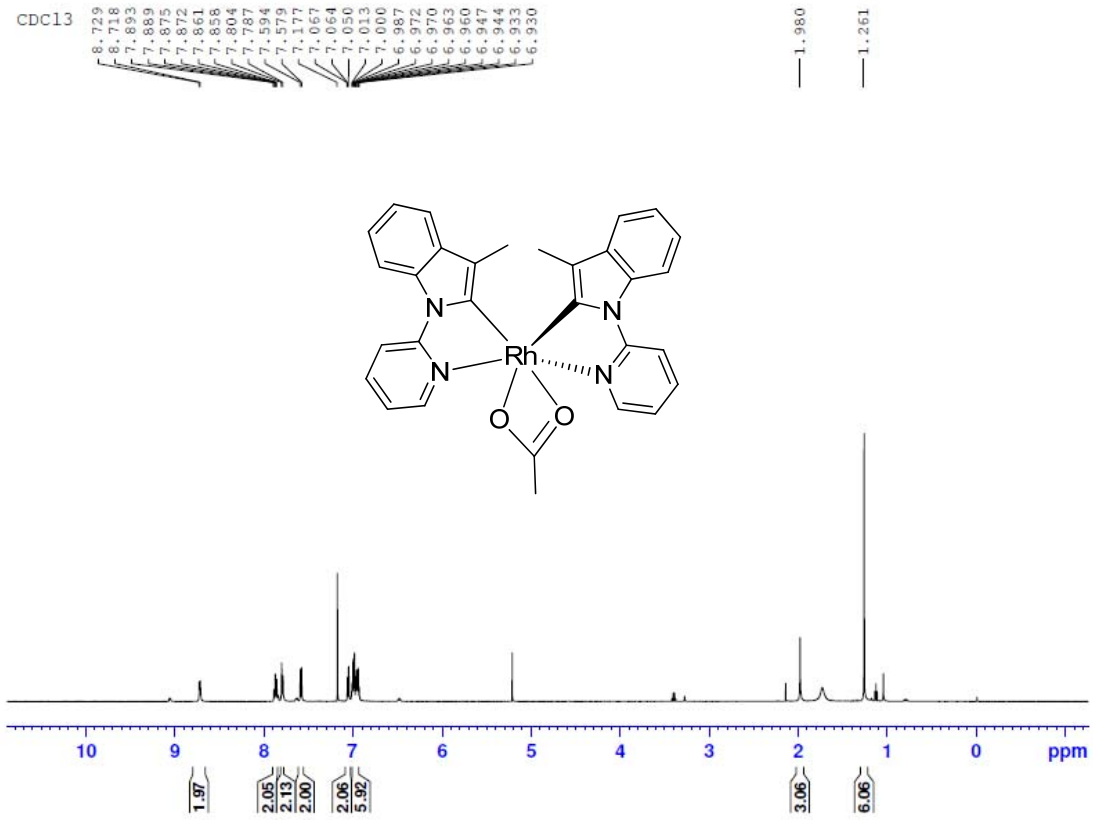

Ph
2

4a


200
180
160
140
120
100
80
60
40
20
0
ppm


CDCl3
7.956
7.941
7.852
7.835
3.752
3.490
2.389
2.381
2.370
2.345
OMe
OMe
3jga
3jag
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.25
2.01
3.00
3.43
12.87


159.82
158.58
150.44
150.12
141.59
141.49
139.48
138.38
138.30
138.10
137.95
137.71
134.65
134.53
133.86
133.62
131.93
131.51
131.43
131.15
131.01
130.53
130.45
129.57
129.47
128.86
128.81
128.55
128.37
128.07
127.71
127.39
126.95
126.10
123.21
123.17
120.52
120.24
117.83
117.70
114.50
114.46
113.95
113.29
104.80
103.34
101.74
101.01
55.33
54.97
21.12
21.09
7.93
7.89
CDCl3
OMe
OMe
3jga
3jag
200
180
160
140
120
100
80
60
40
20
0
ppm


CDCl3
8.729
8.718
7.893
7.889
7.875
7.872
7.861
7.858
7.804
7.787
7.594
7.579
7.177
7.067
7.064
7.050
7.013
7.000
6.987
6.972
6.970
6.963
6.960
6.947
6.944
6.933
6.930
1.980
1.261
N
N
Rh
N
N
O
O
10
9
8
7
6
5
4
3
2
1
0
ppm
1.97
2.05
2.13
2.00
2.06
5.92
3.06
6.06