Supplementary information.

Visible-Light-Induced, Copper(I)-Catalysed C-N Coupling Between o-Phenylenediamine and Terminal Alkynes: One-Pot Synthesis of 3-Phenyl-2-Hydroxy-Quinoxalines

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Experimental section

General: All reactions were conducted under an oxygen atmosphere and oven-dried glasswares were used. All reactions were conducted using a blue-LED arrau as the light source (30 lamps, power density: 40 mW/cm^2 at 460 nm). All solvents were dried according to known methods and distilled prior to use. Starting materials were commercially available (Sigma-Aldrich) and used as received. NMR spectra were recorded ^{1}H NMR at 400 MHz/ ^{13}C NMR at 100 MHz using deuterated $CDCl_3$, $CDCl_3$-DMSO mixture or DMSO.

General procedure:

A dry test tube (20 mL) with a rubber septum and a magnetic stirrer bar was charged with K_2CO_3 (0.52 mmol, 1.05 eqv.) and 5 mol% Cu(I)Cl was added and then followed the addition of dry CH_3CN and CH_3OH (1:1 v/v) via syringe, along with terminal acetylene (0.083 M) and 1, 2-o-phenylenediamine (0.1 M). The yellowish orange transparent suspension was irradiated with blue light from the output of a blue

LED array at room temperature in presence of oxygen atmosphere for 2-5 h until completion of coupling reaction (it was determined by thin layer chromatography). The reaction mixture was diluted using 40 % ethyl acetate in hexane and stirred for 10 min. The mixture was filtered through celite and silica gel pads, and washed with ethyl acetate. The filtrate was concentrated and the residue was purified by flash column chromatography on silica gel to afford desired quinoxaline product.

Preparation of copper phenylacetylide:[1]

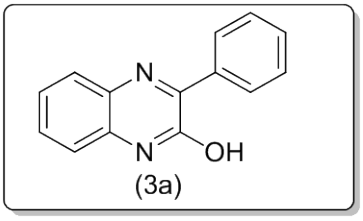
CuI (1.0 g, 5.0 mmol) was dissolved in ammonium hydroxide to form a blue solution. While stirring, this solution was added dropwise to the solution of phenylacetylene (0.5 g, 5.1 mmol) in 50 mL of ethanol. The system was allowed to stand for 15 min to form a yellow precipitate. The precipitate was filtered out and washed with water, ethanol, and diethyl ether, three times each. The solid was vacuum-dried, and 0.65 g (yield 75%) of a bright yellow solid was obtained.

IR (KBr, cm^{-1})[2]: 1931(C-C trible bond), 1596, 1568

UV-Vis λ_{abs} = 475 nm

Spectroscopic Data:

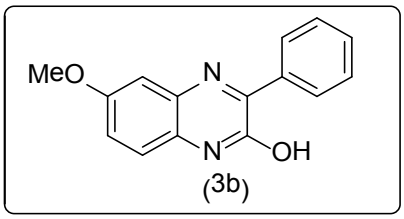
3-phenylquinoxalin-2-ol (3a)



(3a)

Yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$): **δ** 8.14-8.07 (m, 2H), 7.78-7.75 (m, 1 H), 7.56-7.46 (m, 3H), 7.36-7.31 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.2, 135.1, 132.1, 131.1, 129.5, 128.9, 128.6, 128.3, 127.3, 123.0, 114.5; **HRMS** calcd for $C_{14}H_{10}N_2O$: 222.079, found: 222.078.

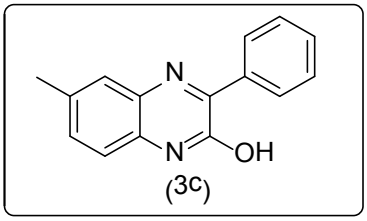
6-methoxy-3-phenylquinoxalin-2-ol (3b)



(3b)

Pale orange solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.27-8.26 (d, 2H), 7.80-7.78 (d, 1H 7.48-7.44 (m, 3H), 6.93-6.90(dd, 1H), 6.70-6.70(s, 1H), 3.84 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ160.5, 155.1, 150.6, 135.5, 133.1, 129.6, 128.9, 128.4, 127.3, 111.9, 96.9, 55.0: **HRMS** calcd for $C_{15}H_{12}N_2O_2$: 252.090, found: 252.089.

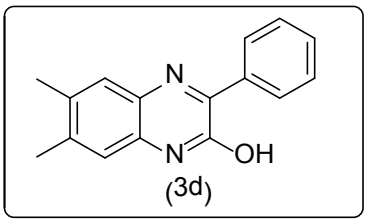
6-methyl-3-phenylquinoxalin-2-ol (3c)



(3c)

Pale yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 12.53 (s,1H), 8.42 -8.38 (m, 2 H), 7.81-7.71 (m, 1H), 7.52-7.51 (m, 3H), 7.30-7.14 (m, 2H), 2.35 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.6, 141.3, 135.7, 134.1, 133.2, 131.7, 131.5, 131.1, 130.3, 130.1, 129.4, 129.3, 129.0, 128.9, 128.1, 125.9, 115.2, 21.7; **HRMS** calcd for $C_{12}H_{10}N_2O$: 236.095, found: 236.095.

6,7-dimethyl-3-phenylquinoxalin-2-ol (3d)

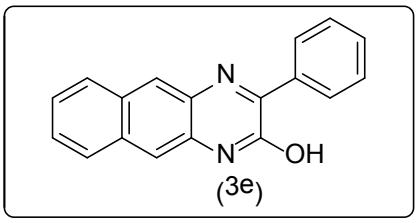


(3d)

Yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.23-8.21 (m, 2H), 7.61 (s, 1H), 7.44-7.42 (m, 3H), 7.00 (s, 1H), 2.30 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.6, 153.4,

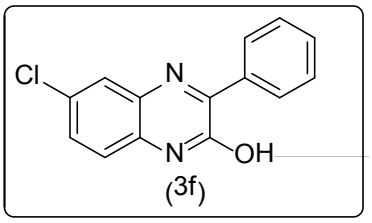
140.6, 135.7, 133.2, 131.6, 130.0, 129.3, 129.1, 128.9, 127.9, 115.2, 20.0, 19.2; HRMS calcd for $C_{16}H_{14}N_2O$: 250.111, found: 250.110.

3-phenylbenzo[g]quinoxalin-2-ol (3e)



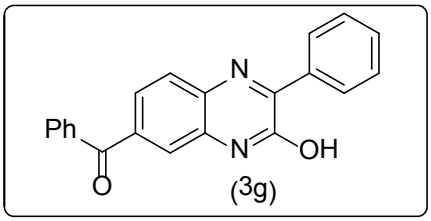
Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85-8.33 (d, 2H), 7.33-7.24 (m, 5H) 7.14-7.13 (t, 2H), 6.84 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ159.0 140.5, 139.2, 134.6, 134.3, 128.8, 125.0, 124.8, 123.9, 122.6, 106.3; HRMS calcd for $C_{18}H_{12}N_2O$: 272.095, found: 272.093.

6-chloro-3-phenylquinoxalin-2-ol (3f)



Yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 12.8 (s, 1 H), 8.22-8.21 (m, 2H), 7.68-7.66 (d, 1H), 7.57 (s, 1H), 7.37-7.36 (m, 4H), 7,14-7.12 (d, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.9, 135.0, 134.8, 132.4, 130.6, 129.7, 129.6, 128.7, 128.1, 127.9, 127.7, 127.4, 126.1, 123.2, 114.3; **HRMS** calcd for $C_{14}H_9ClN_2O$: 256.040, found: 256.060.

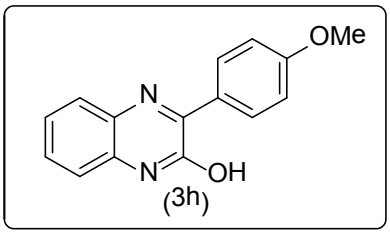
(3-hydroxy-2-phenylquinoxalin-6-yl)(phenyl)methanone (3g)



Pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.32 (s, 1H), 8.26 (s, 1H), 8.21 (s, 1H), 8.09-8.07 (t, 2H), 7.87-7.85 (d, 2H), 7.61-7.58 (m, 3H), 7.51-7.47 (m, 2H); **^{13}C**

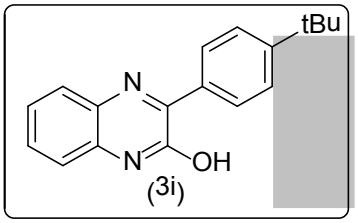
NMR (100 MHz, $CDCl_3$): δ 194.8, 160.51, 142.0, 139.1, 138.6, 136.6, 136.4, 133.6, 133.2, 131.7, 131.6, 131.2, 130.4, 130.0,7, 130.02, 129.8, 129.7, 129.6, 129.0,6, 129.0, 128.1, 127.7, 123.1, 120.4; **HRMS** calcd for $C_{21}H_{14}N_2O_2$: 326.1068, found: 326.102.

4-3-(4-methoxyphenyl)quinoxalin-2-ol (3h)



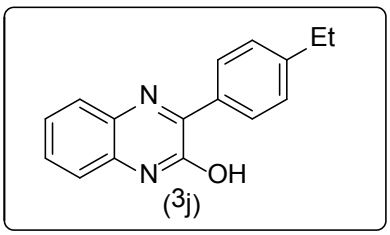
Pale orange solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 12.0 (b, 1 H), 8.23-8.20 (d, 2H), 7.88-7.86 (dd, 1H) 7.45-7.42 (t, 1H), 7.33-7.31(t, 1H), 7.24-7.22(m, 2H), 7.00-6.97 (dd, 2H), 3.87 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.1, 153.4, 132.3, 130.6, 128.9, 128.7, 128.1, 122.9, 114.7, 112.9, 54.8; **HRMS** calcd for $C_{15}H_{12}N_2O_2$: 252.090, found: 252.089.

3-(4-(tert-butyl)phenyl)quinoxalin-2-ol (3i)



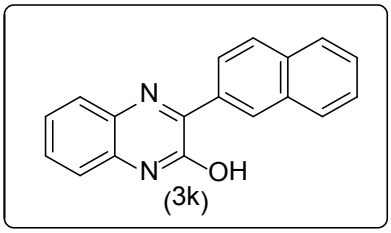
Pale Yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.39-8.36 (m, 2 H), 7.95- 7.92 (m, 1H), 7.57-7.26 (m, 5H), 1.39 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.7, 153.8, 133.3, 132.8, 131.1, 130.1, 129.3, 129.2, 125.2, 124.2, 11.5.4, 34.8, 31.2; **HRMS** calcd for $C_{18}H_{18}N_2O$: 278.142, found: 278.142.

3-(4-ethylphenyl)quinoxalin-2-ol (3j)



Pale Yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.36-8.34 (m, 2H), 7.92-7.91(d, 1H), 7.46-7.33 (m, 5H), 2.74 (q, 2H) , 1.29 (t, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.7, 147.0, 133.3, 133.1, 131.0, 130.0, 129.5, 129.2, 127.7, 124.2, 115.4, 28.8, 15.3; **HRMS** calcd for $C_{16}H_{14}N_2O$: 250.111, found: 250.110.

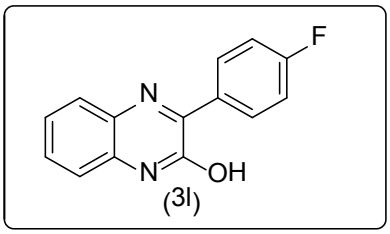
3-(naphthalen-2-yl)quinoxalin-2-ol (3k)



(3k)

Yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 12.20 (b, 1H), 8.94 (s, 1H), 8.28-8.25 (d, 1H), 7.80-7.68 (m, 5H), 7.35-7.14 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.9, 153.4, 133.3, 132.6, 132.1, 131.3, 129.5, 129.4, 128.5, 128.3, 126.8, 125.4, 125.3, 122.8, 114.7; **HRMS** calcd for $C_{18}H_{12}N_2O$: 272.095, found: 272.094.

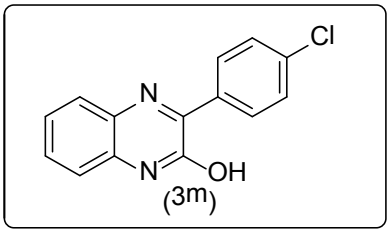
3-(4-fluorophenyl)quinoxalin-2-ol (3l)



(3l)

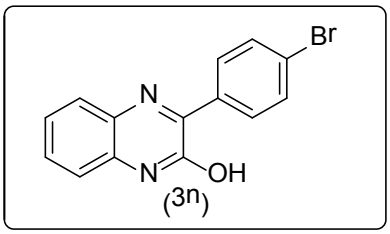
Pale white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 12.0 (b, 1 H), 8.19-8.15 (m, 2H), 7.59-7.58 (d, 1H), 7.22-7.18 (t, 1H), 7.10- 7.02 (m, 2H), 6.91-6.87 (t, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.3, 161.8, 154.6, 152.5, 131.8, 131.3, 130.9, 130.8, 129.3, 128.1, 122.7, 114.6, 114.2, 114.0; **HRMS** calcd for C_{14} H_9FN_2O : 240.070, found: 240.069.

3-(4-chlorophenyl)quinoxalin-2-ol (3m)



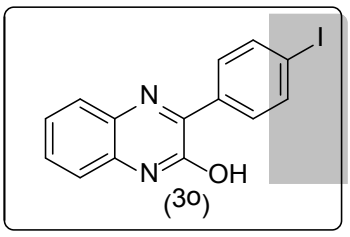
White solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ12. 5 (b, 1 H), 8.29-8.27 (d, 2H), 7.74-7.72 (d, 1H), 7.47-7.17 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.7, 152.6, 135.4, 133.8, 132.0, 131.6, 130.3, 129.7, 128.5, 127.5, 123.0, 114.9; HRMS calcd for $C_{14}H_9ClN_2O$: 256.040, found: 256.041.

3-(4-bromophenyl) quinoxalin-2-ol (3n)



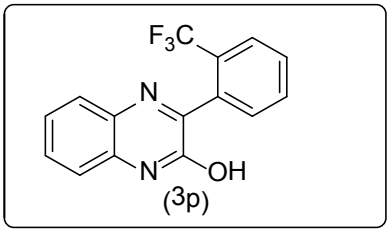
White solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.27-8.25 (d, 2 H), 7.74-7.72 (d, 1H), 7.54-7.52 (d, 2H), 7.41-7.39 (t, 1H), 7.29- 7.26 (d, 1H), 7.24-7.22 (t, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.5, 152.5, 134.4, 131.9, 131.8,130.8, 130.5, 129.9, 128.5, 124.0, 123.1, 115.0; **HRMS** calcd for $C_{14}H_9BrN_2O$: 299.990, found: 299.992.

3-(4-iodophenyl)quinoxalin-2-ol (3p)



Yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.07- 8.04 (d, 2H), 7.82-7.77 (m, 3H), 7.50-7.48 (t, 1H), 7.31-7.27 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.8, 153.4, 137.1, 135.3, 132.2, 131.3, 130.9, 129.0, 123.9, 115.4, 97.8; **HRMS** calcd for $C_{14}H_9IN_2O$: 347.976, found: 347.973.

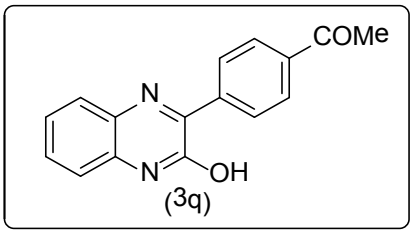
3-(2-(trifluoromethyl)phenyl)quinoxalin-2-ol (3p)



(3p)

Yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 12.0 (b, 1 H), 7.43-7.38 (m, 2H), 7.30-7.11 (m, 4H), 7.03-6.90 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.1, 154.7, 134.5, 132.1, 131.7, 131.4, 130.4, 130.1, 128.9, 128.7, 128.5, 128.2, 126.2, 126.1, 123.3, 115.5; **HRMS** calcd for $C_{15}H_9F_3N_2O$: 290.067, found: 290.065.

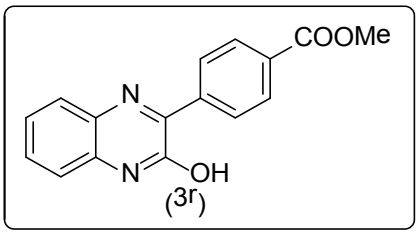
1-(4-(3-hydroxyquinoxalin-2-yl) phenyl)ethanone (3q)



(3q)

Pale yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.43-8.41 (d, 2H), 7.96-7.94 (d, 2H), 7.78-7.76 (d, 1H), 7.45-7.22 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.9, 154.5, 152.7, 139.5, 137.2, 131.9, 130.2, 129.0, 128.7, 127.2, 123.0, 114.9, 26.4; **HRMS** calcd for $C_{16}H_{12}N_2O_2$: 264.090, found: 264.089.

Methyl 4-(3-hydroxyquinoxalin-2-yl) benzoate (3r)

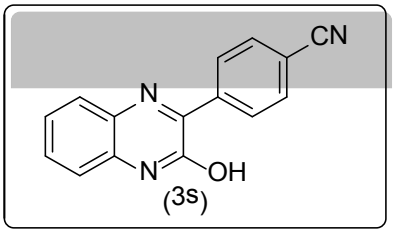


(3r)

Yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.44-8.42 (d, 2 H), 8.02-8.00 (d, 2H), 7.80-7.78 (d, 1H), 7.49-7.46(t, 1H), 7.33-7.25(m, 2H), 3.86 (s, 3H); **^{13}C NMR** (100

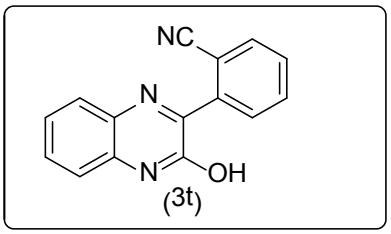
MHz, $CDCl_3$): δ 165.7, 154.4, 152.7, 139.6, 132.0, 131.9, 130.4, 130.3, 129.0, 128.7, 128.3, 123.1, 115.0, 51.8; **HRMS** calcd for $C_{16}H_{12}N_2O3$: 280.085, found: 280.084.

4-(3-hydroxyquinoxalin-2-yl)benzonitrile (3s)



Pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.49-8.47 (d, 2 H), 7.78-7.58 (m, 4H), 7.44-7.21 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.5, 151.8, 139.5, 132.7, 132.0, 131.8, 131.5, 130.5, 129.5, 128.8, 123.2, 118.2, 115.1, 112.4; **HRMS** calcd for $C_{15}H_9N_3O$: 247.075, found: 247.074

2-(3-hydroxyquinoxalin-2-yl)benzonitrile (3t)



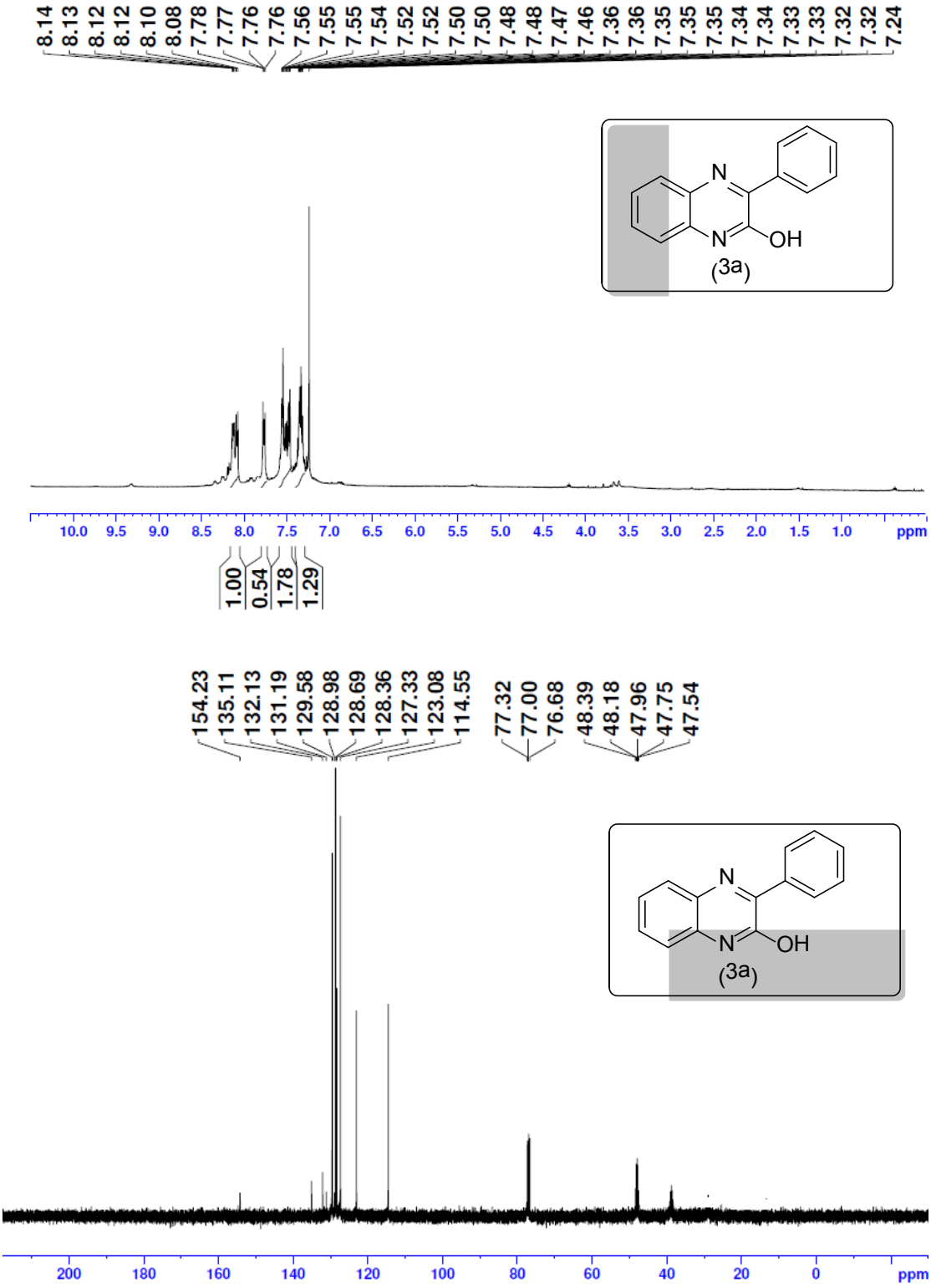
Pale yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95- 7.94 (d, 1H), 7.77-7.76 (d, 1H), 7.69-7.67(d, 1H), 7.58-7.54(t, 1H), 7.44-7.36 (m, 3H), 7.25-7.17 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.4, 153.3, 138.5, 133.5, 132.1, 131.7, 130.8, 130.3, 129.3, 129.0, 123.5, 117.7, 115.4, 112.0; HRMS calcd for $C_{14}H_9N_3O$: 247.075, found: 247.074.

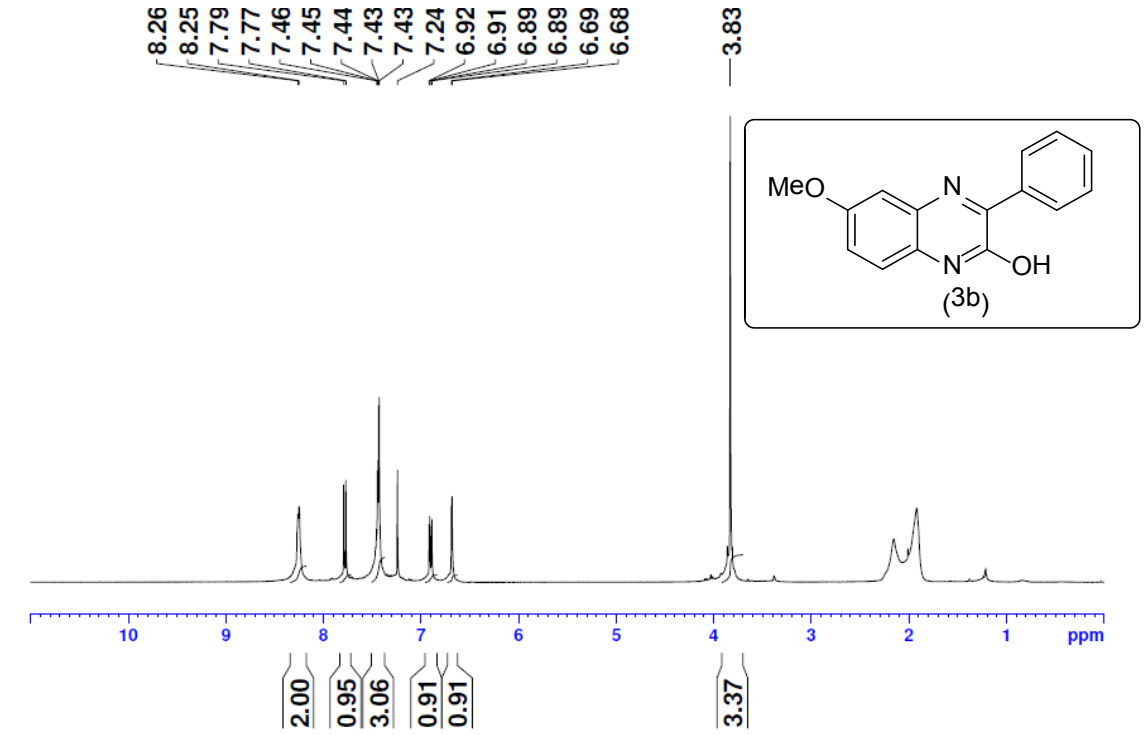
Supplementary references:

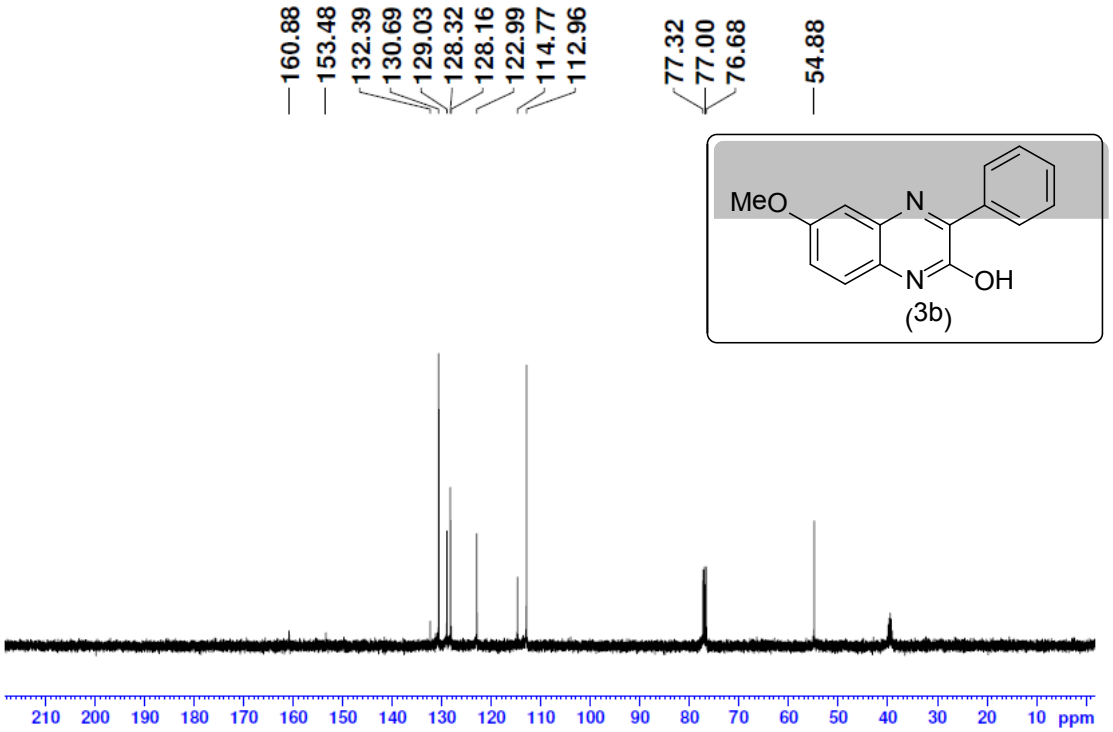
S1. W. Shi, Y. Luo, X. Luo, L. Chao, H. Zhang, J. Wang, A. Lei, *J. Am. Chem. Soc.*, **2008**, *130*, 14713-14720.

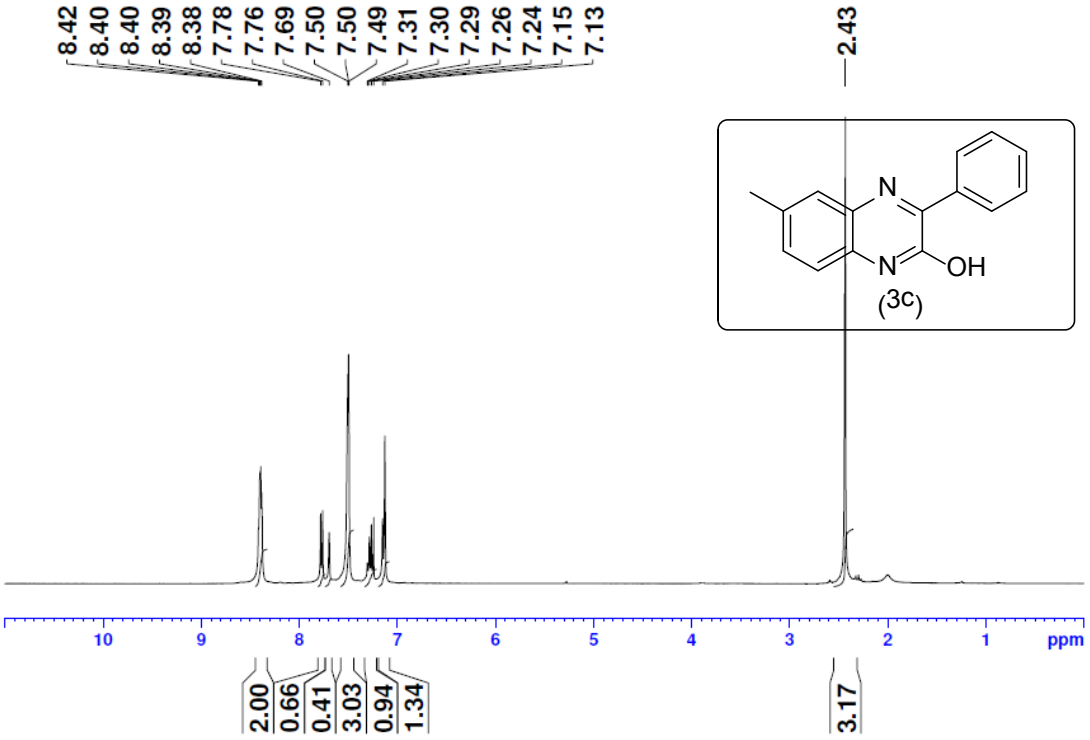
S2. Y. Okamoto and S. K. Kundu, *J. Phys. Chem.*, 1973, **77**, 2677-2680.

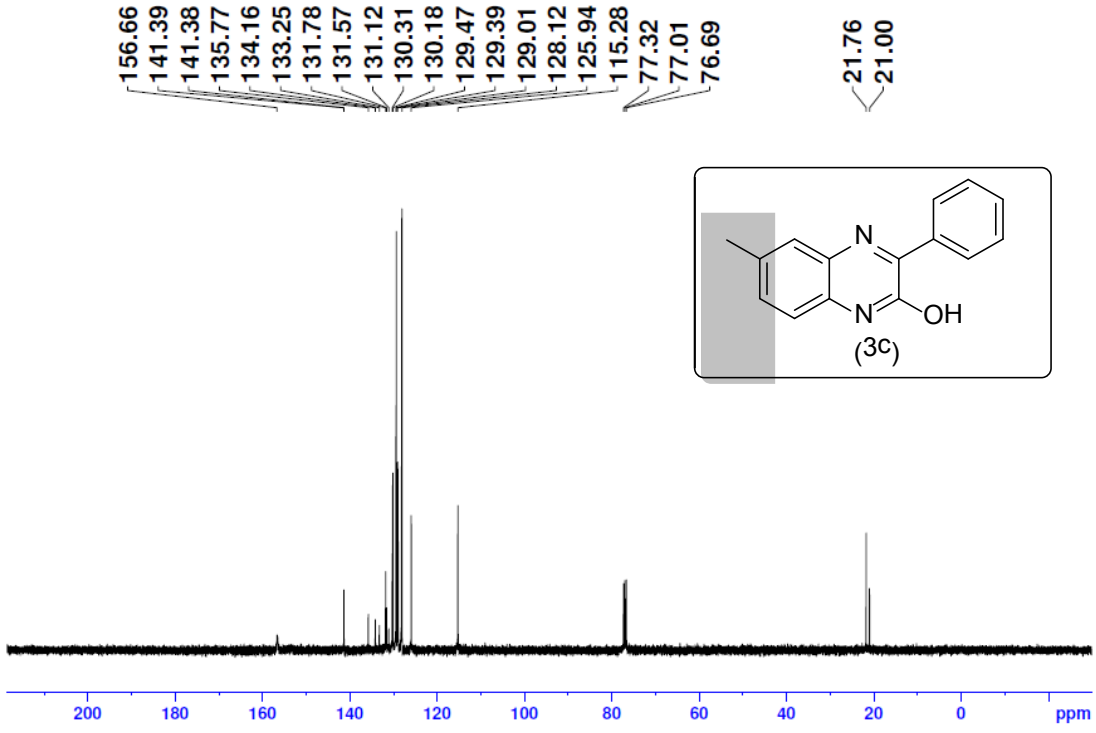
Figure S1. ^{1}H NMR and ^{13}C NMR spectra

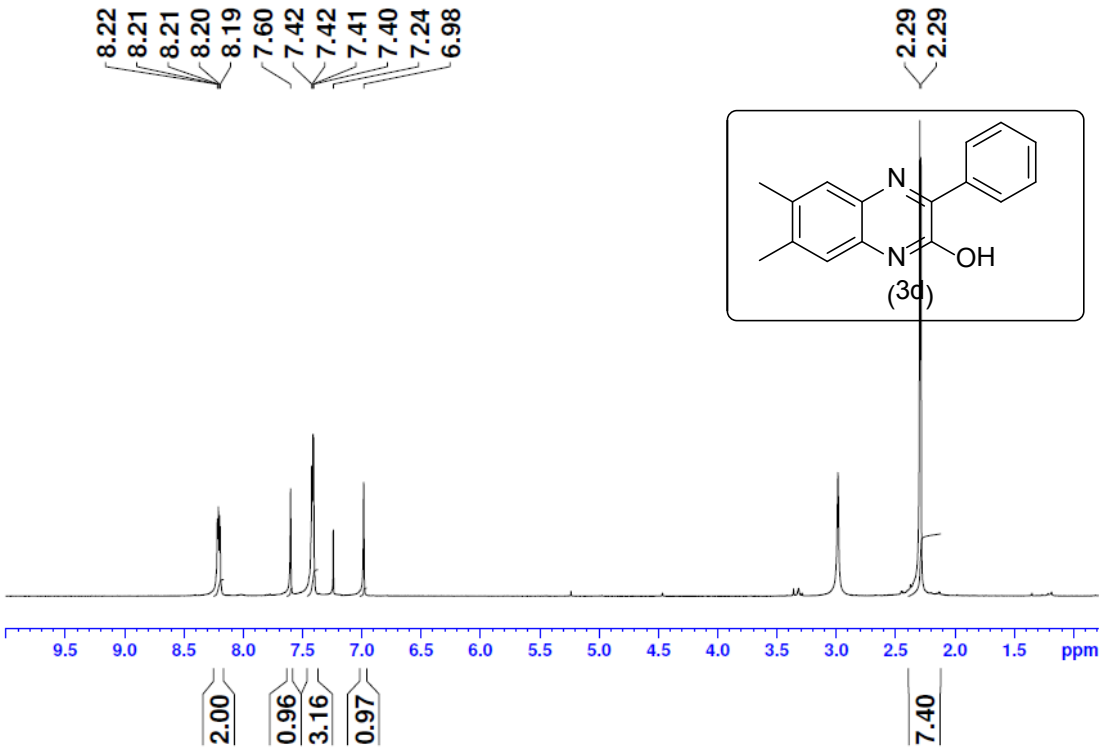


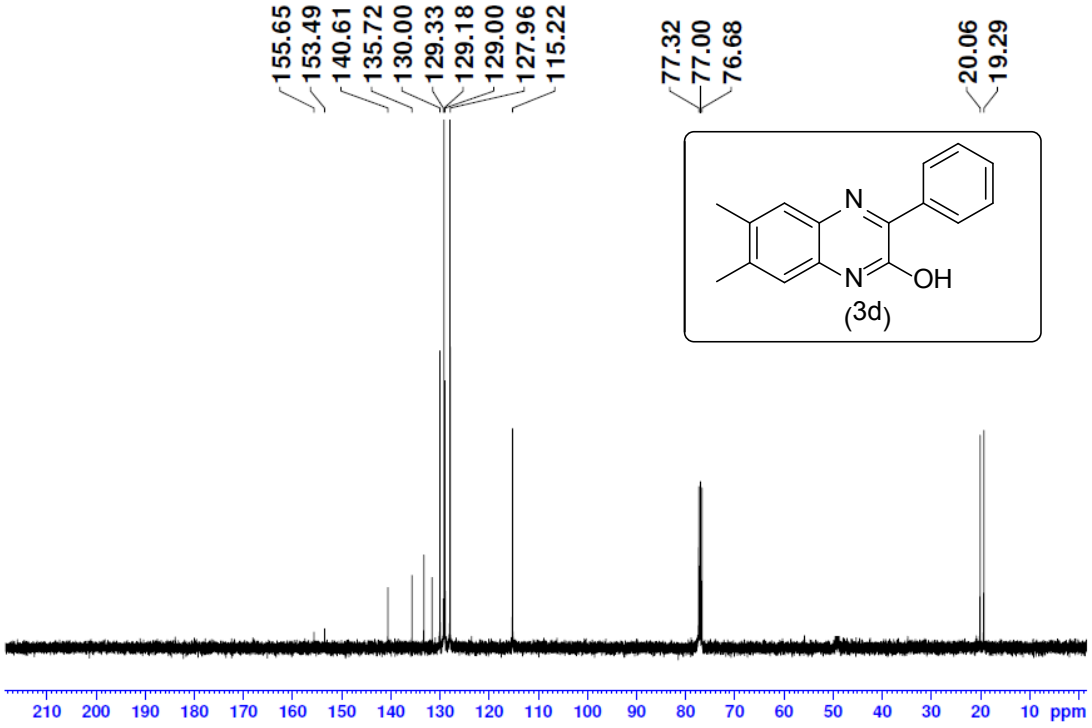


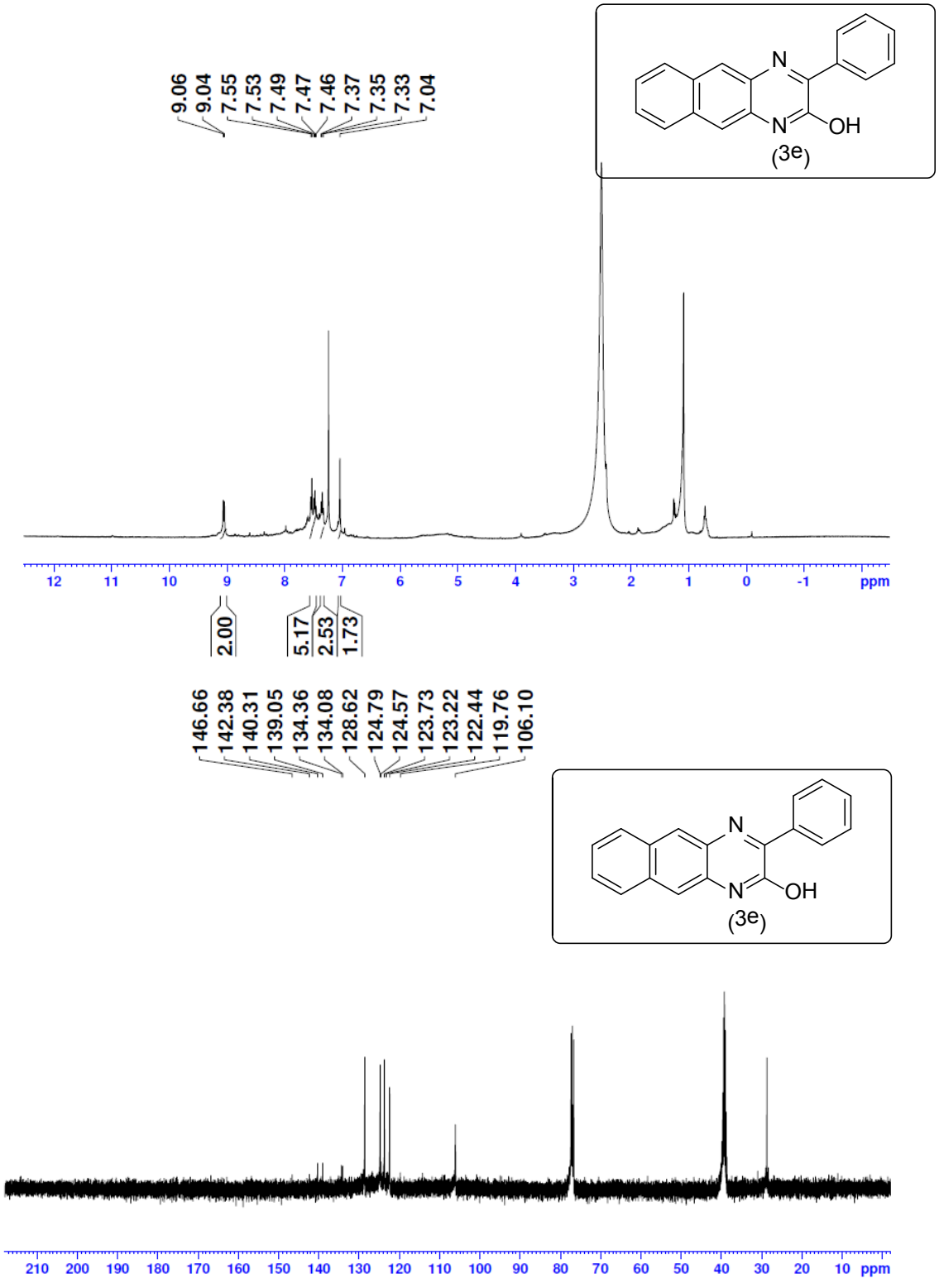


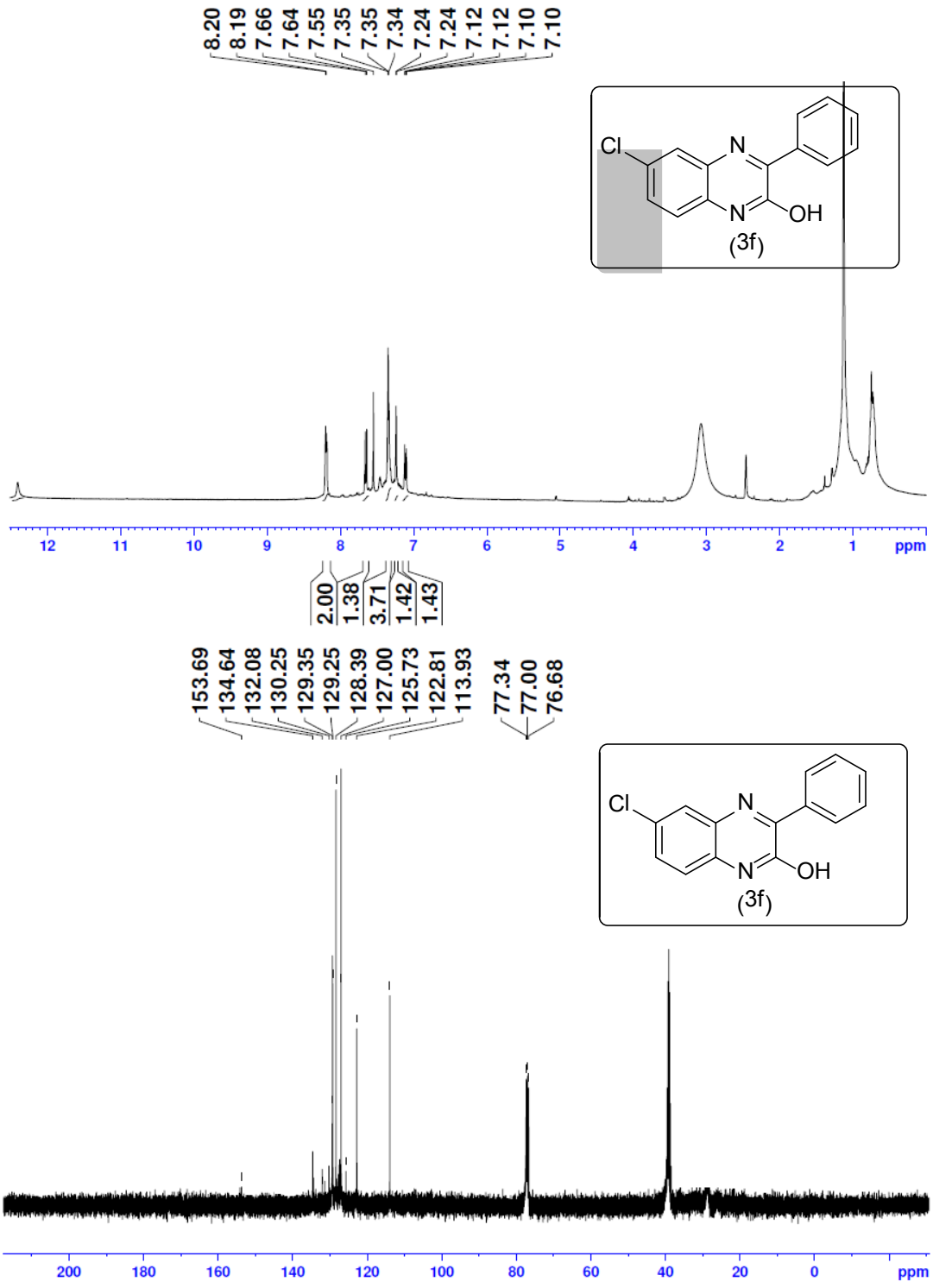


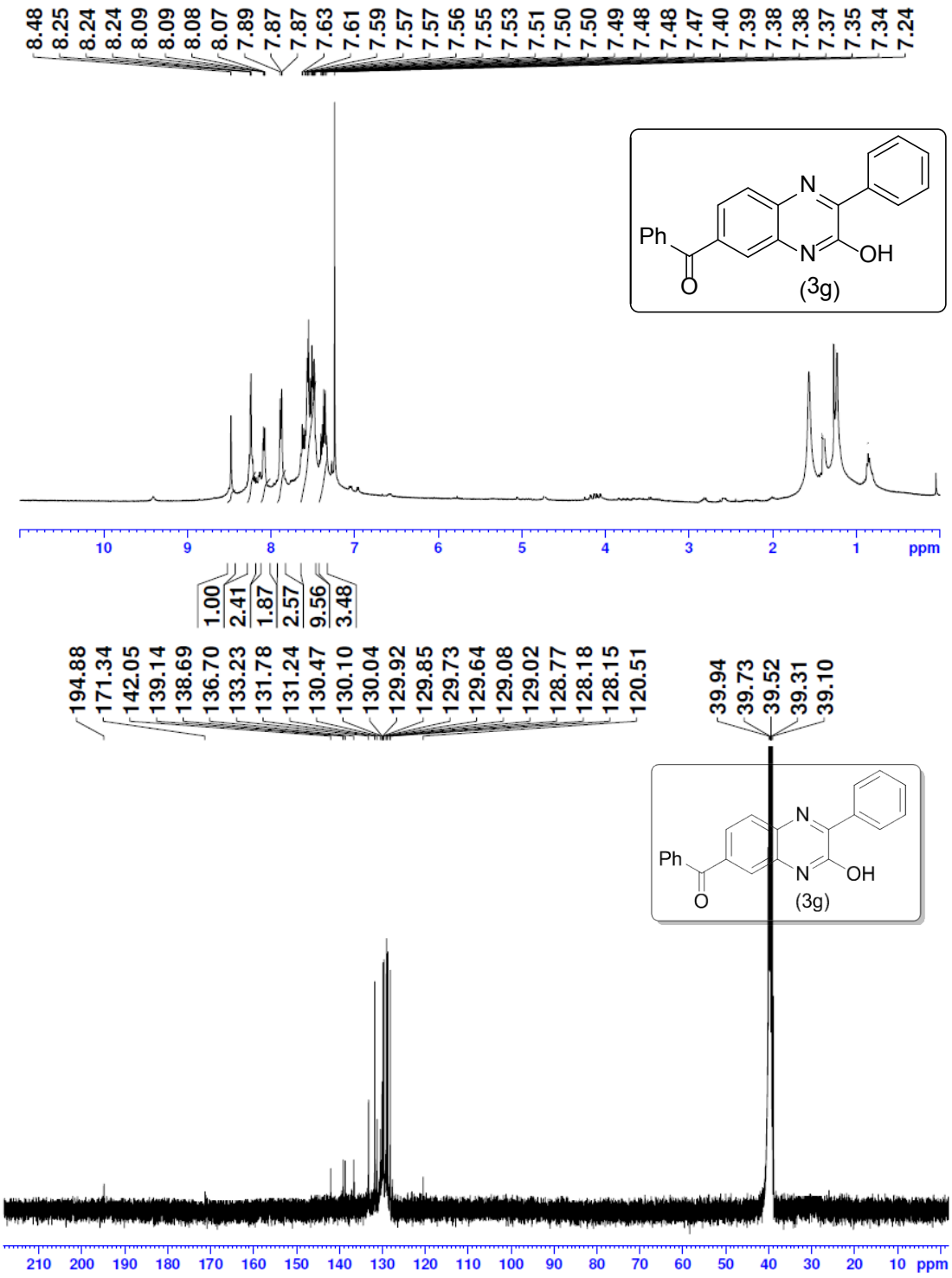


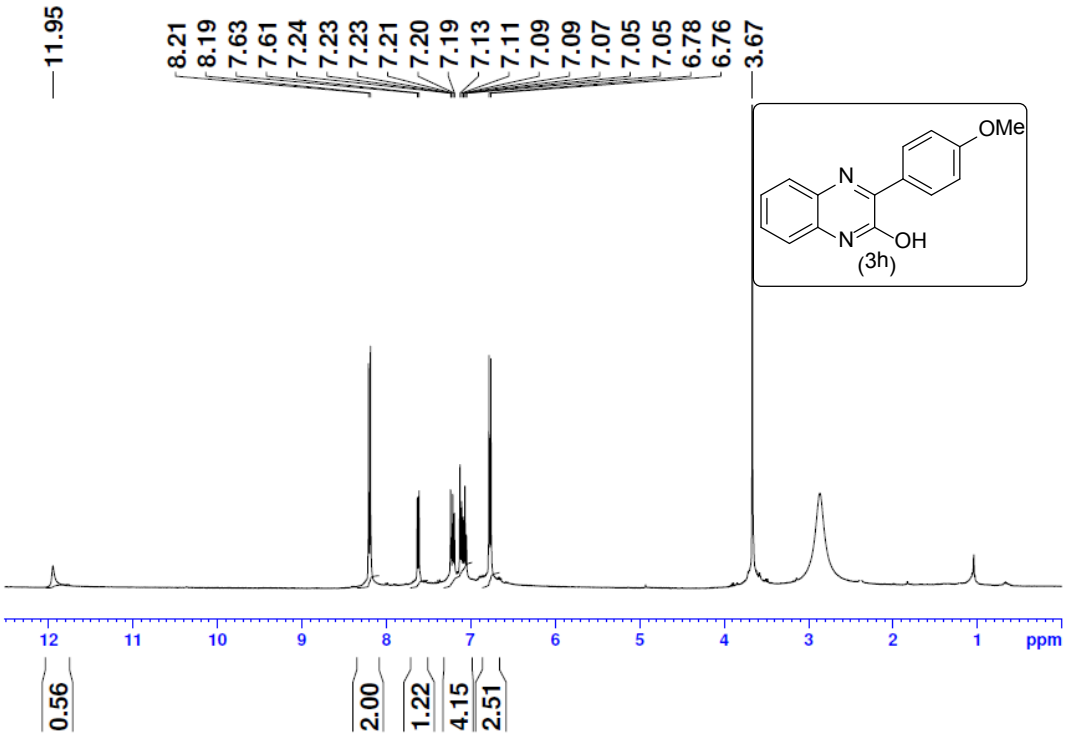


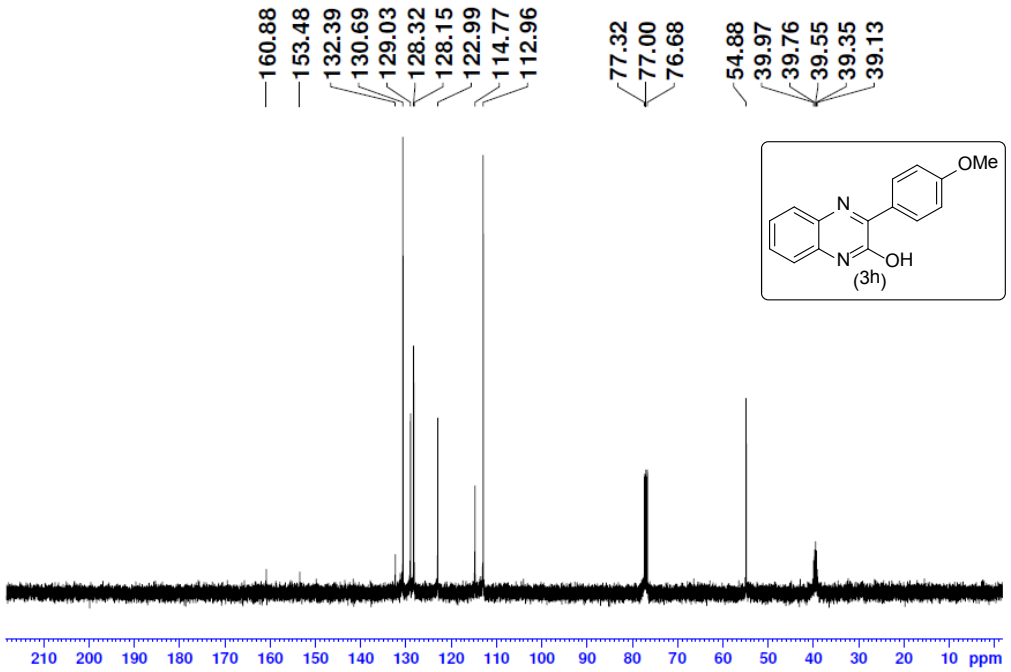


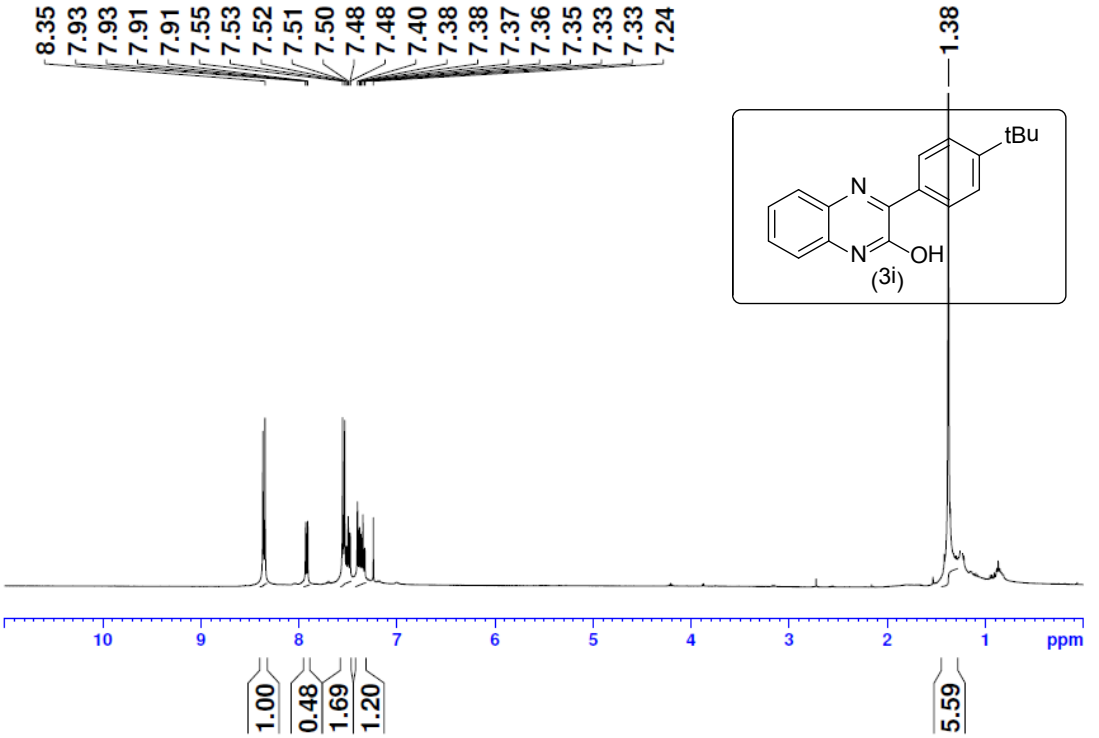


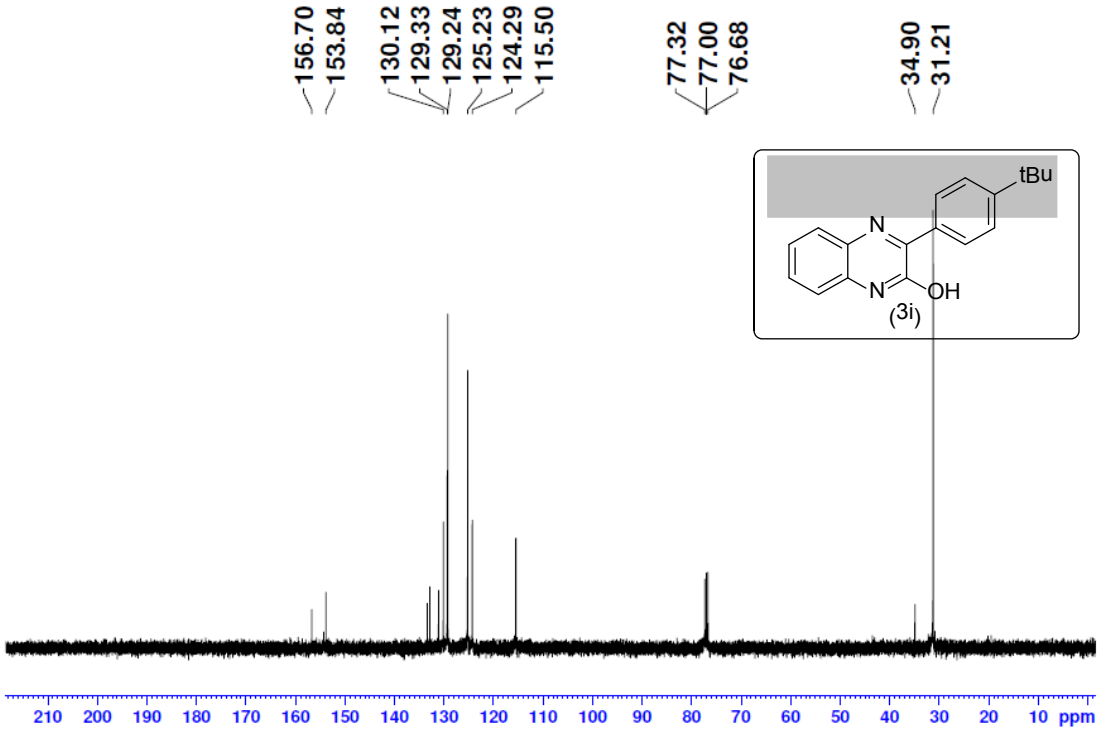


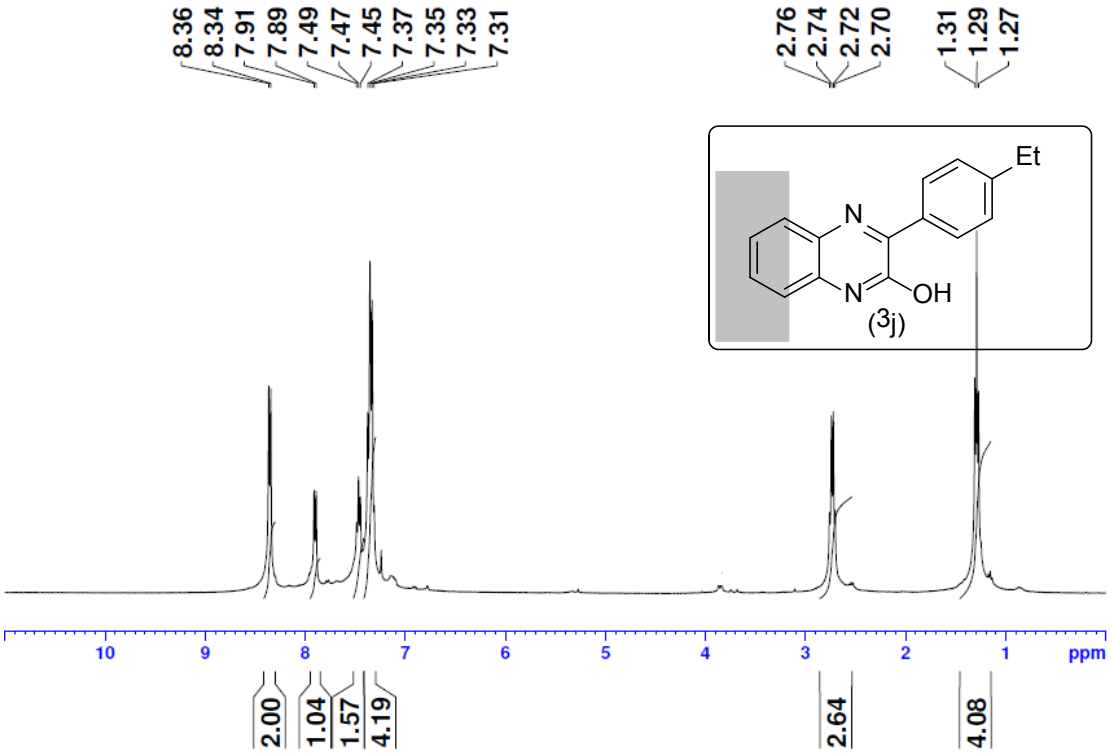


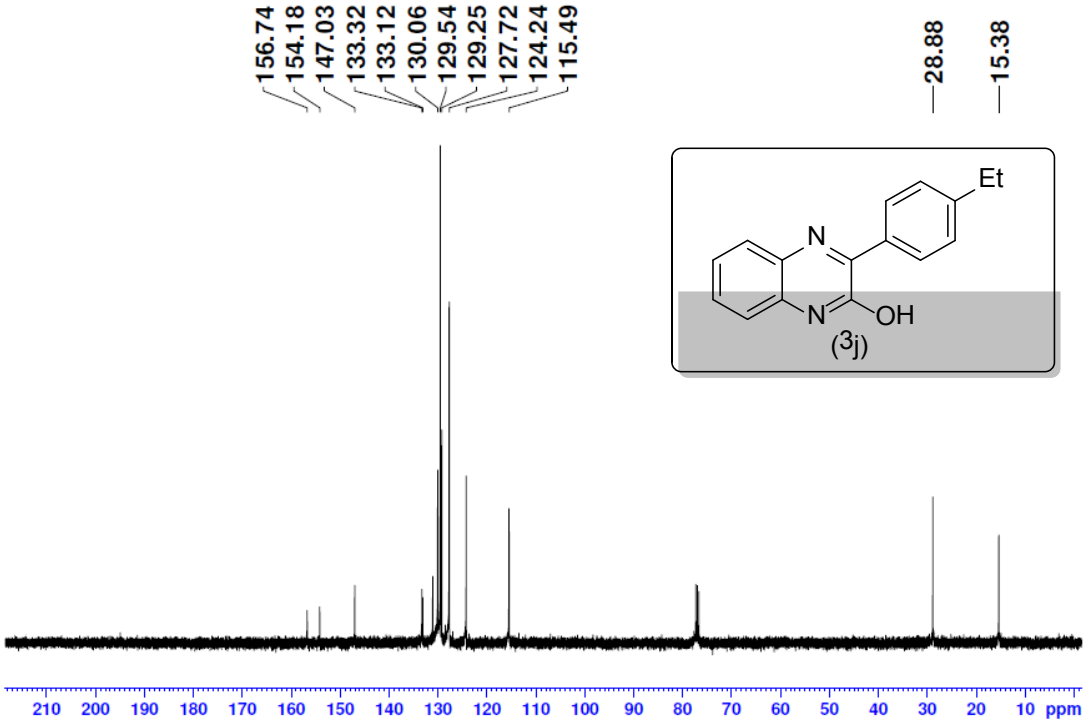


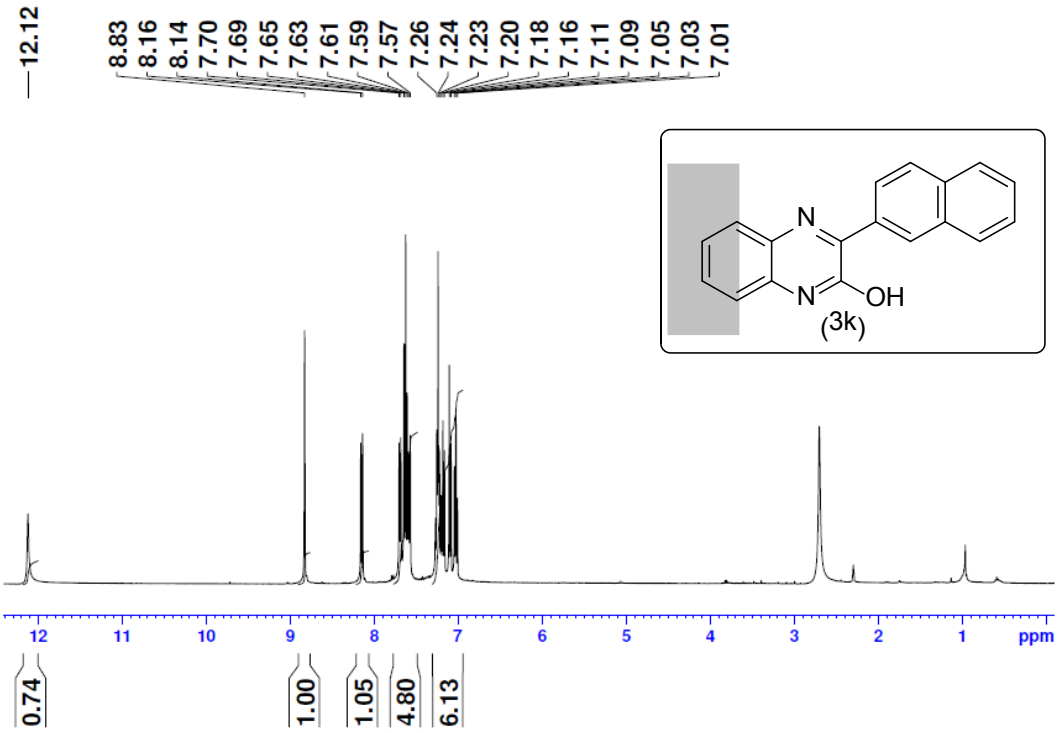


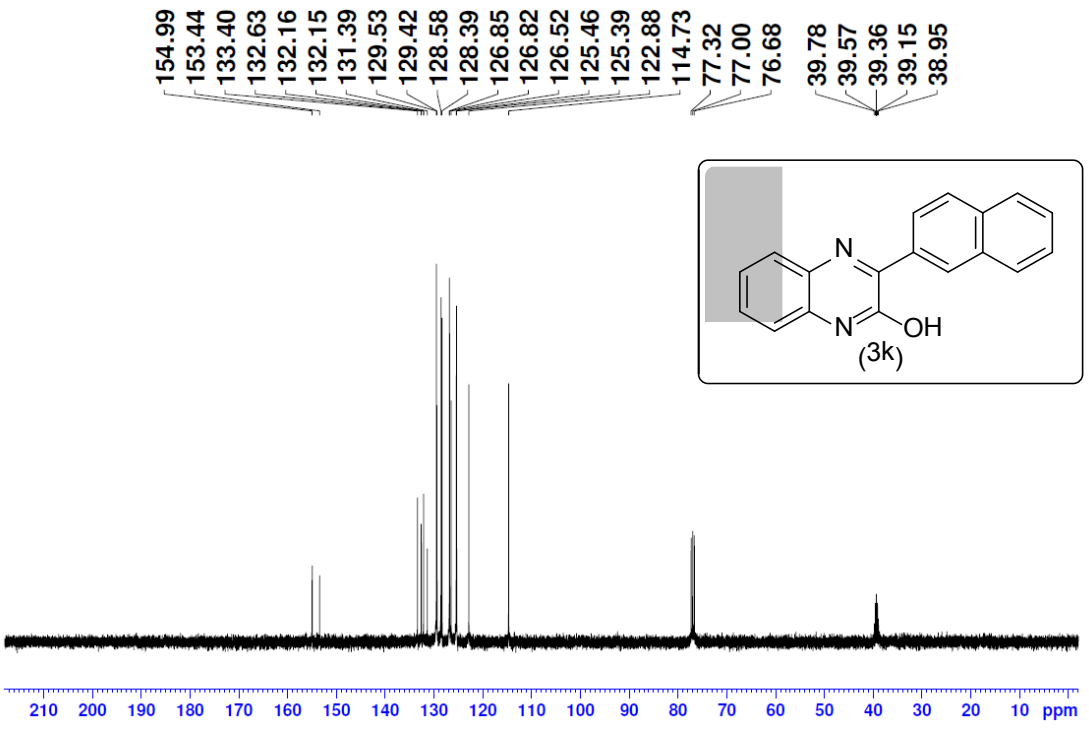


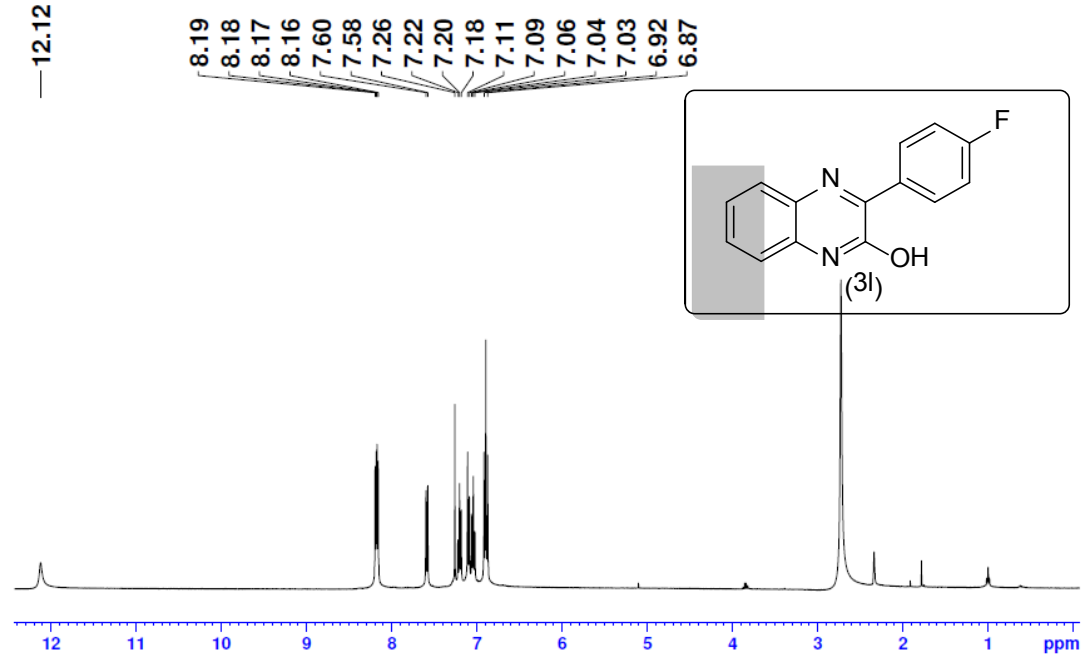


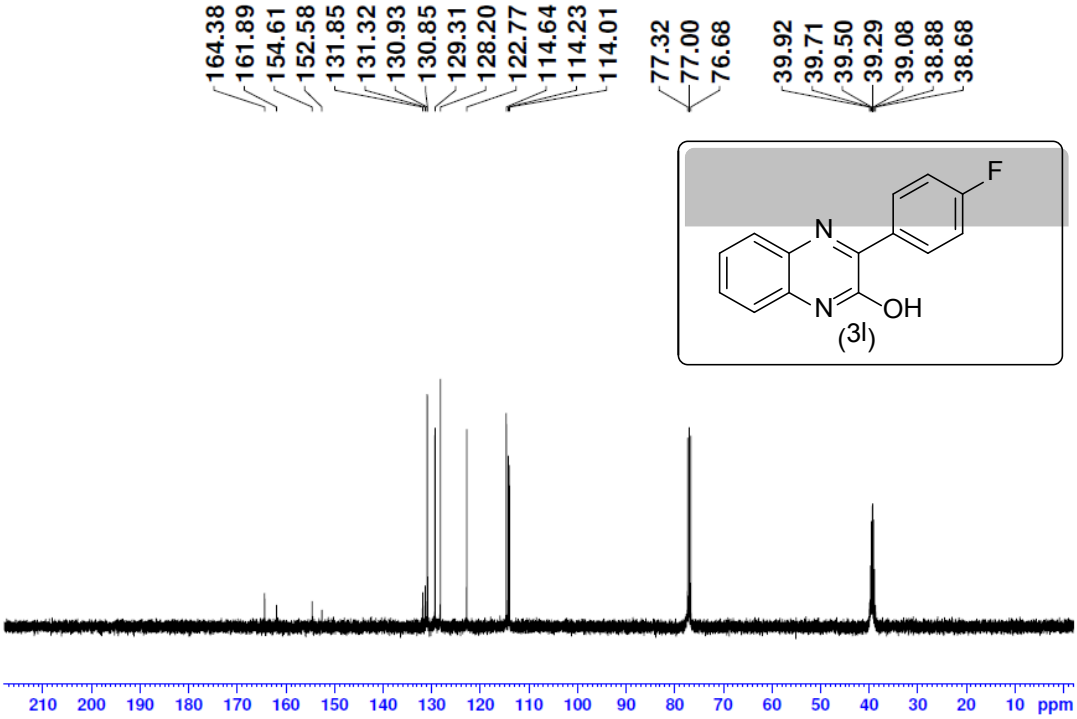


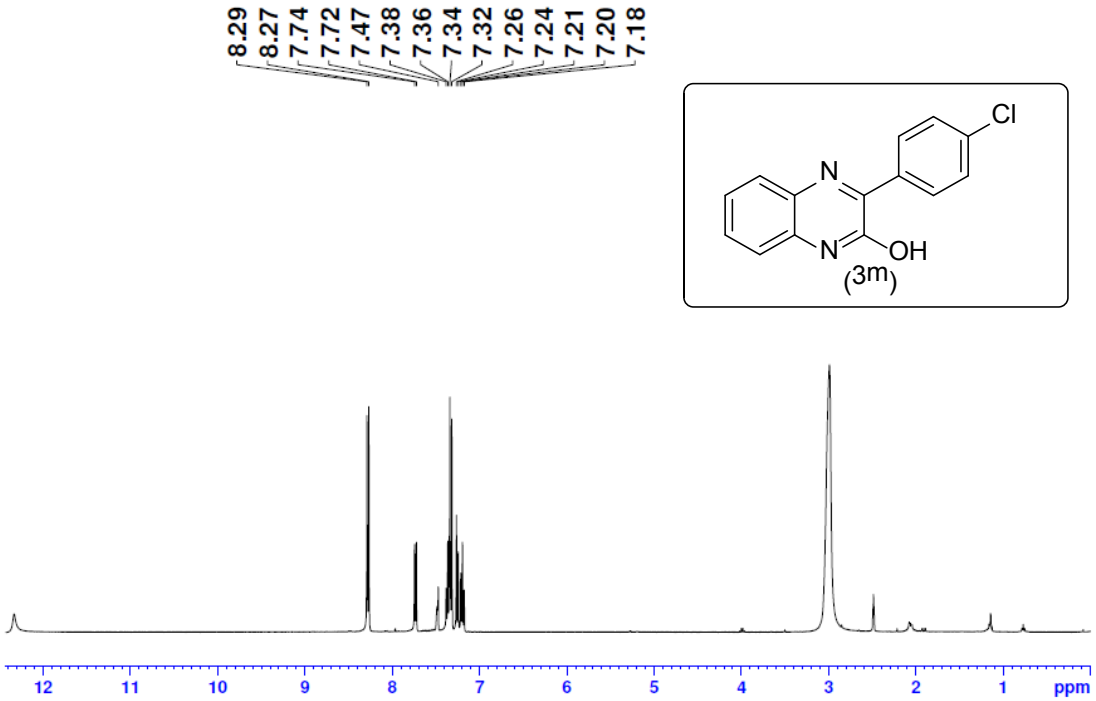


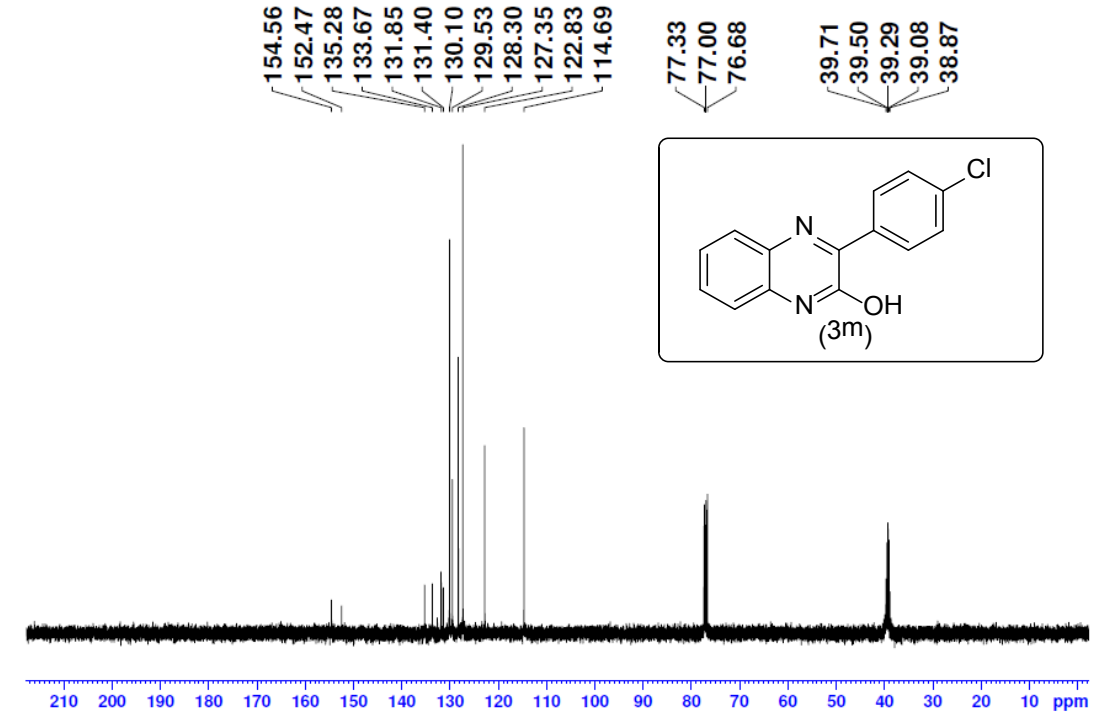


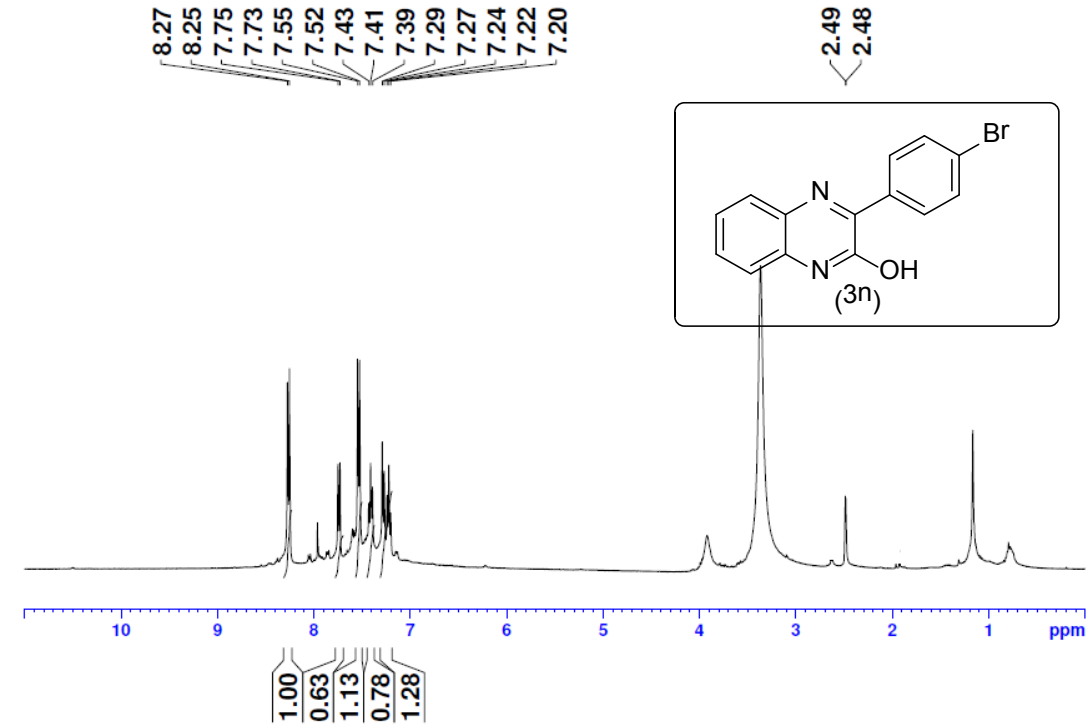


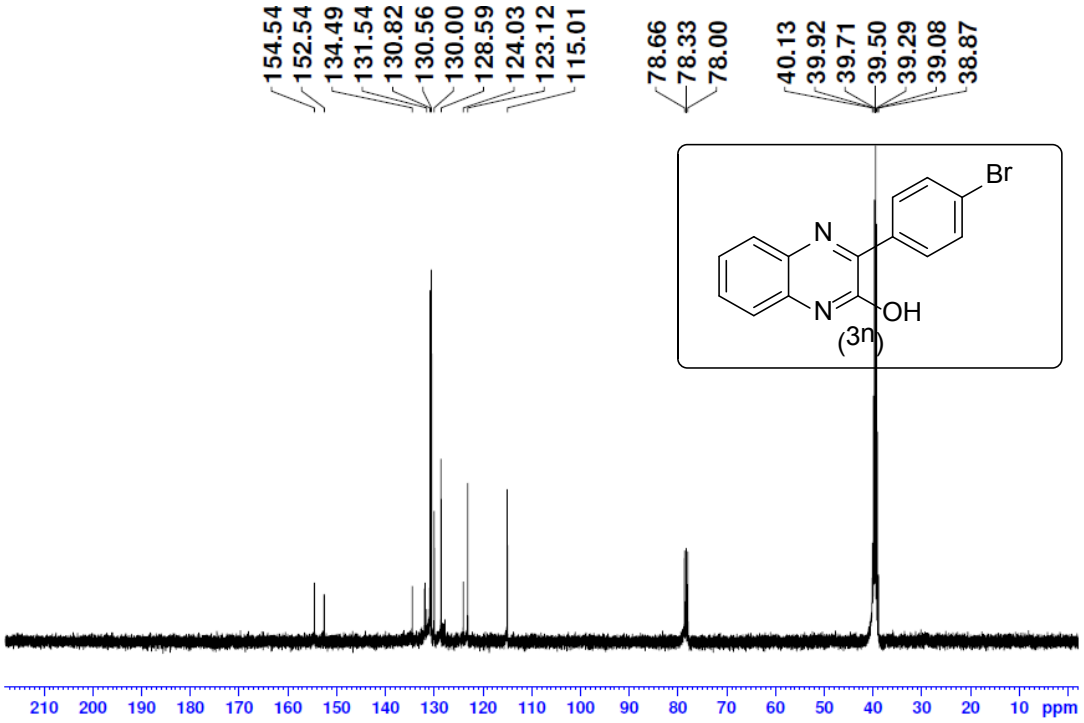


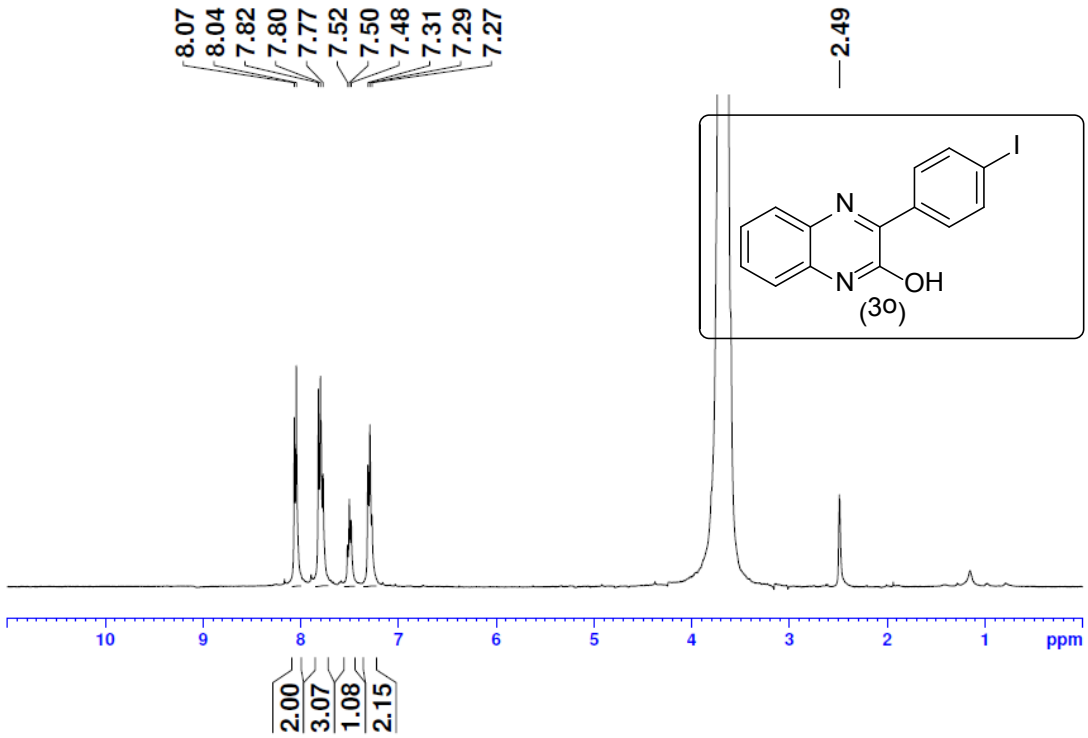


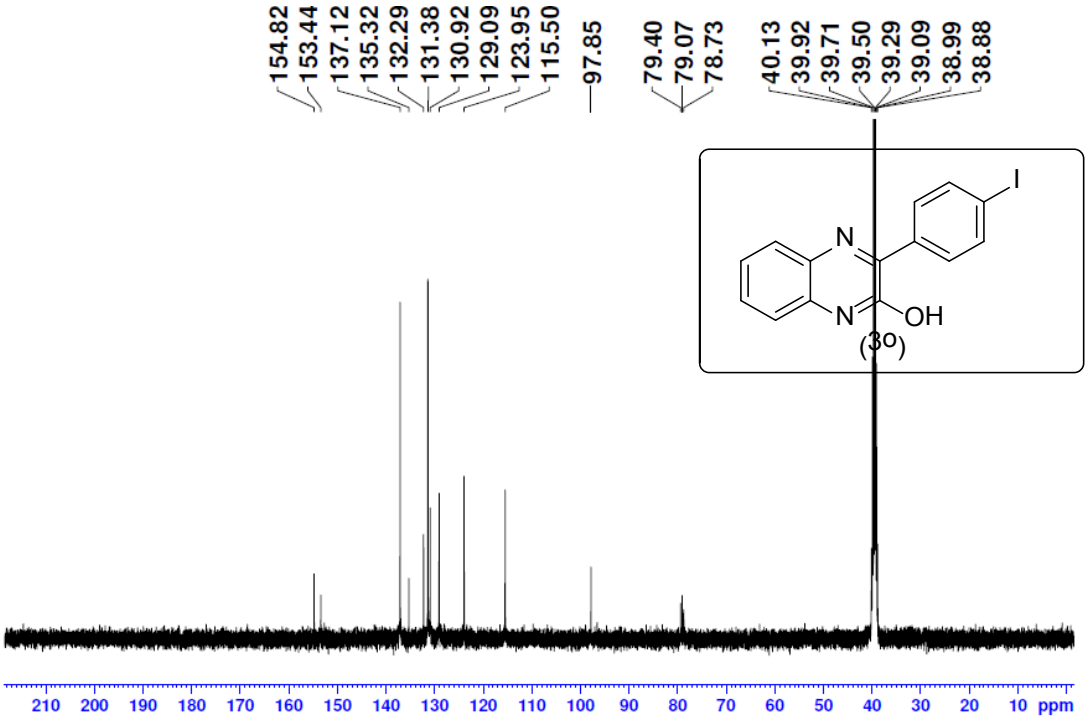


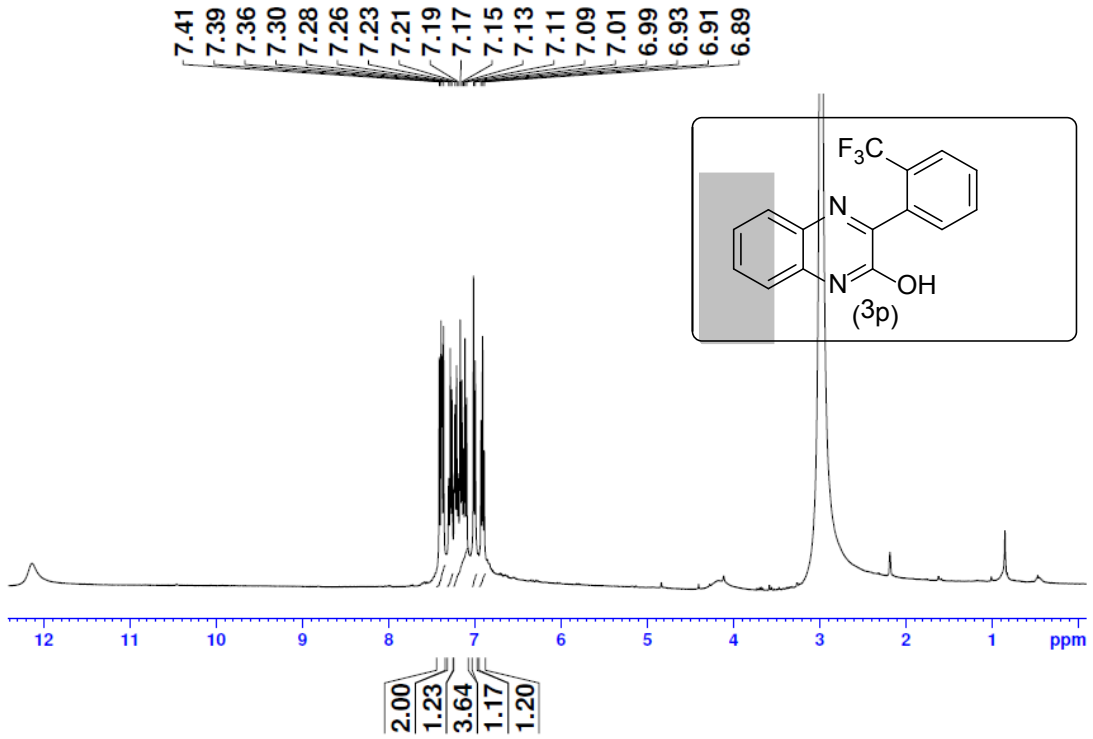


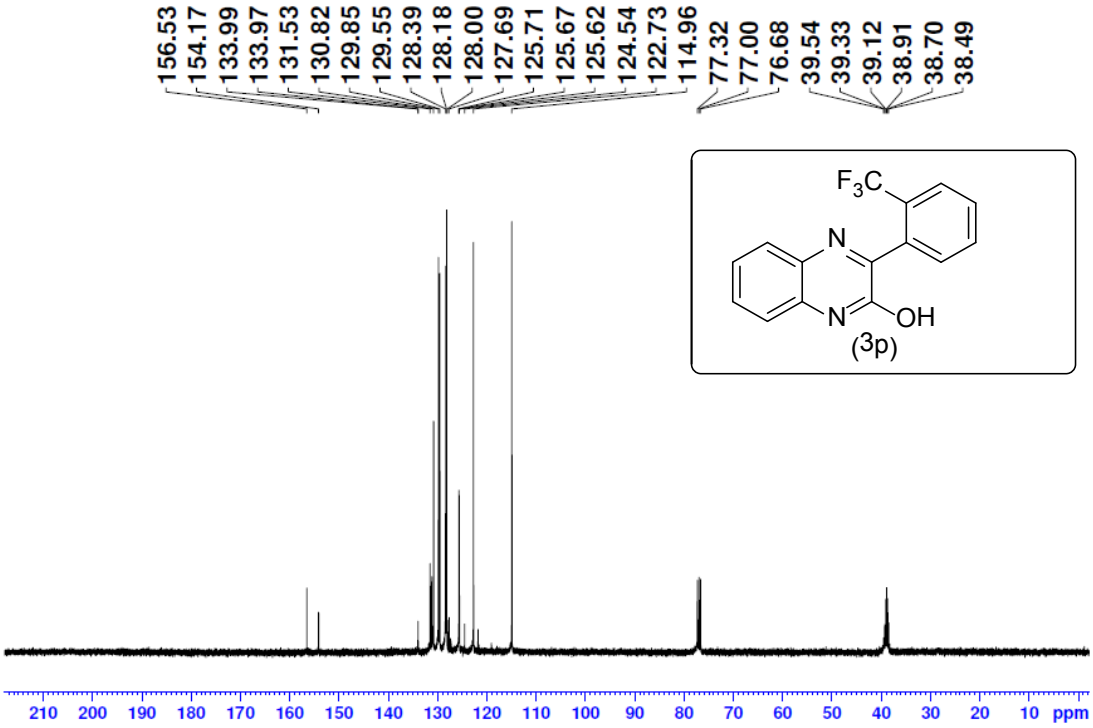


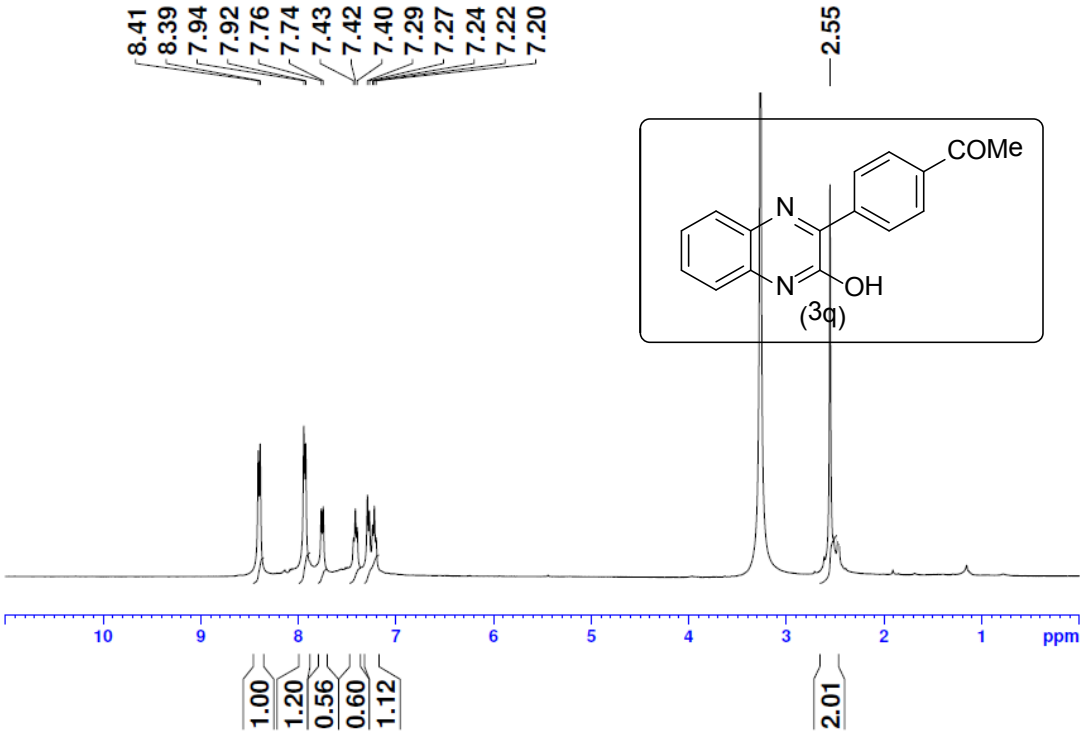


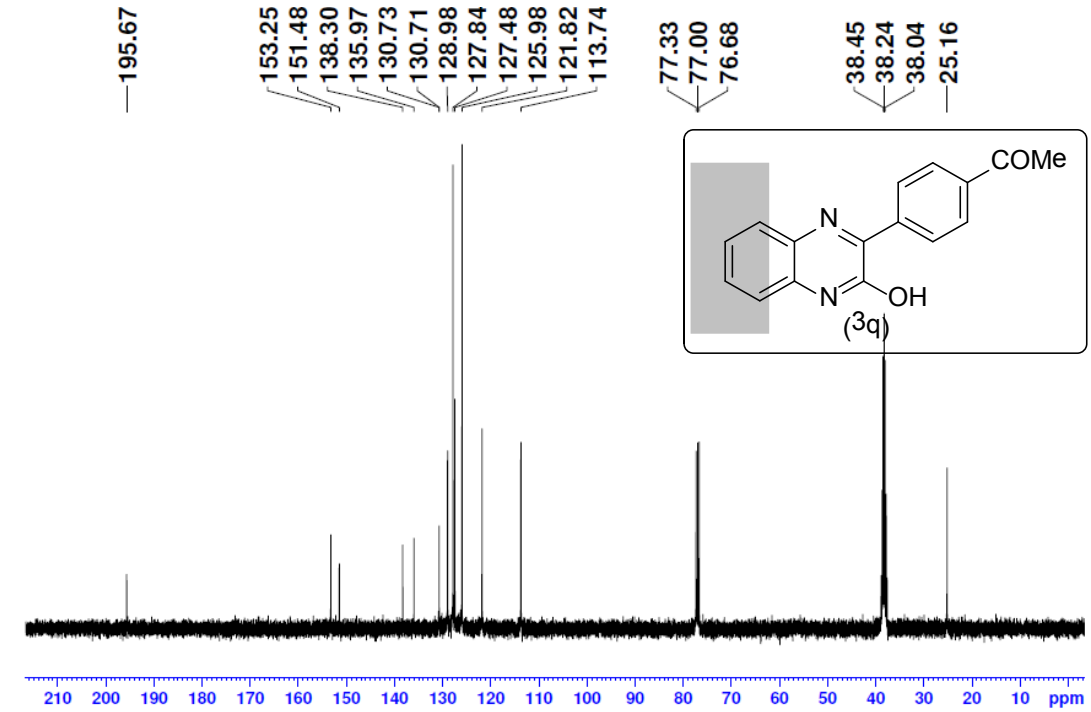


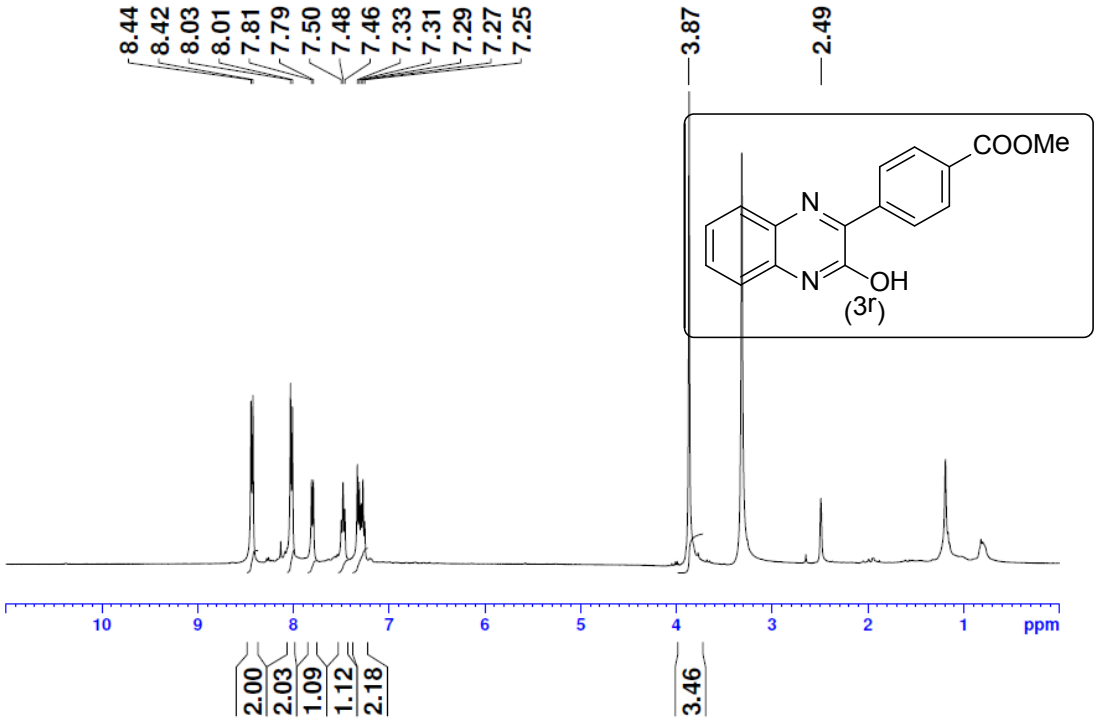


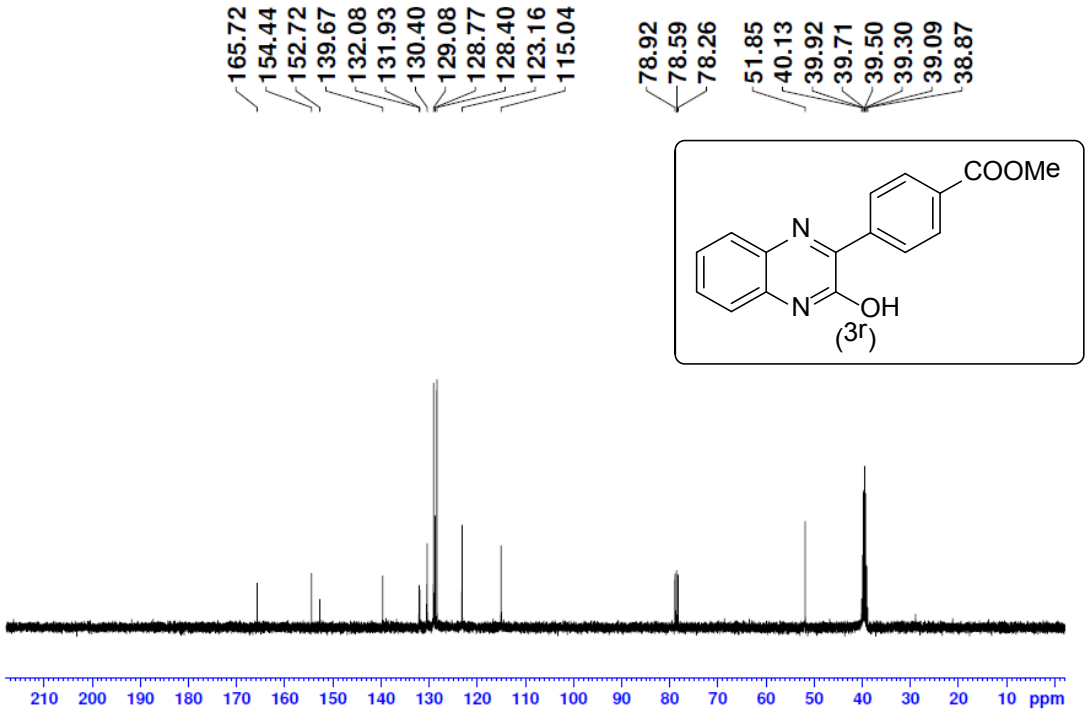


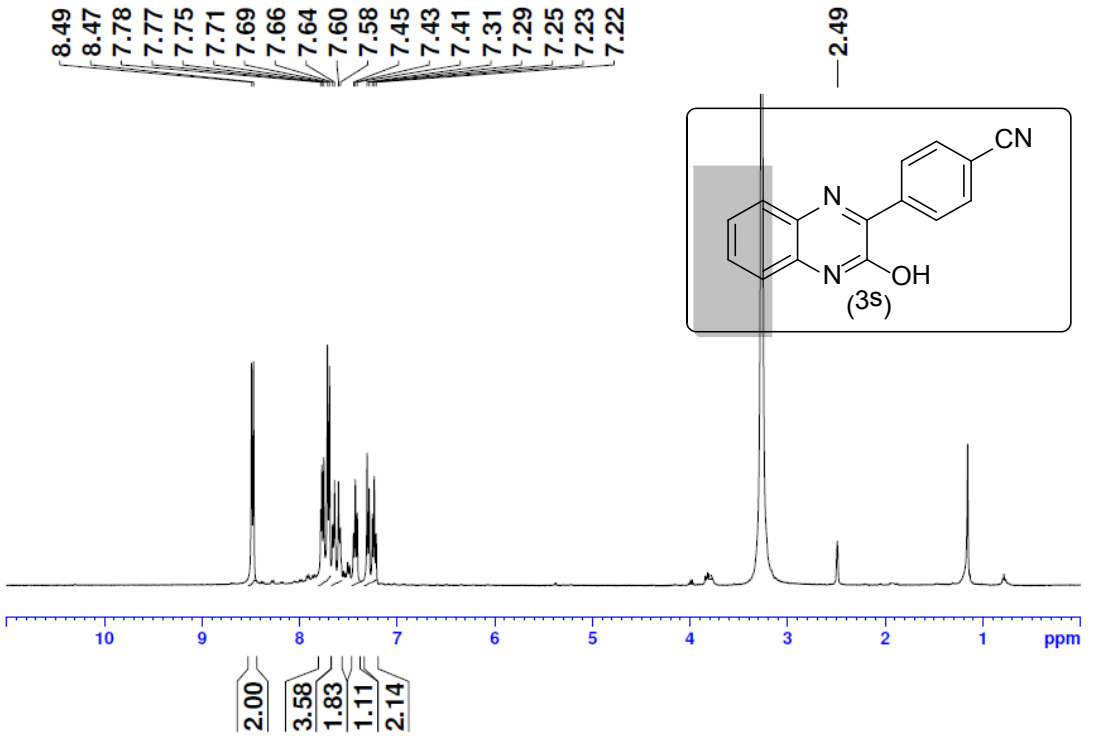


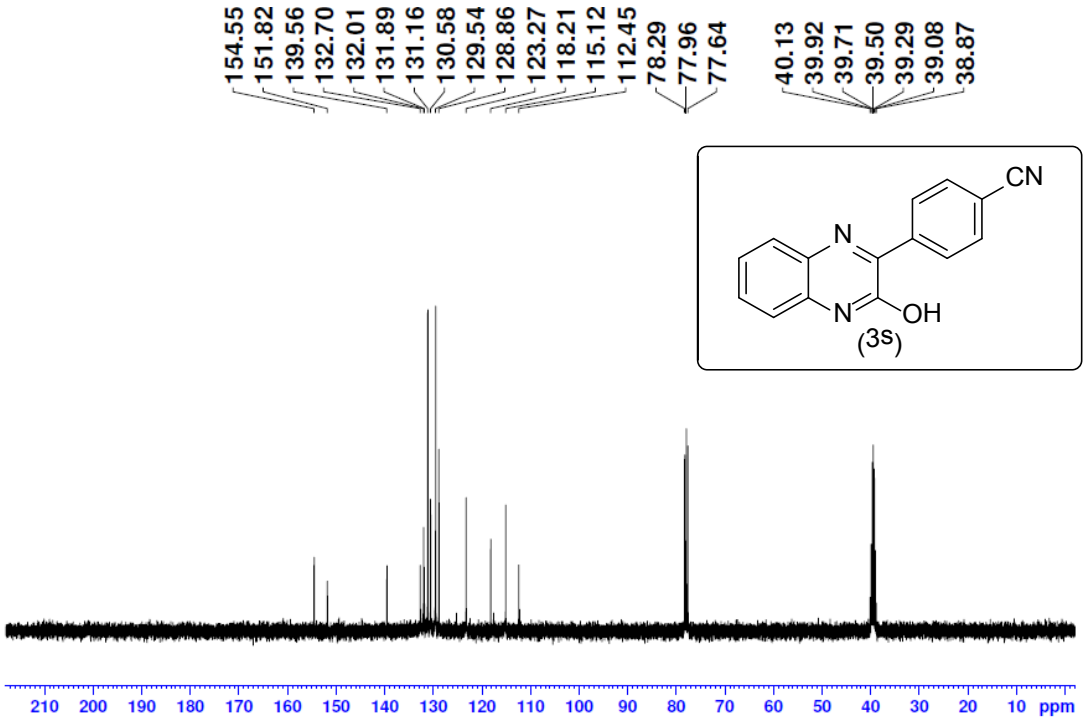


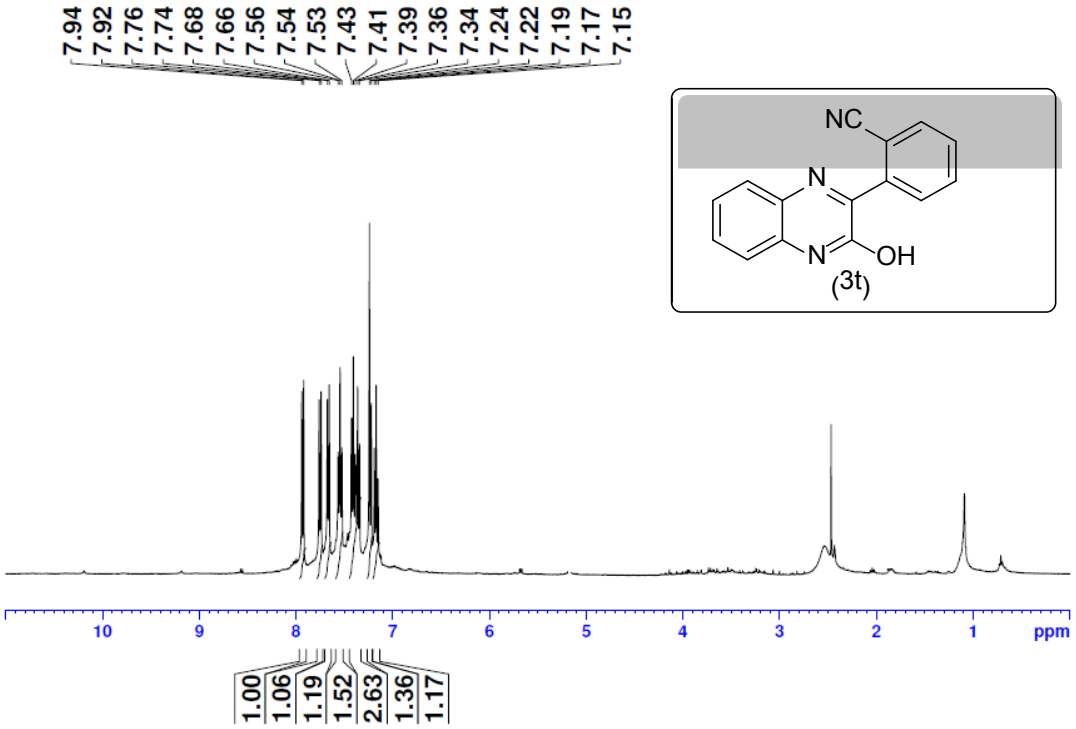


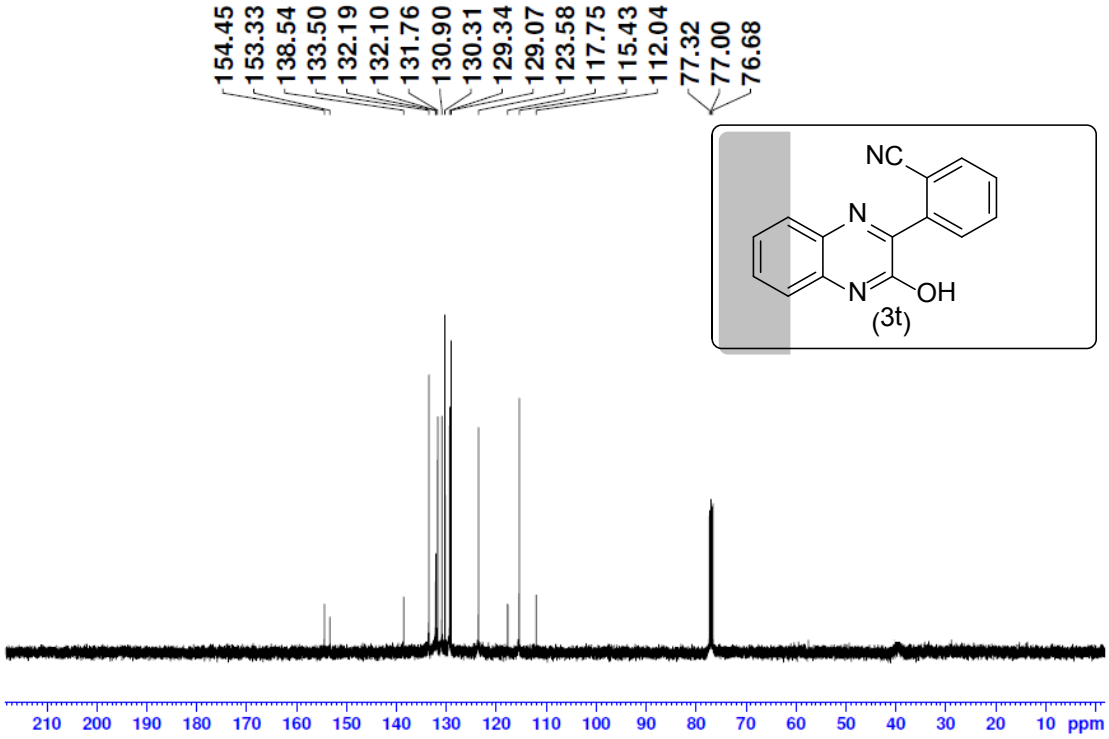












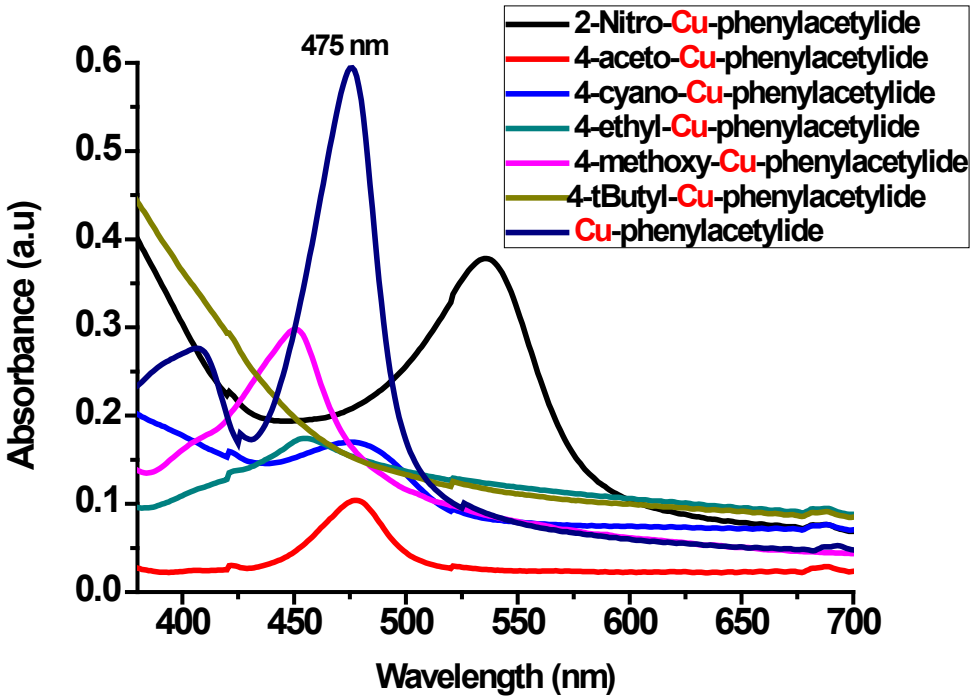


Figure S2. Uv-visible absorption spectra of aryl-copper acetylides.

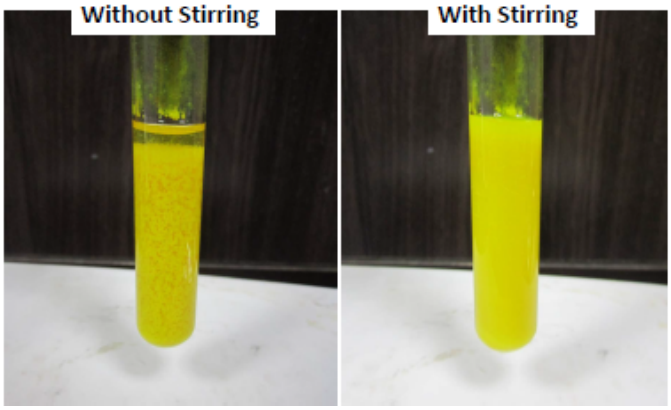


Figure S3. Optical pictures of Cu(I)Cl in CH_3CN-CH_3OH solution in the presence of reaction substrates.