

Supporting Information for

**Bioinspired Aerobic Oxidation of Secondary Amines and Nitrogen Heterocycles
with a Bifunctional Quinone Catalyst**

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Materials and Methods.

General Considerations. All commercially available compounds were purchased from Sigma-Aldrich, and used as received unless otherwise indicated. Solvents were dried over alumina columns prior to use. ^1H and ^{13}C NMR spectra for compound characterization were recorded on Bruker AC-300 MHz, Avance-400 MHz, Avance-500 MHz or Varian Mercury-300 MHz spectrometers. Chemical shift values are given in parts per million relative to residual solvent peaks (^1H and ^{13}C) or liquid NH_3 (^{15}N). High-resolution, exact mass measurements were obtained by the mass spectrometry facility at the University of Wisconsin. Melting points were taken on a Mel-Temp II melting point apparatus. Gas chromatographic analysis of reactions was conducted with a Shimadzu GC-2010Plus gas chromatograph with either a DB-Wax or a RTX-5 column. Flash chromatography was performed using SilicaFlash® P60 (Silicycle, particle size 40-63 μm , 230-400 mesh).

Procedure for Stoichiometric Reaction of phd with 1,2,3,4-tetrahydroisoquinoline:

To a solution of phd (4.0 mg, 0.019 mmol) in $\text{MeCN-}d_3$ (1.0 mL) containing internal standard (1,3,5-trimethoxybenzene) was added 6.0 equiv of 1,2,3,4-tetrahydroisoquinoline (14.5 μL , 0.114 mmol). Reaction progress was monitored by ^1H NMR until completion, at which point solids had formed along the walls of the NMR tube. (The liquids could be decanted, and the solids reconstituted in $\text{DMSO-}d_6$ + 1 drop TFA to give a spectrum which matched authentic 1,10-phenanthroline-5,6-diol, prepared according to the literature procedure¹).

Low Temperature NMR Characterization of Hemiaminal Intermediate A: General considerations for NMR studies: Low temperature characterization data was obtained using Bruker Avance 500 MHz or Varian INOVA 600 MHz spectrometers. Low temperature correlation spectroscopy was acquired using the following pulse parameters: $^1\text{H-}^{13}\text{C}$ HSQC spectral window (f2) of 230 ppm centered at 105 ppm, $j1\text{xh} = 140.0$ Hz, $ni = 256$, and $ns = 2$; $^1\text{H-}^{13}\text{C}$ HMBC spectral window (f2) of 230 ppm centered at 105 ppm, $j\text{nxh} = 8.0$ Hz, $j1\text{xh} = 140.0$ Hz, $ni = 256$, $ns = 4$; $^1\text{H-}^{15}\text{N}$ HMBC spectral window (f2) of 400 ppm centered at 150 ppm, $j\text{nxh} = 7.0$ Hz, $j1\text{xh} = 95.0$ Hz, $ni = 256$, and $ns = 128$. Chemical shift values are given in parts per million relative to residual solvent peaks (^1H and ^{13}C) or liquid NH_3 (^{15}N). Unless otherwise indicated, temperature calibrations were determined using a 4% MeOH in CD_3OD external standard.

General Procedure for NMR sample preparation: A solution of phd (4.0 mg, 0.019 mmol) in 1.0 mL $\text{MeCN-}d_3$ was loaded into an NMR tube. 1,2,3,4-Tetrahydroisoquinoline (14.5 μL , 0.114 mmol, 6.0 equiv) was added, and the sample was frozen in a dry ice/acetone bath to prevent further reaction. The sample was quickly thawed prior to loading into a spectrometer already cooled to -40 °C. When relevant, percent yield was determined from quantitative ^1H NMR spectra (relaxation delay: 25 s) based on 1,3,5-trimethoxybenzene internal standard.

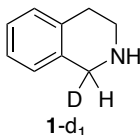
General Procedure for NMR time courses: A solution of (a) phd (4.0 mg, 0.019 mmol), or (b) phd (4.0 mg, 0.019 mmol) and 0.5 equiv $\text{Zn}(\text{OTf})_2$ (3.45 mg, 0.0095 mmol) in 1.0 mL $\text{MeCN-}d_3$ was loaded into an NMR tube. The sample was locked, tuned and shimmed in an NMR spectrometer already at -10 °C. The sample was quickly ejected,

1,2,3,4-tetrahydroisoquinoline (14.5 μ L, 0.114 mmol, 6.0 equiv) was added, and the sample was re-injected into the spectrometer. Quantitative (1 scan) ^1H spectra were acquired every 60 or 120 seconds.

Procedures for aerobic reaction screening

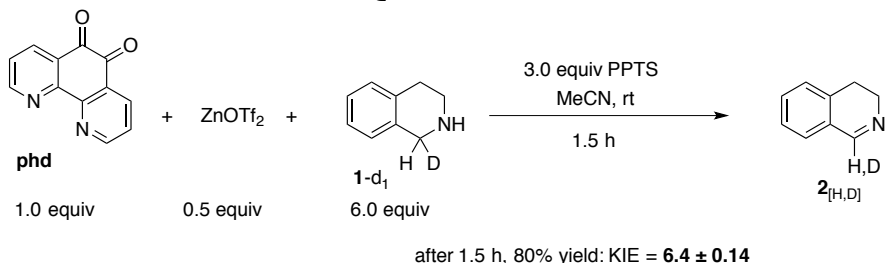
In a disposable culture tube, 1,10-phenanthroline-5,6-dione (5 mol %, 0.065 mmol), ZnI_2 (2.5 mol %, 0.00325 mmol), and PPTS (15 mol %, 0.0195 mmol) were dissolved in 0.5 mL MeCN. 1,2,3,4-Tetrahydroisoquinoline or dibenzylamine (0.130 mmol) was added, and the reaction tube was placed into an aluminum block mounted on a Large Capacity Mixer (Glas-Col) that enabled several reactions to be performed simultaneously under a constant pressure of (approx.) 1 atm O_2 with orbital agitation. The headspace above the tubes was filled and purged with oxygen gas multiple times, and then left under constant pressure of O_2 for 24 h. Upon completion, the tube was removed and internal standard was added. The reaction solvents were removed, and the residue suspended in CDCl_3 and filtered through a short plug of Celite for NMR analysis.

Kinetic Isotope Effect Studies



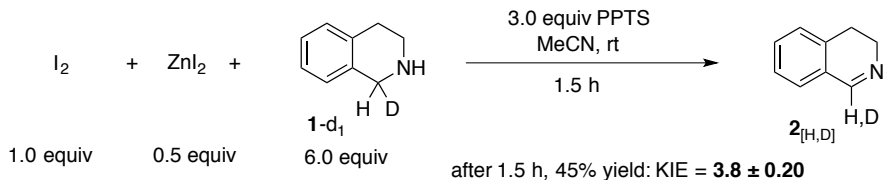
Mono-deuterated 1,2,3,4-tetrahydroisoquinoline, $1-d_1$, was prepared with >99:1 deuterium incorporation according to the literature procedure.²

Stoichiometric Reactions: Quinone-mediated oxidation.



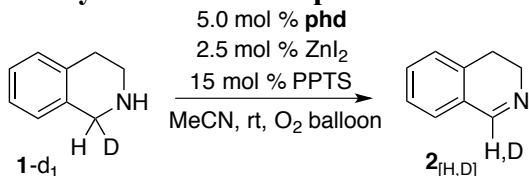
To a solution containing 1.0 equiv **phd** (10.0 mg, 0.047 mmol), 0.5 equiv $\text{Zn}(\text{OTf})_2$ (8.6 mg, 0.023 mmol) and 3.0 equiv PPTS (35.6 mg, 0.141 mmol) in 2.5 mL MeCN was added 6.0 equiv $1-d_1$ (36 μ L, 0.284 mmol). After 1.5 h, a stock solution of 1,3,5-trimethoxybenzene was added and the reaction was concentrated, resuspended in CDCl_3 , and filtered through a celite plug into an NMR tube. Quantitative NMR analysis showed the reaction yield to be 80% based on **phd**. The intrinsic KIE was determined to be 6.4 ± 0.14 (mean \pm s.e.m.) based on three independent experiments.

Stoichiometric Reactions: Iodine/Triiodide-mediated oxidation.



To a solution containing 1.0 equiv I₂ (12.1 mg, 0.047 mmol), 0.5 equiv ZnI₂ (7.6 mg, 0.023 mmol) and 3.0 equiv PPTS (35.6 mg, 0.141 mmol) in 2.5 mL MeCN was added 6.0 equiv **1-d₁** (36 μL, 0.284 mmol). After 1.5 h a stock solution of 1,3,5-trimethoxybenzene was added to the reaction mixture and the reaction was diluted with EtOAc and washed with a saturated solution of sodium thiosulfate. The organic phase was dried, concentrated and redissolved in CDCl₃ for NMR. Quantitative NMR analysis showed the reaction yield to be 45% based on **phd**. The intrinsic KIE was determined to be 3.8 +/- 0.20 (mean +/- s.e.m.) based on five independent experiments.

Catalytic Reactions: Optimized aerobic conditions.



after 24 h, 52% yield: KIE = 6.4 ± 0.19

To a solution containing 5 mol % phd (4.14 mg, 0.0195 mmol), 2.5 mol % ZnI₂ (3.14 mg, 0.00975 mmol), and 15 mol % PPTS (14.9 mg, 0.585 mmol) in 1.6 mL MeCN containing 1,3,5-trimethoxybenzene and under an O₂ atmosphere (balloon) was added **1-d₁** (50 μL, 0.39 mmol). After 24 h the reaction was concentrated, redissolved in CDCl₃, and filtered through a Celite plug. Quantitative NMR analysis showed the reaction yield to be 52% based on **1** (>10 catalyst turnovers). The intrinsic KIE was determined to be 6.4 +/- 0.19 (mean +/- s.e.m.) based on three independent experiments. A sample run to earlier conversion, stopped after 7 h, was measured to have KIE = 6.5.

Procedures for catalytic secondary amine oxidation

Typical procedure for the oxidation of secondary amines is as follows. A 25 mL flask was charged with 1,10-phenanthroline-5,6-dione (10.5 mg, 0.05 mmol, 5 mol %) and amine substrate (1.0 mmol) and 3.0 mL anhydrous MeCN was added. The flask was flushed with O₂ and equipped with an O₂ balloon. A well-dissolved solution of ZnI₂ (7.98 mg, 0.025 mmol, 2.5 mol %) and pyridinium *p*-toluenesulfonic acid, PPTS (37.7 mg, 0.15 mmol, 15 mol %), in 1.0 mL anhydrous MeCN was then added. (Depending on the substrate, once ZnI₂ was added the mixture was observed to change color and/or form a heterogeneous component over the course of the reaction). The reaction was stirred vigorously at room temperature for 24 h or 48 h, or until TLC indicated completion.

Workup A: Following reaction completion, the mixture was concentrated by rotary evaporation, suspended in a minimum of chloroform, and directly chromatographed over SiO₂ using EtOAc/Hexanes or EtOAc.

Workup B: Following reaction completion, the mixture was diluted in 50 mL EtOAc and washed with 25 mL of 1M NaOH. The aqueous phase was extracted with additional EtOAc (2 x 25 mL). The combined organic phases were washed with 25 mL brine, dried over Na₂SO₄, filtered, and concentrated. The reaction crude was then chromatographed over SiO₂ using EtOAc/Hexanes or EtOAc.

Figure S1. Variable Temperature stackplot of phd with 6.0 equiv **1** from 27 °C to -40 °C, resolving species **A** from the dynamic exchange of phd with **1**.

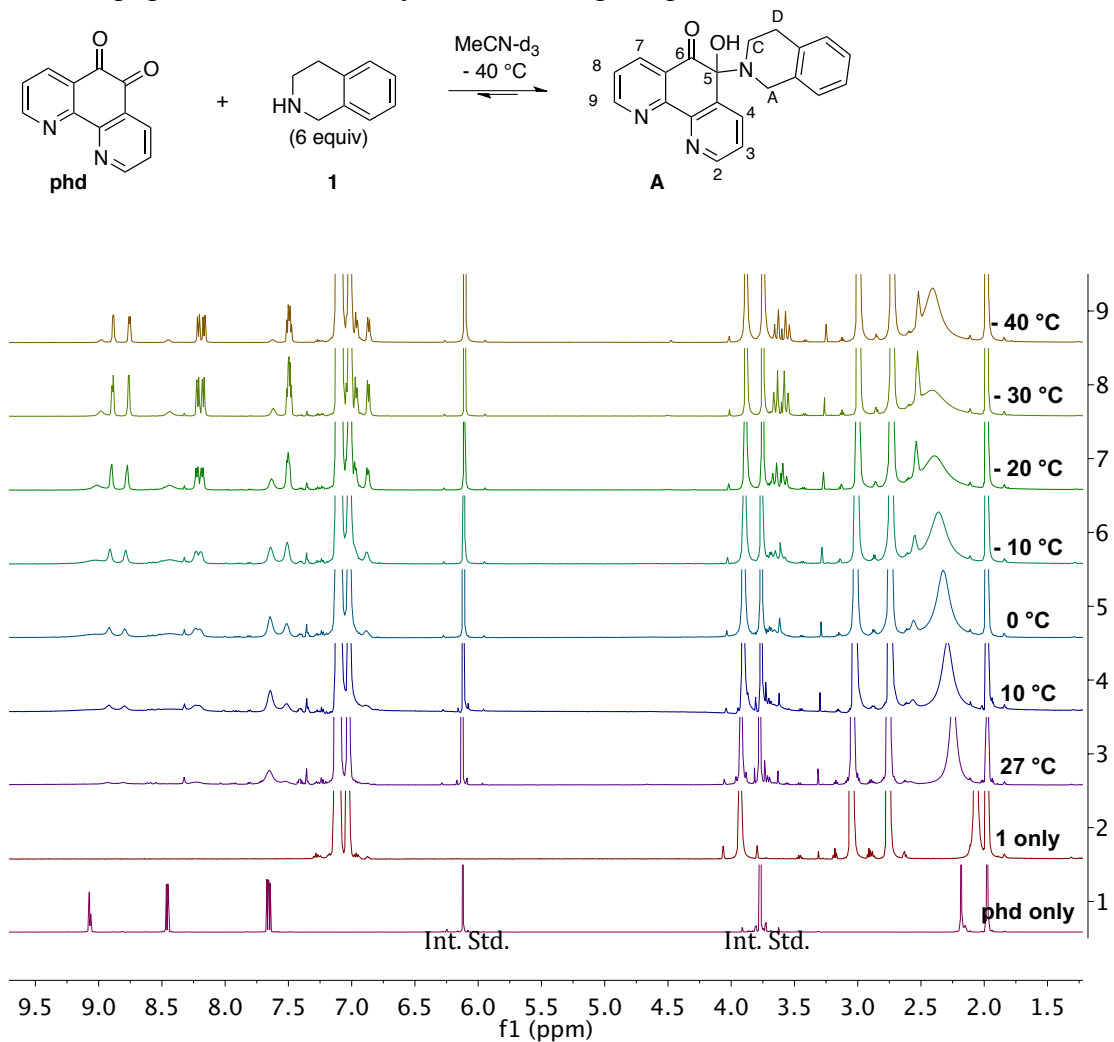


Figure S2. Characterization of Hemiaminal species, A ^1H NMR at $-40\text{ }^\circ\text{C}$.

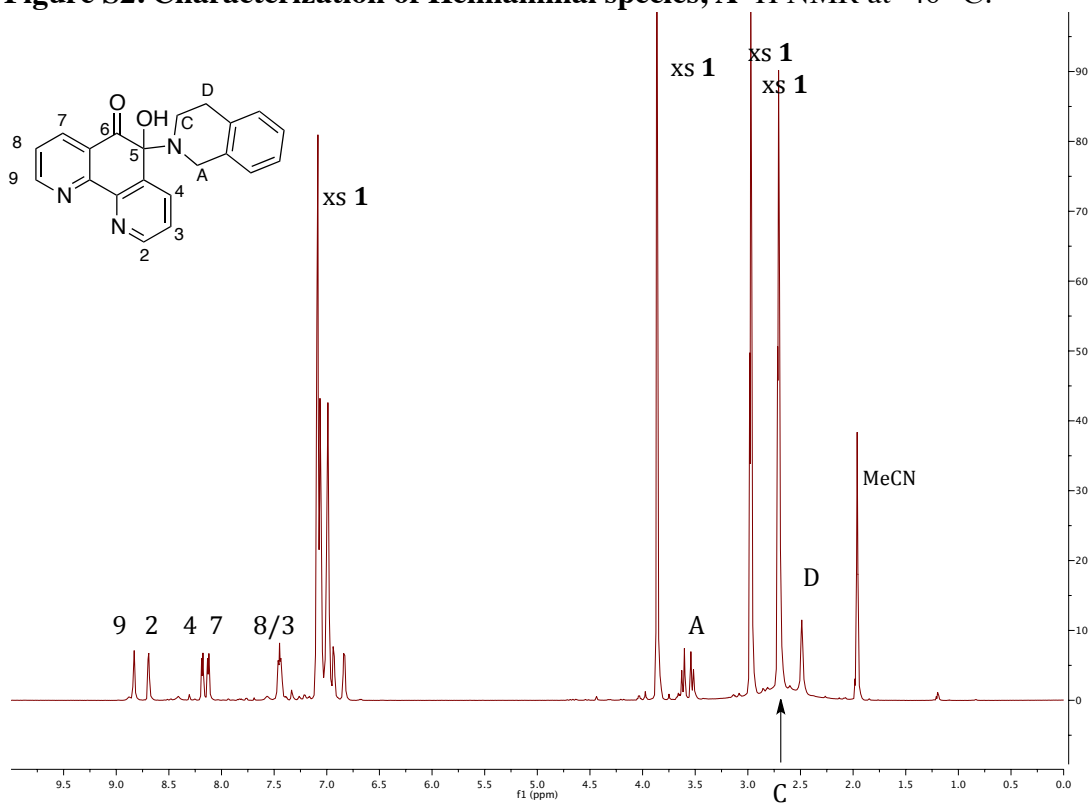


Figure S3. Characterization of Hemiaminal species, A ^1H - ^{13}C HSQC at $-40\text{ }^\circ\text{C}$.

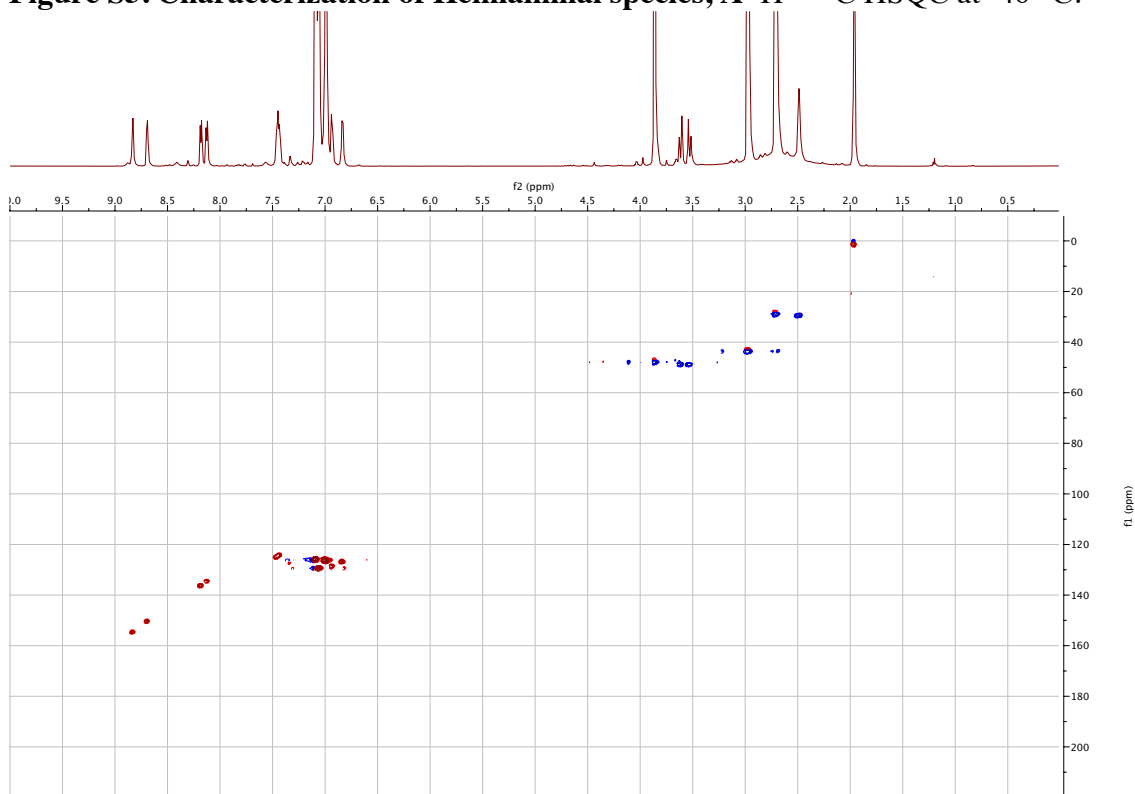


Figure S4. Characterization of Hemiaminal species, A ^1H - ^{13}C HMBC at -40°C .

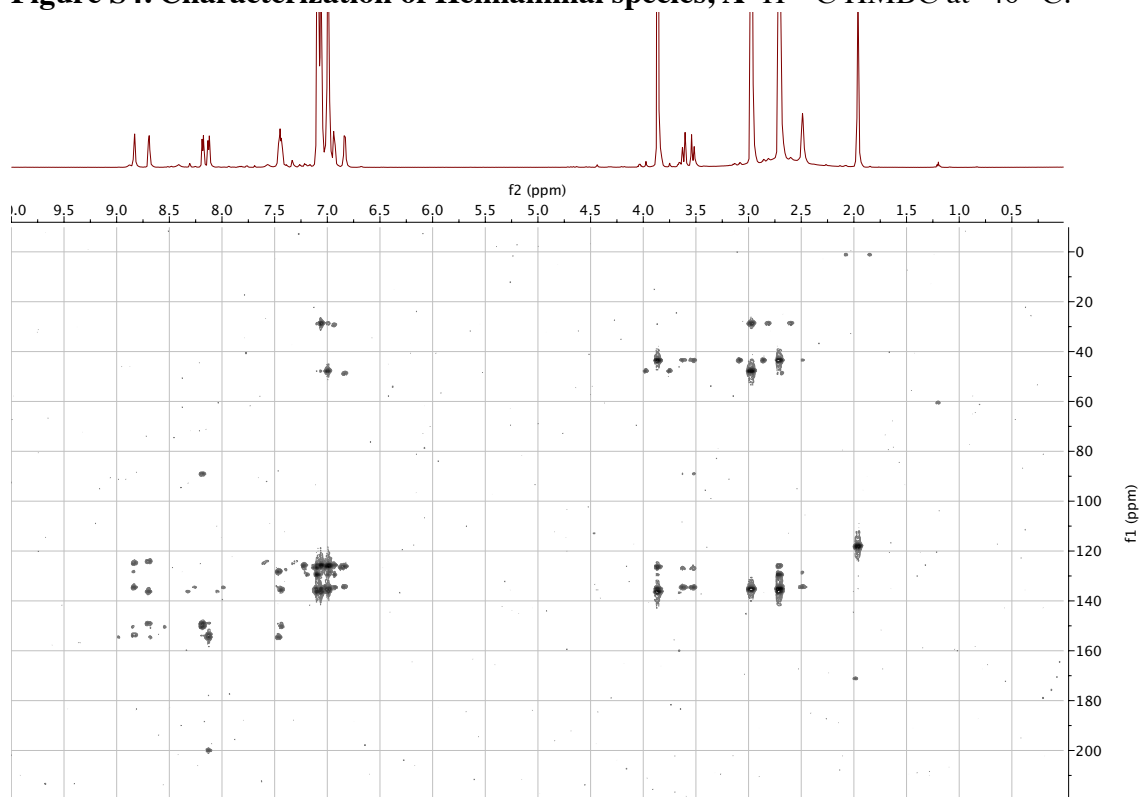


Figure S5. Characterization of Hemiaminal species, A ^1H - ^{15}N HMBC at -40°C .

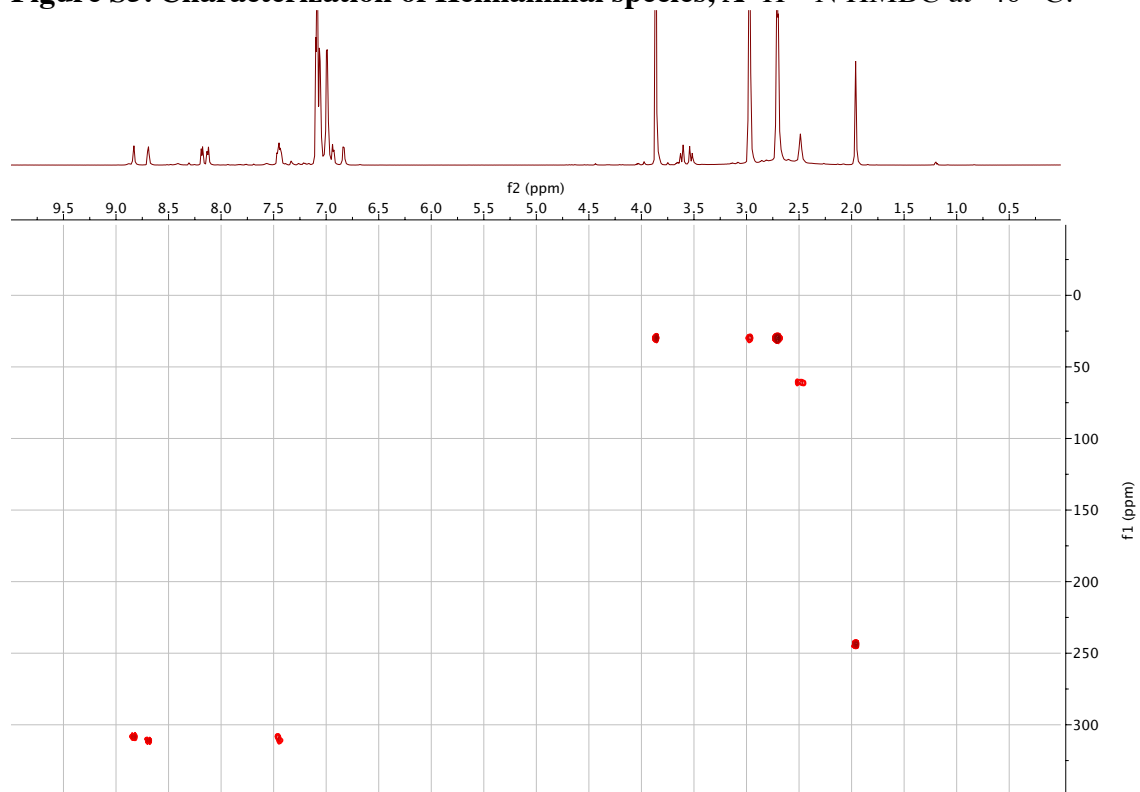


Figure S6. Characterization of Hemiaminal species, A 1D-NOESY at -40 °C. Selective irradiation at 8.12 ppm, mix time 0.3 s. NOE is observed from 4 to 3, A and C. (NOTE: Positive NOE is also observed to free **1** due to the exchange of positively magnetized A/C in species **A** with free **1** – see exchange dynamics).

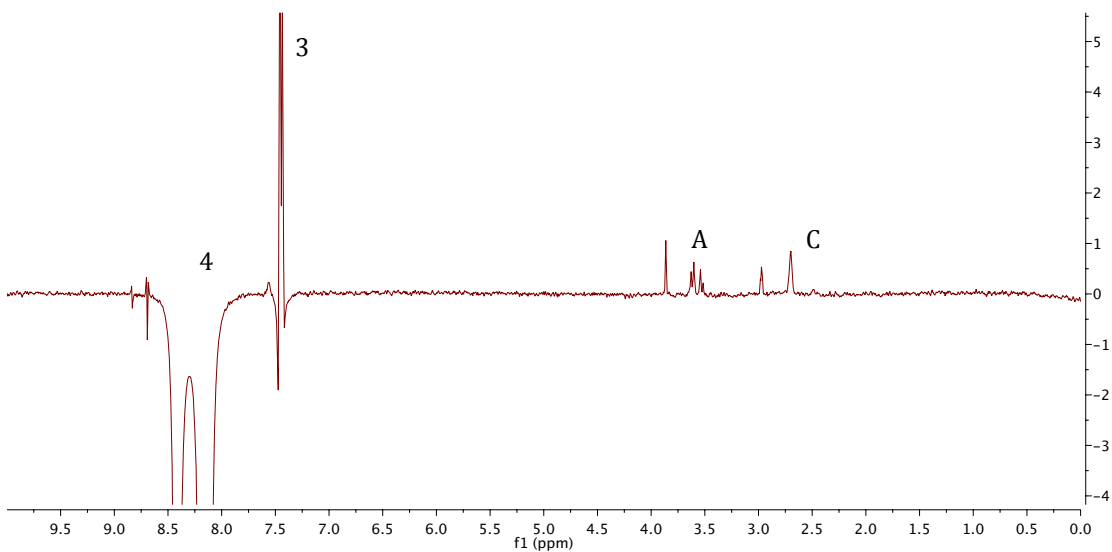


Figure S7. NMR titration of phd with 1, demonstrating equilibrium formation of Hemiaminal species, A ¹H-NMR stackplot at -40 °C.

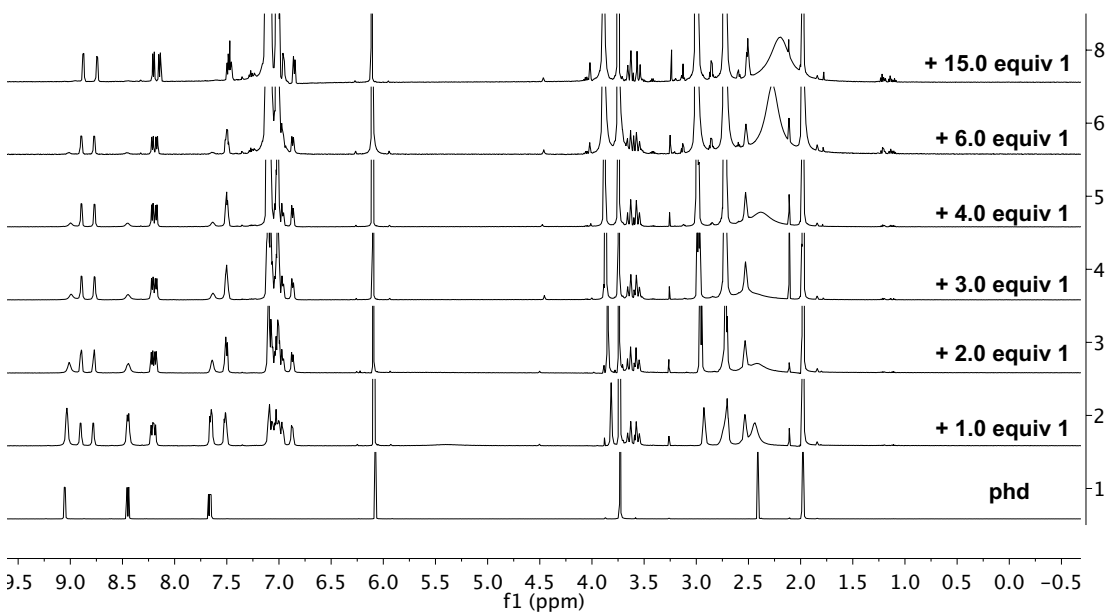


Figure S8. Low Temperature Exchange Dynamics EXSY-1D at $-40\text{ }^{\circ}\text{C}$.
 Selective irradiation at 3.88 ppm with arrayed mix time. Magnetization transfer from free **1** (*) to species **A** (A) indicates exchange.

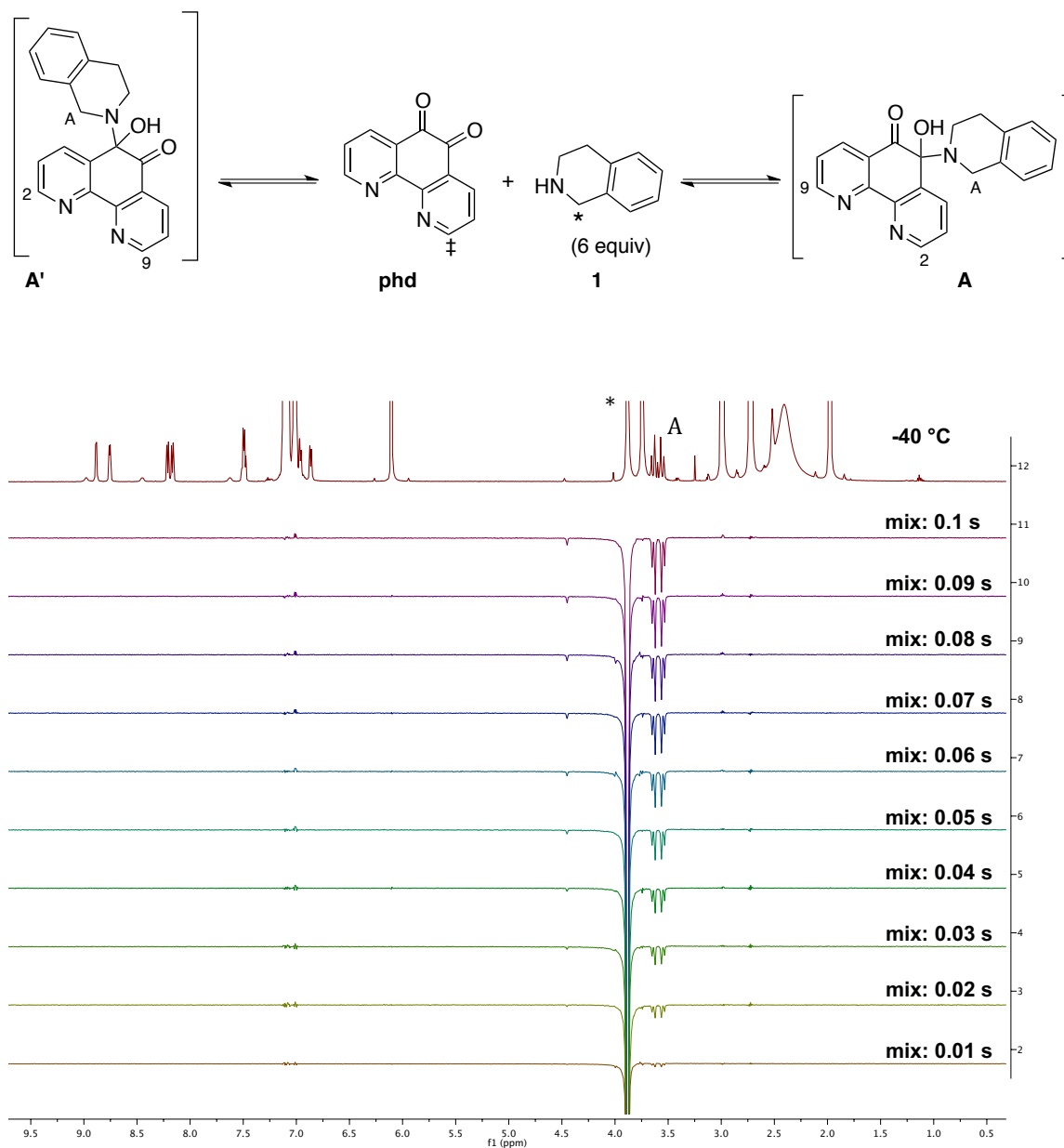


Figure S9. Low Temperature Exchange Dynamics EXSY-1D at -40 °C.

Selective irradiation at 8.12 ppm with arrayed mix time. Magnetization transfer from species A (2) to free phd (‡) to species A' (9) indicates exchange.

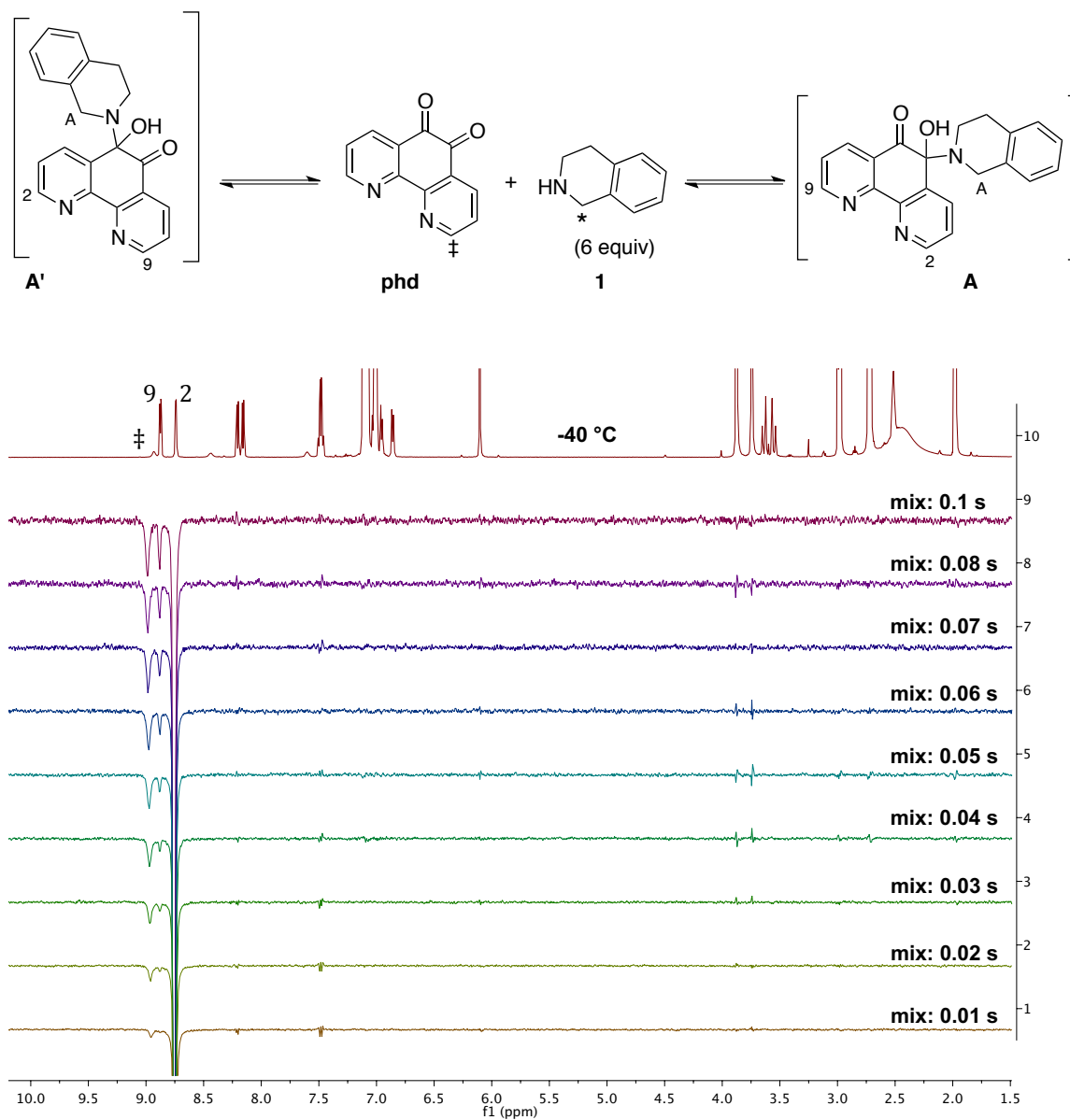


Figure S10. Zn(OTf)₂/phd NMR Titration stackplot and speciation plot.

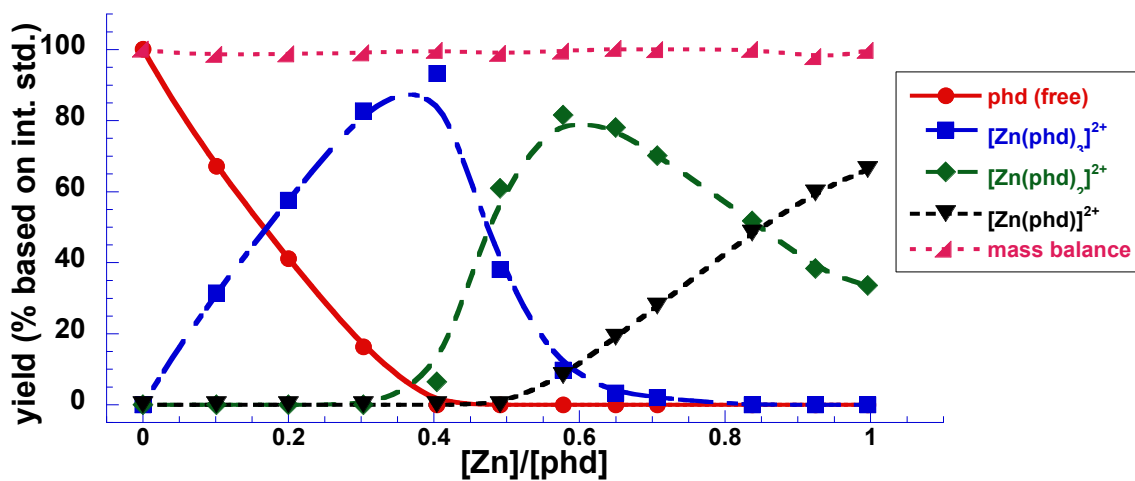
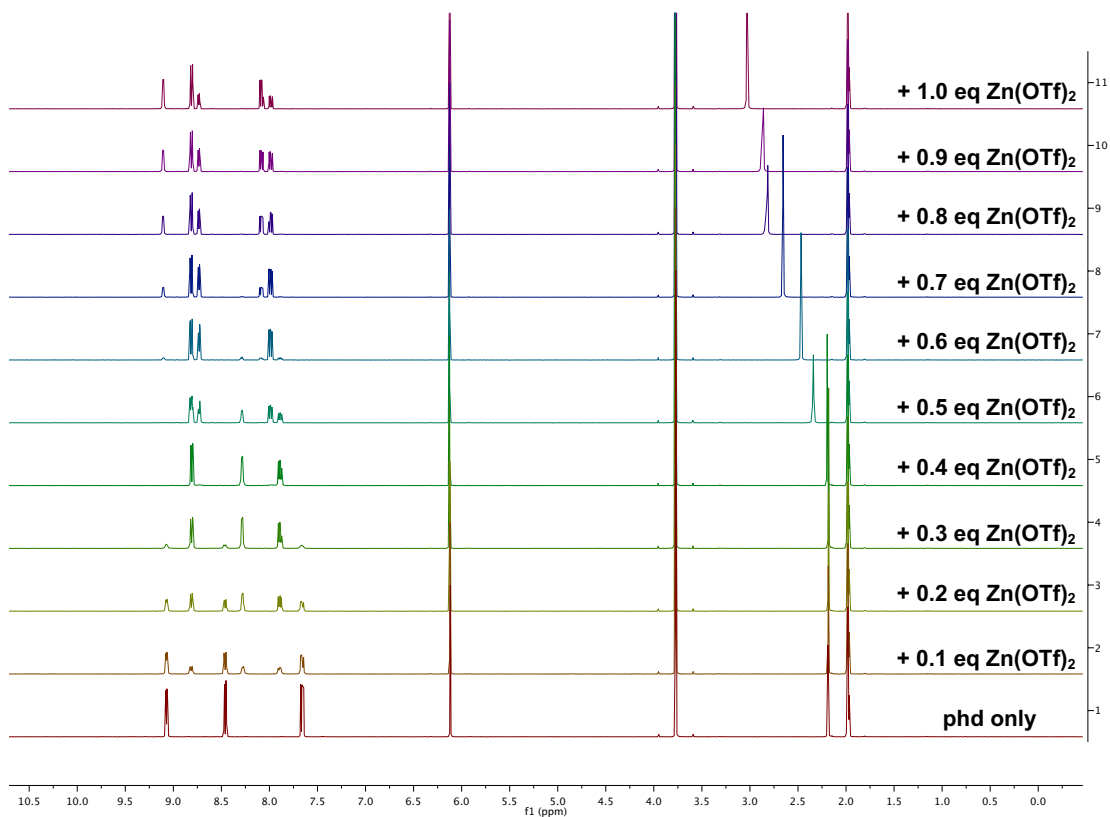


Figure S11. ^1H - ^{15}N HMBC: $\text{Zn}(\text{phd})_3\text{OTf}_2$ Indirect measurement of ^{15}N chemical shift of free phd is 251 ppm (vs NH_3)

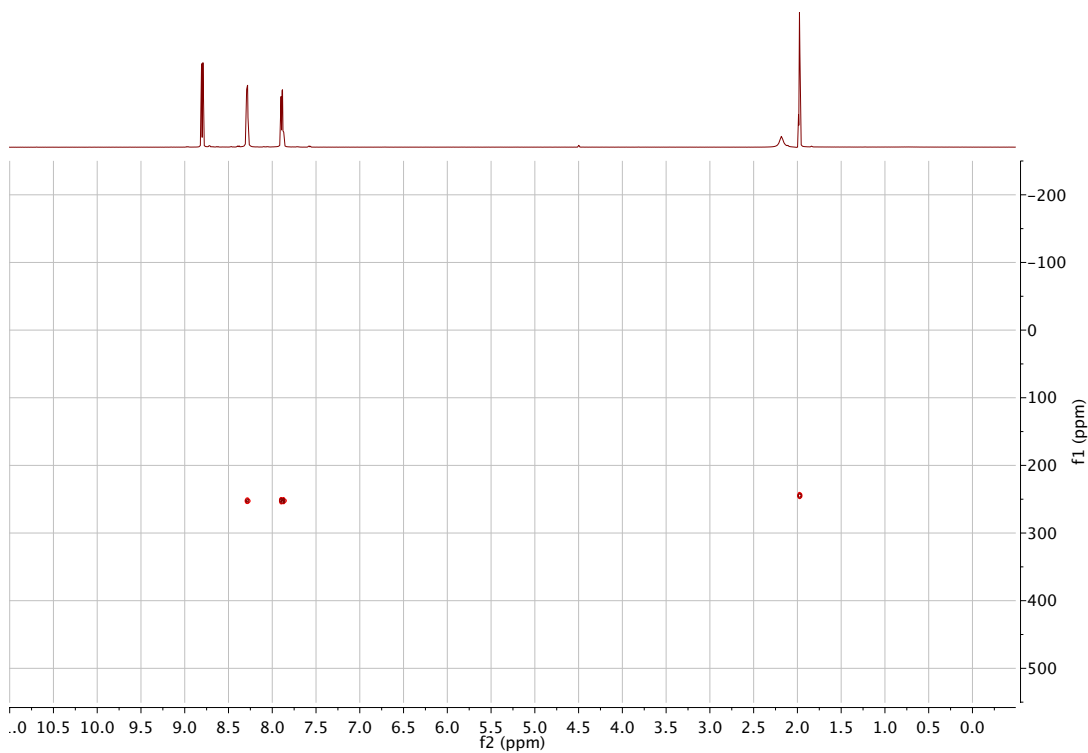
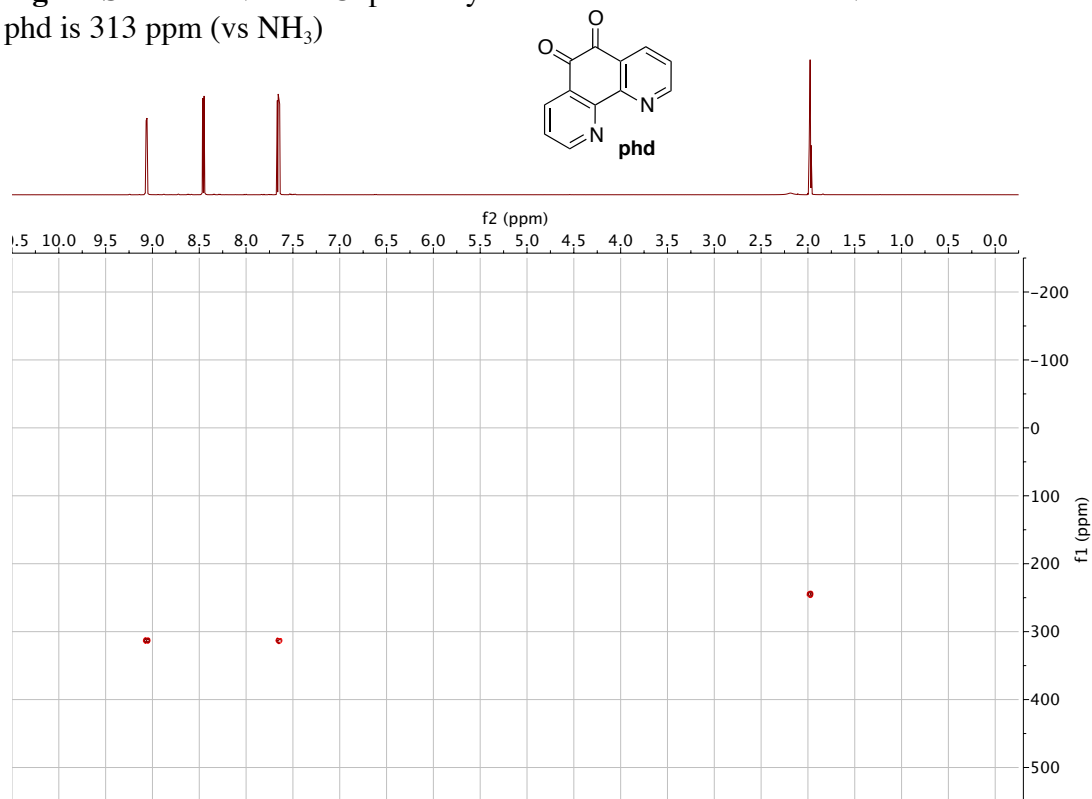
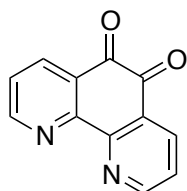


Figure S12. ^1H - ^{15}N HMBC: phd only. Indirect measurement of ^{15}N chemical shift of free phd is 313 ppm (vs NH_3)



Synthesis of 1,10-phenanthroline-5,6-dione, *phd*



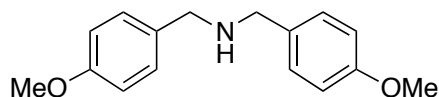
1,10-phenanthroline-5,6-dione, phd

The quinone catalyst, *phd*, was prepared from commercial 1,10-phenanthroline (Sigma Aldrich) according to the method of Eisenberg.³ 1,10-phenanthroline (4.0 g, 22.0 mmol) and KBr (4.1 g, 34.4 mmol) were combined in a flask, and an ice-cooled mixture of H₂SO₄ (40 mL) and HNO₃ (20 mL) was slowly added to the solids. The mixture was heated to reflux for 3 h, and then dumped onto 500 mL ice. The yellow aqueous solution was carefully neutralized with NaOH to pH = 6 - 7, extracted into CHCl₃, dried over MgSO₄, and concentrated to give nearly quantitative 1,10-phenanthroline-5,6-dione. The yellow solids were recrystallized from ethanol to give pale yellow, flat needles (1.65 g, 35%): mp (EtOH): 263-264 °C; ¹H NMR (400 MHz, DMSO) δ 9.01 (dd, 2H, *J* = 4.8, 1.6 Hz), 8.40 (dd, 2H, *J* = 7.6, 1.6 Hz), 7.69 (dd, 2H, *J* = 7.6, 4.8 Hz); ¹³C NMR (101 MHz, DMSO) δ 178.25, 154.83, 152.79, 136.16, 129.60, 125.72; EMM (ESI) Calc for C₁₂H₆N₂O₂ (M+H): 211.0503, found 211.0500. 1,10-phenanthroline-5,6-dione is also commercially available (Sigma Aldrich).

Synthesis and Characterization of Substrates

Acyclic Secondary Amines

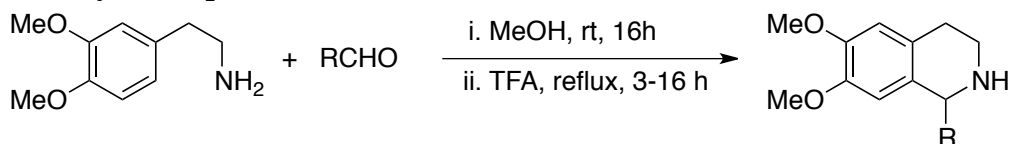
Dibenzylamine was obtained from commercial sources (Sigma Aldrich) and was used as obtained, without further purification. Other acyclic secondary amines were synthesized by reductive amination, according to the literature method.⁴



N,N-bis-(4-methoxybenzyl)amine

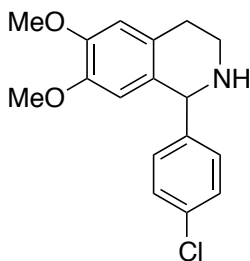
Synthesized according to the representative procedure to give a colorless oil whose spectroscopic data matched those previously reported:⁵ ¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, *J* = 8.6 Hz, 1H), 6.91 (d, *J* = 8.6 Hz, 1H), 3.84 (s, 6H), 3.77 (s, 4H), 1.55 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 158.61, 132.58, 129.34, 113.78, 55.30, 52.51.

Tetrahydroisoquinolines



1,2,3,4-tetrahydroisoquinoline was obtained from commercial sources (Sigma Aldrich) and was used without further purification. 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline was prepared by basification of an aqueous solution of 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline hydrochloride (available from Sigma Aldrich) and extraction of

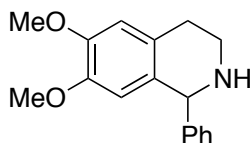
the neutralized compound into organic solvent. 1-substituted tetrahydroisoquinolines were prepared according to the following representative procedure.



1-(4-chlorophenyl)-1,2,3,4-tetrahydro-6,7-dimethoxyisoquinoline

Representative Procedure for Imine Formation: 4-Chlorobenzaldehyde (2.5 g, 17.8 mmol) was dissolved in 100 mL MeOH, and 3,4-dimethoxyphenethylamine (3.0 mL, 17.8 mmol) was added. The reaction was stirred at room temperature for 16 h, forming a white precipitate over this time. The white solids were collected by vacuum filtration, rinsed with 5 mL MeOH, and dried to afford the desired imine as a fine white solid (4.29 g, 79% yield). The filtrate was concentrated, and the remaining solids were suspended in a minimum of methanol, and similarly collected to give an additional 0.548 g, or 89.6% combined yield of the corresponding imine: ^1H NMR (500 MHz, CDCl_3) δ 8.09 (s, 1H), 7.65 (d, $J = 8.4$ Hz, 2H), 7.39 (d, $J = 8.4$ Hz, 2H), 6.6-6.8 (m, 3H), 3.8-3.9 (m, 8H), 2.97 (t, $J = 7.2$ Hz, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 160.12, 148.62, 147.36, 136.53, 134.66, 132.40, 129.19, 128.88, 120.86, 112.41, 111.12, 63.33, 55.89, 55.73, 36.93. [In some instances, when imine products did not precipitate from solution, the solvents were evaporated and the residue triturated with - or recrystallized from - hexanes, diethyl ether, EtOH, or another suitable solvent].

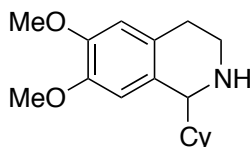
Representative Procedure for Pictet-Spengler: The thus obtained imine (1.67 g, 5.5 mmol) was dissolved in TFA (10 mL) and heated to reflux for 3 h, or until TLC indicated completion. The reaction was cooled, diluted with water and the solution basified by the addition of 1M NaOH. The aqueous solution was extracted (3 x 75 mL EtOAc or CH_2Cl_2), dried over MgSO_4 , and concentrated to give 1.67 g of the title compound as a white solid whose spectroscopic data match those previously reported:⁶ ^1H NMR (500 MHz, CDCl_3) δ 7.30 (d, $J = 8.1$ Hz, 2H), 7.22 (d, $J = 8.2$ Hz, 2H), 6.65 (s, 1H), 6.22 (s, 1H), 5.05 (s, 1H), 3.89 (s, 3H), 3.67 (s, 3H), 3.20 (dt, $J = 11.2, 5.2$ Hz, 1H), 3.06 (ddd, $J = 12.5, 8.5, 4.9$ Hz, 1H), 2.94 (dd, $J = 12.3, 5.9$ Hz, 1H), 2.6-2.85 (m, 1H), 2.26 (s, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 147.76, 147.13, 143.25, 133.14, 130.31, 129.16, 128.55, 127.59, 111.45, 110.70, 60.74, 55.88, 55.85, 41.79, 29.14.



1-phenyl-1,2,3,4-tetrahydro-6,7-dimethoxyisoquinoline

Spectroscopic data match those previously reported.⁷ ^1H NMR (400 MHz, CDCl_3) δ 7.1-7.5 (m, 5H), 6.63 (s, 1H), 6.25 (s, 1H), 5.05 (s, 1H), 3.87 (s, 3H), 3.63 (s, 3H), 3.22 (dt, $J = 12.1, 5.2$ Hz, 1H), 3.05 (ddd, $J = 12.3, 8.2, 4.6$ Hz, 1H), 2.93 (ddd, $J = 14.0, 8.2, 5.3$

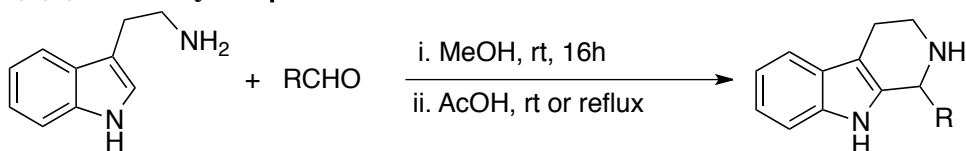
Hz, 1H), 2.75 (dt, $J = 16.0, 4.9$ Hz, 1H), 1.87 (br s, NH); ^{13}C NMR (101 MHz, CDCl_3) δ 147.61, 147.05, 144.90, 129.87, 128.91, 128.41, 127.68, 127.37, 111.42, 110.96, 61.49, 55.87, 55.86, 41.90, 29.35.



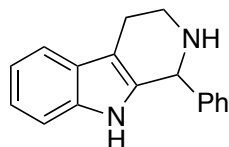
1-cyclohexyl-1,2,3,4-tetrahydro-6,7-dimethoxyisoquinoline

Spectroscopic data match those previously reported.⁷ ^1H NMR (400 MHz, CDCl_3) δ 6.64 (s, 1H), 6.56 (s, 1H), 3.87 (s, 3H), 3.83 (s, 3H), 3.26 (ddd, $J = 12.1, 5.2, 3.6$ Hz, 1H), 2.90 (ddd, $J = 12.1, 9.8, 4.2$ Hz, 1H), 2.76 (ddd, $J = 15.4, 9.8, 5.3$ Hz, 1H), 2.58 (dt, $J = 15.8, 4.0$ Hz, 1H), 1.5-2.0 (m, 6H), 1.0-1.5 (m, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 147.09, 147.06, 130.27, 128.40, 111.71, 109.29, 60.40, 56.10, 55.81, 43.27, 42.50, 30.93, 29.83, 27.09, 26.72, 26.61, 26.38.

1,2,3,4-Tetrahydro- β -carbolines

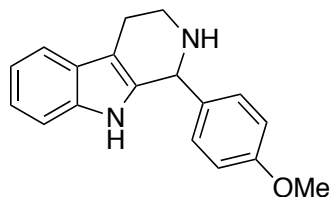


Tetrahydro- β -carbolines were prepared from tryptamine using the general procedure outlined for the preparation of tetrahydroisoquinolines with the modifications described below.



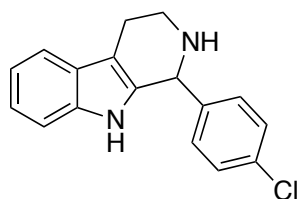
1-phenyl-1,2,3,4-tetrahydro- β -carboline

Representative Procedure for Pictet-Spengler: Following imine formation as indicated above, *N*-benzylidene tryptamine (2.0 g, 8.0 mmol) was dissolved in 20 mL AcOH, and brought to reflux for 30 min. The reaction was cooled, diluted with water, neutralized with 1M NaOH, and extracted into EtOAc (3 x 75 mL). The organic phases were combined, washed with brine, and then dried with Na_2SO_4 to give 1.96 g (7.89 mmol, 98% yield) of the title compound. Spectroscopic data match those previously reported.⁷ ^1H NMR (400 MHz, CDCl_3) δ 7.5-7.6 (m, 2H), 7.28-7.4 (m, 5H), 7.2-7.25 (m, 1H), 7.07-7.17 (m, $J = 7.1, 5.5$ Hz, 2H), 5.17 (t, $J = 1.8$ Hz, 1H), 3.38 (ddd, $J = 12.5, 5.3, 3.7$ Hz, 1H), 3.15 (ddd, $J = 12.9, 8.9, 4.7$ Hz, 1H), 2.7-3.0 (m, 2H), 1.85 (br s, NH); ^{13}C NMR (101 MHz, CDCl_3) δ 141.85, 135.86, 134.55, 128.85, 128.51, 128.21, 127.43, 121.74, 119.42, 118.26, 110.84, 110.27, 58.20, 42.98, 22.59; EMM (ESI) Calc for $\text{C}_{17}\text{H}_{15}\text{ClN}_2$ (M+H): 247.1230, found 247.1224.



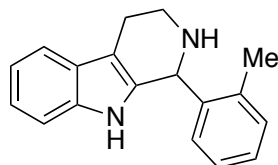
1-(4-methoxyphenyl)-1,2,3,4-tetrahydro-β-carboline

Spectroscopic data match those previously reported.⁷ ¹H NMR (400 MHz, CDCl₃) δ 7.98 (s, 1H), 7.5-7.6 (m, 1H), 7.0-7.25 (m, 5H), 6.86 (d, *J* = 8.3 Hz, 2H), 5.06 (s, 1H), 3.80 (s, 3H), 3.33 (dt, *J* = 12.5, 4.5 Hz, 1H), 3.10 (ddd, *J* = 12.9, 8.8, 4.8 Hz, 1H), 2.7-3.0 (m, 2H), 1.78 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 159.49, 135.91, 134.90, 134.03, 129.71, 127.44, 121.64, 119.32, 118.21, 114.13, 110.90, 110.08, 57.45, 55.38, 42.83, 22.59; EMM (ESI) Calc for C₁₈H₁₈N₂O (M+H): 279.1492, found 279.1482.



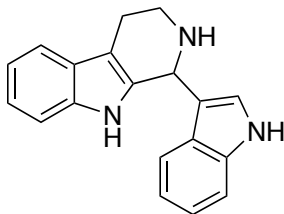
1-(4'-chlorophenyl)-1,2,3,4-tetrahydro-β-carboline

Prepared according to the representative procedure with the following modifications: the reaction was stirred at room temperature for 1.5 h. Spectroscopic data match those previously reported.⁸ ¹H NMR (400 MHz, CDCl₃) δ 7.74 (s, NH), 7.59 (d, *J* = 8.4 Hz, 1H), 7.3-7.4 (m, 2H), 7.0-7.3 (m, 5H, overlaps with CDCl₃ residual peak), 5.14 (t, *J* = 1.8 Hz, 1H), 3.36 (dt, *J* = 12.6, 4.6 Hz, 1H), 3.16 (ddd, *J* = 12.8, 8.6, 4.8 Hz, 1H), 2.75-3.0 (m, 2H), 1.91 (br s, NH); ¹³C NMR (101 MHz, CDCl₃) δ 140.40, 135.93, 134.01, 133.87, 129.92, 128.98, 127.33, 121.94, 119.54, 118.35, 110.91, 110.45, 57.39, 42.68, 22.50; EMM (ESI) Calc for C₁₇H₁₅ClN₂ (M+H): 283.0997, found 283.0995.



1-(2-methylphenyl)-1,2,3,4-tetrahydro-β-carboline

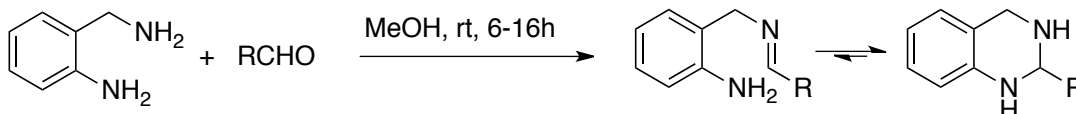
This compound has been previously reported.⁹ ¹H NMR (400 MHz, CDCl₃) δ 8.11 (br s, NH), 7.62 (dd, *J* = 5.7, 3.1 Hz, 1H), 7.3-7.4 (m, 3H), 7.15- 7.3 (m, 3H, overlaps with CDCl₃ residual peak), 7.06 (d, *J* = 7.6 Hz, 1H), 5.39 (t, *J* = 1.8 Hz, 1H), 3.33 (dt, *J* = 12.7, 4.7 Hz, 1H), 3.13 (ddd, *J* = 12.9, 8.4, 4.9 Hz, 1H), 2.8-3.0 (m, 2H), 2.48 (s, 3H), 1.64 (br s, NH); ¹³C NMR (101 MHz, CDCl₃) δ 139.59, 137.13, 135.94, 134.79, 131.07, 128.89, 128.04, 127.44, 126.25, 121.62, 119.34, 118.15, 110.93, 110.42, 54.71, 42.73, 22.68, 19.12; EMM (ESI) Calc for C₁₈H₁₈N₂ (M+H): 263.1543, found 263.1533.



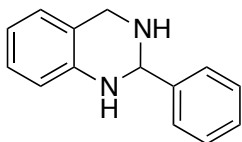
1-(indol-3-yl)-1,2,3,4-tetrahydro-β-carboline

Synthesized according to the literature method.¹⁰ A suspension of tryptamine (2.0 g, mmol) and indole-3-carboxaldehyde (1.99 g, mmol) in 5 mL toluene was heated to reflux for 1 h. After this time, the solvents were removed in vacuo, and the viscous residue dissolved in 20 mL CHCl₃. Trifluoroacetic acid (10 mL) was added, and the reaction was stirred for 24 h. The reaction was then neutralized by the addition of Na₂CO₃ (aq) and extracted into CHCl₃ (3 x 100 ml). The combined organic phases were dried over NaSO₄, concentrated, and chromatographed to afford a pale yellow solid, mp: decomposed at 170 °C; ¹H NMR (500 MHz, DMSO-d₆) δ 10.99 (s, 1H), 10.39 (s, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.37 (dd, *J* = 7.8, 2.6 Hz, 2H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 2.4 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.97 (p, *J* = 7.1 Hz, 2H), 6.88 (t, *J* = 7.5 Hz, 1H), 5.44 (s, 1H), 3.20 (dd, *J* = 11.0, 6.0 Hz, 1H), 3.00 (ddd, *J* = 12.4, 7.6, 4.7 Hz, 1H), 2.80 (q, *J* = 7.4, 6.3 Hz, 1H), 2.6-2.7 (m, 1H); ¹³C NMR (126 MHz, DMSO-d₆) δ 137.02, 136.67, 136.20, 127.44, 126.84, 124.87, 121.42, 120.66, 119.93, 118.78, 118.48, 117.89, 116.30, 111.85, 111.49, 107.92, 50.16, 42.41, 22.82; Calc for C₁₉H₁₇N₃ (M+H): 288.1496, found 288.1495.

Tetrahydroquinazolines

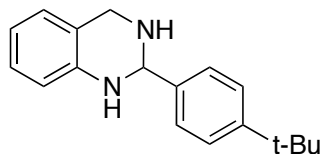


Tetrahydroquinazolines were prepared by condensation of 2-aminobenzylamine with the corresponding aldehyde in MeOH, according to the representative procedure for imine formation, above. Tetrahydroquinazolines exhibit ring-chain tautomerism, resulting in NMR spectra that reflect an equilibrium mixture of species. NMR peak data is given only for the major, ring tautomer unless otherwise indicated.



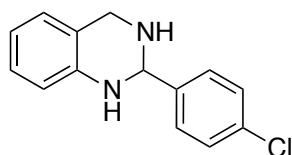
2-phenyl-1,2,3,4-tetrahydroquinazoline

Spectroscopic data match those previously reported.¹¹ Ratio of Ring to Chain (CDCl₃): 15:1; ¹H NMR (400 MHz, CDCl₃) δ 7.56 (m, *J* = 8.8 Hz, 2H), 7.3-7.5 (m, 3H), 7.10 (t, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 7.4 Hz, 1H), 6.77 (t, *J* = 7.4 Hz, 1H), 6.63 (d, *J* = 7.9 Hz, 1H), 5.29 (s, 1H), 4.32 (d, *J* = 16.6 Hz, 1H), 4.04 (d, *J* = 16.7 Hz, 1H), 3.48 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 143.70, 141.49, 128.78, 128.60, 127.33, 126.63, 126.26, 121.20, 118.22, 115.06, 69.60, 46.45.



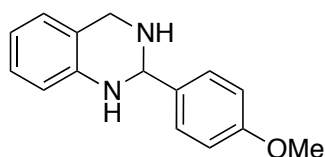
2-(4-tert-butylphenyl)-1,2,3,4-tetrahydroquinazoline

Ratio of Ring to Chain: 13:1 (CDCl₃); mp: 119-122 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.4-7.5 (m, 5H), 7.10 (t, *J* = 7.3 Hz, 1H), 6.99 (d, *J* = 7.4 Hz, 1H), 6.77 (t, *J* = 7.4 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 5.26 (s, 1H), 4.31 (d, *J* = 16.6 Hz, 1H, overlaps with broad peak at 4.24), 4.24 (br s, 1H), 4.04 (d, *J* = 16.6 Hz, 1H), 2.05 (br s, 1H), 1.38 (s, 9H); ¹³C NMR (126 MHz, CDCl₃) δ 151.59, 143.86, 138.66, 127.27, 126.27, 126.24, 125.68, 121.31, 118.10, 115.03, 69.44, 46.65, 34.65, 31.38. EMM (ESI) Calc for C₁₈H₂₂N₂ (M+H): 267.1856, found 267.1844.



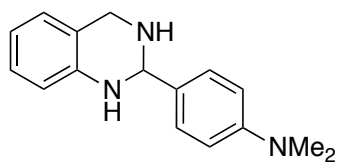
2-(4-chlorophenyl)-1,2,3,4-tetrahydroquinazoline

Spectroscopic data match those previously reported.¹¹ Ratio of Ring to Chain (CDCl₃): 13:1; ¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 7.4 Hz, 1H), 6.77 (td, *J* = 7.5, 1.2 Hz, 1H), 6.63 (d, *J* = 7.9 Hz, 1H), 5.26 (s, 1H), 4.26 (d, *J* = 16.7 Hz, 1H), 3.99 (d, *J* = 16.7 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 143.37, 140.15, 134.20, 128.88, 128.12, 127.38, 126.26, 121.28, 118.42, 115.17, 68.86, 46.15.



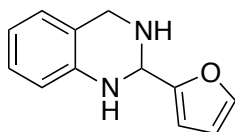
2-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinazoline

Spectroscopic data match those previously reported.¹¹ Ratio of Ring to Chain (CDCl₃): 6:1; ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.9-7.0 (m, 3H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 5.22 (s, 1H), 4.30 (d, *J* = 16.6 Hz, 1H), 4.22 (br s, 1H), 4.02 (d, *J* = 16.6 Hz, 1H), 3.86 (s, 3H), 1.97 (br s, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 159.71, 143.86, 133.93, 127.78, 127.26, 126.23, 121.26, 118.10, 115.02, 114.05, 69.21, 55.36, 46.60.



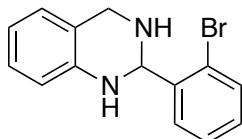
2-(4-N,N-dimethylaminophenyl)-1,2,3,4-tetrahydroquinazoline

Spectroscopic data match those previously reported.¹¹ Ratio of Ring to Chain (CDCl₃): 2:1; ¹H NMR (400 MHz, CDCl₃) δ 8.26 (s, 1H chain tautomer), 7.65 (d, *J* = 8.8 Hz, 2H chain tautomer), 7.41 (d, *J* = 8.6 Hz, 2H ring tautomer), 7.05-7.15 (m, 1H ring tautomer + 1H chain tautomer), 6.98 (d, *J* = 7.4 Hz, 2H chain tautomer), 6.8-6.65 (m, 4H ring tautomer + 3H chain tautomer), 6.60 (d, *J* = 7.9 Hz, 1H, ring tautomer), 5.20 (s, 1H ring tautomer), 4.74 (s, 2H chain tautomer), 4.32 (d, *J* = 16.6 Hz, 1H ring tautomer), 4.19 (s, 1H ring tautomer), 4.04 (d, *J* = 16.5 Hz, 1H ring tautomer), 3.05 (s, 6H chain tautomer), 3.00 (s, 6H ring tautomer). ¹³C NMR (126 MHz, CDCl₃) δ 161.17, 152.13, 150.79, 145.93, 144.10, 129.66, 129.50, 129.15, 128.21, 127.34, 127.19, 126.21, 125.11, 124.24, 121.24, 118.16, 117.87, 115.84, 114.91, 112.55, 111.61, 111.55, 69.40, 63.68, 46.81, 40.65, 40.24 (includes both ring and chain tautomers).



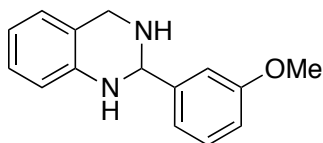
2-(furan-2-yl)-1,2,3,4-tetrahydroquinazoline

Spectroscopic data match those previously reported.¹² Ratio of Ring to Chain (CDCl₃): 18:1; ¹H NMR (400 MHz, CDCl₃) δ 7.45 (t, *J* = 1.2 Hz, 1H), 7.09 (td, *J* = 7.7, 1.5 Hz, 1H), 6.95 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.77 (td, *J* = 7.4, 1.2 Hz, 1H), 6.61 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.35-6.5 (m, 2H), 5.34 (s, 1H), 4.40 (s, 1H), 4.18 (d, *J* = 16.7 Hz, 1H), 3.96 (d, *J* = 16.7 Hz, 1H), 2.07 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 154.12, 142.89, 142.35, 127.35, 126.23, 121.46, 118.48, 115.35, 110.33, 106.70, 63.78, 45.49.



2-(2'-bromophenyl)-1,2,3,4-tetrahydroquinazoline

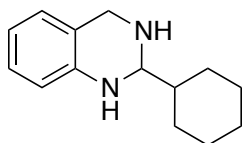
Isolated as a viscous pale yellow oil. Ratio of Ring to Chain (CDCl₃): 48:1; ¹H NMR (500 MHz, CDCl₃) δ 7.64 (d, *J* = 8.3 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.24 (td, *J* = 7.7, 1.7 Hz, 1H), 7.11 (t, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 5.60 (s, 1H), 4.28 (d, *J* = 16.5 Hz, 1H), 3.99 (d, *J* = 16.6 Hz, 1H), 3.0-3.8 (br s, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 143.79, 140.15, 133.30, 133.29, 129.95, 127.90, 127.88, 127.39, 126.37, 123.30, 121.32, 118.42, 115.26, 68.56, 46.24; EMM (ESI) Calc for C₁₄H₁₃BrN₂ (M+H): 289.0335, found 289.0339.



2-(3-methoxyphenyl)-1,2,3,4-tetrahydroquinazoline

Viscous yellow oil. Ratio of Ring to Chain (CDCl₃): 4:1; ¹H NMR (400 MHz, CDCl₃) δ 7.3-7.4 (m, 1H), 7.05-7.2 (m, 3H), 6.99 (dt, *J* = 7.5, 1.2 Hz, 1H), 6.94 (ddd, *J* = 8.3, 2.6,

1.0 Hz, 1H), 6.77 (td, $J = 7.4, 1.2$ Hz, 1H), 6.63 (dd, $J = 8.1, 1.2$ Hz, 1H), 5.24 (s, 1H), 4.30 (d, $J = 16.6$ Hz, 1H), 4.03 (d, $J = 16.6$ Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 159.99, 143.68, 143.18, 129.84, 127.33, 126.27, 121.24, 118.92, 118.23, 115.11, 114.29, 111.96, 69.58, 55.34, 46.51. Calc for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}$ (M+H): 241.1336, found 241.1334.

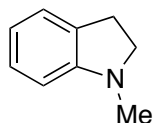


2-cyclohexyl-1,2,3,4-tetrahydroquinazoline

Chain tautomer not observed (CDCl_3); mp: 65-67 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.04 (t, $J = 7.3$ Hz, 1H), 6.92 (d, $J = 7.4$ Hz, 1H), 6.70 (t, $J = 7.4$ Hz, 1H), 6.55 (d, $J = 8.0$ Hz, 1H), 4.15 (d, $J = 16.6$ Hz, 1H), 3.99 (d, $J = 15.7$ Hz, 1H, overlaps with peak at 3.98), 3.98 (s, 1H), 1.9-2.0 (m, 1H), 1.7-1.9 (m, 4H), 1.4-1.6 (m, 1H), 1.0-1.4 (m, 5H); ^{13}C NMR (126 MHz, CDCl_3) δ 144.04, 127.15, 126.09, 121.74, 117.74, 114.96, 71.04, 46.74, 42.87, 28.27, 27.99, 26.52, 26.21, 26.18. EMM (ESI) Calc for $\text{C}_{14}\text{H}_{20}\text{N}_2$ (M+H): 217.1700, found 217.1699.

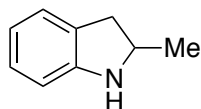
Indolines

Indoline was obtained from commercial sources (Sigma Aldrich), and was used as received without further purification. Methylindolines were prepared by reduction of the corresponding indole using excess NaCNBH_3 in acetic acid, according to literature methods.¹³



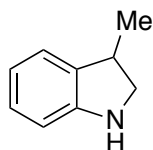
1-methylindoline

Spectroscopic data match those previously reported.¹⁴ ^1H NMR (400 MHz, CDCl_3) δ 7.1-7.2 (m, 2H), 6.75 (t, $J = 7.6$ Hz, 1H), 6.53 (d, $J = 8.0$ Hz, 1H), 3.32 (t, $J = 8.1$ Hz, 2H), 2.97 (t, $J = 8.1$ Hz, 2H), 2.79 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 153.41, 130.37, 127.36, 124.31, 117.88, 107.35, 56.22, 36.37, 28.80.



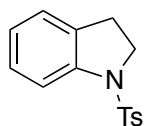
2-methylindoline

Spectroscopic data match those previously reported.¹⁴ ^1H NMR (400 MHz, CDCl_3) δ 7.08 (d, $J = 8.8$ Hz, 1H), 7.02 (td, $J = 7.7, 1.4$ Hz, 1H), 6.70 (td, $J = 7.4, 1.0$ Hz, 1H), 6.61 (d, $J = 7.7$ Hz, 1H), 4.00 (ddq, $J = 8.6, 7.8, 6.2$ Hz, 1H), 3.78 (br s, NH), 3.15 (dd, $J = 15.4, 8.5$ Hz, 1H), 2.65 (dd, $J = 15.5, 7.8$ Hz, 1H), 1.30 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 150.98, 128.91, 127.25, 124.74, 118.54, 109.19, 55.25, 37.79, 22.32.



3-methylindoline

Spectroscopic data match those previously reported.¹³ ¹H NMR (400 MHz, CDCl₃) δ 7.10 (d, *J* = 7.2 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.75 (td, *J* = 7.4, 1.0 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 3.71 (t, *J* = 8.6 Hz, 1H, overlaps with NH), 3.5-3.3 (m, 1H), 3.12 (t, *J* = 8.6 Hz, 1H), 1.34 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 151.25, 134.35, 127.30, 123.38, 118.70, 109.52, 55.47, 36.66, 18.66.

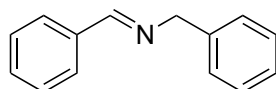


N-toluenesulfonylindoline

Spectroscopic data match those previously reported.¹⁵ ¹H NMR (300 MHz, CDCl₃) δ 7.7-7.6 (m, 3H), 7.24-7.13 (m, 3H), 7.07 (ddd, *J* = 7.4, 1.5, 0.7 Hz, 1H), 6.96 (td, *J* = 7.4, 1.0 Hz, 1H), 3.91 (t, *J* = 8.4 Hz, 2H), 2.87 (t, *J* = 8.8 Hz, 2H), 2.36 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 144.23, 142.22, 134.27, 131.96, 129.85, 127.91, 127.53, 125.30, 123.91, 115.23, 50.15, 28.10, 21.74.

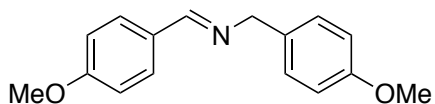
Characterization of Products

Acyclic imines



N-benzylidenebenzylamine, **4**

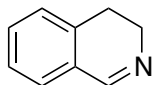
Spectroscopic data match those previously reported.¹⁶ ¹H NMR (300 MHz, CDCl₃) δ 8.37 (s, 1H), 7.78 (m, 2H), 7.21-7.41 (m, 8H), 4.81 (s, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 162.21, 139.56, 136.42, 131.00, 128.83, 128.73, 128.52, 128.22, 127.22, 65.29.



N-(4-methoxybenzylidene)-4-methoxybenzylamine, **5**

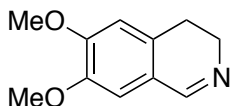
Spectroscopic data match those previously reported.¹⁶ ¹H NMR (300 MHz, CDCl₃) δ 8.30 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 6.8-6.9 (m, 4H), 4.73 (s, 2H), 3.83 (s, 3H), 3.79 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 161.90, 161.12, 158.87, 131.92, 130.02, 129.39, 114.19, 114.12, 64.62, 55.56, 55.51.

3,4-Dihydroisoquinolines



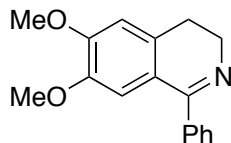
3,4-dihydroisoquinoline, **2**

Spectroscopic data matches those reported in the literature.¹⁷ ¹H NMR (400 MHz, CDCl₃) δ 8.28 (br s, 1H), 7.2-7.3 (m, 3H, overlaps with CDCl₃ residual peak), 7.08 (d, *J* = 8.8 Hz, 1H), 3.70 (td, *J* = 8.0, 1.6 Hz, 2H), 2.68 (t, *J* = 8.0 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 160.83, 136.37, 131.30, 128.45, 127.49, 127.44, 127.17, 47.34, 25.06.



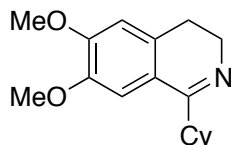
3,4-dihydro-6,7-dimethoxyisoquinoline, **6**

Using workup method B. From 194.6 mg substrate, 176.1 mg (91% yield) of the title compound was collected as a viscous oil. Spectroscopic data matches those reported in the literature.¹⁸ ¹H NMR (400 MHz, CDCl₃) δ 8.21 (br s, 1H), 6.79 (s, 1H), 6.65 (s, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.71 (t, *J* = 7.6 Hz, 2H), 2.66 (t, *J* = 7.6 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 159.69, 151.23, 147.85, 129.90, 121.54, 110.40, 110.38, 56.15, 56.07, 47.35, 24.78; EMM (ESI) Calc for C₁₁H₁₃NO₂ (M+H): 192.1020, found 192.1019.



1-phenyl-3,4-dihydro-6,7-dimethoxyisoquinoline, **7**

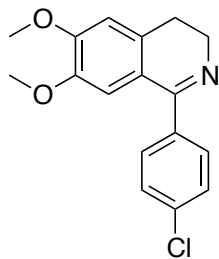
Using workup method B. From 269.0 mg of starting material, 260.7 mg (97.5%) of the title compound was obtained as a white solid, mp: 119-121 °C. Spectroscopic data matches those reported in the literature.¹⁹ ¹H NMR (400 MHz, CDCl₃) δ 7.60 (m, 2H), 7.43 (m, 3H), 6.79 (d, *J* = 5.6 Hz, 2H), 3.95 (s, 3H), 3.81 (t, *J* = 7.2 Hz, 2H), 3.72 (s, 3H), 2.73 (t, *J* = 7.2 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 166.72, 150.90, 147.10, 139.24, 132.63, 129.32, 128.80, 128.20, 121.63, 111.56, 110.28, 56.18, 56.07, 47.76, 26.05; EMM (ESI) Calc for C₁₇H₁₇NO₂ (M+H): 268.1333, found 268.1327.



1-cyclohexyl-3,4-dihydro-6,7-dimethoxyisoquinoline, **8**

Using workup method B. From 274.8 mg starting material, 244.3 mg (89.5% yield) was obtained as a colorless oil that eventually solidifies to an off-white solid; mp: 78-80 °C. Spectroscopic data matches those reported in the literature.²⁰ ¹H NMR (400 MHz, CDCl₃) δ 6.99 (s, 1H), 6.65 (s, 1H), 3.87 (s, 6H), 3.58 (t, *J* = 7.2 Hz, 2H), 2.77 (t, *J* = 10 Hz, 1H), 2.53 (t, *J* = 7.2 Hz, 2H), 1.6-1.9 (m, 5H), 1.2-1.5 (m, 5H); ¹³C NMR (101 MHz, CDCl₃) δ 170.15, 150.55, 147.43, 132.09, 121.69, 110.48, 108.68, 56.38, 55.94, 46.96,

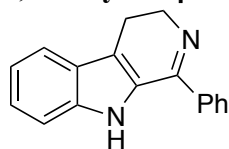
42.27, 31.35, 26.62, 26.32, 26.04; EMM (ESI) Calc for C₁₇H₂₃NO₂ (M+H): 274.1802, found 274.1795.



1-(4-chlorophenyl)-3,4-dihydro-6,7-dimethoxyisoquinoline, 9

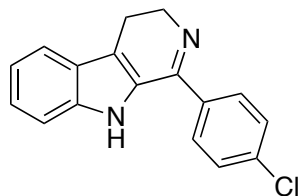
Using workup method B. From 304.8 mg starting material, 284.9 mg (94.0% yield) was obtained as a white crystalline solid, mp: 125-127 °C. Spectroscopic data matches those reported in the literature.²¹ ¹H NMR (500 MHz, CDCl₃) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 6.77 (s, 1H), 6.73 (s, 1H), 3.94 (s, 3H), 3.79 (t, *J* = 8.0 Hz, 2H), 3.73 (s, 3H), 2.72 (t, *J* = 8.0 Hz, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 165.77, 151.09, 147.18, 137.58, 135.39, 132.67, 130.20, 128.45, 121.20, 111.18, 110.35, 56.18, 56.09, 47.69, 25.96; EMM (ESI) Calc for C₁₇H₁₆ClNO₂ (M+H): 302.0943, found 302.0934.

3,4-Dihydro-β-carbolines



1-phenyl-3,4-dihydro-β-carboline, 11

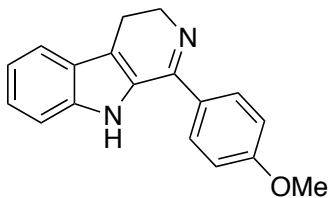
Using workup method A or B. From 249.1 mg of starting material, 200.0 mg collected (80.9% yield) as a pale yellow solid, mp: 211-214 °C. Spectroscopic data matches those reported in the literature.²² ¹H NMR (400 MHz, CDCl₃) δ 8.23 (s, NH), 7.77 (m, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.5-7.6 (m, 3H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 4.08 (t, *J* = 8.4 Hz, 2H), 3.01 (t, *J* = 8.4 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 159.33, 137.67, 136.47, 130.00, 128.90, 127.85, 127.81, 125.63, 124.63, 120.46, 120.06, 117.89, 112.01, 48.98, 19.29; EMM (ESI) Calc for C₁₇H₁₄N₂ (M+H): 247.1230, found 247.1224.



1-(4'-chlorophenyl)-3,4-dihydro-β-carboline, 12

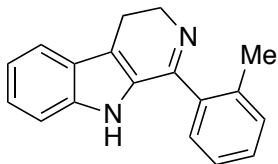
Using workup method A. From 283.9 mg of starting material, 197.3 mg were collected (70% yield) as a light yellow solid, mp: 220-222 °C. Spectroscopic data matches those reported in the literature.⁸ ¹H NMR (400 MHz, CDCl₃) δ 8.08 (br s, NH), 7.65-7.7 (m, 3H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 4.04 (t, *J* = 8.4 Hz, 2H), 2.97 (t, *J* = 8.4 Hz, 2H); ¹³C NMR (101 MHz,

CDCl₃) δ 158.31, 136.55, 136.14, 136.04, 129.23, 129.14, 127.45, 125.61, 124.88, 120.64, 120.12, 118.32, 112.03, 48.99, 19.24; EMM (ESI) Calc for C₁₇H₁₃ClN₂ (M+H): 281.0841, found 281.0835.



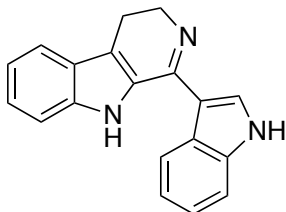
1-(4-methoxyphenyl)-3,4-dihydro- β -carboline, 13

Using workup method A or B. From 277.6 mg of starting material; 241.4 mg collected (87.6% yield) as a pale white solid, mp: 196-197 °C. Spectroscopic data matches those reported in the literature.²² ¹H NMR (400 MHz, CDCl₃) δ 8.18 (br s, NH), 7.70 (d, J = 8.8 Hz, 2H) 7.65 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.28 (t, J = 7.2 Hz, 1H overlaps with CDCl₃ residual peak), 7.18 (t, J = 7.2 Hz, 1H) 7.00 (d, J = 8.8 Hz, 2H), 4.00 (t, J = 8.4 Hz, 2H), 3.86 (s, 3H), 2.95 (t, J = 8.4 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 161.10, 158.70, 136.40, 130.24, 129.33, 127.97, 125.68, 124.52, 120.42, 120.01, 117.89, 114.22, 111.98, 55.46, 48.81, 19.30; EMM (ESI) Calc for C₁₈H₁₆N₂O (M+H): 277.1336, found 277.1326.



1-(2-methylphenyl)-3,4-dihydro- β -carboline, 14

Using workup method B. From 263.7 mg of starting material, 240.7 mg (91% yield) were collected as an off-white solid, decomposed above 180 °C. This compound has been previously reported, but full spectroscopic data have not been reported.⁹ ¹H NMR (500 MHz, CDCl₃) δ 7.87 (s, NH), 7.66 (d, J = 8.0 Hz, 1H), 7.38 (m, 2H), 7.25-7.35 (m, 4H, overlaps with CDCl₃ residual peak), 7.18 (m, 1H), 4.12 (t, J = 8.5 Hz, 2H), 3.04 (t, J = 8.5 Hz, 2H), 2.28 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 160.45, 136.96, 136.56, 136.23, 130.89, 129.21, 128.63, 128.28, 126.10, 125.67, 120.46, 120.12, 116.80, 111.99 48.90, 19.50, 19.33; EMM (ESI) Calc for C₁₈H₁₆N₂ (M+H): 261.1308, found 261.1303.

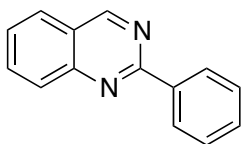


Isoeudistomin U, 15

Using workup method B. Bright yellow solid, slow decomposition >200 °C; Spectroscopic data match those previously reported.^{23,24} ¹H NMR (400 MHz, MeOD-d₄ + 1 drop TFA-d₁) δ 8.30 (s, 1H), 7.93 (d, J = 7.2 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.3-7.45 (m, 3H), 7.19 (t, J = 7.6 Hz, 1H), 4.00

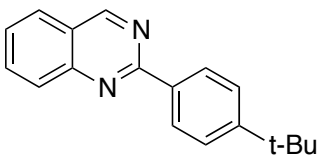
(t, $J = 8.0$ Hz, 2H), 3.29 (m, 2H, overlaps with MeOD- d_4 residual peak); ^{13}C NMR (101 MHz, MeOD- d_4 + 1 drop TFA- d_1) δ 157.04, 137.78, 141.44, 136.53, 128.00, 125.22, 124.98, 124.92, 124.41, 124.92, 124.41, 124.35, 122.89, 121.44, 120.97, 119.57, 112.98, 112.84, 106.00, 41.25, 19.26; EMM (ESI) Calc for $\text{C}_{19}\text{H}_{15}\text{N}_3$ (M+H): 286.1339, found 286.1350.

Quinazolines



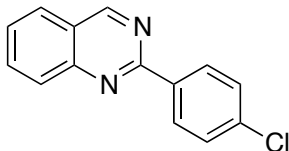
2-phenylquinazoline, **16**

Spectroscopic data matches those reported in the literature.²⁶ Using workup method A. From 210.2 mg of starting material, 174.0 mg (84.4% yield) were isolated as a bright yellow flaky solid, mp: 96-100 °C. ^1H NMR (400 MHz, CDCl_3) δ 9.45 (s, 1H), 8.61 (dd, $J = 8.0, 1.2$ Hz, 2H), 8.08 (d, $J = 8.4$ Hz, 1H), 7.8-7.9 (m, 2H), 7.48-7.62 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 161.13, 160.55, 150.83, 138.09, 134.16, 130.66, 128.70, 128.62, 127.32, 127.18, 123.66; EMM (ESI) Calc for $\text{C}_{14}\text{H}_{10}\text{N}_2$ (M+H): 207.0917, found 207.0921.



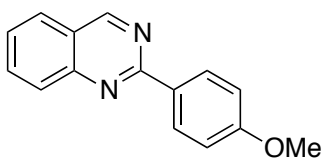
2-(4-tert-butylphenyl)quinazoline, **17**

Using workup method B. From 270 mg of starting material, 226.8 mg (85.3% yield) were collected as a white crystalline solid, mp: 90-91 °C. ^1H NMR (400 MHz, CDCl_3) δ 9.45 (s, 1H), 8.53 (d, $J = 8.4$ Hz, 1H), 8.08 (d, $J = 8.8$ Hz, 1H), 7.8-7.9 (m, 2H), 7.5-7.6 (m, 3H), 1.39 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 161.20, 160.48, 153.99, 150.88, 135.37, 134.04, 128.67, 128.40, 127.16, 127.06, 125.68, 123.56, 34.93, 31.33; EMM (ESI) Calc for $\text{C}_{18}\text{H}_{18}\text{N}_2$ (M+H): 263.1543, found 263.1548.



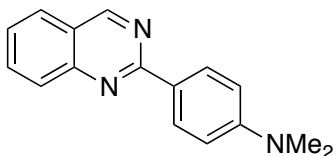
2-(4-chlorophenyl)quinazoline, **18**

Spectroscopic data matches those reported in the literature.²⁶ From 248.1 mg of starting materials, 199.6 mg (81.8% yield) were collected as a fine white crystalline solid; mp: 136-137 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.48 (s, 1H), 8.62 (d, $J = 8.4$ Hz, 2H), 8.10 (d, $J = 8.0$ Hz, 1H), 7.94-7.98 (m, 2H), 7.66 (t, $J = 7.2$ Hz, 1H), 7.35 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 160.59, 160.11, 150.75, 136.89, 136.58, 134.32, 129.94, 128.88, 128.66, 127.52, 127.21, 123.68; EMM (ESI) Calc for $\text{C}_{14}\text{H}_9\text{ClN}_2$ (M+H): 241.0528, found 241.0524.



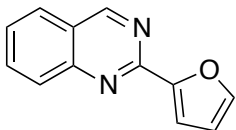
2-(4-methoxyphenyl)-quinazoline, 19

Spectroscopic data matches those reported in the literature.²⁶ From 240 mg of starting material, 151.4 mg (64% yield) as a pale yellow crystalline solid; mp: 92-94 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.45 (s, 1H), 8.61 (d, *J* = 9.2 Hz, 2H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.89-7.93 (m, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.35 (d, *J* = 8.8 Hz, 2H), 3.93 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 161.88, 160.92, 160.44, 150.89, 134.07, 130.78, 130.25, 128.47, 127.18, 126.83, 123.36, 114.02, 55.44; EMM (ESI) Calc for C₁₅H₁₂N₂O (M+H): 237.1023, found 237.1025.



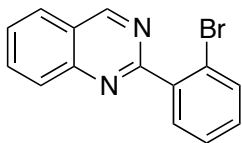
2-(4-(*N,N*-dimethylamino)-phenyl)-quinazoline, 20

This compound has been previously reported.²⁵ Bright yellow needles, mp: 136-138.5 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.36 (s, 1H), 8.51 (d, *J* = 9.2 Hz, 2H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.8-7.9 (m, 2H), 7.49 (t, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 9.2 Hz, 2H), 3.06 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 161.53, 160.27, 152.20, 151.07, 133.86, 129.93, 128.23, 127.17, 126.14, 125.74, 123.11, 111.79, 40.31; EMM (ESI) Calc for C₁₆H₁₅N₃ (M+H): 250.1339, found 250.1334.



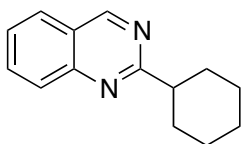
2-(Furan-2-yl)quinazoline, 21

Using workup method A. From 200.7 mg of starting materials, 159.0 mg (81% yield) of the title compound was collected as pale orange needles, mp: 128-130 °C. Spectroscopic data match those previously reported.²⁶ ¹H NMR (400 MHz, CDCl₃) δ 9.37 (s, 1H), 8.09 (d, *J* = 9.2 Hz, 1H), 7.8-7.9 (m, 2H), 7.68 (dd, *J* = 3.6, 2.4 Hz, 1H), 7.59 (td, *J* = 6.9, 0.8 Hz, 1H), 7.45 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.61 (dd, *J* = 3.6, 2.0 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 160.79, 154.16, 152.56, 150.48, 145.40, 134.56, 128.45, 127.32, 123.42, 114.14, 112.37; EMM (ESI) Calc for C₁₂H₈N₂O (M+H): 197.0710, found 197.0707.



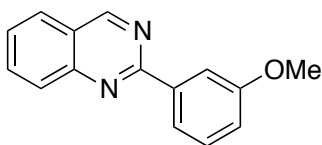
2-(2-bromophenyl)-quinazoline, 22

From 303 mg of starting material, 254.1 mg (85% yield) of the title compound was obtained as a pale yellow viscous oil; ^1H NMR (400 MHz, CDCl_3) δ 9.51 (s, 1H), 8.11 (dd, $J = 8.4, 0.8$ Hz, 1H), 7.9-8.0 (m, 2H), 7.77 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.71 (dd, $J = 8.4, 1.2$ Hz, 1H), 7.66 (dt, $J = 8.0, 1.2$ Hz, 1H), 7.44 (dt, $J = 7.6, 1.2$ Hz, 1H), 7.28 (dt, $J = 7.6, 1.6$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 162.85, 160.30, 150.31, 140.22, 134.47, 133.75, 131.74, 130.47, 128.66, 128.13, 127.53, 127.21, 123.33, 121.97; EMM (ESI) Calc for $\text{C}_{14}\text{H}_9\text{BrN}_2$ (M+H): 285.0022, found 285.0013.



2-cyclohexylquinazoline, 23

From 216.3 mg starting material, 161.9 mg (76.3% yield) of the title compound was recovered as a glassy colorless solid, mp: 34-37 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.27 (s, 1H), 7.90 (d, $J = 8.8$ Hz, 1H), 7.7-7.8 (m, 2H), 7.49 (t, $J = 6.8$ Hz, 1H), 2.97 (tt, $J = 11.6, 3.6$ Hz, 1H), 2.00 (m, 2H), 1.6-1.8 (m, 5H), 1.2-1.4 (m, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.97, 160.42, 150.44, 133.87, 128.08, 127.07, 126.84, 123.31, 47.99, 31.99, 26.36, 26.07; EMM (ESI) Calc for $\text{C}_{14}\text{H}_{16}\text{N}_2$ (M+H): 213.1387, found 213.1387.

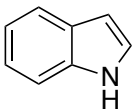


2-(3-methoxyphenyl)quinazoline, 24

Spectroscopic data matches those reported in the literature.²⁷ From 239.3 mg starting material, 169.8 mg (72% yield) of the title compound was obtained as a white crystalline solid, mp: 78-80 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.45 (s, 1H), 8.14 (dt, $J = 8.0, 1.2$ Hz, 1H), 8.10 (m, 1H), 8.00 (d, $J = 8.4$ Hz, 1H), 7.8-7.85 (m, 2H), 7.51 (td, $J = 7.6, 1.2$ Hz, 1H), 7.36 (t, $J = 8.0$ Hz, 1H), 6.97 (ddd, $J = 8.4, 2.8, 0.8$ Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 160.88, 160.48, 160.07, 150.07, 139.56, 134.14, 129.69, 128.72, 127.35, 127.16, 123.70, 121.20, 117.30, 113.06, 55.50; EMM (ESI) Calc for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}$ (M+H): 237.1023, found 237.1032.

Indoles

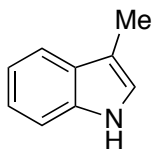
The reaction procedure for the oxidation of indoles was identical to that described above, except that 1.0 mol % ZnI_2 and 1.0 mol % PPTS were used. Workup method A was employed in all instances.



Indole, 25

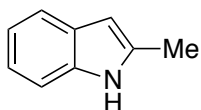
From 112 μl of indoline, using workup method A, obtained 95.1 mg (81.2% yield) of indole. Spectroscopic data were identical to commercially available material. ^1H NMR (400 MHz, CDCl_3) δ 8.01 (br s, NH), 7.64 (d, $J = 7.6$ Hz, 1H), 7.35 (d, $J = 8.4$ Hz, 1H),

7.1-7.25 (m, 3H), 6.54 (t, $J = 2.0$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 135.84, 127.91, 124.26, 122.06, 120.82, 119.90, 111.14, 102.65; EMM (EI) Calc for $\text{C}_8\text{H}_7\text{N}$ (M+H): 117.0573, found 117.1579.



3-methylindole, 26

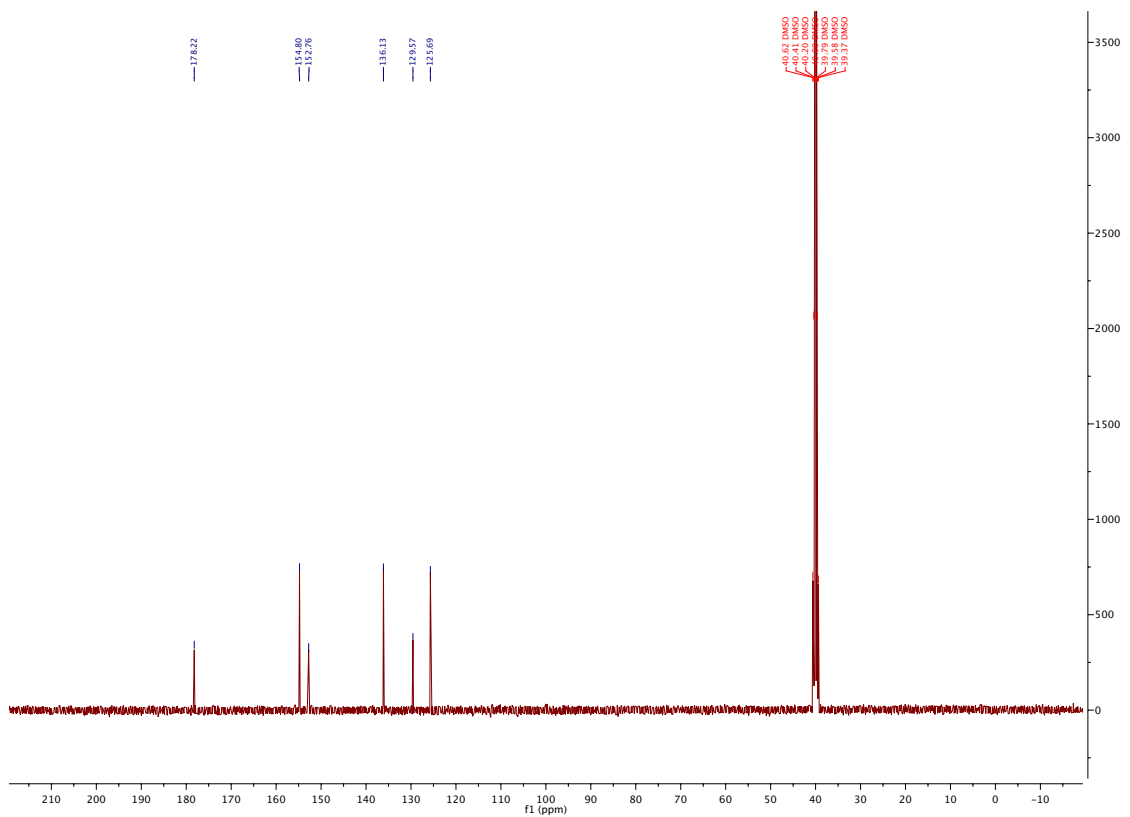
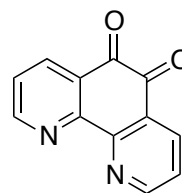
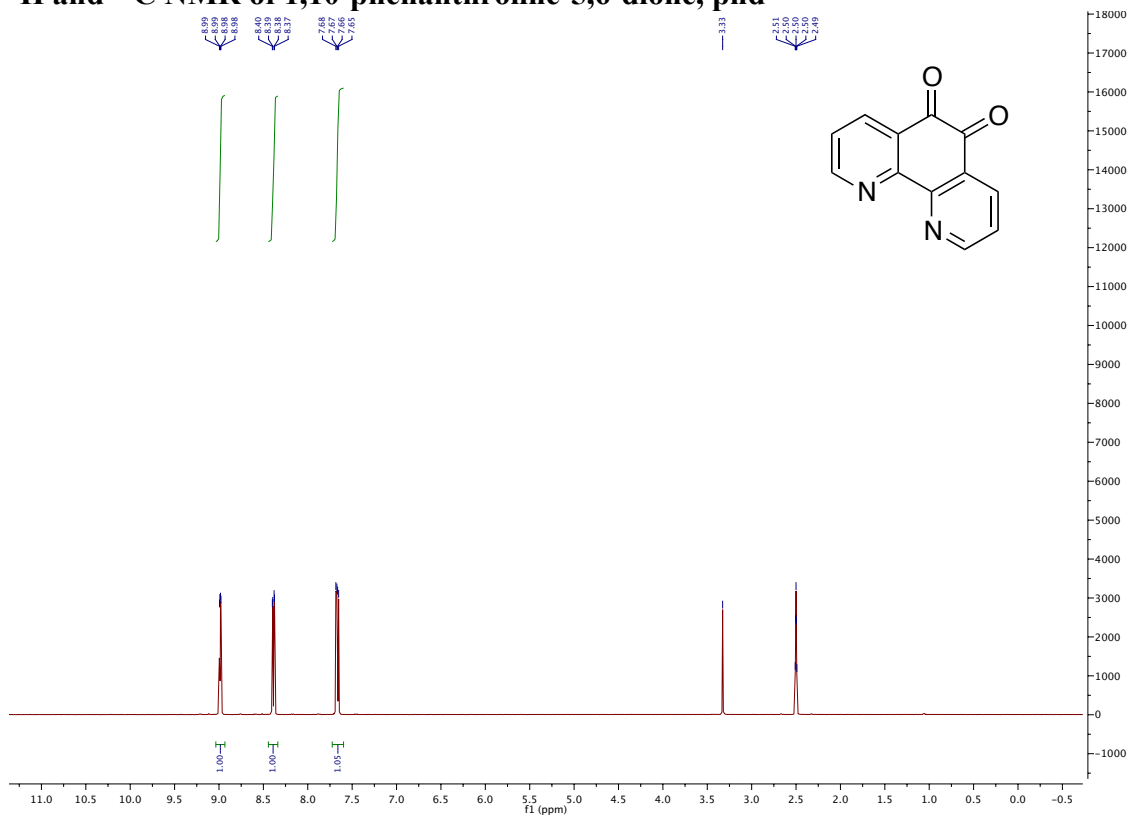
From 135.4 mg of 3-methylindoline, using workup method A, obtained 106.6 mg (79.9% yield) of 3-methylindole as a white solid; mp 95-97 °C to red oil; ^1H NMR (400 MHz, CDCl_3) δ 7.73 (m, 2H), 7.41 (d, $J = 7.6$ Hz, 1H), 7.34 (t, $J = 6.8$ Hz, 1H), 7.28 (t, $J = 7.2$ Hz, 1H), 7.01 (s, 1H), 2.48 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 136.36, 128.39, 121.99, 121.79, 119.25, 118.98, 111.74, 111.13, 9.82; EMM (EI) Calc for $\text{C}_9\text{H}_9\text{N}$ (M+H): 131.0730, found 131.0726. Spectroscopic data were identical to commercially available material.



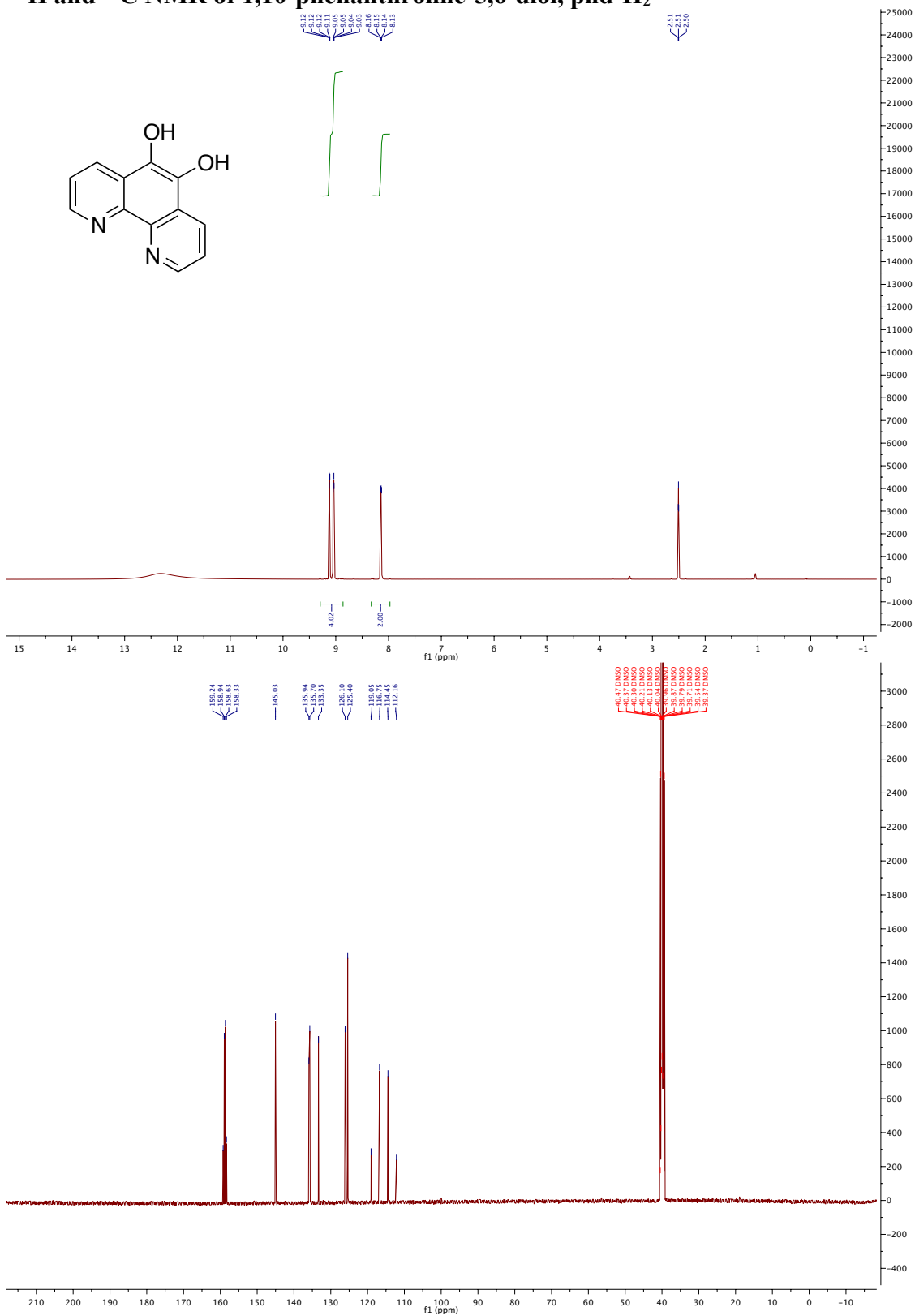
2-methylindole, 27

From 137.6 mg of the corresponding 2-methylindoline, using workup method A, obtained 124.9 mg as a mixture of product and starting material. This mixture was dissolved in hot hexanes, precipitating out 99.0 mg (73% yield) of title compound as white crystals; mp 58-59°C; ^1H NMR (500 MHz, CDCl_3) δ 7.65 (br s, NH), 7.52 (d, $J = 7.5$ Hz, 1H), 7.29 (d, $J = 8.0$ Hz, 1H), 7.05-7.15 (m, 2H), 6.23 (br s, 1H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 136.07, 135.06, 129.10, 120.96, 119.66, 110.22, 100.43, 13.77; EMM (EI) Calc for $\text{C}_9\text{H}_9\text{N}$ (M+H): 131.0730, found 131.0726. Spectroscopic data were identical to commercially available material.

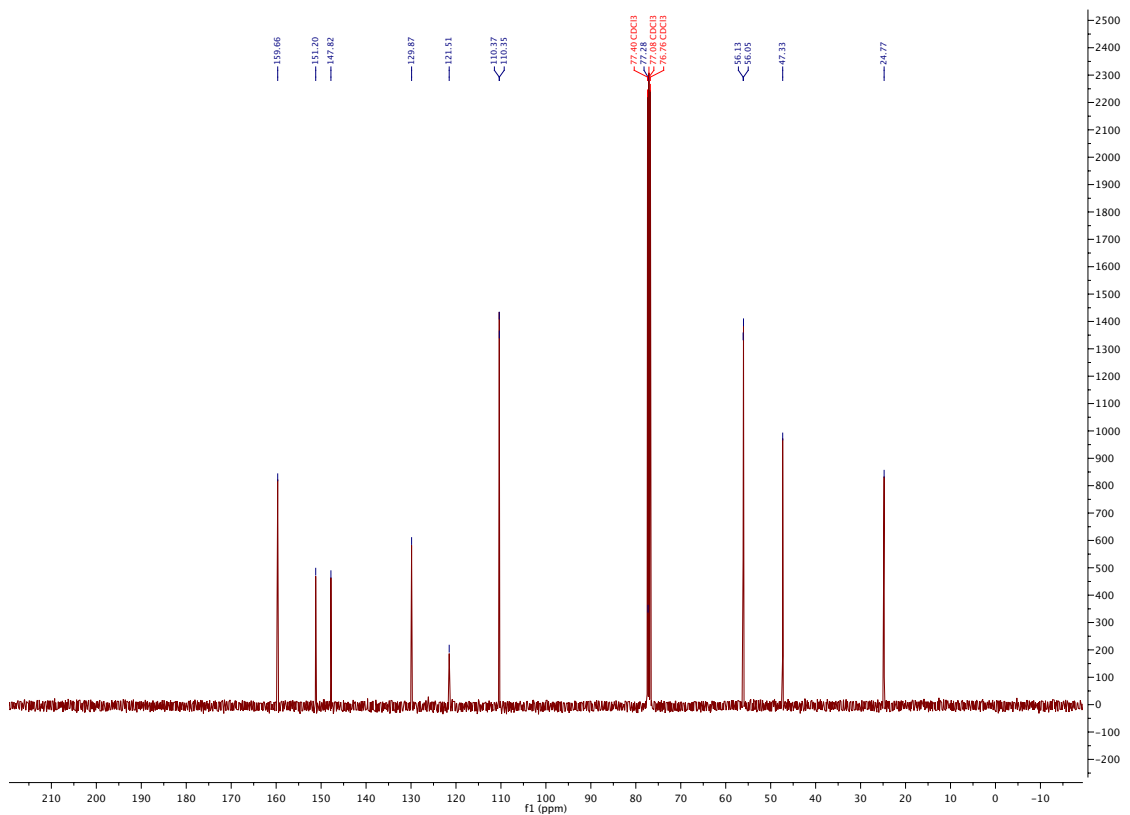
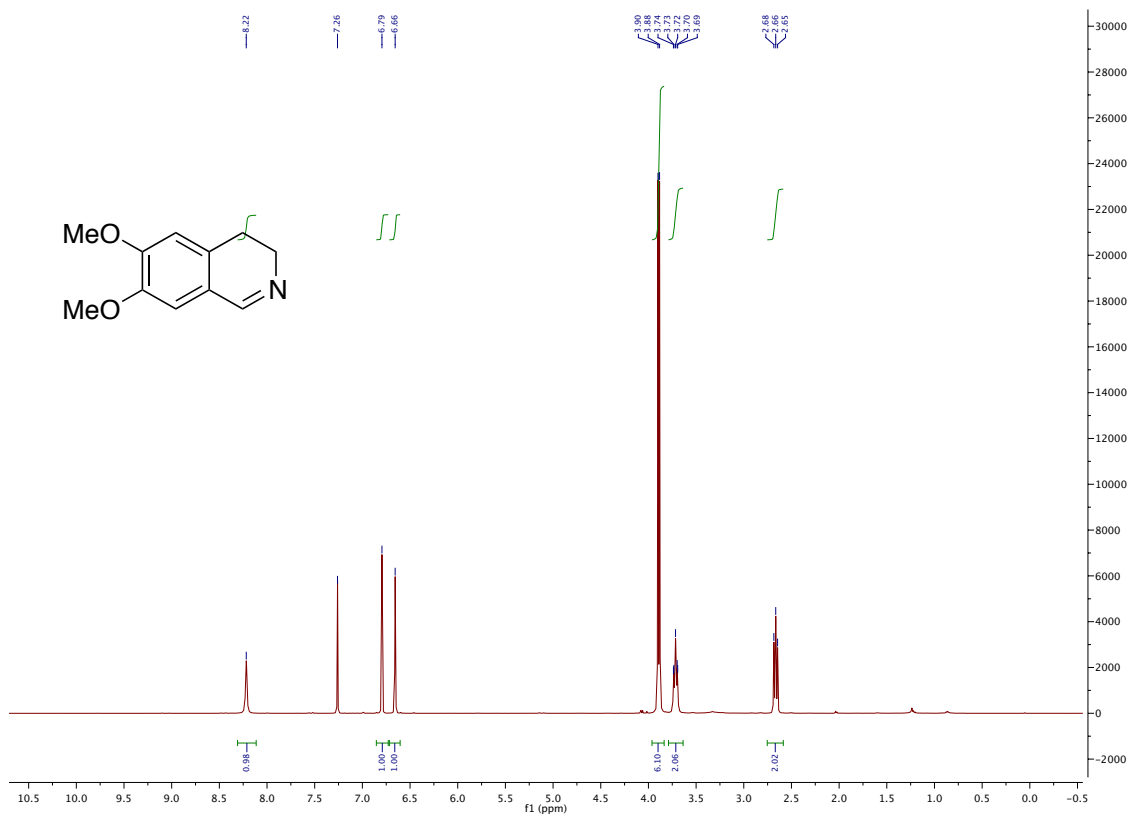
^1H and ^{13}C NMR of 1,10-phenanthroline-5,6-dione, phd

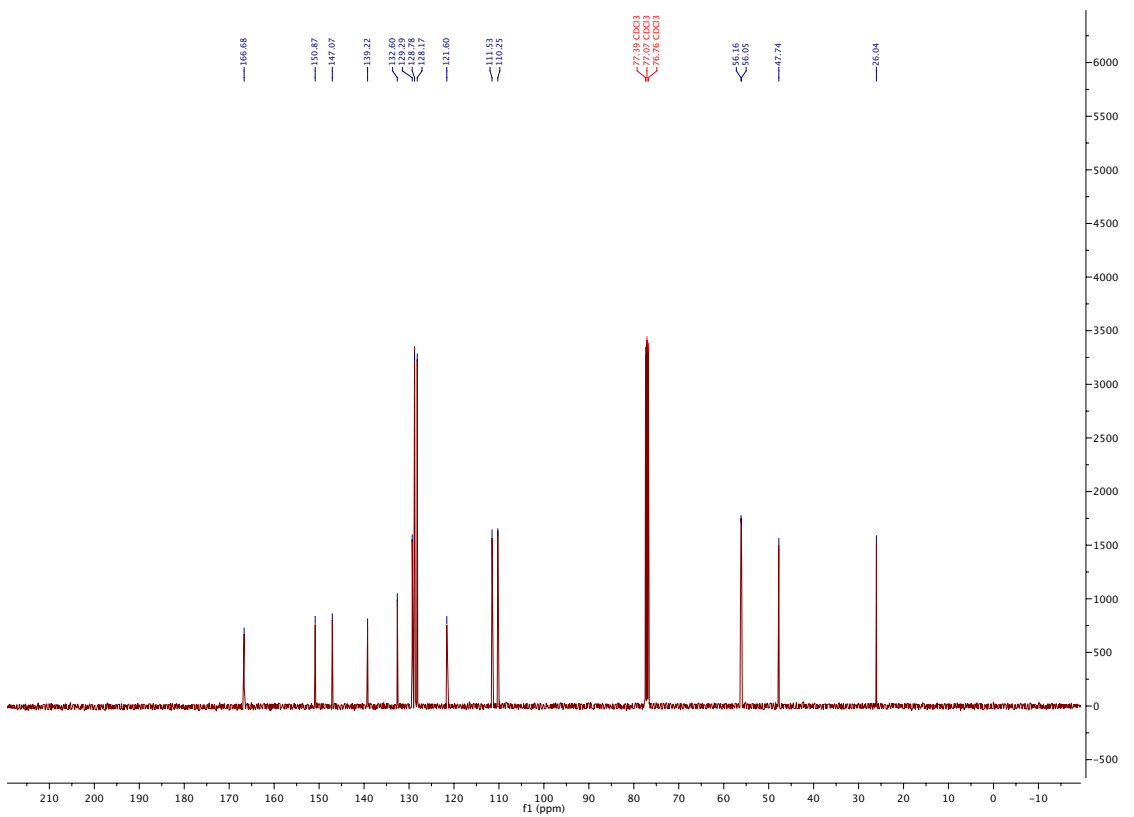
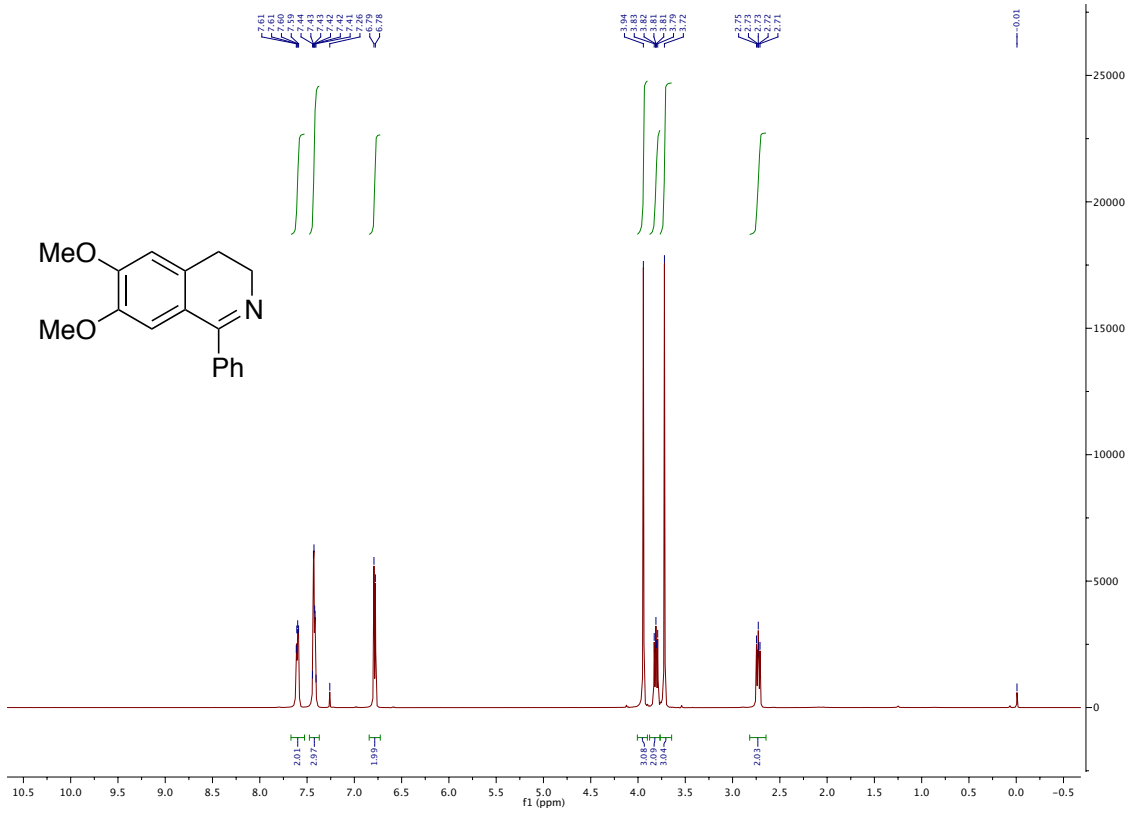


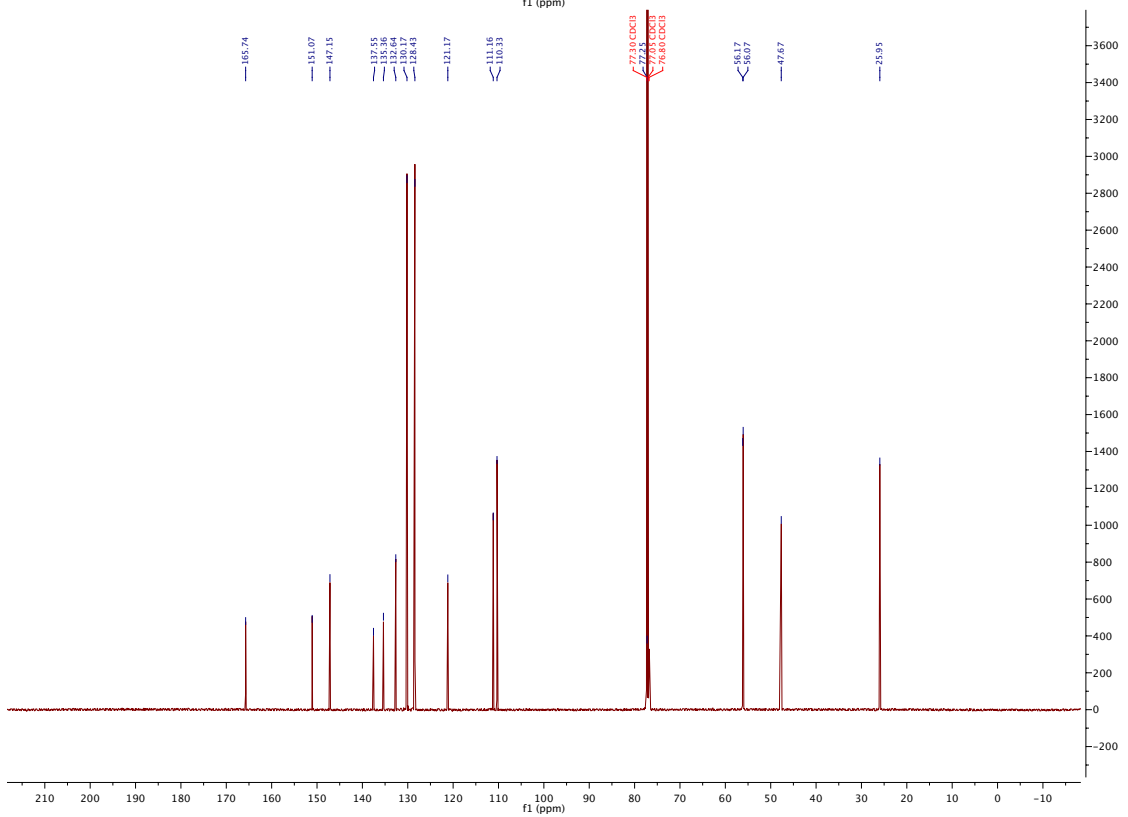
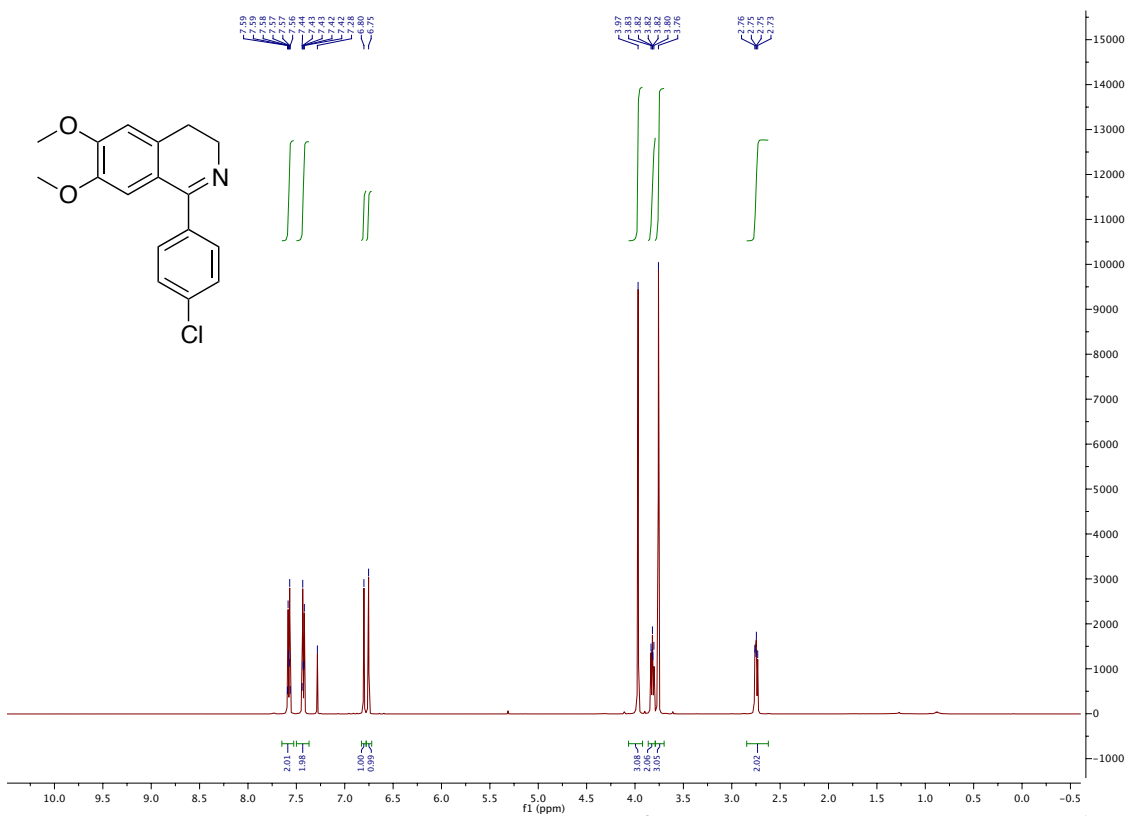
^1H and ^{13}C NMR of 1,10-phenanthroline-5,6-diol, phd-H₂

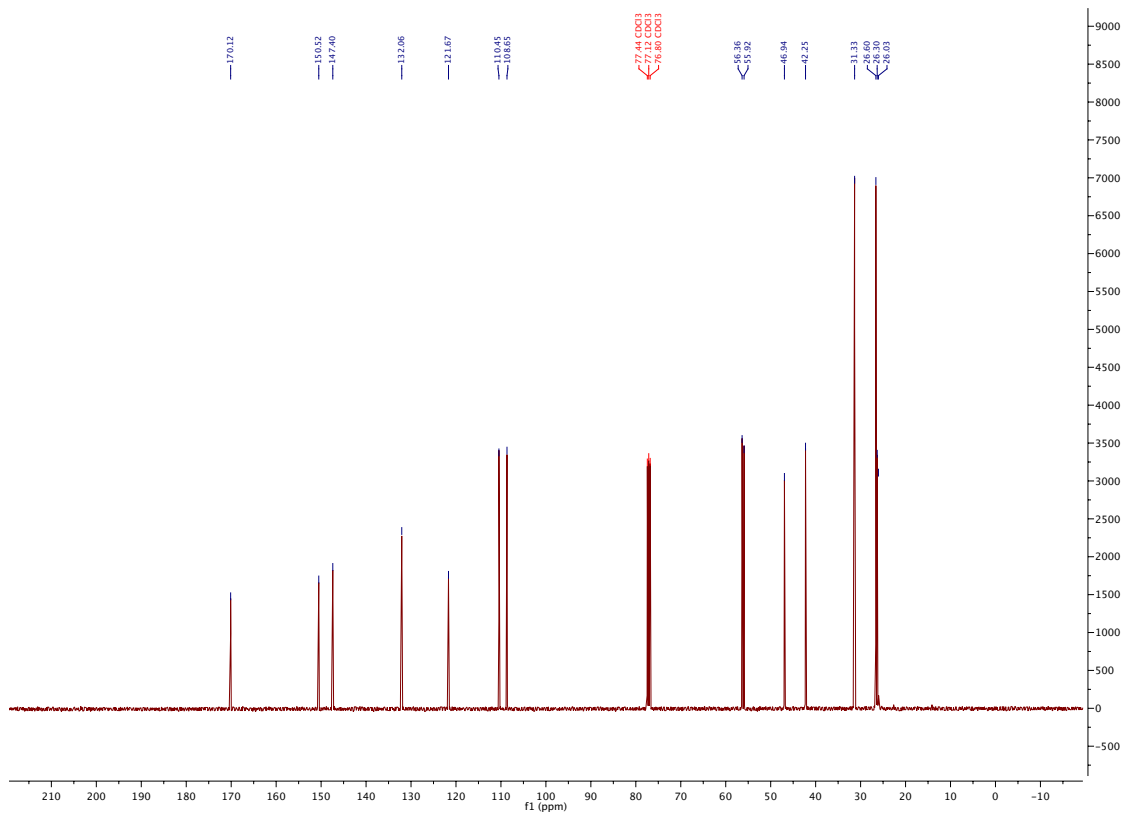
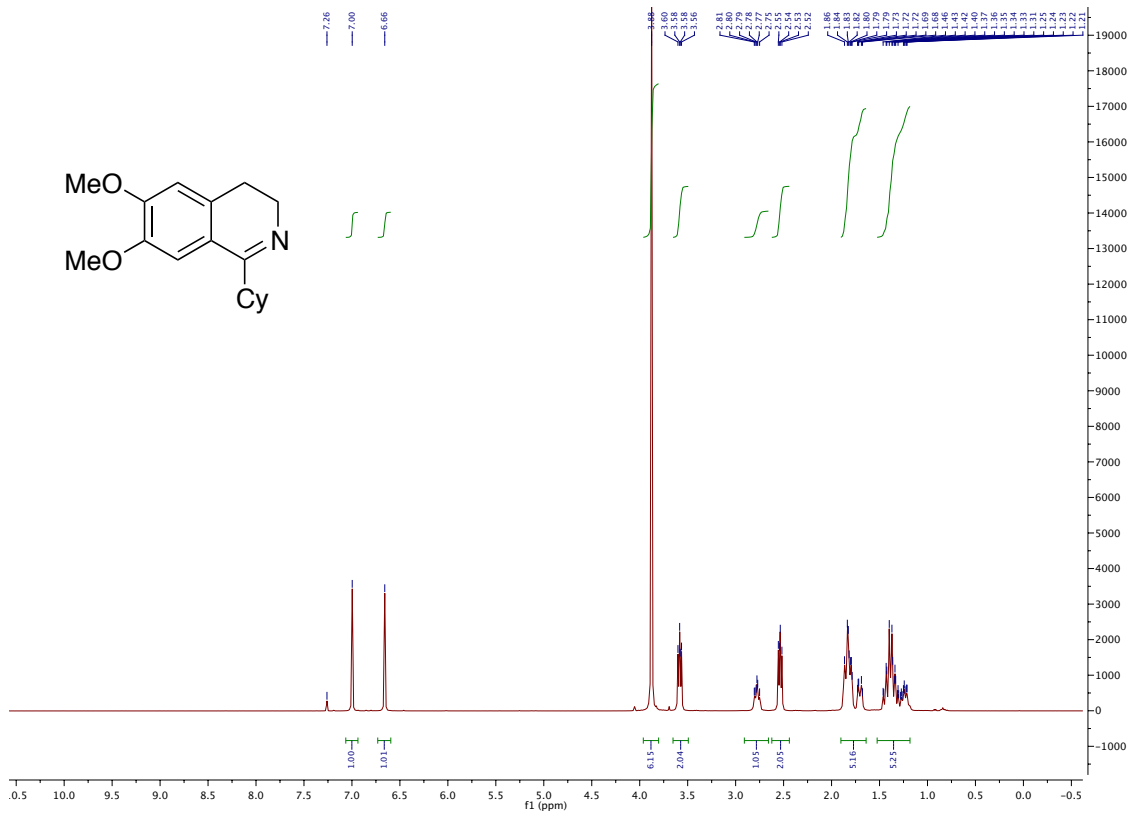


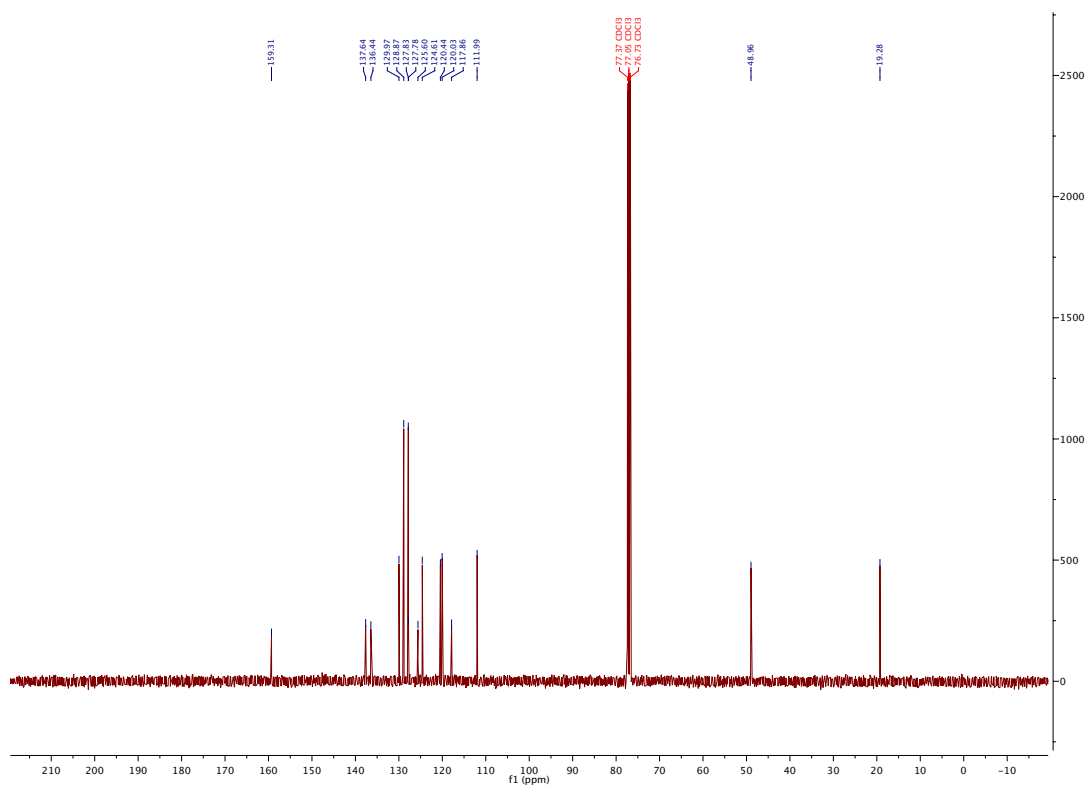
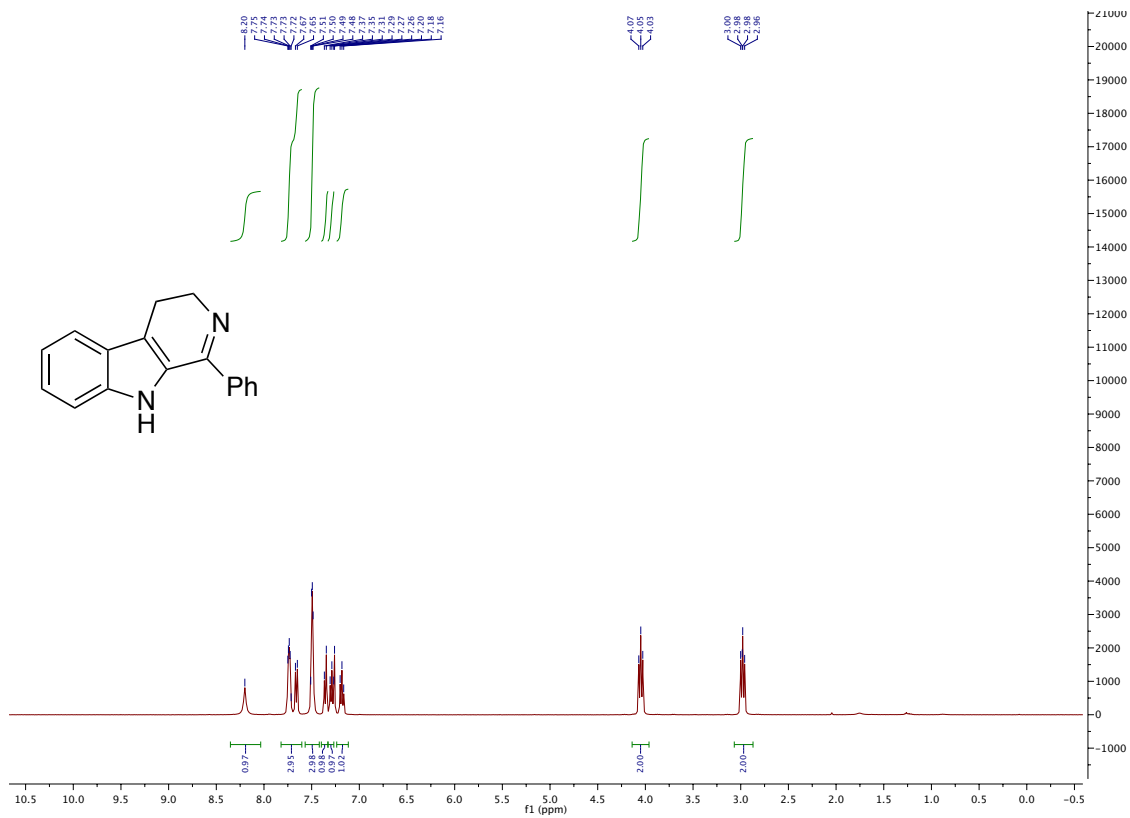
^1H and ^{13}C NMR Spectra of Products

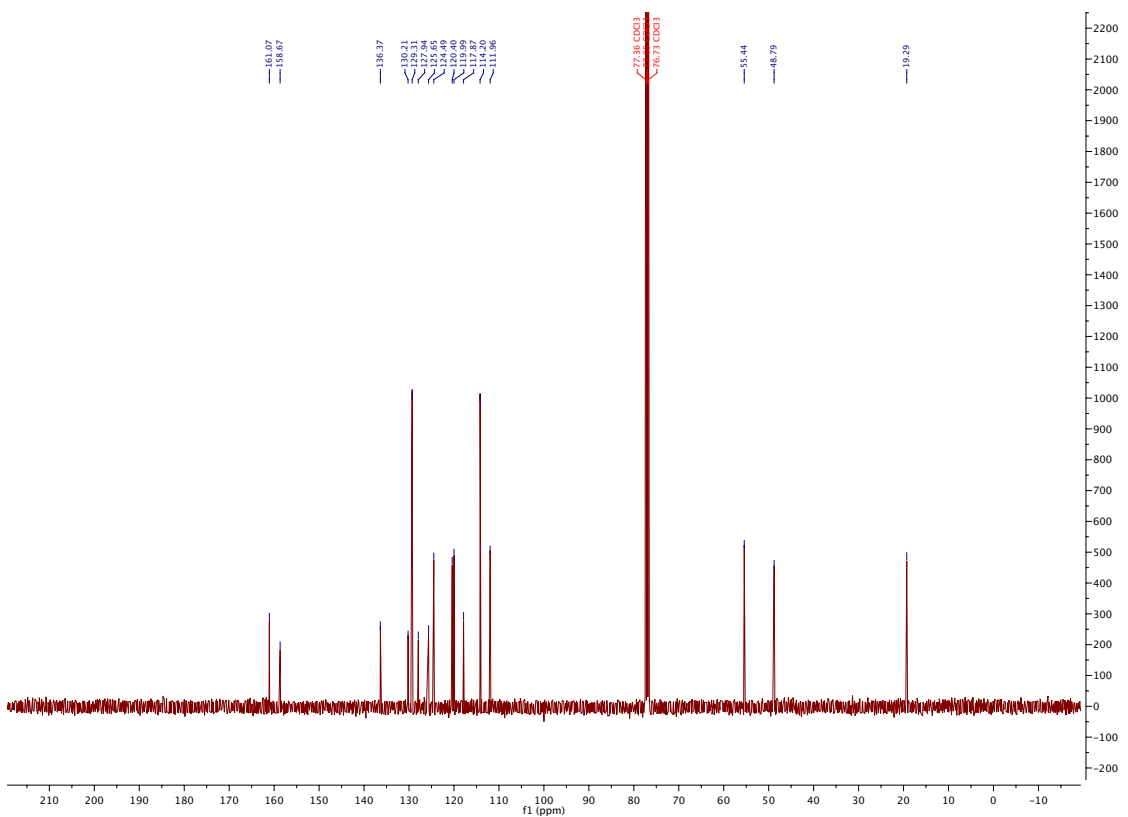
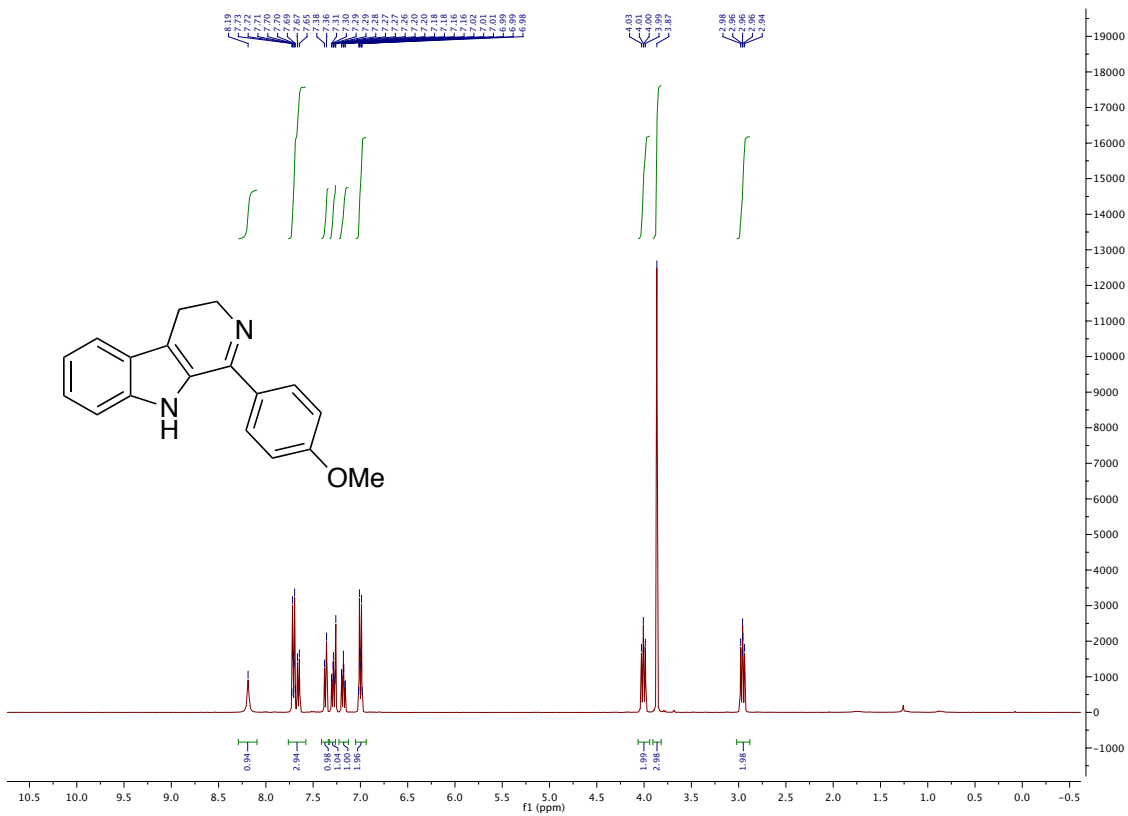


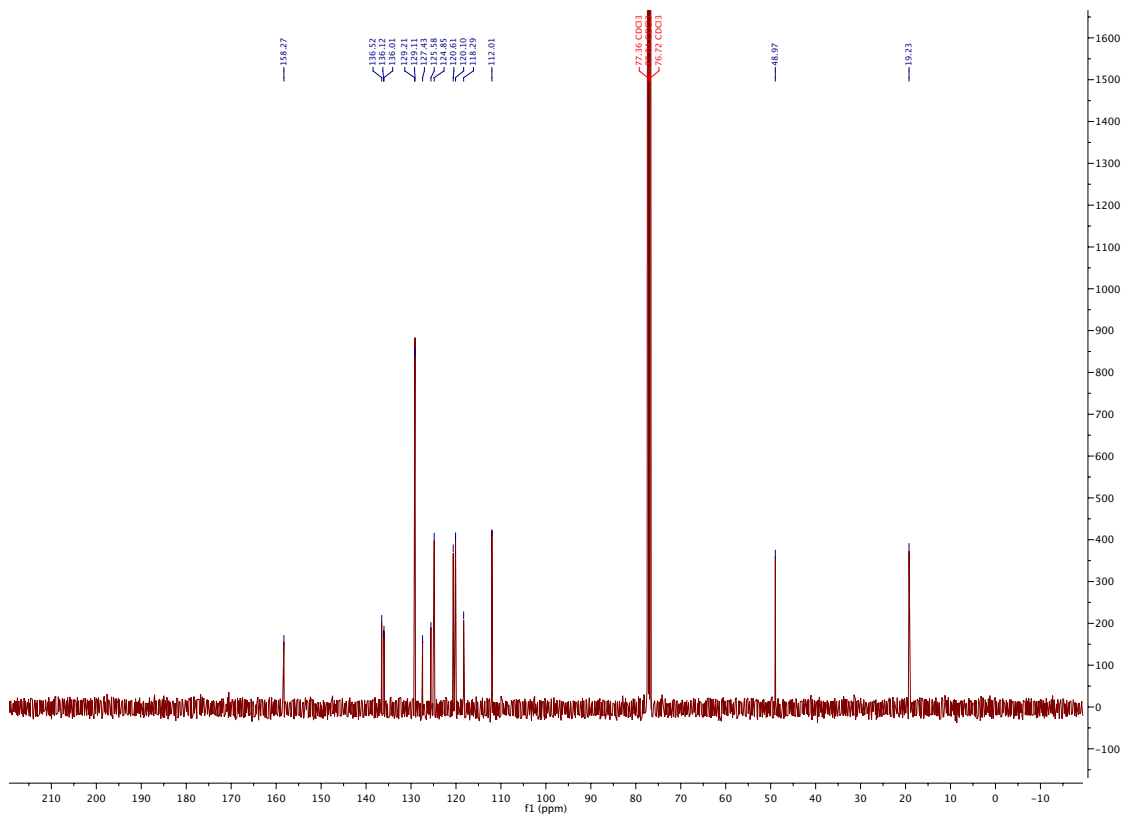
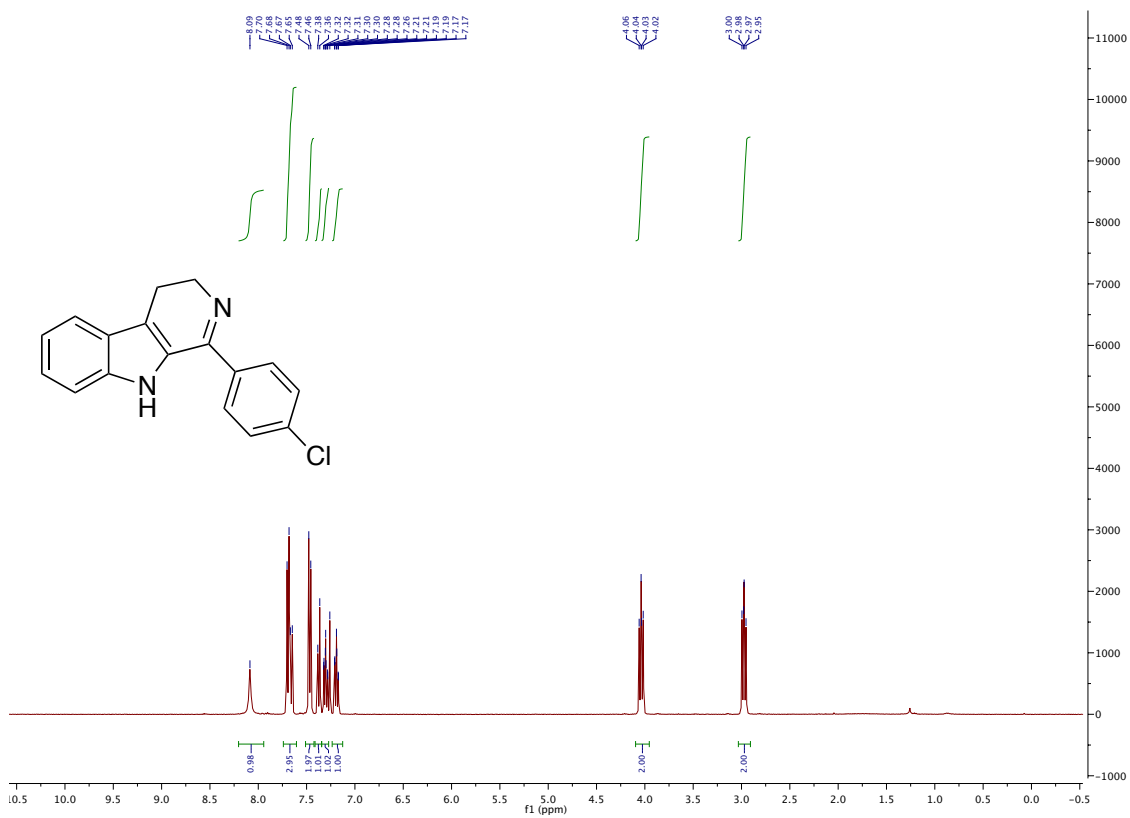


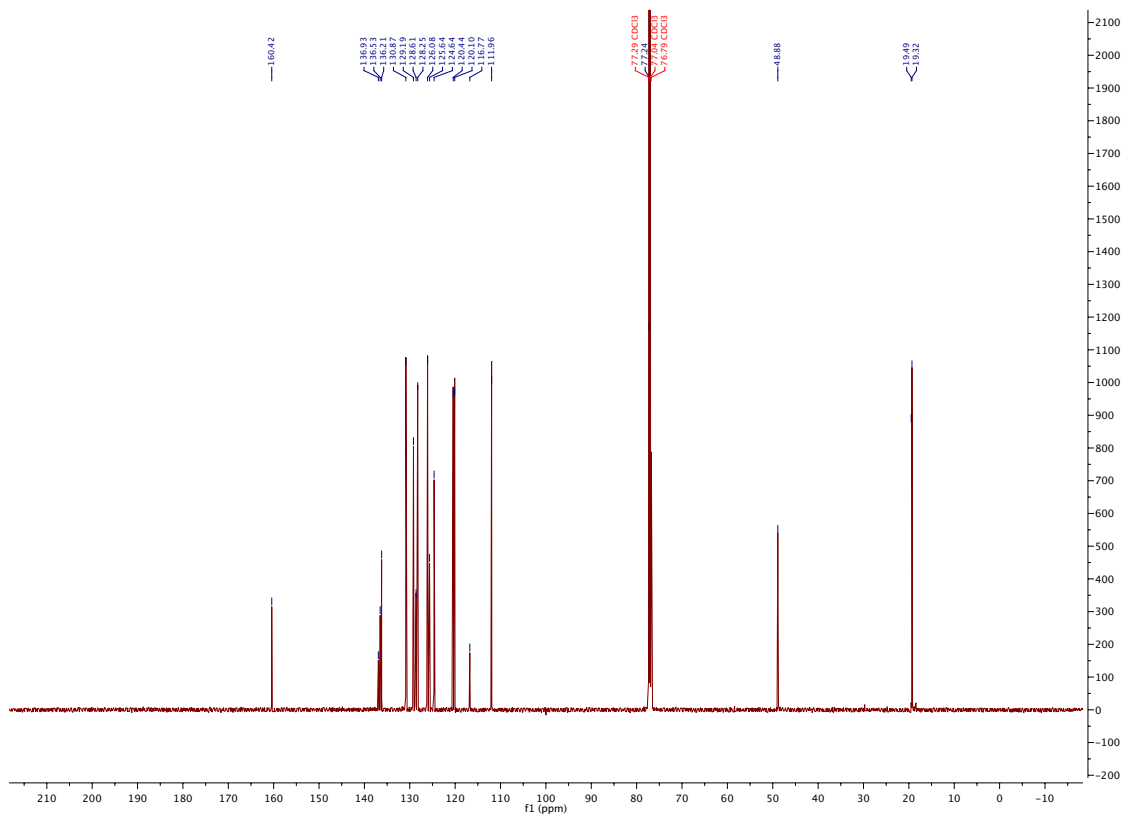
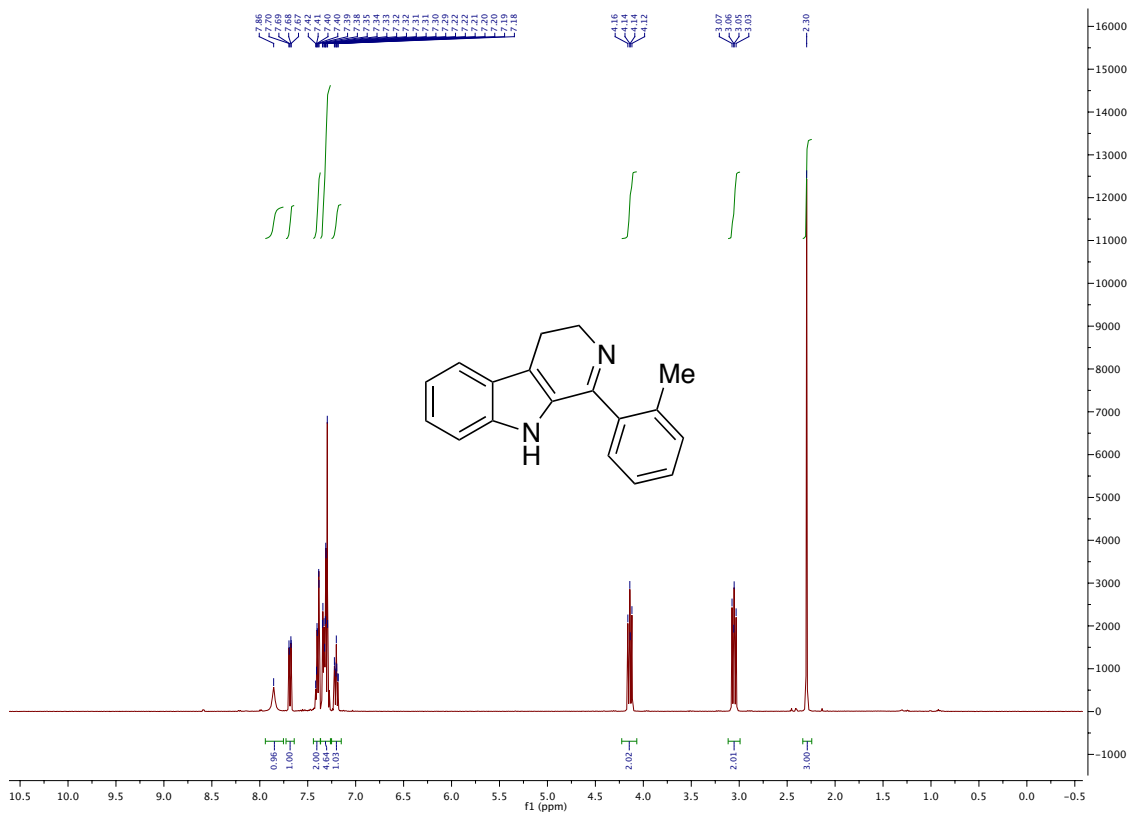


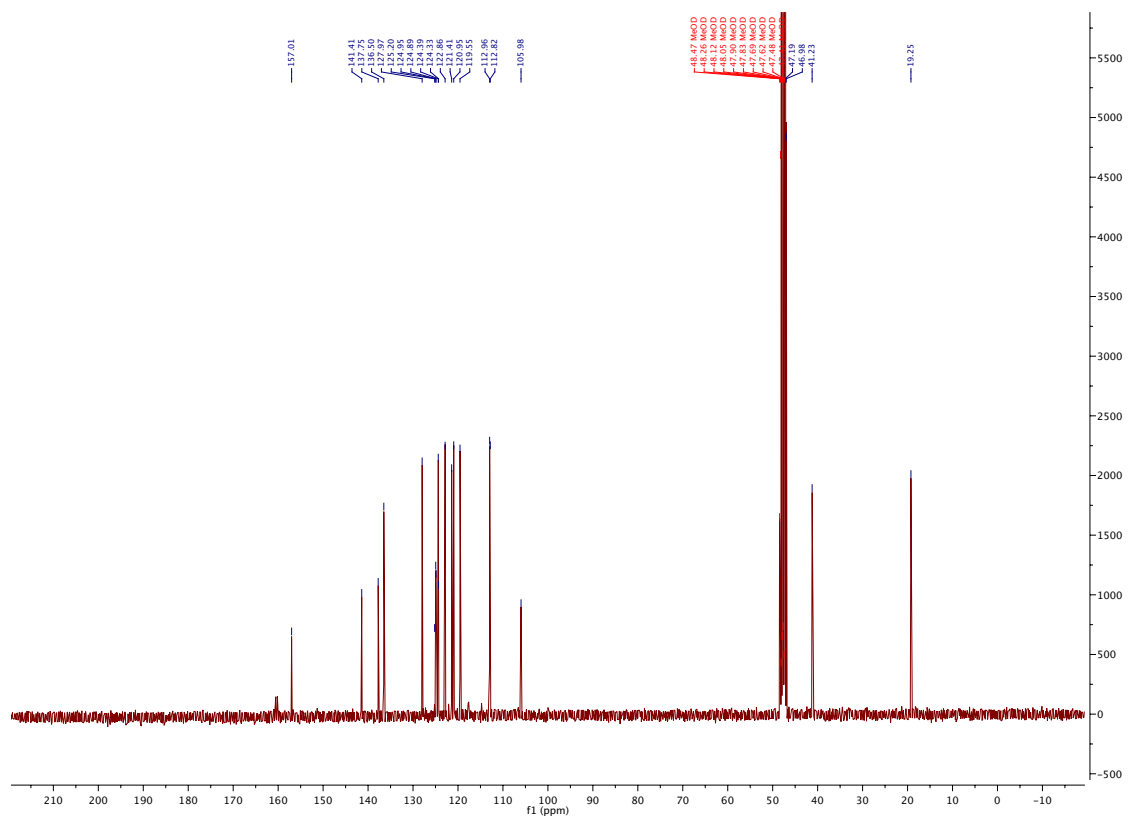
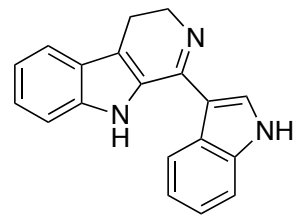
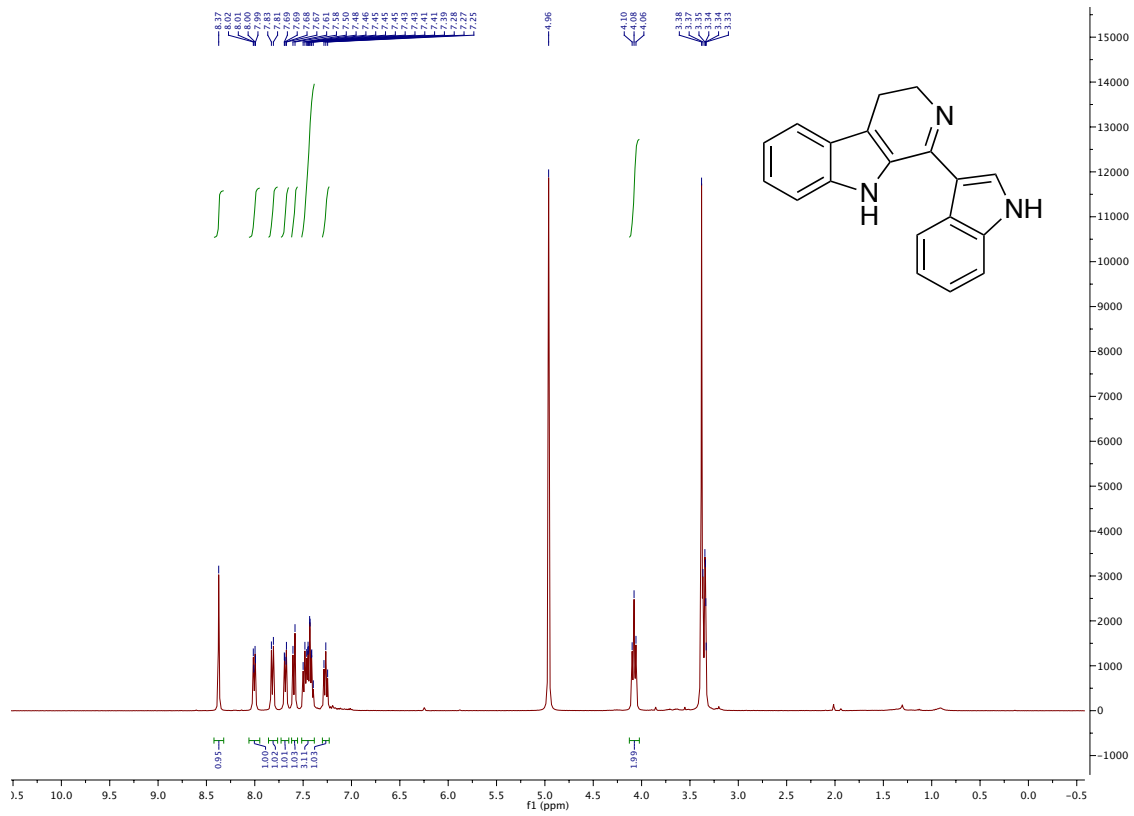


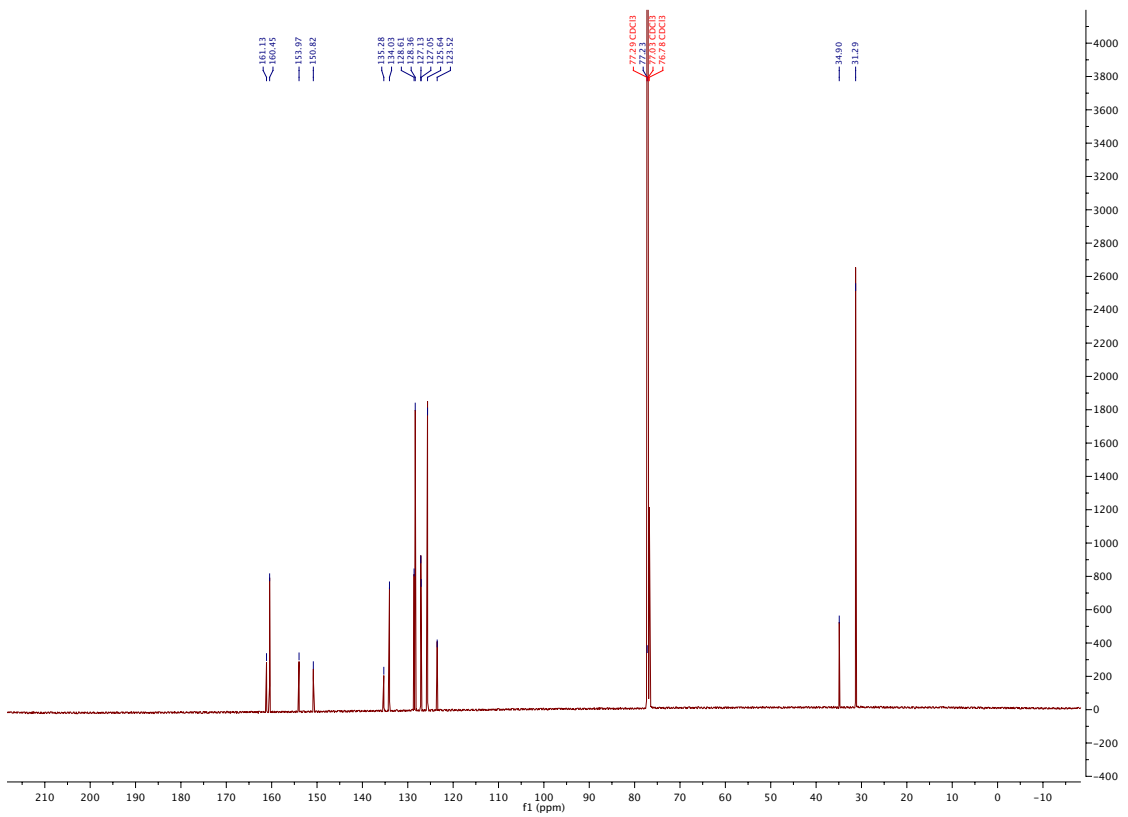
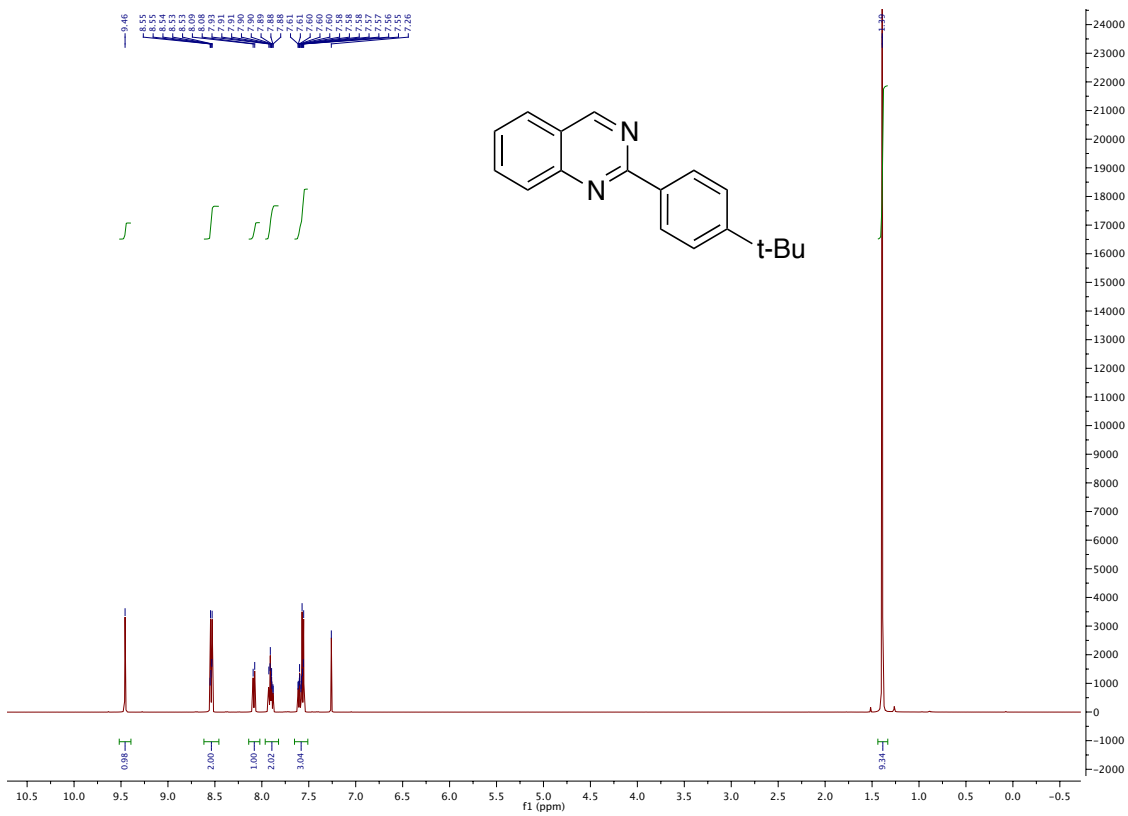


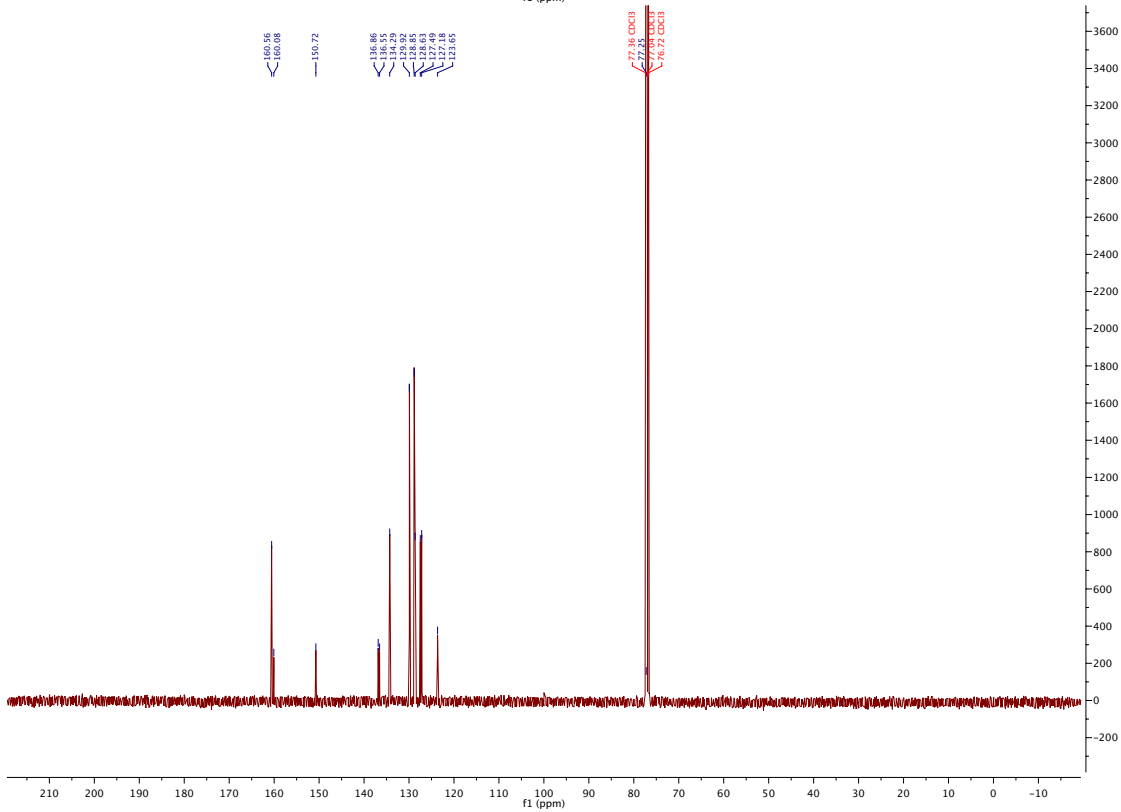
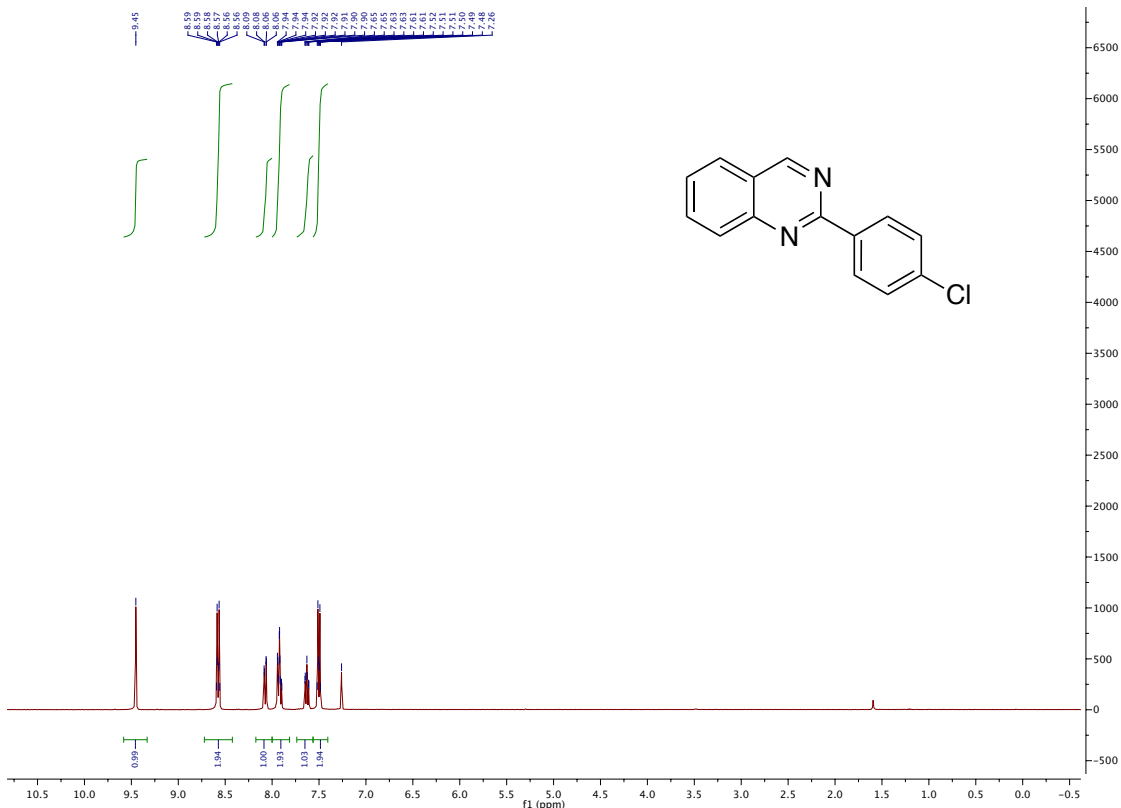


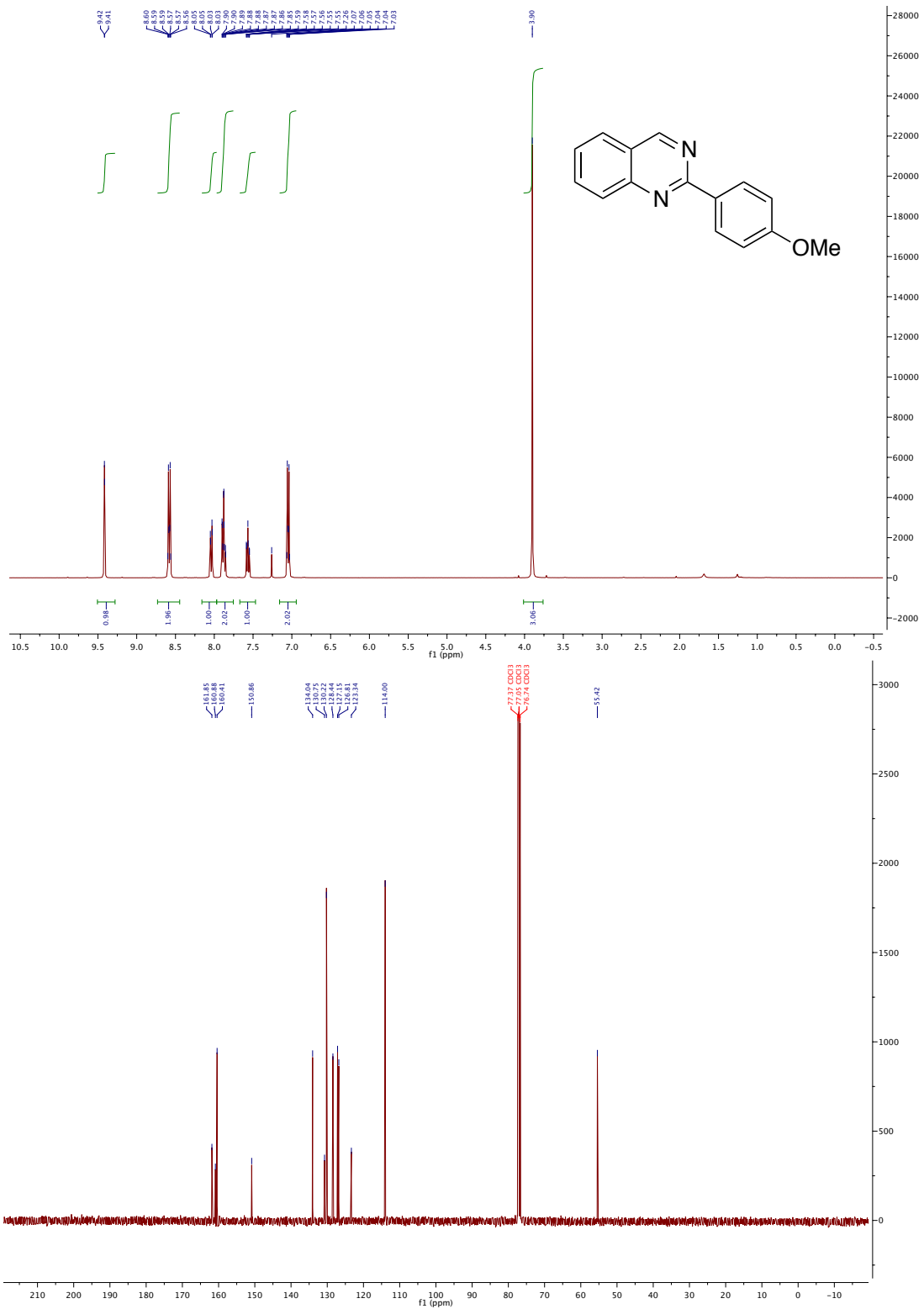


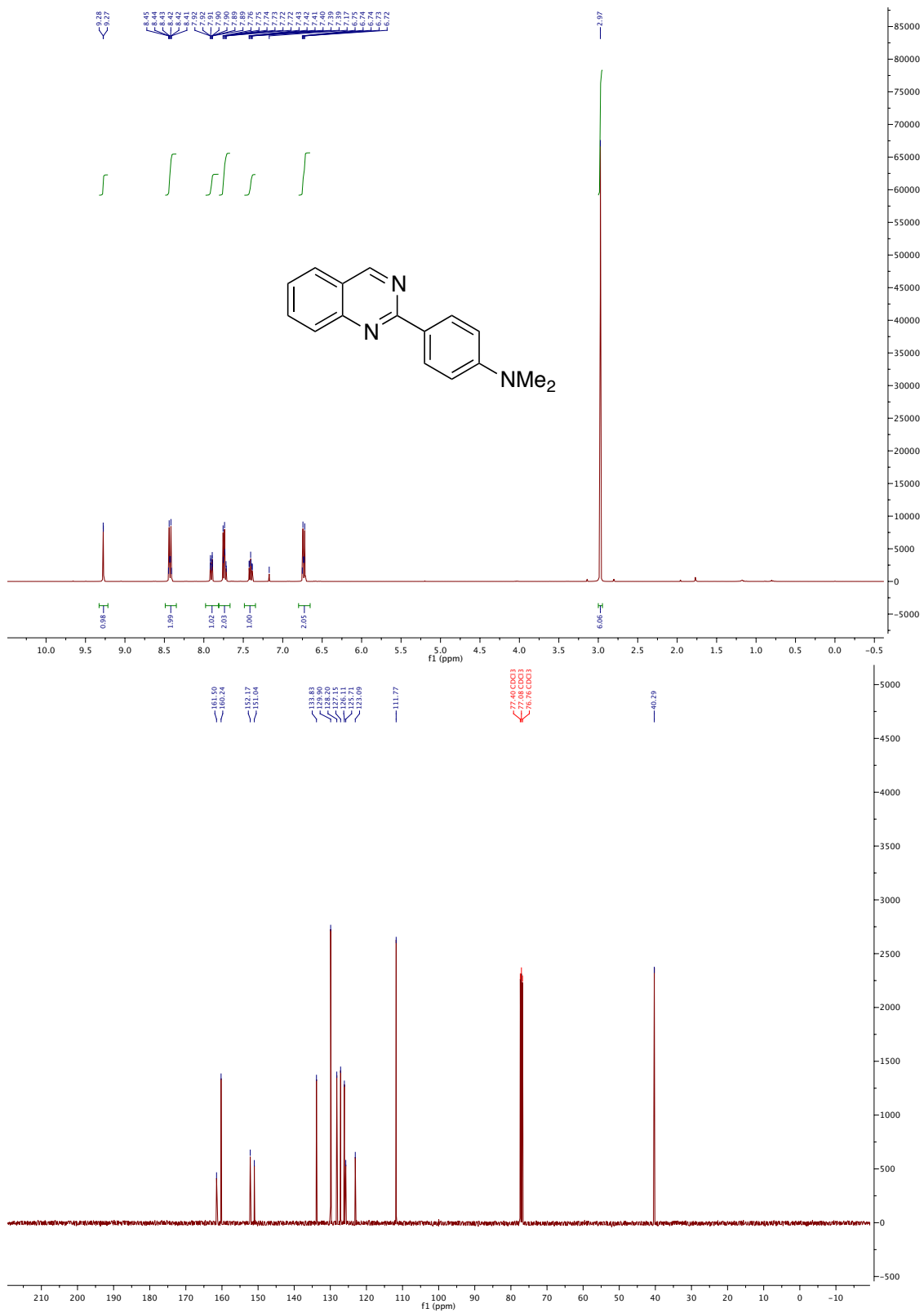


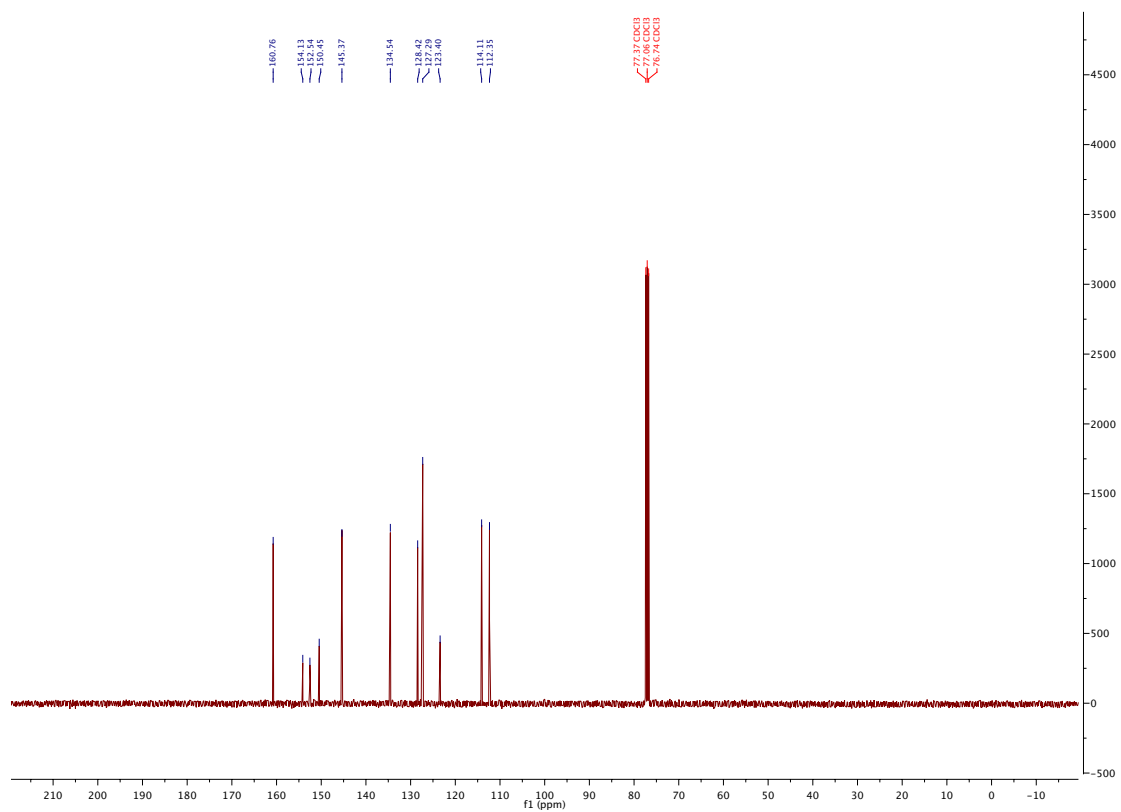
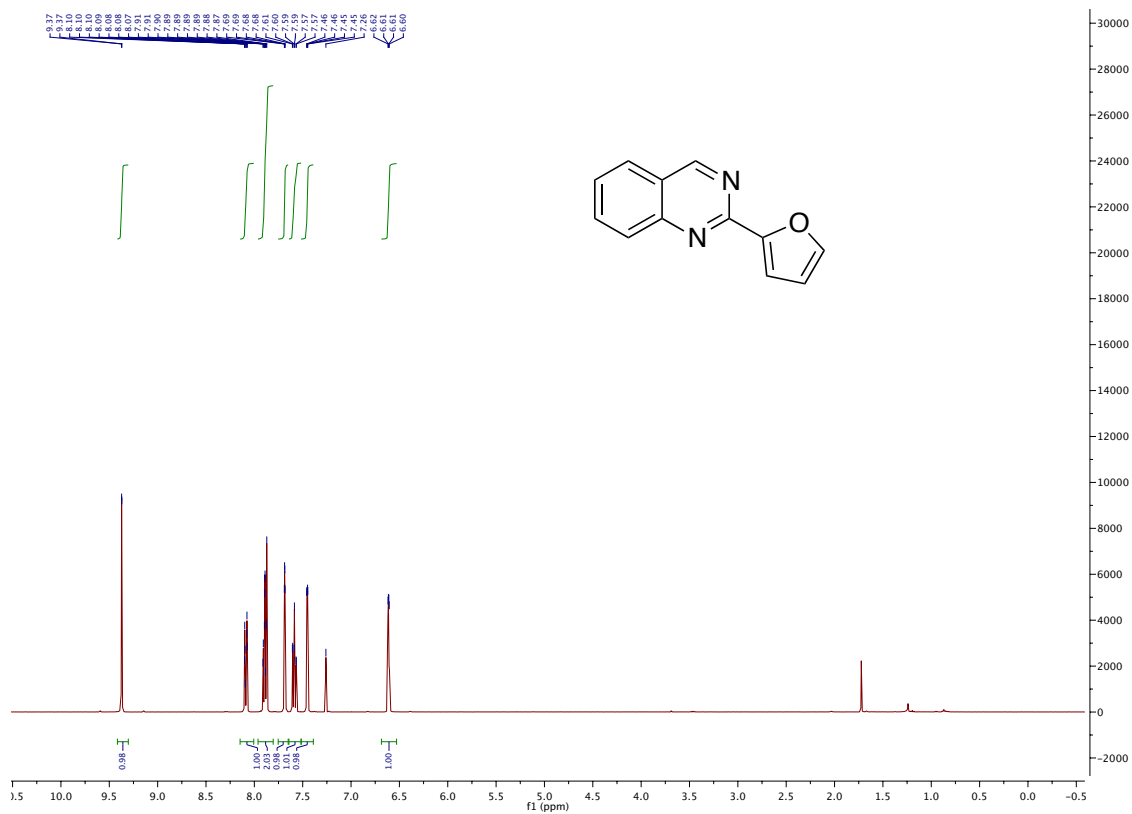


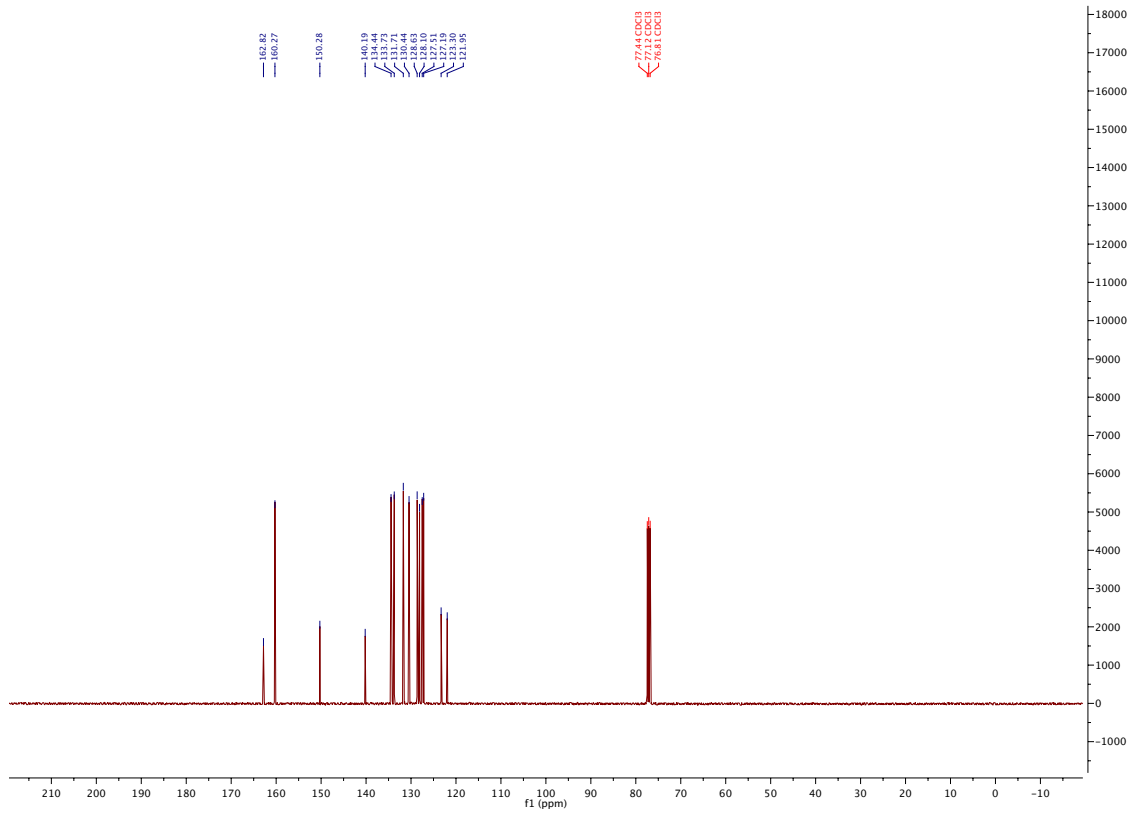
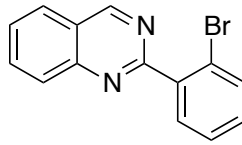
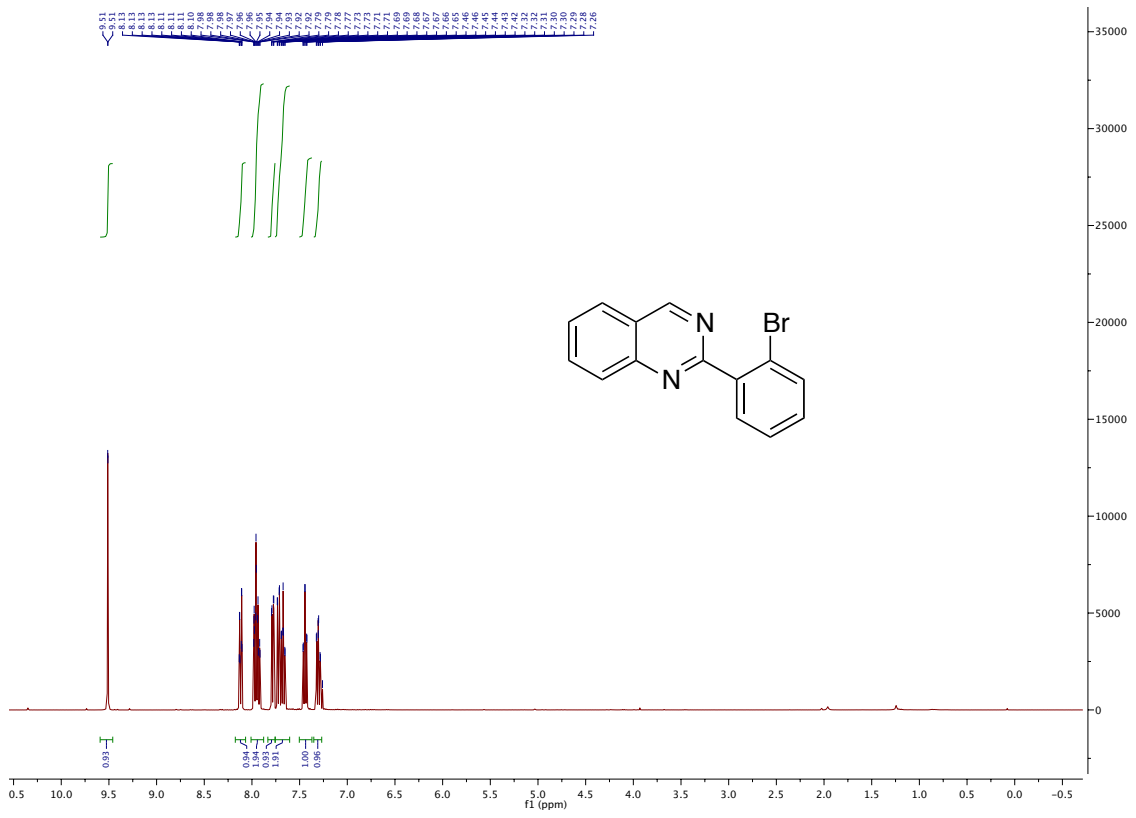


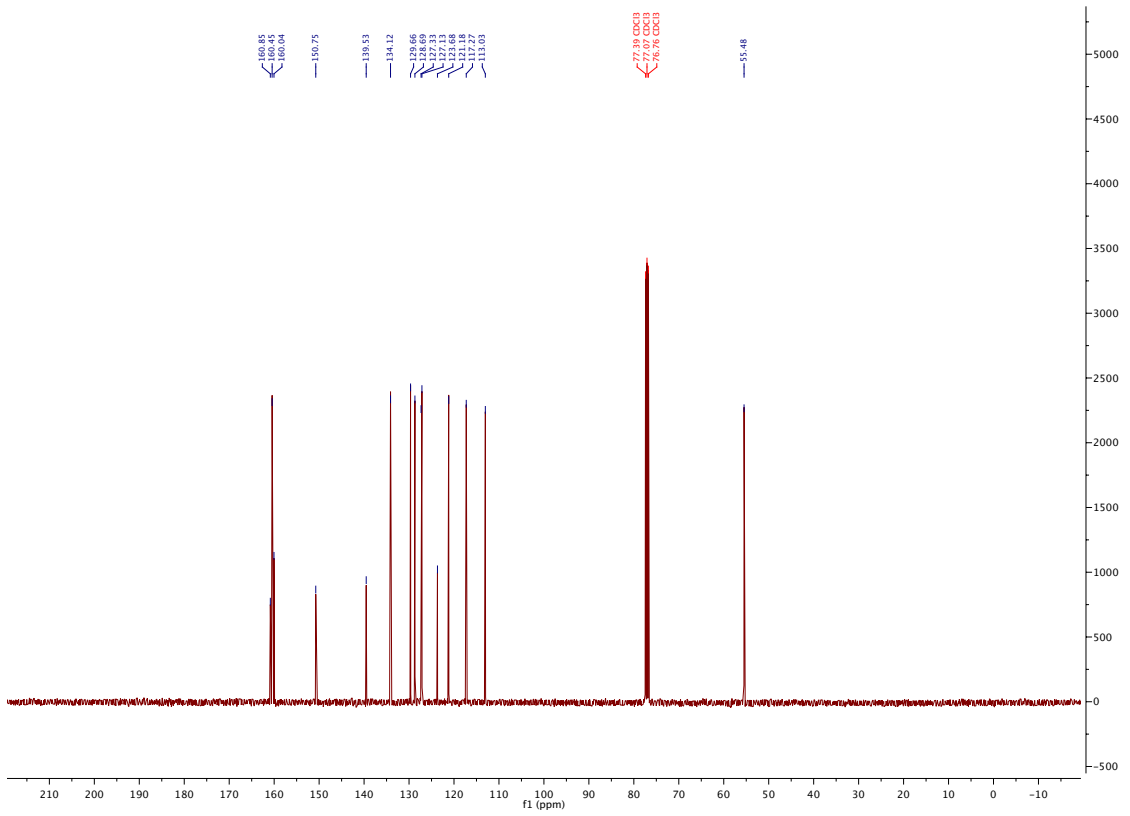
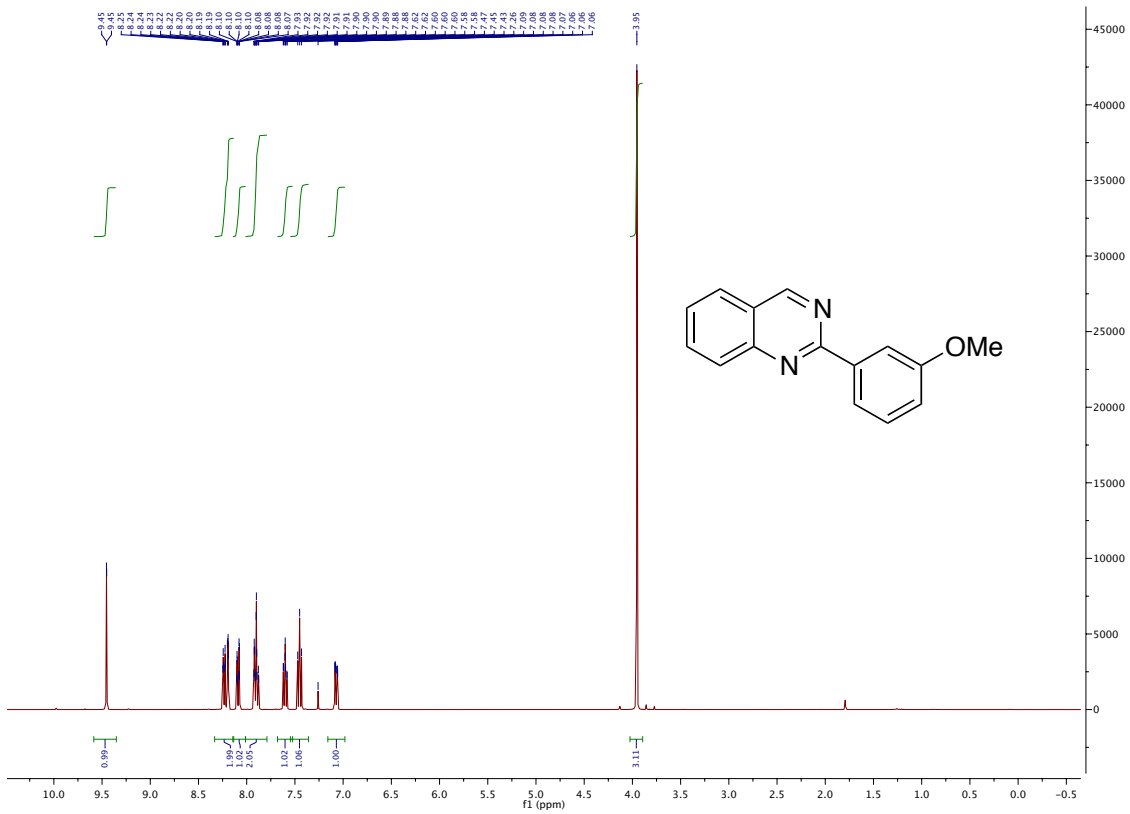


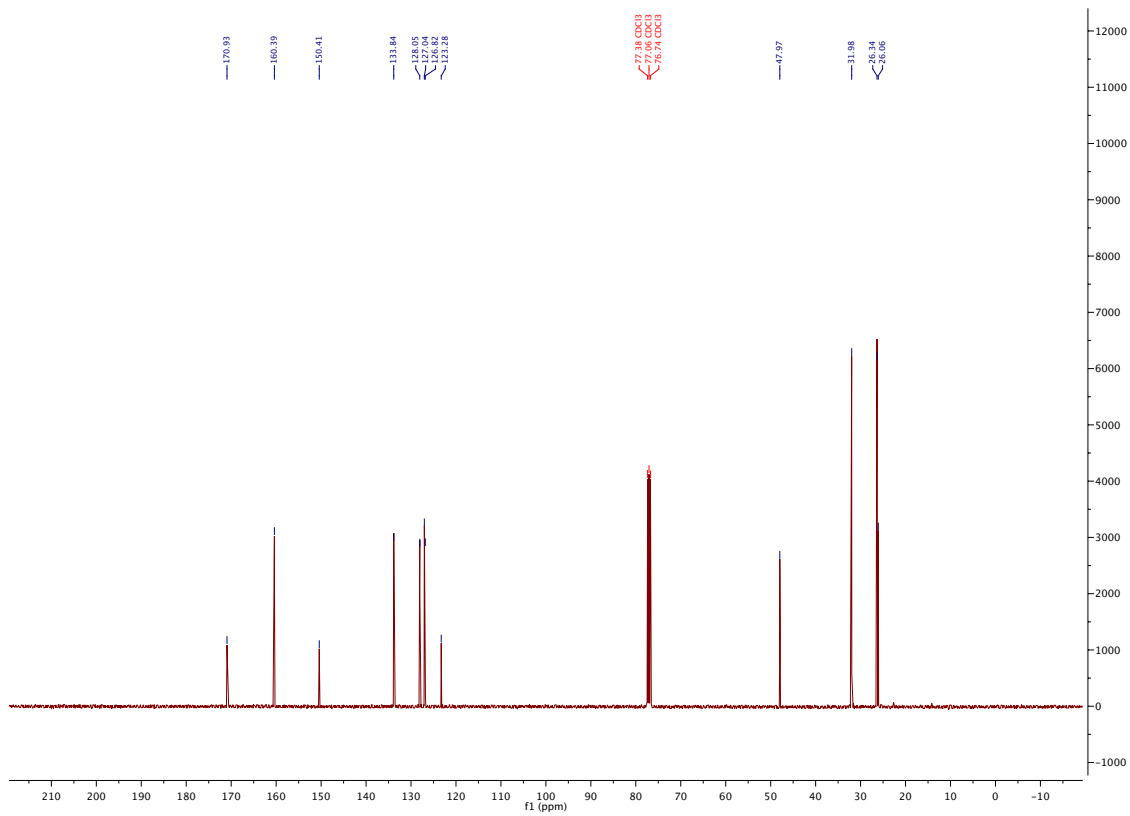
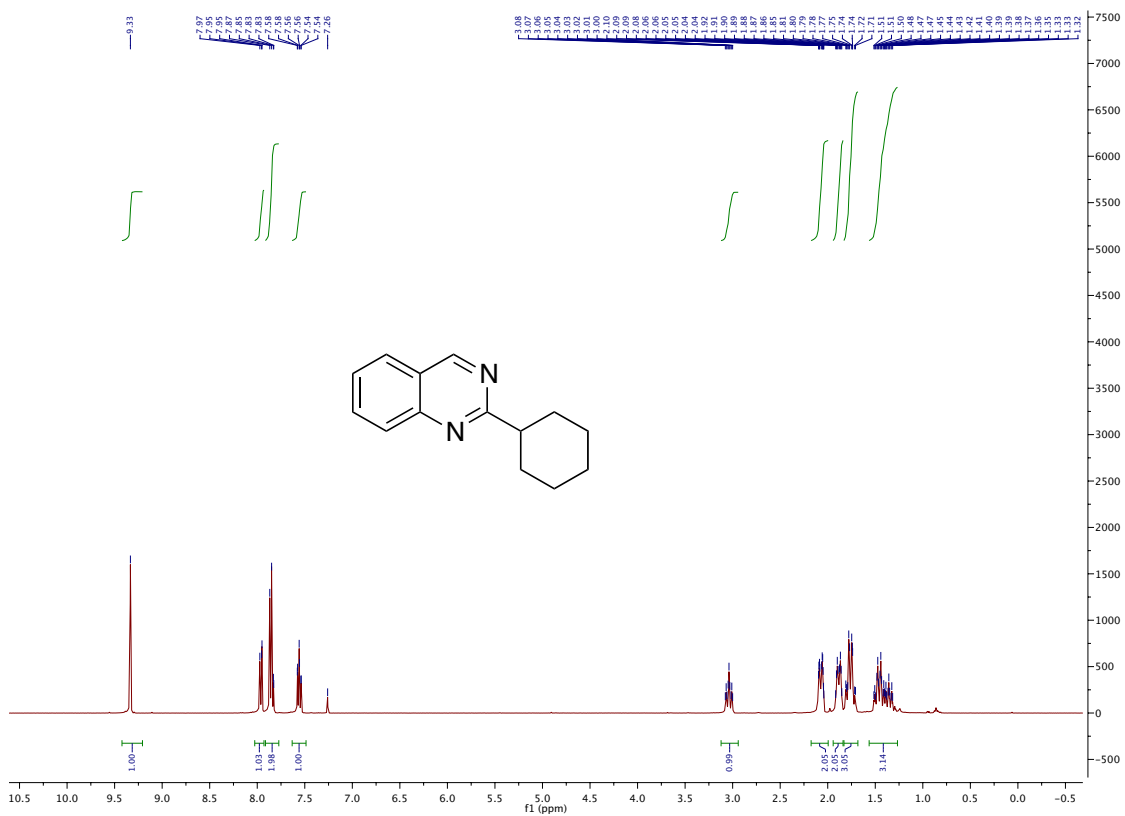


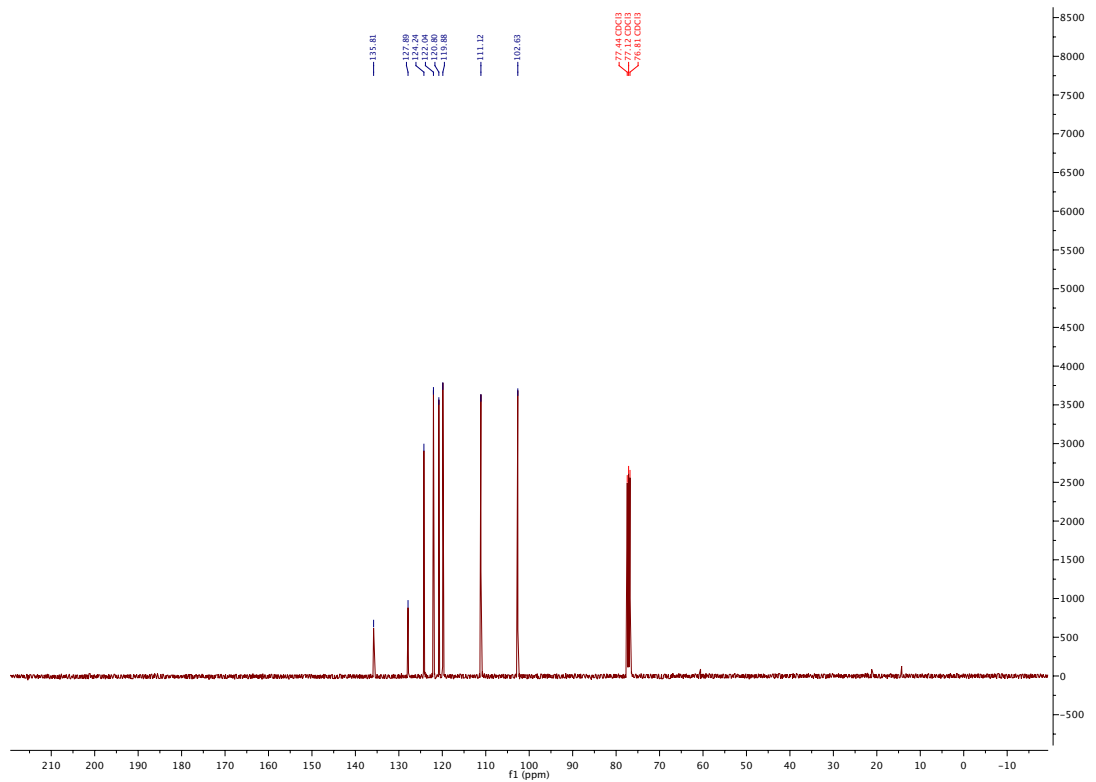
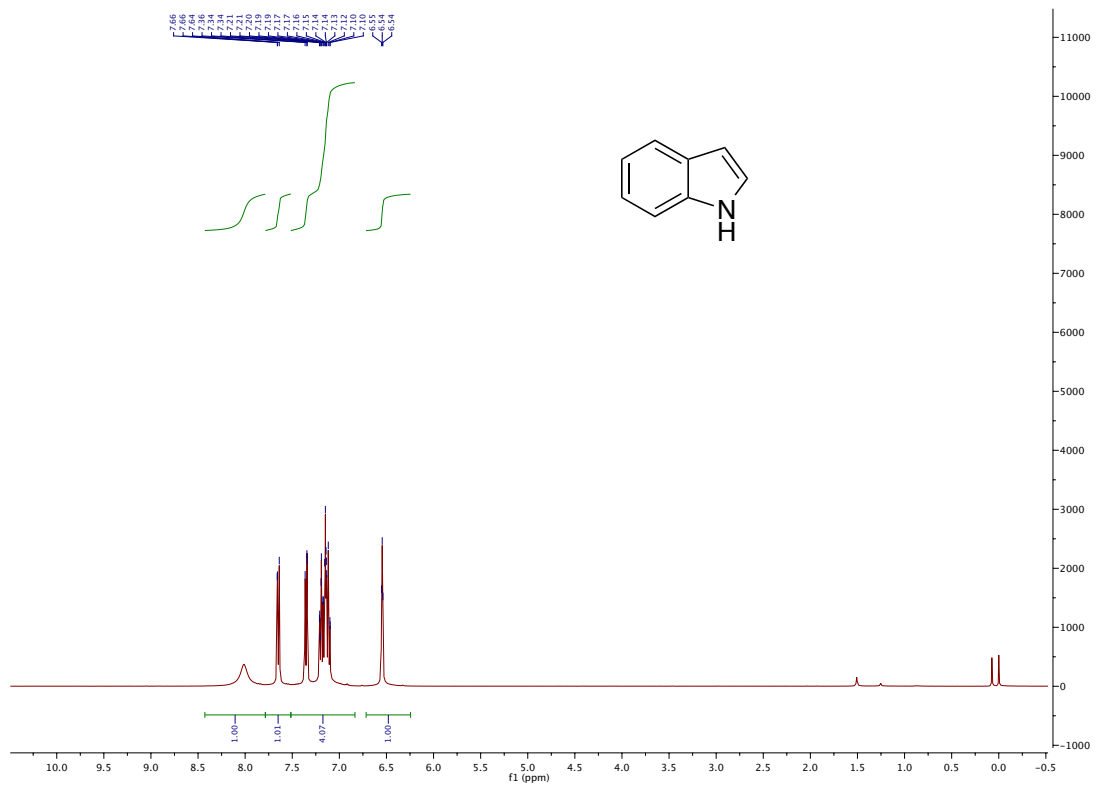


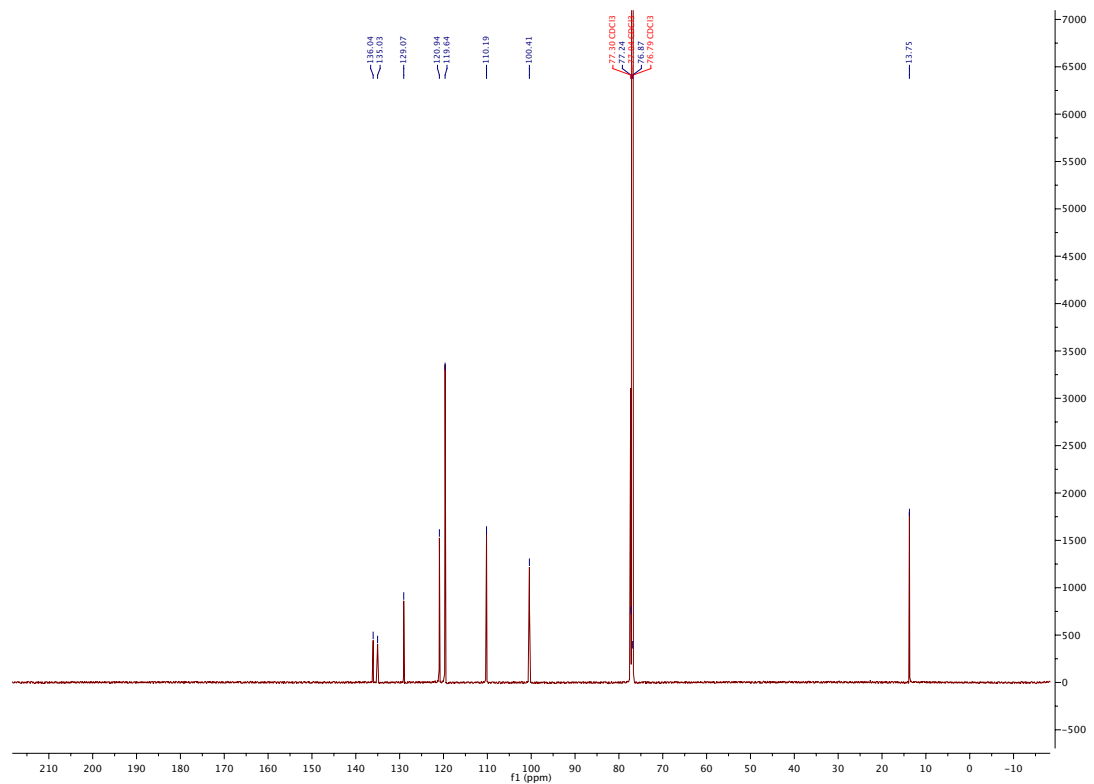
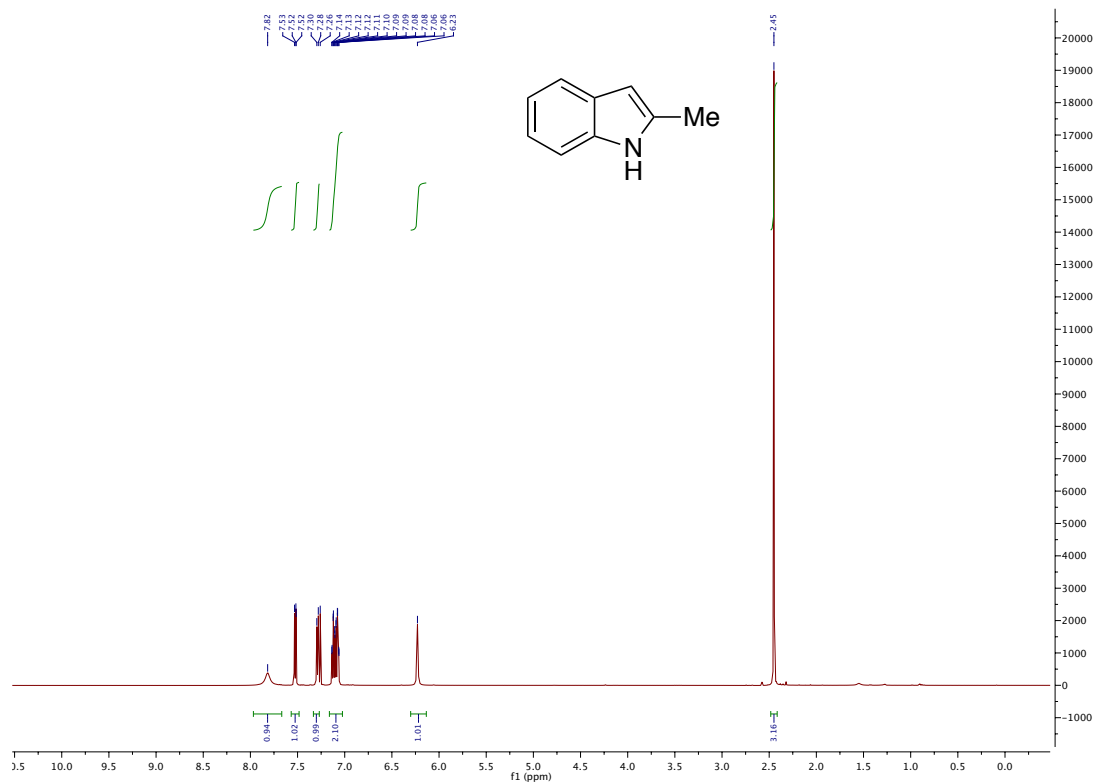


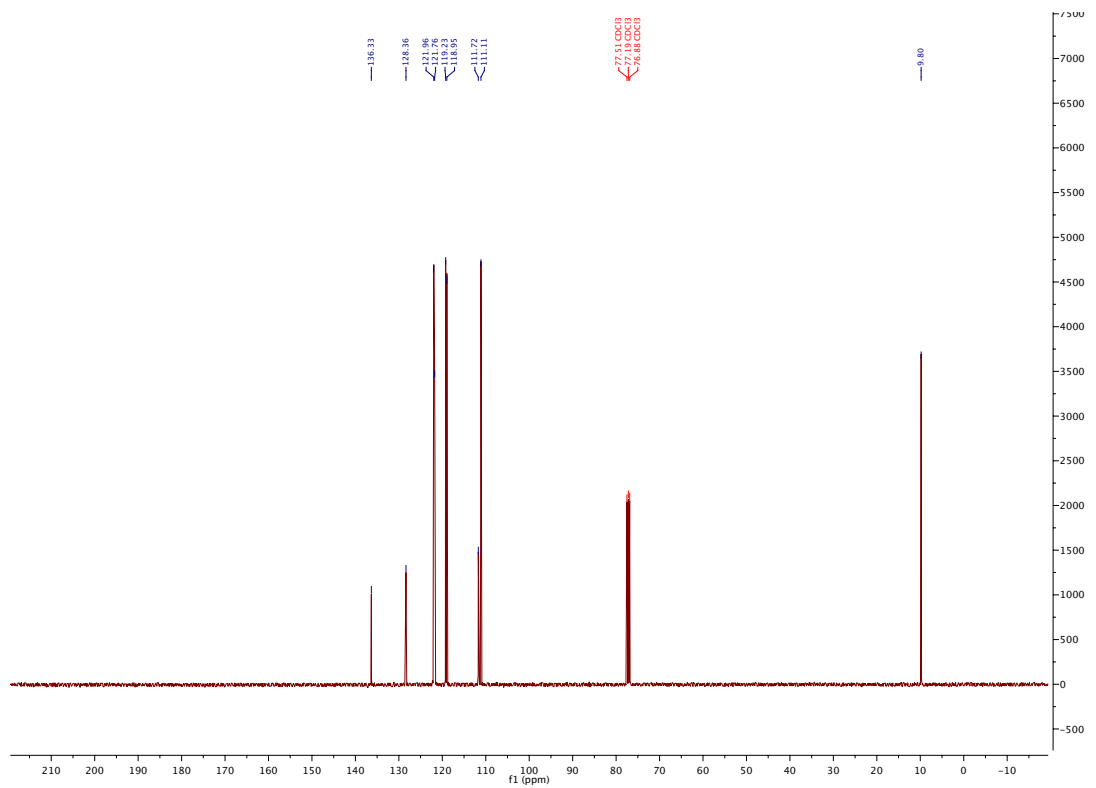
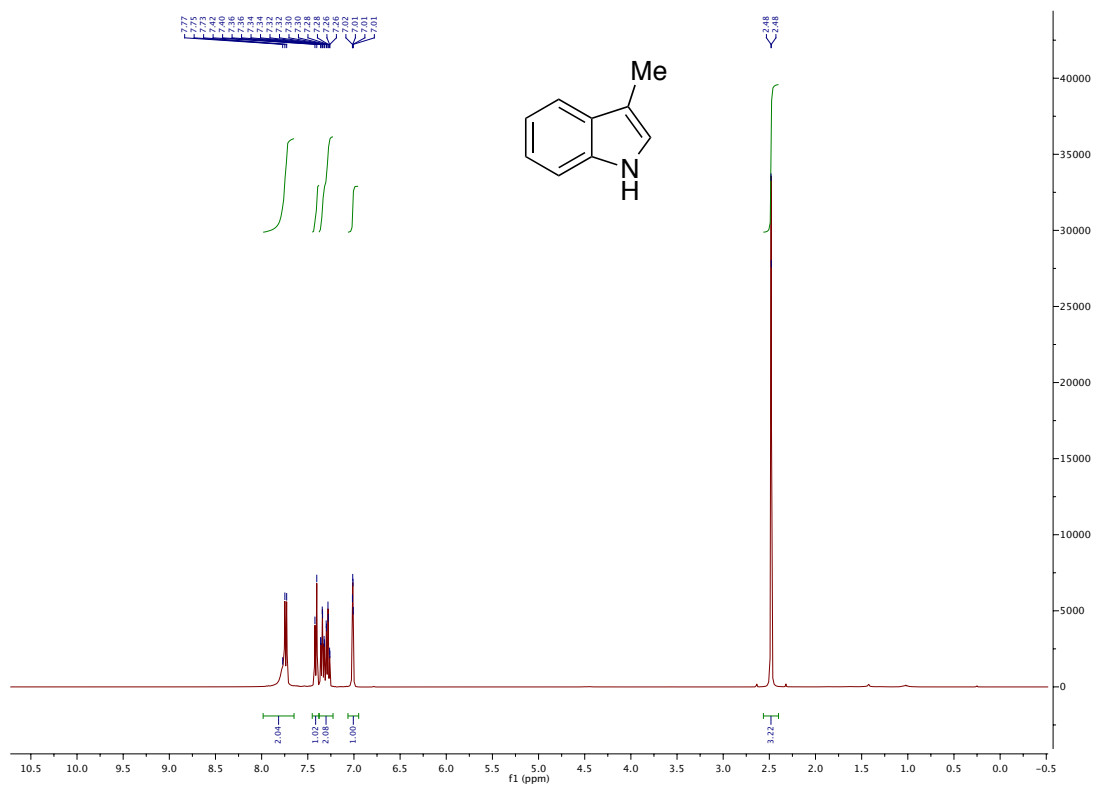












APEXII program suite. The final cell constants were calculated from a set of 9785 strong reflections from the actual data collection.

The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.70 Å. A total of 153282 data were harvested by collecting 6 sets of frames with 0.5° scans in ω and φ with exposure times of 20 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements. [1]

Structure Solution and Refinement

The systematic absences in the diffraction data were consistent for the space groups *Pnma* and *Pna2₁*. The *E*-statistics strongly suggested the centrosymmetric space group *Pnma* that yielded chemically reasonable and computationally stable results of refinement [2-4].

A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

The asymmetric unit contains one Zn complex as well as a heavily disordered non-coordinated triflate anion and two partially occupied acetonitrile molecules. Ligand N3 of the Zn complex is disordered over two positions (major component: 82.0(10)%). Triflate ligand S1 is also disordered over two positions (major component: 92.8(2)%). Bond distance and thermal parameter restraints and constraints were applied to the disordered species to enable a computationally stable and chemically reasonable refinement.

A significant amount of time was invested in identifying and refining the disordered non-coordinated triflate anion and acetonitrile molecules. Bond length restraints were applied to model the diffuse species but the resulting isotropic displacement coefficients suggested that the species were mobile. In addition, the refinement was computationally unstable. Option SQUEEZE of program PLATON [5] was used to correct the diffraction data for diffuse scattering effects and to identify the species. PLATON calculated the upper limit of volume that can be occupied by the species to be 1828 Å³, or 27.3% of the unit cell volume. The program calculated 820 electrons in the unit cell for the diffuse species. This approximately corresponds to one triflate anion (592 electrons/cell) and 1.4 molecules of acetonitrile (246 electrons/cell) in the asymmetric unit. It is very likely that these species are disordered over several positions. Based on these results, the formula for the asymmetric unit is: [(C₁₂H₆N₂O₂)₂(O₃SCF₃)(C₂H₃N)Zn]⁺; [O₃SCF₃]⁻; 1.4 (C₂H₃N). Please note that all derived results in the following tables are based on the known contents. No data are given for the diffusely scattering species.

The final least-squares refinement of 551 parameters against 7908 data resulted in residuals R (based on F^2 for $I \geq 2\sigma$) and wR (based on F^2 for all data) of 0.0365 and 0.0939, respectively.

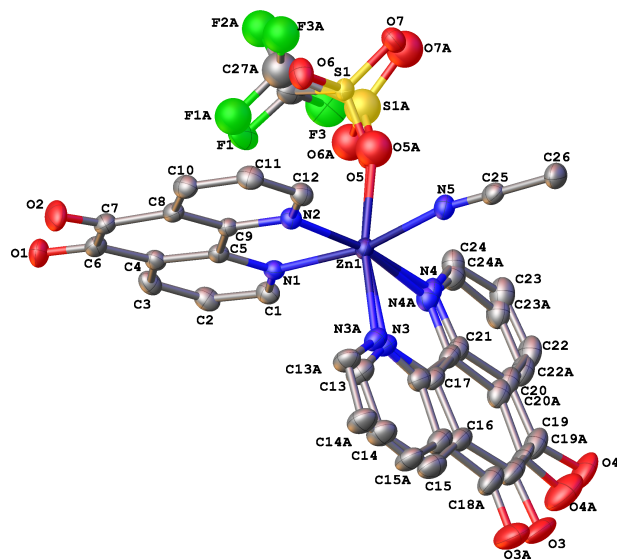
Summary

Crystal data for C_{30.8}H_{19.2}N_{6.4}O₁₀F₆S₂Zn ($M = 882.41$): orthorhombic, space group *Pnma* (no. 62), $a = 21.111(7)$ Å, $b = 22.086(6)$ Å, $c = 14.348(6)$ Å, $V = 6690(4)$ Å³, $Z = 8$, $T = 100.0$ K, $\mu(\text{Mo K}\alpha) = 0.963$ mm⁻¹, $D_{\text{calc}} = 1.752$ g/mm³, 153282 reflections measured ($3.384 \leq 2\theta \leq 55.094$), 7908 unique ($R_{\text{int}} = 0.0451$) which were used in all calculations. The final R_1 was 0.0429 ($I > 2\sigma(I)$) and wR_2 was 0.1159 (all data).

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A molecular drawing of the Zn complex of phd showing the disordered component. All atoms are drawn with 50% probability ellipsoids. All H atoms are omitted for clarity.

Table S1. Crystal data and structure refinement for Stahl171

Identification code	Stahl171
Empirical formula	$[(C_{12}H_6N_2O_2)_2(O_3SCF_3)(C_2H_3N)Zn]^+; [O_3SCF_3]^-; 1.4(C_2H_3N)$
Formula weight	882.41
Temperature/K	100.0
Crystal system	orthorhombic
Space group	<i>Pnma</i>
a/Å	21.111(7)
b/Å	22.086(6)
c/Å	14.348(6)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/Å ³	6690(4)
Z	8
ρ_{calc} mg/mm ³	1.752
μ /mm ⁻¹	0.963
F(000)	3558.0
Crystal size/mm ³	0.733 × 0.133 × 0.119
2 θ range for data collection	3.384 to 55.094°
Index ranges	-27 ≤ h ≤ 27, -28 ≤ k ≤ 28, -18 ≤ l ≤ 18
Reflections collected	153282
Independent reflections	7908[R(int) = 0.0451]
Data/restraints/parameters	7908/616/551
Goodness-of-fit on F ²	1.077
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0365, wR ₂ = 0.0898
Final R indexes [all data]	R ₁ = 0.0431, wR ₂ = 0.0939
Largest diff. peak/hole / e Å ⁻³	0.44/-0.50

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