Supporting Information for

Modular *o*-Quinone Catalyst System for Dehydrogenation of Tetrahydroquinolines under Ambient Conditions

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This Supporting Information file includes:

I. 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. ^{1}H 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 (^{1}H and ^{13}C). High-resolution, exact mass measurements were obtained by the mass spectrometry facility at the University of Wisconsin. C, H, N elemental analyses were carried out by Robertson Microlit Laboratories. Melting points were taken on a Mel-Temp II melting point apparatus. Flash chromatography was performed using SilicaFlash® P60 (Silicycle, particle size 40-63 μm, 230-400 mesh).

Procedure for Multiwell Gas Uptake Kinetics Measurements (Figures 1 and 3)

Each set of data was collected using a 6-well gas uptake apparatus which holds individually calibrated 50 mL round bottom flasks, each connected to a pressure transducer designed to measure the gas pressure within each sealed reaction vessel. Five vessels contained various reaction mixtures, and the sixth well used as a solvent control for variations in pressure. The apparatus was evacuated and filled with O_2 to 600 torr three times. The pressure was established at 600 torr with the flasks heated to 27 °C. Solution A (see below) was added via syringe through a septum, and the pressure and temperature allowed to equilibrate. When the pressure (approximately 700 torr) and temperature (27 °C) stabilized, solution B (see below) was added via syringe through a septum. Data were acquired using custom software written within LabVIEW (National Instruments).

Specific conditions for Figure 1

- "5% phd + 2.5% ZnI_2 + 15% PPTS"

Solution A: phd (4.74 mg, 0.0225 mmol, 0.05 equiv) in 1.0 mL MeCN. Solution B: PPTS (16.98 mg, 0.0676 mmol, 0.15 equiv), ZnI_2 (3.59 mg, 0.0112 mmol, 0.025 equiv) and tetrahydroquinoline (60.1 mg, 0.451 mmol, 1.0 equiv) in 1.0 mL MeCN.

- "2.5% $Fe(phd)_3$ + 1% Bu_4NI"

Solution A: Bu_4NI (1.66 mg, 0.0045 mmol, 0.01 equiv) and tetrahydroquinoline (60.1 mg, 0.451 mmol, 1.0 equiv) in 1.0 mL MeCN. Solution B: $Fe(phd)_3$ $2PF_6$ (11.0 mg, 0.0113 mmol, 0.025 equiv) in 1.0 mL MeCN.

- "2.5% $Ru(phd)_3$ + 1% Bu_4NI"

Solution A: Bu_4NI (1.66 mg, 0.0045 mmol, 0.01 equiv) and tetrahydroquinoline (60.1 mg, 0.451 mmol, 1.0 equiv) in 1.0 mL MeCN. Solution B: $Ru(phd)_3$ $2PF_6$ (11.5 mg, 0.0113 mmol, 0.025 equiv) in 1.0 mL MeCN.

Specific conditions for Figure 3

- "no co-catalyst"

Solution A: tetrahydroquinoline (60.1 mg, 0.451 mmol, 1.0 equiv) in 1.0 mL MeCN. Solution B: $Ru(phd)_3$ $2PF_6$ (11.5 mg, 0.0113 mmol, 0.025 equiv) in 1.0 mL MeCN.

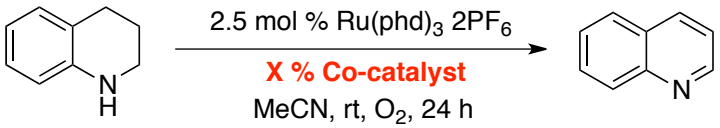
- "1% Bu_4NI"
As "2.5% $Ru(phd)_3$ + 1% Bu_4NI" in Figure 1.

- "5% Co(salophen)"
Co(salophen) (8.41 mg, 0.0225 mmol, 0.05 equiv) was added as a solid to the flask prior to evacuating/backfilling with O_2. Solution A: tetrahydroquinoline (60.1 mg, 0.451 mmol, 1.0 equiv) in 1.0 mL MeCN. Solution B: $Ru(phd)_3$ $2PF_6$ (11.5 mg, 0.0113 mmol, 0.025 equiv) in 1.0 mL MeCN.

Procedures for aerobic reaction screening
In a disposable culture tube, a solution of $[Ru(phd)_3]2PF_6$ (2.5 mol %, 0.065 mmol) in 0.25 mL was added to Bu_4NI (0.5 to 2.5 mol %), Co(salophen) (5.0 mol %), or other co-catalyst (5.0 mol %) in 0.25 mL MeCN. 1,2,3,4-Tetrahydroquinoline (15 μL, 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 1,3,5-trimethoxybenzene was added as an internal standard. The reaction solvents were removed under vacuum, and the residue was suspended in $CDCl_3$ and filtered through a short plug of Celite for NMR analysis. The yield was determined by ^1H NMR spectroscopy (relaxation delay >25 s) versus the internal standard.

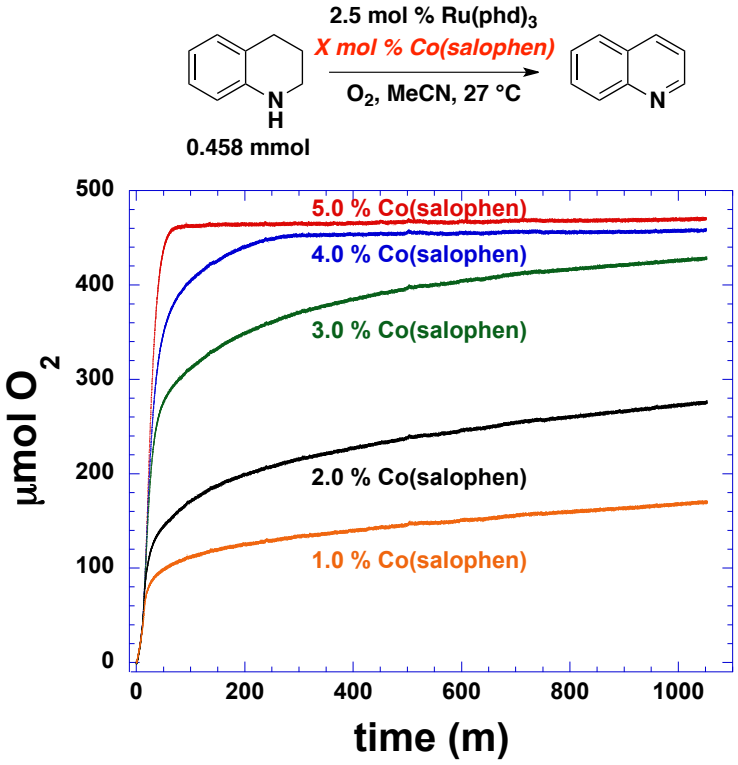
II. Additional Tables and Figures

Table S1. Additional Co-catalyst Screening Data (see above for conditions)



entry	co-catalyst	NMR Yields
1	----	16 %
2	0.5 % TBAI	82 %
3	**1.0 % TBAI**	**93 %**
4	1.5 % TBAI	74 %
5	2.0 % TBAI	61 %
6	2.5 % TBAI	48 %
7	5.0 % Cu(pc)	7 %
8	5.0 % Fe(pc)	79 %
9	5.0 % Co(salpr)	33 %
10	**5.0 % Co(salophen)**	**89 %**

Figure S1. Multiwell gas uptake plot for 1% to 5% Co(salophen)



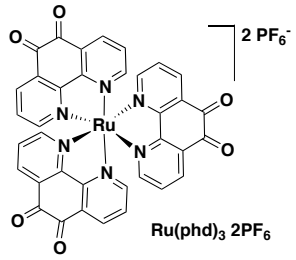
III. Synthesis and Characterization Data

Synthesis and Characterization of Catalysts

1,10-Phenanthroline-5,6-dione, phd, was prepared according to the method previously reported,[1] and is also commercially available. Co(salophen) was prepared according to the method of Backvall,[2] and is also commercially available.

$[Fe(phd)_3](PF_6)_2 H_2O$

$[Fe(phd)_3]2PF_6$ was prepared based on the method reported previously.[3] To a solution of phd (695 mg, 3.3 mmol, 3.2 equiv) in 1:1 EtOH/H_2O was added $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$ (405 mg, 1.03 mmol, 1.0 equiv). The reaction was stirred for 60 minutes at room temperature, and then precipitated with a saturated aqueous solution of NH_4PF_6. The solids were collected and washed sequentially with H_2O, EtOH, and Et_2O. The complex was then dissolved in a minimum of MeCN, filtered through celite, and reprecipitated by slow addition of Et_2O to give 772 mg (76% yield) of the title complex as a black crystalline solid. ^{1}H NMR (500 MHz, CD_3CN) δ 8.66 (dd, J = 7.9, 1.3 Hz, 6H), 7.81 (dd, J = 5.6, 1.4 Hz, 6H), 7.73 (dd, J = 7.9, 5.6 Hz, 6H). ^{13}C NMR (126 MHz, CD_3CN) δ 175.55, 160.32, 158.70, 138.30, 131.37, 129.50; Anal. Calc for $C_{36}H_{20}F_{12}FeN_6O_7P_2$: C, 43.48; H, 2.03; N, 8.45. Found: C, 42.89; H, 2.30; N, 8.71.



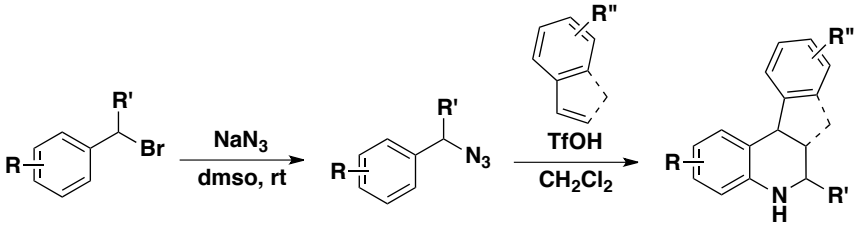
$[Ru(phd)_3]2PF_6$

$Ru(dmso)_4Cl_2$ was prepared from $RuCl_3$ according to a previously reported procedure.[4] $Ru(dmso)_4Cl_2$ (598 mg, 1.23 mmol) and phd (870 mg, 4.13 mmol, 3.3 equiv) were loaded into a round bottom flask and 25 mL of 1:1 $EtOH/H_2O$ was added. The sample was quickly frozen and degassed three times by the method of freeze-pump-thaw. The sample was then equipped with a condenser and refluxed under nitrogen overnight. After cooling to room temperature, the sample was precipitated by the addition of a saturated aqueous solution of NH_4PF_6. Solid was collected, washed with water, EtOH, then Et_2O and dried under vacuum. The sample was then redissolved in a minimum of MeCN and filtered through a pad of celite. The pad was washed with MeCN, and Et_2O was slowly added to the collected filtrate to give 693 mg (55% yield) of $[Ru(phd)_3]2PF_6$ as a brown solid: ^1H NMR (500 MHz, CD_3CN) δ 8.62 (dd, J = 8.1, 1.4 Hz, 6H), 8.13 (d, J = 5.1 Hz, 6H), 7.72 (dd, J = 8.0, 5.6 Hz, 6H); ^{13}C NMR (126 MHz, CD_3CN) δ 175.54, 157.65, 156.78, 137.50, 131.46, 129.56; Anal. Calc for $C_{36}H_{18}F_{12}N_6O_6P_2Ru$: C, 42.33; H, 1.78; N, 8.23. Found: C, 42.12; H, 2.03; N, 8.13.

Synthesis and Characterization of Substrates

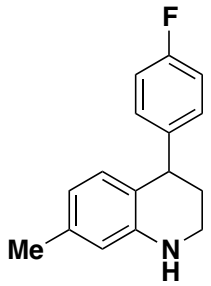
Tetrahydroquinoline, 6-methyltetrahydroquinoline, 6-methoxytetrahydroquinoline, 6-chlorotetrahydroquinoline were obtained from commercial sources and used as received. 2-methyltetrahydroquinoline, 3-methyltetrahydroquinoline, 4-methyltetrahydroquinoline, and 8-methyltetrahydroquinoline were obtained by high-pressure hydrogenation of the corresponding quinoline (commercial) according to literature procedure.[5] 4-phenyltetrahydroquinoline and 3-methyl-4-phenyltetrahydroquinoline were obtained according to literature procedure.[6] 2-butyltetrahydroquinoline, 2-styrenyltetrahydroquinoline were obtained from the method of Miyata.[7] 4-methyl-2-phenyltetrahydroquinoline and 4-methyl-2-(*p*-chlorophenyl)tetrahydroquinoline were obtained according to a literature method.[8]

The synthesis of 4-(*p*-fluorophenyl)-7-methyltetrahydroquinoline, 4-(*m*-acetamidophenyl)-2-methyltetrahydroquinoline, and compound **20** were synthesized according to the following common method. Desired benzylic azide was obtained from the appropriate benzylic bromide based on literature procedure.[9] The hetero-Diels-Alder reaction was carried out according to the procedure of Pearson.[10]

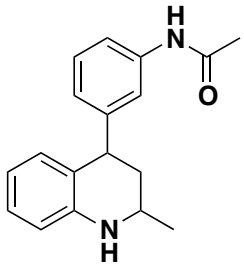


To 400 mL of DMSO was added NaN_3 (1.45g, 22 mmol, 1.1 equiv), and the suspension was allowed to stir for 1 h or until completely dissolved. The appropriate benzylic bromide was then added (20 mmol, 1.0 equiv), and the mixture was stirred at room temperature overnight. After completion, 400 mL H_2O was added and the solution was allowed to cool to room temperature. The mixture was then extracted with 3 x 200 mL Et_2O, and the organic phase was washed with 2 x 100 mL H_2O followed by 1 x 100 mL brine. The organic phase was then dried over $MgSO_4$, and concentrated to give the corresponding azides (yields >90%), which were used without further purification.

A solution of the appropriate benzylic azide was added to CH_2Cl_2 and cooled to 0 °C. TfOH (1.1 equiv) was added, and the solution allowed to stir for 10 min at room temperature. Indene or the appropriate styrene (2.0 equiv) was then added (either at room temperature, or at 0 °C) and the reaction stirred at the indicated temperature until completion (see below). The reaction was quenched by addition of saturated aqueous Na_2CO_3, and extracted into EtOAc (3 x 100 mL). The organic phase was washed with brine, dried over $MgSO_4$, concentrated, and purified by column chromatography.

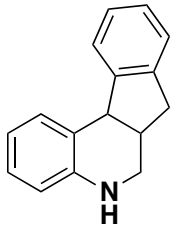


From 3-methylbenzyl azide. 4-fluorostyrene was added at room temperature, and stirred for 1 h at room temperature. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 – 7.06 (m, 2H), 7.03 – 6.92 (m, 2H), 6.61 (d, *J* = 7.6 Hz, 1H), 6.46 – 6.35 (m, 2H), 4.10 (t, *J* = 6.1 Hz, 1H), 3.87 (s, 1H), 3.29 (ddd, *J* = 11.0, 7.2, 3.6 Hz, 1H), 3.21 (ddd, *J* = 11.5, 8.1, 3.4 Hz, 1H), 2.24 (s, 3H), 2.18 (dddd, *J* = 13.3, 8.1, 5.4, 3.5 Hz, 1H), 1.99 (dtd, *J* = 13.0, 7.1, 3.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.33 (d, *J* = 243.9 Hz), 144.74, 142.46 (d, *J* = 3.2 Hz), 137.18, 130.20, 129.96 (d, *J* = 7.8 Hz), 120.43, 118.16, 115.08, 114.84 (d, *J* = 17.3 Hz), 41.81, 39.17, 31.46, 21.18; MS: Calc for $C_{16}H_{16}FN$: 242.1340; Meas: 242.1333.



From (1-azidoethyl)benzene. 3-acetamidostyrene was added at room temperature and stirred at reflux overnight. Mp = 175-180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.49 (m, 1H), 7.29 (m, overlaps with $CHCl_3$, 1H), 7.22 (t, *J* = 1.8 Hz, 1H), 7.14 (br s, 1H), 7.06 – 6.94 (m, 2H), 6.69 – 6.47 (m, 3H), 4.15 (dd, *J* = 12.4, 5.5 Hz, 1H), 3.81 (br s, 1H), 3.60 (dtt, *J* = 12.5, 6.3, 3.1 Hz, 1H), 2.32 – 2.08 (m, 4H), 1.82 (td, *J* = 12.6, 11.1 Hz, 1H),

1.24 (d, J = 6.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.13, 146.97, 145.32, 138.04, 129.75, 129.19, 127.17, 124.75, 124.49, 119.81, 118.06, 117.32, 114.09, 47.62, 44.44, 41.18, 24.67, 22.56; MS: Calc for $C_{18}H_{20}N_2O$: 281.1649; Meas: 281.1649.

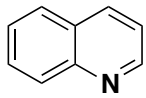


From benzyl azide. Indene was added at 0 °C, and the reaction stirred for 1 h at this temperature. Mp = 89-90 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (m, 2H), 7.29 – 7.21 (m, 1H), 7.18 – 7.11 (m, 2H), 7.04 (td, J = 7.9, 1.5 Hz, 1H), 6.79 (td, J = 7.4, 1.2 Hz, 1H), 6.57 (dd, J = 7.9, 1.2 Hz, 1H), 4.32 (d, J = 6.0 Hz, 1H), 3.84 (br s, 1H), 3.30 – 3.13 (m, 2H), 2.93 – 2.78 (m, 2H), 2.72 (dd, J = 15.7, 1.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.58, 144.81, 141.39, 130.78, 127.07, 126.52, 126.33, 125.25, 124.53, 122.22, 117.60, 114.87, 45.64, 43.14, 37.14, 36.11; MS: Calc for $C_{16}H_{15}N$: 222.1278; Meas: 222.1277.

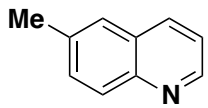
Synthesis and Characterization of Products

General procedure for oxidation of tetrahydroquinolines to quinolines.

A 25 mL round bottom flask equipped with a stir bar was loaded with tetrahydroquinoline (1.0 mmol), $[Ru(phd)_3]2PF_6$ (0.025 mmol, 25.5 mg), and Co(salophen) (0.05 mmol, 18.7 mg). MeCN (4.0 mL) or MeOH (if indicated) was added and the reaction was stirred open to ambient air until TLC indicated completion. (Typically, for reaction times longer than 8 h, the reaction was equipped with an air balloon to minimize solvent evaporation). The crude reaction mixture was then diluted with EtOAc and filtered through a pad of celite. The celite pad was subsequently washed with EtOAc (5 x 50 mL) and the combined filtrate was concentrated *in vacuo*. Purification using SiO_2 chromatography afforded the desired quinoline product.

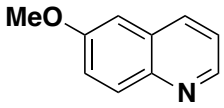


Characterization data matched those of authentic material.[11] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.89 (dd, J = 4.2, 1.7 Hz, 1H), 8.09 (dd, J = 8.3, 1.5 Hz, 2H), 7.76 (dd, J = 8.1, 1.4 Hz, 1H), 7.68 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.50 (ddd, J = 8.0, 6.8, 1.1 Hz, 1H), 7.34 (dd, J = 8.2, 4.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.42, 148.28, 136.02, 129.46, 129.44, 128.26, 127.79, 126.52, 121.06.

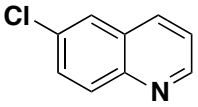


Characterization data matched those of authentic material.[11] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (dd, J = 4.3, 1.7 Hz, 1H), 8.00 (t, J = 9.7 Hz, 2H), 7.57 – 7.45 (m, 2H), 7.30 (dd, J

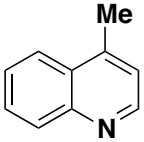
= 8.2, 4.2 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.53, 146.90, 136.34, 135.32, 131.71, 129.11, 128.29, 126.58, 121.04, 21.57; MS: Calc for $C_{10}H_9N$: 144.0808; Meas: 144.0809.



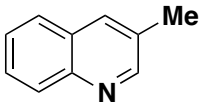
Characterization data matched those of authentic material.[11] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.03 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.99 (d, *J* = 9.2 Hz, 1H), 7.43 – 7.27 (m, 2H), 7.06 (d, *J* = 2.8 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.71, 147.96, 144.45, 134.76, 130.88, 129.29, 122.27, 121.36, 105.10, 55.53; MS: Calc for $C_{10}H_9NO$: 160.0757; Meas: 160.0759.



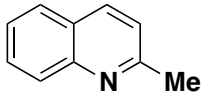
Characterization data matched those of authentic material.[11] Mp = 35-37 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.91 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.14 – 7.99 (m, 2H), 7.80 (d, *J* = 2.3 Hz, 1H), 7.65 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.42 (dd, *J* = 8.3, 4.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.59, 145.62, 134.10, 131.26, 130.10, 129.39, 127.80, 125.39, 120.89; MS: Calc for C_9H_6ClN: 164.0262; Meas: 164.0260.



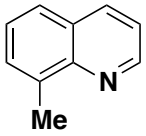
Characterization data matched those of authentic material.[11] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 4.4 Hz, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 8.00 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.71 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.57 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.23 (dd, *J* = 4.4, 1.2 Hz, 1H), 2.71 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.20, 147.99, 144.31, 130.03, 129.12, 128.29, 126.29, 123.82, 121.87, 18.69; MS: Calc for $C_{10}H_9N$: 144.0808; Meas: 144.0812.



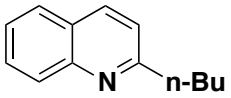
Characterization data matched those of authentic material.[11] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (d, *J* = 2.2 Hz, 1H), 8.06 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.90 (d, *J* = 1.1 Hz, 1H), 7.73 (dd, *J* = 8.1, 0.7 Hz, 1H), 7.64 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.50 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.44, 146.57, 134.66, 130.47, 129.19, 128.43, 128.13, 127.13, 126.55, 18.77 MS: Calc for $C_{10}H_9N$: 144.0808; Meas: 144.0807.



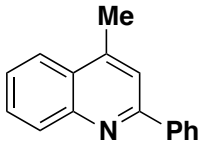
Characterization data matched those of authentic material.[11] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.7 Hz, 2H), 7.77 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.68 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.48 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 2.75 (s, 3H);^{13}C NMR (126 MHz, $CDCl_3$) δ 159.01, 147.89, 136.17, 129.43, 128.65, 127.49, 126.49, 125.67, 122.01, 25.43; MS: Calc for $C_{10}H_9N$: 144.0808; Meas: 144.0810.



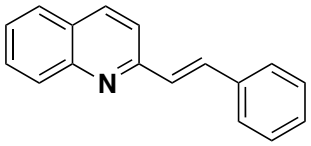
Characterization data matched those of authentic material.[11] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.13 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.57 (dt, *J* = 7.0, 1.3 Hz, 1H), 7.47 – 7.34 (m, 2H), 2.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.27, 147.40, 137.12, 136.30, 129.61, 128.28, 126.30, 125.87, 120.84, 18.15; MS: Calc for $C_{10}H_9N$: 144.0808; Meas: 144.0809.



Characterization data matched those previously reported.[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.00 (m, 2H), 7.77 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.67 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.47 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.29 (d, *J* = 8.5 Hz, 1H), 3.10 – 2.89 (m, 2H), 1.89 – 1.71 (m, 2H), 1.54 – 1.34 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.12, 147.93, 136.15, 129.30, 128.85, 127.48, 126.71, 125.62, 121.38, 39.15, 32.22, 22.71, 14.02; MS: Calc for $C_{13}H_{15}N$: 186.1278; Meas: 186.1276.

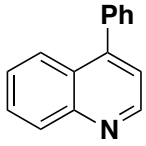


Characterization data matched those of authentic material.[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (ddd, *J* = 9.8, 8.3, 1.4 Hz, 3H), 8.05 – 7.97 (m, 1H), 7.73 (d, *J* = 1.4 Hz, 2H), 7.61 – 7.49 (m, 3H), 7.47 (m, 1H), 2.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.09, 148.16, 144.79, 139.85, 130.33, 129.32, 129.19, 128.78, 127.54, 127.27, 126.02, 123.61, 119.77, 19.03; MS: Calc for $C_{16}H_{13}N$: 220.1121; Meas: 220.1124.

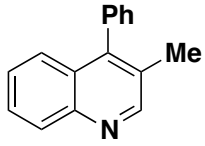


Characterization data matched those previously reported.[13] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.5 Hz, 1H), 8.01 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.75 – 7.68 (m, 1H), 7.67 – 7.53 (m, 5H), 7.42 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.38 – 7.30 (m, 3H), 7.28 – 7.22 (m, 1H);

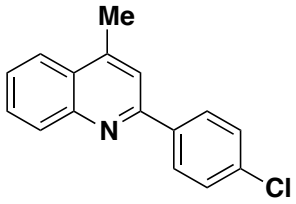
^{13}C NMR (126 MHz, $CDCl_3$) δ 156.01, 148.29, 136.53, 136.35, 134.43, 129.75, 129.23, 129.05, 128.81, 128.64, 127.51, 127.36, 127.28, 126.18, 119.28; MS: Calc for $C_{17}H_{13}N$: 232.1121; Meas: 232.1117.



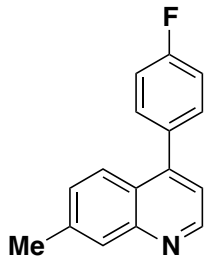
Characterization data matched those previously reported.[14] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.95 (d, *J* = 4.4 Hz, 1H), 8.18 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.93 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.73 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.59 – 7.44 (m, 6H), 7.34 (d, *J* = 4.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.01, 148.71, 148.48, 138.01, 129.88, 129.56, 129.32, 128.59, 128.43, 126.77, 126.63, 125.89, 121.35; MS: Calc for $C_{15}H_{11}N$: 206.0965; Meas: 206.0969.



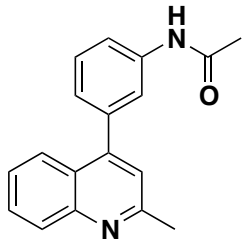
Characterization data matched those previously reported.[15] Mp = 83-85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.56 (td, *J* = 6.8, 1.8 Hz, 0H), 7.52 – 7.27 (m, 5H), 7.20 (d, *J* = 6.9 Hz, 2H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.66, 146.91, 146.25, 136.90, 129.37, 129.25, 128.60, 128.18, 128.03, 127.89, 127.56, 126.42, 125.88,17.60; MS: Calc for $C_{16}H_{13}N$: 220.1121; Meas: 220.1120.



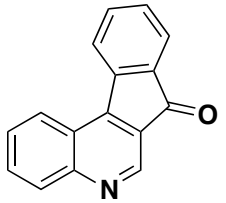
Mp = 65-67 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.5 Hz, 1H), 8.12 (d, *J* = 8.6 Hz, 2H), 8.01 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.73 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.69 (q, *J* = 1.1 Hz, 1H), 7.56 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.49 (d, *J* = 8.8 Hz, 2H), 2.78 (d, *J* = 1.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.73, 148.08, 145.08, 138.21, 135.39, 130.27, 129.51, 128.96, 128.79, 127.30, 126.25, 123.65, 119.34, 19.08; MS: Calc for $C_{16}H_{12}ClN$: 254.0732; Meas: 254.0727.



Compound has been previously reported.[16] Mp = 115-118 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (d, *J* = 4.4 Hz, 1H), 7.88 (s, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.51 – 7.35 (m, 2H), 7.27 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.22 – 7.05 (m, 3H), 2.50 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.88 (d, *J* = 248.1 Hz), 149.94, 148.95, 147.13, 139.74, 134.12 (d, *J* = 3.3 Hz), 131.20 (d, *J* = 8.0 Hz), 129.03, 128.92, 125.25, 124.73, 120.64, 115.63 (d, *J* = 21.6 Hz), 21.73; MS: Calc'd for $C_{16}H_{12}FN$: 238.1027; Meas: 238.1032.

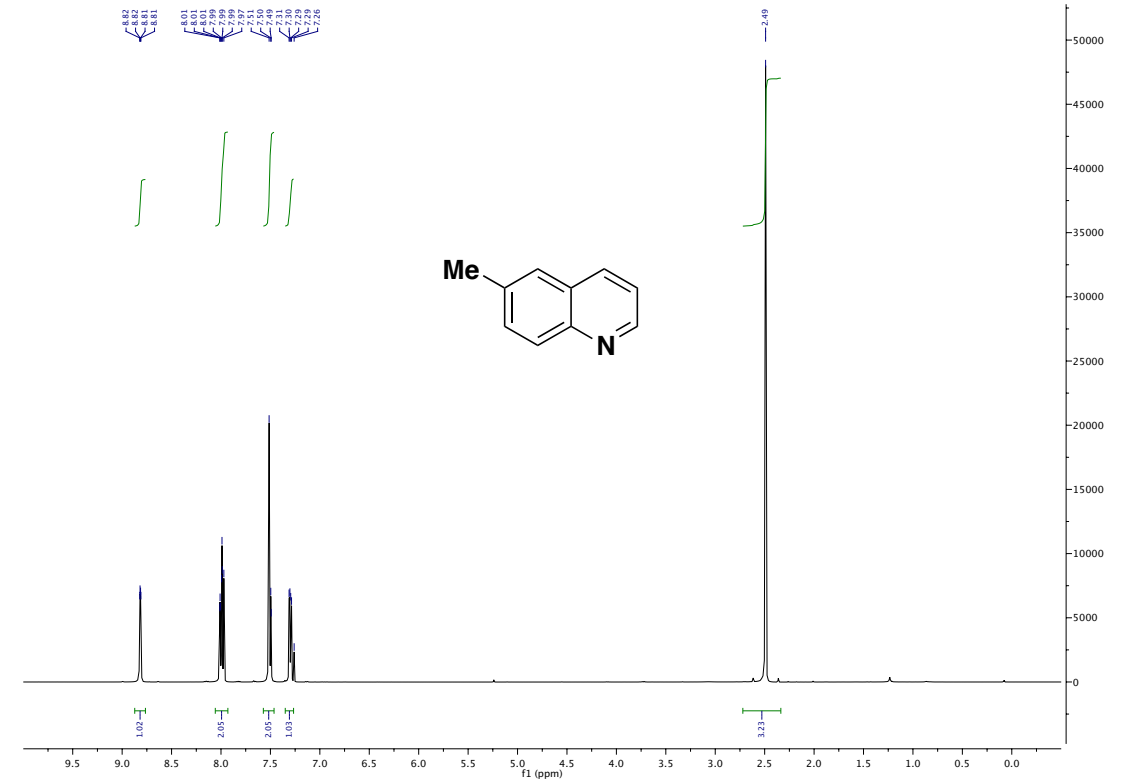


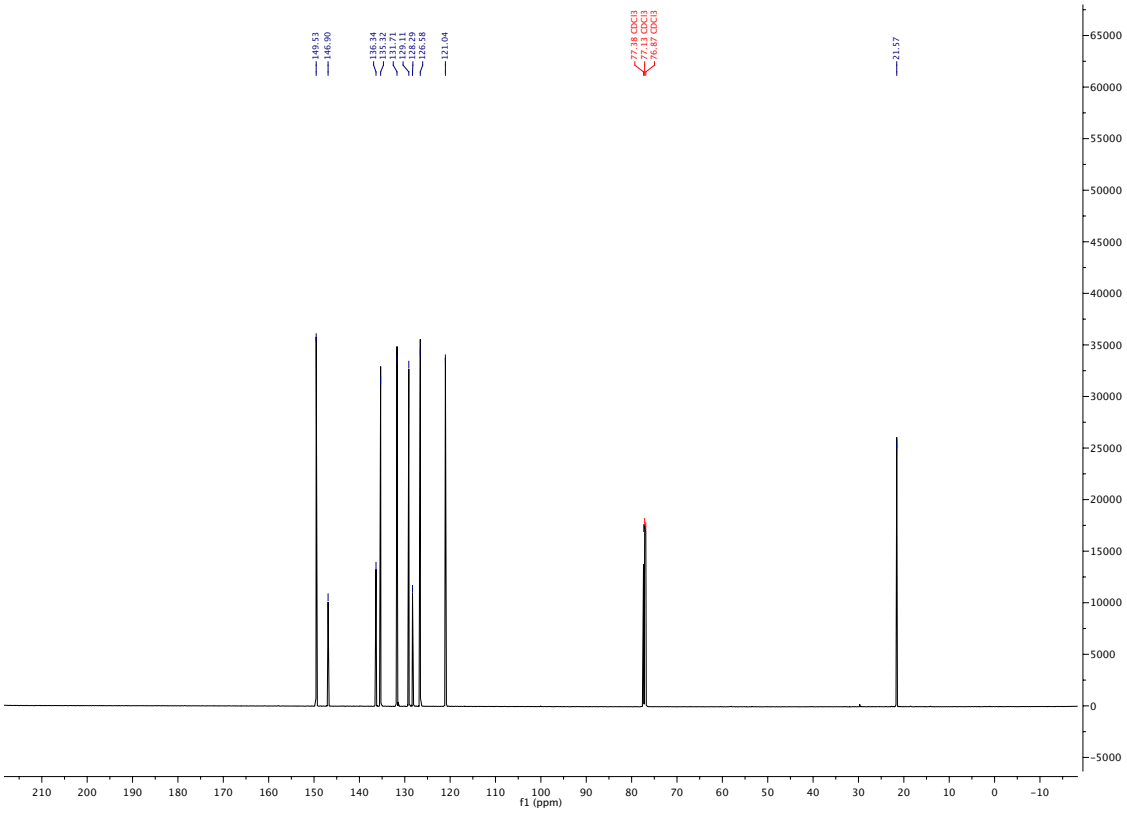
Characterization data matched those previously reported.[17] Mp = 188-190 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.73 – 7.56 (m, 4H), 7.48 – 7.38 (m, 2H), 7.25 – 7.18 (m, 2H), 2.76 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.50, 158.49, 148.29, 148.04, 138.91, 138.22, 129.42, 129.19, 128.89, 125.86, 125.58, 125.38, 124.95, 122.19, 120.77, 119.70, 25.30, 24.65; MS: Calc for $C_{18}H_{16}N_2O$: 277.1336; Meas: 277.1334.

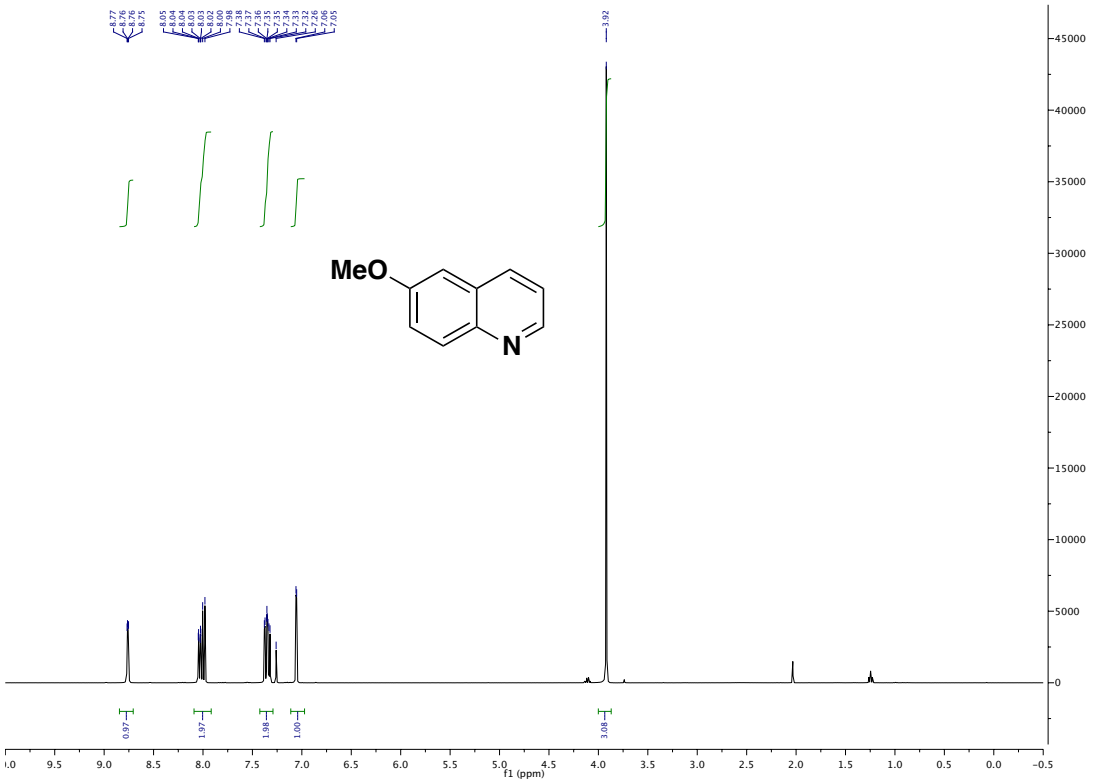


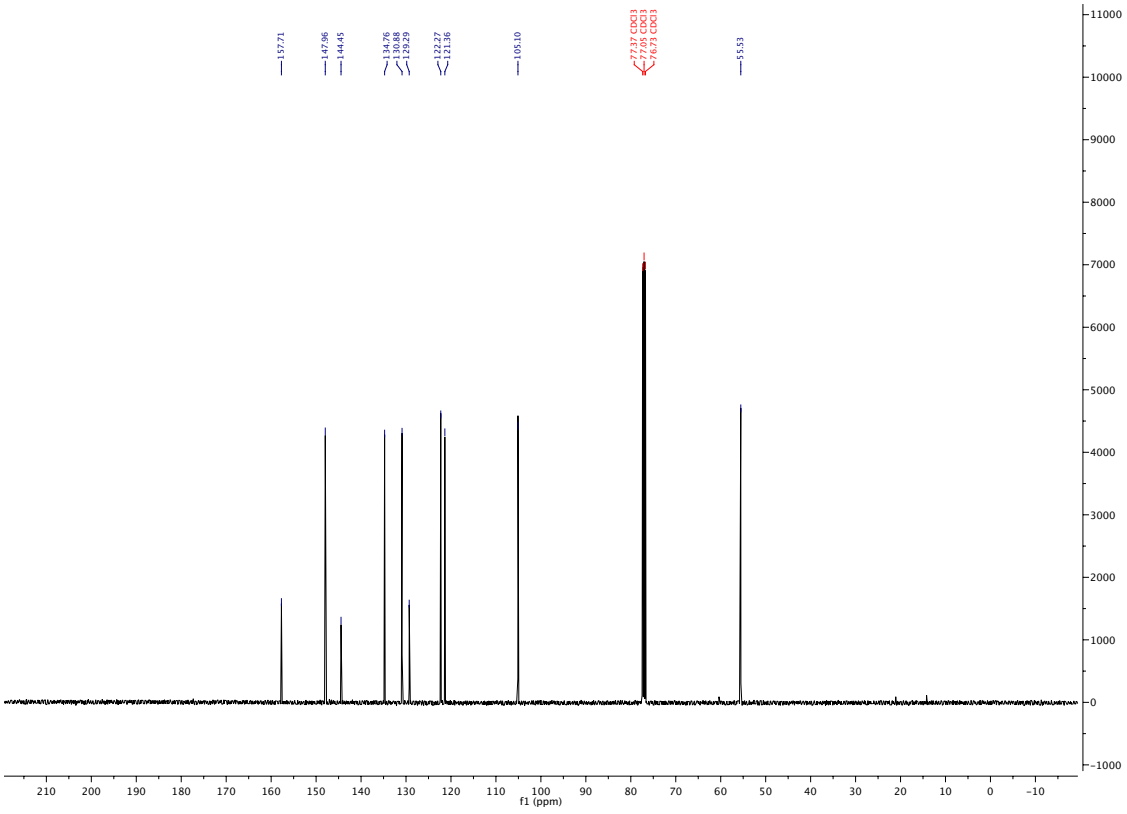
Compound has been previously reported.[18] Mp = 223-224 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.17 (s, 1H), 8.50 (dd, *J* = 8.4, 1.0 Hz, 1H), 8.19 (dt, *J* = 8.5, 0.8 Hz, 1H), 8.14 (d, *J* = 7.5 Hz, 1H), 7.86 (ddd, *J* = 8.2, 6.7, 1.3 Hz, 1H), 7.79 (dt, *J* = 7.4, 0.9 Hz, 1H), 7.71 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1H), 7.64 (td, *J* = 7.6, 1.2 Hz, 1H), 7.51 (td, *J* = 7.4, 0.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.08, 152.66, 151.20, 144.90, 142.57, 134.74, 134.04, 132.18, 131.17, 131.15, 128.26, 125.05, 124.93, 124.87, 124.58, 123.69; MS: Calc for $C_{16}H_9NO$: 232.0757; Meas: 232.0759.

IV. ^{1}H and ^{13}C NMR Data






MeO
N
f1 (ppm)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134.76
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129.89
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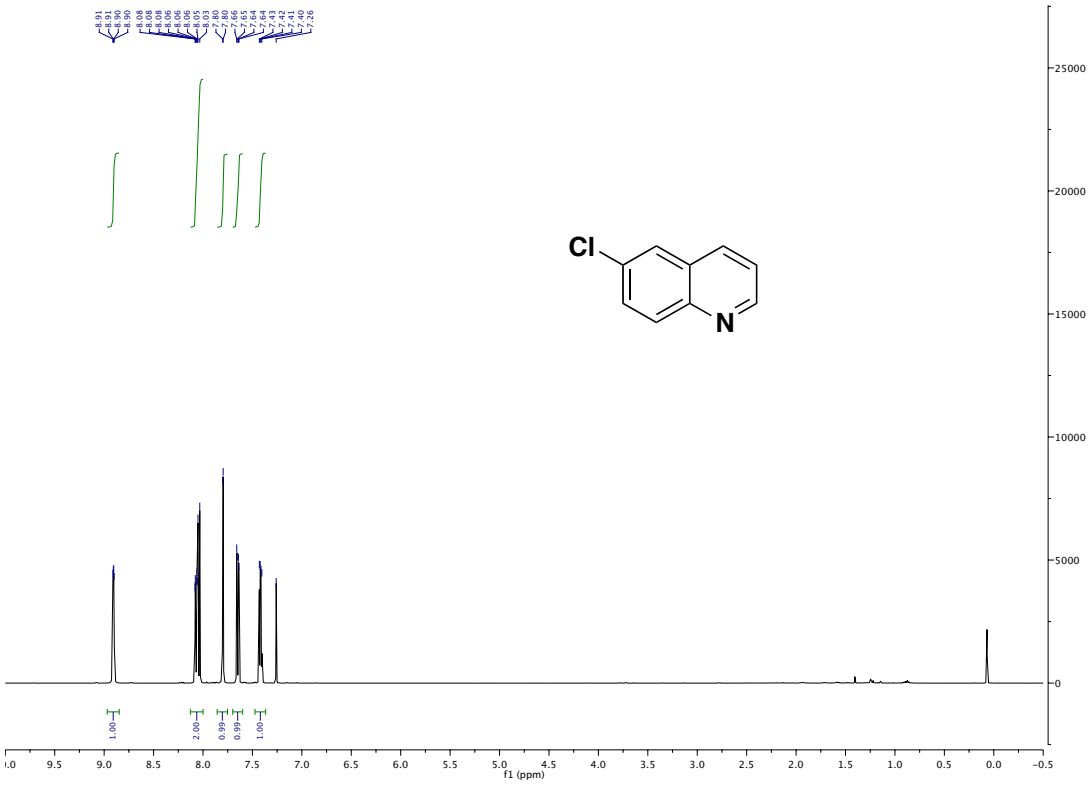
121.56
105.10
77.27 CDCl3
77.05 CDCl3
76.73 CDCl3
55.53
f1 (ppm)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8.91
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8.08
8.08
8.06
8.06
8.06
8.06
8.05
8.03
7.80
7.80
7.66
7.65
7.64
7.64
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7.40
7.26
Cl
N
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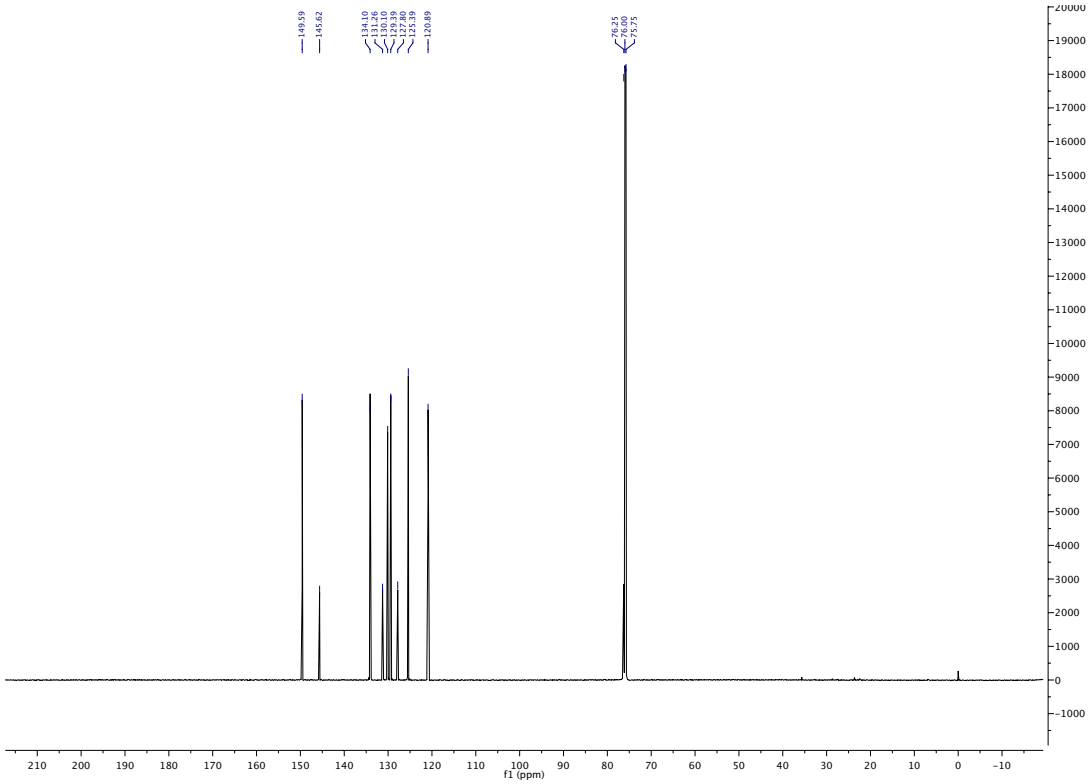
2.00
0.99
0.99
1.00
f1 (ppm)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125.39
120.89
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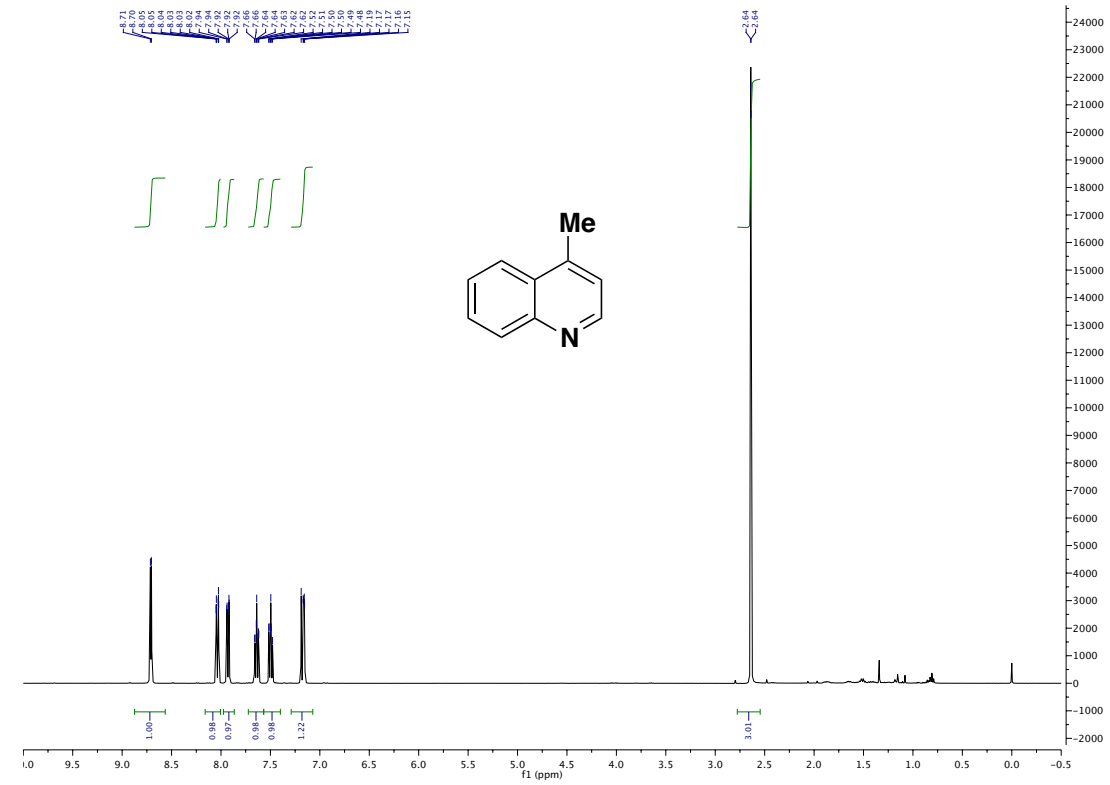
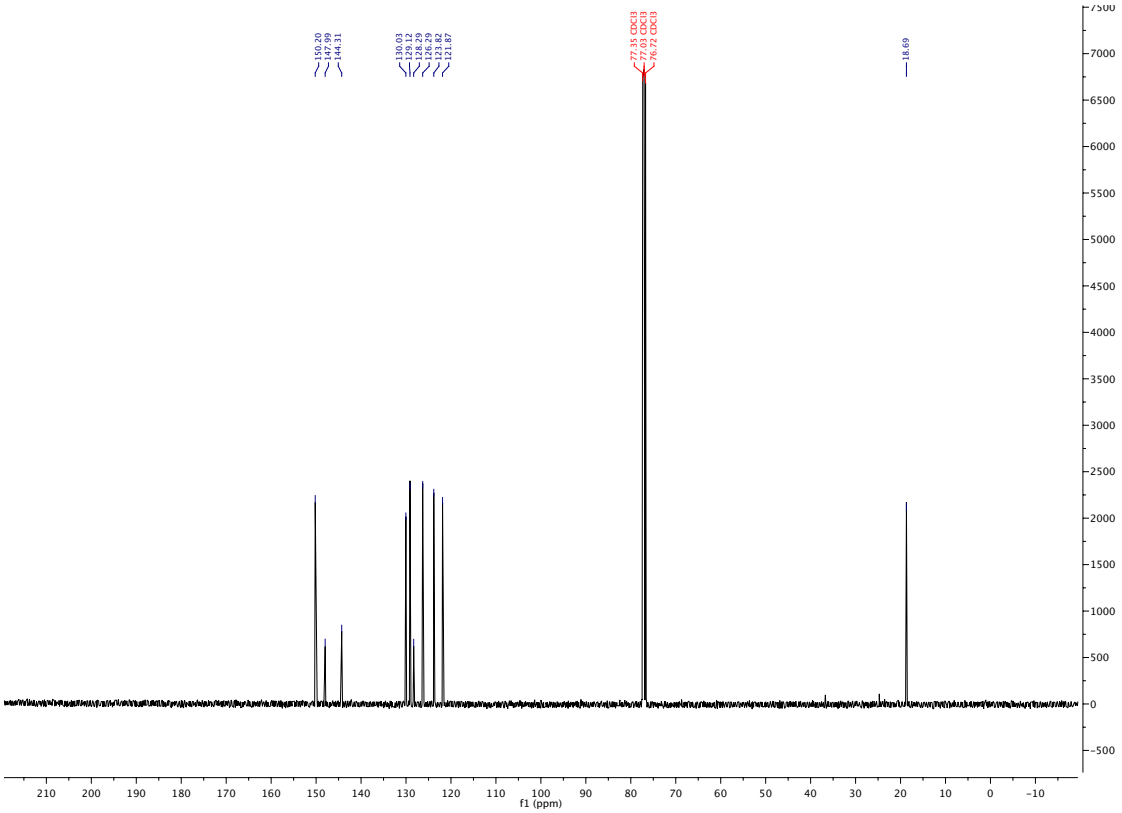
75.75
f1 (ppm)


Me
N
f1 (ppm)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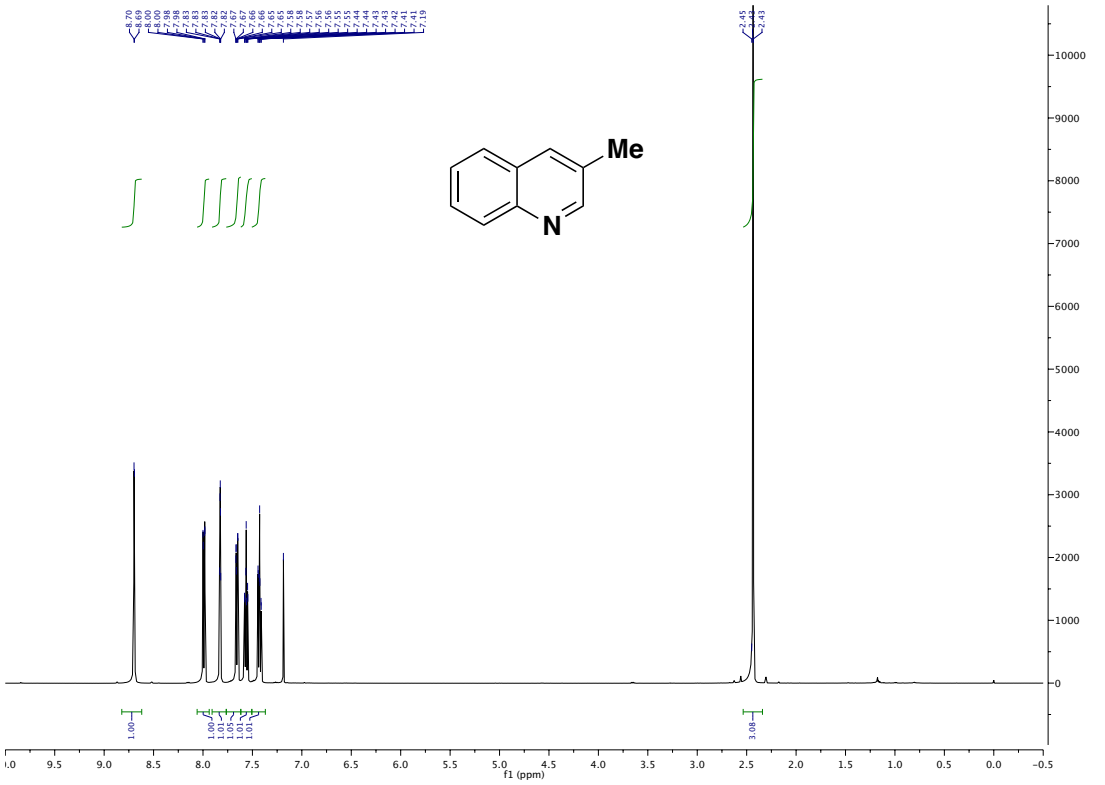
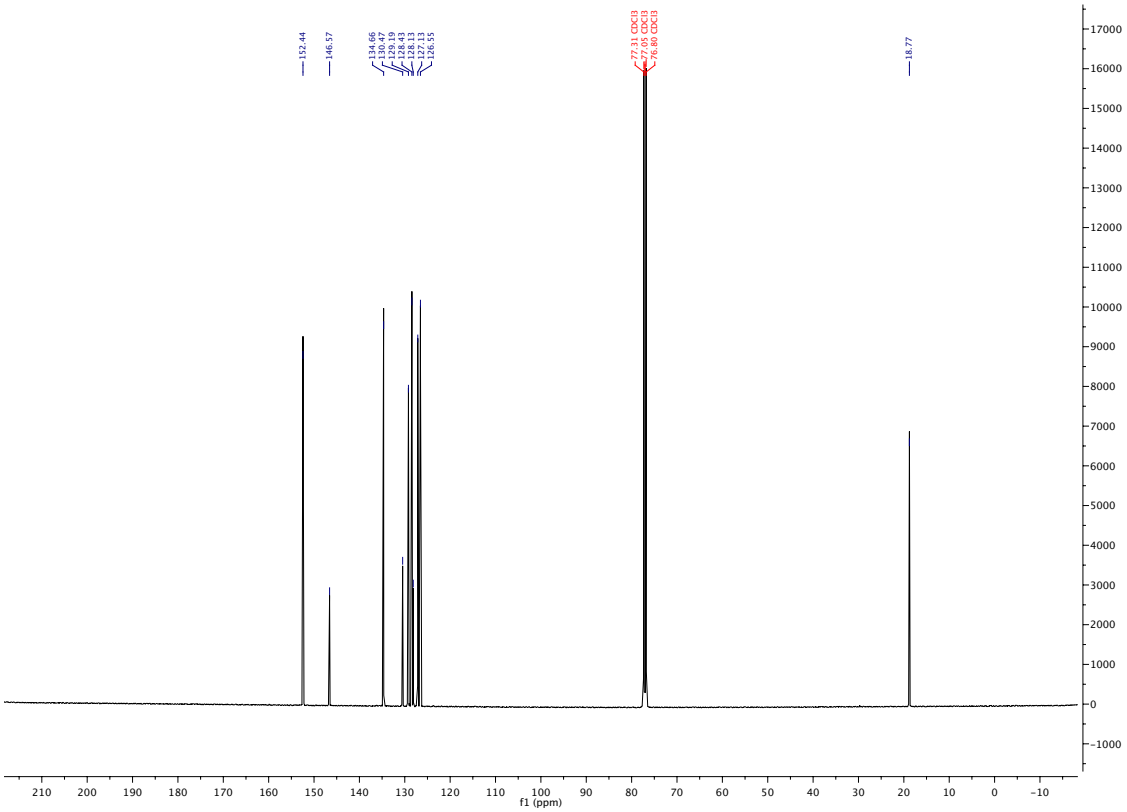

Me
N
f1 (ppm)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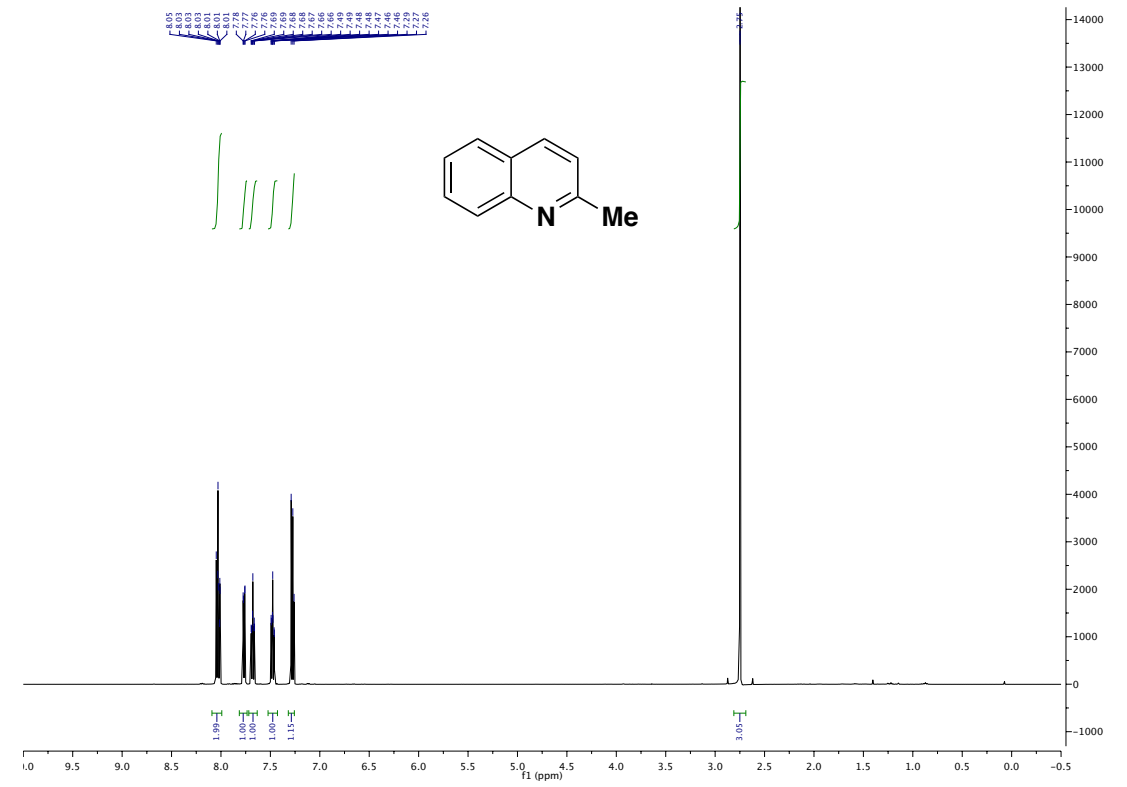
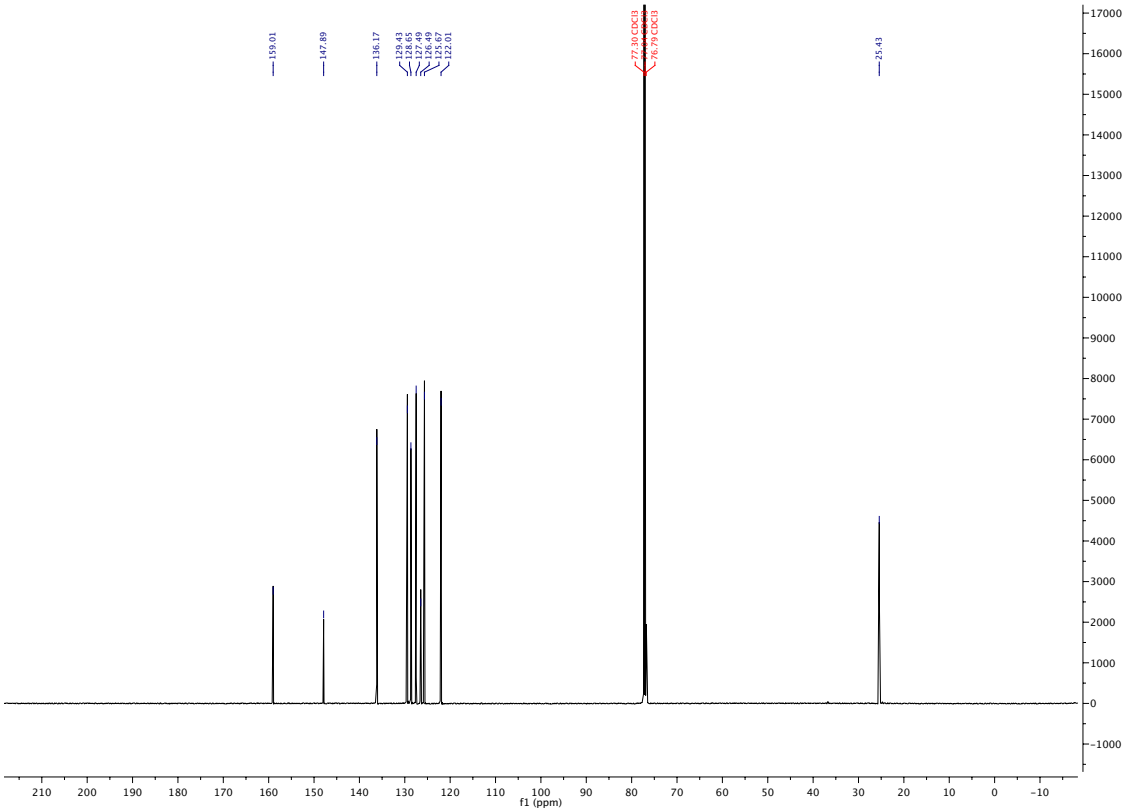
127.13
126.55
77.31 CDCl3
77.05 CDCl3
76.80 CDCl3
18.77
f1 (ppm)


N
Me
f1 (ppm)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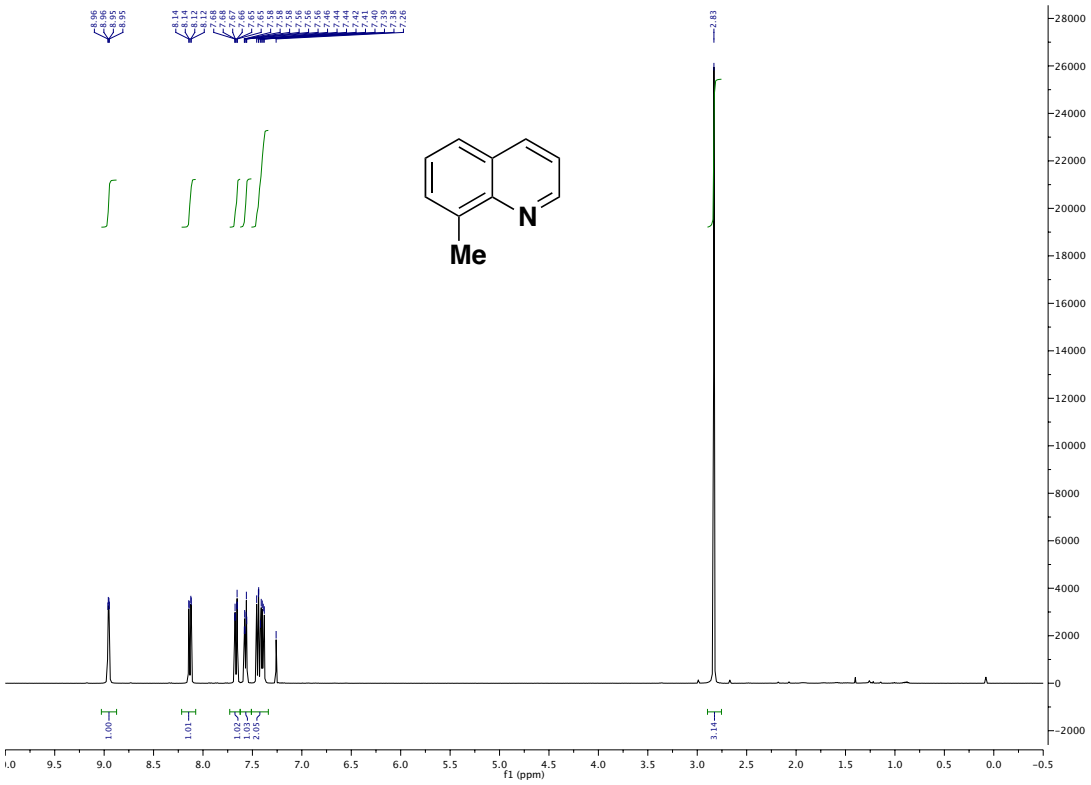
25.43
f1 (ppm)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7.65
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7.58
7.56
7.56
7.46
7.44
7.42
7.41
7.40
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N
Me
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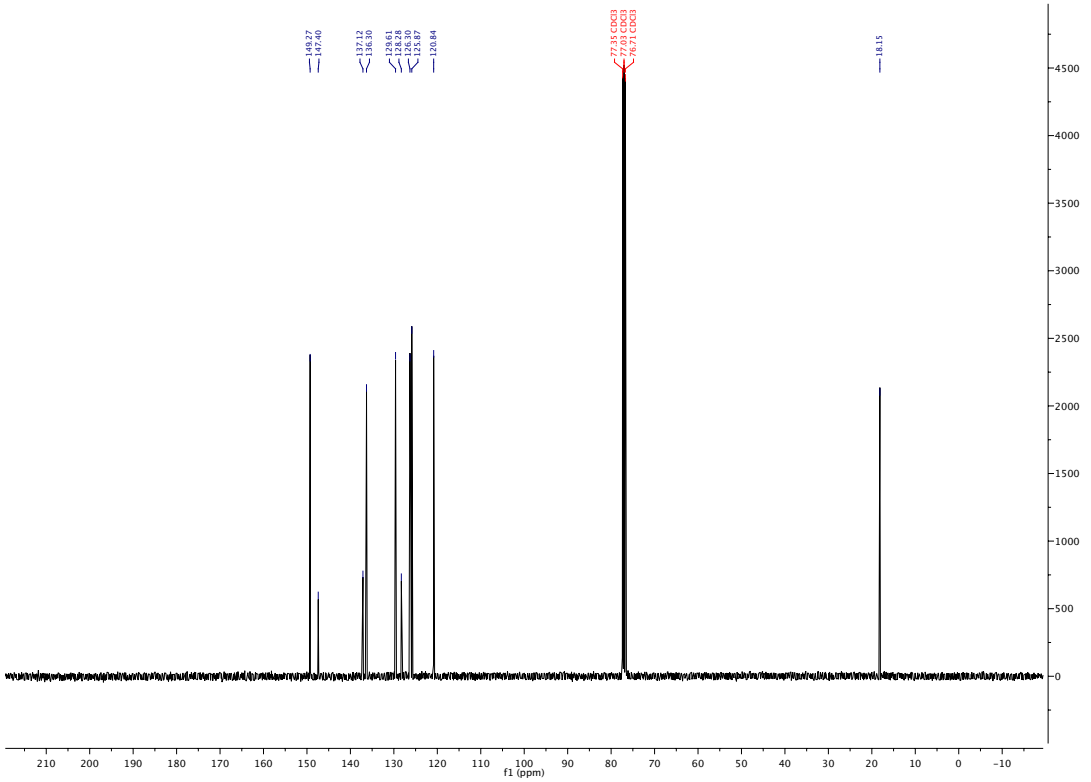
1.01
1.02
1.03
2.05
3.14
f1 (ppm)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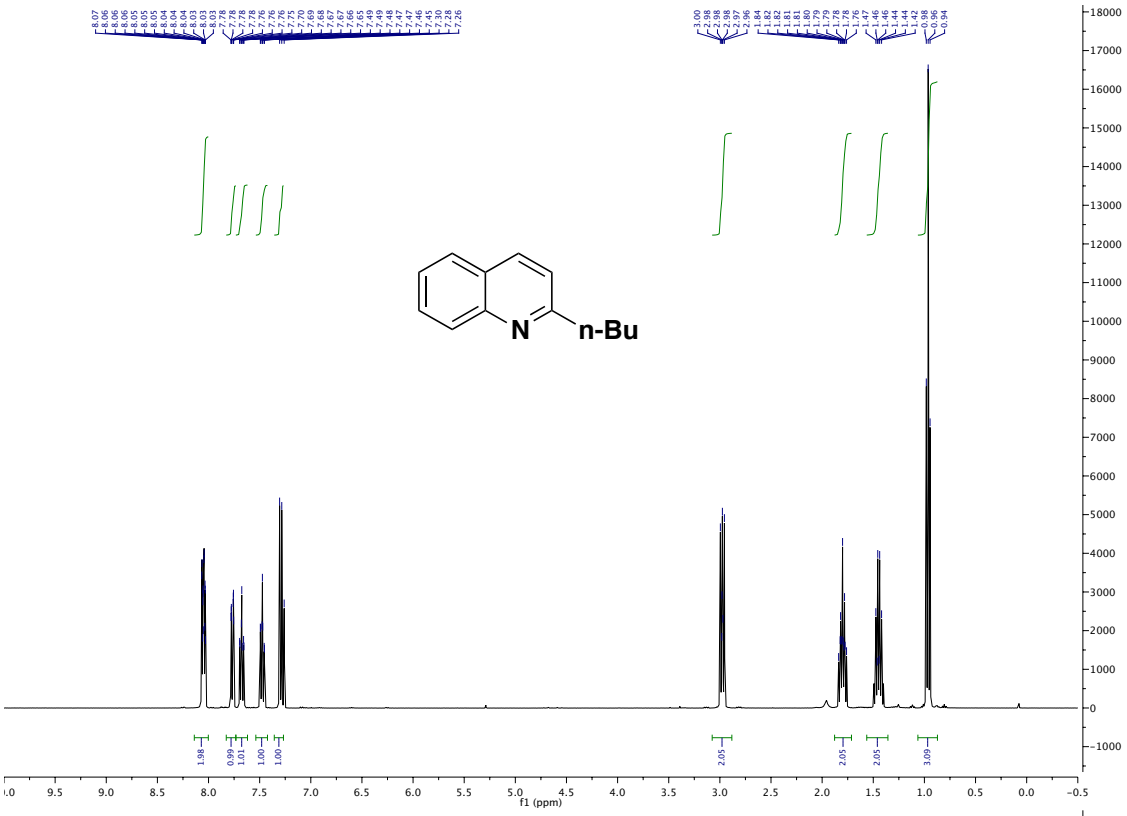
77.03 CDCl3
76.71 CDCl3
18.15
f1 (ppm)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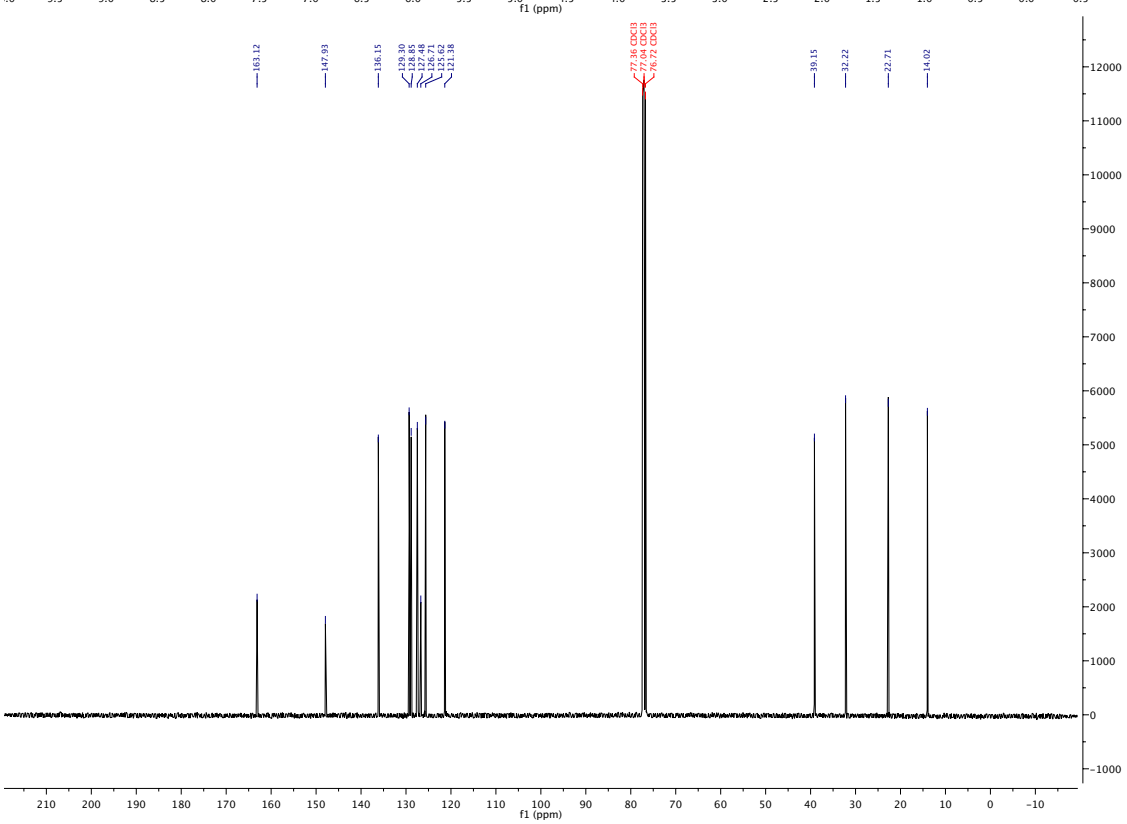
n-Bu
f1 (ppm)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77.04 CDCl3
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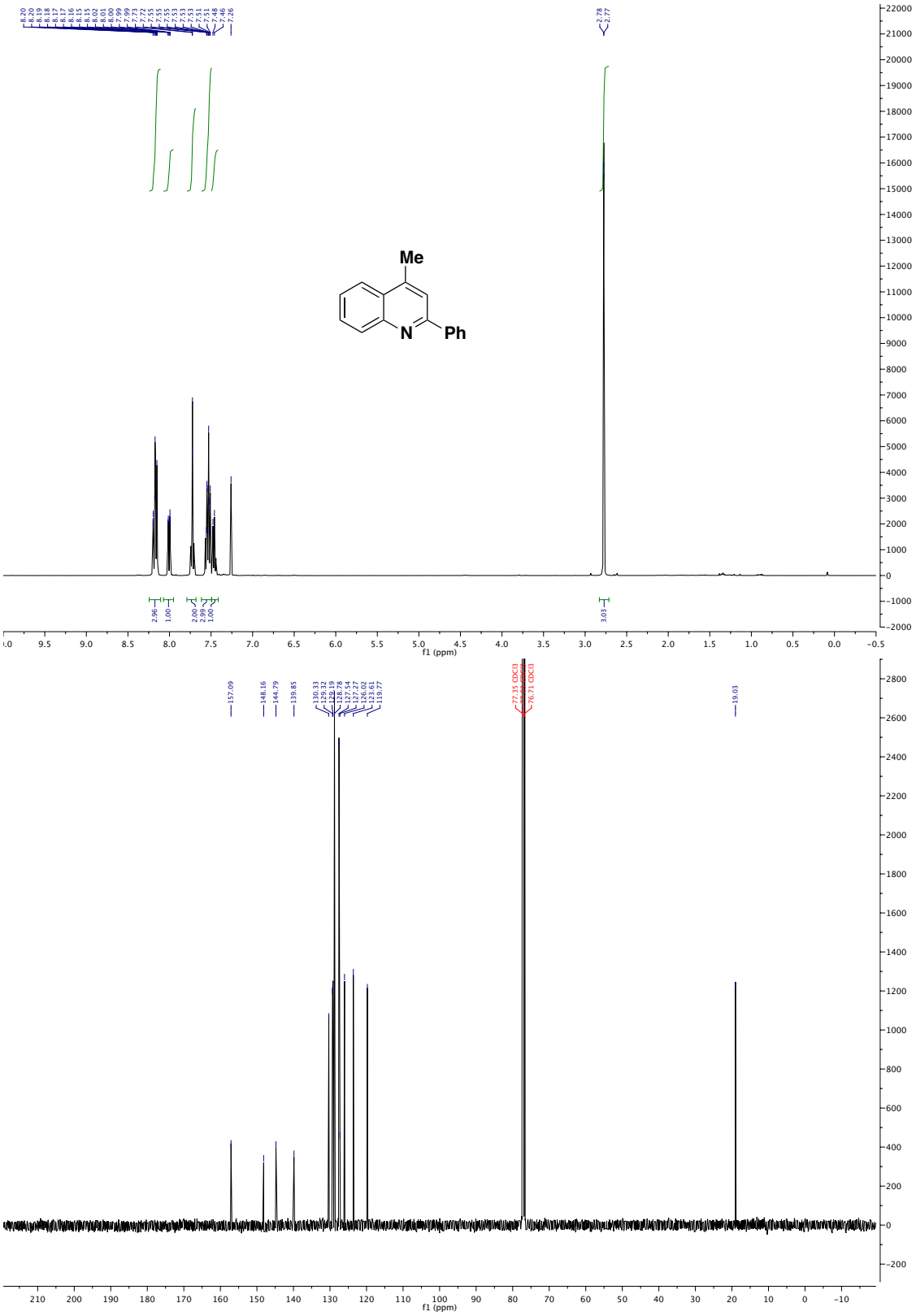
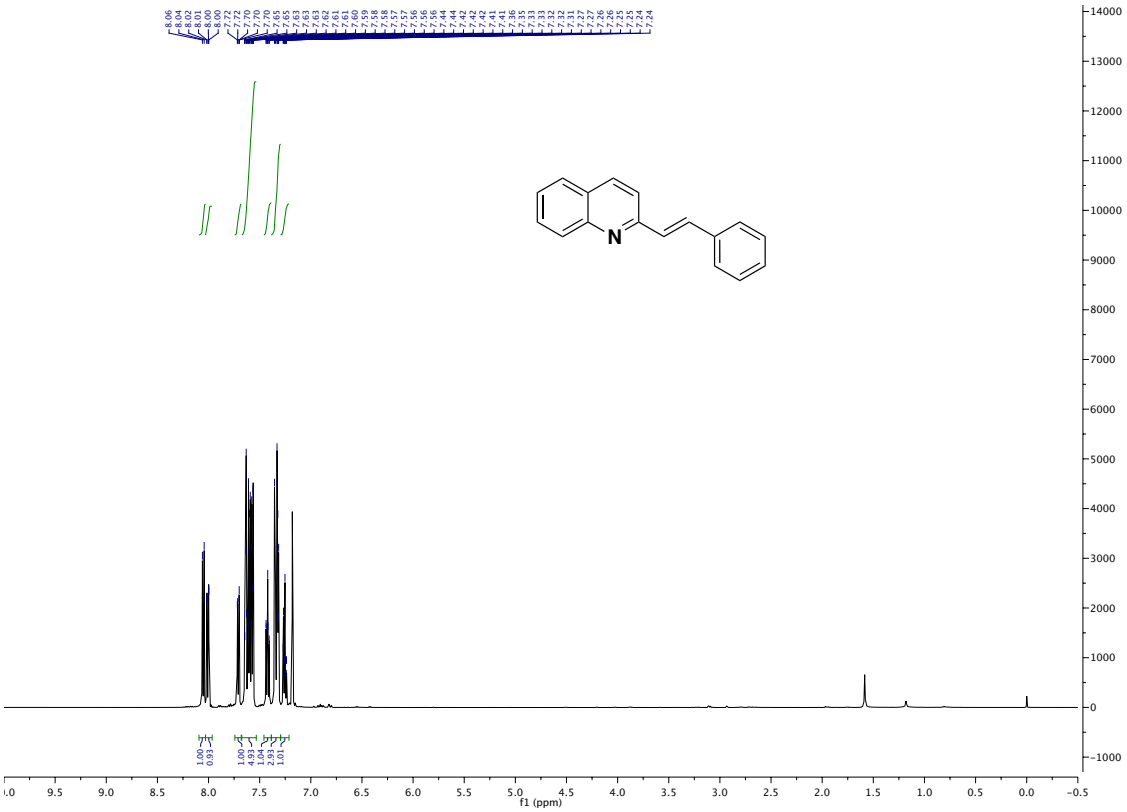
39.15
32.22
22.71
14.02
f1 (ppm)


Me
N
Ph
f1 (ppm)
f1 (ppm)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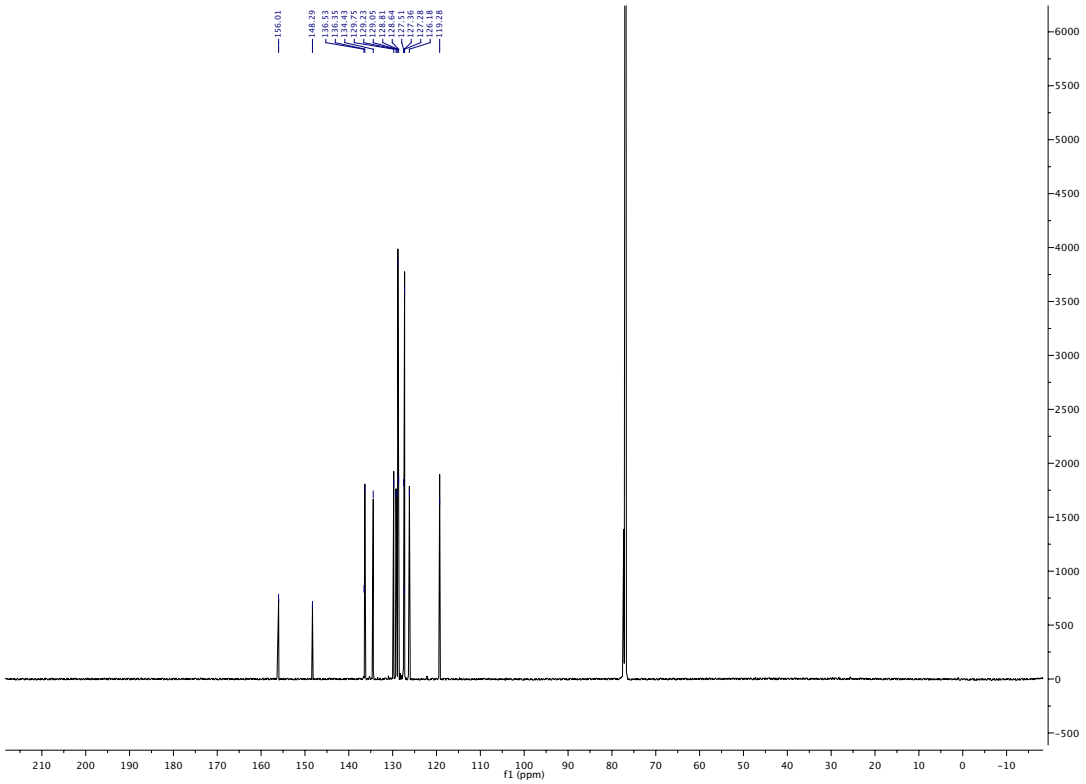
f1 (ppm)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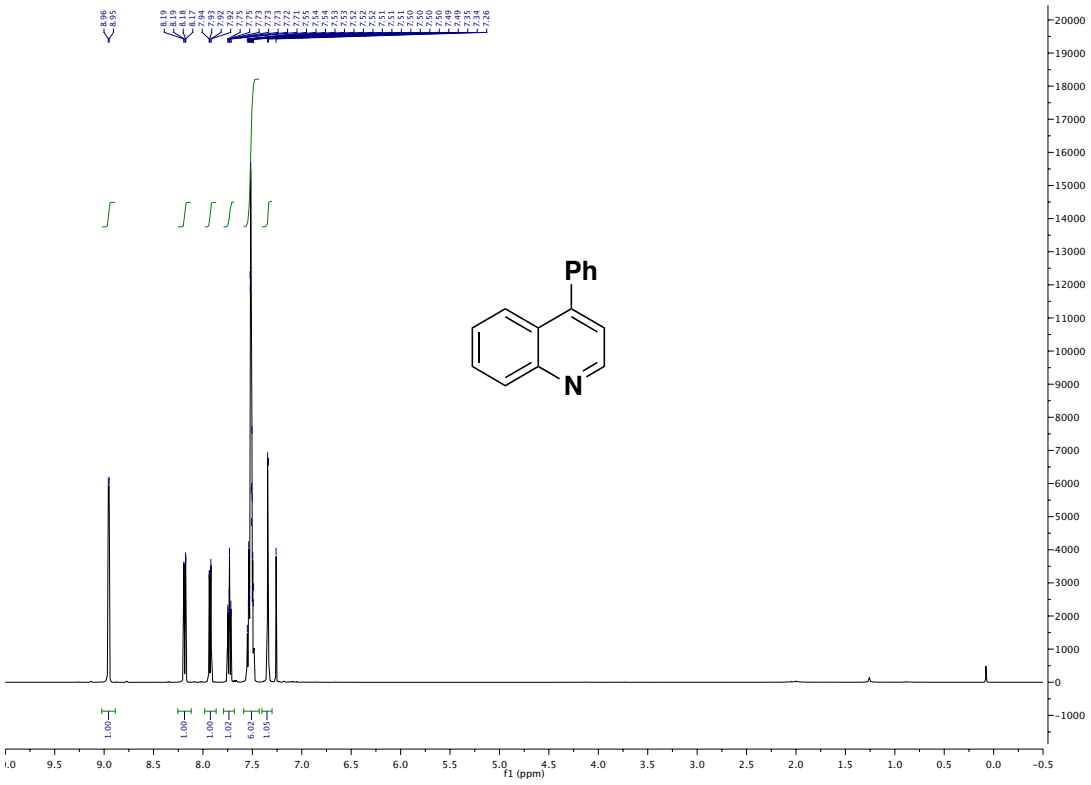
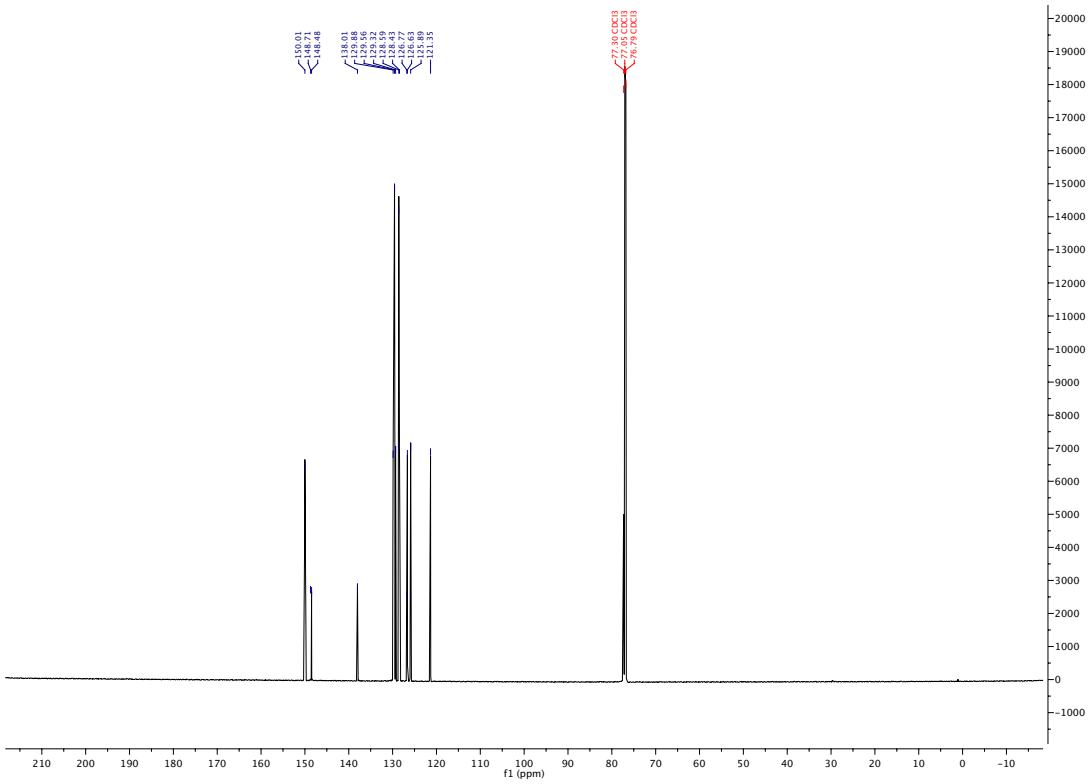

Ph
N
f1 (ppm)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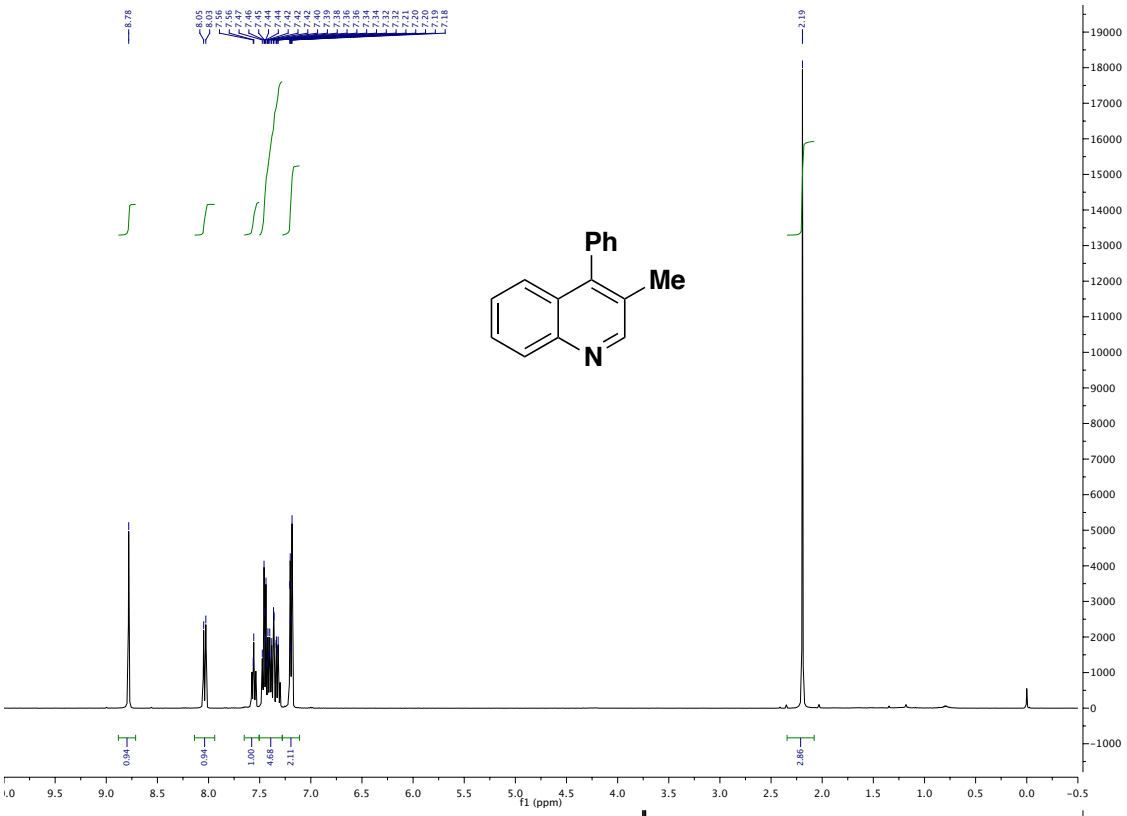
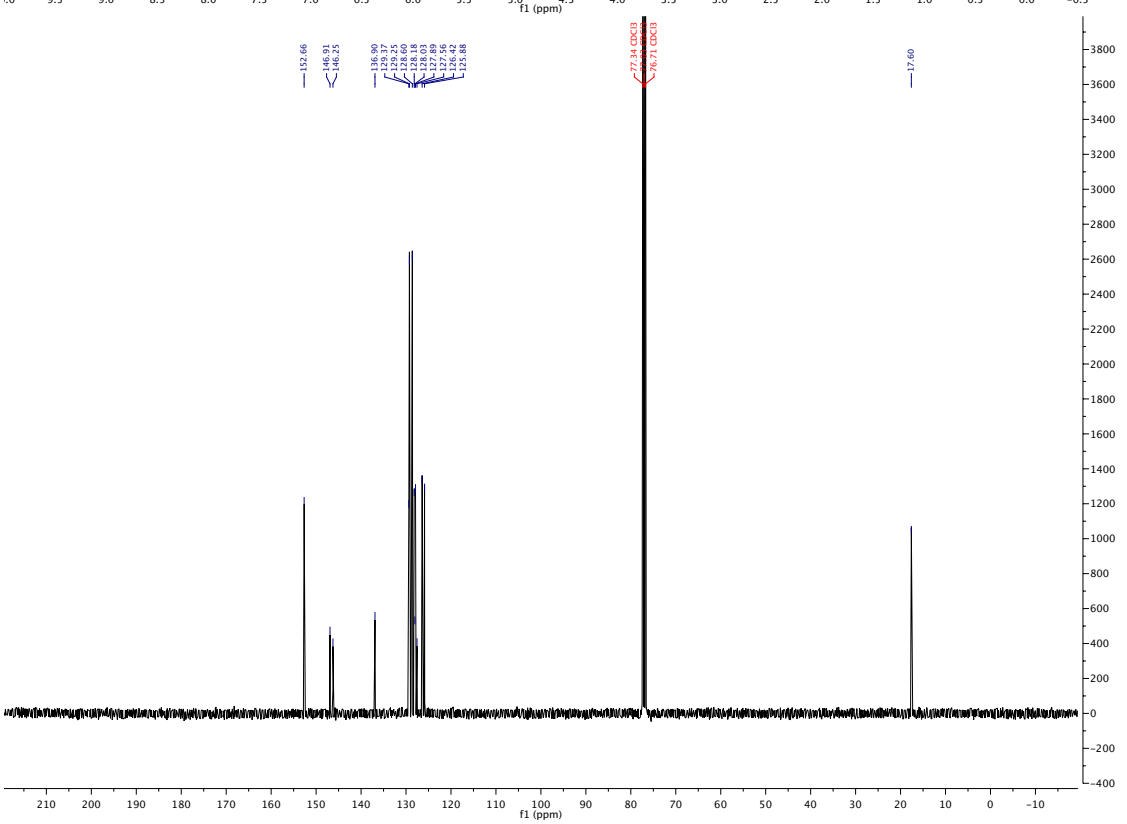

Ph
Me
N
f1 (ppm)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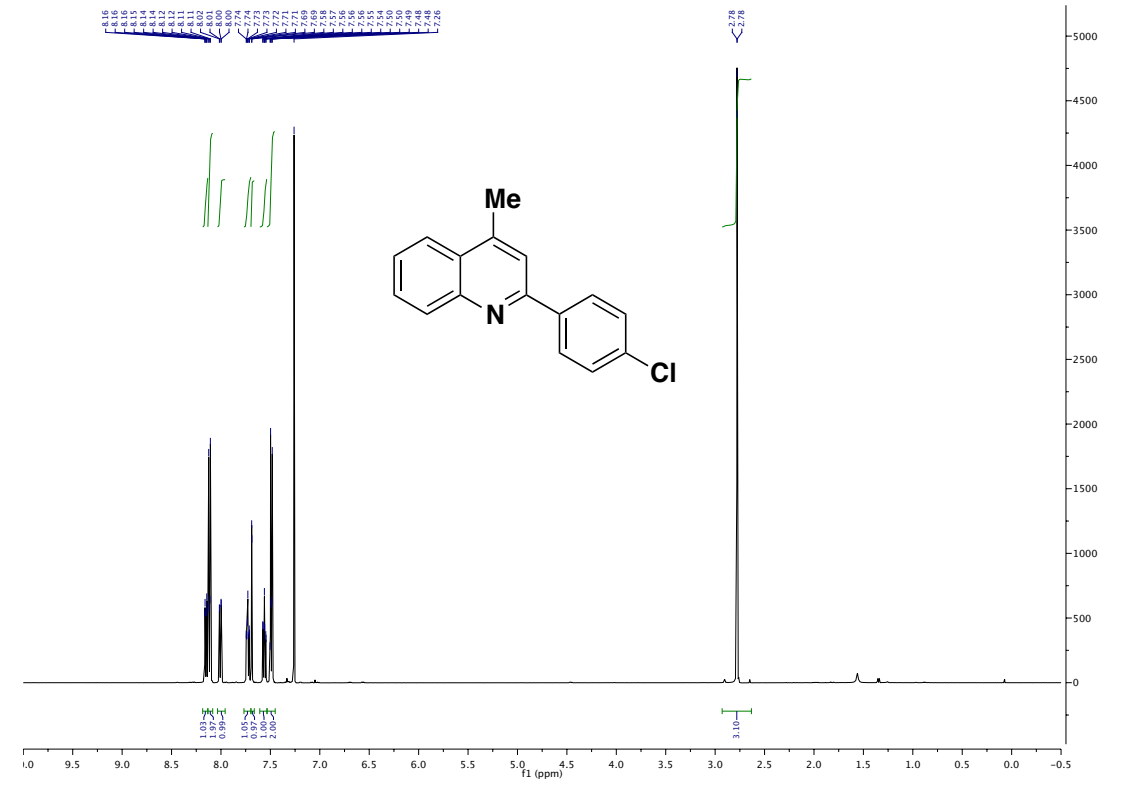
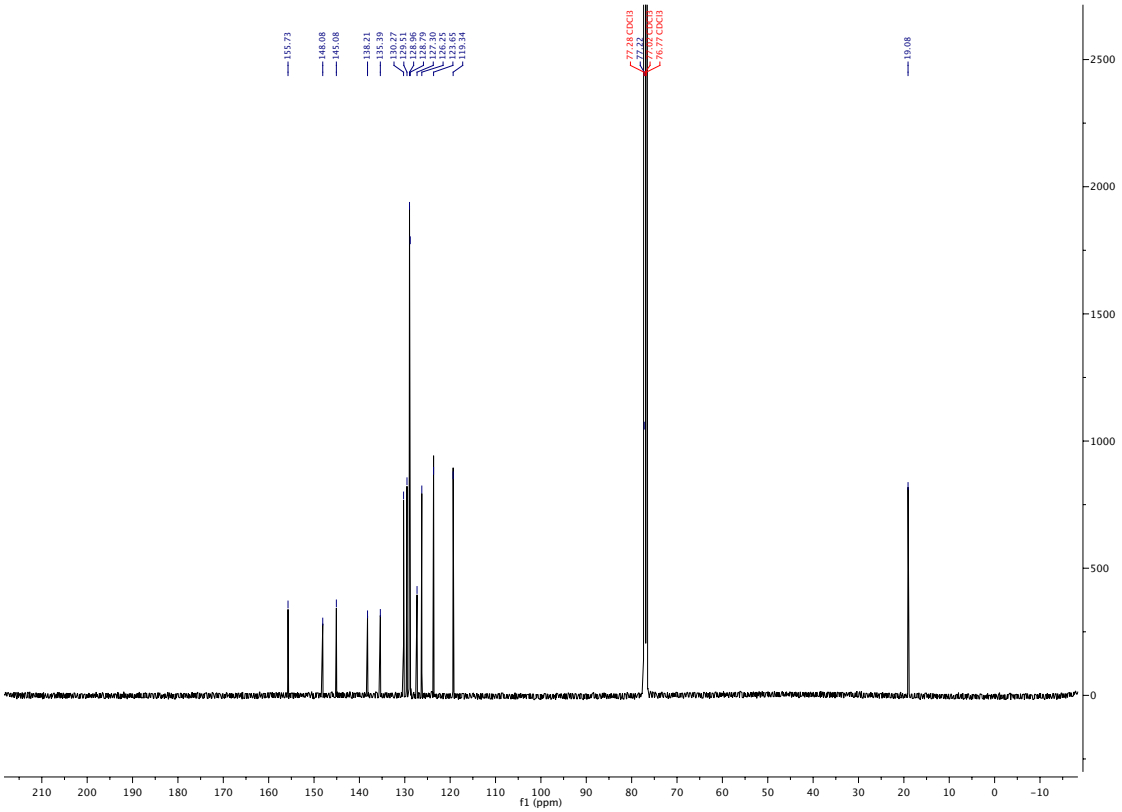

Me
N
Cl
f1 (ppm)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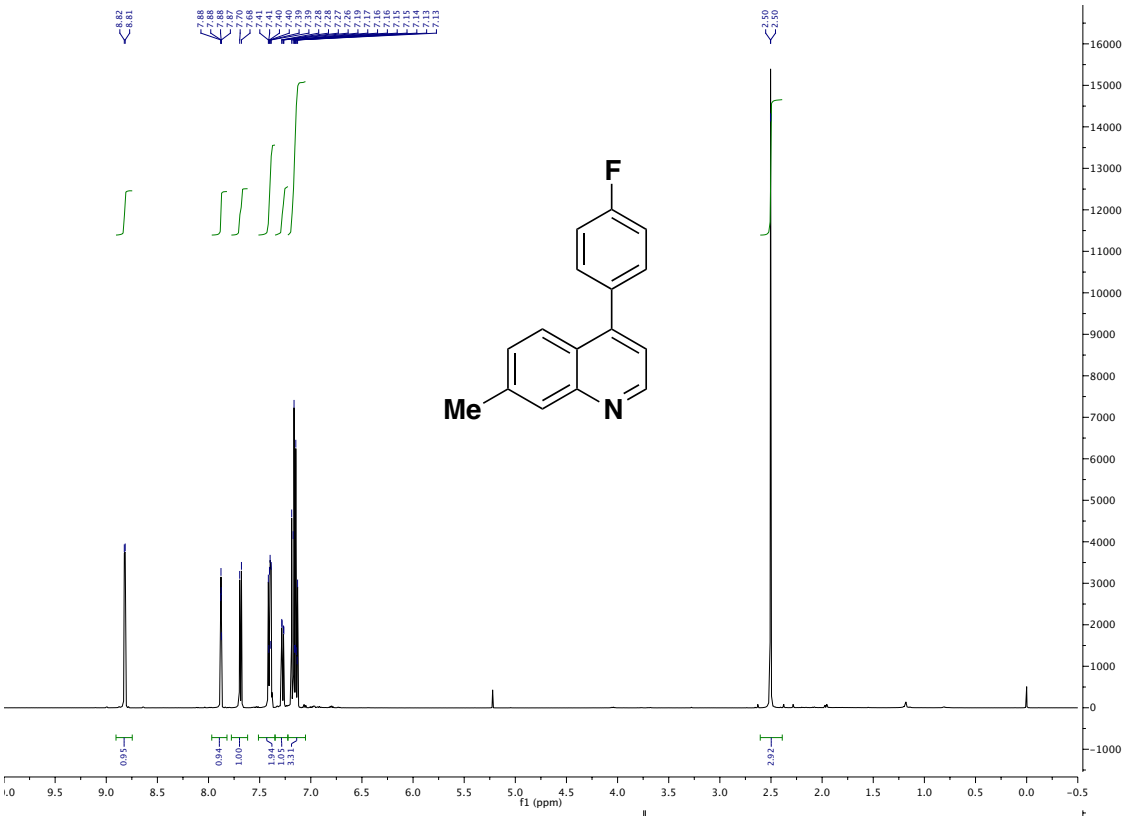
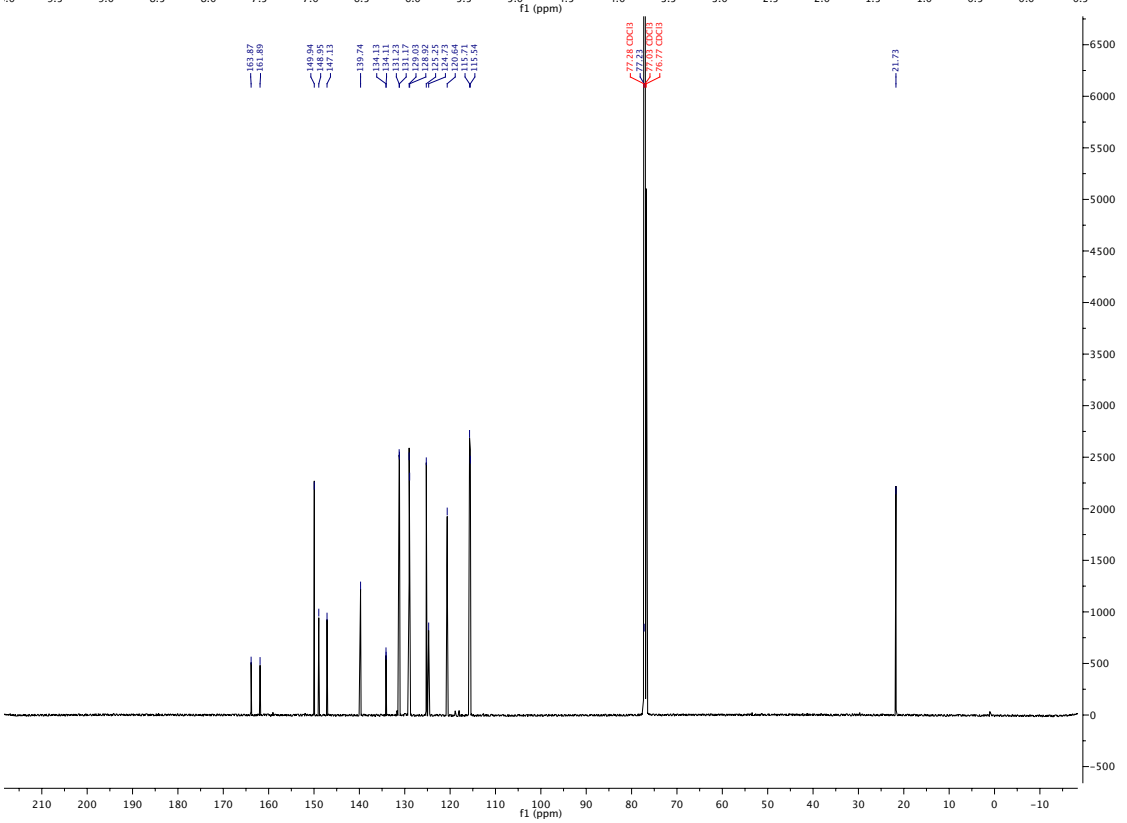
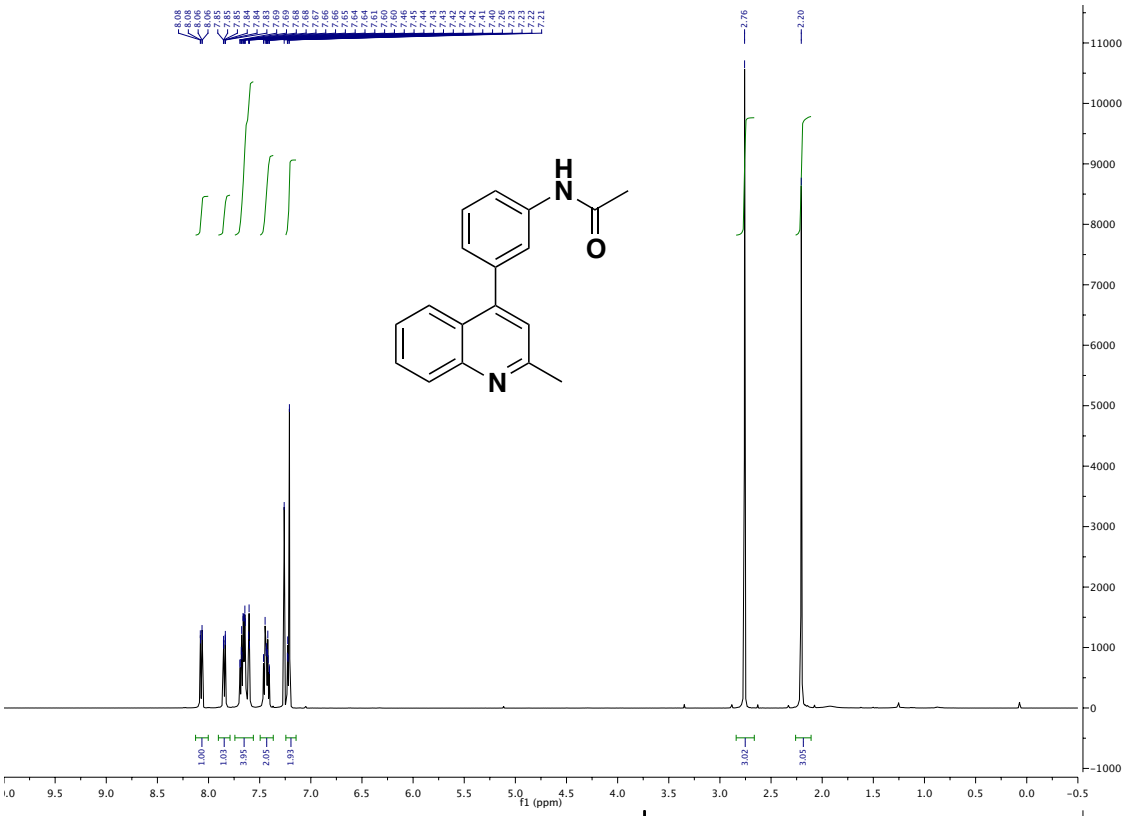
148.08
145.08
138.21
131.39
130.27
129.51
128.96
127.70
127.30
126.25
123.65
119.34
77.28 CDCl3
77.02 CDCl3
76.77 CDCl3
19.08
f1 (ppm)


F
Me
N
f1 (ppm)


f1 (ppm)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8.06
7.85
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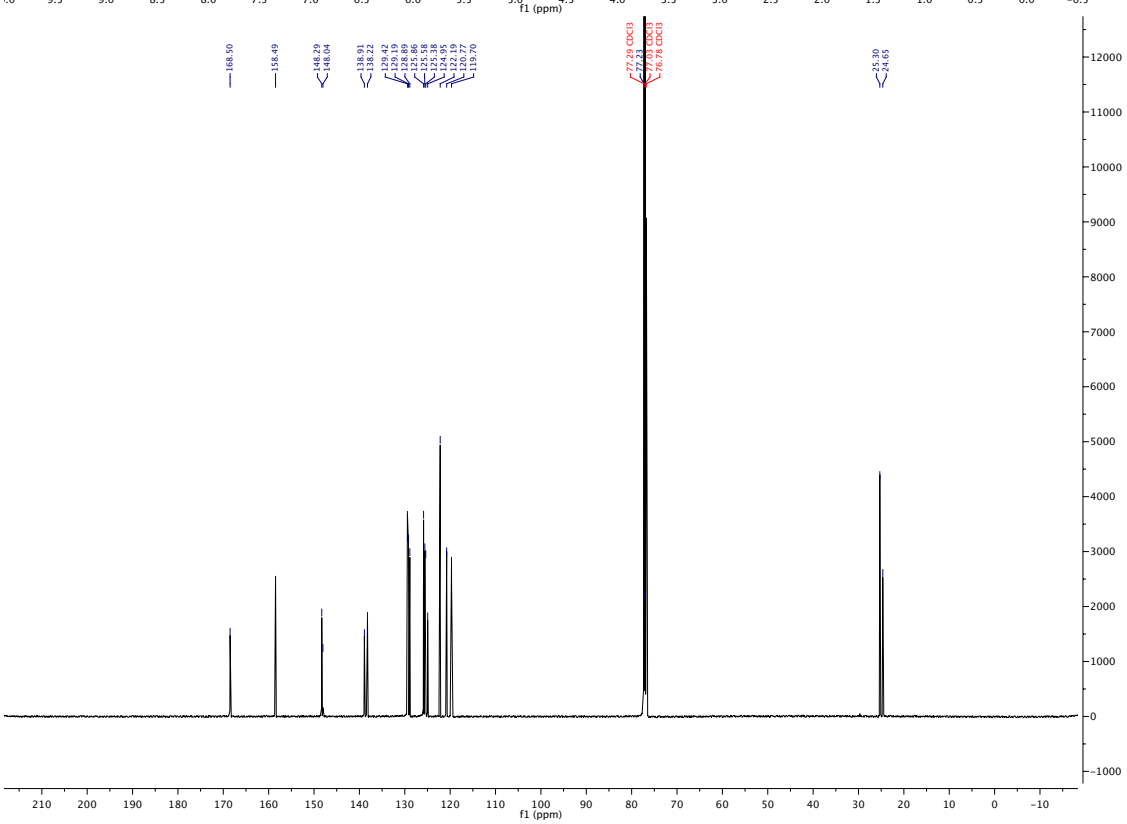
7.69
7.68
7.67
7.66
7.65
7.64
7.61
7.60
7.46
7.45
7.44
7.43
7.42
7.41
7.26
7.23
7.22
7.21
2.76
2.20
H
N
O
N
1.00
1.03
3.95
2.05
1.93
3.02
3.05
f1 (ppm)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158.49
148.29
148.04
138.91
138.22
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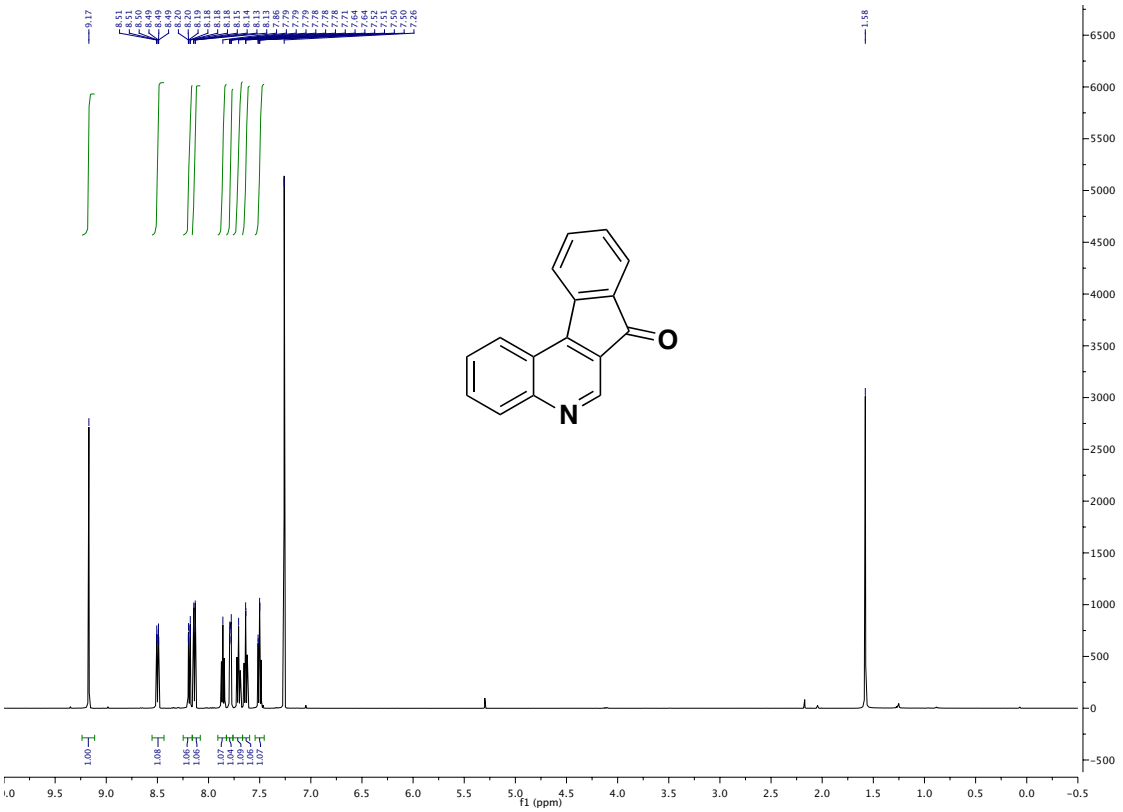
129.19
128.89
125.86
125.58
125.38
124.95
122.19
120.77
119.70
77.29 CDCl3
77.03 CDCl3
76.78 CDCl3
25.30
24.65
f1 (ppm)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8.51
8.50
8.49
8.49
8.48
8.20
8.19
8.18
8.18
8.16
8.15
8.14
8.13
7.86
7.79
7.79
7.79
7.78
7.78
7.78
7.71
7.64
7.64
7.52
7.51
7.50
7.50
7.26
1.58
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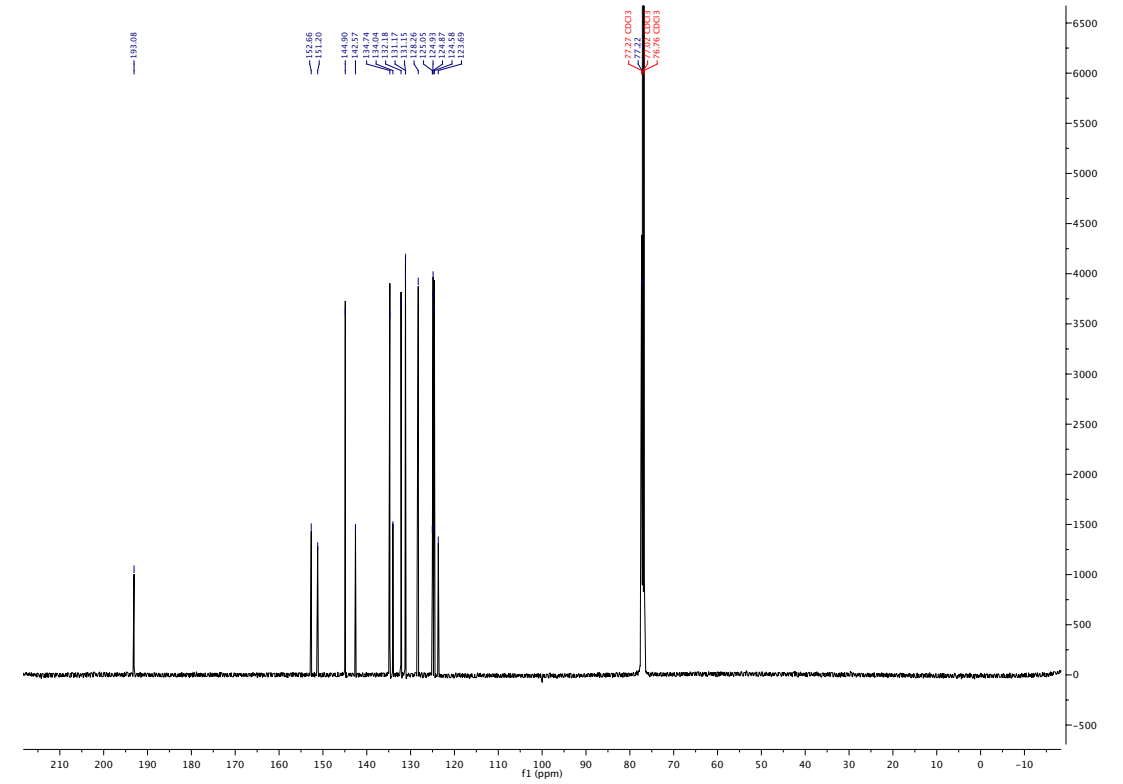
1.04
1.00
1.06
1.07
f1 (ppm)


193.08
153.66
151.20
144.90
142.57
138.74
134.04
132.18
131.17
131.15
128.26
125.85
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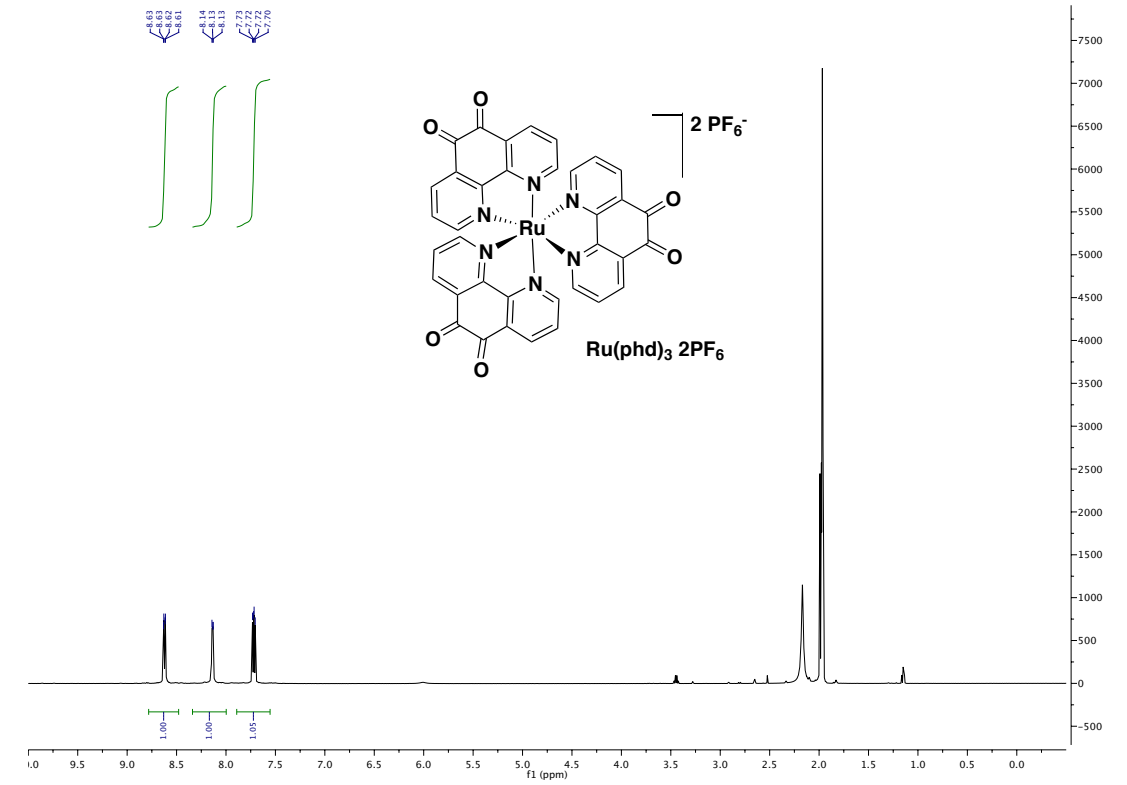
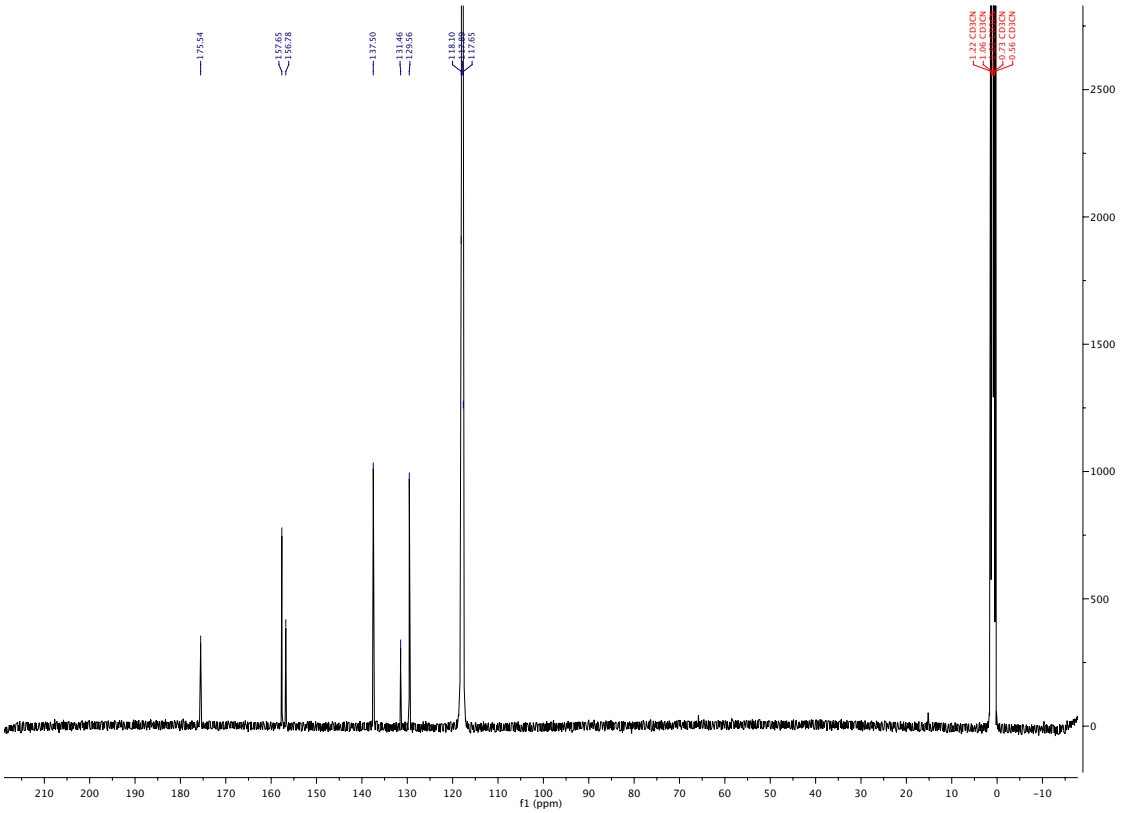
77.27 CDCl3
77.23
77.02
76.76 CDCl3
f1 (ppm)


8.63
8.63
8.62
8.61
8.14
8.13
8.13
7.73
7.72
7.72
7.70
2 PF6-
Ru(phd)3 2PF6
1.00
1.00
1.05
f1 (ppm)


175.54
157.65
156.78
137.50
131.46
129.56
118.10
118.02
117.65
1.22 CD3CN
1.96 CD3CN
2.08 CD3CN
0.73 CD3CN
0.56 CD3CN
f1 (ppm)

V. X Ray Crystallographic Data

Data Collection

A dark red crystal with approximate dimensions 0.27 x 0.12 x 0.07 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker Quazar SMART APEXII diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.96 cm.

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5º in a 6º range about ω with the exposure time of 10 second per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program suite. The final cell constants were calculated from a set of 9849 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 77039 data were harvested by collecting 4 sets of frames with 0.5º scans in ω and ϕ with an exposure time 40 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.[19]

Structure Solution and Refinement

The systematic absences in the diffraction data were uniquely consistent for the space group $P2_12_12_1$ that yielded chemically reasonable and computationally stable results of refinement.[20-22]

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.

There were two fully occupied molecules of acetonitrile solvent in the asymmetric unit. There was a disordered and partially occupied acetonitrile solvent molecule which was set to a chemical occupancy of 50%. Bond distance restraints and thermal parameter constraints were applied to the disordered solvent molecule to ensure a chemically reasonable and computationally stable refinement. The carbonyl (C30, O6) of one of the quinone ligands was disordered over two positions with a major component occupancy of 52(7)% Two perchlorate ions were also in the asymmetric unit. One of them was disordered over two positions with a major component occupancy of 57(2)%. The oxygen atoms of the disordered perchlorate were refined isotropically and bond distance constraints were applied to ensure a chemically reasonable and computationally stable refinement.

The structure was refined as an inversion twin with a minor component contribution of 37(3) %.

The final least-squares refinement of 672 parameters against 12129 data resulted in residuals *R* (based on F^2 for $I \geq 2\sigma$) and *wR* (based on F^2 for all data) of 0.0383 and 0.0934, respectively. The final difference Fourier map had one noticeable peak (ca. 1.00 e/Å^3) in the vicinity of the disordered acetonitrile molecule and could not be accounted for with a chemically reasonable and computationally stable model.

Summary

Crystal Data for $C_{41}H_{25.5}Cl_2N_{8.5}O_{14}Ru$ (M =1033.17): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 13.744(5) Å, b = 14.024(6) Å, c = 20.665(8) Å, V = 3983(3) Å^3, Z = 4, T = 100.0 K, μ(MoKα) = 0.613 mm^{-1}, *Dcalc* = 1.723 g/mm^3, 76925 reflections measured ($3.51 \leq 2\Theta \leq 61.044$), 12129 unique ($R_{int}$ = 0.0586, R_{sigma} = 0.0427) which were used in all calculations. The final R_1 was 0.0383 ($I > 2\sigma(I)$) and wR_2 was 0.0934 (all data).

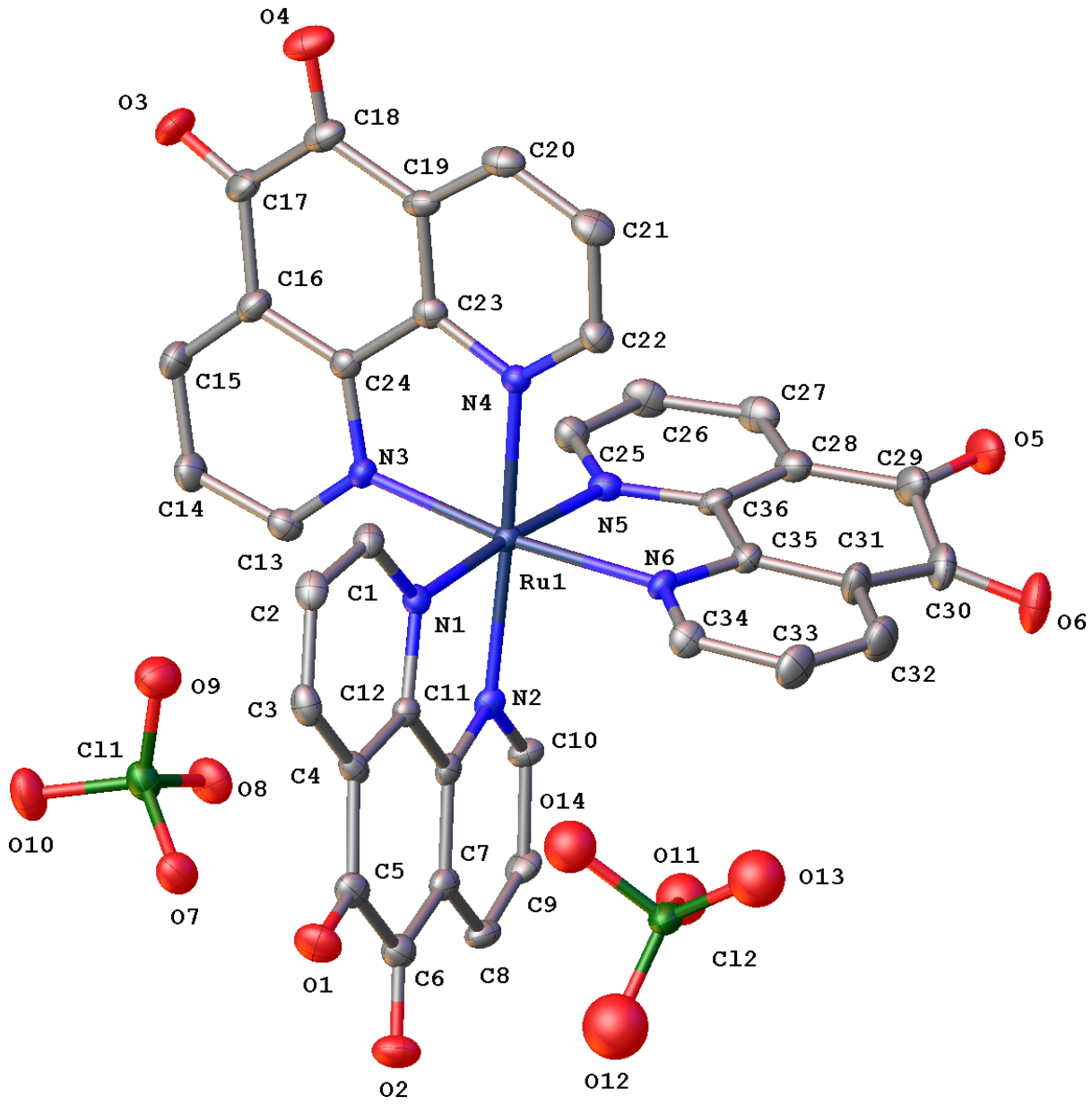


Figure S2. A molecular drawing of the Ruthenium complex of Stahl194 shown with 50% probability ellipsoids. All H atoms, acetonitrile solvent molecules, and minor components of the disordered atoms are omitted for clarity.

Table S2 Crystal data and structure refinement for stahl194.

Identification code	stahl194
Empirical formula	$Ru(C_{12}H_6N_2O_2)_3(ClO_4)_2(CH_3CN)_{2.5}$
Formula weight	1033.17
Temperature/K	100.0
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	13.744(5)
b/Å	14.024(6)
c/Å	20.665(8)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3983(3)
Z	4
ρ_{calc}mg/mm^3	1.723
m/mm^{-1}	0.613
F(000)	2084.0
Crystal size/mm^3	0.274 × 0.124 × 0.074
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	3.51 to 61.044°
Index ranges	-17 ≤ h ≤ 19, -19 ≤ k ≤ 19, -29 ≤ l ≤ 26
Reflections collected	76925
Independent reflections	12129 [R_{int} = 0.0586, R_{sigma} = 0.0427]
Data/restraints/parameters	12129/50/632
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0383, wR_2 = 0.0880
Final R indexes [all data]	R_1 = 0.0489, wR_2 = 0.0934
Largest diff. peak/hole / e Å^{-3}	1.00/-0.73
Flack parameter	0.37(3)

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