Supporting Information

Catalytic Aerobic Dehydrogenation of Nitrogen Heterocycles Using Heterogeneous Cobalt Oxide Supported on Nitrogen-Doped Carbon

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General Considerations

All commercially available metal salts, organic compounds and solvents were used as received. Acetylene Black was obtained as a donated research sample from Soltex (AB 100%). Vulcan XC72R was obtained as a donated research sample from the Cabot Corporation. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 400 and 500 MHz spectrometers and chemical shifts are given in parts per million (ppm) relative to standard tetramethylsilane (0.00 ppm for ^{1}H NMR) or residual solvent peaks for ^{13}C NMR. High resolution mass spectra were obtained using a Water Autospec by the mass spectrometry facility at the University of Wisconsin. Chromatography was performed using an automated Isco Combiflash Rf® system with reusable high performance silica gel 60 (Silicycle) and eluted with hexane/ethyl acetate. Melting points were recorded on a Melt-Temp® apparatus.

Procedure for the Preparation of Co_3O_4-NGr/C Catalysts

Synthesis of the heterogeneous catalysts was performed according to the procedures described by Beller et al. and the optimized catalyst had the same composition as the one previously characterized.[1] In a 50 ml round bottom flask were added $Co(OAc)_2 \cdot 4H_2O$ (25.4 mg, 0.1 mmol) (corresponds to 3wt% Co) and 1,10-phenanthroline monohydrate (45.9 mg, 0.2 mmol) (1:2 ratio) and stirred in EtOH (10 ml) for 30 minutes. Then carbon powder (137.9 mg) was added and the mixture was heated to reflux for 4 hours. After the mixture was cooled to room temperature, the ethanol was evaporated *in vacuo* and the resulting powder was dried at 60 °C under vacuum for 12 hours. The powder was then grinded to fine particles. The ground powder was subsequently placed in a quartz tube, which was placed inside a tube furnace. The quartz tube was evacuated and filled with argon three times, after which a positive flow of argon was maintained through it (~10 ml/min). The tube furnace was then heated to 800 °C over one hour and then held at that temperature for 2 hours. After the tube was cooled the room temperature, a black fine powder was obtained.

General procedures for dehydrogenation reactions: Optimization and experimental data performed on custom parallel reactor – Orbital mixing (Procedure A)

To a disposable 13 mm x 100 mm thick-walled tube were added sequentially catalyst (5 mg corresponding to 2.5 mol% Co), K_2CO_3 (13.8 mg, 0.1 mmol) and substrate **1a** (14.7 mg, 0.1 mmol), followed by MeOH (0.8 ml). The test tube was placed in a custom parallel shaker reactor, preheated to 60 °C, and the headspace was purged for 5 minutes with O_2. The headspace was then filled with O_2 at a pressure of 1 atm. The mixture was allowed to shake (60 rpm) at 60 °C for 4 h, after which the shaking was stopped and the reactor allowed to cool to room temperature. O_2 pressure was released and then to the test tubes was added a known quantity of standard (dibromomethane or 1,3,5-trimethoxybenzene) in $CDCl_3$ and an aliquot was taken from the reaction mixture, filtered through a short pad of celite and analyzed by ^{1}H NMR.

For product isolation, the conditions above were scaled up to 0.5 mmol substrate and carried out in a 75 ml conical flask using the same orbital mixer. After the reaction was completed according to the time specified for each substrate, the reaction mixture was filtered, the flask and filtrate washed 4 times with 2 ml dichloromethane, and the combined organic layers concentrated on the rotatory evaporator. The product was then purified via flash chromatography on silica with hexane/ethyl acetate eluent using standard techniques.

Procedure for dehydrogenation reaction performed with an O_2 balloon – Magnetic stirring (Procedure B)

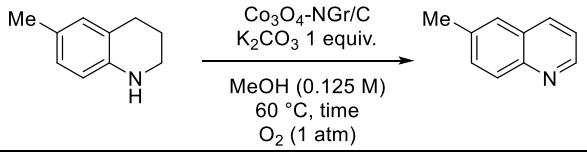
CAUTION: Because of the flammability of methanol and O_2, large scale reactions should be conducted below the LOC of MeOH (approx. 7-8%).[2]

A 20 mm x 150 mm culture tube or 50 ml round bottom flask was equipped with a stir bar, oven dried and capped with a septum. Meanwhile, on a weighing paper were weighed catalyst (25 mg), K_2CO_3 (69.1 mg, 0.5 mmol) and substrate (0.5 mmol) if it is a solid. The solid mixture was added to the test tube followed by addition of the substrate if it is a liquid and methanol (4 ml, 0.125 M). The test tube was capped with a septum immediately. Oxygen from a tank or a balloon was then purged using a 20 gauge needle inserted in the solvent, while the solution was stirring for 10 minutes, after which an O_2 balloon was attached to the test tube, this time the needle not going into the solution and the mixture was placed in an oil bath preheated to 60 °C. The reaction can be monitored by TLC for completion and generally takes longer than with orbital mixing. After completion, the mixture is worked up and purified as above.

For the 10 mmol scale reaction (**1m**, 1.43 g), the reaction components were added as above to a 500 ml round bottom flask equipped with a reflux condenser. The reaction vessel was purged with O_2 for 10 minutes through a 16 gauge needle inserted in the solvent with vigorous stirring, after which two O_2 balloons were attached at the top of the reflux condenser. The reaction was

immersed in an oil bath at 60 °C and monitored by TLC. After 16 h, the reaction was worked up as above and the crude contained analytically pure product obtained in 94% yield (1.31 g).

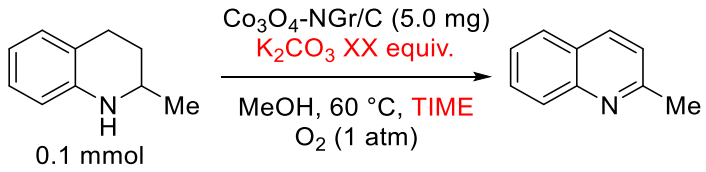
Comparison of Yields between Different Reaction Set-ups

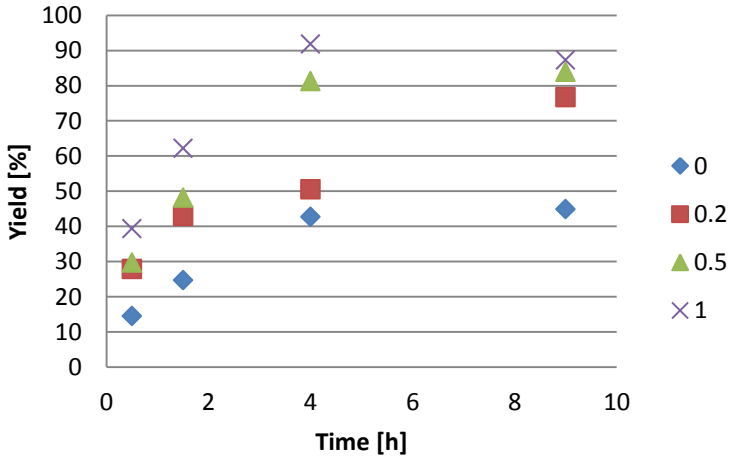


Set-up	Scale	Reaction Time	Yield
Shaker reactor - Orbital Mixing	0.5 mmol	4 h	94% (Isolated)
Round bottom flask - Magnetic Stirring	0.5 mmol	20 h	86% (^{1}H NMR Yield)
Round bottom flask - Magnetic Stirring	10 mmol	16 h	94% (Isolated)
Culture Tube - Magnetic Stirring	0.5 mmol	16 h	93% (Isolated)

Figure S1. Optimization of Reaction Conditions – Base Dependence

Experiments were conducted according to the optimization general procedure A. Nitrogen source for the catalyst was 1,10-phenanthroline, Co:ligand ratio was 1:2. Carbon source was acetylene black. Each time point represents a separate reaction.





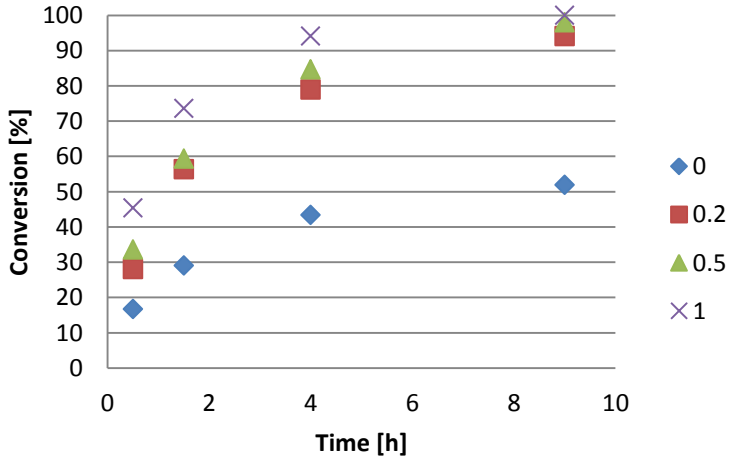
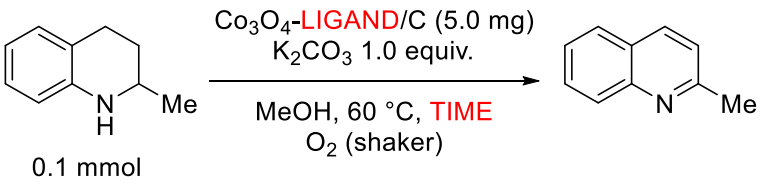
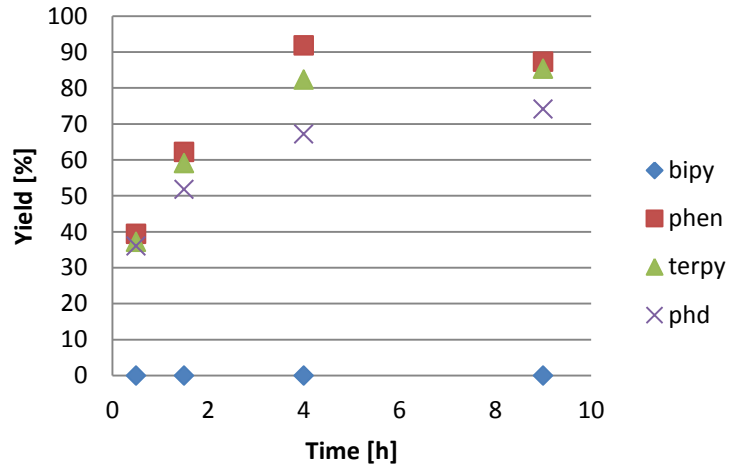


Figure S2. Optimization of Reaction Conditions – Ligand Dependence

Experiments were conducted according to the optimization general procedure A. Carbon source was acetylene black. Co:ligand ratio was 1:2. Each time point represents a separate reaction.





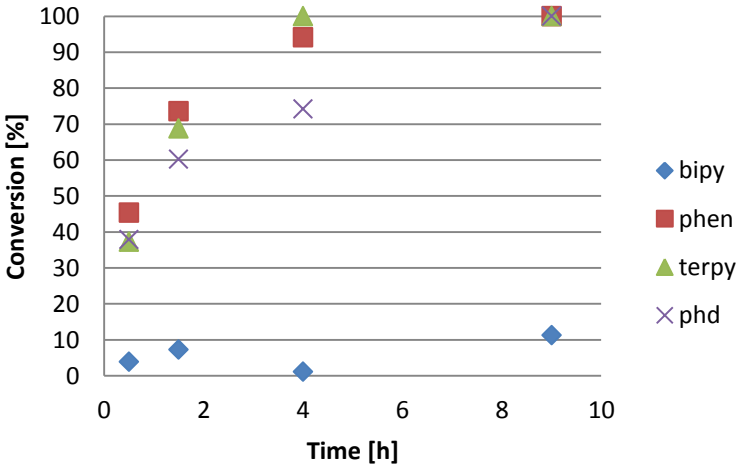
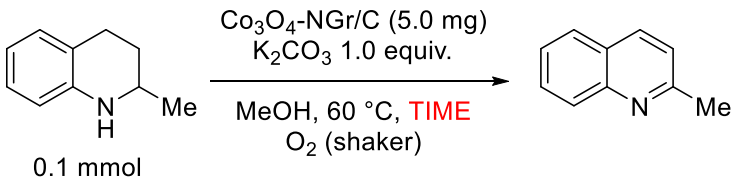
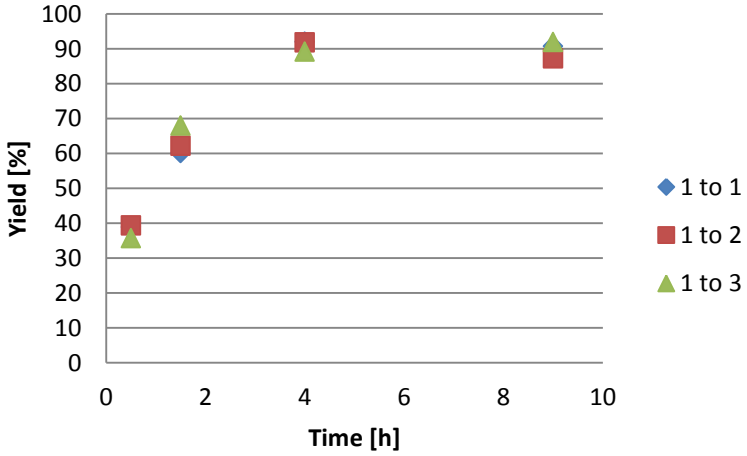


Figure S3. Optimization of Reaction Conditions – Co:Phen Ratio Optimization

Experiments were conducted according to the optimization general procedure A. Nitrogen source for the catalyst was 1,10-phenanthroline, Co:ligand ratio was 1:2. Carbon source was acetylene black. Each time point represents a separate reaction.





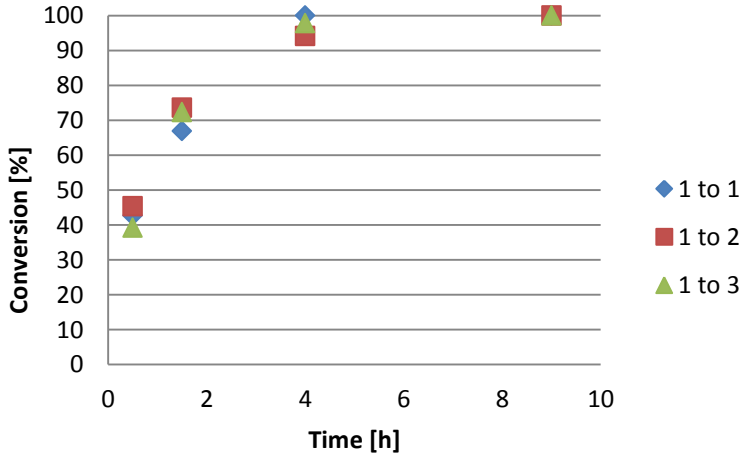
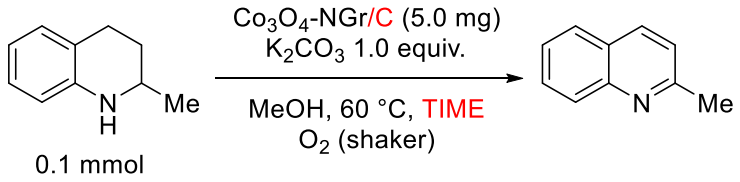
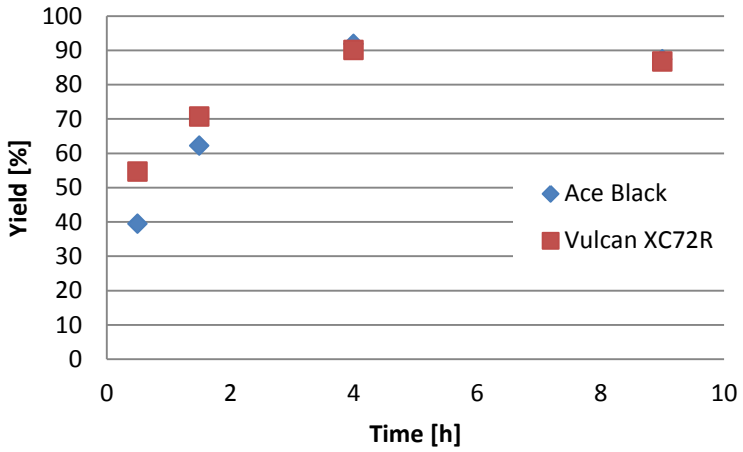


Figure S4. Optimization of Reaction Conditions – Acetylene Black vs. Vulcan XC72R

Experiments were conducted according to the optimization general procedure A. Nitrogen source for the catalyst was 1,10-phenanthroline, Co:ligand ratio was 1:2. Each time point represents a separate reaction.





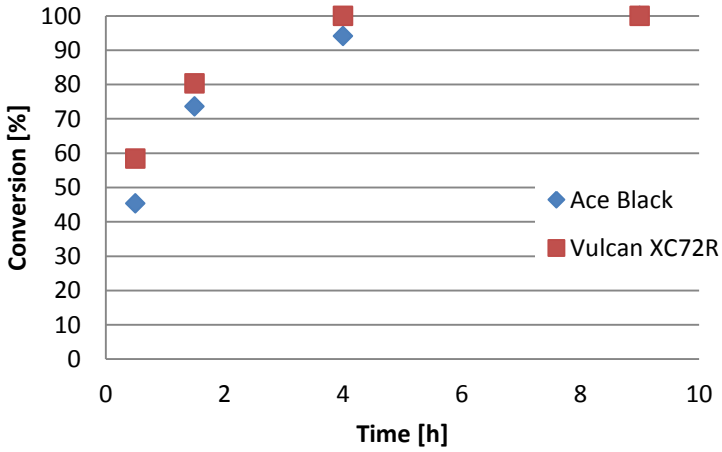
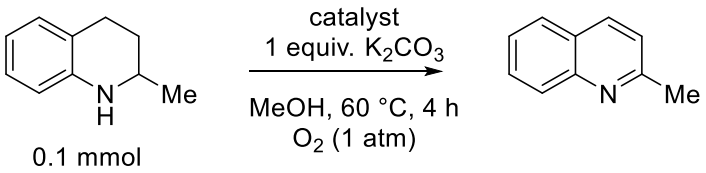


Table S1. Control Reactions for Dehydrogenation of 1,2,3,4-Tetrahydroquinaldine



Entry	Carbon Support	Metal Source	Ligand	Pyrolysis	Yield (Conv)
1	-	-	-	-	-
2	-	$Co(OAc)_2$	-	-	9 (9)
3	-	$Co(OAc)_2$	Phen	-	0 (7)
4	AB	$Co(OAc)_2$	-	-	11 (26)
5	AB	$Co(OAc)_2$	Phen	-	0 (0)
6	AB	$Co(OAc)_2$	-	800 ºC, Ar	0 (8)
7	AB	Co_3O_4	-	800 ºC, Ar	0 (11)
8	**AB**	**$Co(OAc)_2$**	**Phen**	**800 ºC, Ar**	**92 (94)**
9	AB	-	Phen	800 ºC, Ar	0 (1)
10	AB	-	-	800 ºC, Ar	0 (6)
11	AB	-	-	-	0 (4)
12	AB (100 wt%)	-	-	-	0 (2)

Conditions: Substrate (0.1 mmol), 0.8 ml MeOH, 2.5 mol% catalyst, 1 equiv. K_2CO_3, 1 atm O_2, orbital stirring. Yields and conv. determined by ^1H NMR. AB = Acetylene Black; Phen = 1,10-Phenanthroline.

XPS Data for Prepared Catalysts from Table 1

XPS spectra were acquired on a Thermo Scientific K-alpha XPS equipped with an Al Kα X-ray source (1486.5 eV) and spot size of 400 μm. The detector was scanned with a 0.2 eV step size and pass energy of 35 eV. The spectra were referenced to the C 1s peak at 284.8 eV. Instrumentation support from the UW Materials Research Science & Engineering Center and NSF Grant DMR-1121288 is acknowledged.

As expected for this class of catalysts, there were three main peaks observed in the N1s spectra that can be attributed to pyridinic (398.8 ± 0.2 eV), pyrrolic (400.0 ± 0.3 eV), and graphitic (401.3 ± 0.2 eV) nitrogen.[3] An exception is the catalyst prepared using bpy as the nitrogen source; for reasons that are not clear, no nitrogen was detected in this sample by XPS. Figures S5 – S12 present the N1s spectra and Table S2 the surface nitrogen and metal surface compositions.

The metallic XPS spectra show that all of the metals detected by this technique are in an oxidized state. The Co 2p spectra (Figure S13) show the $2p_{3/2}$ and $2p_{1/2}$ peaks at ~780.5 eV and ~796.2 eV, respectively, as expected for Co(II). CoO is known to be unstable and oxidize to Co_3O_4,[4] which can be observed as a decrease in satellite peak intensity. The intensity of the satellite peaks at ~787 and ~803 eV suggest that the catalyst surface contain a mixture of CoO and Co_3O_4; although, the surface concentration is low and a definitive assignment challenging. The Mn 2p spectrum (Figure S14) shows a wide feature at ~642 eV that could be a mixture of Mn(II), Mn(III), and Mn(IV), but definite assignment is challenging due to the low surface concentration. The Fe 2p spectrum (Figure S15) shows a peak at ~ 710.8 eV that can be attributed to Fe_2O_3. The Ni 2p spectrum (Figure S16) contains a peak at ~855.6 eV, which suggests a mixture of NiO and Ni_2O_3.[4,5]

Table S2. Overview of catalyst nitrogen speciation and surface concentrations (atom %).

	Pyridinic			Pyrrolic			Graphitic			Overall			
Catalyst	atom %	% N	BE (eV)	atom %	% N	BE (eV)	atom %	% N	BE (eV)	M atom %	N atom %	M: N	N: M
Co-phen/AB	1.5	50	398.8	0.78	26	399.9	0.71	24	401.3	0.64	2.99	0.21	4.7
Co-bipy/AB	-	-	-	-	-	-	-	-	-	0.37	-	-	-
Co-terpy/AB	0.8	47	398.7	0.29	17	399.6	0.63	37	401.1	0.49	1.72	0.28	3.5
Co-phd/AB	1.04	43	398.7	0.5	21	399.8	0.89	37	401.1	0.6	2.43	0.25	4.1
Mn-phen/AB	1.28	57	398.6	0.61	27	400.2	0.36	16	401.6	0.66	2.25	0.29	3.4
Fe-phen/AB	1.24	54	398.8	0.65	28	399.9	0.4	17	401.2	1.08	2.29	0.47	2.1
Ni-phen/AB	1.16	45	398.9	0.79	30	399.8	0.65	25	401.2	0.84	2.6	0.32	3.1
Co-phen/Vulcan XC72R	1.11	63	399.0	0.34	19	400.3	0.31	18	401.4	0.59	1.76	0.34	3.0

* The metal concentrations should be treated as an upper bound since the satellite peaks were not subtracted from the total area

Figure S5. Fitted N1s spectrum from Co-phen/AB

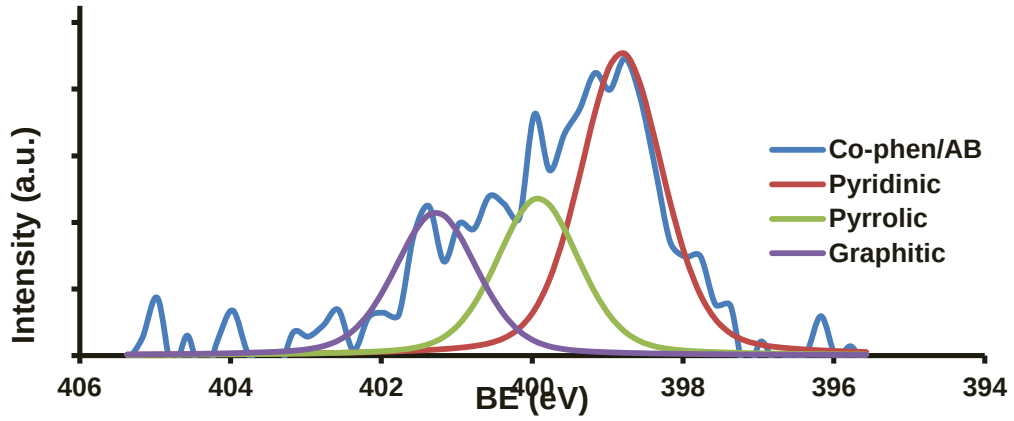


Figure S6. Fitted N1s spectrum from Co-bpy/AB

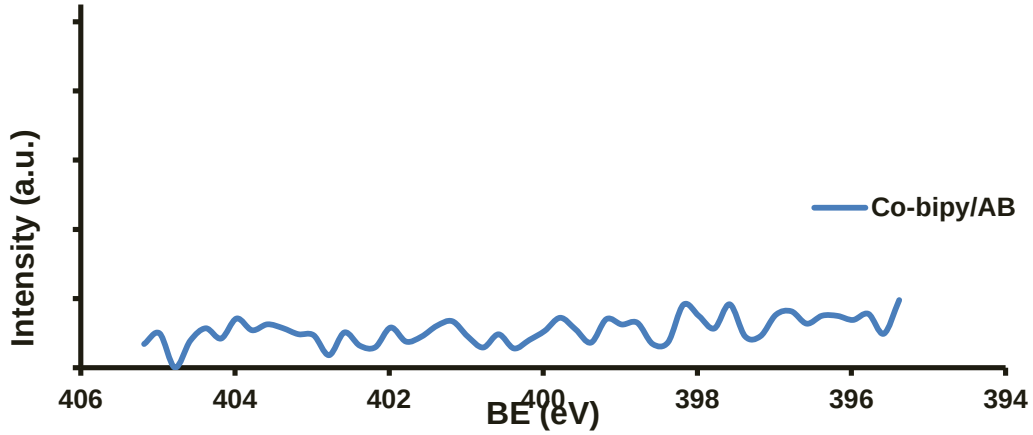


Figure S7. Fitted N1s spectrum from Co-terpy/AB

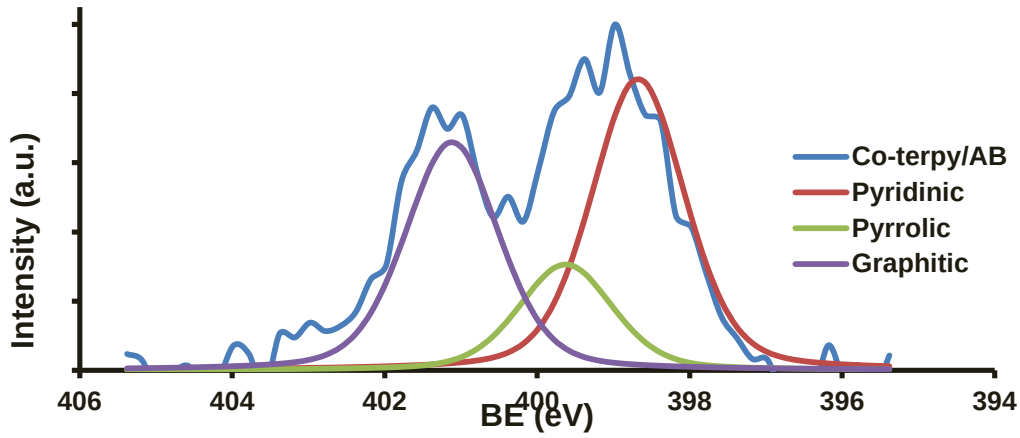


Figure S8. Fitted N1s spectrum from Co-phd/AB

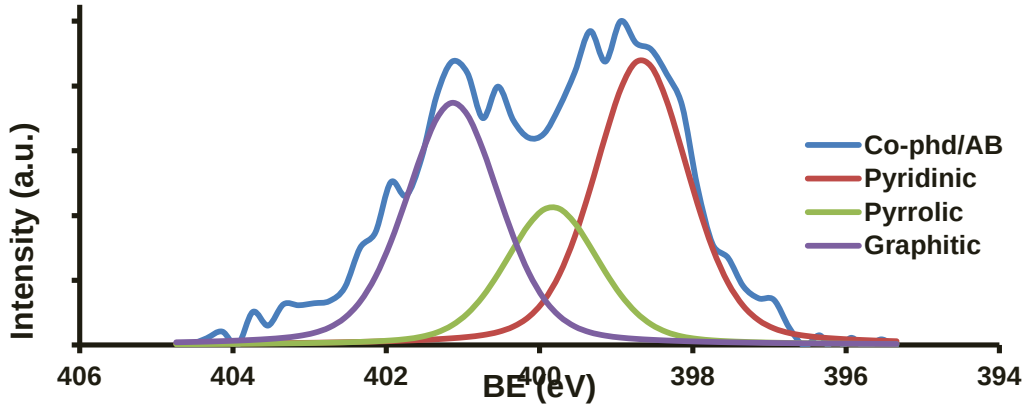


Figure S9. Fitted N1s spectrum from Mn-phen/AB

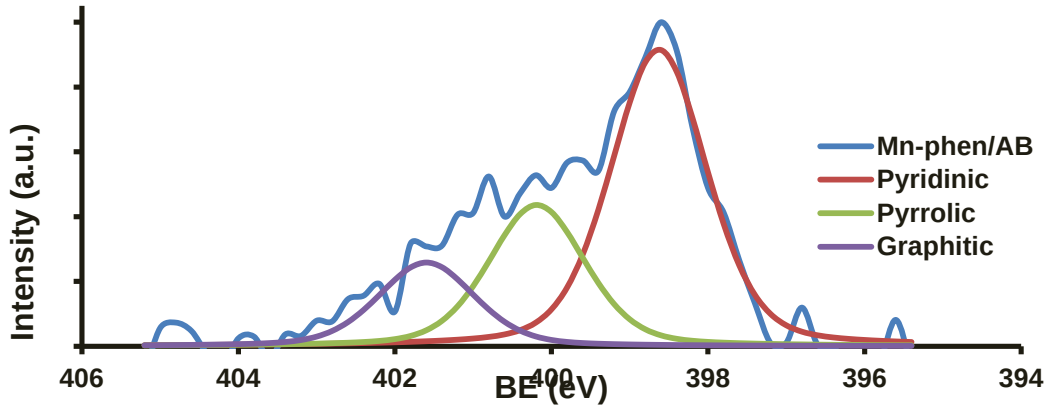


Figure S10. Fitted N1s spectrum from Fe-phen/AB

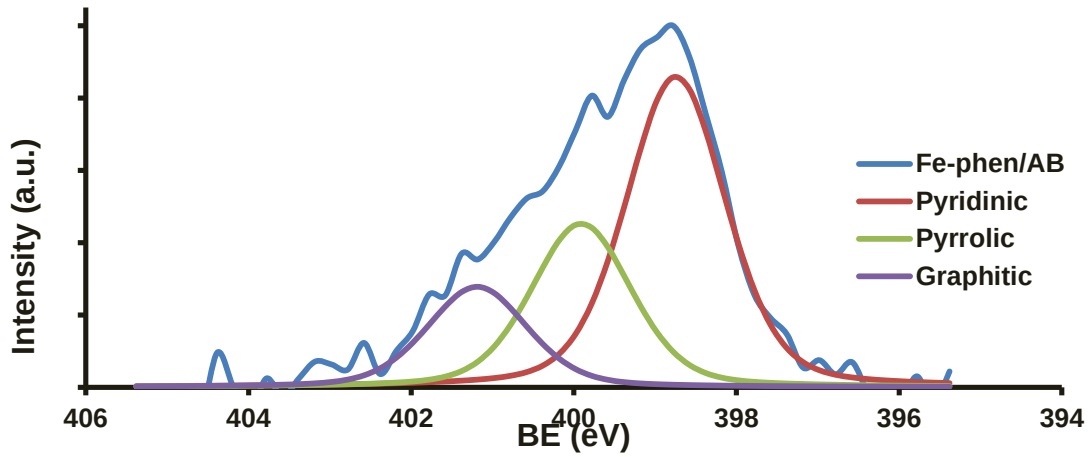


Figure S11. Fitted N1s spectrum from Ni-phen/AB

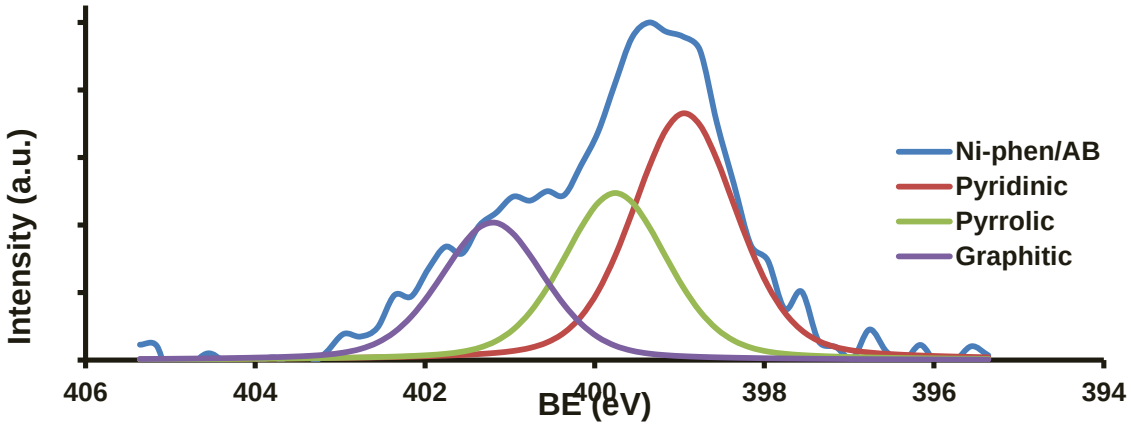


Figure S12. Fitted N1s spectrum from Co-phen/Vulcan XC72R

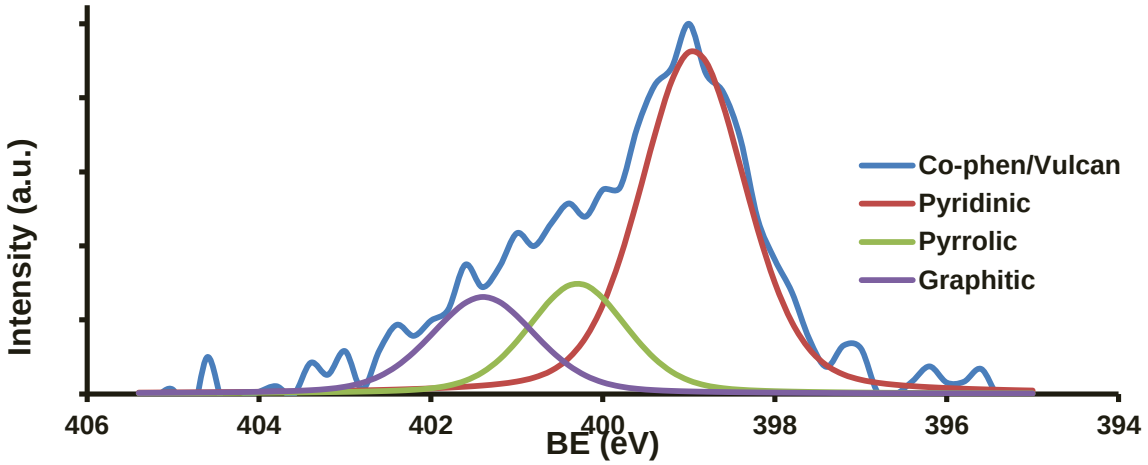


Figure S13. Co 2p spectra

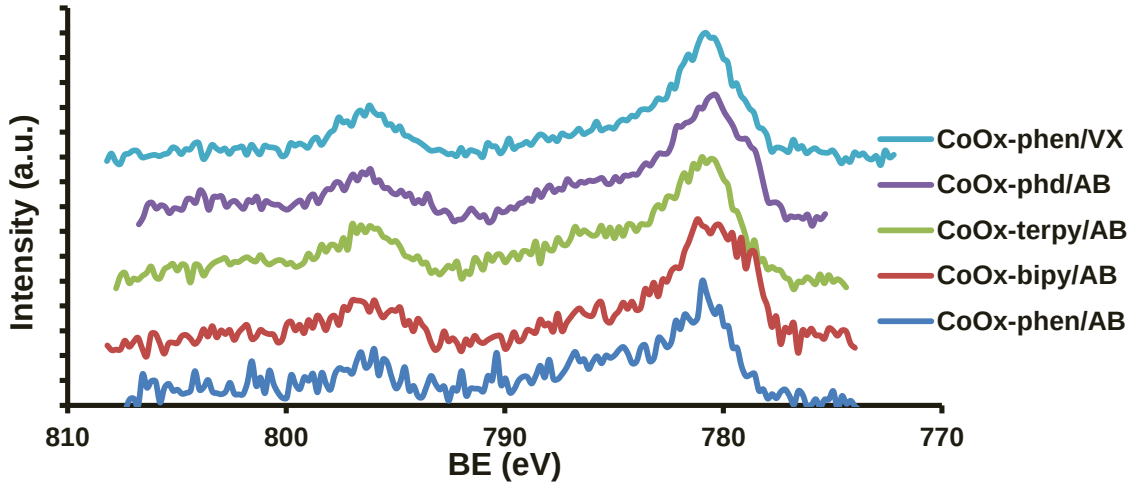


Figure S14. Mn 2p spectra

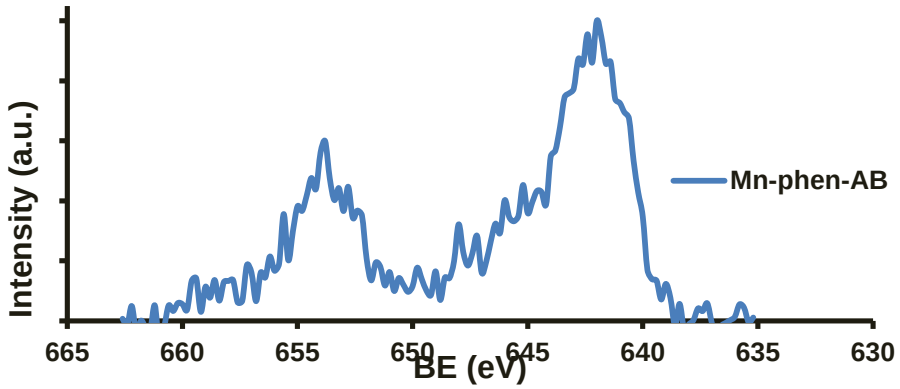


Figure S15. Fe 2p spectra

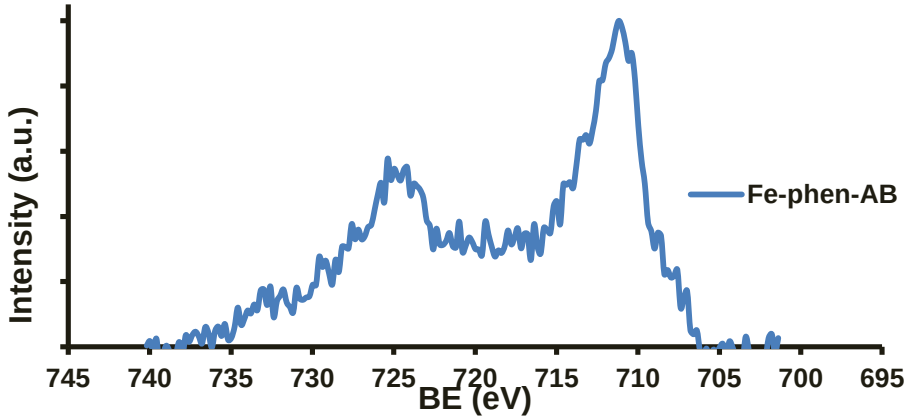
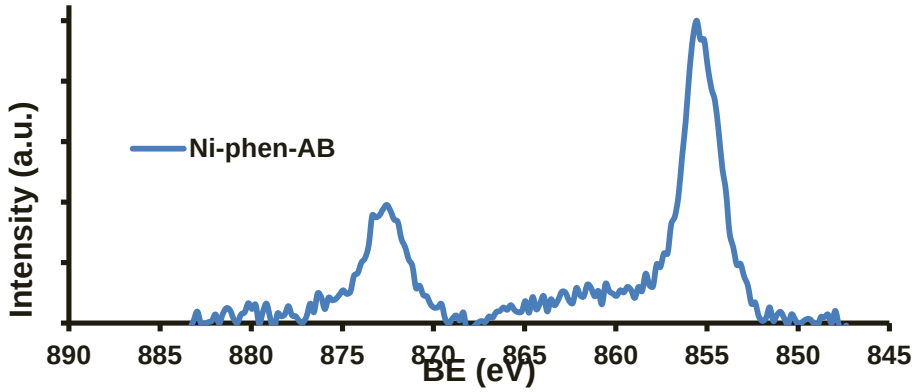


Figure S16. Ni 2p spectra



Powder X-Ray Diffraction (pXRD) Data for Prepared Catalysts from Table 1

Powder X-ray diffraction patterns were recorded at room temperature using a Bruker D8 Advance diffractometer with Cu Kα radiation (λ=1.54056).

For the cobalt catalysts, the patterns agreed with previous measurements by Beller et al.[6] and metallic cobalt was mainly observed whereas weak reflections were observed for CoO. The low metal loading of the catalyst didn't allow for observation of stronger features for other oxidic cobalt species. The only exception was CoO_x-bpy/phen which besides metallic Co displayed two unidentified sharp peaks.

The pattern for MnO_x-phen/AB matched mainly MnO and Mn. For FeO_x-phen/AB, the observed species was iron carbide. For NiO_x-phen/AB, the observed pattern matched metallic Ni.

Figure S17. pXRD patterns for supported cobalt catalysts

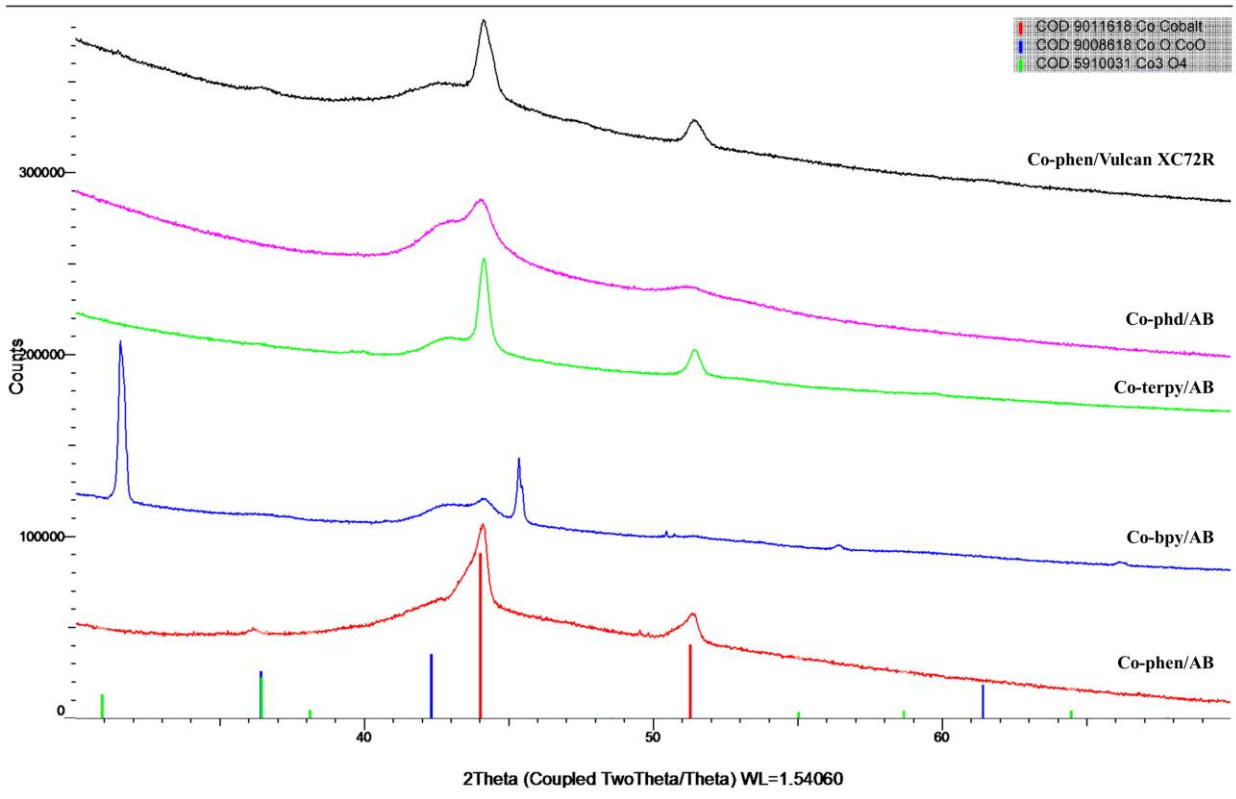


Figure S18. pXRD pattern for Mn-phen/AB

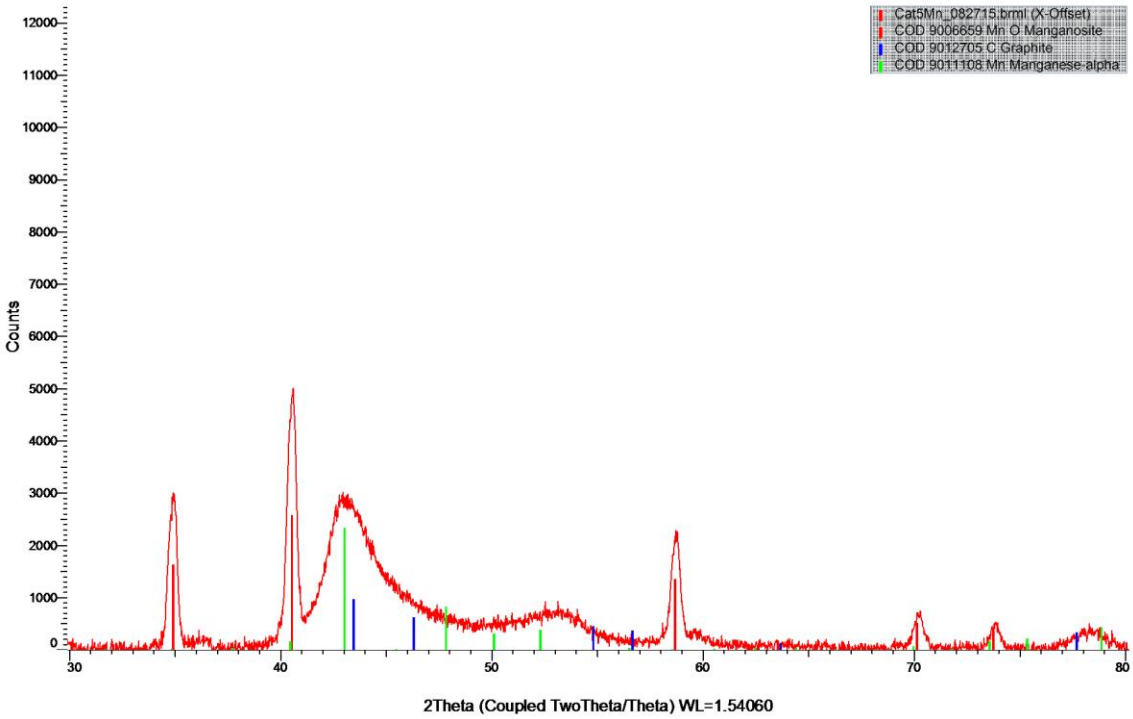


Figure S19. pXRD pattern for Fe-phen/AB

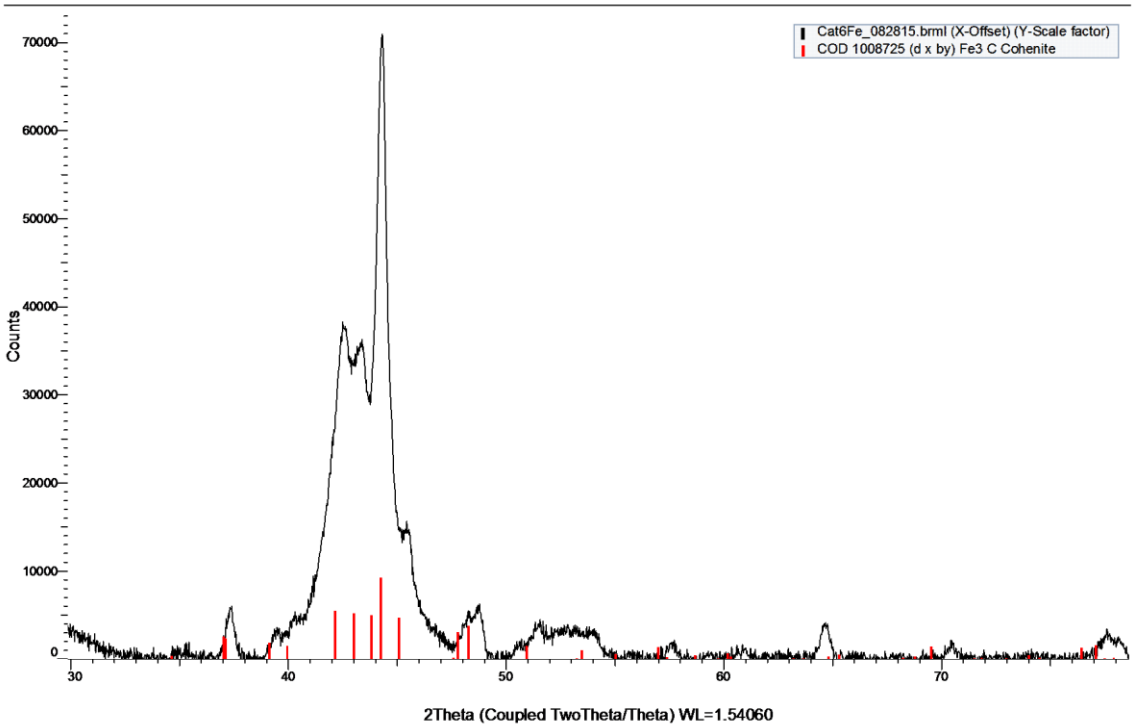
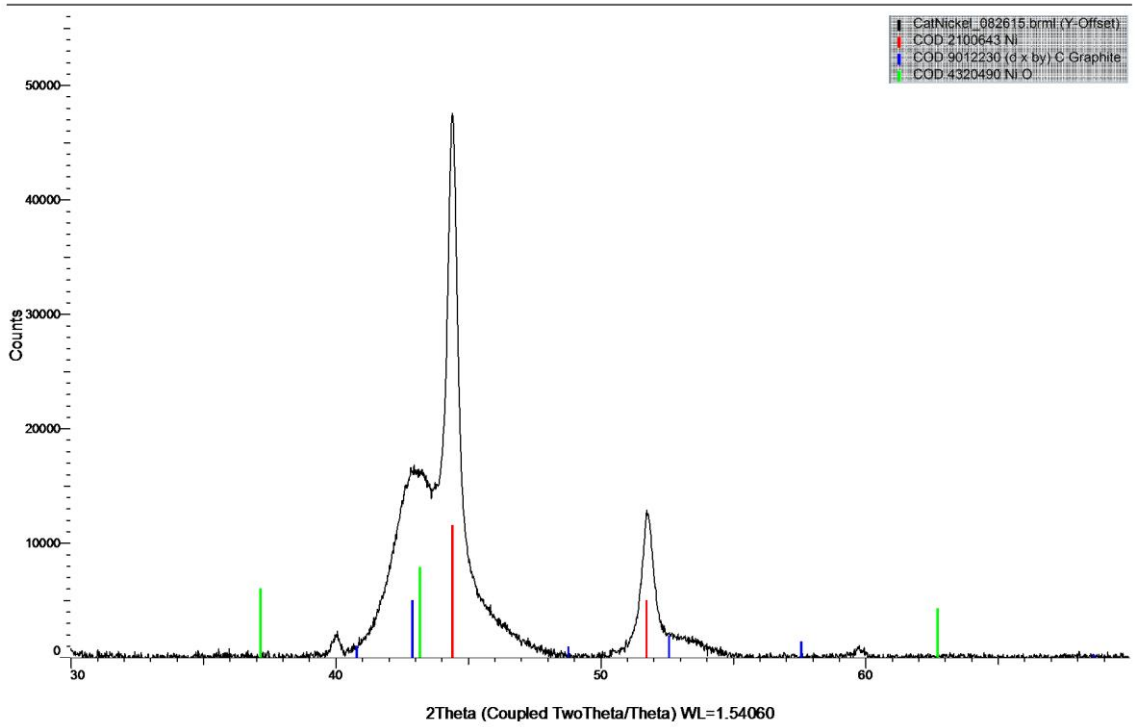


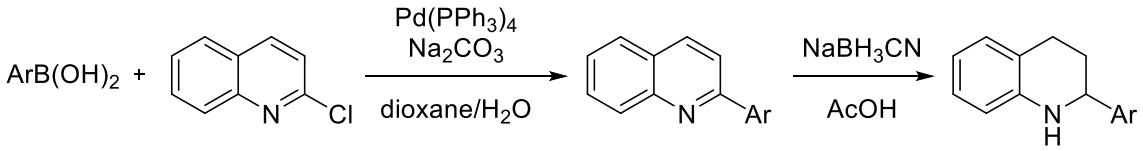
Figure S20. pXRD pattern for Ni-phen/AB



Synthesis and Characterization of Substrate Precursors

Substrates **1a** (1,2,3,4-tetrahydroquinoline), **1b** (2-Methyl-1,2,3,4-tetrahydroquinoline), **1m** (6-Methyl-1,2,3,4-tetrahydroquinoline), **1n** (6-Methoxy-1,2,3,4-tetrahydroquinoline) and **1p** (6-Chloro-1,2,3,4-tetrahydroquinoline) are commercially available. Substrates **1j** (3-Methyl-1,2,3,4-tetrahydroquinoline), **1k** (4-Methyl-1,2,3,4-tetrahydroquinoline) and **1s** (8-Methyl-1,2,3,4-tetrahydroquinoline) were obtained via high pressure hydrogenation of the corresponding quinoline derivatives (commercially available).[7] Substrate **1l** was prepared via a literature procedure.[8] Substrate **1q** was prepared by the bromination of 1,2,3,4-tetrahydroquinoline according to a literature procedure.[9] Substrate **1t** was prepared via methylation of 8-hydroxyquinoline and subsequent reduction according to a literature procedure.[10] The rest of the substrates were prepared according to procedures C and D outlined below.

General Procedures C and D for the Synthesis of 1,2,3,4-Tetrahydroquinoline Substrates 1c-i, 1o, 1r

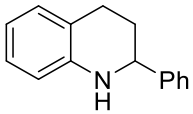


Procedures for the synthesis of these substrates were adapted from procedures described in the literature.[11] None of the reactions employed in substrate synthesis was optimized for maximum yield.

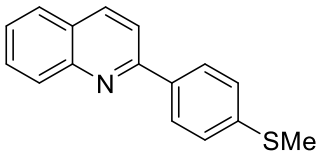
General Procedure C: Procedure performed on 3 to 6 mmol scale. To a Schlenk flask were added 2-chloroquinoline (1 equiv.), arylboronic acid (1.3 equiv.) and sodium carbonate (5 equiv.). The flask was equipped with a reflux condenser and the system was placed under nitrogen. A 4:1 mixture of 1,4-dioxane/water (0.1 M) was added and the resulting suspension was sparged with N_2 while stirring for ten minutes. To this suspension was then added tetrakis(triphenylphosphine)palladium(0) (1 mol%) and the mixture was refluxed overnight. After cooling, the mixture was filtered through a pad of Celite and the filter cake was washed with ethyl acetate. The organic layer was then washed with brine, dried with magnesium sulfate and concentrated on the rotatory evaporator. The resulting residue was purified by column chromatography on silica with hexanes/EtOAc using standard techniques.

General Procedure D: Procedure performed on 2-5 mmol scale. To a round bottom flask was added quinoline (1 equiv.) and glacial acetic acid (0.15 M). To the resulting solution was added $NaBH_3CN$ (2.0 equiv.) in one portion while stirring. The flask was capped with a septum and the reaction mixture was stirred overnight at room temperature. To the flask was then slowly added a saturated aqueous solution of sodium carbonate, along with DCM and the mixture was stirred for further 30 minutes. The organic layer was separated and the aqueous layer was further extracted twice more with DCM. The organic layers are then combined, dried with magnesium sulfate and

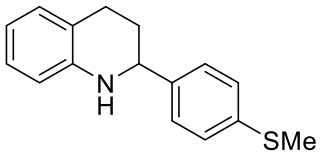
concentrated on the rotatory evaporator. The crude material was then purified by column chromatography on silica with hexanes/EtOAc using standard techniques to obtain the desired 1,2,3,4-tetrahydroquinoline derivative.



2-phenyl-1,2,3,4-tetrahydroquinoline (1c): Prepared via procedure D on 2.5 mmol scale from 2-phenylquinoline (commercially available). Obtained in 79% yield as colorless oil (396 mg). Characterization data matched those previously reported.[11] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 – 7.31 (m, 4H), 7.31 – 7.25 (tt, 7.2, 1.2, 1H), 7.03 – 6.97 (m, 2H), 6.65 (td, *J* = 7.4, 1.2 Hz, 1H), 6.53 (d, *J* = 7.7 Hz, 1H), 4.43 (dd, *J* = 9.4, 3.3 Hz, 1H), 4.03 (s, 1H), 2.92 (ddd, *J* = 16.2, 10.7, 5.5 Hz, 1H), 2.73 (dt, *J* = 16.3, 4.7 Hz, 1H), 2.15 – 2.08 (m, 1H), 2.06 – 1.92 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.80, 144.72, 129.29, 128.56, 127.43, 126.89, 126.53, 120.86, 117.14, 113.95, 56.25, 30.98, 26.39; **HRMS (ESI)** Calcd. for $C_{15}H_{16}N$ ($[M+H]^+$): 210.1278, found: 210.1277.

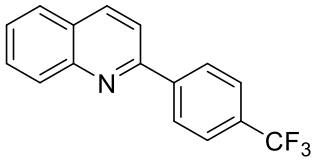


2-(4-(methylthio)phenyl)quinoline: Prepared via procedure C on 4.5 mmol scale with 4-(methylthio)phenylboronic acid (5.85 mmol, 983 mg). Obtained in 50% yield as a white solid (562.5 mgs). Characterization data matched those previously reported.[12] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.6 Hz, 1H), 8.13 (m, 3H), 7.84 (m, 2H), 7.72 (t, *J* = 8.2 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 2.55 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.63, 148.29, 140.38, 136.75, 136.26, 129.67, 129.63, 127.82, 127.44, 127.12, 126.42, 126.18, 118.57, 15.55.

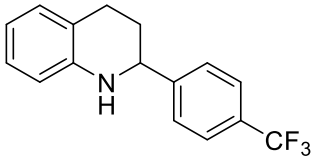


2-(4-(methylthio)phenyl)-1,2,3,4-tetrahydroquinoline (1d): Prepared via procedure D on 2.0 mmol scale from 2-(4-(methylthio)phenyl)quinoline. Obtained in 74% yield as colorless, viscous oil (378 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 3H), 7.04 – 6.96 (m, 2H), 6.65 (td, *J* = 7.5, 0.8 Hz, 1H), 6.53 (d, *J* = 7.8 Hz, 1H), 4.40 (dd, *J* = 9.3, 3.2 Hz, 1H), 4.00 (s, 1H), 2.91 (ddd, *J* = 16.2, 10.6, 5.5 Hz, 1H), 2.72 (dt, *J* = 16.2, 4.8 Hz, 1H), 2.48 (s, 3H), 2.14 – 2.04 (m, 1H), 2.03 – 1.84 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.63,

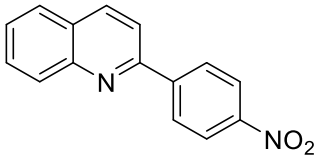
141.81, 137.35, 129.31, 127.09, 126.92, 126.90, 120.85, 117.23, 114.00, 55.81, 30.97, 26.34, 16.06; **HRMS (ESI)** Calcd. for $C_{16}H_{18}NS$ ($[M+H]^+$): 256.1155, found: 256.1154.



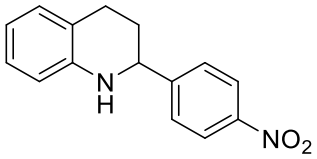
2-(4-(trifluoromethyl)phenyl)quinoline: Prepared via procedure C on 6.0 mmol scale with 4-(trifluoromethyl)phenylboronic acid (7.8 mmol, 1.48 g). Obtained in 48% yield as a white solid (785 mg). Characterization data matched those previously reported.[13] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.28 (t, *J* = 8.2 Hz, 3H), 8.19 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.6 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.82 – 7.72 (m, 3H), 7.61 – 7.53 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.69, 148.27, 142.96, 137.13, 131.1 (q, *J* = 31.4 Hz), 129.99, 129.86, 127.84, 127.52, 127.43, 126.85, 125.73, 124.2 (q, *J* = 272.5 Hz), 118.79.



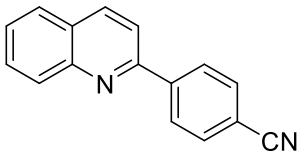
2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroquinoline (1e): Prepared via procedure D on 2.7 mmol scale from 2-(4-(trifluoromethyl)phenyl)quinoline. Obtained in 20% yield as a light yellow, viscous oil (150 mg). Characterization data matched those previously reported.[14] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.09 – 6.94 (m, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.57 (d, *J* = 7.9 Hz, 1H), 4.52 (dd, *J* = 8.9, 3.2 Hz, 1H), 4.05 (s, 1H), 2.91 (ddd, *J* = 15.9, 10.1, 5.4 Hz, 1H), 2.71 (dt, *J* = 16.4, 5.0 Hz, 1H), 2.20 – 2.06 (m, 1H), 2.06 – 1.88 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.92, 144.22, 129.83, 129.51, 129.36, 127.05, 126.88, 125.54 (q, 3.8 Hz), 120.78, 117.57, 114.13, 55.79, 30.88, 25.96; **HRMS (ESI)** Calcd. for $C_{16}H_{15}F_3N$ ($[M+H]^+$): 278.1155, found: 278.1152.



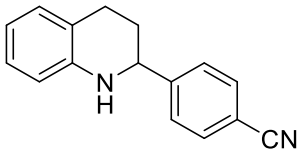
2-(4-(nitrophenyl)quinoline: Prepared via procedure C on 3.0 mmol scale with 4-nitrophenylboronic acid (3.9 mmol, 650 mg). Obtained in 91% yield as a yellow solid (684 mgs). Characterization data matched those previously reported. [13] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.40 – 8.33 (m, 4H), 8.31 (d, *J* = 8.5 Hz, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 8.6 Hz, 1H), 7.91 – 7.85 (m, 1H), 7.79 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.60 (ddd, *J* = 8.1, 6.8, 1.1 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.56, 148.33, 148.29, 145.48, 137.34, 130.24, 129.96, 128.32, 127.57, 127.28, 124.05, 118.76.



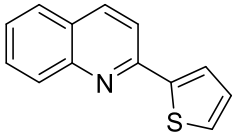
4-(1,2,3,4-tetrahydroquinolin-2-yl)nitrobenzene (1f): Prepared via procedure D on 2.8 mmol scale from 4-(quinolin-2-yl)nitrobenzene. Obtained in 93% yield as orange solid (648 mg). **M.P.** 97-98 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.7 Hz, 2H), 7.56 (d, *J* = 8.7 Hz, 2H), 7.09 – 6.96 (m, 2H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 7.9 Hz, 1H), 4.59 (dd, *J* = 8.6, 3.4 Hz, 1H), 4.10 (s, 1H), 2.91 (ddd, *J* = 15.6, 9.7, 5.3 Hz, 1H), 2.69 (dt, *J* = 16.4, 5.2 Hz, 1H), 2.25 – 2.09 (m, 1H), 2.04 – 1.94 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.45, 147.29, 143.84, 129.39, 127.35, 127.16, 123.88, 120.68, 117.84, 114.24, 55.57, 30.77, 25.66; **HRMS (ESI)** Calcd. for $C_{15}H_{15}N_2O_2$ ($[M+H]^+$): 255.1129, found: 255.1120.



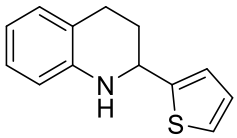
4-(quinolin-2-yl)benzonitrile: Prepared via procedure C on 6.0 mmol scale with 4-cyanophenylboronic acid (7.8 mmol, 1.15 g). Obtained in 96% yield as a white solid (1.32 g). Characterization data matched those previously reported.[15] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 – 8.26 (m, 3H), 8.18 (dd, *J* = 8.6, 1.2 Hz, 1H), 7.93 – 7.84 (m, 2H), 7.84 – 7.73 (m, 3H), 7.59 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.96, 148.27, 143.73, 137.31, 132.63, 130.17, 129.91, 128.09, 127.56, 127.54, 127.15, 118.86, 118.63, 112.75.



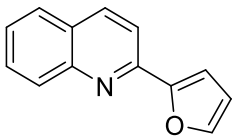
4-(1,2,3,4-tetrahydroquinolin-2-yl)benzonitrile (1g): Prepared via procedure D on 4.0 mmol scale from 4-(quinolin-2-yl)benzonitrile. Obtained in 57% yield as white solid (531 mg). Characterization data matched those previously reported.[16] **M.P.** 97-99 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.12 – 6.91 (m, 2H), 6.68 (t, *J* = 7.4 Hz, 1H), 6.57 (d, *J* = 7.9 Hz, 1H), 4.52 (dd, *J* = 8.6, 3.4 Hz, 1H), 4.07 (s, 1H), 2.89 (ddd, *J* = 15.6, 9.8, 5.3 Hz, 1H), 2.67 (dt, *J* = 16.4, 5.2 Hz, 1H), 2.23 – 2.06 (m, 1H), 2.01 – 1.90 (m, *J* = 13.4, 9.5, 5.0 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.38, 143.92, 132.40, 129.32, 127.26, 127.08, 120.65, 118.83, 117.69, 114.16, 111.12, 55.70, 30.65, 25.64; **HRMS (ESI)** Calcd. for $C_{16}H_{15}N_2$ ($[M+H]^+$): 235.1227, found: 235.1230.



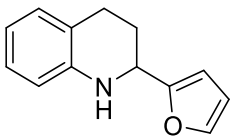
2-(2-thienyl)quinoline: Prepared via procedure C on 6.0 mmol scale with 2-thienylboronic acid (7.8 mmol, 998 mg). Obtained in 99% yield as a yellow solid (1.25 g). Characterization data matched those previously reported.[13] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 – 8.04 (m, 2H), 7.83 – 7.74 (m, 2H), 7.74 – 7.64 (m, 2H), 7.52 – 7.42 (m, 2H), 7.15 (dd, *J* = 5.0, 3.7 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.35, 148.12, 145.41, 136.63, 129.82, 129.28, 128.59, 128.09, 127.49, 127.20, 126.11, 125.85, 117.66.



2-(2-thienyl)-1,2,3,4-tetrahydroquinoline (1h): Prepared via procedure D on 4.0 mmol scale from 2-(2-thienyl)-quinoline. Obtained in 75% yield as yellow, viscous oil (891 mg). Characterization data matched those previously reported.[17] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.10 – 6.86 (m, 4H), 6.66 (td, *J* = 7.4, 1.0 Hz, 1H), 6.54 (d, *J* = 7.8 Hz, 1H), 4.75 (dd, *J* = 9.1, 3.2 Hz, 1H), 4.16 (s, 1H), 2.93 (ddd, *J* = 16.1, 10.4, 5.5 Hz, 1H), 2.77 (dt, *J* = 16.4, 5.0 Hz, 1H), 2.27 – 2.16 (m, 1H), 2.16 – 1.96 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.89, 143.99, 129.29, 126.91, 126.65, 124.08, 123.55, 120.91, 117.69, 114.30, 52.00, 31.83, 26.17; **HRMS (ESI)** Calcd. for $C_{13}H_{14}NS$ ($[M+H]^+$): 216.0842, found: 216.0848.

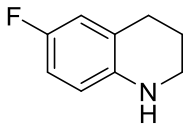


2-(2-furyl)quinoline: Prepared via procedure C on 5.54 mmol scale with 2-furanylboronic acid (7.2 mmol, 807 mg). Obtained in 77% yield as a yellow solid (833 mg). Characterization data matched those previously reported.[13] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 – 8.09 (m, 2H), 7.87 – 7.75 (m, 2H), 7.74 – 7.67 (m, 1H), 7.63 (s, 1H), 7.55 – 7.45 (m, 1H), 7.22 (d, *J* = 3.3 Hz, 1H), 6.59 (dd, *J* = 3.3, 1.7 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.69, 149.03, 148.10, 144.13, 136.68, 129.88, 129.36, 127.57, 127.16, 126.21, 117.48, 112.22, 110.13.

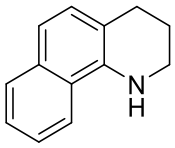


2-(2-furyl)-1,2,3,4-tetrahydroquinoline (1i): Prepared via procedure D on 4.27 mmol scale from 2-(2-furyl)-quinoline. Obtained in 65% yield as yellow, viscous oil (448 mg).

Characterization data matched those previously reported.[17] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 1H), 7.02 – 6.92 (m, 2H), 6.63 (td, *J* = 7.5, 0.7 Hz, 1H), 6.51 (d, *J* = 7.9 Hz, 1H), 6.31 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.18 (d, *J* = 3.2 Hz, 1H), 4.50 (dd, *J* = 8.3, 3.5 Hz, 1H), 4.09 (s, 1H), 2.84 (ddd, *J* = 15.3, 9.3, 5.6 Hz, 1H), 2.72 (dt, *J* = 16.3, 5.5 Hz, 1H), 2.26 – 2.01 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.92, 143.71, 141.56, 129.21, 126.83, 120.90, 117.49, 114.30, 110.14, 105.17, 49.63, 26.86, 25.48; **HRMS (ESI)** Calcd. for $C_{13}H_{14}NO$ ($[M+H]^+$): 200.1070, found: 200.1070.

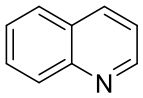


6-Fluoro-1,2,3,4-tetrahydroquinoline (1o): Prepared via a modification of Procedure D on 6.5 mmol scale from 6-fluoroquinoline (commercially available). The substrate (956 mg, 6.5 mmol) was dissolved in 36 ml of absolute ethanol. To this, $NaBH_3CN$ (1.63 g, 26 mmol) was added in one portion. 2.6 ml of 37% HCl(aq.) (26 mmol) was then added dropwise with stirring while checking for heating of the reaction. After the HCl was added, the reaction was stirred for 1 h at room temperature, then at 60 °C for 12 hours, followed by 5 days at room temperature. Reaction was quenched by adding saturated NH_4OH until pH = 9. The reaction mixture is then diluted with water and extracted with DCM (75 ml) 3 times. The combined organic layers were dried over magnesium sulfate and concentrated. Column chromatography of the crude on silica using hexanes/EtOAc provided the product in 55% yield as yellow oil (540 mg). Characterization data matched those previously reported.[18] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.76 – 6.59 (m, 2H), 6.43 – 6.34 (m, 1H), 3.69 (s, 1H), 3.36 – 3.18 (m, 2H), 2.74 (t, *J* = 6.5 Hz, 2H), 1.92 (dt, *J* = 12.0, 6.4 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.47 (d, *J* = 234.5 Hz), 140.95 , 122.80 (d, *J* = 6.7 Hz), 115.64 (d, *J* = 21.6 Hz), 114.92 (d, *J* = 7.6 Hz), 113.22 (d, *J* = 22.4 Hz), 42.11, 27.05, 22.02; **HRMS (ESI)** Calcd. for $C_9H_{11}FN$ ($[M+H]^+$): 152.0871, found: 152.0865.

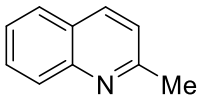


1,2,3,4-tetrahydrobenzo[*h*]quinoline (1r): Prepared via procedure D on 5.0 mmol scale from **benzo[*h*]quinoline**. Obtained in 68% yield as light brown solid (620 mg). Characterization data matched those previously reported.[19] **M.P.** 40-42 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 – 7.65 (m, 2H), 7.44 – 7.32 (m, 2H), 7.17 (d, *J* = 8.45 Hz, 1H), 7.11 (d, *J* = 8.45 Hz, 1H), 4.37 (s, 1H), 3.56 – 3.42 (m, 2H), 2.92 (t, *J* = 6.4 Hz, 2H), 2.04 (dt, *J* = 11.9, 6.4 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.00, 133.02, 128.58, 128.53, 124.92, 124.73, 123.23, 119.39, 116.91, 115.79, 42.44, 27.46, 22.15; **HRMS (ESI)** Calcd. for $C_{13}H_{14}N$ ($[M+H]^+$): 184.1122, found: 184.1121.

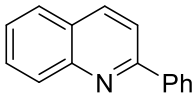
Characterization Data for Isolated Products



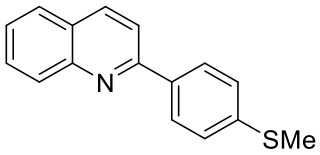
Quinoline (2b): Yield 90% (57.9 mg) after 6 h. Colorless oil. Characterization data matched that of authentic material.[20] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.92 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.21 – 8.02 (m, 2H), 7.81 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.77 – 7.66 (m, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.39 (dd, *J* = 8.3, 4.2 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.42, 148.28, 136.07, 129.46, 128.29, 127.79, 126.55, 121.08. **HRMS (ESI)** Calcd. for C_9H_8N ($[M+H]^+$): 130.0652, found: 130.0654.



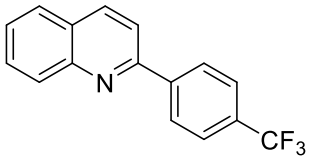
Quinoline (2a): Yield 82% (58.7 mg) after 6 h. Colorless oil. Characterization data matched that of authentic material.[20] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.03 (dd, *J* = 8.3, 4.2 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.73 – 7.62 (m, 1H), 7.47 (t, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 2.75 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.00, 147.88, 136.15, 129.42, 128.64, 127.49, 126.48, 125.66, 122.00, 25.42; **HRMS (ESI)** Calcd. for $C_{10}H_{10}N$ ($[M+H]^+$): 144.0808, found: 144.0806.



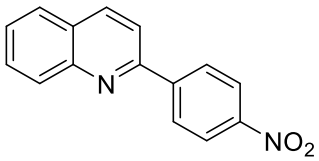
2-Phenylquinoline (2c): Yield 92% (94.2 mg) after 6 h. Yellow solid. Characterization data matched that of authentic material.[20] **M.P.** 80-82 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 – 8.12 (m, 4H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.79 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.71 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1H), 7.55 – 7.40 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.40, 148.35, 139.74, 136.81, 129.80, 129.70, 129.37, 128.90, 127.63, 127.52, 127.23, 126.33, 119.05; **HRMS (ESI)** Calcd. for $C_{15}H_{12}N$ ($[M+H]^+$): 206.0965, found: 206.0969.



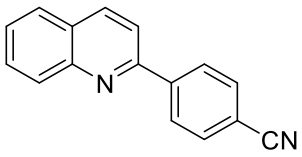
2-(4-(methylthio)phenyl)quinoline (2d): Yield 80% (100.3 mg) after 12 h. White solid. Characterization data matched those previously reported.[12] **M.P.** 128-130 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.6 Hz, 1H), 8.13 (m, 3H), 7.84 (m, 2H), 7.72 (t, *J* = 8.2 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 2.55 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.63, 148.29, 140.38, 136.75, 136.26, 129.67, 129.63, 127.82, 127.44, 127.12, 126.42, 126.18, 118.57, 15.55; **HRMS (ESI)** Calcd. for $C_{16}H_{14}NS$ ($[M+H]^+$): 252.0842, found: 252.0834.



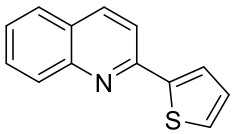
2-(4-(trifluoromethyl)phenyl)quinoline (2e): Yield 90% (121 mg) after 6 h. White solid. Characterization data matched those previously reported.[13] **M.P.** 122-124 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.28 (t, *J* = 8.2 Hz, 3H), 8.19 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.6 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.82 – 7.72 (m, 3H), 7.61 – 7.53 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.69, 148.27, 142.96, 137.13, 131.1 (q, *J* = 31.4 Hz), 129.99, 129.86, 127.84, 127.52, 127.43, 126.85, 125.73, 124.2 (q, *J* = 272.5 Hz), 118.79; **HRMS (ESI)** Calcd. for $C_{16}H_{11}F_3N$ ($[M+H]^+$): 274.0839, found: 274.0844.



2-(4-(nitrophenyl)quinoline (2f): Yield 66% (83 mg) after 16 h. Yellow solid. Characterization data matched those previously reported.[13] **M.P.** 118-120 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.40 – 8.33 (m, 4H), 8.31 (d, *J* = 8.5 Hz, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 8.6 Hz, 1H), 7.91 – 7.85 (m, 1H), 7.79 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.60 (ddd, *J* = 8.1, 6.8, 1.1 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.56, 148.33, 148.29, 145.48, 137.34, 130.24, 129.96, 128.32, 127.57, 127.28, 124.05, 118.76; **HRMS (ESI)** Calcd. for $C_{15}H_{11}N_2O_2$ ($[M+H]^+$): 251.0816, found: 251.0821.

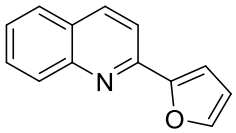


4-(quinolin-2-yl)benzonitrile (2g): Yield 50% (58 mg) after 16 h. White solid. Characterization data matched those previously reported.[15] **M.P.** 112-113 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 – 8.26 (m, 3H), 8.18 (dd, *J* = 8.6, 1.2 Hz, 1H), 7.93 – 7.84 (m, 2H), 7.84 – 7.73 (m, 3H), 7.59 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.96, 148.27, 143.73, 137.31, 132.63, 130.17, 129.91, 128.09, 127.56, 127.54, 127.15, 118.86, 118.63, 112.75; **HRMS (ESI)** Calcd. for $C_{16}H_{11}N_2$ ($[M+H]^+$): 231.0917, found: 231.0915.

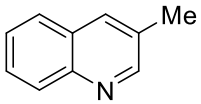


2-(2-thienyl)quinoline (2h): Yield 90% (94.7 mg) after 8 h. Yellow solid. Characterization data matched those previously reported.[13] **M.P.** 126-128 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 – 8.04 (m, 2H), 7.83 – 7.74 (m, 2H), 7.74 – 7.64 (m, 2H), 7.52 – 7.42 (m, 2H), 7.15 (dd, *J* = 5.0,

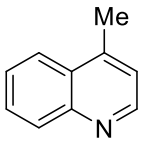
3.7 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.35, 148.12, 145.41, 136.63, 129.82, 129.28, 128.59, 128.09, 127.49, 127.20, 126.11, 125.85, 117.66; **HRMS (ESI)** Calcd. for $C_{13}H_{10}NS$ ($[M+H]^+$): 212.0529, found: 212.0536.



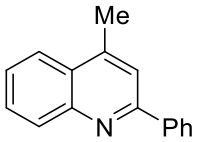
2-(2-furyl)quinoline (2i): Yield 96% (93.9 mg) after 6 h. Yellow solid. Characterization data matched those previously reported.[13] **M.P.** 85-87 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 – 8.09 (m, 2H), 7.87 – 7.75 (m, 2H), 7.74 – 7.67 (m, 1H), 7.63 (s, 1H), 7.55 – 7.45 (m, 1H), 7.22 (d, *J* = 3.3 Hz, 1H), 6.59 (dd, *J* = 3.3, 1.7 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.69, 149.03, 148.10, 144.13, 136.68, 129.88, 129.36, 127.57, 127.16, 126.21, 117.48, 112.22, 110.13; **HRMS (ESI)** Calcd. for $C_{13}H_{10}NO$ ($[M+H]^+$): 196.0757, found: 196.0753.



3-Methylquinoline (2j) Yield 61% (43.5 mg) after 6 h. Colorless liquid. Characterization data matched that of authentic material.[20] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.91 (s, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.68 – 7.58 (m, 1H), 7.58 – 7.41 (m, 1H), 2.51 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.43, 146.57, 134.68, 130.48, 129.18, 128.44, 128.14, 127.13, 126.55, 18.78; **HRMS (ESI)** Calcd. for $C_{10}H_{10}N$ ($[M+H]^+$): 144.0808, found: 144.0804.

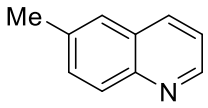


4-Methylquinoline (2k) Yield 90% (64.7 mg) after 6 h. Colorless liquid. Characterization data matched that of authentic material.[20] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 4.4 Hz, 1H), 8.19 – 8.04 (m, 1H), 8.04 – 7.90 (m, 1H), 7.69 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.54 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.19 (dd, *J* = 4.5, 1.1 Hz, 1H), 2.67 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.15, 147.94, 144.30, 129.97, 129.10, 128.26, 126.27, 123.81, 121.85, 18.65; **HRMS (ESI)** Calcd. for $C_{10}H_{10}N$ ($[M+H]^+$): 144.0808, found: 144.0808.

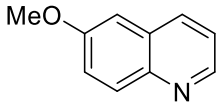


2-Phenyl-4-Methylquinoline (2l): Yield 93% (102.1 mg) after 6 h. Yellow solid. Characterization data matched those previously reported.[21] **M.P.** 60-62 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.95 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.13 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H),

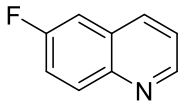
7.60 – 7.53 (m, 1H), 7.49 – 7.34 (m, 2H), 2.83 (t, *J* = 0.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.08, 148.16, 144.81, 139.86, 130.33, 129.35, 129.22, 128.81, 127.57, 127.28, 126.04, 123.65, 119.78, 19.05; **HRMS (ESI)** Calcd. for $C_{16}H_{14}N$ ($[M+H]^+$): 220.1121, found: 220.1129.



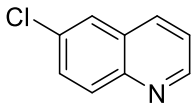
6-Methylquinoline (2m): Yield 94% (65.0 mg, purity of starting material 97%) after 6 h. Yellow liquid. Characterization data matched that of authentic material.[20] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.84 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.61 – 7.50 (m, 2H), 7.34 (dd, *J* = 8.3, 4.2 Hz, 1H), 2.53 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.54, 146.91, 136.39, 135.37, 131.75, 129.11, 128.33, 126.59, 121.07, 21.59; **HRMS (ESI)** Calcd. for $C_{10}H_{10}N$ ($[M+H]^+$): 144.0808, found: 144.0808.



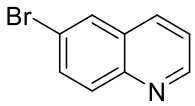
6-Methoxyquinoline (2n): Yield 87% (69.0 mg) after 6 h. Yellow liquid. Characterization data matched that of authentic material.[20] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.77 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.02 (dd, *J* = 16.1, 9.0 Hz, 2H), 7.45 – 7.30 (m, 2H), 7.06 (d, *J* = 2.9 Hz, 1H), 3.93 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.74, 147.96, 144.44, 134.80, 130.87, 129.31, 122.30, 121.38, 105.12, 55.55; **HRMS (ESI)** Calcd. for $C_{10}H_{10}NO$ ($[M+H]^+$): 160.0757, found: 160.0751.



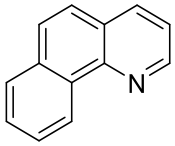
6-Fluoroquinoline (2o): Yield 98% (72.0 mg) after 9 h. Colorless liquid. Characterization data matched those previously reported.[22] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.89 (dd, *J* = 4.1, 1.4 Hz, 1H), 8.17 – 8.06 (m, 2H), 7.50 (td, *J* = 8.8, 2.8 Hz, 1H), 7.46 – 7.38 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.37, 159.40, 149.71 (d, *J* = 2.7 Hz), 145.41, 135.41 (d, *J* = 5.3 Hz), 132.01 (d, *J* = 9.3 Hz), 128.88 (d, *J* = 10.0 Hz), 121.78, 119.76 (d, *J* = 25.7 Hz), 110.70 (d, *J* = 21.6 Hz); **HRMS (ESI)** Calcd. for C_9H_7FN ($[M+H]^+$): 148.0558, found: 148.0558.



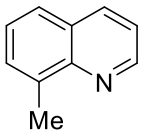
6-Chloroquinoline (2p): Yield 84% (69.1 mg) after 6 h. Yellow solid. Characterization data matched those previously reported.[21] **M.P.** 39-41 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 4.0 Hz, 1H), 8.03 (d, *J* = 9.0 Hz, 2H), 7.77 (d, *J* = 1.9 Hz, 1H), 7.63 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.40 (dd, *J* = 8.3, 4.2 Hz, 1H); **^{13}C NMR** (101 MHz,) δ 150.61, 146.64, 135.11, 132.28, 131.13, 130.40, 128.82, 126.42, 121.91; **HRMS (ESI)** Calcd. for C_9H_7ClN ($[M+H]^+$): 164.0262, found: 164.0261.



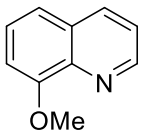
6-Bromoquinoline (2q): Yield 97% (99.8 mg) after 6 h. Yellow liquid. Characterization data matched those previously reported.[23] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.92 (d, *J* = 4.1 Hz, 1H), 8.06 (d, *J* = 8.3 Hz, 1H), 8.03 – 7.93 (m, 2H), 7.78 (dd, *J* = 9.0, 1.8 Hz, 1H), 7.42 (dd, *J* = 8.3, 4.2 Hz, 1H); **^{13}C NMR** (101 MHz,) δ 150.78, 146.87, 135.08, 132.98, 131.27, 129.83, 129.38, 121.93, 120.49; **HRMS (ESI)** Calcd. for C_9H_7BrN (monoisotopic) ($[M+H]^+$): 207.9757, found: 207.9755.



Benzo[*h*]quinoline (2r): Yield 69% (62.0 mg) after 12 h. Light brown solid. Characterization data matched that of authentic material.[20] **M.P.** 37-39 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.30 (d, *J* = 8.7 Hz, 1H), 9.01 (dd, *J* = 4.4, 1.7 Hz, 1H), 8.18 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.92 (d, *J* = 7.4 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.78 – 7.64 (m, 3H), 7.53 (dd, *J* = 8.0, 4.4 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.85, 146.60, 135.84, 133.62, 131.51, 128.22, 127.83, 127.78, 127.10, 126.42, 125.36, 124.36, 121.81; **HRMS (ESI)** Calcd. for $C_{13}H_{10}N$ ($[M+H]^+$): 180.0808, found: 180.0804.



8-Methylquinoline (2s): Yield 72% (51.8 mg) after 9 h. Colorless liquid. Characterization data matched that of authentic material.[20] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.95 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.13 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.57 (d, *J* = 6.9 Hz, 1H), 7.50 – 7.32 (m, 2H), 2.83 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.28, 147.40, 137.11, 136.31, 129.62, 128.27, 126.30, 125.88, 120.85, 18.18; **HRMS (ESI)** Calcd. for $C_{10}H_{10}N$ ($[M+H]^+$): 144.0808, found: 144.0814.



8-Methoxyquinoline (2t): Yield 77% (60.9 mg) after 9 h. Colorless liquid. Characterization data matched that of authentic material.[10] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.93 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.12 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.59 – 7.34 (m, 3H), 7.05 (d, *J* = 7.6 Hz, 1H), 4.09 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.39, 149.25, 140.20, 135.86, 129.33, 126.69, 121.68, 119.53, 107.50, 55.96; **HRMS (ESI)** Calcd. for $C_{10}H_{10}NO$ ($[M+H]^+$): 160.0757, found: 160.0756.

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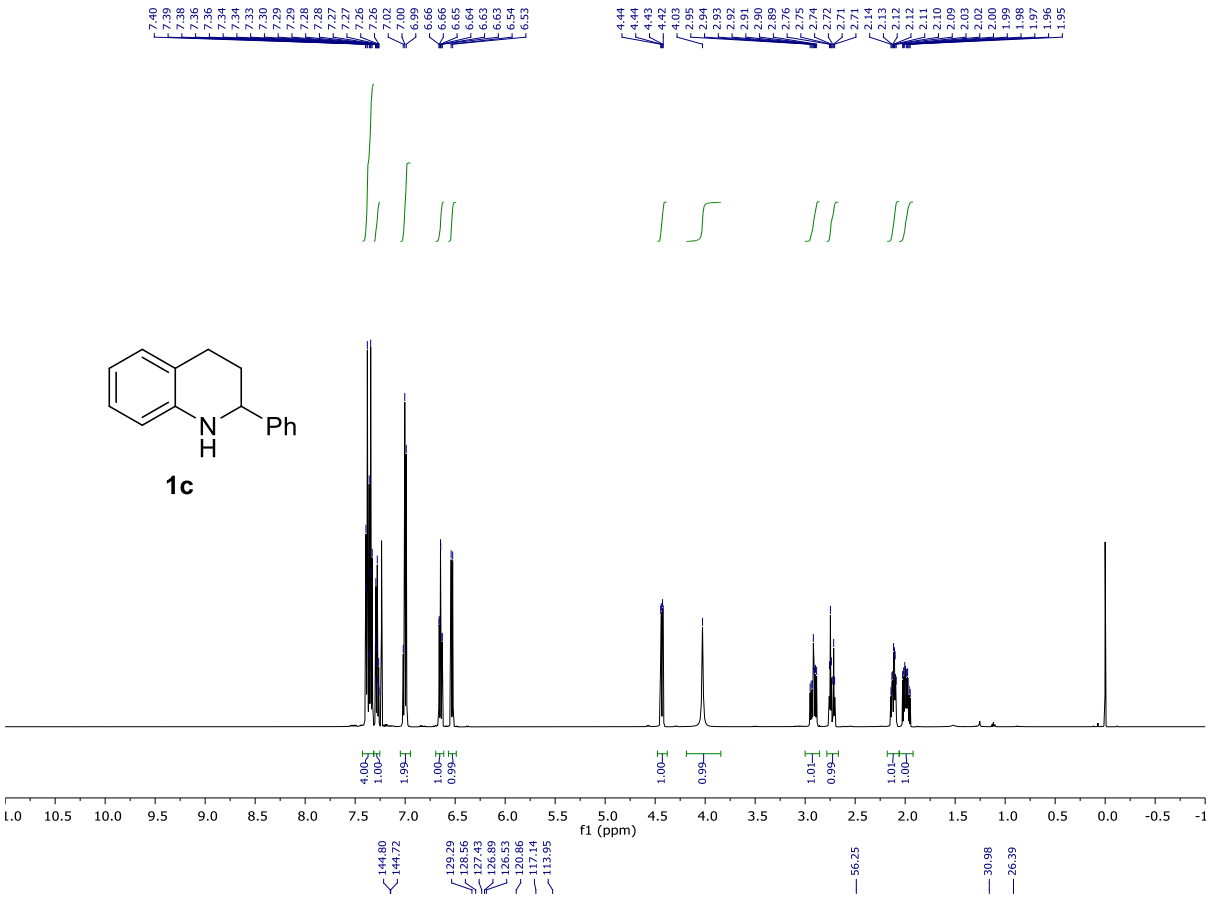
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4.44 4.44 4.43 4.42 4.03 2.95 2.94 2.93 2.92 2.91 2.90 2.89 2.76 2.75 2.74 2.72 2.71 2.71 2.14 2.13 2.12 2.12 2.11 2.10 2.09 2.03 2.02 2.00 1.99 1.98 1.97 1.96 1.95
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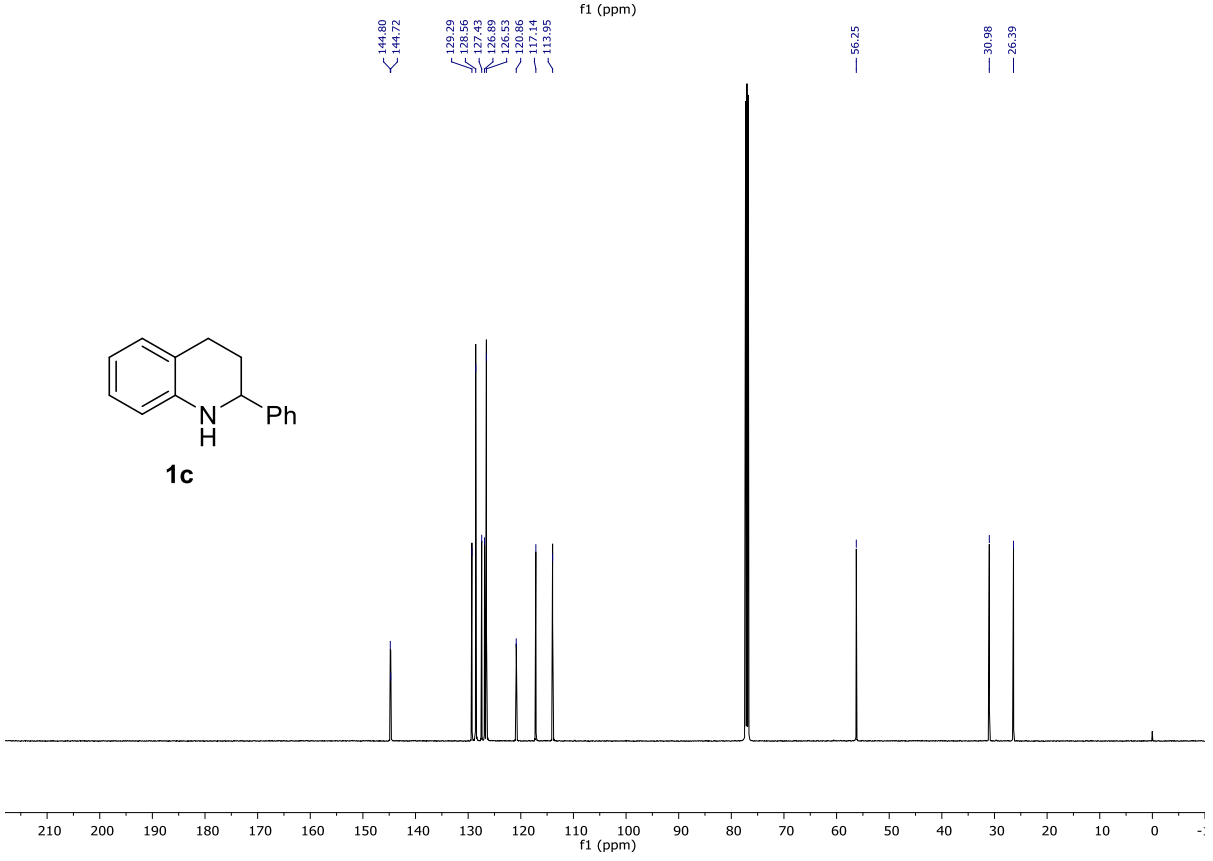
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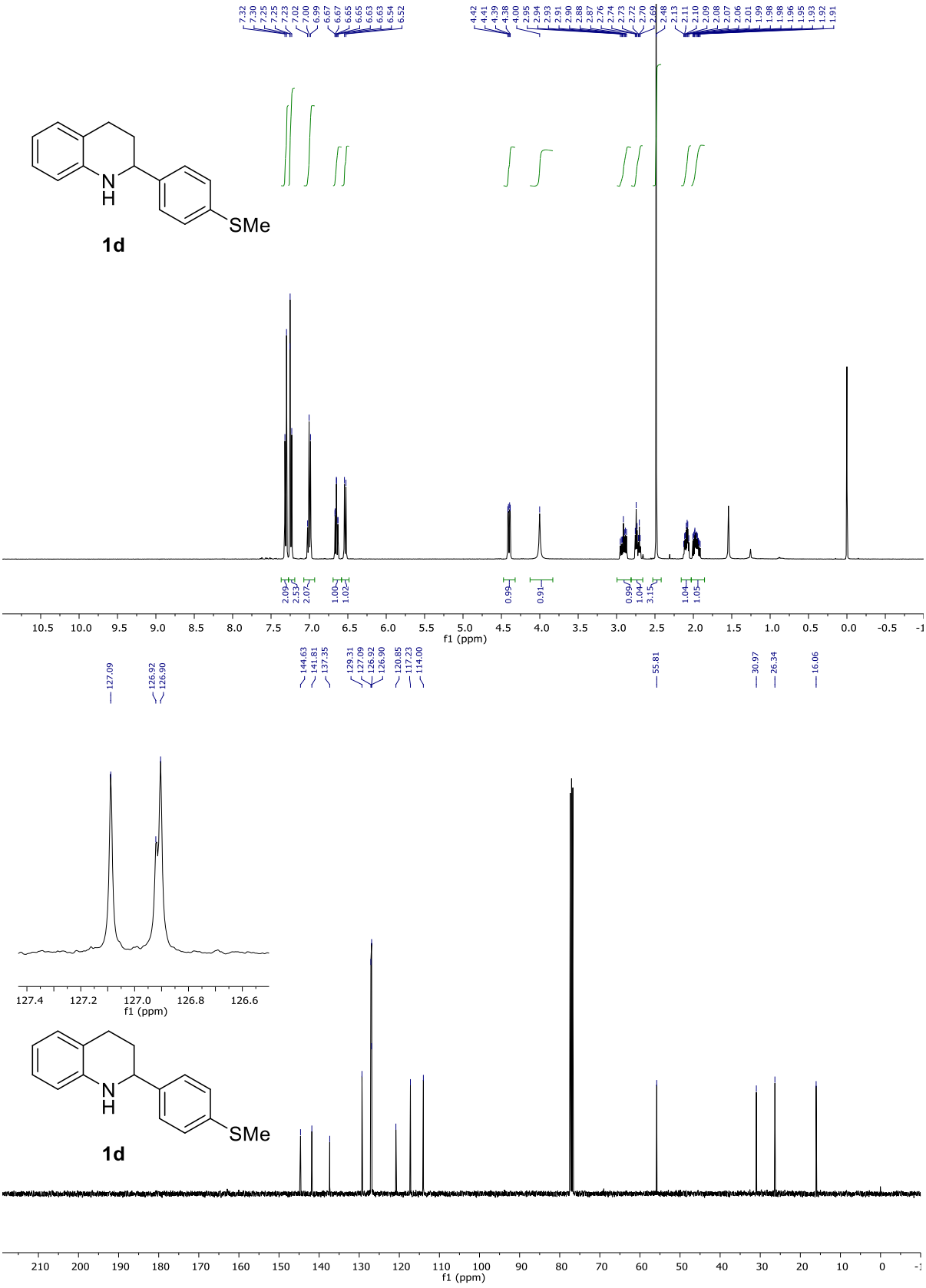
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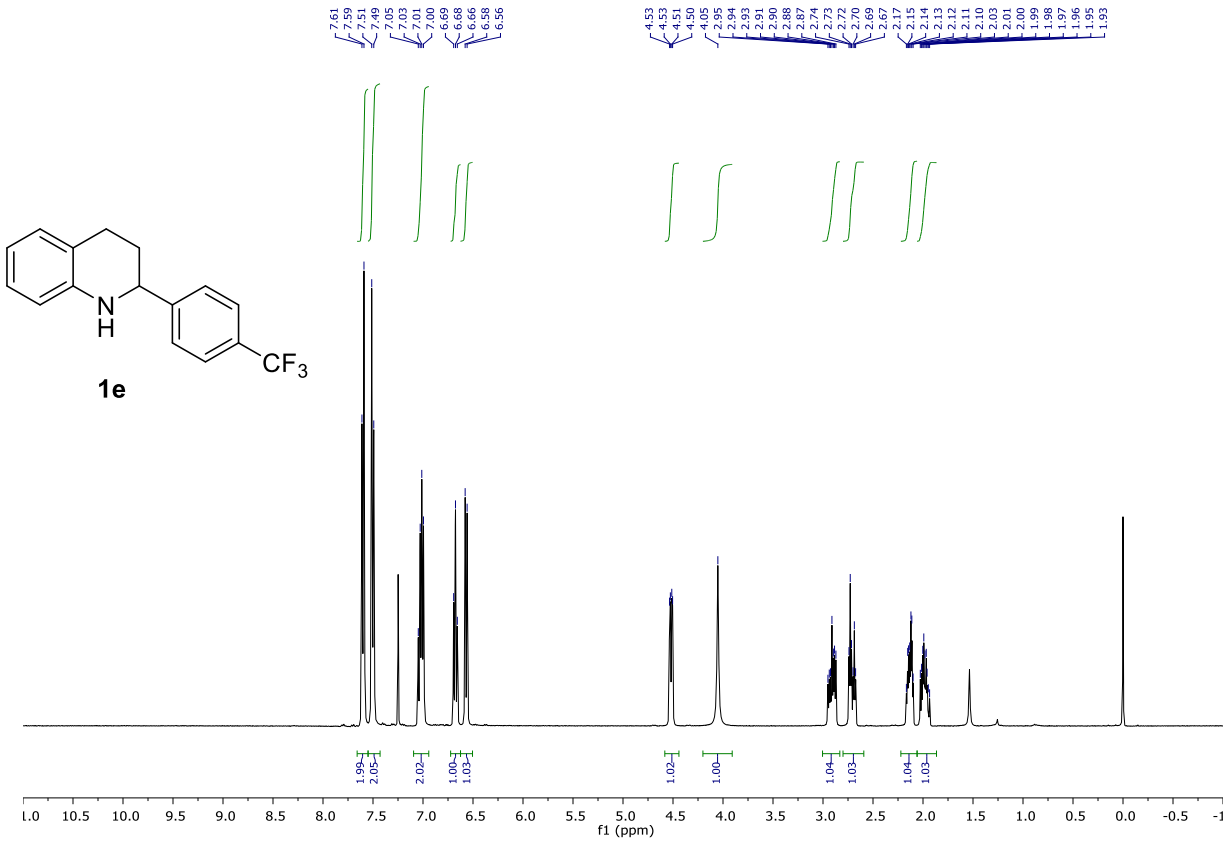
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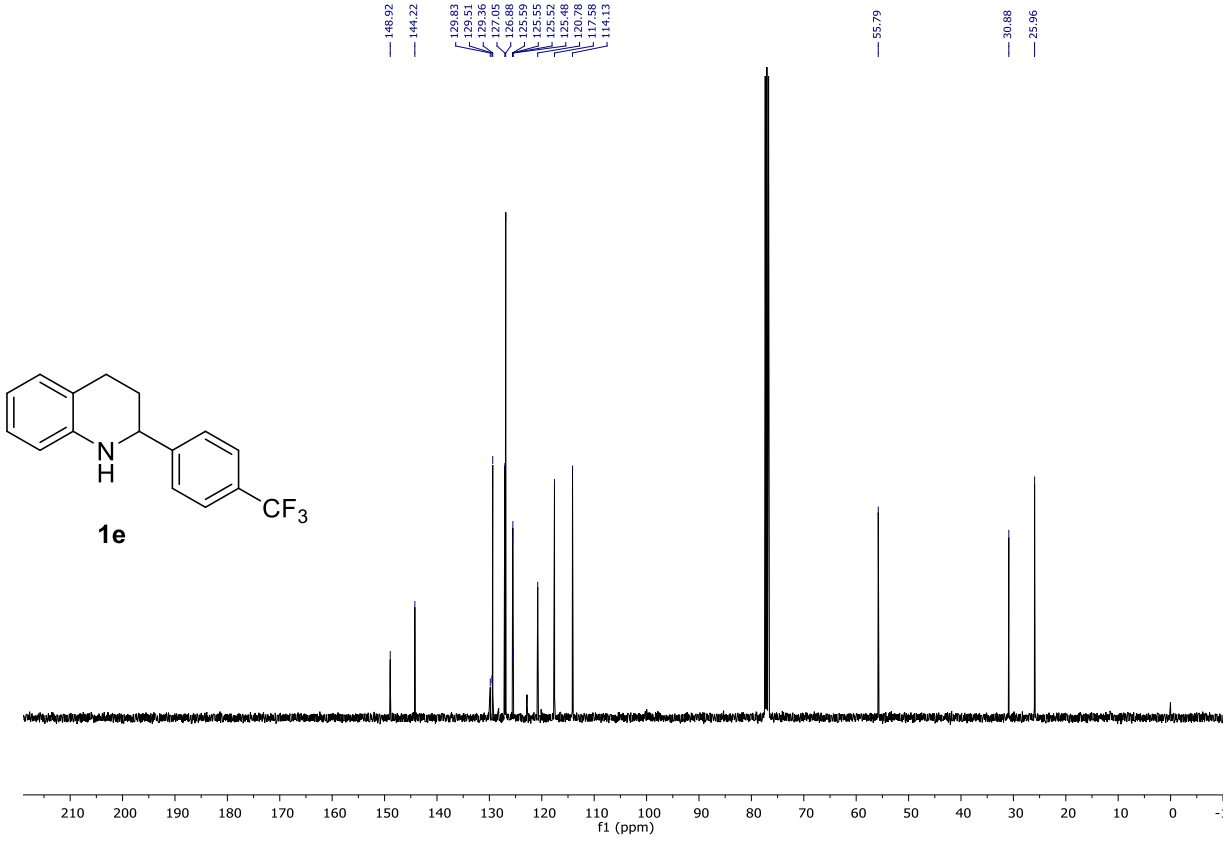
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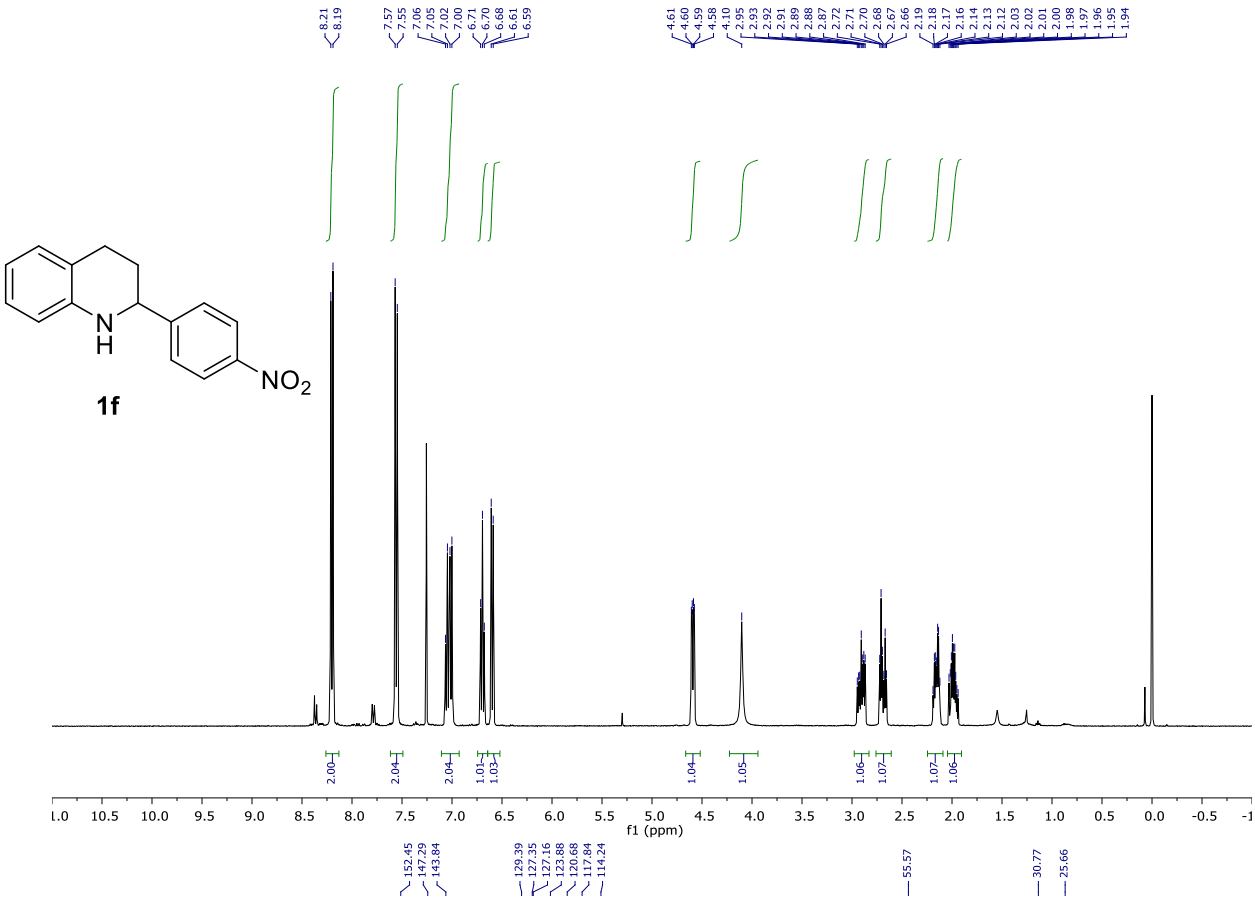
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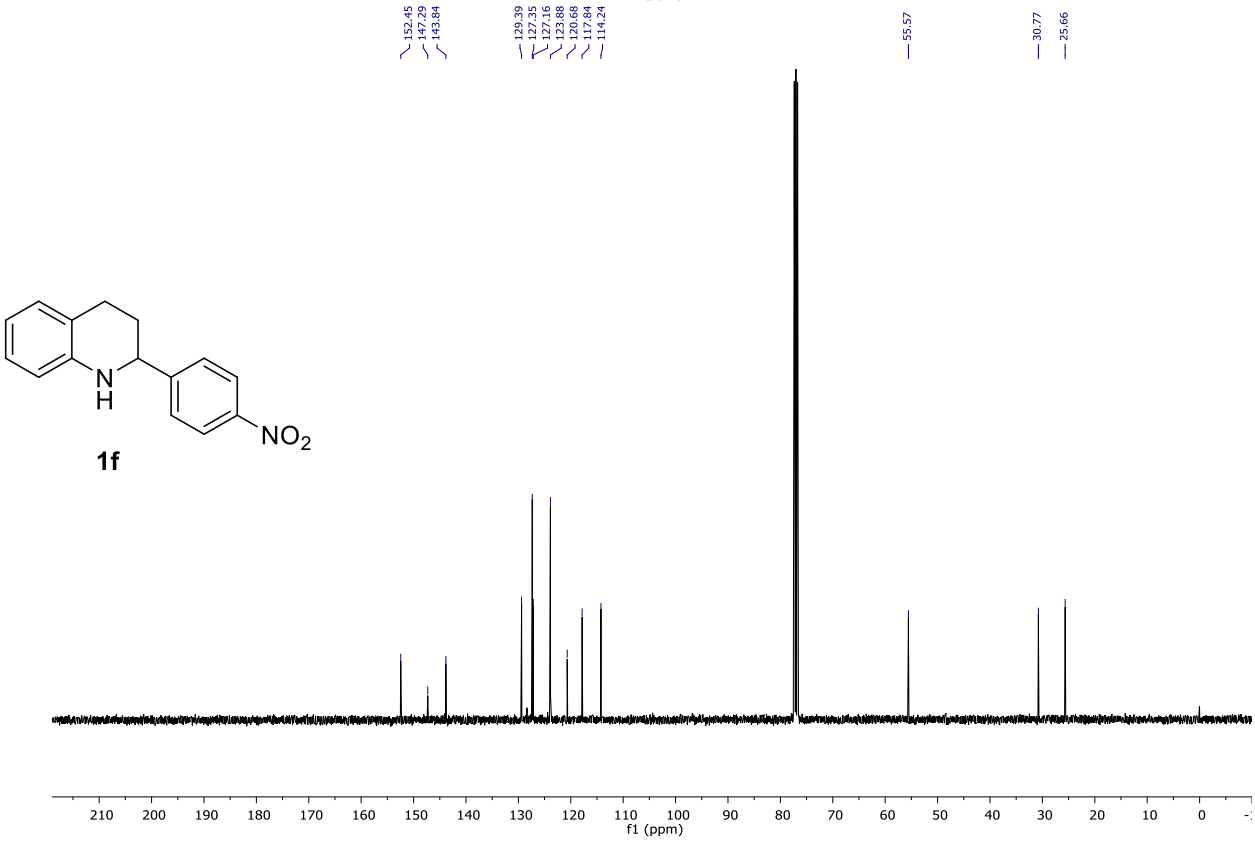
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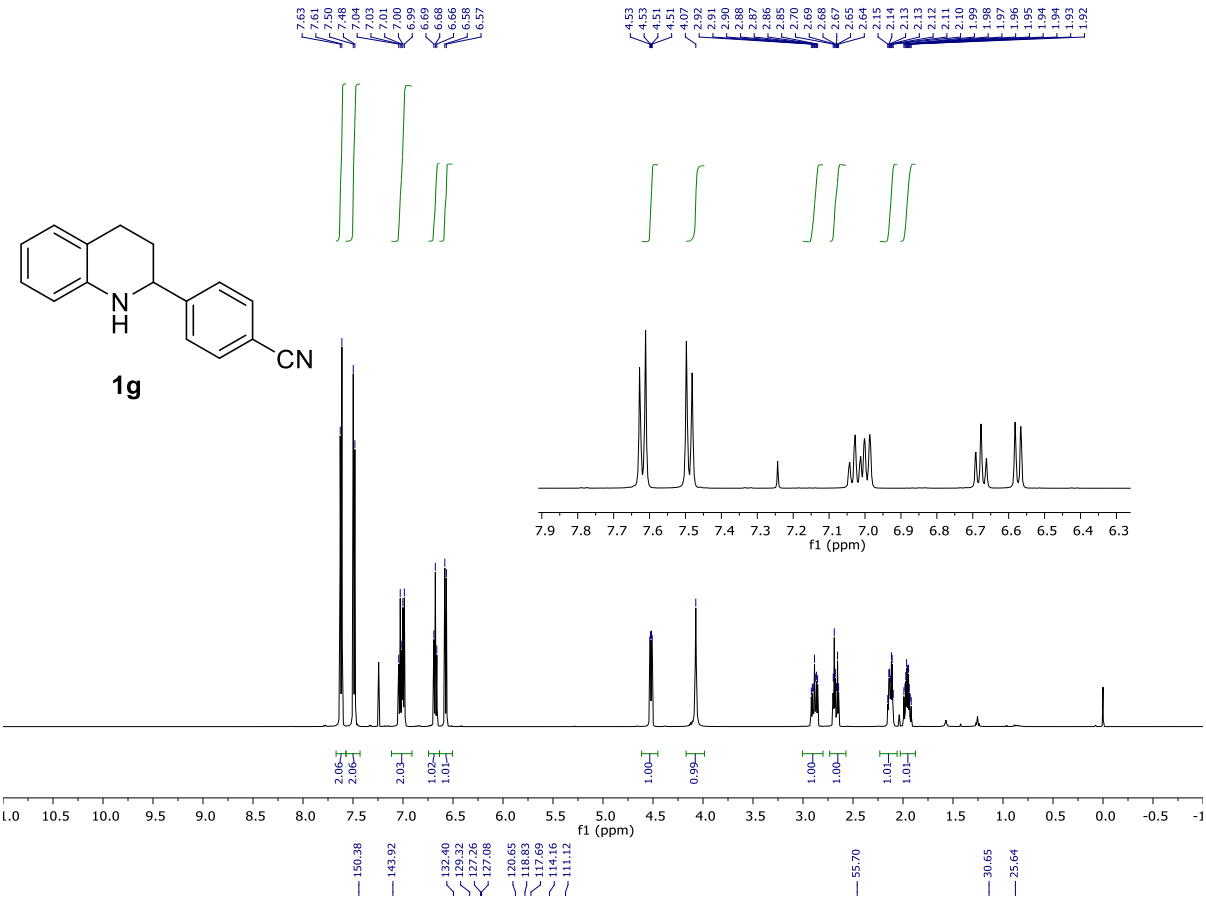
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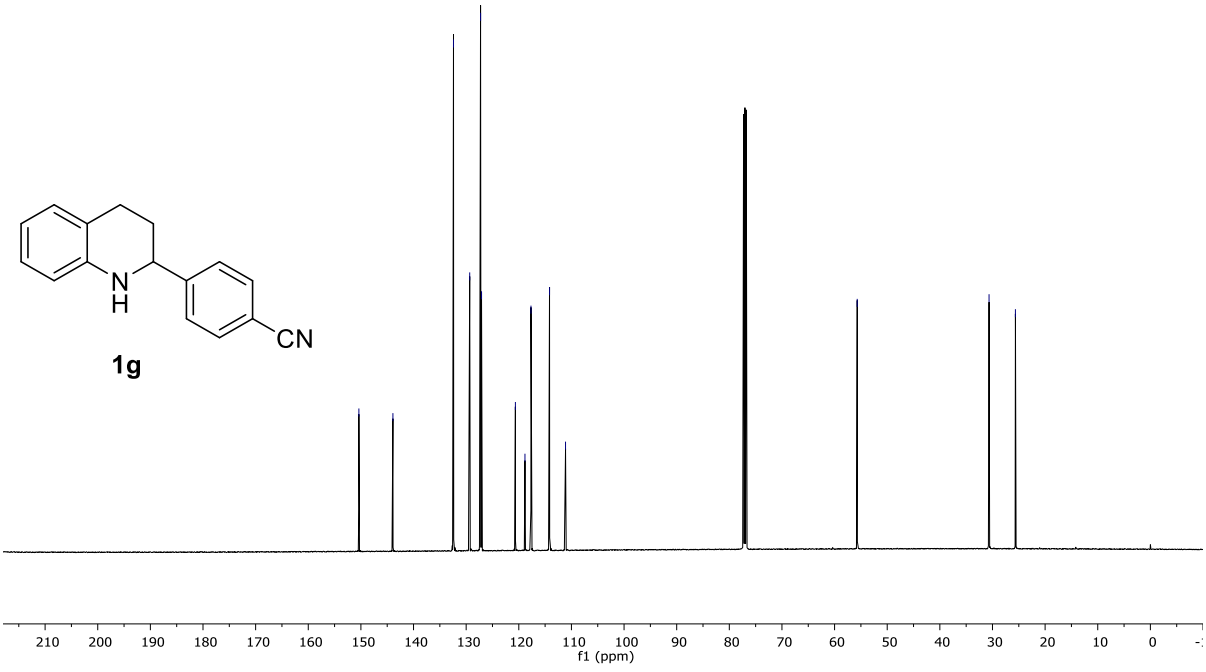
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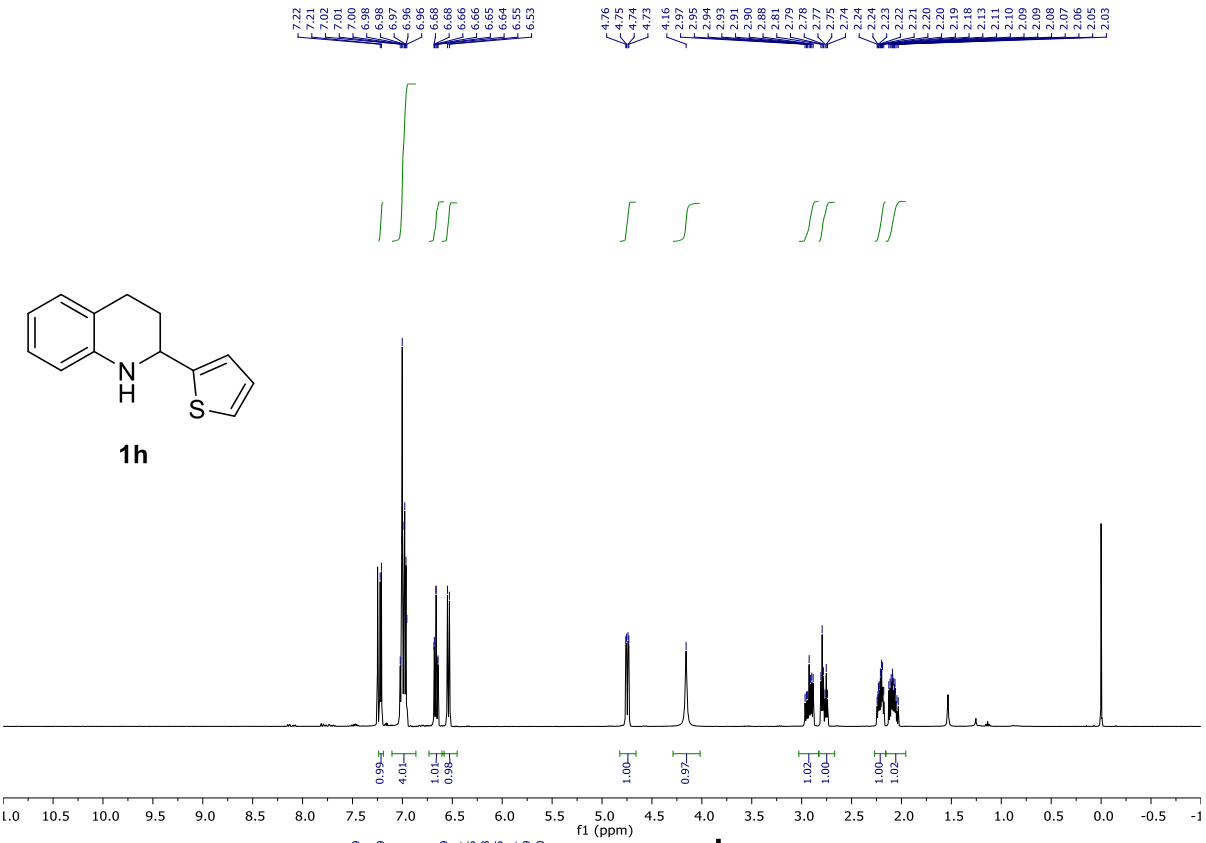
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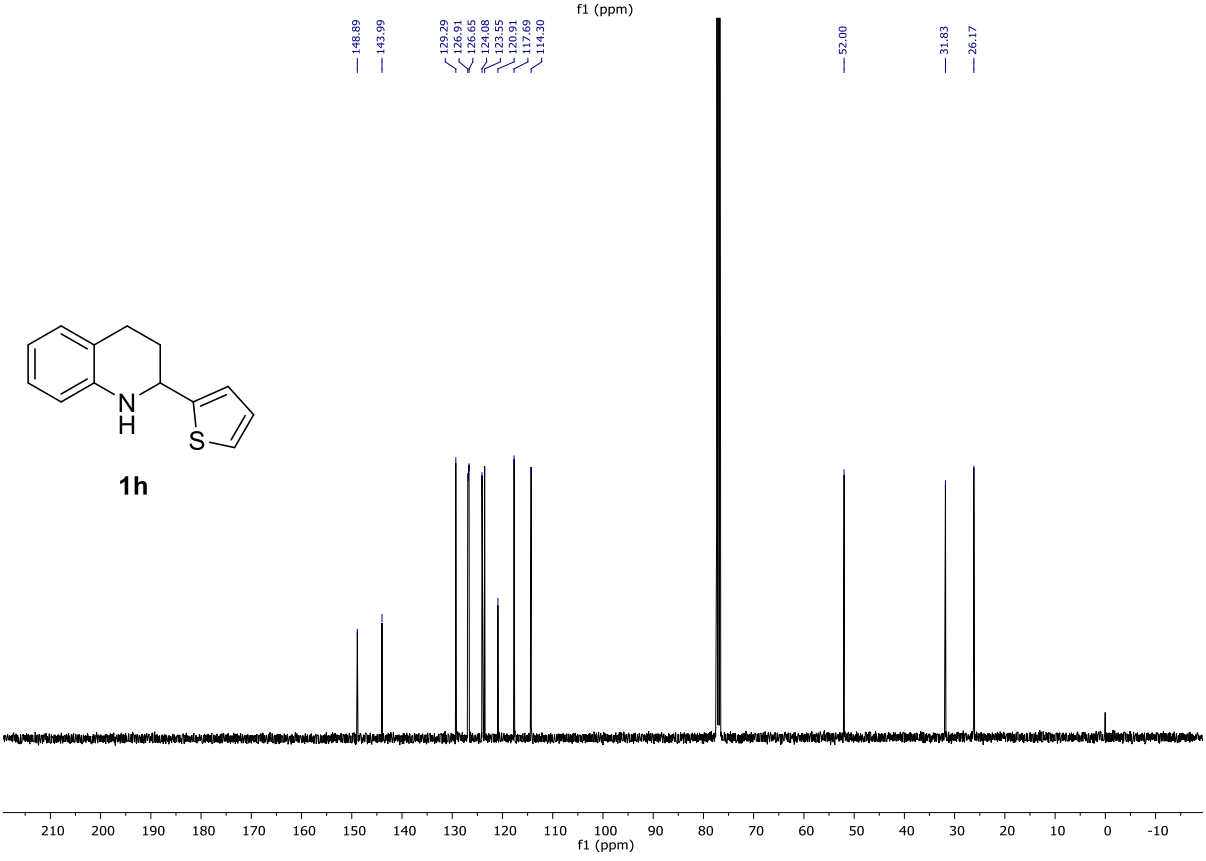
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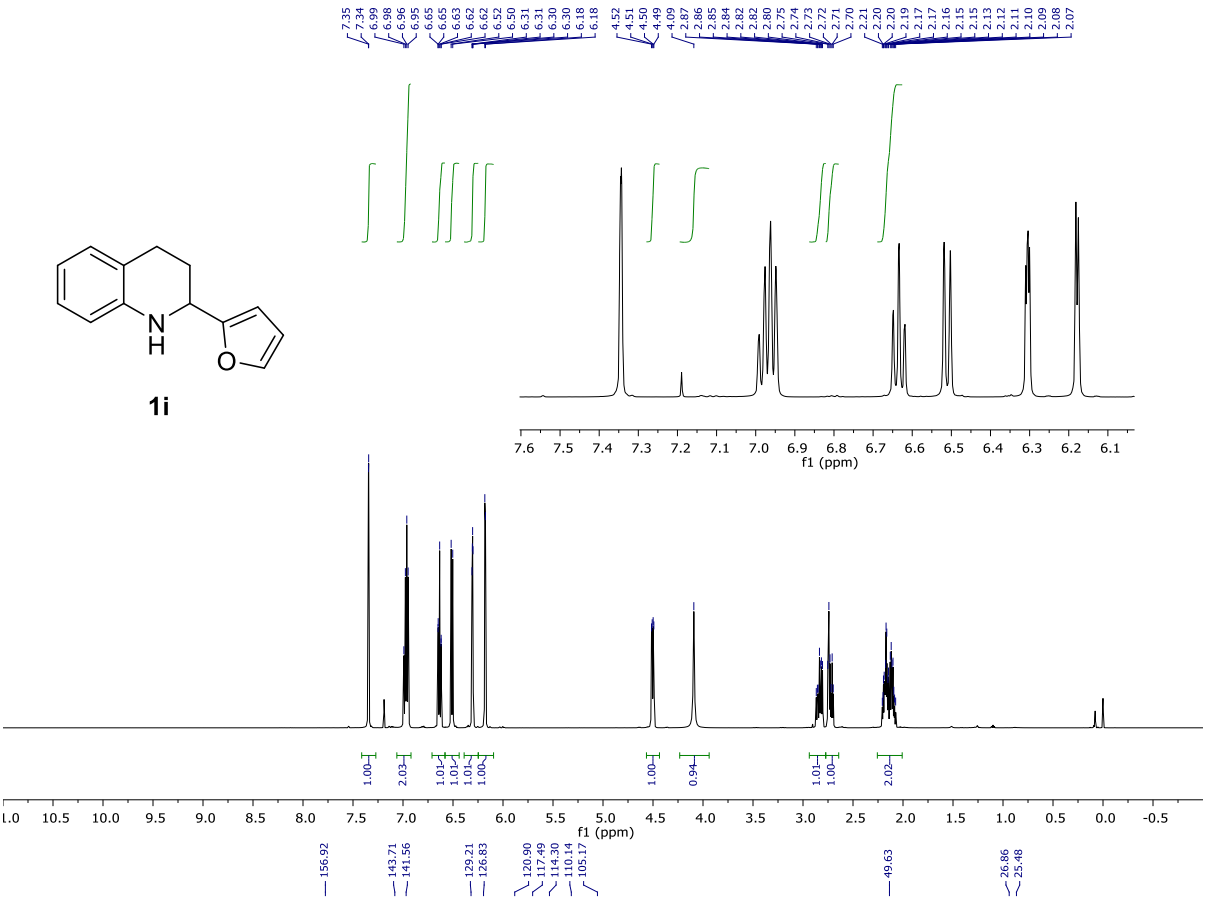
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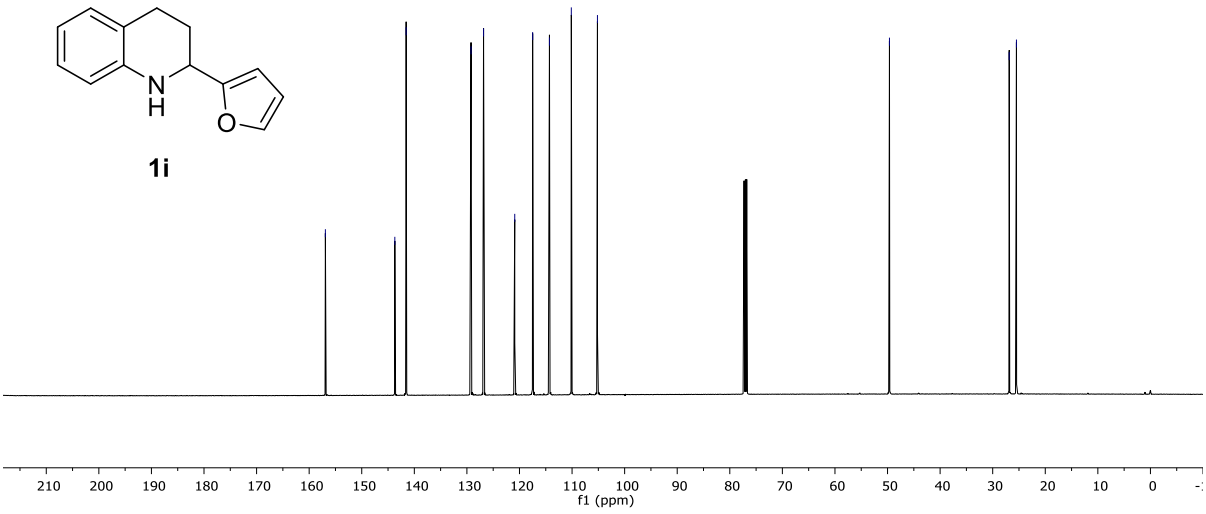
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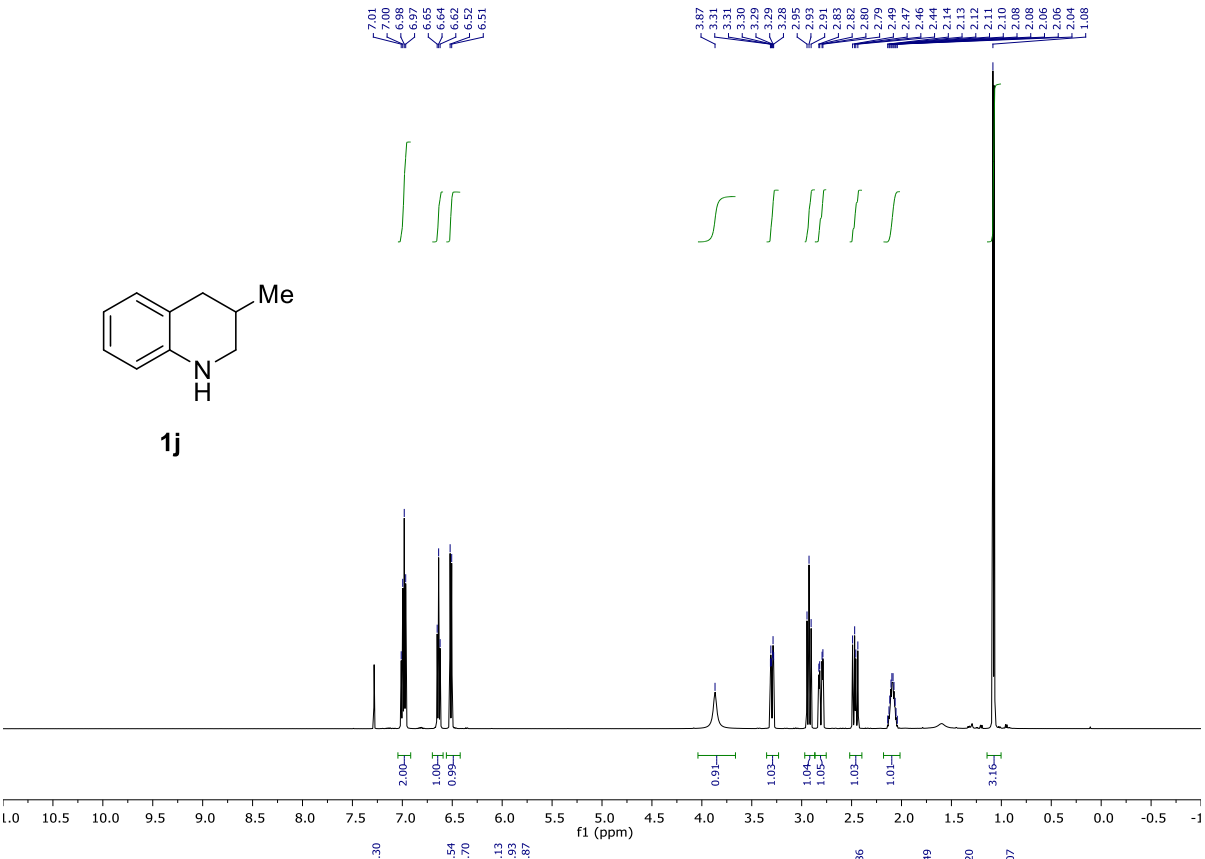
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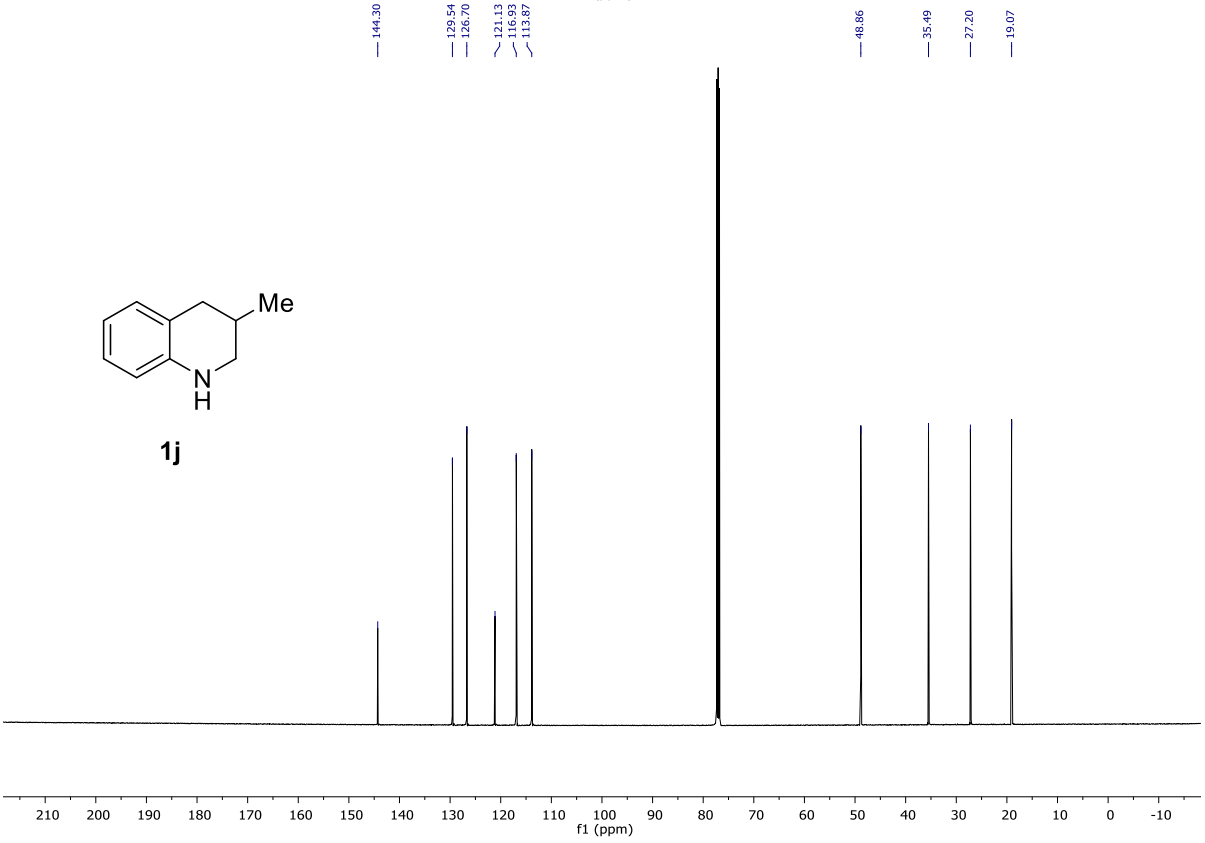
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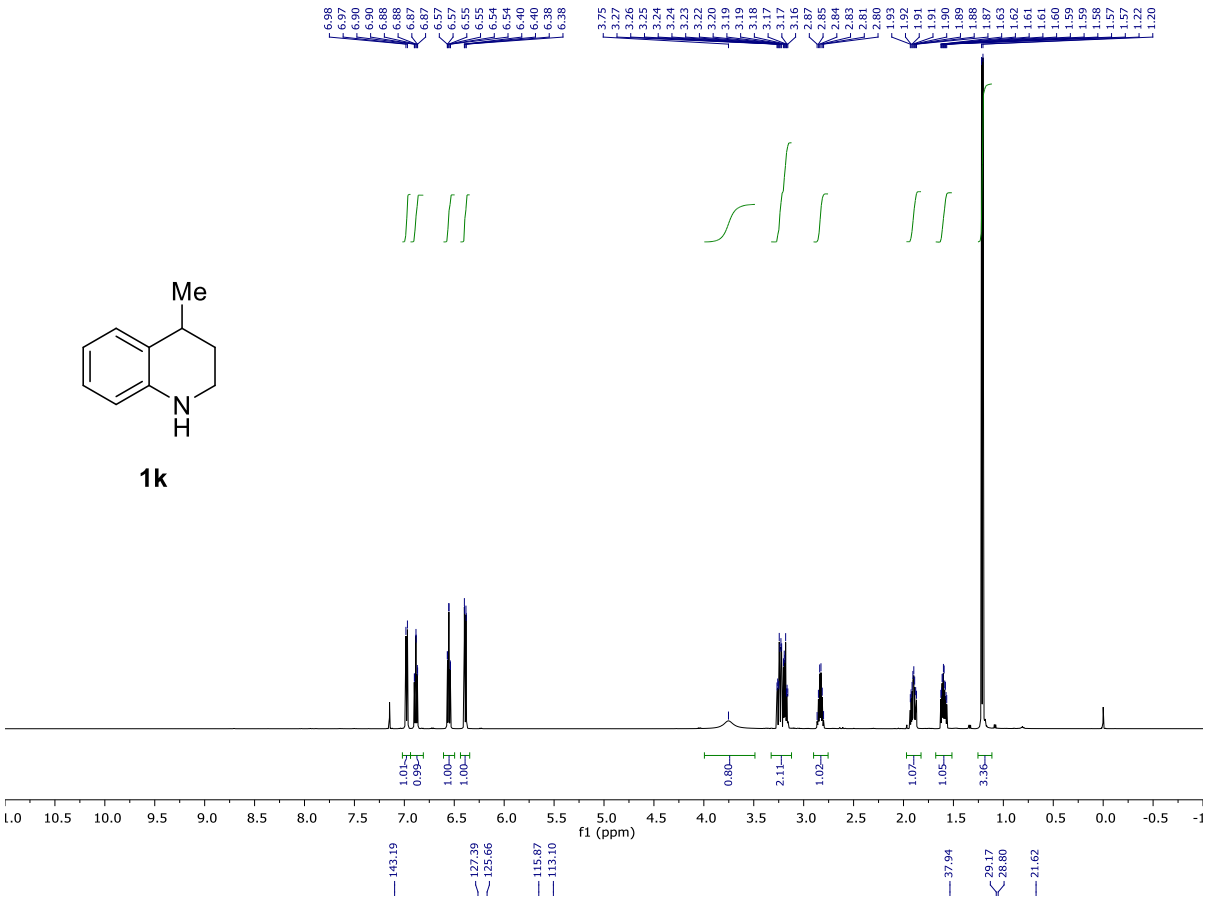
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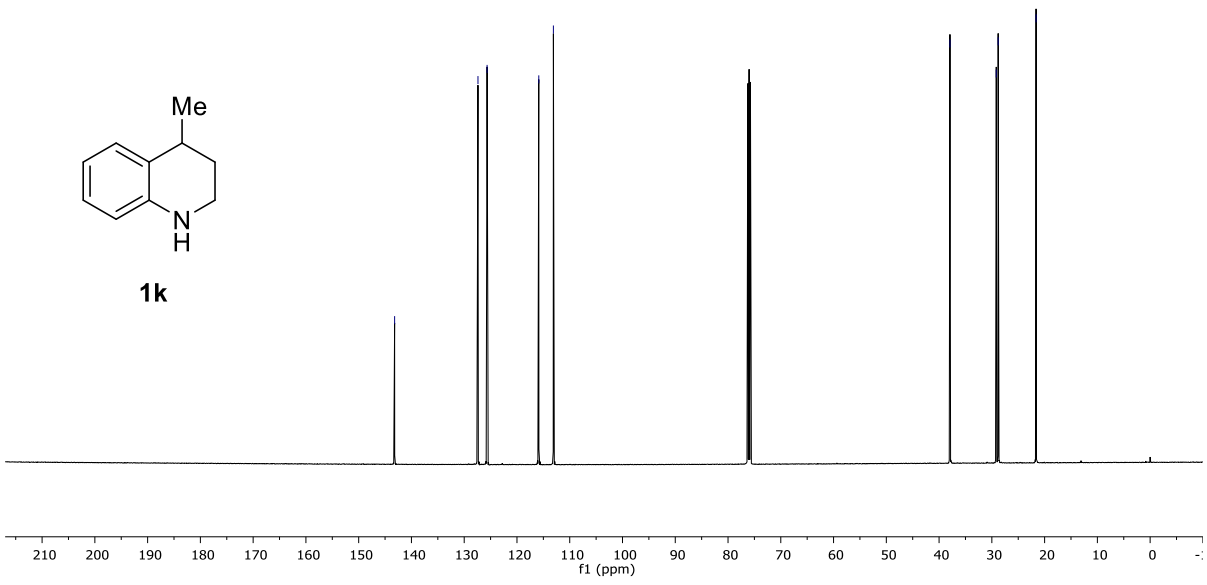
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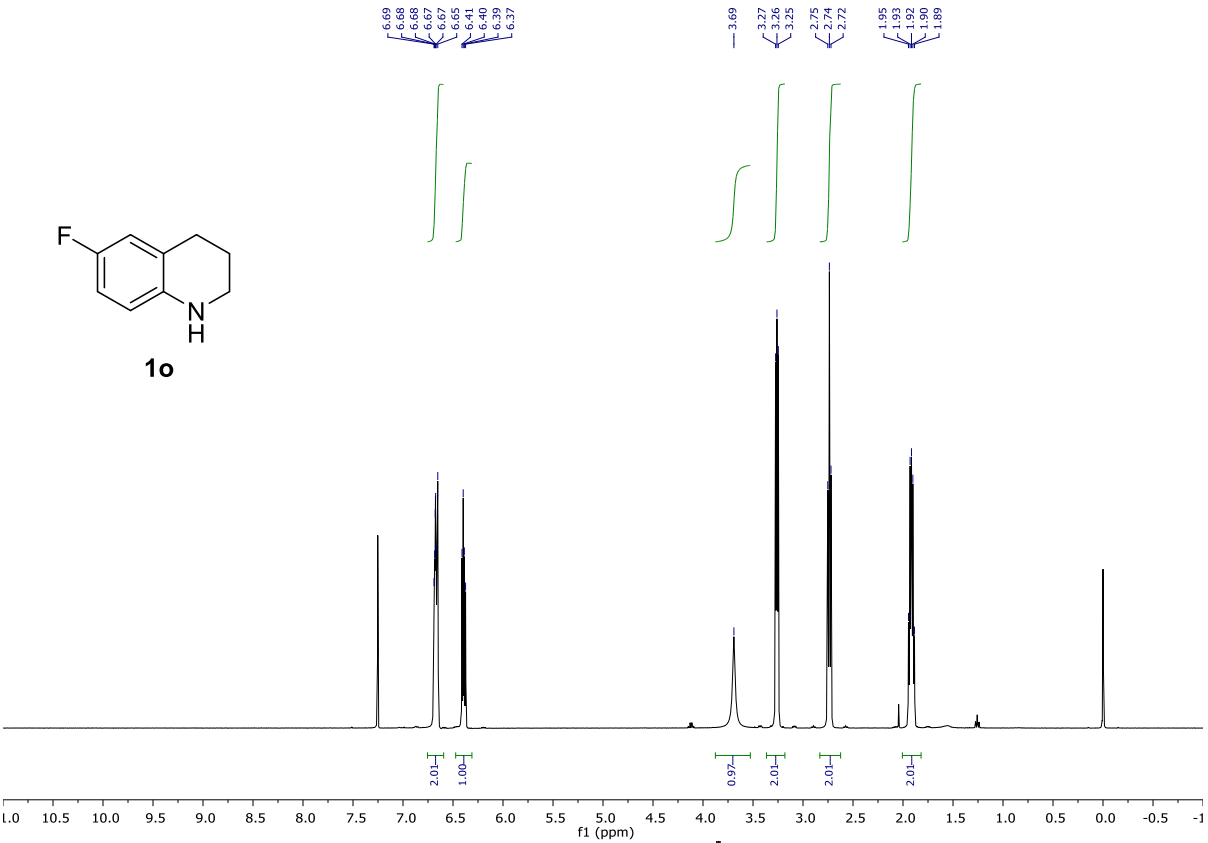
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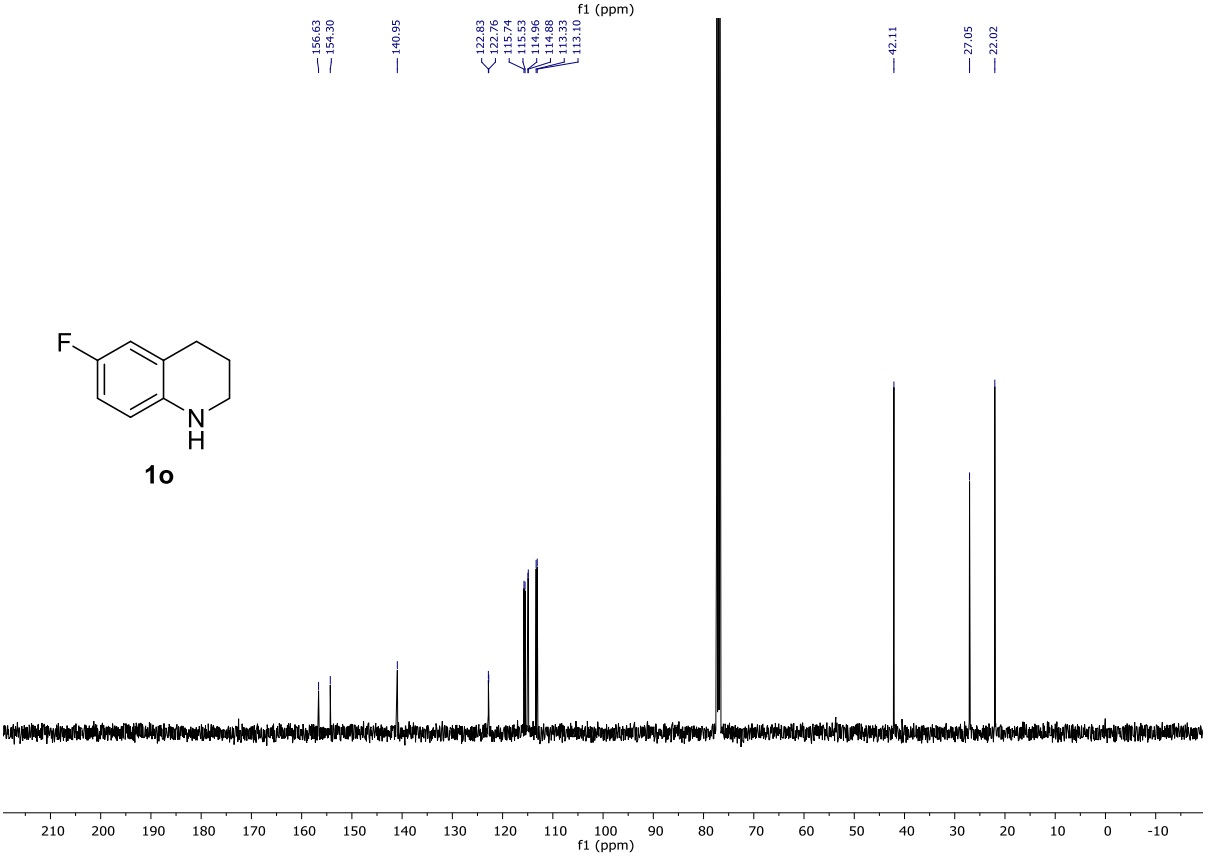
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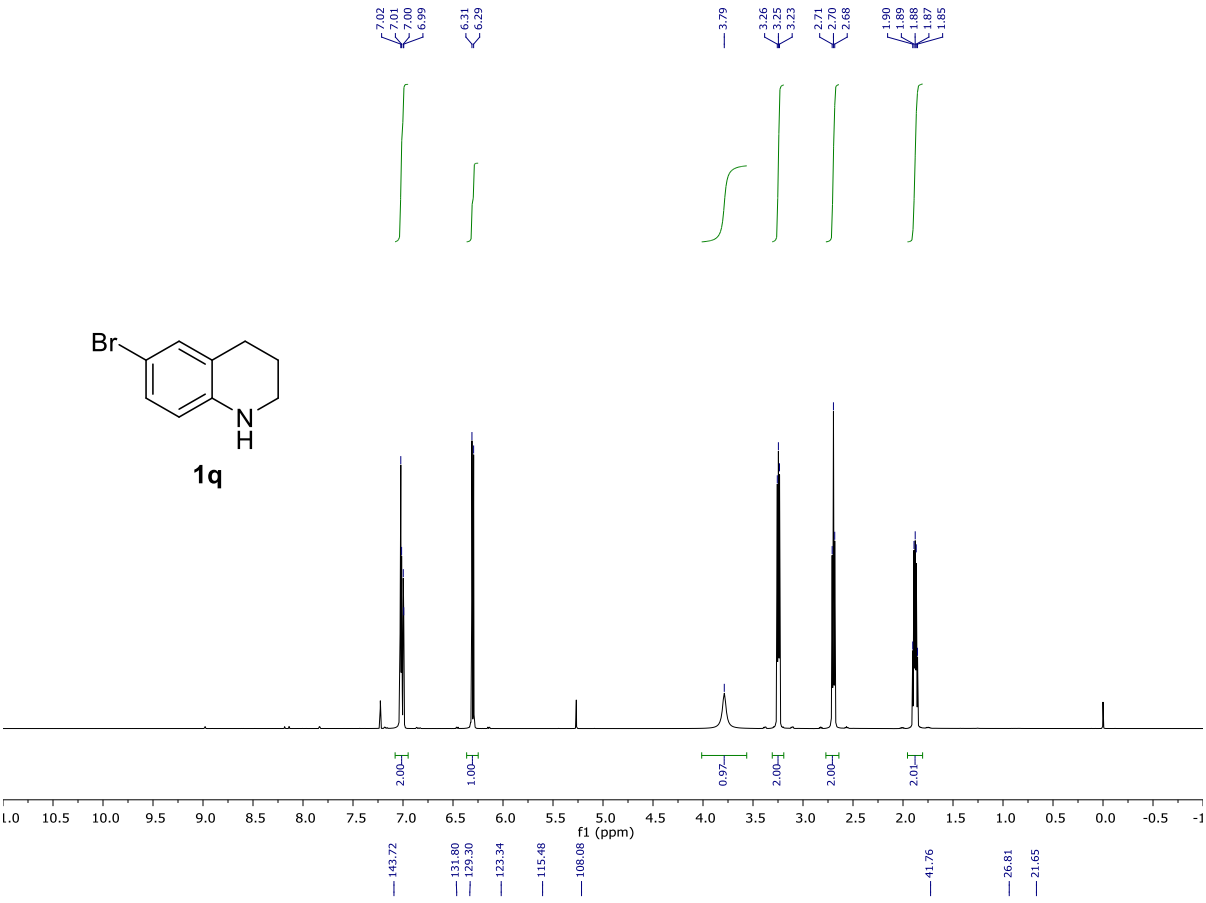
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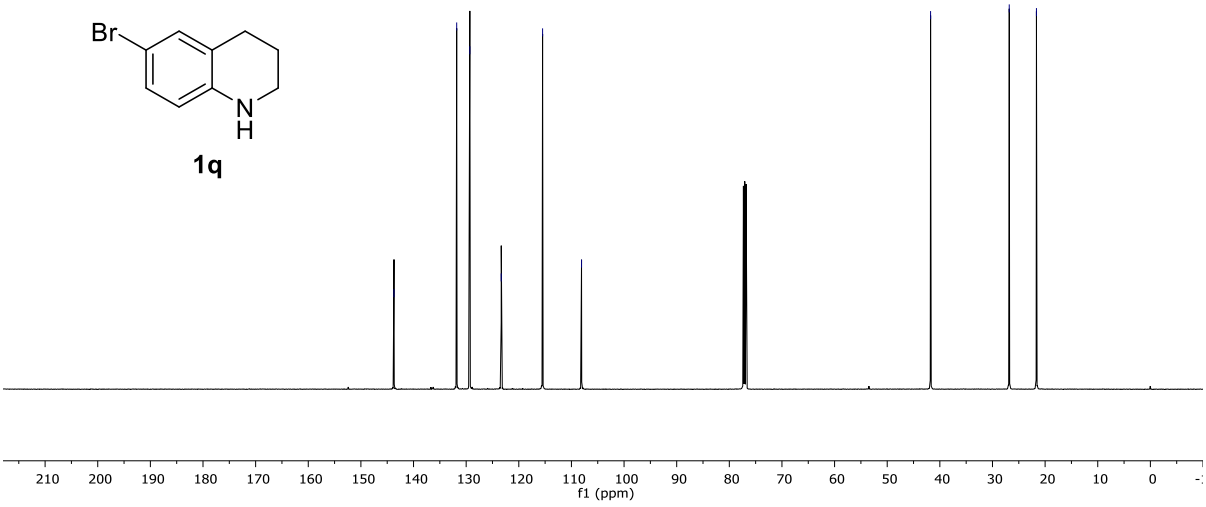
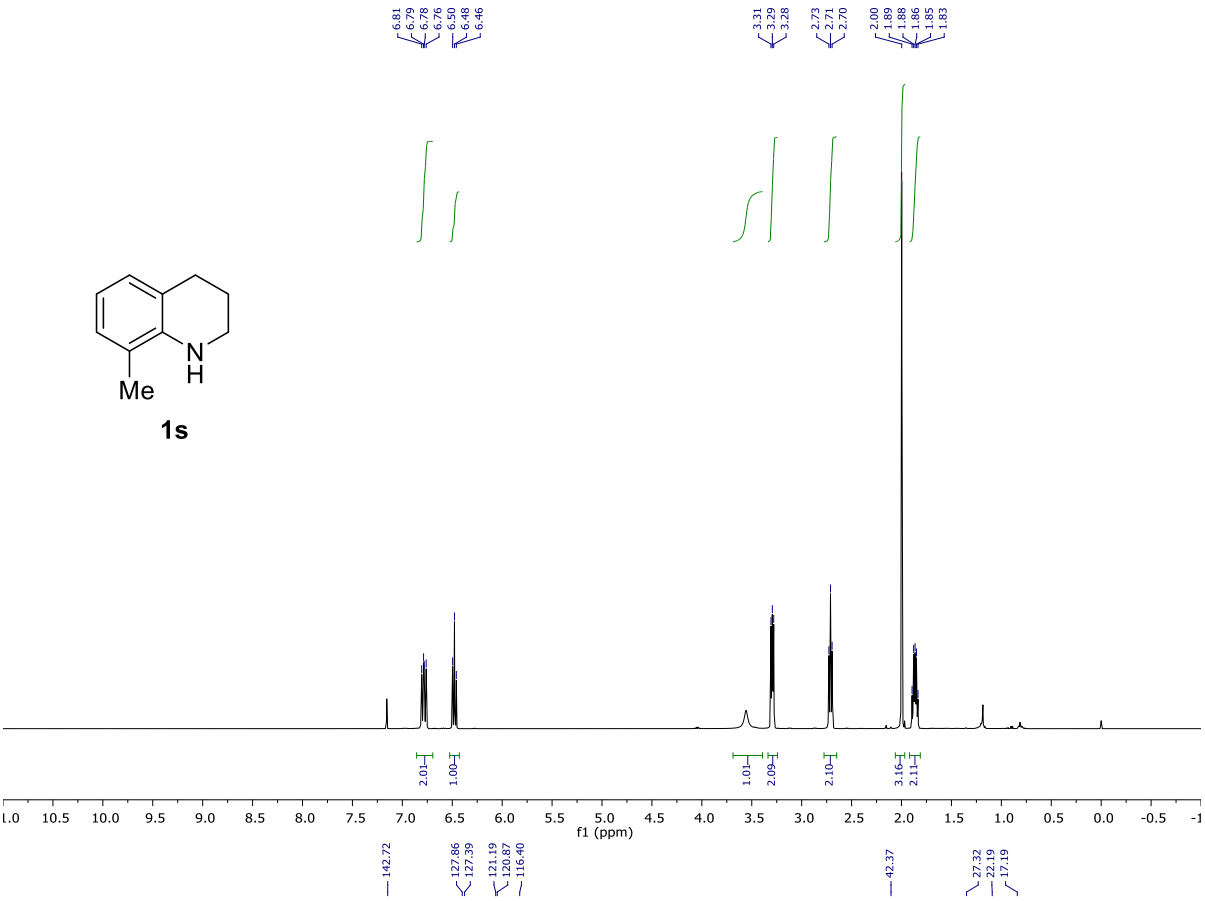
3.23
2.71
2.70
2.68
1.90
1.89
1.88
1.87
1.85
Br
N
H
1q
2.00
1.00
0.97
2.00
2.00
2.01
f1 (ppm)
143.72
131.80
129.30
123.34
115.48
108.08
41.76
26.81
21.65


Br
N
H
1q
f1 (ppm)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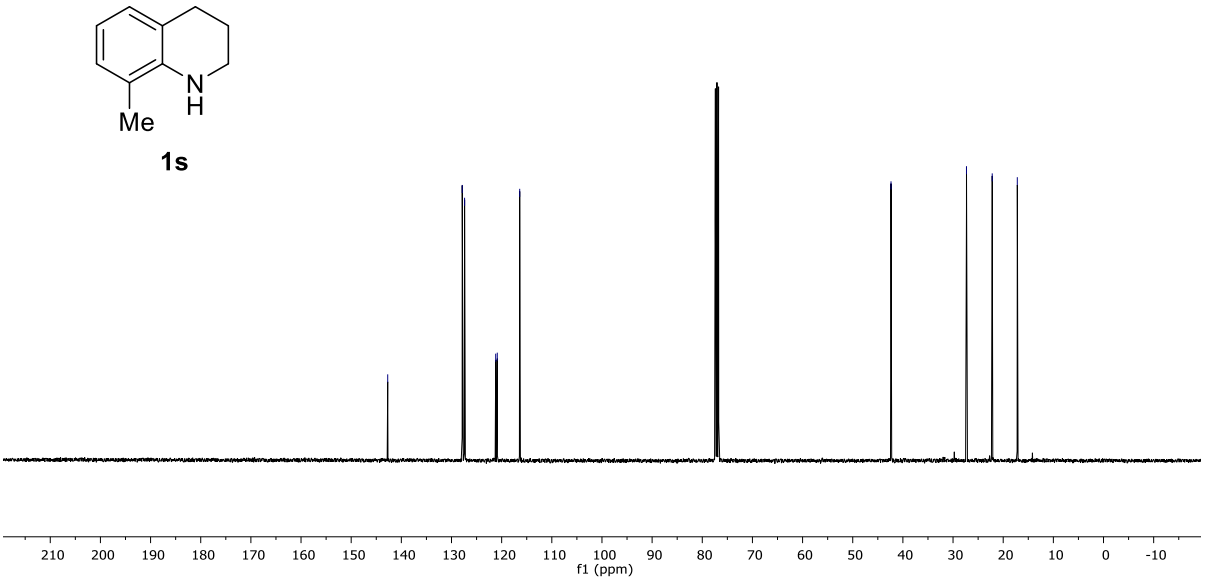
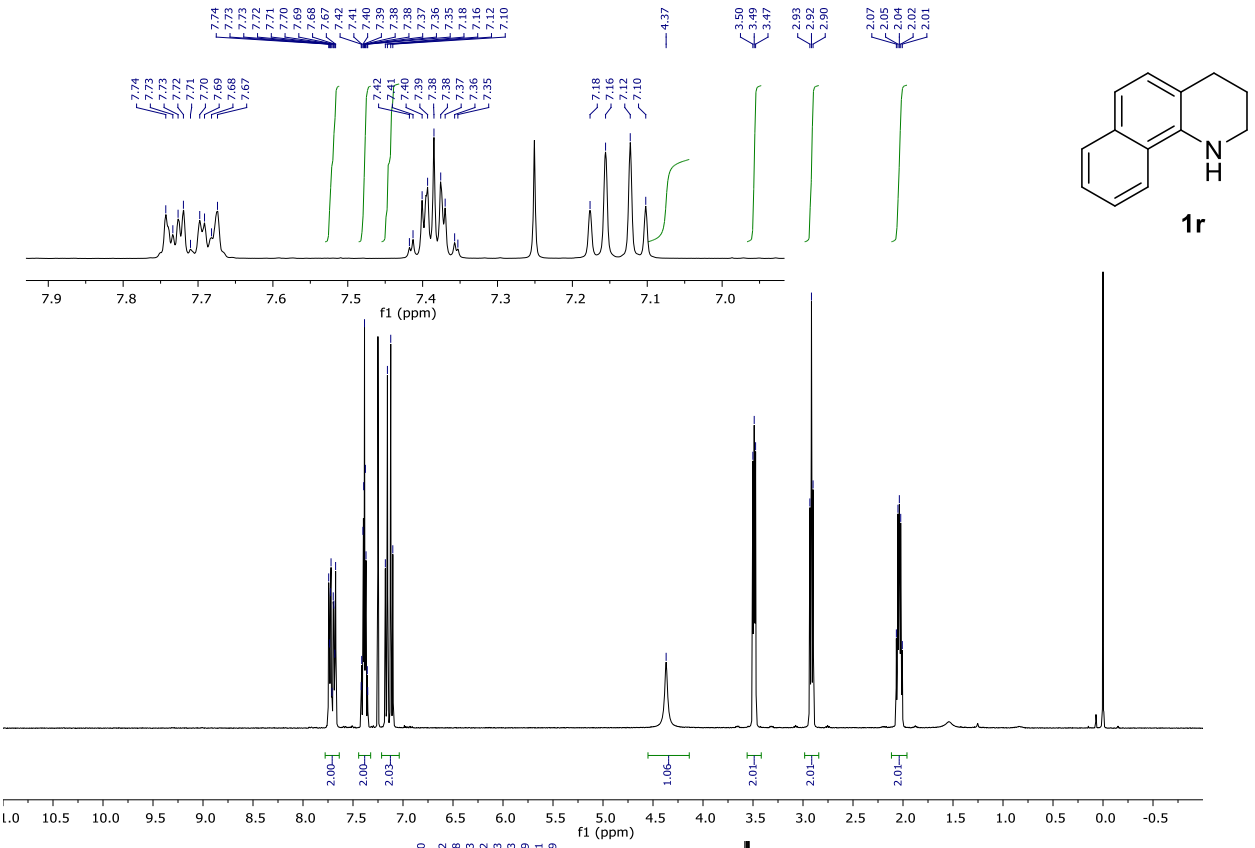
3.28
2.73
2.71
2.70
2.00
1.89
1.88
1.86
1.85
1.83
N
H
Me
1s
2.01
1.00
1.01
2.09
2.10
3.16
2.11
f1 (ppm)
142.72
127.86
127.39
121.19
120.87
116.40
42.37
27.32
22.19
17.19


N
H
Me
1s
f1 (ppm)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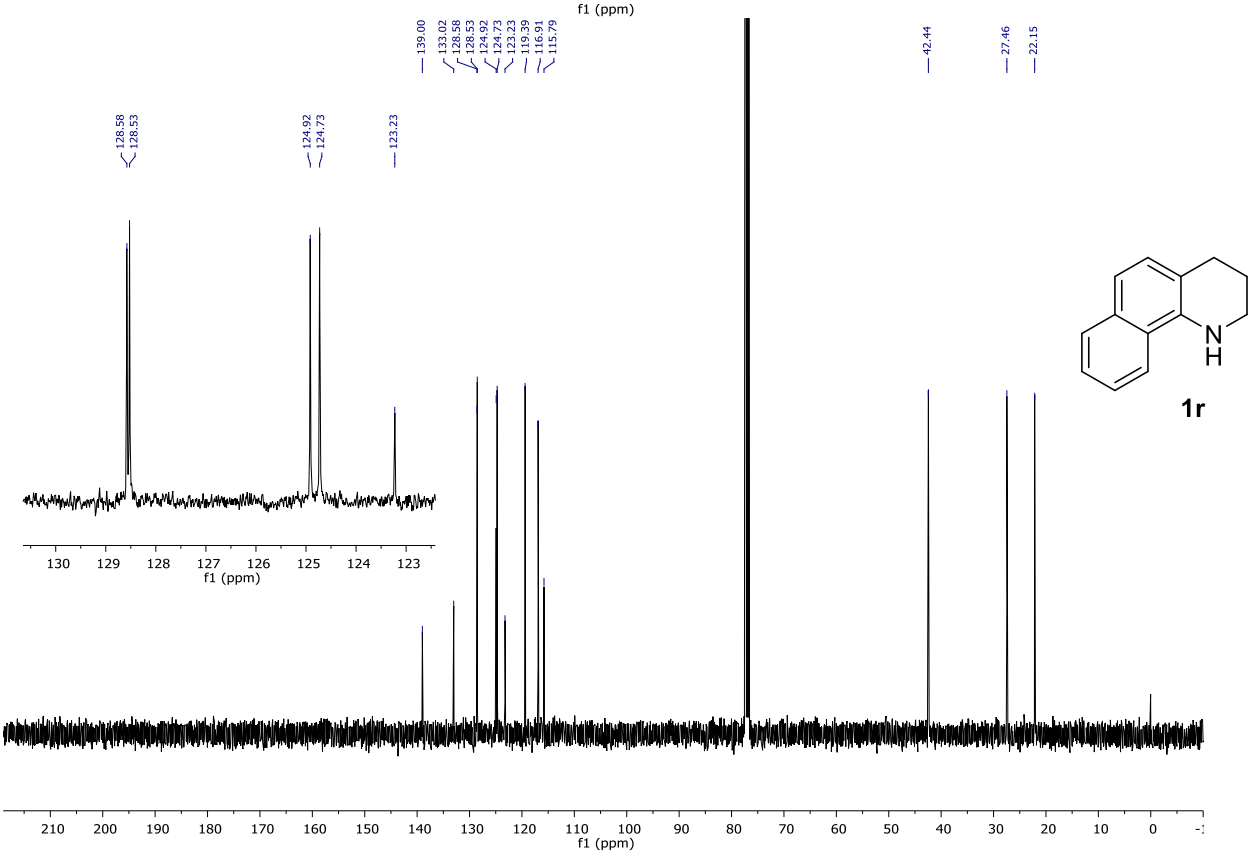
7.73
7.73
7.72
7.71
7.70
7.69
7.68
7.67
7.42
7.41
7.40
7.39
7.38
7.38
7.37
7.36
7.35
7.18
7.16
7.12
7.10
4.37
3.50
3.49
3.47
2.93
2.92
2.90
2.07
2.05
2.04
2.02
2.01
f1 (ppm)
2.00
2.00
2.03
1.06
2.01
2.01
2.01
f1 (ppm)

1r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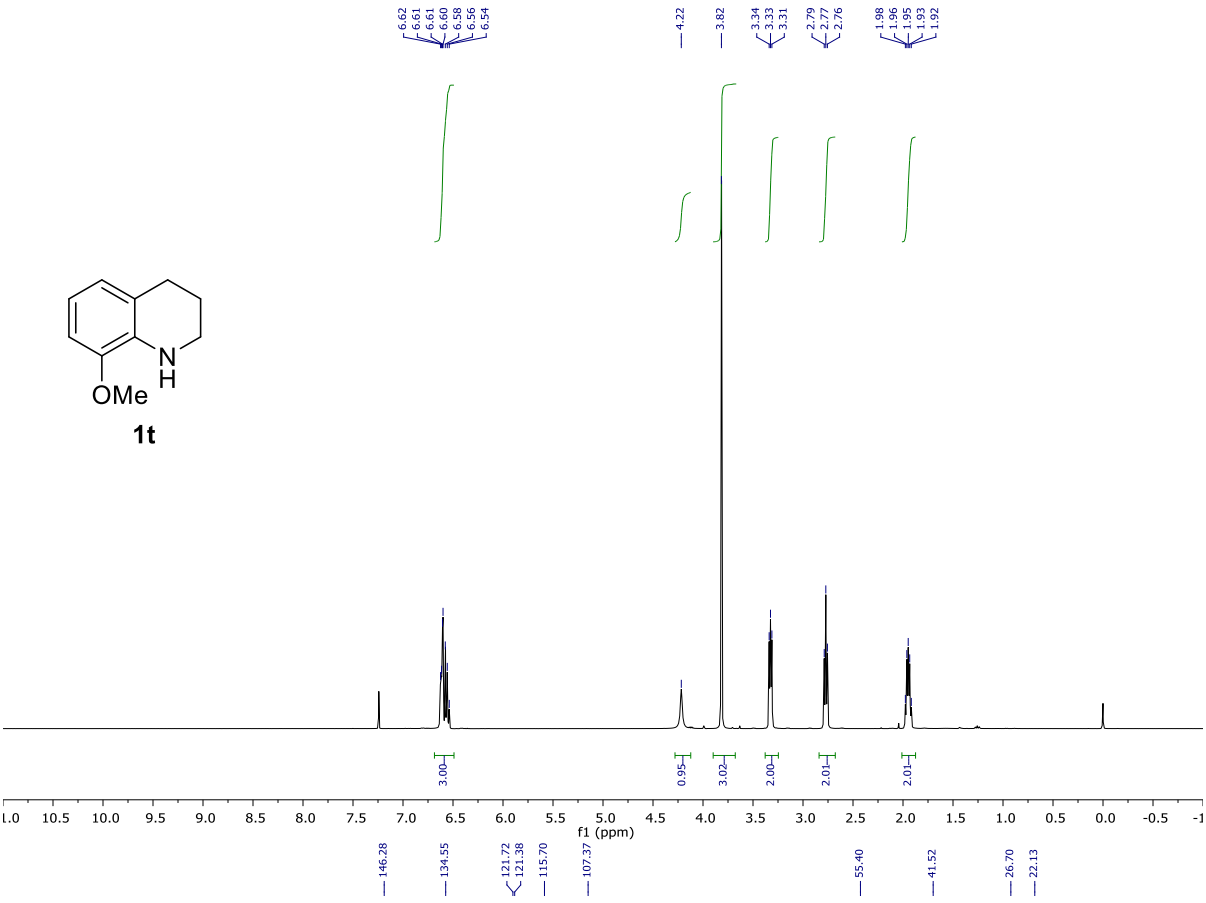
133.02
128.58
128.53
124.92
124.73
123.23
112.39
110.91
115.79
42.44
27.46
22.15
128.58
128.53
124.92
124.73
123.23
f1 (ppm)
f1 (ppm)

1r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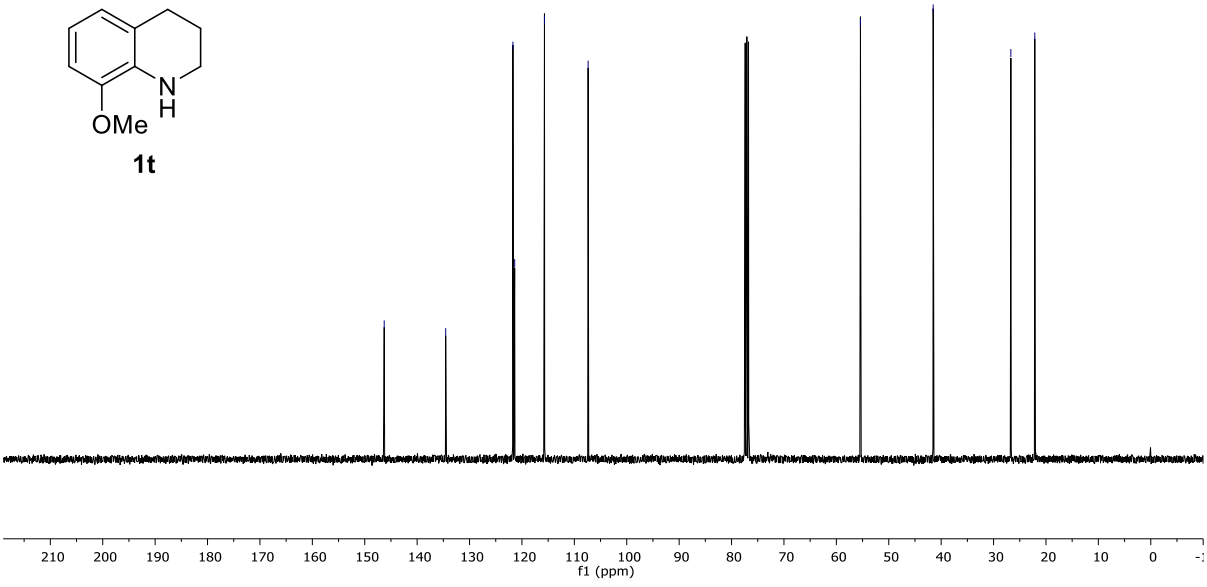
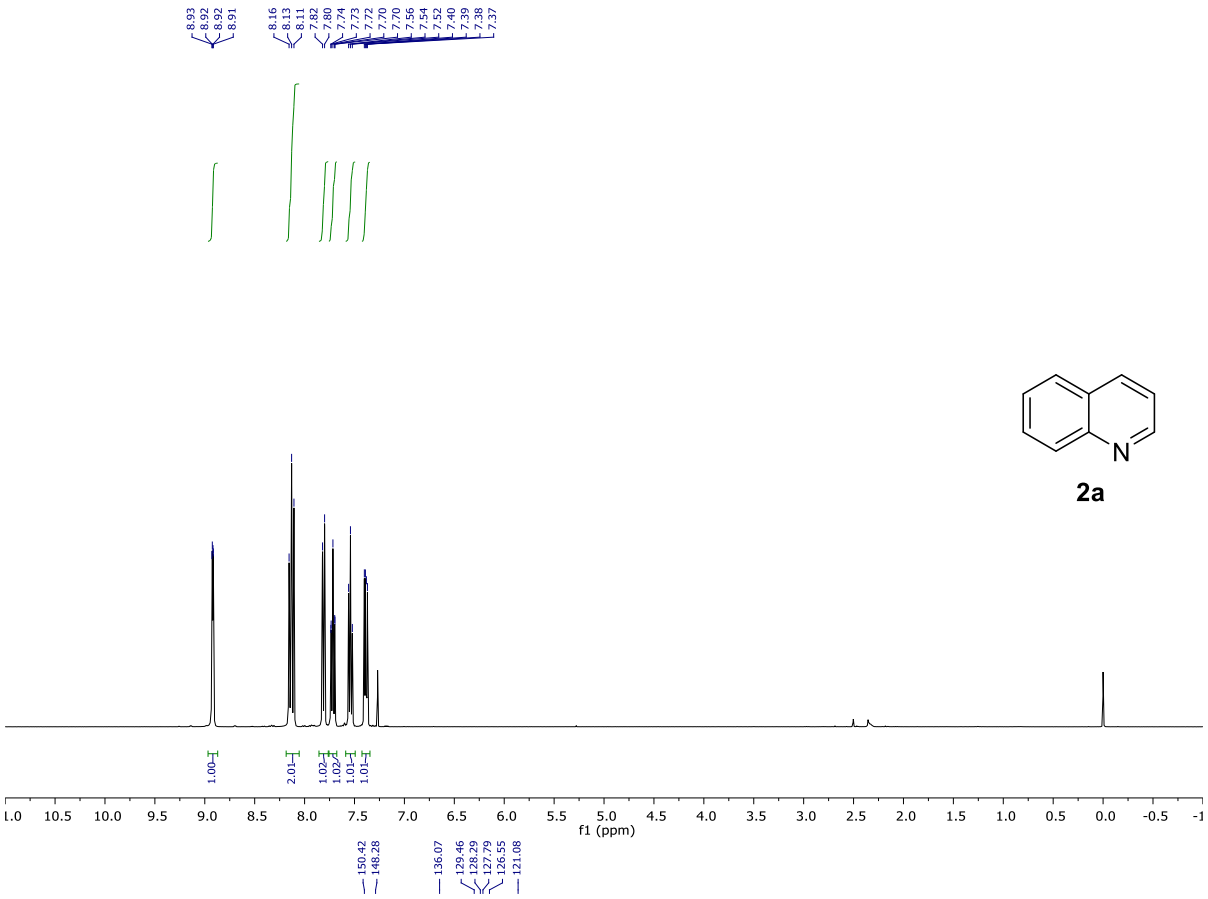
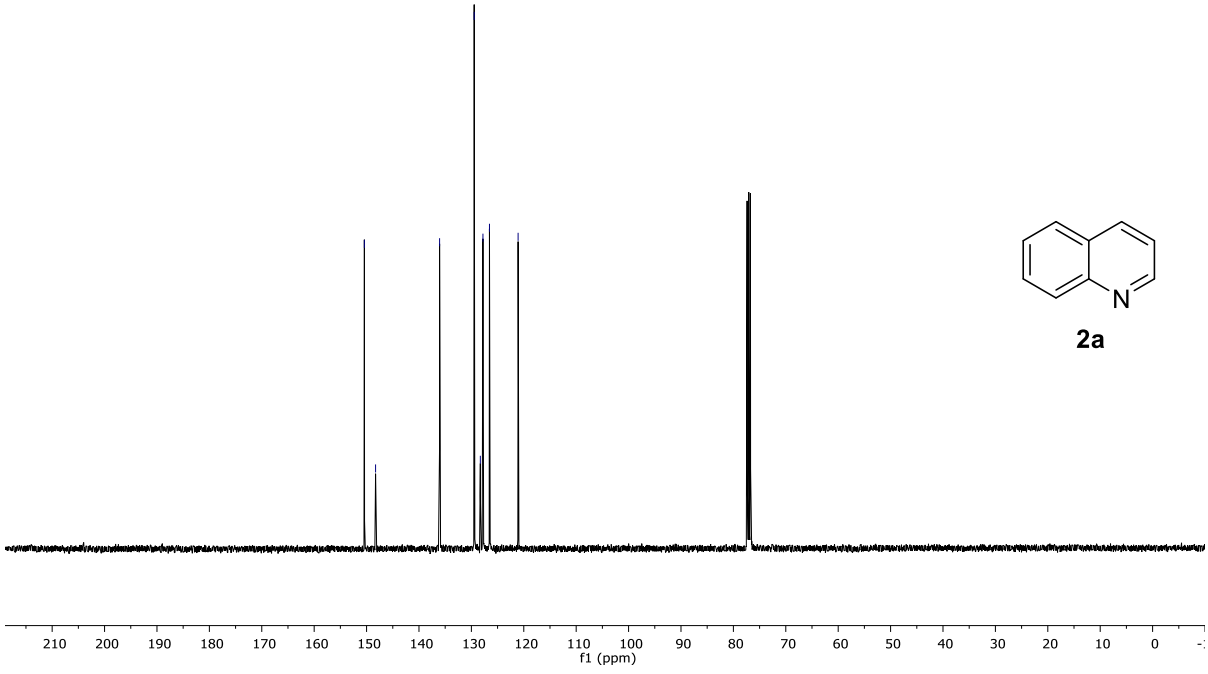
6.58
6.56
6.54
4.22
3.82
3.34
3.33
3.31
2.79
2.77
2.76
1.98
1.96
1.95
1.93
1.92
N
H
OMe
1t
3.00
0.95
3.02
2.00
2.01
2.01
f1 (ppm)
146.28
134.55
121.72
121.38
115.70
107.37
55.40
41.52
26.70
22.13

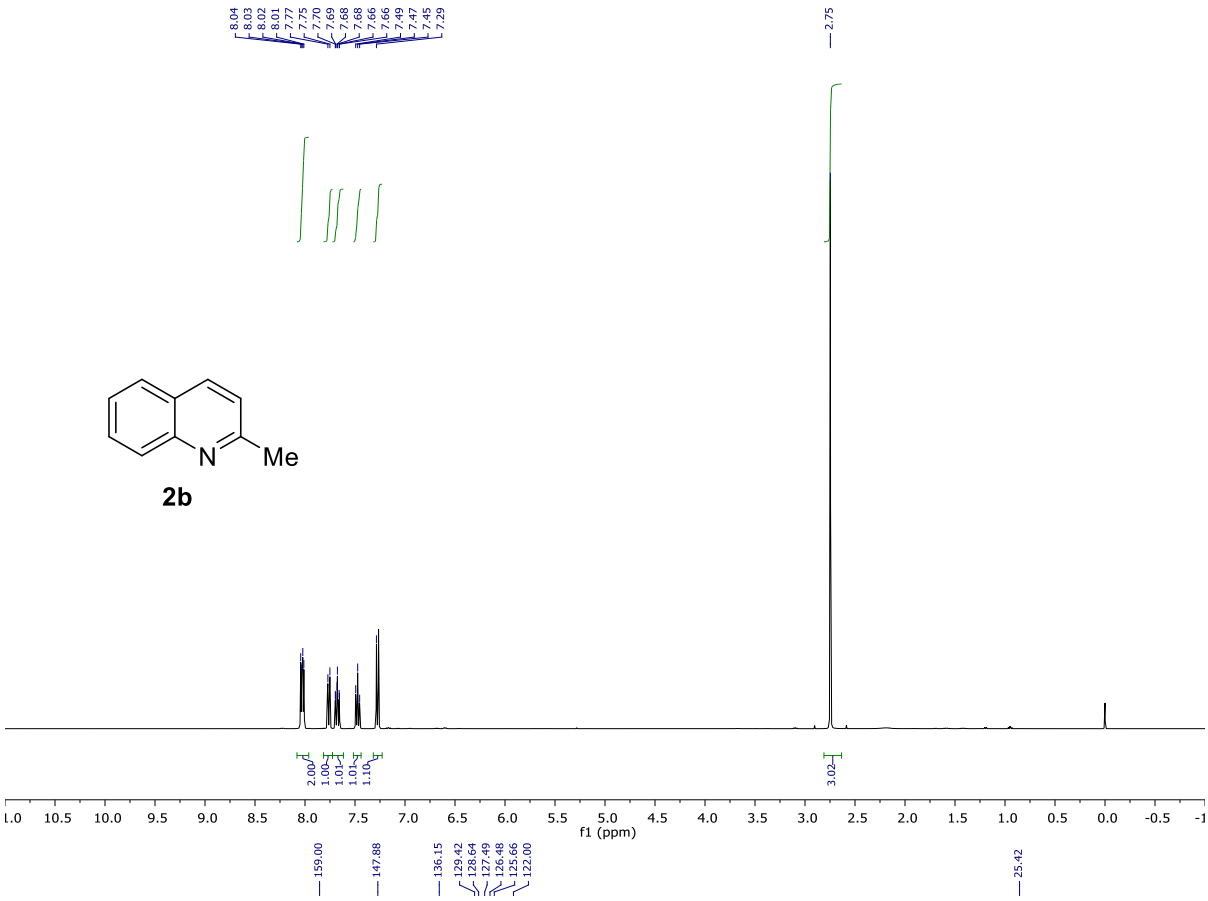

N
H
OMe
1t
f1 (ppm)

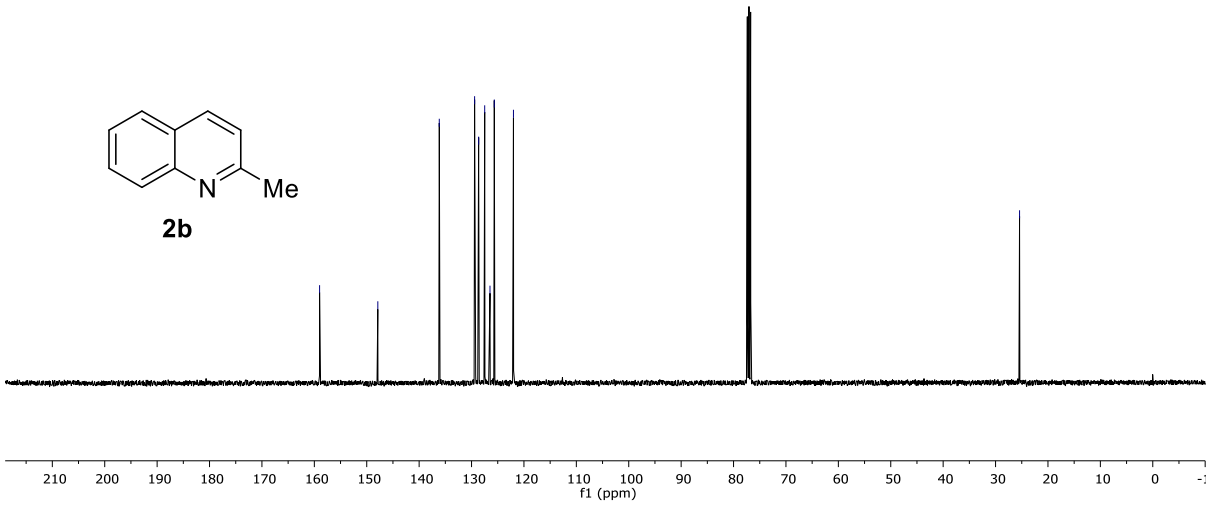

8.93
8.92
8.92
8.91
8.16
8.13
8.11
7.82
7.80
7.74
7.73
7.72
7.70
7.70
7.56
7.54
7.52
7.40
7.39
7.38
7.37
1.00
2.01
1.02
1.02
1.01
1.01
f1 (ppm)

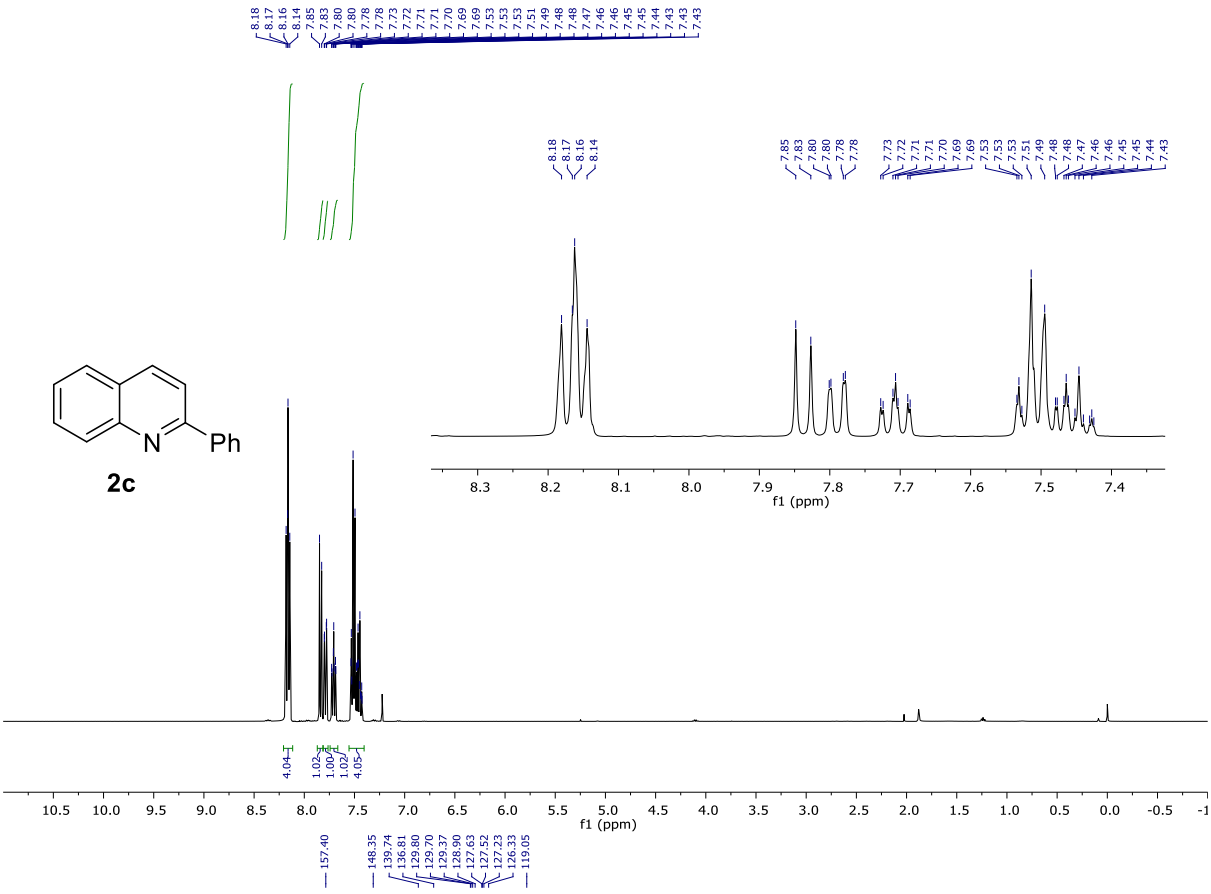
2a

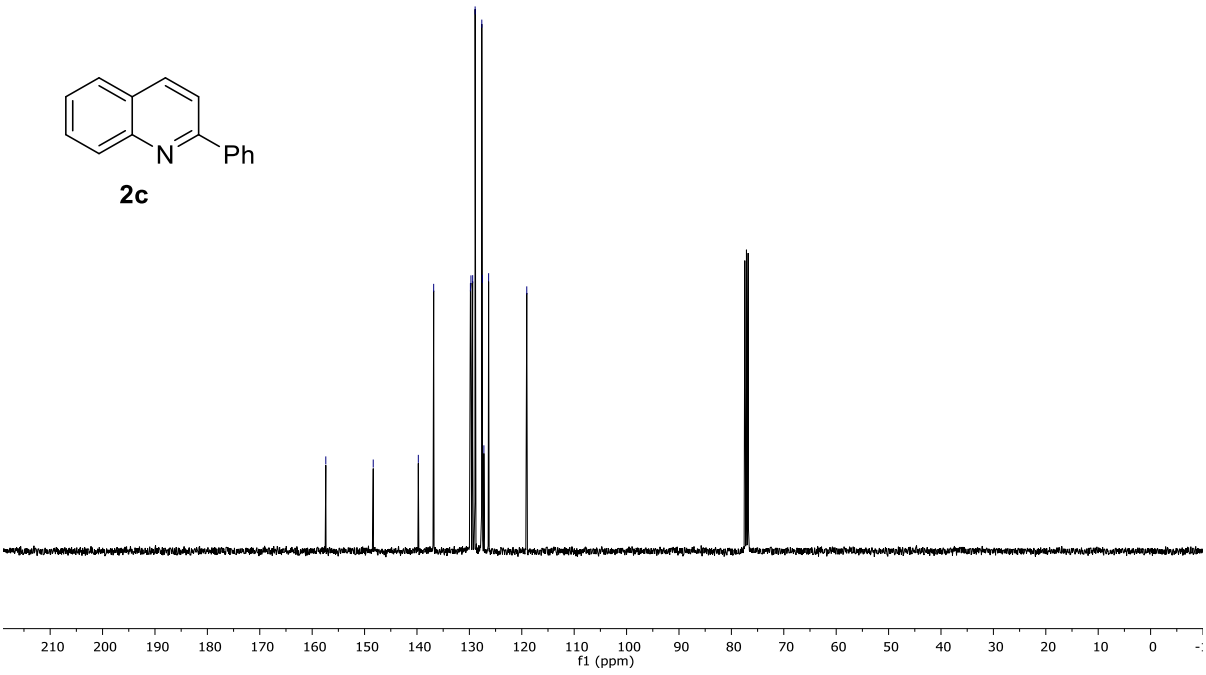

150.42
148.28
136.07
129.46
128.29
127.79
126.55
121.08
f1 (ppm)

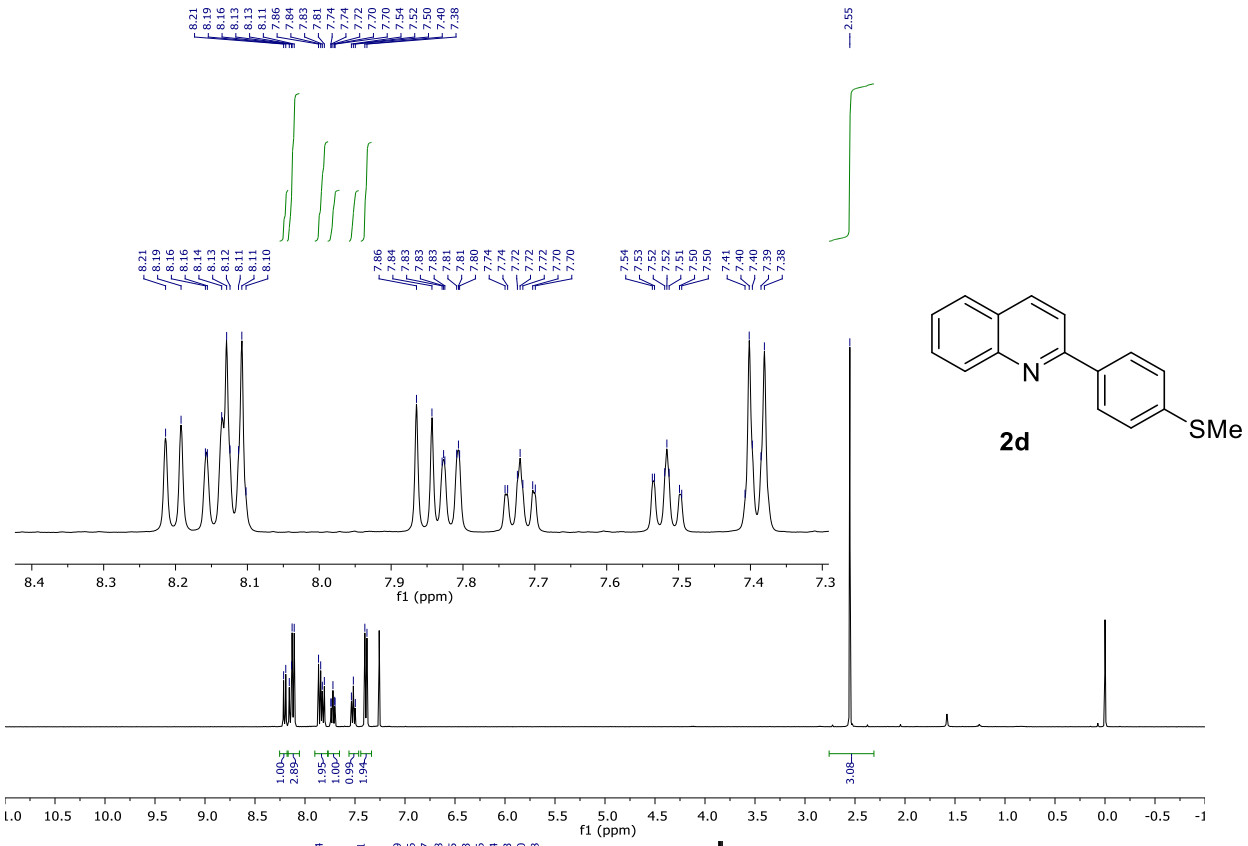
2a


8.04
8.03
8.02
8.01
7.77
7.75
7.70
7.69
7.68
7.68
7.66
7.66
7.49
7.47
7.45
7.29
2.75
N
Me
2b
2.00
1.00
1.01
1.01
1.10
3.02
f1 (ppm)


159.00
147.88
136.15
129.42
128.64
127.49
126.48
125.66
122.00
25.42
N
Me
2b
f1 (ppm)


8.18 8.17 8.16 8.14 7.85 7.83 7.80 7.80 7.78 7.78 7.73 7.72 7.71 7.70 7.69 7.69 7.53 7.53 7.51 7.49 7.48 7.48 7.47 7.46 7.46 7.45 7.45 7.44 7.43 7.43
N
Ph
2c
f1 (ppm)
4.04 1.02 1.00 1.02 4.05
f1 (ppm)


157.40 148.35 139.74 136.81 129.80 129.70 129.37 128.90 127.63 127.52 127.23 126.33 119.05
N
Ph
2c
f1 (ppm)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8.19
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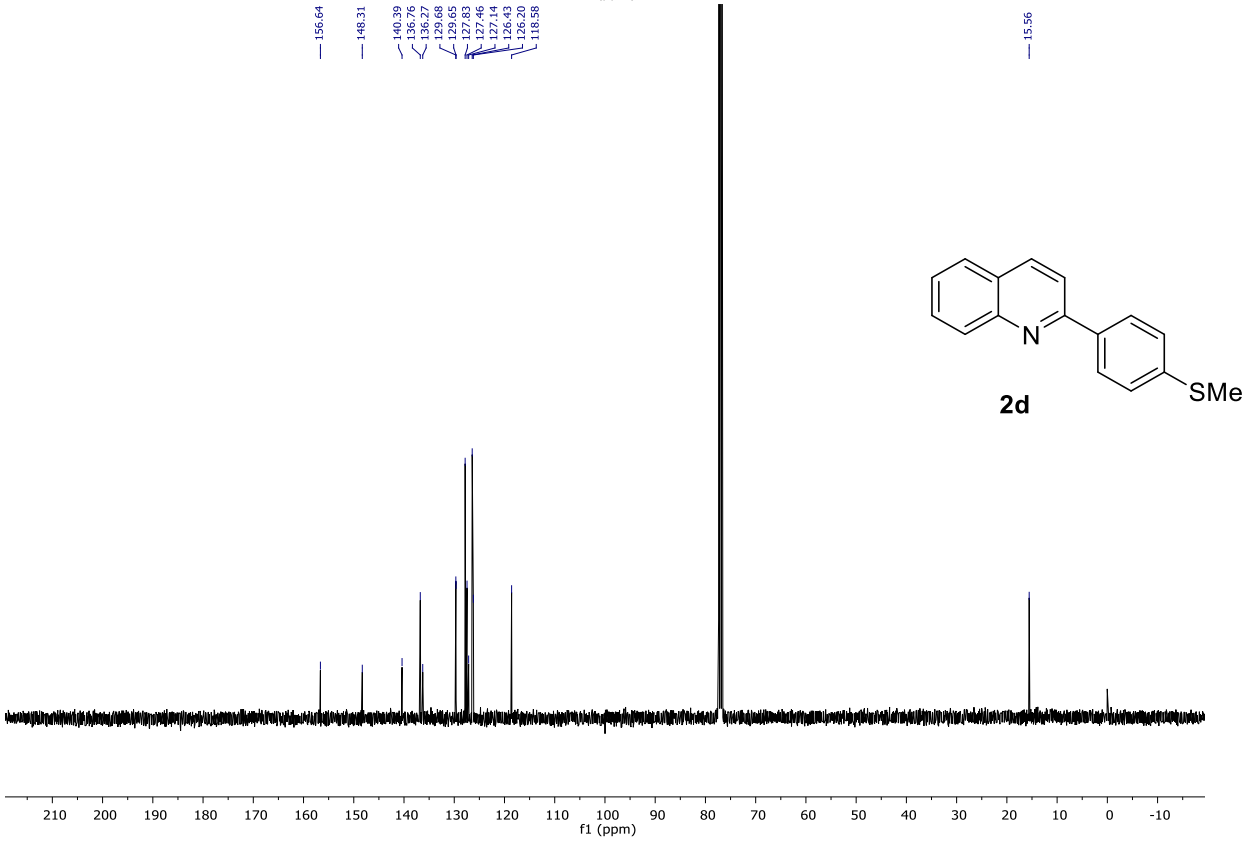
8.11
7.86
7.84
7.83
7.81
7.74
7.72
7.70
7.54
7.52
7.50
7.40
7.38
2.55
7.54
7.53
7.52
7.52
7.51
7.50
7.50
7.41
7.40
7.40
7.39
7.38
7.86
7.84
7.83
7.83
7.81
7.80
7.74
7.74
7.72
7.72
7.72
7.70
7.70
8.21
8.19
8.16
8.16
8.14
8.13
8.12
8.11
8.11
8.10
N
SMe
2d
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
f1 (ppm)
1.00
2.89
1.95
1.00
0.99
1.94
3.08
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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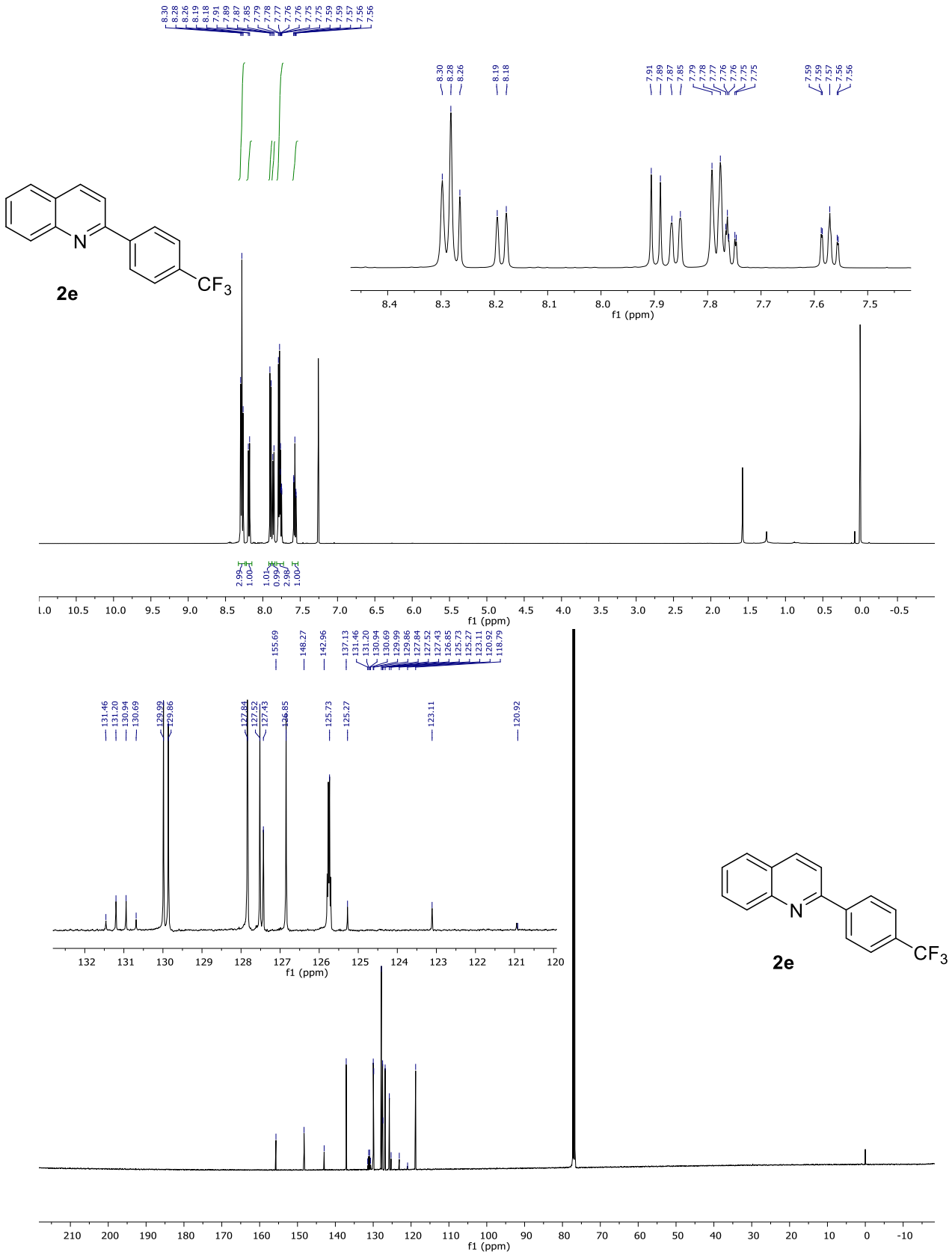
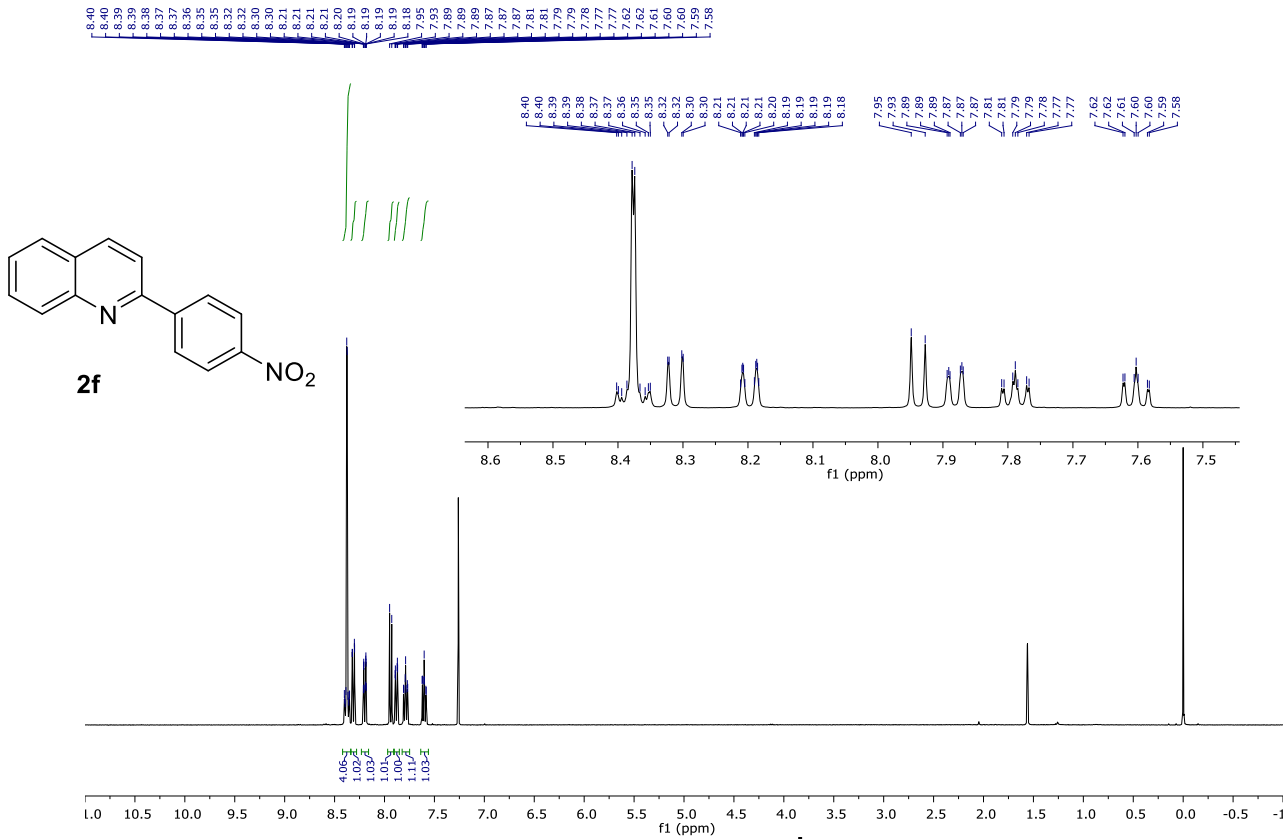
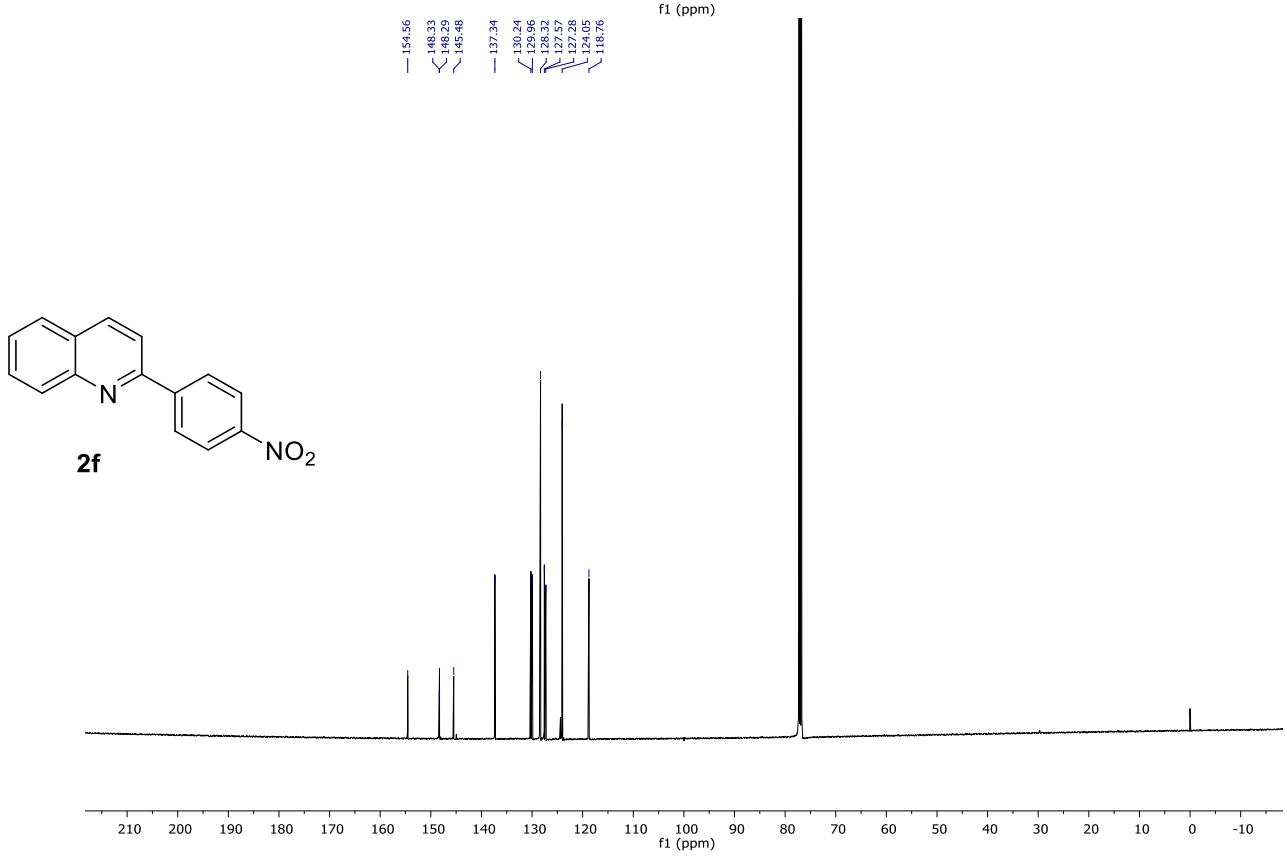
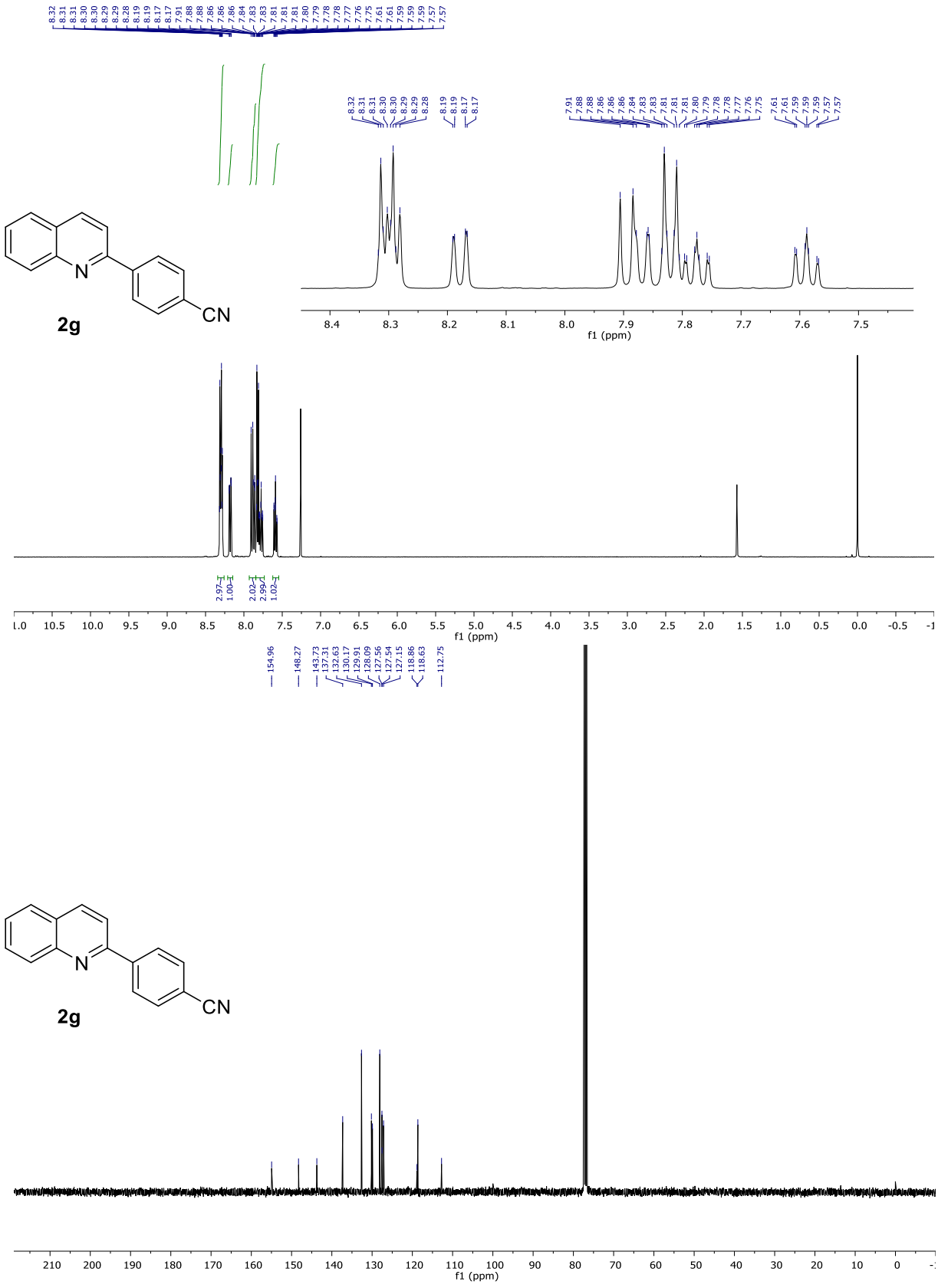
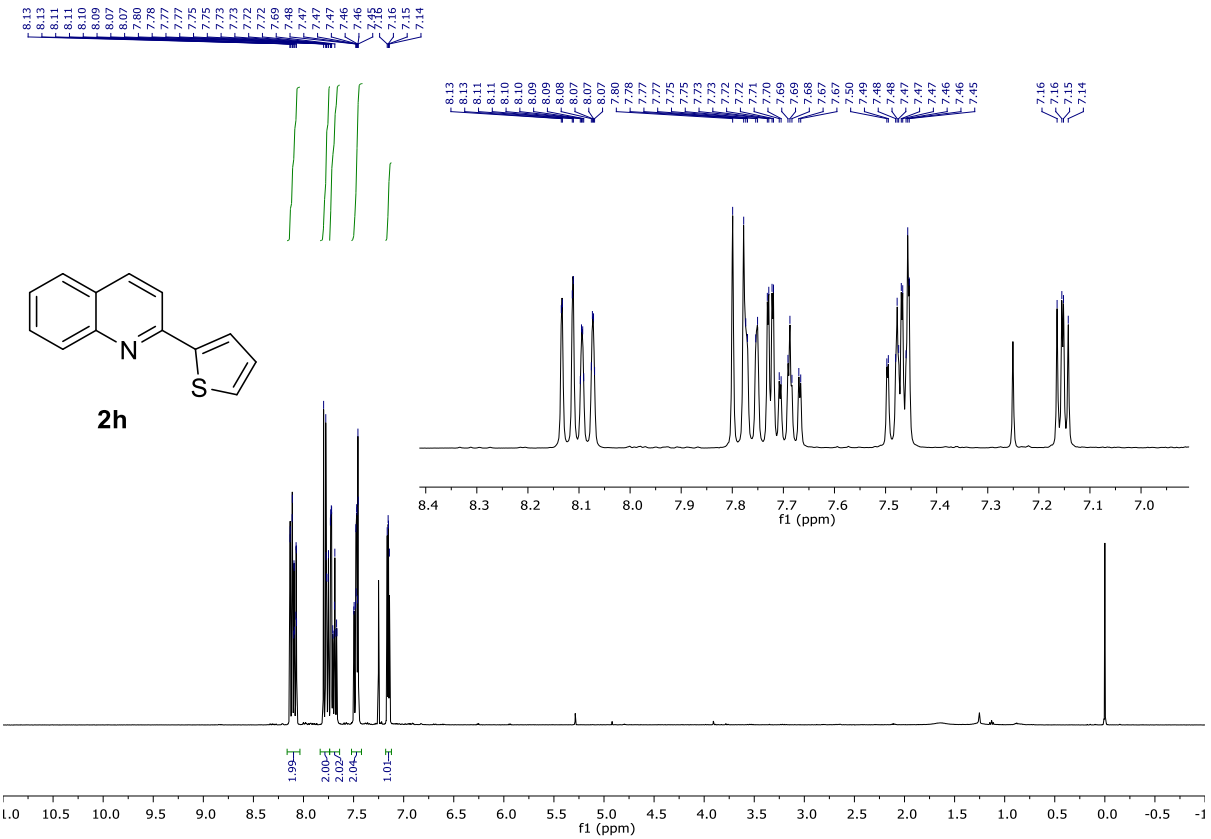
148.31
140.39
136.76
136.27
129.68
129.65
127.83
127.46
127.14
126.43
126.20
118.58
15.56
N
SMe
2d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

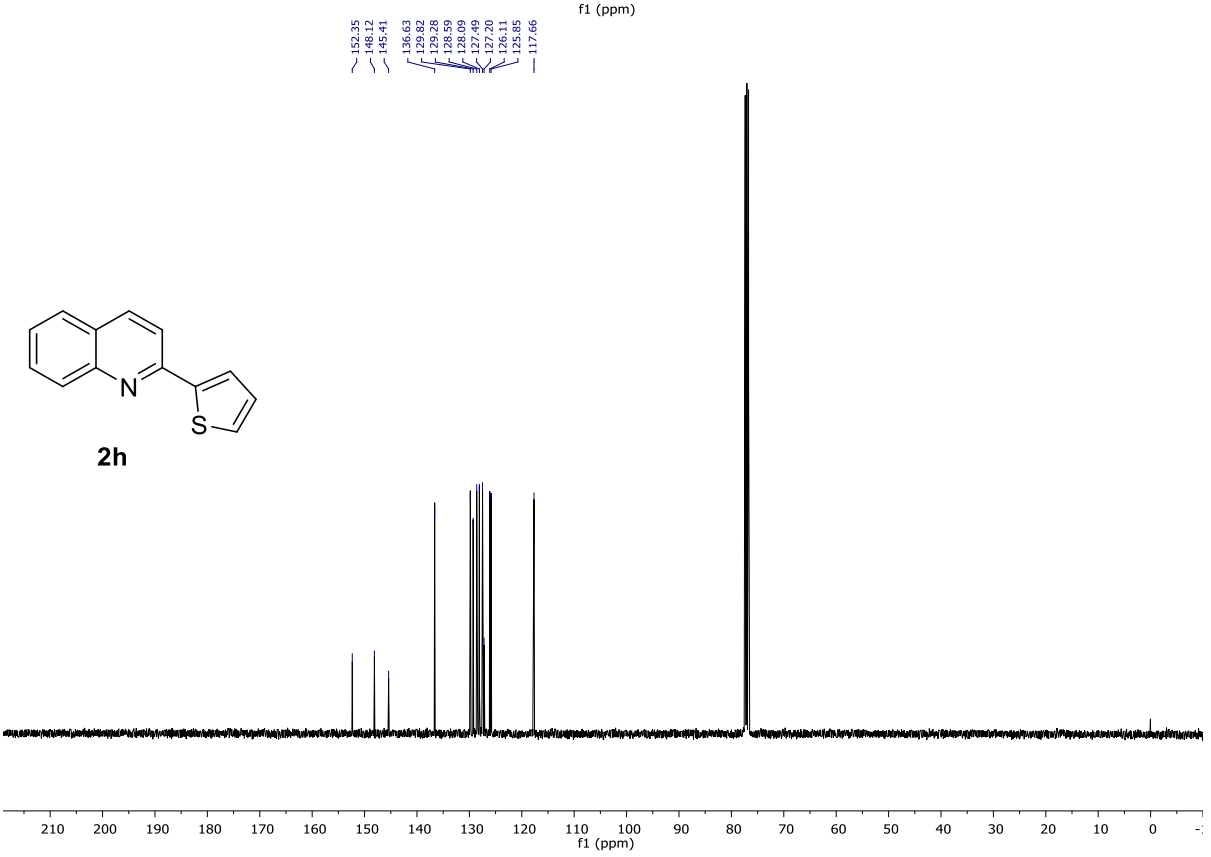

8.30
8.28
8.26
8.19
8.18
7.91
7.89
7.87
7.85
7.79
7.78
7.77
7.76
7.76
7.75
7.75
7.59
7.57
7.56
7.56
2e
CF3
f1 (ppm)
155.69
148.27
142.96
137.13
131.46
131.20
130.94
130.69
129.99
129.86
127.84
127.52
127.43
126.85
125.73
125.27
123.11
120.92
118.79
2e
CF3
f1 (ppm)

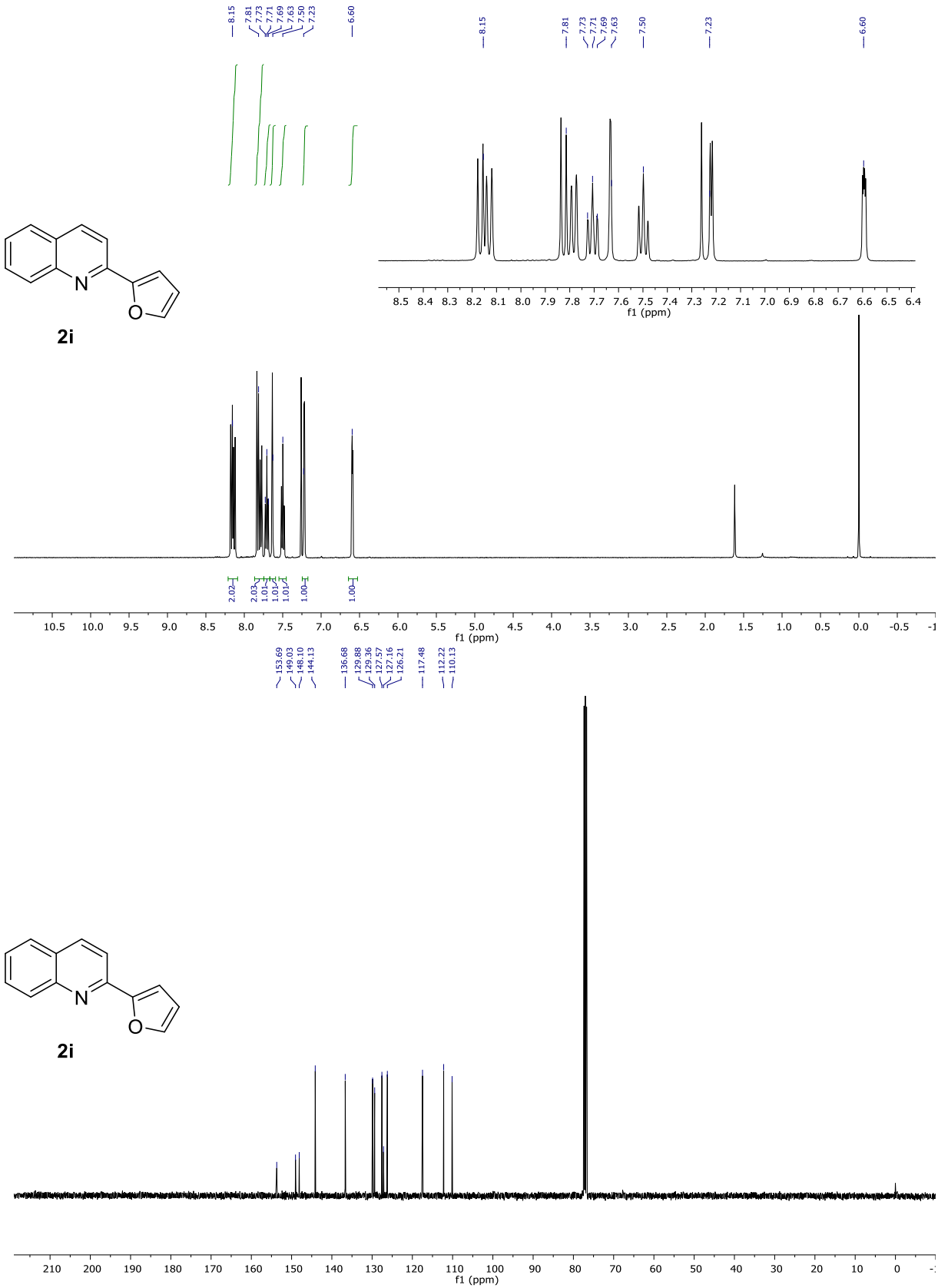

2f
f1 (ppm)

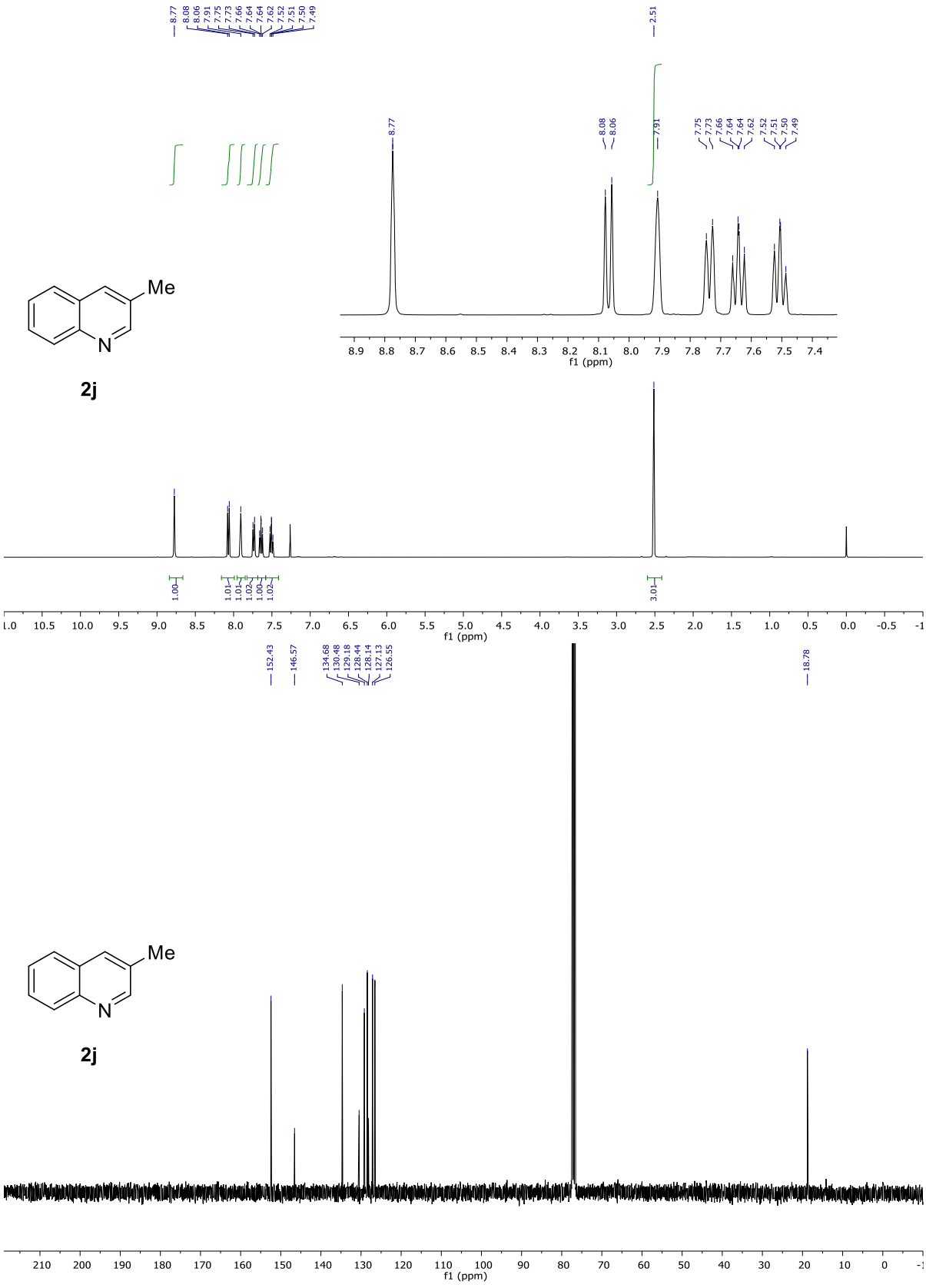

2f
f1 (ppm)


2g
f1 (ppm)
2g
f1 (ppm)


2h
f1 (ppm)


2h
f1 (ppm)


8.15
7.81
7.73
7.71
7.69
7.63
7.50
7.23
6.60
N
O
2i
f1 (ppm)
2.02
2.03
1.01
1.01
1.02
1.00
1.00
153.69
149.03
148.10
144.13
136.68
129.88
129.36
127.57
127.16
126.21
117.48
112.22
110.13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7.73
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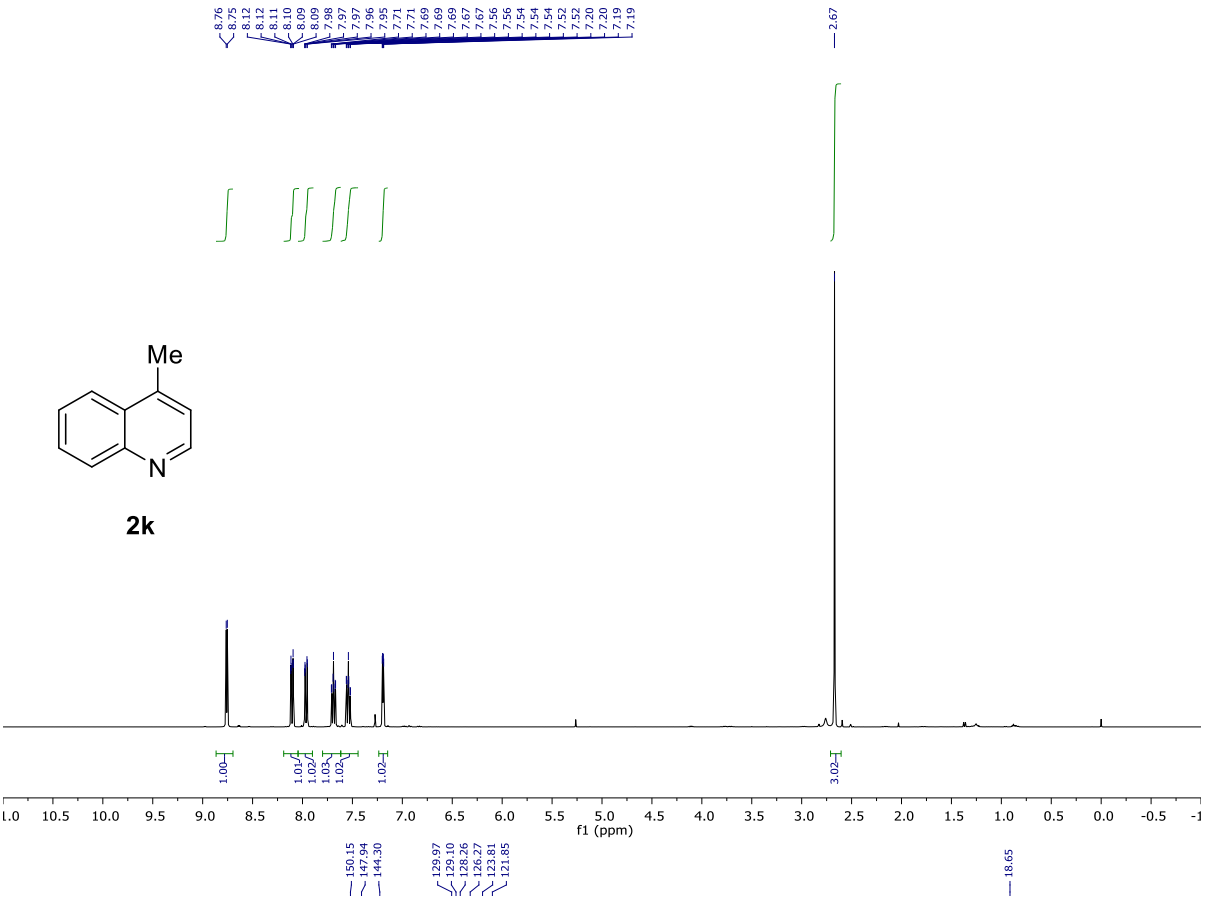
7.64
7.64
7.62
7.52
7.51
7.50
7.49
2.51
Me
N
2j
f1 (ppm)
1.00
1.01
1.01
1.02
1.00
1.02
3.01
152.43
146.57
134.68
130.48
129.18
128.44
128.14
127.13
126.55
18.78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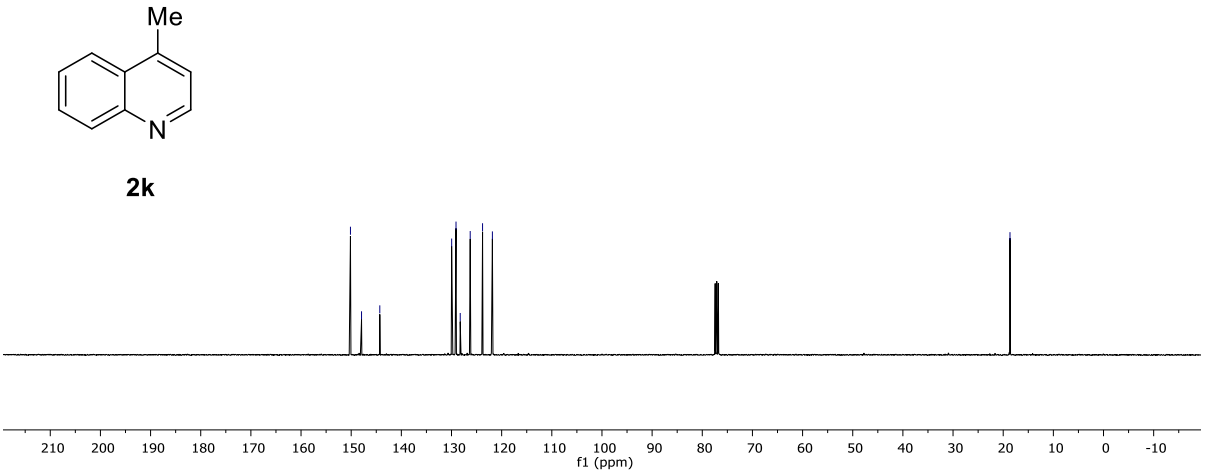
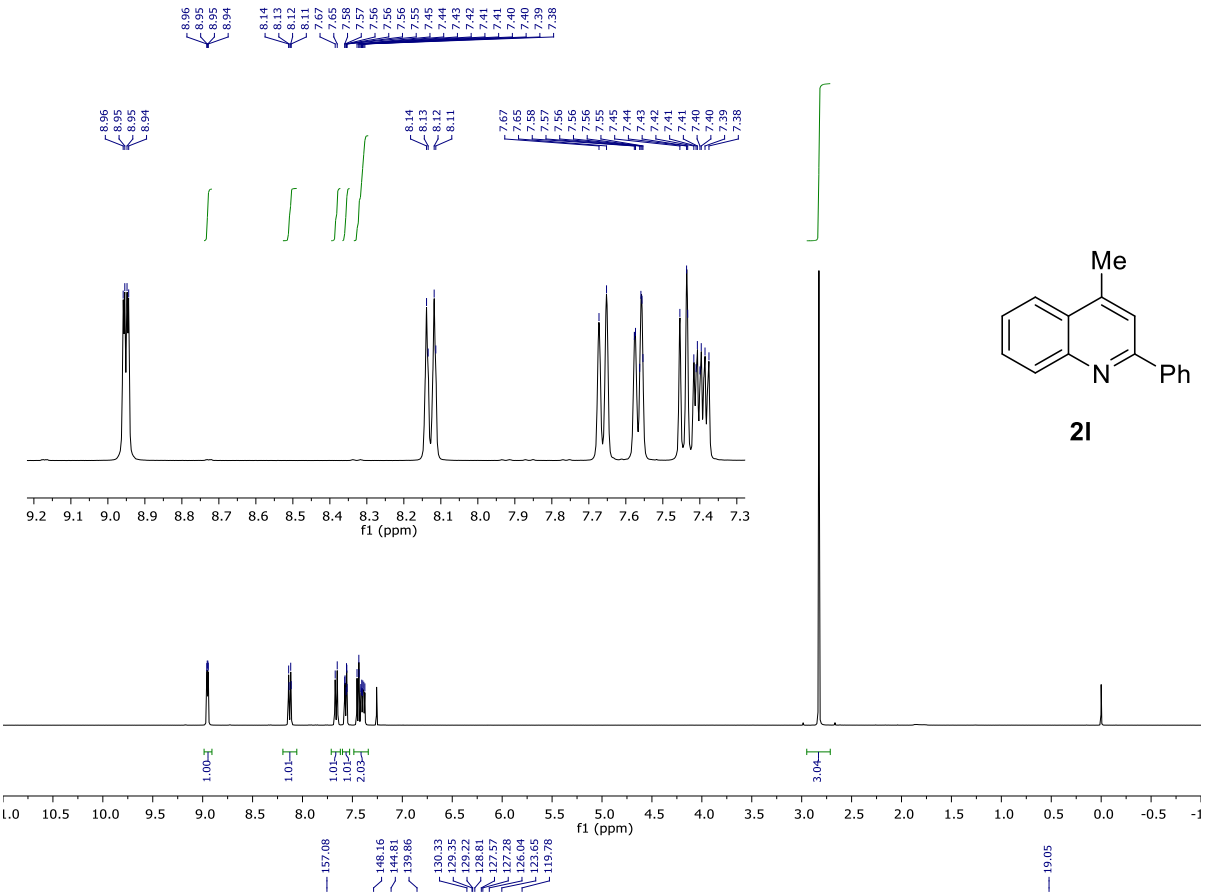
8.09
8.09
7.98
7.97
7.97
7.96
7.95
7.71
7.71
7.69
7.69
7.69
7.67
7.67
7.56
7.56
7.54
7.54
7.54
7.52
7.52
7.20
7.20
7.19
7.19
2.67
Me
N
2k
1.00
1.01
1.02
1.03
1.02
1.02
3.02
f1 (ppm)
150.15
147.94
144.30
129.97
129.10
128.26
126.27
123.81
121.85
18.65


Me
N
2k
f1 (ppm)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8.11
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7.65
7.58
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7.56
7.56
7.56
7.55
7.45
7.44
7.43
7.42
7.41
7.41
7.40
7.40
7.39
7.38
f1 (ppm)
1.00
1.01
1.01
1.01
2.03
3.04
157.08
148.16
144.81
139.86
130.33
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128.81
127.57
127.28
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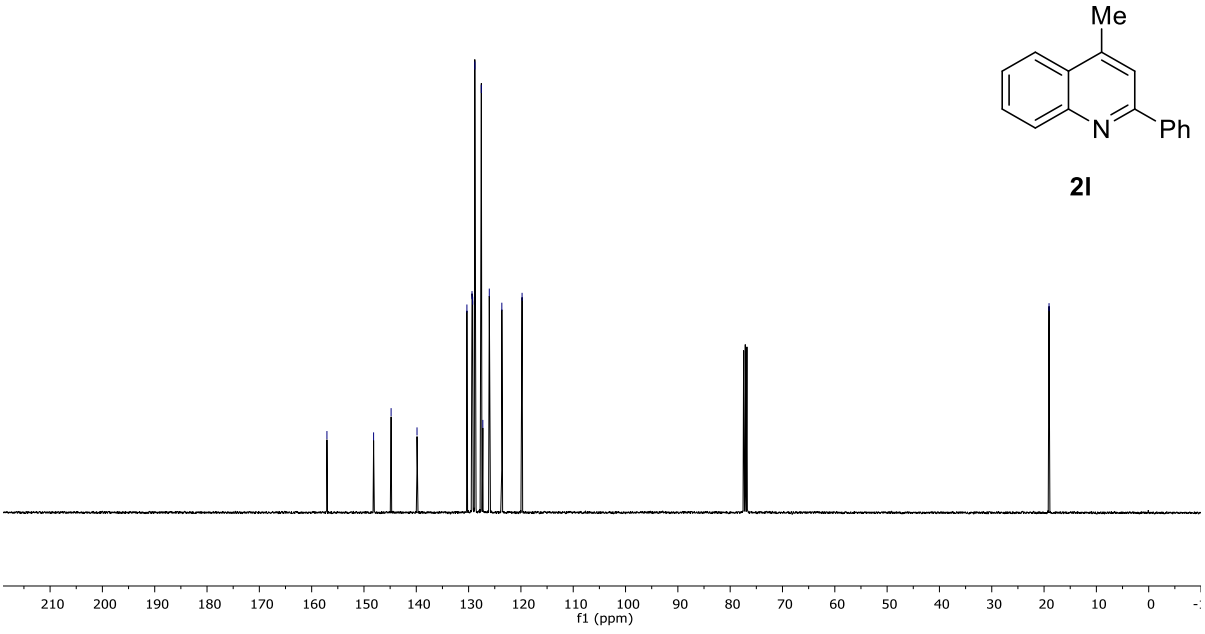
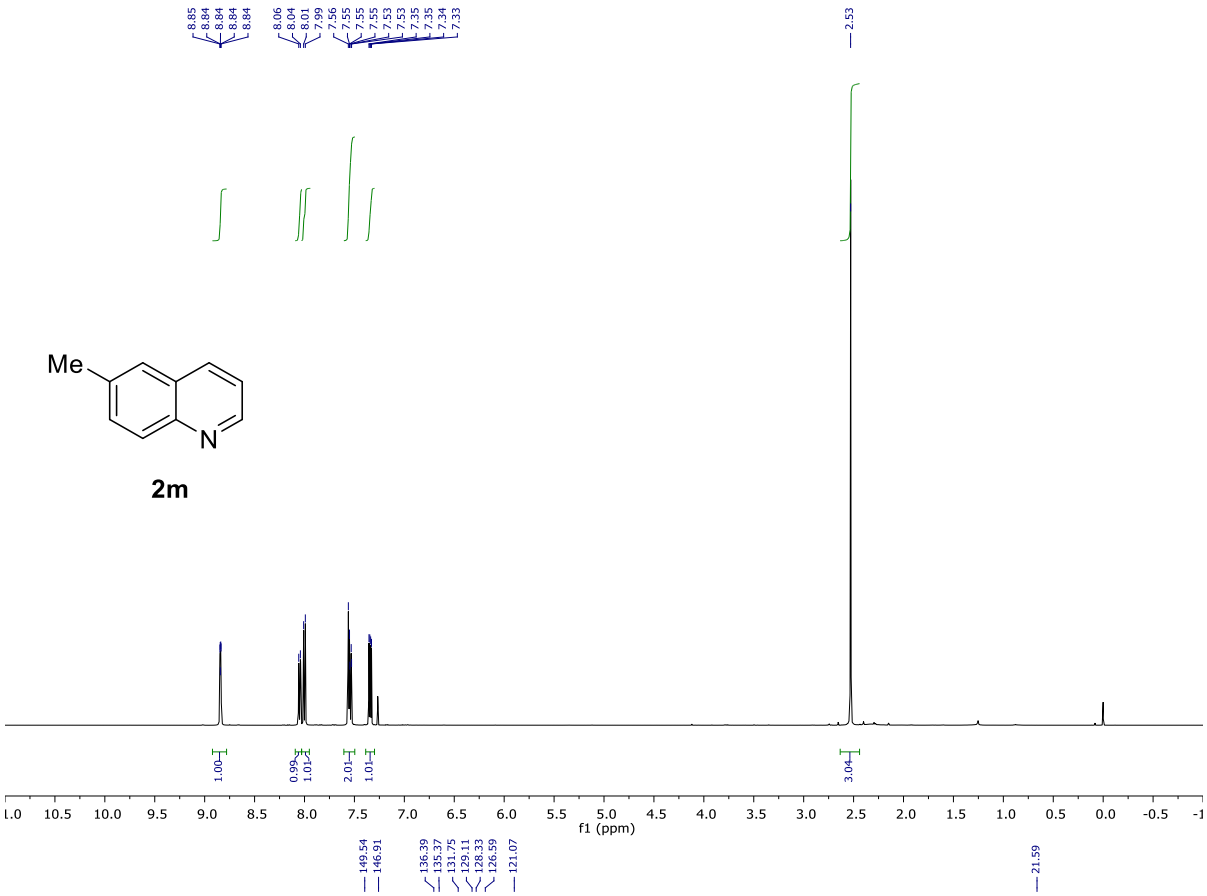
123.65
119.78
19.05
Me
N
Ph
2l


Me
N
Ph
2l
f1 (ppm)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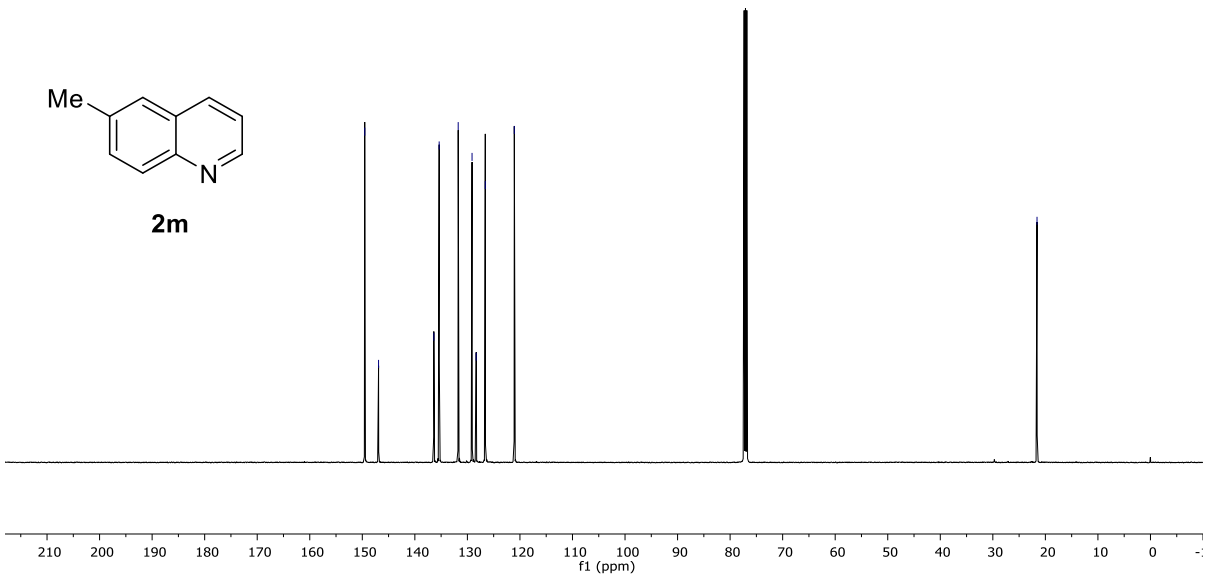
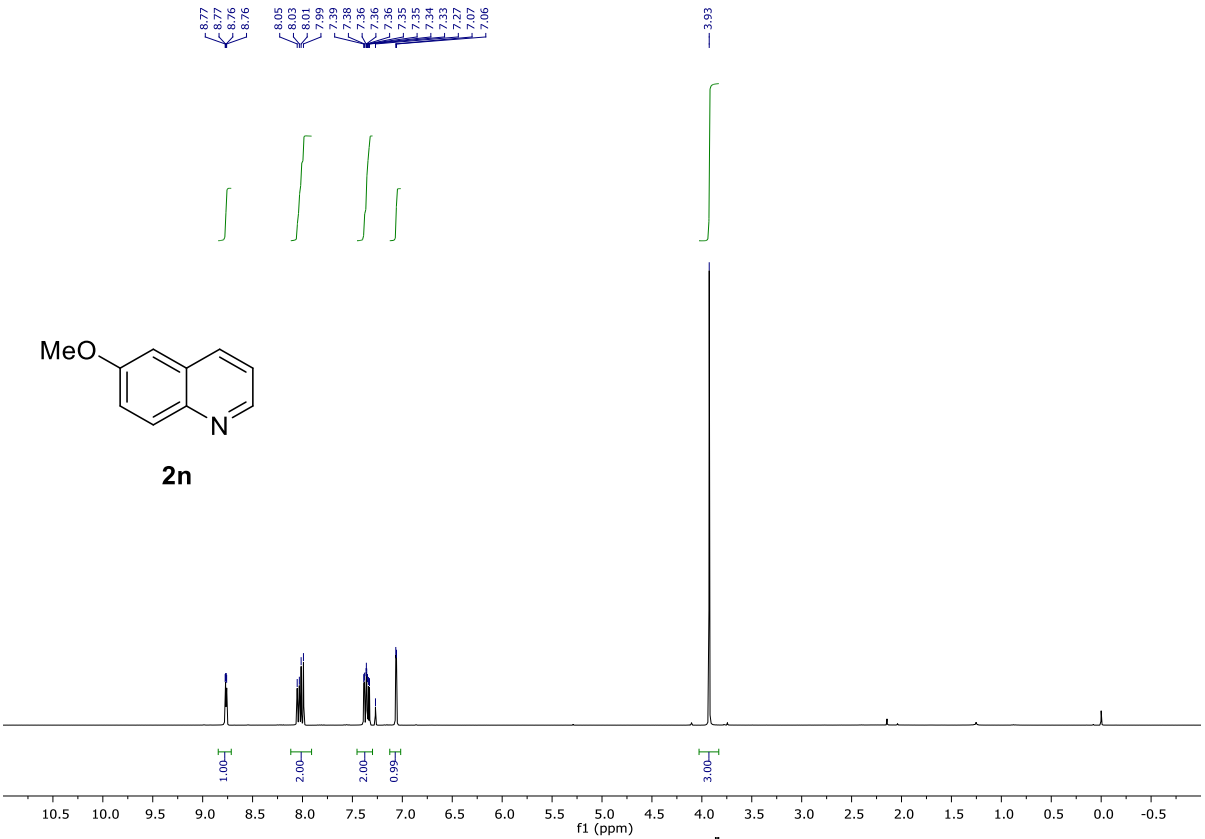
8.84
8.84
8.84
8.06
8.04
8.01
7.99
7.56
7.55
7.55
7.53
7.53
7.35
7.35
7.34
7.33
2.53
Me
N
2m
1.00
0.99
1.01
2.01
1.01
3.04
f1 (ppm)
149.54
146.91
136.39
135.37
131.75
129.11
128.33
126.59
121.07
21.59


Me
N
2m
f1 (ppm)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8.77
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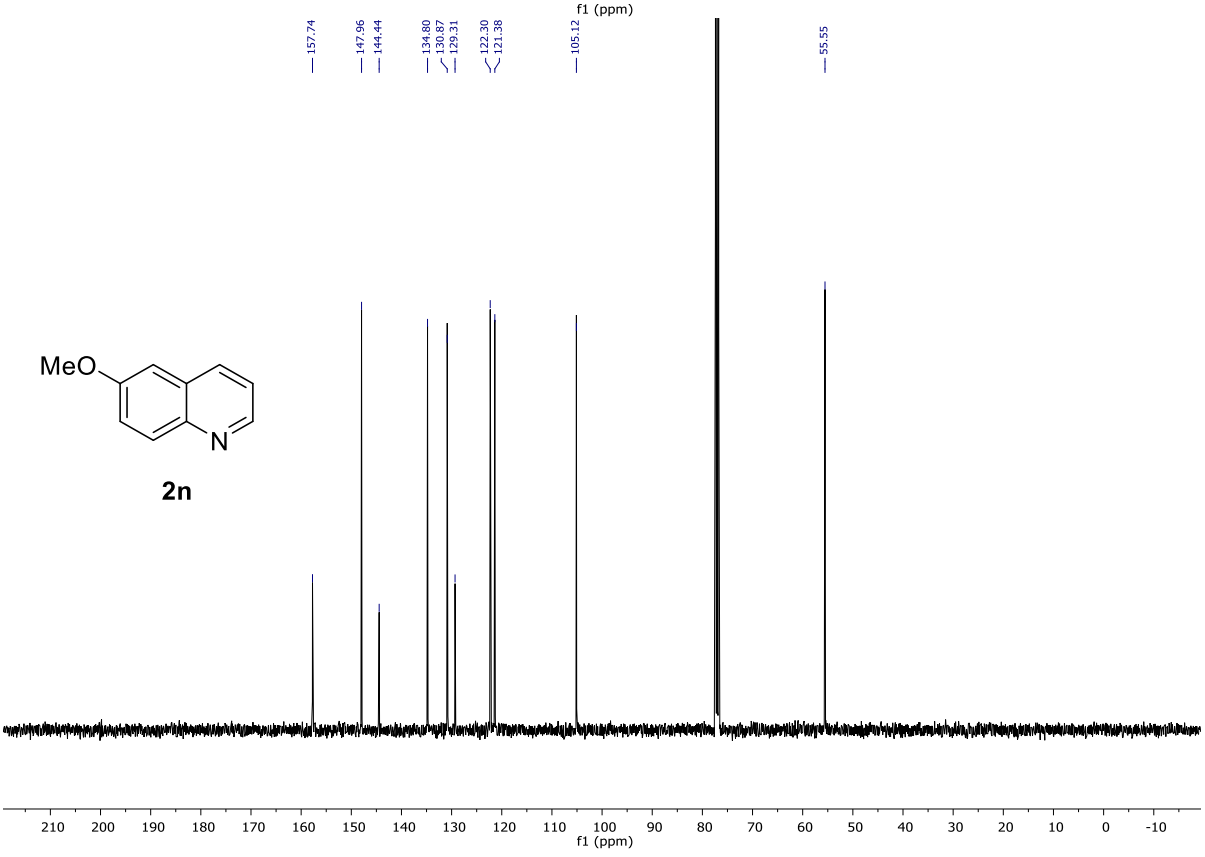
8.76
8.05
8.03
8.01
7.99
7.39
7.38
7.36
7.36
7.36
7.35
7.35
7.34
7.33
7.27
7.07
7.06
3.93
MeO
N
2n
1.00
2.00
2.00
0.99
3.00
f1 (ppm)


157.74
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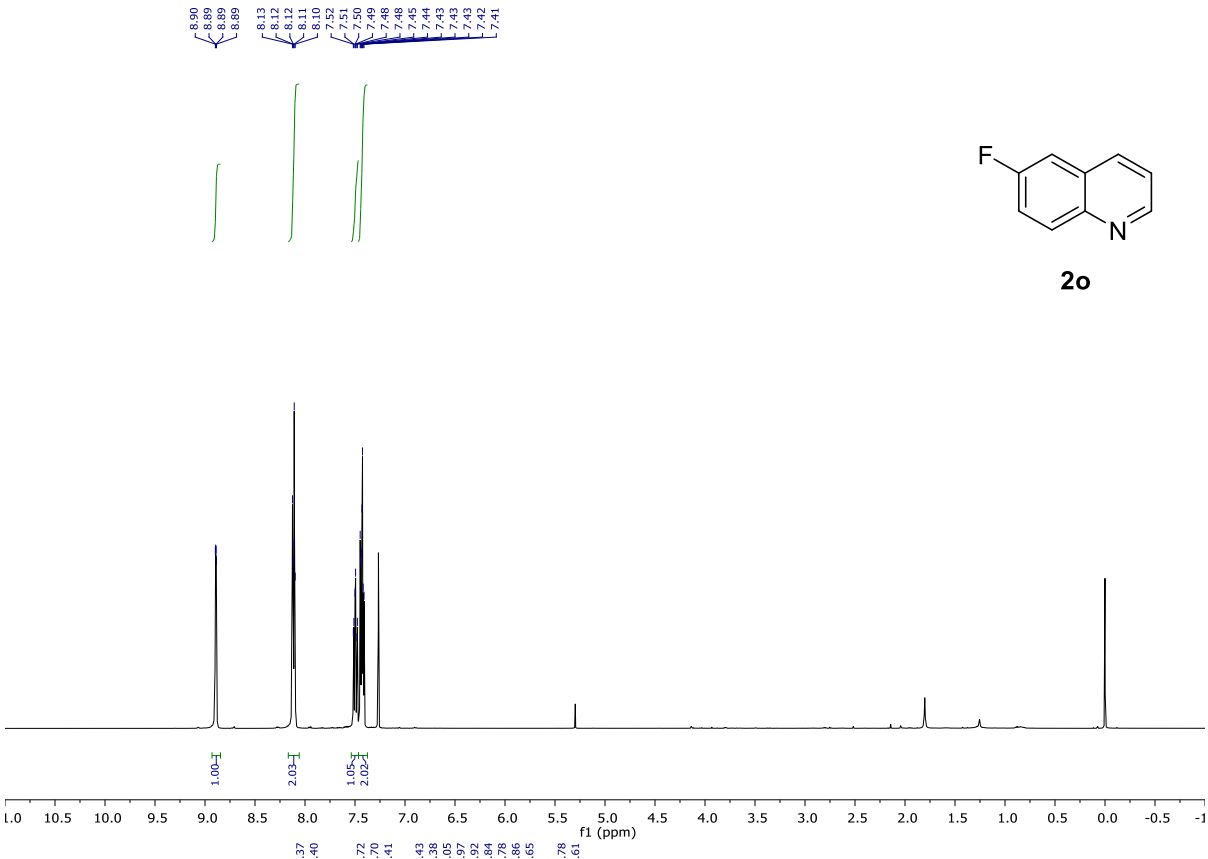
130.87
129.31
122.30
121.38
105.12
55.55
MeO
N
2n
f1 (ppm)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8.12
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7.51
7.50
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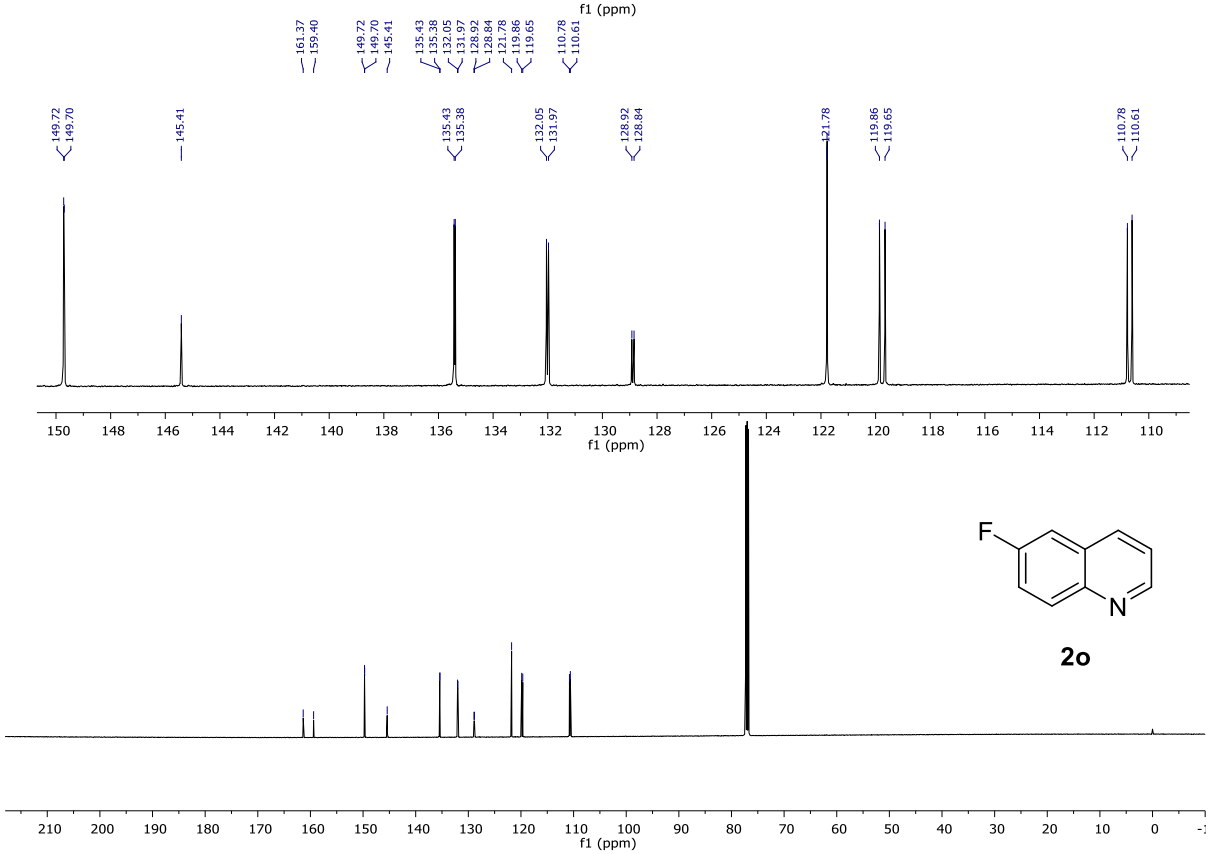
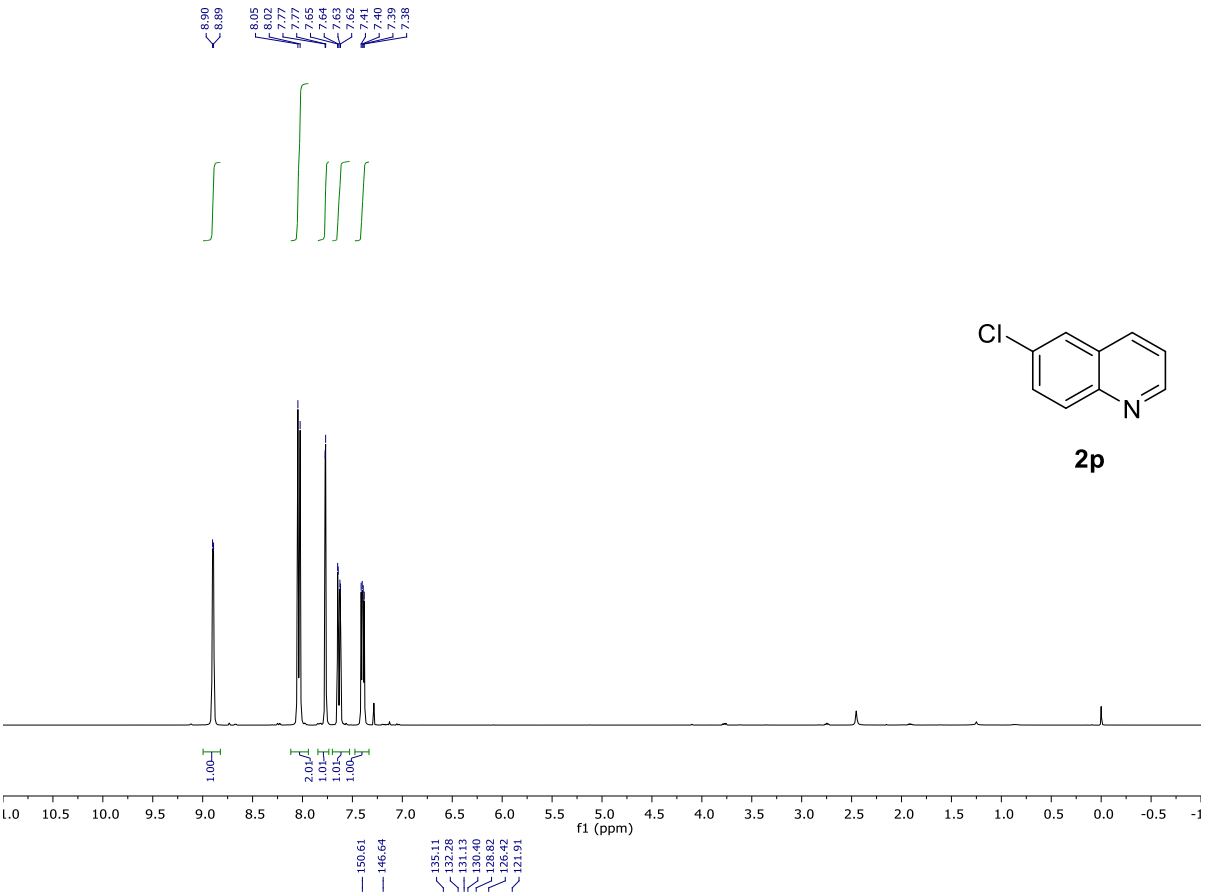
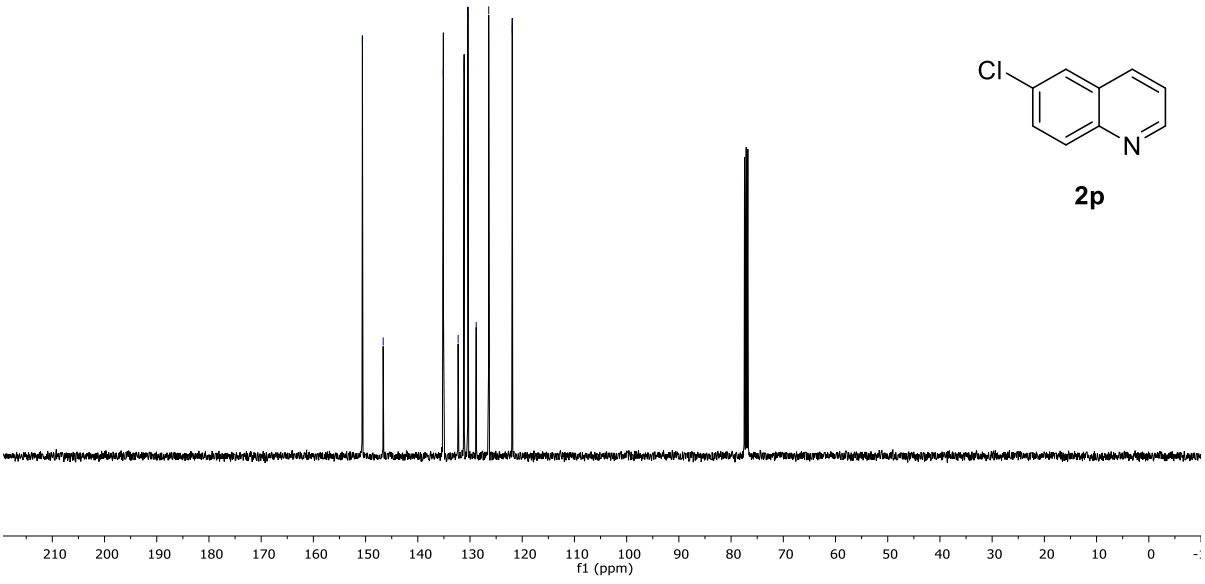
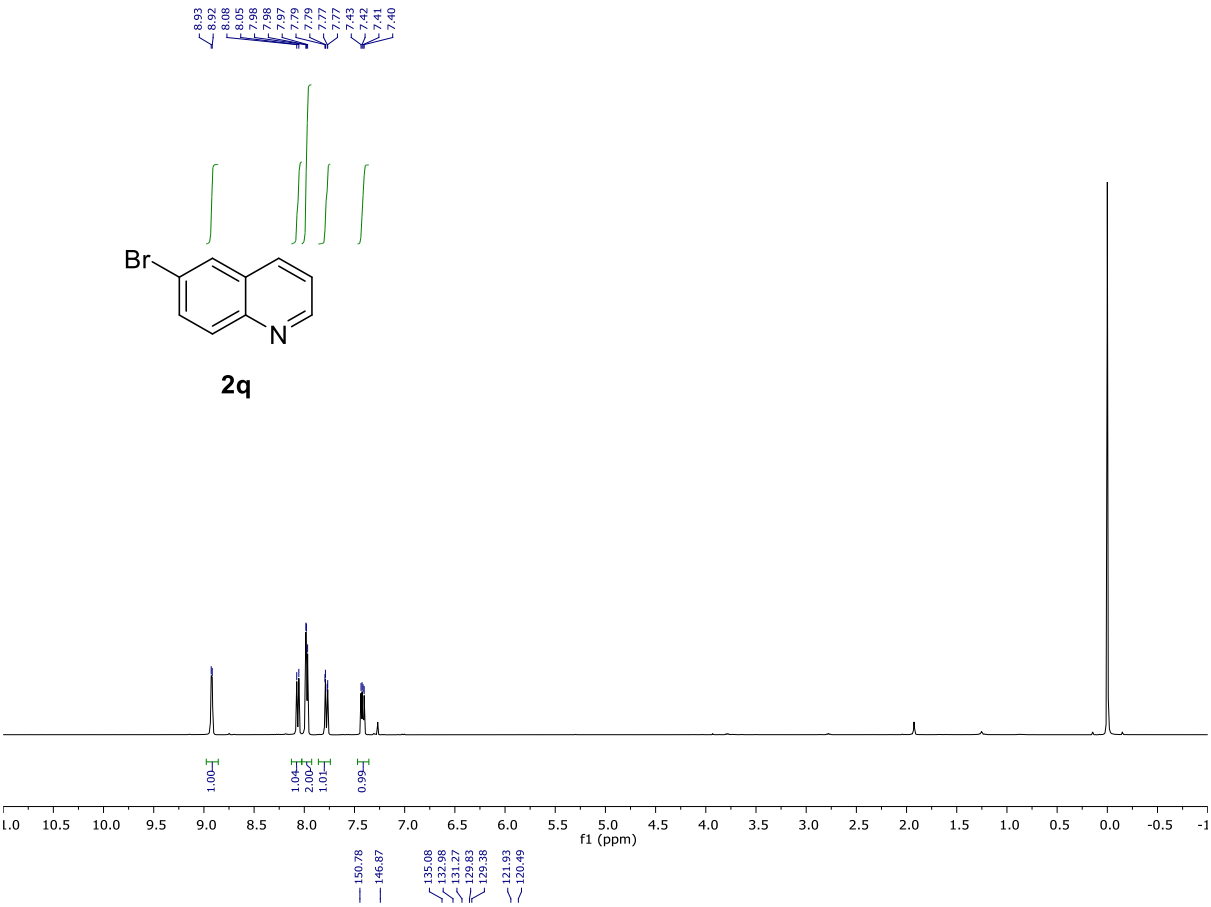
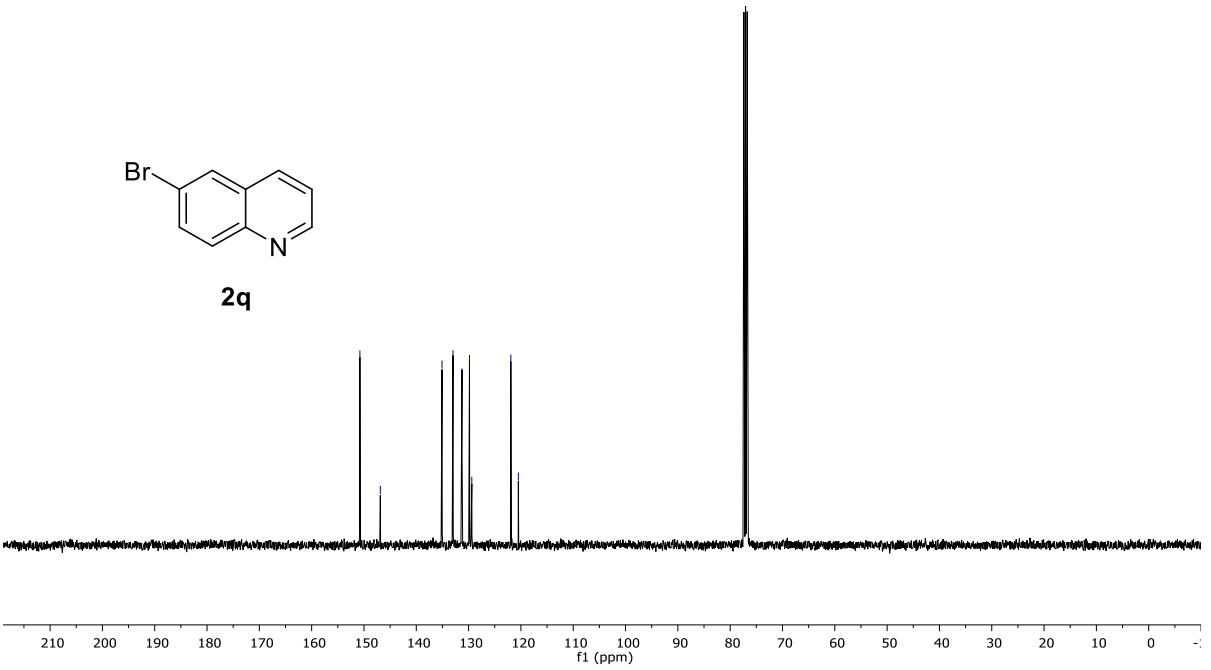
7.48
7.48
7.45
7.44
7.43
7.43
7.43
7.42
7.41
F
N
2o
1.00
2.03
1.05
2.02
f1 (ppm)

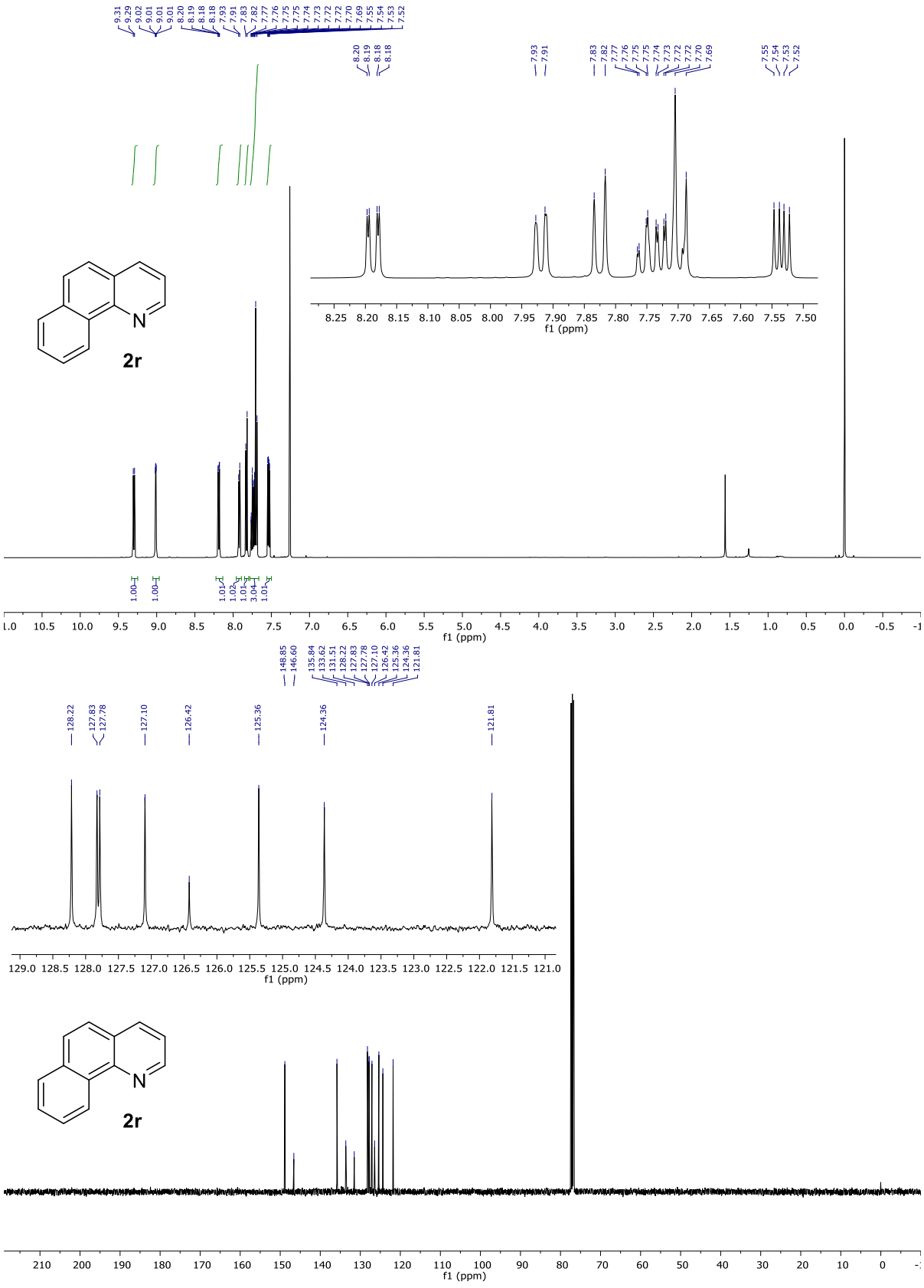

161.37
159.40
149.72
149.70
145.41
135.43
135.38
132.05
131.97
128.92
128.84
121.78
119.86
119.65
110.78
110.61
f1 (ppm)
F
N
2o

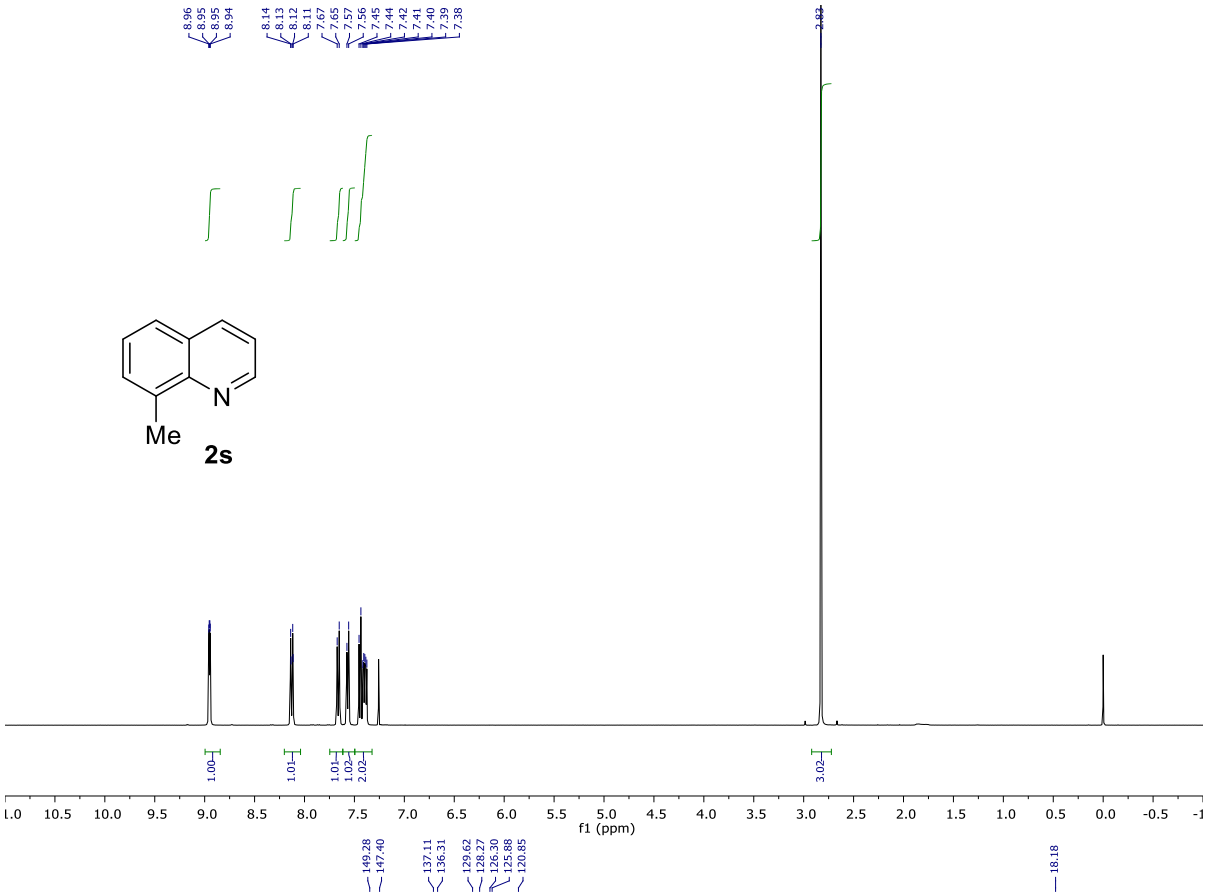

8.90
8.89
8.05
8.02
7.77
7.77
7.65
7.64
7.63
7.62
7.41
7.40
7.39
7.38
Cl
N
2p
1.00
2.01
1.01
1.01
1.00
f1 (ppm)

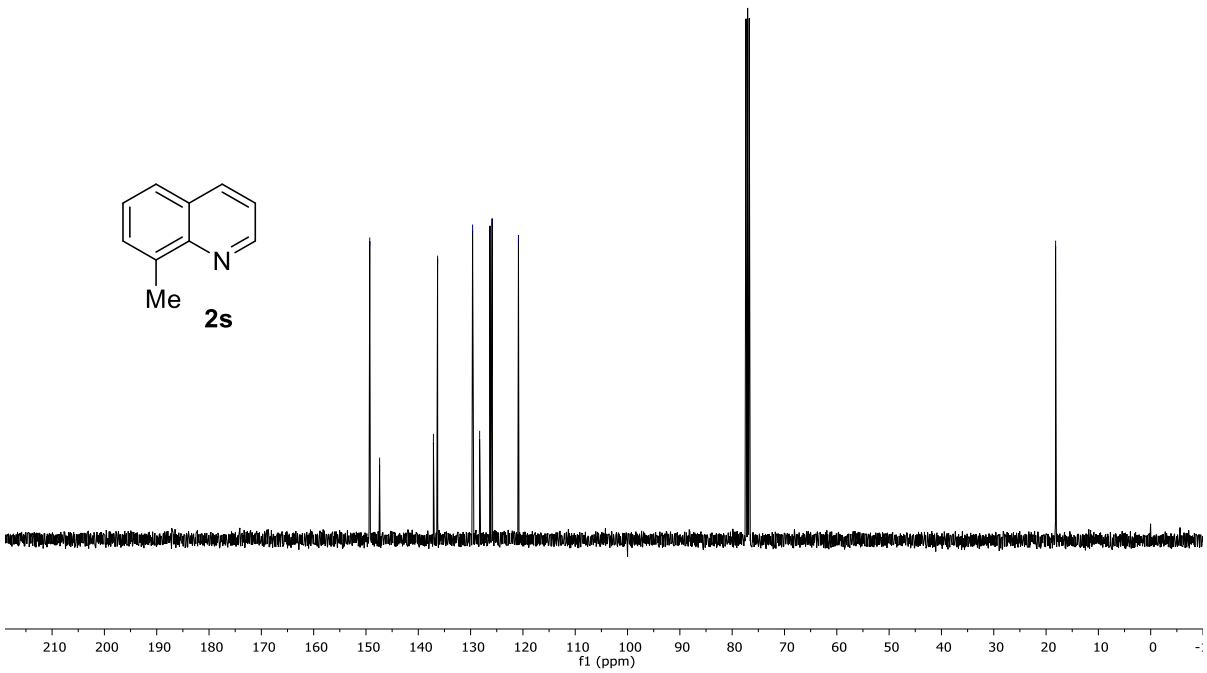

150.61
146.64
135.11
132.28
131.13
130.40
128.82
126.42
121.91
Cl
N
2p
f1 (ppm)

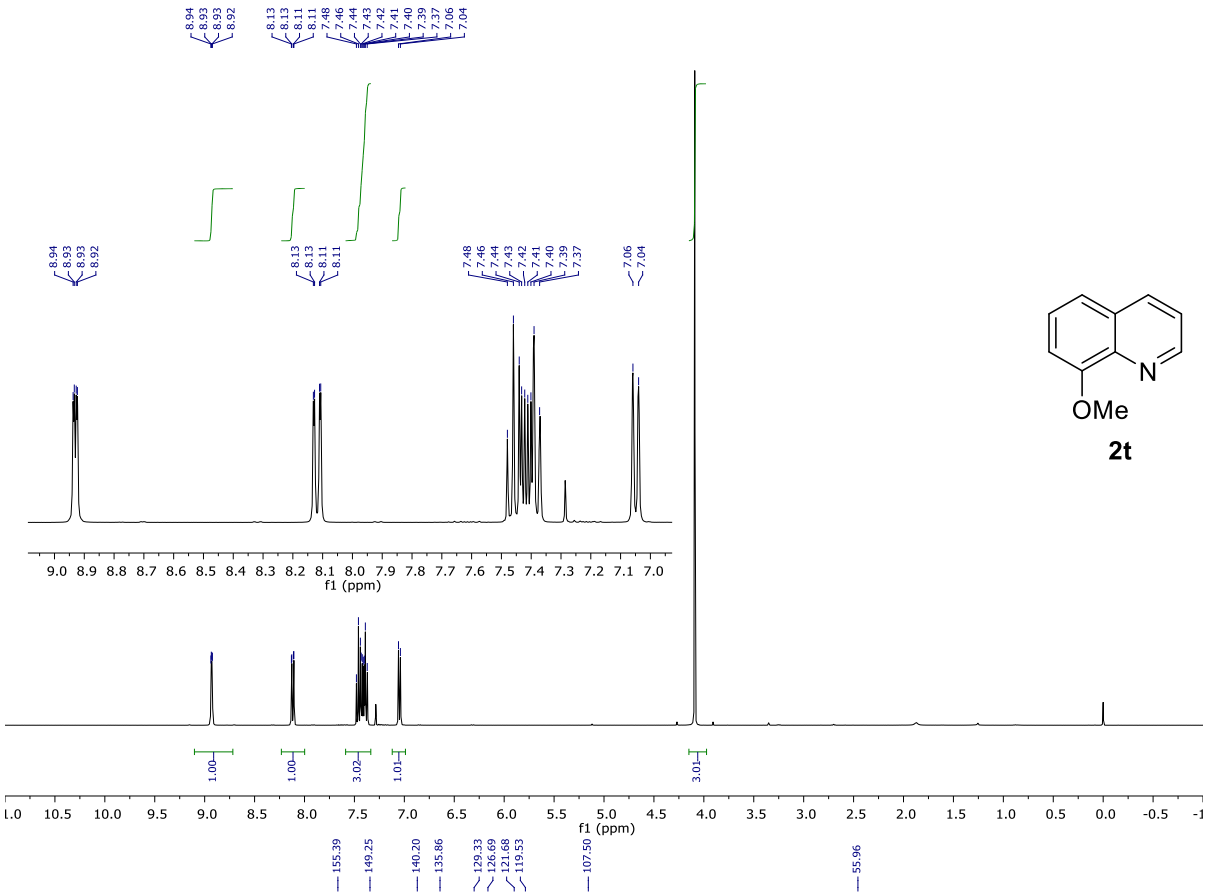

8.93
8.92
8.08
8.05
7.98
7.98
7.97
7.79
7.79
7.77
7.77
7.43
7.42
7.41
7.40
Br
N
2q
1.00
1.04
2.00
1.01
0.99
f1 (ppm)

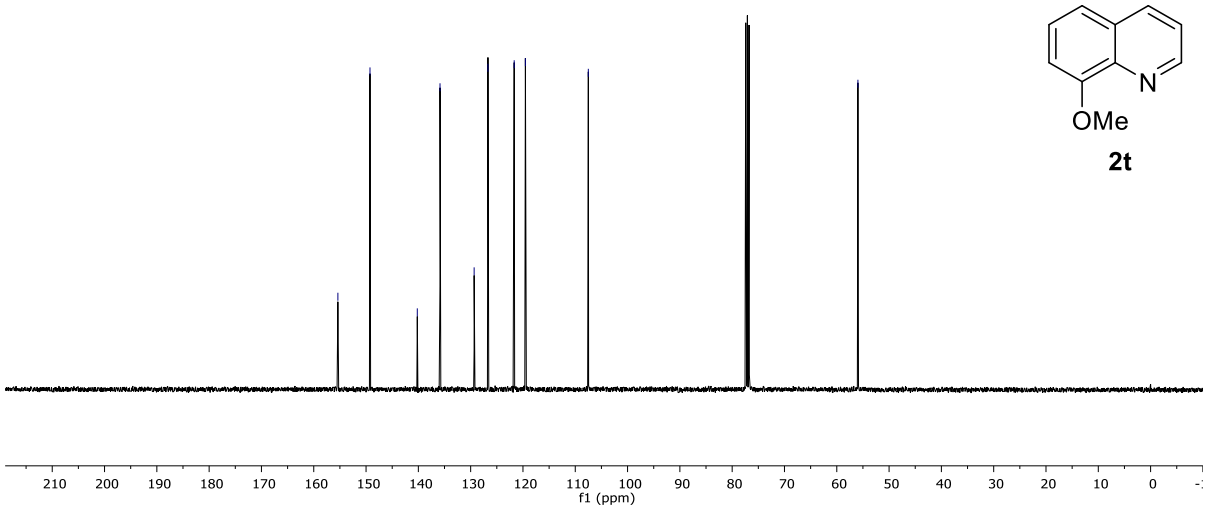

150.78
146.87
135.08
132.98
131.27
129.83
129.38
121.93
120.49
Br
N
2q
f1 (ppm)


9.31
9.29
9.02
9.01
9.01
9.01
8.20
8.19
8.18
8.18
7.93
7.91
7.83
7.82
7.77
7.76
7.75
7.74
7.73
7.72
7.70
7.69
7.55
7.54
7.53
7.52
2r
f1 (ppm)
148.85
146.60
135.84
133.62
131.51
128.22
127.83
127.78
127.10
126.42
125.36
124.36
121.81
2r
f1 (ppm)


8.96
8.95
8.95
8.94
8.14
8.13
8.12
8.11
7.67
7.65
7.57
7.56
7.45
7.44
7.42
7.41
7.40
7.39
7.38
2.82
N
Me
2s
1.00
1.01
1.01
1.02
2.02
3.02
f1 (ppm)


149.28
147.40
137.11
136.31
129.62
128.27
126.30
125.88
120.85
18.18
N
Me
2s
f1 (ppm)


8.94
8.93
8.93
8.92
8.13
8.13
8.11
8.11
7.48
7.46
7.44
7.43
7.42
7.41
7.40
7.39
7.37
7.06
7.04
9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
1.00
1.00
3.02
1.01
3.01
f1 (ppm)
N
OMe
2t


155.39
149.25
140.20
135.86
129.33
126.69
121.68
119.53
107.50
55.96
f1 (ppm)
N
OMe
2t