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ELECTRONIC SUPPLEMENTARY INFORMATION

Cobalt-catalysed Transfer Hydrogenation of Quinolines and Related Heterocycles Using Formic Acid under mild Conditions

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1. GENERAL INFORMATION

All the chemicals were purchased and used without further purification. Phosphine ligands **L1**[1] and **L3**[2] were synthetized following reported reaction procedures. Conversions and yields of reduction reactions were determined by GC-FID, HP 6890 with FID detector, column HP530 m x 250 mm x 0.25 µm. Mass spectra were recorded on a GC-MS Agilent 5973 Network equipped with a mass selective detector. NMR spectra of the isolated products were recorded using Bruker AV-300 (300 MHZ for ^{1}H) and Bruker AV-400 (400 MHz for ^{1}H) spectrometers. NMR chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane and were referenced to the residual proton resonance and the natural abundance ^{13}C resonance of the solvents. For the NMR experiments $CDCl_3$ or CD_3OD were used as solvent. Coupling constants (*J*) are expressed in Hz. Abbreviations used in the reported NMR experiments: b, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. All measurements were carried out at room temperature unless otherwise stated. HRMS measurements of the all isolated products were performed using the electrospray ionization technique in UPLC (ultra-pressure) equipment.

2. EXPERIMENTAL PROCEDURES

General procedure for the transfer hydrogenation of quinoline (1a): A 25 mL schlenk containing a stirring bar was sequentially charged under argon with $Co(BF_4)_2 \cdot 6H_2O$ (1.7 mg, 0.005 mmol, 2 mol%), ligand **L1** (4.0 mg, 0.005 mmol, 2 mol%), quinoline **1a** (29.6 μL, 0.25 mmol), *n*-hexadecane (30.0 mg) as an internal standard and dry *i*-PrOH (2 mL) as solvent. Then, the schlenk was sealed and set in an oil bath at 80 ºC during 10 min. Next, the reaction mixture was cooled to room temperature and formic acid (95.0 μL, 2.5 mmol, 10 eq) was added under argon atmosphere. Afterwards, the schlenk was placed into an oil bath at 80 °C during 20 h. Finally, the reaction was cooled, diluted with ethyl acetate and analysed by GC.

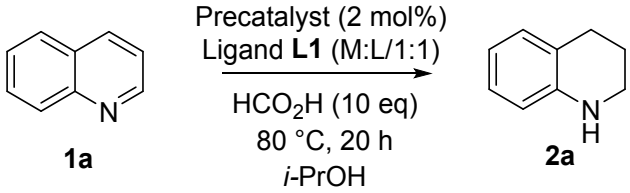
General procedure for the homogeneity tests in the transfer hydrogenation of quinoline (1a): A 25 mL schlenk containing a stirring bar was sequentially charged under argon with $Co(BF_4)_2 \cdot 6H_2O$ (1.7 mg, 0.005 mmol, 2 mol%), ligand **L1** (4.0 mg, 0.005 mmol, 2 mol%), quinoline **1a** (29.6 μL, 0.25 mmol), *n*-hexadecane (30.0 mg) as an internal standard and dry *i*-PrOH (2 mL) as solvent. Then, the schlenk was sealed and set in an oil bath at 80 ºC during 10 min. Next, the reaction mixture was cooled to room temperature and formic acid (95.0 μL, 2.5 mmol, 10 eq) and the corresponding quantity of Hg as additive (1.25 or 2.5 mol%, 0.5 or 1 eq to Co) was added under argon atmosphere. Afterwards, the schlenk was placed into an oil bath at 80 °C during 20 h. Finally, the reaction was cooled, diluted with ethyl acetate and analysed by GC.

Synthesis of (*E*)-6-styrylquinoline (1i) through Mizoroki-Heck cross coupling[3]: A 100 mL round-bottomed flask containing a stirring bar was sequentially charged under argon with $Pd(OAc)_2$ (68.0 mg, 0.3 mmol, 5 mol%), PPh_3 (236.0 mg, 0.9 mmol, 15 mol%), 6-Br-quinoline **1d** (812.0 μL, 6.0 mmol), styrene **S1** (1.03 mL, 9 mmol, 1.5 eq), dry DMF (10 mL) as solvent and Et_3N (1.7 mL, 12 mmol, 2 eq). Afterwards, the round-bottomed flask was sealed and set in an oil bath at 140 ºC during 16 h. When the reaction was complete, the crude reaction mixture was allowed to reach room temperature. Then, 50 mL of diethyl ether were added, the mixture was filtered under gravity and the solid residue was washed with diethyl ether (3 x 5 mL). The solvent was removed under reduced pressure. Finally, reaction mixture was purified by silica gel column chromatography (*n*-heptane/AcOEt mixtures) obtaining the desired product **1i** as white solid (870.0 mg, 69%).

General procedure for the transfer hydrogenation of N-heterocycles: A 25 mL schlenk containing a stirring bar was sequentially charged under argon with $Co(BF_4)_2 \cdot 6H_2O$ (2.5-8 mol%), ligand **L2** (2.5-8 mol%), N-heterocycle (0.25 mmol) and dry *i*-PrOH (2 mL) as solvent. Then, the schlenk was sealed and set in an oil bath at 80 ºC during 10 min. Next, the reaction mixture was cooled to room temperature and formic acid (95.0 μL, 2.5 mmol, 10 eq) was added under argon atmosphere. Afterwards, the schlenk was placed into an oil bath at 80-100 ºC during 20 h. Finally, the reaction was cooled and diluted with ethyl acetate. To determine the isolated yield of the hydrogenated products, the reaction mixture was purified by silica gel column chromatography (*n*-hexane/AcOEt mixtures) to give the corresponding desired N-heteroarene. For the isolation of compounds **2q** and **2r** (*n*-heptane/AcOEt mixtures) with 5% of triethylamine was used.

3. ADDITIONAL TABLES

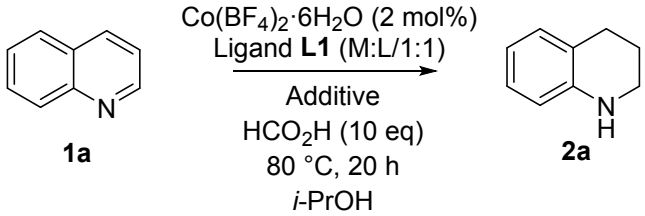
Table S1. Transfer hydrogenation of quinoline **1a** using formic acid: influence of the metal precatalyst



Entry[a]	Precatalyst	Conv. (%)[b]	**2a** (%)[b]
1	**$Co(BF_4)_2 \cdot 6H_2O$**	**>99**	**97**
2	$Co(acac)_3$	-	-
3	$Co(acac)_2 \cdot H_2O$	7	4
4	CoF_2	-	-
5	$CoBr_2$	-	-
6	$Co(NO_3)_2 \cdot 6H_2O$	-	-
7	$CoSO_4 \cdot 7H_2O$	45	42
8	$Co(ClO_4)_2 \cdot 4H_2O$	-	-
9	$CoCl_2$	-	-
10	$Fe(BF_4)_2 \cdot 6H_2O$	-	-
11	$Cu(BF_4)_2 \cdot 6H_2O$	-	-
12	$Zn(BF_4)_2 \cdot 6H_2O$	-	-

[a] Standard reaction conditions: quinoline **1a** (29.6 μL, 0.25 mmol), metal precatalyst (0.005 mmol, 2 mol%), ligand **L1** (4.0 mg, 0.005 mmol, 2 mol%), HCO_2H (95.0 μL, 2.5 mmol, 10 eq) and dry *i*-PrOH (2 mL) at 80°C during 20 h. [b] Conversion of **1a** and yield of product **2a** were calculated by GC using hexadecane as internal standard.

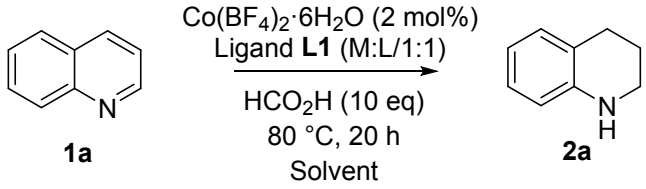
Table S2. Homogenity studies for the [Co/**L1**]-catalysed transfer hydrogenation of quinoline **1a** using formic acid



Entry[a]	Additive (eq. to Co)	Conv. (%)[b]	**2a** (%)[b]
1	none	>99	97
2	Hg (0.5)	99	95
3	Hg (1)	>99	97

[a] Standard reaction conditions: quinoline **1a** (29.6 μL, 0.25 mmol), $Co(BF_4)_2 \cdot 6H_2O$ (1.70 mg, 0.005 mmol, 2 mol%), ligand **L1** (4.0 mg, 0.005 mmol, 2 mol%), HCO_2H (95.0 μL, 2.5 mmol, 10 eq), Hg (0.5-1 eq to Co) and dry *i*-PrOH (2 mL) at 80°C during 20 h. [b] Conversion of **1a** and yield of product **2a** were calculated by GC using hexadecane as internal standard.

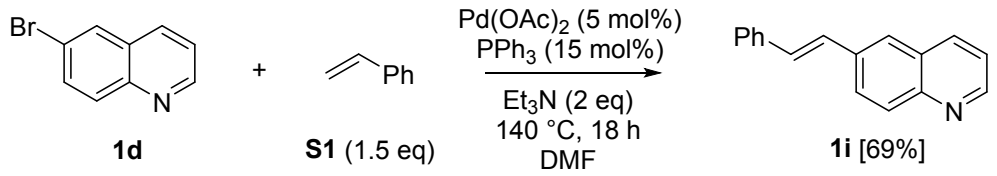
Table S3. Solvent effect in the [Co/**L1**]-catalysed transfer hydrogenation of quinoline **1a** using formic acid



Entry[a]	Solvent	Conv. (%)[b]	**2a** (%)[b]
1	***i*-PrOH**	**>99**	**97**
2	*i*-PrOH/H_2O (10:1)	20	17
3	EtOH	>99	93
4	2-methoxyethanol	-	-
5	*t*-amylOH	90	84
6	1-pentanol	94	92
7	3-pentanol	26	24
8	3-hexanol	-	-
9	propylene glycol	75	74
10	1,4-dioxane	4	-
11	*n*-Bu_2O	2	-
12	DMF	18	12
13	DMSO	3	-
14	*m*-xylene	-	-
15	toluene	71	67

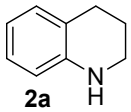
[a] Standard reaction conditions: quinoline **1a** (29.6 μL, 0.25 mmol), $Co(BF_4)_2 \cdot 6H_2O$ (1.70 mg, 0.005 mmol, 2 mol%), ligand **L1** (4.0 mg, 0.005 mmol, 2 mol%), HCO_2H (95.0 μL, 2.5 mmol, 10 eq) and dry solvent (2 mL) at 80°C during 20 h. [b] Conversion of **1a** and yield of product **2a** were calculated by GC using hexadecane as internal standard.

4. ADDITIONAL SCHEMES



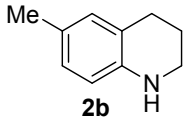
Scheme S1. Synthesis of (E)-6-styrylquinoline **1i** through Mizoroki-Heck cross coupling between 6-Br-quinoline **1d** and styrene **S1**. Isolated yield of the product after purification by column chromatography on silica is given.

5. CHARACTERIZATION DATA OF THE ISOLATED PRODUCTS



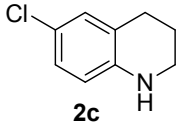
2a

1,2,3,4-tetrahydroquinoline (2a).[4] Isolated yield: 90%. GC-MS (m/z, $M^{+\cdot}$ 132), major peaks found: 132 (100%), 118 (20%), 104 (8%), 91 (6%), 77 (12%), 65 (6%). (The NMR spectrum is consistent with the reported data). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.07-6.97 (m, 2H), 6.66 (ddd, *J* = 7.6, 7.6, 1.4, 1H), 6.52 (d, *J* = 8.0, 1H), 3.66 (bs, NH), 3.34 (t, *J* = 5.6, 2H), 2.82 (t, *J* = 6.4, 2H), 2.05-1.87 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 144.83 (C), 129.56 (CH), 126.76 (CH), 121.47 (C), 116.96 (CH), 114.24 (CH), 42.04 (N-CH_2), 27.04 (CH_2), 22.24 (CH_2).



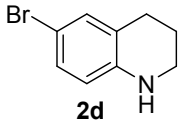
2b

6-methyl-1,2,3,4-tetrahydroquinoline (2b).[5] Isolated yield: 89%. GC-MS (m/z, $M^{+\cdot}$ 146), major peaks found: 146 (100%), 132 (40%), 117 (23%), 91 (15%), 72 (11%), 65 (11%). (The NMR spectrum is consistent with the reported data). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.83-6.78 (m, 2H), 6.53-6.35 (m, 1H), 3.48 (bs, NH), 3.35-3.23 (m, 2H), 2.76 (t, *J* = 6.4, 2H), 2.23 (s, 3H), 2.05-1.87 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 142.44 (C), 130.10 (CH), 127.26 (CH), 126.26 (C), 121.62 (C), 114.48 (CH), 42.20 (N-CH_2), 26.93 (CH_2), 22.46 (CH_2), 20.43 (CH_3). HRMS (ESI) [$M+H^+$; calculated for $C_{10}H_{13}N$: 148.1120] found m/z 148.1120.



2c

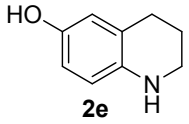
6-chloro-1,2,3,4-tetrahydroquinoline (2c).[6] Isolated yield: 88%. GC-MS (m/z, $M^{+\cdot}$ 167), major peaks found: 169 (33%), 167 (100%), 138 (10%), 132 (15%), 130 (50%), 117 (42%), 103 (14%), 77 (21%), 65 (19%). (The NMR spectrum is consistent with the reported data). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.92-6.88 (m, 2H), 6.41-6.36 (m, 1H), 3.59 (bs, NH), 3.33-3.22 (m, 2H), 2.73 (t, *J* = 6.4, 2H), 1.98-1.85 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 143.40 (C), 129.14 (CH), 126.61 (CH), 122.97 (C), 121.25 (C), 115.19 (CH), 41.96 (N-CH_2), 26.97 (CH_2), 21.85 (CH_2). HRMS (ESI) [$M+H^+$; calculated for $C_9H_{10}ClN$ (^{37}Cl): 170.0546] found m/z 170.0545 and [$M+H^+$; calculated for $C_9H_{10}ClN$ (^{35}Cl): 168.0574] found m/z 168.0575.



2d

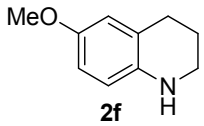
6-bromo-1,2,3,4-tetrahydroquinoline (2d).[6] Isolated yield: 78%. GC-MS (m/z, $M^{+\cdot}$ 212), major peaks found: 213 (98%), 211 (100%), 184 (8%), 130 (80%), 117 (60%), 103 (12%), 89 (10%), 77 (24%), 65 (22%), 51 (20%). (The NMR spectrum is consistent with the reported data). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.14-6.95 (m, 2H), 6.34 (d, *J* = 8.2, 1H), 3.65 (bs, NH), 3.31-3.24 (m, 2H), 2.72 (t, *J* = 6.4, 2H), 1.96-1.84 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ:

143.79 (C), 132.00 (CH), 129.49 (CH), 123.55 (C), 115.67 (CH), 108.38 (C), 41.91 (N-CH_2), 26.94 (CH_2), 21.79 (CH_2). HRMS (ESI) [M+H$^+$; calculated for $C_9H_{10}BrN$ (^{81}Br): 214.0049] found m/z 214.0052 and [M+H$^+$; calculated for $C_9H_{10}BrN$ (^{79}Br): 212.0069] found m/z 212.0072.



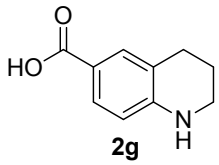
2e

1,2,3,4-tetrahydroquinolin-6-ol (2e).[7] Isolated yield: 76%. GC-MS (m/z, $M^{+\cdot}$ 149), major peaks found: 149 (100%), 133 (20%), 117 (18%), 89 (25%), 77 (15%), 63 (18%). (The NMR spectrum is consistent with the reported data). ^{1}H NMR (300 MHz, CD_3OD) δ: 6.49-6.41 (m, 2H), 6.43-6.41 (m, 1H), 4.90 (bs, NH+OH), 3.17-3.09 (m, 2H), 2.68 (t, *J* = 6.6, 2H), 1.92-1.82 (m, 2H). ^{13}C NMR (75 MHz, CD_3OD) δ: 150.70 (C), 138.69 (C), 125.38 (C), 118.23 (CH), 116.76 (CH), 114.76 (CH), 43.41 (N-CH_2), 27.92 (CH_2), 23.56 (CH_2). HRMS (ESI) [M+H$^+$; calculated for $C_9H_{11}NO$: 150.0913] found m/z 150.0914.



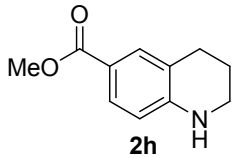
2f

6-methoxy-1,2,3,4-tetrahydroquinoline (2f).[8] Isolated yield: 80%. GC-MS (m/z, $M^{+\cdot}$ 163), major peaks found: 163 (50%), 148 (100%), 130 (10%), 118 (12%), 103 (10%), 91 (12%), 77 (12%). (The NMR spectrum is consistent with the reported data). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.63-6.55 (m, 2H), 6.46 (d, *J* = 8.5, 1H), 3.73 (s, 3H), 3.37 (bs, NH), 3.30-3.22 (m, 2H), 2.76 (t, *J* = 6.5, 2H), 2.00-1.86 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 151.88 (C), 138.87 (C), 122.96 (C), 115.65 (CH), 114.91 (CH), 112.93 (CH), 55.85 (O-CH_3), 42.38 (N-CH_2), 27.20 (CH_2), 22.47 (CH_2). HRMS (ESI) [M+H$^+$; calculated for $C_{10}H_{13}NO$: 164.1069] found m/z 164.1069.



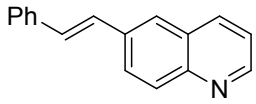
2g

1,2,3,4-tetrahydroquinoline-6-carboxylic acid (2g).[9] Isolated yield: 82%. GC-MS (m/z, $M^{+\cdot}$ 177), major peaks found: 177 (100%), 160 (10%), 148 (8%), 132 (35%), 117 (25%), 91 (10%), 77 (14%). (The NMR spectrum is consistent with the reported data). ^{1}H NMR (300 MHz, CD_3OD) δ: 7.48-7.42 (m, 2H), 6.30 (d, *J* = 9.1, 1H), 4.80 (bs, NH+OH), 3.32-3.07 (m, 2H), 2.62 (t, *J* = 6.3, 2H), 1.89-1.60 (m, 2H). ^{13}C NMR (75 MHz, CD_3OD) δ: 171.02 (C=O), 151.22 (C), 132.39 (CH), 130.43 (CH), 120.50 (C), 117.31 (C), 113.38 (CH), 42.33 (CH_2), 28.17 (CH_2), 22.51 (CH_2). HRMS (ESI) [M$^+$; calculated for $C_{10}H_{11}NO_2$: 178.0862] found m/z 178.0862.



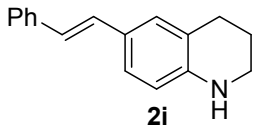
2h

methyl 1,2,3,4-tetrahydroquinoline-6-carboxylate (2h).[10] Isolated yield: 98%. GC-MS (m/z, $M^{+\cdot}$ 191), major peaks found: 191 (100%), 160 (100%), 132 (30%), 117 (15%), 104 (10%), 77 (12%). (The NMR spectrum is consistent with the reported data). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.71-7.56 (m, 2H), 6.45-6.34 (m, 1H), 4.34 (bs, NH), 3.83 (s, 3H), 3.40-3.29 (m, 2H), 2.76 (t, *J* = 6.3, 2H), 2.01-1.84 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 167.65 (C=O), 148.90 (C), 131.42 (CH), 129.24 (CH), 120.02 (C), 117.56 (C), 112.74 (CH), 51.55 (O-CH_3), 41.84 (N-CH_2), 27.02 (CH_2), 21.54 (CH_2). HRMS (ESI) [M+H^+; calculated for $C_{11}H_{13}NO_2$: 192.1019] found m/z 192.1017.



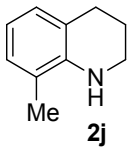
1i

(E)-6-styrylquinoline (1i).[11] Isolated yield: 69%. GC-MS (m/z, $M^{+\cdot}$ 231), major peaks found: 231 (85%), 230 (100%), 216 (15%), 202 (16%), 115 (14%), 101 (7%). (The NMR spectrum is consistent with the reported data). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.87 (dd, *J* = 4.2, 1.7, 1H), 8.14 (dd, *J* = 8.3, 1.4, 1H), 8.09 (d, *J* = 8.9, 1H), 7.98 (dd, *J* = 8.9, 2.0, 1H), 7.83 (d, *J* = 1.9, 1H), 7.60-7.55 (m, 2H), 7.43-7.36 (m, 3H), 7.31 (dt, *J* = 4.6, 1.9, 1H), 7.27 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 150.28 (CH), 148.24 (C), 137.15 (C), 136.09 (CH), 135.73 (C), 130.35 (CH), 129.94 (CH), 128.93 (2xCH), 128.74 (C), 128.15 (CH), 128.00 (CH), 127.40 (CH), 126.80 (2xCH), 126.07 (CH), 121.68 (CH). HRMS (ESI) [M+H^+; calculated for $C_{17}H_{13}N$: 232.1120] found m/z 232.1122.



2i

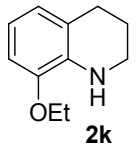
(E)-6-styryl-1,2,3,4-tetrahydroquinoline (2i). Isolated yield: 89%. GC-MS (m/z, $M^{+\cdot}$ 235), major peaks found: 235 (100%), 206 (10%), 178 (9%), 130 (5%), 103 (8%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.50 (dd, *J* = 8.4, 1.4, 2H), 7.36 (t, *J* = 7.6, 2H), 7.27-7.15 (m, 3H), 7.04, 6.91 (ABq, J_{AB} = 16.3, 2H), 6.48 (d, *J* = 8.0, 1H), 3.57 (bs, NH), 3.34 (t, *J* = 6.3, 2H), 2.82 (t, *J* = 6.4, 2H), 2.07-1.88 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 144.67 (C), 138.34 (C), 129.16 (CH), 128.67 (2xCH), 127.95 (CH), 126.69 (CH), 126.42 (C), 126.07 (2xCH), 125.54 (CH), 124.09 (CH), 121.40 (C), 114.28 (CH), 42.08 (N-CH_2), 27.15 (CH_2), 22.16 (CH_2). HRMS (ESI) [M+H^+; calculated for $C_{17}H_{17}N$: 236.1433] found m/z 236.1431.



2j

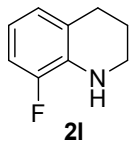
8-methyl-1,2,3,4-tetrahydroquinoline (2j).[12] Isolated yield: 93%. GC-MS (m/z, $M^{+\cdot}$ 146), major peaks found: 146 (100%), 132 (40%), 117 (20%), 91 (15%), 72 (11%), 65 (11%). (The NMR spectrum is consistent with the reported

data). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.90 (t, *J* = 7.5, 2H), 6.60 (t, *J* = 7.4, 1H), 3.60 (bs, NH), 3.47-3.33 (m, 2H), 2.83 (t, *J* = 6.4, 2H), 2.11 (s, 3H), 2.04-1.91 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 142.79 (C), 127.94 (CH), 127.47 (CH), 121.27 (C), 120.95 (C), 116.49 (CH), 42.43 (N-CH_2), 27.39 (CH_2), 22.25 (CH_2), 17.26 (CH_3).



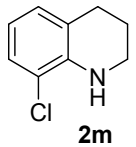
2k

8-ethoxy-1,2,3,4-tetrahydroquinoline (2k).[13] Isolated yield: 93%. GC-MS (m/z, $M^{+\cdot}$ 177), major peaks found: 177 (50%), 148 (100%), 131 (20%), 120 (7%), 103 (15%), 91 (11%). (The NMR spectrum is consistent with the reported data). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.72-6.46 (m, 3H), 4.29 (bs, NH), 4.06 (q, *J* = 7.0, 2H), 3.44-3.31 (m, 2H), 2.81 (t, *J* = 6.4, 2H), 2.08-1.87 (m, 2H), 1.45 (t, *J* = 7.0, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 145.64 (C), 134.66 (C), 121.64 (CH), 121.46 (C), 115.77 (CH), 108.32 (CH), 63.63 (O-CH_2), 41.58 (N-CH_2), 26.79 (CH_2), 22.23 (CH_2), 15.12 (CH_3). HRMS (ESI) [M^+; calculated for $C_{11}H_{15}NO$: 178.1226] found m/z 178.1225.



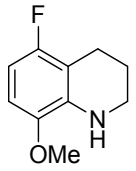
2l

8-fluoro-1,2,3,4-tetrahydroquinoline (2l).[10] Isolated yield: 82%. GC-MS (m/z, $M^{+\cdot}$ 151), major peaks found: 151 (85%), 150 (100%), 135 (15%), 130 (9%), 122 (10%), 109 (9%), 75 (20%). (The NMR spectrum is consistent with the reported data). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.84-6.71 (m, 2H), 6.51 (td, *J* = 7.8, 5.3, 1H), 3.57 (bs, NH), 3.35 (t, *J* = 5.7, 2H), 2.79 (t, *J* = 6.4, 2H), 2.02-1.91 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 151.04 (d, $J^{1}_{C\text{-}F}$ = 237.5, C), 133.28 (d, $J^{2}_{C\text{-}F}$ = 12.2, C), 124.59 (d, $J^{4}_{C\text{-}F}$ = 2.9, CH), 123.72 (d, $J^{3}_{C\text{-}F}$ = 3.6, C), 115.65 (d, $J^{3}_{C\text{-}F}$ = 7.4, CH), 112.26 (d, $J^{2}_{C\text{-}F}$ = 18.3, CH), 41.39 (N-CH_2), 26.66 (d, $J^{4}_{C\text{-}F}$ = 3.0, CH_2), 21.91 (CH_2). ^{19}F NMR (282 MHz, $CDCl_3$) δ: -138.58 (dd, $J^{3}_{F\text{-}H}$ = 11.2, $J^{4}_{F\text{-}H}$ = 5.2, 1F). HRMS (ESI) [$M+H^+$; calculated for $C_9H_{10}NF$: 152.0870] found m/z 152.0868.



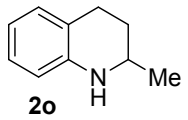
2m

8-chloro-1,2,3,4-tetrahydroquinoline (2m).[14] Isolated yield: 90%. GC-MS (m/z, $M^{+\cdot}$ 167), major peaks found: 169 (33%), 167 (100%), 152 (8%), 132 (13%), 130 (40%), 117 (25%), 104 (15%), 77 (20%), 65 (14%). (The NMR spectrum is consistent with the reported data). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.18-7.00 (m, 1H), 6.87 (dd, *J* = 7.5, 1.1, 1H), 6.52 (t, *J* = 7.7, 1H), 4.41 (bs, NH), 3.40 (t, *J* = 5.5, 2H), 2.79 (t, *J* = 6.4, 2H), 2.06-1.83 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 140.78 (C), 127.77 (CH), 126.88 (CH), 122.76 (C), 118.18 (C), 116.41 (CH), 41.91 (N-CH_2), 27.32 (CH_2), 21.75 (CH_2). HRMS (ESI) [$M+H^+$; calculated for $C_9H_{10}ClN$ (^{37}Cl): 170.0546] found m/z 170.0543 and [$M+H^+$; calculated for $C_9H_{10}ClN$ (^{35}Cl): 168.0574] found m/z 168.0573.



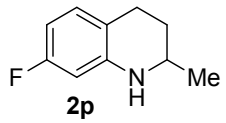
2n

5-fluoro-8-methoxy-1,2,3,4-tetrahydroquinoline (2n).[13] Isolated yield: 97%. GC-MS (m/z, $M^{+\cdot}$ 181), major peaks found: 181 (60%), 166 (100%), 151 (20%), 121 (15%), 109 (10%), 83 (10%). (The NMR spectrum is consistent with the reported data). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.51 (dd, *J* = 8.8, 4.9, 1H), 6.28 (t, *J* = 9.0, 1H), 4.24 (bs, NH), 3.80 (s, 3H), 3.36-3.27 (m, 2H), 2.74 (t, *J* = 6.5, 2H), 2.01-1.89 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 156.07 (d, $J^{1}_{C\text{-}F}$ = 234.3, C), 142.31 (C), 135.79 (d, $J^{3}_{C\text{-}F}$ = 8.7, C), 108.89 (d, $J^{2}_{C\text{-}F}$ = 23.4, C), 107.25 (d, $J^{3}_{C\text{-}F}$ = 10.2, CH), 100.50 (d, $J^{2}_{C\text{-}F}$ = 23.9, CH), 55.89 (O-CH_3), 40.95 (N-CH_2), 21.19 (CH_2), 19.93 (d, $J^{3}_{C\text{-}F}$ = 3.8, CH_2). ^{19}F NMR (282 MHz, $CDCl_3$) δ: -128.18 (dd, $J^{3}_{F\text{-}H}$ = 9.0, $J^{4}_{F\text{-}H}$ = 5.0, 1F). HRMS (ESI) [M+H$^+$; calculated for $C_{10}H_{12}FNO$: 182.0975] found m/z 182.0976.



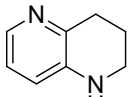
2o

2-methyl-1,2,3,4-tetrahydroquinoline (2o).[4] Isolated yield: 78%. GC-MS (m/z, $M^{+\cdot}$ 147), major peaks found: 147 (35%), 132 (100%), 117 (20%), 104 (18%), 91 (8%), 77 (11%), 65 (9%). (The NMR spectrum is consistent with the reported data). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.15-7.08 (m, 2H), 6.76 (ddd, *J* = 7.3, 7.3, 0.9, 1H), 6.60 (dd, *J* = 8.3, 0.7, 1H), 3.75 (bs, NH), 3.57-3.46 (m, 1H), 3.06-2.82 (m, 2H), 2.11-2.01 (m, 1H), 1.80-1.65 (m, 1H), 1.34 (d, *J* = 6.3, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 144.74 (C), 129.22 (CH), 126.64 (CH), 121.01 (C), 116.91 (CH), 114.01 (CH), 47.10 (N-CH), 30.10 (CH_2), 26.58 (CH_2), 22.57 (CH_3). HRMS (ESI) [M+H$^+$; calculated for $C_{10}H_{13}N$: 148.1120] found m/z 148.1119.



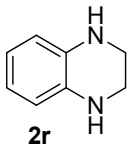
2p

7-fluoro-2-methyl-1,2,3,4-tetrahydroquinoline (2p).[15] Isolated yield: 84%. GC-MS (m/z, $M^{+\cdot}$ 165), major peaks found: 165 (29%), 150 (100%), 135 (16%), 109 (5%), 95 (5%), 75 (11%). (The NMR spectrum is consistent with the reported data). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.91-6.83 (m, 1H), 6.29 (td, *J* = 8.5, 2.6, 1H), 6.17 (dd, *J* = 10.9, 2.5, 1H), 3.75 (bs, NH), 3.40 (dqd, *J* = 9.3, 6.3, 3.0, 1H), 2.86-2.62 (m, 2H), 1.93 (dddd, *J* = 12.9, 5.4, 3.8, 2.9, 1H), 1.56 (dddd, *J* = 12.9, 11.0, 9.8, 5.7, 1H), 1.21 (d, *J* = 6.3, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 162.24 (d, $J^{1}_{C\text{-}F}$ = 240.5, d, C), 145.93 (d, $J^{3}_{C\text{-}F}$ = 10.8, C), 130.16 (d, $J^{3}_{C\text{-}F}$ = 9.8, CH), 116.63 (C), 103.44 (d, $J^{2}_{C\text{-}F}$ = 21.6, CH), 100.26 (d, $J^{2}_{C\text{-}F}$ = 24.4, CH), 47.13 (N-CH), 30.09 (CH_2), 26.09 (CH_2), 22.59 (CH_3). ^{19}F NMR (282 MHz, $CDCl_3$) δ: -116.73-(-116.83) (m, 1F). HRMS (ESI) [M+H$^+$; calculated for $C_{10}H_{12}FN$: 166.1026] found m/z 166.1026.



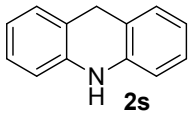
2q

1,2,3,4-tetrahydro-1,5-naphthyridine (2q).[10] Isolated yield: 88%. GC-MS (m/z, $M^{+\cdot}$ 134), major peaks found: 134 (95%), 133 (100%), 119 (15%), 106 (14%), 79 (10%), 66 (9%), 52 (7%). (The NMR spectrum is consistent with the reported data). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (dd, *J* = 4.7, 1.3, 1H), 6.87 (dd, *J* = 8.0, 4.7, 1H), 6.72 (dd, *J* = 8.1, 1.4, 1H), 3.59 (bs, NH), 3.28 (t, *J* = 5.4, 2H), 2.92 (t, *J* = 6.5, 2H), 2.09-1.94 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 142.60 (C), 141.14 (C), 137.60 (CH), 122.07 (CH), 120.47 (CH), 41.56 (N-CH_2), 30.20 (CH_2), 21.76 (CH_2). HRMS (ESI) [M^+; calculated for $C_8H_{10}N_2$: 135.0916] found m/z 135.0916.



2r

1,2,3,4-tetrahydroquinoxaline (2r).[16] Isolated yield: 90%. GC-MS (m/z, $M^{+\cdot}$ 134), major peaks found: 134 (85%), 133 (100%), 119 (5%), 103 (10%), 92 (12%), 77 (10%), 66 (8%). (The NMR spectrum is consistent with the reported data). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.62-6.55 (m, 2H), 6.53-6.47 (m, 2H), 3.42 (s, 4H), 3.31 (bs, 2NH). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 133.77 (2xC), 118.86 (2xCH), 114.82 (2xCH), 41.48 (2xCH_2). HRMS (ESI) [$M+H^+$; calculated for $C_8H_{10}N_2$: 135.0916] found m/z 135.0916.



2s

9,10-dihydroacridine (2s).[17] Isolated yield: 78%. GC-MS (m/z, $M^{+\cdot}$ 181), major peaks found: 181 (45%), 180 (100%), 152 (10%), 90 (10%), 76 (5%). (The NMR spectrum is consistent with the reported data). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.17-7.07 (m, 4H), 6.89 (ddd, *J* = 7.4, 7.4, 1.2, 2H), 6.68 (d, *J* = 7.9, 2H), 5.96 (bs, NH), 4.08 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 140.22 (2xC), 128.71 (2xCH), 127.10 (2xCH), 120.73 (2xCH), 120.13 (2xC), 113.55 (2xCH), 31.49 (CH_2). HRMS (ESI) [$M+H^+$; calculated for $C_{13}H_9N$: 180.0807] found m/z 180.0807.

6. REFERENCES

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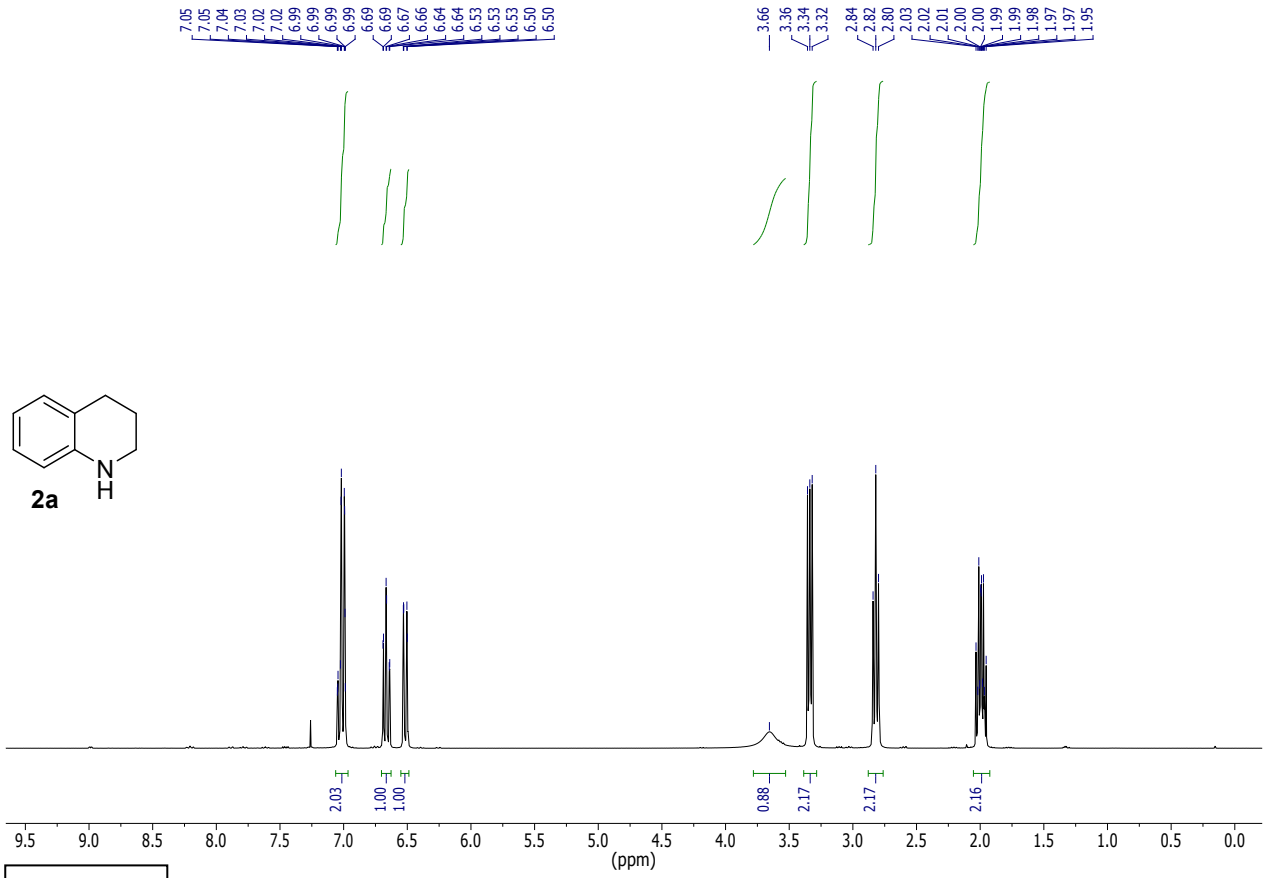
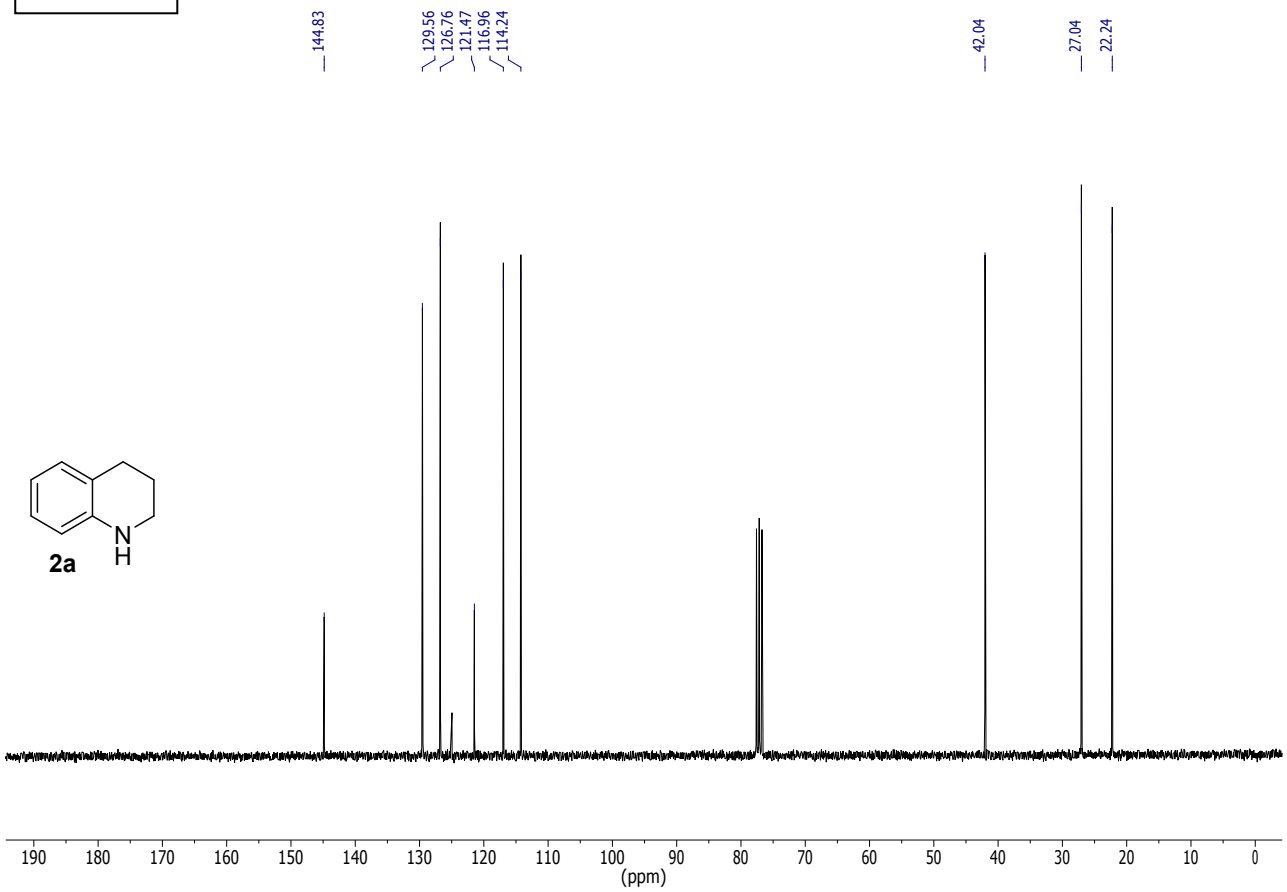
7. NMR SPECTRA OF THE ISOLATED PRODUCTS

^{1}H NMR



^{13}C NMR



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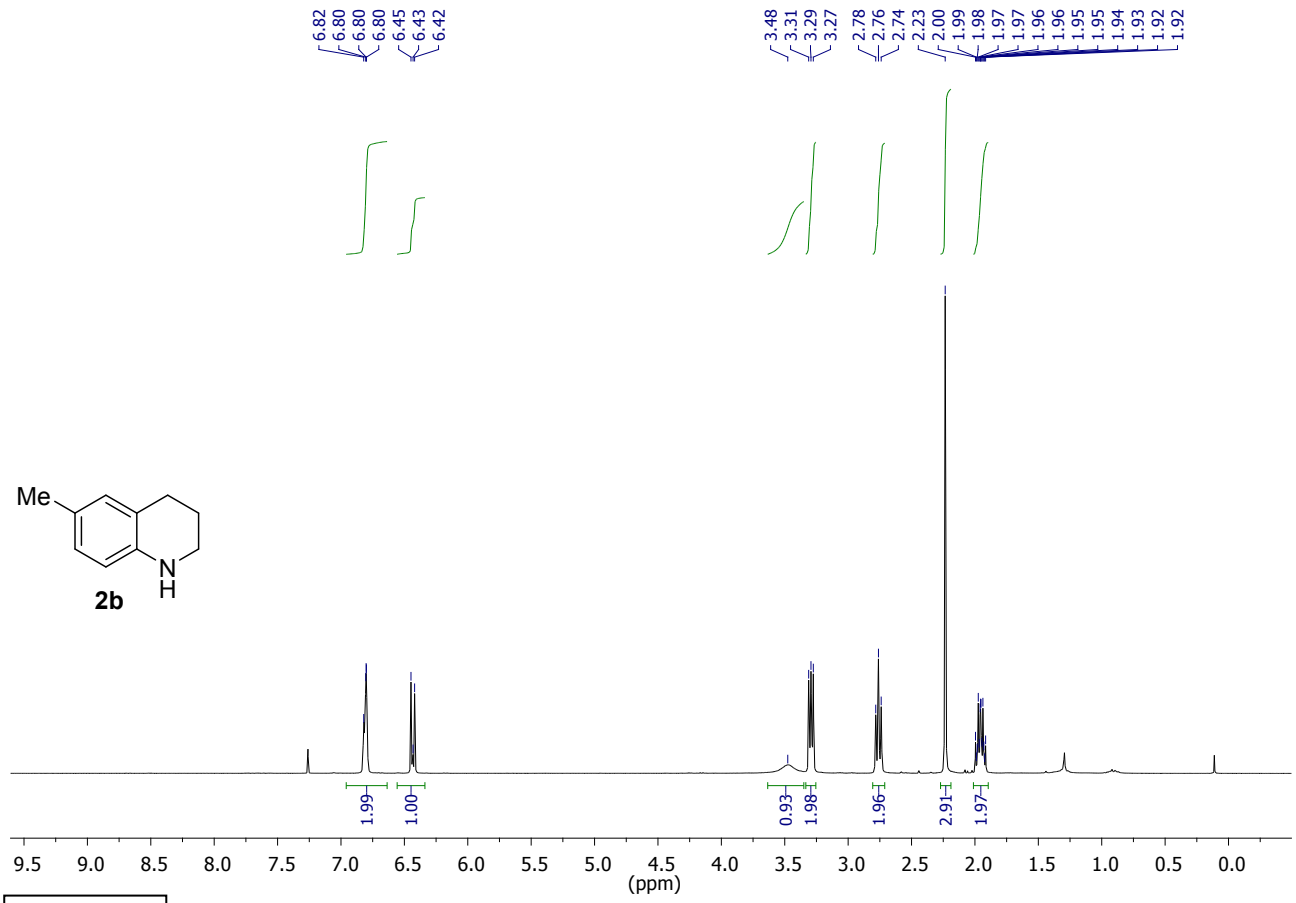

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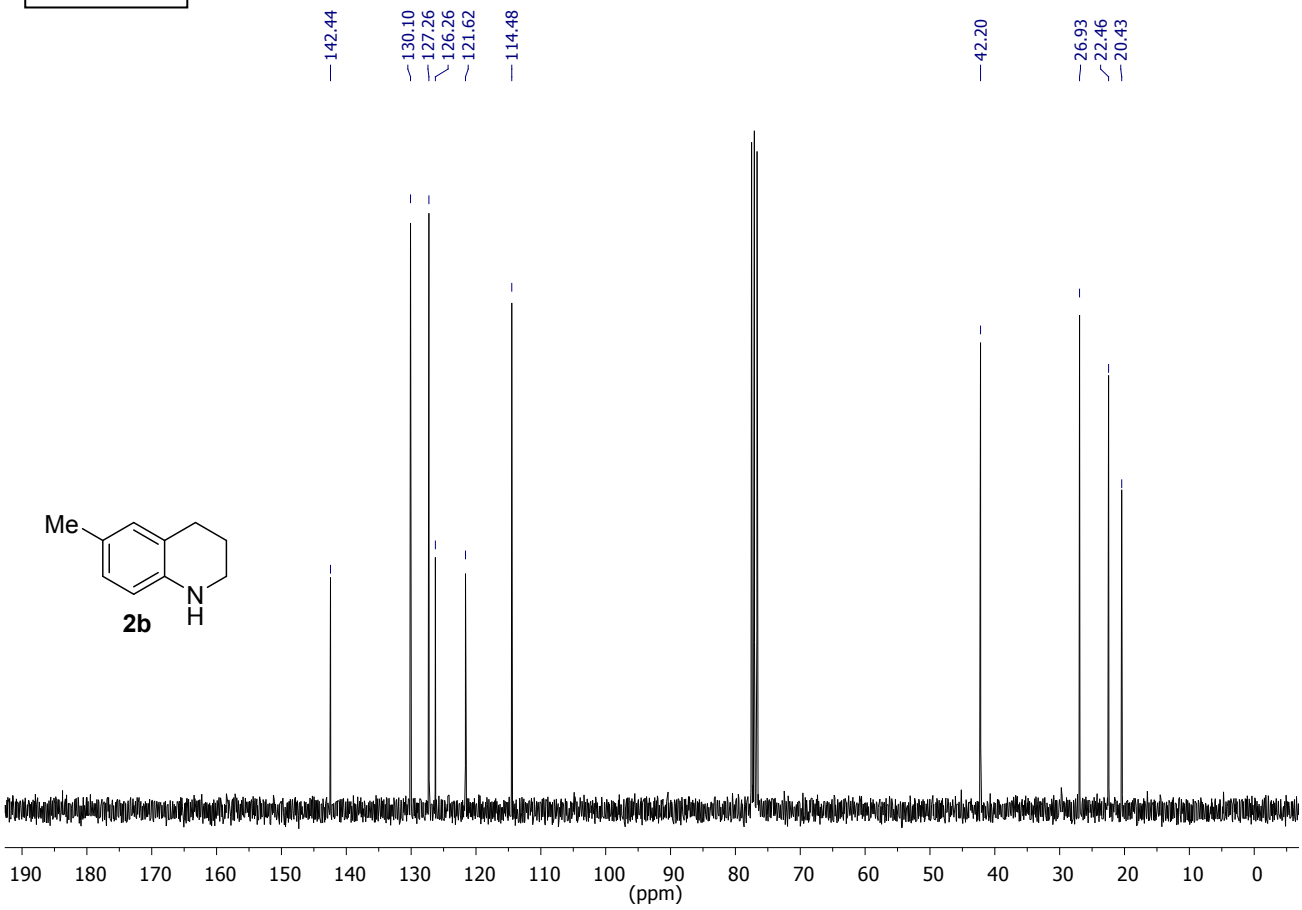

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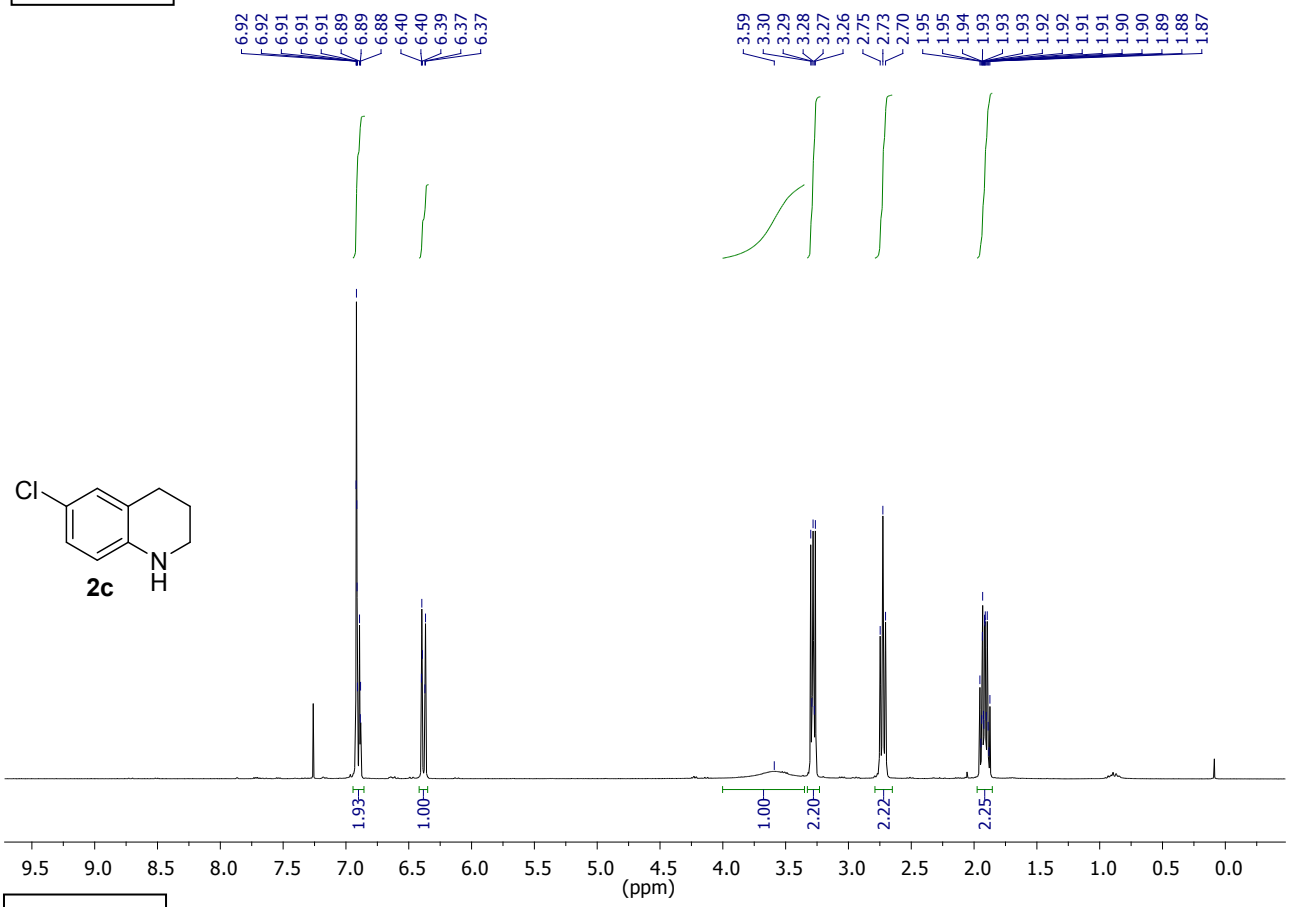

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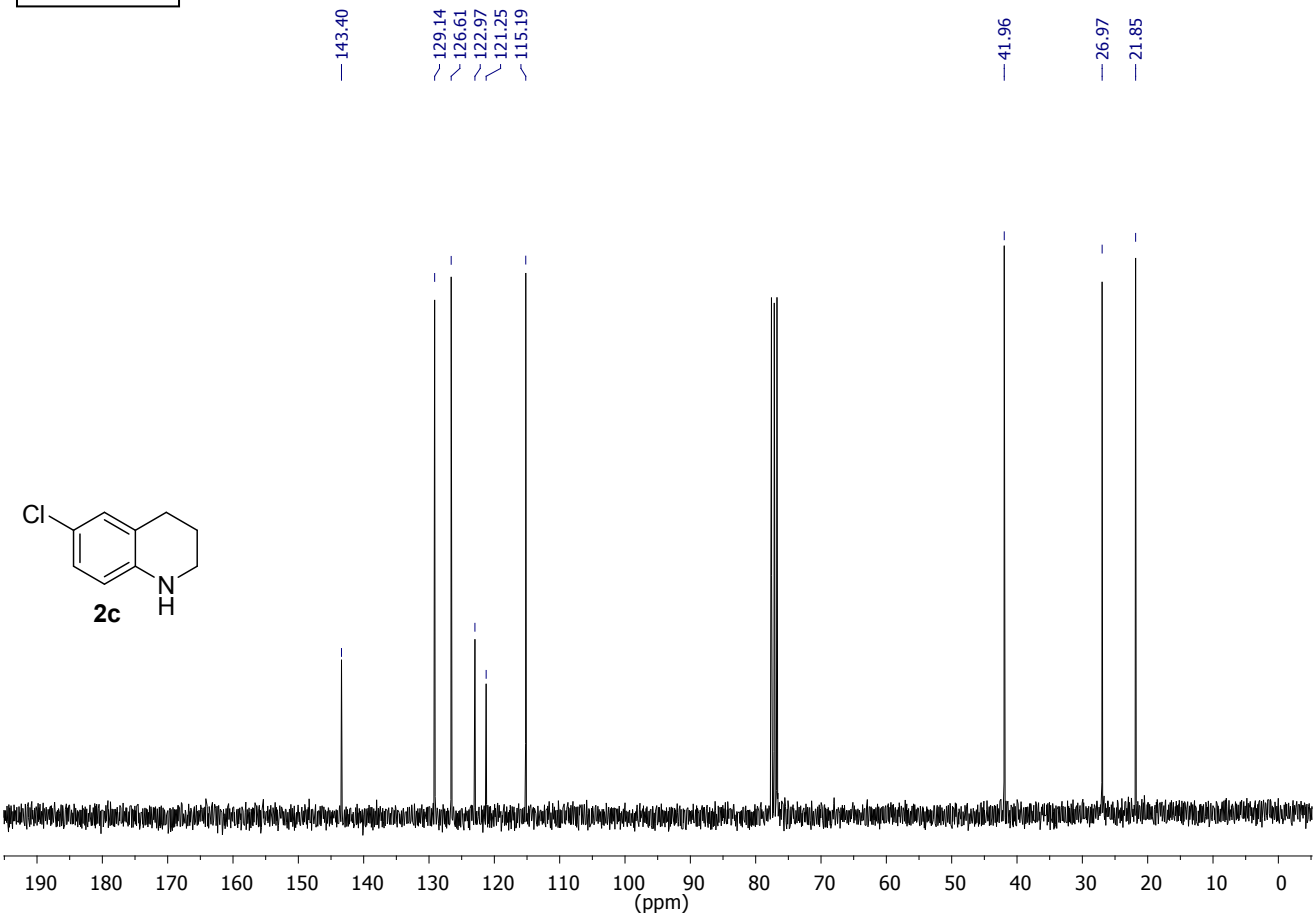

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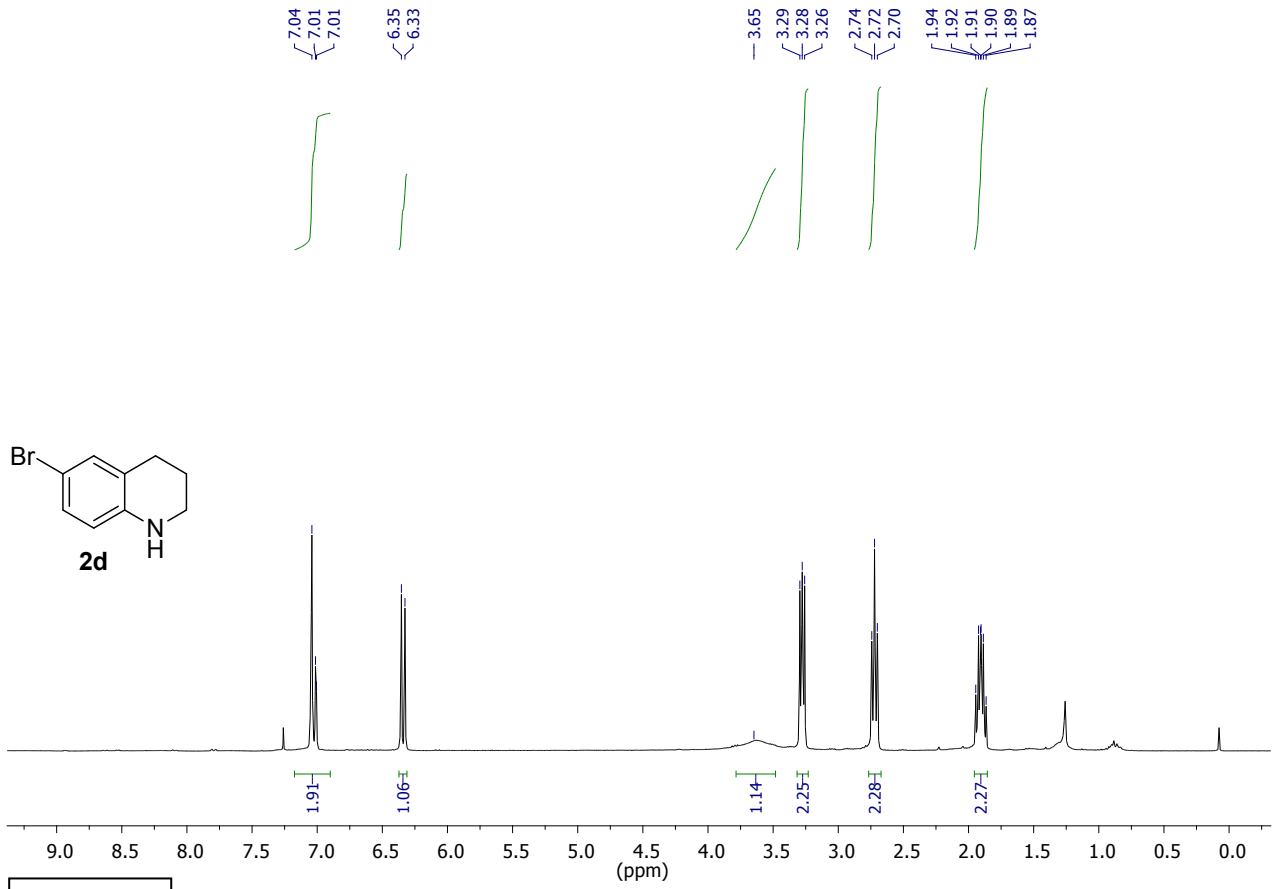

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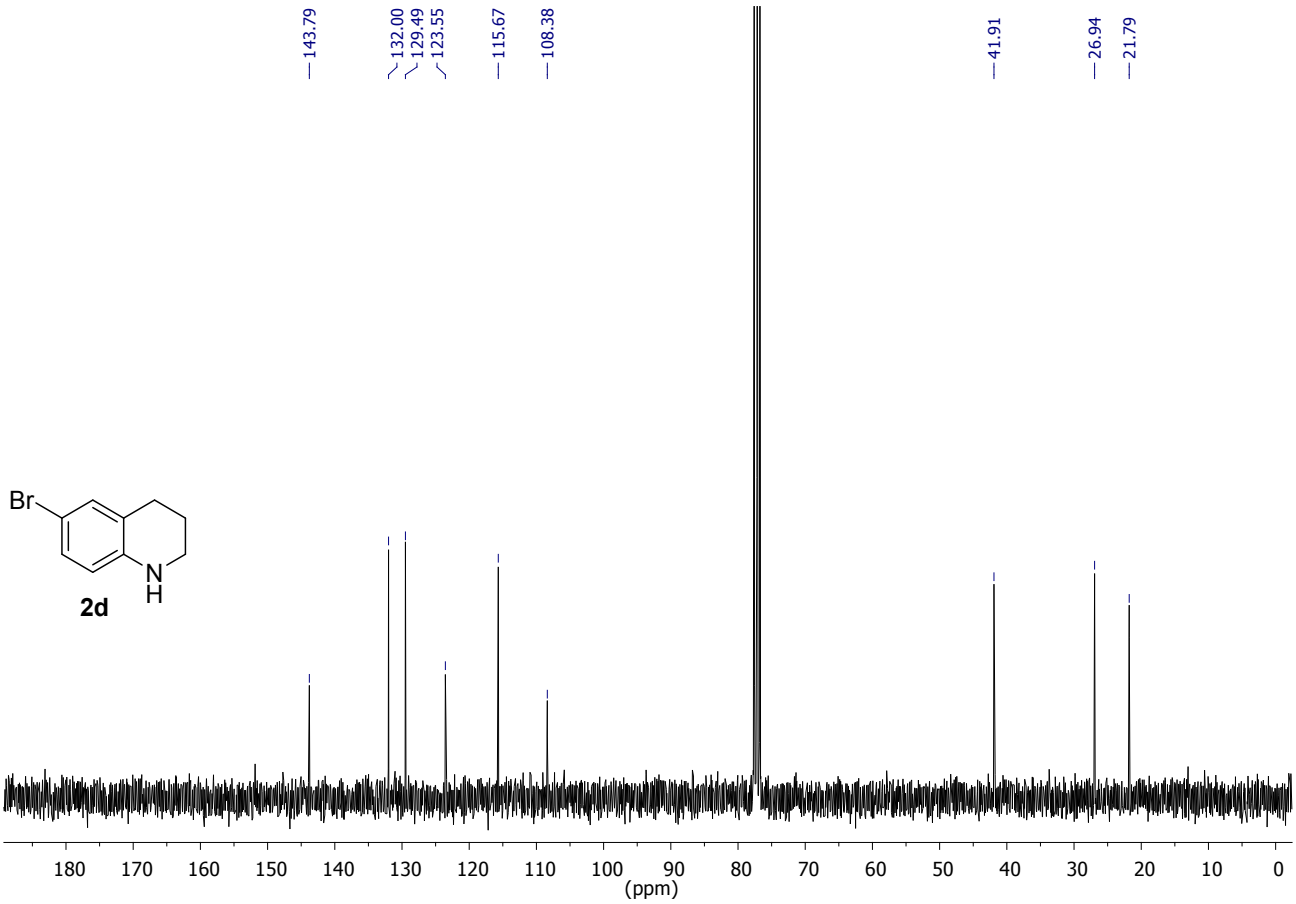

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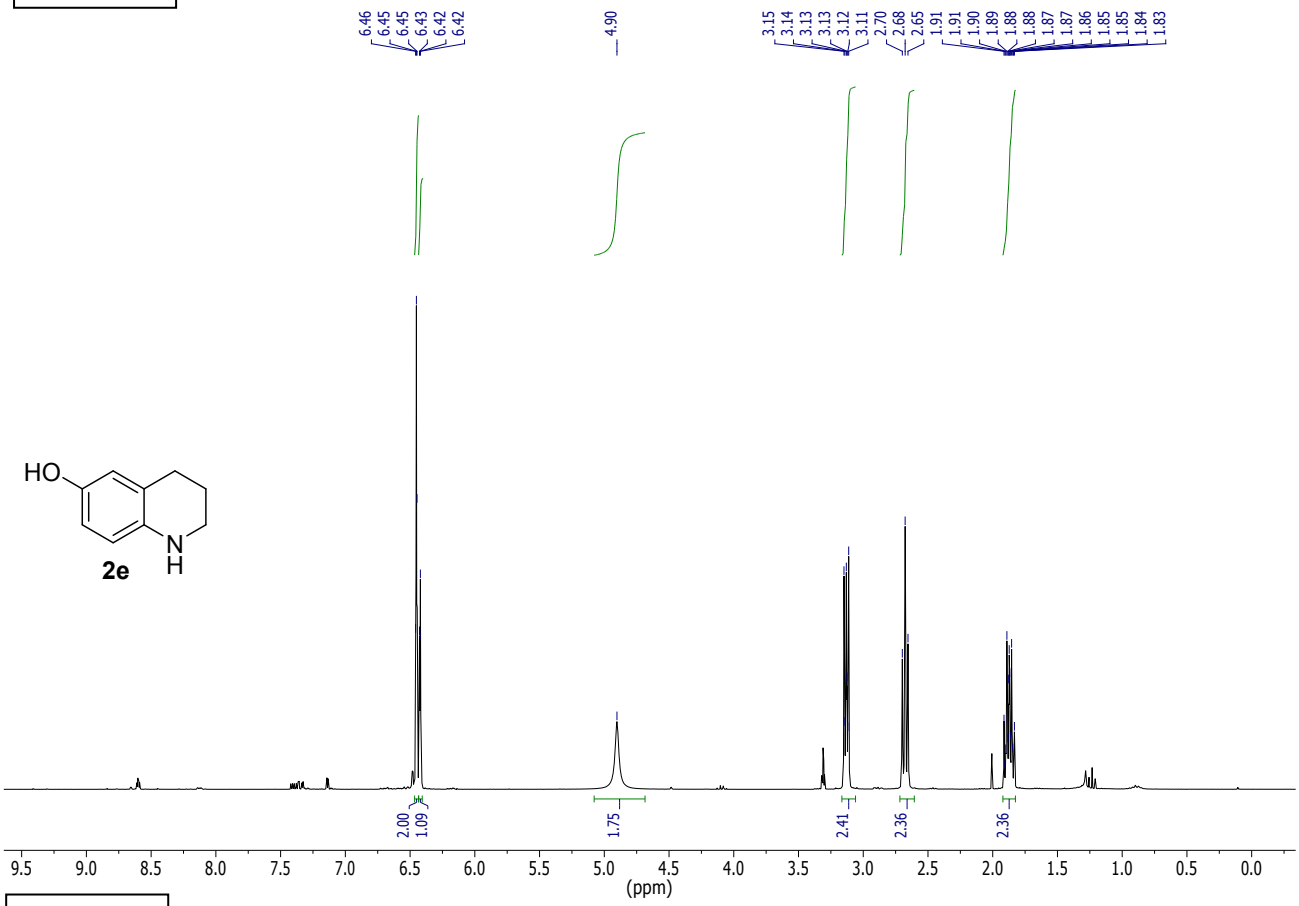

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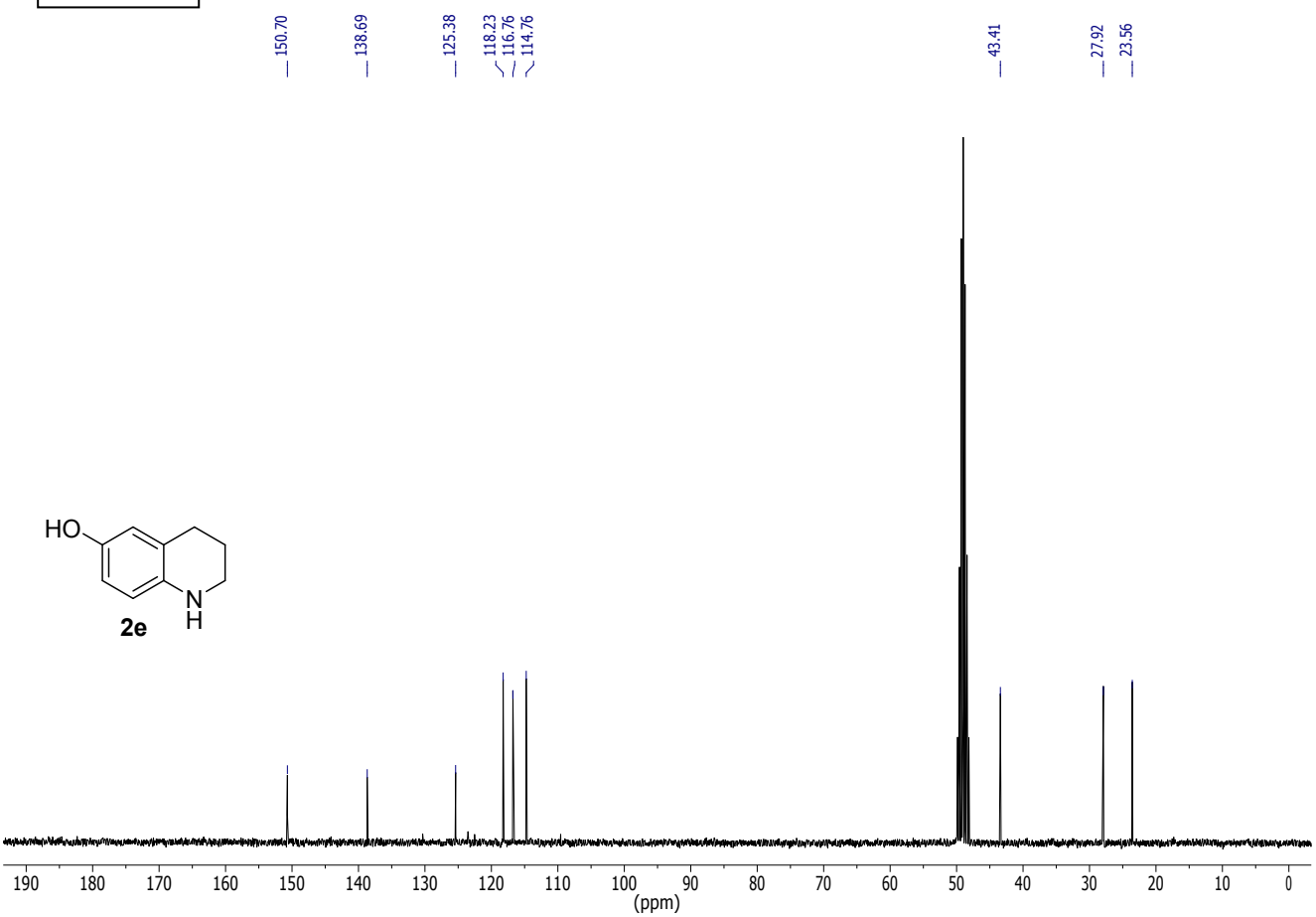
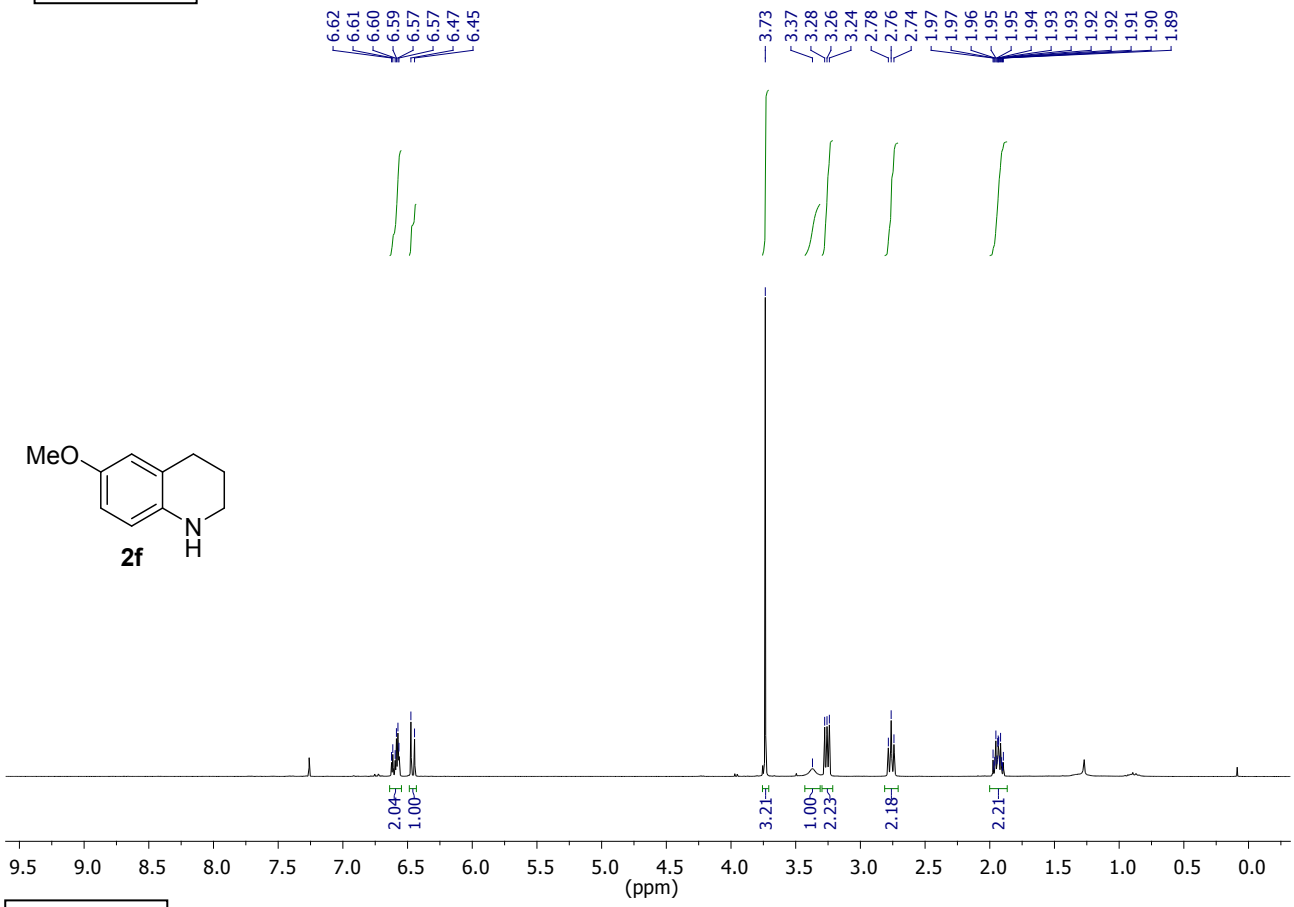
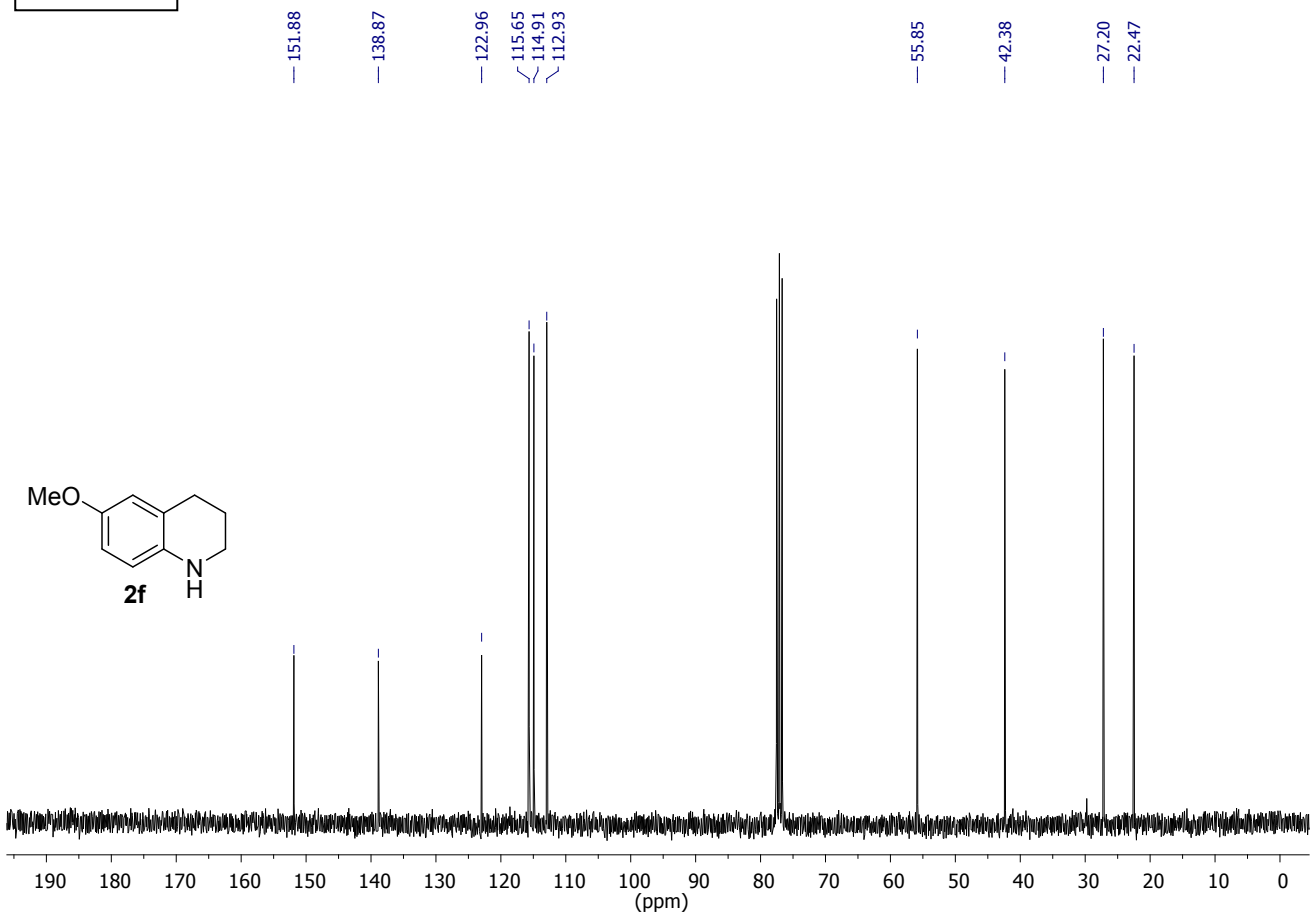


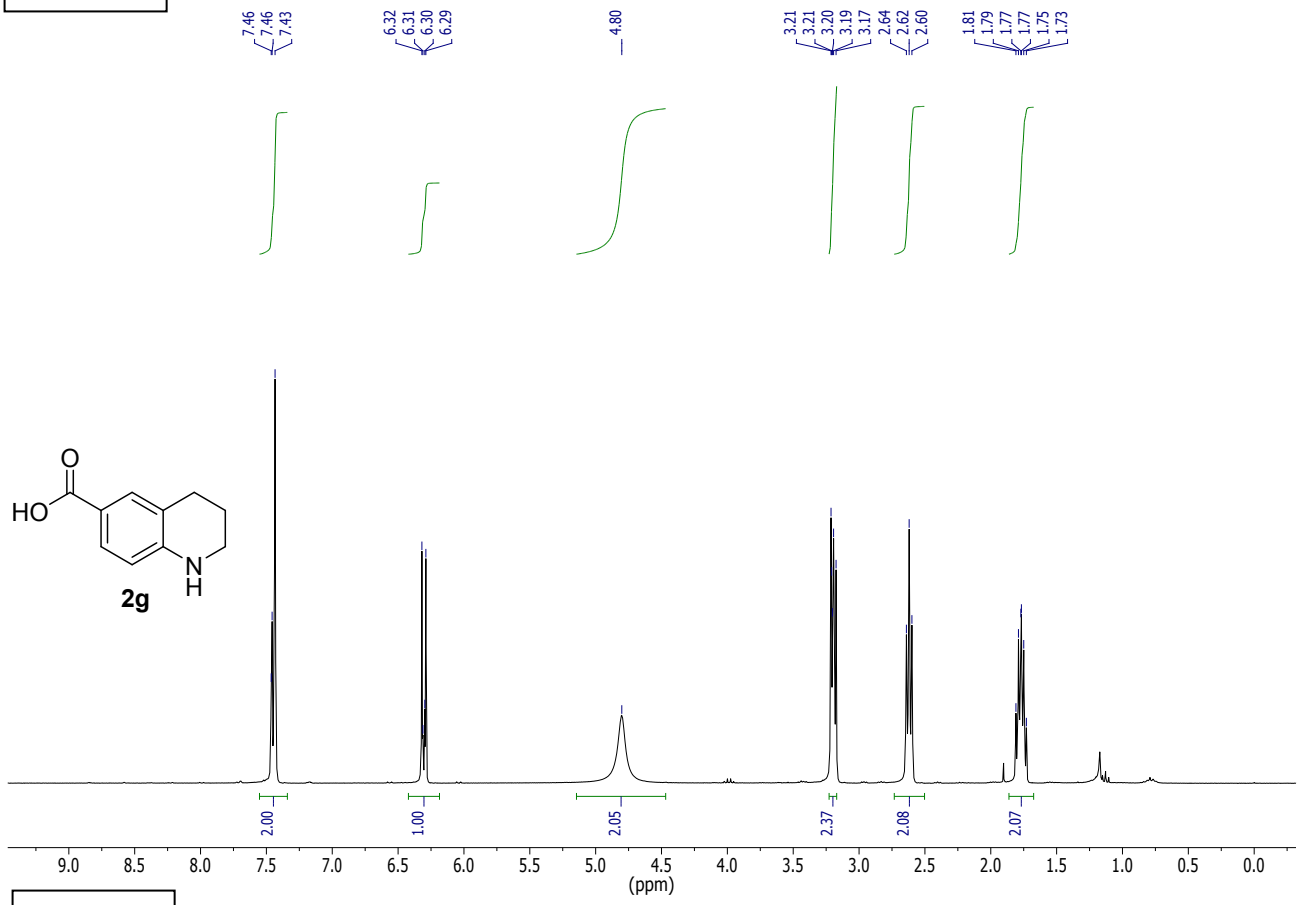
^{1}H NMR



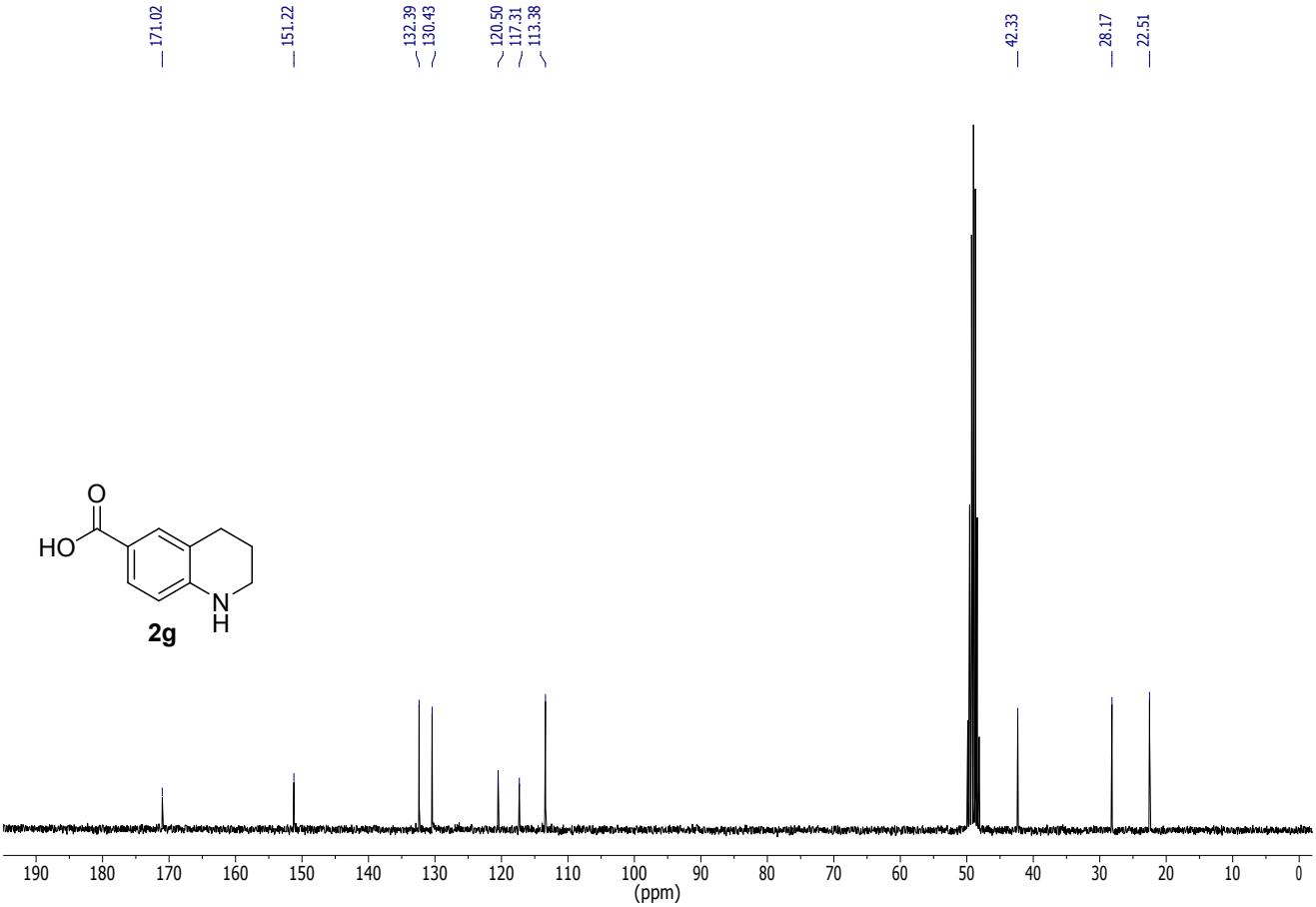
^{13}C NMR



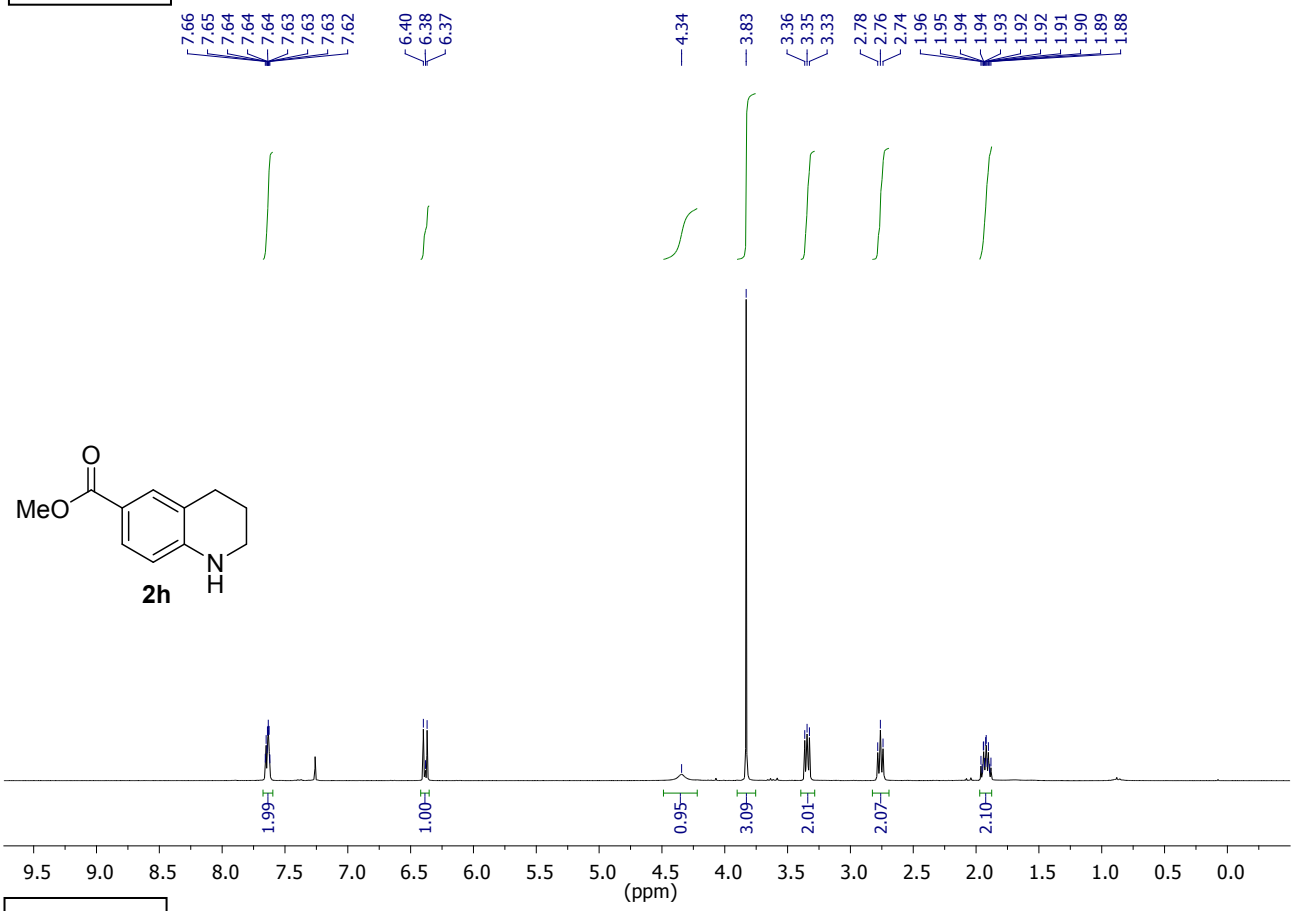
^{1}H NMR



^{13}C NMR



^{1}H NMR



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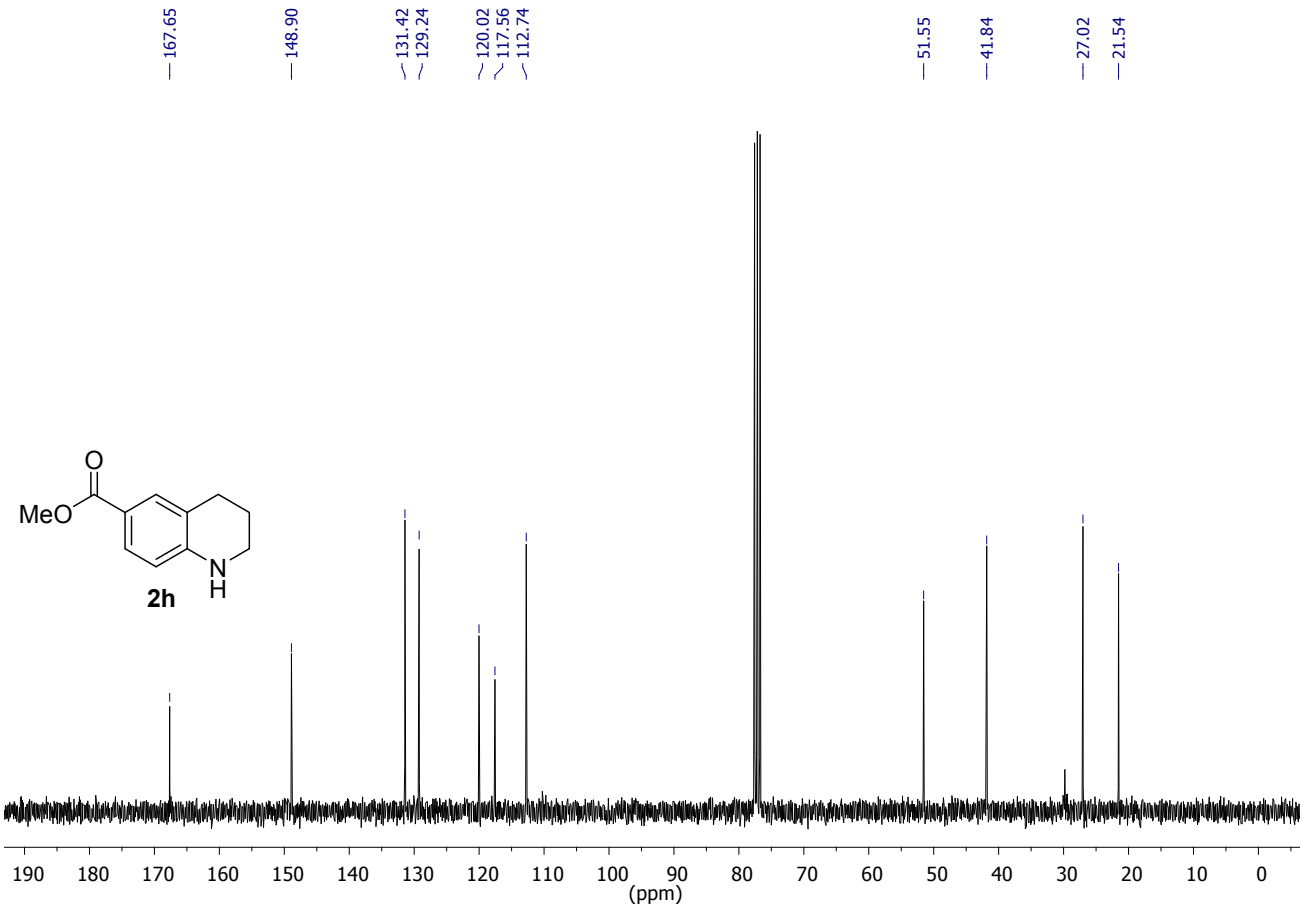
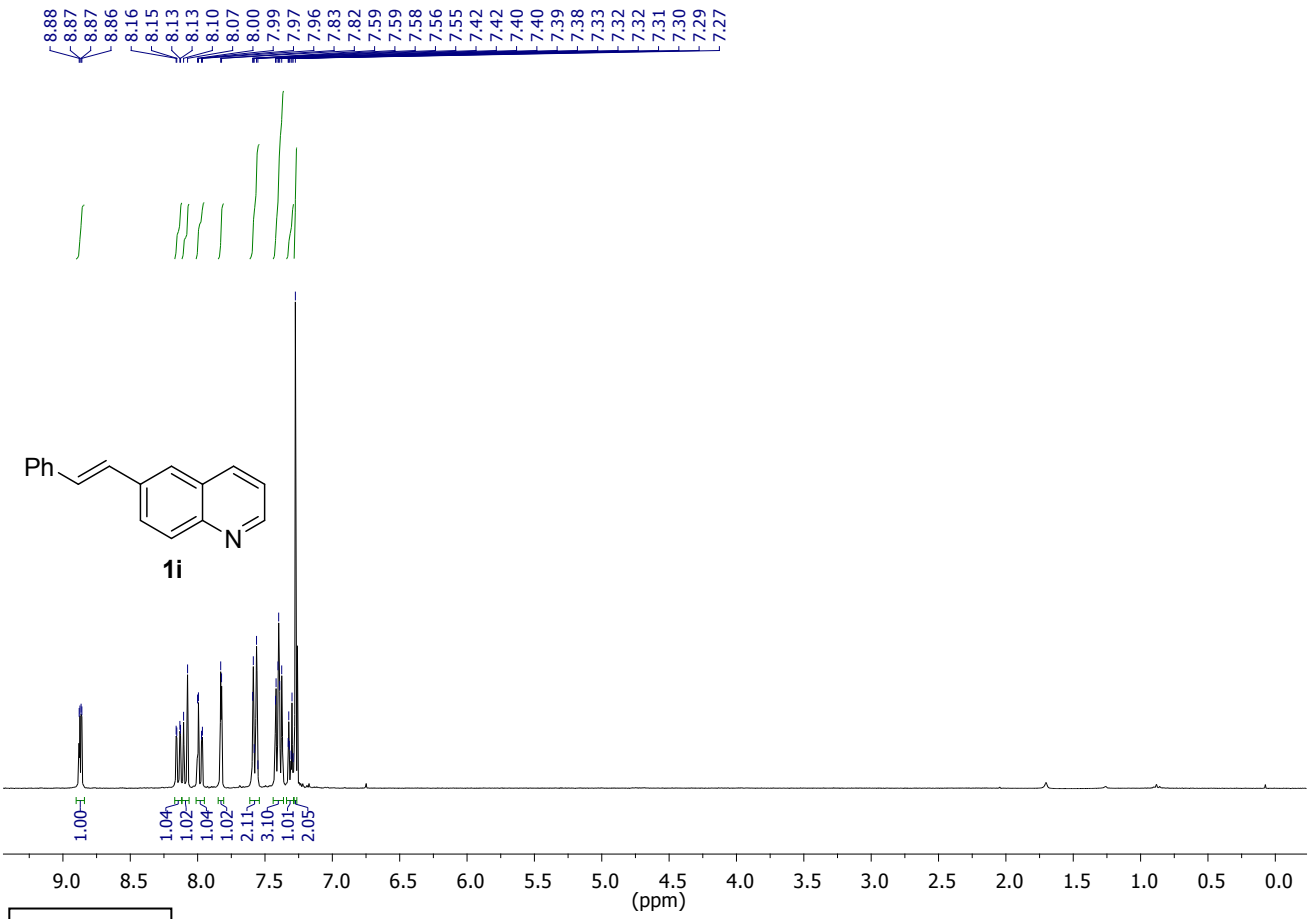
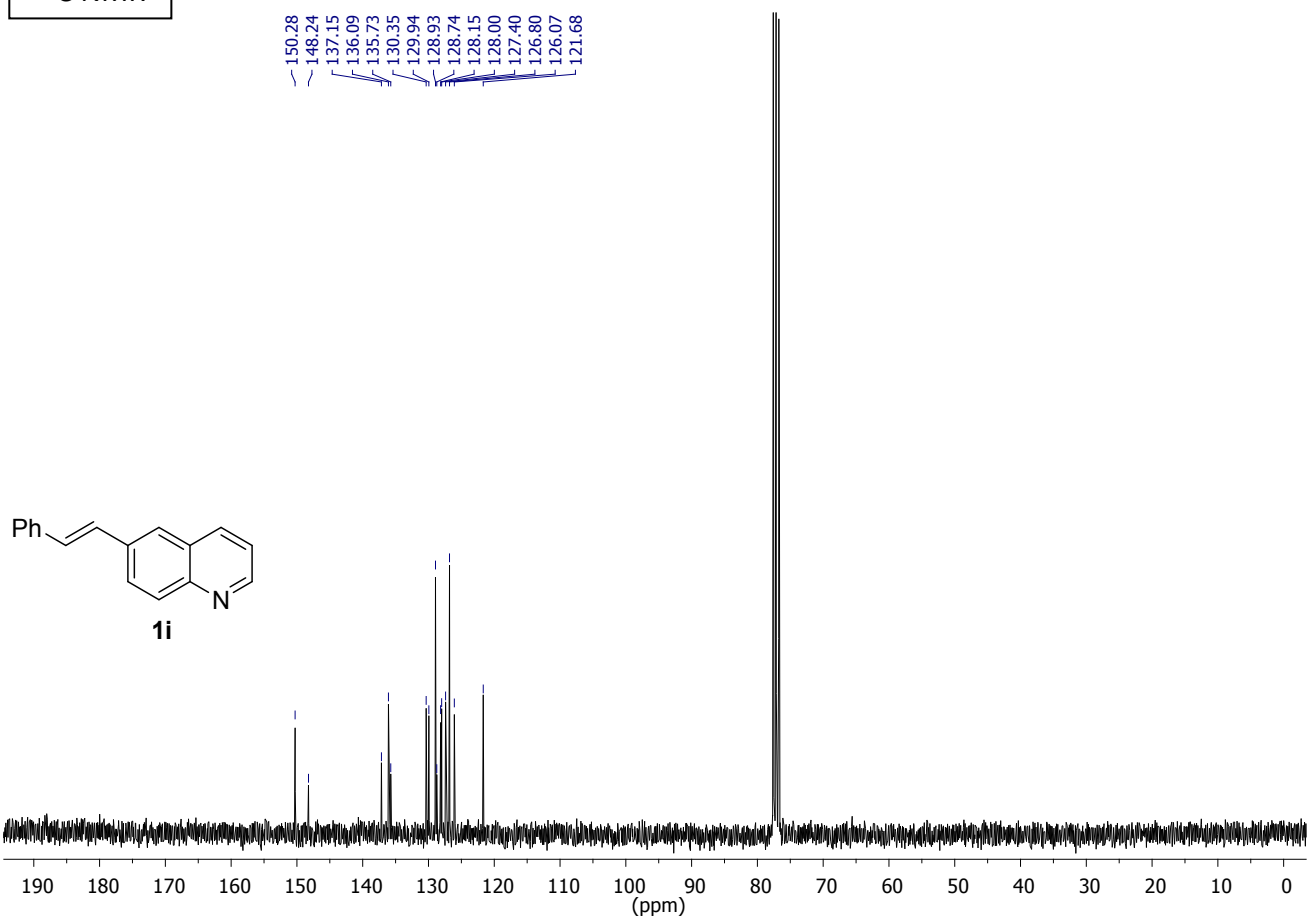


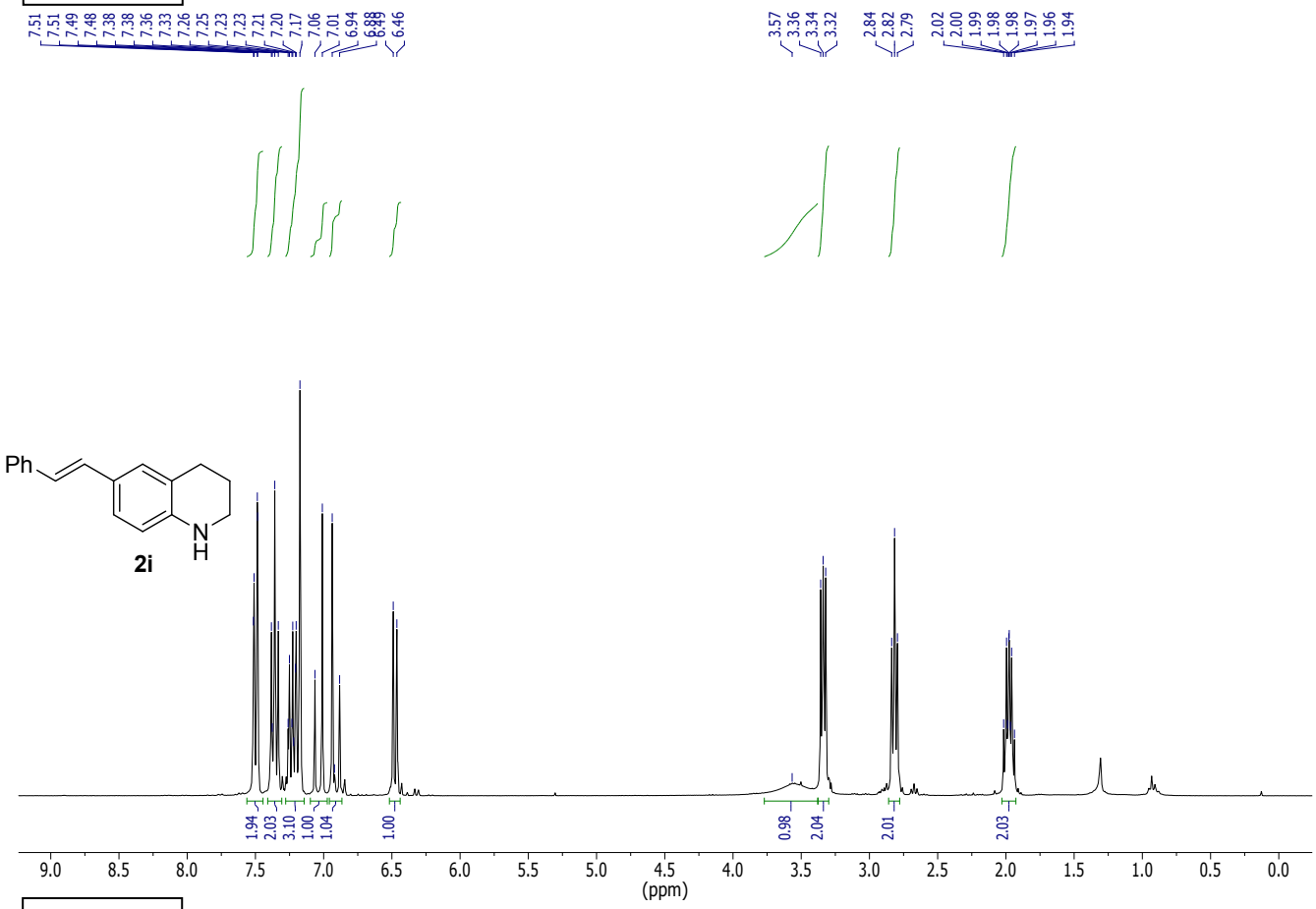
^{1}H NMR



^{13}C NMR



^{1}H NMR



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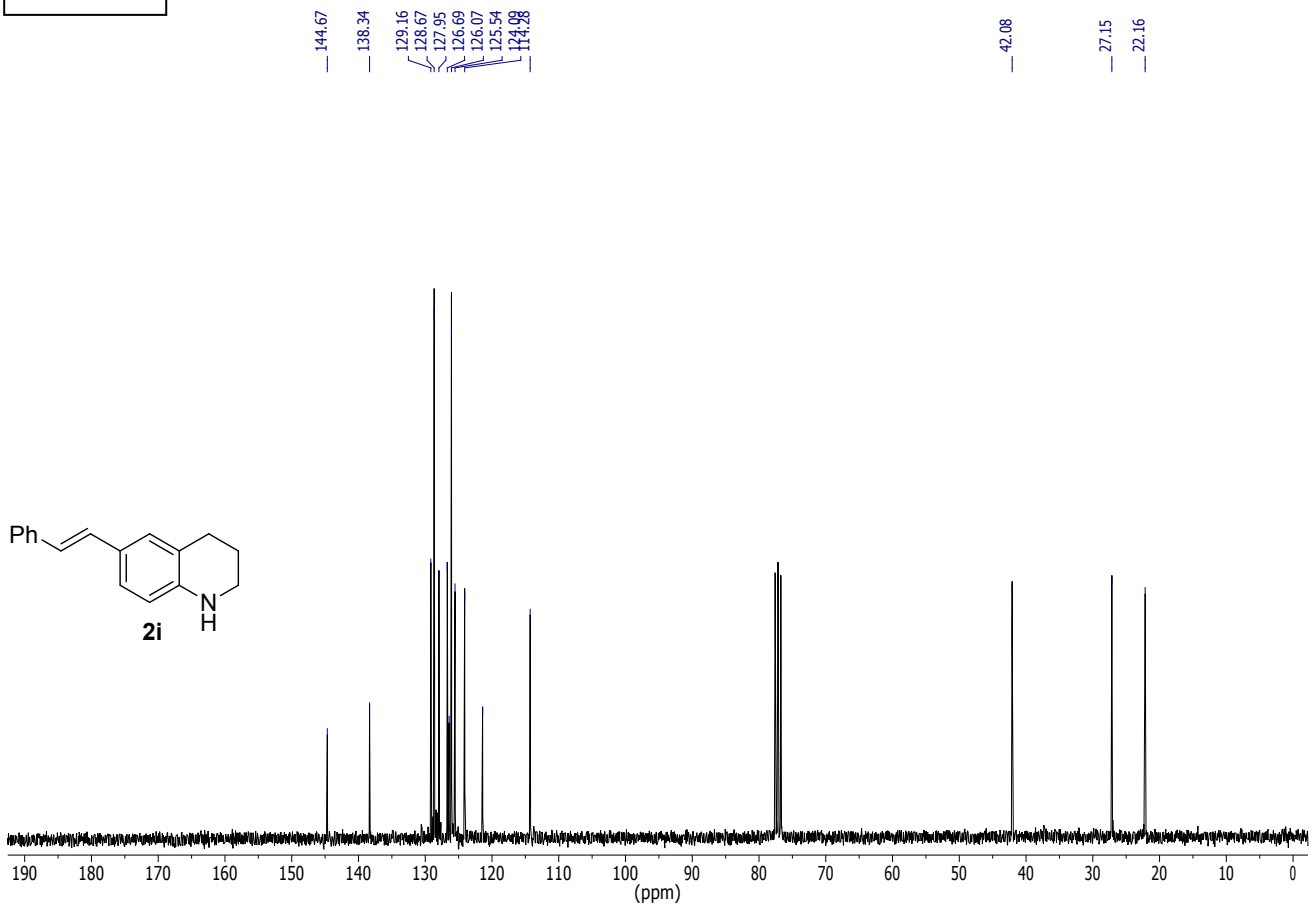
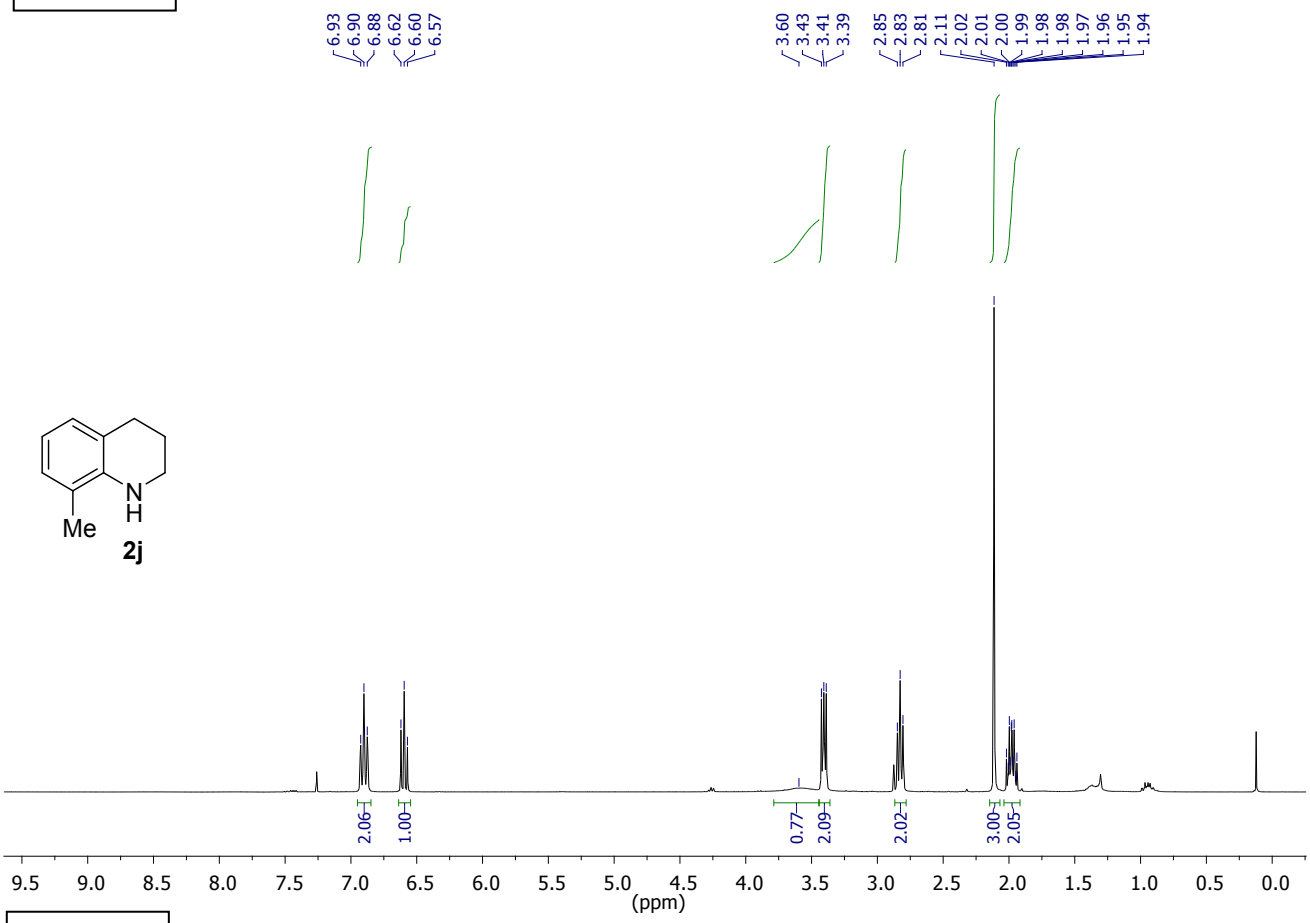


^{1}H NMR



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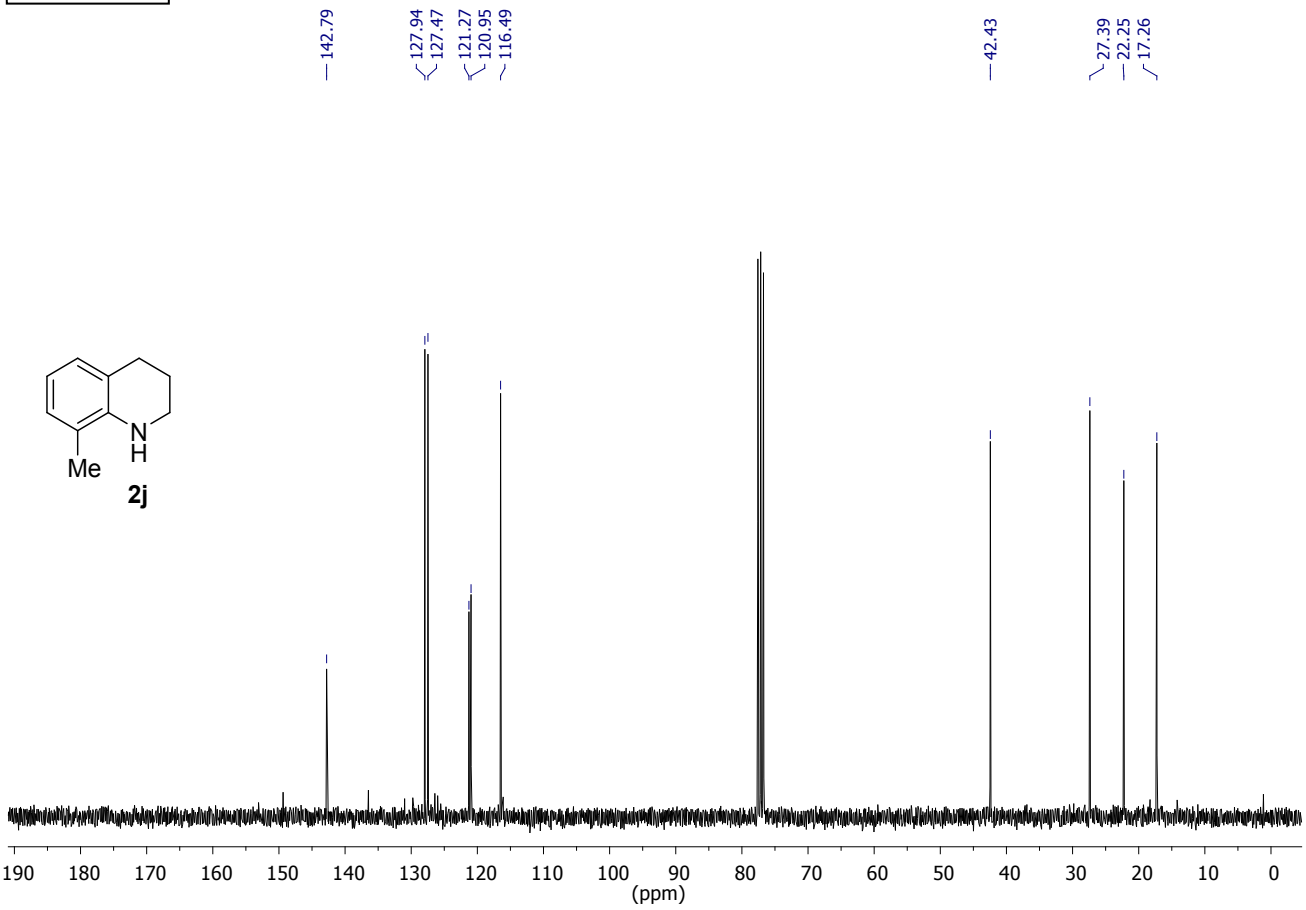
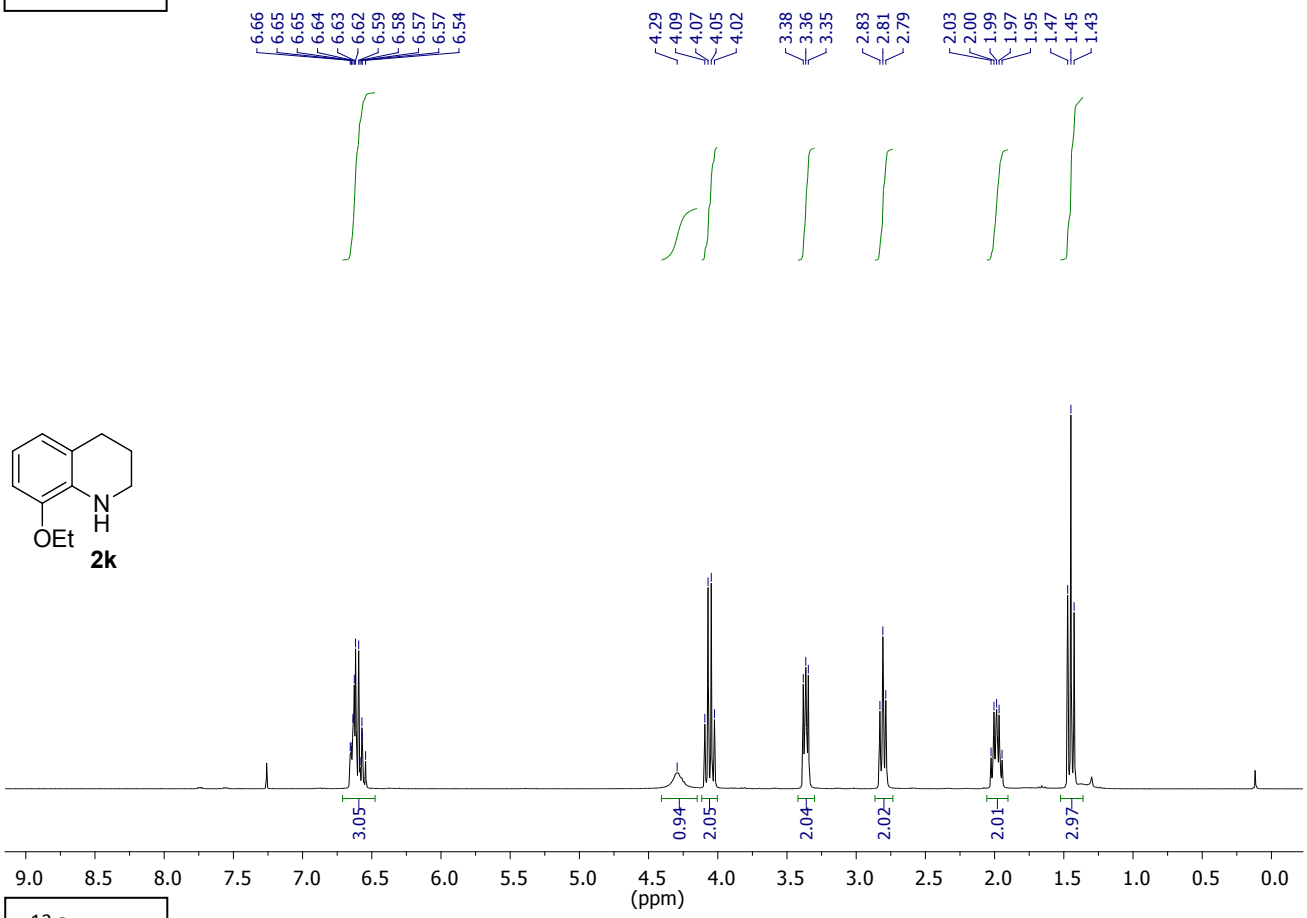
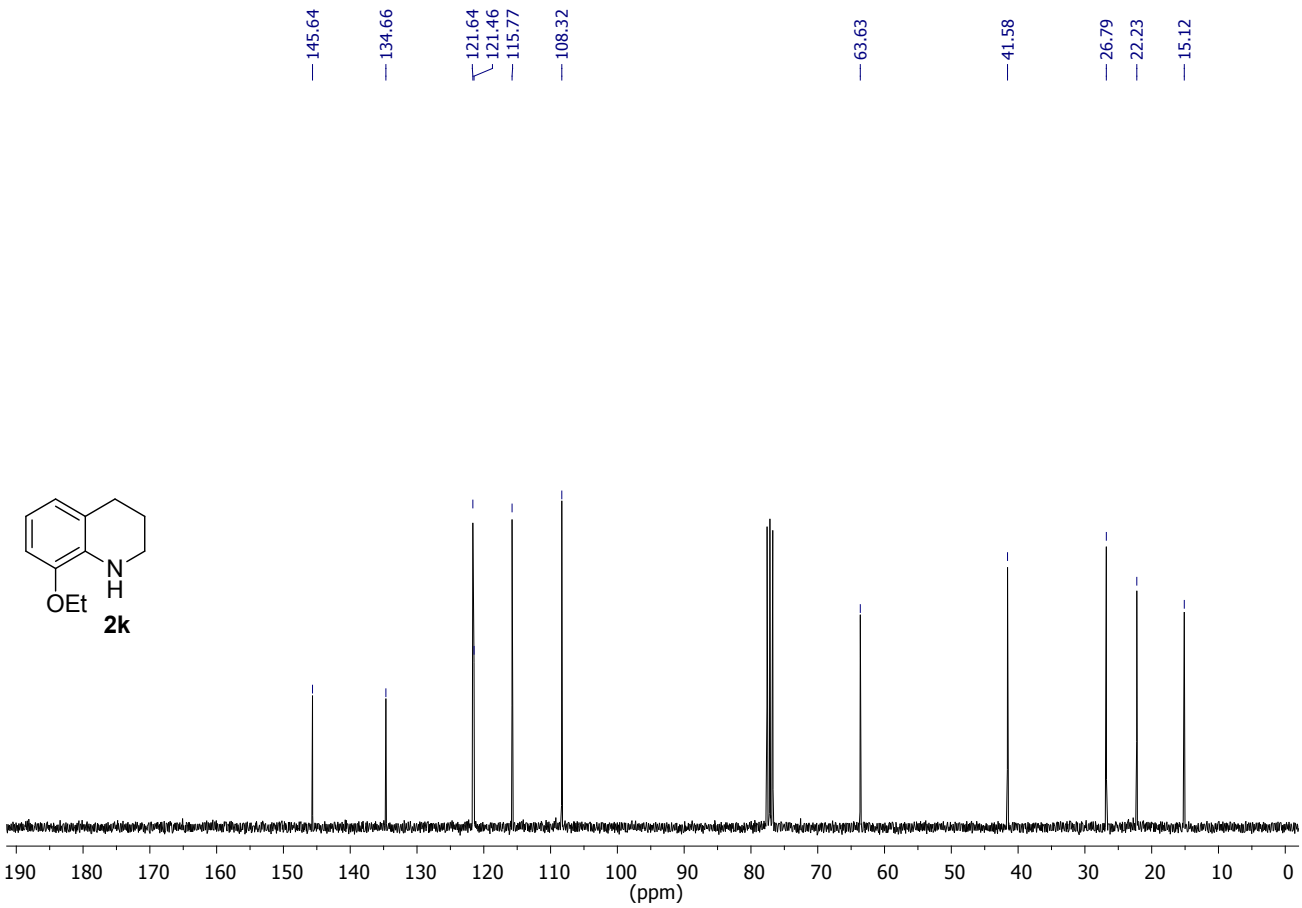


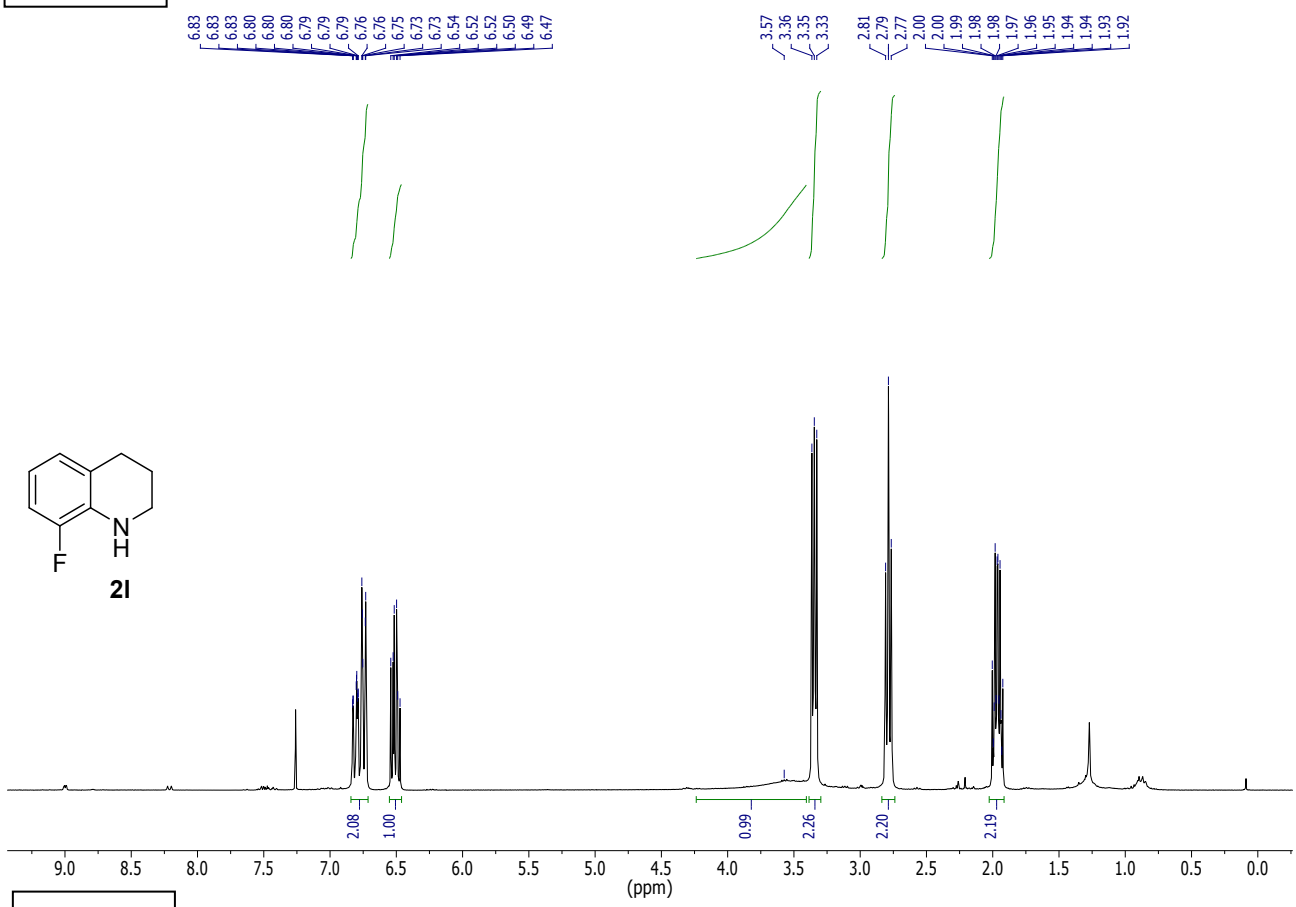
^{1}H NMR



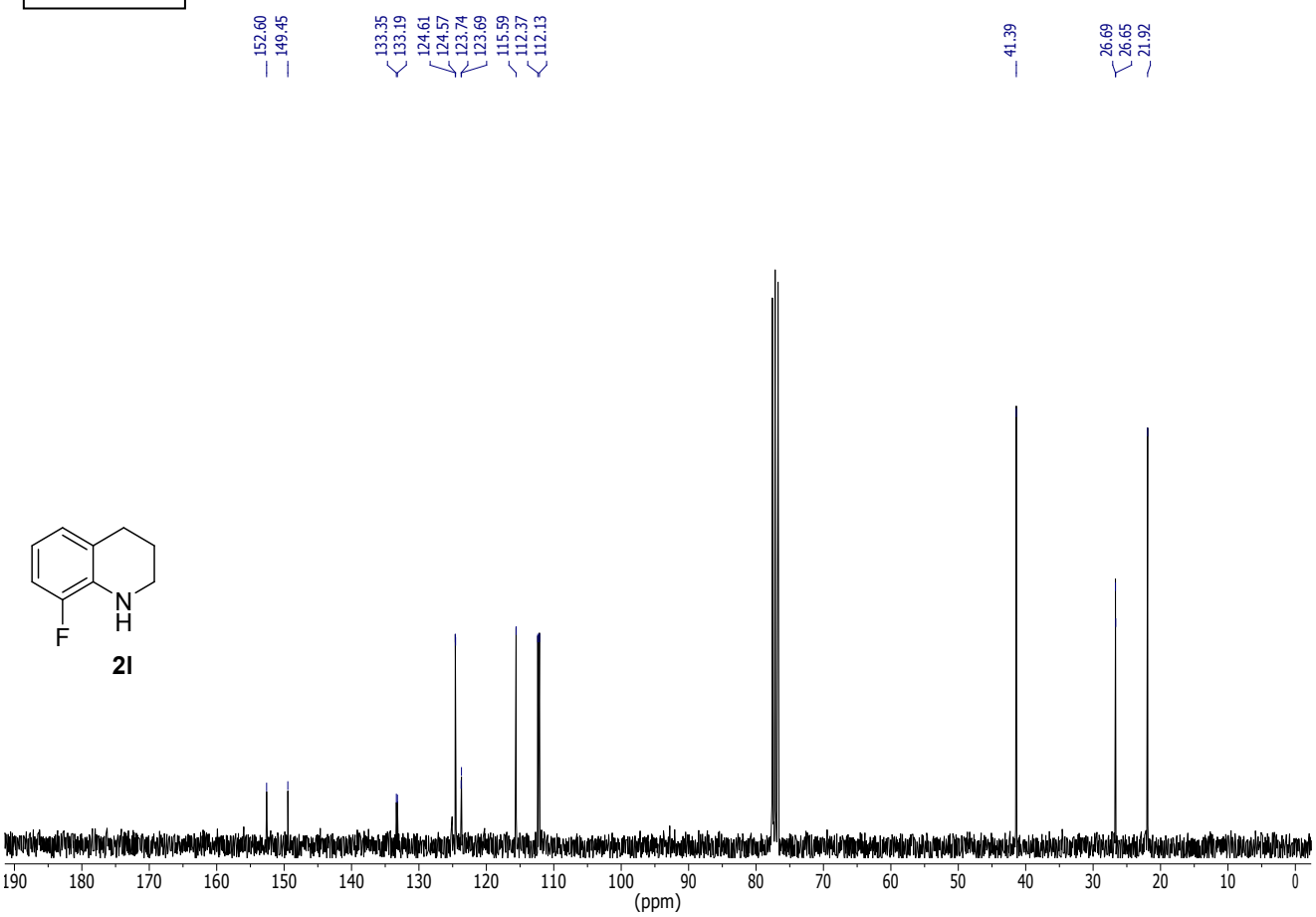
^{13}C NMR



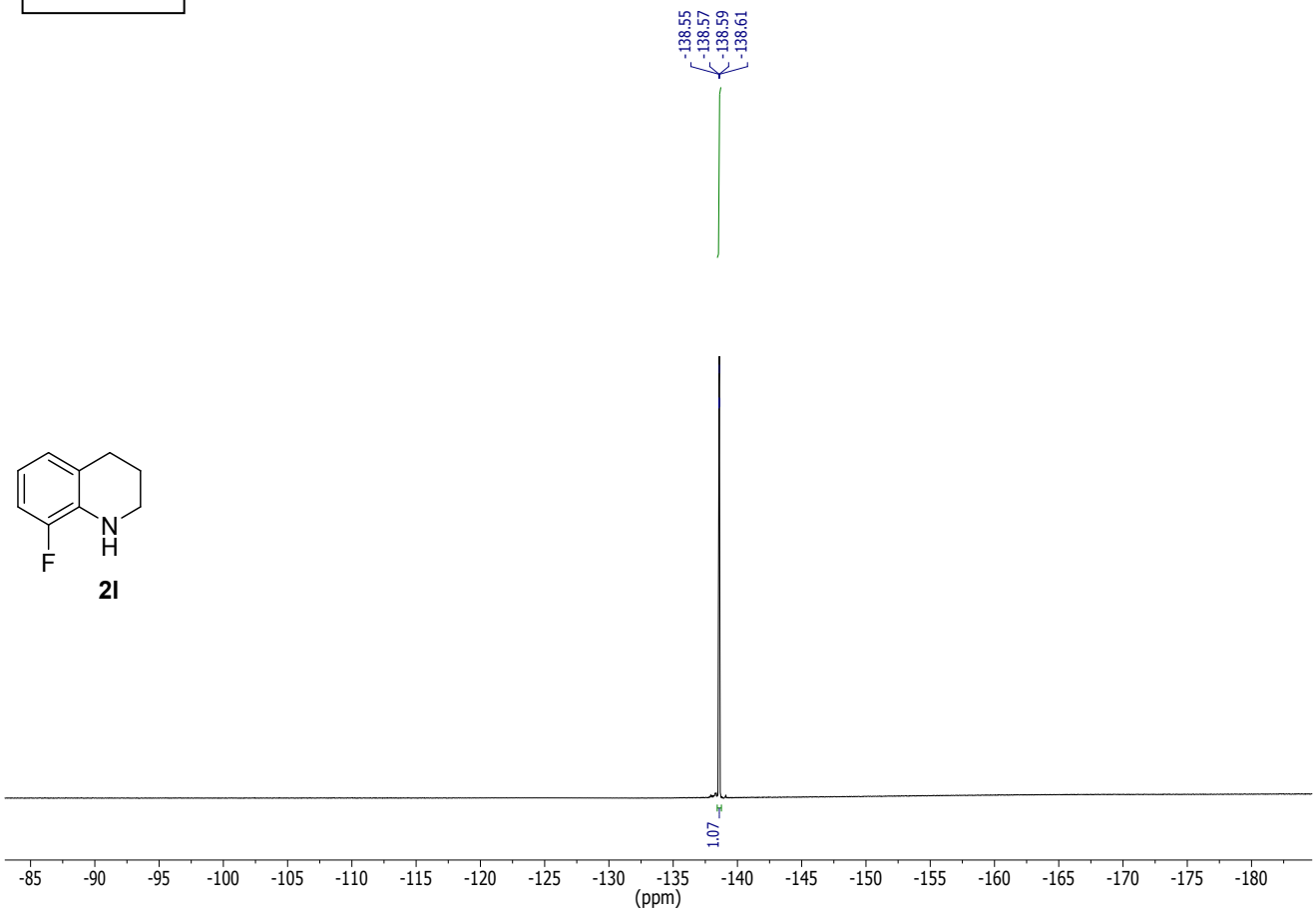
^{1}H NMR



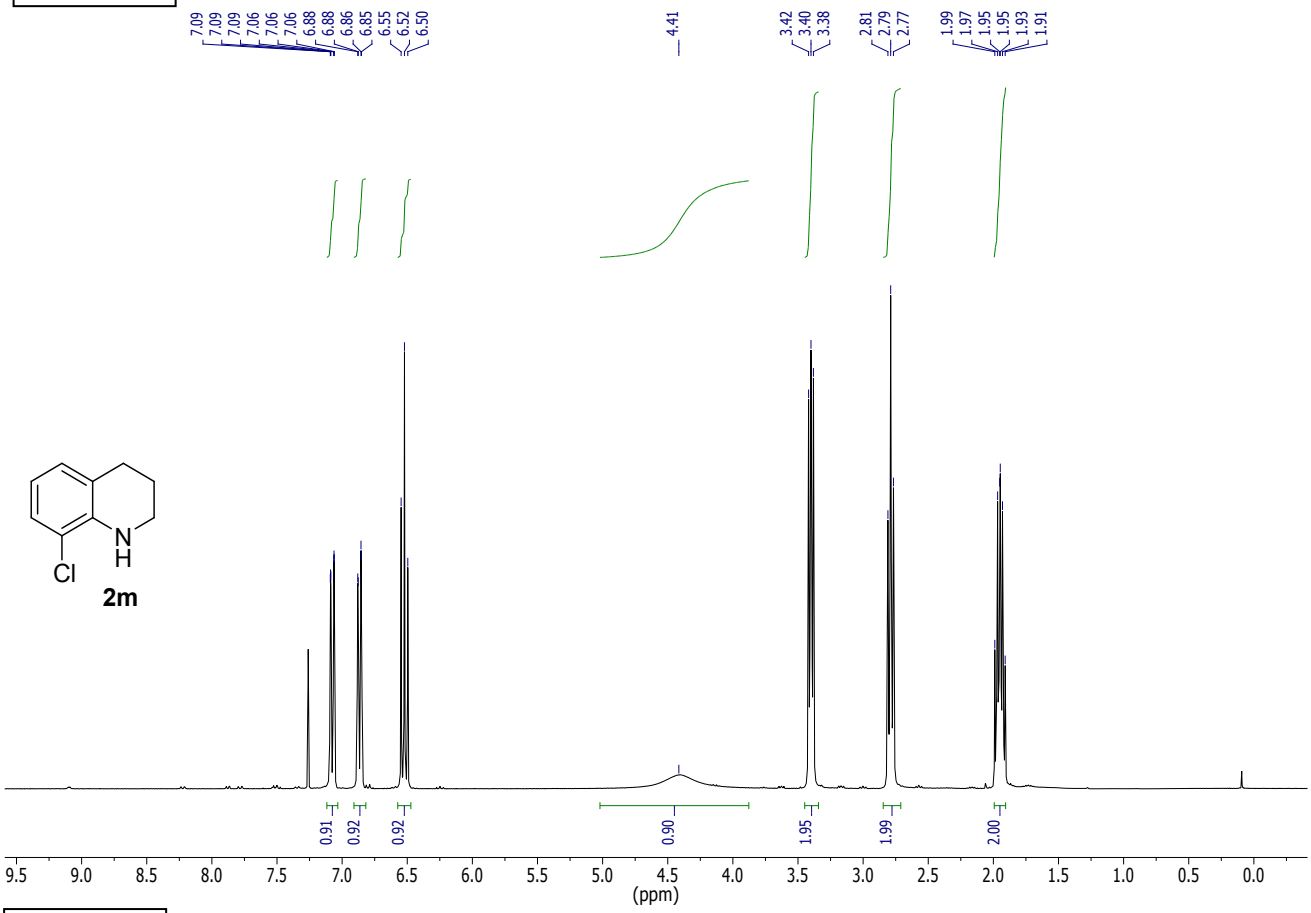
^{13}C NMR



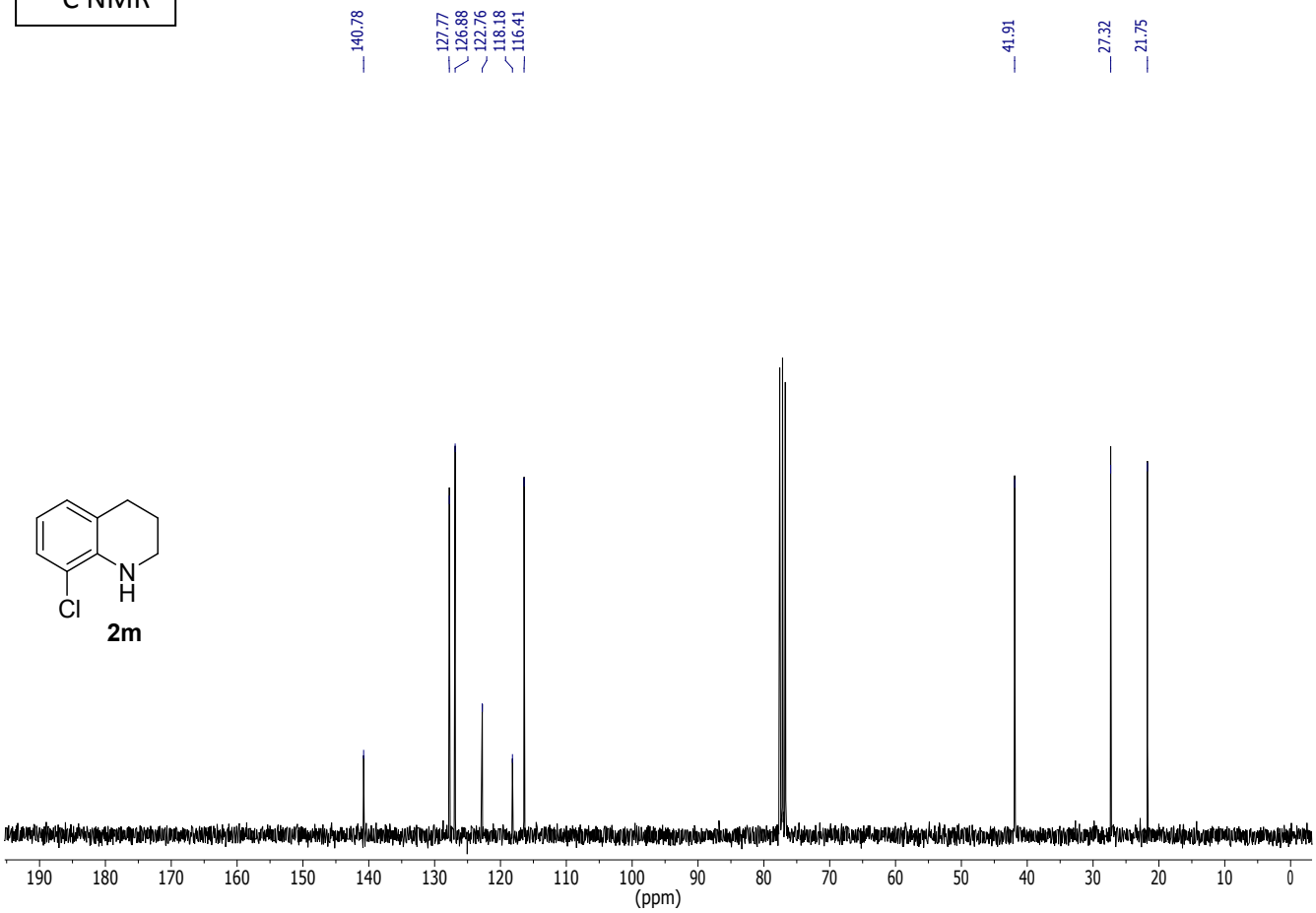
^{19}F NMR


-138.55
-138.57
-138.59
-138.61
N
H
F
2l
1.07
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180
(ppm)

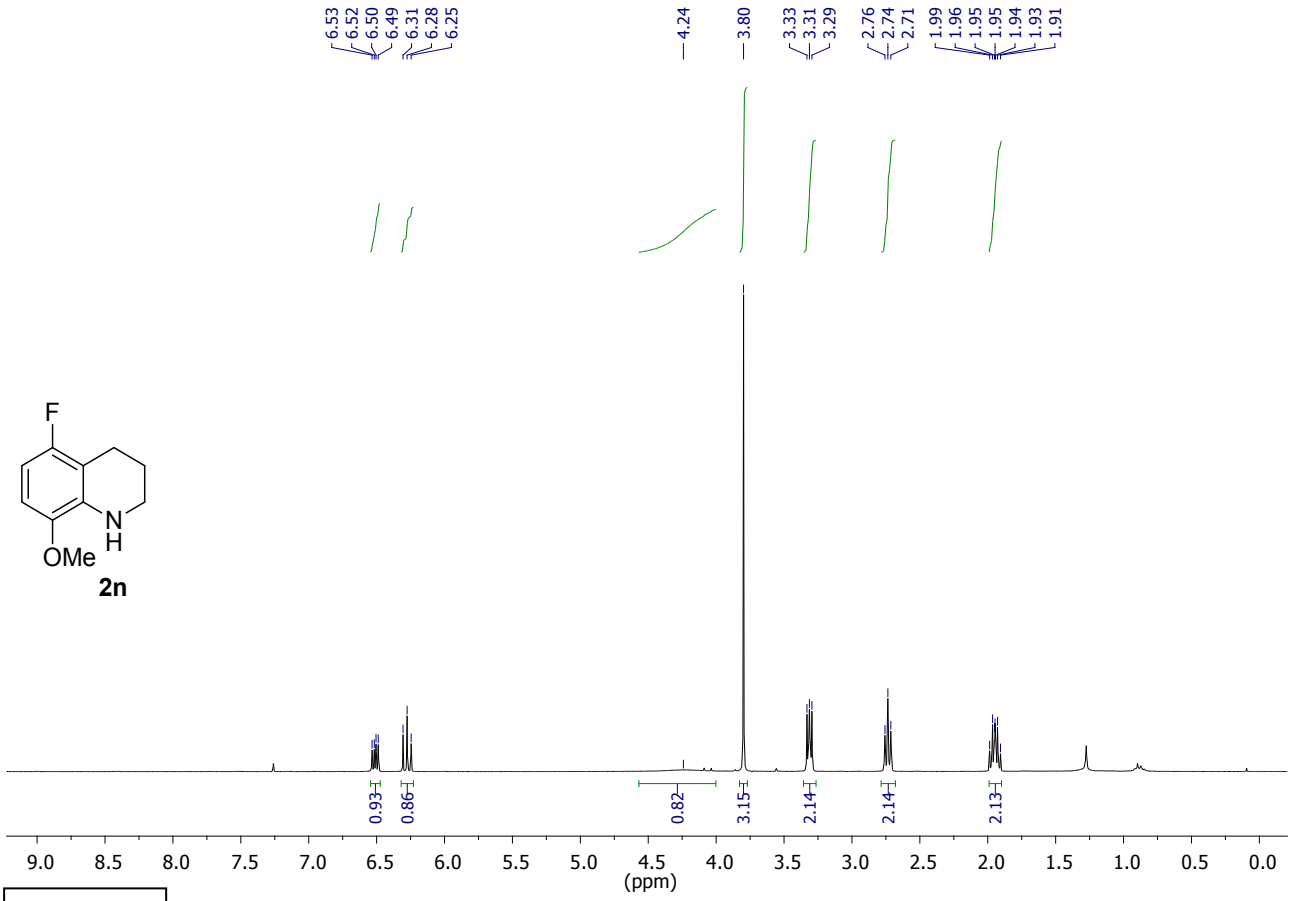
^{1}H NMR



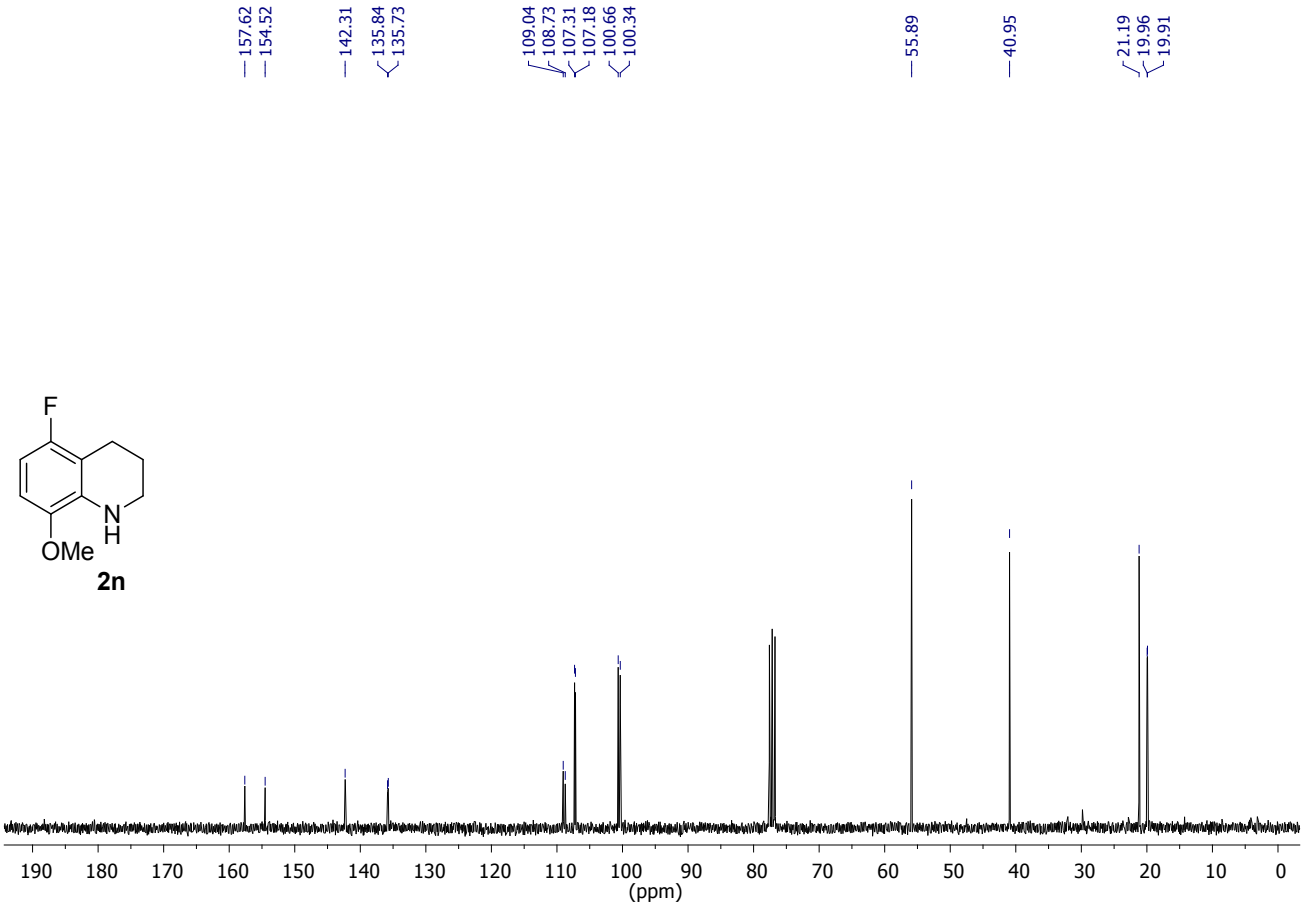
^{13}C NMR



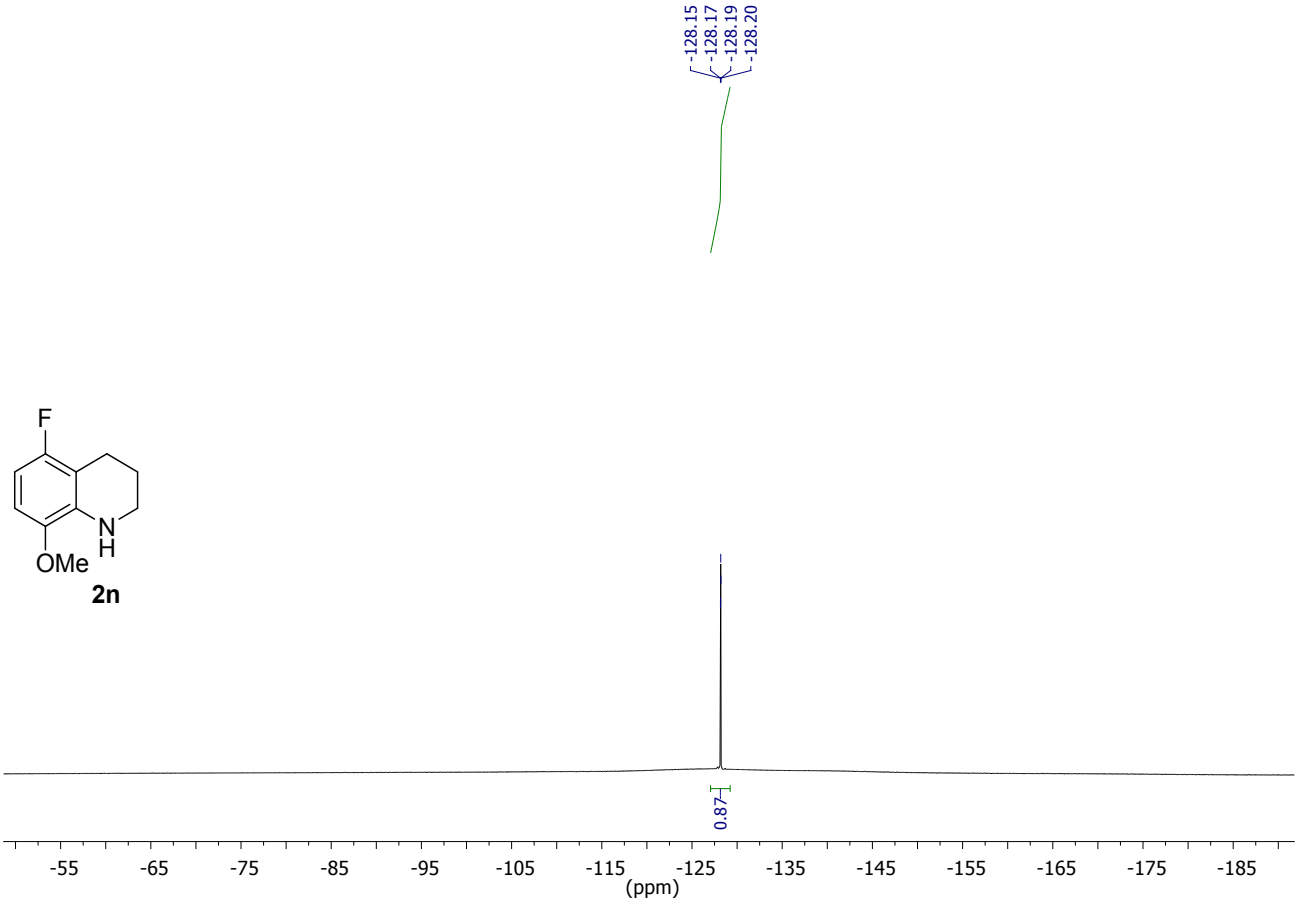
^{1}H NMR



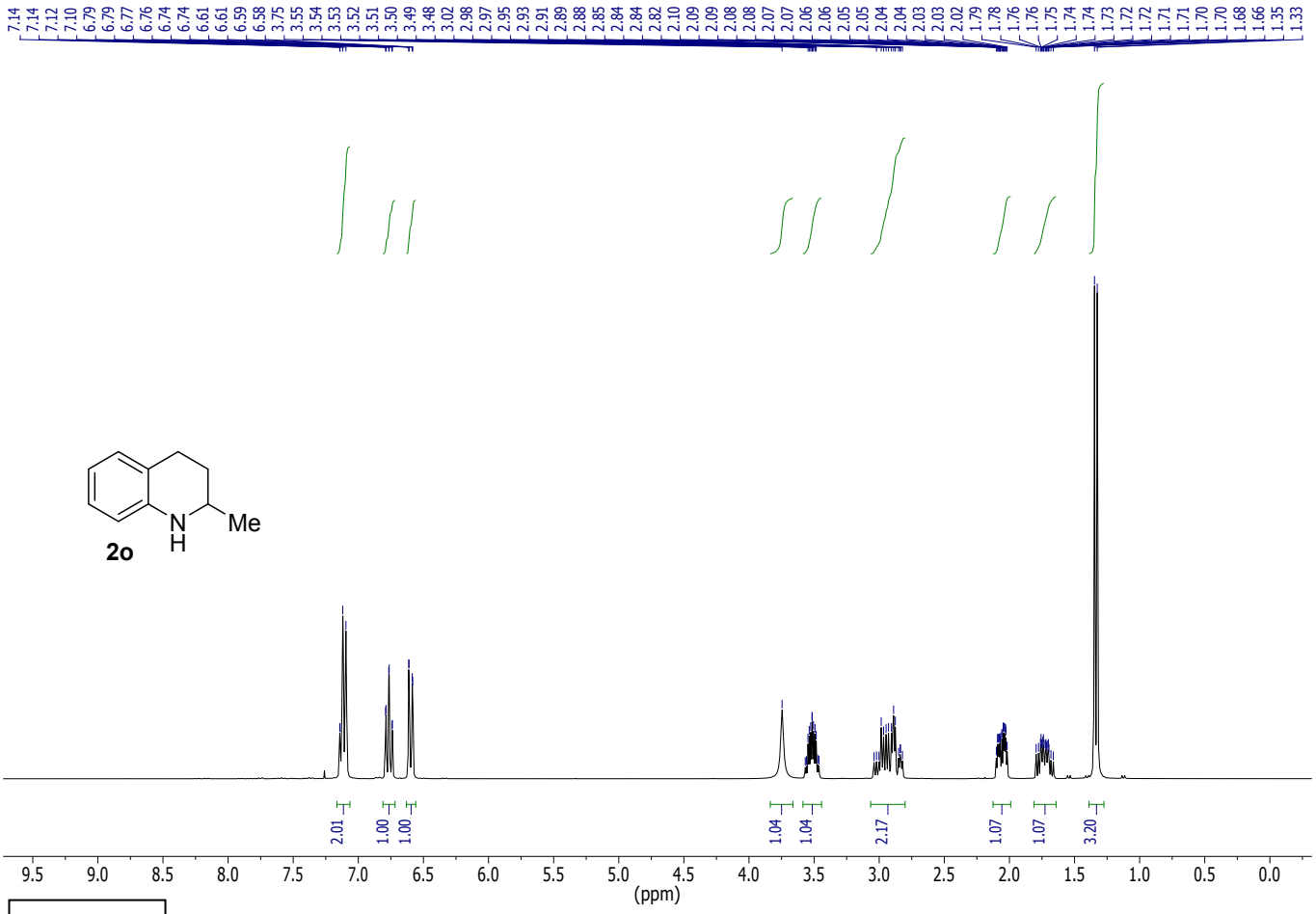
^{13}C NMR



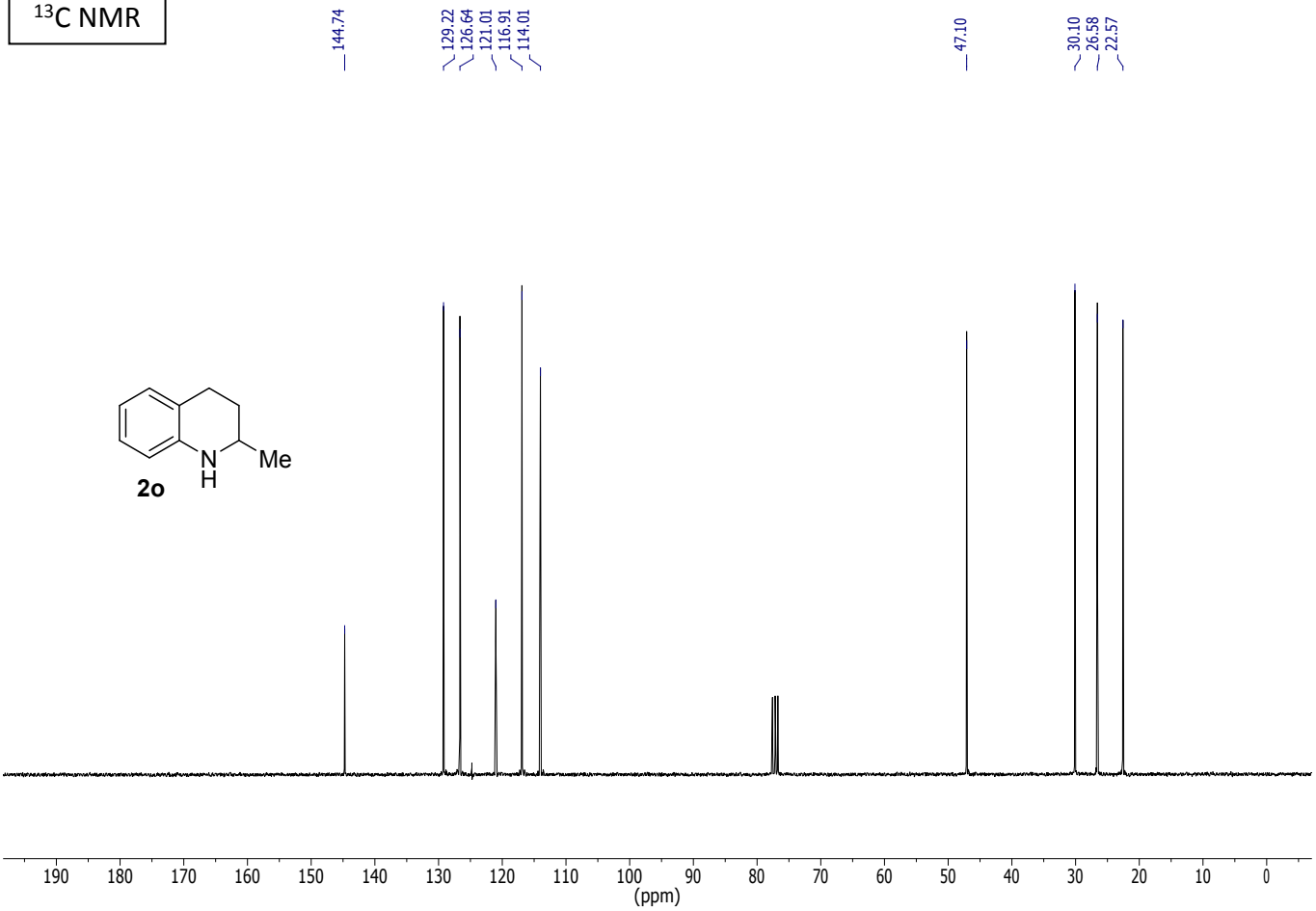
^{19}F NMR


-128.15
-128.17
-128.19
-128.20
F
N
H
OMe
2n
0.87
-55
-65
-75
-85
-95
-105
-115
-125
-135
-145
-155
-165
-175
-185
(ppm)

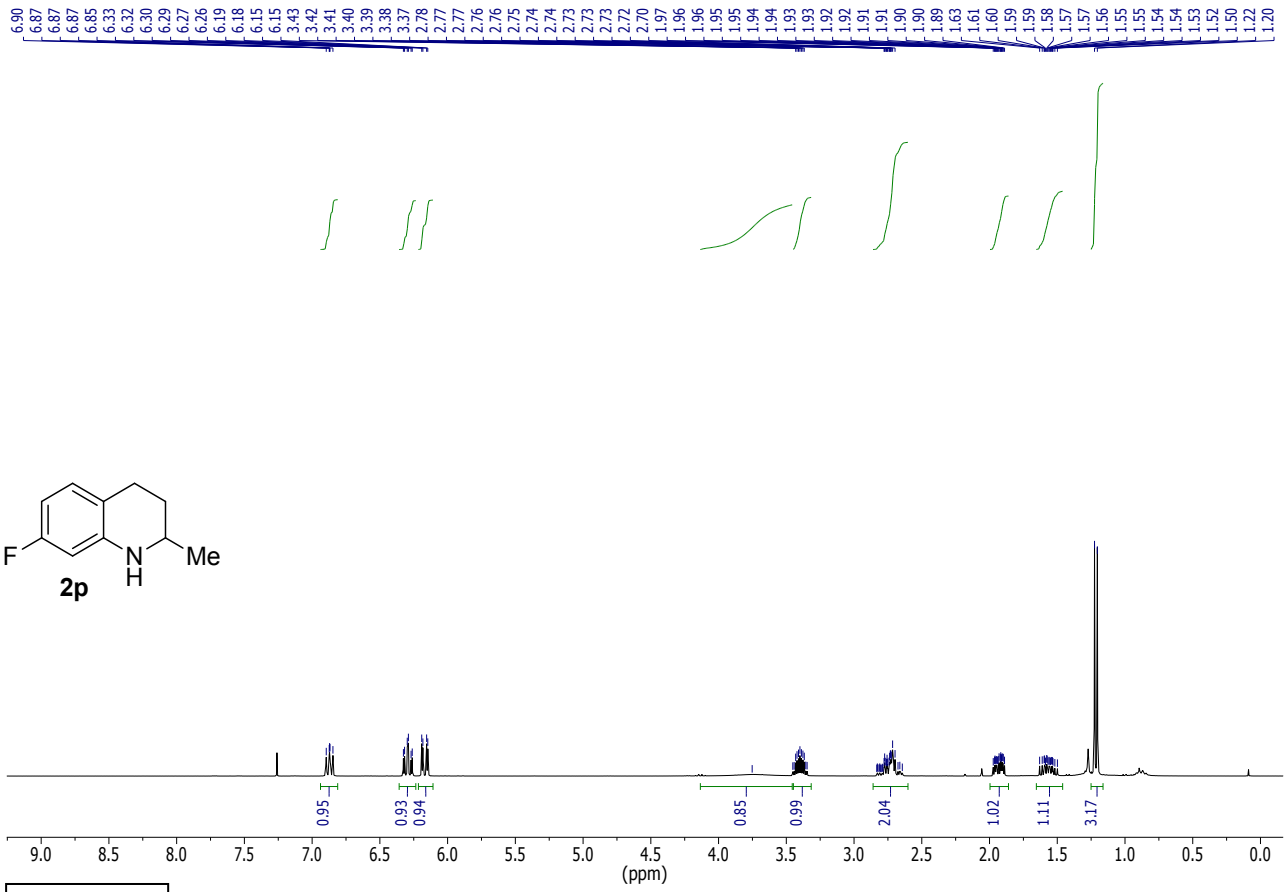
^{1}H NMR



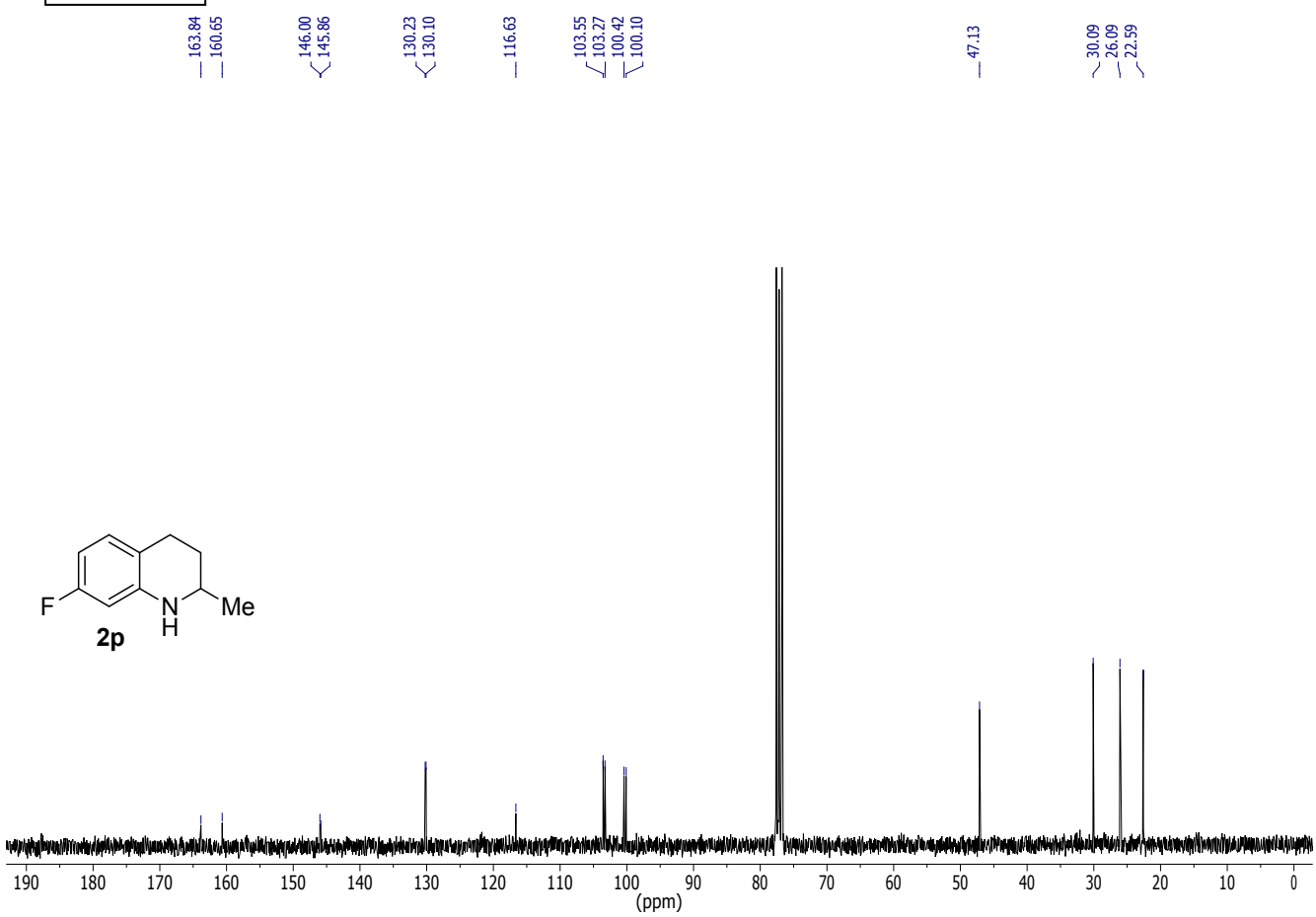
^{13}C NMR



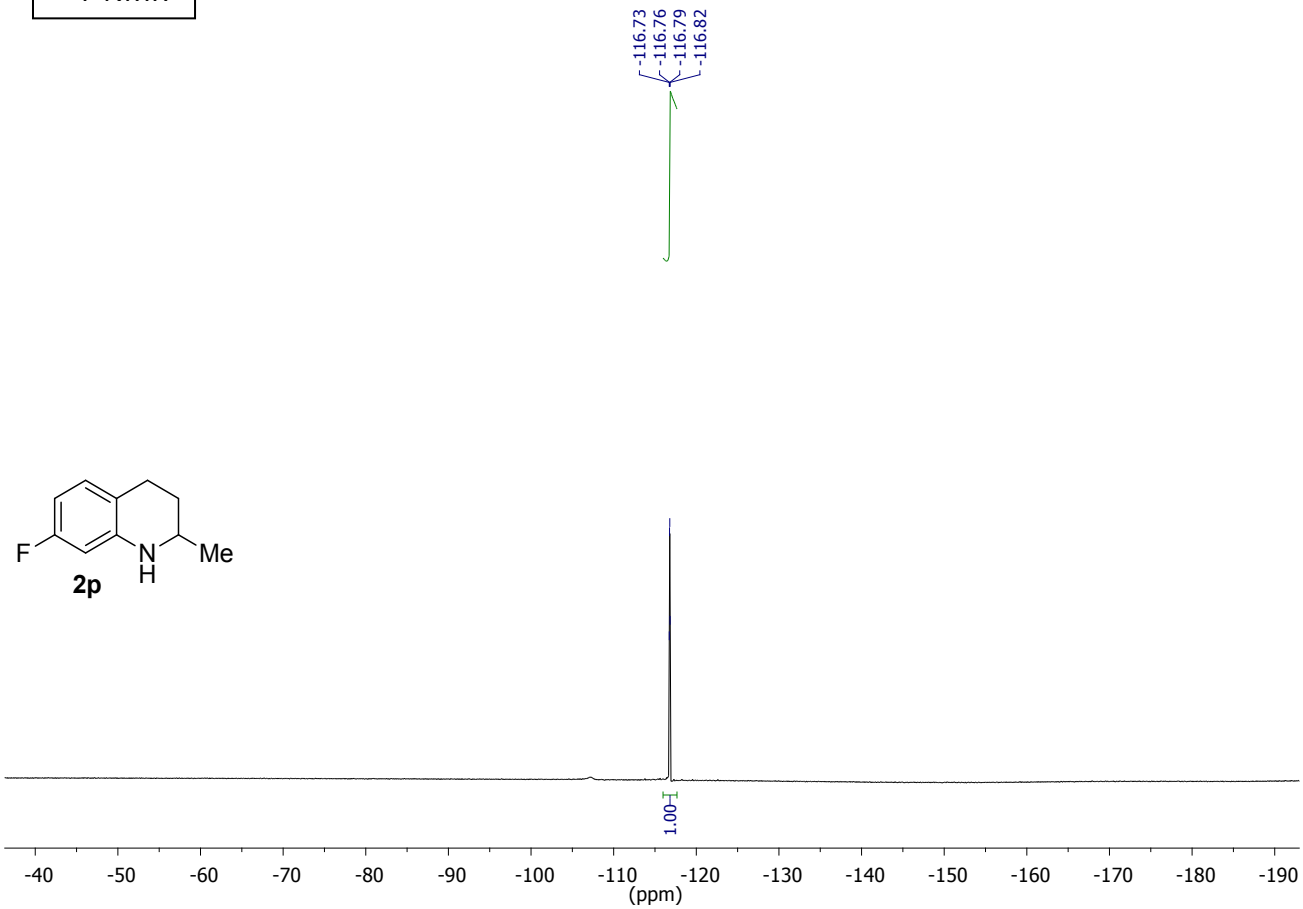
^{1}H NMR



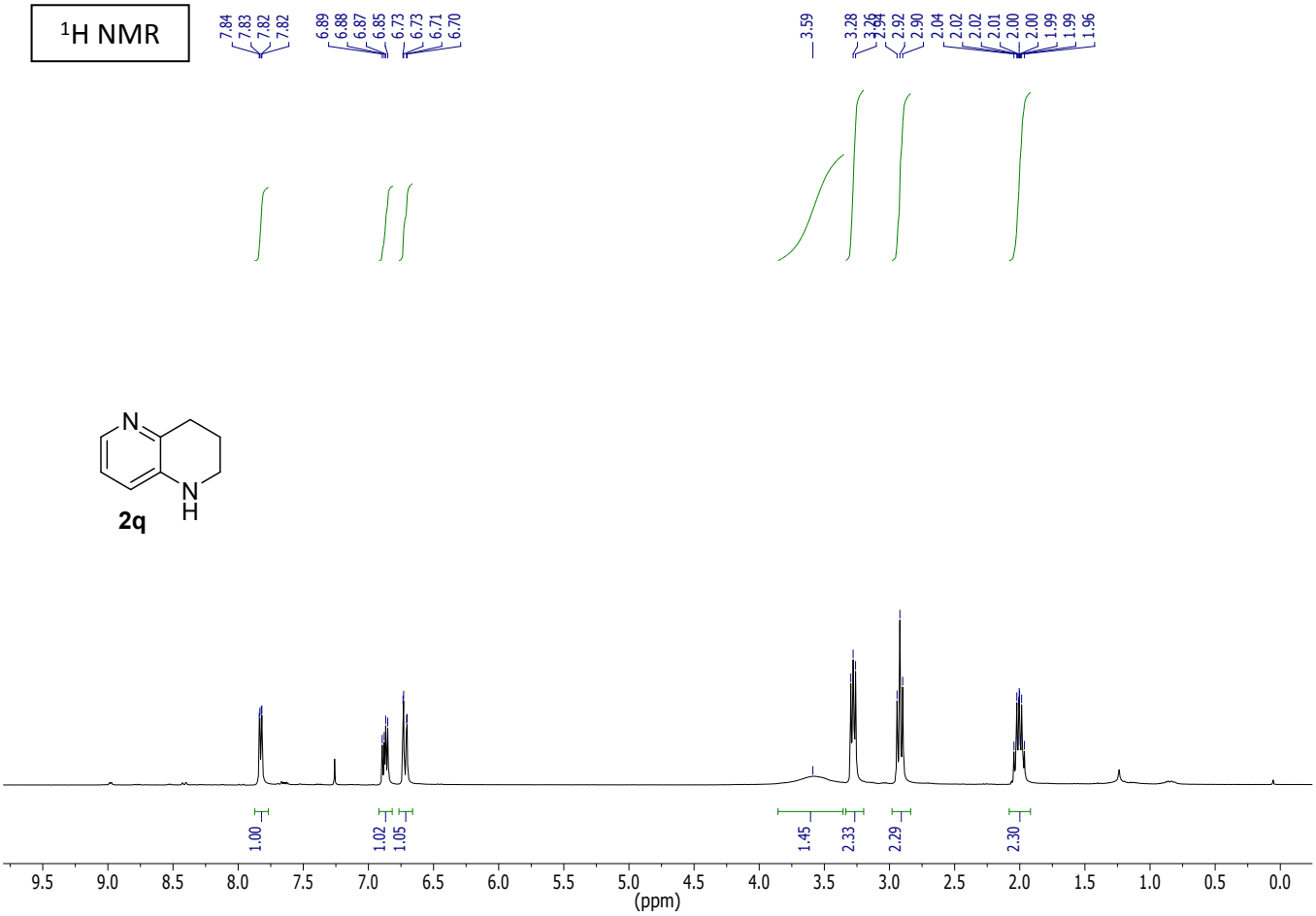
^{13}C NMR



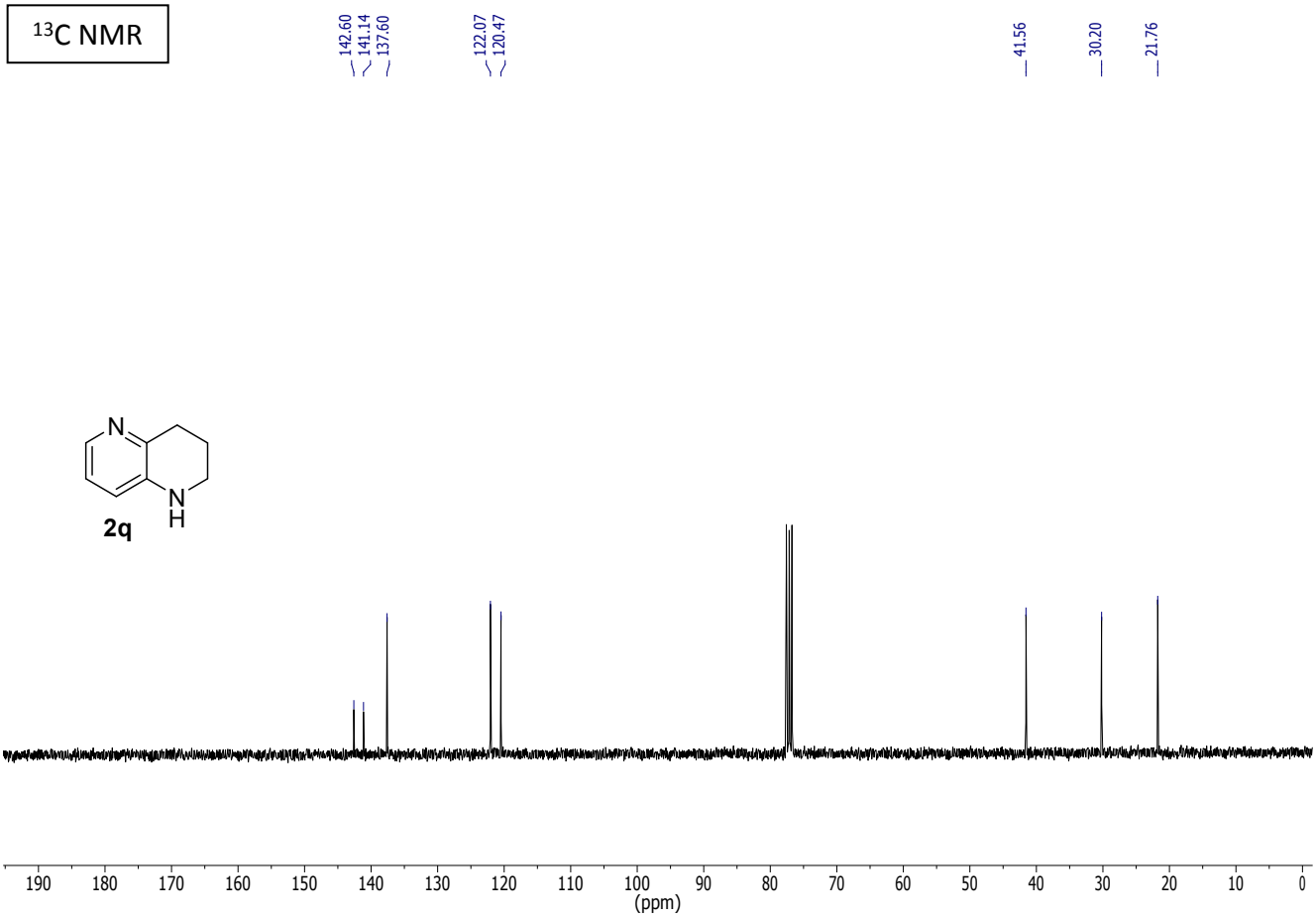
^{19}F NMR


-116.73
-116.76
-116.79
-116.82
F
N
H
Me
2p
1.00
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
(ppm)

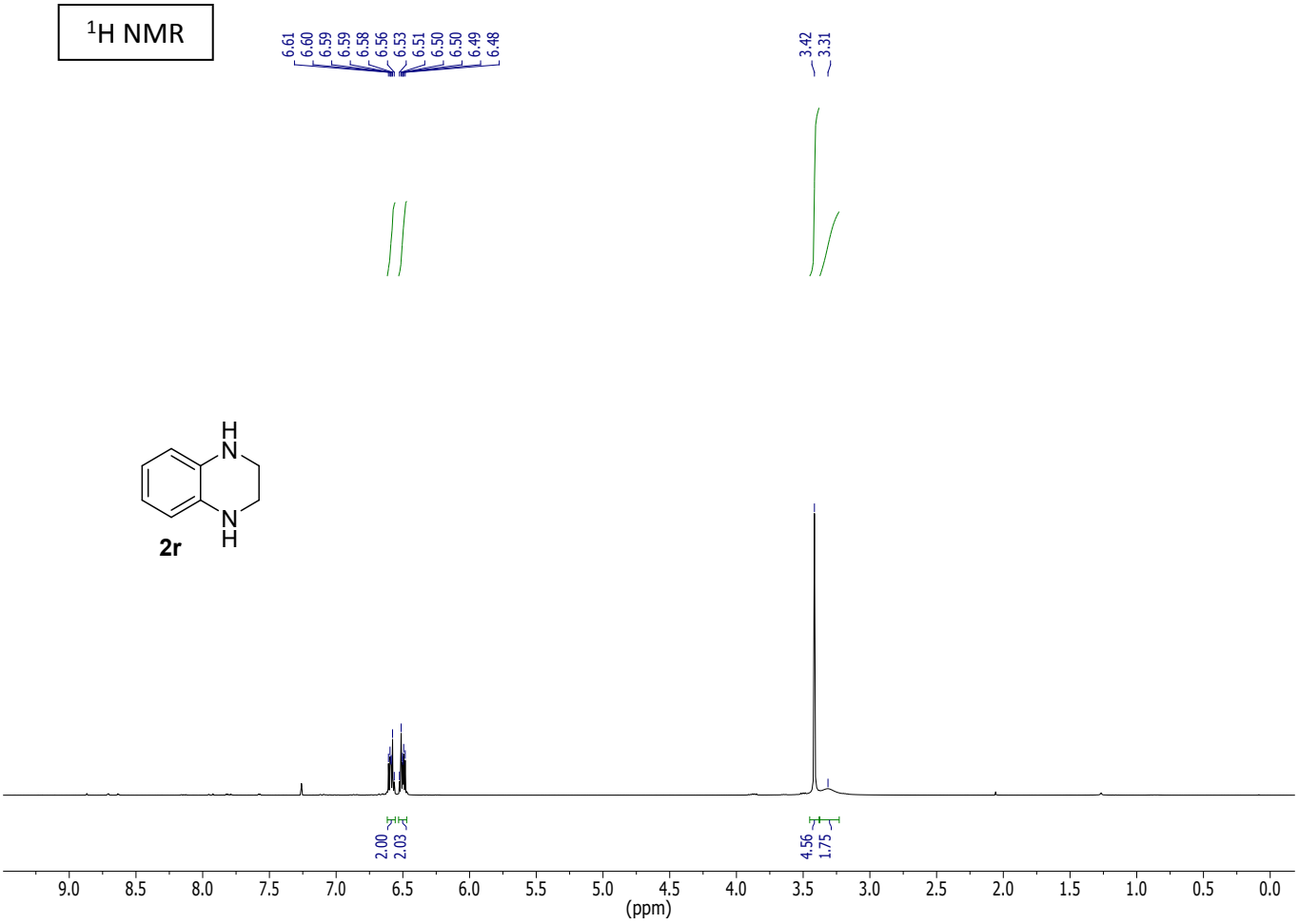
^{1}H NMR



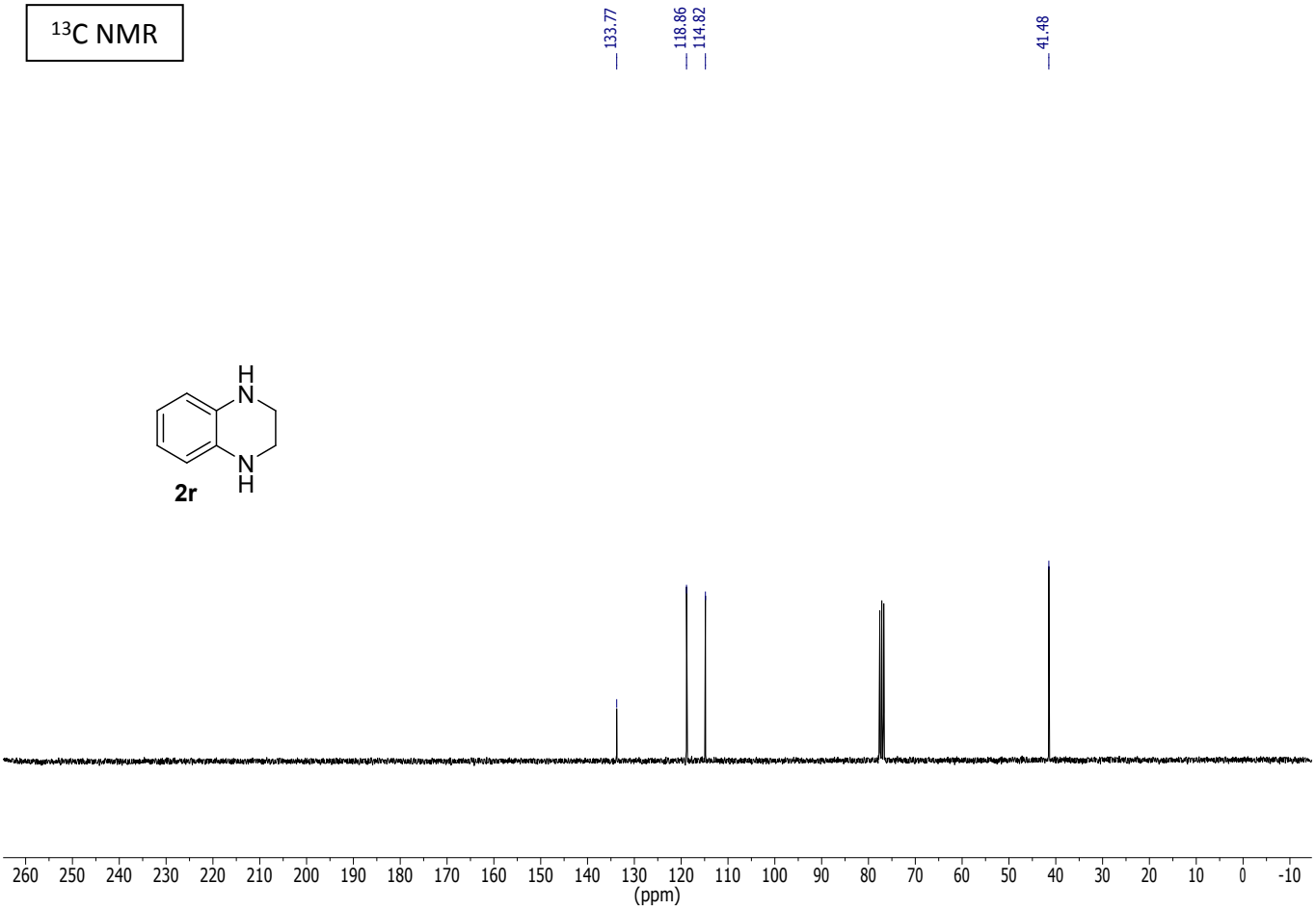
^{13}C NMR



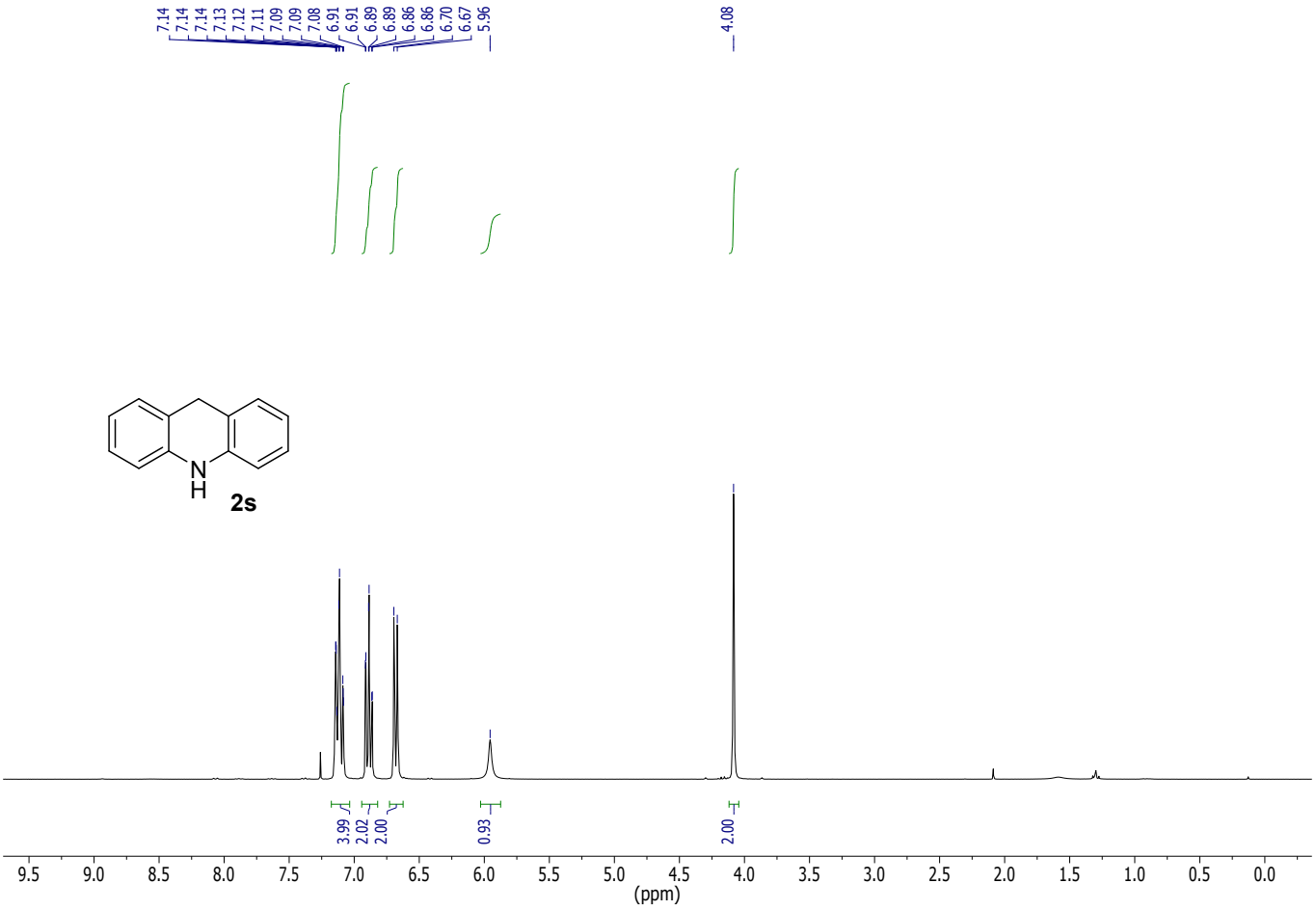
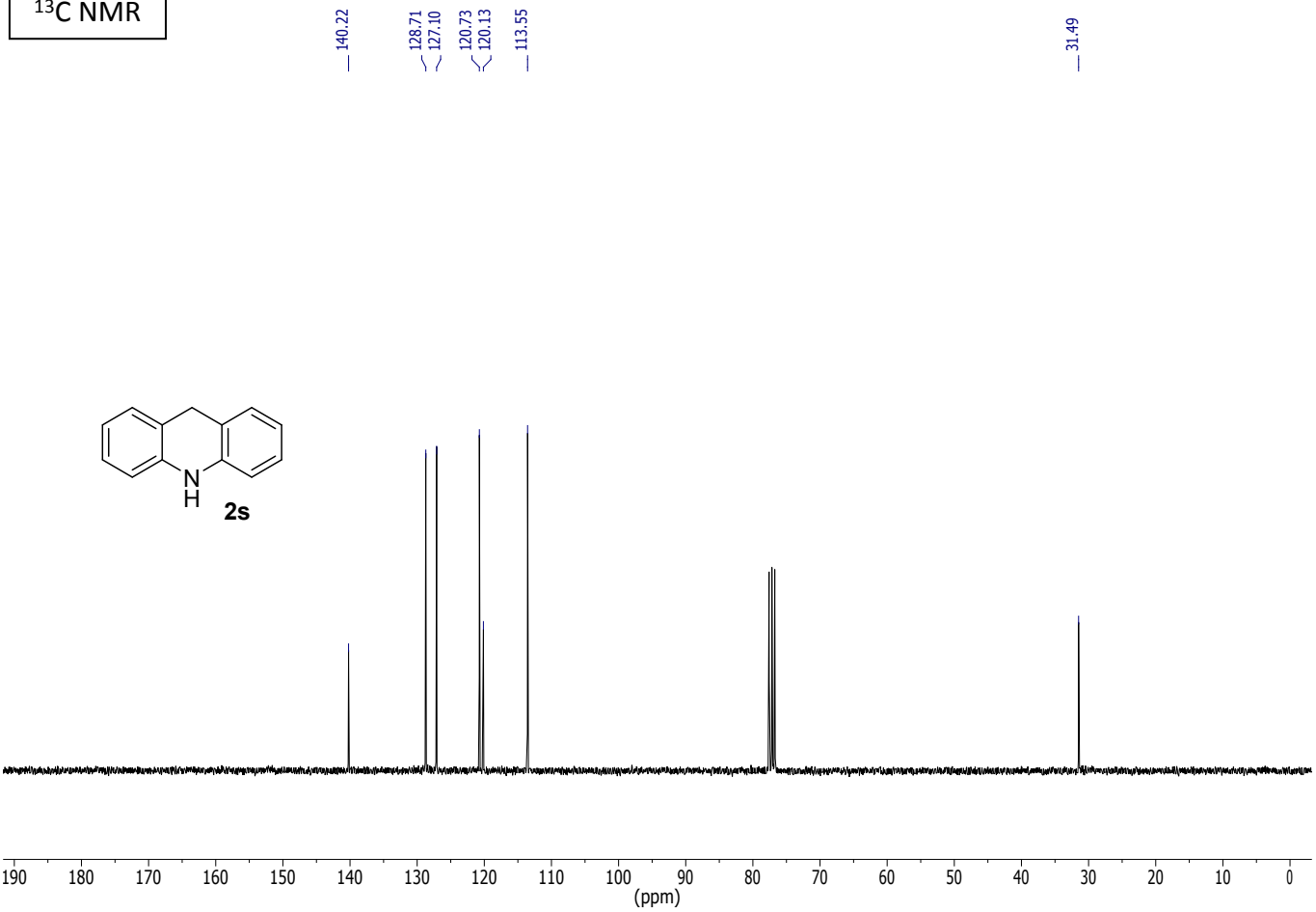
^{1}H NMR



^{13}C NMR



^{1}H NMR



^{13}C NMR