Supporting Information

$B(C_6F_5)_3$-promoted hydrogenations of N-heterocycles with ammonia borane

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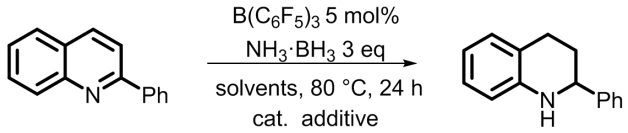
1. General Information

Procedure for the synthesis of **1o-1u**, please see article.[31] Unless otherwise noted, otherwise noted, reagents were obtained from commercial suppliers and were used without further purification. ^{1}H NMR (400 MHz or 600 MHz) and ^{13}C NMR (150 MHz) spectra were obtained on Bruker 400 M or 600 M nuclear resonance spectrometers. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet. Flash column chromatography was performed using 200-300 mesh silica gel.

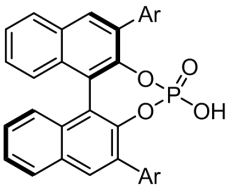
General Procedure for the Hydrogenations of N-Heterocycles: To a mixture of an appropriate N-heterocycles (0.5 mmol) and $B(C_6F_5)_3$ (5 mol %) in a standard Schlenk tube, 1.5 mmol of ammonia borane for quinoline derivatives and quinoxaline derivatives was added. The mixture was evacuated and backfilled with N_2 (3 times). Then, the solvent (1.5 mL) was added via syringe, and the mixture was stirred at 80 °C for 8 h. The resulting reaction mixture was concentrated under reduced pressure and purified by column chromatography using petroleum ether/ethyl acetate to afford the corresponding products.

General Procedure for the Asymmetric Hydrogenations of N-Heterocycles: To a mixture of an appropriate N-heterocycles (0.1 mmol), $B(C_6F_5)_3$ (5 mol%), PA (10 mol%) and additive (0.1 mmol) in a standard Schlenk tube, 0.3 mmol of ammonia borane for quinoline derivatives was added. The mixture was evacuated and backfilled with N_2 (3 times). Then, the solvent (1.5 mL) was added via syringe, and the mixture was stirred at 80 °C for 8 h. The resulting reaction mixture was concentrated under reduced pressure and purified by column chromatography using petroleum ether/ethyl acetate to afford the corresponding products.

Table S1 Optimization studies for the asymmetric transfer hydrogenation of **1o**[a]



Entry	Cat. 5 mol%	Solvent	Additive 5 mol%	Yield (%)	ee (%)[b]
1	S1a	toluene	-	65	0
2	S1b	toluene	-	63	0
3	S1c	toluene	-	66	12
4	S1d	toluene	-	50	13
5	S1e	toluene	-	55	0
6	quinine	toluene	-	57	0
7	chinchonine	toluene	-	62	3
8	S1c	DCE	-	70	5
9	S1c	DCM	-	71	10
10	S1c	THF	-	66	3
11	S1c	toluene	NEt_3	70	10
12	S1c	toluene	DMAP	65	17
13	S1c	toluene	py	72	15
14	S1c	toluene	$PhNH_2$	65	10
15	S1c	toluene	Bn_2NH	60	14
16	S1c	toluene	4-morpholino pyridine	75	20



(R)

S1a: Ar = 1-naphthyl

S1b: Ar = 2-naphthyl

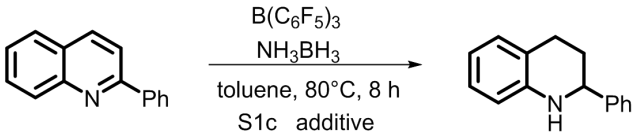
S1c: Ar = 9-anthracenyl

S1d: Ar = 9-phenanthyl

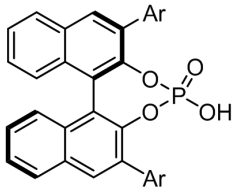
S1e: Ar = 3,5-$(CF_3)_2$-C_6H_3

[a] Reaction conditions: substrates (0.1 mmol, 1 equiv.) and ammonia borane (0.3 mmol, 3 equiv.) with $B(C_6F_5)_3$ (5 mol %) in solvent (1.5 mL) at 80 °C for 8 h. [b] The ee values were determined by HPLC.

Table S2 Other effect on the asymmetric transfer hydrogenation of **1o**[a]



Entry	$B(C_6F_5)_3$ mol%	S1c mol%	Additive mol%	ee (%)[b]
1	5	10	10	21
2	5	20	20	22
3	10	20	20	23
4	20	20	20	13
5	5	10	50	23
6	5	10	100	24



(R)

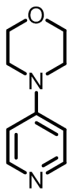
S1a: Ar = 1-naphthyl

S1b: Ar = 2-naphthyl

S1c: Ar = 9-anthracenyl

S1d: Ar = 9-phenanthyl

S1e: Ar = 3,5-$(CF_3)_2$-C_6H_3



4-morpholinopyridine

additive

[a] Reaction conditions: substrates (0.1 mmol, 1 equiv.) and ammonia borane (0.3 mmol, 3 equiv.) with $B(C_6F_5)_3$, S1c in toluene (1.5 mL) at 80 °C for 8 h. [b] The ee values were determined by HPLC.

The optimum reaction condition is as follows: substrates (0.1 mmol, 1 equiv.) and ammonia borane (0.3 mmol, 3 equiv.) with $B(C_6F_5)_3$ (5 mol%), S1c (10 mol%) and 4-morpholinopyridine (0.1 mmol, 1 equiv.) in toluene (1.5 mL) at 80 °C for 8 h.

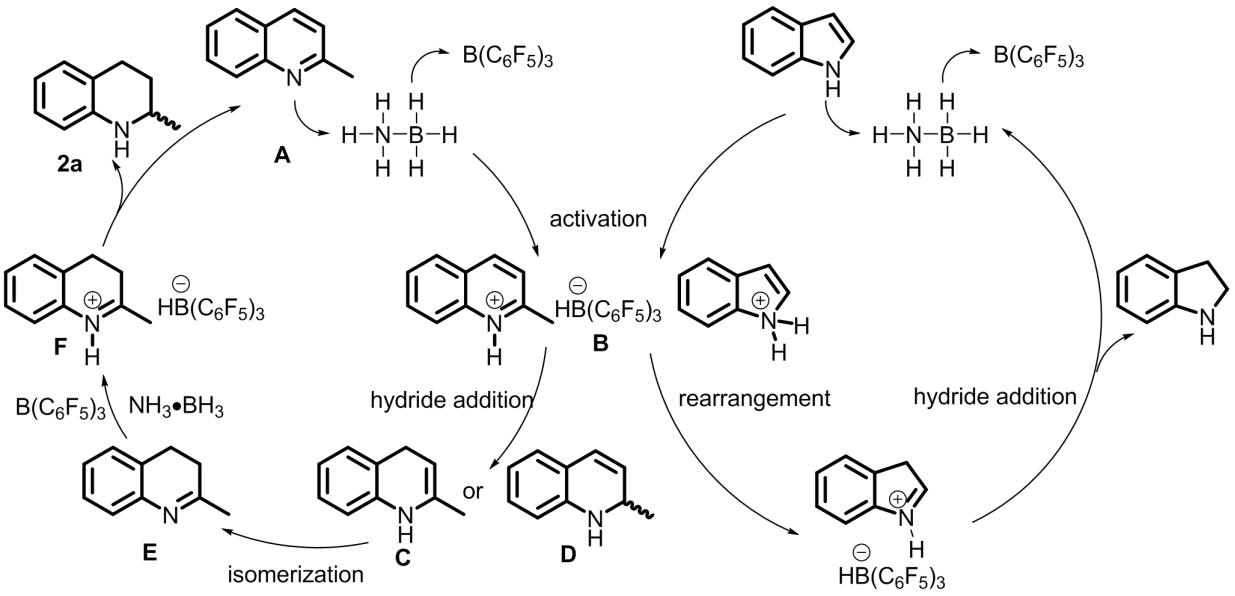
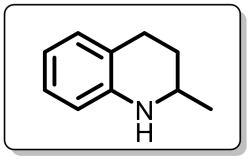


Fig. 1 Proposed catalytic cycle for the hydrogenations of N-heterocycles.

Based on relevant reports in the literature,[9, 17, 19] a plausible reaction mechanism for this $B(C_6F_5)_3$-promoted hydrogenation of N-heterocycles with ammonia borane has been proposed in Fig. 1. We assume that the FLPs of quinaldine and $B(C_6F_5)_3$ can split the N−H and B−H bonds of ammonia borane to generate zwitterion species (**B**). The location of the subsequent hydride attack could occur at the 2- or 4- position of quinaldine, because both sites are electrophilic. On the one hand, attacking at the 4- position would produce a transient enamine (**C**). On the other hand, attacking by hydride at the 2-position would generate the 1,2-dihydro-quinoline which can undergo 1,3 proton shifts to regenerate an imine (**D**). As a result, either attacking at the 4- position or at the 2- position, it would give the same intermediate product (**E**). Subsequently, the FLPs of imine **E** and $B(C_6F_5)_3$ activate ammonia borane to generate zwitterion species (**F**). Finally, imines were hydrogenated giving the reductive products (**2a**) with catalyst $B(C_6F_5)_3$ released. In addition, the mechanism for the hydrogenations of indole is similar to that of quinaldine.

2. Experimental Details

2-methyl-1,2,3,4-tetrahydroquinoline (**2a**)[1]

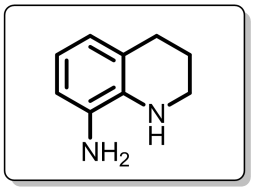


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.11 – 6.88 (m, 2H), 6.64 (td, *J* = 7.4, 1.1 Hz, 1H), 6.58 – 6.40 (m, 1H), 3.69 (s, 1H), 3.43 (dqd, *J* = 9.3, 6.2, 2.8 Hz, 1H), 2.98 – 2.69 (m, 2H), 1.96 (ddt, *J* = 12.5, 6.1, 3.2 Hz, 1H), 1.63 (m, 1H), 1.24 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 144.8, 129.4, 126.8, 121.2, 117.1, 114.1, 47.3, 30.2, 26.7, 22.7.

HPLC (OJ-H, elute: Hexanes/i-PrOH = 90/10, detector: 254 nm, flow rate: 0.5 mL/min), t_1 = 19.9 min (major), t_2 = 22.0 min (minor).

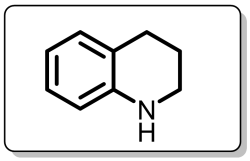
1,2,3,4-tetrahydroquinolin-8-amine (**2b**)[1]



^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.69 – 6.47 (m, 3H), 3.39 – 3.32 (m, 2H), 3.28 (s, 3H), 2.78 (t, *J* = 6.4 Hz, 2H), 1.92 (dt, *J* = 11.0, 6.3 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 133.9, 133.8, 123.4, 121.2, 118.2, 114.2, 42.6, 27.1, 22.4.

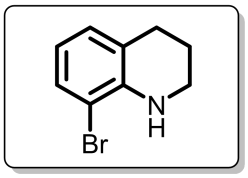
1,2,3,4-tetrahydroquinoline (**2c**)[1]



^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.05 – 6.92 (m, 2H), 6.62 (td, *J* = 7.4, 1.2 Hz, 1H), 6.49 (d, *J* = 7.9 Hz, 1H), 3.77 (s, 1H), 3.38 – 3.26 (m, 2H), 2.78 (t, *J* = 6.5 Hz, 2H), 2.02 – 1.91 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 144.8, 129.6, 126.8, 121.6, 117.1, 114.3, 42.1, 27.1, 22.3.

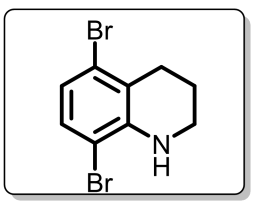
8-bromo-1,2,3,4-tetrahydroquinoline (**2d**)[2]



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 7.4 Hz, 1H), 6.46 (t, *J* = 7.7 Hz, 1H), 4.44 (s, 1H), 3.40 (t, *J* = 5.6 Hz, 2H), 2.79 (t, *J* = 6.4 Hz, 2H), 2.08 – 1.85 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 141.8, 130.1, 128.5, 122.9, 117.0, 108.8, 42.1, 27.5, 21.8.

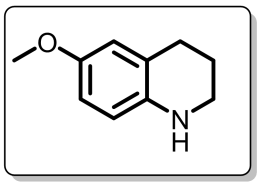
5,8-dibromo-1,2,3,4-tetrahydroquinoline (**2e**)[1]



^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.43 – 3.29 (m, 1H), 2.78 (t, *J* = 6.5 Hz, 1H), 2.05 – 1.89 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 143.3, 130.7, 124.6, 122.0, 120.6, 107.6, 77.4, 41.6, 28.4, 21.9.

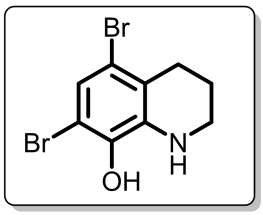
6-methoxy-1,2,3,4-tetrahydroquinoline (**2f**)[1]



^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.61 (dd, *J* = 8.6, 3.0 Hz, 1H), 6.57 (d, *J* = 2.7 Hz, 1H), 6.48 (d, *J* = 8.6 Hz, 1H), 3.74 (d, *J* = 1.0 Hz, 3H), 3.73 – 3.69 (m, 1H), 3.31 – 3.19 (m, 2H), 2.76 (t, *J* = 6.5 Hz, 2H), 2.02 – 1.86 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 152.0, 138.7, 123.1, 115.8, 115.0, 113.0, 55.9, 42.5, 27.2, 22.5.

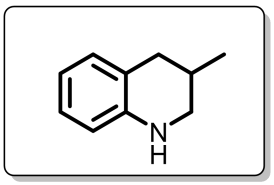
5,7-dibromo-1,2,3,4-tetrahydroquinolin-8-ol (**2g**)[3]



^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.96 (s, 1H), 5.17 (s, 1H), 4.44 (s, 1H), 3.31 (t, *J* = 5.5 Hz, 2H), 2.71 (t, *J* = 6.5 Hz, 2H), 1.96 (dd, *J* = 6.6, 4.9 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 138.0, 135.5, 120.4, 120.4, 116.3, 106.7, 40.9, 27.6, 21.8.

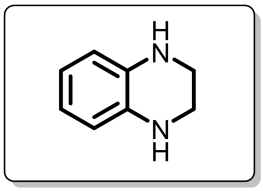
3-methyl-1,2,3,4-tetrahydroquinoline (**2h**)[1]



^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.95 (t, *J* = 6.9 Hz, 2H), 6.62 (t, *J* = 7.4 Hz, 1H), 6.52 (d, *J* = 8.0 Hz, 1H), 3.28 (d, *J* = 11.2 Hz, 1H), 2.90 (t, *J* = 10.4 Hz, 1H), 2.78 (dd, *J* = 16.1, 4.8 Hz, 1H), 2.43 (dd, *J* = 16.2, 10.2 Hz, 1H), 2.07 (s, 1H), 1.26 (s, 1H), 1.05 (dd, *J* = 6.6, 1.9 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 144.0, 129.7, 126.9, 121.6, 117.4, 114.3, 49.0, 35.6, 27.3, 19.2.

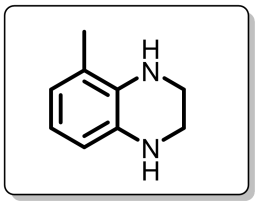
1,2,3,4-tetrahydroquinoxaline (**2i**)[1]



^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.59 (dd, *J* = 5.7, 3.5 Hz, 2H), 6.50 (dd, *J* = 5.6, 3.6 Hz, 2H), 3.50 (s, 2H), 3.42 (s, 4H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 133.5, 119.1, 115.1, 41.4.

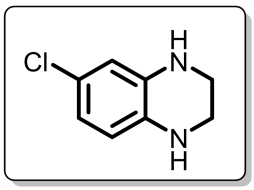
5-methyl-1,2,3,4-tetrahydroquinoxaline (**2j**)[1]



^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.65 – 6.51 (m, 2H), 6.43 (dd, *J* = 6.7, 2.6 Hz, 1H), 3.63 – 3.47 (m, 4H), 3.46 – 3.39 (m, 2H), 2.12 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 133.2, 131.7, 122.2, 120.4, 118.0, 112.9, 41.8, 41.2, 17.0.

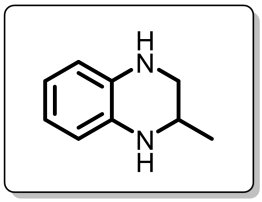
6-chloro-1,2,3,4-tetrahydroquinoxaline (**2k**)[4]



^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.51 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.44 (d, *J* = 2.3 Hz, 1H), 6.38 (d, *J* = 8.2 Hz, 1H), 3.58 (s, 2H), 3.38 (s, 4H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 134.8, 132.0, 123.3, 118.0, 115.4, 114.0, 41.1.

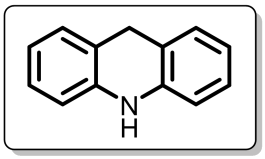
2-methyl-1,2,3,4-tetrahydroquinoxaline (**2l**)[1]



^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.60 (dd, *J* = 5.7, 3.4 Hz, 2H), 6.52 (dt, *J* = 6.0, 3.1 Hz, 2H), 3.68 (s, 2H), 3.50 (d, *J* = 8.4 Hz, 1H), 3.39 – 3.25 (m, 1H), 3.03 (t, *J* = 9.6 Hz, 1H), 1.20 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 133.5, 133.1, 119.0, 119.0, 114.8, 114.7, 48.3, 45.9, 19.9.

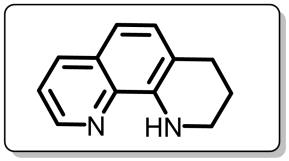
9,10-dihydroacridine (**2m**)[1]



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 – 7.03 (m, 4H), 6.86 (t, *J* = 7.4 Hz, 2H), 6.67 (d, *J* = 7.8 Hz, 2H), 5.95 (s, 1H), 4.07 (s, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 140.2, 128.7, 127.1, 120.8, 120.1, 113.6, 31.5.

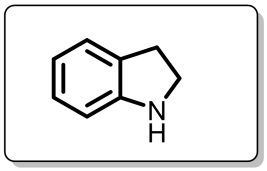
1,2,3,4-tetrahydro-1,10-phenanthroline (**2n**)[1]



^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.68 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.01 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.29 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 5.93 (s, 1H), 3.53 (t, *J* = 5.5 Hz, 2H), 2.92 (t, *J* = 6.3 Hz, 2H), 2.15 – 2.00 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 147.0, 140.8, 137.6, 136.1, 129.2, 127.5, 120.7, 116.8, 113.2, 41.4, 27.2, 21.9.

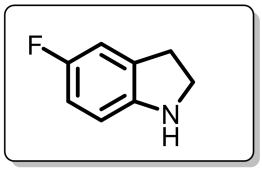
Indoline (**4a**)[5]



^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.13 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.03 (td, *J* = 7.6, 1.2 Hz, 1H), 6.72 (td, *J* = 7.4, 1.0 Hz, 1H), 6.67 (d, *J* = 7.7 Hz, 1H), 3.79 – 3.62 (m, 1H), 3.56 (t, *J* = 8.4 Hz, 2H), 3.04 (t, *J* = 8.4 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 151.2, 129.6, 127.4, 124.8, 119.1, 109.9, 47.4, 29.9.

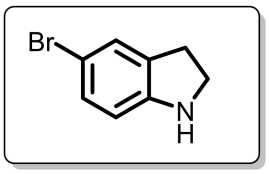
5-fluoroindoline (**4b**)[5]



^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.84 (ddt, *J* = 8.4, 2.4, 1.1 Hz, 1H), 6.71 (m, 1H), 6.54 (dd, *J* = 8.4, 4.3 Hz, 1H), 3.56 (t, *J* = 8.4 Hz, 2H), 3.47 (s, 1H), 3.01 (td, *J* = 8.4, 1.1 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.0, 156.4, 147.5, 131.3, 131.3, 113.3, 113.2, 112.2, 112.1, 109.8, 109.7, 48.1, 30.3, 30.3.

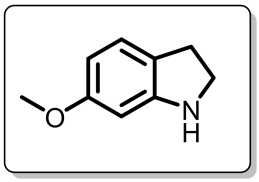
5-bromoindoline (**4c**)[6]



^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.19 (dt, *J* = 2.2, 1.2 Hz, 1H), 7.12 – 7.07 (m, 1H), 6.49 (d, *J* = 8.3 Hz, 1H), 3.73 – 3.61 (m, 1H), 3.56 (t, *J* = 8.4 Hz, 2H), 3.01 (tt, *J* = 8.3, 1.0 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 150.7, 131.9, 129.9, 127.7, 110.6, 110.2, 47.7, 29.8.

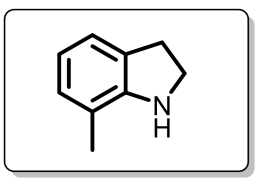
6-methoxyindoline (**4d**)[7]



^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.00 (dt, *J* = 8.4, 1.2 Hz, 1H), 6.25 (d, *J* = 7.2 Hz, 2H), 3.76 (s, 3H), 3.56 (t, *J* = 8.3 Hz, 2H), 2.96 (td, *J* = 8.3, 1.1 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.9, 153.0, 124.8, 121.7, 103.4, 96.4, 55.5, 55.5, 48.1, 29.1.

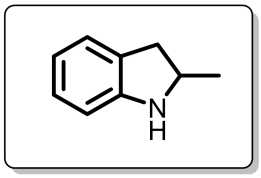
7-methylindoline (**4e**)[8]



^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.05 – 6.99 (m, 1H), 6.94 – 6.86 (m, 1H), 6.69 (t, *J* = 7.4 Hz, 1H), 3.59 (t, *J* = 8.4 Hz, 2H), 3.08 (td, *J* = 8.4, 0.9 Hz, 2H), 2.17 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 150.2, 128.7, 128.2, 122.2, 119.0, 118.9, 47.3, 30.2, 17.0.

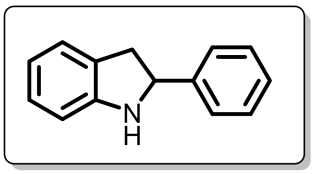
2-methylindoline (**4f**)[5]



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.08 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.01 (td, *J* = 7.6, 1.2 Hz, 1H), 6.69 (td, *J* = 7.4, 1.0 Hz, 1H), 6.61 (d, *J* = 7.7 Hz, 1H), 4.07 – 3.91 (m, 1H), 3.52 (s, 1H), 3.15 (dd, *J* = 15.4, 8.5 Hz, 1H), 2.64 (dd, *J* = 15.4, 7.8 Hz, 1H), 1.30 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 150.9, 129.1, 127.4, 124.8, 118.7, 109.4, 55.4, 37.8, 22.4.

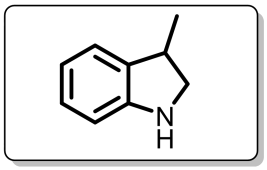
2-phenylindoline (**4g**)[9]



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.41 (m, 2H), 7.40 – 7.33 (m, 2H), 7.32 – 7.26 (m, 1H), 7.16 – 7.03 (m, 2H), 6.76 (td, *J* = 7.4, 1.0 Hz, 1H), 6.69 (d, *J* = 7.7 Hz, 1H), 4.97 (t, *J* = 9.0 Hz, 1H), 4.03 (s, 1H), 3.46 (dd, *J* = 15.6, 9.2 Hz, 1H), 3.01 (ddt, *J* = 15.6, 8.7, 1.1 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 150.5, 144.3, 129.1, 128.7, 128.4, 127.7, 127.6, 126.5, 125.3, 124.7, 119.3, 109.4, 63.6, 39.6.

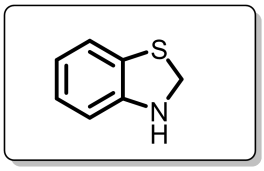
3-methylindoline (**4h**)[6]



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.14 – 6.98 (m, 2H), 6.75 (t, *J* = 7.4 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 3.71 (t, *J* = 8.7 Hz, 1H), 3.38 (q, *J* = 7.7 Hz, 1H), 3.12 (t, *J* = 8.6 Hz, 2H), 1.33 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 151.2, 134.5, 127.4, 123.5, 118.9, 109.7, 55.5, 36.7, 18.7.

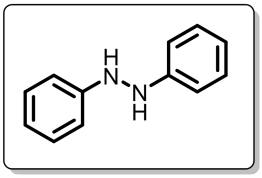
2,3-dihydrobenzo[d]thiazole (**4i**)[1]



^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 – 6.80 (m, 2H), 6.67 – 6.24 (m, 2H), 4.93 – 4.71 (m, 1H), 2.70 (d, *J* = 3.8 Hz, 2H).

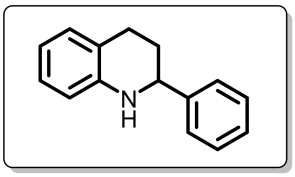
^{13}C NMR (150 MHz, $CDCl_3$) δ 150.4, 137.1, 132.2, 118.5, 116.3, 109.9, 30.5.

1,2-diphenylhydrazine (**5**)[10]



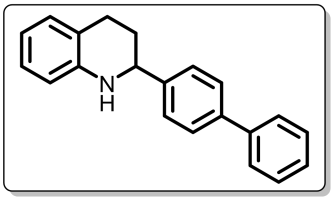
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 – 7.16 (m, 5H), 6.88 – 6.84 (m, 5H), 5.62 (s, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 149.0, 129.5, 120.0, 112.4.

2-phenyl-1,2,3,4-tetrahydroquinoline (**2o**)[31]



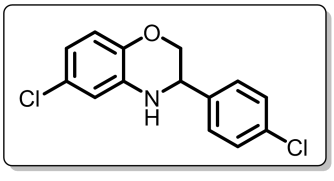
^{1}H NMR (400 MHz, Chloroform-d): δ 7.42 – 7.35 (m, 4H), 7.32 – 7.30 (m, 1H), 7.05 – 7.01 (m, 2H), 6.69 – 6.65 (m, 1H), 6.57 – 6.55 (m, 1H), 4.47 – 4.44 (dd, *J* = 9.2, 3.2 Hz, 1H), 4.06 (s, 1H), 2.97 – 2.90 (m, 1H), 2.79 – 2.72 (m, 1H), 2.16 – 2.11 (m, 1H), 2.06 – 1.99 (m, 1H);
^{13}C NMR (150 MHz, $CDCl_3$): δ 145.0, 144.9, 129.4, 128.7, 127.6, 127.0, 126.7, 121.0, 117.3, 114.1, 56.4, 31.1, 26.5.
HPLC (OD-H, elute: Hexanes/i-PrOH = 80/20, detector: 254 nm, flow rate: 1.0 mL/min), t_1 = 7.5 min (minor), t_2 = 9.5 min (major).

2-([1,1'-biphenyl]-4-yl)-1,2,3,4-tetrahydroquinoline (**2p**)[31]



^{1}H NMR (400 MHz, Chloroform-d): δ 7.64 – 7.61 (m, 4H), 7.58 – 7.46 (m, 4H), 7.40 – 7.36 (m, 1H), 7.08 – 7.04 (m, 2H), 6.70 (t, *J* = 7.2 Hz, 1H), 6.60 (d, *J* = 8.4 Hz, 1H), 4.52 (dd, *J* = 9.2, 3.2 Hz, 1H), 4.16 (s, 1H), 3.02 – 2.94 (m, 1H), 2.83 – 2.77 (m, 1H), 2.23 – 2.16 (m, 1H), 2.12 – 2.02 (m, 1H);
^{13}C NMR (150 MHz, $CDCl_3$): δ 144.8, 144.0, 141.0, 140.6, 129.5, 128.9, 127.5, 127.4, 127.2, 127.1, 127.1, 121.0, 117.4, 114.2, 56.1, 31.1, 26.5.
HPLC (OD-H, elute: Hexanes/i-PrOH = 80/20, detector: 254 nm, flow rate: 1.0 mL/min), t_1 = 13.4 min (minor), t_2 = 18.7 min (major).

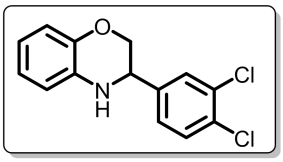
6-chloro-3-(4-chlorophenyl)-3,4-dihydro-2H-benzo[b][1,4]oxazine (**2q**)[31]



^{1}H NMR (400 MHz, Chloroform-d): δ 7.33 (dd, *J* = 21.2, 8 Hz, 4H), 6.76 – 6.74 (m, 1H), 6.65 – 6.64 (m, 2H), 4.48 (d, *J* = 8.4 Hz, 1H), 4.24 (d, *J* = 10.4 Hz, 1H), 3.95 – 3.90 (m, 2H).
^{13}C NMR (150 MHz, $CDCl_3$): δ 142.1, 137.4, 134.6, 134.4, 129.2, 128.6, 126.4, 118.8, 117.7, 115.0, 70.7, 53.5.

HPLC (OD-H, elute: Hexanes/i-PrOH = 80/20, detector: 254 nm, flow rate: 1.0 mL/min), t_1 = 9.0 min (minor), t_2 = 15.3 min (major).

3-(3,4-dichlorophenyl)-3,4-dihydro-2H-benzo[b][1,4]oxazine (**2r**)[31]

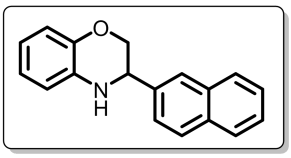


^{1}H NMR (400 MHz, Chloroform-d): δ 7.51 (d, *J* = 2.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.24 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.86 – 6.81 (m, 2H), 6.75 – 6.68 (m, 2H), 4.49 (dd, *J* = 8.0, 2.8 Hz, 1H), 4.26 (dd, *J* = 10.4, 2.8 Hz, 1H), 3.99 – 3.93 (m, 2H);

^{13}C NMR (150 MHz, $CDCl_3$): δ 143.6, 139.8, 133.3, 133.2, 132.5, 130.9, 129.3, 126.6, 121.9, 119.5, 116.9, 115.7, 70.6, 53.4.

HPLC (OD-H, elute: Hexanes/i-PrOH = 80/20, detector: 254 nm, flow rate: 1.0 mL/min), t_1 = 13.0 min (minor), t_2 = 27.5 min (major).

3-(naphthalen-2-yl)-3,4-dihydro-2H-benzo[b][1,4]oxazine (**2s**)[31]

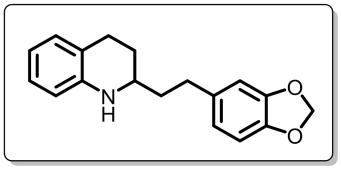


^{1}H NMR (400 MHz, Chloroform-d): δ 7.89 – 7.86 (m, 4H), 7.53 – 7.51 (m, 3H), 6.91 – 6.84 (m, 2H), 6.77 – 6.72 (m, 2H), 4.68 (dd, *J* = 8.4, 2.4 Hz, 1H, CH2), 4.37 (dd, *J* = 10.4, 2.4 Hz, 1H), 4.12 – 4.07 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 143.6, 136.6, 133.9, 133.4, 133.4, 128.7, 128.0, 127.8, 126.4, 126.3, 126.2, 125.0, 121.6, 119.0, 116.7, 115.5, 71.0, 54.4.

HPLC (OD-H, elute: Hexanes/i-PrOH = 80/20, detector: 254 nm, flow rate: 1.0 mL/min), t_1 = 16.9 min (minor), t_2 = 32.0 min (major).

2-(2-(benzo[d][1,3]dioxol-5-yl)ethyl)-1,2,3,4-tetrahydroquinoline (**2t**)[31]

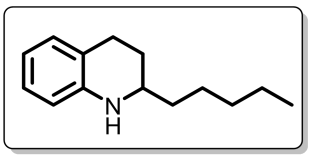


^{1}H NMR (400 MHz, Chloroform-d): δ 6.97 – 6.95 (m, 2H), 6.76 – 6.71 (m, 2H), 6.67 – 6.62 (m, 2H), 6.48 (d, J = 8.0 Hz, 1H), 5.93 (s, 2H), 3.82 (br, 1H), 3.30 – 3.28 (m, 1H), 2.86 – 2.65 (m, 4H), 2.01 – 1.98 (m, 1H), 1.82 – 1.77 (m, 2H), 1.72 – 1.62 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 147.8, 145.8, 144.5, 135.7, 129.4, 126.9, 121.5, 121.2, 117.3, 114.4, 108.9, 108.4, 100.9, 51.1, 38.6, 32.0, 28.0, 26.3.

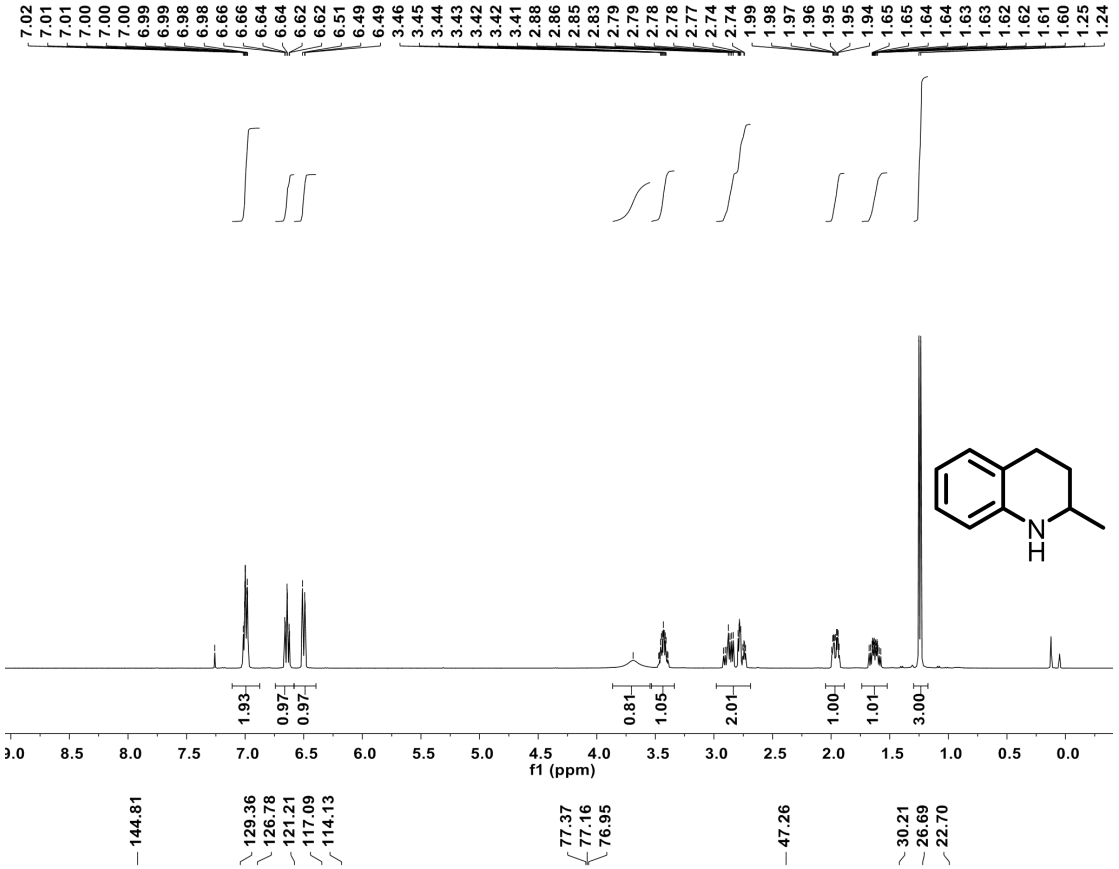
HPLC (OD-H, elute: Hexanes/i-PrOH = 80/20, detector: 254 nm, flow rate: 1.0 mL/min), t_1 = 11.1 min (minor), t_2 = 14.2 min (major).

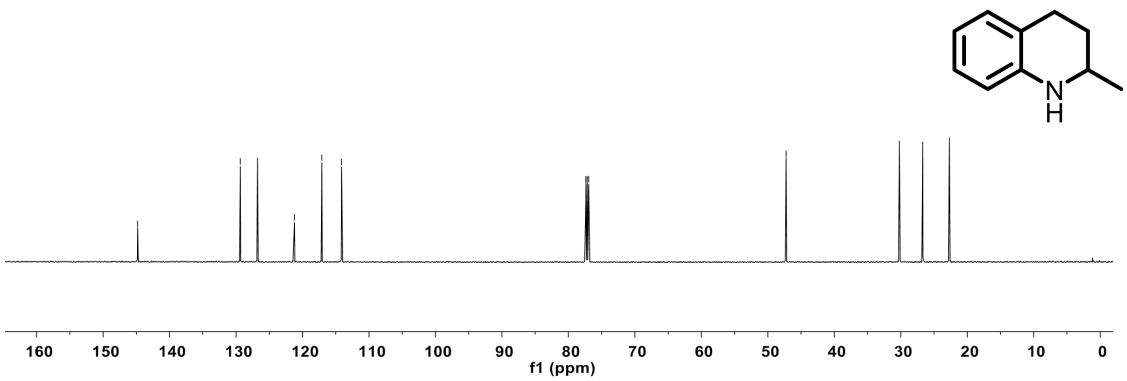
2-pentyl-1,2,3,4-tetrahydroquinoline (**2u**)[31]

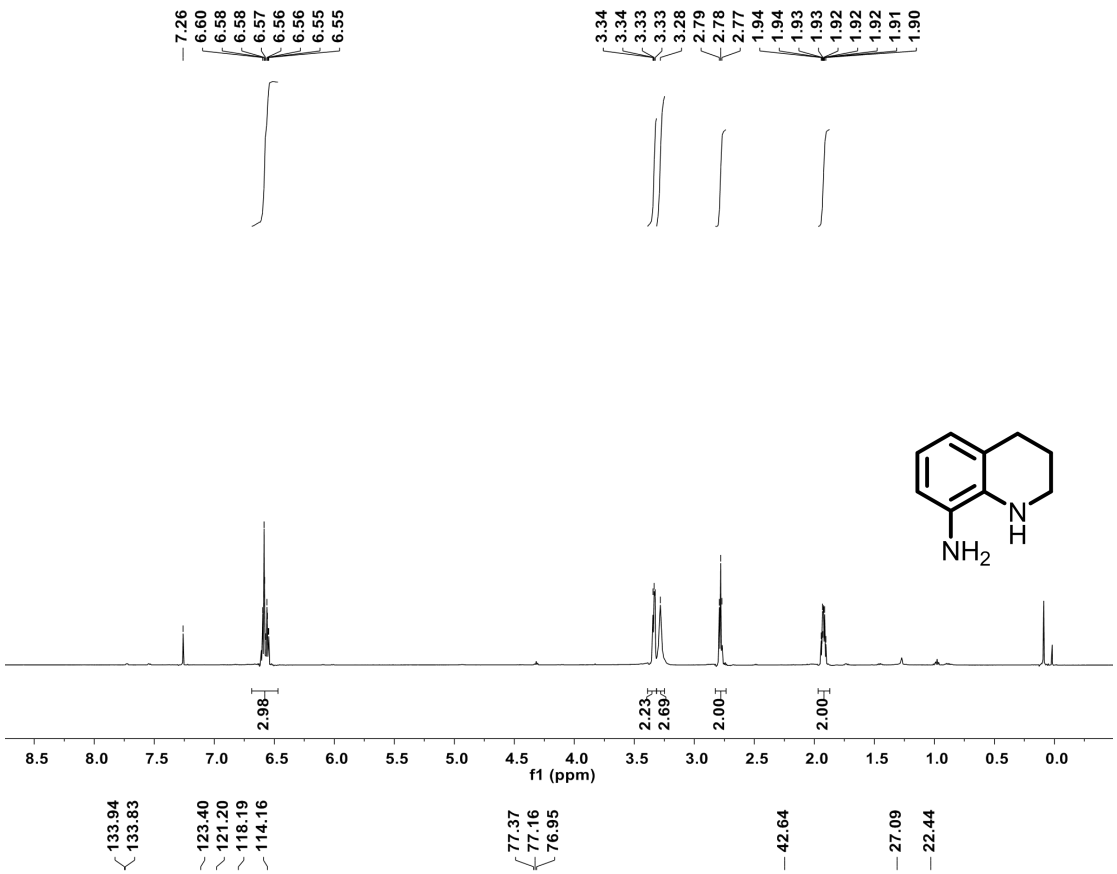


^{1}H NMR (400 MHz, Chloroform-d): δ 6.96 – 6.95 (m, 2H), 6.62 – 6.59 (m, 1H), 6.50 – 6.48 (m, 1H), 3.25 – 3.24 (m, 1H), 2.82 – 2.71 (m, 2H), 2.05 – 1.95 (m, 1H), 1.61 – 1.50 (m, 1H), 1.49 – 1.47 (m, 2H), 1.41 – 1.27 (m, 7H), 0.92 – 0.90 (m, 3H);
^{13}C NMR (150 MHz, $CDCl_3$): δ 144.8, 129.4, 126.8, 121.6, 117.1, 114.2, 51.8, 36.8, 32.1, 28.2, 26.6, 25.5, 22.8, 14.2.
HPLC (OD-H, elute: Hexanes/i-PrOH = 90/10, detector: 254 nm, flow rate: 0.5 mL/min), t_1 = 12.4 min (major), t_2 = 13.5 min (minor).

3 NMR Spectra






7.26
6.60
6.58
6.58
6.57
6.56
6.56
6.55
6.55
3.34
3.34
3.33
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3.28
2.79
2.78
2.77
1.94
1.94
1.93
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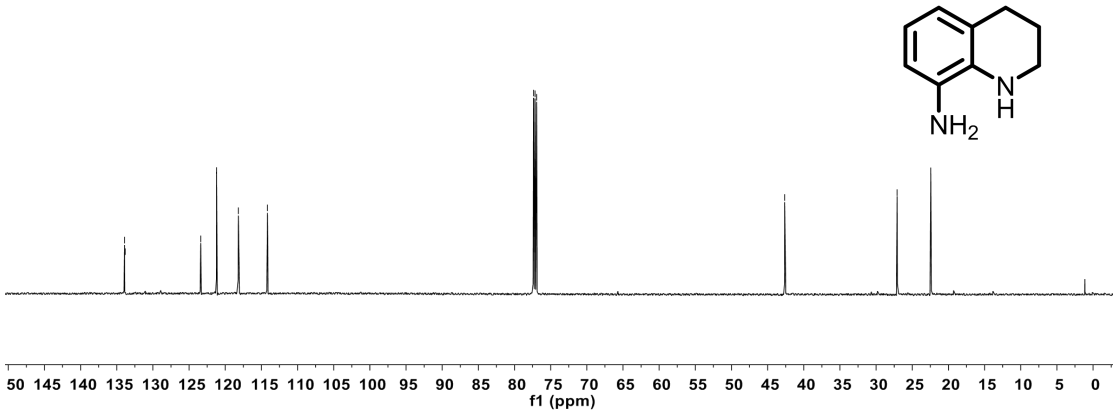
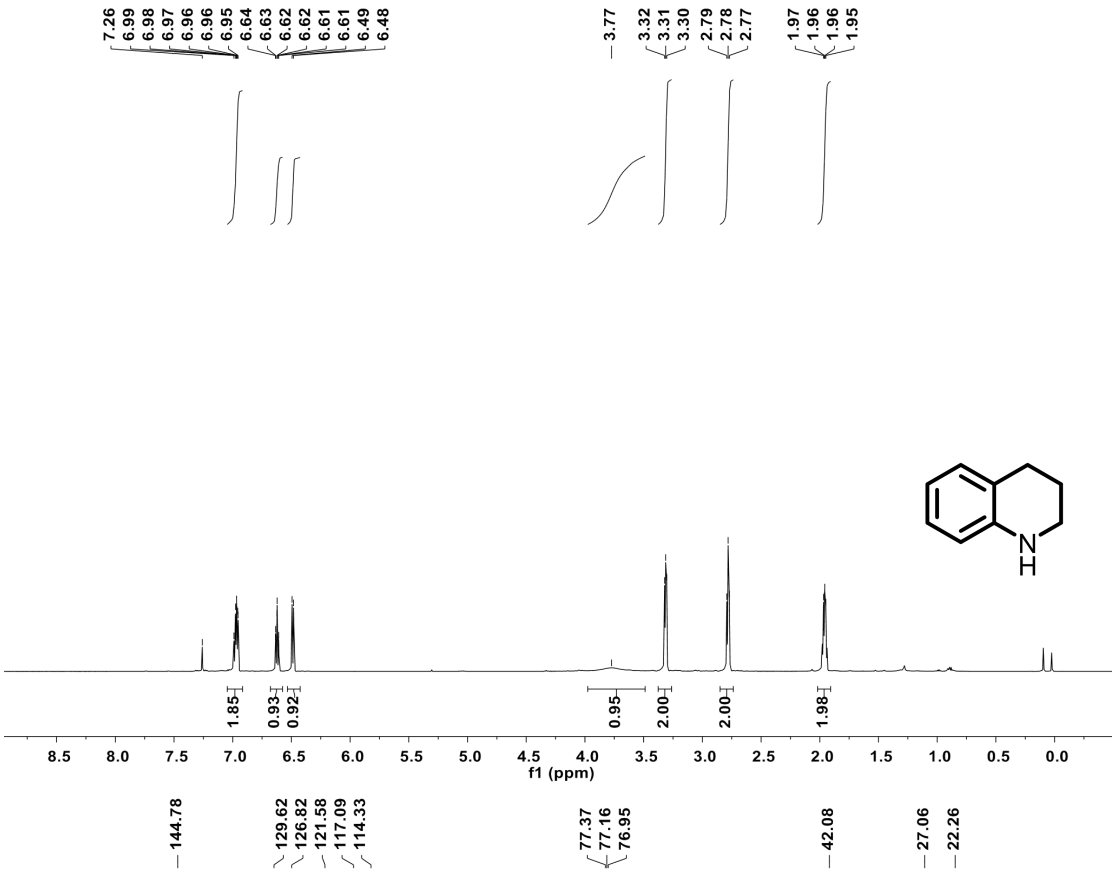
2.23
2.69
2.00
2.00
f1 (ppm)


133.94
133.83
123.40
121.20
118.19
114.16
77.37
77.16
76.95
42.64
27.09
22.44
NH2
f1 (ppm)


7.26
6.99
6.98
6.97
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6.95
6.64
6.63
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6.62
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6.49
6.48
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3.30
2.79
2.78
2.77
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1.96
1.95
N
H
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0.93
0.92
0.95
2.00
2.00
1.98
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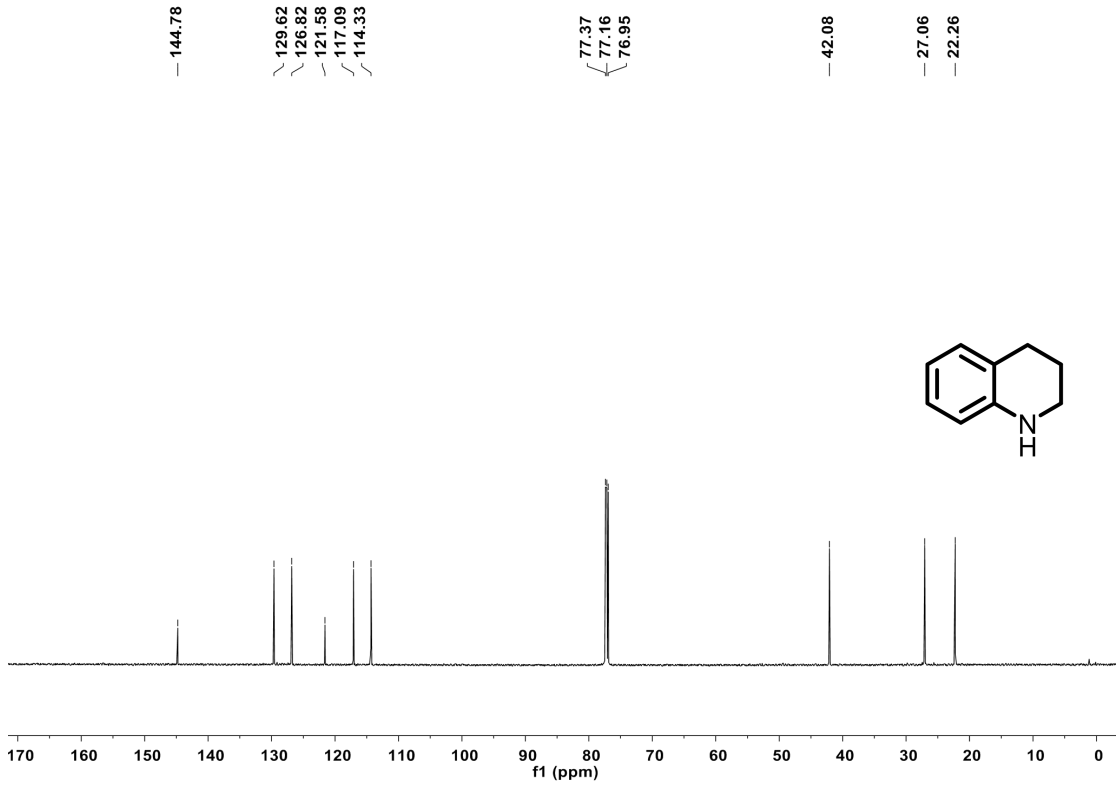
f1 (ppm)


144.78
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126.82
121.58
117.09
114.33
77.37
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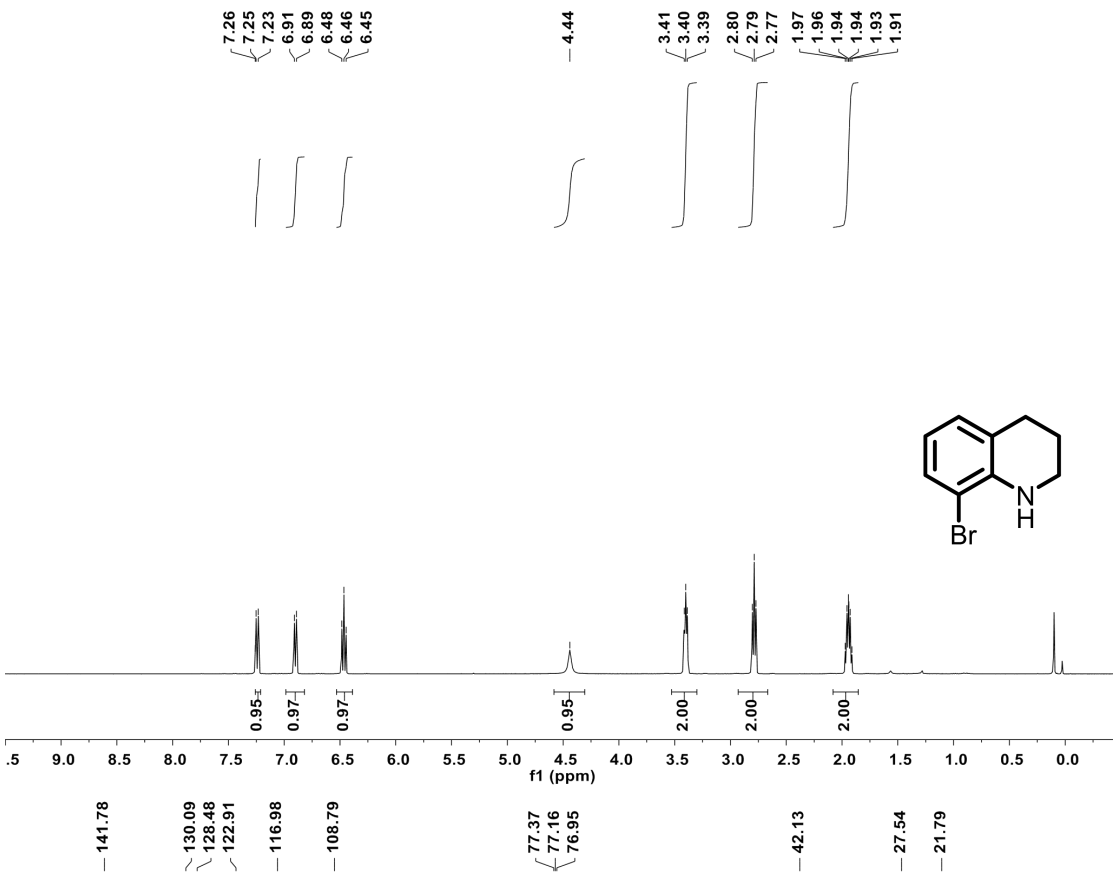
76.95
42.08
27.06
22.26
N
H
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.26
7.25
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4.44
3.41
3.40
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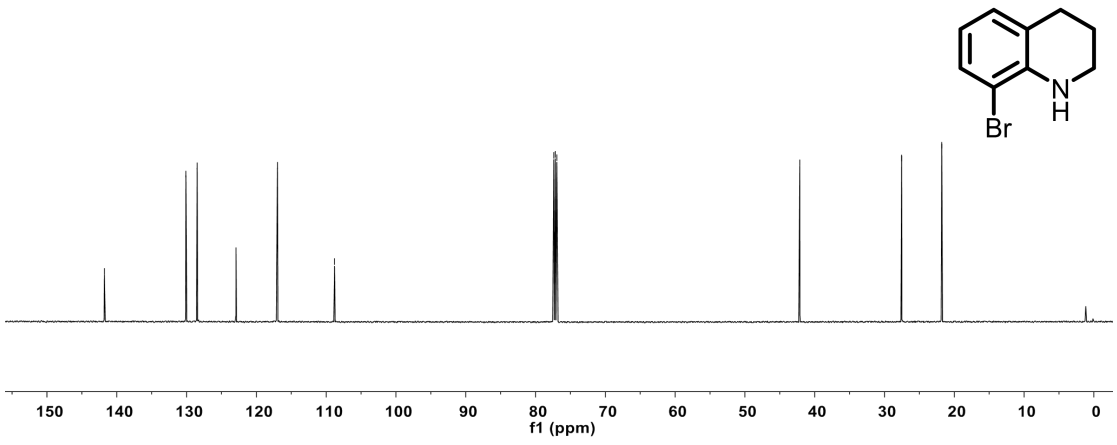
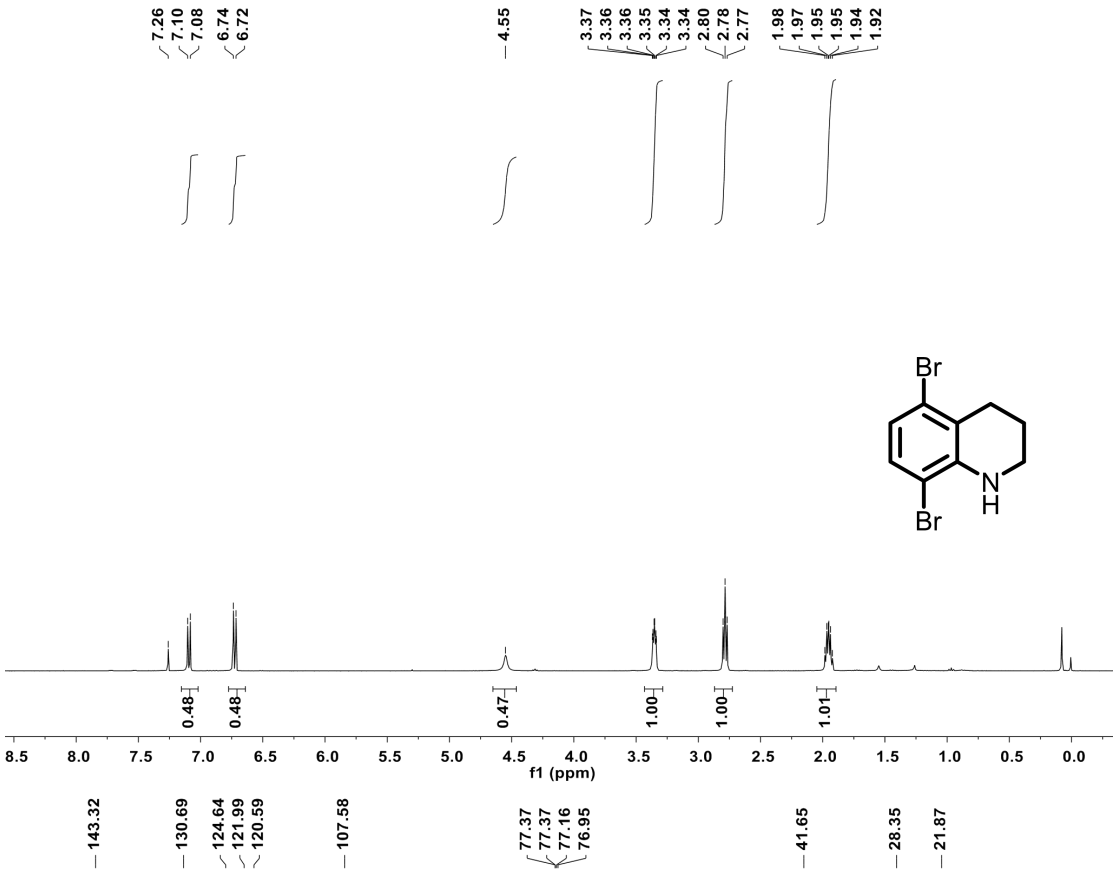
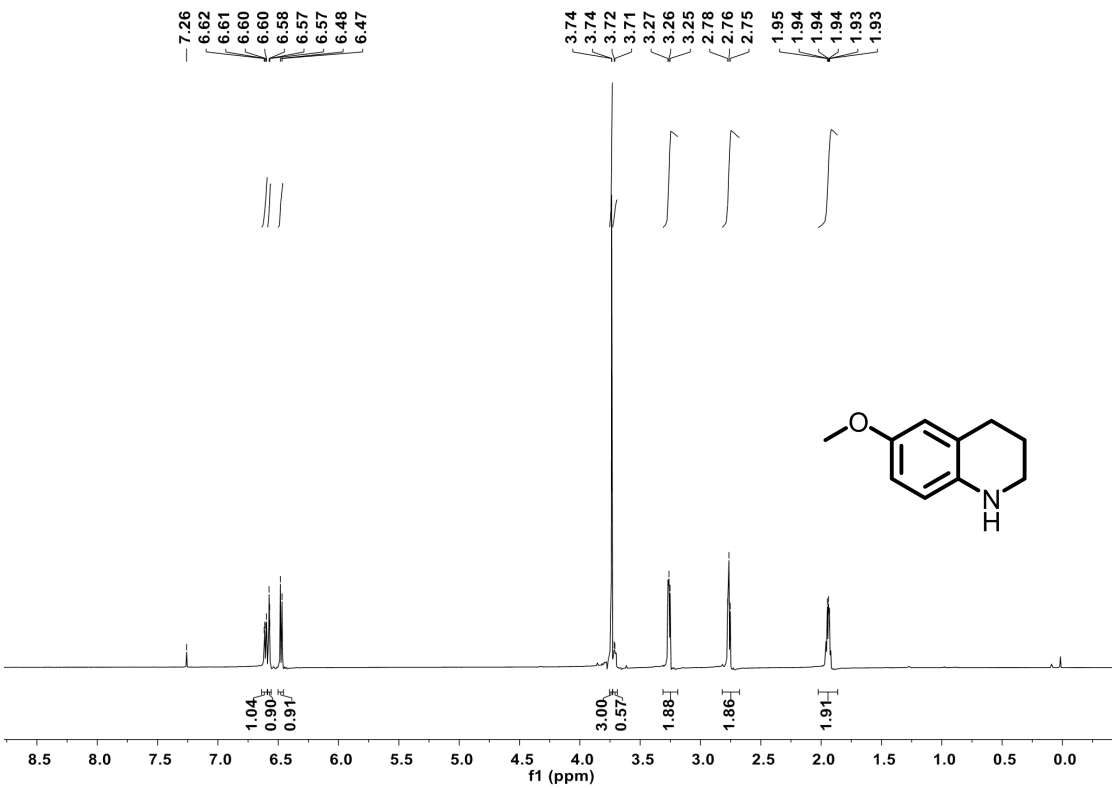
2.79
2.77
1.97
1.96
1.94
1.94
1.93
1.91
Br
N
H
0.95
0.97
0.97
0.95
2.00
2.00
2.00
f1 (ppm)

141.78
130.09
128.48
122.91
116.98
108.79
77.37
77.16
76.95
42.13
27.54
21.79


Br
N
H
f1 (ppm)


7.26
7.10
7.08
6.74
6.72
4.55
3.37
3.36
3.36
3.35
3.34
3.34
2.80
2.78
2.77
1.98
1.97
1.95
1.95
1.94
1.92
Br
N
H
Br
0.48
0.48
0.47
1.00
1.00
1.01
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
f1 (ppm)
143.32
130.69
124.64
121.99
120.59
107.58
77.37
77.37
77.16
76.95
41.65
28.35
21.87
Br
N
H
Br
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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6.62
6.61
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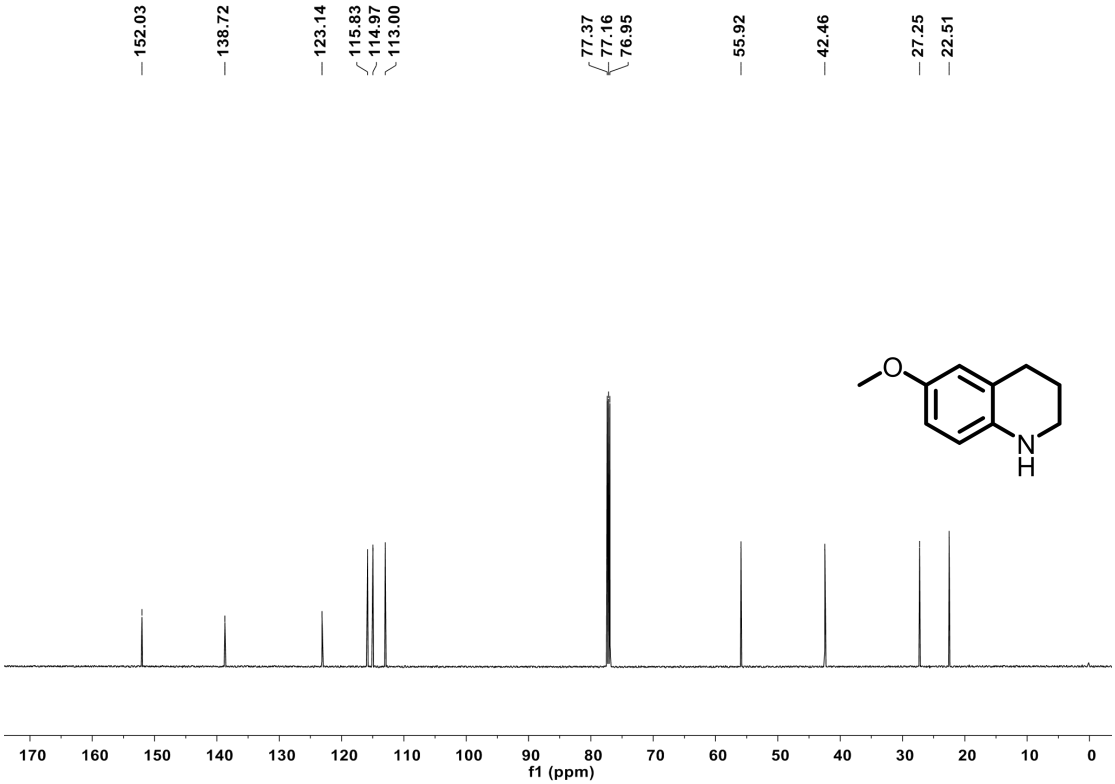
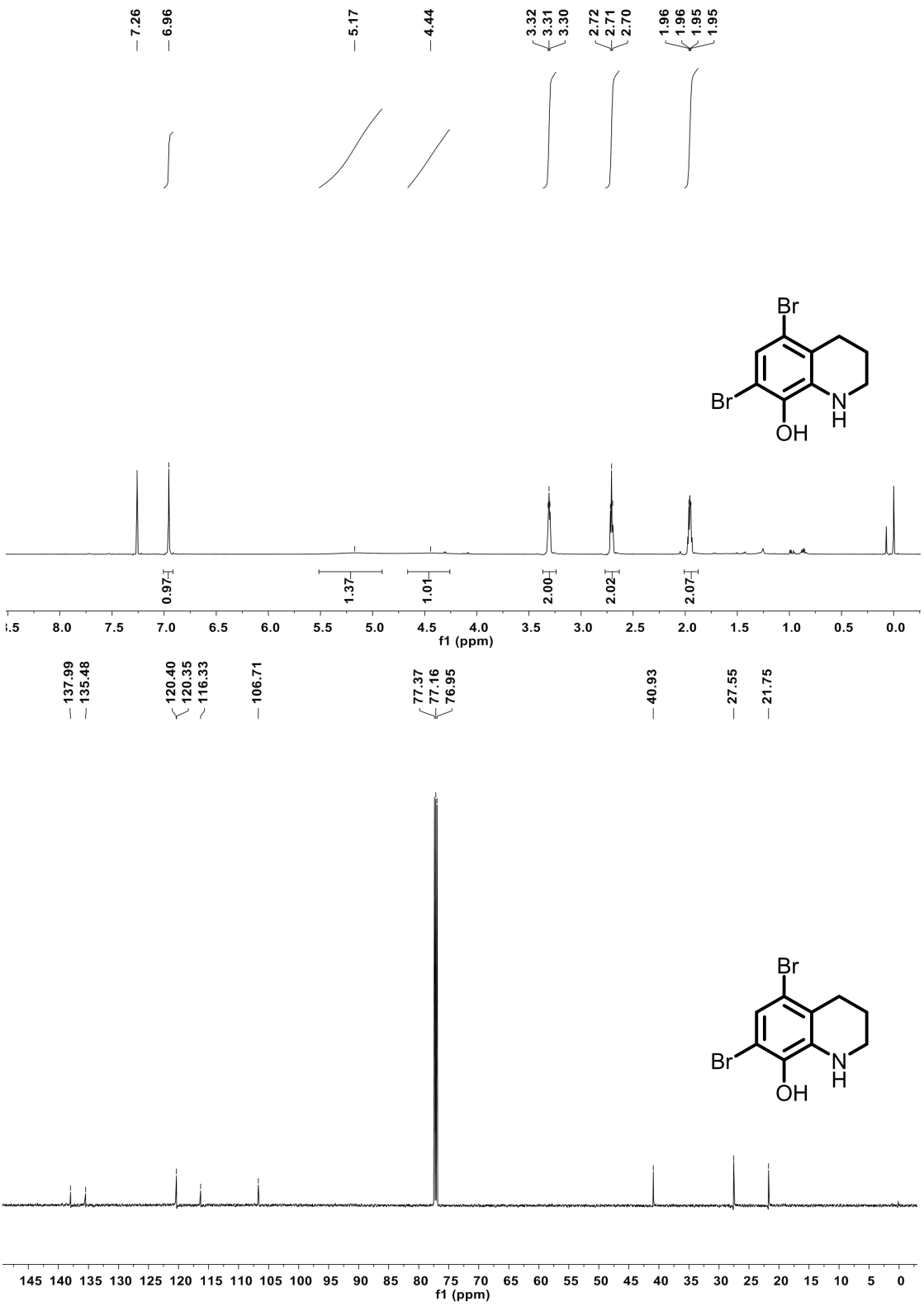
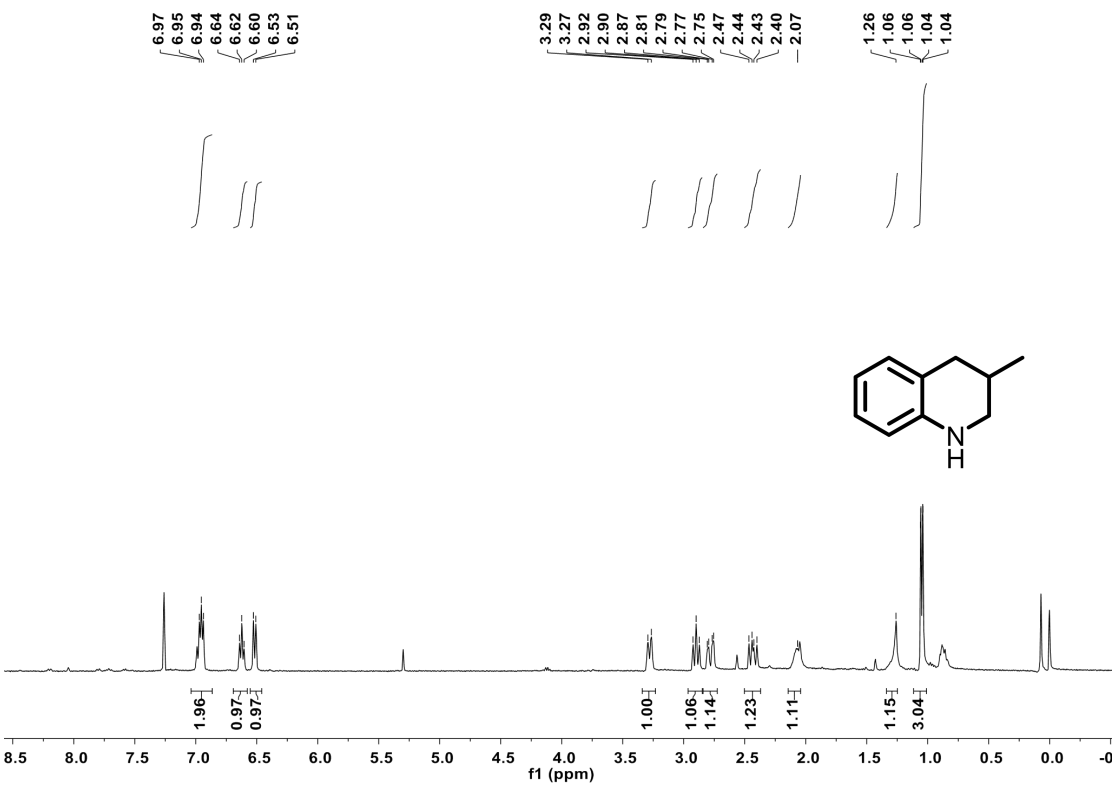
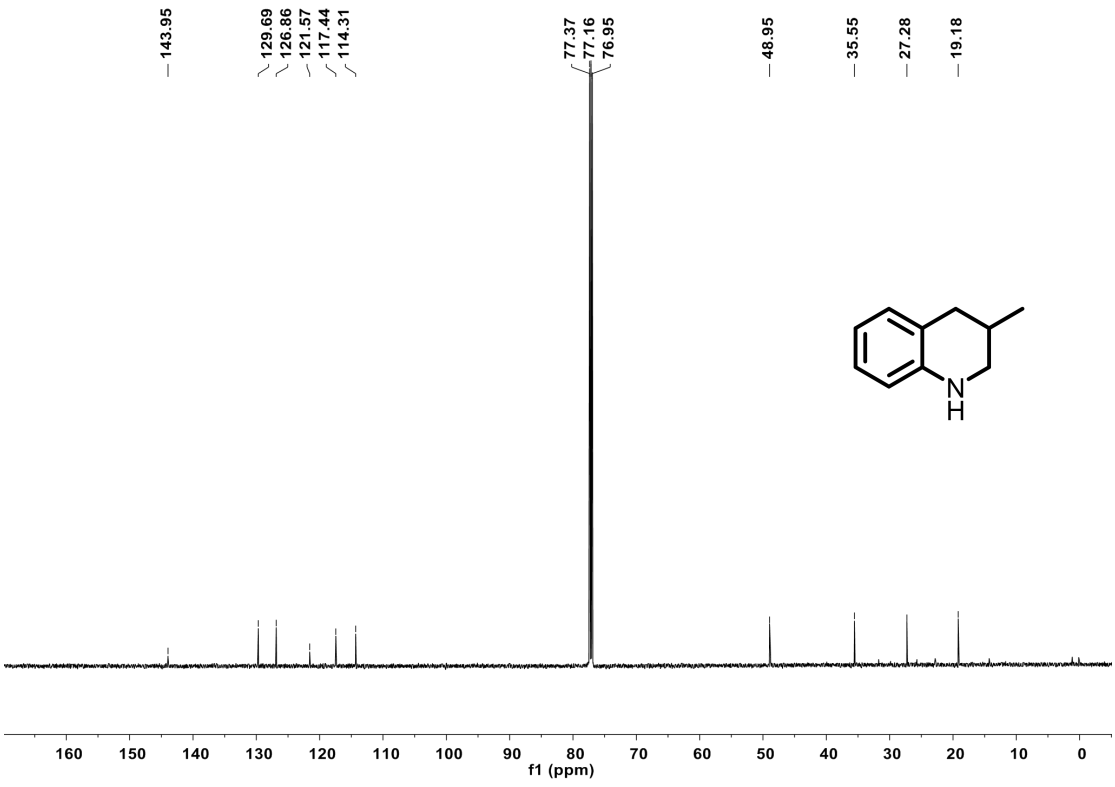
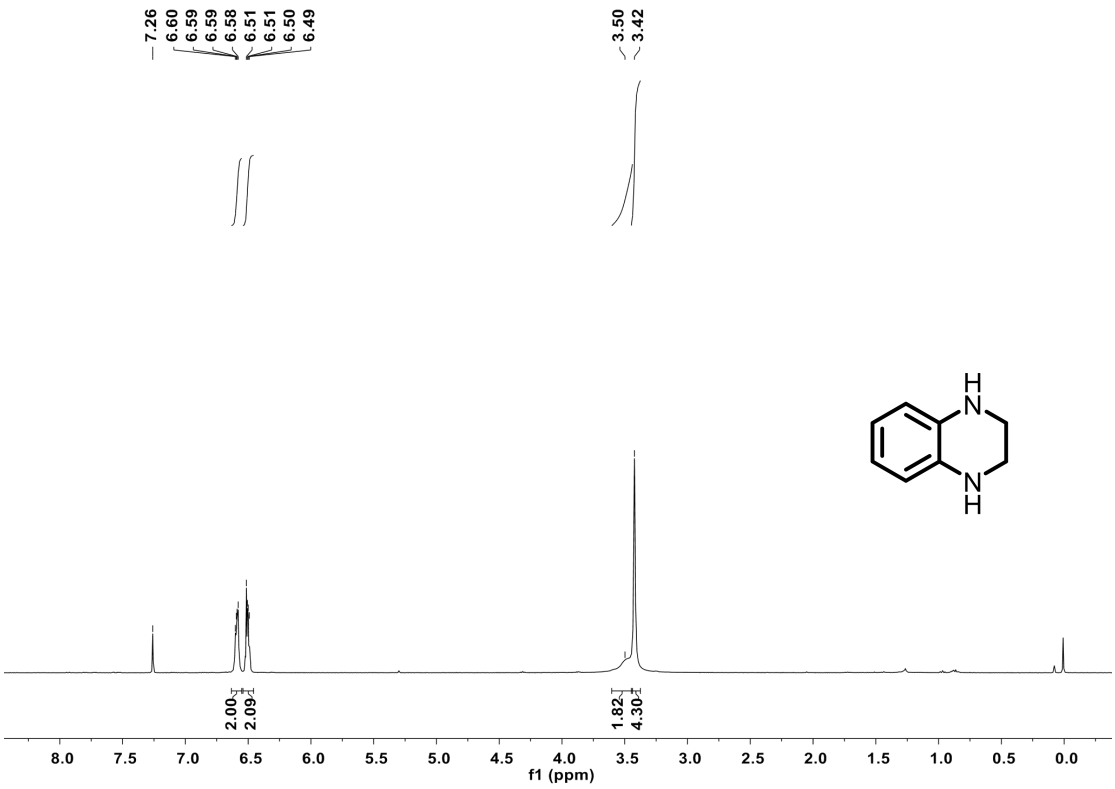
6.60
6.58
6.57
6.57
6.48
6.47
3.74
3.74
3.72
3.71
3.27
3.26
3.25
2.78
2.76
2.75
1.95
1.94
1.94
1.94
1.93
1.93
O
N
H
1.04
0.90
0.91
3.00
0.57
1.88
1.86
1.91
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

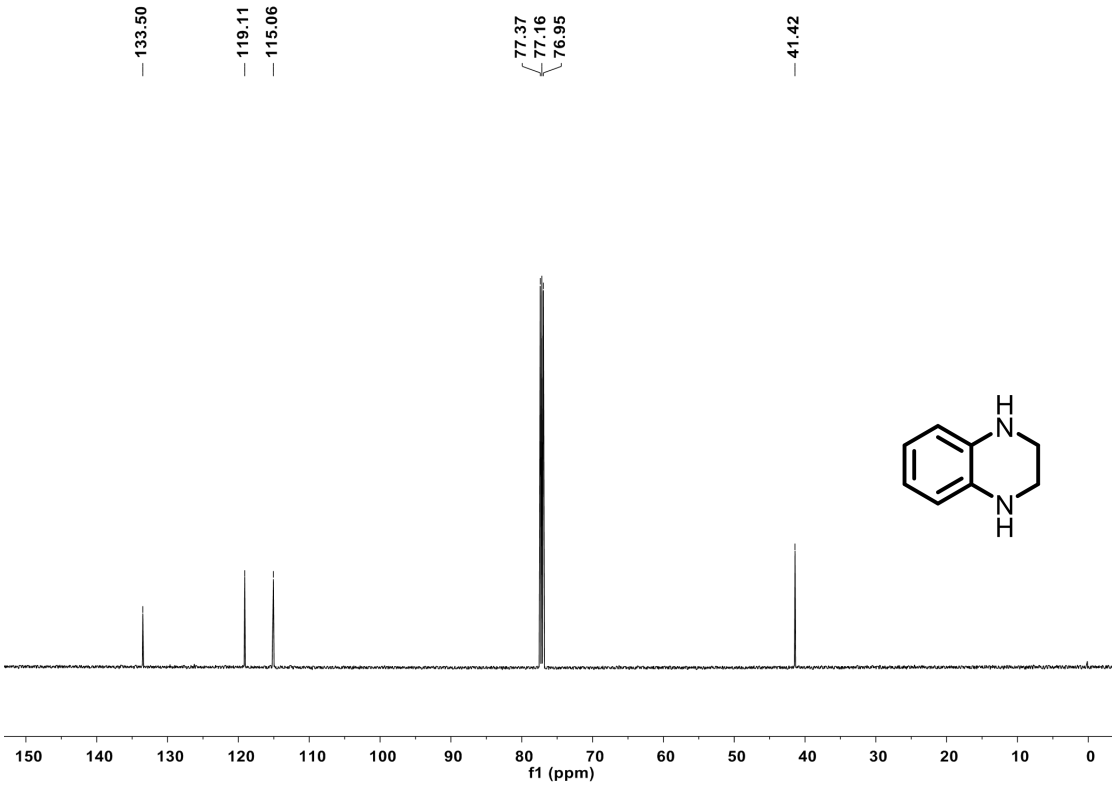

152.03
138.72
123.14
115.83
114.97
113.00
77.37
77.16
76.95
55.92
42.46
27.25
22.51
O
N
H
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

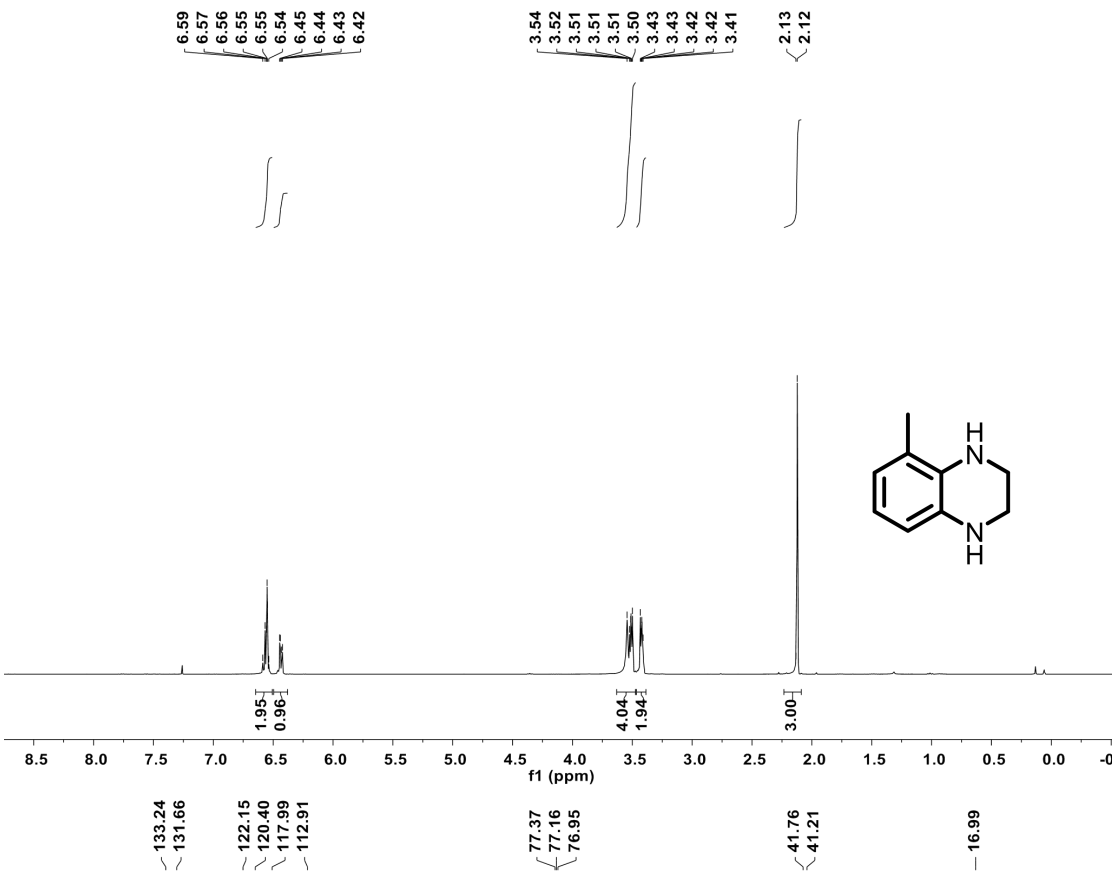

7.26
6.96
5.17
4.44
3.32
3.31
3.30
2.72
2.71
2.70
1.96
1.96
1.95
1.95
Br
Br
N
H
OH
0.97
1.37
1.01
2.00
2.02
2.07
f1 (ppm)
137.99
135.48
120.40
120.35
116.33
106.71
77.37
77.16
76.95
40.93
27.55
21.75
Br
Br
N
H
OH
f1 (ppm)

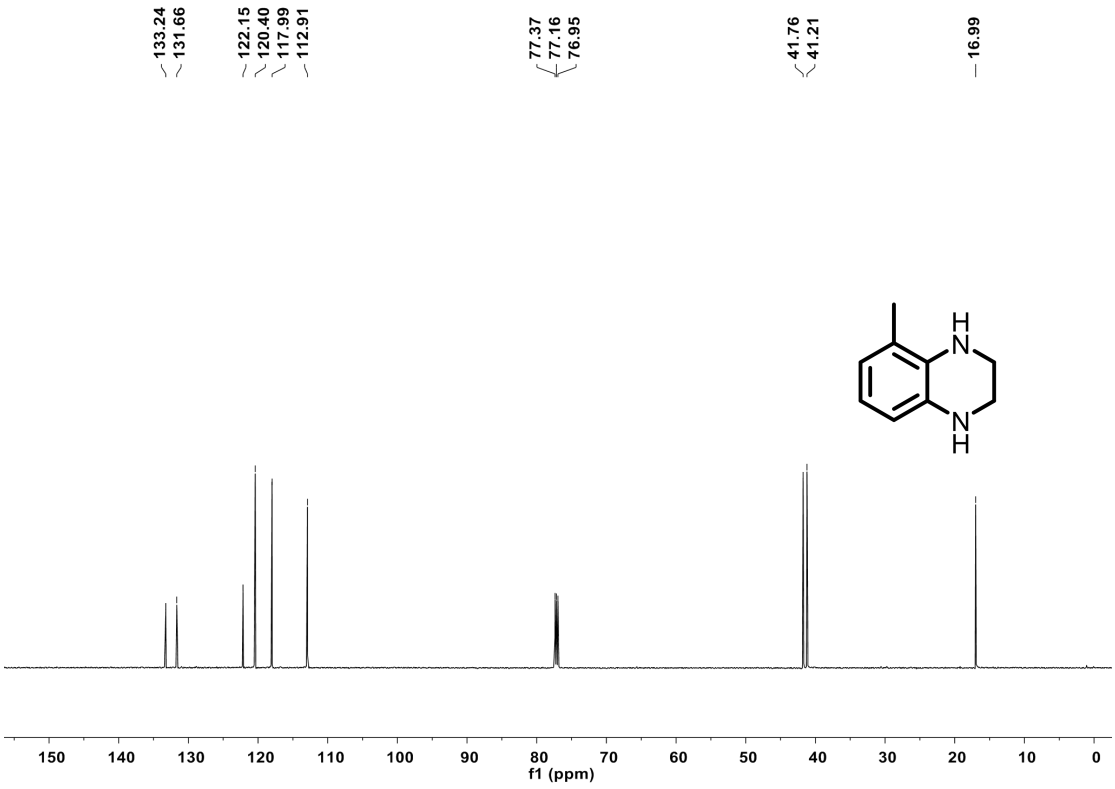

6.97
6.95
6.94
6.64
6.62
6.60
6.53
6.51
3.29
3.27
2.92
2.90
2.87
2.81
2.79
2.77
2.75
2.47
2.44
2.43
2.40
2.07
1.26
1.06
1.06
1.04
1.04
N
H
1.96
0.97
0.97
1.00
1.06
1.14
1.23
1.11
1.15
3.04
f1 (ppm)

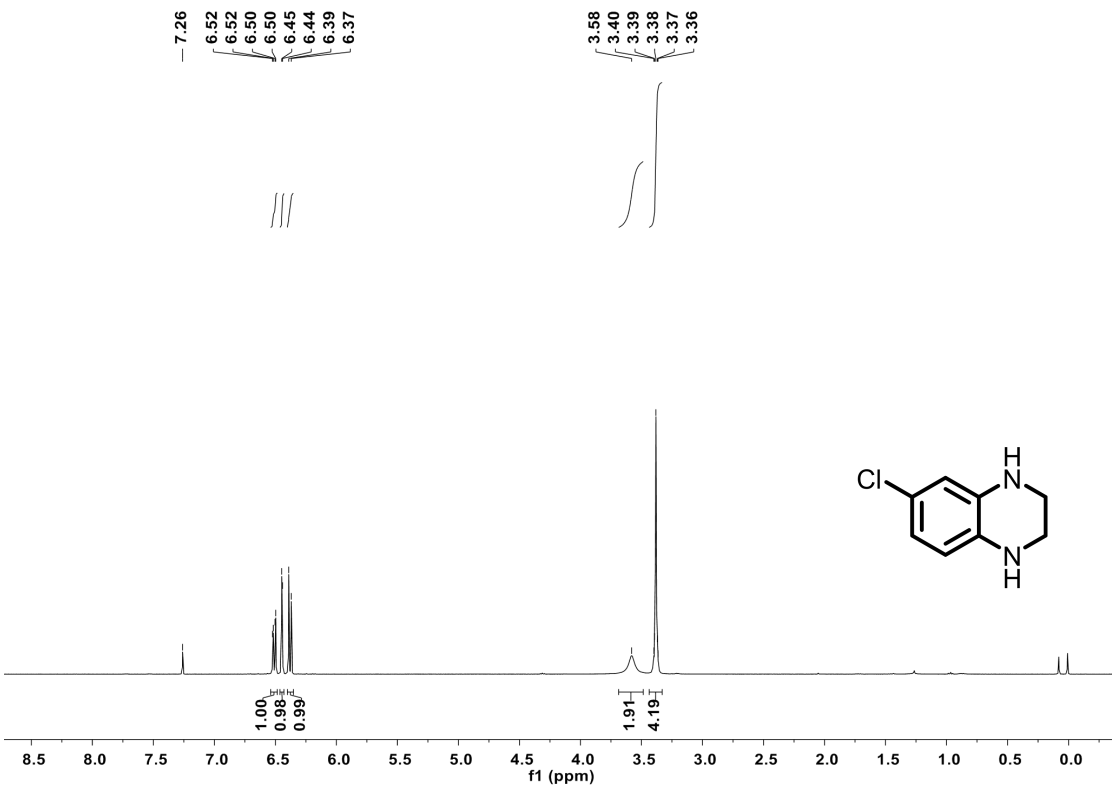

143.95
129.69
126.86
121.57
117.44
114.31
77.37
77.16
76.95
48.95
35.55
27.28
19.18
N
H
f1 (ppm)

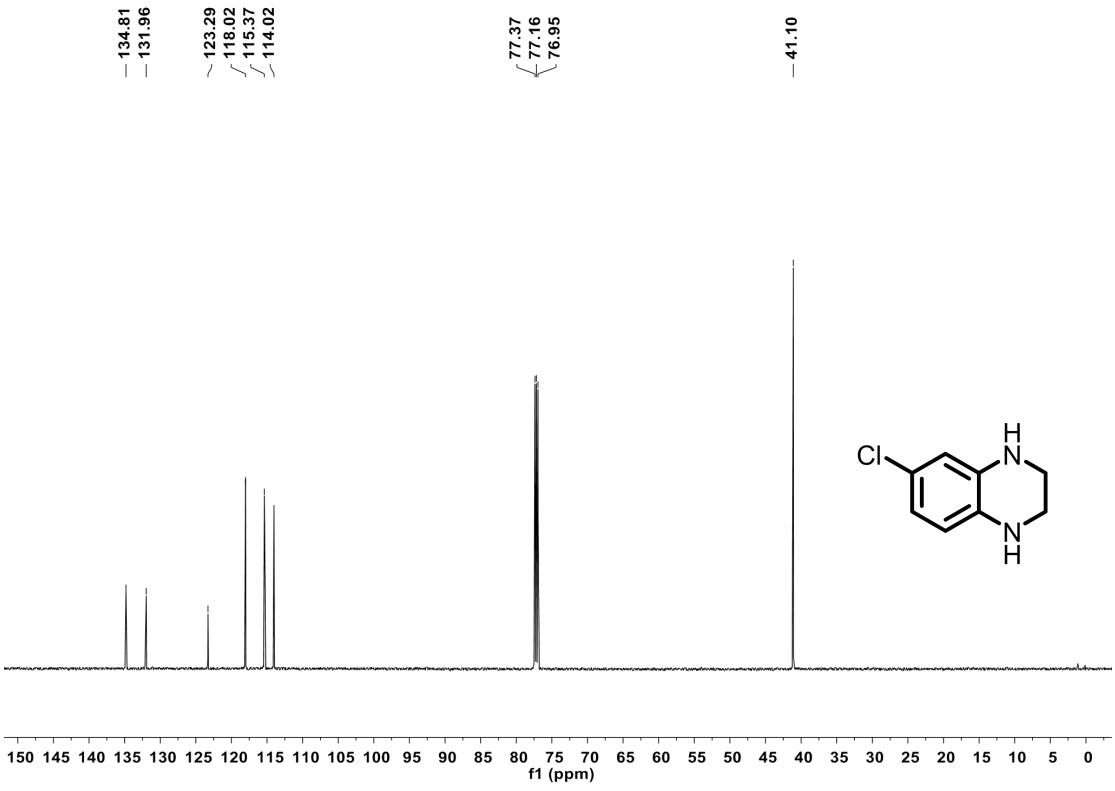

7.26
6.60
6.59
6.59
6.58
6.51
6.51
6.50
6.49
3.50
3.42
H
N
N
H
2.00
2.09
1.82
4.30
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

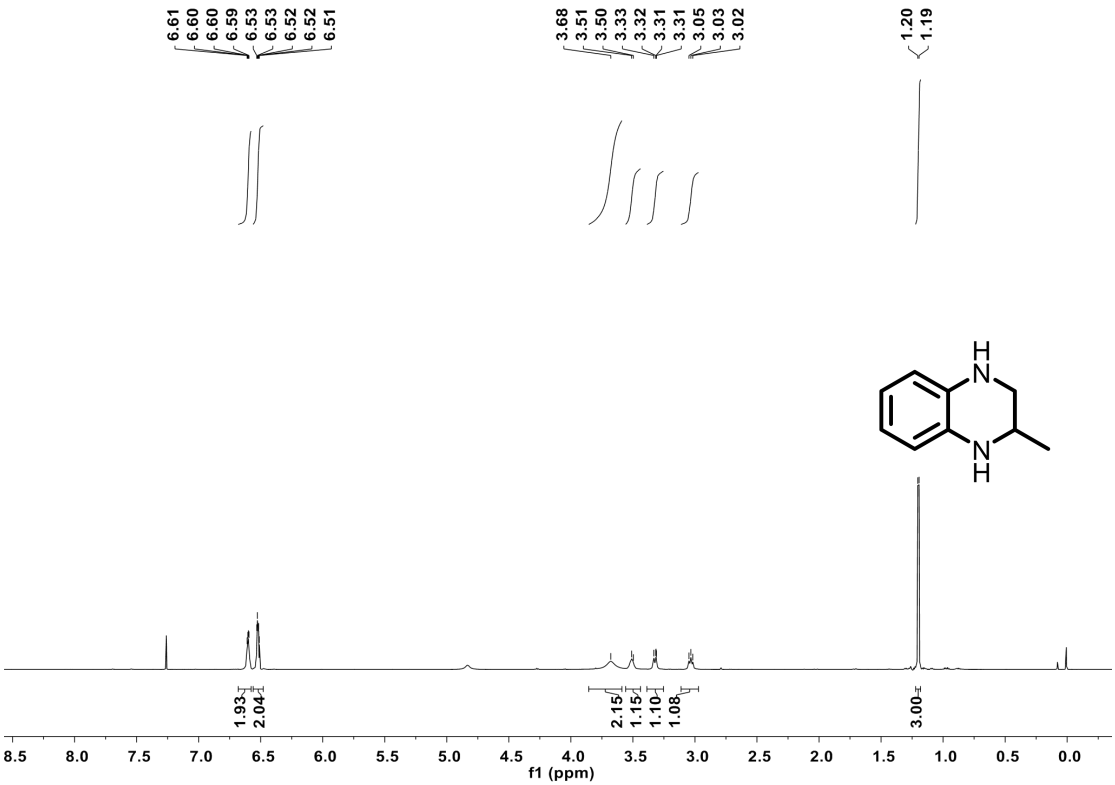

133.50
119.11
115.06
77.37
77.16
76.95
41.42
H
N
N
H
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

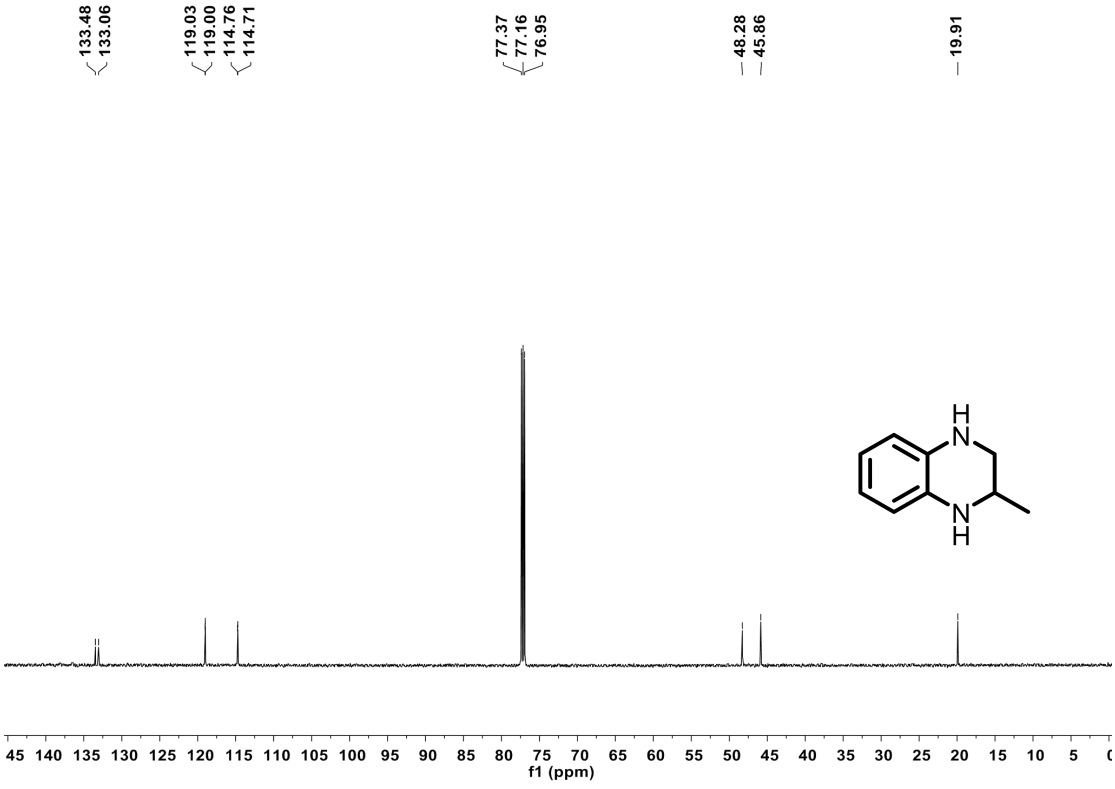

6.59
6.57
6.56
6.55
6.55
6.54
6.45
6.44
6.43
6.42
3.54
3.52
3.51
3.51
3.51
3.50
3.43
3.43
3.42
3.42
3.41
2.13
2.12
1.95
0.96
4.04
1.94
3.00
f1 (ppm)

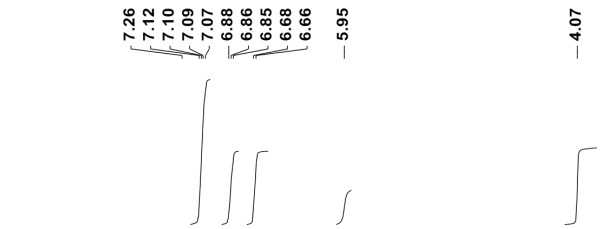

133.24
131.66
122.15
120.40
117.99
112.91
77.37
77.16
76.95
41.76
41.21
16.99
f1 (ppm)

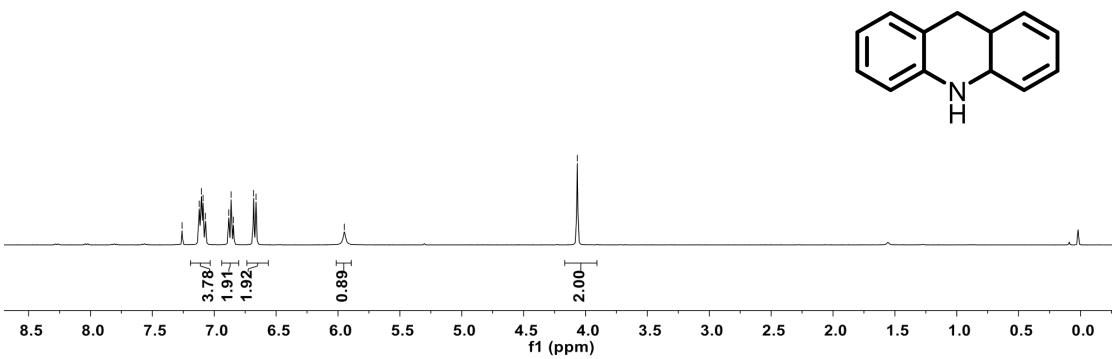

7.26
6.52
6.52
6.50
6.50
6.45
6.44
6.39
6.37
3.58
3.40
3.39
3.38
3.37
3.36
Cl
H
N
N
H
1.00
0.98
0.99
1.91
4.19
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

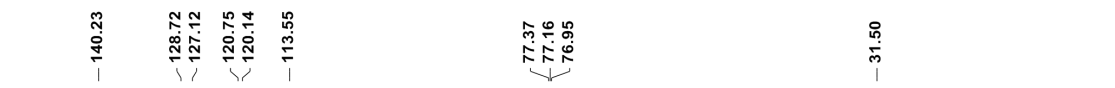

134.81
131.96
123.29
118.02
115.37
114.02
77.37
77.16
76.95
41.10
Cl
H
N
N
H
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

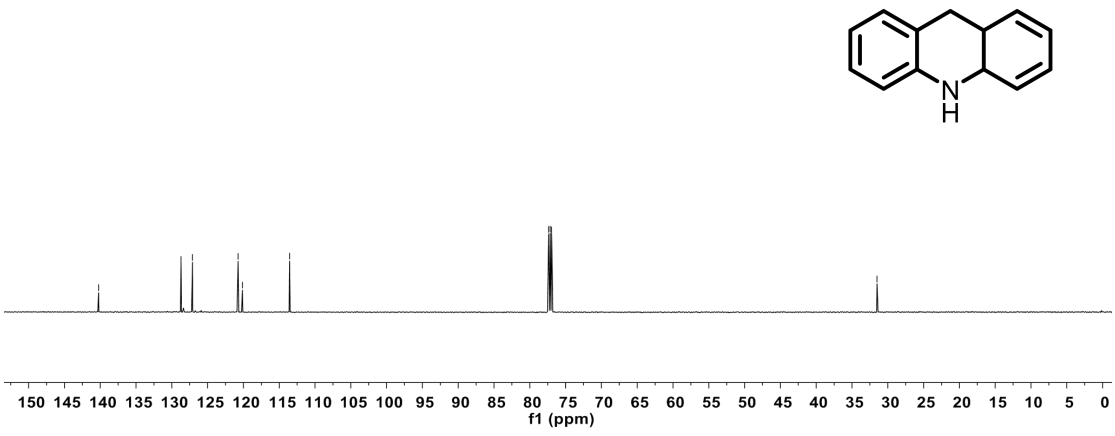

6.61
6.60
6.60
6.59
6.53
6.53
6.52
6.52
6.51
3.68
3.51
3.50
3.33
3.32
3.31
3.31
3.05
3.03
3.02
1.20
1.19
1.93
2.04
2.15
1.15
1.10
1.08
3.00
f1 (ppm)

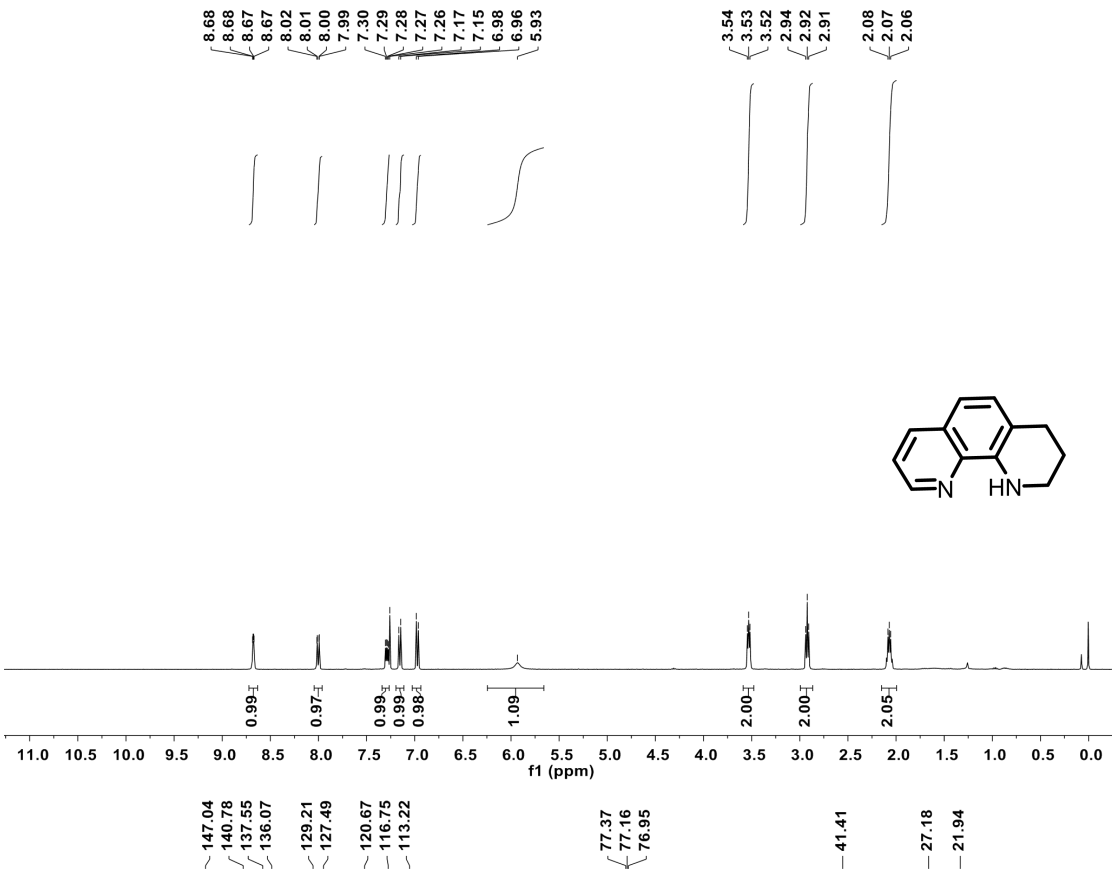

133.48
133.06
119.03
119.00
114.76
114.71
77.37
77.16
76.95
48.28
45.86
19.91
f1 (ppm)


7.26
7.12
7.10
7.09
7.07
6.88
6.86
6.85
6.68
6.66
5.95
4.07


3.78
1.91
1.92
0.89
2.00
f1 (ppm)


140.23
128.72
127.12
120.75
120.14
113.55
77.37
77.16
76.95
31.50


f1 (ppm)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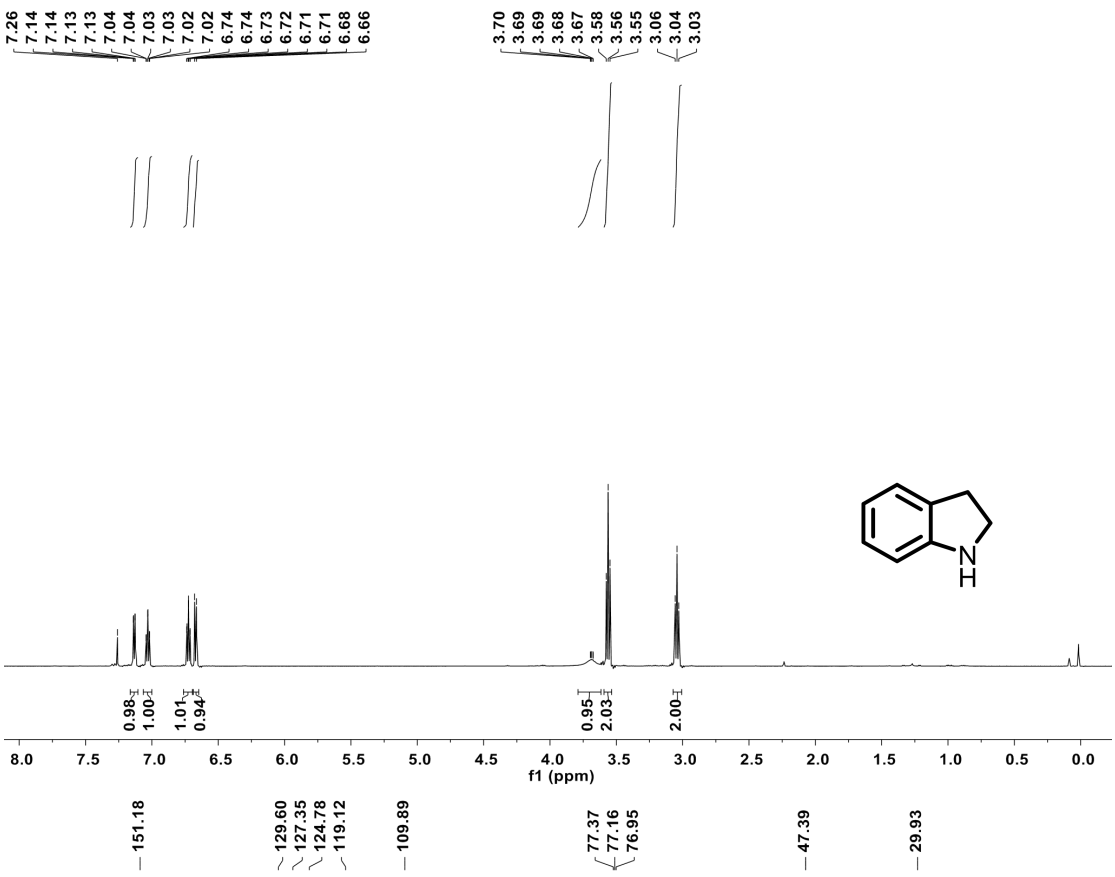
8.68
8.67
8.67
8.02
8.01
8.00
7.99
7.30
7.29
7.28
7.27
7.26
7.17
7.15
6.98
6.96
5.93
3.54
3.53
3.52
2.94
2.92
2.91
2.08
2.07
2.06
N
HN
0.99
0.97
0.99
0.99
0.98
1.09
2.00
2.00
2.05
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
147.04
140.78
137.55
136.07
129.21
127.49
120.67
116.75
113.22
77.37
77.16
76.95
41.41
27.18
21.94
N
HN
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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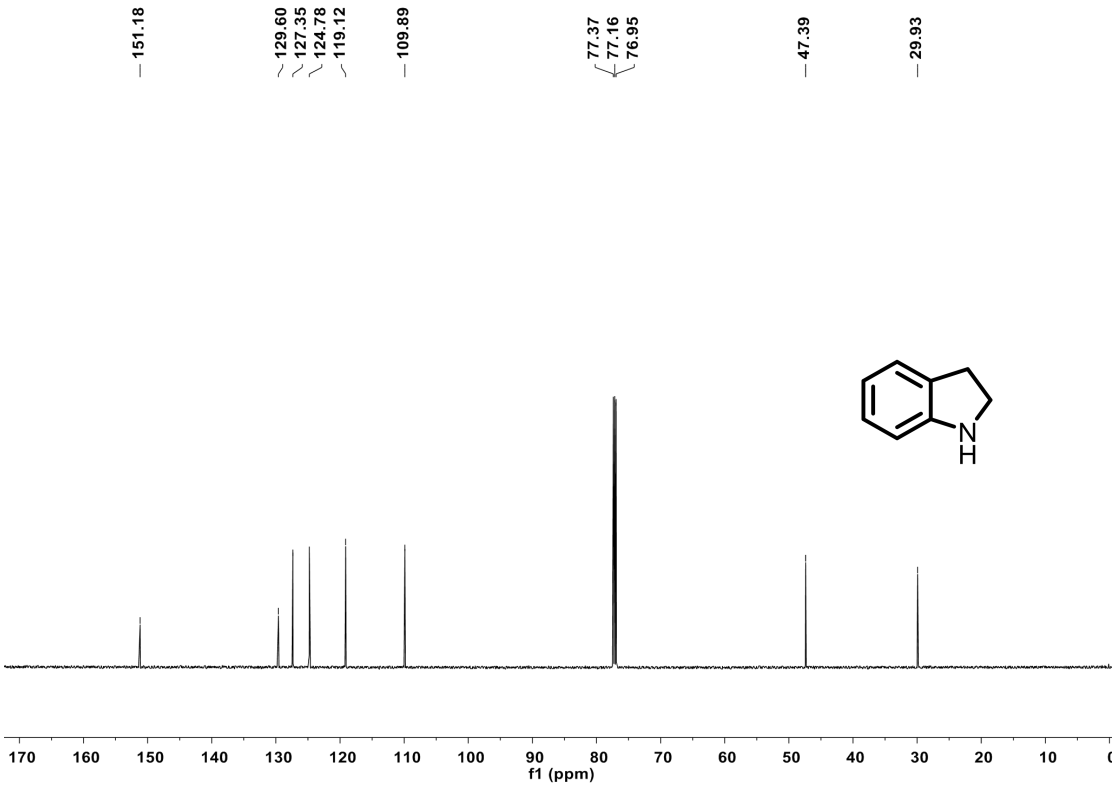
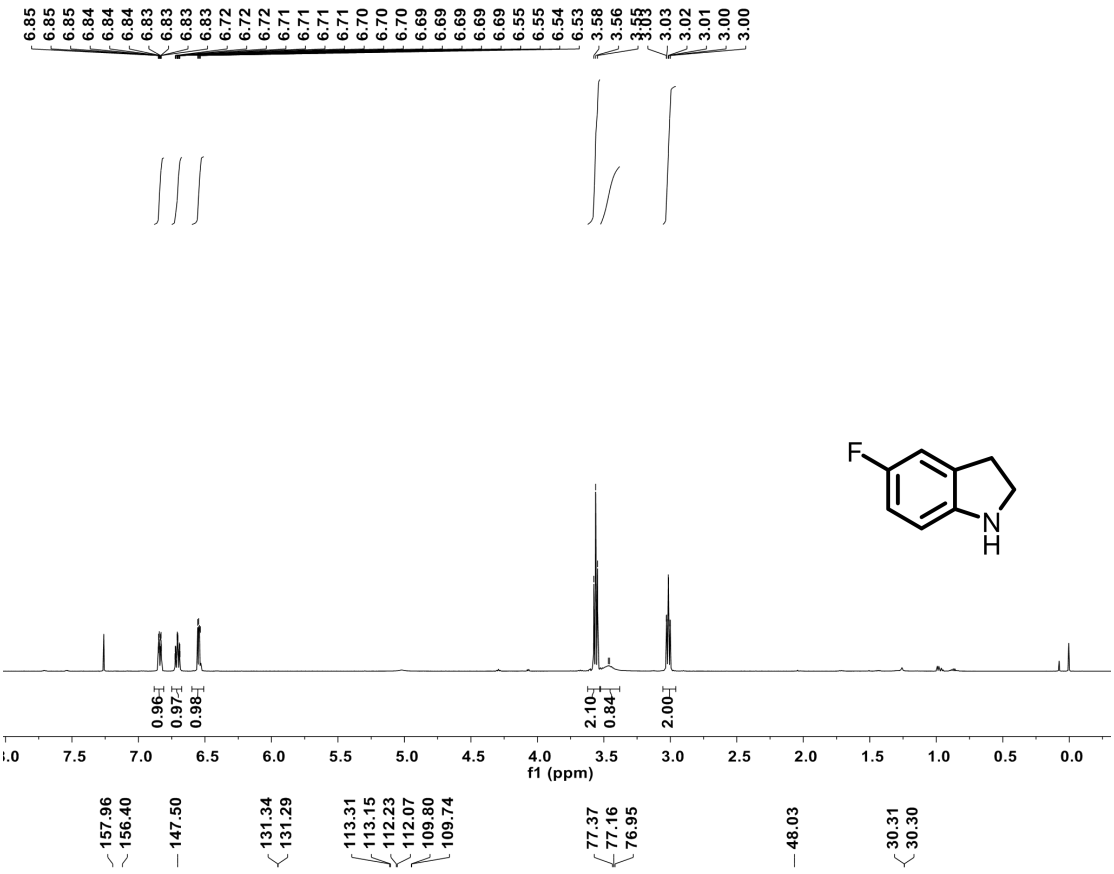
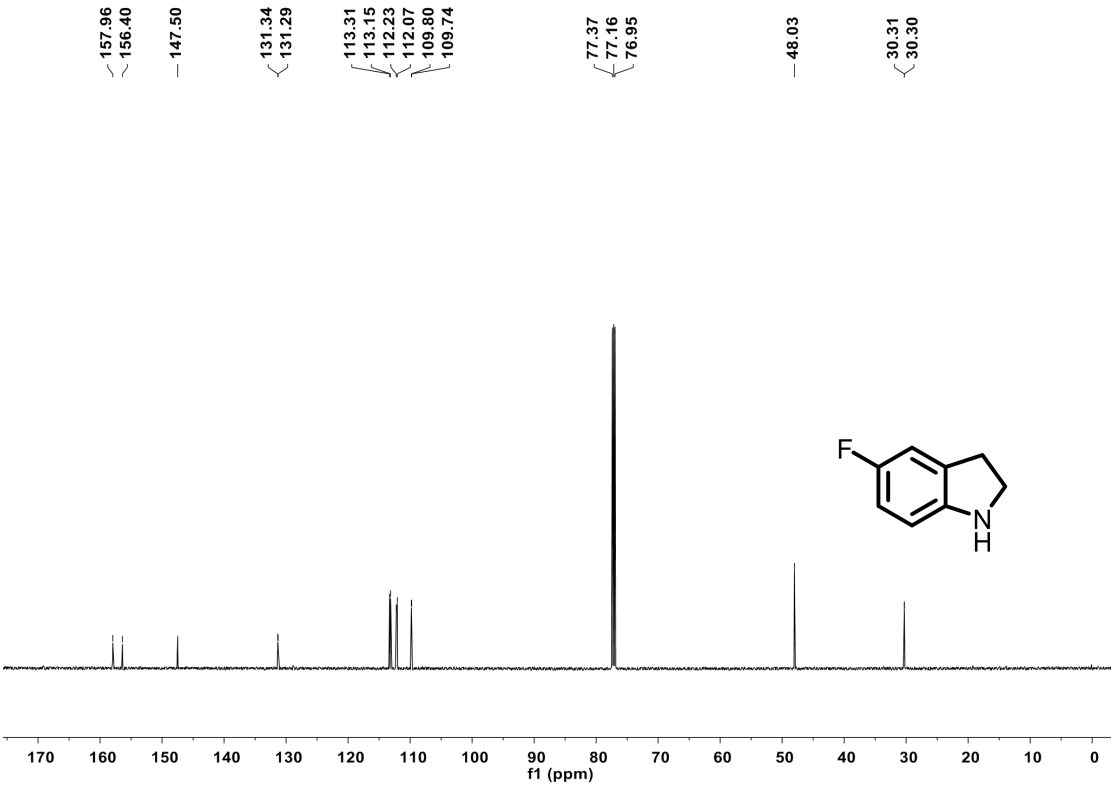
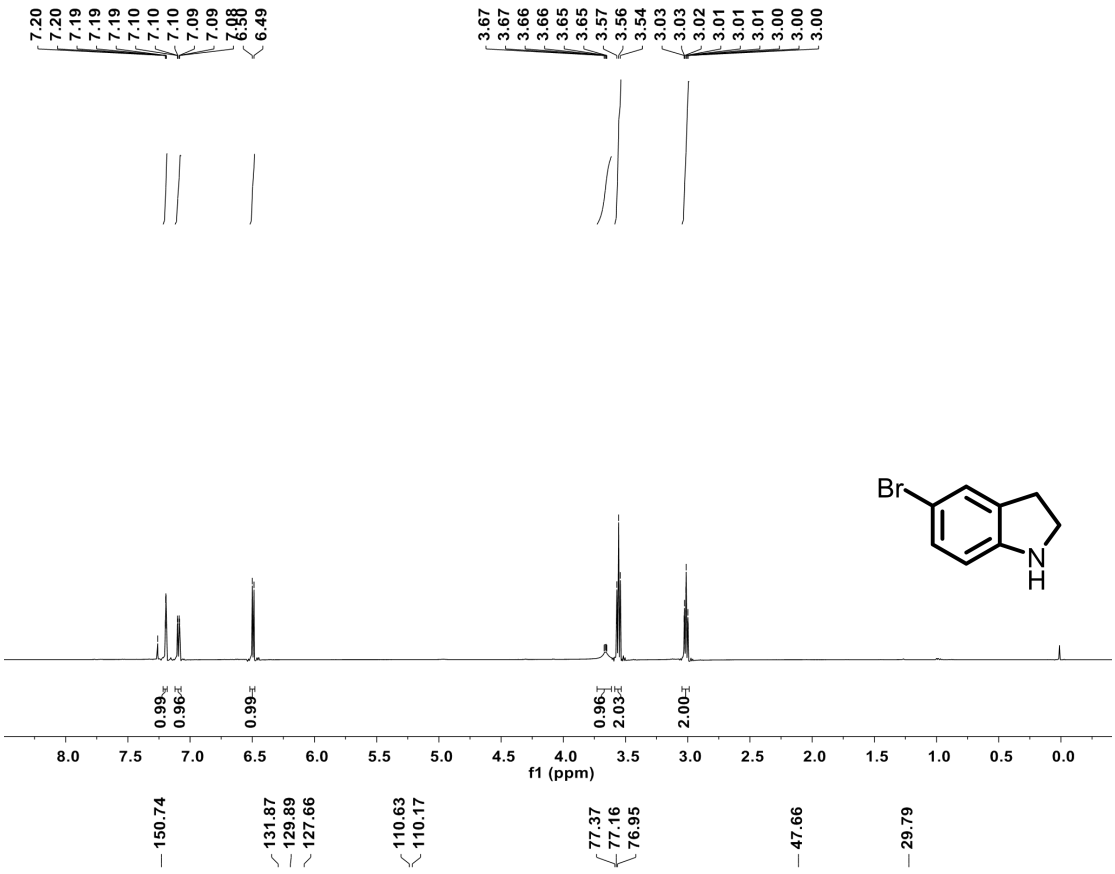
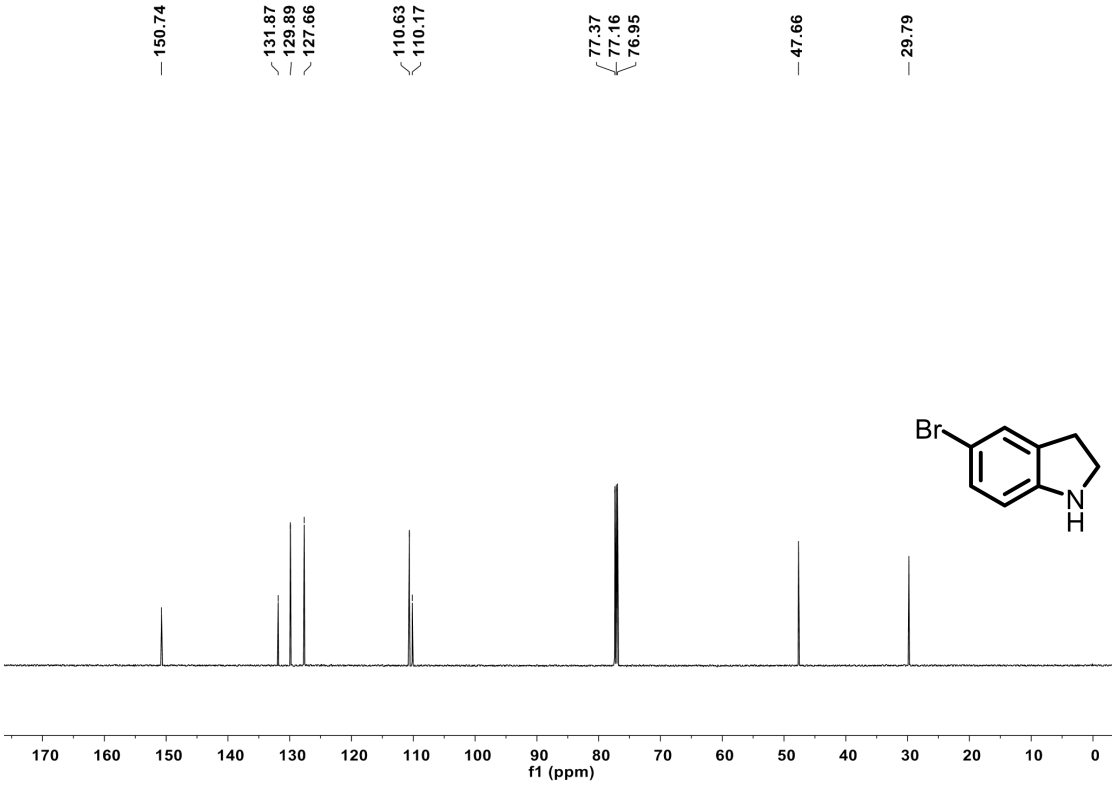
7.14
7.14
7.13
7.13
7.04
7.04
7.03
7.03
7.02
7.02
6.74
6.74
6.73
6.72
6.71
6.71
6.68
6.66
3.70
3.69
3.69
3.68
3.67
3.58
3.56
3.55
3.06
3.04
3.03
0.98
1.00
1.01
0.94
0.95
2.03
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
N
H

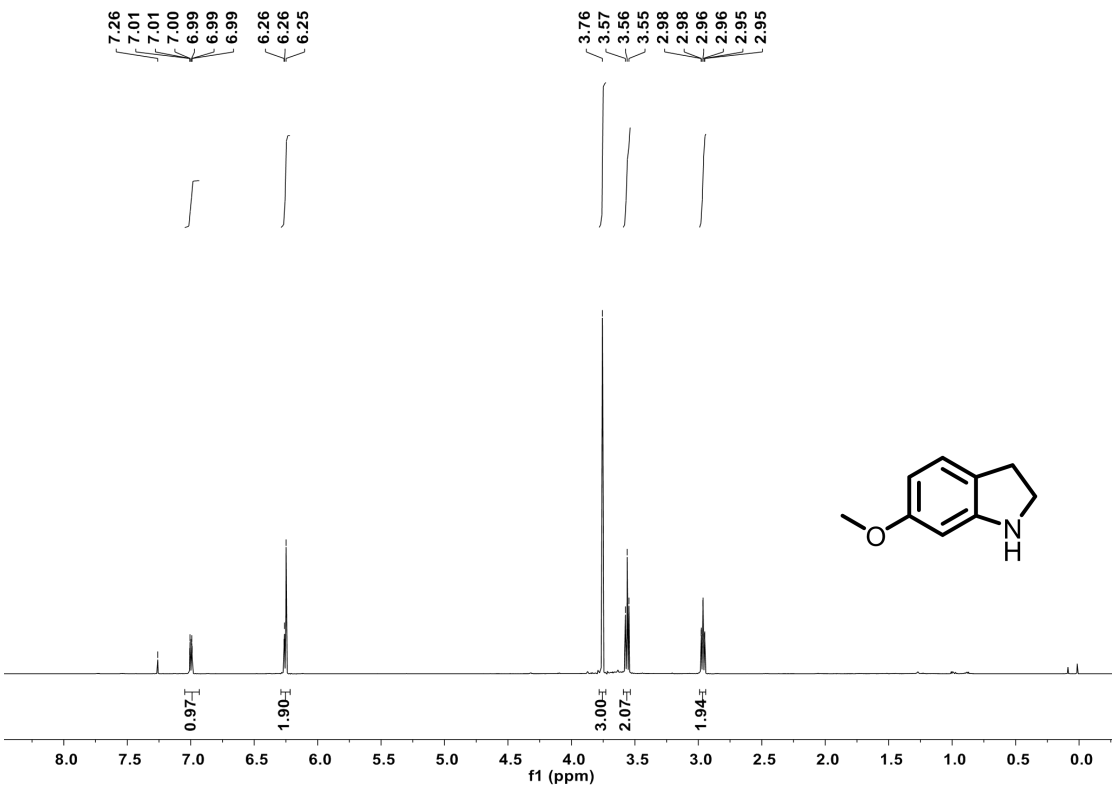

151.18
129.60
127.35
124.78
119.12
109.89
77.37
77.16
76.95
47.39
29.93
N
H
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

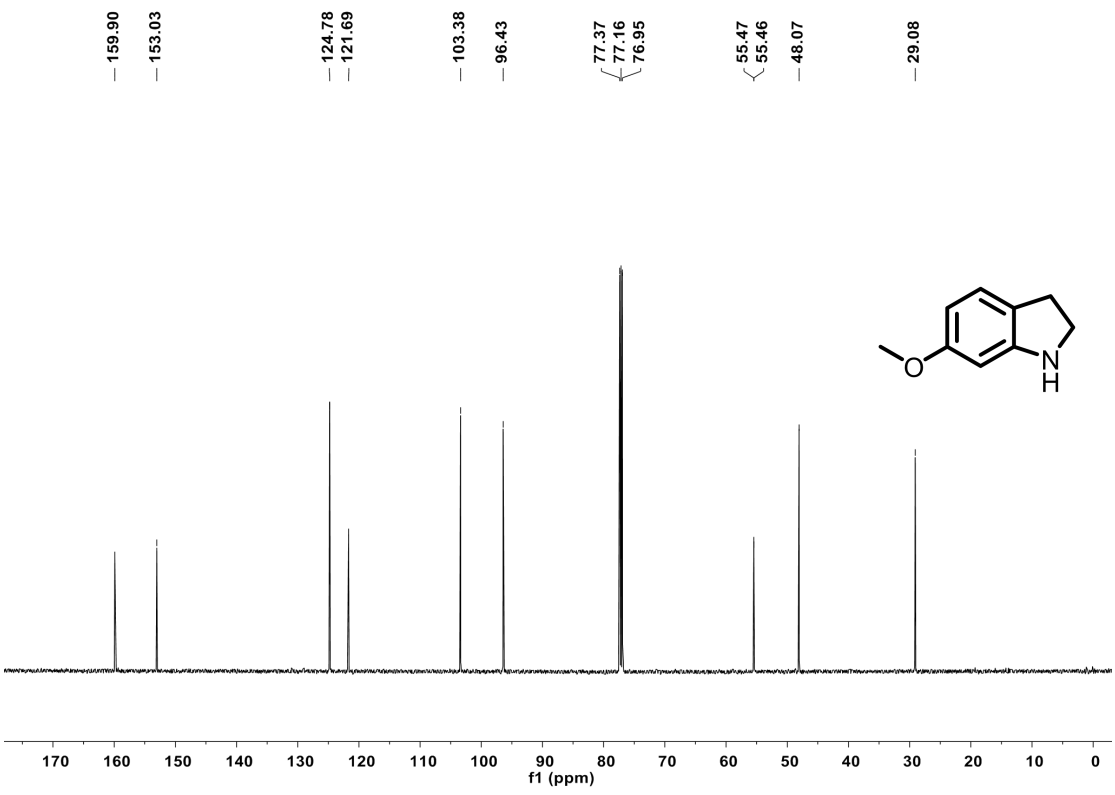

6.85 6.85 6.85 6.84 6.84 6.84 6.83 6.83 6.83 6.83 6.72 6.72 6.72 6.71 6.71 6.71 6.71 6.70 6.70 6.70 6.69 6.69 6.69 6.69 6.69 6.55 6.55 6.54 6.53 3.58 3.56 3.03 3.03 3.02 3.01 3.00 3.00
F
N
H
0.96 0.97 0.98 2.10 0.84 2.00
f1 (ppm)

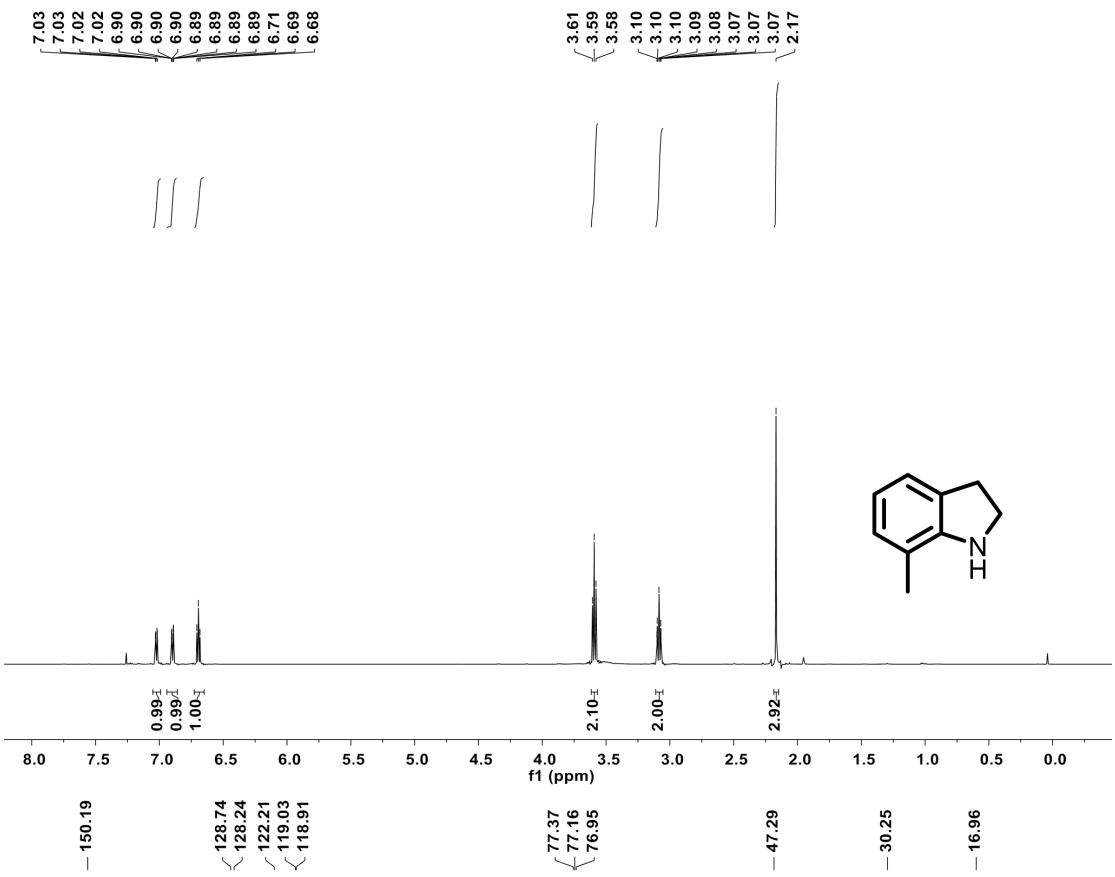

157.96 156.40 147.50 131.34 131.29 113.31 113.15 112.23 112.07 109.80 109.74 77.37 77.16 76.95 48.03 30.31 30.30
F
N
H
f1 (ppm)


7.20
7.20
7.19
7.19
7.19
7.10
7.10
7.10
7.09
7.09
7.08
6.50
6.49
3.67
3.67
3.66
3.66
3.65
3.65
3.57
3.56
3.54
3.03
3.03
3.02
3.01
3.01
3.01
3.00
3.00
3.00
Br
N
H
0.99
0.96
0.99
0.96
2.03
2.00
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
f1 (ppm)


150.74
131.87
129.89
127.66
110.63
110.17
77.37
77.16
76.95
47.66
29.79
Br
N
H
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.26
7.01
7.01
7.00
6.99
6.99
6.99
6.26
6.26
6.25
3.76
3.57
3.56
3.55
2.98
2.98
2.96
2.96
2.95
2.95
0.97
1.90
3.00
2.07
1.94
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
f1 (ppm)
O
N
H


159.90
153.03
124.78
121.69
103.38
96.43
77.37
77.16
76.95
55.47
55.46
48.07
29.08
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
O
N
H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3.58
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3.10
3.10
3.09
3.08
3.07
3.07
3.07
2.17
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0.99
1.00
2.10
2.00
2.92
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7.0
6.5
6.0
5.5
5.0
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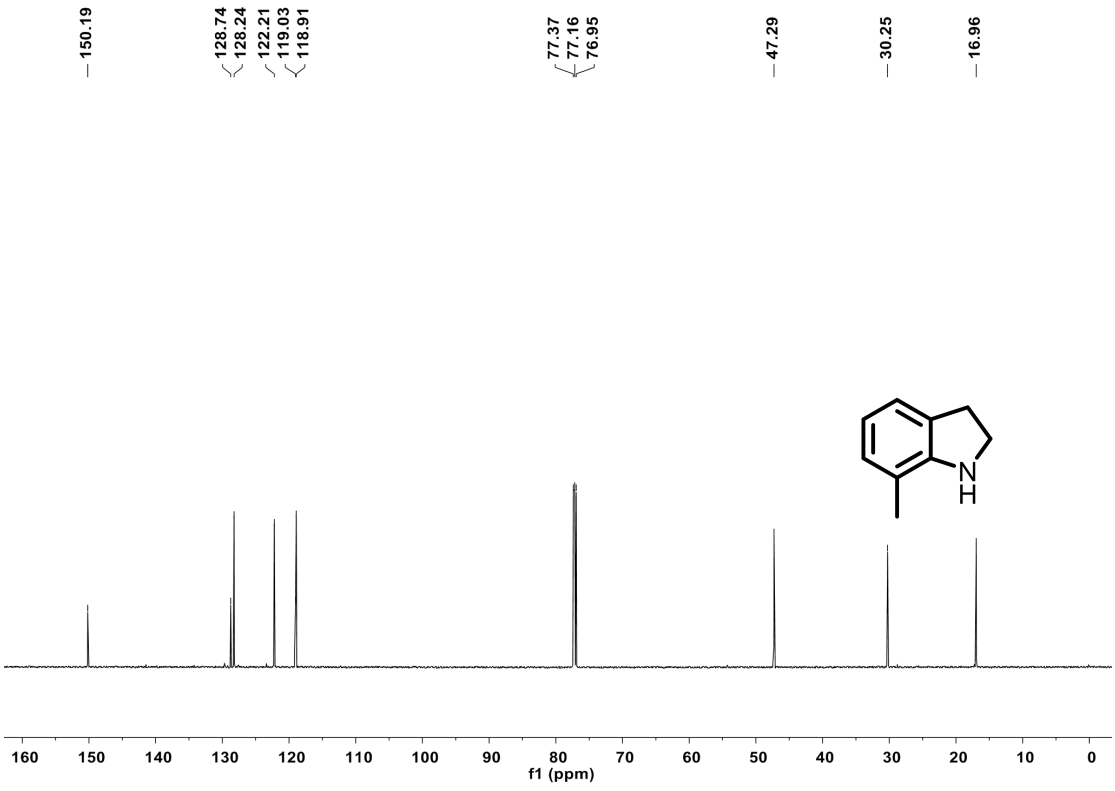
f1 (ppm)
N
H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16.96
160
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110
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90
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70
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50
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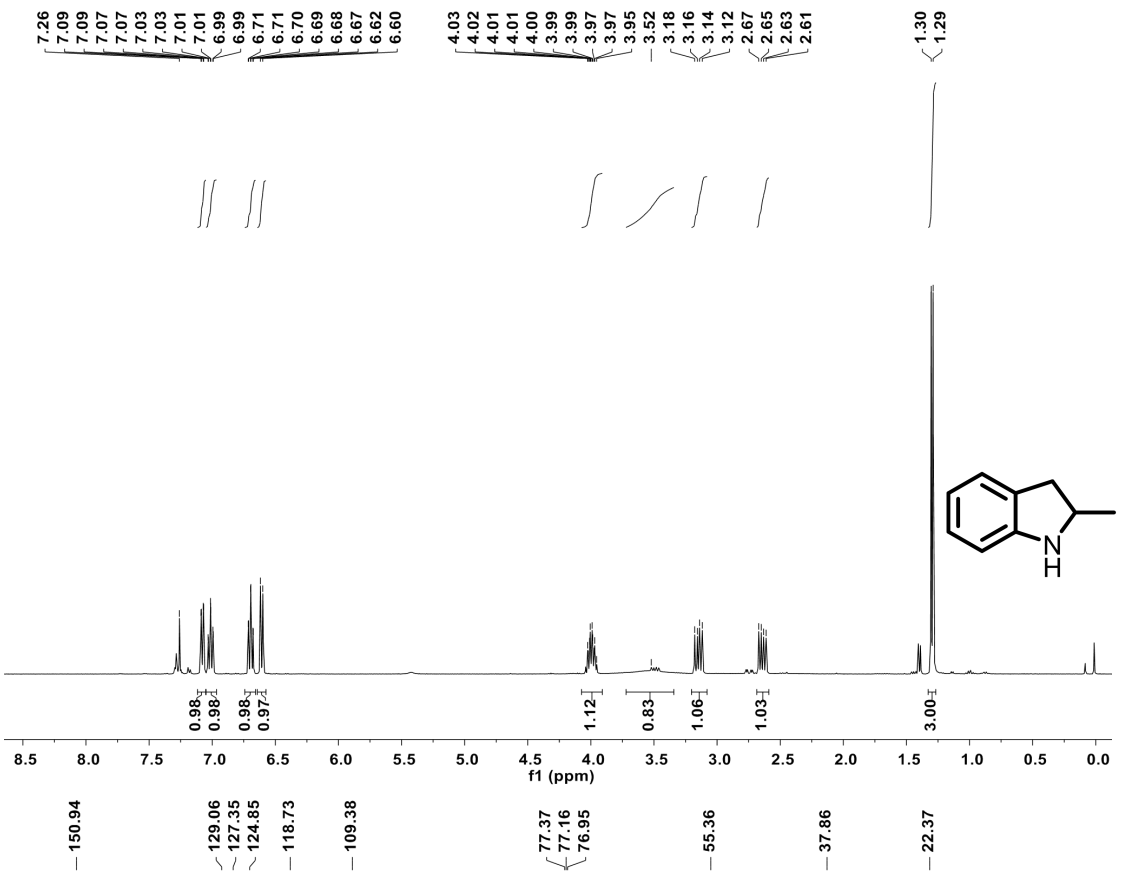
30
20
10
0
f1 (ppm)
N
H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3.16
3.14
3.12
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2.63
2.61
1.30
1.29
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0.98
0.98
0.97
1.12
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1.06
1.03
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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2.0
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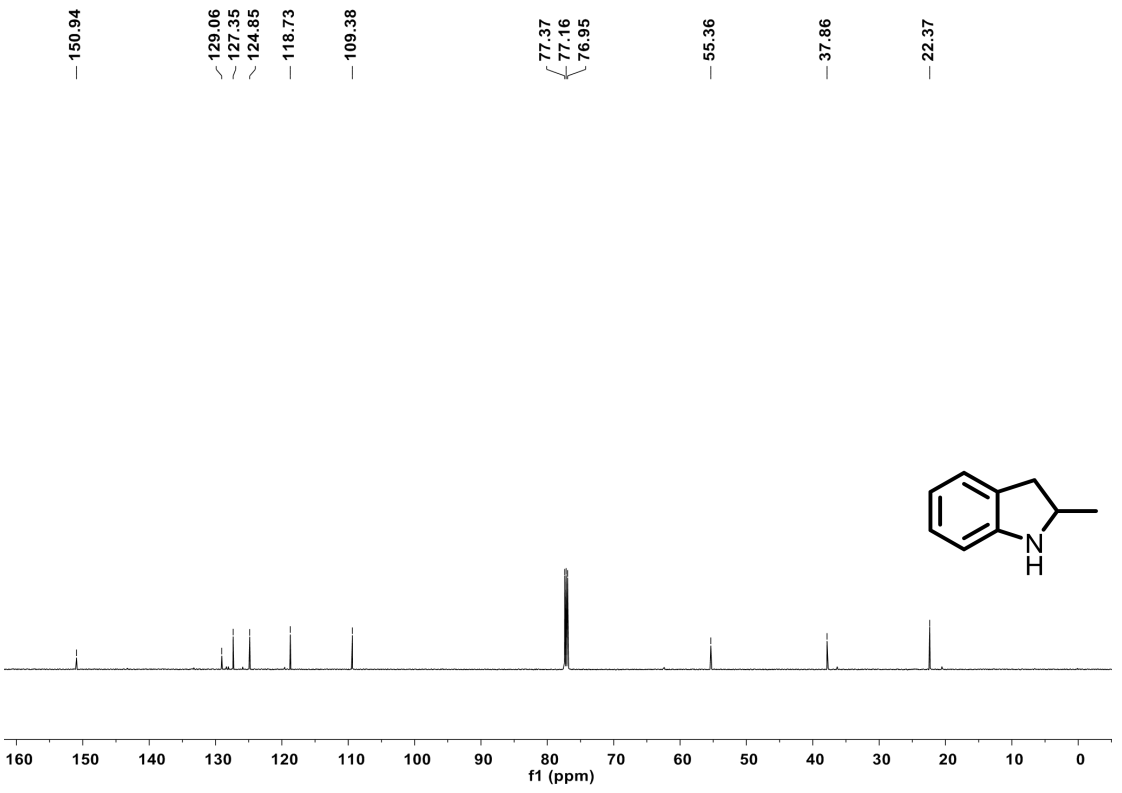
0.5
0.0
f1 (ppm)
N
H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55.36
37.86
22.37
160
150
140
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110
100
90
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70
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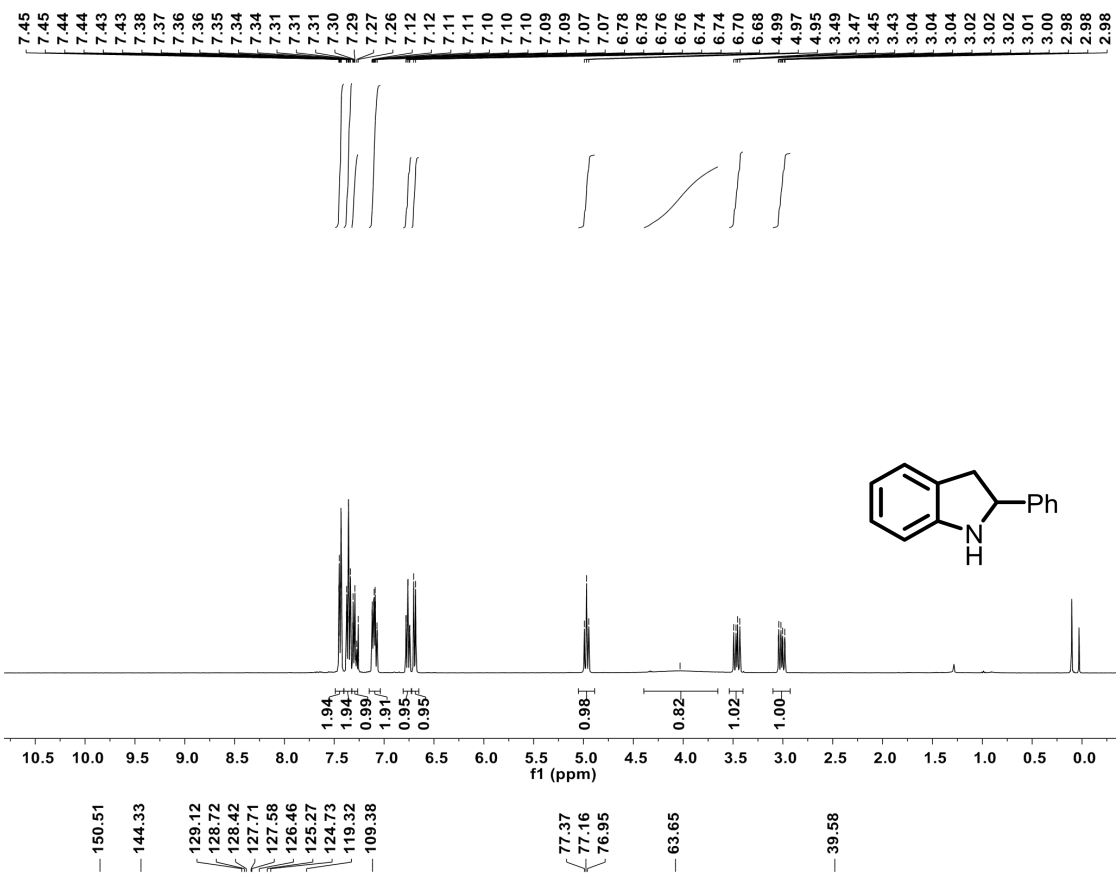
50
40
30
20
10
0
f1 (ppm)
N
H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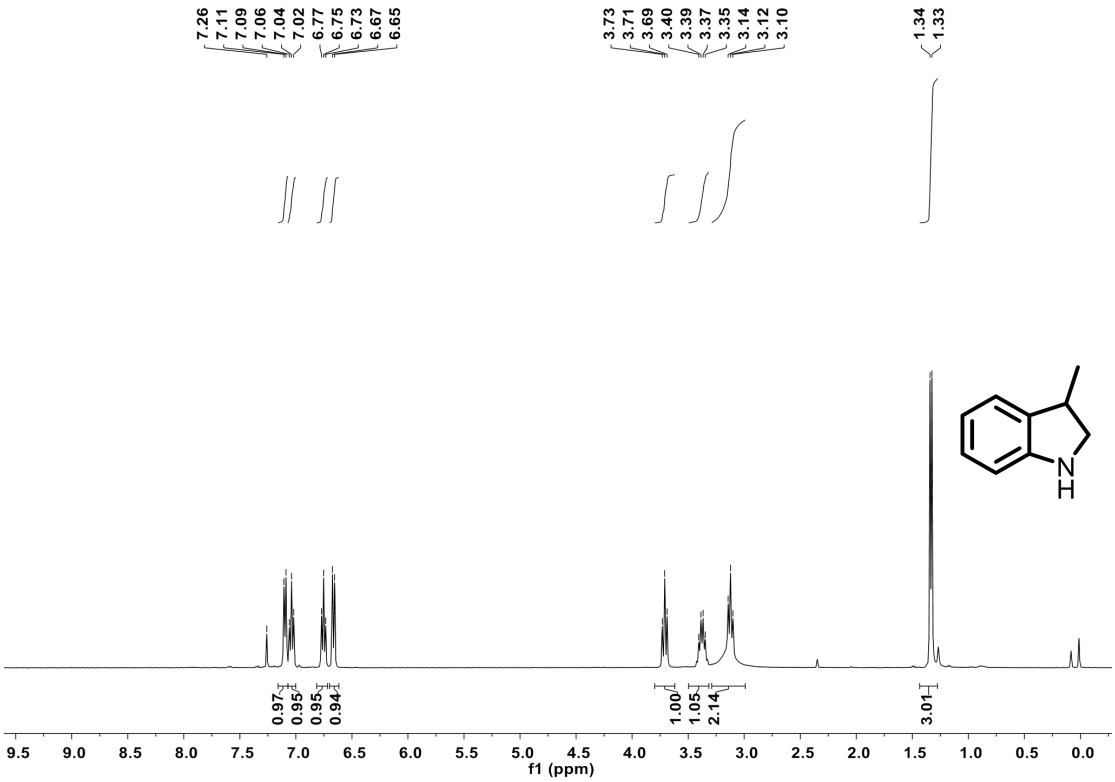
Ph
N
H
1.94 1.94 0.99 1.91 0.95 0.95 0.98 0.82 1.02 1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
150.51 144.33 129.12 128.72 128.42 127.71 127.58 126.46 125.27 124.73 119.32 109.38 77.37 77.16 76.95 63.65 39.58
Ph
N
H
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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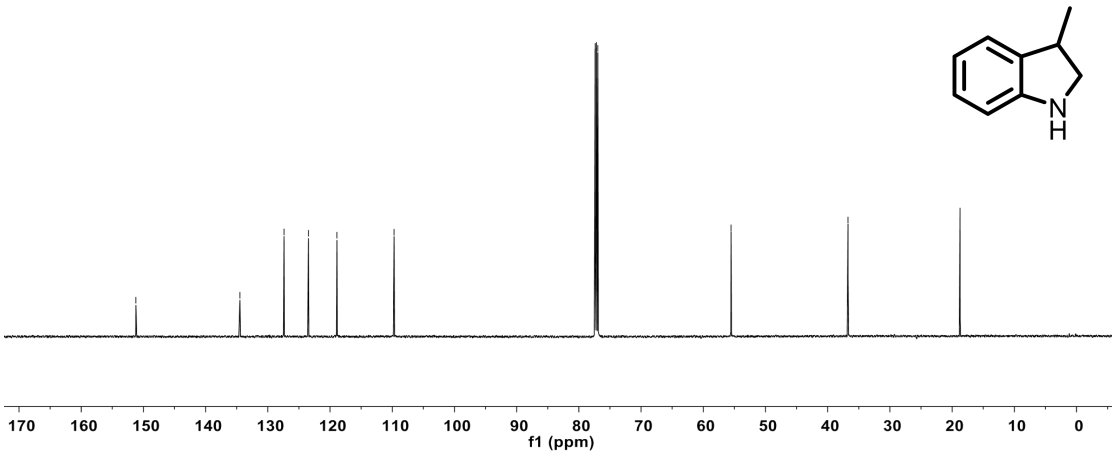
6.67
6.65
3.73
3.71
3.69
3.40
3.39
3.37
3.35
3.14
3.12
3.10
1.34
1.33
0.97
0.95
0.95
0.94
1.00
1.05
2.14
3.01
f1 (ppm)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134.49
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123.48
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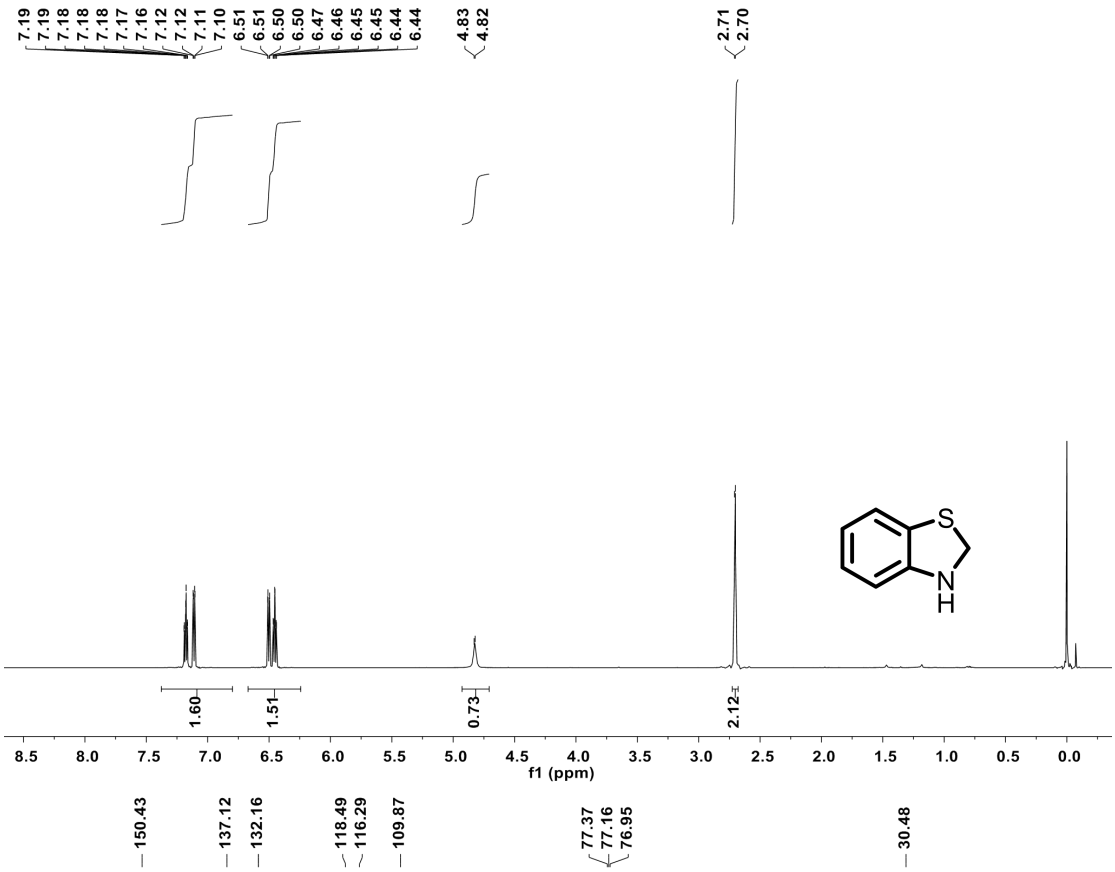
77.37
77.16
76.95
55.53
36.74
18.73
f1 (ppm)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7.19
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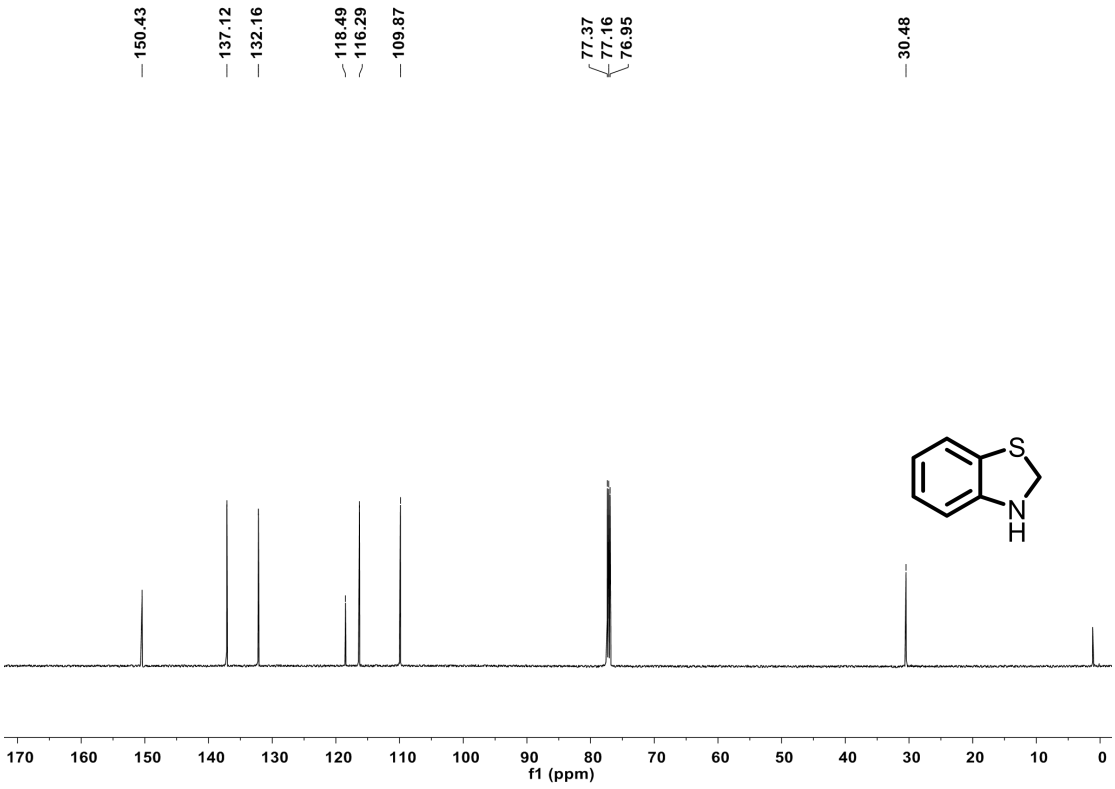
7.18
7.18
7.17
7.16
7.12
7.12
7.11
7.10
6.51
6.51
6.50
6.50
6.47
6.46
6.45
6.45
6.44
6.44
4.83
4.82
2.71
2.70
S
N
H
1.60
1.51
0.73
2.12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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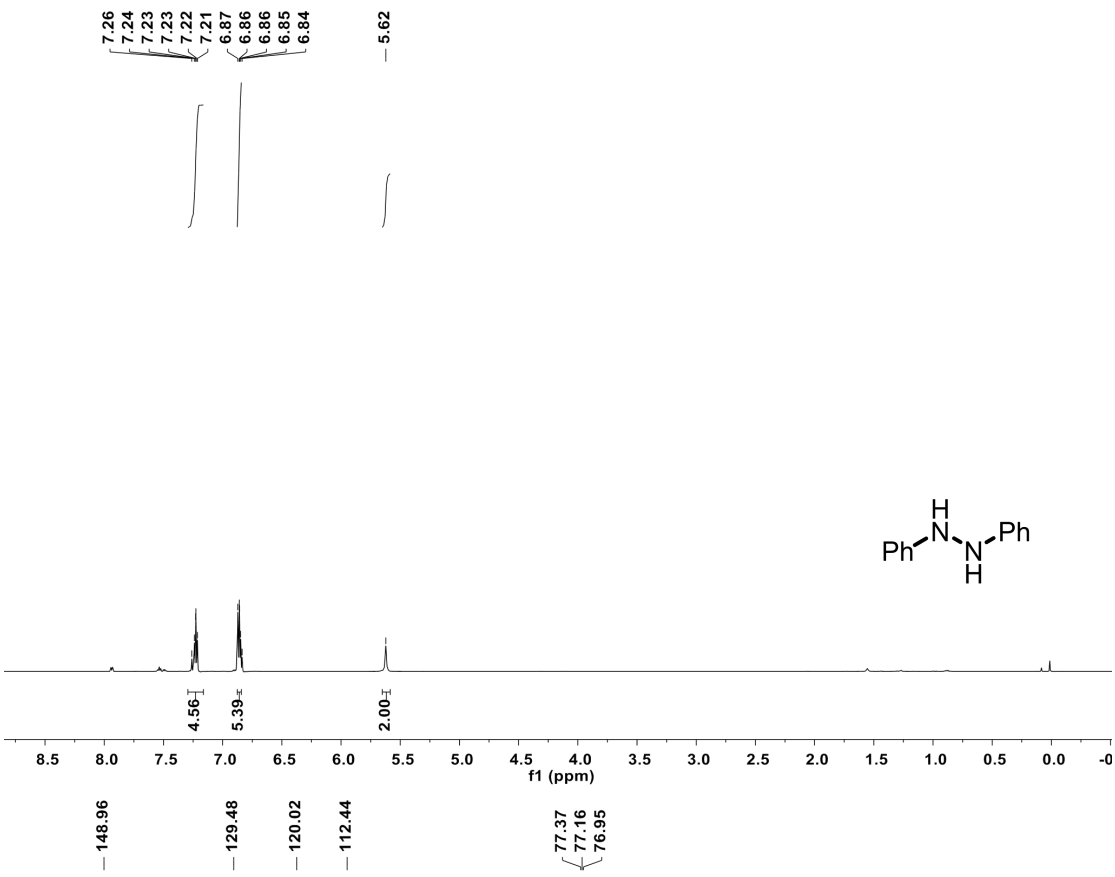
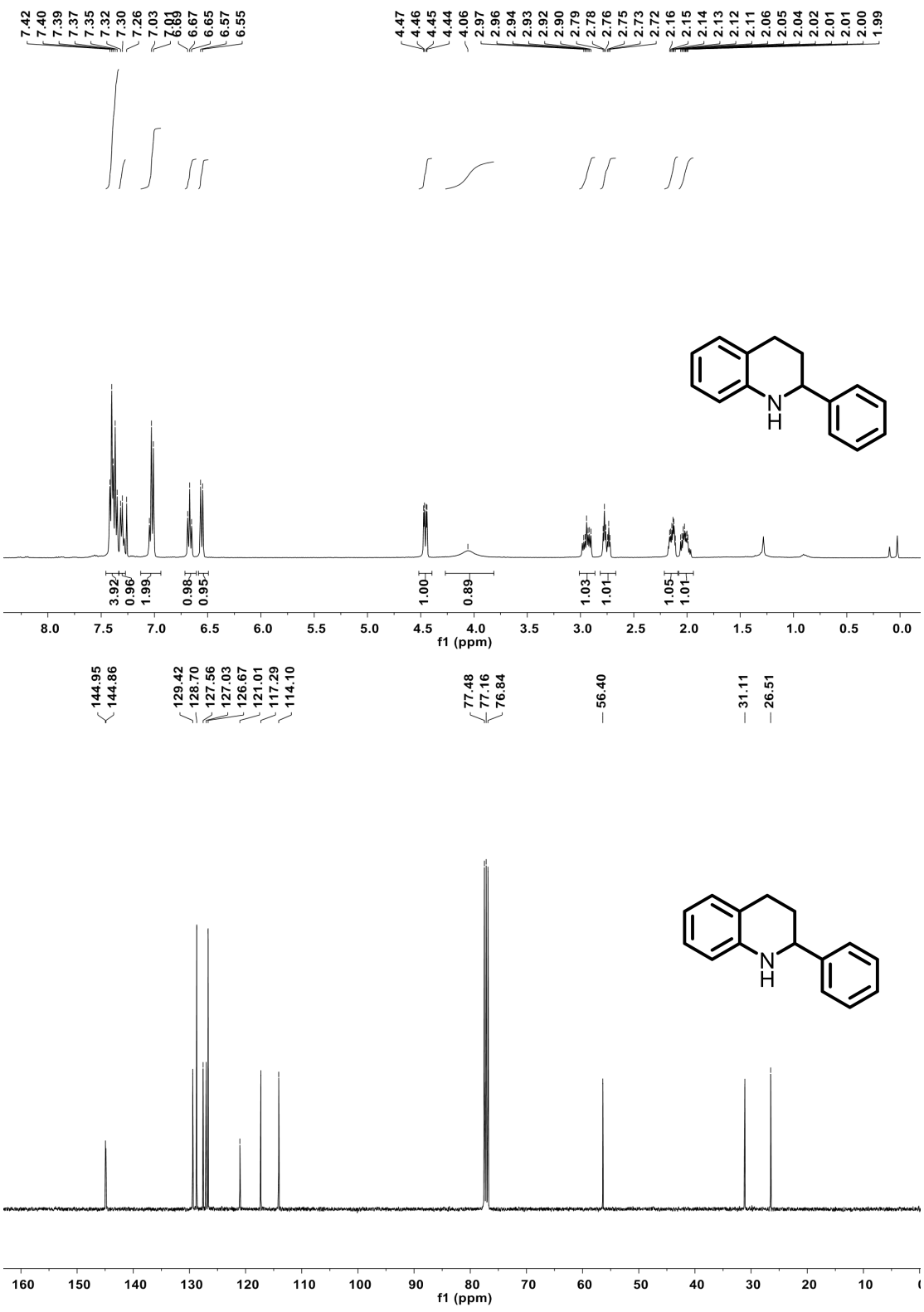
137.12
132.16
118.49
116.29
109.87
77.37
77.16
76.95
30.48
S
N
H
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.26
7.24
7.23
7.23
7.22
7.21
6.87
6.86
6.86
6.85
6.84
5.62
4.56
5.39
2.00
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
f1 (ppm)
148.96
129.48
120.02
112.44
77.37
77.16
76.95
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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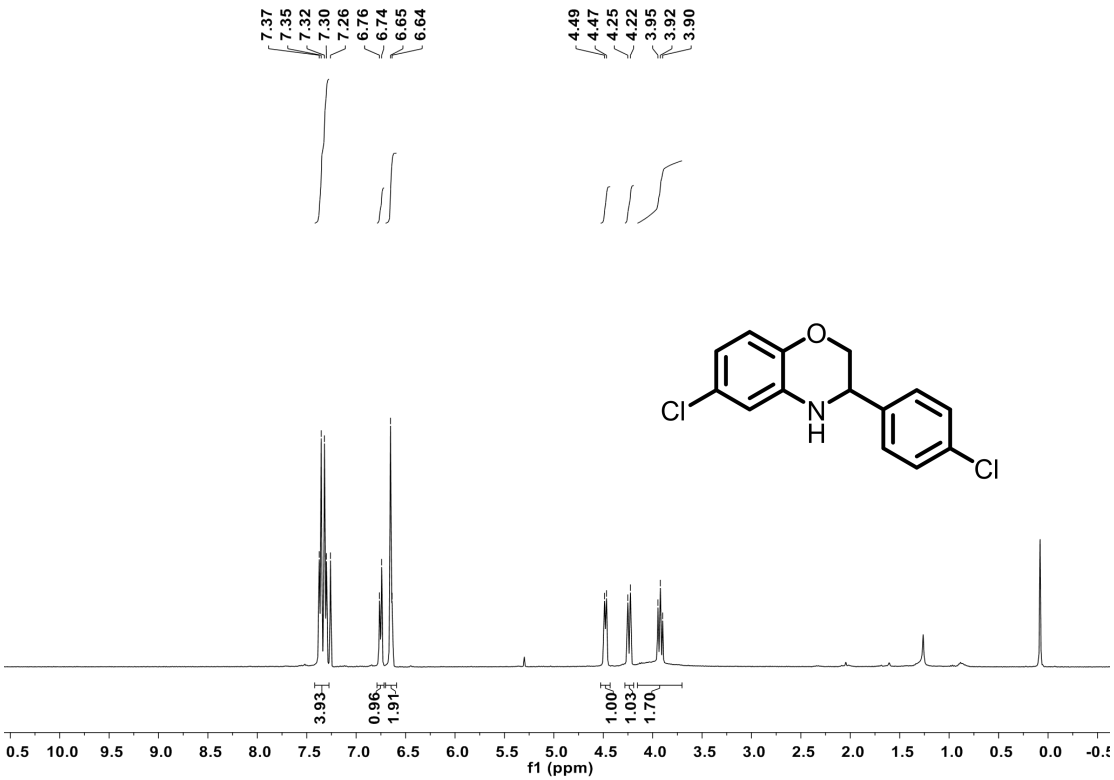
7.32
7.30
7.26
7.03
7.01
6.89
6.67
6.65
6.57
6.55
4.47
4.46
4.45
4.44
4.06
2.97
2.96
2.94
2.93
2.92
2.90
2.79
2.78
2.76
2.75
2.73
2.72
2.16
2.15
2.14
2.13
2.12
2.11
2.06
2.05
2.04
2.02
2.01
2.01
2.00
1.99
N
H
3.92
0.96
1.99
0.98
0.95
1.00
0.89
1.03
1.01
1.05
1.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
144.95
144.86
129.42
128.70
127.56
127.03
126.67
121.01
117.29
114.10
77.48
77.16
76.84
56.40
31.11
26.51
N
H
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.64 7.64 7.63 7.62 7.62 7.61 7.50 7.49 7.48 7.48 7.46 7.40 7.38 7.36 7.28 7.08 7.06 7.04 6.72 6.70 6.68 6.61 6.59 4.54 4.53 4.52 4.51 3.02 3.01 3.00 2.98 2.97 2.95 2.94 2.83 2.82 2.81 2.79 2.78 2.77 2.20 2.18 2.18 2.09 2.08
N H
4.02 4.08 1.03 2.02 1.01 1.00 1.00 0.96 1.04 1.05 1.05 1.36
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.
f1 (ppm)
144.82 144.02 141.00 140.57 129.45 128.92 127.45 127.40 127.21 127.12 127.07 121.04 117.37 114.16 77.48 77.16 76.84 56.12 31.10 26.51
N H
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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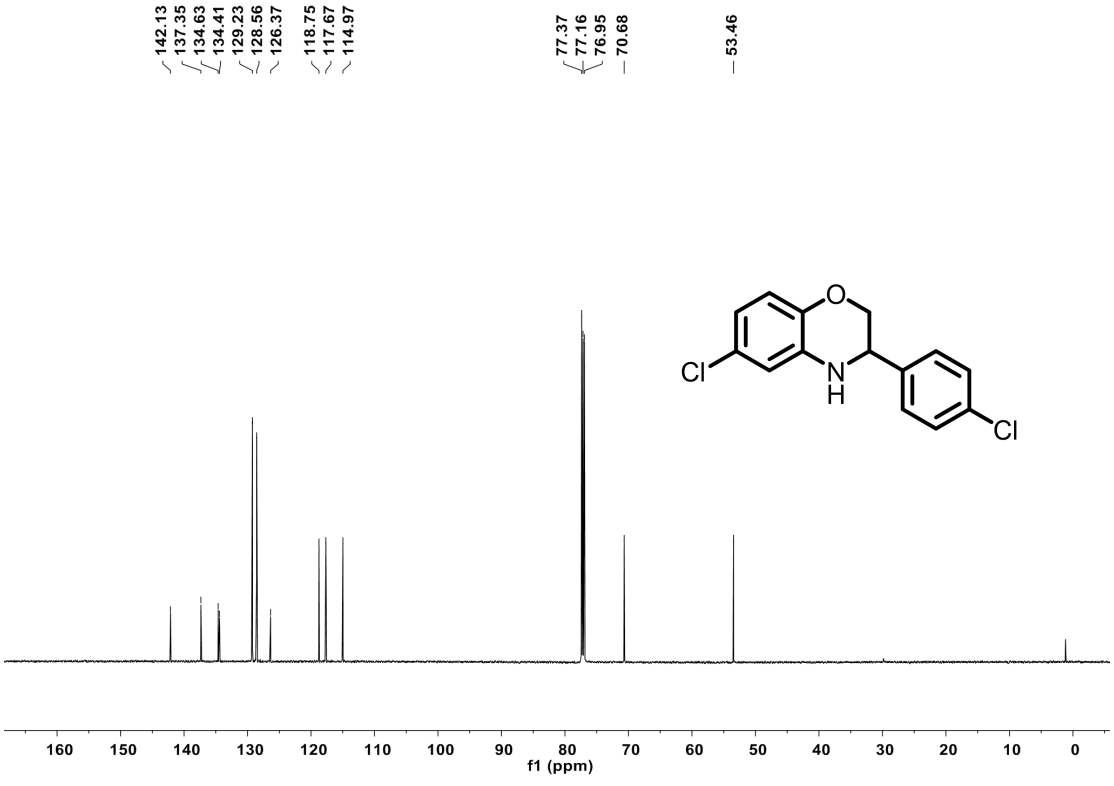
7.35
7.32
7.30
7.26
6.76
6.74
6.65
6.64
4.49
4.47
4.25
4.22
3.95
3.92
3.90
O
Cl
N
H
Cl
3.93
0.96
1.91
1.00
1.03
1.70
f1 (ppm)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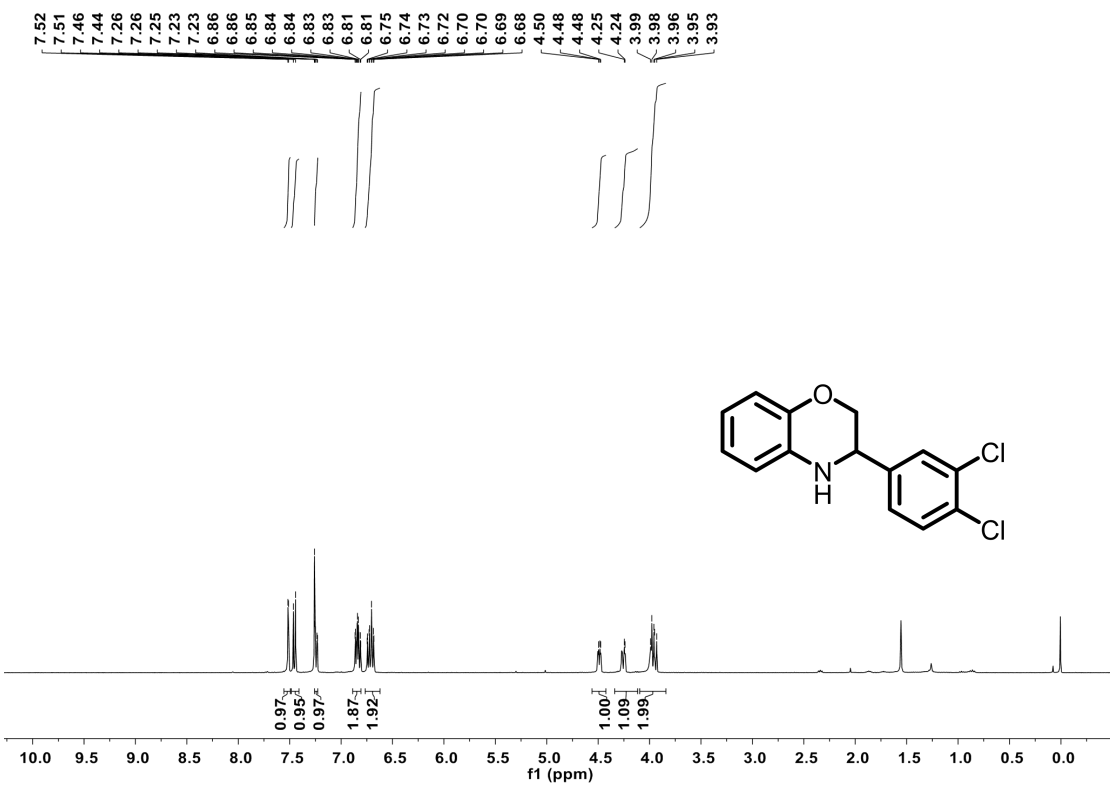
137.35
134.63
134.41
129.23
128.56
126.37
118.75
117.67
114.97
77.37
77.16
76.95
70.68
53.46
O
Cl
N
H
Cl
f1 (ppm)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7.51
7.46
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7.26
7.25
7.23
7.23
6.86
6.86
6.85
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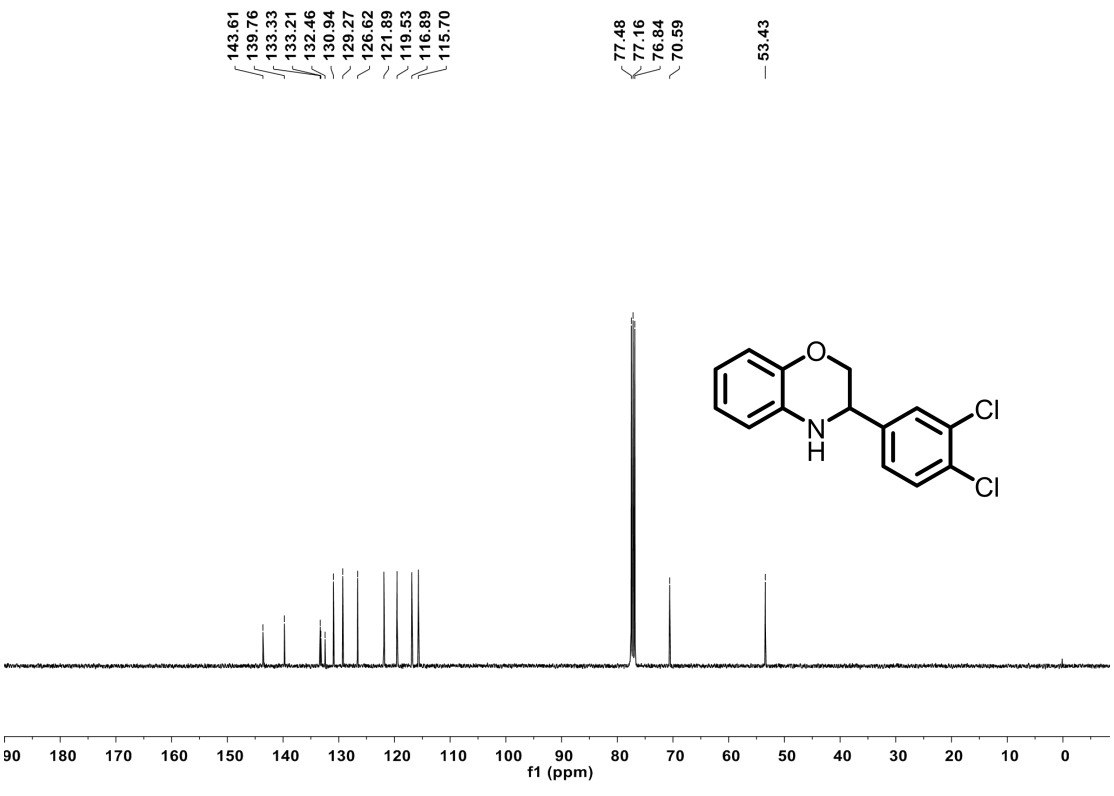
6.84
6.83
6.83
6.81
6.81
6.75
6.74
6.73
6.72
6.70
6.70
6.69
6.68
4.50
4.48
4.48
4.25
4.24
3.99
3.98
3.96
3.95
3.93
O
N
H
Cl
Cl
0.97
0.95
0.97
1.87
1.92
1.00
1.09
1.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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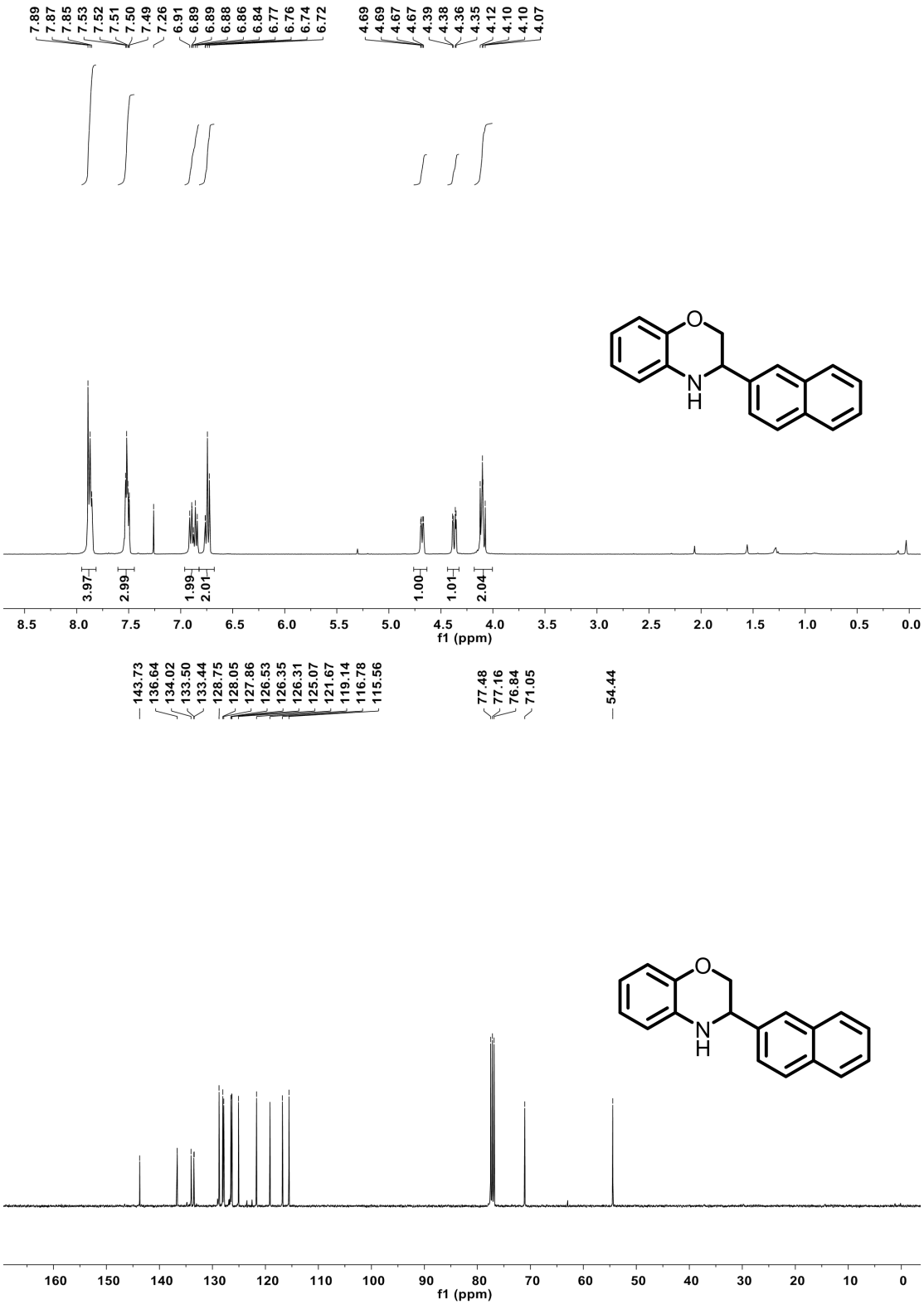
132.46
130.94
129.27
126.62
121.89
119.53
116.89
115.70
77.48
77.16
76.84
70.59
53.43
O
N
H
Cl
Cl
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.51
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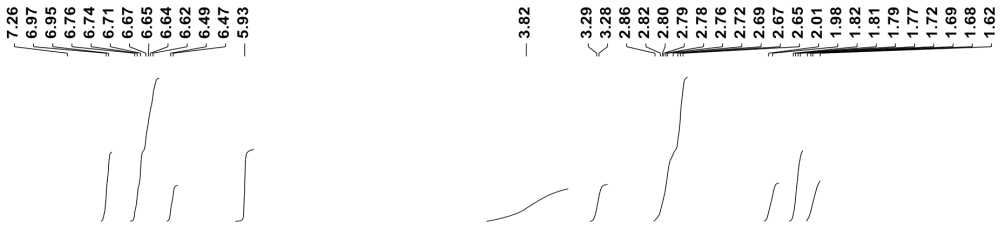
7.49
7.26
6.91
6.89
6.89
6.88
6.86
6.84
6.77
6.76
6.74
6.72
4.69
4.69
4.67
4.67
4.39
4.38
4.36
4.35
4.12
4.10
4.10
4.07
O
N
H
3.97
2.99
1.99
2.01
1.00
1.01
2.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
143.73
136.64
134.02
133.50
133.44
128.75
128.05
127.86
126.53
126.35
126.31
125.07
121.67
119.14
116.78
115.56
77.48
77.16
76.84
71.05
54.44
O
N
H
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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6.71
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6.64
6.62
6.49
6.47
5.93
3.82
3.29
3.28
2.86
2.82
2.80
2.79
2.78
2.76
2.72
2.69
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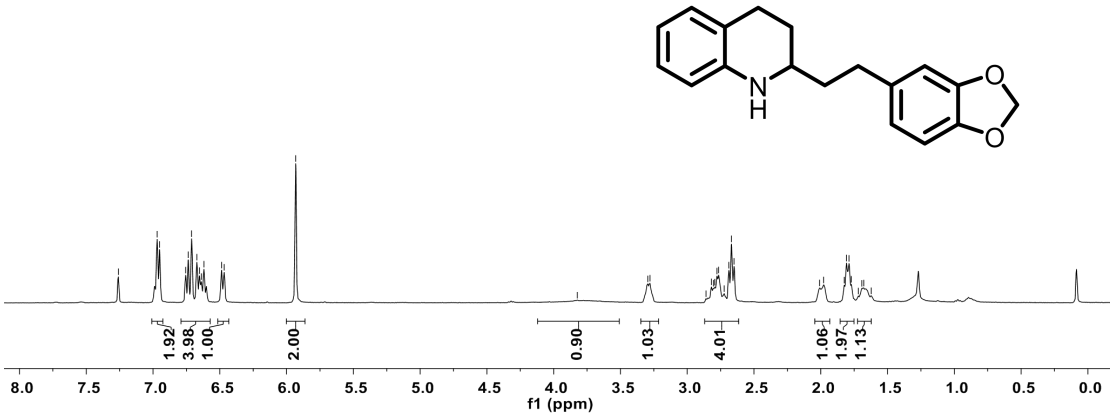
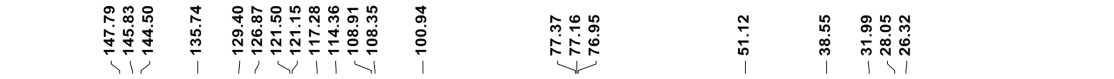
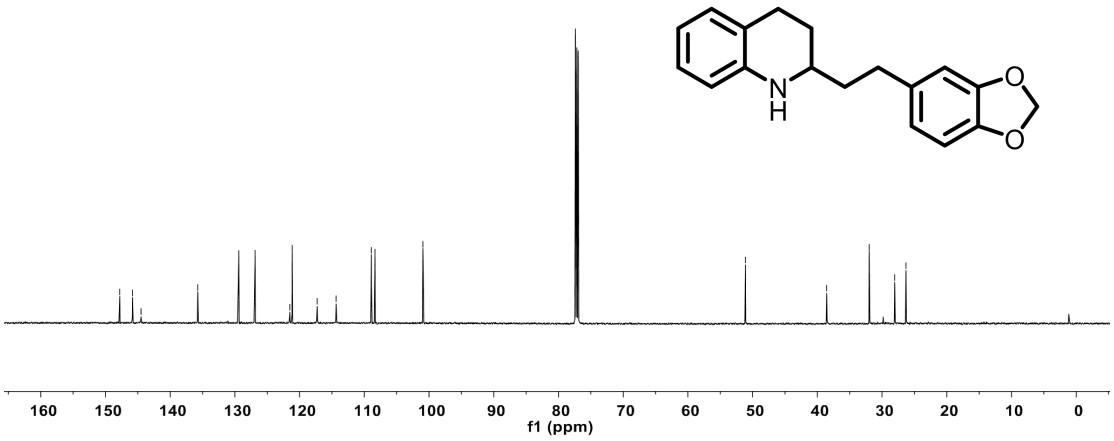
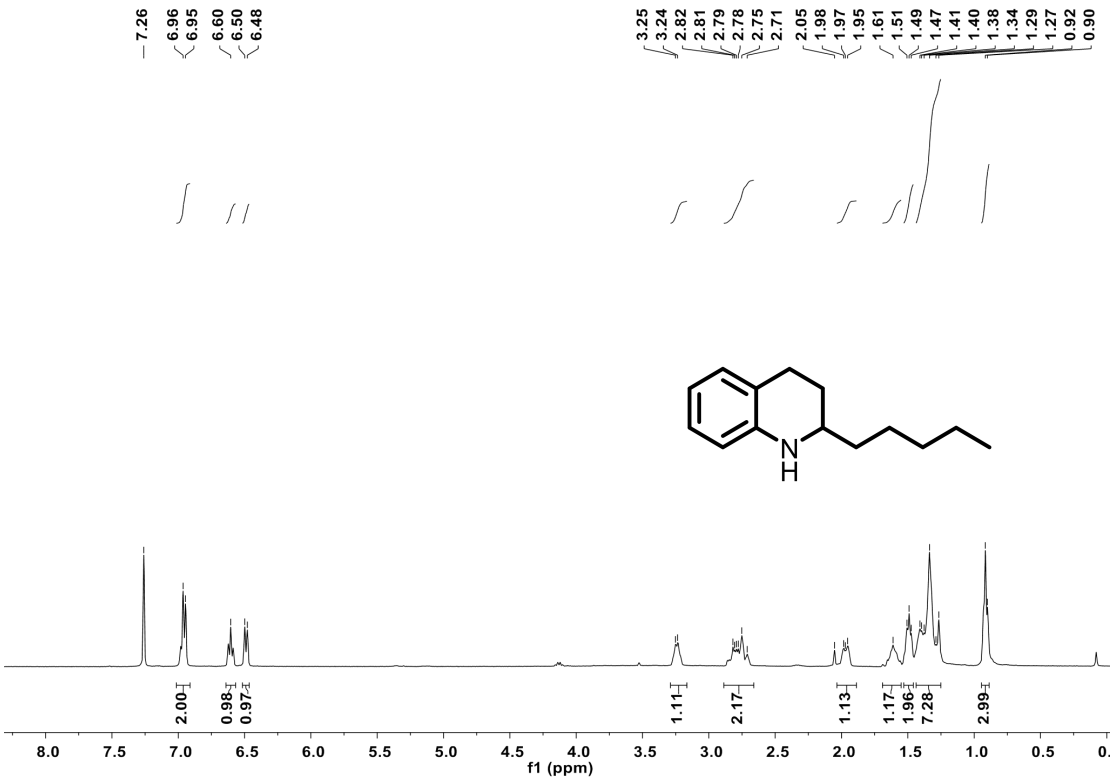
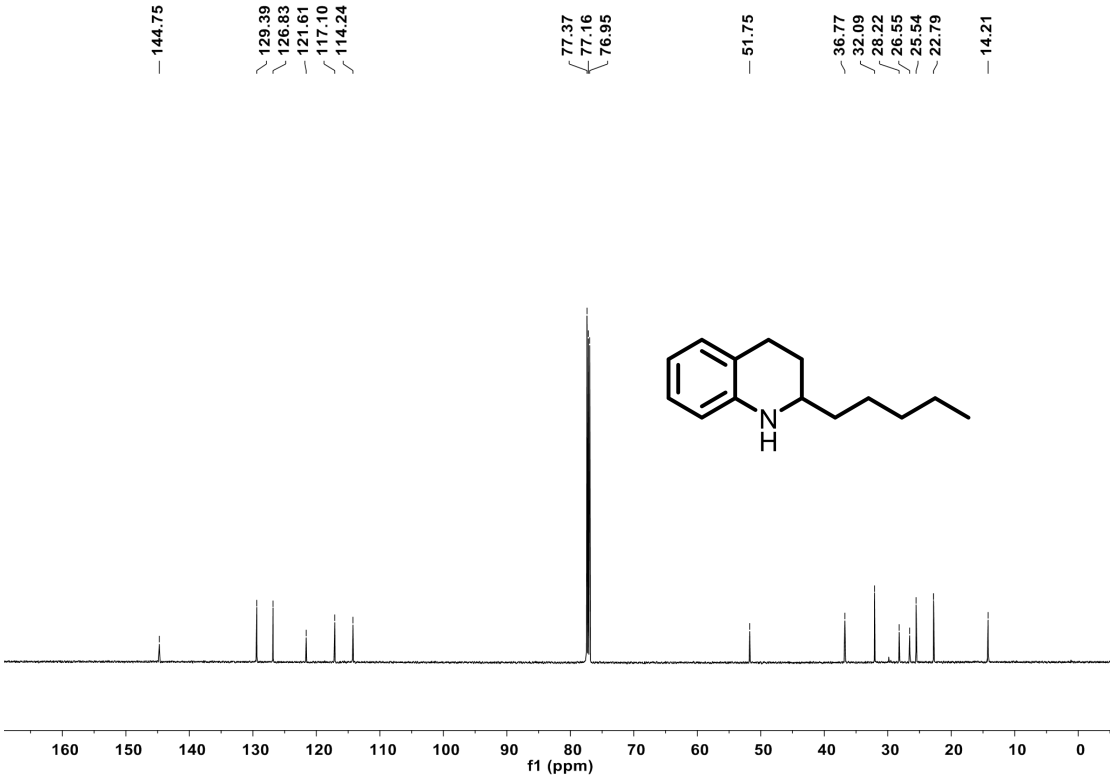
1.81
1.79
1.77
1.72
1.69
1.68
1.62


N
H
O
O
1.92
3.98
1.00
2.00
0.90
1.03
4.01
1.06
1.97
1.13
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
f1 (ppm)


147.79
145.83
144.50
135.74
129.40
126.87
121.50
121.15
117.28
114.36
108.91
108.35
100.94
77.37
77.16
76.95
51.12
38.55
31.99
28.05
26.32


N
H
O
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.26
6.96
6.95
6.60
6.50
6.48
3.25
3.24
2.82
2.81
2.79
2.78
2.75
2.71
2.05
1.98
1.97
1.95
1.61
1.51
1.49
1.47
1.41
1.40
1.38
1.34
1.29
1.27
0.92
0.90
N
H
2.00
0.98
0.97
1.11
2.17
1.13
1.17
1.96
7.28
2.99
f1 (ppm)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117.10
114.24
77.37
77.16
76.95
51.75
36.77
32.09
28.22
26.55
25.54
22.79
14.21
N
H
f1 (ppm)

4 References

1. Y. Xia, X. Sun, L. Zhang, K. Luo, and L. Wu, *Chem. Eur. J.*, 2016, **22**, 17151-17155.
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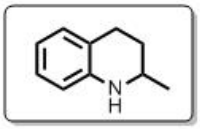
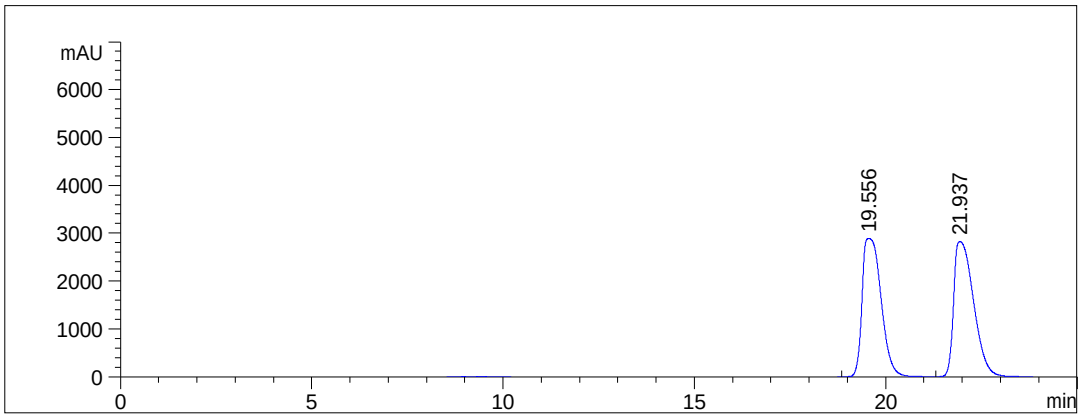
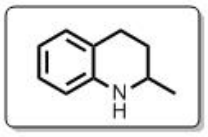
HPLC trace of racemic 2-methyl-1,2,3,4-tetrahydroquinoline (**2a**)

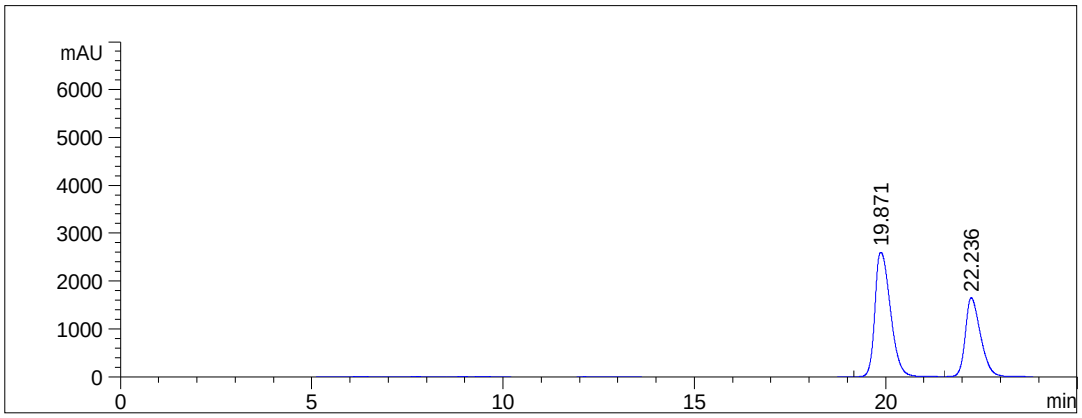




峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	19.556	BB	0.5354	9.90900e4	2894.65039	49.3286
2	21.937	BBA	0.5601	1.01787e5	2826.70313	50.6714

HPLC trace of enantioenriched 2-methyl-1,2,3,4-tetrahydroquinoline (**2a**)





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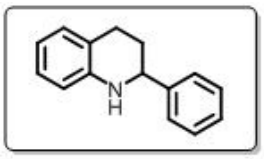
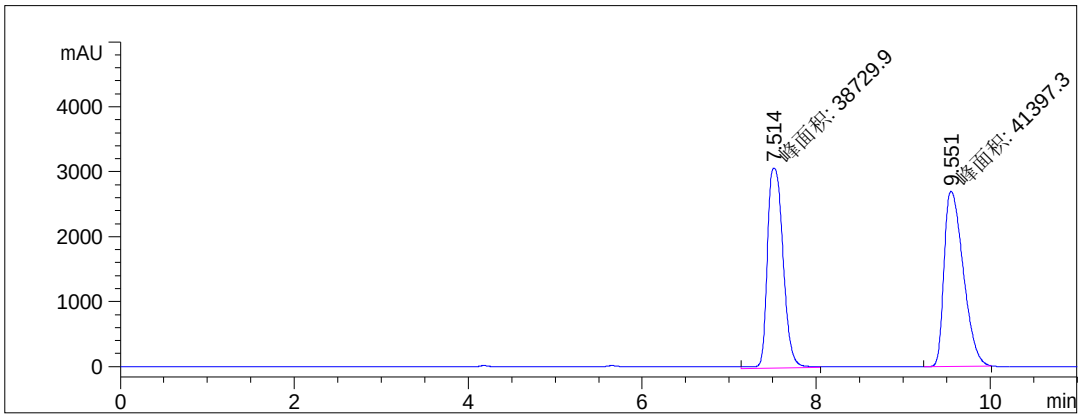
1	19.871	BB	0.4315	7.28534e4	2603.49487	61.6164
2	22.236	BB	0.4175	4.53837e4	1652.17798	38.3836

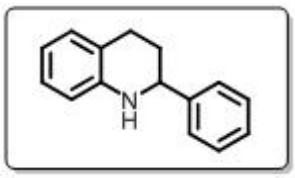
HPLC trace of racemic 2-phenyl-1,2,3,4-tetrahydroquinoline (**2o**)

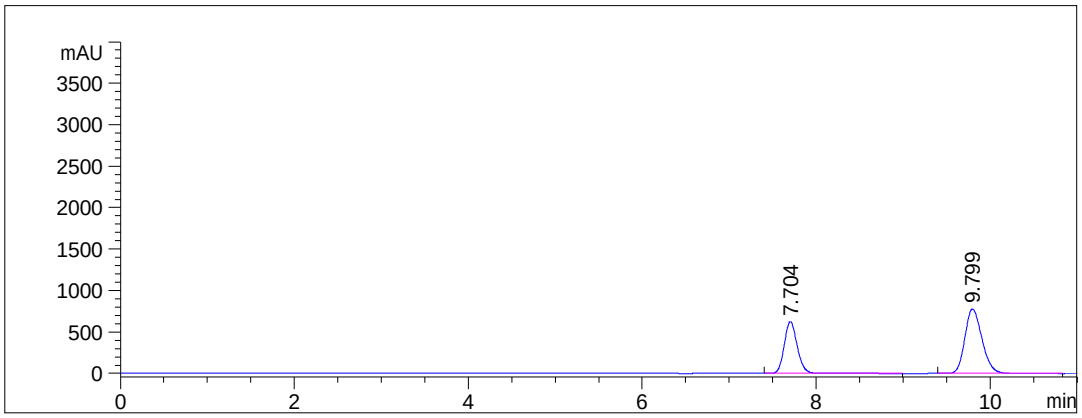




峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.514	MM	0.2098	3.87299e4	3076.91602	48.3355
2	9.551	MM	0.2557	4.13973e4	2698.10034	51.6645

HPLC trace of enantioenriched 2-phenyl-1,2,3,4-tetrahydroquinoline (**2o**)





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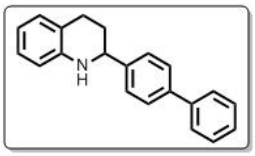
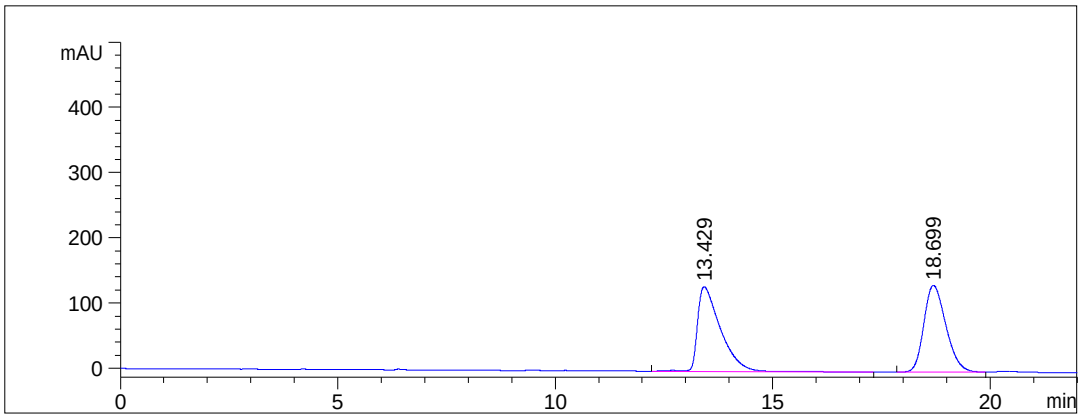
1	7.704	BB	0.1590	6429.29492	624.83246	37.8103
2	9.799	BB	0.2110	1.05748e4	775.82117	62.1897

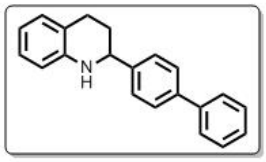
HPLC trace of racemic 2-([1,1'-biphenyl]-4-yl)-1,2,3,4-tetrahydroquinoline (**2p**)

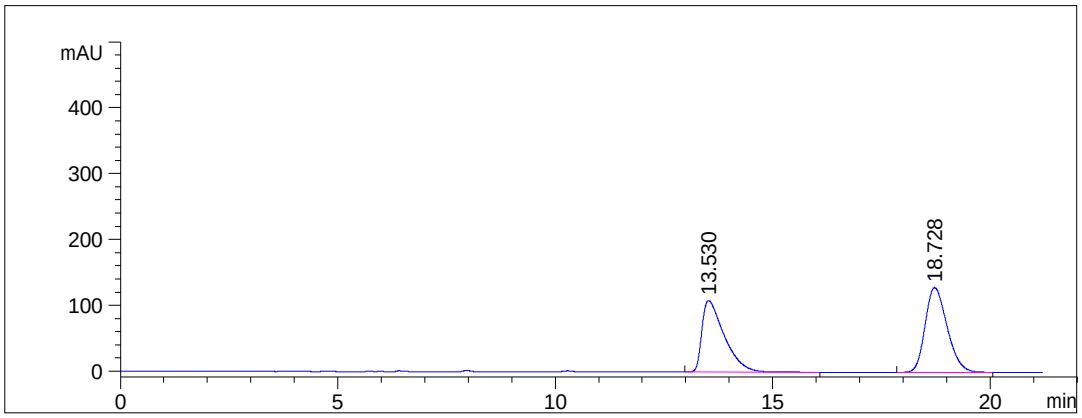




峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	13.429	VB R	0.5370	4719.20020	129.55571	50.2877
2	18.699	BB	0.5448	4665.21143	132.80237	49.7123

HPLC trace of enantioenriched 2-([1,1'-biphenyl]-4-yl)-1,2,3,4-tetrahydroquinoline(**2p**)





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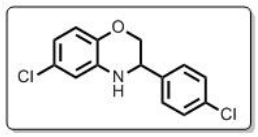
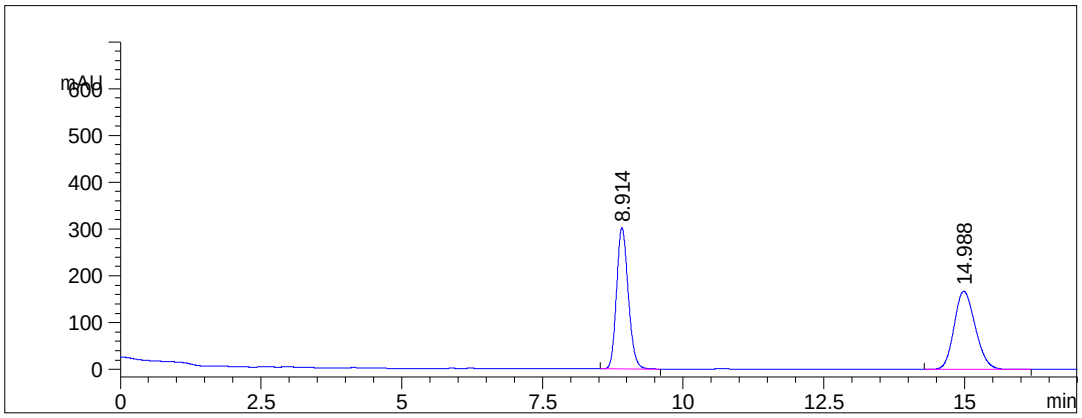
1	13.530	BB	0.5310	3877.11279	108.47720	46.2327
2	18.728	BB	0.5434	4508.97314	128.50739	53.7673

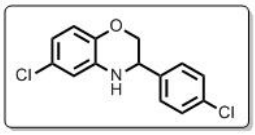
HPLC trace of racemic 6-chloro-3-(4-chlorophenyl)-3,4-dihydro-2H-benzo [b][1,4]oxazine (**2q**)

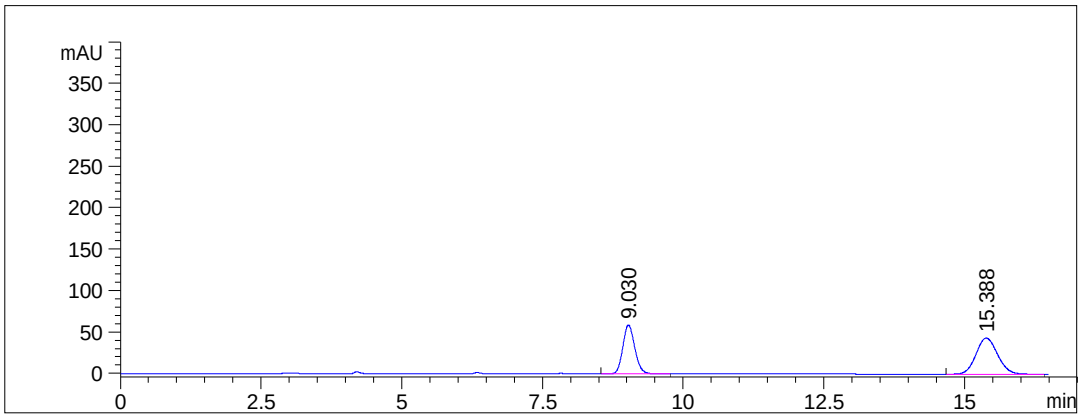




峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.914	BB	0.2238	4367.47803	301.92303	50.0061
2	14.988	BB	0.4071	4366.41650	166.98267	49.9939

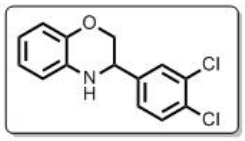
HPLC trace of enantioenriched 6-chloro-3-(4-chlorophenyl)-3,4-dihydro-2H-benzo[b][1,4]oxazine (**2q**)

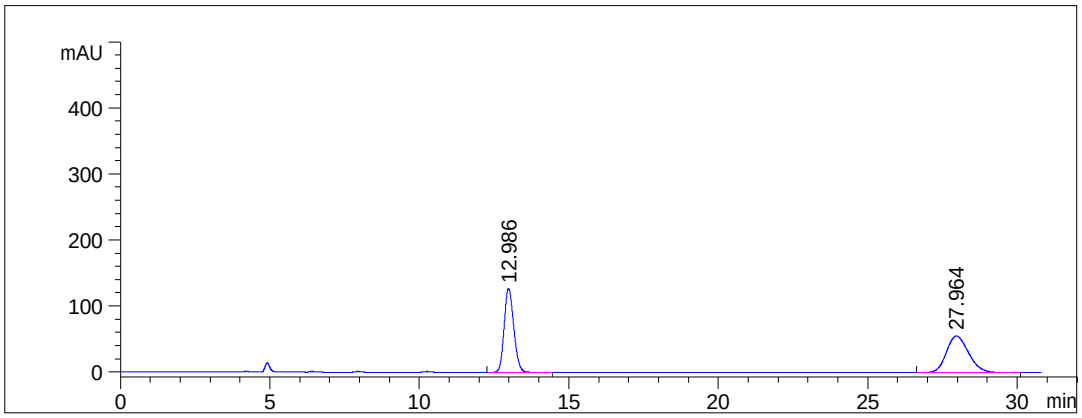




峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.030	BB	0.2289	874.26501	58.99132	43.0263
2	15.388	BB	0.4143	1157.66626	43.52600	56.9737

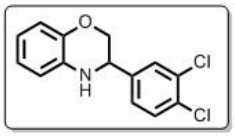
HPLC trace of racemic 3-(3,4-dichlorophenyl)-3,4-dihydro-2H-benzo[b][1,4]oxazine (**2r**)

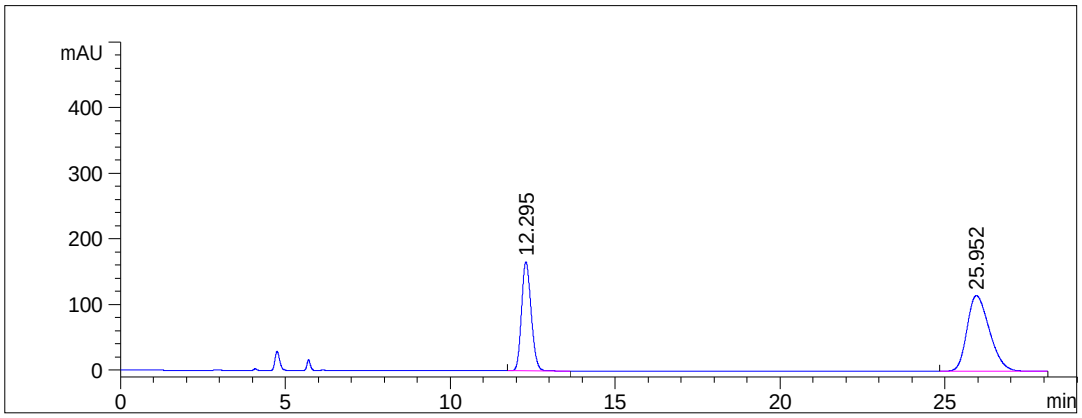




峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.986	BB	0.3450	2820.04761	127.02346	50.0846
2	27.964	BB	0.7913	2810.52612	55.08429	49.9154

HPLC trace of enantioenriched 3-(3,4-dichlorophenyl)-3,4-dihydro-2H-benzo[b][1,4]oxazine (**2r**)





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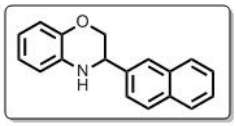
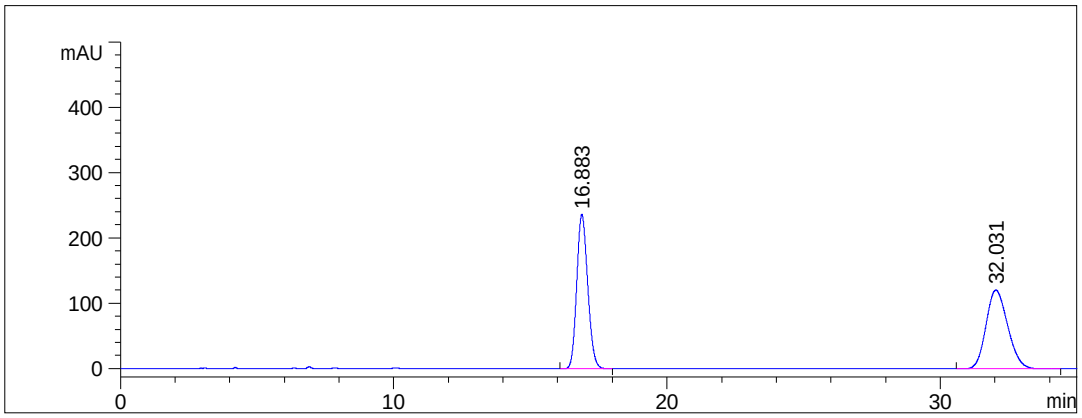
1	12.295	BB	0.3159	3368.27759	165.90019	38.3180
2	25.952	BBA	0.7306	5422.05322	115.10542	61.6820

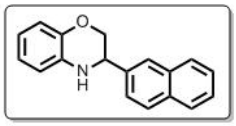
HPLC trace of racemic 3-(naphthalen-2-yl)-3,4-dihydro-2H-benzo[b][1,4]oxazine (**2s**)

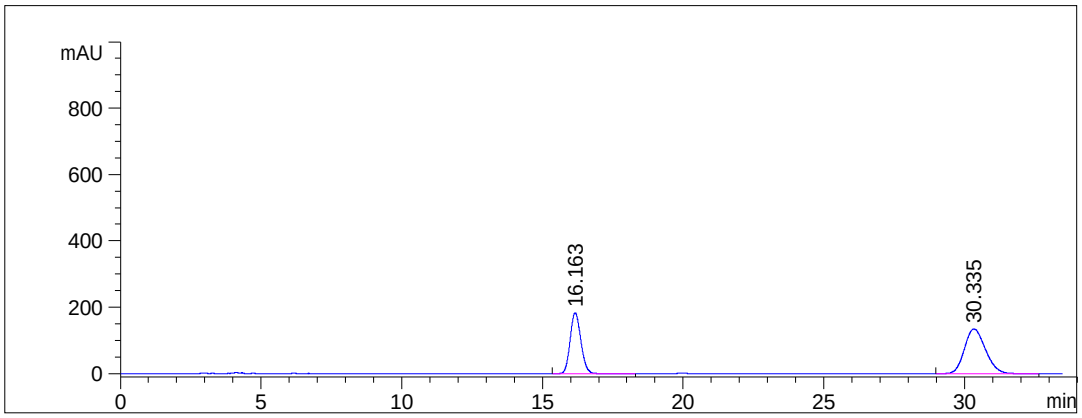




峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	16.883	BB	0.4350	6621.44922	236.26204	49.8799
2	32.031	BB	0.8574	6653.34717	120.63855	50.1201

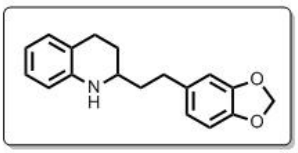
HPLC trace of enantioenriched 3-(naphthalen-2-yl)-3,4-dihydro-2H-benzo [b][1,4]oxazine (**2s**)

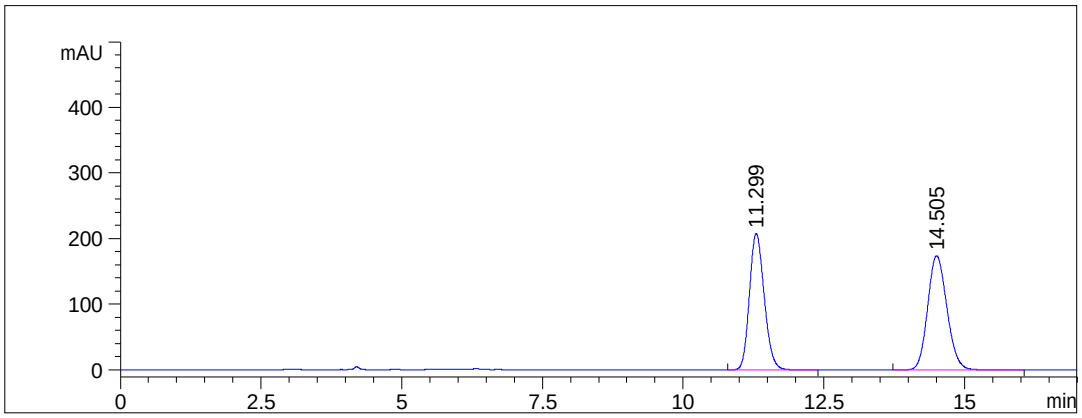




峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	16.163	BB	0.4102	4852.91943	183.72993	41.0660
2	30.335	BB	0.8037	6964.46045	134.58812	58.9340

HPLC trace of racemic 2-(2-(benzo[d][1,3]dioxol-5-yl) ethyl)-1,2,3,4-tetrahydroquinoline (**2t**)





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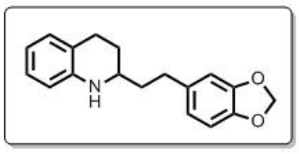
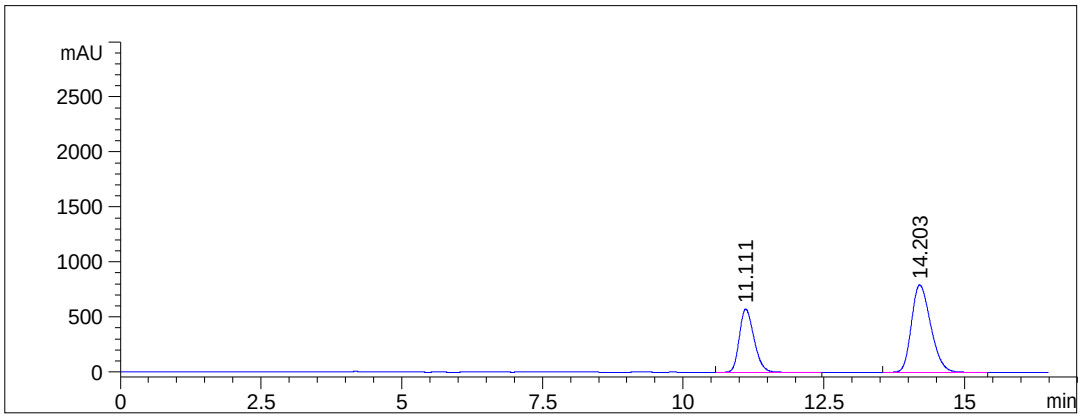
1	11.299	BB	0.2828	3791.93921	207.93303	47.8923
2	14.505	BB	0.3687	4125.70020	173.95863	52.1077

HPLC trace of enantioenriched 2-(2-(benzo[d][1,3]dioxol-5-yl) ethyl)-1,2,3,4-tetrahydroquinoline (**2t**)





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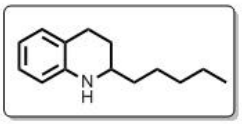
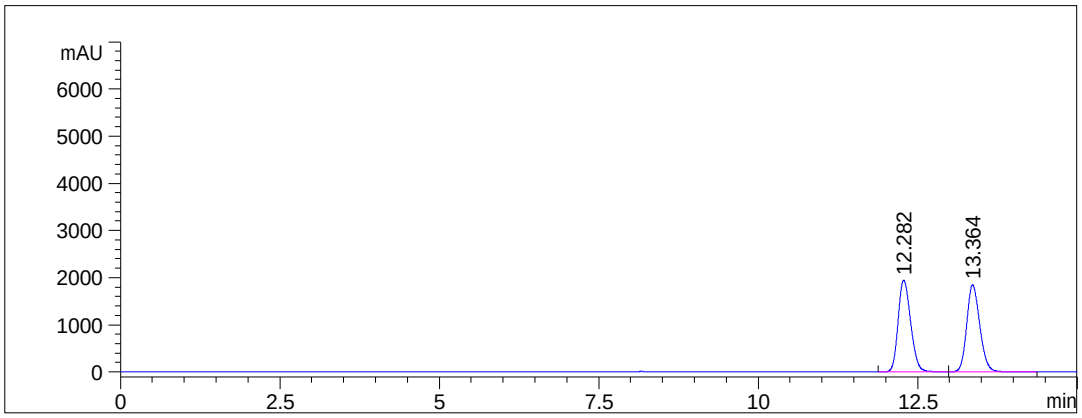
1	11.111	BB	0.2798	1.03722e4	574.06506	35.5270
2	14.203	BB	0.3689	1.88231e4	793.17834	64.4730

HPLC trace of racemic 2-pentyl-1,2,3,4-tetrahydroquinoline (**2u**)





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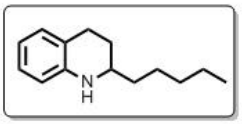
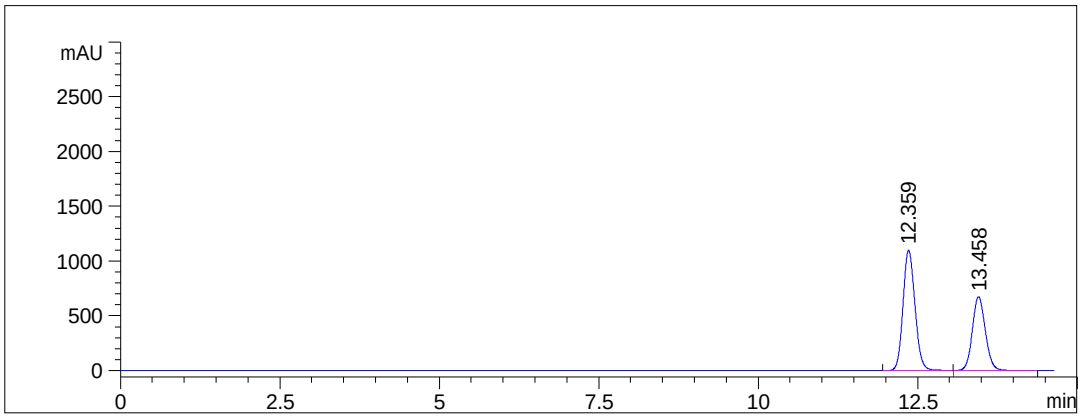
1	12.282	BB	0.2126	2.66411e4	1947.52844	50.0071
2	13.364	BB	0.2232	2.66335e4	1847.40735	49.9929

HPLC trace of enantioenriched 2-pentyl-1,2,3,4-tetrahydroquinoline (**2u**)





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1	12.359	BB	0.2010	1.43224e4	1099.21130	59.9234
2	13.458	BBA	0.2199	9578.76367	673.74420	40.0766