Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Transfer hydrogenation of pyridinium and quinolinium species using ethanol as a hydrogen source to access saturated N-heterocycles

Suman Yadav, Dhananjay Chaudhary, Naveen Kumar Maurya, Dharmendra Kumar, Km Ishu, and Malleswara Rao Kuram*****

Medicinal and Process Chemistry Division, CSIR-Central Drug Research Institute,

Lucknow- 226031, U.P., India

Academy of Scientific & Innovative Research (AcSIR),

Ghaziabad 201002, India

Email: malleswara.kuram@cdri.res.in

TABLE OF CONTENTS

1. General Information

Unless otherwise noted, all the reactions were performed using oven-dried schlenk tubes under nitrogen. The reactions were monitored by Merck silica gel 60 F_{254} precoated plates (0.25 mm) visualizing under UV light (254 nm) or I_2 staining. Temperature mentioned for any reaction is corresponding to the oil bath temperature. Column chromatography was performed using silica gel 60-120 Å or 100-200 Å mesh of Merck Company.

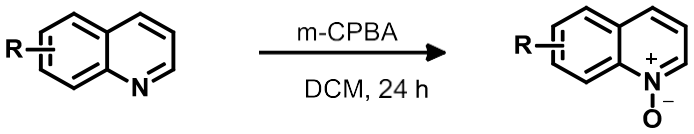
All the commercial reagents and anhydrous solvents were purchased from Sigma- Aldrich, Alfa Aesar, Merck, Spectrochem, Avra Synthesis Pvt. Ltd. and directly used as received without any further purification. Pentamethylcyclopentadienyl iridium dichloride dimer ($[IrCp^*Cl_2]_2$) catalyst was purchased from TCI. 7-Methylquinoline was purchased from TCI that contain 25% 5-methylquinoline at maximum. 3-Ethylquinoline,[1] 3-Phenylquinoline,[2] 6-Phenylquinoline,[3] and 6-ethylester quinoline[4] were prepared according to literature procedures.

Analytical Methods

^1H, ^{13}C and ^{19}F nuclear magnetic resonance spectra were recorded on Bruker Advance III 400 MHz spectrometer at 25 °C. NMRs of the products were measured in $CDCl_3$. The chemical shifts in ^1H NMR and $^{13}C\{1H\}$ NMR spectra are reported in parts per million (ppm) and are referenced to the residual solvent signal as the internal standard; ^1H NMR spectra ($CDCl_3$ δ 7.26 ppm) and ^{13}C ($CDCl_3$ δ 77.16). The coupling constant (J) was reported in Hertz (Hz). Splitting patterns are denoted as "s" for singlet; "d" for doublet; "t" for triplet; "q" for quartet; "sext" for sextet; "sept" for septet; "m"for multiplet, "br" for broad; "dt" for doublet of triplets; "td" for triplet of doublets. ESI-HRMS were recorded on AGILENT 6520 Q-TOF spectrometer. IR spectra were recorded with Agilent Cary 630 FTIR Spectrometer.

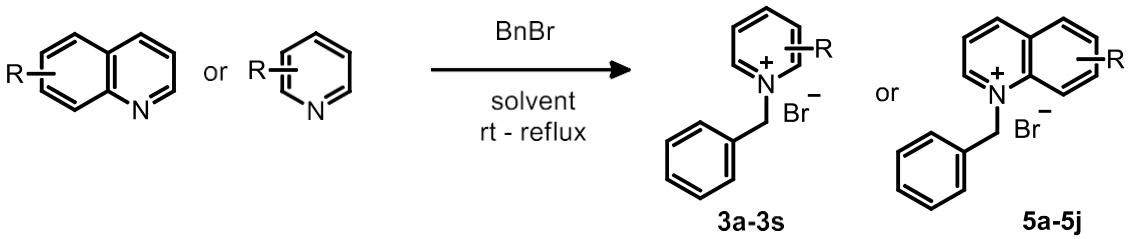
2. Experimental Procedures

(a) General procedure for the synthesis of quinoline *N*-oxides:[5a-d]



To a solution of the corresponding quinoline (0.5 mmol) in DCM (5 mL) was added m-CPBA (1.5 equiv) at 0 °C. The reaction mixture was allowed to stir at room temperature for 16-24 h. The reaction mixture was diluted with DCM and washed with $NaHCO_3$ followed by brine solution. The combined organic part was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with 80% ethyl acetate in hexane to 100% ethyl acetate as the eluent. Pure quinoline *N*-oxides were obtained with 70−90% yields.

(b) General procedure for the synthesis of pyridinium and quinolinium salts:[6a-h]



A mixture of the corresponding quinoline/pyridines (1.0 equiv) and benzyl bromides (2.0 equiv) in acetone/CH_3CN/toluene was stirred at reflux for 24-30 h. The solvent was removed under reduced pressure. Resulting precipitate was washed with diethyl ether and dried under vacuum to give the desired pyridinium and quinolinium salts.

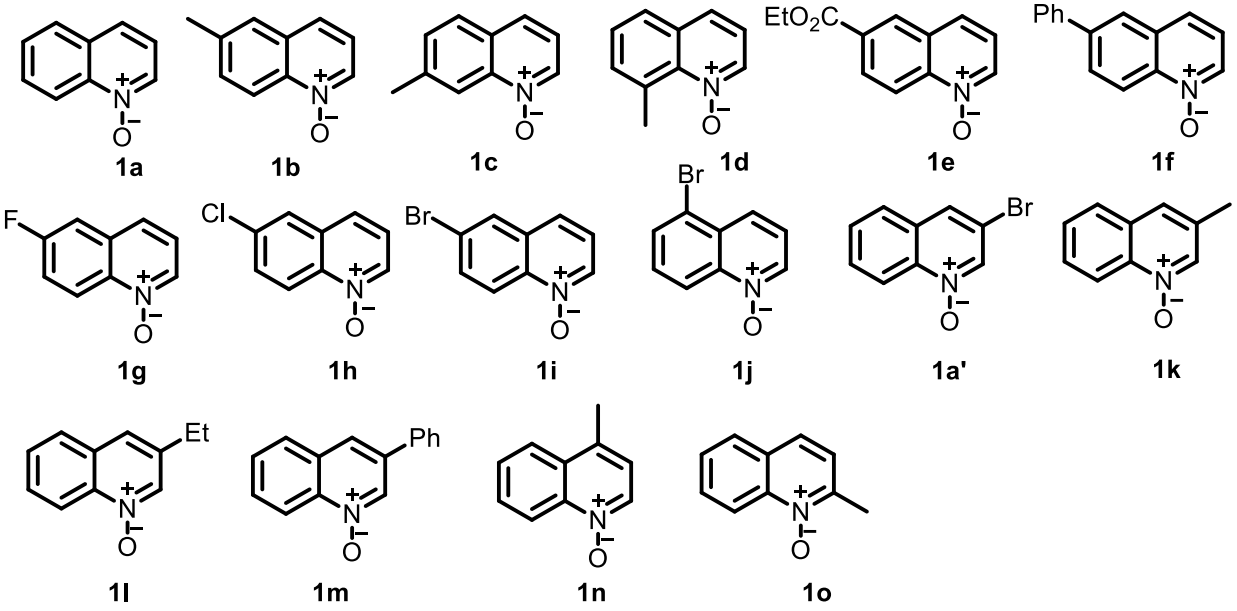
Acetone was used as a solvent for **3b**-**3d**, **3f**, **3h**-**3l**, **3n**-**3p**, **3r**, **3s**, **5e**, and **5f**-**5h**.

Acetonitrile was used as a solvent for **3m**, **3q**, **5a**-**5d**, **5i**, and **5j**.

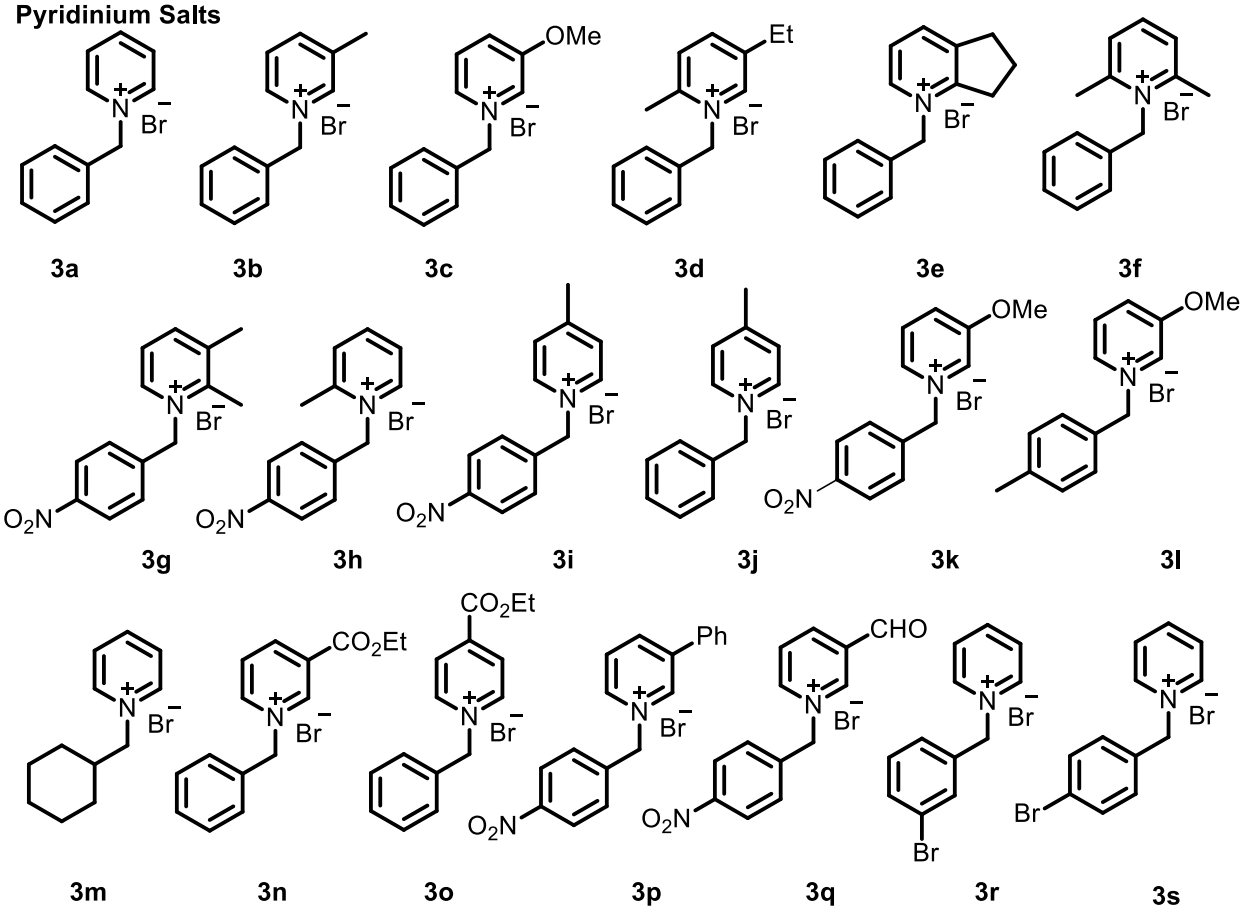
Toluene was used as a solvent for **3e** and **3g**.

(c) Substrates employed in the reaction:

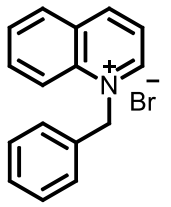
Quinoline N-oxides:



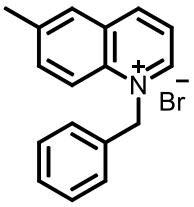
Pyridinium Salts



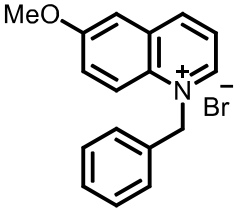
Quinolinium Salts:



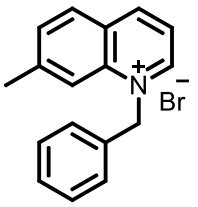
5a



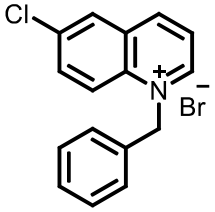
5b



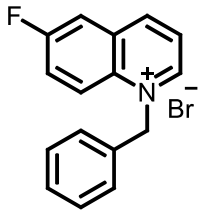
5c



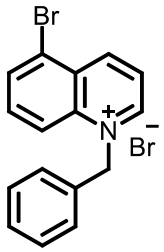
5d



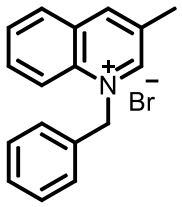
5e



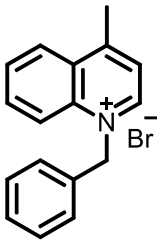
5f



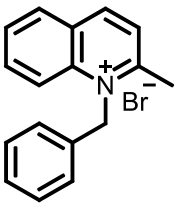
5g



5h

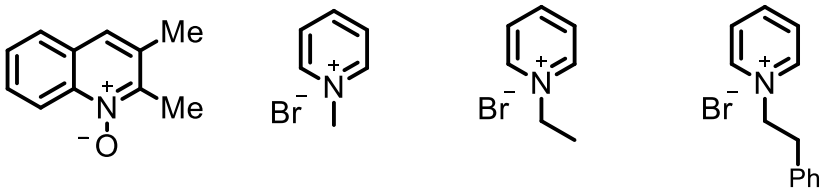


5i



5j

(d) Unsuccessful substrates:



no desired product

trace

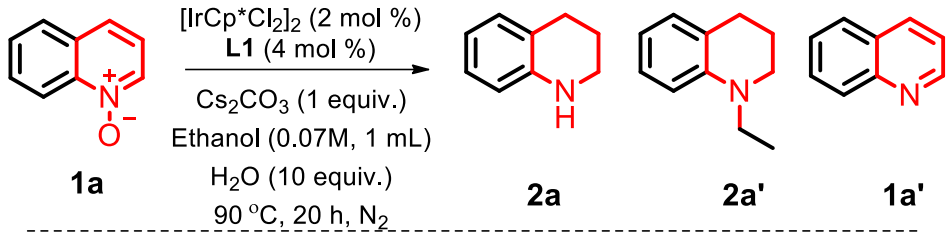
(e) General procedure for the transfer hydrogenation of quinolines N-oxides (Condition A):

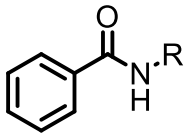
To an oven dried Schlenk tube, was charged with quinoline N-oxide (**1**) (0.5 mmol), $[IrCp^*Cl_2]_2$ (2.0 mol %), Ligand (4.0 mol %) and Cs_2CO_3 (1.0 equiv.), and exchanged with nitrogen and vacuum three times. Then ethanol (3.6 mL) and H_2O (10 equiv.) was added in the reaction tube under N_2 atm. The reaction mixture was stirred at 90 ^oC for 20-24 h. Upon completion, the reaction mixture was cooled, diluted with DCM, filtered through Celite and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (1-10% hexane/ethyl acetate as eluent) to yield the corresponding product.

(f) General procedure for the transfer hydrogenation of pyridinium and quinolinium salts (Condition B):

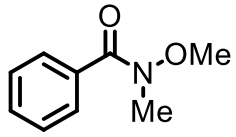
To an oven dried Schlenk tube, was charged with N-heteroarenium Salts (**3** or **5**) (0.5 mmol), $[IrCp^*Cl_2]_2$ (2 mol %), Ligand (4 mol %), KI (3.0 equiv) and DABCO (1.0 equiv.), and exchanged with nitrogen and vacuum three times. After adding ethanol (5-6 mL), the reaction mixture was stirred at 90 ^oC for 20-24 h. Upon completion, the reaction mixture was cooled, diluted with DCM, filtered through Celite and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (1-10% hexane/ethyl acetate as eluent) to yield the corresponding product.

(g) Optimization of the reaction conditions with quinoline N-oxide:

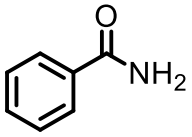




R = OMe, **L1;**
R = OPiv, **L2;**
R = Me, **L3**
R = Ph, **L4**



L5

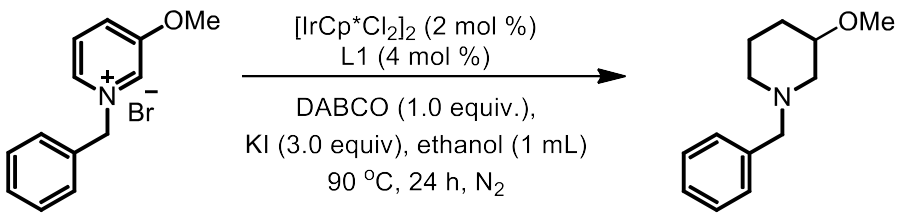


L6

Entry	Deviation from the standard conditions	Yield (%) of 2a
1	None	85 (70)[b]
2	Without ligand	46[b]
3	K_2CO_3/NaOAc/Na_2CO_3 instead of Cs_2CO_3	n.d.
4	Et_3N instead of Cs_2CO_3	n.d.
5	Cs_2CO_3 (0.5 equiv)	65
6	Cs_2CO_3 (0.2 equiv)	30
7	Ethanol (0.5mL, 0.14M)	85
8	Ethanol (1.0 mL, 0.069M)	83
9	Ethanol (1.5 mL, 0.046M)	trace
10	50 °C	trace
11	$Pd(OAc)_2$	n.d.
12	$NiCl_2$	n.d.
13	$CpMn(CO)_3$	n.d.

[a]Reaction conditions: **1a** (0.068 mmol), $[IrCp^*Cl_2]_2$ (2 mol %), **L** (4 mol %), Cs_2CO_3 (1 equiv.), H_2O (10 equiv.), ethanol (1 mL) at 90 °C for 20 h under N_2. [1]HNMR yield using 1,3,5-trimethoxybenzene as internal standard. n.d. = not detected. [b]Isolated yield.

(h) Optimization of the reaction conditions with pyridinium salt:



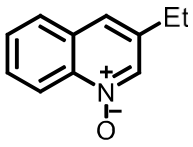
3c **4c**

Entry	Deviation from the standard conditions	Yield (%) of 4c
1	None	78[b]
2	Without base	n.d.
3	Without ligand	33
4	With **L5** instead of **L1**	62
5	With **L6** instead of **L1**	64%
6	With CyJohnPhos instead of **L1**	n.d.
7	With 1,10-phen instead of **L1**	n.d.
8	With PPh_3 instead of **L1**	n.d.
9	MeOH instead of ethanol	75
10	$[Ir(COD)Cl_2]_2$ instead of $[IrCp^*Cl_2]_2$-catalyst	n.d.
11	Pyridine N-oxide instead of pyridinium salt	n.d.
13	70 °C	Trace
14	KI (1.0 equiv)	60
15	KI (2.0 equiv)	64

[a]Reaction conditions: **3c** (0.036 mmol), $[IrCp^*Cl_2]_2$ (2.0 mol %), **L1** (4.0 mol %), DABCO (1.0 equiv.), KI (3.0 equiv.), ethanol (1 mL) at 90 °C for 24 h under N_2.(b) isolated yield.

3. Characterization data of Starting material

3-ethylquinoline 1-oxide (1l)



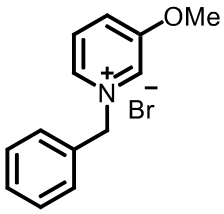
The representative general procedure **2(a)** was followed, using 3-Ethylquinoline (250 mg, 1.6 mmol) for 24 h. Purification by column chromatography (eluted with 90% EtOAc in hexane) furnished **1l** (236 mg, 85% yield) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.60 (d, J = 8.7 Hz, 1H), 8.39 (d, J = 0.9 Hz, 1H), 7.71 (d, J = 8.2 Hz, 1H), 7.62–7.59 (m, 1H), 7.53–7.50 (m, 1H), 7.47 (s, 1H), 2.67 (q, J = 7.6 Hz, 2H), 1.25 (t, J = 7.6 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 139.8, 137.4, 136.6, 130.3, 129.5, 128.7, 127.6, 124.6, 119.5, 26.2, 14.7.

HRMS (ESI): Exact mass calculated for $C_{11}H_{11}NO$ $[M+H]^+$: 174.0924, found: 174.0917.

1-benzyl-3-methoxypyridin-1-ium bromide (3c)



The representative general procedure **2(b)** was followed, using 3-methoxy pyridine (300 mg, 2.7 mmol) reflux for 24 h to give **3c** (750 mg, 99%) as a yellow solid.

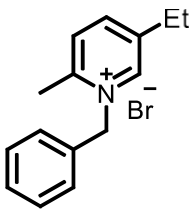
^{1}H NMR (400 MHz, DMSO-d_6): δ 9.31 (br, 1H), 8.91–8.89 (m, 1H), 8.27 (d, J = 8.7 Hz, 1H), 8.12–8.08 (m, 1H), 7.63 (br, 2H), 7.42 (br, 2H), 5.93 (br, 2H), 4.02 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 158.6, 137.5, 134.9, 133.2, 131.2, 129.8, 129.6, 129.3, 129.2, 63.5, 58.1.

Melting point: 143-145 °C;

HRMS (ESI): Exact mass calculated for $C_{13}H_{14}NO$ $[M]^+$: 200.1070, found: 200.1073.

1-benzyl-5-ethyl-2-methylpyridin-1-ium bromide (3d)



The representative general procedure **2(b)** was followed, using 5-ethyl-2-methylpyridine (300 mg, 2.5 mmol) reflux for 24 h to give **3d** (600 mg, 82%) as a white solid.

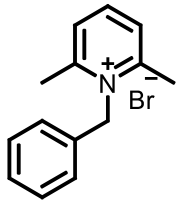
^{1}H NMR (400 MHz, D_2O): δ 8.59 (s, 1H), 8.26 (d, J = 8.2 Hz, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.40–7.39 (br, 3H), 7.18–7.16 (m, 2H), 5.72 (s, 2H), 2.76 (q, J = 7.6 Hz, 2H), 2.65 (s, 3H), 1.21 (t, J = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 153.4, 145.9, 145.5, 142.4, 133.7, 130.4, 129.7, 129.2, 127.8, 60.7, 25.2, 19.9, 14.8.

Melting point: 170-172 °C;

HRMS (ESI): Exact mass calculated for $C_{15}H_{18}N$ $[M]^+$: 212.1434, found: 212.1442.

1-benzyl-2,6-dimethylpyridin-1-ium bromide (3f)



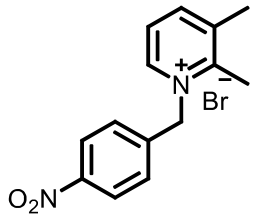
The representative general procedure **2(b)** was followed, using 2,6-dimethylpyridine (300 mg, 2.8 mmol) reflux for 24 h to give **3f** (470 mg, 60%) as a sticky solid.

^{1}H NMR (400 MHz, DMSO-d_6): δ 8.49 (t, J = 7.9 Hz, 1H), 8.02 (d, J = 7.9 Hz, 2H), 7.45–7.38 (m, 3H), 7.05 (d, J = 6.9 Hz, 2H), 5.92 (s, 2H), 2.76 (s, 6H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 156.7, 145.7, 132.8, 129.8, 128.7, 128.5, 126.0, 55.9, 21.5.

HRMS (ESI): Exact mass calculated for $C_{14}H_{16}N$ $[M]^+$: 198.1277, found: 198.1281.

2,3-dimethyl-1-(4-nitrobenzyl)pyridin-1-ium bromide (3g)



The representative general procedure **2(b)** was followed, using 2,3-dimethylpyridine (250 mg, 2.3 mmol) reflux for 24 h to give **3g** (550 mg, 74%) as a white solid.

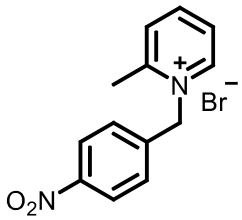
^{1}H NMR (400 MHz, D_2O): δ 8.68 (br, 1H), 8.33 (d, J = 6.9 Hz, 1H), 8.21 (br, 2H), 7.83–7.79 (m, 1H), 7.31 (d, J = 8.3 Hz, 2H), 5.96 (s, 2H), 2.59 (s, 3H), 2.48 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 155.6, 147.9, 146.8, 144.7, 141.3, 139.8, 128.9, 125.6, 124.6, 60.6, 19.8, 17.6.

Melting point: 190-192 °C;

HRMS (ESI): Exact mass calculated for $C_{14}H_{15}N_2O_2$ $[M]^+$: 243.1128, found: 243.1138.

2-methyl-1-(4-nitrobenzyl)pyridin-1-ium bromide (3h)



The representative general procedure **2(b)** was followed, using 2-methylpyridine (200 mg, 2.1 mmol) reflux for 24 h to give **3h** (600 mg, 92%) as a white solid.

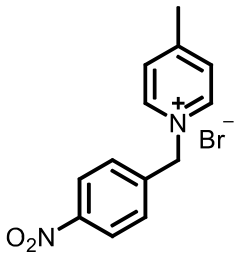
^{1}H NMR (400 MHz, D_2O): δ 8.83(br, 1H), 8.47-8.44 (m, 1H), 8.21-8.18 (m, 2H), 7.97–7.94 (m, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 5.94 (s, 2H), 2.71 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 156.4, 148.0, 146.9, 146.7, 140.9, 130.9, 129.3, 126.6, 124.7, 59.9, 20.5.

Melting point: 205-207 °C;

HRMS (ESI): Exact mass calculated for $C_{13}H_{13}N_2O_2$ $[M]^+$: 229.0972, found: 229.0984.

4-methyl-1-(4-nitrobenzyl)pyridin-1-ium bromide (3i)



The representative general procedure **2(b)** was followed, using 4-methylpyridine (250 mg, 2.7 mmol) reflux for 24 h to give **3i** (730 mg, 87%) as a white solid.

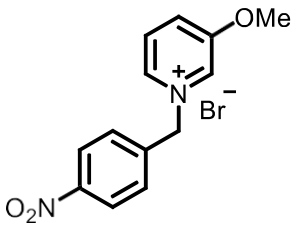
^{1}H NMR (400 MHz, D_2O): δ 8.68 (d, *J* = 6.6 Hz, 2H), 8.22 (d, *J* = 8.8 Hz, 2H), 7.86 (d, *J* = 6.4 Hz, 2H), 7.55 (d, *J* = 8.7 Hz, 2H), 5.82 (s, 2H), 2.60 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 161.4, 148.3, 144.5, 141.9, 130.4, 129.3, 124.6, 61.6, 22.0.

Melting point: 178-180 °C;

HRMS (ESI): Exact mass calculated for $C_{13}H_{13}N_2O_2$ $[M]^+$: 229.0972, found: 229.0986.

3-methoxy-1-(4-nitrobenzyl)pyridin-1-ium bromide (3k)



The representative general procedure **2(b)** was followed, using 3- methoxypyridine (200 mg, 1.8 mmol) and 4-nitrobenzyl bromide (1.2 equiv) reflux for 24 h to give **3k** (510 mg, 87%) as a yellow solid.

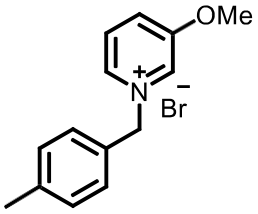
^{1}H NMR (400 MHz, D_2O): δ 8.60 (br, 1H), 8.50 (d, J = 5.9 Hz, 1H), 8.23 (d, J = 8.7 Hz, 2H), 8.12 (dd, J = 8.9 Hz, 2.3 Hz, 1H), 7.97–7.94 (m, 1H), 7.57 (d, J = 8.7 Hz, 2H), 5.87 (s, 2H), 3.96 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 158.8, 148.3, 141.7, 137.9, 133.6, 131.6, 130.5, 129.5, 124.5, 62.5, 58.1.

Melting point: 188-190 °C;

HRMS (ESI): Exact mass calculated for $C_{13}H_{13}N_2O_3$ $[M]^+$: 245.0921, found: 245.0928.

3-methoxy-1-(4-methylbenzyl)pyridin-1-ium bromide (3l)



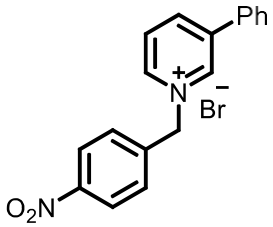
The representative general procedure **2(b)** was followed, using 3-methoxypyridine (200 mg, 1.8 mmol) and 4-methylbenzyl bromide (1.2 equiv) reflux for 24 h to give **3l** (470 mg, 89%) as a sticky solid.

^{1}H NMR (400 MHz, D_2O): δ 8.49 (s, 1H), 8.42 (d, J = 5.8 Hz, 1H), 8.02 (d, J = 8.9 Hz, 1H), 7.89–7.81 (m, 1H), 7.31–7.29 (m, 2H), 7.25 (br, 2H), 5.64 (s, 2H), 3.93 (s, 3H), 2.27 (s, 3H).

^{13}C NMR (100 MHz, D_2O): δ 158.8, 140.5, 136.4, 131.9, 130.5, 130.1, 129.7, 128.9, 128.6, 64.6, 57.2, 20.3.

HRMS (ESI): Exact mass calculated for $C_{14}H_{16}NO$ $[M]^+$: 214.1226, found: 214.1229.

1-(4-nitrobenzyl)-3-phenylpyridin-1-ium bromide (3p)



The representative general procedure **2(b)** was followed, using 3-phenylpyridine (250 mg, 1.6 mmol) and 4-nitrobenzyl bromide (1.2 equiv) reflux for 24 h to give **3p** (567 mg, 95%) as a white solid.

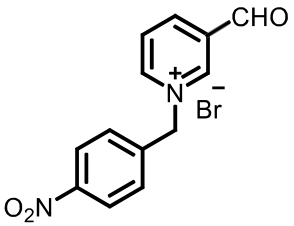
^{1}H NMR (400 MHz, DMSO-d_6): δ 9.79 (s, 1H), 9.21 (d, J = 5.3 Hz, 1H), 9.02–8.99 (m, 1H), 8.31–8.28 (m, 3H), 7.96–7.88 (m, 4H), 7.66–7.58 (m, 3H), 6.14 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 148.4, 143.9, 143.8, 143.7, 141.7, 140.6, 133.5, 130.8, 130.6, 129.9, 129.1, 128.1, 124.6, 62.7.

Melting point: 216-218 °C;

HRMS (ESI): Exact mass calculated for $C_{18}H_{15}N_2O_2$ $[M]^+$: 291.1128, found: 291.1137.

3-formyl-1-(4-nitrobenzyl)pyridin-1-ium bromide (3q)



The representative general procedure **2(b)** was followed, using nicotinaldehyde (250 mg, 2.3 mmol) and 4-nitrobenzyl bromide (1.2 equiv) reflux for 24 h to give **3q** (557 mg, 75%) as a white solid.

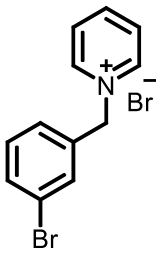
^{1}H NMR (400 MHz, DMSO-d_6): δ 10.17 (s, 1H), 9.82 (s, 1H), 9.45 (d, J = 5.9 Hz, 1H), 9.07 (dt, J = 8.0 Hz, 1.3 Hz, 1H), 8.41 (dd, J = 6.3 Hz, 1H), 8.31 (d, J = 8.8 Hz, 2H), 7.85 (d, J = 8.7 Hz, 2H), 6.16 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 189.1, 148.9, 148.5, 147.2, 145.9, 141.2, 135.4, 130.8, 129.6, 124.6, 62.9.

Melting point: 228-230 °C;

HRMS (ESI): Exact mass calculated for $C_{13}H_{11}N_2O_3$ $[M+CH_3OH]^+$: 275.1026, found: 275.1035.

1-(3-bromobenzyl)pyridin-1-ium bromide (3r)



The representative general procedure **2(b)** was followed, using pyridine (250 mg, 3.2 mmol) and 3-bromobenzyl bromide (1.2 equiv) reflux for 24 h to give **3r** (947 mg, 90%) as a white solid.

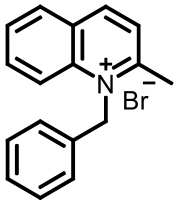
^{1}H NMR (400 MHz, DMSO-d_6): δ 9.35–9.29 (br, 2H), 8.66 (t, J = 7.7 Hz, 1H), 8.23–8.19 (m, 2H), 7.91–7.89 (m, 1H), 7.63–7.62 (br, 2H), 7.44–7.40 (m, 1H), 5.98 (br, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 146.6, 145.4, 137.2, 132.7, 132.2, 131.8, 129.0, 128.6, 122.7, 62.4.

Melting point: 102-104 °C;

HRMS (ESI): Exact mass calculated for $C_{12}H_{11}BrN$ $[M]^+$: 248.0069, found: 248.0074.

1-benzyl-2-methylquinolin-1-ium bromide (5j)



The representative general procedure **2(b)** was followed, using 2-methylquinoline (750 mg, 5.2 mmol) and benzyl bromide (1.2 equiv) reflux for 24 h to give **5j** (408 mg, 25%) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.27 (d, J = 8.5 Hz, 1H), 8.48 (d, J = 8.1 Hz, 1H), 8.41 (d, J = 8.9 Hz, 1H), 8.26 (d, J = 8.5 Hz, 1H), 8.18–8.13 (m, 1H), 7.98 (t, J = 7.5 Hz, 1H), 7.40–7.32 (m, 3H), 7.13 (d, J = 6.8 Hz, 2H), 6.35 (s, 2H), 3.09 (s, 3H).

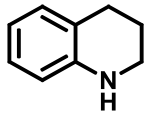
^{13}C NMR (100 MHz, DMSO-d_6): δ 162.2, 147.2, 139.4, 135.9, 133.7, 131.2, 129.7, 128.9, 128.6, 126.3, 126.2, 119.7, 54.9, 23.3.

Melting point: 185-187 °C;

HRMS (ESI): Exact mass calculated for $C_{17}H_{16}N$ $[M]^+$: 234.1277, found: 234.1283.

4. Characterization data of isolated products

1,2,3,4-tetrahydroquinoline (2a):[7]



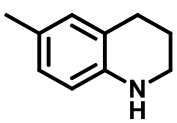
The representative general procedure **A** was followed, using **1a** (73 mg, 0.5 mmol) for 19 h. Purification by column chromatography (eluted with 3% EtOAc in hexane) furnished **2a** (47 mg, 70% yield) as a colourless oil. R_f 0.51 (10% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.95–6.92 (m, 2H), 6.58 (t, J = 7.9 Hz, 1H), 6.43 (d, J = 7.8 Hz, 1H), 3.59 (br s, 1H), 3.27–3.25 (m, 2H), 2.74 (t, J = 6.3 Hz, 2H), 1.94–1.89 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 144.9, 129.6, 126.8, 121.5, 116.9, 114.2, 42.0, 27.0, 22.3.

HRMS (ESI): Exact mass calculated for $C_9H_{11}N$ $[M+H]^+$: 134.0970, found: 134.0961.

6-methyl-1,2,3,4-tetrahydroquinoline (2b):[7a]



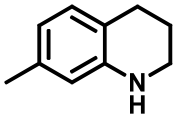
The representative general procedure **A** was followed, using **1b** (80 mg, 0.5 mmol) for 20 h. Purification by column chromatography (eluted with 3% EtOAc in hexane) furnished **2b** (47 mg, 64% yield) as colourless oil. R_f 0.51 (10% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.78–6.76 (m, 2H), 6.40 (d, J = 8.6 Hz, 1H), 3.26–3.24 (m, 2H), 2.72 (t, J = 6.4 Hz, 2H), 2.19 (s, 3H), 1.95–1.89 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.4, 130.1, 127.3, 126.3, 121.6, 114.5, 42.2, 26.9, 22.5, 20.4.

HRMS (ESI): Exact mass calculated for $C_{10}H_{13}N$ $[M+H]^+$: 148.1126, found: 148.1117.

7-methyl-1,2,3,4-tetrahydroquinoline (2c):[7a]



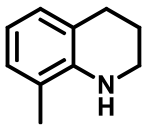
The representative general procedure **A** was followed, using **1c** (80 mg, 0.5 mmol) for 20 h. Purification by column chromatography (eluted with 2% EtOAc in hexane) furnished **2c** (62 mg, 84% yield) as Yellow oil. R_f 0.5 (10% EtOAc in hexane).

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.86 (d, J = 7.6 Hz, 1H), 6.46 (dd, J = 7.6, 1.0 Hz, 1H), 6.33 (s, 1H), 3.32–3.29 (m, 2H), 2.75 (t, J = 6.4 Hz, 2H), 2.25 (s, 3H), 1.99–1.91 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 144.6, 136.4, 129.4, 118.6, 117.9, 114.8, 42.0, 26.6, 22.4, 21.1.

HRMS (ESI): Exact mass calculated for $C_{10}H_{13}N$ $[M+H]^+$: 148.1126, found: 148.1116.

8-methyl-1,2,3,4-tetrahydroquinoline (2d)[7a]



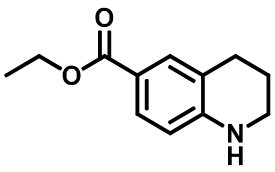
The representative general procedure **A** was followed, using **1d** (80 mg, 0.5 mmol) for 21 h. Purification by column chromatography (eluted with 3% EtOAc in hexane) furnished **2d** (39 mg, 53% yield) as colourless oil. R_f 0.51 (10% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80–6.75 (m, 2H), 6.47 (t, J = 7.4 Hz, 1H), 3.54 (br s, 1H), 3.29–3.27 (m, 2H), 2.70 (t, J = 6.4 Hz, 2H), 1.99 (s, 3H), 1.89–1.83 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7, 127.9, 127.4, 121.2, 120.9, 116.4, 42.4, 27.3, 22.2, 17.2.

HRMS (ESI): Exact mass calculated for $C_{10}H_{13}N$ $[M+H]^+$: 148.1126, found: 148.1118.

ethyl 1,2,3,4-tetrahydroquinoline-6-carboxylate (2e)[7g]



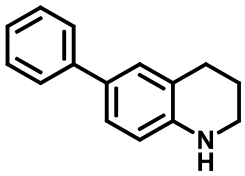
The representative general procedure **A** was followed, using **1e** (109 mg, 0.5 mmol), $[IrCp^*Cl_2]_2$ (5 mol%), **L1** (10 mol%) and Cs_2CO_3 (1.5 equiv.) for 21 h. Purification by column chromatography (eluted with 10% EtOAc in hexane) furnished **2e** (80 mg, 78% yield) as yellow solid. R_f 0.2 (10% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.56 (m, 2H), 6.31 (d, J = 9.0 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.28–3.26 (m, 2H), 2.69 (t, J = 6.3 Hz, 2H), 1.88–1.82 (m, 2H), 1.27 (t, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 148.7, 131.2, 129.0, 119.9, 117.8, 112.6, 60.1, 41.7, 26.9, 21.5, 14.5.

HRMS (ESI): Exact mass calculated for $C_{12}H_{15}NO_2$ $[M+H]^+$: 206.1181, found: 206.1166.

6-phenyl-1,2,3,4-tetrahydroquinoline (2f)[7f]



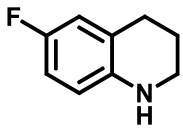
The representative general procedure **A** was followed, using **1f** (111 mg, 0.5 mmol) for 19 h. Purification by column chromatography (eluted with 3% EtOAc in hexane) furnished **2f** (51 mg, 49% yield) as colourless oil. R_f 0.51 (10% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 7.4 Hz, 2H), 7.29 (t, J = 7.7 Hz, 2H), 7.17–7.13 (m, 3H), 6.44 (d, J = 7.9 Hz, 1H), 3.24–3.22 (m, 2H), 2.74 (t, J = 6.4 Hz, 2H) 1.91–1.85 (m, 2H).

^{13}C NMR (100MHz, $CDCl_3$): δ 143.2, 140.4, 128.8, 127.5, 127.1, 125.2, 124.8, 124.5, 120.5, 113.4, 40.9, 26.1, 21.1.

HRMS (ESI): Exact mass calculated for $C_{15}H_{15}N$ $[M+H]^+$: 210.1283, found: 210.1274.

6-fluoro-1,2,3,4-tetrahydroquinoline (2g)[7b]



The representative general procedure **A** was followed, using **1g** (82 mg, 0.5 mmol) for 19 h. Purification by column chromatography (eluted with 5% EtOAc in hexane) furnished **2g** (58 mg, 77% yield) as colourless oil. R_f 0.41 (10% EtOAc in hexane).

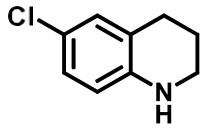
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.69–6.65 (m, 2H), 6.41 (dd, J = 9.4 Hz, 4.8 Hz, 1H), 3.27–3.25 (m, 2H), 2.74 (t, J = 6.5 Hz, 2H), 1.95–1.89 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.5 (J^1 = 233.0 Hz), 140.9, 122.8 (J^3 = 6.6 Hz), 115.6 (J^2 = 21.6 Hz), 114.9 (J^3 = 7.5 Hz), 113.2 (J^2 = 22.0 Hz), 42.1, 27.0, 21.9.

^{19}F NMR (376 MHz): δ –128.4Hz.

HRMS (ESI): Exact mass calculated for $C_9H_{10}FN$ $[M+H]^+$: 152.0876, found: 152.0868.

6-chloro-1,2,3,4-tetrahydroquinoline (2h)[7b]



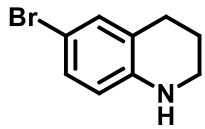
The representative general procedure **A** was followed, using **1h** (89 mg, 0.5 mmol) for 19 h. Purification by column chromatography (eluted with 3% EtOAc in hexane) furnished **2h** (42 mg, 50% yield) as yellow oil. R_f 0.51 (10% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.82–6.79 (m, 2H), 6.30–6.27 (m, 1H), 3.69 (br s, 1H), 3.20–3.17 (m, 2H), 2.63 (t, J = 6.4 Hz, 2H), 1.85–1.79 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.2, 129.0, 126.5, 122.8, 121.1, 115.1, 41.8, 26.9, 21.7.

HRMS (ESI): Exact mass calculated for $C_9H_{10}ClN$ $[M+H]^+$: 168.0580, found: 168.0576.

6-bromo-1,2,3,4-tetrahydroquinoline (2i)[7b]



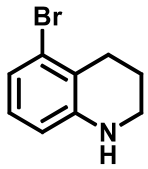
The representative general procedure **A** was followed, using **1i** (111mg, 0.5 mmol) for 19 h. Purification by column chromatography (eluted with 5% EtOAc in hexane) furnished **2i** (65 mg, 62% yield) as yellow oil. R_f 0.3 (10% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97–6.93 (m, 2H), 6.25 (d, J = 8.4 Hz, 1H), 3.21-3.18 (m, 2H), 2.64 (t, J = 6.4 Hz, 2H), 1.86-1.79 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 143.7, 131.9, 129.4, 123.4, 115.5, 108.2, 41.8, 26.8, 21.7.

HRMS (ESI): Exact mass calculated for $C_9H_{10}BrN$ $[M+H]^+$: 212.0075, found: 212.0062.

5-bromo-1,2,3,4-tetrahydroquinoline (2j)[7c]



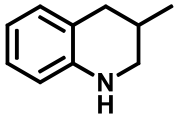
The representative general procedure **A** was followed, using **1j** (111 mg, 0.5 mmol) for 19 h. Purification by column chromatography (eluted with 3% EtOAc in hexane) furnished **2j** (87 mg, 82% yield) as yellow oil. R_f 0.51 (10% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.85–6.77 (m, 2H), 6.38 (d, *J* = 7.8 Hz, 1H), 3.25–3.22 (m, 2H), 2.75 (t, *J* = 6.5 Hz, 2H), 1.96–1.92 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 146.5, 127.6, 125.9, 120.8, 120.7, 113.2, 41.5, 27.7, 22.2.

HRMS (ESI): Exact mass calculated for $C_9H_{10}BrN$ $[M+H]^+$: 212.0075, found: 212.0068.

3-methyl-1,2,3,4-tetrahydroquinoline (2k)[7a]



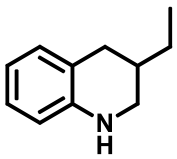
The representative general procedure **A** was followed, using **1k** (80 mg, 0.5 mmol), Cs_2CO_3 (1.5 equiv), without water at 85 ^{o}C for 24 h. Purification by column chromatography (eluted with 3% EtOAc in hexane) furnished **2k** (68 mg, 92% yield) as colourless oil. R_f 0.51 (10% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97–6.92 (m, 2H), 6.59 (t, *J* = 7.3 Hz, 1H), 6.47 (d, *J* = 7.9 Hz, 1H), 3.27–3.23 (m, 1H), 2.90–2.85 (m, 1H), 2.79–2.74 (m, 1H), 2.42 (dd, *J* = 16.0 Hz, 10.2 Hz, 1H), 2.10–1.98 (m, 1H), 1.03 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.3, 129.6, 126.7, 121.1, 116.9, 113.9, 48.9, 35.5, 27.2, 19.1.

HRMS (ESI): Exact mass calculated for $C_{10}H_{13}N$ $[M+H]^+$: 148.1126, found: 148.1114.

3-ethyl-1,2,3,4-tetrahydroquinoline (2l)[7e]



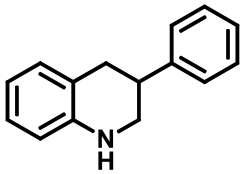
The representative general procedure **A** was followed, using **1l** (87 mg, 0.5 mmol),), Cs_2CO_3 (1.5 equiv), without water at 85 ^{o}C for 24 h. Purification by column chromatography (eluted with 3% EtOAc in hexane) furnished **2l** (65 mg, 81% yield) as colourless oil. R_f 0.51 (10% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.89–6.86 (m, 2H), 6.52 (td, *J* = 7.3 Hz, 1.0 Hz, 1H), 6.40 (d, *J* = 7.6 Hz, 1H), 3.27–3.23 (m, 1H), 2.86–2.81 (m, 1H), 2.77–2.71 (m, 1H), 2.35 (dd, *J* = 16 Hz, 10.2 Hz 1H), 1.80-1.69 (m, 1H), 1.34–1.27 (m, 2H), 0.91 (t, *J* =7.5 Hz, 3H).

^{13}C NMR (125MHz, $CDCl_3$): δ 144.6, 129.6, 126.7, 121.1, 116.9, 113.9, 47.0, 34.0, 33.4, 26.6, 11.5.

HRMS (ESI): Exact mass calculated for $C_{11}H_{15}N$ $[M+H]^+$: 162.1283, found: 162.1275.

3-phenyl-1,2,3,4-tetrahydroquinoline (2m)[7d]



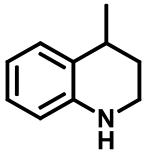
The representative general procedure **A** was followed, using **1m** (45 mg, 0.2 mmol), Cs_2CO_3 (1.5 equiv), without water at 85 °C for 24 h. Purification by column chromatography (eluted with 5% EtOAc in hexane) furnished **2m** (35 mg, 84% yield) as yellow oil. R_f 0.3 (10% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28–7.24 (m, 2H), 7.18–7.15 (m, 3H), 6.95–6.92 (m, 2H), 6.57 (td, *J*=7.3, 0.9 Hz, 1H), 6.46 (d, *J* = 7.5 Hz, 1H), 3.93 (br s, 1H), 3.39–3.35 (m, 1H), 3.28-3.22 (m, 1H), 3.10–3.03 (m, 1H), 2.97–2.86 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 143.9, 129.6, 128.6, 127.2, 127.0, 126.7, 121.4, 117.1, 114.0, 48.4, 38.7, 34.6.

HRMS (ESI): Exact mass calculated for $C_{15}H_{15}N$ $[M+H]^+$: 210.1283, found: 210.1288.

4-methyl-1,2,3,4-tetrahydroquinoline (2n)[7a]



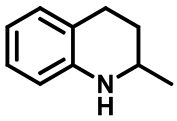
The representative general procedure **A** was followed, using **1n** (80 mg, 0.5 mmol), Cs_2CO_3 (1.5 equiv), without water at 85 °C for 24 h. Purification by column chromatography (eluted with 3% EtOAc in hexane) furnished **2n** (28 mg, 38% yield) as colourless oil. R_f 0.51 (10% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 (d, *J* = 7.6 Hz, 1H), 6.90–6.86 (m, 1H), 6.55 (td, *J* = 7.4 Hz, 1.2 Hz, 1H), 6.39 (dd, *J* = 7.9 Hz, 1.1 Hz, 1H), 3.28–3.16 (m, 2H), 2.88–2.80 (m, 1H), 1.94–1.87 (m, 1H), 1.64–1.56 (m, 1H), 1.21 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.3, 128.4, 126.7, 126.6, 116.9, 114.2, 39.0, 30.2, 29.9, 22.6.

HRMS (ESI): Exact mass calculated for $C_{10}H_{13}N$ $[M+H]^+$: 148.1126, found: 148.1117.

2-methyl-1,2,3,4-tetrahydroquinoline (2o)[7a]



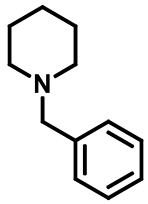
The representative general procedure **A** was followed, using **1o** (80 mg, 0.5 mmol), Cs_2CO_3 (1.5 equiv), without water at 85 ^{0}C for 24 h. Purification by column chromatography (eluted with 3% EtOAc in hexane) furnished **2o** (17 mg, 23% yield) as colourless oil. R_f 0.41 (10% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.89–6.86 (m, 2H), 6.52 (td, J = 7.4 Hz, 1.0 Hz, 1H), 6.40-6.38 (m, 1H), 3.36–3.28 (m, 1H), 3.10 (br s, 1H), 2.79–2.71 (m, 1H), 2.67–2.61 (m, 1H), 1.88–1.82 (m, 1H), 1.56–1.46 (m, 1H), 1.13 (d, J = 6.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.7, 129.3, 126.7, 121.2, 117.0, 114.0, 47.2, 30.1, 26.6, 22.6.

HRMS (ESI): Exact mass calculated for $C_{10}H_{13}N$ $[M+H]^+$: 148.1126, found: 148.1113.

1-benzylpiperidine (4a)[8a]



The title compound was prepared according to General Procedure **B** using salt **3a** (125 mg, 0.5 mmol) for 24 h. The crude material was purified by column chromatography (95:5 Hexane: EtOAc) to give amine **4a** (70 mg, 79%) as a yellow oil.

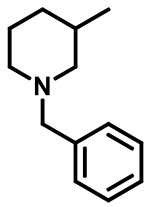
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.19 (m, 4H), 7.18–7.13 (m, 1H), 3.39 (s, 2H), 2.29 (br, 4H), 1.52–1.47 (m, 4H), 1.38–1.31 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 129.3, 128.1, 126.9, 63.9, 54.4, 25.9, 24.4.

HRMS (ESI): Exact mass calculated for $C_{12}H_{17}N$ $[M+H]^+$: 176.1439, found: 176.1437.

IR (neat) (cm^{-1}): 2926, 2857, 2798, 1738, 1618, 1455, 1384, 1269, 1110, 1072, 737.

1-benzyl-3-methylpiperidine (4b)[8b]



The title compound was prepared according to General Procedure **B** using salt **3b** (66 mg, 0.25 mmol), KI (2.0 equiv) for 24h. The crude material was purified by column chromatography (95:5 Hexane: EtOAc) to give amine **4b** (30 mg, 63%) as a yellow oil.

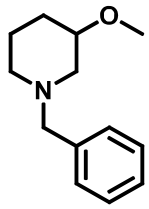
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24–7.20 (m, 4H), 7.19–7.14 (m, 1H), 3.40 (s, 2H), 2.74–2.69 (m, 2H), 1.78 (td, J = 10.9, 3.7 Hz, 1H), 1.63–1.43 (m, 6H), 0.76 (d, J = 6.3 Hz, 3H).

^{13}C NMR (100MHz, $CDCl_3$): δ 128.7, 119.8, 118.5, 117.3, 53.9, 52.2, 44.3, 23.4, 21.5, 15.9, 10.1.

HRMS (ESI): Exact mass calculated for C13H19N $[M+H]^+$: 190.1596, found: 190.1598.

IR (neat) (cm^{-1}): 2927, 2793, 2757, 1732, 1612, 1452, 1383, 1156, 1117, 1070, 904, 858, 738, 698.

1-benzyl-3-methoxypiperidine (4c)



The title compound was prepared according to General Procedure **B** using salt **3c** (80 mg, 0.29 mmol), KI (2.0 equiv) for 24 h. The crude material was purified by column chromatography (93:7 Hexane: EtOAc) to give amine **4c** (46 mg, 78%) as a yellow oil.

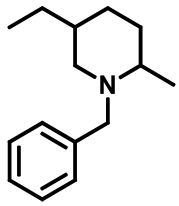
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24–7.15 (m, 5H), 3.46 (dd, J = 17.5Hz, 13.1Hz, 2H), 3.25 (s, 3H), 3.23–3.20 (m, 1H), 2.85–2.82 (m, 1H), 2.59–2.54 (m, 1H), 2.00–1.85 (m, 3H), 1.69–1.61 (m, 1H), 1.49–1.39 (m, 1H), 1.21–1.11 (m, 1H).

^{13}C NMR (100MHz, $CDCl_3$): δ 138.0, 129.2, 128.1, 126.9, 76.3, 63.3, 57.7, 56.0, 53.4, 29.8, 23.1.

HRMS (ESI): Exact mass calculated for $C_{13}H_{19}NO$ $[M+H]^+$: 206.1545, found: 206.1548.

IR (neat) (cm^{-1}): 2932, 2861, 2803, 1731, 1611, 1452, 1382, 1157, 1101, 740, 699.

1-benzyl-5-ethyl-2-methylpiperidine (4d)



The title compound was prepared according to General Procedure **B** using salt **3d** (146 mg, 0.5 mmol). The crude material was purified by column chromatography (95:5 Hexane: EtOAc) to give amine **4d** (65 mg, 60%) as a colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27–7.13 (m, 5H), 3.98 (d, J = 13.6 Hz, 1H), 3.11 (d, J = 13.6 Hz, 1H), 2.73–2.69 (m, 1H), 2.10–2.04 (m, 1H), 1.69–1.65 (m, 1H), 1.60–1.55 (m, 1H), 1.47 (t,

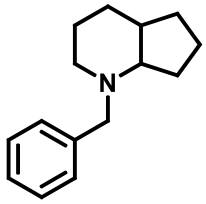
11.1 Hz, 1H), 1.33–1.25 (m, 2H), 1.12 (d, J = 6.1 Hz, 3H), 1.09–0.93 (m, 2H), 0.82–0.75 (m, 1H), 0.72 (t, J = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 139.3, 129.2, 128.0, 126.6, 59.3, 58.2, 56.9, 37.9, 35.0, 31.0, 27.2, 21.0, 11.3.

HRMS (ESI): Exact mass calculated for $C_{15}H_{23}N$ $[M+H]^+$: 218.1909, found: 218.1899.

IR (neat) (cm^{-1}): 2923, 2786, 1612, 1452, 1380, 1114, 1067, 734, 697.

1-benzyloctahydro-1H-cyclopenta[b]pyridine (4e)[8c]



The title compound was prepared according to General Procedure **B** using salt **3e** (145 mg, 0.5 mmol). The crude material was purified by column chromatography (95:5 Hexane: EtOAc) to give amine **4e** (26 mg, 24%) as a colourless oil.

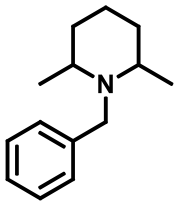
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25–7.13 (m, 5H), 3.69 (d, J = 13.8 Hz, 1H), 3.21 (d, J = 13.8 Hz, 1H), 2.71 (q, J = 5.1 Hz, 1H), 2.50–2.46 (m, 1H), 2.08–2.03 (m, 1H), 1.92–1.87 (m, 1H), 1.82–1.74 (m, 2H), 1.56–1.41 (m, 6H), 1.38–1.31 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 139.9, 128.8, 128.0, 126.5, 64.0, 59.7, 49.8, 39.1, 28.1, 25.9, 25.5, 23.1, 21.5.

HRMS (ESI): Exact mass calculated for $C_{15}H_{21}N$ $[M+H]^+$: 216.1752, found: 216.1757.

IR (neat) (cm^{-1}): 2923, 2786, 1612, 1452, 1380, 1067, 1114, 734, 697.

1-benzyl-2,6-dimethylpiperidine (4f)[8a]



The title compound was prepared according to General Procedure **B** using salt **3f** (139 mg, 0.5 mmol). The crude material was purified by column chromatography (95:5 Hexane: EtOAc) to give amine **4f** (51 mg, 50%, 64:36 dr) as an orange oil as an inseparable mixture of diasteroisomers. The major diastereomer was identified as **cis** by comparison with literature data.[8a]

Data for the major diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (d, J = 7.7 Hz, 2H), 7.20 (t, J = 7.6 Hz, 2H), 7.13–7.09 (m, 1H), 3.73 (s, 2H), 2.42–2.39 (m, 2H), 1.52–1.45 (m, 3H), 1.24–1.21 (m, 3H), 0.99 (d, J = 6.2 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 142.1, 128.0, 127.9, 126.0, 57.3, 53.7, 34.6, 24.3, 22.1.

Data for the minor diastereomer:

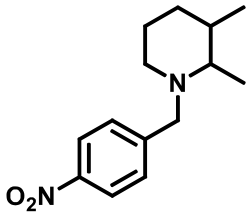
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (d, J = 7.7 Hz, 2H), 7.20 (t, J = 7.6 Hz, 2H), 7.13–7.09 (m, 1H), 3.84 (d, J = 14.0 Hz, 1H), 3.33 (d, J = 14.0 Hz, 1H), 2.82 (m, 2H), 1.58–1.53 (m, 3H), 1.29–1.26 (m, 3H), 0.93 (d, J = 6.5 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 141.5, 128.3, 128.0, 126.3, 53.7, 49.6, 32.8, 19.4, 15.9.

HRMS (ESI): Exact mass calculated for $C_{14}H_{21}N$ $[M+H]^+$: 204.1752, found: 204.1745.

IR (neat) (cm-1): 2925, 2857, 1732, 1606, 1455, 1380, 1311, 1063, 724.

2,3-dimethyl-1-(4-nitrobenzyl)piperidine (4g)[8a]



The title compound was prepared according to General Procedure **b** using salt **3g** (162 mg, 0.5 mmol). The crude material was purified by column chromatography (90:10 Hexane: EtOAc) to give amine **4g** (20 mg, 16%) as a yellow oil.

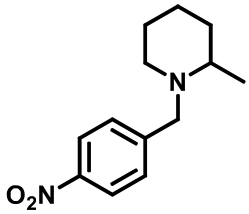
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 8.3 Hz, 2H), 3.64 (d, J = 14.7 Hz, 1H), 3.52 (d, J = 14.7 Hz, 1H), 2.69–2.65 (m, 1H), 2.42–2.37 (m, 1H), 2.19 (dt, J = 11.4, 4.3 Hz, 1H), 1.87–1.79 (m, 1H), 1.54–1.35 (m, 3H), 1.27–1.17 (m, 1H), 0.83 (d, J = 6.7 Hz, 3H), 0.79 (d, J = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 148.7, 146.9, 128.9, 123.4, 58.6, 58.2, 46.9, 34.9, 27.7, 24.9, 17.8, 6.9.

HRMS (ESI): Exact mass calculated for $C_{14}H_{20}N_2O_2$ $[M+H]^+$: 249.1603, found: 249.1604.

IR (neat) (cm^{-1}): 2925, 2341, 1605, 1520, 1449, 1382, 1344, 1063, 850, 737, 691.

2-methyl-1-(4-nitrobenzyl)piperidine (4h)



The title compound was prepared according to General Procedure **b** using salt **3h** (155 mg, 0.5 mmol). The crude material was purified by column chromatography (90:10 Hexane: EtOAc) to give amine **4h** (63 mg, 54%) as a yellow oil.

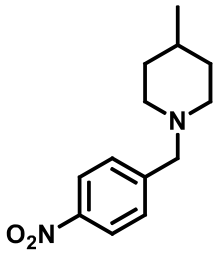
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 8.7 Hz, 2H), 7.45 (d, J = 8.7 Hz, 2H), 3.98 (d, J = 14.5 Hz, 1H), 3.2 (d, J = 14.5 Hz, 1H), 2.59 (dt, J = 11.4, 3.8 Hz, 1H), 2.33–2.26 (m, 1H), 1.97–1.90 (m, 1H), 1.63–1.59 (m, 2H), 1.49–1.37 (m, 2H), 1.35–1.24 (m, 2H), 1.06 (d, J = 6.2 Hz, 3H).

^{13}CNMR(100MHz,$CDCl_3$): δ 148.4, 146.9, 129.3, 123.4, 58.0, 56.7, 52.5, 34.6, 25.9, 23.7, 19.3.

HRMS (ESI): Exact mass calculated for $C_{13}H_{18}N_2O_2$ $[M+H]^+$: 235.1447, found: 235.1451.

IR (neat) (cm^{-1}): 2928, 2856, 2793, 1738, 1602, 1520, 1382, 1345, 1110, 1074, 853, 769, 736.

4-methyl-1-(4-nitrobenzyl)piperidine ((4i)



The title compound was prepared according to General Procedure **b** using salt **3i** (155 mg, 0.5 mmol) for 27 h. The crude material was purified by column chromatography (90:10 Hexane: EtOAc) to give amine **4i** (66 mg, 56%) as a yellow oil.

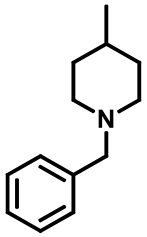
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 8.8 Hz, 2H), 3.48 (s, 2H), 2.74–2.69 (m, 2H), 1.91 (td, J = 11.5 Hz, 2.4 Hz, 2H), 1.55–1.51 (m, 2H), 1.35–1.24 (m, 1H), 1.22–1.12 (m, 2H), 0.85 (d, J = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 147.1, 147.0, 129.4, 123.4, 62.6, 54.1, 34.3, 30.6, 21.8.

HRMS (ESI): Exact mass calculated for $C_{13}H_{18}N_2O_2$ $[M+H]^+$: 235.1447, found: 235.1436.

IR (neat) (cm^{-1}): 2923, 2864, 2799, 1602, 1520, 1453, 1382, 1109, 1025, 979, 854, 694.

1-benzyl-4-methylpiperidine (4j)[8b]



The title compound was prepared according to General Procedure **b** using salt **3j** (132 mg, 0.5 mmol). The crude material was purified by column chromatography (95:5 Hexane: EtOAc) to give amine **4j** (44 mg, 46%) as a colourless oil.

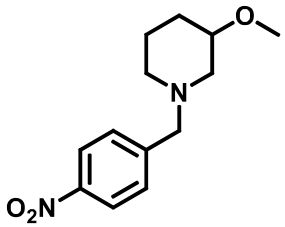
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13–7.02 (m, 5H), 3.29 (s, 2H), 2.65 (d, J = 11.6 Hz, 2H), 1.74 (td, J = 11.4 Hz, 1.8 Hz, 2H), 1.41–1.38 (m, 2H), 1.21–1.12 (m, 1H), 1.07 (qd, J = 3.6 Hz, 2H), 0.72 (d, J = 6.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7, 129.3, 128.1, 126.9, 63.6, 53.9, 34.4, 30.8, 21.9.

HRMS (ESI): Exact mass calculated for $C_{13}H_{19}N$ $[M+H]^+$: 190.1596, found: 190.1590.

IR (neat) (cm^{-1}): 2923, 2858, 1619, 1384, 1063, 756, 457.

3-methoxy-1-(4-nitrobenzyl)piperidine (4k)



The title compound was prepared according to General Procedure **B** using salt **3k** (162 mg, 0.5 mmol) for 27 h. The crude material was purified by column chromatography (90:10 Hexane: EtOAc) to give amine **4k** (90 mg, 72%) as a yellow oil.

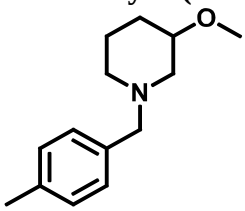
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 8.7 Hz, 2H), 7.43 (d, J = 8.8 Hz, 2H), 3.53 (s, 2H), 3.26 (s, 3H), 3.24–3.21 (m, 1H), 2.77 (dd, J = 10.6 Hz, 3.4 Hz, 1H), 2.54–2.49 (m, 1H), 2.07–1.95 (m, 2H), 1.90–1.86 (m, 1H), 1.72–1.65 (m, 1H), 1.51–1.40 (m, 1H), 1.25–1.21 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 147.1, 146.5, 129.4, 123.5, 76.1, 62.3, 57.9, 56.1, 53.6, 29.5, 23.0.

HRMS (ESI): Exact mass calculated for C13H18N2O3 $[M+H]^+$: 251.1396, found: 251.1386.

IR (neat) (cm^{-1}): 2933, 2859, 2913, 1737, 1602, 1454, 1381, 1158, 1015, 942, 858, 741, 697, 491.

3-methoxy-1-(4-methylbenzyl)piperidine (4l)



The title compound was prepared according to General Procedure **B** using salt **3l** (147 mg, 0.5 mmol) for 27 h. The crude material was purified by column chromatography (95:5 Hexane: EtOAc) to give amine **4l** (73 mg, 68%) as a yellow oil.

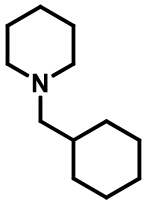
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 7.8 Hz, 2H), 3.44 (d, J = 13.0 Hz, 1H), 3.39 (d, J = 13.0 Hz, 1H), 3.25 (s, 3H), 3.24–3.19 (m, 1H), 2.84–2.82 (m, 1H), 2.57–2.52 (m, 1H), 2.25 (s, 3H), 1.98–1.84 (m, 3H), 1.68–1.60 (m, 1H), 1.48–1.35 (m, 1H), 1.21–1.10 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 136.5, 134.9, 129.2, 128.8, 76.3, 63.0, 57.7, 56.1, 53.3, 29.9, 23.2, 21.1.

HRMS (ESI): Exact mass calculated for $C_{14}H_{22}NO$ $[M+H]^+$: 220.1701, found: 220.1695.

IR (neat) (cm^{-1}): 2932, 2863, 2801, 1618, 1512, 1450, 1382, 1158, 942, 873, 807, 602,484.

1-(cyclohexylmethyl)piperidine (4m)



The title compound was prepared according to General Procedure **B** using salt **3m** (128 mg, 0.5 mmol) for 24 h. The crude material was purified by column chromatography (97:3 Hexane: EtOAc) to give amine **4m** (50 mg, 55%) as a colourless oil.

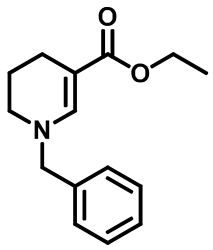
^{1}H NMR (400 MHz, $CDCl_3$); δ 2.25 (br, 3H), 2.01 (d, J = 7.0 Hz, 2H), 1.71–1.56 (m, 5H), 1.53–1.47 (m, 4H), 1.45–1.31 (m, 3H), 1.20–1.06 (m, 4H), 0.84–0.74 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 66.7, 55.2, 35.2, 32.2, 26.8, 26.2, 25.9, 24.6.

HRMS (ESI): Exact mass calculated for $C_{12}H_{23}N$ $[M+H]^+$: 182.1909, found: 182.1905.

IR (neat) (cm^{-1}): 2924, 2861, 1734, 1632, 1454, 1384, 1255, 1104, 949, 761.

ethyl 1-benzyl-1,4,5,6-tetrahydropyridine-3-carboxylate (4n)[8d]



The title compound was prepared according to General Procedure **B** using salt **3n** (161 mg, 0.5 mmol), Cs_2CO_3 (1.0 equiv) and KI (1.0 equiv) for 24 h. The crude material was purified by column chromatography (95:5 Hexane: EtOAc) to give amine **4n** (45 mg, 37%) as a yellow oil.

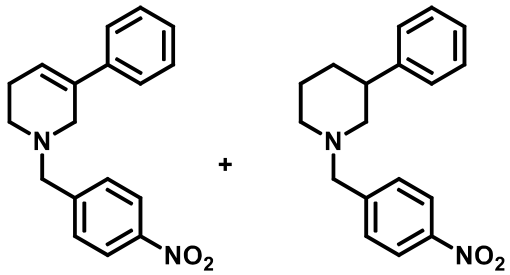
^{1}H NMR (500 MHz, $CDCl_3$); δ 7.47 (br, 1H), 7.29-7.26 (m, 1H), 7.23-7.19 (m, 1H), 7.14 (d, J = 7.2 Hz, 2H), 4.21 (s, 2H), 4.08 (q, J = 7.1 Hz, 2H), 2.92–2.90 (m, 2H), 2.22 (t, J = 6.3 Hz, 2H), 1.74–1.69 (m, 2H), 1.19 (t, J = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 168.8, 146.2, 137.1, 128.7, 127.7, 127.4, 94.9, 59.7, 58.9, 45.5, 21.3, 20.0, 14.7.

HRMS (ESI): Exact mass calculated for $C_{15}H_{19}NO_2$ $[M+H]^+$: 246.1494, found: 246.1484.

IR (neat) (cm^{-1}): 2929, 2856, 1674, 1614, 1442, 1382, 1295, 1261, 1151, 1091, 735, 699.

1-(4-nitrobenzyl)-5-phenyl-1,2,3,4-tetrahydropyridine (4p+4p')[8e,8b]



4p **4p'**

The title compound was prepared according to General Procedure **B** using salt **3p** (287 mg, 0.75 mmol), IrCp*Cl_2 (2.5 mol%), Ligand (8 mol%), KI (3.0 equiv) and DABCO (1.0 equiv),for 48 h. The crude material was purified by column chromatography (99.5:0.5; DCM:MeOH) to give amine **4p+4p'** (54 mg, 24%) colourless oil as an inseparable mixture of partial and fully hydrogenated product.

1H NMR of product 4p:

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (d, J = 8.7 Hz, 2H), 7.50 (d, J = 8.6 Hz, 2H), 7.73 - 7.22 (m, 4H), 7.16 – 7.15 (m, 1H), 6.08 – 6.06 (m, 1H), 3.70 (s, 2H), 3.29 – 3.28 (m, 2H), 2.56 (t, J = 5.74 Hz, 2H), 2.31 – 2.27 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 147.3, 146.5, 139.9, 135.2, 129.5, 128.4, 127.2, 124.9, 123.6, 122.5, 61.9, 54.7, 49.5, 26.3.

HRMS (ESI): Exact mass calculated for $C_{18}H_{18}N_2O_2$ $[M+H]^+$: 295.1447, found: 295.1445.

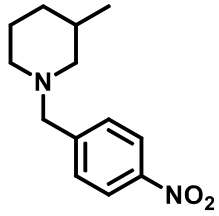
1H NMR of product 4p':

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.7 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 7.21 - 7.17 (m, 2H), 7.13 – 7.09 (m, 3H), 3.53 (d, *J* = 3.9 Hz, 2H), 2.86 – 2.73 (m, 3H), 2.03 – 1.95 (m, 2H), 1.88 – 1.85 (m, 1H), 1.73 – 1.60 (m, 2H), 1.39 (qd, *J* = 12.4 Hz, *J* = 4.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 147.1, 146.7, 144.4, 129.4, 128.4, 127.2, 126.4, 123.5, 62.6, 61.2, 54.0, 42.9, 31.5, 25.8.

HRMS (ESI): Exact mass calculated for $C_{18}H_{20}N_2O_2$ $[M+H]^+$: 297.1603, found: 297.1617.

3-methyl-1-(4-nitrobenzyl)piperidine (4q')



The title compound was prepared according to General Procedure **B** using salt **3q** (323mg, 1.0 mmol), $[IrCp^*Cl_2]_2$ (4.0 mol%), **L1** (8.0 mol%), KI (3.0 equiv) and DABCO (1.0 equiv) for 48 h. The crude material was purified by column chromatography (95:5; Hexane:EA)) to give amine **4q'** (27 mg, 11%) colourless oil.

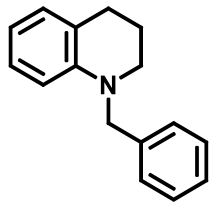
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J=8.7 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 2H), 3.35 (s, 2H), 2.57–2.51 (m, 2H), 1.73 (td, *J* = 11.1, 3.2 Hz, 1H), 1.54–1.32 (m, 5H), 0.74–0.68 (m, 1H), 0.65 (d, *J* = 6.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 147.1, 129.4, 123.4, 62.7, 62.0, 54.2, 32.8, 31.1, 25.5, 19.6.

HRMS (ESI): Exact mass calculated for $C_{13}H_{18}N_2O_2$ $[M+H]^+$: 235.1447, found: 235.1444.

IR (neat) (cm^{-1}): 2926, 2856, 2796, 1731, 1603, 1522, 1453, 1383, 1345, 1110, 1066, 857, 740, 695.

1-benzyl-1,2,3,4-tetrahydroquinoline (6a)[8h]



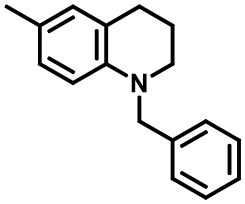
The title compound was prepared according to General Procedure **B** using salt **5a** (150 mg, 0.5 mmol) for 24 h. The crude material was purified by column chromatography (100:0 Hexane: EtOAc) to give amine **6a** (77 mg, 70%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24–7.12 (m, 5H), 6.89–6.86 (m, 2H), 6.48 (t, J = 7.3 Hz, 1H), 6.42 (d, J = 8.4 Hz, 1H), 4.38 (s, 2H), 3.28–3.25 (m, 2H), 2.73 (t, J = 6.3 Hz, 2H), 1.95–1.89 (m, 2H).

^{13}CNMR(100MHz,$CDCl_3$): δ 145.7, 139.0, 129.0, 128.6, 127.2, 126.8, 126.6, 122.3, 115.9, 111. 0, 55.2, 49.9, 28.3, 22.4.

HRMS (ESI): Exact mass calculated for $C_{16}H_{17}N$ $[M+H]^+$: 224.1439, found: 224.1433.

1-benzyl-6-methyl-1,2,3,4-tetrahydroquinoline (6b)[8h]



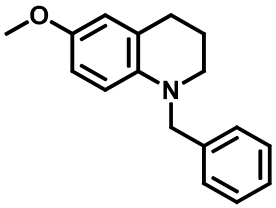
The title compound was prepared according to General Procedure **B** using salt **5b** (157 mg, 0.5 mmol). The crude material was purified by column chromatography (99:1 Hexane: EtOAc) to give amine **6b** (83 mg, 70%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24–7.09 (m, 5H), 6.71–6.68 (m, 2H), 6.33 (d, J = 8.2 Hz, 1H), 4.34 (s, 2H), 3.23–3.19 (m, 2H), 2.71–2.65 (m, 2H), 2.12 (s, 3H), 1.93–1.86 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 139.3, 129.8, 128.6, 127.6, 126.8, 126.7, 125.0, 122.4, 111.3, 55.5, 49.9, 28.2, 22.6, 20.3.

HRMS (ESI): Exact mass calculated for $C_{17}H_{19}N$ $[M+H]^+$: 238.1596, found: 238.1598.

1-benzyl-6-methoxy-1,2,3,4-tetrahydroquinoline (6c)[8h]



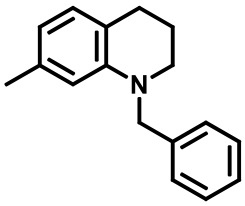
The title compound was prepared according to General Procedure **B** using salt **5c** (165 mg, 0.5 mmol). The crude material was purified by column chromatography (98:2; Hexane:EtOAc) to give amine **6c** (114 mg, 90%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$); δ 7.23–7.09 (m, 5H), 6.51–6.46 (m, 2H), 6.37–6.34 (m, 1H), 4.31 (s, 2H), 3.61 (s, 3H), 3.19–3.17 (m, 2H), 2.69 (t, J = 6.2 Hz, 2H), 1.95–1.86 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.9, 140.4, 139.4, 128.6, 126.8, 126.7, 123.8, 115.3, 112.5, 112.3, 56.0, 55.8, 49.9, 28.5, 22.6.

HRMS (ESI): Exact mass calculated for $C_{17}H_{19}NO$ $[M+H]^+$: 254.1545, found: 254.1543.

1-benzyl-7-methyl-1,2,3,4-tetrahydroquinoline (6d)



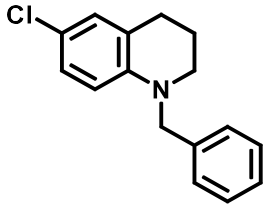
The title compound was prepared according to General Procedure **B** using salt **5d** (157 mg, 0.5 mmol). The crude material was purified by column chromatography (99:1; Hexane:EtOAc) to give amine **6d** (109 mg, 92%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.11 (m, 5H), 6.78 (d, J = 7.4 Hz, 1H), 6.33–6.27 (m, 2H), 4.38 (s, 2H), 3.24–3.21 (m, 2H), 2.68 (t, J = 5.9 Hz, 2H), 2.09 (s, 3H), 1.90–1.86 (m, 2H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.6, 139.2, 136.8, 128.9, 128.6, 126.8, 126.7, 119.4, 116.8, 111.6, 55.2, 49.8, 27.9, 22.3, 21.7.

HRMS (ESI): Exact mass calculated for $C_{17}H_{19}N$ $[M+H]^+$: 238.1596, found: 238.1581.

1-benzyl-6-chloro-1,2,3,4-tetrahydroquinoline (6e)



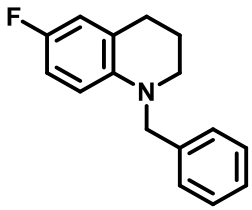
The title compound was prepared according to General Procedure **B** using salt **5e** (67 mg, 0.2 mmol). The crude material was purified by column chromatography (98:2 Hexane:EtOAc) to give amine **6e** (24 mg, 47%) as a colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25–7.14 (m, 5H), 6.86–6.79 (m, 2H), 6.31 (d, J = 8.7 Hz, 1H), 4.37 (s, 2H), 3.29–3.27 (m, 2H), 2.69 (t, J = 6.3 Hz, 2H), 1.94–1.89 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 144.1, 138.4, 128.7, 128.6, 126.9, 126.8, 126.5, 123.9, 120.3, 112.0, 55.2, 49.9, 28.1, 22.2.

HRMS (ESI): Exact mass calculated for $C_{16}H_{16}ClN$ $[M+H]^+$: 258.1050, found: 258.1051.

1-benzyl-6-fluoro-1,2,3,4-tetrahydroquinoline (6f)



The title compound was prepared according to General Procedure **B** using salt **5f** (84 mg, 0.26 mmol). The crude material was purified by column chromatography (96:4; Hexane:EtOAc) to give amine **6f** (29 mg, 47%) as a colourless oil.

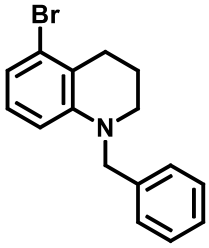
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27–7.15 (m, 5H), 6.65–6.56 (m, 2H), 6.31 (dd, J = 8.9, 4.7 Hz, 1H), 4.36 (s, 2H), 3.27–3.24 (m, 2H), 2.72 (t, J = 6.3 Hz, 2H), 1.96–1.90 (m, 2H).

^{13}C NMR (125MHz, $CDCl_3$): δ 154.8 (d, J = 232.5 Hz), 142.1, 138.9, 128.6, 126.8, 126.6, 123.7 (d, J = 6.7 Hz), 115.4 (d, J = 21.7 Hz), 113.1 (d, J = 21.5 Hz), 111.7 (d, J = 7.3 Hz), 55.8, 49.9, 28.3, 22.3.

^{19}F NMR (376 MHz, $CDCl_3$); δ -130.12.

HRMS (ESI): Exact mass calculated for $C_{16}H_{16}FN$ $[M+H]^+$: 242.1345, found: 242.1342.

1-benzyl-5-bromo-1,2,3,4-tetrahydroquinoline (6g)



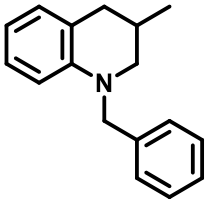
The title compound was prepared according to General Procedure **B** using salt **5g** (90 mg, 0.24 mmol). The crude material was purified by column chromatography (98:2; Hexane:EtOAc) to give amine **6g** (31 mg, 43%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–7.15 (m, 5H), 6.77–6.69 (m, 2H), 6.36 (d, J = 8.0 Hz, 1H), 4.40 (s, 2H), 3.29–3.27 (m, 2H), 2.79 (t, J = 6.5 Hz, 2H), 1.98–1.92 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 138.4, 128.7, 127.8, 126.9, 126.5, 125.6, 121.5, 119.9, 110.2, 55.6, 49.8, 28.7, 22.2.

HRMS (ESI): Exact mass calculated for $C_{16}H_{16}BrN$ $[M+H]^+$: 302.0544, found: 302.0545.

1-benzyl-3-methyl-1,2,3,4-tetrahydroquinoline (6h)[8h]



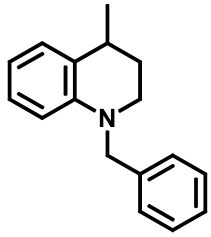
The title compound was prepared according to General Procedure **B** using salt **5h** (157 mg, 0.5 mmol). The crude material was purified by column chromatography (99:1; Hexane:EtOAc) to give amine **6h** (115 mg, 97%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.12 (m, 5H), 6.89–6.88 (m, 2H), 6.51–6.41 (m, 2H), 4.39 (s, 2H), 3.21–3.17 (m, 1H), 2.97–2.91 (m, 1H), 2.75–2.71 (m, 1H), 2.45–2.39 (m, 1H), 2.12–2.03 (m, 1H), 0.98–0.95 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.2, 139.0, 129.2, 128.6, 127.2, 126.8, 126.6, 121.9, 115.9, 110.8, 56.9, 55.2, 36.6, 27.4, 19.1.

HRMS (ESI): Exact mass calculated for $C_{17}H_{19}N$ $[M+H]^+$: 238.1596, found: 238.1595.

1-benzyl-4-methyl-1,2,3,4-tetrahydroquinoline (6i)[8i]



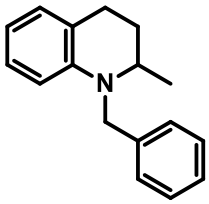
The title compound was prepared according to General Procedure **B** using salt **5i** (157 mg, 0.5 mmol). The crude material was purified by column chromatography (99:1; Hexane:EtOAc) to give amine **6i** (26 mg, 22%) as a blue oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.14 (m, 5H), 7.00–6.99 (m, 1H), 6.91–6.88 (m, 1H), 6.53 (td, J = 7.4, 0.9 Hz, 1H), 6.43 (d, J = 8.2 Hz, 1H), 4.41 (s, 2H), 3.36–3.32 (m, 1H), 3.26–3.22 (m, 1H), 2.91–2.85 (m, 1H), 2.01–1.95 (m, 1H), 1.69–1.64 (m, 1H), 1.24 (d, J = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 138.9, 128.6, 127.9, 127.3, 127.1, 126.8, 126.6, 115.9, 110.0, 55.2, 46.7, 31.1, 29.7, 22.3.

HRMS (ESI): Exact mass calculated for $C_{17}H_{19}N$ $[M+H]^+$: 238.1596, found: 238.1595.

1-ethyl-2-methyl-1,2,3,4-tetrahydroquinoline (6j)



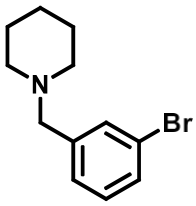
The title compound was prepared according to General Procedure **B** using salt **5j** (157 mg, 0.5 mmol). The crude material was purified by column chromatography (99:1; Hexane:EtOAc) to give amine **6j** (78 mg, 66%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24–7.12 (m, 5H), 6.92 (d, J = 7.3 Hz, 1H), 6.88–6.84 (m, 1H), 6.49 (td, , J = 7.3 Hz, 0.9 Hz, 1H), 6.32 (d, J = 8.2 Hz, 1H), 4.43 (dd, , J = 17.3 Hz, 2H), 3.54–3.47 (m, 1H), 2.88–2.80 (m, 1H), 2.67 (dt, J = 16.1, 4.6 Hz, 1H), 2.01–1.92 (m, 1H), 1.79–1.72 (m, 1H), 1.10 (d, J=6.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 144.8, 139.5, 128.8, 128.5, 127.1, 126.6, 126.3, 121.8, 115.5, 111.4, 53.4, 53.0, 28.2, 24.1, 19.0.

HRMS (ESI): Exact mass calculated for $C_{17}H_{19}N$ $[M+H]^+$: 238.1596, found: 238.1598.

1-(3-bromobenzyl)piperidine (4r)[8g]



The title compound was prepared according to General Procedure **B** using salt **3r** (165 mg, 0.5 mmol). The crude material was purified by column chromatography (95:5; Hexane:EtOAc) to give amine **4r (**71 mg, 56%) as a yellow oil.

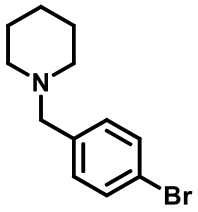
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (br, 1H), 7.28 (d, J = 7.9 Hz, 1H), 7.18-7.15 (m, 1H), 7.10-7.07 (m, 1H), 3.35 (s, 2H), 2.28 (br, 4H), 1.52–1.47 (m, 4H), 1.38–1.34 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 141.3, 131.9, 129.9, 129.7, 127.7, 122.3, 63.2, 54.5, 25.9 24.3.

HRMS (ESI): Exact mass calculated for $C_{12}H_{16}BrN$ $[M+H]^+$: 254.0544, found: 254.0540.

IR (neat) (cm^{-1}): 2929, 2858, 2794, 2317, 1600, 1384, 1064, 875, 771, 671.

1-(4-bromobenzyl)piperidine (4s)[8f]



The title compound was prepared according to General Procedure **B** using salt **3s** (329 mg, 1.0 mmol). The crude material was purified by column chromatography (95:5; Hexane:EtOAc) to give amine **4s** (173 mg, 69%) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 8.2 Hz, 2H), 3.32 (s, 2H), 2.26 (br, 4H), 1.50–1.46 (m, 4H), 1.36–1.33 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 137.8, 131.2, 130.8, 120.6, 63.1, 54.5, 25.9,24.3.

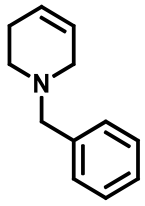
HRMS (ESI): Exact mass calculated for $C_{12}H_{16}BrN$ $[M+H]^+$: 254.0544, found: 254.0545.

IR (neat) (cm^{-1}): 2931, 2855, 2791, 1621, 1484, 1443, 1384, 1304, 1153, 1109, 1013, 906, 806, 493.

5. Gram scale synthesis of 4a: General procedure **B** was followed with **3a** (1.0 g, 3.99 mmol), $[IrCp^*Cl_2]_2$ (63mg, 2.0 mol %), **L1** (24 mg, 4.0 mol %), KI (1.99 g, 3.0 equiv.) and DABCO (0.448 g, 1.0 equiv.) and ethanol (8.0 mL) at 90 ^{o}C for 24 h. The residue was purified by column chromatography to give **4a** as a yellow oil (344 mg, 49% yield).

6. Control experiment

(a) Synthesis of 1-benzyl-1,2,3,6-tetrahydropyridine (4a'):[9]

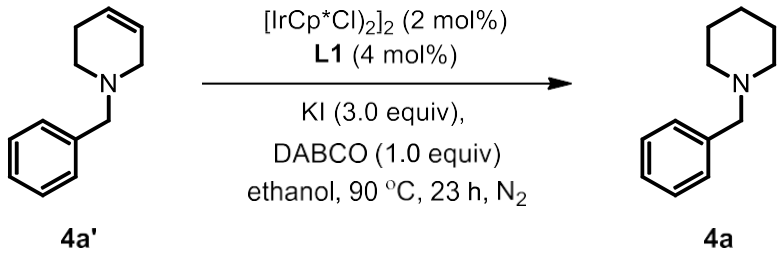


The benzylpyridinium bromide (**3a**) (300mg, 1.19 mmol) was dissolved in MeOH (5 ml), and cooled to 0 ^{o}C, then $NaBH_4$ (1.5 equiv.) was added portion wise. The reaction mixture was stirred at 0 ^{o}C for 4 h. The reaction was quenched with water and extracted with ethyl acetate, resulting solution was washed with brine, dried over Na_2SO_4, concentrated on rotary evaporator to give 1-benzyl-1,2,3,6-tetrahydropyridine**(4a')** in 80% yield (165 mg, 0.952 mmol) as a yellow oil and used for next reaction without column purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28–7.14 (m, 5H), 5.69–5.55 (m, 2H), 3.49 (s, 2H), 2.90–2.87 (m, 2H), 2.47 (t, J = 5.7 Hz, 2H), 2.11–2.05 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 129.2, 128.2, 127.1, 125.4, 125.6, 62.9, 52.8, 49.7, 26.2.

(b) Transfer hydrogenation of 1,2-dihydroquinoline with EtOH

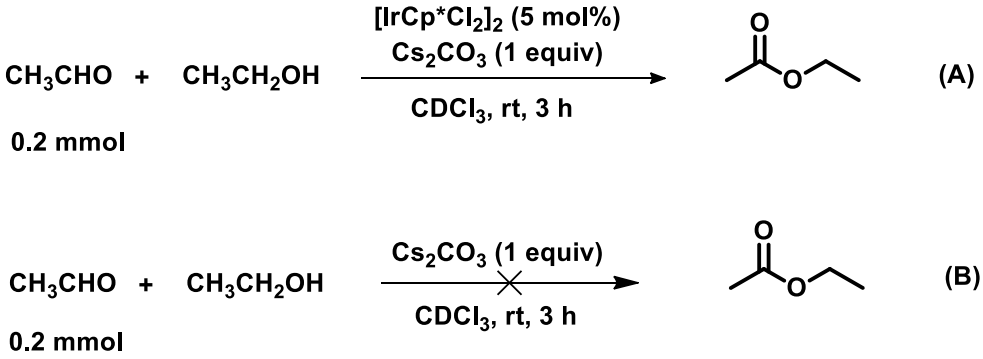


4a' **4a**

The general procedure **B** was followed using **4a'** (10mg, 0.058 mmol), ethanol (0.5 mL) for 23 h. The yield of **4a** is 80%, determined by NMR using 1,3,5-trimethoxybenzene as an internal standard.

(c) Study of the Conversion of CH_3CHO to EtOAc[10]

To study the formation of EtOAc as a byproduct, we conducted NMR experiments. Treatment of CH_3CHO (0.2 mmol) with ethanol (1.7 mmol), $[IrCp^*Cl_2]_2$ (5 mol%), and base (1 equiv) in $CDCl_3$ (0.5 mL) in 3h at rt led to the conversion of CH_3CHO to EtOAc (eq **A**) (Identified in 1H NMR, Figure 1). Without the Iridium catalyst, EtOAc was not detected in NMR spectra (eq **B**) (Figure 2). Therefore, the acetaldehyde generated may be converted to ethyl acetate under Ir-catalyzed conditions, avoiding catalyst poisoning in the optimized reaction conditions.[10]



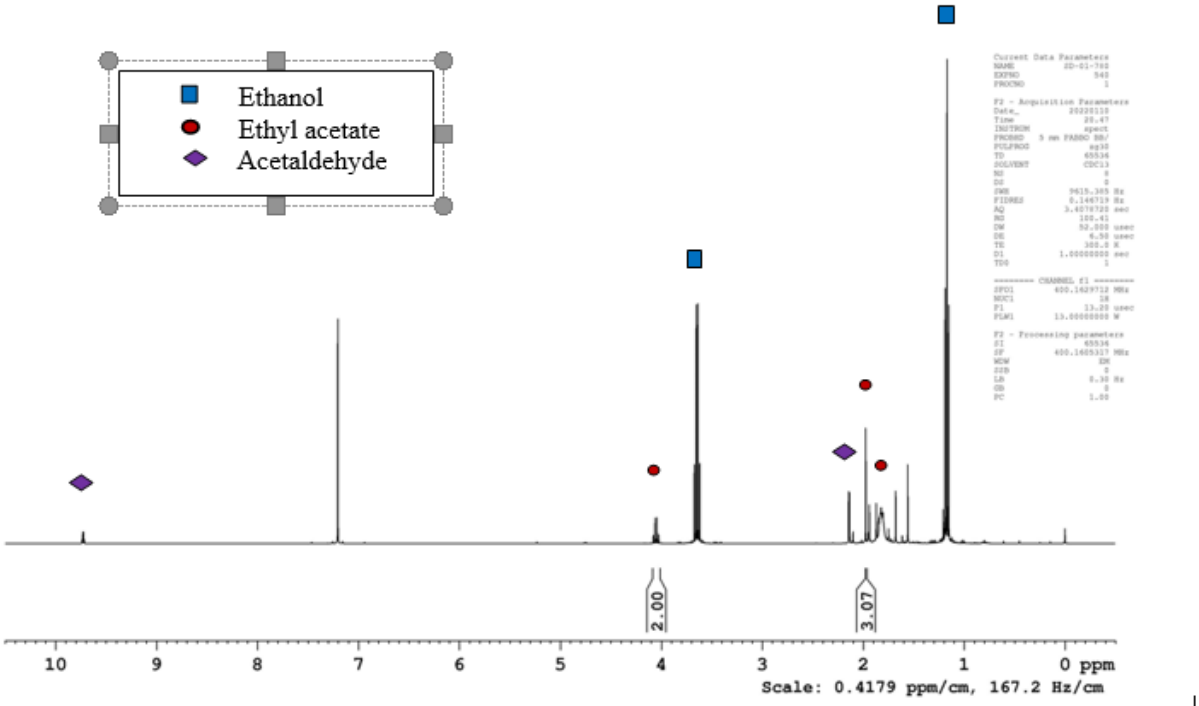


Figure 1:1H NMR (400 MHz, $CDCl_3$) with Iridium metal.

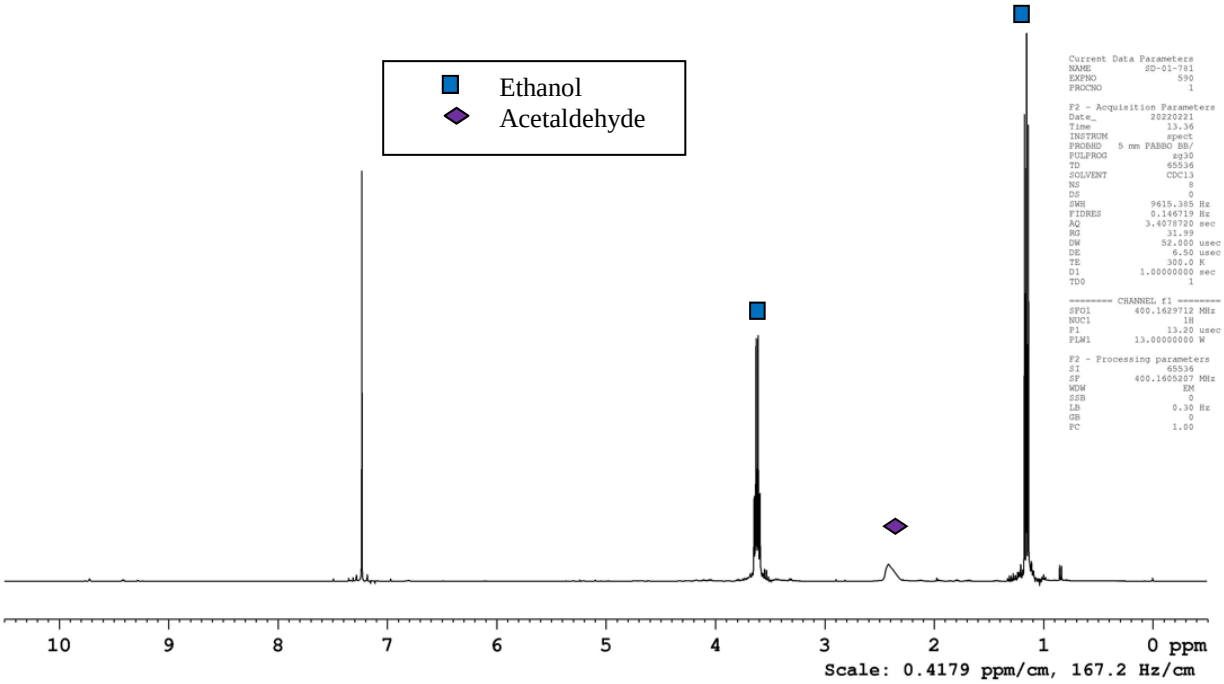


Figure 2: 1H NMR (400 MHz, $CDCl_3$) without Iridium metal.

7. Formation of Iridium Hydride:[11] To study the formation of Iridium hydride, $[IrCp^*Cl_2]_2$ (1.0 equiv), **L1** (2 equiv) and base (Cs_2CO_3 or DABCO, 1 equiv) was dissolved in ethanol and stirred at 90 ^oC for 12 h. NMR analysis of the crude reaction mixture provided the formation of Ir-H.[11]

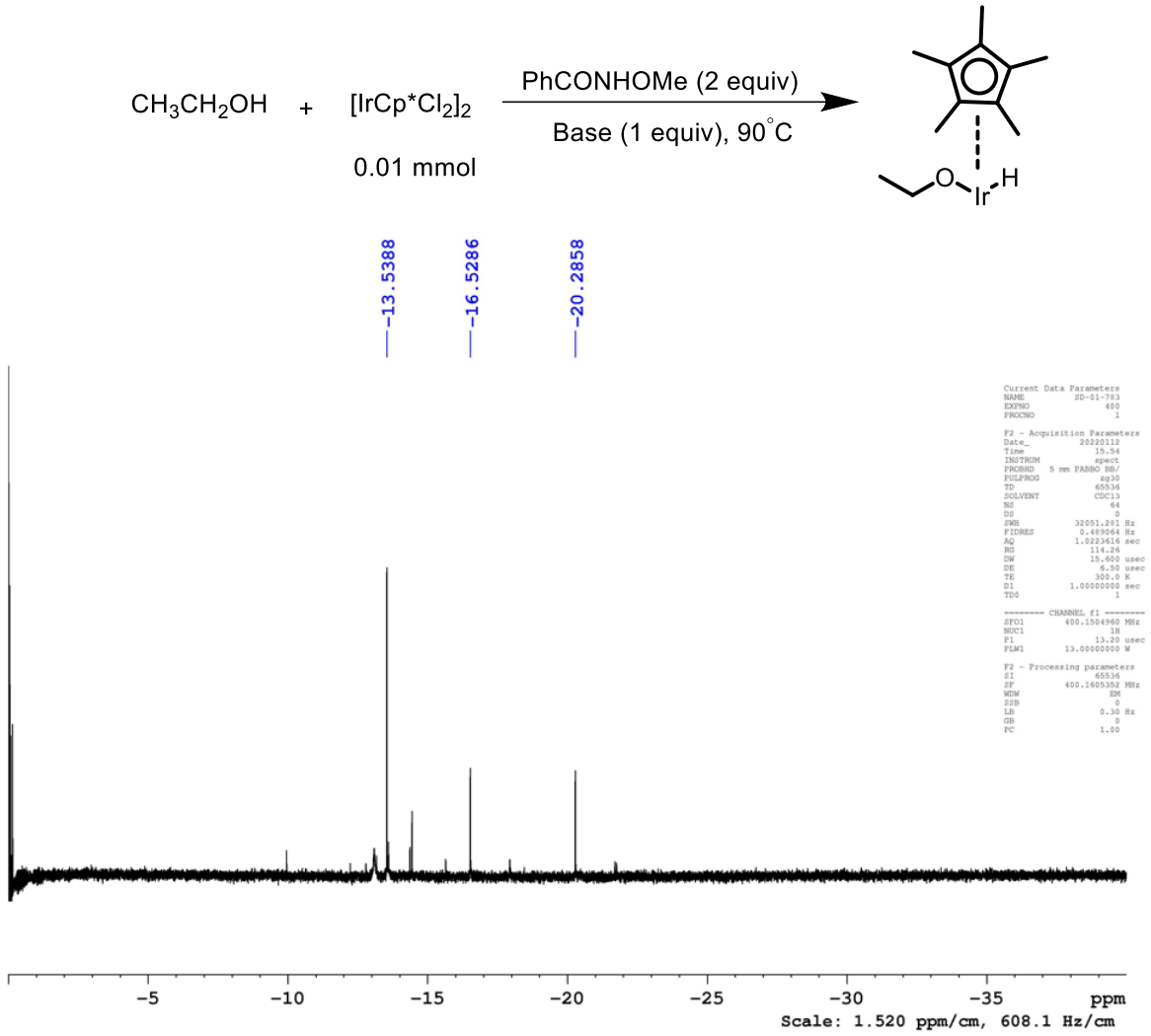


Figure 3:1H NMR (400 MHz, $CDCl_3$, Cs_2CO_3 base) spectrum from (-35 ppm to 0 ppm range).

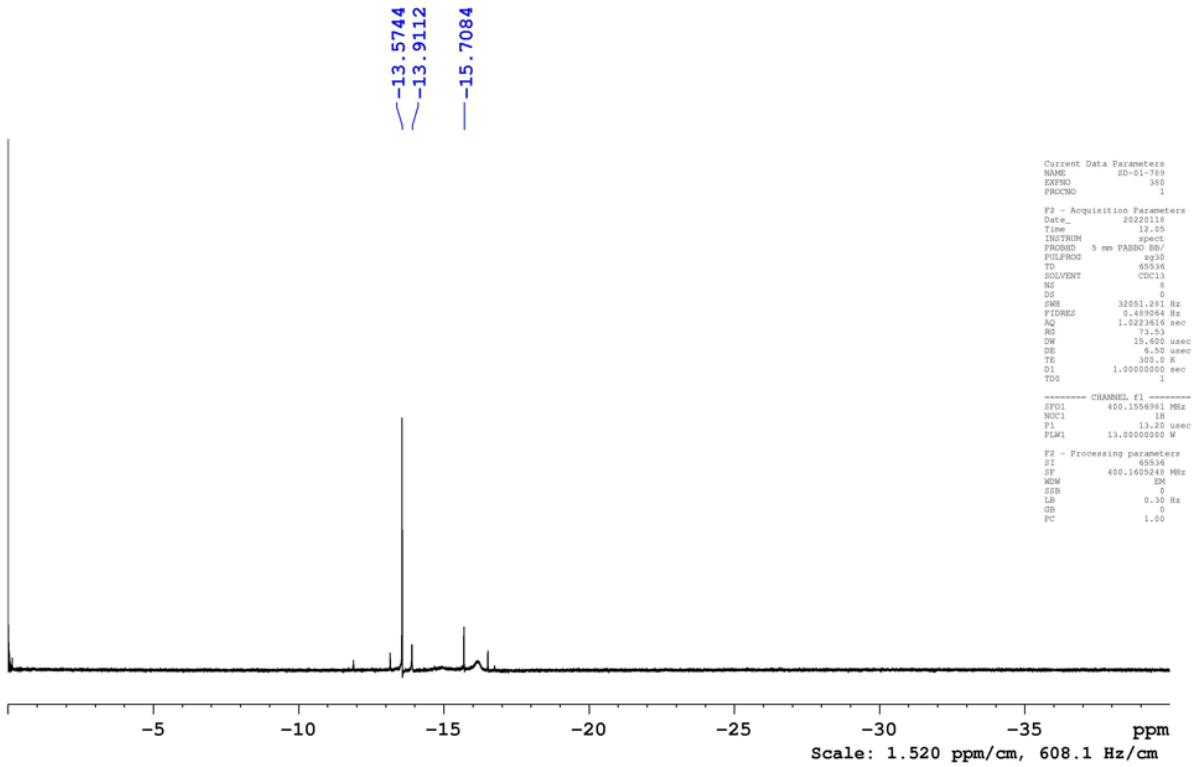


Figure 4: 1H NMR (400 MHz, $CDCl_3$, DABCO base) spectrum from (-35 ppm to 0 ppm range).

8. References

(1) Anand, N.; Koley, S.; Ramulu, B. J.; Singh, M. S. Metal-free aerobic one-pot synthesis of substituted/annulated quinolines from alcohols via indirect Friedländer annulation. *Org. Biomol. Chem*. **2015**, *13*, 9570.

(2) Yan, R.; Liu, X.; Pan, C.; Zhou, X.; Li, X.; Kang, X.; Huang, G. Aerobic Synthesis of Substituted Quinoline from Aldehyde and Aniline: Copper-Catalyzed Intermolecular C-H Active and C-C Formative Cyclization. *Org. Lett*. **2013,** *15*, 4876.

(3) Preindl, J.; Chakrabarty, S.; Waser, J. Dearomatization of electron poor six-membered N-heterocycles through [3 + 2] annulation with aminocyclopropanes. *Chem. Sci*. **2017**, *8*, 7112.

(4) Sagi, K.; Fujita, K.; Sugiki, M.; Takahashi, M.; Takehana, S.; Tashiro, K.; Kayahara, T.; Yamanashi, M.; Fukuda, Y.; Oono, S.; Okajima, A.; Iwata, S.; Shoji, M.; Sakurai, K. Optimization of a coagulation factor VIIa inhibitor found in factor Xa inhibitor library. *Bioorg. Med. Chem.* **2005**, *13*, 1487.

(5) (a) Li, P.; Zhao, J.; Xia, C.; Li, F. The development of carbene-stabilized N–O radical coupling strategy in metal-free regioselective C–H azidation of quinolone N-oxides. *Org. Chem. Front.* **2015**, *2*, 1313. (b) Bering, L.; Antonchick, A. P. Regioselective Metal-Free Cross Coupling of Quinoline N-Oxides with

Boronic Acids. *Org. Lett*. **2015**, *17*, 3134. (c) Biswas, A.; Karmakar, U.; Nandi, S.; Samanta, R. Copper-Catalyzed Direct, Regioselective Arylamination of N-Oxides: Studies To Access Conjugated π-Systems. *J. Org. Chem*. **2017**, *82*, 8933. (d) Zhang, Y.; Zhang, S.; Xu, G.; Li, M.; Tang, C.; Fan, W. Cu-Catalyzed carbamoylation *versus* amination of quinoline N-oxide with formamides. *Org. Biomol. Chem.*, **2019**, *17*, 309.

(6) (a) Renom-Carrasco, M.; Gajewski, P.; Pignataro, L.; de Vries, J. G.; Piarulli, U.; Gennari, C.; Lefort, L. Asymmetric Hydrogenation of 3-Substituted Pyridinium Salts. *Chem. Eur. J.* **2016**, *22*, 9528. (b) Qu, B.; Mangunuru, H. P. R.; Wei, X.; Fandrick, K. R.; Desrosiers, J.-N.; Sieber, J. D.; Kurouski, D.; Haddad, N.; Samankumara, L. P.; Lee, H.; Savoie, J.; Ma, S.; Grinberg, N.; Sarvestani, M.; Yee, N. K.; Song, J. J.; Senanayake, C. H. Synthesis of Enantioenriched 2-Alkyl Piperidine Derivatives through Asymmetric Reduction of Pyridinium Salts. *Org. Lett.* **2016**, *18*, 4920. (c) Peng, H.; Li, T.; Tian, D.; Yang, H.; Xu, G.; Tang, W. Metal-free reduction of unsaturated carbonyls, quinones, and pyridinium salts with tetrahydroxydiboron/water. *Org. Biomol. Chem.* **2021**, *19*, 4327. (d) Wang, R.; Gu, X.; Li, Q.; Gao, J.; Shi, B.; Xu, G.; Zhu, T.; Tian, H.; Zhao, C. Aggregation Enhanced Responsiveness of Rationally Designed Probes to Hydrogen Sulfide for Targeted Cancer Imaging. *J. Am. Chem. Soc.* **2020**, *142*, 15084. (e) Shirota, H.; Matsuzaki, H.; Ramati, S.; Wishart, J. F. Effects of Aromaticity in Cations and Their Functional Groups on the Low-Frequency Spectra and Physical Properties of Ionic Liquids. *J. Phys. Chem. B* **2015**, *119*, 9173. (f) Yau, H. M.; Croft, A. K.; Harper, J. B. 'One-pot' Hammett plots: a general method for the rapid acquisition of relative rate data. *Chem. Commun*. **2012**, *48*, 8937. (g) Yang, J.; Zhao, H.; Tan, Z.; Cao, L.; Jiang, H.; Ci, C.; Dixneuf, P. H.; Zhang, M. *syn*-Selective Construction of Fused Heterocycles by Catalytic Reductive Tandem Functionalization of N-Heteroarenes. *ACS Catal.* **2021**, *11*, 9271. (h) Tan, Z.; Ci, C.; Yang, J.; Wu, Y.; Cao, L.; Jiang, H.; Zhang, M. Catalytic Conversion of N-Heteroaromatics to Functionalized Arylamines by Merging Hydrogen Transfer and Selective Coupling. *ACS Catal*. **2020**, *10*, 5243.

(7) (a) Yang, C.-H.; Chen, X.; Li, H.; Wei, W.; Yang, Z.; Chang, J. Iodine catalyzed reduction of quinolines under mild reaction conditions. *Chem. Commun*. **2018**, *54*, 8622. (b) Cui, X.; Huang, W.; Wu, L. Zirconium-hydride-catalyzed transfer hydrogenation of quinolines and indoles with ammonia borane. *Org. Chem. Front*. **2021**, *8*, 5002. (c) Butt, M.; Zhao, Y.; Feng, X.; Lu, Y.; Jin, T.; Yamamoto, Y.; Bao, M. Unsupported Nanoporous Gold-Catalyzed Chemoselective Reduction of Quinolines Using Formic Acid as a Hydrogen Source. *ChemistrySelect* **2019**, *4*, 6572. (d) Wang, Y.; Dong, B.; Wang, Z.; Cong, X.; Bi, X. Silver-Catalyzed Reduction of Quinolines in Water. *Org. Lett*. **2019**, *21*, 3631. (e) Zhang, J.; An, Z.; Zhu, Y.; Shu, X.; Song, H.; Jiang, Y.; Wang, W.; Xiang, X.; Xu, L.; He, J. $Ni^0/Ni^{\delta+}$ Synergistic Catalysis on a Nanosized Ni Surface for Simultaneous Formation of C−C and C−N Bonds. *ACS Catal*. **2019**, *9*, 11438. (f) Clohessy, T, A.; Roberts, A.; Manas, E. S.; Patel, V. K.; Anderson, N. A.; Watson, A. J. B. Chemoselective One-Pot Synthesis of Functionalized Aminoazaheterocycles Enabled by COware. *Org. Lett*. **2017**, *19*, 6368. (g) Wu, J.; Barnard, J. H.; Zhang, Y.; Talwar, D.; Robertson, C. M.; Xiao, J. Robust cyclometallated Ir(III) catalysts for the homogeneous hydrogenation of N-heterocycles under mild conditions. *Chem. Commun.* **2013**, *49*, 7052.

(8) (a) Wu, J.; Tang, W.; Pettman, A.; Xiao, J. Efficient and Chemoselective Reduction of Pyridines to Tetrahydropyridines and Piperidines *via* Rhodium-Catalyzed Transfer Hydrogenation. *Adv. Synth. Catal*. **2013**, *355*, 35. (b) Chamberlain, A. E. R.; Paterson, K. J.; Armstrong, R. J.; Twin, H. C.; Donohoe, T. J. A hydrogen borrowing annulation strategy for the stereocontrolled synthesis of saturated aza-heterocycles. *Chem. Commun.* **2020**, *56*, 3563. (c) Qu, B.; Mangunuru, H. P. R.; Wei, X.; Fandrick, K. R.; Desrosiers, J.-N.; Sieber, J. D.; Kurouski, D.; Haddad, N.; Samankumara, L. P.; Lee, H.; Savoie, J.; Ma, S.; Grinberg, N.; Sarvestani, M.; Yee, N. K.; Song, J. J.; Senanayake, C. H. Synthesis of Enantioenriched 2-Alkyl Piperidine Derivatives through Asymmetric Reduction of Pyridinium Salts. *Org. Lett.* **2016**, *18*, 4920. (d) He, Y.; Wang, F.; Zhang, X.; Fan, X. $C(sp^3)$–H dehydrogenation and $C(sp^2)$–H alkoxy carbonylation of inactivated cyclic amines towards functionalized N-heterocycles. *Chem. Commun.* **2017**, *53*, 4002. (e) Renom-Carrasco, M.; Gajewski, P.; Pignataro, L.; de Vries, J. G.; Piarulli, U.; Gennari, C.; Lefort, L. Asymmetric Hydrogenation of 3-Substituted Pyridinium Salts. *Chem. Eur. J.* **2016**, *22*, 9528. (f) Taylor, N. J.; Emer,

E.; Preshlock, S.; Schedler, M.; Tredwell, M.; Verhoog, S.; Mercier, J.; Genicot, C.; Gouverneur, V. Derisking the Cu-Mediated ^{18}F-Fluorination of Heterocyclic Positron Emission Tomography Radioligands. *J. Am. Chem. Soc.* **2017**, *139*, 8267. (g) Tan, P. W.; Haughey, M.; Dixon, D. J. Palladium(II)-catalysed ortho-arylation of N-benzylpiperidines. *Chem. Commun.* **2015**, *51*, 4406. (h) Kaga, A.; Hayashi, H.; Hakamata, H.; Oi, M.; Uchiyama, M.; Takita, R.; Chiba, S. Nucleophilic Amination of Methoxy Arenes Promoted by a Sodium Hydride/Iodide Composite. *Angew. Chem. Int. Ed.* **2017**, *56*, 11807. (i) Vieira, T. O.; Alper, H. Rhodium(I)-catalyzed hydroaminomethylation of 2-isopropenylanilines as a novel route to 1,2,3,4-tetrahydroquinolines. *Chem. Commun.* **2007**, 2710.

(9) Karabiyikoglu, S.; Brethomé, A. V.; Palacin, T.; Paton, R. S.; Fletcher, S. P. Enantiomerically enriched tetrahydropyridine allyl chlorides. *Chem. Sci.* **2020**, *11*, 4125.

(10) (a) Y. Wang, Z. Huang, X. Leng, H. Zhu, G. Liu and Z. Huang, *J. Am. Chem. Soc.*, **2018**, *140*, 4417; (b) Wang, Y.; Huang, Z.; Huang. Z. Catalyst as colour indicator for endpoint detection to enable selective alkyne trans-hydrogenation with ethanol. *Nature catalysis* **2019**, *2*, 529.

(11) Itoh, S.; Yoshimura, K.; Tsukamoto, Y.; Obora, Y. Iridium Complex-Catalyzed C2-Extension of Primary Alcohols with Ethanol via a Hydrogen Autotransfer Reaction. *J. Org. Chem*. **2020**, *85*, 11952.

9. NMR Spectra

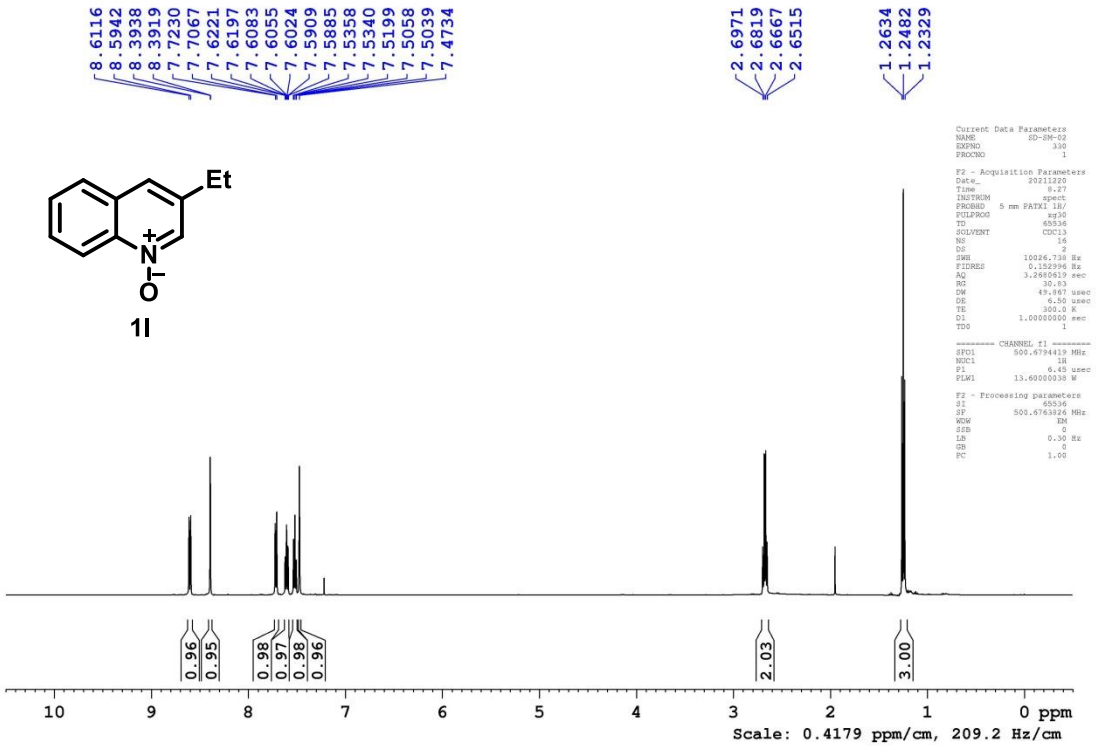


Figure S-1: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **1l**

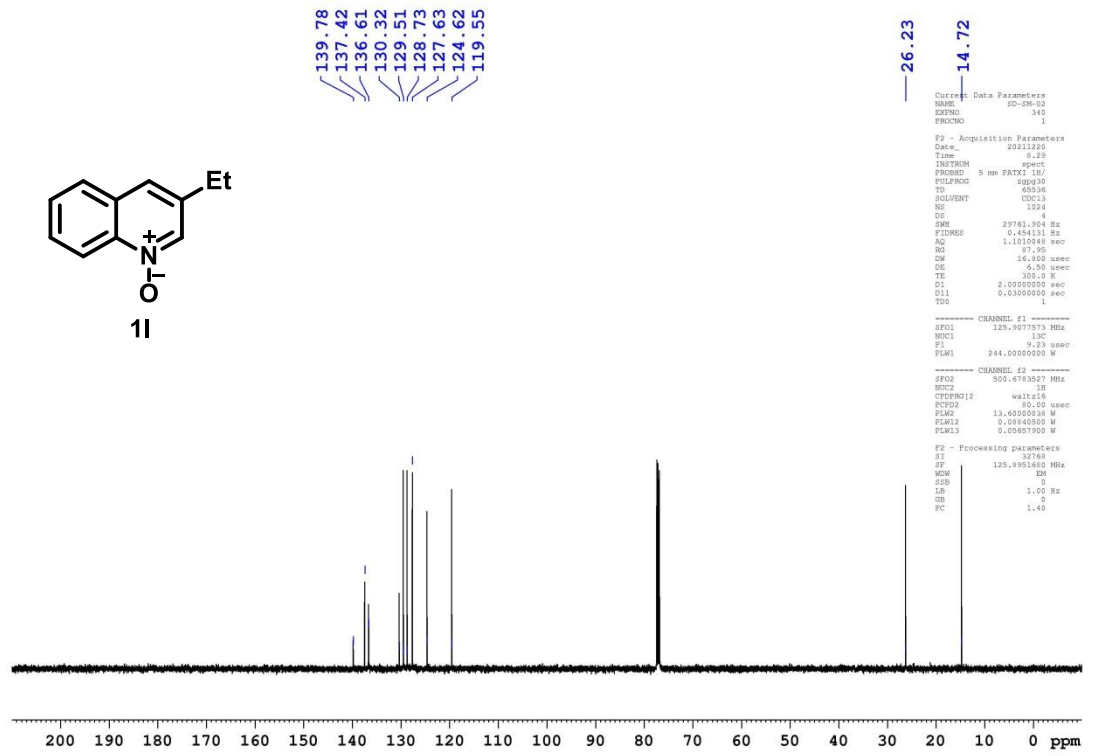


Figure S-2: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **1l**

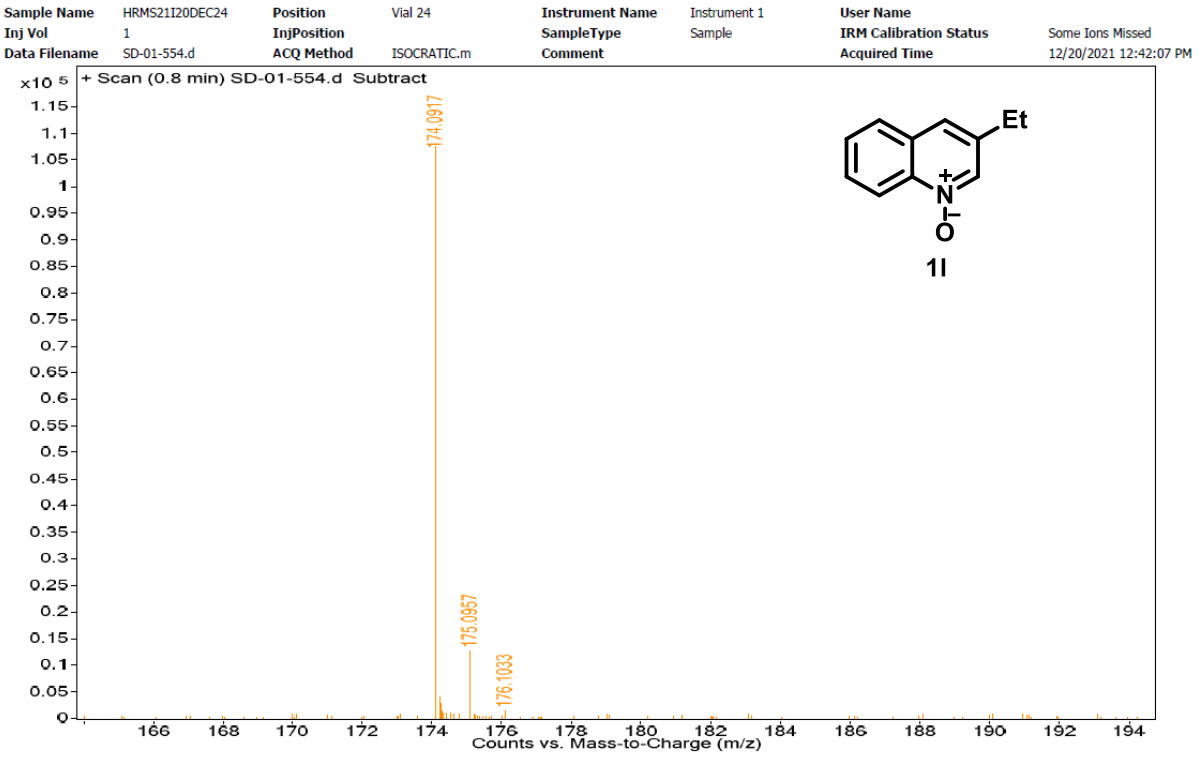


Figure S-3 HRMS spectrum of compound **1l**

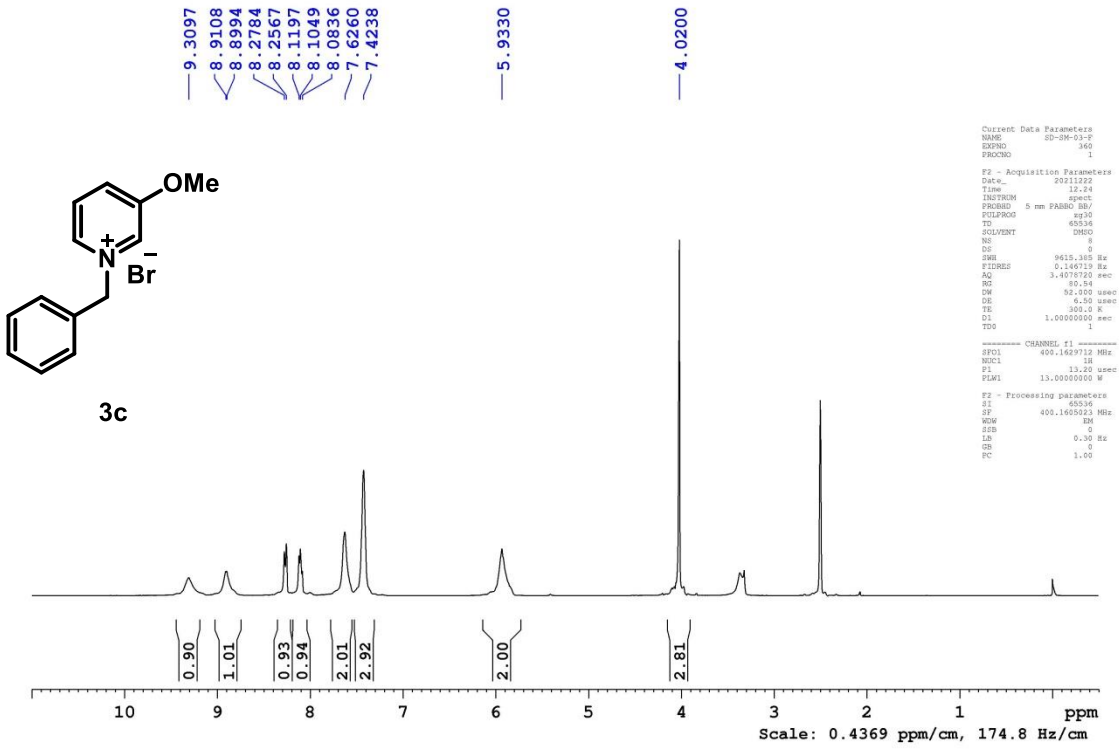


Figure S-4: ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound **3c**

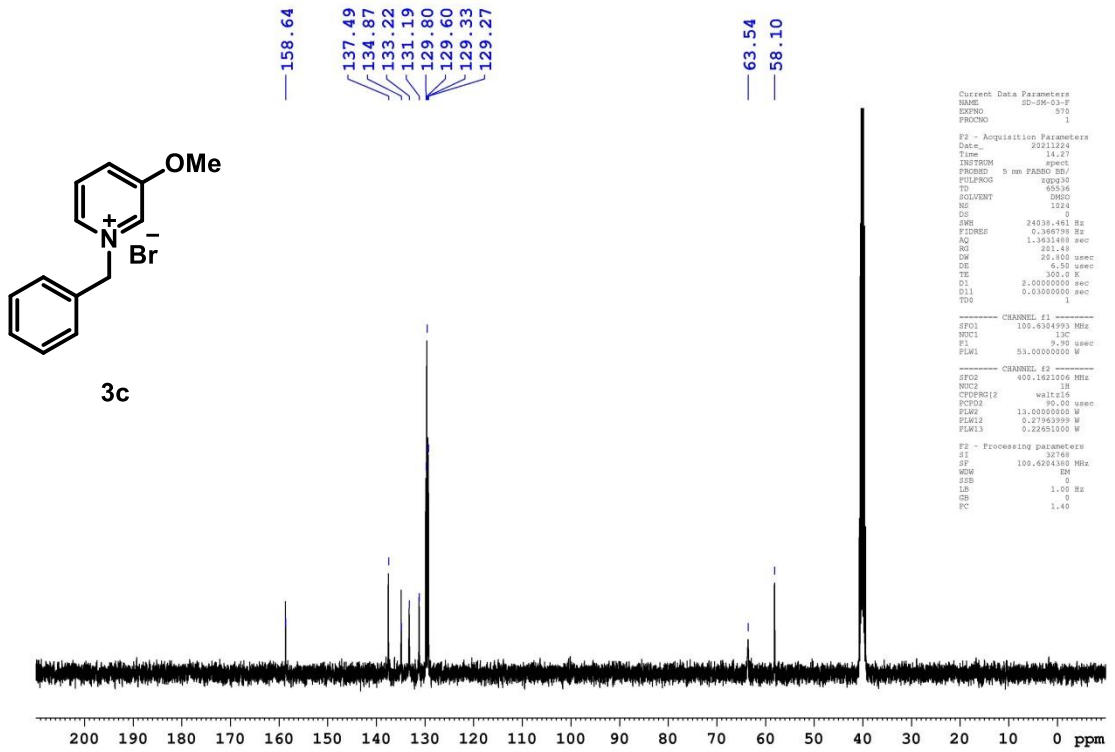


Figure S-5: ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound **3c**

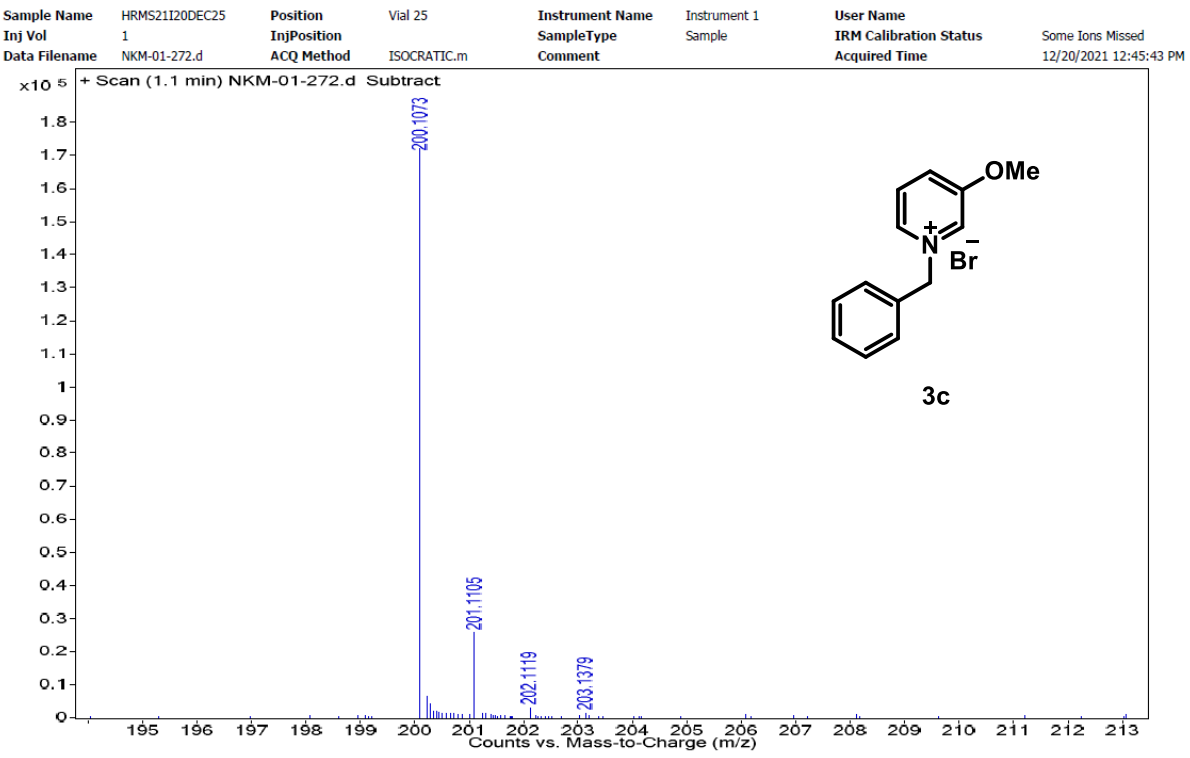


Figure S-6 HRMS spectrum of compound **3c**

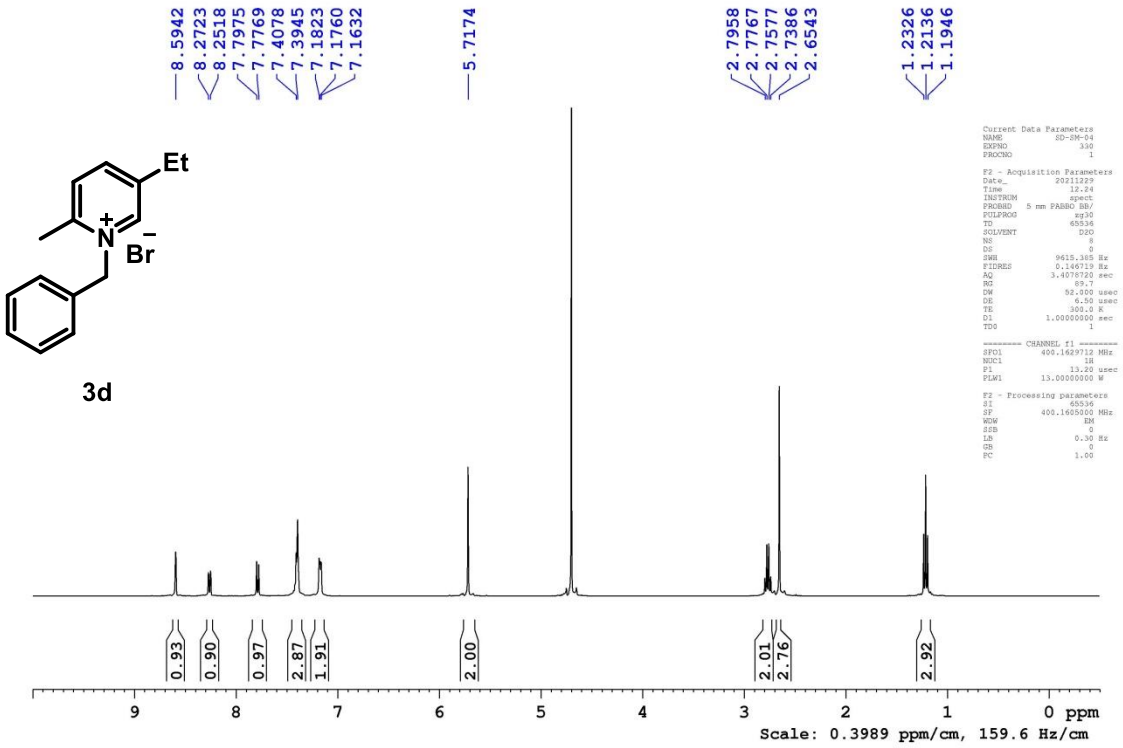


Figure S-7: ^{1}H NMR (400 MHz, D_2O) spectrum of compound **3d**

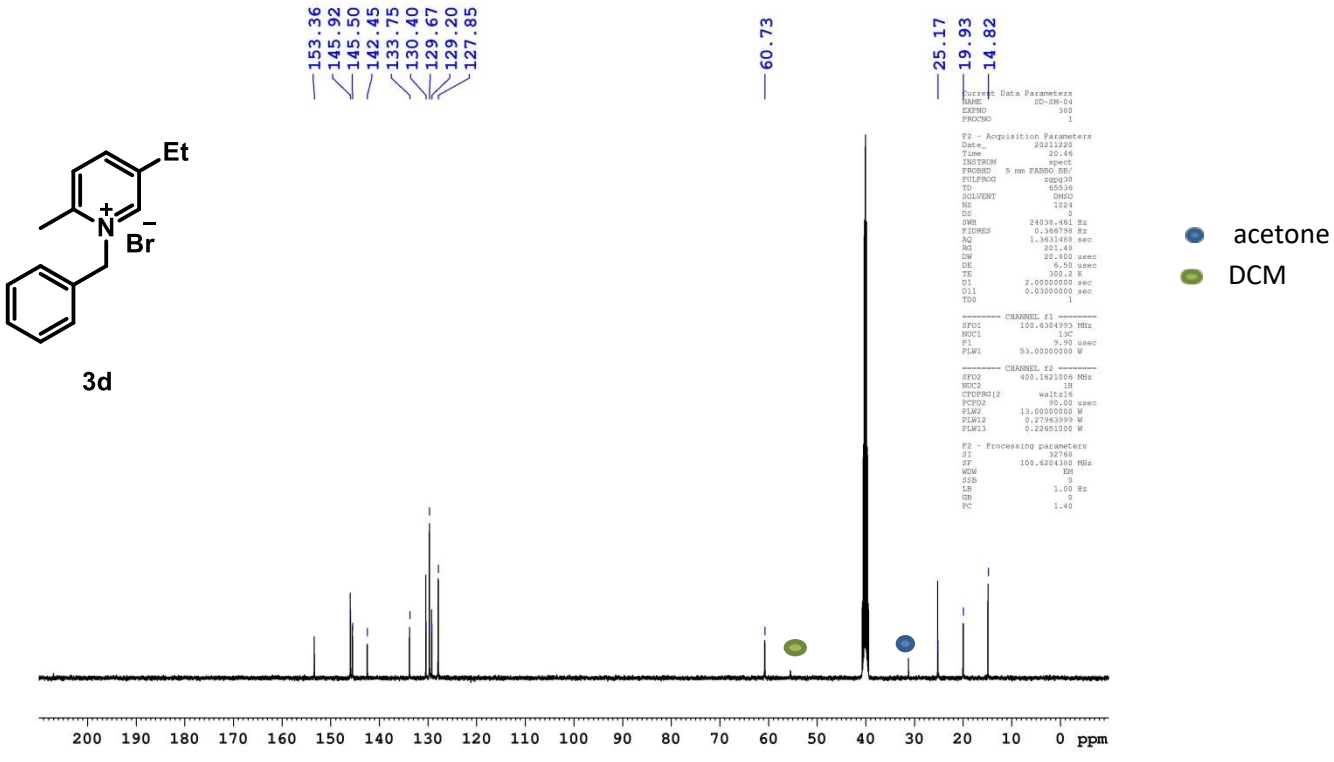


Figure S-8: ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound **3d**

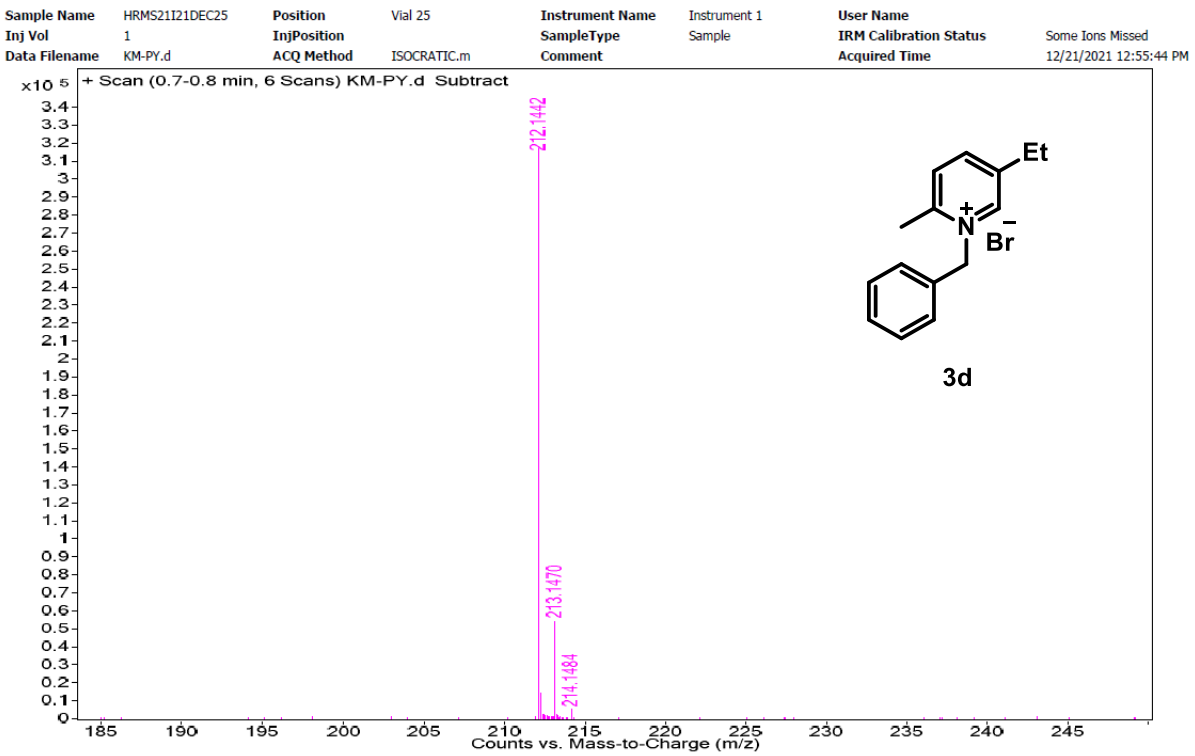


Figure S-9 HRMS spectrum of compound **3d**

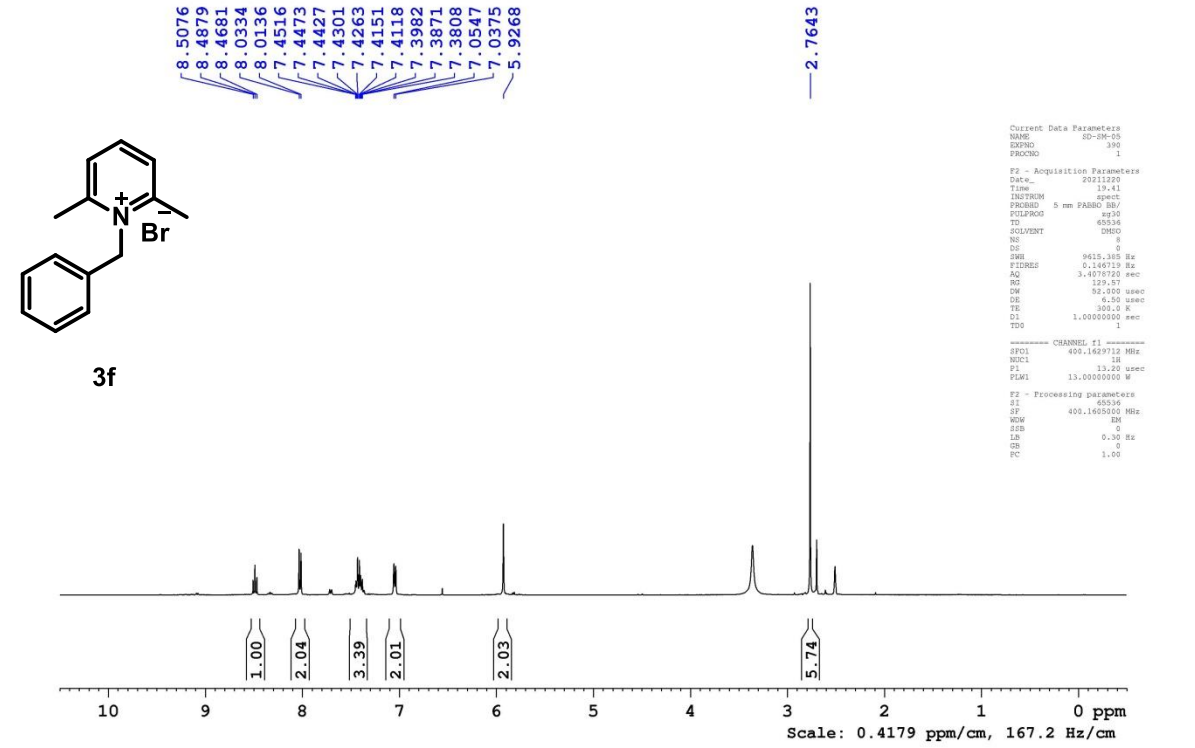


Figure S-10: ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound **3f**

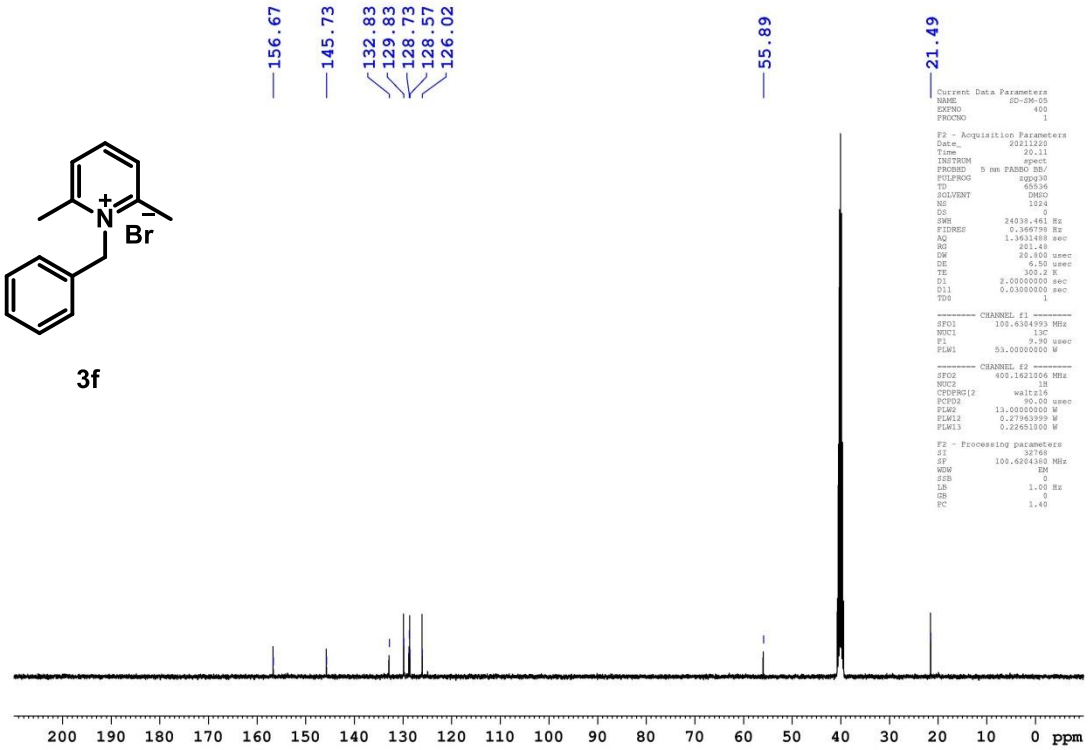


Figure S-11: ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound **3f**

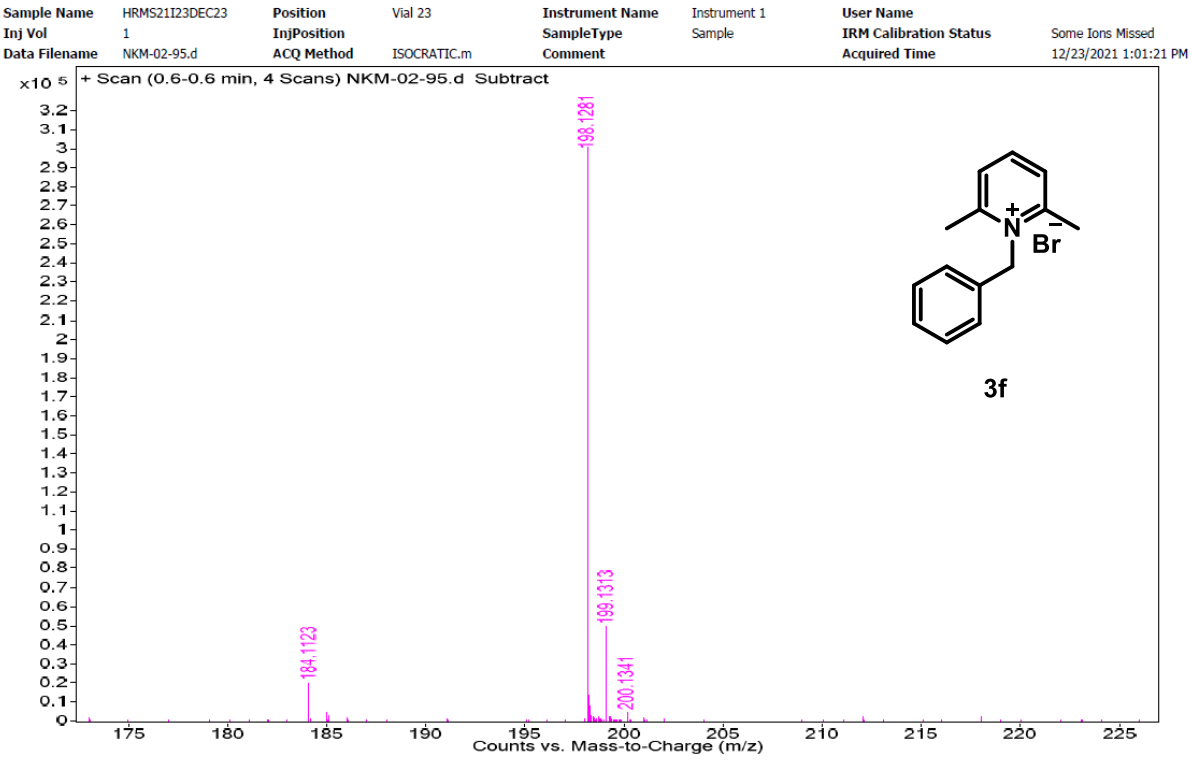


Figure S-12 HRMS spectrum of compound **3f**

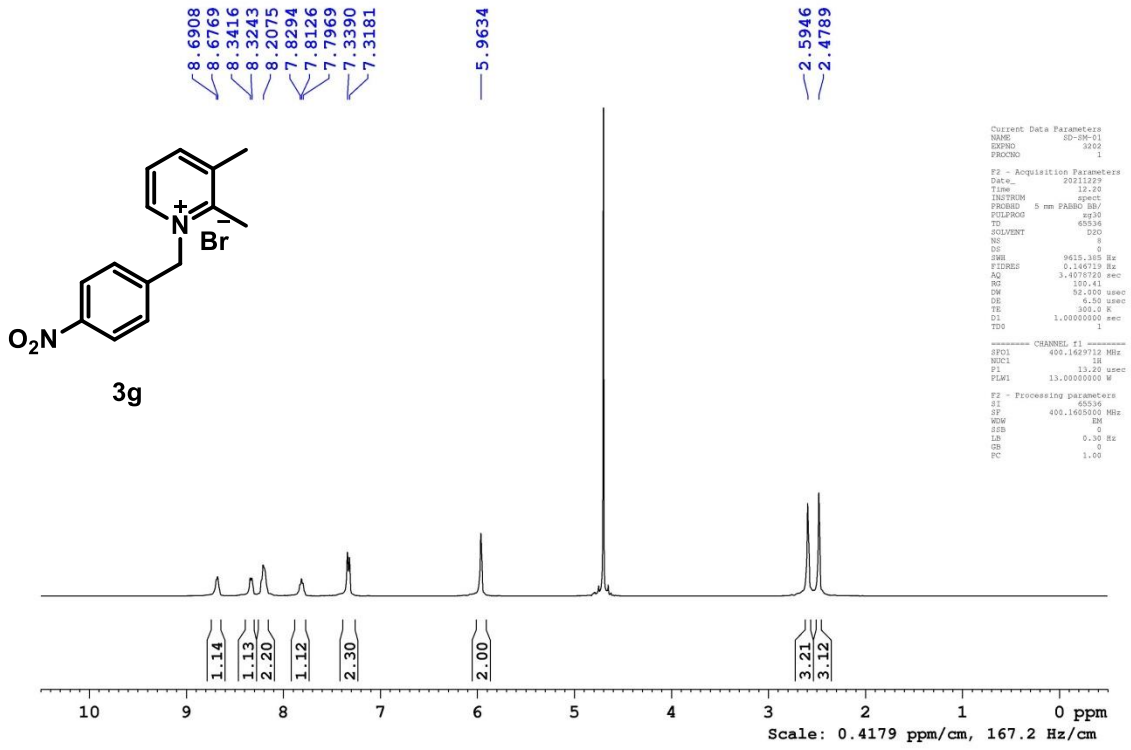


Figure S-13: ^{1}H NMR (400 MHz, D_2O) spectrum of compound **3g**

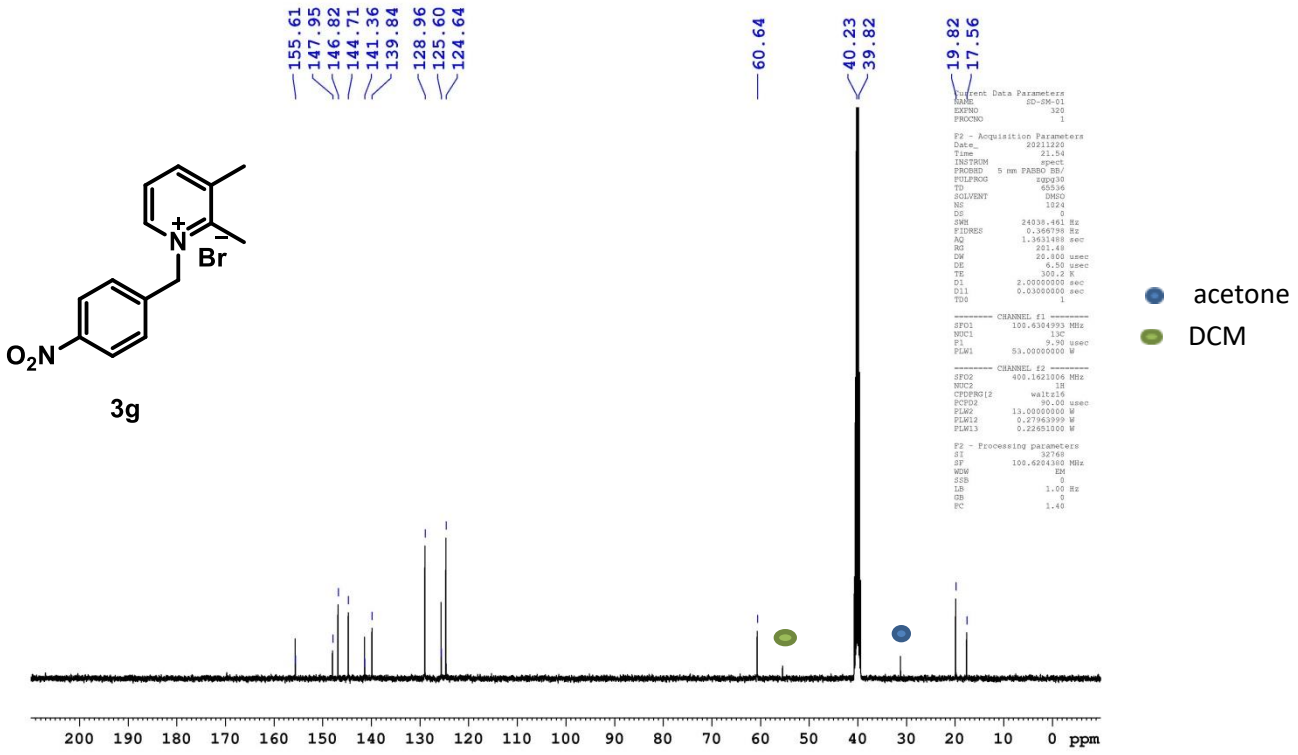


Figure S-14: ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound **3g**

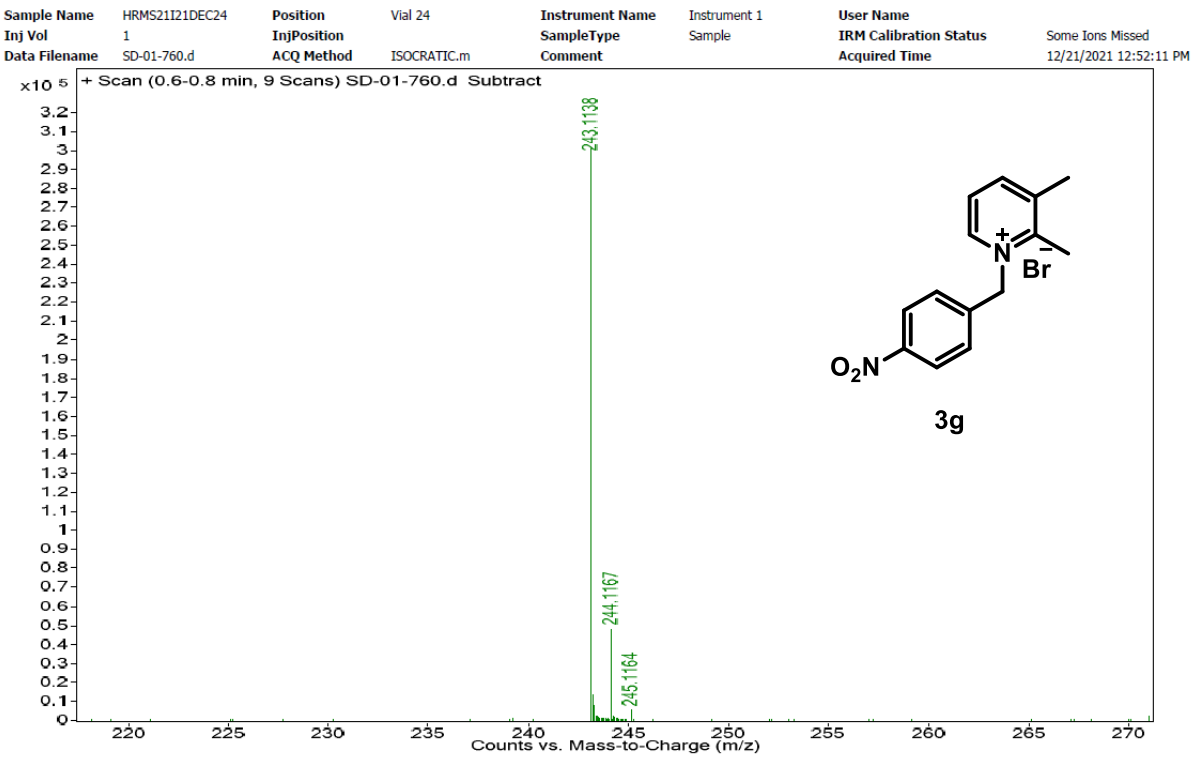


Figure S-15 HRMS spectrum of compound **3g**

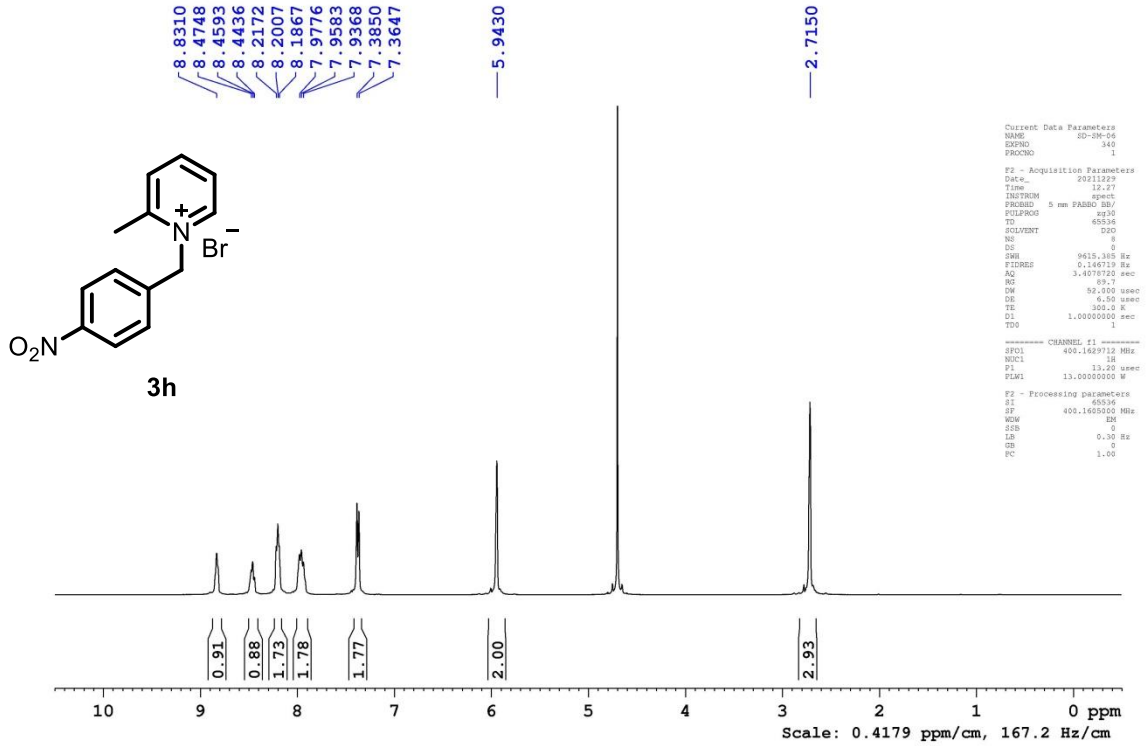


Figure S-16: ^{1}H NMR (400 MHz, D_2O) spectrum of compound **3h**

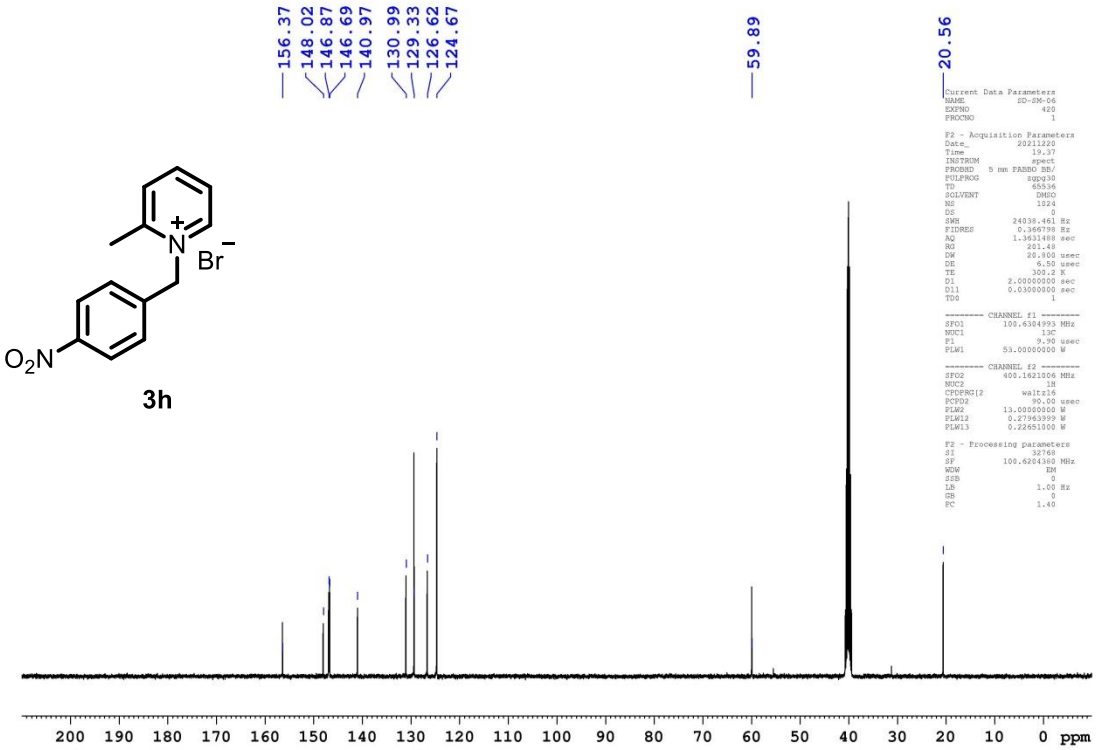


Figure S-17: ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound **3h**

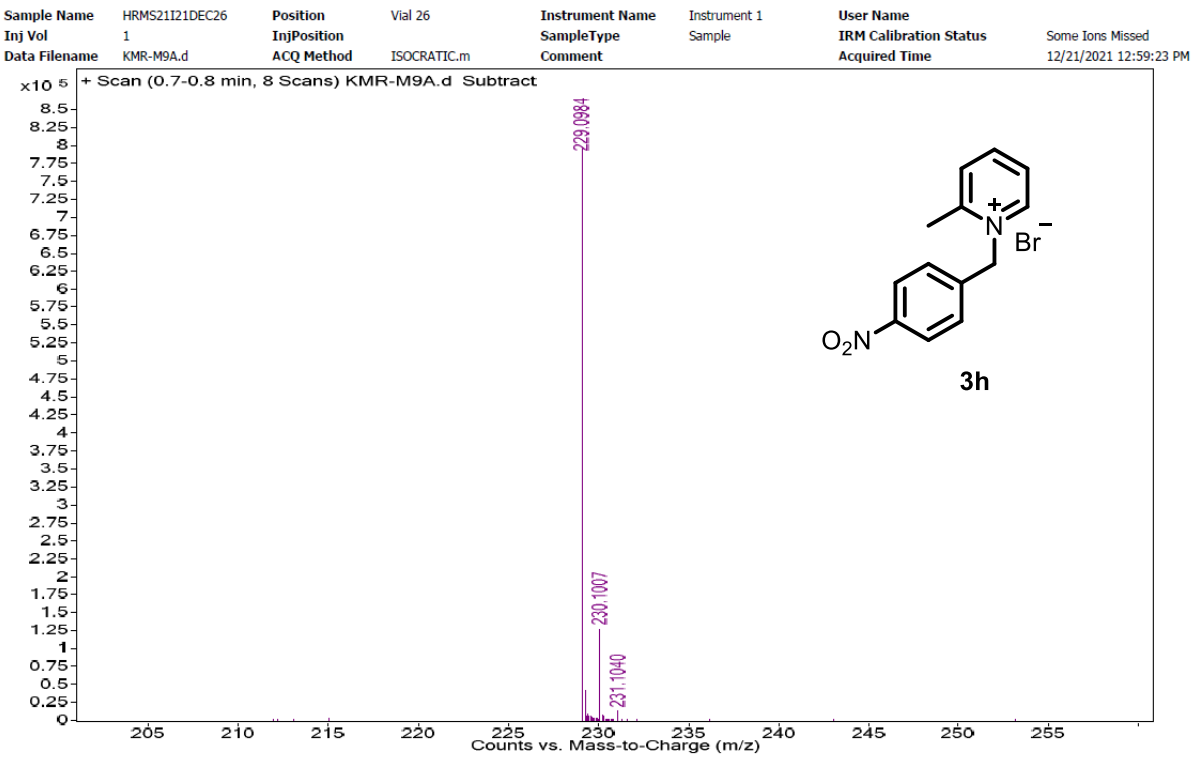


Figure S-18 HRMS spectrum of compound **3h**

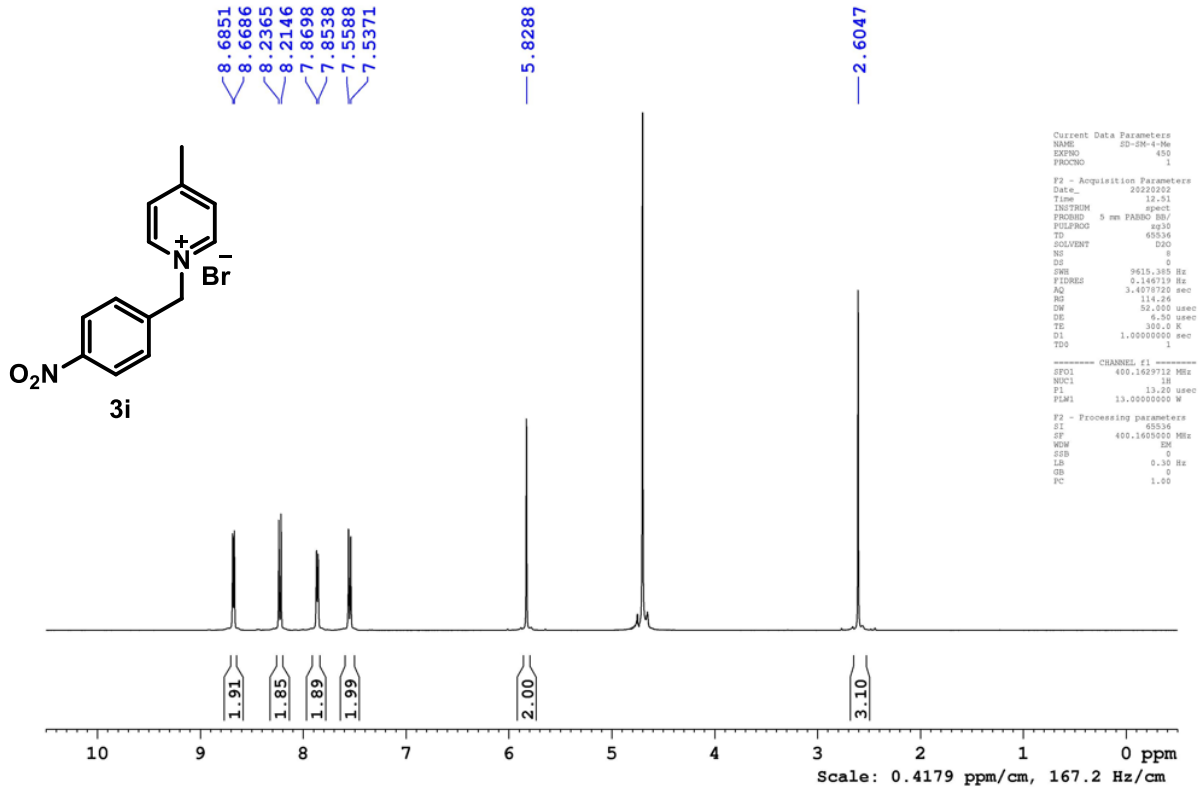


Figure S-19: ^{1}H NMR (400 MHz, D_2O) spectrum of compound **3i**

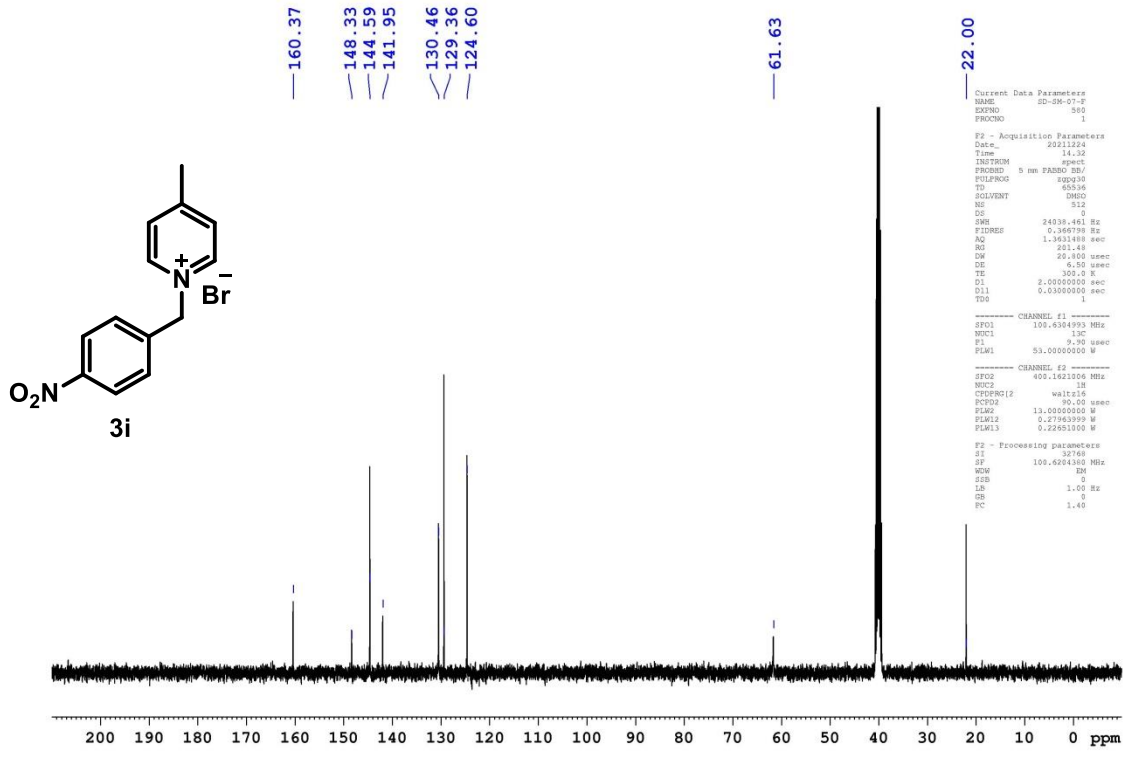


Figure S-20: ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound **3i**

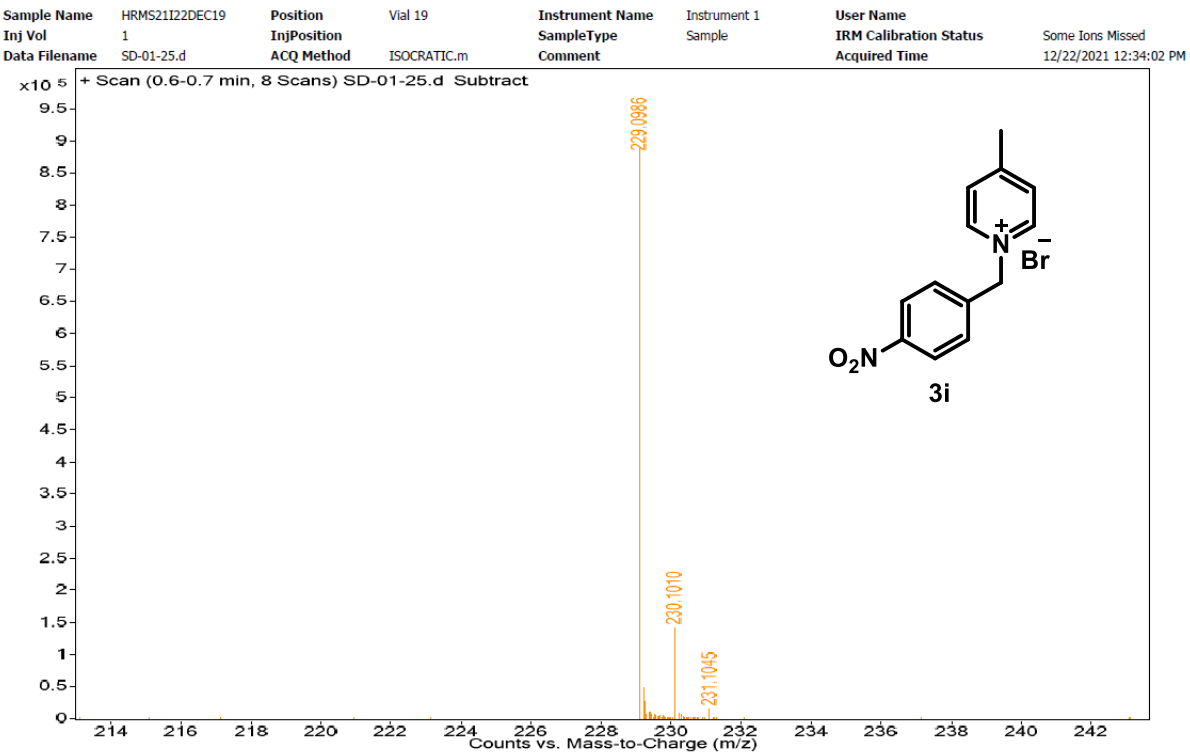


Figure S-21 HRMS spectrum of compound **3i**

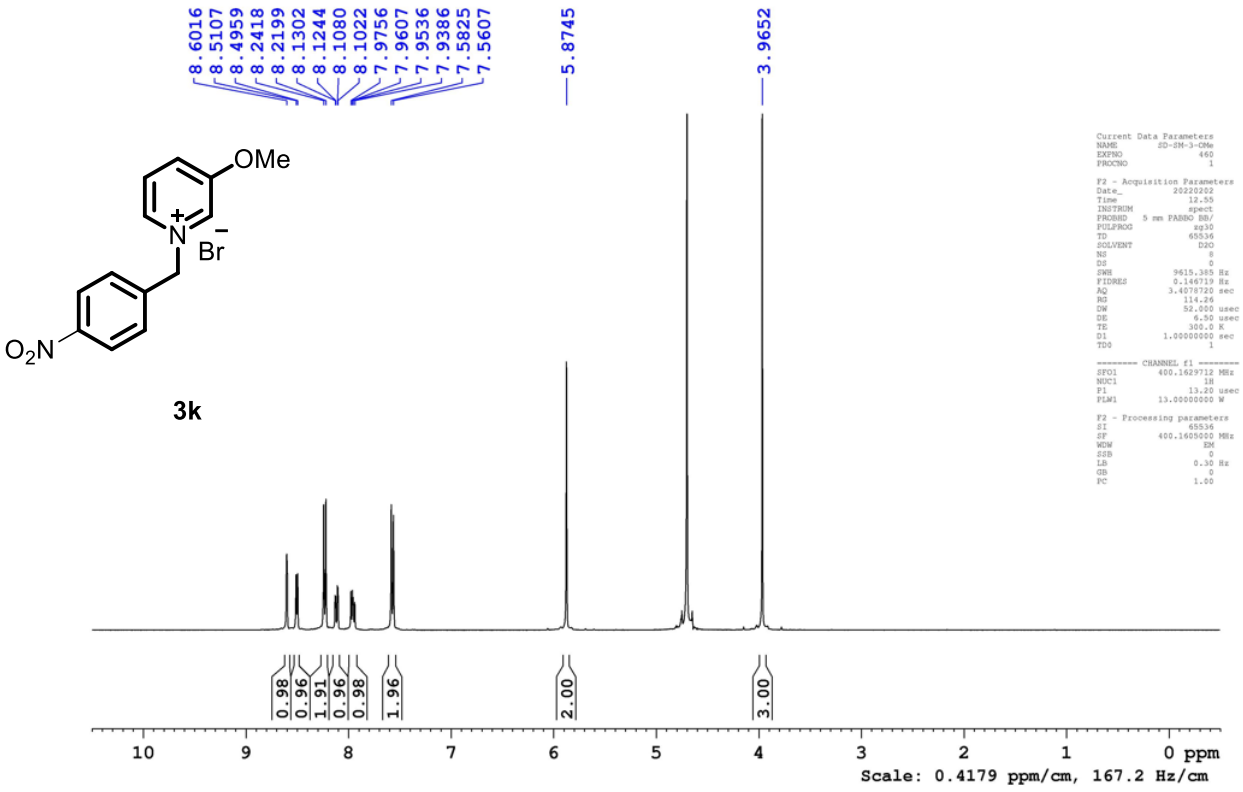


Figure S-22: ^{1}H NMR (400 MHz D_2O) spectrum of compound **3k**

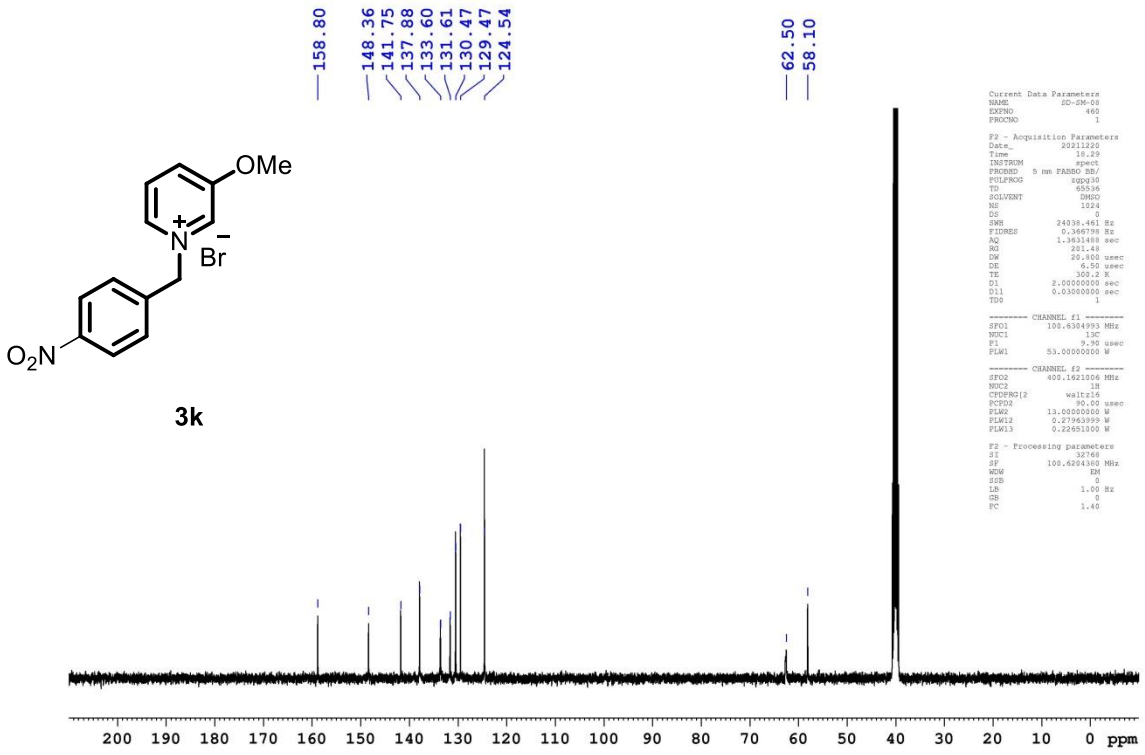


Figure S-23: ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound **3k**

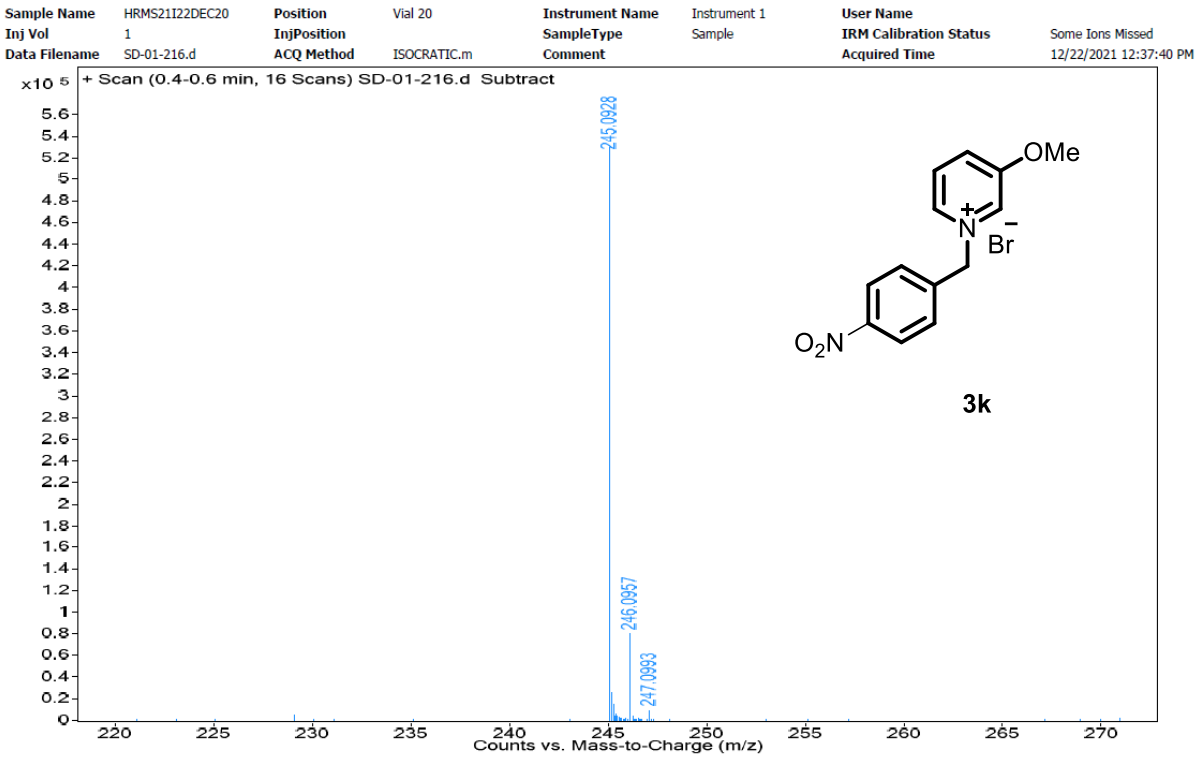


Figure S-24 HRMS spectrum of compound **3k**

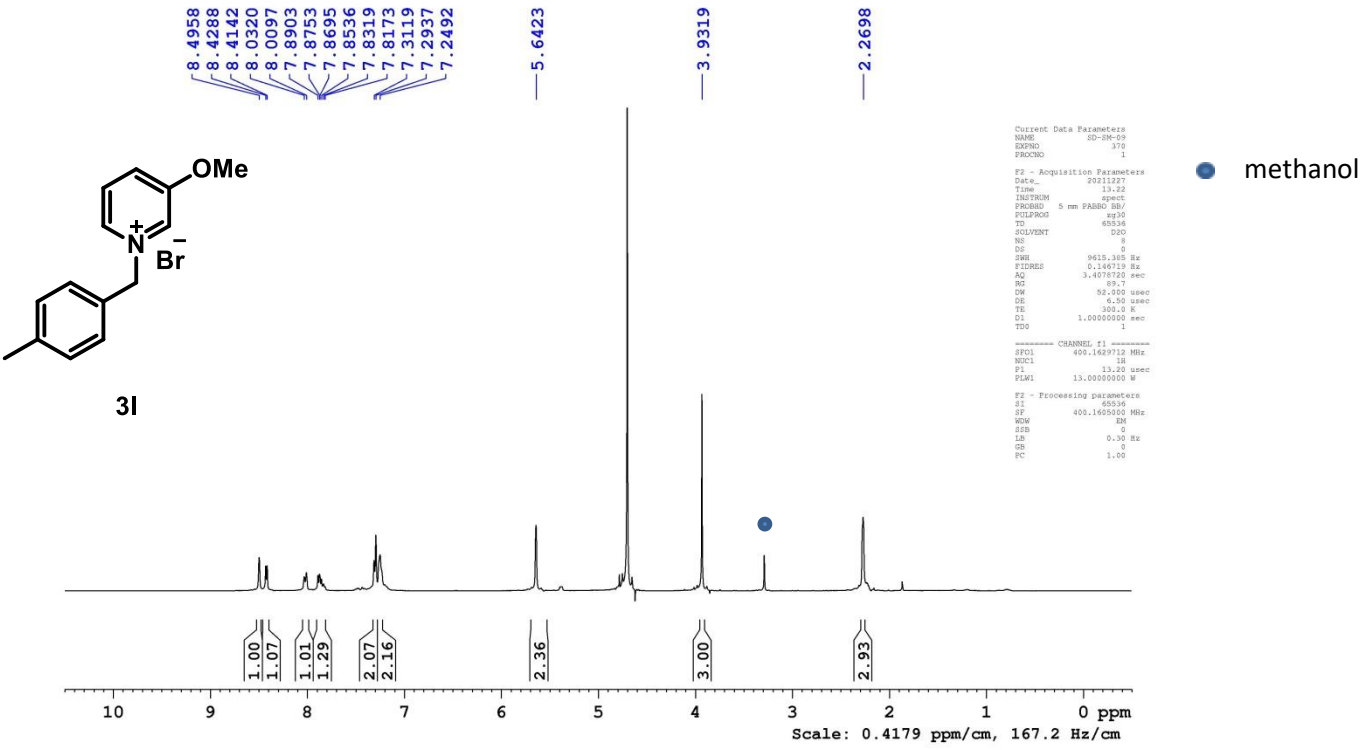


Figure S-25: ^{1}H NMR (400 MHz, D_2O) spectrum of compound **3l**

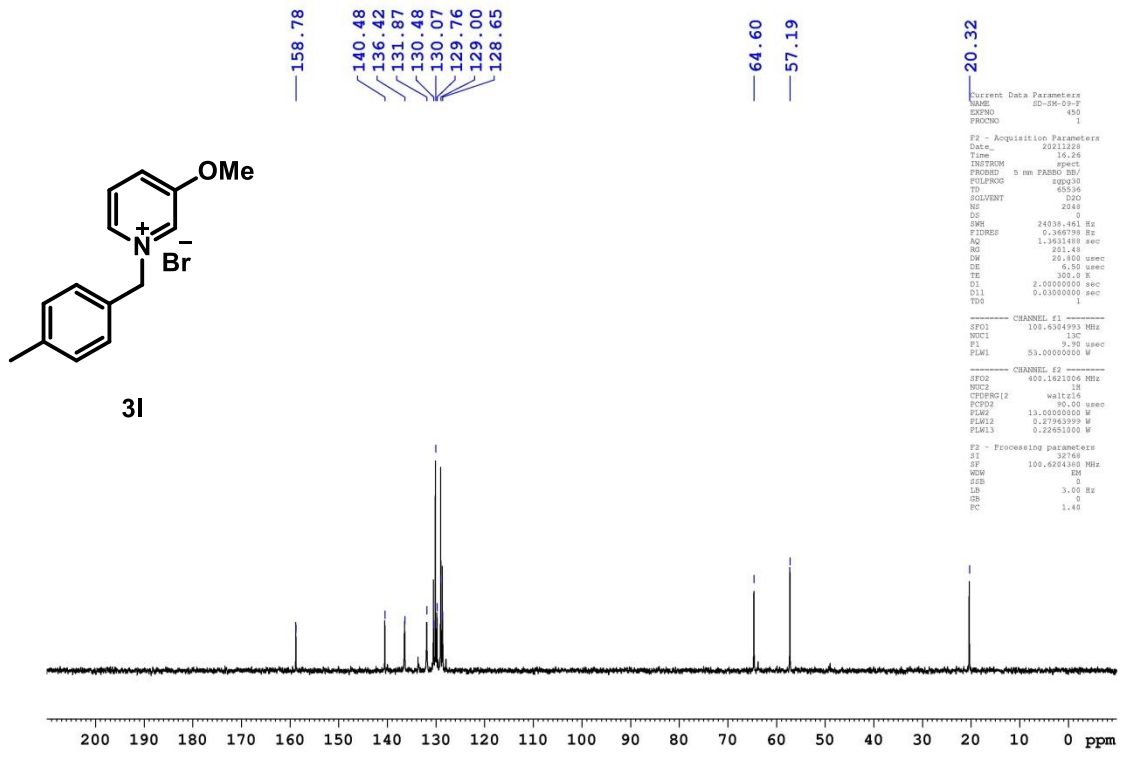


Figure S-26: ^{13}C NMR (100 MHz, D_2O) spectrum of compound **3l**

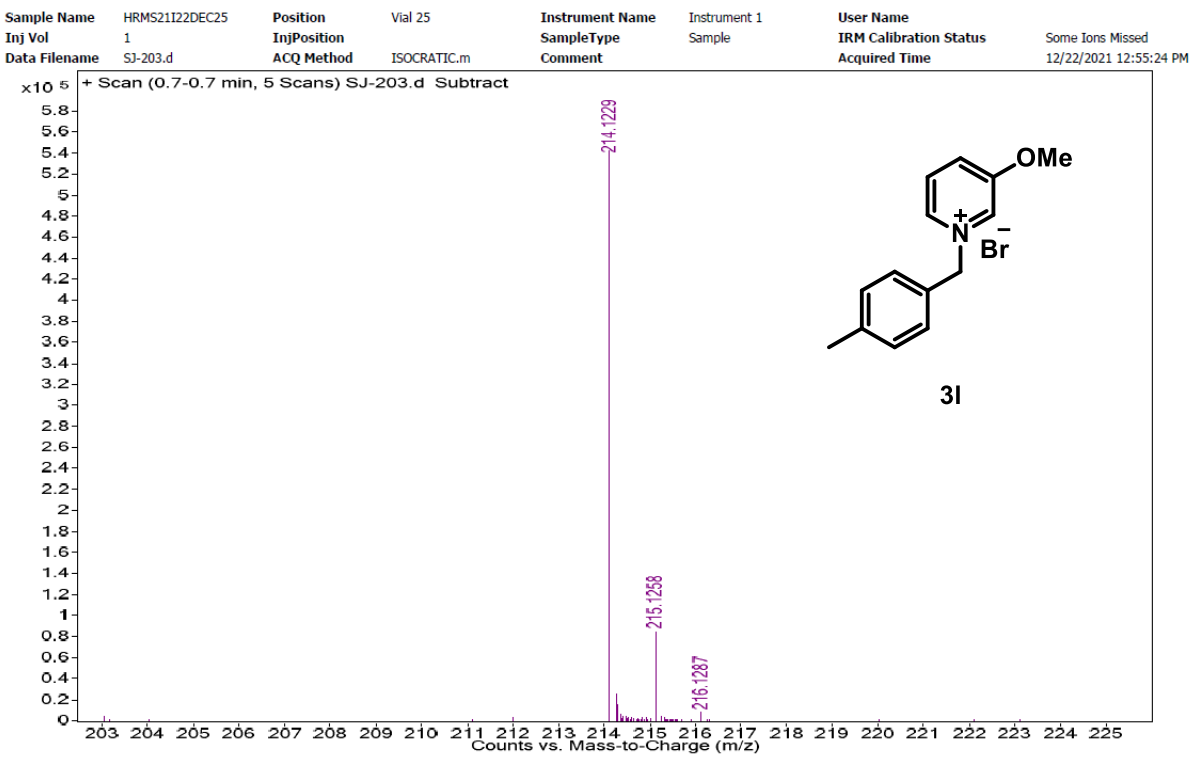


Figure S-27 HRMS spectrum of compound **3l**

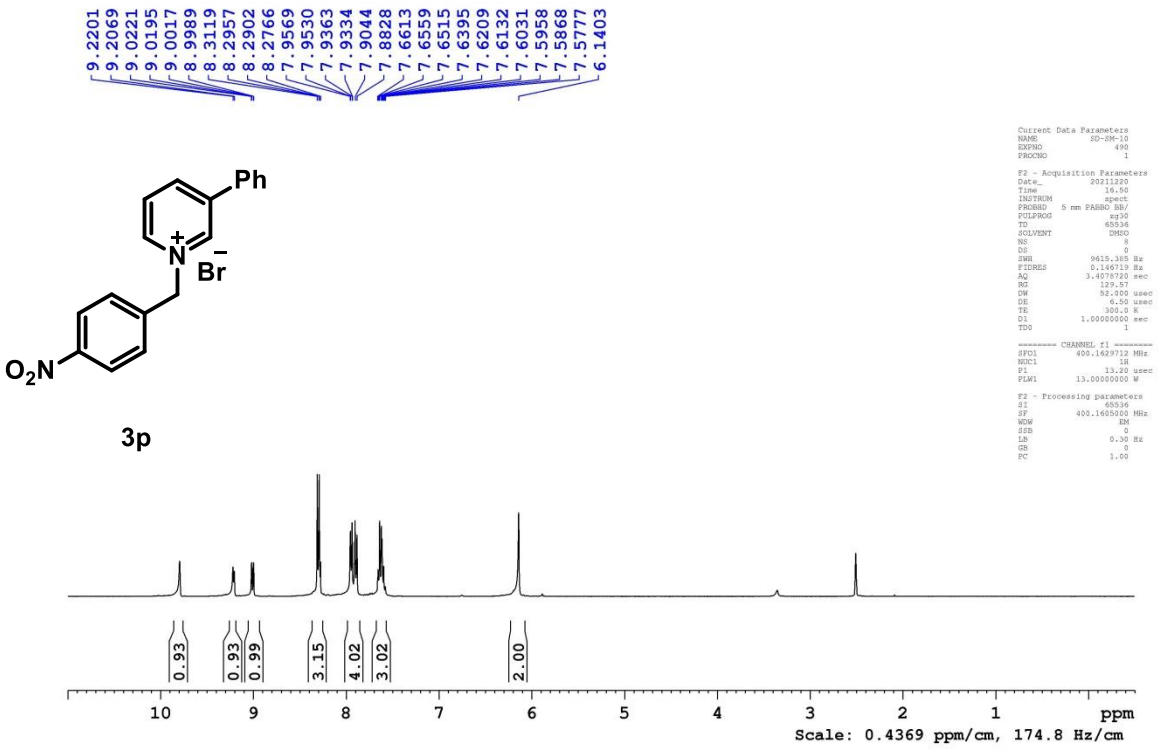


Figure S-28: ^{1}H NMR (400 MHz, DMSO-d$_6$) spectrum of compound **3p**

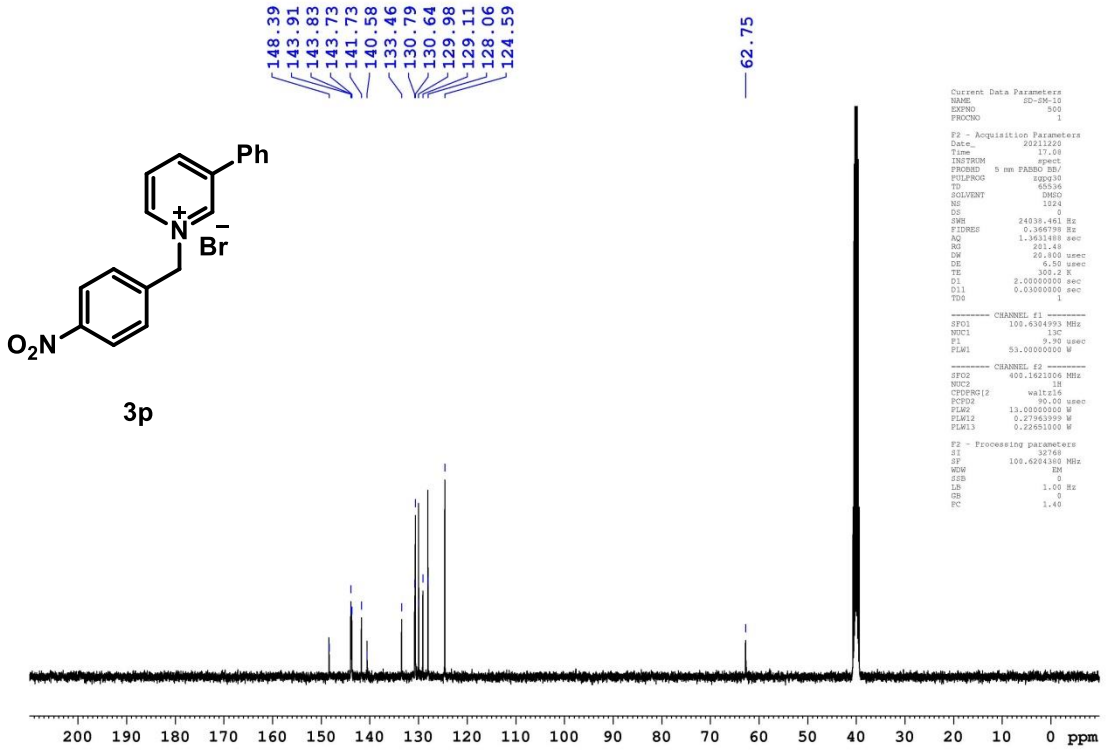


Figure S-29: ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound **3p**

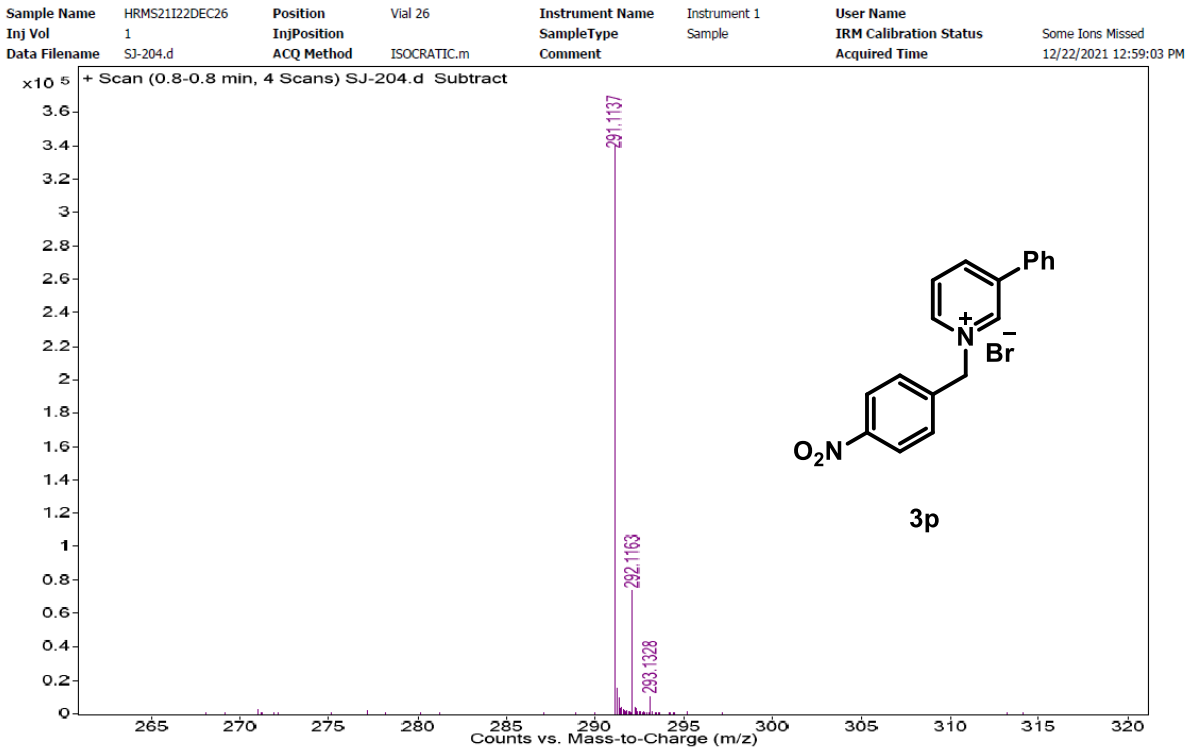


Figure S-30 HRMS spectrum of compound **3p**

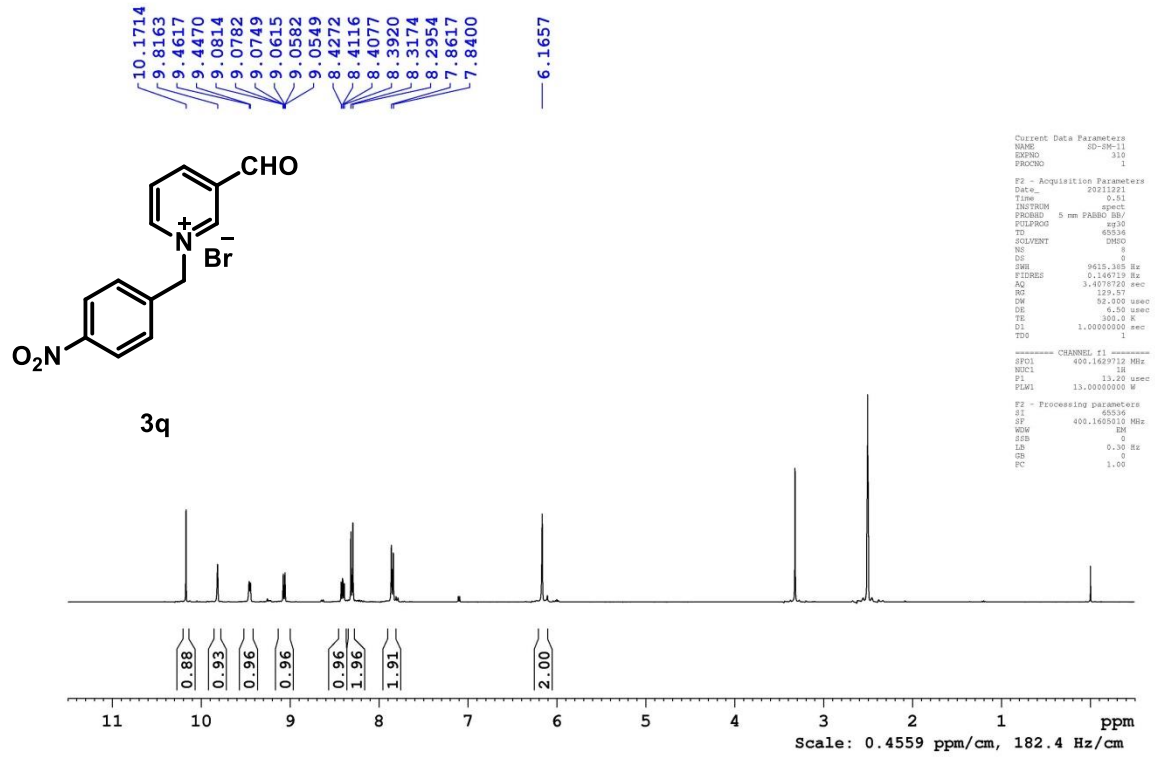


Figure S-31: ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound **3q**

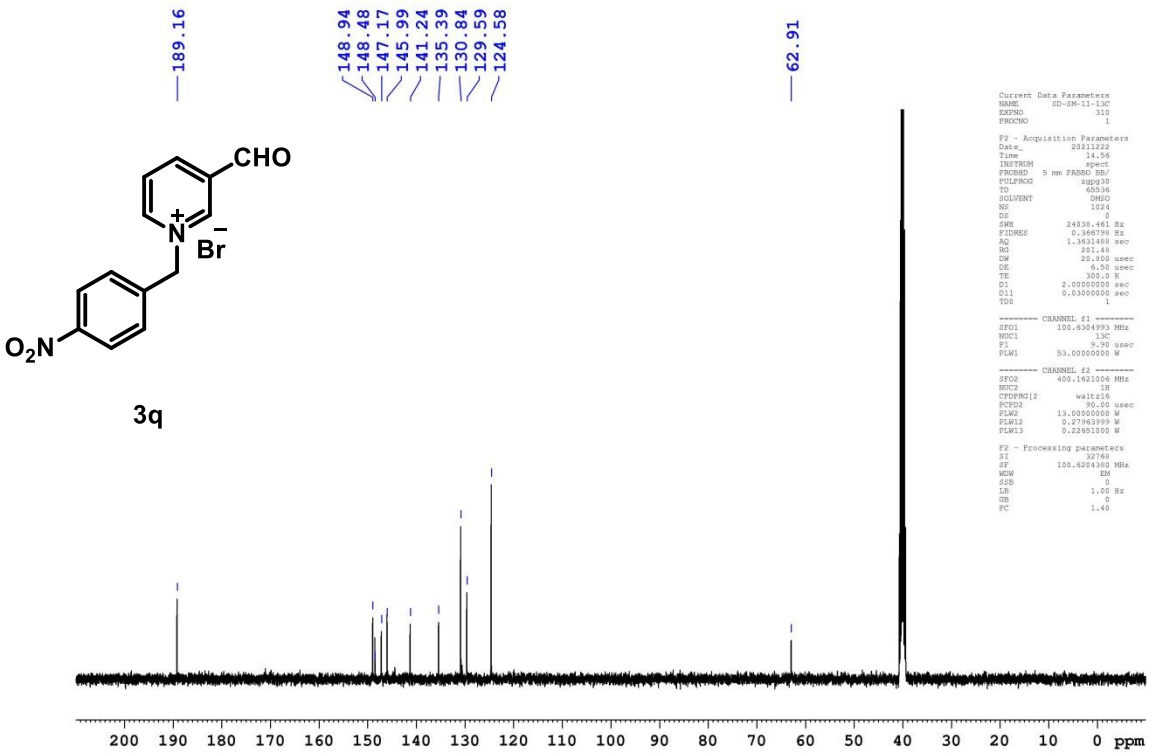


Figure S-32: ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound **3q**

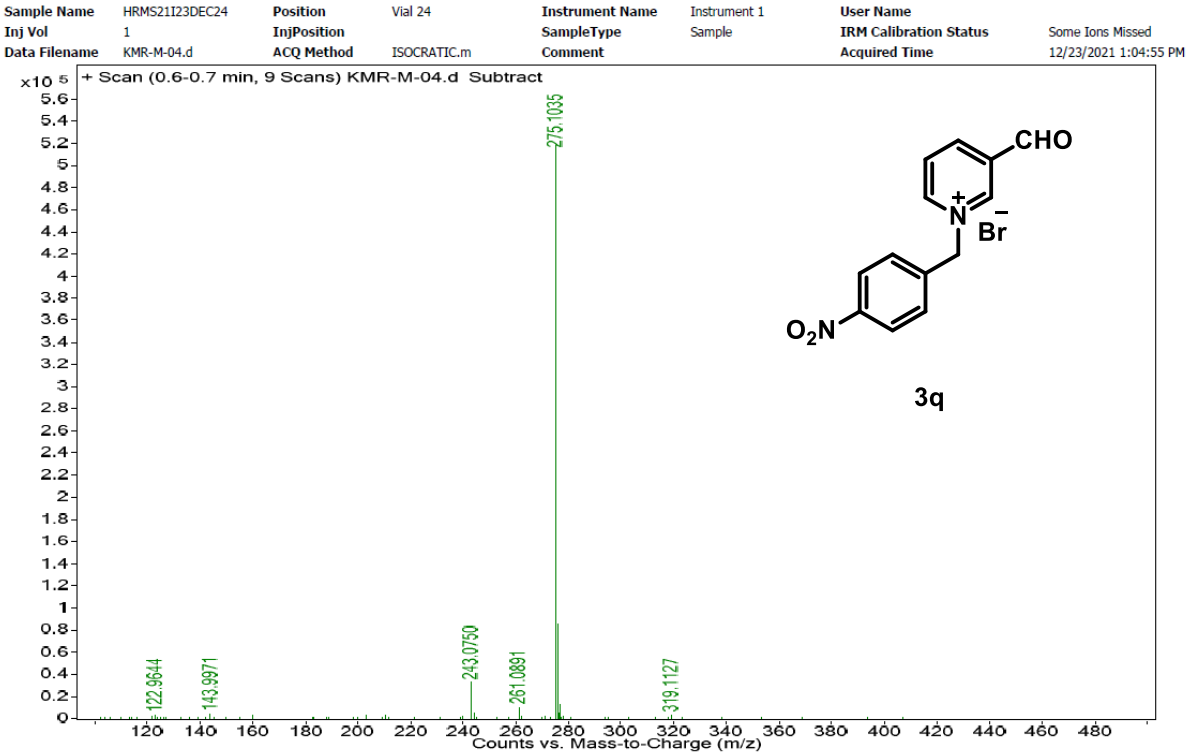


Figure S-33 HRMS spectrum of compound **3q**

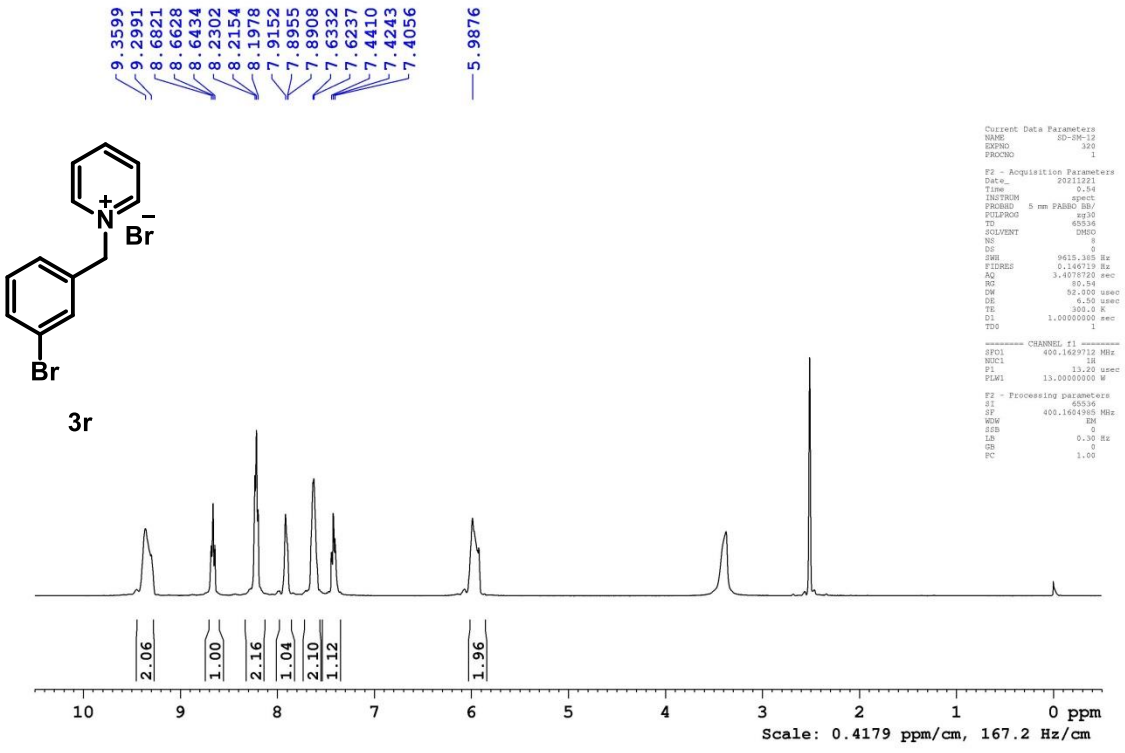


Figure S-34: ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound **3r**

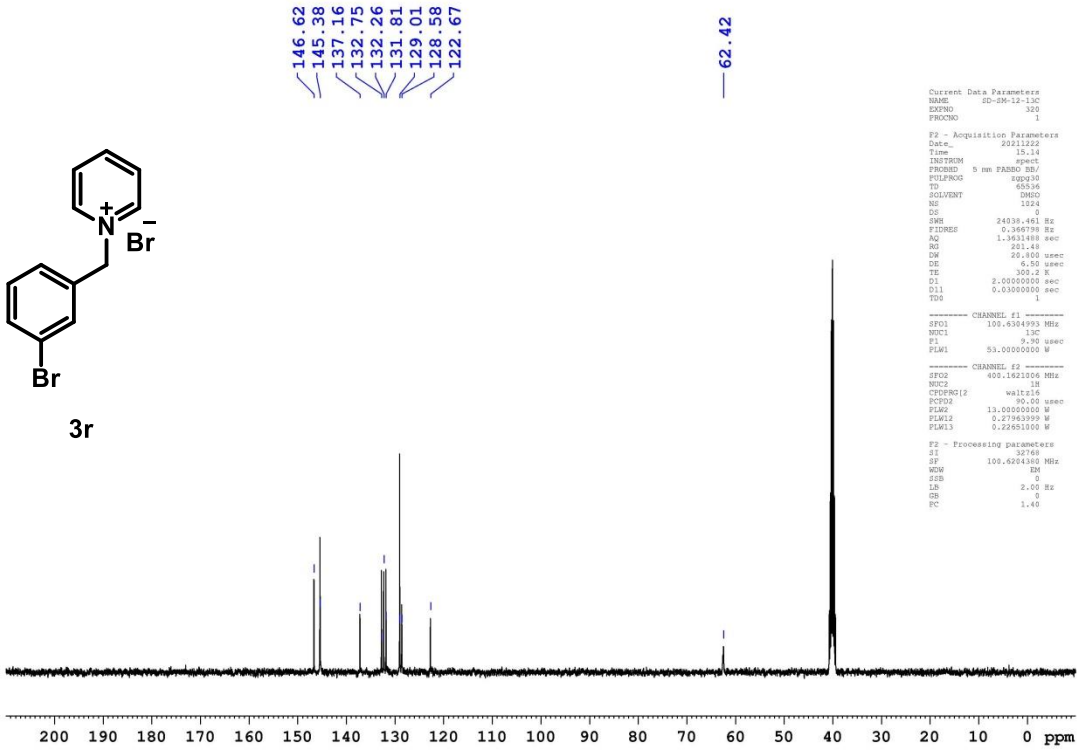


Figure S-35: ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound **3r**

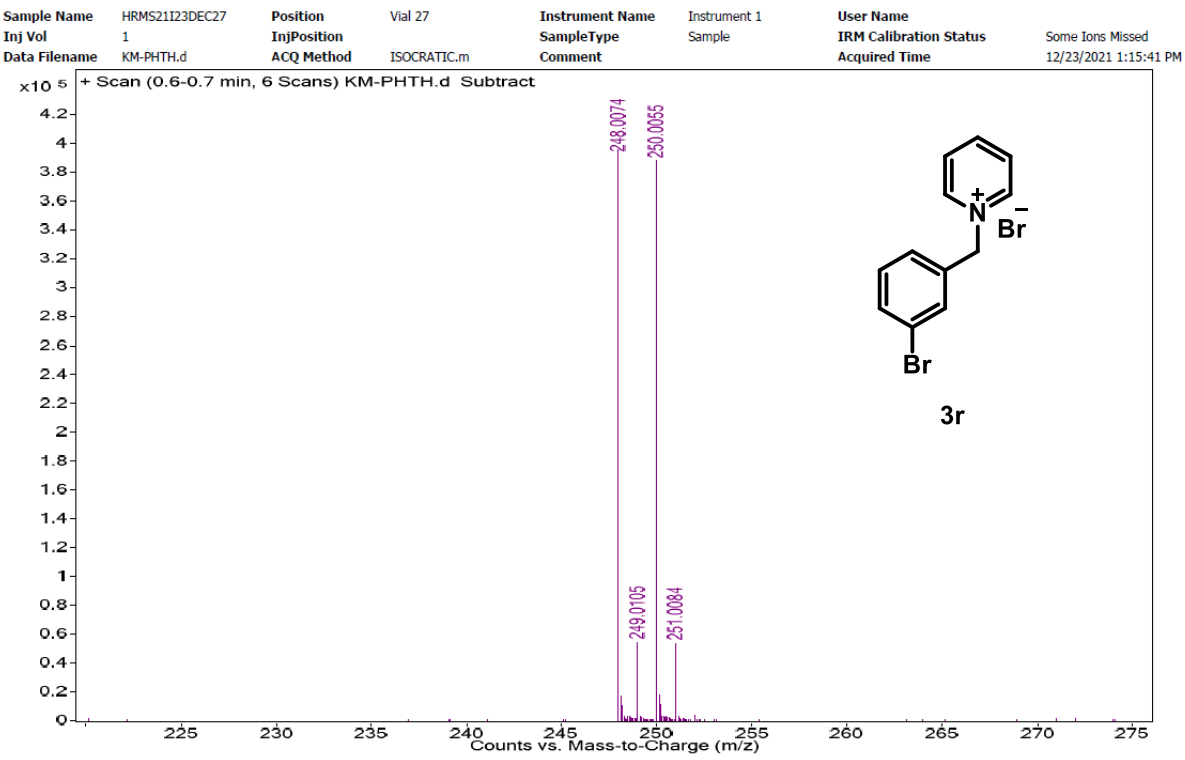


Figure S-36 HRMS spectrum of compound **3r**

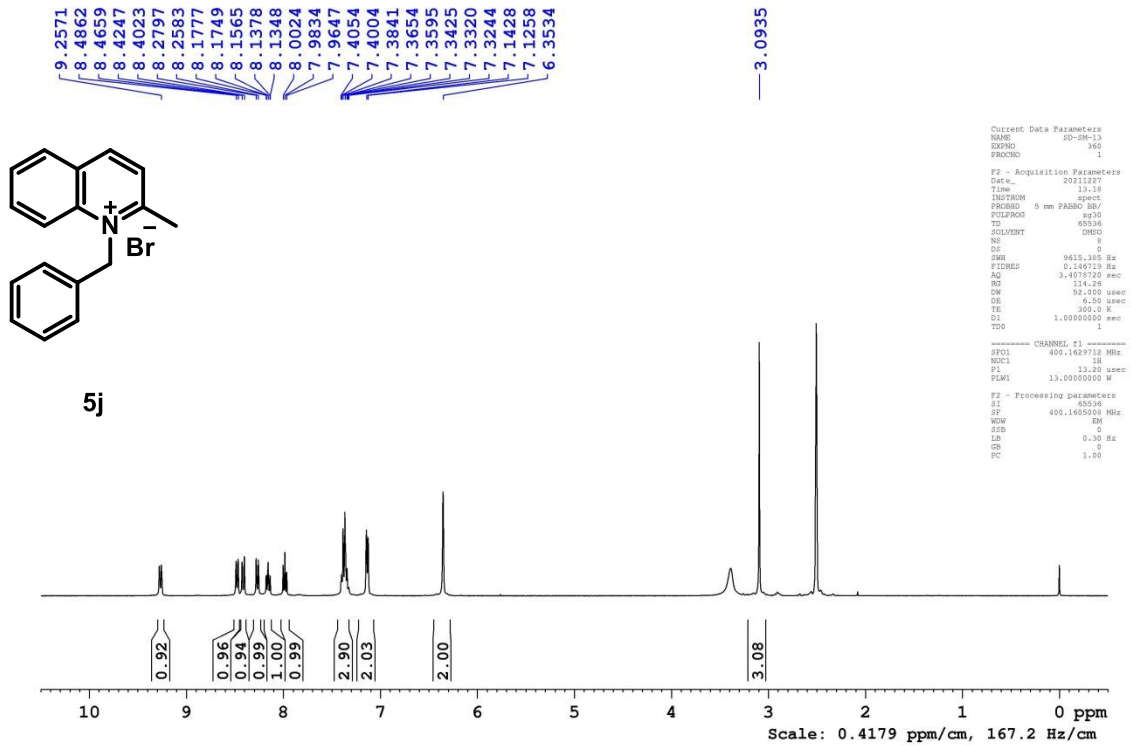


Figure S-37: ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound **5j**

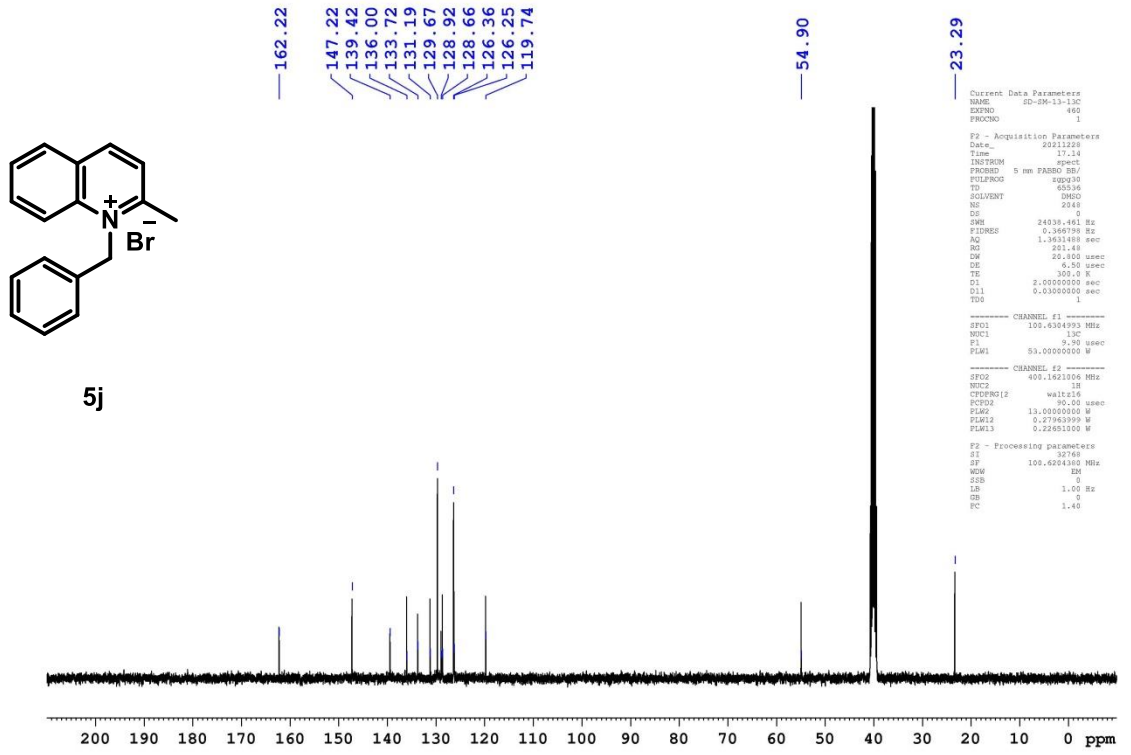


Figure S-38: ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound **5j**

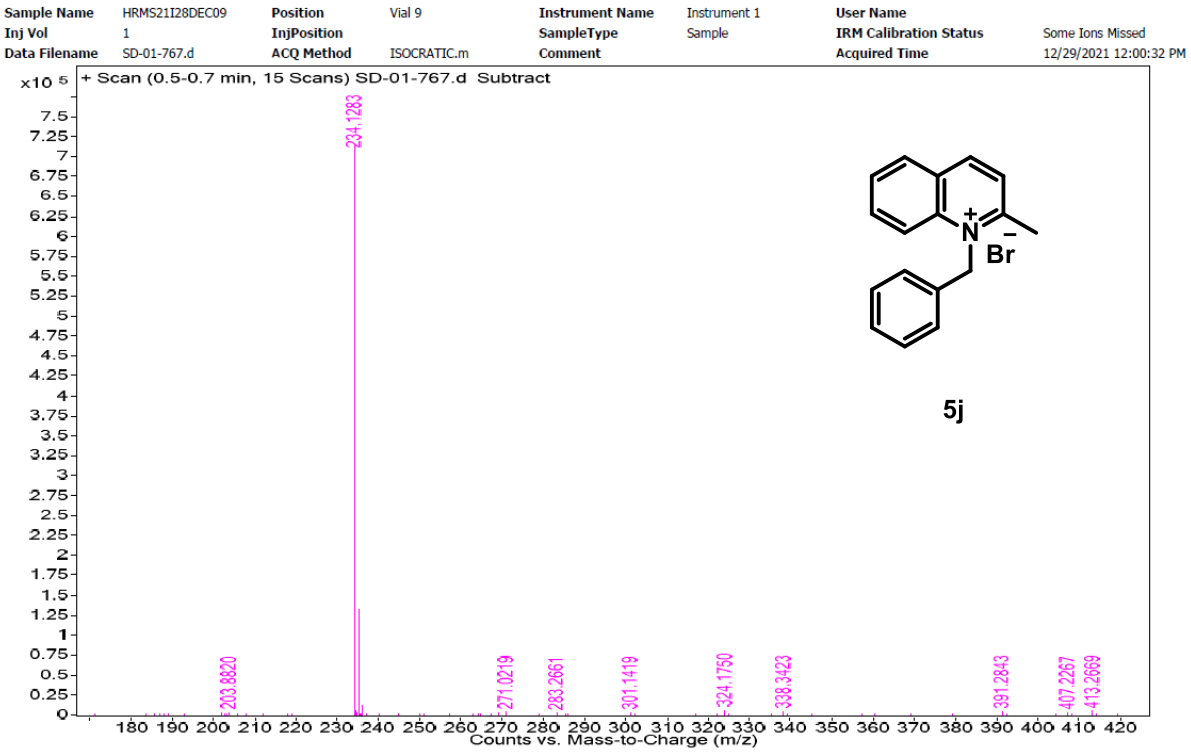


Figure S-39 HRMS spectrum of compound **5j**

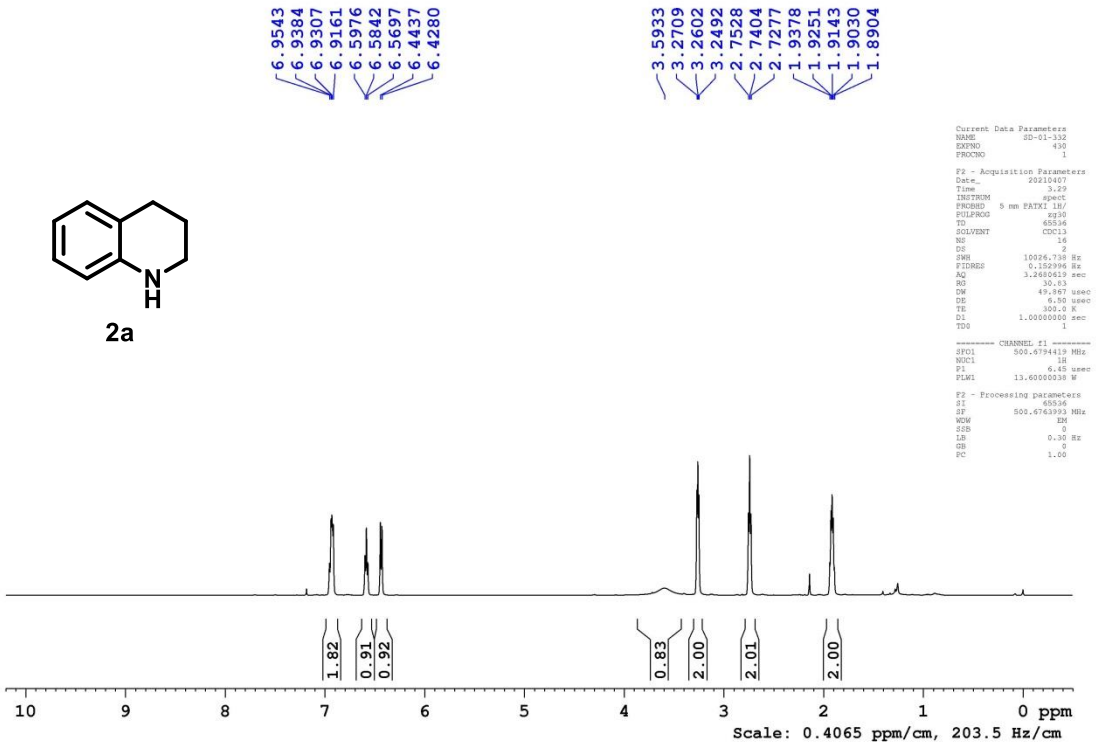


Figure S-40: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2a**

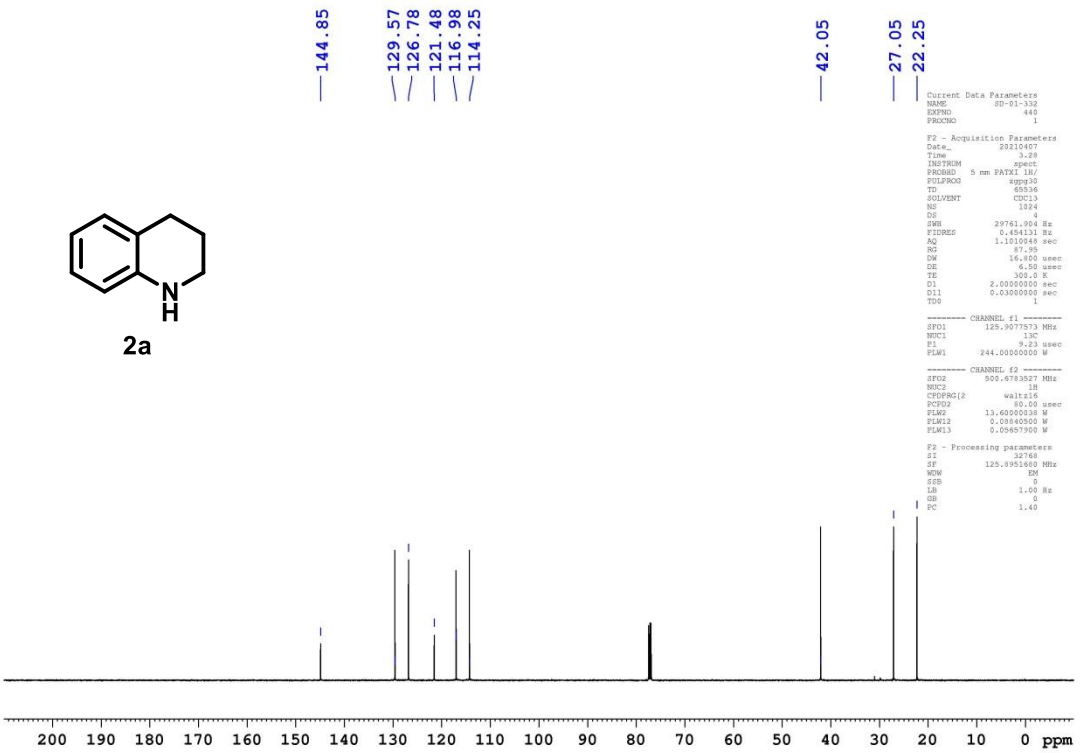


Figure S-41: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2a**

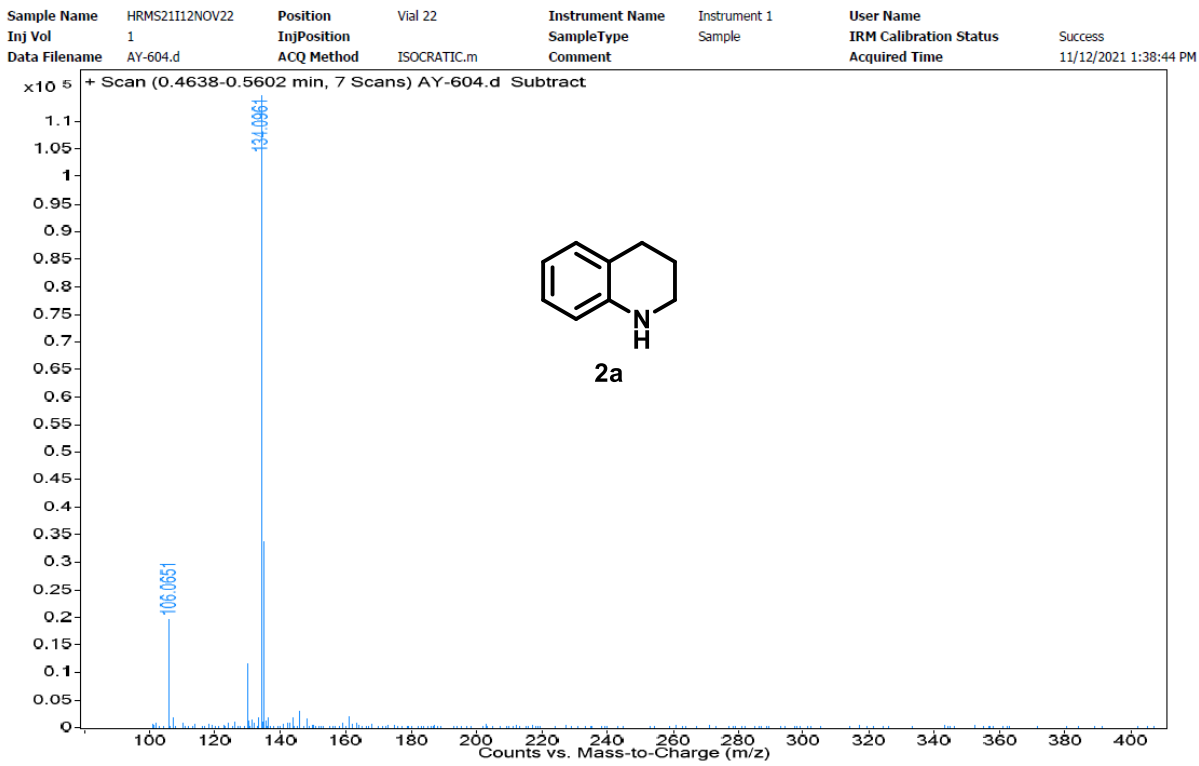


Figure S-42 HRMS spectrum of compound **2a**

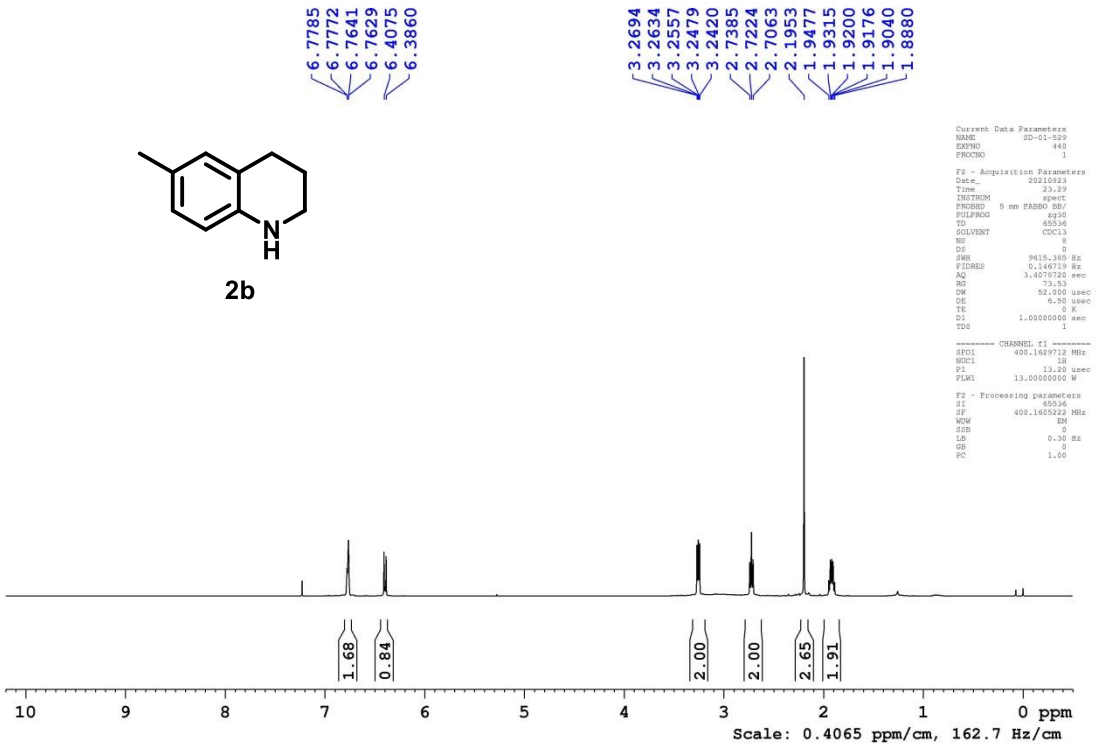


Figure S-43: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **2b**

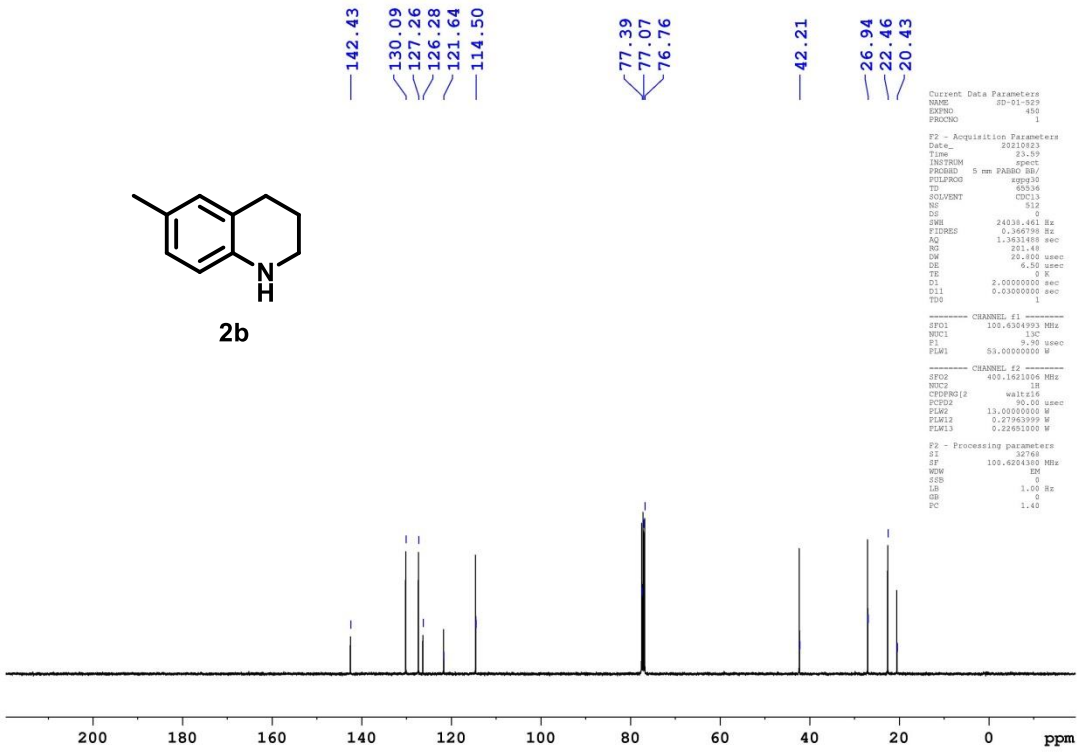


Figure S-44: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **2b**

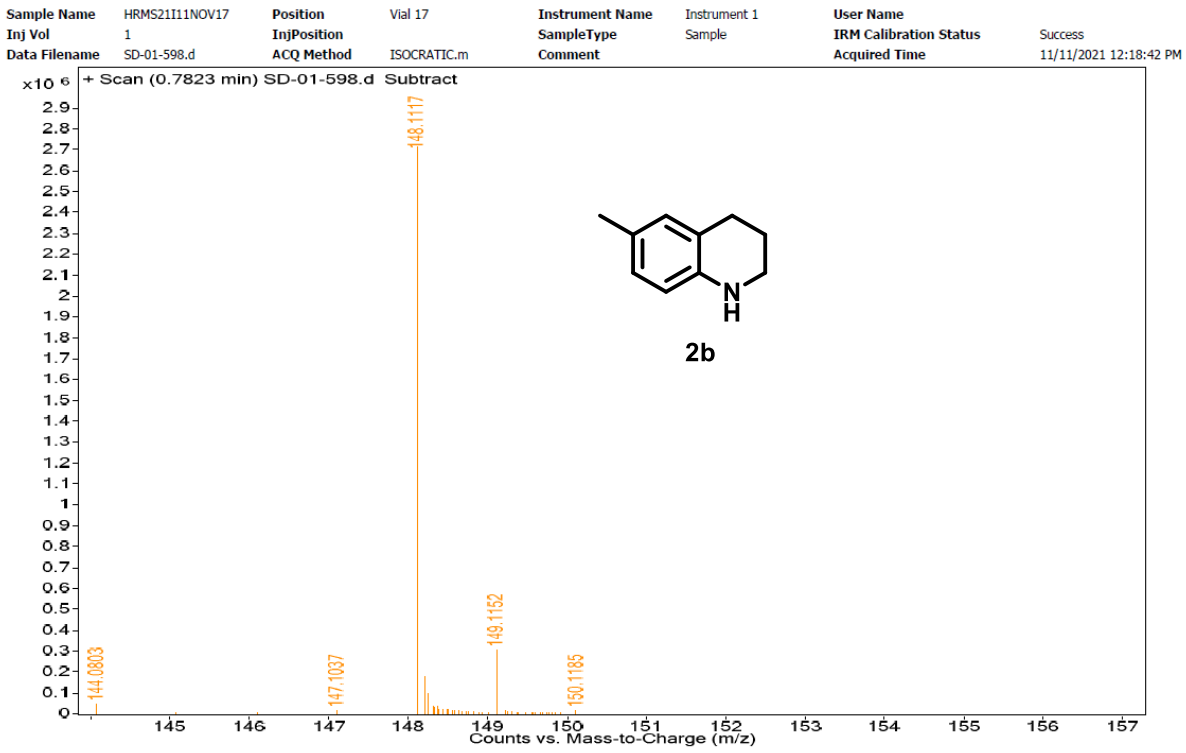


Figure S-45: HRMS spectrum of compound **2b**

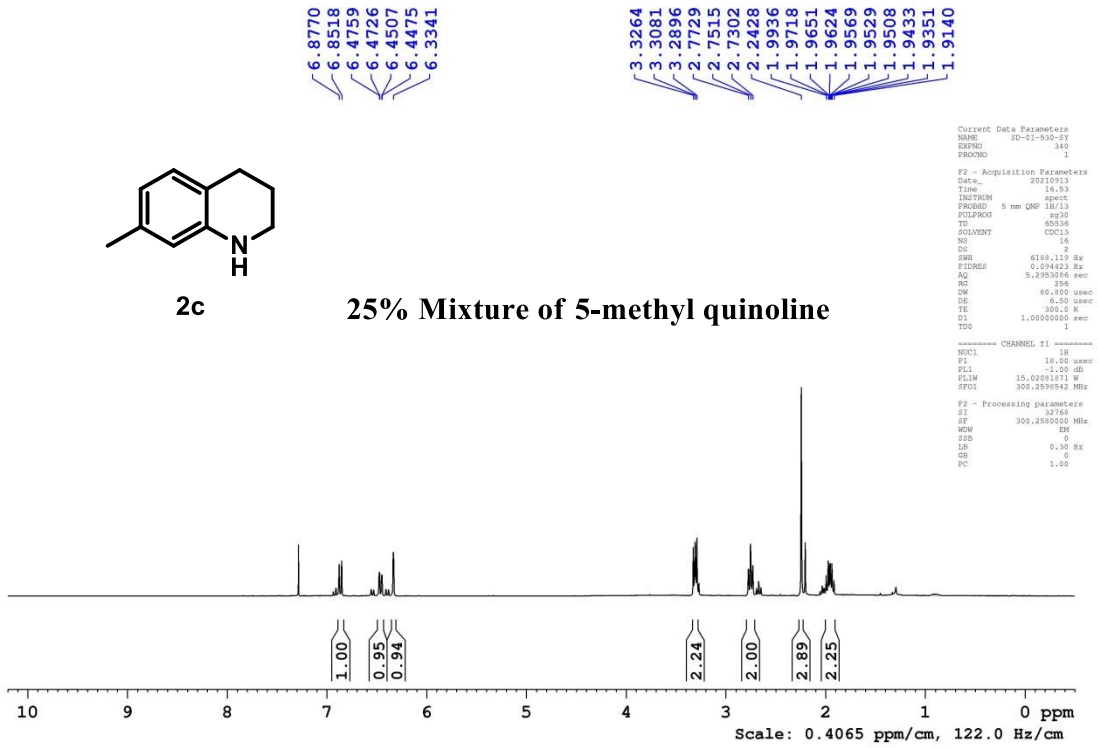


Figure S-46: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **2c**

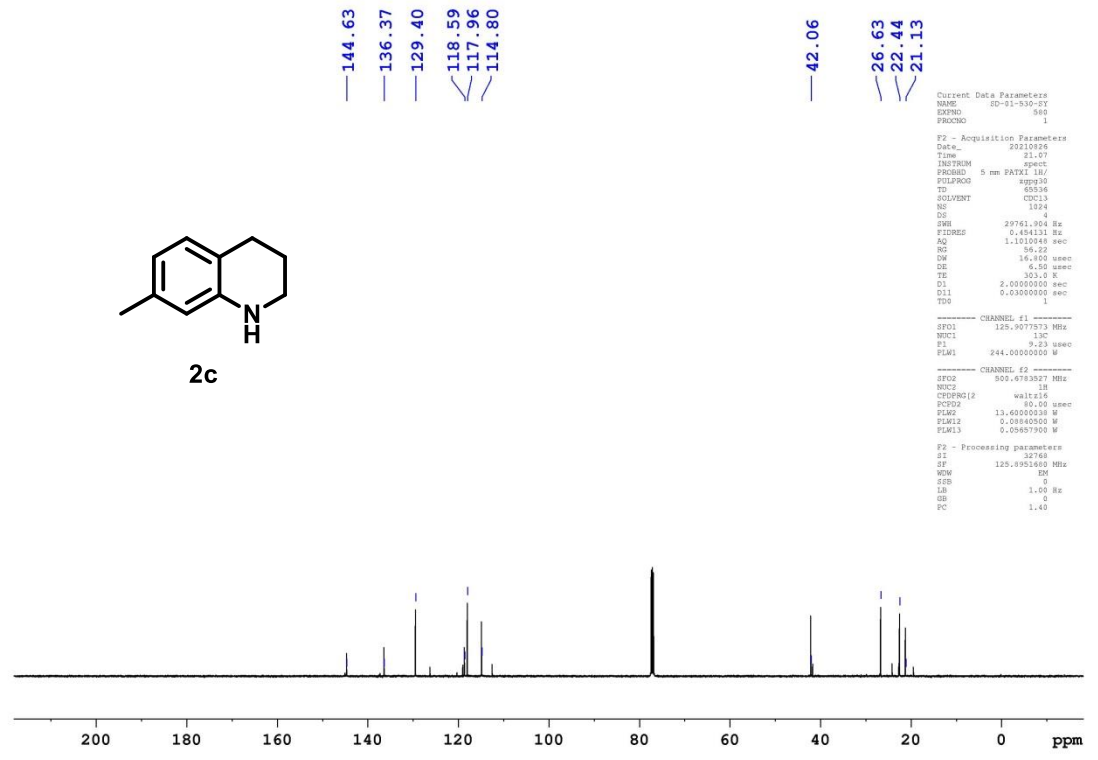


Figure S-47: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2c**

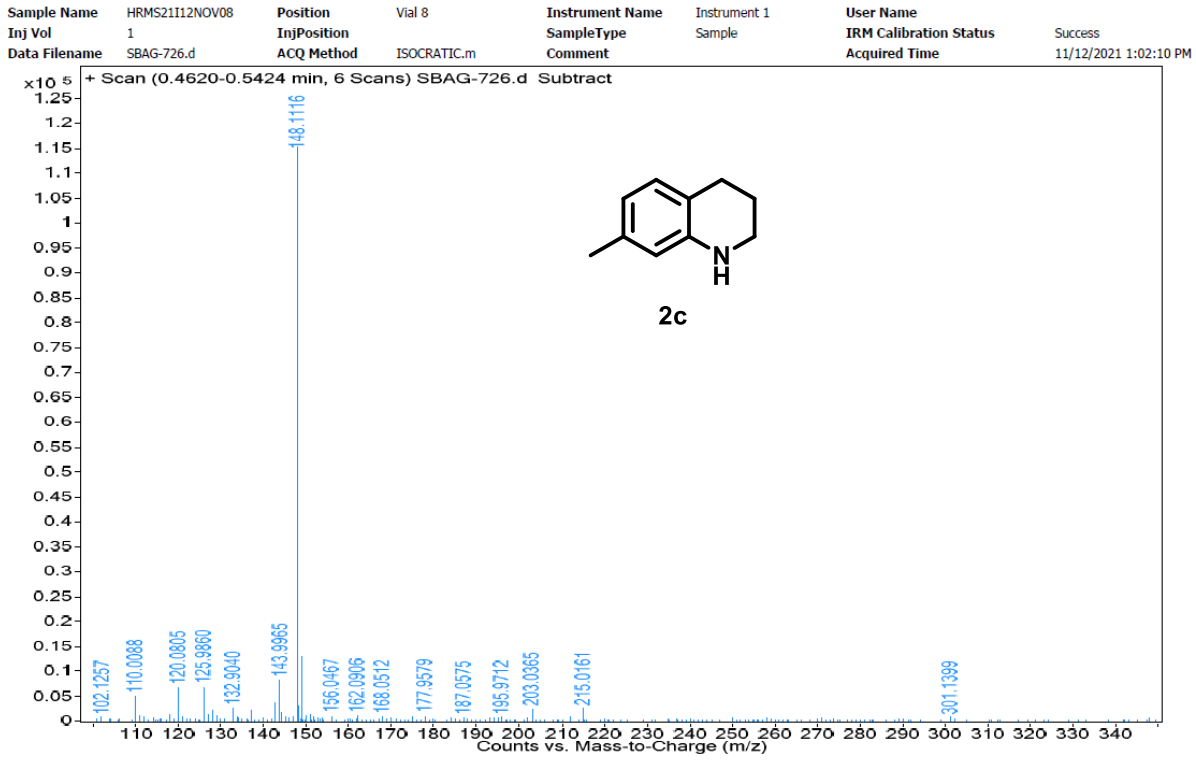


Figure S-48 HRMS spectrum of compound **2c**

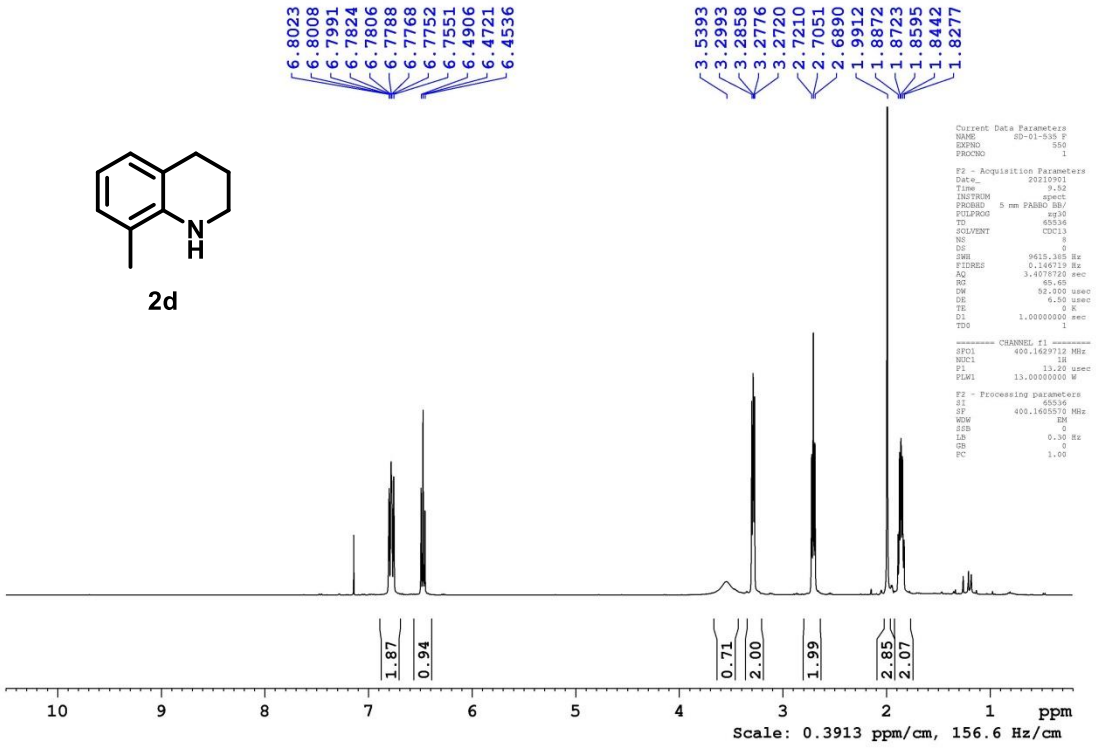


Figure S-49: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **2d**

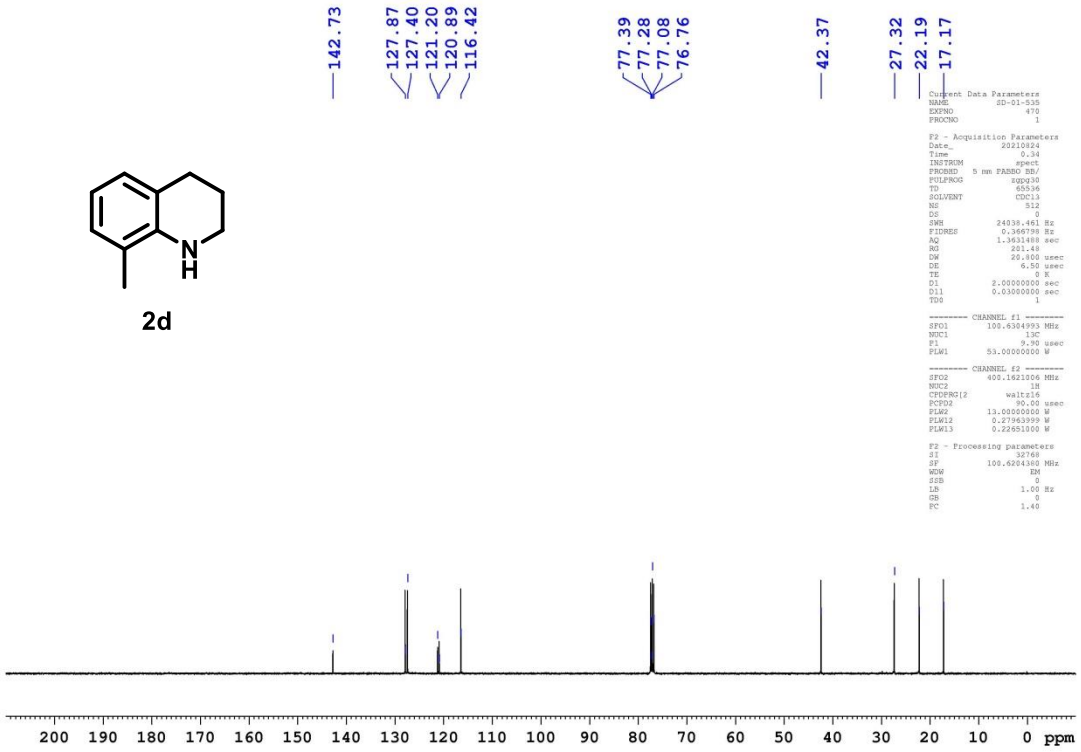


Figure S-50: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **2d**

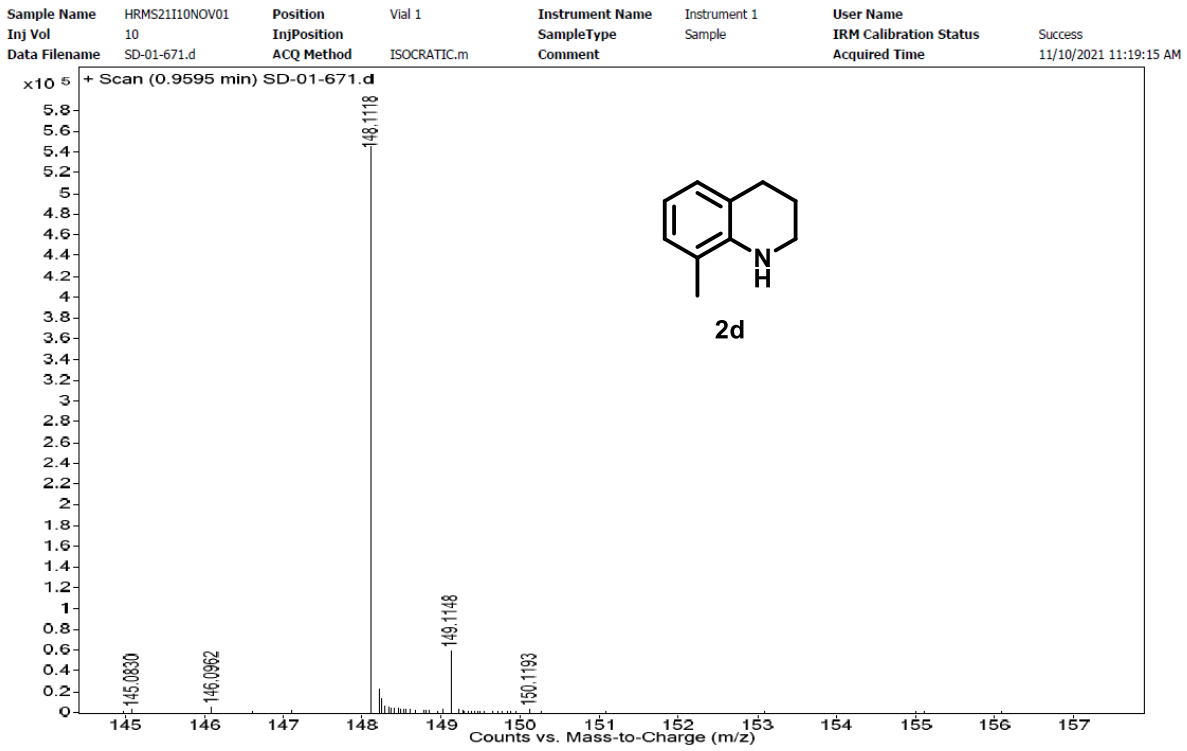


Figure S-51 HRMS spectrum of compound **2d**

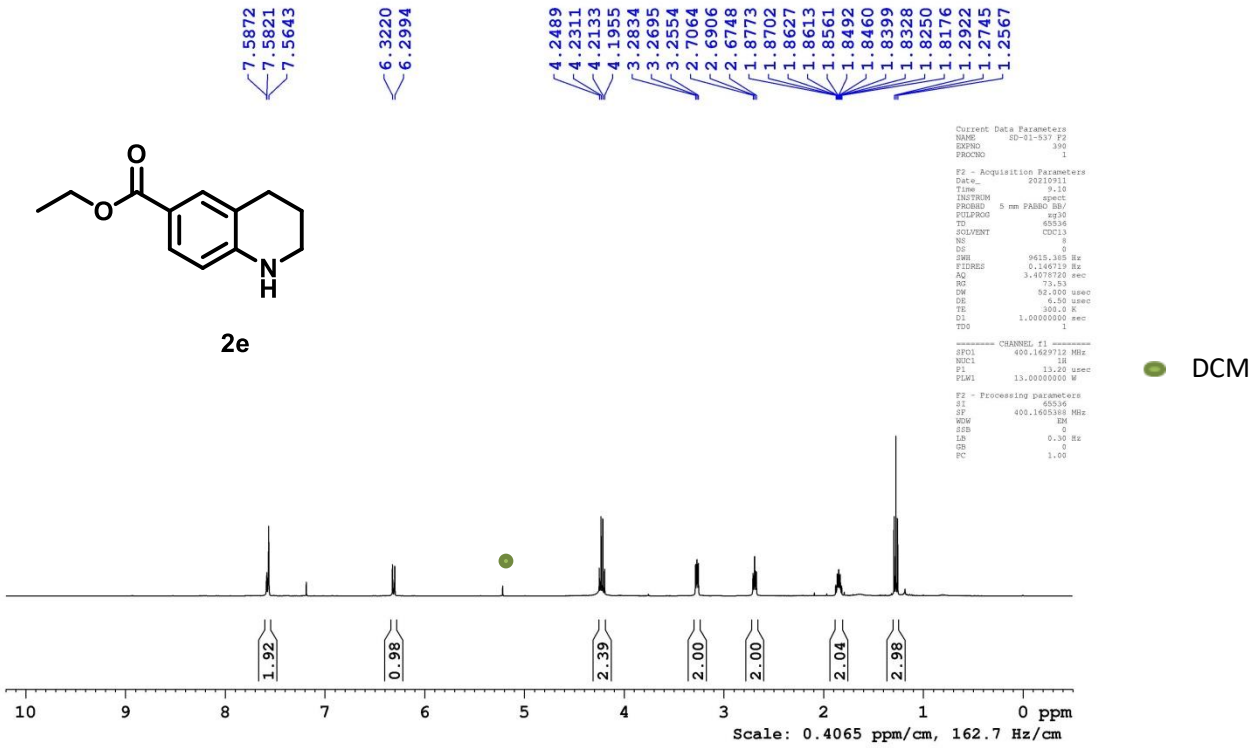


Figure S-52: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **2e**

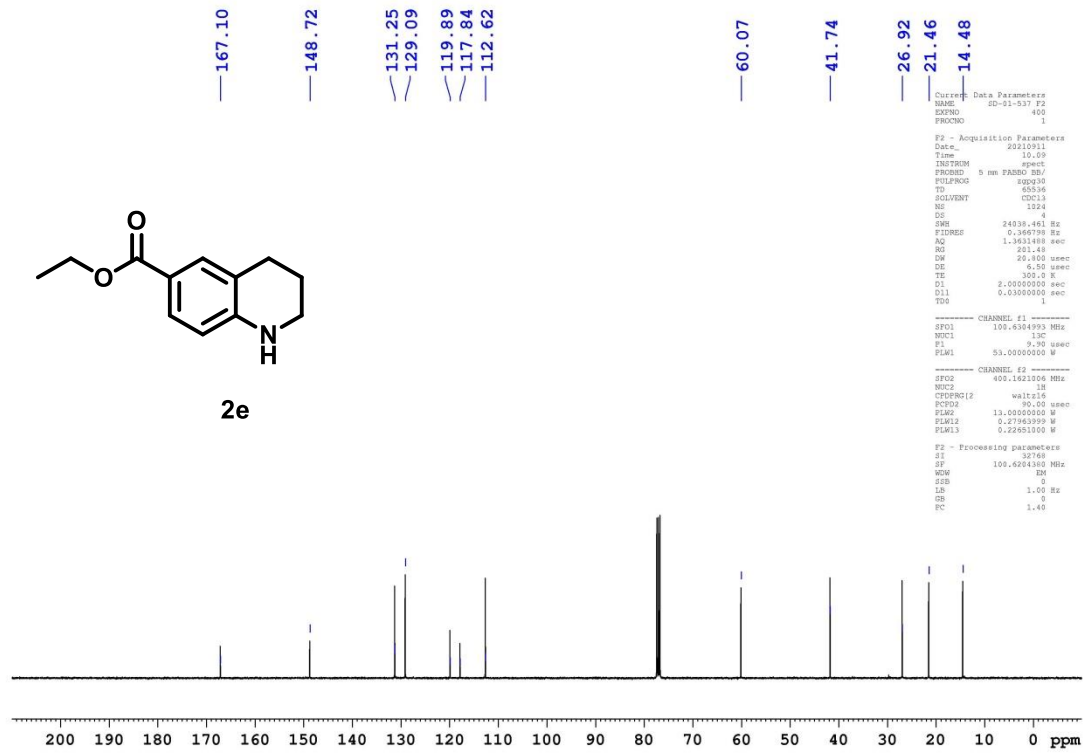


Figure S-53: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **2e**

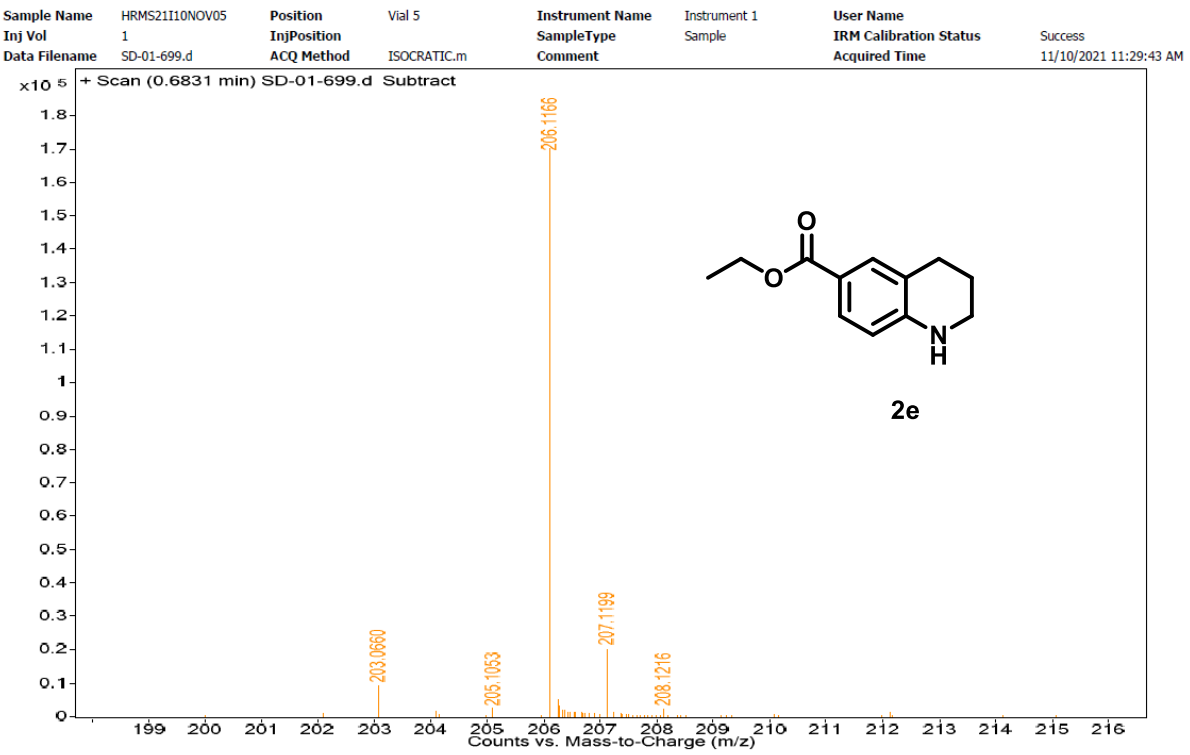


Figure S-54 HRMS spectrum of compound **2e**

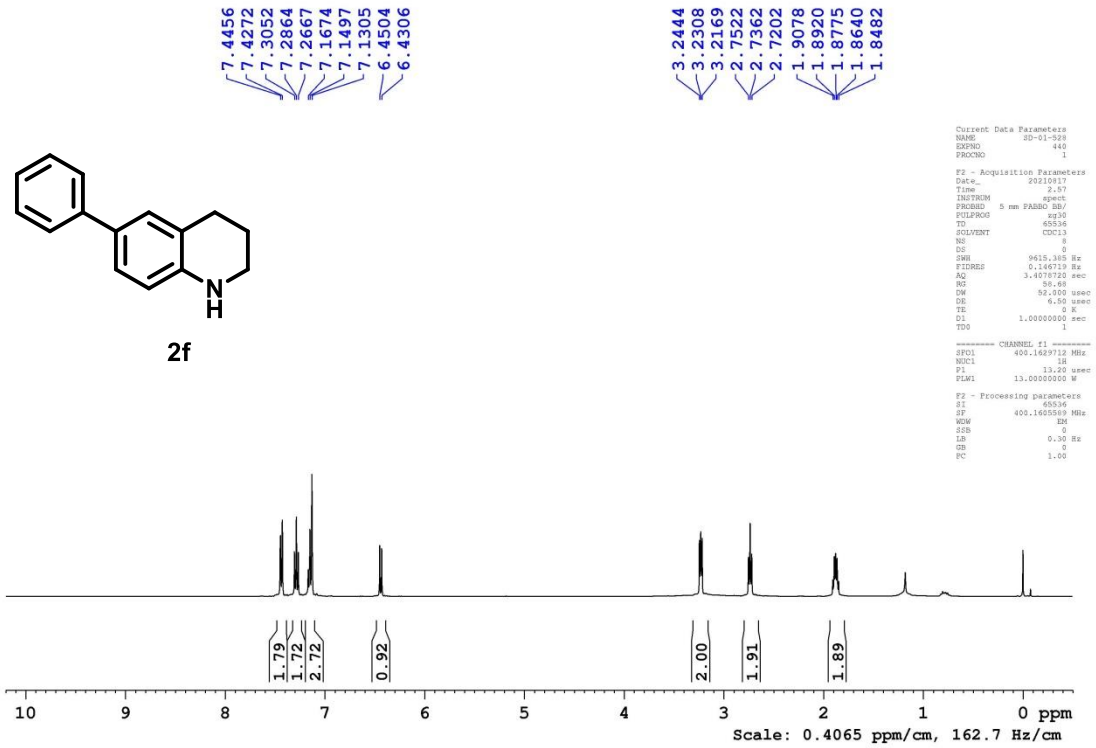


Figure S-55: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **2f**

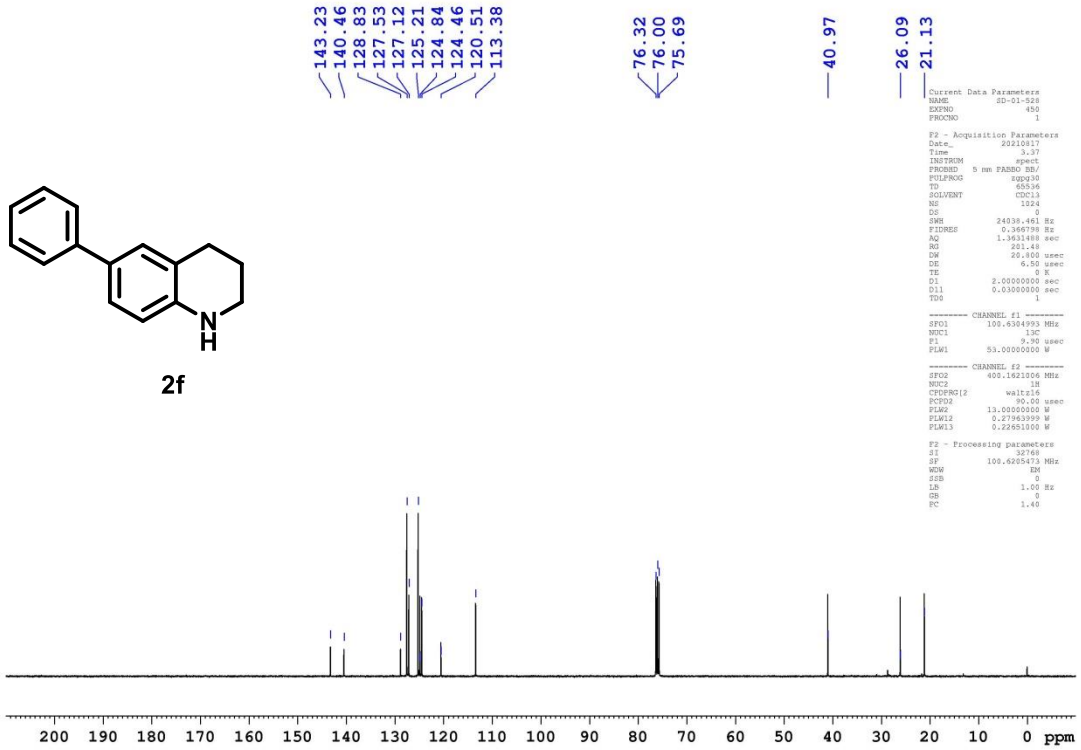


Figure S-56: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **2f**

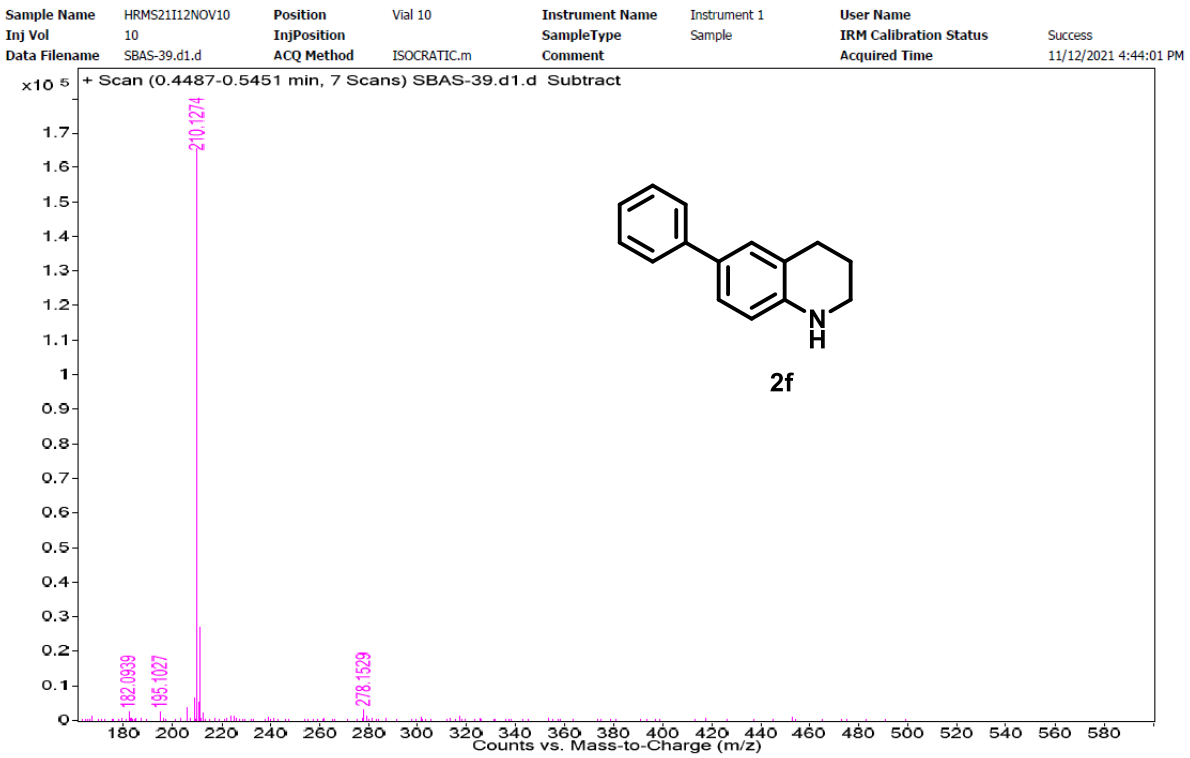


Figure S-57 HRMS spectrum of compound **2f**

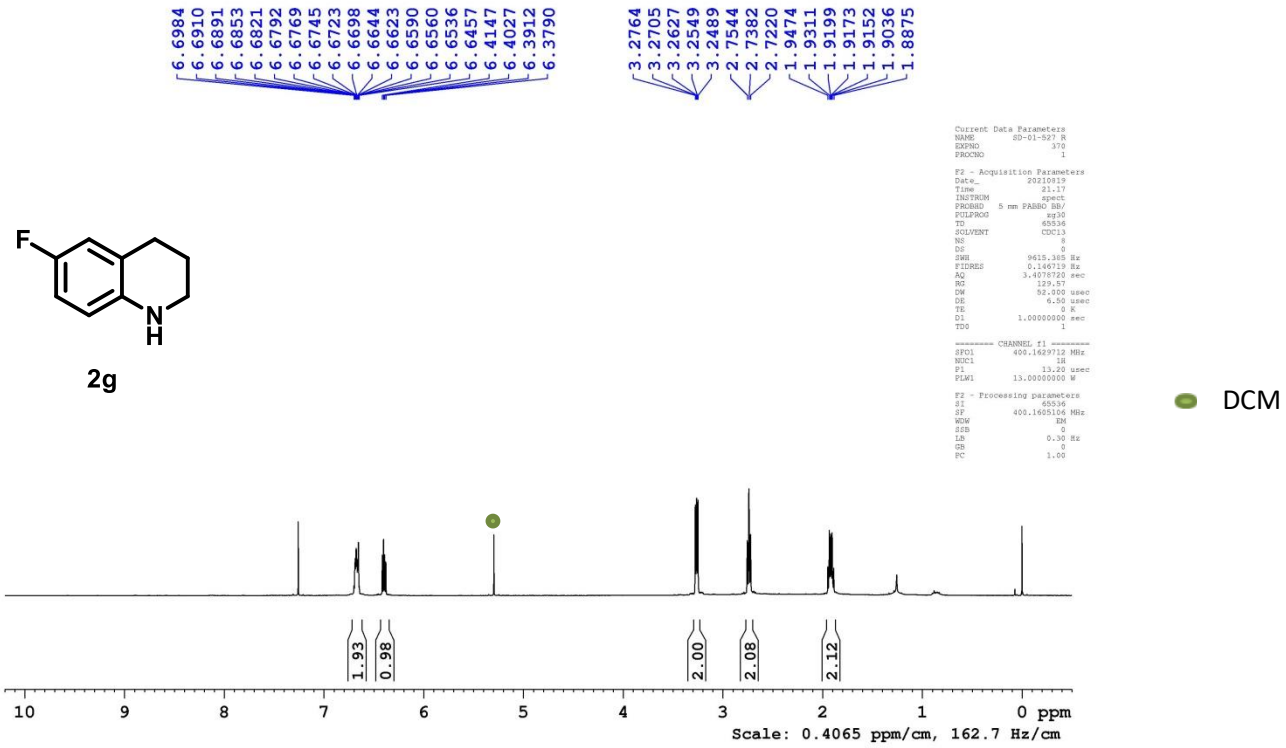


Figure S-58: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **2g**

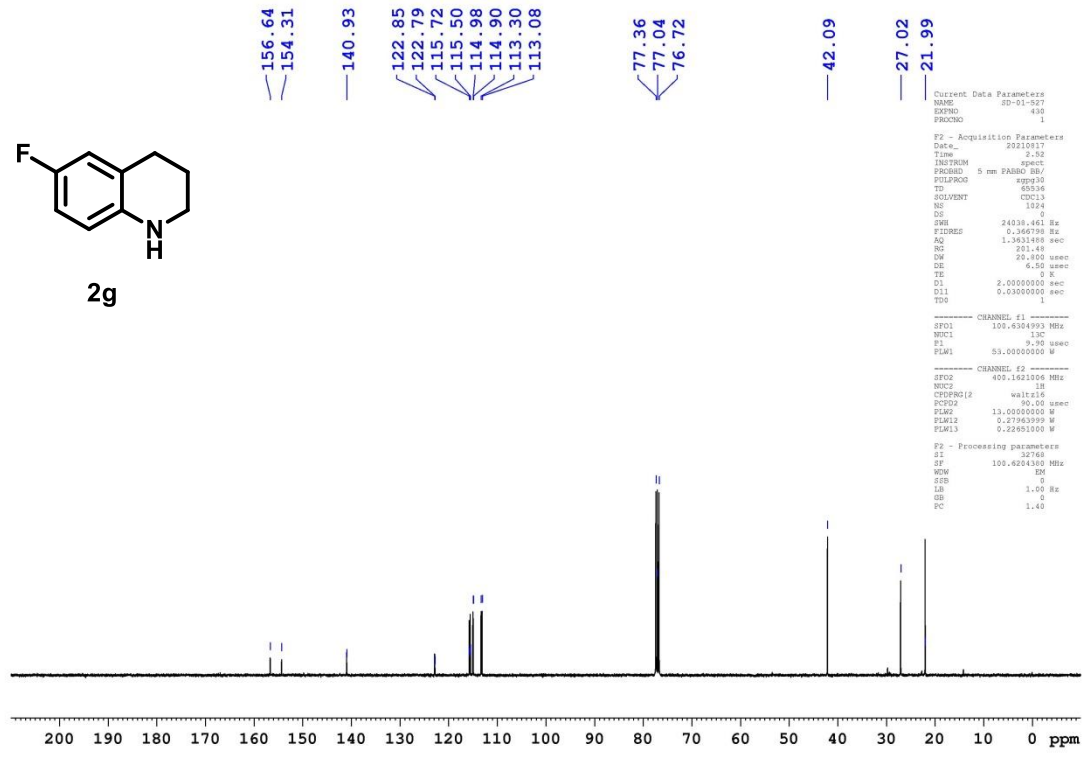


Figure S-59: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **2g**

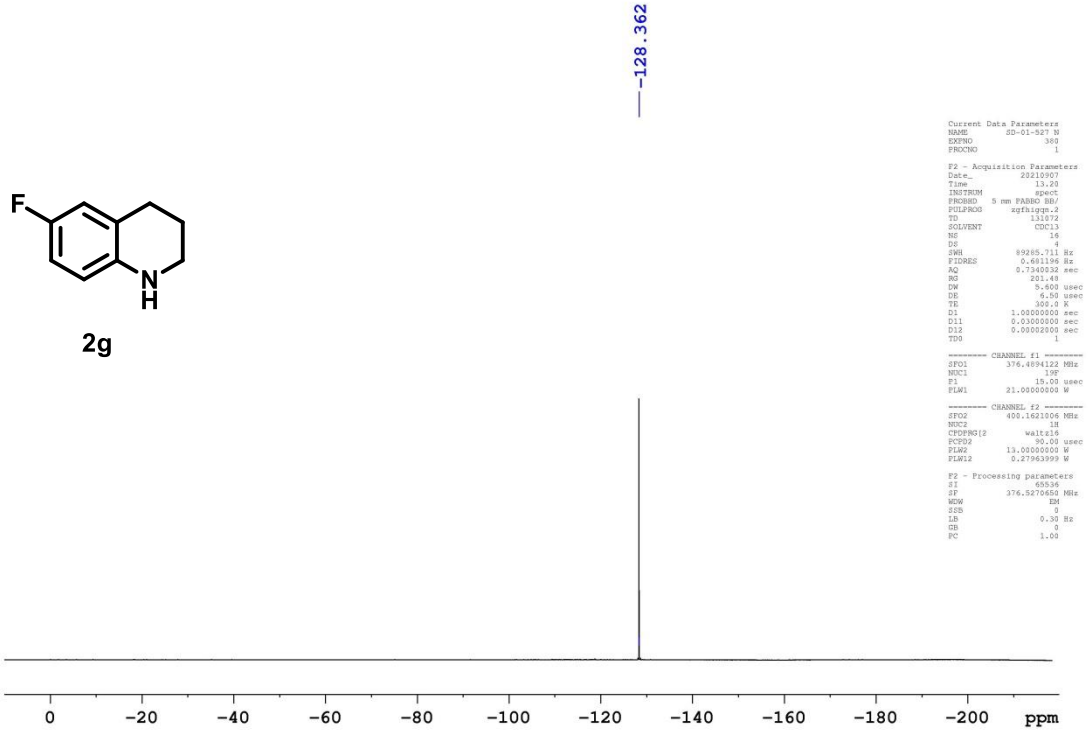


Figure S-60: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **2g**

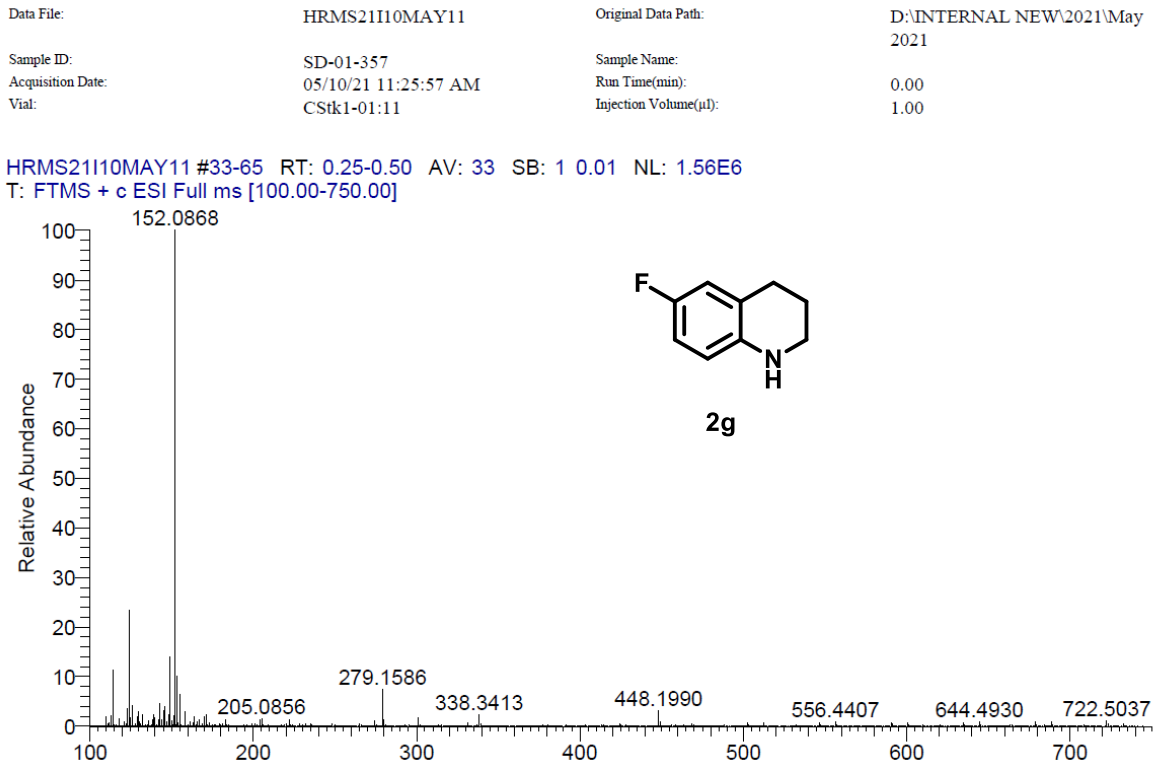


Figure S-61 HRMS spectrum of compound **2g**

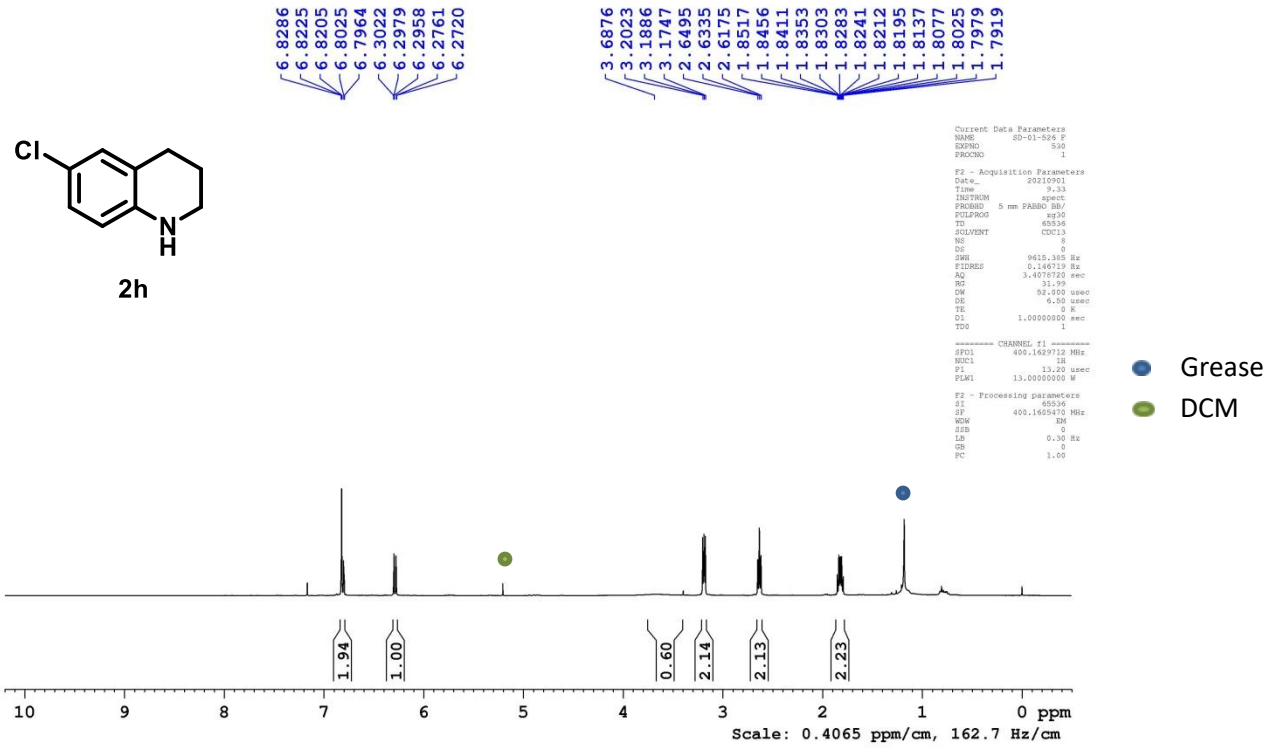


Figure S-62: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **2h**

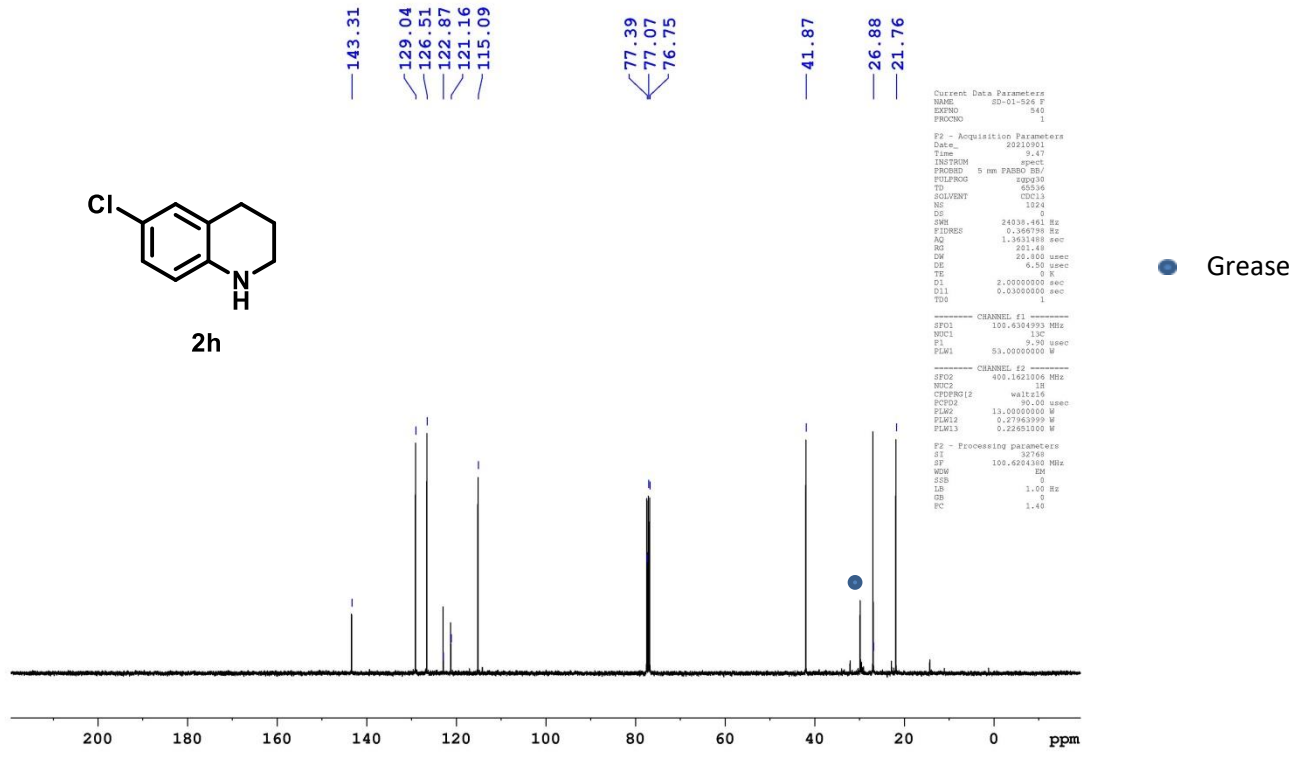


Figure S-63: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **2h**

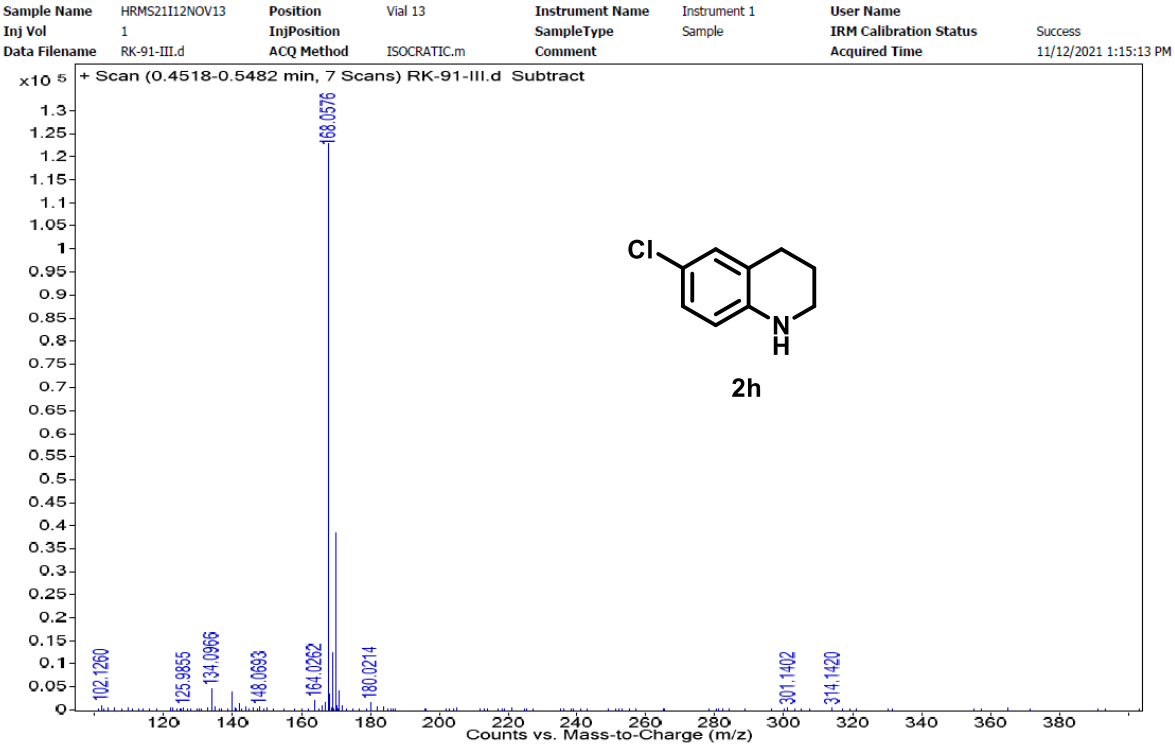


Figure S-64 HRMS spectrum of compound **2h**

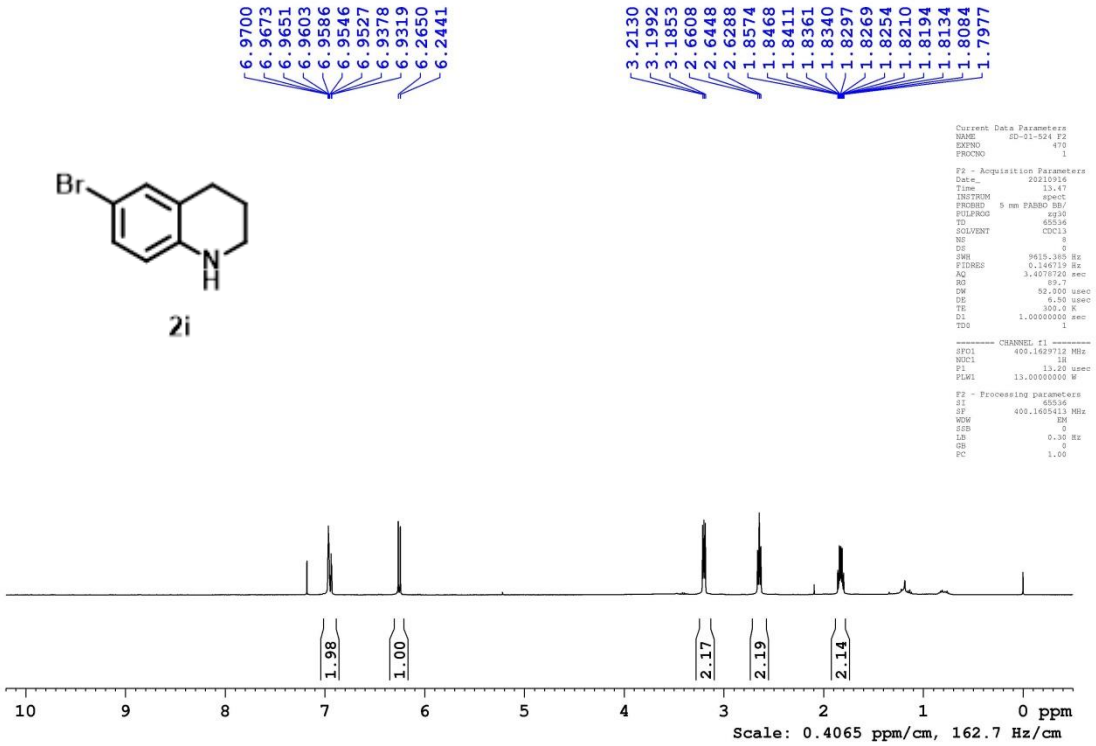


Figure S-65: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **2i**

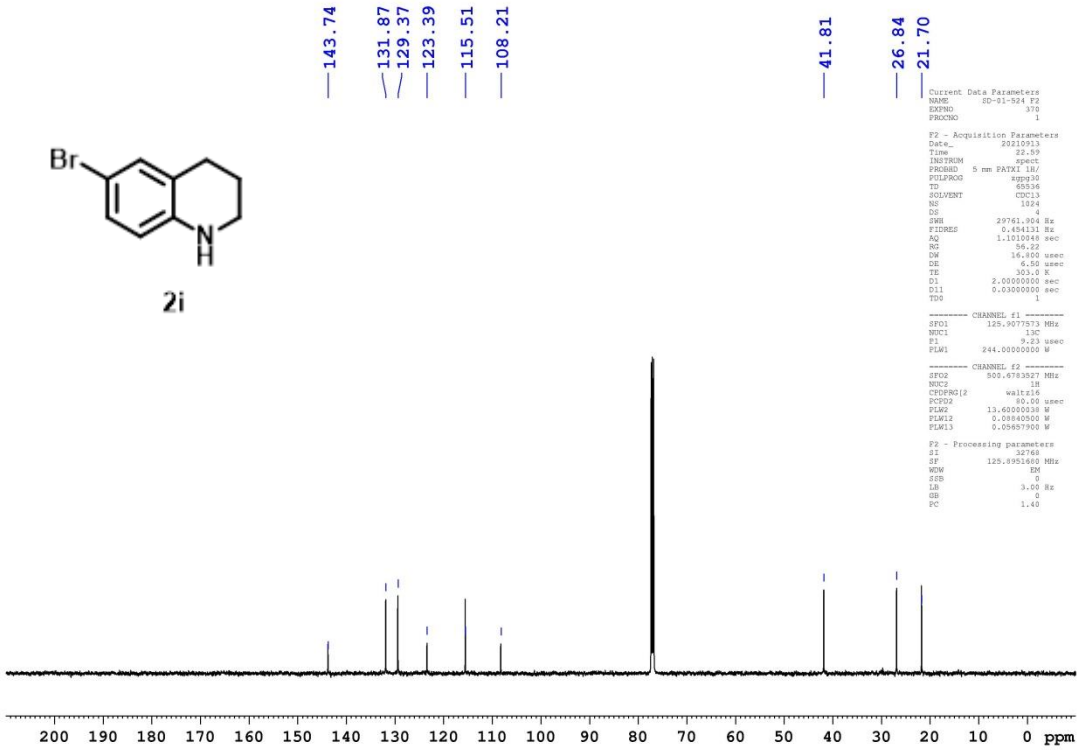


Figure S-66: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2i**

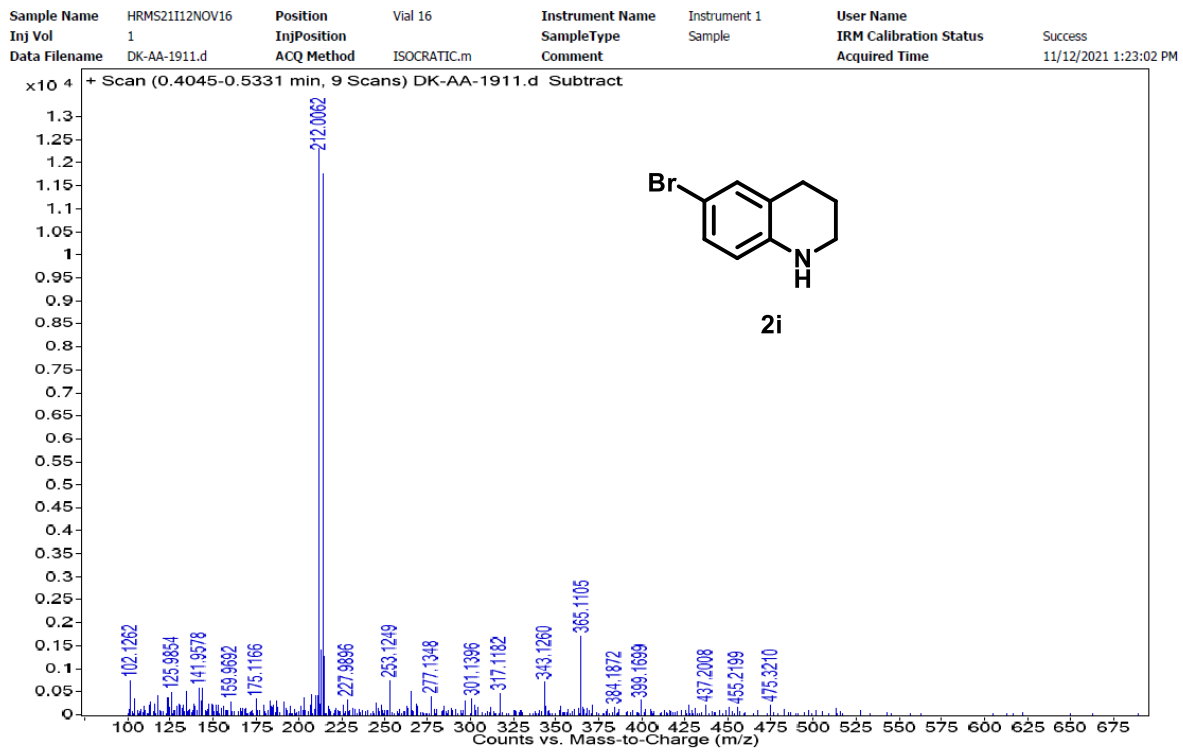


Figure S-67: HRMS spectrum of compound **2i**

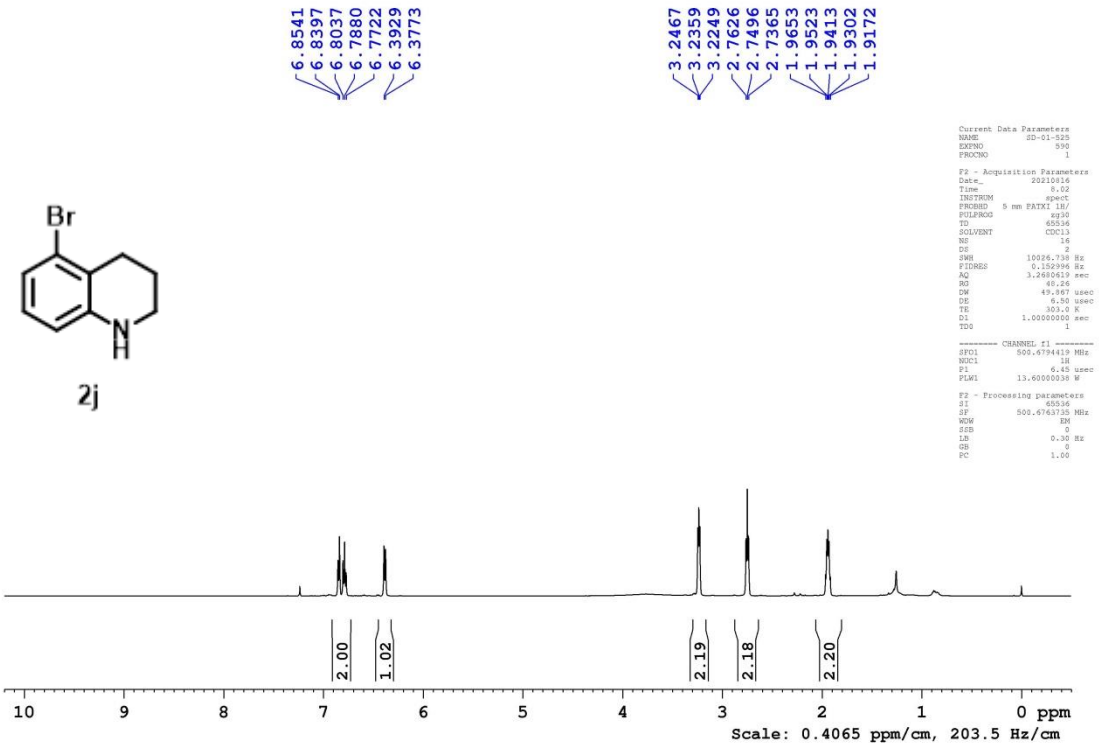


Figure S-68: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2j**

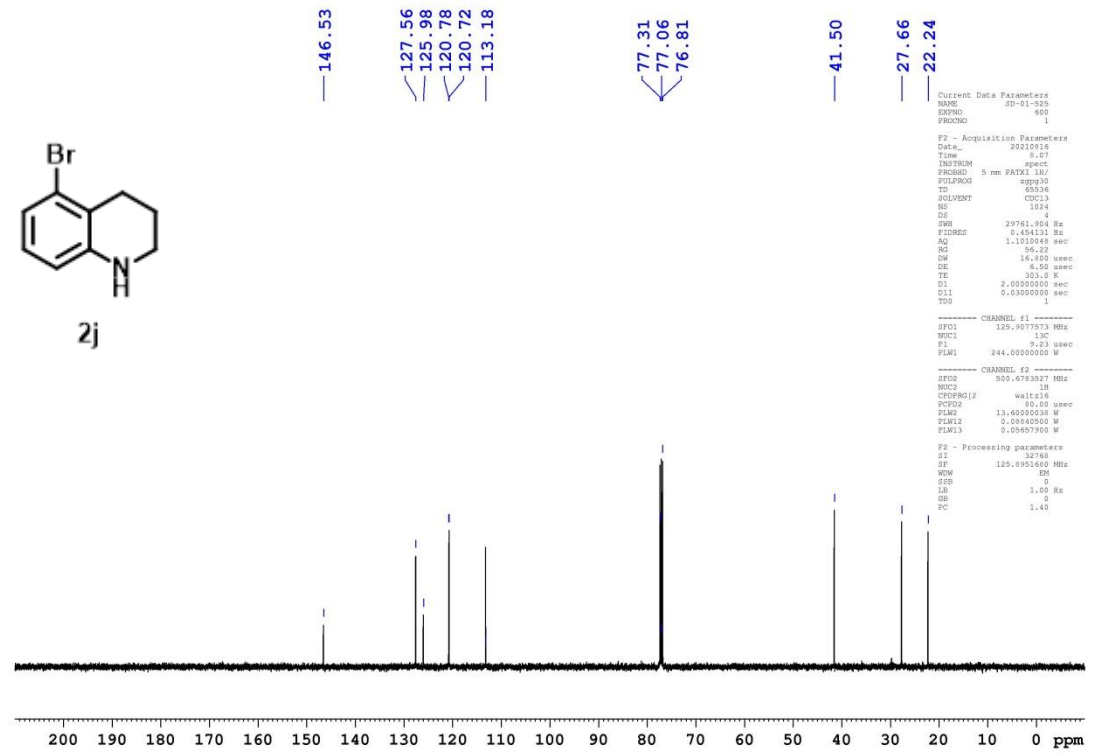


Figure S-69: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2j**

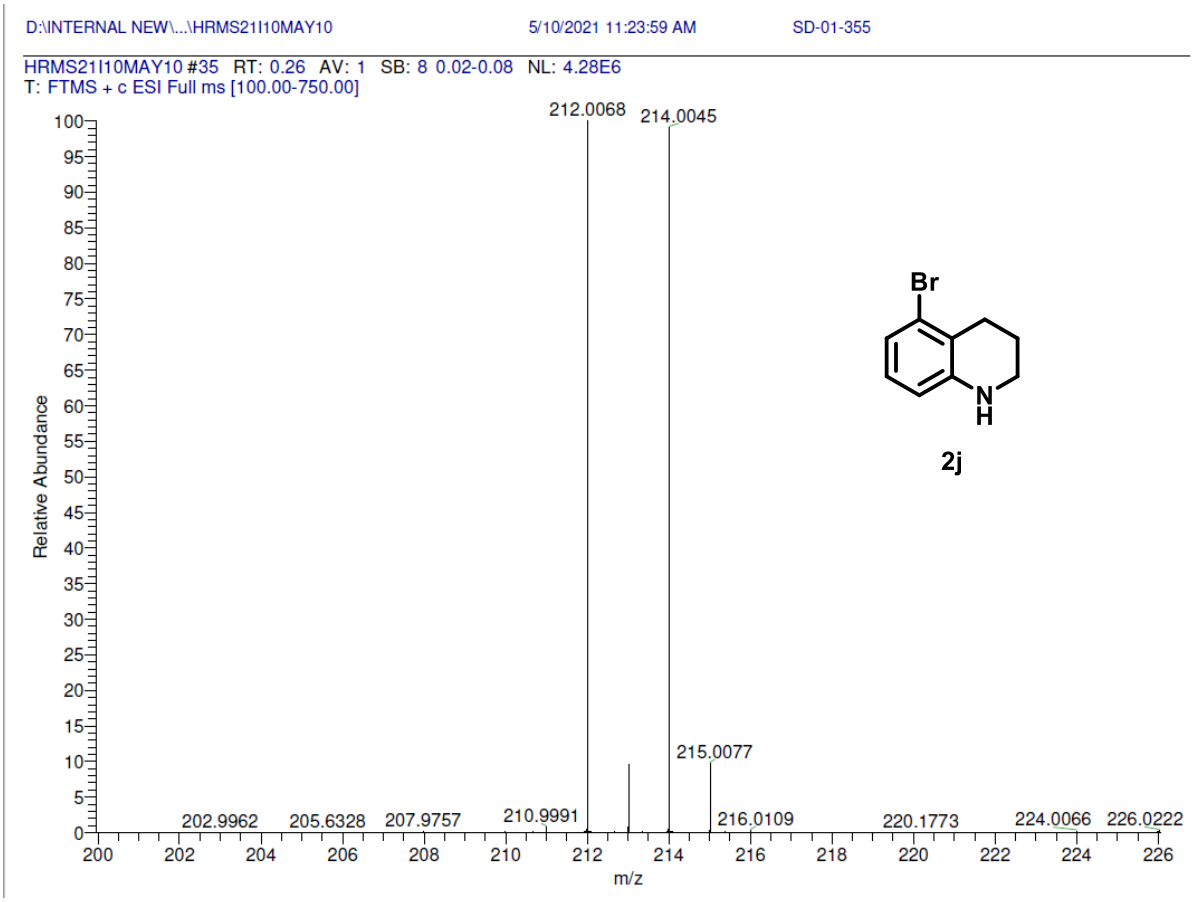


Figure S-70: HRMS spectrum of compound **2j**

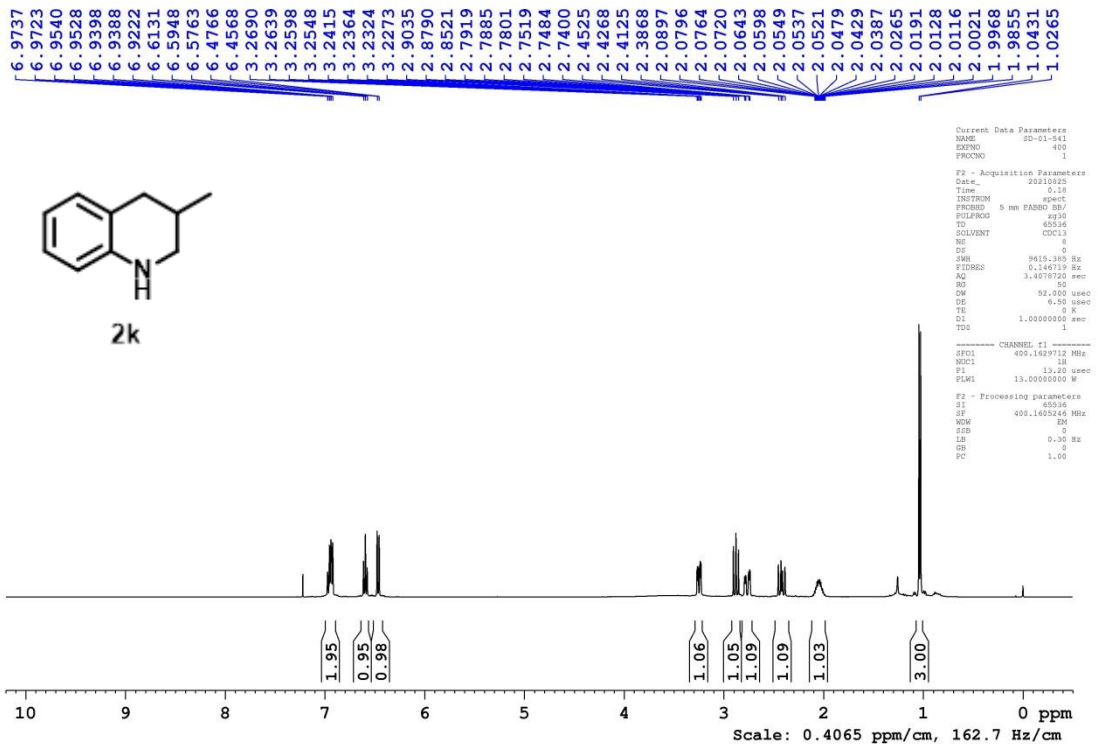


Figure S-71: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **2k**

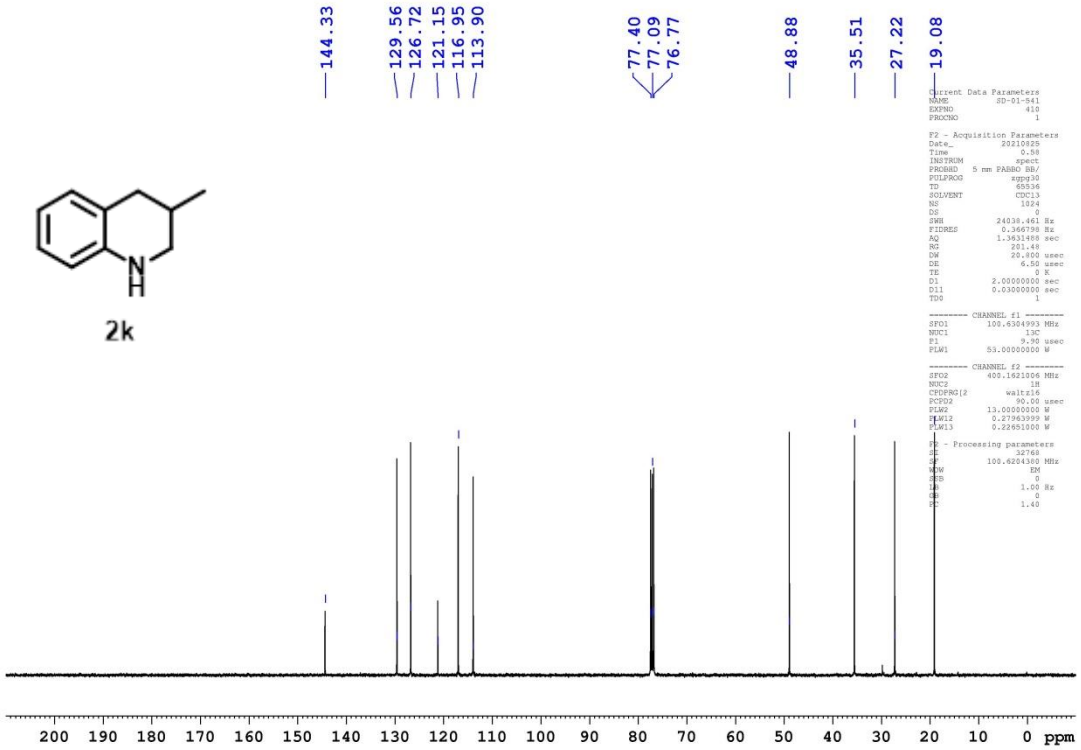


Figure S-72: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **2k**

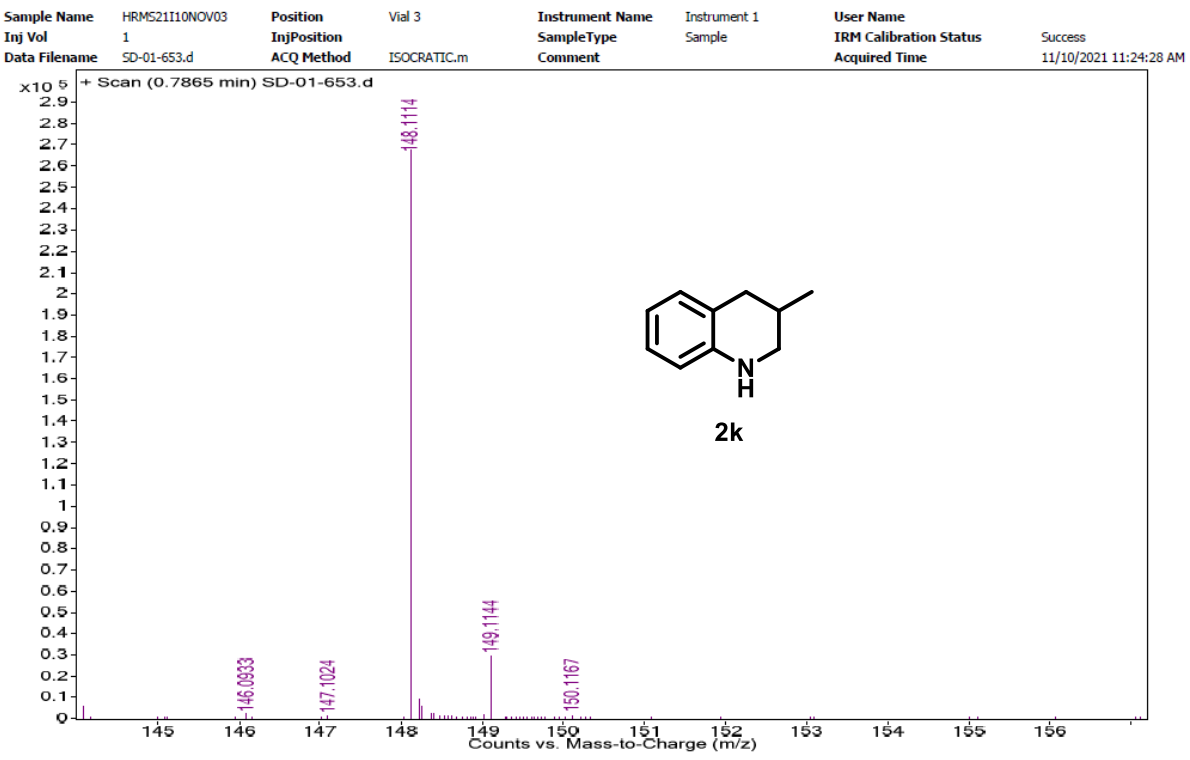


Figure S-73: HRMS spectrum of compound **2k**

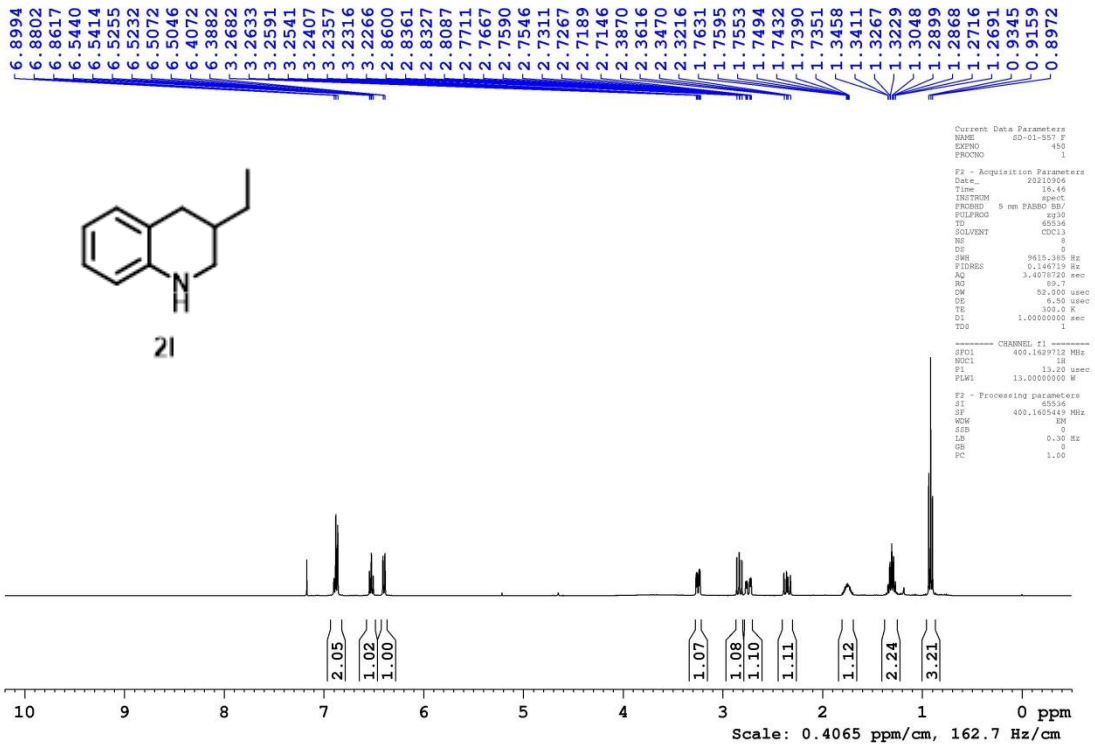


Figure S-74: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **2l**

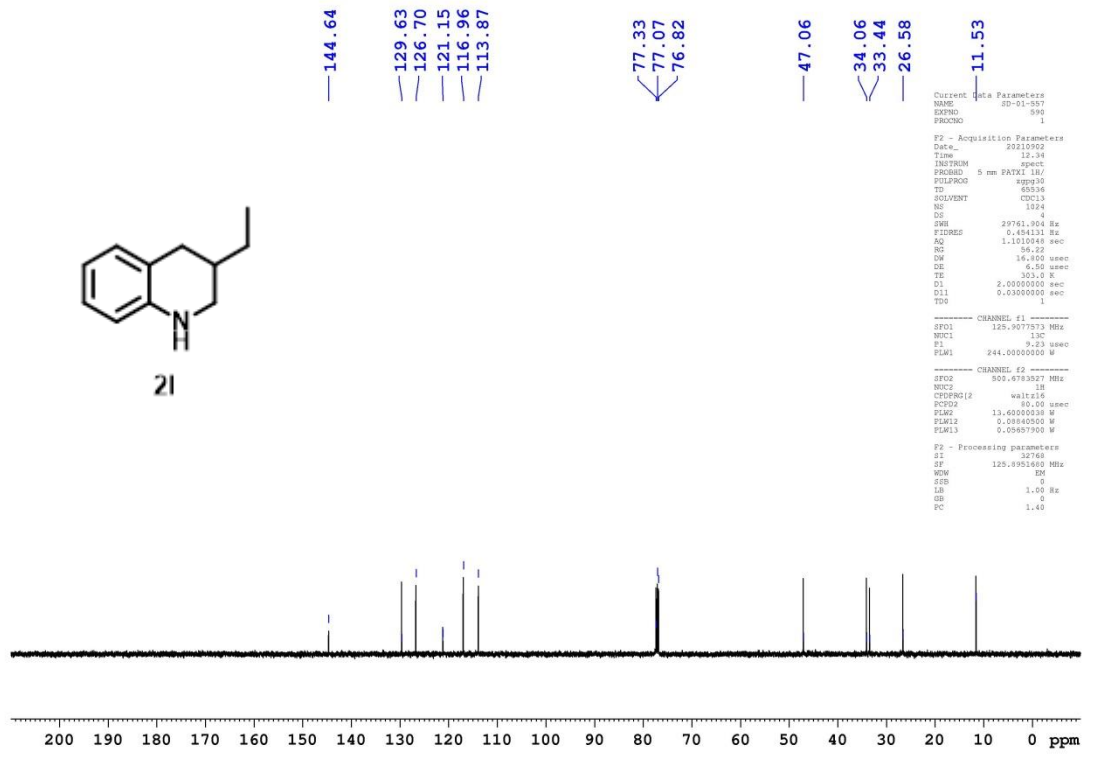


Figure S-75: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2l**

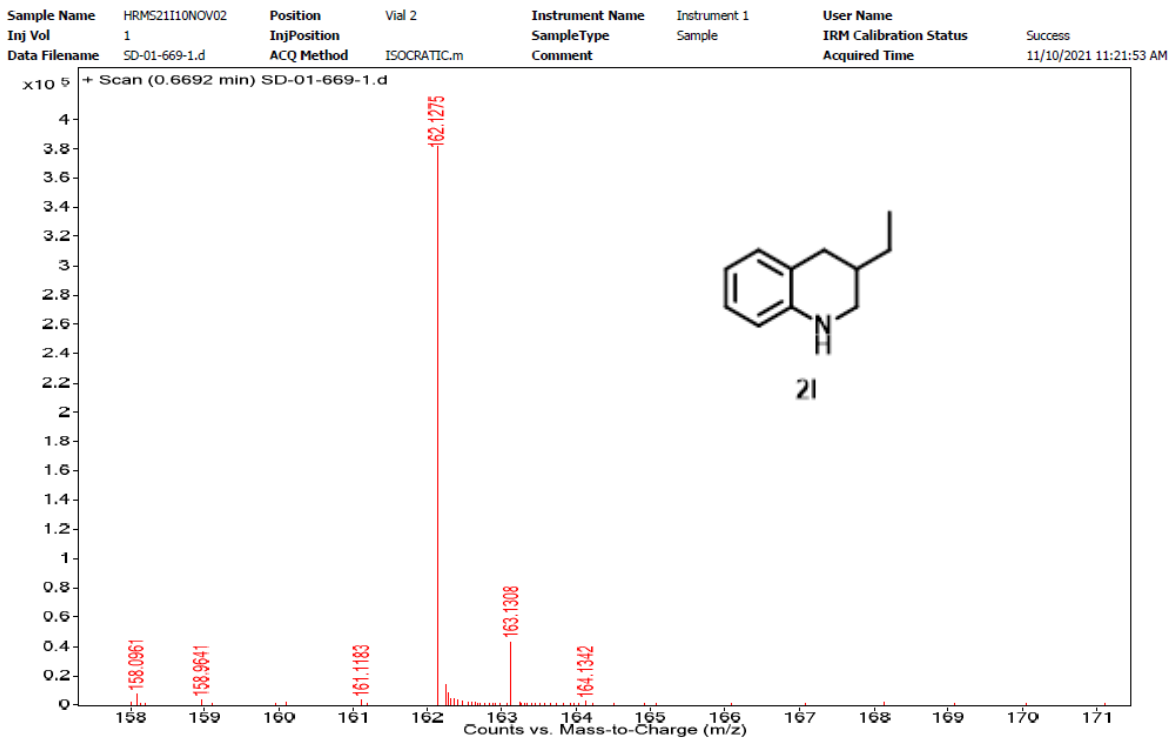


Figure S-76: HRMS spectrum of compound **2l**

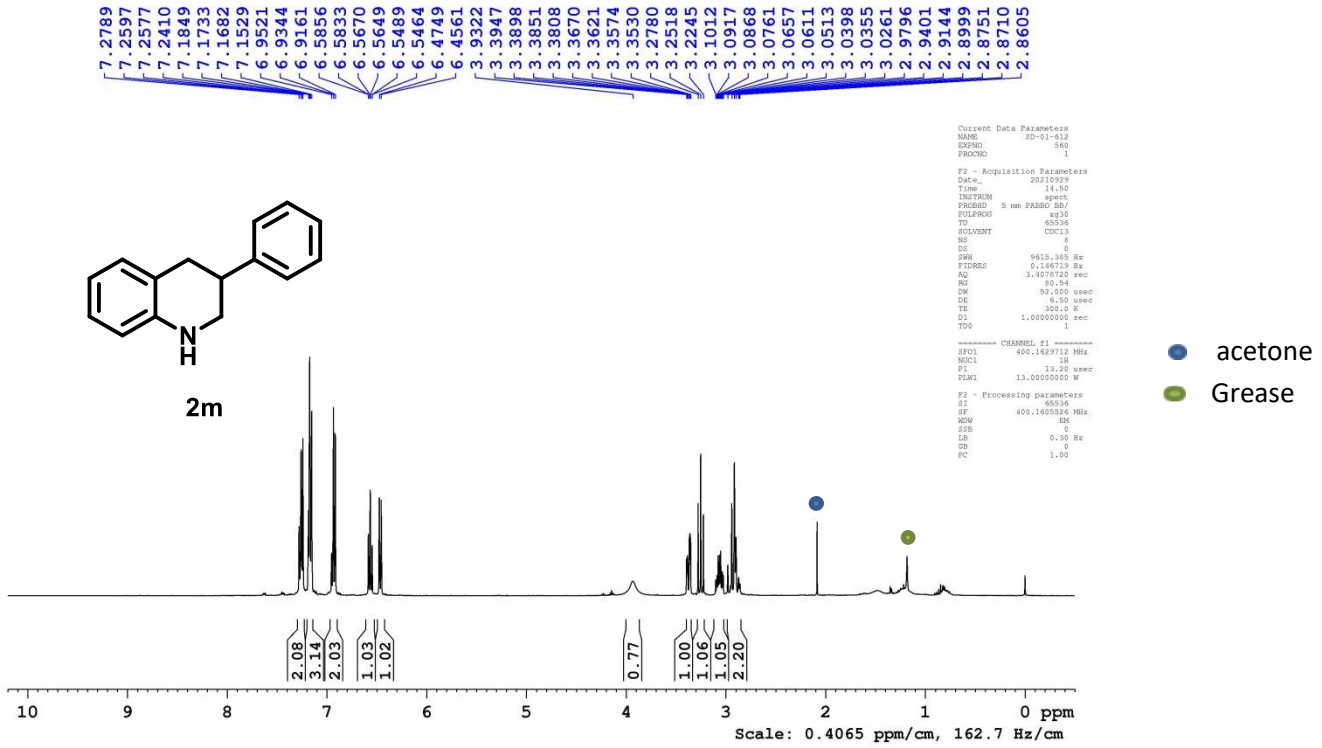


Figure S-77: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **2m**

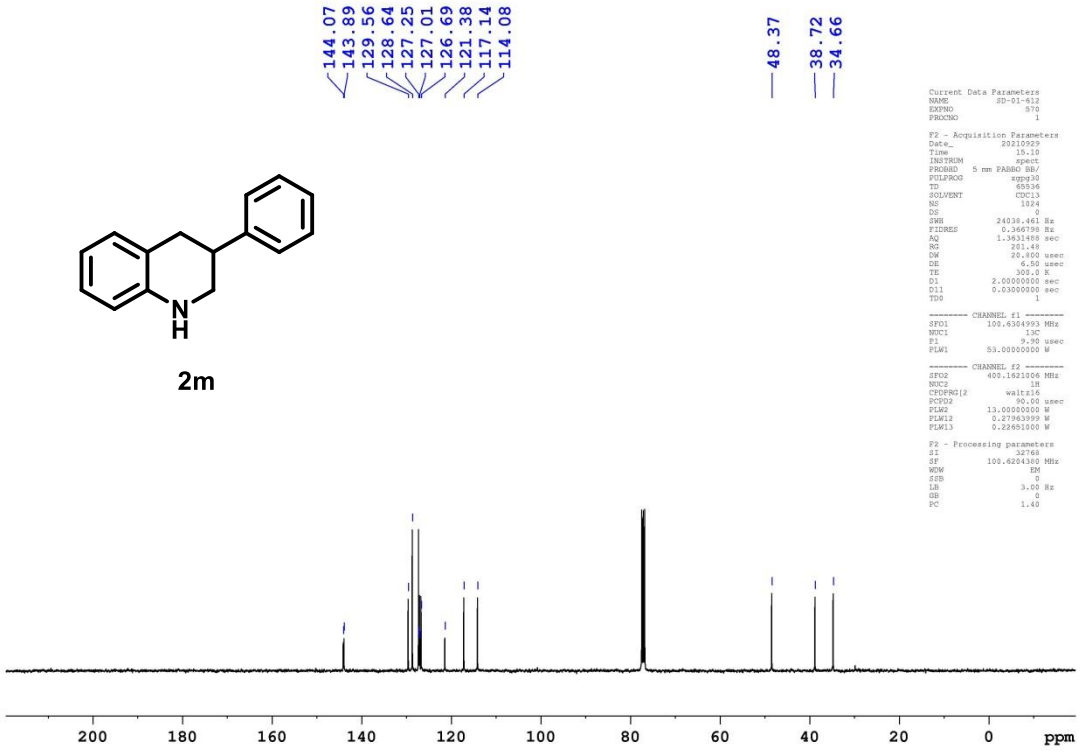


Figure S-78: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **2m**

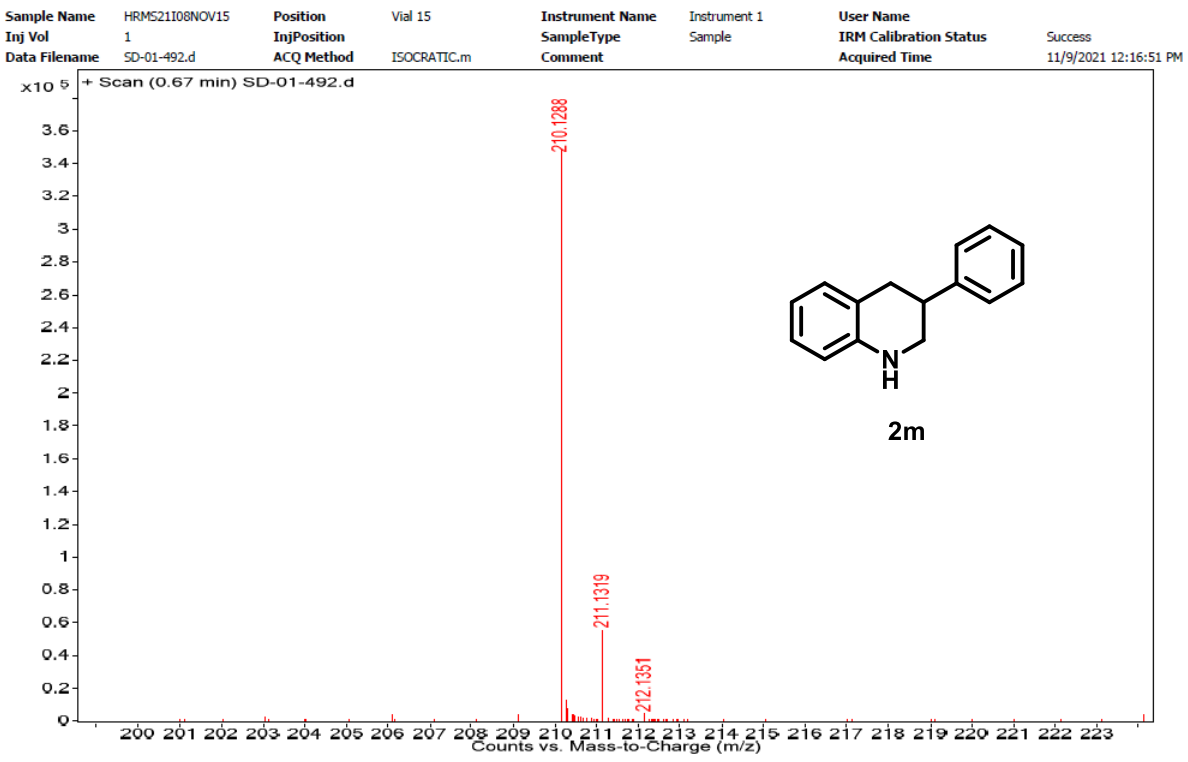


Figure S-79: HRMS spectrum of compound **2m**

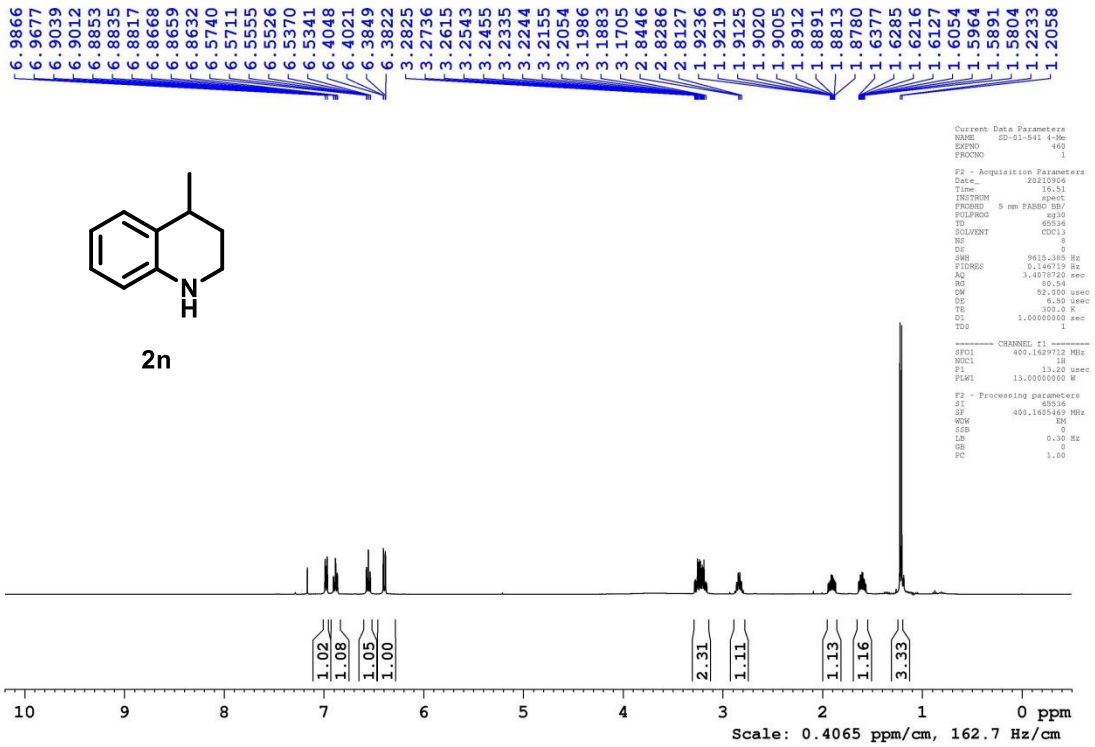


Figure S-80: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **2n**

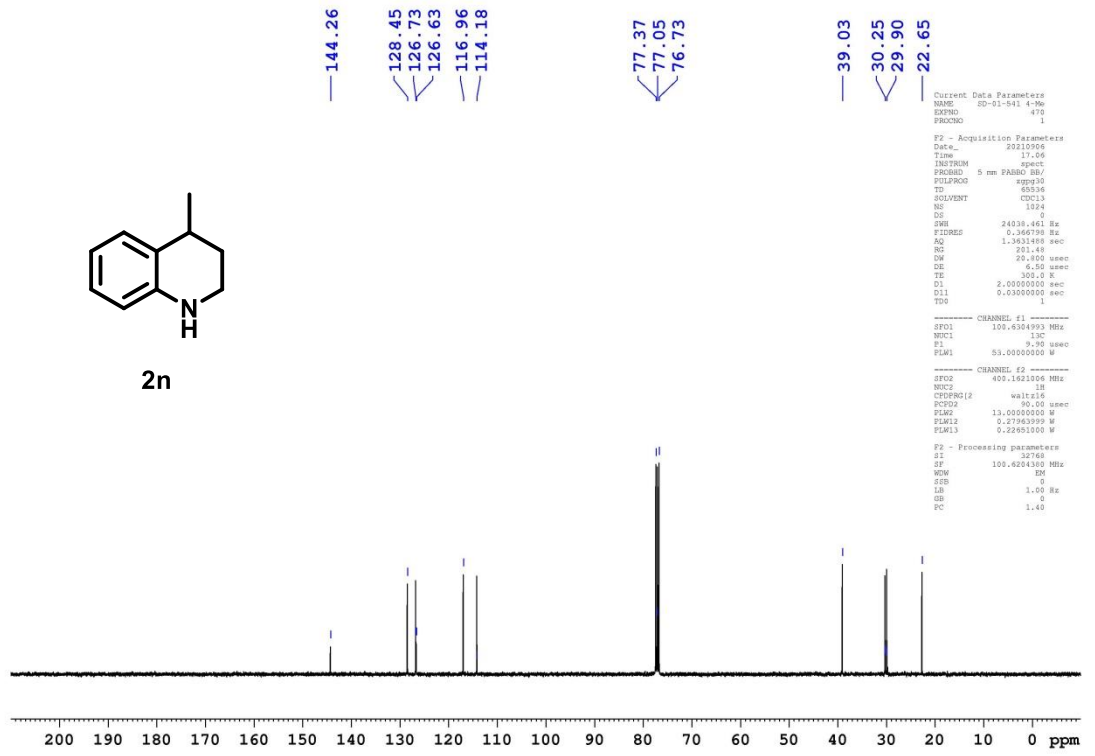


Figure S-81: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **2n**

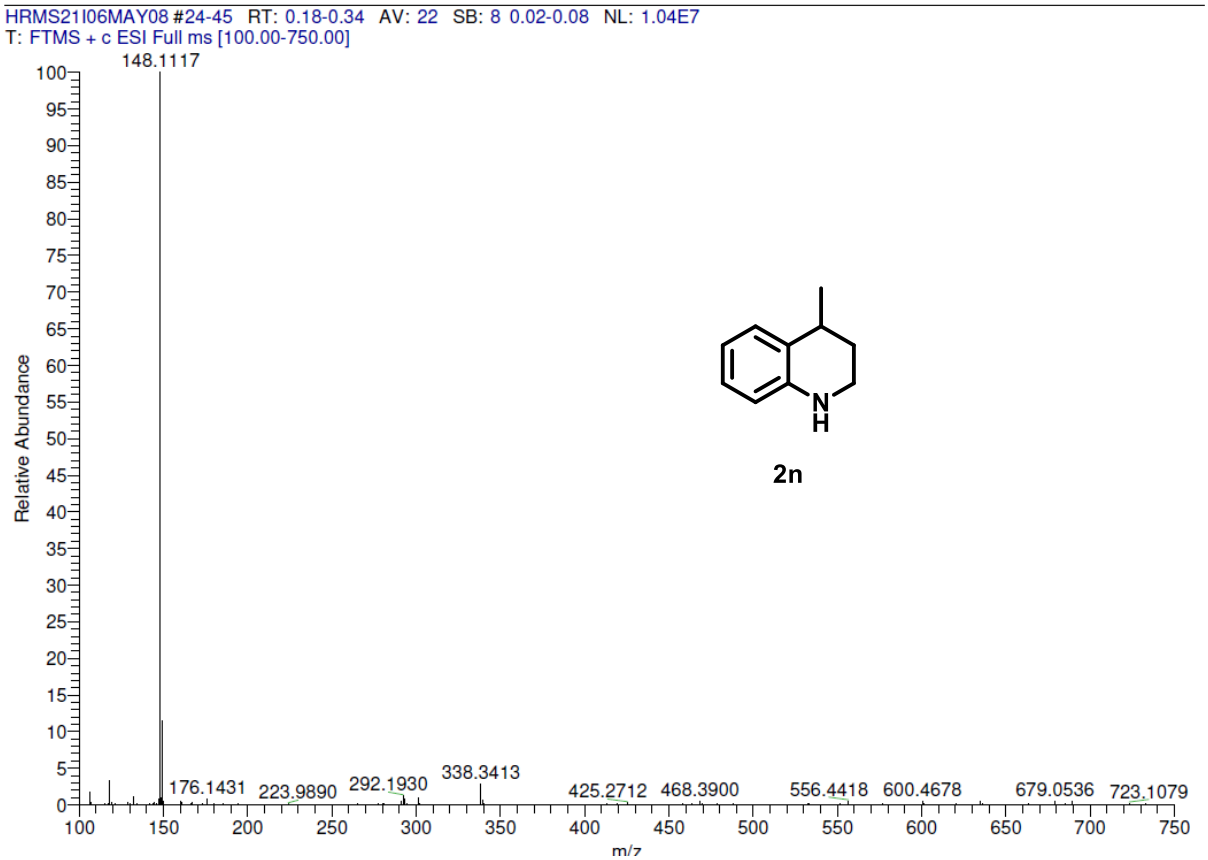


Figure S-82: HRMS spectrum of compound **2n**

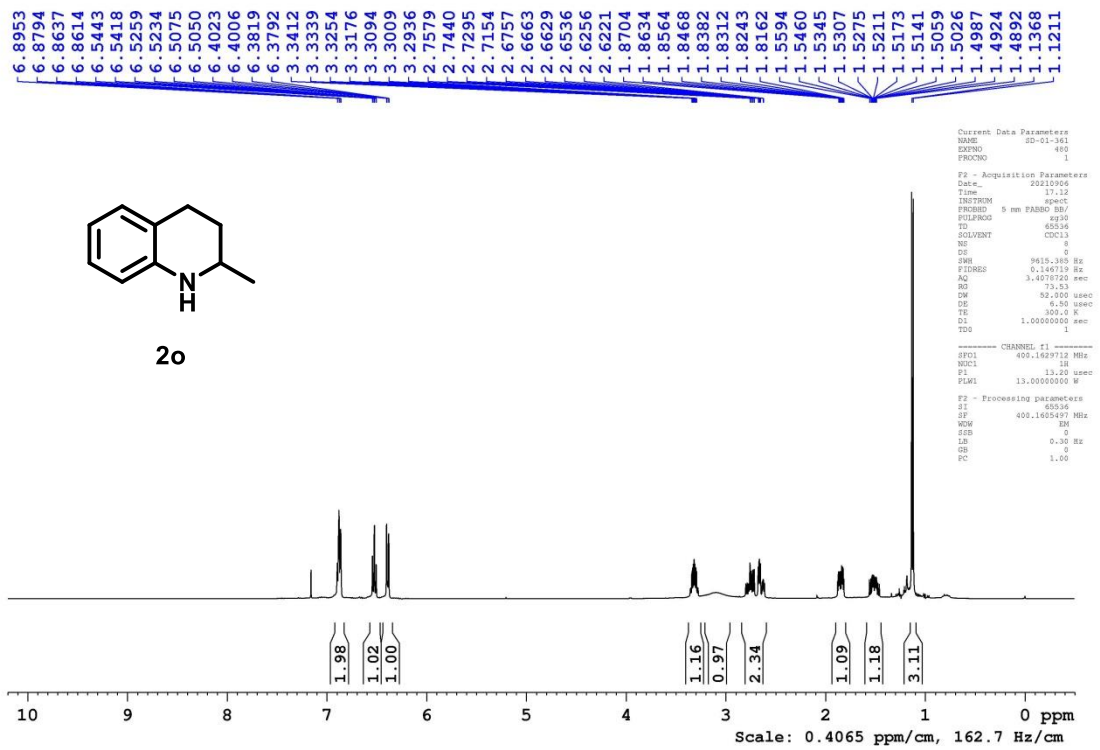


Figure S-83: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **2o**

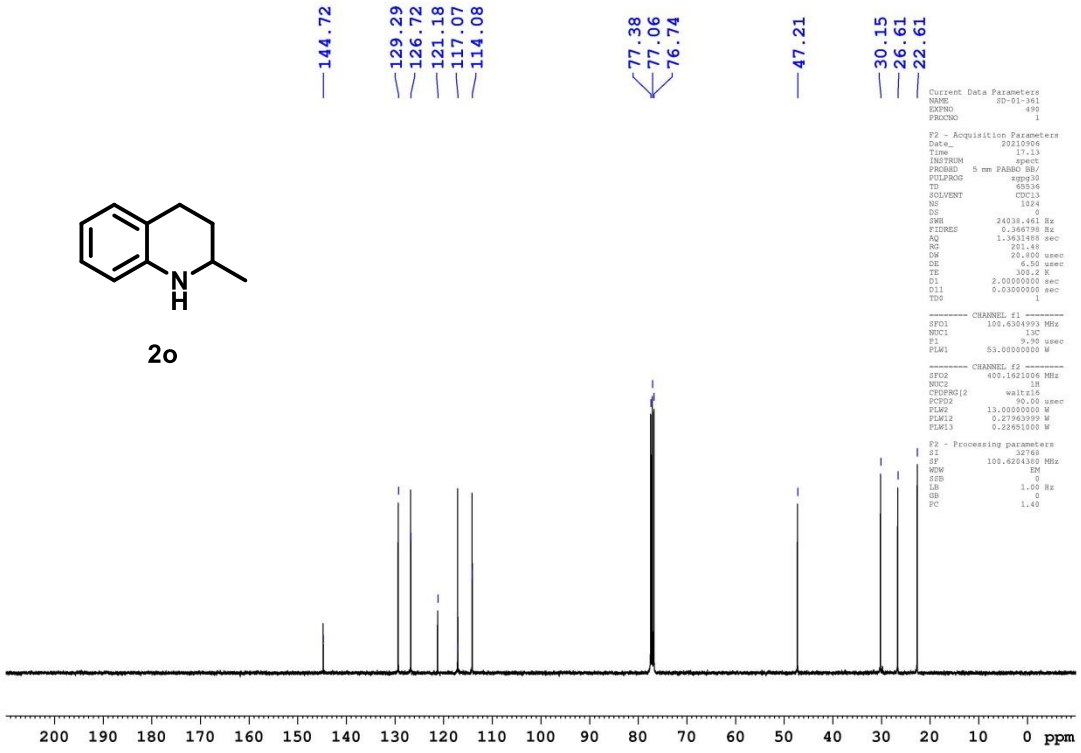


Figure S-84: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **2o**

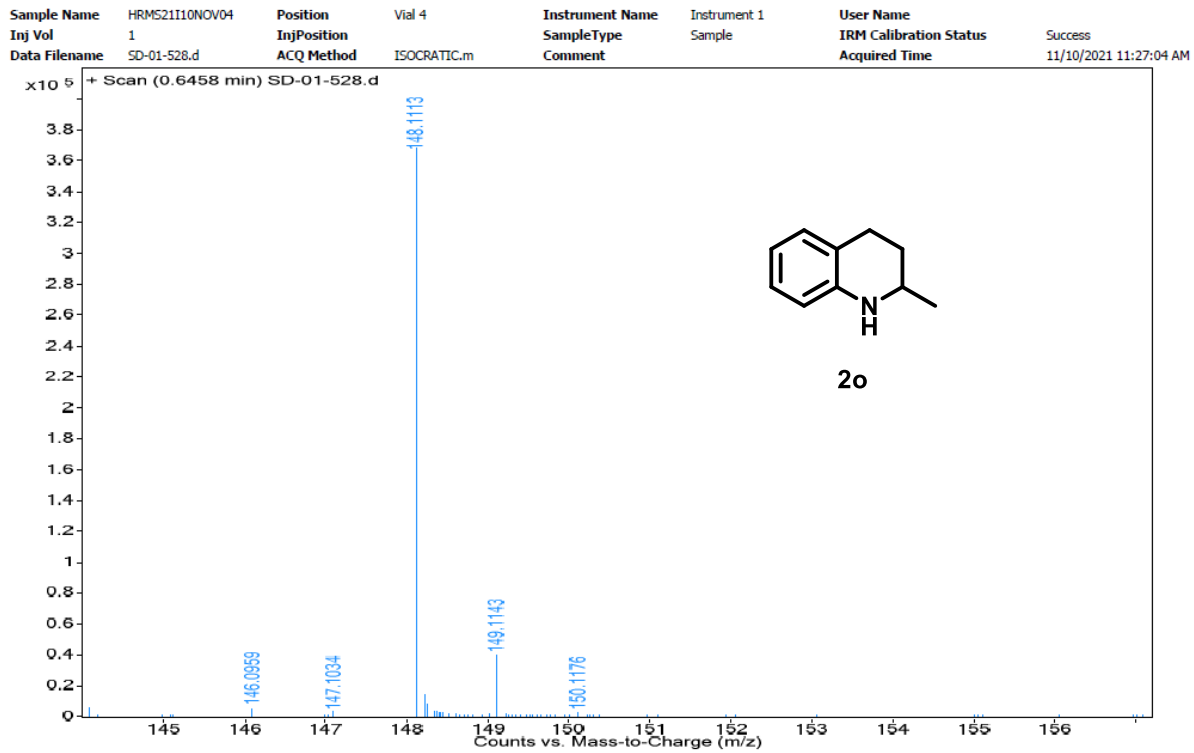


Figure S-85: HRMS spectrum of compound **2o**

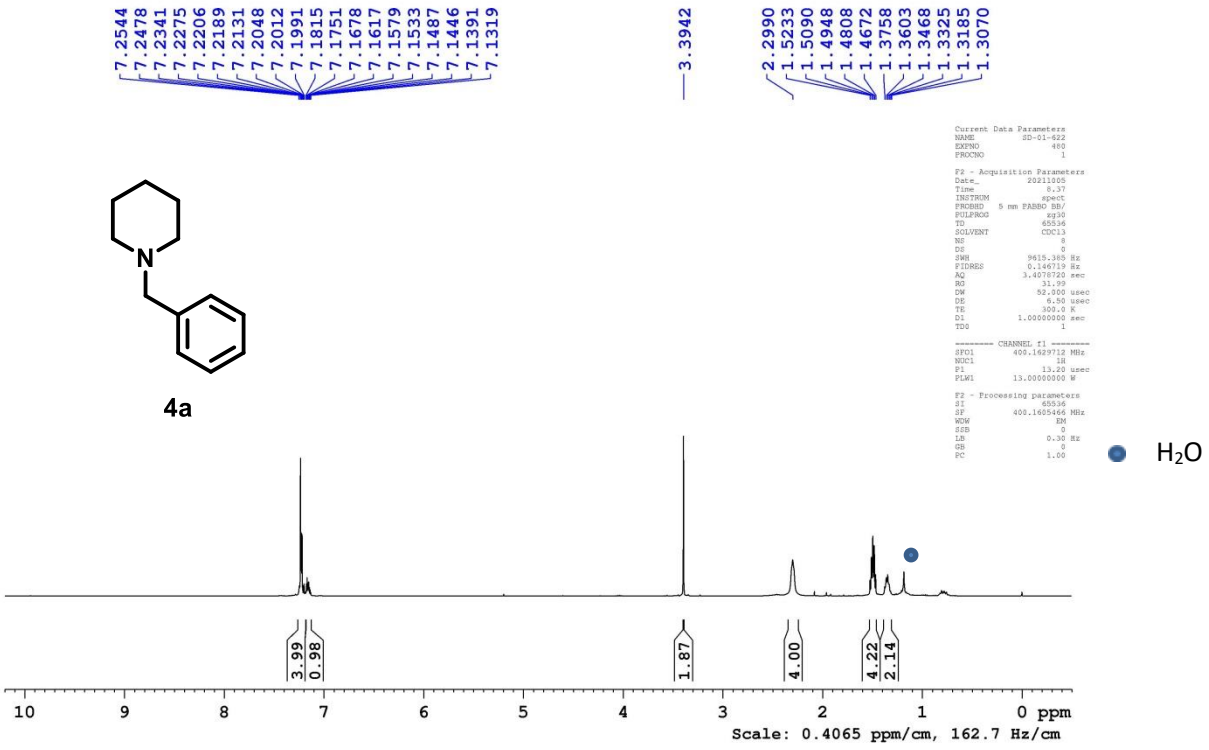


Figure S-86: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4a**

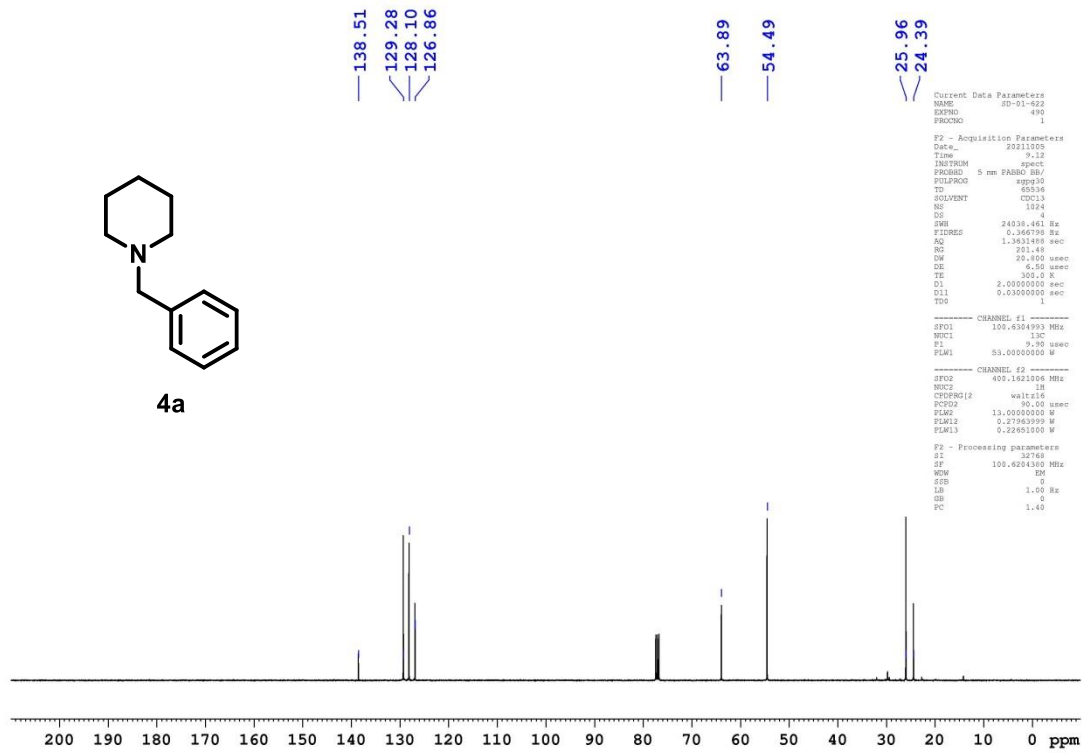


Figure S-87: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4a**

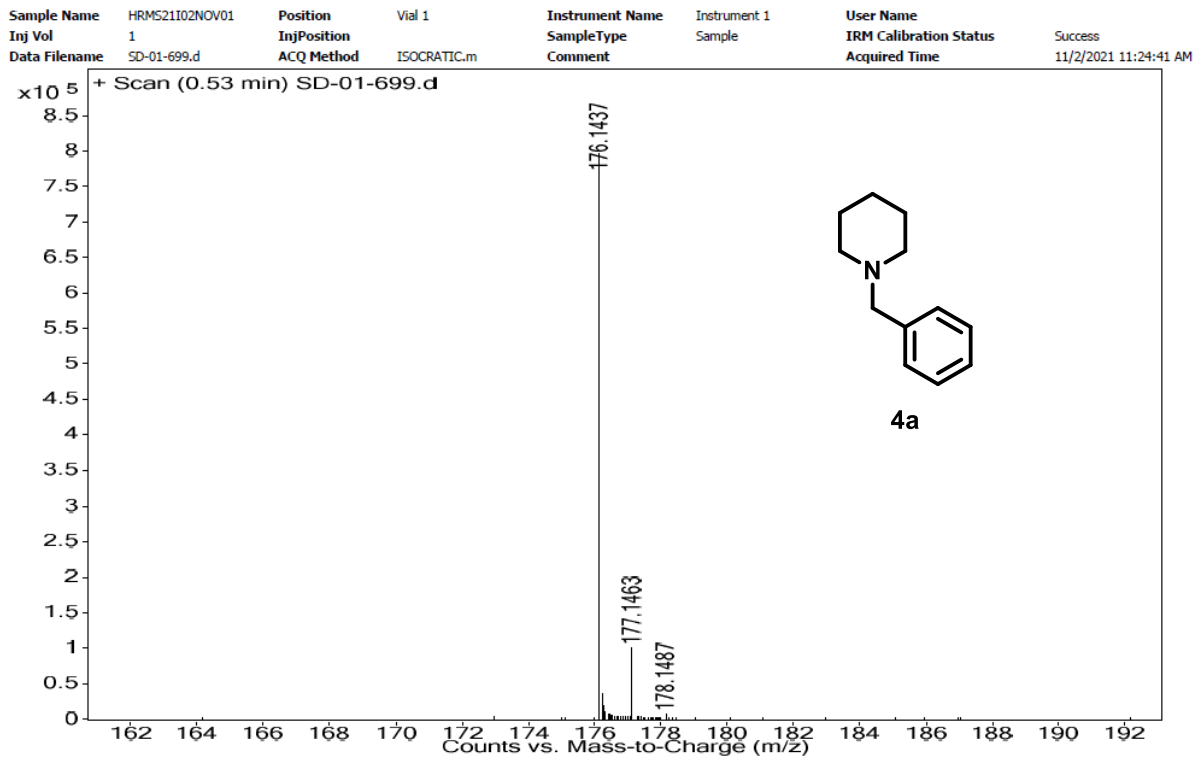


Figure S-88: HRMS spectrum of compound **4a**

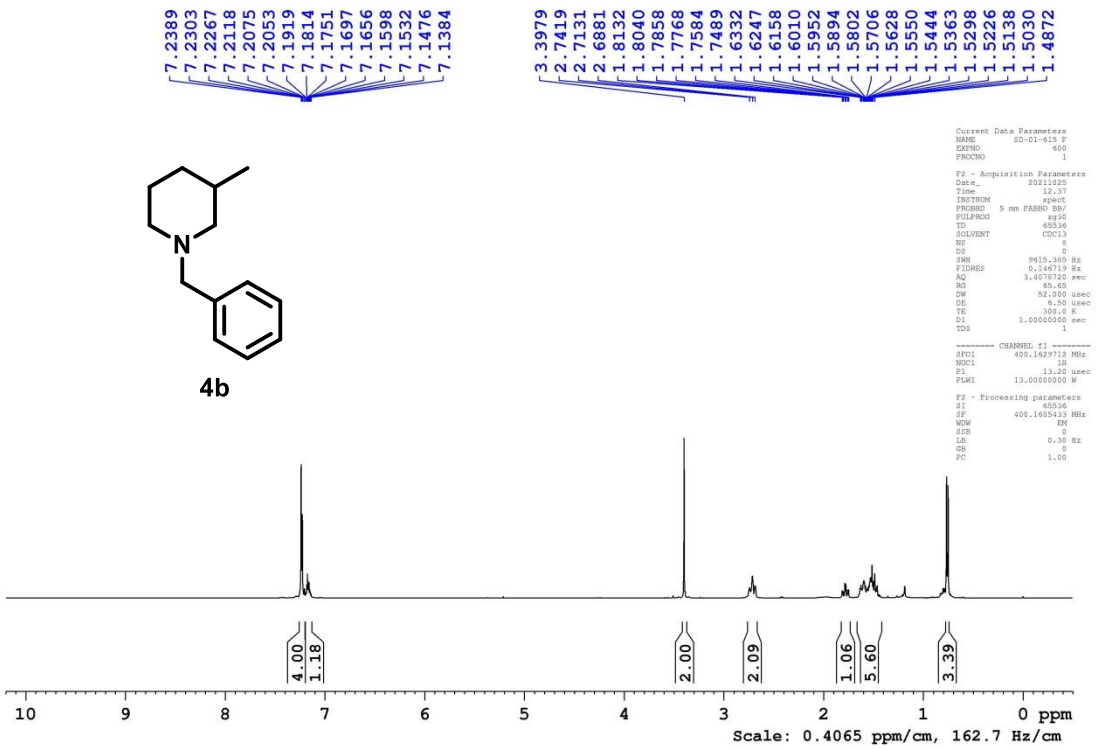


Figure S-89: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4b**

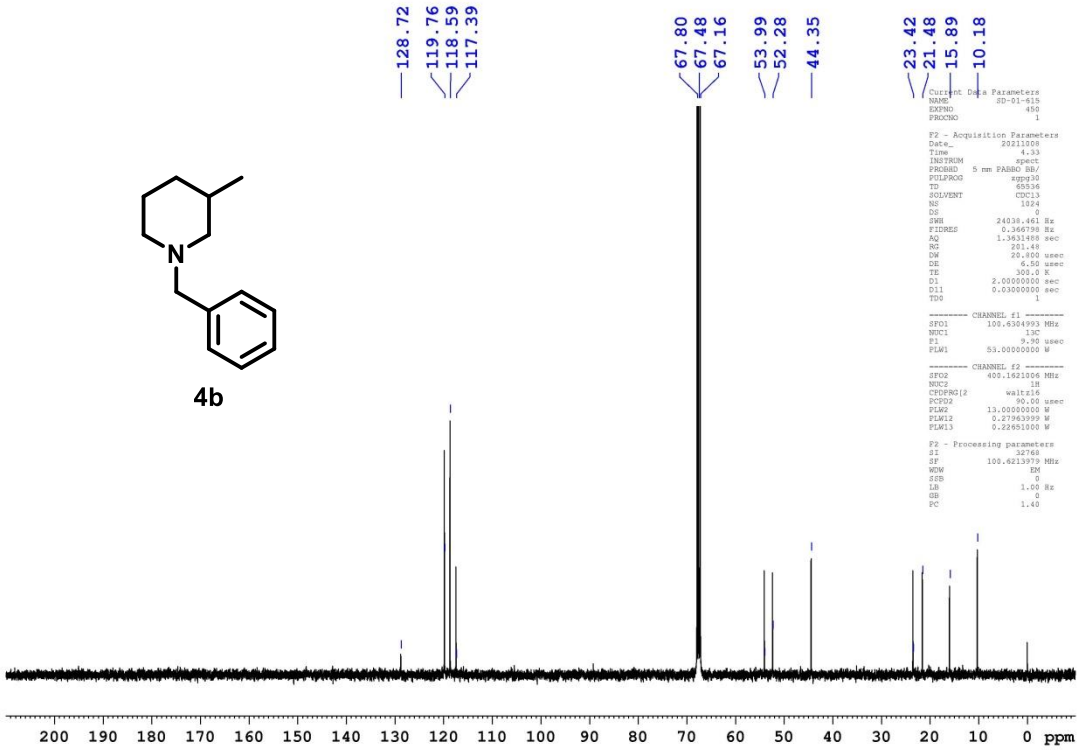


Figure S-90: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4b**

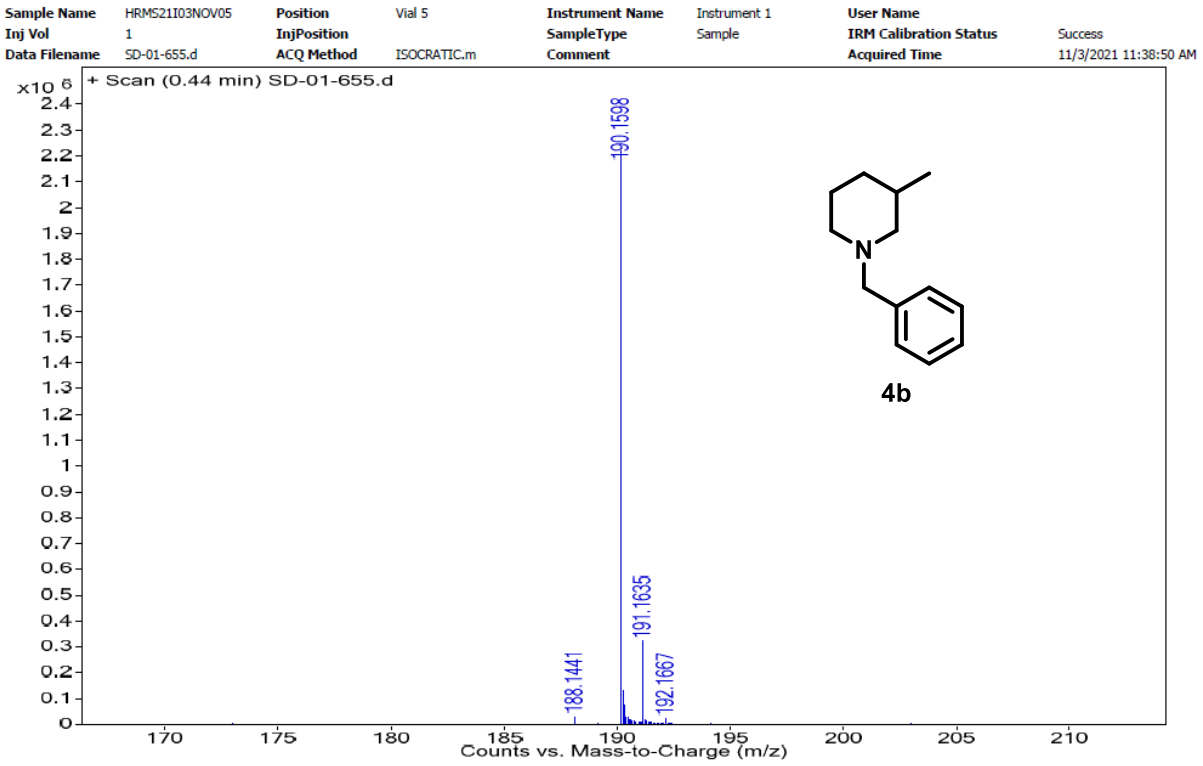


Figure S-91: HRMS spectrum of compound **4b**

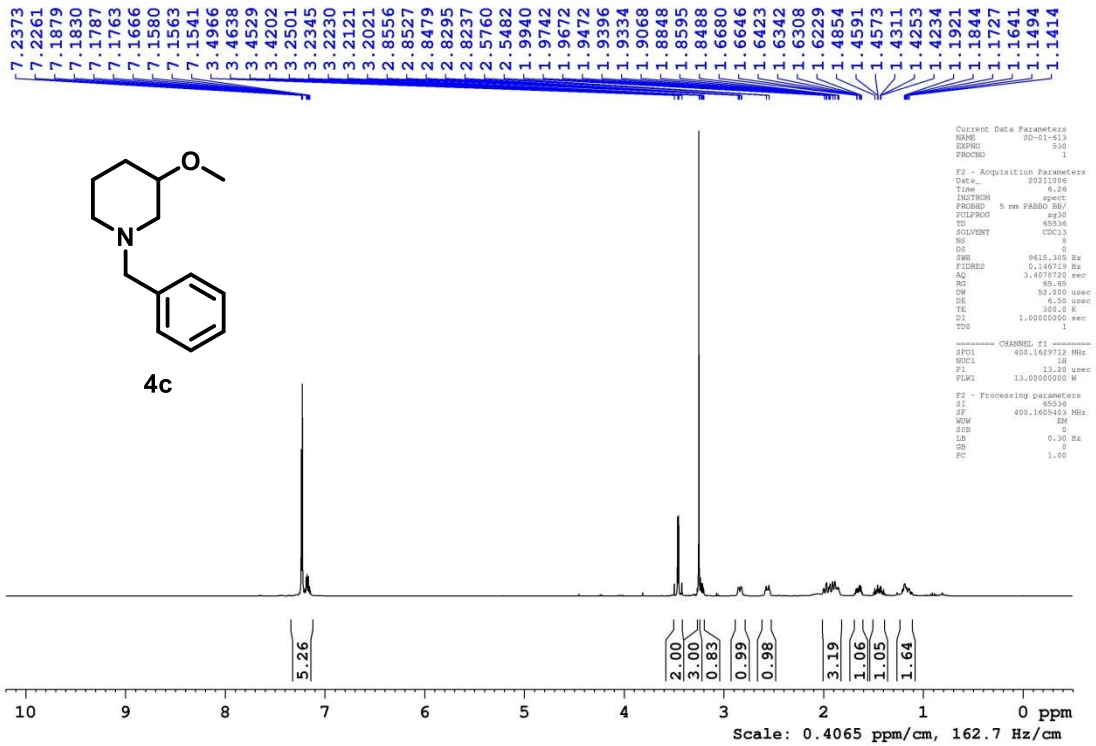


Figure S-92: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4c**

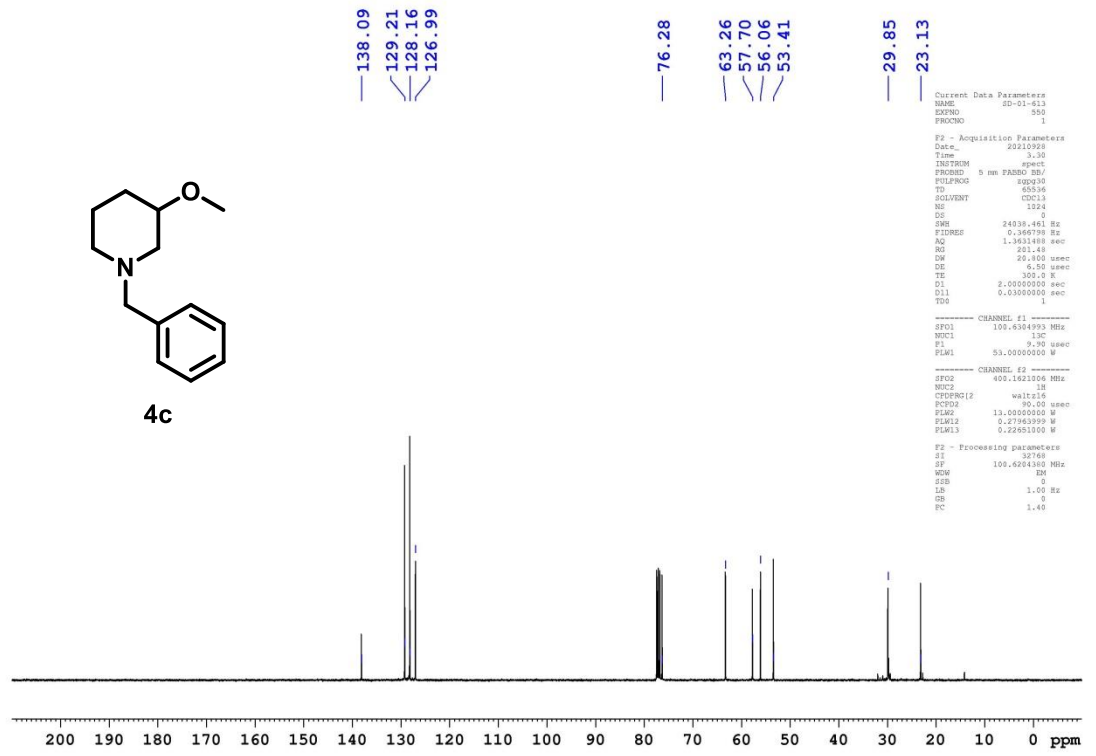


Figure S-93: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4c**

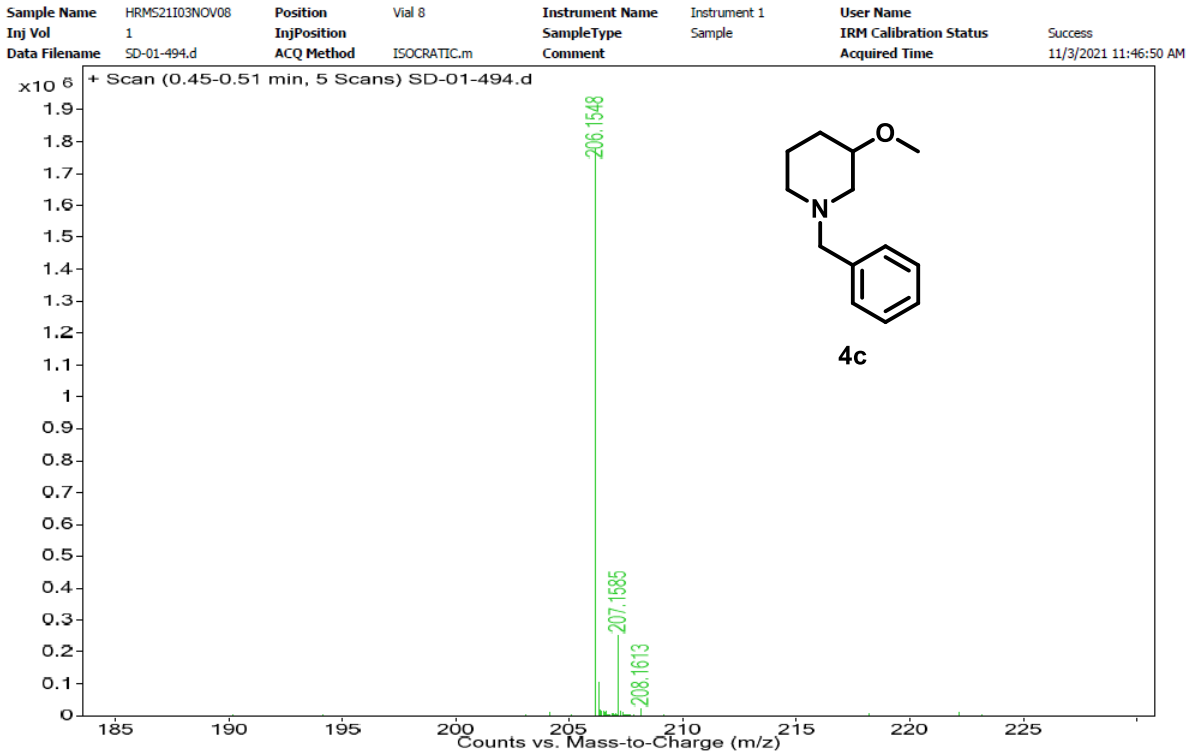


Figure S-94: HRMS spectrum of compound **4c**

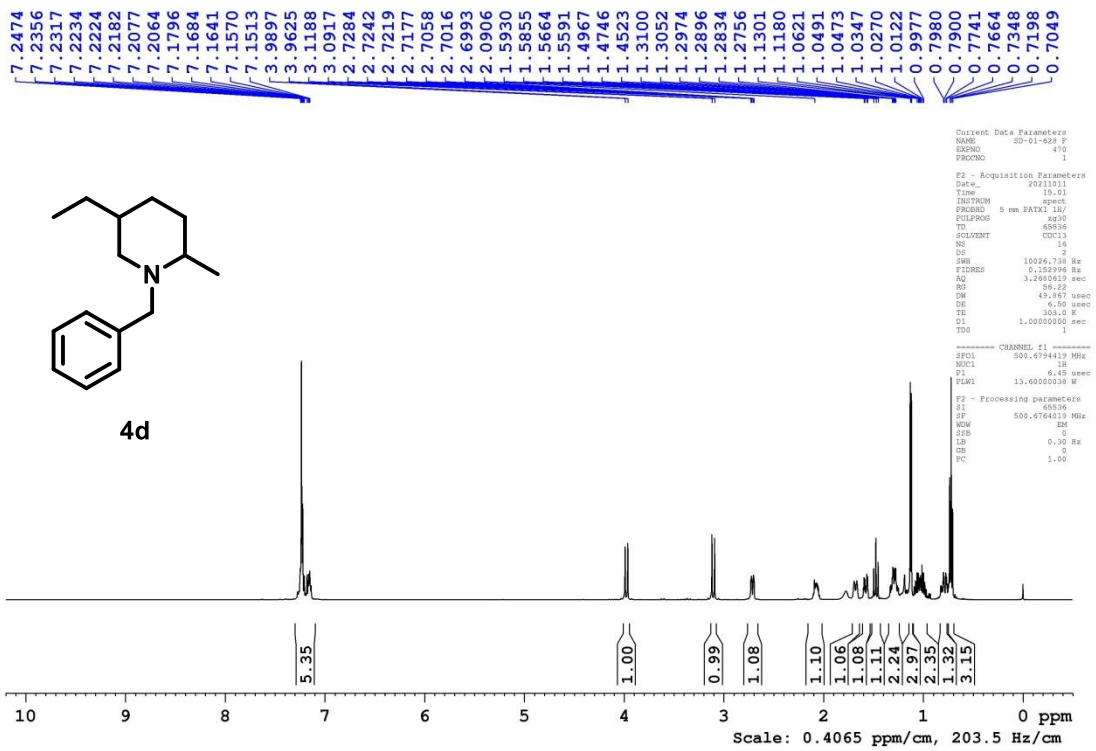


Figure S-95: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4d**

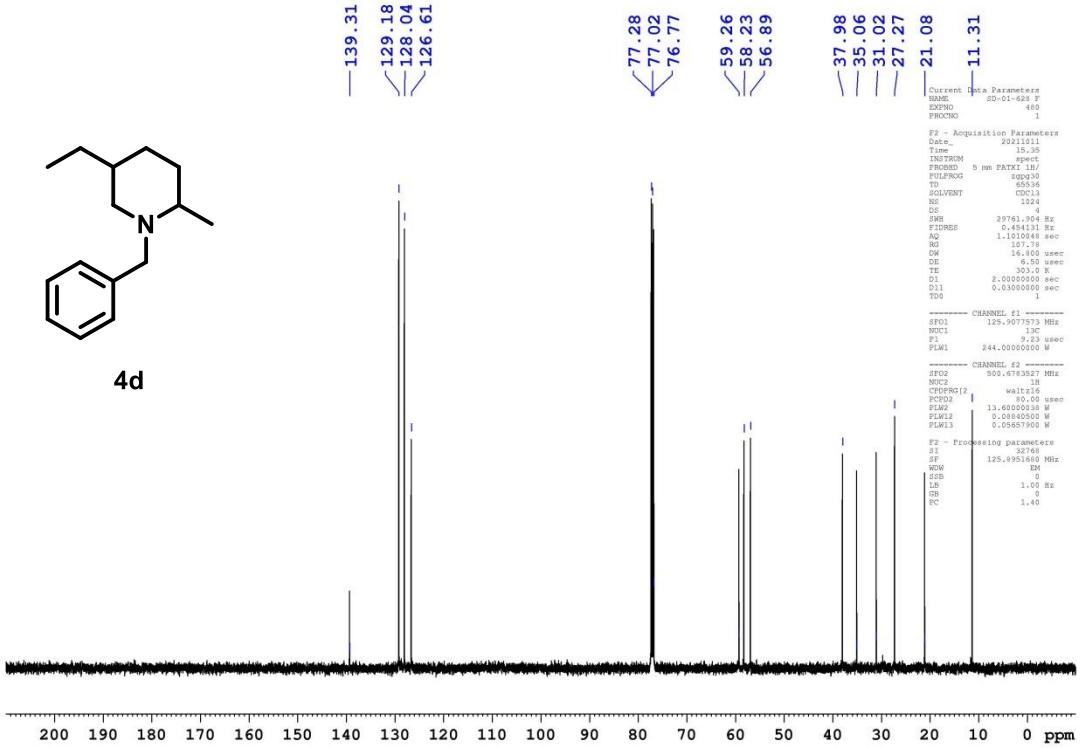


Figure S-96: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4d**

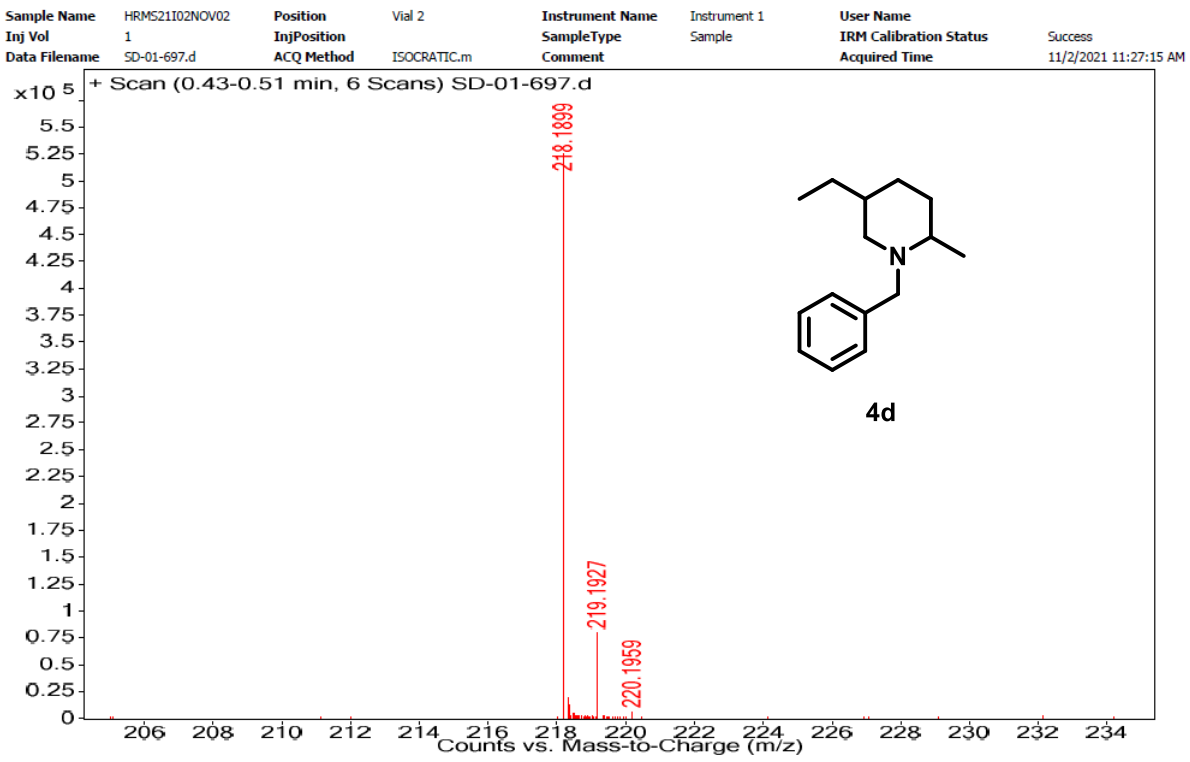


Figure S-97: HRMS spectrum of compound **4d**

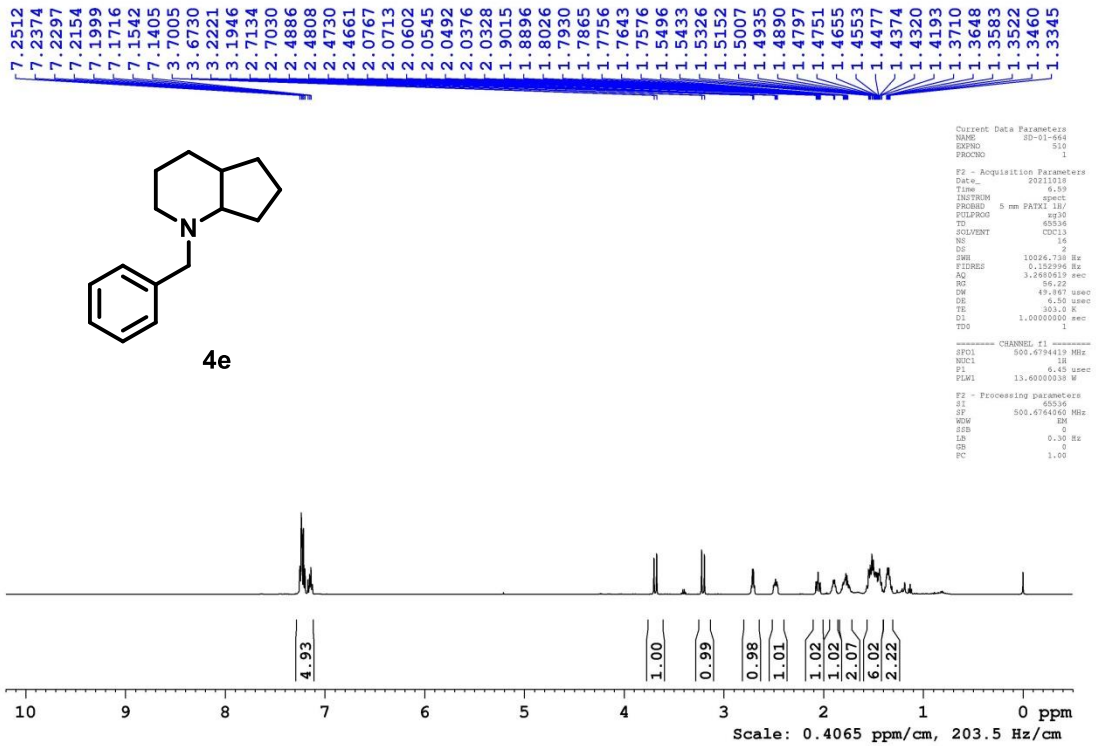


Figure S-98: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4e**

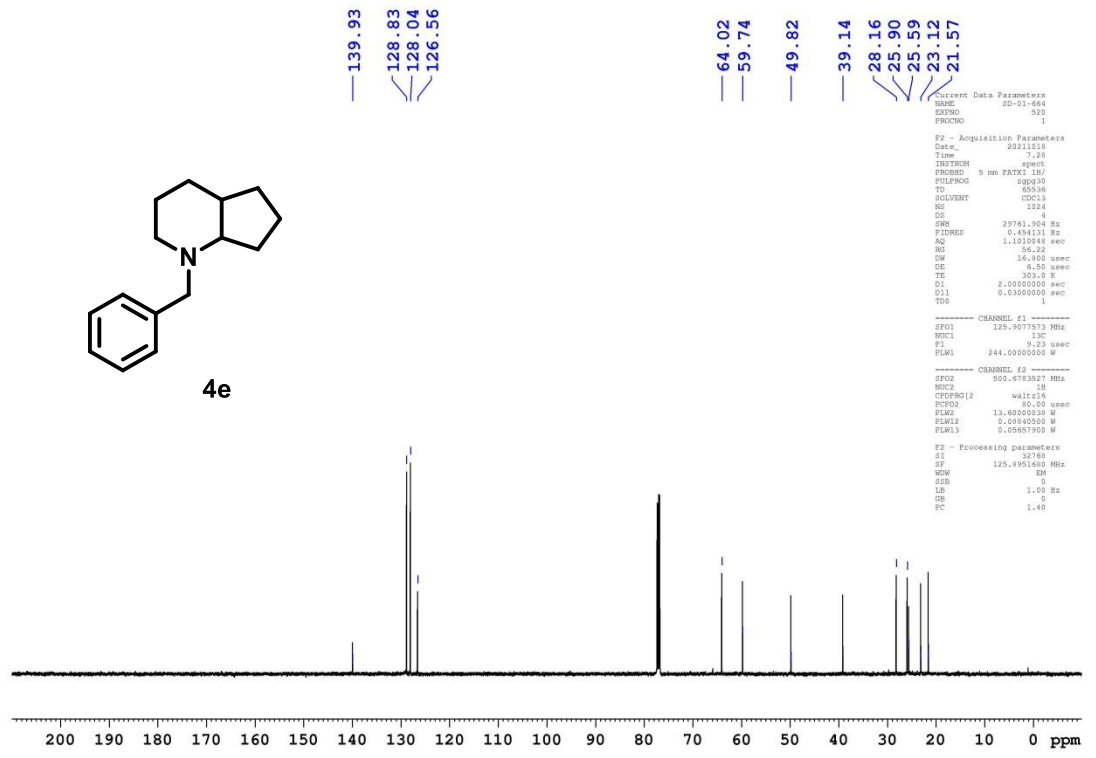


Figure S-99: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4e**

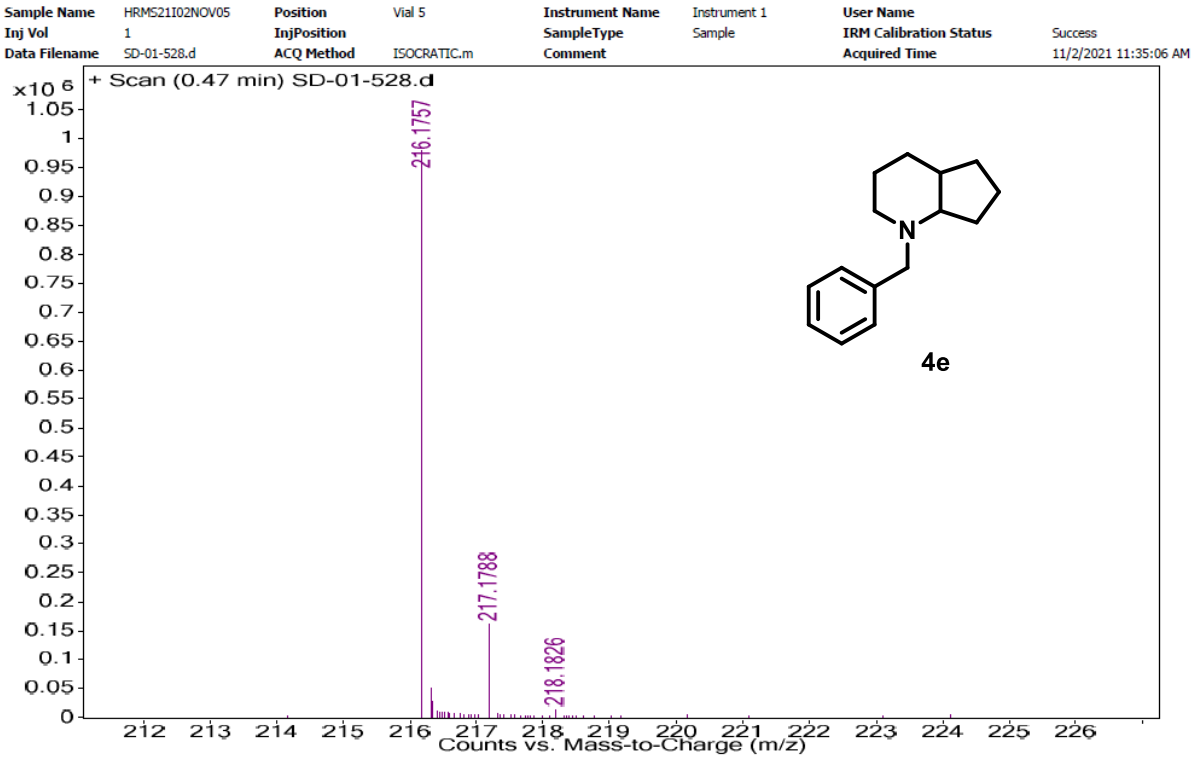


Figure S-100: HRMS spectrum of compound **4e**

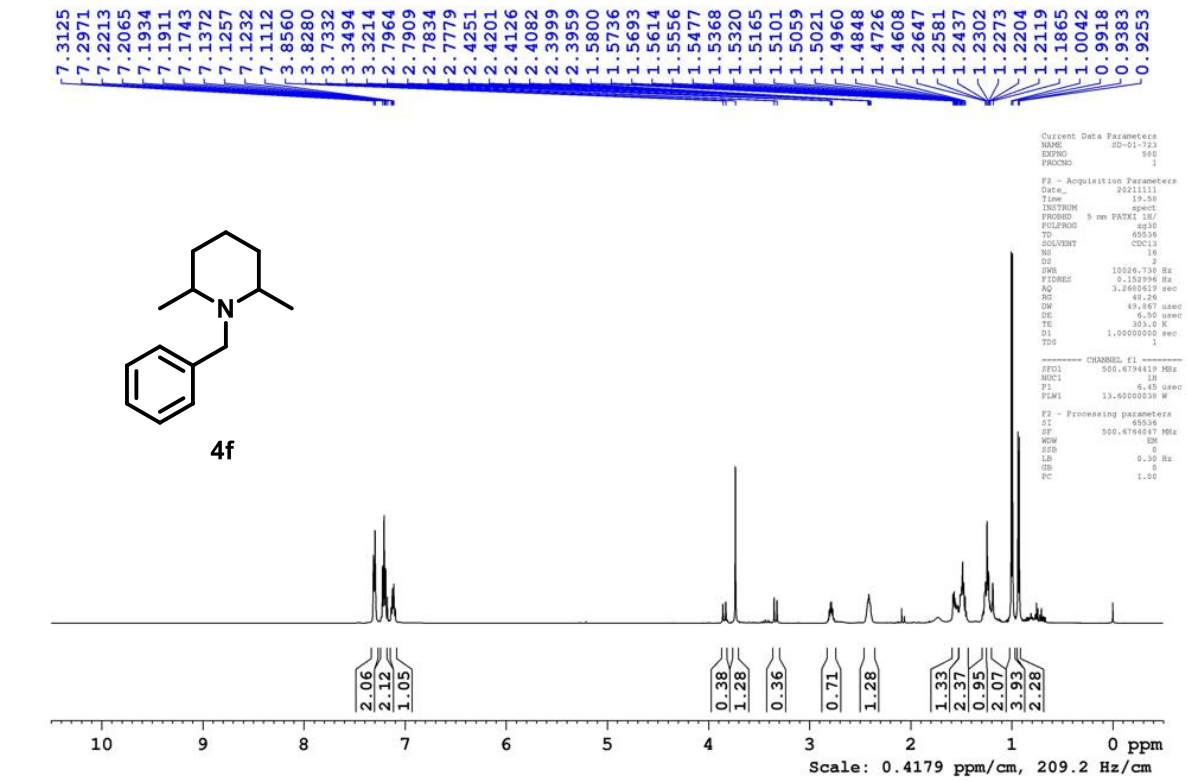


Figure S-101: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4f**

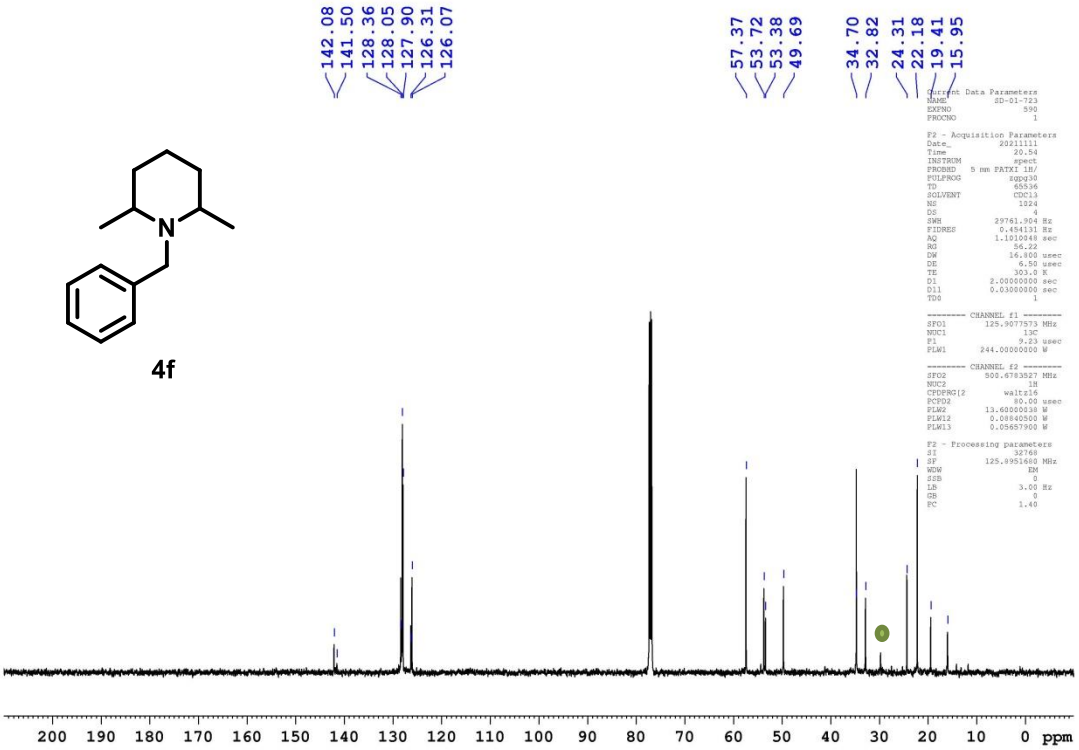


Figure S-102: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4f**

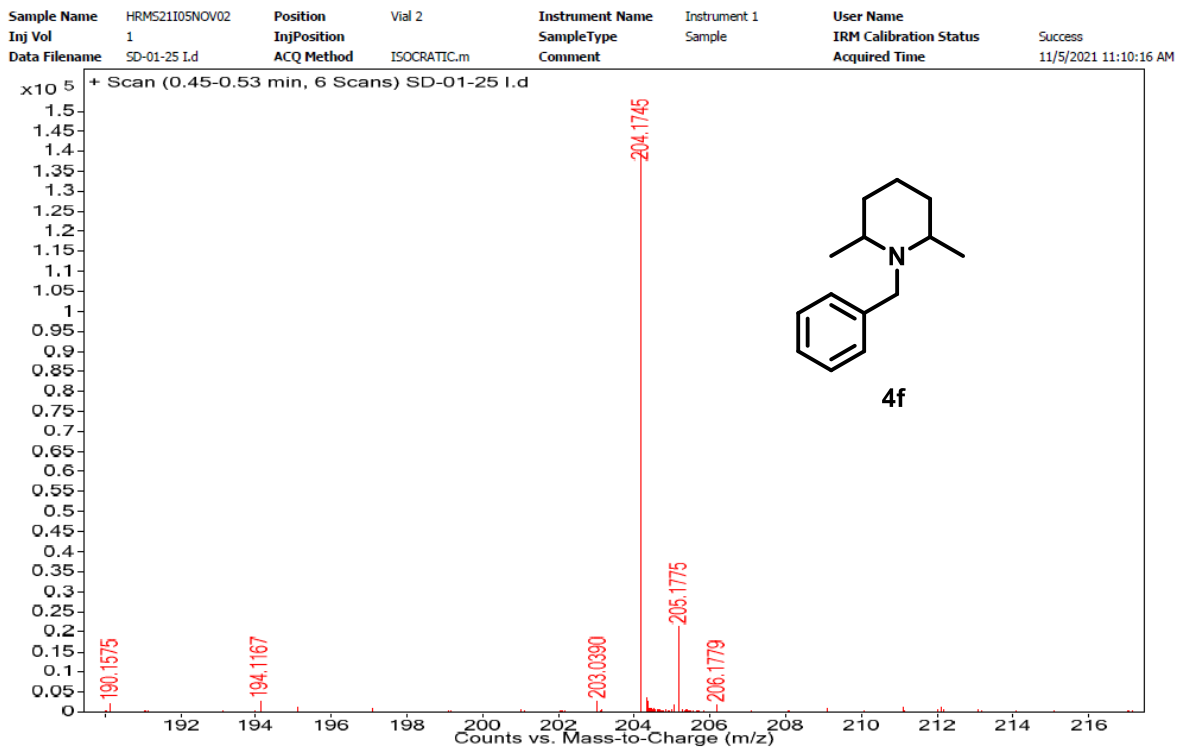


Figure S-103: HRMS spectrum of compound **4f**

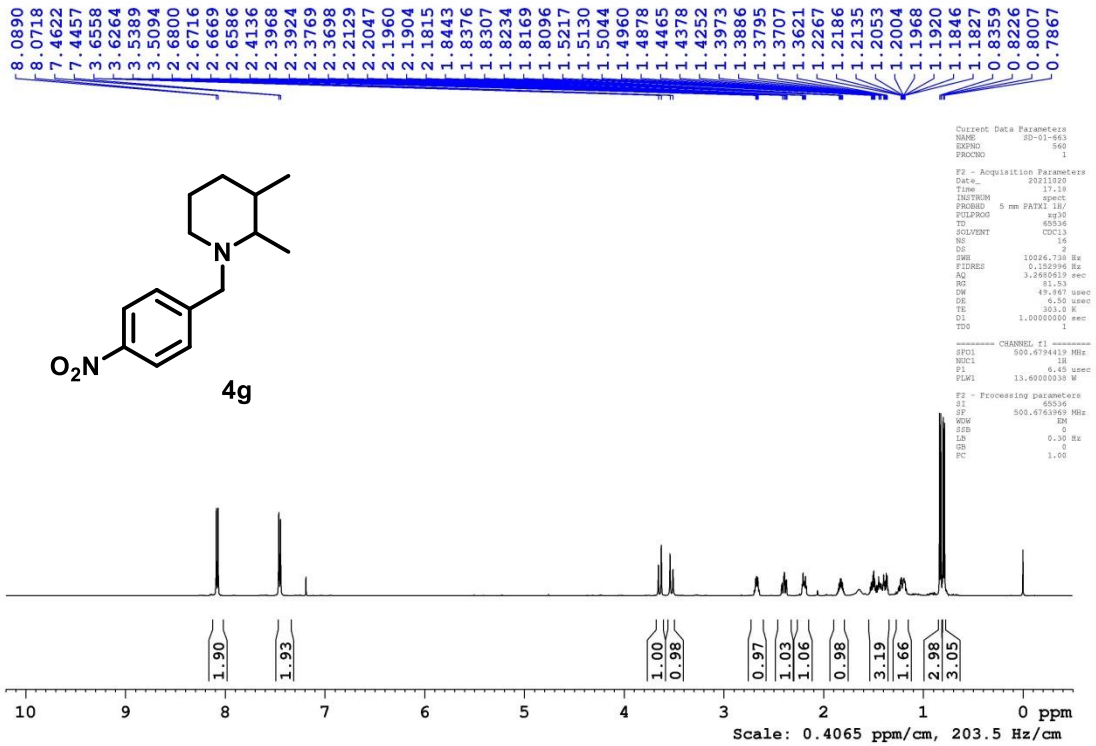


Figure S-104: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4g**

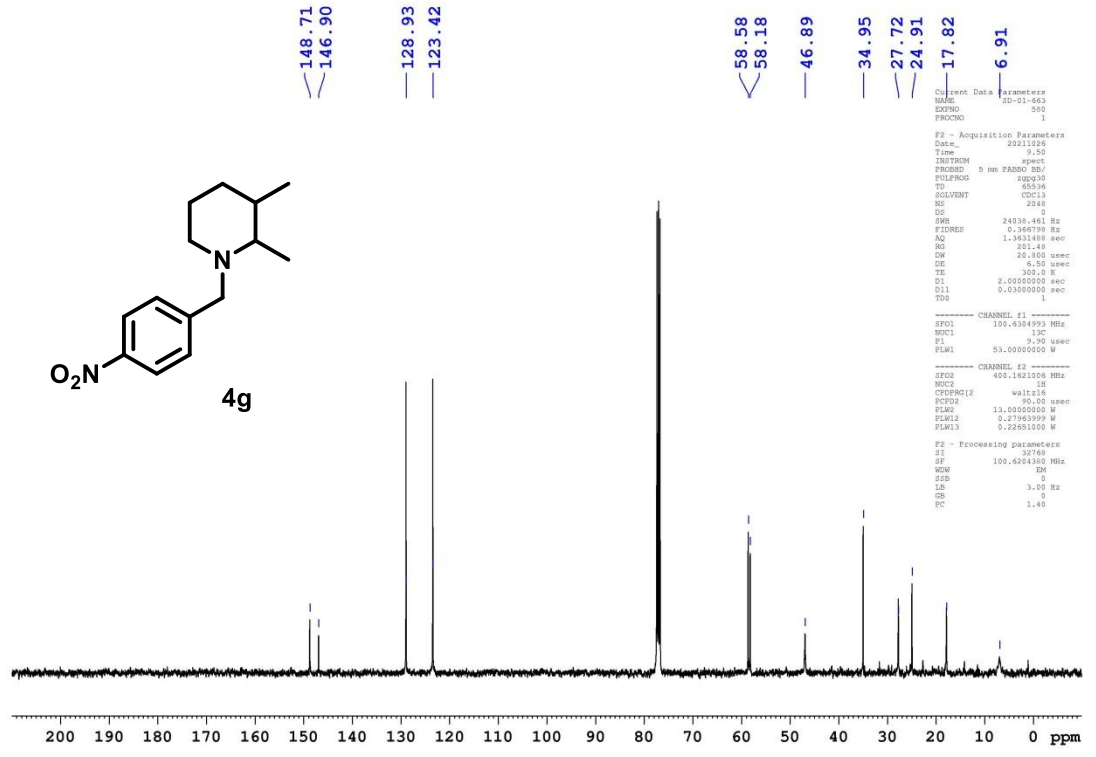


Figure S-105: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4g**

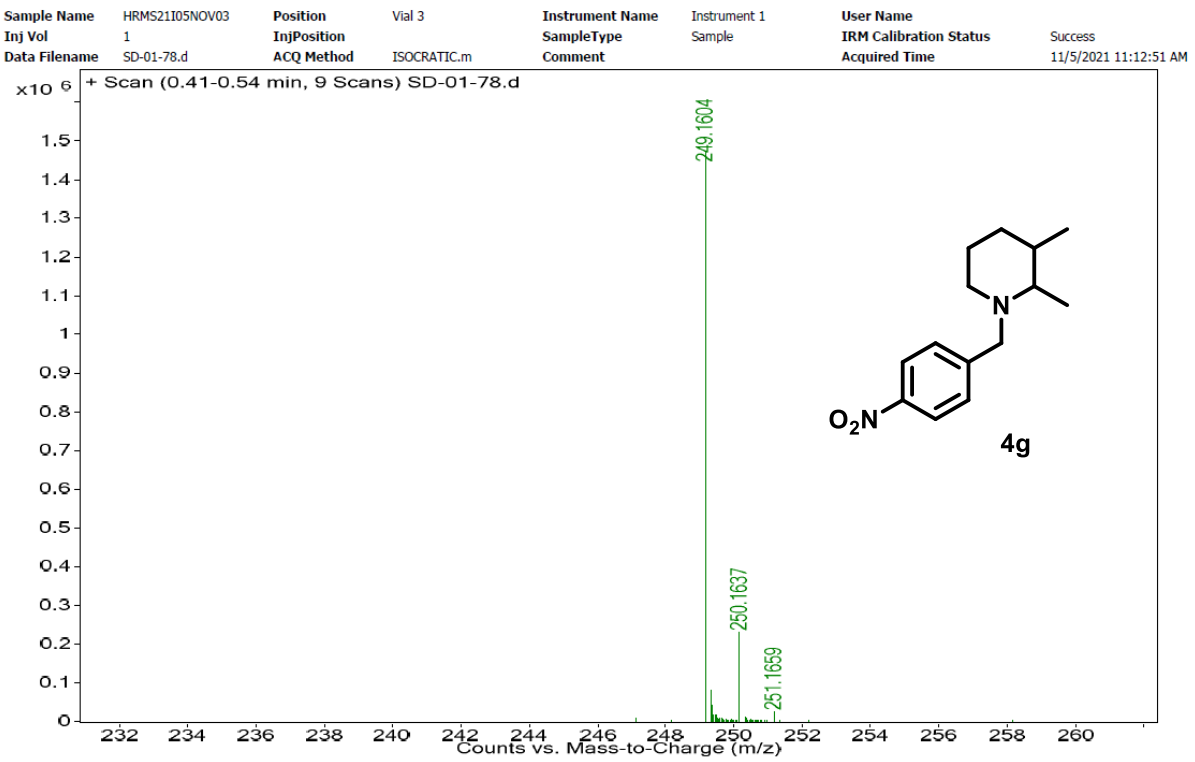


Figure S-106: HRMS spectrum of compound **4g**

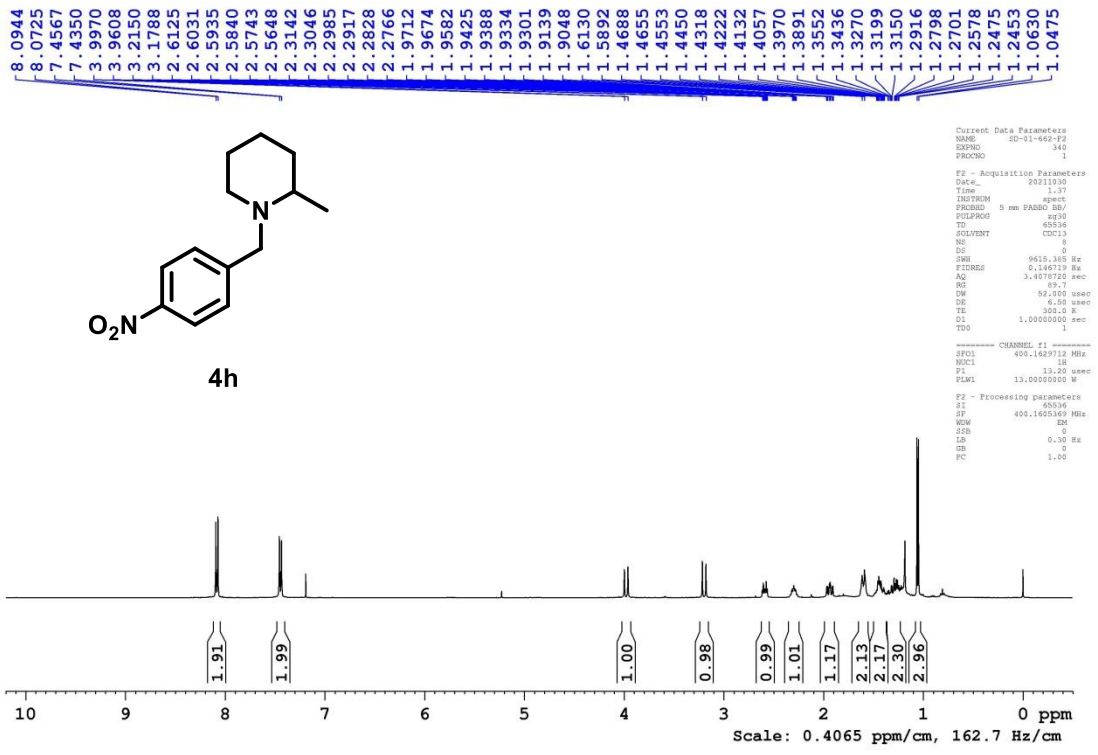


Figure S-107: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4h**

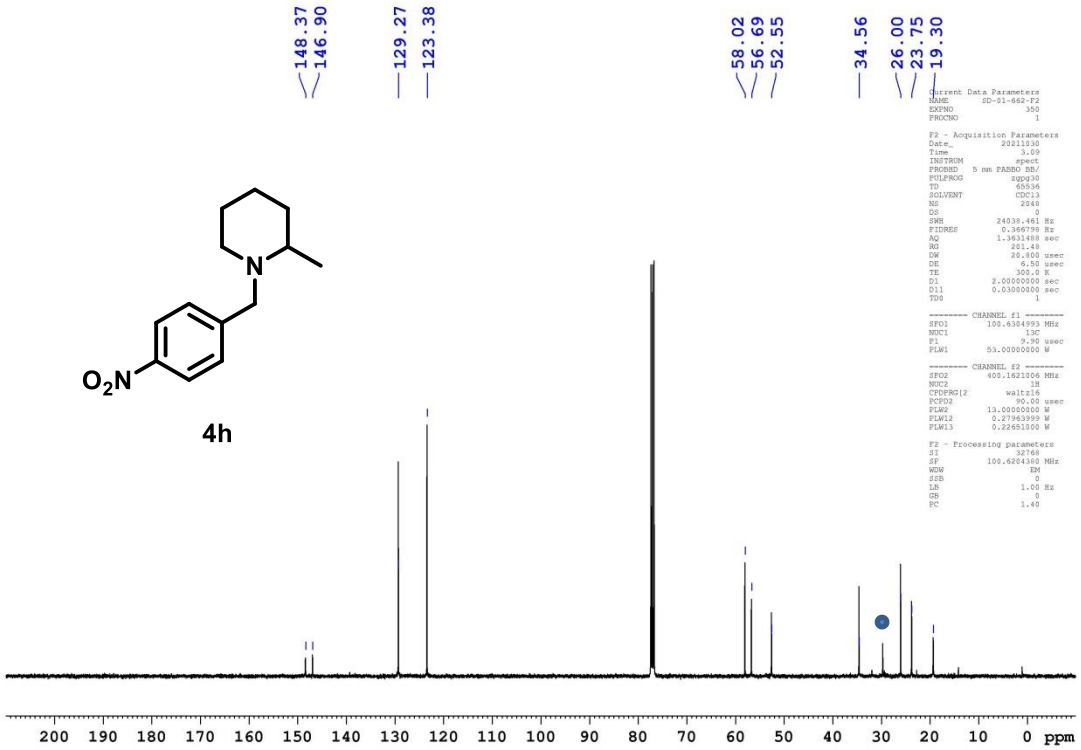


Figure S-108: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4h**

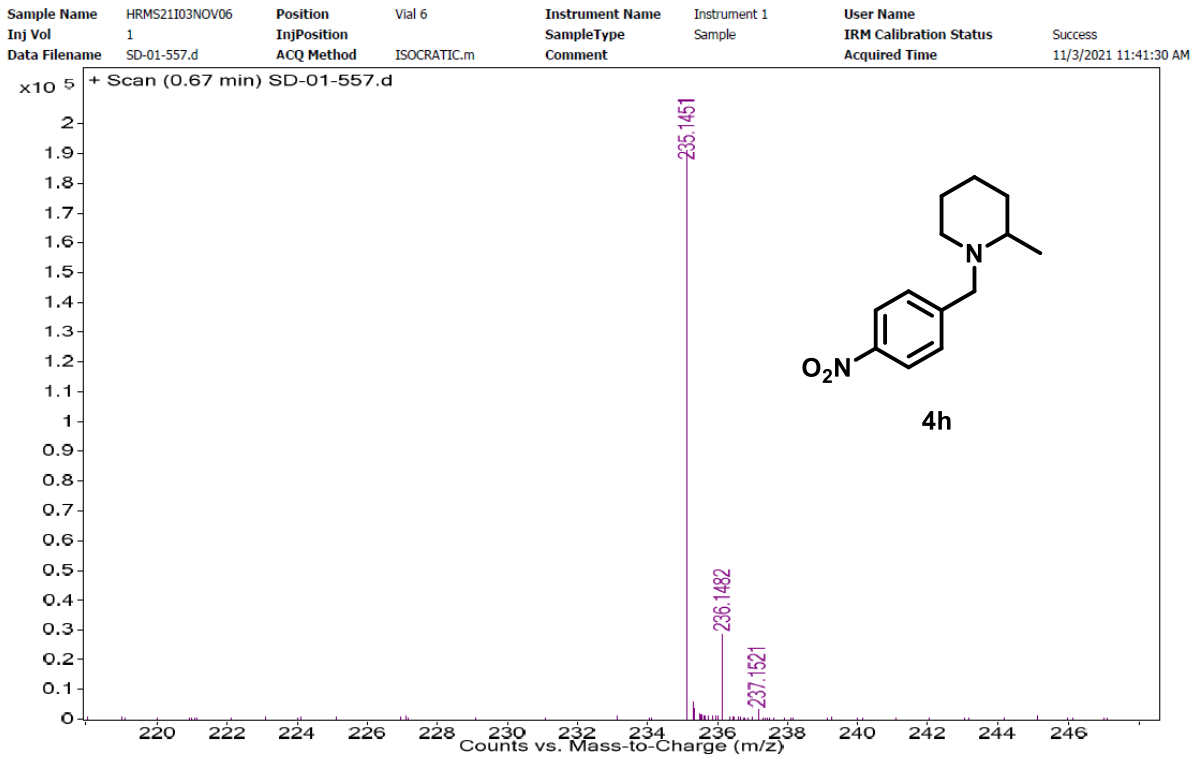


Figure S-109: HRMS spectrum of compound **4h**

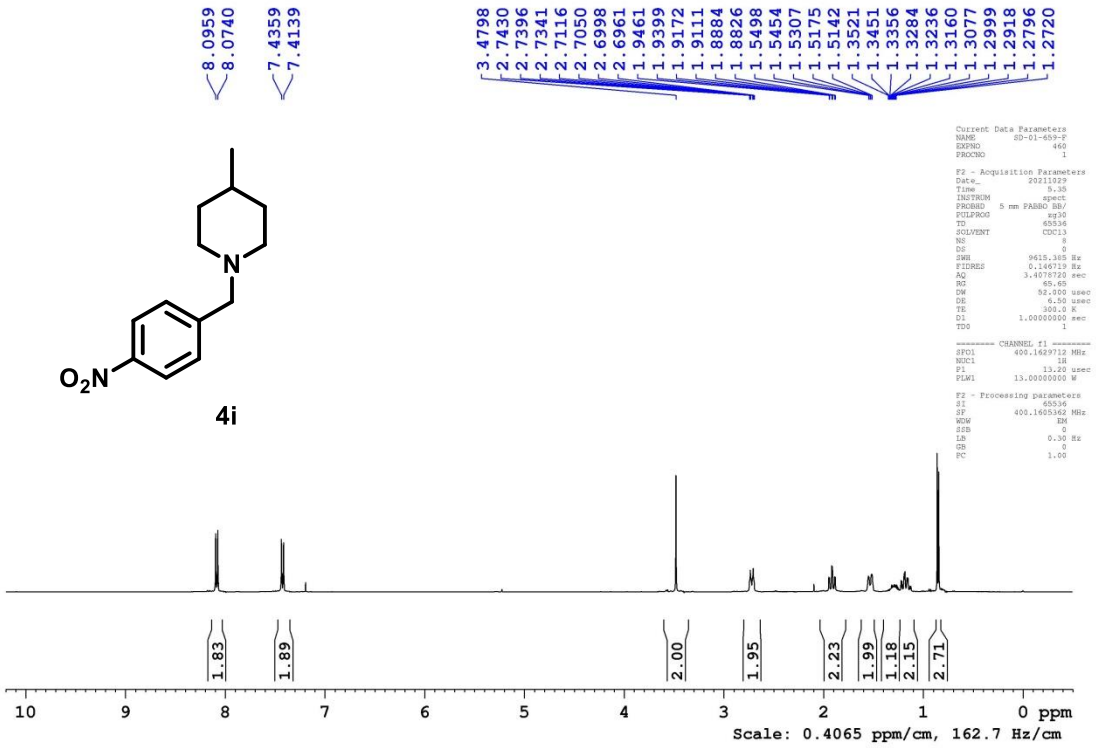


Figure S-110: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4i**

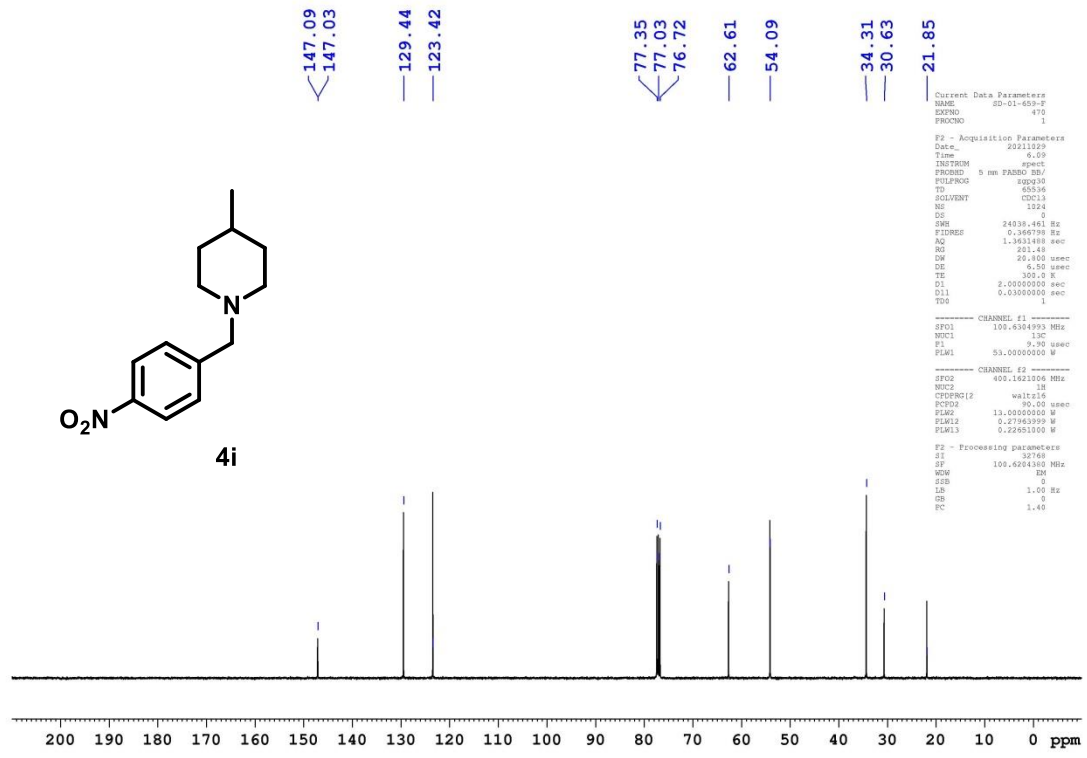


Figure S-111: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4i**

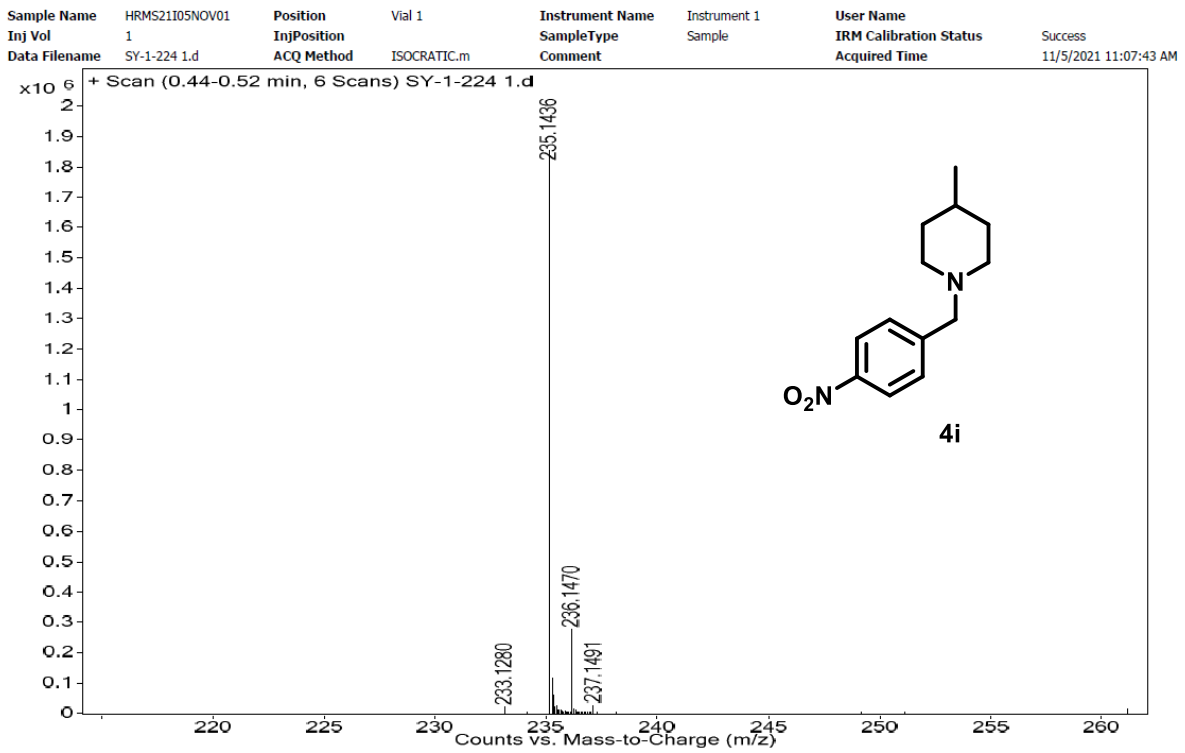


Figure S-112: HRMS spectrum of compound **4i**

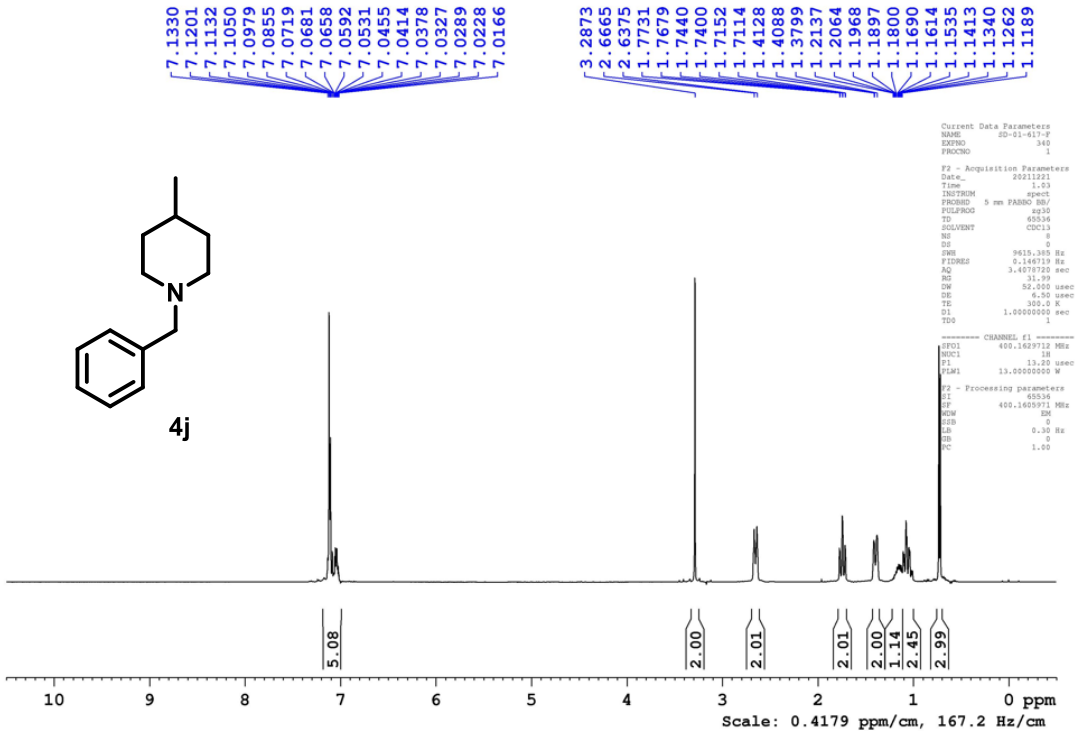


Figure S-113: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4j**

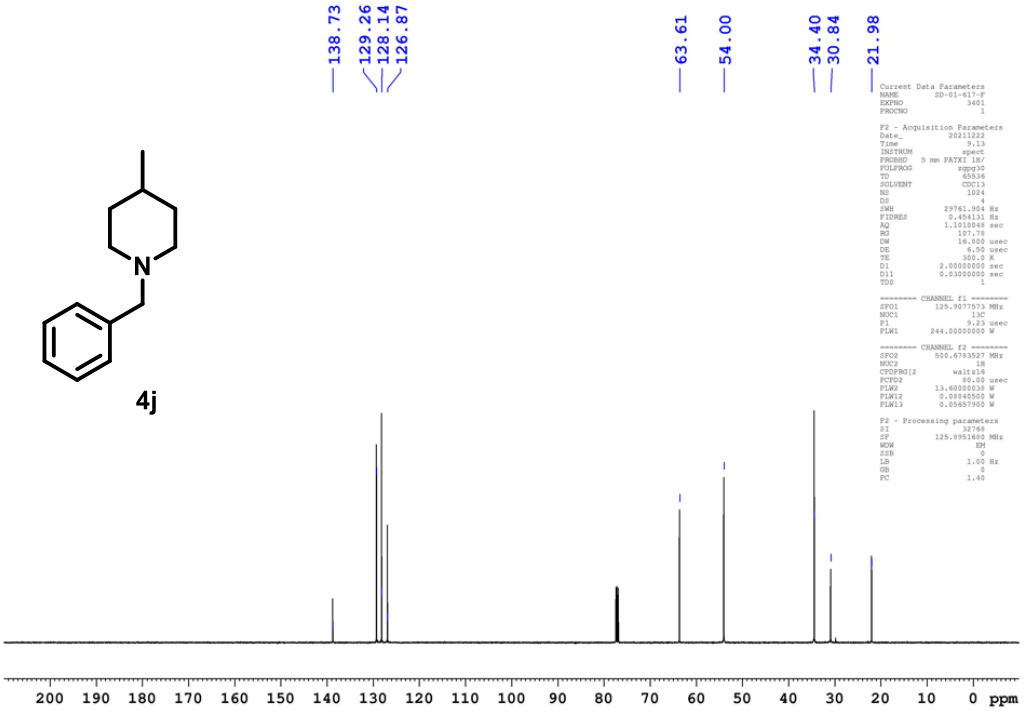


Figure S-114: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4j**

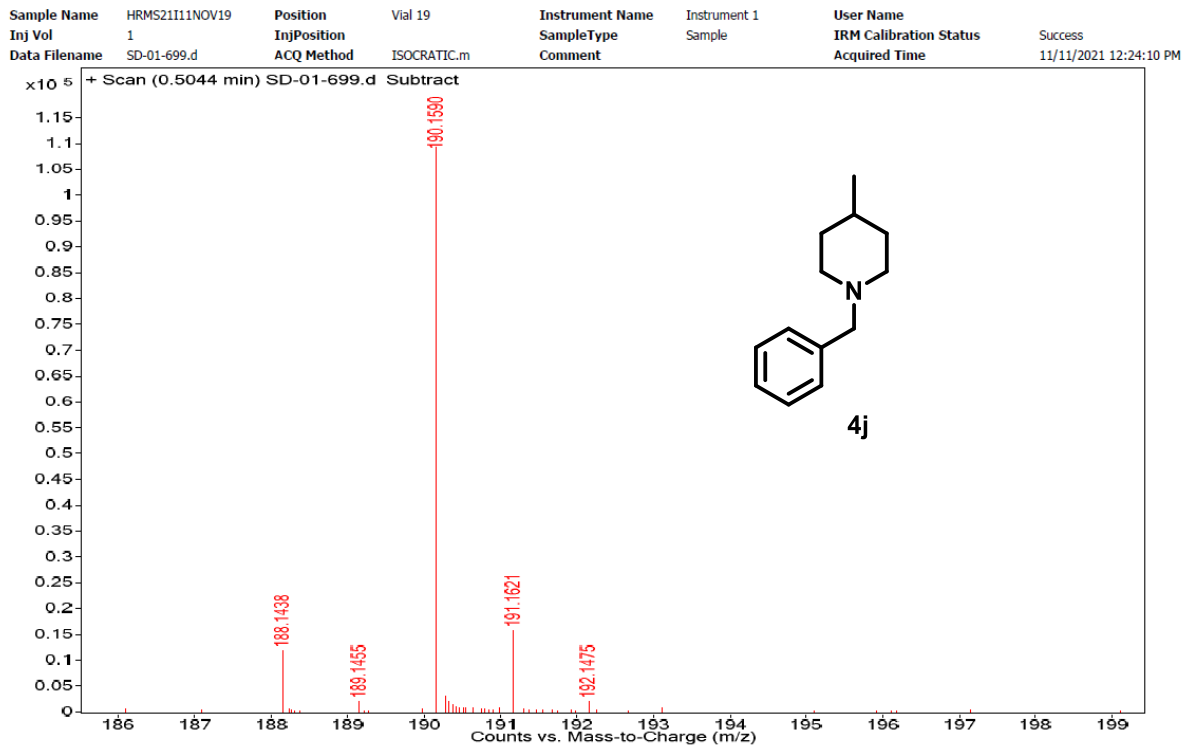


Figure S-115: HRMS spectrum of compound **4j**

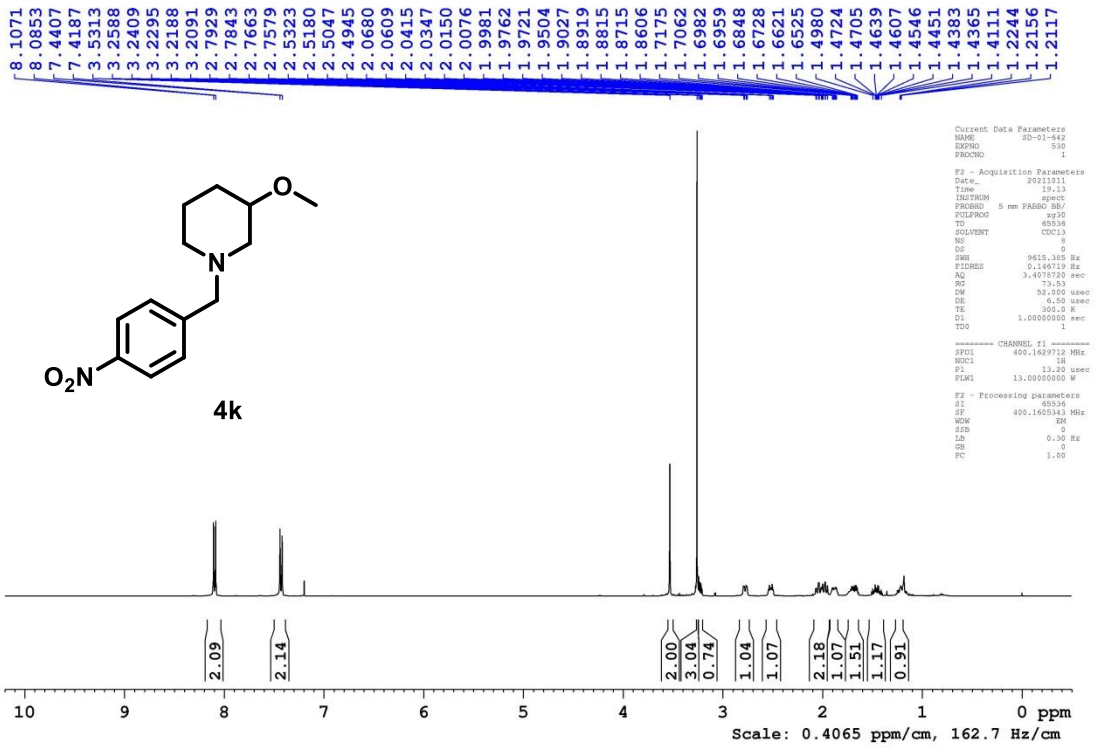


Figure S-116: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4k**

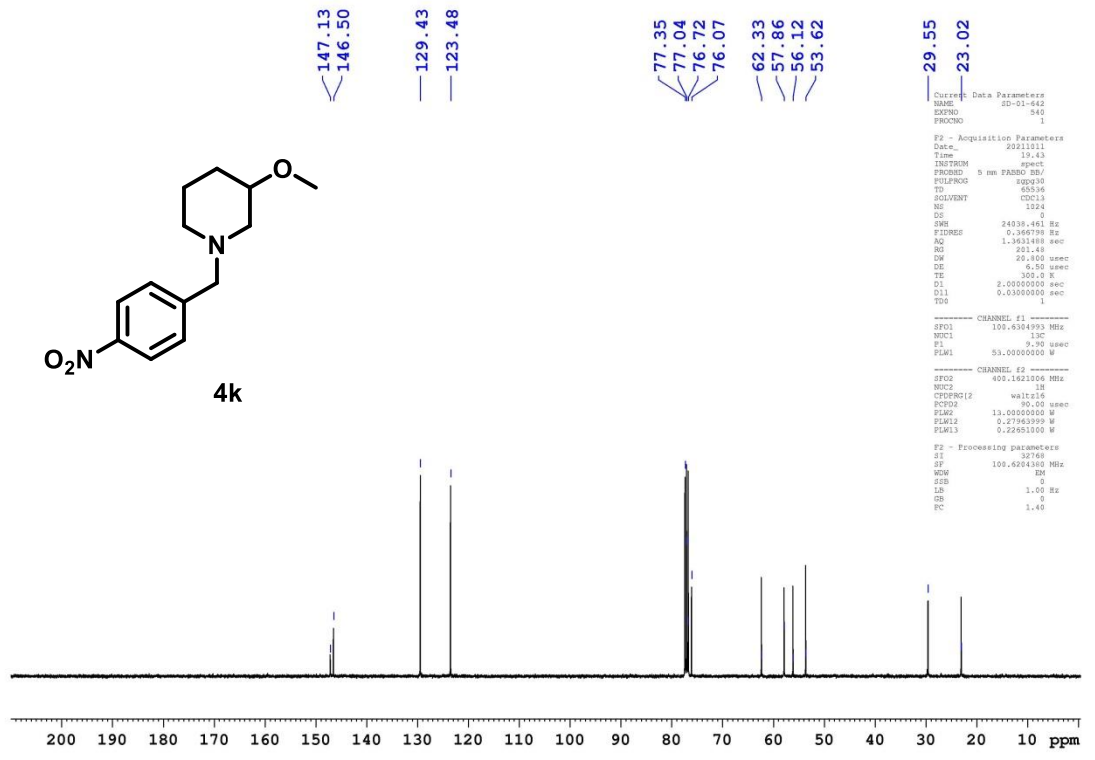


Figure S-117: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4k**

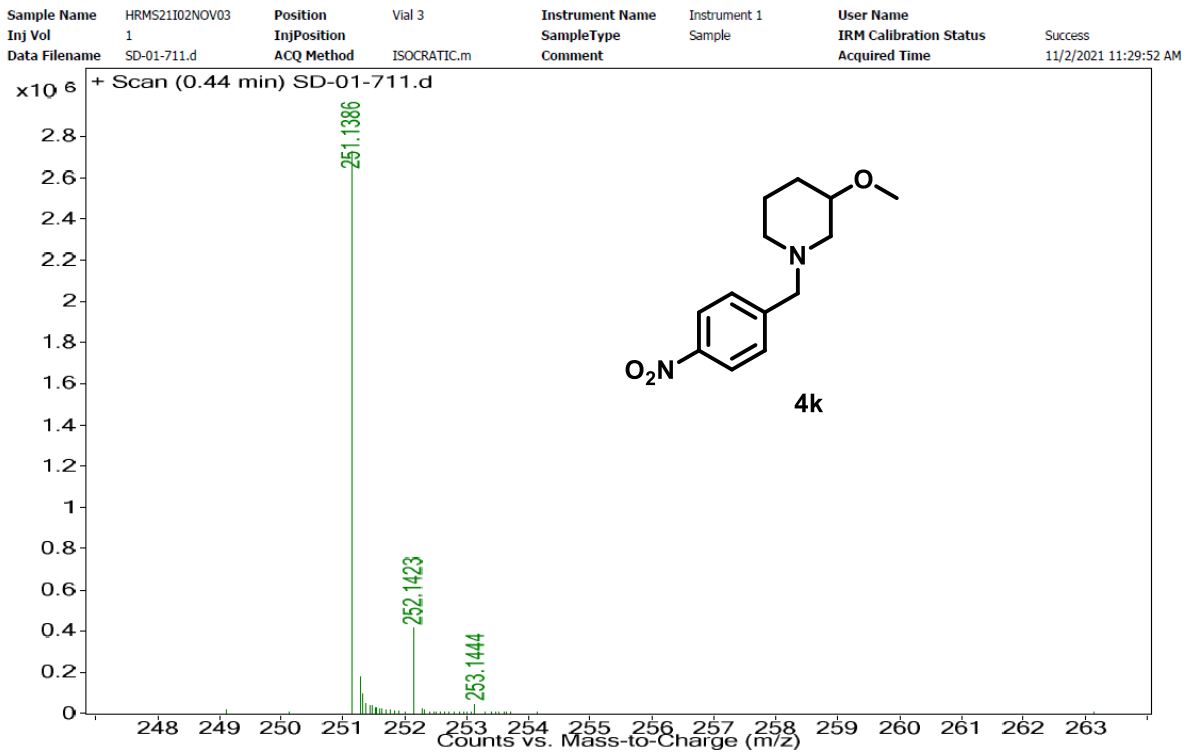


Figure S-118: HRMS spectrum of compound **4k**

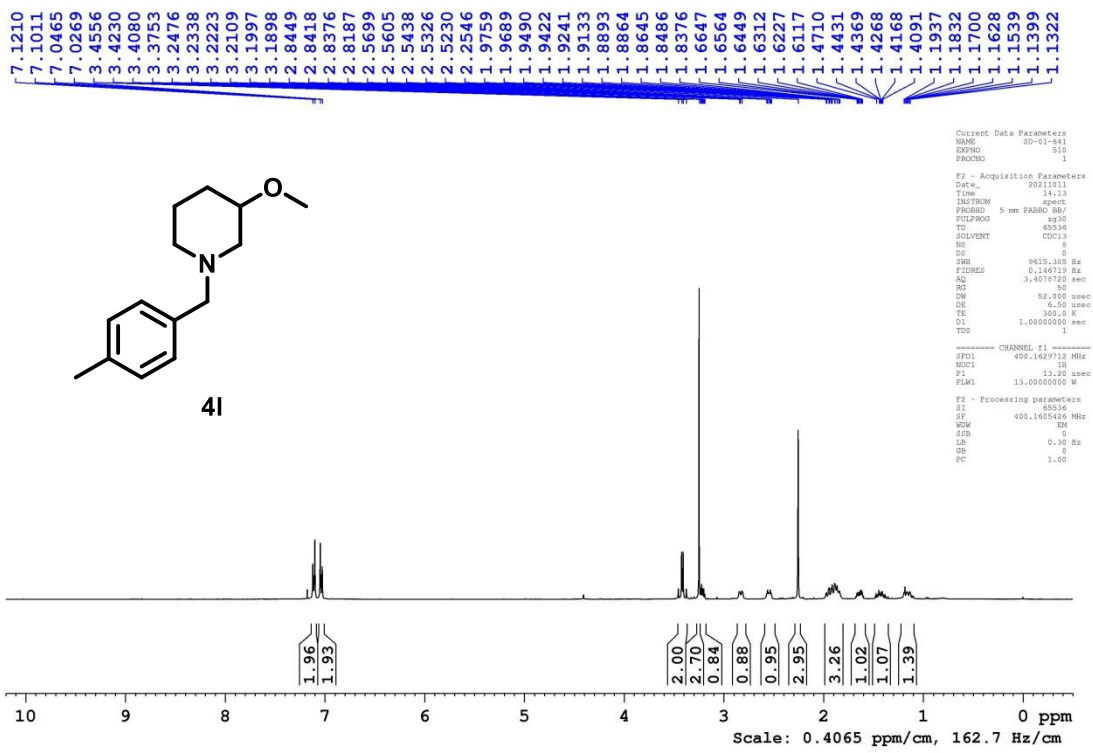


Figure S-119: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4l**

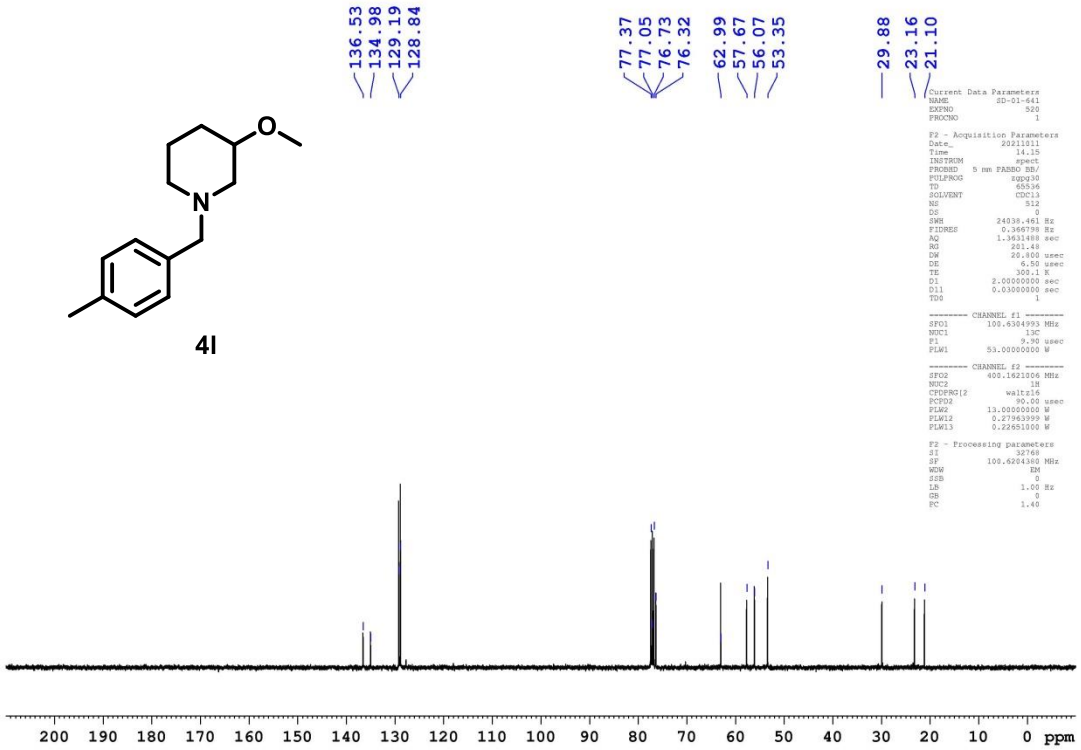


Figure S-120: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4l**

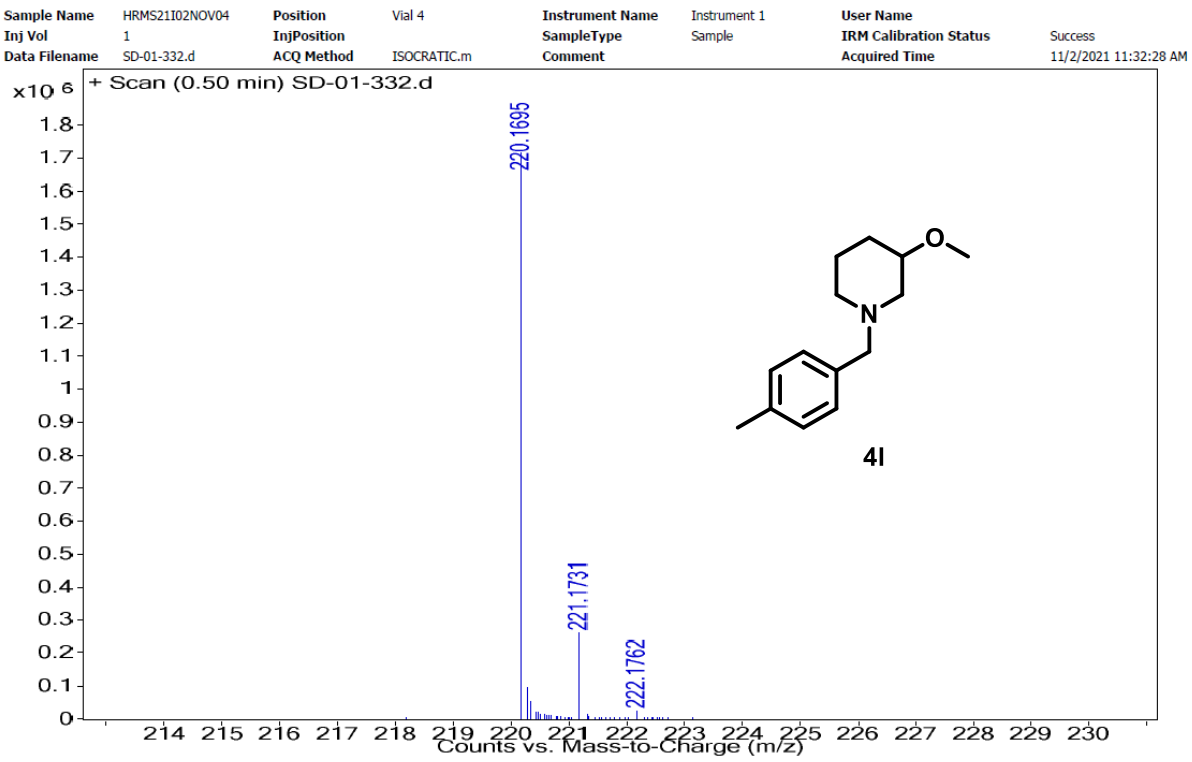


Figure S-121: HRMS spectrum of compound **4l**

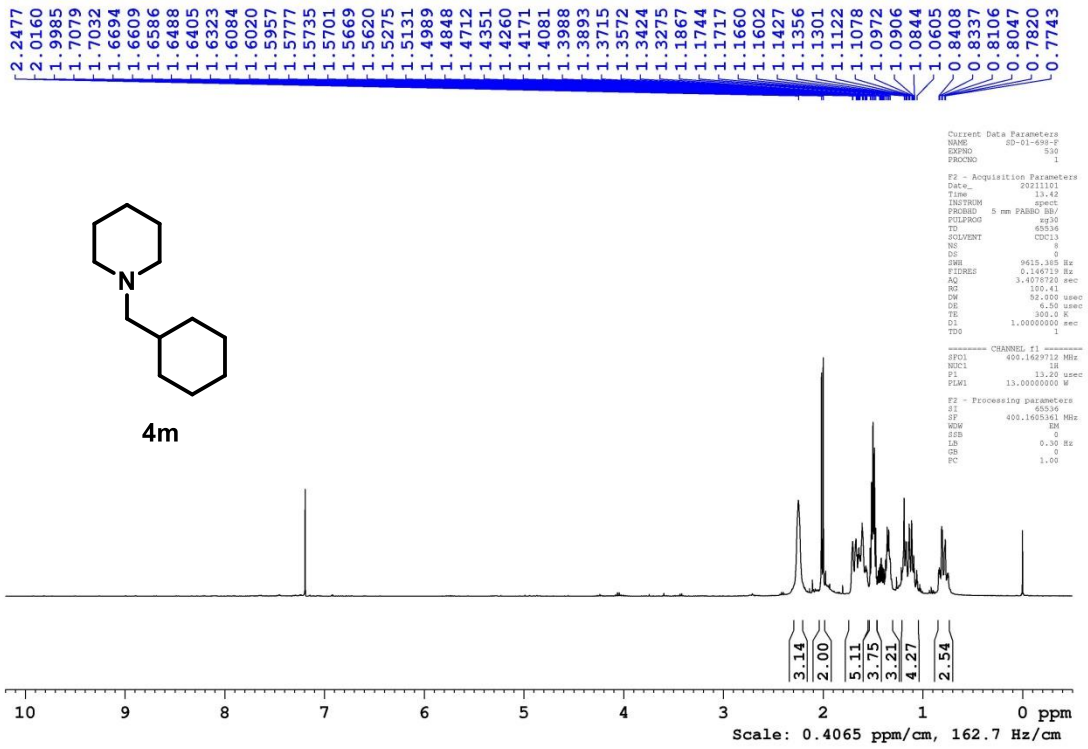


Figure S-122: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4m**

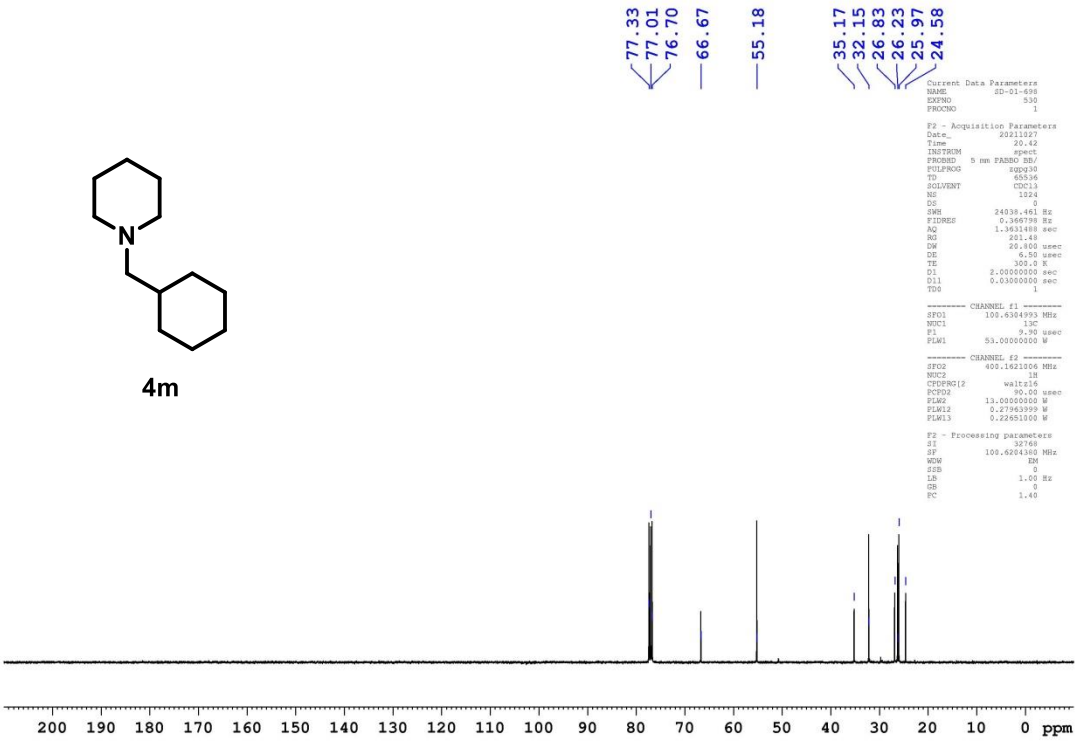


Figure S-123: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4m**

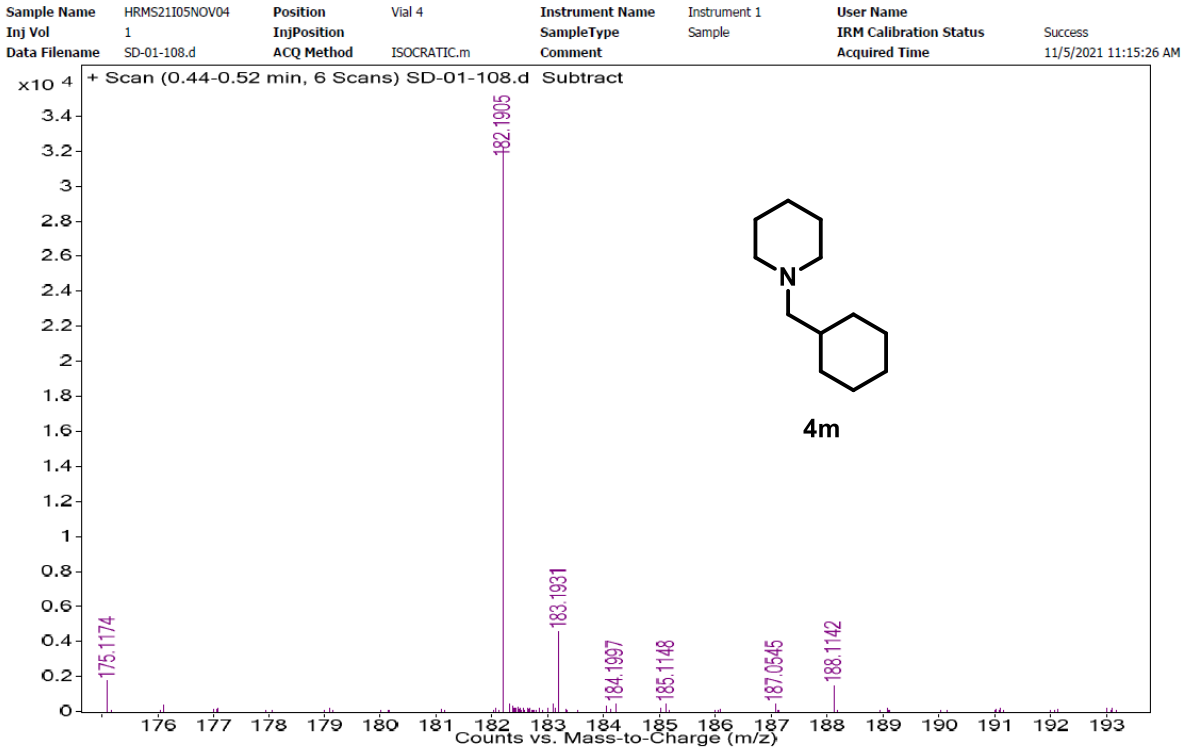


Figure S-124: HRMS spectrum of compound **4m**

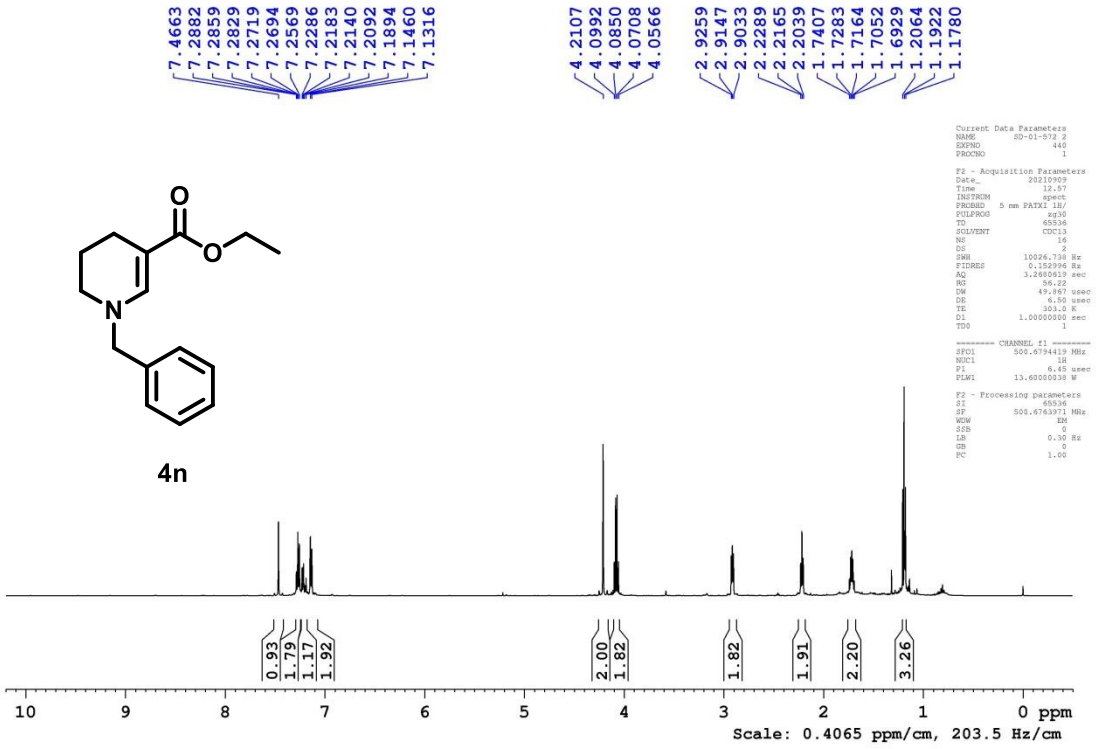


Figure S-125: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4n**

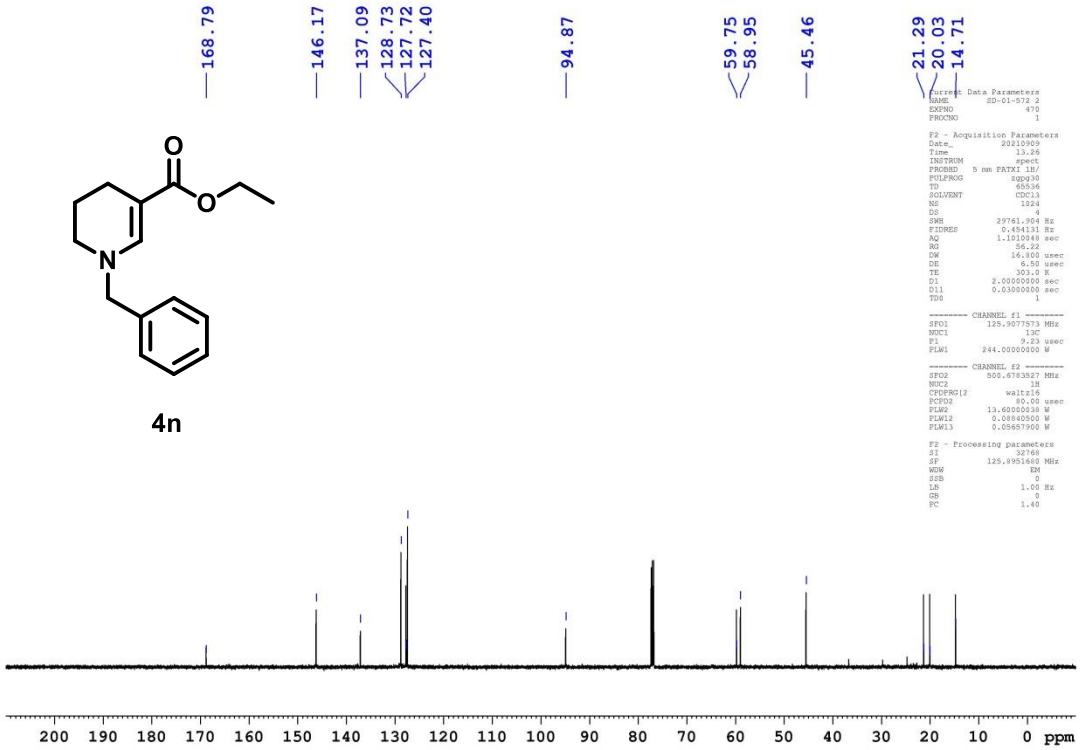


Figure S-126: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4n**

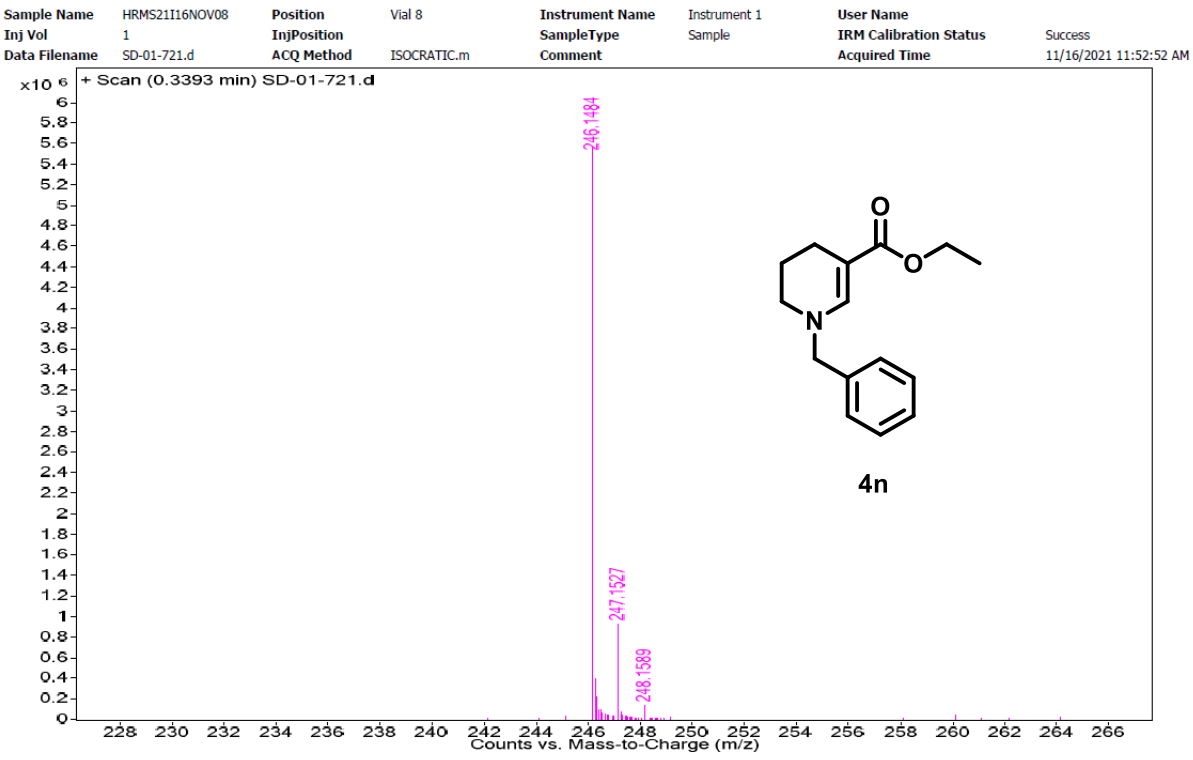


Figure S-127: HRMS spectrum of compound **4n**

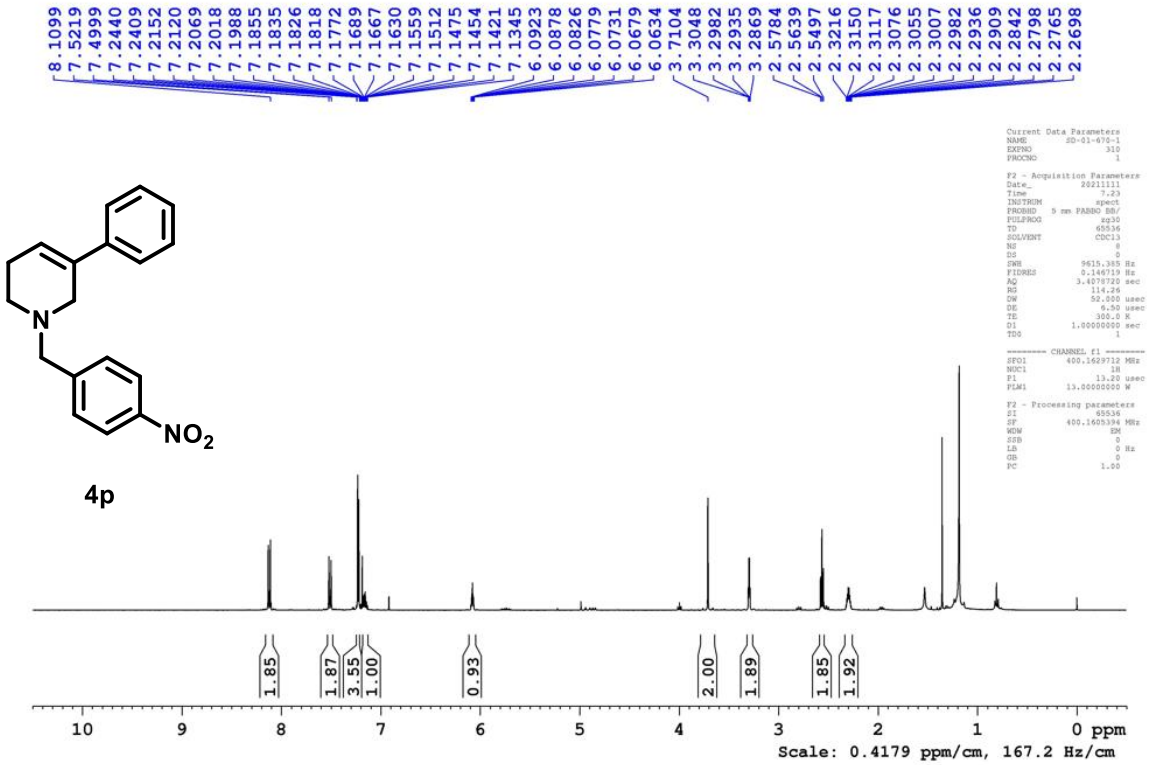


Figure S-128: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4p**

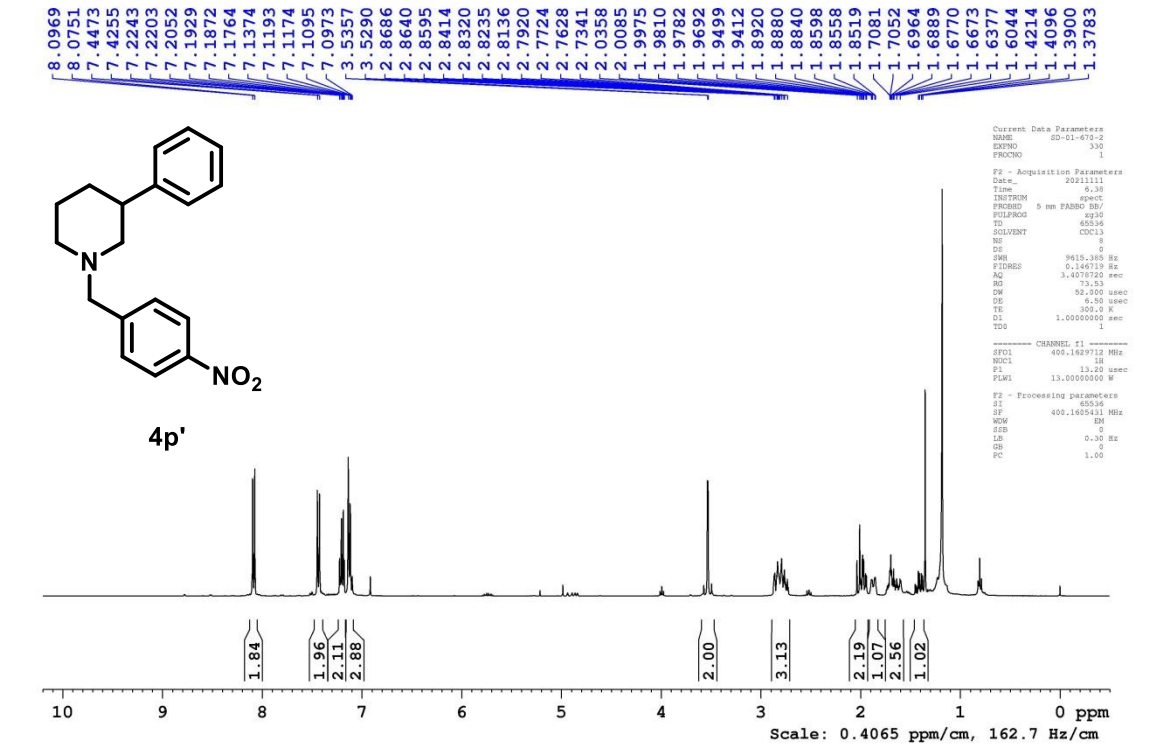


Figure S-129: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4p'**

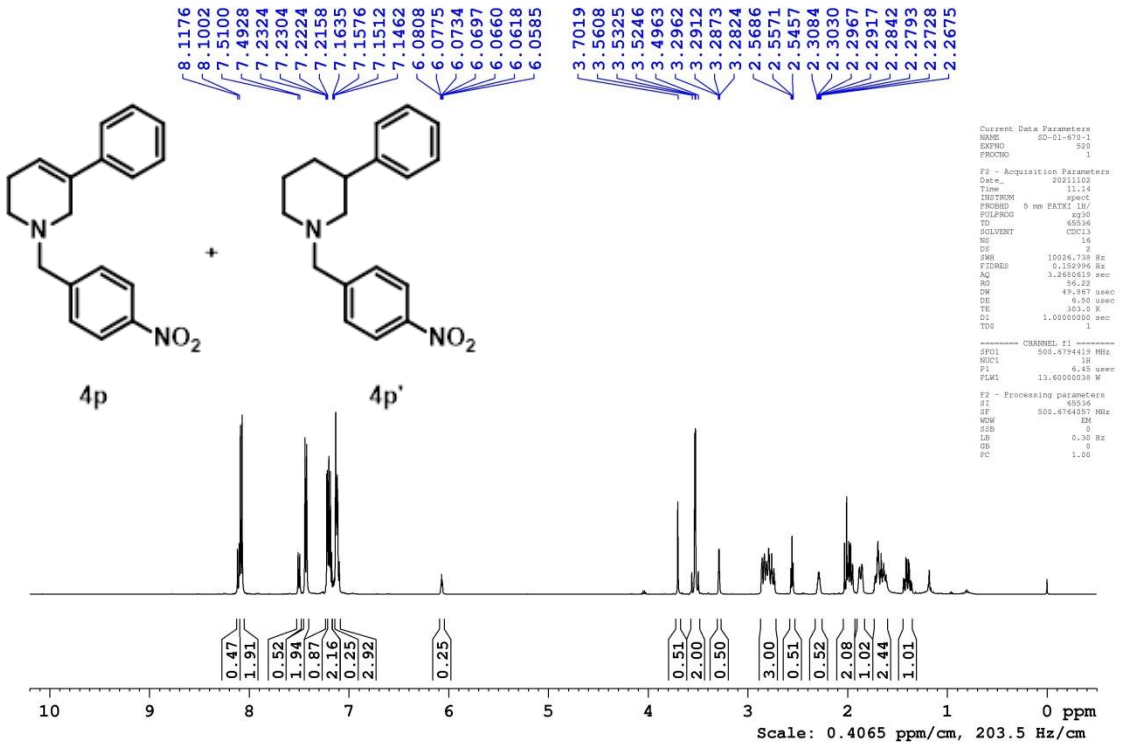


Figure S-130: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4p + 4p'**

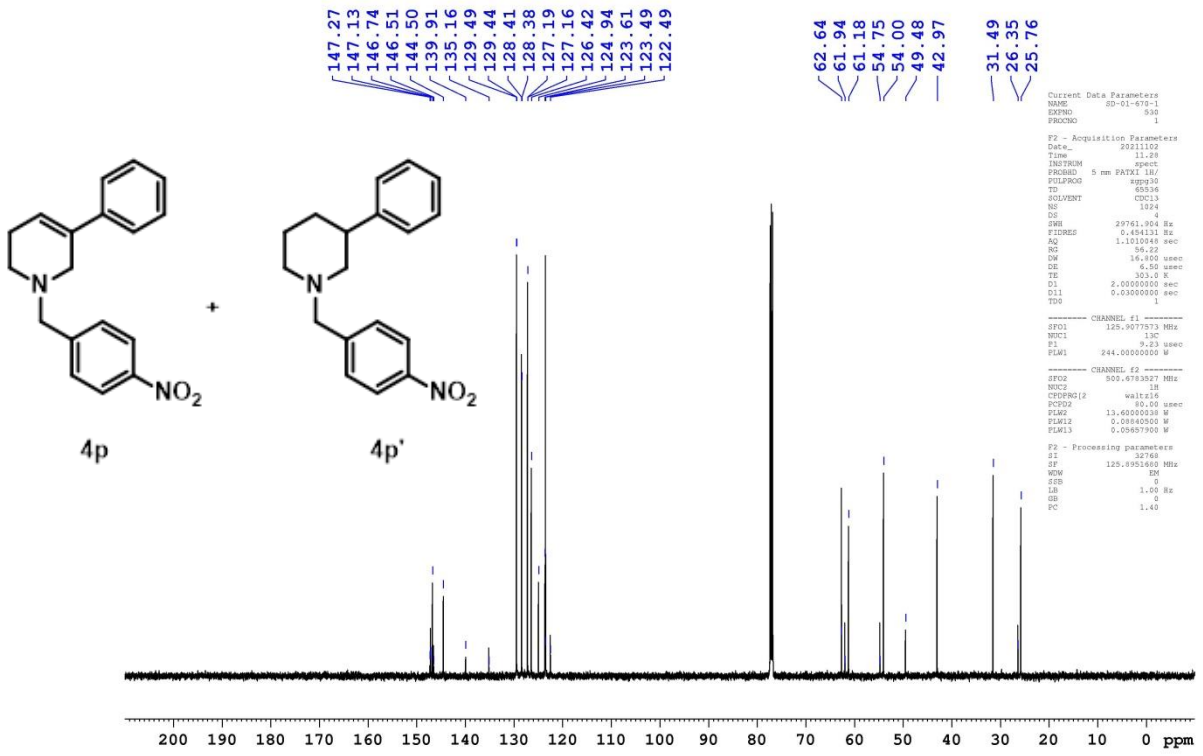


Figure S-131: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4p + 4p'**

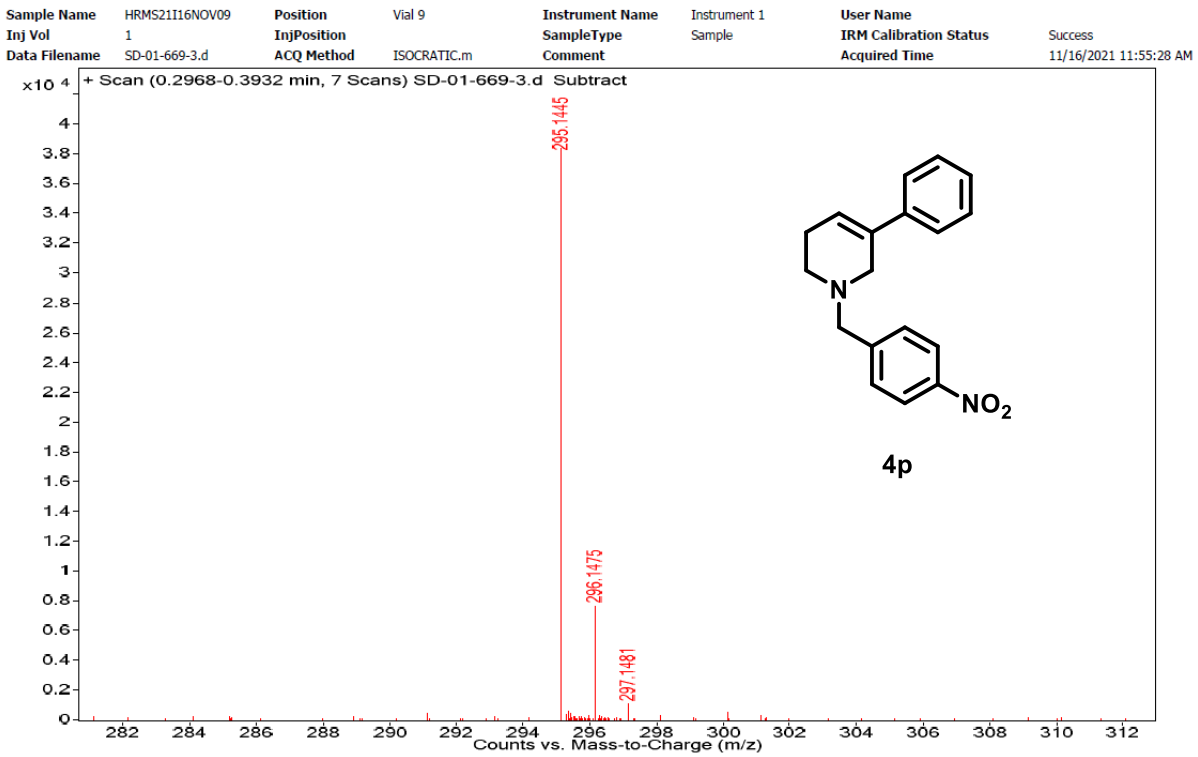


Figure S-132: HRMS spectrum of compound **4p**

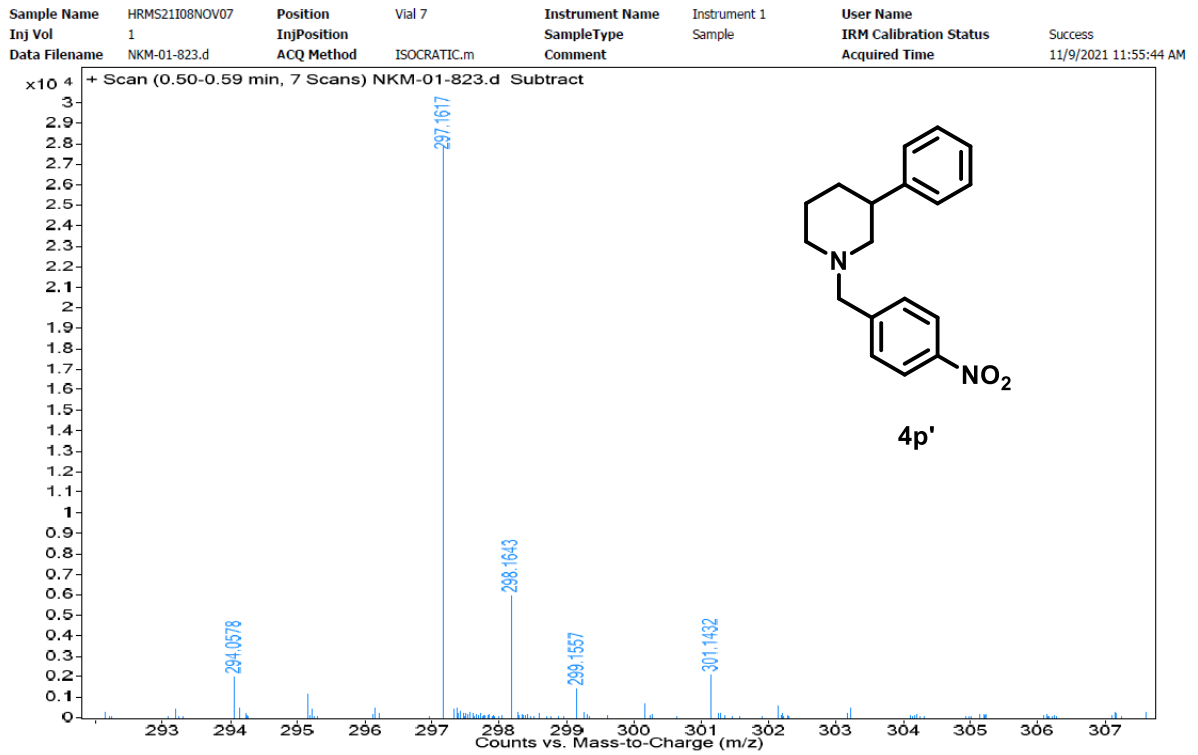


Figure S-133: HRMS spectrum of compound **4p'**

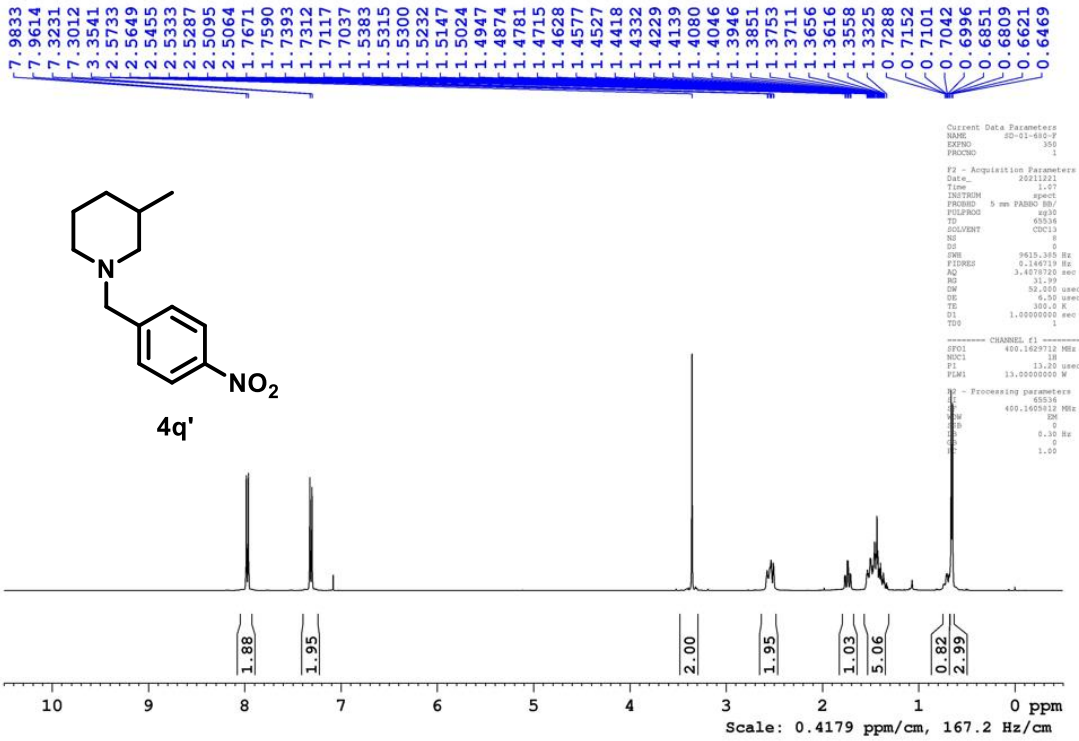


Figure S-134: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4q'**

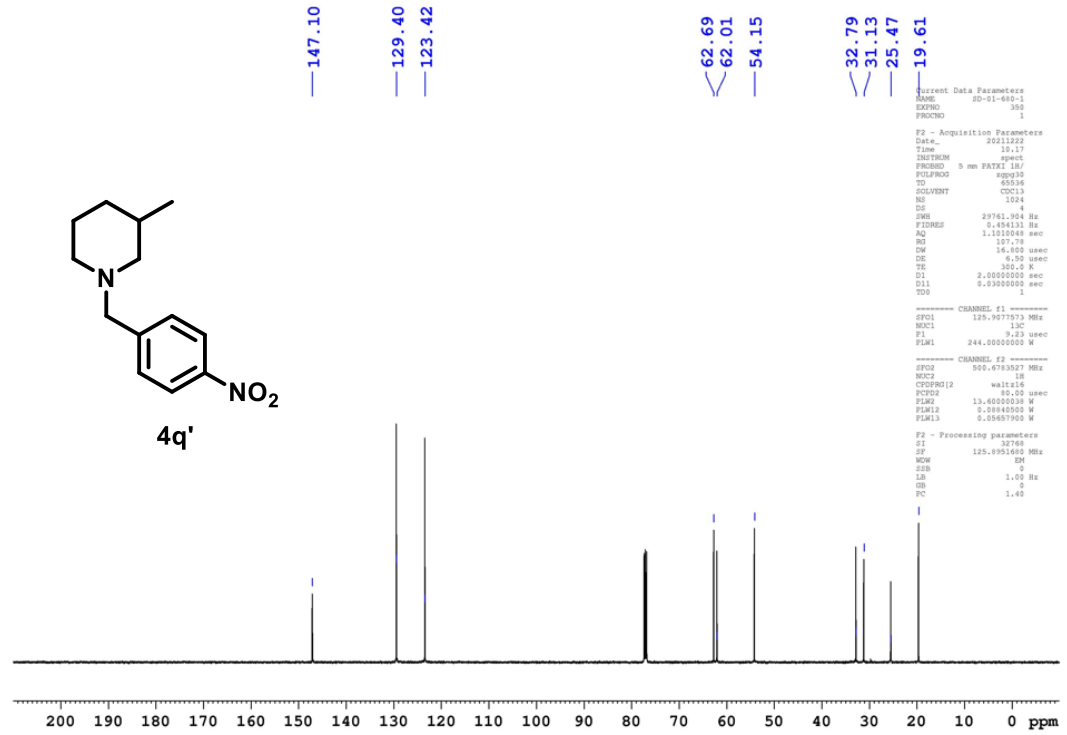


Figure S-135: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4q'**

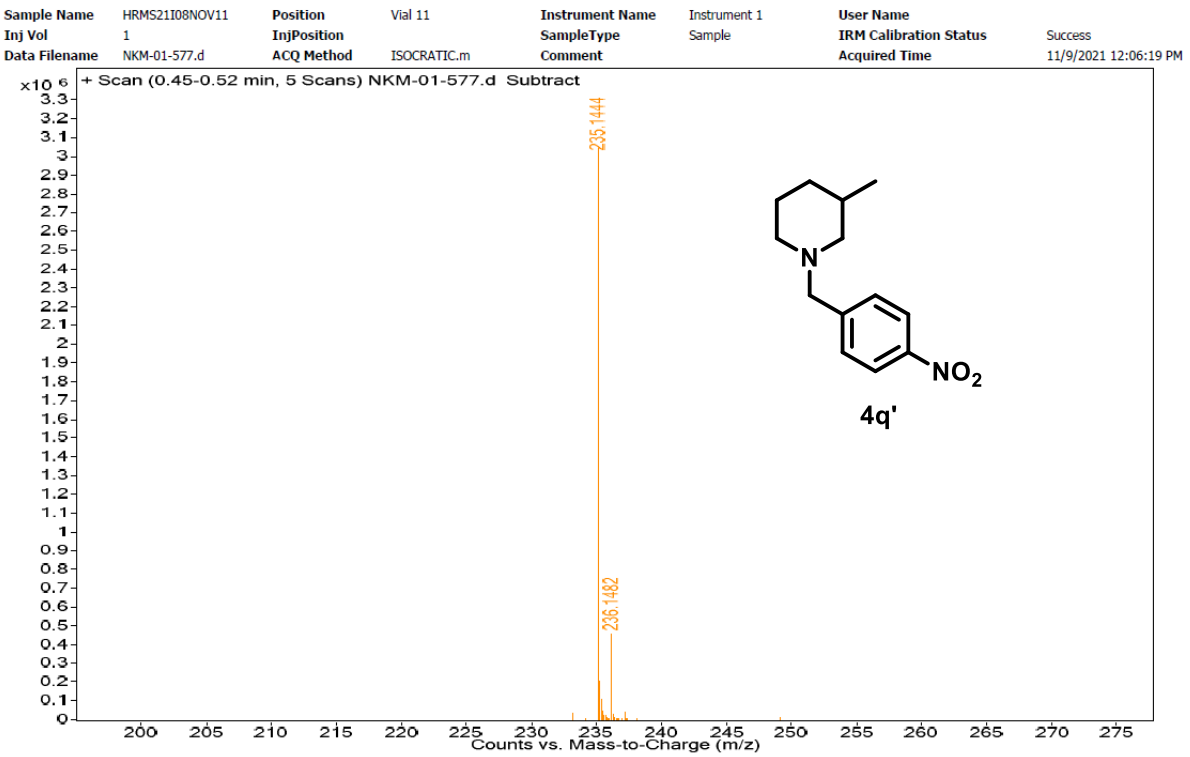


Figure S-136: HRMS spectrum of compound **4q'**

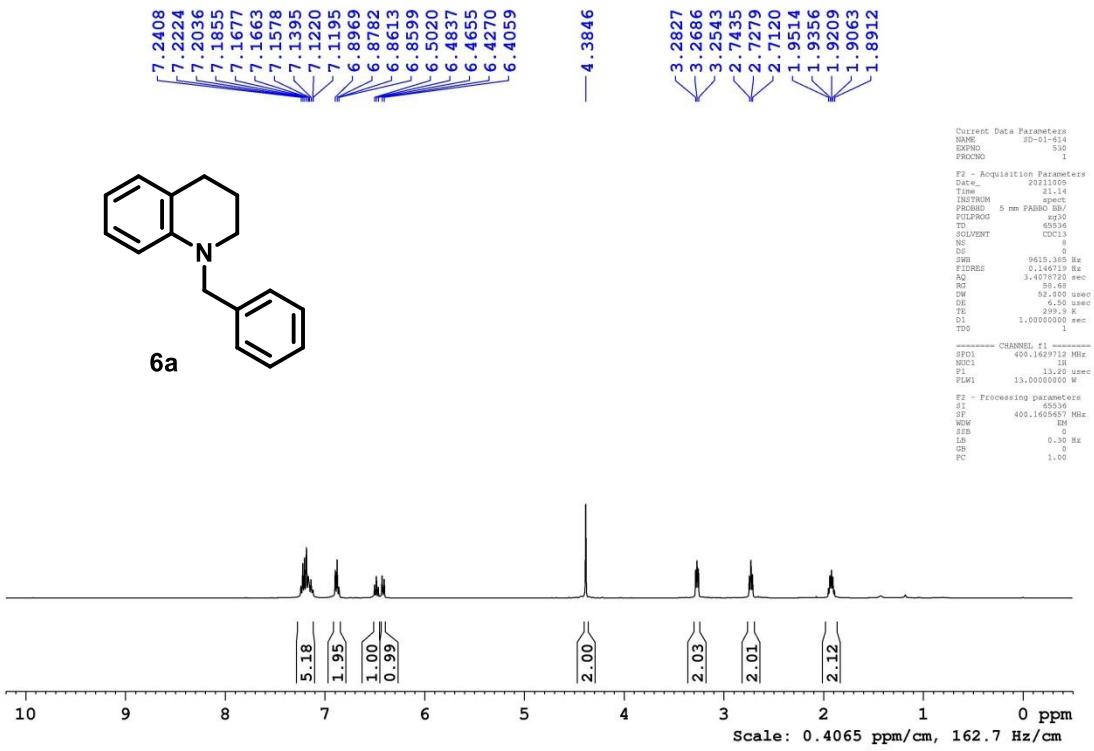


Figure S-137: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6a**

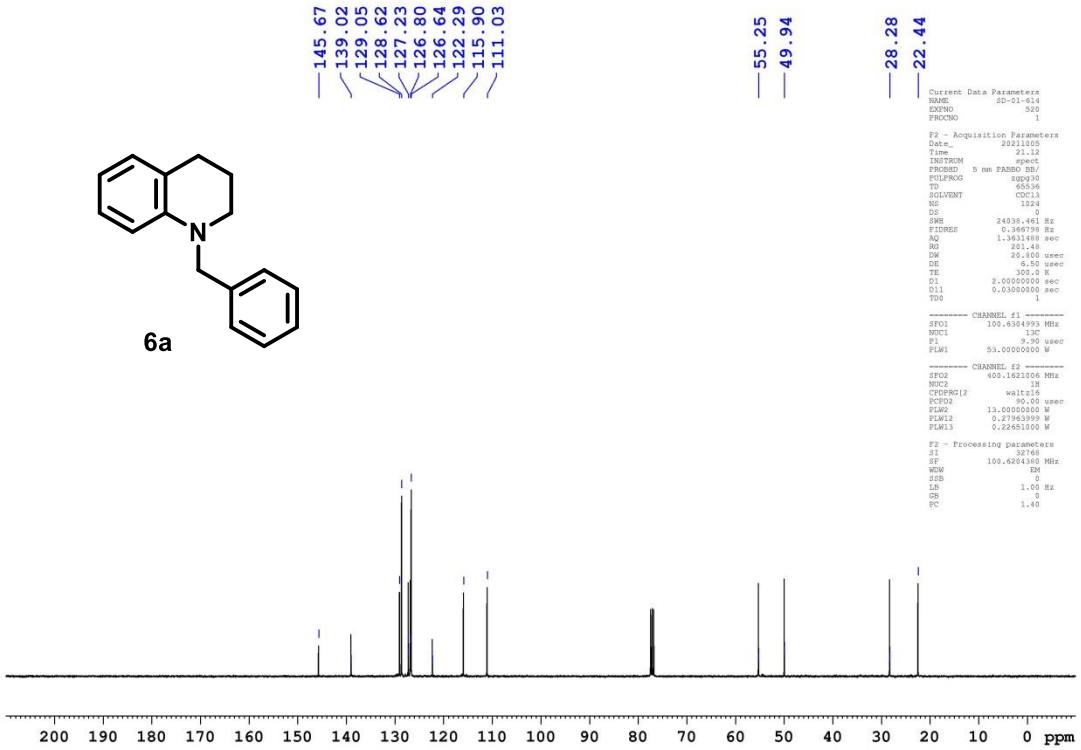


Figure S-138: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6a**

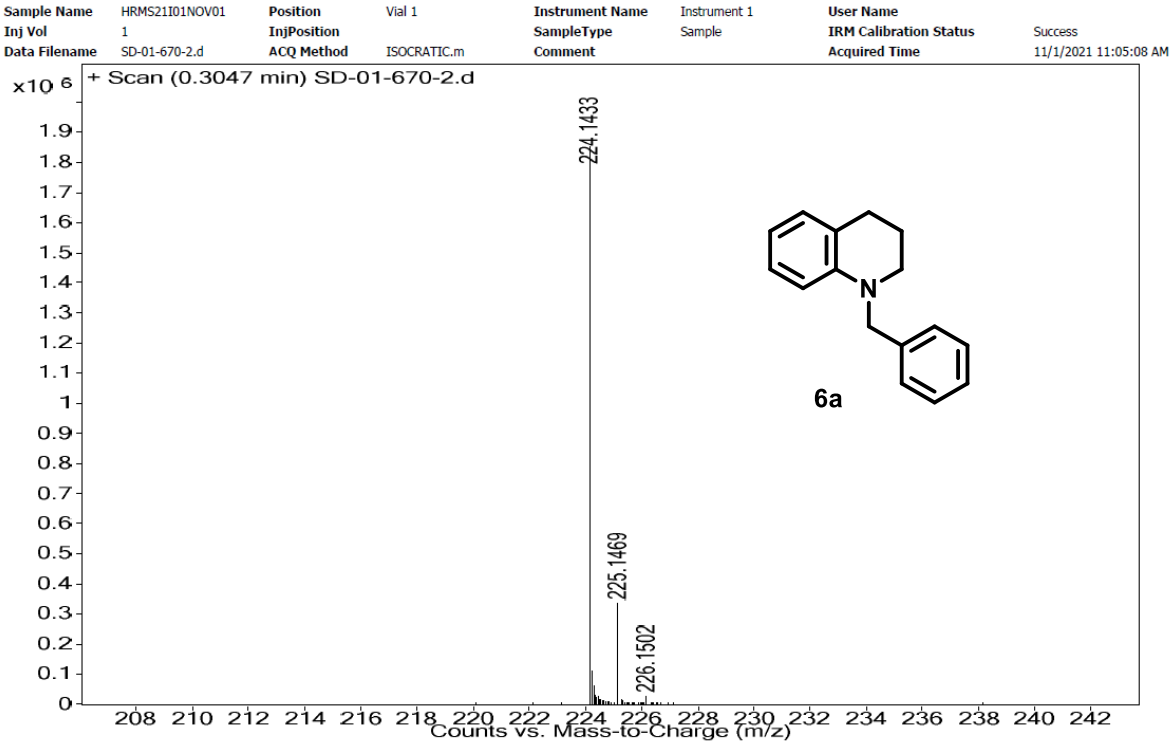


Figure S-139: HRMS spectrum of compound **6a**

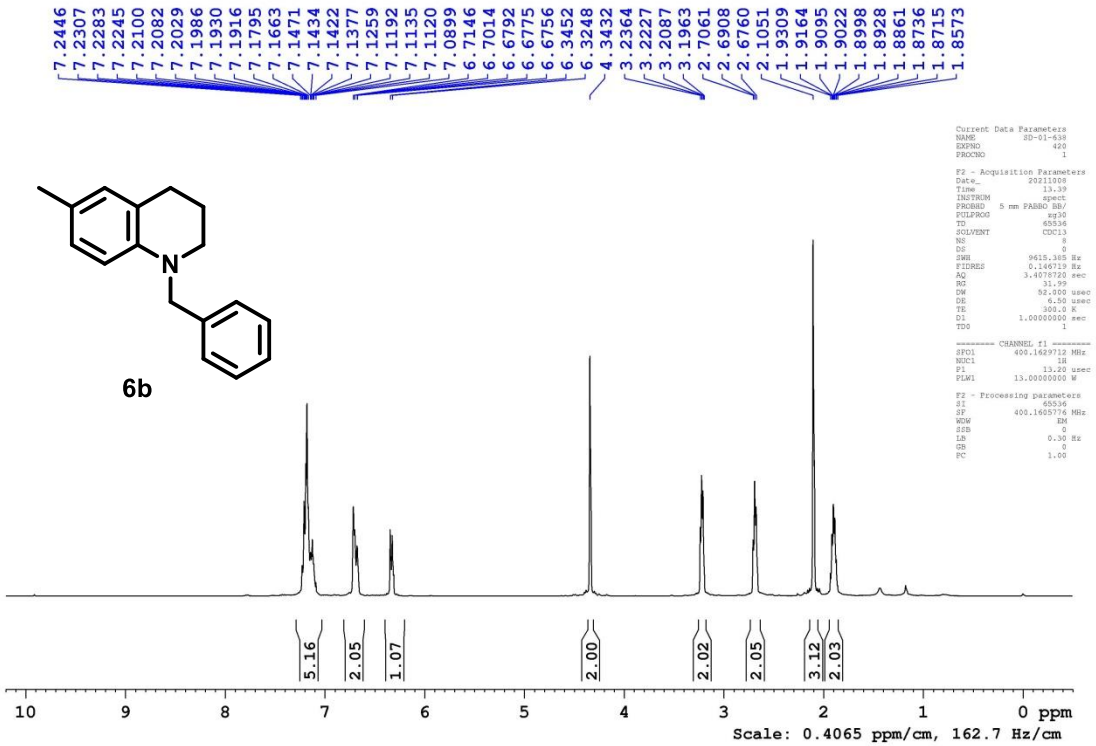


Figure S-140: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6b**

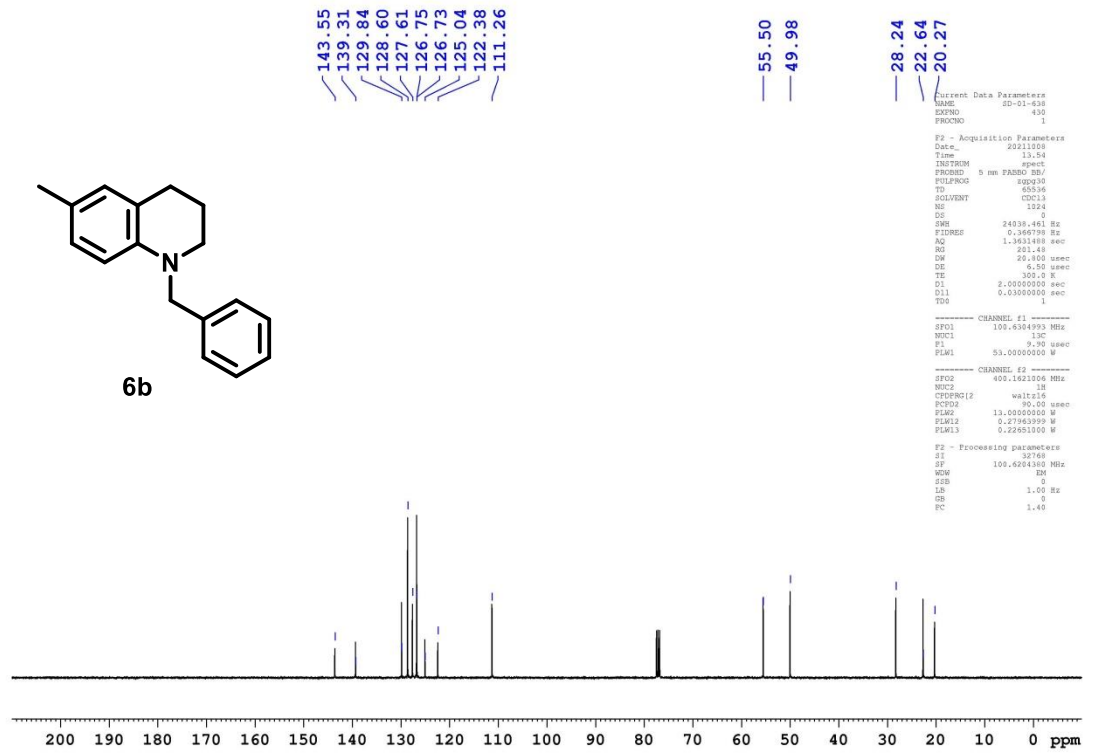


Figure S-141: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6b**

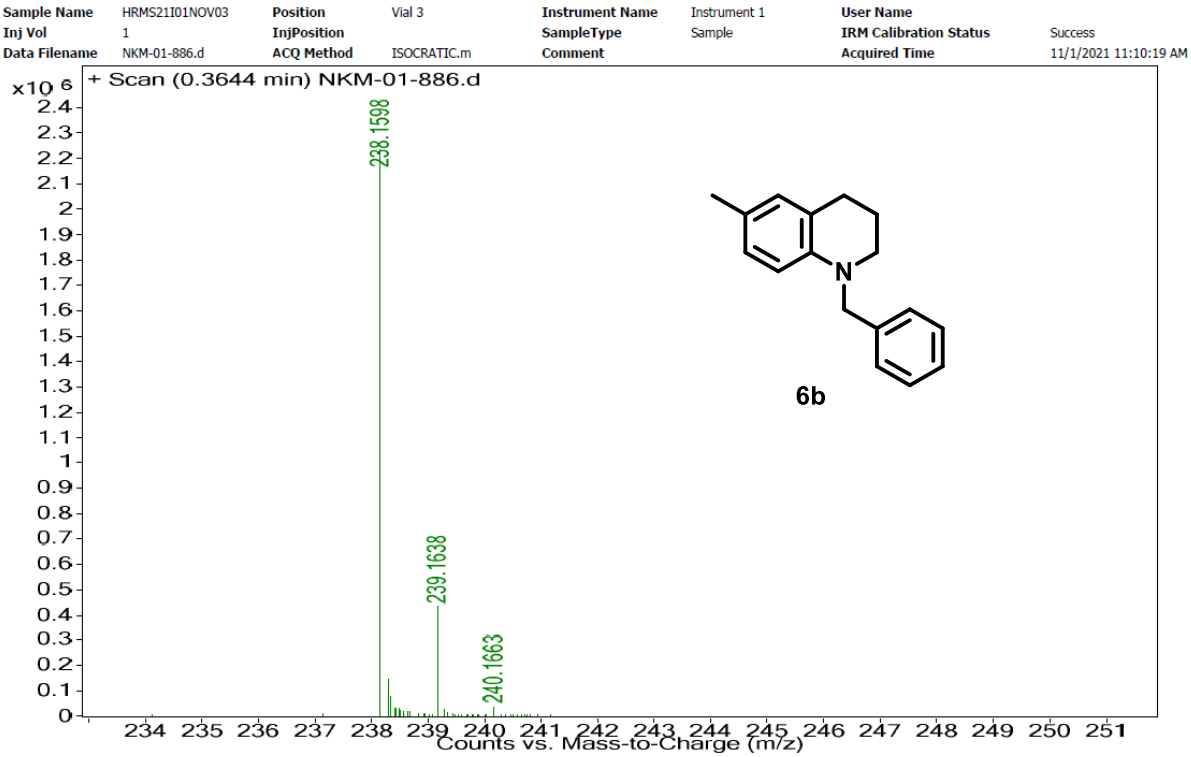


Figure S-142: HRMS spectrum of compound **6b**

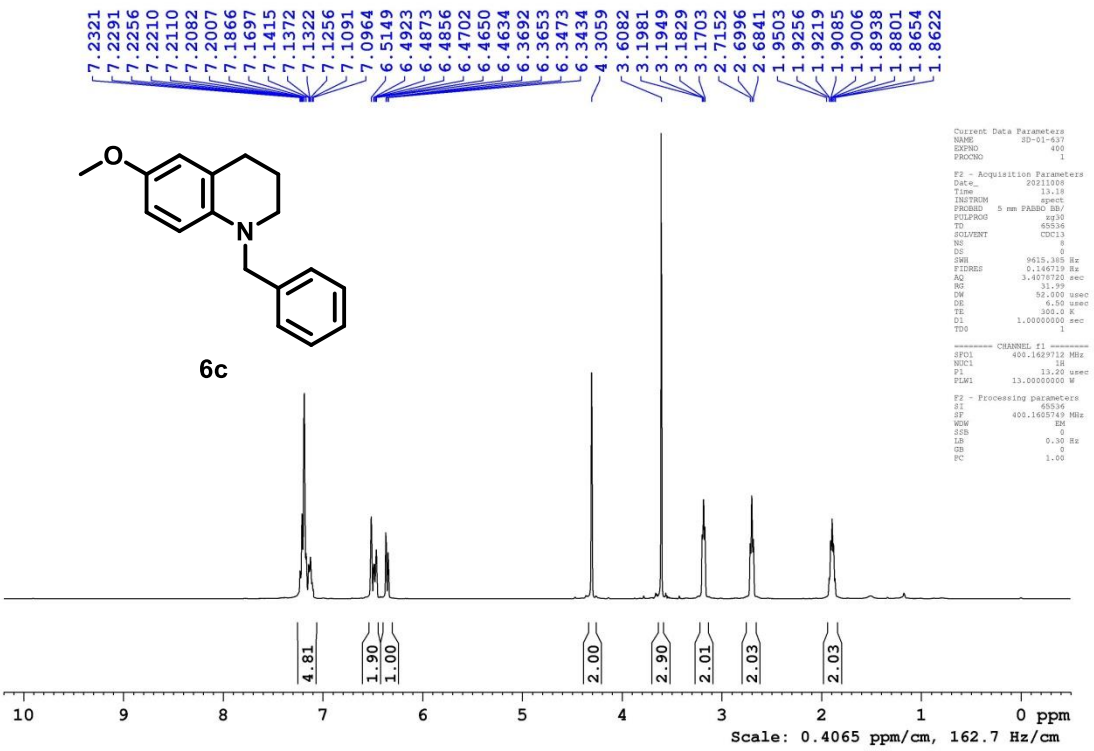


Figure S-143: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6c**

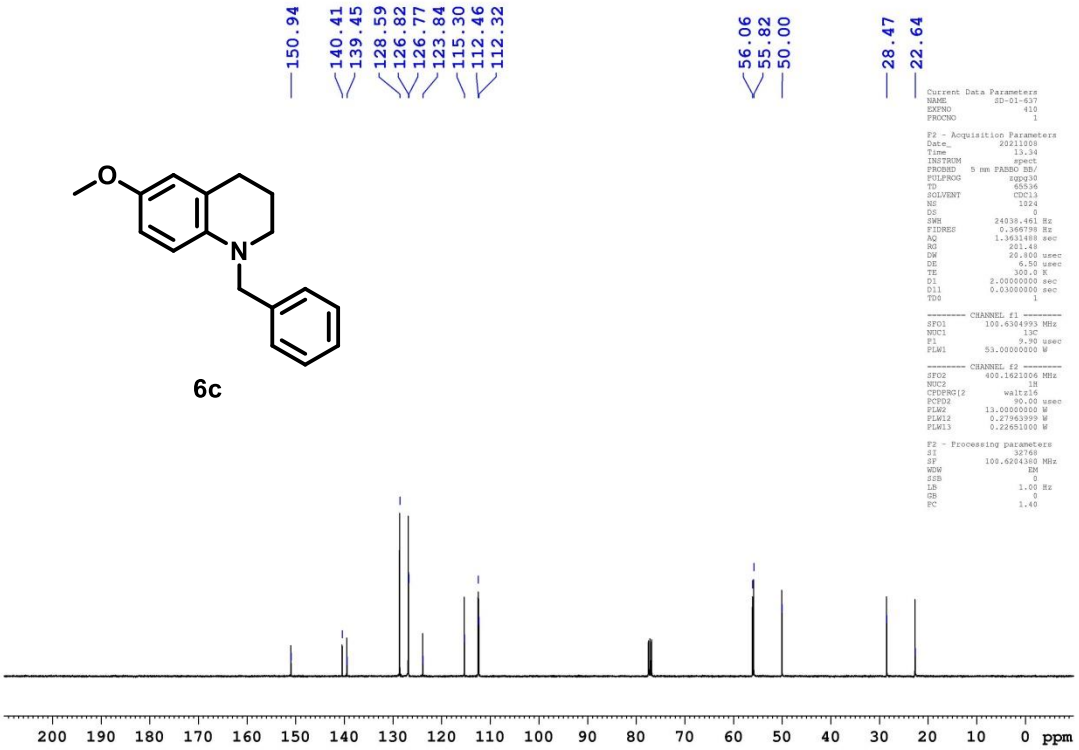


Figure S-144: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6c**

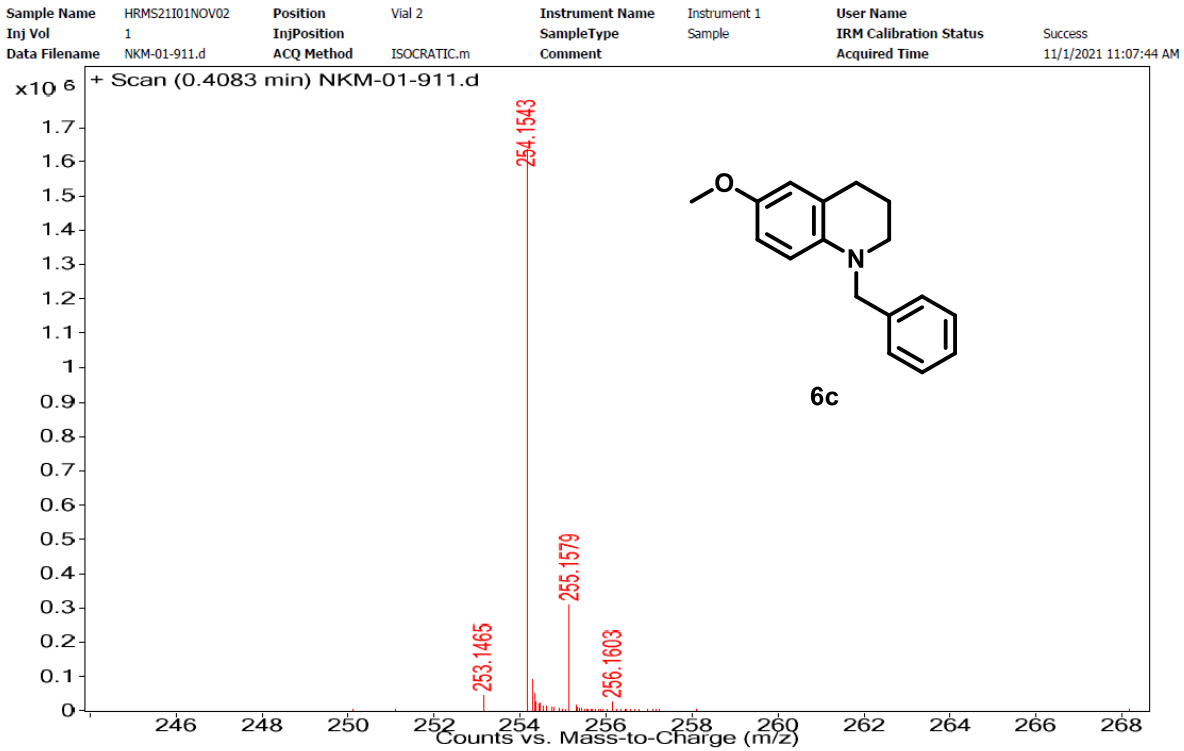


Figure S-145: HRMS spectrum of compound **6c**

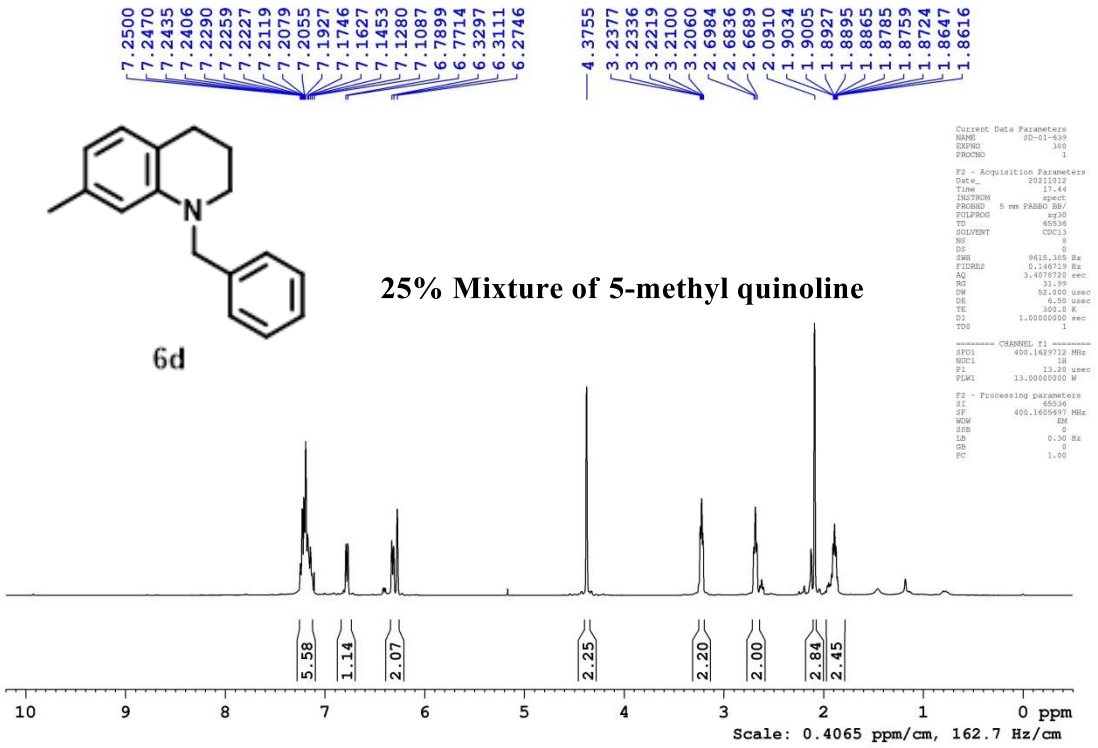


Figure S-146: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6d**

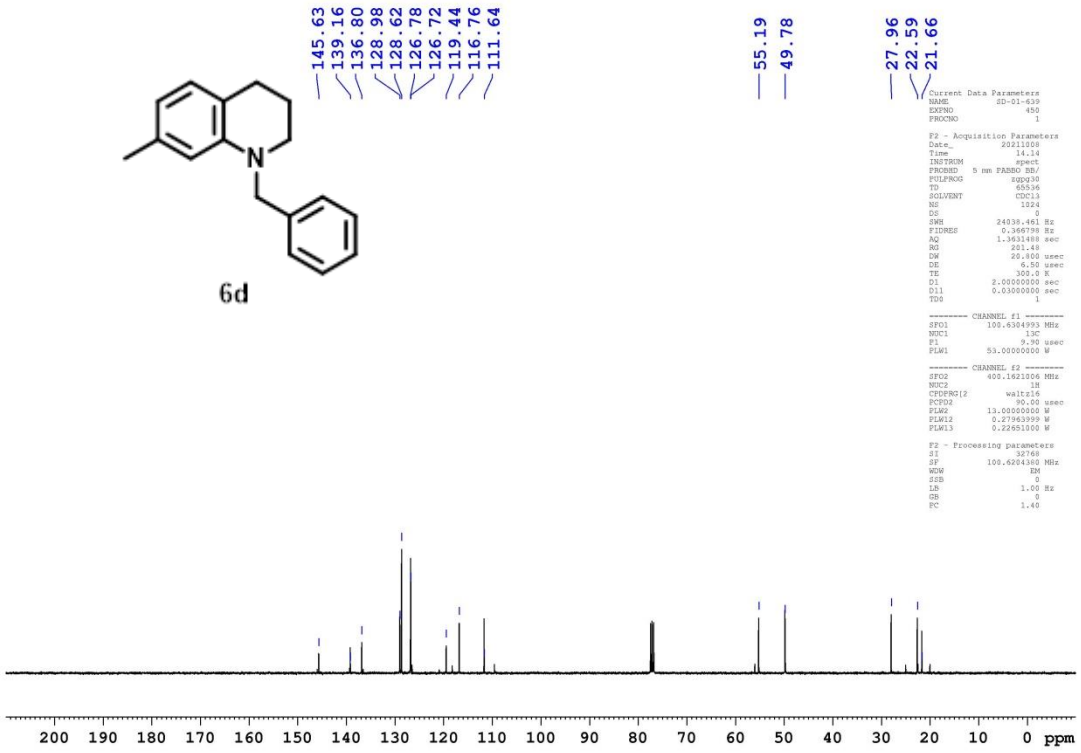


Figure S-147: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6d**

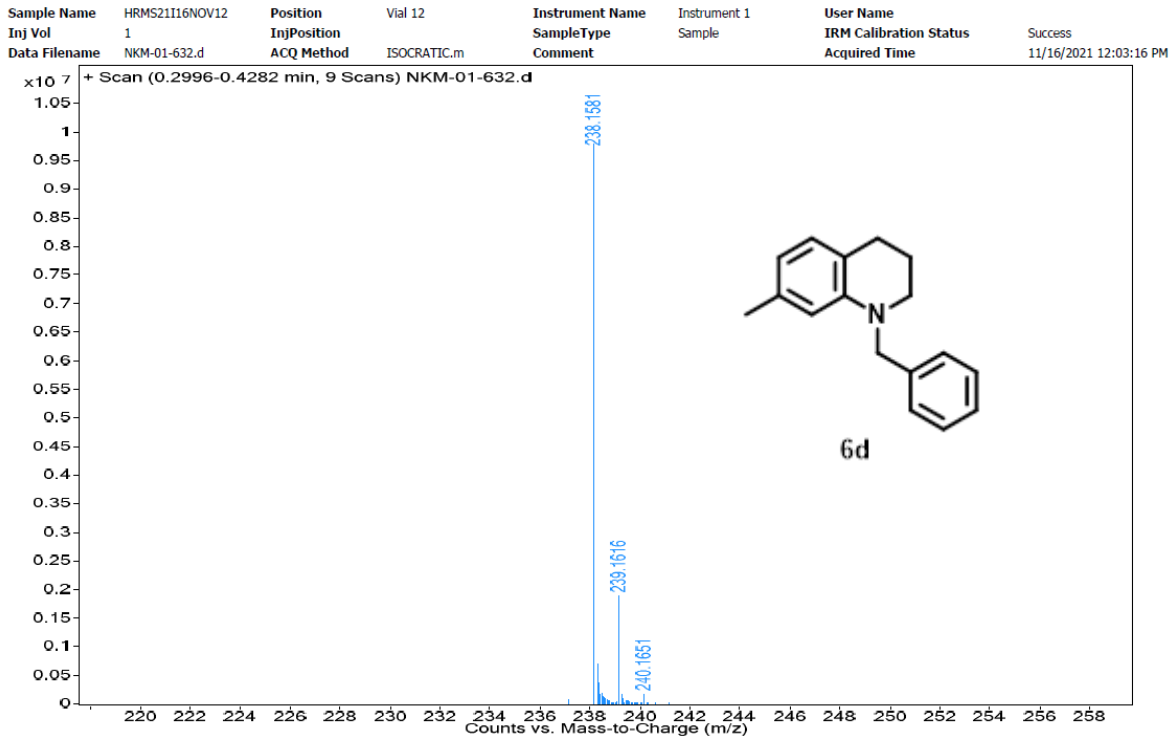


Figure S-148: HRMS spectrum of compound **6d**

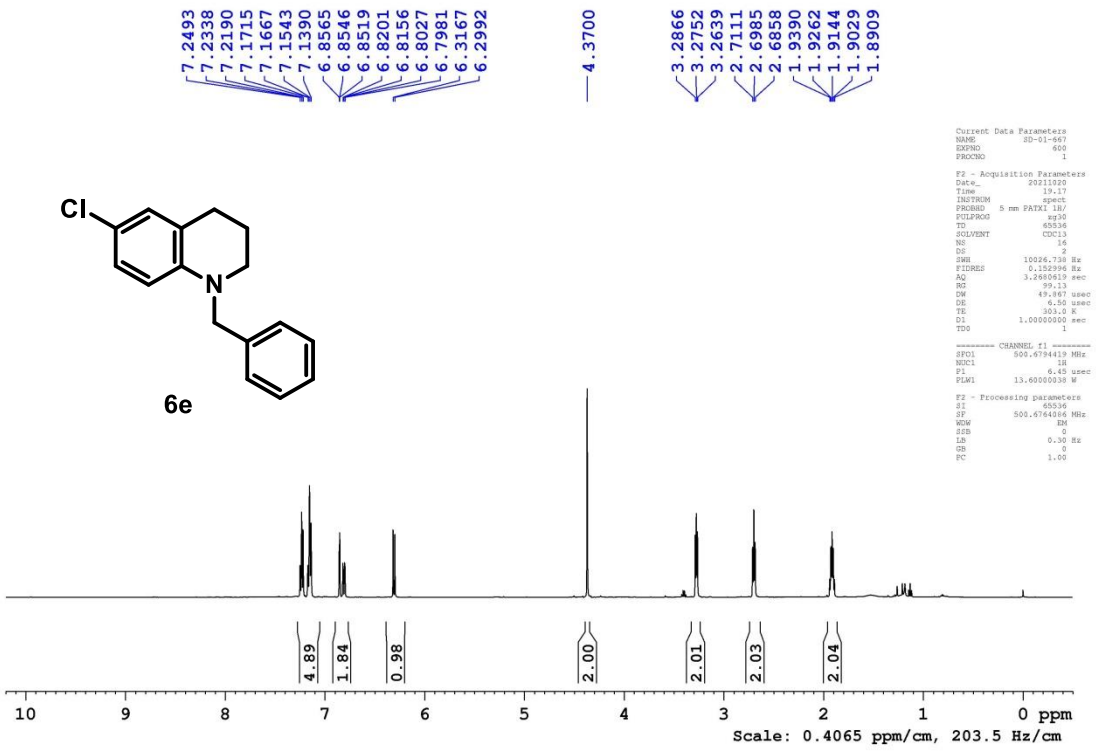


Figure S-149: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **6e**

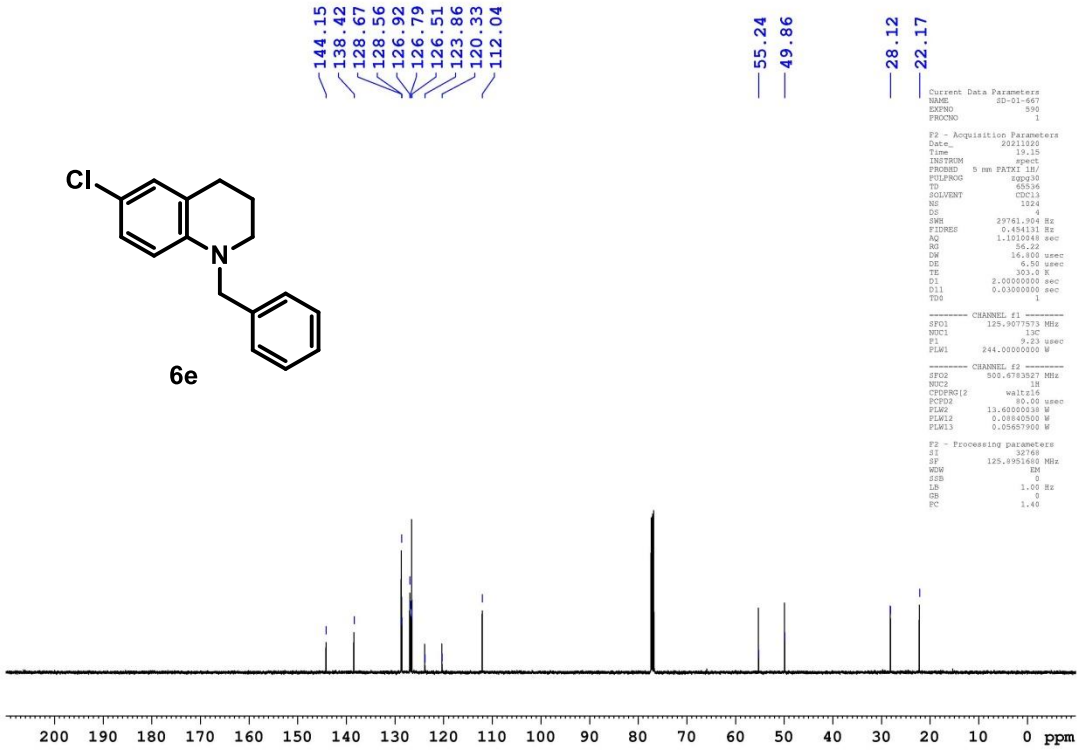


Figure S-150: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **6e**

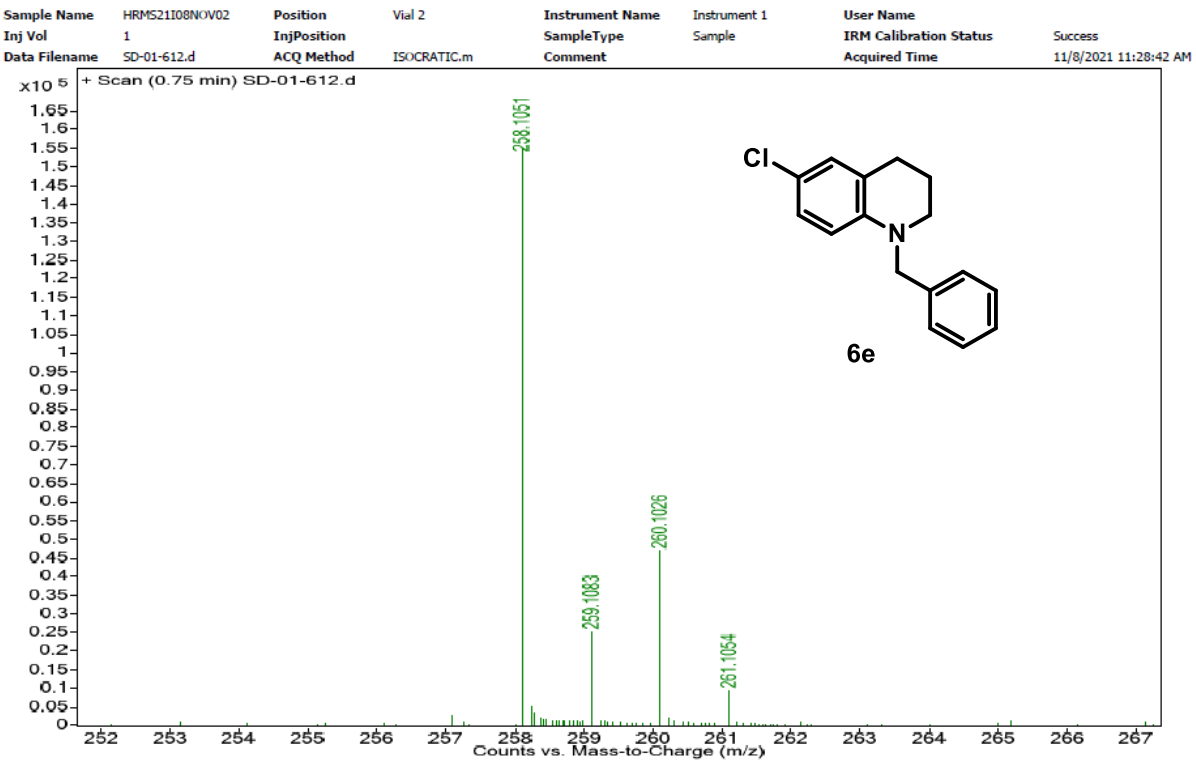


Figure S-151: HRMS spectrum of compound **6e**

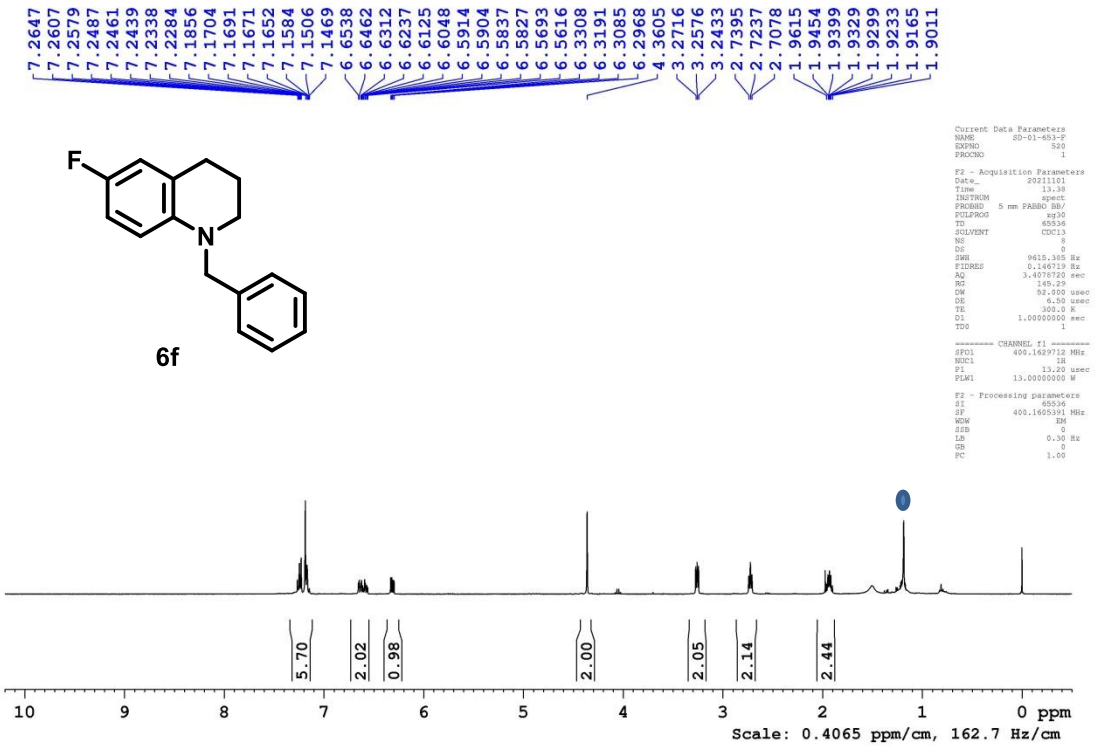


Figure S-152: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6f**

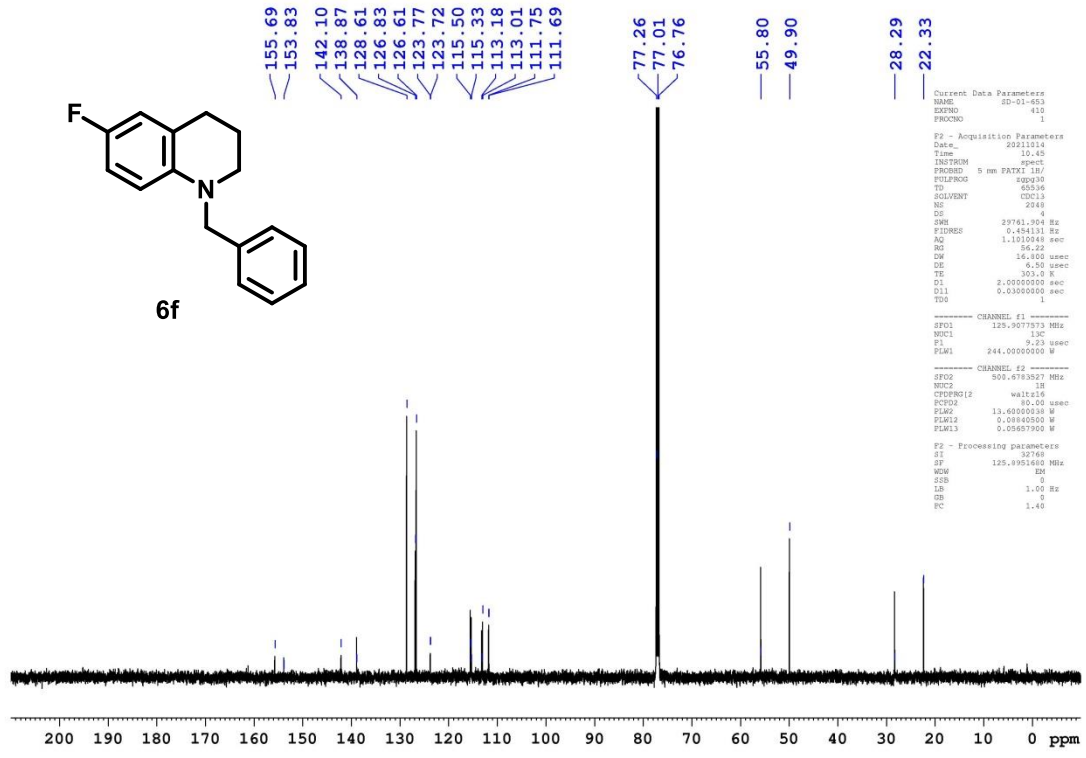


Figure S-153: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **6f**

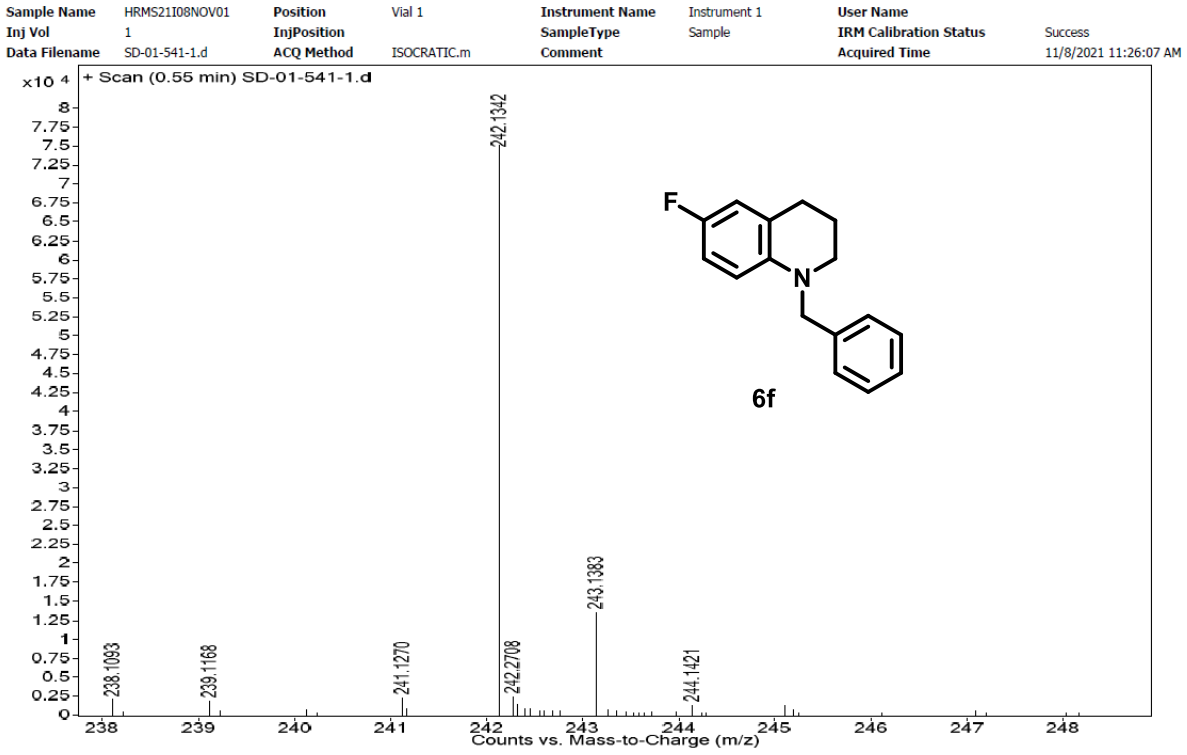


Figure S-154: HRMS spectrum of compound **6f**

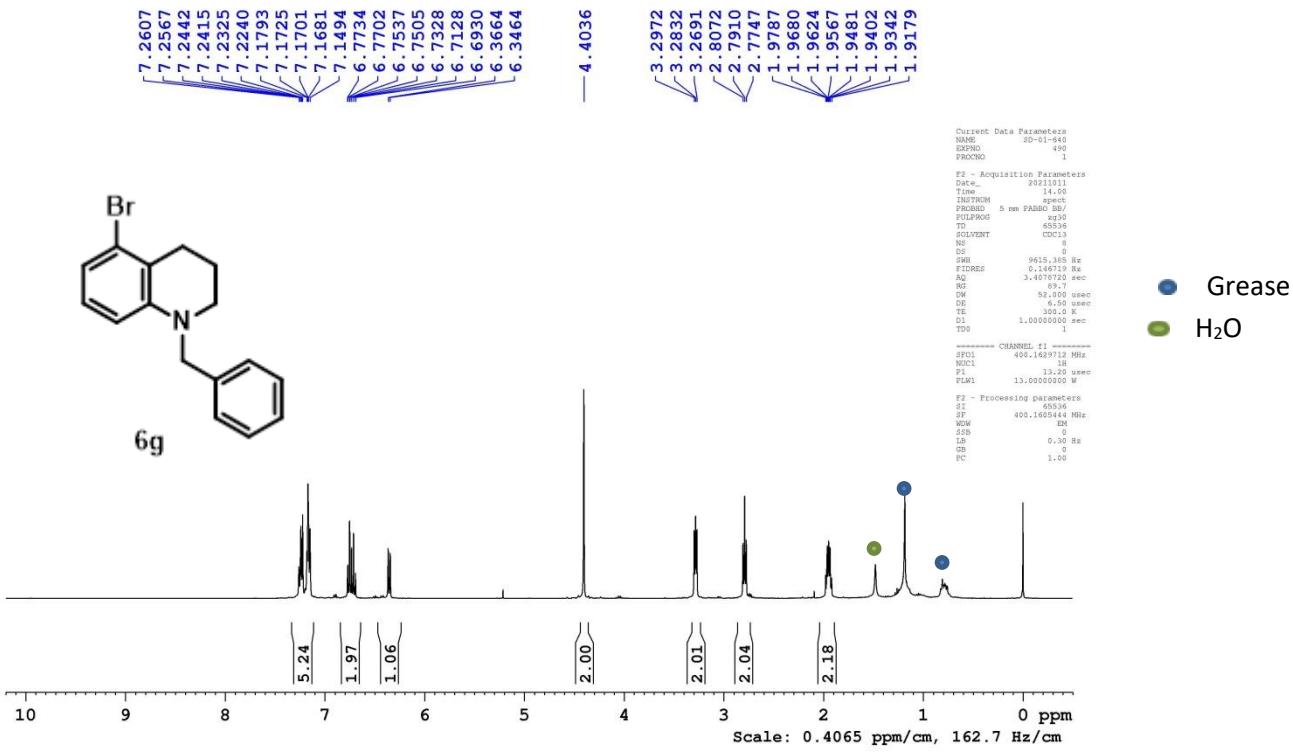


Figure S-155: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6g**

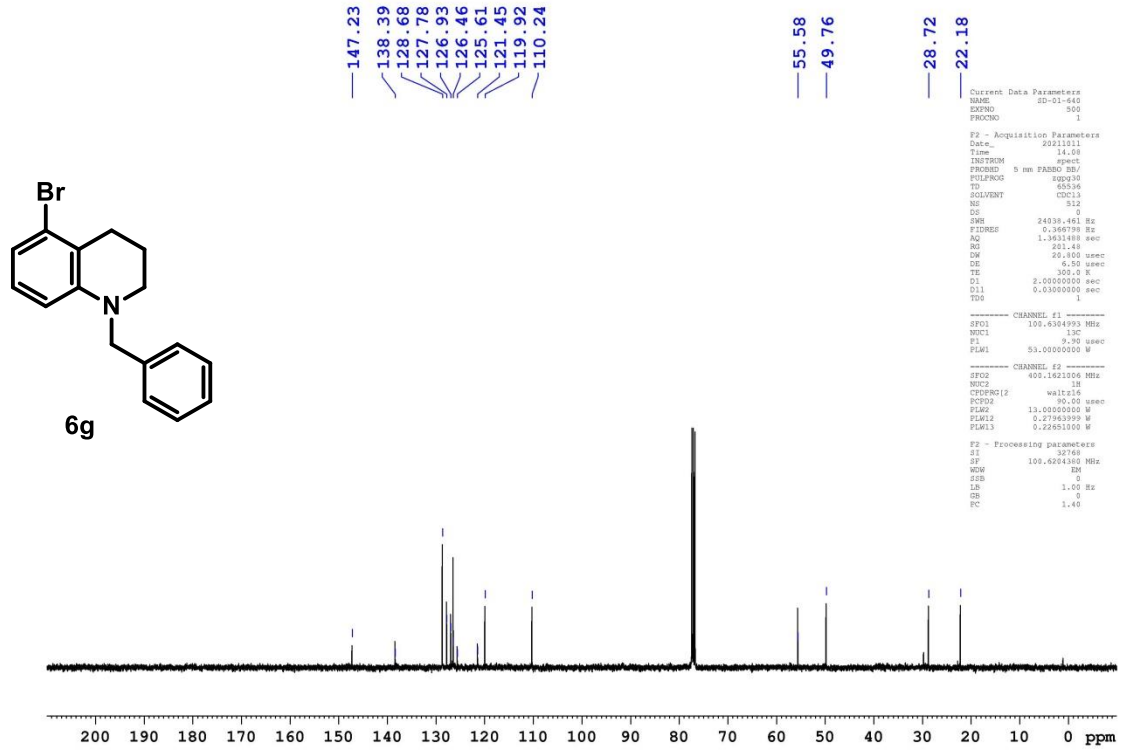


Figure S-156: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6g**

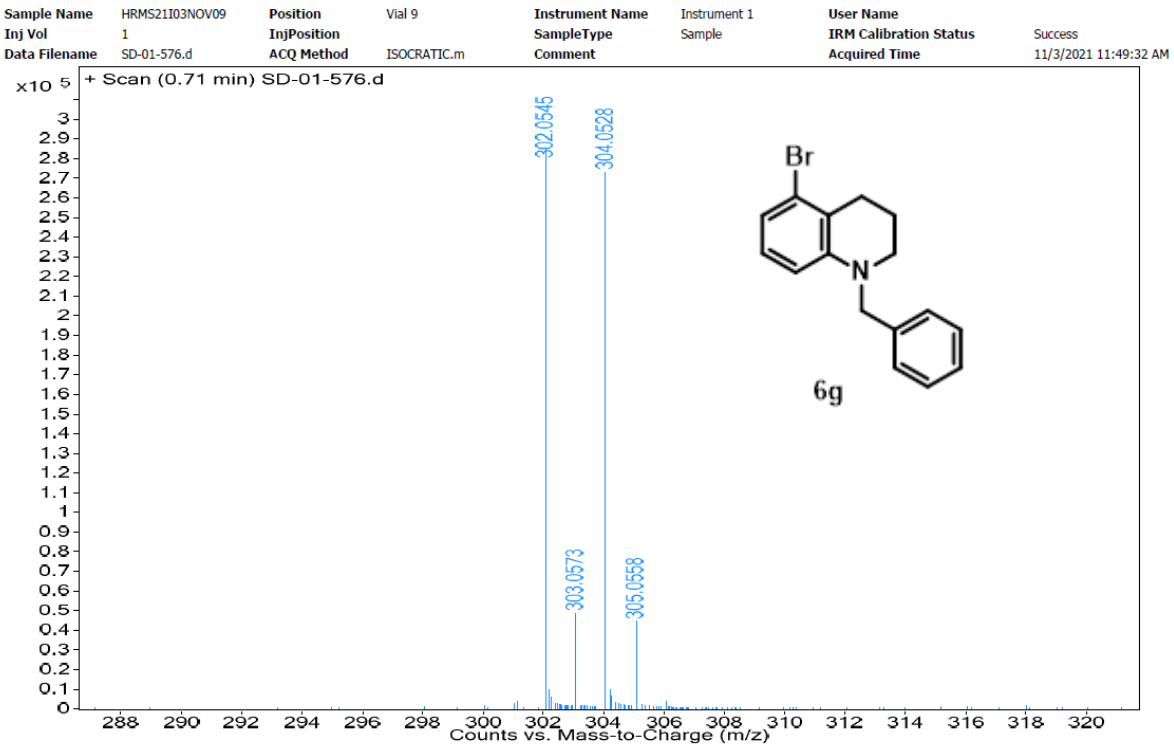


Figure S-157: HRMS spectrum of compound **6g**

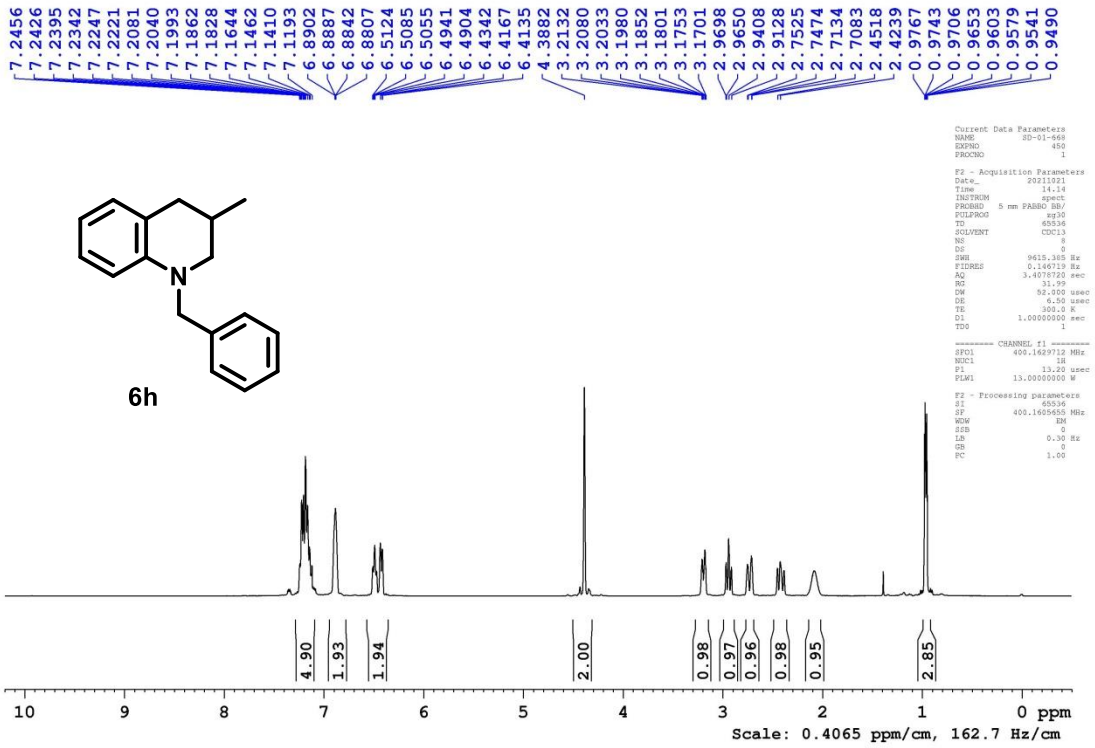


Figure S-158: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6h**

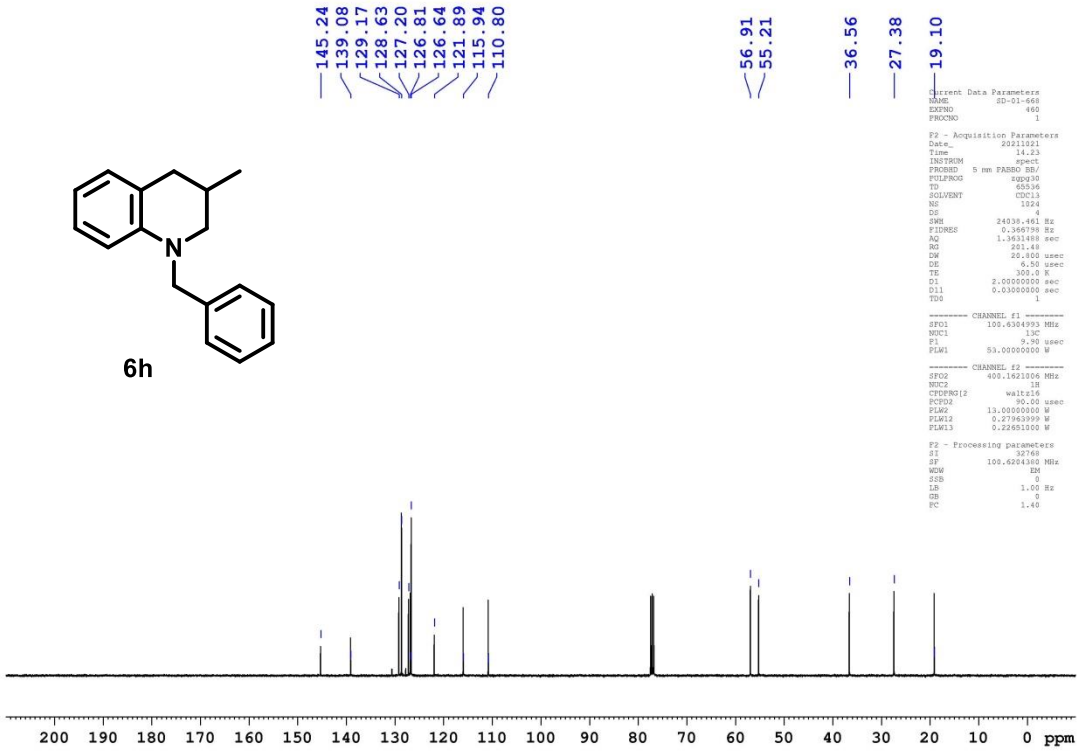


Figure S-159: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6h**

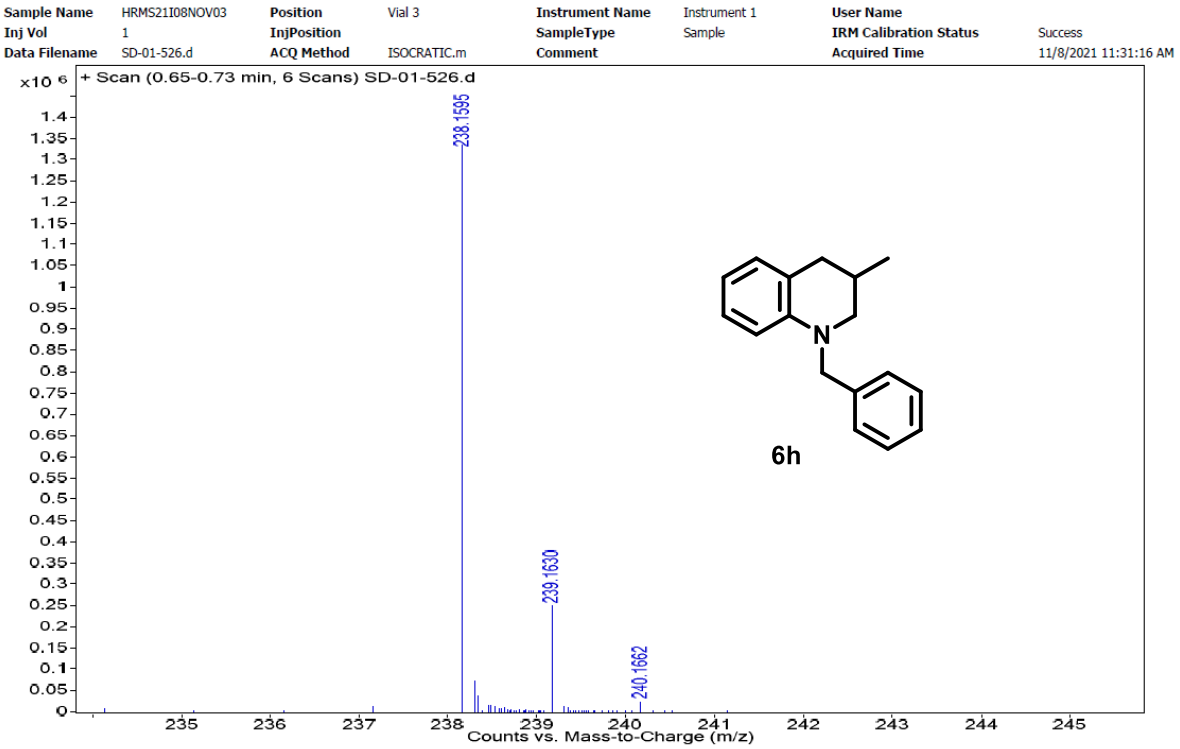


Figure S-160: HRMS spectrum of compound **6h**

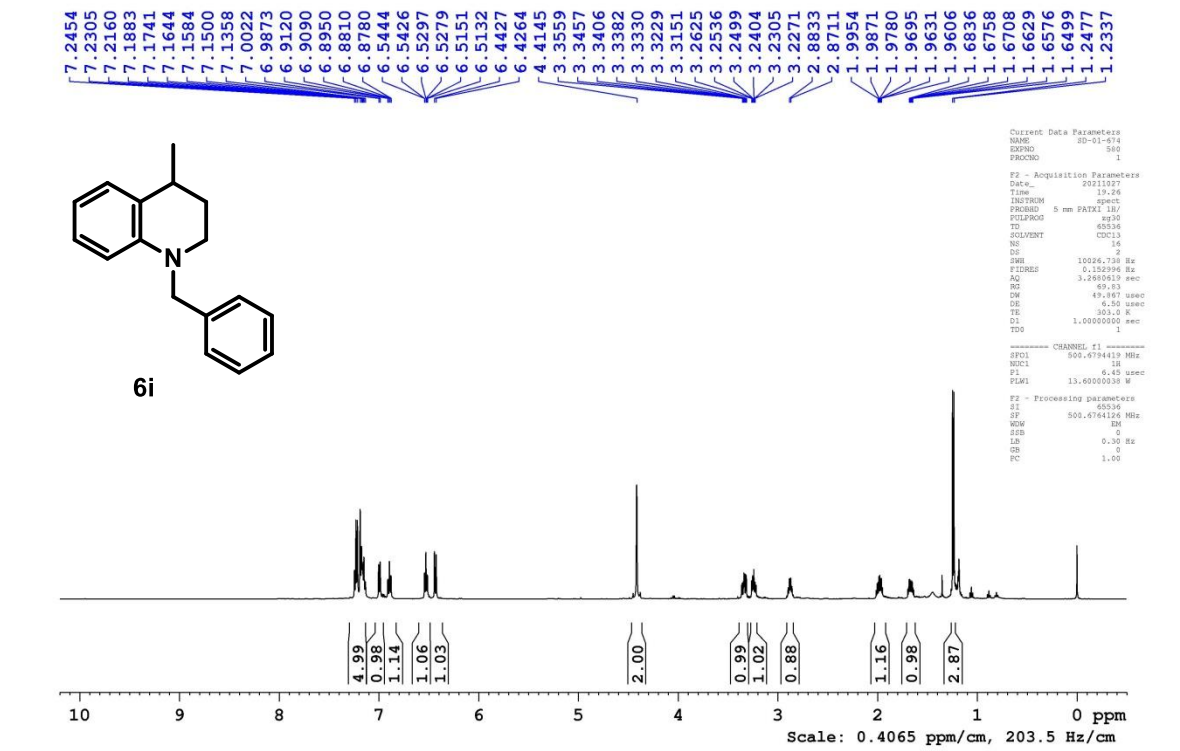


Figure S-161: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **6i**

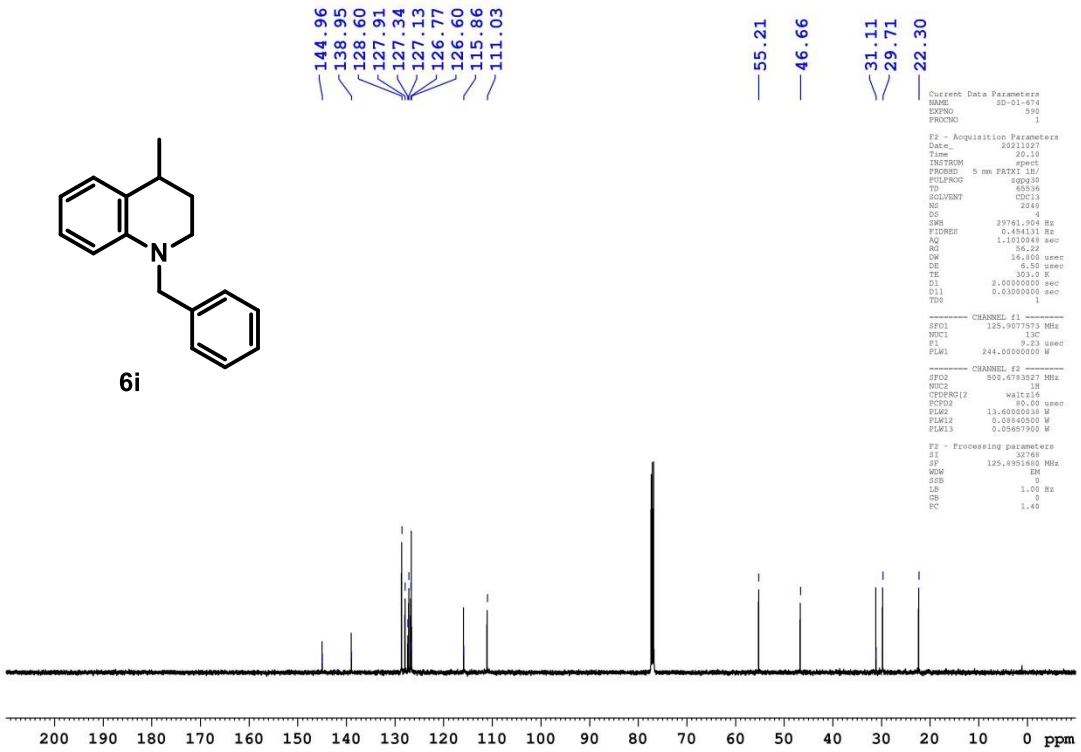


Figure S-162: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **6i**

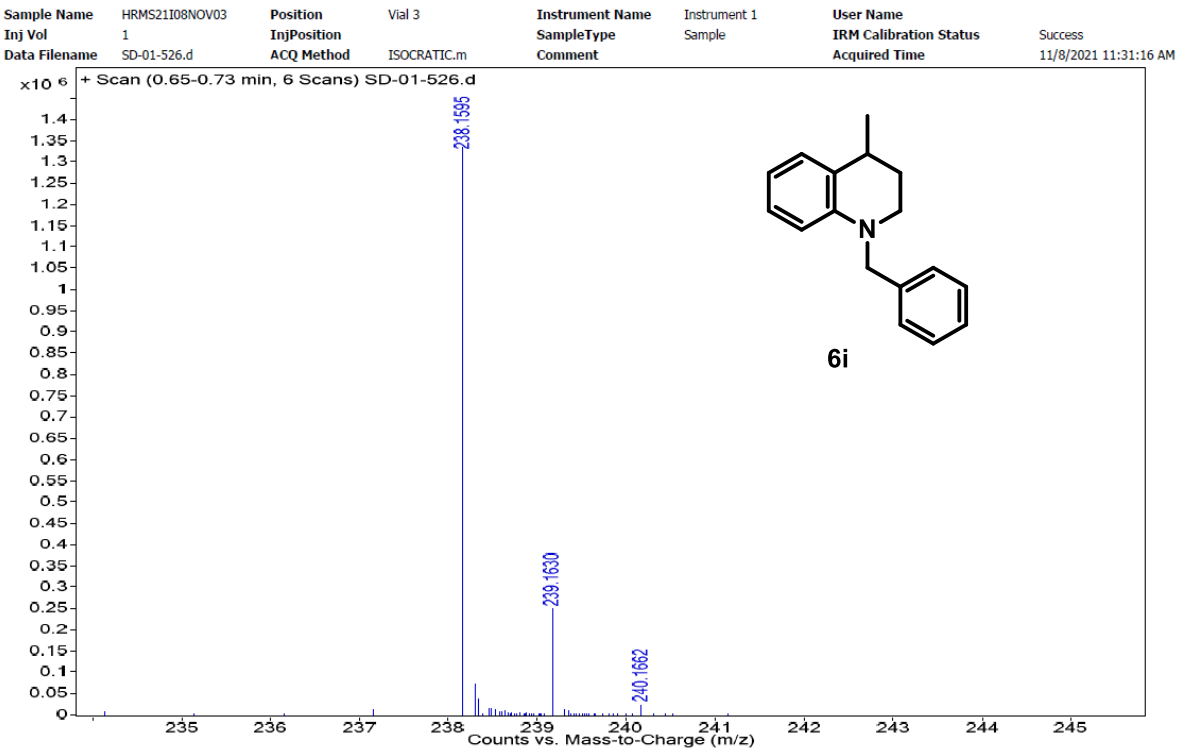


Figure S-163: HRMS spectrum of compound **6i**

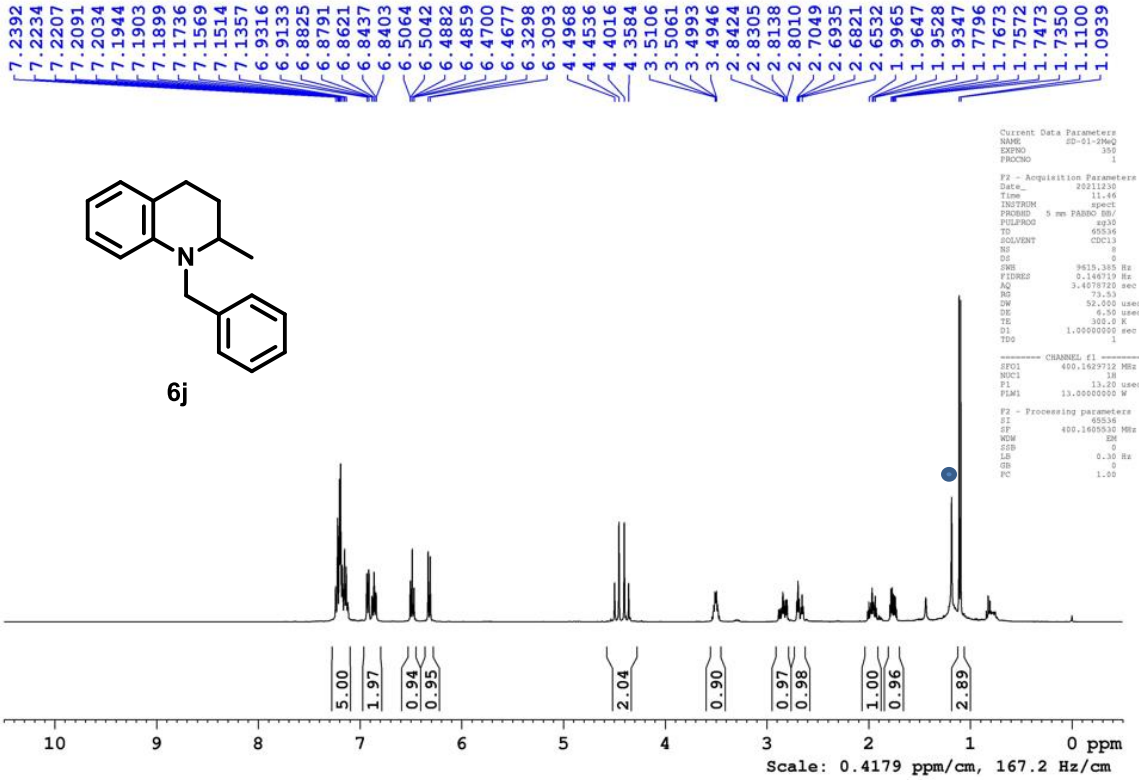


Figure S-164: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6j**

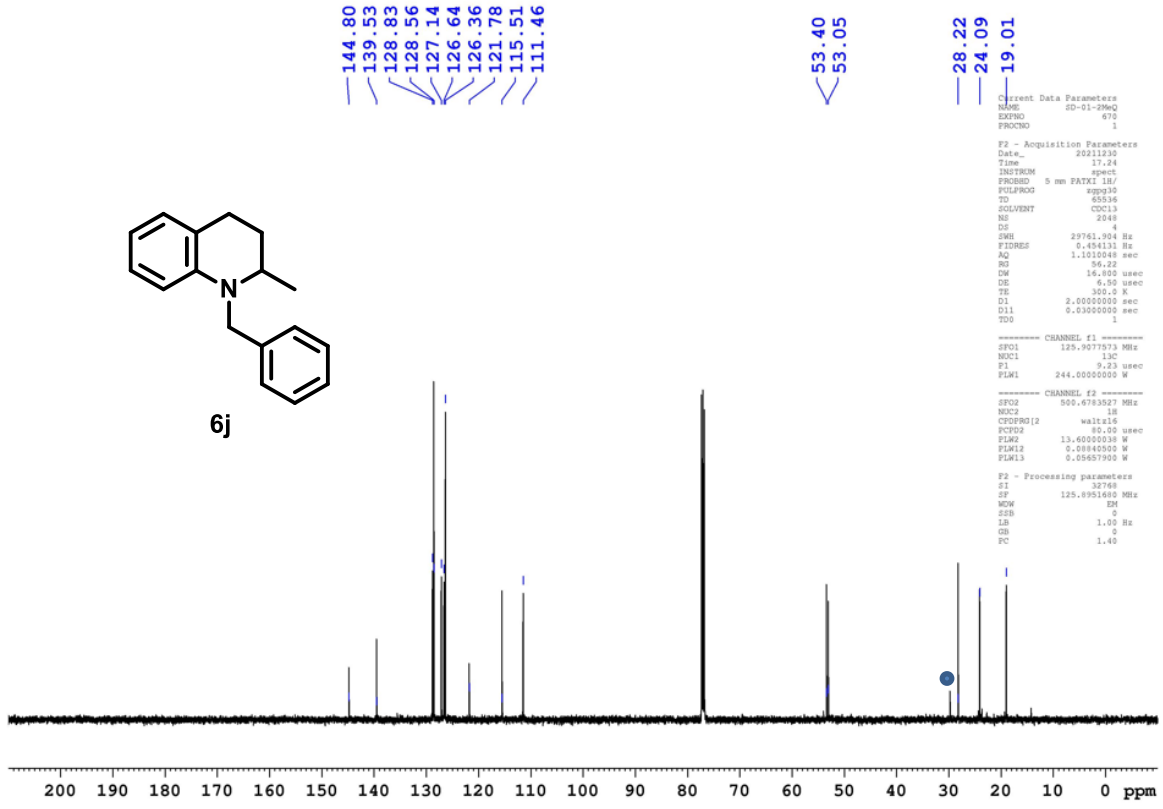


Figure S-165: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **6j**

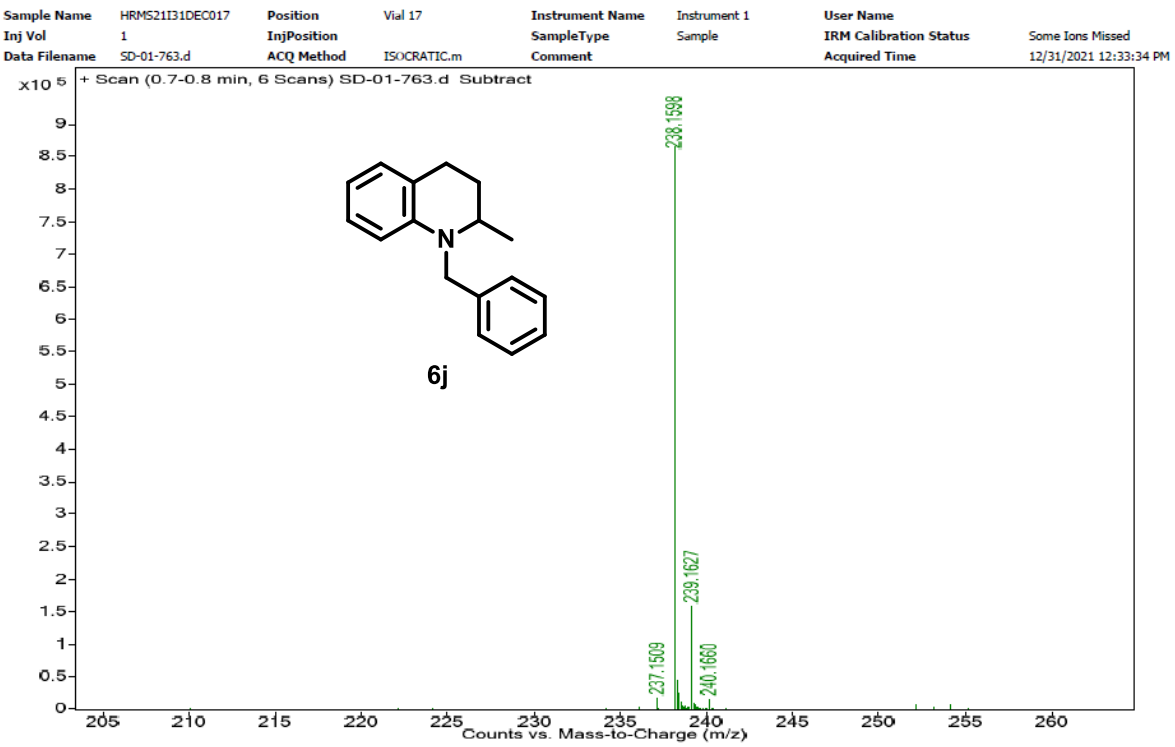


Figure S-166: HRMS spectrum of compound **6j**

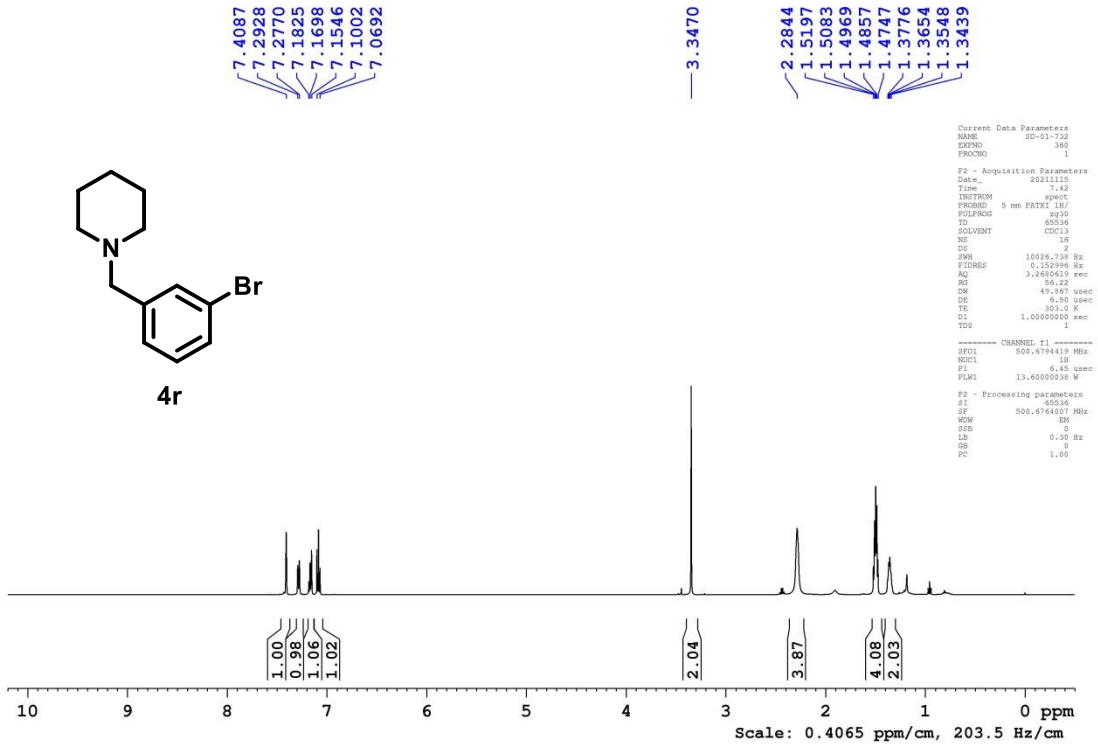


Figure S-167: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4r**

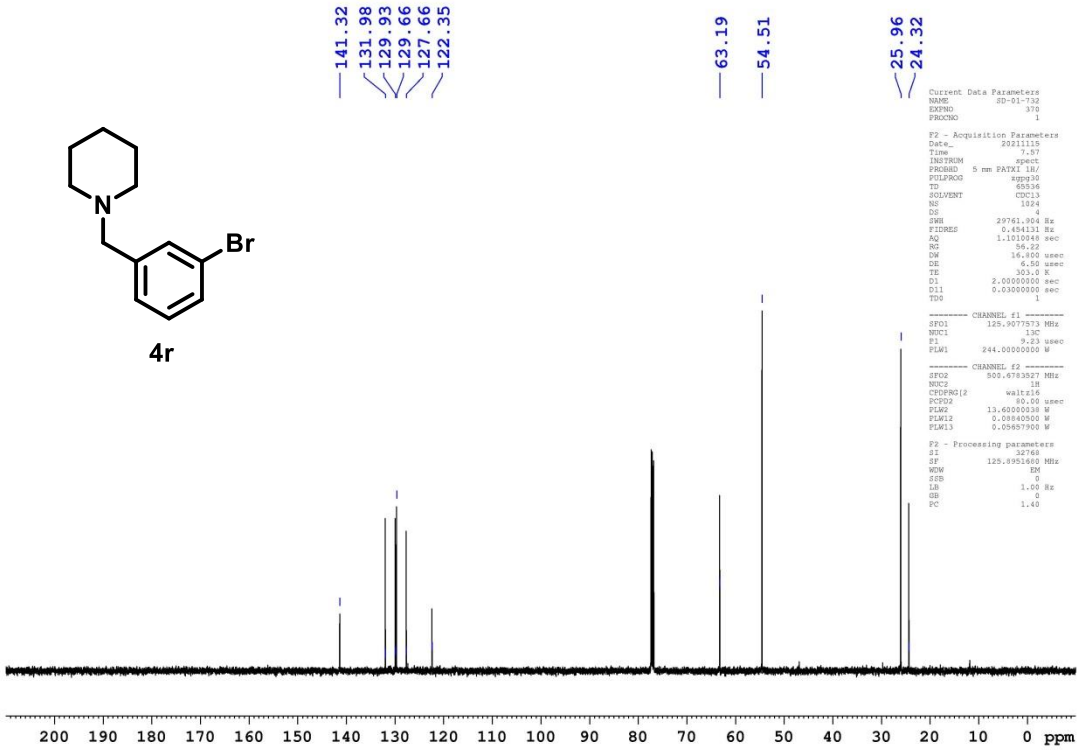


Figure S-168: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4r**

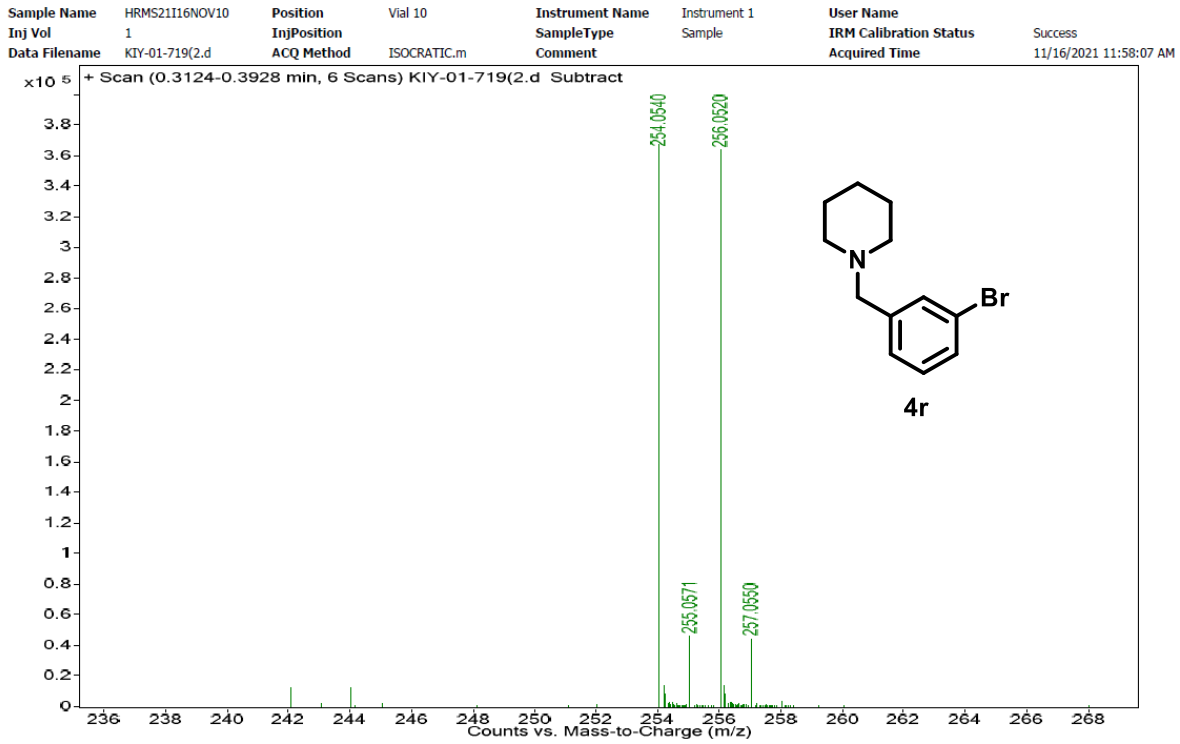


Figure S-169: HRMS spectrum of compound **4r**

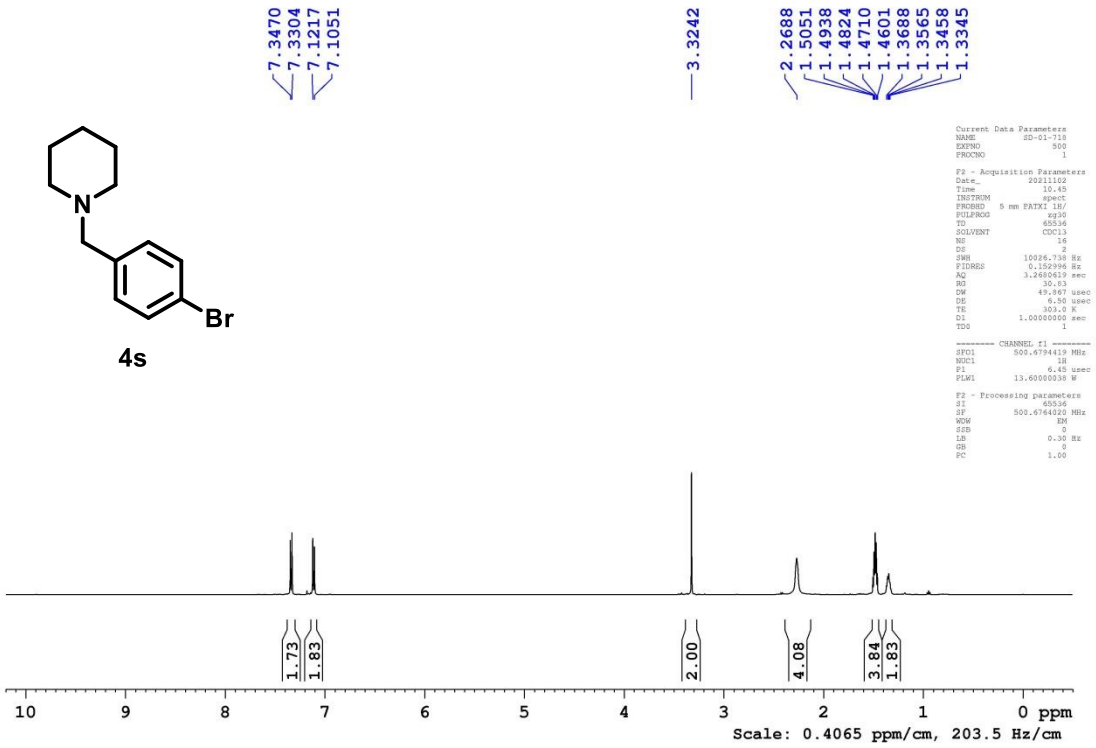


Figure S-170: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4s**

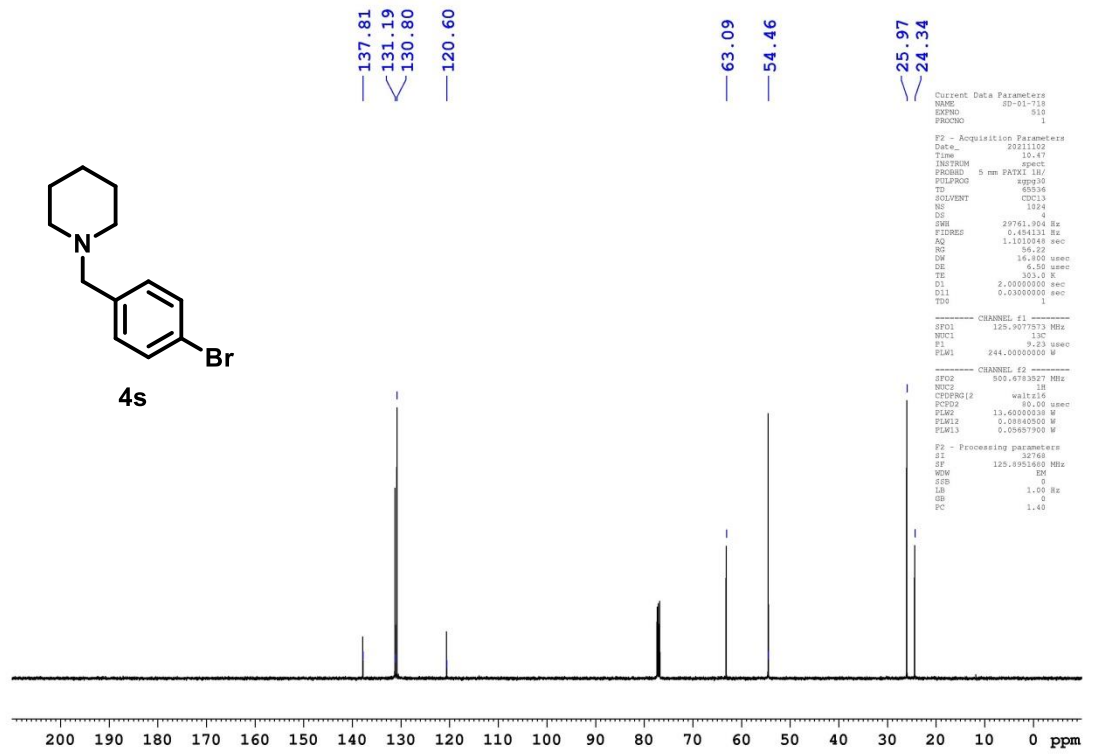


Figure S-171: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4s**

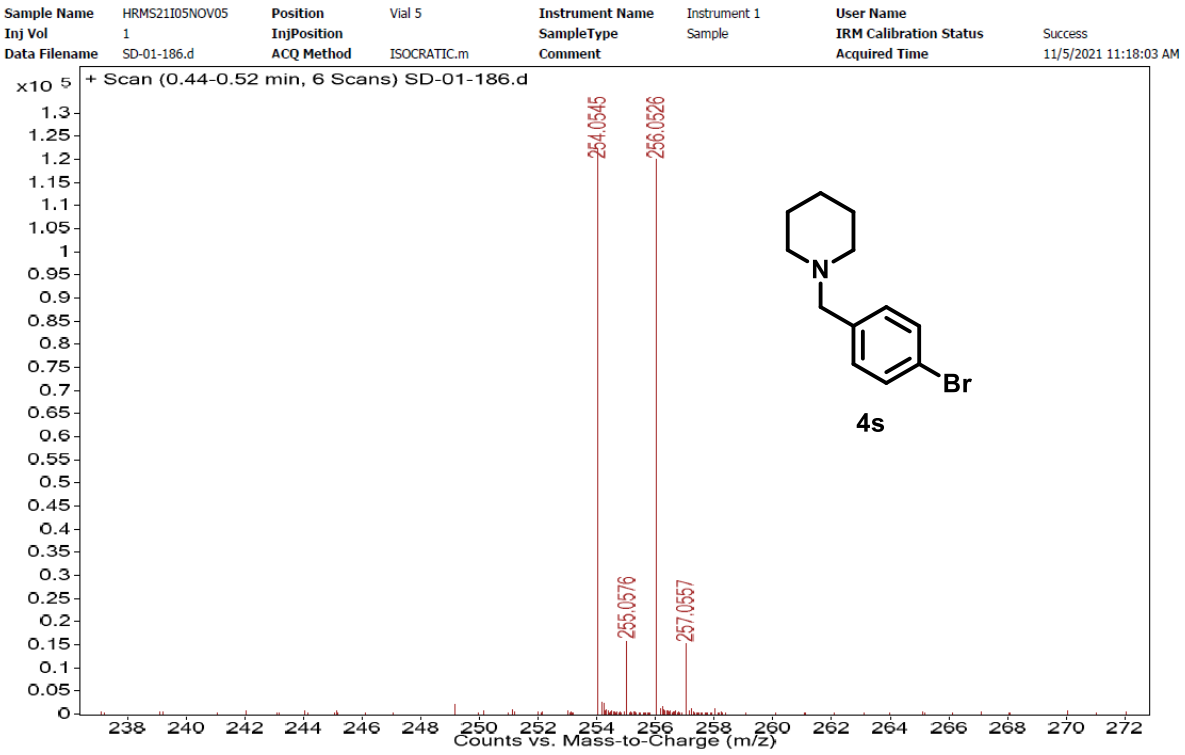


Figure S-172: HRMS spectrum of compound **4s**