Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Copper-Catalysed Oxidative *α*-C(sp^3)–H Nitroalkylation of (Hetero)aryl-fused Cyclic Amines

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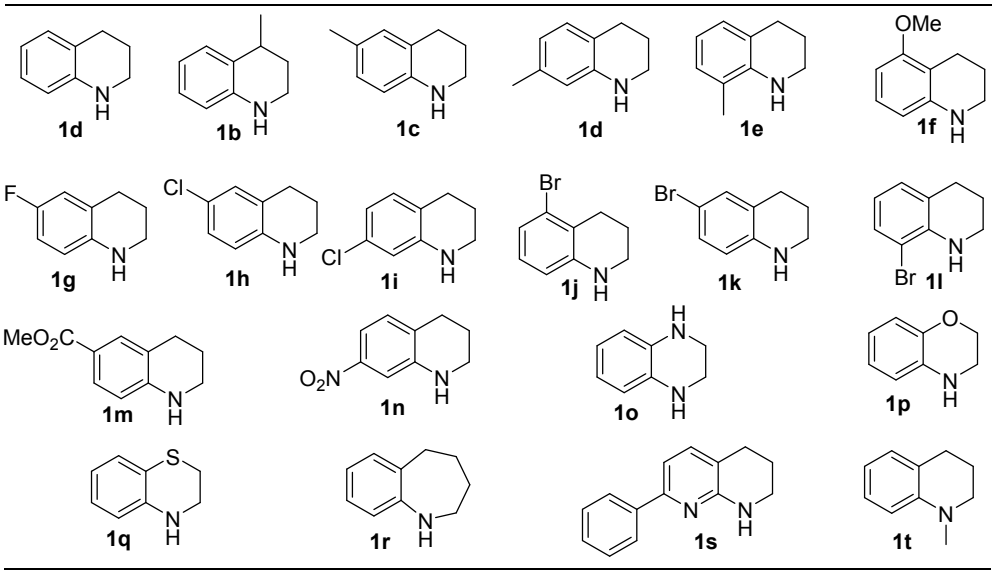
1. General information

All the obtained products were characterized by melting points (m.p), ^{1}H-NMR, ^{13}C-NMR and infrared spectra (IR). Melting points were measured on an Electrothemal SGW-X4 microscopy digital melting point apparatus and are uncorrected; IR spectra were recorded on a FTLA2000 spectrometer; ^{1}H-NMR and ^{13}C-NMR spectra were obtained on Bruker-400 and referenced to $CHCl_3$ (7.26 ppm for ^{1}H, and 77.2 ppm for ^{13}C) or DMSO-d_6 (2.50 ppm for ^{1}H, and 39.5 ppm for ^{13}C). Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm; Unless otherwise stated, all the reagents were purchased from commercial sources (*J*&KChemic, TCI, Fluka, Acros, SCRC), used without further purification.

2. Substrates preparation

General Procedure for the Preparation of tetrahydroquinolines



Scheme S1. (Hetero)arene-fused cyclic amines employed for the reaction

Substrates tetrahydroquinolines **1** were prepared by the hydrogenation of the corresponding quinolines according to the literature method.[1] To a solution of quinolines (5.0 mmol, 1.0 equiv) in AcOH (25 mL) at 0 °C was added $NaBH_3CN$

(1.26 g, 20.0 mmol, 4 equiv) in portions. The reaction was stirred at room temperature for 4 hours. Then, 40% NaOH saturated solution was added slowly at 0℃ and the reaction mixture was extracted with ethyl acetate three times. The combined organic layers were washed by water and saturated sodium chloride solution, then dried over $MgSO_4$ and filtered, and the filtrate was concentrated under reduced pressure. The remaining residue was purified through column chromatography on silica gel, and elution with petroleum ether/ethyl acetate (20:1) gave the products.

Reference

[1] (a) C. Aubry, A. Patel, S. Mahale, B. Chaudhuri, J. -D. Maréchal, M. J. Sutcliffe, P. R. Jenkins, Tetrahedron Lett. 2005, **46**, 1423-1425; (b) R. Adam, J. R. Cabrero-Antonino, A. Spannenberg, K. Junge, R. Jackstell, M. Beller, Angew. Chem. Int. Ed. 2017, **56**, 3216-3220.

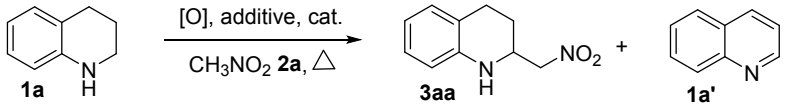
[2] J. Jeong, S.Park and S. Chang, *Chem. Sci.*, 2016, **7**, 5362.

3. Optimization of the reaction conditions

The coupling of tetrahydroquinoline **1a** and nitromethane **2a** was chosen as a model reaction. First, it was performed at 110 ^oC for 12 h under N_2 protection in the presence of a CuCl/TBHP system and 3 equiv of K_2CO_3. Gratifyingly, the expected 2-nitromethylated product **3aa** was obtained in 42% isolated yield (Table S1, entry1). Then, we tested several copper catalyst precursors, the results showed that the utilization of Cu(I) exhibited better chemoselectivity than Cu (II) in the generation of the desired product, and CuI was the best choice (entries 2-4). Interestingly, the addition of 20 mol % of TEMPO to the reaction exclusively produced the desired product **3aa** with significantly improved yield (entry 5). Thus, we chose CuI/TEMPO as a preferred combination, several oxidants were further tested (Table S1, entries 6-9). It showed that molecular O_2 was able to afford a similar yield as TBHP (entry 6), whereas other oxidants were less effective. Noteworthy, the use of O_2 in the absence of TEMPO only resulted in a 62% yield (entry 10). The evaluation of catalyst and base loadings, reaction temperature and time (entries 11-14) showed that an optimal yield (89%) was obtained, when the reaction was conducted at 80 ^oC for 18 h in the

presence of 15 mol % of CuI, 20 mol % of TEMPO and 2.5 equiv of K_2CO_3 by using O_2 or TBHP as the oxidant (entries 14-15).

Table S1. Screening of the Optimal Conditions[a]



Entry	Oxidant	Catalyst	Additive	**3aa**, Yield %[b]	**1a'**, Yield %
1	TBHP	CuCl	-	42	5
2	TBHP	$CuCl_2$	-	trace	90
3	TBHP	CuI	-	74	trace
4	TBHP	CuBr	-	30	15
5	TBHP	CuI	TEMPO	83	trace
6	O_2	CuI	TEMPO	81	10
7	DDQ	CuI	TEMPO	trace	5
8	DTBP	CuI	TEMPO	7	trace
9	DCP	CuI	TEMPO	51	5
10	O_2	CuI	-	62	trace
11[c]	O_2	CuI	TEMPO	(65, 87, 85)	(30, trace,15)
12[d]	O_2	CuI	TEMPO	(82, 87,78)	trace
13[e]	O_2	CuI	TEMPO	(78, 87, 85)	(5, trace, 18)
14[f]	O_2	CuI	TEMPO	(58, 89, 68)	trace
15	TBHP	CuI	TEMPO	89	trace

[a]Conditions: unless otherwise stated, the reaction in nitromethane **2a** (1.0 mL) was performed with **1a** (0.1 mmol), catalyst (50 mol %), additive (3 eq.), oxidant (3 eq.) at 110 °C for 12 h under N_2 protection. [b]Isolated yield. [c]Yields are with respect to the use of 2, 2.5 and 3.0 equiv of K_2CO_3, respectively. [d]Yields correlate with use of 0.15, 0.20 and 0.25 equiv of CuI, respectively. [e]Yields are with respecte to the temperatures at 60, 80 and 110 °C, respectively. [f]Yields are with respect to the time of 12, 18 and 24 h, respectively.

4. Typical procedure for the synthesis of 3

Typical procedure for the synthesis of 3aa

The mixture of 1,2,3,4-tetrahydroquinoline **1a** (40 mg, 0.3 mmol), K_2CO_3 (104 mg, 0.75 mmol), TEMPO (9.3 mg, 0.06mmol) and CuI (8.5 mg, 0.045 mmol) in nitromethane **2a** (1.0 mL) equipped with an O_2 balloon was stirred at 80 °C for 18 h. After cooling down to room temperature, the resulting mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica gel eluting with petroleum ether / ethyl acetate (10:1), which afforded **3aa** as a yellow solid (51 mg, 89% yield).

General procedure for the synthesis of 3ba-3sa

The mixture of 1,2,3,4-tetrahydroquinoline **1** (0.3 mmol), K_2CO_3 (104 mg, 0.75 mmol), TEMPO (9.3 mg, 0.06mmol) and CuI (8.5 mg, 0.045 mmol) in nitromethane **2a** (1.0 mL) equipped with an O_2 balloon was stirred at 80 °C for 18 h. After cooling down to room temperature, the resulting mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica gel eluting with petroleum ether / ethyl acetate (10:1), which afforded **3**.

General procedure for the synthesis of 3ta, 3ab, 3eb, 3ub, 3pb, 3ac, 3fc, 3uc, 3pc

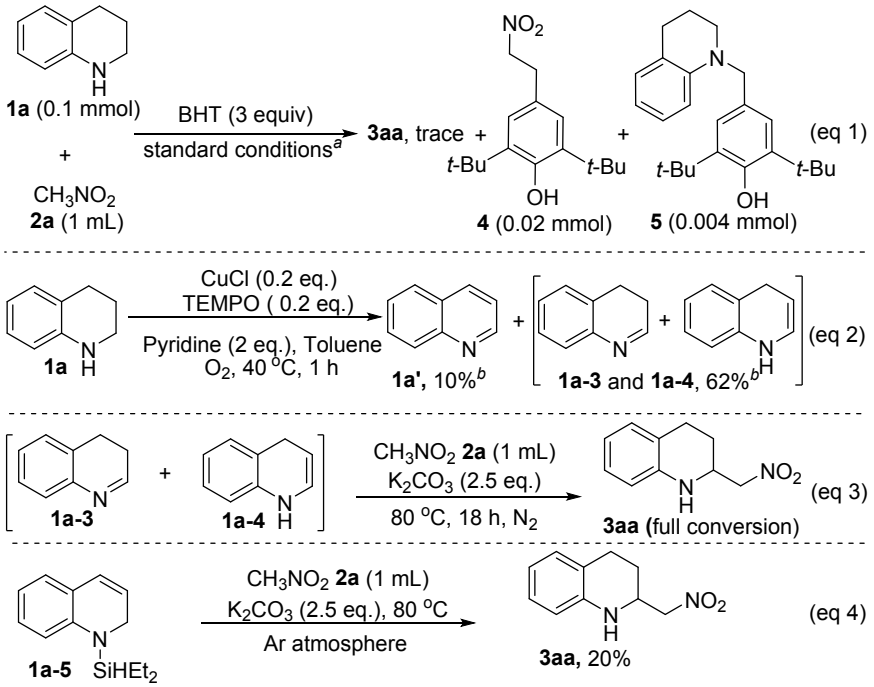
Under N_2 atmosphere, cyclic amine **1** (0.3 mmol), K_2CO_3 (104 mg, 0.75 mmol), TEMPO (9.3 mg, 0.06mmol) and CuI (8.5 mg, 0.045 mmol), TBHP (0.6 mmol) and nitroalkane **2** (1 mL), were introduced into a Schlenk tube (25 mL), successively. Then, the Schlenk tube was closed and the resulting mixture was stirred at 80 °C for 18 h. After cooling down to room temperature, the reaction mixture was concentrated by removing the solvent under vacuum, and product **3** was obtained by purification of the residue with preparative TLC on silica gel eluting with petroleum ether / ethyl acetate (10 : 1).

5. Transformation of the obtained products 3

Nitromethyl tetrahydroquinolines **3** (0.2 mmol) charged with a H_2 balloon were

treated overnight in MeOH at 40 °C with 10 mol % of 10% Pd/C, After cooling down to room temperature, the reaction mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica gel eluting with petroleum ether / ethyl acetate (1:2), which afforded **3'**.

6. The control experiments



Scheme S2. The control experiments

General procedure for the synthesis of compound 4 and 5

Under N_2 atmosphere, the mixture of 1,2,3,4-tetrahydroquinoline **1a** (40 mg, 0.3 mmol), K_2CO_3 (104 mg, 0.75 mmol), TEMPO (9.3 mg, 0.06mmol), TBHP (54mg, 0.6 mmol), BHT (660mg, 0.6 mmol) and CuI (8.5 mg, 0.045 mmol) in nitromethane **2a** (1.0 mL) was introduced into a Schlenk tube (25 mL) was stirred at 80 °C for 18 h. After cooling down to room temperature, the resulting mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica gel eluting with petroleum ether / ethyl acetate (20:1), which afforded compound **4** as a yellow oil, and compound **5** as a yellow oil (see Figure S1).

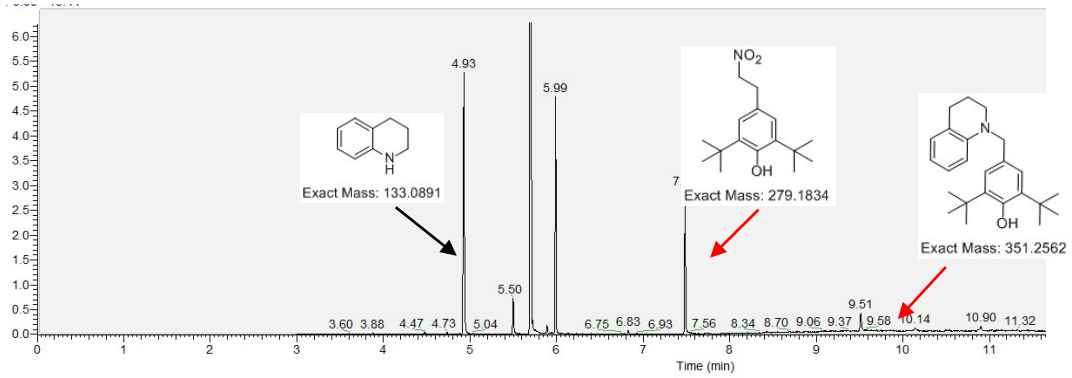
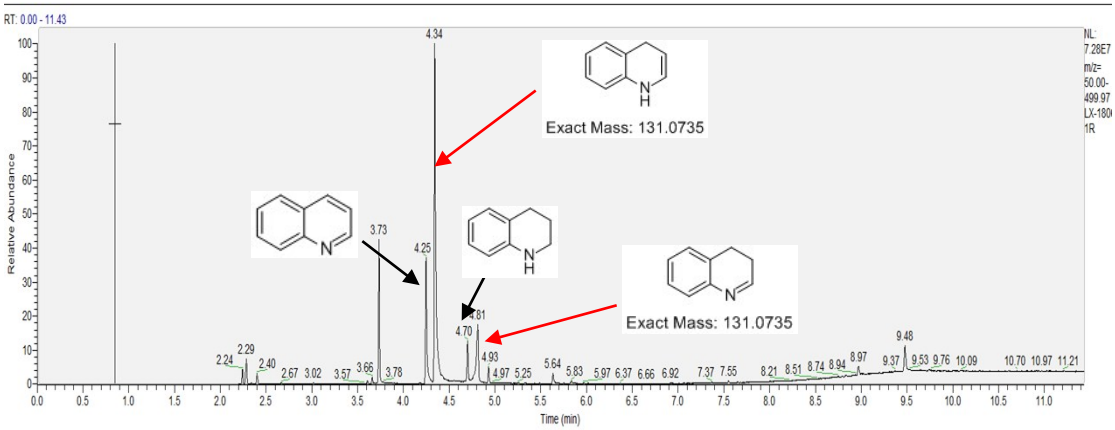


Figure S1. GC-MS of compound **4** and compound **5**

Synthesis of dihydroquinolines 1a-3 and 1a-4 and their further conversion to 3aa

The mixture of 1,2,3,4-tetrahydroquinolines **1a** (0.2 mmol), pyridine (0.4 mmol), TEMPO (0.04 mmol) and CuCl (0.04 mmol) in toluene (1 mL) was stirred at 45 °C for 1 hours under 1 atm of O_2 atmosphere (using O_2 balloon). Then, the mixture was filtered by celite to remove CuCl under stringent argon protection, which gave rise to the mixture of dihydroquinolines (**1a-3** and **1a-4**, see Figure S2) in a 62% combined yield and quinoline **1a'** in 10% yield. The peak of retention time at 4.35 min is assigned to enamine **1a-4** due to the initial loss of H and acetylene fragments (m/e = 104), whereas the peak at 4.81 min is assigned to imine **1a-3** due to the initial loss of H and HCN fragments (m/e = 103). It is very important to note that both **1a-3 and 1a-4** are extremely unstable. So, after removing the solvent, the mixture of the filtrate under argon protection was treated with **2a** (1 mL) and K_2CO_3 (2.5 eq.) at 80 °C for 18 h, dihydroquinolines were fully converted into product **3aa**, and quinoline **1a'** remained unchanged.



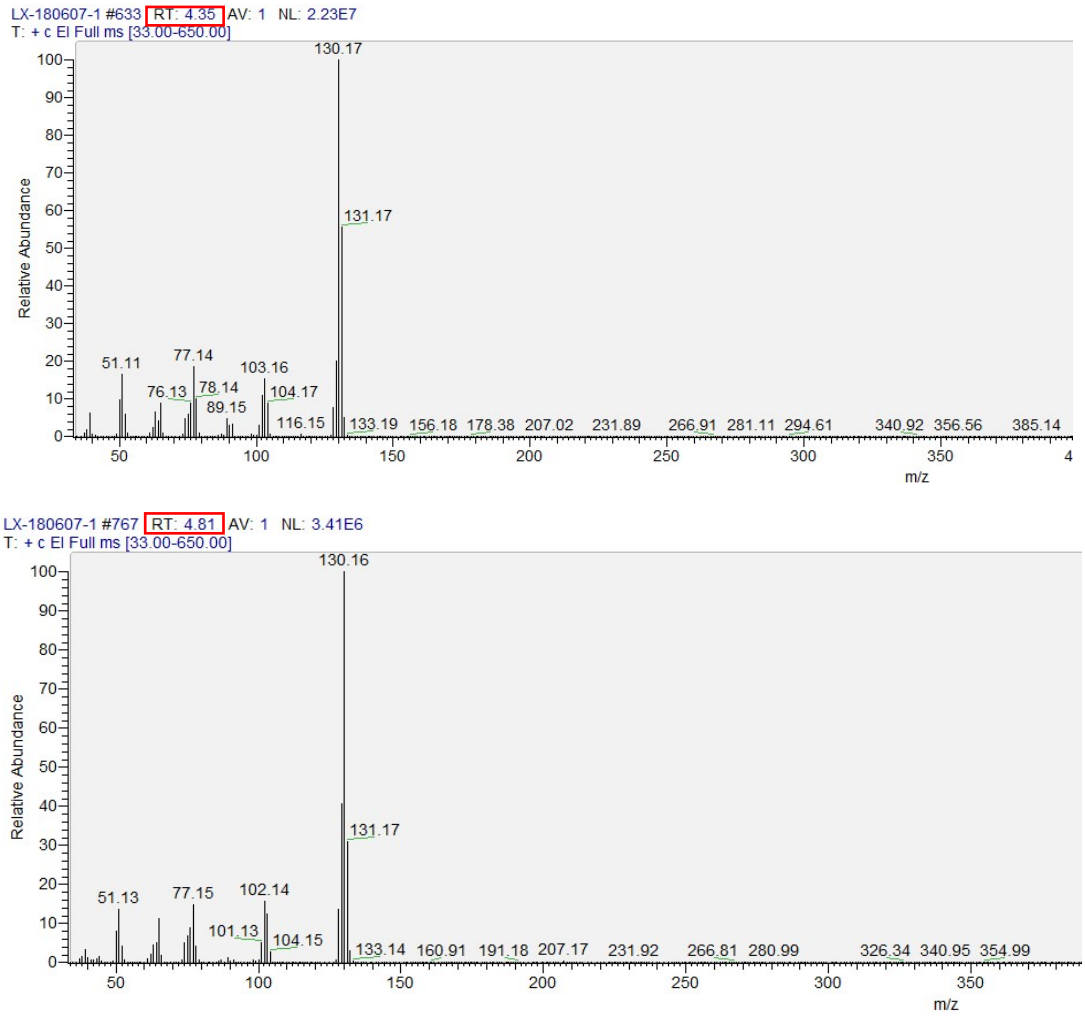


Figure S2. GC-MS of **1a-3** and **1a-4**

Synthesis of N-silylated dihydroquinoline 1a-5 and its further conversion to 3aa

In consideration that dihydroquinolines (**1a-3** and **1a-4**, see Figure S2) are extremely unstable, we prepared a relatively stable N-silylated dihydroquinoline **1a-5** according to Chang's method.[2] Initially, diethylsilane (1.5 mmol, 1.5 equiv) was added to a solution of $[Cp^*IrCl_2]_2$ (0.014 mmol, 1.4 mol %) in C_6D_6 (1 mL, 1M) in a Schlenk tube (25 mL) under argon atmosphere, and the solution was shaken briefly. After 5 minutes, quinoline **1a'** (1 mmol, 1.0 equiv) were added into the solution under Ar atmosphere, and it was reacted at 55 ^oC overnight. The ^1H NMR analysis of this crude reaction solution proved the generation of N-silylated dihydroquinoline **1a-5** (see Figure S3). The above mixture was treated with K_2CO_3 (2.5 eq.) and **2a** (1 mL) at 80 ^oC under argon protection for 18 h, which generated product **3aa** in 20% GC yield.

Noteworthy, the low product yield is due to the easy decomposition of **1a-5.**

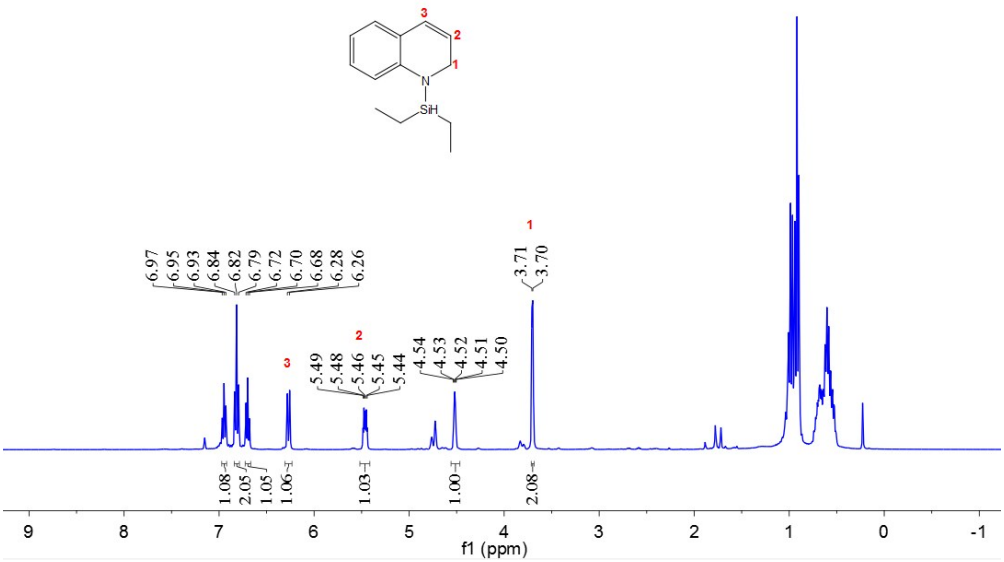
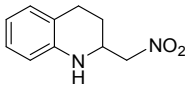


Figure S3. ^{1}H NMR (400 MHz, C_6D_6) of compound **1a-5**

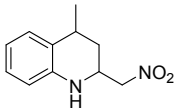
7. Analytic data of the obtained compound

(1) 2-(nitromethyl)-1,2,3,4-tetrahydroquinoline (**3aa**)



Yellow oil. Isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1, v/v, R_f = 0.45). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.03 (dd, *J* = 18.1, 7.7 Hz, 2H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 4.49 (d, *J* = 6.3 Hz, 3H), 4.22 – 4.08 (m, 1H), 2.94 – 2.72 (m, 2H), 2.06 – 1.98 (m, 1H), 1.86 (dt, *J* = 13.2, 6.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.50, 129.30, 127.28, 120.31, 118.24, 114.88, 79.92, 49.06, 24.81, 24.57, IR (KBr): 3447, 2993, 2927, 2839, 2061, 1606, 1486, 1393, 1356, 785, 750 cm^{-1}. HRMS (ESI): Calcd. for $C_{10}H_{13}N_2O_2$ $[M+H]^+$: 193.0972; found: 193.0969.

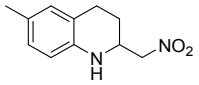
(2) 4-methyl-2-(nitromethyl)-1,2,3,4-tetrahydroquinoline (**3ba**)



Yellow oil. Isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1, v/v, R_f = 0.45). The ratio of diastereomers is 2.5:1.0, the major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (d, *J* = 7.6 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.71 (t, *J* = 7.4 Hz, 1H), 6.54 (d, *J* = 8.0 Hz, 1H), 4.46 (d, *J* = 6.3 Hz, 2H), 4.39 (dd, *J* = 12.9, 8.8 Hz, 1H), 4.16 – 4.05 (m, 1H), 2.91 (p, *J* = 6.4 Hz, 1H), 1.83 (ddd, *J* = 13.6, 8.4, 5.4 Hz, 1H), 1.72 (ddd, *J* = 13.1, 5.7, 3.9 Hz, 1H), 1.65 – 1.43 (m, 1H), 1.35 (d, *J* = 6.9 Hz, 1H), 1.32 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.99, 128.26, 127.23, 118.35, 114.99, 114.90, 80.39, 46.28, 32.47, 28.60, 23.00. IR (KBr): 3451, 2992,

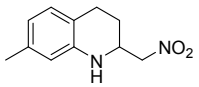
2826, 1602, 1483, 785cm^{-1}. HRMS (ESI): Calcd. for $C_{11}H_{15}N_2O_2$ $[M+H]^+$: 207.1128; found: 207.1124.

(3) 6-methyl-2-(nitromethyl)-1,2,3,4-tetrahydroquinoline (**3ca**)



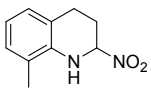
Brown oil. Isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1, v/v, R_f = 0.4). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* =8.4 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.07 (s, 1H), 5.63 (dq, *J* = 9.9, 5.0 Hz, 1H), 4.50 – 4.34 (m, 2H), 2.94 – 2.74 (m, 2H), 2.36 (s, 3H), 2.14 – 2.04 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.98, 133.97, 129.63, 128.92, 125.32, 117.13, 72.56, 46.98, 23.62, 23.16, 20.90, IR (KBr): 3429.96, 2988.78, 2932.41, 2837.37, 2722.37, 2061.51, 1609.18, 1552.63, 1498.68, 1449.53, 1304.54, 787.61, 719 cm^{-1}. HRMS (ESI): Calcd. for $C_{11}H_{15}N_2O_2$ $[M+H]^+$: 207.1128; found: 207.1126.

(4) 7-methyl-2-(nitromethyl)-1,2,3,4-tetrahydroquinoline (**3da**)



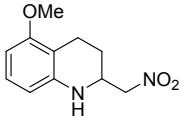
Brown oil. Isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1, v/v, R_f = 0.46). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86 (d, *J* = 7.5 Hz, 1H), 6.51 (d, *J* = 7.6 Hz, 1H), 6.37 (s, 1H), 4.45 (d, *J* = 6.3 Hz, 2H), 4.25 (s, 1H), 4.12 – 4.06 (m, 1H), 2.85 – 2.66 (m, 2H), 2.22 (s, 3H), 2.04 – 1.97 (m, 1H), 1.85 – 1.76 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.24, 137.06, 129.16, 119.24, 117.34, 115.42, 79.91, 49.09, 25.04, 24.15, 21.11, IR (KBr): 3440, 2987, 2832, 2718, 2062, 1610, 1486, 1448, 885, 787 cm^{-1}. HRMS (ESI): Calcd. for $C_{11}H_{15}N_2O_2$ $[M+H]^+$: 207.1128; found: 207.1121.

(5) 8-methyl-2-(nitromethyl)-1,2,3,4-tetrahydroquinoline (**3ea**)



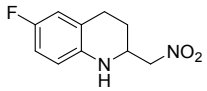
Brown oil. Isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1, v/v, R_f = 0.52). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.91 (d, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 7.4 Hz, 1H), 6.63 (t, *J* = 7.4 Hz, 1H), 4.48 (d, *J* = 6.3 Hz, 2H), 4.20 (s, 1H), 4.17 – 4.11 (m, 1H), 2.91 – 2.71 (m, 2H), 2.09 (s, 3H), 2.06 – 1.98 (m, 1H), 1.84 (td, *J* = 13.2, 7.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.48, 128.40, 127.13, 122.03, 119.75, 117.71, 80.06, 49.39, 24.83, 24.79, 17.05, IR (KBr): 3441, 2990, 2929, 2062, 1601, 1482, 1393, 1362, 1176, 783 cm^{-1}. HRMS (ESI): Calcd. for $C_{11}H_{15}N_2O_2$ $[M+H]^+$: 207.1128; found: 207.1133.

(6) 5-methoxy-2-(nitromethyl)-1,2,3,4-tetrahydroquinoline (**3fa**)



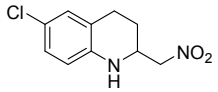
Brown solid. m.p.:98-99 ^{o}C. Isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1, v/v, R_f = 0.42). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97 (t, *J* = 8.0 Hz, 1H), 6.27 (d, *J* = 8.1 Hz, 1H), 6.20 (d, *J* = 8.0 Hz, 1H), 4.45 (d, *J* = 6.2 Hz, 2H), 4.05 (d , *J* = 5.9 Hz, 1H), 3.79 (s, 3H), 2.68 (tq, *J* = 17.4, 8.4, 6.4 Hz, 2H), 1.79 (dq, *J* = 13.3, 6.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.77, 143.34, 127.31, 108.78, 108.11, 100.18, 79.58, 55.31, 48.70, 24.58, 18.37, IR (KBr): 3444, 2989, 2832, 2718, 2062, 1604, 1486, 1449, 1398, 1363, 1177, 1006, 786 cm^{-1}. HRMS (ESI): Calcd. for $C_{11}H_{15}N_2O_3$ $[M+H]^+$: 223.1077; found: 223.1074.

(7) 6-fluoro-2-(nitromethyl)-1,2,3,4-tetrahydroquinoline (**3ga**)



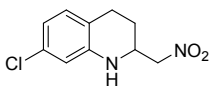
Brown oil. Isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1, v/v, R_f = 0.25). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (dd, *J* = 9.0, 5.0 Hz, 1H), 7.06 (t, *J* = 8.5 Hz, 1H), 6.98 (d, *J* = 8.6 Hz,1H), 5.59 (dt, *J* = 10.4, 5.2 Hz, 1H), 4.50 – 4.37 (m, 2 H), 2.92 (ddd, *J* = 15.7, 9.9 5.3 Hz, 1H), 2.83-2.75 (m, 1H), 2.12 (tq, *J* = 14.4, 5.3, 4.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.56, 160.11, 132.64, 132.61, 127.93, 127.86, 119.35, 119.26, 115.65, 115.53, 115.43, 115.30, 72.73, 47.06, 23.65, 23.47, IR (KBr): 3442, 2988, 2830, 2716, 2062, 1609, 1491, 1397, 1367, 1173, 1003, 787, 774 cm^{-1}. HRMS (ESI): Calcd. for $C_{10}H_{11}FN_2NaO_2$ $[M+Na]^+$: 233.0697; found: 233.0670.

(8) 6-chloro-2-(nitromethyl)-1,2,3,4-tetrahydroquinoline (**3ha**)



Yellow oil. Isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1, v/v, R_f = 0.32). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.96 (d, *J* = 6.9 Hz, 2H), 6.46 (d, *J* = 9.2 Hz, 1H), 4.54 – 4.42 (m, 2H), 4.36 (s, 1H), 4.09 (tt, *J* = 8.0, 4.4 Hz, 1H), 2.86 – 2.66 (m, 2H), 2.04 – 1.96 (m, 1H), 1.83 – 1.75 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.06, 128.84, 127.14, 122.67, 121.78, 115.93, 79.73, 48.96, 24.49, 24.47, IR (KBr): 3421, 2986, 2831, 2061, 1607, 1488, 1365, 1123, 1006, 789, 617 cm^{-1}. HRMS (ESI): Calcd. for $C_{10}H_{12}ClN_2O_2$ $[M+H]^+$: 227.0582; found: 227.0579.

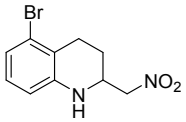
(9) 7-chloro-2-(nitromethyl)-1,2,3,4-tetrahydroquinoline (**3ia**)



Brown oil. Isolated by preparative TLC Isolated by flash column chromatography (petroleum ether/ethyl acetate = 10/1, v/v, R_f = 0.56). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.96 (d, *J* = 6.7 Hz, 2H), 6.46 (d, *J* = 8.9 Hz, 1H), 4.42 – 4.34 (m, 2H), 4.29 (s, 1H), 4.05 – 4.00 (m, 1H), 2.82 (dq, *J* = 14.1, 6.9 Hz, 1H), 2.75 – 2.66 (m, 1H), 2.00 (dq, *J* = 12.1, 6.1 Hz, 1H), 1.79 (dt, *J* = 13.4, 6.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.04, 128.83, 127.15, 122.73, 121.77, 115.93, 79.74, 48.98, 24.50, IR (KBr): 3435,

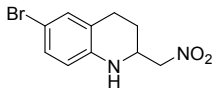
2986, 2717, 2062, 1607, 1488, 1433, 1364, 1175, 1006, 789 cm^{-1}. HRMS (ESI): Calcd. for $C_{10}H_{12}ClN_2O_2$ $[M+H]^+$: 227.0582; found: 227.0583.

(10) 5-bromo-2-(nitromethyl)-1,2,3,4-tetrahydroquinoline (**3ja**)



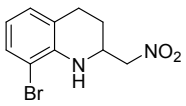
Brown oil. Isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1, v/v, R_f = 0.63).^{1}H NMR (400 MHz, $CDCl_3$): δ 6.88 (d, *J* = 7.9 Hz, 1H), 6.80 (t, *J* = 7.9 Hz, 1H), 6.42 (d, *J* = 8.0 Hz, 1H), 4.50 – 4.31 (m, 2H), 4.08 (tt, *J* = 7.7, 4.4 Hz, 1H), 2.82 – 2.67 (m, 2H), 2.07 – 2.01 (m, 1H), 1.82 – 1.76 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.02, 128.15, 125.58, 122.12, 119.78, 113.99, 79.41, 48.65, 25.32, 24.84, IR (KBr): 3444, 97, 2831, 2062, 1609, 1486, 1397, 1363, 1176, 1005, 788, 733 cm^{-1}. HRMS (ESI): Calcd. for $C_{10}H_{12}BrN_2O_2$ $[M+H]^+$: 271.0077; found: 271.0081.

(11) 6-bromo-2-(nitromethyl)-1,2,3,4-tetrahydroquinoline (**3ka**)



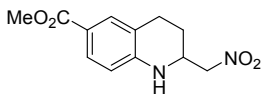
Yellow solid. m.p.: 44-45 ^{o}C. Isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1, v/v, R_f = 0.55). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (s, 2H), 6.44 (d, *J* = 9.1 Hz, 1H), 4.50 – 4.36 (m, 3H), 4.14 – 4.09 (m, 1H), 2.84 (dt, *J* = 14.2, 6.9 Hz, 1H), 2.77 – 2.68 (m, 1H), 2.05 – 2.00 (m, 1H), 1.81 (dq, *J* = 13.5, 7.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.51, 131.70, 129.99, 122.28, 116.35, 109.78, 79.71, 48.90, 24.43, IR (KBr): 3440, 2988, 2720, 2062, 1604, 1486, 1448, 1397, 1363, 1176, 1005, 788 cm^{-1}. HRMS (ESI): Calcd. for $C_{10}H_{12}BrN_2O_2$ $[M+H]^+$: 271.0077; found: 271.0069.

(12) 8-bromo-2-(nitromethyl)-1,2,3,4-tetrahydroquinoline (**3la**)



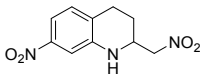
Brown oil. Isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1, v/v, R_f = 0.6). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 7.3 Hz, 1H), 6.55 (t, *J* = 7.5Hz, 1H), 4.95 (s, 1H), 4.50 (d, *J* = 6.3 Hz, 2H), 4.24 – 4.12 (m, 1H), 2.92 – 2.83 (m, 1H), 2.82 – 2.69 (m, 1H), 2.05 – 2.00 (m, 1H), 1.81 (dd, *J* = 13.0, 6.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.84, 130.69, 128.36, 121.93, 228.55, 109.49, 79.93, 49.32, 25.00, 24.58, IR (KBr): 3440, 2987, 2718, 2061, 1607, 1488, 1399, 1364, 1175, 1005, 788, 732 cm^{-1}. HRMS (ESI): Calcd. for $C_{10}H_{12}BrN_2O_2$ $[M+H]^+$: 271.0077; found: 271.0070.

(13) methyl 2-(nitromethyl)-1,2,3,4-tetrahydroquinoline-6-carboxylate (**3ma**)



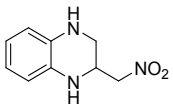
Yellow solid, m.p. 64-65 °C. Isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1, v/v, R_f = 0.28). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (s, 1H), 7.69 (s, 1H), 6.51 (d, *J* = 8 Hz, 1H), 4.79 (s, 1H), 4.53 – 4.44 (m, 2H), 4.22 – 4.16 (m, 1H), 3.85 (s, 3H), 2.97 – 2.73 (m, 2 H), 2.08 – 2.00 (m, 1H), 1.88 – 1.80 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.20, 146.57, 131.19, 129.41, 119.36, 119.18, 113.76, 79.68, 51.63, 48.82, 24.33, 24.27, IR (KBr): 3411, 1987, 2948, 2838, 2063, 1698, 1608, 1554, 1489, 1366, 1249, 1136, 1004, 832, 781, 726, 619 cm^{-1}. HRMS (ESI): Calcd. for $C_{12}H_{15}N_2O_4$ $[M+H]^+$: 273.0846; found: 273.0850.

(14) 7-nitro-2-(nitromethyl)-1,2,3,4-tetrahydroquinoline (**3na**)



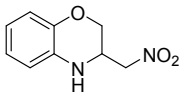
Yellow solid, m.p.: 52-53 °C. Isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1, v/v, R_f = 0.33). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.42 (d, *J* = 2.0 Hz, 1H), 7.31 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.14 (d, *J* = 8.2 Hz, 1H), 6.74 (s, 1H), 4.74 (dd, *J* = 12.9, 4.6 Hz, 1H), 4.60 (dd, *J* = 12.9, 8.3 Hz, 1H), 4.10 (d, *J* = 6.4Hz, 1H), 2.84 – 2.69 (m, 2H), 1.86 (dd, *J* = 12.9, 5.4 Hz, 1H), 1.77 (dq, *J* = 12.7, 6.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 147.21, 144.90, 129.99, 127.92, 110.60, 107.76, 80.06, 48.41, 24.44, 23.01. IR (KBr): 3439, 2987, 2830, 2719, 2062, 1608, 1487, 1445, 13986, 1363, 1175, 1005, 899, 788 cm^{-1}. HRMS (ESI): Calcd. for $C_{10}H_{11}N_3NaO_4$ $[M+Na]^+$: 260.0642; found: 260.0644.

(15) 2-(nitromethyl)-1,2,3,4-tetrahydroquinoxaline (**3oa**)



Brown oil. Isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1, v/v, R_f = 0.22). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.56 (q, *J* = 8.4, 6.0 Hz, 2H), 6.46 (dd, *J* = 6.5, 2.3 Hz, 2H), 4.58 – 4.43 (m, 2H), 4.16 (dq, *J* = 7.6, 3.5 Hz, 1H), 3.42 – 3.35 (m, 1H), 3.22 – 3.14 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 132.45, 131.15, 119.95, 119.31, 115.13, 115.01, 78.38, 48.95, 42.68, IR (KBr): 3442, 2988, 2830, 2720, 2062, 1607, 1487, 1398, 1364, 1176, 1005, 900, 787 cm^{-1}. HRMS (ESI): Calcd. for $C_9H_{12}N_3O_2$ $[M+H]^+$: 194.0924; found: 194.0930.

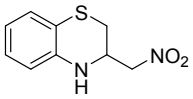
(16) 3-(nitromethyl)-3,4-dihydro-2*H*-benzo[*b*] [1,4] oxazine (**3pa**)



Yellow oil. Isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1, v/v, R_f = 0.42). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.82 (d, *J* = 7.5 Hz, 2H), 6.70 (t, *J* = 7.6 Hz, 1H), 6.63 (d, *J* = 7.7 Hz, 1H), 4.62 – 4.51 (m, 2H), 4.24 (dt, *J* = 8.3, 4.1 Hz, 1H), 4.18 – 4.13 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.07, 131.01, 122.59, 119.50, 117.17, 115.97, 76.72, 65.45, 48.42, IR (KBr): 3439, 2987, 2830, 2719, 2061, 1606, 1489, 1398, 1364, 1176, 1005, 900, 788 cm^{-1}. HRMS (ESI): Calcd. for $C_9H_{11}N_2O_3$

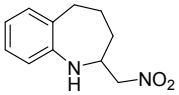
[M+H]$^+$: 195.0764; found: 195.0771.

(17) 3-(nitromethyl)-3,4-dihydro-2*H*-benzo[*b*] [1,4] thiazine (**3qa**)



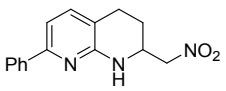
Yellow oil. Isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1, v/v, R_f = 0.53). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.03 (d, *J* = 7.8 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.69 (t, *J* = 7.5 Hz, 1H), 6.54 (d, *J* = 8.1 Hz, 1H), 4.72 (dd, *J* = 13.1, 8.4 Hz, 1H), 4.59 (dd, *J* = 13.1, 4.2 Hz, 1H), 4.52 (dq, *J* = 7.7, 3.7 Hz, 1H), 3.13 (dd, *J* = 13.2, 3.3 Hz, 1H), 2.87 (dd, *J* = 13.2, 3.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.48, 128.20, 126.60, 118.94, 116.05, 114.65, IR (KBr): 3441, 2989, 2830, 2723, 2062, 1603, 1485, 1396, 1363, 1177, 1005, 787 cm^{-1}. HRMS (ESI): Calcd. for $C_9H_{10}N_2NaO_2S$ [M+Na]$^+$: 233.0355; found: 233.0352.

(18) 2-(nitromethyl)-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine (**3ra**)



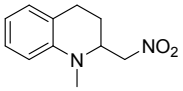
Yellow oil. Isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1, v/v, R_f = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 – 7.04 (m, 2H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 7.7 Hz, 1H), 5.51 – 5.43 (m, 1H), 4.34 (d, *J* = 12.7 Hz, 1H), 4.17 (s, 1H), 3.79 (s, 1H), 2.82 – 2.76 (m, 2H), 1.99 – 1.90 (m, 1H), 1.76 (dt, *J* = 12.8, 6.1 Hz, 1H), 1.68 (dt, *J* = 10.7, 6.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.45, 134.14, 130.39, 127.13, 122.44, 121.33, 18.68, 54.59, 35.04, 34.36, 23.92, IR (KBr): 3440, 2988, 2830, 2720, 2062, 1606, 1485, 1397, 1363, 1177, 1065, 1005 787 cm^{-1}. HRMS (ESI): Calcd. for $C_{11}H_{15}N_2O_2$ [M+H]$^+$: 207.1128; found: 207.1124.

(19) (S)-2-(nitromethyl)-7-phenyl-1,2,3,4-tetrahydro-1,8-naphthyridine (**3sa**)



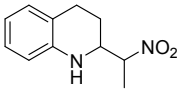
Yellow oil. Isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1, v/v, R_f = 0.21). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.7 Hz, 2H), 7.45 – 7.33 (m, 3H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 5.51 (s, 1H), 4.47 (d, *J* = 6.5 Hz, 2H), 4.26 (dd, *J* = 6.4, 2.9 Hz, 1H), 2.80 (dq, *J* = 17.4, 10.2 Hz, 2H), 2.04 (dd, *J* = 11.6, 4.7 Hz, 1H), 1.84 (dt, *J* = 13.2, 7.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.61, 154.41, 139.48, 137.37, 128.68, 128.63, 126.74, 113.85, 111.08. 79.61, 49.12, 24.22, 23.83. IR (KBr): 3444.58, 2990.79, 2829.99, 2063.13, 1603.68, 1481.74, 1396.11, 1361.92, 1177.91, 1006.17, 786.62, 551.49 cm^{-1}. HRMS (ESI): Calcd. for $C_{15}H_{16}N_3O_2$ [M+H]$^+$: 270.1237; found: 270.1242.

(20) 2-methyl-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (**3ta**)



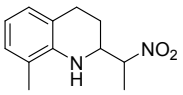
Yellow oil. Isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1, v/v, R_f = 0.71). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (t, *J* = 7.7Hz, 1H), 7.03 (d, *J* = 7.3 Hz, 1H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 8.2 Hz, 1H), 4.55 (dd, *J* = 11.2, 5.9 Hz, 1H), 4.46 – 4.36 (m, 1H), 4.17 – 4.12 (m, 1H), 3.00 (s, 3H), 2.86 – 2.77 (m, 2H), 2.08 – 1.96 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.73, 129.22, 127.67, 121.03, 117.35, 111.62, 75.99, 57.97, 38.27, 23.49, 23.00. IR (KBr): 3438, 3208, 2991, 2849, 1333, 1555, 1487, 1178, 1005, 789 cm^{-1}. HRMS (ESI): Calcd. for $C_{11}H_{15}N_2O_2$ $[M+1]^+$: 207.1128; found: 207.1131.

(21) 2-(1-nitroethyl)-1,2,3,4-tetrahydroquinoline (**3ab**)



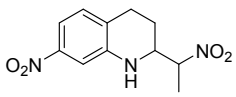
Yellow oil. Isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1, v/v, R_f = 0.17). The ratio of diastereomers is 1.1:1.0, the major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 – 6.94 (m, 2H), 6.56 (d, *J* = 7.9 Hz, 1H), 6.50 (d, *J* = 8.0 Hz, 1H), 4.64 – 4.55 (m, 1H), 4.10 (s, 1H), 3.88 – 3.82 (m, 1H), 2.88 – 2.79 (m, 2H), 2.08 – 1.91 (m, 2H), 1.60 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.59, 129.21, 127.38, 120.41, 118.11, 114.89, 87.58, 54.01, 24.45, 16.19, 14.57. IR (KBr): 3441, 2960, 2830, 2719, 2062, 1609, 1482, 1443, 1396, 1364, 1117, 1006, 883, 786 cm^{-1}. HRMS (ESI): Calcd. for $C_{11}H_{15}N_2O_2$ $[M+H]^+$: 207.1128; found: 207.1125.

(22) 8-methyl-2-(1-nitroethyl)-1,2,3,4-tetrahydroquinoline (**3eb**)



Yellow oil. Isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1, v/v, R_f = 0.5). The ratio of diastereomers is 1.2:1.0, the major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97 – 6.92 (m, 2H), 6.65 (t, *J* = 7.4 Hz, 1H), 4.67 – 4.58 (m, 1H), 3.93 – 3.88 (m, 1H), 2.89 – 2.81 (m, 2H), 2.15 (s, 3H), 1.92 – 1.75 (m, 2H), 1.62 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.51, 128.43, 127.02, 121.97, 120.23, 117.55, 87.59, 54.30, 24.56, 23.26, 16.99, 16.03. IR (KBr): 3676, 3279, 3178, 1710, 1517, 1333, 1283, 1047, 869, 818, 741 cm^{-1}. HRMS (ESI): Calcd. for $C_{12}H_{16}N_2NaO_2$ $[M+Na]^+$: 243.1104; found: 243.1101.

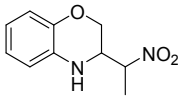
(23) 7-nitro-2-(1-nitroethyl)-1,2,3,4-tetrahydroquinoline (**3nb**)



Yellow oil. Isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1, v/v, R_f = 0.2).The ratio of diastereomers is 1.0:1.0, the major isomer: ^{1}H NMR (400 MHz,

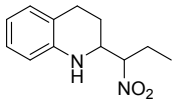
$CDCl_3$): δ 7.40 (s, 1H), 7.07 (d, *J* = 8.2 Hz, 2H), 4.68 (p, *J* = 6.5 Hz, 1H), 3.93 – 3.90 (m, 1H), 2.94 – 2.87 (m, 2H), 1.94 – 1.85 (m, 2H), 1.62 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.46, 143.75, 129.58, 127.35, 112.44, 108.84, 85.54, 53.35, 24.50, 22.36, 16.06. IR (KBr): 3628, 3285, 3048, 2766.55, 1680.53, 1544.82, 1499.01, 1321.80, 1010.72, 802.70, 748.64 cm^{-1}. HRMS (ESI): Calcd. for $C_{11}H_{13}N_3NaO_4$ $[M+Na]^+$: 274.0798; found: 274.0796.

(24) 3-(1-nitroethyl)-3,4-dihydro-2H-benzo[b] [1,4] oxazine (**3pb**)



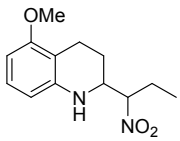
Yellow oil. Isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1, v/v, R_f = 0.34).The ratio of diastereomers is 1.0:1.0, the major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.82 (t, *J* = 7.6 Hz, 2H), 6.73 – 6.62 (m, 1H), 6.59 (d, *J* = 8.5 Hz, 1H), 4.80 – 4.74 (m, 1H), 4.13 – 4.05 (m, 3H), 1.64 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.26, 131.21, 122.56, 119.07, 116.98, 115.76, 84.00, 64.07, 53.42, 16.42. IR (KBr): 3673, 3281, 2930, 1701, 1546, 1488, 1309, 1006, 804, 759 cm^{-1}. HRMS (ESI): Calcd. for $C_{10}H_{13}N_2O_3$ $[M+H]^+$: 209.0921; found: 209.0924.

(25) 2-(1-nitropropyl)-1,2,3,4-tetrahydroquinoline (**3ac**)



Yellow oil. Isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1, v/v, R_f = 0.51). The ratio of diastereomers is 1.5:1.0, the major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.99 (t, *J* = 7.0 Hz, 2H), 6.54 (d, *J* = 8.0 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 1H), 4.45 – 4.54 (m, 1H), 4.14 (s, 1H), 3.87 – 3.72 (m, 1H), 2.84 – 2.74 (m, 2H), 2.03 – 1.95 (m, 4H), 1.01 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.62, 129.31, 127.12, 120.60, 118.04, 114.55, 92.72, 53.35, 24.62, 24.05, 23.44, 10.42. IR (KBr): 3441, 2988, 2831, 2720, 2062, 1604, 1484, 1397, 1363, 1179, 1067, 1006, 787, 730 cm^{-1}. HRMS (ESI): Calcd. for $C_{12}H_{17}N_2O_2$ $[M+H]^+$: 221.1285; found: 221.1283.

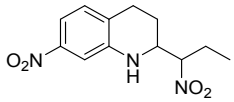
(26) 5-methoxy-2-(1-nitropropyl)-1,2,3,4-tetrahydroquinoline (**3fc**)



Yellow oil. Isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1, v/v, R_f = 0.44). The ratio of diastereomers is 1.4:1.0, the major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97 (t, *J* = 8.1 Hz, 1H), 6.27 (d, *J* = 8.1 Hz, 1H), 6.20 (d, *J* = 8.1 Hz, 1H), 4.50 (ddd, *J* = 10.5, 6.5, 3.2 Hz, 1H), 4.13 (s, 1H), 3.79 (s, 3H), 3.72 (td, *J* = 6.8, 3.4 Hz, 1H), 2.80 – 2.64 (m, 2H), 2.19 – 2.07 (m, 1H), 1.92 (dtd, *J* = 13.0, 9.3, 8.2, 4.6, 2H), 1.78 (dt, *J* = 13.5, 6.8 Hz, 1H), 0.99 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.96, 143.69, 127.32, 109.25, 107.92, 100.18, 92.61, 55.44, 53.09, 23.95,

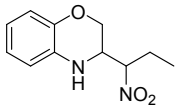
23.13, 18.63, 10.55. IR (KBr): 3439, 2987, 2831, 2720, 2062, 1604, 1485, 1398, 1363, 1177, 1064, 1006, 787 cm^{-1}. HRMS (ESI): Calcd. for $C_{13}H_{19}N_2O_3$ $[M+H]^+$: 251.1390; found: 251.1358.

(27) 7-nitro-2-(1-nitropropyl)-1,2,3,4-tetrahydroquinoline (**3nc**)



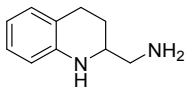
Yellow oil. Isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1, v/v, R_f = 0.36). The ratio of diastereomers is 1.2:1.0, the major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (s, 1H), 7.07 (dd, *J* = 8.2, 4.4 Hz, 2H), 4.61 (s, 1H), 4.49 – 4.44 (m, 1H), 2.94 – 2.76 (m, 2H), 2.17 – 2.01 (m, 4H), 1.01 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.48, 134.10, 129.53, 127.15, 112.44, 108.70, 93.84, 52.52, 24.44, 23.48, 22.53, 10.04. IR (KBr): 3437, 2987, 2830, 2721, 2062, 1607, 1485, 1397, 1357, 1178, 1066, 1005, 875, 787, 739 cm^{-1}. HRMS (ESI): Calcd. for $C_{12}H_{16}N_3O_4$ $[M+H]^+$: 266.1135; found: 266.1139.

(28) 3-(1-nitropropyl)-3,4-dihydro-2*H*-benzo[*b*] [1,4] oxazine (**3pc**)



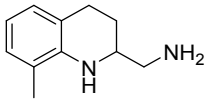
Brown oil. Isolated by preparative TLC (petroleum ether/ethyl acetate = 10/1, v/v, R_f = 0.54). The ratio of diastereomers is 1.4:1.0, the major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.83 (t, *J* = 7.7 Hz, 2H), 6.58 (d, *J* = 8.2, 2H), 4.64 (qd, *J* = 8.8, 7.9, 3.8 Hz, 1H), 4.25 (dd, *J* = 11.4, 2.6 Hz, 1H), 4.14 – 4.09 (m, 2H), 3.89 (s, 1H), 2.17 – 2.01 (m, 2H), 1.01 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.12, 131.22, 122.57, 119.12, 117.00, 115.85, 91.32, 64.22, 52.55, 23.87. IR (KBr): 3421, 2985, 2942, 2885, 2720, 2061, 1605, 1550, 1494, 1394, 1364, 1177, 1109, 1051, 1006, 787, 748 cm^{-1}. HRMS (ESI): Calcd. for $C_{11}H_{15}N_2O_3$ $[M+H]^+$: 245.0897; found: 245.0896.

(29) (1,2,3,4-tetrahydroquinolin-2-yl) methanamine **(3aa')**



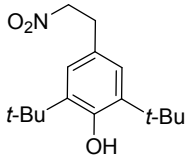
Yellow oil. Isolated by preparative TLC (petroleum ether/ethyl acetate = 1/2, v/v, R_f = 0.25). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.99-6.93 (m, 2H), 6.61 (t, *J* = 7.4 Hz, 1H), 6.52 (d, *J* = 7.9 Hz, 1H), 3.26 (s, 1H), 2.95 - 2.88 (m, 1H), 2.83 (td, *J* = 10.8, 5.5 Hz, 1H), 2.76 – 2.71 (m, 1H), 2.69 (d, *J* = 16.3 Hz, 1), 1.94 – 1.90 (m, 1H), 1.68 – 1.62 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 144.61, 129.30, 126.93, 121.45, 117.15, 114.37, 53.36, 26.30, 26.03, IR (KBr): 3357, 2921, 2850, 1661, 1606, 1494, 1384, 1097, 1035, 801, 750 cm^{-1}. HRMS (ESI): Calcd. for $C_{10}H_{15}N_2$ $[M+H]^+$: 163.1230; found: 163.1229.

(30) (8-methyl-1,2,3,4-tetrahydroquinolin-2-yl) methanamine **(3ea')**



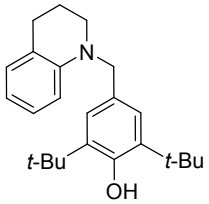
Yellow oil. Isolated by preparative TLC (petroleum ether/ethyl acetate = 1/2, v/v, R_f = 0.32). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.87 (dd, *J* = 14.4, 7.3 Hz, 2H), 6.56 (t, *J* = 7.4 Hz, 2H), 3.30 (tt, *J* = 7.8, 3.8 Hz, 1H), 2.95 (dd, *J* = 12.3, 3.8 Hz, 1H), 2.89 – 2.84 (m, 1H), 2.78 – 2.73 (m, 1H), 2.12 (s, 3H), 1.96 – 1.91 (m, 1H), 1.66 (ddt, *J* = 9.6, 7.5, 5.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 142.57, 128.07, 127.16, 121.36, 120.89, 116.57, 53.66, 47.58, 26.59, 25.98, 17.32, IR (KBr): 3369, 2923, 2851, 1664, 1599, 1493, 1477, 1309, 1265, 615, 602 cm^{-1}. HRMS (ESI): Calcd. for $C_{11}H_{17}N_2$ $[M+H]^+$: 177.1386; found: 177.1382.

(31) 2,6-di-*tert*-butyl-4-(2-nitroethyl) phenol (compound **4**)



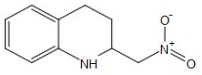
Yellow oil. Isolated by preparative TLC (petroleum ether/ethyl acetate = 20/1, v/v, R_f = 0.72). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 (s, 2H), 5.16 (s, 1H), 4.57 (t, *J* = 7.8 Hz, 2H), 3.24 (t, *J* = 7.7 Hz, 2H), 1.43 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.04, 136.47, 126.20, 125.14, 34.33, 33.60, 30.23. IR (KBr): 3698, 3287, 3057, 1706, 1244, 1503, 1440, 1325, 810, 749.88 cm^{-1}. HRMS (ESI): Calcd. for $C_{16}H_{25}NNaO_3$ $[M+Na]^+$: 302.1727; found: 302.1724.

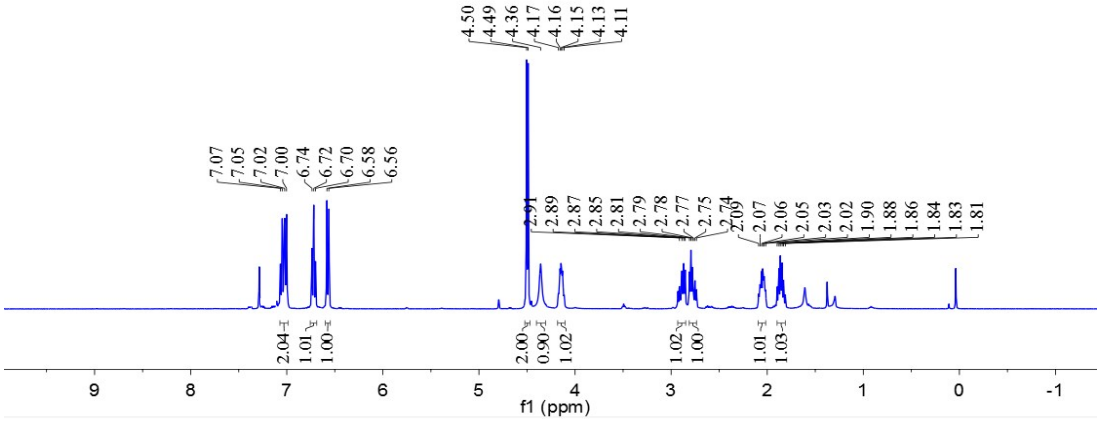
(32) 2,6-di-*tert*-butyl-4-((3,4-dihydroquinolin-1(2*H*)-yl) methyl) phenol (compound **5**)



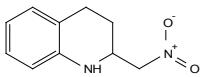
Yellow oil. Isolated by preparative TLC (petroleum ether/ethyl acetate = 20/1, v/v, R_f = 0.8). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.07 (s, 2H), 6.99 (dd, *J* = 17.9, 7.5 Hz, 2H), 6.52 – 6.55 (m, 2H), 5.10 (s, 1H), 4.39 (s, 2H), 3.34 – 3.31 (m, 2H), 2.81 (t, *J* = 6.3 Hz, 2H), 1.99 (p, *J* = 6.1 Hz, 2H), 1.42 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.66, 136.09, 129.22, 129.04, 127.23, 123.51, 122.43, 115.75, 111.38, 55.24, 49.64, 34.47, 28.48, 22.60. IR (KBr): 3641, 2957, 2921, 1602, 1574, 1434, 1233, 1194, 1156, 1117, 971, 881, 803, 743 cm^{-1}. HRMS (ESI): Calcd. for $C_{24}H_{34}NO$ $[M+H]^+$: 352.2635; found: 352.2637.

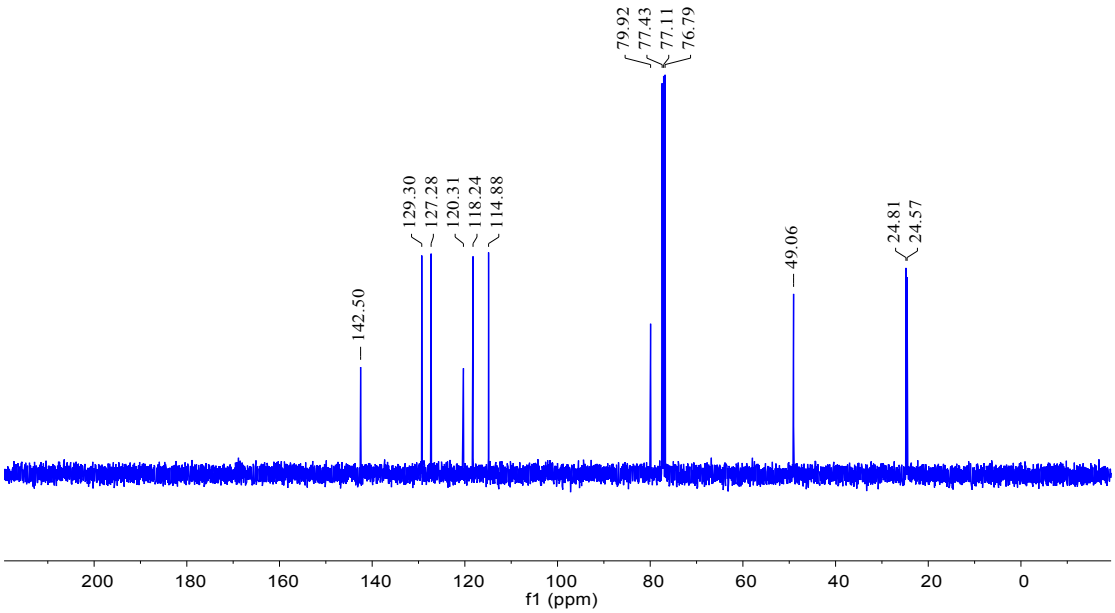
8. NMR spectra of products



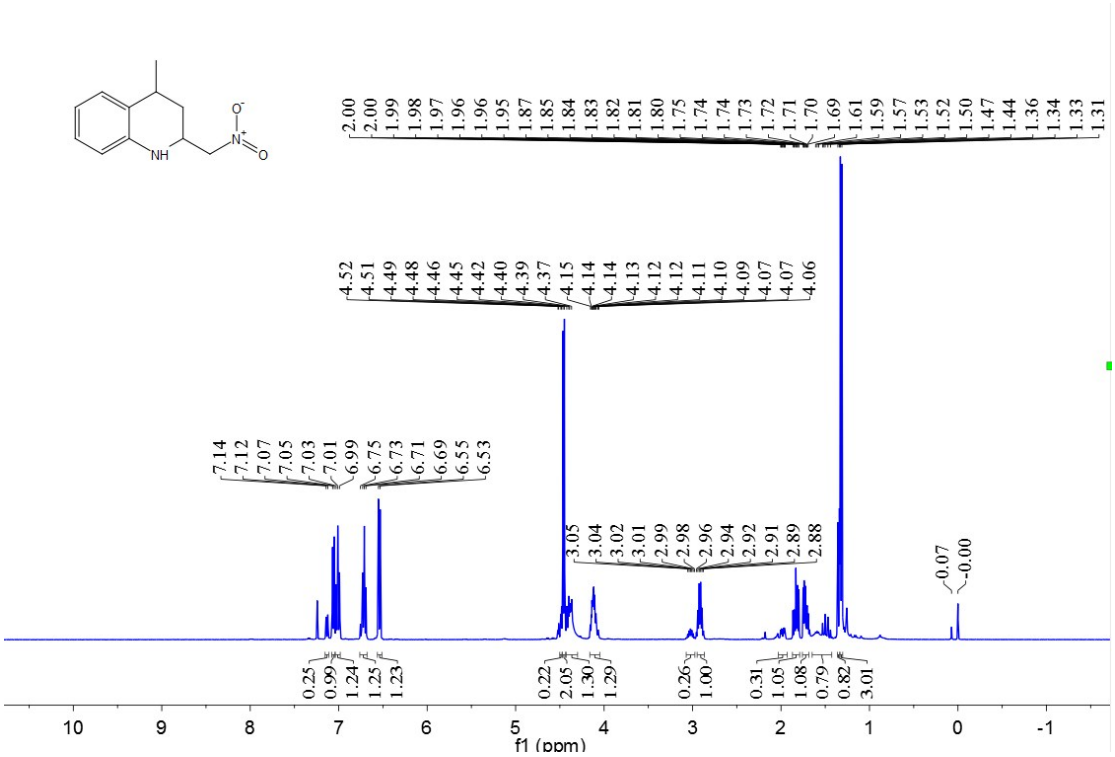


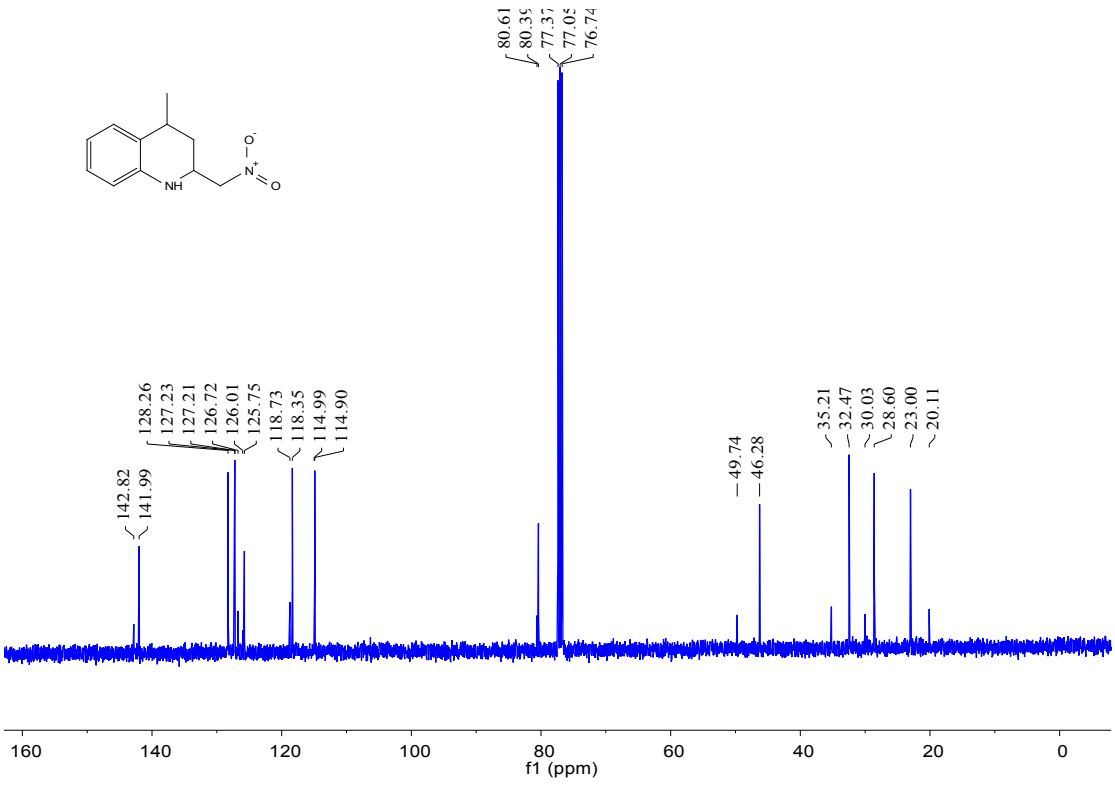
NMR spectra of 2-(nitromethyl)-1,2,3,4-tetrahydroquinoline (3aa)



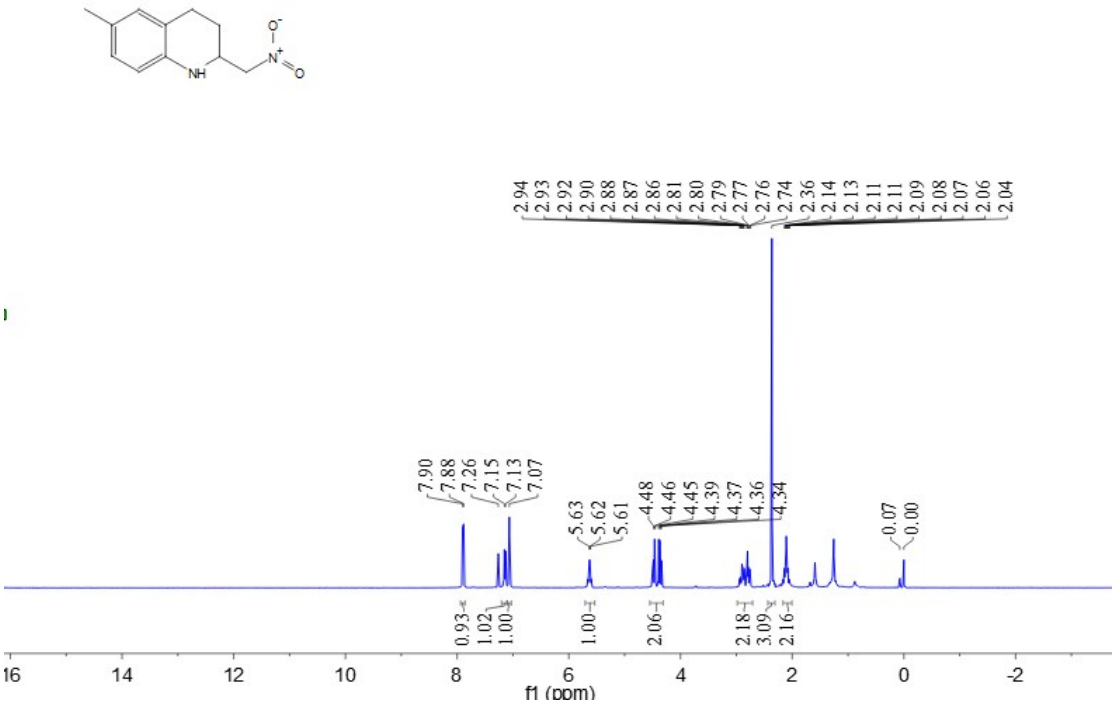


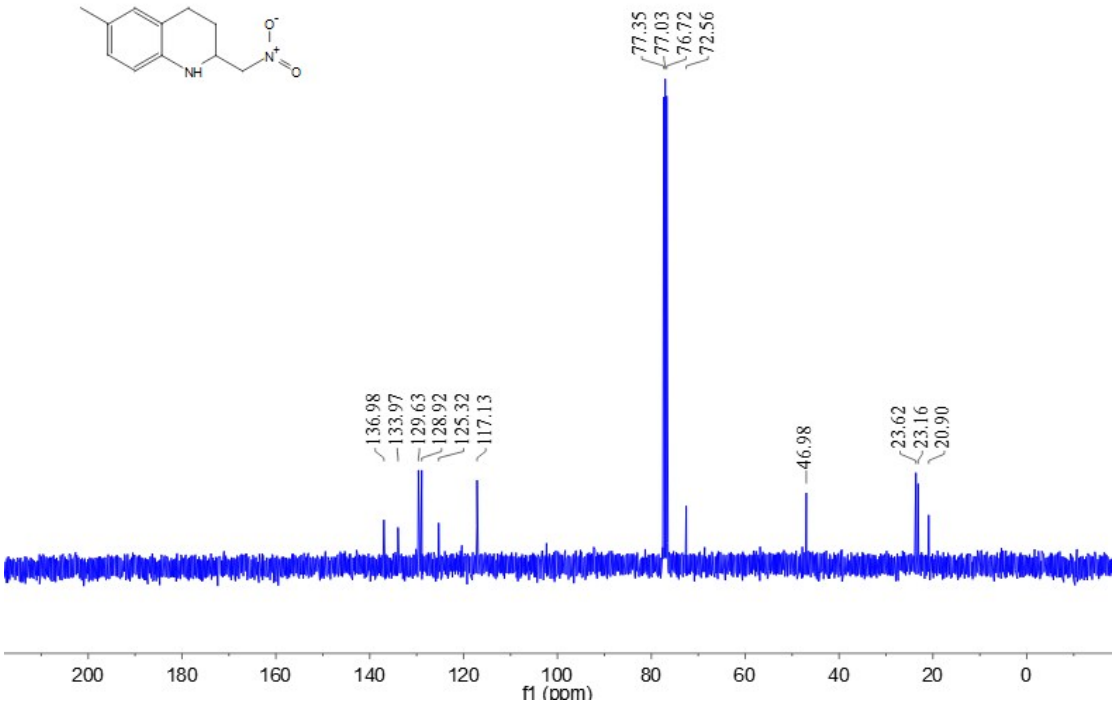
NMR spectra of 4-methyl-2-(nitromethyl)-1,2,3,4-tetrahydroquinoline (3ba)



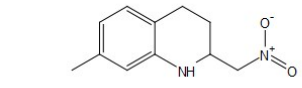


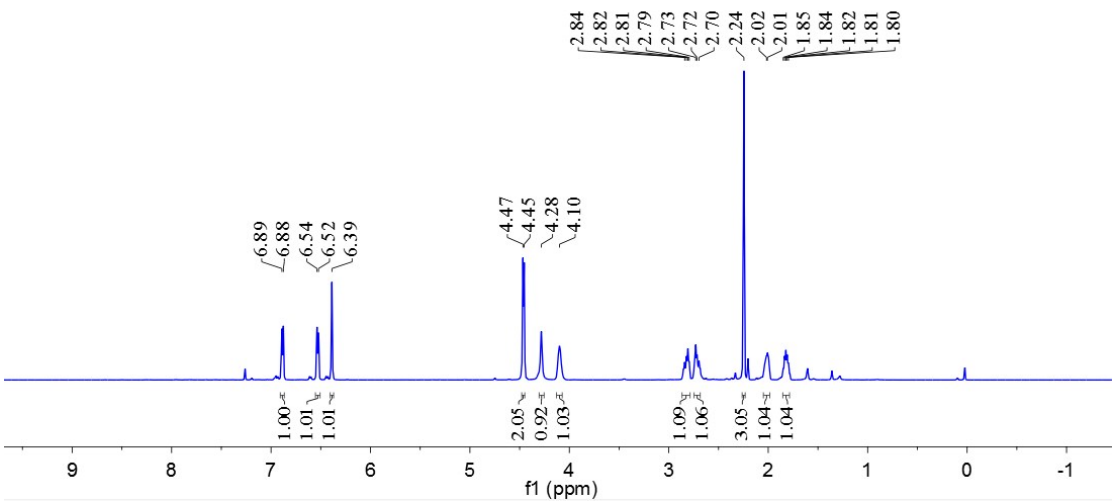
NMR spectra of 6-methyl-2-(nitromethyl)-1,2,3,4-tetrahydroquinoline (3ca)

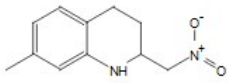


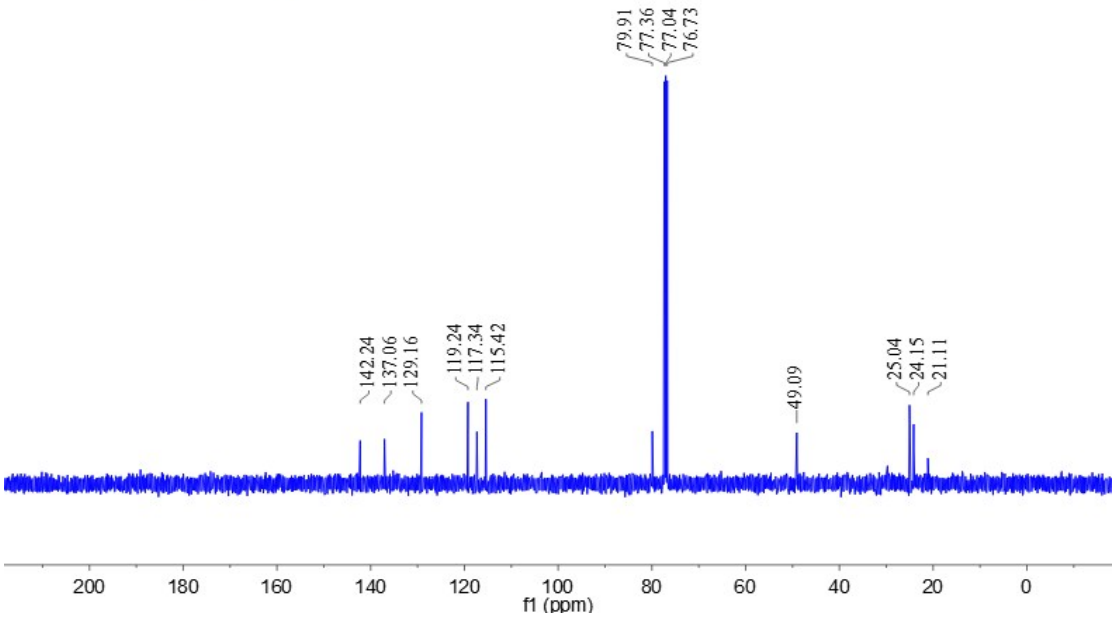


NMR spectra of 7-methyl-2-(nitromethyl)-1,2,3,4-tetrahydroquinoline (3da)

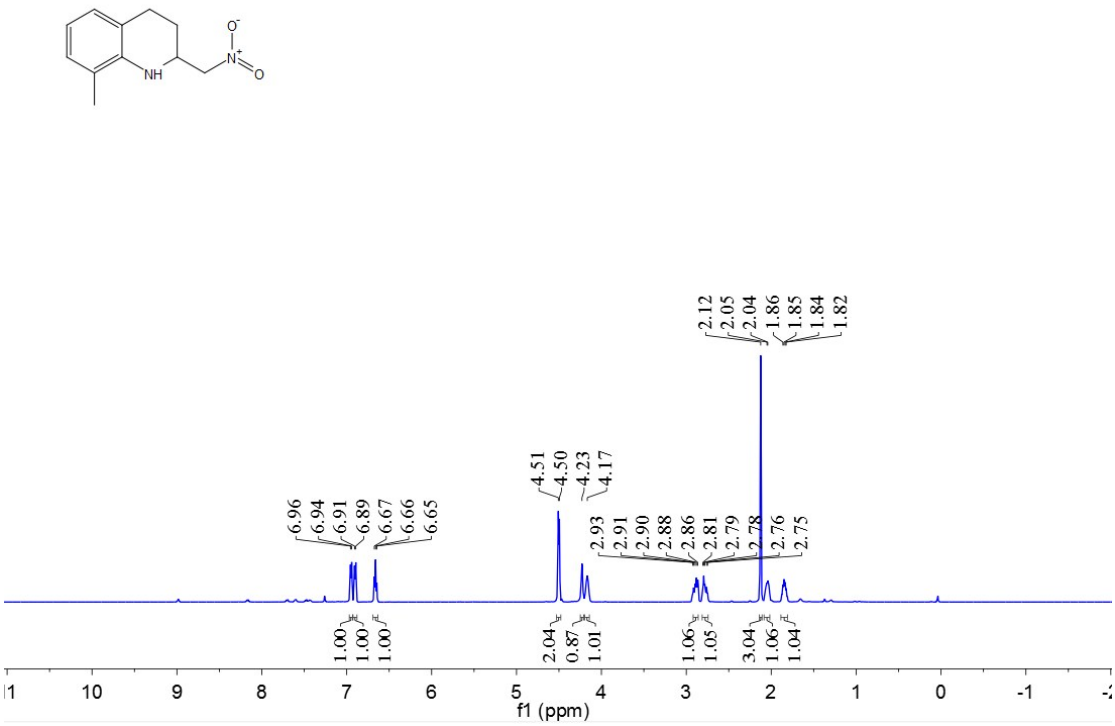


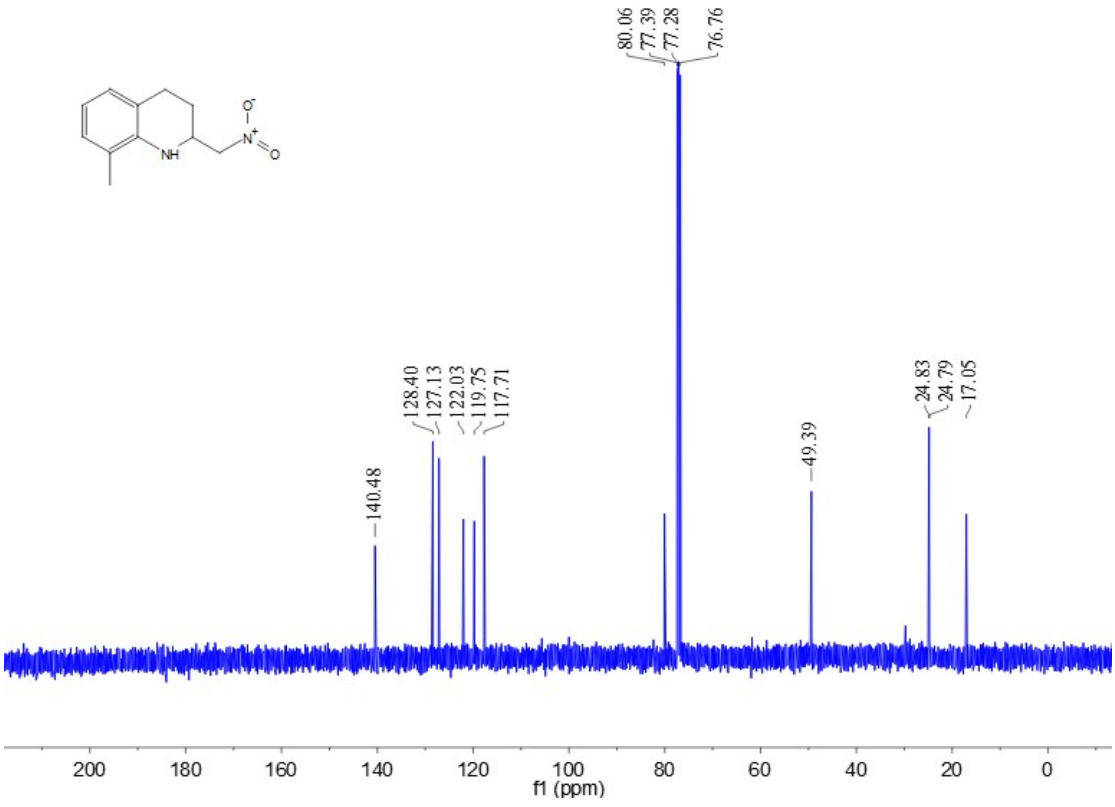




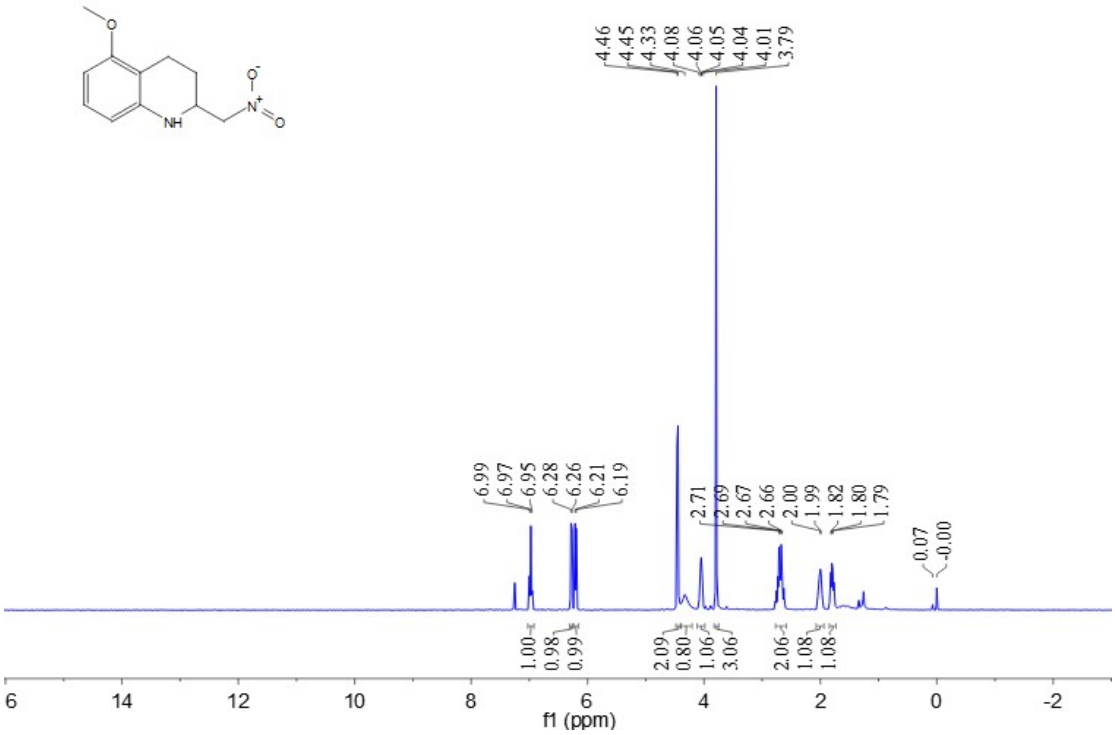


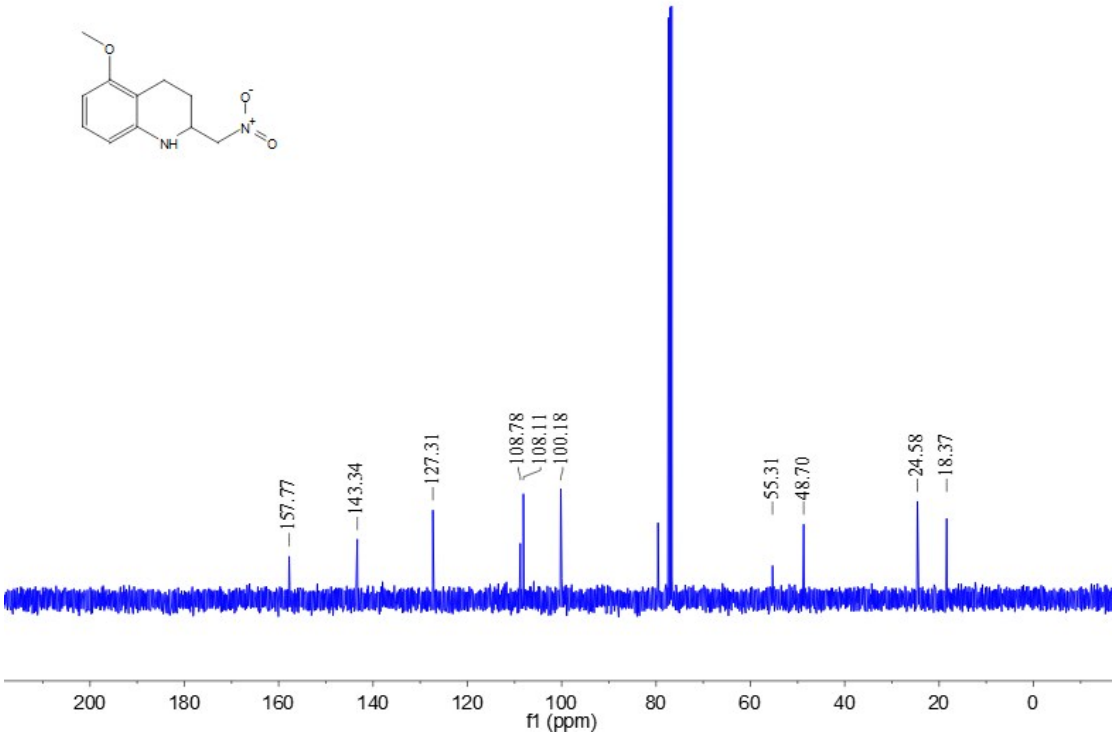
NMR spectra of 8-methyl-2-(nitromethyl)-1,2,3,4-tetrahydroquinoline (3ea)



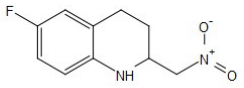


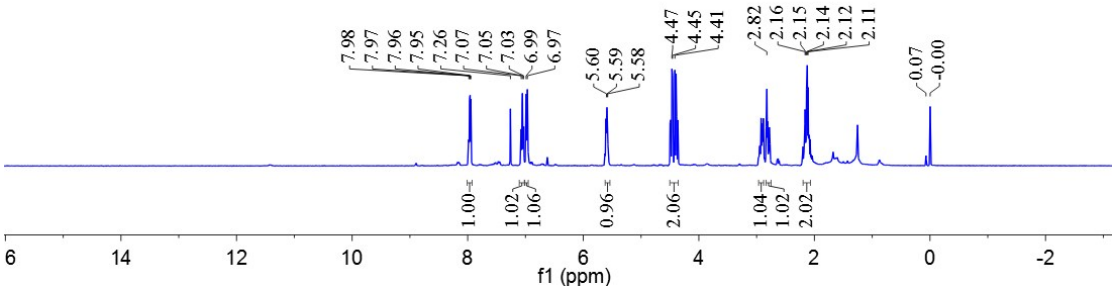
NMR spectra of 5-methoxy-2-(nitromethyl)-1,2,3,4-tetrahydroquinoline (3fa)

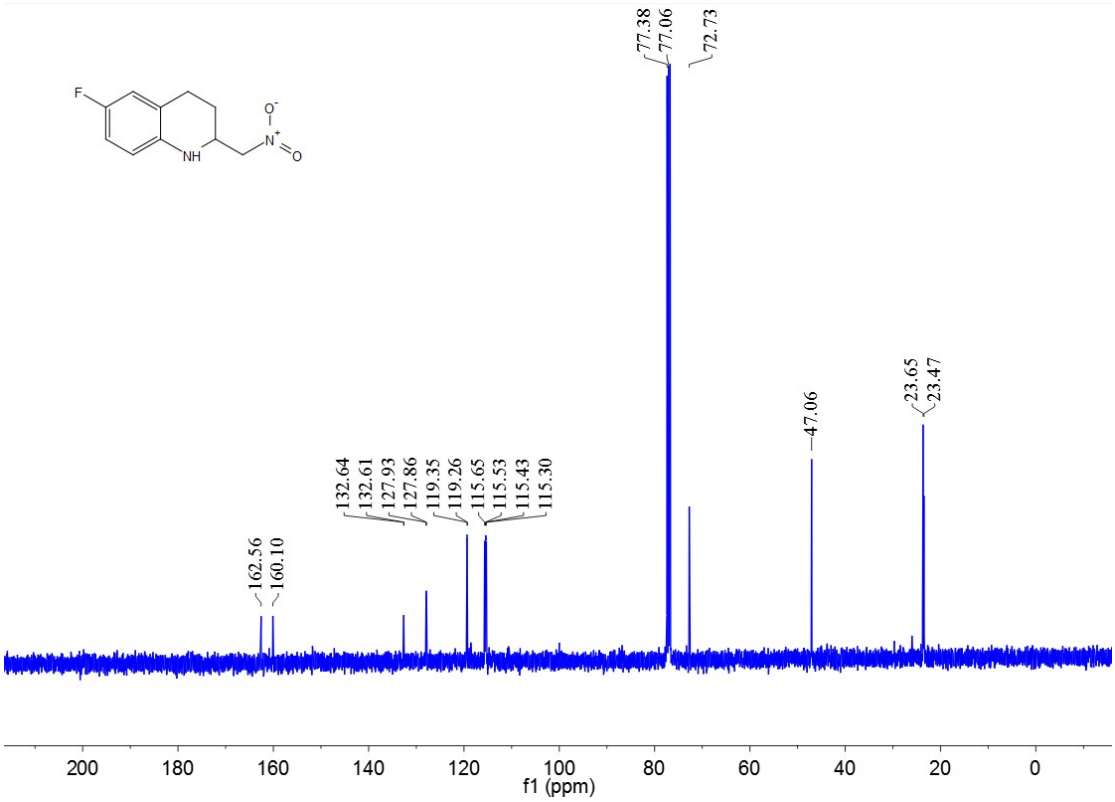


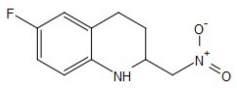


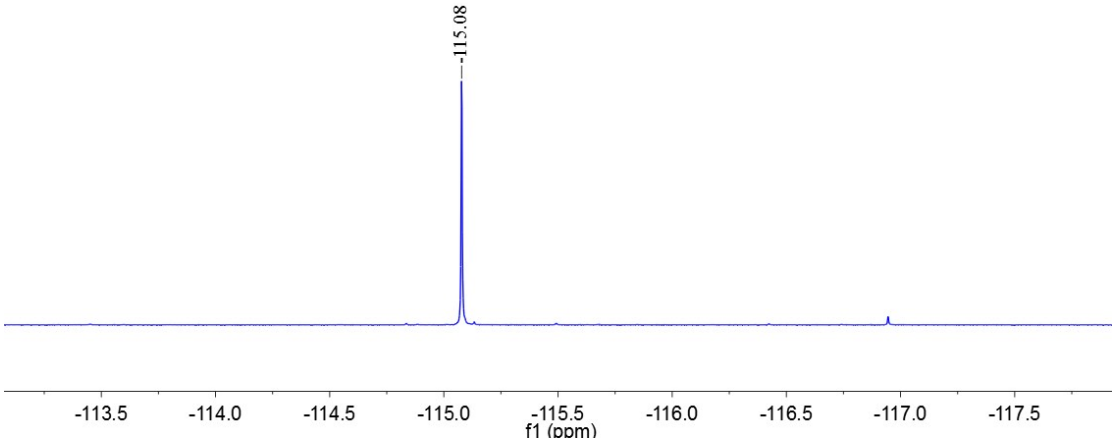
NMR spectra of 6-fluoro-2-(nitromethyl)-1,2,3,4-tetrahydroquinoline (3ga)



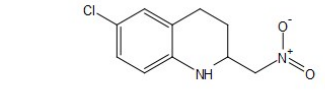


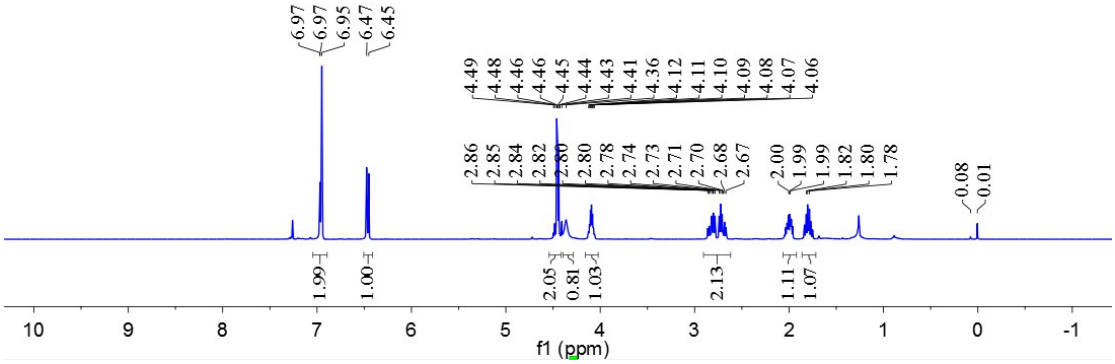


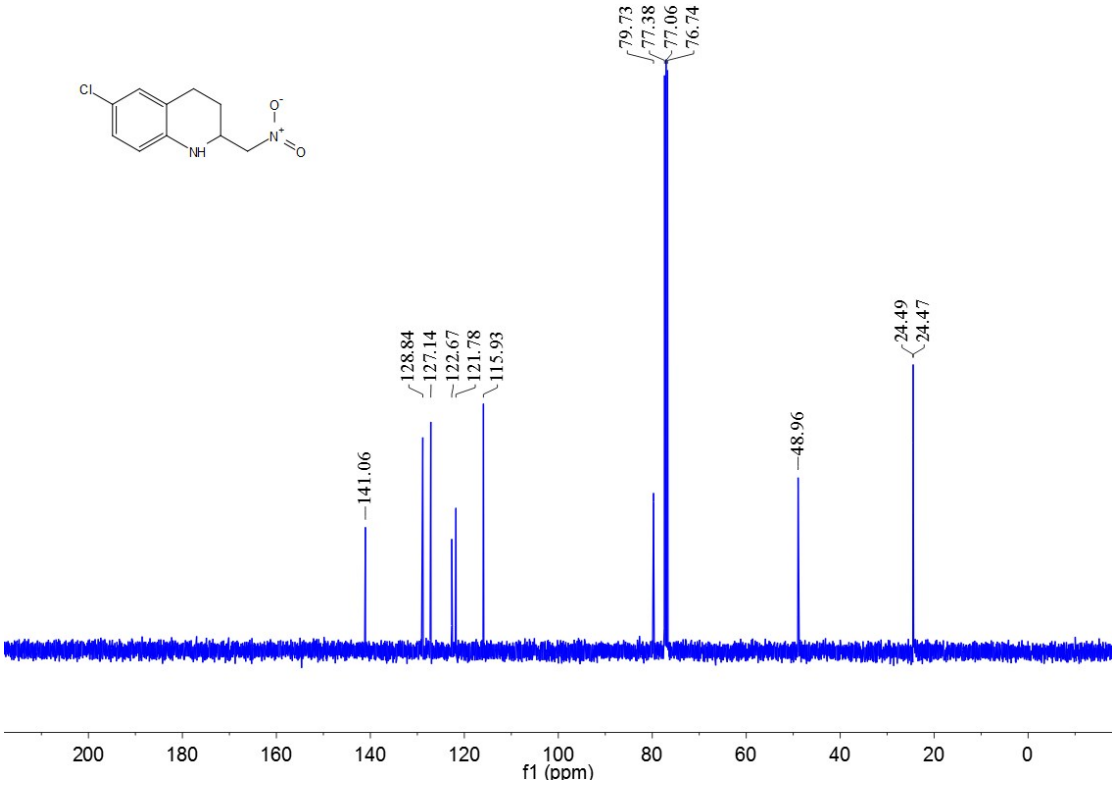

F
NH
O
N
O


-115.08
-113.5
-114.0
-114.5
-115.0
-115.5
-116.0
-116.5
-117.0
-117.5
f1 (ppm)

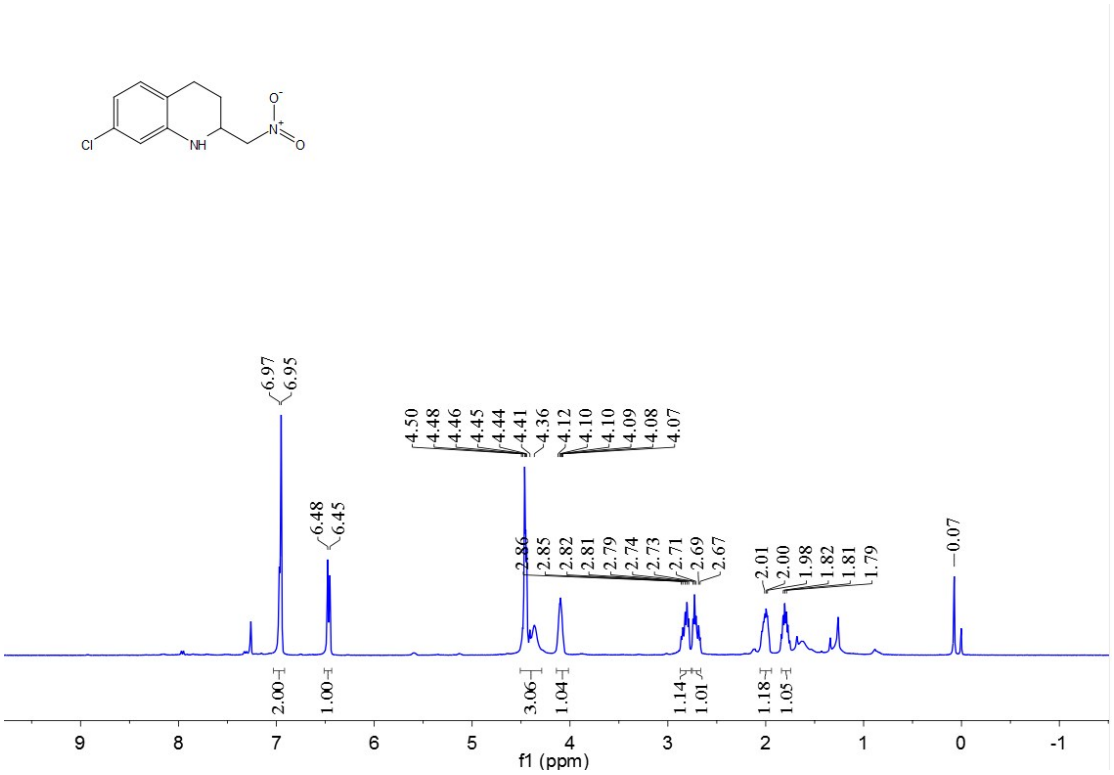
NMR spectra of 6-chloro-2-(nitromethyl)-1,2,3,4-tetrahydroquinoline (3ha)

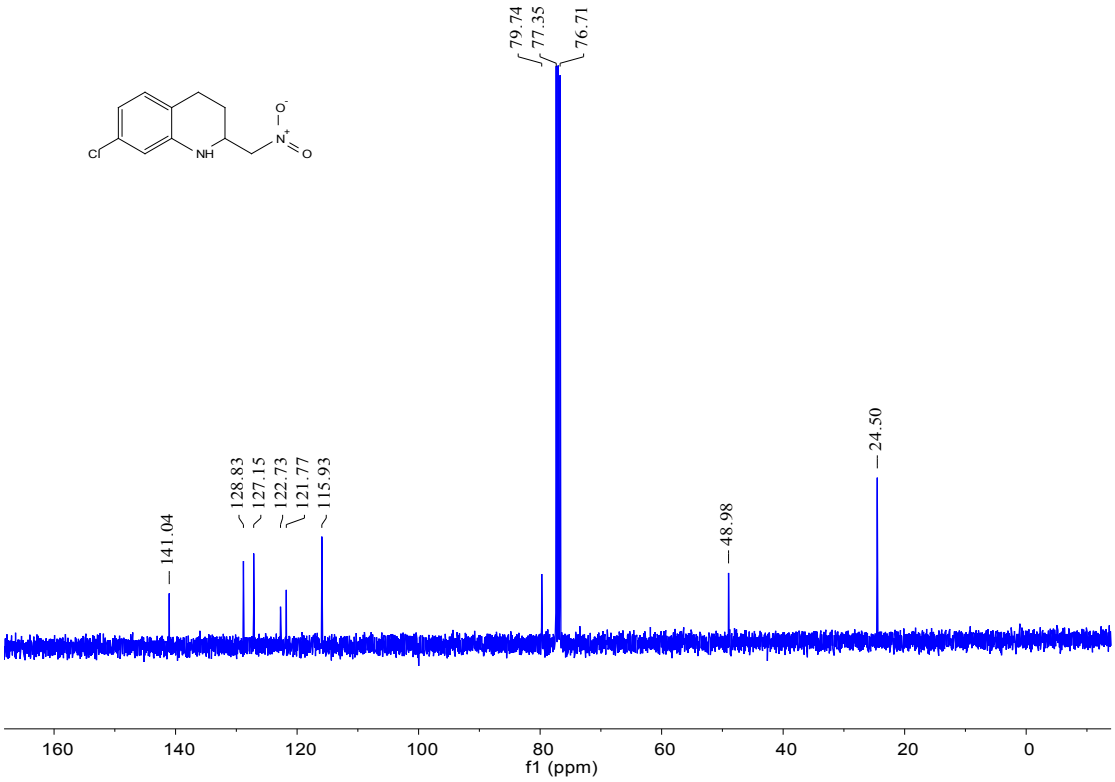




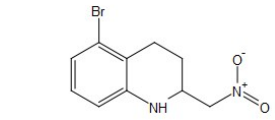


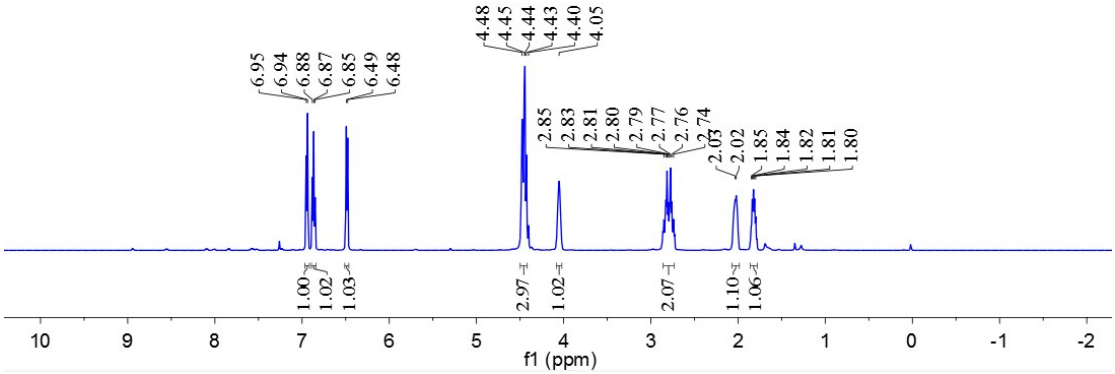
NMR spectra of 7-chloro-2-(nitromethyl)-1,2,3,4-tetrahydroquinoline (3ia)

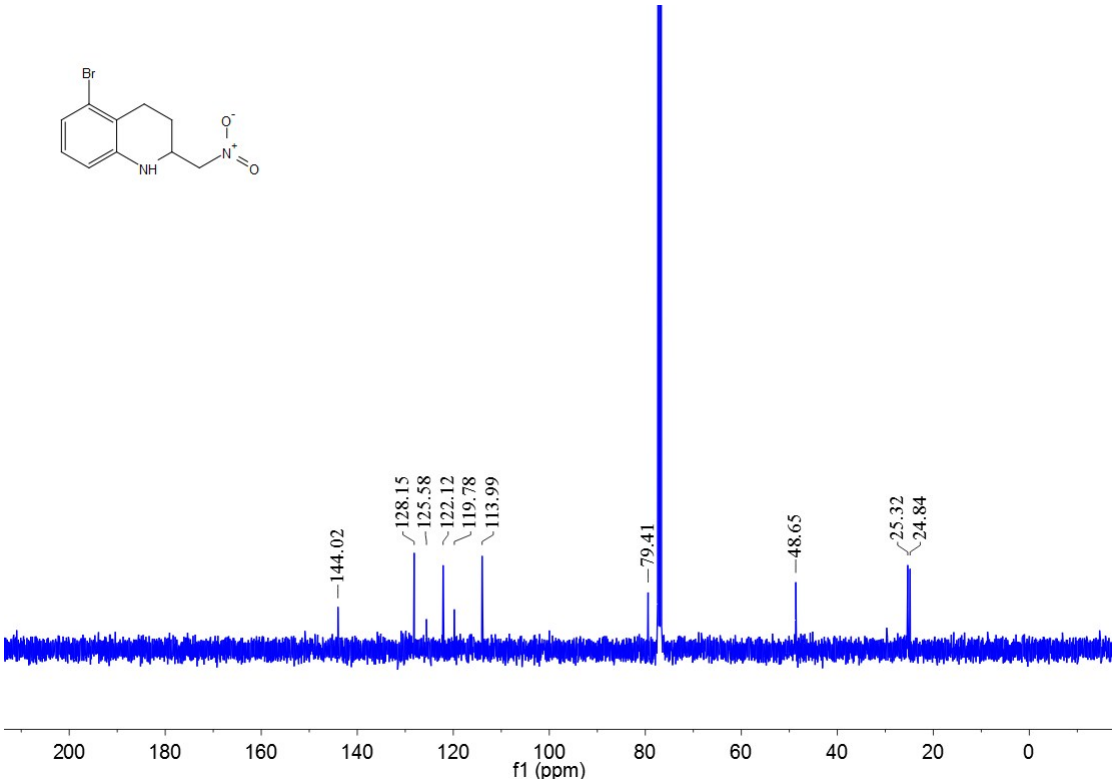




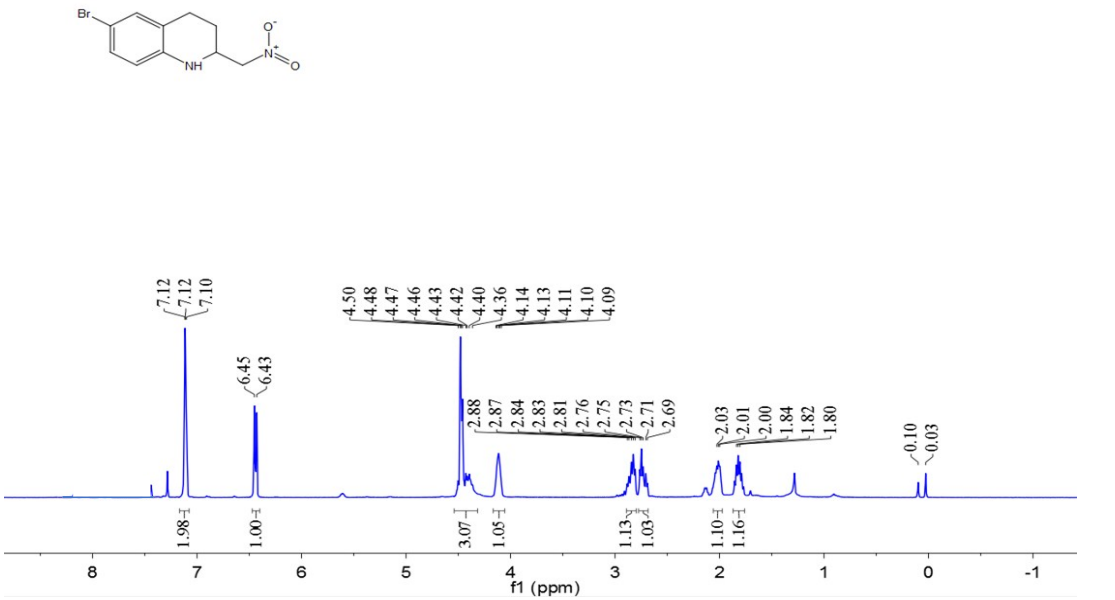
NMR spectra of 5-bromo-2-(nitromethyl)-1,2,3,4-tetrahydroquinoline (3ja)

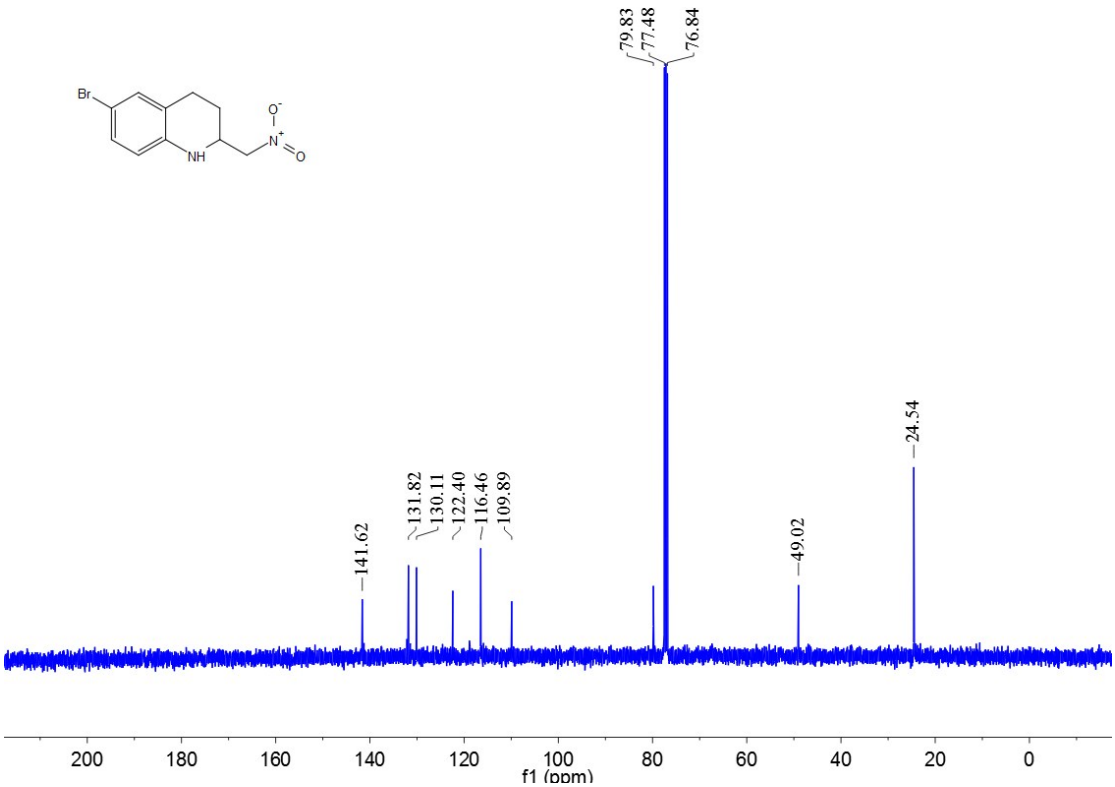




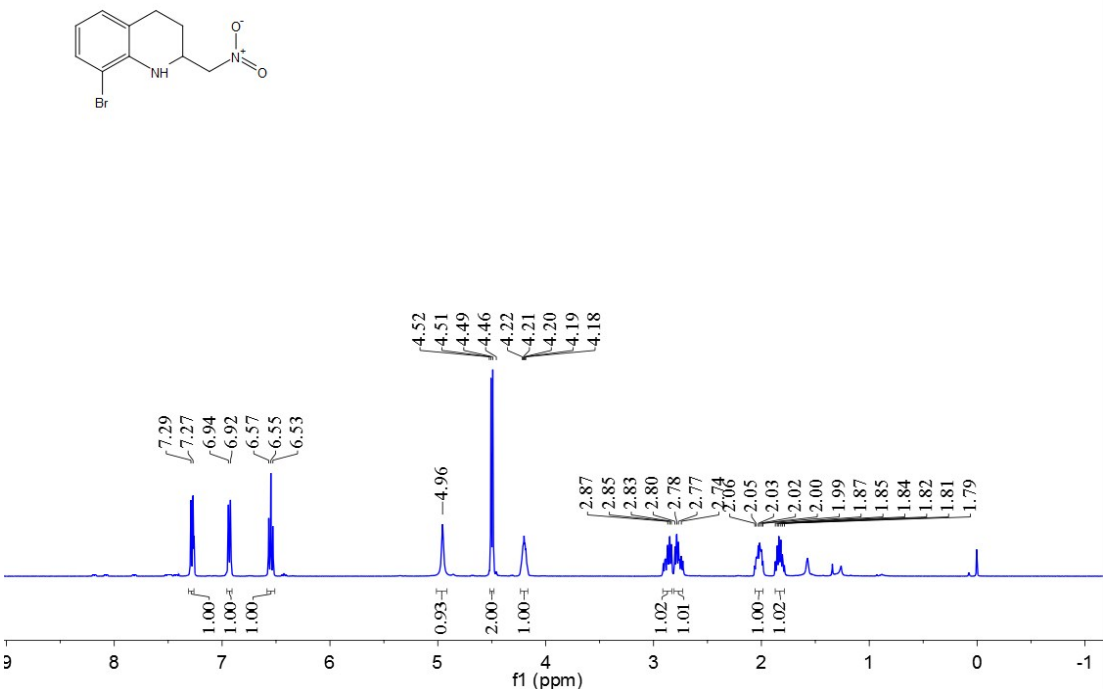


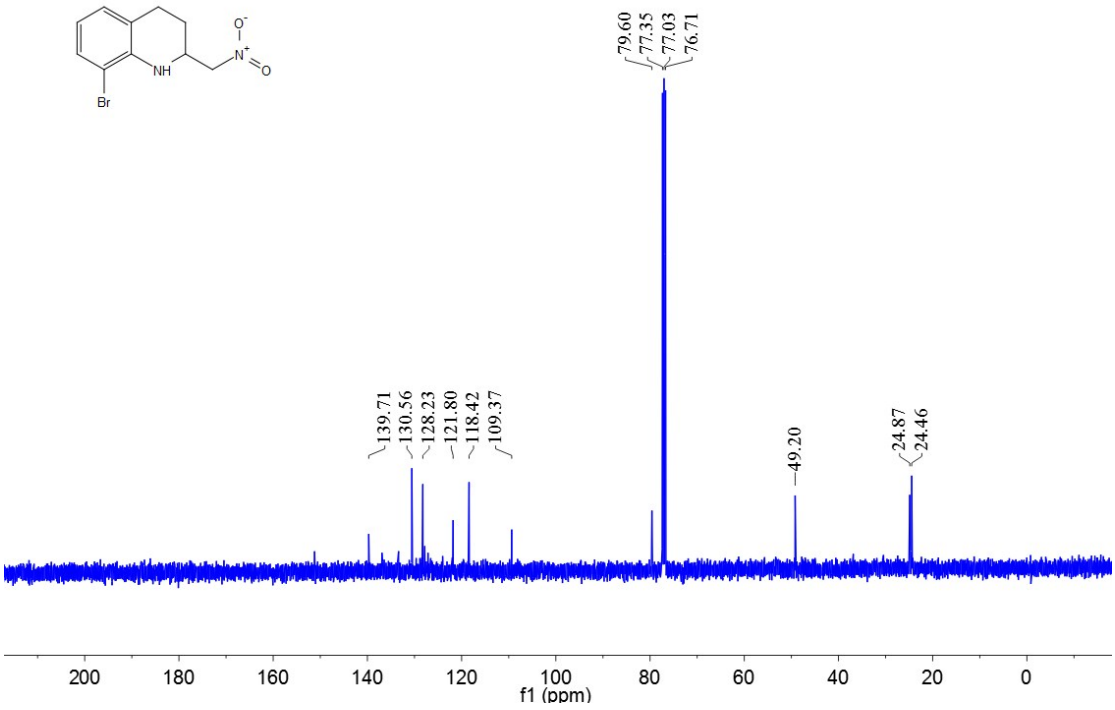
NMR spectra of 6-bromo-2-(nitromethyl)-1,2,3,4-tetrahydroquinoline (3ka)





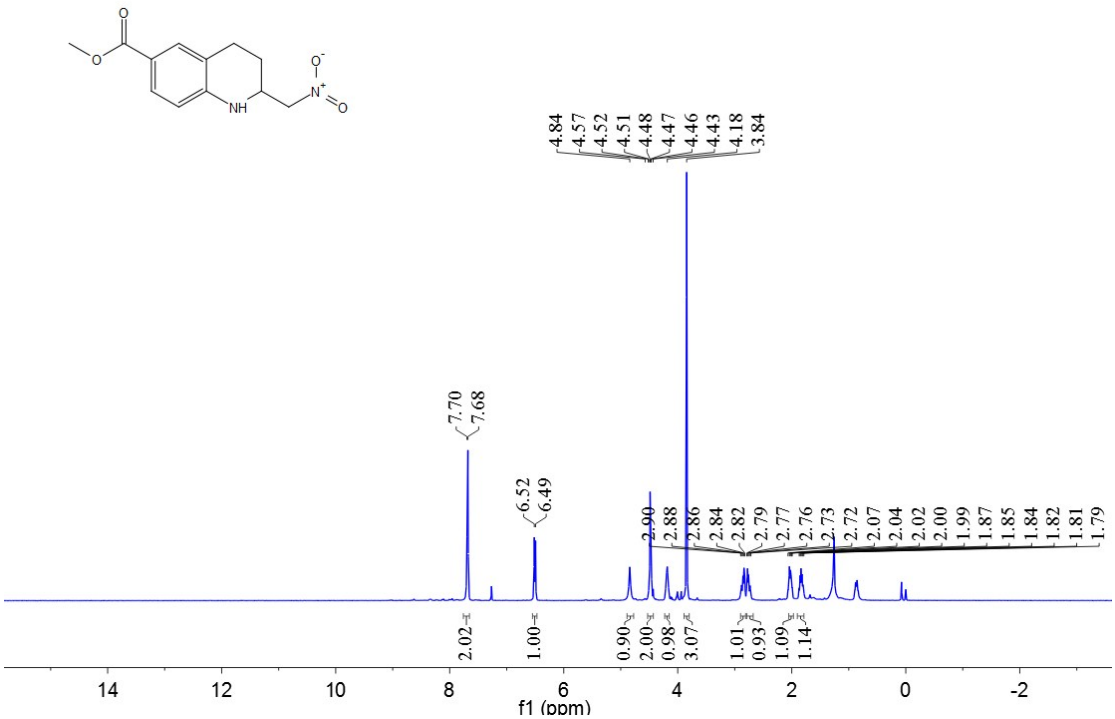
NMR spectra of 8-bromo-2-(nitromethyl)-1,2,3,4-tetrahydroquinoline (3la)

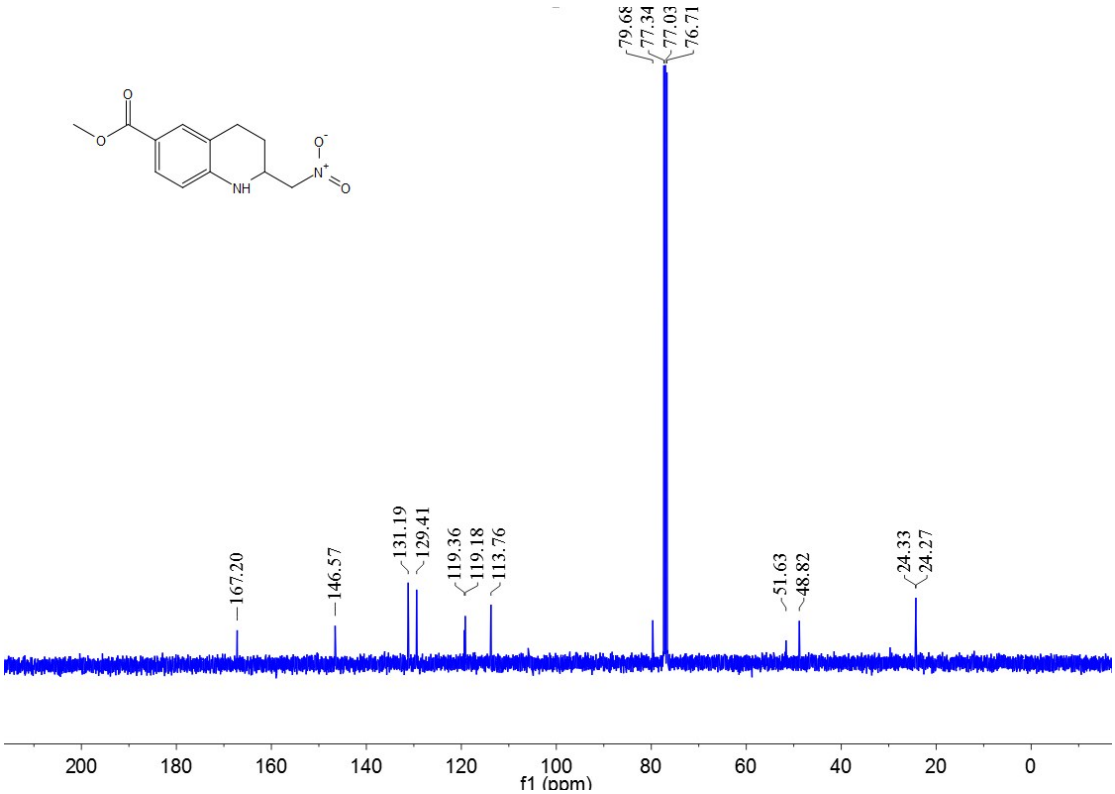




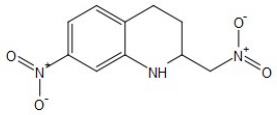
NMR spectra of methyl 2-(nitromethyl)-1,2,3,4-tetrahydroquinoline-6-

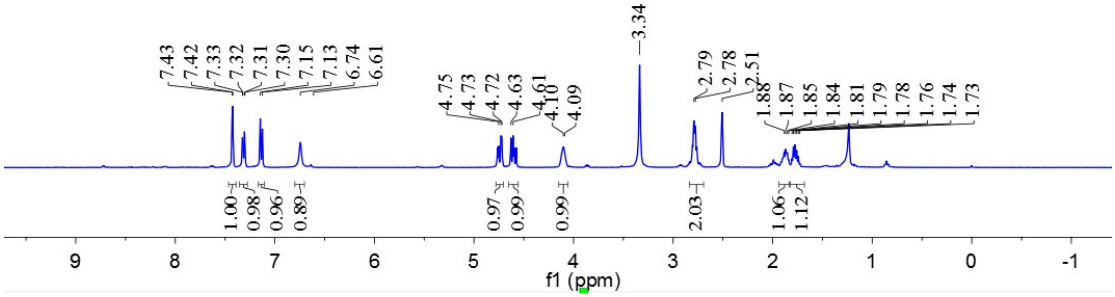
carboxylate (3ma)

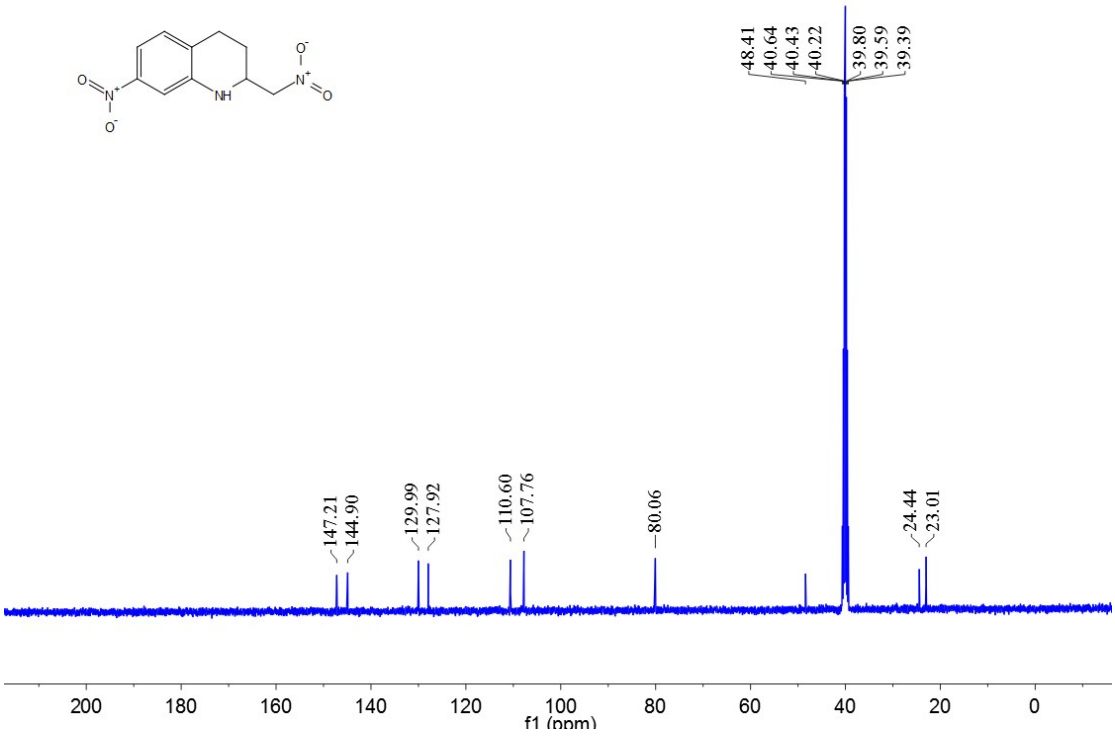




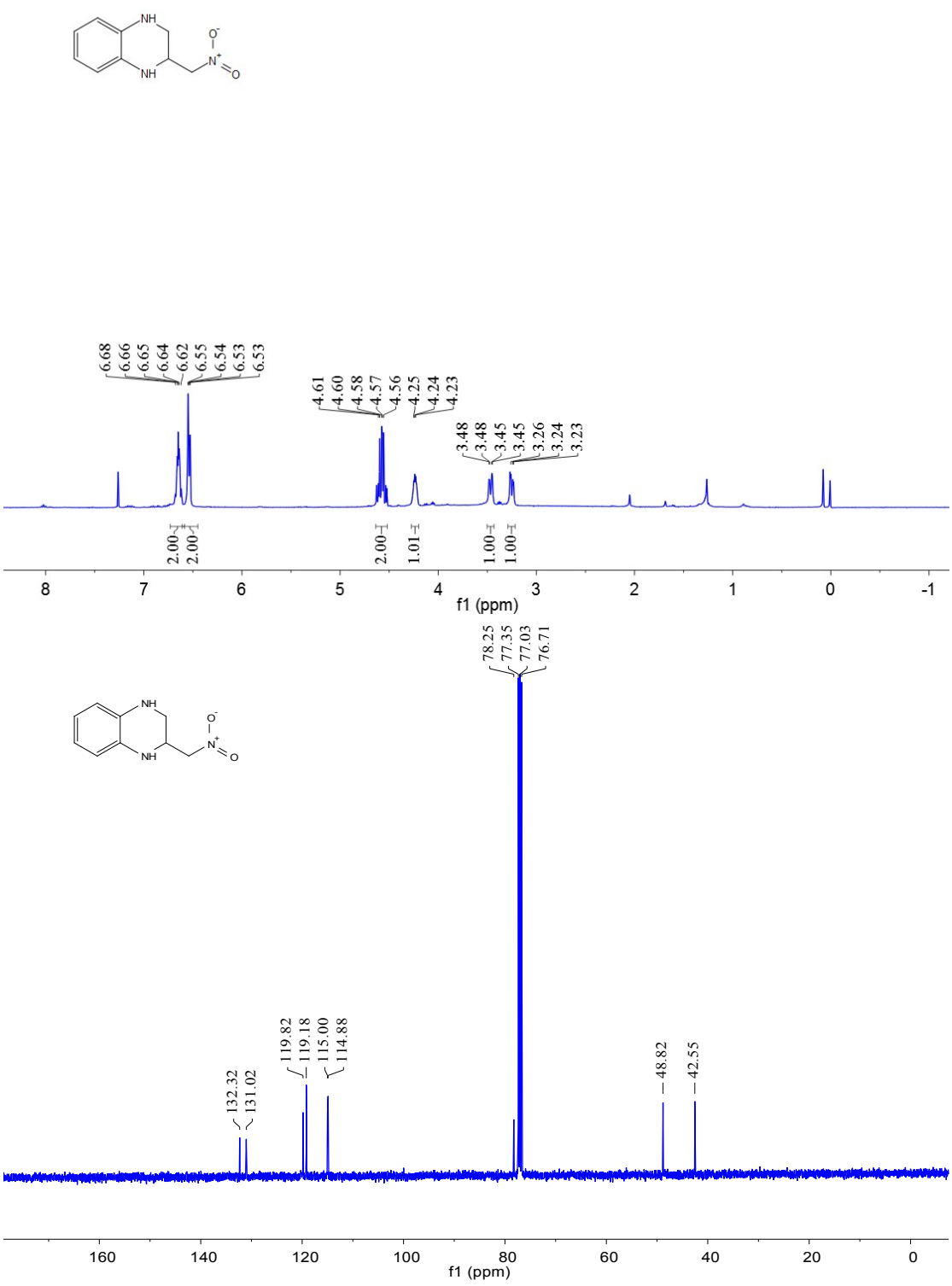
NMR spectra of 7-nitro-2-(nitromethyl)-1,2,3,4-tetrahydroquinoline (3na)



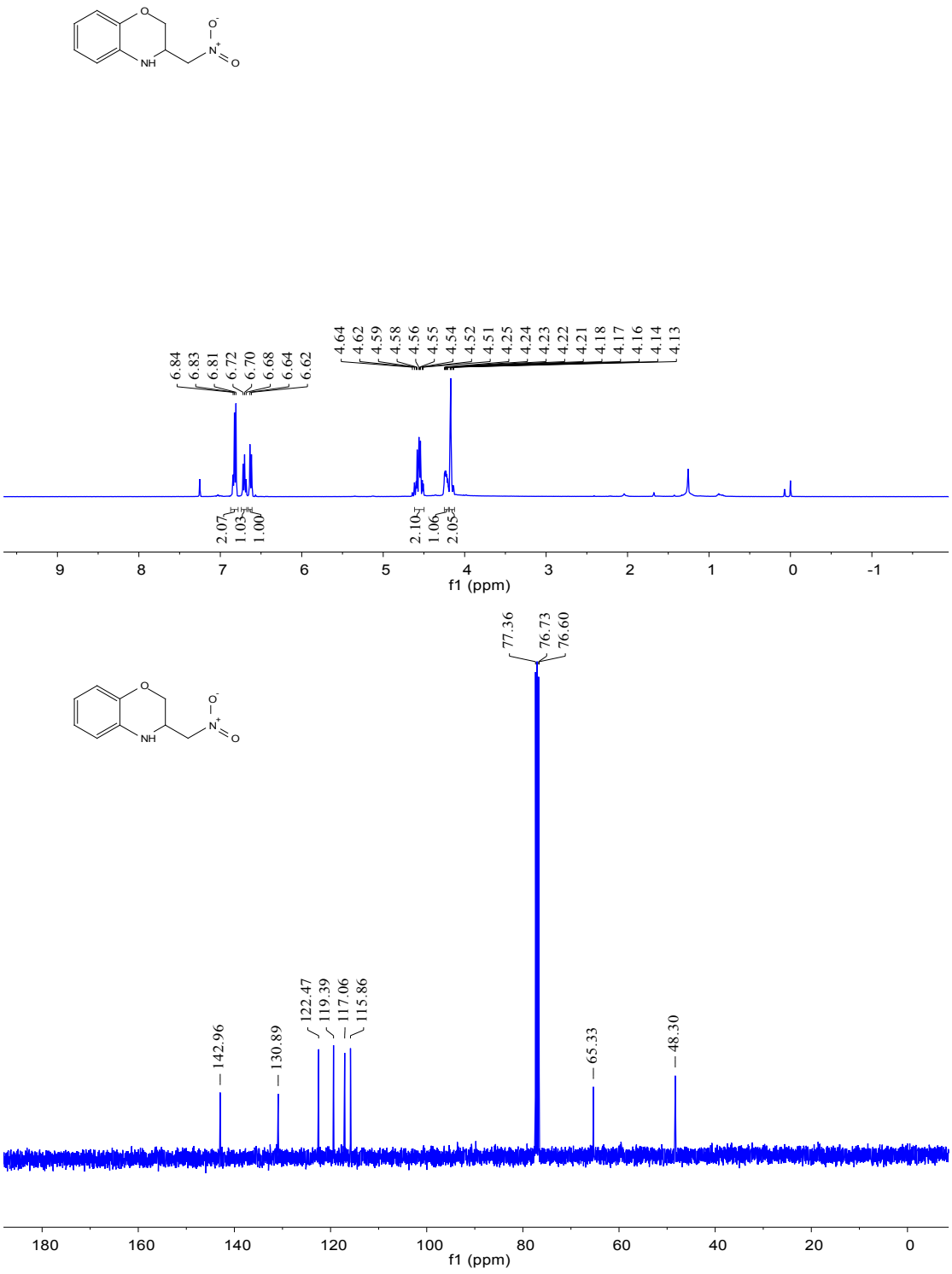




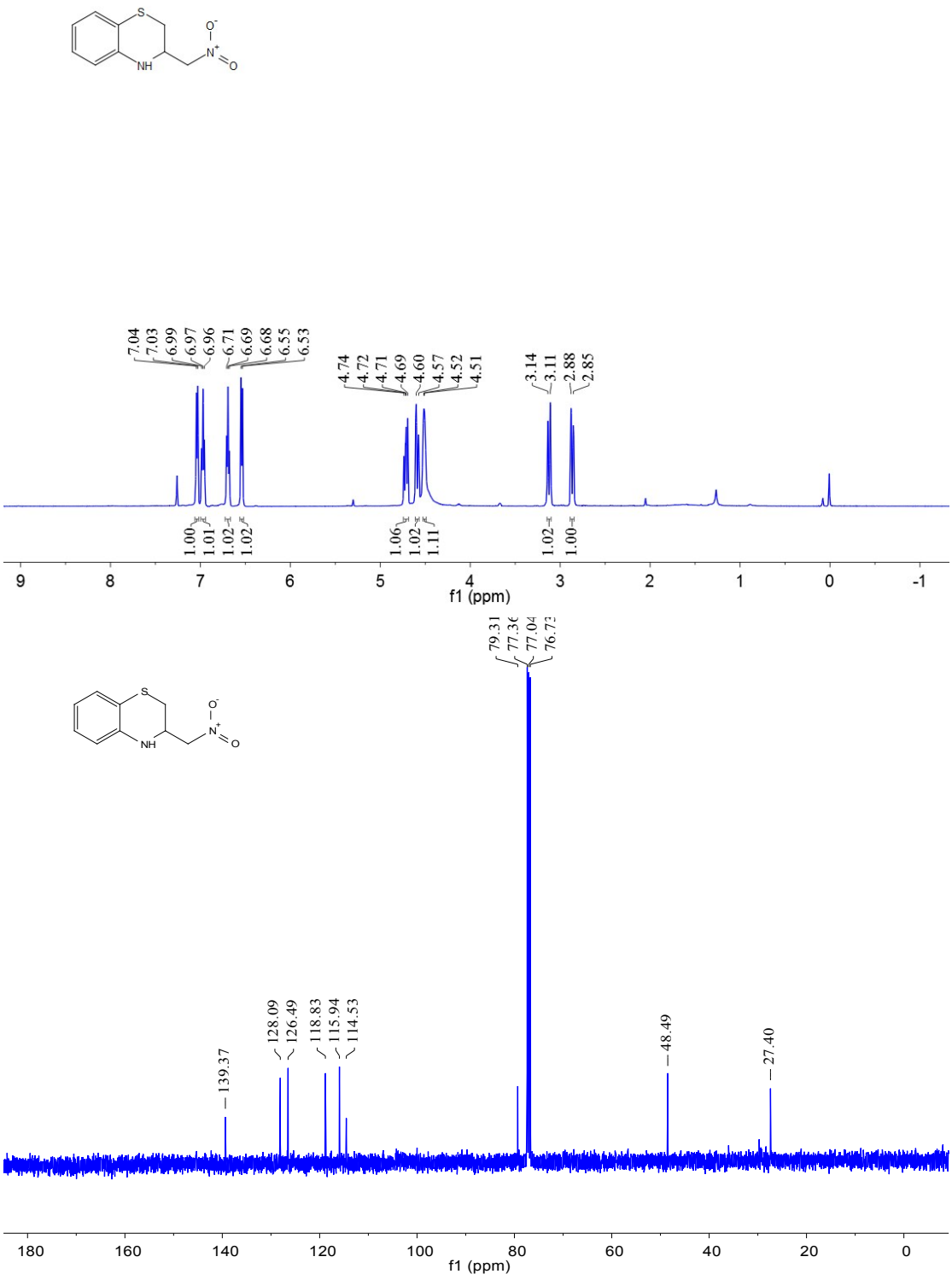
NMR spectra of 2-(nitromethyl)-1,2,3,4-tetrahydroquinoxaline (3oa)



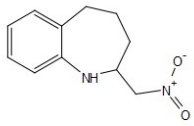
NMR spectra of 3-(nitromethyl)-3,4-dihydro-2*H*-benzo[*b*] [1,4] oxazine (3pa)

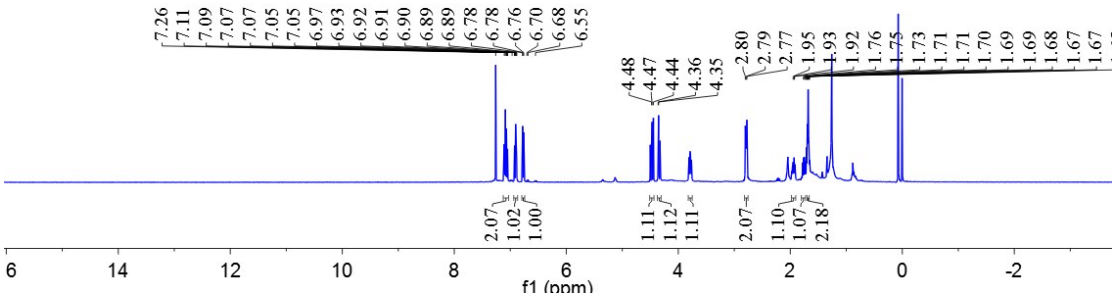


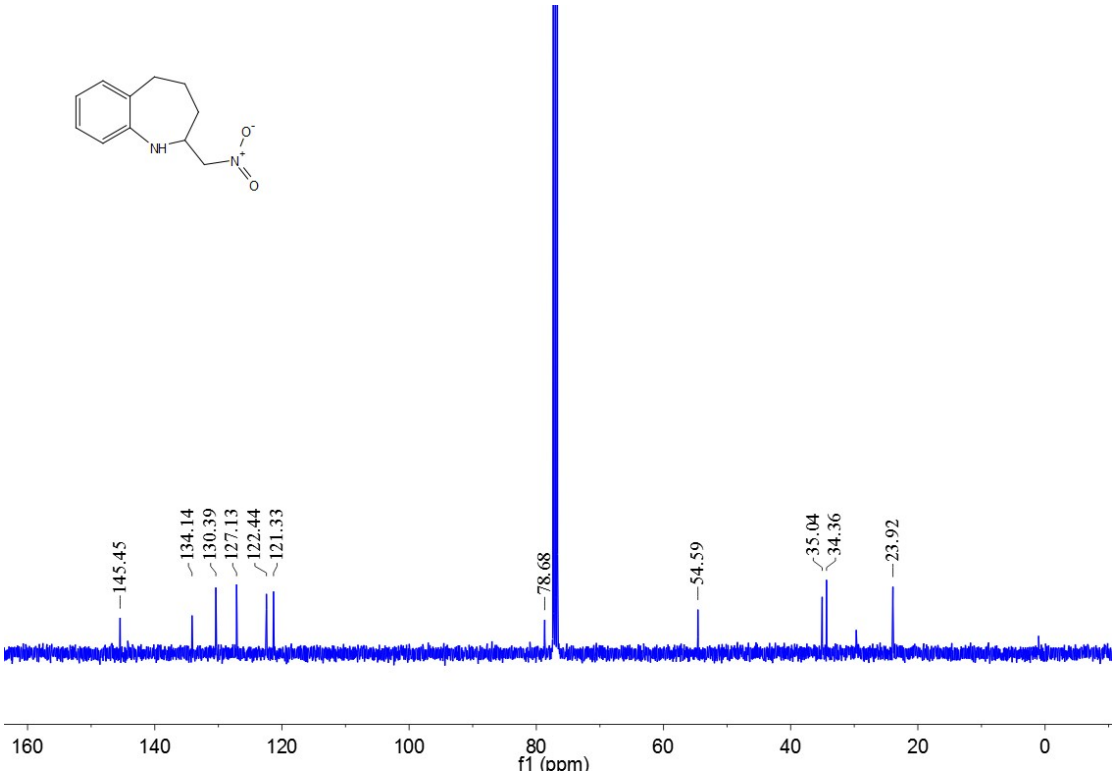
NMR spectra of 3-(nitromethyl)-3,4-dihydro-2*H*-benzo[*b*] [1,4] thiazine (3qa)



NMR spectra of 2-(nitromethyl)-2,3,4,5-tetrahydro-1*H*-benzo[*b*] azepine (3ra)

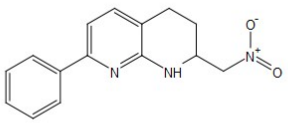


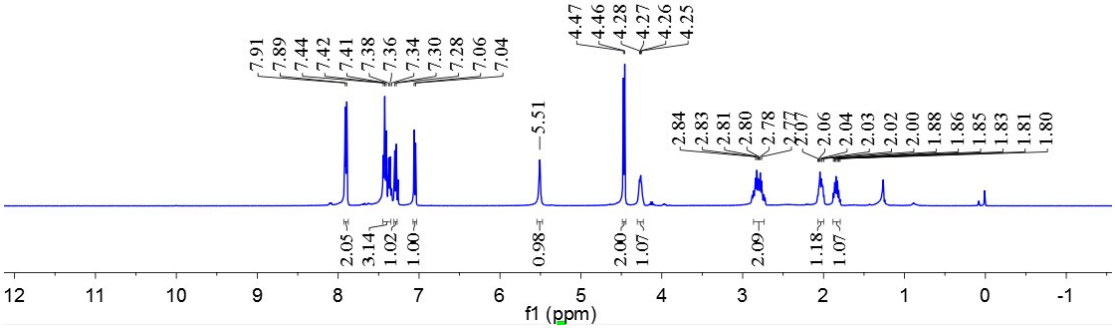


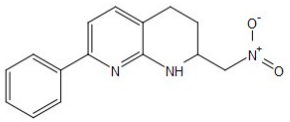


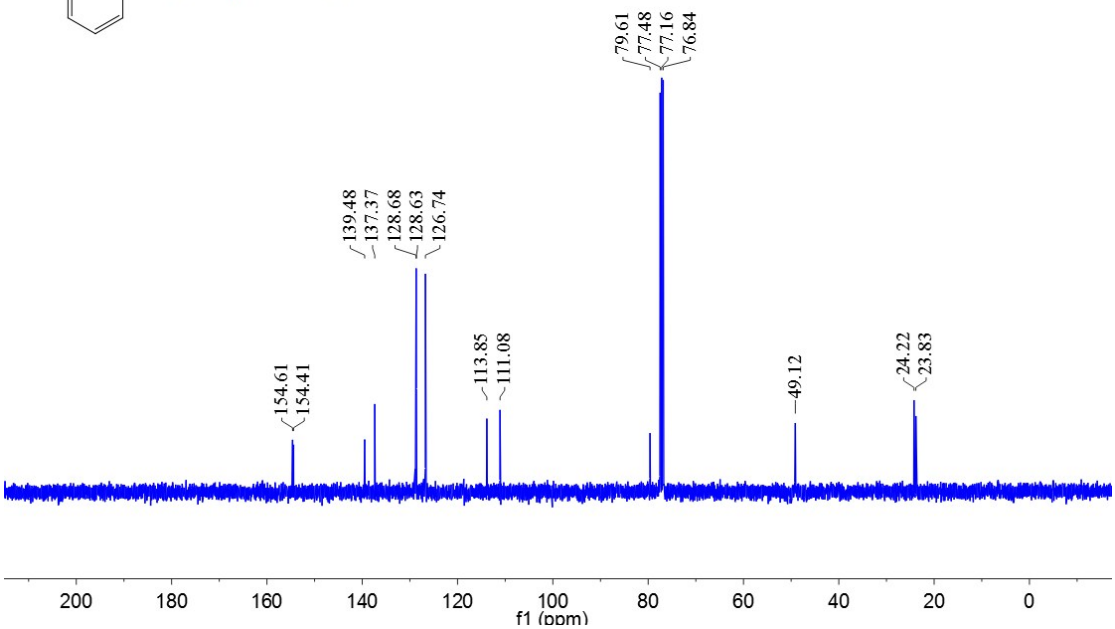
NMR spectra of (S)-2-(nitromethyl)-7-phenyl-1,2,3,4-tetrahydro-1,8-

naphthyridine (3sa)

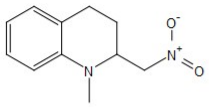


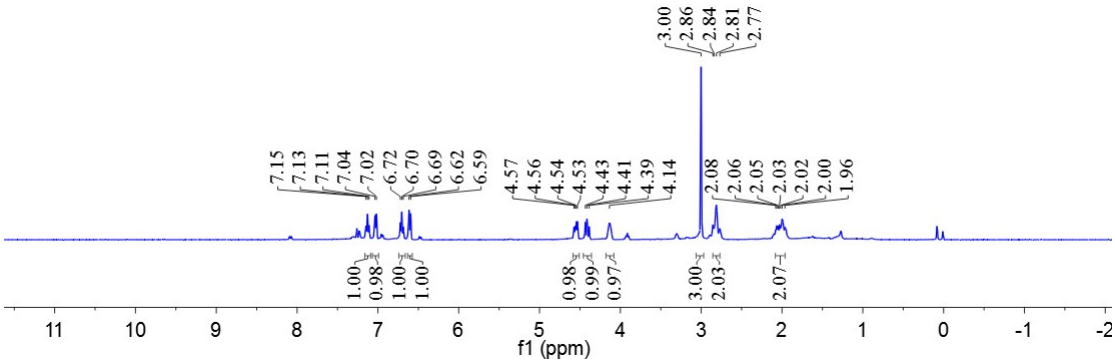


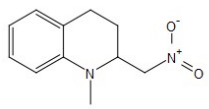




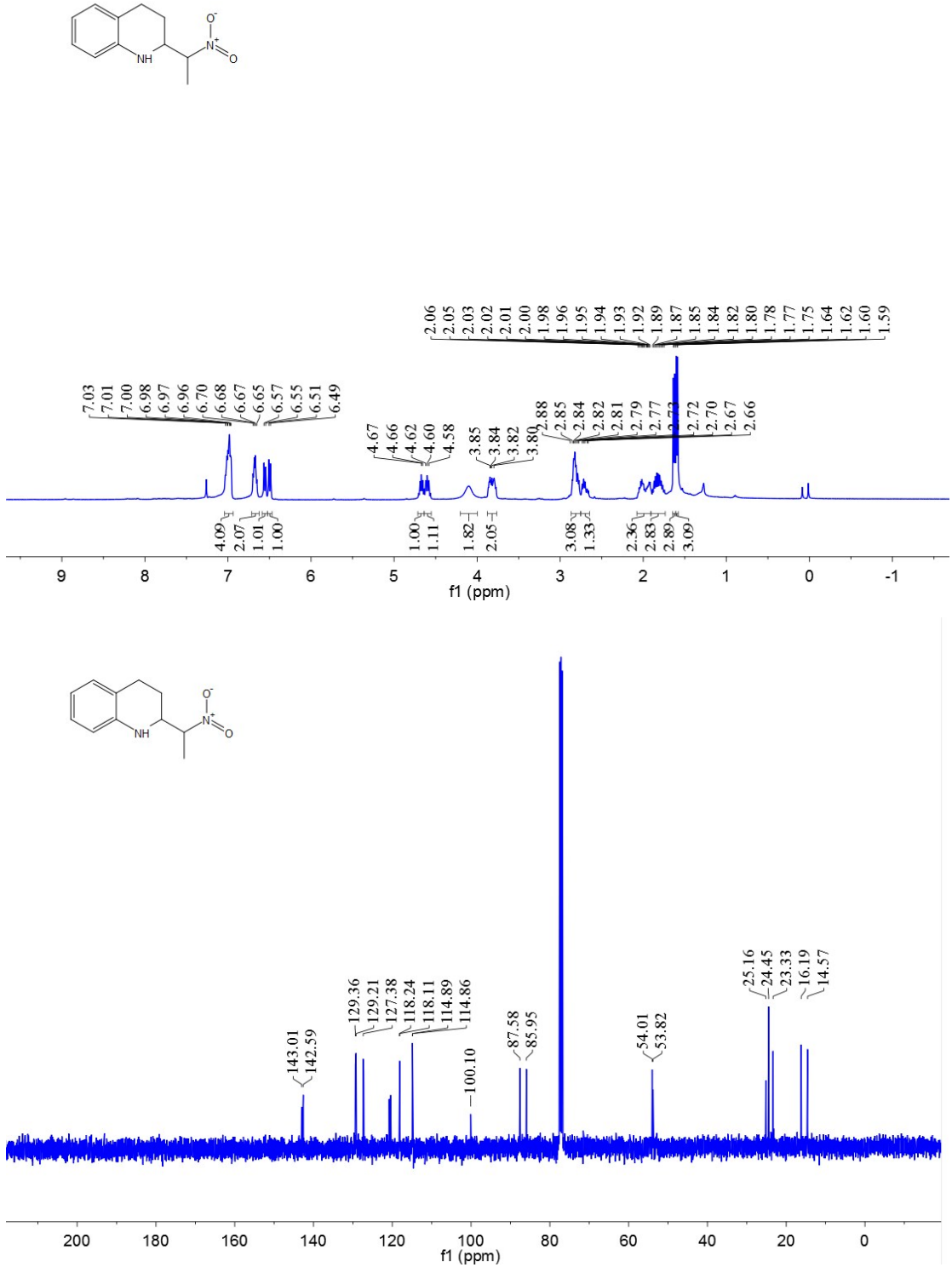
NMR spectra of 1-methyl-2-(nitromethyl)-1,2,3,4-tetrahydroquinoline (3ta)



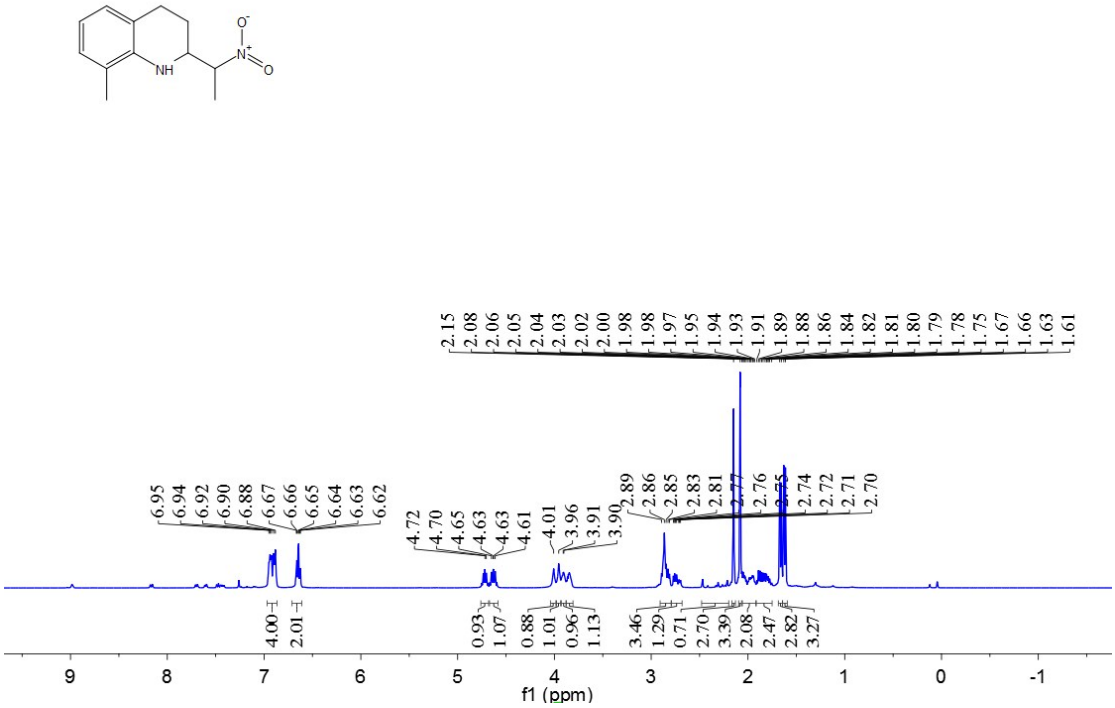


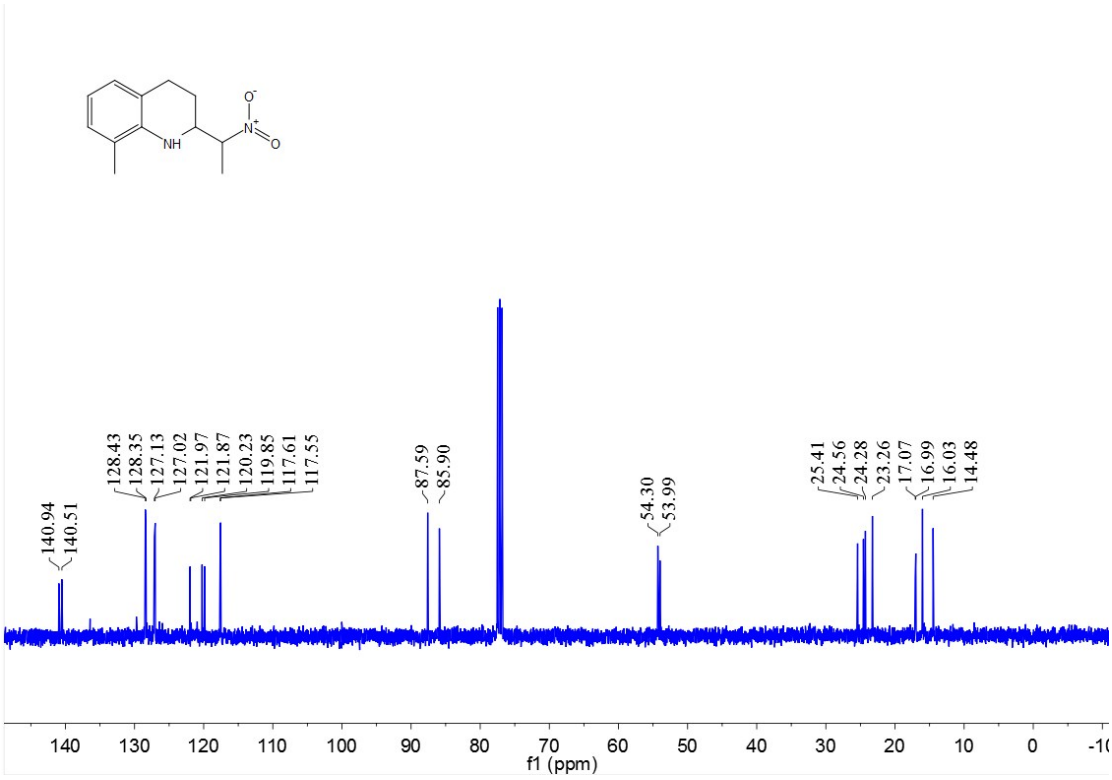


NMR spectra of 2-(1-nitroethyl)-1,2,3,4-tetrahydroquinoline (3ab)

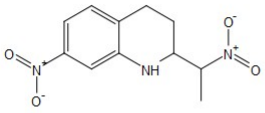


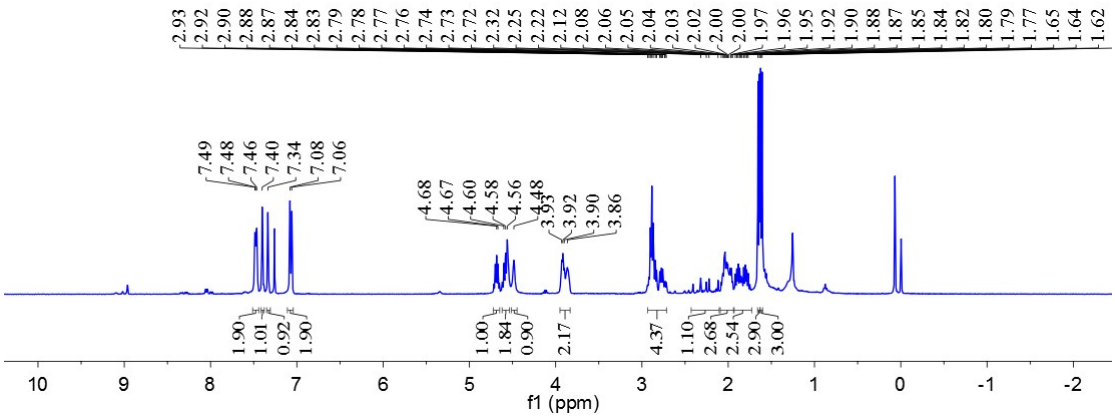
NMR spectra of 8-methyl-2-(1-nitroethyl)-1,2,3,4-tetrahydroquinoline (3eb)

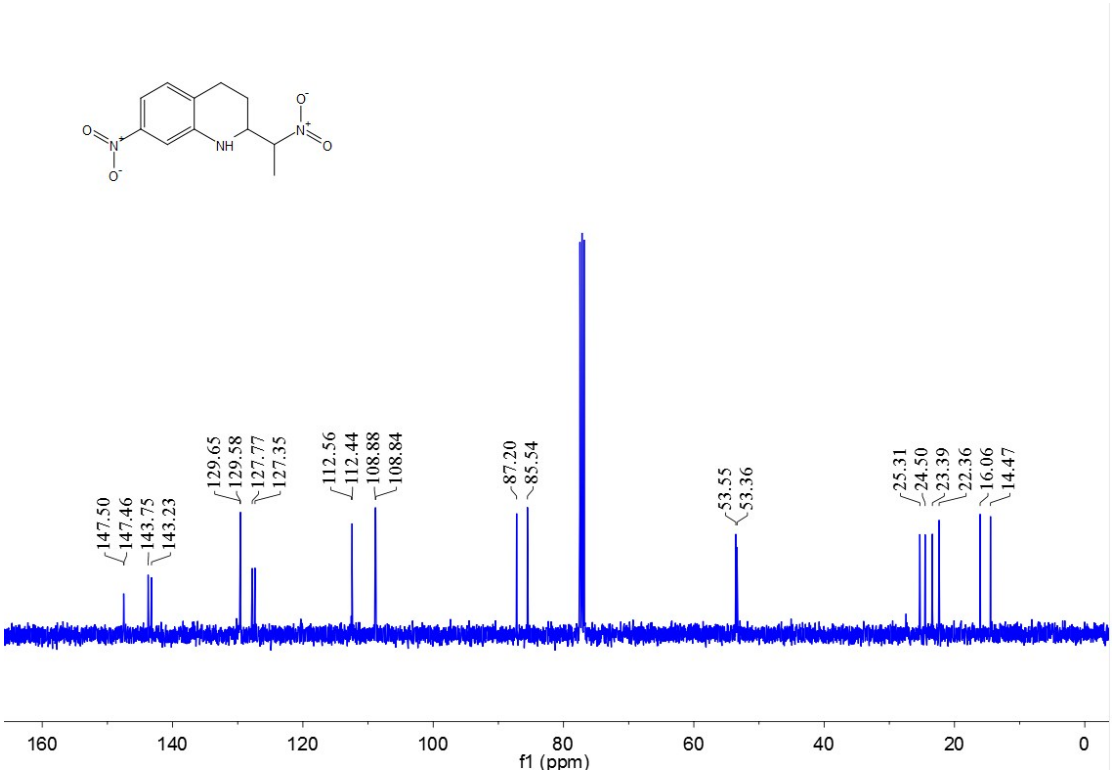




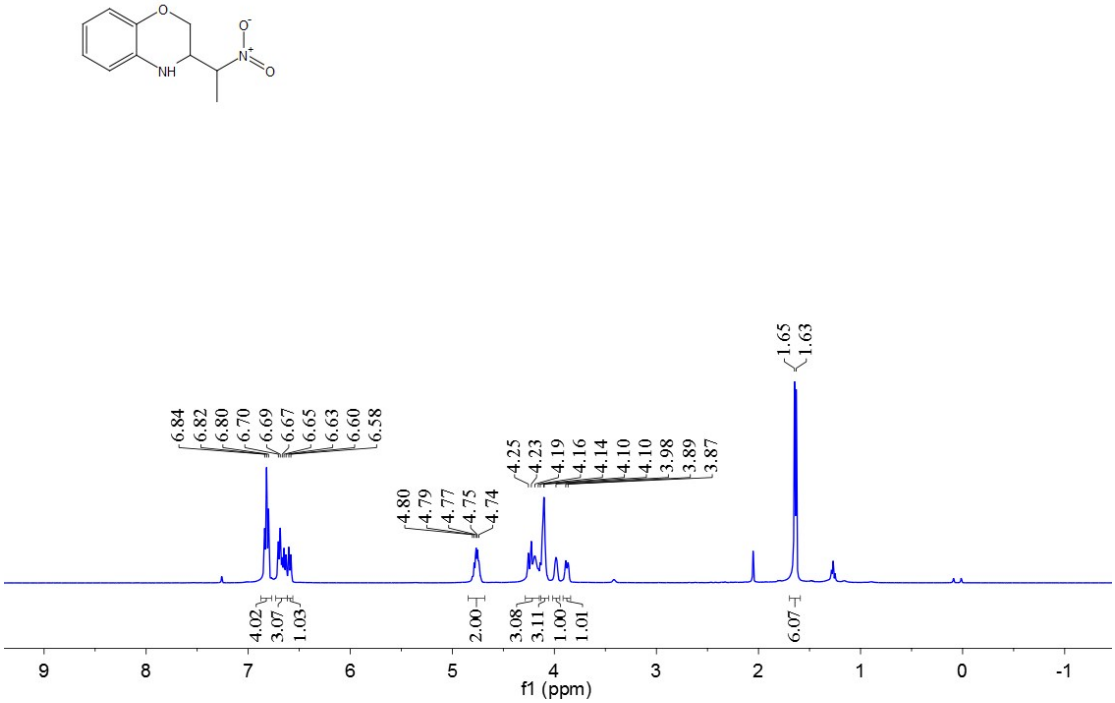
NMR spectra of 7-nitro-2-(1-nitroethyl)-1,2,3,4-tetrahydroquinoline (3nb)

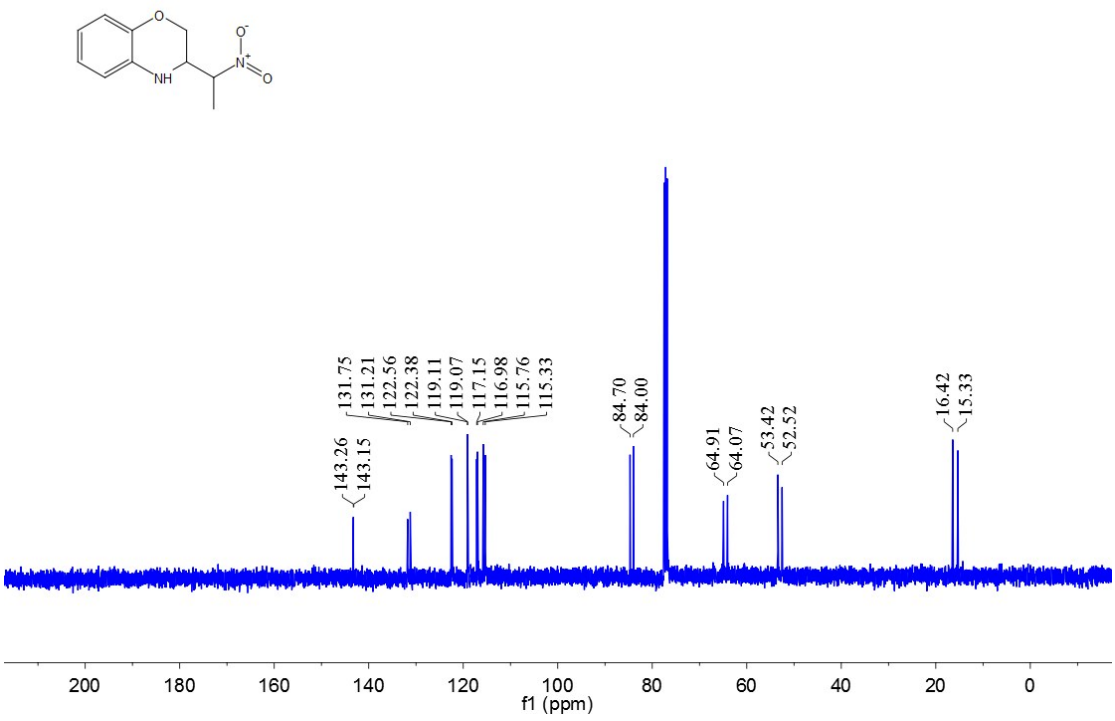




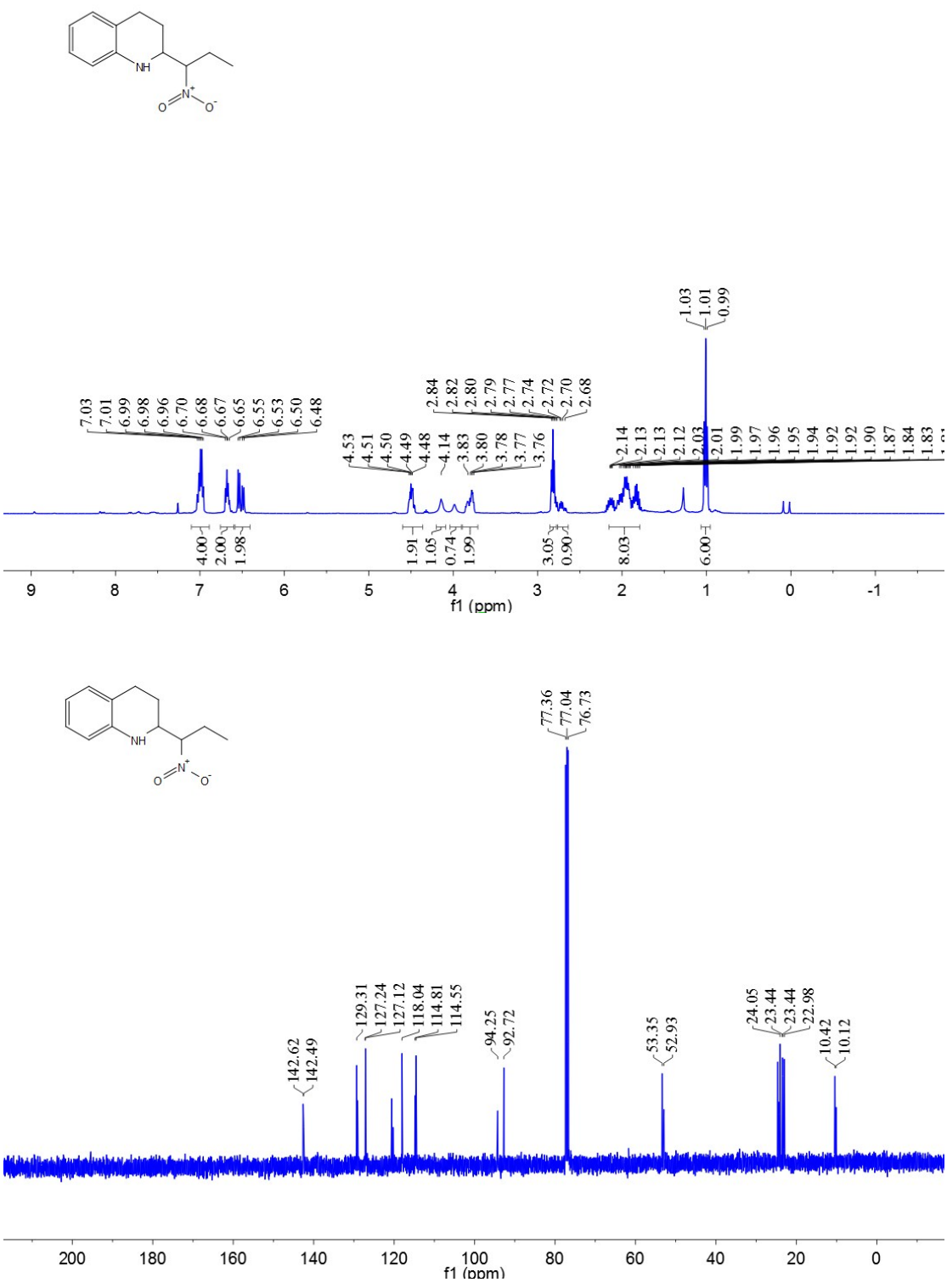


NMR spectra of 3-(1-nitroethyl)-3,4-dihydro-2*H*-benzo[*b*] [1,4] oxazine (3pb)

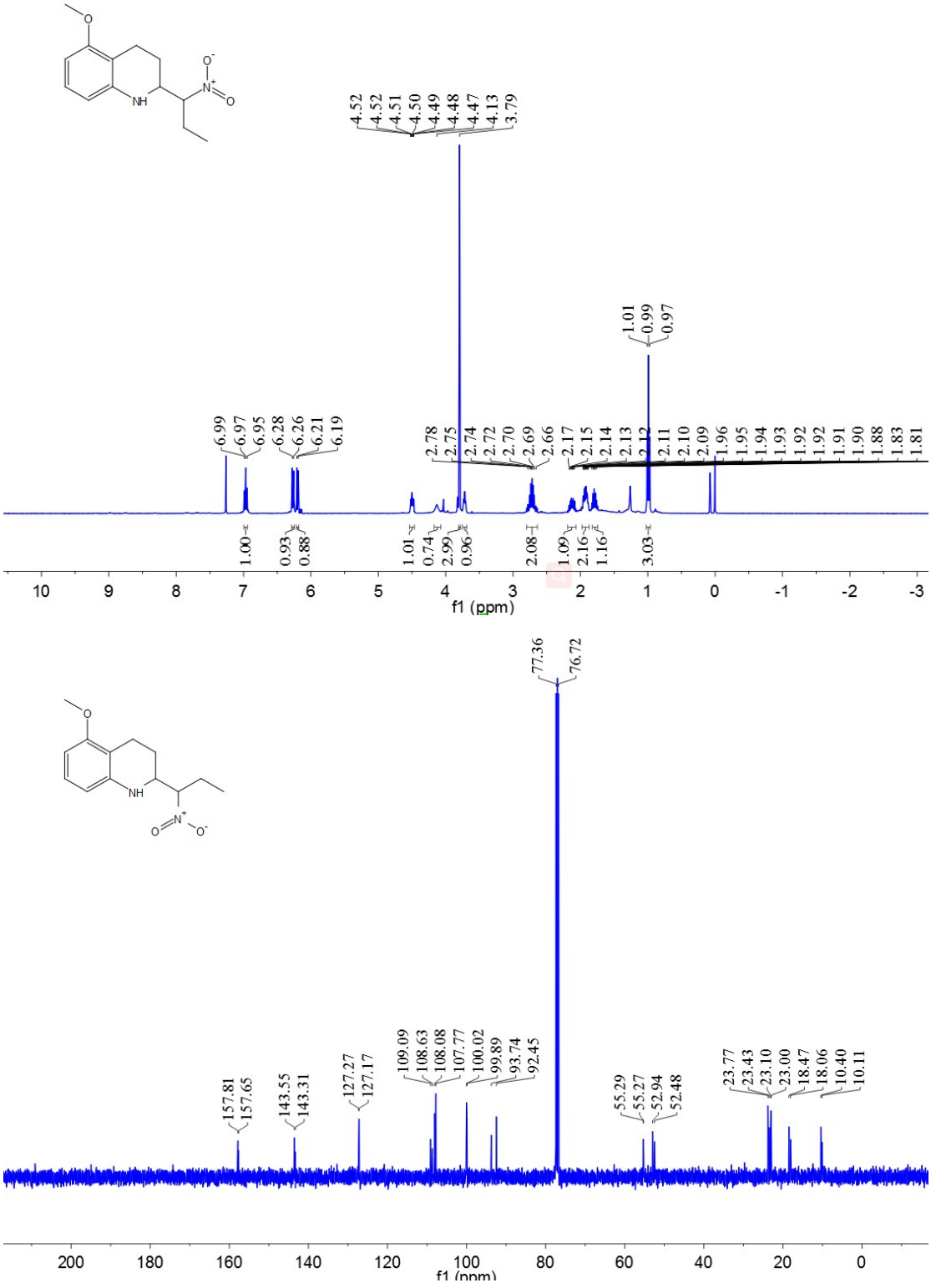




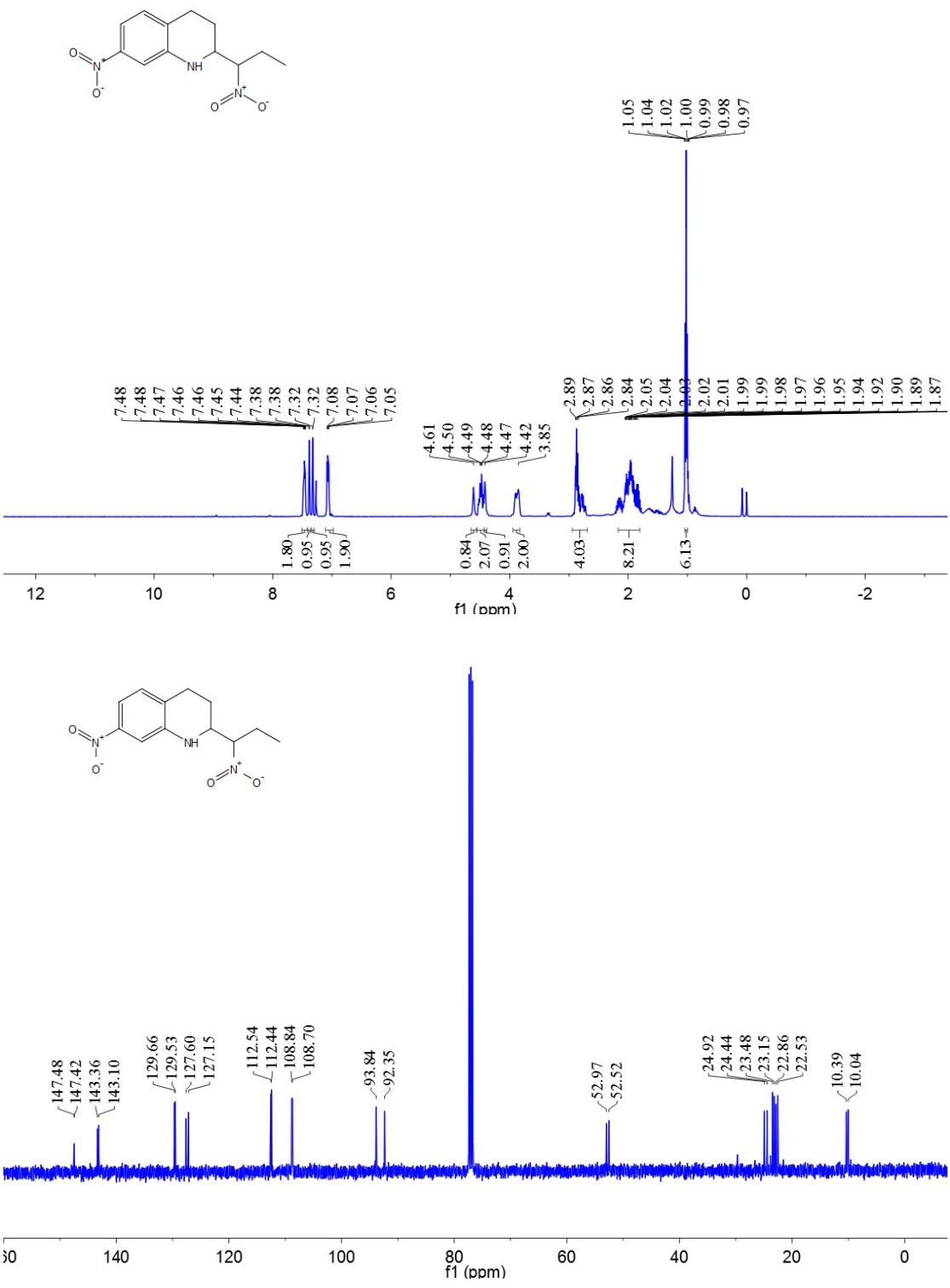
NMR spectra of 2-(1-nitropropyl)-1,2,3,4-tetrahydroquinoline (3ac)



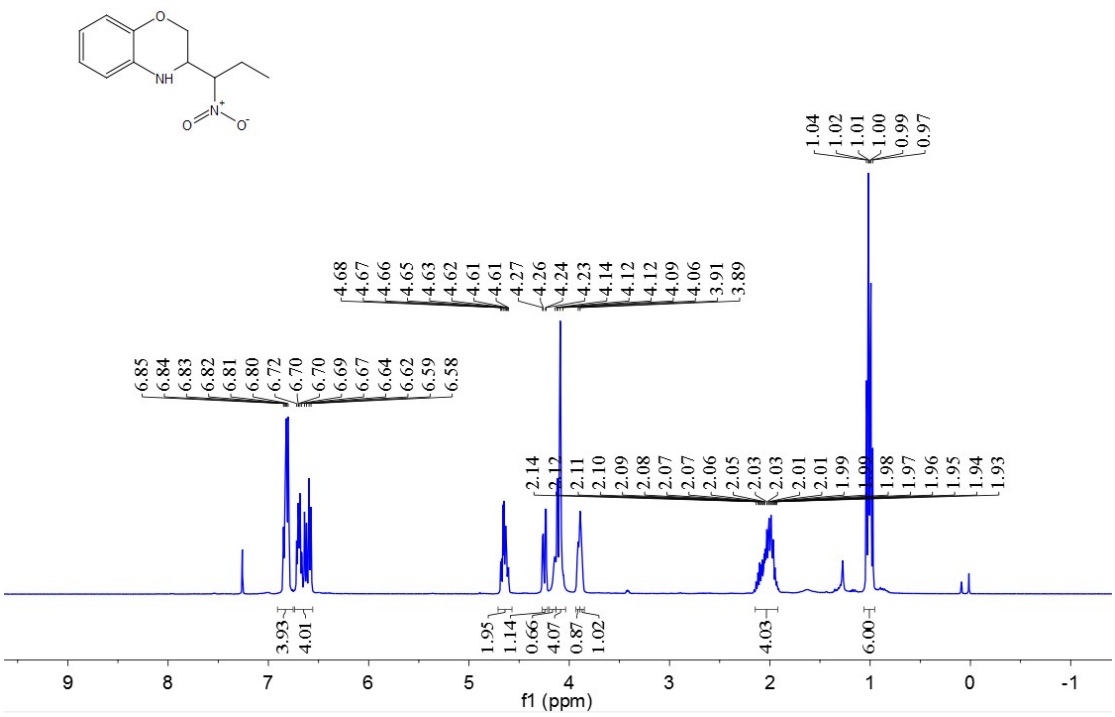
NMR spectra of 5-methoxy-2-(1-nitropropyl)-1,2,3,4-tetrahydroquinoline (3fc)

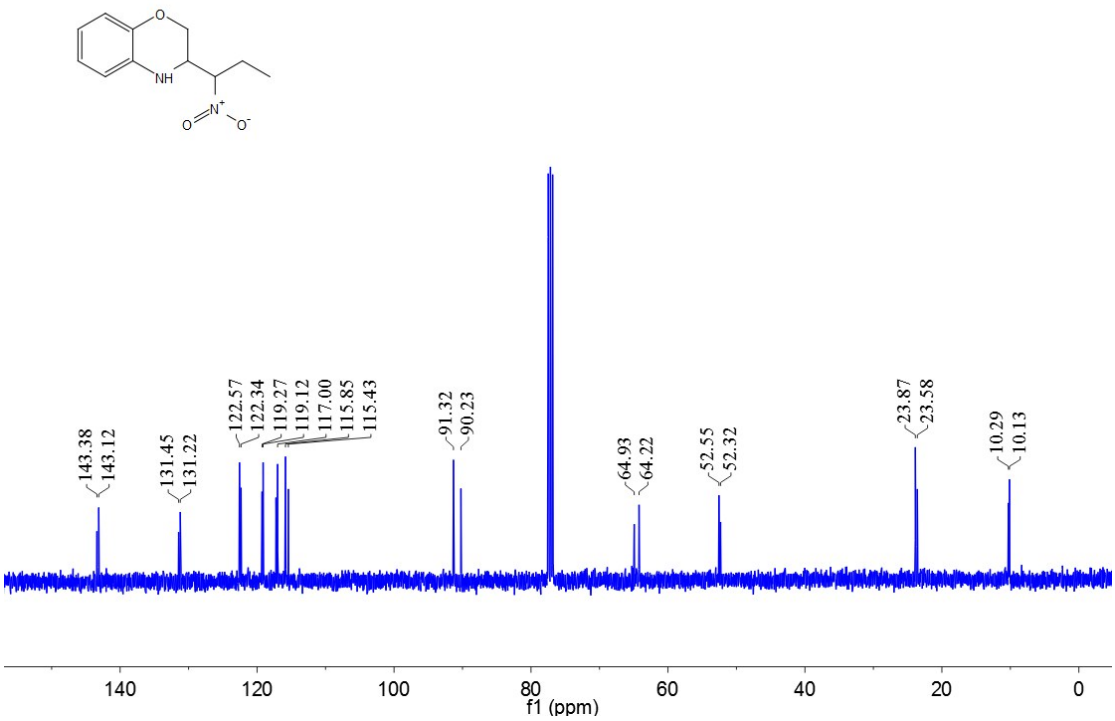


NMR spectra of 7-nitro-2-(1-nitropropyl)-1,2,3,4-tetrahydroquinoline (3nc)

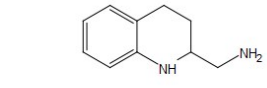


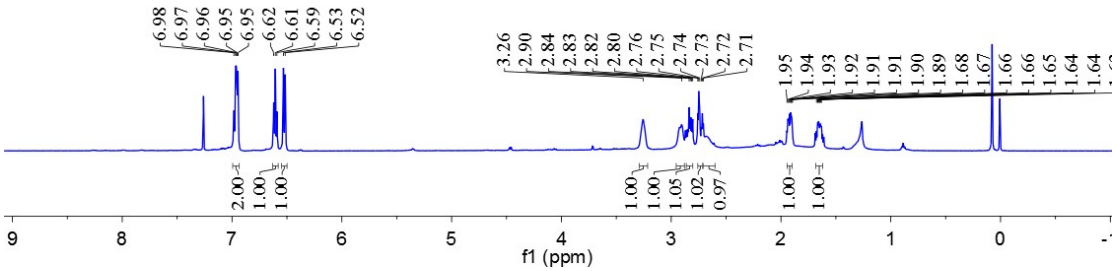
NMR spectra of 3-(1-nitropropyl)-3,4-dihydro-2*H*-benzo[*b*] [1,4] oxazine (3pc)

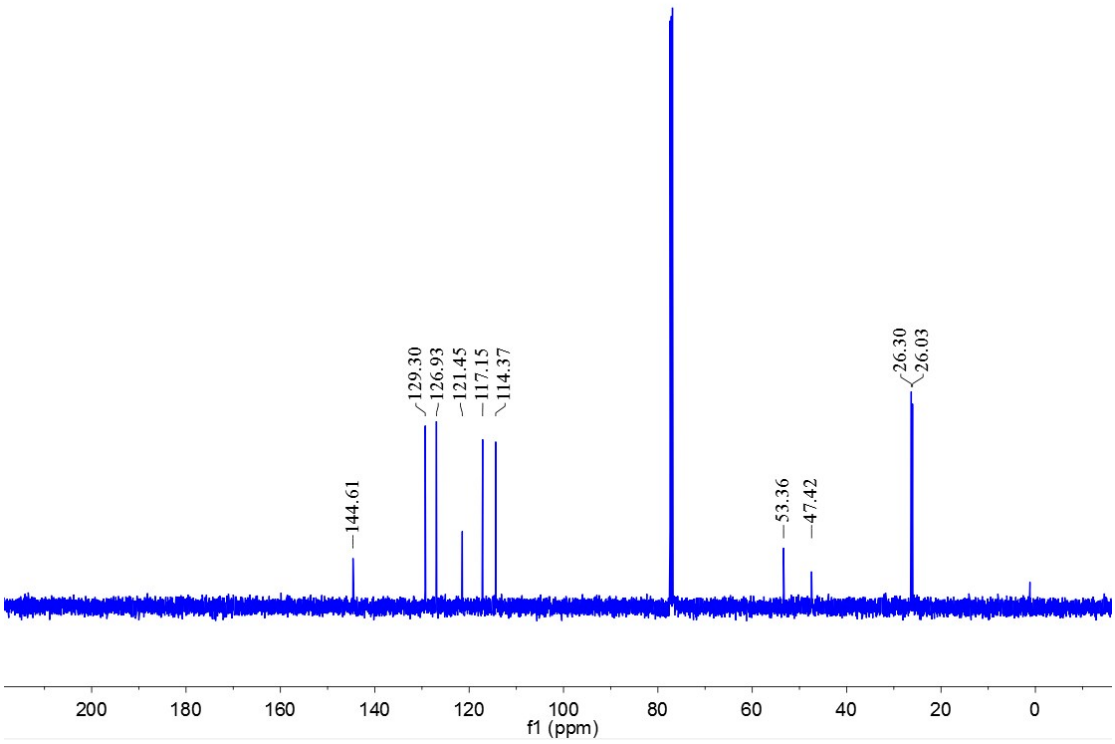




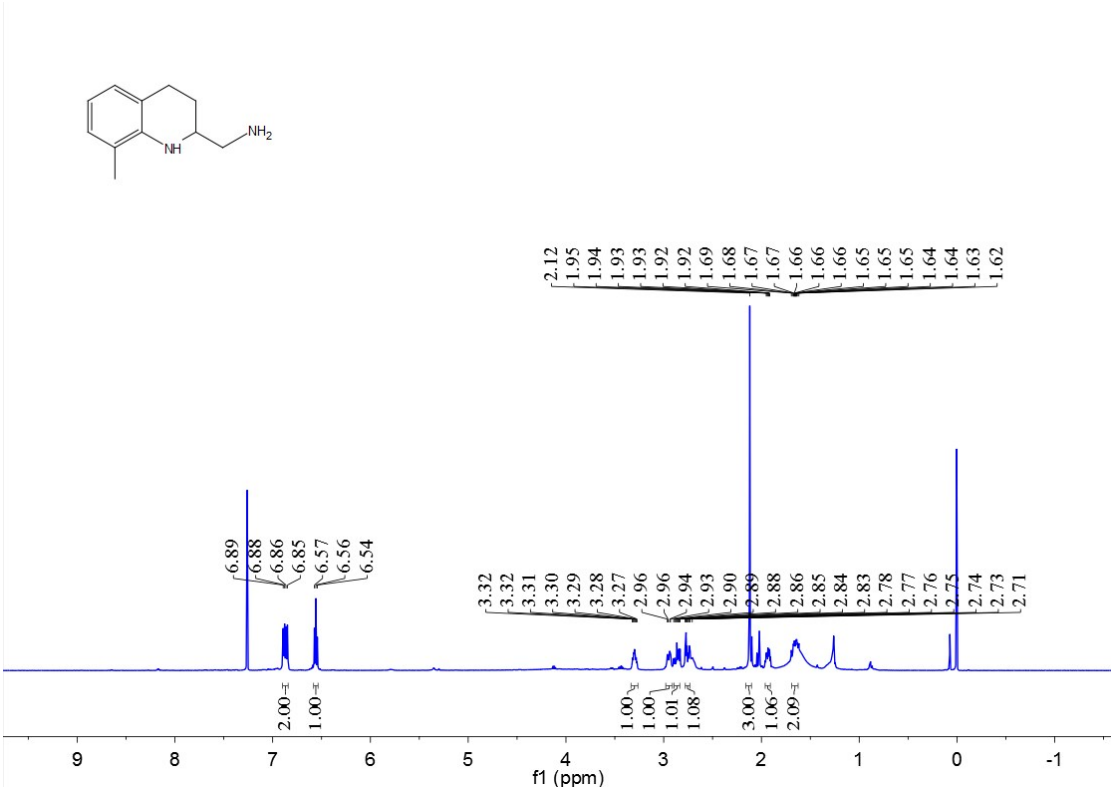
NMR spectra of (1,2,3,4-tetrahydroquinolin-2-yl) methanamine (3aa')

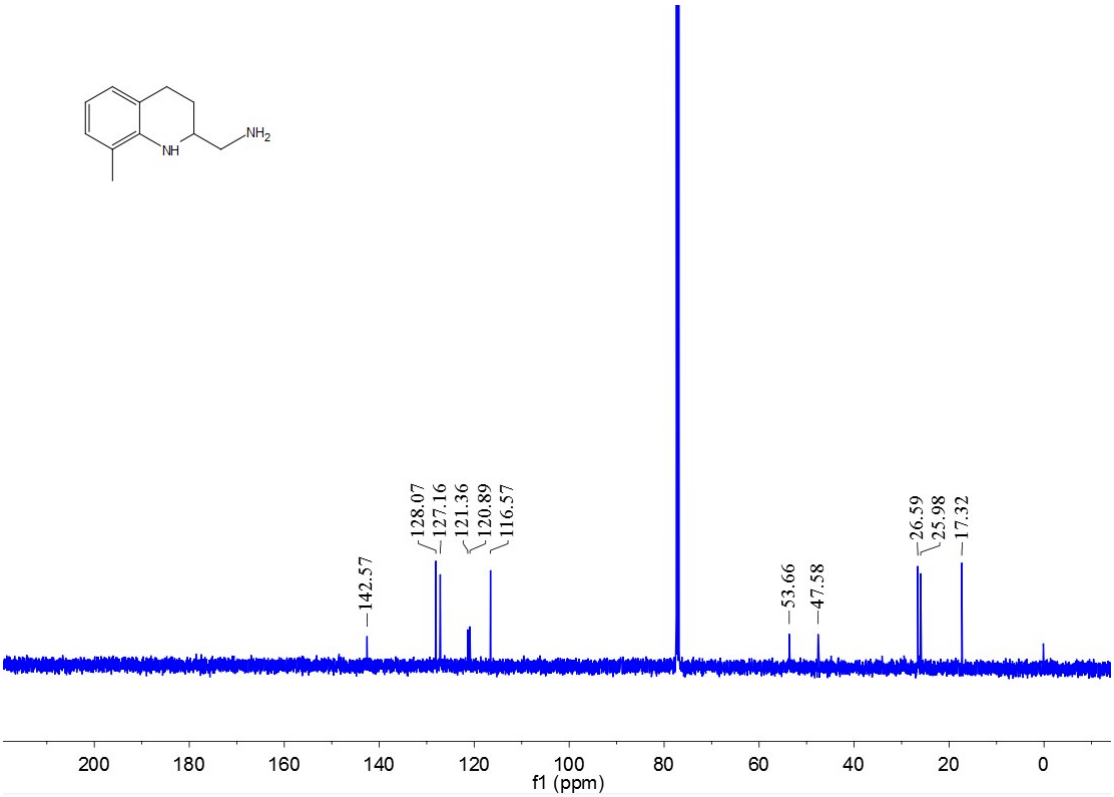




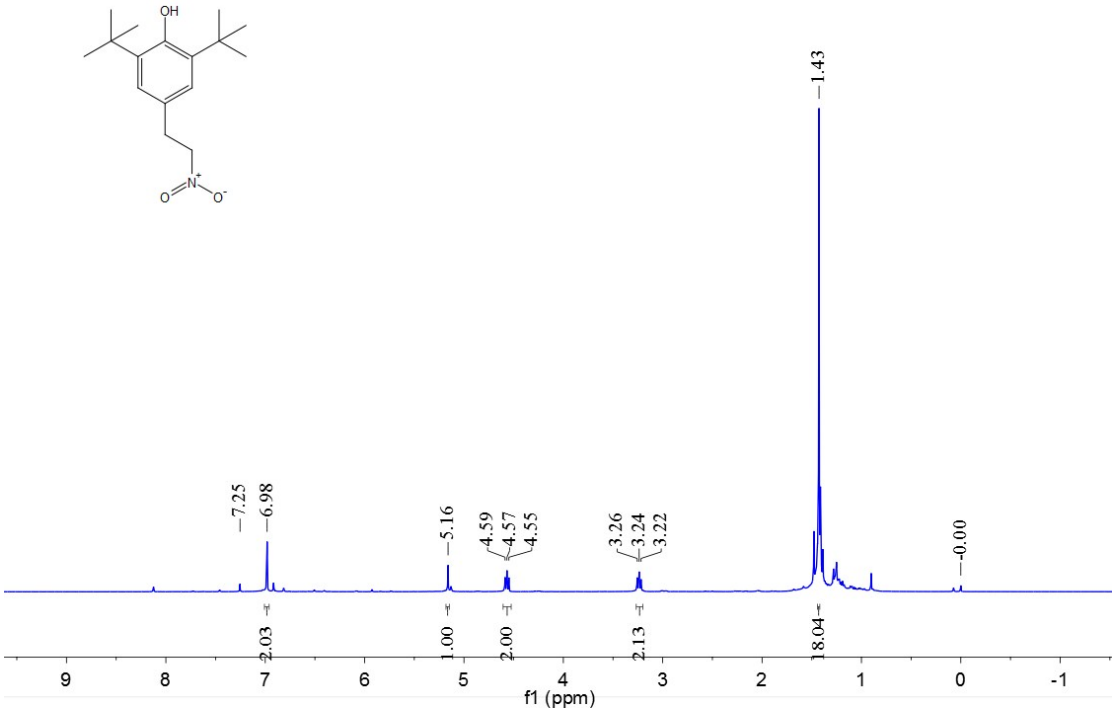


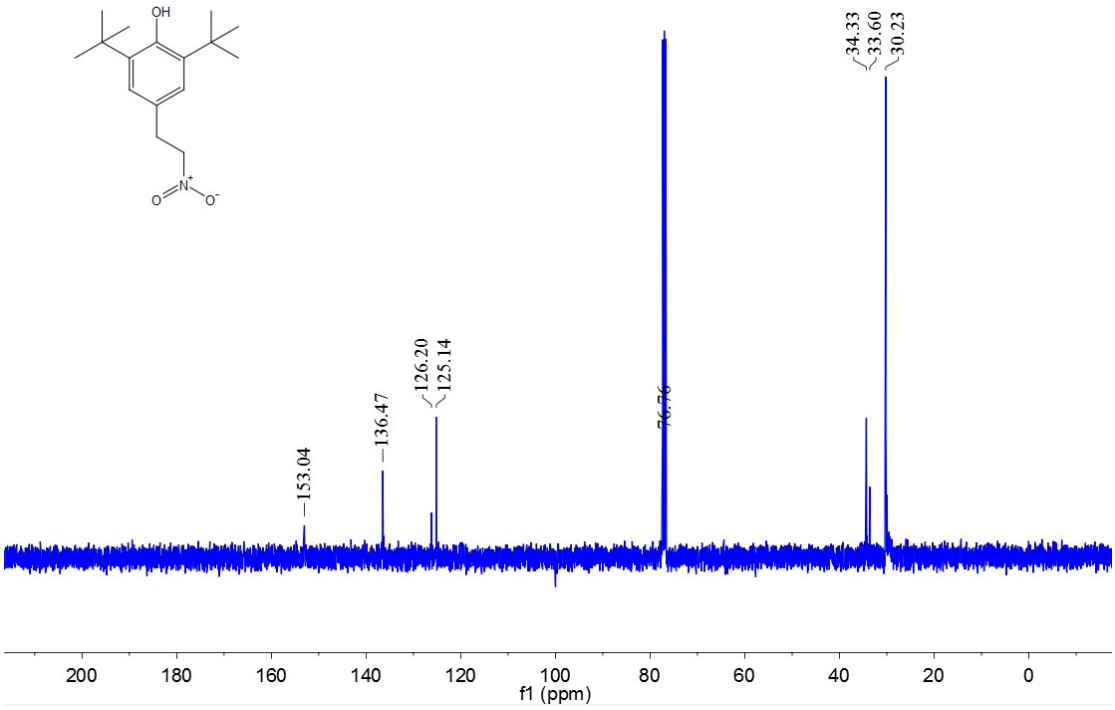
NMR spectra of (8-methyl-1,2,3,4-tetrahydroquinolin-2-yl) methanamine (3ea')





NMR spectra of 2,6-di-*tert*-butyl-4-(2-nitroethyl) phenol (compound 4)





NMR spectra of 2,6-di-*tert*-butyl-4-((3,4-dihydroquinolin-1(2*H*)-yl) methyl)

phenol (compound 5)