Supporting Information

for

Diboron-Assisted Palladium-Catalyzed Transfer Hydrogenation of N-Heteroaromatics with Water as Hydrogen Donor and Solvent

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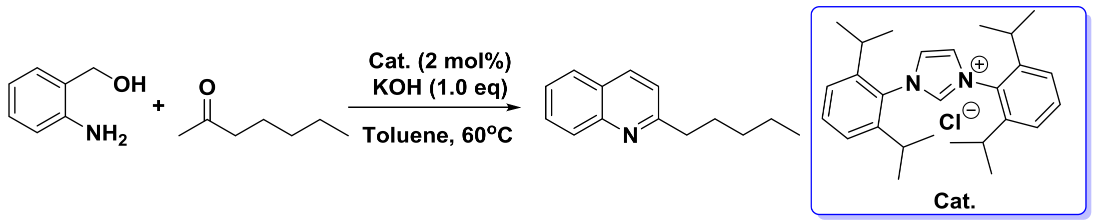
I. General methods

Unless otherwise noted, otherwise noted, all reagents were obtained from commercial suppliers and were used without further purification. ^{1}H, ^{13}C spectra were recorded in $CDCl_3$ on a Bruker AVIII-500M spectrometers. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet. Column chromatography was performed using silica gel (200-300 mesh).

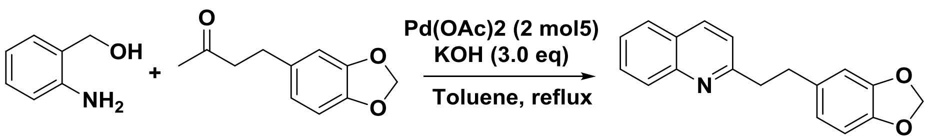
II. Preparation of 1h, 1i, 1p-t

Typical procedure for preparation of 1h [1]



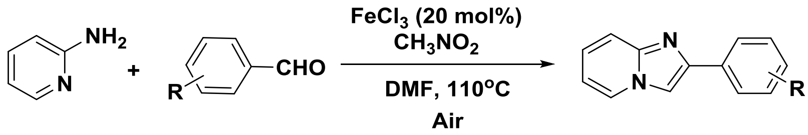
A mixture of 2-aminobenzyl alcohol (0.246 g, 2 mmol), heptan-2-one (0.456g, 4 mmol), KOH (0.11g, 2 mmol), catalyst (0.017g, 0.04 mmol) and toluene (10 ml) was placed in a round bottom flask and allowed to react at 60℃ for 2h. After the solution was cooled to room temperature, the solid was filtered over celite and washed with methylene dichloride. The filtrate was evaporated under reduced pressure, and the product was purified by flash chromatography using petroleum ether and ethyl acetate as eluent.

Typical procedure for preparation of 1i [2]



A mixture of 2-aminobenzyl alcohol (0.246 g, 2 mmol), acetophenone (0.480 g, 4 mmol), KOH (0.336 g, 6 mmol), $Pd(OAc)_2$ (0.0090 g, 0.04 mmol) and toluene (6 mL) was placed in a round bottom flask and allowed to react at reflux temperature for 24 h. After the brown black solution was cooled to room temperature, the solid was filtered over celite and washed with methylene dichloride. The filtrate was evaporated under reduced pressure, and the product was purified by flash chromatography using petroleum ether and ethyl acetate as eluent.

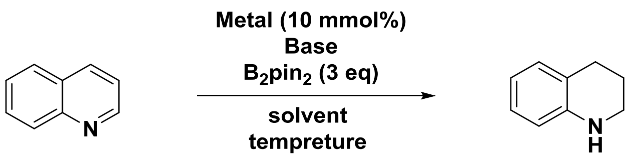
Typical procedure for preparation of 1p-t [3]



A mixture of 2-aminopyridine (94 mg, 1 mmol) and 4-chlorobenzaldehyde (1.1 mmol) was heated in presence of anhydrous $FeCl_3$ (20 mol%) in nitromethane (2 mL) and DMF (1 mL) at 110 °C for 5 h (TLC). After completion, the reaction mixture was cooled to room temperature and extracted with dichloromethane (10 mL) followed by washing with brine (5 mL) and dried over Na_2SO_4. After evaporation of solvent the crude product was purified by column chromatography on silica gel using petroleum ether/ethylacetate as eluent.

III. Palladium-catalyzed transfer hydrogenation

i. General procedure for reaction optimization



1a 2a

General optimization procedure: To a Schenk tube equipped with a stir bar, 152.4mg of B_2pin_2 (0.6 mmol), 4.5mg $Pd(OAc)_2$ (0.02 mmol) were added. The

Schenk tube was capped with a septum, degassed and backfilled with N_2 for at least three times. Then, the solvent (2.0 ml) and 25.8mg quinoline (0.2 mmol) were added via syringe. The mixture was stirred at room temperature for about 10h. Then, the mixture was extracted with ethyl acetate, repeat three times. The combined organic layer was evaporated under reduced pressure, and the product was purified by flash chromatography using petroleum ether and ethyl acetate as eluent.

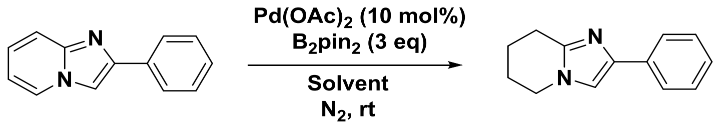
Reaction optimization

Entry	Metal	Base (x eq)	Solvent	T (℃)	Yield (%) [b]
1[c]	CuBr	Cs_2CO_3 (2)	CH_3CN	60	18
2[c]	$Pd(OAc)_2$	Cs_2CO_3 (2)	CH_3CN	60	42
3	$Pd(OAc)_2$	Cs_2CO_3 (2)	CH_3CN	60	62
4[d]	$Pd(OAc)_2$	Cs_2CO_3 (2)	CH_3CN	60	< 10
5	$Pd(OAc)_2$	Cs_2CO_3 (2)	CH_3CN/H_2O (1:1)	60	95
6	$Pd(OAc)_2$	Cs_2CO_3 (0.5)	CH_3CN/H_2O (1:1)	60	93
7	$Pd(OAc)_2$	Cs_2CO_3 (0.5)	H_2O	60	94
8	$Pd(OAc)_2$	Cs_2CO_3 (0.5)	H_2O	rt	94
9	**$Pd(OAc)_2$**	**-**	**H_2O**	**rt**	**95**
10	-	Cs_2CO_3 (0.5)	H_2O	rt	42
11[e]	$Pd(OAc)_2$	-	H_2O	rt	trace
12	$Pd_2(dba)_3$	-	H_2O	rt	65
13	$Pd(PPh_3)_4$	-	H_2O	rt	20
14	CuBr	-	H_2O	rt	trace
15	$Cu(OTf)_2$	-	H_2O	rt	trace
16[f]	$Pd(OAc)_2$	-	H_2O	rt	89
17[f]	$Pd(OAc)_2$	-	CH_3CN	rt	93
18	$Pd(OAc)_2$	-	H_2O	rt	92

[a] General procedure: **1a** (0.2 mmol), B_2pin_2 (0.6 mmol), solvent (2 ml), under N_2. [b] isolated yield. [c] B_2pin_2 (0.4 mmol).[d] PPh_3 (0.04 mmol) was used [e] under air. [f] B_2pin_2

was replaced with HBpin (0.6 mmol)

ii. Solvent effects on the hydrogenation of 1p [a]



Entry	Solvent	Yield (%) [b]
1	H_2O	95%
2	H_2O/CH_3CN (1:1)	45%
3	H_2O/CH_3CN (1:2)	38%
4	CH_3CN	trace

[a] All reactions were carried out with **1p** (0.2 mmol) under Cond. A: $Pd(OAc)_2$ (10 mol%), B_2pin_2 (3 eq), H_2O (2 ml), N_2, rt; [b] isolated yields;

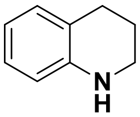
IV. The procedure for the synthesis of 4

2-methyl-1,2,3,4-tetrahydroquinoline **2b** (0.25 g, 1.7 mmol) was synthesized according Cond. A. Then, To a Schenk tube equipped with a stir bar, 4-methylbenzenesulfonyl chloride (0.38 g, 2 mmol) was added. The Schenk tube was capped with a septum, degassed and backfilled with N_2 for at least three times. Then, pyridine (1 mL) and **2b** (0.25 g, 1.7 mmol) were added via syringe. The reaction mixture was stirred at 60 ^{o}C for 3 h. Then, after the reaction mixture was cooled down, filtered off the solid. Ethyl acetate was added to the filtrate. Then, washed the organic layer exhaustively with HCl (0.01 M) and water. The combined organic layer was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure, and the product was purified by flash chromatography using petroleum ether and ethyl acetate as eluent.

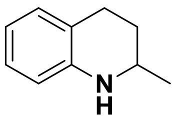
V. References

1. S. Santra, S. Mitra, A. K. Bagdi, A. Majee, A. Hajra, Tetrahedron Lett. **2014**, *55*, 5151.
2. X. Jiang, C. Wang, Y. Wei, D. Xue, Z. Liu, J. Xiao, *Chem. Eur. J.* **2014**, *20*, 58.
3. Y. Zhu, C. Cai, *RSC Adv.* **2014**, *4*, 52911.

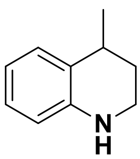
VI. Analytic data of products



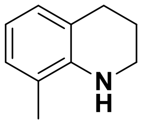
1,2,3,4-tetrahydroquinoline (**2a**): shallow yellow oil (**cond. A**: 94%, 25.0 mg; **cond. B**: 95%, 25.3 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 – 6.94 (m, 2H), 6.64 (td, *J* = 7.4, 1.1 Hz, 1H), 6.51 (dd, *J* = 7.9, 0.7 Hz, 1H), 3.35 – 3.31 (m, 2H), 2.80 (t, *J* = 6.4 Hz, 2H), 2.01 – 1.95 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.78 (s), 129.53 (s), 126.73 (s), 121.47 (s), 116.97 (s), 114.21 (s), 42.01 (s), 26.99 (s), 22.20 (s).



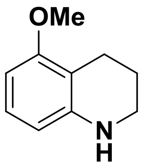
2-methyl-1,2,3,4-tetrahydroquinoline (**2b**): shallow yellow oil (**cond. A**: 87%, 25.6 mg; **cond. B**: 85%, 25.0 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 – 6.94 (m, 2H), 6.63 (td, *J* = 7.4, 1.1 Hz, 1H), 6.50 (dd, *J* = 8.3, 1.0 Hz, 1H), 3.72 (s, 1H), 3.43 (dqd, *J* = 12.6, 6.3, 2.8 Hz, 1H), 2.87 (ddd, *J* = 17.1, 11.6, 5.7 Hz, 1H), 2.76 (ddd, *J* = 16.3, 5.1, 3.6 Hz, 1H), 2.00 – 1.92 (m, 1H), 1.66 – 1.59 (m, 1H), 1.24 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.78 (s), 129.28 (s), 126.70 (s), 121.13 (s), 116.99 (s), 114.01 (s), 47.18 (s), 30.14 (s), 26.61 (s), 22.63 (s).



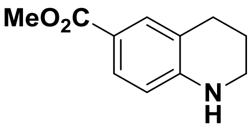
4-methyl-1,2,3,4-tetrahydroquinoline (**2c**): shallow yellow oil (**cond. A**: 82%, 24.1 mg; **cond. B**: 80%, 23.5 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (d, *J* = 7.6 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.69 (t, *J* = 7.4 Hz, 1H), 6.52 (d, *J* = 8.0 Hz, 1H), 3.38 (ddd, *J* = 11.8, 8.6, 3.5 Hz, 1H), 3.34 – 3.28 (m, 1H), 3.01 – 2.91 (m, 1H), 2.03 (ddd, *J* = 12.9, 8.8, 4.6 Hz, 1H), 1.73 (dtd, *J* = 9.9, 6.4, 3.6 Hz, 1H), 1.34 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.27 (s), 128.47 (s), 126.69 (d, *J* = 14.4 Hz), 116.97 (s), 114.19 (s), 39.03 (s), 30.25 (s), 29.90 (s), 22.69 (s).



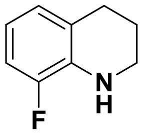
8-methyl-1,2,3,4-tetrahydroquinoline (**2d**): shallow yellow oil (**cond. A**: 94%, 27.6 mg; **cond. B**: 92%, 27.0 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.97 – 6.86 (m, 2H), 6.59 (t, *J* = 7.4 Hz, 1H), 3.46 – 3.38 (m, 2H), 2.82 (t, *J* = 6.4 Hz, 2H), 2.11 (s, 3H), 2.01 – 1.94 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.70 (s), 127.84 (s), 127.38 (s), 121.20 (s), 120.88 (s), 116.40 (s), 42.35 (s), 27.30 (s), 22.17 (s), 17.17 (s).



5-methoxy-1,2,3,4-tetrahydroquinoline (**2e**): shallow yellow oil (**cond. A**: 94%, 30.6 mg; **cond. B**: 94%, 30.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.96 (t, *J* = 8.1 Hz, 1H), 6.25 (d, *J* = 8.1 Hz, 1H), 6.19 (d, *J* = 8.0 Hz, 1H), 3.82 (s, 3H), 3.31 – 3.23 (m, 2H), 2.69 (t, *J* = 6.6 Hz, 2H), 2.01 – 1.91 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.95 (s), 145.87 (s), 126.65 (s), 109.85 (s), 107.69 (s), 99.16 (s), 55.27 (s), 41.56 (s), 21.96 (s), 20.59 (s).

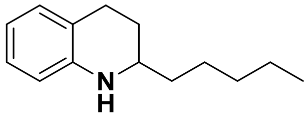


methyl 1,2,3,4-tetrahydroquinoline-6-carboxylate (**2f**): shallow yellow solid (**cond. A**: trace; **cond. B**: 90%, 34.4 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 4.3, 2.3 Hz, 2H), 6.40 (d, *J* = 8.9 Hz, 1H), 4.40 (s, 1H), 3.85 (s, 3H), 3.39 – 3.31 (m, 2H), 2.78 (t, *J* = 6.3 Hz, 2H), 1.97 – 1.90 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.57 (s), 148.84 (s), 131.30 (s), 129.12 (s), 119.88 (s), 117.34 (s), 112.63 (s), 51.45 (s), 41.71 (s), 26.92 (s), 21.41 (s).

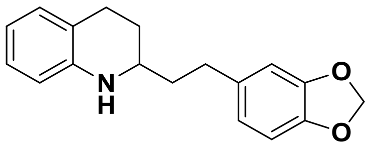


8-fluoro-1,2,3,4-tetrahydroquinoline (**2g**): shallow yellow oil (**cond. A**: 82%, 24.7 mg; **cond. B**: 92%, 30.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$) 6.85 – 6.79 (m, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 6.53 (td, *J* = 7.8, 5.4 Hz, 1H), 4.03 (s, 1H), 3.40 – 3.34 (m, 2H), 2.81 (t, *J* = 6.4 Hz, 2H), 2.02 – 1.95 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.85 (s), 149.96 (s), 133.18 (d, *J* = 12.2 Hz), 124.48

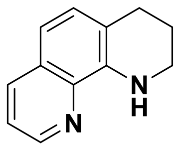
(d, *J* = 2.9 Hz), 123.60 (d, *J* = 3.7 Hz), 115.51 (d, *J* = 7.5 Hz), 112.14 (d, *J* = 18.2 Hz), 41.28 (s), 26.56 (d, *J* = 3.0 Hz), 21.80 (s).



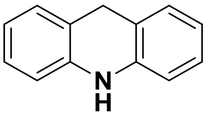
2-pentyl-1,2,3,4-tetrahydroquinoline (**2h**): shallow yellow oil (**cond. A**: 83%, 33.7g; **cond. B**: 92%, 32.5 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.99 (t, *J* = 7.5 Hz, 2H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 1H), 3.30 – 3.22 (m, 1H), 2.85 (ddd, *J* = 16.5, 11.1, 5.6 Hz, 1H), 2.76 (dt, *J* = 16.3, 4.7 Hz, 1H), 2.03 – 1.96 (m, 1H), 1.67 – 1.59 (m, 1H), 1.52 (dd, *J* = 14.0, 7.0 Hz, 2H), 1.46 – 1.34 (m, 6H), 0.95 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.75 (s), 129.26 (s), 126.70 (s), 121.42 (s), 116.89 (s), 114.05 (s), 51.62 (s), 36.71 (s), 31.99 (s), 28.15 (s), 26.47 (s), 25.43 (s), 22.68 (s), 14.09 (s).



2-(2-(benzo[d][1,3]dioxol-5-yl)ethyl)-1,2,3,4-tetrahydroquinoline (**2i**): white solid (**cond. A**: 75%, 42.1g; **cond. B**: 79%, 44.4 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00 (t, *J* = 7.7 Hz, 2H), 6.78 (d, *J* = 7.9 Hz, 1H), 6.75 (d, *J* = 1.5 Hz, 1H), 6.70 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.65 (td, *J* = 7.4, 1.0 Hz, 1H), 6.50 (d, *J* = 7.8 Hz, 1H), 5.96 (s, 2H), 3.79 (s, 1H), 3.36 – 3.28 (m, 1H), 2.90 – 2.74 (m, 2H), 2.73 – 2.66 (m, 2H), 2.02 (dddd, *J* = 12.8, 5.5, 4.4, 3.2 Hz, 1H), 1.86 – 1.78 (m, 2H), 1.75 – 1.66 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.69 (s), 145.73 (s), 144.52 (s), 135.67 (s), 129.28 (s), 126.76 (s), 121.32 (s), 121.05 (s), 117.08 (s), 114.17 (s), 108.81 (s), 108.25 (s), 100.84 (s), 51.00 (s), 38.51 (s), 31.90 (s), 27.99 (s), 26.24 (s).

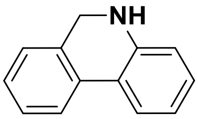


1,2,3,4-tetrahydro-1,10-phenanthroline (**2j**): yellow oil (**cond. A**: trace; **cond. B**: 90%, 33.1 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.03 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.31 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.18 (d, *J* = 8.2 Hz, 1H), 7.00 (d, *J* = 8.2 Hz, 1H), 5.96 (s, 1H), 3.58 – 3.51 (m, 2H), 2.95 (t, *J* = 6.4 Hz, 2H), 2.13 – 2.06 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.94 (s), 140.69 (s), 137.50 (s), 135.87 (s), 129.06 (s), 127.37 (s), 120.54 (s), 116.58 (s), 113.10 (s), 41.29 (s), 27.05 (s), 21.84 (s).

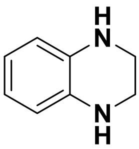


9,10-dihydroacridine

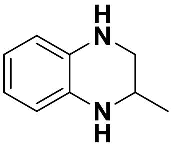
9,10-dihydroacridine (**2k**): white solid (**cond. A**: trace; **cond. B**: 73%, 26.4 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (dd, *J* = 14.4, 7.5 Hz, 4H), 6.91 (td, *J* = 7.4, 0.8 Hz, 2H), 6.71 (d, *J* = 7.8 Hz, 2H), 5.98 (s, 1H), 4.11 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.15 (s), 128.65 (s), 127.03 (s), 120.67 (s), 120.07 (s), 113.49 (s), 31.42 (s).



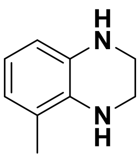
5,6-dihydrophenanthridine (**2l**):white solid (**cond. A**: 75%, 27.2 mg; Cond. B: 69%, 24.9 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 9.7, 3.5 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 7.4 Hz, 1H), 7.14 (dd, *J* = 10.8, 4.3 Hz, 2H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.70 (dd, *J* = 7.9, 0.7 Hz, 1H), 4.42 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.72 (s), 132.76 (s), 132.08 (s), 128.82 (s), 127.68 (s), 127.14 (s), 126.03 (s), 123.61 (s), 122.43 (s), 122.08 (s), 119.30 (s), 115.15 (s), 46.40 (s).



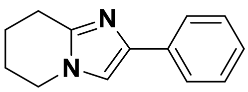
1,2,3,4-tetrahydroquinoxaline (2**m**):brown oil (**cond. A**: 79%, 21.2 mg; **cond. B**: 83%, 22.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.62 (dd, *J* = 5.8, 3.4 Hz, 2H), 6.53 (dd, *J* = 5.7, 3.4 Hz, 2H), 3.48 (s, 2H), 3.44 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.69 (s), 118.77 (s), 114.73 (s), 41.40 (s).



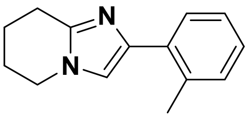
2-methyl-1,2,3,4-tetrahydroquinoxaline (**2n**):brown oil (**cond. A**: 85%, 25.2 mg; **cond. B**: 92%, 27.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.62 (dd, *J* = 5.7, 3.4 Hz, 2H), 6.56 – 6.51 (m, 2H), 3.58 – 3.51 (m, 1H), 3.34 (dd, *J* = 10.7, 2.8 Hz, 3H), 3.07 (dd, *J* = 10.6, 8.3 Hz, 1H), 1.22 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.55 (s), 133.17 (s), 118.74 (s), 114.51 (d, *J* = 5.9 Hz), 48.25 (s), 45.73 (s), 19.91 (s).



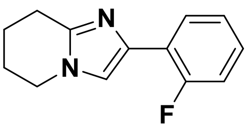
5-methyl-1,2,3,4-tetrahydroquinoxaline (**2o**): red-orange oil (**cond. A**: 75%, 22.2 mg; **cond. B**: 92%, 27.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.58 – 6.50 (m, 2H), 6.43 (dd, *J* = 6.8, 2.2 Hz, 1H), 3.55 – 3.49 (m, 2H), 3.46 – 3.41 (m, 2H), 2.11 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.16 (s), 131.65 (s), 122.20 (s), 120.47 (s), 118.03 (s), 112.93 (s), 41.76 (s), 41.22 (s), 16.95 (s).



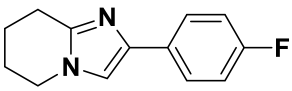
2-phenyl-5,6,7,8-tetrahydroimidazo[1,2-a]pyridine (**2p**): white solid (**cond. A**: 95%, 36.8 mg; **cond. B**: 93%, 36.9mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.24 – 7.19 (m, 1H), 7.05 (s, 1H), 3.95 (t, *J* = 5.8 Hz, 2H), 2.93 (t, *J* = 6.3 Hz, 2H), 2.01 – 1.91 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.24 (s), 140.47 (s), 134.46 (s), 128.47 (s), 126.42 (s), 124.67 (s), 113.88 (s), 44.84 (s), 24.62 (s), 23.04 (s), 21.15 (s).



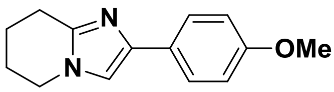
2-(o-tolyl)-5,6,7,8-tetrahydroimidazo[1,2-a]pyridine (**2q**): yellow solid (**cond. A**: 90%, 38.1 mg; **cond. B**: 92%, 39.4 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.27 – 7.21 (m, 2H), 7.20 – 7.15 (m, 1H), 6.93 (s, 1H), 4.03 (t, *J* = 5.9 Hz, 2H), 2.96 (t, *J* = 6.3 Hz, 2H), 2.49 (s, 3H), 2.06 – 1.97 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.29 (s), 139.52 (s), 134.56 (s), 133.70 (s), 130.60 (s), 128.34 (s), 126.44 (s), 125.87 (s), 116.58 (s), 44.84 (s), 24.52 (s), 23.11 (s), 21.88 (s), 21.22 (s).



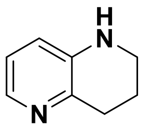
2-(2-fluorophenyl)-5,6,7,8-tetrahydroimidazo[1,2-a]pyridine (**2r**): yellow solid (**cond. A**: 94%, 40.6 mg; **cond. B**: 93%, 40.1 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 – 8.08 (m, 1H), 7.26 (d, *J* = 4.1 Hz, 1H), 7.21 – 7.13 (m, 2H), 7.10 – 7.03 (m, 1H), 3.98 (t, *J* = 5.8 Hz, 2H), 2.94 (t, *J* = 6.3 Hz, 2H), 2.03 – 1.92 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.54 (d, *J* = 247.4 Hz), 144.75 (s), 133.77 (s), 127.34 (d, *J* = 4.3 Hz), 127.14 (d, *J* = 8.4 Hz), 124.21 (d, *J* = 3.2 Hz), 122.15 (d, *J* = 12.7 Hz), 118.20 (d, *J* = 14.4 Hz), 115.34 (d, *J* = 22.1 Hz), 44.87 (s), 24.53 (s), 23.02 (s), 21.16 (s).



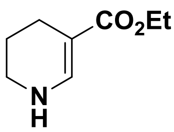
2-(4-fluorophenyl)-5,6,7,8-tetrahydroimidazo[1,2-a]pyridine (**2s**): yellow solid (**cond. A**: 93%, 40.1 mg; **cond. B**: 94%, 40.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 8.8, 5.5 Hz, 2H), 7.04 (t, *J* = 8.8 Hz, 2H), 7.00 (s, 1H), 3.96 (t, *J* = 5.9 Hz, 2H), 2.92 (t, *J* = 6.3 Hz, 2H), 2.03 – 1.91 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.74 (d, *J* = 244.6 Hz), 145.31 (s), 139.66 (s), 130.68 (d, *J* = 3.1 Hz), 126.19 (d, *J* = 7.8 Hz), 115.30 (d, *J* = 21.5 Hz), 113.51 (s), 44.85 (s), 24.56 (s), 23.02 (s), 21.11 (s).



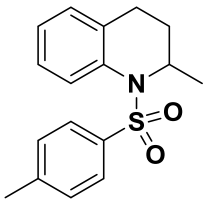
2-(4-methoxyphenyl)-5,6,7,8-tetrahydroimidazo[1,2-a]pyridine (**2t**): yellow solid (**cond. A**: 94%, 42.8 mg; **cond. B**: 95%, 43.3 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.7 Hz, 2H), 6.95 (s, 1H), 6.90 (d, *J* = 8.7 Hz, 2H), 3.94 (t, *J* = 5.8 Hz, 2H), 3.81 (s, 3H), 2.91 (t, *J* = 6.2 Hz, 2H), 2.00 – 1.90 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.41 (s), 145.00 (s), 140.31 (s), 127.34 (s), 125.88 (s), 113.90 (s), 112.81 (s), 55.25 (s), 44.77 (s), 24.58 (s), 23.05 (s), 21.15 (s).



1,2,3,4-tetrahydro-1,5-naphthyridine (**2u**): shallow yellow oil (**cond. A**: 75%, 20.1 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 4.7, 1.2 Hz, 1H), 6.90 (dd, *J* = 8.0, 4.7 Hz, 1H), 6.74 (dd, *J* = 8.0, 1.3 Hz, 1H), 3.34 – 3.27 (m, 2H), 2.95 (t, *J* = 6.5 Hz, 2H), 2.04 (ddd, *J* = 11.2, 8.8, 6.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.68 (s), 140.94 (s), 137.82 (s), 121.91 (s), 120.26 (s), 41.51 (s), 30.22 (s), 21.74 (s).



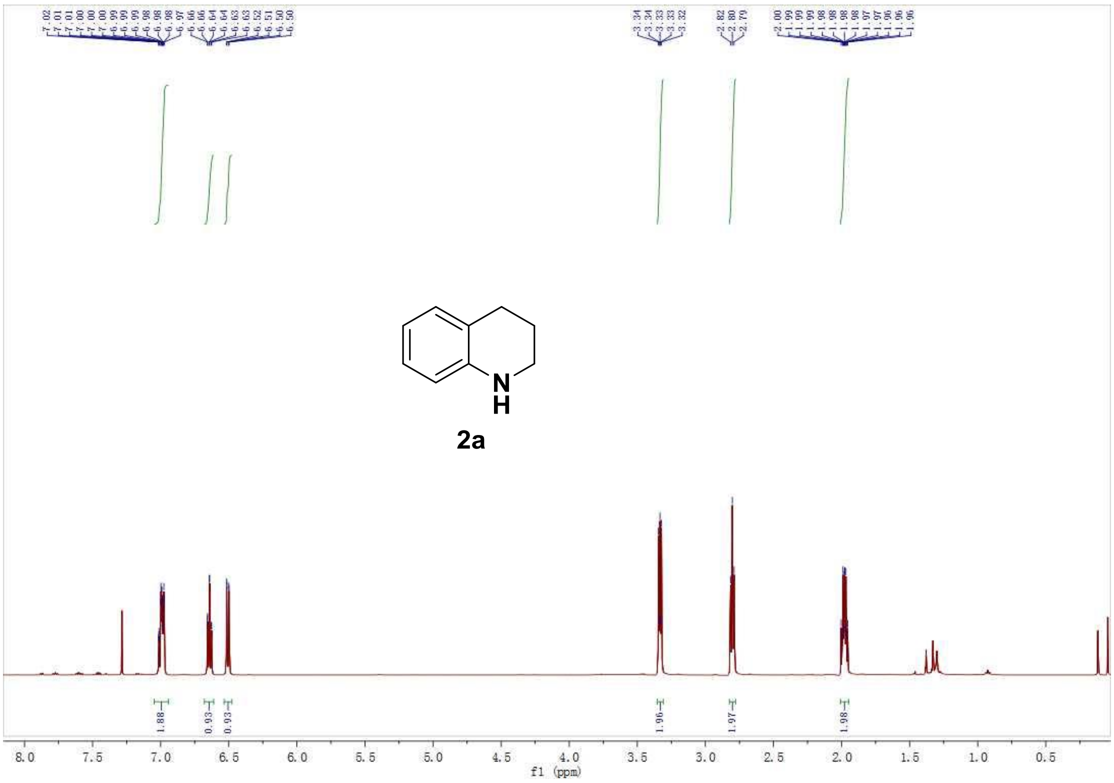
ethyl 1,4,5,6-tetrahydropyridine-3-carboxylate (**2v**): colorless oil (**cond. A** 75%, 23.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 6.2 Hz, 1H), 4.45 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.24 – 3.18 (m, 2H), 2.36 – 2.31 (m, 2H), 1.84 – 1.79 (m, 2H), 1.26 (t, *J* = 6.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.84 (s), 142.72 (s), 95.64 (s), 58.92 (s), 40.74 (s), 20.99 (s), 20.62 (s), 14.65 (s).

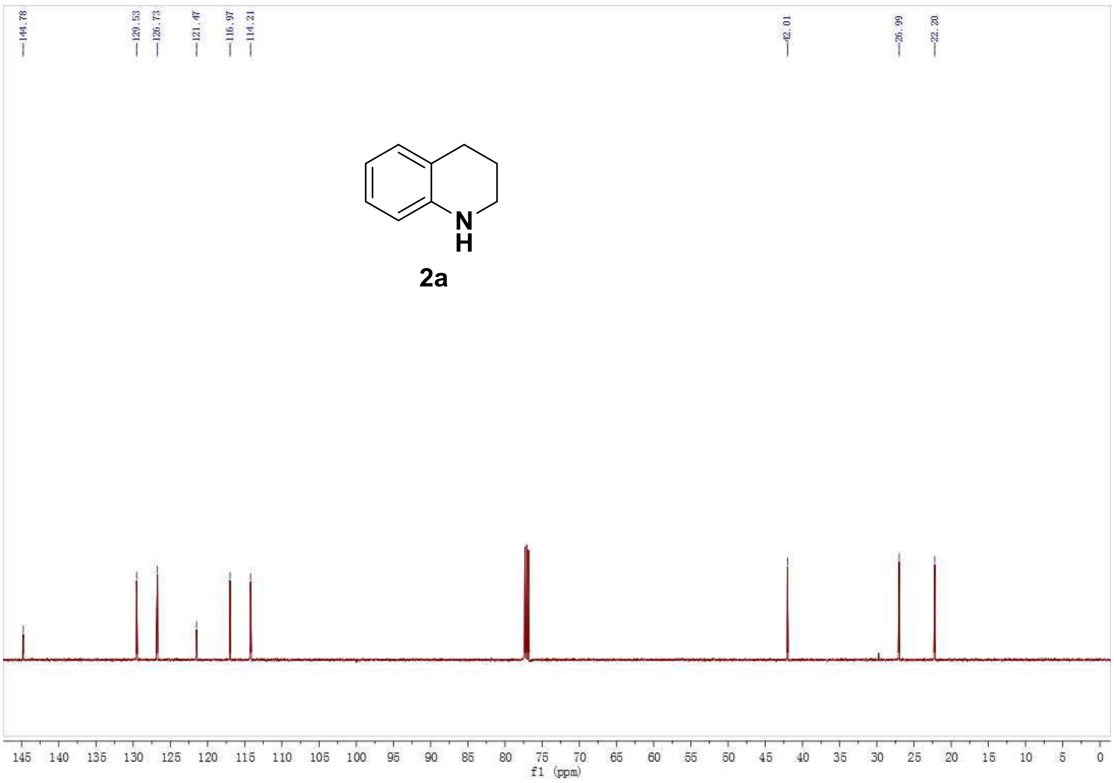


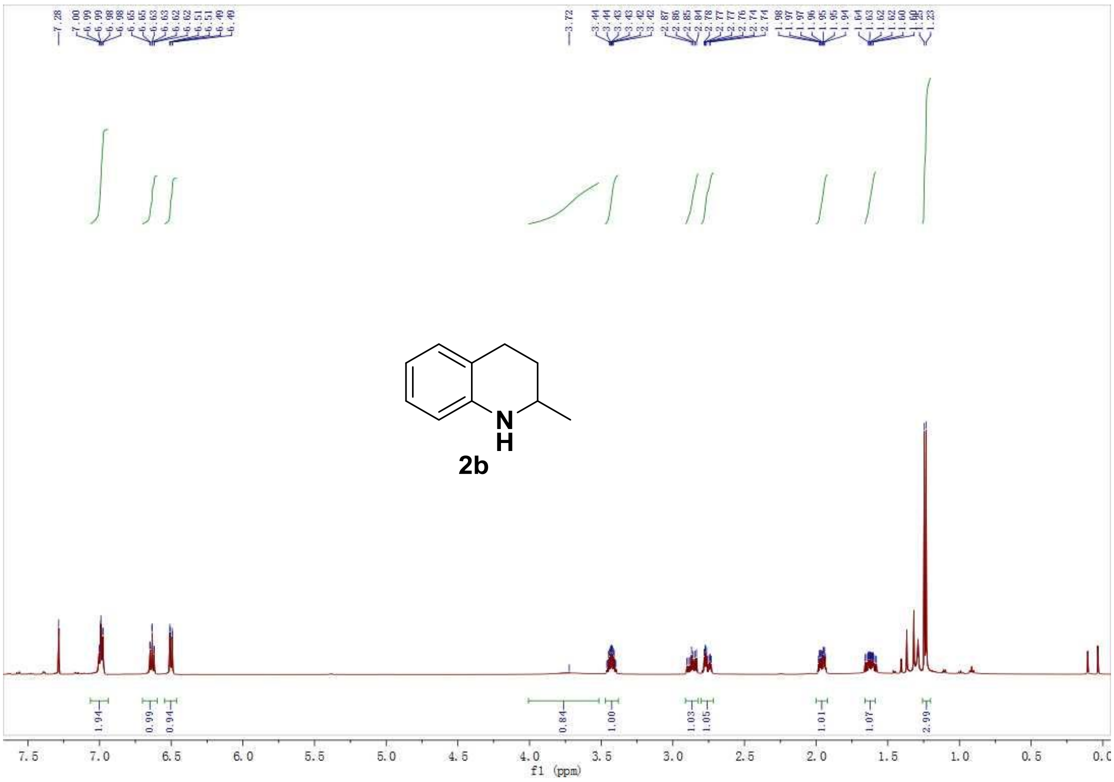
2-methyl-1-tosyl-1,2,3,4-tetrahydroquinoline (**4**): colorless oil (80%, 204.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 7.4 Hz, 1H), 4.42 – 4.34 (m, 1H), 2.39 (s, 3H), 1.87 – 1.76 (m, 2H), 1.39 – 1.27 (m, 5H).^{13}C NMR (126 MHz, $CDCl_3$) δ

143.27 (s), 136.38 (s), 135.17 (s), 133.39 (s), 129.40 (s), 127.95 (s), 127.51 (s), 127.02 (s), 126.67 (s), 125.51 (s), 52.28 (s), 30.03 (s), 24.63 (s), 21.59 (d, J = 14.0 Hz).

VII. ^{1}H and ^{13}C NMR spectra of products



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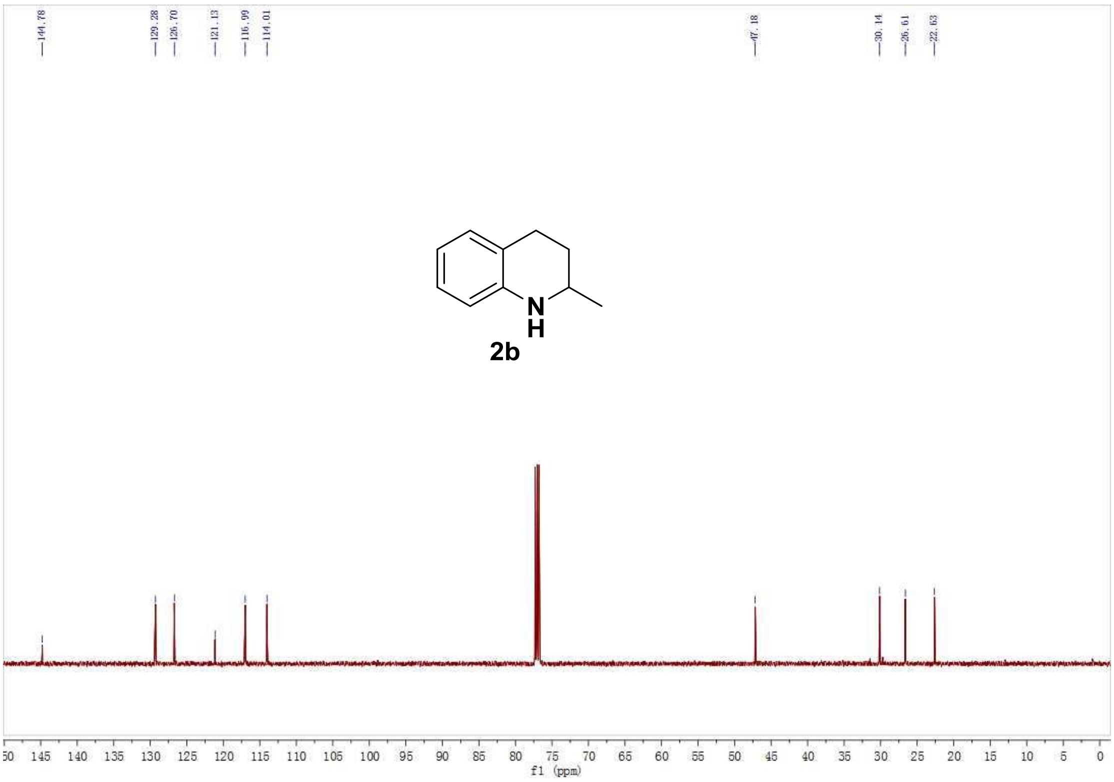
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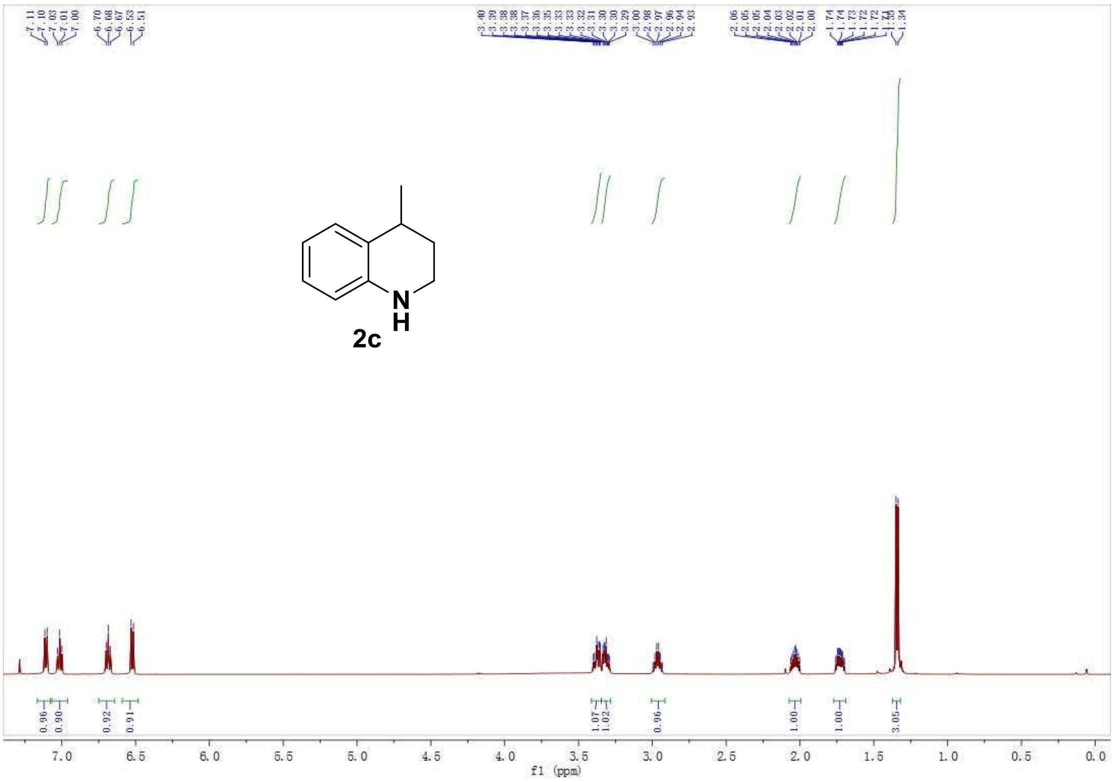
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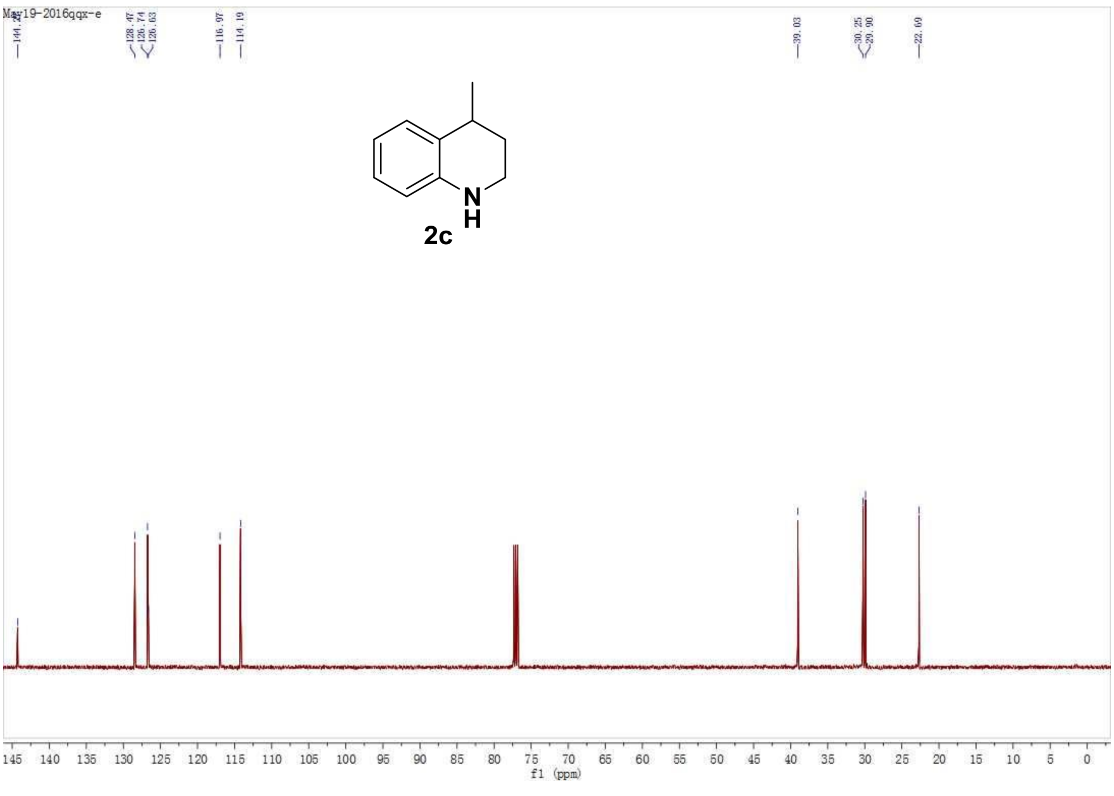
f1 (ppm)


May19-2016qqx-e
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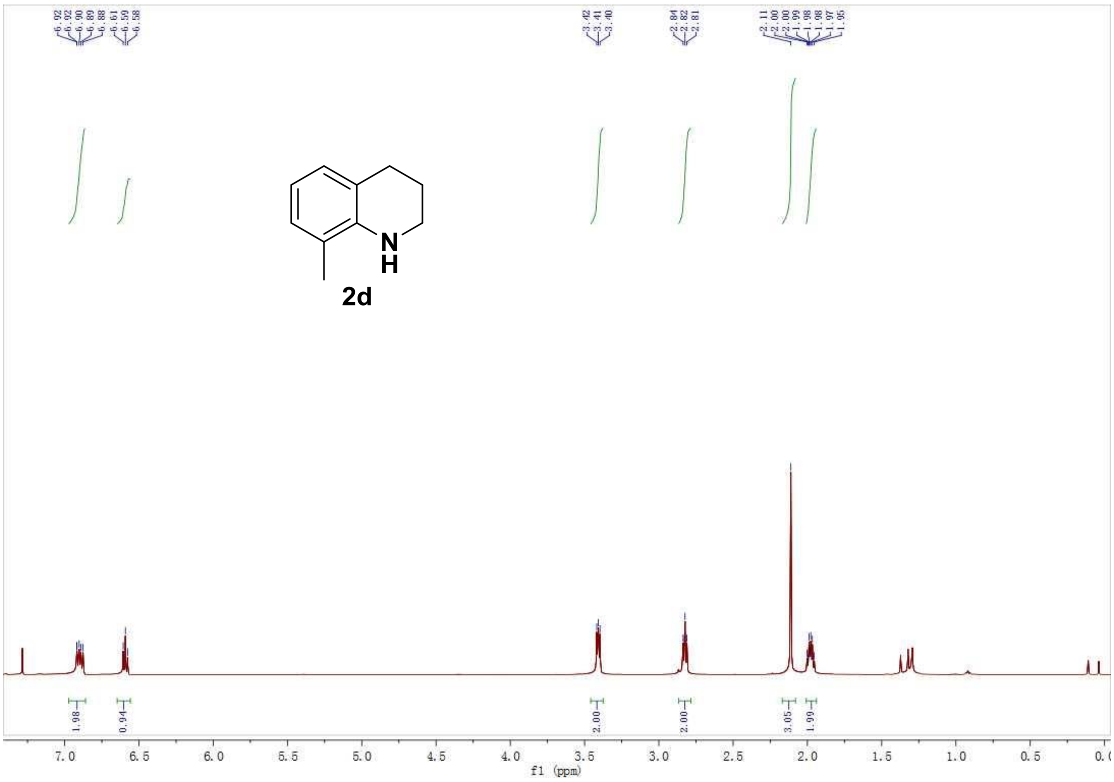
H
f1 (ppm)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2.84 2.82 2.81
2.11 2.00 2.00 1.99 1.98 1.98 1.97 1.95
N
H
2d
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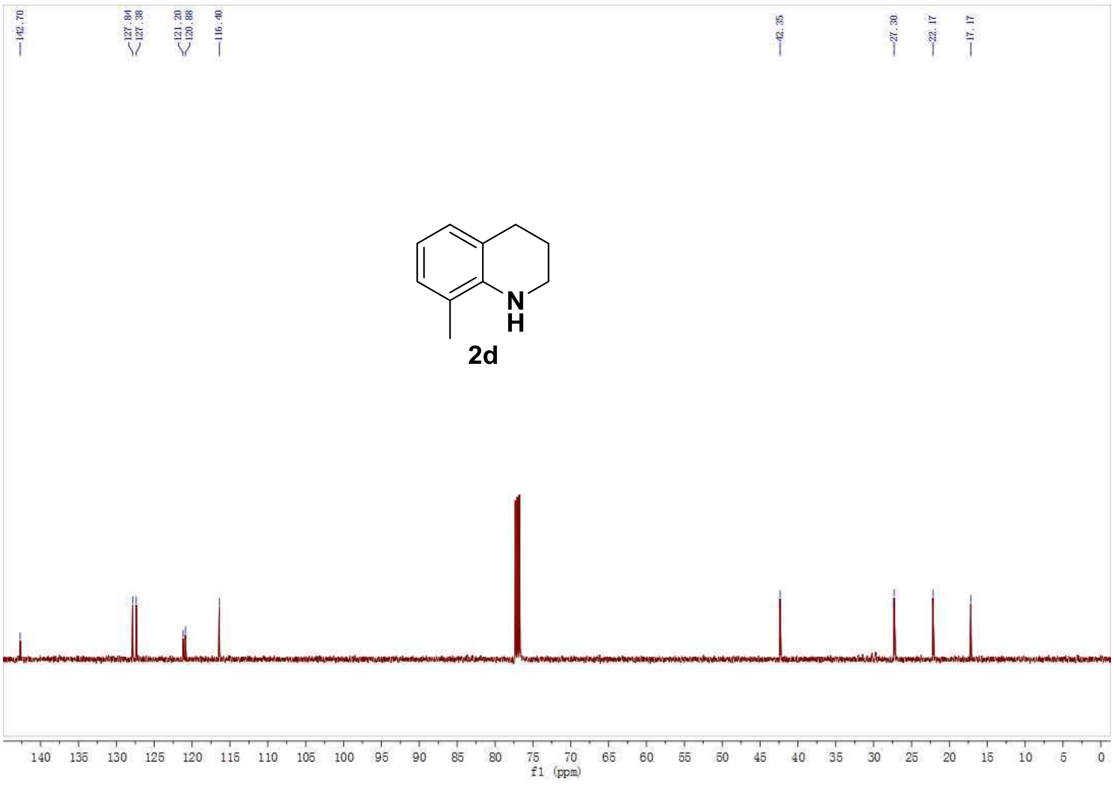
0.94
2.00
2.00
3.05
1.99
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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N
H
2d
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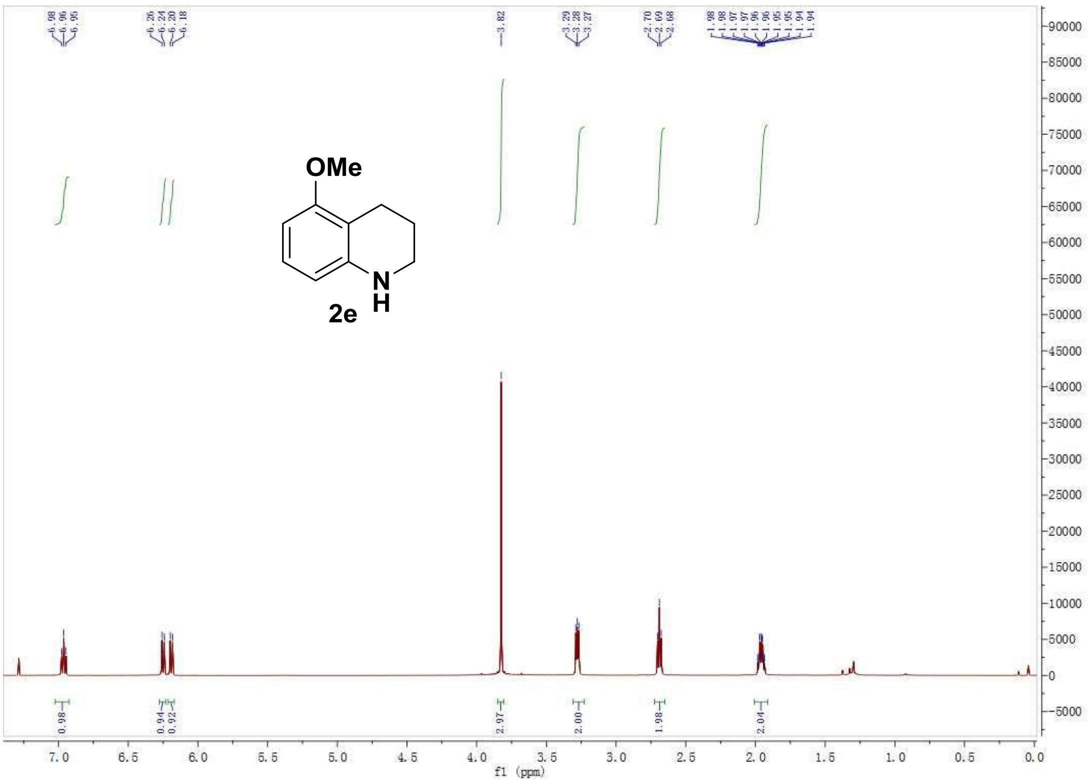
f1 (ppm)



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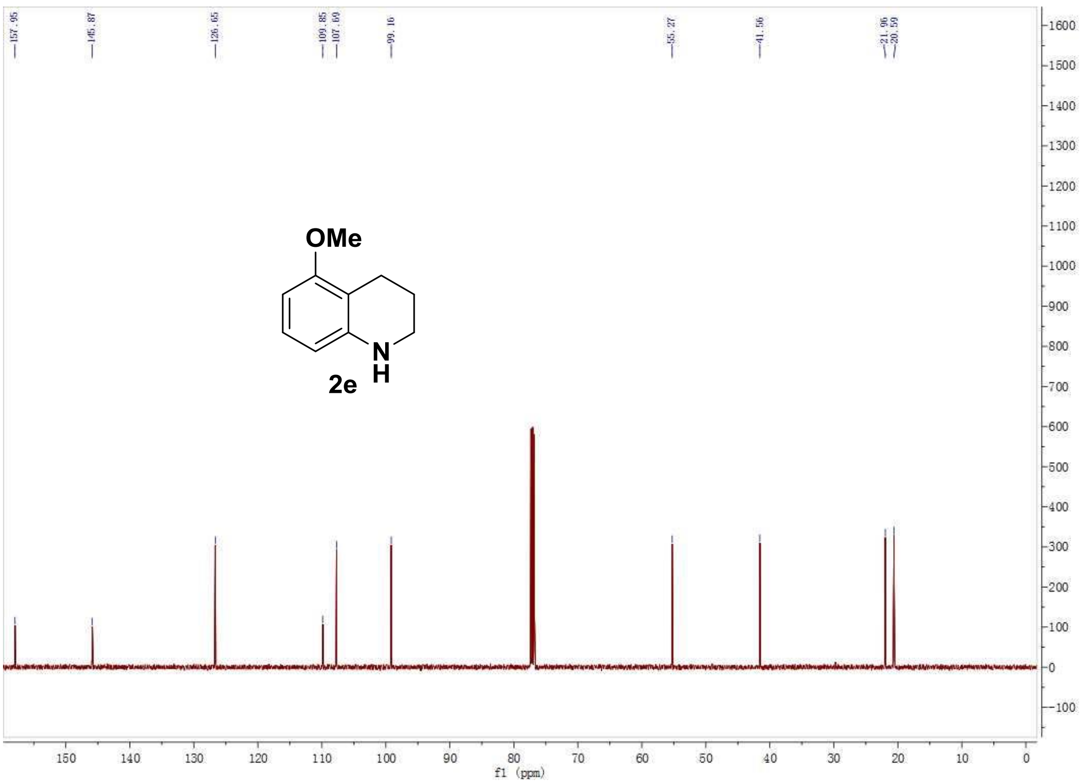
H
2e
f1 (ppm)



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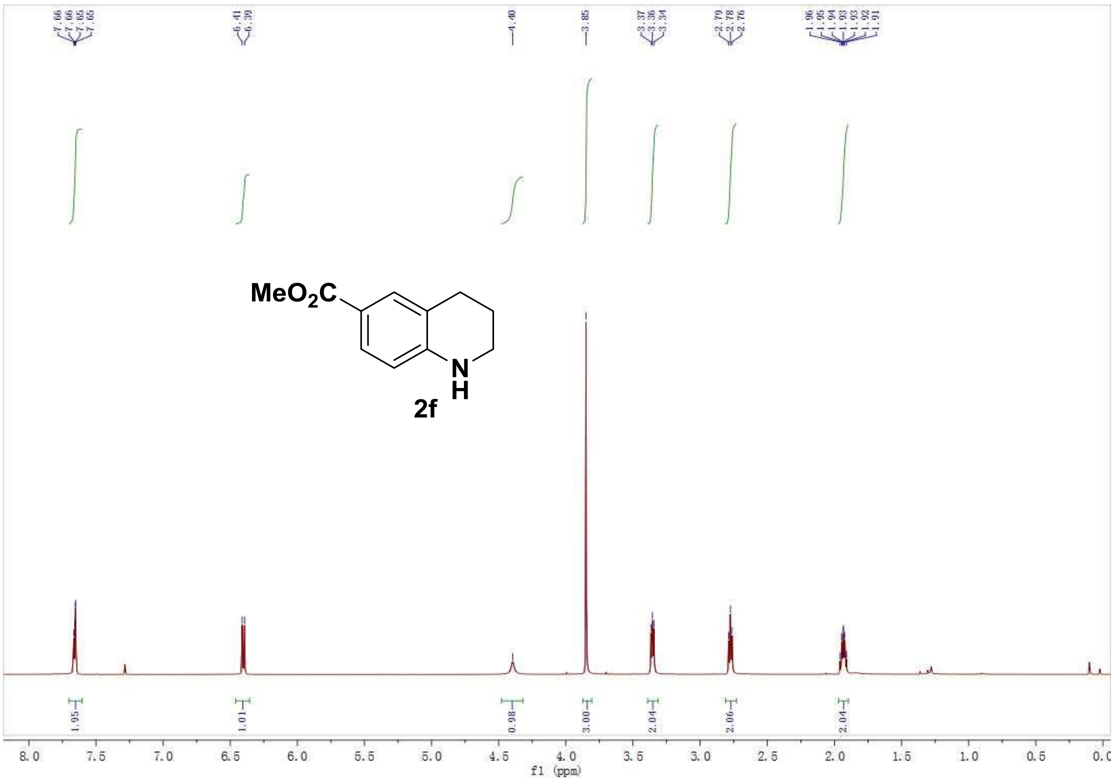
2e
f1 (ppm)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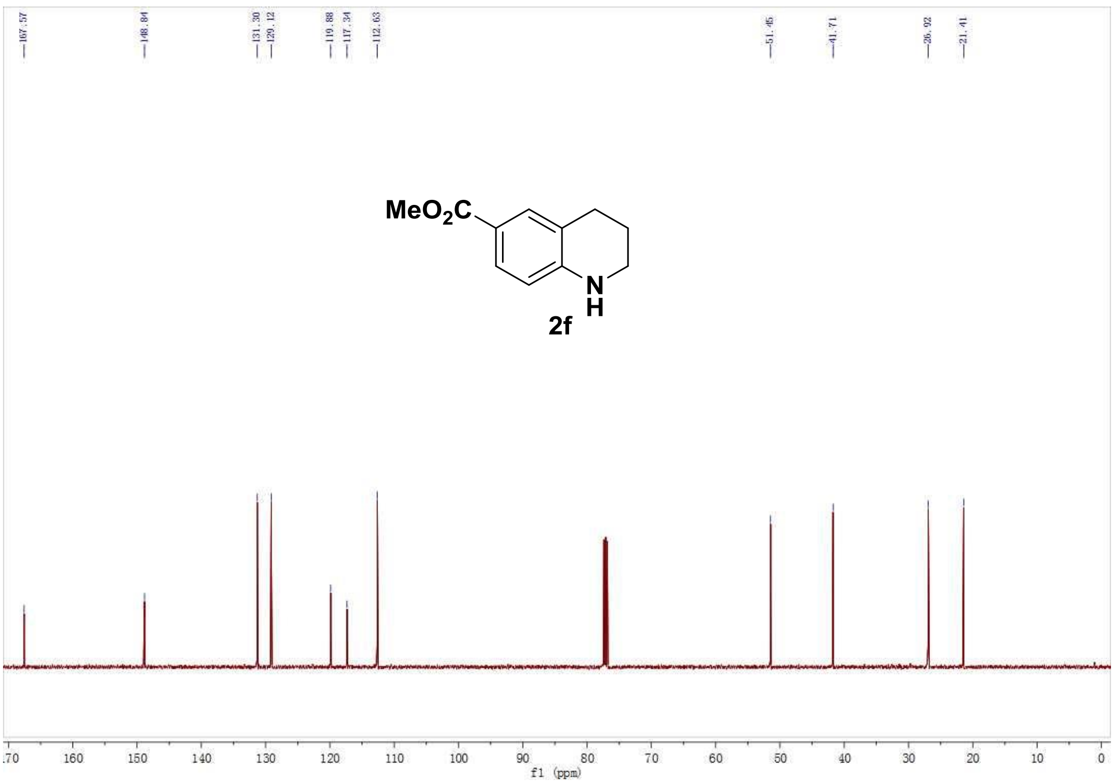
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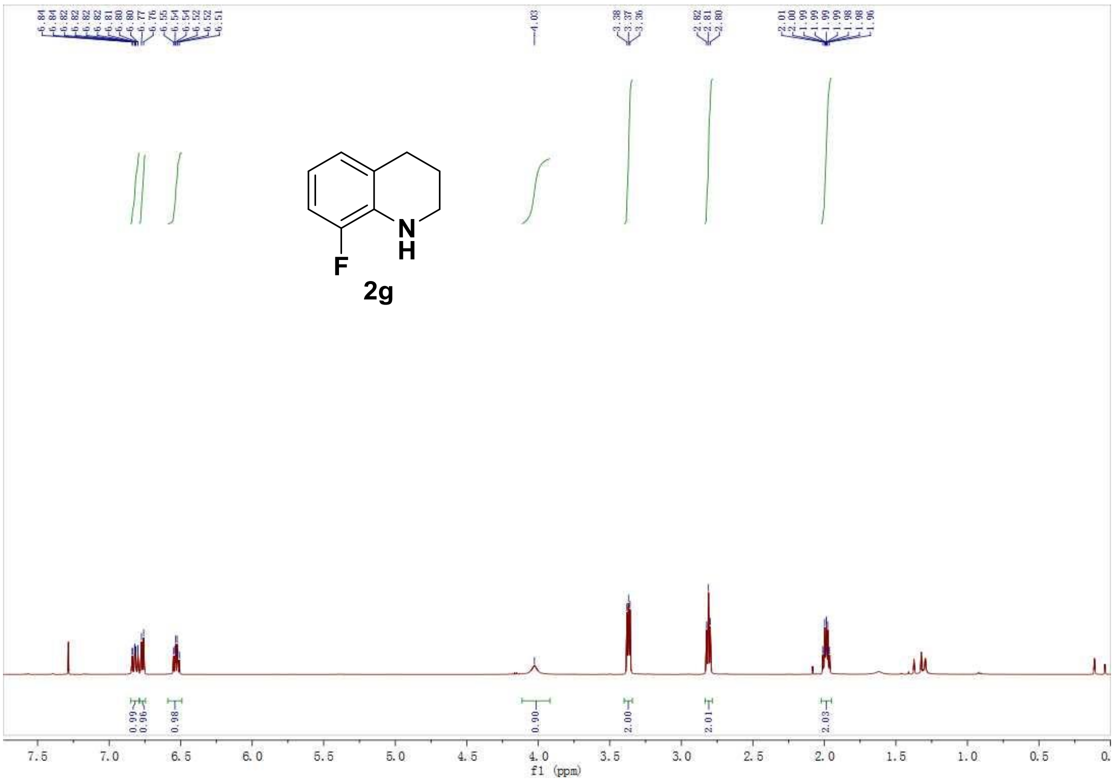

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3.37
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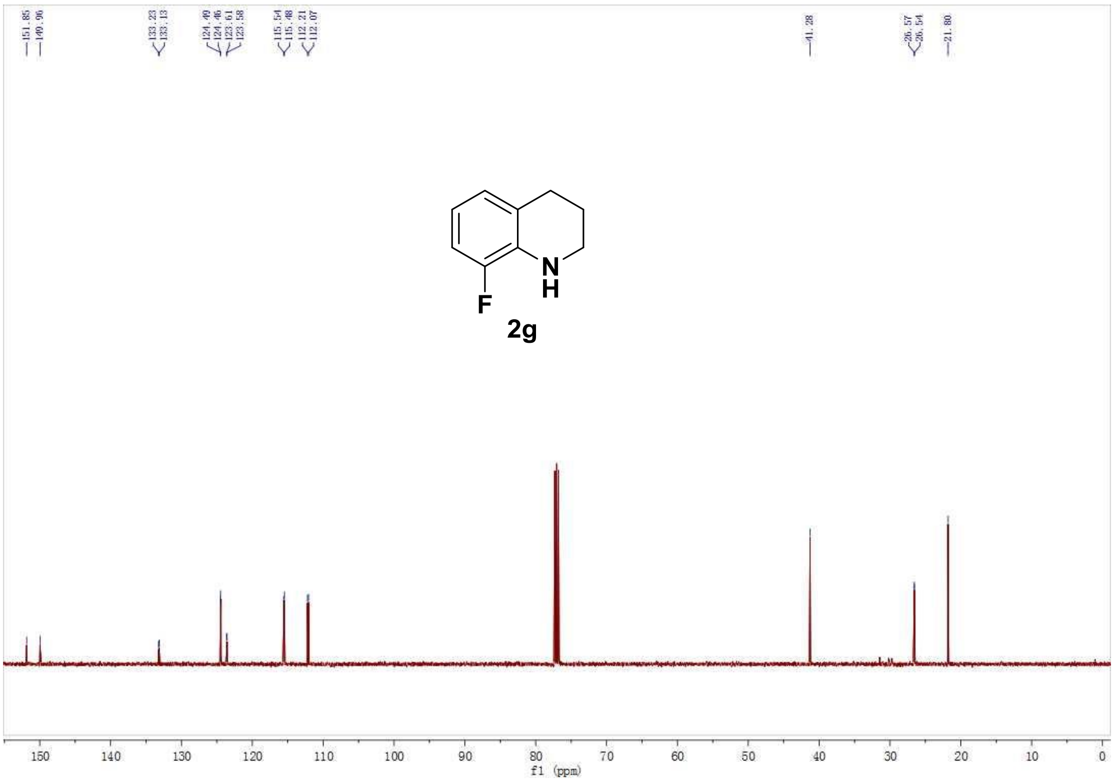

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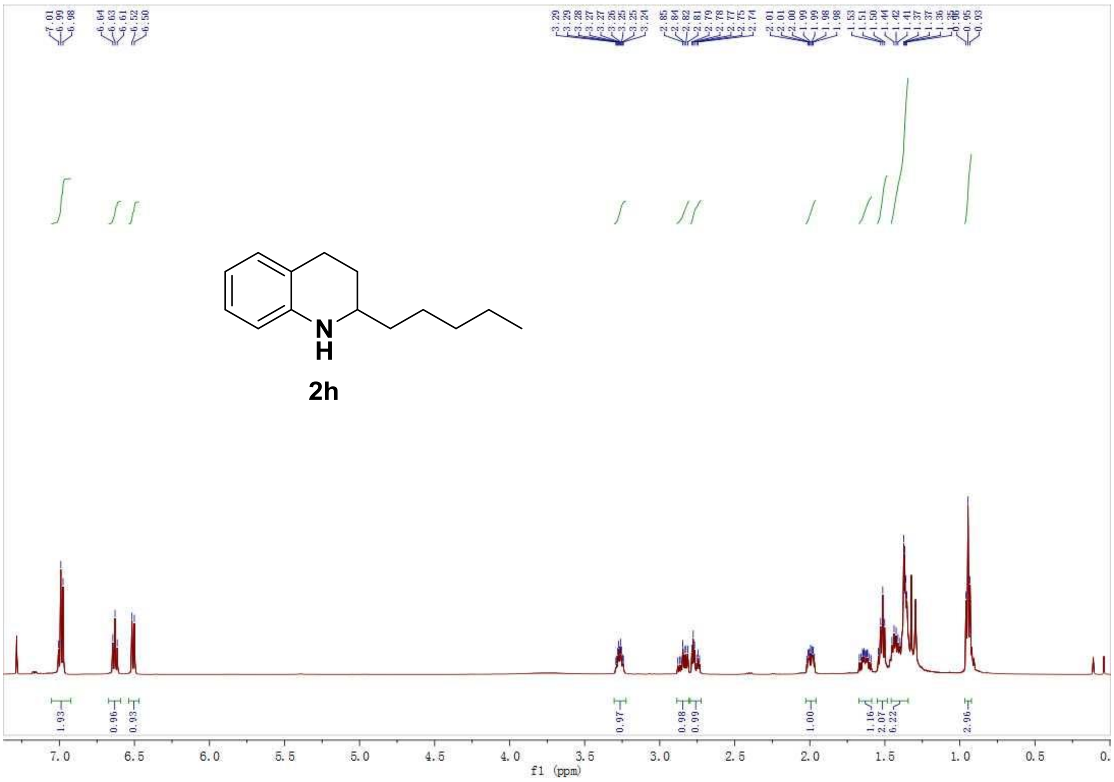
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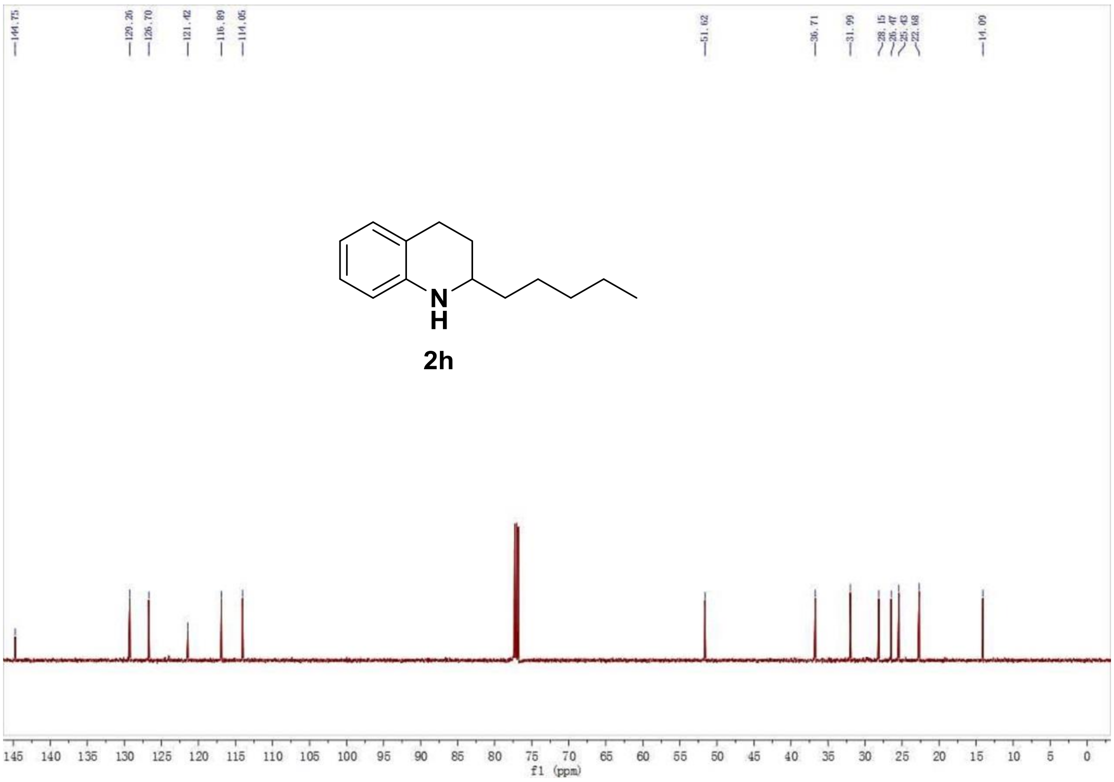
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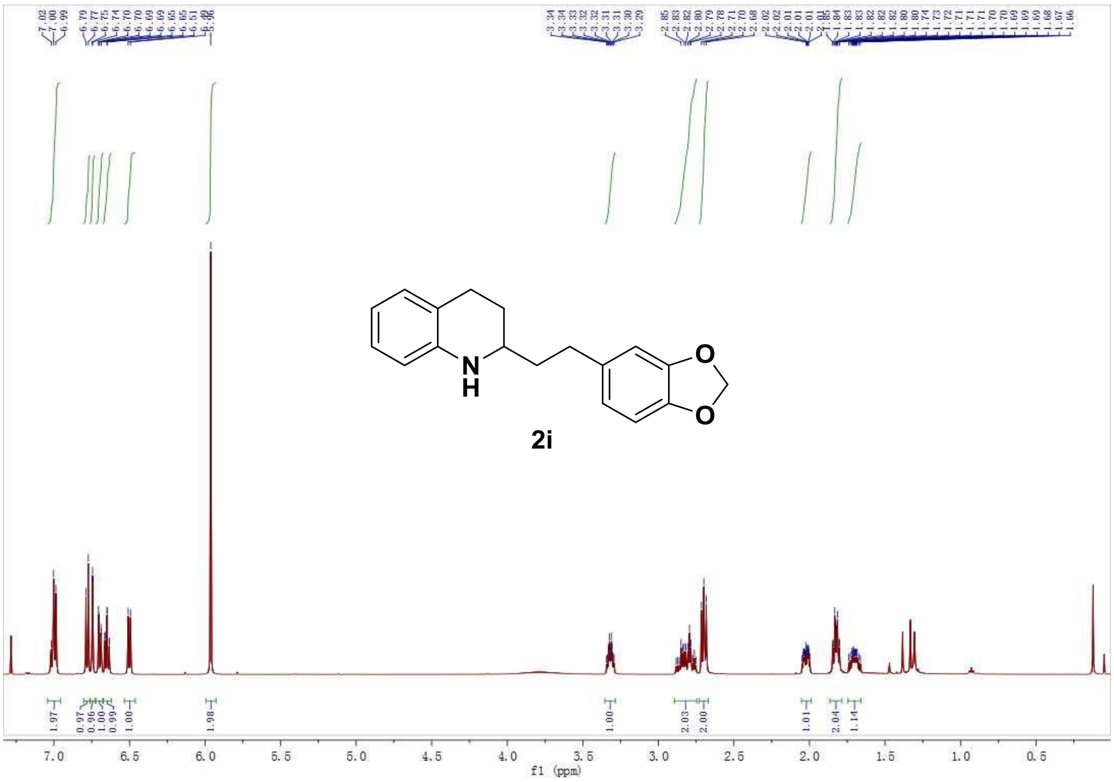
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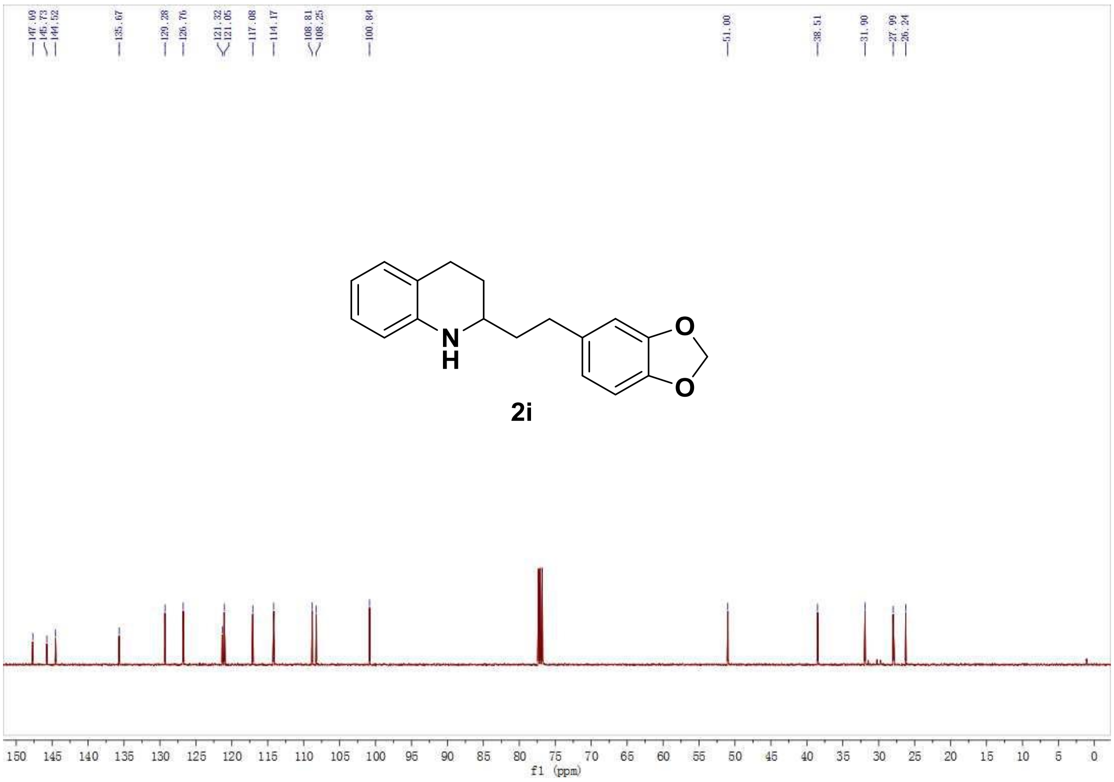
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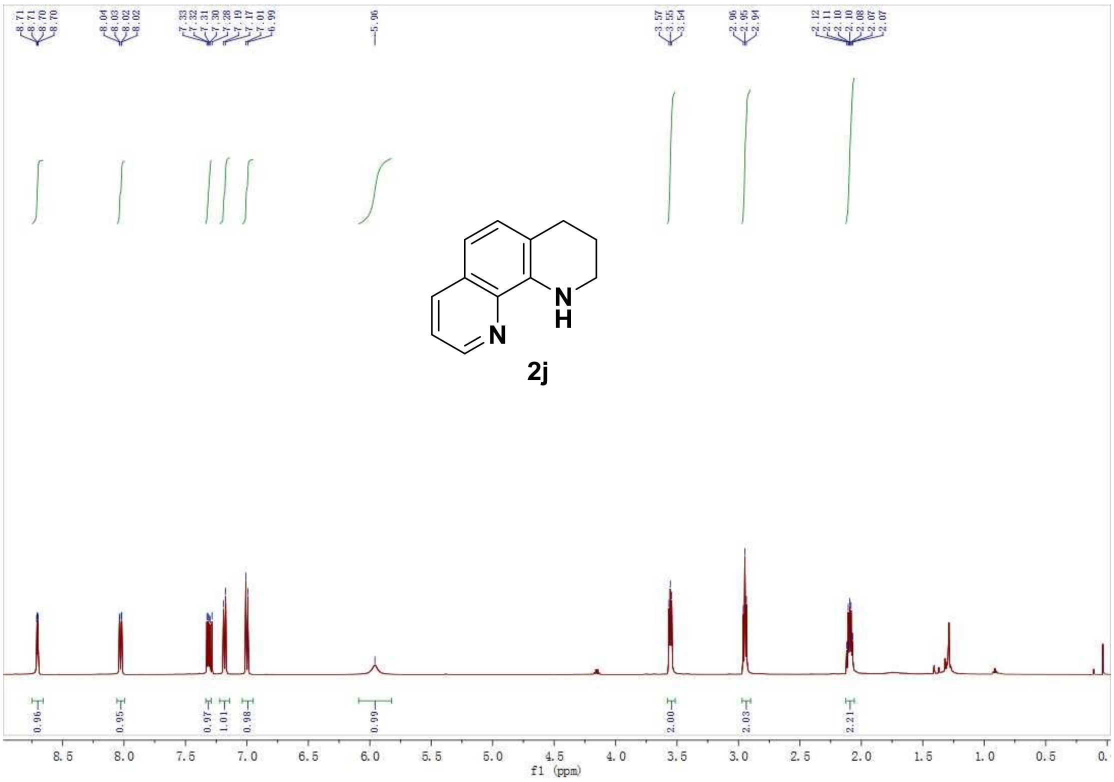
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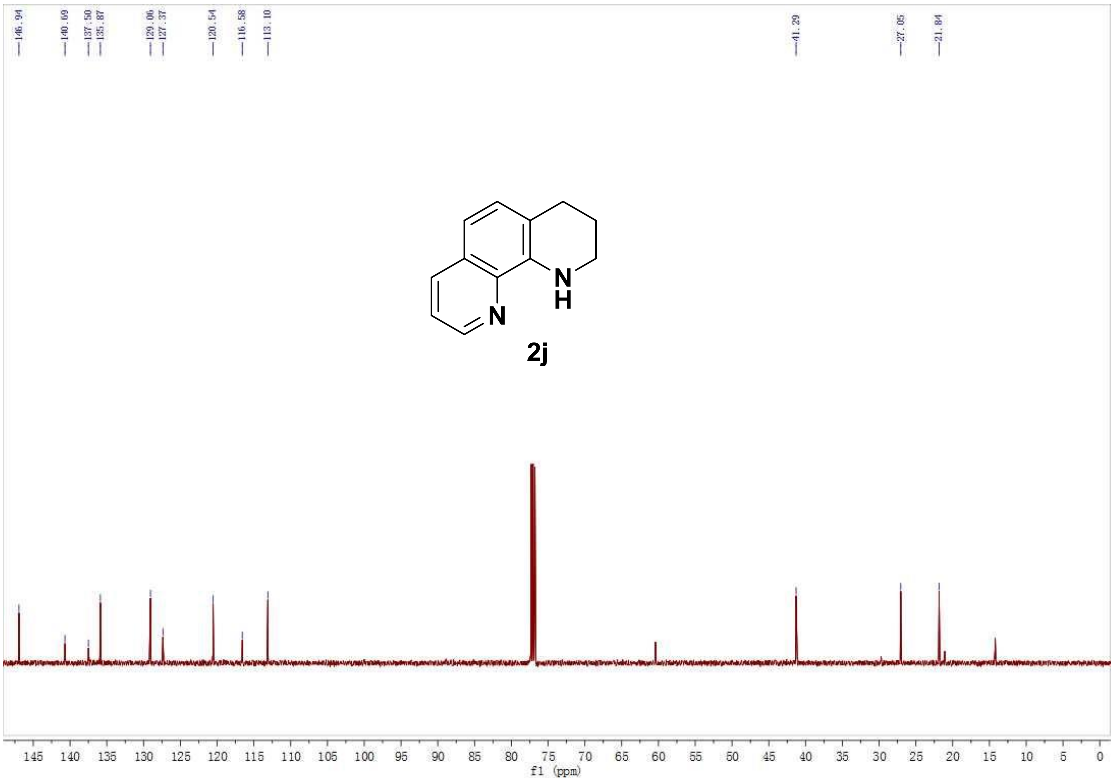
2j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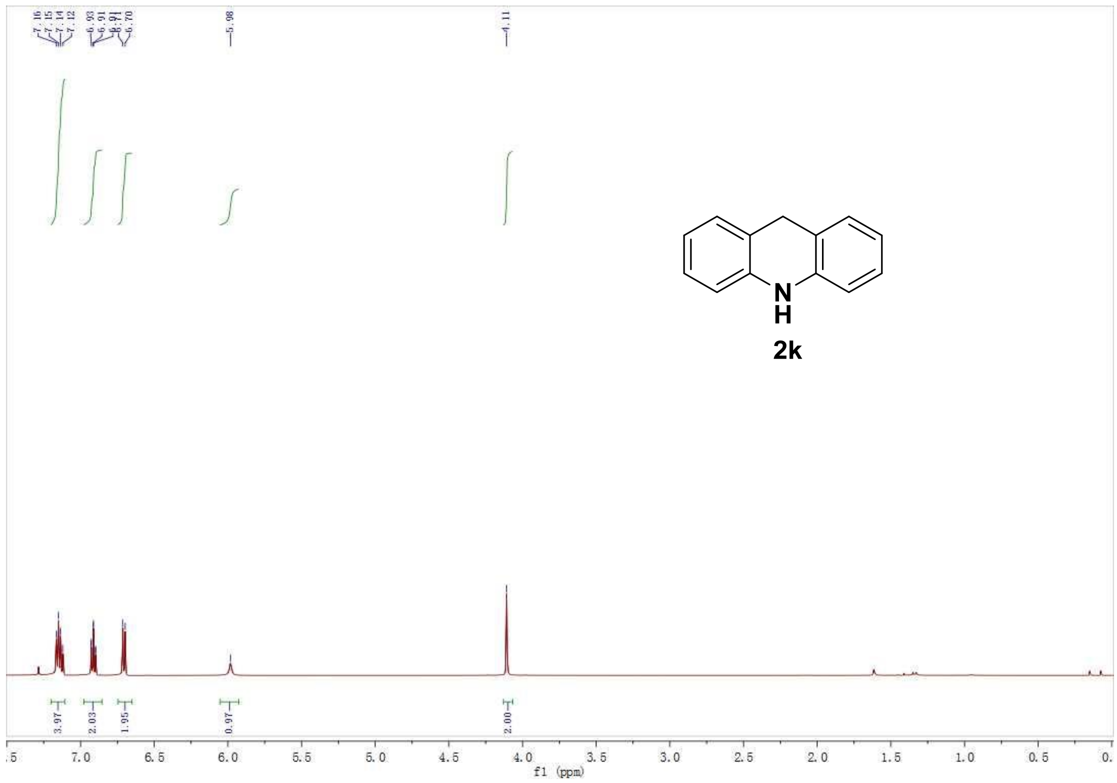
2j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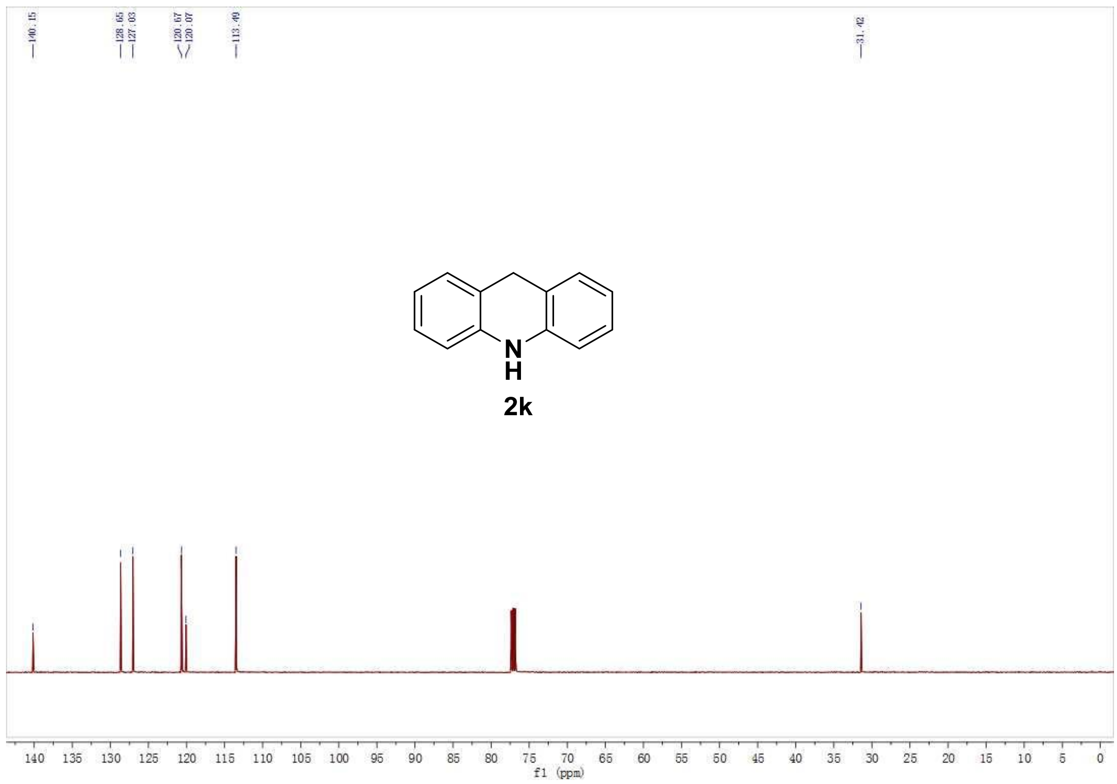
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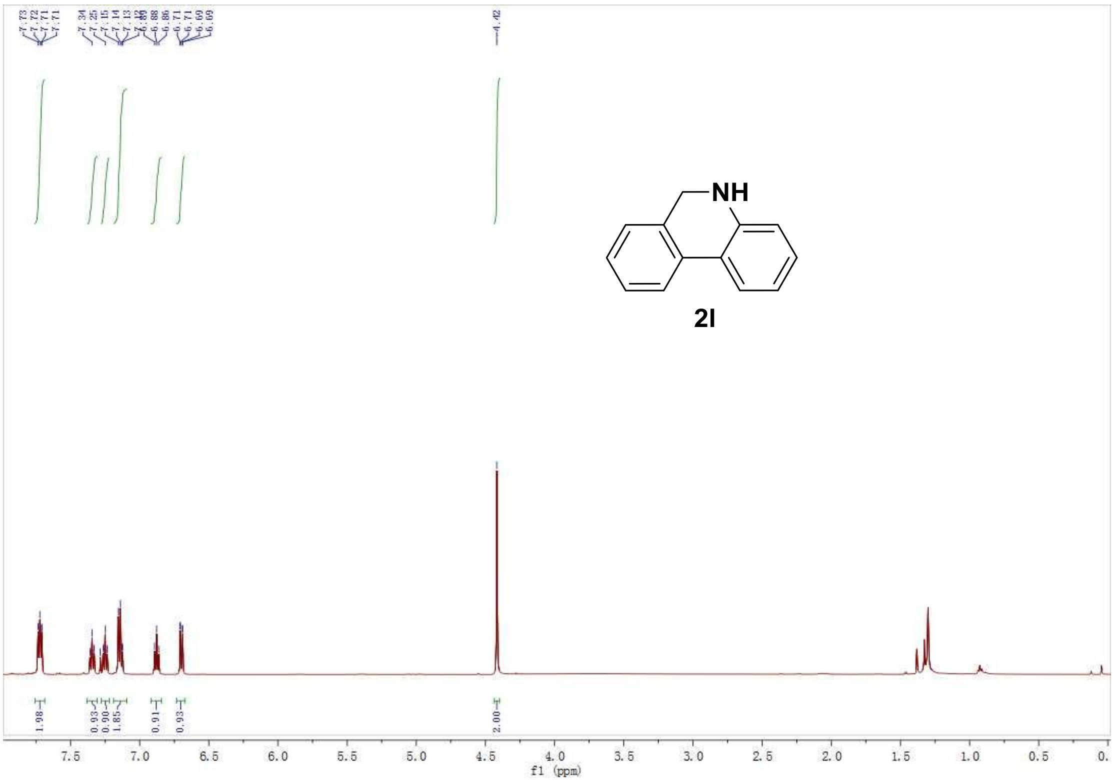
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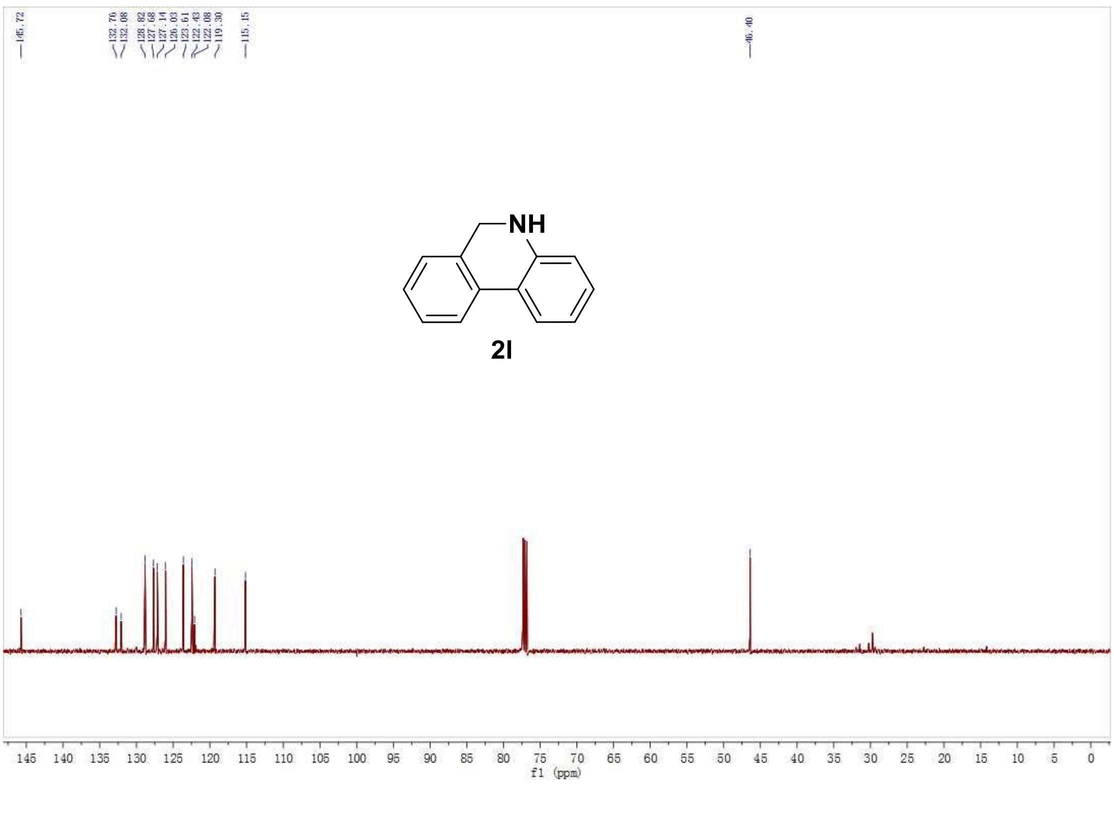
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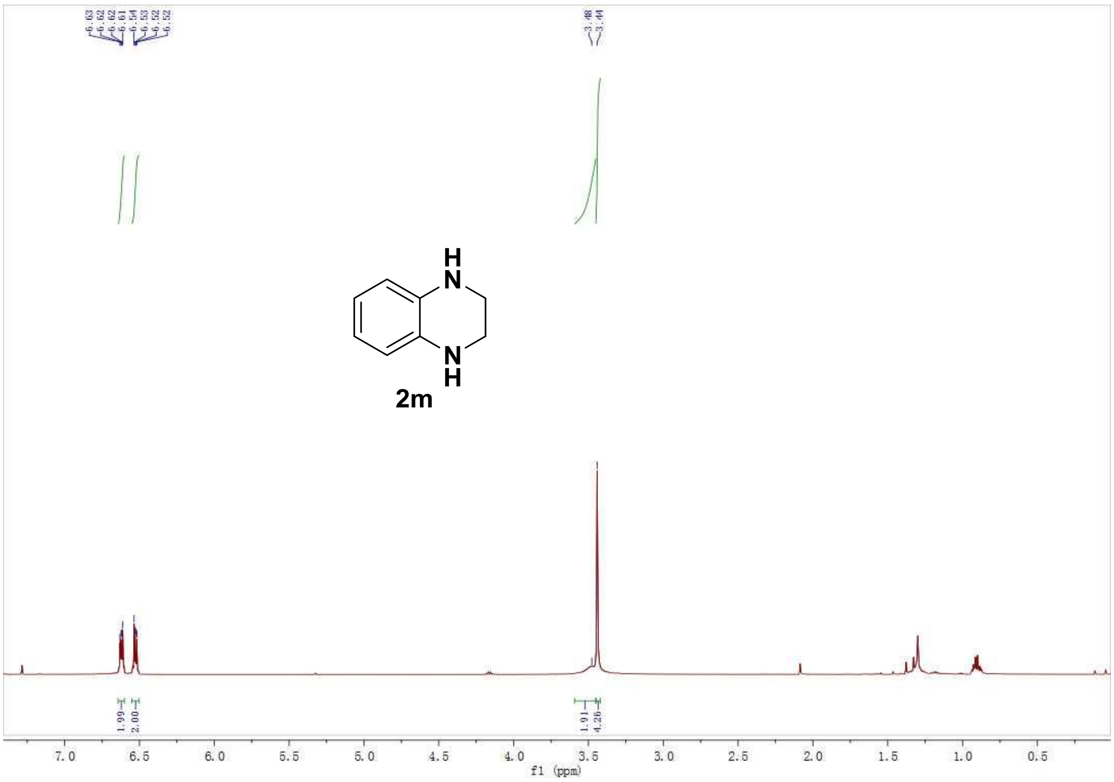
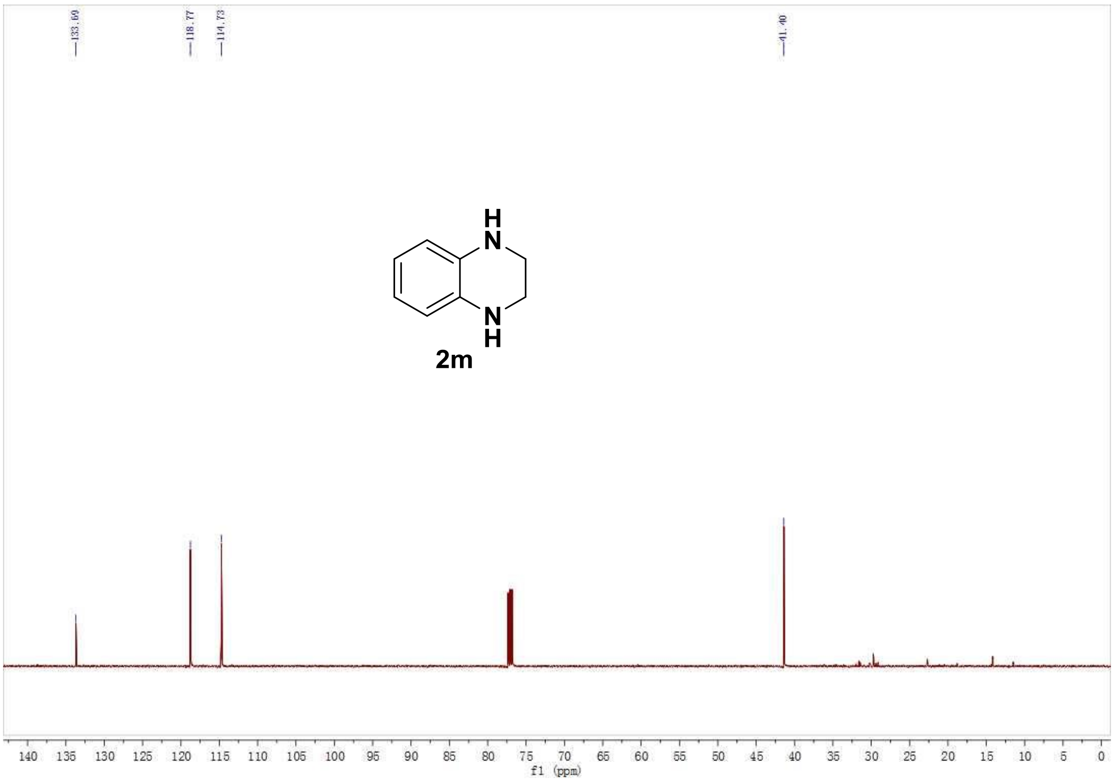
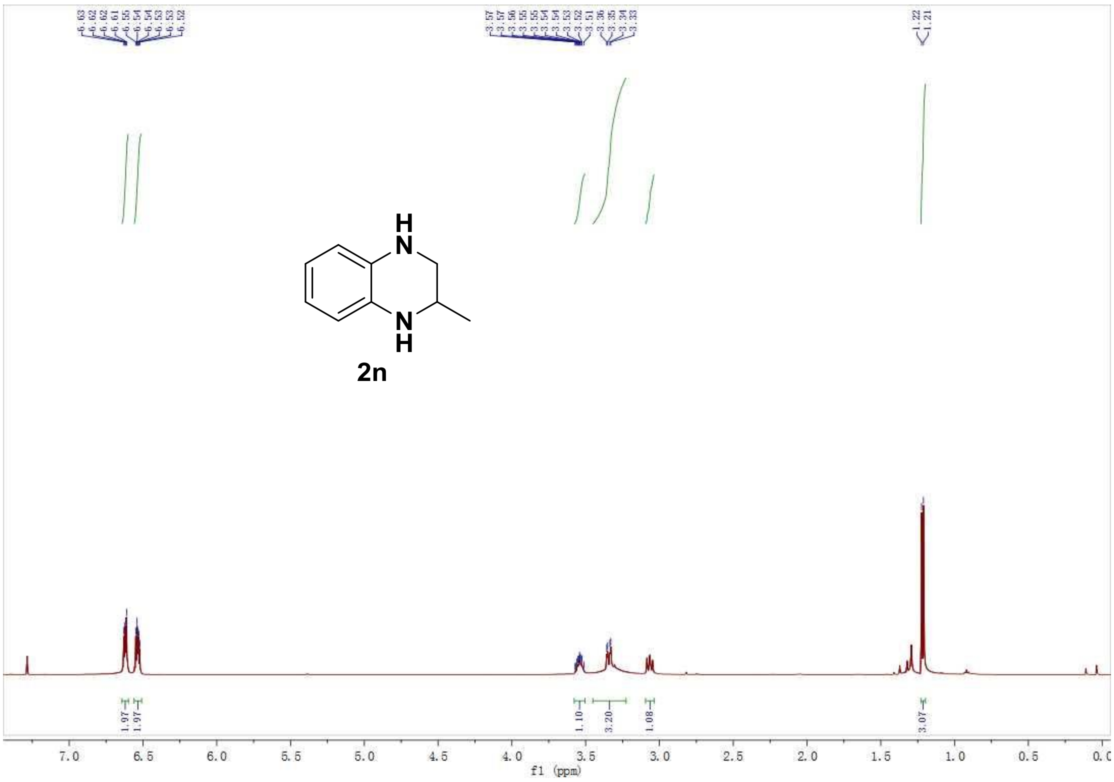
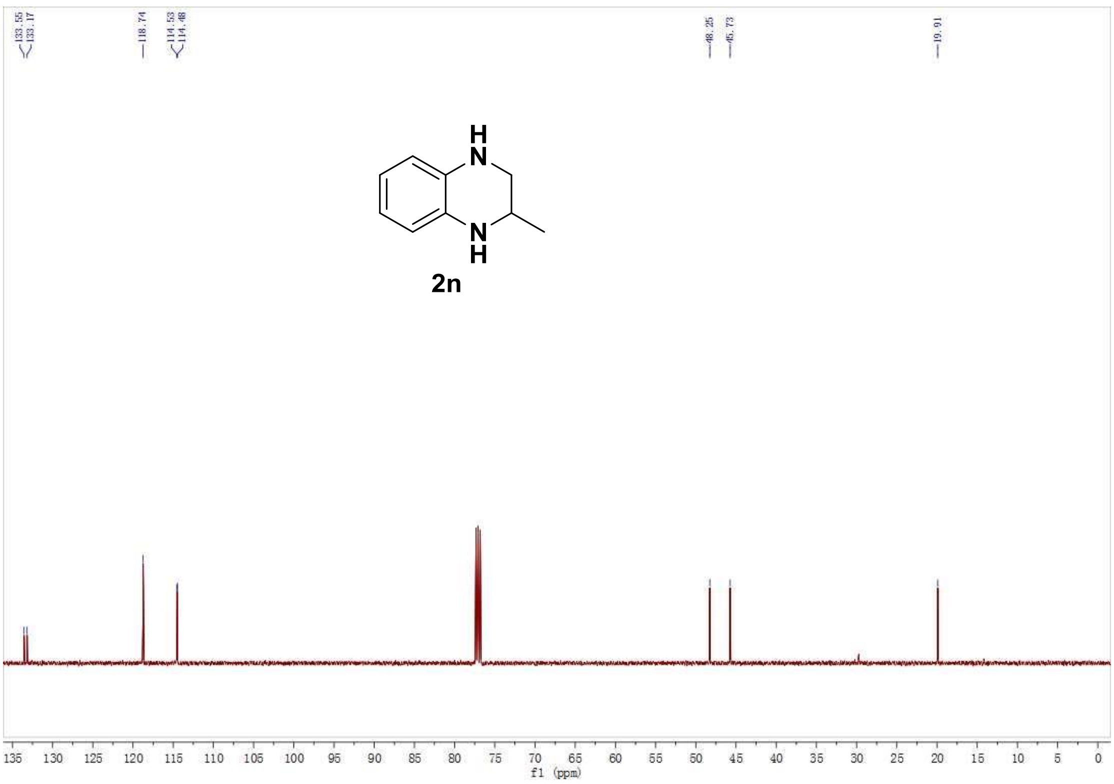
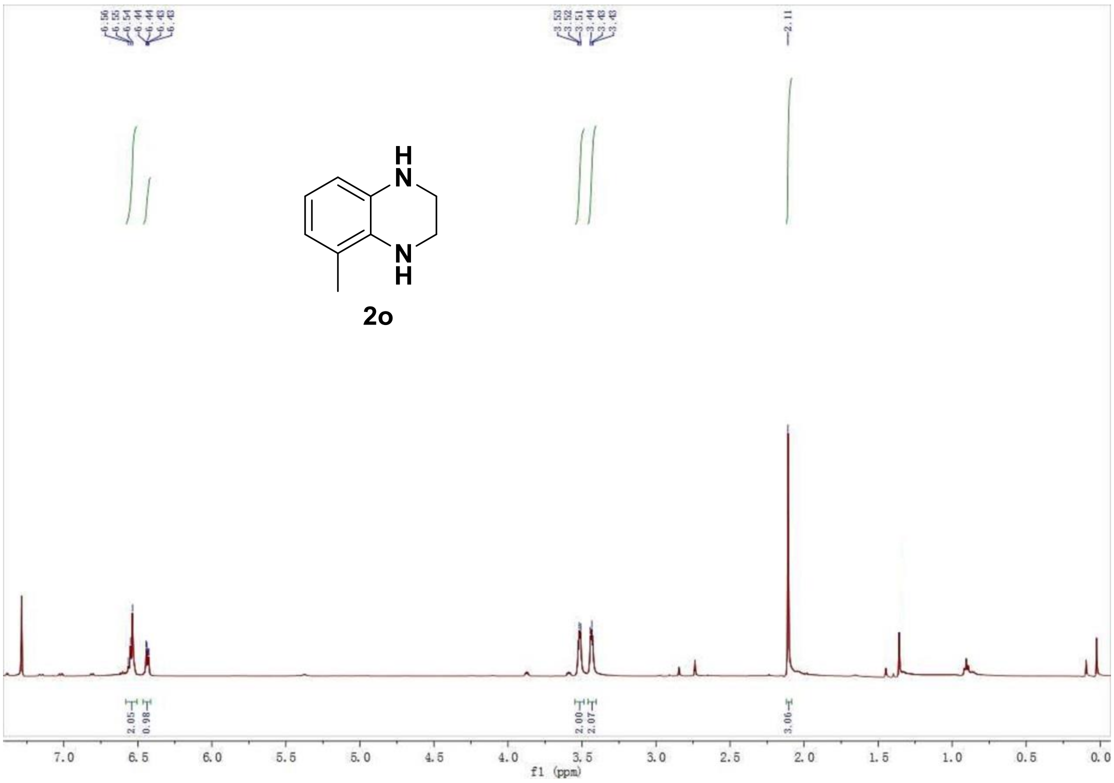
2l
f1 (ppm)

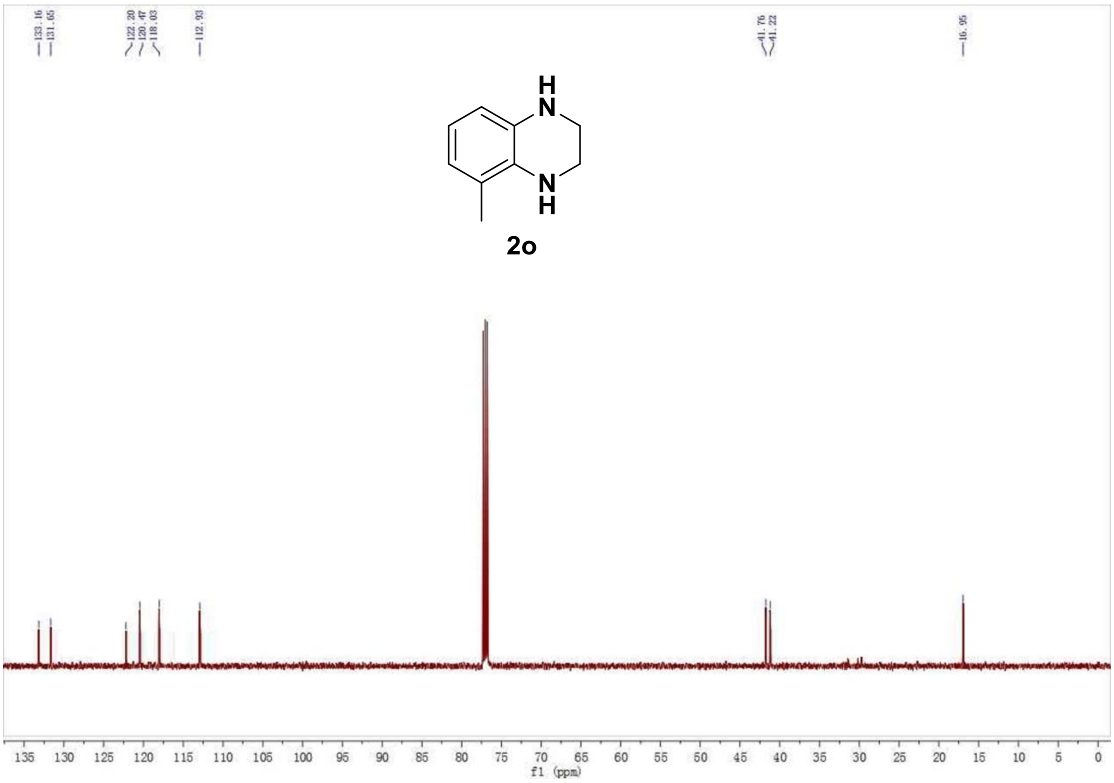

6.63
6.62
6.62
6.61
6.54
6.53
6.52
6.52
3.48
3.44
1.99
2.00
1.91
4.20
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

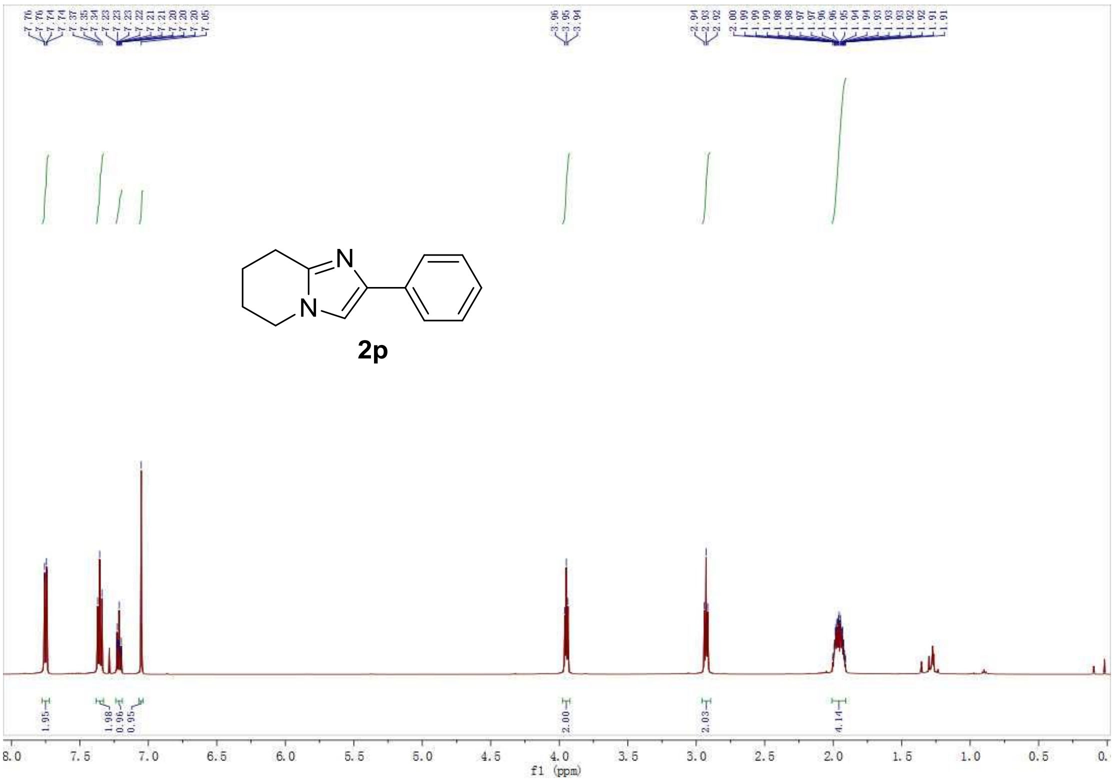

133.69
118.77
114.73
41.40
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

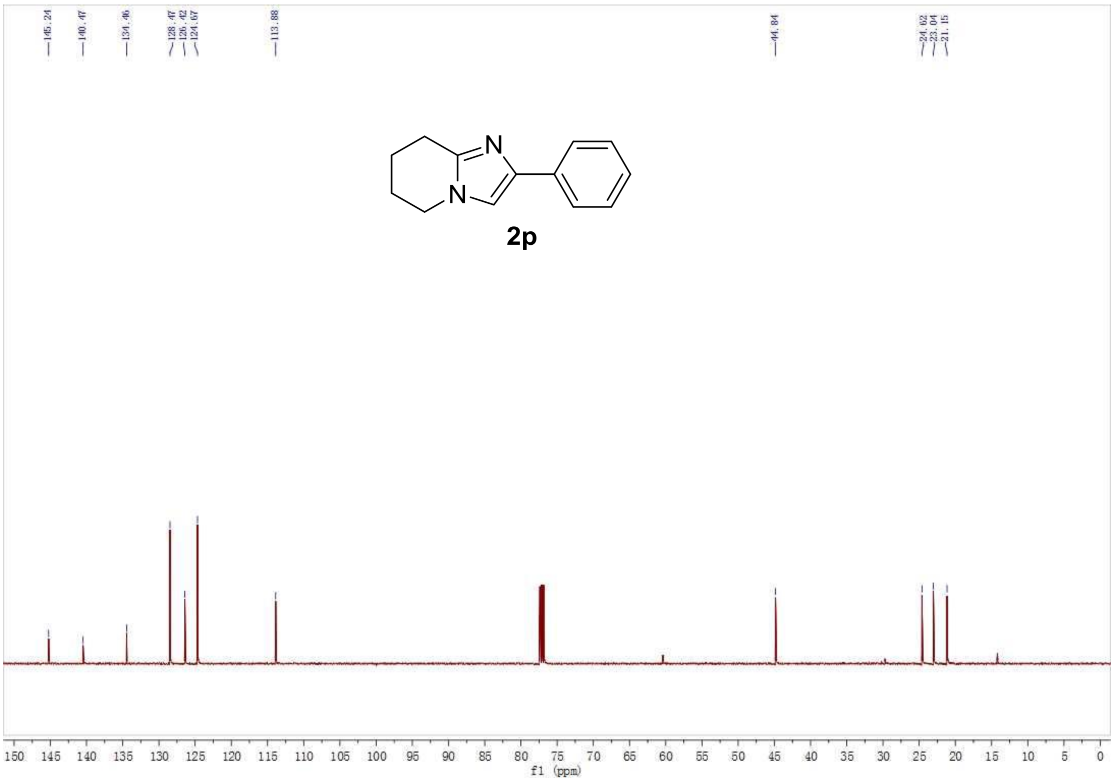

6.63 6.62 6.62 6.61 6.55 6.54 6.54 6.53 6.53 6.52
3.57 3.57 3.56 3.55 3.55 3.54 3.54 3.53 3.52 3.52 3.51 3.36 3.35 3.34 3.33
1.22 1.21
H
N
N
H
2n
1.97 1.97 1.10 3.20 1.08 3.07
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

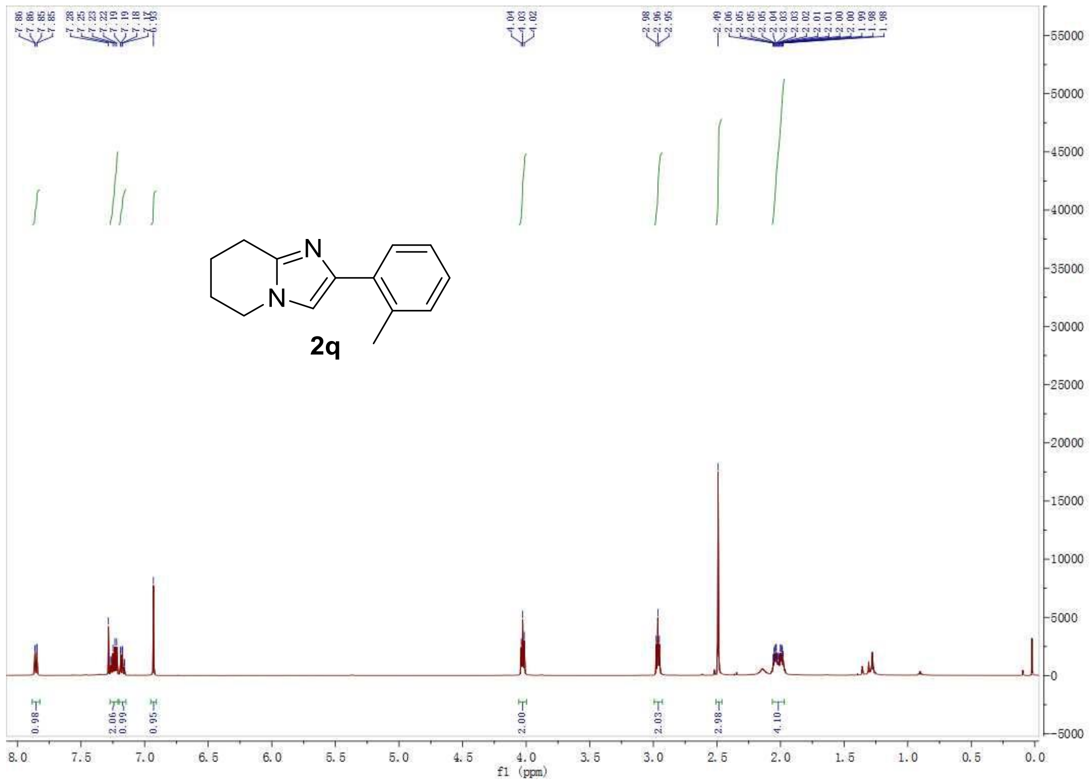

133.55 133.17
118.74
114.53 114.48
48.25
45.73
19.91
H
N
N
H
2n
135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)


6.56
6.55
6.54
6.44
6.44
6.43
6.43
3.53
3.52
3.51
3.44
3.43
3.43
2.11
H
N
N
H
2o
2.05
0.98
2.00
2.07
3.06
f1 (ppm)

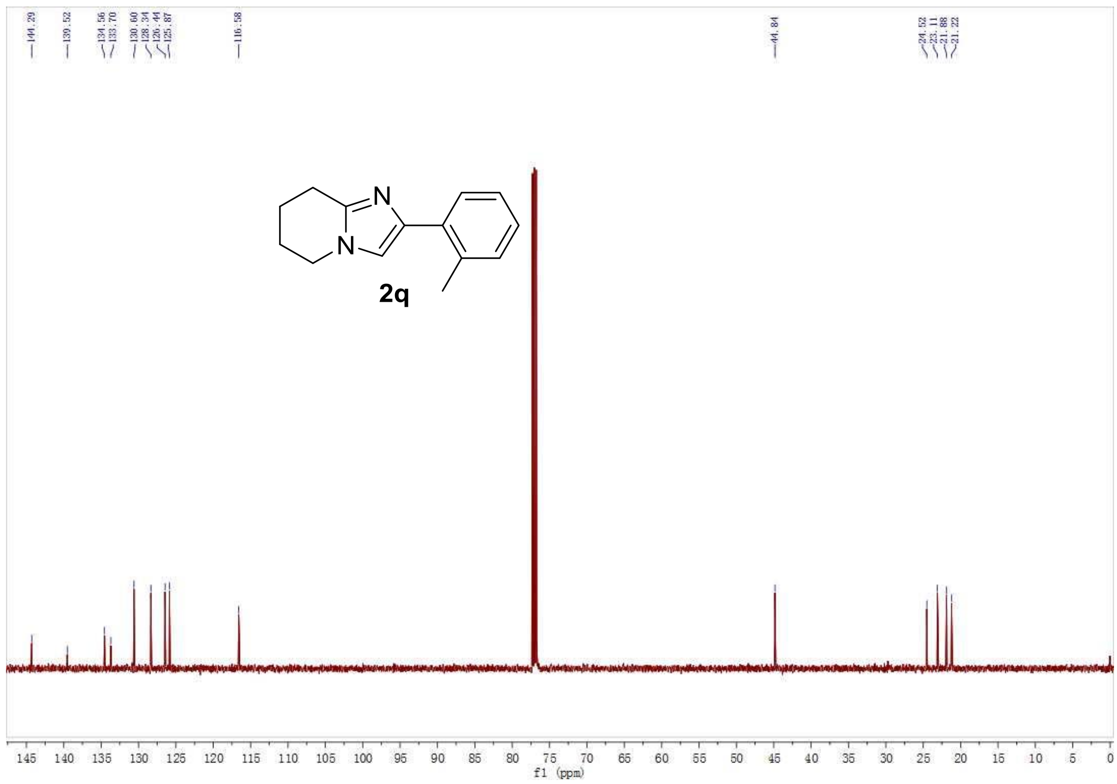

133.16
131.65
122.20
120.47
118.03
112.93
41.76
41.22
16.95
H
N
N
H
2o
f1 (ppm)


2p
f1 (ppm)

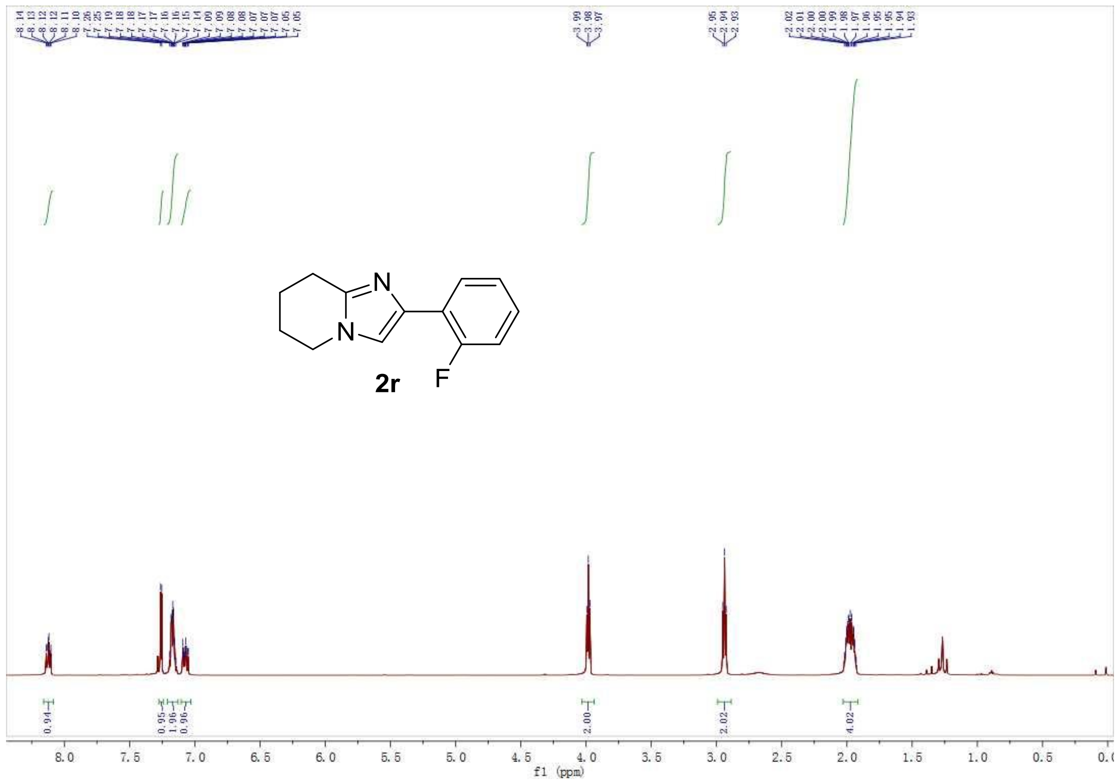

2p
f1 (ppm)

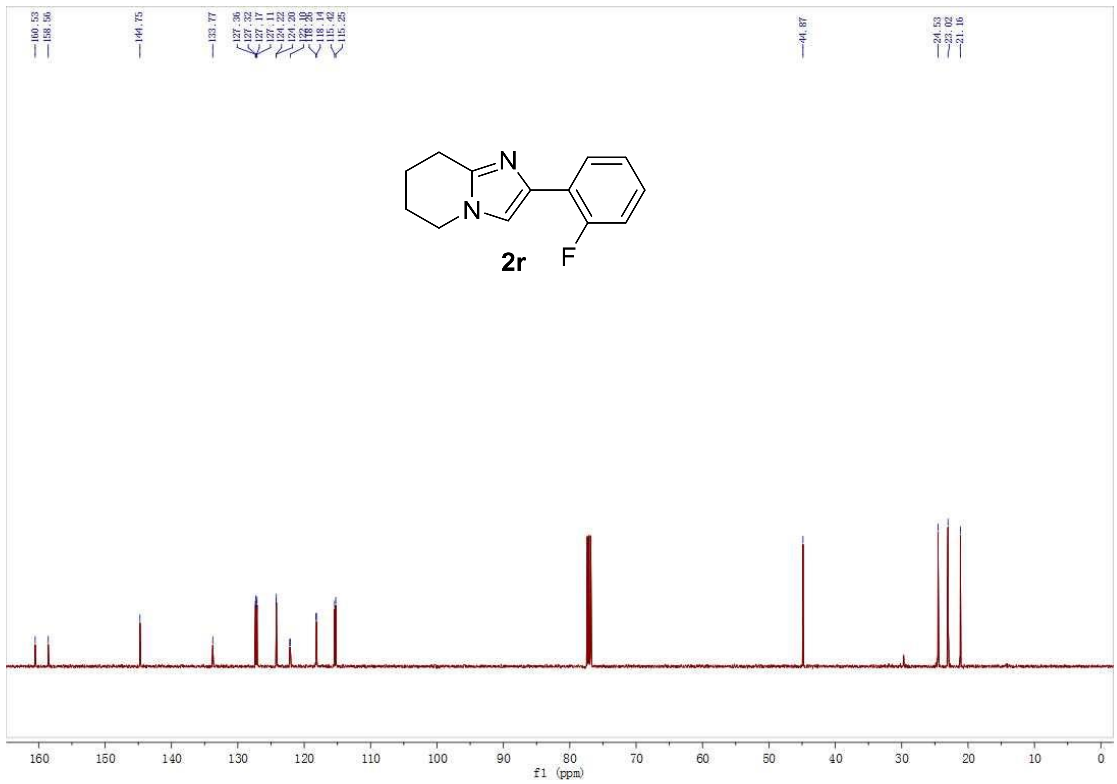


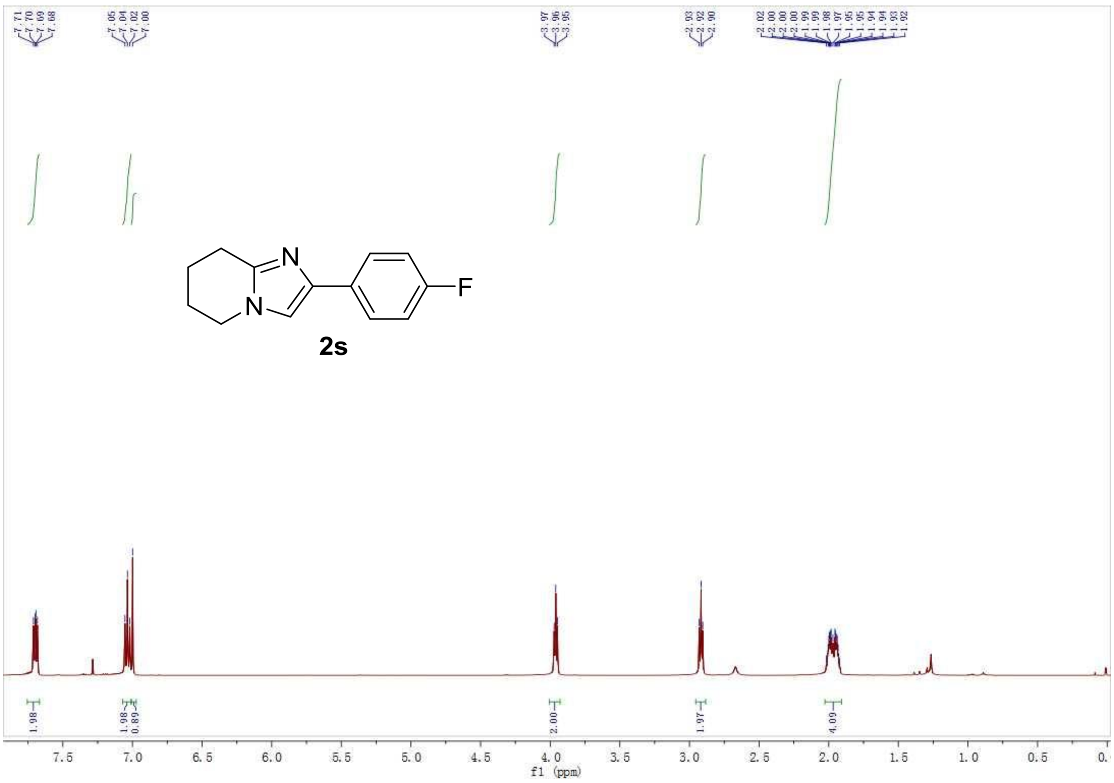
2q
f1 (ppm)

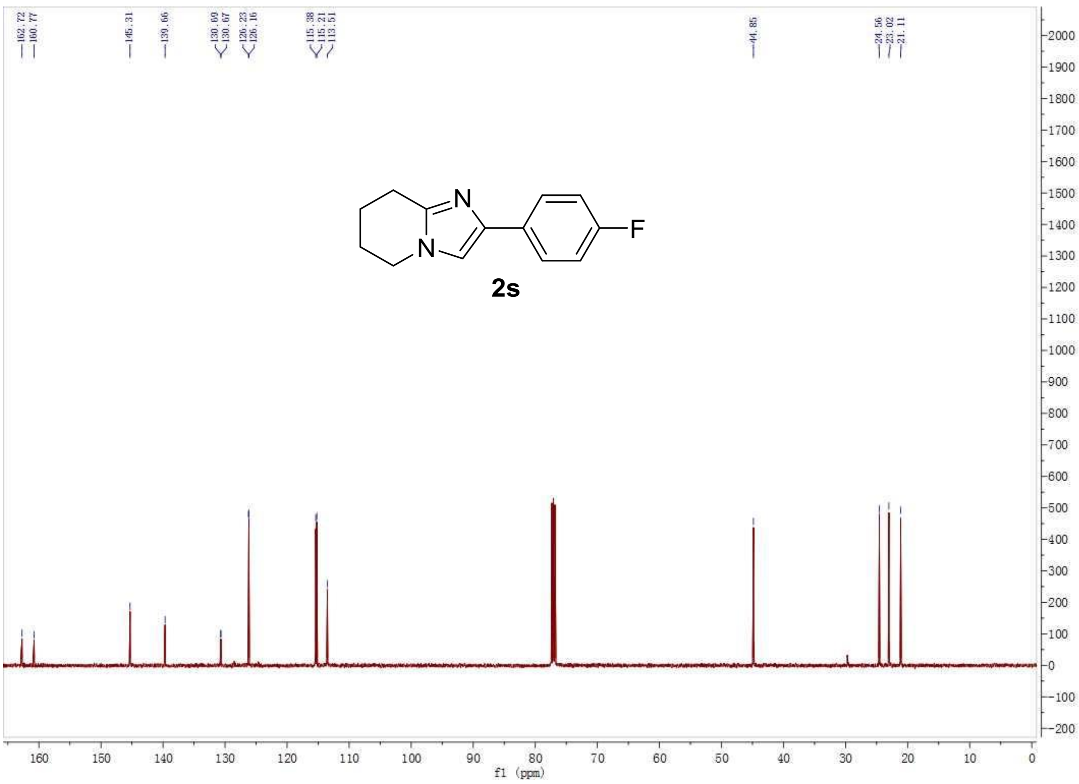


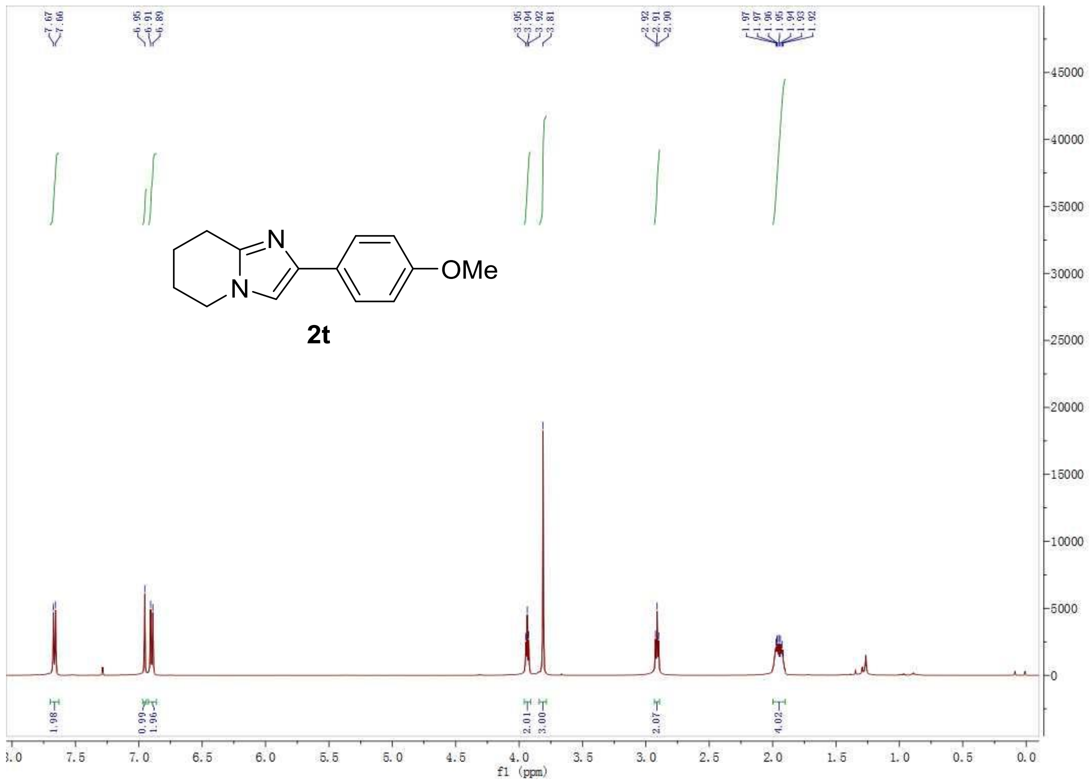
144.29
139.52
134.56
133.70
130.60
128.34
126.44
125.87
116.58
44.84
24.52
23.11
21.88
21.22
2q
f1 (ppm)



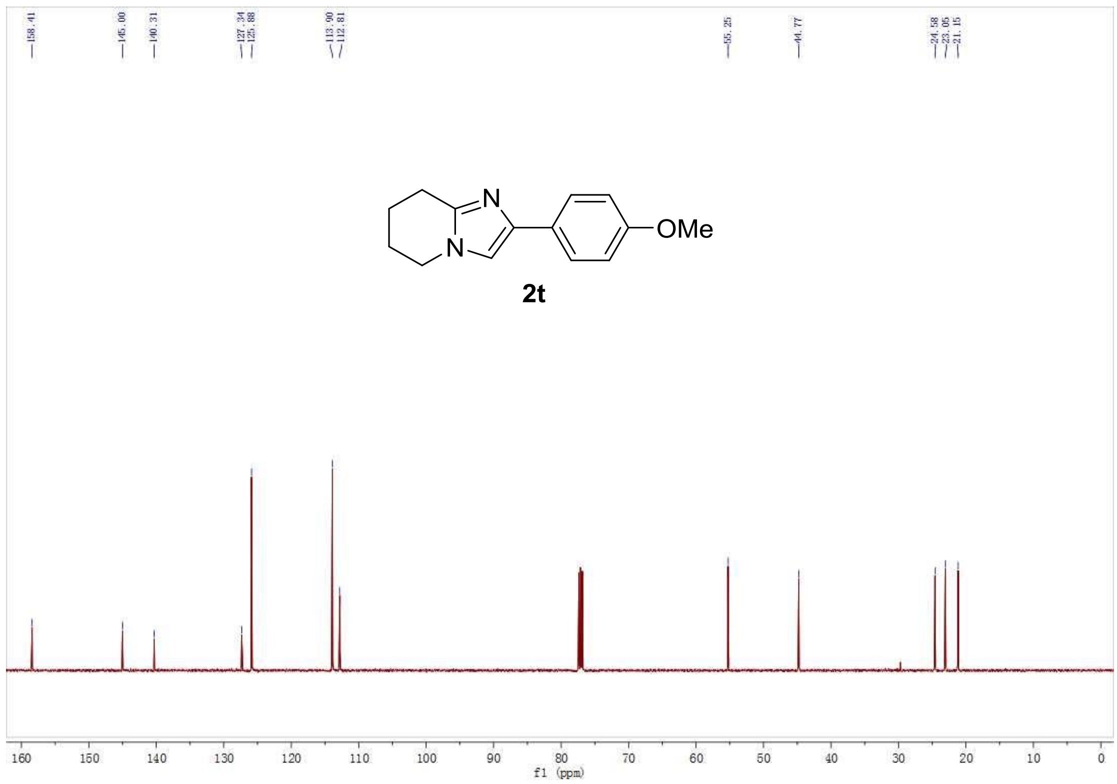



7.71
7.70
7.69
7.68
7.05
7.04
7.02
7.00
3.97
3.96
3.95
2.93
2.92
2.90
N
N
F
2s
1.98
1.98
0.89
2.00
1.97
4.09
f1 (ppm)

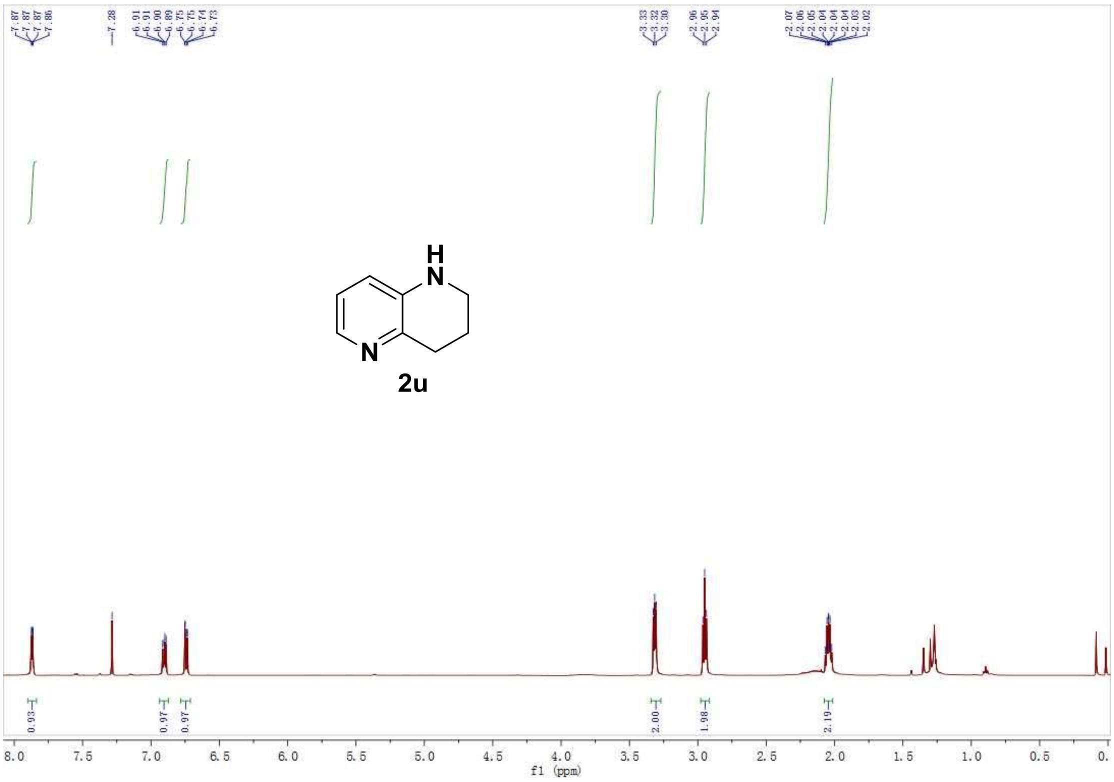

162.72
160.77
145.31
139.66
130.69
130.67
126.23
126.16
115.38
115.21
113.51
44.85
24.56
23.02
21.11
N
N
F
2s
f1 (ppm)



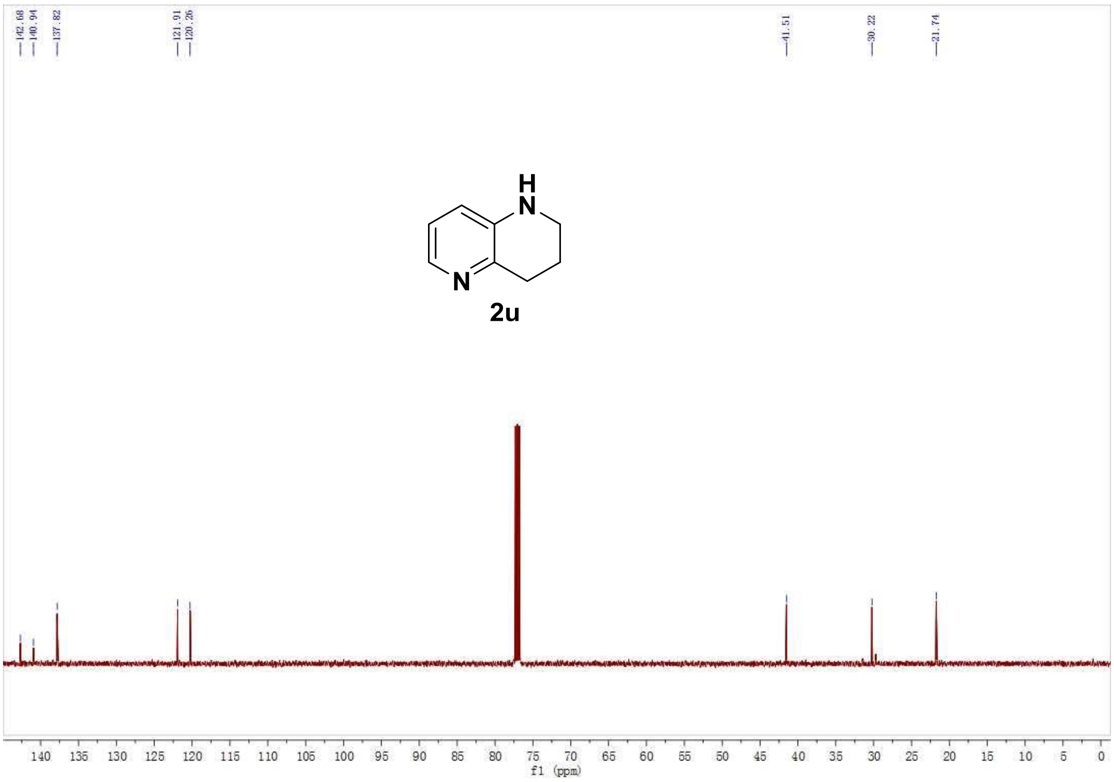
OMe
2t
f1 (ppm)



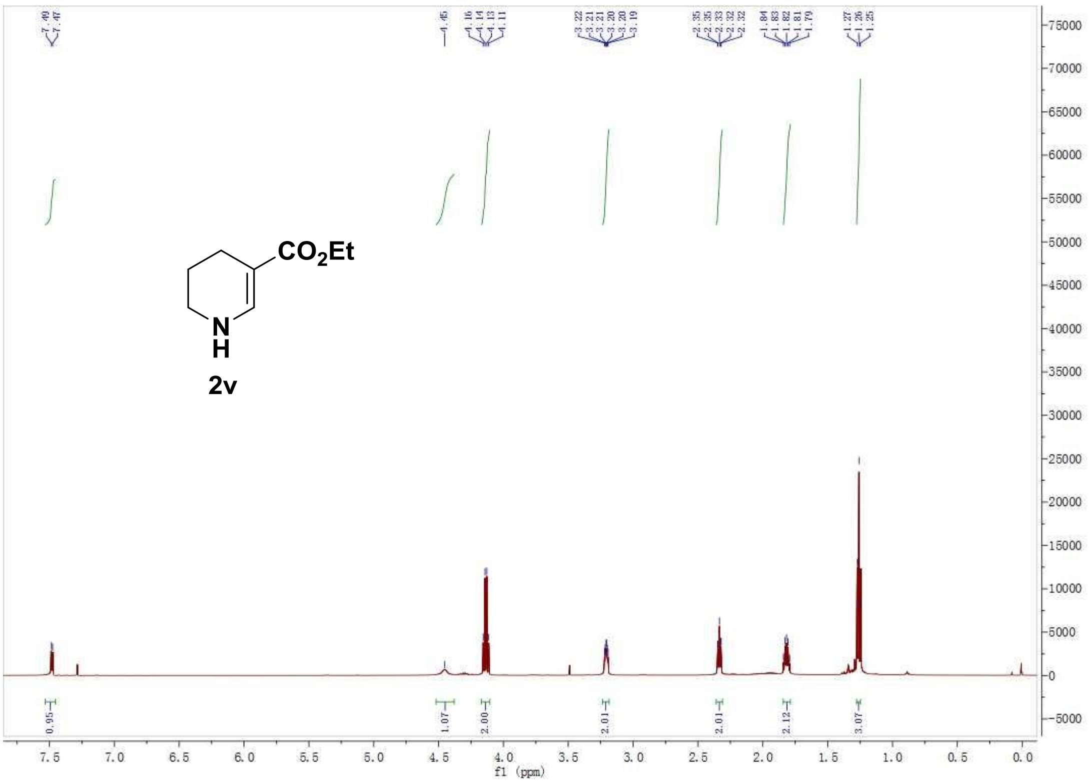
OMe
2t
f1 (ppm)

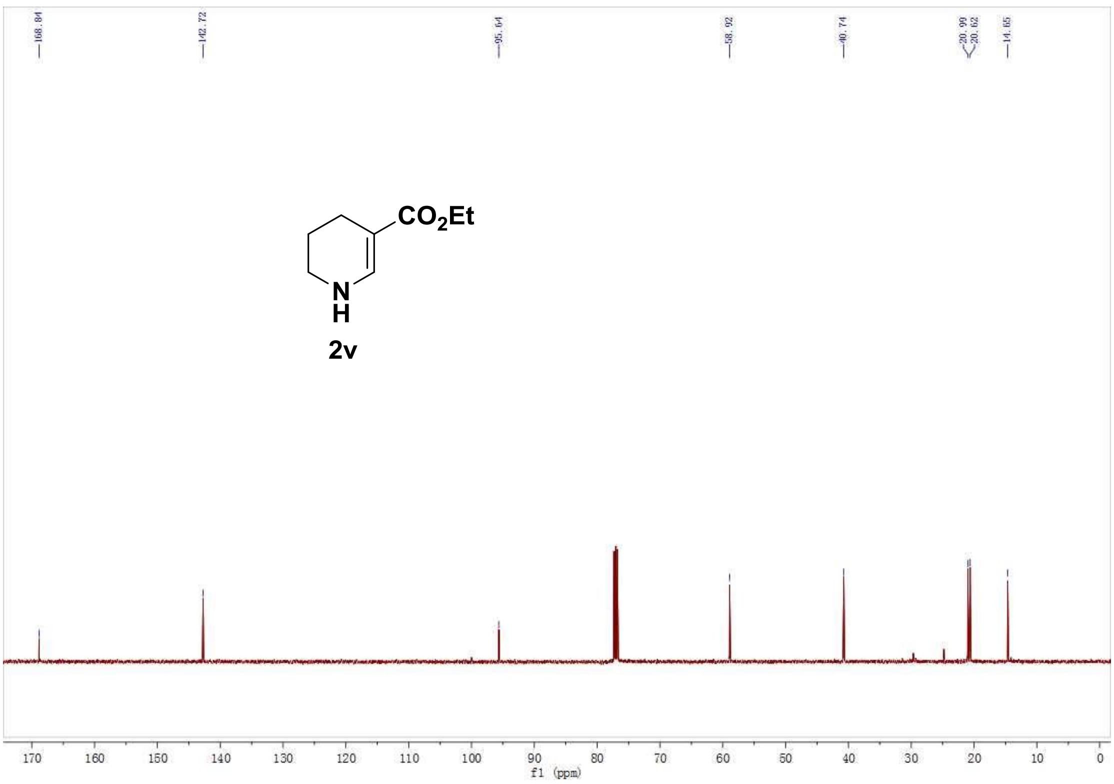


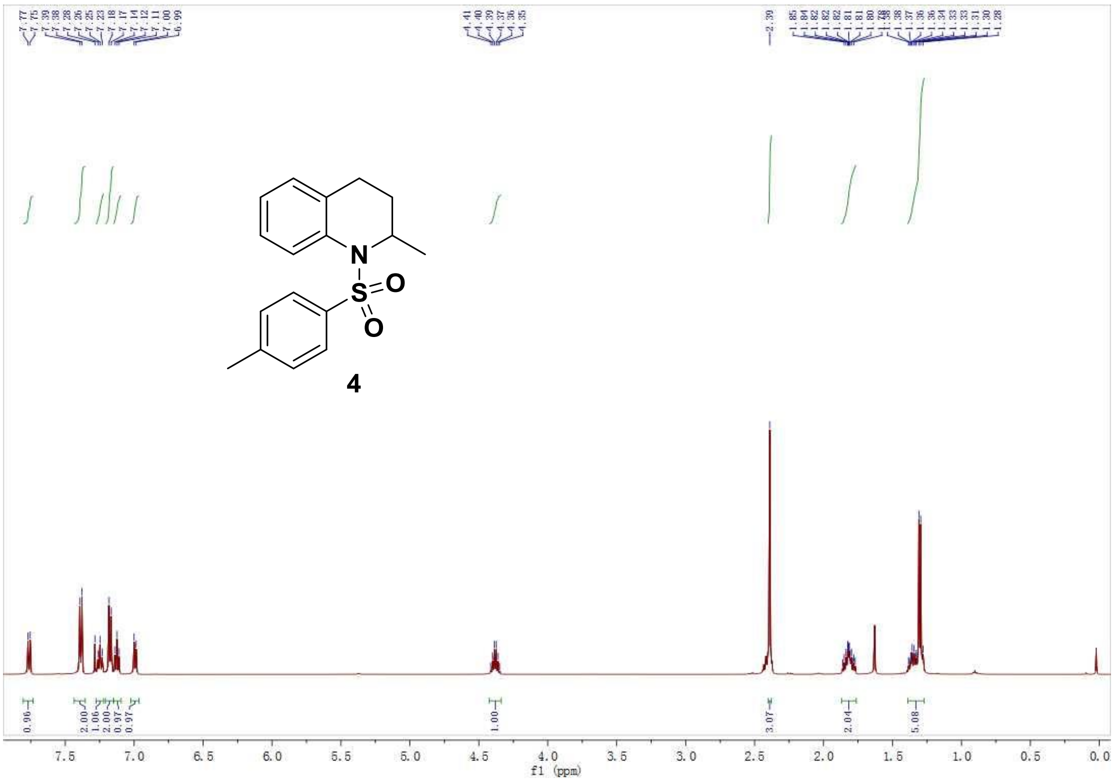
2u
0.93
0.97
0.97
2.00
1.98
2.19
f1 (ppm)

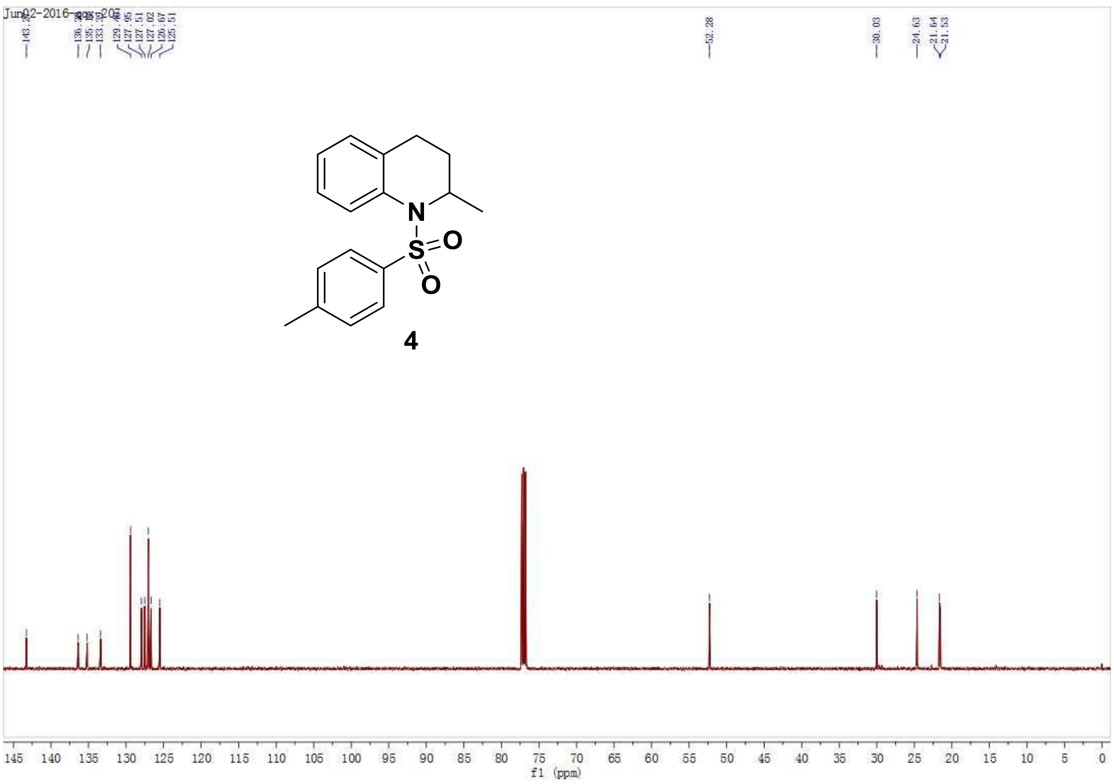


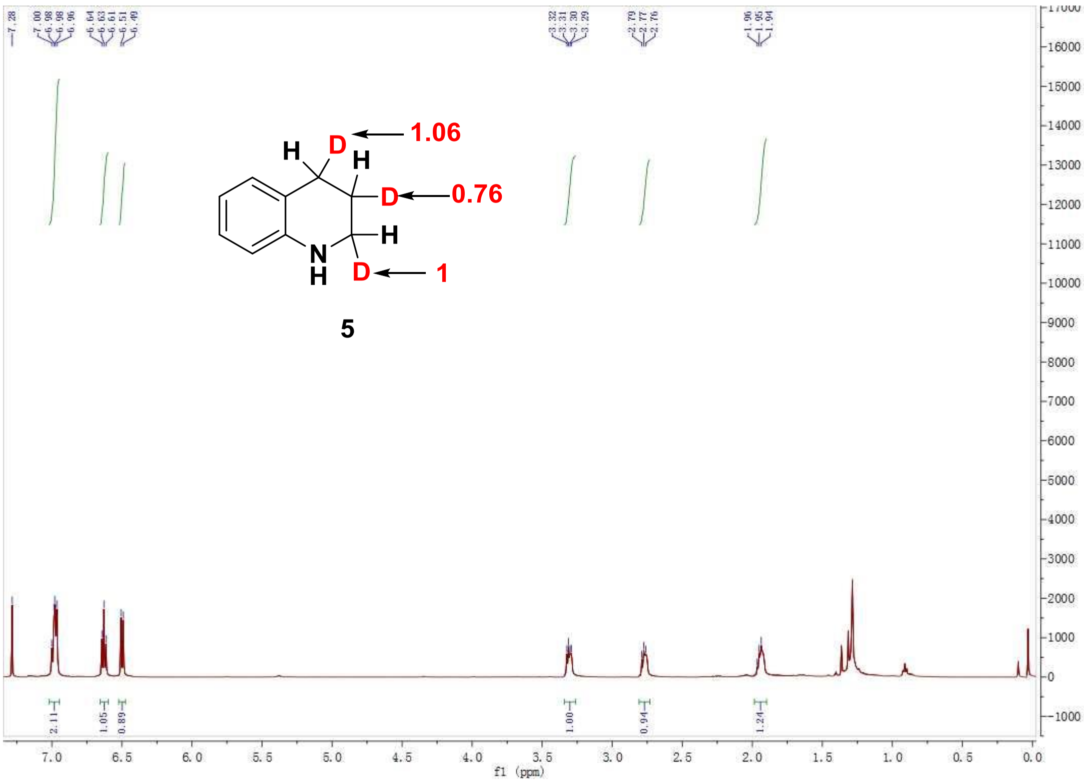
142.68
140.94
137.82
121.91
120.26
41.51
30.22
21.74
2u
f1 (ppm)


CO2Et
N
H
2v


CO2Et
N
H
2v


N
S
O
O
4
f1 (ppm)


Jun02-2016
N
S
O
O
4
f1 (ppm)


1.06
0.76
1
5
f1 (ppm)

VIII. ^{11}B NMR spectra of products

HOBpin was detected by ^{11}B NMR spectra in the crude reaction mixture of Condtion A.