Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Iron-Catalyzed Regioselective Protoboration of Alkene on *N*-heterocycles

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Supporting Information

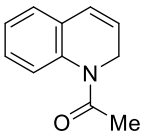
1. General Considerations

All manipulations were conducted with Schlenk tube. ^{1}H-NMR spectras were recorded on BrukerAVIII-400 spectrometers, JNM-ECZ400S/L1 and JNM-ECZ600R/S1 spectrometers. Chemical shifts (in ppm) were referenced to Chloroform-d (δ = 7.26 ppm) in Chloroform-d as an internal standard. Data werereported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t =triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constants (Hz), integration and assignment.^{13}C-NMR spectras were obtained by using the same NMR spectrometers and were calibrated by Chloroform-d (δ = 77.00 ppm). ^{19}F-NMR spectra were obtained by the same NMR. High resolution mass spectrometry (HRMS) data were obtained on a QTOF mass analyzer with electrospray ionization (ESI) through a Waters Acquity UPLC Class I/Xevo G2 Q-Tof. HPLC data were collected on a Shimadzu LC-2030 spectrometer. Melting points were measured on a WRS-1A digital melting point apparatus and are uncorrected. Substrates were purchased from Aldrich, TCI, Acros, Energy, Aladdin, or synthesized according to the procedures outlined below. THF was distilled from sodium benzophenone prior to use. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. For the heating reaction, the heat source is an oil bath.

2. Synthesis of Substrates

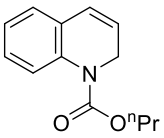
2.1 Synthesis of 1,2-Dihydroquinoline

These substrates were prepared according to the corresponding literature reports. Analytical data (^{1}H NMR, ^{13}C NMR) matches with the literature.[1,2]



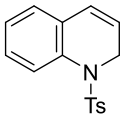
1a

1-(quinolin-1(2*H*)-yl)ethan-1-one



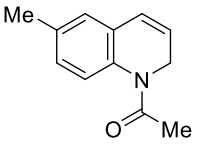
1b

propyl quinoline-1(2*H*)-carboxylate



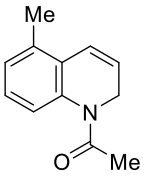
1c

1-tosyl-1,2-dihydroquinoline



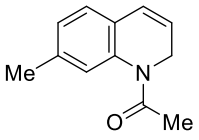
1d

1-(6-methylquinolin-1(2*H*)-yl)ethan-1-one



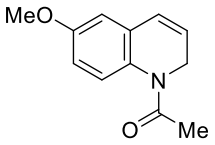
1e

1-(5-methylquinolin-1(2*H*)-yl)ethan-1-one



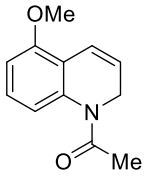
1f

1-(7-methylquinolin-1(2*H*)-yl)ethan-1-one



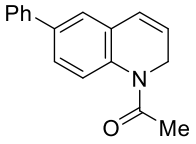
1g

1-(6-methoxyquinolin-1(2*H*)-yl)ethan-1-one



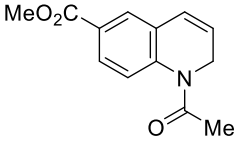
1h

1-(5-methoxyquinolin-1(2*H*)-yl)ethan-1-one



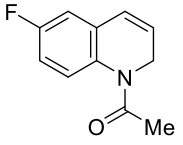
1i

1-(6-phenylquinolin-1(2*H*)-yl)ethan-1-one



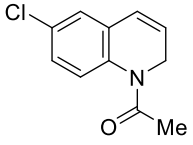
1j

methyl 1-acetyl-1,2-dihydroquinoline-6-carboxylate



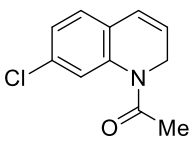
1k

1-(6-fluoroquinolin-1(2*H*)-yl)ethan-1-one



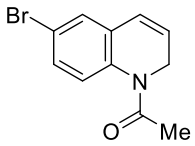
1l

1-(6-chloroquinolin-1(2*H*)-yl)ethan-1-one



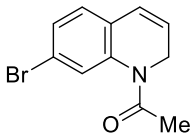
1m

1-(7-chloroquinolin-1(2*H*)-yl)ethan-1-one



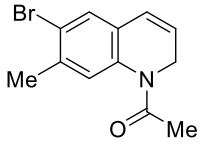
1n

1-(6-bromoquinolin-1(2*H*)-yl)ethan-1-one



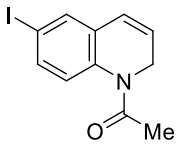
1o

1-(7-bromoquinolin-1(2*H*)-yl)ethan-1-one



1p

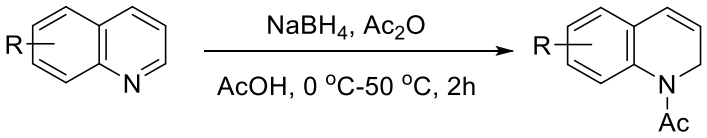
1-(6-bromo-7-methylquinolin-1(2*H*)-yl)ethan-1-one



1q

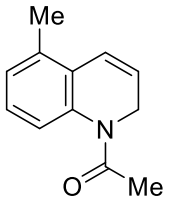
1-(6-iodoquinolin-1(2*H*)-yl)ethan-1-one

1e, **1i, 1j**, **1m**, **1p**, and **1q** were synthesized according to the literature. (General procedure A)[2]



1

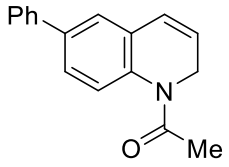
Sodium borohydride (3.01 g, 80.0 mmol) was added portionwise to a mixture of quinoline (2.47 g, 19.1 mmol), acetic anhydride (10.2 mL) and acetic acid (31.0 mL) at 0 ℃. After the addition of complete, the mixture was warmed to 50 ℃ for 30 min. The reaction mixture was concentrated under vacuum, diluted with water and neutralized with aqueous Na_2CO_3 . This was then extracted with CH_2Cl_2 three times and the organic extract was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (ethyl acetate : petroleum ether = 1 : 3), followed by bulb-to-bulb distillation to give the corresponding 1,2-dihydroquinoline **1** (1.22 g, 7.0 mmol, 37%) as a colorless oil. The 1,2-dihydropyridines were immediately used in the next borylation reaction in order to prevent decomposition.



1e

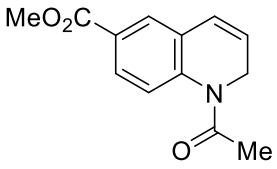
1-(5-methylquinolin-1(2*H*)-yl)ethan-1-one (1e). The general procedure A was followed using 5-methylquinoline (0.72 g, 5.0 mmol, 1.0 equiv.). Purification of this material by chromatography

on silica gel (ethyl acetate : petroleum ether = 1 : 3) afforded product **1e** as a colorless oil (0.69 g , 74 % yield): R_f = 0.4 (ethyl acetate : petroleum ether = 1 : 2); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.10 (t, *J* = 7.7 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 2H), 6.71 (d, *J* = 9.7 Hz, 1H), 6.15 (dt, *J* = 9.7, 4.2 Hz, 1H), 4.50-4.35 (m, 2H), 2.34 (s, 3H), 2.17 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 169.9, 137.0, 133.9, 127.9, 127.5, 127.2, 126.4, 123.1, 121.7, 40.6, 22.2, 18.8 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{12}H_{14}NO$ $(M + H)^+$: 188.1075, found 188.1083.



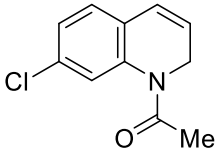
1i

1-(6-phenylquinolin-1(2*H*)-yl)ethan-1-one (1i). The general procedure A was followed using 6-phenylquinoline (1.03 g, 5.0 mmol, 1.0 equiv.). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 3) afforded product **1i** as a colorless oil (0.84 g , 67 % yield): R_f = 0.4 (ethyl acetate : petroleum ether = 1 : 2); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.60-7.55 (m, 2H), 7.47-7.42 (m, 3H), 7.39-7.18 (m, 3H), 6.59 (d, *J* = 9.5 Hz, 1H), 6.13 (dt, *J* = 8.8, 4.0 Hz, 1H), 4.49 (s, 2H), 2.26 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 167.0, 140.1, 138.5, 136.2, 128.9, 128.8, 127.4, 126.8, 126.2, 125.6, 125.0, 124.0, 41.6, 29.3, 22.5 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{17}H_{16}NO$ $(M + H)^+$: 250.1232, found 250.1242.



1j

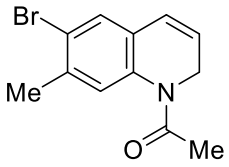
Methyl 1-acetyl-1,2-dihydroquinoline-6-carboxylate (1k). The general procedure A was followed using methyl quinoline-6-carboxylate (0.94 g, 5.0 mmol, 1.0 equiv.). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 3) afforded product **1k** as a colorless oil (0.52 g , 45 % yield): R_f = 0.4 (ethyl acetate : petroleum ether = 1 : 2); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.88 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.78 (d, *J* = 2.0 Hz, 1H), 7.32 (s, 1H), 6.57 (d, J = 9.6 Hz, 1H), 6.13 (dt, *J* = 9.4, 4.1 Hz, 1H), 4.52-4.39 (m, 2H), 3.91 (s, 3H), 2.25 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 169.4, 165.7, 140.4, 128.3, 128.0, 127.5, 127.3, 126.4, 125.4, 123.0, 51.7, 41.8, 22.2 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{14}NO_3$ $(M + H)^+$: 232.0974, found 232.0979.



1m

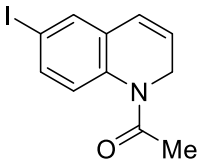
1-(7-chloroquinolin-1(2*H*)-yl)ethan-1-one (1m). The general procedure A was followed using 7-chloroquinoline (0.82 g, 5.0 mmol, 1.0 equiv.). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 3) afforded product **1m** as a colorless oil (0.75 g , 72 % yield): Rf = 0.4 (ethyl acetate : petroleum ether = 1 : 2); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ:

7.39-7.04 (m, 2H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.49 (d, *J* = 9.5 Hz, 1H), 6.07 (dt, *J* = 9.2, 4.1 Hz, 1H), 4.40 (s, 2H), 2.22 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 169.3, 137.5, 131.8, 127.2, 126.9, 125.1, 123.6, 41.4, 22.1 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{11}H_{11}ClNO$ $(M + H)^+$: 208.0529 found 208.0534.



1p

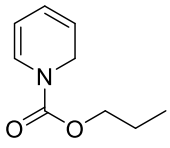
1-(6-bromo-7-methylquinolin-1(2*H*)-yl)ethan-1-one (1p). The general procedure A was followed using 6-bromo-7-methylquinoline (1.11 g, 5.0 mmol, 1.0 equiv.). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 3) afforded product **1q** as a colorless oil (0.80 g, 60 % yield): R_f = 0.4 (ethyl acetate : petroleum ether = 1 : 2); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.28 (s, 2H), 6.45 (d, *J* = 9.5 Hz, 1H), 6.08 (dt, *J* = 8.9, 4.0 Hz, 1H), 4.42 (s, 2H), 2.39 (s, 3H), 2.21 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 169.7, 136.5, 136.0, 129.6, 128.5, 125.9, 125.0, 120.9, 41.2, 23.0, 22.4 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{12}H_{13}BrNO$ $(M + H)^+$: 266.0181, found 266.0184.



1q

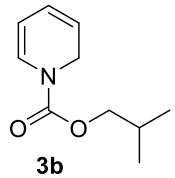
1-(6-iodoquinolin-1(2*H*)-yl)ethan-1-one (1q). The general procedure A was followed using 6-iodoquinoline (1.28 g, 5.0 mmol, 1.0 equiv.). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 3) afforded product **1q** as a colorless oil (0.96 g, 64 % yield): R_f = 0.4 (ethyl acetate : petroleum ether = 1 : 2); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.51 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.43 (d, *J* = 1.9 Hz, 1H), 6.92 (s, 1H), 6.44 (d, *J* = 9.6 Hz, 1H), 6.12 (dt, *J* = 8.9, 4.0 Hz, 1H), 4.43 (s, 2H), 2.20 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 169.5, 136.4, 135.6, 134.8, 131.0, 129.1, 125.5, 125.0, 89.3, 41.4, 22.3 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{11}H_{11}INO$ $(M + H)^+$: 299.9885, found299.9895.

2.2 Synthesis of 1,2-Dihydropyridine



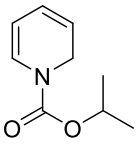
3a

propyl pyridine-1(2*H*)-carboxylate



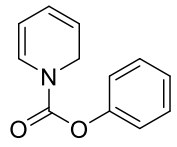
3b

isobutyl pyridine-1(2*H*)-carboxylate



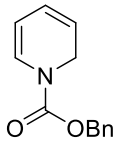
3c

isopropyl pyridine-1(2*H*)-carboxylate



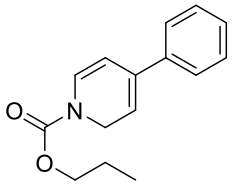
3d

phenyl pyridine-1(2*H*)-carboxylate



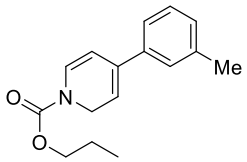
3e

benzyl pyridine-1(2*H*)-carboxylate



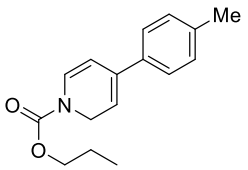
3f

propyl 4-phenylpyridine-1(2*H*)-carboxylate



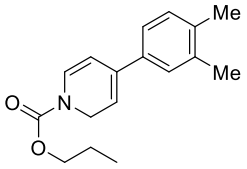
3g

propyl 4-(*m*-tolyl)pyridine-1(2*H*)-carboxylate



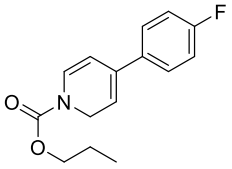
3h

propyl 4-(*p*-tolyl)pyridine-1(2*H*)-carboxylate



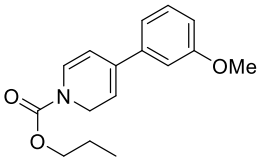
3i

propyl 4-(3,4-dimethylphenyl)pyridine-1(2*H*)-carboxylate



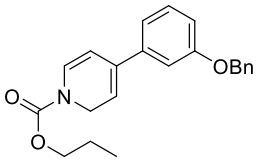
3j

propyl 4-(4-fluorophenyl)pyridine-1(2*H*)-carboxylate



3k

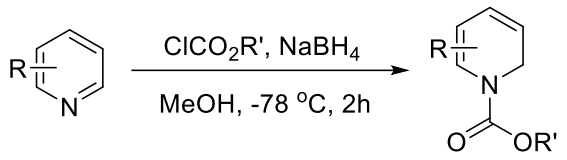
propyl 4-(3-methoxyphenyl)pyridine-1(2*H*)-carboxylate



3l

propyl 4-(3-(benzyloxy)phenyl)pyridine-1(2*H*)-carboxylate

The 4-arylpyridines were synthesized through the standard Suzuki-Miyaura coupling reaction of 4-bromopyridine and the corresponding arylboronic acids according to the literature procedure. (General procedure B)[3]

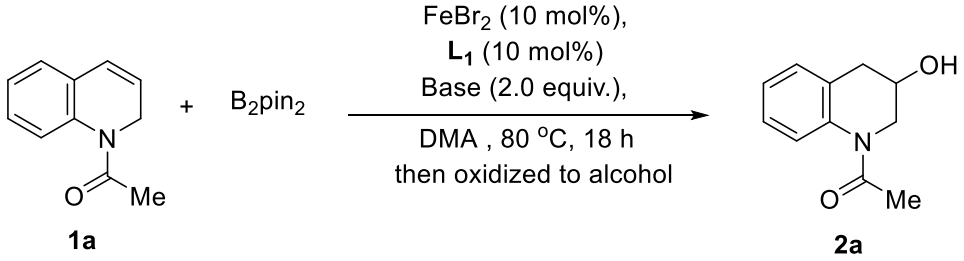


3

Chloroformate (30.0 mmol, 1.0 equiv.) was added dropwise under nitrogen to a MeOH solution (100.0 mL) of $NaBH_4$ (567.0 mg, 15.0 mmol, 0.5 equiv.), pyridine (2.4 mL, 30.0 mmol, 1.0 equiv.) at −78 °C. The reaction was maintained at -78 ℃ for 2 h and then quenched by water. The mixture was extracted with CH_2Cl_2 three times. The combined organic layer was then dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by a short pad of silica gel with ethyl acetate : petroleum ether (1 : 20) as an eluent. The solvent was removed by evaporation under reduced pressure to obtain **3** as a clear liquid, which was immediately used in the next borylation reaction in order to prevent decomposition.

3. **The effect of different reaction conditions**

Table S1. The effect of different bases. [a]

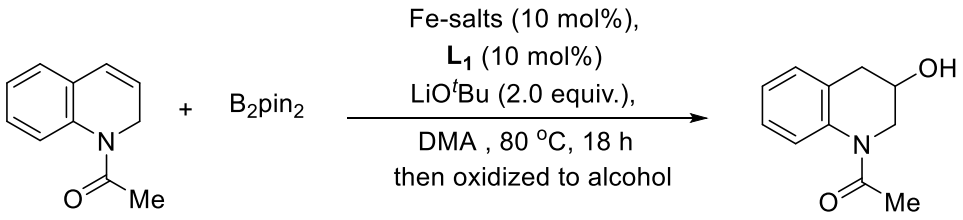


1a **2a**

Entry	Bases	Yield (%)[b]
1	LiO^{t}Bu	87
2	NaO^{t}Bu	51
3	KO^{t}Bu	75
4	Li_2CO_3	trace
5	LiOMe	60
6	LiOAc	0

[a] Standard conditions: **1a** (0.2 mmol), B_2pin_2 (0.4 mmol), $FeBr_2$ (0.02 mmol), **L$_1$** (0.02 mmol), Base (0.4 mmol), DMA (1.0 mL), at 80 °C for 18 h. Then $NaBO_3 \cdot 4H_2O$ (0.6 mmol), THF (2 mL), H_2O (2 mL), 25 °C, 3 h. [b] isolated yield.

Table S2. The effect of different [Fe]-salts. [a]

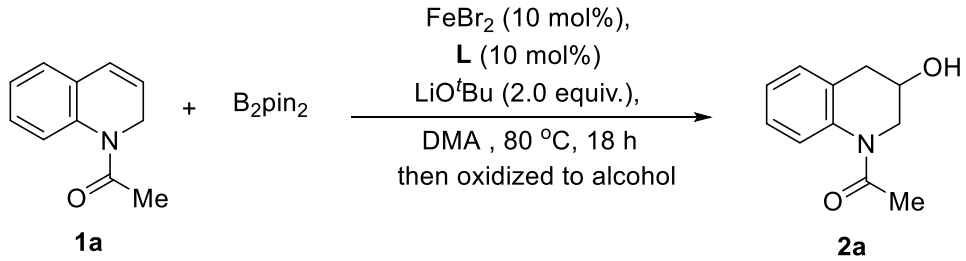


1a **2a**

Entry	Fe-salts	Yield (%)[b]
1	$FeBr_2$	87
2	$FeBr_3$	58
3	$FeCl_3$	70
4	$Fe(acac)_2$	0
5	$FeCl_2$	74
6	$Fe(OTs)_2$	68
7	$Fe(OTs)_3$	43
8	$Fe(acac)_3$	47

[a] Standard conditions: **1a** (0.2 mmol), B_2pin_2 (0.4 mmol), Fe-salts (0.02 mmol), $\mathbf{L_1}$ (0.02 mmol), LiO^tBu (0.4 mmol), DMA (1.0 mL), at 80 °C for 18 h. Then $NaBO_3 \cdot 4H_2O$ (0.6 mmol), THF (2 mL), H_2O (2 mL), 25 °C, 3 h. [b] isolated yield.

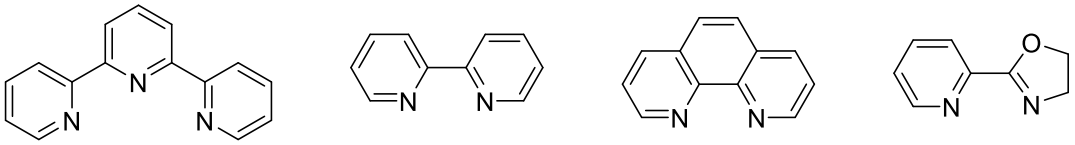
Table S3. The effect of different ligands. [a]



1a **2a**

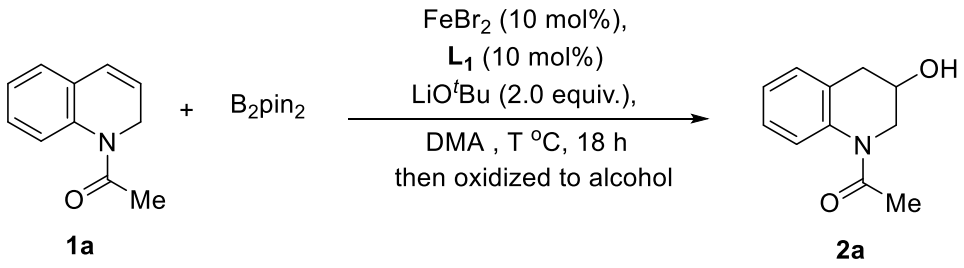
Entry	Ligands	Yield (%)[b]
1	L_1	87
2	L_2	45
3	L_3	69
4	L_4	60

[a] Standard conditions: **1a** (0.2 mmol), B_2pin_2 (0.4 mmol), $FeBr_2$ (0.02 mmol), **L** (0.02 mmol), LiO^tBu (0.4 mmol), DMA (1.0 mL), at 80 °C for 18 h. Then $NaBO_3 \cdot 4H_2O$ (0.6 mmol), THF (2 mL), H_2O (2 mL), 25 °C, 3 h.
[b] isolated yield.



L_1 L_2 L_3 L_4

Table S4. The effect of different temperature. [a]



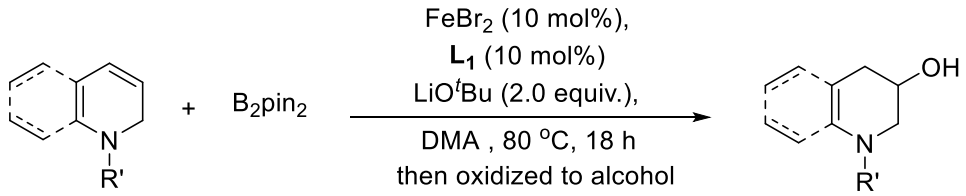
1a **2a**

Entry	Temperature (°C)	Yield (%)[b]
1	40	28
2	60	62
3	70	84
4	80	87
5	90	78
6	100	58

[a] Standard conditions: **1a** (0.2 mmol), B_2pin_2 (0.4 mmol), $FeBr_2$ (0.02 mmol), $\mathbf{L_1}$ (0.02 mmol), LiO^{t}Bu (0.4 mmol), DMA (1.0 mL), at T °C for 18 h. Then $NaBO_3 \cdot 4H_2O$ (0.6 mmol), THF (2 mL), H_2O (2 mL), 25 °C, 3 h. [b] isolated yield.

4. General procedure for the reaction

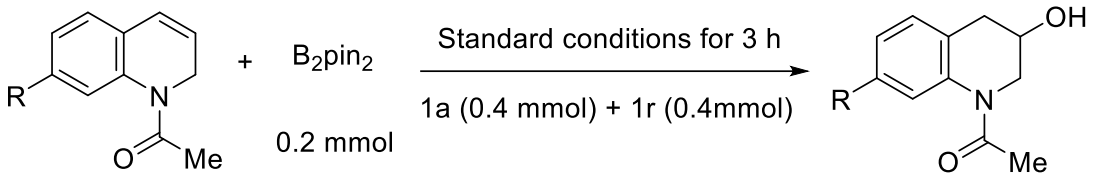
General procedure (C) :



1 or 3 **2 or 4**

In an oven dried 10-mL Schlenk tube, which contained a stirring bar, was charged with $FeBr_2$ (4.3 mg, 0.02 mmol, 10 mol%), **L_1** (4.7 mg, 0.02 mmol, 10 mol%), B_2pin_2 (102 mg, 0.4 mmol, 2.0 equiv), and LiO^tBu (32 mg, 0.4 mmol, 2.0 equiv.). The tube was evacuated and back-filled under a N_2 flow (this sequence was repeated three times), then anhydrous DMA (1.0 mL) was added under N_2. The tube was stirred at 25 ℃ for 60 min. After above, **1** or **3** (0.2 mmol, 1.0 equiv.) was added subsequently under N_2, the tube was stirred at 80 ^oC for 18 h. Then, the reaction mixture was diluted with EtOAc (2.0 mL), and it was extracted with EtOAc (2 mL × 3). The organic layer was combined and dried over Na_2SO_4, filtered and concentrated in vacuo to get the crude product. Then the crude product was dissolved in THF (2.0 mL), $NaBO_3$ $4H_2O$ (92.3 mg, 0.6 mmol, 3.0 equiv.) and H_2O (2.0 mL) were added, the resulting mixture was allowed to stir at 25 ℃ for three hours. The reaction mixture diluted with EtOAc (2.0 mL) and H_2O (2.0 mL), then it was extracted with EtOAc (2.0 mL × 3), the organic layer was combined, washed with brine and dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel chromatography (ethyl acetate/petroleum ether) to afford the product **2** or **4**.

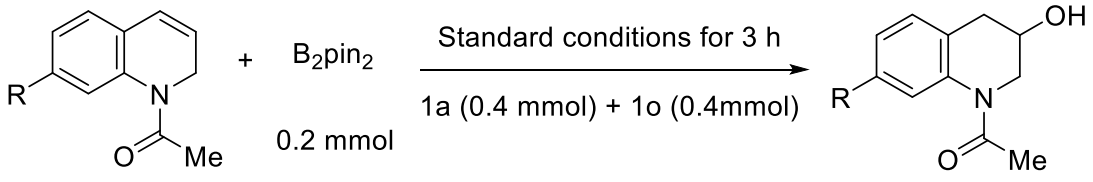
5. The effect of substituent electricity.



1a: R = H
1r: R = OMe

2a : **2r** =4.8 : 1
32% : 7%

In an oven dried 10-mL Schlenk tube, which contained a stirring bar, was charged with $FeBr_2$ (4.3 mg, 0.02 mmol, 10 mol%), $\mathbf{L_1}$ (4.7 mg, 0.02 mmol, 10 mol%), B_2pin_2 (51 mg, 0.2 mmol, 1.0 equiv), and LiO^tBu (16 mg, 0.2 mmol, 1.0 equiv.). The tube was evacuated and back-filled under a N_2 flow (this sequence was repeated three times), then anhydrous DMA (1.0 mL) was added under N_2. The tube was stirred at 25 ℃ for 60 min. After above, **1a** (69.2 mg, 0.4 mmol, 2.0 equiv.) and **1r** (81.3 mg, 0.4 mmol, 2.0 equiv.) was added subsequently under N_2, the tube was stirred at 80 ^oC for 3 h. Then, the reaction mixture was diluted with EtOAc (2.0 mL), and it was extracted with EtOAc (2 mL× 3). The organic layer was combined and dried over Na_2SO_4, filtered and concentrated in vacuo to get the crude product. Then the crude product was dissolved in THF (2.0 mL), $NaBO_3 \cdot 4H_2O$ (0.6 mmol) and H_2O (2.0 mL) were added, the resulting mixture was allowed to stir at 25 ℃ for three hours. The reaction mixture diluted with EtOAc (2.0 mL) and H_2O (2.0 mL), then it was extracted with EtOAc (2.0 mL × 3), the organic layer was combined, washed with brine and dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel chromatography (ethyl acetate : petroleum ether = 1 : 1) to afford the product **2a** (12.3 mg, 32% yield) and **2r** (3.1 mg, 7% yield).



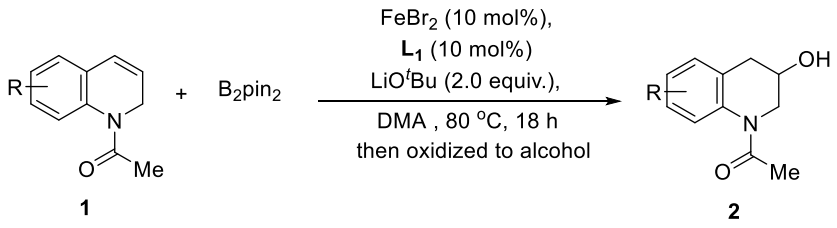
1a: R = H
1o: R = Br

2a : **2o** = 1 : 8.3
7% : 58%

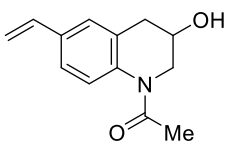
In an oven dried 10-mL Schlenk tube, which contained a stirring bar, was charged with $FeBr_2$ (4.3 mg, 0.02 mmol, 10 mol%), $\mathbf{L_1}$ (4.7 mg, 0.02 mmol, 10 mol%), B_2pin_2 (51 mg, 0.2 mmol, 1.0 equiv), and LiO^tBu (16 mg, 0.2 mmol, 1.0 equiv.). The tube was evacuated and back-filled under a N_2 flow (this sequence was repeated three times), then anhydrous DMA (1.0 mL) was added under N_2. The tube was stirred at 25 ℃ for 60 min. After above, **1a** (69.2 mg, 0.4 mmol, 2.0 equiv.) and **1o** (100.8 mg, 0.4 mmol, 2.0 equiv.) was added subsequently under N_2, the tube was stirred at 80 ^oC for 3 h. Then, the reaction mixture was diluted with EtOAc (2.0 mL), and it was extracted with EtOAc (2 mL× 3). The organic layer was combined and dried over Na_2SO_4, filtered and concentrated in vacuo to get the crude product. Then the crude product was dissolved in THF (2.0 mL), $NaBO_3 \cdot 4H_2O$ (0.6 mmol) and H_2O (2.0 mL) were added, the resulting mixture was allowed to stir at 25 ℃ for three hours. The reaction mixture diluted with EtOAc (2.0 mL) and H_2O (2.0 mL), then it was extracted with EtOAc (2.0 mL × 3), the organic layer was combined, washed with brine and dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by

silica gel chromatography (ethyl acetate : petroleum ether = 1 : 1) to afford the product **2a** (2.7 mg, 7% yield) and **2o** (31,3 mg, 58% yield).

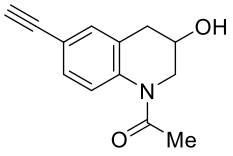
6. Unsuccessful substrates



1 **2**



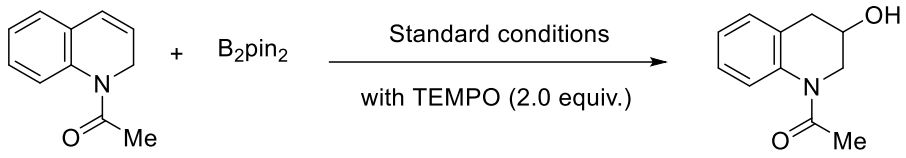
2s:Trace



2t:NR

[a] Standard conditions: **1** (0.2 mmol), B_2pin_2 (0.4 mmol), $FeBr_2$ (0.02 mmol), $\mathbf{L_1}$ (0.02 mmol), LiO^tBu (0.4 mmol), DMA (1.0 mL), at 80 °C for 18 h. Then $NaBO_3 \cdot 4H_2O$ (0.6 mmol), THF (2 mL), H_2O (2 mL), 25 °C, 3 h. [b] isolated yield.

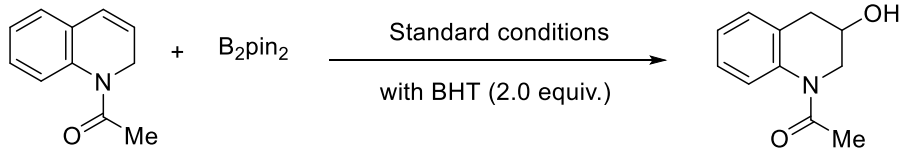
7. Radical traping experiments.



1a **2a**

24% yield

In an oven dried 10-mL Schlenk tube, which contained a stirring bar, was charged with $FeBr_2$ (4.3 mg, 0.02 mmol, 10 mol%), **L_1** (4.7 mg, 0.02 mmol, 10 mol%), B_2pin_2 (102 mg, 0.4 mmol, 2.0 equiv), and LiO^tBu (32 mg, 0.4 mmol, 2.0 equiv.). The tube was evacuated and back-filled under a N_2 flow (this sequence was repeated three times), then anhydrous DMA (1.0 mL) was added under N_2. The tube was stirred at 25 ℃ for 60 min. After above, **1a** (34.6 mg, 0.2 mmol, 1.0 equiv.) and 2,2,6,6-Tetramethylpiperidine 1-oxyl (TEMPO) (62.6 mg, 0.4 mmol, 2.0 equiv.) was added subsequently under N_2, the tube was stirred at 80 ^oC for 18 h. Then, the reaction mixture was diluted with EtOAc (2.0 mL), and it was extracted with EtOAc (2 mL × 3). The organic layer was combined and dried over Na_2SO_4, filtered and concentrated in vacuo to get the crude product. Then the crude product was dissolved in THF (2.0 mL), $NaBO_3 \cdot 4H_2O$ (0.6 mmol) and H_2O (2.0 mL) were added, the resulting mixture was allowed to stir at 25 ℃ for three hours. The reaction mixture diluted with EtOAc (2.0 mL) and H_2O (2.0 mL), then it was extracted with EtOAc (2.0 mL × 3), the organic layer was combined, washed with brine and dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel chromatography (ethyl acetate : petroleum ether = 1 : 1) to afford the product **2a** (9.2 mg, 24% yield).

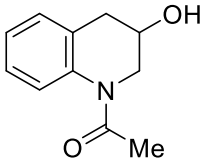


1a **2a**

78% yield

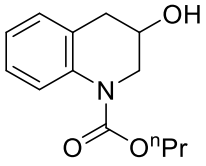
In an oven dried 10-mL Schlenk tube, which contained a stirring bar, was charged with $FeBr_2$ (4.3 mg, 0.02 mmol, 10 mol%), **L1** (4.7 mg, 0.02 mmol, 10 mol%), B_2pin_2 (102 mg, 0.4 mmol, 2.0 equiv), and LiO^tBu (32 mg, 0.4 mmol, 2.0 equiv.). The tube was evacuated and back-filled under a N_2 flow (this sequence was repeated three times), then anhydrous DMA (1.0 mL) was added under N_2. The tube was stirred at 25 ℃ for 60 min. After above, **1a** (34.6 mg, 0.2 mmol, 1.0 equiv.) and 2,6-di-tert-butyl-4-methylphenol (BHT) (88.1 mg, 0.4 mmol, 2.0 equiv.) was added subsequently under N_2, the tube was stirred at 80 ^oC for 18 h. Then, the reaction mixture was diluted with EtOAc (2.0 mL), and it was extracted with EtOAc (2 mL × 3). The organic layer was combined and dried over Na_2SO_4, filtered and concentrated in vacuo to get the crude product. Then the crude product was dissolved in THF (2.0 mL), $NaBO_3 \cdot 4H_2O$ (92.3 mg, 0.6 mmol, 3.0 equiv.) and H_2O (2.0 mL) were added, the resulting mixture was allowed to stir at 25 ℃ for three hours. The reaction mixture diluted with EtOAc (2.0 mL) and H_2O (2.0 mL), then it was extracted with EtOAc (2.0 mL × 3), the organic layer was combined, washed with brine and dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel chromatography (ethyl acetate : petroleum ether = 1 : 1) to afford the product **2a** (29.8 mg, 78% yield).

8. Analytical data for compounds



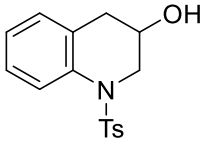
2a

1-(3-hydroxy-3,4-dihydroquinolin-1(2*H*)-yl)ethan-1-one (2a). The general procedure C was followed using 1-(quinolin-1(2*H*)-yl)ethan-1-one (**1a**, 34.6 mg, 0.2 mmol). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 1) afforded product **2a** as a colorless oil (33.3 mg, 87 % yield): R_f = 0.2 (ethyl acetate : petroleum ether = 1 : 1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.34-7.01 (m, 4H), 4.41-4.23 (m, 1H), 4.00-3.72 (m, 2H), 3.42 (s, 1H), 3.07 (dd, *J* = 16.3, 5.0 Hz, 1H), 2.79 (dd, *J* = 16.5, 5.3 Hz, 1H), 2.24 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 170.9, 138.7, 129.9, 129.5, 126.2, 125.6, 124.2, 65.8, 49.5, 35.7, 22.8 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{11}H_{14}NO_2$ $(M + H)^+$: 191.1024, found 191.1028.



2b

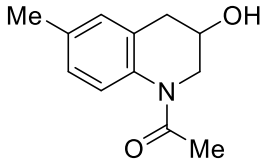
propyl 3-hydroxy-3,4-dihydroquinoline-1(2*H*)-carboxylate (2b). The general procedure C was followed using propyl quinoline-1(2*H*)-carboxylate (**1b**, 43.5 mg, 0.2 mmol). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 1) afforded product **2b** as a colorless oil (43.3 mg, 92 % yield): R_f = 0.5 (ethyl acetate : petroleum ether = 1 : 1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.66 (d, *J* = 8.1 Hz, 1H), 7.21-7.15 (m, 1H), 7.11 (d, *J* = 6.6 Hz, 1H), 7.04 (m, 1H), 4.27 (m, 1H), 4.15 (t, *J* = 6.7 Hz, 2H), 3.86-3.74 (m, 2H), 3.09 (dd, *J* = 16.5, 5.2 Hz, 1H), 2.81 (dd, *J* = 16.5, 5.5 Hz, 1H), 2.26 (d, *J* = 4.6 Hz, 1H), 1.70 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 155.4, 137.6, 129.4, 126.6, 126.2, 124.1, 123.8, 67.8, 64.9, 50.4, 36.0, 22.2, 10.5 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{18}NO_3$ $(M + H)^+$: 236.1287, found 236.1295.



2c

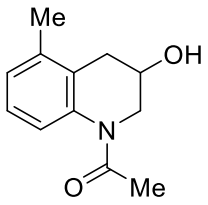
1-tosyl-1,2,3,4-tetrahydroquinolin-3-ol (2c). The general procedure C was followed using 1-tosyl-1,2-dihydroquinoline (**1c**, 57.1 mg, 0.2 mmol). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 1) afforded product **2c** as a colorless oil (46.1 mg, 72 % yield): R_f = 0.5 (ethyl acetate : petroleum ether = 1 : 2); **^{1}H NMR** ($CDCl_3$, 600 MHz) δ: 7.70 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.21 (dd, *J* = 22.9, 8.1 Hz, 3H), 7.11-7.03 (m, 2H), 4.06-4.01 (m, 2H), 3.62 (dd, *J* = 14.3, 8.1 Hz, 1H), 2.77 (dd, *J* = 16.2, 5.2 Hz, 1H), 2.53 (dd, *J* = 16.2, 6.5 Hz, 1H), 2.39 (s, 3H), 1.90 (s, 1H); **^{13}C NMR** ($CDCl_3$, 151 MHz) δ: 143.8, 136.6, 136.1, 129.8, 129.7, 127.5, 127.0, 127.0, 125.1, 123.6, 64.1, 52.1, 35.8, 21.6 ppm;

HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{18}NO_3S$ $(M + H)^+$: 304.1007, found 304.1010.



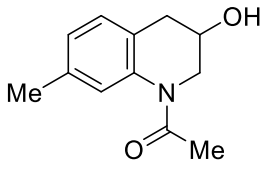
2d

1-(3-hydroxy-6-methyl-3,4-dihydroquinolin-1(2*H*)-yl)ethan-1-one (2d). The general procedure C was followed using 1-(6-methylquinolin-1(2*H*)-yl)ethan-1-one (**1d**, 37.5 mg, 0.2 mmol). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 1) afforded product **2d** as a colorless oil (35.7 mg, 87 % yield): R_f = 0.2 (ethyl acetate : petroleum ether = 1 : 1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 6.98 (d, *J* = 5.9 Hz, 3H), 4.27-4.19 (m, 1H), 4.18-3.76 (m, 2H), 3.71 (dd, *J* = 12.9, 5.7 Hz, 1H), 2.99 (dt, *J* = 17.5, 5.7 Hz, 1H), 2.73 (dd, *J* = 16.4, 5.6 Hz, 1H), 2.30 (s, 3H), 2.21 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 170.6, 136.0, 135.1, 129.6, 126.5, 123.6, 65.5, 49.3, 35.5, 22.4, 20.6 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{12}H_{16}NO_2$ $(M + H)^+$: 206.1181, found 206.1190.



2e

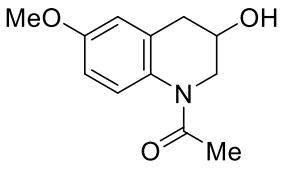
1-(3-hydroxy-5-methyl-3,4-dihydroquinolin-1(2*H*)-yl)ethan-1-one (2e). The general procedure C was followed using 1-(5-methylquinolin-1(2*H*)-yl)ethan-1-one (**1e**, 37.5 mg, 0.2 mmol). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 1) afforded product **2e** as a colorless oil (27.1 mg, 66 % yield): R_f = 0.2 (ethyl acetate : petroleum ether = 1 : 1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.27-6.87 (m, 3H), 4.33 (h, *J* = 4.9 Hz, 1H), 4.01-3.70 (m, 2H), 2.98 (dd, *J* = 17.3, 6.0 Hz, 1H), 2.79 (s, 1H), 2.67 (dd, *J* = 17.3, 5.0 Hz, 1H), 2.25 (d, *J* = 5.8 Hz, 6H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 171.2, 138.8, 137.5, 127.0, 125.6, 122.2, 65.6, 48.8, 33.6, 22.8, 19.4 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{12}H_{16}NO_2$ $(M + H)^+$: 206.1181 found 206.1185.



2f

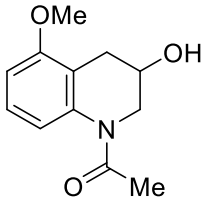
1-(3-hydroxy-7-methyl-3,4-dihydroquinolin-1(2*H*)-yl)ethan-1-one (2f). The general procedure C was followed using 1-(7-methylquinolin-1(2H)-yl)ethan-1-one (**1f**, 37.5 mg, 0.2 mmol). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 1) afforded product **2f** as a colorless oil (30.0 mg, 73 % yield): R_f = 0.2 (ethyl acetate : petroleum ether = 1 : 1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.01 (dd, *J* = 41.4, 7.6 Hz, 3H), 4.29 (p, *J* = 5.0 Hz, 1H), 3.83 (q, *J* = 13.1, 7.4 Hz, 2H), 3.15-2.84 (m, 2H), 2.75 (dd, *J* = 16.3, 5.2 Hz, 1H), 2.33 (s,

3H), 2.25 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 170.9, 138.6, 138.5, 136.0, 129.2, 126.4, 124.8, 66.0, 49.7, 35.4, 22.8, 21.2 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{12}H_{16}NO_2$ $(M + H)^+$: 206.1181, found 206.1180.



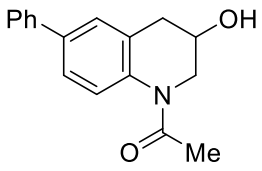
2g

1-(3-hydroxy-6-methoxy-3,4-dihydroquinolin-1(2*H*)-yl)ethan-1-one (2g). The general procedure C was followed using 1-(6-methoxyquinolin-1(2*H*)-yl)ethan-1-one (**1g**, 40.6 mg, 0.2 mmol). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 1) afforded product **2g** as a colorless oil (33.8 mg, 80 % yield): R_f = 0.2 (ethyl acetate : petroleum ether = 1 : 1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.03 (s, 1H), 6.82-6.61 (m, 2H), 4.37-4.27 (m, 1H), 3.79 (m, 5H), 3.02 (d, *J* = 13.8 Hz, 1H), 2.86-2.55 (m, 2H), 2.21 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 170.9, 157.4, 132.1, 131.6, 125.1, 114.1, 112.0, 66.2, 55.4, 49.6, 36.0, 22.5 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{12}H_{16}NO_3$ $(M + H)^+$: 222.1130, found 222.1124.



2h

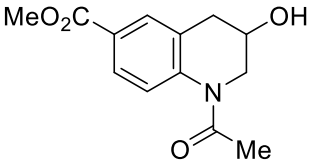
1-(3-hydroxy-5-methoxy-3,4-dihydroquinolin-1(2*H*)-yl)ethan-1-one (2h). The general procedure C was followed using 1-(5-methoxyquinolin-1(2*H*)-yl)ethan-1-one (**1h**, 40.6 mg, 0.2 mmol). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 1) afforded product **2h** as a colorless oil (19.9 mg, 45 % yield): R_f = 0.2 (ethyl acetate : petroleum ether = 1:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.16 (t, *J* = 8.2 Hz, 1H), 6.68 (d, *J* = 8.3 Hz, 2H), 4.28 (t, *J* = 6.8 Hz, 1H), 3.83 (s, 5H), 3.00 (dd, *J* = 18.0, 6.1 Hz, 1H), 2.79 (s, 1H), 2.70 (dd, *J* = 18.0, 4.6 Hz, 1H), 2.26 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 171.3, 157.6, 139.6, 126.1, 118.0, 116.8, 106.6, 65.0, 55.5, 48.9, 30.4, 23.0 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{12}H_{16}NO_3$ $(M + H)^+$: 222.1130, found 222.1128.



2i

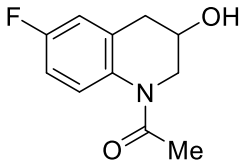
1-(3-hydroxy-6-phenyl-3,4-dihydroquinolin-1(2*H*)-yl)ethan-1-one (2i). The general procedure C was followed using 1-(6-phenylquinolin-1(2*H*)-yl)ethan-1-one (**1i**, 49.9 mg, 0.2 mmol). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 1) afforded product **2i** as a colorless oil (37.2 mg, 70 % yield): R_f = 0.2 (ethyl acetate : petroleum ether = 1 : 1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.55 (d, *J* = 7.3 Hz, 2H), 7.50-7.25 (m, 6H), 4.33 (q,

J = 4.6 Hz, 1H), 3.87 (s, 2H), 3.34-3.06 (m, 2H), 2.86 (dd, *J* = 16.5, 5.1 Hz, 1H), 2.28 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 171.2, 140.3, 138.7, 138.0, 129.0, 128.2, 127.5, 127.0, 125.1, 124.7, 65.9, 49.9, 36.1, 23.1 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{17}H_{18}NO_2$ $(M + H)^+$: 268.1338 found 268.1333.



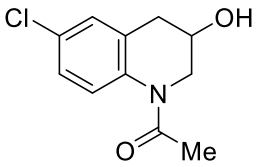
2j

methyl 1-acetyl-3-hydroxy-1,2,3,4-tetrahydroquinoline-6-carboxylate (2j). The general procedure C was followed using methyl 1-acetyl-1, 2-dihydroquinoline-6-carboxylate (**1j**, 46.3 mg, 0.2 mmol). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 1) afforded product **2j** as a colorless oil (20.9 mg, 42 % yield): R_f = 0.2 (ethyl acetate : petroleum ether = 1 : 1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.83 (d, *J* = 8.9 Hz, 2H), 7.37 (d, *J* = 9.4 Hz, 1H), 4.26 (m, 1H), 3.89 (s, 4H), 3.78 (d, *J* = 4.9 Hz, 2H), 3.07 (dd, *J* = 16.7, 5.4 Hz, 1H), 2.82 (dd, *J* = 16.7, 5.2 Hz, 1H), 2.25 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 170.9, 166.4, 142.3, 130.9, 128.8, 127.3, 126.4, 125.9, 64.7, 52.0, 50.2, 35.6, 23.1 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{16}NO_4$ $(M + H)^+$: 250.1079, found 250.1077.



2k

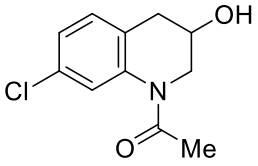
1-(6-fluoro-3-hydroxy-3,4-dihydroquinolin-1(2*H*)-yl)ethan-1-one (2k). The general procedure C was followed using 1-(6-fluoroquinolin-1(2*H*)-yl)ethan-1-one (**1k**, 38.2 mg, 0.2 mmol). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 1) afforded product **2k** as a colorless oil (36.8 mg, 88 % yield): R_f = 0.2 (ethyl acetate : petroleum ether = 1 : 1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.21-6.66 (m, 3H), 4.31 (q, *J* = 4.4 Hz, 1H), 3.85 (s, 2H), 3.05 (d, *J* = 11.5 Hz, 2H), 2.79 (dd, *J* = 16.8, 4.4 Hz, 1H), 2.22 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 170.9, 161.3, 158.2, 134.6, 132.3, 125.7, 116.0, 113.0, 65.4, 49.5, 35.8, 22.6 ppm; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ: -116.31, -117.43; **HRMS** (ESI-TOF) *m/z* calcd for $C_{11}H_{13}FNO_2$ $(M + H)^+$: 210.0930, found 210.0920.



2l

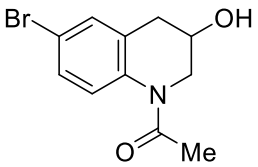
1-(6-chloro-3-hydroxy-3,4-dihydroquinolin-1(2*H*)-yl)ethan-1-one (2l). The general procedure C was followed using 1-(6-chloroquinolin-1(2*H*)-yl)ethan-1-one (**1l**, 41.5 mg, 0.2 mmol). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 1) afforded product **2l** as a colorless oil (38.8 mg, 86 % yield): R_f = 0.2 (ethyl acetate : petroleum

ether = 1 : 1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.33-6.92 (m, 3H), 4.26 (p, *J* = 4.6 Hz, 1H), 3.81 (dd, *J* = 12.0, 4.9 Hz, 2H), 3.56 (s, 1H), 3.02 (dd, *J* = 16.7, 5.0 Hz, 1H), 2.76 (dd, *J* = 16.8, 4.8 Hz, 1H), 2.22 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 170.9, 137.0, 131.7, 130.7, 129.1, 126.1, 125.4, 65.0, 49.3, 35.5, 22.8 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{11}H_{13}ClNO_2$ $(M + H)^+$: 226.0625, found 226.0637.



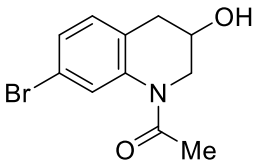
2m

1-(7-chloro-3-hydroxy-3,4-dihydroquinolin-1(2*H*)-yl)ethan-1-one (2m). The general procedure C was followed using 1-(7-chloroquinolin-1(2*H*)-yl)ethan-1-one (**1m**, 41.5 mg, 0.2 mmol). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 1) afforded product **2m** as a colorless oil (31.6 mg, 70 % yield): R_f = 0.2 (ethyl acetate : petroleum ether = 1 : 1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.18 (d, *J* = 81.3 Hz, 3H), 4.26 (m, 1H), 3.78 (dt, *J* = 23.3, 11.7 Hz, 3H), 3.02 (dd, *J* = 16.7, 5.4 Hz, 1H), 2.75 (dd, *J* = 16.8, 4.9 Hz, 1H), 2.24 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 170.9, 139.2, 131.3, 130.4, 125.4, 124.2, 65.0, 49.6, 35.2, 22.9 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{11}H_{13}ClNO_2$ $(M + H)^+$: 226.0635, found 226.0631.



2n

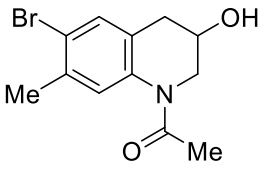
1-(6-bromo-3-hydroxy-3,4-dihydroquinolin-1(2*H*)-yl)ethan-1-one (2n). The general procedure C was followed using 1-(6-bromoquinolin-1(2*H*)-yl)ethan-1-one (**1n**, 50.4 mg, 0.2 mmol). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 1) afforded product **2n** as a colorless oil (44.3 mg, 82 % yield): R_f = 0.2 (ethyl acetate : petroleum ether = 1 : 1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.42-6.92 (m, 3H), 4.32-4.22 (m, 1H), 3.91-3.62 (m, 2H), 3.38 (s, 1H), 3.03 (dd, *J* = 16.8, 5.1 Hz, 1H), 2.77 (dd, *J* = 16.8, 4.7 Hz, 1H), 2.22 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 170.9, 137.6, 132.1, 129.1, 125.8, 118.5, 65.1, 49.5, 35.4, 22.8 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{11}H_{13}BrNO_2$ $(M + H)^+$: 270.0130, found 270.0135.



2o

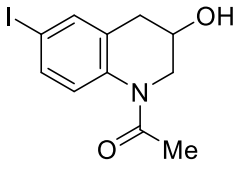
1-(7-bromo-3-hydroxy-3,4-dihydroquinolin-1(2*H*)-yl)ethan-1-one (2o). The general procedure C was followed using 1-(7-bromoquinolin-1(2*H*)-yl)ethan-1-one (**1o**, 50.4 mg, 0.2 mmol). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 1) afforded product **2o** as a colorless oil (35.7 mg, 66 % yield): R_f = 0.2 (ethyl acetate : petroleum

ether = 1 : 1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.74-7.11 (m, 2H), 7.02 (d, *J* = 8.0 Hz, 1H), 4.27 (h, *J* = 4.9 Hz, 1H), 3.84-3.65 (m, 2H), 3.54 (s, 1H), 3.00 (dd, *J* = 16.8, 5.4 Hz, 1H), 2.74 (dd, *J* = 16.8, 4.9 Hz, 1H), 2.25 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 170.9, 139.7, 130.8, 128.3, 127.1, 119.0, 65.0, 49.8, 35.3, 22.9 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{11}H_{13}BrNO_2$ $(M + H)^+$: 270.0130, found 270.0134.



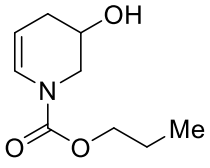
2p

1-(6-bromo-3-hydroxy-7-methyl-3,4-dihydroquinolin-1(2*H*)-yl)ethan-1-one (2p). The general procedure C was followed using 1-(6-bromo-7-methylquinolin-1(2*H*)-yl)ethan-1-one (**1p**, 53.2 mg, 0.2 mmol). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 1) afforded product **2p** as a colorless oil (36.4 mg, 64 % yield): R_f = 0.2 (ethyl acetate : petroleum ether = 1 : 1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.30 (d, *J* = 10.2 Hz, 2H), 4.26-4.19 (m, 1H), 3.75 (s, 3H), 2.98 (dd, *J* = 16.6, 5.1 Hz, 1H), 2.72 (dd, *J* = 16.6, 5.0 Hz, 1H), 2.35 (s, 3H), 2.22 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 170.8, 137.5, 135.5, 132.6, 129.0, 126.2, 121.0, 65.1, 49.8, 35.0, 22.9, 22.6 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{12}H_{15}BrNO_2$ $(M + H)^+$: 284.0286, found 284.0283.



2q

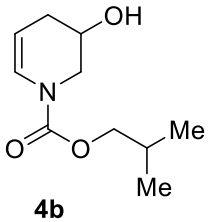
1-(3-hydroxy-6-iodo-3,4-dihydroquinolin-1(2*H*)-yl)ethan-1-one (2q). The general procedure C was followed using 1-(6-iodoquinolin-1(2*H*)-yl)ethan-1-one (**1q**, 59.8 mg, 0.2 mmol). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 1) afforded product **2q** as a colorless oil (45.0 mg, 71 % yield): R_f = 0.2 (ethyl acetate : petroleum ether = 1 : 1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.49 (d, *J* = 6.4 Hz, 2H), 6.95 (s, 1H), 4.25 (h, *J* = 4.8 Hz, 1H), 3.79 (dt, *J* = 17.3, 8.8 Hz, 2H), 3.48 (s, 1H), 3.00 (dd, *J* = 15.8, 6.2 Hz, 1H), 2.74 (dd, *J* = 16.8, 4.9 Hz, 1H), 2.22 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 170.8, 138.1, 135.0, 132.2, 126.0, 89.5, 64.9, 49.5, 35.2, 22.9 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{11}H_{13}INO_2$ $(M + H)^+$: 317.9991, found 317.9999.



4a

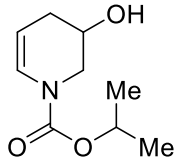
propyl 3-hydroxy-3,4-dihydropyridine-1(2*H*)-carboxylate (4a). The general procedure C was followed using propyl pyridine-1(2*H*)-carboxylate (**3a**, 33.5 mg, 0.2 mmol). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 3) afforded product

4a as a colorless oil (30.0 mg, 81 % yield): R_f = 0.4 (ethyl acetate : petroleum ether = 1 : 3); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 6.90 (d, *J* = 8.2 Hz, 0.5H), 6.79 (d, *J* = 8.2 Hz, 0.5H), 4.92-4.82 (m, 0.5H), 4.83-4.71 (m, 0.5H), 4.10 (t, *J* = 6.2 Hz, 3H), 3.71-3.49 (m, 2H), 3.03-2.91 (m, 0.5H), 2.85-2.71 (m, 0.5H), 2.37 (d, *J* = 17.3 Hz, 1H), 2.09 (d, *J* = 17.5 Hz, 1H), 1.69 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 154.1, 153.7, 125.2, 124.6, 102.8, 102.5 , 67.6, 67.5, 63.1, 47.8, 47.5, 30.1, 22.1, 10.3 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_9H_{16}NO_3$ $(M + H)^+$: 186.1130, found 186.1138.



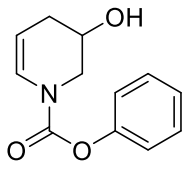
4b

isobutyl 3-hydroxy-3,4-dihydropyridine-1(2*H*)-carboxylate (4b). The general procedure C was followed using isobutyl pyridine-1(2*H*)-carboxylate (**3b**, 36.2 mg, 0.2 mmol). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 3) afforded product **4b** as a colorless oil (29.9 mg, 75 % yield): R_f = 0.4 (ethyl acetate : petroleum ether = 1 : 3); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 6.89 (d, *J* = 8.1 Hz, 0.5H), 6.79 (d, *J* = 8.2 Hz, 0.5H), 4.90-4.84 (m, 0.5H), 4.81 (dd, *J* = 7.8, 3.7 Hz, 0.5H), 4.12 (s, 1H), 3.92 (d, *J* = 6.7 Hz, 2H), 3.66 (t, *J* = 9.7 Hz, 1H), 3.55 (d, *J* = 6.8 Hz, 1H), 3.20 (s, 0.5H), 3.01 (s, 0.5H), 2.34 (s, 1H), 2.08 (d, *J* = 17.4 Hz, 1H), 1.96 (dt, *J* = 13.4, 6.7 Hz, 1H), 0.95 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 154.0, 153.7, 125.1, 124.5, 102.9, 102.5, 72.1, 71.9, 47.7, 47.5, 30.1, 27.7, 18.9 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{10}H_{18}NO_3$ $(M + H)^+$: 200.1287, found 200.1296.



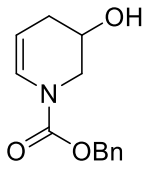
4c

isopropyl 3-hydroxy-3,4-dihydropyridine-1(2*H*)-carboxylate (4c). The general procedure C was followed using isopropyl pyridine-1(2*H*)-carboxylate (**3c**, 33.4 mg, 0.2 mmol). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 3) afforded product **4c** as a colorless oil (28.5 mg, 77 % yield): R_f = 0.4 (ethyl acetate : petroleum ether = 1 : 3); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 6.92 (d, *J* = 7.9 Hz, 0.5H), 6.84-6.76 (m, 0.5H), 4.98 (dq, J = 12.5, 6.2 Hz,1H), 4.90-4.81 (m, 0.5H), 4.80-4.69 (m, 0.5H), 4.14 (s, 1H), 3.67-3.55 (m, 2H), 2.55 (s, 0.5H), 2.37 (d, *J* = 17.4 Hz, 1.5H), 2.15-2.01 (m, 1H), 1.28 (d, *J* = 6.3 Hz, 6H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 153.6, 153.3, 125.3, 124.9, 102.3, 102.2, 69.7, 63.2, 47.8, 47.5, 30.2, 22.0 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_9H_{16}NO_3$ $(M + H)^+$: 186.1130, found 186.1133.



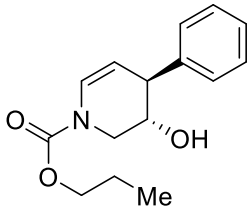
4d

phenyl 3-hydroxy-3,4-dihydropyridine-1(2*H*)-carboxylate (4d). The general procedure C was followed using phenyl pyridine-1(2*H*)-carboxylate (**3d**, 40.2 mg, 0.2 mmol). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 3) afforded product **4d** as a colorless oil (30.7 mg, 70 % yield): R_f = 0.4 (ethyl acetate : petroleum ether = 1 : 3); **^{1}H NMR** ($CDCl_3$, 600 MHz) δ: 7.37 (t, *J* = 7.9 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.15-7.12 (m, 2H), 6.99 (dt, *J* = 8.3, 1.9 Hz, 0.5H), 6.95-6.92 (m, 0.5H), 5.00-4.93 (m, 0.5H), 4.92 (dd, *J* = 8.2, 4.0 Hz, 0.5H), 4.19-4.15 (m, 1H), 3.86-3.70 (m, 1H), 3.68 (d, *J* = 4.6 Hz, 1H), 2.43-2.33 (m, 2H), 2.12 (dt, *J* = 16.9, 4.3 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 151 MHz) δ: 152.5, 152.1, 150.9, 150.8, 129.3, 125.7, 125.0, 124.6, 121.5, 104.1, 104.0, 63.0, 48.4, 47.8, 30.1 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{12}H_{14}NO_3$ $(M + H)^+$: 220.0974, found 220.0971.



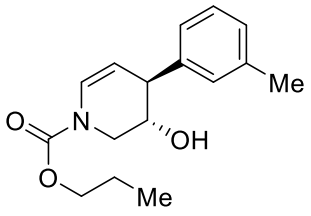
4e

benzyl 3-hydroxy-3,4-dihydropyridine-1(2*H*)-carboxylate (4e). The general procedure C was followed using benzyl pyridine-1(2*H*)-carboxylate (**3e**, 43.1 mg, 0.2 mmol). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 3) afforded product **4e** as a colorless oil (30.8 mg, 66 % yield): R_f = 0.4 (ethyl acetate : petroleum ether = 1 : 3); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.38-7.31 (m, 5H), 6.93 (d, *J* = 7.8 Hz, 0.5H), 6.82 (d, *J* = 8.0 Hz, 0.5H), 5.18 (d, *J* = 4.0 Hz, 2H), 4.81-4.76 (m, 1H), 4.13 (d, *J* = 13.7 Hz,1H), 3.63 (p, *J* = 11.2, 9.1 Hz, 2H), 2.38-2.05 (m, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 153.9, 153.5, 136.0, 128.5, 128.2, 128.1, 125.3, 124.8, 102.9, 102.8, 67.8, 67.6, 63.2, 63.1, 47.9, 47.7, 30.2 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{16}NO_3$ $(M + H)^+$: 234.1130, found 234,1140.



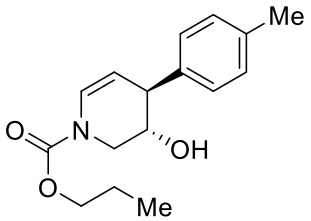
4f

propyl 3-hydroxy-4-phenyl-3,4-dihydropyridine-1(2*H*)-carboxylate (4f). The general procedure C was followed using propyl 4-phenylpyridine-1(2*H*)-carboxylate (**3f**, 48.7 mg, 0.2 mmol). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 3) afforded product **4f** as a colorless oil (38.2 mg, 73 % yield): R_f = 0.5 (ethyl acetate : petroleum ether = 1 : 3); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.35-7.23 (m, 5H), 7.13 (d, *J* = 8.0 Hz, 0.5H), 7.02 (d, *J* = 8.1 Hz, 0.5H), 4.89 (dd, *J* = 28.1, 6.5 Hz, 1H), 4.11 (d, *J* = 5.6 Hz, 2H), 3.87 (s, 1H), 3.65 (t, *J* = 10.3 Hz, 1H), 3.58-3.48 (m, 1H), 3.41 (s, 1H), 2.57 (dd, *J* = 36.6, 4.4 Hz, 1H), 1.69 (dq, *J* = 12.9, 6.8 Hz, 2H), 0.97 (dt, *J* = 13.7, 7.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 153.9, 153.5, 141.9, 128.5, 128.3, 127.0, 125.9, 125.4, 105.6, 105.4, 69.6, 67.8, 67.7, 46.9, 45.2, 45.0, 22.1, 10.3 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{15}H_{20}NO_3$ $(M + H)^+$: 262.1443, found 262.1452.



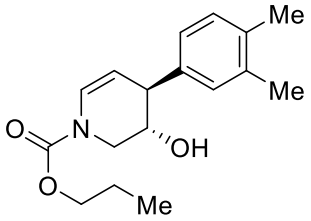
4g

propyl 3-hydroxy-4-(m-tolyl)-3,4-dihydropyridine-1(2*H*)-carboxylate (4g). The general procedure C was followed using propyl propyl 4-(m-tolyl)pyridine-1(2*H*)-carboxylate (**3g**, 51.5 mg, 0.2 mmol). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 3) afforded product **4g** as a colorless oil (38.0 mg, 69 % yield): R_f = 0.5 (ethyl acetate : petroleum ether = 1 : 3); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.20 (t, *J* = 7.7 Hz, 1H), 7.03 (q, *J* = 11.8, 9.2 Hz, 4H), 4.94-4.80 (m, 1H), 4.14-4.07 (m, 2H), 3.85 (s, 1H), 3.66 (d, *J* = 12.6 Hz, 1H), 3.51 (dd, *J* = 12.0, 7.2 Hz, 1H), 3.36 (s, 1H), 2.79 (d, *J* = 4.9 Hz, 0.5H), 2.68 (d, *J* = 6.0 Hz, 0.5H), 2.33 (s, 3H), 1.69 (dq, *J* = 13.5, 6.9 Hz, 2H), 0.97 (dt, *J* = 13.6, 7.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 153.9, 153.5, 141.8, 138.1, 128.9, 128.3, 127.6, 125.7, 125.3, 125.2, 105.8, 105.7, 69.5, 67.7, 67.6, 46.8, 45.2, 45.0, 22.1, 21.3, 10.3 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{16}H_{22}NO_3$ $(M + H)^+$: 276.1600, found 276.1606.



4h

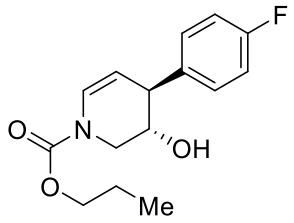
propyl 3-hydroxy-4-(p-tolyl)-3,4-dihydropyridine-1(2*H*)-carboxylate (4h). The general procedure C was followed using propyl propyl 4-(p-tolyl)pyridine-1(2*H*)-carboxylate (**3h**, 51.5 mg, 0.2 mmol). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 3) afforded product **4h** as a colorless oil (40.2 mg, 73 % yield): R_f = 0.5 (ethyl acetate : petroleum ether = 1 : 3); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.14 (s, 4.5H), 7.02 (d, *J* = 8.0 Hz, 0.5H), 4.88 (dd, *J* = 34.2, 6.4 Hz, 1H), 4.13 (q, *J* = 5.9, 5.5 Hz, 2H), 3.87 (s, 1H), 3.67 (t, *J* = 13.4 Hz, 1H), 3.59 -3.50 (m, 1H), 3.39 (s, 1H), 2.33 (s, 3H), 2.22-2.14 (m, 1H), 1.70 (dd, *J* = 13.1, 6.7 Hz, 2H), 0.97 (dt, J = 14.3, 7.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 154.0, 153.5, 138.8, 136.8, 129.3, 128.2, 125.9, 125.4, 105.6, 105.5, 69.8, 67.8, 67.7, 46.6, 45.2, 45.0, 22.2, 21.0, 10.4 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{16}H_{22}NO_3$ $(M + H)^+$: 276.1600, found 276.1604.



4i

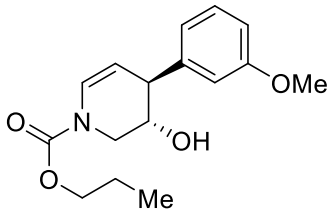
propyl 4-(3,4-dimethylphenyl)-3-hydroxy-3,4-dihydropyridine-1(2*H*)-carboxylate (4i). The general procedure C was followed using propyl

4-(3,4-dimethylphenyl)pyridine-1(2*H*)-carboxylate (**3i**, 54.3 mg, 0.2 mmol). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 3) afforded product **4i** as a colorless oil (29.5 mg, 51 % yield): Rf = 0.5 (ethyl acetate : petroleum ether = 1 : 3); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.17-6.97 (m, 4H), 4.94 (d, *J* = 5.7 Hz, 0.5H), 4.86 (d, *J* = 5.9 Hz, 0.5H), 4.13 (s, 3H), 3.83-3.58 (m, 3H), 2.26 (d, *J* = 5.0 Hz, 6H), 1.75-1.67 (m, 2H), 1.45 (d, J = 5.9 Hz, 1H), 1.02-0.94 (m, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 154.1, 153.6, 136.9, 136.5, 136.4, 135.8, 130.3, 130.0, 126.4, 126.3, 125.8, 105.2, 105.1, 67.8, 67.7, 66.0, 45.8, 43.5, 43.4, 22.2, 19.8, 19.3, 10.4 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{17}H_{24}NO_3$ $(M + H)^+$: 290.1756, found 290.1758.



4j

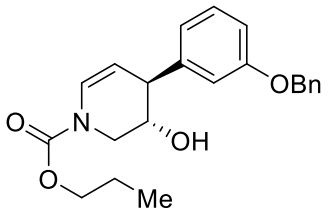
propyl 4-(4-fluorophenyl)-3-hydroxy-3,4-dihydropyridine-1(2*H*)-carboxylate (4j). The general procedure C was followed using propyl 4-(4-fluorophenyl)pyridine-1(2*H*)-carboxylate (**3j**, 52.3 mg, 0.2 mmol). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 3) afforded product **4j** as a colorless oil (35.2 mg, 63 % yield): R_f = 0.5 (ethyl acetate : petroleum ether = 1:3); **^{1}H NMR** ($CDCl_3$, 600 MHz) δ: 7.21 (dd, *J* = 8.4, 5.5 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 0.5H), 7.01 (t, *J* = 8.5 Hz, 2.5H), 4.94-4.77 (m, 1H), 4.11 (d, *J* = 6.4 Hz, 2H), 3.84 (s, 1H), 3.64 (dd, *J* = 19.9, 14.2 Hz, 1H), 3.53 (dd, *J* = 12.8, 7.1 Hz, 1H), 3.40 (s, 1H), 2.80 (d, *J* = 5.0 Hz, 0.5H), 2.69-2.50 (m, 0.5H), 1.70 (dq, *J* = 16.9, 7.0 Hz, 2H), 1.01-0.94 (m, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 163.0, 160.6, 153.9, 153.5, 137.6, 129.8, 126.1, 125.6, 115.4, 115.2, 105.5, 105.2, 69.6, 67.9, 67.8, 46.1, 45.2, 45.0, 22.1, 10.3 ppm; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ: -115.70 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{15}H_{19}FNO_3$ $(M + H)^+$: 280.1349, found 280.1350



4k

propyl 3-hydroxy-4-(3-methoxyphenyl)-3,4-dihydropyridine-1(2*H*)-carboxylate (4k). The general procedure C was followed using propyl 4-(3-methoxyphenyl)pyridine-1(2*H*)-carboxylate (**3k**, 54.7 mg, 0.2 mmol). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 3) afforded product **4k** as a colorless oil (25.1 mg, 43 % yield): R_f = 0.4 (ethyl acetate : petroleum ether = 1 : 3); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.23 (d, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 7.7 Hz, 0.5H), 7.01 (d, *J* = 8.2 Hz, 0.5H), 6.87-6.75 (m, 3H), 4.92 (d, *J* = 6.0 Hz, 0.5H), 4.88-4.80 (m, 0.5H), 4.16-4.07 (m, 2H), 3.89 (s, 1H), 3.79 (s, 3H), 3.72-3.62 (m, 1H), 3.54 (dd, *J* = 11.7, 5.7 Hz, 1H), 3.39 (s, 1H), 2.45 (d, *J* = 22.0 Hz, 1H), 1.77-1.62 (m, 2H), 0.97 (dt, *J* = 12.9, 7.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 159.7, 153.9, 153.5, 143.5, 129.6, 126.0, 125.5,

120.6, 114.1, 114.0, 112.3, 112.1, 105.4, 105.3, 69.5, 67.8, 67.7, 55.1, 47.0, 45.3, 45.0, 22.1, 10.3 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{16}H_{22}NO_4$ $(M + H)^+$: 292.1549, found 292.1563.

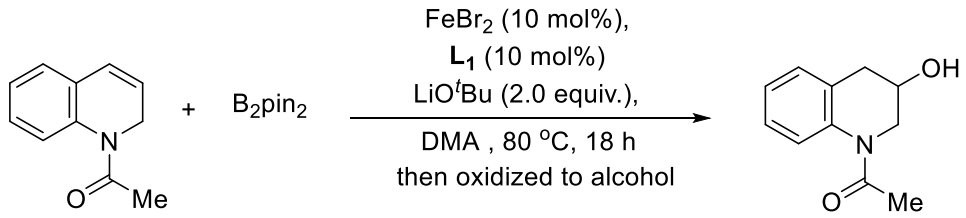


4l

propyl 4-(3-(benzyloxy)phenyl)-3-hydroxy-3,4-dihydropyridine-1(2*H*)-carboxylate (4l). The general procedure C was followed using propyl 4-(3-(benzyloxy)phenyl)pyridine-1(2*H*)-carboxylate (**3l**, 69.9 mg, 0.2 mmol). Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 3) afforded product **4l** as a colorless oil (29.4 mg, 40 % yield): R_f = 0.6 (ethyl acetate : petroleum ether = 1 : 3); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.45-7.36 (m, 4H), 7.34-7.25 (m, 2H), 7.14 (d, *J* = 8.4 Hz, 0.5H), 7.02 (d, *J* = 8.0 Hz, 0.5H), 6.94-6.83 (m, 3H), 5.06 (s, 2H), 4.89 (dd, *J* = 34.5, 6.9 Hz, 1H), 4.14 (s, 3H), 3.81-3.57 (m, 3H), 1.76-1.64 (m, 2H), 1.45 (d, *J* = 6.8 Hz, 1H), 0.98 (d, *J* = 7.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 159.1, 154.0, 153.6, 140.8, 136.8, 129.7, 128.6, 128.0, 127.5, 126.5, 126.1, 121.6, 115.9, 113.7, 113.6, 104.7, 70.0, 67.8, 65.9, 45.9, 43.8, 29.7, 22.2, 10.4. ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{22}H_{26}NO_4$ $(M + H)^+$: 368.1862, found 368.1851.

9. Further transformations for the product

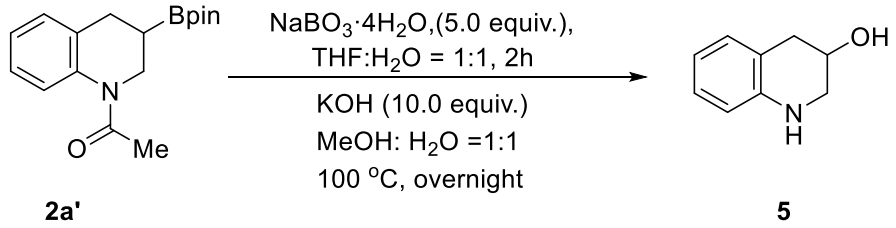
9-1 Gram scale reaction



1a **2a'**

In an oven dried 100-mL Schlenk tube, which contained a stirring bar, was charged with $FeBr_2$ (129 mg, 0.6 mmol, 10 mol%), **L_1** (141 mg, 0.6 mmol, 10 mol%), B_2pin_2 (3.06 g, 12 mmol, 2.0 equiv.), and LiO^tBu (0.96 g, 12 mmol, 2.0 equiv.). The tube was evacuated and back-filled under a N_2 flow (this sequence was repeated three times), then anhydrous DMA (30.0 mL) was added under N_2. The tube was stirred at 25 ℃ for 60 min. After above, **1a** (1.04 g, 6 mmol, 1.0 equiv.) was added subsequently under N_2, the tube was stirred at 80 °C for 18 h. Then, the reaction mixture was diluted with EtOAc (20.0 mL), and it was extracted with EtOAc (20.0 mL × 3). The organic layer was combined and dried over Na_2SO_4, filtered and concentrated in vacuo to get the crude product. Then the crude product was dissolved in THF (20.0 mL), $NaBO_3$ $4H_2O$ (2.77g, 18 mmol, 3.0 equiv.) and H_2O (20.0 mL) were added, the resulting mixture was allowed to stir at 25 ℃ for three hours. The reaction mixture diluted with EtOAc (2.0 mL) and H_2O (2.0 mL), then it was extracted with EtOAc (2.0 mL × 3), the organic layer was combined, washed with brine and dried over Na_2SO_4, filtered and concentrated in vacuo. Purification of this material by chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 3) afforded product **2a'** as a colorless oil (1.12 g , 62 % yield): R_f = 0.3 (ethyl acetate : petroleum ether = 1 : 3).

9-2 Procedure for synthesis of **5** [4]

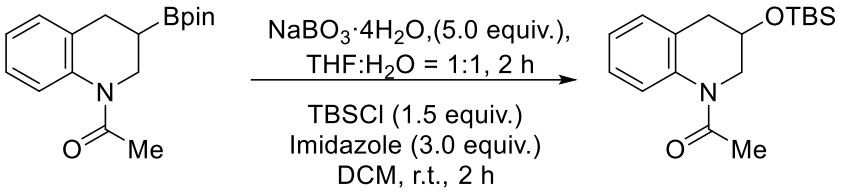


2a' **5**

In an oven dried 10-mL Schlenk tube, which contained a stirring bar, was charged with the solution of **2a'** (60.2 mg, 0.2 mmol, 1.0 equiv.) in THF (2.0 mL), $NaBO_3$•$4H_2O$ (154 mg, 1.0 mmol, 5.0 equiv.) and H_2O (2.0 mL) were added. The resulting mixture was allowed to stir at 25 ℃ for three hours. The reaction mixture diluted with EtOAc (5.0 mL) and H_2O (5.0 mL). Then it was extracted with EtOAc (5.0 mL × 3). The organic layer was combined and dried over Na_2SO_4, filtered and concentrated by rotary evaporation. The resulting crude material was used in the next reaction without further purifification. To a solution of this intermediate in a mixture of MeOH and H_2O (1 : 1, 5.5 mL) was added KOH (112 mg, 2.0 mmol, 10.0 equiv.) at 25 ℃. The resulting mixture was heated to 100 ℃. After the reaction was completed, the reaction mixture was extracted with DCM, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was purifified by silica gel chromatography using petroleum ether / ethyl acetate as an eluent (ethyl acetate : petroleum ether = 1 : 2) to afffford product **5** as a colorless oil (26.0 mg , 87 %

yield): R_f = 0.3 (ethyl acetate : petroleum ether = 1 : 2); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.06-6.94 (m, 2H), 6.69 (td, *J* = 7.4, 1.1 Hz, 1H), 6.54 (d, *J* = 7.9 Hz, 1H), 4.25 (tq, *J* = 4.5, 2.4 Hz, 1H), 3.85 (d, *J* = 49.2 Hz, 1H), 3.34 (d, *J* = 11.2 Hz, 1H), 3.25 (m, 1H), 3.05 (dd, *J* = 16.5, 4.0 Hz, 1H), 2.79 (dd, *J* = 16.9, 3.6 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 143.6, 130.6, 127.0, 118.6, 118.1, 114.2, 63.4, 47.6, 35.4 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_9H_{12}NO$ $(M + H)^+$: 150.0919, found 150.0923.

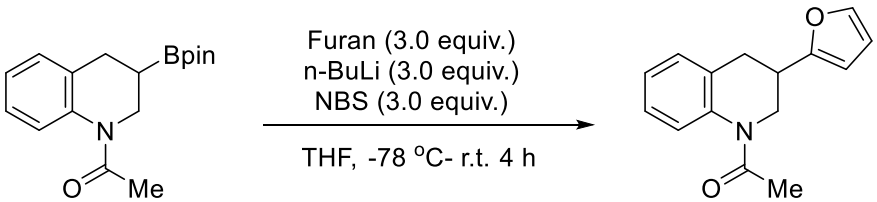
9-3 Procedure for synthesis of **6** [5]



2a' **6**

2a' (60.2 mg, 0.2 mmol, 1.0 equiv.) was dissolved in THF (2.0 mL), $NaBO_3$•$4H_2O$ (154 mg, 1.0 mmol, 5.0 equiv.) and H_2O (2.0 mL) were added, then the reaction was allowed to stir at 25 ℃ for three hours. The reaction mixture diluted with EtOAc (5.0 mL) and H_2O (5.0 mL), then it was extracted with EtOAc (5.0 mL × 3), the organic layer was combined, washed with brine and dried over Na_2SO_4, filtered and concentrated in vacuo. The resulting crude material was used in the next reaction without further purifification. Then the crude product was dissolved in DCM 2 mL), then imidazole (42.0 mg, 0.6 mmol, 3.0 equiv.) and TBSCl (45.2 mg, 0.3 mmol, 1.5 equiv.) were added. After stirring at room temperature for 12 h, the reaction was quenched by addition of saturated $NaHCO_3$ (5 mL) solution, and the resulting mixture was extracted with EtOAc (5.0 mL × 3). The organic layer was combined and dried over Na_2SO_4. Then filtered and concentrated by rotary evaporation. The residue was purifified by silica gel chromatography using petroleum ether/ ethyl acetate as an eluent (ethyl acetate : petroleum ether = 1 : 10) to afffford product **6** as a colorless oil (57.4 mg , 94 % yield): R_f = 0.5 (ethyl acetate : petroleum ether = 1 : 10); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.20-6.99 (m, 4H), 4.19 (m, 1H), 3.96 (s, 1H), 3.62 (dd, *J* = 12.5, 6.5 Hz, 1H), 3.00 (dd, *J* = 16.0, 5.1 Hz, 1H), 2.73 (dd, *J* = 16.0, 6.4 Hz, 1H), 2.24 (s, 3H), 0.87 (s, 9H), 0.10 (s, 6H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 170.2, 138.8, 129.9, 129.2, 126.0, 125.2, 124.2, 66.6, 49.7, 37.1, 25.7, 22.9, 17.9, -4.9 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{17}H_{28}NO_2Si$ $(M + H)^+$: 306.1894, found 306.1889.

9-4 Procedure for synthesis of **7** [6]

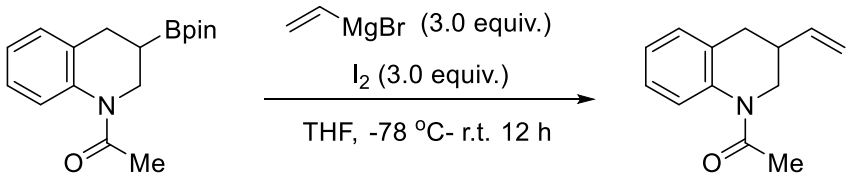


2a' **7**

In an oven dried 25-mL Schlenk tube, which containing a stirring bar was charged with furan (40.8 mg, 0.6 mmol, 3.0 equiv.) and 1.0 mL of dry THF. Then ^{n}BuLi (2.5 M in hexane, 0.6 mL, 0.6 mmol, 3.0 equiv.) was added dropwise under -78 °C. The mixture was warmed to room

temperature and stirred for 2 h. Subsequently, the reaction mixture was cooled back to 0 °C and a solution of compound **2a'** (60.2 mg, 0.2 mmol, 1.0 equiv.) in THF (1.0 mL) was added dropwise. The resulting mixture was stirred at the same temperature for 1 h. Then a solution of NBS (107.0 mg, 0.6 mmol, 3.0 equiv.) in THF (1 mL) was added dropwise and stirred 1 h at -78 °C. After completion of the reaction, the reaction mixture was quenched with saturated solution of $Na_2S_2O_3$ (3 mL) at 25 °C. Then it was extracted with EtOAc (5.0 mL × 3). The organic layer was combined and dried over Na_2SO_4. Then filtered and concentrated by rotary evaporation. The residue was purifified by silica gel chromatography using petroleum ether / ethyl acetate as an eluent (ethyl acetate : petroleum ether = 1 : 3) to afffford product **7** as a colorless oil (25.1 mg , 52 % yield): R_f = 0.3 (ethyl acetate : petroleum ether = 1 : 3); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.37-7.32 (m, 1H), 7.28-7.01 (m, 4H), 6.34-6.25 (m, 1H), 6.08 (d, *J* = 3.2 Hz, 1H), 4.22 (s, 1H), 3.77 (dd, *J* = 12.6, 9.2 Hz, 1H), 3.34 (m, 1H), 3.15 (dd, *J* = 16.1, 6.0 Hz, 1H), 2.98 (dd, *J* = 15.9, 9.1 Hz, 1H), 2.21 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 170.1, 155.5, 141.6, 128.8, 126.2, 125.2, 124.5, 110.2, 105.2, 34.9, 31.9, 29.7, 23.0 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{15}H_{16}NO_2$ $(M + H)^+$: 242.1181, found 242.1177.

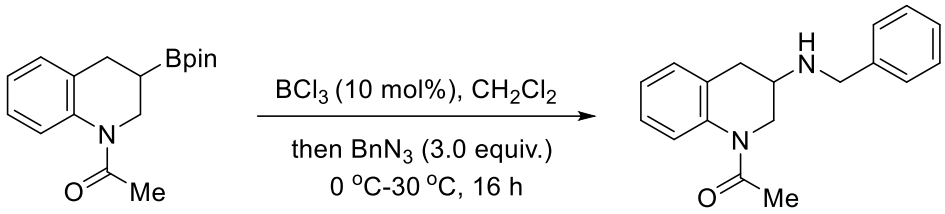
9-5 Procedure for synthesis of **8** [6]



2a' **8**

In an oven dried 10-mL Schlenk tube, which contained a stirring bar, was charged with **2a'** (60.2 mg, 0.2 mmol, 1.0 equiv.), the tube was then evacuated and back-filled under a N_2 flow (this sequence was repeated three times). Then THF (2.0 mL) and vinylMgBr (0.80 mL, 1 M in THF, 0. 80 mmol) was added at 25 ℃, The resulting mixture was allowed to stir at same temperature for 0.5 h. A solution of I_2 (203 mg, 0.8 mmol, 2 mL MeOH) was then slowly added to the reaction mixture at -78 ℃ and stirred for 0.5 h. Then a solution of NaOMe (130 mg, 2.4 mmol, 2.4 mL MeOH) was added slowly at -78 ℃. The resulting mixture was then warmed to 25 °C and stirred for 1 h. The reaction mixture was quenched by saturated aqueous $Na_2S_2O_3$ (5 mL), then it was extracted with EtOAc (10 mL × 3). The organic layer was combined and dried over Na_2SO_4, filtered and concentrated by rotary evaporation. The residue was purified by silica gel chromatography (ethyl acetate : petroleum ether = 1 : 3) to afford the product **8** as a yellow oil (34.6 mg, 86% yield): R_f = 0.4(ethyl acetate : petroleum ether = 1 : 3); **^{1}H NMR** ($CDCl_3$, 400 MHz) : 7.32-7.02 (m, 4H), 5.80 (ddd, *J* = 17.1, 10.3, 6.7 Hz, 1H), 5.17-5.06 (m, 2H), 4.03 (d, *J* = 10.4 Hz, 1H), 3.47 (dd, *J* = 12.6, 9.0 Hz, 1H), 2.90 (m, 1H), 2.63 (d, *J* = 10.5 Hz, 2H), 2.24 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz) : 170.0, 139.0, 128.6, 126.0, 125.0, 124.3, 115.4, 47.5, 39.4, 33.0, 23.1 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{16}NO$ $(M + H)^+$: 202.1232, found 202.1236.

9-6 Procedure for synthesis of **9** [7]



2a' **9**

In an oven-dried reaction vial, CH_2Cl_2 solution of BCl_3 (1.0 M, 0.5 mL, 0.5 mmol) was added under nitrogen atmosphere. The CH_2Cl_2 solution (1.0 mL) of the crude product of compound **2a'** (60.2 mg, 0.2 mmol, 1.0 equiv.) was added to the reaction vial with stirring at room temperature. After 4 h, the volatile materials were removed under reduced pressure, and dry CH_2Cl_2 (1.0 mL) was added to the resultant product. The reaction vial was cooled to 0 ℃, and benzylazide (80.0 mg, 0.6 mmol, 3.0 equiv.) was added to the mixture. After stirred for 16 h at 0 ℃, the reaction mixture was quenched by adding NaOH aq. (2.0 M), extracted three times with EtOAc, dried over Na_2SO_4. Then filtered and concentrated by rotary evaporation. The residue was purifified by silica gel chromatography using petroleum ether/ ethyl acetate as an eluent (ethyl acetate : petroleum ether = 1 : 3) to afffford product **9** as a colorless oil (27.5 mg , 49 % yield): R_f = 0.3 (ethyl acetate : petroleum ether = 1 : 3); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.33-7.08 (m, 9H), 4.06 (s, 1H), 3.87 (d, *J* = 6.3 Hz, 2H), 3.60 (s, 1H), 3.18 (p, *J* = 5.8 Hz, 1H), 3.03 (dd, *J* = 15.9, 5.8 Hz, 1H), 2.63 (dd, *J* = 15.9, 7.3 Hz, 1H), 2.23 (s, 3H), 1.62 (s, 1H); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ: 170.1, 140.0, 129.1, 128.4, 128.0, 127.0, 126.1, 125.2, 124.1, 52.8, 51.1, 34.4, 22.9 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{18}H_{21}N_2O$ $(M + H)^+$: 283.1572, found 283.1567.

10. References.

1. M. Jiao, J. Gao and X. Fang, Enantioselective Synthesis of 4-Cyanotetrahydroquinolines via Ni-Catalyzed Hydrocyanation of 1,2-Dihydroquinolines, *Org. Lett*., 2020, **22**, 8566.

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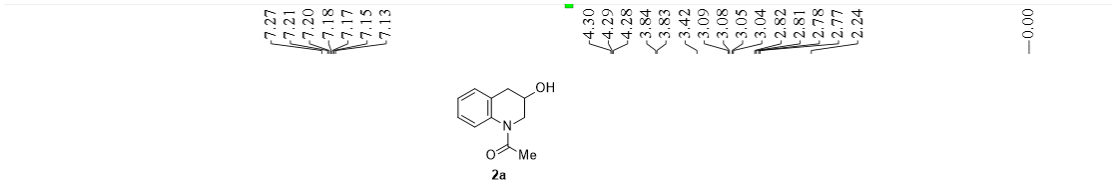
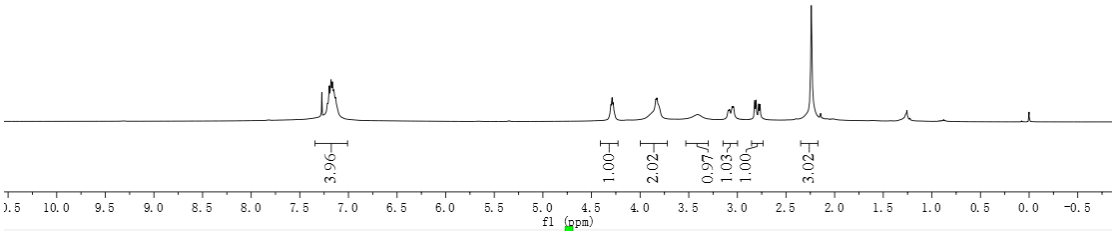
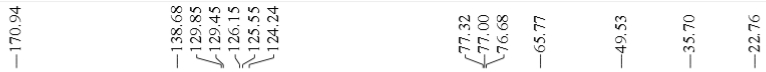
11. NMR spectra of products.

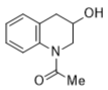


2a

^{1}H NMR (400 MHz, Chloroform-*d*)

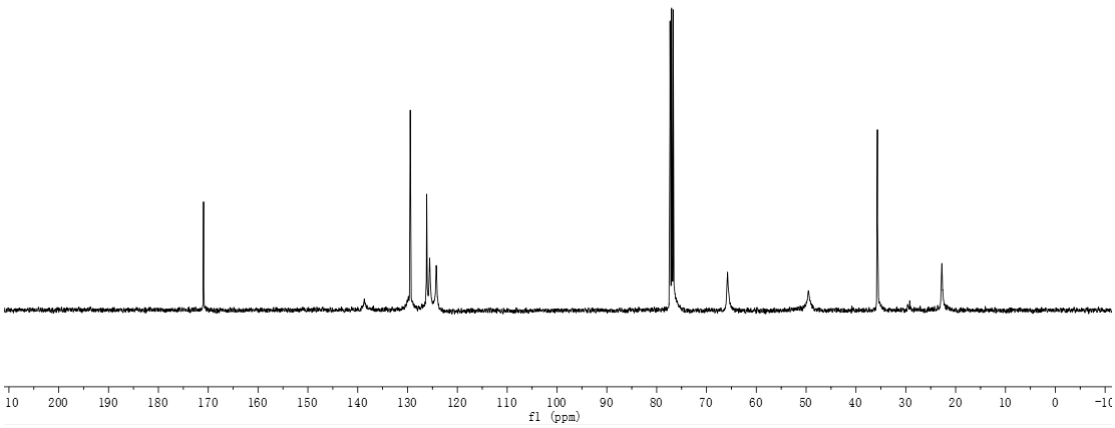


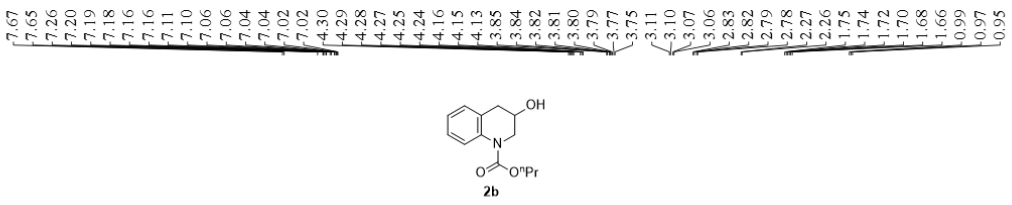




2a

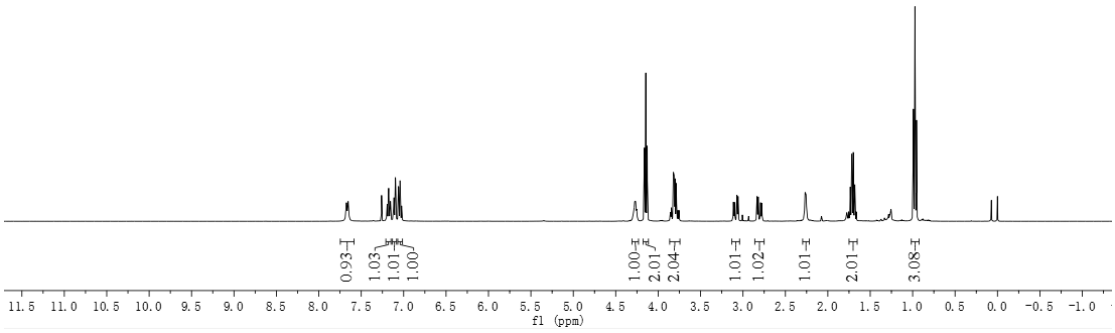
^{13}C NMR (101 MHz, Chloroform-*d*)

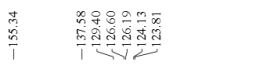




2b

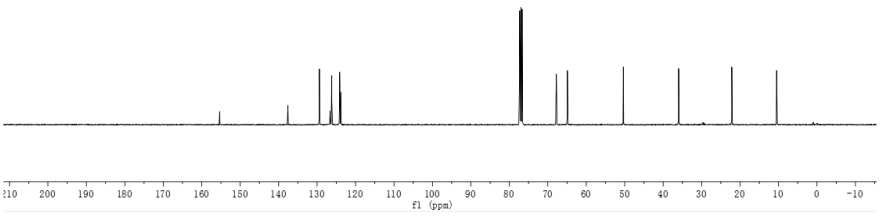
^{1}H NMR (400 MHz，Chloroform-*d*)

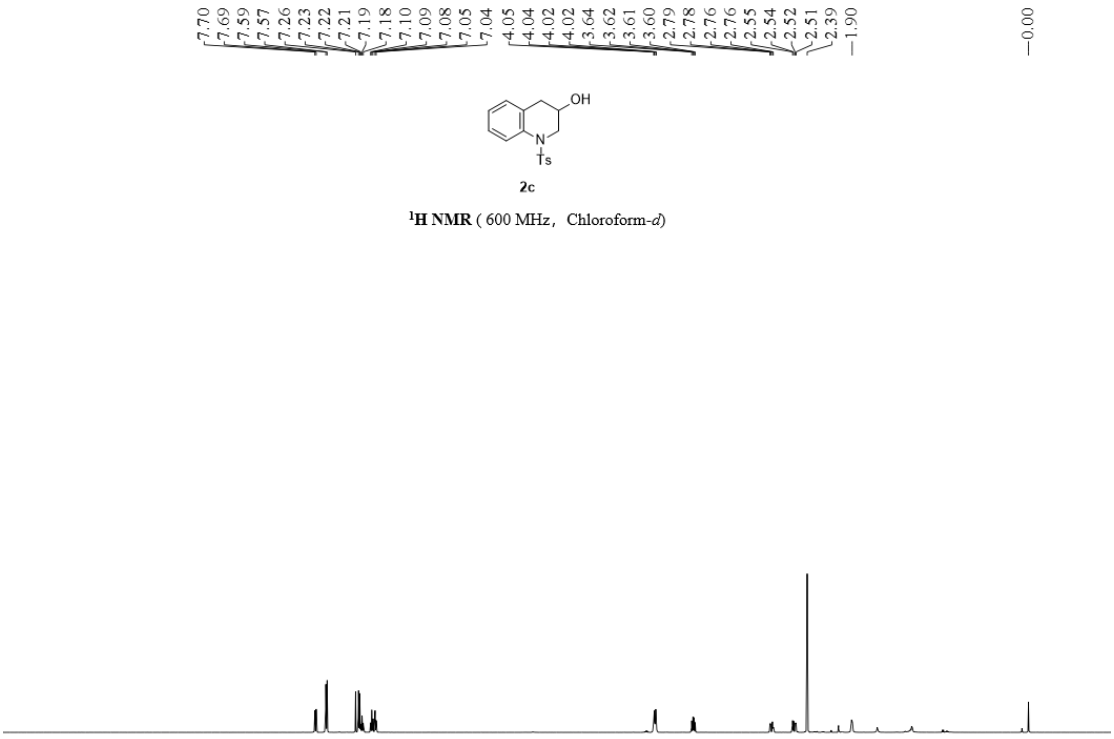




2b

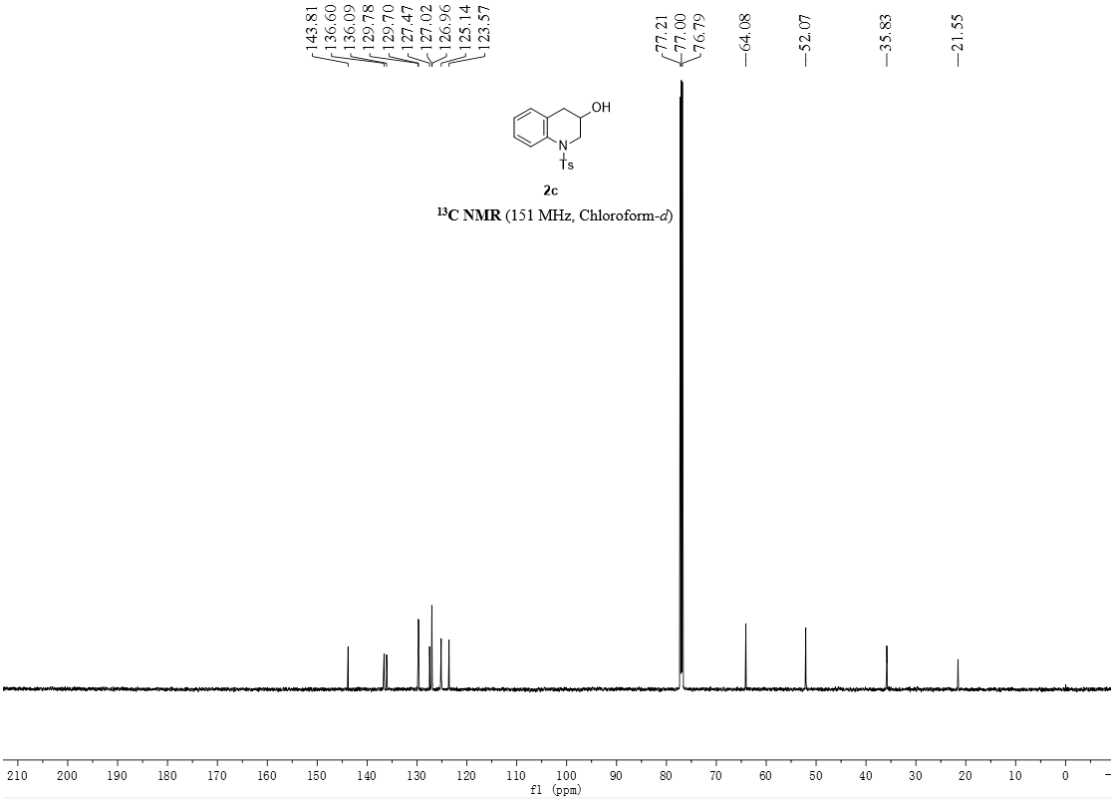
^{13}C NMR (101 MHz, Chloroform-*d*)





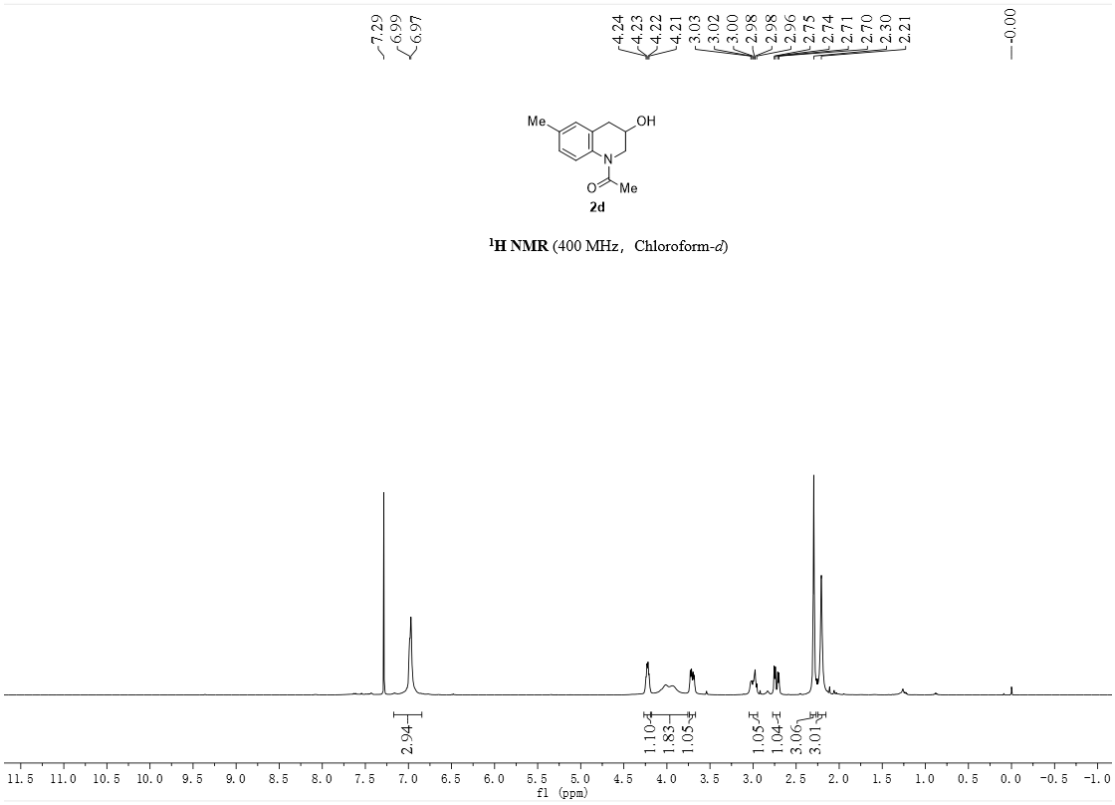
2c

^{1}H NMR (600 MHz，Chloroform-*d*)

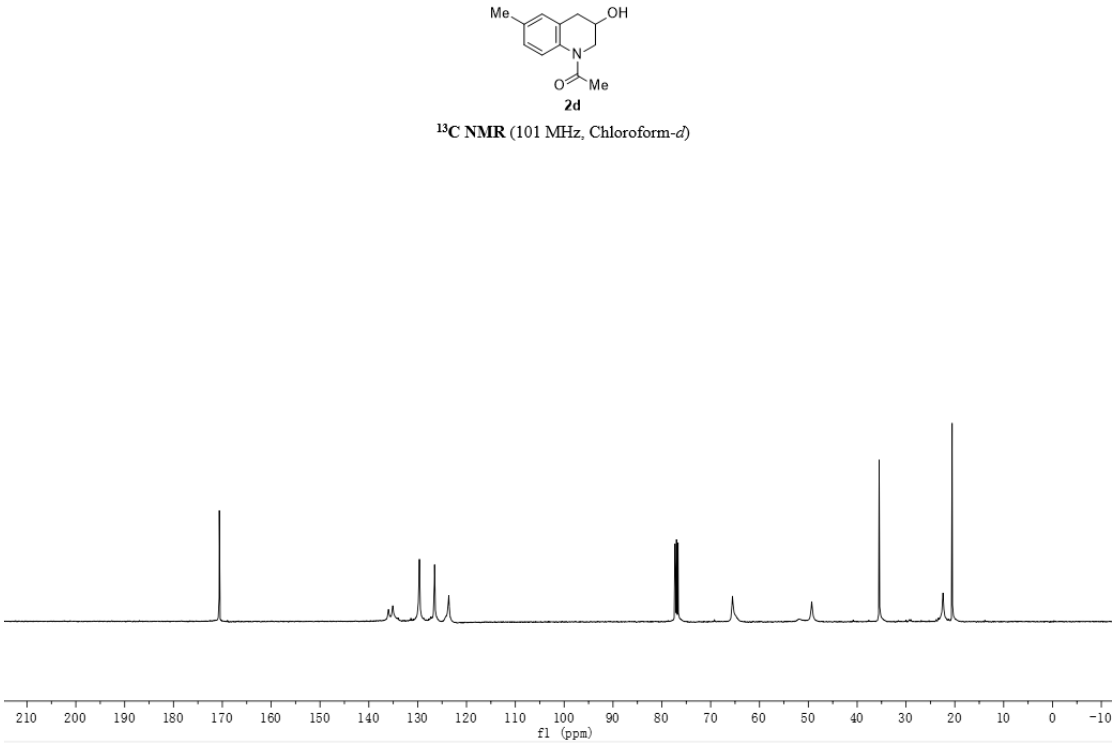


2c

^{13}C NMR (151 MHz, Chloroform-*d*)



^{1}H NMR (400 MHz, Chloroform-*d*)



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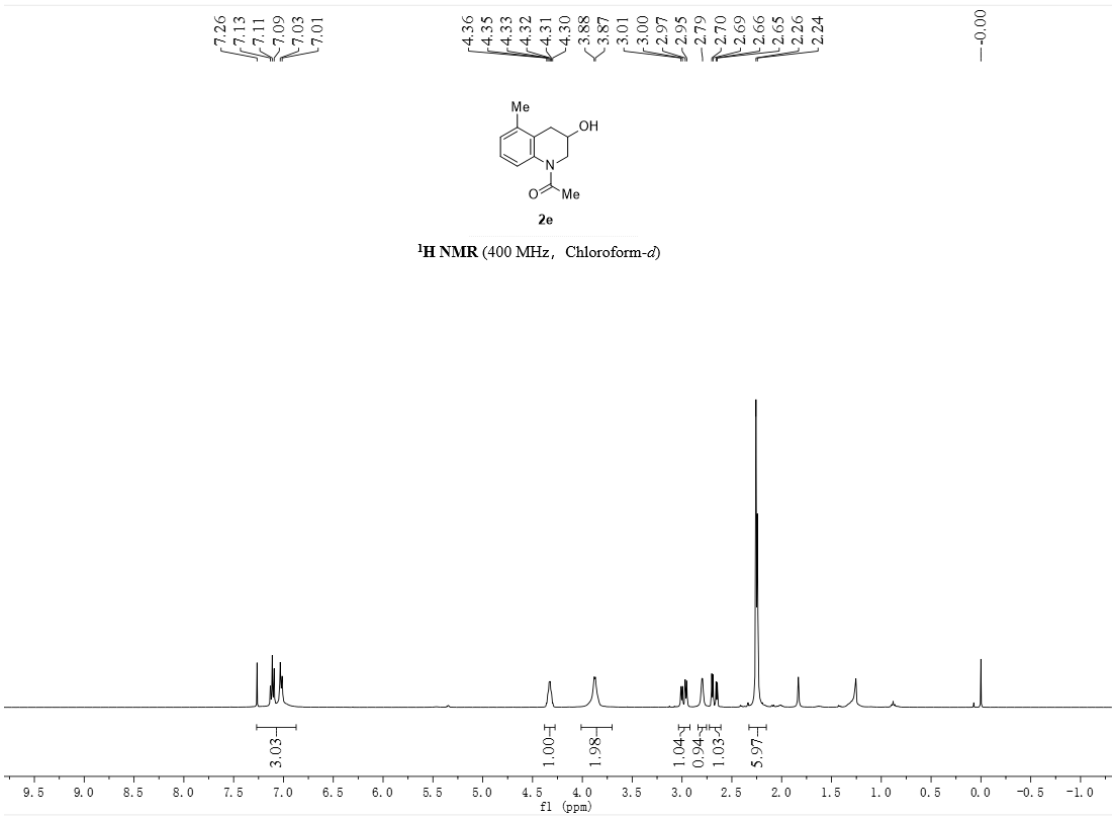
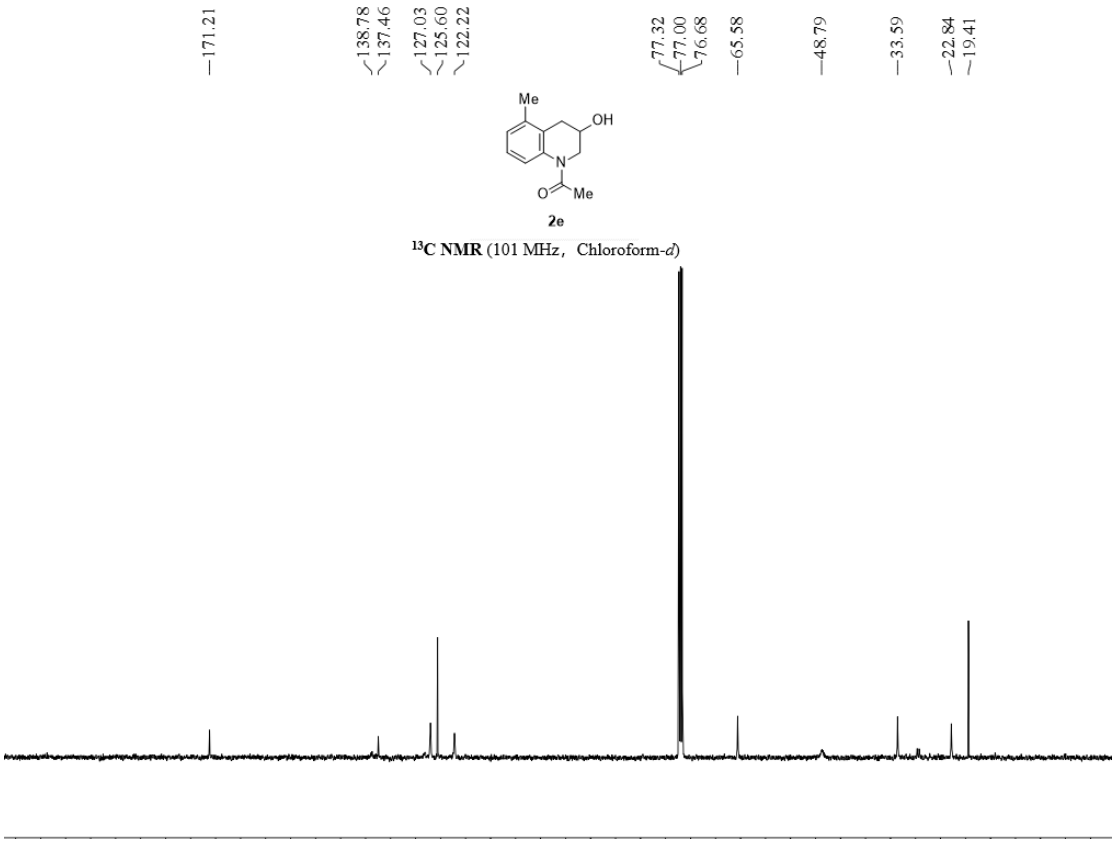


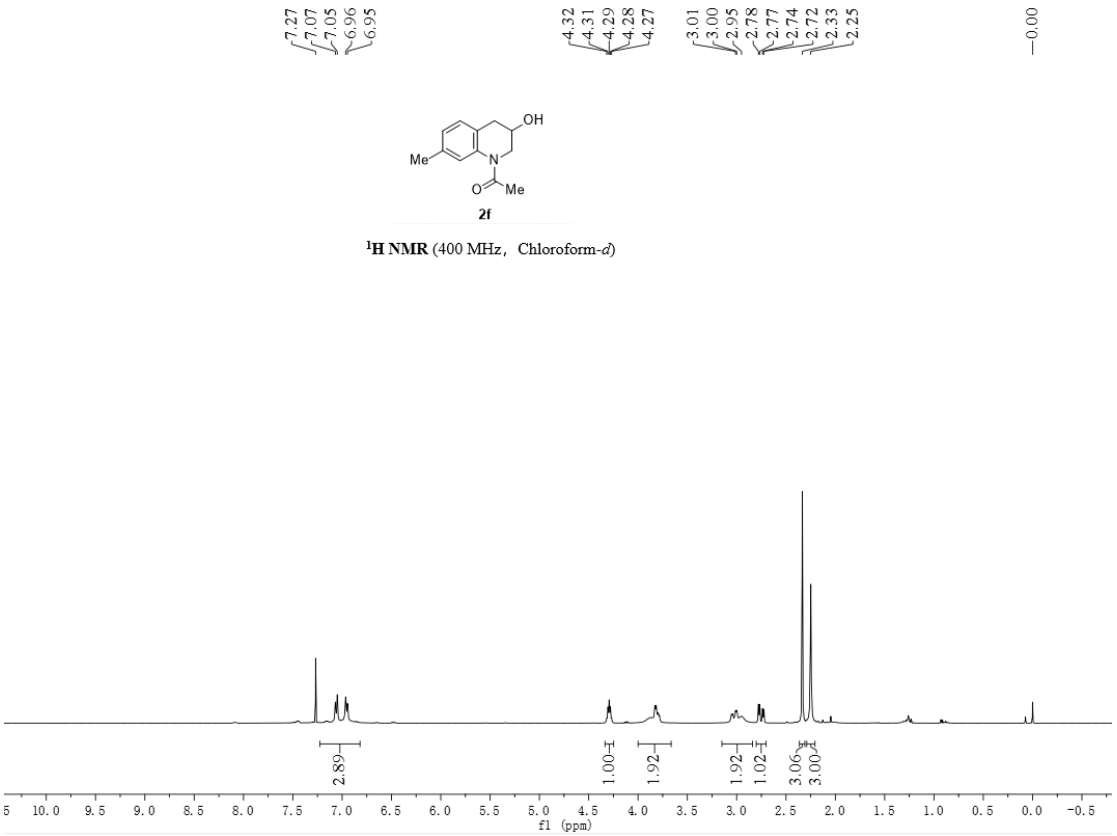
2e

^{1}H NMR (400 MHz，Chloroform-*d*)



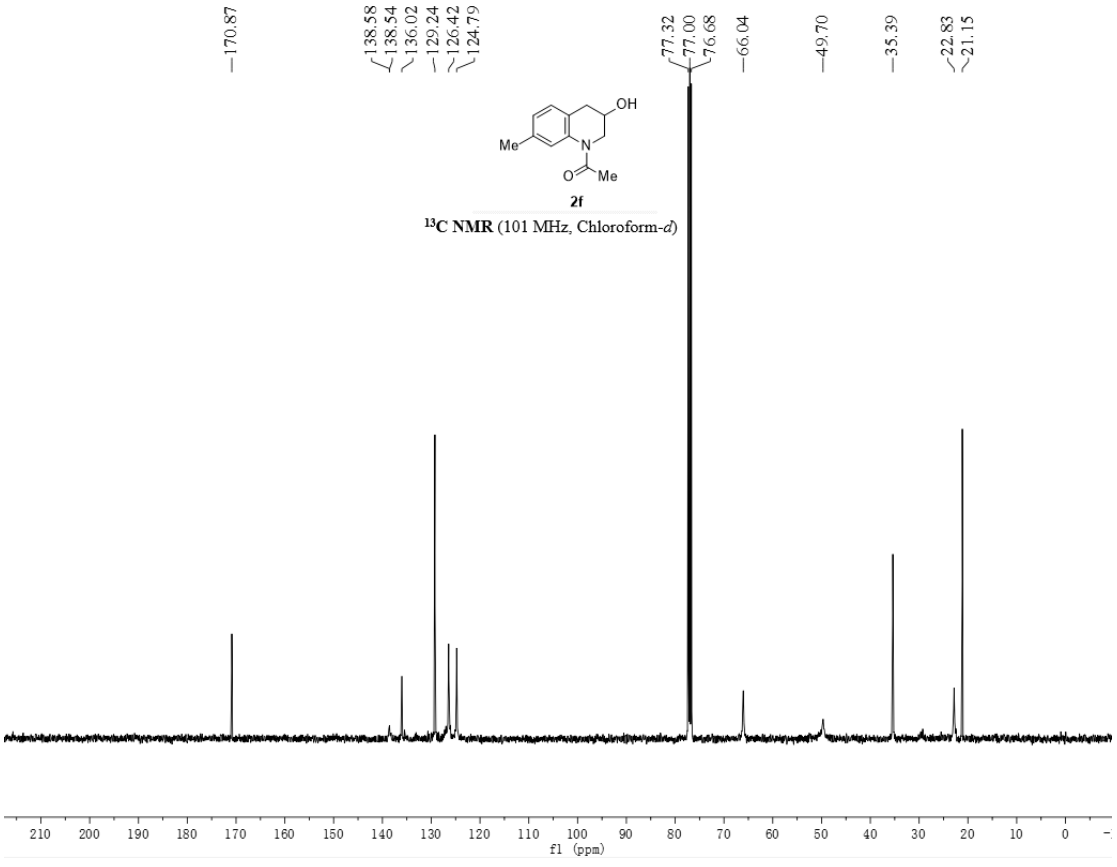
2e

^{13}C NMR (101 MHz，Chloroform-*d*)



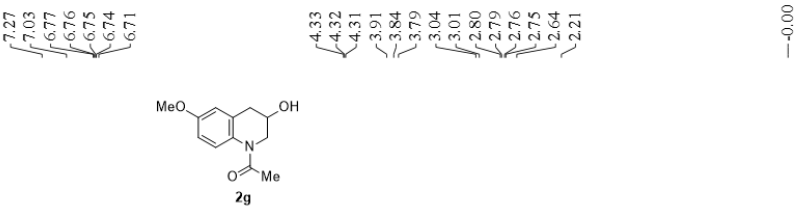
2f

^{1}H NMR (400 MHz, Chloroform-*d*)



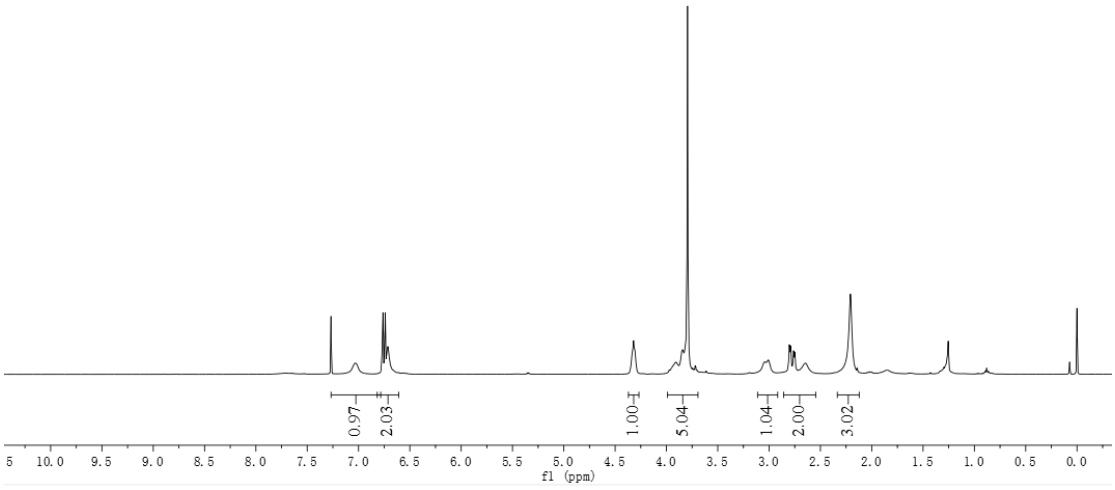
2f

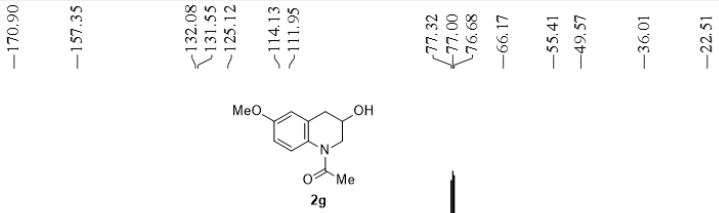
^{13}C NMR (101 MHz, Chloroform-*d*)



2g

^{1}H NMR (400 MHz, Chloroform-*d*)





2g

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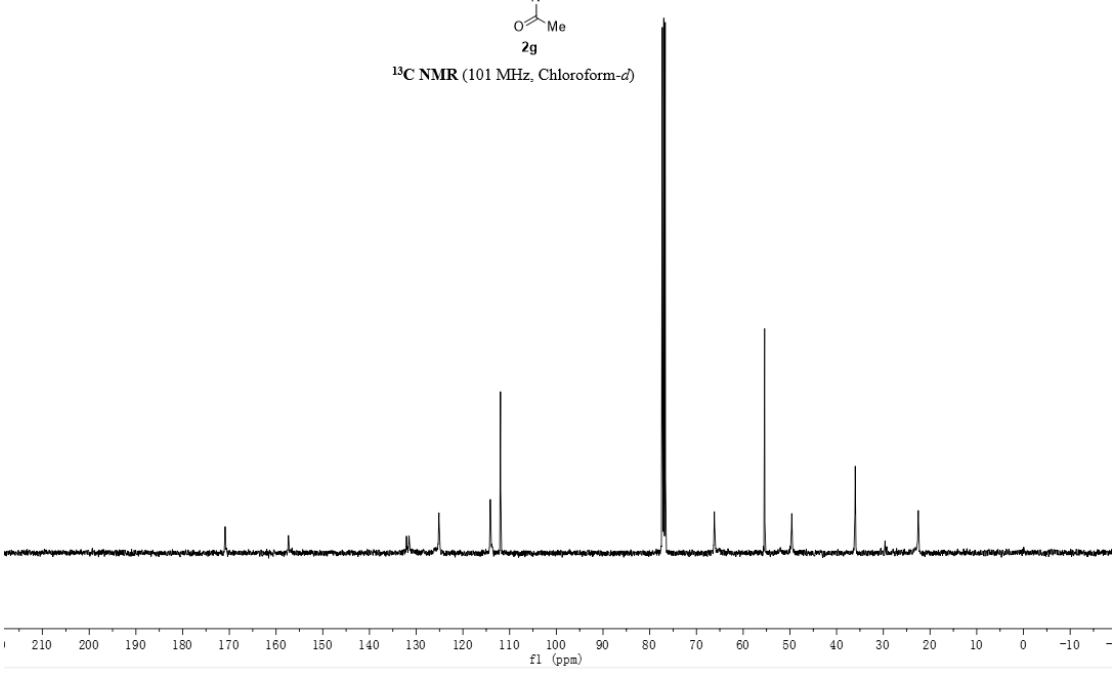
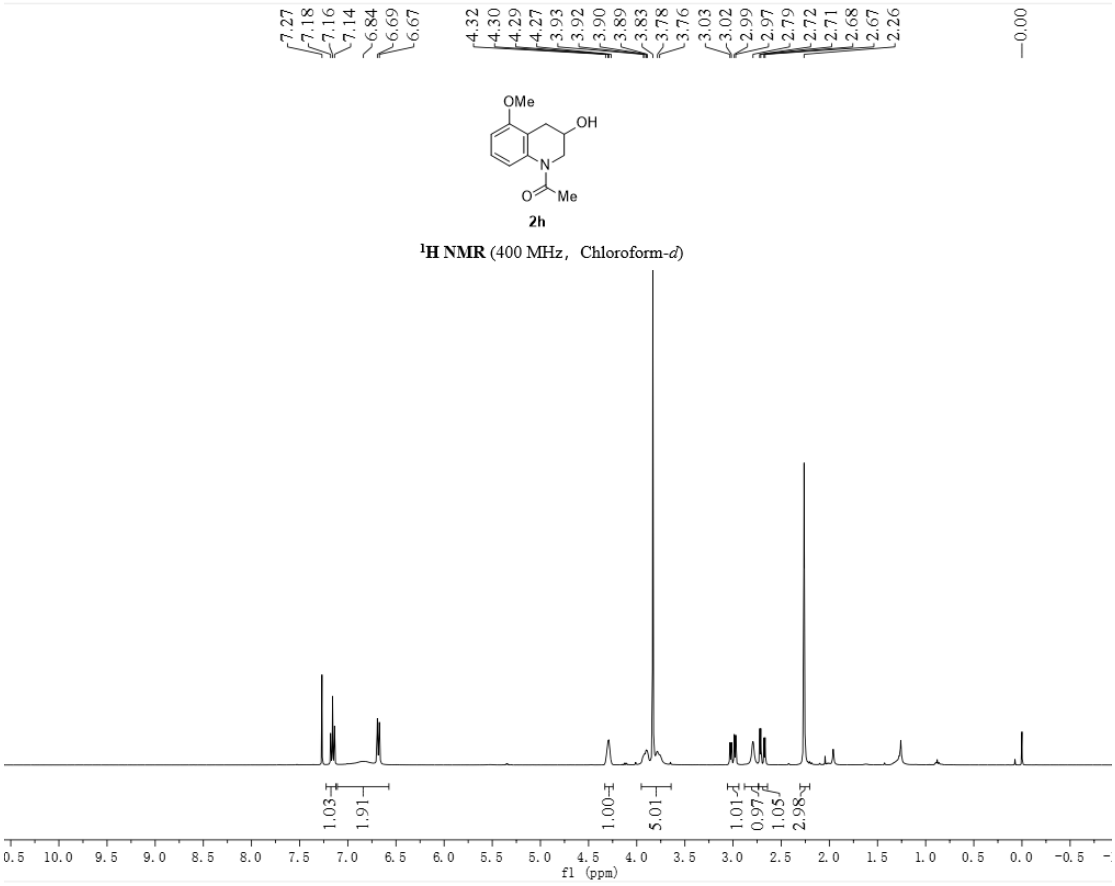
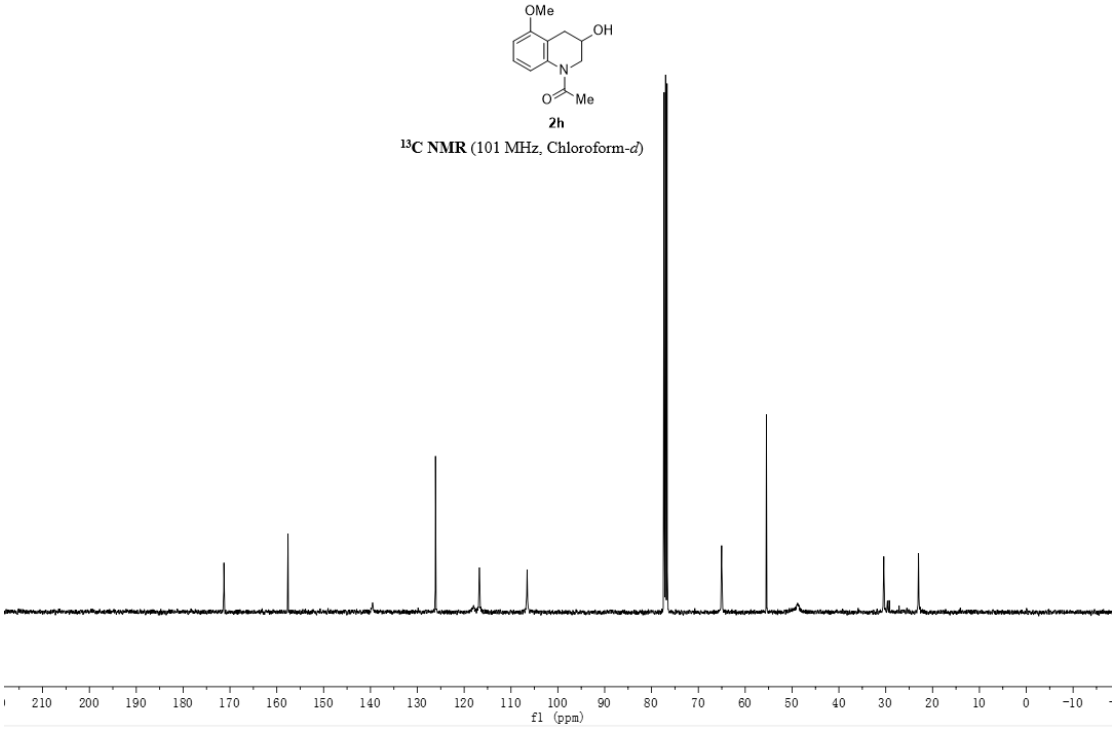




2h

^{1}H NMR (400 MHz, Chloroform-*d*)



2h

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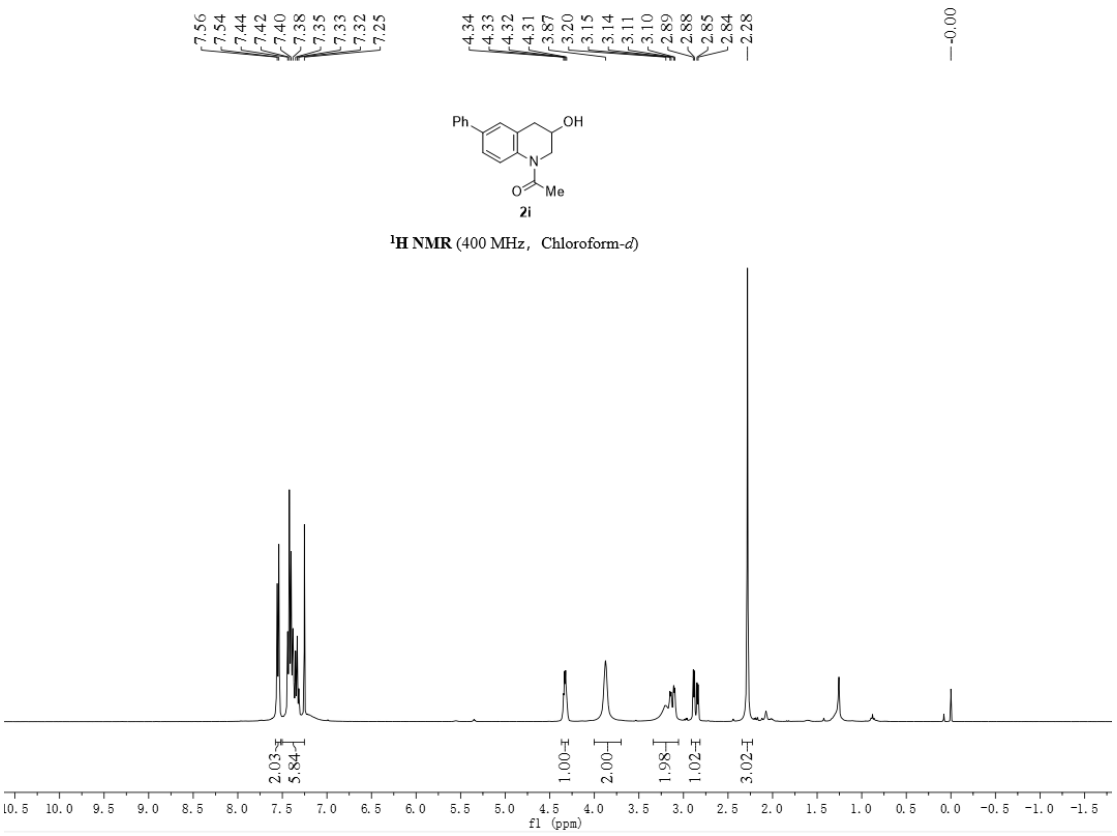
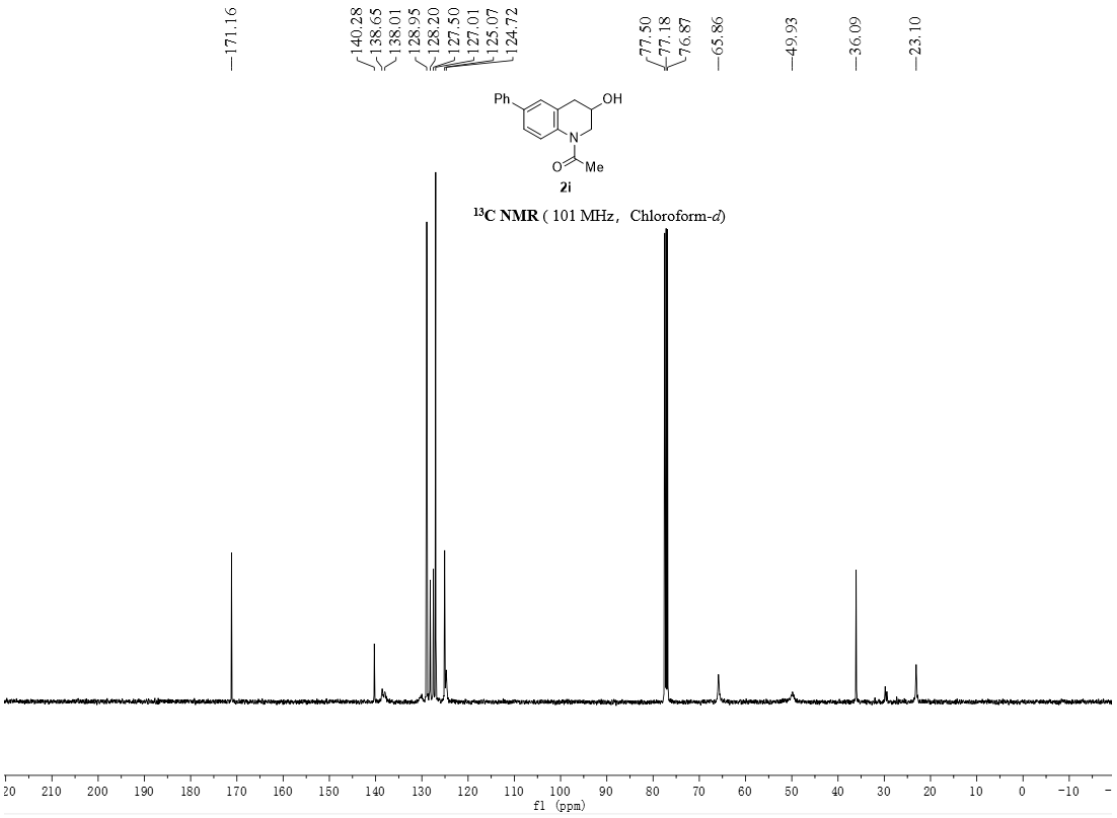


^{1}H NMR (400 MHz, Chloroform-*d*)



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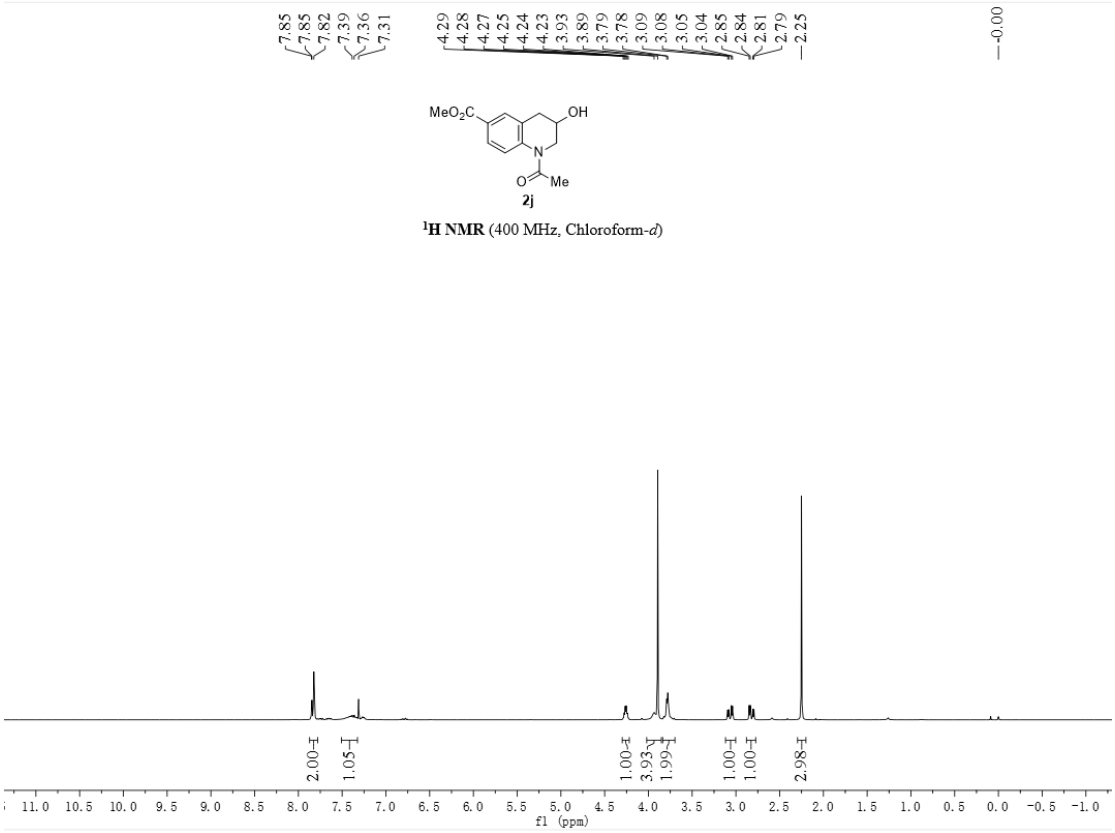
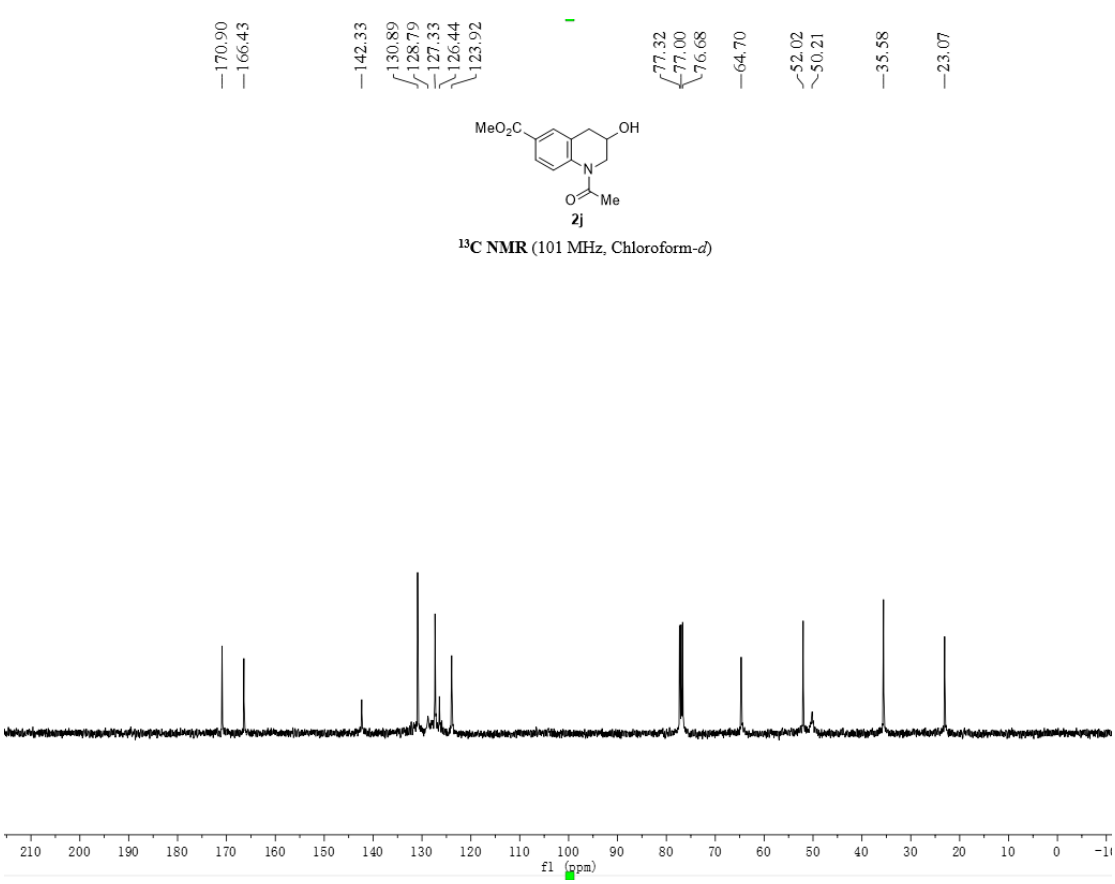
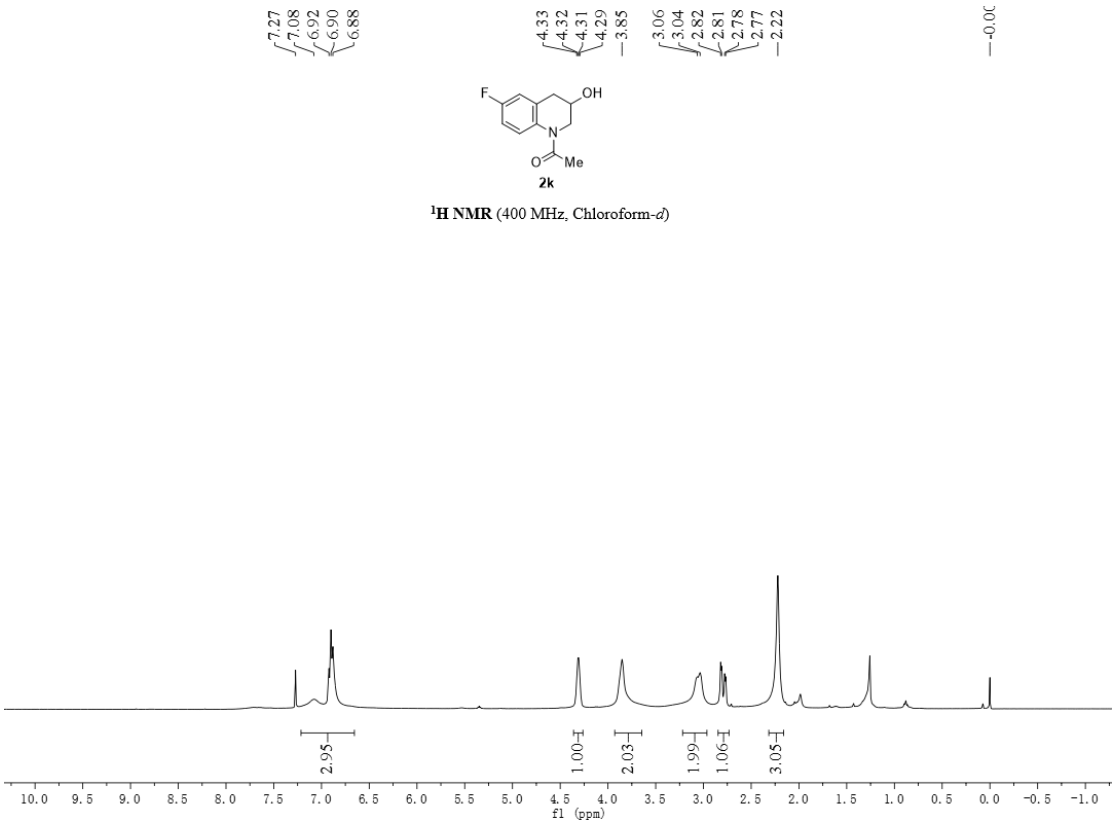


^{1}H NMR (400 MHz, Chloroform-*d*)

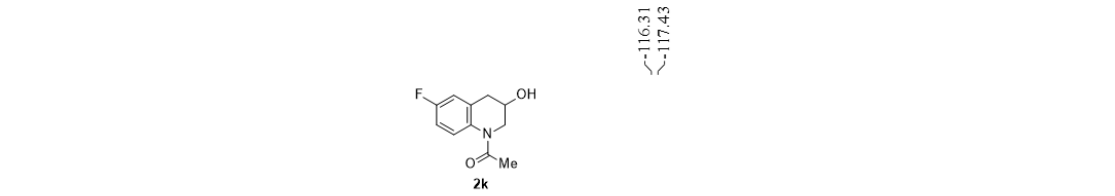


^{13}C NMR (101 MHz, Chloroform-*d*)



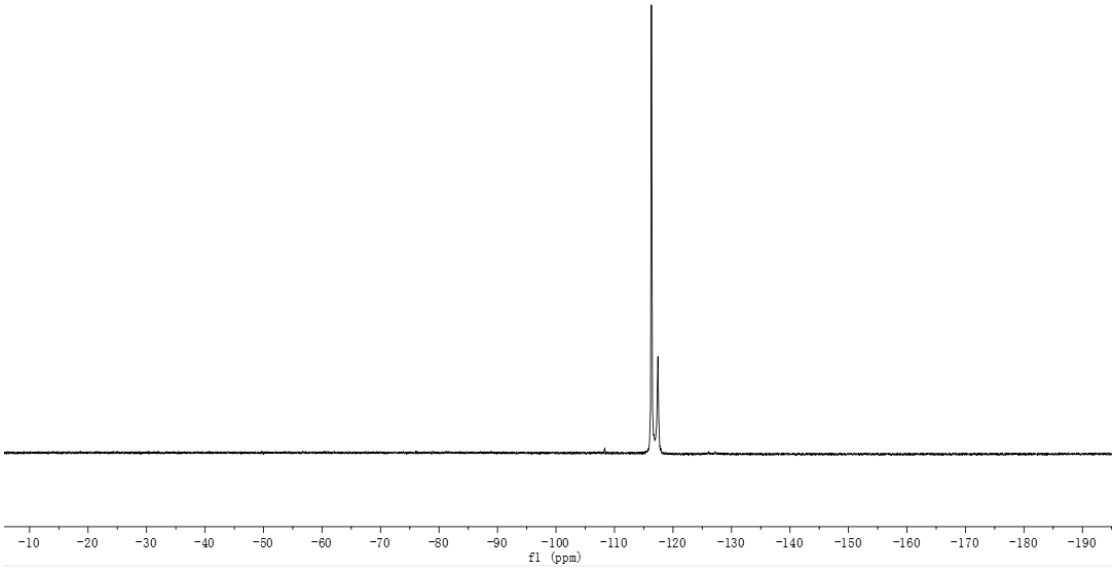
^{1}H NMR (400 MHz, Chloroform-*d*)

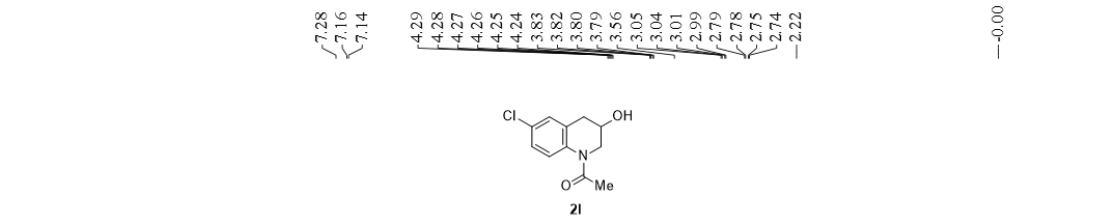
^{13}C NMR (101 MHz, Chloroform-*d*)



2k

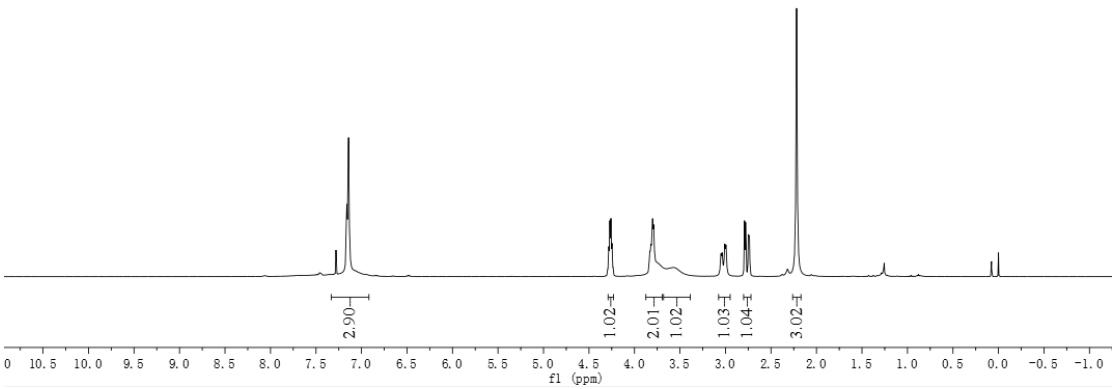
^{19}F NMR (376 MHz，Chloroform-*d*)

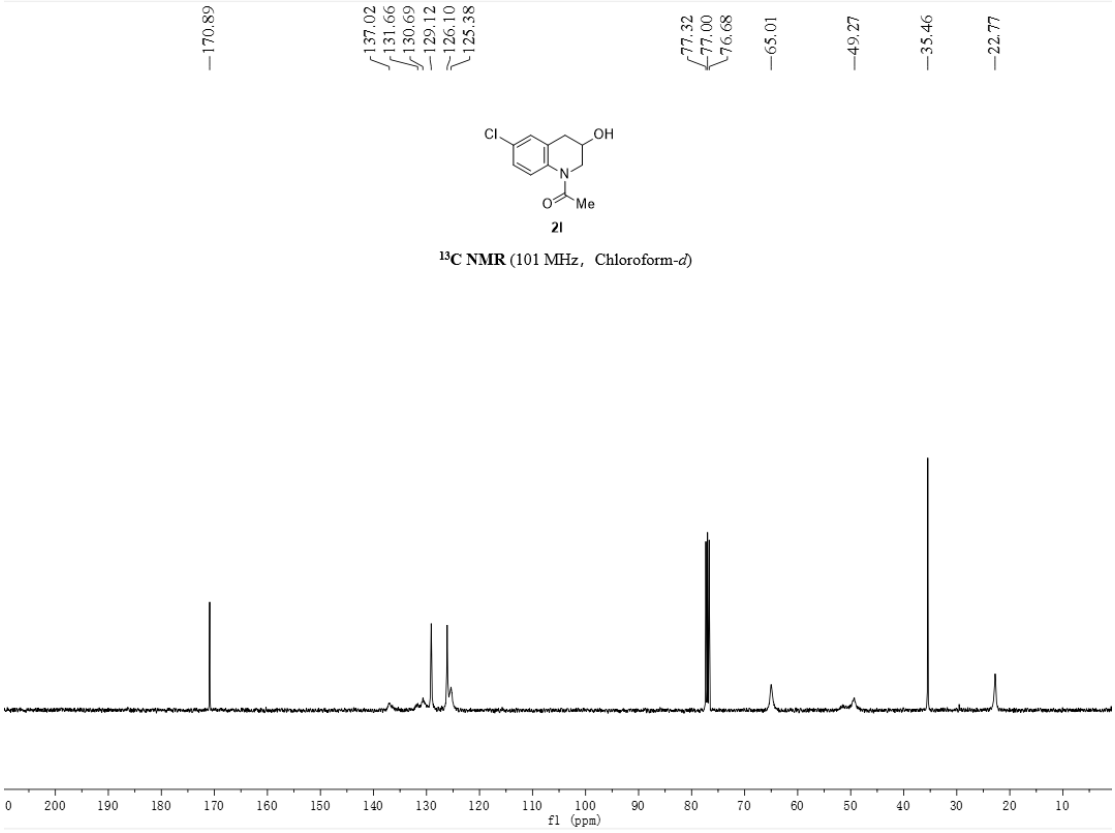




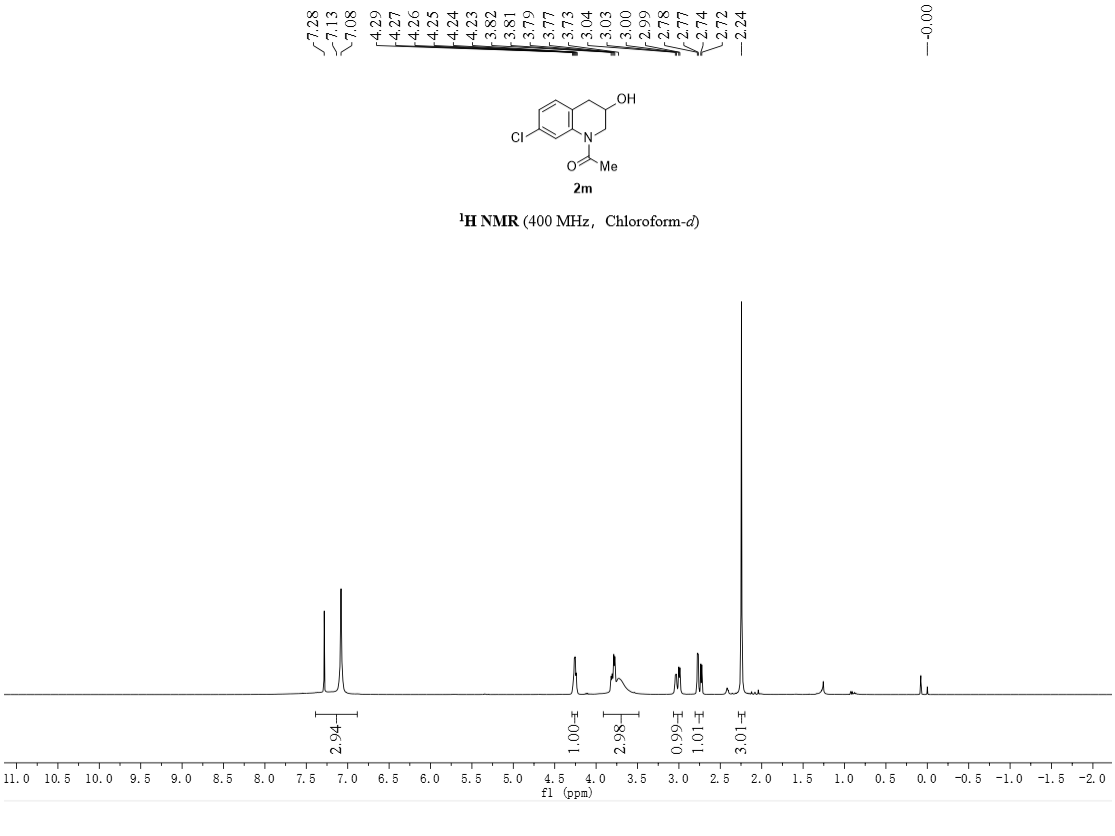
2l

^{1}H NMR (400 MHz，Chloroform-*d*)

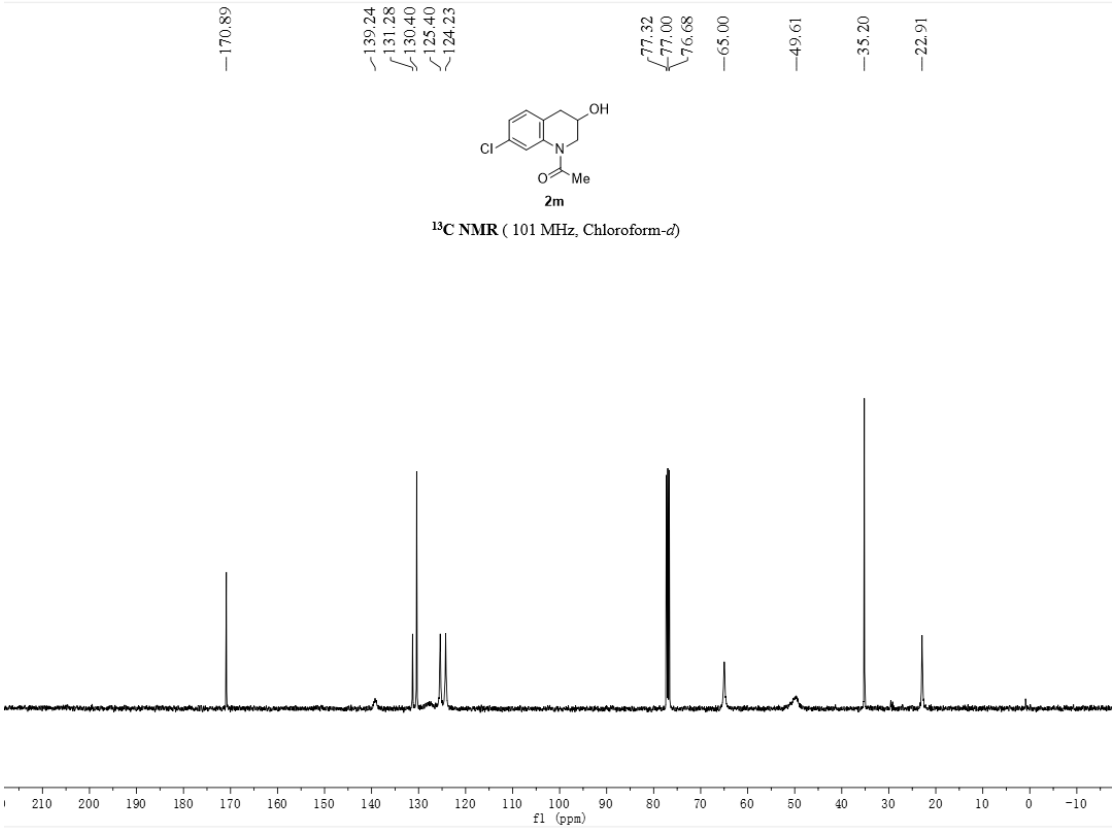




^{13}C NMR (101 MHz, Chloroform-*d*)

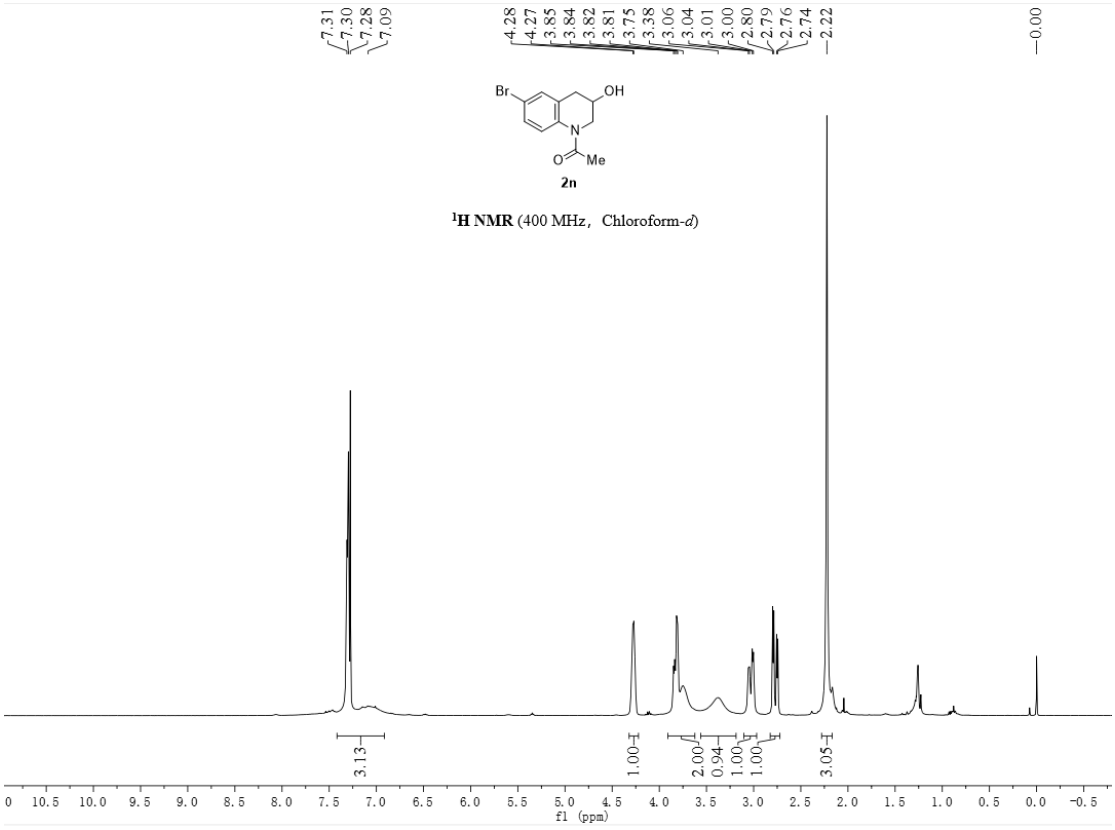


^{1}H NMR (400 MHz, Chloroform-*d*)



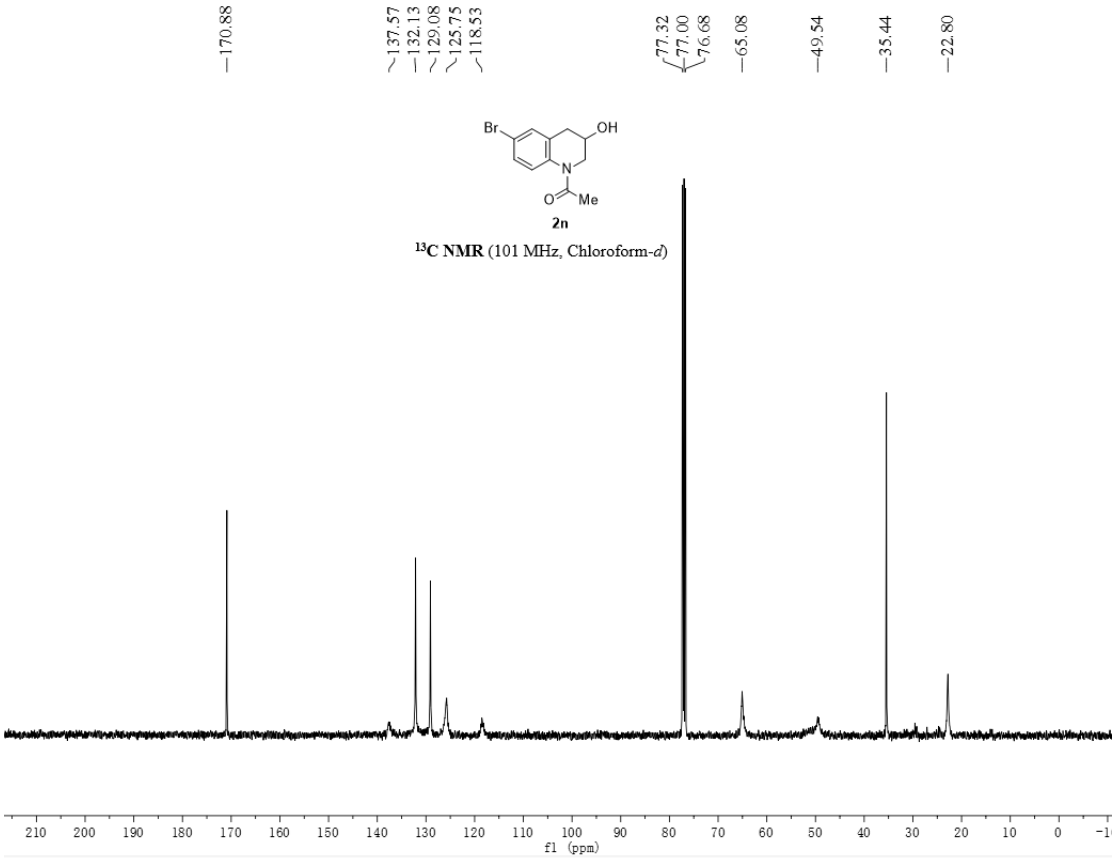
2m

^{13}C NMR (101 MHz, Chloroform-*d*)

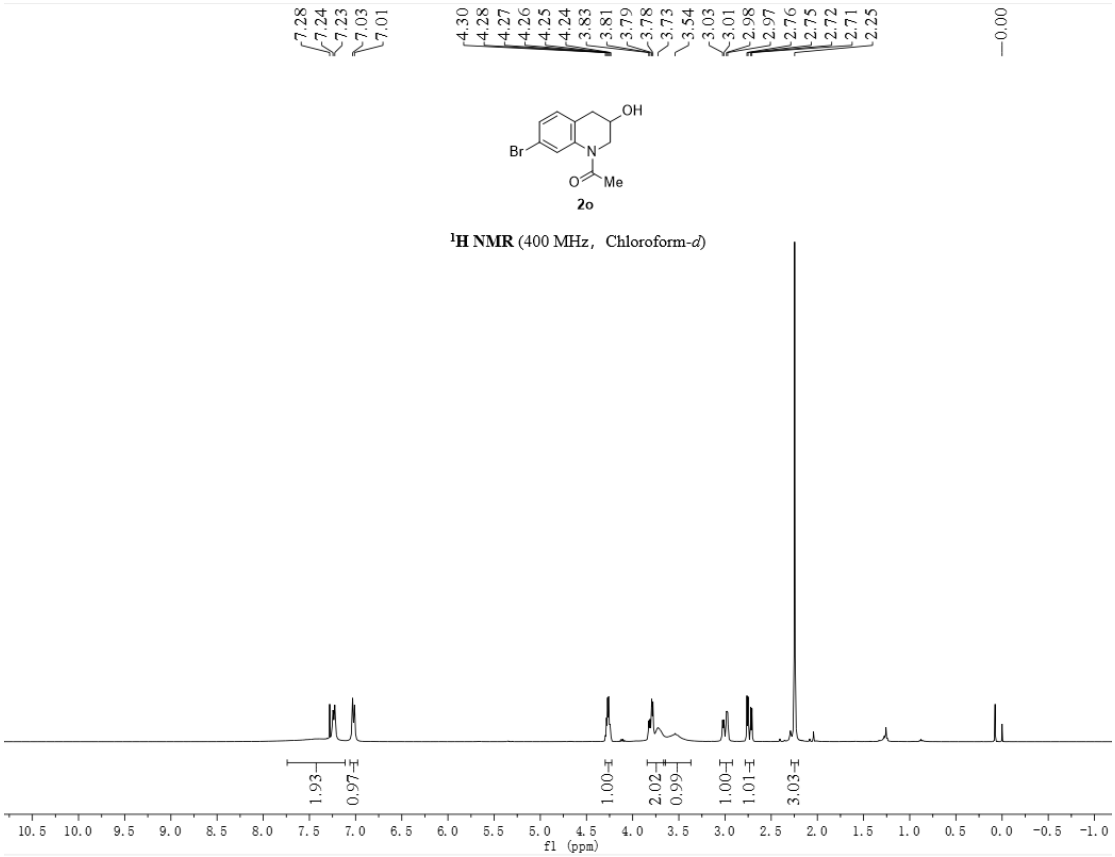


2n

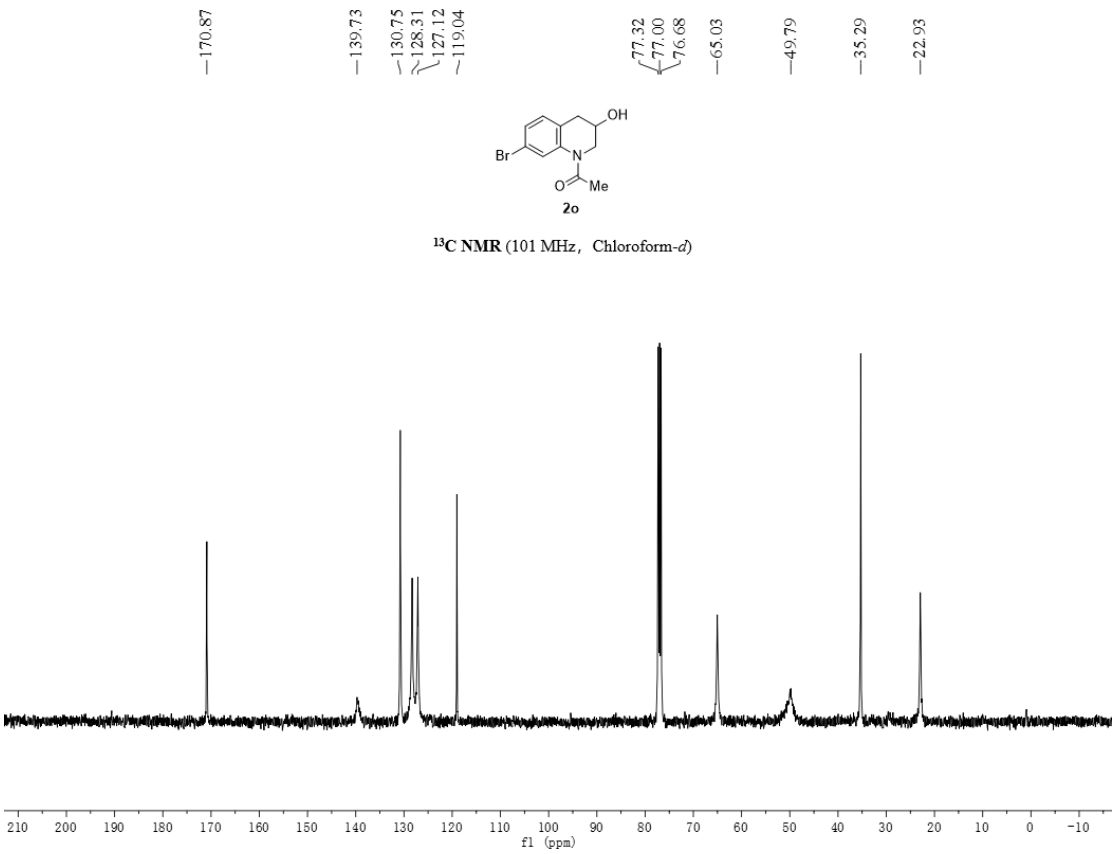
^{1}H NMR (400 MHz，Chloroform-*d*)



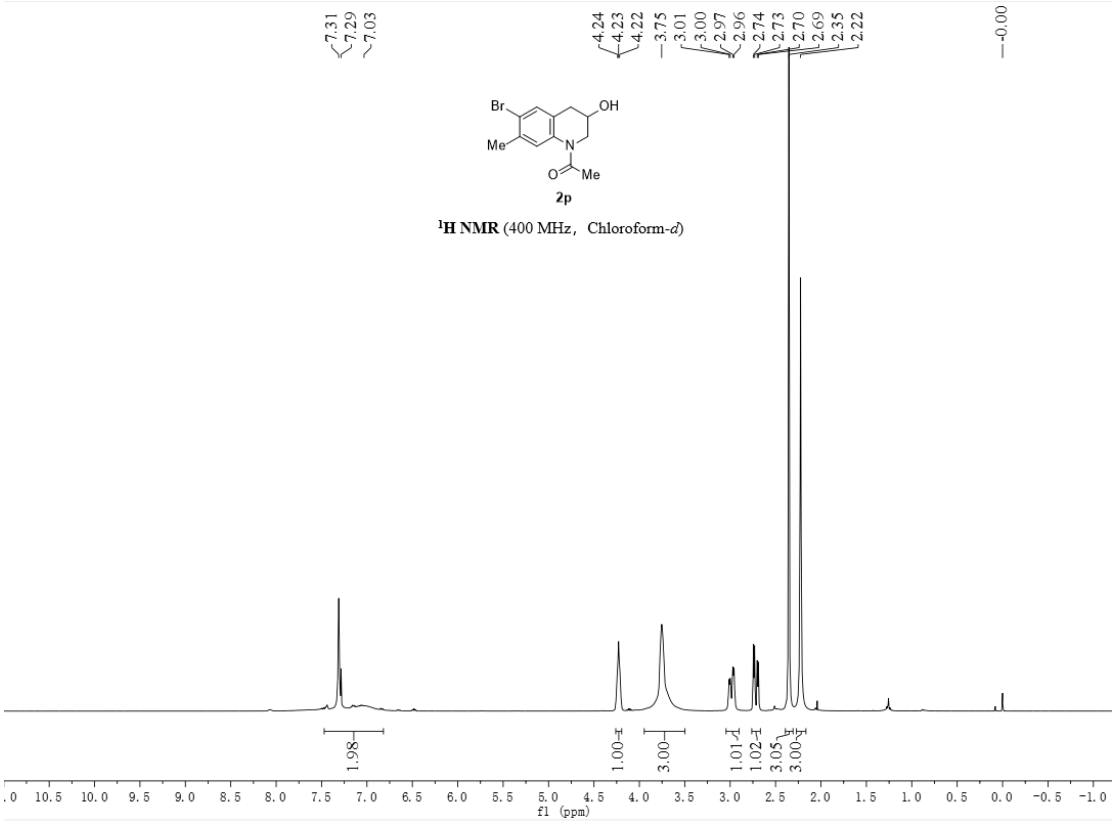
^{13}C NMR (101 MHz, Chloroform-*d*)



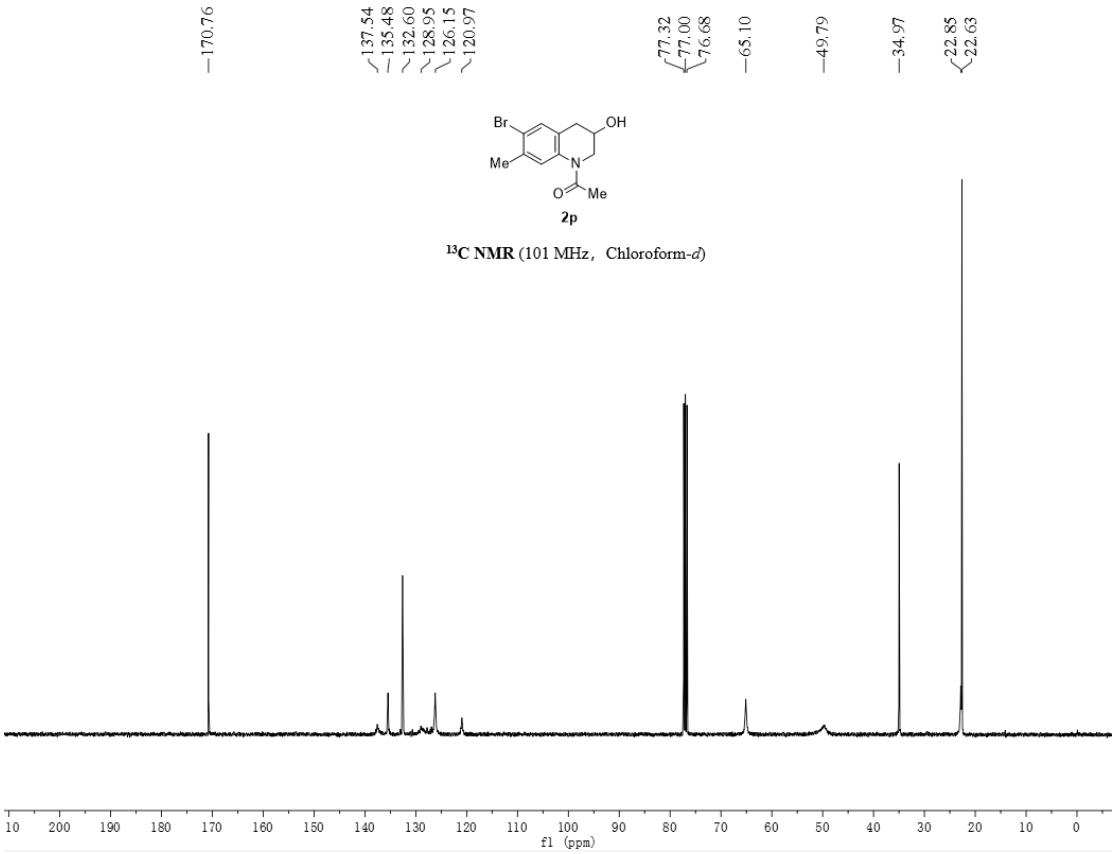
^{1}H NMR (400 MHz, Chloroform-*d*)



^{13}C NMR (101 MHz, Chloroform-*d*)

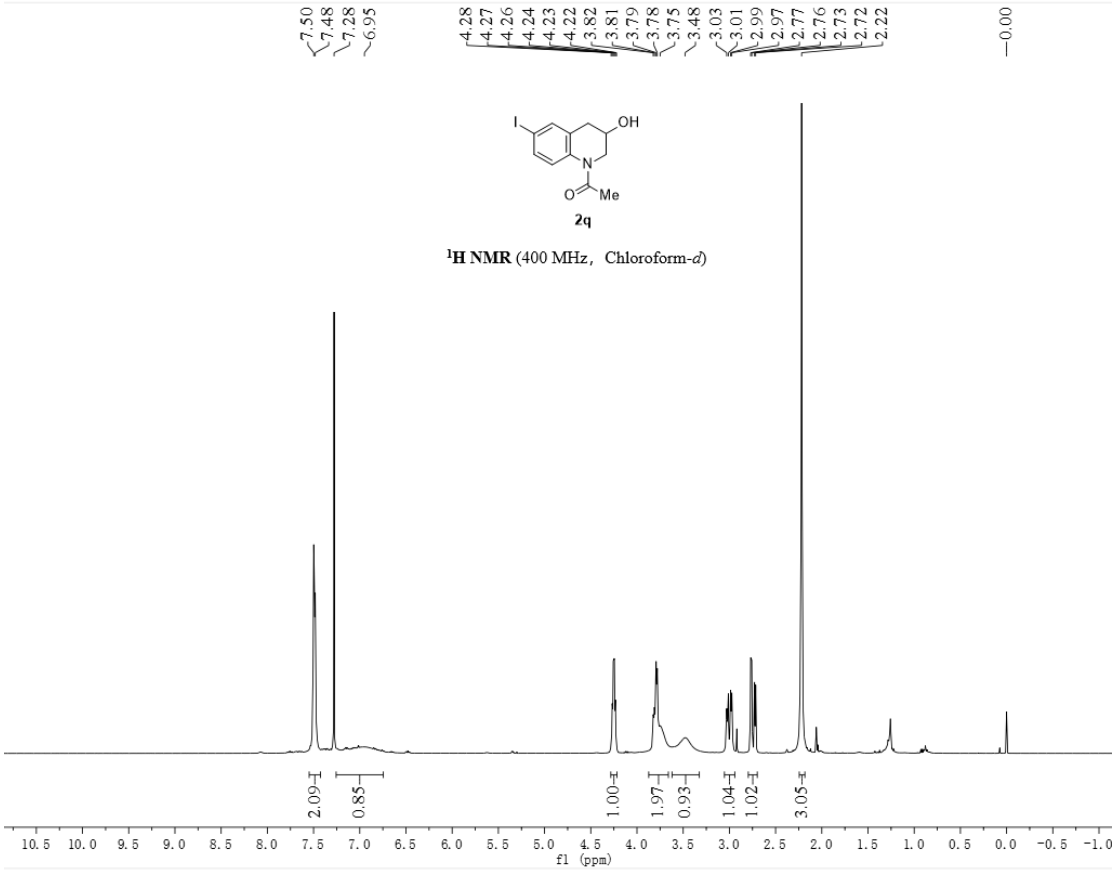


^{1}H NMR (400 MHz, Chloroform-*d*)



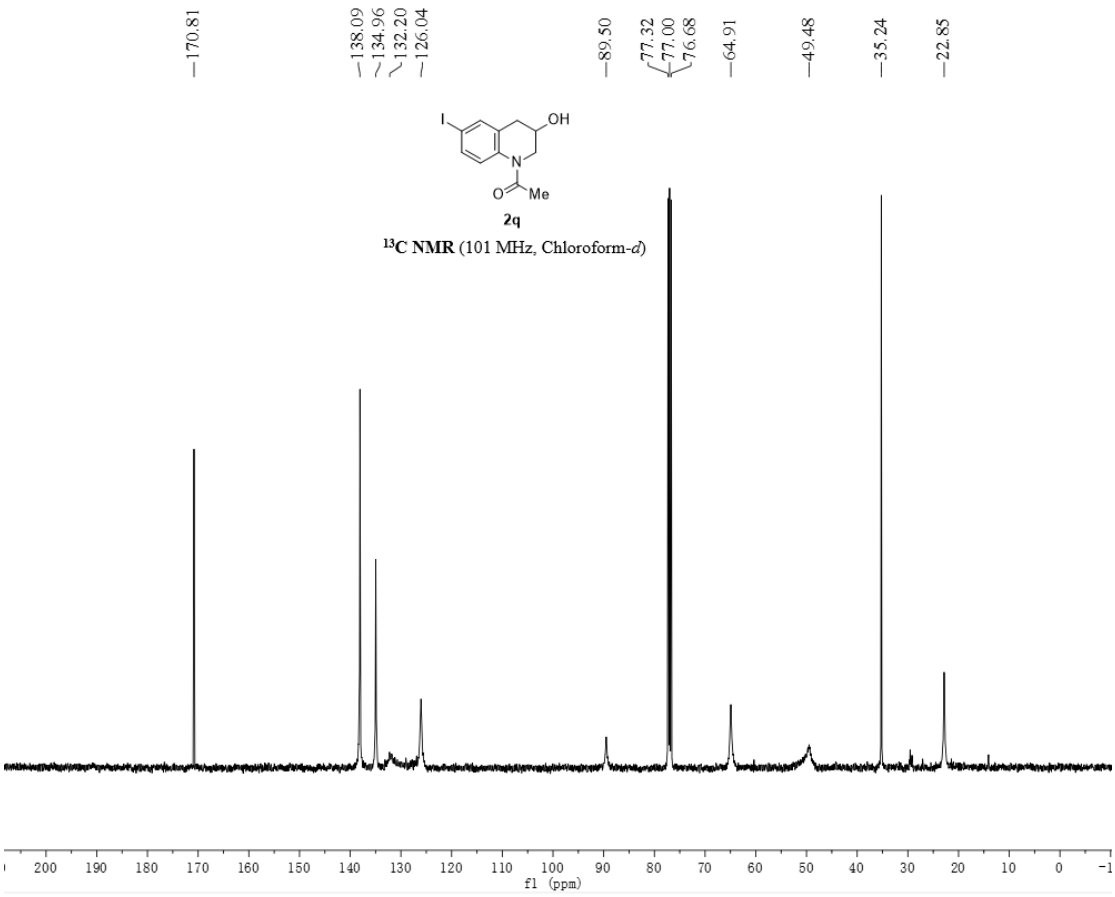
2p

^{13}C NMR (101 MHz, Chloroform-*d*)

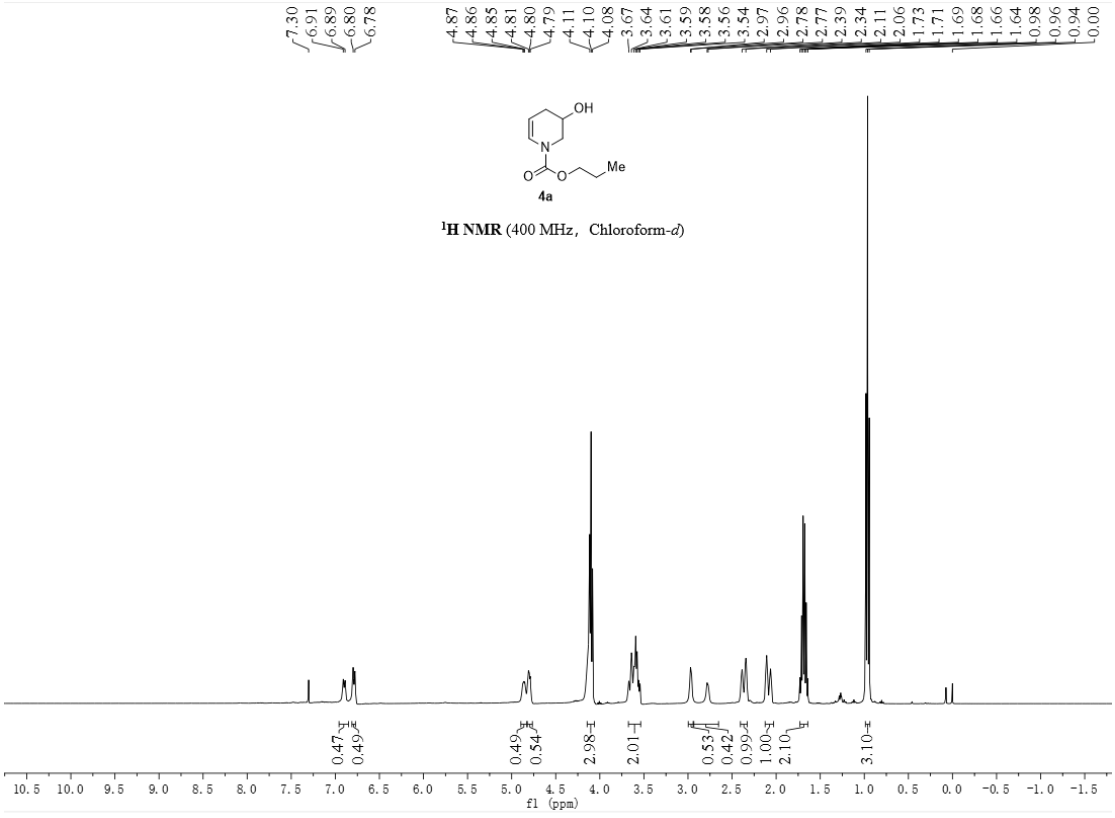


2q

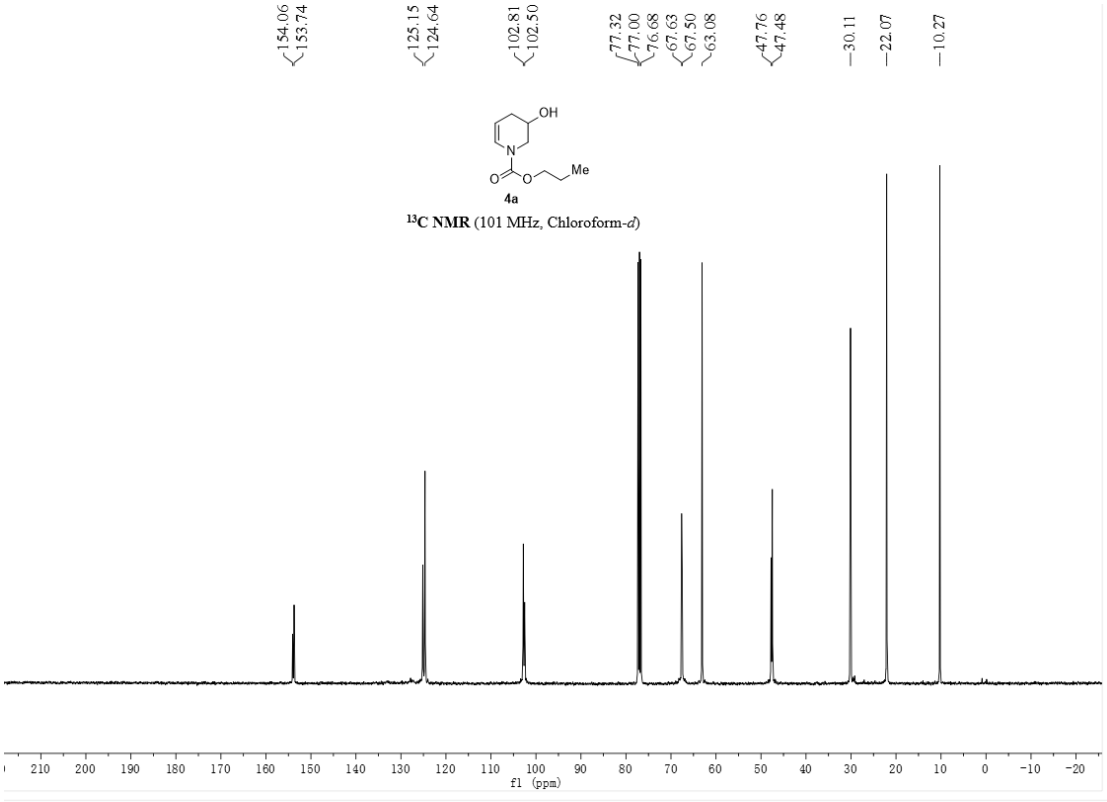
^{1}H NMR (400 MHz, Chloroform-*d*)



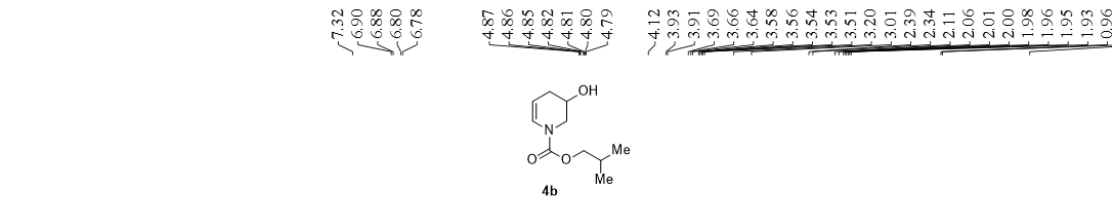
^{13}C NMR (101 MHz, Chloroform-*d*)



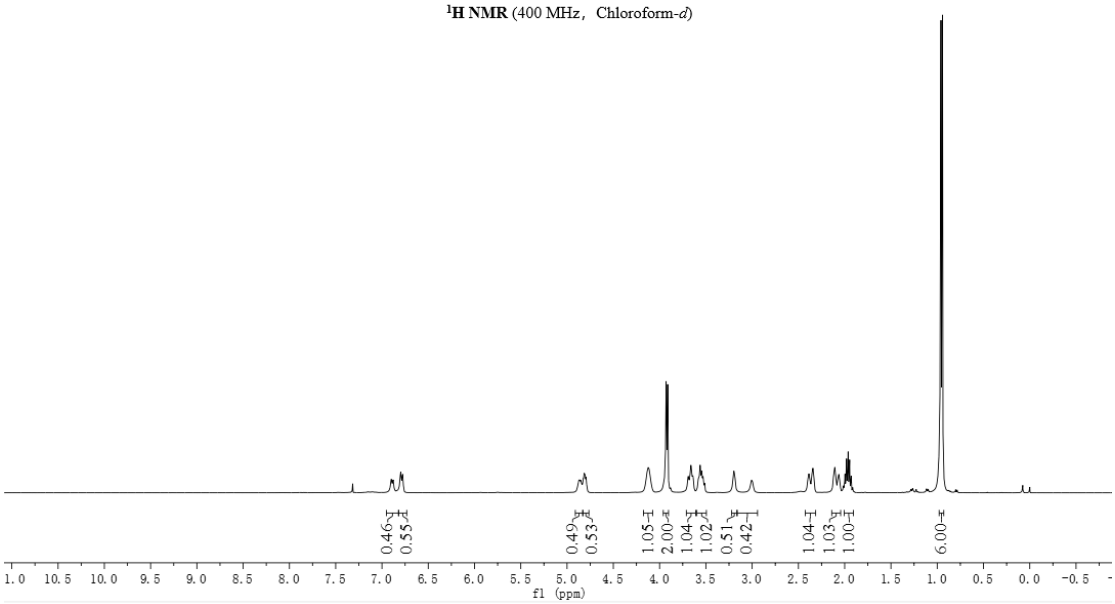
^{1}H NMR (400 MHz, Chloroform-*d*)

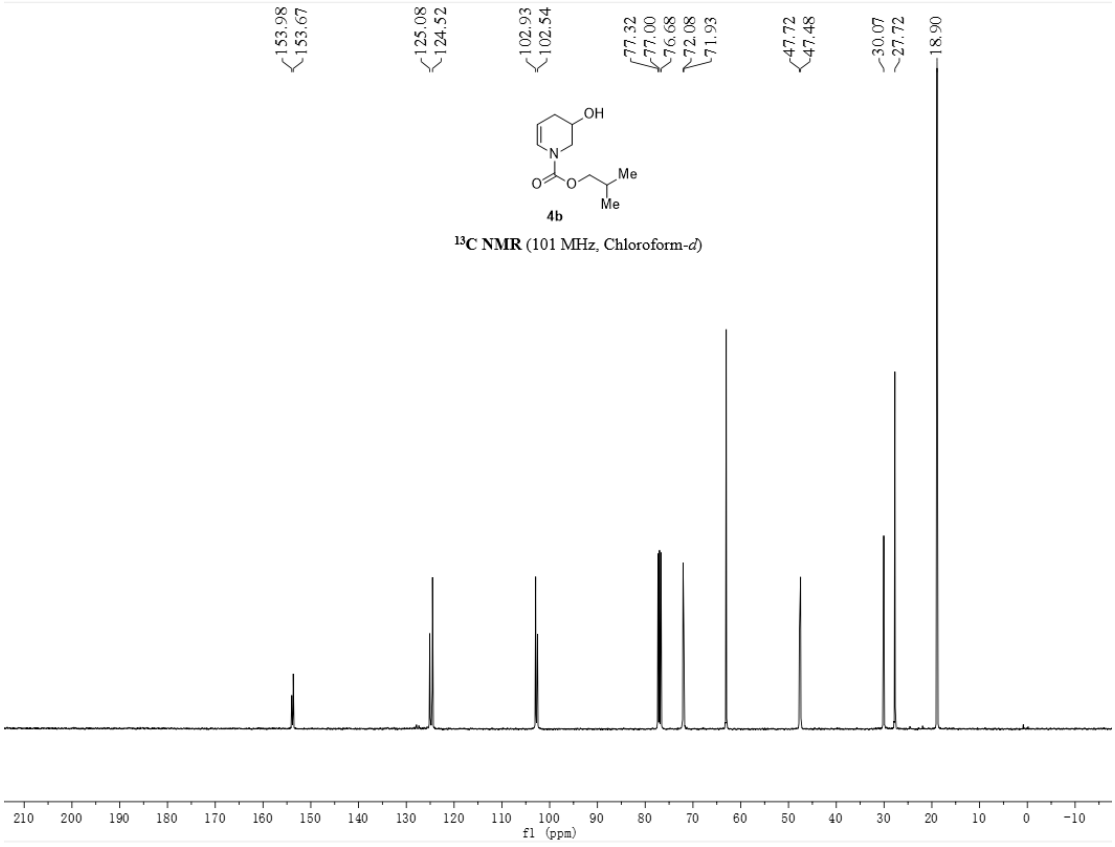


^{13}C NMR (101 MHz, Chloroform-*d*)



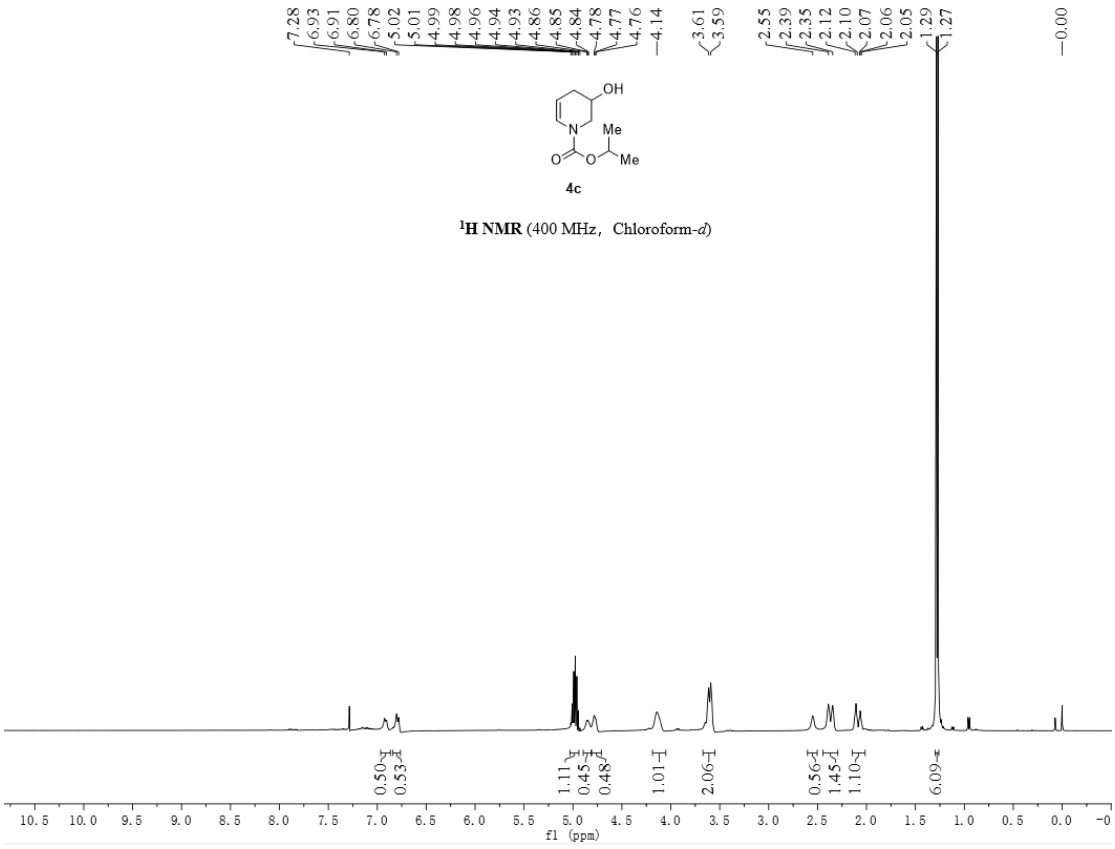
^{1}H NMR (400 MHz, Chloroform-*d*)





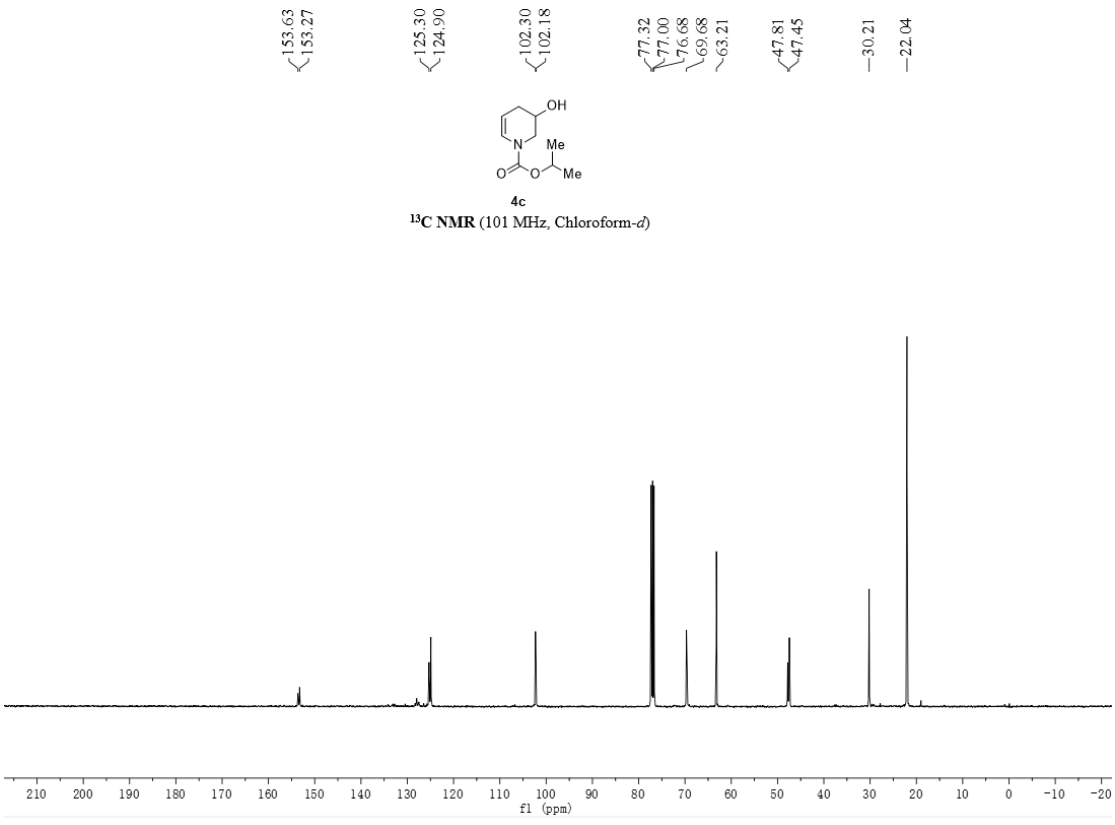
4b

^{13}C NMR (101 MHz, Chloroform-*d*)



4c

^{1}H NMR (400 MHz, Chloroform-*d*)

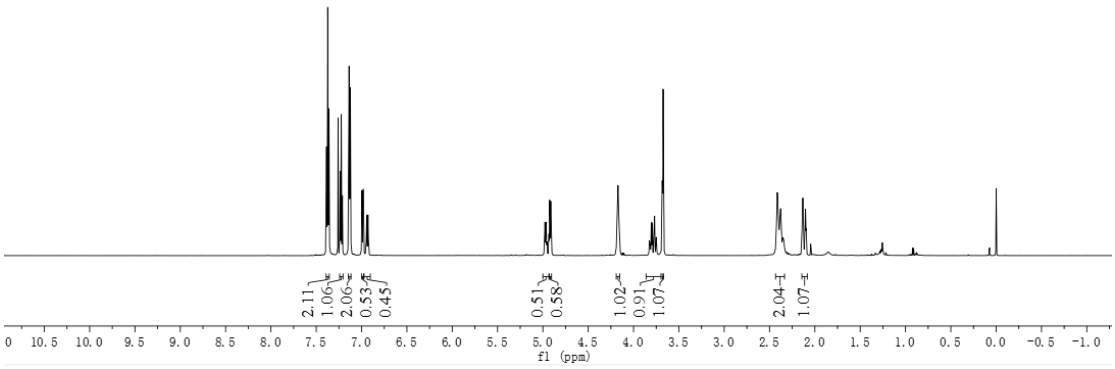


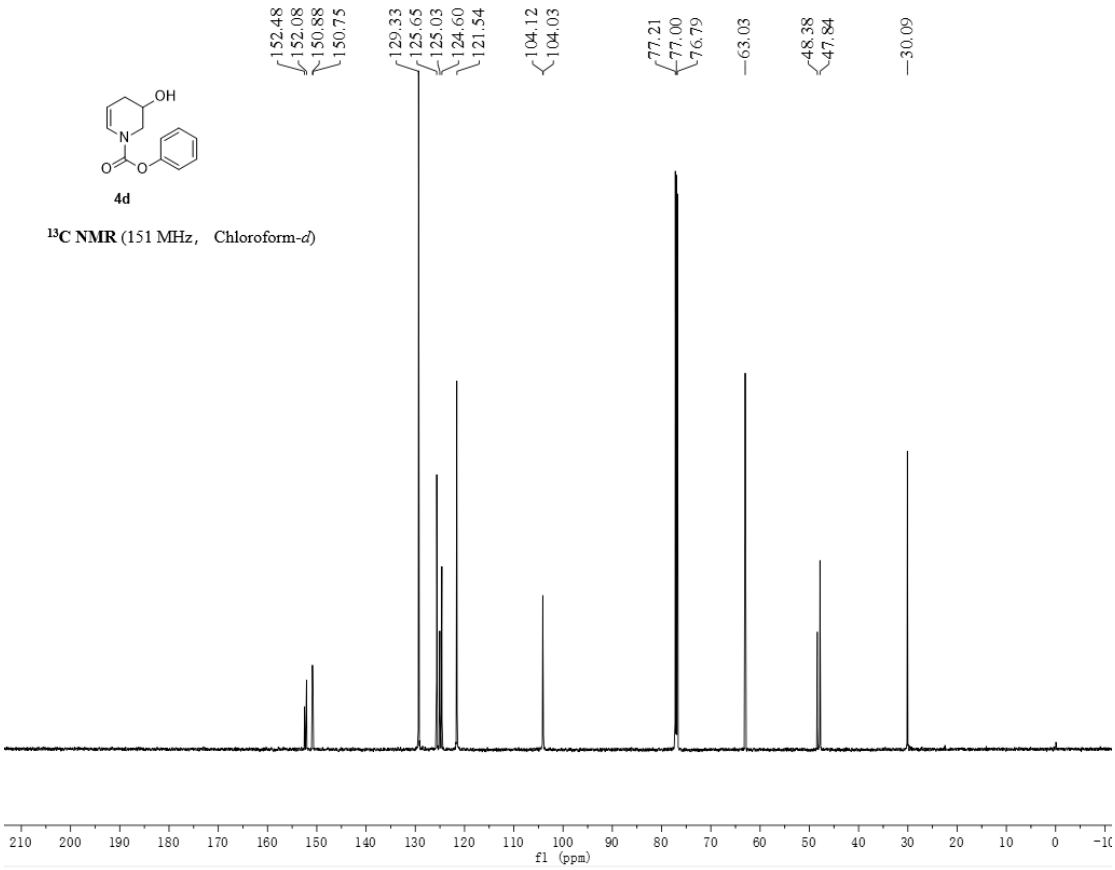
4c

^{13}C NMR (101 MHz, Chloroform-*d*)

4d

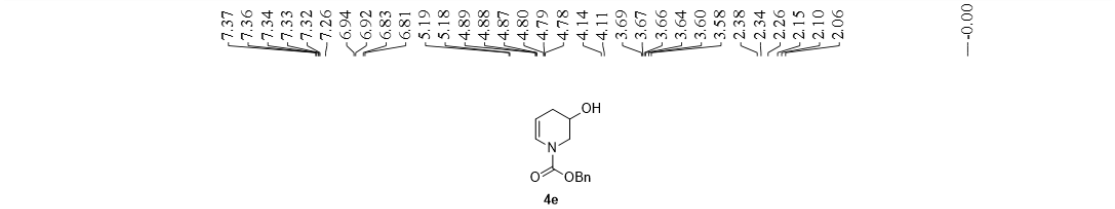
^{1}H NMR (600 MHz, Chloroform-*d*)





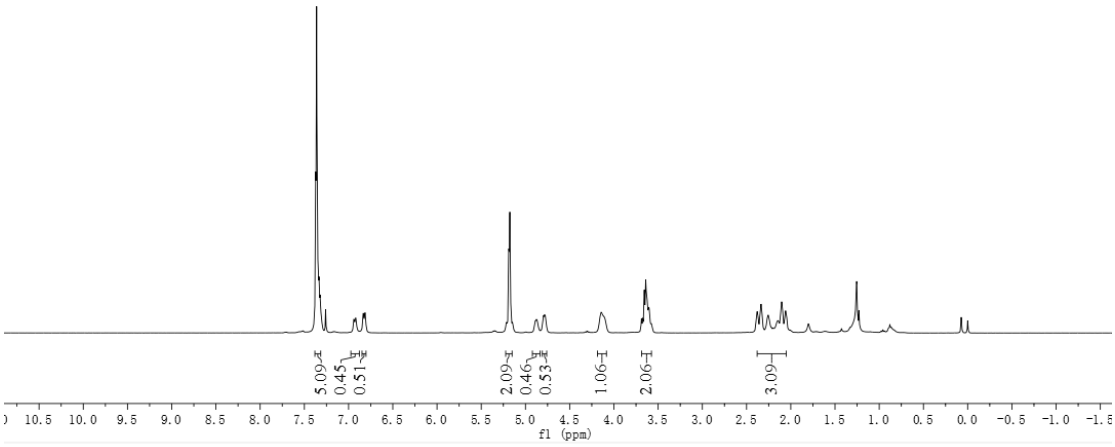
4d

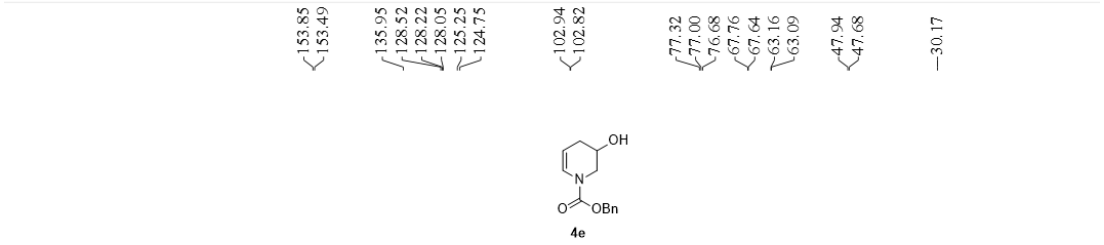
^{13}C NMR (151 MHz, Chloroform-*d*)



4e

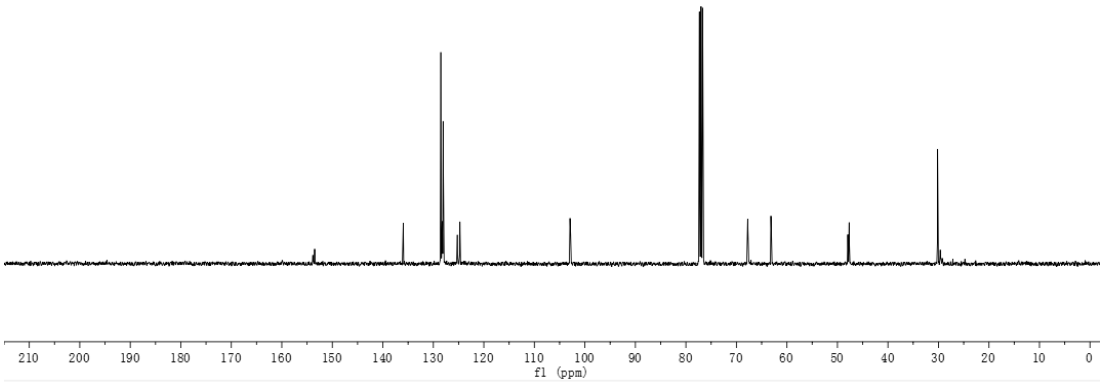
^{1}H NMR (400 MHz, Chloroform-*d*)

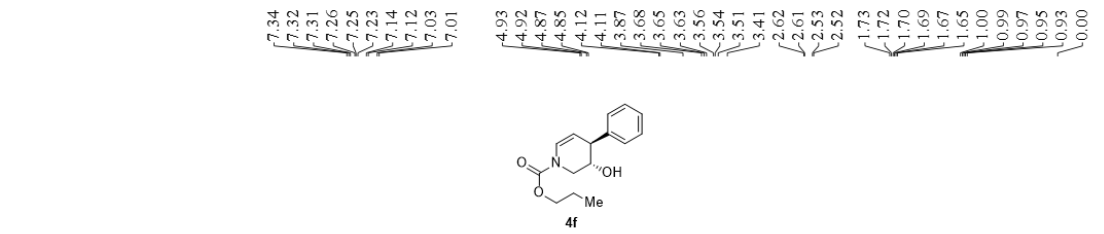




4e

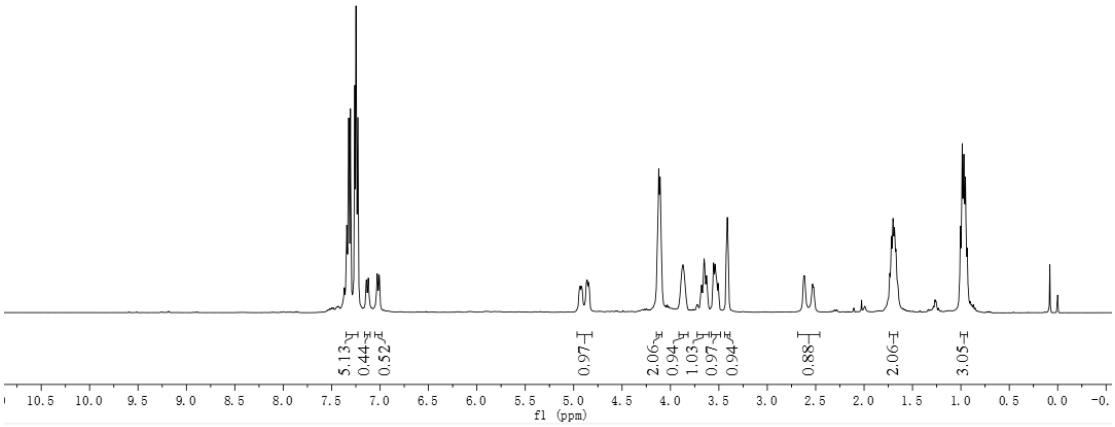
^{13}C NMR (101 MHz，Chloroform-*d*)

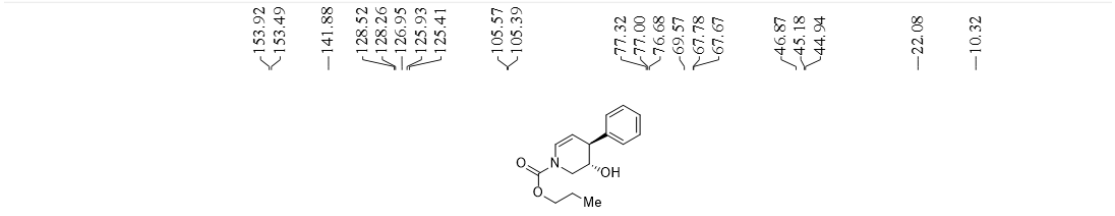




4f

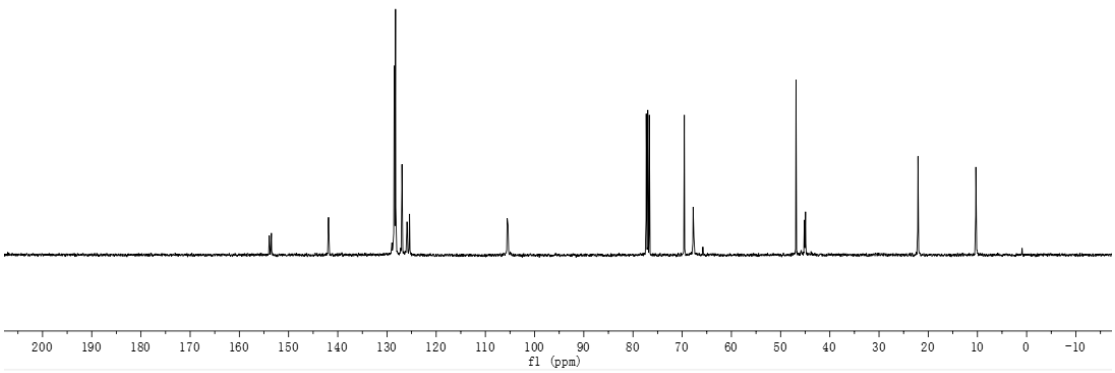
^{1}H NMR (400 MHz，Chloroform-*d*)

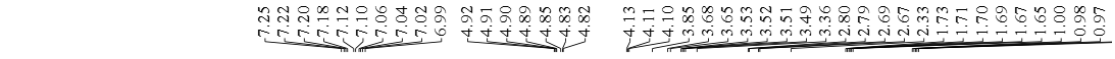


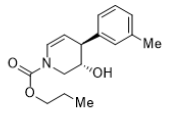


4f

^{13}C NMR (101 MHz, Chloroform-*d*)

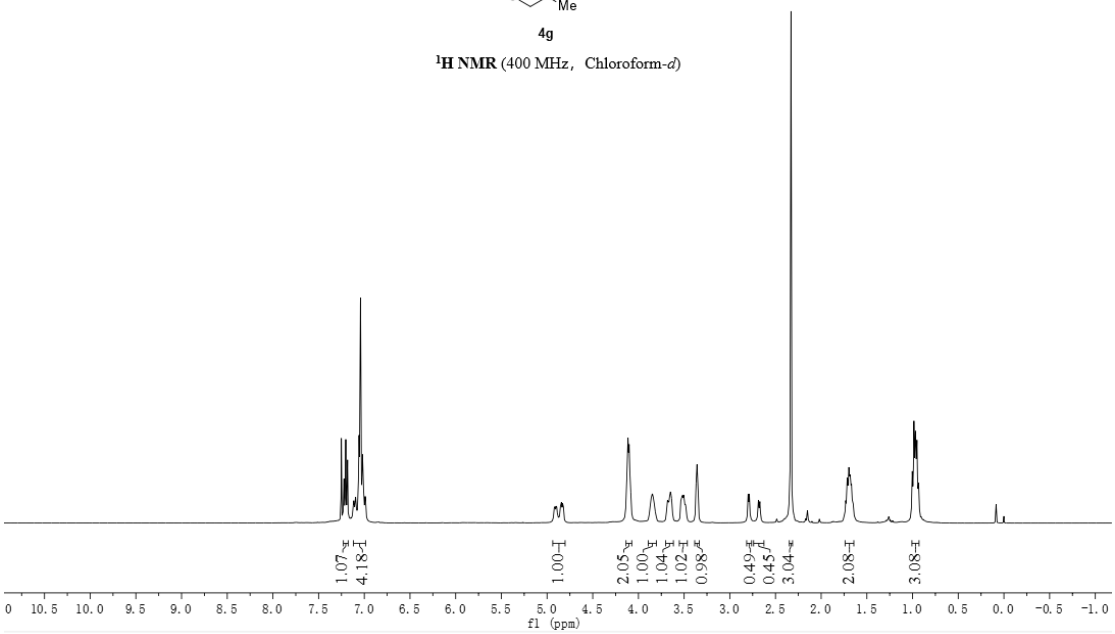


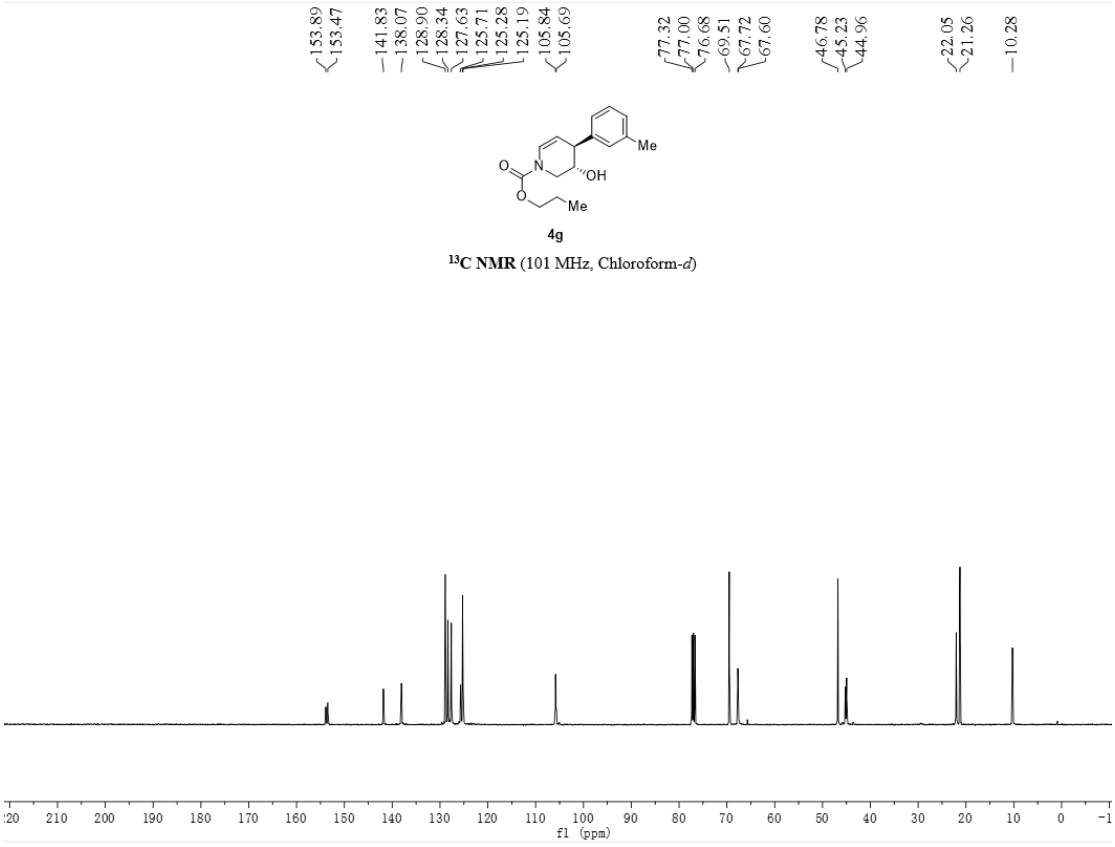




4g

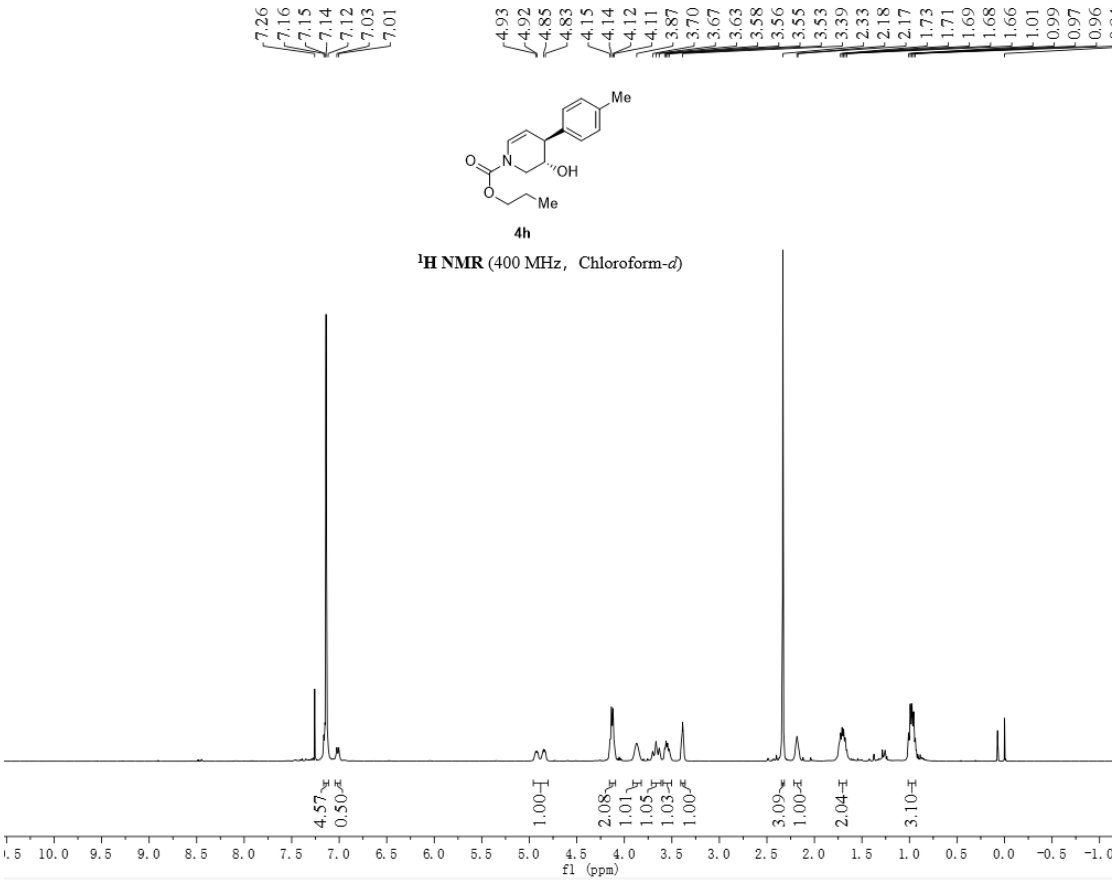
^{1}H NMR (400 MHz, Chloroform-*d*)





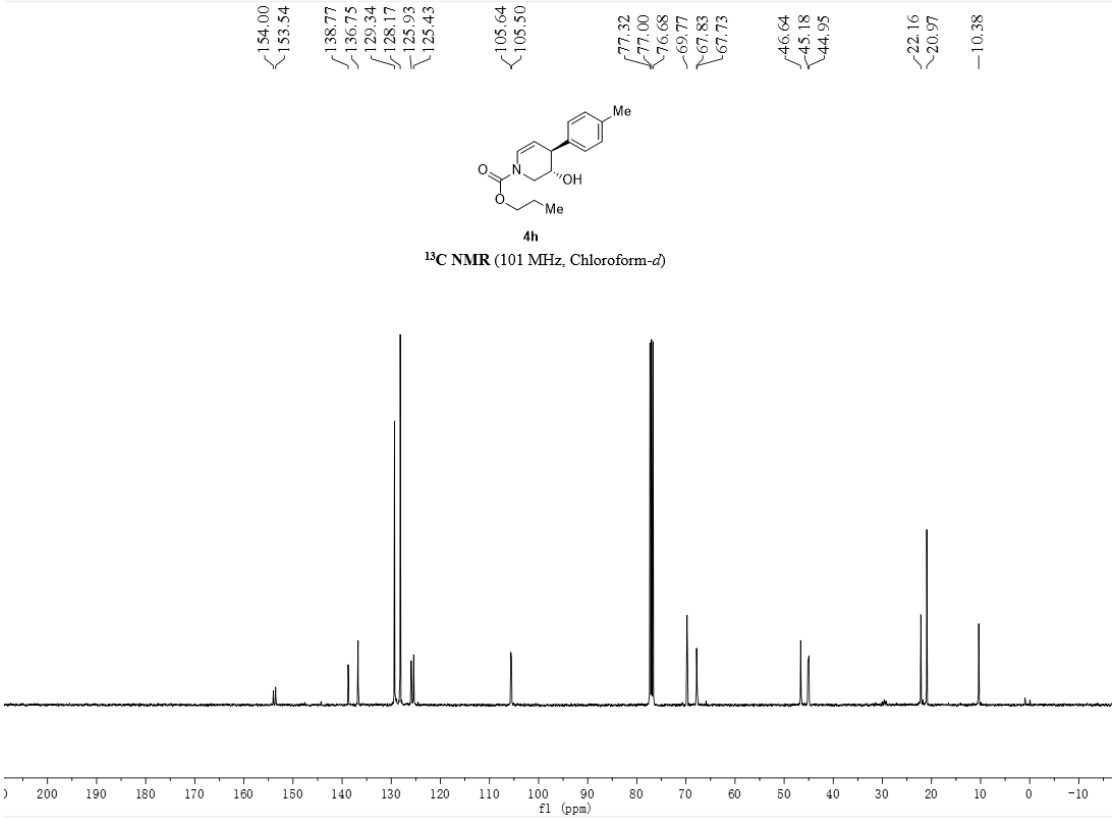
4g

^{13}C NMR (101 MHz, Chloroform-*d*)



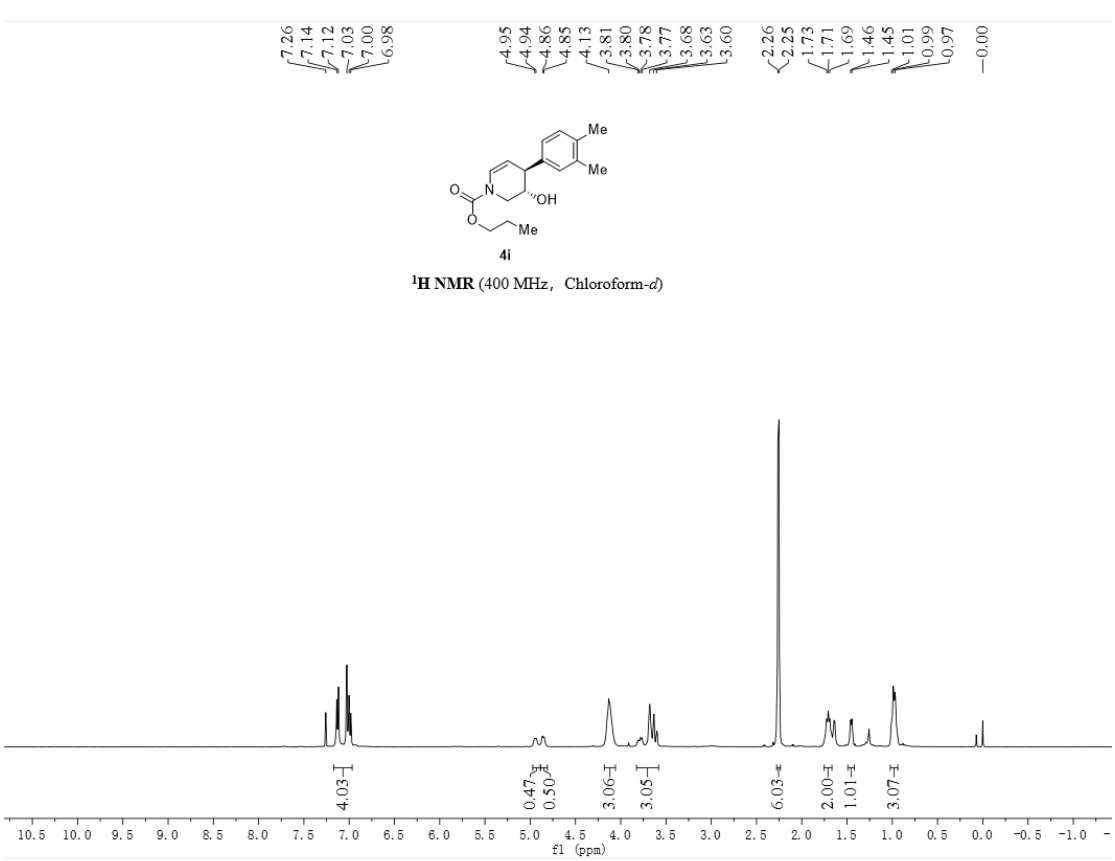
4h

^{1}H NMR (400 MHz, Chloroform-*d*)



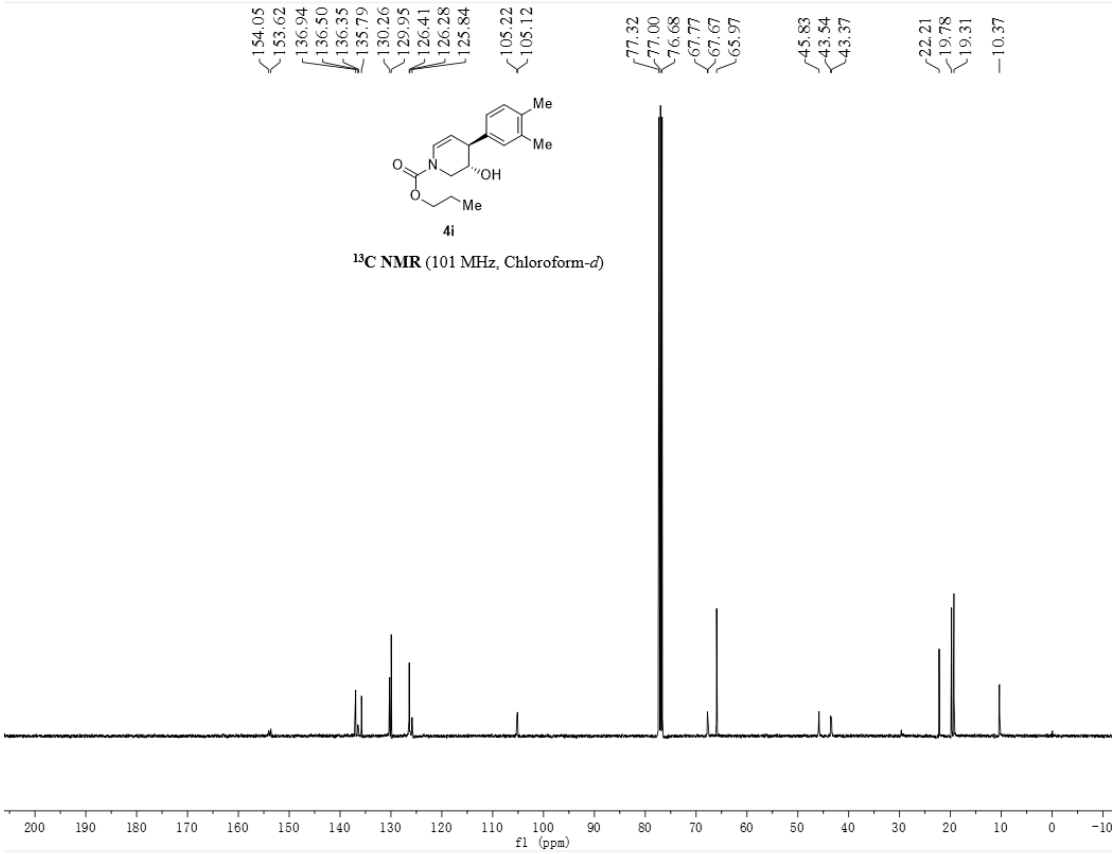
4h

^{13}C NMR (101 MHz, Chloroform-*d*)



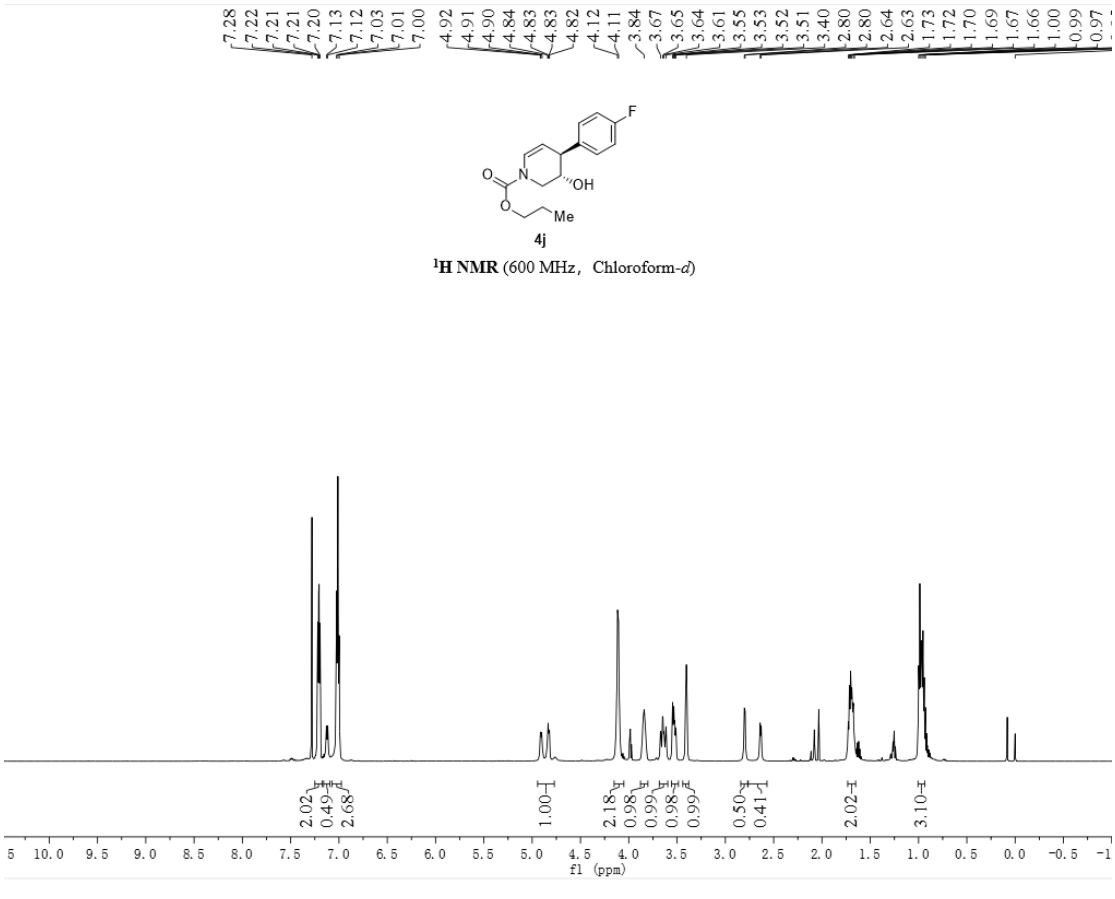
4i

^{1}H NMR (400 MHz, Chloroform-*d*)



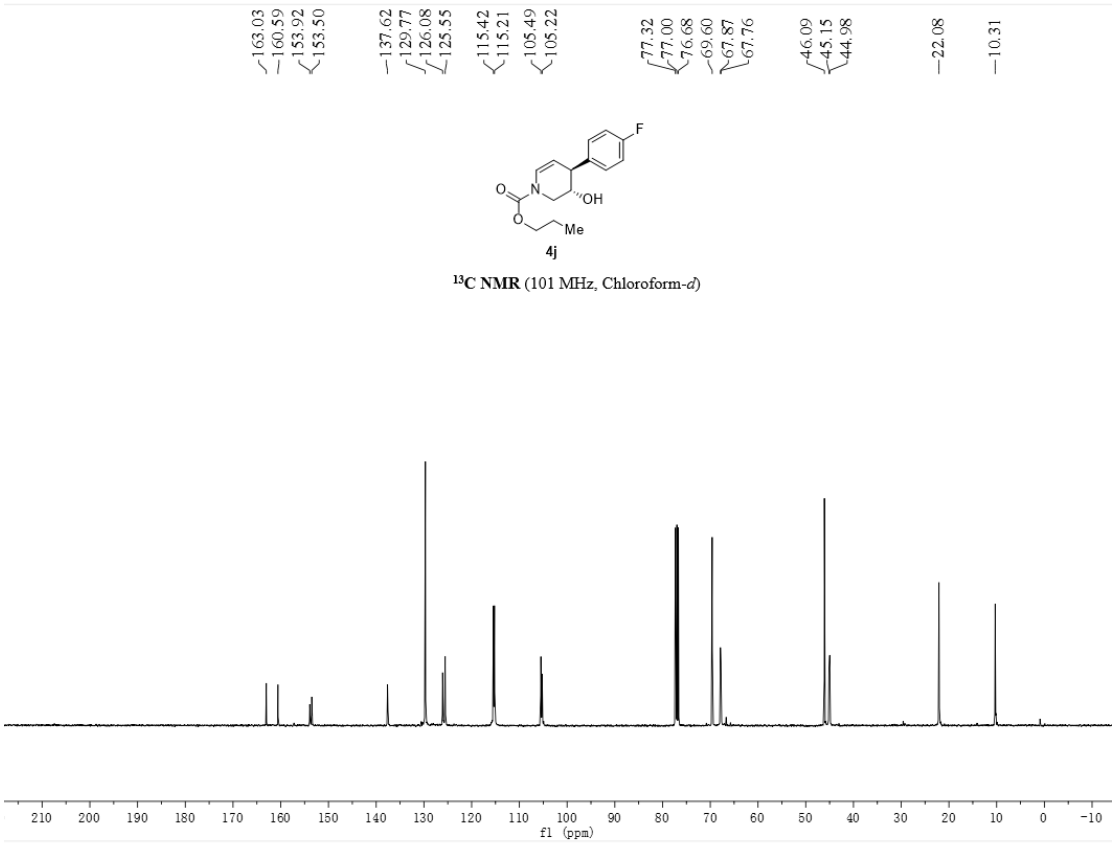
4i

^{13}C NMR (101 MHz, Chloroform-*d*)

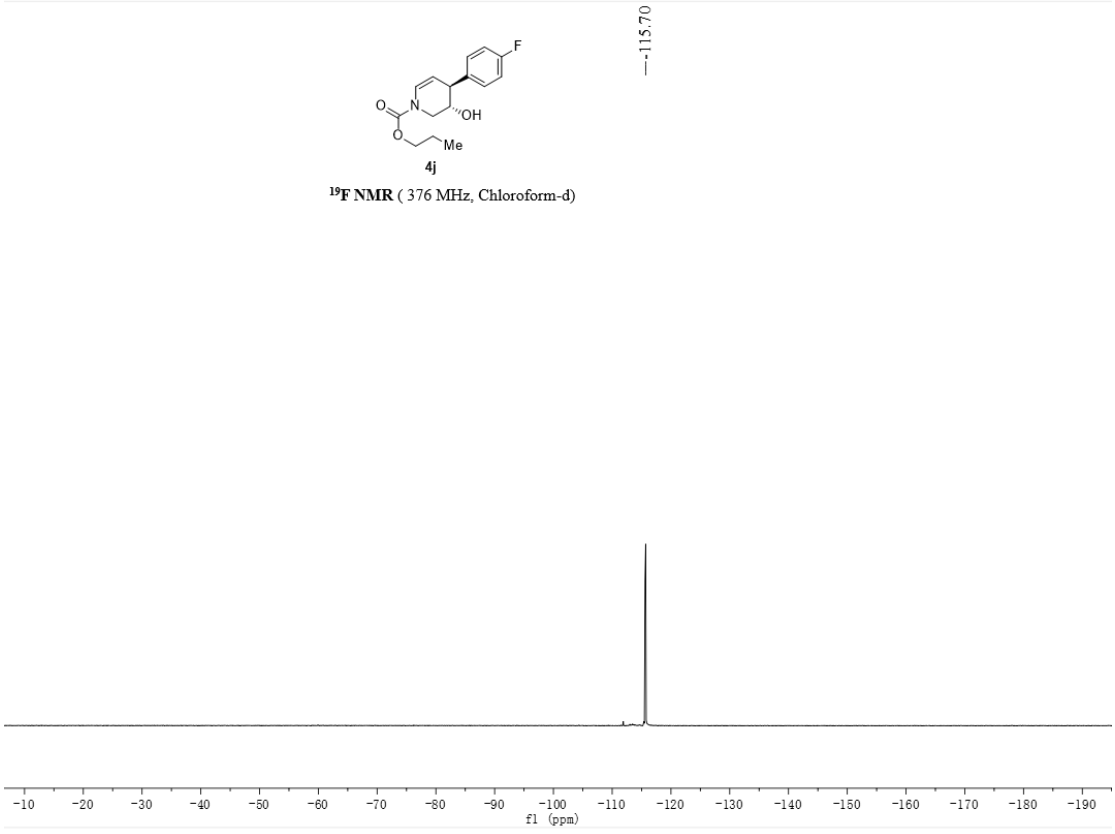


4j

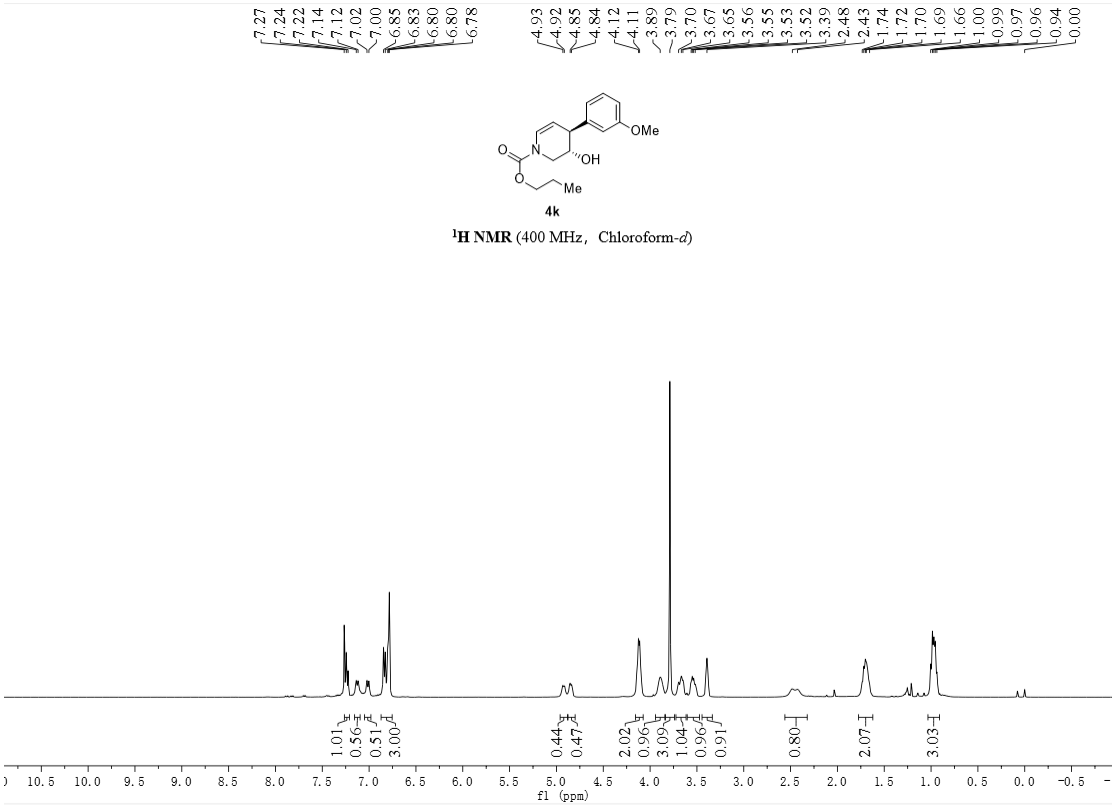
^{1}H NMR (600 MHz，Chloroform-*d*)



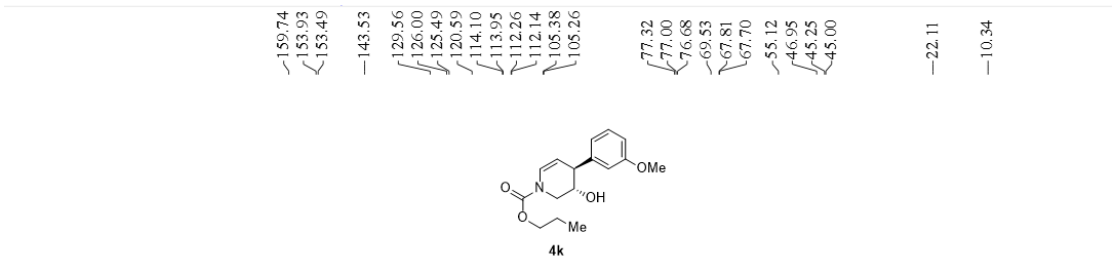
^{13}C NMR (101 MHz, Chloroform-*d*)



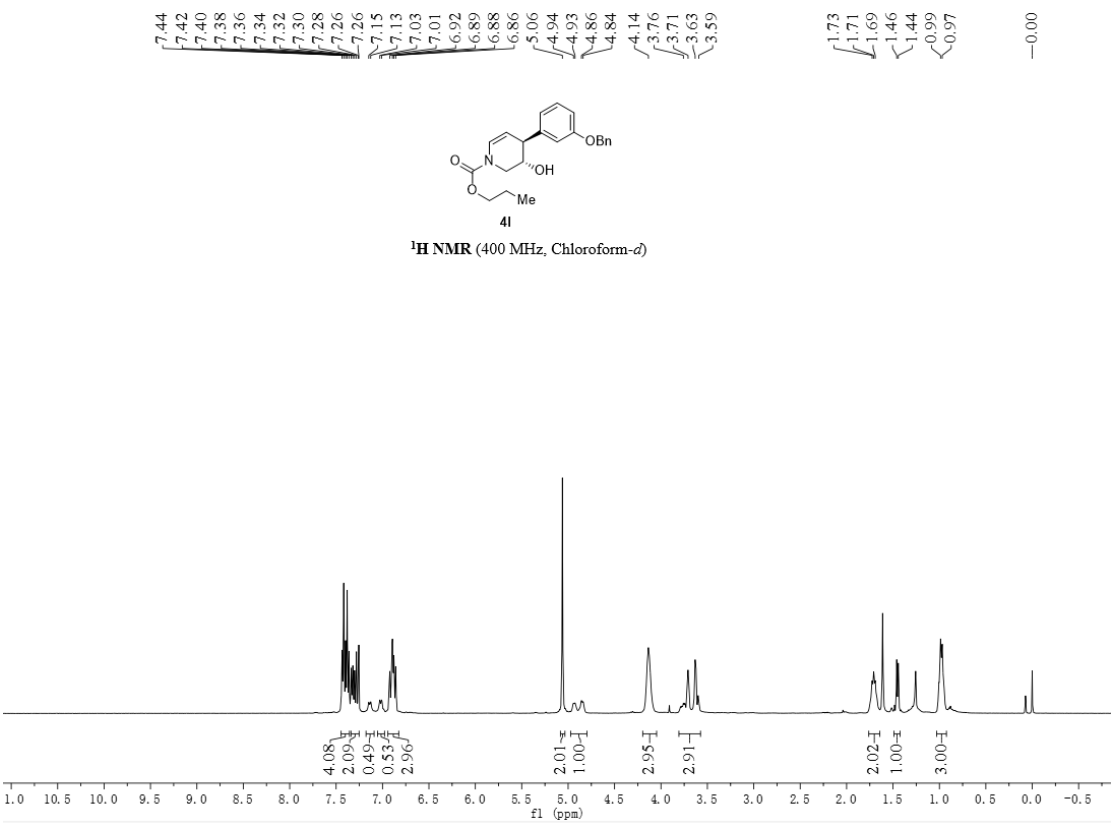
^{19}F NMR (376 MHz, Chloroform-d)



^{1}H NMR (400 MHz, Chloroform-*d*)

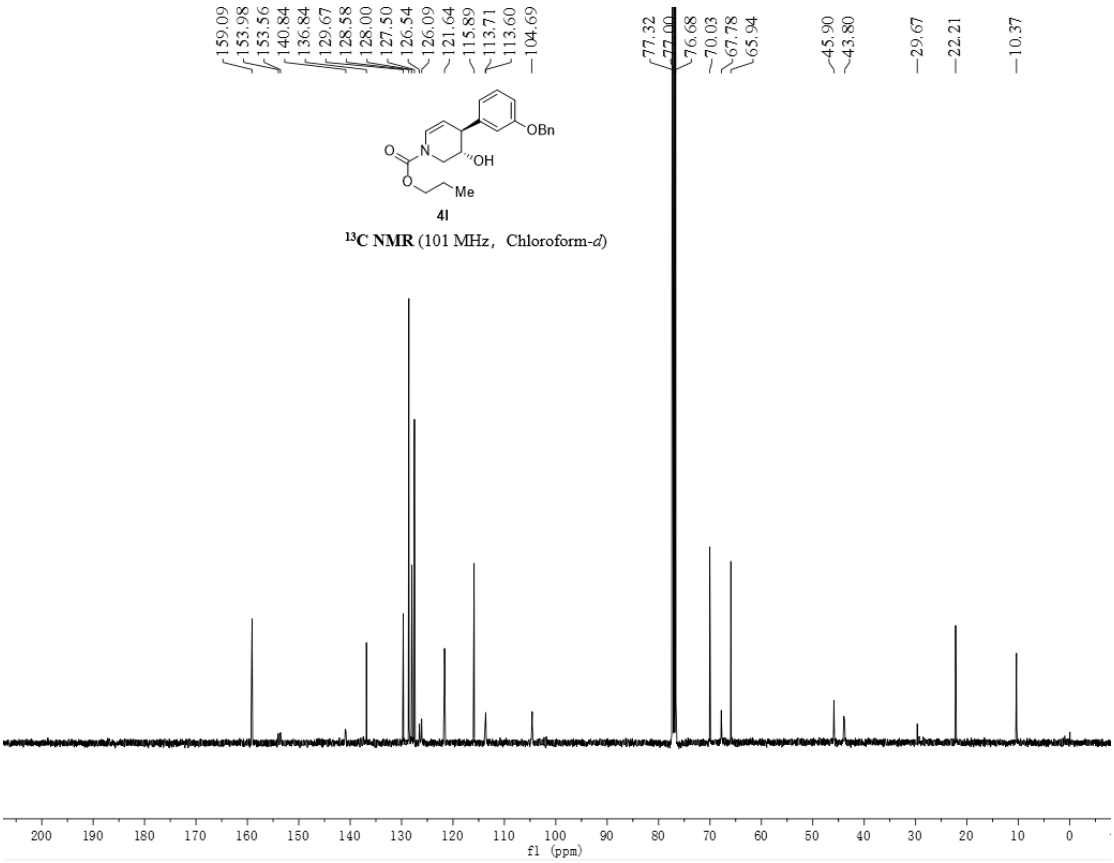


^{13}C NMR (101 MHz, Chloroform-*d*)



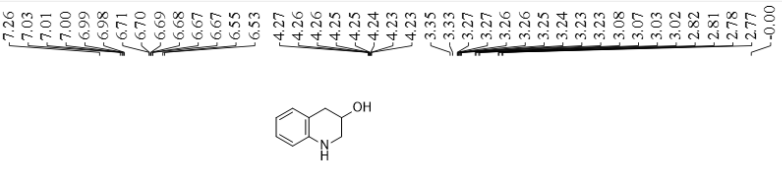
4l

^{1}H NMR (400 MHz, Chloroform-*d*)



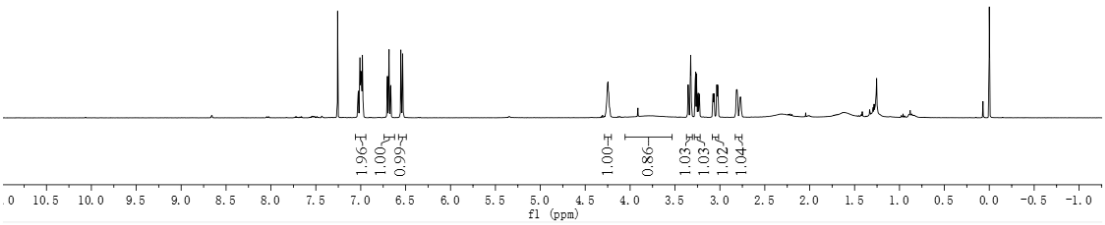
4l

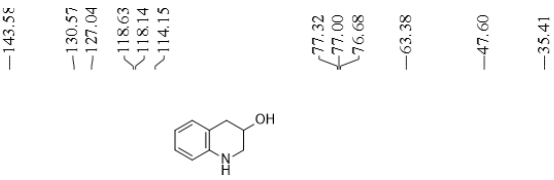
^{13}C NMR (101 MHz, Chloroform-*d*)



5

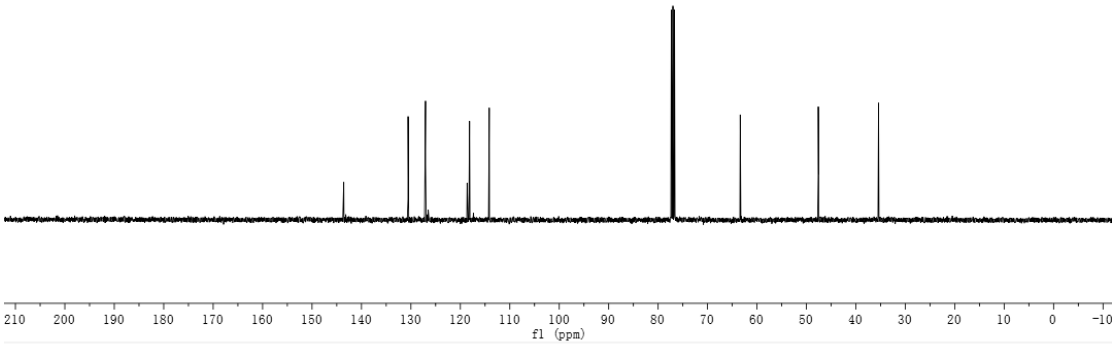
^{1}H NMR (400 MHz, Chloroform-*d*)

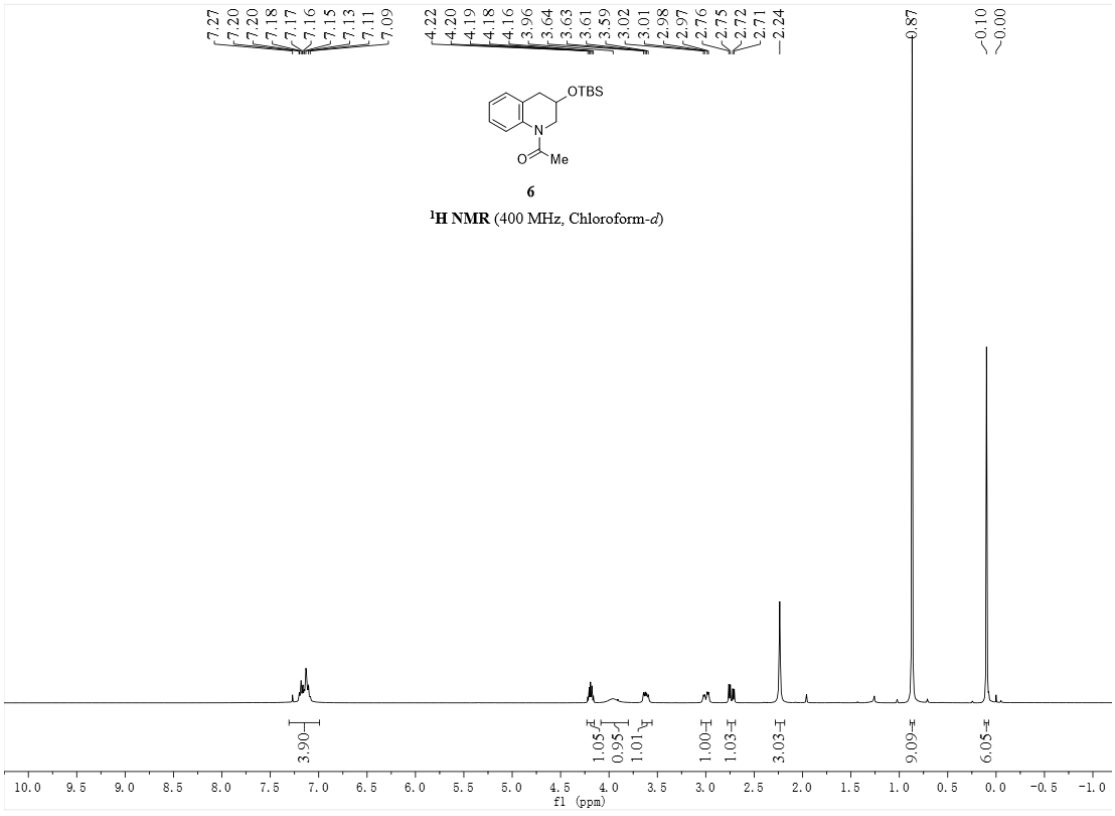




5

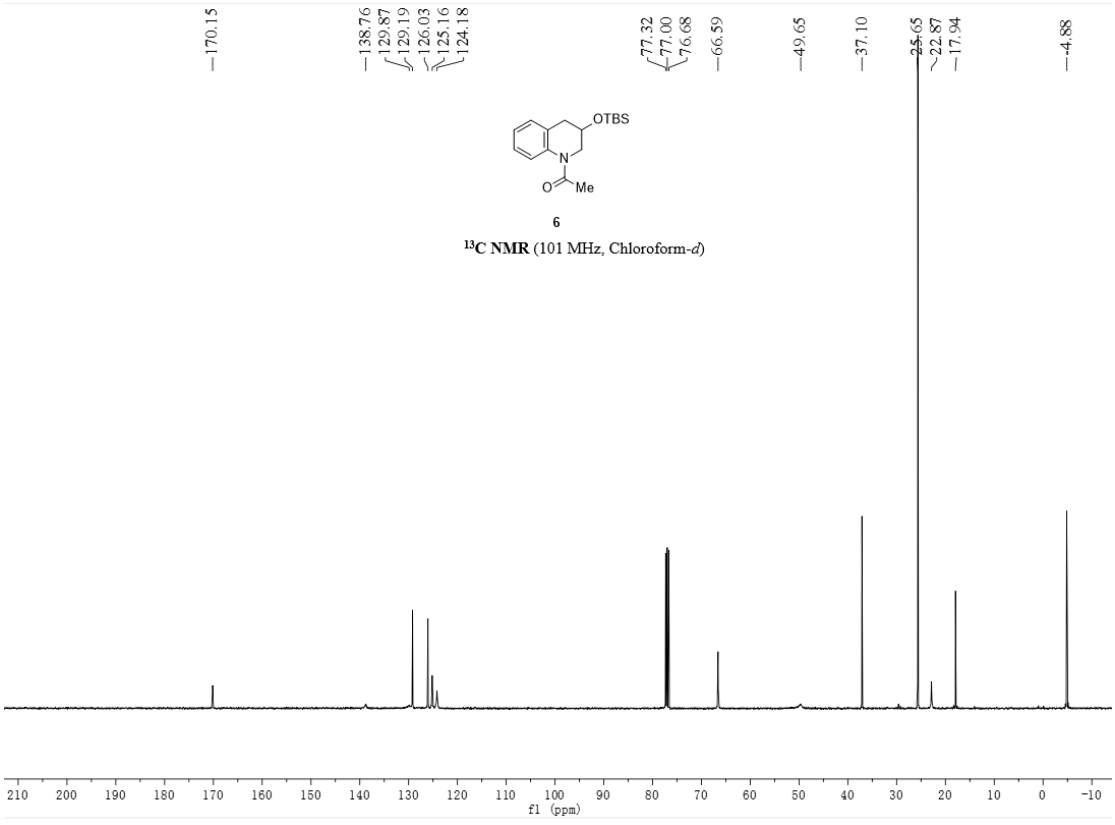
^{13}C NMR (101 MHz, Chloroform-*d*)





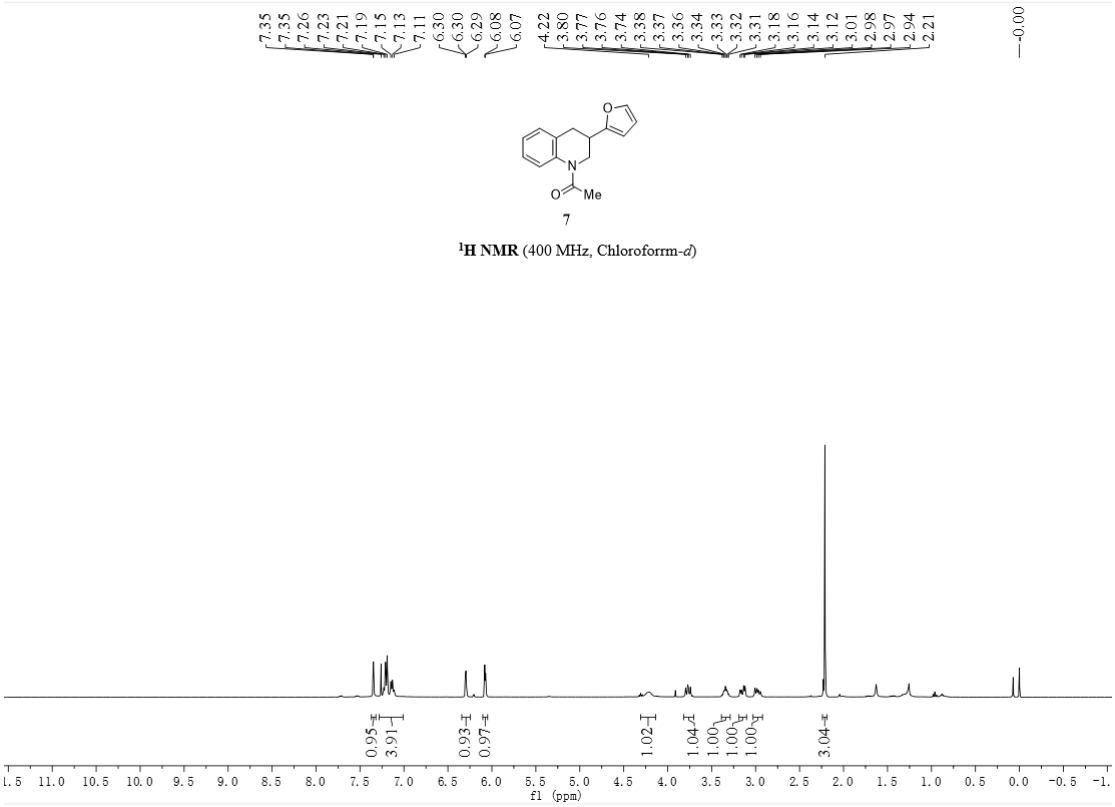
6

^{1}H NMR (400 MHz, Chloroform-*d*)



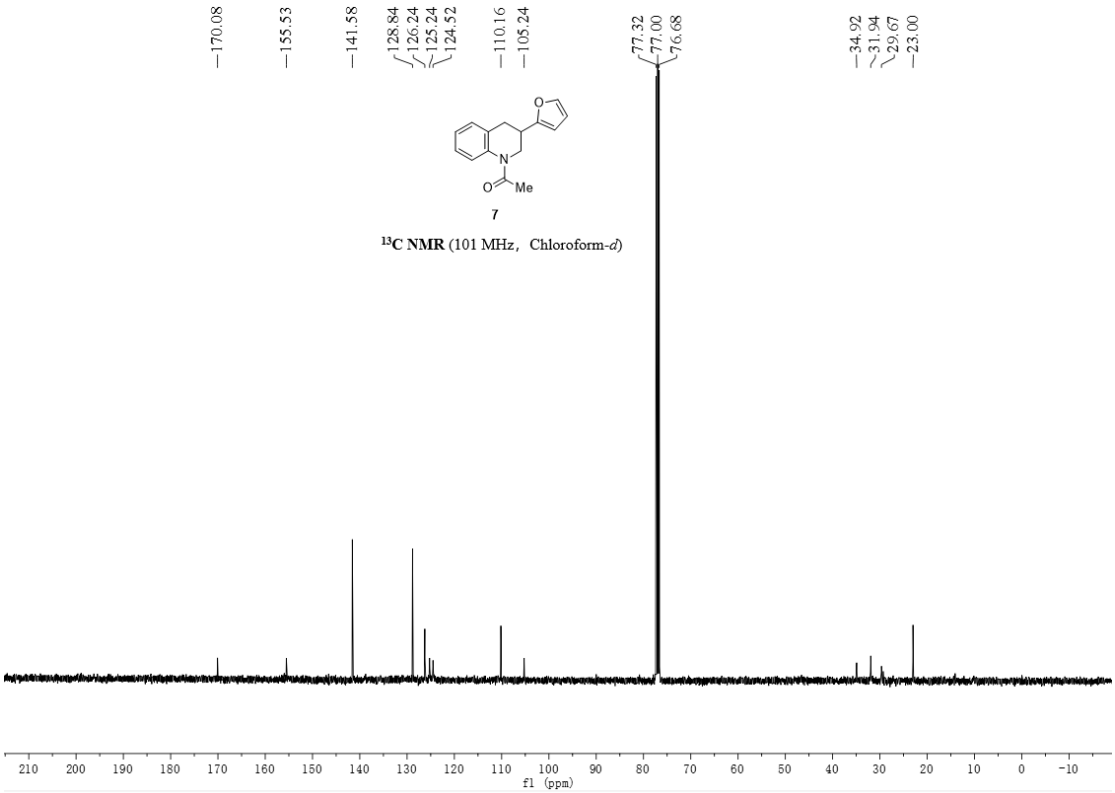
6

^{13}C NMR (101 MHz, Chloroform-*d*)



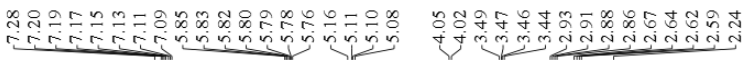
7

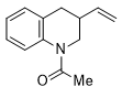
^{1}H NMR (400 MHz, Chloroformm-*d*)



7

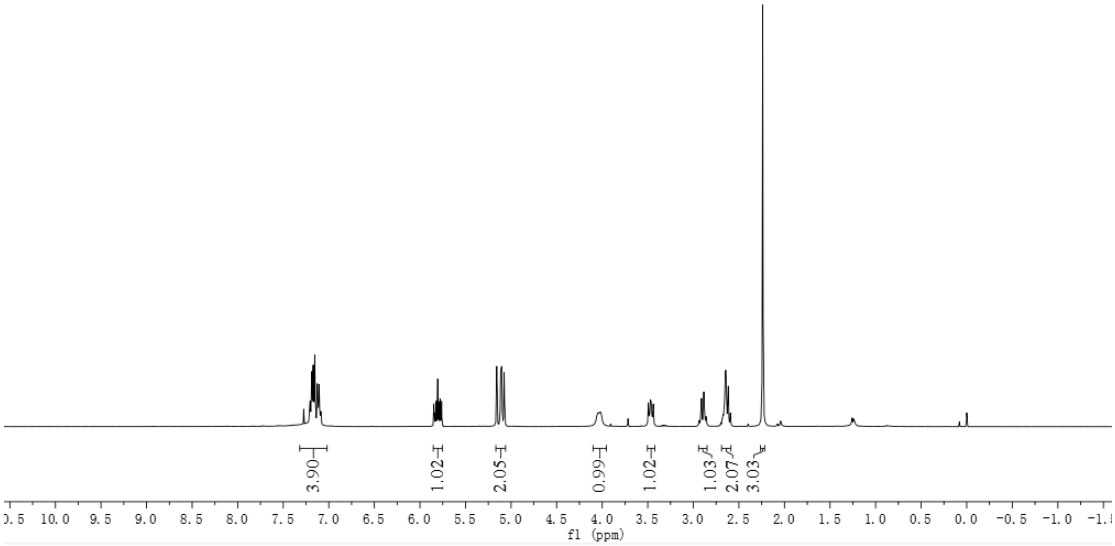
^{13}C NMR (101 MHz, Chloroform-*d*)

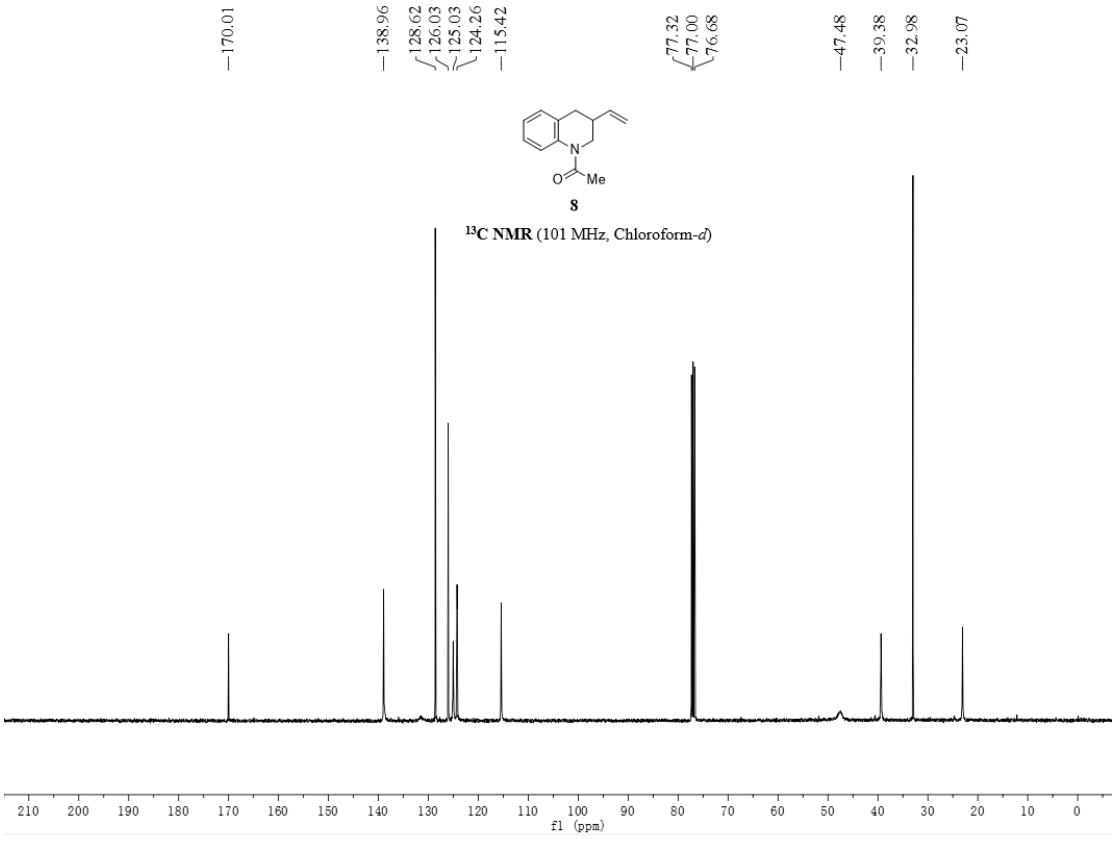




8

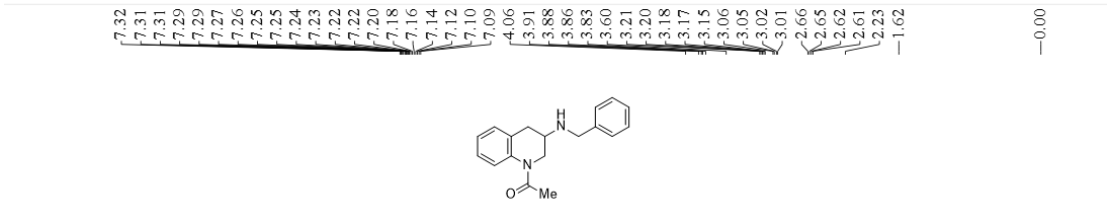
^{1}H NMR (400 MHz, Chloroform-*d*)





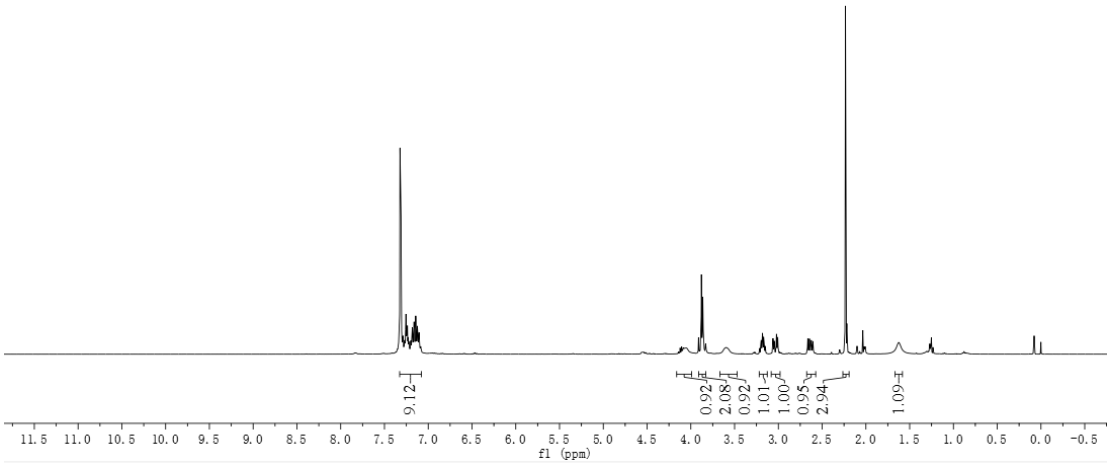
8

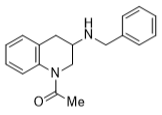
^{13}C NMR (101 MHz, Chloroform-*d*)



9

^{1}H NMR (400 MHz, Chloroform-*d*)





9

^{13}C NMR (101 MHz, Chloroform-*d*)