Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

for

Cu/Pd Cooperatively Catalyzed Tandem Intramolecular anti-Markovnikov Hydroarylation of Unsaturated Amides: Facile Construction of 3,4-Dihydroquinolinones via Borylation/Intramolecular C(sp^3)-C(sp^2) Cross Coupling

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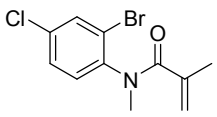
1. General Information

All reagents and solvents were purchased from Adamas Reagent, energy chemical company, J&K Scientific Ltd, Bide Pharmatech Ltd and Tansoole and used without further purification. Unless otherwise stated, all experiments were conducted in a Schlenk tube under N_2 atmosphere which had been oven-dried. All reagents were dry. Reactions were monitored by TLC or GC-MS analysis. Flash column chromatography was performed over silica gel (200-300 mesh).

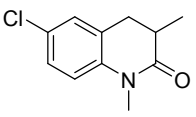
^1H NMR (in $CDCl_3$ or DMSO-d_6), ^{19}F NMR (in $CDCl_3$) and ^{13}C NMR spectra (in $CDCl_3$) were recorded at ambient temperature using 500 MHz spectrometers (500 MHz ^1H, 125 MHz ^{13}C, 471 MHz ^{19}F). The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. High-resolution mass spectra data were obtained by peak matching.

2. Optimization of Experimental Conditions

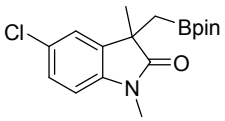


1a, 0.2 mmol

$(Bpin)_2$ (1.5 equiv), $Pd(dba)_2$ (10 mol %)
CuBr (10 mol %), xantphos (10 mol %)
toluene(dry), N_2, 110 ^oC, 12 h



2a



3a

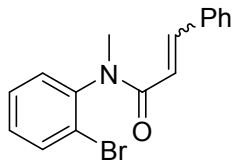
entry	base (1.5 equiv)	yield (%) **2a**	**3a**
1	NaO^tBu		17
2	LiO^tBu		23
3	Cs_2CO_3	41	5
4	K_2CO_3	39	4
5	Na_2CO_3	43	3
6	DBU	31	10
7	$NaHCO_3$		28
8	K_3PO_4		39
9	K_2HPO_4	36	22
10	Li_2CO_3	31	5
11	NaOAc		37
12	NaOMe		36

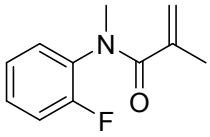
Reaction conditions: all reactions were performed on 0.2 mmol scale with respect to 1a; yields were determined by GC by utilizing dodecane as internal standard. The reaction mixture contained approximately 0.3% w/w water.

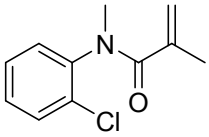
The method to determine the water contamination:
Instrument: Automatic Karl Fischer moisture analyzer MKC-520D, Electronic Balance AT261/1994392H2054. Method: GB/T 6283-2008.

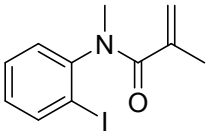
Reaction Mixture	Before Reaction	Reaction Over
Water Contamination (w/w)	0.0041	0.0024

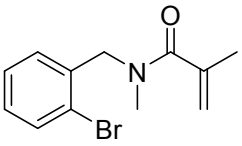
Some incompatible substrates

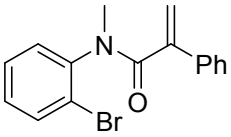


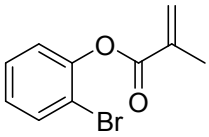


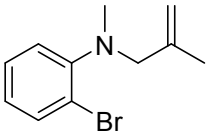




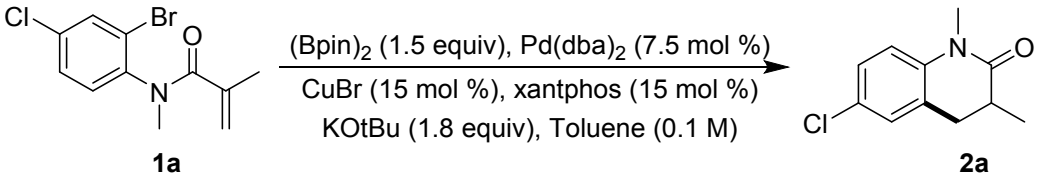






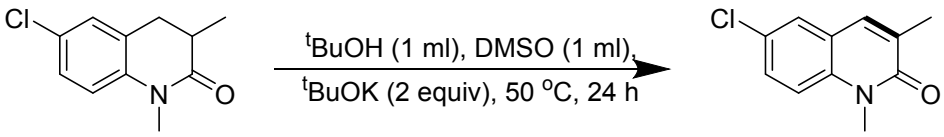


3. General Process for the Synthesis of 2a and 6a



1a **2a**

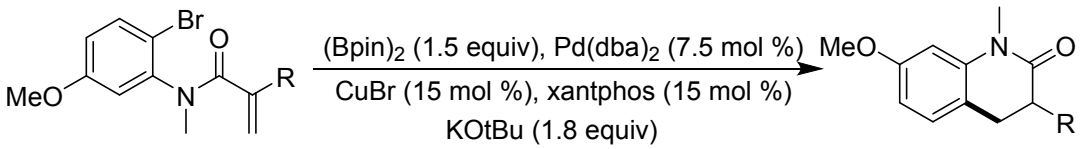
To a 25 mL Schlenk tube, under a nitrogen atmosphere, was added 0.20 mmol of unsaturated amide (**1**) followed by 0.30 mmol of $(Bpin)_2$ (1.5 equiv), 0.015 mmol of $Pd(dba)_2$ (0.075 equiv), 0.03 mmol of CuBr (0.15 equiv), 0.03 mmol of xantphos (0.15 equiv), 0.36 mmol of KO^{t}Bu (1.8 equiv), in toluene (2 mL). The Schlenk tube was sealed and stirred at 110 ^{o}C for further 12 h. Then, the reaction mixture was washed by water, and extracted with EA. Then the organic layers were dried with Na_2SO_4, and concentrated to dryness. The crude product was purified by silica gel chromatography (silica gel, PE: EA = 10:1 – 6:1, v/v) to afford the product **2** (31.7 mg, 75%) as a light yellow oil.



2a, 0.18 mmol **6a**, 68%

To a 25 mL tube was added 0.18 mmol of 6-chloro-1,3-dimethyl-3,4-dihydroquinolin-2(1*H*)-one (**2a**) and 0.36 mmol of KO^{t}Bu (2.0 equiv), in DMSO (1 mL) and tert butanol (1mL). The tube was sealed and stirred at 50 ^{o}C for further 24 h under air. Then, the reaction mixture was extracted with EA/H_2O. Then the organic layers were dried with Na_2SO_4, and concentrated to dryness. The crude product was purified by silica gel chromatography (silica gel, PE: EA = 10:1 – 6:1, v/v) to afford the product **6a** (25.5 mg, 68%) as a light yellow solid.

4. General Process for the Synthesis of 2m and 2n on 1.5 mmol



1m, R=Me
1n, R=H

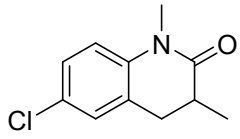
2m, R=Me
2n, R=H

To a 25 mL Schlenk tube, under a nitrogen atmosphere, was added 1.50 mmol of unsaturated amide (**1m** or **1n**) followed by 2.3 mmol of $(Bpin)_2$ (1.5 equiv), 0.225 mmol of CuBr (0.15 equiv), 0.225 mmol of xantphos (0.15 equiv), 2.7 mmol of KO^tBu (1.8 equiv), in toluene (8 mL). The Schlenk tube was sealed and stirred at 110 ^oC for further 10 min, subsequently, 0.113 mmol of $Pd(dba)_2$ (0.075 equiv) in 2 ml toluene was added with syringe, and stirred overnight at the same temperature. Then, the reaction mixture was cooled to room temperature, washed by water, and extracted with EA. Then the organic layers were dried with Na_2SO_4, and concentrated to dryness. The crude product was purified by silica gel chromatography (silica gel, PE: EA = 10:1 – 6:1, v/v) to afford the product (**2m**, 191 mg, 60 %; **2n**, 205 mg, 70%) as a light yellow solid.

Caution: The reactants were added by order.

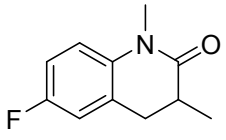
5. Characterization Data for Products

6-Chloro-1,3-dimethyl-3,4-dihydroquinolin-2(1*H*)-one (2a)[1]



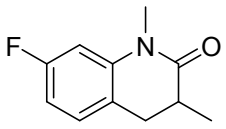
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE: EA =10:1 - 6:1, v/v) to give the product as a yellow oil (31.7 mg, 75%).^{1}H NMR (500 MHz, DMSO) δ 7.31 – 7.27 (m, 2H), 7.09 – 7.06 (m, 1H), 3.23 (s, 3H), 2.92 (dd, *J* = 15.3, 5.4 Hz, 1H), 2.64 (dd, *J* = 15.2, 11.8 Hz, 1H), 2.55 (dt, *J* = 12.6, 6.4 Hz, 1H), 1.11 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.8, 139.0, 127.8, 127.7, 127.4, 127.2, 115.6, 35.2, 31.0, 29.9, 15.6.

6-Fluoro-1,3-dimethyl-3,4-dihydroquinolin-2(1*H*)-one (2b)



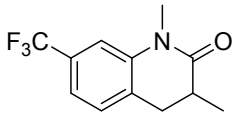
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE: EA =10:1 - 6:1, v/v) to give the product as a yellow oil (34.7 mg, 90%). ^{1}H NMR (500 MHz, DMSO) δ 7.12 – 7.05 (m, 3H), 3.23 (s, 3H), 2.91 (dd, *J* = 15.4, 5.5 Hz, 1H), 2.64 (dd, *J* = 15.3, 11.7 Hz, 1H), 2.53 (dt, *J* = 14.8, 4.4 Hz, 1H), 1.11 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.7, 158.3 (d, *J* = 240.9 Hz), 136.6 (d, *J* = 2.5 Hz), 127.7 (d, *J* = 7.6 Hz), 115.5 (d, *J* = 8.2 Hz), 114.9 (d, *J* = 22.8 Hz), 113.5 (d, *J* = 22.1 Hz), 35.2, 33.2, 30.0, 15.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -121.0. HRMS (ESI, m/z) calcd for $C_{11}H_{13}FNO$ $[M+H]^+$: 194.0976; found: 194.0978.

7-Fluoro-1,3-dimethyl-3,4-dihydroquinolin-2(1*H*)-one (2c)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE: EA =10:1 - 6:1, v/v) to give the product as a yellow oil (23.5 mg, 61%).^{1}H NMR (500 MHz, DMSO) δ 7.21 (dd, *J* = 7.8, 6.9 Hz, 1H), 6.96 (dd, *J* = 11.3, 2.5 Hz, 1H), 6.81 (td, *J* = 8.5, 2.5 Hz, 1H), 3.23 (s, 3H), 2.90 (dd, *J* = 14.5, 4.9 Hz, 1H), 2.56 (ddd, *J* = 19.1, 13.1, 9.2 Hz, 2H), 1.11 (d, *J* = 6.6 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 173.0, 162.2 (d, *J* = 241.6 Hz), 141.7 (d, *J* = 10.1 Hz), 128.7 (d, *J* = 9.3 Hz), 121.1 (d, *J* = 3.1 Hz), 108.7 (d, *J* = 21.0 Hz), 102.5 (d, *J* = 26.5 Hz), 35.5, 32.6, 29.8, 15.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -114.2. HRMS (ESI, m/z) calcd for $C_{11}H_{13}FNO$ $[M+H]^+$: 194.0976; found: 194.0976.

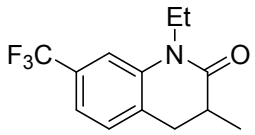
1,3-Dimethyl-7-(trifluoromethyl)-3,4-dihydroquinolin-2(1*H*)-one (2d)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE: EA =10:1 - 6:1, v/v) to give the

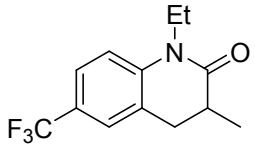
product as a yellow solid (34.1 mg, 70%, mp: 78.4-79.6 °C)). ^{1}H NMR (500 MHz, DMSO) δ 7.44 (d, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.31 (s, 1H), 3.30 (s, 3H), 3.07 – 2.99 (m, 1H), 2.77 – 2.69 (m, 1H), 2.63 – 2.55 (m, 1H), 1.13 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.8, 140.9, 129.9 (d, *J* = 32.3 Hz), 129.5 (d, *J* = 0.9 Hz), 128.2, 124.0 (d, *J* = 270.5 Hz), 119.4 (q, *J* = 3.7 Hz), 111.1 (q, *J* = 3.7 Hz), 35.1, 33.1, 29.9, 15.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.5. HRMS (ESI, m/z) calcd for $C_{12}H_{13}F_3NO$ $[M+H]^+$: 244.0944; found: 244.0944.

1-Ethyl-3-methyl-7-(trifluoromethyl)-3,4-dihydroquinolin-2(1*H*)-one (2e)



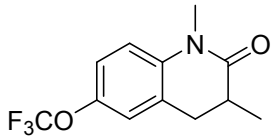
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE: EA =10:1 - 6:1, v/v) to give the product as a yellow solid (31.9 mg, 62%, mp: 52.9-53.3 °C).^{1}H NMR (500 MHz, DMSO) δ 7.59 (d, *J* = 7.0 Hz, 2H), 7.29 (d, *J* = 9.2 Hz, 1H), 4.02 – 3.84 (m, 2H), 3.02 (dd, *J* = 15.4, 5.5 Hz, 1H), 2.70 (dd, *J* = 15.3, 12.0 Hz, 1H), 2.63 – 2.55 (m, 1H), 1.12 (dt, *J* = 7.1, 3.7 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.2, 139.9, 130.1, 129.8 (d, *J* = 7.1 Hz), 128.5, 124.0 (d, *J* = 271.3 Hz), 119.2 (q, *J* = 3.9 Hz), 111.0 (q, *J* = 3.9 Hz), 37.7, 35.1, 33.3, 15.5, 12.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.5. HRMS (ESI, m/z) calcd for $C_{13}H_{15}F_3NO$ $[M+H]^+$: 258.1100; found: 258.1101.

1-Ethyl-3-methyl-6-(trifluoromethyl)-3,4-dihydroquinolin-2(1*H*)-one (2f)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE: EA =10:1 - 6:1, v/v) to give the product as a light yellow solid (30.8 mg, 60%, mp: 49.1-49.7 °C). ^{1}H NMR (500 MHz, DMSO) δ 7.59 (d, *J* = 5.7 Hz, 2H), 7.31 – 7.27 (m, 1H), 4.02 – 3.83 (m, 2H), 3.02 (dd, *J* = 15.4, 5.4 Hz, 1H), 2.70 (dd, *J* = 15.2, 12.1 Hz, 1H), 2.64 – 2.55 (m, 1H), 1.12 (dt, *J* = 7.0, 3.7 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.4, 142.2, 126.3, δ 125.2, 125.1 (q, *J* = 3.6 Hz), 124.7 (q, *J* = 3.9 Hz), 124.0 (dd, *J* = 111.6, 78.8 Hz), 114.2, 37.7, 35.1, 33.2, 15.5, 12.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -61.9. HRMS (ESI, m/z) calcd for $C_{13}H_{15}F_3NO$ $[M+H]^+$: 258.1100; found: 258.1103.

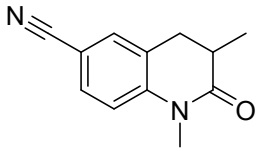
1,3-Dimethyl-6-(trifluoromethoxy)-3,4-dihydroquinolin-2(1H)-one (2g)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE: EA =10:1 - 6:1, v/v) to give the product as a light yellow oil (38.3 mg, 74%).^{1}H NMR (500 MHz, DMSO) δ 7.25 (d, *J* = 9.1 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 1H), 3.26 (s, 3H), 2.96 (dd, *J* = 15.4, 5.5 Hz, 1H), 2.68 (dd, *J* = 15.3, 12.1 Hz, 1H), 2.61 – 2.52 (m, 1H), 1.12 (d, *J* = 6.8 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 172.8, 144.1 (dd, *J* = 3.7, 1.9 Hz), 139.1, 127.4, 120.5 (q, *J* = 255.0 Hz), 119.9, 117.4, 115.3, 35.1, 33.1,

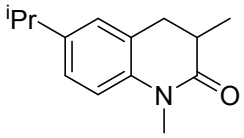
30.0, 15.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -58.2. HRMS (ESI, m/z) calcd for $C_{12}H_{13}F_3NO_2$ [M+H] $^+$: 260.0893; found: 260.0893.

1,3-Dimethyl-2-oxo-1,2,3,4-tetrahydroquinoline-6-carbonitrile (2h)



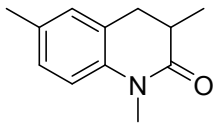
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE: EA =10:1 - 5:1, v/v) to give the product as a light yellow oil (13.5 mg, 32%). ^{1}H NMR (500 MHz, DMSO) δ 7.74 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.69 (s, 1H), 7.23 (d, *J* = 8.5 Hz, 1H), 3.27 (s, 3H), 2.98 (dd, *J* = 15.3, 5.4 Hz, 1H), 2.70 (dd, *J* = 15.2, 12.1 Hz, 1H), 2.65 – 2.56 (m, 1H), 1.13 (d, *J* = 6.7 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 172.8, 144.1, 132.0, 131.2, 126.6, 118.8, 114.8, 105.7, 35.0, 32.8, 29.9, 15.6. HRMS (EI, m/z) calcd for $C_{12}H_{12}N_2O$ [M+H] $^+$: 200.0950; found: 200.0956.

6-Isopropyl-1,3-dimethyl-3,4-dihydroquinolin-2(1*H*)-one (2i)



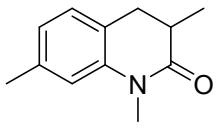
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE: EA =10:1 - 5:1, v/v) to give the product as a light yellow oil (40 mg, 92%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.02 (d, *J* = 1.6 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 3.34 (s, 3H), 2.93 – 2.82 (m, 2H), 2.63 (ddt, *J* = 13.5, 11.9, 9.0 Hz, 2H), 1.27 – 1.23 (m, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.1, 143.3, 138.2, 125.9, 125.6, 125.0, 114.3, 35.5, 33.4, 33.3, 29.7, 24.02, 24.03, 15.7. HRMS (ESI, m/z) calcd for $C_{14}H_{20}NO$ [M+H] $^+$: 218.1539; found: 218.1540.

1,3,6-Trimethyl-3,4-dihydroquinolin-2(1*H*)-one (2j)[1]



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE: EA =10:1 - 6:1, v/v) to give the product as a light yellow oil (28.2 mg, 74%). ^{1}H NMR (500 MHz, DMSO) δ 7.05 (d, *J* = 8.2 Hz, 1H), 7.01 (s, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 3.22 (s, 3H), 2.86 (dd, *J* = 15.0, 5.3 Hz, 1H), 2.59 (dd, *J* = 14.7, 11.8 Hz, 1H), 2.54 – 2.46 (m, 2H), 2.24 (s, 3H), 1.10 (d, *J* = 6.8 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 173.0, 138.0, 132.1, 128.6, 127.7, 125.5, 114.3, 35.5, 33.3, 29.8, 20.5, 15.7.

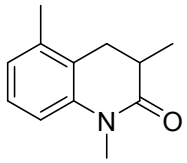
1,3,7-Trimethyl-3,4-dihydroquinolin-2(1*H*)-one (2k)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE: EA =10:1 - 6:1, v/v) to give the product as

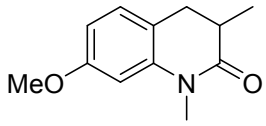
a light yellow oil (26.1 mg, 70%).[1]H NMR (500 MHz, DMSO) δ 7.07 (d, *J* = 7.5 Hz, 1H), 6.90 (s, 1H), 6.81 (dd, *J* = 7.5, 0.7 Hz, 1H), 3.24 (s, 3H), 2.85 (dd, *J* = 14.8, 5.2 Hz, 1H), 2.60 – 2.54 (m, 1H), 2.53 – 2.45 (m, 1H), 2.30 (s, 3H), 1.10 (d, *J* = 6.7 Hz, 3H). [13]C NMR (125 MHz, $CDCl_3$) δ 173.3, 140.2, 137.1, 127.6, 123.2, 122.7, 115.3, 35.6, 32.9, 29.8, 21.5, 15.7. HRMS (ESI, m/z) calcd for $C_{12}H_{16}NO$ $[M+H]^+$: 190.1226; found: 190.1226.

1,3,5-Trimethyl-3,4-dihydroquinolin-2(1*H*)-one (2l)



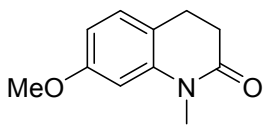
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE: EA =10:1 - 6:1, v/v) to give the product as a light yellow oil (22.7 mg, 60%). [1]H NMR (500 MHz, DMSO) δ 7.14 (t, *J* = 7.8 Hz, 1H), 6.90 (dd, *J* = 14.2, 7.8 Hz, 2H), 3.23 (s, 3H), 2.98 – 2.89 (m, 1H), 2.53 – 2.43 (m, 2H), 2.25 (s, 3H), 1.14 (d, *J* = 6.3 Hz, 3H).[13]C NMR (126 MHz, $CDCl_3$) δ 173.1, 140.5, 135.5, 126.8, 124.7, 124.3, 112.6, 35.0, 30.1, 29.6, 19.5, 15.8. HRMS (ESI, m/z) calcd for $C_{12}H_{16}NO$ $[M+H]^+$: 190.1226; found: 190.1228.

7-Methoxy-1,3-dimethyl-3,4-dihydroquinolin-2(1*H*)-one (2m) [1]



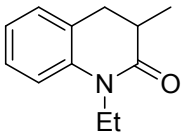
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE: EA =10:1 - 4:1, v/v) to give the product as a light yellow solid (26 mg, 63%, mp: 78.8-79.6 °C). [1]H NMR (500 MHz, $CDCl_3$) δ 7.05 (d, *J* = 8.8 Hz, 1H), 6.55 – 6.52 (m, 2H), 3.81 (s, 3H), 3.33 (s, 3H), 2.90 – 2.83 (m, 1H), 2.65 – 2.56 (m, 2H), 1.24 (d, *J* = 6.5 Hz, 3H). [13]C NMR (125 MHz, $CDCl_3$) δ 173.4, 159.1, 141.4, 128.3, 117.9, 106.4, 102.2, 55.4, 35.8, 32.5, 29.8, 15.7.

7-Methoxy-1-methyl-3,4-dihydroquinolin-2(1*H*)-one (2n) [2]



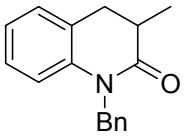
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE: EA =10:1 - 4:1, v/v) to give the product as a light yellow solid (29.5 mg, 77%, mp: 77.1-78.2 °C). [1]H NMR (500 MHz, $CDCl_3$) δ 7.06 (d, *J* = 7.8 Hz, 1H), 6.56 – 6.52 (m, 2H), 3.81 (s, 3H), 3.32 (s, 3H), 2.85 – 2.81 (m, 2H), 2.62 (dd, *J* = 8.4, 6.3 Hz, 2H). [13]C NMR (125 MHz, $CDCl_3$) δ 170.6, 159.1, 141.6, 128.1, 118.4, 106.4, 102.4, 55.4, 32.0, 29.5, 24.5.

1-Ethyl-3-methyl-3,4-dihydroquinolin-2(1H)-one (2o) [1]



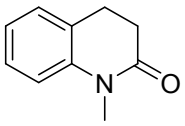
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE: EA =10:1 - 6:1, v/v) to give the product as a light yellow oil (31.9 mg, 85%).^{1}H NMR (500 MHz, DMSO) δ 7.27 – 7.22 (m, 1H), 7.20 (d, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 6.98 (td, *J* = 7.4, 1.0 Hz, 1H), 3.98 – 3.80 (m, 2H), 2.88 (dd, *J* = 15.1, 5.3 Hz, 1H), 2.61 (dd, *J* = 15.0, 11.9 Hz, 1H), 2.56 – 2.47 (m, 1H), 1.11 (dt, *J* = 7.1, 3.7 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.6, 139.4, 128.1, 127.4, 126.0, 122.5, 114.4, 37.6, 35.5, 33.5, 15.6, 12.8.

1-Benzyl-3-methyl-3,4-dihydroquinolin-2(1*H*)-one (2p) [1]



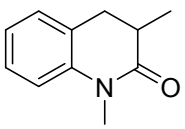
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE: EA =10:1 - 6:1, v/v) to give the product as a light yellow oil (35.4 mg, 70%). ^{1}H NMR (500 MHz, DMSO) δ 7.30 (t, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 4H), 7.14 – 7.08 (m, 1H), 6.95 (t, *J* = 7.2 Hz, 1H), 6.89 (d, *J* = 8.1 Hz, 1H), 5.14 (dd, *J* = 60.3, 16.4 Hz, 2H), 3.04 – 2.93 (m, 1H), 2.80 – 2.67 (m, 2H), 1.20 (d, *J* = 6.1 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3, 139.7, 137.2, 128.7, 128.0, 127.4, 127.0, 126.3, 125.8, 122.8, 115.3, 46.5, 35.6, 33.5, 15.7.

1-Methyl-3,4-dihydroquinolin-2(1*H*)-one (2q) [3]



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE: EA =10:1 - 6:1, v/v) to give the product as a light yellow oil (26.4 mg, 83%).^{1}H NMR (500 MHz, DMSO) δ 7.25 (td, *J* = 8.1, 1.6 Hz, 1H), 7.21 (dd, *J* = 7.3, 1.0 Hz, 1H), 7.10 – 7.05 (m, 1H), 7.00 (td, *J* = 7.4, 1.0 Hz, 1H), 3.24 (s, 3H), 2.88 – 2.81 (m, 2H), 2.52 (dd, *J* = 8.4, 6.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5, 140.6, 127.7, 127.4, 126.2, 122.7, 114.6, 31.7, 29.5, 25.3.

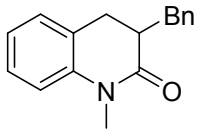
1,3-Dimethyl-3,4-dihydroquinolin-2(1*H*)-one (2r) [1]



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE: EA =10:1 - 6:1, v/v) to give the product as

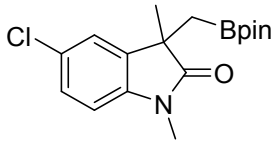
a light yellow oil (33 mg, 94%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 1H), 7.16 (d, *J* = 7.3 Hz, 1H), 7.01 (td, *J* = 7.4, 0.9 Hz, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 3.36 (s, 3H), 2.93 (dd, *J* = 14.8, 5.1 Hz, 1H), 2.70 (dd, *J* = 14.7, 11.2 Hz, 1H), 2.62 (ddd, *J* = 13.6, 9.2, 6.0 Hz, 1H), 1.26 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3, 140.4, 127.9, 127.4, 125.8, 122.7, 114.5, 35.5, 33.3, 29.8, 15.7.

3-Benzyl-1-methyl-3,4-dihydroquinolin-2(1*H*)-one (2s)



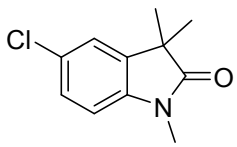
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE: EA =10:1 - 6:1, v/v) to give the product as a light yellow oil (20 mg, 40%) with **4s** of 9% (determined by ^{1}H NMR). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.28 – 7.21 (m, 2H), 7.17 (d, *J* = 7.1 Hz, 2H), 7.07 (t, *J* = 5.3 Hz, 1H), 7.01 (ddd, *J* = 8.1, 6.5, 2.8 Hz, 2H), 3.40 (s, 3H), 3.31 (dd, *J* = 13.7, 3.9 Hz, 1H), 2.81 (dt, *J* = 9.7, 5.4 Hz, 2H), 2.62 – 2.52 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.1, 140.2, 139.1, 129.2, 128.4, 128.2, 127.4, 126.3, 125.1, 122.9, 114.4, 42.4, 35.5, 29.9, 29.3. HRMS (ESI, m/z) calcd for $C_{17}H_{18}NO$ $[M+H]^+$: 252.1383; found: 252.1384.

5-Chloro-1,3-dimethyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3a) [4]



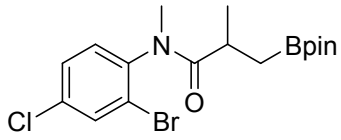
The reaction was performed following the general procedure but without CuBr and ligand. The residue was purified by flash column chromatograph (silica gel, PE: EA =8:1 - 5:1, v/v) to give the product as a light yellow solid (48 mg, 71%).^{1}H NMR (500 MHz, DMSO) δ 7.43 (d, *J* = 2.0 Hz, 1H), 7.29 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 3.09 (s, 3H), 1.32 – 1.16 (m, 3+2H), 0.96 (s, 6H), 0.90 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.2, 141.9, 137.5, 127.5, 127.3, 123.4, 108.5, 83.2, 45.7, 26.3, 25.2, 25.0, 24.7, 24.4.

5-Chloro-1,3,3-trimethylindolin-2-one (4a) [4]



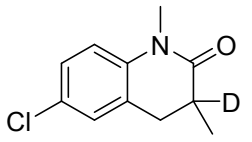
The reaction was performed following the general procedure but without CuBr and ligand. The residue was purified by flash column chromatograph (silica gel, PE: EA =8:1 - 5:1, v/v) to give the product as a light yellow solid (7.8 mg, 18%).^{1}H NMR (500 MHz, DMSO) δ 7.49 (d, *J* = 2.1 Hz, 1H), 7.32 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 3.12 (s, 3H), 1.27 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.8, 141.2, 137.4, 127.8, 127.5, 122.9, 108.9, 44.4, 26.3, 24.2.

***N*-(2-bromo-4-chlorophenyl)-N,2-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanamide (5a)** [5]



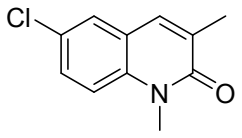
The reaction was performed following the general procedure but without Pd salt. The residue was purified by flash column chromatograph (silica gel, PE: EA =8:1 - 5:1, v/v) to give the product as a colorless liquid (55 mg, 66%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 2.2 Hz, 1H), 7.44 – 7.20 (m, 2H), 3.13 (d, *J* = 2.2 Hz, 3H), 2.47 – 2.35 (m, 1H), 1.21 (d, *J* = 10.3 Hz, 12H), 1.10 – 1.05 (m, 1H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.96 – 0.78 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.4, 141.8, 141.6*, 134.5*, 134.4, 133.5*, 133.4, 131.2, 130.5*, 129.0*, 128.9, 124.3*, 123.8, 83.0, 82.8*, 36.1*, 36.0, 33.5*, 32.9, 24.9, 24.8*, 24.7, 24.6*, 19.9, 19.4*.

6-chloro-1,3-dimethyl-3,4-dihydroquinolin-2(1*H*)-one-3-*d* *(D-2a)*



The reaction was performed following the general procedure but with additional 28 equiv D_3COD. The residue was purified by flash column chromatograph (silica gel, PE: EA =8:1 - 5:1, v/v) to give the product as a colorless liquid (30 mg, 71%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.15 – 7.12 (m, 1H), 6.87 (d, *J* = 8.6 Hz, 1H), 3.32 (s, 3H), 2.89 (dd, *J* = 13.1, 2.6 Hz, 1H), 2.69 – 2.56 (m, 1.65H), 1.26 – 1.22 (m, 3H).

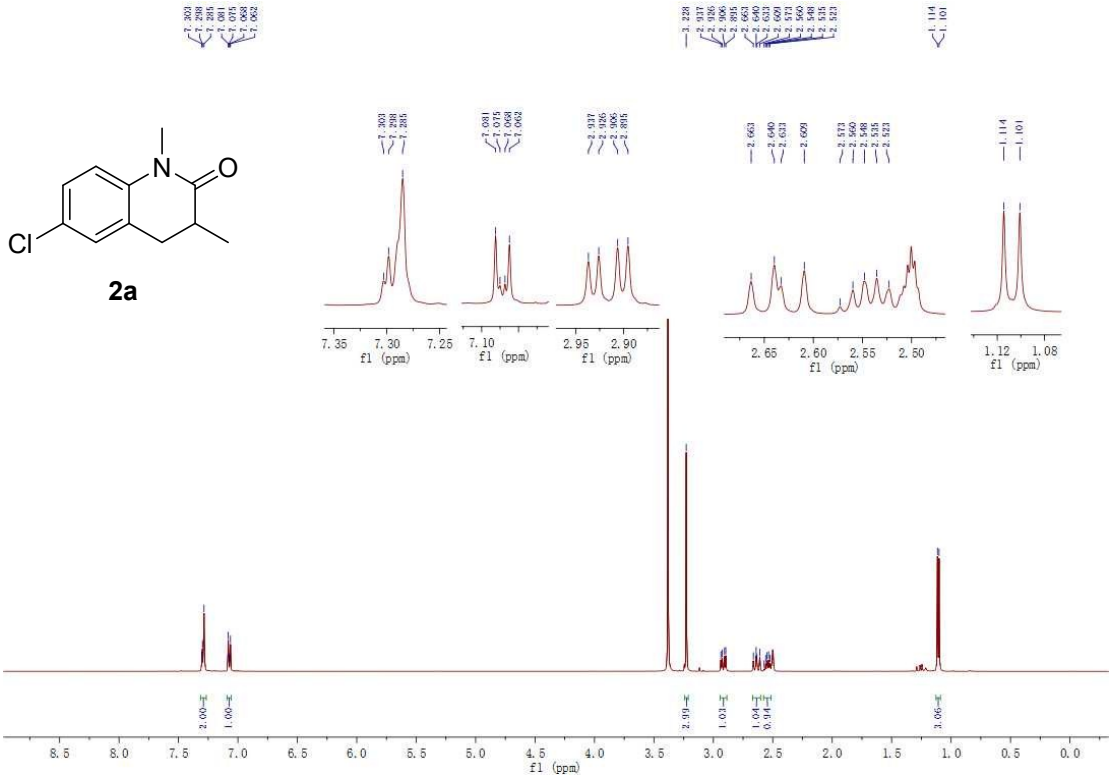
6-Chloro-1,3-dimethylquinolin-2(1H)-one (6a) [6]

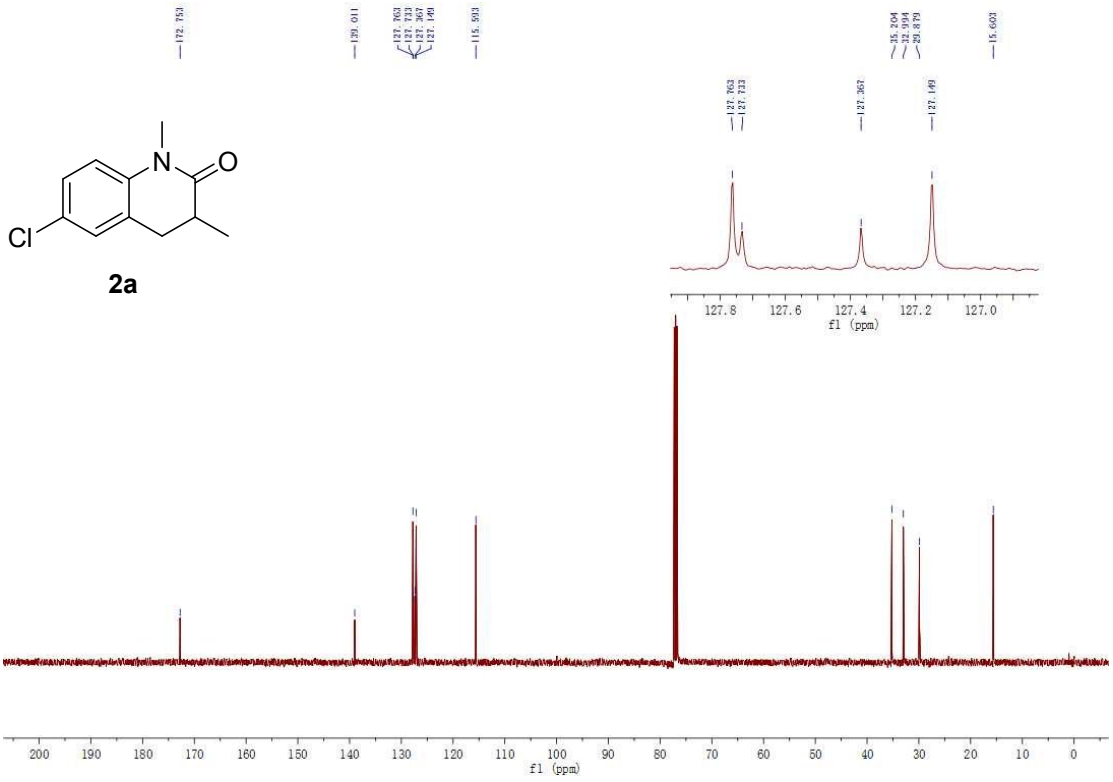


The reaction was performed following the general procedure for **6a.** The residue was purified by flash column chromatograph (silica gel, PE: EA =10:1 - 6:1, v/v) to give the product as a light yellow solid (25 mg, 68%, mp: 61.2-62.3 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dt, *J* = 8.9, 2.3 Hz, 3H), 7.26 (d, *J* = 8.9 Hz, 1H), 3.72 (s, 3H), 2.26 (d, *J* = 1.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5, 137.6, 134.4, 131.6, 129.2, 127.3, 126.8, 121.7, 115.3, 29.9, 17.9.

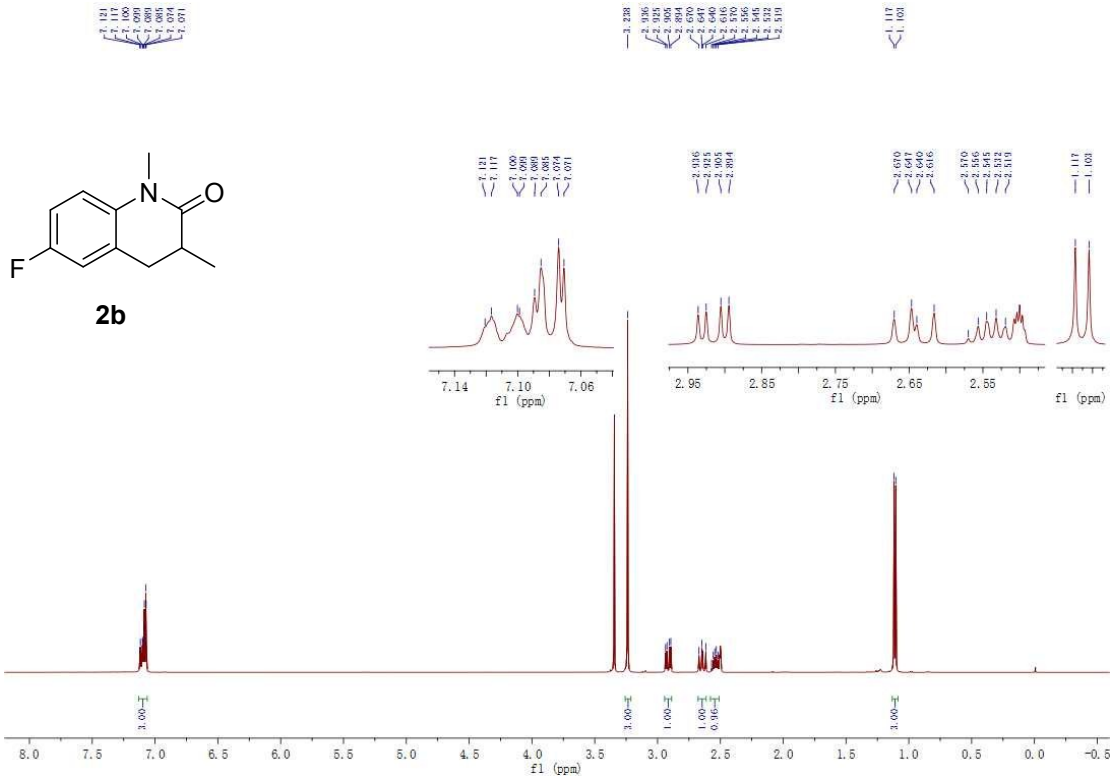
6. NMR Spectroscopic Data

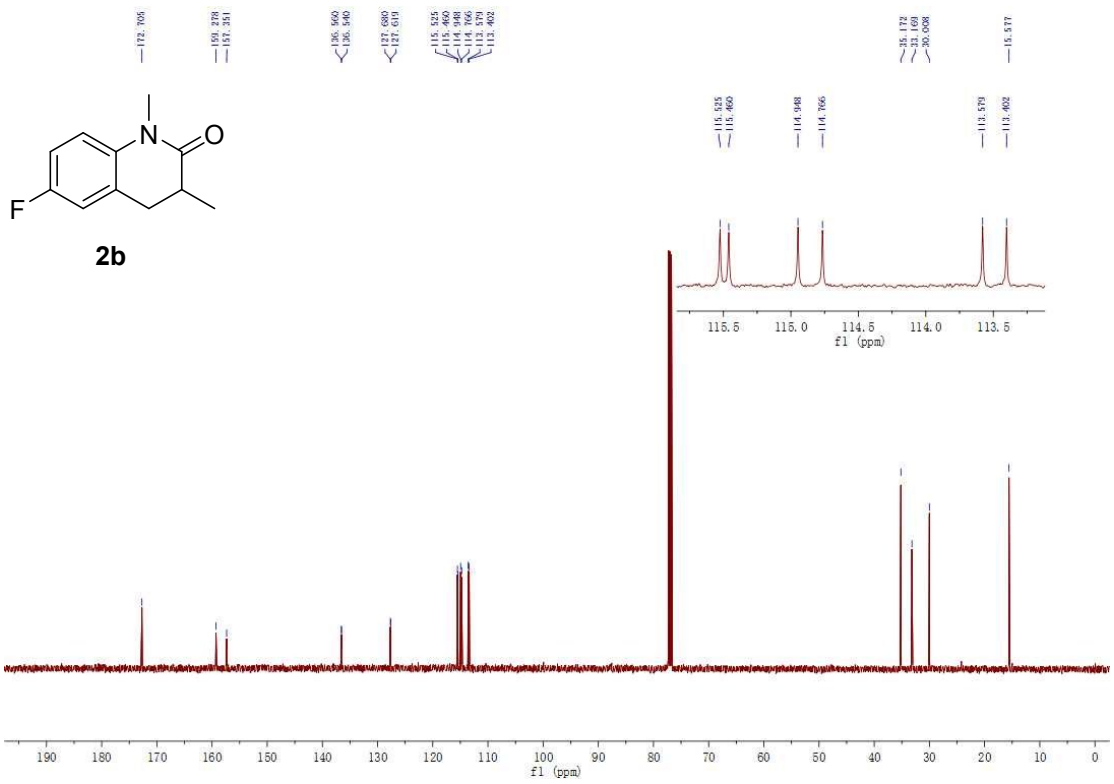
6-Chloro-1,3-dimethyl-3,4-dihydroquinolin-2(1*H*)-one (2a)

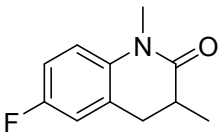




6-Fluoro-1,3-dimethyl-3,4-dihydroquinolin-2(1*H*)-one (2b)

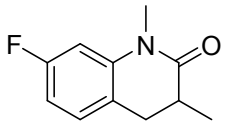




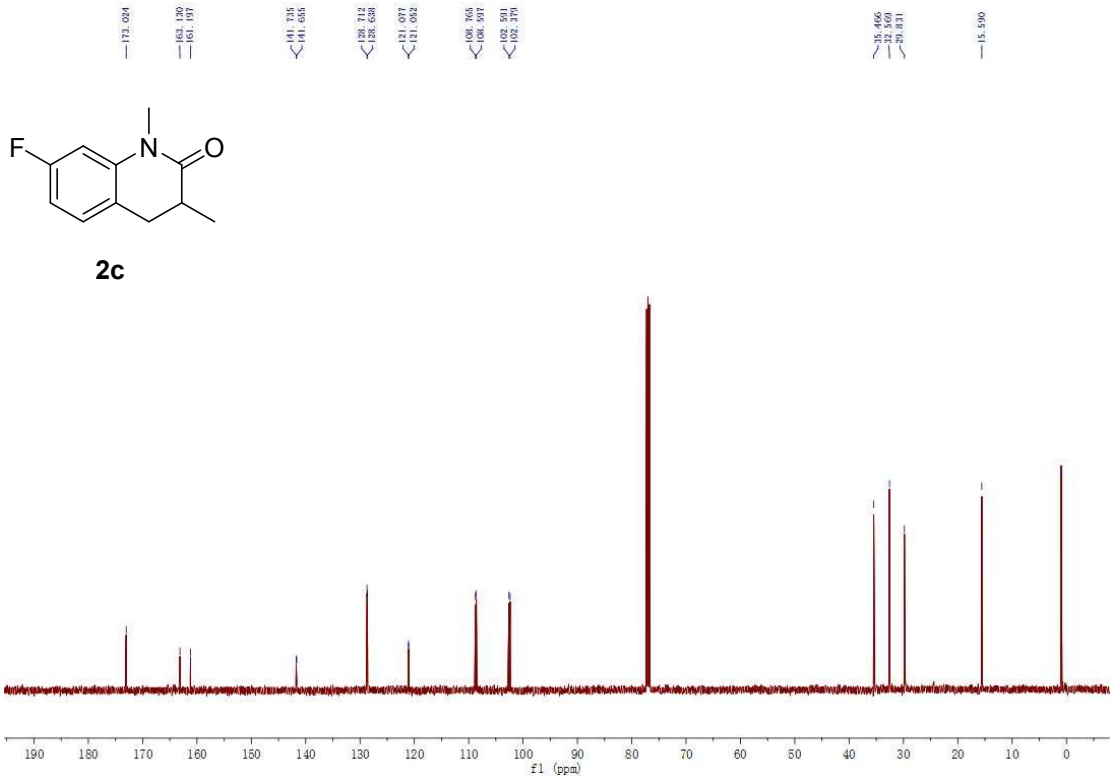


2b

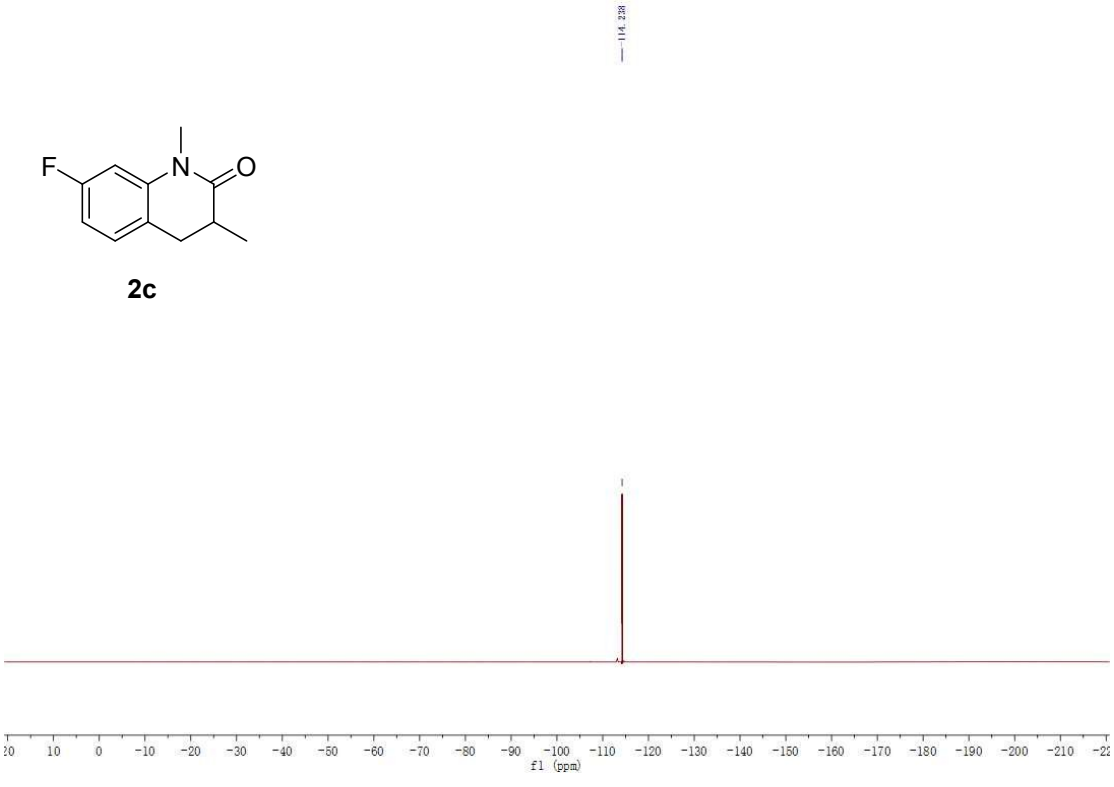
7-Fluoro-1,3-dimethyl-3,4-dihydroquinolin-2(1*H*)-one (2c)



2c

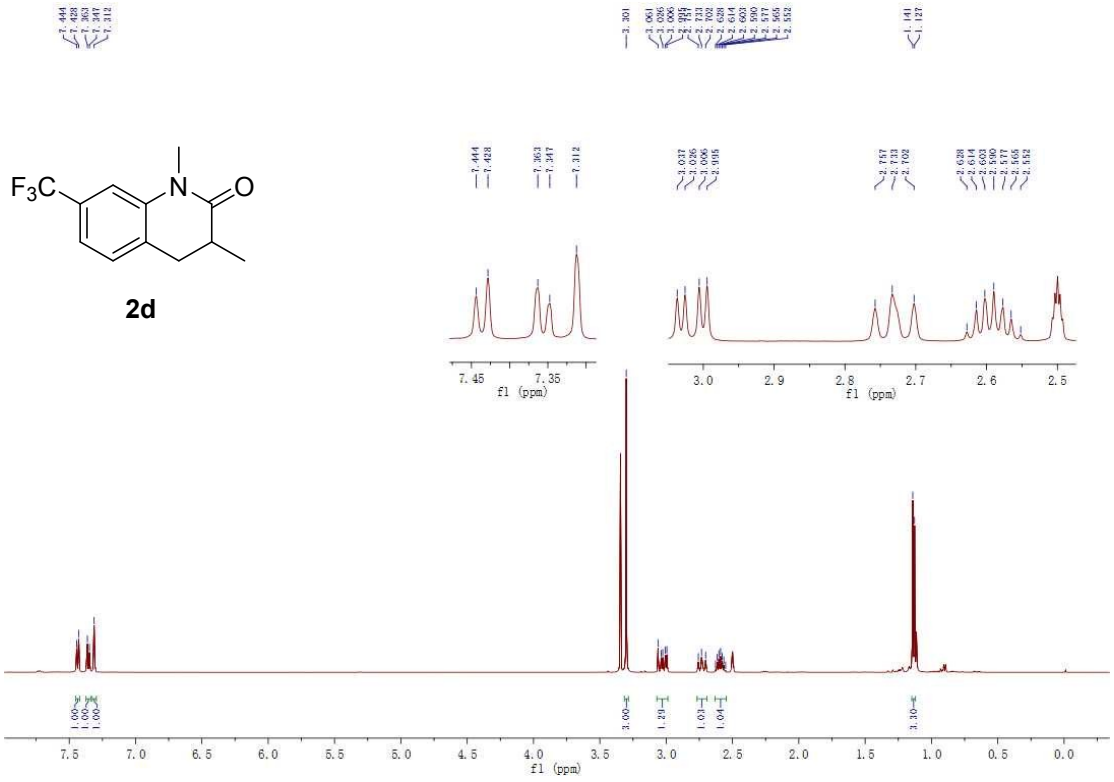

173.024
163.120
161.197
141.735
141.655
128.712
128.638
121.077
121.052
108.765
108.597
102.591
102.379
35.466
32.569
29.831
15.590
F
N
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

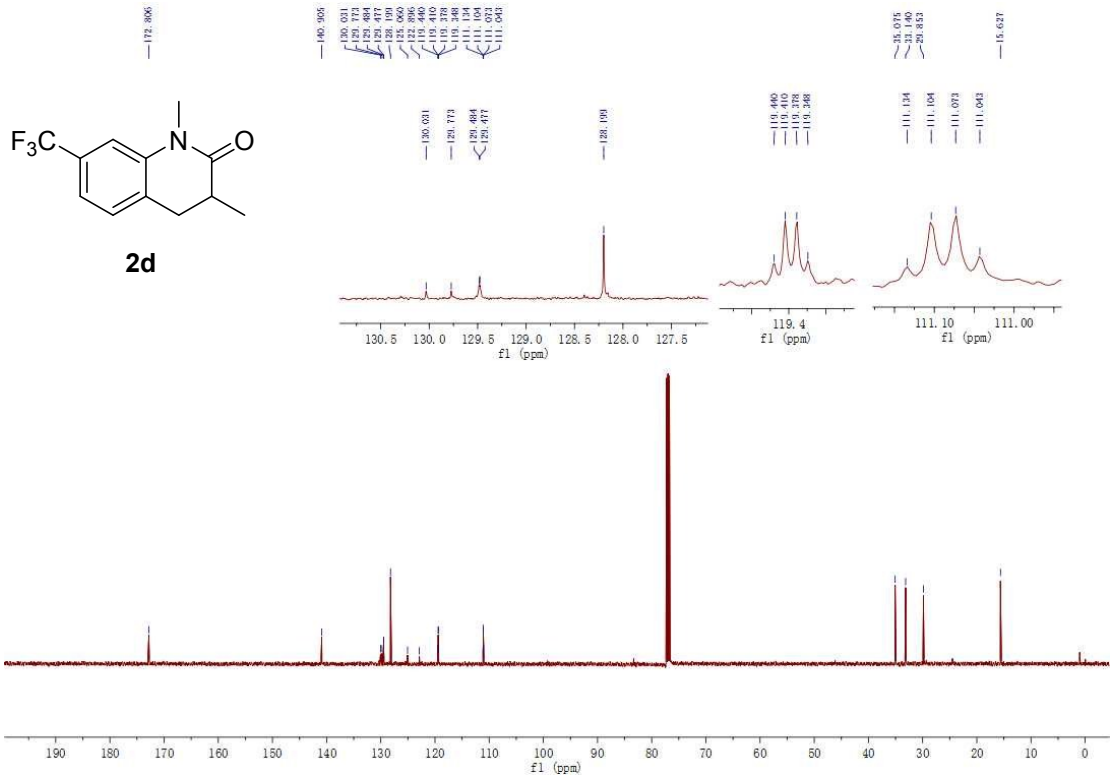
2c

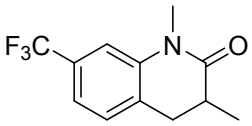

114.238
F
N
O
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

2c

1,3-Dimethyl-7-(trifluoromethyl)-3,4-dihydroquinolin-2(1*H*)-one (2d)

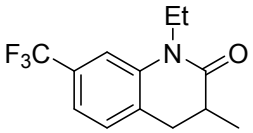




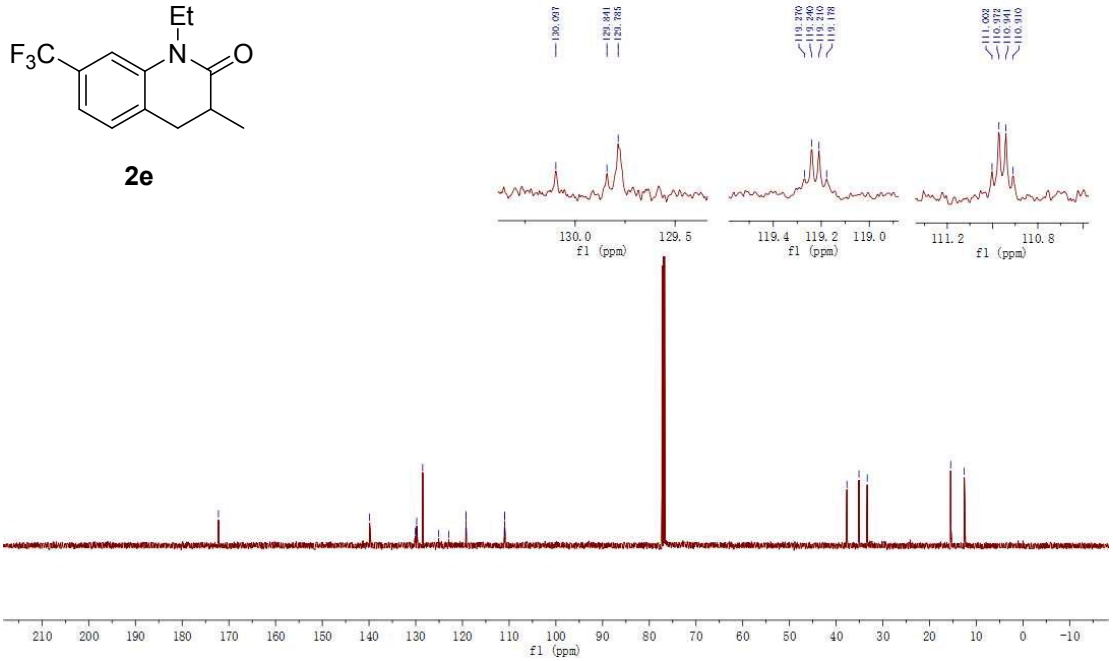


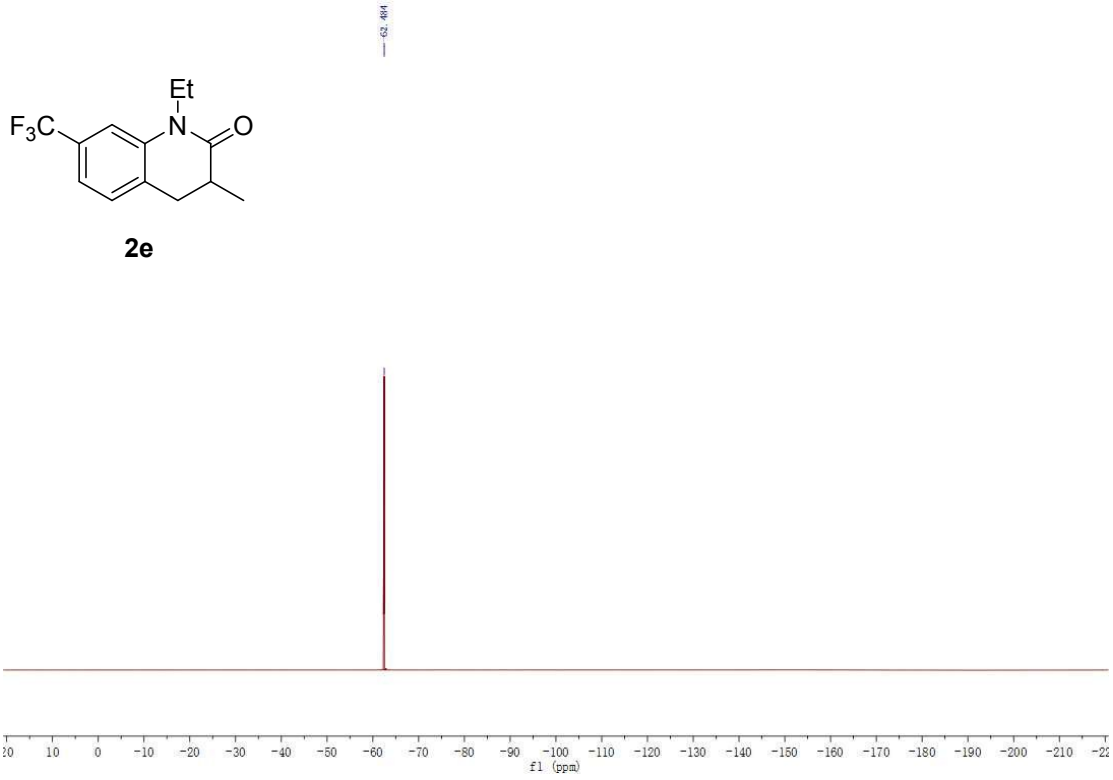
2d

1-Ethyl-3-methyl-7-(trifluoromethyl)-3,4-dihydroquinolin-2(1*H*)-one (2e)

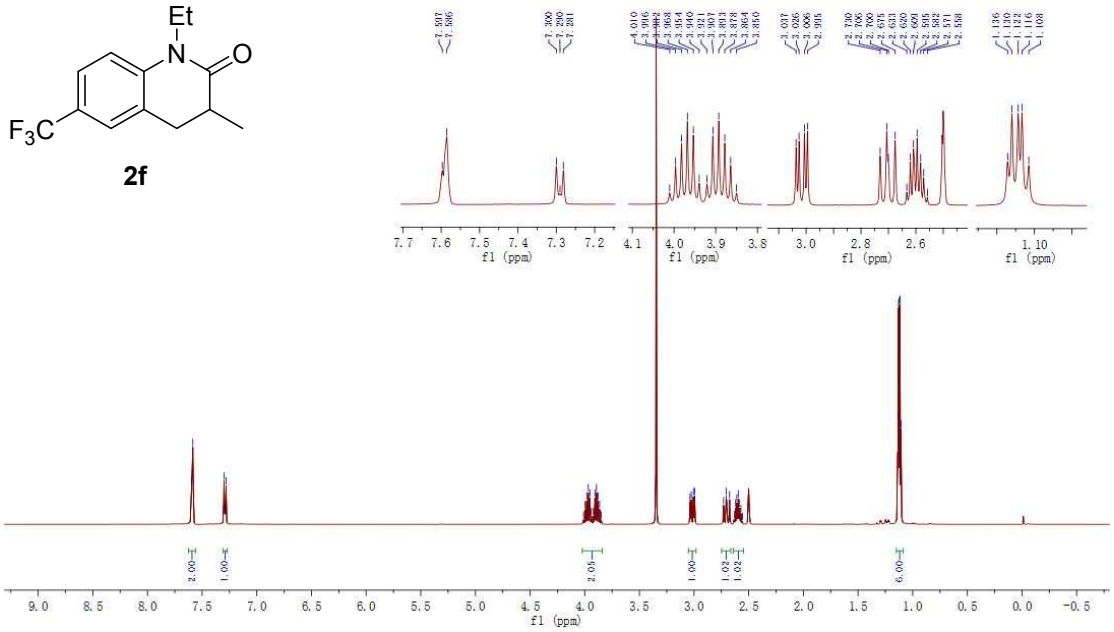


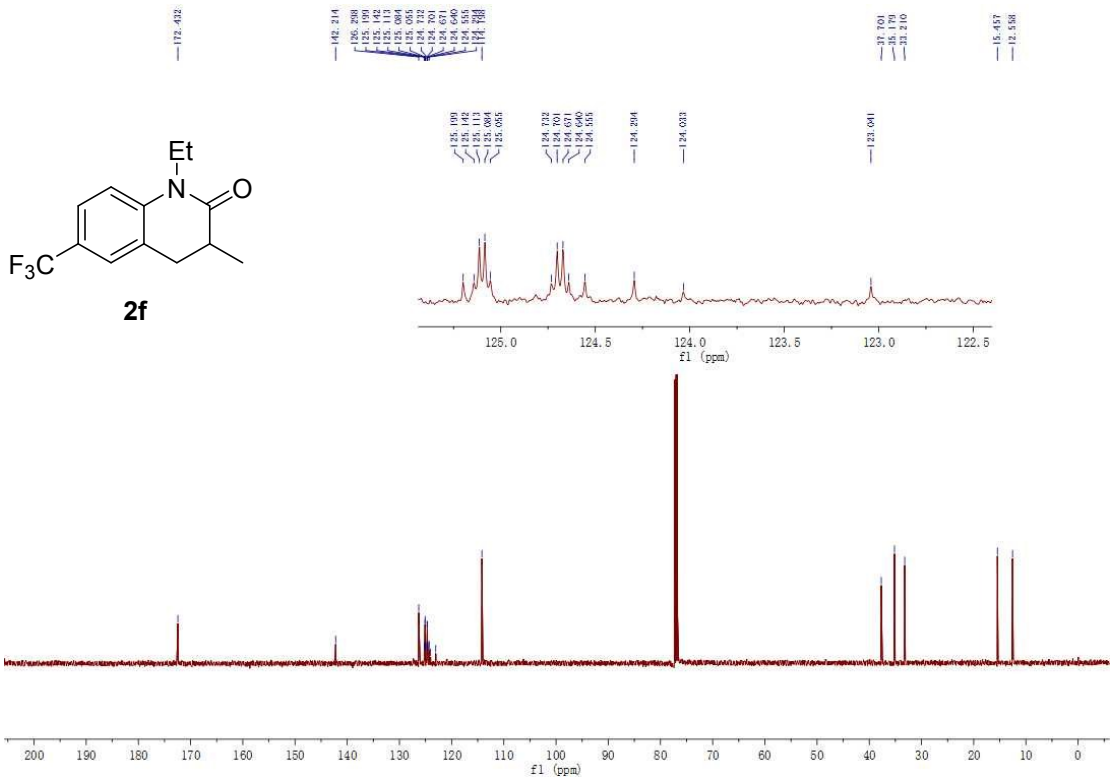
2e

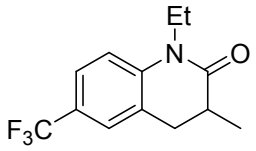

Et
N
O
F3C
2e


Et
N
O
F3C
2e

1-Ethyl-3-methyl-6-(trifluoromethyl)-3,4-dihydroquinolin-2(1*H*)-one (2f)

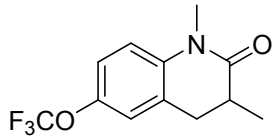




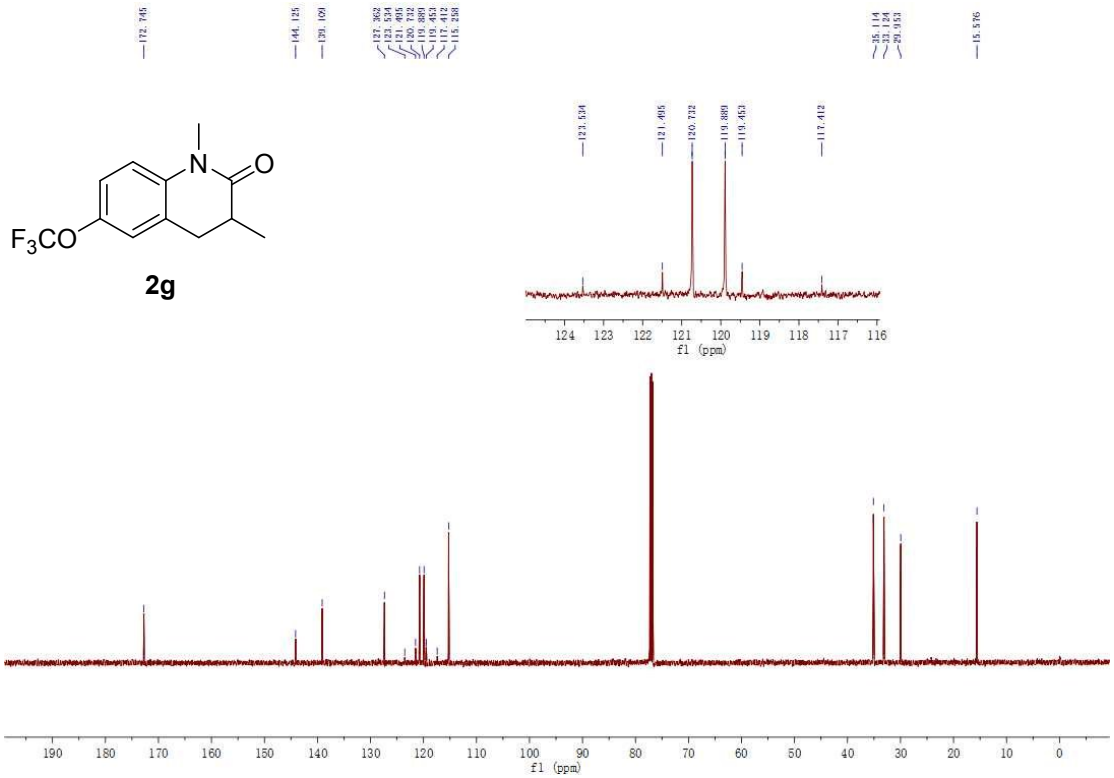


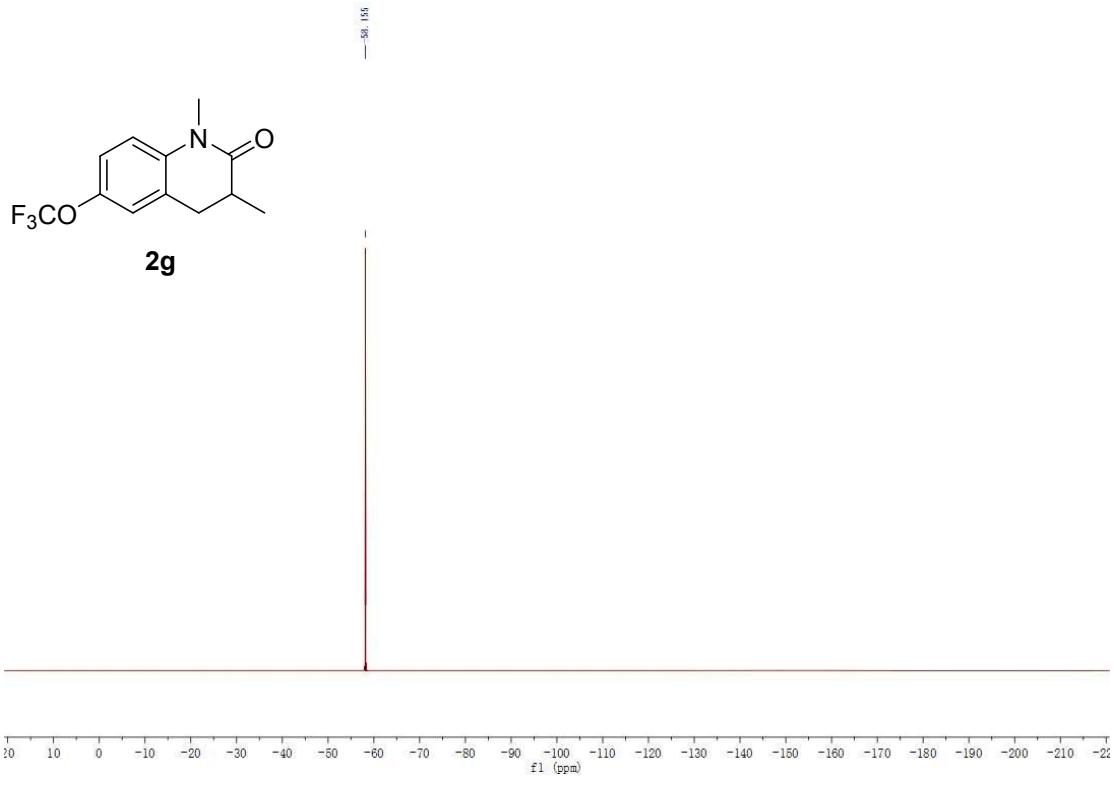
2f

1,3-Dimethyl-6-(trifluoromethoxy)-3,4-dihydroquinolin-2(1H)-one (2g)

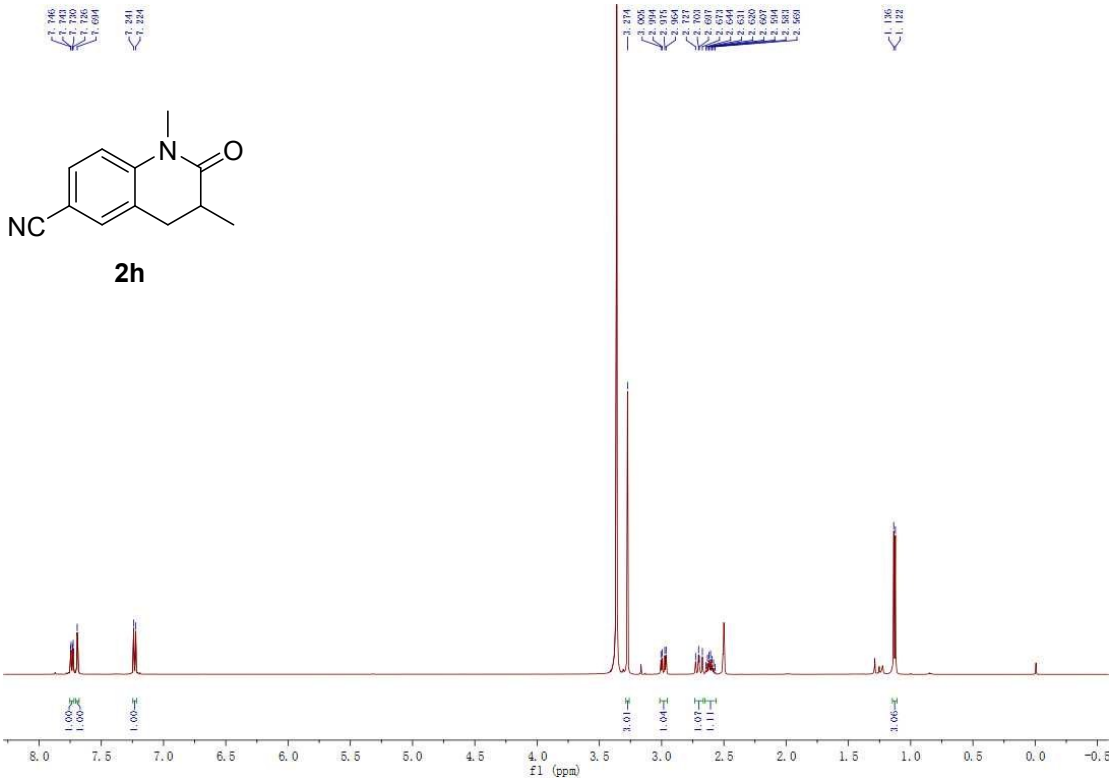


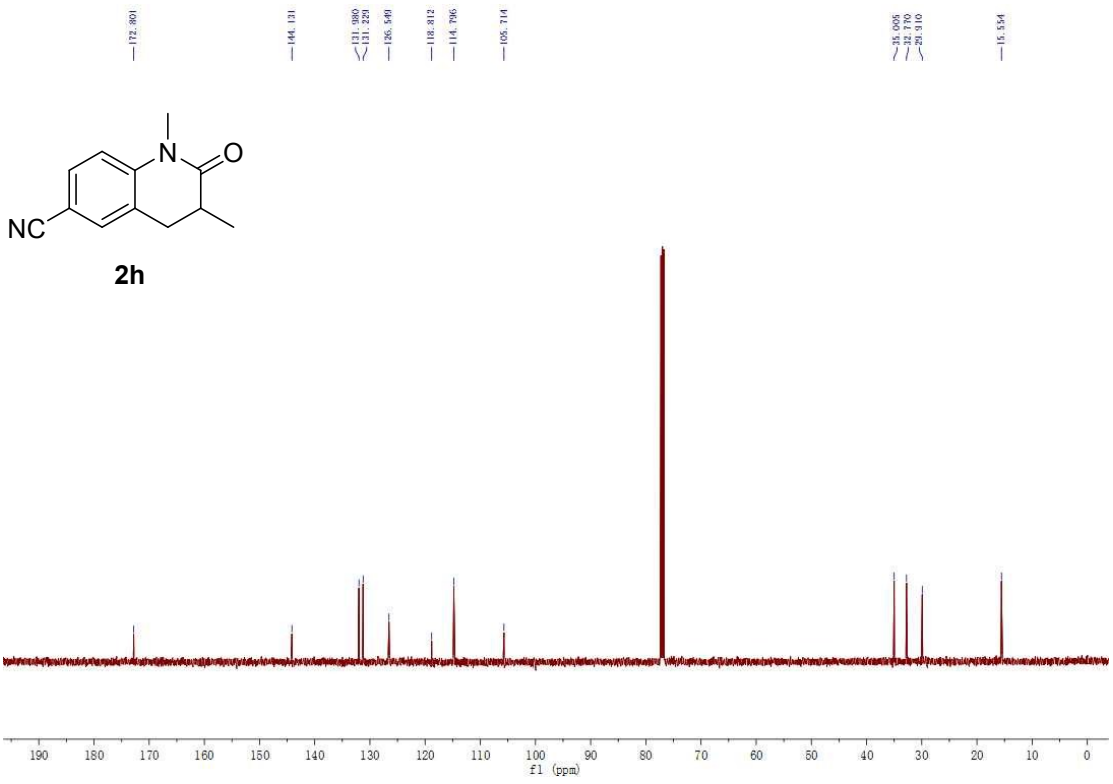
2g


172.745
144.125
129.109
127.362
123.534
121.495
120.732
119.889
119.453
117.412
115.258
35.114
33.124
29.951
15.576
F3CO
2g
123.534
121.495
120.732
119.889
119.453
117.412
124 123 122 121 120 119 118 117 116
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

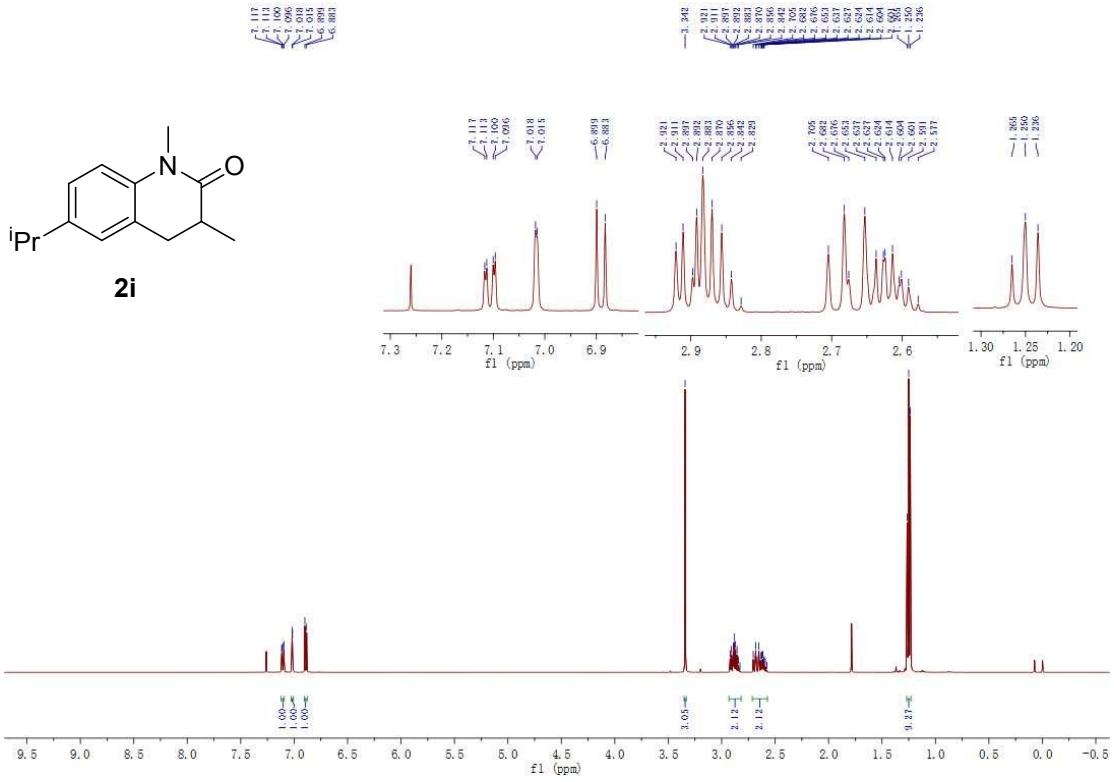

58.155
F3CO
2g
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)

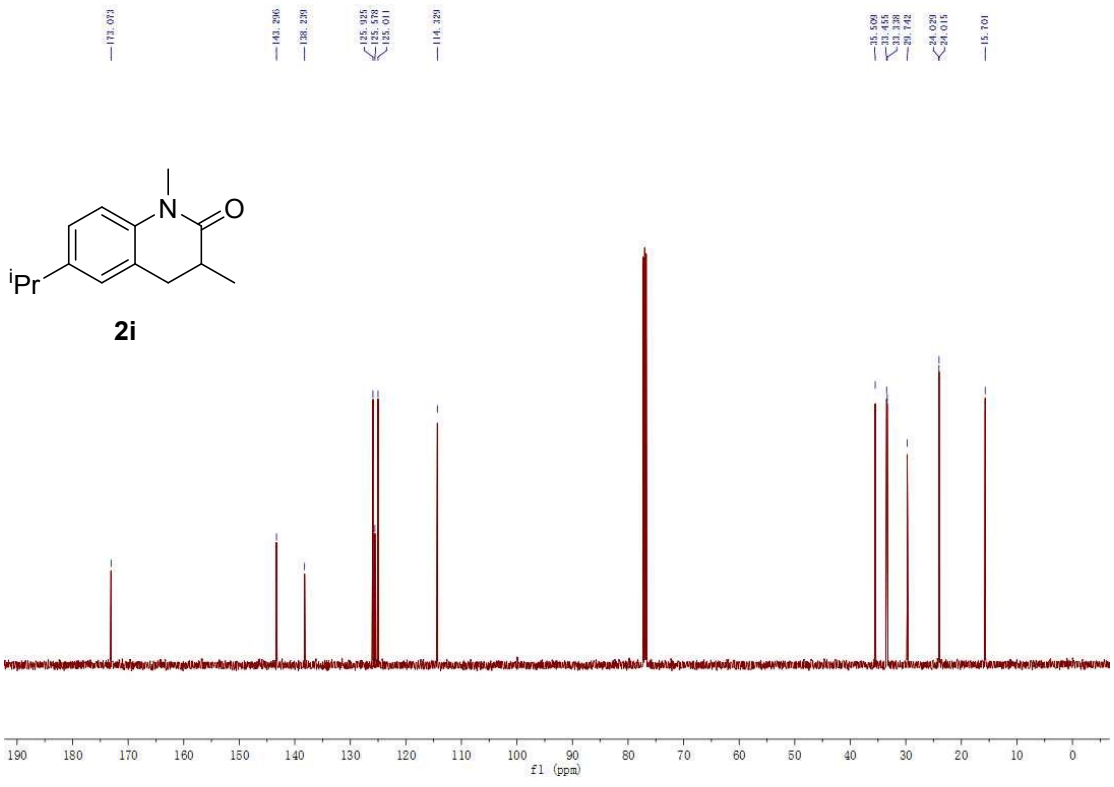
1,3-Dimethyl-2-oxo-1,2,3,4-tetrahydroquinoline-6-carbonitrile (2h)



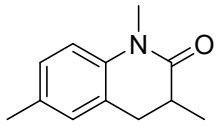


6-Isopropyl-1,3-dimethyl-3,4-dihydroquinolin-2(1*H*)-one (2i)

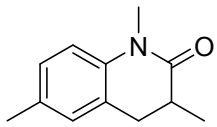




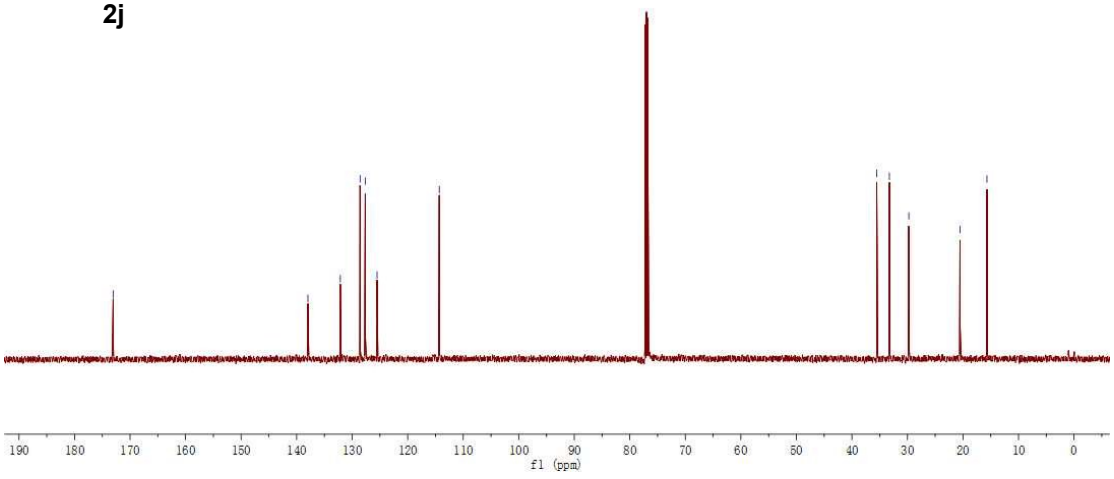
1,3,6-Trimethyl-3,4-dihydroquinolin-2(1*H*)-one (2j)



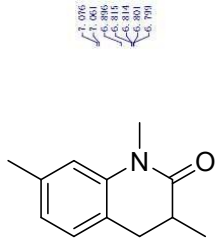
2j



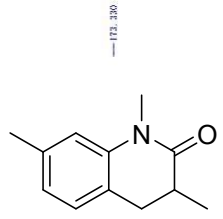
2j



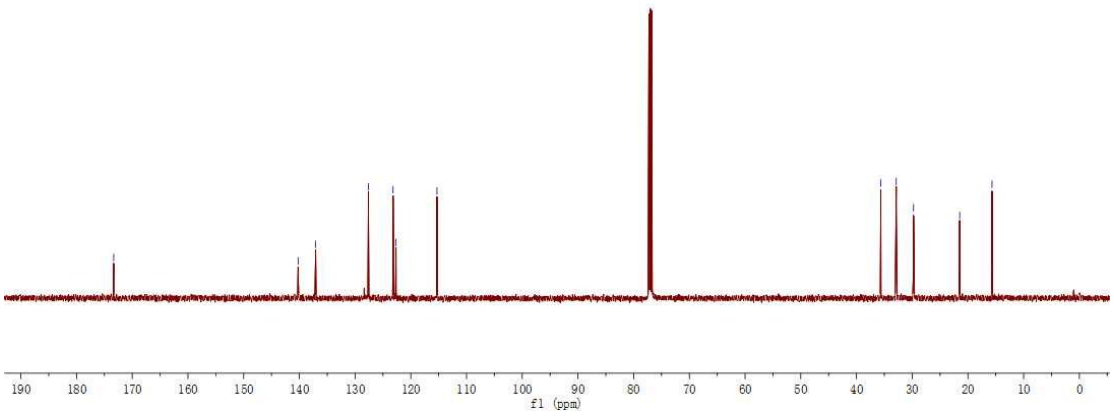
1,3,7-Trimethyl-3,4-dihydroquinolin-2(1*H*)-one (2k)



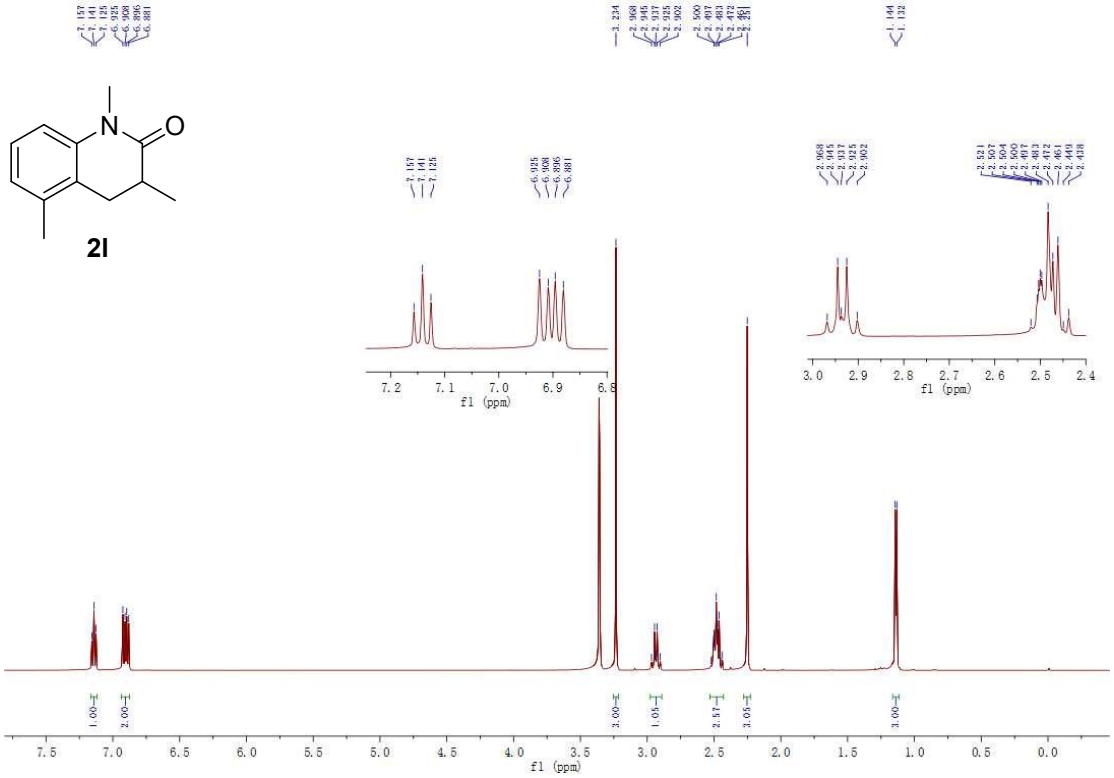
2k

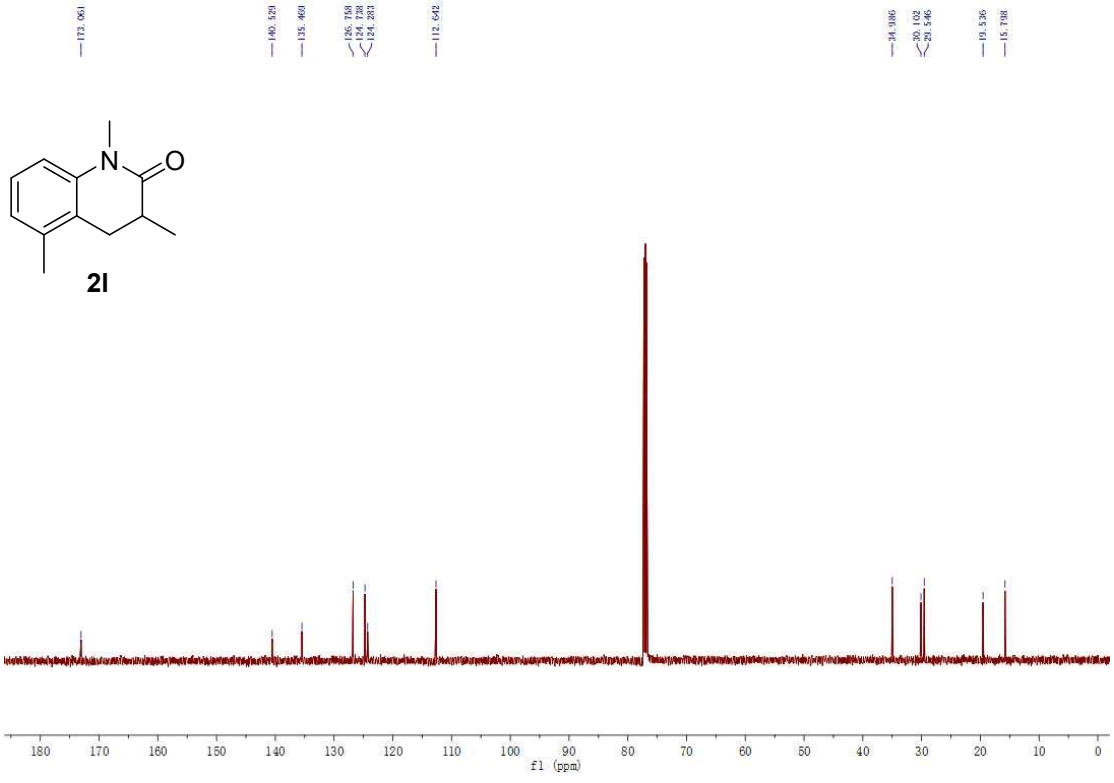


2k

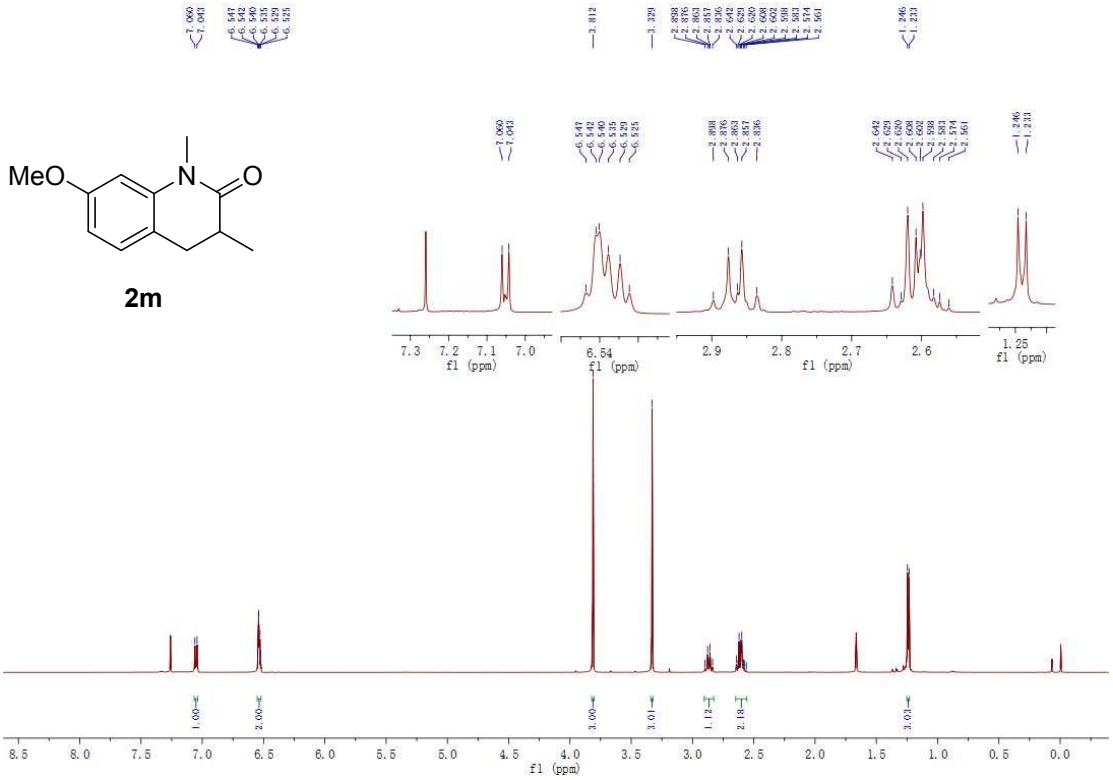


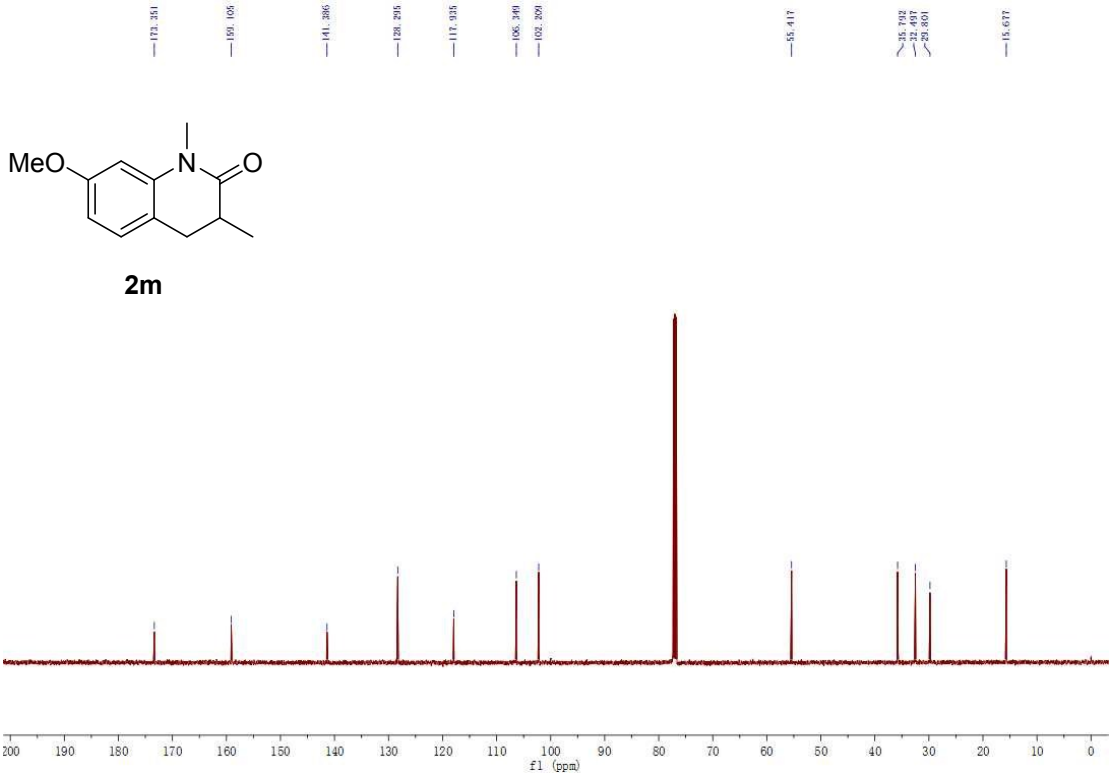
1,3,5-Trimethyl-3,4-dihydroquinolin-2(1*H*)-one (2l)



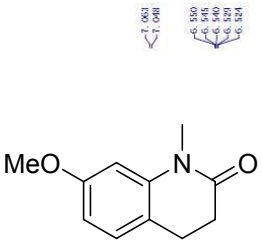


7-Methoxy-1,3-dimethyl-3,4-dihydroquinolin-2(1*H*)-one (2m)

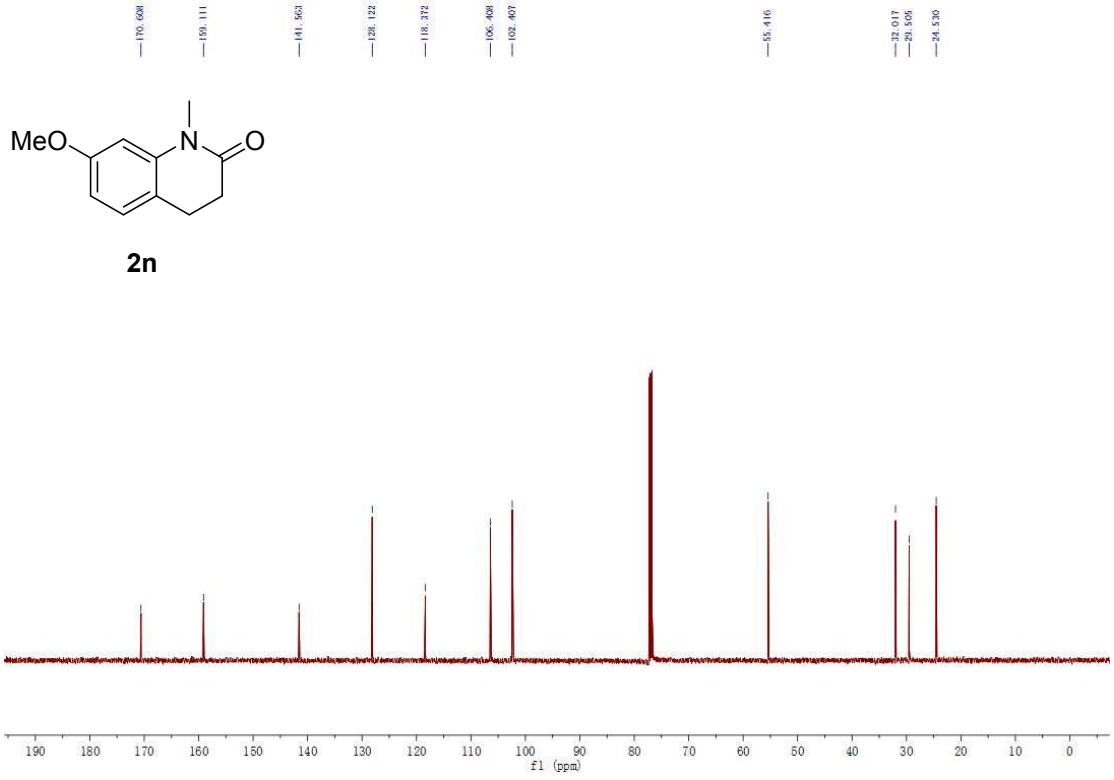




7-Methoxy-1-methyl-3,4-dihydroquinolin-2(1*H*)-one (2n)

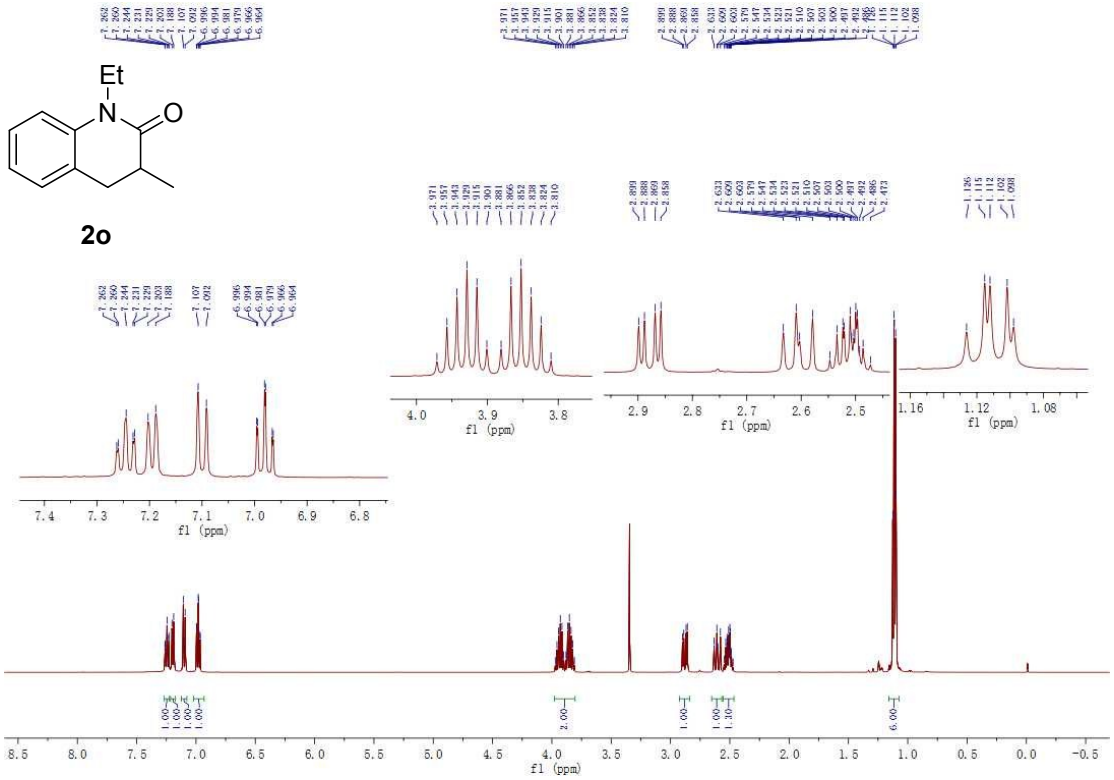


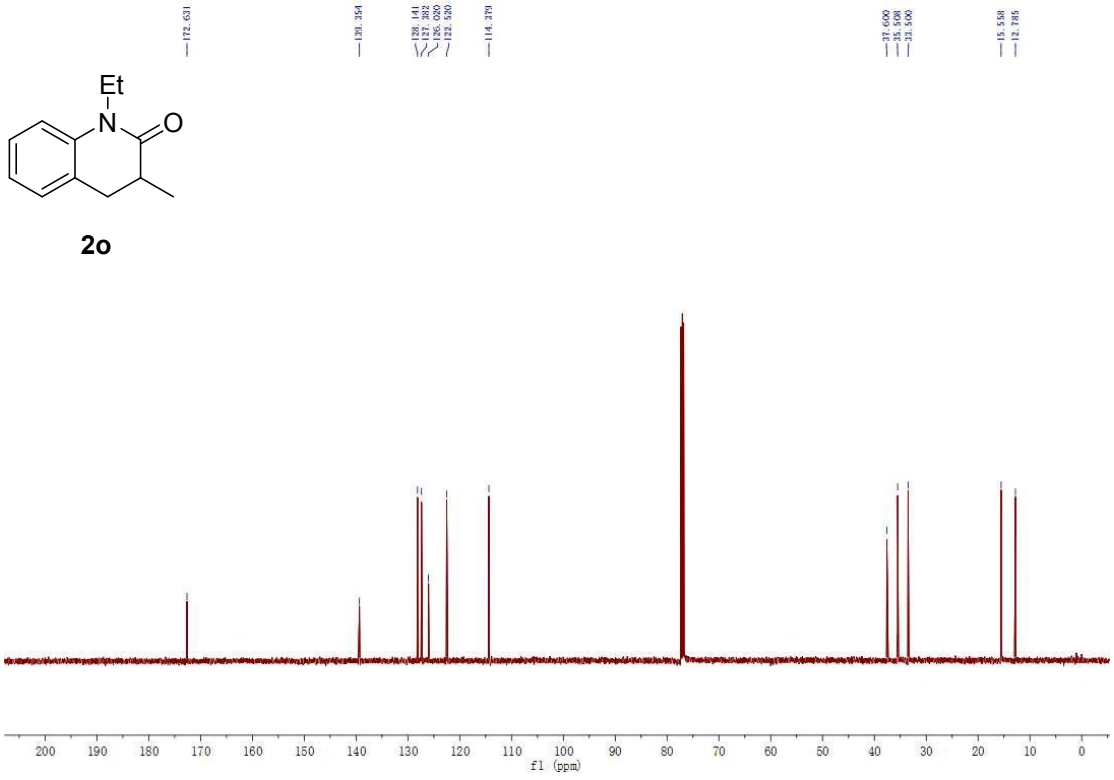
2n



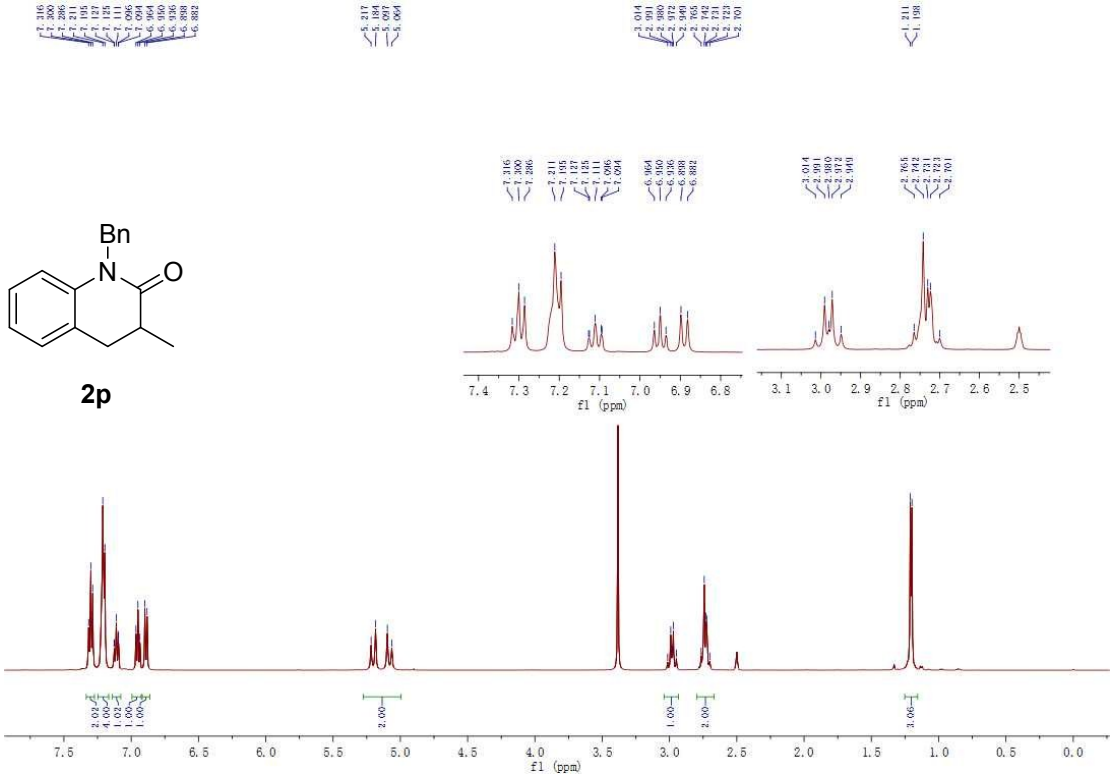
2n

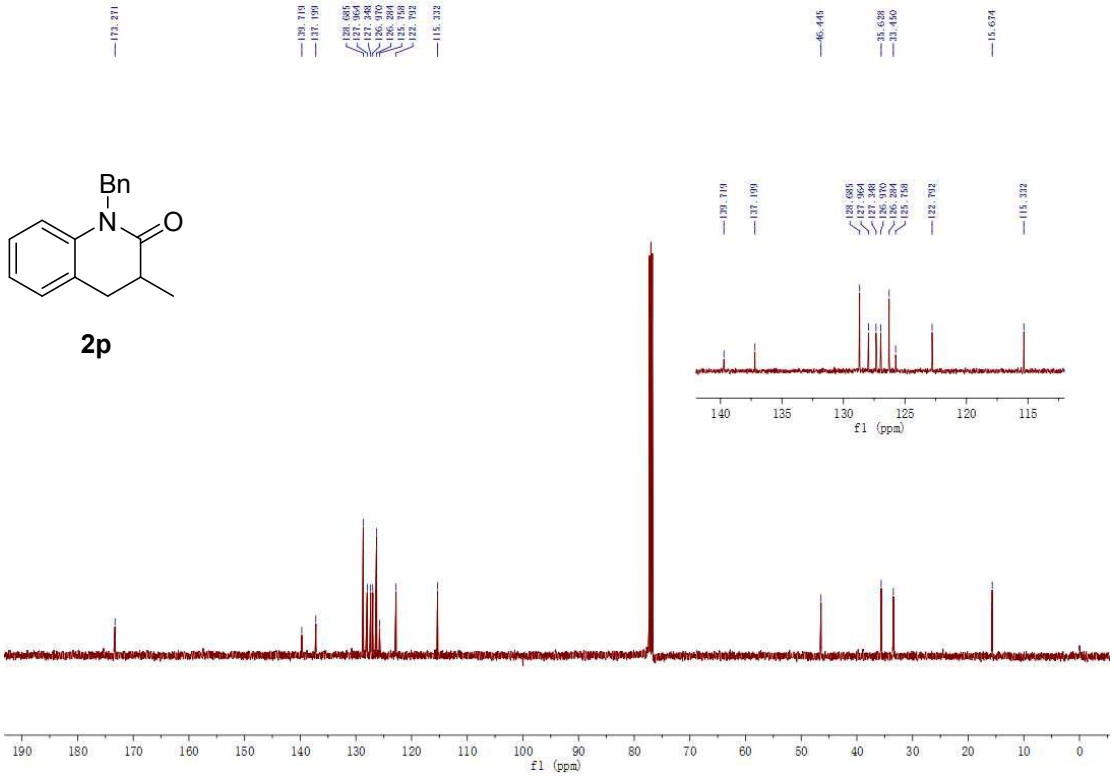
1-Ethyl-3-methyl-3,4-dihydroquinolin-2(1H)-one (2o)



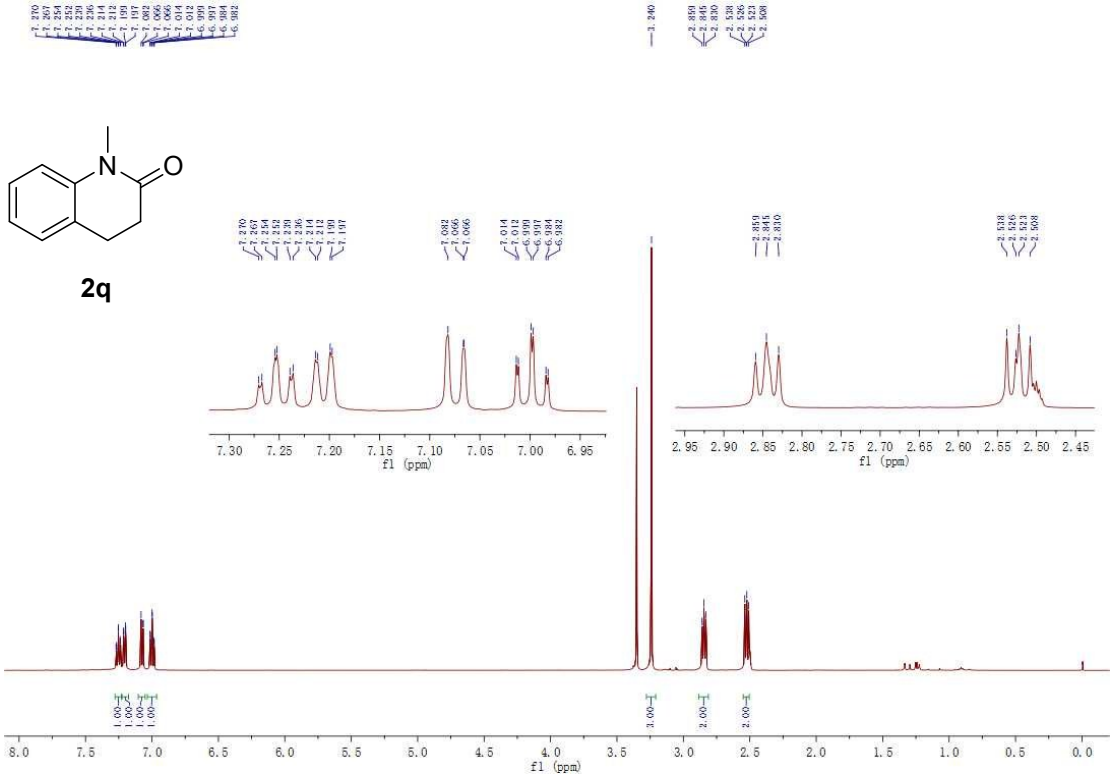


1-Benzyl-3-methyl-3,4-dihydroquinolin-2(1*H*)-one (2p)

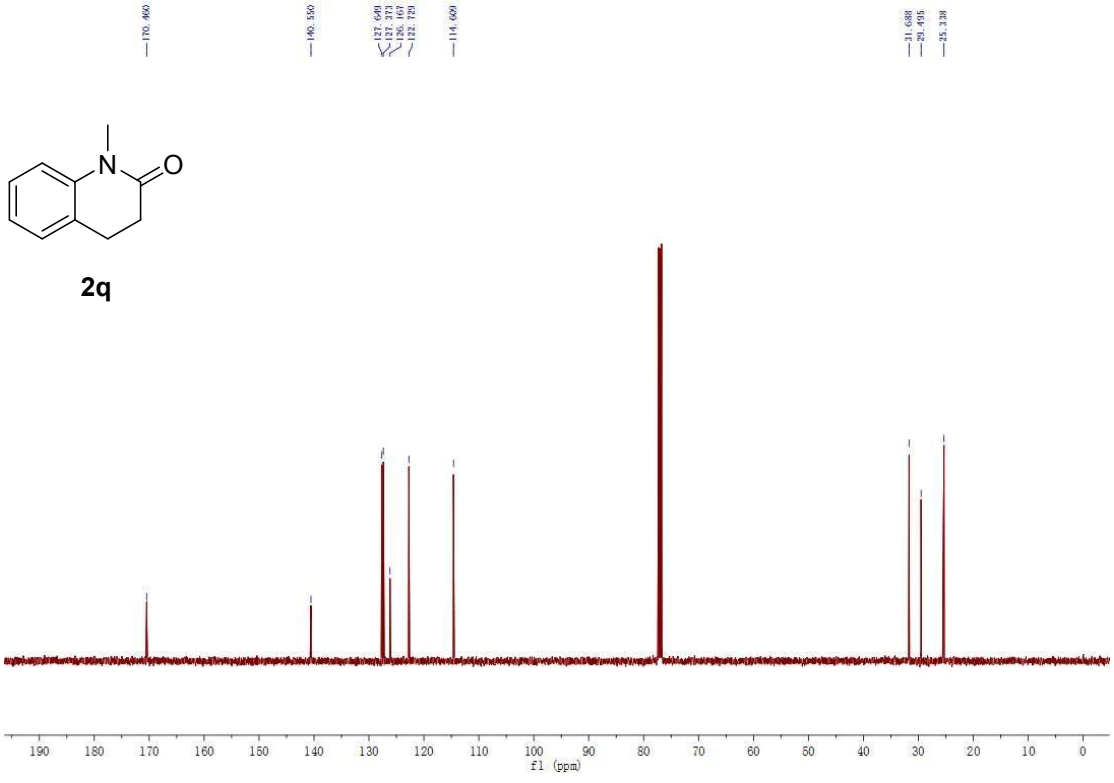




1-Methyl-3,4-dihydroquinolin-2(1*H*)-one (2q)



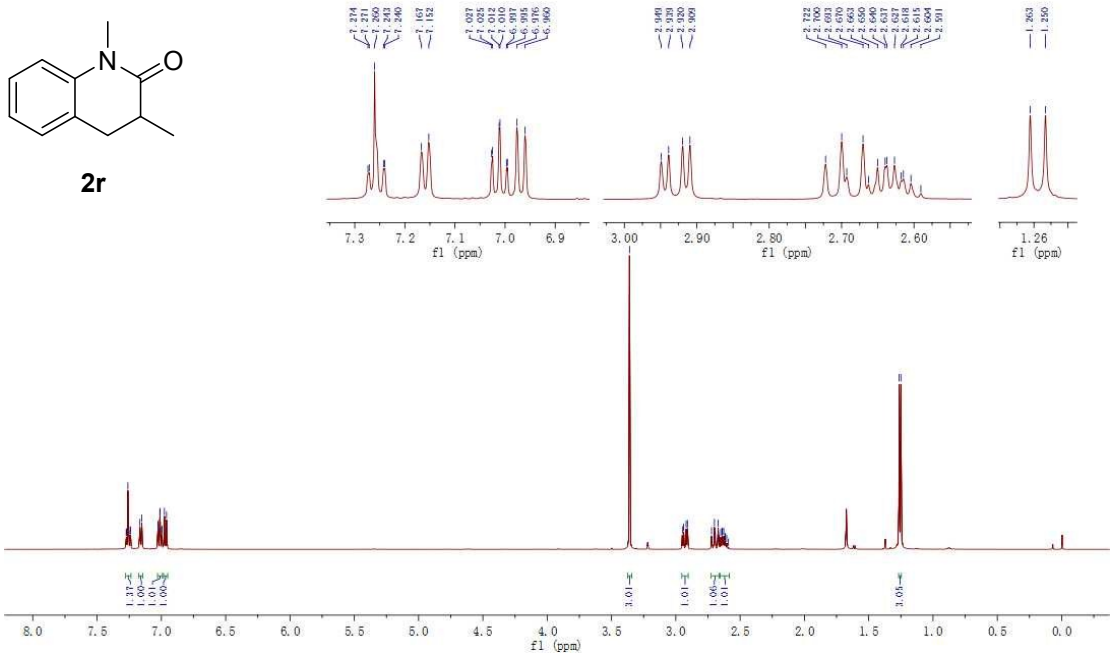
2q

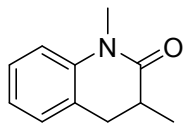


2q

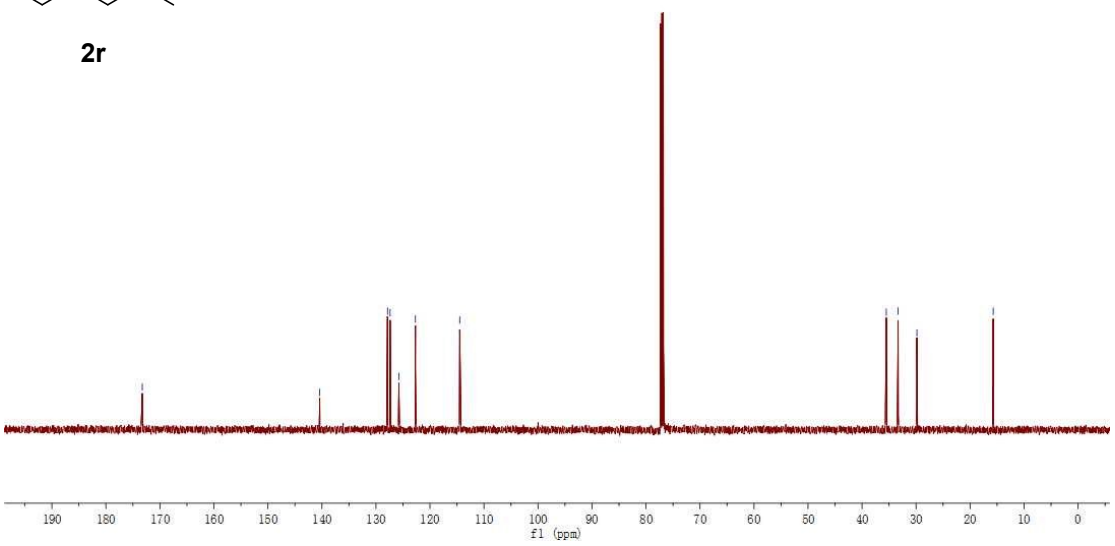
1,3-Dimethyl-3,4-dihydroquinolin-2(1*H*)-one (2r)

2r

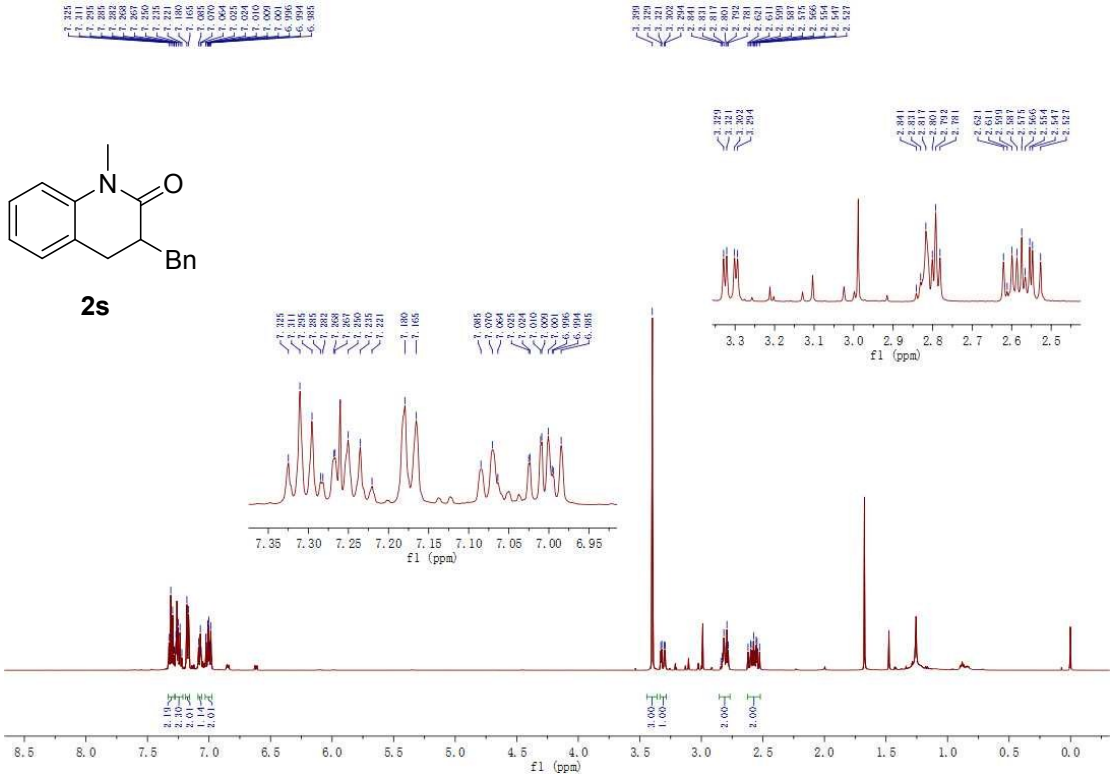


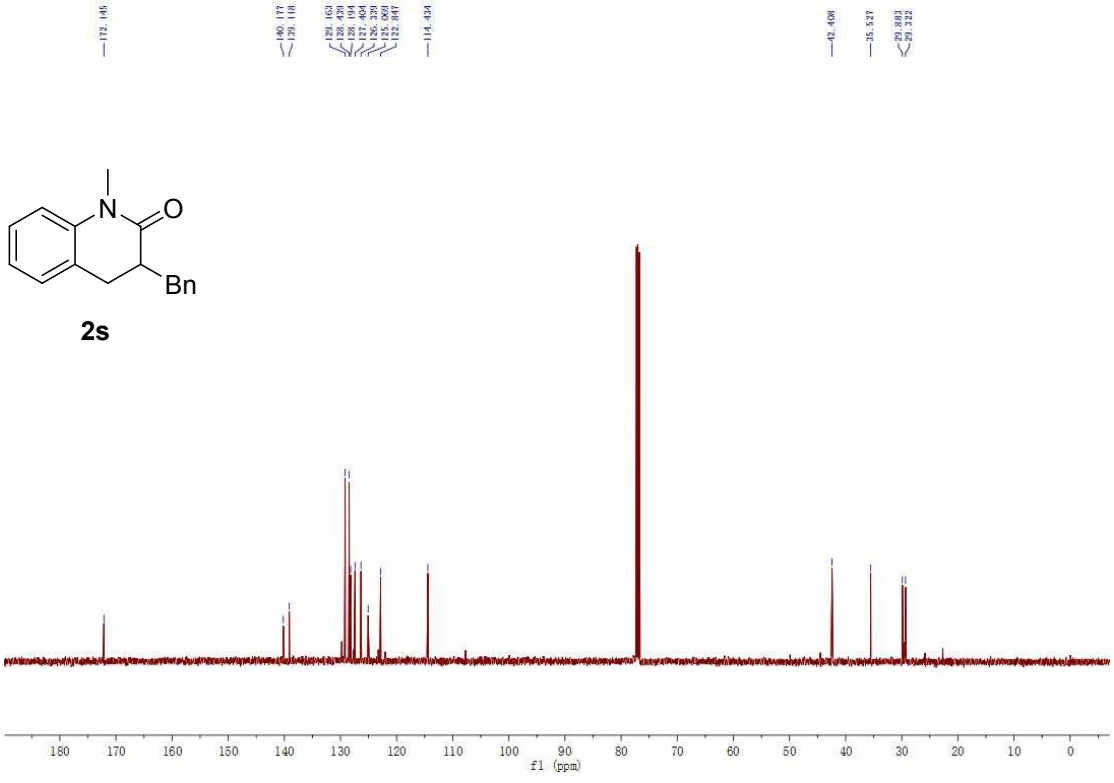


2r

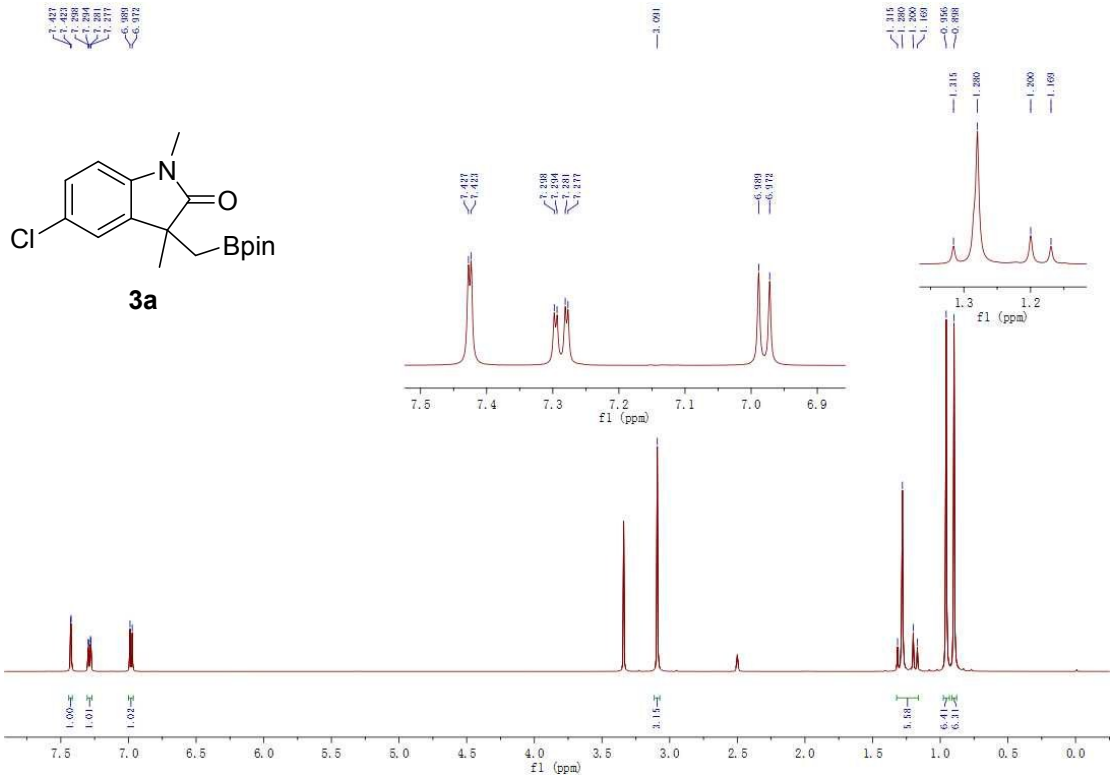


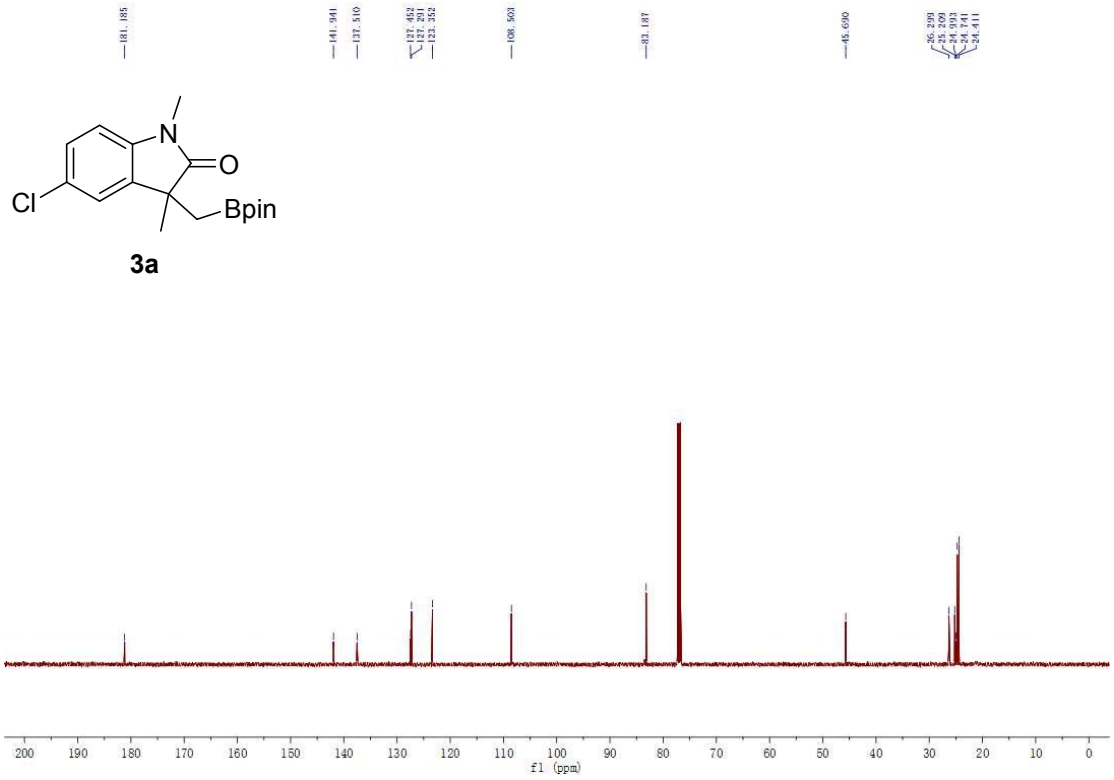
3-Benzyl-1-methyl-3,4-dihydroquinolin-2(1*H*)-one (2s)（with 9% **4s**）



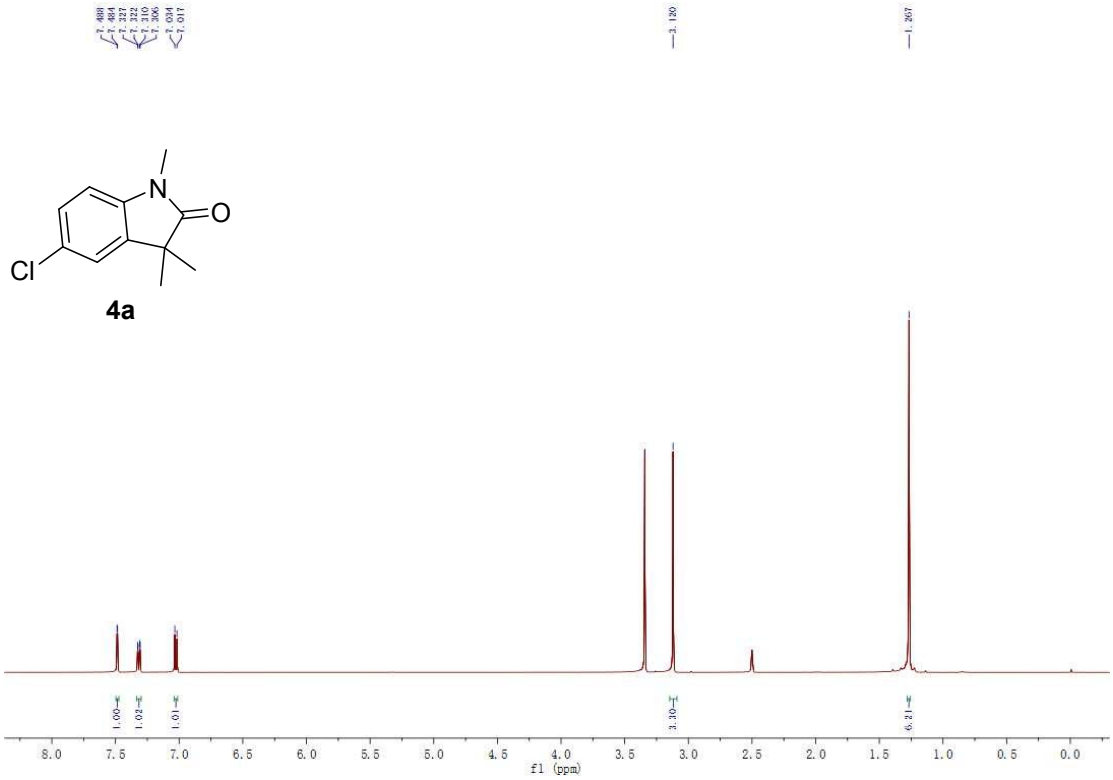


5-Chloro-1,3-dimethyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3a)

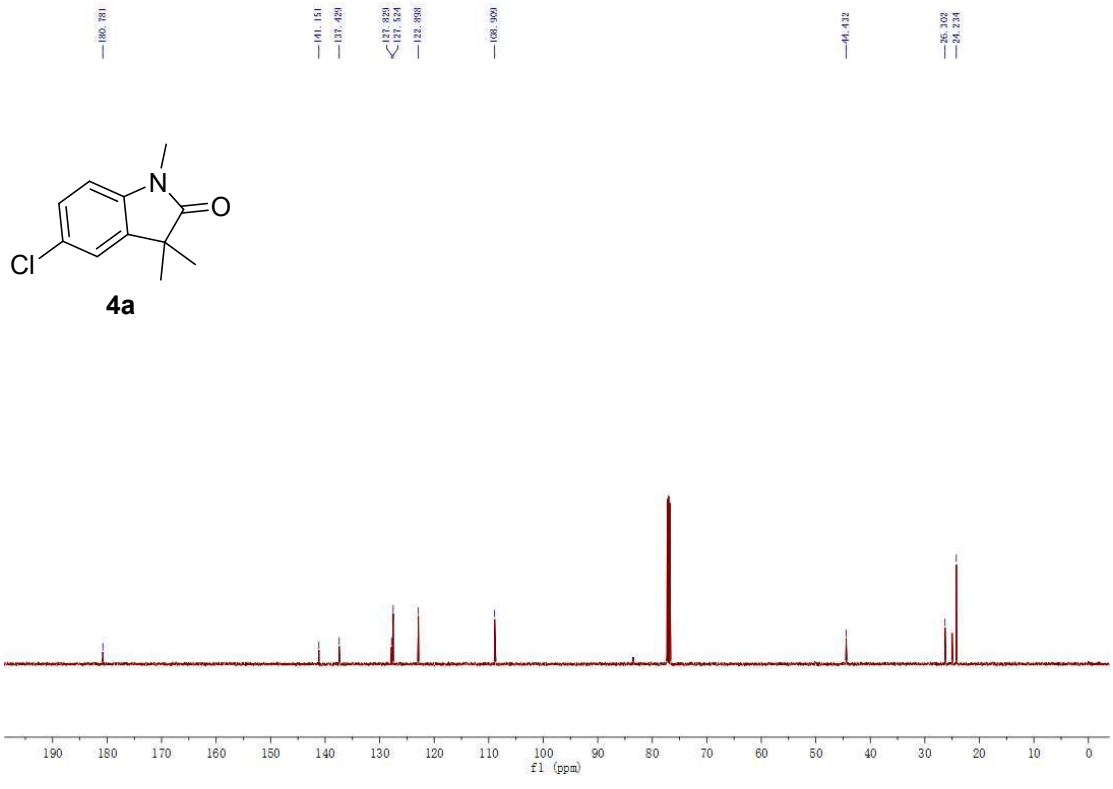




5-Chloro-1,3,3-trimethylindolin-2-one (4a)

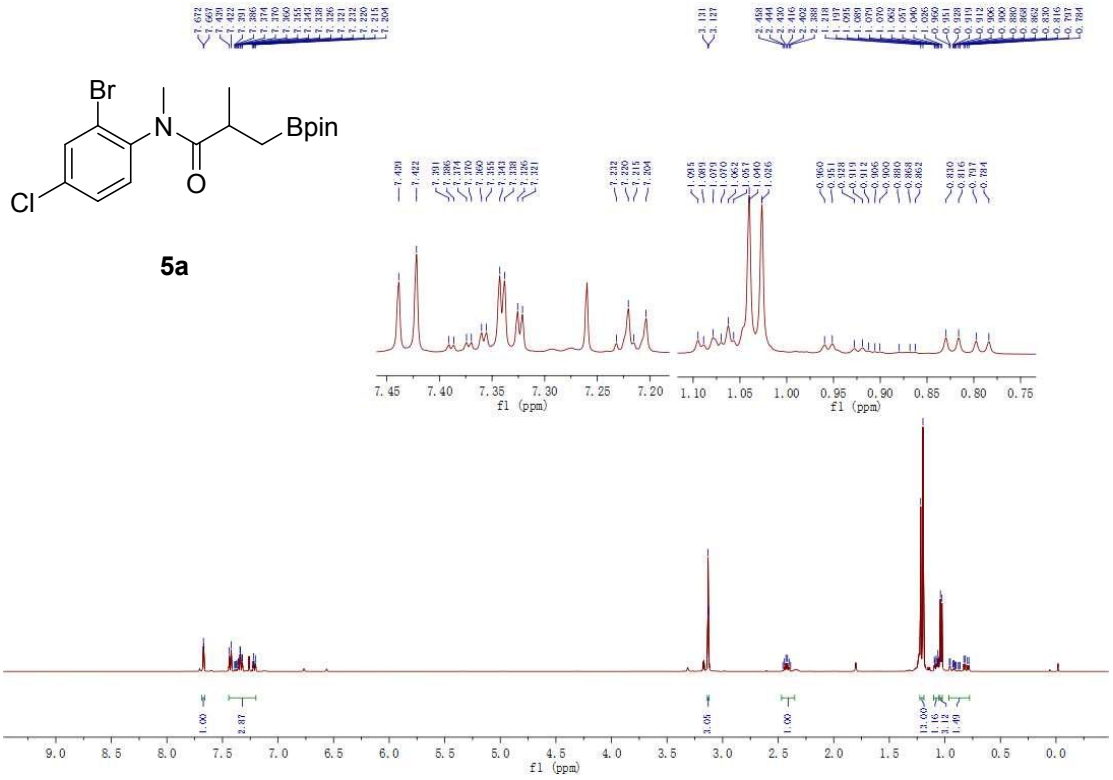


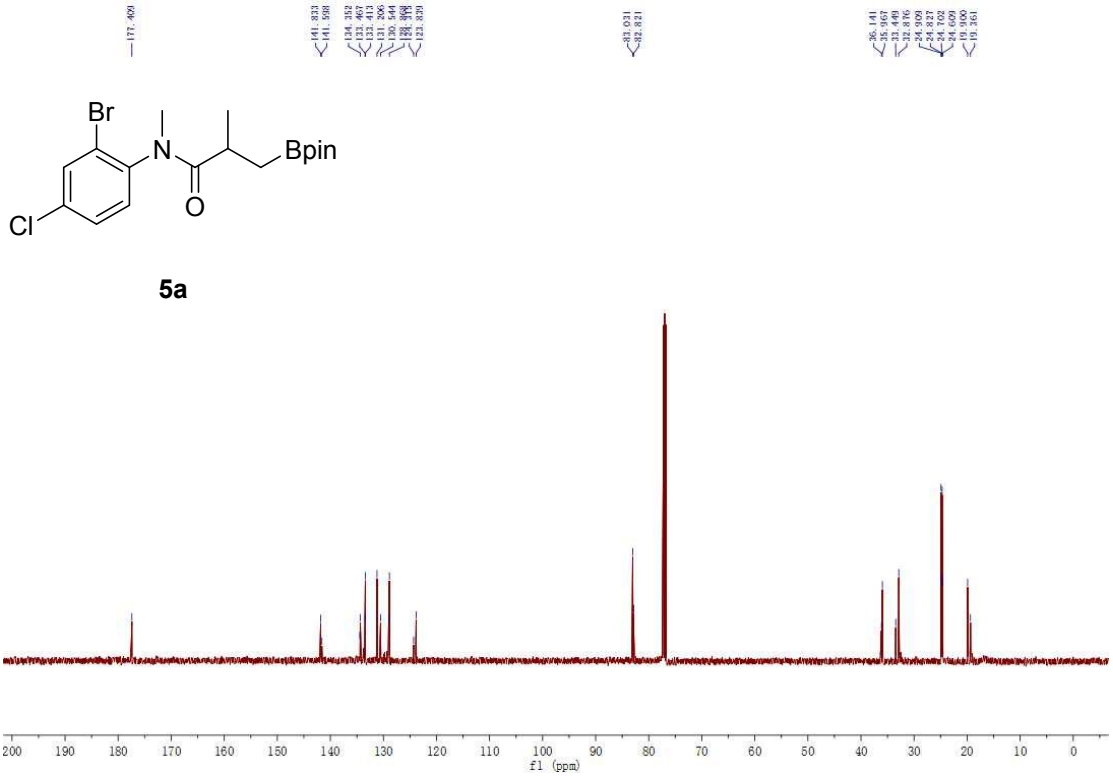
4a



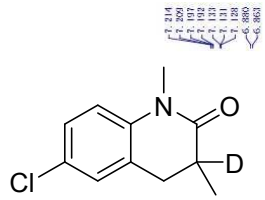
4a

***N*-(2-bromo-4-chlorophenyl)-*N*,2-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanamide (5a)**

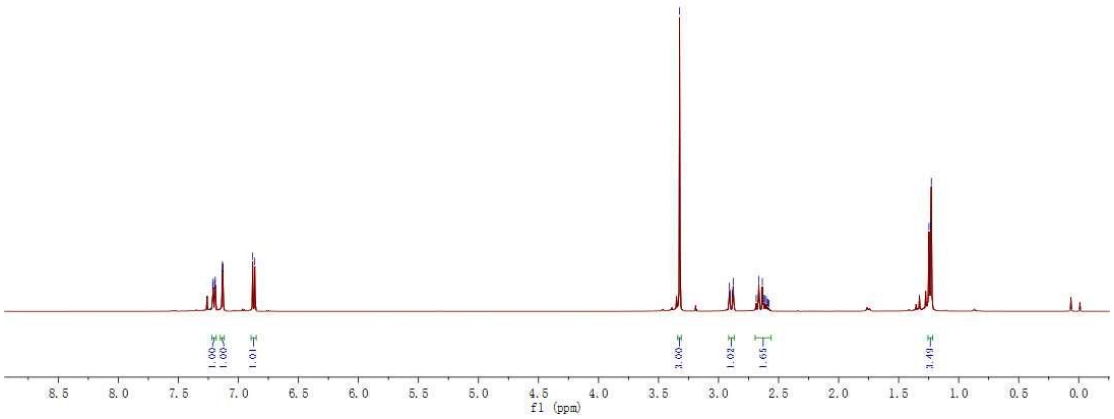




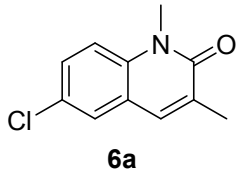
6-chloro-1,3-dimethyl-3,4-dihydroquinolin-2(1*H*)-one-3-*d* *(D-2a)*



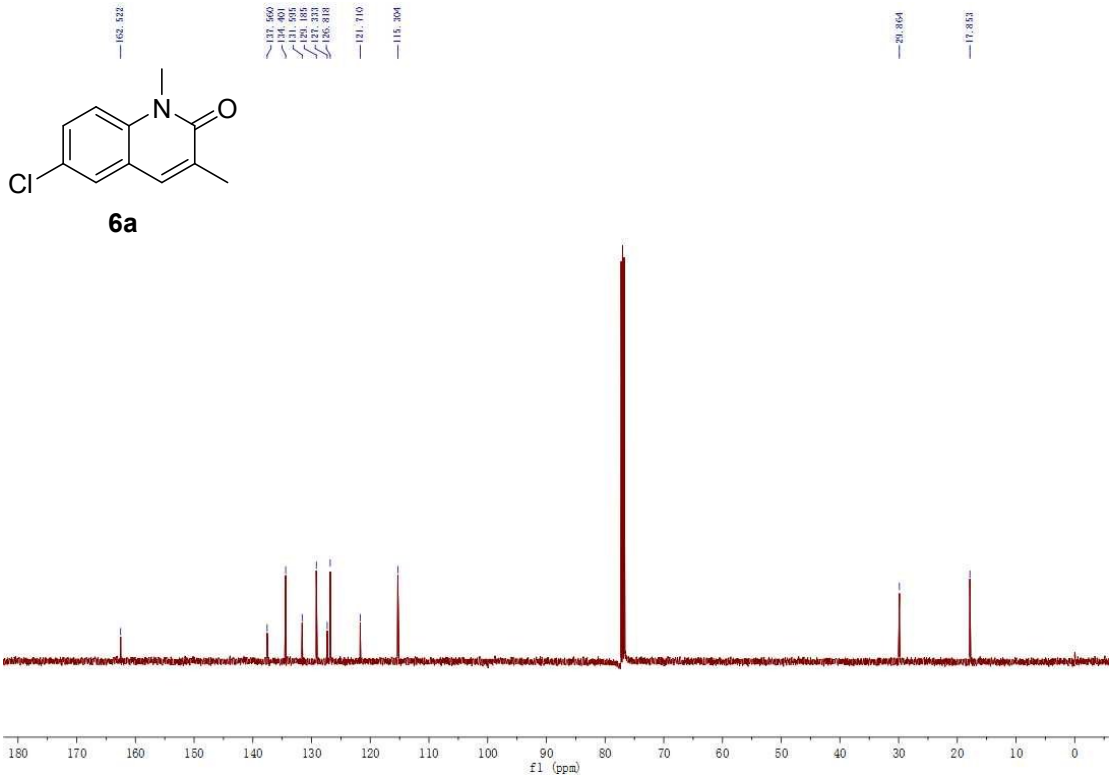
D-**2a**



6-Chloro-1,3-dimethylquinolin-2(1*H*)-one (6a)



6a


162.522
137.960
134.601
131.991
129.185
127.333
126.818
121.710
115.304
29.864
17.853
N
O
Cl
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

6a

7. References

1. T. Nishio, H. Asai and T. Miyazaki, *Helvetica Chimica Acta*., 2000, **83**, 1475.
2. Y. Chen, A. Turlik and T. R. Newhouse, *J. Am. Chem. Soc.*, 2016, **138**, 1166−1169.
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4. F. Wei, L. Wei, L. Zhou, C.-H. Tung, Y. Ma and Z. Xu, *Asian J. Org. Chem*., 2016, **5**, 971.
5. H. Chea, H.-S. Sim and J. Yuna, *Adv. Synth. Catal.*, 2009, **351**, 855 – 858.
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