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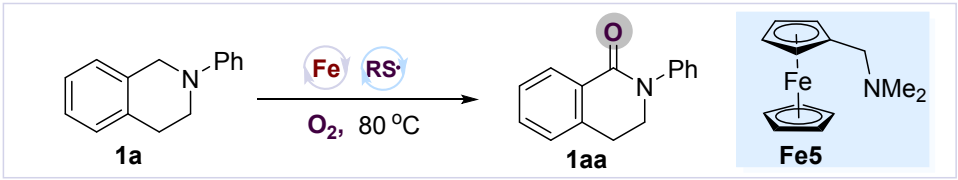
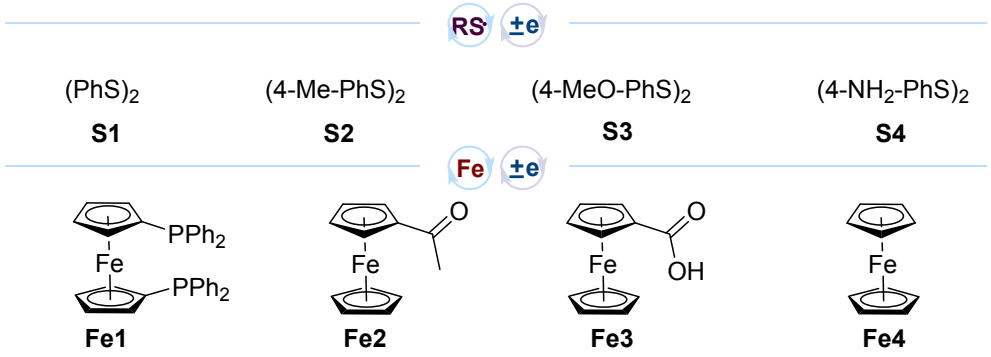
General information: ^{1}H NMR and ^{13}C NMR spectra were recorded on an Agilent 400 MHz or 600 MHz DD2 spectrometer at ambient temperature. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. NMR yield was determined by ^{1}H NMR using mesitylene as an internal standard before working up the reaction.

Materials: All reagents were obtained from commercial suppliers, unless noted otherwise. MeCN, DCM and Toluene were distilled under reduced pressure with CaH_2. 1,4-Dioxane and THF were distilled with sodium and benzophenone before used.

Optimization of the Iron-catalyzed Oxygenation of amine. [a]

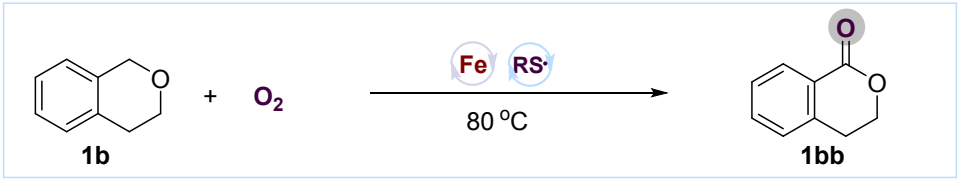


Entry	[Fe]	[Additive 10 mol%]	Temperature	Base	Solvent (0.5 mL)	Yield (%)[b]
1	Fe1	S1	80 °C		1,4-dioxane	17
2	Fe2	S1	80 °C		1,4-dioxane	21
3	Fe3	S1	80 °C		1,4-dioxane	15
4	Fe4	S1	80 °C		1,4-dioxane	25
5	Fe5	S1	80 °C		1,4-dioxane	43
6	Fe5	S2	80 °C		1,4-dioxane	31
7	Fe5	S3	80 °C		1,4-dioxane	35
8	Fe5	S4	80 °C		1,4-dioxane	39
9	Fe5	S1	80 °C	Na_2CO_3 (0.1 eq.)	1,4-dioxane	47
10	Fe5	S1	80 °C	K_2CO_3 (0.1 eq.)	1,4-dioxane	54
11	Fe5	S1	80 °C	K_3PO_4 (0.1 eq.)	1,4-dioxane	57
12	***Fe5***	***S1***	***80 °C***	***Na_3PO_4 (0.1 eq.)***	***1,4-dioxane***	***(66%)***
13	Fe5	S1	80 °C	Na_3PO_4 (0.05 eq.)	1,4-dioxane	53%
14	Fe5	S1	80 °C	Na_3PO_4 (0.2 eq.)	1,4-dioxane	50%
15	Fe5	S1	90 °C	Na_3PO_4 (0.1 eq.)	1,4-dioxane	65
16	Fe5	S1	60 °C	Na_3PO_4 (0.1 eq.)	1,4-dioxane	41
17	Fe5	S1	40 °C	Na_3PO_4 (0.1 eq.)	1,4-dioxane	16
18	Fe5	S1	rt	Na_3PO_4 (0.1 eq.)	1,4-dioxane	trace
19	Fe5	S1	80 °C	Na_3PO_4 (0.1 eq.)	toluene	20
20	Fe5	S1	80 °C	Na_3PO_4 (0.1 eq.)	MeCN	<5
21	Fe5	S1	80 °C	Na_3PO_4 (0.1 eq.)	DCE	<5
22	Fe5	S1	80 °C	Na_3PO_4 (0.1 eq.)	THF	<10

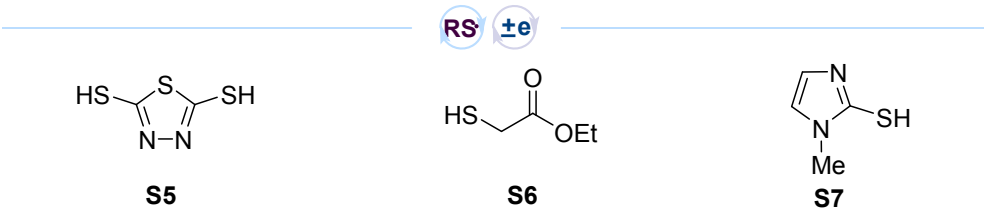


[a]Reaction conditions (unless otherwise specified): **1a** (0.3 mmol, 1.0 equiv), O_2 (1 atm), [Fe] (0.03 mmol, 0.1 equiv), disulfide (0.03 mmol, 0.1 equiv), dioxane (0.5 mL), 80 °C, 15 h. [b]Determined by ^{1}H NMR using mesitylene as an internal standard. The isolated yield is shown in parentheses.

Optimization of the Iron-Catalyzed Oxygenation of Isochroman.[a]



Entry	[Fe]	[Additive 10 mol%]	Temperature	Solvent (0.5 mL)	Yield (%)[b]
1	Fe1		80 °C	MeCN	trace
2	Fe1	S5	80 °C	MeCN	trace
3	Fe1	S6	80 °C	MeCN	< 5
4	Fe1	S7	80 °C	MeCN	< 5
5	Fe1	S1	80 °C	MeCN	7
6	Fe1	S1	80 °C	DCE	trace
7	Fe1	S1	80 °C	Toluene	13
8	Fe1	S1	80 °C	THF	16
9	Fe1	S1	*80 °C*	DMSO	17
10	Fe1	S1	80 °C	Acetone	19
11	Fe1	S1	80 °C	MeOH	8
12	***Fe1***	***S1***	***80 °C***	***1,4-dioxane***	***74% (75%)***
13	Fe1	S1	80 °C	*i*Pr$_2$O	66%
14	Fe1	S1	*80 °C*	diglyme	65%
15	Fe2	S1	80 °C	1,4-dioxane	66
16	Fe3	S1	80 °C	1,4-dioxane	56
17	Fe4	S1	80 °C	1,4-dioxane	57
18	Fe1		80 °C	1,4-dioxane	trace
19	Fe(ClO$_4$)$_2$	S1	80 °C	1,4-dioxane	trace
20	Fe(ClO$_4$)$_2$		80 °C	1,4-dioxane	11

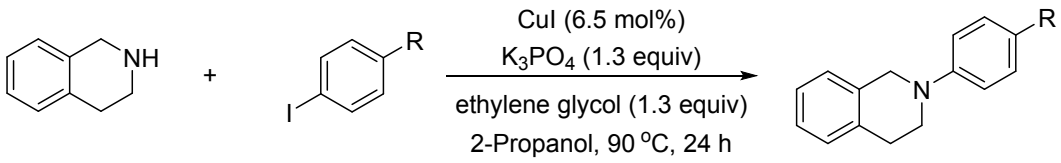


S5 **S6** **S7**

[a]Reaction conditions (unless otherwise specified): **1b** (0.3 mmol, 1.0 equiv), O_2 (1 atm), [Fe] (0.03 mmol, 0.1 equiv), additive (0.03 mmol, 0.1 equiv), 1,4-dioxane (0.5 mL), 80 °C, 15 h. [b]Determined by ^{1}H NMR using mesitylene as an internal standard. The isolated yield is shown in parentheses.

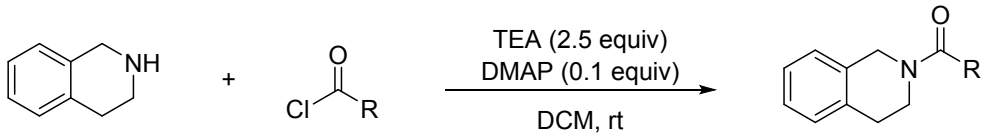
Synthesis and Characterization data of amine derivatives

General procedure 1:



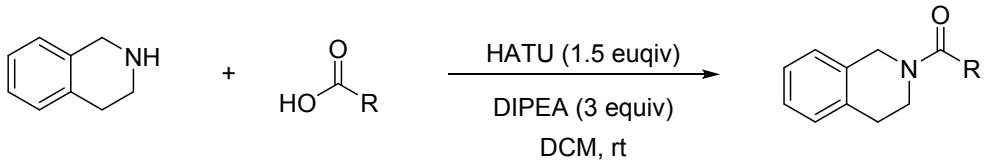
To a 25 ml of Schlenk tube was added CuI (1.0 mmol) and K_3PO_4 (20.0 mmol), then 2-propanol (10 mL), ethylene glycol (20.0 mmol), 1,2,3,4-tetrahydroisoquinoline (15.0 mmol), iodobenzene (15.0 mmol) were added under argon atmosphere. The reaction mixture was heated to 90 ^oC and allowed to react for 24 h. The reaction was quenched with water, and the mixture was extracted with Et_2O for three times. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated to give a crude product, and the residue was purified with silica gel chromatography to give product.

General procedure 2:



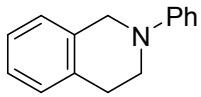
To a solution of DMAP (0.5 mmol) in DCM (20 mL) at room temperature under argon atmosphere, was successively added 1,2,3,4-tetrahydroisoquinoline (5.0 mmol), triethylamine (12.5 mmol) and corresponding acyl chloride (5.0 mmol). After stirring for 10 h at room temperature, the reaction was quenched with water, and the mixture was extracted with DCM for three times. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated to give a crude product, and the residue was purified with silica gel chromatography to give product.

General procedure 3:

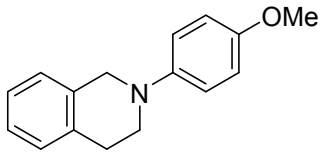


To a solution of condensation agent HATU (7.5 mmol), carboxylic acid (5.0 mmol) in DCM (20 mL) at room temperature under argon atmosphere, was successively added

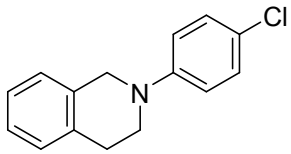
N,*N*-diisopropylethylamine (15.0 mmol), 1,2,3,4-tetrahydroisoquinoline (5.0 mmol), triethylamine (12.5 mmol) and corresponding carboxylic acid (5.0 mmol). After stirring for 10 h at room temperature, the reaction was quenched with water, and the mixture was extracted with DCM for three times. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated to give a crude product, and the residue was purified with silica gel chromatography to give product.



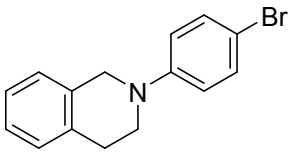
2-Phenyl-1,2,3,4-tetrahydroisoquinoline (1a) The title compound was prepared according to general procedure 1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, *J* = 8.4 Hz, 2 H), 7.24-7.18 (m, 4 H), 7.03 (d, *J* = 8.4 Hz, 2 H), 6.88 (t, *J* = 7.6 Hz, 1H), 4.46 (s, 2 H), 3.61 (t, *J* = 6.0 Hz, 2 H), 3.03 (t, *J* = 6.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 134.9, 134.5, 129.2, 128.5, 126.5, 126.3, 126.0, 118.6, 115.1, 50.7, 46.5, 29.1.



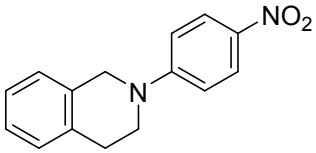
2-(4-Methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (2a) The title compound was prepared according to general procedure 1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.13 (m, 4 H), 7.00 (d, *J* = 8.8 Hz, 2 H), 6.88 (d, *J* = 8.8 Hz, 2 H), 4.31 (s, 2 H), 3.79 (s, 3 H), 3.46 (t, *J* = 6.0 Hz, 2 H), 3.00 (t, *J* = 6.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 145.3, 134.5, 134.5, 128.7, 126.5, 126.2, 125.9, 118.0, 114.5, 55.6, 52.6, 48.4, 29.1.



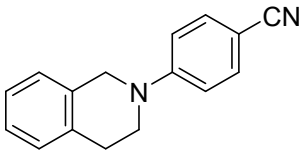
2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline (3a) The title compound was prepared according to general procedure 1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.13 (m, 6 H), 6.87 (d, *J* = 8.8 Hz, 2 H), 4.37 (s, 2 H), 3.52 (t, *J* = 6.0 Hz, 2 H), 2.97 (t, *J* = 6.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 134.7, 134.1, 129.0, 128.5, 126.5, 126.5, 126.1, 123.3, 116.1, 50.6, 46.5, 28.9.



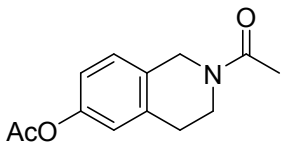
2-(4-Bromophenyl)-1,2,3,4-tetrahydroisoquinoline (4a) The title compound was prepared according to general procedure 1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.2 Hz, 2 H), 7.21-7.14 (m, 4 H), 6.83 (d, *J* = 7.2 Hz, 2 H), 4.38 (s, 2 H), 3.53 (t, *J* = 5.6 Hz, 2 H), 2.98 (t, *J* = 5.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 134.7, 134.0, 131.9, 128.5, 126.5, 126.1, 116.4, 110.4, 50.4, 46.3, 28.9.



2-(4-Nitrophenyl)-1,2,3,4-tetrahydroisoquinoline (5a) The title compound was prepared according to general procedure 1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.0 Hz, 2 H), 7.25-7.20 (m, 4 H), 6.18 (d, *J* = 8.0 Hz, 2 H), 4.56 (s, 2 H), 3.69 (t, *J* = 5.6 Hz, 2 H), 3.02 (t, *J* = 5.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 137.4, 134.8, 133.0, 128.0, 127.1, 126.6, 126.4, 126.1, 111.1, 48.7, 44.7, 28.9.

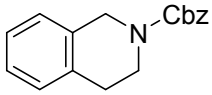


4-(3,4-Dihydroisoquinolin-2(1*H*)-yl)benzonitrile (6a) The title compound was prepared according to general procedure 1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.8 Hz, 2 H), 7.25-7.17 (m, 4 H), 6.85 (d, *J* = 8.8 Hz, 2 H), 4.49 (s, 2 H), 3.62 (t, *J* = 6.0 Hz, 2 H), 2.99 (t, *J* = 6.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 134.8, 133.4, 133.3, 128.1, 126.8, 126.4, 126.4, 120.3, 112.5, 98.5, 48.7, 44.5, 28.8.

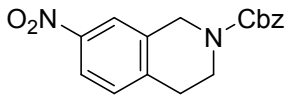


2-Acetyl-1,2,3,4-tetrahydroisoquinolin-6-yl acetate (7a) The title compound was prepared according to general procedure 2. ^{1}H NMR (400 MHz, $CDCl_3$, rotomers seen) δ 7.11 (dd, *J* = 16.0, 8.0 Hz, 1 H), 6.92-6.87 (m, 2 H), 4.69 (s, 1.2 H), 4.58 (s, 0.8 H), 3.79 (t, *J* = 5.6 Hz, 0.8 H), 3.65 (t, *J* = 5.6 Hz, 1.2 H), 2.88 (t, *J* = 5.6 Hz, 1.2 H), 2.82

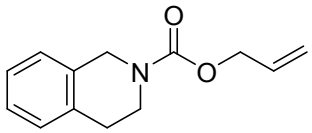
(t, J = 5.6 Hz, 0.8 H), 2.27 (s, 3.0 H), 2.15 (s, 3.0 H). ^{13}C NMR (100 MHz, $CDCl_3$, rotomers seen) δ 169.6, 169.5, 169.3, 149.2, 149.0, 136.5, 135.3, 131.1, 130.1, 127.7, 127.0, 121.8, 121.2, 119.9, 119.7, 47.7, 43.7, 43.6, 39.1, 29.4, 28.5, 21.8, 21.6, 21.0.



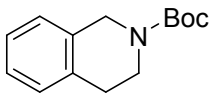
Benzyl 3,4-dihydroisoquinoline-2(1*H*)-carboxylate (8a) The title compound was prepared according to general procedure 2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.32 (m, 5 H), 7.20-7.10 (m, 4 H), 5.21 (s, 2 H), 4.67 (s, 2 H), 3.74 (s (br), 2 H), 2.87 (s (br), 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 136.7, 134.5, 134.4, 133.3, 132.9, 128.7, 128.4, 127.9, 127.9, 126.4, 126.2, 67.1, 45.7, 41.5, 41.3, 28.9, 28.7.



Benzyl 7-nitro-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (9a) The title compound was prepared according to general procedure 2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.97 (m, 2 H), 7.38-7.25 (m, 6 H), 5.18 (s, 2 H), 4.73 (s, 2 H), 3.76 (t, J = 6.0 Hz, 2 H), 2.94 (s (br), 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 146.5, 142.1, 136.3, 134.6, 129.8, 128.5, 128.2, 128.0, 121.5, 67.5, 45.5, 40.7, 29.0.

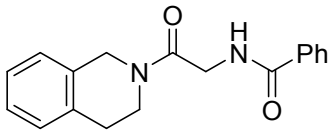


Allyl 3,4-dihydroisoquinoline-2(1*H*)-carboxylate (10a) The title compound was prepared according to general procedure 2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.11 (m, 4 H), 6.03-6.93 (m, 1 H), 5.33 (d, J = 17.2 Hz, 1 H), 5.23 (d, J = 10.4 Hz, 1 H), 4.65 (s, 4 H), 3.72 (t, J = 6.0 Hz, 2 H), 2.86 (t, J = 6.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 134.5, 133.4, 133.0, 128.7, 128.5, 126.4, 126.2, 117.4, 66.0, 45.6, 41.5, 28.9.

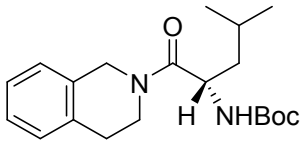


***tert*-Butyl 3,4-dihydroisoquinoline-2(1*H*)-carboxylate (11a)** The title compound was prepared according to general procedure 2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.10 (m, 4 H), 4.58 (s, 2 H), 3.65 (t, J = 5.6 Hz, 2 H), 2.84 (t, J = 5.6 Hz, 2 H), 1.50 (s, 9 H).

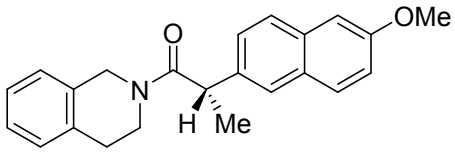
^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 134.7, 133.7, 128.6, 126.2, 126.1, 79.7, 45.8, 40.6, 28.9, 28.4.



***N*-(2-(3,4-Dihydroisoquinolin-2(1*H*)-yl)-2-oxoethyl)benzamide (12a)** The title compound was prepared according to general procedure 3. ^{1}H NMR (400 MHz, $CDCl_3$, rotomers seen) δ 7.85 (d, *J* = 7.6 Hz, 2.0 H), 7.50 (t, *J* = 7.2 Hz, 1.0 H), 7.43 (t, *J* = 7.2 Hz, 3.0 H), 7.25-7.11 (m, 4.0 H), 4.77 (s, 1.1 H), 4.62 (s, 0.9 H), 4.35-4.32 (m, 2.0 H), 3.88 (t, *J* = 6.0 Hz, 0.9 H), 3.68 (t, *J* = 6.0 Hz, 1.1 H), 2.94 (t, *J* = 6.0 Hz, 1.1 H), 2.90 (t, *J* = 6.0 Hz, 0.9 H). ^{13}C NMR (100 MHz, $CDCl_3$, rotomers seen) δ 167.1, 166.9, 134.5, 133.8, 133.7, 132.6, 131.5, 131.5, 128.8, 128.5, 128.3, 127.2, 127.0, 126.8, 126.7, 126.6, 126.5, 126.1, 45.9, 44.4, 42.1, 41.9, 40.1, 29.0, 28.2.

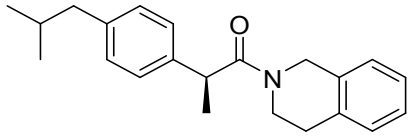


***tert*-Butyl (*S*)-(1-(3,4-dihydroisoquinolin-2(1*H*)-yl)-4-methyl-1-oxopentan-2-yl) carbamate (13a)** The title compound was prepared according to general procedure 3. ^{1}H NMR (400 MHz, $CDCl_3$, rotomers seen) δ 7.22-7.08 (m, 4.0 H), 5.33 (t, *J* = 9.2 Hz, 1.0 H), 4.79-4.71 (m, 3.0 H), 3.97- 3.79 (m, 1.0 H), 3.74-3.66 (m, 1.0 H), 3.01-2.90 (m, 1.0 H), 2.86 (t, *J* = 6.0 Hz, 1.0 H), 1.77-1.69 (m, 1.0 H), 1.59-1.47 (m, 1.0 H), 1.42 (s, 9.0 H), 1.40-1.31 (m, 1.0 H), 1.02 (d, *J* = 3.6 Hz, 1.8 H), 1.00 (d, *J* = 3.6 Hz, 1.2 H), 0.93 (d, *J* = 6.8 Hz, 1.8 H), 0.89 (d, *J* = 6.8 Hz, 1.2 H). ^{13}C NMR (100 MHz, $CDCl_3$, rotomers seen) δ 172.0, 171.8, 155.6, 134.8, 133.9, 133.0, 132.1, 128.8, 128.3, 127.0, 126.6, 126.4, 126.1, 79.5, 49.0, 48.8, 47.0, 44.5, 43.0, 43.0, 42.9, 40.3, 29.4, 28.3, 24.6, 23.4, 21.9, 21.8.



(*S*)-1-(3,4-Dihydroisoquinolin-2(1*H*)-yl)-2-(6-methoxynaphthalen-2-yl)propan-1-one (14a) The title compound was prepared according to general procedure 3. ^{1}H NMR

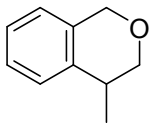
(400 MHz, $CDCl_3$, rotomers seen) δ 7.71-7.64 (m, 3 H), 7.39 (d, *J* = 8.4 Hz, 1 H), 7.15-7.09 (m, 5 H), 6.98 (d, *J* = 7.6 Hz, 0.6 H), 6.86 (d, *J* = 7.6 Hz, 0.4 H), 4.79 (dd, *J* = 29.2, 17.2 Hz, 1.2 H), 4.69 (d, *J* = 16.0 Hz, 0.4 H), 4.35 (d, *J* = 16.0 Hz, 0.4 H), 4.13-4.01 (m, 1.4 H), 3.90 (s, 3 H), 3.73-3.55 (m, 1.6 H), 2.89-2.77 (m, 0.8 H), 2.68-2.61 (m, 0.6 H), 2.38-2.31 (m, 0.6 H), 1.55 (d, *J* = 6.8 Hz, 3.0 H). ^{13}C NMR (100 MHz, $CDCl_3$, rotomers seen) δ 172.7, 172.6, 157.5, 137.1, 136.8, 135.0, 134.1, 133.4, 132.6, 129.1, 129.0, 128.6, 128.2, 127.5, 126.7, 126.6, 126.4, 126.3, 126.1, 125.9, 125.5, 119.0, 118.9, 105.6, 55.3, 47.3, 44.6, 43.6, 43.0, 40.2, 29.1, 28.5, 20.8, 20.7.



(*S*)-1-(3,4-Dihydroisoquinolin-2(1*H*)-yl)-2-(4-isobutylphenyl)propan-1-one (16a) The title compound was prepared according to general procedure 3. ^1H NMR (400 MHz, $CDCl_3$, rotomers seen) δ 7.18-7.13 (m, 7 H), 7.00 (d, *J* = 7.6 Hz, 0.6 H), 6.87 (d, *J* = 7.6 Hz, 0.4 H), 4.86 (d, *J* = 17.2 Hz, 0.6 H), 4.68 (d, *J* = 17.2 Hz, 0.6 H), 4.62 (d, *J* = 16.0 Hz, 0.4 H), 4.37 (d, *J* = 16.0 Hz, 0.4 H), 3.98-3.90 (m, 1.4 H), 3.76-3.70 (m, 0.4 H), 3.63-3.53 (m, 1.4 H), 2.85-2.80 (m, 0.6 H), 2.66-2.60 (m, 0.6 H), 2.45-2.40 (m, 2.0 H), 2.35-2.27 (m, 0.6 H), 1.89-1.75 (m, 1.0 H), 1.47 (d, *J* = 6.0 Hz, 3.0 H), 0.88 (d, *J* = 6.4 Hz, 3.0 H). ^{13}C NMR (100 MHz, $CDCl_3$, rotomers seen) δ 172.7, 140.1, 139.2, 138.9, 135.0, 134.1, 133.5, 132.7, 129.6, 129.5, 128.6, 128.2, 126.9, 126.8, 126.6, 126.3, 126.3, 126.1, 125.8, 47.2, 44.9, 44.6, 43.3, 43.0, 40.2, 30.1, 30.1, 29.0, 28.4, 22.3, 20.7.

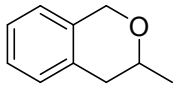
Synthesis and Characterization data of isochroman derivatives

Isochroman derivatives were synthesized according to the methods reported in the literature.[1-6]

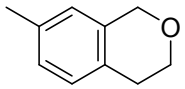


4-Methylisochromane (2b)[1] ^1H NMR (400 MHz, $CDCl_3$) δ 7.26-7.16 (m, 3 H), 6.99 (d, *J* = 7.6 Hz, 1 H), 4.80 (dd, *J* = 20.8, 15.2 Hz, 2 H), 3.99 (dd, *J* = 11.2, 4.4 Hz, 1 H),

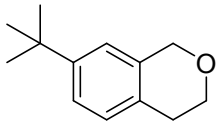
3.69 (dd, J = 11.2, 5.6 Hz, 1 H), 2.99-2.92 (m, 1 H), 1.33 (d, J = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 134.2, 127.7, 126.5, 125.8, 124.1, 71.3, 68.3, 31.8, 19.2.



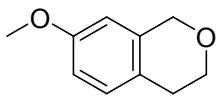
3-Methylisochromane (3b) [1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19-7.16 (m, 2 H), 7.13-7.09 (m, 1 H), 7.01 (t, J = 4.4 Hz, 2 H), 4.89-4.81 (m, 2 H), 3.88-3.79 (m, 1 H), 2.73 (d, J = 6.8 Hz, 2 H), 1.38 (d, J = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.6, 133.4, 128.6, 126.3, 125.9, 124.1, 70.9, 68.1, 35.7, 21.6.



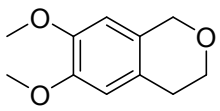
7-Methylisochromane (4b) [1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, J = 8.0 Hz, 1 H), 7.02 (d, J = 8.0 Hz, 1 H), 6.83 (s, 1 H), 4.78 (s, 2 H), 4.00 (t, J = 6.0 Hz, 2 H), 2.85 (t, J = 6.0 Hz, 2 H), 2.34 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4, 134.6, 130.0, 128.7, 127.1, 124.8, 67.9, 65.4, 27.9, 21.0.



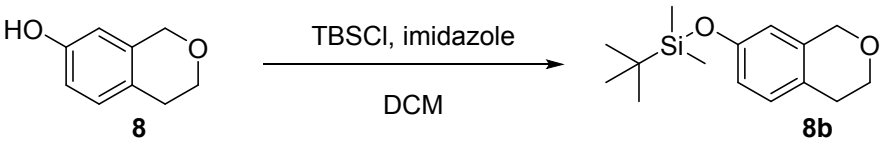
7-(*tert*-Butyl)isochromane (5b)[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 8.0 Hz, 1 H), 7.09 (d, J = 8.0 Hz, 1 H), 7.02 (s, 1 H), 4.80 (s, 2 H), 3.99 (t, J = 5.6 Hz, 2 H), 2.84 (t, J = 5.6 Hz, 2 H), 1.33 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 134.4, 130.2, 128.5, 123.5, 121.0, 68.2, 65.5, 34.4, 31.3, 27.9.



7-Methoxyisochromane (6b) [1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, J = 8.0 Hz, 1 H), 6.75 (d, J = 8.0 Hz, 1 H), 6.53 (s, 1 H), 4.75 (s, 2 H), 3.96 (t, J = 5.6 Hz, 2 H), 3.78 (s, 3 H), 2.80 (t, J = 5.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 135.8, 129.7, 125.1, 112.6, 109.0, 68.0, 65.6, 55.2, 27.5.

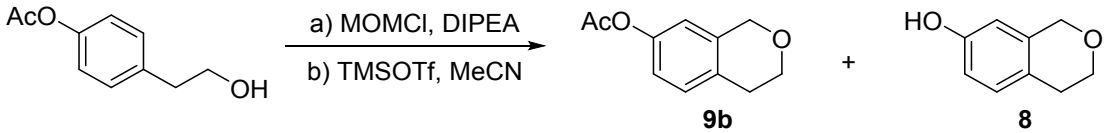


6,7-Dimethoxyisochromane (7b)[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.61 (s, 1 H), 6.47 (s, 1 H), 4.70 (s, 2 H), 3.95 (t, *J* = 5.6 Hz, 2 H), 3.85 (s, 3 H), 3.83 (s, 3 H), 2.77 (t, *J* = 5.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 147.5, 126.6, 125.0, 111.7, 107.3, 67.6, 65.4, 55.9, 27.8.



To a 25 mL two neck round bottom flask was added **8** (200 mg, 1.3 mmol), TBSCl (292 mg, 1.95 mmol), imidazole (176 mg, 2.6 mmol) and 6 mL CH_2Cl_2 at 0 ^{o}C under N_2, the mixture was stirred for 3 h at room temperature, then the mixture was poured into water and extracted with CH_2Cl_2, the combined organic phases were dried over Na_2SO_4, concentrated in vacuo, and the residue was purified by silica gel chromatography to give **8b** with a quantitative yield.

***tert*-Butyl(isochroman-7-yloxy)dimethylsilane (8b)** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, *J* = 8.0 Hz, 1 H), 6.66 (d, *J* = 8.0 Hz, 1 H), 6.47 (s, 1 H), 4.71 (s, 2 H), 3.95 (t, *J* = 5.6 Hz, 2 H), 2.78 (t, *J* = 5.6 Hz, 2 H), 0.98 (s, 9 H), 0.18 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 135.8, 129.7, 125.7, 118.4, 115.5, 67.9, 65.6, 27.6, 25.7, 18.2, -4.4.



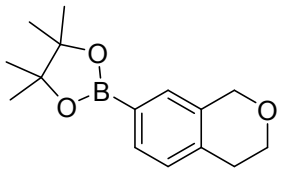
a) A mixture of 4-(2-hydroxyethyl)phenyl acetate (known compound)[1] (2.5 g, 13.9 mmol), DIPEA (4.6 mL, 27.8 mmol), MOMCl (1.6 mL, 20.9 mmol) in dry 30 mL CH_2Cl_2 was allowed react for 10 h under N_2 at room temperature, then the mixture was poured into water and extracted with CH_2Cl_2, the combined organic phases were

washed with 30 mL 1 N HCl, dried over Na_2SO_4, concentrated in vacuo, the crude product can move forward without purification.

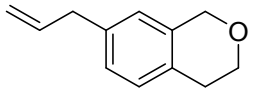
b) The residue was dissolved in 30 mL MeCN, then TMSOTf (13.9 mmol, 1.0 equiv) was added at 0 °C and the mixture was stirred at room temperature for 16 h, then the reaction was quenched by saturated $NaHCO_3$ solution and extracted with ethyl acetate, dried over Na_2SO_4, concentrated in vacuo, the reaction crude was purified with silica gel chromatography to provide the product **9b** (1.3 g, 50% yield) and byproduct **8** (416 mg, 20% yield).

Isochroman-7-yl acetate (9b)[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.0 Hz, 1 H), 6.87 (d, *J* = 8.0 Hz, 1 H), 6.71 (s, 1 H), 4.74 (s, 2 H), 3.94 (t, *J* = 5.2 Hz, 2 H), 2.82 (t, *J* = 5.2 Hz, 2 H), 2.27 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 148.5, 136.0, 130.7, 129.8, 119.6, 117.2, 67.6, 65.2, 27.7, 21.0.

Isochroman-7-ol (8) ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (d, *J* = 8.0 Hz, 1 H), 6.66 (d, *J* = 8.0 Hz, 1 H), 6.43 (s, 1 H), 6.27 (s, 1 H), 4.71 (s, 2 H), 3.98 (t, *J* = 5.6 Hz, 2 H), 2.78 (t, *J* = 5.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 135.5, 130.0, 124.7, 114.0, 110.7, 67.8, 65.7, 27.4.

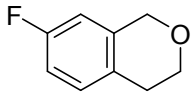


2-(Isochroman-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10b) This compound was synthesized via cross-coupling from **14b** according to the literature.[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.6 Hz, 1 H), 7.44 (s, 1 H), 7.12 (d, *J* = 7.6 Hz, 1 H), 4.78 (s, 2 H), 3.96 (t, *J* = 5.6 Hz, 2 H), 2.86 (t, *J* = 5.6 Hz, 2 H), 1.33 (s, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 134.3, 132.6, 130.9, 128.3, 83.7, 67.9, 65.2, 28.6, 24.8. HRMS: Calculated for $(M+Na)^+$:283.1478; Found: 283.1466.

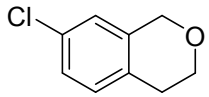


7-Allylisochromane (11b) This compound was synthesized via cross-coupling from **14b** according to the literature.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, *J* = 7.6 Hz, 1

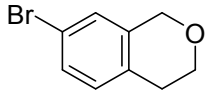
H), 7.00 (d, *J* = 7.6 Hz, 1 H), 6.82 (s, 1 H), 6.00-5.90 (m, 1 H), 5.10-5.05 (m, 2 H), 4.76 (s, 2 H), 3.97 (t, *J* = 5.6 Hz, 2 H), 3.34 (d, *J* = 6.8 Hz, 2 H), 2.83 (t, *J* = 5.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 137.4, 134.9, 130.9, 128.9, 126.7, 124.4, 115.8, 68.0, 65.5, 39.9, 28.0.



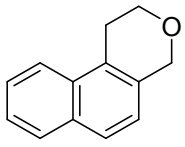
7-Fluoroisochromane (12b)[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (t, *J* = 7.2 Hz, 1 H), 6.85 (t, *J* = 8.4 Hz, 1 H), 6.67 (d, *J* = 9.2 Hz, 1 H), 4.72 (s, 2 H), 3.95 (t, *J* = 6.0 Hz, 2 H), 2.80 (t, *J* = 6.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0 (d, *J* = 243.0 Hz), 136.6 (d, *J* = 6.7 Hz), 130.3 (d, *J* = 7.8 Hz), 128.7 (d, *J* = 3.1 Hz), 113.4 (d, *J* = 21.2 Hz), 110.9 (d, *J* = 21.5 Hz), 67.7, 65.3, 27.6.



7-Chloroisochromane (13b)[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.0 Hz, 1 H), 7.03 (t, *J* = 8.0 Hz, 1 H), 6.96 (s, 1 H), 4.71 (s, 2 H), 3.94 (t, *J* = 6.0 Hz, 2 H), 2.80 (t, *J* = 6.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 131.6, 131.5, 130.2, 126.5, 124.4, 67.5, 65.2, 27.7.

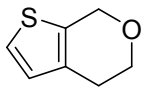


7-Bromoisochromane (14b)[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.0 Hz, 1 H), 7.12 (s, 1 H), 6.98 (d, *J* = 8.0 Hz, 1 H), 4.71 (s, 2 H), 3.94 (t, *J* = 5.6 Hz, 2 H), 2.78 (t, *J* = 5.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 132.1, 130.5, 129.4, 127.3, 119.5, 67.4, 65.1, 27.8.

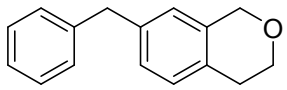


1,4-Dihydro-2*H*-benzo[*f*]isochromene (15b)[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 1 H), 7.85 (d, *J* = 8.0 Hz, 1 H), 7.70 (d, *J* = 8.4 Hz, 1 H), 7.56 (t, *J* = 8.0 Hz, 1 H), 7.50 (t, *J* = 8.0 Hz, 1 H), 7.11 (d, *J* = 8.4 Hz, 1 H), 4.93 (s, 2 H), 4.16 (t, *J* = 5.6

Hz, 2 H), 3.18 (t, *J* = 5.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.2, 132.0, 132.0, 128.5, 128.2, 126.3, 126.2, 125.3, 122.8, 122.4, 68.2, 65.2, 25.1.



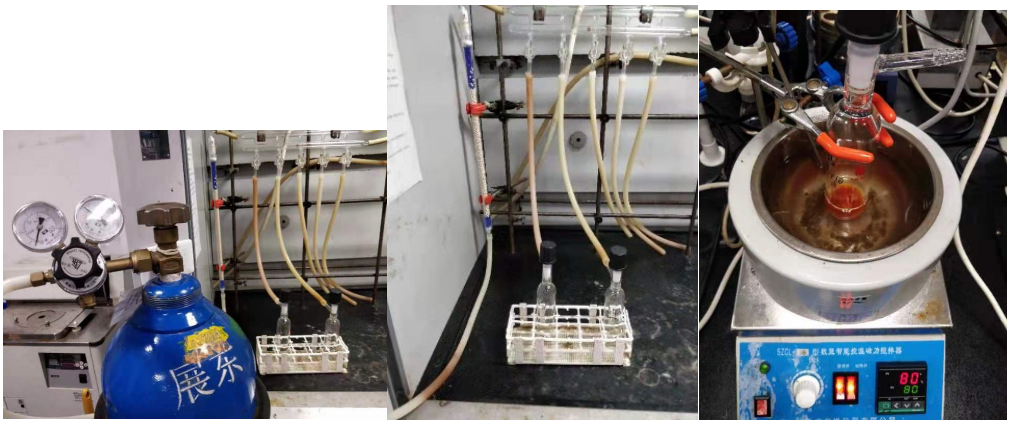
4,7-Dihydro-5*H*-thieno[2,3-*c*]pyran (16b)[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 5.2 Hz, 1 H), 6.83 (d, *J* = 5.2 Hz, 1 H), 4.83 (s, 2 H), 3.96 (t, *J* = 5.6 Hz, 2 H), 2.76 (t, *J* = 5.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.7, 126.9, 122.4, 65.6, 65.0, 26.1.



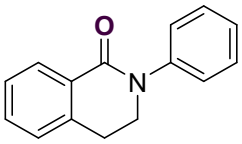
7-Benzylisochromane (22b) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.27 (m, 2 H), 7.21-7.18 (m, 3 H), 7.07-6.99 (m, 2 H), 6.81 (s, 1 H), 4.73 (s, 2 H), 3.99-3.93 (m, 4 H), 2.83 (t, *J* = 5.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 138.9, 134.9, 130.9, 129.0, 128.8, 128.4, 127.0, 126.1, 124.7, 68.0, 65.4, 41.6, 28.0. HRMS: Calculated for $(M+H)^+$:225.1273; Found: 225.1268.

General procedure for the oxygenation reaction

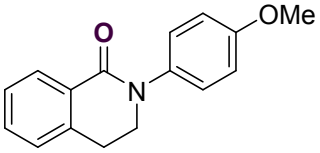
To a 25 ml of Schlenk tube was added **Fe1** or **Fe5** (0.03 mmol, 0.1 equiv) and phenyl disulfide (6.5 mg, 0.03 mmol, 0.1 equiv) under air. The reaction tube was degassed with O_2 (1 atm, 3 times), then substrates (0.30 mmol, 1.0 equiv) and freshly distilled 1,4-dioxane (0.5 mL) were added. The reaction mixture was heated to 80 ^{o}C and allowed to react for 15 h. The mixture was concentrated, and the residue was purified with silica gel chromatography to give product.



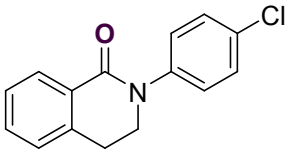
Characterization data of products



2-Phenyl-3,4-dihydroisoquinolin-1(2*H*)-one (1aa) The product (44 mg, 66% yield) as a white solid was purified with silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.6 Hz, 2 H), 7.46 (td, *J* =7.6, 1.6 Hz, 1 H), 7.43-7.35 (m, 5 H), 7.27-7.23 (m, 2 H), 3.99 (t, *J* = 6.4 Hz, 2 H), 3.14 (t, *J* = 6.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 143.1, 138.3, 132.0, 129.7, 128.9, 128.7, 127.2, 126.9, 126.2, 125.3, 49.4, 28.6. HRMS: Calculated for $(M+H)^+$: 224.1069; Found: 224.1073.

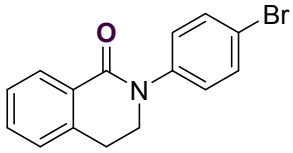


2-(4-Methoxyphenyl)-3,4-dihydroisoquinolin-1(2*H*)-one (2aa) The product (37 mg, 50% yield) as a white solid was purified with silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.6 Hz, 1 H), 7.46 (t, *J* = 7.6 Hz, 1 H), 7.37 (t, *J* = 7.6 Hz, 1 H), 7.30 (d, *J* = 8.8 Hz, 2 H), 7.24 (d, *J* = 7.6 Hz, 1 H), 6.94 (d, *J* = 8.8 Hz, 2 H), 3.95 (t, *J* = 6.4 Hz, 2 H), 3.83 (s, 3 H), 3.14 (t, *J* = 6.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 157.8, 138.3, 136.1, 131.9, 129.8, 128.7, 127.1, 126.9, 126.7, 114.2, 55.5, 49.7, 28.7. HRMS: Calculated for $(M+H)^+$: 254.1175; Found: 254.1178.

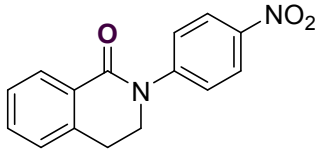


2-(4-Chlorophenyl)-3,4-dihydroisoquinolin-1(2*H*)-one (3aa) The product (49 mg, 63% yield) as a white solid was purified with silica gel chromatography. ^{1}H NMR (400

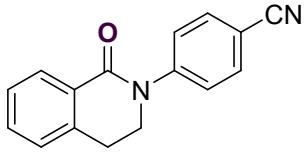
MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 1 H), 7.39 (t, *J* = 7.6 Hz, 1 H), 7.31-7.23 (m, 5 H), 7.16 (d, *J* = 7.6 Hz, 1 H), 3.88 (t, *J* = 6.4 Hz, 2 H), 3.05 (t, *J* = 6.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 141.5, 138.2, 132.2, 131.4, 129.3, 128.9, 128.7, 127.2, 127.0, 126.5, 49.2, 28.5. HRMS: Calculated for $(M+Na)^+$: 280.0499; Found: 280.0502.



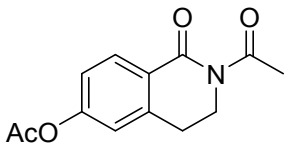
2-**(4-Bromophenyl)-3,4-dihydroisoquinolin-1(2*H*)-one (4aa)** The product (56 mg, 62% yield) as a white solid was purified with silica gel chromatography. ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.6 Hz, 1 H), 7.53 (d, *J* = 8.8 Hz, 2 H), 7.49 (t, *J* = 7.6 Hz, 1 H), 7.39 (t, *J* = 7.6 Hz, 1 H), 7.29 (d, *J* = 8.8 Hz, 2 H), 7.25 (d, *J* = 7.6 Hz, 1 H), 3.97 (t, *J* = 6.4 Hz, 2 H), 3.15 (t, *J* = 6.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 142.0, 138.2, 132.2, 131.8, 129.3, 128.7, 127.2, 127.0, 126.8, 119.3, 49.2, 28.5. HRMS: Calculated for $(M+H)^+$: 302.0175; Found: 302.0179.



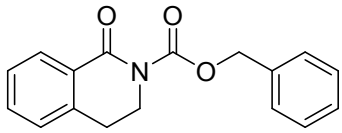
2-(4-Nitrophenyl)-3,4-dihydroisoquinolin-1(2*H*)-one (5aa) The product (38 mg, 47% yield) as a white solid was purified with silica gel chromatography. ^1H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 9.2 Hz, 2 H), 8.16 (d, *J* = 7.6 Hz, 1 H), 7.61 (d, *J* = 9.2 Hz, 2 H), 7.51 (td, *J* = 7.6, 1.2 Hz, 1 H), 7.41 (t, *J* = 7.6 Hz, 1 H), 7.28 (d, *J* = 7.6 Hz, 1 H), 4.08 (t, *J* = 6.4 Hz, 2 H), 3.19 (t, *J* = 6.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 148.6, 144.7, 138.2, 132.8, 129.0, 128.9, 127.5, 127.1, 124.8, 124.2, 49.0, 28.4.



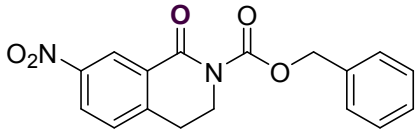
4-(1-Oxo-3,4-dihydroisoquinolin-2(1*H*)-yl)benzonitrile (6aa) The product (56 mg, 75% yield) as a white solid was purified with silica gel chromatography. ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.6 Hz, 1 H), 7.67 (d, *J* = 8.4 Hz, 2 H), 7.53 (d, *J* = 8.4 Hz, 2 H), 7.49 (t, *J* = 7.6 Hz, 1 H), 7.38 (t, *J* = 7.6 Hz, 1 H), 7.25 (d, *J* =7.6 Hz, 1 H), 4.02 (t, *J* = 6.4 Hz, 2 H), 3.16 (t, *J* = 6.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 146.8, 138.1, 132.6, 128.9, 128.8, 127.3, 127.0, 125.0, 118.6, 108.8, 48.8, 28.3. HRMS: Calculated for $(M+H)^+$: 249.1022; Found: 249.1027.



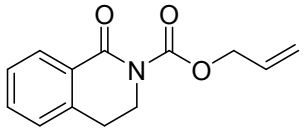
2-Acetyl-1-oxo-1,2,3,4-tetrahydroisoquinolin-6-yl acetate (7aa) The product (49 mg, 66% yield) as a white solid was purified with silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.8 Hz, 1 H), 7.08 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 1 H), 7.00 (s, 1 H), 4.09 (t, *J* = 6.0 Hz, 2 H), 2.96 (t, *J* = 6.0 Hz, 2 H), 2.63 (s, 3 H), 2.30 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 168.7, 164.9, 154.3, 142.0, 131.4, 126.5, 120.7, 120.3, 41.5, 28.1, 27.5, 21.1.



Benzyl 1-oxo-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (8aa) The product (55 mg, 65% yield) as a white solid was purified with silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.6 Hz, 1 H), 7.49 (t, *J* = 7.6 Hz, 2 H), 7.41-7.31 (m, 5 H), 7.22 (d, *J* = 7.6 Hz, 1 H), 5.37 (s, 2 H), 4.09 (t, *J* = 6.0 Hz, 2 H), 3.02 (t, *J* = 6.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 154.5, 139.5, 135.4, 133.1, 129.7, 129.0, 128.6, 128.3, 128.1, 127.3, 127.2, 68.7, 44.8, 28.2. HRMS: Calculated for $(M+Na)^+$: 304.0944; Found: 304.0947.

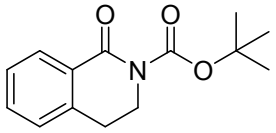


Benzyl 7-nitro-1-oxo-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (9aa) The product (60 mg, 61% yield) as a white solid was purified with silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (d, *J* = 2.8 Hz, 1 H), 8.32 (dd, *J* = 8.4 Hz, *J* = 2.4 Hz, 1 H), 7.50-7.47 (m, 2 H), 7.44-7.34 (m, 4 H), 5.38 (s, 2 H), 4.13 (t, *J* = 6.0 Hz, 2 H), 3.13 (t, *J* = 6.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 154.0, 147.6, 145.9, 135.0, 130.4, 128.7, 128.6, 128.5, 128.1, 127.3, 125.0, 69.2, 44.0, 28.3.

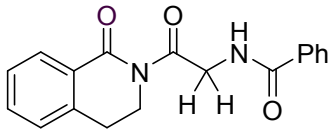


Allyl 1-oxo-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (10aa) The product (42 mg, 60% yield) as a white solid was purified with silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.6 Hz, 1 H), 7.49 (t, *J* = 7.6 Hz, 1 H), 7.37 (t, J = 7.6 Hz,

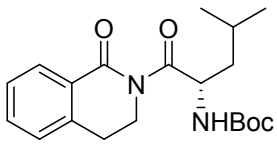
1 H), 7.23 (d, *J* = 7.6 Hz, 1 H), 6.07-5.98 (m, 1 H), 5.49 (d, *J* = 17.2 Hz, 1 H), 5.31 (d, *J* = 10.4 Hz, 1 H), 4.82 (d, *J* = 5.2 Hz, 2 H), 4.09 (t, *J* = 6.0 Hz, 2 H), 3.03 (t, *J* = 6.0 Hz, 2 H). ^{13}C NMR (100 MHz, CDCl3) δ 163.7, 154.4, 139.5, 133.1, 131.5, 129.8, 129.0, 127.3, 127.2, 118.9, 67.7, 44.7, 28.3. HRMS: Calculated for $(M+Na)^+$: 254.0787; Found: 254.0793.



***tert*-Butyl 1-oxo-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (11aa)** The product (52 mg, 70% yield) as a white solid was purified with silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.6 Hz, 1 H), 7.46 (t, *J* = 7.6 Hz, 1 H), 7.34 (t, *J* = 7.6 Hz, 1 H), 7.20 (d, *J* = 7.6 Hz, 1 H), 3.98 (t, *J* = 6.0 Hz, 2 H), 3.00 (t, *J* = 6.0 Hz, 2 H), 1.58 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 153.1, 139.5, 132.8, 129.6, 129.3, 127.2, 127.1, 83.2, 44.4, 28.3, 28.1. HRMS: Calculated for $(M+Na)^+$: 270.1100; Found: 270.1105.

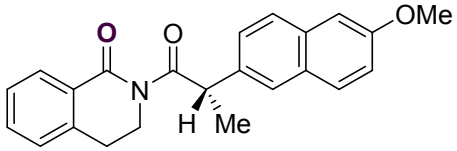


***N*-(2-Oxo-2-(1-oxo-3,4-dihydroisoquinolin-2(1*H*)-yl)ethyl)benzamide (12aa)** The product (58 mg, 63% yield) as a white solid was purified with silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.0 Hz, 1 H), 7.86 (d, *J* = 7.6 Hz, 2 H), 7.56-7.49 (m, 2 H), 7.46-7.39 (m, 3 H), 7.27 (d, *J* = 7.6 Hz, 1 H), 7.17 (t, *J* = 5.2 Hz, 1 H), 4.95 (d, *J* = 5.2 Hz, 2 H), 4.16 (t, *J* = 6.8 Hz, 2 H), 3.04 (t, *J* = 6.8 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 167.4, 165.4, 139.9, 134.1, 133.7, 131.5, 129.6, 128.6, 128.5, 127.5, 127.3, 127.1, 47.4, 42.1, 27.9. HRMS: Calculated for $(M+Na)^+$: 331.1053; Found: 331.1057.

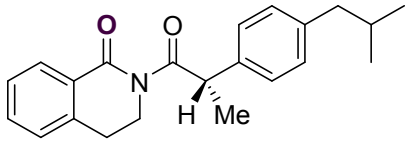


***tert*-Butyl(*S*)-(4-Methyl-1-oxo-1-(1-oxo-3,4-dihydroisoquinolin-2(1*H*)-yl)pentan-2-yl)carbamate (13aa)** The product (71 mg, 71% yield) as a white solid was purified with silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.08 (m, 4 H), 5.33 (t, *J* = 9.2 Hz, 1 H), 4.79-4.62 (m, 3 H), 7.31 (d, *J* = 5.2 Hz, 1 H), 4.82 (t, *J* = 1.2 Hz, 2 H), 4.48 (t, *J* = 1.2 Hz, 2 H), 4.19 (s, 5 H), 4.04 (t, *J* = 4.0 Hz, 2 H), 3.18 (t, *J* = 4.0 Hz,

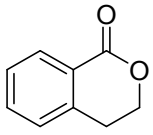
2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 165.7, 139.9, 133.3, 129.6, 128.7, 127.7, 127.4, 75.9, 71.6, 71.5, 70.4, 45.0, 29.0. HRMS: Calculated for $(M+H)^+$: 361.2121; Found: 361.2124.



(*S*)-2-(2-(6-Methoxynaphthalen-2-yl)propanoyl)-3,4-dihydroisoquinolin-1(2*H*)-one (14aa) The product (54 mg, 50% yield) as a white solid was purified with silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.6 Hz, 1 H), 7.71 (s, 1 H), 7.68 (dd, *J* = 8.4, 3.2 Hz, 2 H), 7.49 (dd, *J* = 8.4, 2.0 Hz, 1 H), 7.44 (td, *J* = 7.6, 1.6 Hz, 1 H), 7.33 (t, *J* = 7.6 Hz, 1 H), 7.16 (d, *J* = 7.6 Hz, 1 H), 7.11-7.07 (m, 2 H), 5.33 (q, *J* = 6.8 Hz, 1 H), 4.18-4.12 (m, 1 H), 4.04-3.98 (m, 1 H), 3.88 (s, 3 H), 2.93-2.80 (m, 2 H), 1.62 (d, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.9, 165.4, 157.4, 140.1, 136.8, 133.5, 133.2, 129.6, 129.3, 129.0, 128.9, 127.2, 127.0, 126.9, 126.3, 118.6, 105.5, 55.2, 46.8, 42.8, 28.2, 20.0.

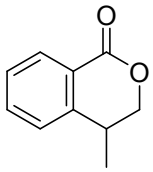


(*S*)-2-(2-(4-Isobutylphenyl)propanoyl)-3,4-dihydroisoquinolin-1(2*H*)-one (16aa) The product (46 mg, 46% yield) as a white solid was purified with silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.0 Hz, 1 H), 7.46 (t, *J* = 7.6 Hz, 1 H), 7.34 (t, *J* = 7.6 Hz, 1 H), 7.25 (d, *J* = 7.6 Hz, 2 H), 7.19 (d, *J* = 7.6 Hz, 1 H), 7.05 (d, *J* = 8.0 Hz, 2 H), 5.15 (q, *J* = 6.8 Hz, 1 H), 4.16-4.10 (m, 1 H), 4.01-3.94 (m, 1 H), 2.89-2.85 (m, 2 H), 2.40 (d, *J* = 7.2 Hz, 2 H), 1.86-1.76 (m, 1 H), 1.54 (d, *J* = 6.8 Hz, 3 H), 0.85 (d, *J* = 6.4 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 165.4, 140.1, 138.7, 133.2, 129.5, 129.1, 129.0, 127.6, 127.2, 46.4, 45.0, 42.9, 30.0, 28.2, 22.3, 19.9.

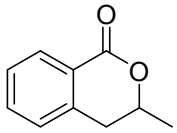


Isochroman-1-one (1bb) The product (33 mg, 75% yield) as a white solid was purified with silica gel chromatography. This compound is known.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.6 Hz, 1 H), 7.52 (t, *J* = 7.6 Hz, 1 H), 7.38 (t, *J* = 7.6 Hz, 1 H), 7.25 (d, *J* = 7.6 Hz, 1 H), 4.52 (t, *J* = 6.0 Hz, 2 H), 3.05 (t, *J* = 6.0 Hz, 2 H). ^{13}C NMR (100

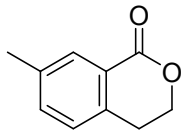
MHz, $CDCl_3$) δ 165.1, 139.5, 133.6, 130.4, 127.6, 127.2, 125.3, 67.3, 27.8. HRMS: Calculated for $C_9H_8O_2$ $(M+Na)^+$: 171.0416; Found: 171.0419.



4-Methylisochroman-1-one (2bb) The product (38 mg, 79% yield) as a colorless liquid was purified with silica gel chromatography. This compound is known.[1] ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 7.6 Hz, 1 H), 7.56 (t, J = 7.6 Hz, 1 H), 7.37 (t, J = 7.6 Hz, 1 H), 7.28 (d, J = 7.6 Hz, 1 H), 4.49 (dd, J = 10.8, 4.0 Hz, 1 H), 4.22 (dd, J = 10.8, 6.8 Hz, 1 H), 3.18-3.10 (m, 1 H), 1.35 (d, J = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 144.5, 133.8, 130.4, 127.5, 125.6, 124.3, 72.4, 31.7, 16.6. HRMS: Calculated for $C_{10}H_{10}O_2$ $(M+Na)^+$: 185.0573; Found: 185.0575.

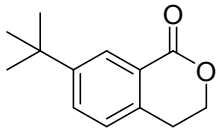


3-**Methylisochroman-1-one (3bb)** The product (39 mg, 80% yield) as a white solid was purified with silica gel chromatography. This compound is known.[1] ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 7.6 Hz, 1 H), 7.51 (t, J = 7.6 Hz, 1 H), 7.36 (t, J = 7.6 Hz, 1 H), 7.21 (d, J = 7.6 Hz, 1 H), 4.70-4.61 (m, 1 H), 2.98-2.88 (m, 2 H), 1.49 (d, J = 6.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 139.0, 133.6, 130.1, 127.5, 127.2, 124.9, 75.0, 34.8, 20.8. HRMS: Calculated for $C_{10}H_{10}O_2$ $(M+Na)^+$: 185.0573; Found: 185.0575.

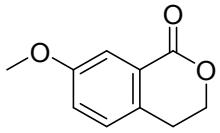


7-Methylisochroman-1-one (4bb) The product (39 mg, 80% yield) as a colorless liquid was purified with silica gel chromatography. This compound is known.[1] ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1 H), 7.32 (d, J = 7.6 Hz, 1 H), 7.13 (d, J = 7.6 Hz, 1 H), 4.49 (t, J = 6.0 Hz, 1 H), 2.99 (t, J = 6.0 Hz, 1 H), 2.36 (s, 3 H). ^{13}C NMR (100 MHz,

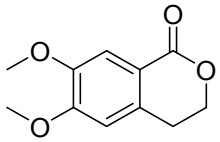
$CDCl_3$) δ 165.3, 137.5, 136.5, 134.5, 130.5, 127.0, 125.0, 67.4, 27.4, 20.9. HRMS: Calculated for $C_{10}H_{10}O_2$ $(M+Na)^+$: 185.0573; Found: 185.0575.



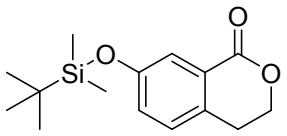
7-(*tert*-Butyl)isochroman-1-one (5bb) The product (45 mg, 74% yield) as a colorless liquid was purified with silica gel chromatography. This compound is known.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 2.0 Hz, 1 H), 7.57 (dd, J = 8.0, J = 2.0 Hz, 1 H), 7.20 (d, J = 8.0 Hz, 1 H), 4.51 (t, J = 6.0 Hz, 2 H), 3.02 (t, J = 6.0 Hz, 2 H), 1.33(s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 150.9, 136.6, 130.9, 127.04, 127.0, 124.8, 67.3, 34.7, 31.1, 27.3. HRMS: Calculated for $C_{13}H_{16}O_2$ $(M+Na)^+$: 227.1042; Found: 227.1044.



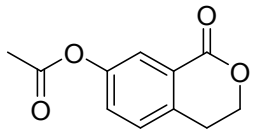
7-Methoxyisochroman-1-one (6bb) The product (40 mg, 75% yield) as a colorless liquid was purified with silica gel chromatography. This compound is known.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 2.8 Hz, 1 H), 7.15 (d, J = 8.4 Hz, 1 H), 7.15 (dd, J = 8.4, J = 2.8 Hz, 1 H), 4.50 (t, J = 6.0 Hz, 2 H), 3.82 (s, 3 H), 2.97 (t, J = 6.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 158.9, 131.8, 128.4, 126.0, 121.5, 113.0, 67.6, 55.6, 27.0. HRMS: Calculated for $C_{10}H_{10}O_3$ $(M+Na)^+$: 201.0522; Found: 201.0524.



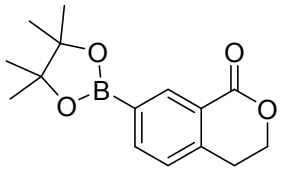
6,7-Dimethoxyisochroman-1-one (7bb) The product (41 mg, 66% yield) as a white solid was purified with silica gel chromatography. This compound is known.[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1 H), 6.67 (s, 1 H), 4.50 (t, J = 6.0 Hz, 2 H), 3.93 (s, 3 H), 3.90 (s, 3 H), 2.97 (t, J = 6.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 153.5, 148.4, 133.9, 117.3, 111.7, 109.0, 67.3, 56.16, 56.12, 27.4. HRMS: Calculated for $C_{11}H_{12}O_4Na$ $(M+Na)^+$: 231.0627; Found: 231.0630.



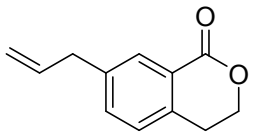
7-((*tert*-Butyldimethylsilyl)oxy)isochroman-1-one (8bb) The product (52 mg, 62% yield) as a white solid was purified with silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 2.4 Hz, 1 H), 7.11 (d, *J* = 8.4 Hz, 1 H), 6.99 (dd, *J* = 8.4, 2.4 Hz, 1 H), 4.48 (t, *J* = 6.0 Hz, 2 H), 2.96 (t, *J* = 6.0 Hz, 2 H), 0.96 (s, 9 H), 0.19 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 155.0, 132.2, 128.3, 126.1, 126.0, 120.9, 67.5, 27.0, 25.6, 25.5, 18.1, -4.5. HRMS: Calculated for $(M+NH_4)^+$: 296.1676; Found: 296.1666.



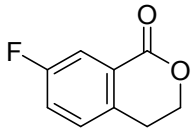
1-Oxoisochroman-7-yl acetate (9bb) The product (43 mg, 70% yield) as a colorless crystal was purified with silica gel chromatography. This compound is known.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1 H), 7.28-7.23 (m, 2 H), 4.51 (t, *J* = 6.0 Hz, 2 H), 3.02 (t, *J* = 6.0 Hz, 2 H), 2.29 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 164.2, 149.8, 136.9, 128.4, 127.2, 126.3, 123.1, 67.3, 27.2, 20.9. HRMS: Calculated for $C_{11}H_{10}O_4Na$ $(M+Na)^+$: 229.0471; Found: 229.0462.



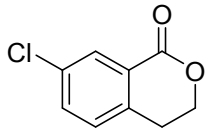
7-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)isochroman-1-one (10bb) The product (49 mg, 60% yield) as a white solid was purified with silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1 H), 7.92 (d, *J* = 7.6 Hz, 1 H), 7.24 (d, *J* = 7.6 Hz, 1 H), 4.50 (t, *J* = 6.0 Hz, 2 H), 3.05 (t, *J* = 6.0 Hz, 2 H), 1.32 (s, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 142.2, 139.6, 137.0, 126.6, 124.6, 84.1, 67.1, 28.0, 24.8. HRMS: Calculated for $(M+H)^+$: 275.1451; Found: 275.1440.



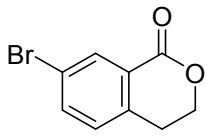
7-Allylisochroman-1-one (11bb) The product (23 mg, 40% yield) as a colorless liquid was purified with silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1 H), 7.37 (d, *J* = 8.0 Hz, 1 H), 7.19 (d, *J* = 8.0 Hz, 1 H), 5.99-5.89 (m, 1 H), 5.11 (s, 1 H), 5.07 (m, 1 H), 4.52 (t, *J* = 6.0 Hz, 2 H), 3.42 (d, *J* = 6.4 Hz, 2 H), 3.03 (t, *J* = 6.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 139.8, 137.3, 136.4, 134.0, 130.2, 127.3, 125.2, 116.6, 67.4, 39.6, 27.5. HRMS: Calculated for $(M+Na)^+$: 211.0729; Found: 211.0721.



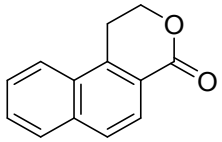
7-Fluoroisochroman-1-one (12bb) The product (35 mg, 71% yield) as a colorless crystal was purified with silica gel chromatography. This compound is known.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 1 H), 7.25-7.22 (m, 2 H), 4.52 (t, *J* = 6.0 Hz, 2 H), 3.02 (t, *J* = 6.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 162.0 (d, *J* = 245.7 Hz), 135.3 (d, *J* = 3.3 Hz), 129.1 (d, *J* = 7.4 Hz), 126.9 (d, *J* = 7.5 Hz), 121.0 (d, *J* = 21.8 Hz), 116.7 (d, *J* = 23.1 Hz), 67.4, 27.1. HRMS: Calculated for $C_9H_7FO_2$ $(M+Na)^+$: 189.0322; Found: 189.0324.



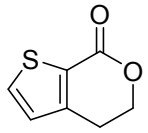
7-Chloroisochroman-1-one (13bb) The product (43mg, 79% yield) as a white solid was purified with silica gel chromatography. This compound is known.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1 H), 7.48 (d, *J* = 8.0 Hz, 1 H), 7.21 (d, *J* = 8.0 Hz, 1 H), 4.52 (t, *J* = 6.0 Hz, 2 H), 3.02 (t, *J* = 6.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 137.7, 133.7, 130.1, 128.7, 126.7, 67.2, 27.2. HRMS: Calculated for $C_9H_7ClO_2$ $(M+Na)^+$: 205.0026; Found: 205.0028.



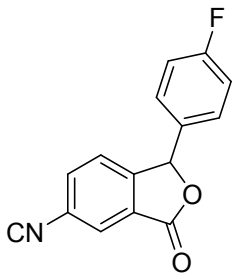
7-**Bromoisochroman-1-one (14bb)** The product (54 mg, 80% yield) as a white solid was purified with silica gel chromatography. This compound is known.[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1 H), 7.64 (d, *J* = 8.0 Hz, 1 H), 7.15 (d, *J* = 8.0 Hz, 1 H), 4.52 (t, *J* = 6.0 Hz, 2 H), 3.01 (t, *J* = 6.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 138.2, 136.5, 133.0, 128.9, 126.9, 121.3, 67.2, 27.3. HRMS: Calculated for $C_9H_7BrO_2$ $(M+Na)^+$: 248.9521; Found: 248.9523.



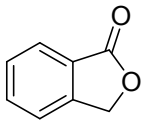
1,2-Dihydro-4*H*-benzo[*f*]isochromen-4-one (15bb) The product (36 mg, 61% yield) as a white solid was purified with silica gel chromatography. This compound is known.[9] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 1 H), 8.02-8.00 (m, 1 H), 7.91-7.88 (m, 1 H), 7.82 (d, *J* = 8.4 Hz, 1 H), 7.66-7.59 (m, 2 H), 4.66 (t, *J* = 6.0 Hz, 2 H), 3.42 (t, *J* = 6.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 138.5, 135.5, 129.7, 128.8, 128.6, 127.7, 127.1, 125.1, 124.3, 122.3, 66.6, 24.1. HRMS: Calculated for $C_{13}H_{10}O_2$ $(M+Na)^+$: 221.0573; Found: 221.0575.



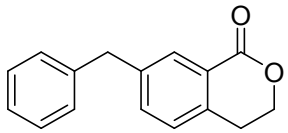
4,5-Dihydro-7*H*-thieno[2,3-*c*]pyran-7-one (16bb) The product (21 mg, 46% yield) as a white solid was purified with silica gel chromatography. This compound is known.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 5.2 Hz, 1 H), 6.98 (d, *J* = 5.2 Hz, 1 H), 4.57 (t, *J* = 6.0 Hz, 1 H), 3.00 (t, *J* = 6.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 147.4, 134.4, 126.6, 126.5, 68.3, 25.1. HRMS: Calculated for $C_7H_6O_2S$ $(M+Na)^+$: 176.9980; Found: 176.9983.



1-(4-Fluorophenyl)-3-oxo-1,3-dihydroisobenzofuran-5-carbonitrile (17bb) The product (38 mg, 50% yield) as a light yellow solid was purified with silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1 H), 8.30 (s, 1 H), 7.98 (d, *J* = 8.0 Hz, 1 H), 7.79 (dd, *J* = 7.6, 5.6 Hz, 2 H), 7.61 (d, *J* = 7.6 Hz, 1 H), 7.16 (t, *J* = 8.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 188.2, 166.3 (d, *J* = 256.4 Hz), 144.4, 136.3, 135.6, 133.8, 132.5 (d, *J* = 9.7 Hz), 132.4 (d, *J* = 2.9 Hz), 129.3, 116.8, 116.3(d, *J* = 22.0 Hz), 114.9. HRMS: Calculated for $(M-H)^-$: 252.0466; Found: 252.0465.

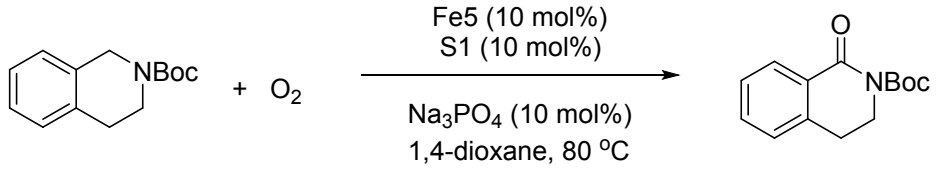


Isobenzofuran-1(3*H*)-one (18bb) The product (21 mg, 52% yield) as a white solid was purified with silica gel chromatography. This compound is known.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 1 H), 7.68 (t, *J* = 7.6 Hz, 1 H), 7.54 (t, *J* = 7.6 Hz, 1 H), 7.51 (d, *J* = 7.6 Hz, 1 H), 5.32 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 146.5, 134.0, 129.0, 125.7, 122.1, 69.6.



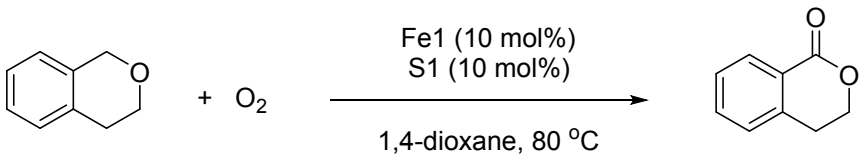
7-Benzylisochroman-1-one (22bb) The product (31 mg, 44% yield) as a light yellow liquid was purified with silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1 H), 7.35 (d, *J* = 7.6 Hz, 1 H), 7.29 (t, *J* = 7.6 Hz, 2 H), 7.23-7.17 (m, 4 H), 4.51 (t, *J* = 6.0 Hz, 2 H), 4.01 (s, 2 H), 3.01 (t, *J* = 6.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 141.0, 140.2, 137.3, 134.2, 130.5, 128.8, 128.6, 127.4, 126.3, 125.2, 67.3, 41.4, 27.4. HRMS: Calculated for $(M+Na)^+$: 261.0886; Found: 261.0881.

Radical Inhibtion Experiments



Entry	Additive	Yield
1	None	70%
2	TEMPO (10 mol%)	39%
3	BHT (10 mol%)	28%
4	TEMPO (100 mol%)	37%
5	BHT (100 mol%)	19%

To a 25 mL of Schlenk tube were added **Fe5** (7.3 mg, 0.03 mmol, 0.1 equiv), phenyl disulfide (6.5 mg, 0.03 mmol, 0.1 equiv), additive (0.1-1.0 equiv) under air. The mixture was then evacuated and backfilled with O_2 (3 times), then amine (0.30 mmol, 1 equiv) and freshly distilled 1,4-dioxane (0.5 mL) were added subsequently. The reaction mixture was heated to 80 °C and allowed to react for 15 h. The reaction was cooled to room temperature and mesitylene (0.3 mmol) was added. The yield was determined by ^{1}H NMR.

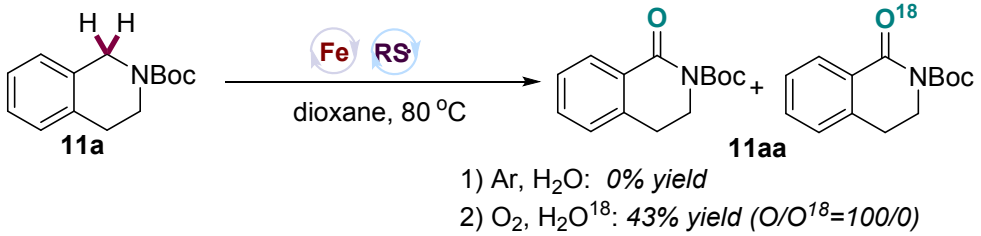


Entry	Additive	Yield
1	None	75%
2	TEMPO (10 mol%)	60%
3	BHT (10 mol%)	18%
4	TEMPO (100 mol%)	trace
5	BHT (100 mol%)	trace

To a 25 mL of Schlenk tube were added **Fe1** (16.6 mg, 0.03 mmol, 0.1 equiv), phenyl disulfide (6.5 mg, 0.03 mmol, 0.1 equiv), additive (0.1-1.0 equiv) under air. The mixture was then evacuated and backfilled with O_2 (3 times), then isochroman (0.30 mmol, 1 equiv) and freshly distilled 1,4-dioxane (0.5 mL) were added subsequently. The reaction mixture was heated to 80 °C and allowed to react for 15 h. The reaction

was cooled to room temperature and mesitylene (0.3 mmol) was added. The yield was determined by ^{1}H NMR.

Isotope Labeling Experiments



1) To a 25 mL of Schlenk tube were added **Fe5** (7.3 mg, 0.03 mmol, 0.1 equiv), phenyl disulfide (6.5 mg, 0.03 mmol, 0.1 equiv) under air. The mixture was then evacuated and backfilled with Ar (3 times), then amine (0.30 mmol, 1 equiv), H_2O^{18} (0.05 mL) and freshly distilled 1,4-dioxane (0.5 mL) were added subsequently. The reaction mixture was heated to 80 °C and allowed to react for 15 h. The reaction was cooled to room temperature and mesitylene (0.3 mmol) was added. No desired product was detected.

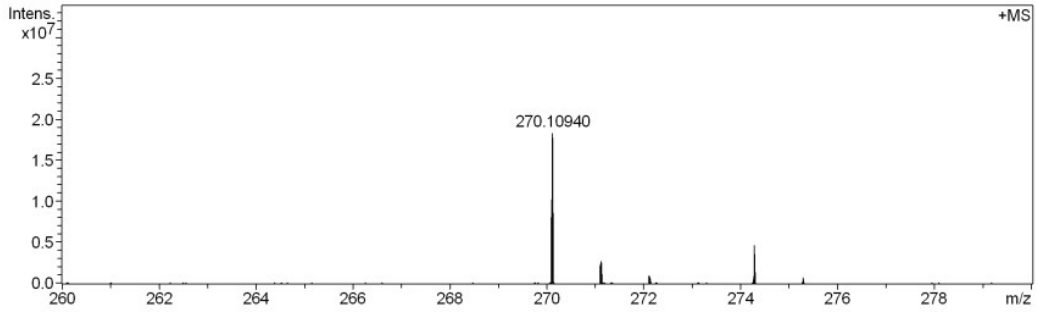
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\201809\BJ-180926-140-5_000002.d	Acquisition Date	9/28/2018 2:51:42 PM
Method	4_17_Mass_range_pos_7T	Operator	
Sample Name	BJ-180926-140-5	Instrument	solariX
Comment			

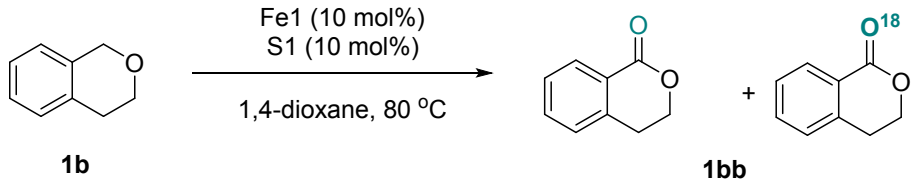
Acquisition Parameter

Polarity	Positive	n/a	n/a	No. of Laser Shots	200
n/a	n/a	No. of Cell Fills	1	Laser Power	20.0 lp
Broadband Low Mass	53.8 m/z	n/a	n/a	n/a	n/a
Broadband High Mass	1100.0 m/z	n/a	n/a	n/a	n/a
Acquisition Mode	Single MS	n/a	n/a		
Pulse Program	basic	n/a	n/a	Calibration Date	Sun Apr 8 02:39:02 2018
Source Accumulation	0.025 sec	n/a	n/a	Data Acquisition Size	524288
Ion Accumulation Time	0.025 sec	n/a	n/a	Apodization	Sine-Bell Multiplication
Flight Time to Acq. Cell	0.001 sec				



Meas. m/z	#	Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSig ma	rdb	e⁻ Conf	N-R ule
248.12746	1	C 14 H 18 N O 3	100.00	248.12812	2.65	2.68	12.1	6.5	even	ok
270.10940	1	C 14 H 17 N Na O 3	100.00	270.11006	2.47	2.81	20.9	6.5	even	ok

2) To a 25 mL of Schlenk tube were added **Fe5** (7.3 mg, 0.03 mmol, 0.1 equiv), phenyl disulfide (6.5 mg, 0.03 mmol, 0.1 equiv) under air. The mixture was then evacuated and backfilled with O_2 (3 times), then amine (0.30 mmol, 1 equiv), H_2O^{18} (0.05 mL) and freshly distilled 1,4-dioxane (0.5 mL) were added subsequently. The reaction mixture was heated to 80 °C and allowed to react for 15 h. The reaction was cooled to room temperature and mesitylene (0.3 mmol) was added. The yield was determined by ^{1}H NMR. The ratio of the product was determined by HRMS.



1b **1bb**

1) Ar, H_2O^{18}: *0% yield*
2) O_2, H_2O^{18}: *46% yield (O/O^{18}=6/1)*

1) To a 25 mL of Schlenk tube were added dppf (16.6 mg, 0.03 mmol, 0.1 equiv), phenyl disulfide (6.5 mg, 0.03 mmol, 0.1 equiv) under air. The mixture was then

evacuated and backfilled with Ar (3 times), then isochroman (0.30 mmol, 1 equiv), H_2O^{18} (0.05 mL) and freshly distilled 1,4-dioxane (0.5 mL) were added subsequently. The reaction mixture was heated to 80 °C and allowed to react for 15 h. The reaction was cooled to room temperature and mesitylene (0.3 mmol) was added. No desired product was detected.

2) To a 25 mL of Schlenk tube were added dppf (16.6 mg, 0.03 mmol, 0.1 equiv), phenyl disulfide (6.5 mg, 0.03 mmol, 0.1 equiv) under air. The mixture was then evacuated and backfilled with O_2 (3 times), then isochroman (0.30 mmol, 1 equiv), H_2O^{18} (0.05 mL) and freshly distilled 1,4-dioxane (0.5 mL) were added subsequently. The reaction mixture was heated to 80 °C and allowed to react for 15 h. The reaction was cooled to room temperature and mesitylene (0.3 mmol) was added. The yield was determined by ^{1}H NMR. The ratio of the product was determined by HRMS.

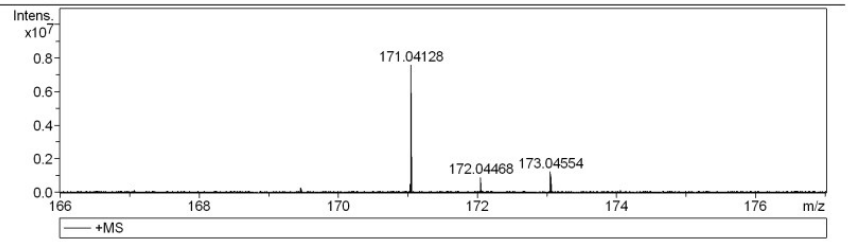
Mass Spectrum List Report

Analysis Info 7/4/2018 11:26:54 AM

Analysis Name	D:\Data\201807\XBJ-180704_000001.d		
Method	4_17_Mass_range_pos_7T	Operator	
Sample Name	XBJ-180704	Instrument	solariX
Comment			

Acquisition Parameter

Polarity	Positive	n/a	n/a	No. of Laser Shots	200
n/a	n/a	No. of Cell Fills	1	Laser Power	20.0 lp
Broadband Low Mass	53.8 m/z	n/a	n/a	n/a	n/a
Broadband High Mass	1100.0 m/z	n/a	n/a	n/a	n/a
Acquisition Mode	Single MS	n/a	n/a		
Pulse Program	basic	n/a	n/a	Calibration Date	Sun Apr 8 02:39:02 2018
Source Accumulation	0.015 sec	n/a	n/a	Data Acquisition Size	524288
Ion Accumulation Time	0.015 sec	n/a	n/a	Apodization	Sine-Bell Multiplication
Flight Time to Acq. Cell	0.001 sec				



m/z	z	I	Res.
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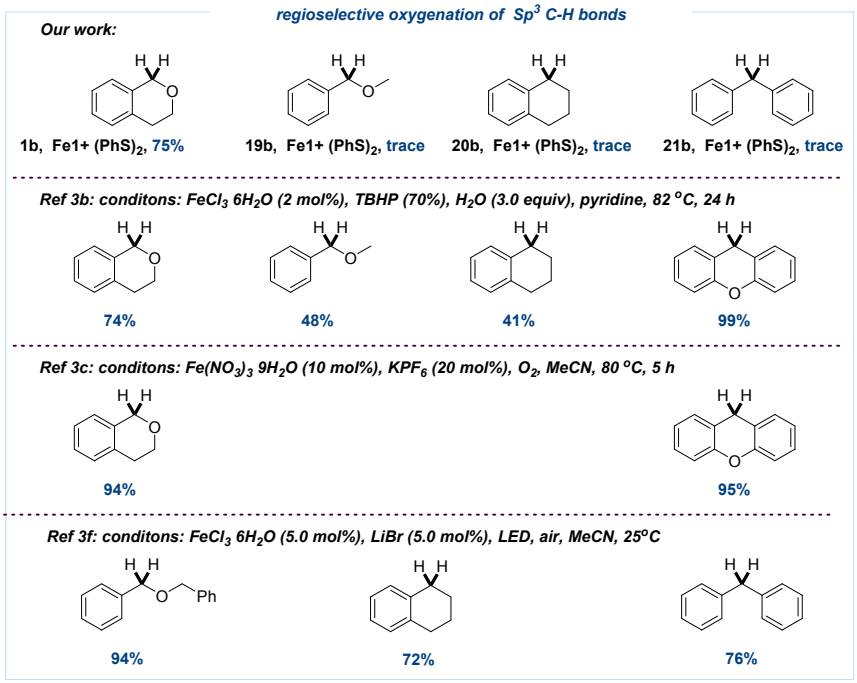
171.04128		7591248	49979
171.04528		531311	116998
171.04746		244012	119211
172.04468		931120	52260
173.04554		1266455	50957

Some results on iron-catalyzed oxygenation of Sp^3 C-H bonds



References:

1) A. Gonzalez-de-Castro, C. M. Robertson and J. Xiao, *J. Am. Chem. Soc.*, **2014**, *136*, 8350−8360.

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5) K. T. Tarantino, P. Liu and R. R. Knowles, *J. Am. Chem. Soc.*, **2013**, *135*, 10022–10025.

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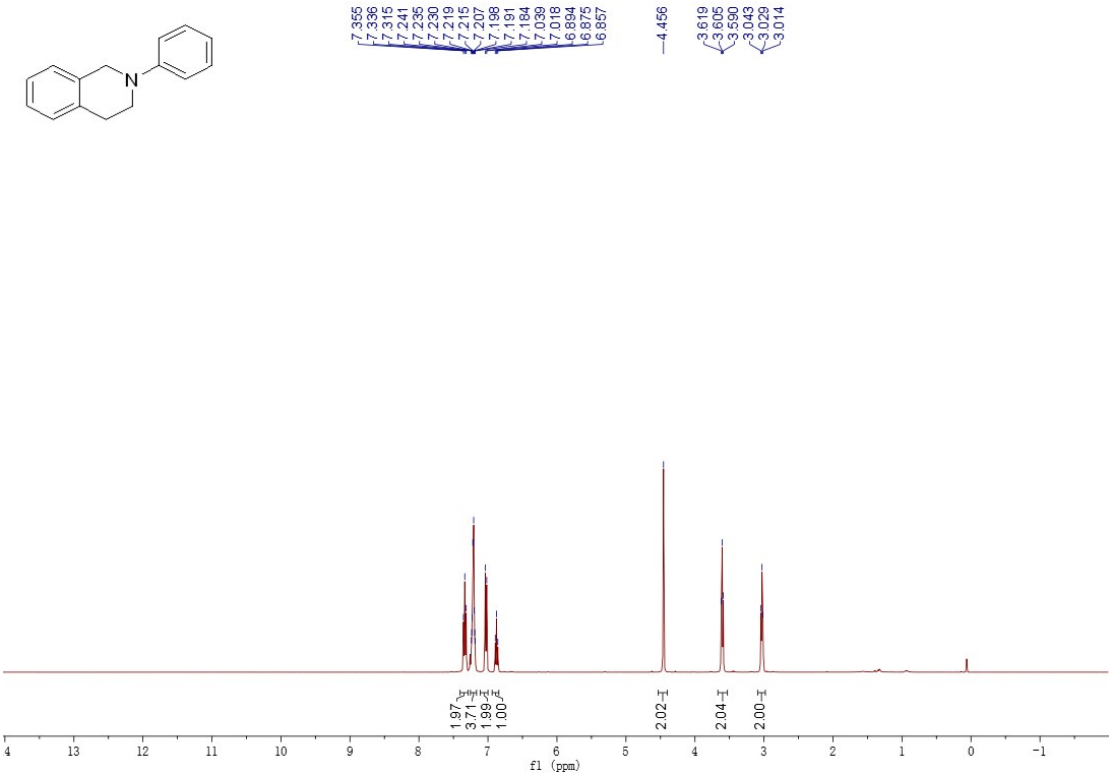
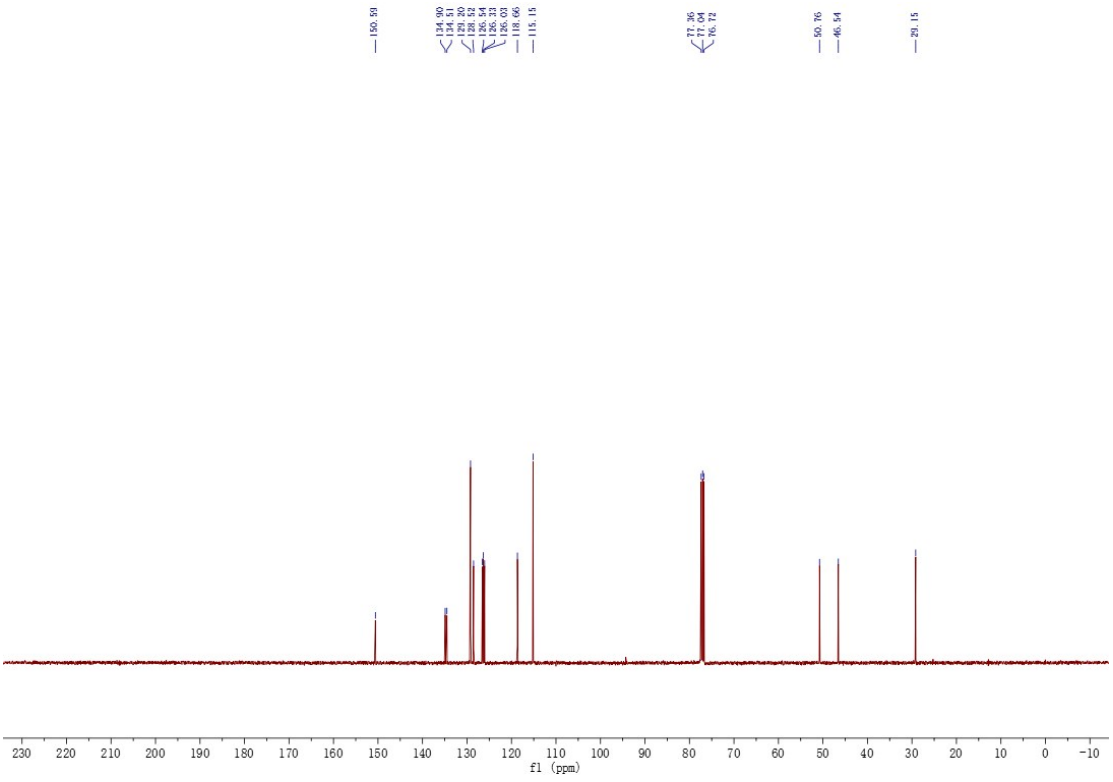
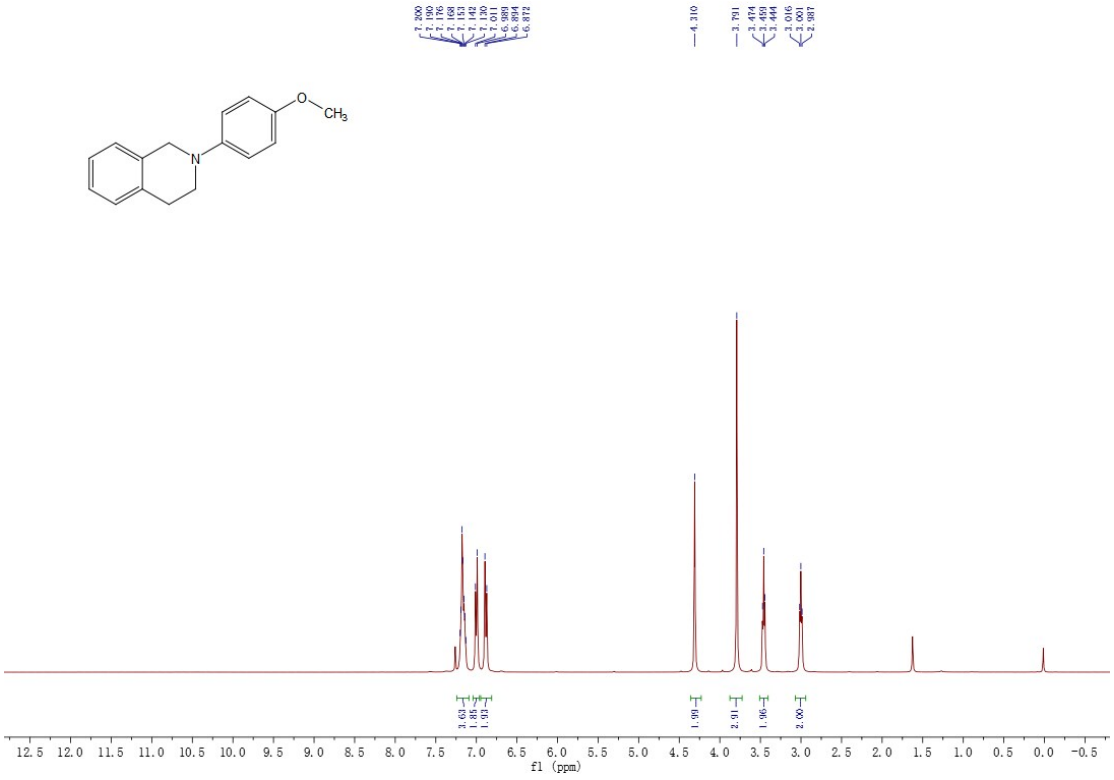
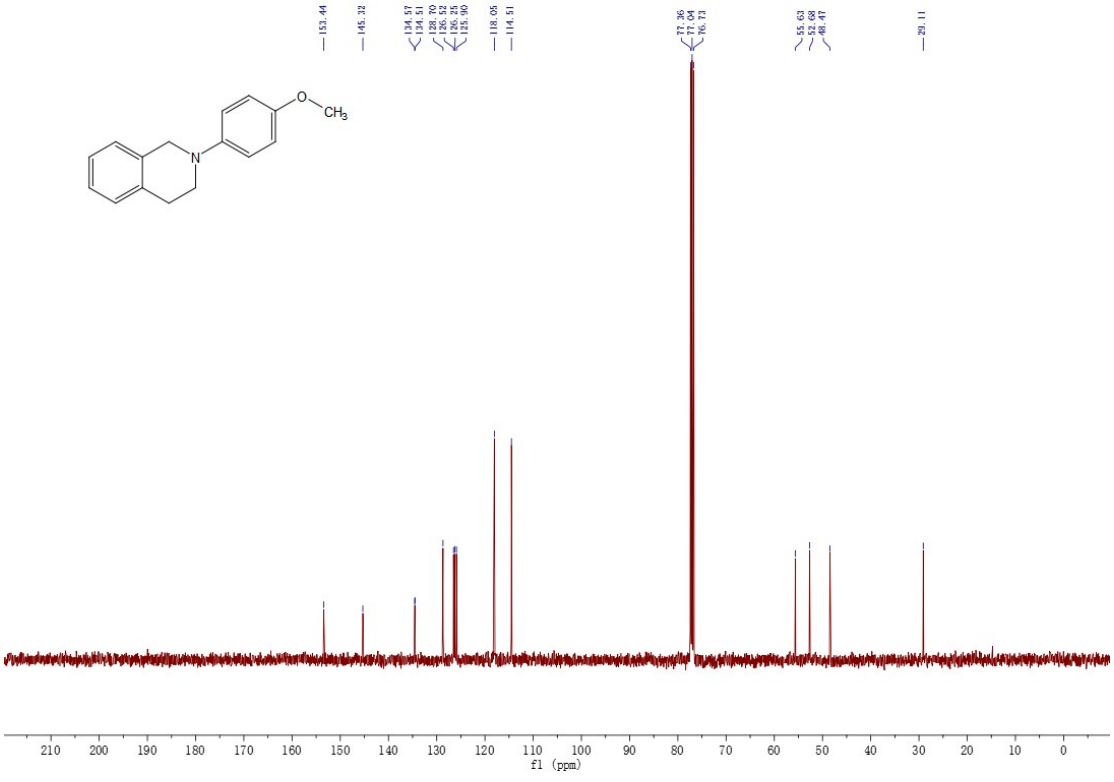
2-Phenyl-1,2,3,4-tetrahydroisoquinoline (1a)



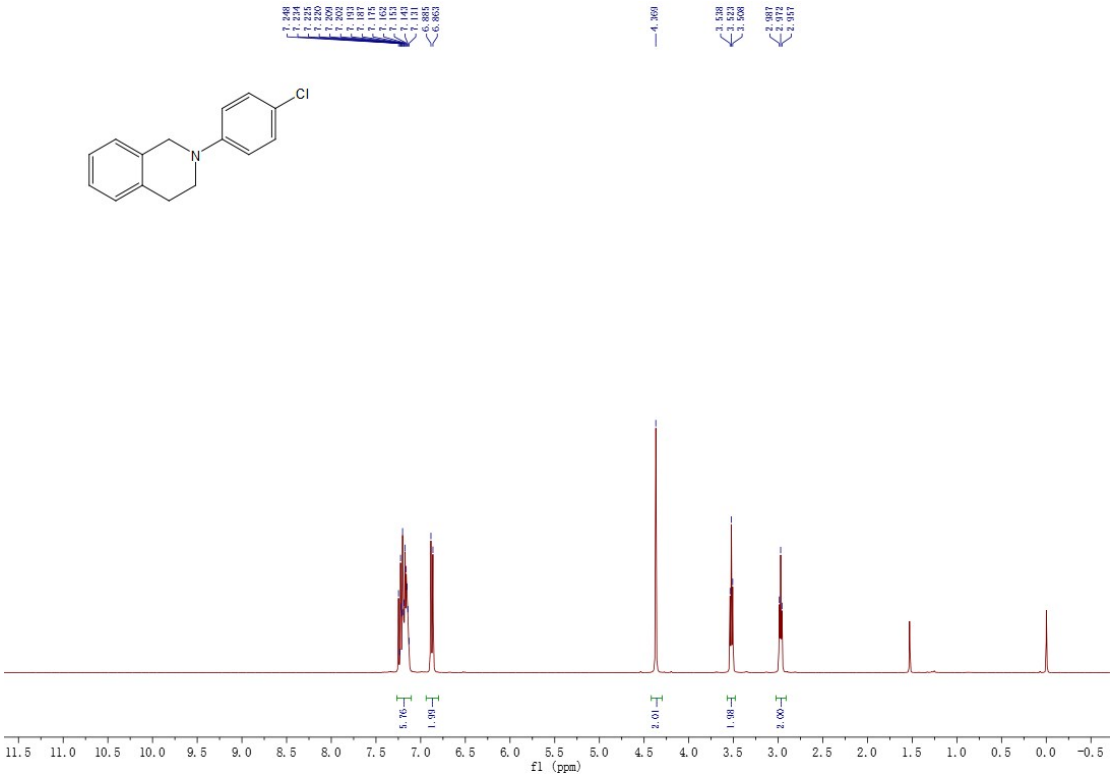


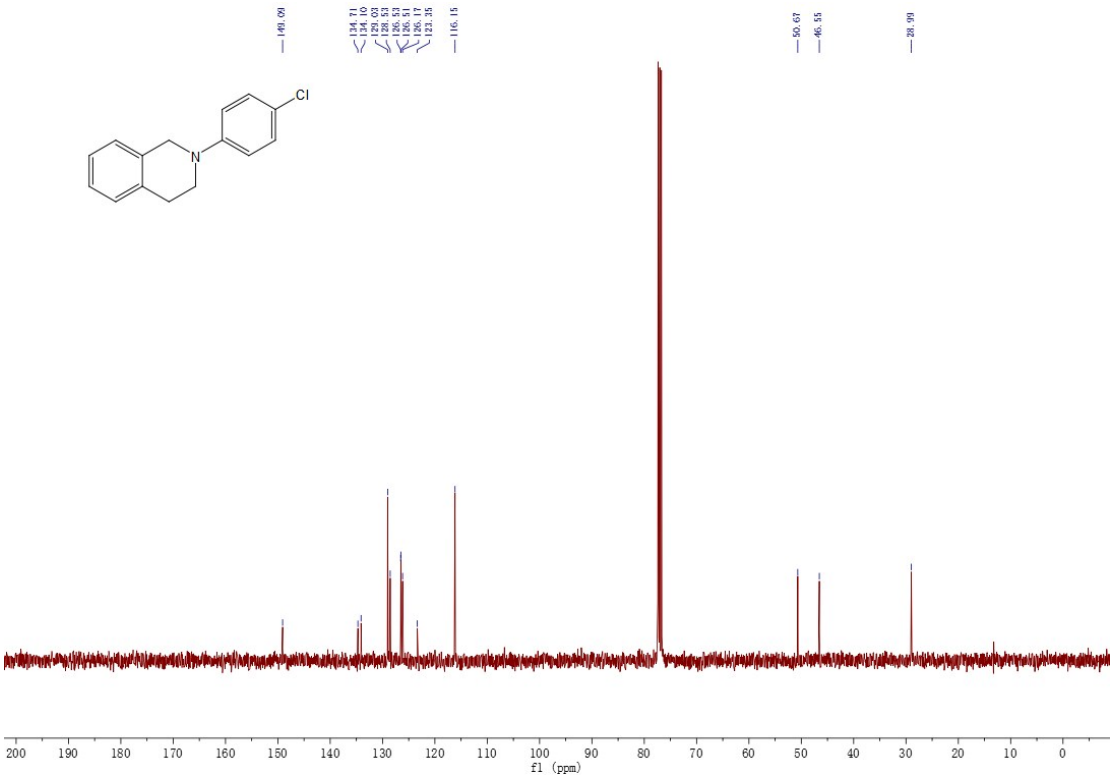
2-(4-Methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (2a)



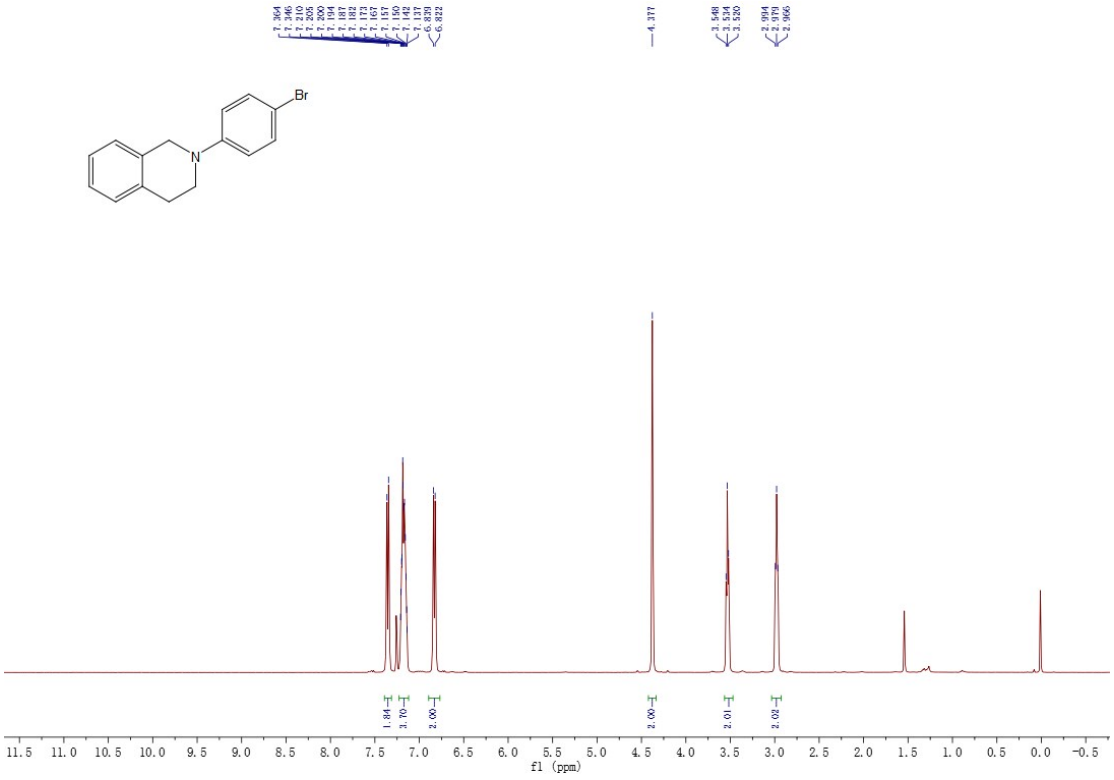


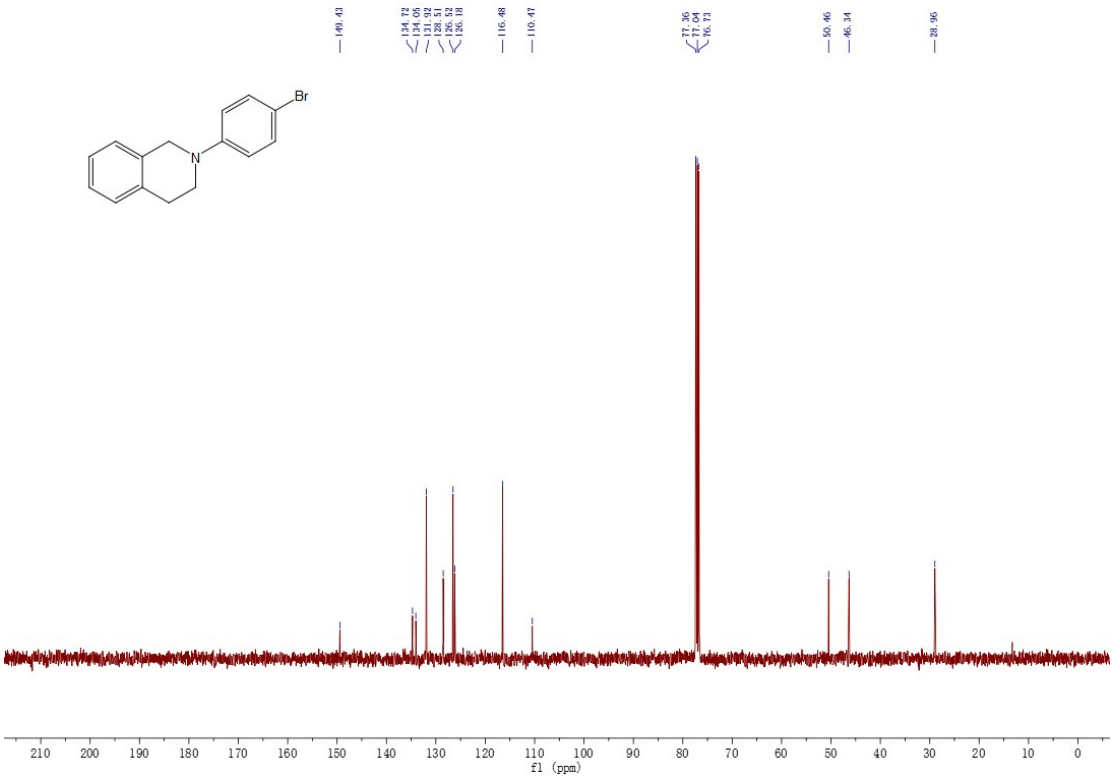
2-(4-Chlorophenyl)-1,2,3,4-tetrahydroisoquinoline (3a)



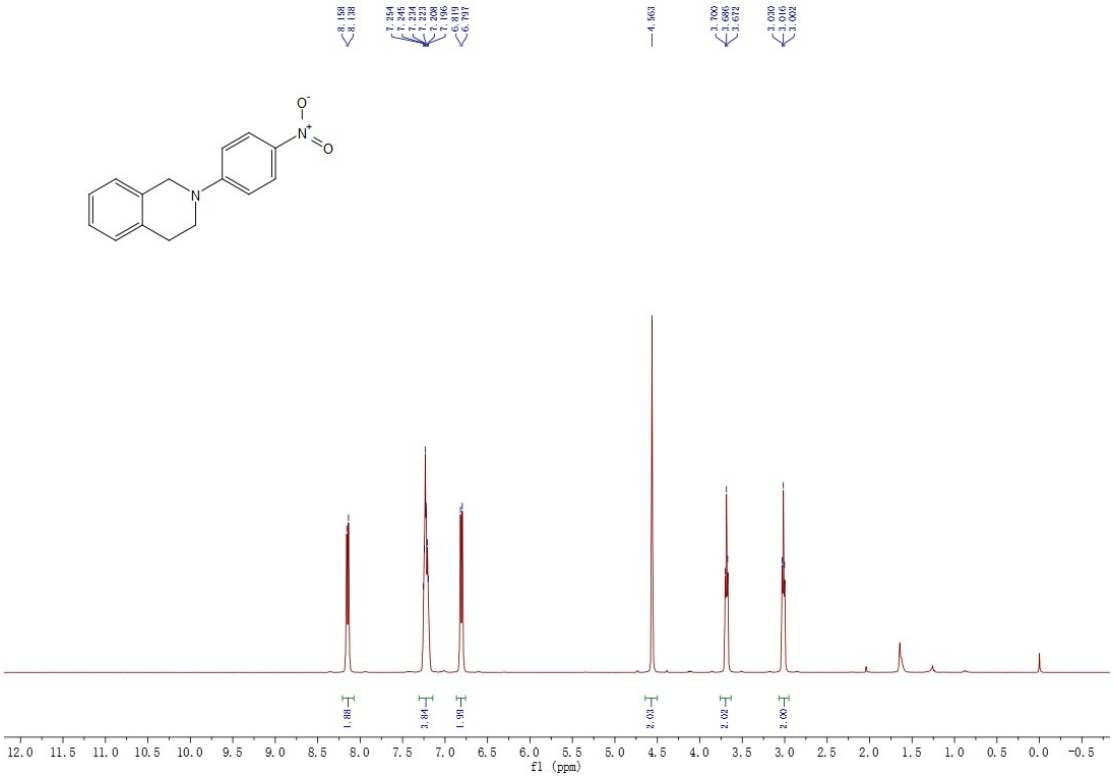


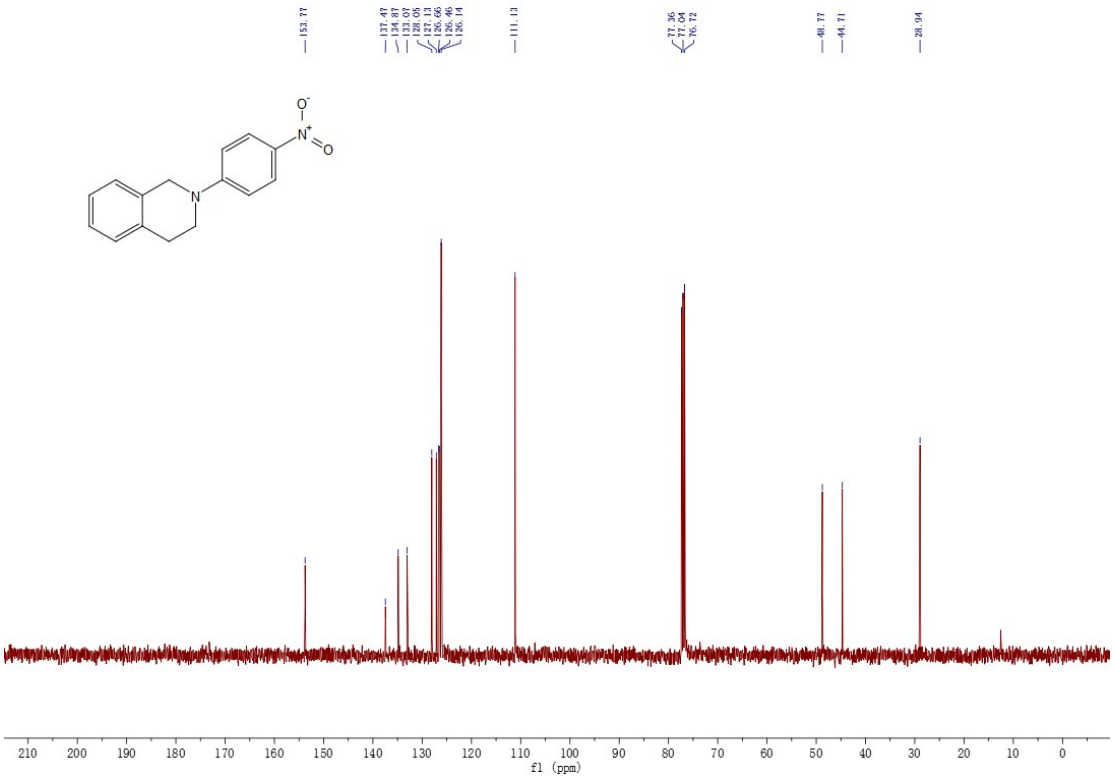
2-(4-Bromophenyl)-1,2,3,4-tetrahydroisoquinoline (4a)



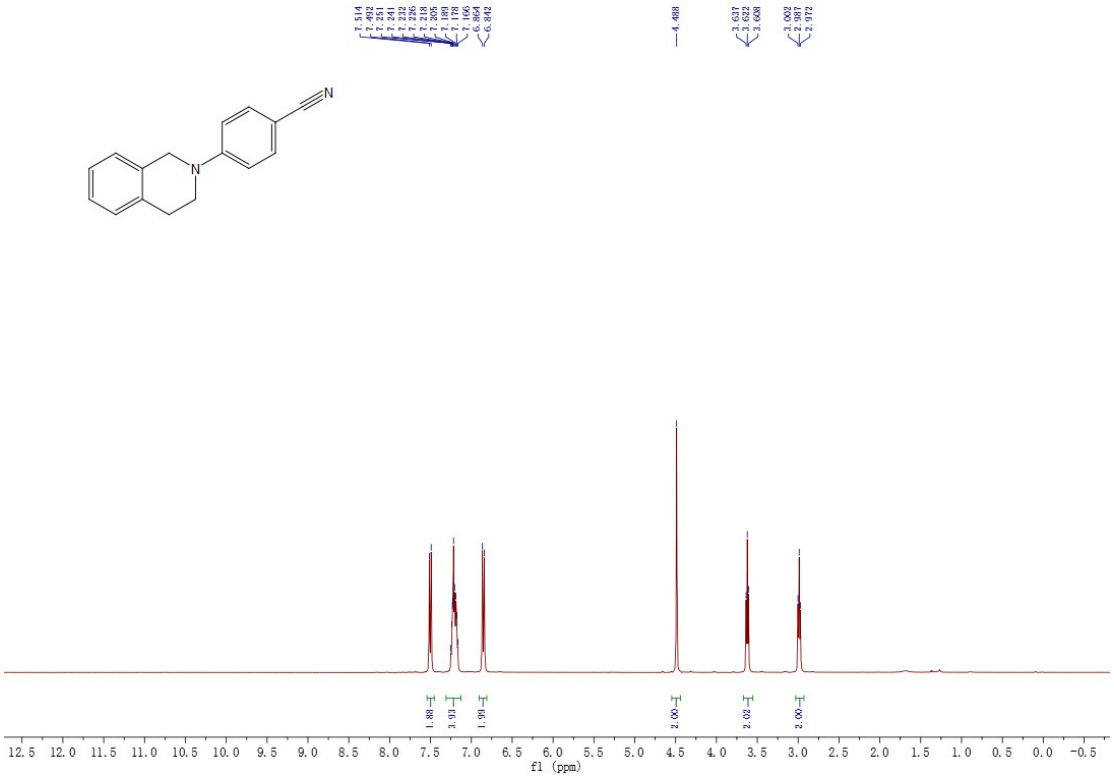


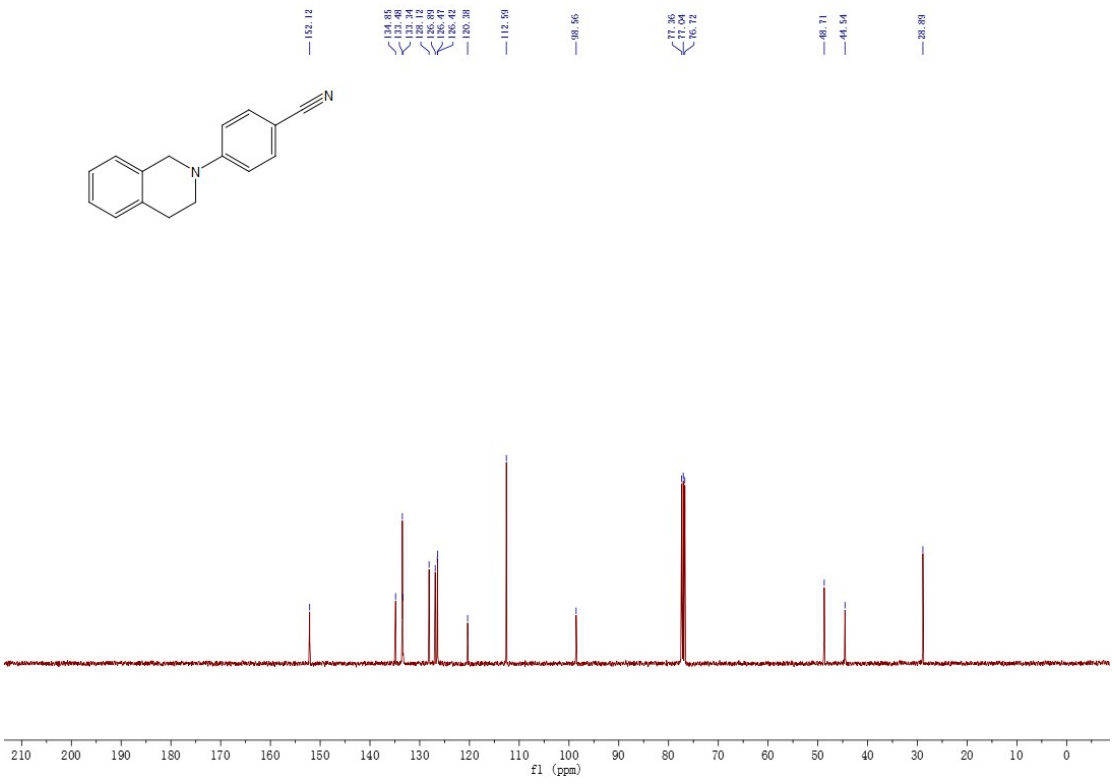
2-(4-Nitrophenyl)-1,2,3,4-tetrahydroisoquinoline (5a)



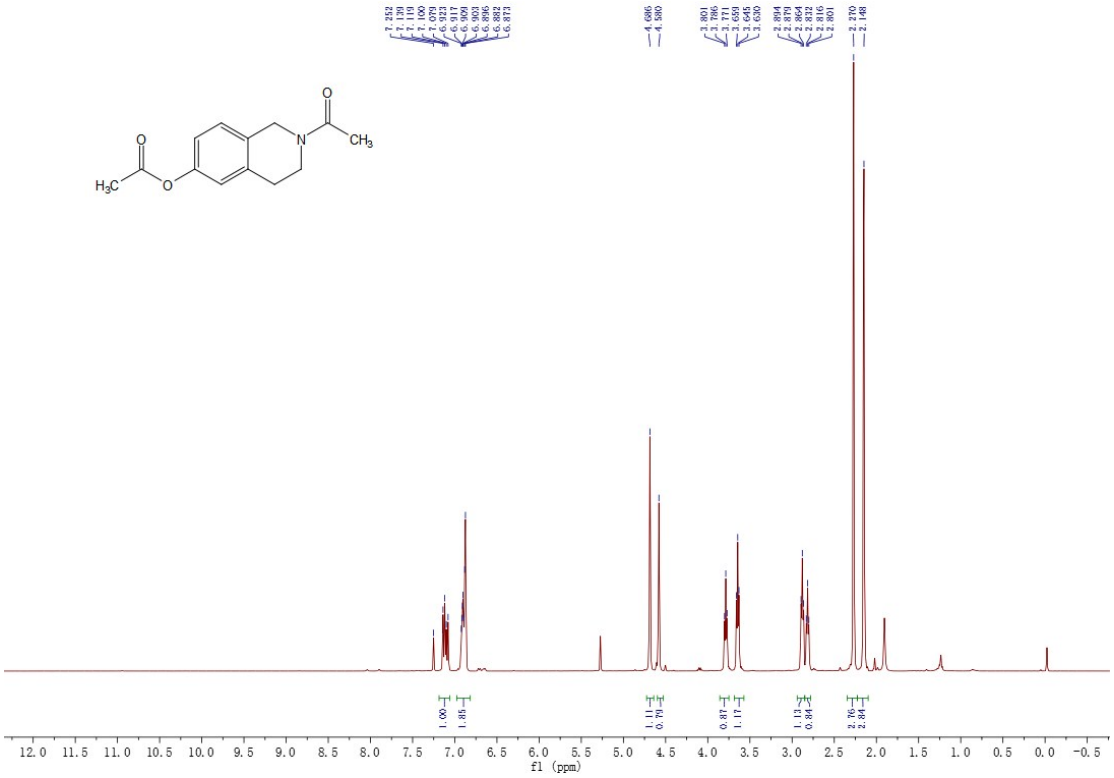


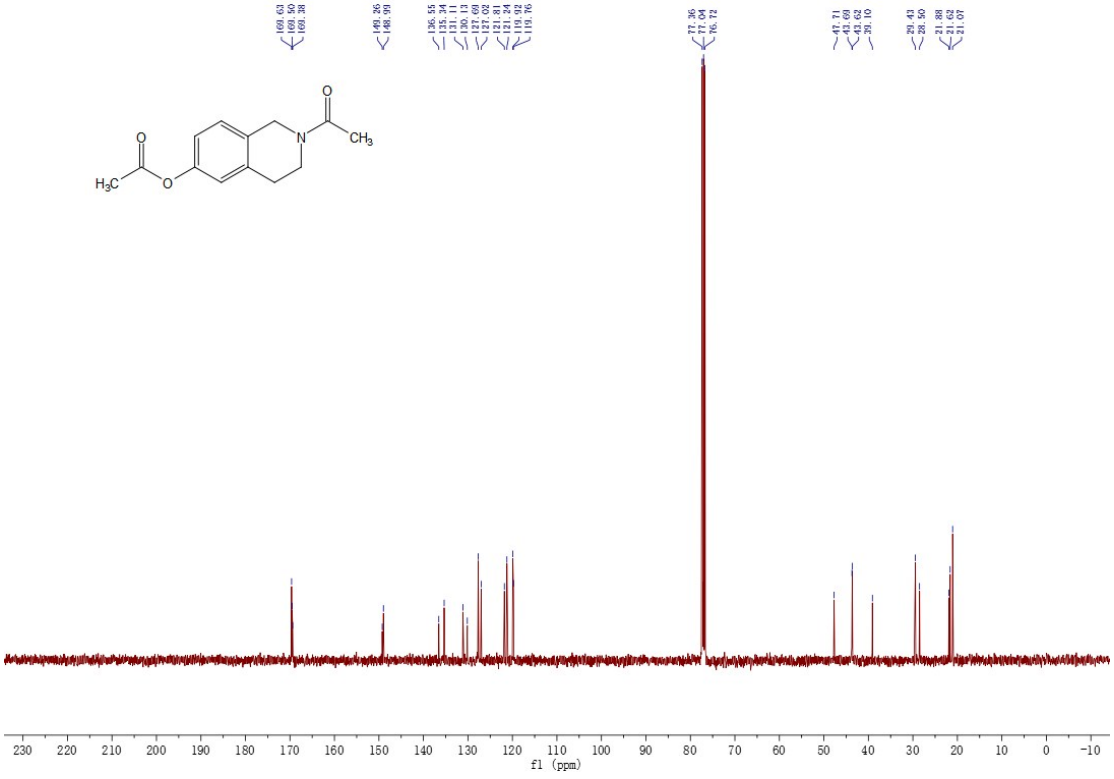
4-(3,4-Dihydroisoquinolin-2(1*H*)-yl)benzonitrile (6a)



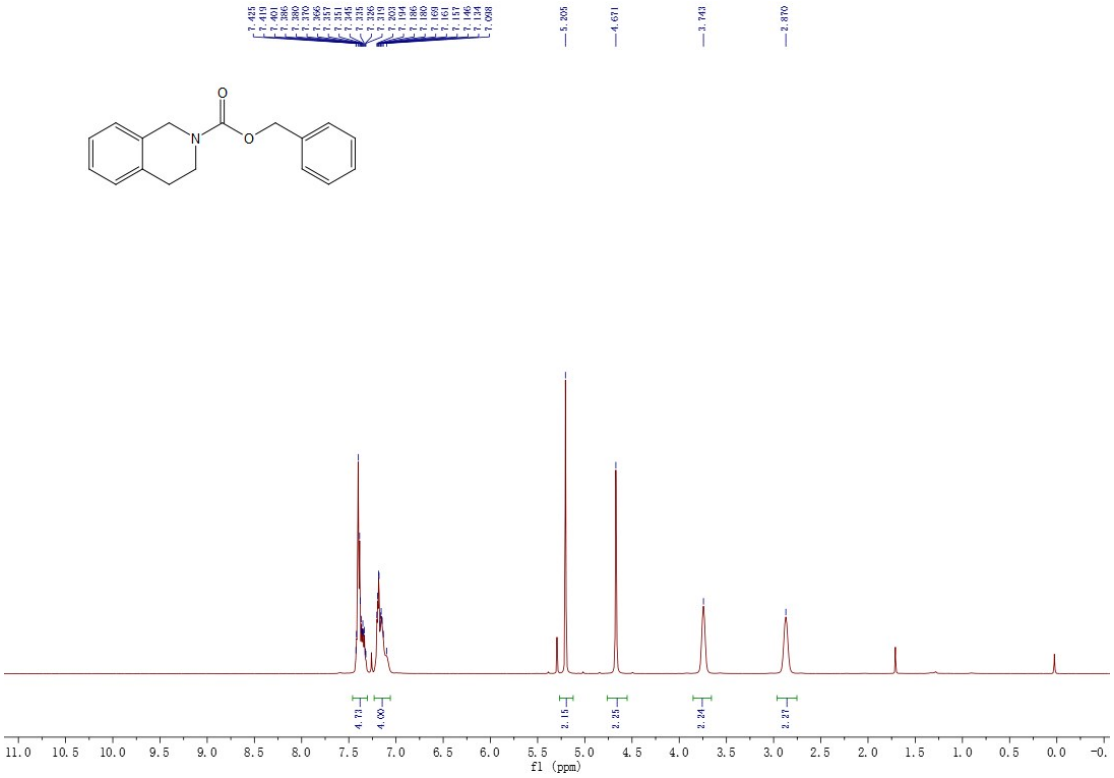


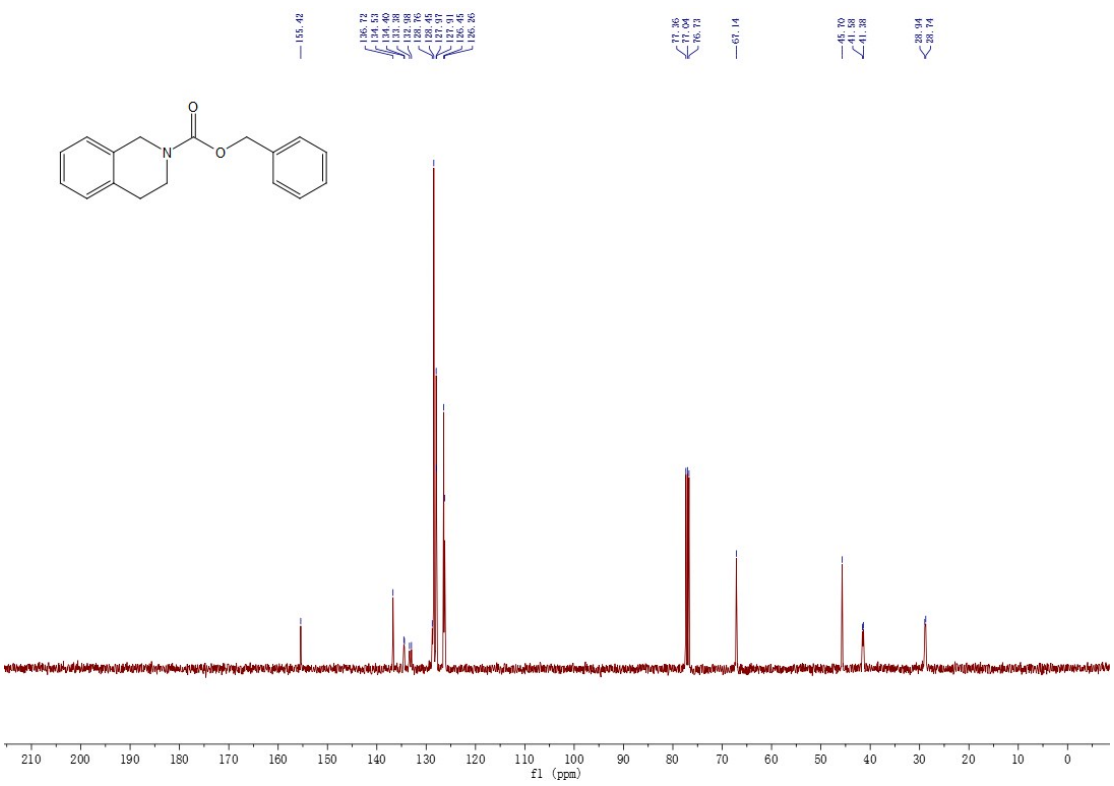
2-Acetyl-1,2,3,4-tetrahydroisoquinolin-6-yl acetate (7a)



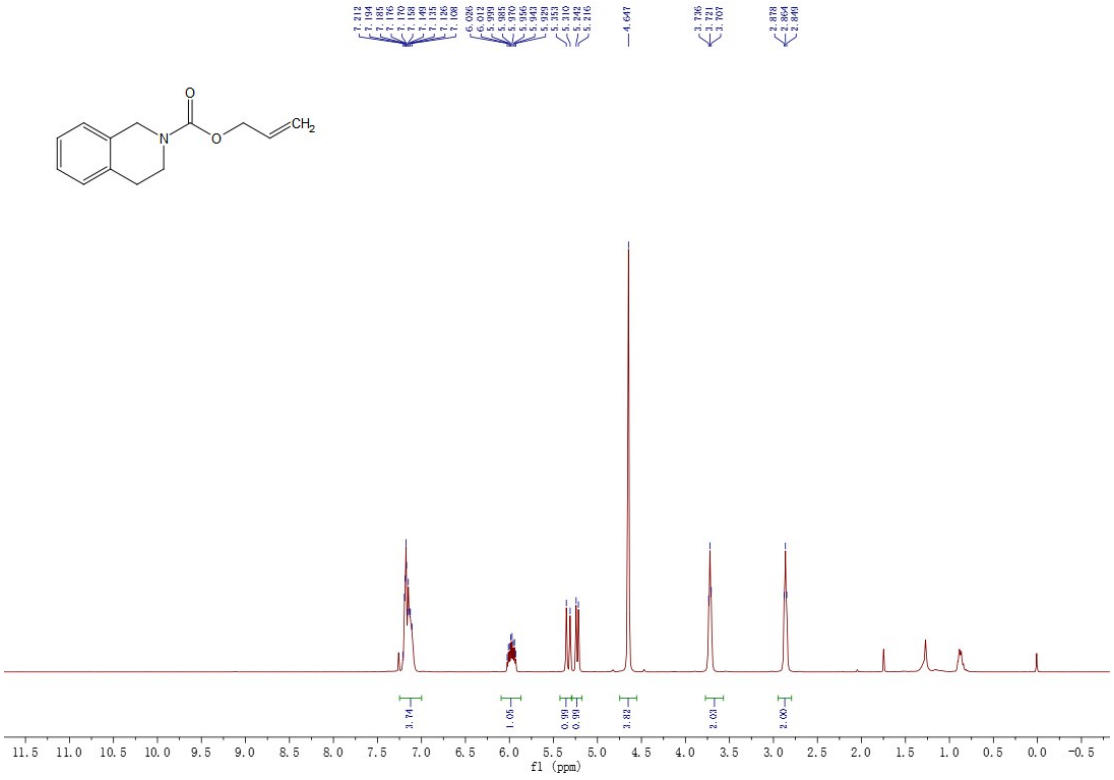


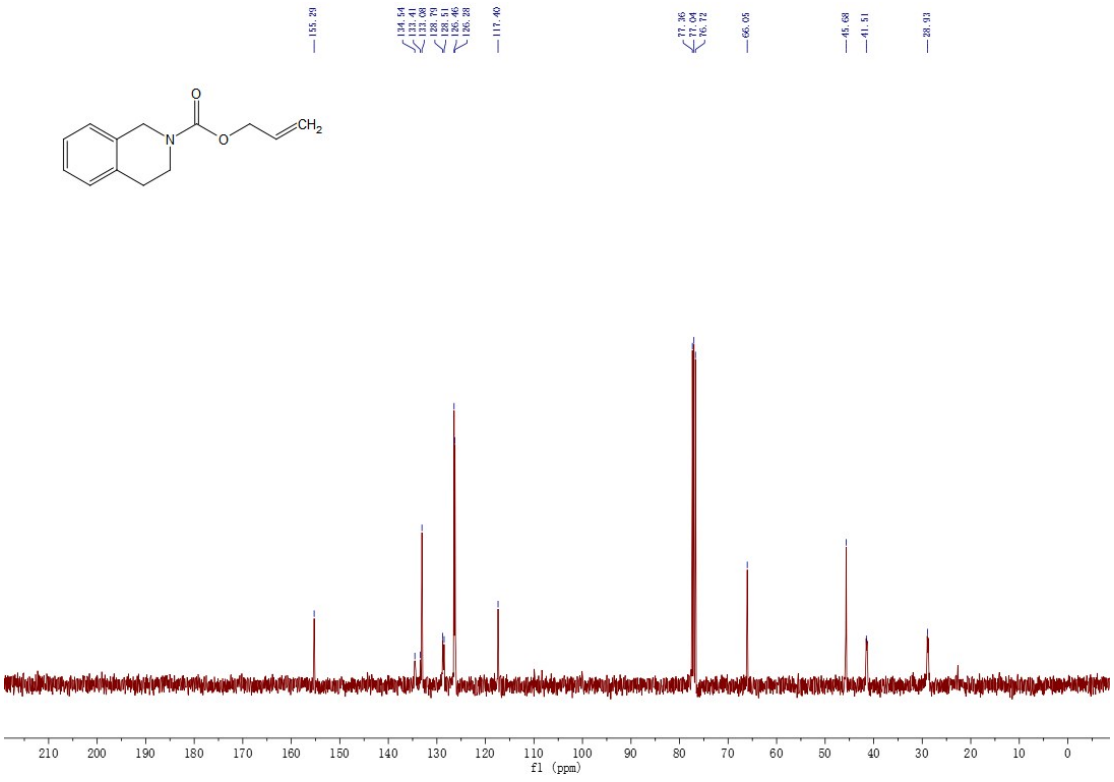
Benzyl 3,4-dihydroisoquinoline-2(1*H*)-carboxylate (8a)



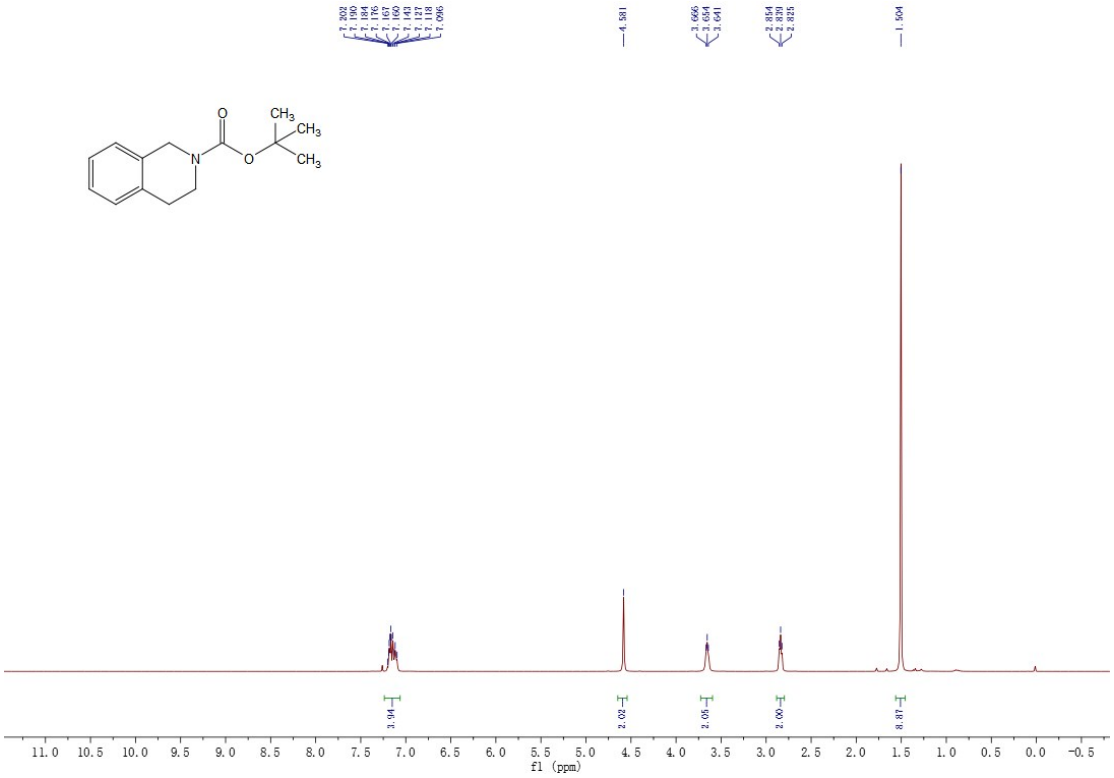


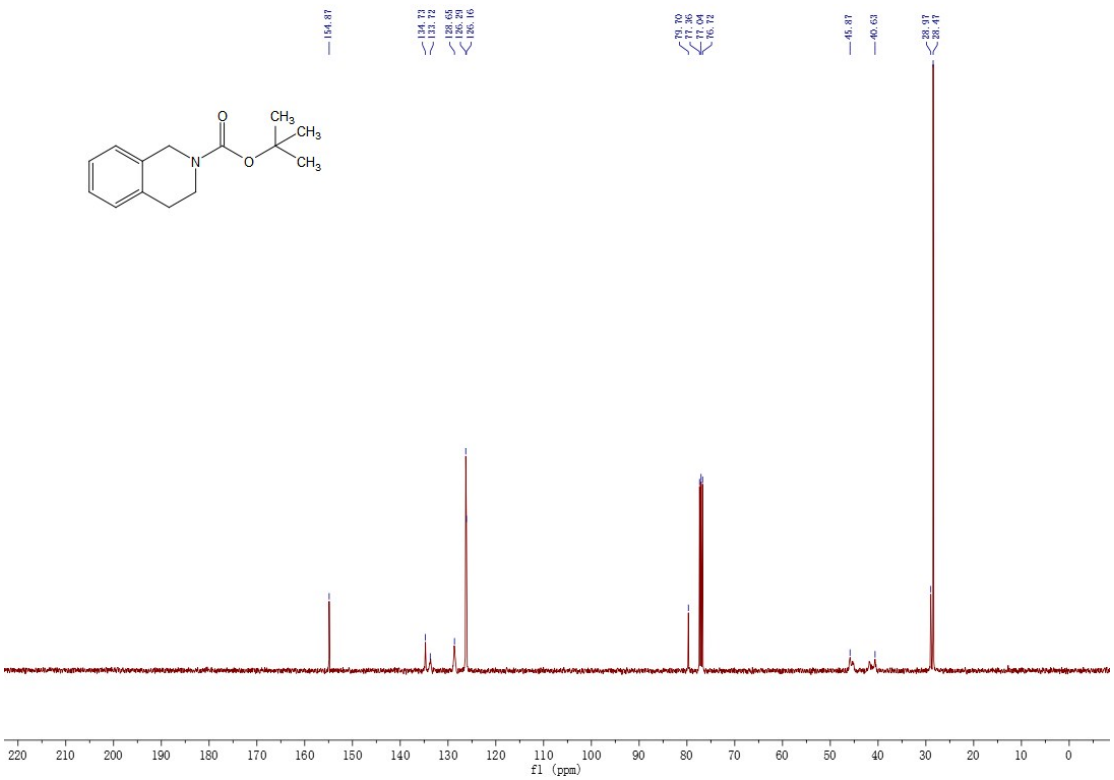
Allyl 3,4-dihydroisoquinoline-2(1*H*)-carboxylate (10a)



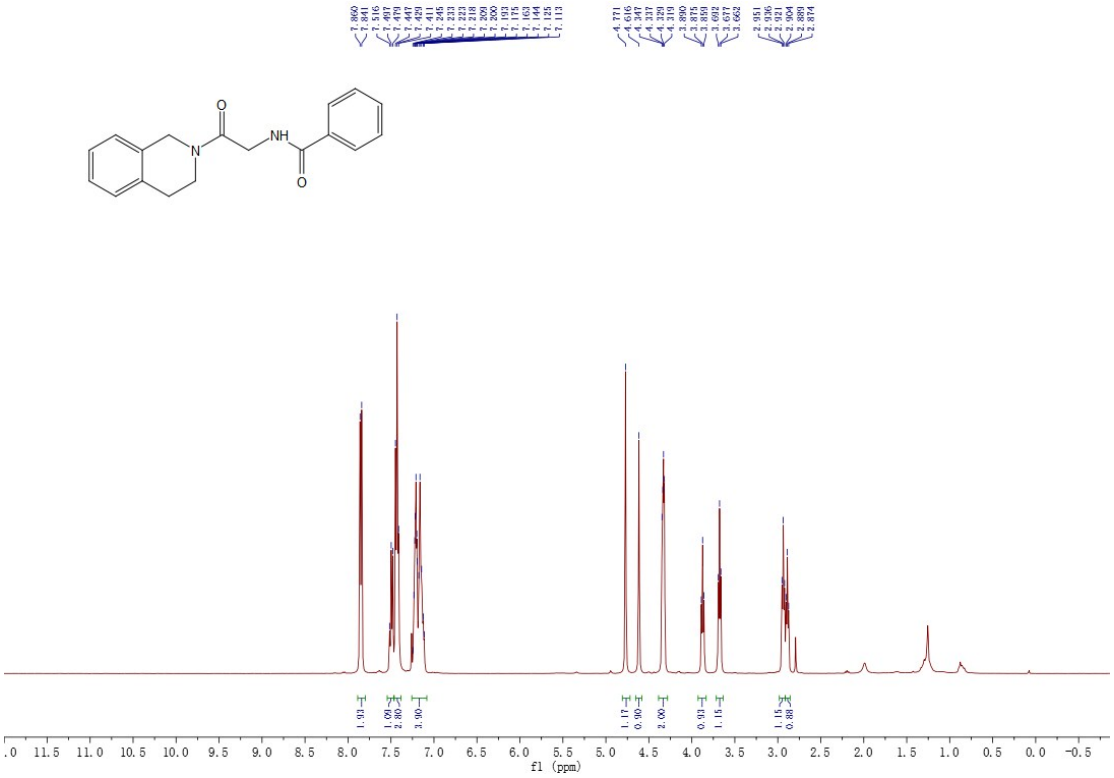


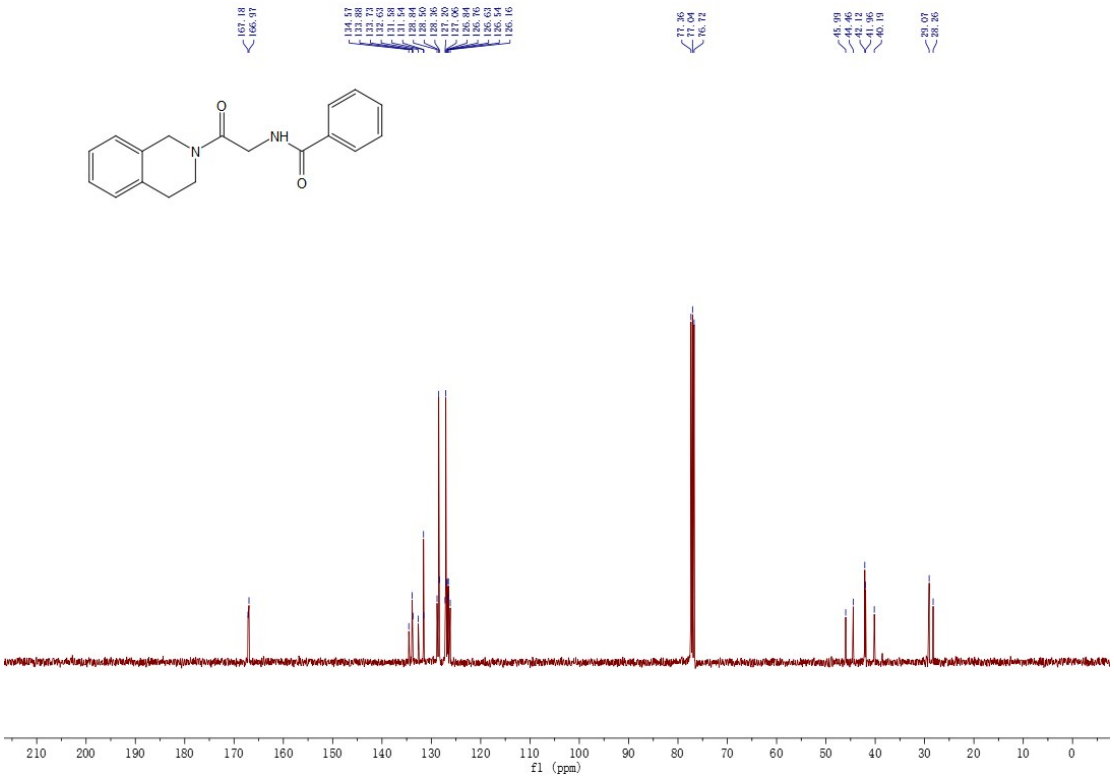
tert-Butyl 3,4-dihydroisoquinoline-2(1*H*)-carboxylate (11a)



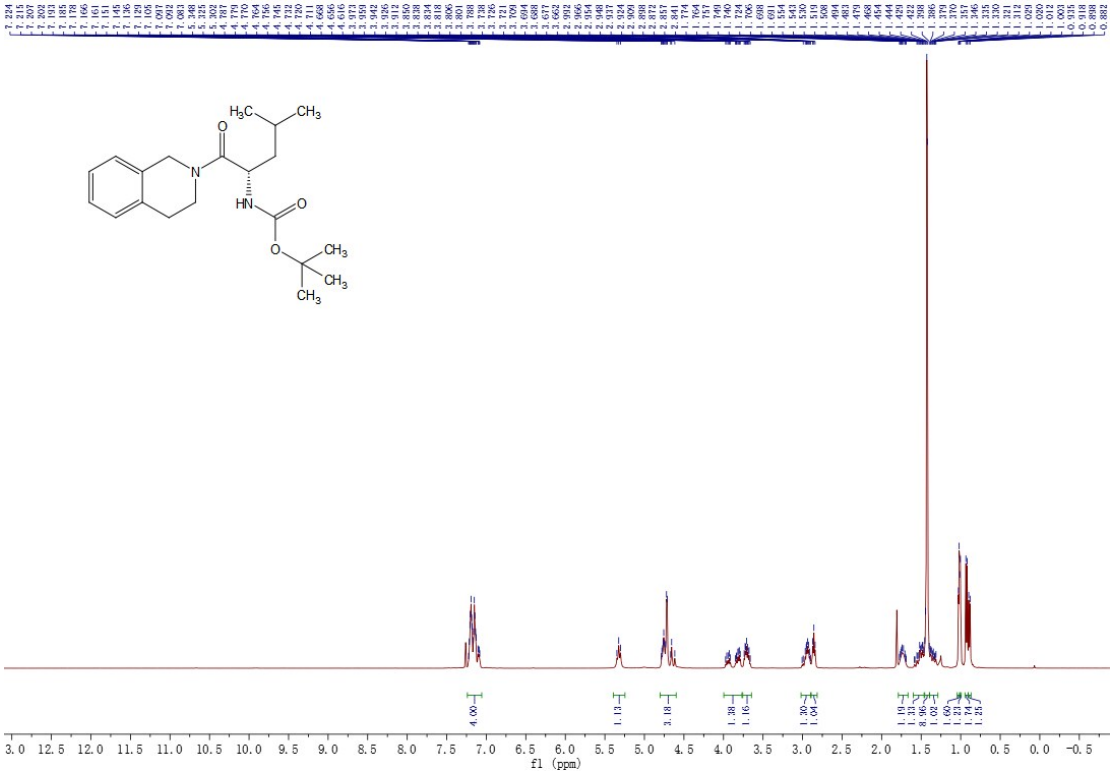


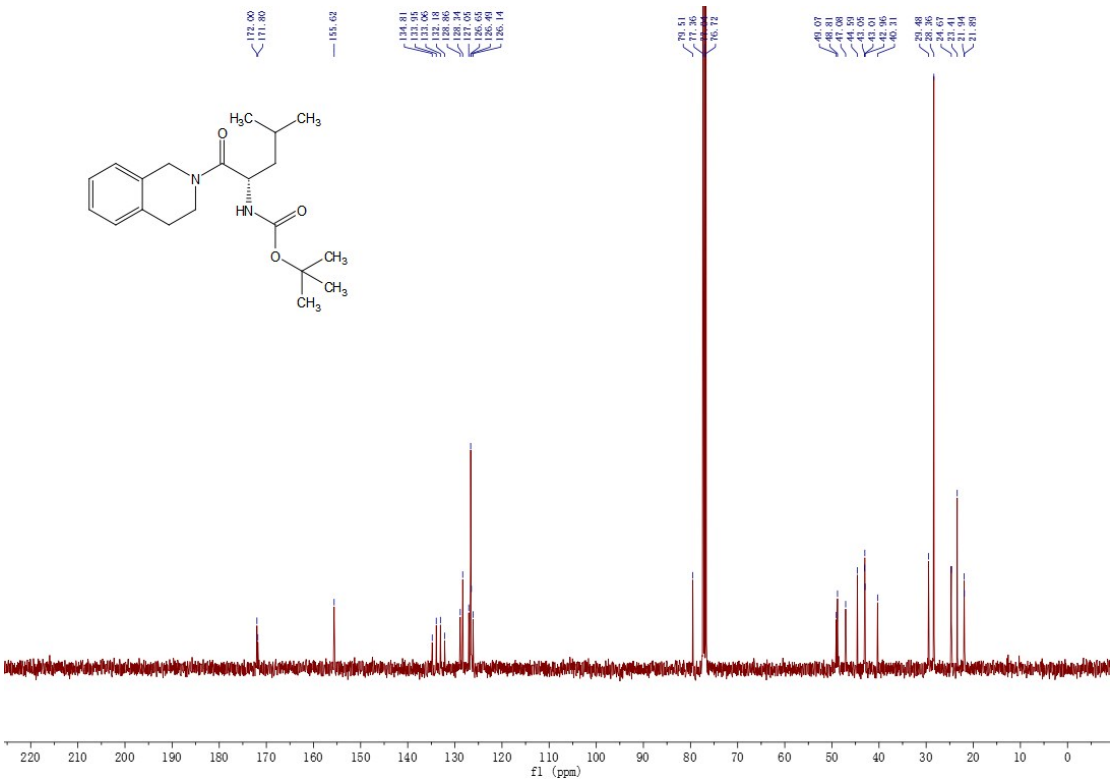
N-(2-(3,4-dihydroisoquinolin-2(1*H*)-yl)-2-oxoethyl)benzamide (12a)



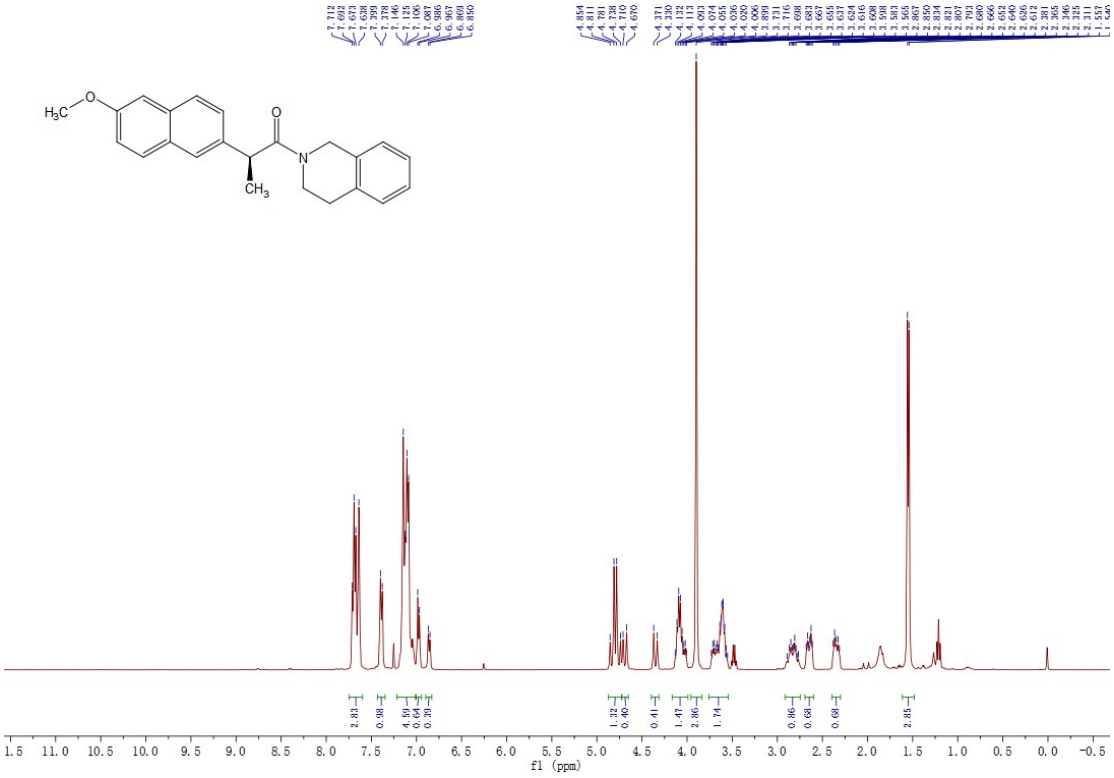


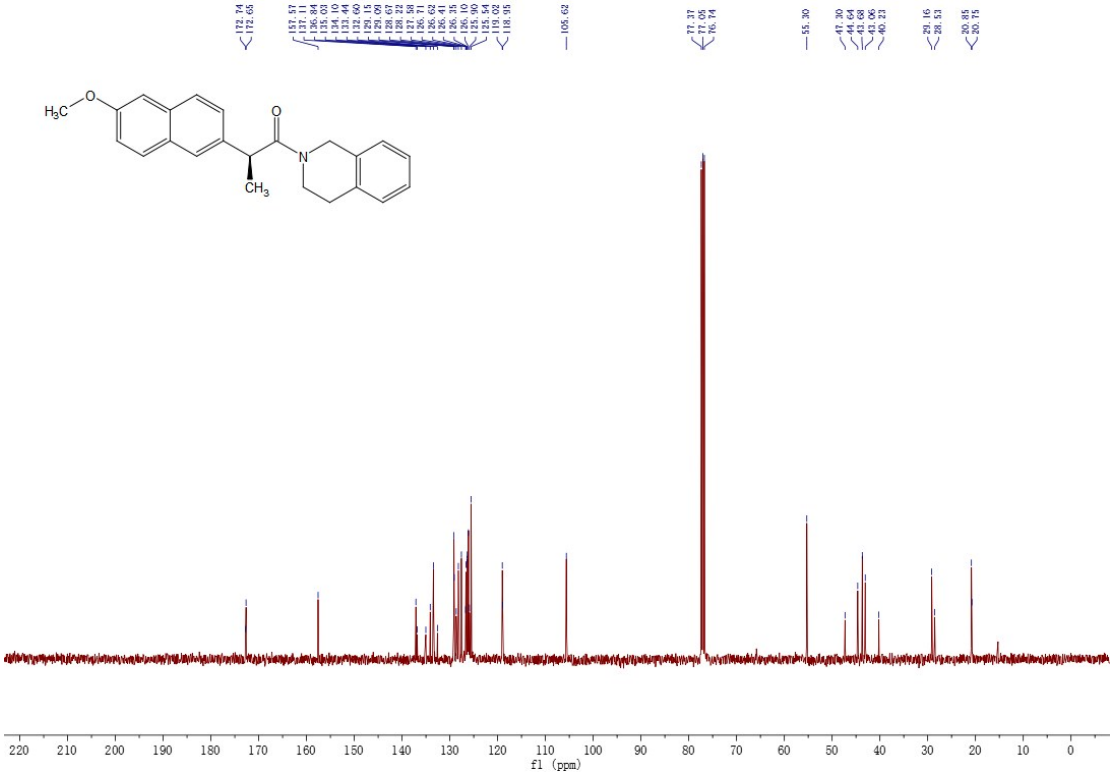
***tert*-Butyl (*S*)-(1-(3,4-dihydroisoquinolin-2(1*H*)-yl)-4-methyl-1-oxopentan-2-yl) carbamate (13a)**



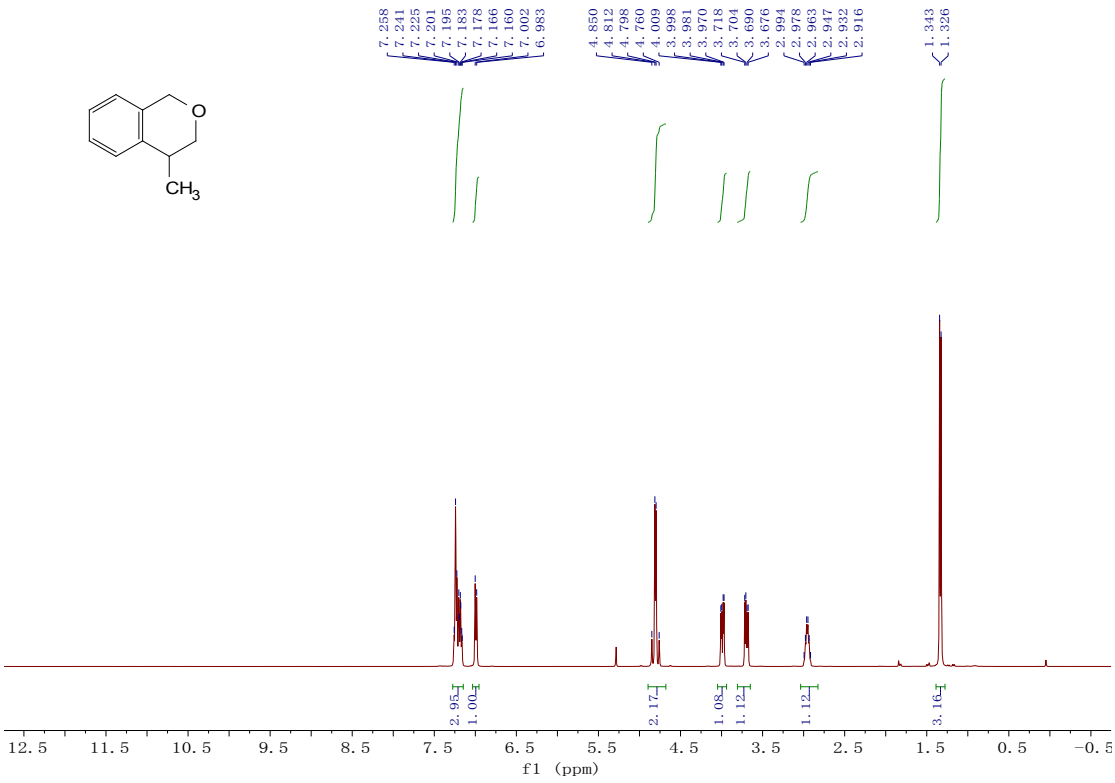


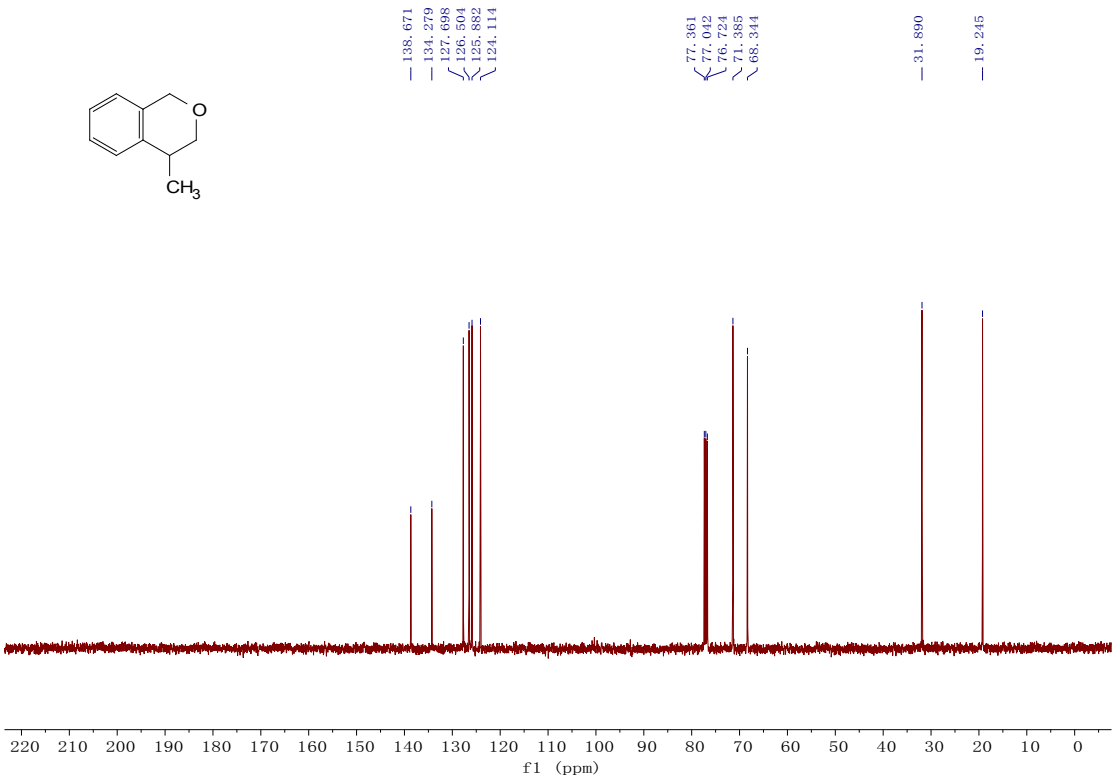
(*S*)-1-(3,4-dihydroisoquinolin-2(1H)-yl)-2-(6-methoxynaphthalen-2-yl)propan-1-one (14a)



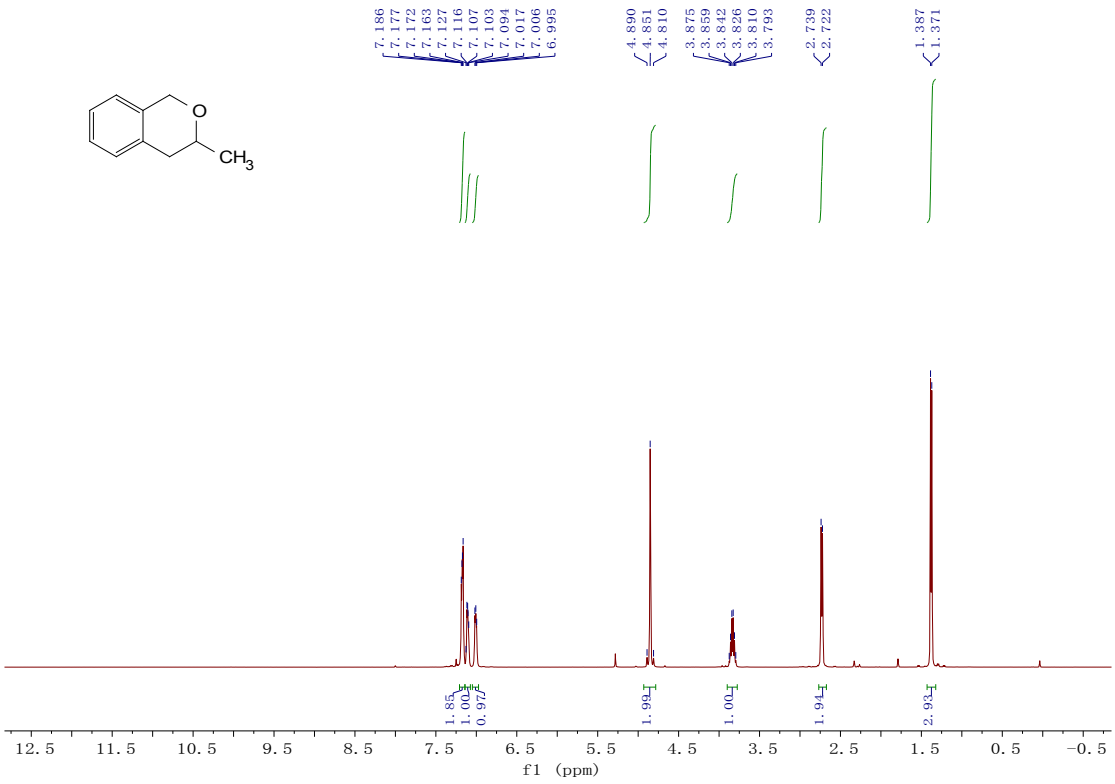


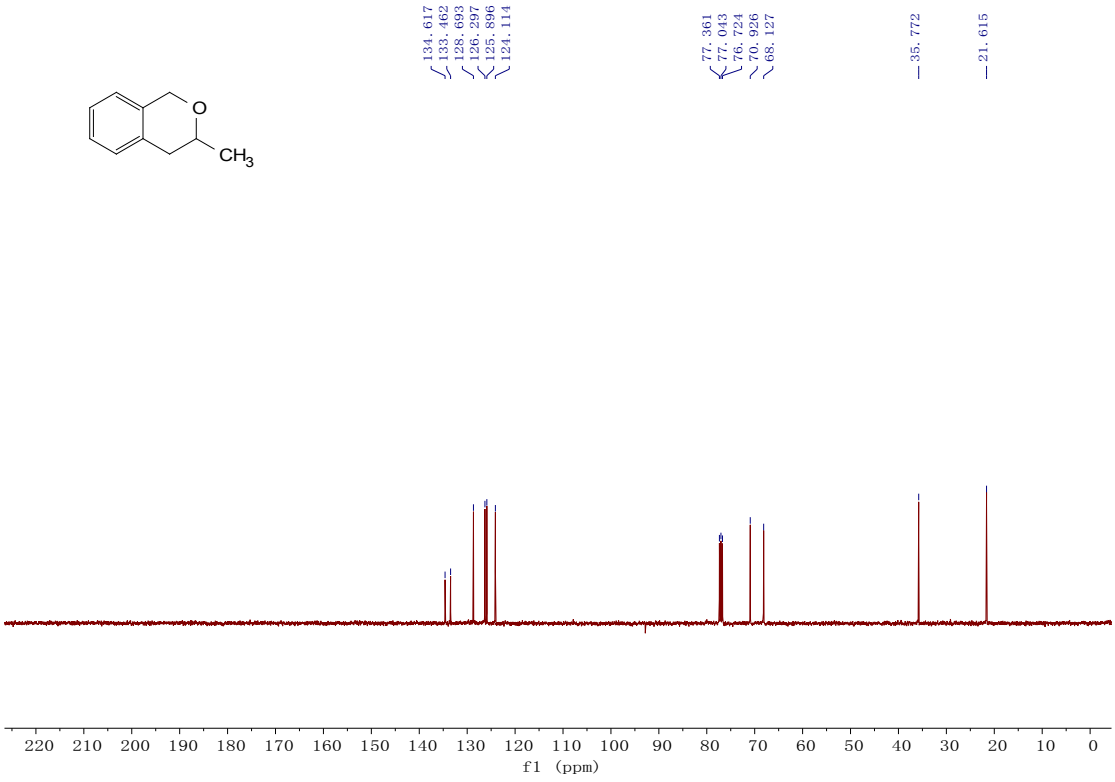
4-Methylisochromane (2b)



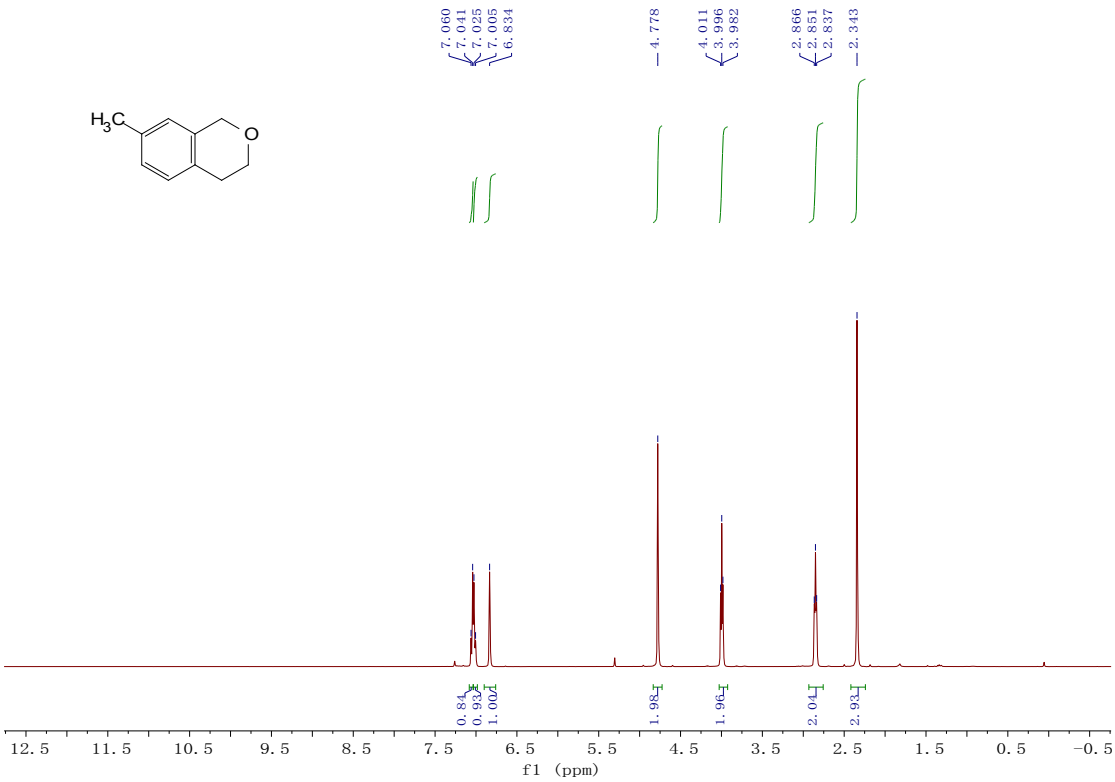


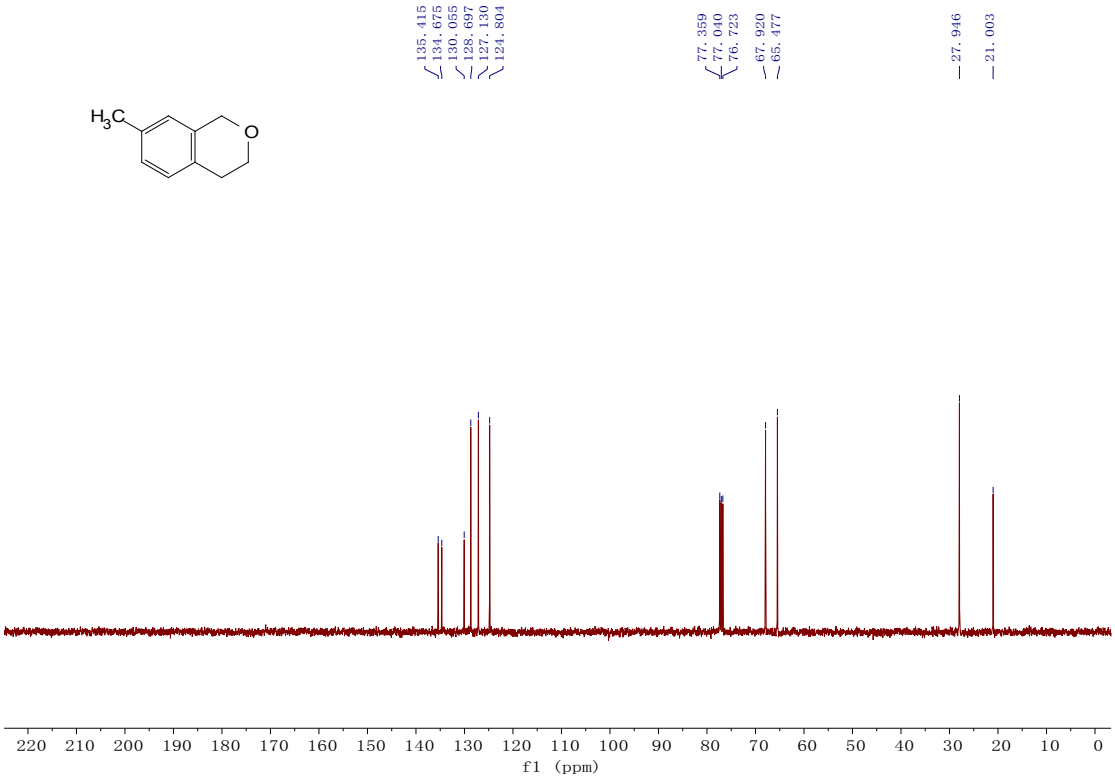
3-Methylisochromane (3b)



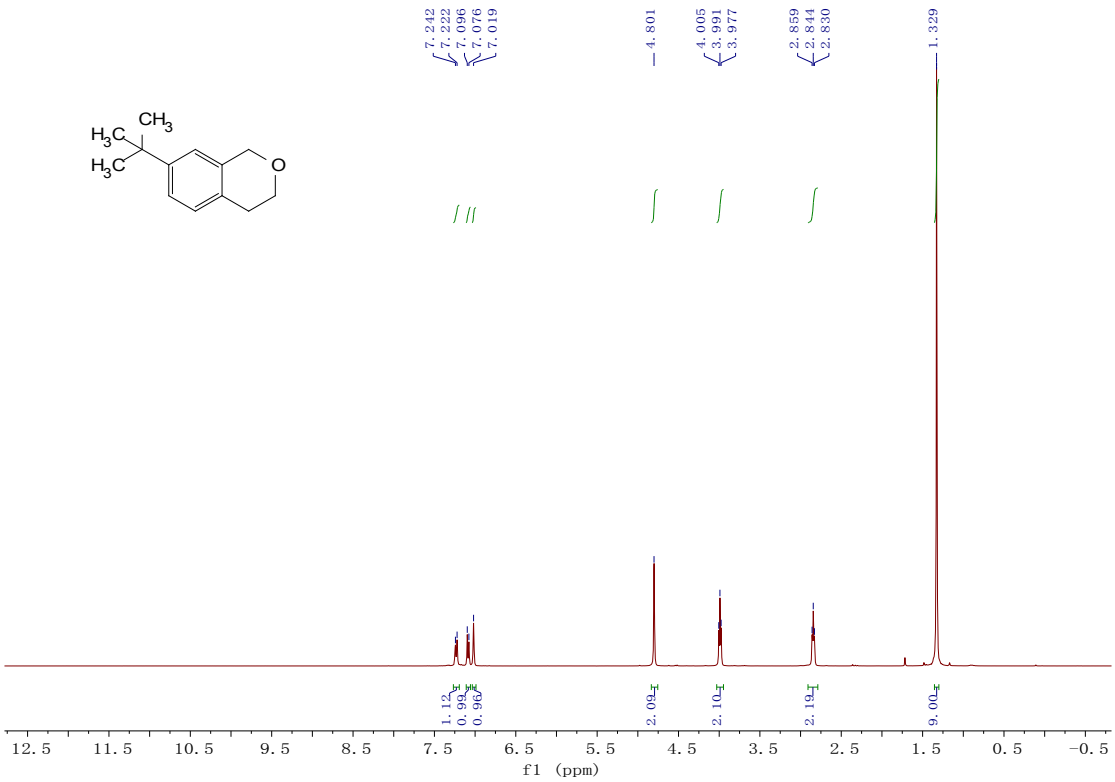


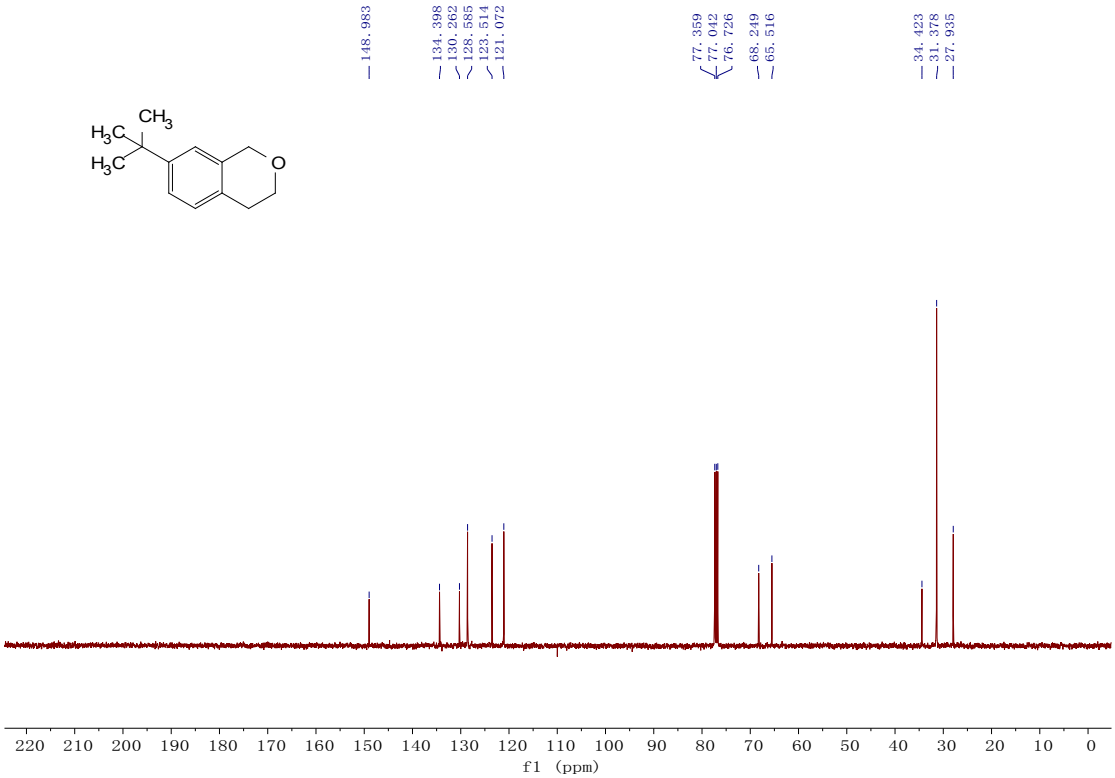
7-Methylisochromane (4b)



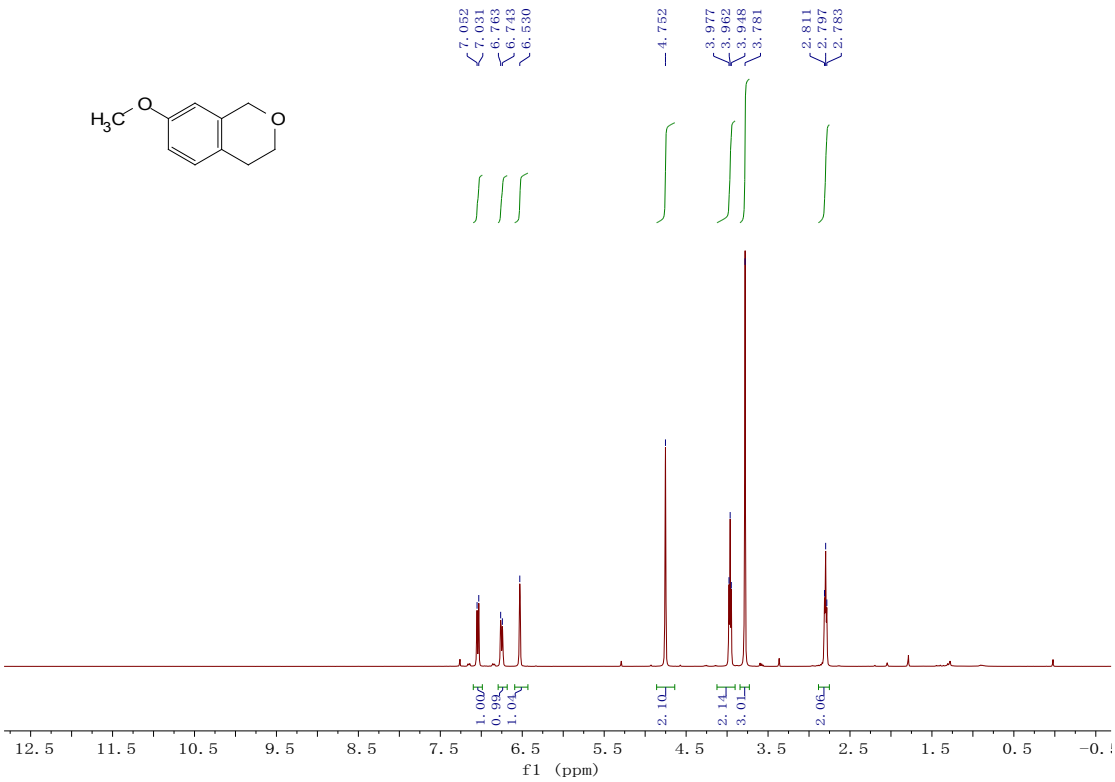


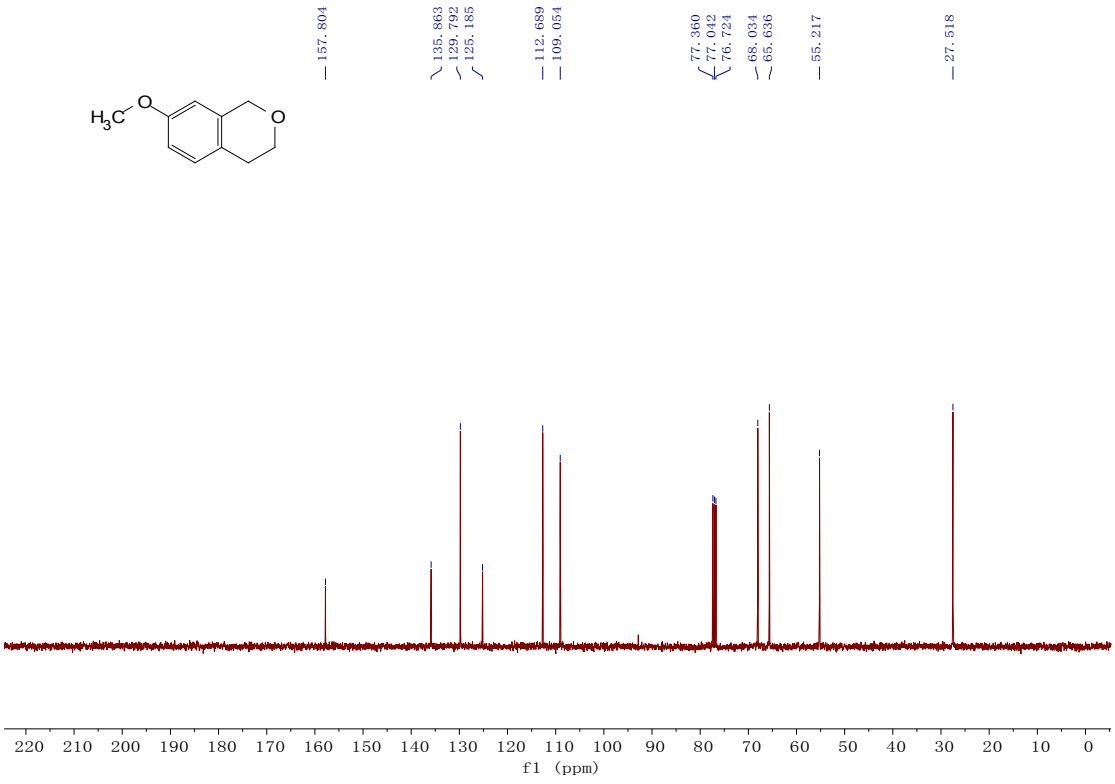
7-(*tert*-Butyl)isochromane (5b)



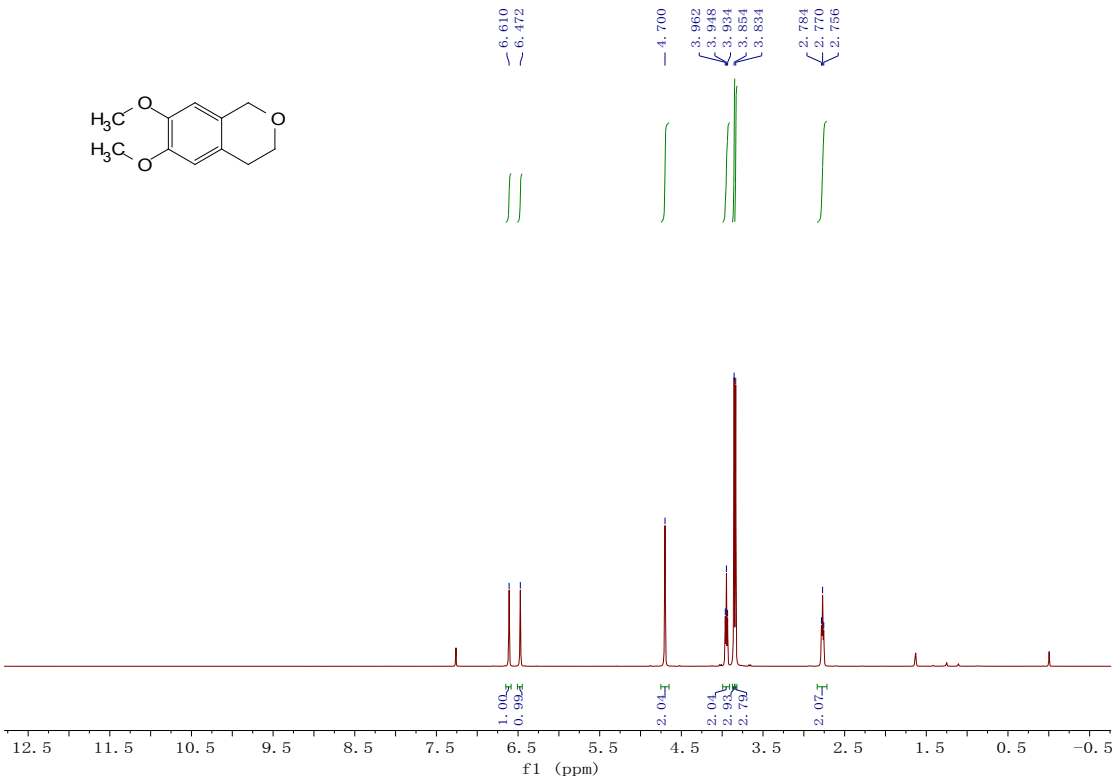


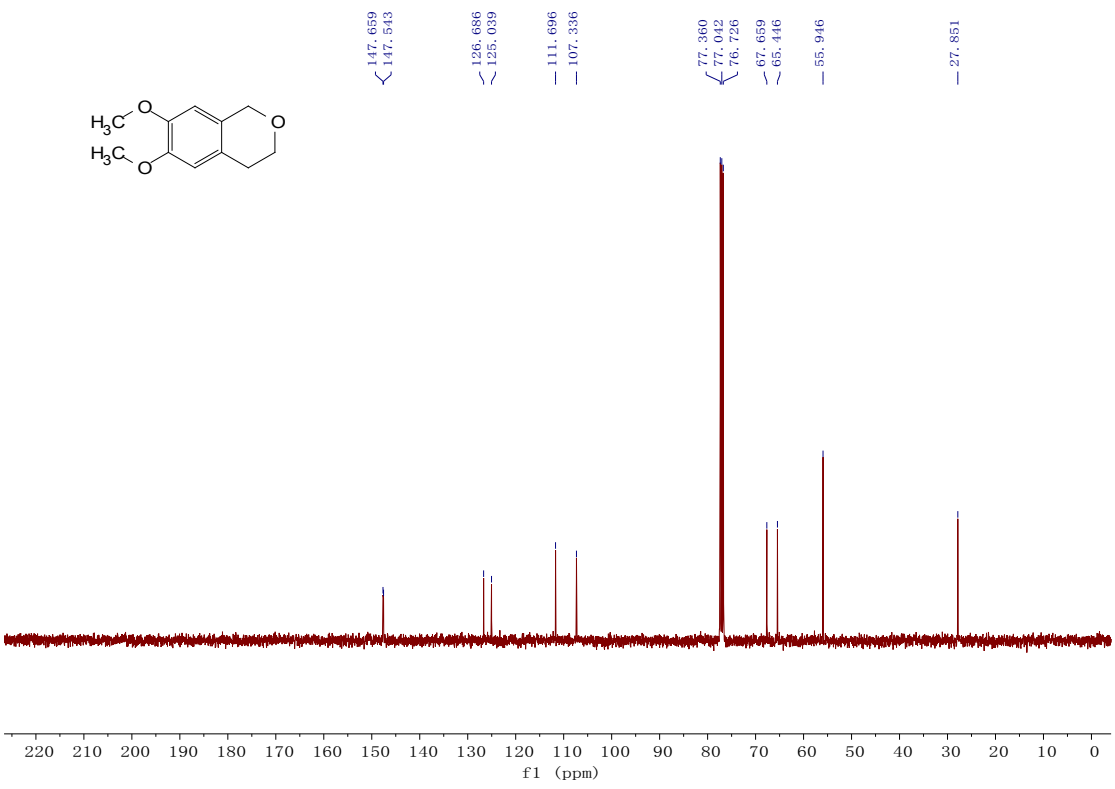
7-Methoxyisochromane (6b)



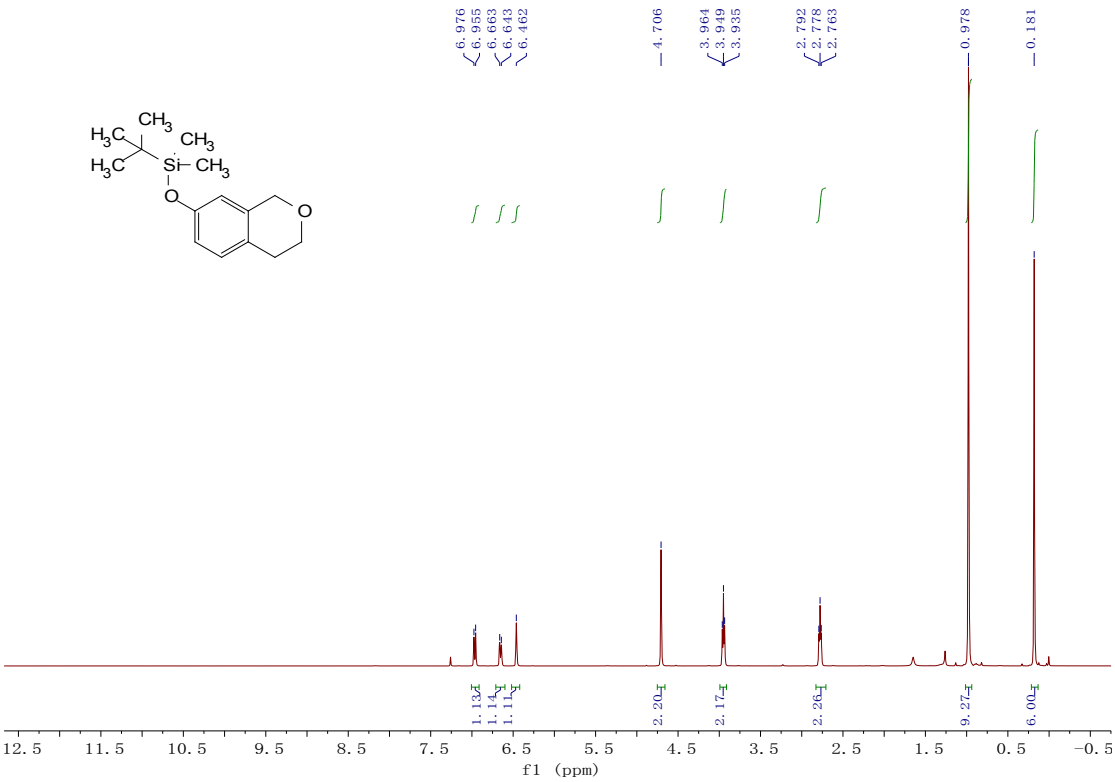


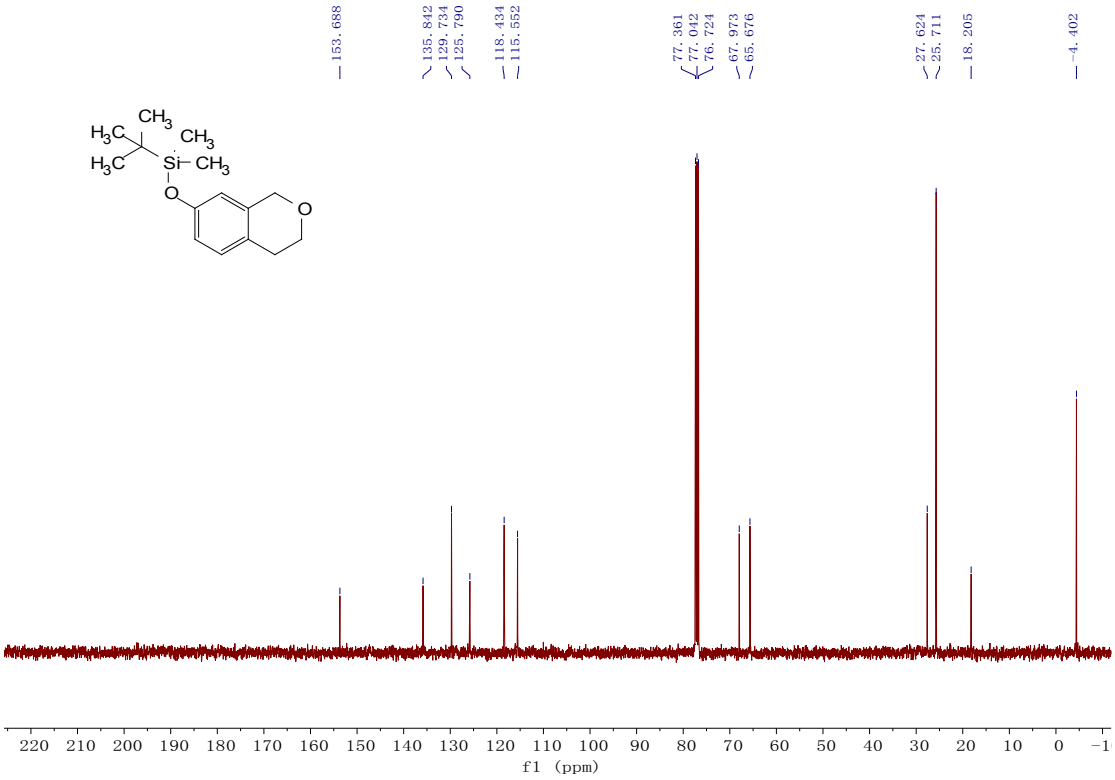
6,7-Dimethoxyisochromane (7b)



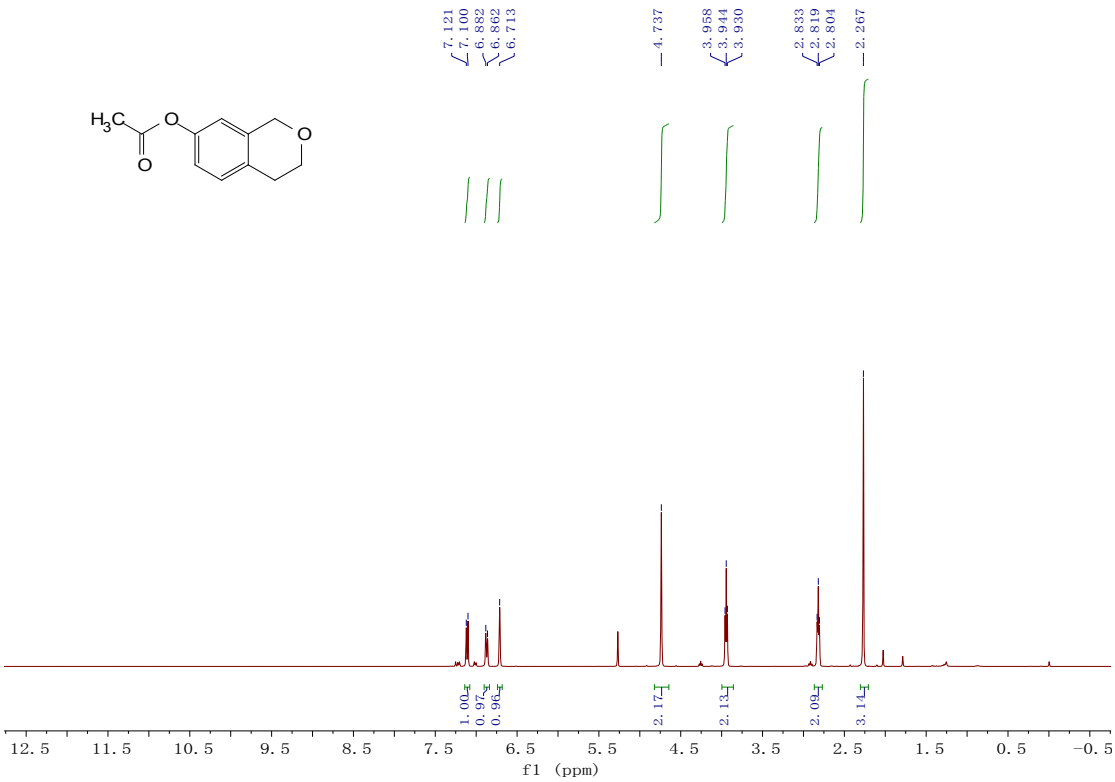


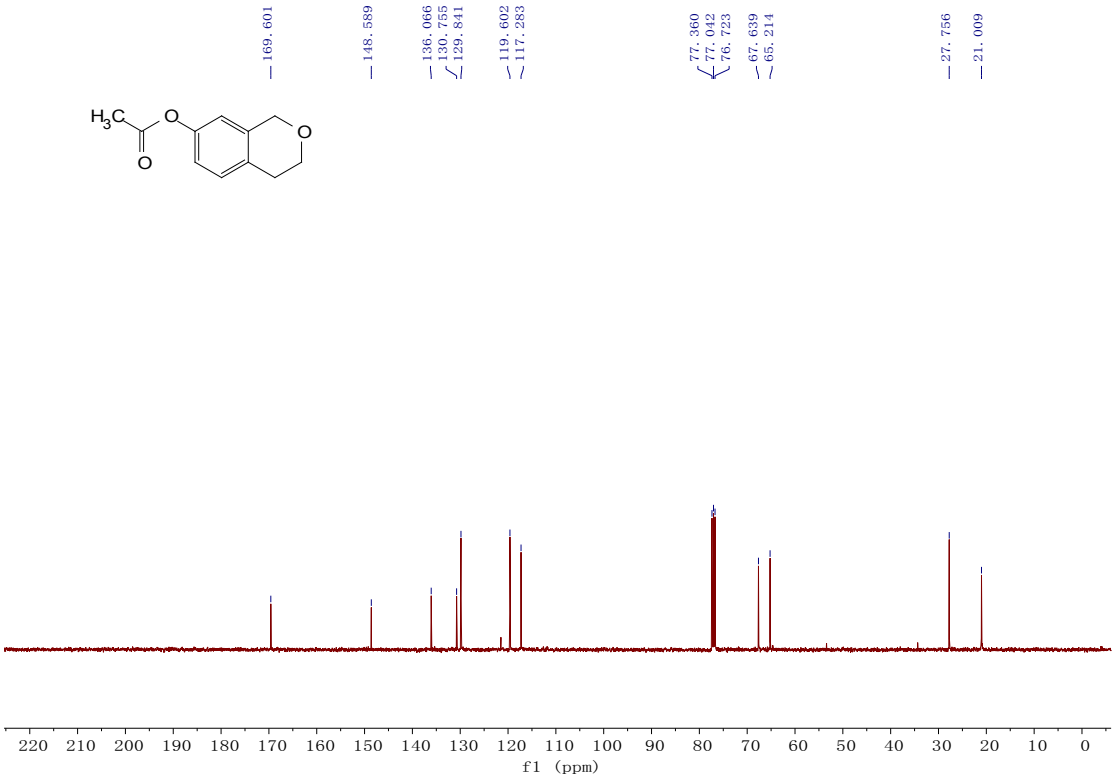
tert-Butyl(isochroman-7-yloxy)dimethylsilane (8b)



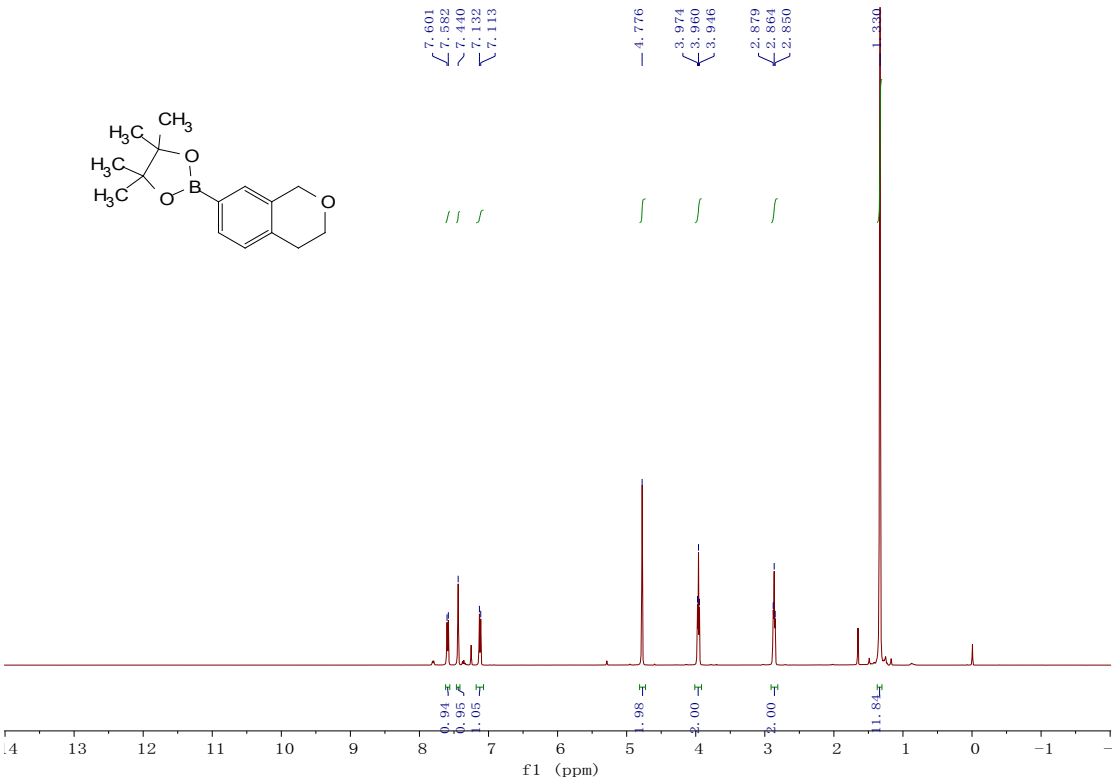


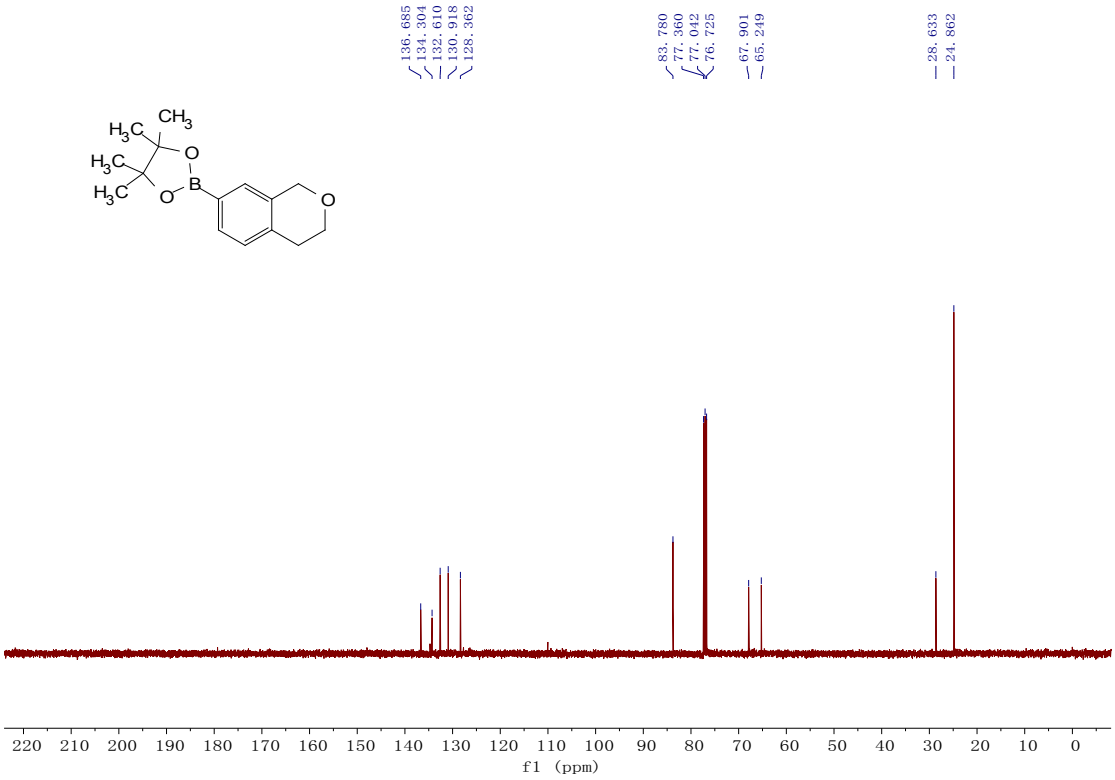
Isochroman-7-yl acetate (9b)



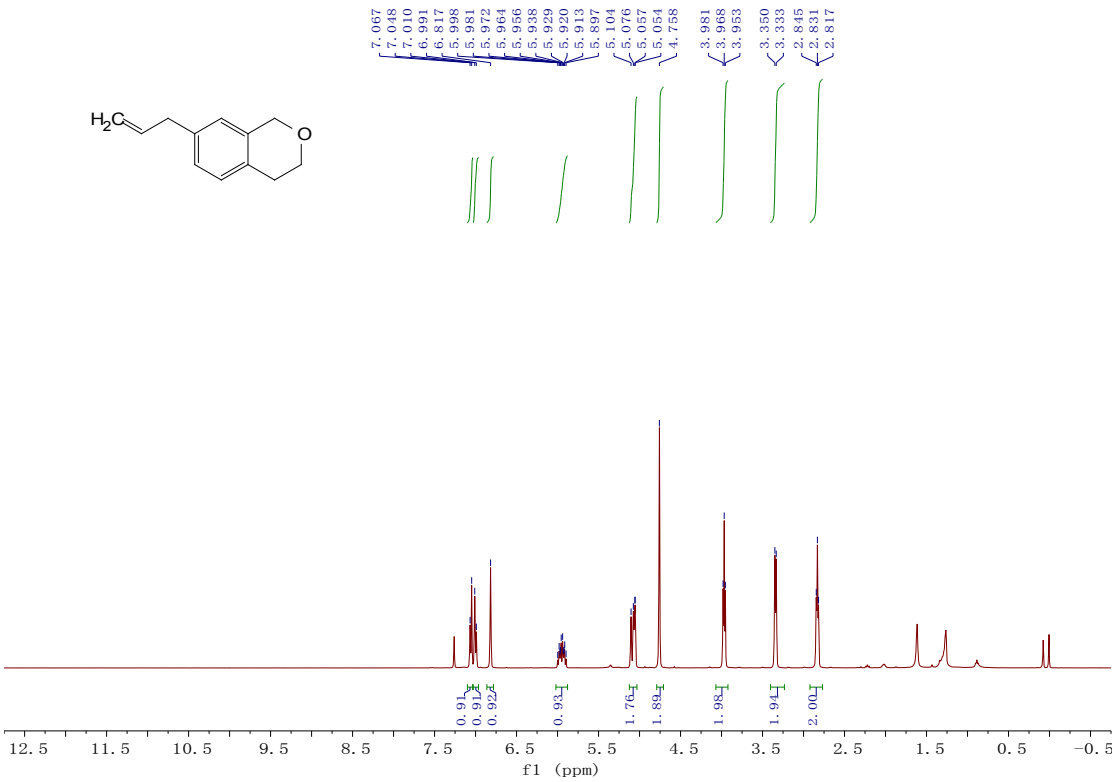


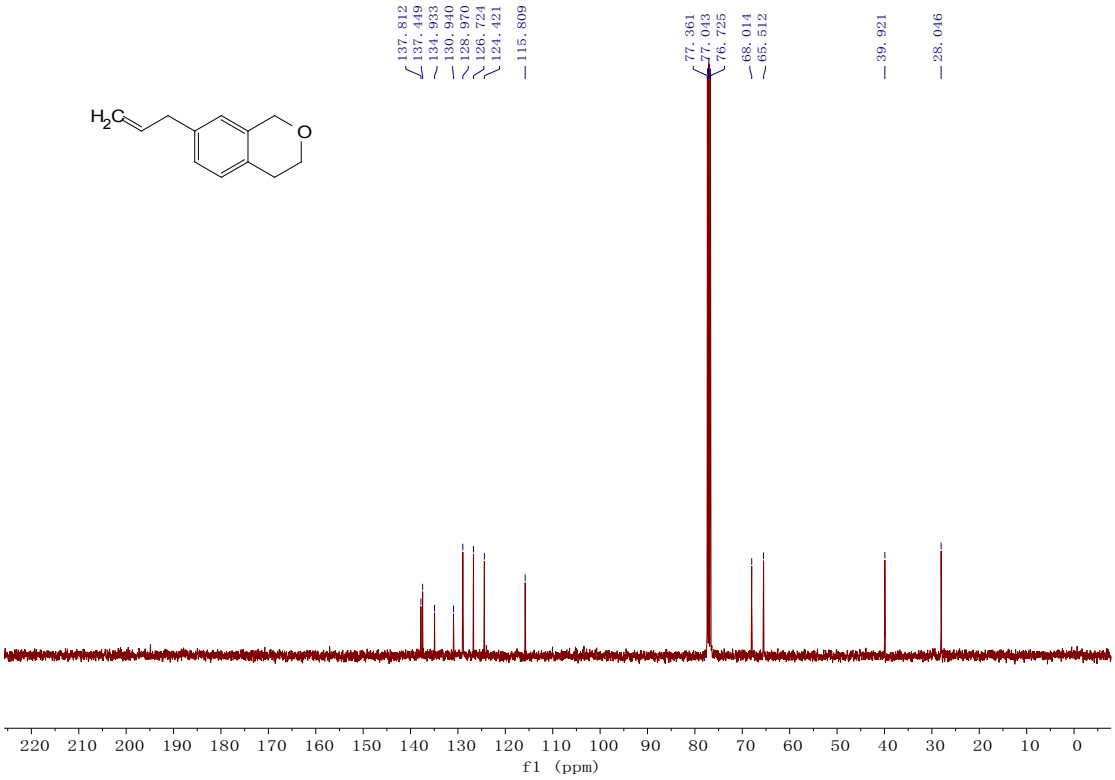
2-(Isochroman-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10b)



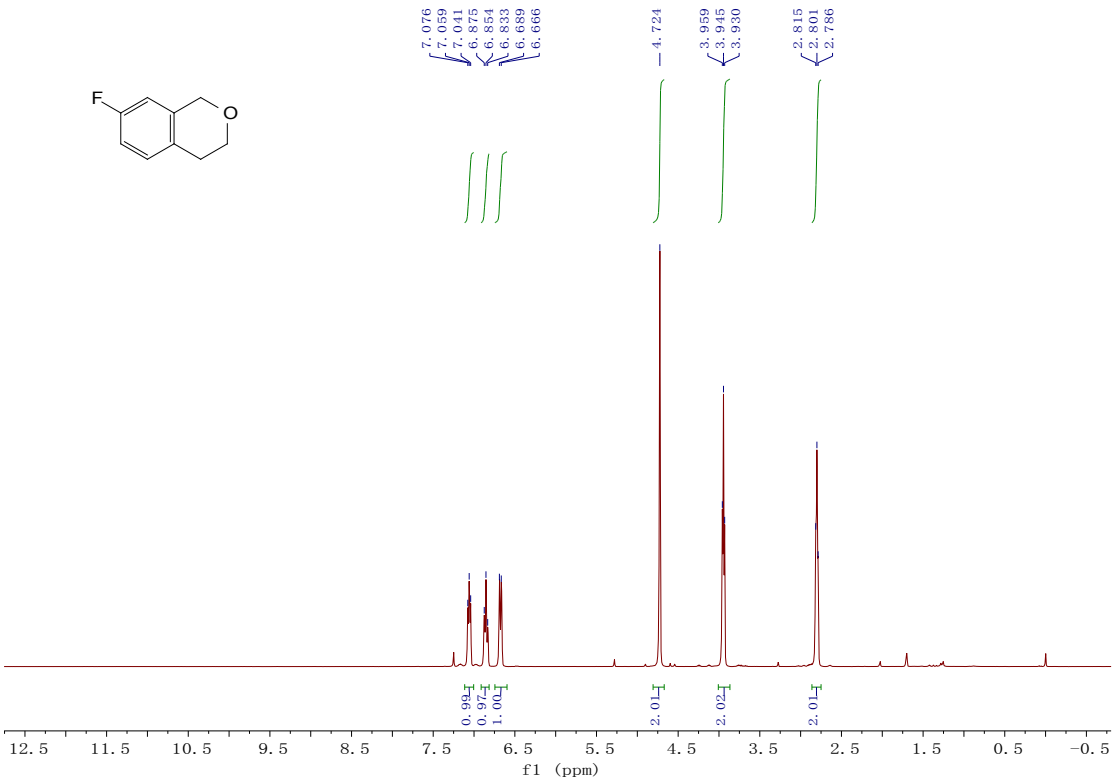


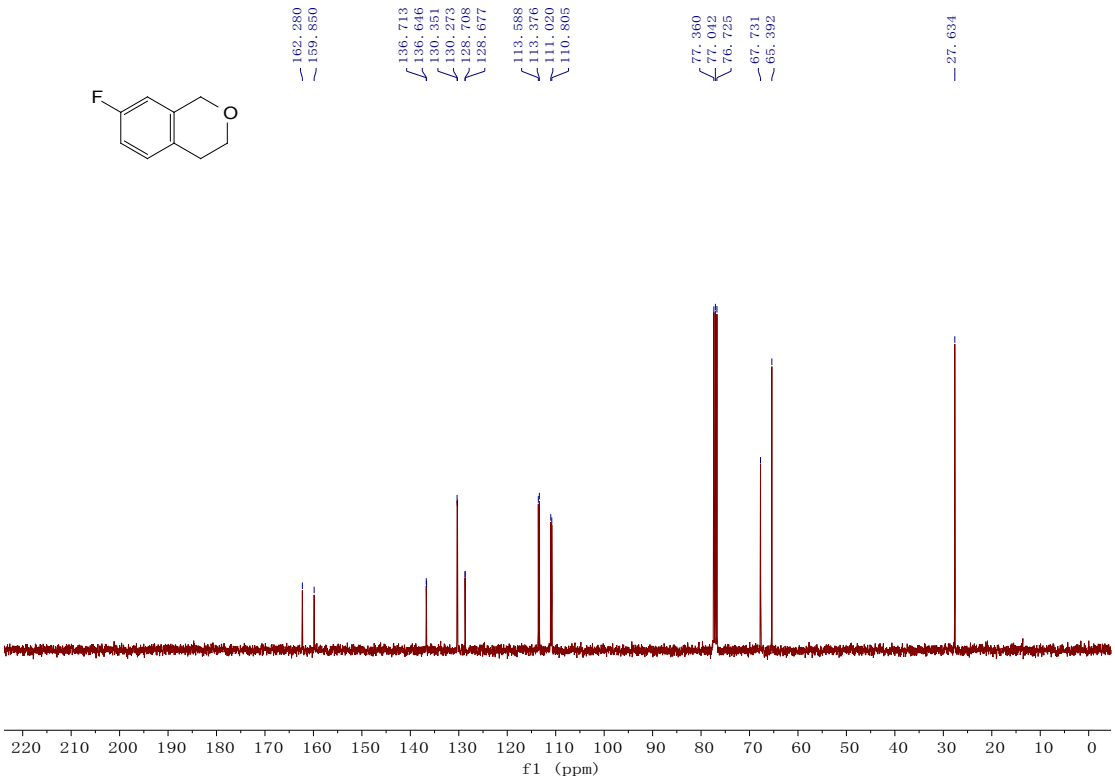
7-Allylisochromane (11b)



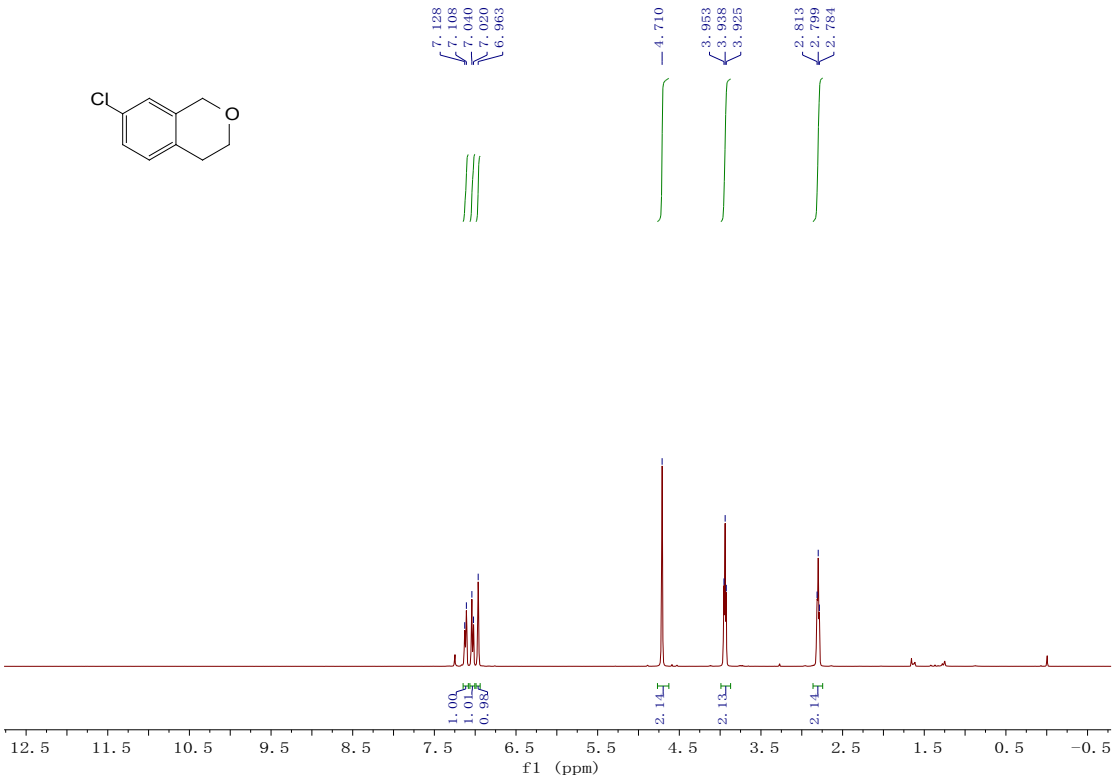


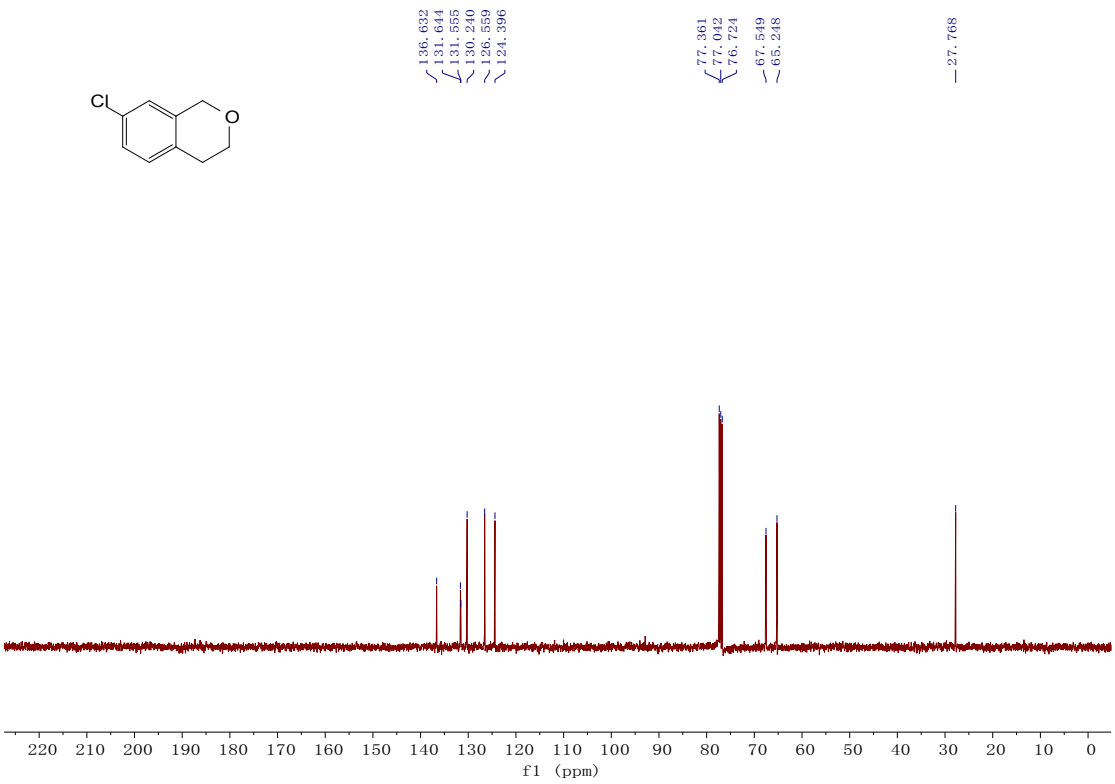
7-Fluoroisochromane (12b)



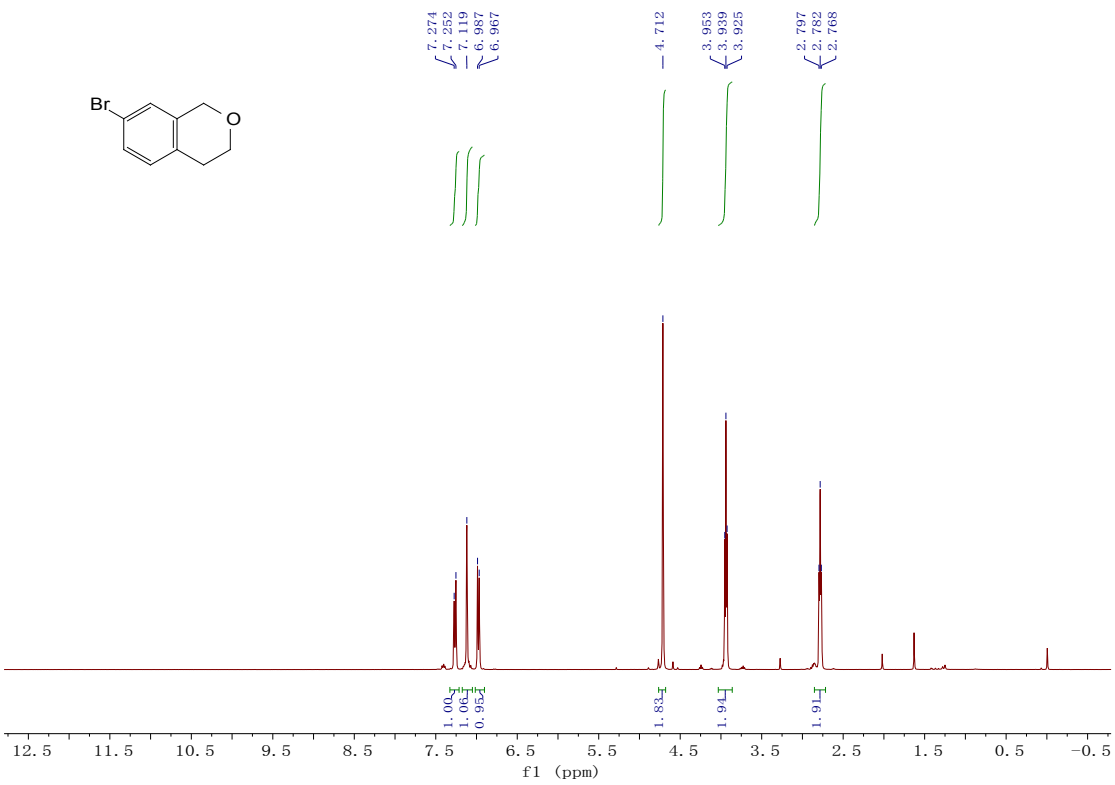


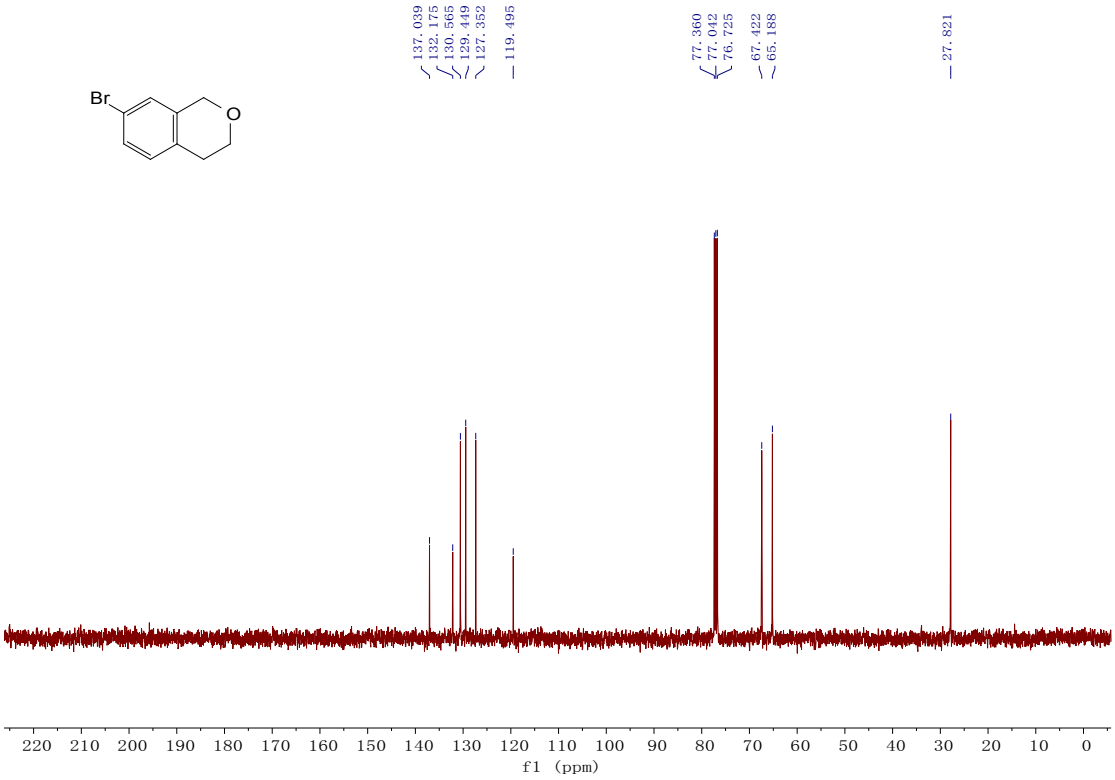
7-Chloroisochromane (13b)



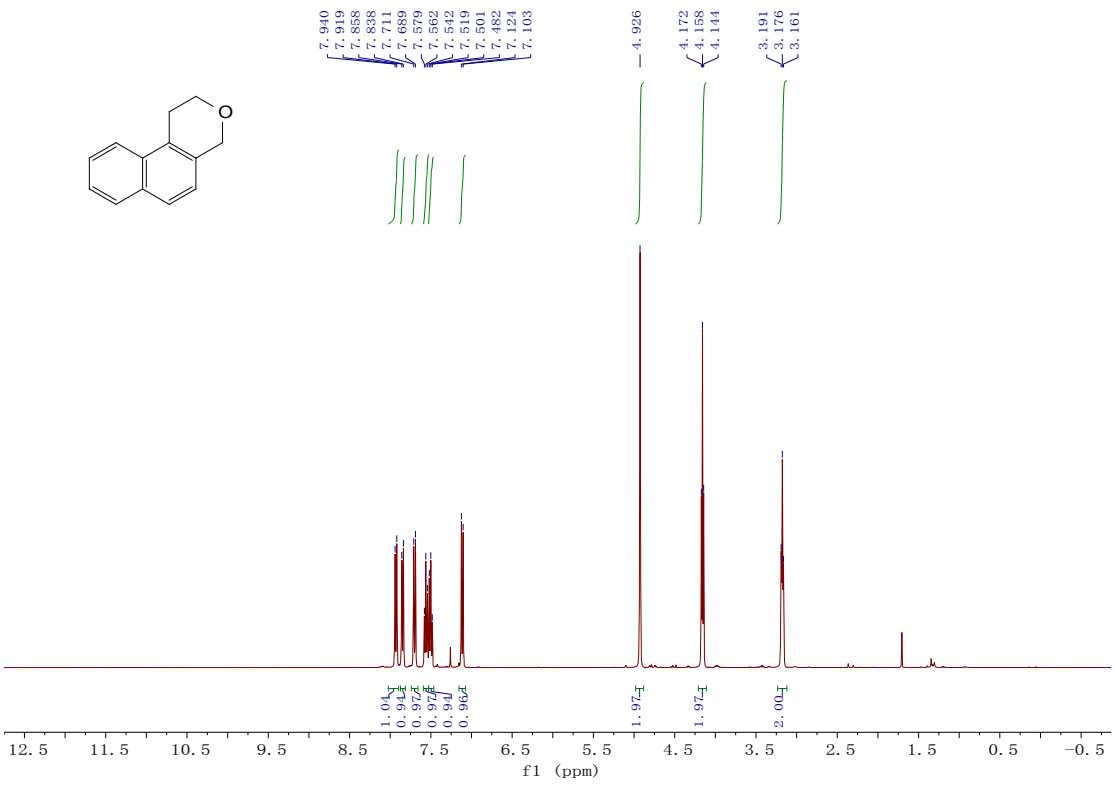


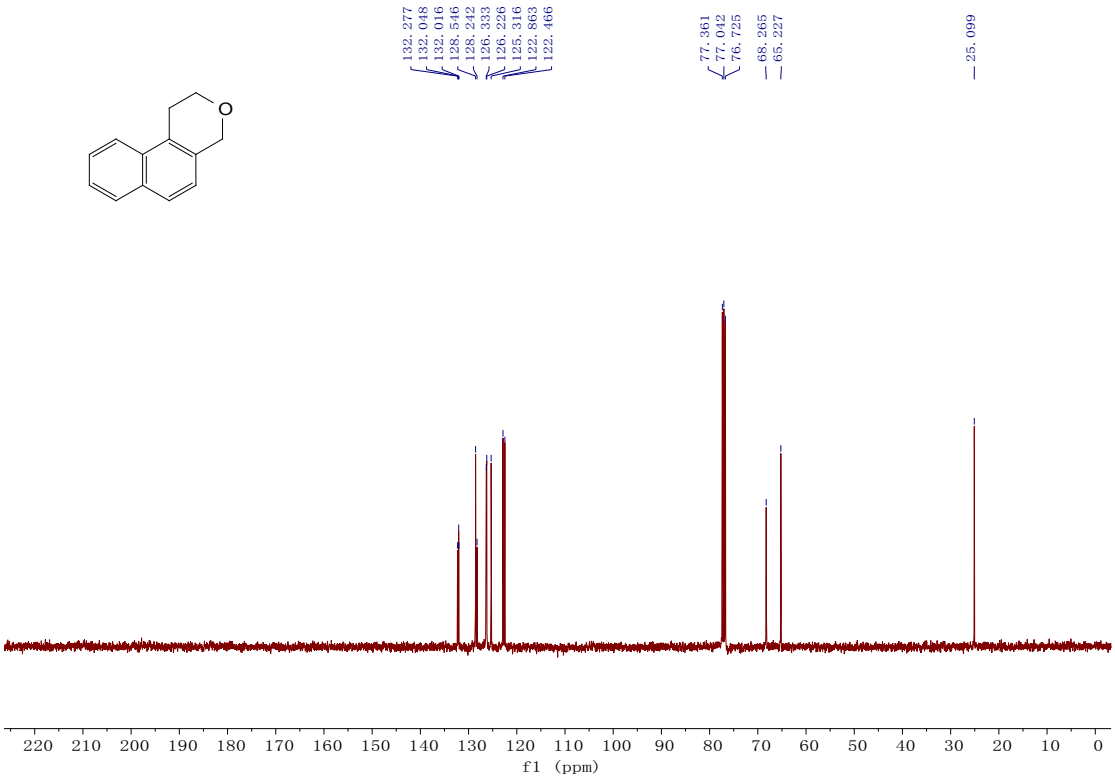
7-Bromoisochromane (14b)



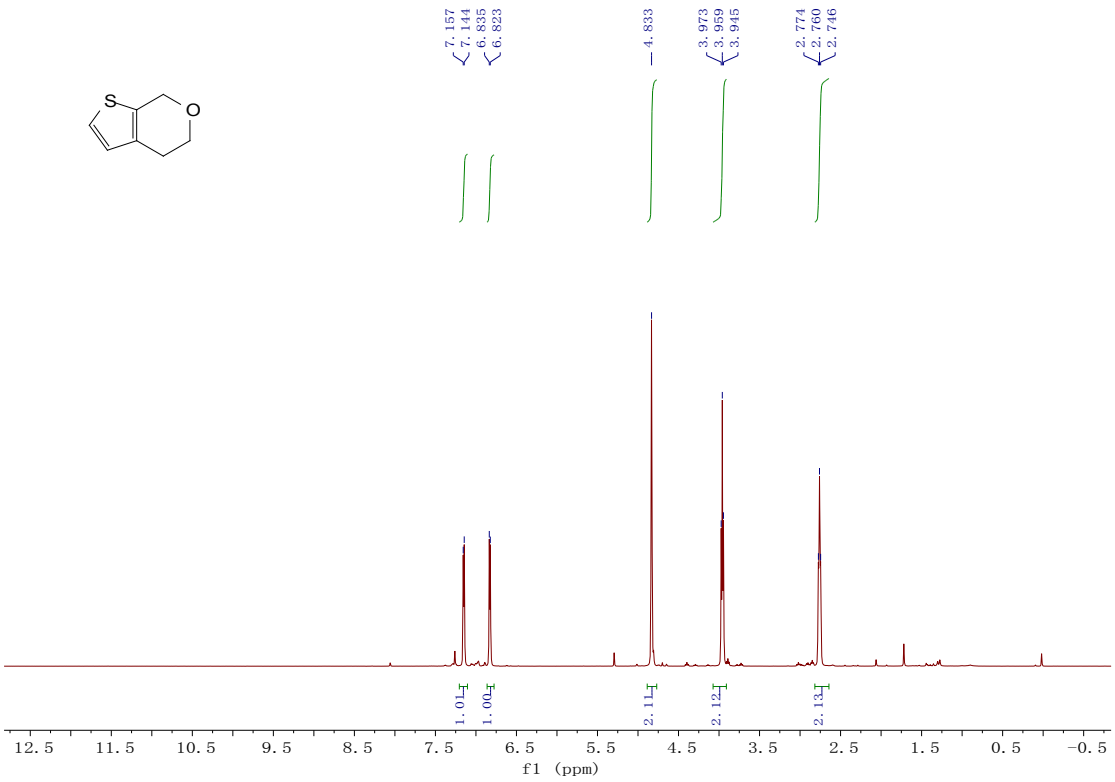


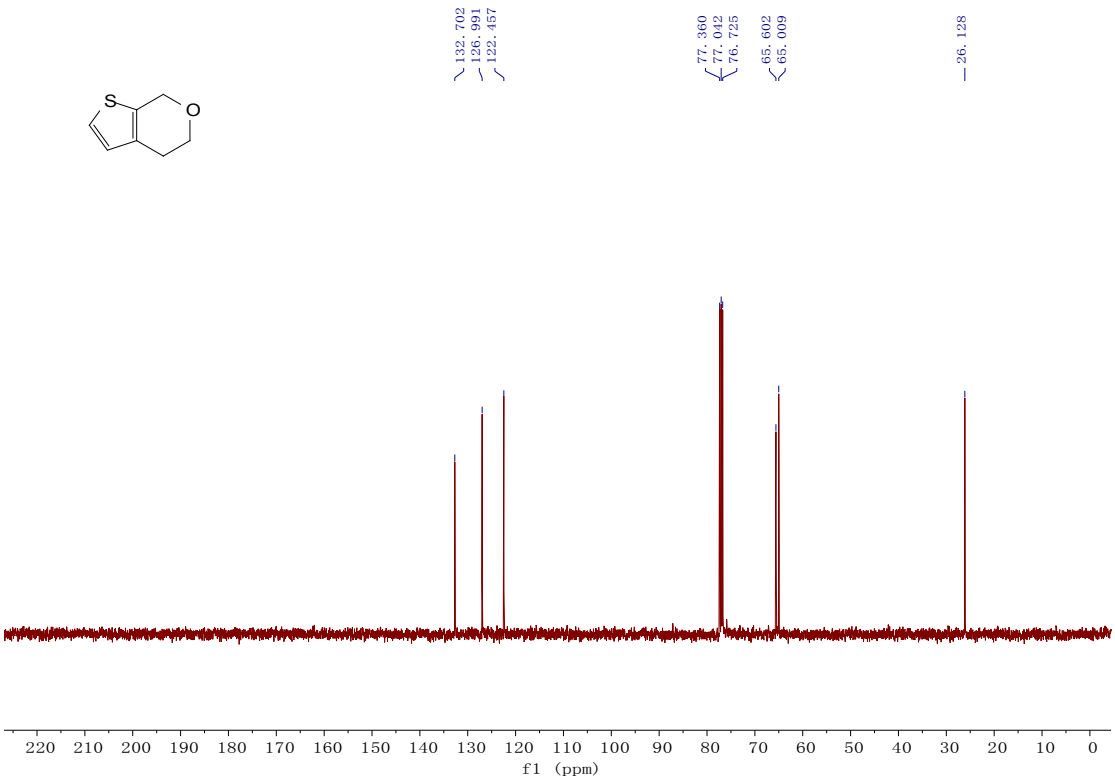
3,4-Dihydro-1*H*-benzo[*h*]isochromene (15b)



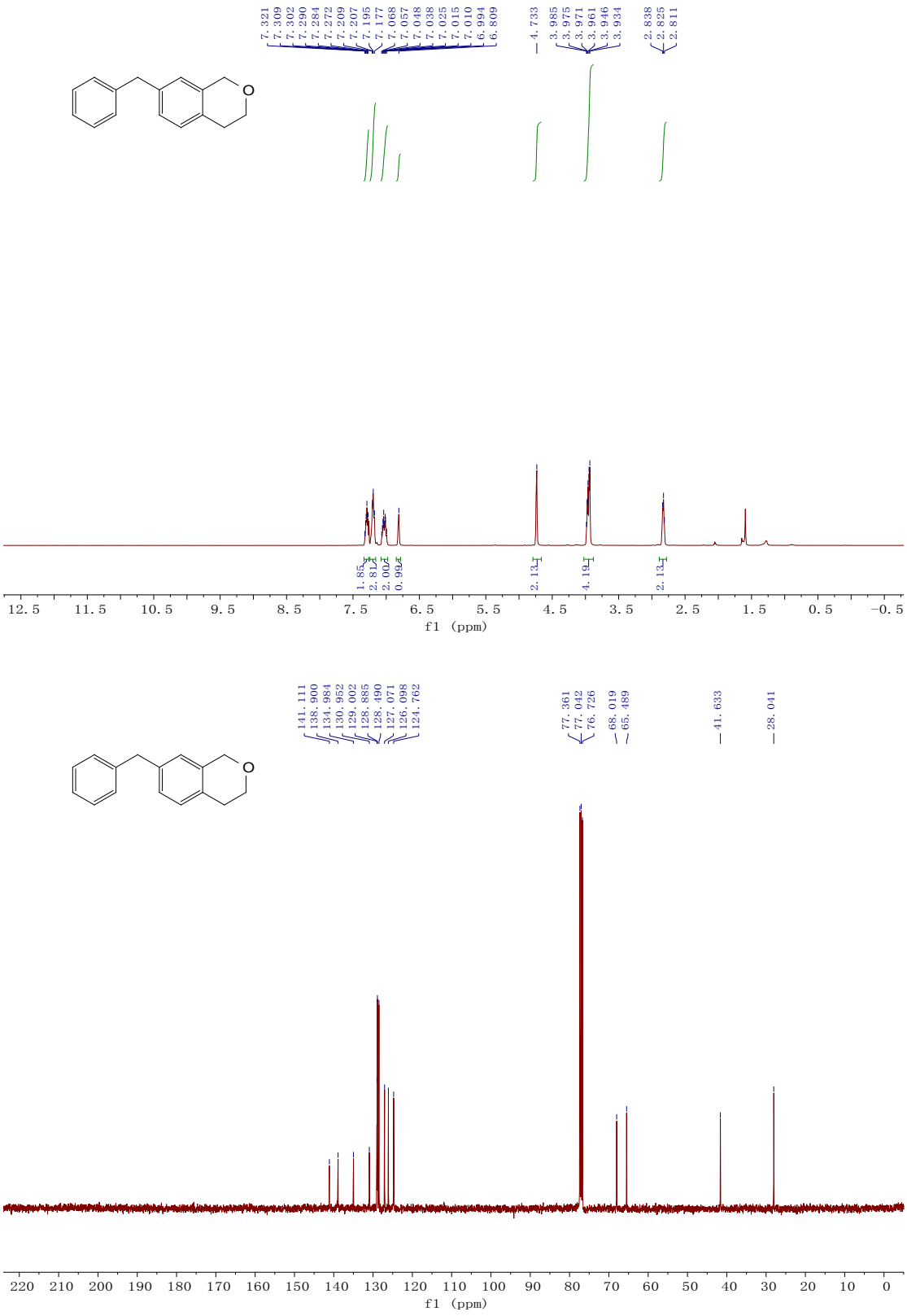


4,7-Dihydro-5*H*-thieno[2,3-*c*]pyran (16b)

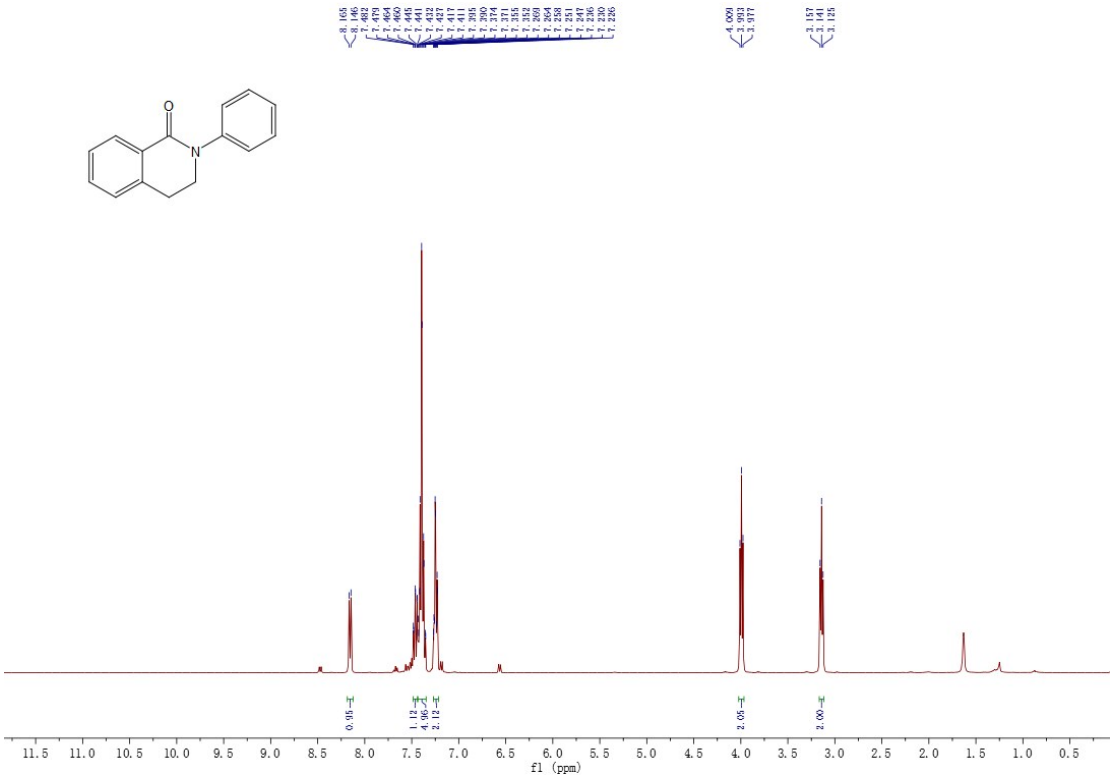

7.157
7.144
6.835
6.823
4.833
3.973
3.959
3.945
2.774
2.760
2.746
1.01
1.00
2.11
2.12
2.13
12.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5
f1 (ppm)

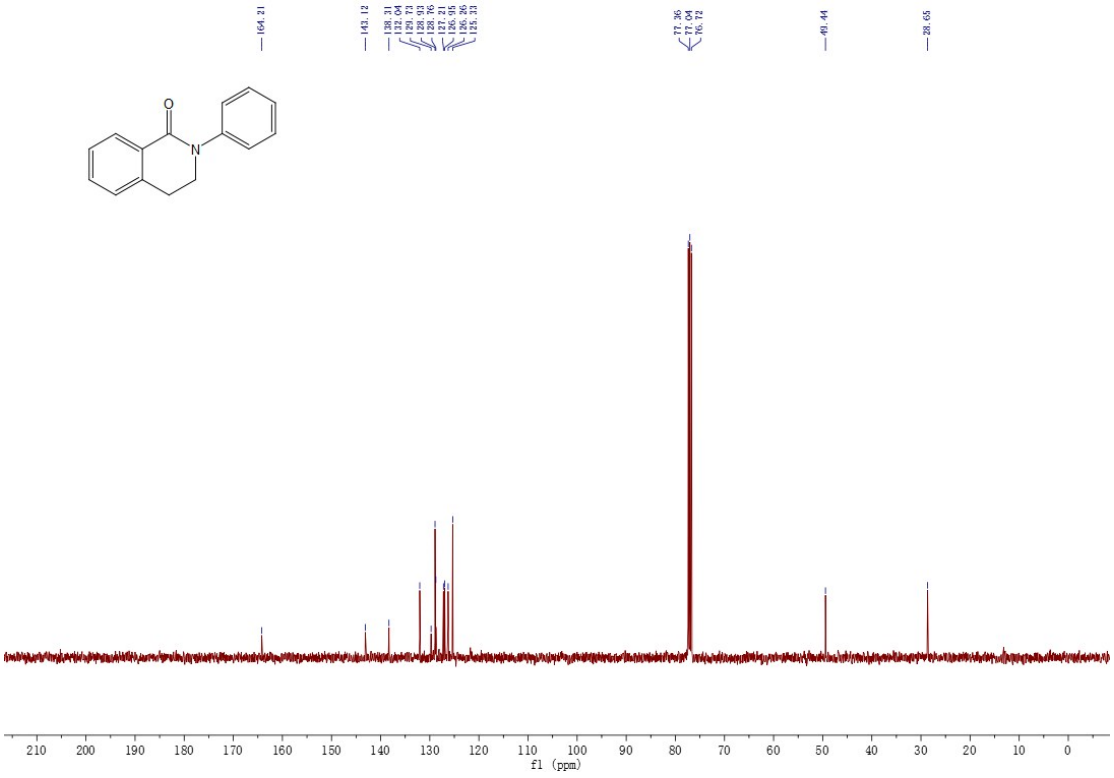

132.702
126.991
122.457
77.360
77.042
76.725
65.602
65.009
26.128
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

7-Benzylisochromane (22b)

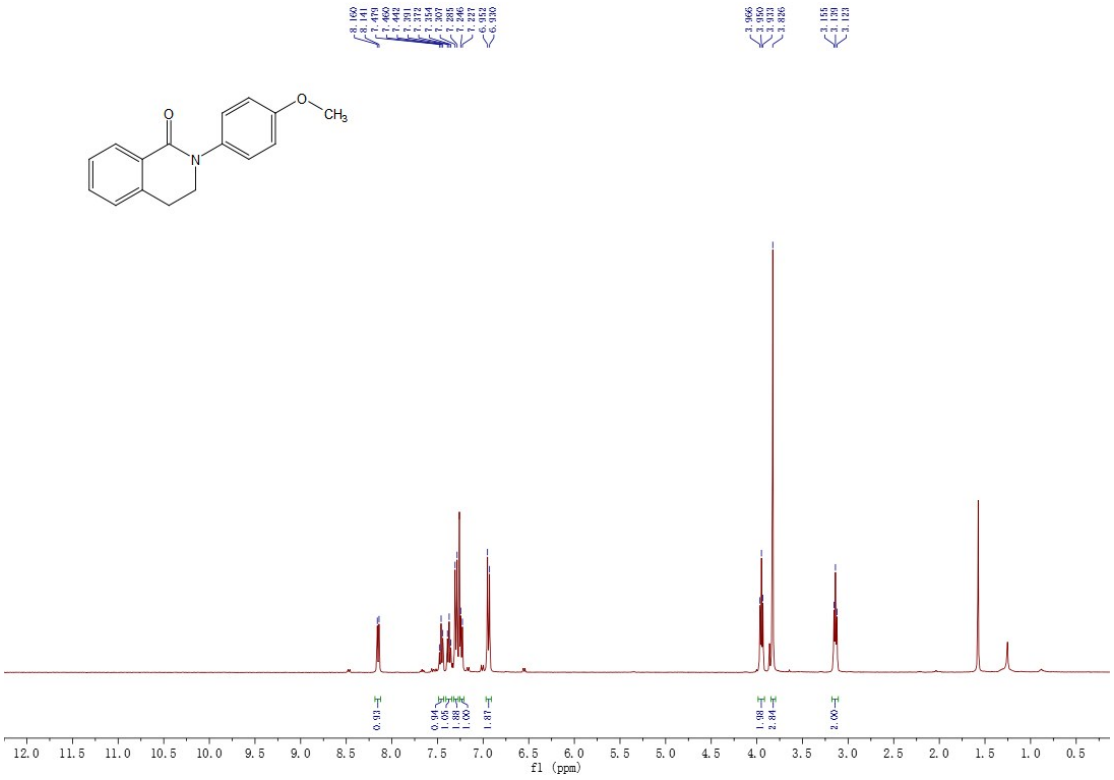


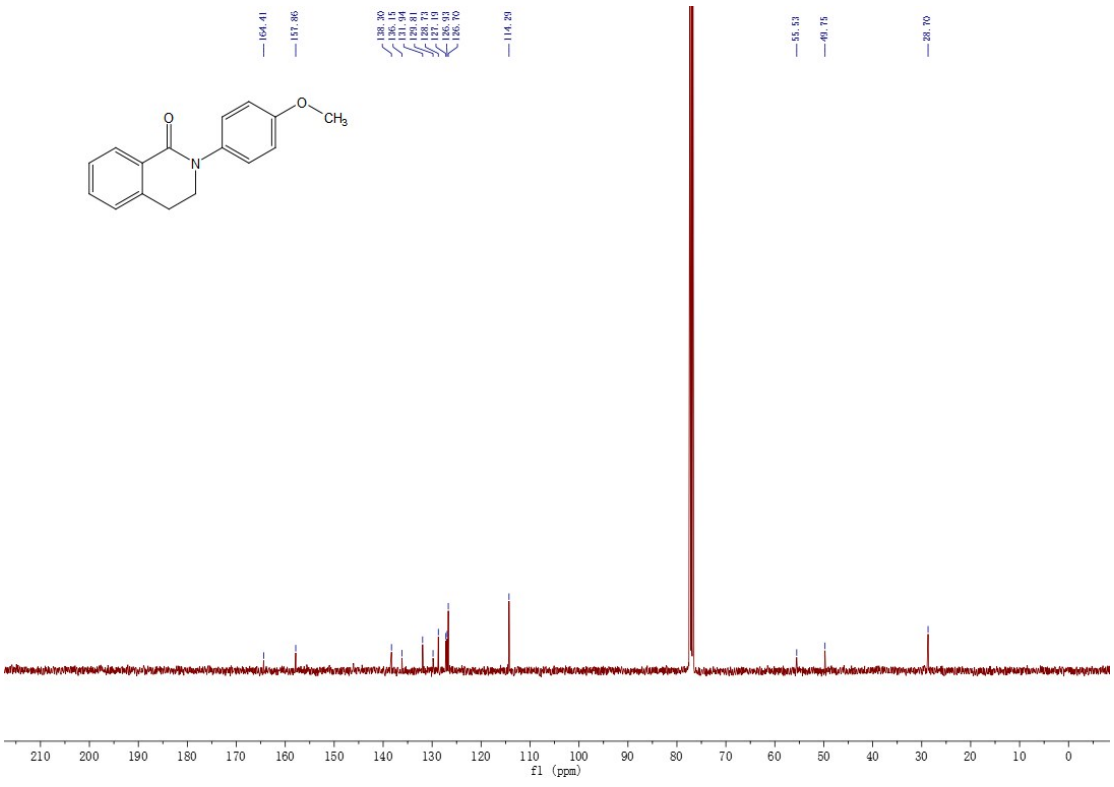
2-Phenyl-3,4-dihydroisoquinolin-1(2*H*)-one (1aa)



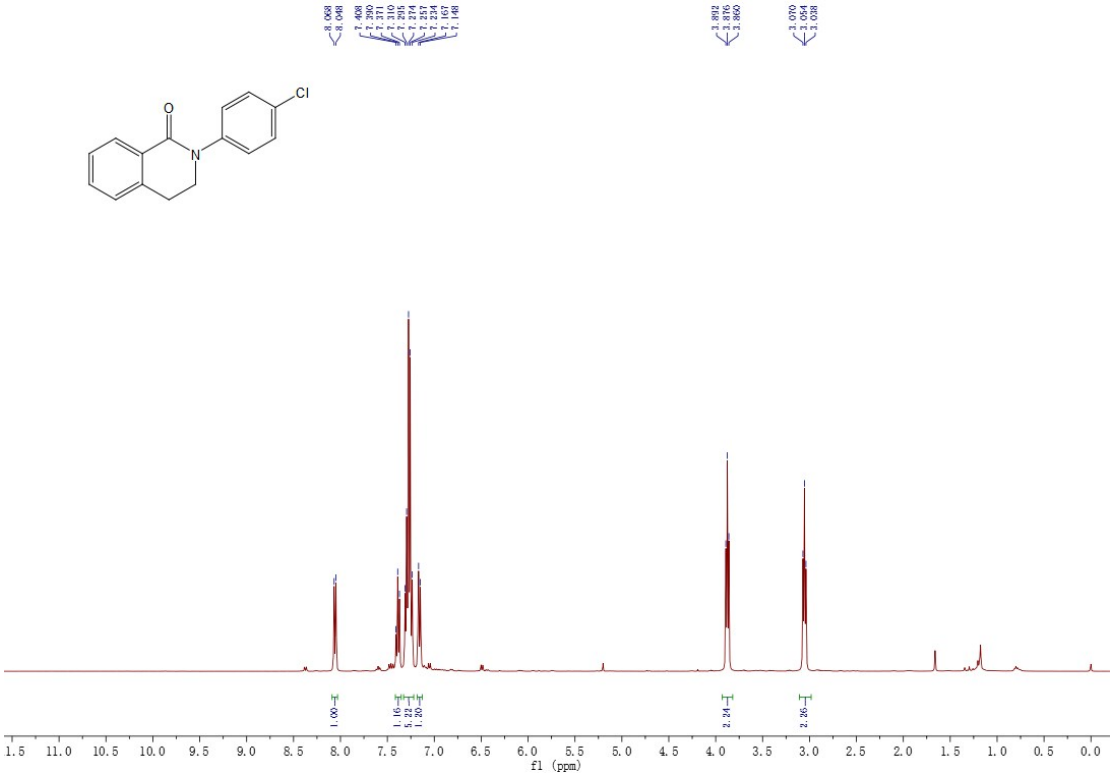


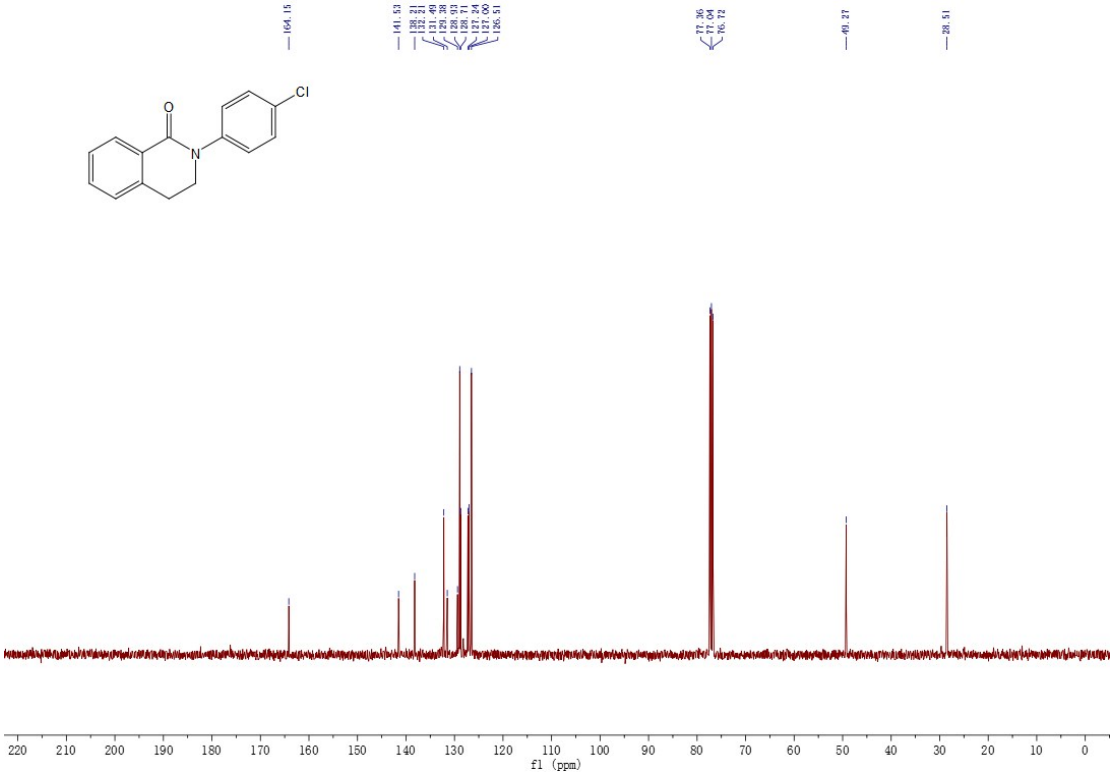
2-(4-Methoxyphenyl)-3,4-dihydroisoquinolin-1(2*H*)-one (2aa)



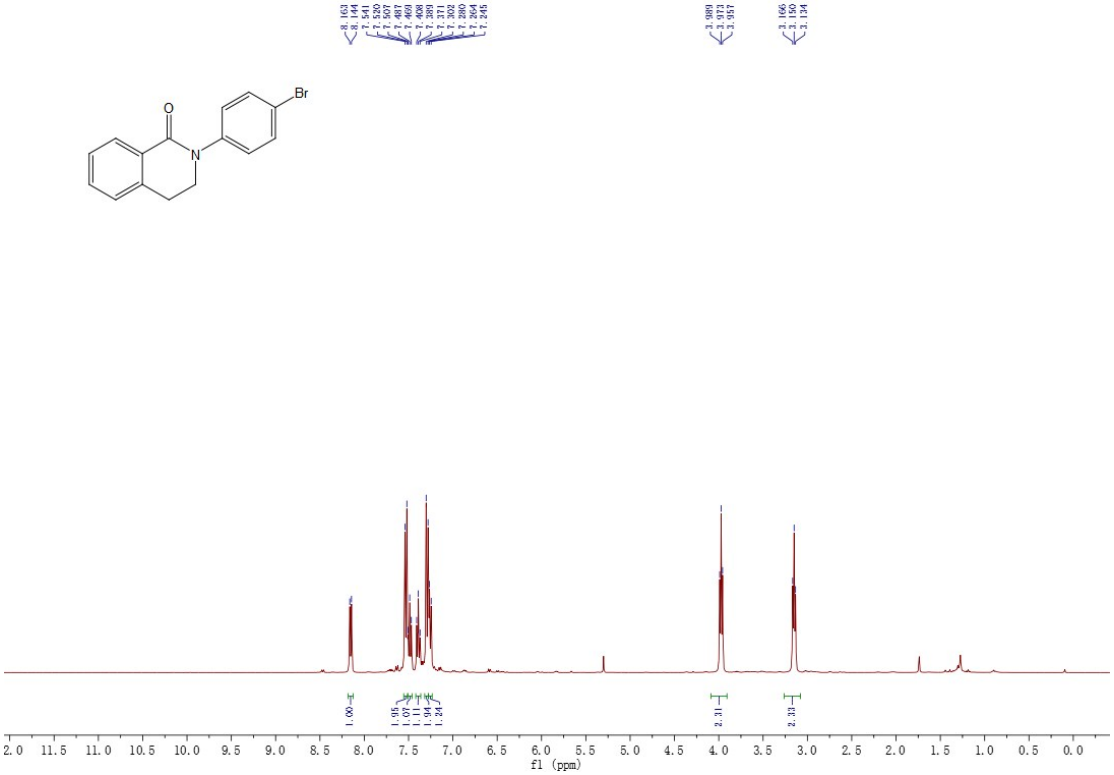


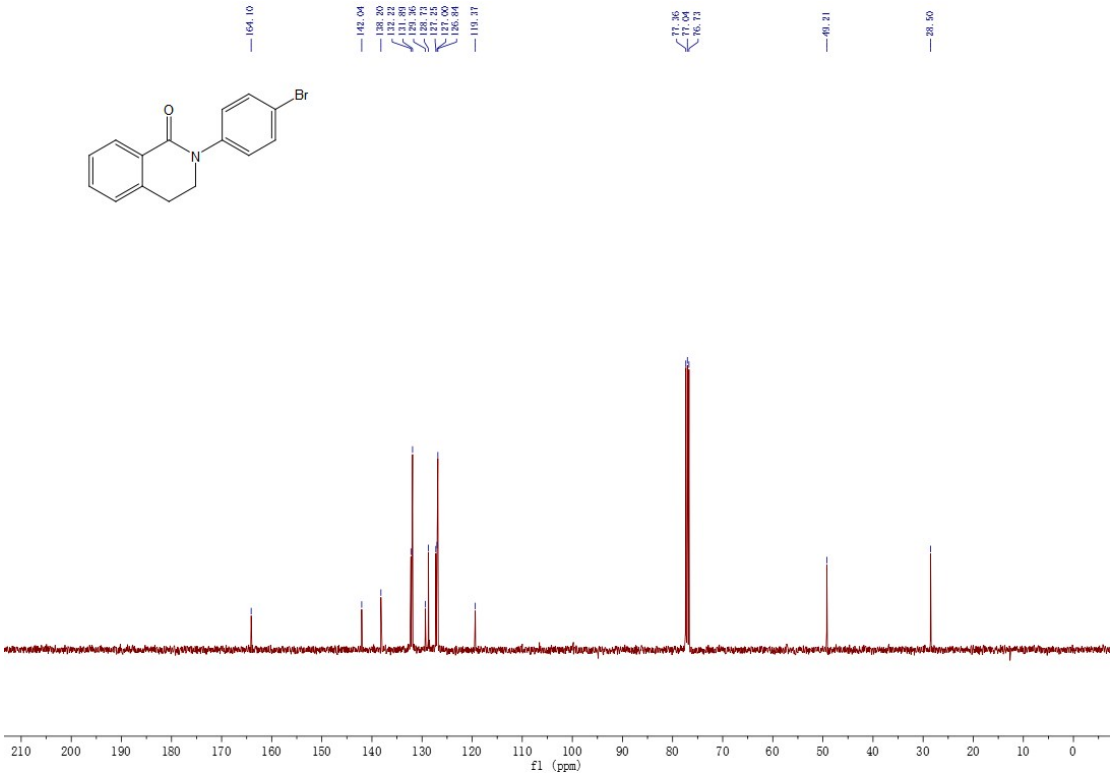
3-(4-Chlorophenyl)-3,4-dihydroisoquinolin-1(2*H*)-one (3aa)



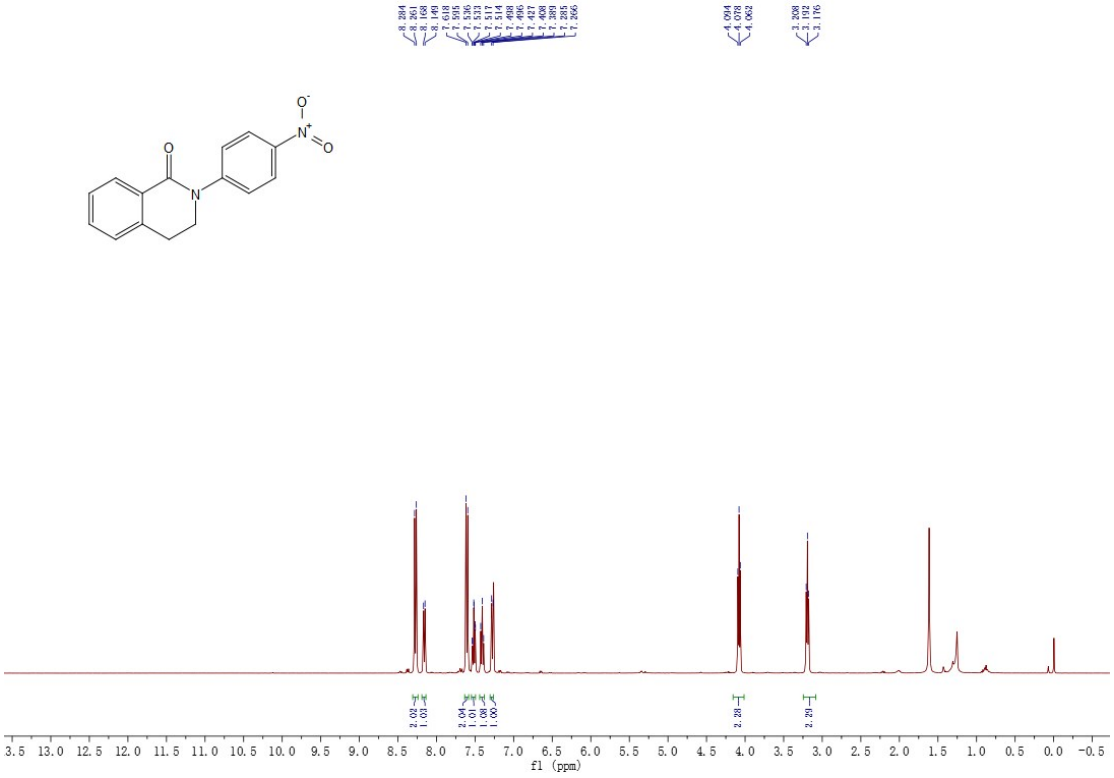


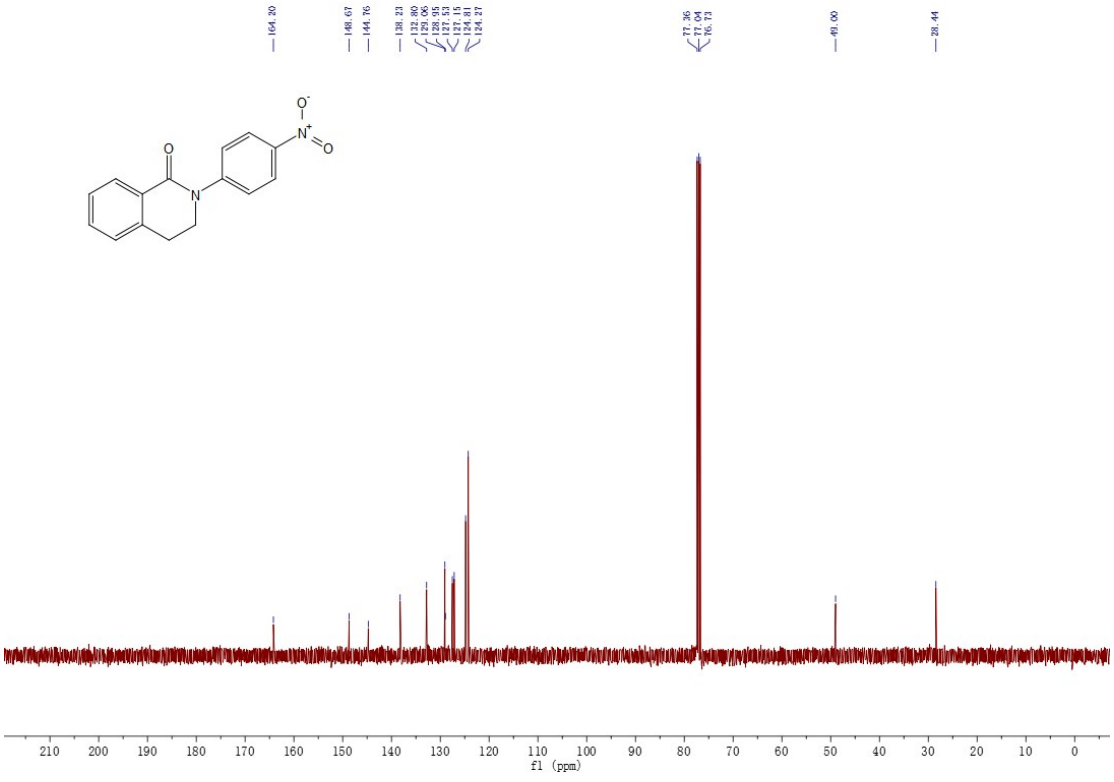
2-(4-Bromophenyl)-3,4-dihydroisoquinolin-1(2*H*)-one (4aa)



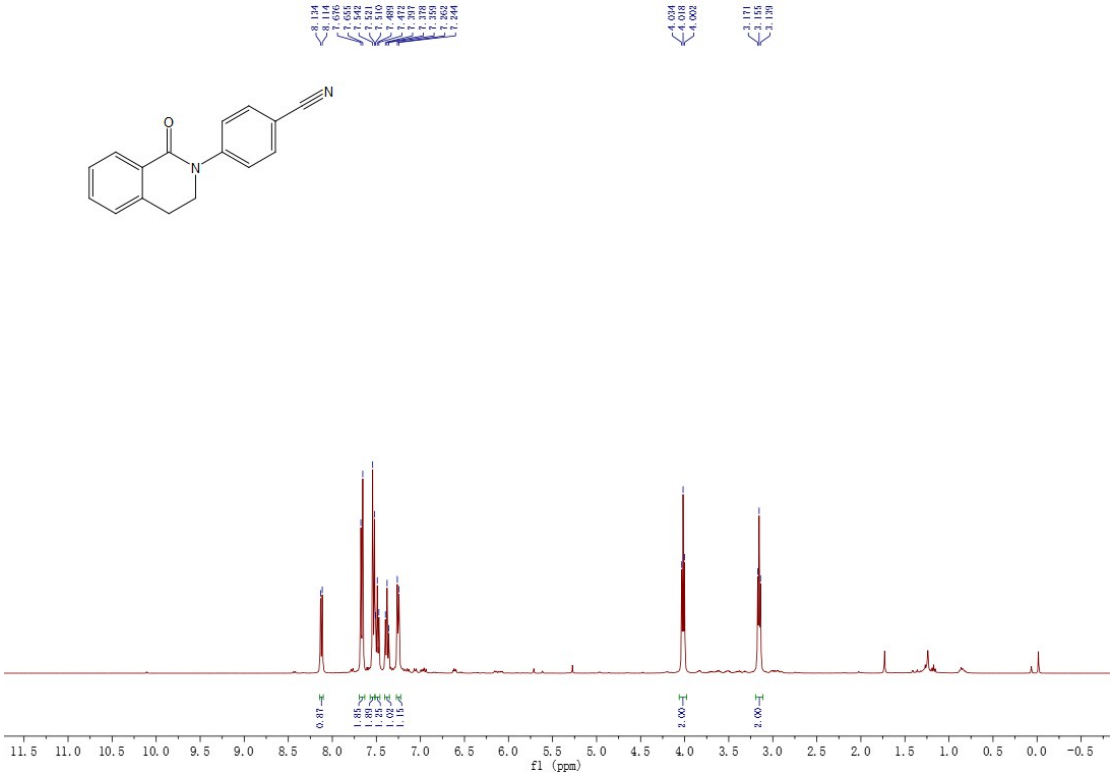


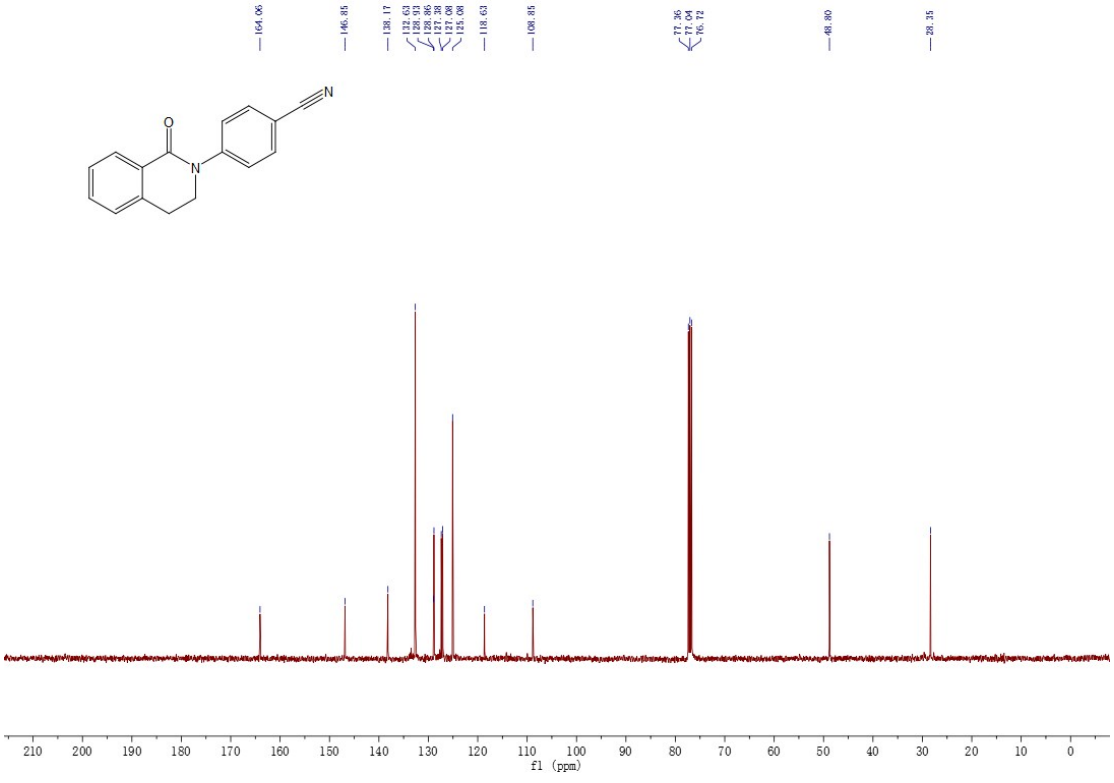
2-(4-Nitrophenyl)-3,4-dihydroisoquinolin-1(2*H*)-one (5aa)



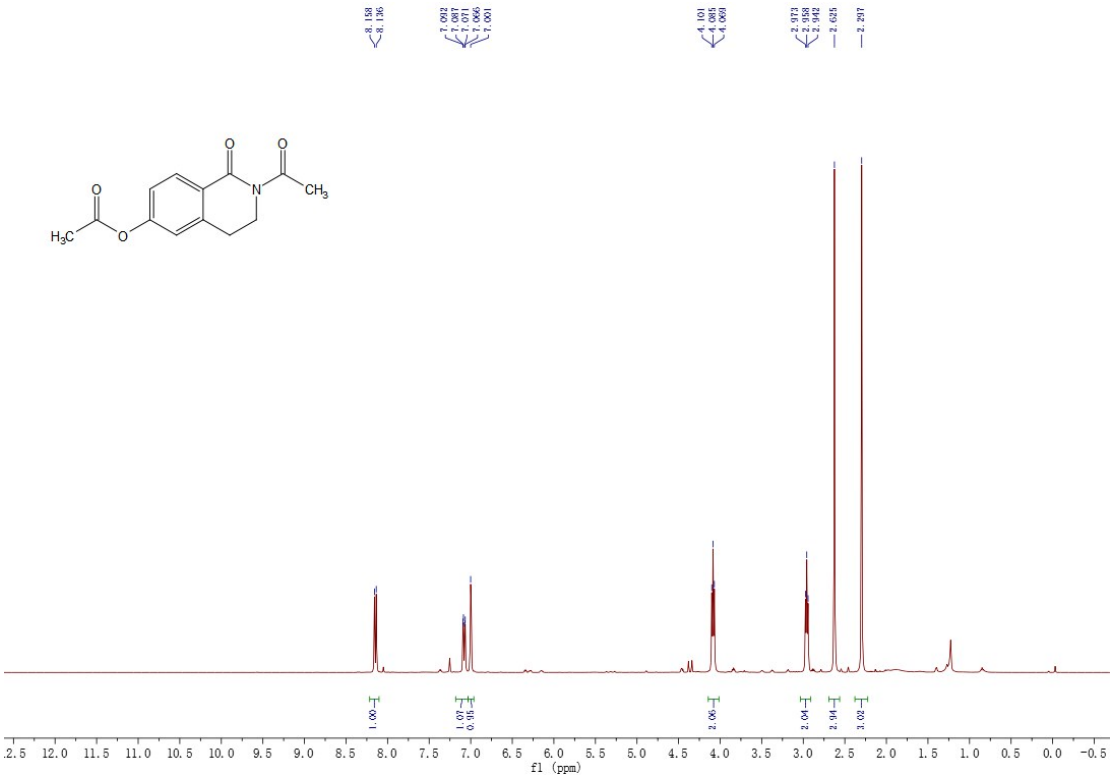


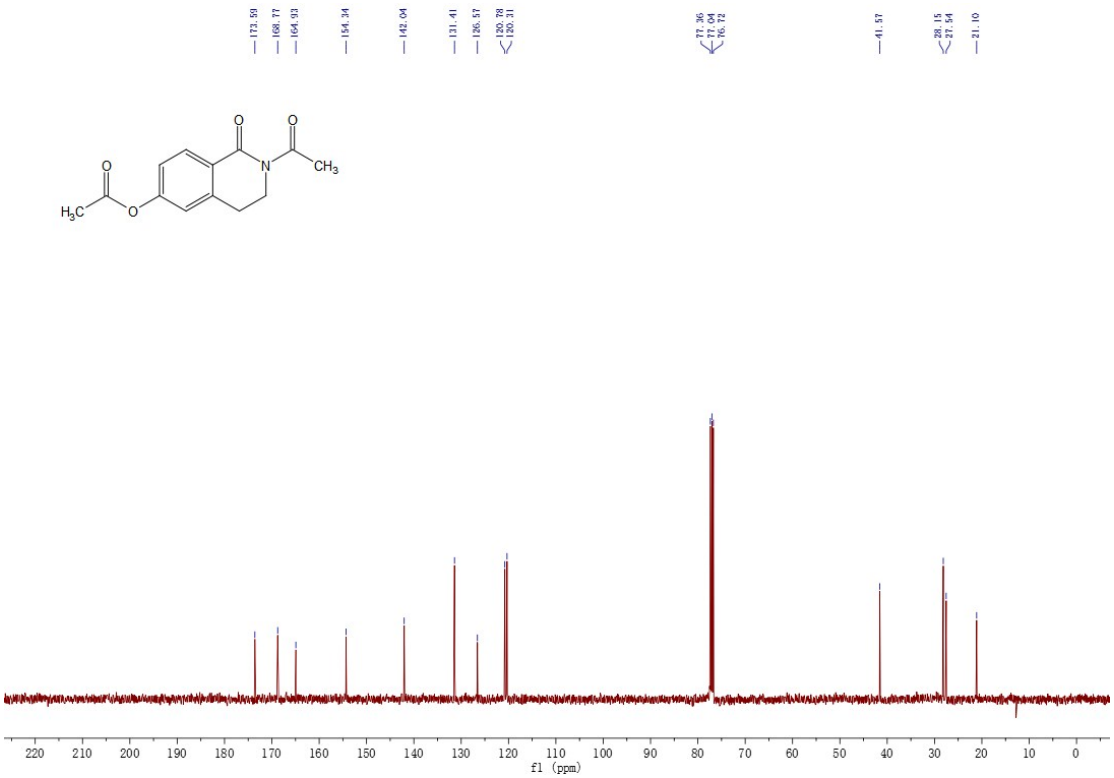
4-(1-Oxo-3,4-dihydroisoquinolin-2(1*H*)-yl)benzonitrile (6aa)



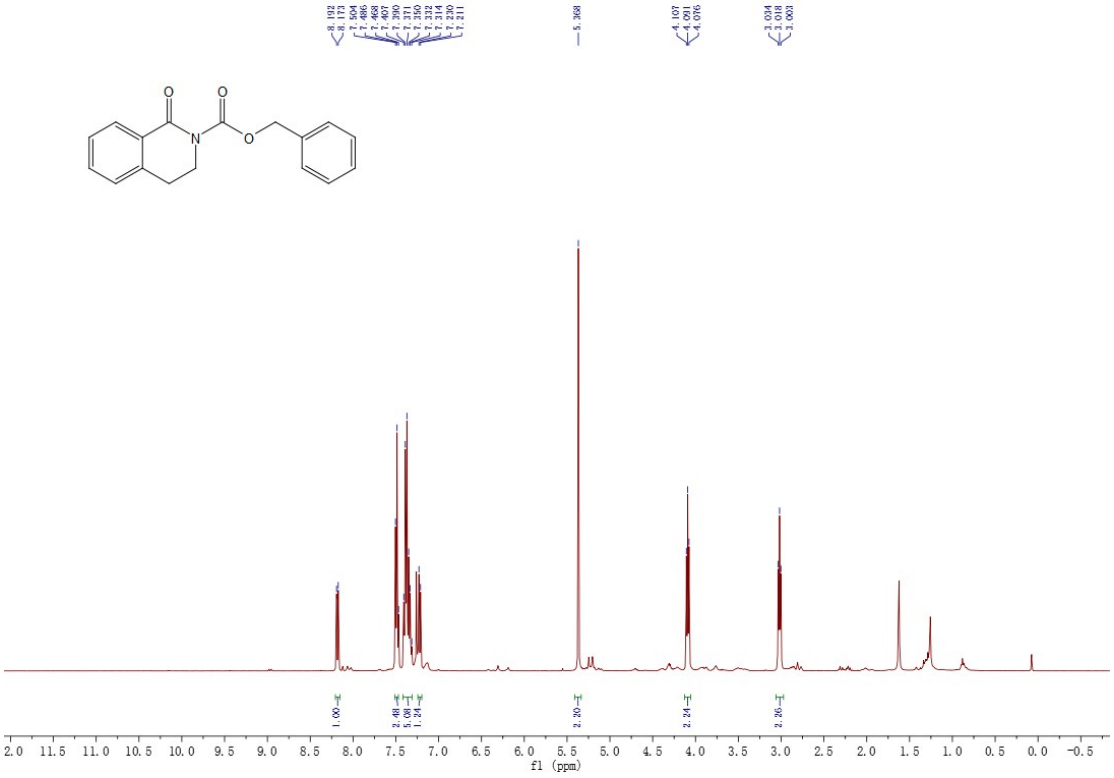


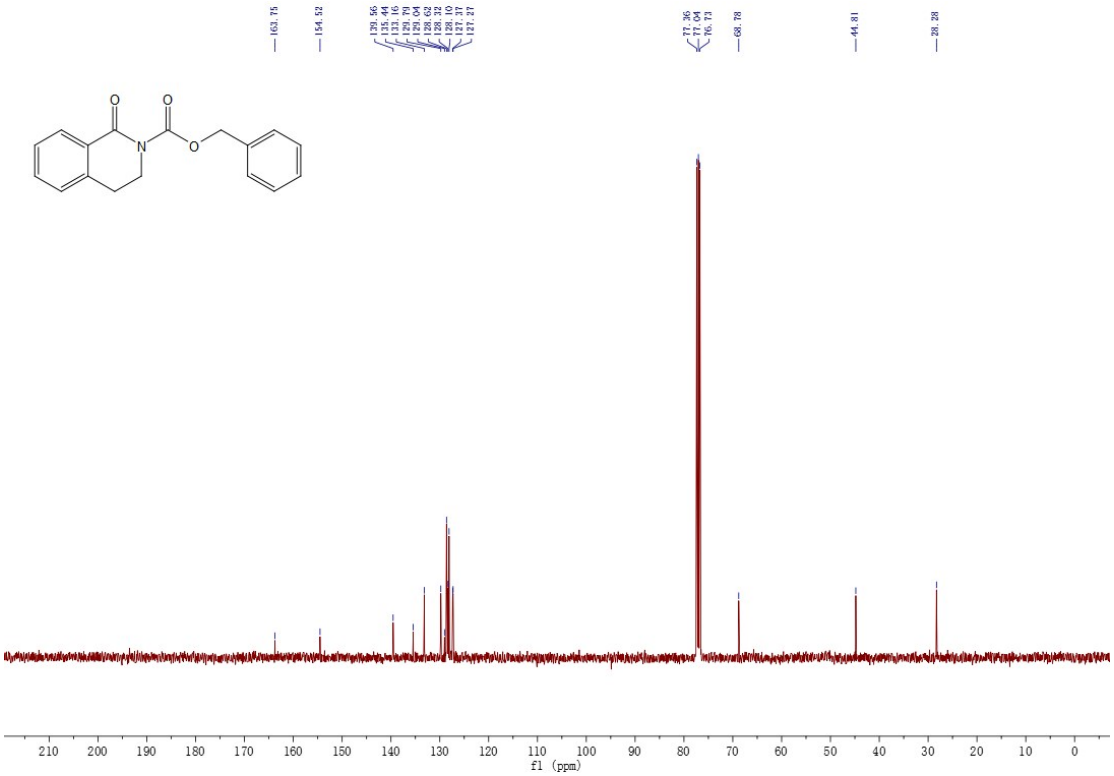
2-Acetyl-1-oxo-1,2,3,4-tetrahydroisoquinolin-6-yl acetate (7aa)



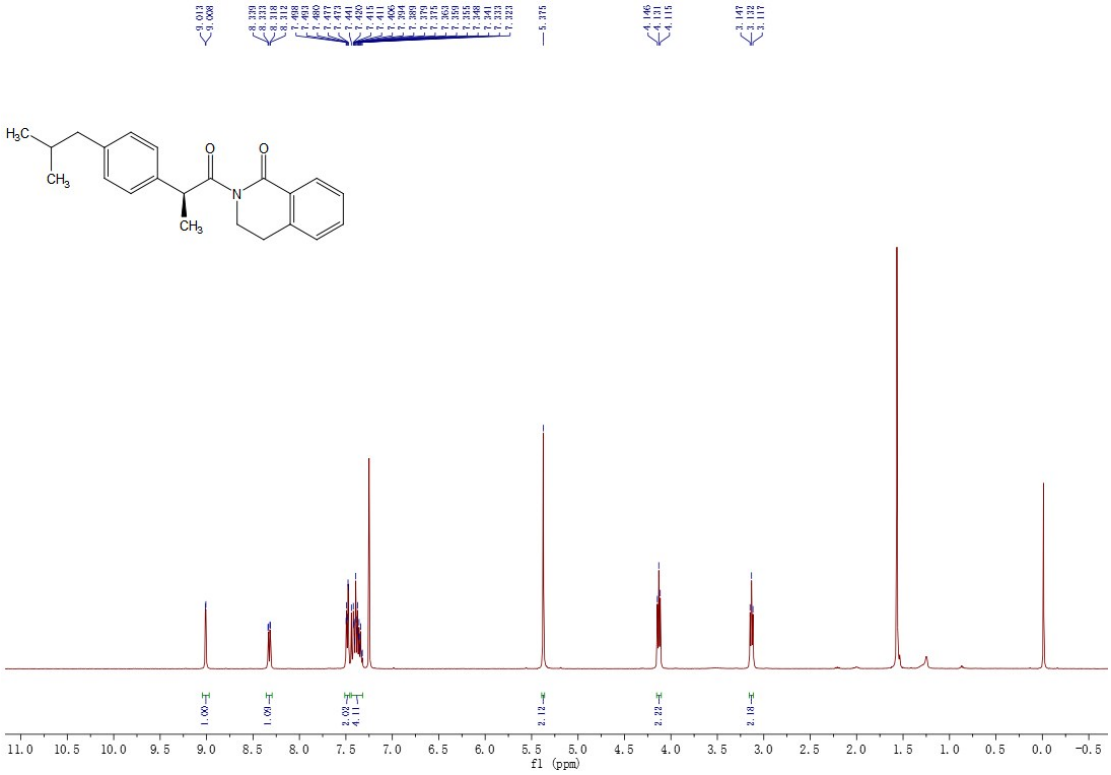


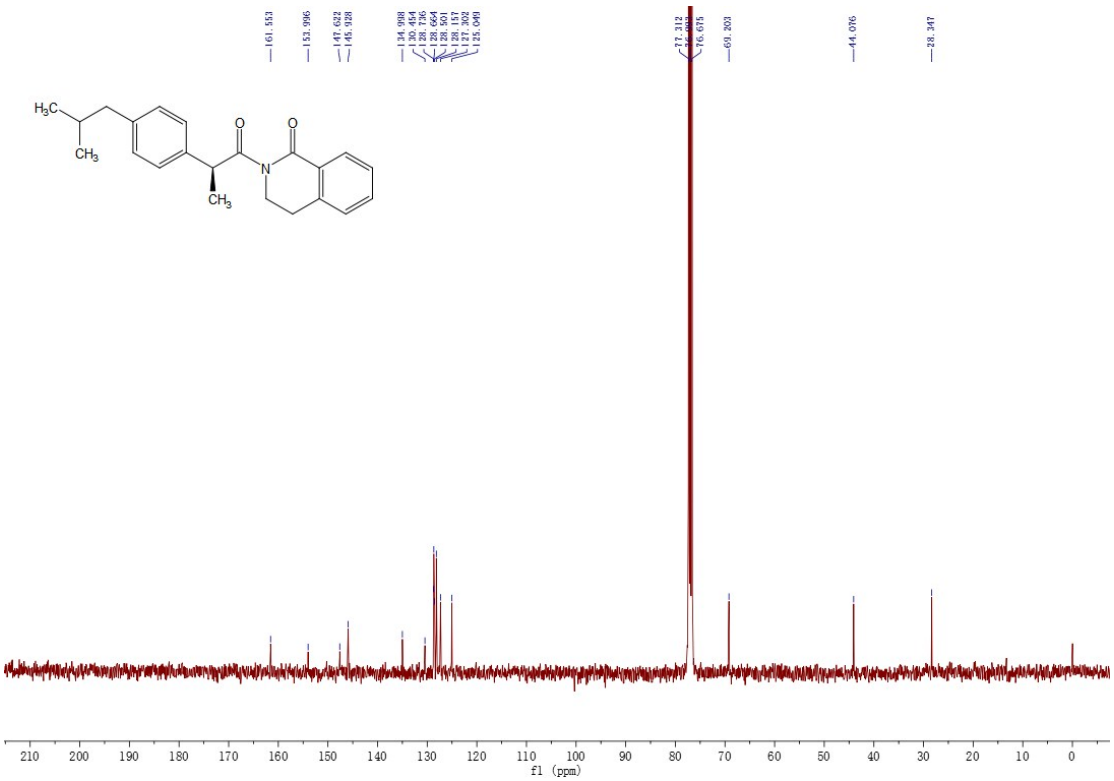
Benzyl 1-oxo-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (8aa)



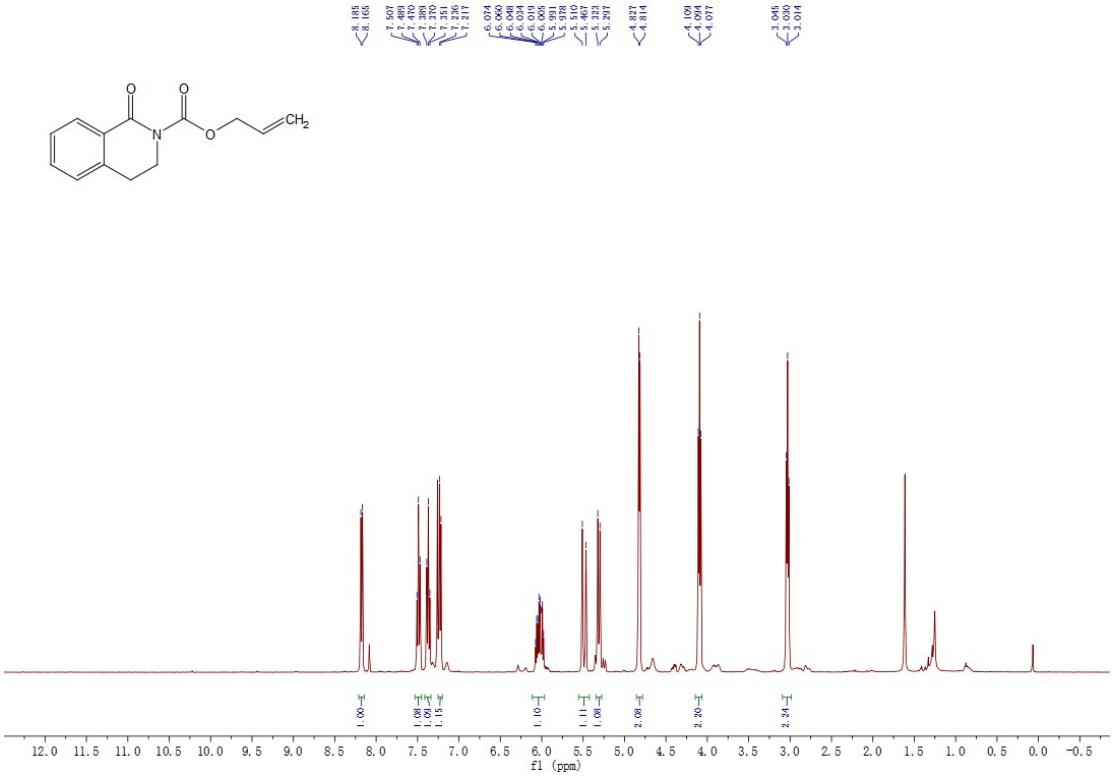


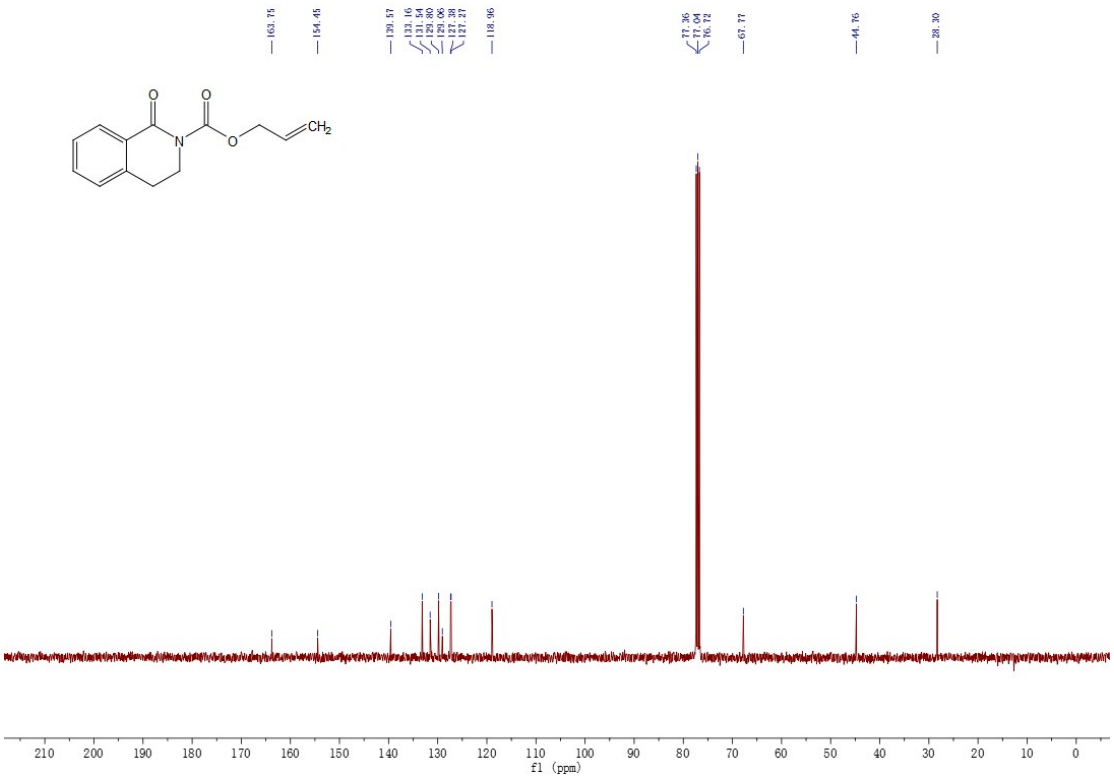
Benzyl 7-nitro-1-oxo-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (9aa)



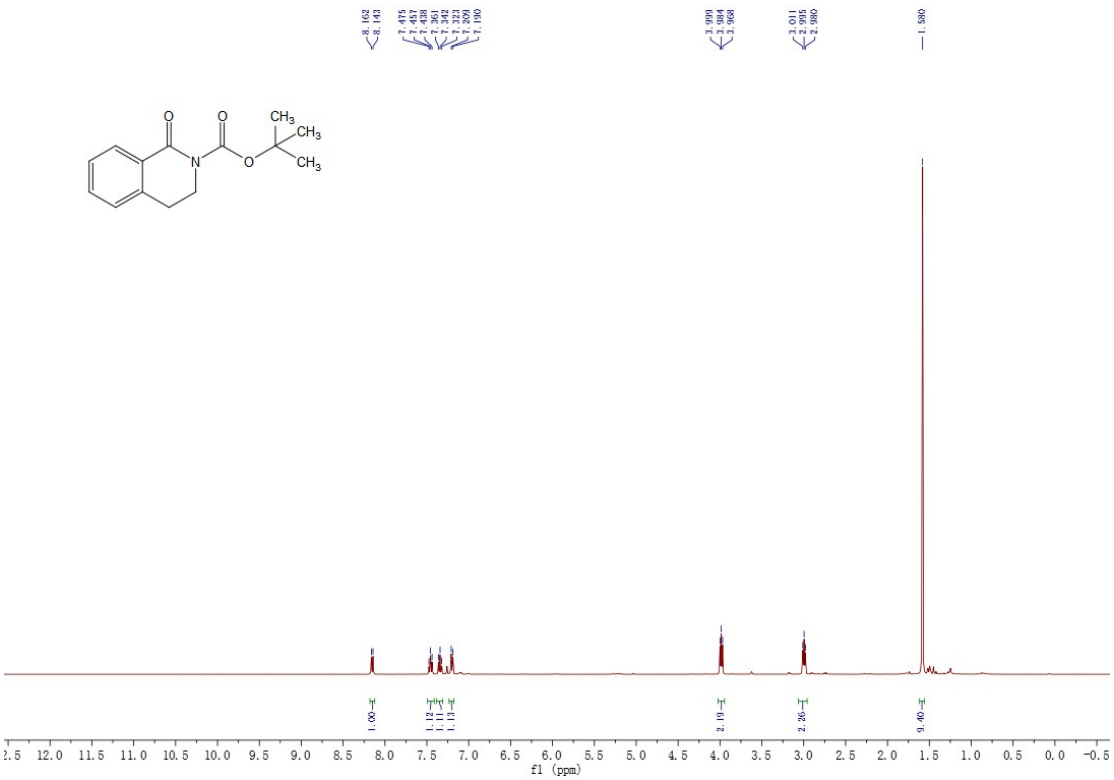


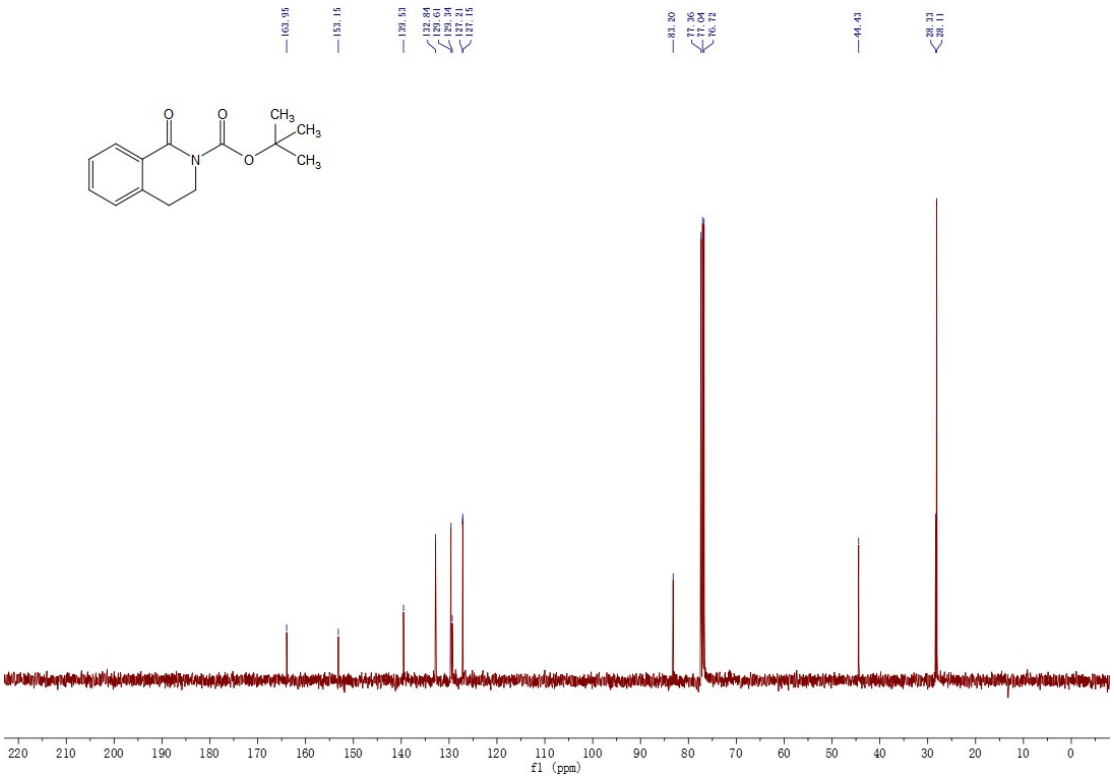
Allyl 1-oxo-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (10aa)



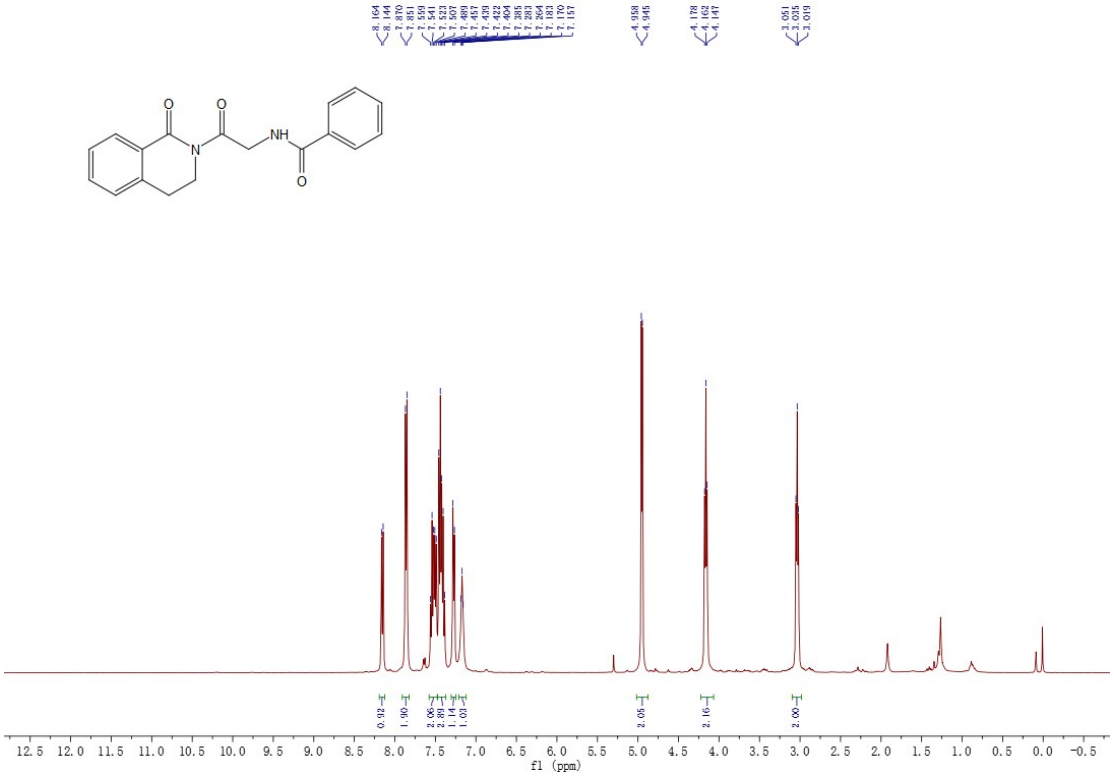


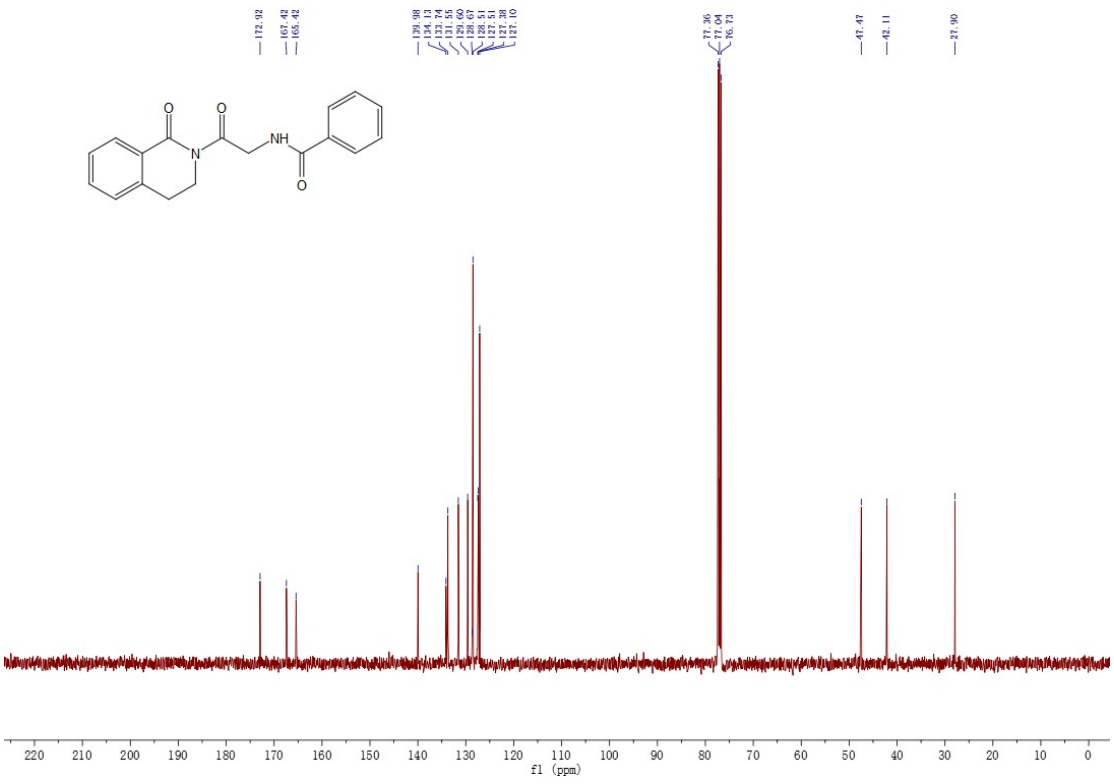
tert-Butyl 1-oxo-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (11aa)



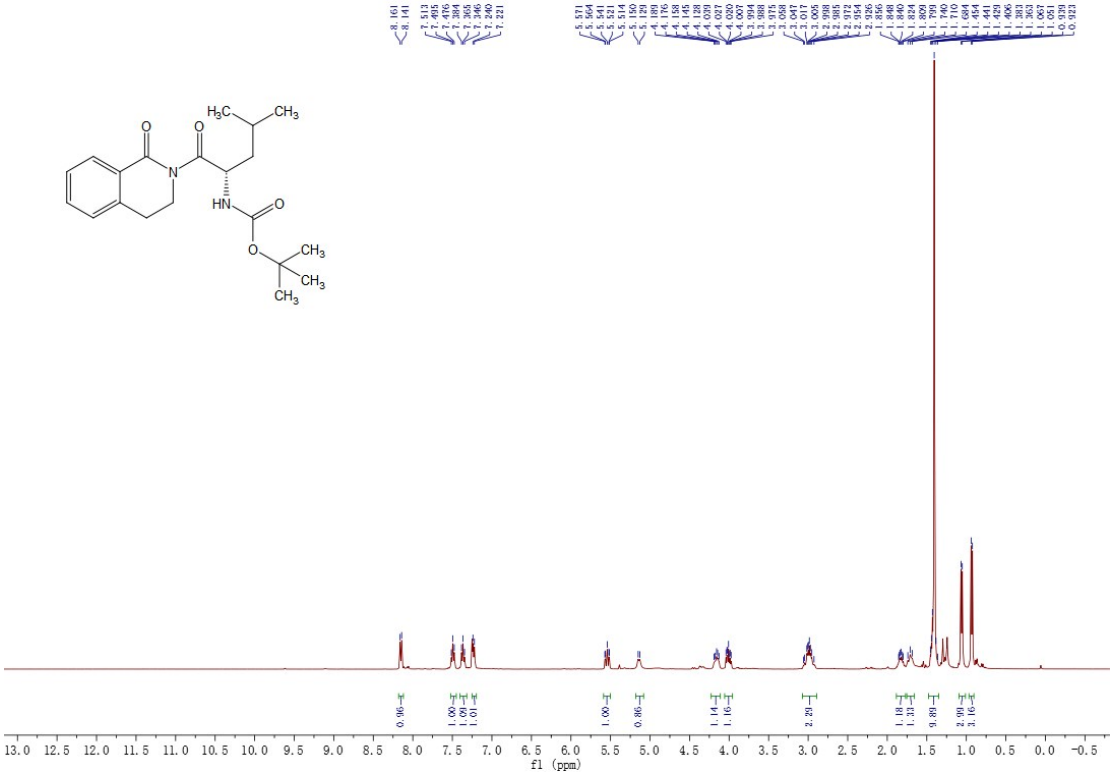


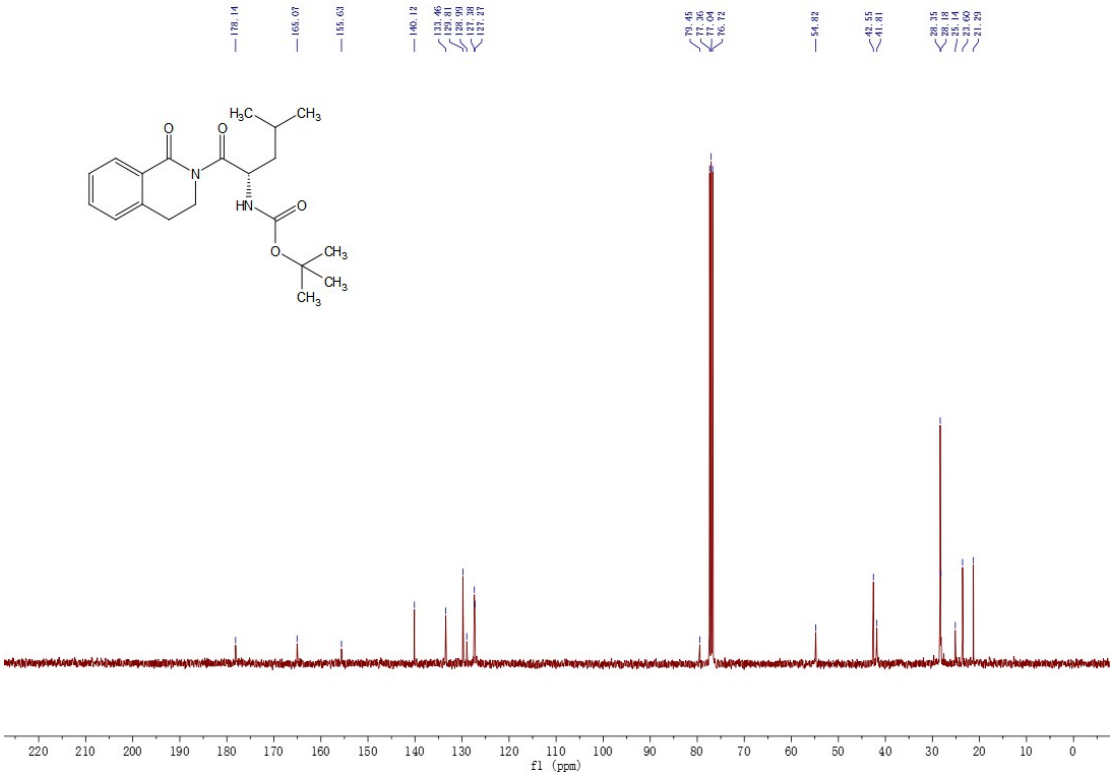
_N_-(2-oxo-2-(1-oxo-3,4-dihydroisoquinolin-2(1_H_)-yl)ethyl)benzamide (12aa)



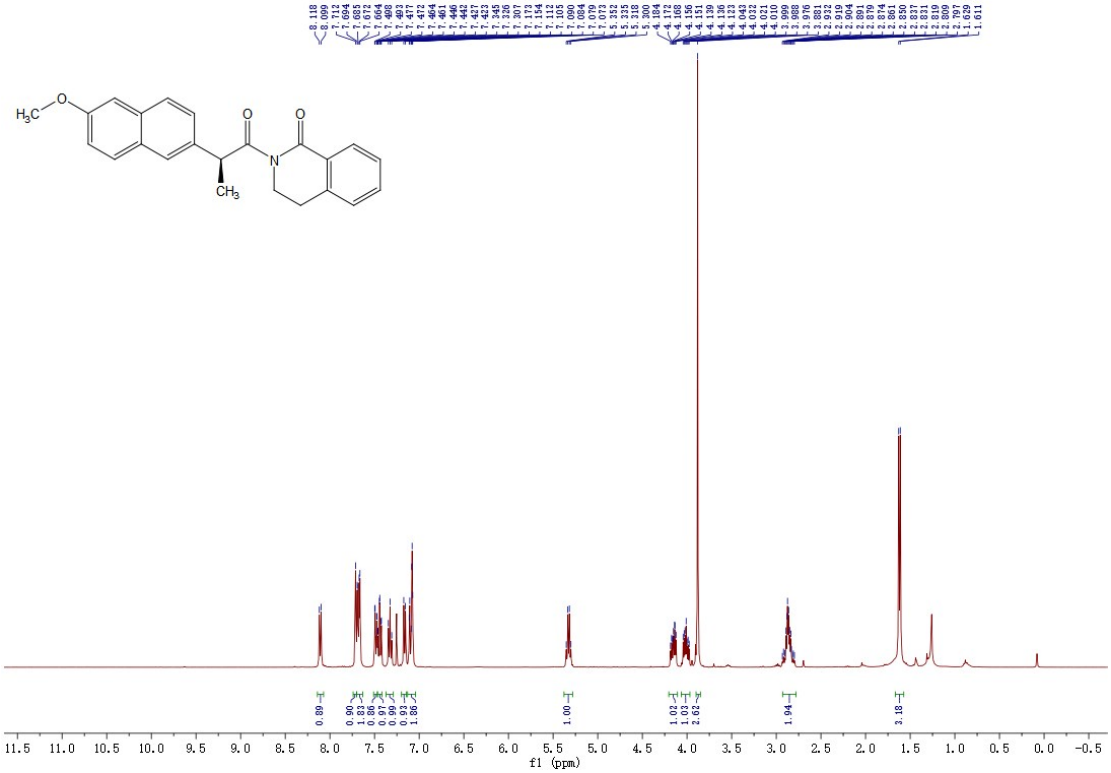


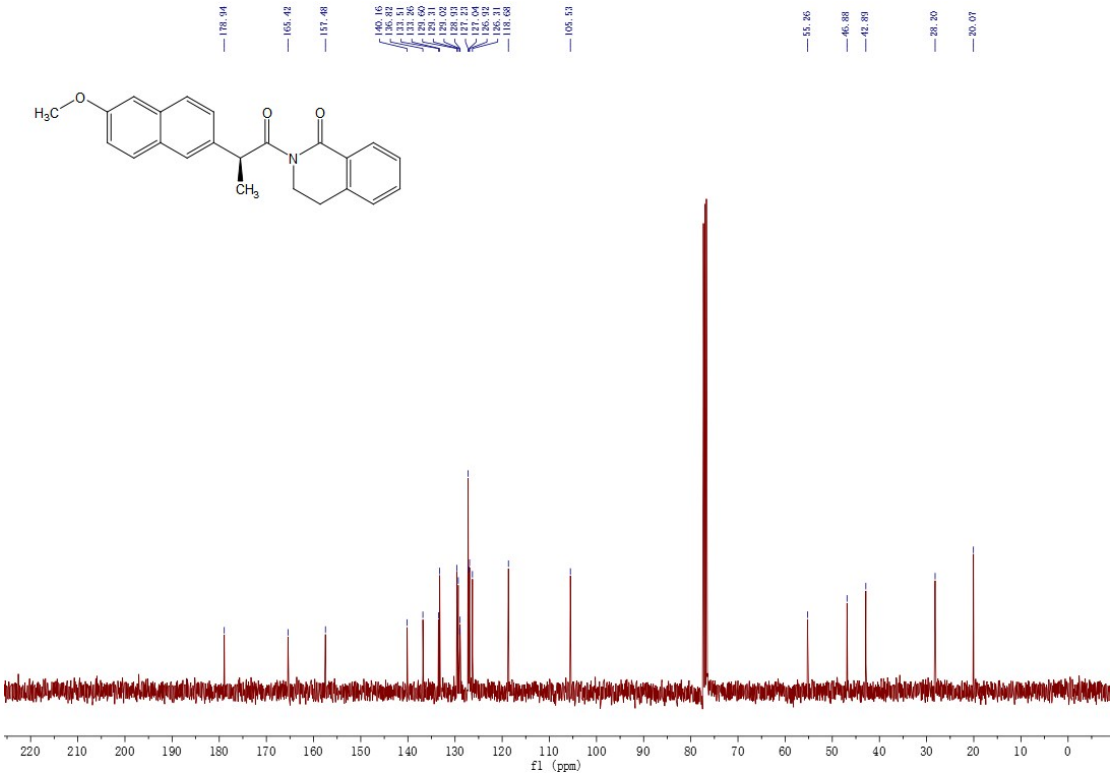
tert-Butyl(_S_)-(4-Methyl-1-oxo-1-(1-oxo-3,4-dihydroisoquinolin-2(1_H_)-yl)pentan-2-yl)carbamate (13aa)



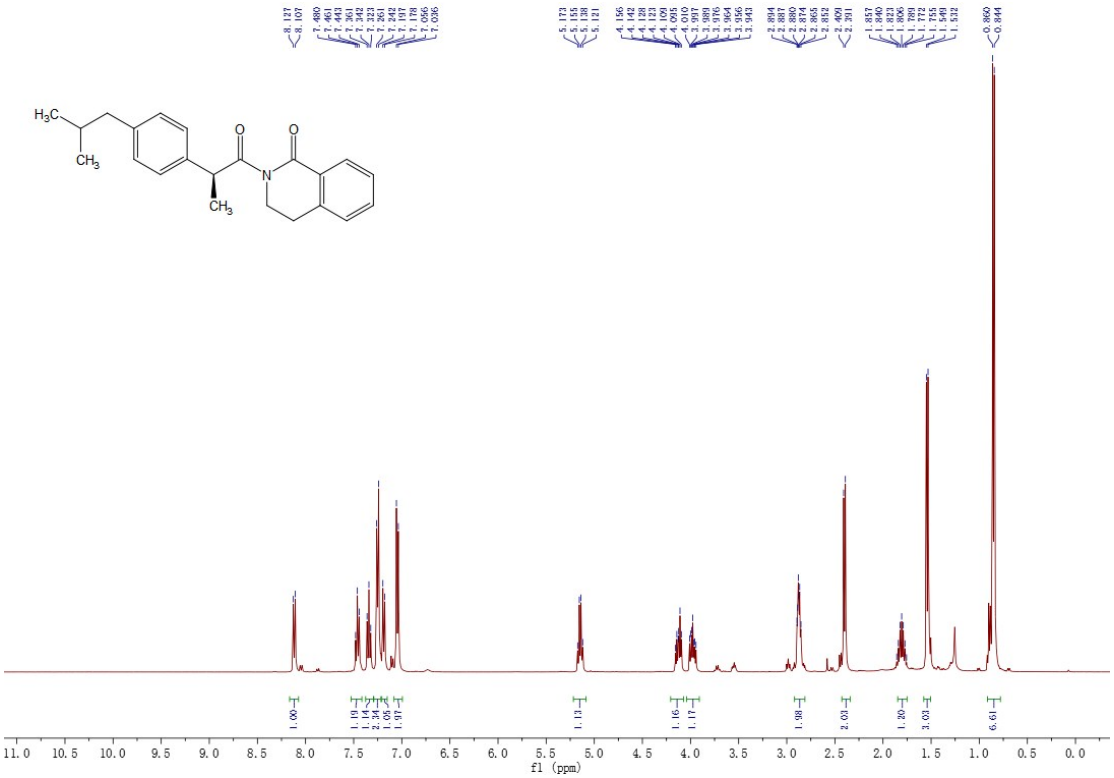


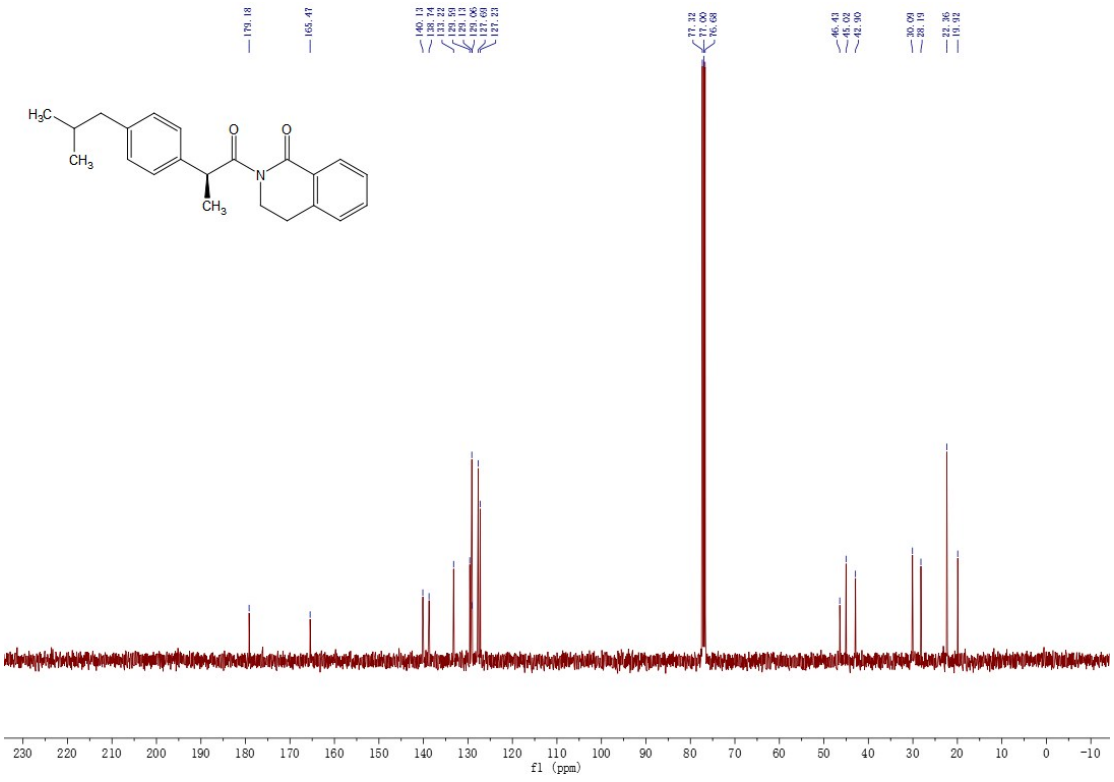
(*S*)-2-(2-(6-Methoxynaphthalen-2-yl)propanoyl)-3,4-dihydroisoquinolin-1(2*H*)-one (14aa)



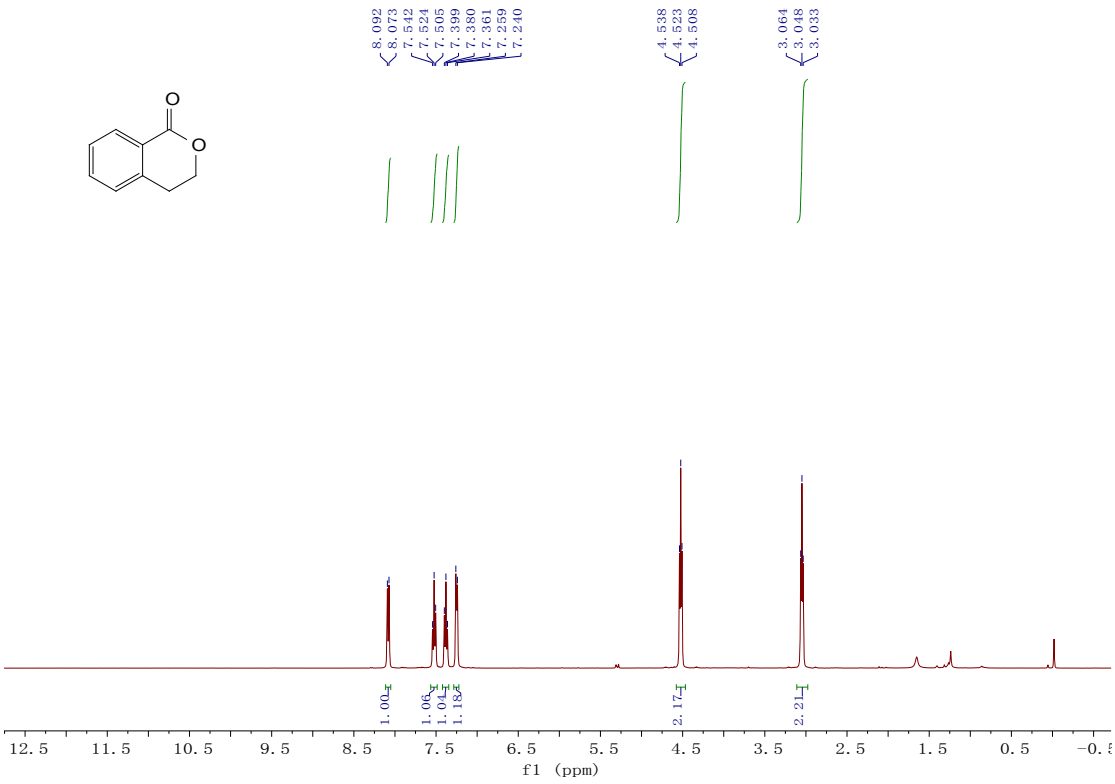


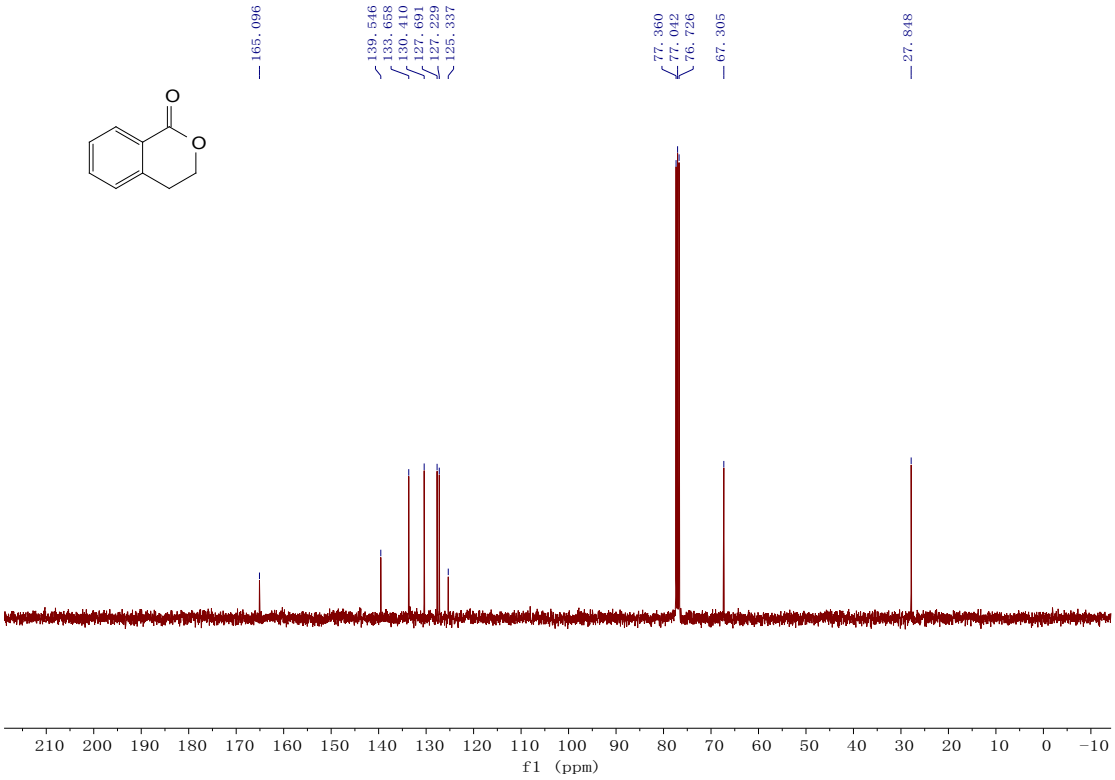
(*S*)-2-(2-(4-Isobutylphenyl)propanoyl)-3,4-dihydroisoquinolin-1(2*H*)-one (15aa)



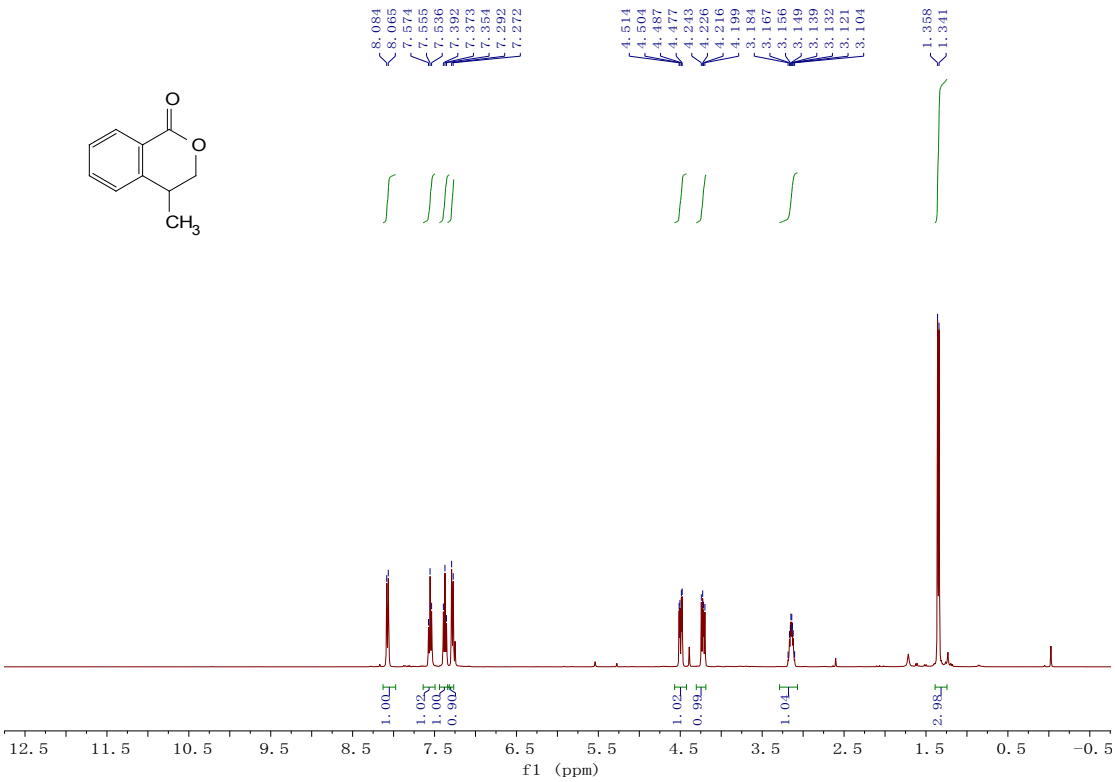


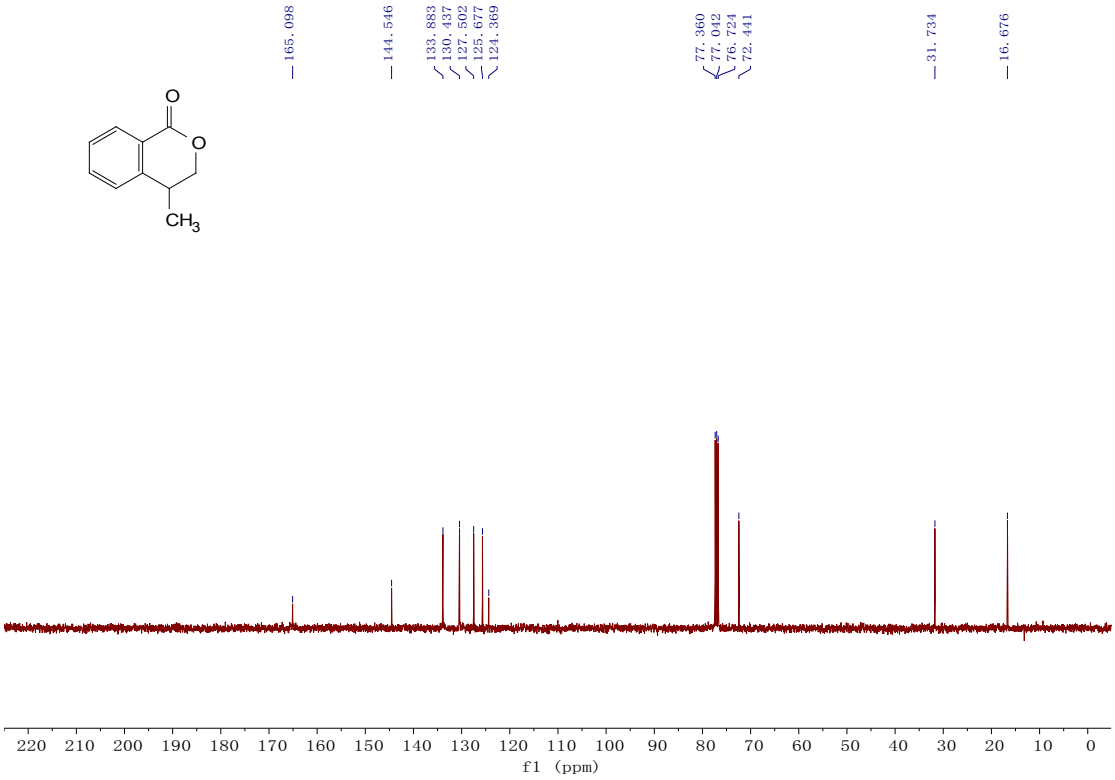
Isochroman-1-one (1bb)



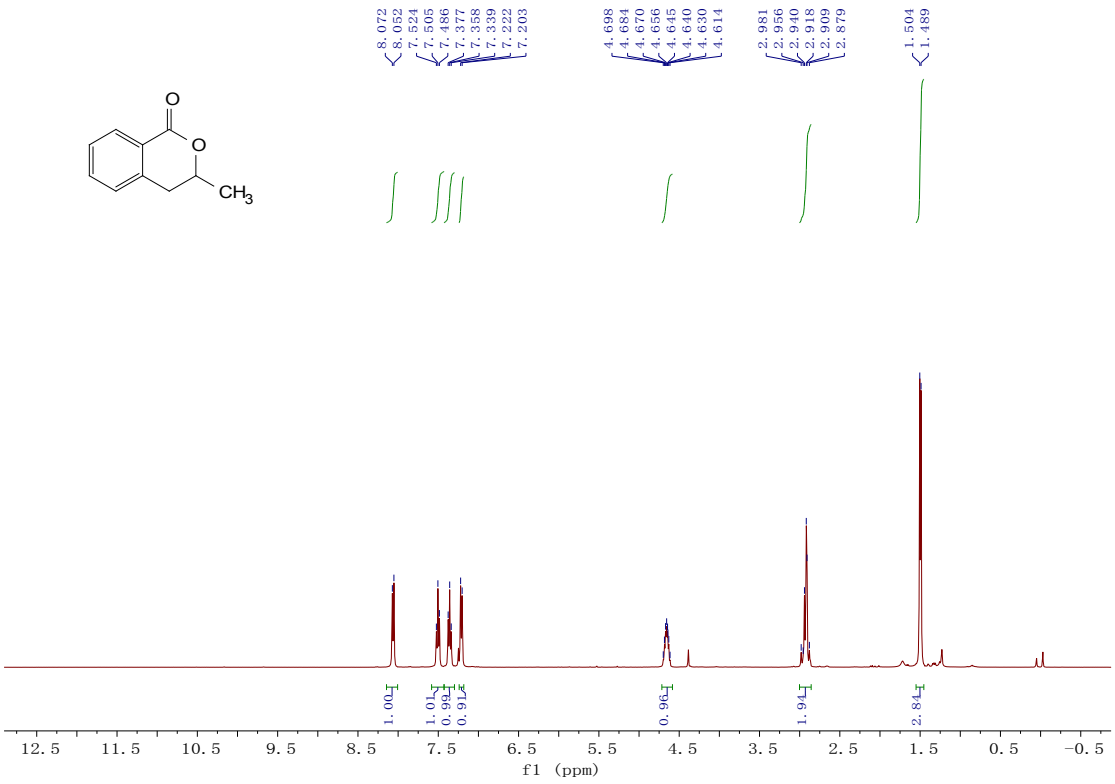


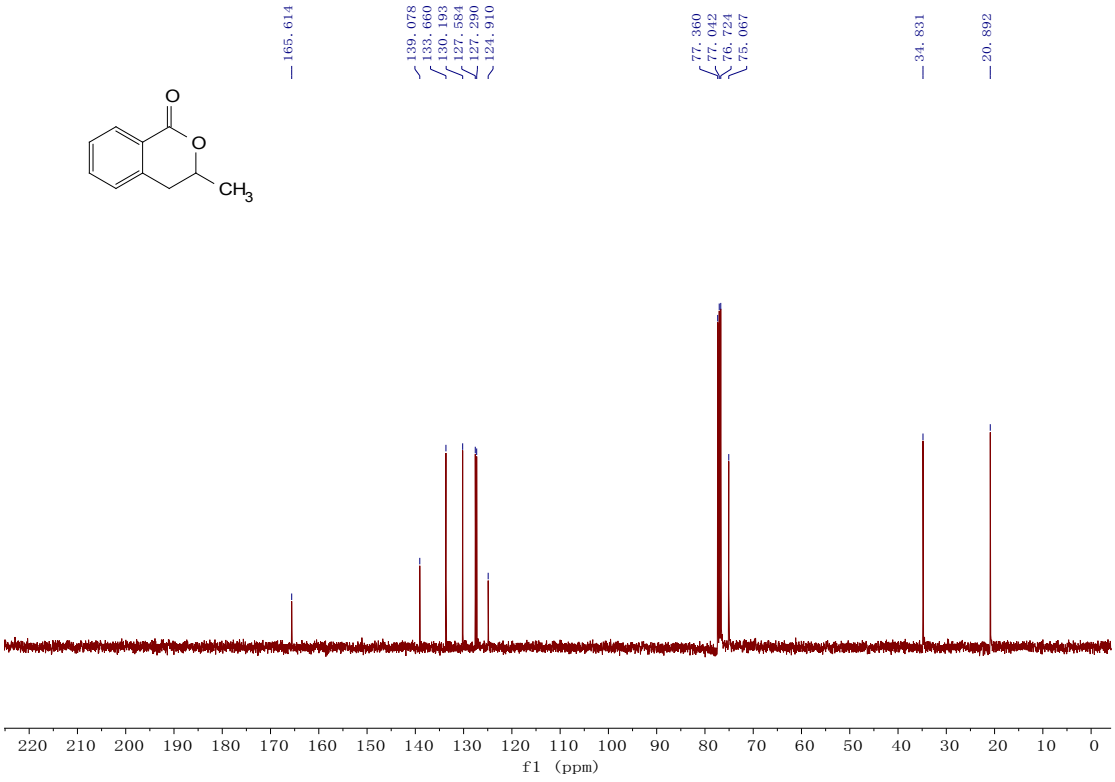
4-Methylisochroman-1-one (2bb)



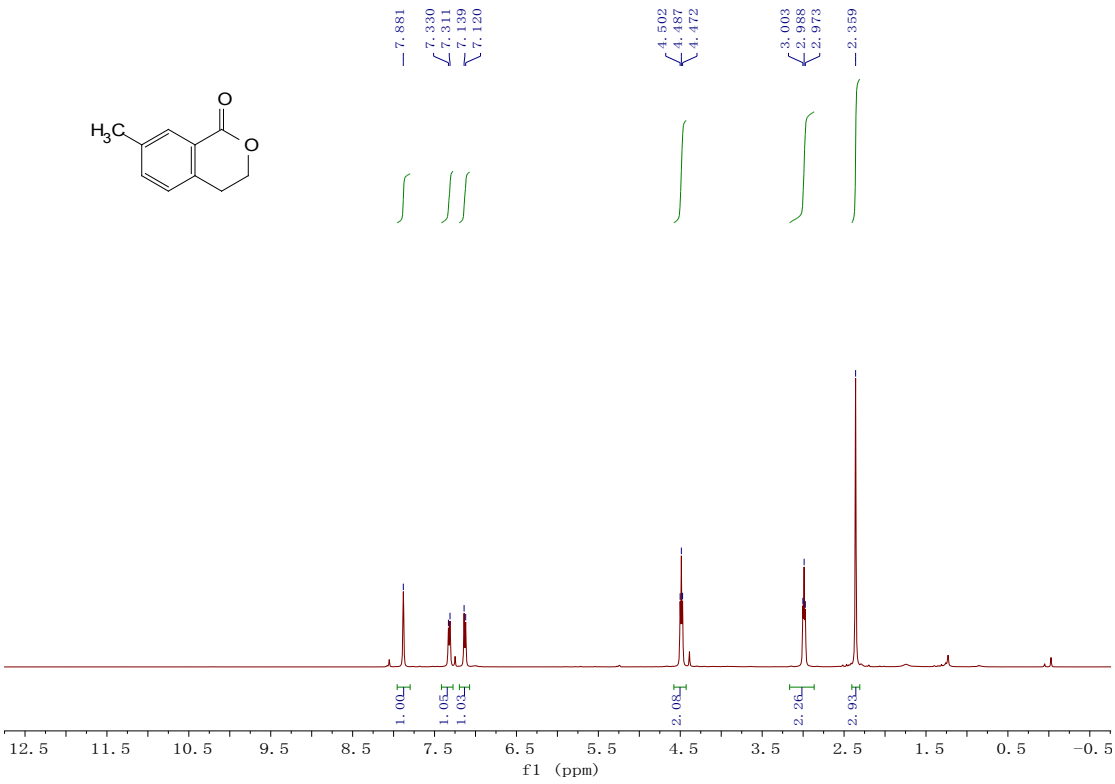


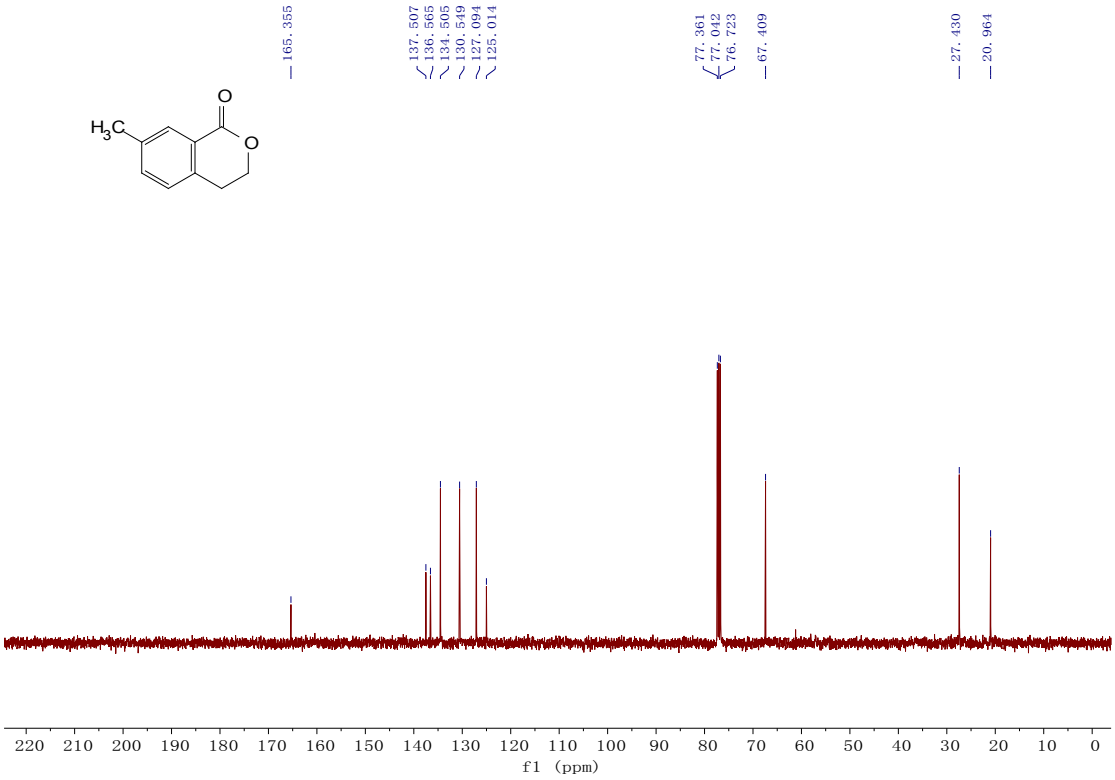
3-Methylisochroman-1-one (3bb)



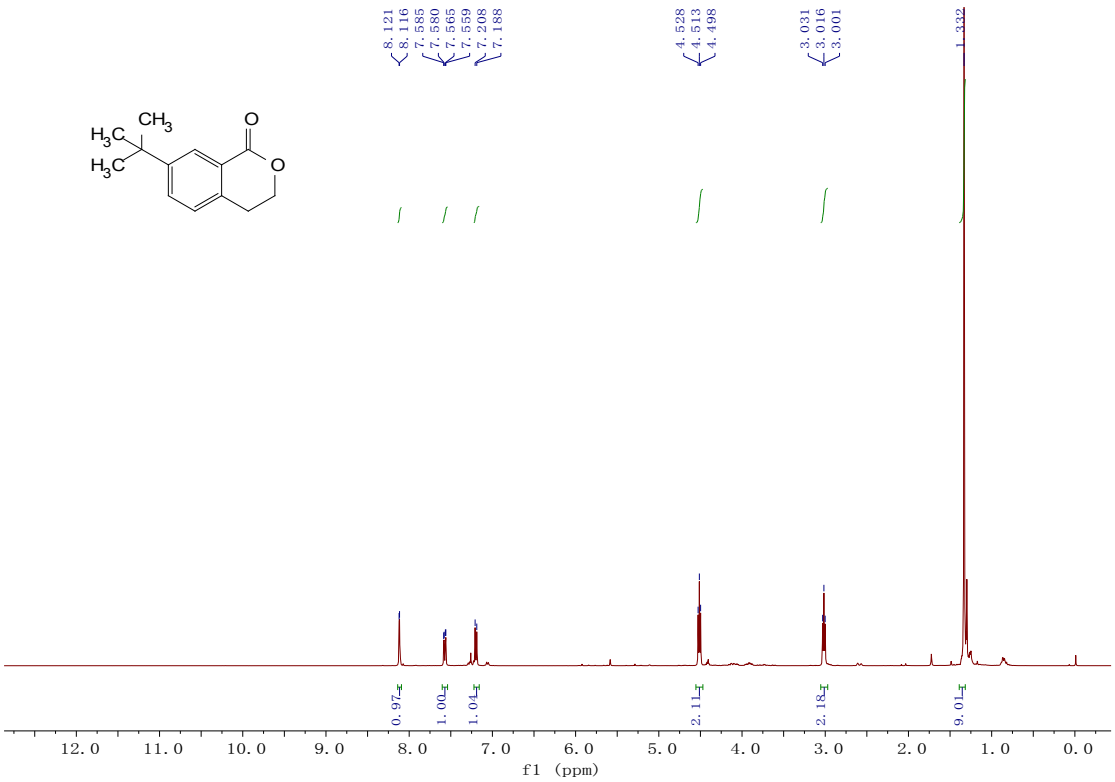


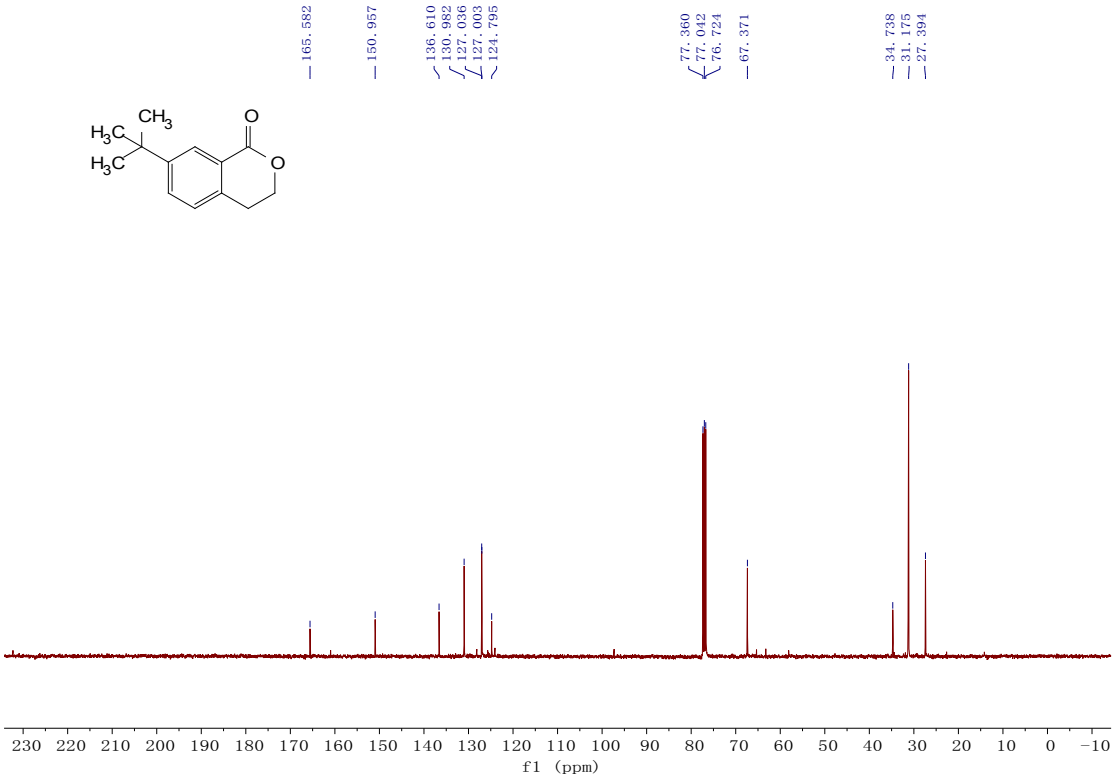
7-Methylisochroman-1-one (4bb)



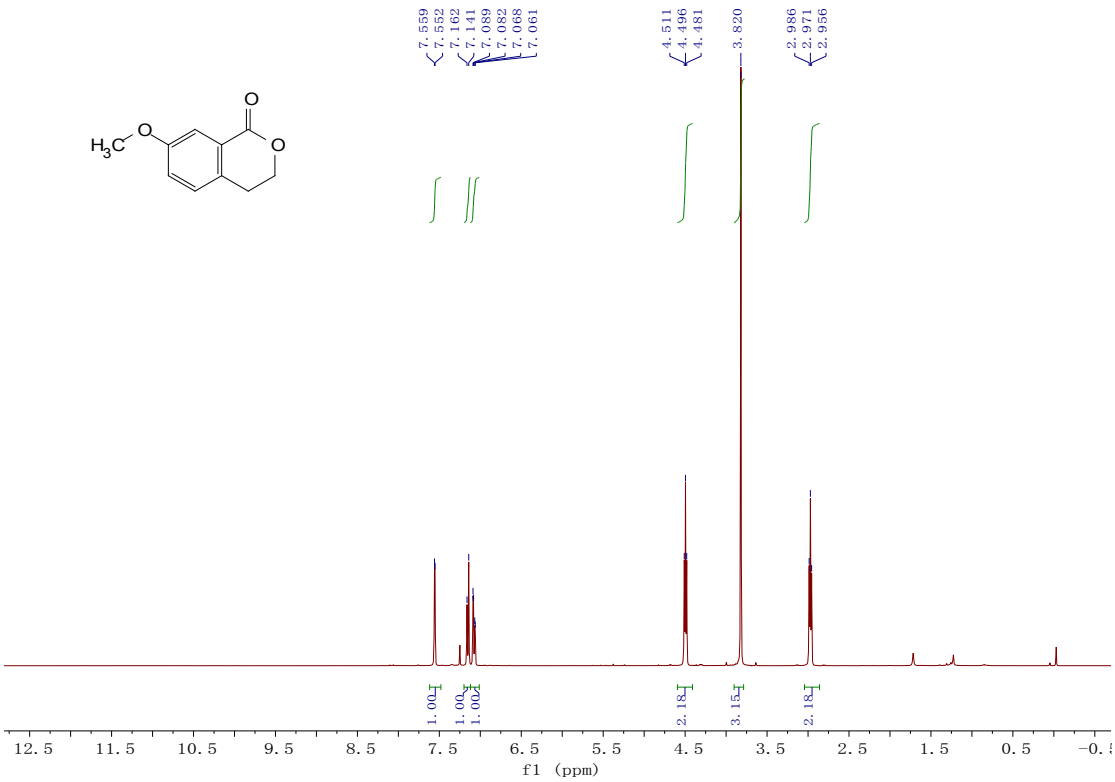


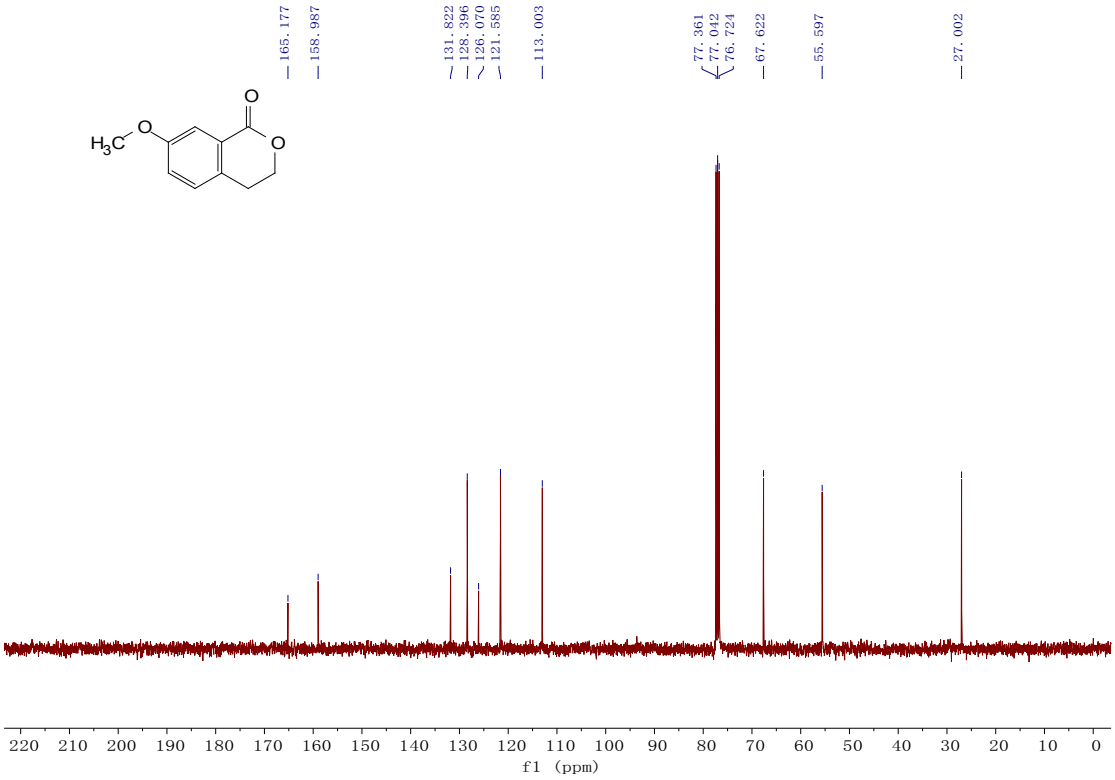
7-(*tert*-Butyl)isochroman-1-one (5bb)



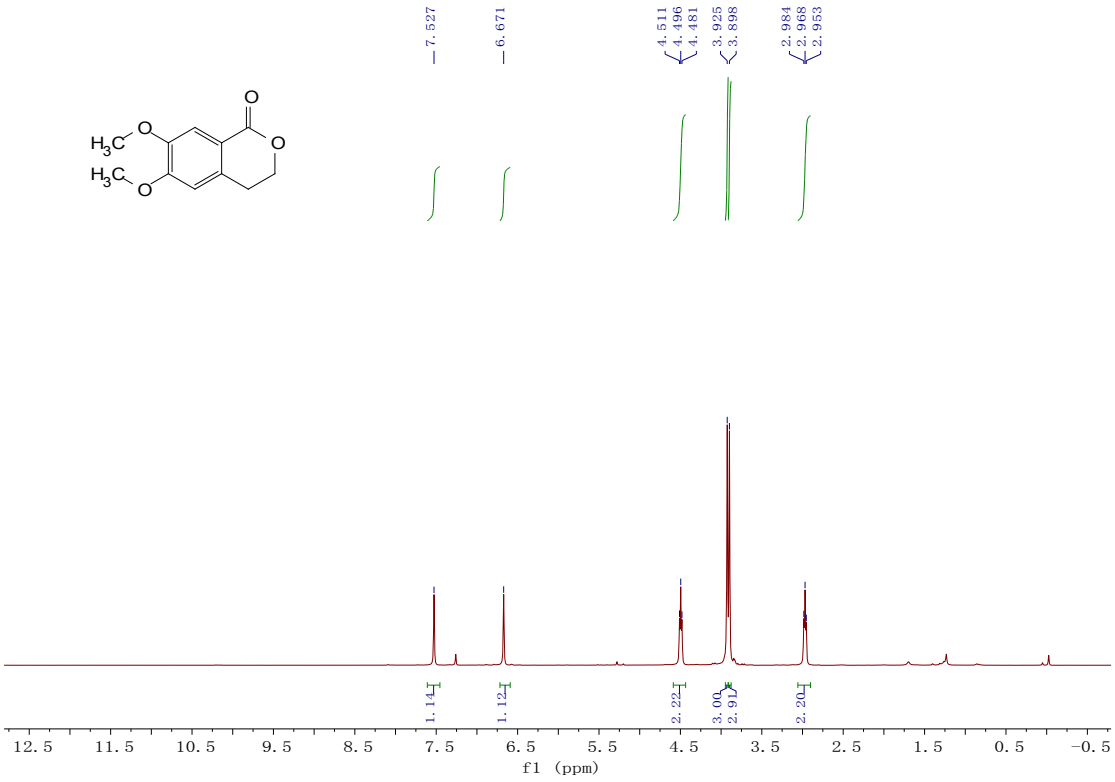


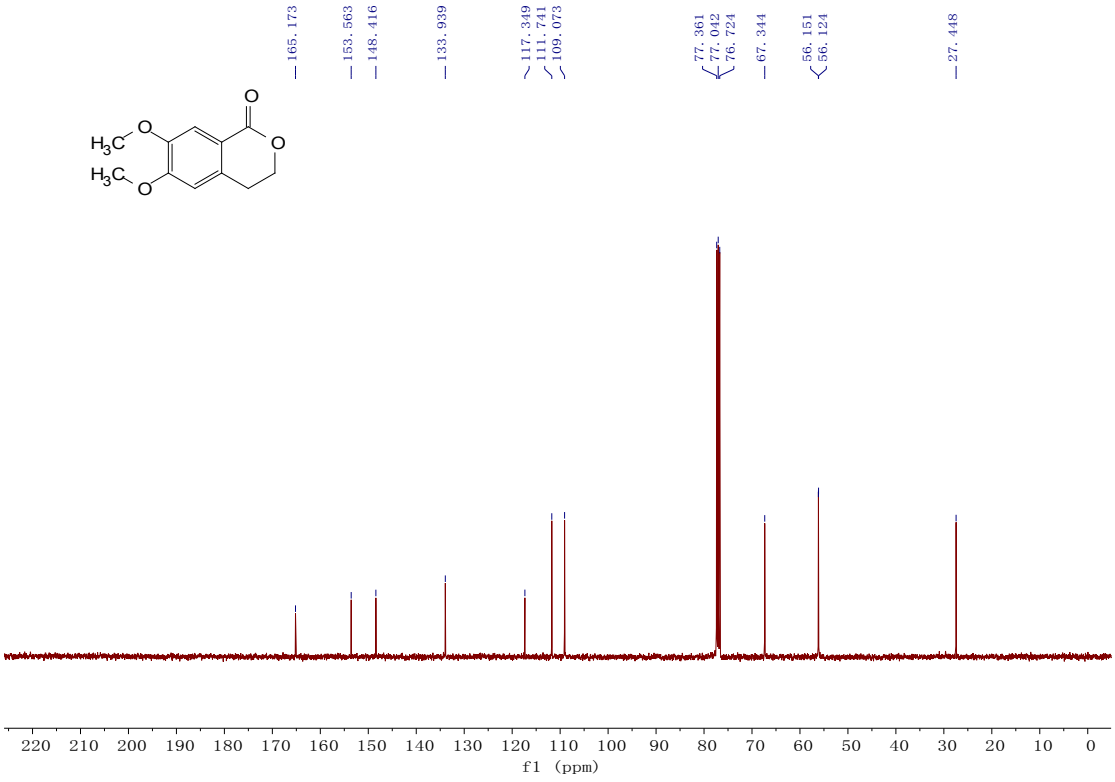
7-Methoxyisochroman-1-one (6bb)



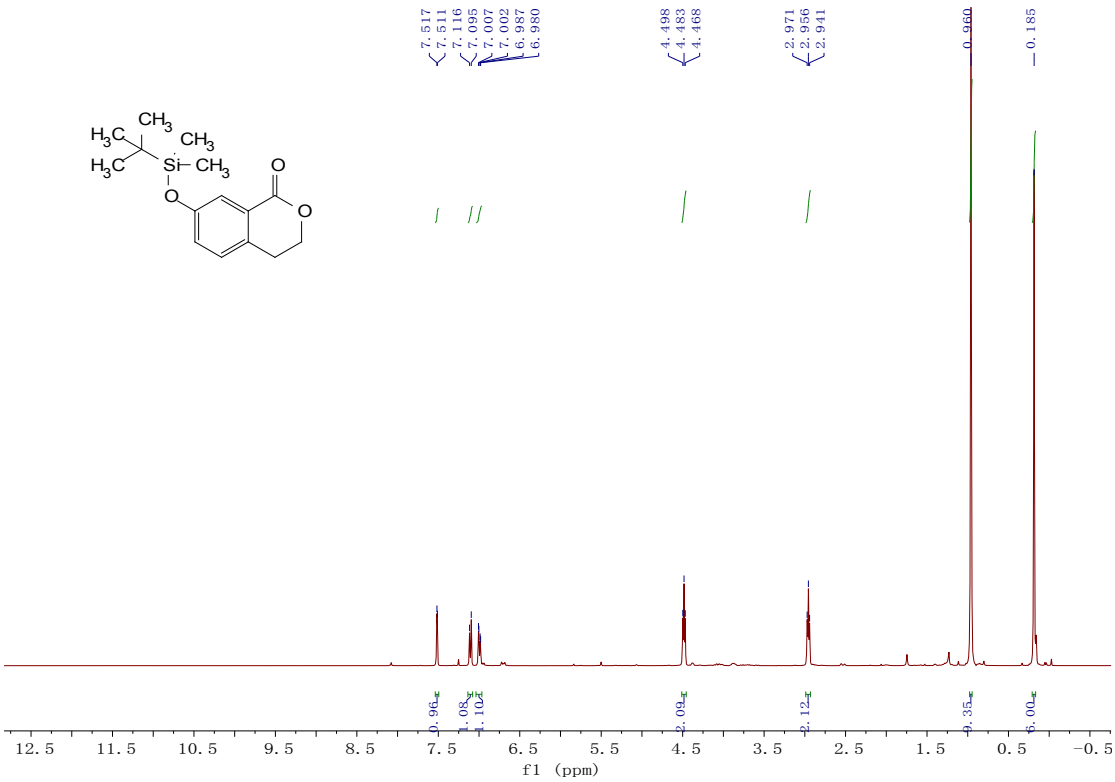


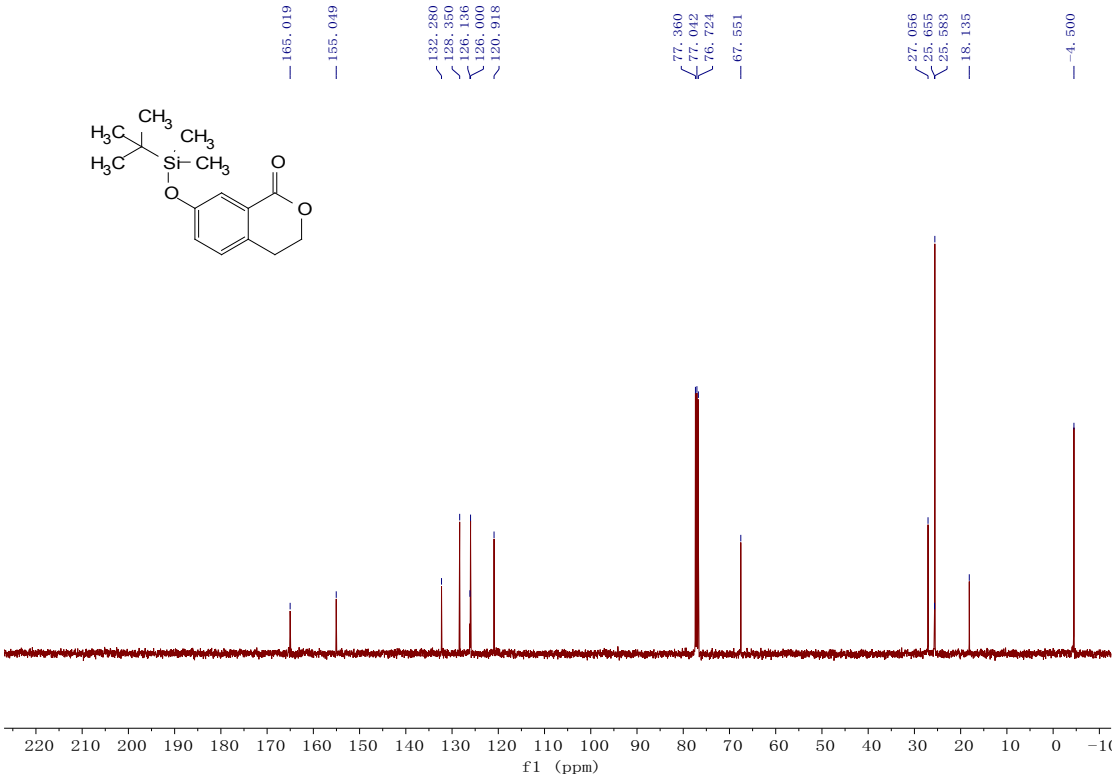
6,7-Dimethoxyisochroman-1-one (7bb)



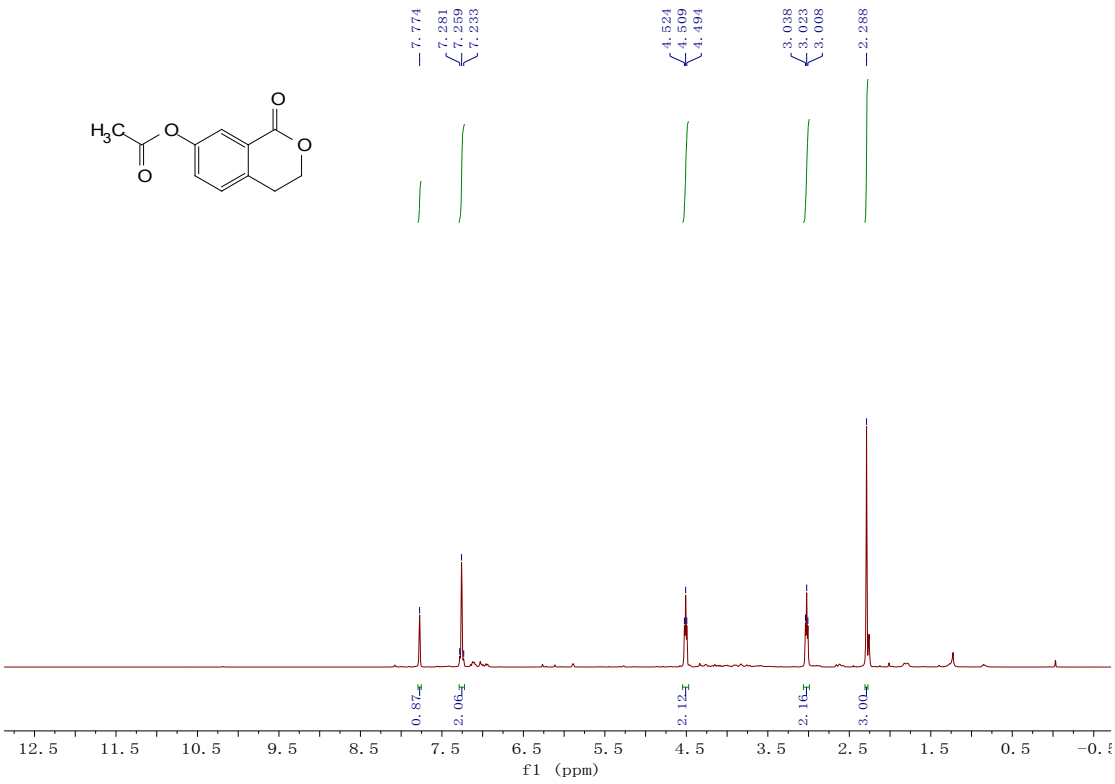


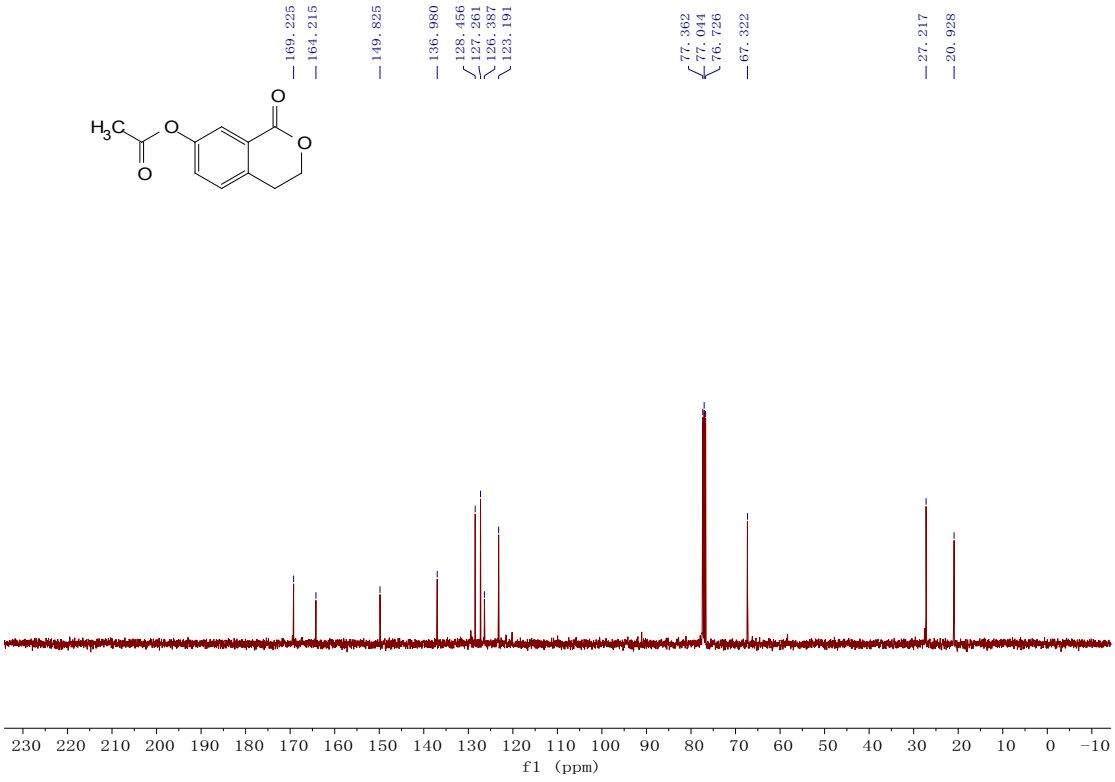
7-((*tert*-Butyldimethylsilyl)oxy)isochroman-1-one (8bb)



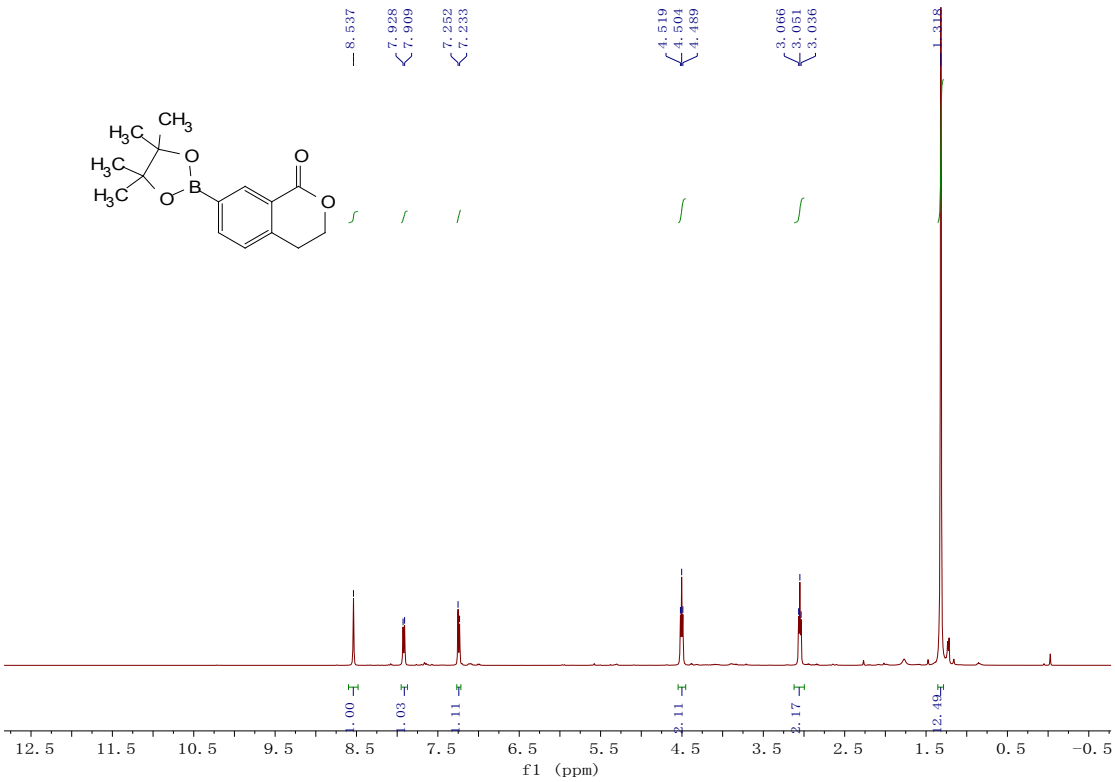


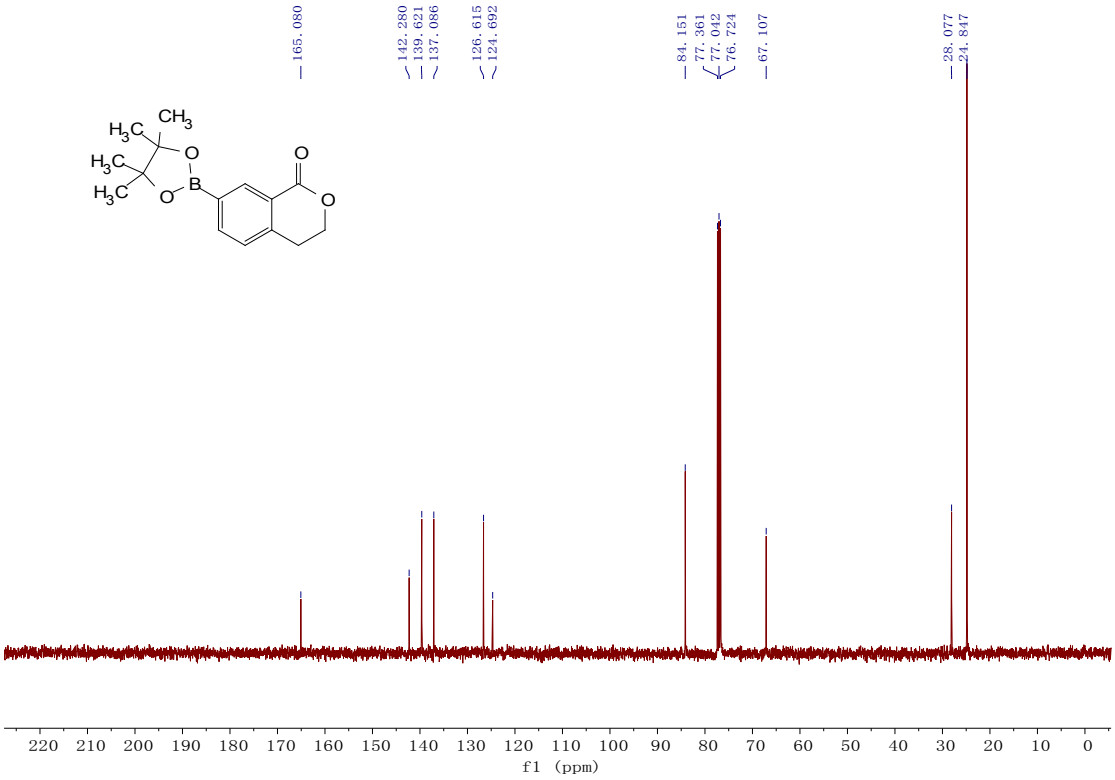
1-Oxoisochroman-7-yl acetate (9bb)



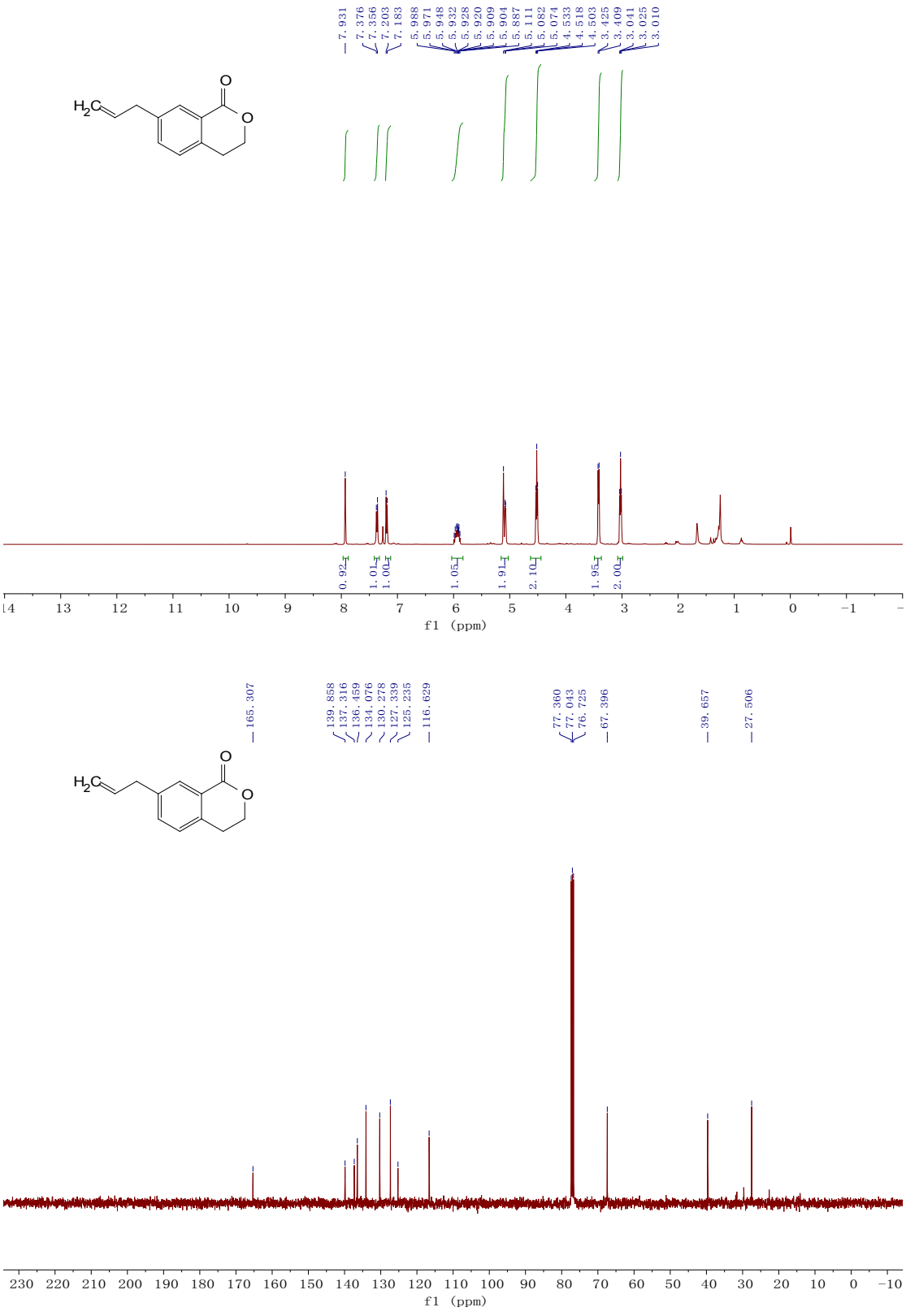


7-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)isochroman-1-one (10bb)

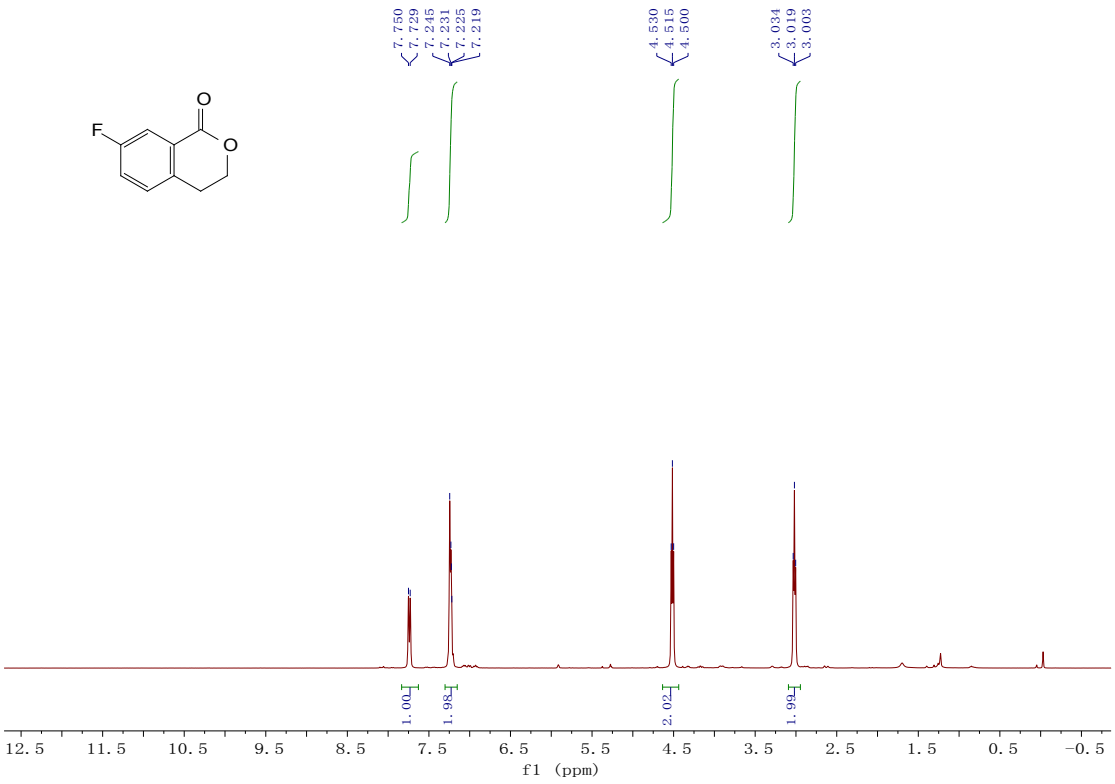


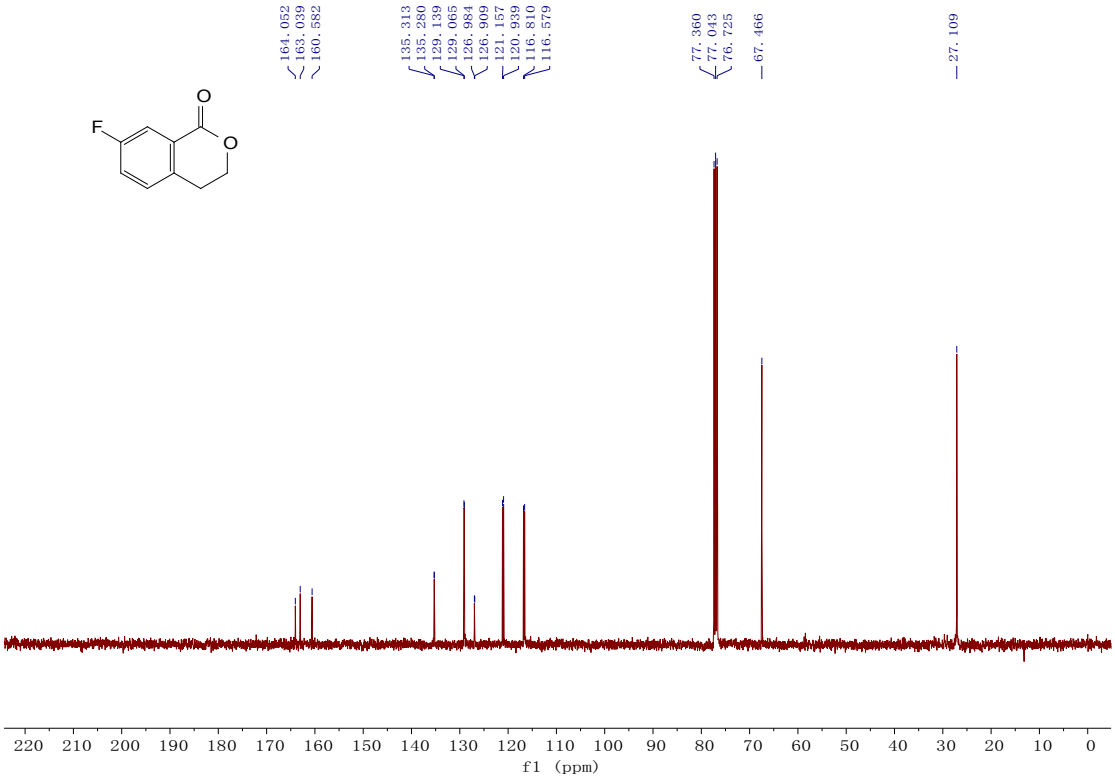


7-Allylisochroman-1-one (11bb)

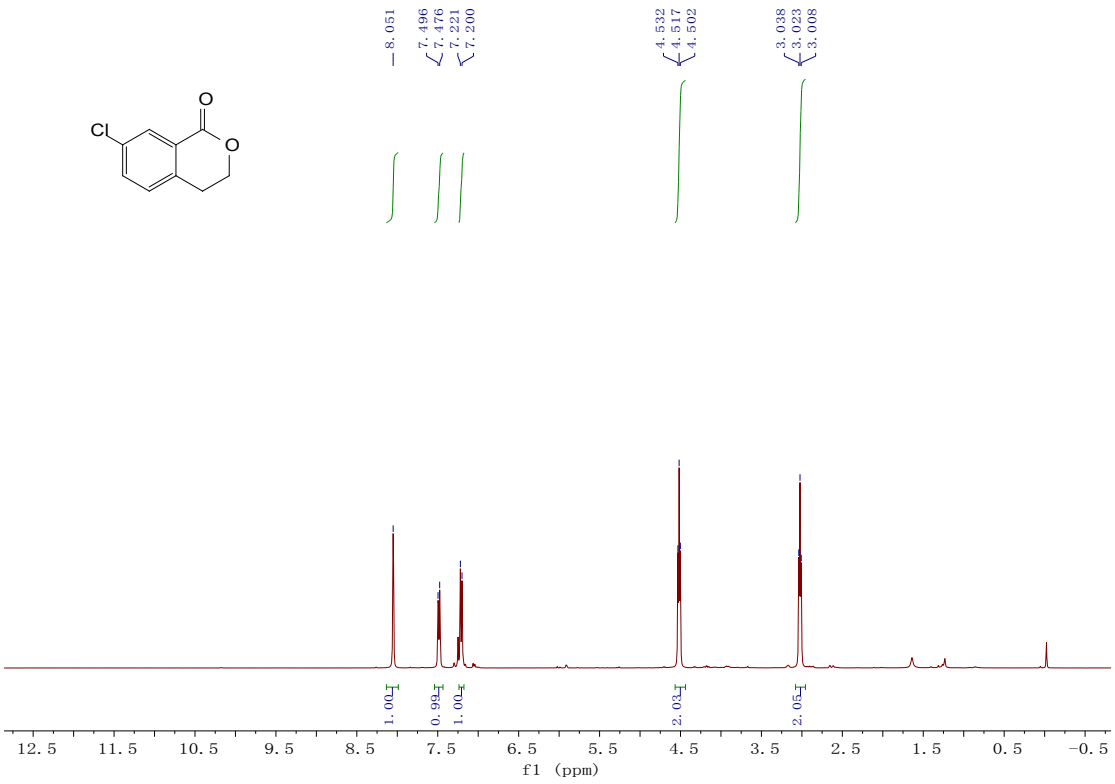


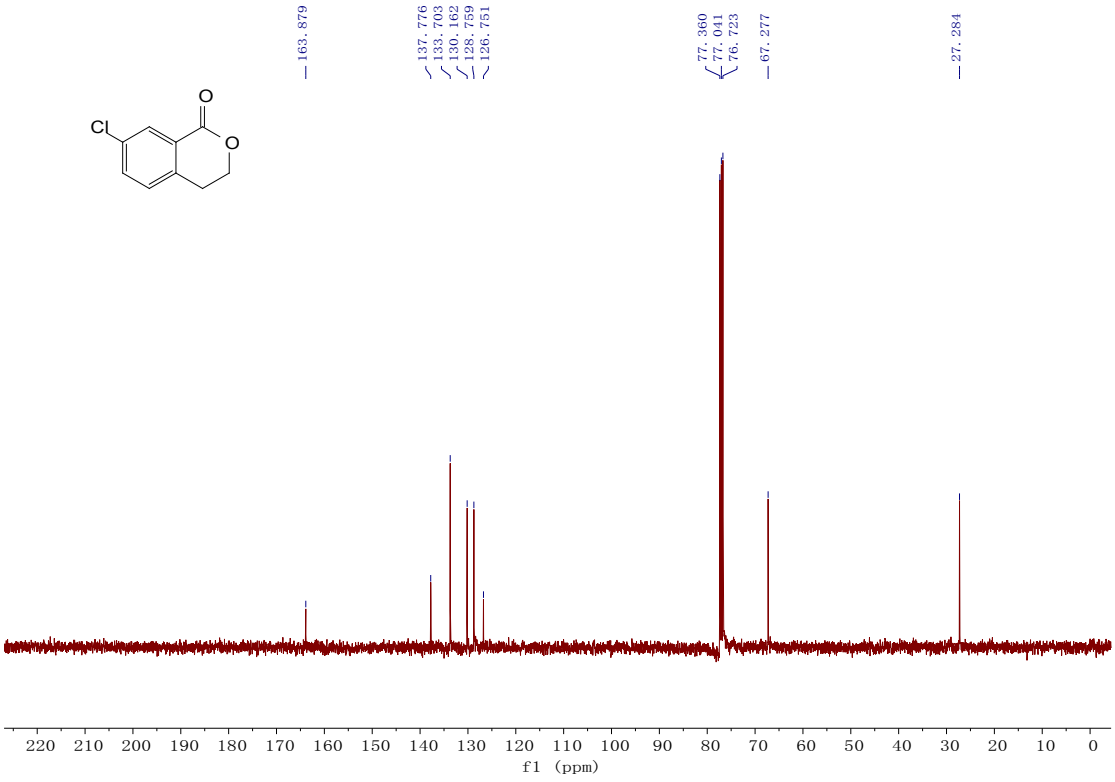
7-Fluoroisochroman-1-one (12bb)



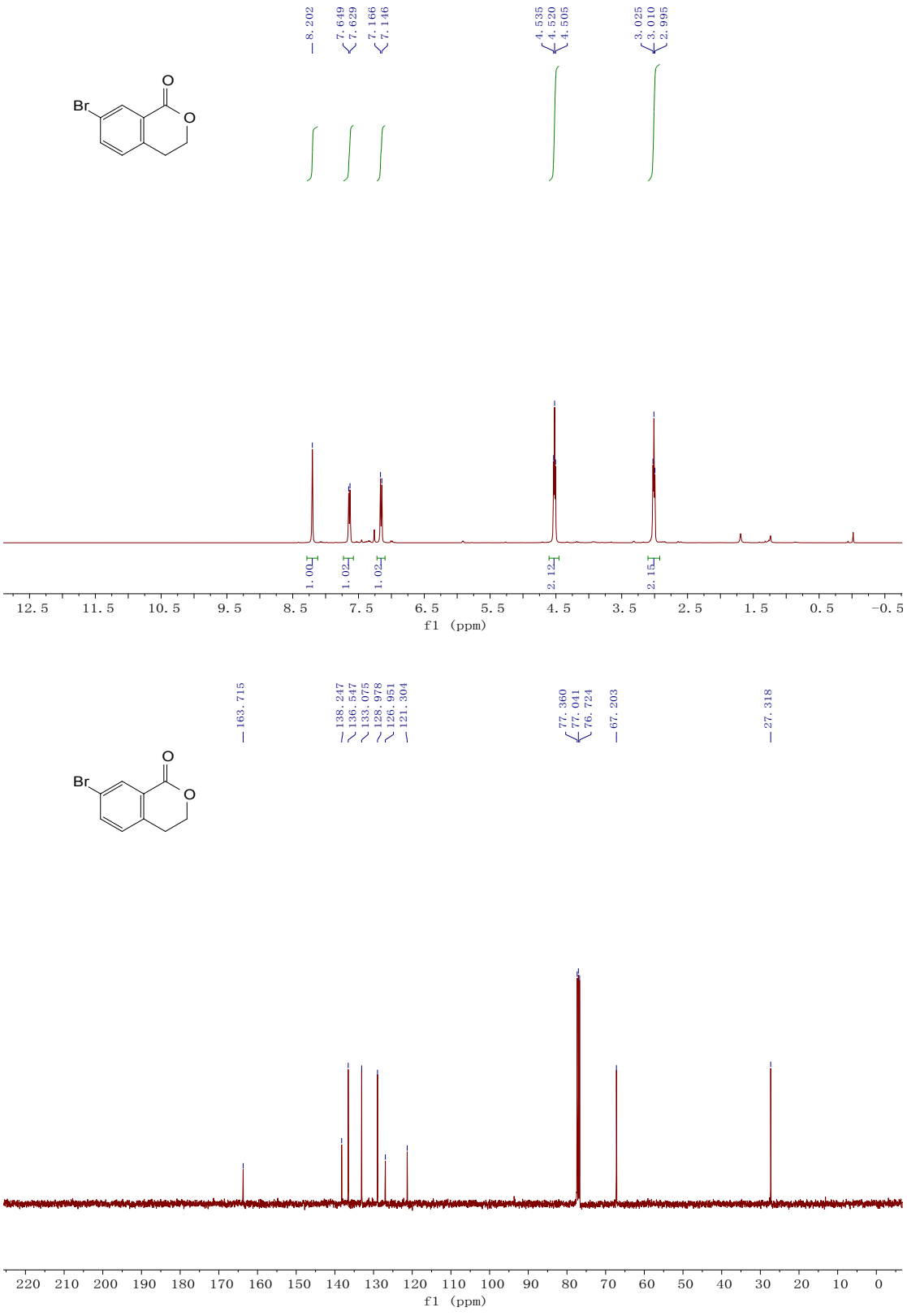


7-Chloroisochroman-1-one (13bb)

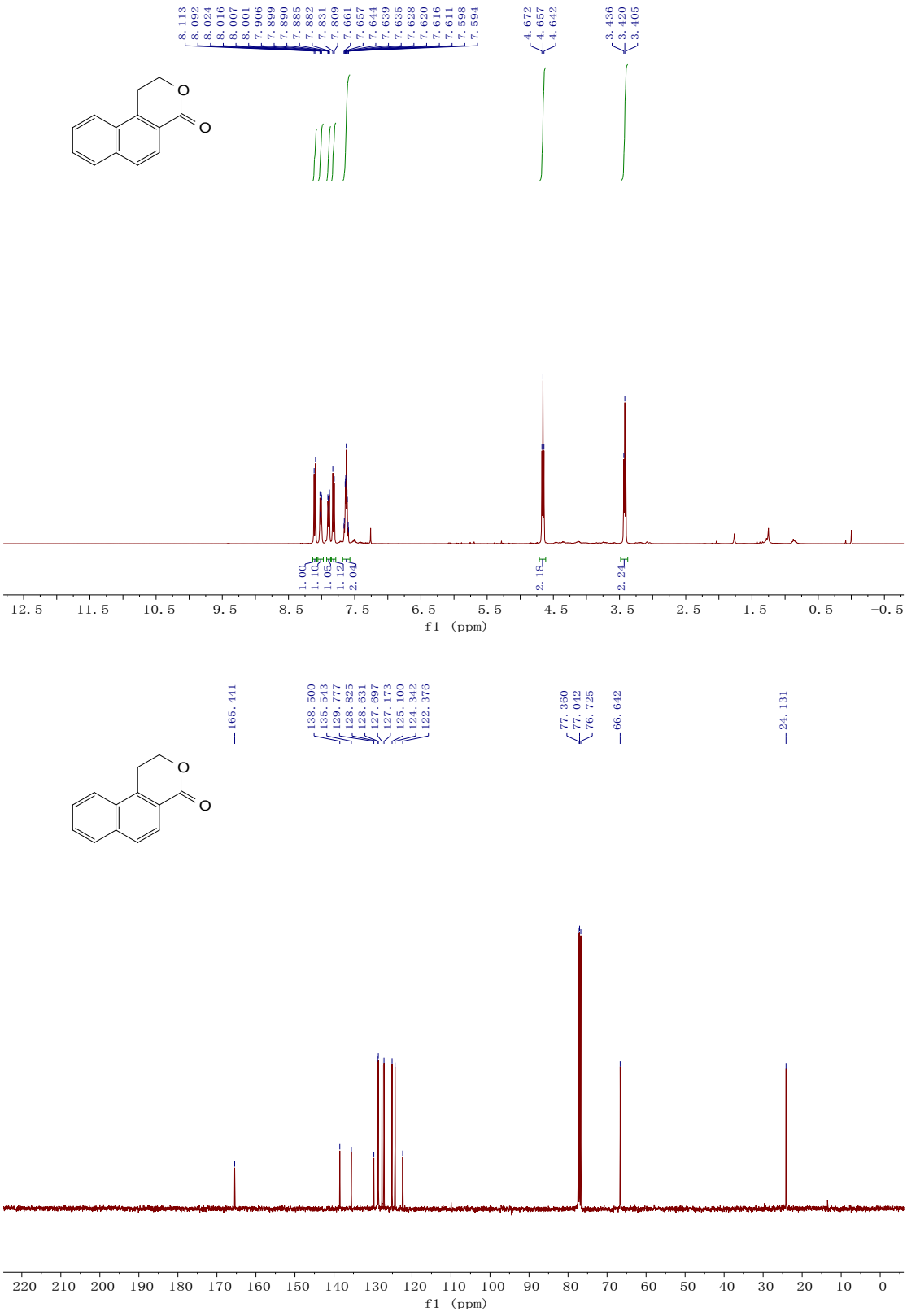




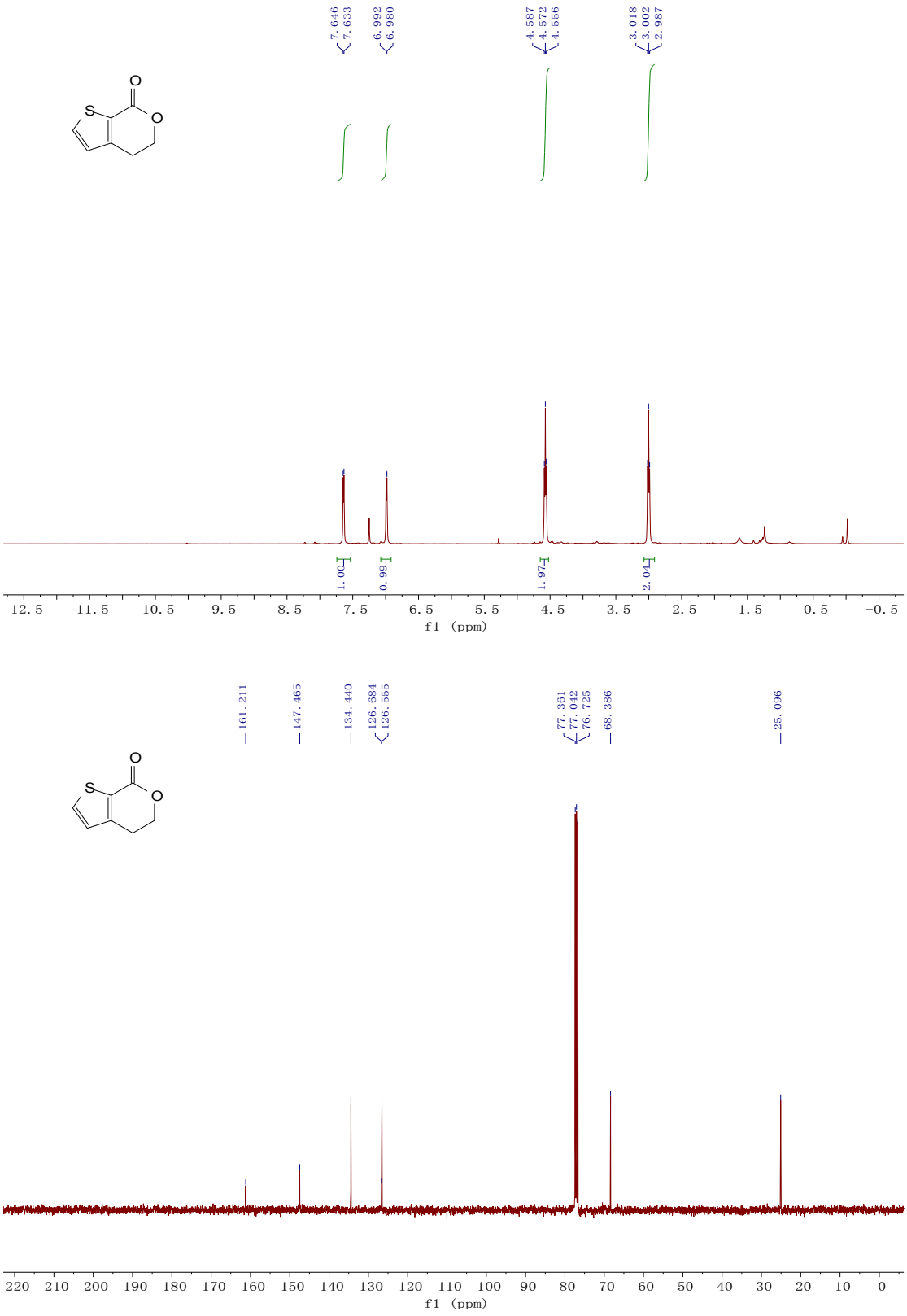
7-Bromoisochroman-1-one (14bb)



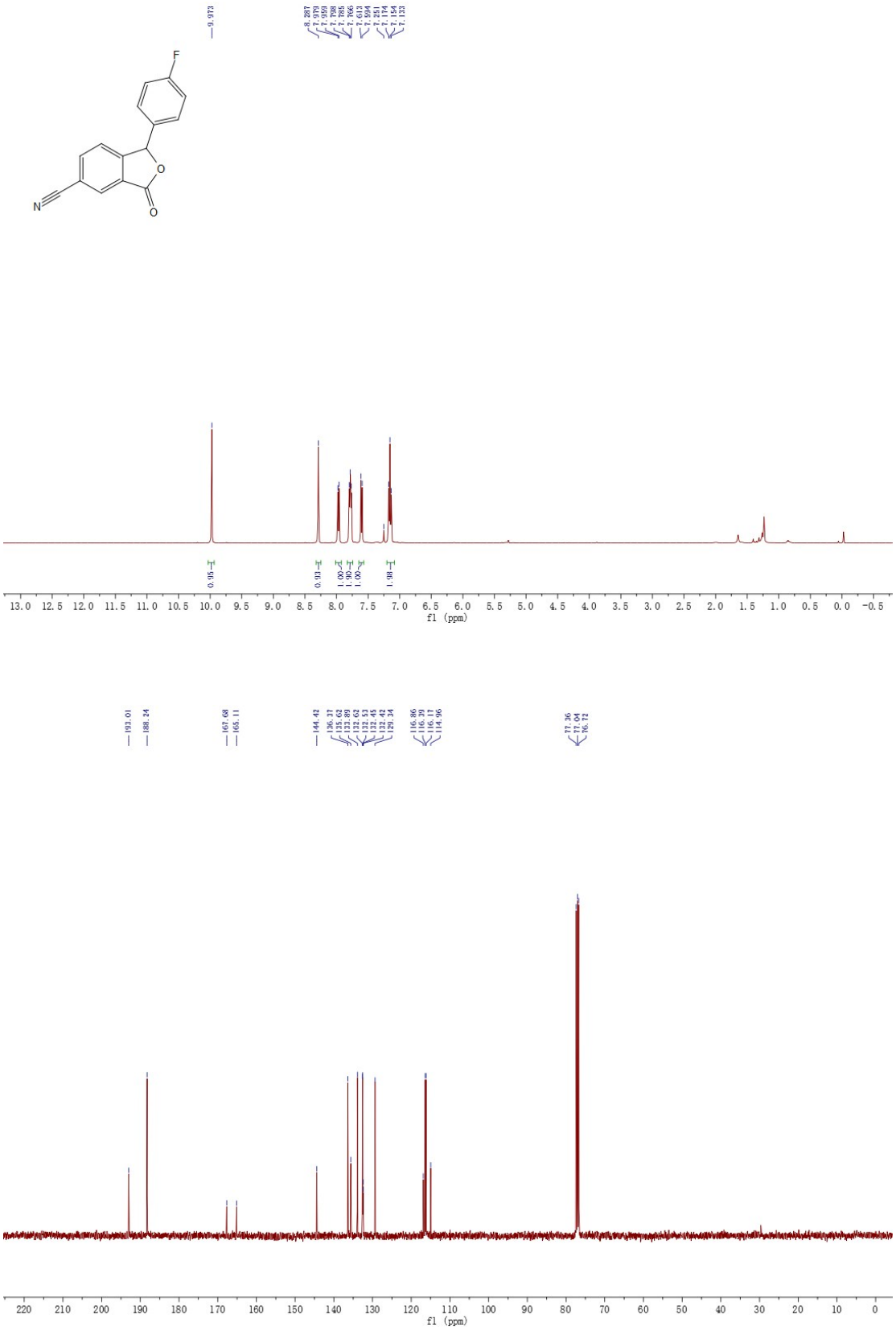
3,4-Dihydro-1*H*-benzo[*h*]isochromen-1-one (15bb)



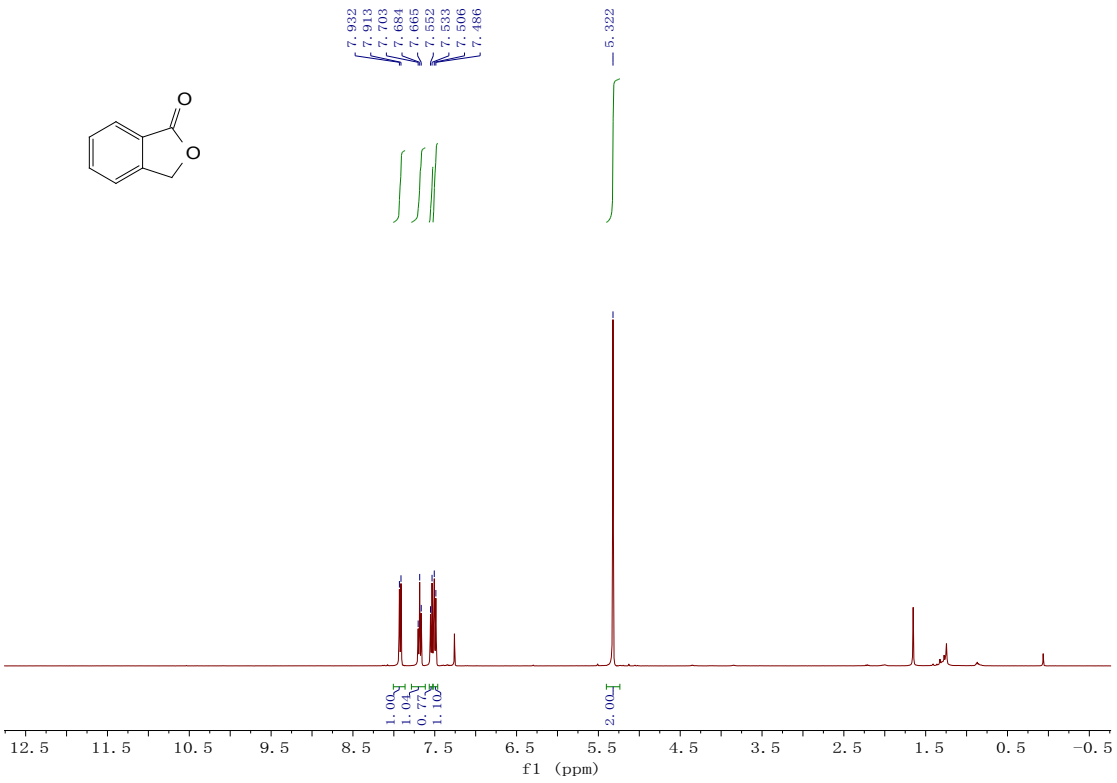
4,5-Dihydro-7*H*-thieno[2,3-*c*]pyran-7-one (16bb)

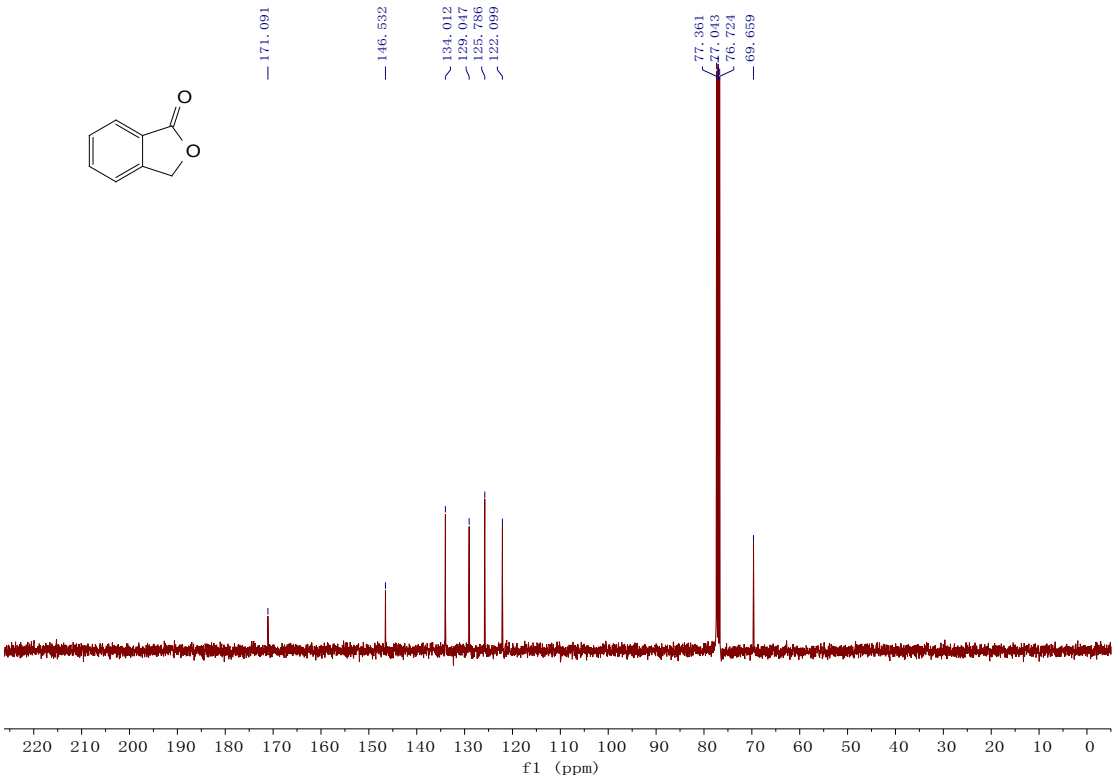


1-(4-Fluorophenyl)-3-oxo-1,3-dihydroisobenzofuran-5-carbonitrile (17bb)



Isobenzofuran-1(3*H*)-one (18bb)





7-Benzylisochroman-1-one (22bb)