Electronic Supporting Information
Nickel-Catalysed Reductive C-N bond Cross-coupling between Aryl Halides and *N*-Chloroamides

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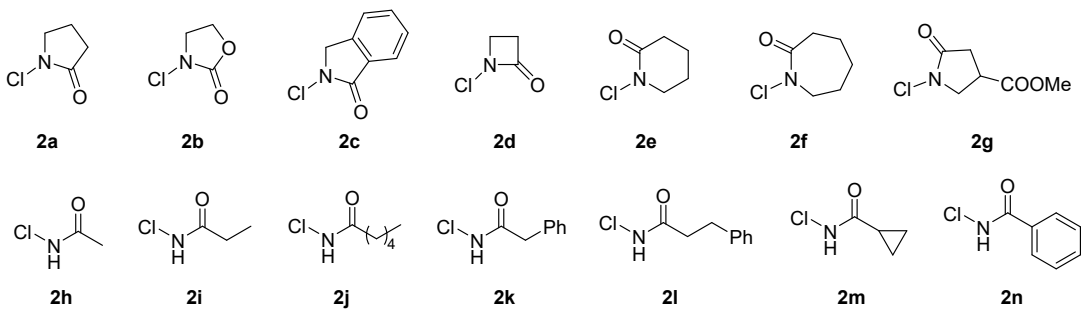
1. Materials and Methods

General Information: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance Neo 600M spectrometer and are calibrated using residual undeuterated solvent ($CDCl_3$ at 7.26 ppm ^{1}H NMR, 77.16 ppm ^{13}C NMR; CD_3OD at 3.31 ppm ^{1}H NMR, 49.00 ppm ^{13}C NMR; DMSO-d_6 at 2.50 ppm ^{1}H NMR, 39.52 ppm ^{13}C NMR). ^{19}F NMR was recorded on a Bruker Avance Neo 600M spectrometer ($CFCl_3$ as an external standard and low field is positive). 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 ^{19}F NMR using benzotrifluoride as an internal standard before working up the reaction. Melting points were determined by WRS-1C melting-point apparatus of Shanghai INESA Physico-Optical Instrument Co.,Ltd.

Materials: All reagents were used as received from commercial sources and used without further purification. Superdry solvents, DMF, DMA, NMP, THF, 1,4-dioxane and MeCN were purchased form Adamas chemicals. Anhydrous $NiCl_2$ and ligands were purchased from Adamas chemicals and used as received.

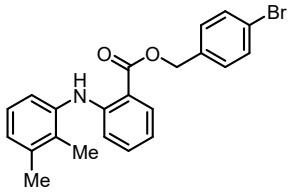
2. Preparation of *N*-chloroamides 2

The preparation of cyclic *N*-chloroamides **2a**-**2g** and primary *N*-chloroamides **2h**-**2n** were according to the literature.[1] The typical procedure for the preparation of **2a** is as follows: to a 100 mL round-bottom flask were added 2-pyrrolidinone (1 equiv) and DCM with stirring. The clear solution was cooled to 0 ℃ with an ice-water bath, and trichloroisocyanuric acid (1.05 equiv) was added. The reaction was stirred overnight at room temperature. After the complete consumption of the 2-pyrrolidinone monitored by TLC, the reaction was filtered through a pad of Celite and concentrated on a rotary evaporator to afford a white solid that is used without further purification.



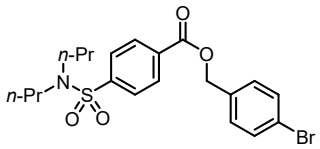
3. Preparation of Pharmaceutical-Derived Aryl Bromides

The general procedure for the preparation of pharmaceutical-derived 4-bromobenzyl ester is according to the literature.[2] Typical procedure for the preparation of **1w** is as follows: to a 250 mL round-bottom flask were added mefenamic acid (11 mmol, 1.1 equiv) and 4-bromophenyl methanol (10 mmol, 1 equiv). Then DCM (100 mL), 4-dimethylaminopyridine (DMAP) (2 mmol, 0.2 equiv) and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI) (12 mmol, 1.2 equiv) were added. The reaction was stirred at room temperature overnight. Upon completion, the reaction mixture was diluted with DCM, washed with aqueous $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 50/1) to give the corresponding 4-bromobenzyl 2-((2,3-dimethylphenyl)amino)benzoate **1w** as a white solid.

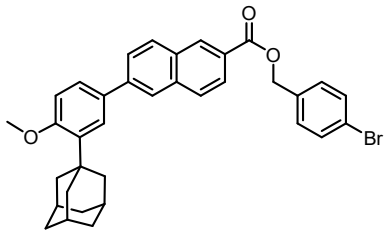


4-Bromobenzyl 2-((2,3-dimethylphenyl)amino)benzoate (1w). The product (4.0 g, 97% yield) as a white solid (m.p. 92.2 – 92.5 °C) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 50/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.23 (s, 1H), 7.98 (dd, J = 8.0, 1.5 Hz, 1H), 7.49 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 7.24 – 7.19 (m, 1H), 7.14 (d, J = 7.7 Hz, 1H), 7.08 (t, J = 7.7 Hz, 1H), 7.00 (d, J = 7.3 Hz, 1H), 6.74 (d, J = 8.5 Hz, 1H), 6.65 – 6.61 (m, 1H), 5.27 (s, 2H), 2.30 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.3, 149.8, 138.7, 138.3, 135.4, 134.5, 132.6, 131.8, 131.6, 129.8, 127.0, 126.1, 123.3, 122.3, 116.2, 113.8, 110.5, 65.5, 20.7, 14.1. MS (ESI): m/z

(%) 410.1 ([M+H]$^+$). HRMS (ESI) Calculated for $C_{22}H_{21}BrNO_2$ ([M+H]$^+$): 410.0750; Found: 410.0748.



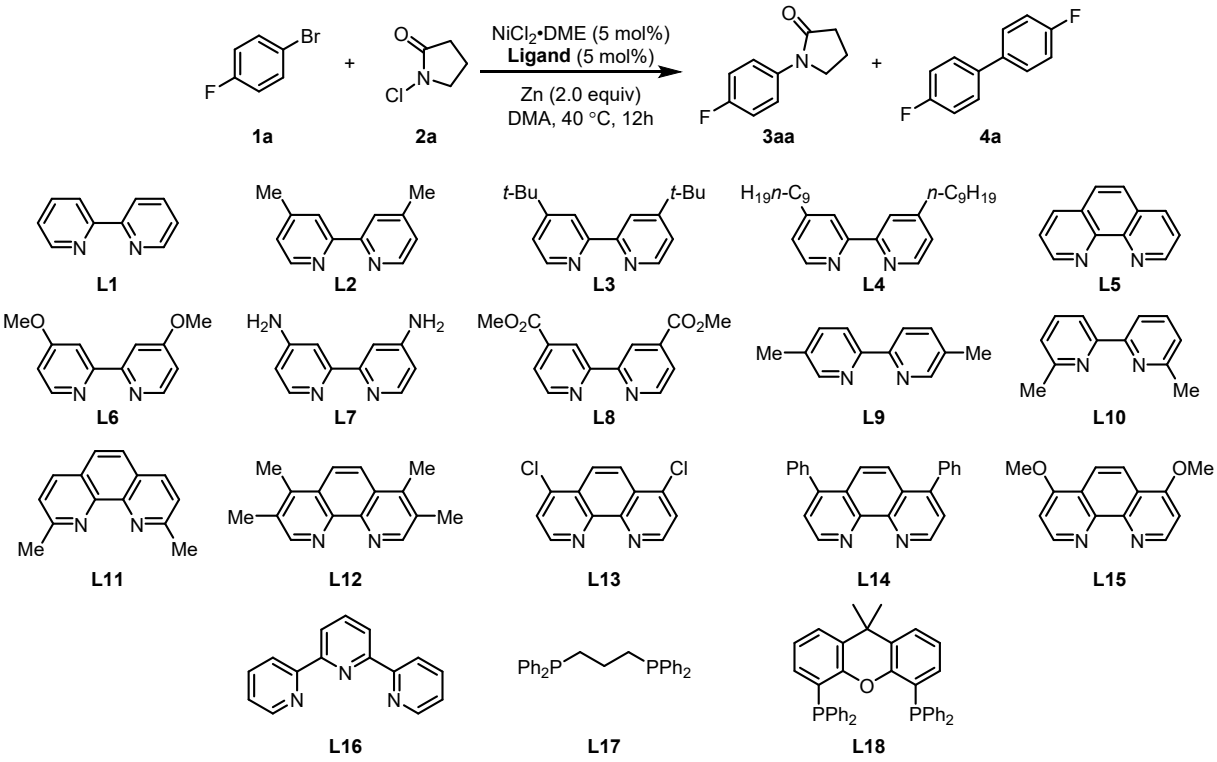
4-Bromobenzyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (1x). The product (1.8 g, 77% yield, 5 mmol of (4-bromophenyl) methanol was used) as a white solid (m.p. 58.6 – 59.5 ℃) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, *J* = 6.9 Hz, 2H), 7.85 (d, *J* = 6.8 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 6.5 Hz, 2H), 5.31 (s, 2H), 3.11 – 3.03 (m, 4H), 1.58 – 1.46 (m, 4H), 0.84 (t, *J* = 6.4 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.9, 144.5, 134.6, 133.2, 131.8, 130.3, 130.1, 127.0, 122.6, 66.5, 49.9, 21.9, 11.2. MS (ESI): m/z (%) 454.1 ([M+H]$^+$). HRMS (ESI) Calculated for $C_{20}H_{25}BrNO_4S$ ([M+H]$^+$): 454.0682; Found: 454.0679.



4-Bromobenzyl 6-(3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthoate (1y). The p-r oduct (471.2 mg, 81% yield, 1 mmol of (4-bromophenyl) methanol was used) as a white s-o lid (m.p. 202.5 – 204.8 ℃) was purified with silica gel chromatography (Petroleum ether/E-t hyl acetate = 50/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.09 (d, *J* = 8.3 Hz, 1H), 8.02 (s, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 8.6 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.62 (s, 1H), 7.55 (d, *J* = 8.2 Hz, 3H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 1H), 5.38 (s, 2H), 3.91 (s, 3H), 2.20 (s, 6H), 2.12 (s, 3H), 1.82 (s, 6H). ^{13}C NMR (151 MHz, C DCl_3) δ 166.7, 159.1, 141.7, 139.1, 136.2, 135.3, 132.6, 131.9, 131.3, 131.1, 130.1, 129.8, 1 28.4, 126.70, 126.66, 126.1, 125.9, 125.7, 124.8, 122.4, 112.2, 66.1, 55.3, 40.7, 37.3, 37.3, 2 9.2. MS (DART): m/z (%) 598.2 ([M+NH_4]$^+$). HRMS (DART) Calculated for $C_{35}H_{37}BrNO_3$ ([M+N H_4]$^+$): 598.1951; Found: 598.1952.

4. Optimization of Nickel Catalyzed Electrophilic Amidation of Aryl Bromide 1a with *N*-chloroamide 2a

Table S1. Ligand effect on Ni-catalyzed electrophilic amidation of aryl bromide 1a with *N*-chloroamides 2a.[a]

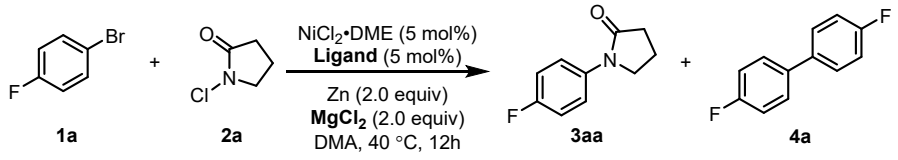


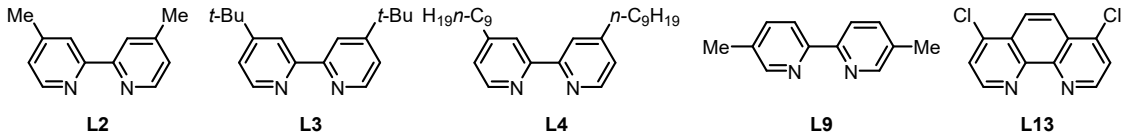
Entry	Ligand	**3aa,** yield (%)[b]	**4a,** yield (%)[b]
1	**L1**	ND	ND
2	**L2**	2	ND
3	**L3**	1	ND
4	**L4**	2	ND
5	**L5**	ND	ND
6	**L6**	ND	ND
7	**L7**	ND	ND
8	**L8**	ND	5
9	**L9**	4	ND
10	**L10**	ND	ND
11	**L11**	ND	ND
12	**L12**	ND	1
13	**L13**	1	ND
14	**L14**	ND	12

15	**L15**	ND	ND
16	**L16**	ND	ND
17	**L17**	ND	ND
18	**L18**	ND	ND

[a]Reaction conditions (unless otherwise specified): **1a** (0.4 mmol, 1.0 equiv), **2a** (1.5 equiv), and DMA (3 mL). [b]Determined by ^{19}F NMR using benzotrifluoride as an internal standard.

Table S2. Ligand effect on Ni-catalyzed electrophilic amidation of aryl bromide 1a with *N*-chloroamides 2a in the presence of $MgCl_2$.[a]

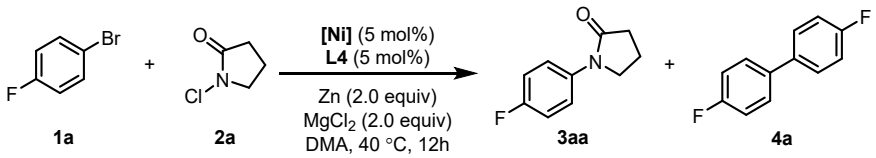




Entry	Ligand	**3aa,** yield (%)[b]	**4a,** yield (%)[b]
1	**L2**	19	1
2	**L3**	3	6
3	**L4**	22	2
4	**L9**	17	4
5	**L13**	6	1

[a]Reaction conditions (unless otherwise specified): **1a** (0.4 mmol, 1.0 equiv), **2a** (1.5 equiv), and DMA (3 mL). [b]Determined by ^{19}F NMR using benzotrifluoride as an internal standard.

Table S3. Screening of nickel catalysts for Ni-catalyzed electrophilic amidation of aryl bromide 1a with *N*-chloroamides 2a.[a]

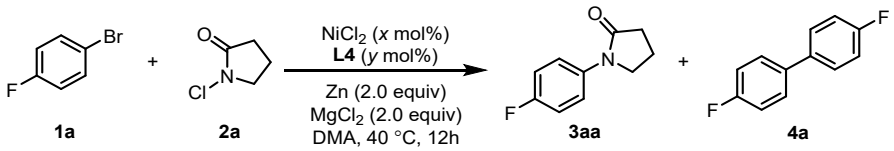


Entry	[Ni]	**3aa,** yield (%)[b]	**4a,** yield (%)[b]
1	$NiCl_2$·DME	22	2
2	$NiBr_2$·DME	16	2
3	$NiBr_2$·$3H_2O$	13	2
4	$NiCl_2(PPh_3)_2$	19	7

5	$NiCl_2$(dppp)	18	4
6	$NiCl_2$(dppe)	11	4
7	$NiBr_2(PPh_3)_2$	21	7
8	$NiCl_2$(dppf)	13	9
9	$Ni(oac)_2 \cdot 4H_2O$	21	2
10	$Ni(acac)_2$	ND	ND
11	$NiCl_2 \cdot 6H_2O$	13	3
12	$NiCl_2$	35	4

[a]Reaction conditions (unless otherwise specified): **1a** (0.4 mmol, 1.0 equiv), **2a** (1.5 equiv), and DMA (3 mL). [b]Determined by ^{19}F NMR using benzotrifluoride as an internal standard.

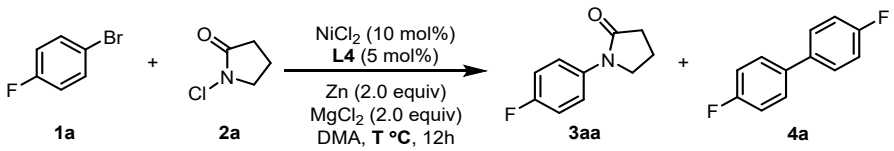
Table S4. Screening of ratio of $NiCl_2$/L4.[a]



Entry	$NiCl_2$ (x)/**L4** (y)	**3aa,** yield (%)[b]	**4a,** yield (%)[b]
1	5/5	35	4
2	5/10	14	3
3	10/5	79	3
4	10/10	67	6

[a]Reaction conditions (unless otherwise specified): **1a** (0.4 mmol, 1.0 equiv), **2a** (1.5 equiv), and DMA (3 mL). [b]Determined by ^{19}F NMR using benzotrifluoride as an internal standard.

Table S5. Temperature effect on Ni-catalyzed electrophilic amidation of aryl bromide 1a with *N*-chloroamides 2a.[a]

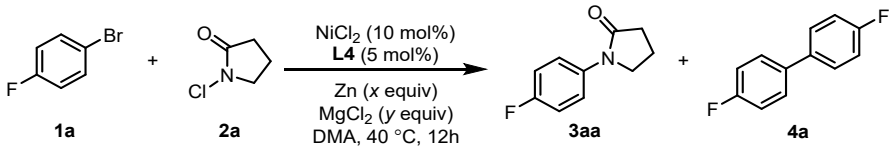


Entry	Temperature (°C)	**3aa,** yield (%)[b]	**4a,** yield (%)[b]
1	30℃	56	3
2	35℃	68	5
3	40℃	79	3

4	45℃	68	9
5	50℃	66	6
6	55℃	62	7

[a]Reaction conditions (unless otherwise specified): **1a** (0.4 mmol, 1.0 equiv), **2a** (1.5 equiv), and DMA (3 mL). [b]Determined by ^{19}F NMR using benzotrifluoride as an internal standard.

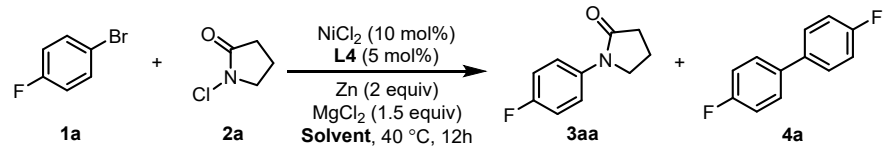
Table S6. Screening of ratio of Zn/$MgCl_2$.[a]



Entry	Zn (x)/$MgCl_2$ (y)	**3aa,** yield (%)[b]	**4a,** yield (%)[b]
1	2/2	79	3
2	2/3	32	20
3	3/3	38	33
4	3/4	29	36
5	2/1.5	80	2
6	3/2	70	10

[a]Reaction conditions (unless otherwise specified): **1a** (0.4 mmol, 1.0 equiv), **2a** (1.5 equiv), and DMA (3 mL). [b]Determined by ^{19}F NMR using benzotrifluoride as an internal standard.

Table S7. Solvent effect on Ni-catalyzed electrophilic amidation of aryl bromide 1a with *N*-chloroamides 2a.[a]

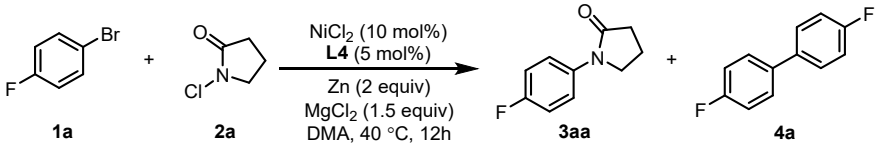


Entry	Solvent	**3aa,** yield (%)[b]	**4a,** yield (%)[b]
1	DMA	80	2
2	DMF	54	1
3	NMP	72	5
4	MeCN	ND	ND
5	1,4-dioxane	ND	ND
6	THF	ND	ND

[a]Reaction conditions (unless otherwise specified): **1a** (0.4 mmol, 1.0 equiv), **2a** (1.5 equiv), and DMA (3 mL).

[b]Determined by ^{19}F NMR using benzotrifluoride as an internal standard.

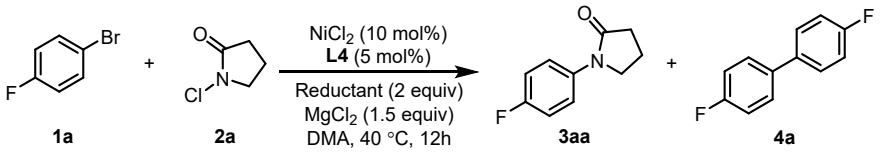
Table S8. Screening of equivalent of *N*-chloroamides 2a.[a]



Entry	Equiv of **2a**	**3aa,** yield (%)[b]	**4a,** yield (%)[b]
1	1.2	73	4
2	1.5	80	2
3	1.8	78	2
4	2	ND	ND

[a]Reaction conditions (unless otherwise specified): **1a** (0.4 mmol, 1.0 equiv), **2a** (1.5 equiv), and DMA (3 mL).
[b]Determined by ^{19}F NMR using benzotrifluoride as an internal standard.

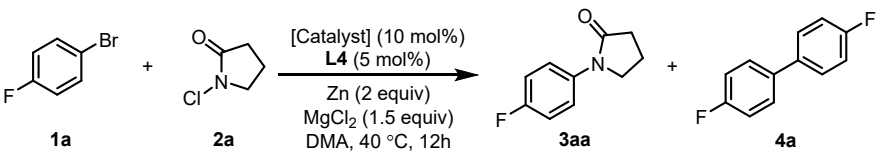
Table S9. Screening of other reductants.[a]



Entry	Reductant	**3aa,** yield (%)[b]	**4a,** yield (%)[b]
1	Zn	80	2
2	Mn	ND	ND
3	In	ND	ND
4	Fe	ND	ND

[a]Reaction conditions (unless otherwise specified): **1a** (0.4 mmol, 1.0 equiv), **2a** (1.5 equiv), and DMA (3 mL).
[b]Determined by ^{19}F NMR using benzotrifluoride as an internal standard.

Table S10. Control experiments.[a]



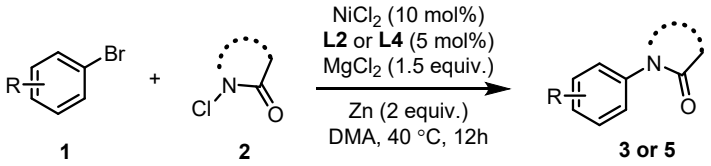
Entry	[Catalyst]	Ligand	**3aa,** yield (%)[b]	**4a,** yield (%)[b]
1	$NiCl_2$	**L4**	80	2

2	none	**L4**	ND	ND
3	$NiCl_2$	none	ND	ND
4	none	none	ND	ND
5	CuBr	**L4**	ND	ND

[a]Reaction conditions (unless otherwise specified): **1a** (0.4 mmol, 1.0 equiv), **2a** (1.5 equiv), and DMA (3 mL).

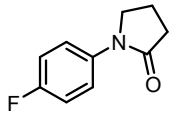
[b]Determined by ^{19}F NMR using benzotrifluoride as an internal standard.

5. General Procedure for Ni-Catalyzed Electrophilic Amination of Aryl Bromide 1 with *N*-chloroamides 2



To a 25 mL of Schlenk tube were added *N*-chloroamides **2** (0.6 mmol, 1.5 equiv), Zn (0.8 mmol, 2 equiv), ligand (5 mol%), $NiCl_2$ (10 mol%) and $MgCl_2$ (0.6 mmol, 1.5 equiv). The tube was evacuated and backfilled with argon for 3 times, then aryl bromide **1** (0.4 mmol, 1.0 equiv) and DMA (3 mL) were added under argon, and the tube was sealed with a Teflon cap. The resulting mixture was stirred at 40 ℃. After stirring for 12 h, the reaction mixture was diluted with ethyl acetate and filtered through a pad of Celite, then the filtrate was extracted with ethyl acetate and washed with brine. The organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography to give the corresponding products **3** and **5**. Isolated yields are based on the average of two runs under identical conditions.

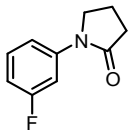
6. Characterization Data for Compounds 3 and 5



1-(4-Fluorophenyl)pyrrolidin-2-one (3aa). Known compound[3]. The product (50.2 mg, 70% yield) as a white solid (m.p. 55.5 – 55.6 ℃) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 1/1). ^1H NMR (600 MHz, $CDCl_3$) δ 7.59 – 7.49 (m, 2H), 7.08 – 6.96 (m, 2H), 3.80 (t, *J* = 7.1 Hz, 2H), 2.57 (t, *J* = 8.1 Hz, 2H), 2.13 (p, *J* = 7.6 Hz, 2H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -117.8 – -117.9 (m, 1F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.2, 159.5 (d, *J* = 244.2 Hz), 135.6 (d, *J* = 2.7 Hz), 121.7 (d, *J* = 8.0 Hz), 115.5 (d, *J* = 22.3 Hz), 49.0, 32.6, 18.0.

Gram-scale synthesis of compound 3aa

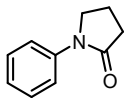
To a 100 mL of Schlenk tube were added Zn (20 mmol, 2 equiv.), 4,4'-dinonyl-2,2'-bpy (5 mol%), $NiCl_2$ (10 mol%) and $MgCl_2$ (15 mmol, 1.5 equiv). The tube was evacuated and backfilled with argon for 3 times, then DMA (30 mL) and the DMA solution of **1a** (10 mmol, 1 equiv) and **2a** (15 mmol, 1.5 equiv) were added under argon, and the tube was sealed with a Teflon cap. The resulting mixture was at 40 ℃. After stirring for 12h, the reaction mixture was then diluted with ethyl acetate and filtered through a pad of Celite and the filtrate was concentrated and extracted with ethyl acetate, washed with brine. The organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 1/1) to give the corresponding products **3aa** as a white solid (1.1 g, 63% yield).



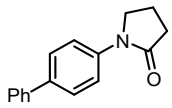
1-(3-Fluorophenyl)pyrrolidin-2-one (3ab). Known compound[3]. The product (50.7 mg, 71% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 1/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 – 7.48 (m, 1H), 7.28 – 7.23 (m, 2H), 6.81 – 6.75 (m, 1H), 3.77 (t, *J* = 7.1 Hz, 2H), 2.55 (t, *J* = 8.1 Hz, 2H), 2.15 – 2.05 (m, 2H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -111.5 – -111.7 (m, 1F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.4, 162.8 (d, *J* = 244.4 Hz), 141.0 (d, *J* = 10.5 Hz), 129.9 (d, *J* = 9.3 Hz), 114.7 (d, *J* = 3.0 Hz), 111.0 (d, *J* = 21.3 Hz), 107.1 (d, *J* = 26.2 Hz), 48.6, 32.8, 17.8.

1-(2-Fluorophenyl)pyrrolidin-2-one (3ac). Known compound[3]. The product (24.0 mg, 34% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 2/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.8 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.17 – 7.09 (m, 2H), 3.81 (t, *J* = 7.0 Hz, 2H), 2.55 (t, *J* = 8.1 Hz, 2H), 2.23 – 2.16 (m, 2H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -119.8

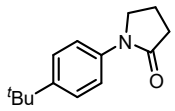
– -120.1 (m, 1F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.9, 157.2 (d, *J* = 250.3 Hz), 128.4 (d, *J* = 8.0 Hz), 128.0 (d, *J* = 1.8 Hz), 126.4 (d, *J* = 11.8 Hz), 124.5 (d, *J* = 3.7 Hz), 116.7 (d, *J* = 20.1 Hz), 50.1, 31.2, 19.1.



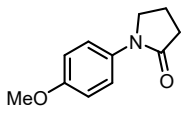
1-Phenylpyrrolidin-2-one (3b). Known compound[3]. The product (31.5 mg, 49% yield) as a white solid (m.p. 62.7 – 65.3 ℃) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 2/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.7 Hz, 2H), 7.42 – 7.31 (m, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 3.86 (t, *J* = 7.0 Hz, 2H), 2.60 (t, *J* = 8.1 Hz, 2H), 2.15 (p, *J* = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.3, 139.5, 128.9, 124.6, 120.1, 48.9, 32.9, 18.1.



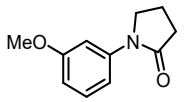
1-([1,1'-Biphenyl]-4-yl)pyrrolidin-2-one (3c). Known compound[4]. The product (59.9 mg, 63% yield, **L2** was used) as a white solid (m.p. 183.0 – 183.7 ℃) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 1/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.7 Hz, 2H), 7.64 – 7.55 (m, 4H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 3.90 (t, *J* = 7.0 Hz, 2H), 2.64 (t, *J* = 8.1 Hz, 2H), 2.18 (p, *J* = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.4, 140.6, 138.8, 137.3, 128.9, 127.5, 127.3, 127.0, 120.3, 48.9, 32.9, 18.1.



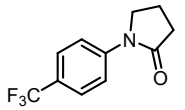
1-(4-(*Tert*-butyl)phenyl)pyrrolidin-2-one (3d). Known compound[5]. The product (40.1 mg, 46% yield) as a white solid (m.p. 70.0 – 71.5 ℃) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 2/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.7 Hz, 2H), 7.38 (d, *J* = 8.7 Hz, 2H), 3.84 (t, *J* = 7.0 Hz, 2H), 2.59 (t, *J* = 8.0 Hz, 2H), 2.18 – 2.09 (m, 2H), 1.31 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.2, 147.5, 136.9, 125.7, 119.9, 48.9, 34.4, 32.7, 31.4, 18.2.



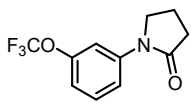
1-(4-Methoxyphenyl)pyrrolidin-2-one (3e). Known compound[3]. The product (38.3 mg, 50% yield) as a white solid (m.p. 114.1 – 114.9 ℃) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 1/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.9 Hz, 2H), 3.83 – 3.74 (m, 5H), 2.56 (t, *J* = 8.1 Hz, 2H), 2.16 – 2.08 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.1, 156.7, 132.8, 122.0, 114.2, 55.6, 49.3, 32.6, 18.2.



1-(3-Methoxyphenyl)pyrrolidin-2-one (3f). Known compound[6]. The product (39.5 mg, 52% yield) as a white solid (m.p. 58.7 – 59.1 ℃) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 2/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (t, *J* = 2.3 Hz, 1H), 7.26 (t, *J* = 8.6 Hz, 1H), 7.12 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.70 (dd, *J* = 8.2, 2.4 Hz, 1H), 3.84 (t, *J* = 7.0 Hz, 2H), 3.81 (s, 3H), 2.60 (t, *J* = 8.1 Hz, 2H), 2.14 (p, *J* = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.4, 160.0, 140.7, 129.5, 112.1, 110.1, 106.1, 55.4, 49.0, 33.0, 18.0.

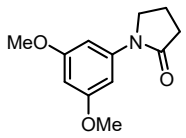


1-(4-(Trifluoromethyl)phenyl)pyrrolidin-2-one (3g). Known compound[7]. The product (54.4 mg, 59% yield) as a white solid (m.p. 133.5 – 135.1 ℃) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 3/2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 3.88 (t, *J* = 7.1 Hz, 2H), 2.63 (t, *J* = 8.1 Hz, 2H), 2.19 (p, *J* = 7.7 Hz, 2H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.2 (s, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.8, 142.5, 126.1 (q, *J* = 3.8 Hz), 126.1 (q, *J* = 32.8 Hz), 124.3 (q, *J* = 271.7 Hz), 119.3, 48.6, 32.9, 18.0.

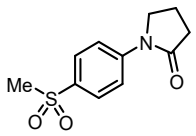


1-(3-(Trifluoromethoxy)phenyl)pyrrolidin-2-one (3h). Known compound. The product (50.8 mg, 52% yield) as a white solid (m.p. 46.7 – 47.5 ℃) was purified with silica gel chromatography

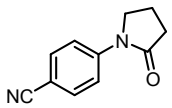
(Petroleum ether/Ethyl acetate = 3/2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.35 (t, *J* = 8.3 Hz, 1H), 6.98 (d, *J* = 9.0 Hz, 1H), 3.83 (t, *J* = 7.1 Hz, 2H), 2.60 (t, *J* = 8.1 Hz, 2H), 2.16 (p, *J* = 7.6 Hz, 2H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -57.8 (s, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.5, 149.5, 140.9, 129.9, 120.6 (q, *J* = 257.4 Hz), 117.6, 116.4, 112.5, 48.6, 32.8, 17.9. MS (ESI): m/z (%) 246.1 ($[M+H]^+$). HRMS (ESI) Calculated for $C_{11}H_{11}F_3NO_2$ ($[M+H]^+$): 246.0736; Found: 246.0730.



1-(3,5-Dimethoxyphenyl)pyrrolidin-2-one (3i). Known compound[8]. The product (34.5 mg, 39% yield) as a white solid (m.p. 83.8 – 84.3 ℃) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 2/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.85 (d, *J* = 2.2 Hz, 2H), 6.26 (t, *J* = 2.2 Hz, 1H), 3.81 (t, *J* = 7.1 Hz, 3H), 3.78 (s, 5H), 2.59 (t, *J* = 8.1 Hz, 2H), 2.13 (p, *J* = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.5, 161.0, 141.3, 98.6, 96.7, 55.5, 49.1, 33.1, 18.0.

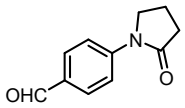


1-(4-(Methylsulfonyl)phenyl)pyrrolidin-2-one (3j). The product (42.7 mg, 45% yield) as a white solid (m.p. 179.4 – 180.7 ℃) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 1/3). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.8 Hz, 2H), 7.83 (d, *J* = 8.8 Hz, 2H), 3.88 (t, *J* = 7.0 Hz, 2H), 3.01 (s, 3H), 2.63 (t, *J* = 8.1 Hz, 2H), 2.19 (p, *J* = 7.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.0, 144.1, 135.2, 128.4, 119.4, 48.5, 44.7, 32.8, 17.9. MS (ESI): m/z (%) 240.1 ($[M+H]^+$). HRMS (ESI) Calculated for $C_{11}H_{14}NO_3S$ ($[M+H]^+$): 240.0689; Found: 240.0691.

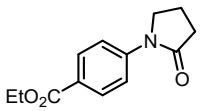


4-(2-Oxopyrrolidin-1-yl)benzonitrile (3k). Known compound[4]. The product (27.8 mg, 37% yield) as a white solid (m.p. 116.2 – 117.4 ℃) was purified with silica gel chromatography (Petroleum

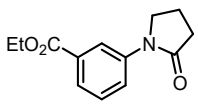
ether/Ethyl acetate = 2/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.8 Hz, 2H), 3.86 (t, *J* = 7.1 Hz, 2H), 2.63 (t, *J* = 8.1 Hz, 2H), 2.19 (p, *J* = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.9, 143.3, 133.0, 119.3, 119.0, 107.1, 48.3, 32.9, 17.8.



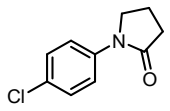
4-(2-Oxopyrrolidin-1-yl)benzaldehyde (3l). The product (21.8 mg, 29% yield) as a white solid (m.p. 121.7 – 122.5 ℃) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 1/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.92 (s, 1H), 7.88 – 7.84 (m, 2H), 7.83 – 7.79 (m, 2H), 3.90 (t, *J* = 7.0 Hz, 2H), 2.63 (t, *J* = 8.1 Hz, 2H), 2.19 (p, *J* = 7.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.2, 174.9, 144.8, 132.1, 130.8, 119.1, 48.6, 33.0, 17.9. MS (ESI): m/z (%) 190.1 ($[M+H]^+$). HRMS (ESI) Calculated for $C_{11}H_{12}NO_2$ ($[M+H]^+$): 190.0863; Found: 190.0866.



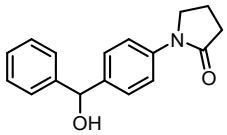
Ethyl 4-(2-oxopyrrolidin-1-yl)benzoate (3m). Known compound[9] The product (41.3 mg, 44% yield) as a white solid (m.p. 94.1 – 94.9 ℃) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 2/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.7 Hz, 2H), 7.66 (d, *J* = 7.7 Hz, 2H), 4.41 – 4.23 (m, 2H), 3.92 – 3.73 (m, 2H), 2.65 – 2.44 (m, 2H), 2.25 – 2.01 (m, 2H), 1.48 – 1.27 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.6, 166.1, 143.3, 130.3, 125.7, 118.5, 60.8, 48.4, 32.8, 17.8, 14.3.



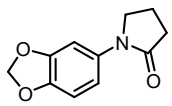
Ethyl 3-(2-oxopyrrolidin-1-yl)benzoate (3n). The product (51.7 mg, 56% yield) as a white solid (m.p. 75.7 – 76.9 ℃) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 3/2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 – 8.04 (m, 1H), 8.03 (t, *J* = 1.9 Hz, 1H), 7.82 – 7.79 (m, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.90 (t, *J* = 7.0 Hz, 2H), 2.62 (t, *J* = 8.1 Hz, 2H), 2.17 (p, *J* = 7.6 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.5, 166.4, 139.7, 131.2, 129.0, 125.5, 124.7, 120.3, 61.3, 48.8, 32.8, 18.1, 14.4. MS (ESI): m/z (%) 234.1 ($[M+H]^+$). HRMS (ESI) Calculated for $C_{13}H_{16}NO_3$ ($[M+H]^+$): 234.1125; Found: 234.1120.



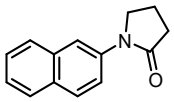
1-(4-Chlorophenyl)pyrrolidin-2-one (3o). Known compound[3]. The product (45.3 mg, 58% yield) as a white solid (m.p. 93.0 – 93.8 ℃) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 1/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 3.80 (t, *J* = 6.9 Hz, 2H), 2.58 (t, *J* = 8.0 Hz, 2H), 2.14 (p, *J* = 7.4 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.4, 138.1, 129.6, 128.9, 121.1, 48.8, 32.8, 18.0.



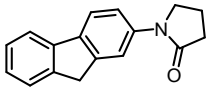
1-(4-(Hydroxy(phenyl)methyl)phenyl)pyrrolidin-2-one (3p). The product (47.7 mg, 45% yield) as a colorless colloidal oil was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 1/2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.6 Hz, 2H), 7.35 – 7.31 (m, 4H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 5.73 (s, 1H), 3.75 (t, *J* = 7.0 Hz, 2H), 3.35 (s, 1H), 2.49 (t, *J* = 8.1 Hz, 2H), 2.06 (p, *J* = 7.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.5, 144.0, 140.4, 138.4, 128.4, 127.4, 127.0, 126.5, 119.9, 75.5, 48.8, 32.6, 17.9. MS (ESI): m/z (%) 268.1 ($[M+H]^+$). HRMS (ESI) Calculated for $C_{17}H_{18}NO_2$ ($[M+H]^+$): 268.1332; Found: 268.1332.



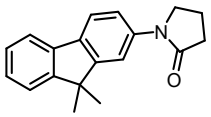
1-(Benzo[d][1,3]dioxol-5-yl)pyrrolidin-2-one (3q). Known compound[10]. The product (35.2 mg, 43% yield) as a white solid (m.p. 90.6 – 91.2 ℃) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 1/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (d, *J* = 2.0 Hz, 1H), 6.83 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 5.92 (s, 2H), 3.77 (t, *J* = 7.0 Hz, 2H), 2.55 (t, *J* = 8.1 Hz, 2H), 2.11 (p, *J* = 7.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.1, 147.8, 144.5, 133.8, 113.3, 107.9, 103.0, 101.3, 49.6, 32.6, 18.0.



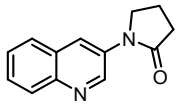
1-(Naphthalen-2-yl)pyrrolidin-2-one (3r). Known compound[11]. The product (43.1 mg, 51% yield) as a white solid (m.p. 125.5 – 126.3 ℃) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 3/2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.9 Hz, 1H), 7.89 – 7.76 (m, 4H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 3.93 (t, *J* = 7.0 Hz, 2H), 2.63 (t, *J* = 8.0 Hz, 2H), 2.16 (p, *J* = 7.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.5, 137.3, 133.6, 130.7, 128.6, 127.7, 127.6, 126.4, 125.3, 119.9, 116.8, 49.1, 32.9, 18.1.



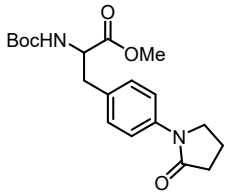
1-(9*H*-Fluoren-2-yl)pyrrolidin-2-one (3s). The product (57.7 mg, 58% yield) as a white solid (m.p. 202.4 – 202.9℃) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 1/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.75 (dd, *J* = 7.9, 3.2 Hz, 2H), 7.56 – 7.48 (m, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.30 – 7.26 (m, 1H), 3.94 – 3.88 (m, 4H), 2.64 (t, *J* = 8.1 Hz, 2H), 2.18 (p, *J* = 7.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.3, 144.1, 143.4, 141.4, 138.4, 138.3, 126.9, 126.5, 125.1, 120.0, 119.8, 118.8, 117.3, 49.4, 37.2, 32.9, 18.2. MS (ESI): m/z (%) 250.1 ($[M+H]^+$). HRMS (ESI) Calculated for $C_{17}H_{16}NO$ ($[M+H]^+$): 250.1226; Found: 250.1226.



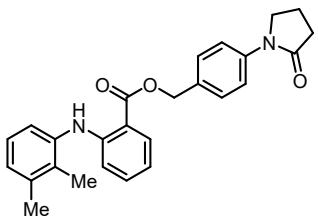
1-(9,9-Dimethyl-9*H*-fluoren-2-yl)pyrrolidin-2-one (3t). The product (48.8 mg, 40% yield) as a white solid (m.p. 113.1 – 114.3 ℃) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 3/2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 1.9 Hz, 1H), 7.72 – 7.67 (m, 2H), 7.49 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.43 (d, *J* = 7.3 Hz, 1H), 7.36 – 7.27 (m, 2H), 3.92 (t, *J* = 6.9 Hz, 2H), 2.63 (t, *J* = 8.1 Hz, 2H), 2.16 (p, *J* = 7.2 Hz, 2H), 1.50 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.2, 154.4, 153.8, 138.9, 138.8, 135.6, 127.1, 127.0, 122.6, 120.2, 119.8, 118.8, 114.7, 49.3, 47.1, 32.9, 27.3, 18.1. MS (ESI): m/z (%) 278.2 ($[M+H]^+$). HRMS (ESI) Calculated for $C_{19}H_{20}NO$ ($[M+H]^+$): 278.1539; Found: 278.1534.



1-(Quinolin-3-yl)pyrrolidin-2-one (3u). The product (32.7 mg, 39% yield) as a white solid (m.p. 122.3 – 125.6 ℃) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 1/3). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.21 (d, *J* = 2.6 Hz, 1H), 8.32 (d, *J* = 2.5 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.62 – 7.58 (m, 1H), 7.49 (t, *J* = 7.9 Hz, 1H), 3.93 (t, *J* = 7.0 Hz, 2H), 2.61 (t, *J* = 8.1 Hz, 2H), 2.19 (p, *J* = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.8, 145.2, 143.8, 133.2, 129.1, 128.5, 127.9, 127.7, 127.1, 123.9, 48.3, 32.3, 18.1. MS (ESI): m/z (%) 213.1 ($[M+H]^+$). HRMS (ESI) Calculated for $C_{13}H_{13}N_2O$ ($[M+H]^+$): 213.1022; Found: 213.1030.

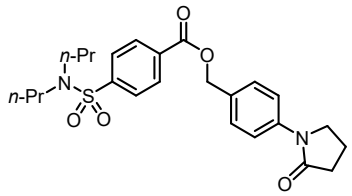


Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(4-(2-oxopyrrolidin-1-yl)phenyl)propanoate (3v). The product (73.7 mg, 51% yield) as a colorless colloidal oil was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 1/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.6 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 4.97 (d, *J* = 7.7 Hz, 1H), 4.59 – 4.49 (m, 1H), 3.82 (t, *J* = 7.1 Hz, 2H), 3.70 (s, 3H), 3.12 – 2.98 (m, 2H), 2.58 (t, *J* = 8.1 Hz, 2H), 2.14 (p, *J* = 7.6 Hz, 2H), 1.40 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.3, 172.3, 155.2, 138.5, 132.1, 129.8, 120.0, 80.0, 54.5, 52.3, 48.8, 37.7, 32.8, 28.4, 18.1. MS (ESI): m/z (%) 385.2 ($[M+Na]^+$). HRMS (ESI) Calculated for $C_{19}H_{26}N_2NaO_5$ ($[M+Na]^+$): 385.1734; Found: 385.1736.

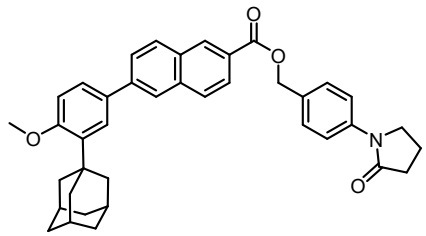


4-(2-Oxopyrrolidin-1-yl)benzyl 2-((2,3-dimethylphenyl)amino)benzoate (3w). The product (72.7 mg, 44% yield, **L2** was used) as a white solid (m.p. 143.9 – 147.0 ℃) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 1/2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.25 (s, 1H),

7.98 (d, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.22 (t, *J* = 7.9 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 8.5 Hz, 1H), 6.63 (t, *J* = 7.5 Hz, 1H), 5.32 (s, 2H), 3.85 (t, *J* = 7.0 Hz, 2H), 2.60 (t, *J* = 8.1 Hz, 2H), 2.32 (s, 3H), 2.17 (s, 3H), 2.16 – 2.11 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.4, 168.5, 149.7, 139.5, 138.8, 138.3, 134.4, 132.6, 132.3, 131.7, 128.9, 126.9, 126.0, 123.2, 120.0, 116.2, 113.8, 110.8, 65.9, 48.8, 32.9, 20.7, 18.1, 14.1. MS (ESI): m/z (%) 415.2 ($[M+H]^+$). HRMS (ESI) Calculated for $C_{26}H_{27}N_2O_3$ ($[M+H]^+$): 415.2016; Found: 415.2008.

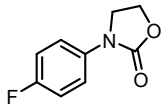


4-(2-Oxopyrrolidin-1-yl)benzyl 4-(*N,N*-dipropylsulfamoyl)benzoate (3x). The product (100.2 mg, 55% yield, **L2** was used) as a white solid (m.p. 104.1 – 104.4 °C) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 1/2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 5.34 (s, 2H), 3.86 (t, *J* = 7.0 Hz, 2H), 3.07 (t, *J* = 7.7Hz, 4H), 2.60 (t, *J* = 8.1 Hz, 2H), 2.16 (p, *J* = 7.5 Hz, 2H), 1.57 – 1.46 (m, 4H), 0.84 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.4, 165.1, 144.4, 139.8, 133.5, 131.5, 130.4, 129.3, 127.1, 120.0, 67.0, 50.0, 48.8, 32.8, 22.0, 18.1, 11.2. MS (ESI): m/z (%) 459.2 ($[M+H]^+$). HRMS (ESI) Calculated for $C_{24}H_{31}N_2O_5S$ ($[M+H]^+$): 459.1948; Found: 459.1950.



4-(2-Oxopyrrolidin-1-yl)benzyl 6-(3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthoate (3y). The product (36 mg, 31% yield, 50 °C, and 0.2 mmol of the corresponding aryl bromine were used) as a white solid (m.p. 207 °C) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 1/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.09 (d, *J* = 8.6 Hz, 1H), 8.01 (s, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.6 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.67 (d,

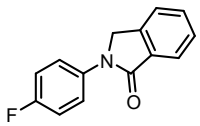
J = 7.9 Hz, 2H), 7.61 (s, 1H), 7.56 – 7.49 (m, 3H), 6.99 (d, *J* = 8.4 Hz, 1H), 5.40 (s, 2H), 3.90 (s, 3H), 3.87 (t, *J* = 7.0 Hz, 2H), 2.62 (t, *J* = 8.0 Hz, 2H), 2.19 (s, 6H), 2.18 – 2.14 (m, 2H), 2.11 (s, 3H), 1.81 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.5, 166.8, 159.1, 141.6, 139.6, 139.1, 136.2, 132.7, 132.3, 131.4, 131.1, 129.9, 129.2, 128.4, 127.0, 126.6, 126.1, 125.9, 125.8, 124.9, 120.1, 112.3, 66.6, 55.3, 48.9, 40.8, 37.4, 37.3, 32.9, 29.3, 18.2. MS (ESI): m/z (%) 608.3 ([M+Na]$^+$). HRMS (ESI) Calculated for $C_{39}H_{39}NNaO_4$ ([M+Na]$^+$): 608.2771; Found: 608.2765.



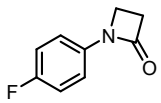
3-(4-Fluorophenyl)oxazolidin-2-one (5a). Known compound[12]. The product (47.3 mg, 65% yield) as a white solid (m.p. 72.2 – 74.5 ℃) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 1/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 2H), 7.08 – 7.00 (m, 2H), 4.48 – 4.42 (m, 2H), 4.04 – 3.99 (m, 2H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -118.5 – -118.7 (m, 1F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3 (d, *J* = 243.9 Hz), 155.5, 134.4 (d, *J* = 2.6 Hz), 120.1 (d, *J* = 8.0 Hz), 115.8 (d, *J* = 22.5 Hz), 61.4, 45.5.

Gram-scale synthesis of compound 5a

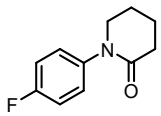
To a 100 mL of Schlenk tube were added Zn (30 mmol, 2 equiv), 4,4'-dinonyl-2,2'-bpy (5 mol%), $NiCl_2$ (10 mol%) and $MgCl_2$ (22.5 mmol, 1.5 equiv). The tube was evacuated and backfilled with argon for 3 times, then DMA (30 mL) and DMA solution of **1a** (15 mmol, 1 equiv) and **2b** (22.5 mmol, 1.5 equiv)were added under argon, and the tube was sealed with a Teflon cap. The resulting mixture was stirred at 40 ℃. After stirring for 12h, the reaction mixture was diluted with ethyl acetate and filtered through a pad of Celite, then the filtrate was concentrated and extracted with ethyl acetate, washed with brine. The organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 1/1) to give the corresponding products **5a** as a white solid (1.4 g, 53% yield).



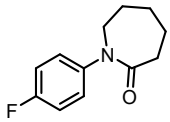
2-(4-Fluorophenyl)isoindolin-1-one (5b). Known compound[13]. The product (39.1 mg, 43% yield) as a white solid (m.p. 174.4 – 178.3 °C) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 1/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2 Hz, 1H), 7.85 – 7.78 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.1 Hz, 2H), 7.14 – 7.07 (m, 2H), 4.82 (s, 2H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -117.8 – -117.9 (m, 1F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.5, 159.7 (d, *J* = 244.5 Hz), 140.1, 135.7 (d, *J* = 2.8 Hz), 133.1, 132.3, 128.6, 124.3, 122.8, 121.4 (d, *J* = 7.9 Hz), 116.0 (d, *J* = 22.4 Hz), 51.1.



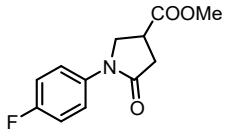
1-(4-Fluorophenyl)azetidin-2-one (5c). Known compound[14]. The product (27.9 mg, 42% yield, 50 °C, **L9**, the corresponding aryl iodide and 1.0 equiv of **2d** were used) as a white solid (m.p. 96.4 – 96.6°C) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 1/2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 2H), 7.06 – 6.98 (m, 2H), 3.61 (t, *J* = 4.4 Hz, 2H), 3.12 (t, *J* = 4.4 Hz, 2H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -118.3 – -118.4 (m, 1F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.3, 159.1 (d, *J* = 243.0 Hz), 135.0 (d, *J* = 2.6 Hz), 117.6 (d, *J* = 7.8 Hz), 116.0 (d, *J* = 22.8 Hz), 38.3, 36.4.



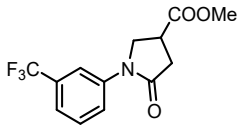
1-(4-Fluorophenyl)piperidin-2-one (5d). Known compound[4]. The product (24.4 mg, 32% yield, 50 °C, **L6**, and the corresponding aryl iodide were used) as a white solid (m.p. 103.6 – 104.0 °C) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 1/2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 – 7.17 (m, 2H), 7.10 – 7.03 (m, 2H), 3.60 (t, *J* = 5.8 Hz, 2H), 2.55 (t, *J* = 6.2 Hz, 2H), 1.98 – 1.88 (m, 4H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -115.3 – -115.4 (m, 1F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.3, 161.1 (d, *J* = 246.0 Hz), 139.4 (d, *J* = 3.1 Hz), 128.1 (d, *J* = 8.4 Hz), 116.1 (d, *J* = 22.6 Hz), 52.0, 32.9, 23.7, 21.6.



1-(4-Fluorophenyl)azepan-2-one (5e). The product (29.8 mg, 36% yield, 50 ℃, **L6**, and the corresponding aryl iodide were used) as a yellow oil was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 1/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 (dd, *J* = 8.2, 5.2 Hz, 2H), 7.01 (t, *J* = 8.5 Hz, 2H), 3.68 (d, *J* = 6.2 Hz, 2H), 2.66 (d, *J* = 6.1 Hz, 2H), 1.78 (s, 6H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -115.8 – -115.9 (m, 1F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.7, 160.8 (d, *J* = 245.7 Hz), 140.5 (d, *J* = 3.1 Hz), 127.9 (d, *J* = 8.4 Hz), 115.8 (d, *J* = 22.6 Hz), 53.1, 37.5, 29.7, 28.8, 23.4. MS (ESI): m/z (%) 208.1 ([M+H]$^+$). HRMS (ESI) Calculated for $C_{12}H_{15}FNO$ ([M+H]$^+$): 208.1132; Found: 208.1130.

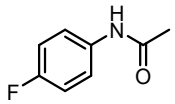


Methyl 1-(4-fluorophenyl)-5-oxopyrrolidine-3-carboxylate (5f). Known compound[15]. The product (39.0 mg, 41% yield) as a white solid (m.p. 96.8 – 97.2 ℃) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 1/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 8.8, 4.6 Hz, 2H), 7.05 (t, *J* = 8.6 Hz, 2H), 4.08 (dd, *J* = 9.7, 6.6 Hz, 1H), 4.00 (t, *J* = 9.2 Hz, 1H), 3.77 (s, 3H), 3.36 (p, *J* = 8.1 Hz, 1H), 2.95 – 2.81 (m, 2H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -116.9 – -117.1 (m, 1F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.9, 171.5, 159.8 (d, *J* = 245.0 Hz), 134.9 (d, *J* = 2.8 Hz), 122.1 (d, *J* = 8.0 Hz), 115.7 (d, *J* = 22.4 Hz), 52.7, 50.7, 35.9, 35.4.

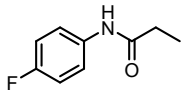


Methyl 5-oxo-1-(3-(trifluoromethyl)phenyl)pyrrolidine-3-carboxylate (5g). The product (67.0 mg, 58% yield, 50℃ and **L2** were used) as a yellow oil was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 3/2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.81 (d, *J* = 8.3 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 4.10 (dd, *J* = 9.8, 6.5 Hz, 1H), 4.04 (t, *J* = 9.2 Hz, 1H), 3.75 (s, 3H), 3.36 (p, *J* = 8.1 Hz, 1H), 2.95 – 2.81 (m, 2H).^{19}F NMR (565 MHz, $CDCl_3$) δ -

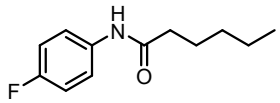
62.7 (s, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.7, 171.8, 139.3, 131.3 (q, J = 32.4 Hz), 129.5, 123.9 (q, J = 272.6 Hz), 122.9, 121.3 (q, J = 3.7 Hz), 116.3 (q, J = 3.9 Hz), 52.7, 50.1, 35.7, 35.4. MS (ESI): m/z (%) 288.1 ($[M+H]^+$). HRMS (ESI) Calculated for $C_{13}H_{13}F_3NO_3$ ($[M+H]^+$): 288.0842; Found: 288.0846.



***N*-(4-fluorophenyl)acetamide (5h).** Known compound[3]. The product (40.7 mg, 56% yield) as a white solid (m.p. 205.6 – 205.8 ℃) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 1/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.47 – 7.41 (m, 2H), 6.99 (t, J = 8.6 Hz, 2H), 2.15 (s, 3H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -117.9 – -118.0 (m, 1F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.5, 159.4 (d, J = 243.7 Hz), 133.9 (d, J = 2.7 Hz), 121.9 (d, J = 7.9 Hz), 115.6 (d, J = 22.5 Hz), 24.4.

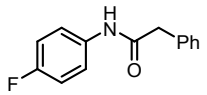


***N*-(4-fluorophenyl)propionamide (5i).** Known compound[16]. The product (30.2 mg, 45% yield, 1.7 equiv of **2i** was used) as a white solid (m.p. 122.3 ℃) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 2/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.51 – 7.40 (m, 2H), 6.95 (t, J = 8.6 Hz, 2H), 2.35 (q, J = 7.6 Hz, 2H), 1.20 (t, J = 7.6 Hz, 3H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -118.2 – -118.3 (m, 1F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.6, 159.4 (d, J = 243.4 Hz), 134.2 (d, J = 3.1 Hz), 122.0 (d, J = 7.7 Hz), 115.6 (d, J = 22.5 Hz), 30.6, 9.8.

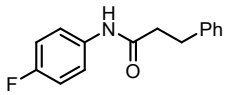


***N*-(4-fluorophenyl)hexanamide (5j).** Known compound[17]. The product (33.5 mg, 40% yield, **L3** was used) as a white solid (m.p. 90.8 – 91.2 ℃) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.50 – 7.42 (m, 2H), 6.97 (t, J = 8.6 Hz, 2H), 2.32 (t, J = 7.6 Hz, 2H), 1.70 (p, J = 7.4 Hz, 2H), 1.36 – 1.28 (m, 4H), 0.89 (t, J = 7.0 Hz, 3H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -118.1 – -118.3 (m, 1F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9,

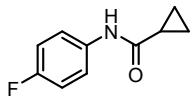
159.4 (d, J = 243.5 Hz), 134.1 (d, J = 2.7 Hz), 121.9 (d, J = 7.8 Hz), 115.6 (d, J = 22.4 Hz), 37.7, 31.5, 25.5, 22.5, 14.0.



***N*-(4-fluorophenyl)-2-phenylacetamide (5k).** Known compound[18]. The product (22.9 mg, 25% yield, **L3** and the corresponding aryl iodide were used) as a white solid (m.p. 131.5 – 132.8 ℃) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 6/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.30 (m, 7H), 7.19 (s, 1H), 6.96 (t, J = 8.5 Hz, 2H), 3.72 (s, 2H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -117.7 – -117.8 (m, 1F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.3, 159.6 (d, J = 243.7 Hz), 134.5, 133.7 (d, J = 2.7 Hz), 129.7, 129.4, 127.9, 121.9 (d, J = 7.9 Hz), 115.7 (d, J = 22.6 Hz), 44.8.

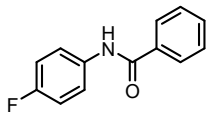


***N*-(4-fluorophenyl)-3-phenylpropanamide (5l).** Known compound[19]. The product (28.7 mg, 30% yield, 1.2 equiv of **2l** was used) as a white solid (m.p. 95.6 – 103.1 ℃) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.38 – 7.32 (m, 2H), 7.30 – 7.23 (m, 2H), 7.23 – 7.16 (m, 3H), 6.93 (t, J = 8.6 Hz, 2H), 3.01 (t, J = 7.7 Hz, 2H), 2.62 (t, J = 7.7 Hz, 2H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -117.8 – - 117.9 (m, 1F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.8, 159.5 (d, J = 243.7 Hz), 140.6, 133.8 (d, J = 2.7 Hz), 128.8, 128.5, 126.5, 122.1 (d, J = 7.9 Hz), 115.6 (d, J = 22.5 Hz), 39.3, 31.7.



***N*-(4-fluorophenyl)cyclopropanecarboxamide (5m).** The product (36.9 mg, 52% yield) as a white solid (m.p. 159.8 – 160.0 ℃) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 8/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.49 – 7.41 (m, 2H), 6.98 (t, J = 8.4 Hz, 2H), 1.53 – 1.44 (m, 1H), 1.07 (p, J = 3.7 Hz, 2H), 0.86 – 0.80 (m, 2H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -118.3 – -118.5 (m, 1F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.1, 159.4 (d, J = 243.2 Hz), 134.3, 121.7 (d, J = 7.7 Hz), 115.7 (d, J = 22.5 Hz), 15.7, 8.1. MS (DART): m/z (%) 180.1 ($[M+H]^+$). HRMS

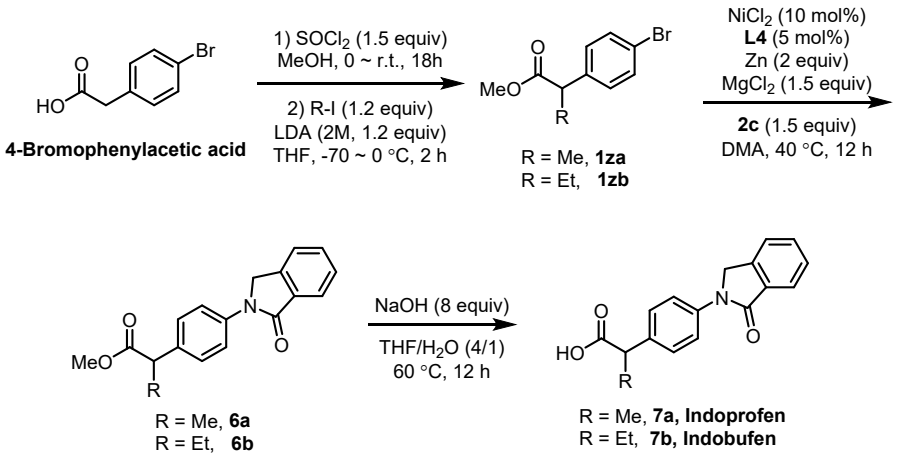
(DART) Calculated for $C_{10}H_{11}FNO$ ([M+H]$^+$): 180.0819; Found: 180.0818.



***N*-(4-fluorophenyl)benzamide (5n).** Known compound[16]. The product (47.0 mg, 55% yield, the corresponding aryl iodide was used) as a white solid (m.p. 179.0 – 179.1 °C) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10/1). ^{1}H NMR (600 MHz, Acetone-d_6) δ 9.61 (s, 1H), 7.99 (d, J = 7.5 Hz, 2H), 7.91 – 7.82 (m, 2H), 7.57 (t, J = 7.3 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.13 (t, J = 8.8 Hz, 2H). ^{19}F NMR (565 MHz, Acetone-d_6) δ -120.5 – -120.6 (m, 1F). ^{13}C NMR (151 MHz, Acetone-d_6) δ 166.3, 159.8 (d, J = 240.8 Hz), 136.6 (d, J = 2.5 Hz), 136.1, 132.4, 129.3, 128.3, 122.9 (d, J = 7.8 Hz), 115.9 (d, J = 22.4 Hz).

7. Synthetic applications

A. Synthesis of Indoprofen (7a) and Indobufen (7b)



Synthesis of methyl 2-(4-bromophenyl)propanoate (1za) and methyl 2-(4-bromophenyl)but-a noate (1zb).

In a 250 mL round-bottom flask, 4-bromophenylacetic acid (20 mmol, 1.0 equiv) and MeOH (100 mL) was added. The reaction suspension was stirred and cooled to 0 °C with ice bath. Thionyl chloride (30 mmol, 1.5 equiv) was then added dropwise. The reaction was allowed to warm to room temperature and stirred overnight. MeOH was evaporated and the residue was extracted with ethyl acetate, washed with $NaHCO_3$ solution and brine, the organic layer was dried over Na_2SO_4 and evaporated to give methyl 2-(4-bromophenyl)acetate as a yellow oil (4.6 g, 99% yield) without further purification. To a

solution of methyl 2-(4-bromophenyl)acetate (20 mmol, 1 equiv) in THF (200 mL) was added LDA (2M, 24 mmol, 1.2 equiv) at -70 ℃ under N_2. After addition, the reaction mixture was stirred for 30 min at 0 ℃. The mixture was then cooled to -70 ℃ again and iodomethane (24 mmol, 1.2 equiv) was added. After addition, the reaction mixture was stirred for 1 hour at 0 ℃. The mixture was quenched with water and extracted with ethyl acetate. The organic extracts were washed with brine, dried over anhydrous Na_2SO_4 and concentrated, the residue was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 30/1) to give **1za** as a yellow oil (4.3 g, 88% yield, known compound[20]). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 3.68 (q, *J* = 7.2 Hz, 1H), 3.65 (s, 3H), 1.48 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.5, 139.5, 131.8, 129.3, 121.1, 52.2, 44.9, 18.5.

The preparation of **1zb** was the same with **1za**, as an orange oil (4.5 g, 87% yield, known compound[21]). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 3.66 (s, 3H), 3.42 (t, *J* = 7.7 Hz, 1H), 2.12 – 2.02 (m, 1H), 1.82 – 1.70 (m, 1H), 0.88 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.2, 138.2, 131.8, 129.9, 121.3, 52.9, 52.2, 26.8, 12.2.

Synthesis of methyl 2-(4-(1-oxoisoindolin-2-yl)phenyl)propanoate (6a) and methyl 2-(4-(1-oxoisoindolin-2-yl)phenyl)butanoate (6b).

To a 25 mL of Schlenk tube were added **2c** (0.6 mmol, 1.5 equiv), Zn (0.8 mmol, 2.0 equiv), **L4** (5 mol%), $NiCl_2$ (10 mol%) and $MgCl_2$ (0.6 mmol, 1.5 equiv). The tube was evacuated and backfilled with argon for 3 times, then **1za** (0.4 mmol, 1.0 equiv) and DMA (3 mL) were added under argon, and the tube was sealed with a Teflon cap. The resulting mixture was stirred at 40 ℃. After stirring for 12 h, the reaction mixture was diluted with ethyl acetate and filtered through a pad of Celite, then the filtrate was extracted with ethyl acetate and washed with brine. The organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 5/1) to give the product **6a** (49.0 mg, 42% yield, known compound[22]) as a white solid (m.p. 130.4 – 131.4 ℃). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 1H), 7.82 (d, *J* = 8.6 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 4.84 (s, 2H), 3.74 (q, *J* = 7.2 Hz, 1H), 3.67 (s, 3H), 1.52 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.1, 167.6, 140.2, 138.6, 136.8, 133.3, 132.3, 128.6, 128.4, 124.4, 122.8, 119.9, 52.2, 50.9, 45.0, 18.7.

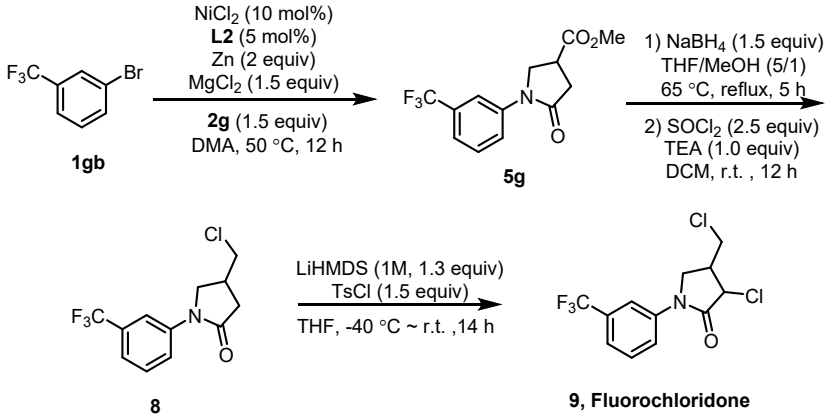
The preparation of **6b** (58.0 mg, 47% yield, known compound[21]) was the same with **6a**., as a white solid (m.p. 123.8 – 124.9 ℃). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.5 Hz, 1H), 7.82 (d, *J* = 8.7 Hz, 2H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 4.85 (s, 2H), 3.67 (s, 3H), 3.47 (t, *J* = 7.7 Hz, 1H), 2.16 – 2.06 (m, 1H), 1.86 – 1.77 (m, 1H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.6, 167.6, 140.2, 138.7, 135.3, 133.3, 132.2, 128.9, 128.6, 124.3, 122.8, 119.8, 52.9, 52.1, 50.9, 26.8, 12.3.

Synthesis of indoprofen (7a) and indobufen (7b).

In a 25 mL round-bottom flask, **6a** (0.2 mmol, 1.0 equiv) and THF/H_2O (5 mL, 4/1) was added. Then NaOH (1.6 mmol, 8 equiv) was added and stirred 12 h at 60 ℃. THF was then evaporated and the residue was diluted with ethyl acetate, then 2M HCl was added to adjust pH to 1~2, the organic layer was washed with brine, dried over Na_2SO_4 and evaporated to give **7a** (52.0 mg, 99% yield) as a white solid (m.p. 206.9 – 207.7 ℃) without further purification. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.30 (s, 1H), 7.85 (d, *J* = 8.6 Hz, 2H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.70 – 7.65 (m, 2H), 7.57 – 7.52 (m, 1H), 7.35 (d, *J* = 8.6 Hz, 2H), 5.01 (s, 2H), 3.69 (q, *J* = 7.1 Hz, 1H), 1.38 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 175.4, 166.5, 141.0, 138.2, 137.0, 132.4, 132.2, 128.2, 127.9, 123.3, 123.2, 119.5, 50.5, 44.1, 18.5. MS (ESI): m/z (%) 282.1 ([M+H]$^+$). HRMS (ESI) Calculated for $C_{17}H_{16}NO_3$ ([M+H]$^+$): 282.1125; Found: 282.1124.

The preparation of **7b** (48.0 mg, 99% yield) was the same with **7a**, as a white solid (m.p. 147.6 – 149.6 ℃) without further purification. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.31 (s, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.70 – 7.64 (m, 2H), 7.54 (t, *J* = 6.9 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 2H), 5.01 (s, 2H), 3.43 (t, *J* = 7.6 Hz, 1H), 2.03 – 1.93 (m, 1H), 1.73 – 1.63 (m, 1H), 0.84 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 174.8, 166.6, 141.0, 138.3, 135.4, 132.4, 132.2, 128.3, 128.2, 123.3, 123.2, 119.4, 52.0, 50.4, 26.1, 12.0. MS (ESI): m/z (%) 296.1 ([M+H]$^+$). HRMS (ESI) Calculated for $C_{18}H_{18}NO_3$ ([M+H]$^+$): 296.1281; Found: 296.1278.

B. Synthesis of Fluorochloridone (9)



Synthesis of methyl 5-oxo-1-(3-(trifluoromethyl)phenyl)pyrrolidine-3-carboxylate (5g).

To a 25 mL of Schlenk tube were added **2g** (0.6 mmol, 1.5 equiv), Zn (0.8 mmol, 2 equiv), **L2** (5 mol%), $NiCl_2$ (10 mol%) and $MgCl_2$ (0.6 mmol, 1.5 equiv). The tube was evacuated and backfilled with argon for 3 times, then **1gb** (0.4 mmol, 1.0 equiv) and DMA (3 mL) were added under argon, and the tube was sealed with a Teflon cap. The resulting mixture was stirred for 12 h at 50 °C. After, the reaction mixture was diluted with ethyl acetate and filtered through a pad of Celite, then the filtrate was extracted with ethyl acetate and washed with brine. The organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 3/2) to give the product **5g** as a yellow oli (67.0 mg, 58% yield).

Synthesis of 4-(chloromethyl)-1-(3-(trifluoromethyl)phenyl)pyrrolidin-2-one (8).

In a 25 mL round-bottom flask, methanol (3 mL) was added dropwise to a suspension of **5g** (1.1 mmol, 1 equiv) and sodium borohydride (3.3 mmol, 3.0 equiv) in THF (15 mL) under reflux at 65 °C. The reaction mixture was stirred for 5 h at the same reaction temperature and evaporated in vacuo. The residue was triturated with ice-water and extracted with ethyl acetate, the organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated. Then dichloromethane (30 mL), triethylamine (0.8 mmol, 1.0 equiv) and thionyl chloride (1.9 mmol, 2.5 equiv) were added, the mixture was stirred overnight at room temperature. After, the reaction mixture was extracted with DCM, and the organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 8/1) to give the product **8** as a brown oil (167.0 mg, 57% yield for two steps). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, J = 5.6 Hz, 2H), 7.48 (t, J = 8.3 Hz, 1H), 7.40 (d, J = 7.7 Hz, 1H), 4.02 (t, J = 8.9 Hz 1H), 3.77 (dd, J = 9.8, 6.0 Hz, 1H),

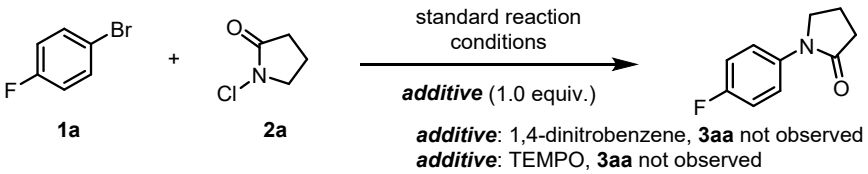
3.69 (dd, J = 11.2, 5.4 Hz, 1H), 3.62 (dd, J = 11.1, 7.4 Hz, 1H), 2.96 – 2.87 (m, 1H), 2.81 (dd, J = 17.3, 8.9 Hz, 1H), 2.53 (dd, J = 17.3, 7.1 Hz, 1H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.6 (s, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.6, 139.6, 131.4 (q, J = 32.5 Hz), 129.6, 124.0 (d, J = 272.5 Hz), 123.0, 121.3 (q, J = 3.8 Hz), 116.4 (q, J = 4.2 Hz), 51.7, 46.6, 36.8, 33.4. MS (ESI): m/z (%) 278.1 ($[M+H]^+$). HRMS (ESI) Calculated for $C_{12}H_{12}ClF_3NO$ ($[M+H]^+$): 278.0554; Found: 278.0558.

Synthesis of Fluorochloridone (9).

In a 50 mL double necked bottle, **8** (0.2 mmol, 1.0 equiv) in THF (5 mL) was cooled to -40 ℃ and LiHMDS (0.3 mmol, 1.3 equiv) was added under N_2. The resulting solution was stirred for 40 min and the tosyl chloride (0.3 mmol, 1.5 equiv) in THF (2 mL) was then added. After warming the solution to room temperature to quench reaction. The solution was extracted with ethyl acetate, and the organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 6/1) to give **9** as a yellow oil (36.0 mg, 64% yield, known compound[23]). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, J = 8.3 Hz, 1H), 7.76 (s, 1H), 7.44 (t, J = 8.0 Hz, 1H), 7.34 (d, J = 7.7 Hz, 1H), 4.06 (dd, J = 9.8, 5.9 Hz, 1H), 3.77 (d, J = 9.8 Hz, 1H), 2.16 – 2.09 (m, 1H), 2.08 – 1.99 (m, 1H), 1.28 – 1.20 (m, 1H), 0.82 (q, J = 4.1 Hz, 1H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.7 (s, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.6, 140.1, 131.3 (q, J = 32.4 Hz), 129.5, 124.1 (q, J = 272.6 Hz), 122.6, 120.6 (q, J = 3.8 Hz), 115.9 (q, J = 4.0 Hz), 50.3, 21.9, 13.0, 11.6.

8. Mechanistic Studies

Radical Inhibition Experiments



Procedure: To a 25 mL of Schlenk tube were added *N*-chloroamides **2a** (0.6 mmol, 1.5 equiv), Zn (0.8 mmol, 2 equiv), **L4** (5 mol%), $NiCl_2$ (10 mol%), $MgCl_2$ (0.6 mmol, 1.5 equiv) and 1,4-dinitrobenzene (1.0 equiv) or TEMPO (1.0 equiv). The tube was evacuated and backfilled with argon for 3 times, then aryl bromide **1a** (0.4 mmol, 1.0 equiv) and DMA (3 mL) were added under argon, and the tube was sealed with a Teflon cap. The resulting mixture was stirred at 40 ℃. After stirring

for 12 h, the reaction mixture was diluted with ethyl acetate. The yield was determined by ^{19}F-NMR with benzotrifluoride as the internal standard. When 1.0 equiv of 1,4-dinitrobenzene was added, the product **3aa** was not detected. When 1.0 equiv of TEMPO was added, **3aa** was not detected.

9. DFT calculations

Computational details:

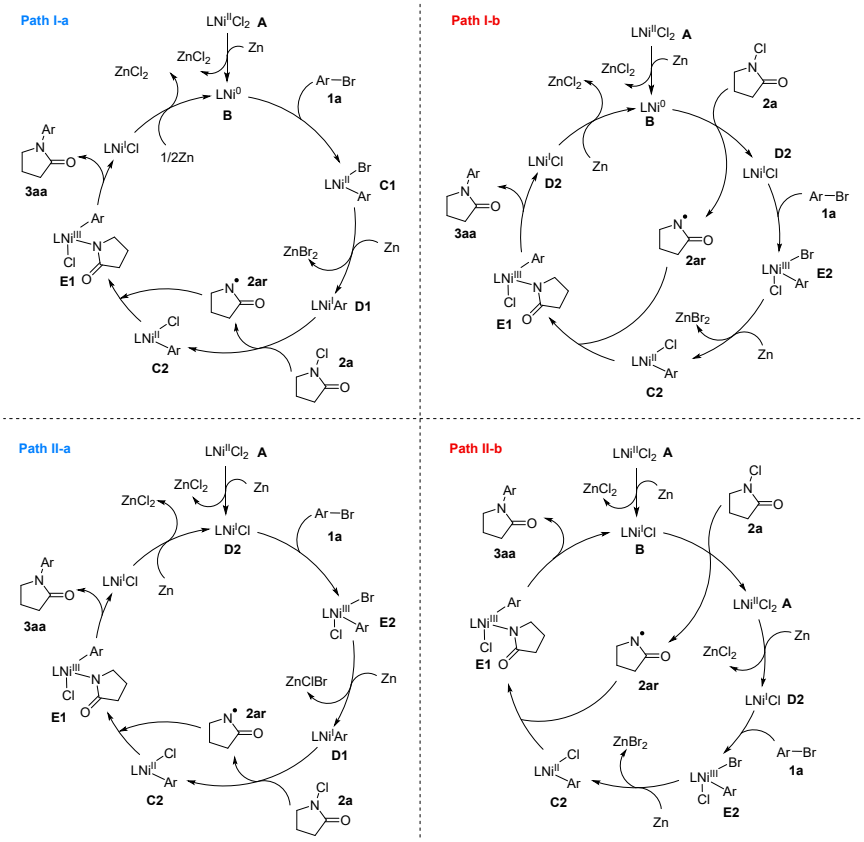
Geometry optimizations and frequency analyses were performed at the (U)PBE0-D3(BJ)/def2-SVP-SMD-(DMA) level of theory as well as the thermal corrections to free energy (G_{corr}) at the temperature of 313 K using Gaussian 16 program[24]. Single-point energies (SP) were calculated in gas phase at the RI-(U)PWPB95-D3BJ/def2-QZVPP-SMD-(DMA)[25] level of theory with def2/J[26] and def2-QZVPP/C[27] as auxiliary basis sets using ORCA 5.0.2 program[28]. The Gibbs free energies of solvation (ΔG_{solv}) were calculated at the M052X/6-31G(d) level of theory using SMD model of solvation. CYLview20 was utilized to generate 3D structures.[29] Imaginary frequencies were inspected to determine the stationary points (no imaginary frequencies) or transition states (only one imaginary frequency). All transition states were confirmed by IRC calculations using the same theory level with geometry optimization. The thermal-corrected, solvated Gibbs free energies were calculated as $G = SP + G_{corr} + \Delta G_{solv}$. Zn atom was used as the model of the Zn powder for simplicity.[30] ***Note***: Superscript in the top left corner of the structure name denotes spin multiplicity. For instance, ^{1}**B** and ^{3}**B** mean **B** in the the singlet state and triplet state respectively. All energies are in kcal/mol.

Table S11. Energies of intermediates and transition states

Structure	SP (Hartree)	G_{corr} (Hartree)	ΔG_{solv} (Hartree)	Imaginary frequency (cm^{-1})
^{3}**A**	-3002.77585796	0.164739000	-0.051404530	none
^{1}**B**	-2082.237833802	0.169353000	-0.041147280	none
^{3}**B**	-2082.249162441	0.168075000	-0.026194720	none
CP1	-4987.347627603	0.236680000	-0.024018290	none
CP2	-2828.408668075	0.256682000	-0.037246820	none
^{3}**C1**	-4987.404874179	0.236525000	-0.043252240	none
^{3}**C2**	-2873.348110060	0.238855000	-0.049108750	none
^{2}**D1**	-2413.111523350	0.239770000	-0.034613790	none
^{2}**D2**	-2542.546782566	0.165058000	-0.027389150	none
^{2}**E1**	-3159.318664786	0.335287000	-0.051746490	none

^{2}E2	-5447.606795742	0.239998000	-0.053331070	none
Zn	-1779.476967127	-0.016798000	-0.012988630	none
$ZnCl_2$	-2699.952888172	-0.025495000	-0.072500140	none
$ZnBr_2$	-6928.072941632	-0.031669000	-0.011837010	none
ZnClBr	-4813.991048259	-0.030347000	-0.062486570	none
1a	-2905.063596138	0.048840000	-0.009028710	none
2a	-746.118421692	0.068561000	-0.015551028	none
3aa	-616.810835350	0.145723000	-0.017412599	none
2ar	-285.891787700	0.065172000	-0.014592707	none
TS1	-4987.344809291	0.238558000	-0.025564930	-98.75
TS2	-3159.234776914	0.326542000	-0.051941540	-148.29
TS3	-3159.264734676	0.327609000	-0.056237350	-16.05
TS4	-3159.304394805	0.333599000	-0.046886760	-315.47
TS5	-2828.405000690	0.257419000	-0.037601700	-663.3
TS6	-5447.600166903	0.238355000	-0.043167100	-84.04
TS7	-3288.669720802	0.257716000	-0.050490220	-61.57

Scheme S1. Proposed mechanism of the reaction



Based on the literature report and preliminary mechanistic experiment, a reaction mechanism involving amidyl radical was proposed, which may follow two pathways where the reaction was

initiated from LNi^0 (B) or $LNi^{I}Cl$ (D) complexes. And in each pathway, two possible processes were considered whether the active Ni species reacted with **1a** or **2a** first. The free energy profile for both pathways were calculated and depicted in Figure S1.

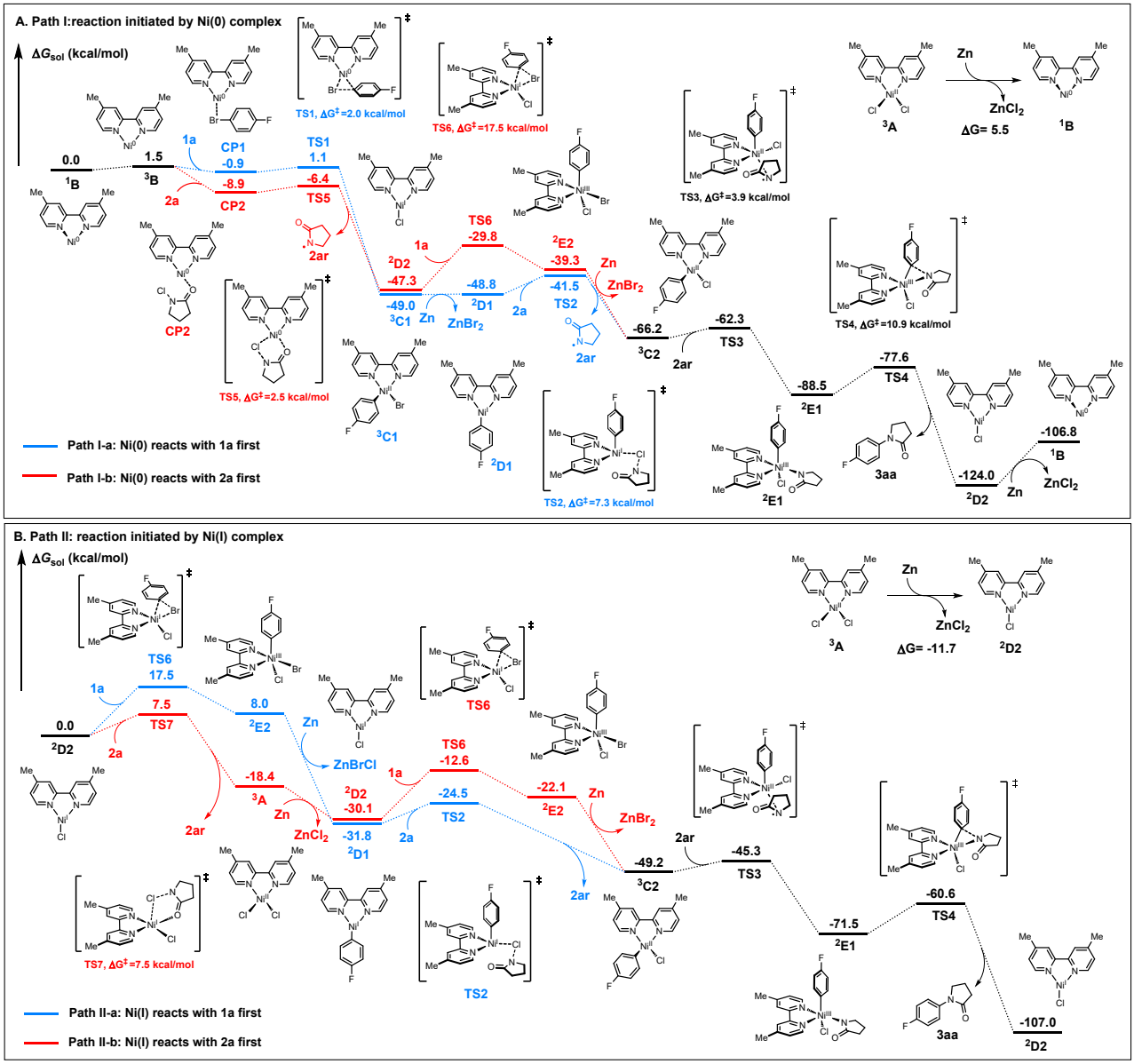


Figure S1. Free energy profile for mechanistic pathways of Ni-catalyzed electrophilic amidation. Calculated at RI-(U)PBWPB95-D3(BJ)/def2-QZVPP-SMD-(DMA)//(U)PBE0-D3(BJ)/def2-SVP-SMD-(DMA) level of theory. (A) Path I: reaction initiated by Ni (0) complex ^{1}B. (B) Path II: reaction initiated by Ni (I) complex ^{2}D2.

Both active nickel species could be generated through reduction of $LNi^{II}Cl_2$ (^{3}**A**) by Zn with free energy changes of 5.5 kcal/mol and -11.7 kcal/mol respectively. For pathway I, Ni^0 complex ^{1}**B** first underwent an intersystem crossing/conformational change to form the triplet spin state ^{3}**B**[31]. In path

I-a, ^{3}**B** bound with **1a** to form complex **CP1** that went through oxidative addition via **TS1** to form ^{3}**C1** with free energy barrier of 2.0 kcal/mol. ^{3}**C1** was then reduced to ^{2}**D1** that reacted with **2a** through chlorine abstraction to via **TS2** to produce amidyl radical **2ar** and ^{3}**C2** with free energy barrier of 7.3 kcal/mol. The radical **2ar** oxidized ^{3}**C2** to form ^{2}**E1** via **TS3** with free energy barrier of 3.9 kcal/mol. ^{2}**E1** finally went through reductive elimination via **TS4** to form **3aa** and ^{2}**D2** with free energy barrier of 10.9 kcal/mol. ^{1}**B** was regenerated by reduction of ^{2}**D2**. In comparison, path I-b begun with the binding of ^{3}**B** with **2a** to form **CP2** that underwent chlorine abstraction to produce radical **2ar** and ^{2}**D2** via **TS5** with free energy barrier of 2.5 kcal/mol. ^{2}**D2** then reacted with **1a** by oxidative addition to form ^{2}**E2** via **TS6** with a high free energy barrier of 17.5 kcal/mol. ^{2}**E2** was reduced by Zn to form ^{3}**C2**, and subsequent process was same as path I-a.

Path II was initiated with Ni^{I} complex ^{2}**D2**. In path II-a, ^{2}**D2** reacted with **1a** to form ^{2}**E2** by oxidative addition via **TS6** (barrier 17.5 kcal/mol). ^{2}**E2** was reduced to ^{2}**D1** which abstracted chlorine atom from **2a** to generate **2ar** and ^{3}**C2** via **TS2** (barrier 7.3 kcal/mol). Comparatively, in path II-b, ^{2}**D2** first reacted with **2a** by chlorine abstraction to produce **2ar** and ^{3}**A** via **TS7** (barrier 7.5 kcal/mol). ^{3}**A** was then reduced to ^{2}**D2** that went through oxidative addition with **2a** to form ^{2}**E2** via **TS6** (barrier 17.5 kcal/mol). ^{2}**E2** was reduced by Zn to form ^{3}**C2** which proceeded the following process. Although the reduction of ^{3}**A** to ^{1}**B** is thermodynamically disfavored compared with that of ^{3}**A to** ^{2}**D2**, the free energy barriers related to ^{3}**B** (**TS1**, 2.0 kcal/mol; **TS2**, 7.3 kcal/mol) are much lower than that related to ^{2}**D2** (**TS6**, 17.5 kcal/mol; **TS7**, 7.5 kcal/mol), indicating path I-a is more kinetically favored. Therefore, a rational pathway would be that the reaction of Ni^{0} (**B**) and **1a** was the initial step, namely path I-a.

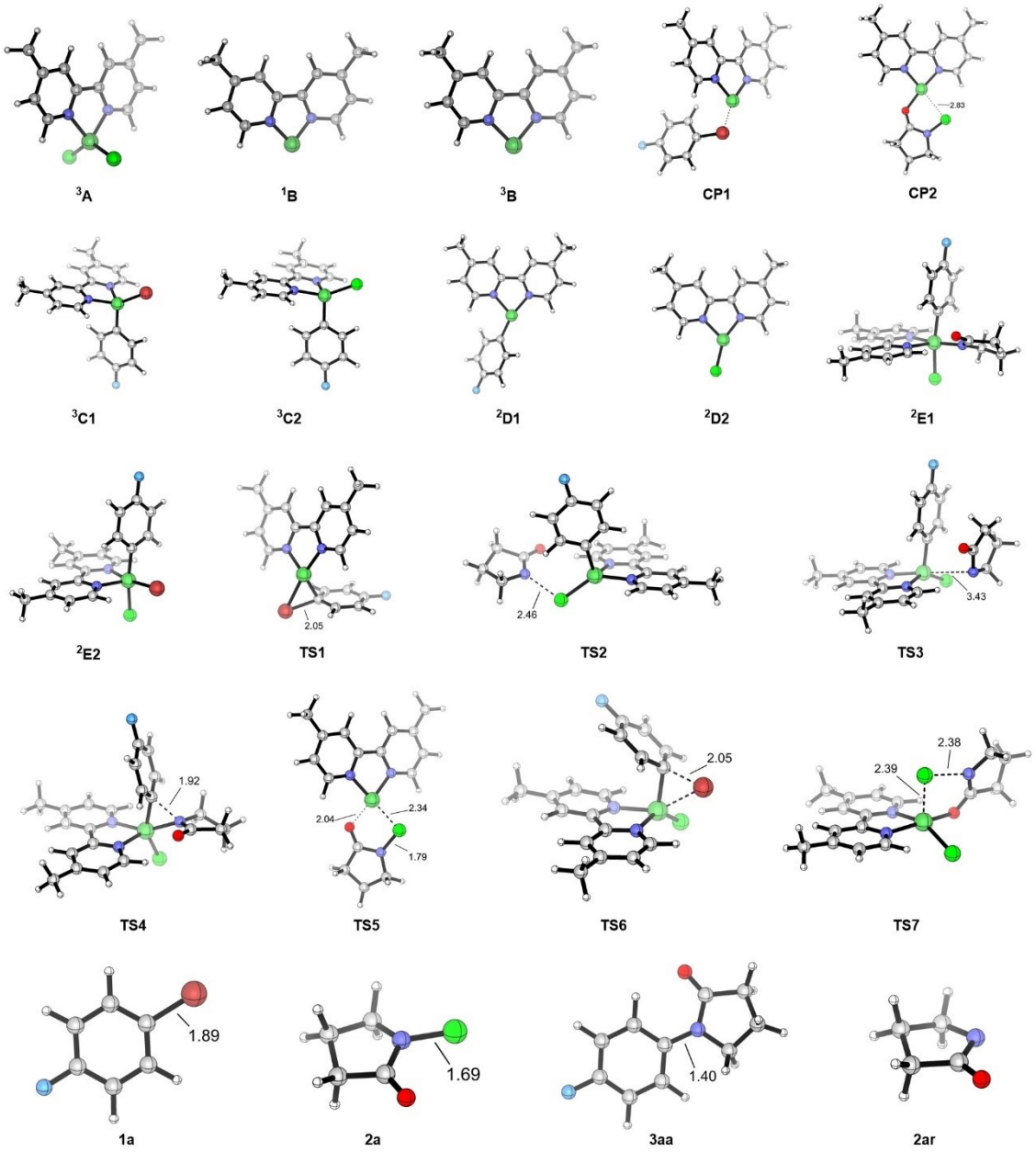


Figure S2. Optimized structures in the mechanism.

Cartesian coordinates

^{3}A

C	0.71481100	1.06188900	-0.00249500
C	2.63521900	-0.23176100	0.08227500
C	3.44746800	0.89167600	0.08721200
C	2.86446500	2.16515200	0.04301600
C	1.46921400	2.23380800	-0.00477200

C	-0.76427400	1.02660400	-0.05273300
C	-2.62045700	-0.35662000	-0.15076500
C	-3.48567500	0.72645700	-0.14827200
C	-2.96442300	2.02591700	-0.09082400
C	-1.57408200	2.16068900	-0.04243700
H	3.05577200	-1.24056100	0.10888500
H	4.53261400	0.77439300	0.12314500
H	0.97809500	3.20679900	-0.04852200
H	-2.99208200	-1.38416200	-0.18619600
H	-4.56392200	0.55761700	-0.18716500
H	-1.12997700	3.15541700	0.00994900
N	-1.29754200	-0.20489400	-0.10633400
N	1.30644700	-0.14334200	0.04228200
C	3.70717200	3.39762400	0.04191600
H	4.36574300	3.41146600	-0.84117100
H	3.09405500	4.30856800	0.03538800
H	4.36103800	3.41826200	0.92793900
C	-3.86515700	3.21656200	-0.07598300
H	-3.29626600	4.15544900	-0.05057900
H	-4.51378500	3.22058900	-0.96611200
H	-4.52913000	3.18437400	0.80253300
Ni	0.03843900	-1.69877500	0.01123000
Cl	0.34016100	-2.67373200	-1.97907400
Cl	-0.21583500	-2.42467100	2.11372100

^{1}B

C	0.70663700	0.37785000	-0.06849900
C	2.58581600	-1.02862500	-0.26300300
C	3.45137500	0.02081000	-0.08534100
C	2.93807700	1.34889200	0.06310200

C	1.56649300	1.49167600	0.08528600
C	-0.70662800	0.37785200	0.06850600
C	-2.58581900	-1.02860200	0.26302600
C	-3.45137000	0.02083100	0.08535400
C	-2.93805500	1.34891400	-0.06310700
C	-1.56647700	1.49168500	-0.08530300
H	2.96152300	-2.04562000	-0.41784000
H	4.52931300	-0.15940400	-0.10010300
H	1.12376100	2.47395100	0.27364300
H	-2.96153200	-2.04559300	0.41787600
H	-4.52931000	-0.15937500	0.10011900
H	-1.12374000	2.47395600	-0.27366700
N	-1.23773500	-0.88532100	0.34527800
N	1.23773900	-0.88532900	-0.34525100
C	3.87219300	2.50590400	0.22940500
H	4.55306500	2.59595900	-0.63460500
H	3.32662100	3.45516100	0.33284700
H	4.51349700	2.38244500	1.11919200
C	-3.87219000	2.50589700	-0.22941400
H	-3.32661300	3.45507800	-0.33351200
H	-4.51396500	2.38209400	-1.11881800
H	-4.55262600	2.59633000	0.63490500
Ni	-0.00001200	-2.20031900	-0.00001100

^{3}B

C	0.71494400	0.31624400	-0.00000300
C	2.65846700	-1.00260200	-0.00007200
C	3.49054100	0.10102200	-0.00006300
C	2.90404900	1.40065200	0.00001800
C	1.52734600	1.48454400	0.00005600

C	-0.71494200	0.31624400	-0.00001300
C	-2.65846800	-1.00259800	0.00009100
C	-3.49053700	0.10102800	0.00008800
C	-2.90404200	1.40065700	-0.00001700
C	-1.52734100	1.48454300	-0.00007300
H	3.07876300	-2.01418500	-0.00010700
H	4.57499200	-0.02830400	-0.00010000
H	1.05153200	2.46787000	0.00016200
H	-3.07876700	-2.01418000	0.00014000
H	-4.57498900	-0.02829400	0.00014200
H	-1.05152600	2.46786800	-0.00019500
N	-1.32135100	-0.93023000	0.00003800
N	1.32135200	-0.93022800	-0.00004000
C	3.77393900	2.61844900	0.00008500
H	4.43446500	2.63328500	-0.88342600
H	3.17992800	3.54368800	0.00013100
H	4.43445400	2.63319200	0.88360600
C	-3.77394200	2.61844600	-0.00008200
H	-3.17994300	3.54369400	-0.00009400
H	-4.43444900	2.63320400	-0.88361100
H	-4.43448300	2.63324500	0.88341800
Ni	-0.00000200	-2.30241600	-0.00000500

CP1

C	-2.74292100	-0.06510700	0.22379400
C	-2.68677000	-2.39777500	0.48263300
C	-3.97994700	-2.44239400	0.96248700
C	-4.71070400	-1.22351300	1.08382000
C	-4.07745600	-0.05625500	0.71161800
C	-2.01381700	1.09485000	-0.18610000

C	0.00600300	1.89546800	-1.06288200
C	-0.43009800	3.20514300	-1.05677800
C	-1.74437100	3.48688400	-0.58015100
C	-2.51419300	2.42507500	-0.15281600
H	-2.10083600	-3.31678300	0.37787300
H	-4.42849500	-3.39774800	1.24292400
H	-4.61139300	0.89331900	0.79119200
H	1.01227600	1.65146400	-1.42187400
H	0.22402000	4.00434000	-1.41164400
H	-3.52499800	2.60935100	0.21816000
N	-0.73327900	0.85992900	-0.64715600
N	-2.06517400	-1.26632200	0.11884100
C	-6.11477200	-1.23627600	1.59994300
H	-6.15805100	-1.66374900	2.61599100
H	-6.54581600	-0.22544400	1.63353800
H	-6.76247600	-1.86710000	0.96797700
C	-2.24845900	4.89522000	-0.55507800
H	-3.27527900	4.95427700	-0.16681300
H	-1.60456100	5.53398500	0.07279600
H	-2.23565200	5.33665300	-1.56591700
Ni	-0.29669700	-1.04240800	-0.56708400
Br	1.87033000	-1.46785700	-1.37863100
C	3.01554200	-0.60983000	-0.10170100
C	4.39229600	-0.76024300	-0.22629500
C	2.43369200	0.14408000	0.91159300
C	5.21737800	-0.12796000	0.70140400
H	4.83122300	-1.35730000	-1.02852000
C	3.26280000	0.77392600	1.83590800
H	1.34657500	0.24336100	0.97457400
C	4.63938400	0.62723200	1.71492800

H	6.30395800	-0.21843800	0.64210800
H	2.84790400	1.37653500	2.64655800
F	5.43280100	1.23103000	2.60019600

CP2

C	2.18836500	0.65991900	0.03520200
C	0.88276900	2.60195800	0.16010300
C	1.98828000	3.43099500	0.15175200
C	3.28564600	2.84195800	0.07751800
C	3.36055700	1.46650400	0.02164700
C	2.17804700	-0.76727000	-0.00720100
C	0.82627800	-2.67891900	-0.00172600
C	1.91275300	-3.53359200	-0.07288500
C	3.22150700	-2.97023300	-0.11552000
C	3.33352500	-1.59541800	-0.08199700
H	-0.12246500	3.03383300	0.22359700
H	1.86228200	4.51464900	0.20244000
H	4.33949800	0.98413200	-0.03179100
H	-0.19522300	-3.07429800	0.03363200
H	1.76424000	-4.61550800	-0.09515100
H	4.32459900	-1.13656800	-0.11444000
N	0.92682400	-1.34793300	0.03060700
N	0.94224100	1.26537300	0.10069500
C	4.50605000	3.70786400	0.06325400
H	4.55396700	4.34048800	0.96587200
H	5.42846400	3.11150800	0.01275200
H	4.49372400	4.39596600	-0.79917800
C	4.42138200	-3.86182000	-0.19361900
H	5.35734100	-3.28521100	-0.21557100
H	4.46036300	-4.54893900	0.66856200

H	4.38598500	-4.49534300	-1.09607900
Ni	-0.49614400	-0.00101400	0.10555500
Cl	-2.65924400	1.73985700	-0.46396000
N	-3.73389100	0.48899500	-0.09100400
C	-5.16793000	0.62488300	-0.30654100
C	-3.29228000	-0.76528900	0.14348900
C	-5.67619300	-0.66719700	0.33734900
H	-5.54380200	1.53321800	0.18303900
H	-5.37943500	0.68133400	-1.38724700
C	-4.50569700	-1.64472700	0.21924700
O	-2.11408600	-1.10460000	0.24254600
H	-6.58995400	-1.02955700	-0.14996700
H	-5.90040900	-0.48168300	1.39776200
H	-4.53480000	-2.22514400	-0.71923400
H	-4.41707700	-2.35799700	1.04987700

^{3}C1

C	-1.91249100	0.35803800	-0.65539400
C	-0.72370200	2.16612800	-1.47785400
C	-1.70534400	2.44551200	-2.41585500
C	-2.85058300	1.63967600	-2.47746400
C	-2.94019900	0.57994600	-1.57144600
C	-1.91287200	-0.73923400	0.33778900
C	-0.73335600	-1.73088900	2.06476600
C	-1.70533600	-2.70520200	2.23303700
C	-2.83931400	-2.69774100	1.41005300
C	-2.92722600	-1.68947100	0.44640700
H	0.18086100	2.77588700	-1.40215000
H	-1.57867200	3.28979600	-3.09693400
H	-3.81629400	-0.06962100	-1.58432900

H	0.16692500	-1.71481400	2.68540600
H	-1.57697500	-3.47052700	3.00145900
H	-3.78983100	-1.65350200	-0.22035800
N	-0.83701000	-0.77268900	1.14327800
N	-0.82632200	1.14812800	-0.62281000
C	-3.92893000	1.90913000	-3.47482800
H	-3.52786200	1.85360900	-4.49932800
H	-4.75523600	1.19161700	-3.38294900
H	-4.32970600	2.92674300	-3.34385500
C	-3.91633200	-3.71956000	1.56965400
H	-4.60908900	-3.71453900	0.71744100
H	-3.48968600	-4.72774500	1.67964000
H	-4.49772800	-3.51490000	2.48404400
Ni	0.57274500	0.62378300	0.73592500
C	1.84489800	-0.44822600	-0.33328400
C	3.23120500	-0.22945100	-0.23747000
C	1.43673600	-1.44834900	-1.23343100
C	4.16427900	-0.95736400	-0.98363500
H	3.60913500	0.54075300	0.44513300
C	2.34100900	-2.19306200	-1.99618200
H	0.36947500	-1.66922300	-1.35699900
C	3.69763200	-1.93167900	-1.85487800
H	5.23977000	-0.77865800	-0.89957700
H	2.01096200	-2.96804900	-2.69334900
F	4.58017000	-2.64047400	-2.58085100
Br	1.34452700	2.39212000	2.12415100

^{3}C2

C	1.83072600	-0.61819700	-0.30940400
C	0.75528900	-2.65811800	-0.09004500

C	1.68052500	-3.28697300	-0.90882700
C	2.73448900	-2.54304200	-1.45715100
C	2.79788800	-1.18335000	-1.13978300
C	1.80559200	0.80807700	0.08782500
C	0.68134300	2.41319800	1.31861300
C	1.56700900	3.40489300	0.92496700
C	2.62583100	3.08208900	0.06552500
C	2.73139300	1.75290900	-0.35261100
H	-0.07640900	-3.20080500	0.36746600
H	1.58191900	-4.35425500	-1.11874300
H	3.60623900	-0.57209700	-1.54324900
H	-0.16143200	2.63552400	1.97897100
H	1.43034600	4.42707700	1.28441900
H	3.53885000	1.46185300	-1.02569600
N	0.80099300	1.14835500	0.91363400
N	0.83051200	-1.35838800	0.19435100
C	3.75176100	-3.18678500	-2.34098200
H	3.26478800	-3.66870000	-3.20329600
H	4.48533700	-2.45897200	-2.71249200
H	4.28922800	-3.97837800	-1.79471800
C	3.59877700	4.12233700	-0.38326300
H	4.34612500	3.70854300	-1.07337900
H	3.07440300	4.95001600	-0.88629700
H	4.12332700	4.55665900	0.48276100
Ni	-0.52199700	-0.34944800	1.30202700
C	-1.98531000	0.13841600	0.05191200
C	-3.25803200	-0.44163700	0.21141100
C	-1.84013200	1.01620000	-1.03745100
C	-4.32755500	-0.16903800	-0.64727100
H	-3.42427700	-1.13799300	1.04136600

C	-2.88703400	1.30987200	-1.91705100
H	-0.87528100	1.50279700	-1.22356700
C	-4.11963100	0.70787600	-1.70310300
H	-5.31189700	-0.62535300	-0.51056500
H	-2.76067100	1.99459900	-2.76019000
F	-5.13660800	0.98109600	-2.53971600
Cl	-1.20960700	-1.81341000	2.88836200

^{2}D1

C	-2.27685100	-0.43709600	0.02287500
C	-1.63858300	-2.65881800	-0.04847600
C	-2.94948700	-3.08890500	0.07911600
C	-3.98152200	-2.14599200	0.19140100
C	-3.61675500	-0.79831200	0.16036100
C	-1.79725100	0.95908100	-0.03950300
C	0.07528300	2.29234800	-0.25015500
C	-0.69005300	3.45268900	-0.22656200
C	-2.07971200	3.35955900	-0.09813500
C	-2.62903300	2.07512400	-0.00608600
H	-0.81648500	-3.37442700	-0.13267600
H	-3.16723600	-4.15931100	0.09324800
H	-4.38660100	-0.02955400	0.24456200
H	1.16351700	2.33647100	-0.34983000
H	-0.20127700	4.42596600	-0.30852900
H	-3.71004900	1.95568900	0.08613700
N	-0.45857500	1.07562900	-0.15272800
N	-1.29955100	-1.36289100	-0.07586200
C	-5.40612600	-2.57156000	0.33921700
H	-5.71014700	-3.21237400	-0.50369000
H	-5.53934100	-3.16732000	1.25657000

H	-6.08405600	-1.70847700	0.38420400
C	-2.95543600	4.57020300	-0.06729800
H	-3.65860800	4.56078900	-0.91553900
H	-3.56319300	4.58786500	0.85109600
H	-2.36667100	5.49611600	-0.11516800
Ni	0.52316600	-0.68248600	-0.15309800
C	2.44970500	-0.51177400	-0.05691200
C	3.35325600	-1.34168900	-0.76200600
C	3.07089400	0.44894100	0.77645100
C	4.74471300	-1.23184000	-0.66503900
H	2.96596500	-2.12147400	-1.42855500
C	4.45677100	0.58902000	0.90152200
H	2.44962500	1.13242300	1.36775100
C	5.27637700	-0.26050600	0.17123600
H	5.41735000	-1.88679300	-1.22620100
H	4.90610200	1.34276600	1.55440600
F	6.61357900	-0.14008300	0.27744700

^{2}D2

C	0.17349100	-1.09911000	0.00000500
C	2.46679500	-0.78656000	0.00003200
C	2.70115100	-2.15240100	0.00002100
C	1.61476200	-3.04069800	-0.00000300
C	0.33308100	-2.48568600	-0.00001000
C	-1.12524600	-0.39892700	0.00000100
C	-2.14650200	1.67888400	-0.00001300
C	-3.40898700	1.10979800	-0.00002100
C	-3.54302200	-0.28713900	-0.00001200
C	-2.36548400	-1.03738100	-0.00000100
H	3.28851600	-0.06454300	0.00004800

H	3.72766900	-2.52614600	0.00003100
H	-0.53806800	-3.14284200	-0.00003100
H	-2.01679700	2.76431500	-0.00001800
H	-4.29082000	1.75473800	-0.00003400
H	-2.42175000	-2.12722600	0.00000600
N	-1.02086500	0.94991500	-0.00000300
N	1.23485800	-0.26895500	0.00002400
C	1.82871200	-4.51984000	-0.00003300
H	2.40905600	-4.82773400	0.88442200
H	0.87666000	-5.06768200	0.00006600
H	2.40885300	-4.82771900	-0.88462900
C	-4.88983800	-0.93458000	0.00001700
H	-4.81286900	-2.03036300	-0.00039400
H	-5.46964100	-0.62635300	0.88482500
H	-5.47003300	-0.62569100	-0.88429600
Ni	0.77659900	1.64021800	0.00001100
Cl	2.30782500	3.19860400	-0.00002100

^{2}E1

C	-2.28320600	0.41247200	-0.23763200
C	-1.29653800	2.08112400	-1.50670100
C	-2.48481000	2.78883700	-1.58427600
C	-3.63124600	2.28749100	-0.95236800
C	-3.51061800	1.07306800	-0.27380900
C	-2.05328400	-0.88185100	0.43329600
C	-0.47373900	-2.49925800	0.92501900
C	-1.41602700	-3.27296600	1.58966100
C	-2.74002300	-2.82790700	1.68723100
C	-3.04762600	-1.60021600	1.09476200

H	-0.38761400	2.44155000	-1.99442700
H	-2.51668200	3.72944700	-2.13792500
H	-4.38035200	0.64170000	0.22306100
H	0.58653400	-2.77183500	0.87093300
H	-1.11303700	-4.22154500	2.03876600
H	-4.06514400	-1.21150100	1.15082000
N	-0.79335900	-1.33610800	0.35805000
N	-1.20470000	0.92950900	-0.84295100
C	-4.92688100	3.02723600	-1.00898800
H	-5.23106700	3.19362000	-2.05434000
H	-5.72805100	2.48331700	-0.49121700
H	-4.82124800	4.02100300	-0.54523800
C	-3.77459500	-3.62952600	2.40699400
H	-4.77358200	-3.18359500	2.31031300
H	-3.80709100	-4.65953600	2.01939500
H	-3.52728500	-3.69913100	3.47868000
Ni	0.42769300	-0.17215700	-0.81008800
C	1.13228700	0.93169200	0.57153900
C	1.67770400	2.14871200	0.16098100
C	1.09190500	0.61002500	1.92666800
C	2.17053600	3.05837900	1.09968100
H	1.72984300	2.41068600	-0.90045900
C	1.58116800	1.51232700	2.87501900
H	0.69179300	-0.34657500	2.26340700
C	2.11051800	2.72169300	2.44528400
H	2.59828000	4.01705000	0.79676400
H	1.55718300	1.28202300	3.94298900
F	2.58025000	3.58819800	3.35539700
N	2.19010700	-0.84528200	-0.93432500
C	3.00694600	-0.30283000	-2.00450700

C	2.91117600	-1.58368000	-0.07728600
C	4.22709700	-1.22502600	-2.04198400
H	2.44034600	-0.28817300	-2.94817300
H	3.31051600	0.74000300	-1.78090800
C	4.34644500	-1.65853100	-0.58939600
O	2.51880300	-2.12245300	0.95903100
H	5.12339700	-0.73080900	-2.44431000
H	4.00599900	-2.09843500	-2.67679800
H	4.94427200	-0.94449400	0.00540800
H	4.77022300	-2.66008700	-0.42859500
Cl	-0.22369400	-1.11193300	-2.79923700

^{2}E2

C	-1.91656100	-0.36793900	0.54423200
C	-0.90640700	-2.41715000	0.91851500
C	-1.95674900	-2.83768000	1.72070500
C	-3.03950900	-1.97807900	1.95055400
C	-3.00417200	-0.72059800	1.34182300
C	-1.78741400	0.92227600	-0.16378500
C	-0.46339900	2.15806100	-1.61286500
C	-1.36329800	3.21486400	-1.60424500
C	-2.52589300	3.12584500	-0.83184200
C	-2.72737100	1.94610300	-0.10621600
H	-0.03998100	-3.05259200	0.71519800
H	-1.93082200	-3.83413900	2.16692800
H	-3.82942800	-0.02293800	1.49151200
H	0.45487700	2.19656500	-2.20376200
H	-1.15222800	4.10660900	-2.19760500
H	-3.62367100	1.83188300	0.50475100
N	-0.67441300	1.05264800	-0.90580300

N	-0.89319300	-1.21193900	0.35373600
C	-4.18845800	-2.40010500	2.80604300
H	-3.83536700	-2.72135300	3.79832900
H	-4.91805500	-1.58962800	2.93585700
H	-4.70307700	-3.26388900	2.35523100
C	-3.52335900	4.23542000	-0.77409600
H	-4.51257100	3.88274600	-1.10612700
H	-3.64208900	4.59191100	0.26140100
H	-3.22311700	5.08305300	-1.40406400
Ni	0.51521800	-0.51314700	-0.91683000
Cl	-0.52708100	-1.22828700	-2.80318800
C	1.57306400	0.41262100	0.39022200
C	1.43532200	0.26854400	1.76777000
C	2.45740200	1.35732100	-0.13001700
C	2.17605900	1.07880500	2.63316300
H	0.75833600	-0.47446300	2.19395100
C	3.20128600	2.17290600	0.72486100
H	2.58742000	1.47205800	-1.21064600
C	3.04486600	2.01866300	2.09643200
H	2.08342800	0.98365000	3.71778700
H	3.89878800	2.91937500	0.33736600
F	3.75624100	2.79760000	2.92460400
Br	2.24047000	-2.11607200	-0.90043300

TS1

C	-1.96830200	-0.83779900	-0.30115600
C	-0.50397100	-2.45666000	-1.16612200
C	-1.44963700	-3.45672500	-1.07851600
C	-2.74557600	-3.13356000	-0.57692100
C	-2.98098100	-1.82945100	-0.19562800

C	-2.12369600	0.53342700	0.07664800
C	-1.09612700	2.63602700	0.21233700
C	-2.22282700	3.22863900	0.74437500
C	-3.38245000	2.42749700	0.95939500
C	-3.31163900	1.09249900	0.62100400
H	0.50129800	-2.67143000	-1.54466500
H	-1.20356600	-4.47456400	-1.38796900
H	-3.96296800	-1.55374400	0.19477400
H	-0.19037600	3.22626400	0.03663800
H	-2.21855100	4.29184400	0.99329800
H	-4.18281100	0.45270200	0.77715500
N	-1.02114700	1.34082100	-0.11961100
N	-0.73066800	-1.18617400	-0.80448400
C	-3.79619700	-4.19325900	-0.47496900
H	-3.46082600	-5.01899200	0.17498900
H	-4.73813400	-3.79668900	-0.07008200
H	-4.00446800	-4.63812700	-1.46262300
C	-4.62141500	3.03713900	1.53441500
H	-5.42705900	2.29733000	1.64436500
H	-4.42008200	3.47904100	2.52478900
H	-4.98997700	3.85725300	0.89544800
Ni	0.53335800	0.32366100	-0.84508500
Br	2.41283900	1.93948300	-1.07073300
C	2.25977200	0.26850200	0.11297400
C	2.84127600	-0.90291100	-0.40753400
C	2.08977900	0.44247400	1.49918600
C	3.12137900	-1.96023600	0.45793300
H	3.05218200	-1.00056900	-1.47497100
C	2.37915100	-0.61490300	2.34823200
H	1.69298100	1.37803000	1.89763100

C	2.88208600	-1.80246800	1.81531700
H	3.54000400	-2.89692300	0.08368200
H	2.22027200	-0.53104200	3.42563700
F	3.16085200	-2.81074800	2.64586700

TS2

C	-2.22701300	-1.32713700	0.33611600
C	-0.14132200	-2.24727800	0.77650600
C	-0.70733400	-3.25289000	1.54923600
C	-2.09562000	-3.30093800	1.72337300
C	-2.85728900	-2.30926100	1.09652800
C	-2.94297200	-0.22930500	-0.35471000
C	-2.69544800	1.64723500	-1.68992900
C	-4.06023400	1.89104300	-1.68428800
C	-4.91030800	1.03139400	-0.97564700
C	-4.32370100	-0.04362800	-0.30190000
H	0.94575000	-2.17556900	0.63004800
H	-0.06145300	-4.00085100	2.01471000
H	-3.94255000	-2.31261300	1.20554200
H	-2.00301200	2.30290600	-2.22511400
H	-4.45977100	2.74892800	-2.22927900
H	-4.95293300	-0.73218900	0.26354100
N	-2.15528500	0.61266200	-1.04513500
N	-0.89054200	-1.31304300	0.18730800
C	-2.73670500	-4.35481500	2.56523600
H	-2.61058700	-4.11061900	3.63343500
H	-3.81346200	-4.43546000	2.36304200
H	-2.26448400	-5.33450100	2.40092700
C	-6.38428600	1.26661200	-0.93584200
H	-6.91201700	0.45027400	-0.42500000

H	-6.60584300	2.20814100	-0.40749900
H	-6.78892000	1.36941700	-1.95457100
Ni	-0.17295300	0.18944800	-0.94371400
C	0.49944600	1.58475800	0.28296900
C	1.86142900	1.93709500	0.30762000
C	-0.33115800	2.24920800	1.20280700
C	2.37560200	2.89643700	1.18567300
H	2.55651000	1.43775400	-0.37605500
C	0.15088800	3.21159800	2.09529200
H	-1.40259300	2.01951900	1.23821800
C	1.50447300	3.51959600	2.06859700
H	3.43632200	3.16186200	1.19598000
H	-0.50437800	3.72166700	2.80662000
F	1.98260500	4.44374400	2.92014300
Cl	1.49842600	-0.66008900	-2.30002800
N	3.62537900	-0.76955700	-1.06511000
C	4.77964500	-0.24421400	-1.73089600
C	3.81569800	-1.46345800	0.05377400
C	5.93237300	-0.96698100	-1.00657400
H	4.76023800	-0.46054700	-2.81112300
H	4.84206100	0.85475900	-1.61584400
C	5.32325900	-1.33962400	0.34333700
O	3.01201700	-2.04783000	0.77186400
H	6.83846000	-0.34849900	-0.93441100
H	6.19086700	-1.88216400	-1.56168700
H	5.44754600	-0.54278100	1.09677900
H	5.70071500	-2.27662400	0.77693300

TS3

C	2.73070700	-0.20822000	-0.03138000

C	2.25481300	-2.37968400	-0.68277700
C	3.48727900	-2.83344100	-0.23896700
C	4.38770400	-1.92828000	0.33924500
C	3.98700900	-0.59272800	0.43526600
C	2.21161700	1.17741200	0.02856300
C	0.41283200	2.55452600	-0.45863200
C	1.06811000	3.66516000	0.05279000
C	2.35743900	3.52595000	0.58229000
C	2.92516800	2.24877600	0.56341600
H	1.52634700	-3.04986100	-1.14717700
H	3.74613000	-3.88921700	-0.34437100
H	4.66162800	0.14204200	0.87619900
H	-0.60258900	2.61771200	-0.86381200
H	0.57026700	4.63723300	0.04235200
H	3.92620400	2.09782100	0.96960900
N	0.97444600	1.34370100	-0.47135200
N	1.89060000	-1.10194500	-0.57726600
C	5.72145300	-2.38075400	0.83577900
H	6.27679600	-2.89869500	0.03834100
H	6.32645000	-1.53902700	1.19830100
H	5.59838400	-3.10225900	1.65951000
C	3.09069200	4.69882400	1.14532100
H	2.51829100	5.15065500	1.97131900
H	4.08368400	4.41576000	1.52002700
H	3.21385000	5.48008900	0.37807200
Ni	0.07432100	-0.37724000	-1.07542400
C	-1.05366900	-0.83014200	0.49055300
C	-1.83838600	-1.99801800	0.45129400
C	-1.07075500	-0.11094100	1.69766200
C	-2.60588400	-2.42842600	1.53786400

H	-1.85971700	-2.59412800	-0.46776000
C	-1.82959600	-0.51002900	2.80195500
H	-0.48323200	0.80864000	1.79573700
C	-2.58868100	-1.66828700	2.69990100
H	-3.21382000	-3.33620700	1.49543700
H	-1.84100800	0.06216700	3.73349000
F	-3.32270100	-2.06537000	3.75379400
N	-2.66651500	1.66302600	-1.39710600
C	-3.23277600	0.60254700	-2.14879100
C	-3.28941400	1.72301100	-0.15353000
C	-4.39582400	-0.03391000	-1.36593200
H	-3.51365000	0.97690800	-3.15276500
H	-2.39931800	-0.10561100	-2.37297700
C	-4.29305400	0.60329600	0.01589300
O	-3.02712300	2.59657800	0.65355000
H	-4.31005100	-1.12916800	-1.33624600
H	-5.35618900	0.20727000	-1.84518600
H	-3.89154600	-0.08556500	0.77703500
H	-5.23928400	1.00141500	0.41072600
Cl	-0.57104400	-1.65899300	-2.86489300

TS4

C	2.28235800	-0.22998800	-0.38632300
C	1.39975200	-2.04628900	-1.51187500
C	2.61749500	-2.70810300	-1.49983200
C	3.72528800	-2.10209600	-0.89056500
C	3.53902000	-0.83514800	-0.33326600
C	1.98572500	1.12077900	0.13812400
C	0.36142900	2.73961900	0.40766300
C	1.27386000	3.62413900	0.97142100

C	2.60419900	3.23238600	1.14127000
C	2.94965200	1.94735700	0.70823000
H	0.51776200	-2.47992200	-1.99033000
H	2.70465300	-3.69251300	-1.96481500
H	4.37948100	-0.32540800	0.13925800
H	-0.69616800	2.99497700	0.31099900
H	0.93955200	4.61593500	1.28335000
H	3.97913800	1.60181500	0.81251500
N	0.70569500	1.51787300	0.00196700
N	1.24003600	-0.84546600	-0.95782400
C	5.05094100	-2.78942200	-0.84648700
H	5.37920900	-3.06427500	-1.86113100
H	5.82155900	-2.15645100	-0.38639500
H	4.97862100	-3.72555900	-0.26981900
C	3.61989200	4.12872300	1.77043900
H	3.25235000	5.16047000	1.85284000
H	3.86385600	3.77135000	2.78464000
H	4.55794700	4.12770400	1.19527800
Ni	-0.52360600	0.12437500	-0.89488500
C	-1.25570300	-0.73077600	0.68504500
C	-1.44112300	-2.11408400	0.51927300
C	-1.07088100	-0.21229200	1.97785600
C	-1.39420800	-2.97213200	1.61714600
H	-1.59529200	-2.53768300	-0.47662600
C	-1.03654500	-1.06849400	3.07554600
H	-0.96348700	0.86184400	2.12309600
C	-1.19366700	-2.43665400	2.88231100
H	-1.51186100	-4.05159000	1.49525700
H	-0.88185400	-0.68050700	4.08547000
F	-1.15340500	-3.25786400	3.94474500

N	-2.41616100	0.27923300	-0.46119000
C	-3.33917500	-0.53897100	-1.24015700
C	-3.06093300	1.32960000	0.12200400
C	-4.48545300	0.41661200	-1.55450700
H	-2.83911300	-0.92439700	-2.13959800
H	-3.69011600	-1.39609700	-0.63523200
C	-4.51265900	1.30366900	-0.32075300
O	-2.56769700	2.14652100	0.88692300
H	-5.42980800	-0.10819600	-1.75691300
H	-4.22373800	1.01538500	-2.44153500
H	-5.09994600	0.85047900	0.49831400
H	-4.88895400	2.32403800	-0.47718100
Cl	-0.67018800	0.32191800	-3.19992900

TS5

C	-2.13849000	-0.66939200	0.06492800
C	-0.84584800	-2.62216400	0.13601600
C	-1.95586000	-3.43757600	0.25137700
C	-3.24859900	-2.83405200	0.26876800
C	-3.31685000	-1.46040600	0.17465100
C	-2.11482900	0.75616000	-0.01634200
C	-0.74754900	2.65337400	-0.15132400
C	-1.82781400	3.51741200	-0.16901000
C	-3.14207200	2.96730300	-0.11057600
C	-3.26446700	1.59555600	-0.03388200
H	0.15966000	-3.05755200	0.11443700
H	-1.83805300	-4.52088700	0.32366900
H	-4.29244600	-0.96887200	0.18921200
H	0.27734300	3.03895200	-0.18965400
H	-1.67078500	4.59677600	-0.22482300

H	-4.25947600	1.14682100	0.01307900
N	-0.85941900	1.32436100	-0.08219900
N	-0.90261400	-1.28917800	0.04116300
C	-4.47383100	-3.68479500	0.38771200
H	-4.45311500	-4.28060300	1.31598500
H	-5.39200000	-3.07990600	0.38813700
H	-4.53670400	-4.40629600	-0.44451000
C	-4.33554800	3.87011600	-0.13223700
H	-5.27655900	3.30391500	-0.07951500
H	-4.31094700	4.57786000	0.71359600
H	-4.35199600	4.48154700	-1.05029700
Ni	0.57915000	-0.01561800	-0.09291600
Cl	2.30604900	-1.23170100	-1.10183200
N	3.59504100	-0.52139600	-0.08164800
C	5.00247500	-0.67570600	-0.41208000
C	3.28307800	0.65594400	0.50081900
C	5.63166100	0.23629800	0.64705900
H	5.31028500	-1.72600100	-0.32579400
H	5.19563100	-0.32253200	-1.43928000
C	4.57473500	1.31660000	0.88956500
O	2.13545000	1.08815900	0.63701500
H	6.59607700	0.64007800	0.31279000
H	5.79890400	-0.33825200	1.56975600
H	4.69839700	2.18343700	0.21707800
H	4.53093700	1.69790900	1.91893000

TS6

C	1.82634600	-1.02634100	0.17158700
C	0.54041300	-2.94017700	0.04134800
C	1.62257700	-3.70044300	-0.37546000

C	2.87322800	-3.09039000	-0.53495700
C	2.95720900	-1.72576400	-0.24889200
C	1.84096100	0.41445000	0.51174800
C	0.59605400	2.15792500	1.38052400
C	1.65078900	3.04780000	1.23419100
C	2.86143500	2.59770500	0.69106100
C	2.94490200	1.24868100	0.33458300
H	-0.44732600	-3.39165000	0.16278300
H	1.48945300	-4.76584800	-0.57593100
H	3.91454900	-1.21294800	-0.34905100
H	-0.36331900	2.45927200	1.81056900
H	1.52956800	4.08869700	1.54237800
H	3.87254500	0.85916600	-0.08701200
N	0.68951000	0.88005200	1.01819400
N	0.63257300	-1.63470800	0.30370300
C	4.06304600	-3.87119600	-0.98791300
H	3.87914200	-4.31293500	-1.98025500
H	4.96211100	-3.24312900	-1.04592000
H	4.26203400	-4.70714800	-0.29875600
C	4.01142500	3.53019800	0.49035800
H	3.78440500	4.24548400	-0.31732700
H	4.20048800	4.12230000	1.39869200
H	4.92912400	2.99008200	0.22071400
Ni	-0.87542700	-0.40844600	0.92405000
Cl	-2.06854900	0.20775500	2.77644900
C	-1.65919600	0.20477200	-0.82338500
C	-0.74316200	0.18600800	-1.89582500
C	-2.29864700	1.41049600	-0.46607400
C	-0.33825600	1.38214400	-2.47233000
H	-0.30884300	-0.75667800	-2.23331600

C	-1.89015900	2.60407700	-1.05258900
H	-3.05357700	1.41016400	0.32142800
C	-0.90373600	2.57739100	-2.03187100
H	0.41208400	1.39916200	-3.26633700
H	-2.33107300	3.55786200	-0.75337600
F	-0.50540200	3.72920900	-2.59044000
Br	-2.72832600	-1.51890000	-0.49595000

TS7

C	-1.74189200	1.21093100	-0.14491900
C	0.17836800	2.41774400	-0.59012900
C	-0.49061200	3.62643100	-0.44747500
C	-1.85439900	3.62636600	-0.13703500
C	-2.47809000	2.38253300	0.01180100
C	-2.31971300	-0.14596100	-0.00645400
C	-1.88020700	-2.41196700	-0.13178700
C	-3.18849000	-2.73269400	0.20242200
C	-4.10944500	-1.70657100	0.44551300
C	-3.64993100	-0.39083900	0.33025400
H	1.24184300	2.37231900	-0.83706600
H	0.05171900	4.56443400	-0.58368100
H	-3.54273900	2.33814400	0.24558000
H	-1.12433600	-3.17304500	-0.34672500
H	-3.48895600	-3.78054000	0.27089500
H	-4.33725600	0.43749800	0.50683300
N	-1.46117600	-1.15202500	-0.23132500
N	-0.43157200	1.24361000	-0.44278700
C	-2.61649700	4.89645200	0.05301700
H	-2.12899100	5.73849700	-0.45723900
H	-3.64932900	4.80134200	-0.31185300

H	-2.67140500	5.14306800	1.12684000
C	-5.51996100	-2.00414000	0.83620600
H	-5.90106400	-2.88983500	0.30758800
H	-5.57156500	-2.22323500	1.91612700
H	-6.18347500	-1.15153700	0.63640200
Ni	0.51299900	-0.59161900	-0.54707900
Cl	1.02618400	-0.72273300	1.77903500
N	3.22299700	-0.31829500	0.97085100
C	4.48861400	-0.35680900	1.65042800
C	3.24283500	0.16143900	-0.24376900
C	5.36873400	0.55298300	0.76847600
H	4.40013900	0.01197600	2.68430700
H	4.87484300	-1.39130500	1.69888000
C	4.67740000	0.51542500	-0.59616400
O	2.27268500	0.29389500	-1.02902100
H	6.41732800	0.22534900	0.74297000
H	5.34375000	1.57852100	1.16783800
H	5.06504800	-0.28543200	-1.24931700
H	4.72382600	1.45736500	-1.16104000
Cl	1.09047100	-2.56081900	-1.59588400

1a

C	2.44496100	0.00000000	0.00000000
C	1.77111100	-1.21464600	-0.00000300
C	0.37805700	-1.21453300	-0.00000100
C	-0.30770700	0.00000000	-0.00000300
C	0.37805700	1.21453300	-0.00000300
C	1.77111100	1.21464600	0.00000100
H	2.33551100	-2.14949700	0.00000300
H	-0.16550600	-2.16112100	0.00000100

H	-0.16550600	2.16112100	-0.00000600
H	2.33551300	2.14949600	0.00000200
F	3.78033700	0.00000100	0.00000200
Br	-2.19933100	0.00000000	0.00000100

2a

C	-1.89149200	-0.90849300	-0.19177000
C	-1.82000800	0.57961100	0.14301600
C	-0.49346700	-1.43397700	0.13893200
H	-2.67164100	-1.44457700	0.36455900
H	-2.08514500	-1.04172000	-1.26669900
H	-2.08255600	0.78083900	1.19604700
H	-2.45120100	1.22280100	-0.48533500
H	-0.17203200	-2.25381400	-0.51907600
H	-0.40171000	-1.76538100	1.18869700
N	0.30746600	-0.24632300	-0.09231000
C	-0.35938800	0.94977100	-0.01384200
O	0.14595800	2.04852800	-0.03828100
Cl	1.99591100	-0.31079900	0.00095300

3aa

C	-3.31378100	-1.06289200	-0.36898100
C	-3.44062300	0.33549700	0.21015000
C	-1.87209600	-1.44289800	-0.05095100
H	-4.03042400	-1.78361300	0.04646000
H	-3.45558500	-1.03218900	-1.46037300
H	-3.71439700	0.31648300	1.27986000
H	-4.15486400	0.99389200	-0.30256500
H	-1.43365200	-2.11188900	-0.80540400
H	-1.78384900	-1.93711600	0.93291400
N	-1.17338800	-0.16143800	-0.03700800

C	-2.04087500	0.90030800	0.12065100
O	-1.73549200	2.07361900	0.20477400
C	0.22664400	-0.09368400	-0.02207000
C	0.97458600	-1.26603600	0.18271300
C	0.91559100	1.11717800	-0.21974300
C	2.36671700	-1.23420000	0.18972800
H	0.47682100	-2.22180000	0.34739100
C	2.30640400	1.14901300	-0.20918600
H	0.34987800	2.03355900	-0.37065900
C	3.01738700	-0.02562400	-0.00591700
H	2.94747800	-2.14514000	0.35029800
H	2.84451600	2.08711800	-0.36354300
F	4.35689000	0.00909200	0.00090300

2ar

C	-1.38965800	0.66951600	-0.20087900
C	-0.00561000	1.18893200	0.15935800
C	-1.25797700	-0.83095200	0.09755400
H	-2.20634900	1.14300800	0.36003200
H	-1.58729200	0.81525100	-1.27442700
H	0.05396500	1.49908100	1.21785200
H	0.36352000	2.02619600	-0.44886300
H	-1.89908400	-1.49065900	-0.51197000
H	-1.54316900	-1.05735300	1.15036500
N	0.11134400	-1.20258700	-0.03394000
C	0.87463200	-0.03419100	-0.00011600
O	2.08883500	-0.05965500	-0.07386400

10. Supplementary Reference

(1) (a) Larionov, O. V.; Kozhushkov, S. I.; Meijere, A. d. New Protocol for Efficient N -

Chlorinations of Amides and Carbamates. *Synthesis* **2003**, 1916–1919; (b) Pastoriza, C.; Antelo, J. M.; Amoedo, F. A.; Parajó, M. Kinetic study of the formation reaction of N-chloro-2-oxazolidinone. *J. Phys. Org. Chem.* **2015**, *28*, 602–611.

(2) Zhang, Y.-L.; Yang, L.; Wu, J.; Zhu, C.; Wang, P. Vinyl Sulfonium Salts as the Radical Acceptor for Metal-Free Decarboxylative Alkenylation. *Org. Lett.* **2020**, *22*, 7768–7772.

(3) Györke, G.; Dancsó, A.; Volk, B.; Bezúr, L.; Hunyadi, D.; Szalóki, I.; Milen, M. Direct Use of Copper-Containing Minerals in Goldberg Arylation of Amides. *Catal. Lett.* **2023**, *153*, 503–521.

(4) Chowdhury, S.; Chauhan, G.; Kumar, A.; Chaturvedi, B.; Behera, C. Copper-Mediated Intramolecular Amidation/C−N-Coupling Cascade Sequence: Straightforward One-Pot Synthesis of N-Aryl γ- and δ-Lactams by Using Amino Acids as Precursors. *Eur. J. Org. Chem.* **2022**, *2022*.

(5) De, S.; Yin, J.; Ma, D. Copper-Catalyzed Coupling Reaction of (Hetero)Aryl Chlorides and Amides. *Org. Lett.* **2017**, *19*, 4864–4867.

(6) Tan, B.; Teo, Y.-C. Mild and Efficient Cobalt-Catalyzed Cross-Coupling of Aliphatic Amides and Aryl Iodides in Water. *Synlett* **2015**, *26*, 1697–1701.

(7) Chang, R. K.; Clairmont, B. P.; Lin, S.; MacArthur, A. H. R. Amidation of Aryl Chlorides Using a Microwave-Assisted, Copper-Catalyzed Concurrent Tandem Catalytic Methodology. *Organometallics* **2019**, *38*, 4448–4454.

(8) Jette, C. I.; Geibel, I.; Bachman, S.; Hayashi, M.; Sakurai, S.; Shimizu, H.; Morgan, J. B.; Stoltz, B. M. Palladium-Catalyzed Construction of Quaternary Stereocenters by Enantioselective Arylation of γ-Lactams with Aryl Chlorides and Bromides. *Angew. Chem. Int. Ed.* **2019**, *58*, 4297–4301.

(9) Luo, H.; Wang, G.; Feng, Y.; Zheng, W.; Kong, L.; Ma, Y.; Matsunaga, S.; Lin, L. Photoinduced Nickel-Catalyzed Carbon-Heteroatom Coupling. *Chem. Eur. J.* **2023**, *29*, e202202385.

(10) Deepake, S. K.; Kumar, M.; Kumar, P.; Das, U. α-Angelica Lactone Catalyzed Oxidation of Pyrrolidines to Lactams. *Eur. J. Org. Chem.* **2022**, *2022*.

(11) Bathini, T.; Rawat, V.; Sreedhar, B. Selective Copper-Catalyzed N-Arylation of Lactams with Arylboronic Acids under Base- and Ligand-Free Conditions. *Synlett* **2015**, *26*, 1348–1351.

(12) Fehr, L.; Sewald, L.; Huber, R.; Kaiser, M. Facile Multicomponent Synthesis of Oxazolidinones from Primary Amines and Cesium (Hydrogen)Carbonate. *Eur. J. Org. Chem.* **2023**, *26*.

(13) Xie, X.; Guo, X.; Qiao, K.; Shi, L. Visible-light promoted photocatalyst-free aerobic α-

oxidation of tertiary amines to amides. *Org. Biomol. Chem.* **2022**, *20*, 8031–8036.

(14) Song, G.; Li, Q.; Nong, D.-Z.; Song, J.; Li, G.; Wang, C.; Xiao, J.; Xue, D. Ni-Catalyzed Photochemical C-N Coupling of Amides with (Hetero)aryl Chlorides. *Chem. Eur. J.* **2023**, e202300458.

(15) Chang, K.; Shi, Y.; Chen, J.; He, Z.; Xu, Z.; Zhao, Z.; Zhu, W.; Li, H.; Xu, Y.; Li, B.; Qian, X. The discovery of new plant activators and scaffolds with potential induced systemic resistance: from jasmonic acid to pyrrolidone. *Med. Chem. Commun.* **2016**, *7*, 1849–1857.

(16) Mair, B. A.; Fouad, M. H.; Ismailani, U. S.; Munch, M.; Rotstein, B. H. Rhodium-Catalyzed Addition of Organozinc Iodides to Carbon-11 Isocyanates. *Org. Lett.* **2020**, *22*, 2746–2750.

(17) Wang, J.; Ren, J.; Zhu, Y.-P.; Sun, X.-Q.; Hu, P.-F.; Mu, X.; Zeng, B.-B. Practical povidone iodine catalyzed transamidation from primary amides and amines. *Tetrahedron Lett.* **2023**, *116*, 154312.

(18) Yu, W.; Yang, S.; Xiong, F.; Fan, T.; Feng, Y.; Huang, Y.; Fu, J.; Wang, T. Palladium-catalyzed carbonylation of benzylic ammonium salts to amides and esters via C-N bond activation. *Org. Biomol. Chem.* **2018**, *16*, 3099–3103.

(19) Nozawa-Kumada, K.; Saga, S.; Matsuzawa, Y.; Hayashi, M.; Shigeno, M.; Kondo, Y. Copper-Catalyzed Oxidative Benzylic C(sp3)-H Cyclization for the Synthesis of β-Lactams. *Chem. Eur. J.* **2020**, *26*, 4496–4499.

(20) Ying, X.; Li, Y.; Li, L.; Li, C. Nickel-Catalyzed C-I-Selective C(sp2)-C(sp3) Cross-Electrophile Coupling of Bromo(iodo)arenes with Alkyl Bromides. *Angew. Chem. Int. Ed.* **2023**, *62*, e202304177.

(21) Deng, H.-P.; Zhou, Q.; Wu, J. Microtubing-Reactor-Assisted Aliphatic C-H Functionalization with HCl as a Hydrogen-Atom-Transfer Catalyst Precursor in Conjunction with an Organic Photoredox Catalyst. *Angew. Chem. Int. Ed.* **2018**, *57*, 12661–12665.

(22) Thapa, P.; Corral, E.; Sardar, S.; Pierce, B. S.; Foss, F. W. Isoindolinone Synthesis: Selective Dioxane-Mediated Aerobic Oxidation of Isoindolines. *J. Org. Chem.* **2019**, *84*, 1025–1034.

(23) Feng Qiang; Chang Bo; Yue Zongqiang; Zhang Xiaoling; He Bing. Synthesis method for improving purity of fluorochloridone. CN113087648A.

(24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.;

Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16 Rev. C.01;* Wallingford, CT, 2016.

(25) (a) Goerigk, L.; Grimme, S. Efficient and Accurate Double-Hybrid-Meta-GGA Density Functionals-Evaluation with the Extended GMTKN30 Database for General Main Group Thermochemistry, Kinetics, and Noncovalent Interactions. *J. Chem. Theory Comput.* **2011**, *7*, 291–309; (b) Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

(26) Weigend, F. Accurate Coulomb-fitting basis sets for H to Rn. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057–1065.

(27) Hellweg, A.; Hättig, C.; Höfener, S.; Klopper, W. Optimized accurate auxiliary basis sets for RI-MP2 and RI-CC2 calculations for the atoms Rb to Rn. *Theor Chem Acc* **2007**, *117*, 587–597.

(28) Neese, F. Software update: The ORCA program system—Version 5.0. *WIREs Comput. Mol. Sci.* **2022**, *12*, e1606.

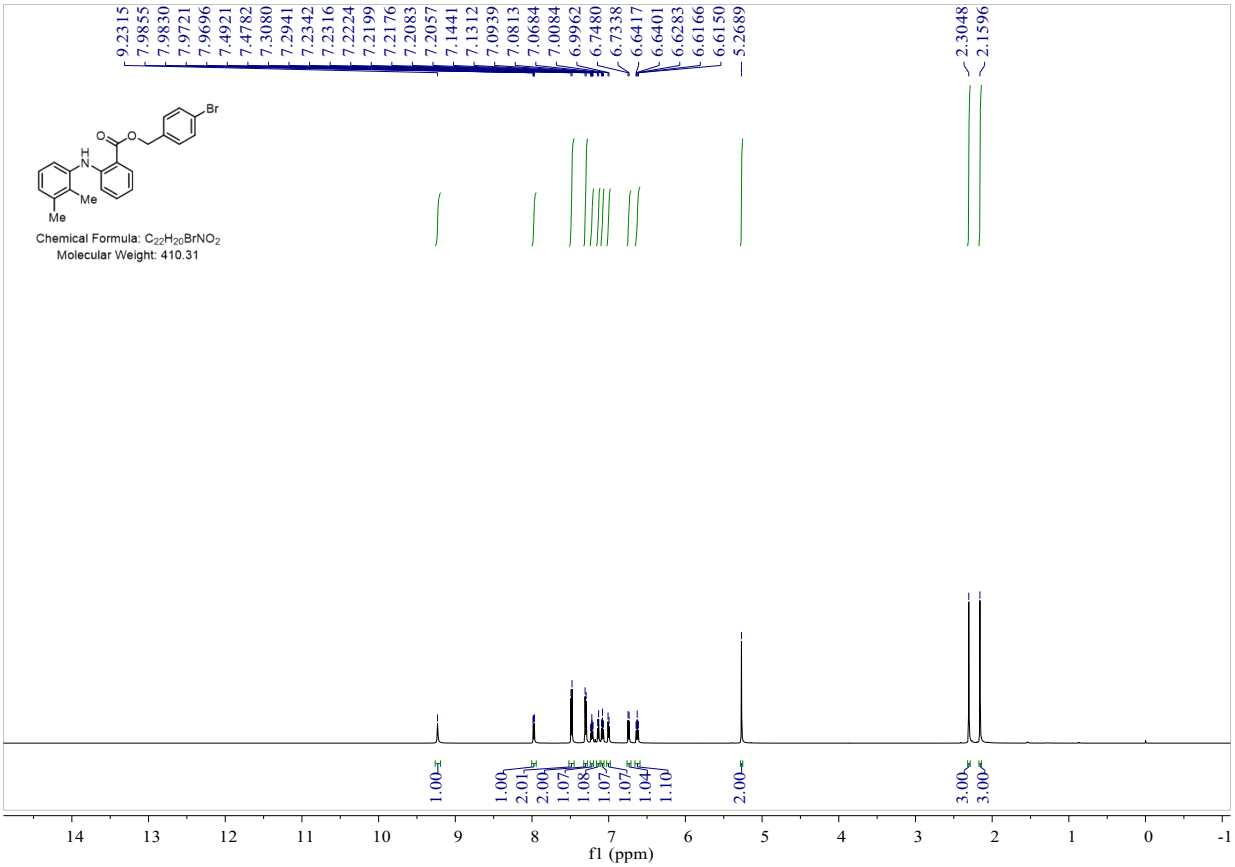
(29) Legault, C. Y. *CYLview20;* Université de Sherbrooke, 2020 (http://www.cylview.org).

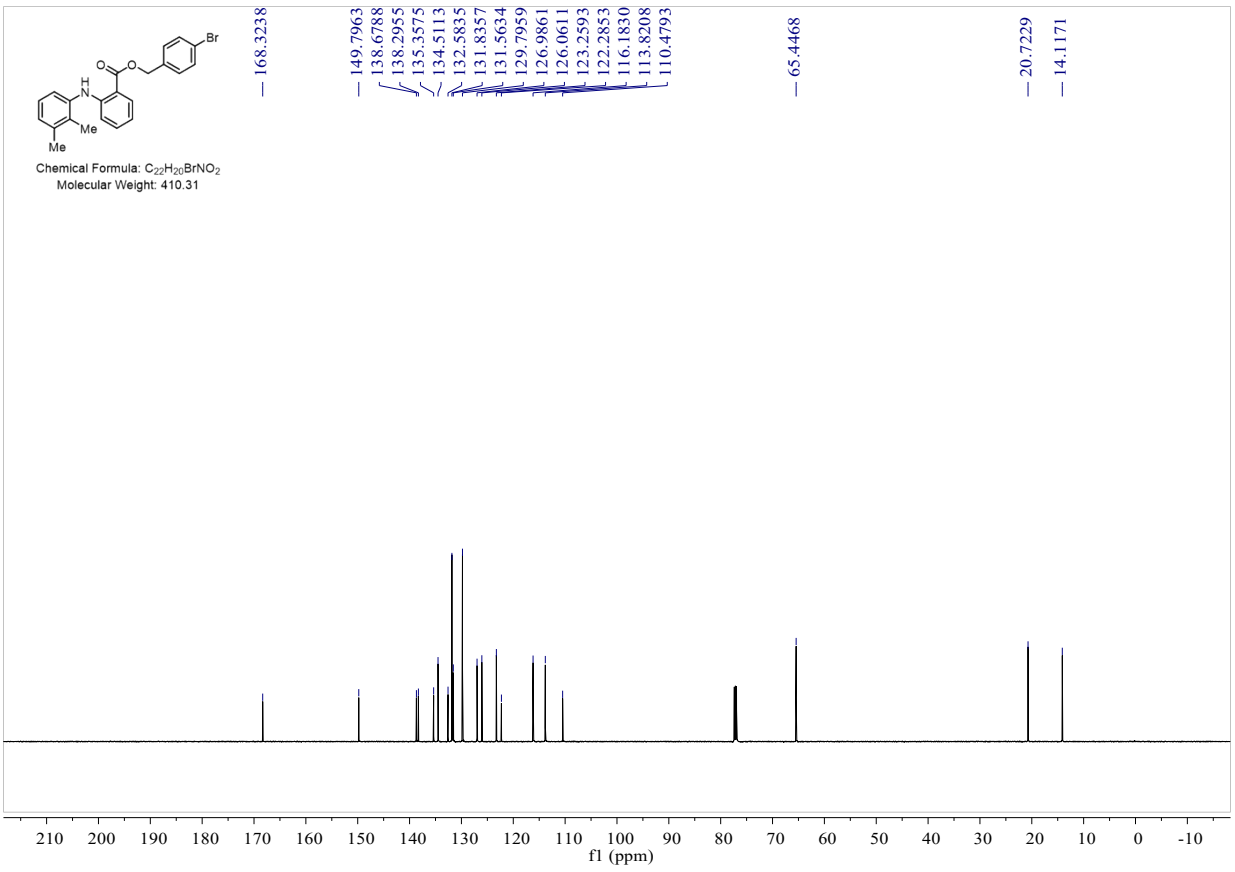
(30) Sayyed, F. B.; Tsuji, Y.; Sakaki, S. The crucial role of a Ni(I) intermediate in Ni-catalyzed carboxylation of aryl chloride with CO2: a theoretical study. *Chem. Commun.* **2013**, *49*, 10715–10717.

(31) Yuan, M.; Song, Z.; Badir, S. O.; Molander, G. A.; Gutierrez, O. On the Nature of C(sp3)–C(sp2) Bond Formation in Nickel-Catalyzed Tertiary Radical Cross-Couplings: A Case Study of Ni/Photoredox Catalytic Cross-Coupling of Alkyl Radicals and Aryl Halides. *J. Am. Chem. Soc.* **2020**, *142*, 7225–7234.

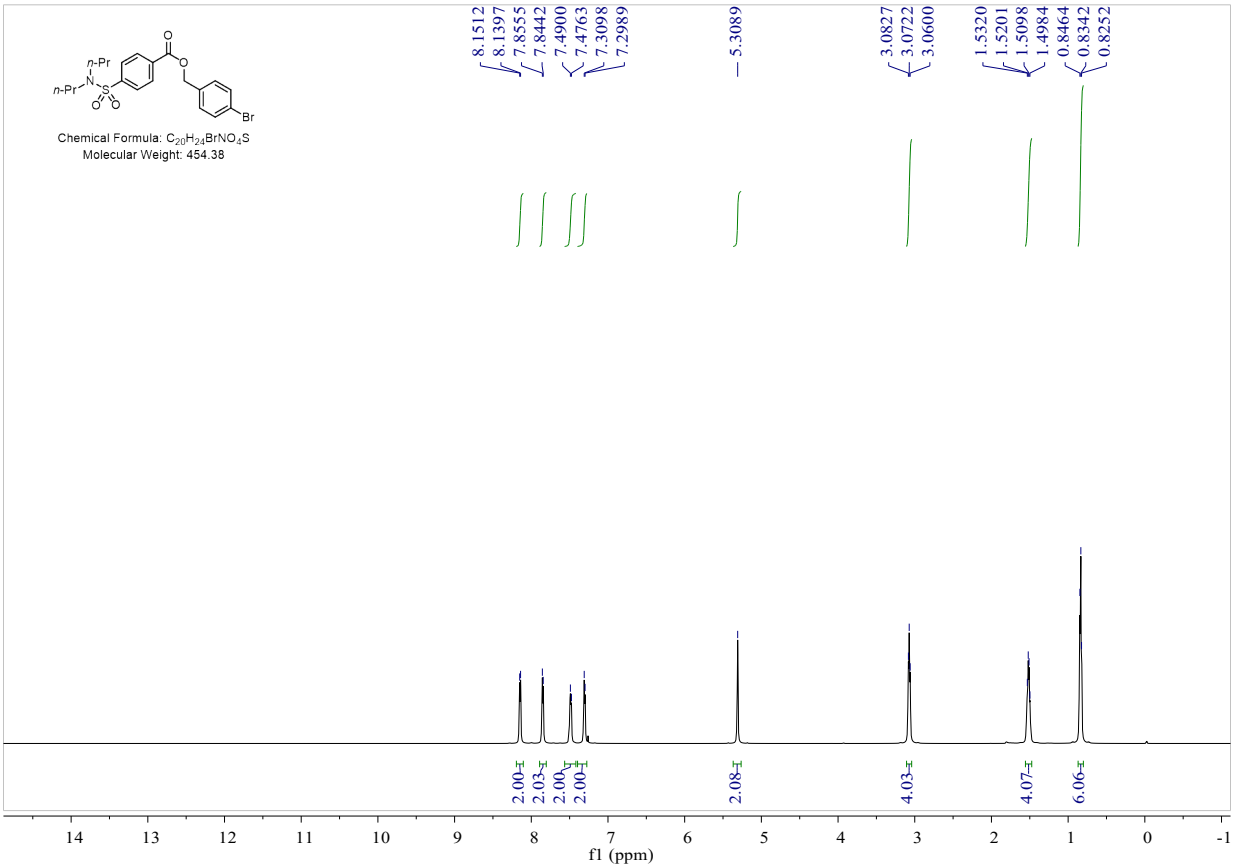
11. Characterization Spectra for compounds 1w, 1x and 1y

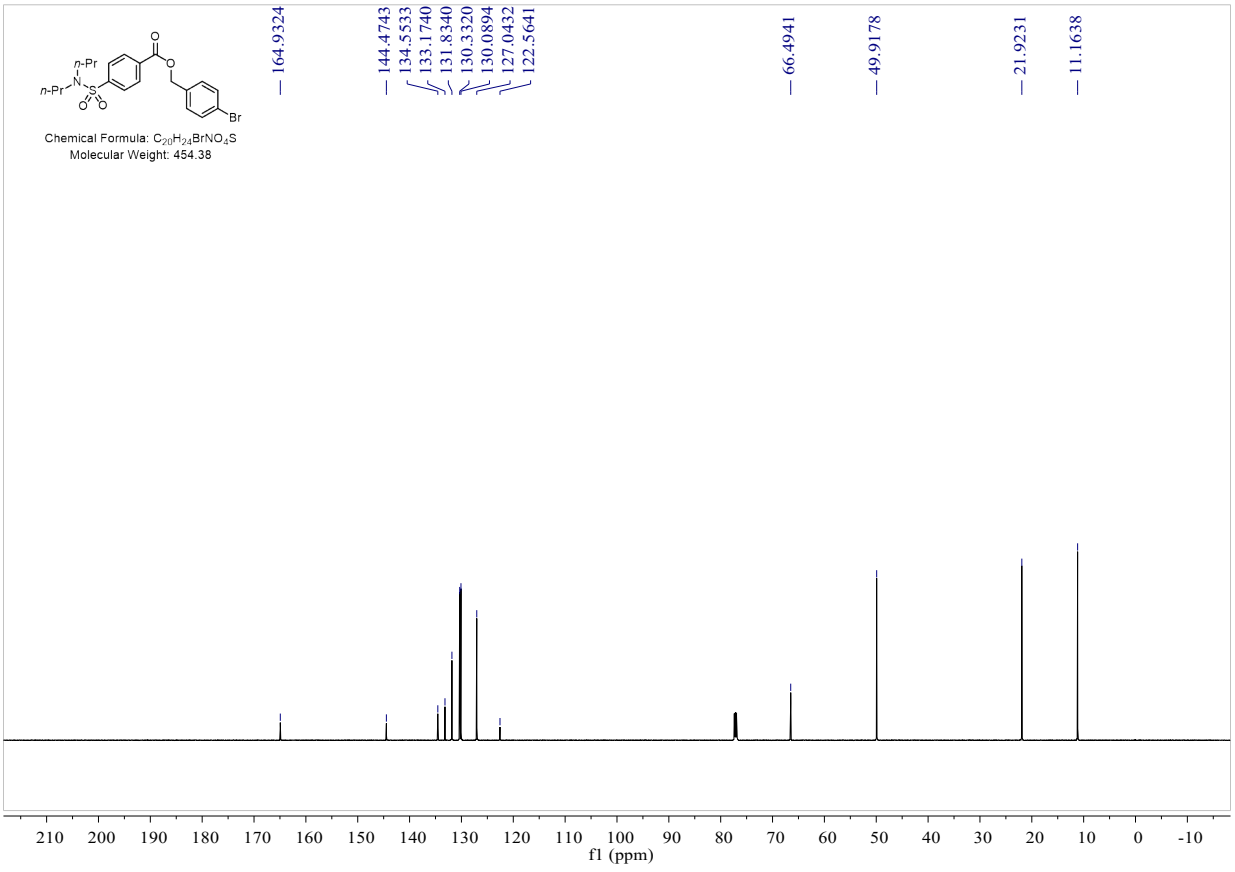
4-Bromobenzyl 2-((2,3-dimethylphenyl)amino)benzoate (1w).



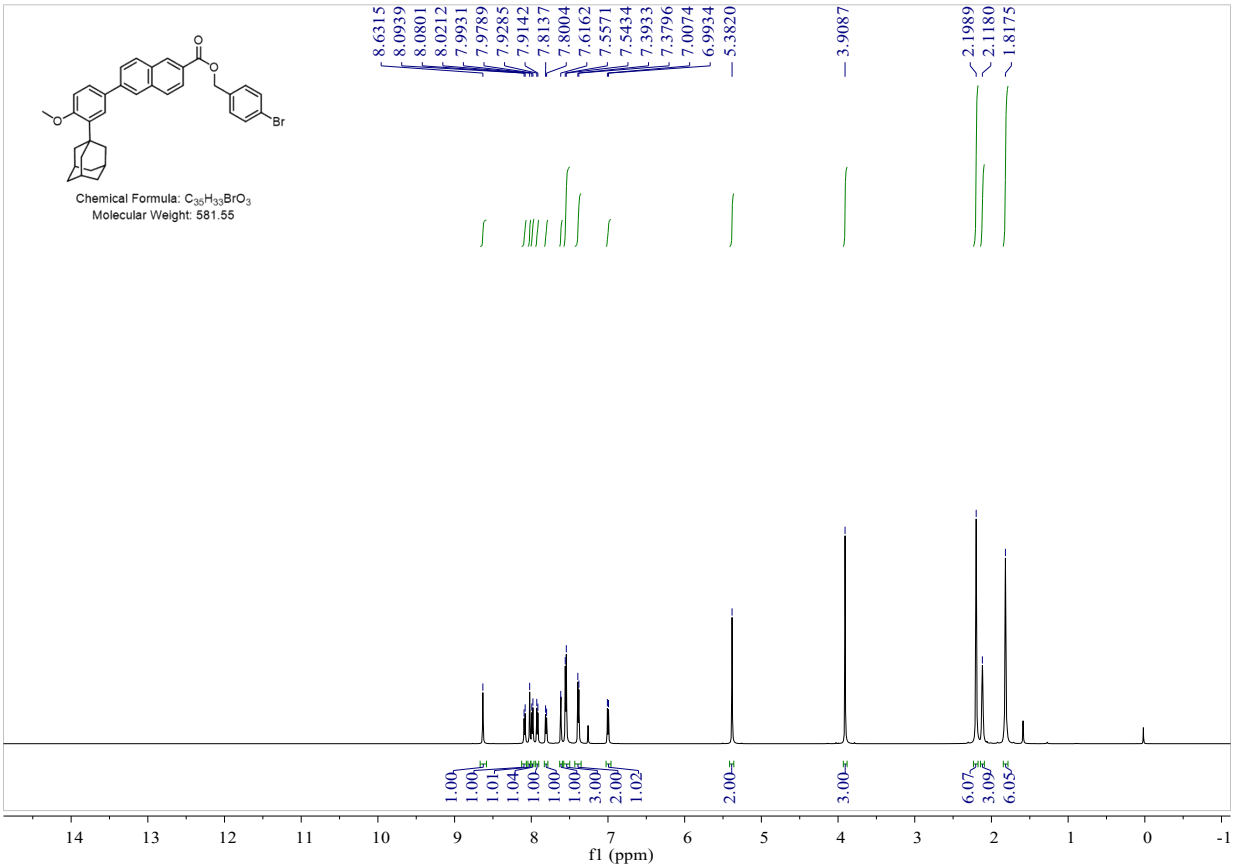


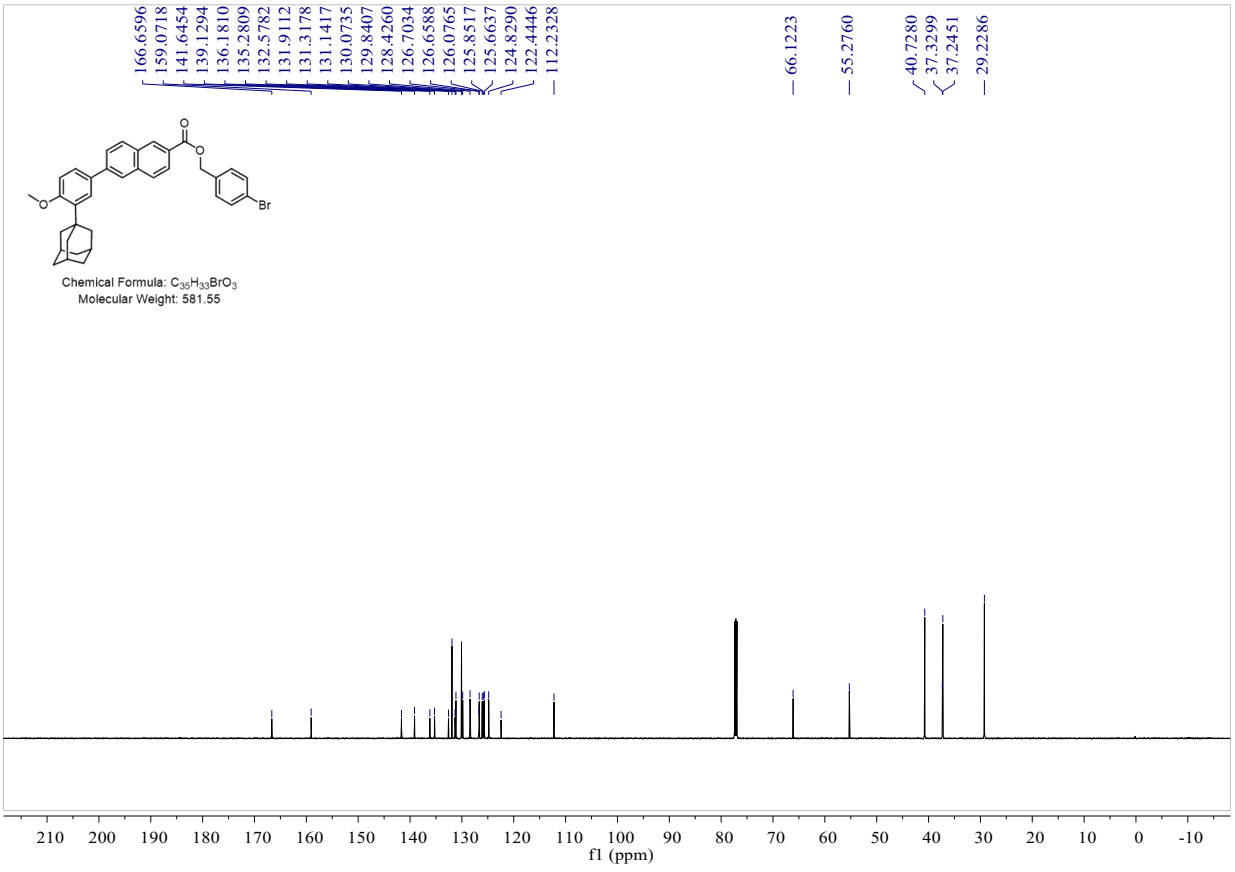
4-Bromobenzyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (1x).





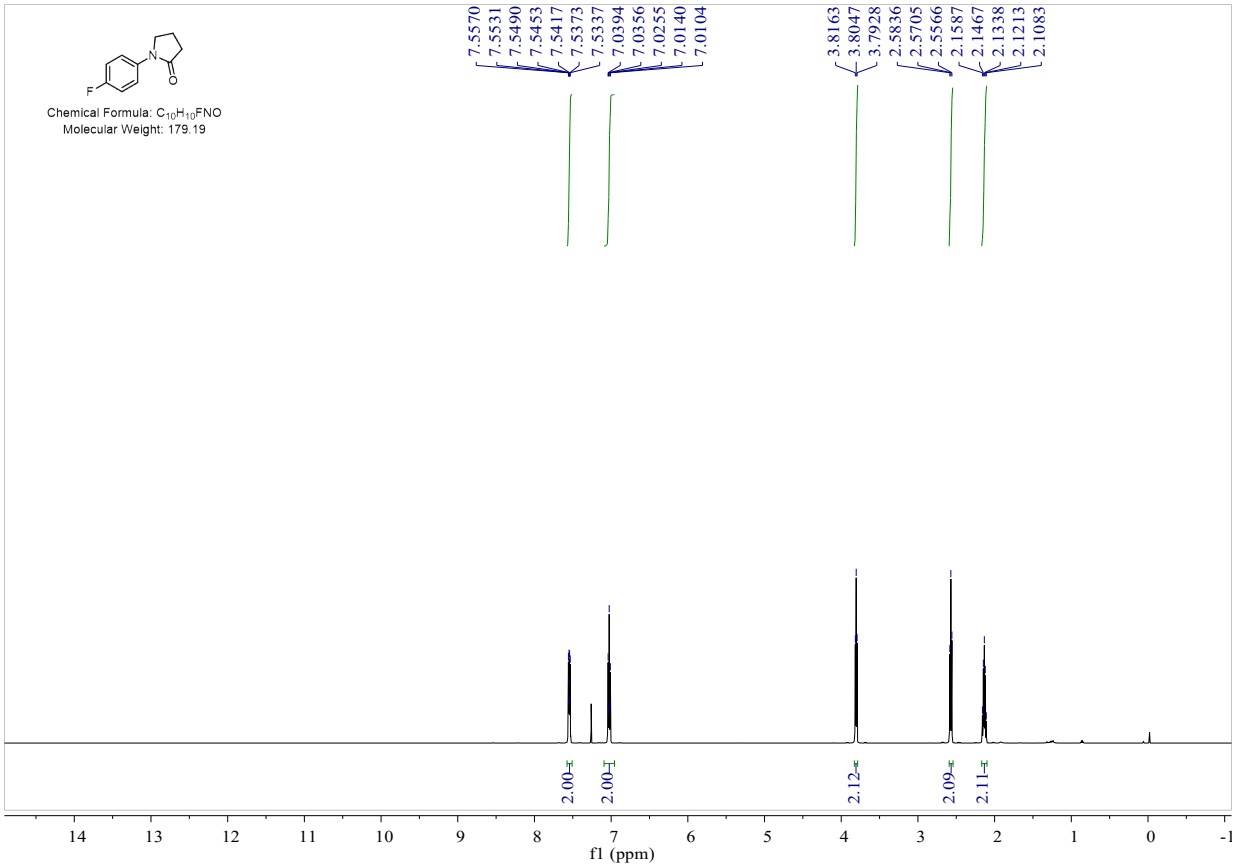
4-Bromobenzyl 6-(3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthoate (1y).

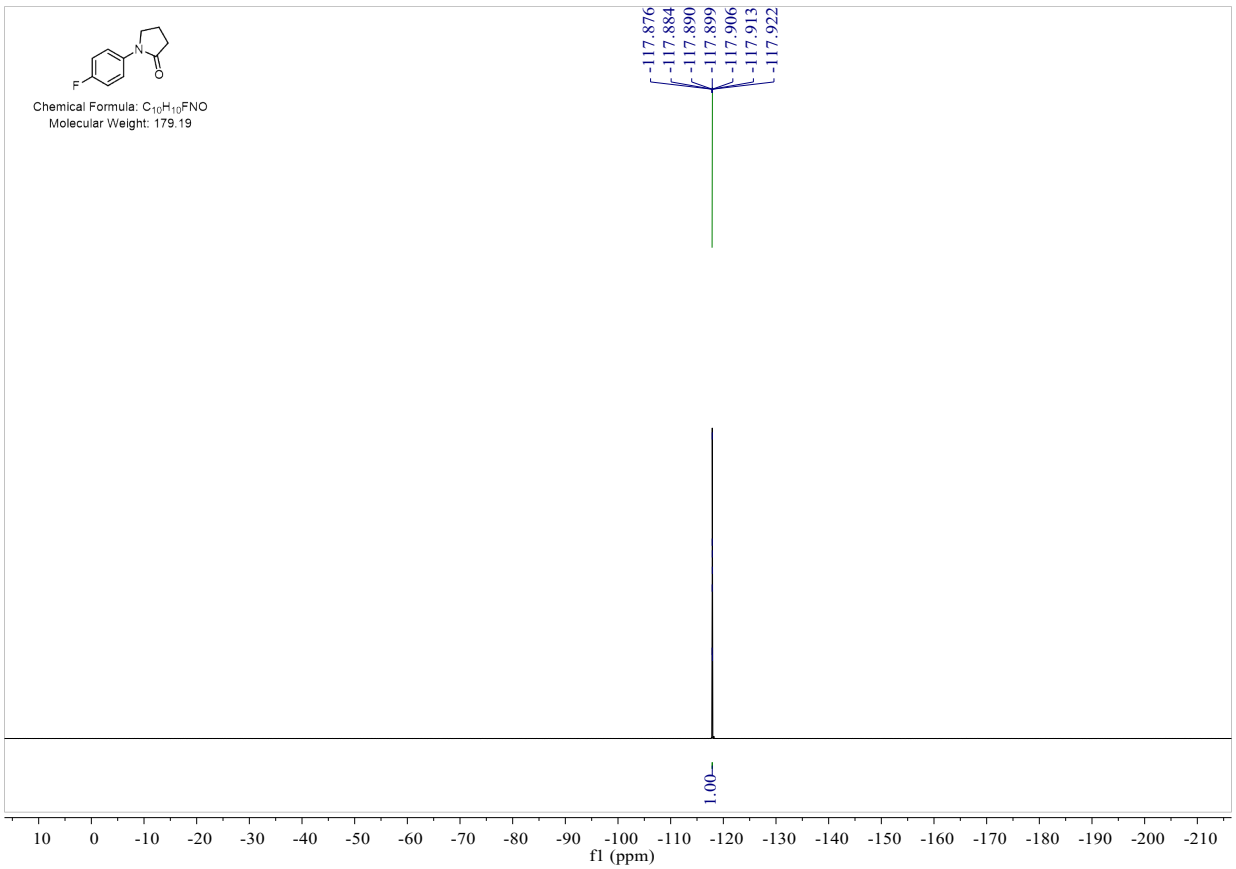


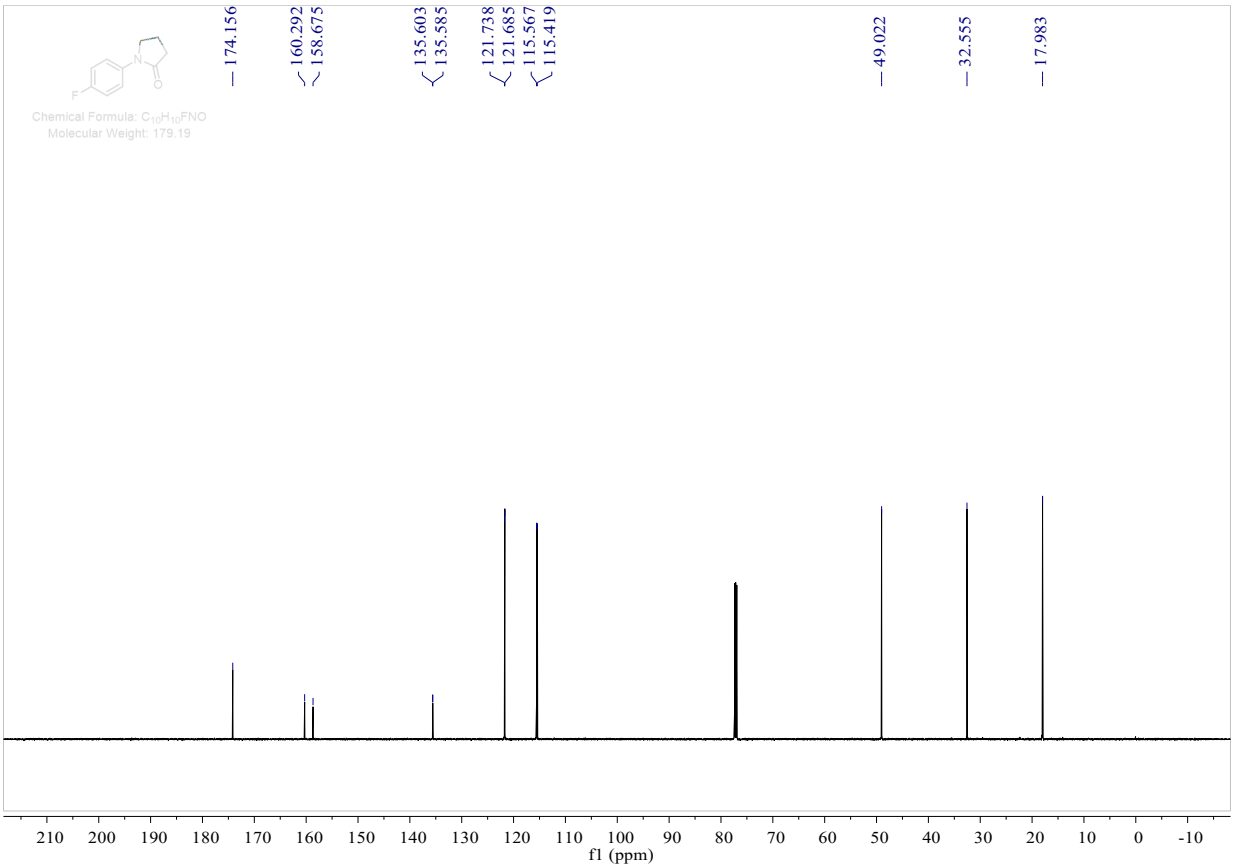


12. Characterization Spectra for compounds 3-9.

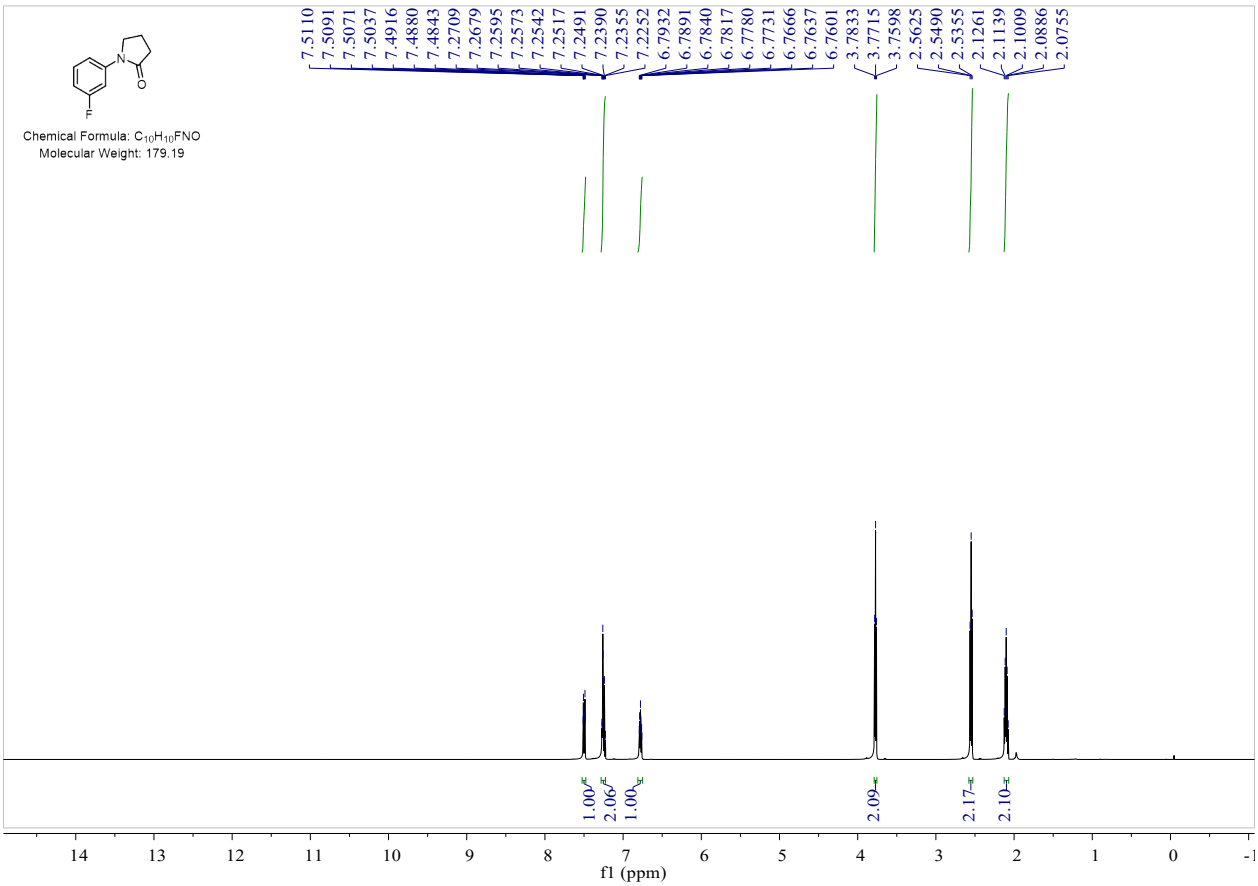
1-(4-Fluorophenyl)pyrrolidin-2-one (3aa).

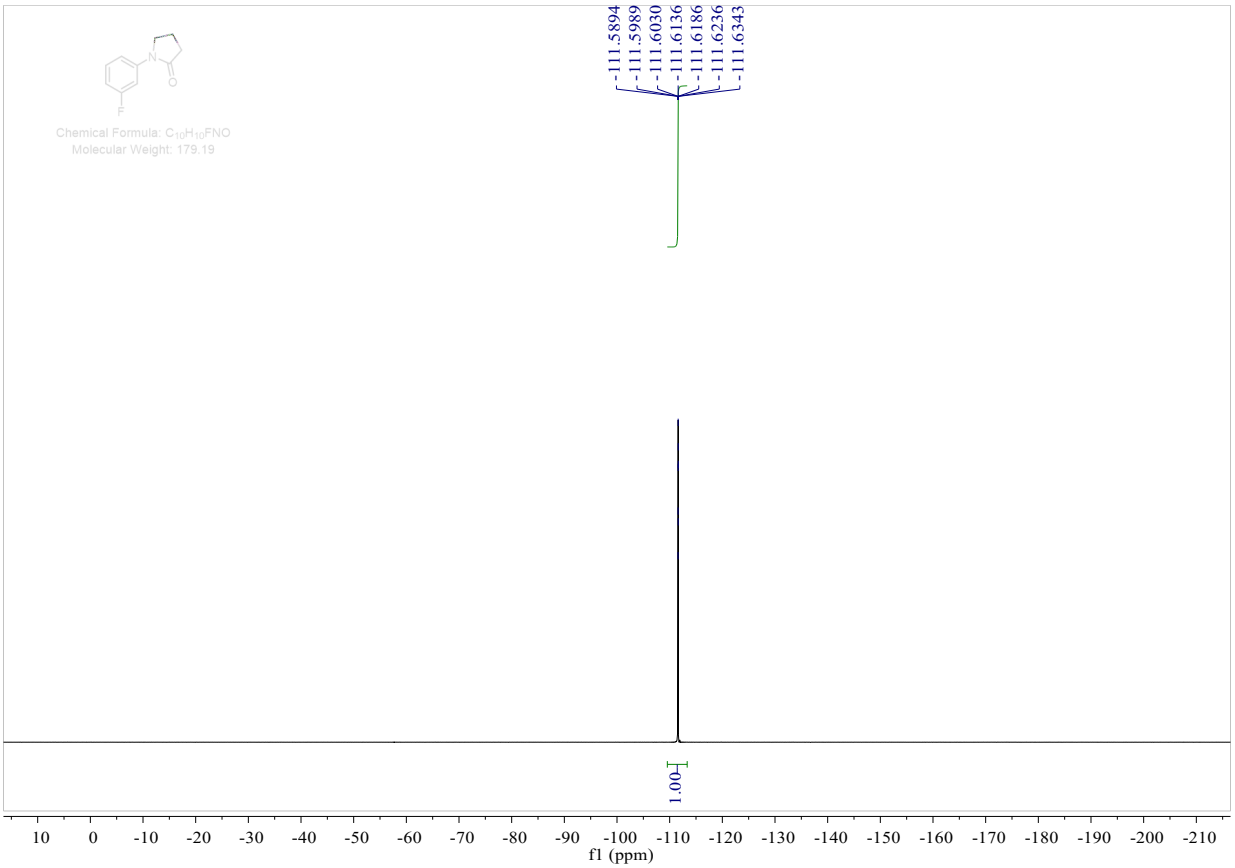


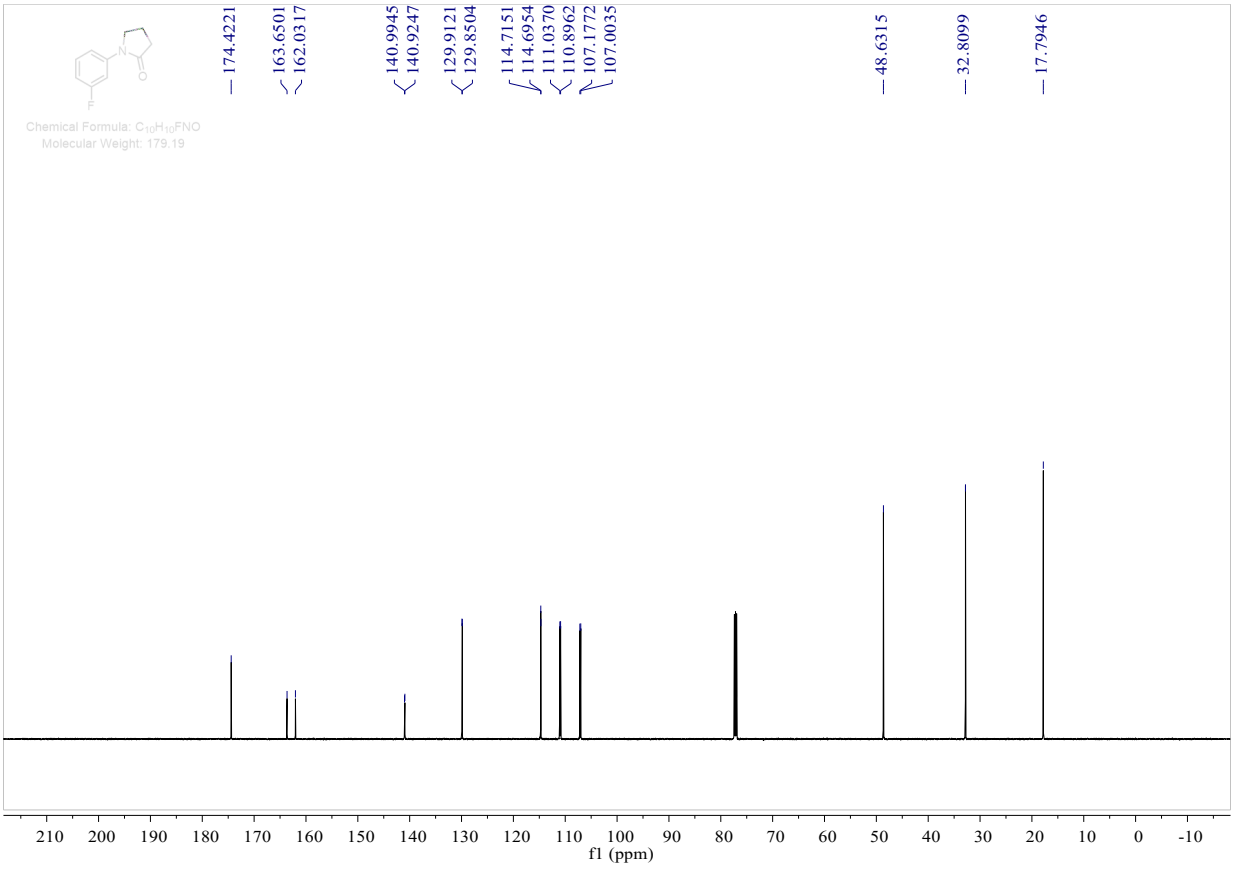




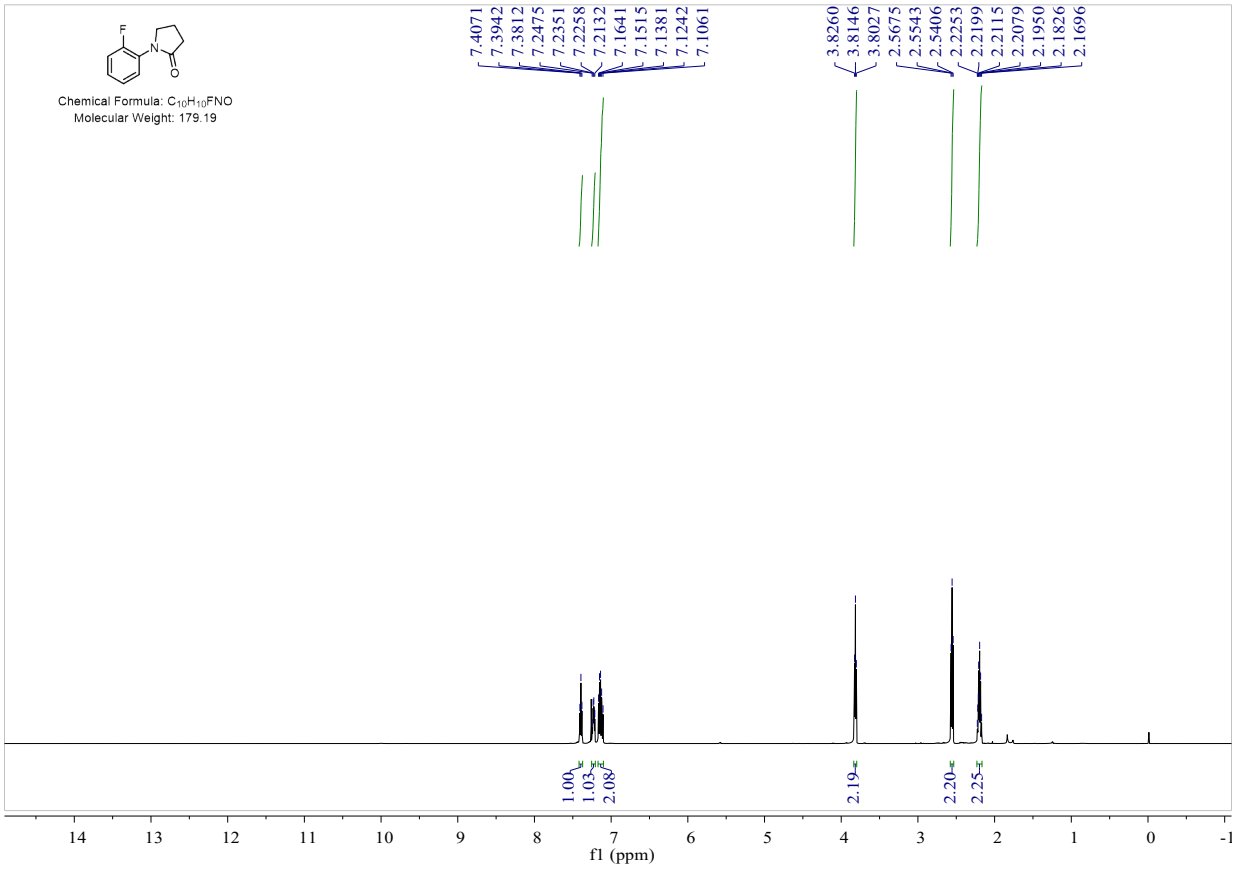
1-(3-Fluorophenyl)pyrrolidin-2-one (3ab).

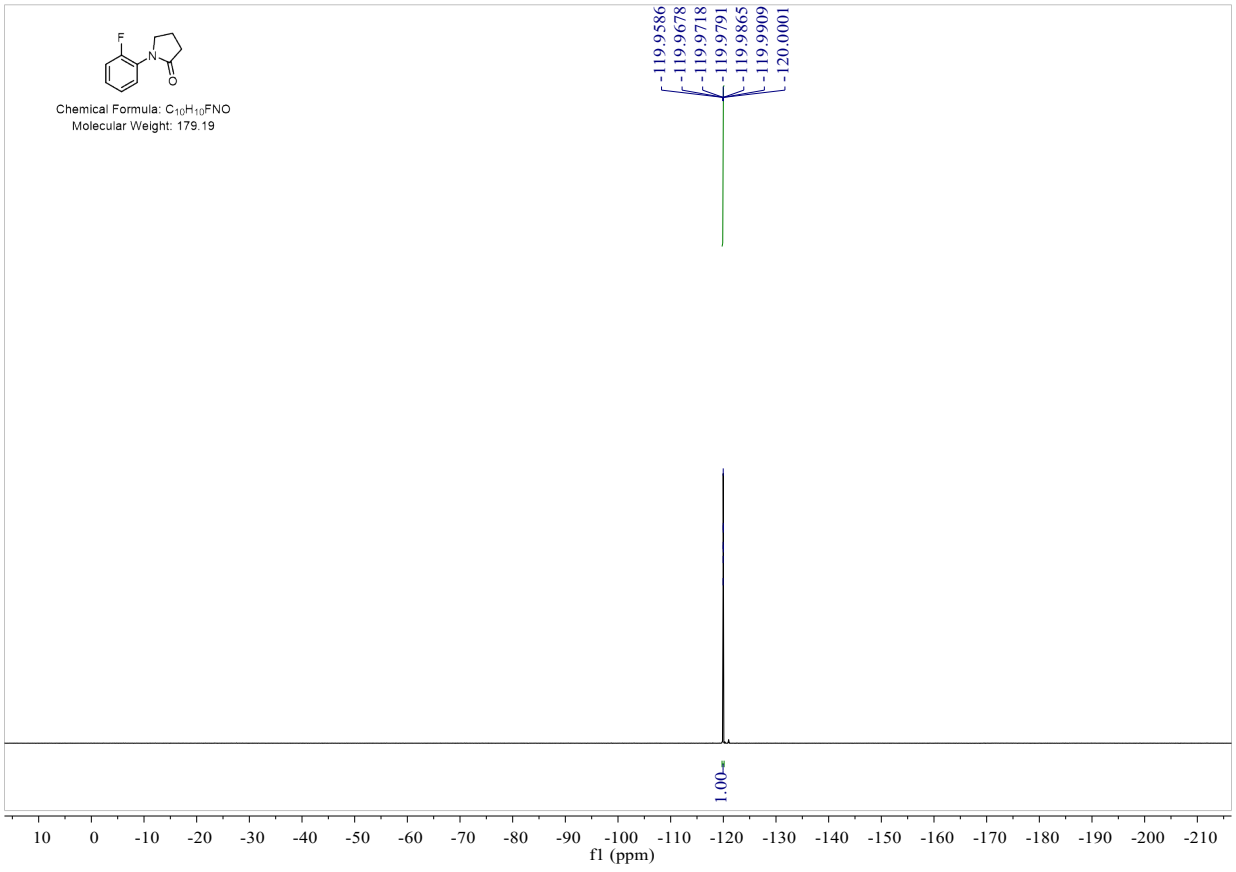


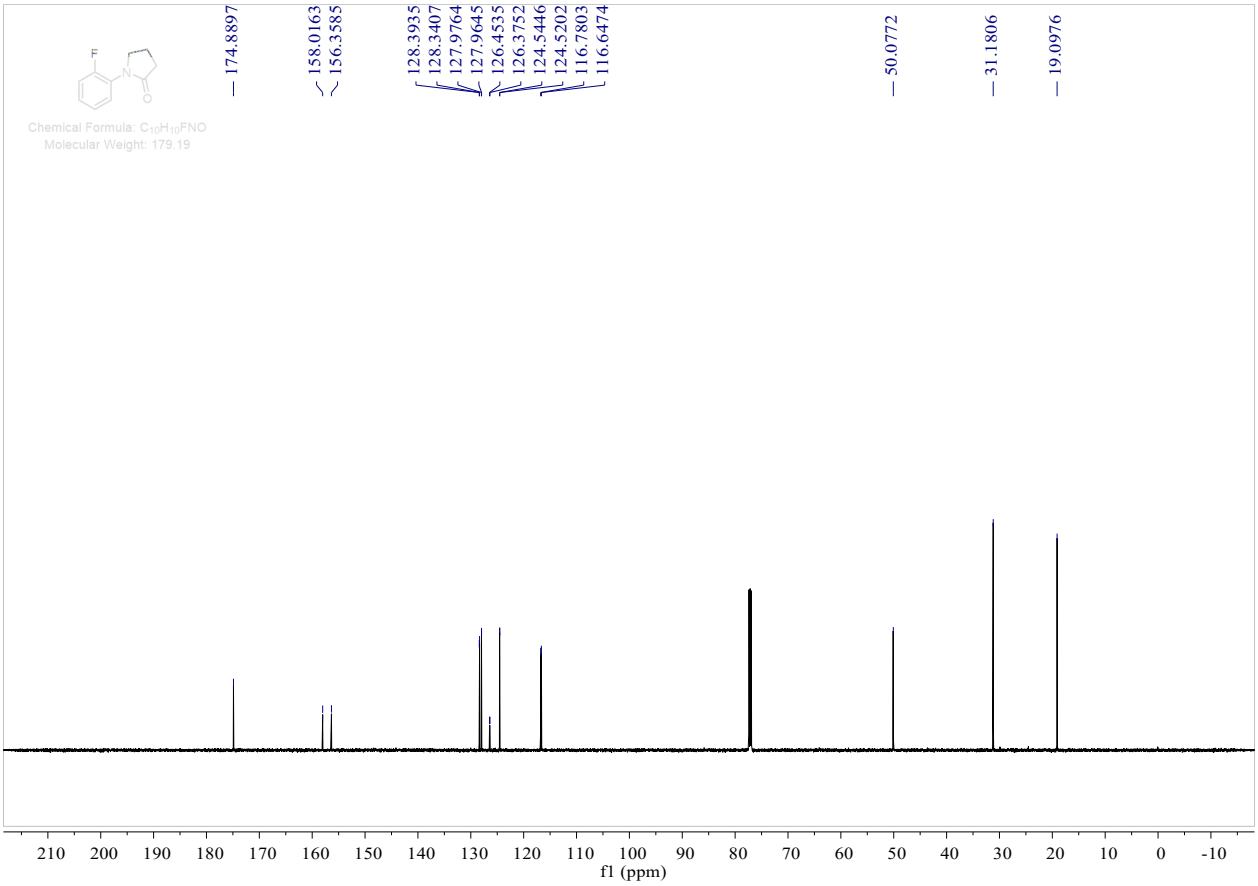

-111.5894
-111.5989
-111.6030
-111.6136
-111.6186
-111.6236
-111.6343
Chemical Formula: C10H10FNO
Molecular Weight: 179.19
1.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


174.4221
163.6501
162.0317
140.9945
140.9247
129.9121
129.8504
114.7151
114.6954
111.0370
110.8962
107.1772
107.0035
48.6315
32.8099
17.7946
Chemical Formula: C10H10FNO
Molecular Weight: 179.19
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

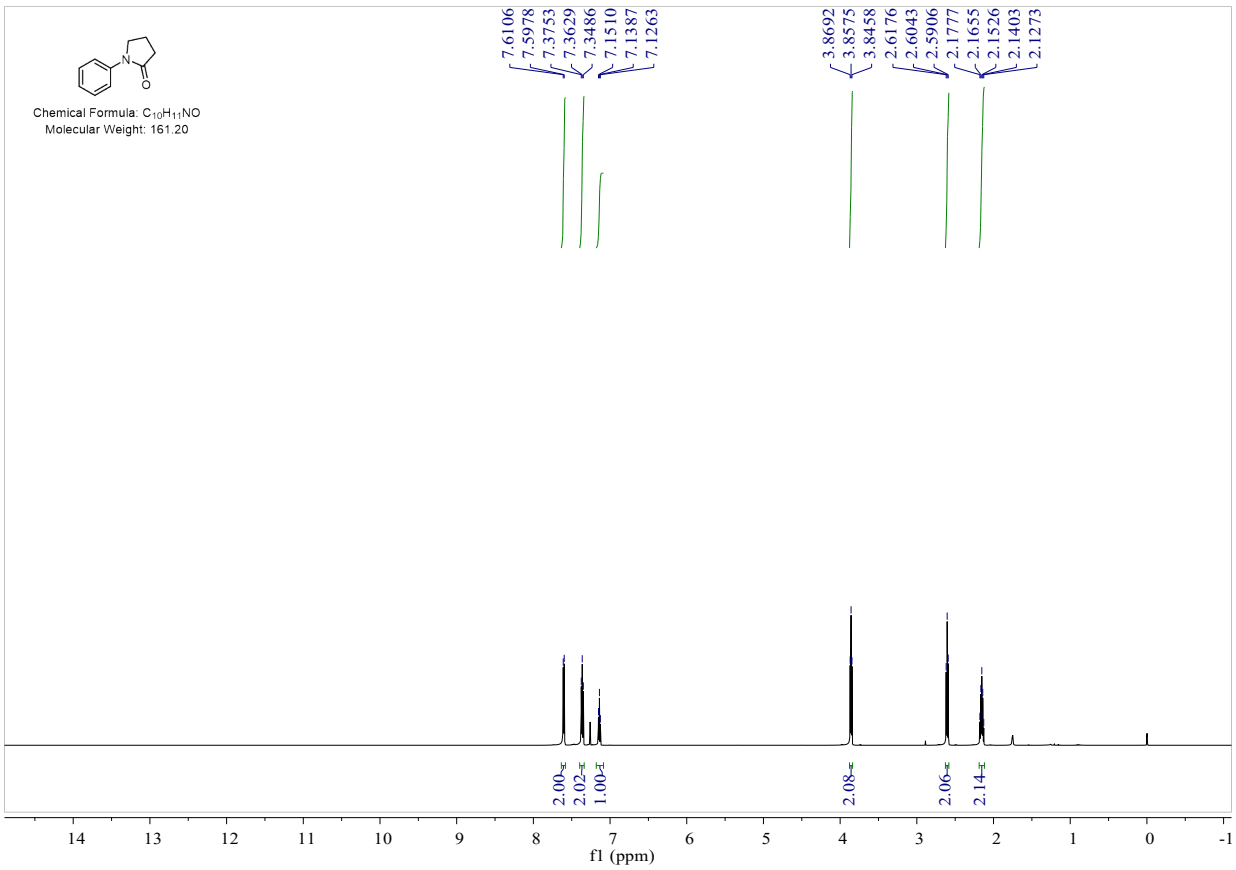
1-(2-Fluorophenyl)pyrrolidin-2-one (3ac).

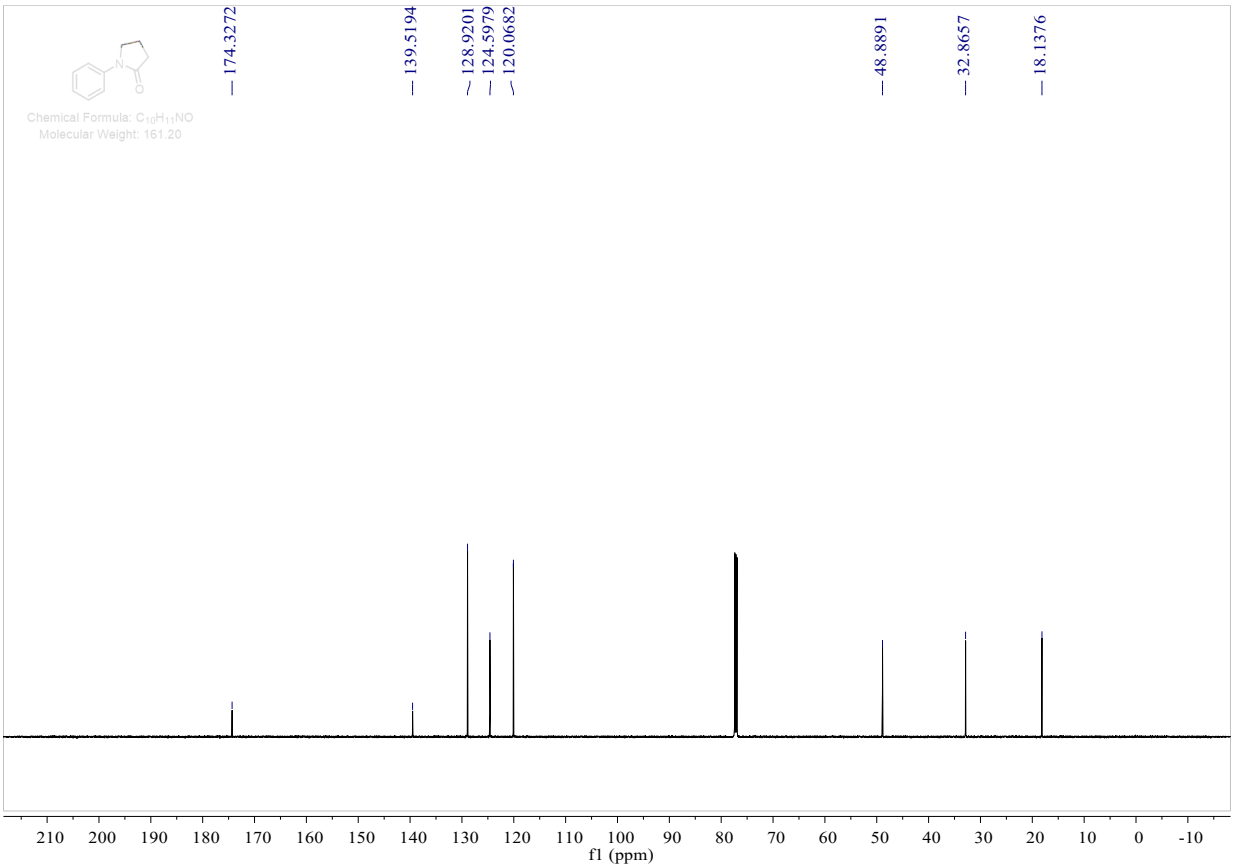




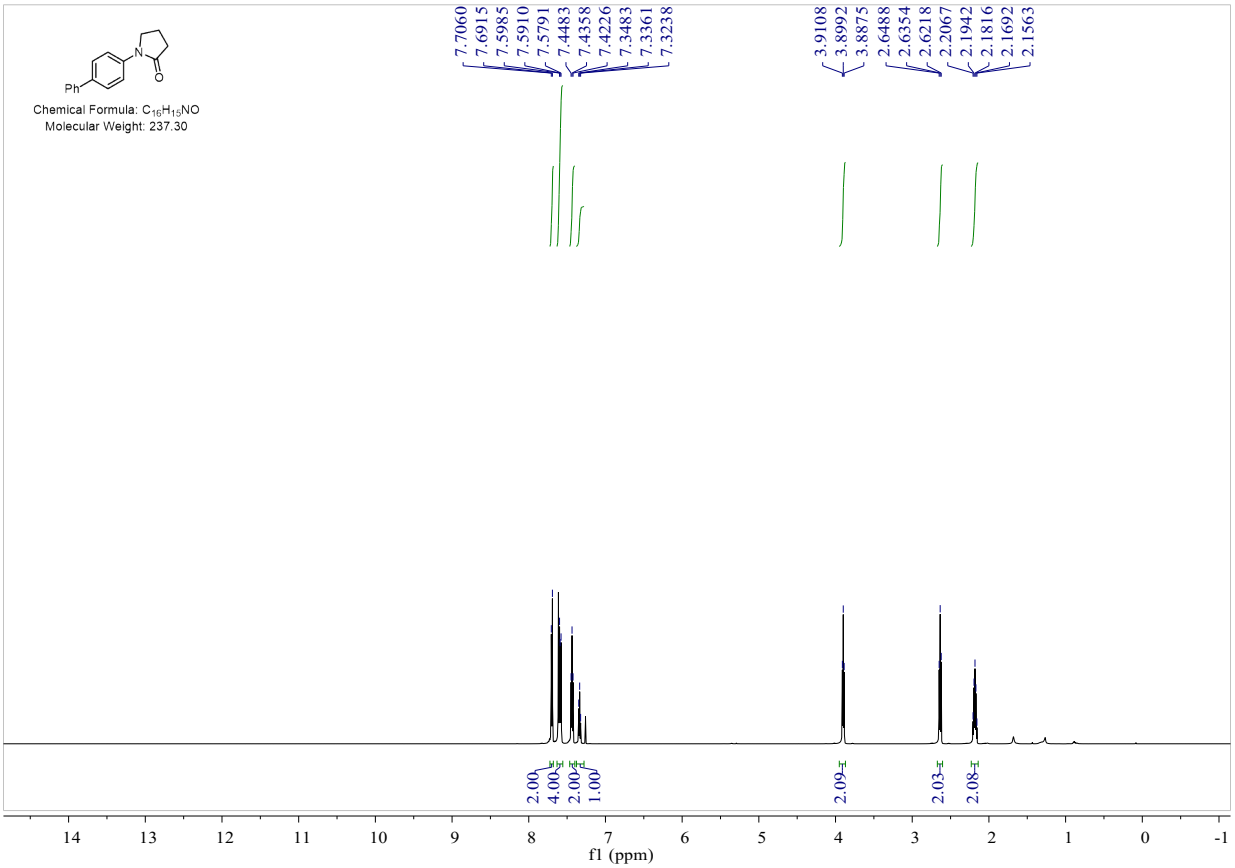


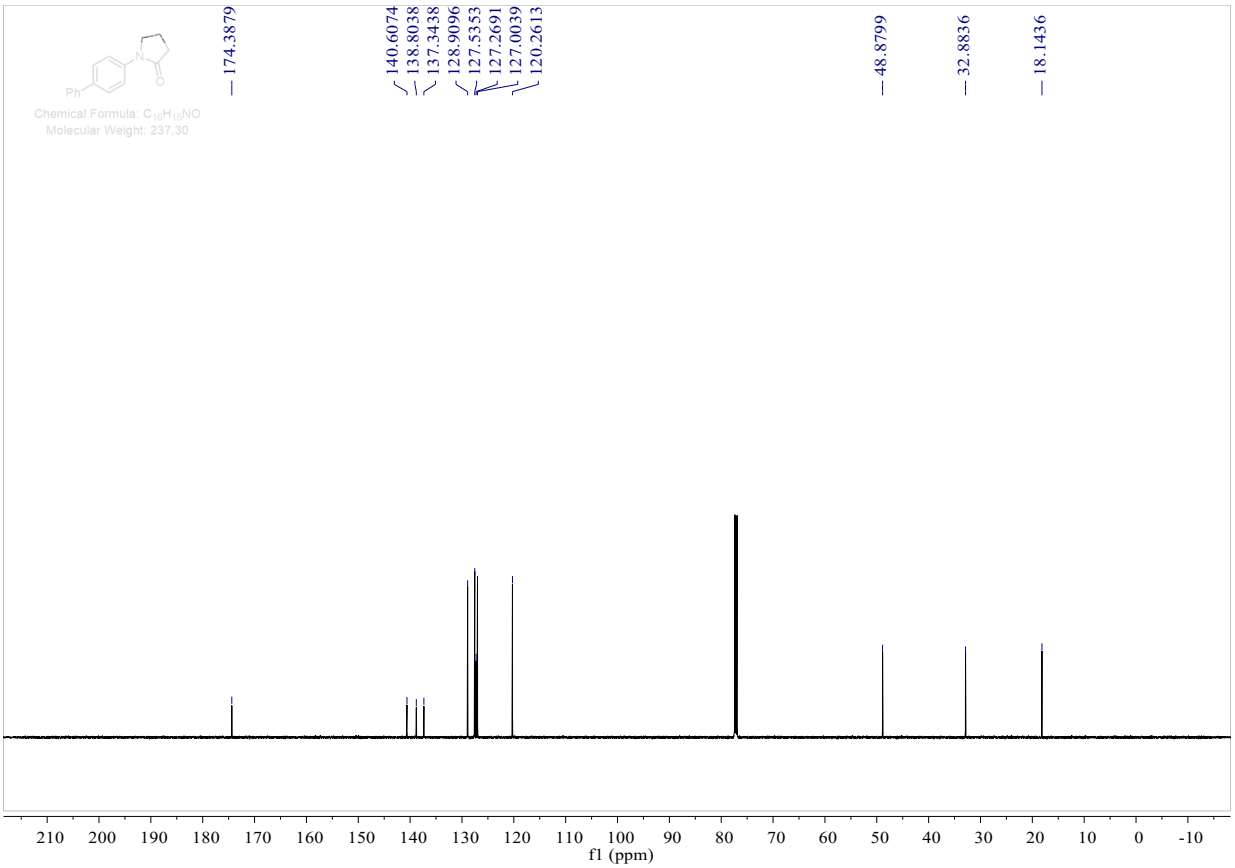
1-Phenylpyrrolidin-2-one (3b).



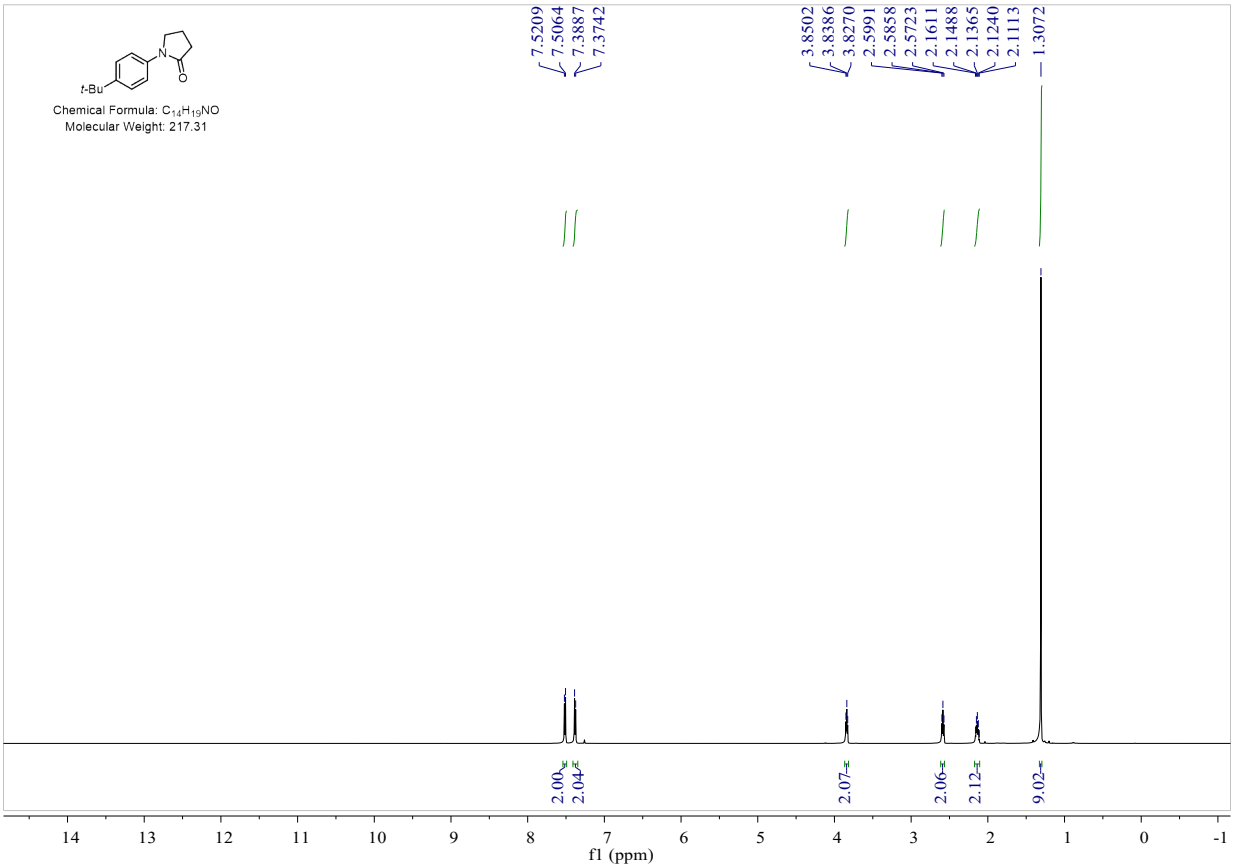


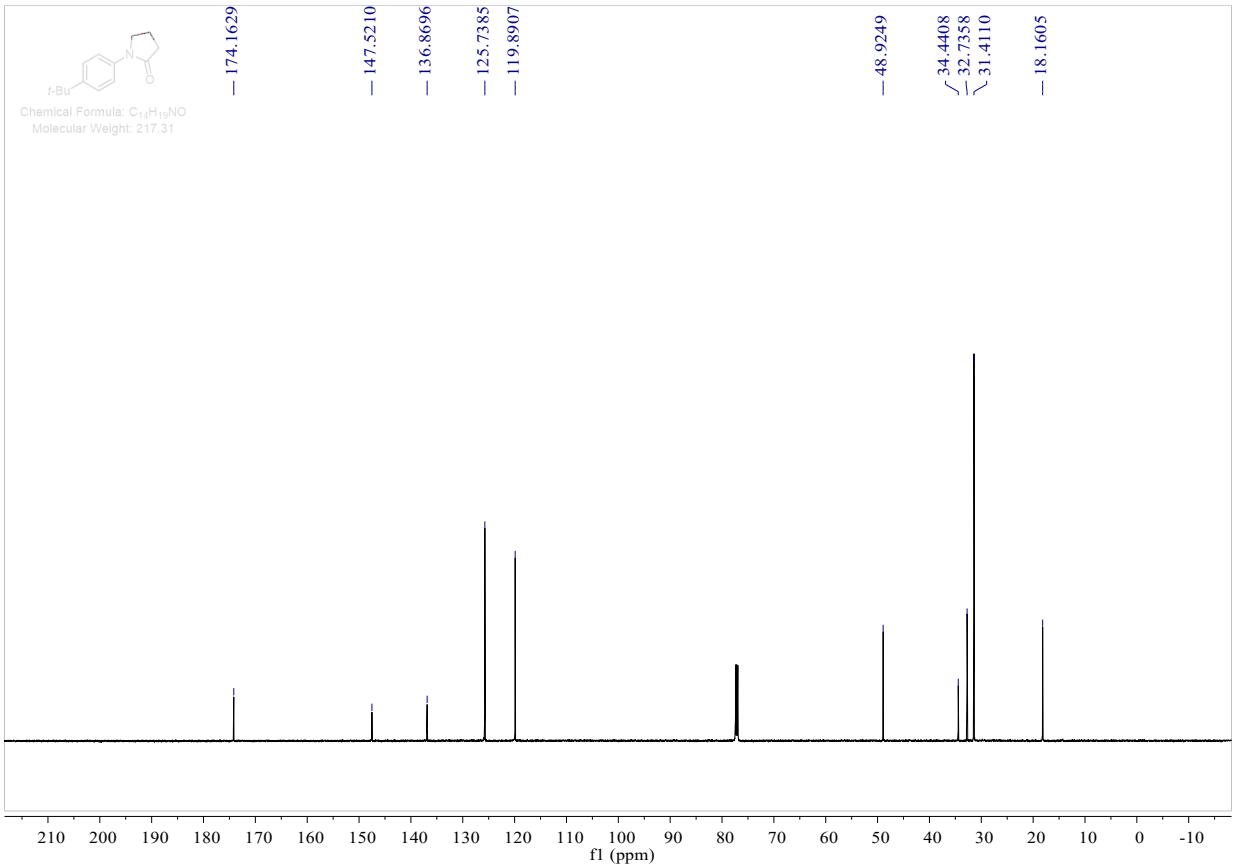
1-([1,1'-Biphenyl]-4-yl)pyrrolidin-2-one (3c).



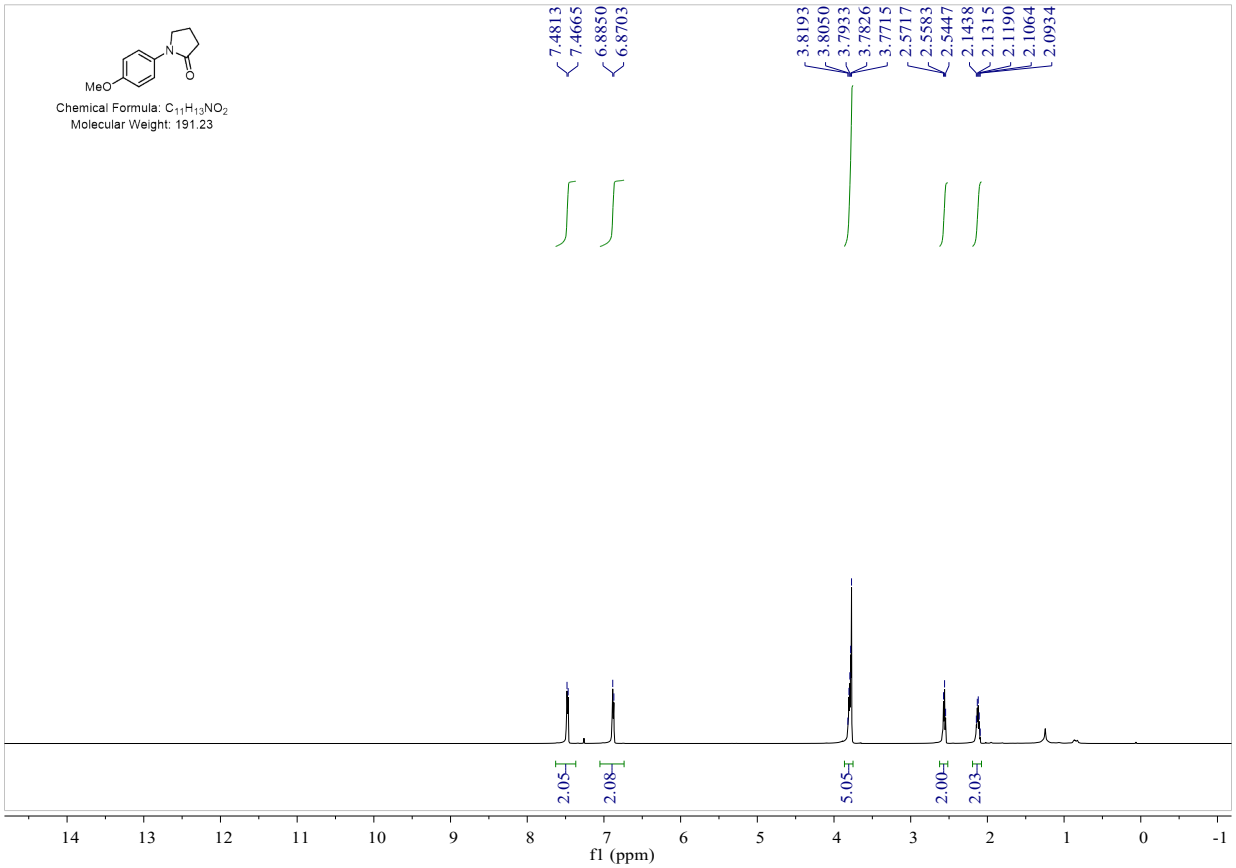


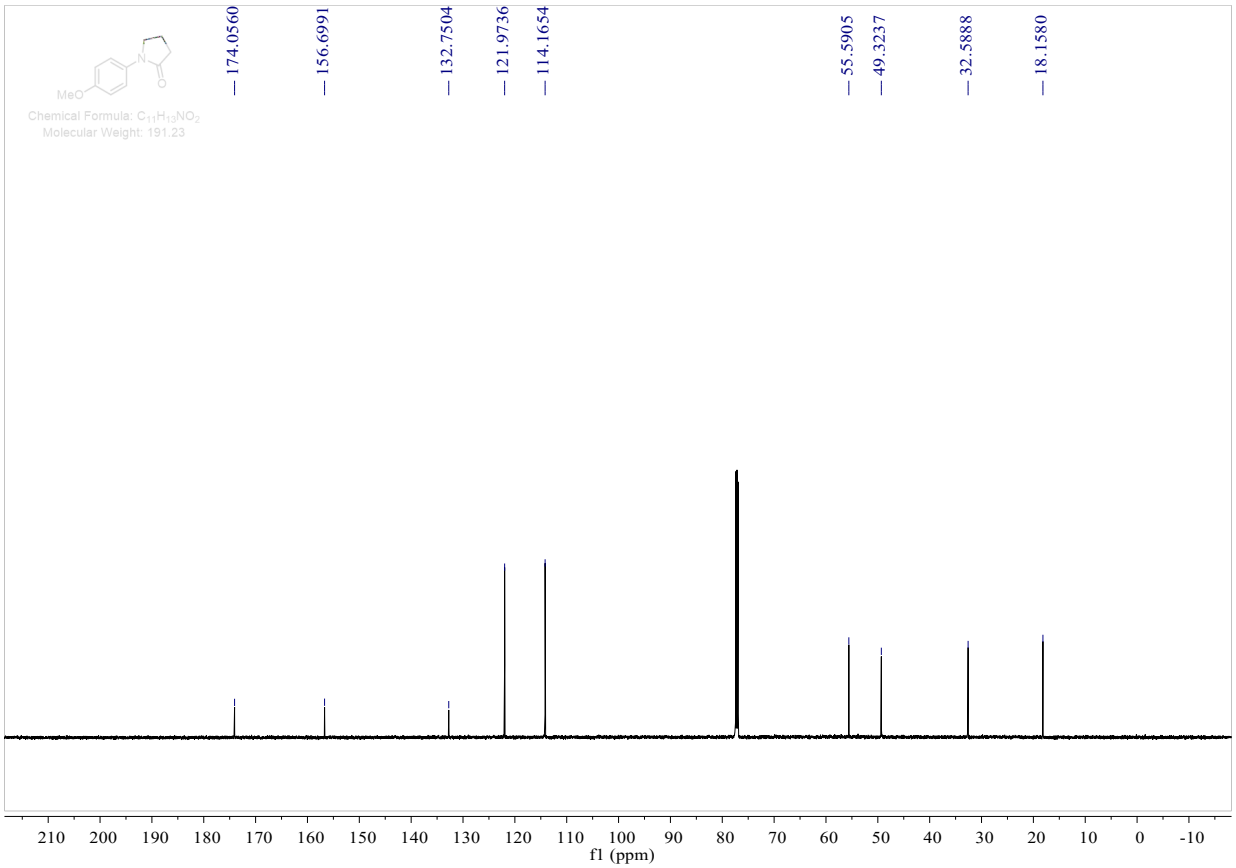
1-(4-(*Tert*-butyl)phenyl)pyrrolidin-2-one (3d).



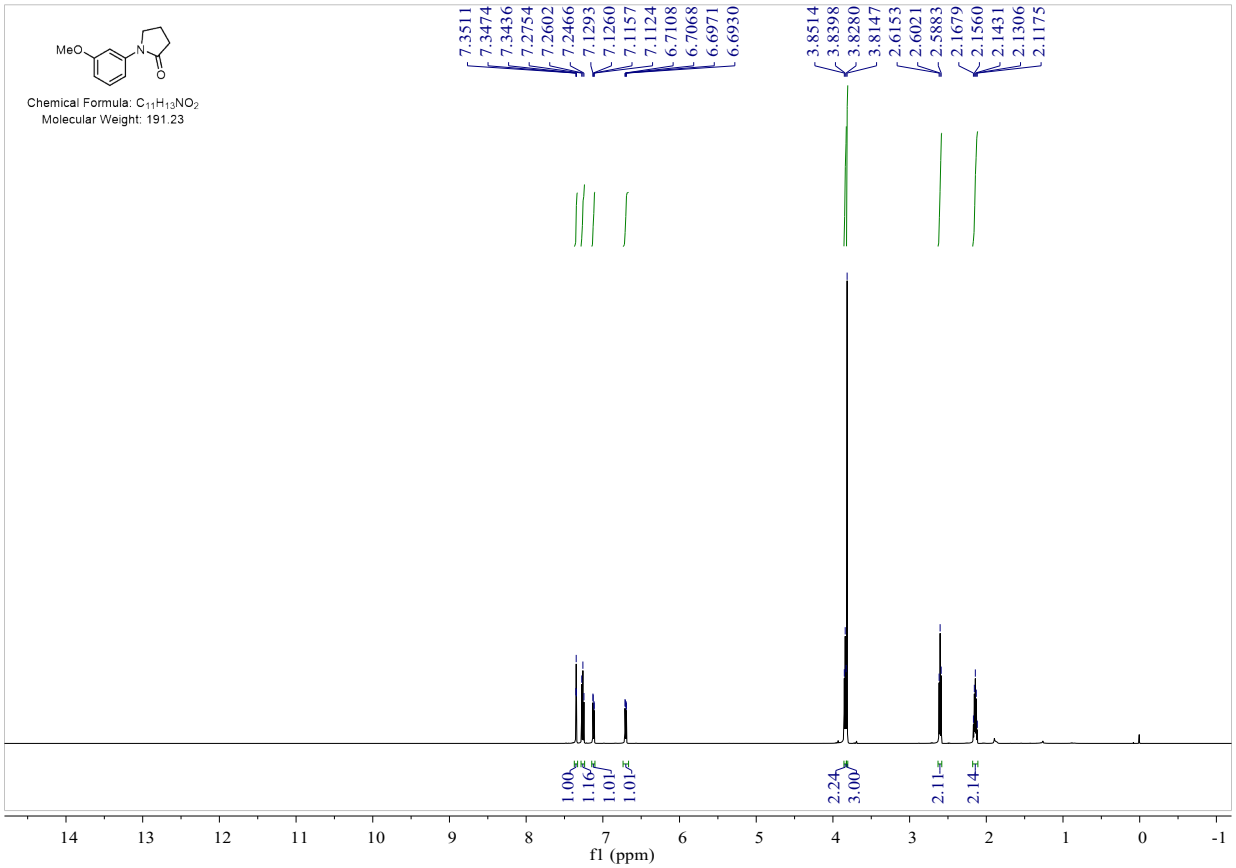


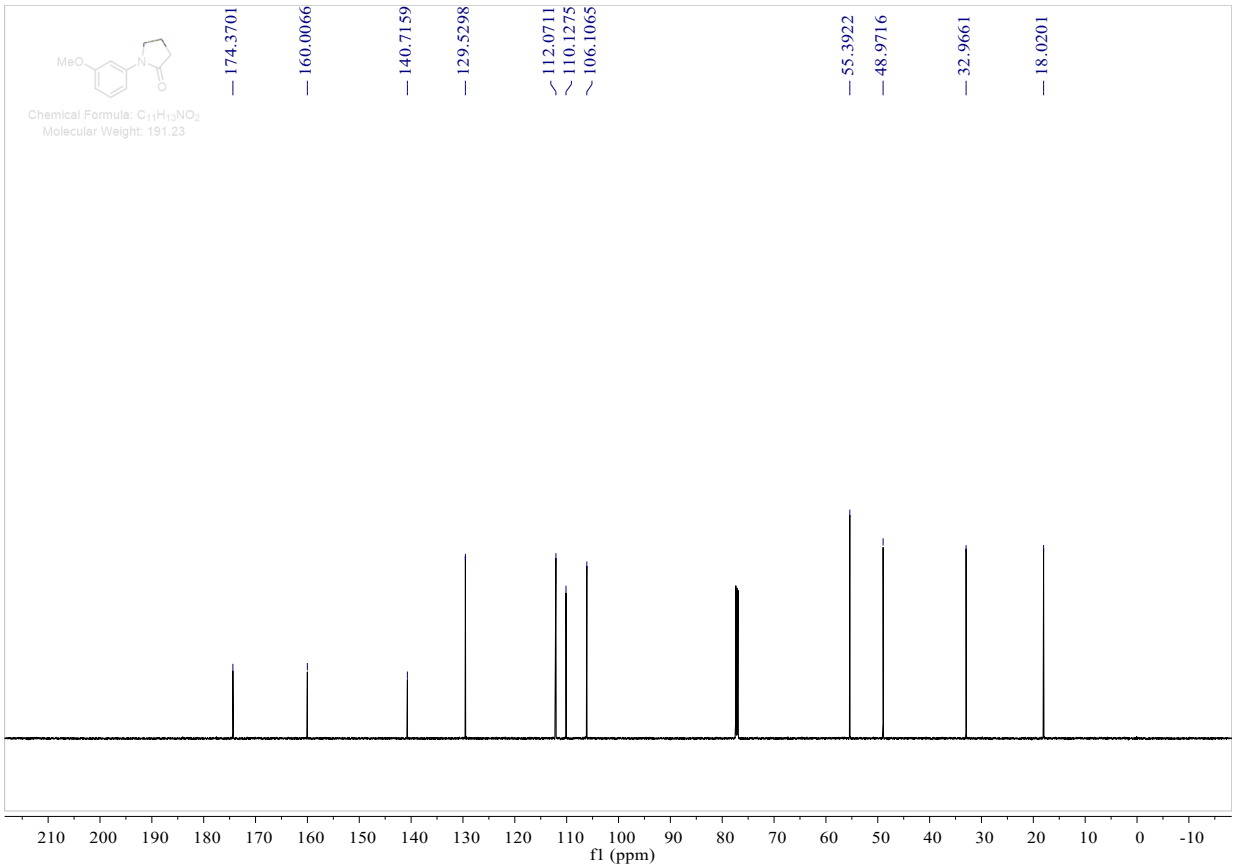
1-(4-Methoxyphenyl)pyrrolidin-2-one (3e).



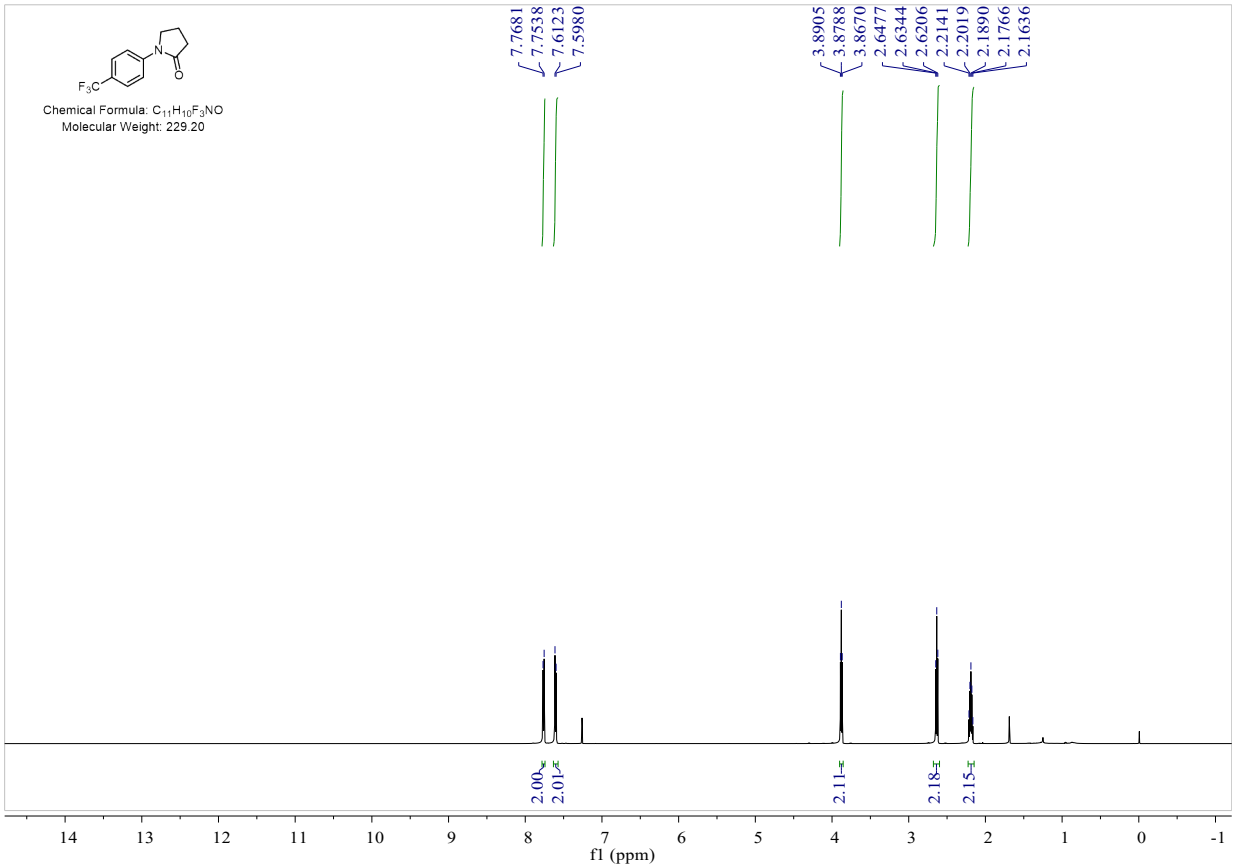


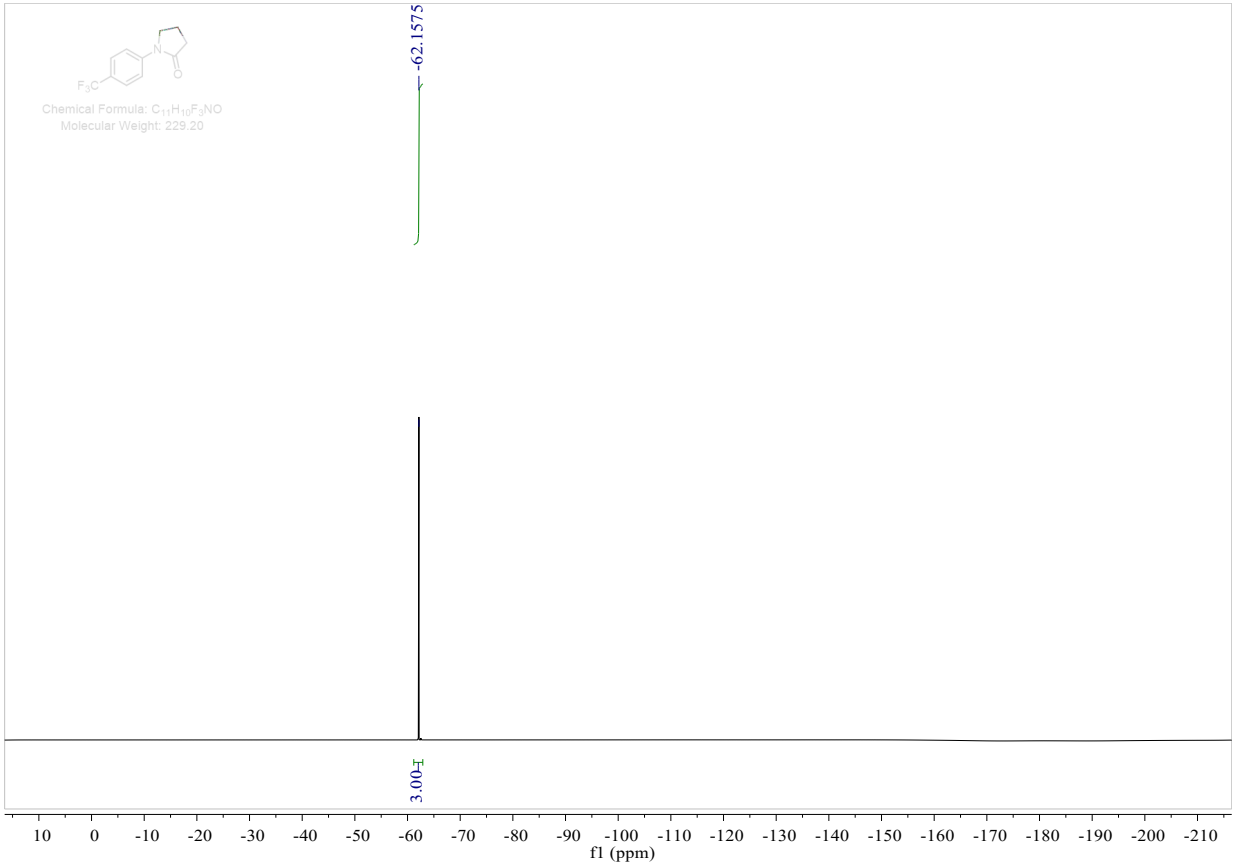
1-(3-Methoxyphenyl)pyrrolidin-2-one (3f).





1-(4-(Trifluoromethyl)phenyl)pyrrolidin-2-one (3g).

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3.00
Chemical Formula: C11H10F3NO
Molecular Weight: 229.20
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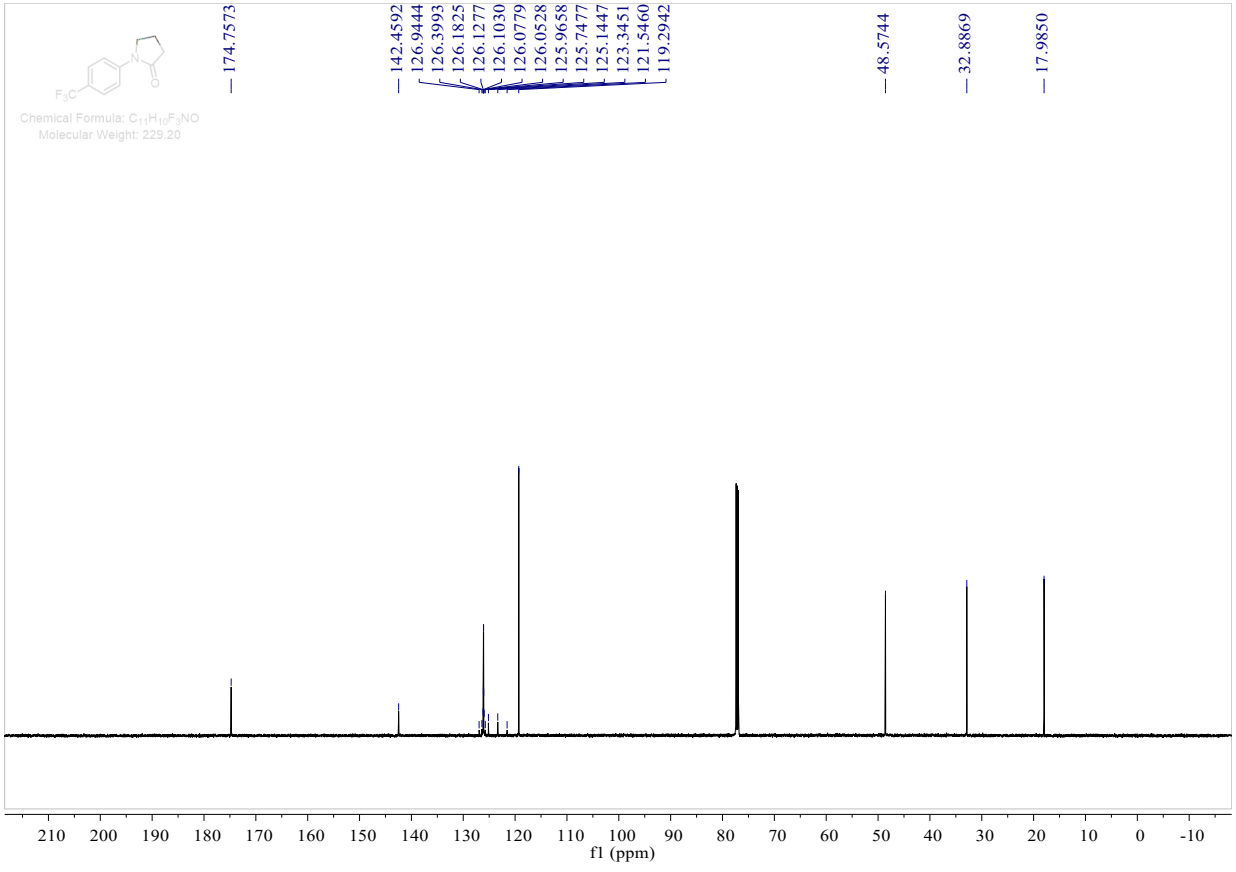
f1 (ppm)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126.0779
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125.1447
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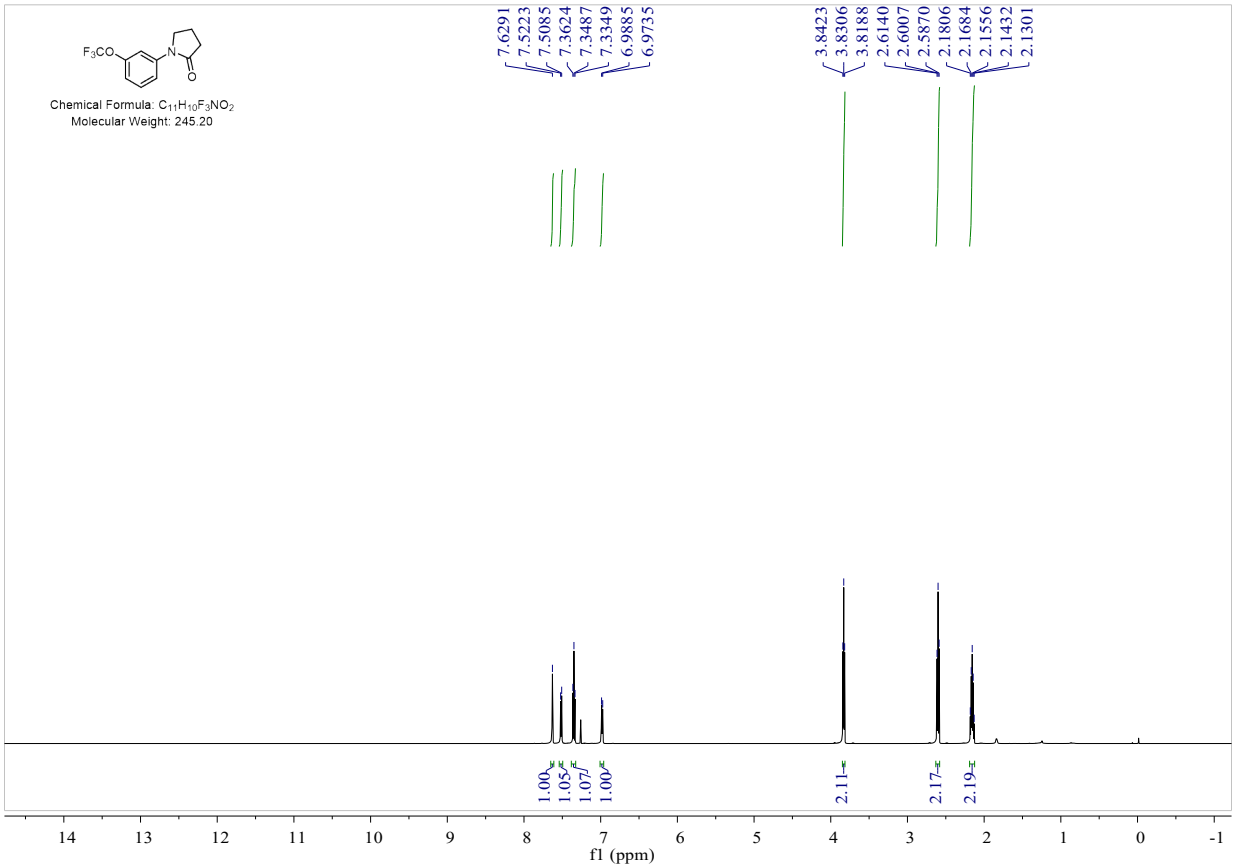
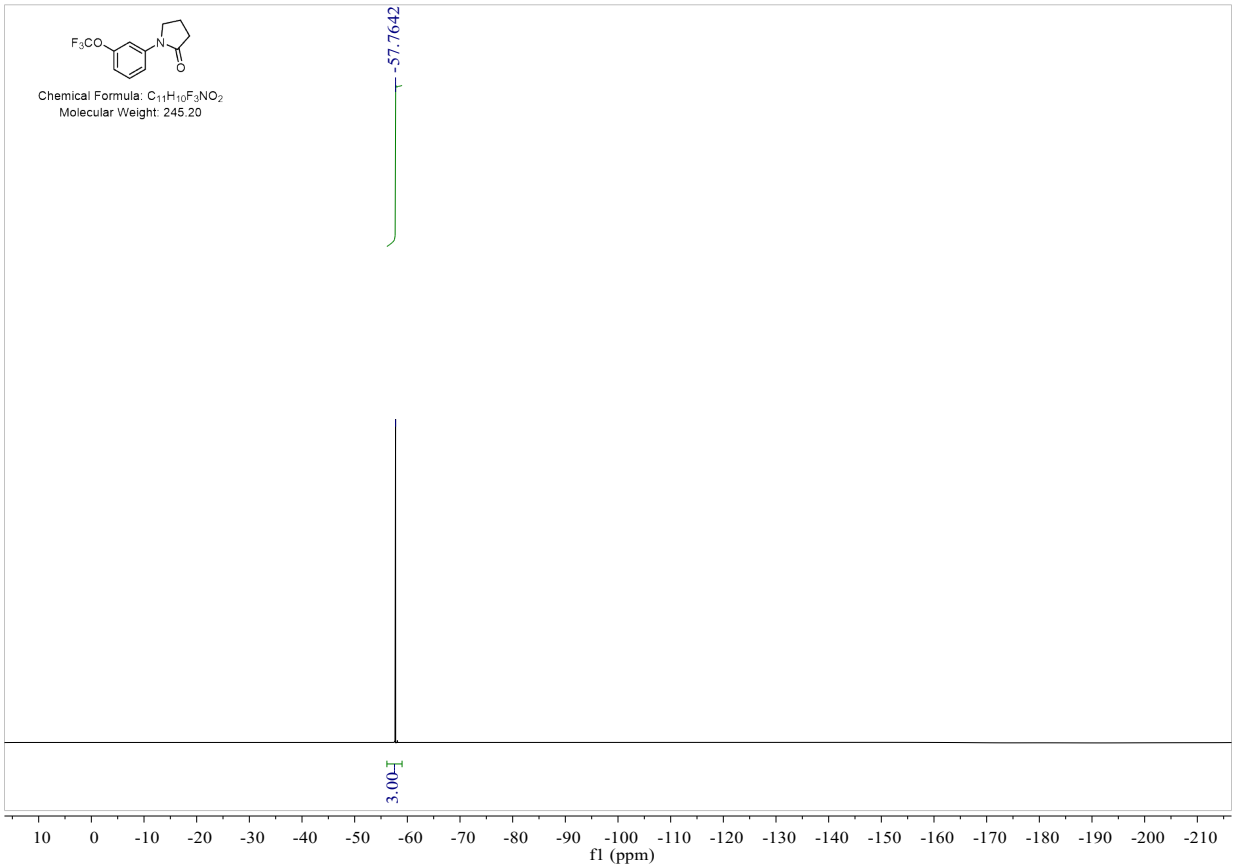
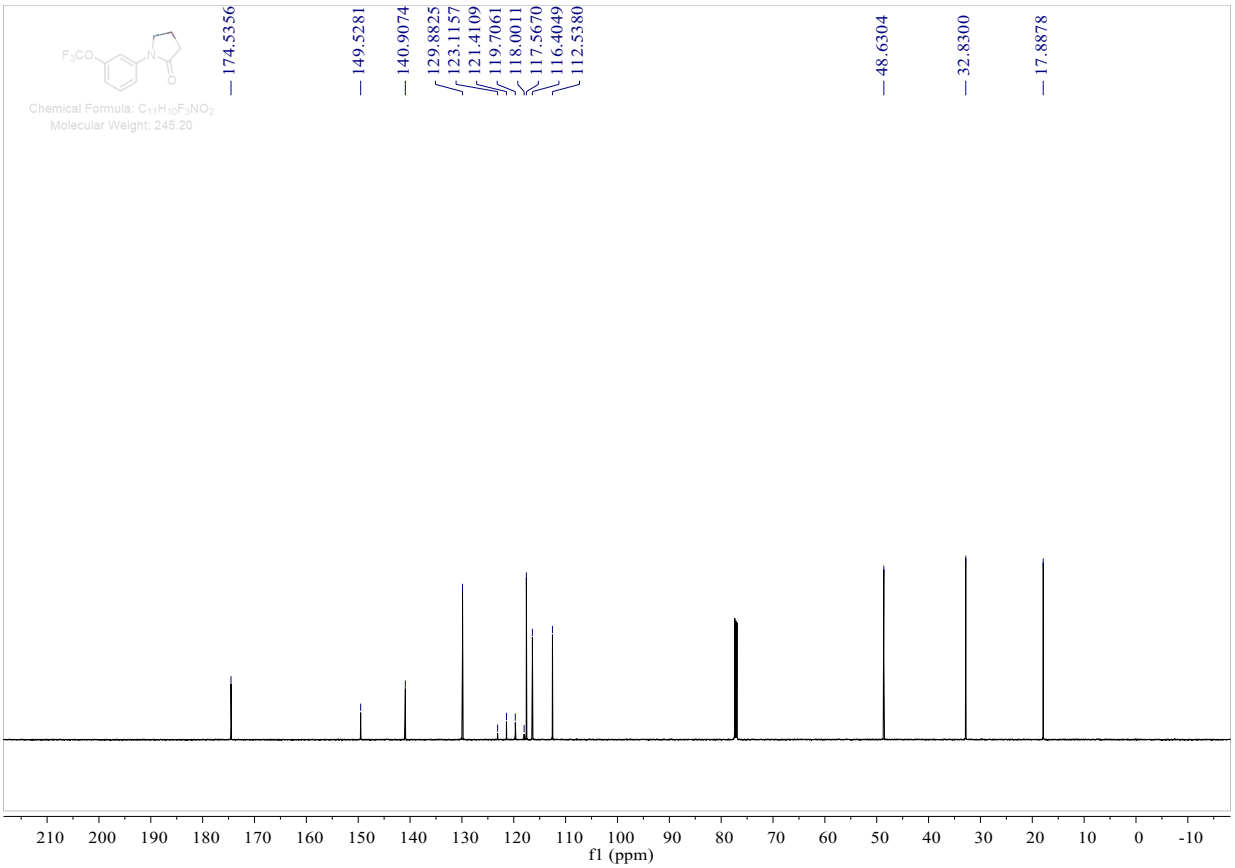
121.5460
119.2942
48.5744
32.8869
17.9850
Chemical Formula: C11H10F3NO
Molecular Weight: 229.20
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

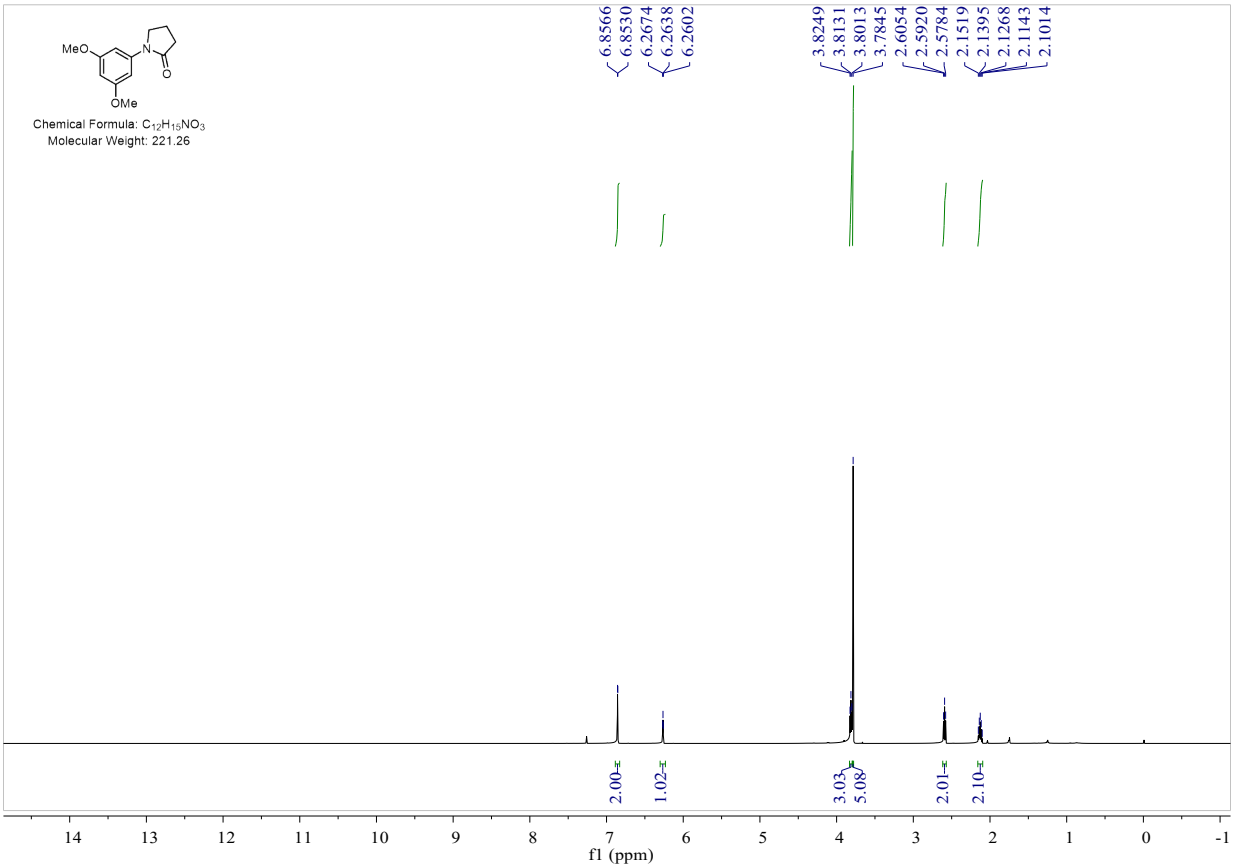
1-(3-(Trifluoromethoxy)phenyl)pyrrolidin-2-one (3h).

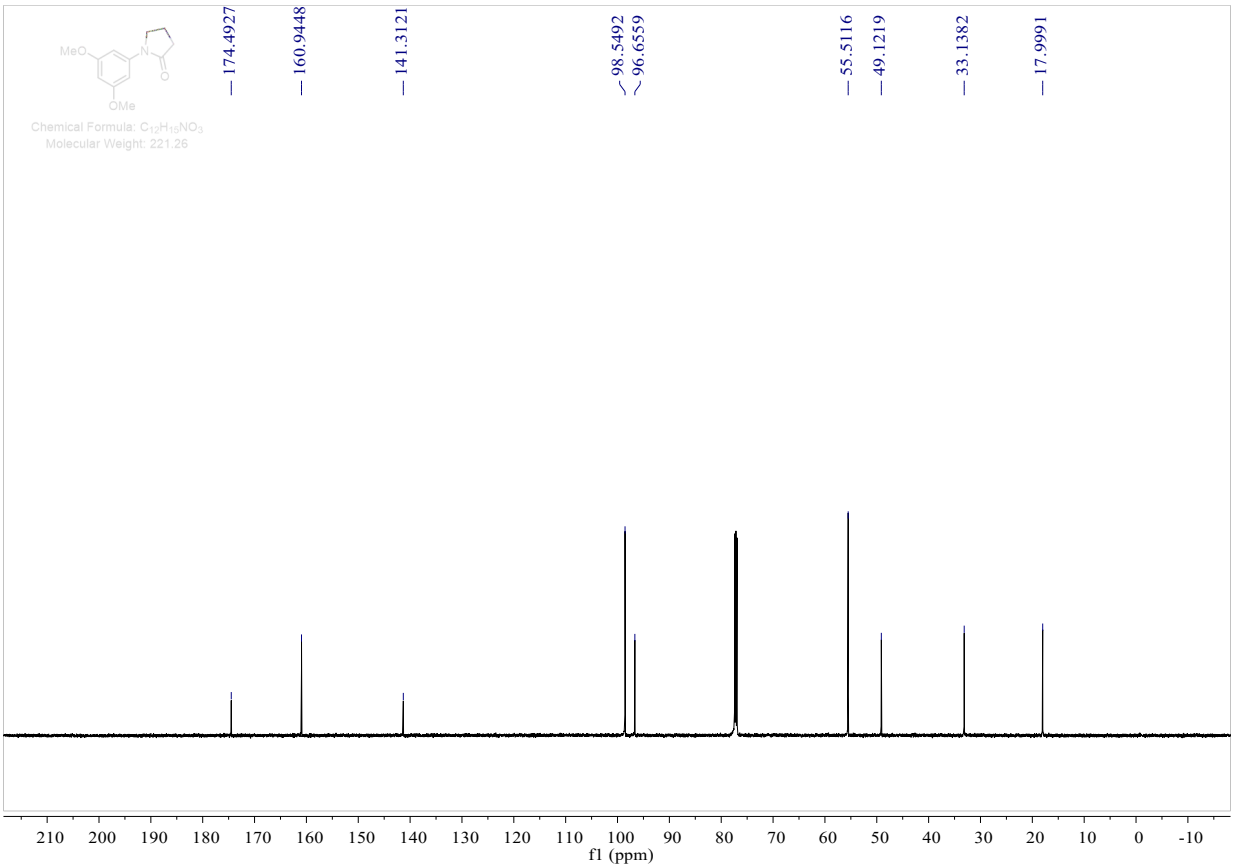




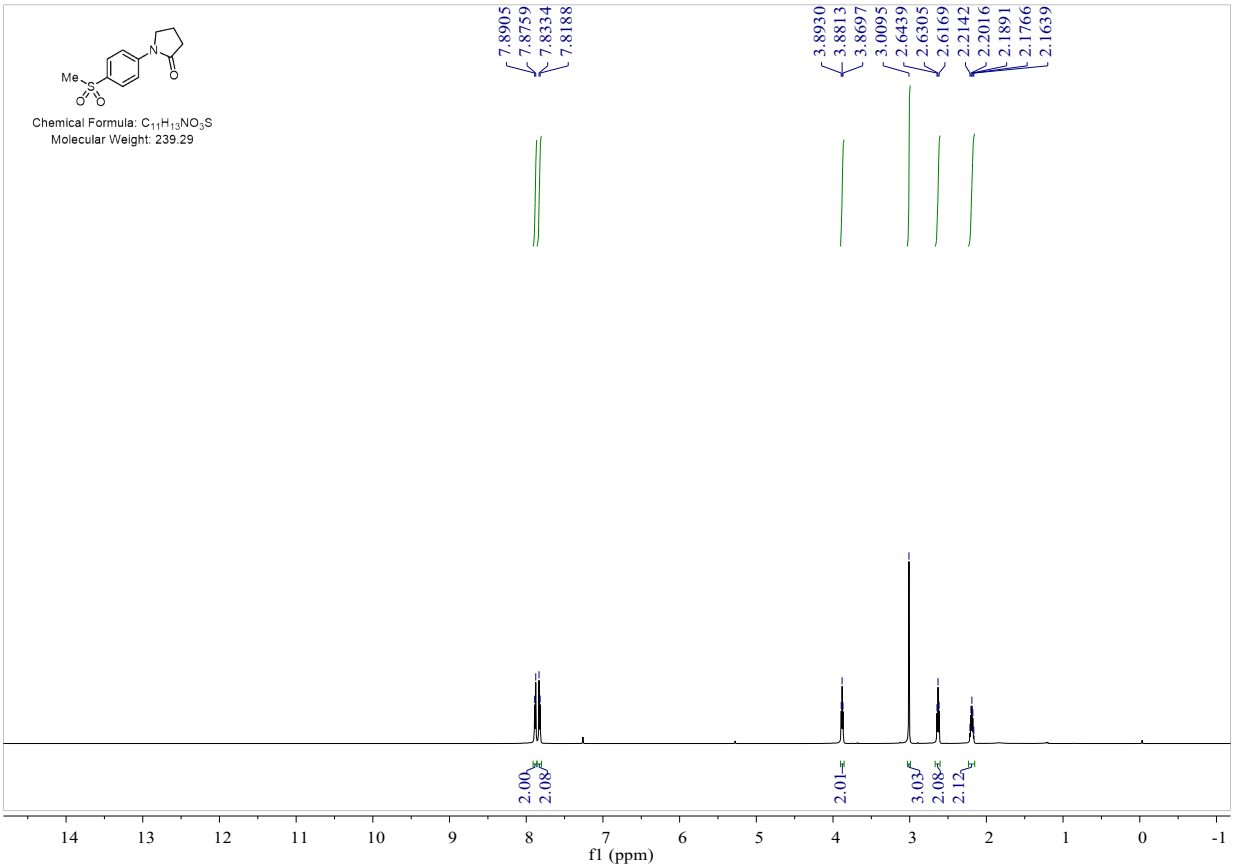


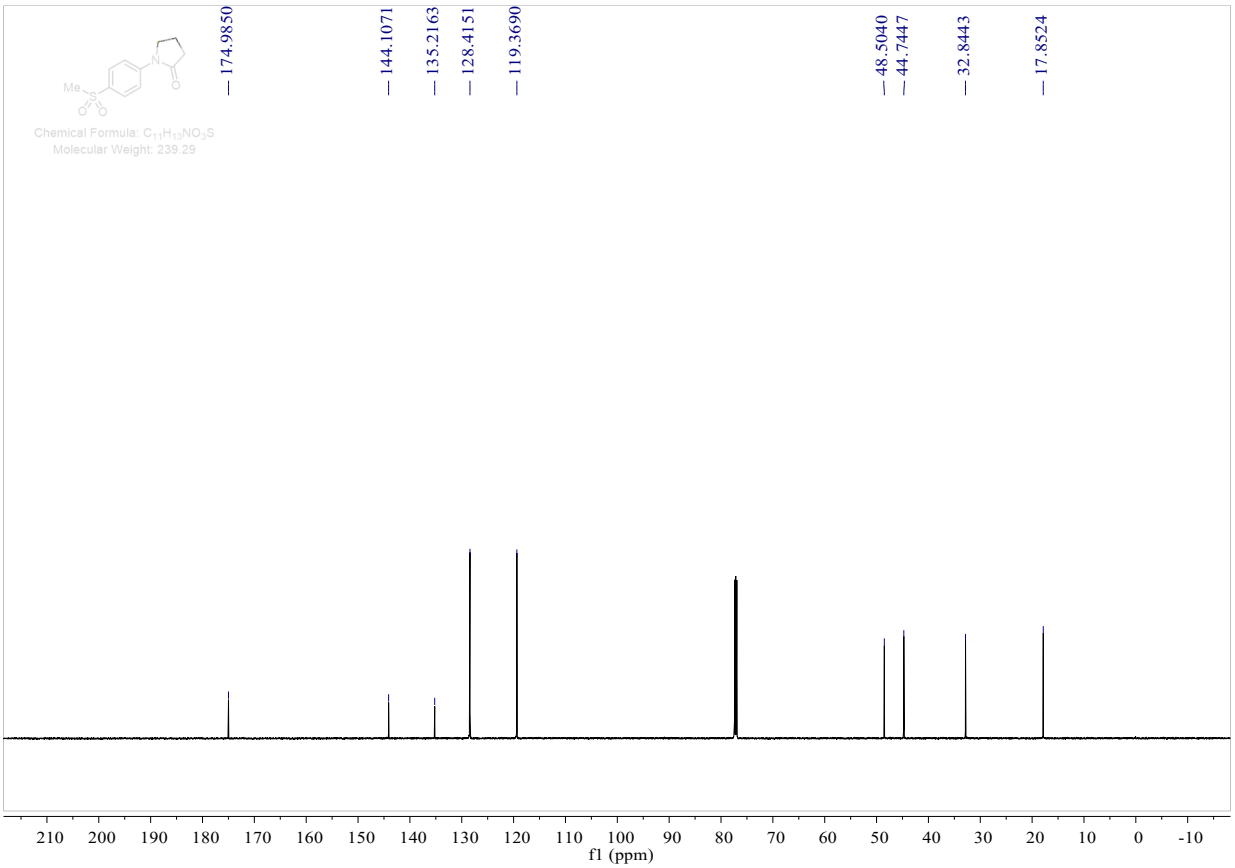
1-(3,5-Dimethoxyphenyl)pyrrolidin-2-one (3i).



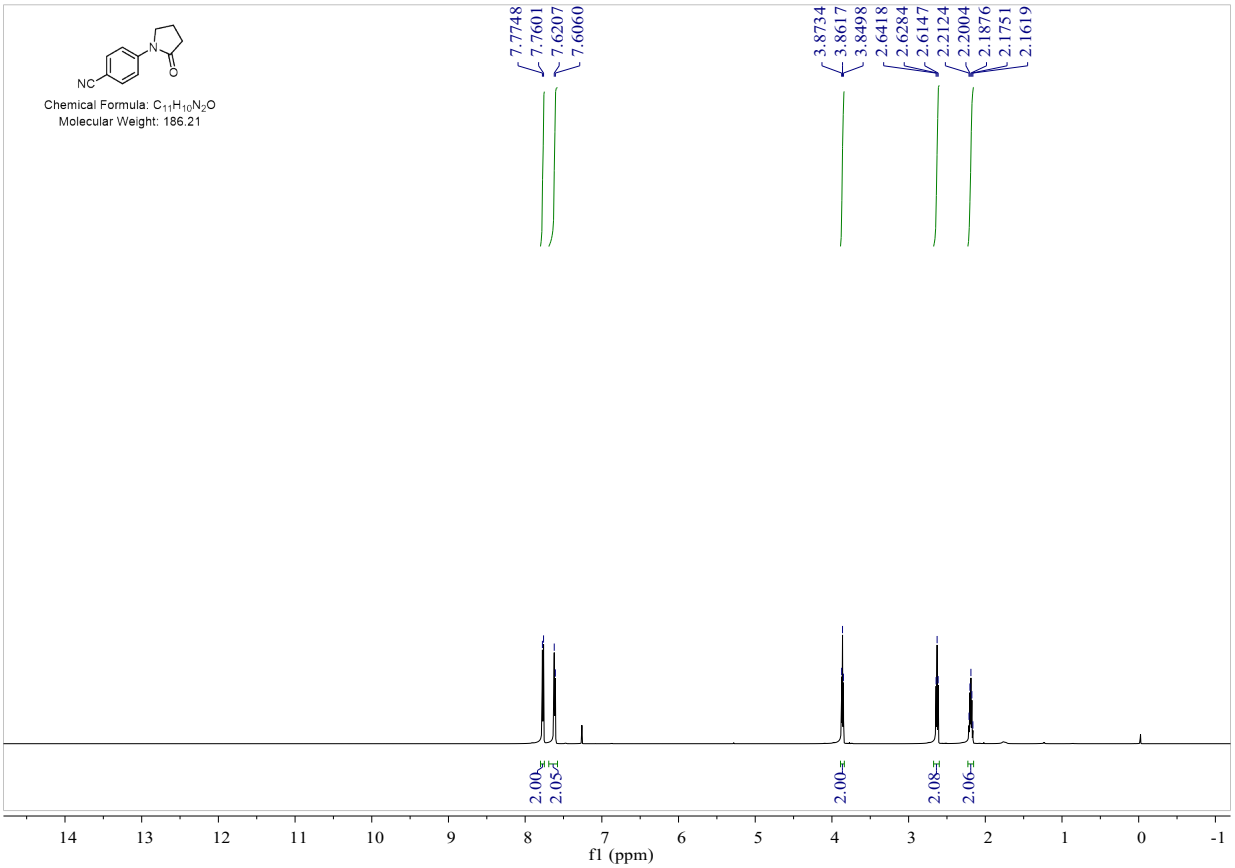


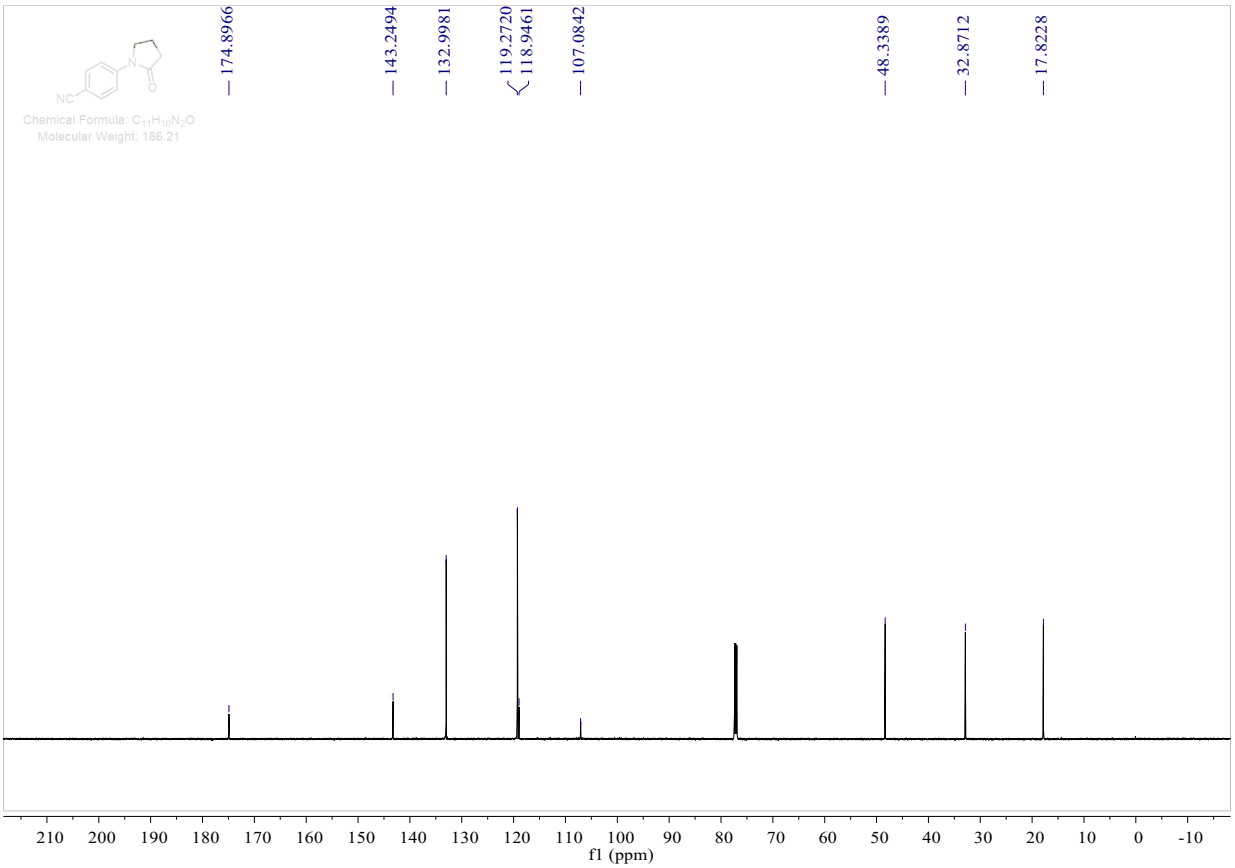
1-(4-(Methylsulfonyl)phenyl)pyrrolidin-2-one (3j).



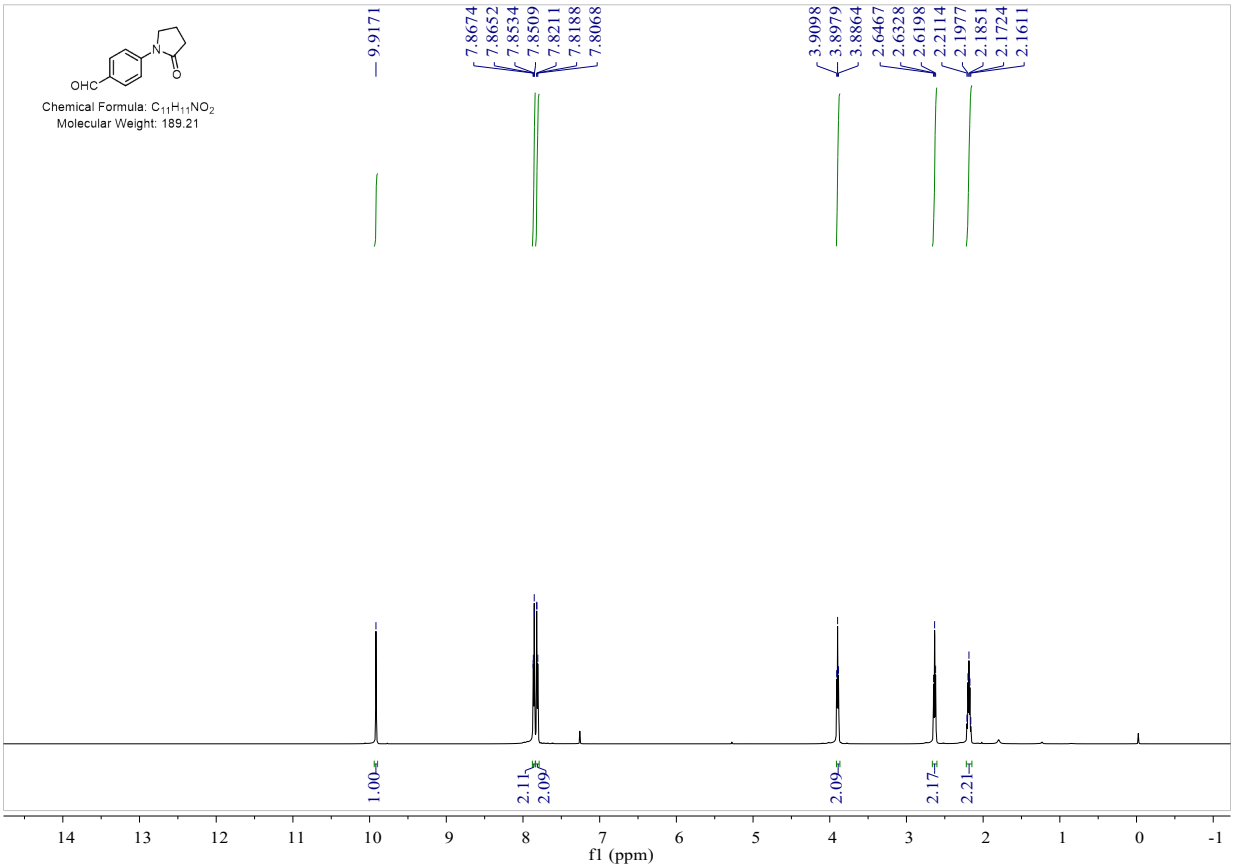


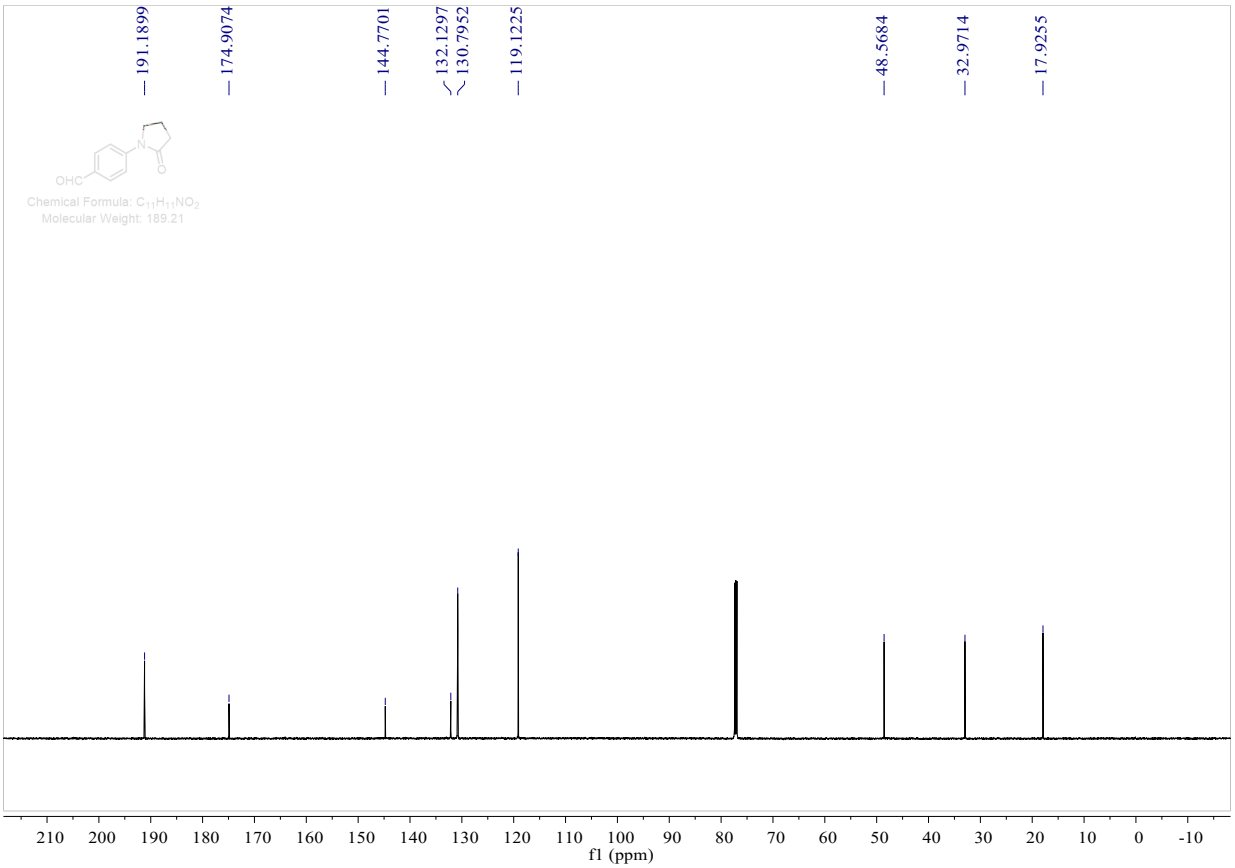
4-(2-Oxopyrrolidin-1-yl)benzonitrile (3k).



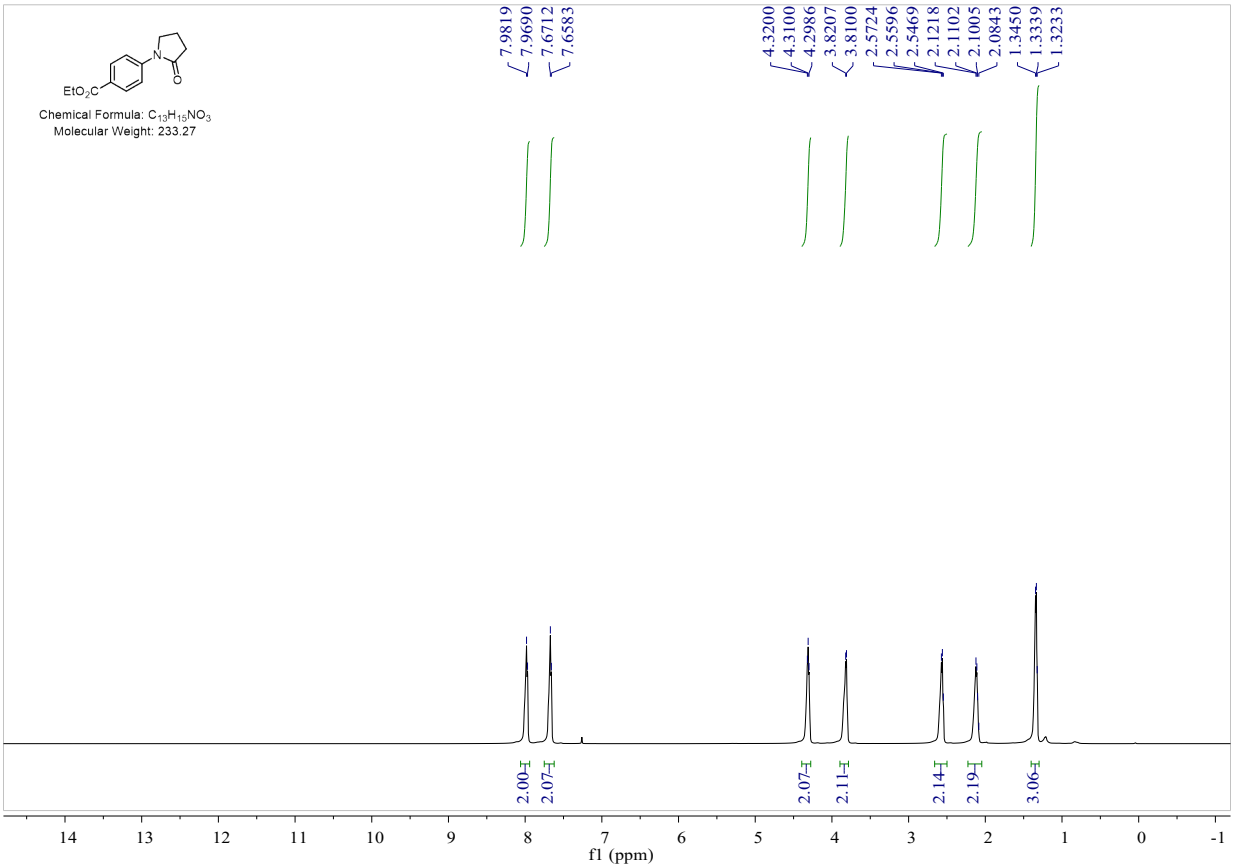


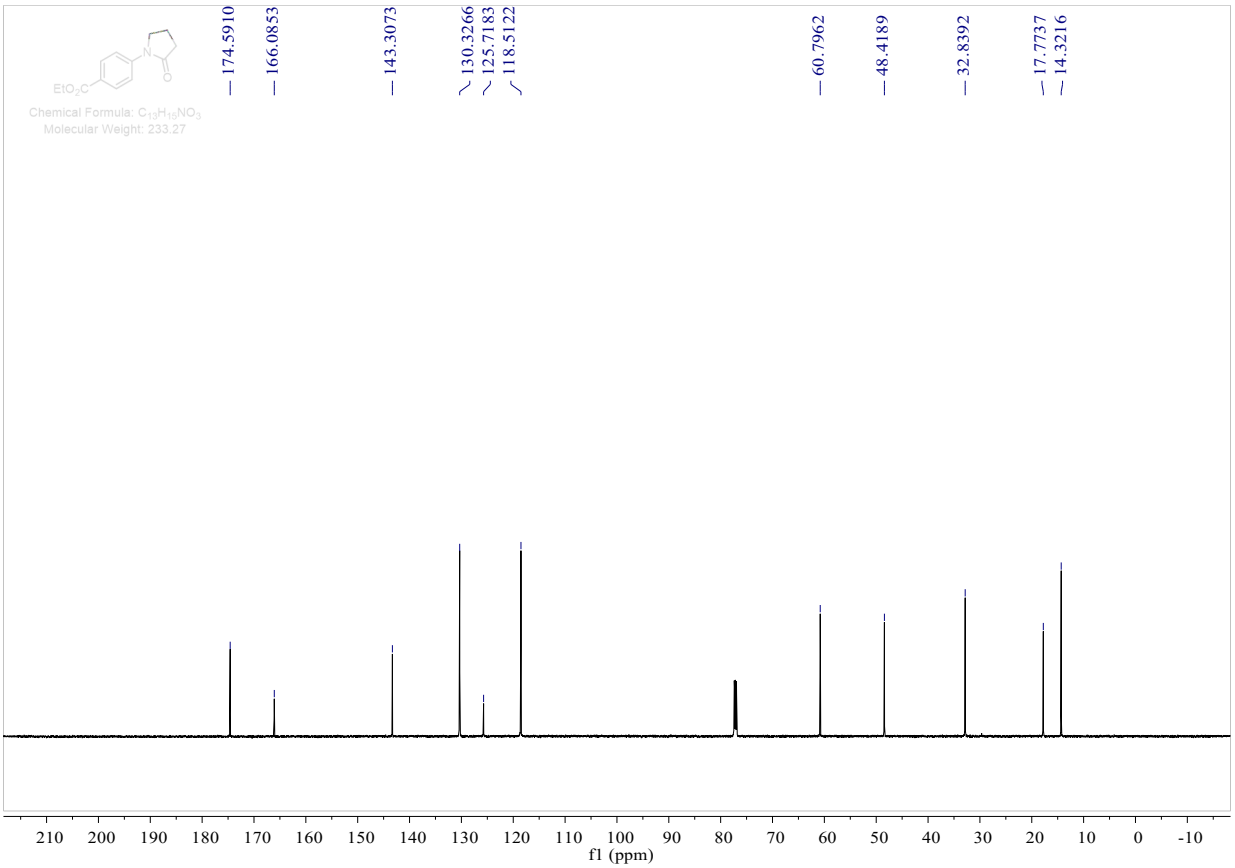
4-(2-Oxopyrrolidin-1-yl)benzaldehyde (3l).



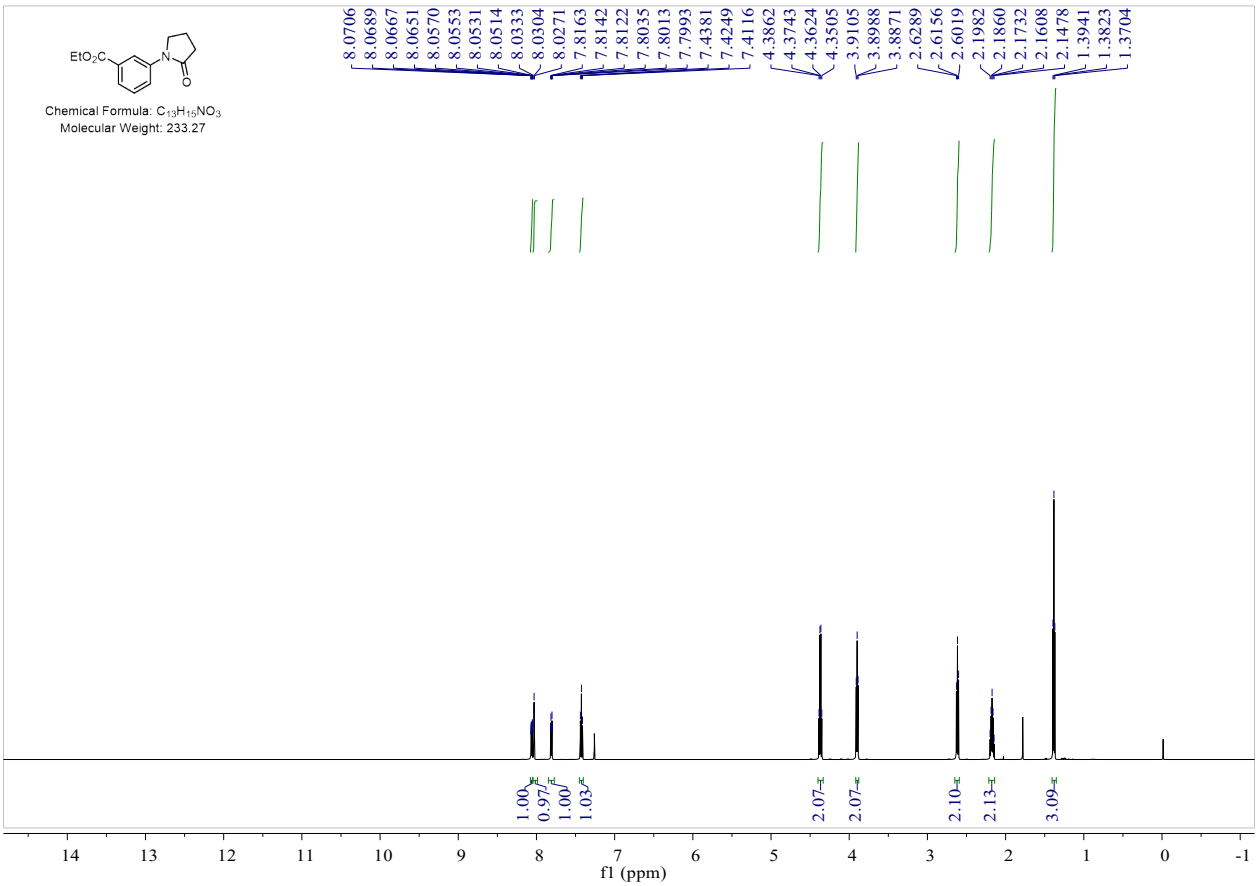


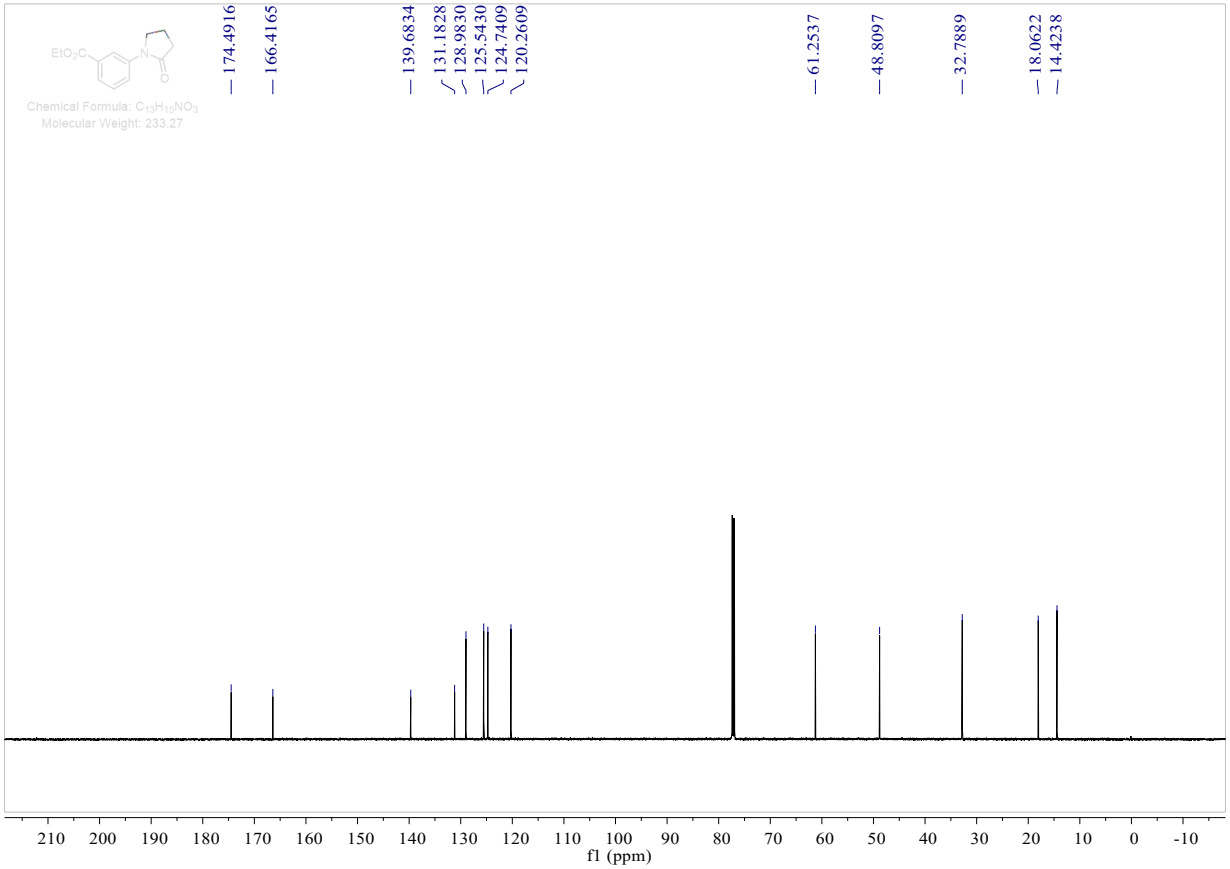
Ethyl 4-(2-oxopyrrolidin-1-yl)benzoate (3m).



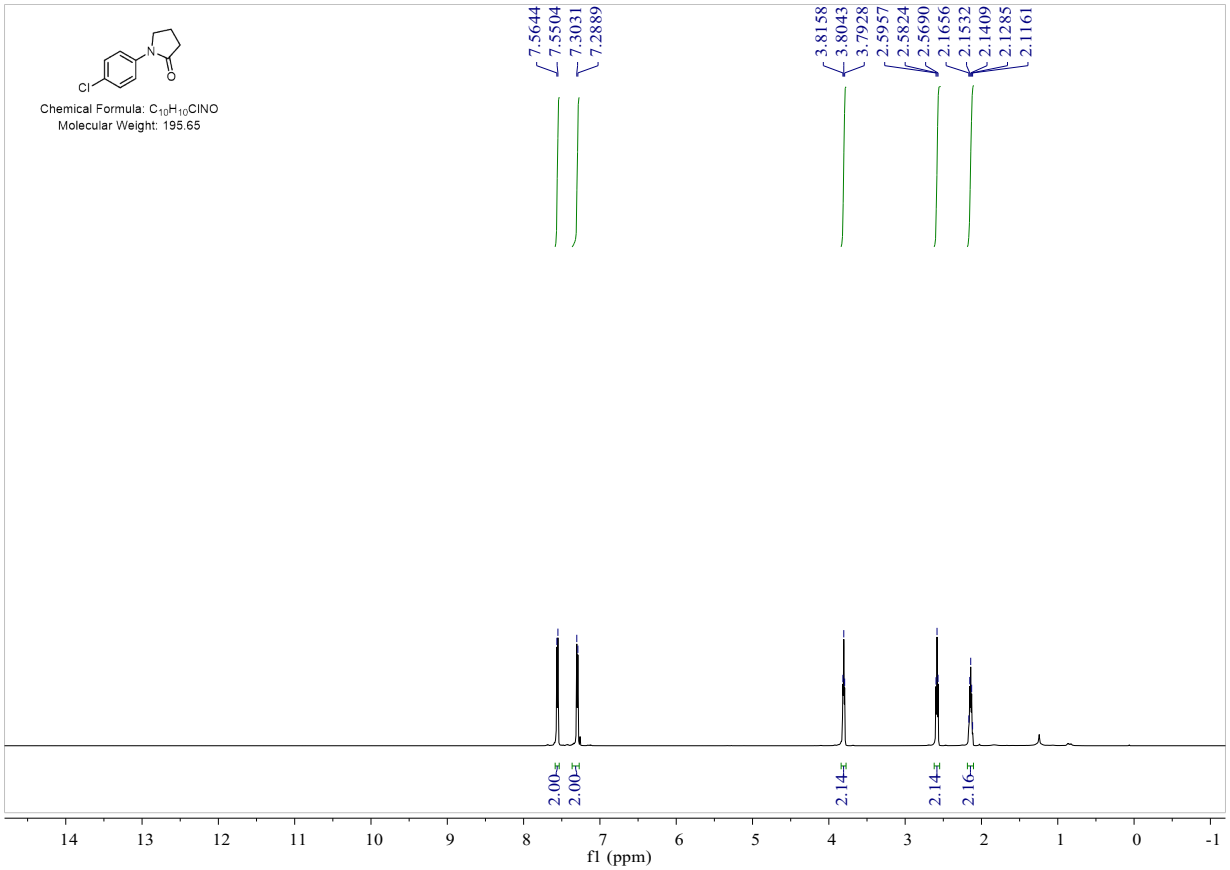


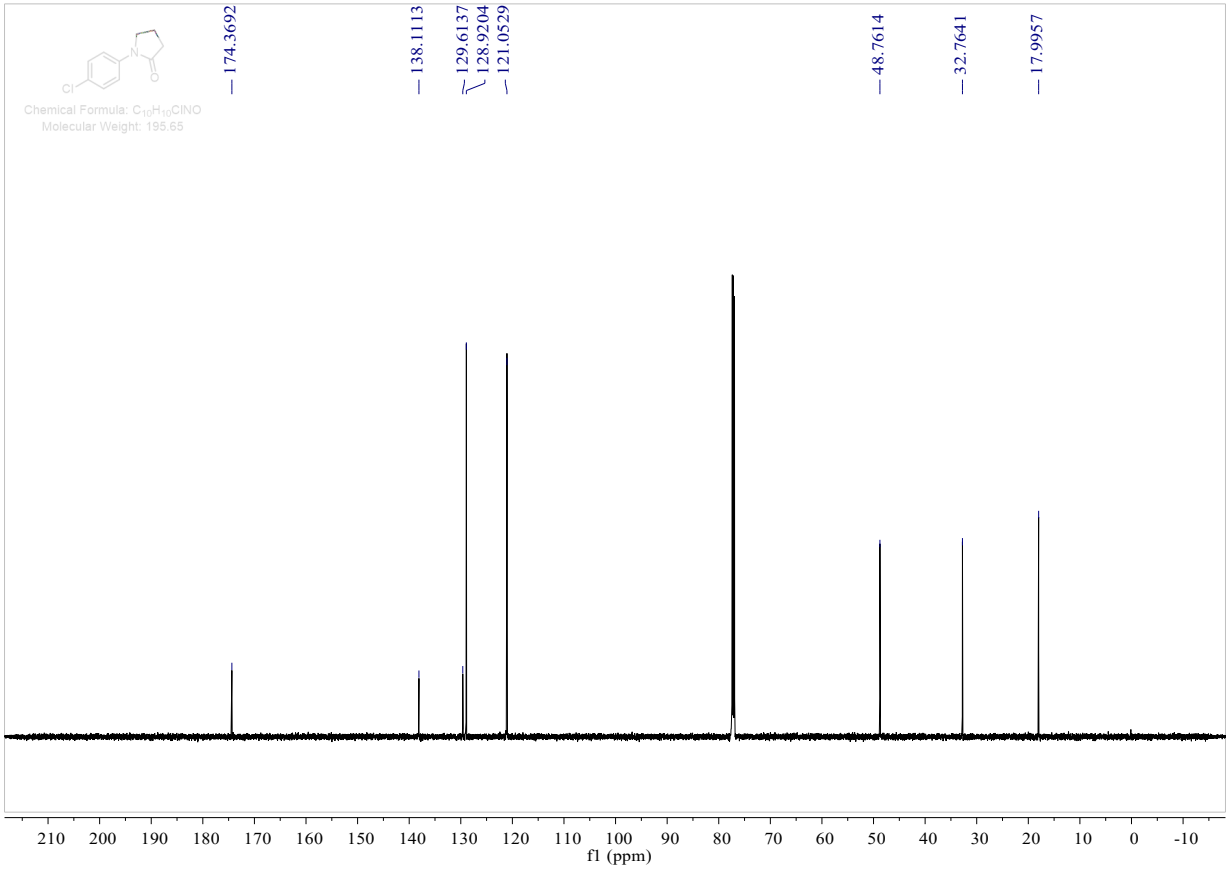
Ethyl 3-(2-oxopyrrolidin-1-yl)benzoate (3n).



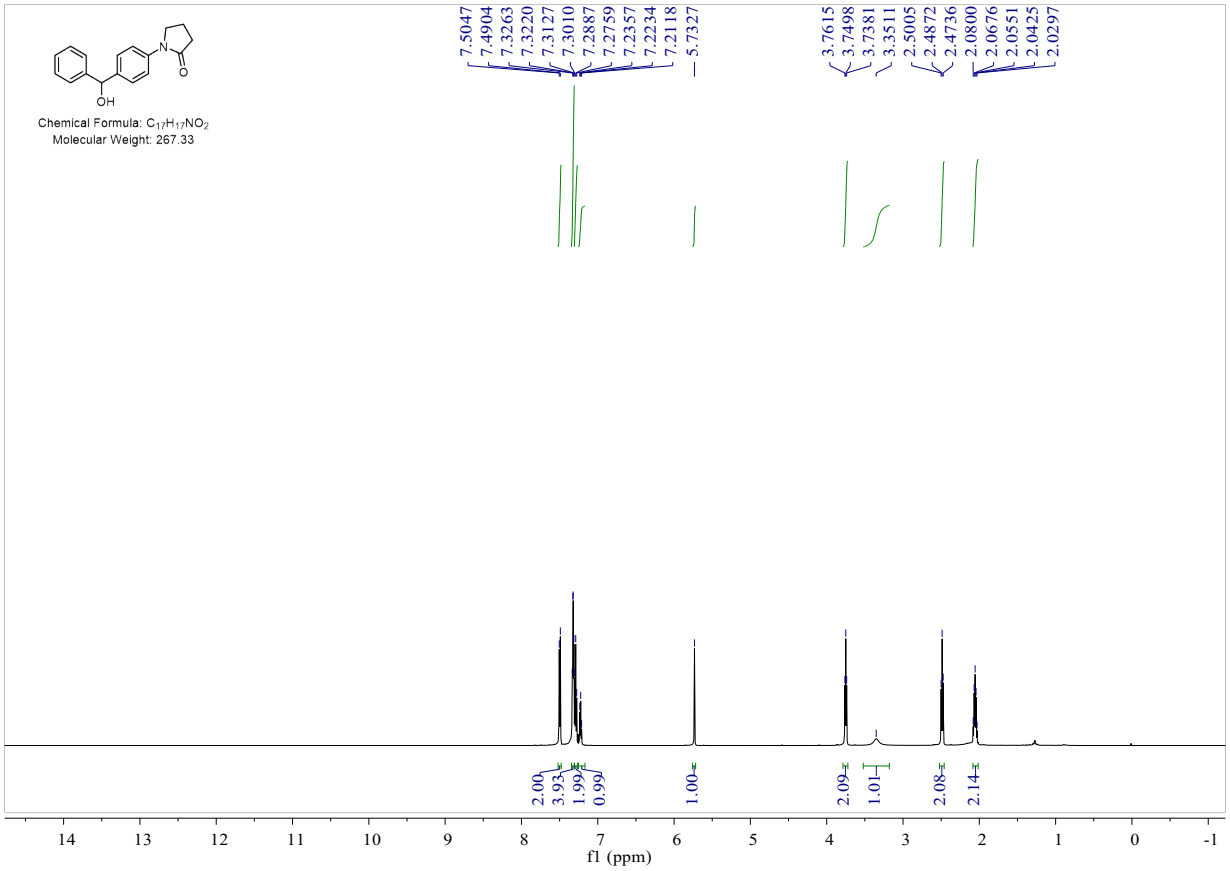


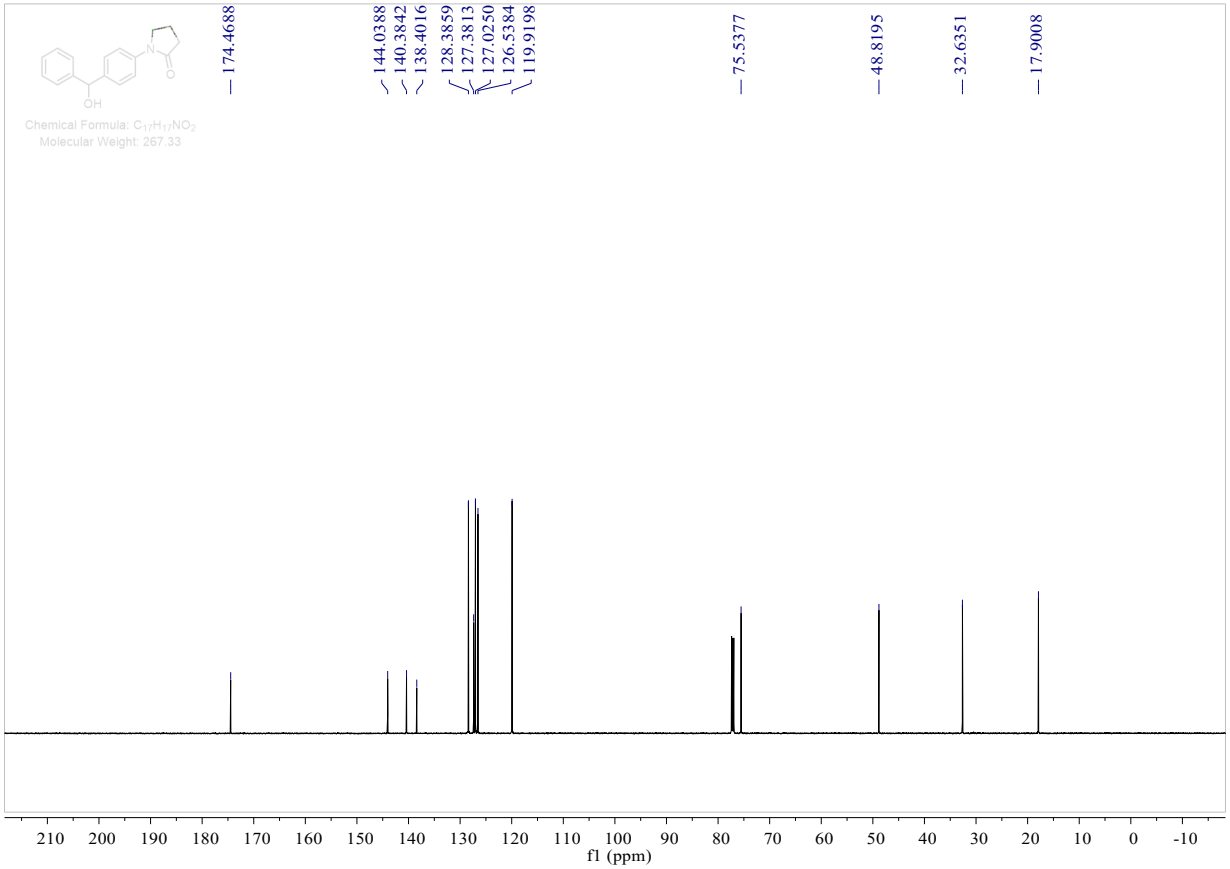
1-(4-Chlorophenyl)pyrrolidin-2-one (3o).



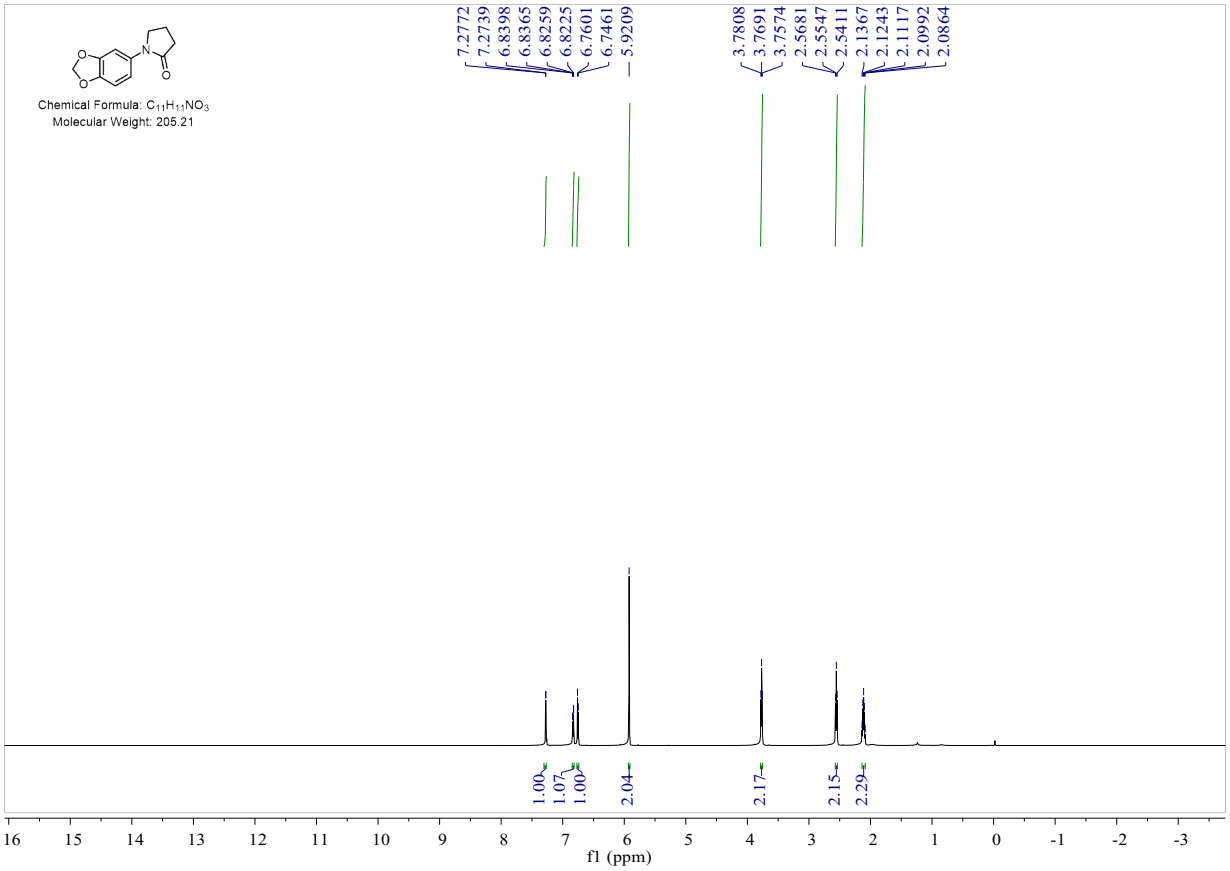


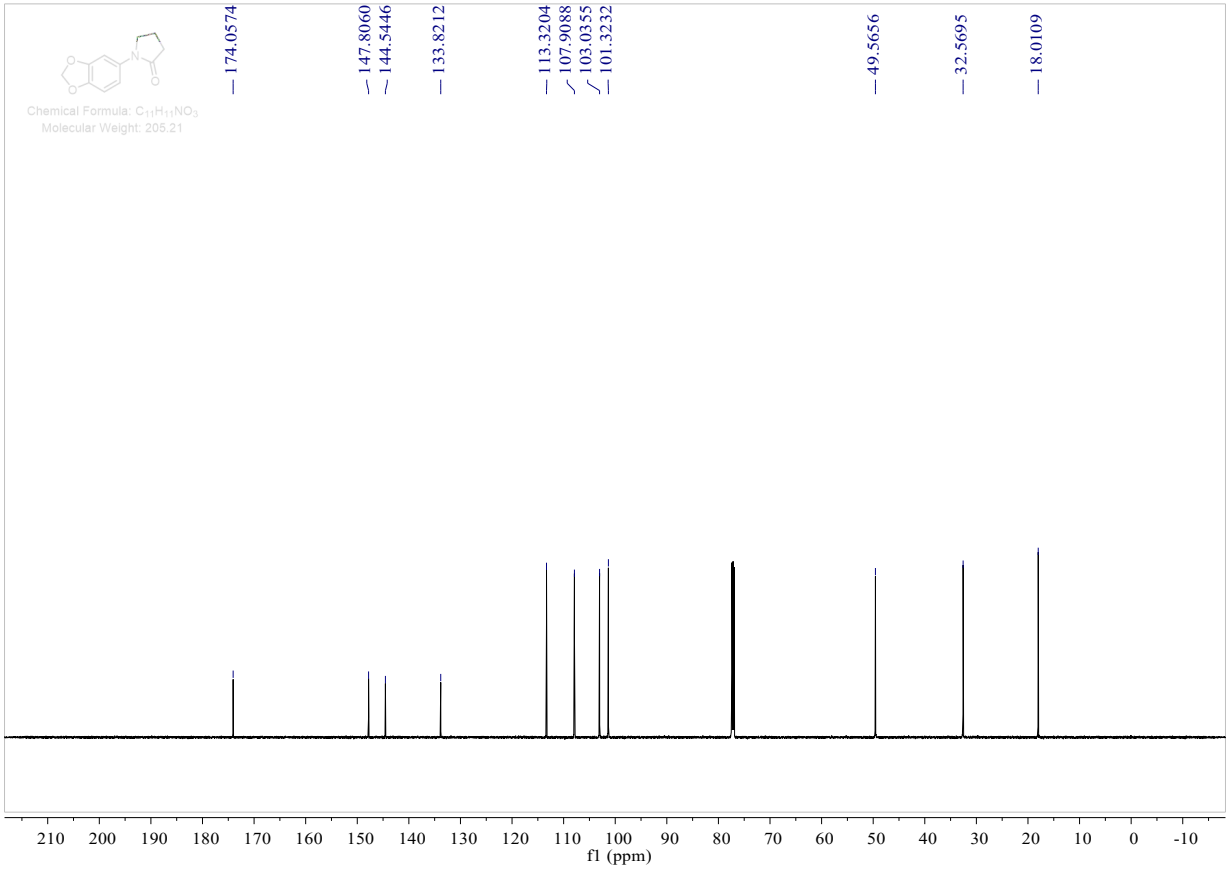
1-(4-(Hydroxy(phenyl)methyl)phenyl)pyrrolidin-2-one (3p).



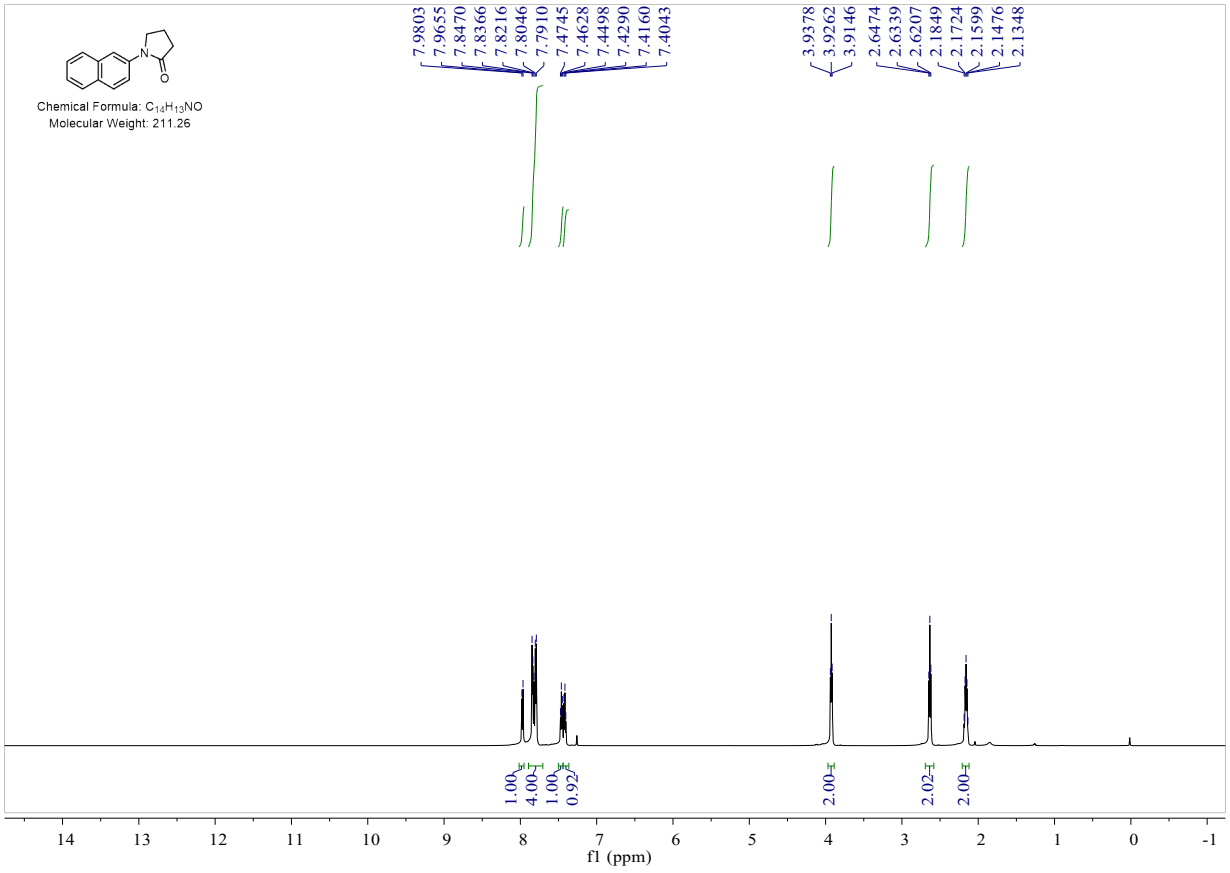


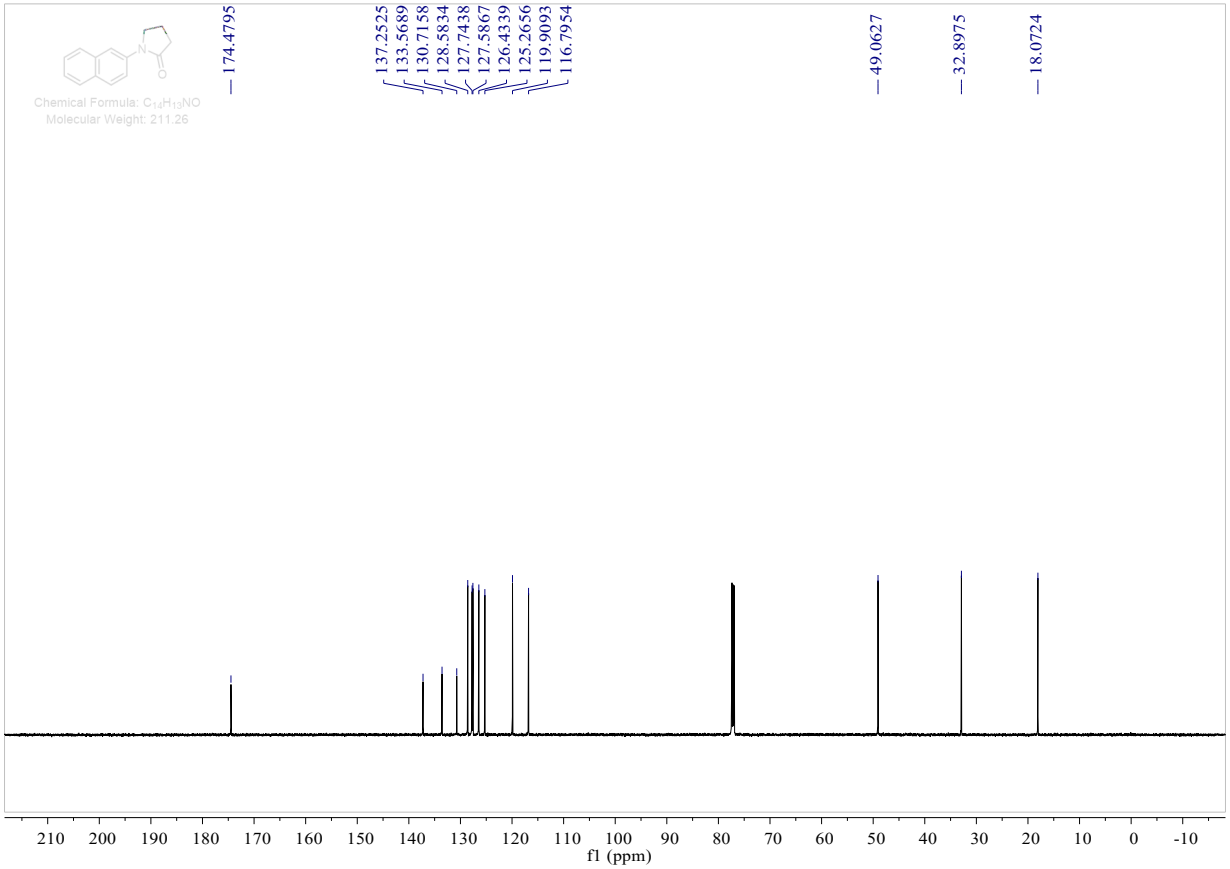
1-(Benzo[d][1,3]dioxol-5-yl)pyrrolidin-2-one (3q).



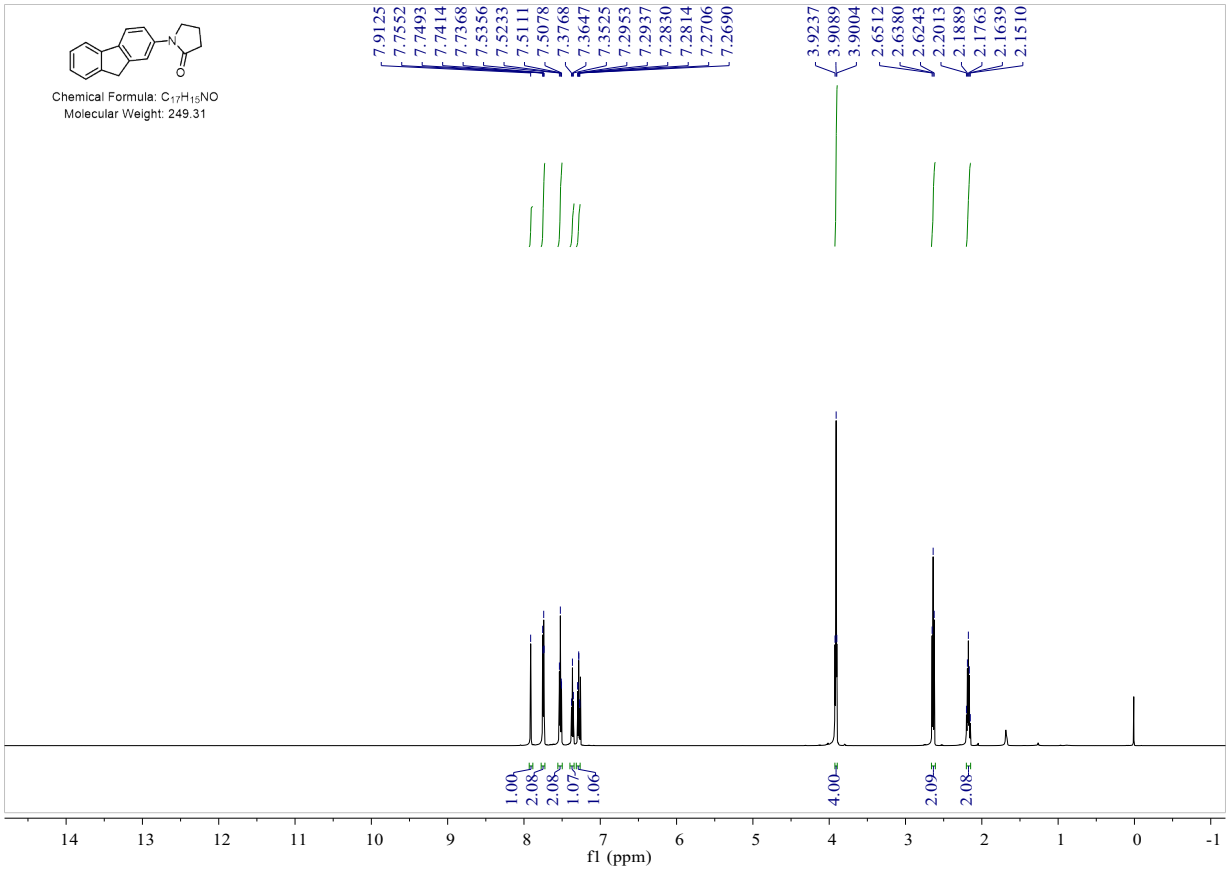


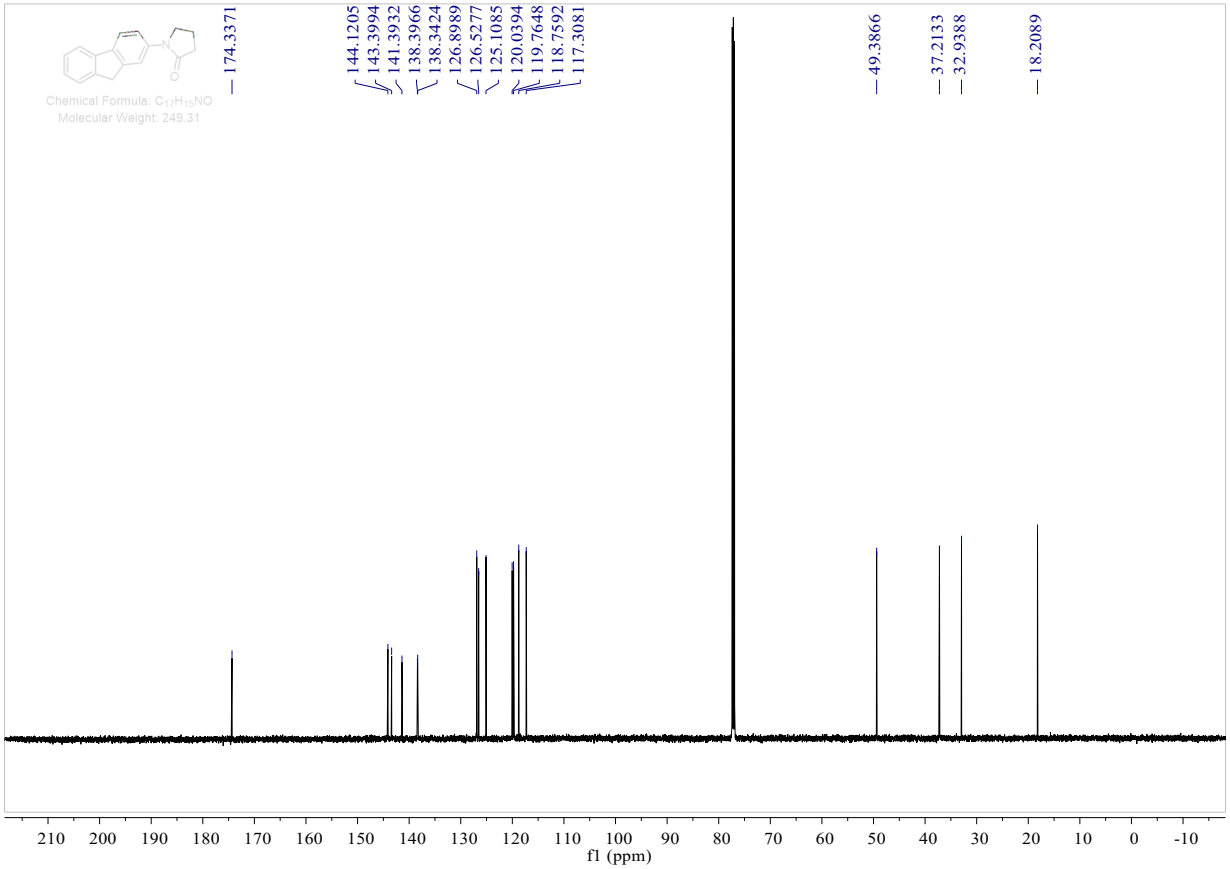
1-(Naphthalen-2-yl)pyrrolidin-2-one (3r).



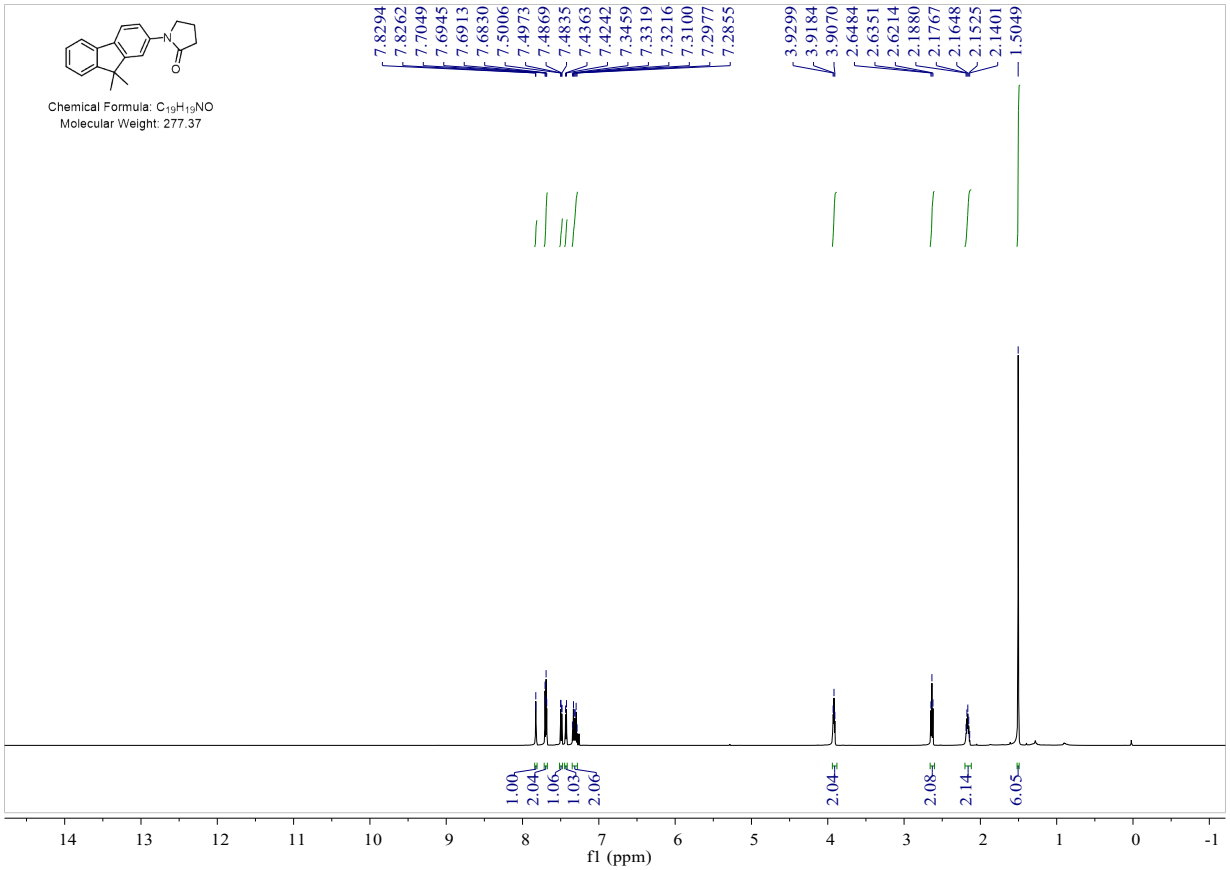


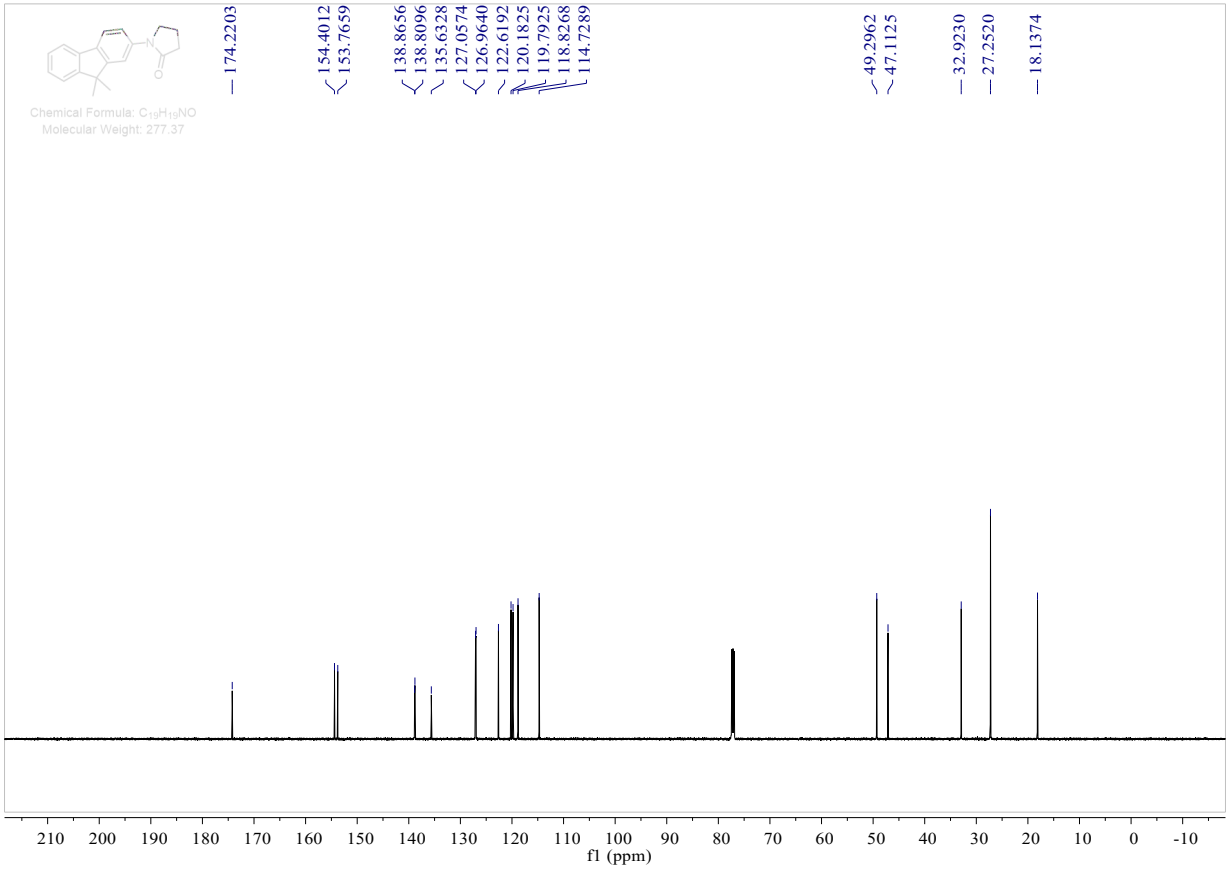
1-(9*H*-Fluoren-2-yl)pyrrolidin-2-one (3s).



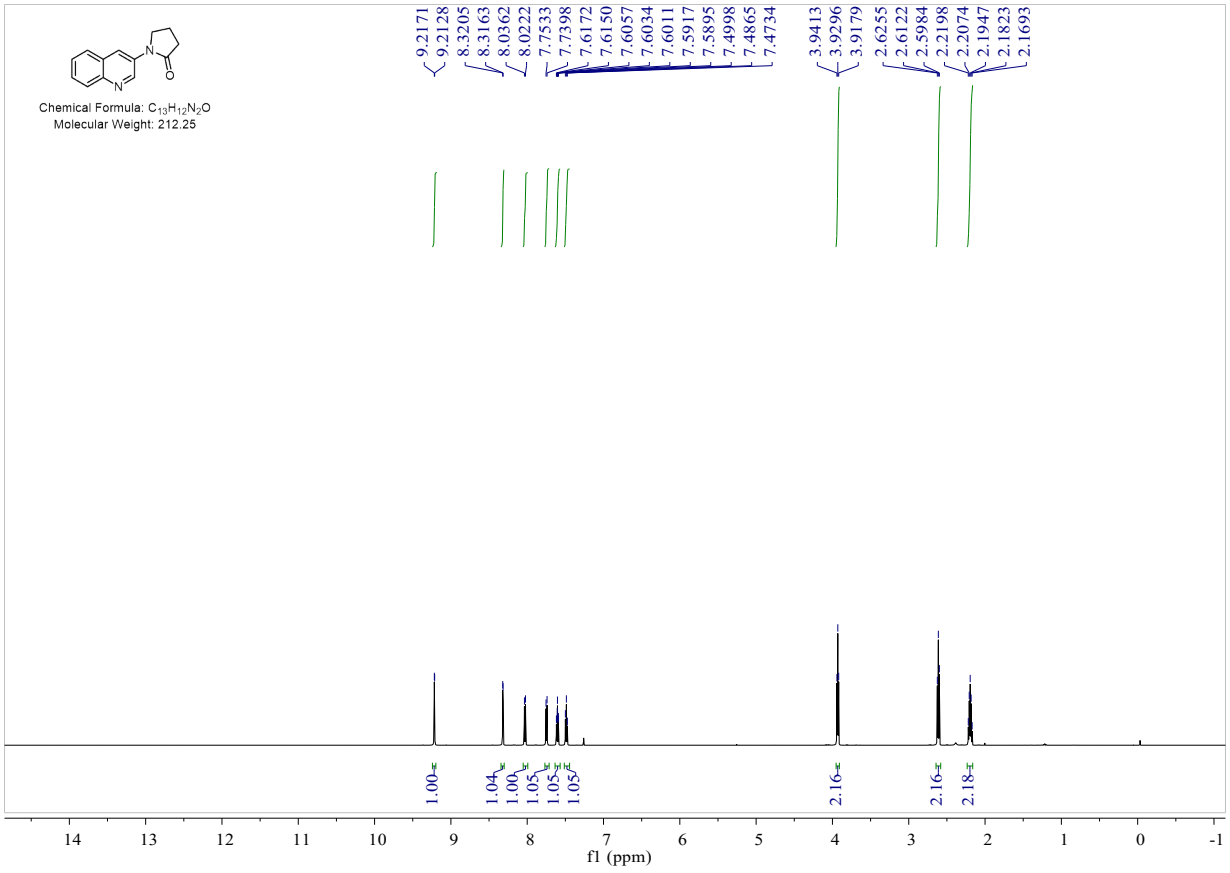


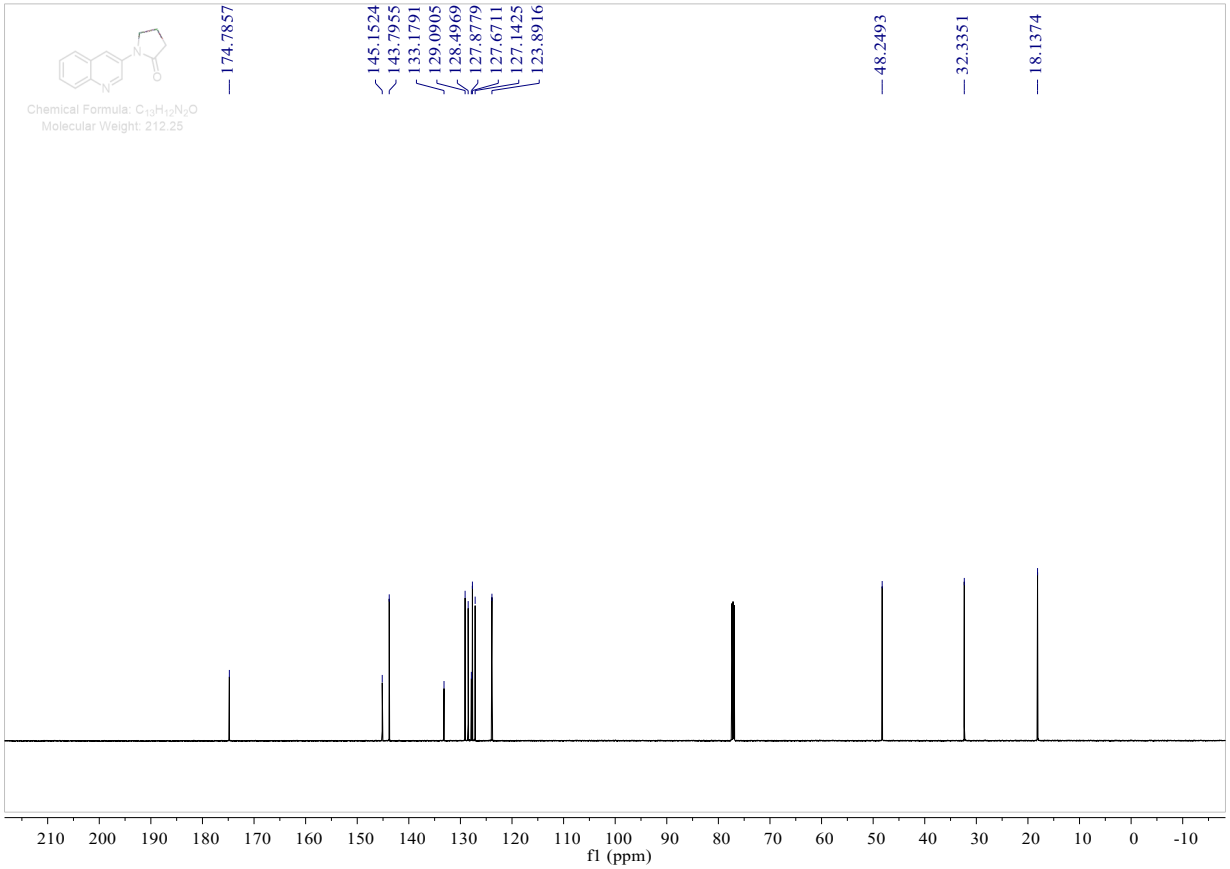
1-(9,9-Dimethyl-9*H*-fluoren-2-yl)pyrrolidin-2-one (3t).



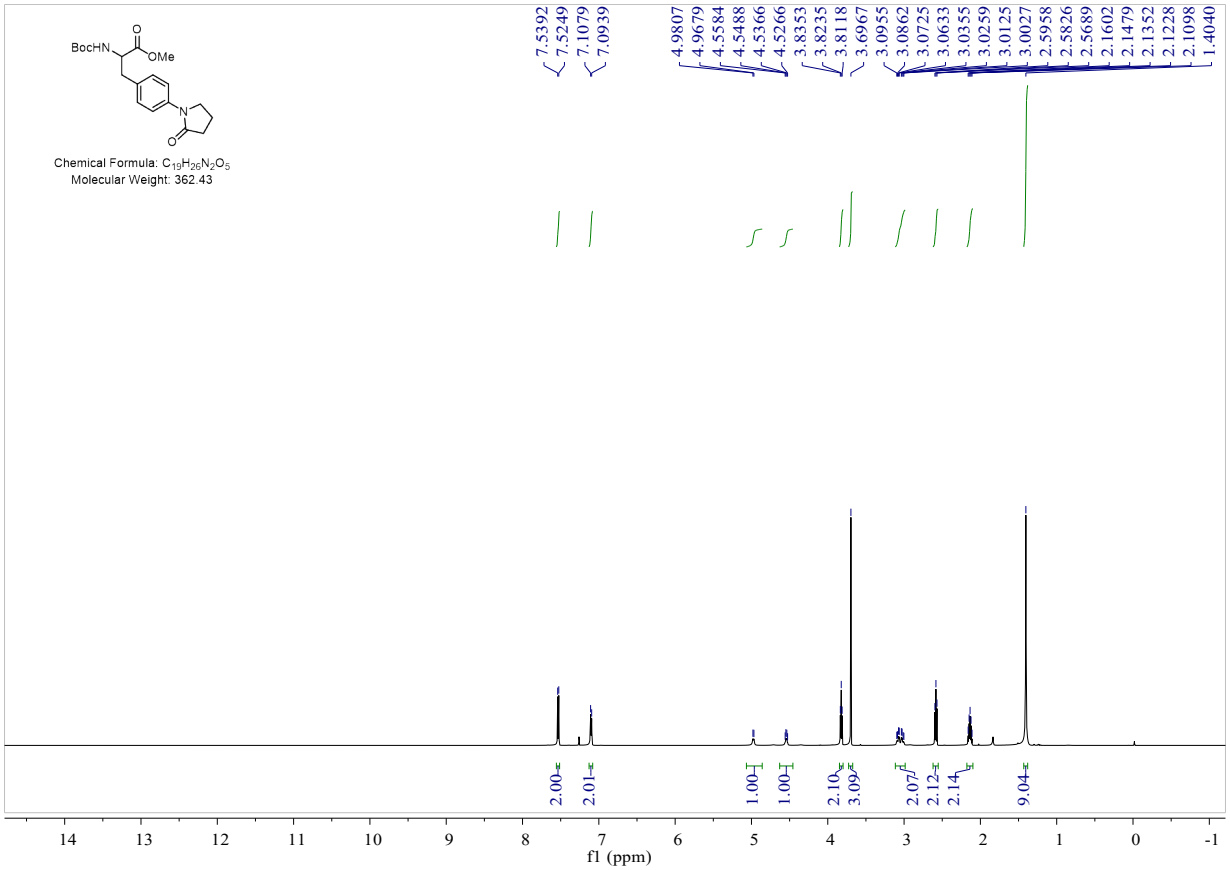


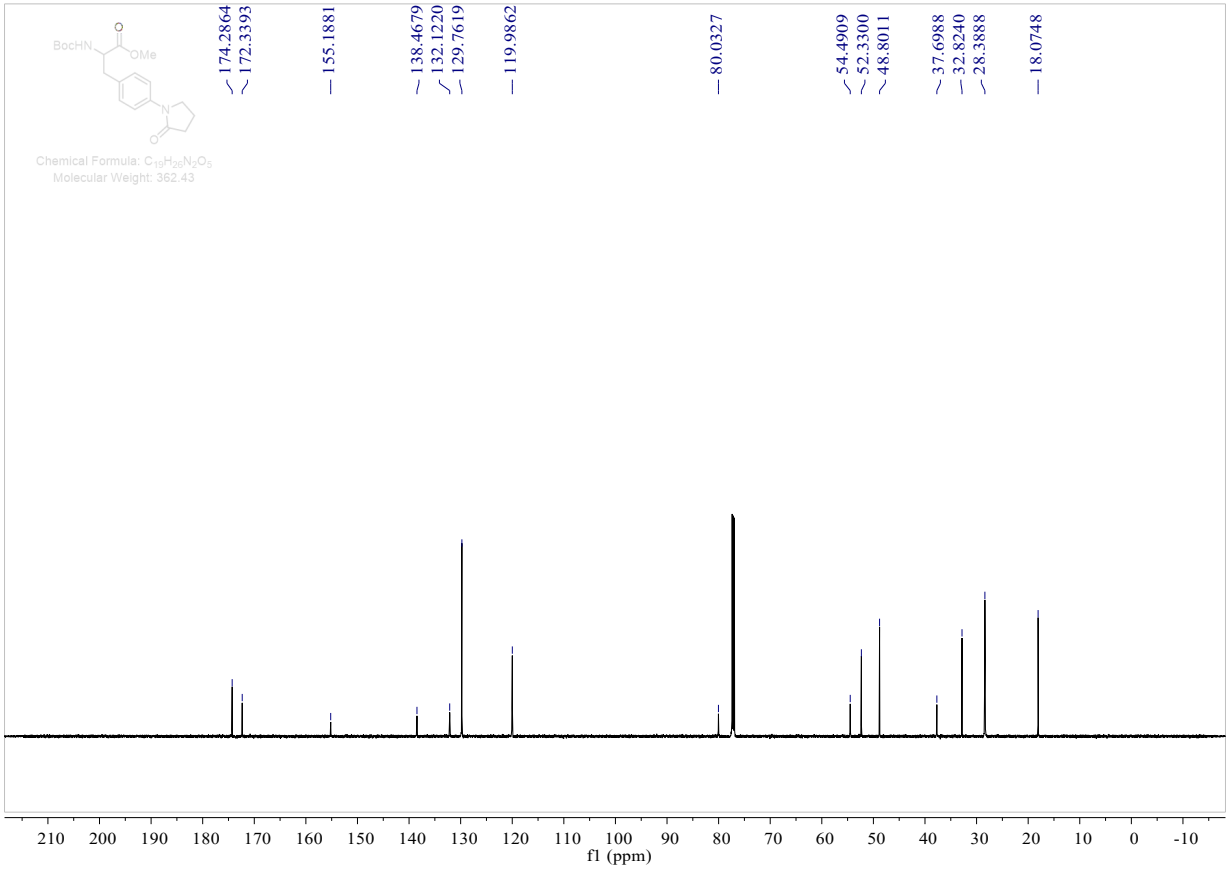
1-(Quinolin-3-yl)pyrrolidin-2-one (3u).



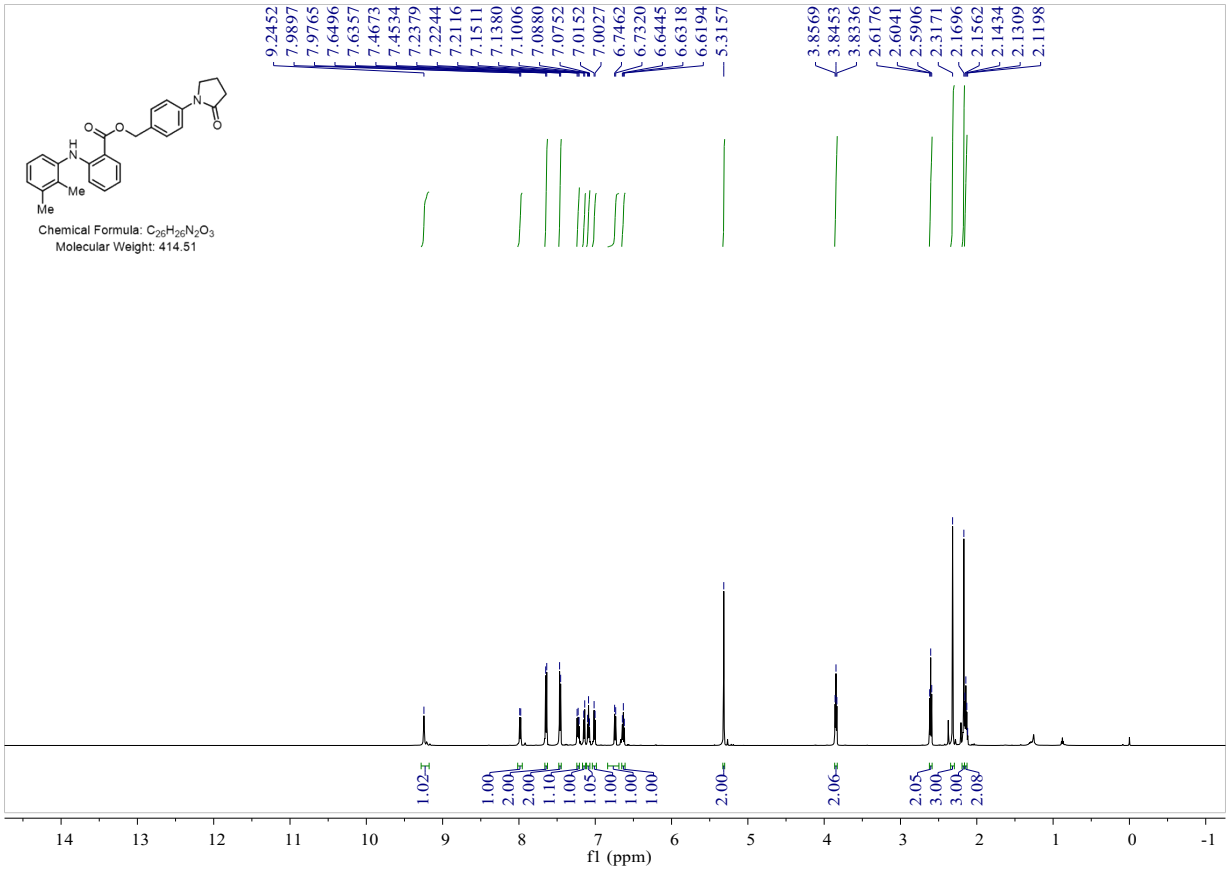


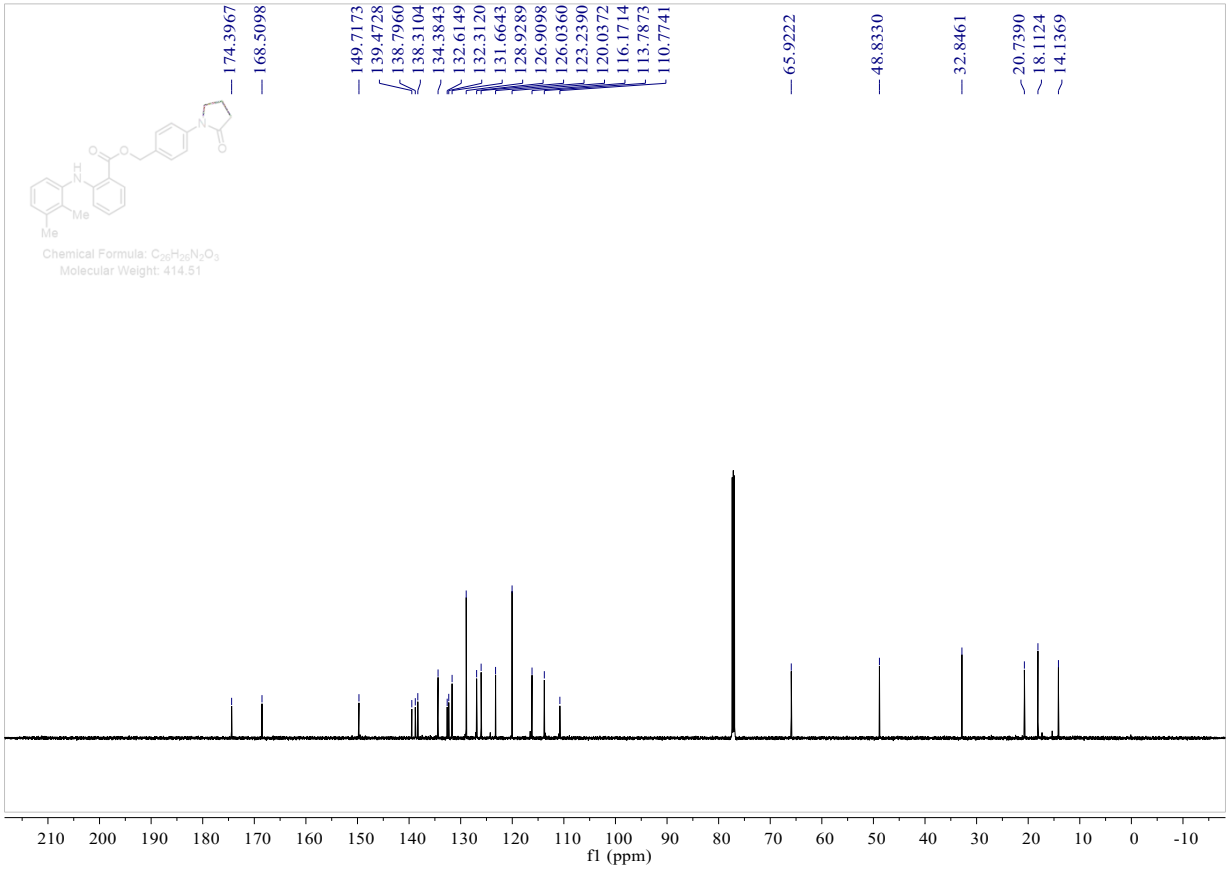
Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(4-(2-oxopyrrolidin-1-yl)phenyl)propanoate (3v).



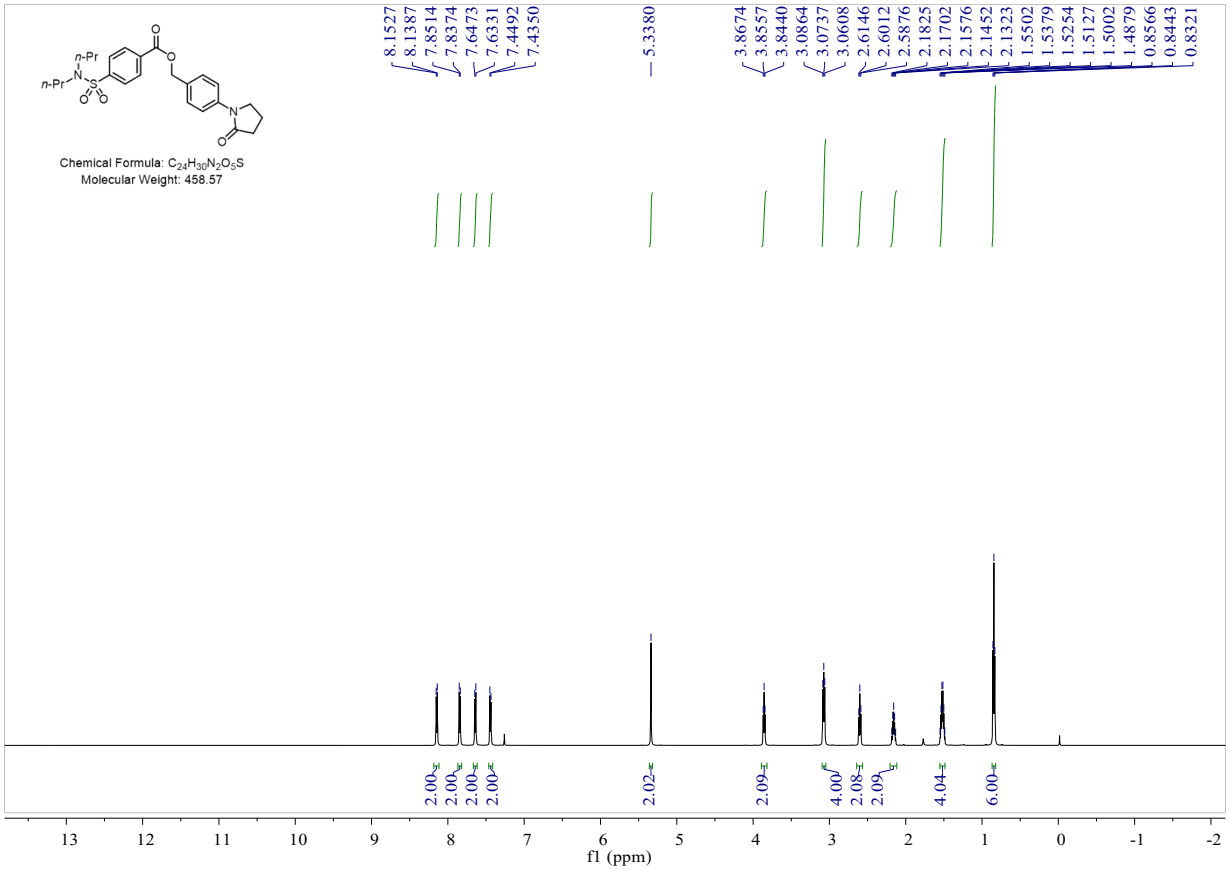


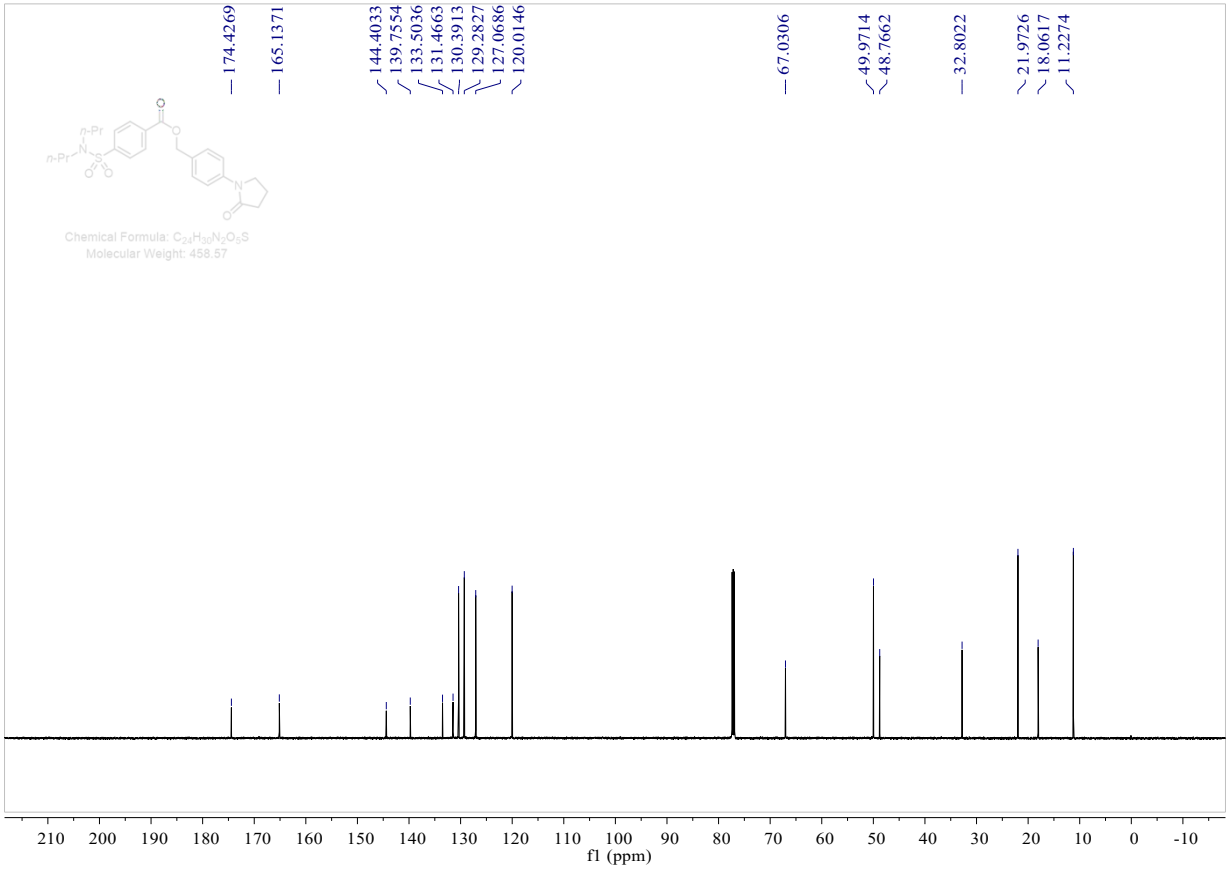
4-(2-Oxopyrrolidin-1-yl)benzyl 2-((2,3-dimethylphenyl)amino)benzoate (3w).



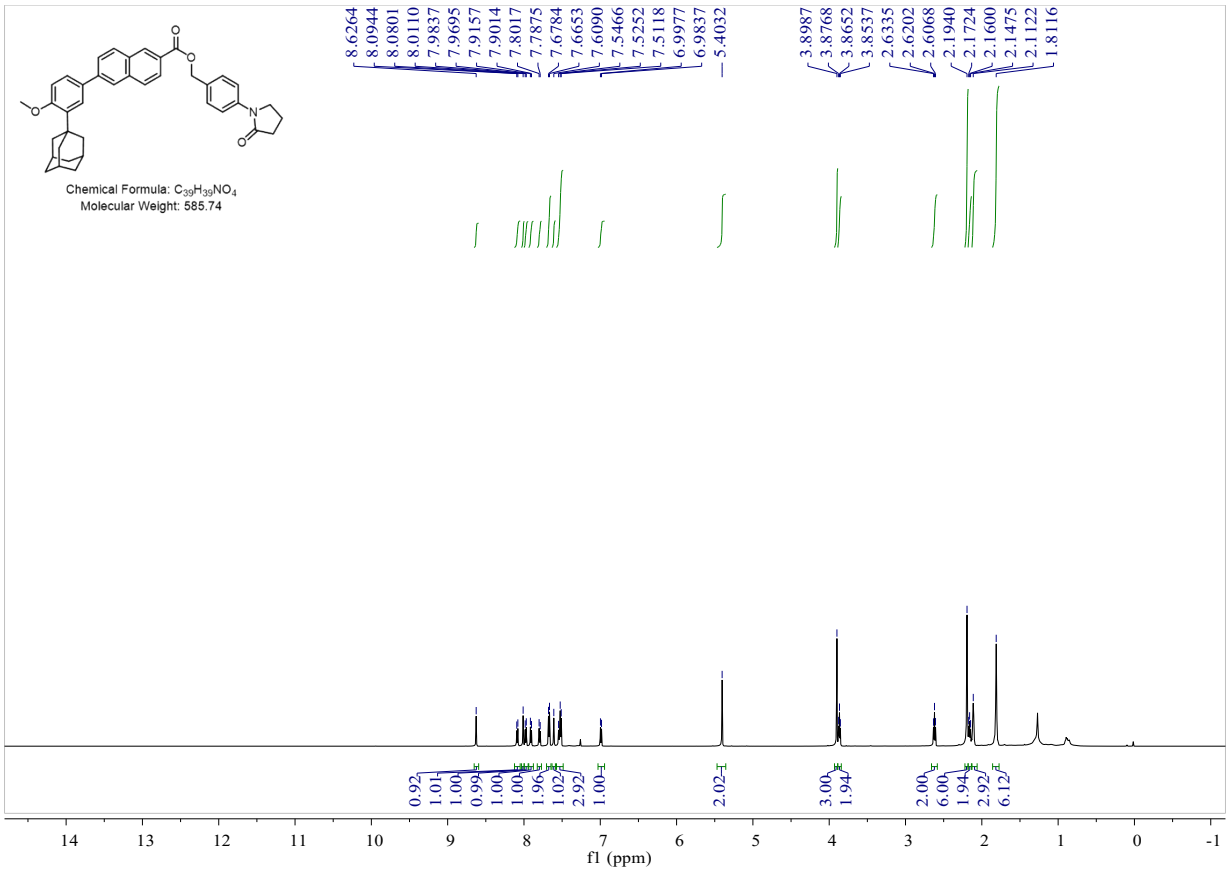


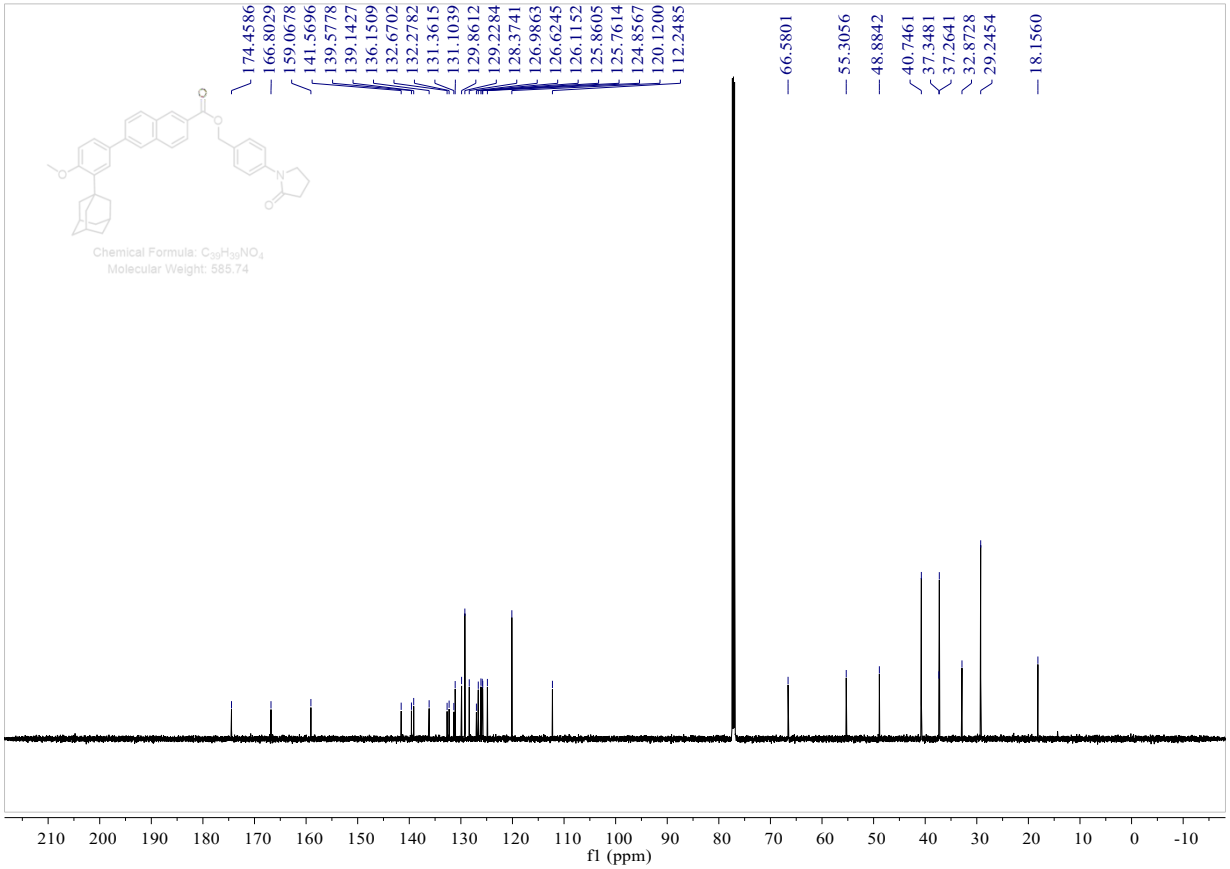
4-(2-Oxopyrrolidin-1-yl)benzyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (3x).



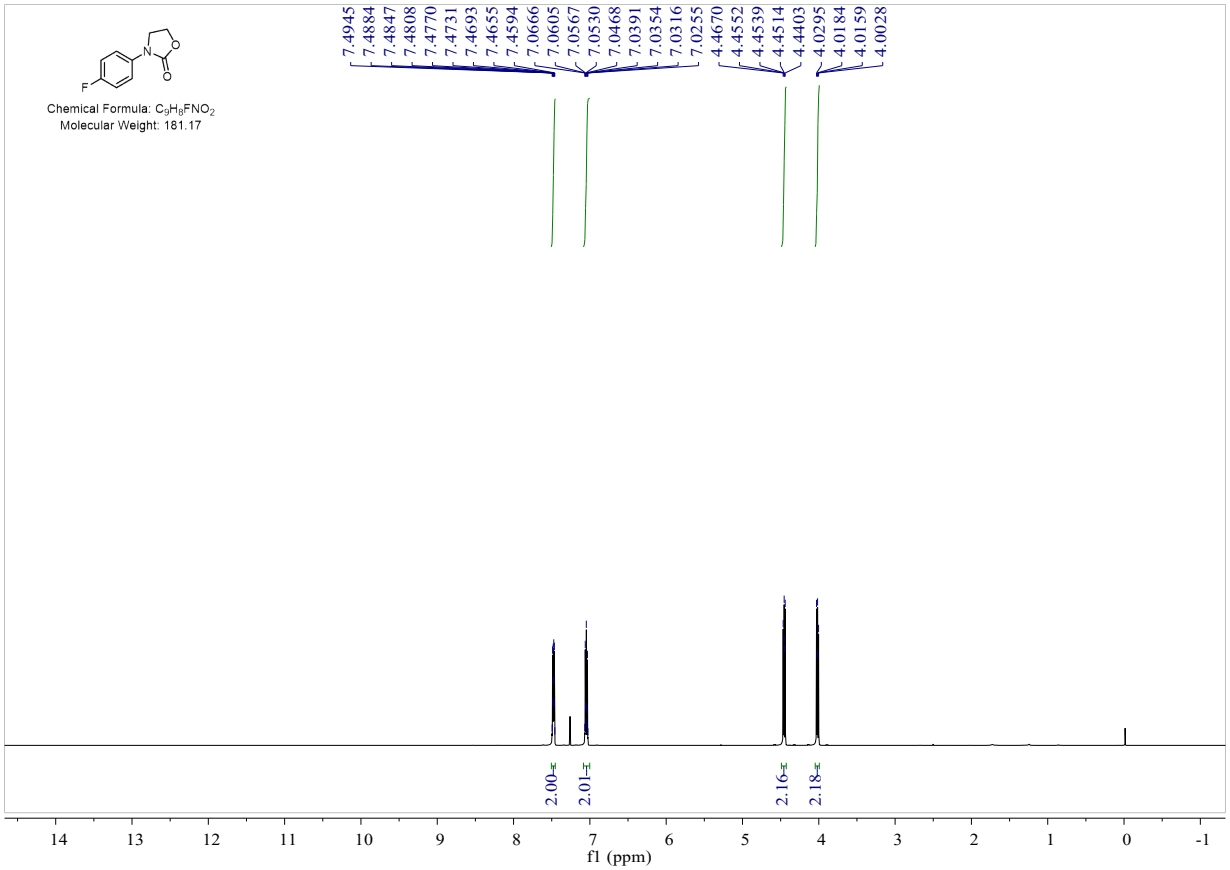


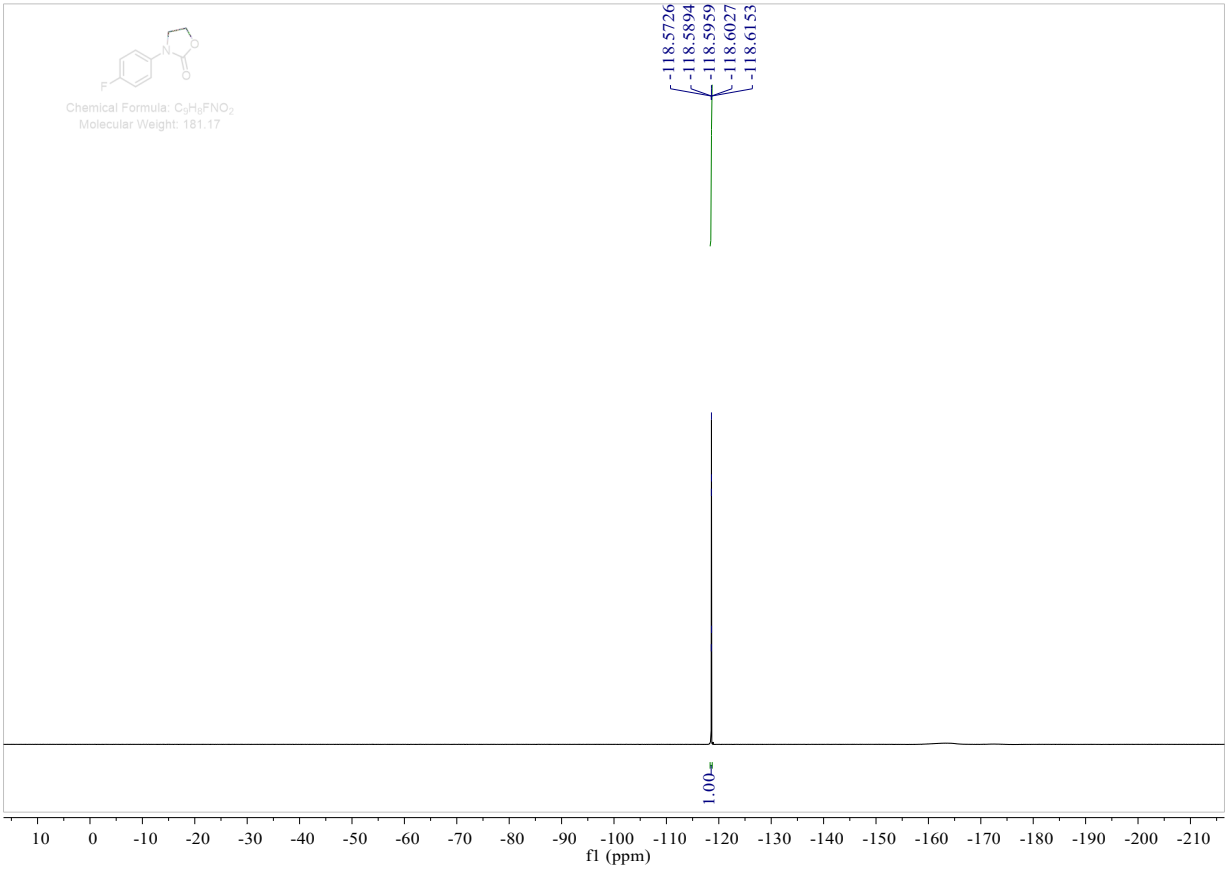
4-(2-Oxopyrrolidin-1-yl)benzyl 6-(3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthoate (3y).





3-(4-Fluorophenyl)oxazolidin-2-one (5a).




Chemical Formula: C9H6FNO2
Molecular Weight: 181.17
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-118.5959
-118.6027
-118.6153
1.00
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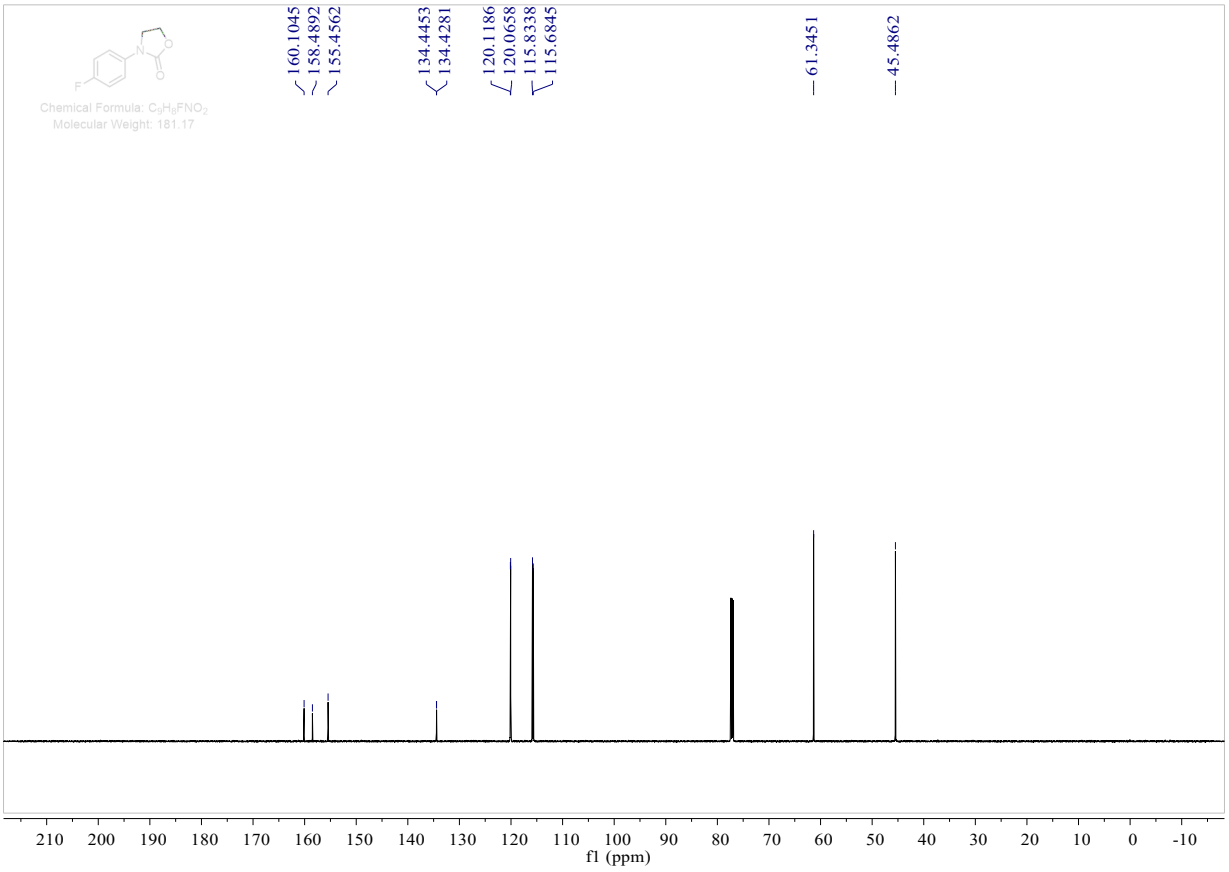
f1 (ppm)


Chemical Formula: C9H6FNO2
Molecular Weight: 181.17
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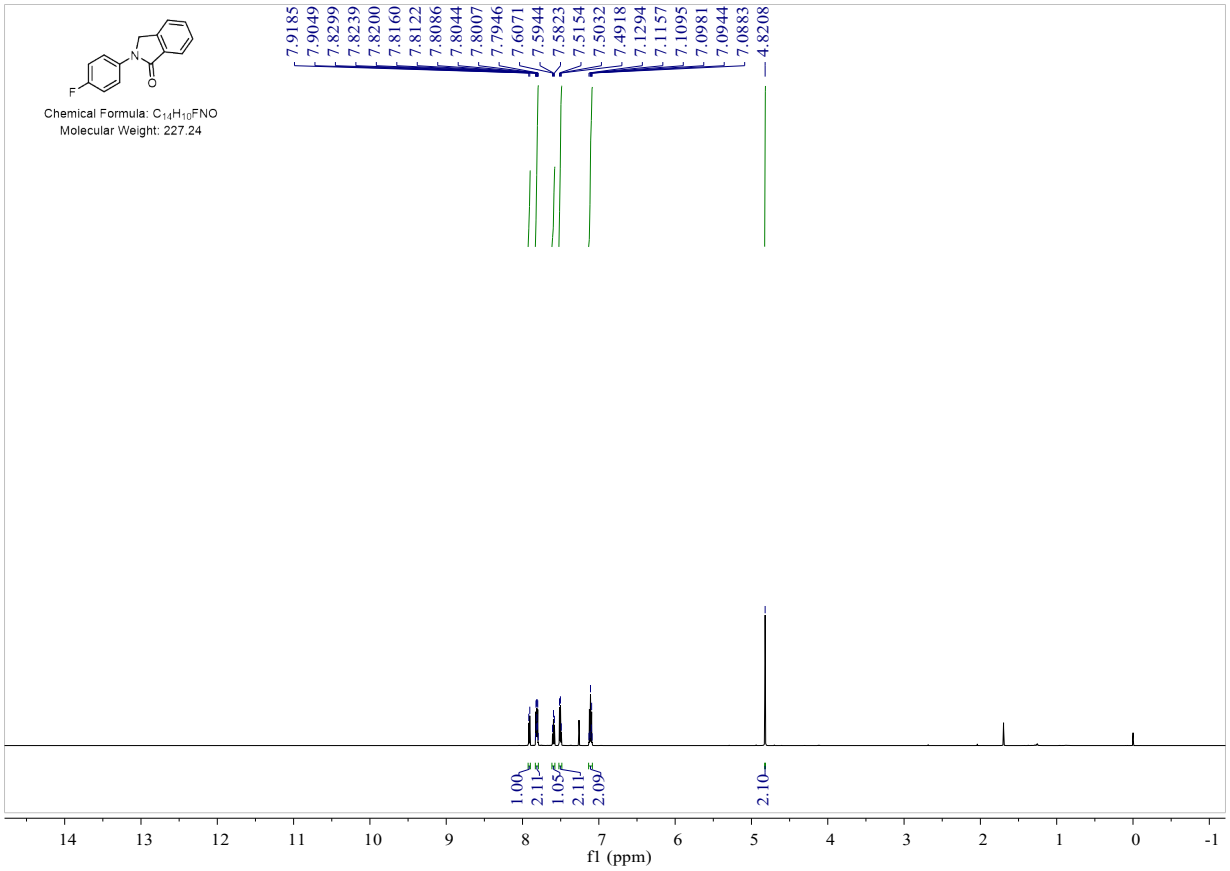
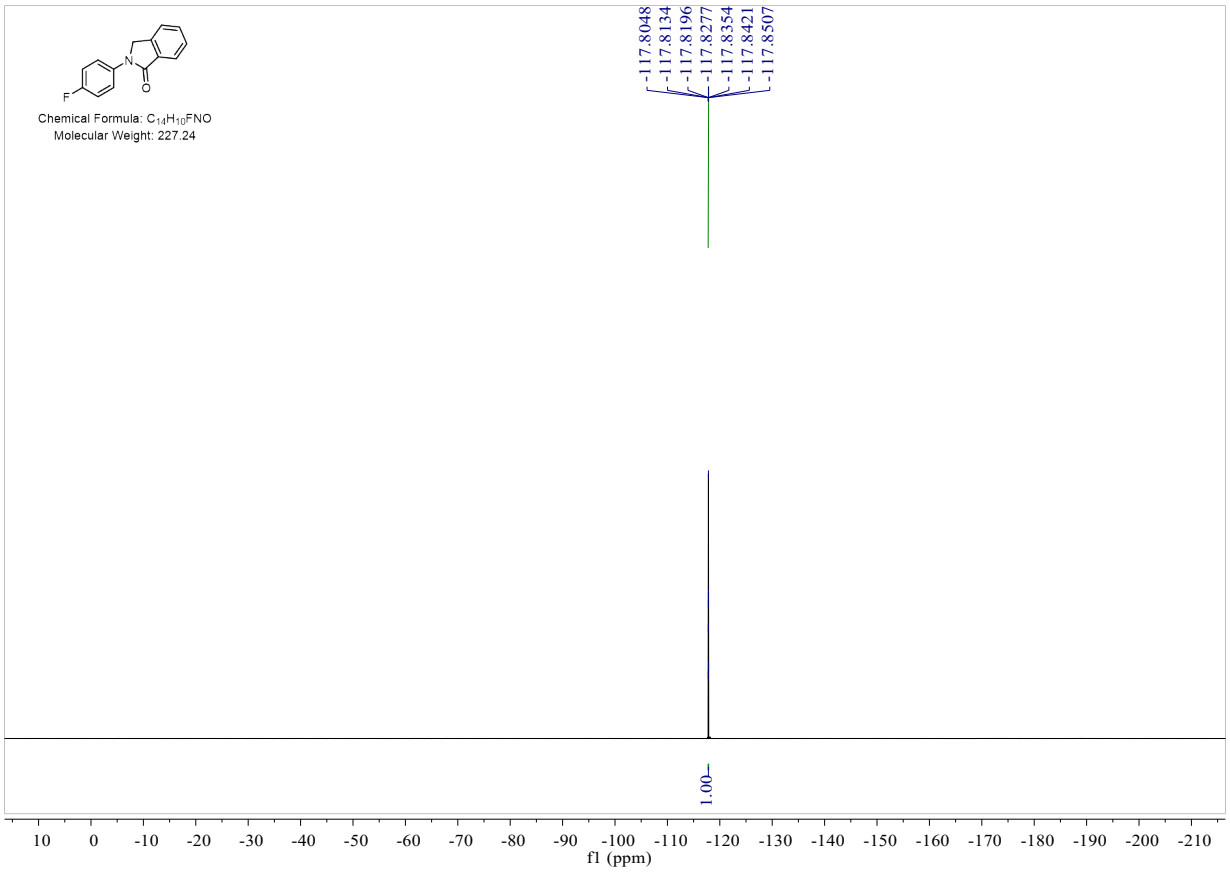
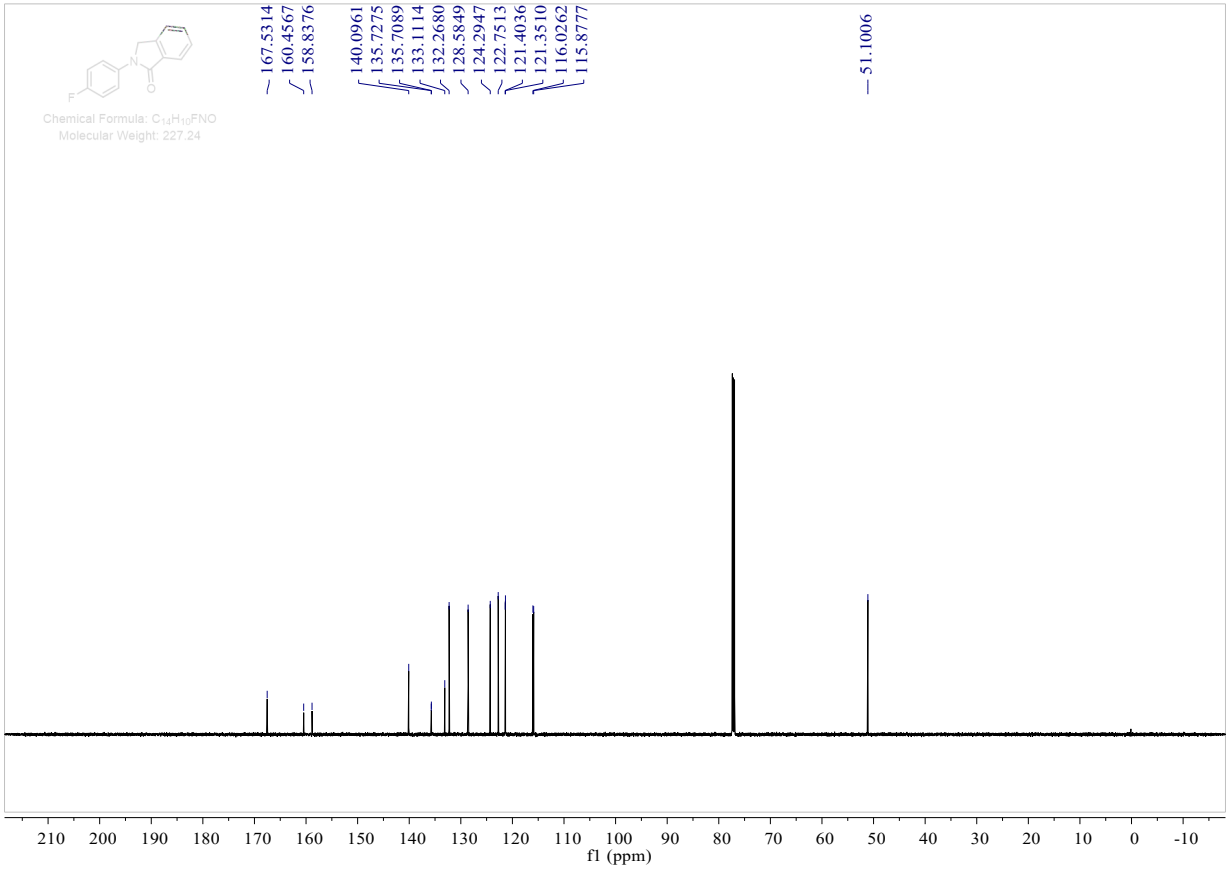
155.4562
134.4453
134.4281
120.1186
120.0658
115.8338
115.6845
61.3451
45.4862
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

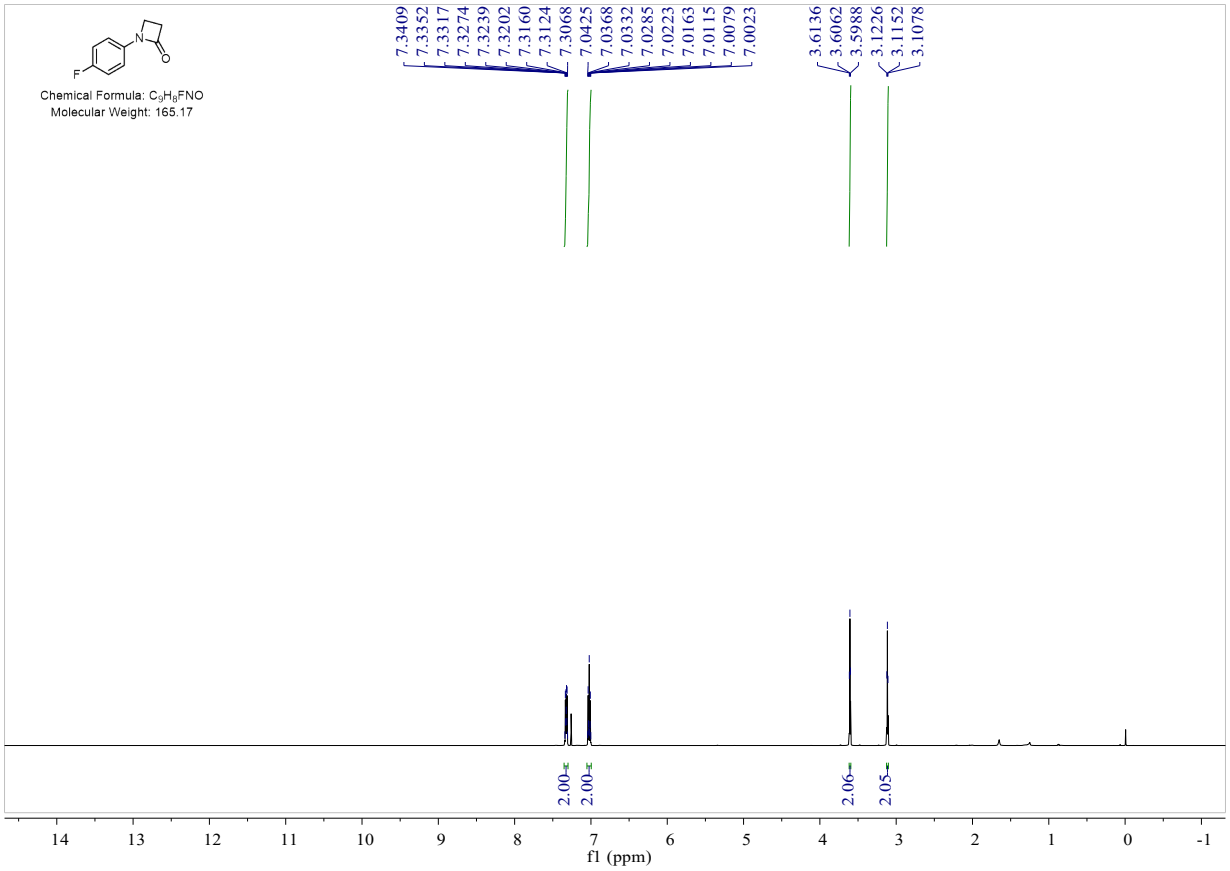
2-(4-Fluorophenyl)isoindolin-1-one (5b).

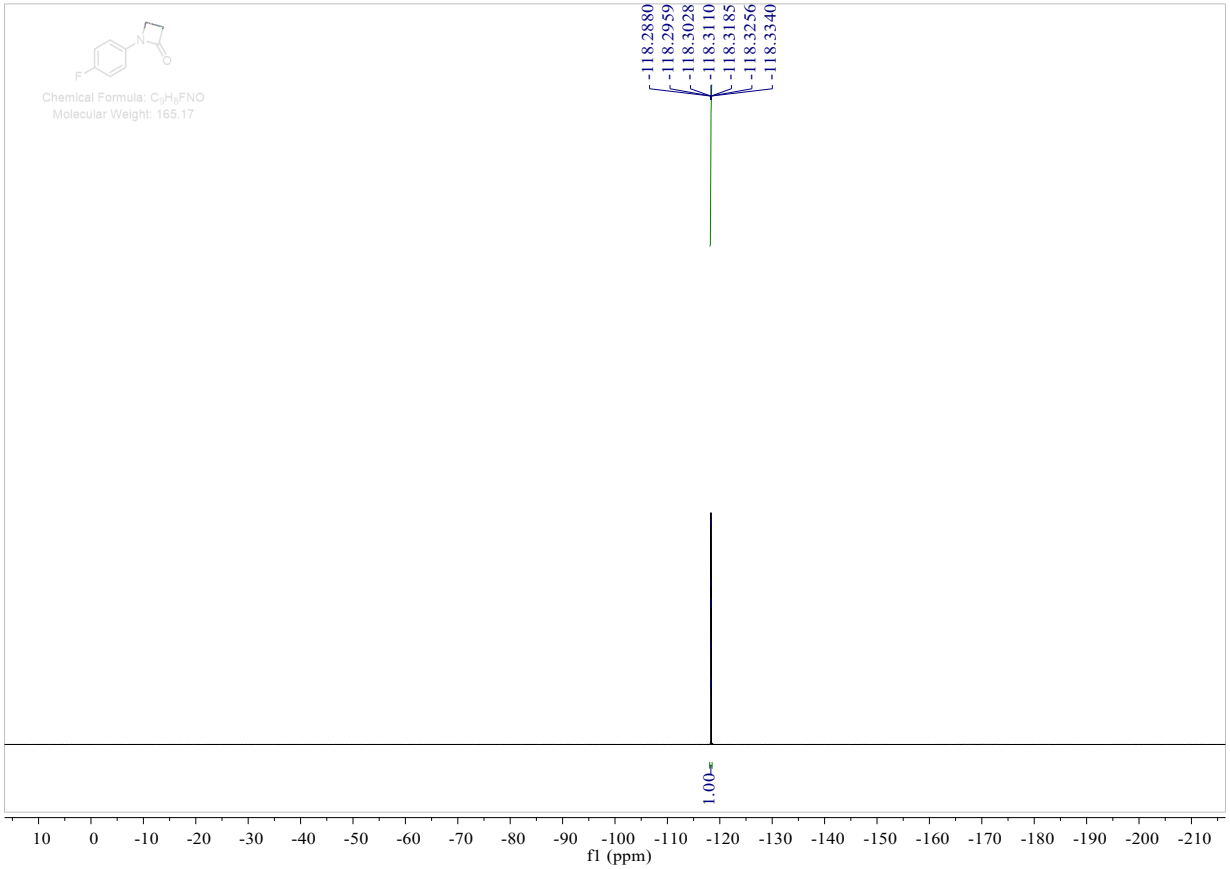






1-(4-Fluorophenyl)azetidin-2-one (5c).




Chemical Formula: C8H6FNO
Molecular Weight: 165.17
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-118.3028
-118.3110
-118.3185
-118.3256
-118.3340
1.00
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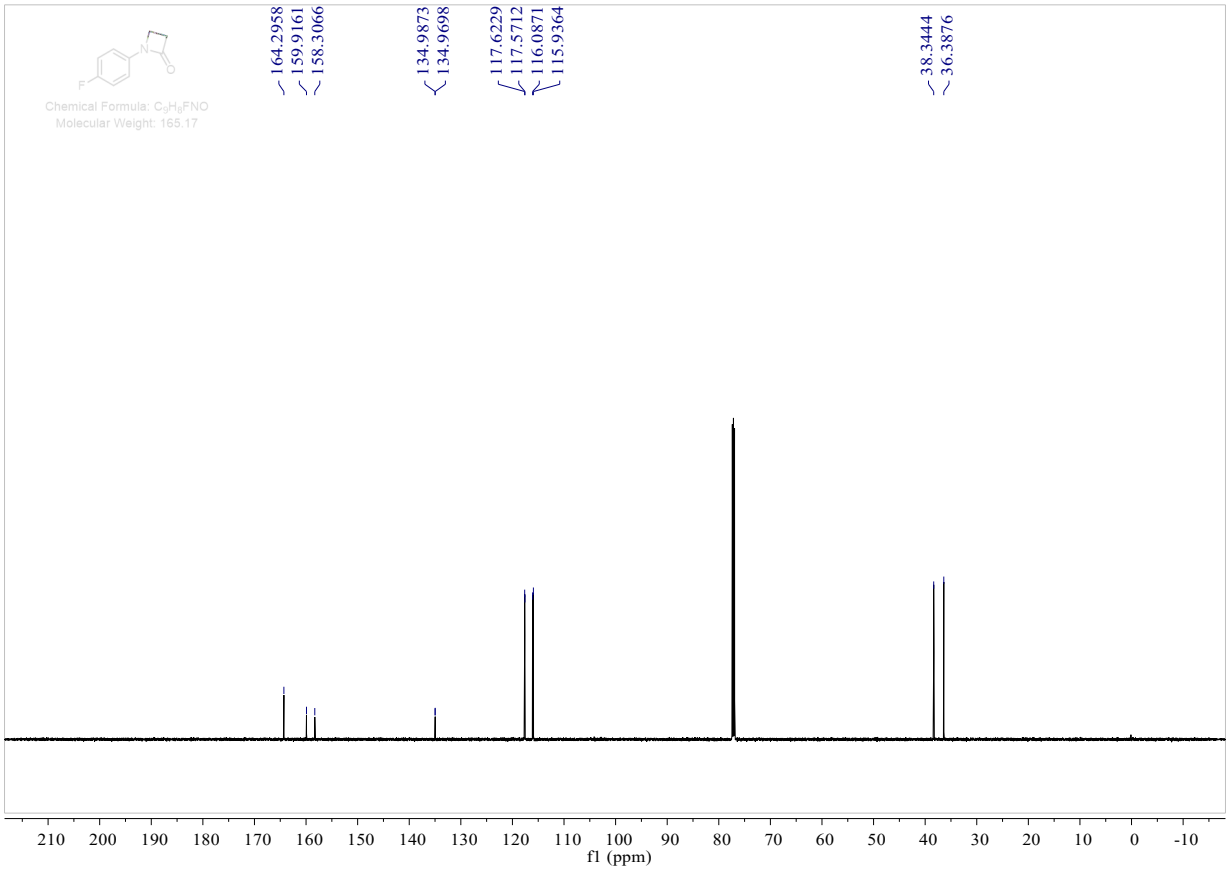
f1 (ppm)


Chemical Formula: C8H6FNO
Molecular Weight: 165.17
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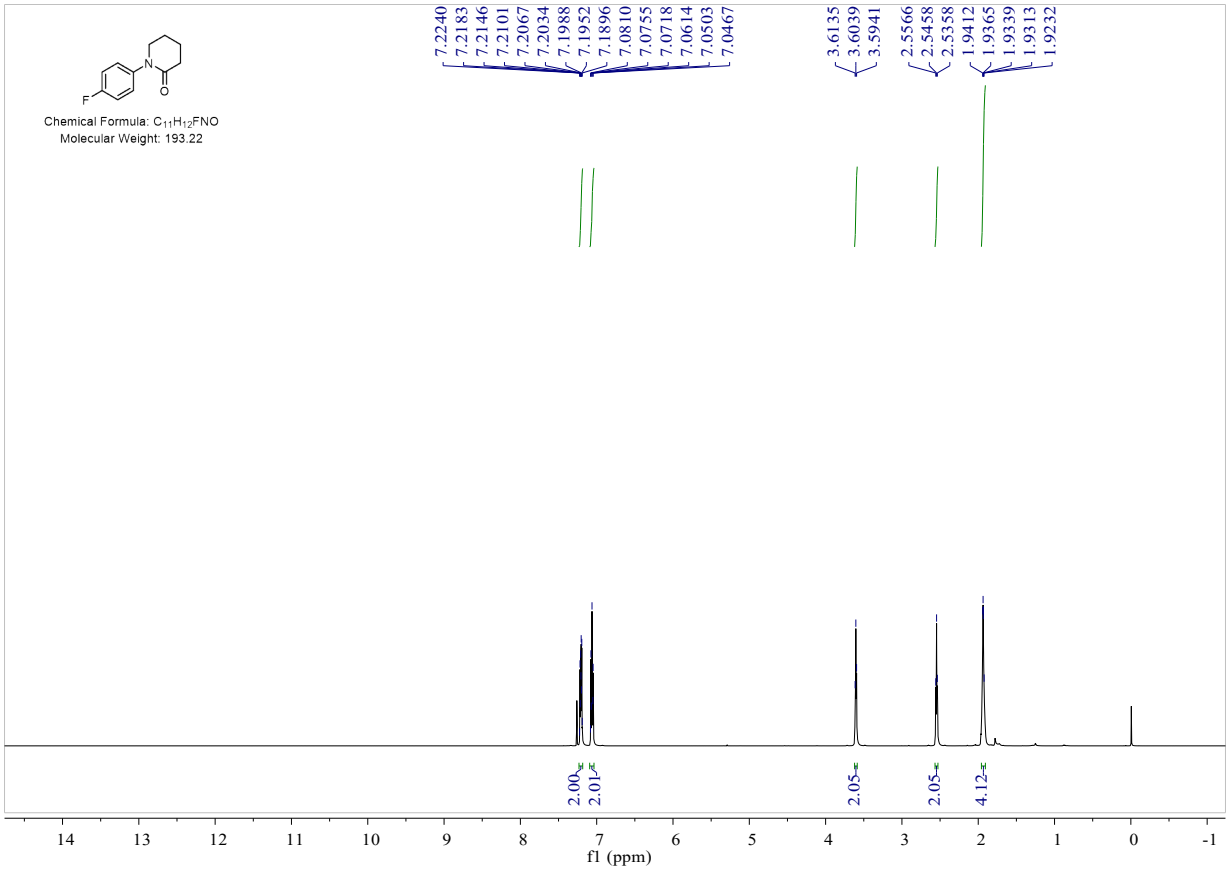
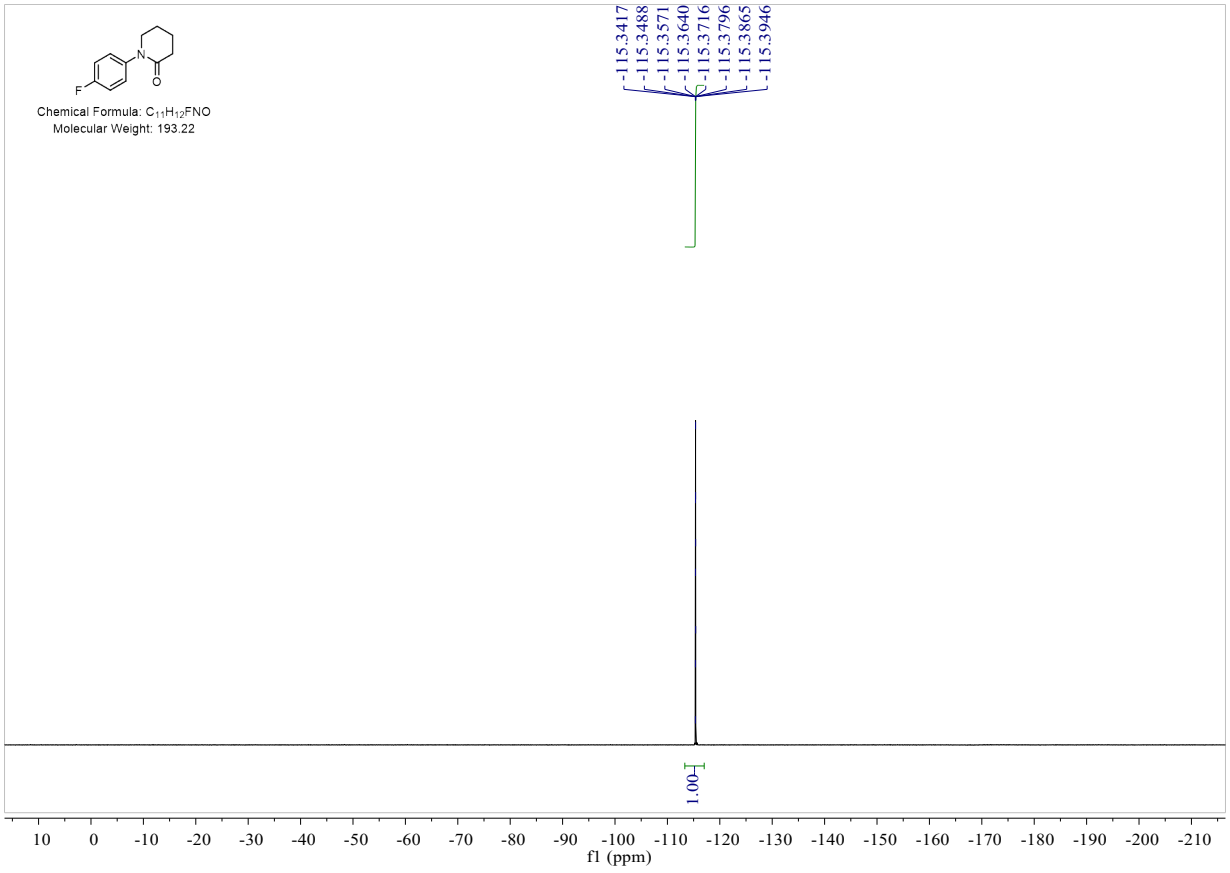
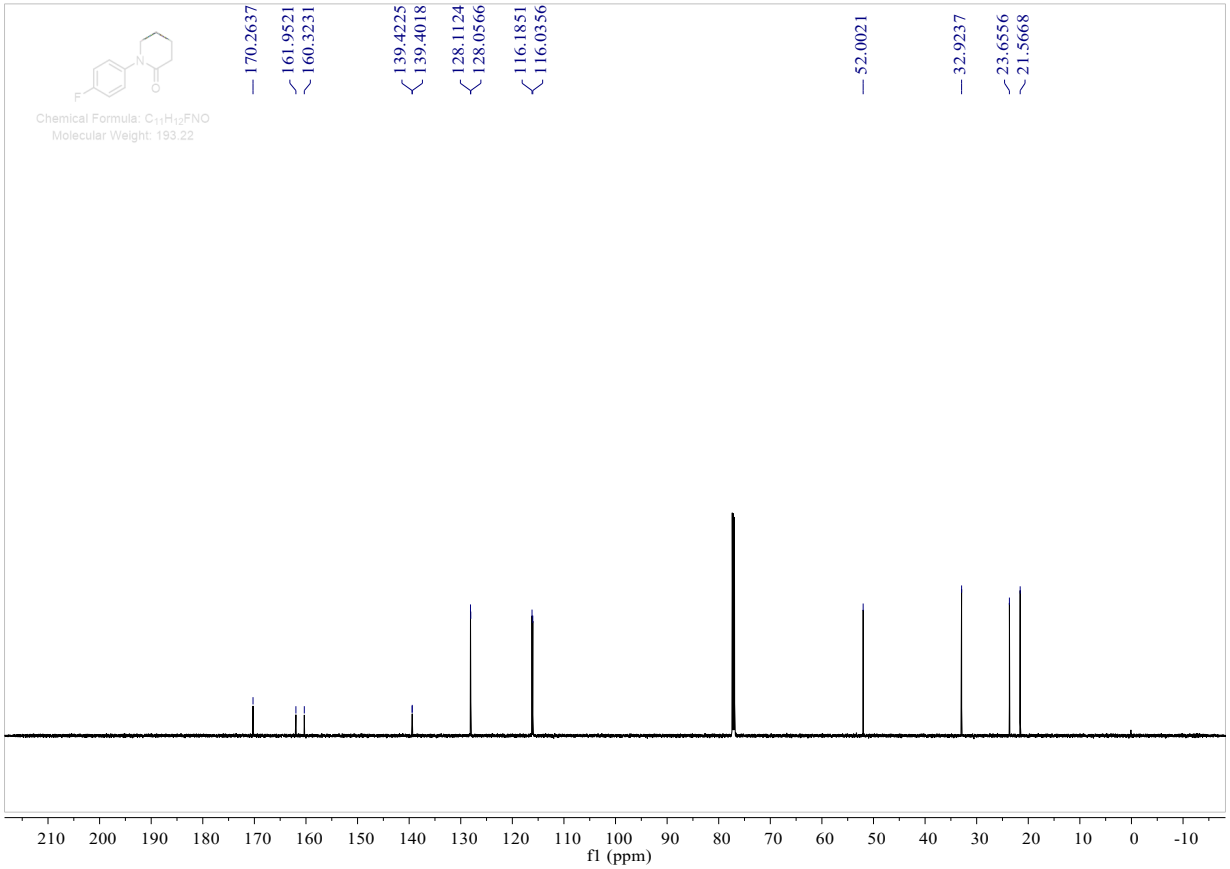
158.3066
134.9873
134.9698
117.6229
117.5712
116.0871
115.9364
38.3444
36.3876
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

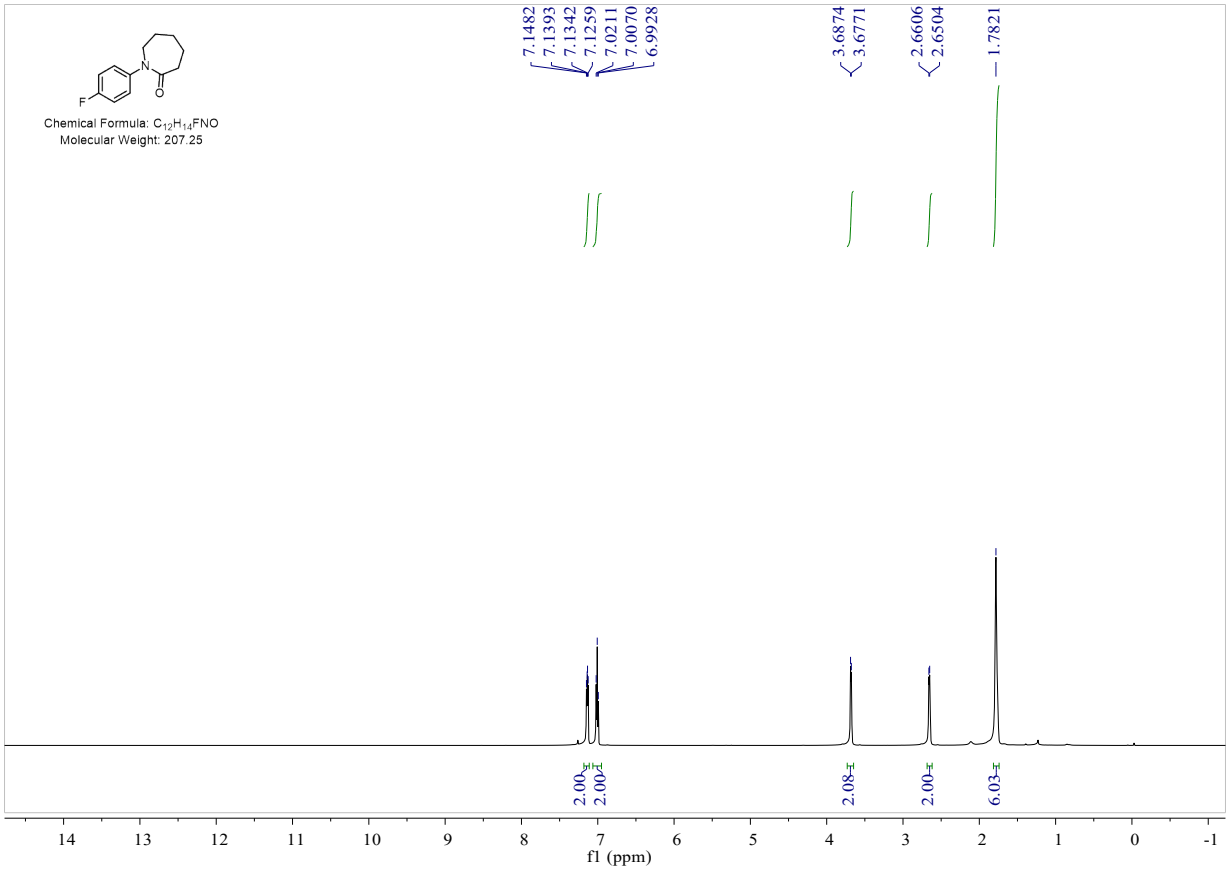
1-(4-Fluorophenyl)piperidin-2-one (5d).

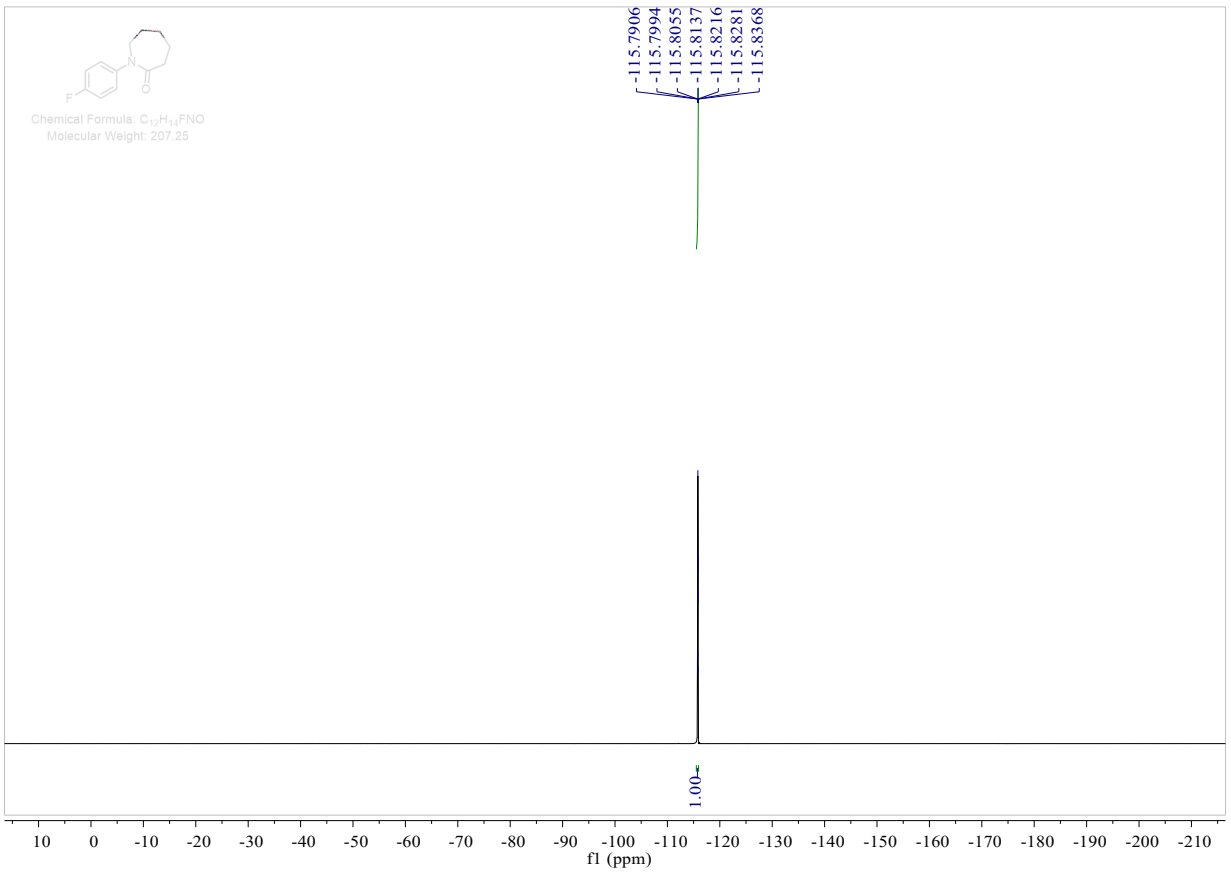






1-(4-Fluorophenyl)azepan-2-one (5e).




Chemical Formula: C12H14FNO
Molecular Weight: 207.25
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-115.8055
-115.8137
-115.8216
-115.8281
-115.8368
1.00
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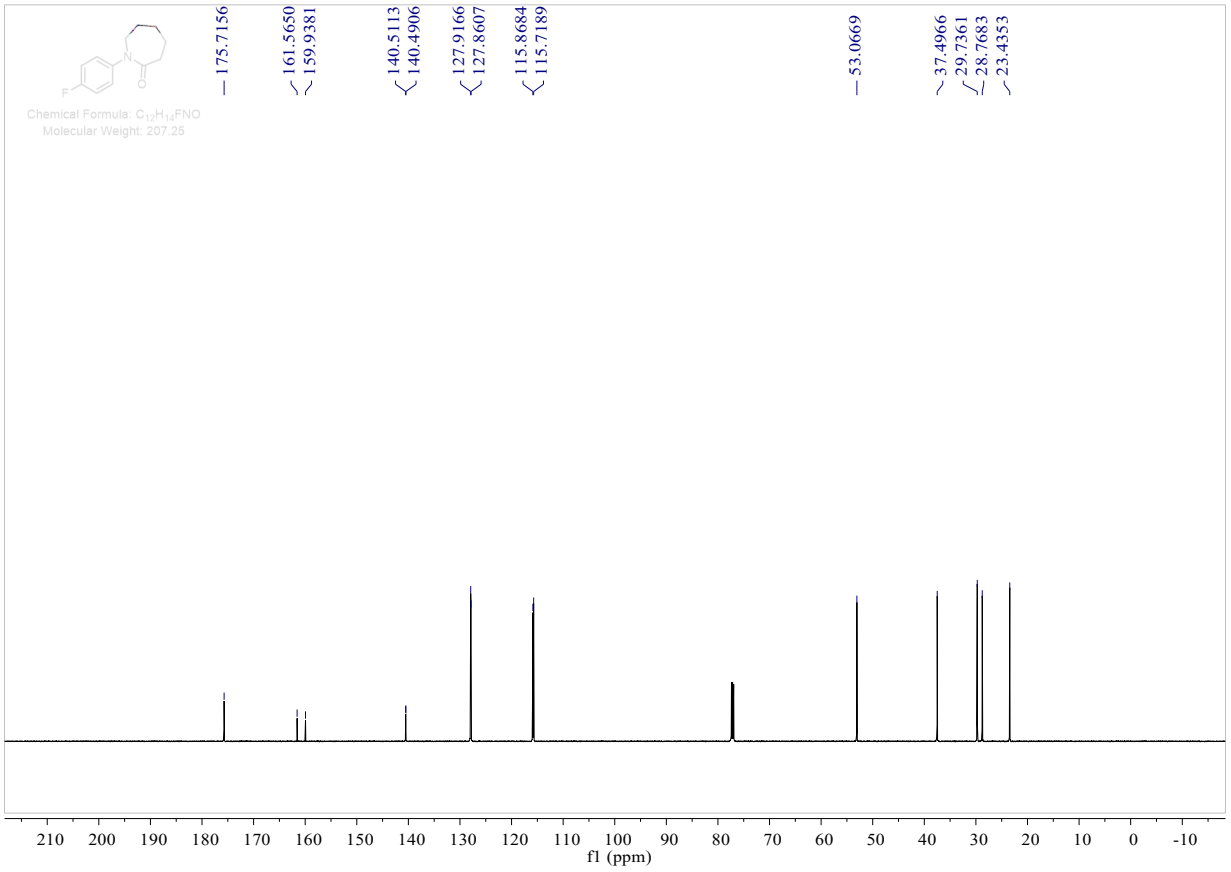
f1 (ppm)


Chemical Formula: C12H14FNO
Molecular Weight: 207.25
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159.9381
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140.4906
127.9166
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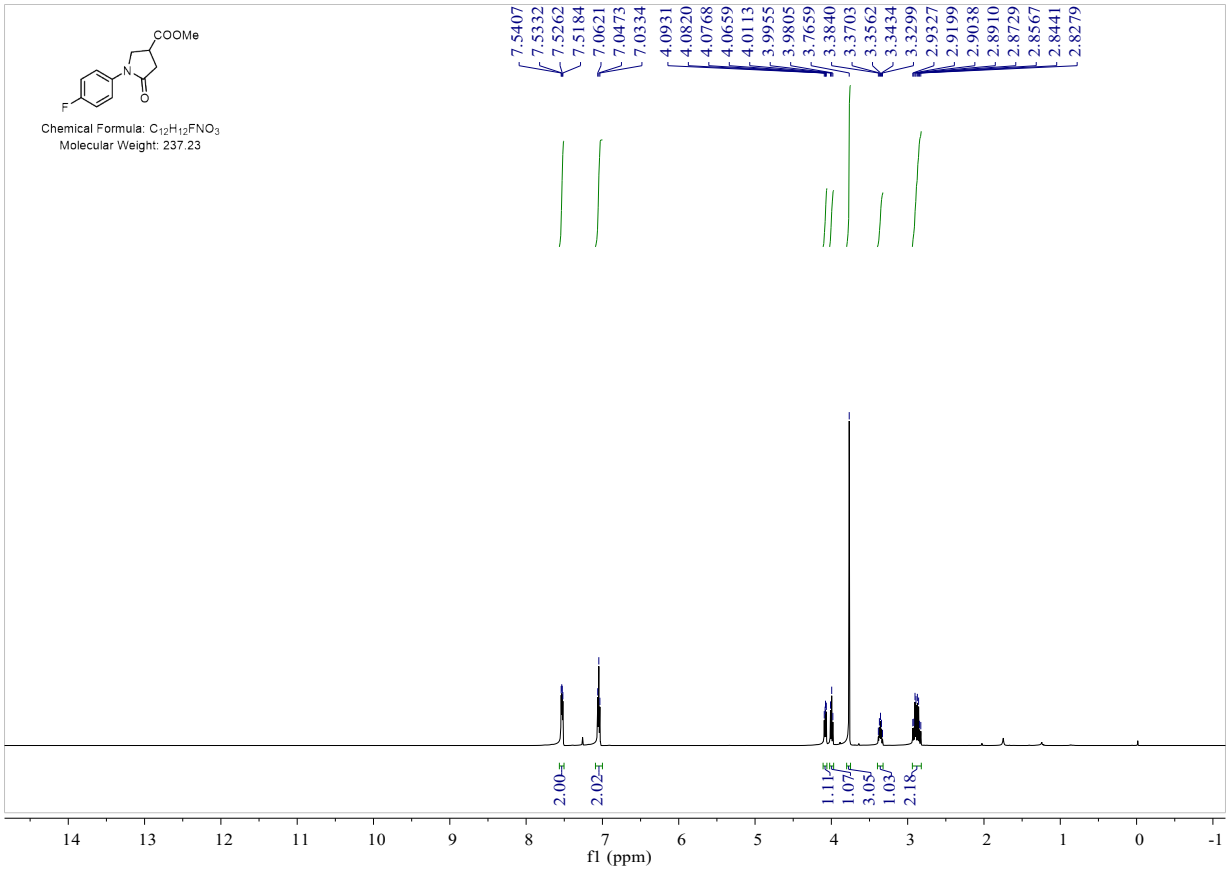
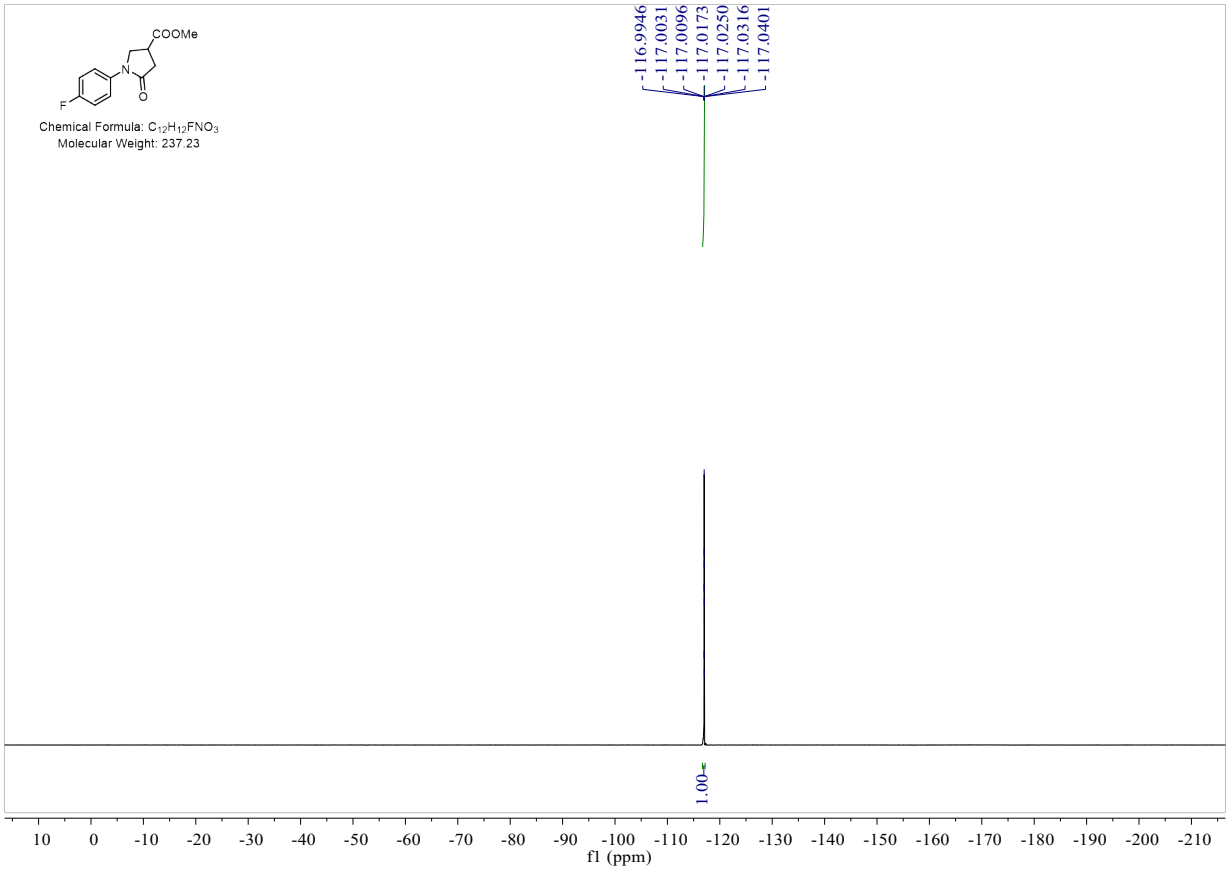
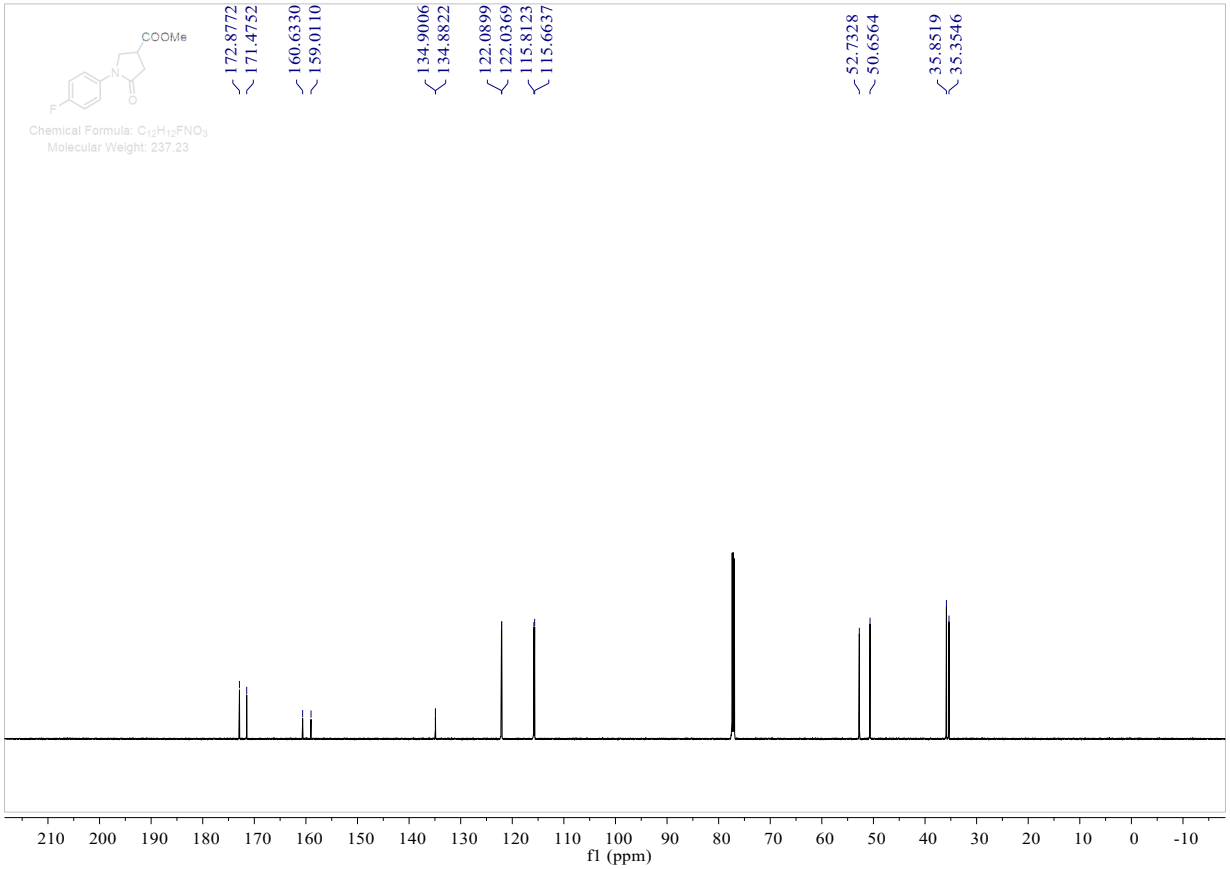
115.7189
53.0669
37.4966
29.7361
28.7683
23.4353
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

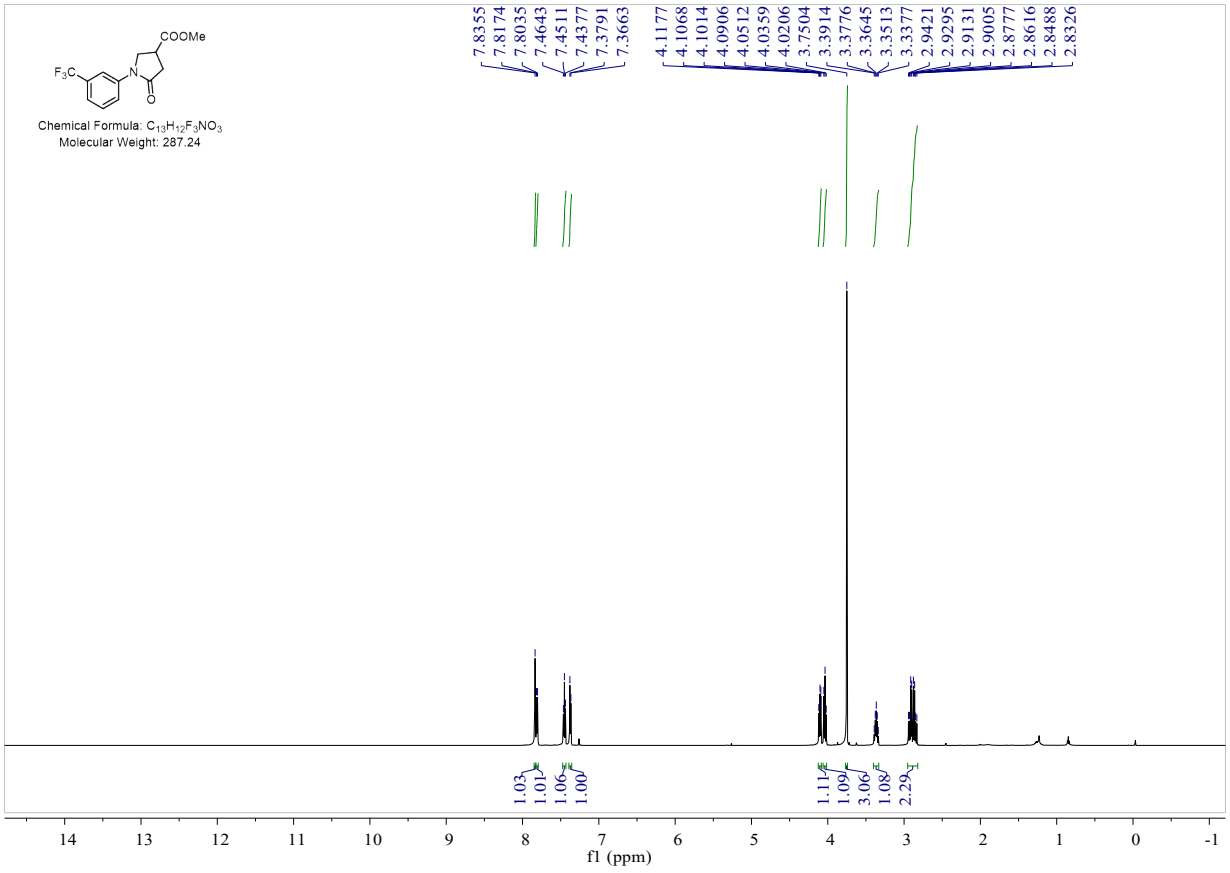
Methyl 1-(4-fluorophenyl)-5-oxopyrrolidine-3-carboxylate (5f).

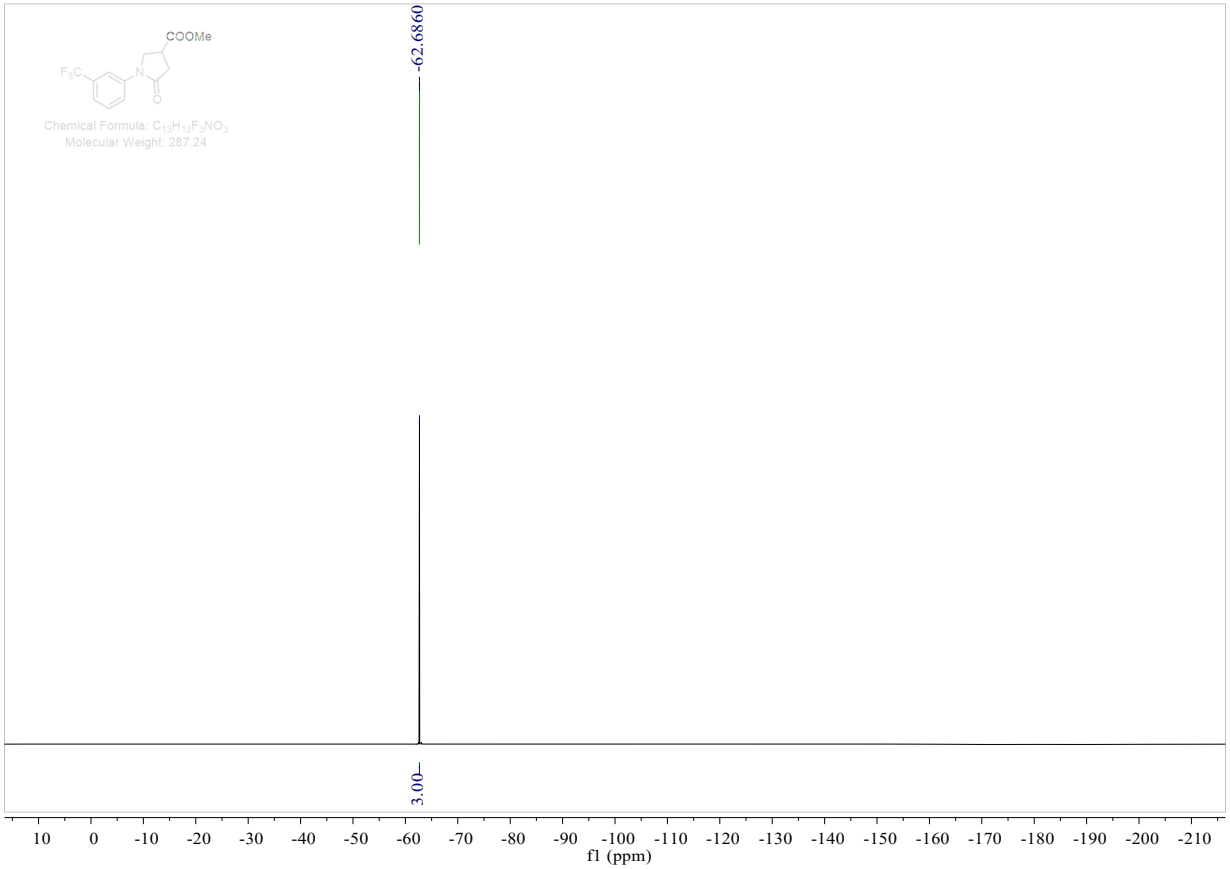






Methyl 5-oxo-1-(3-(trifluoromethyl)phenyl)pyrrolidine-3-carboxylate (5g).




COOMe
F3C
Chemical Formula: C13H10F3NO3
Molecular Weight: 287.24
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3.00
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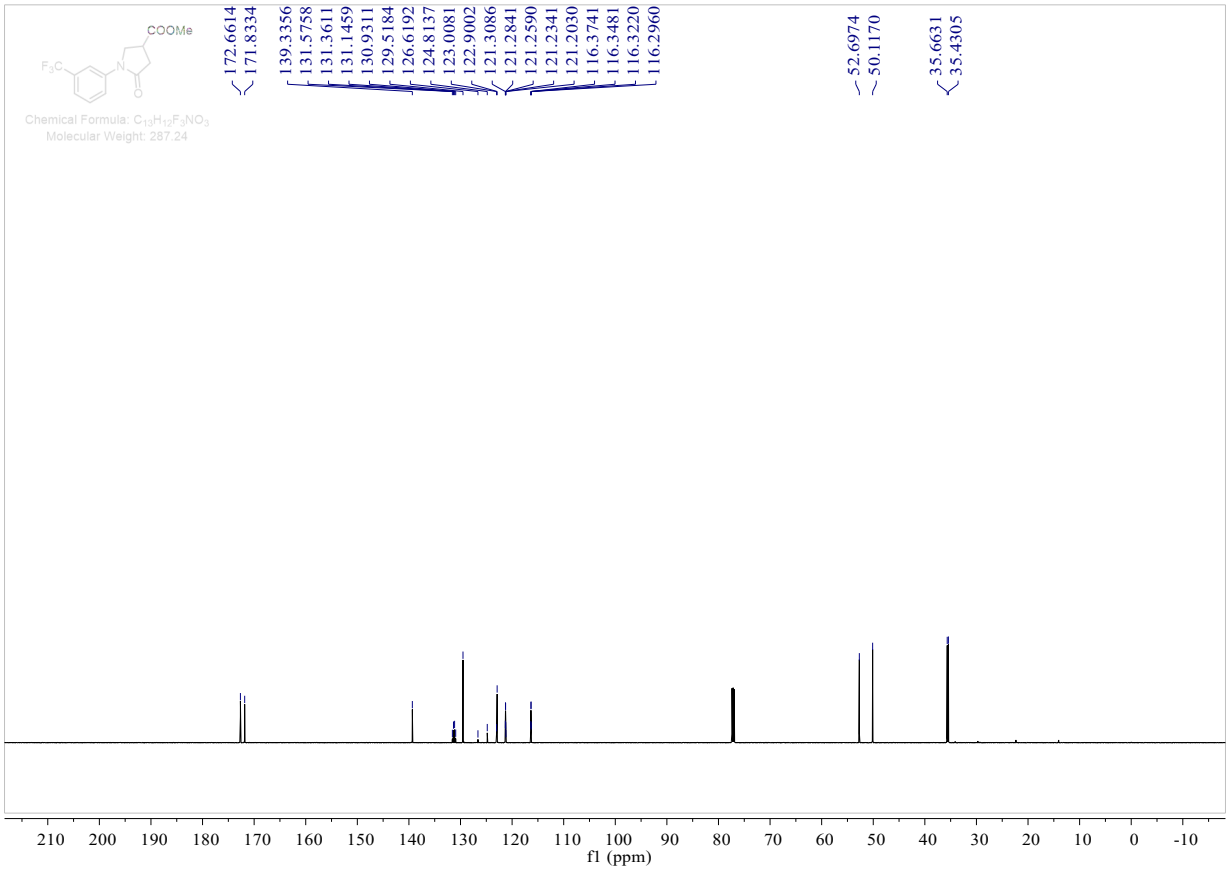
f1 (ppm)


COOMe
F3C
Chemical Formula: C13H10F3NO3
Molecular Weight: 287.24
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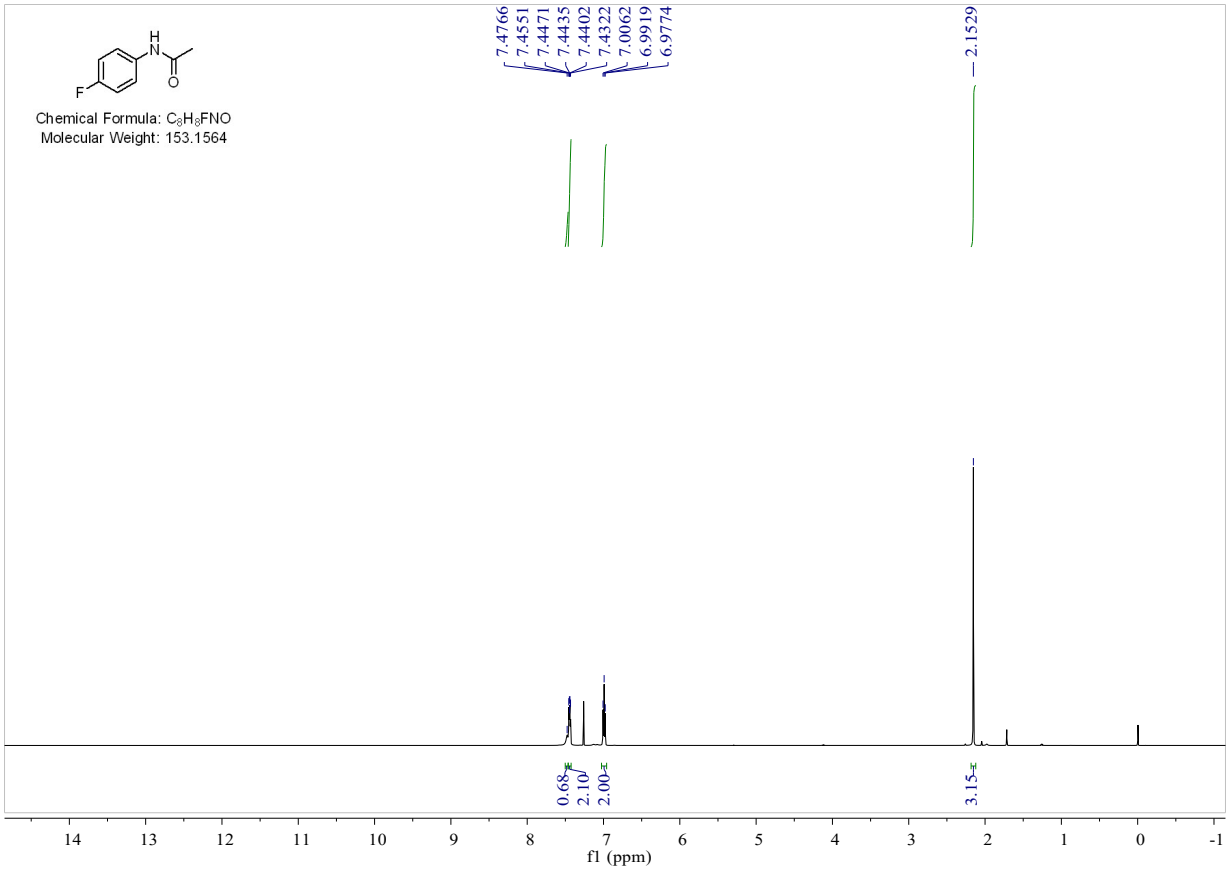
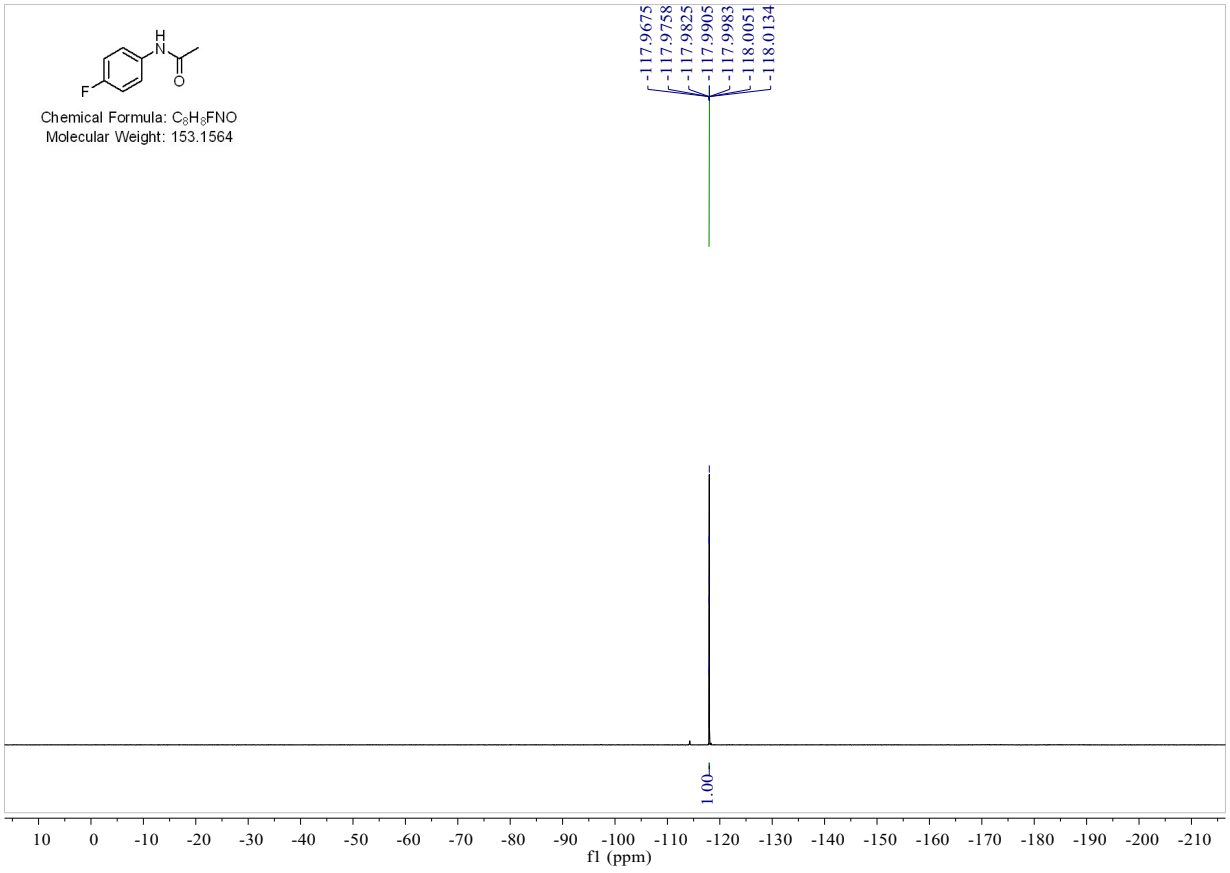
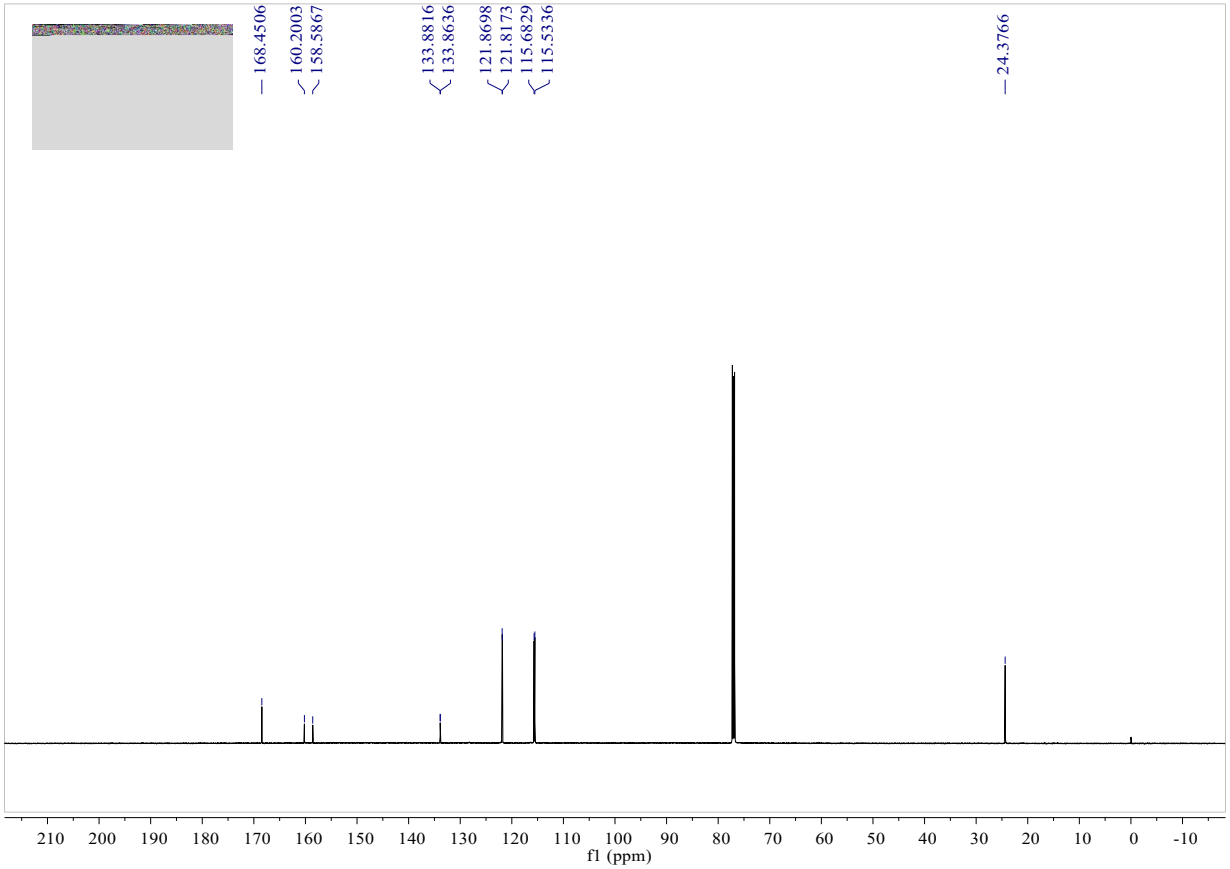
139.3356
131.5758
131.3611
131.1459
130.9311
129.5184
126.6192
124.8137
123.0081
122.9002
121.3086
121.2841
121.2590
121.2341
121.2030
116.3741
116.3481
116.3220
116.2960
52.6974
50.1170
35.6631
35.4305
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

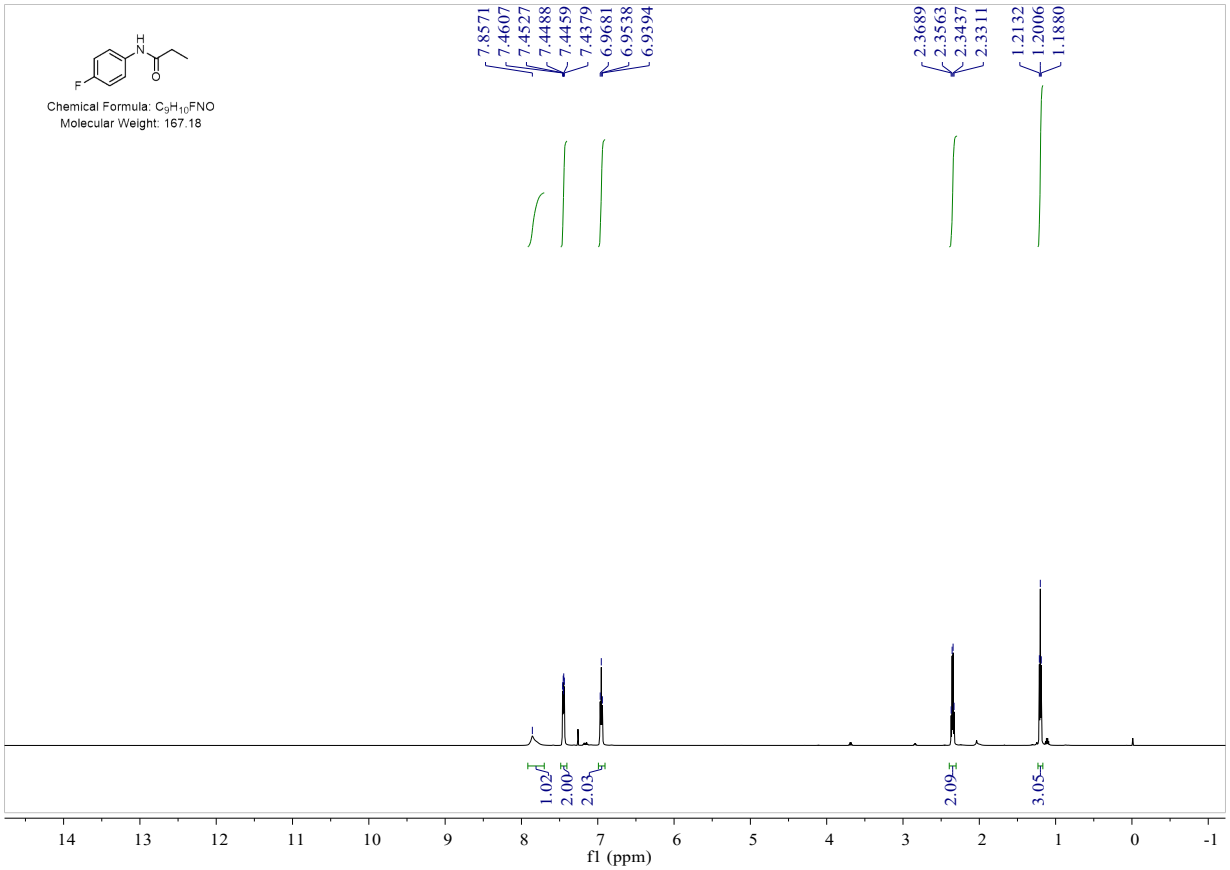
N-(4-fluorophenyl)acetamide (5h).

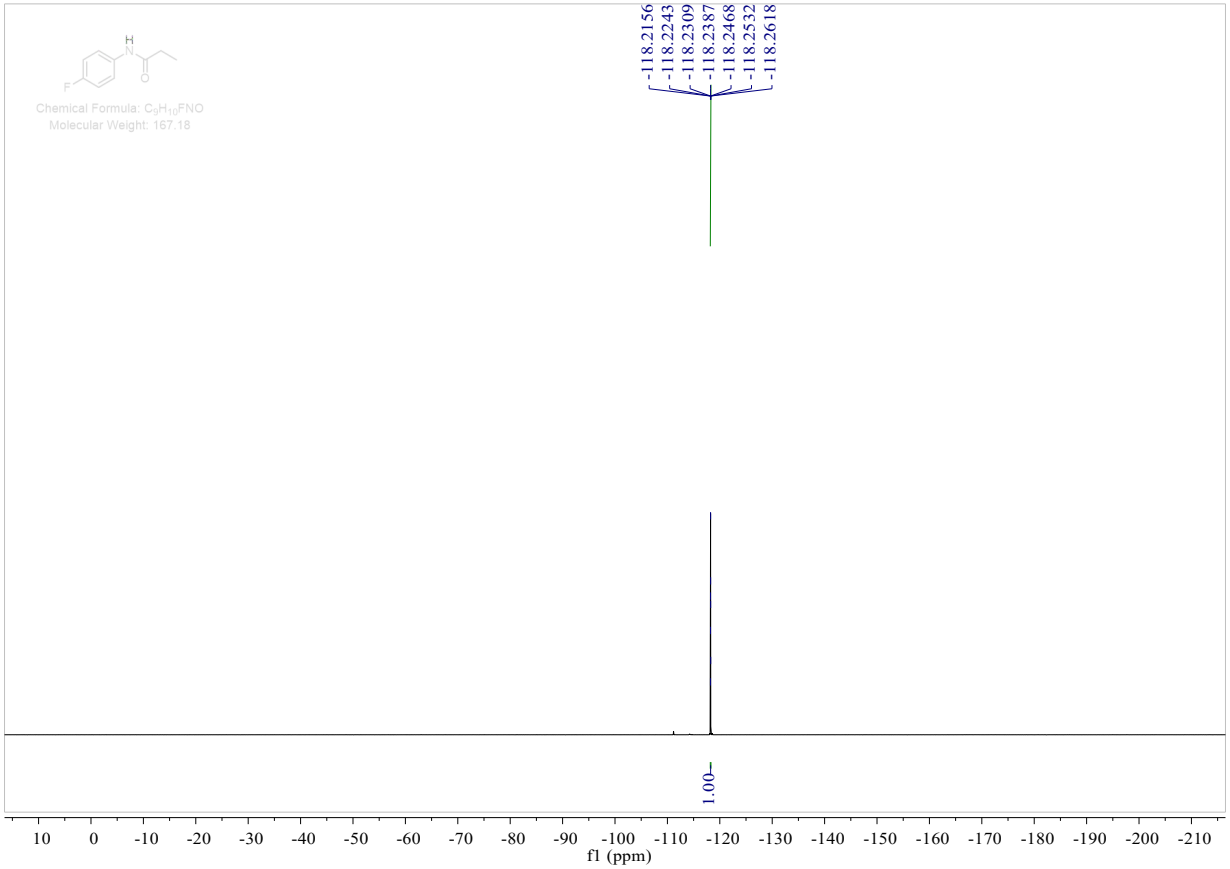






***N*-(4-fluorophenyl)propionamide (5i).**

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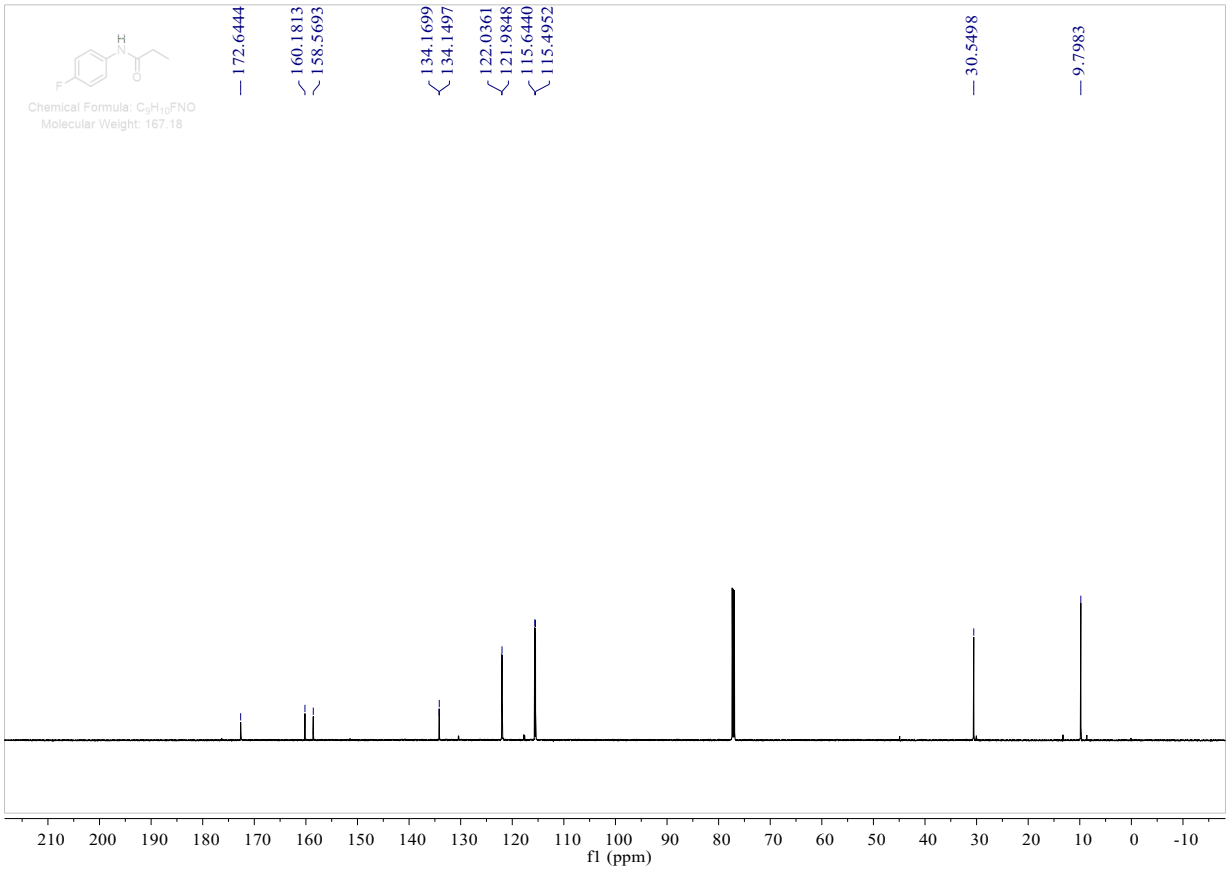
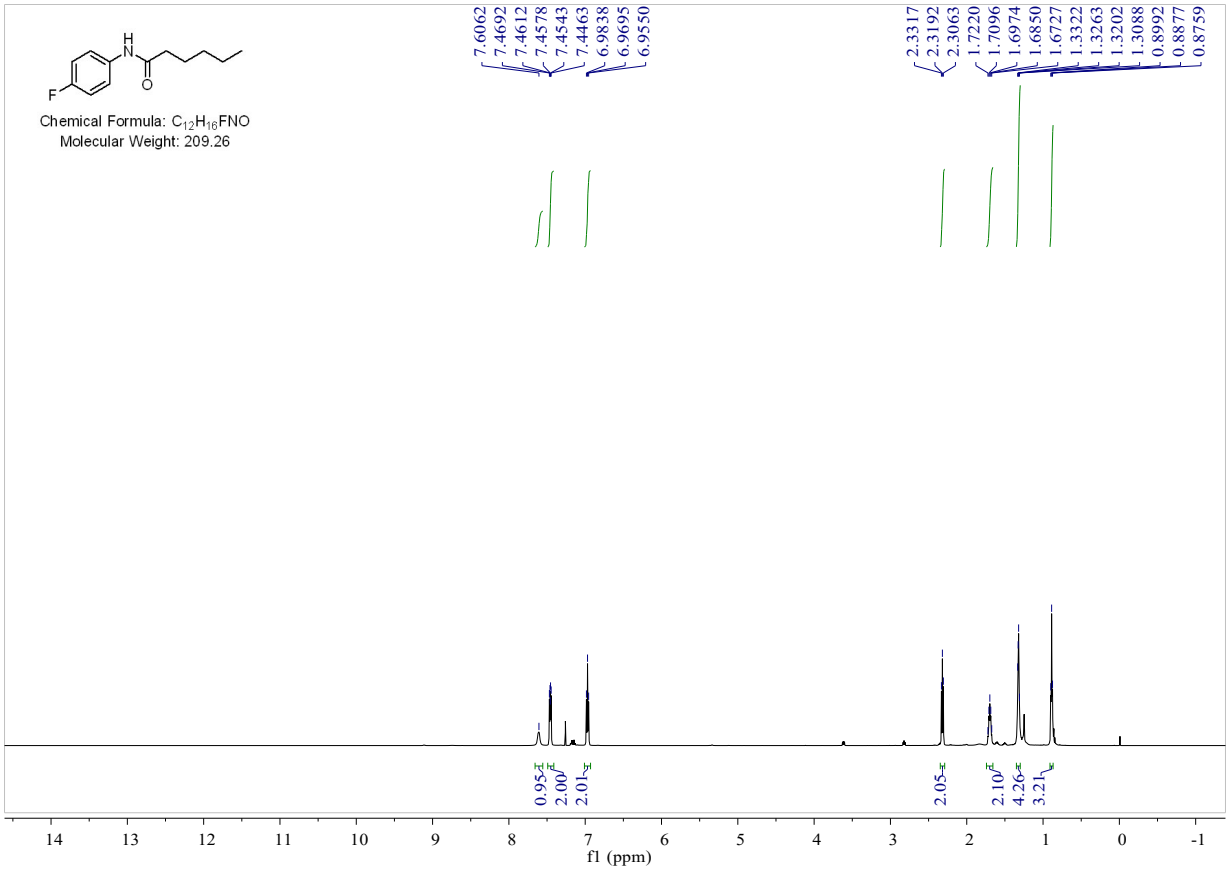
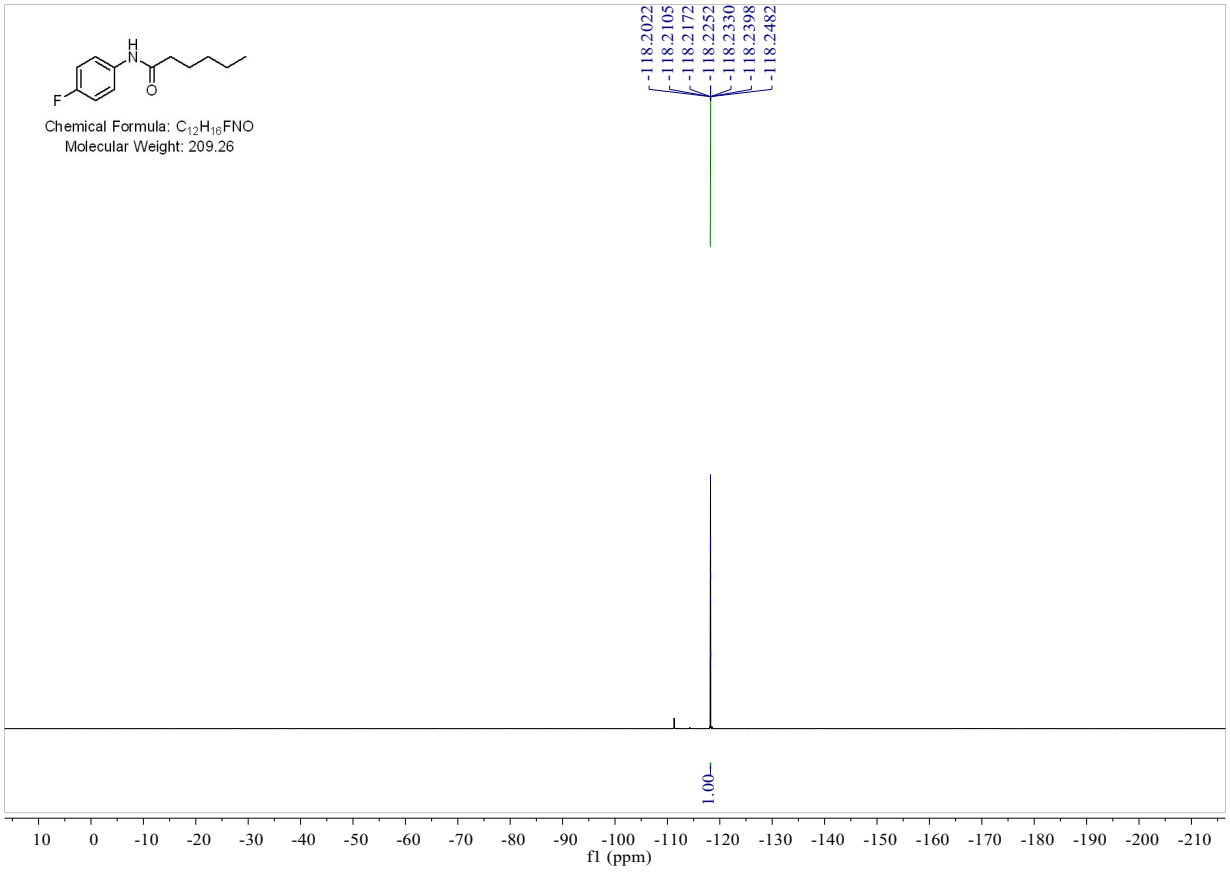
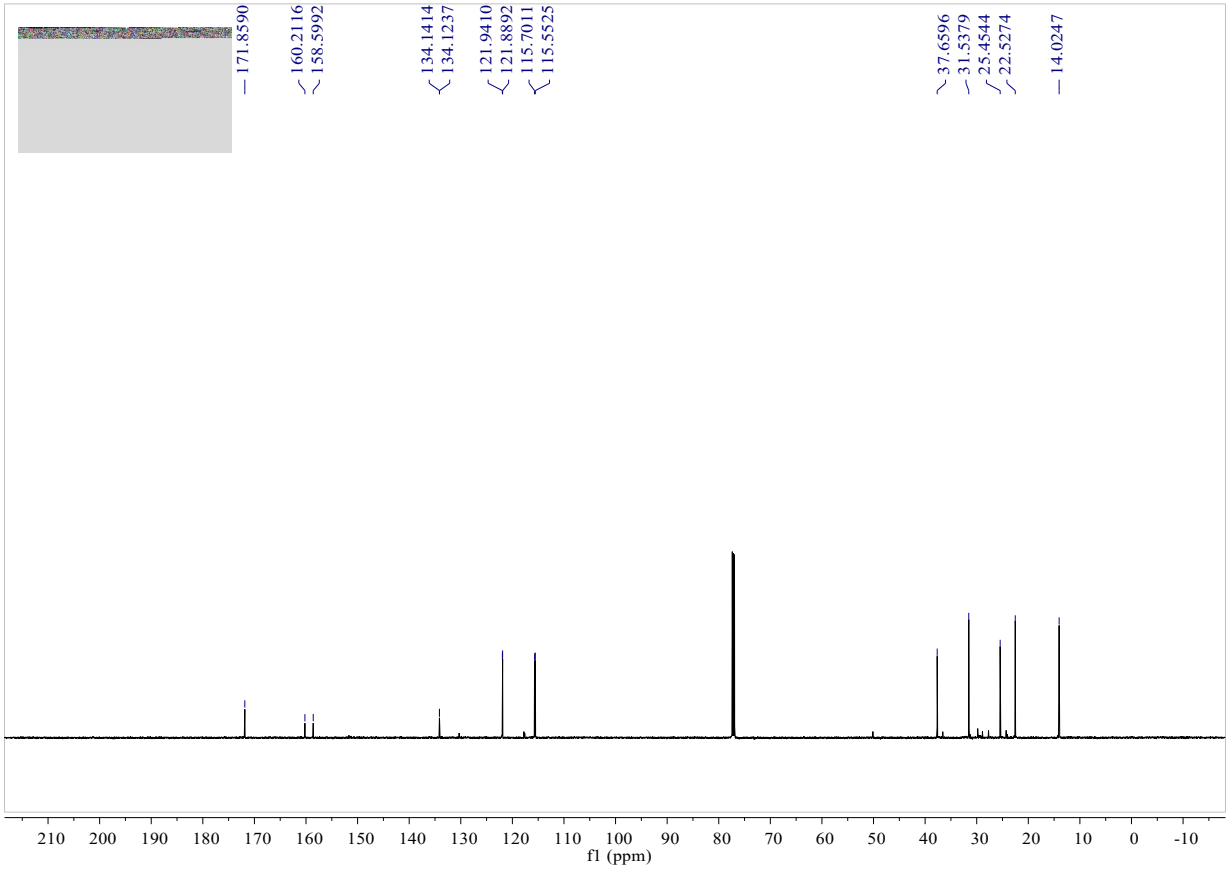
-118.2309
-118.2387
-118.2468
-118.2532
-118.2618
Chemical Formula: C9H10FNO
Molecular Weight: 167.18
1.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


172.6444
160.1813
158.5693
134.1699
134.1497
122.0361
121.9848
115.6440
115.4952
30.5498
9.7983
Chemical Formula: C9H10FNO
Molecular Weight: 167.18
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

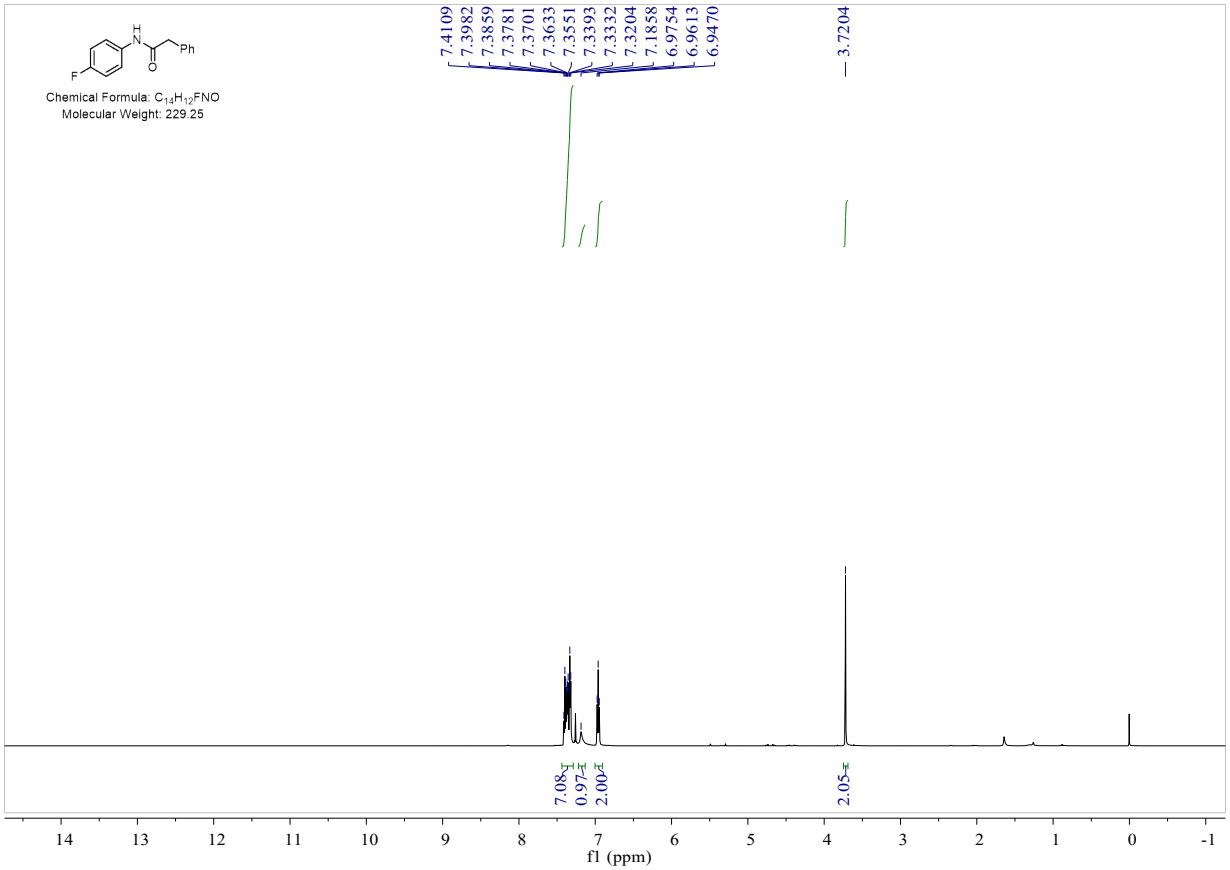
N-(4-fluorophenyl)hexanamide (5j).

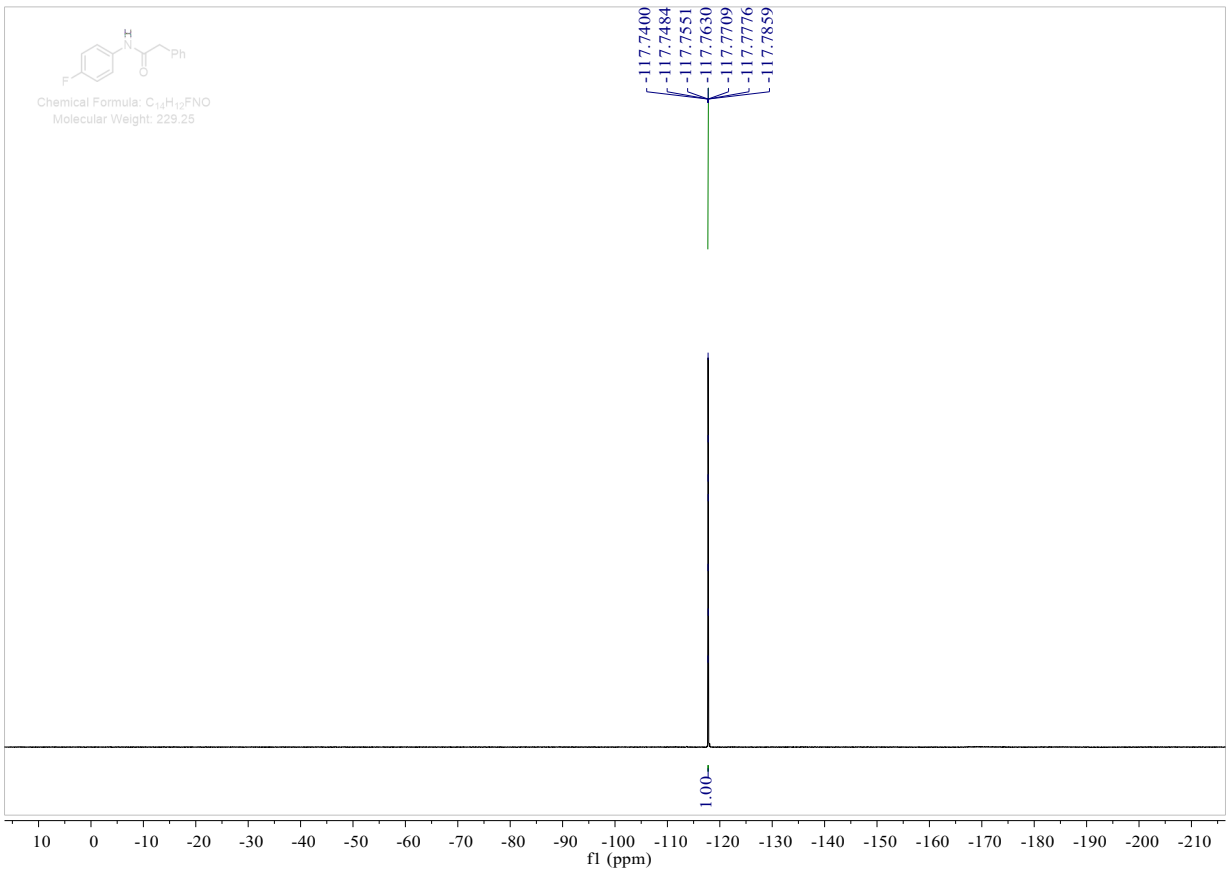






N-(4-fluorophenyl)-2-phenylacetamide (5k).




Chemical Formula: C14H12FNO
Molecular Weight: 229.25
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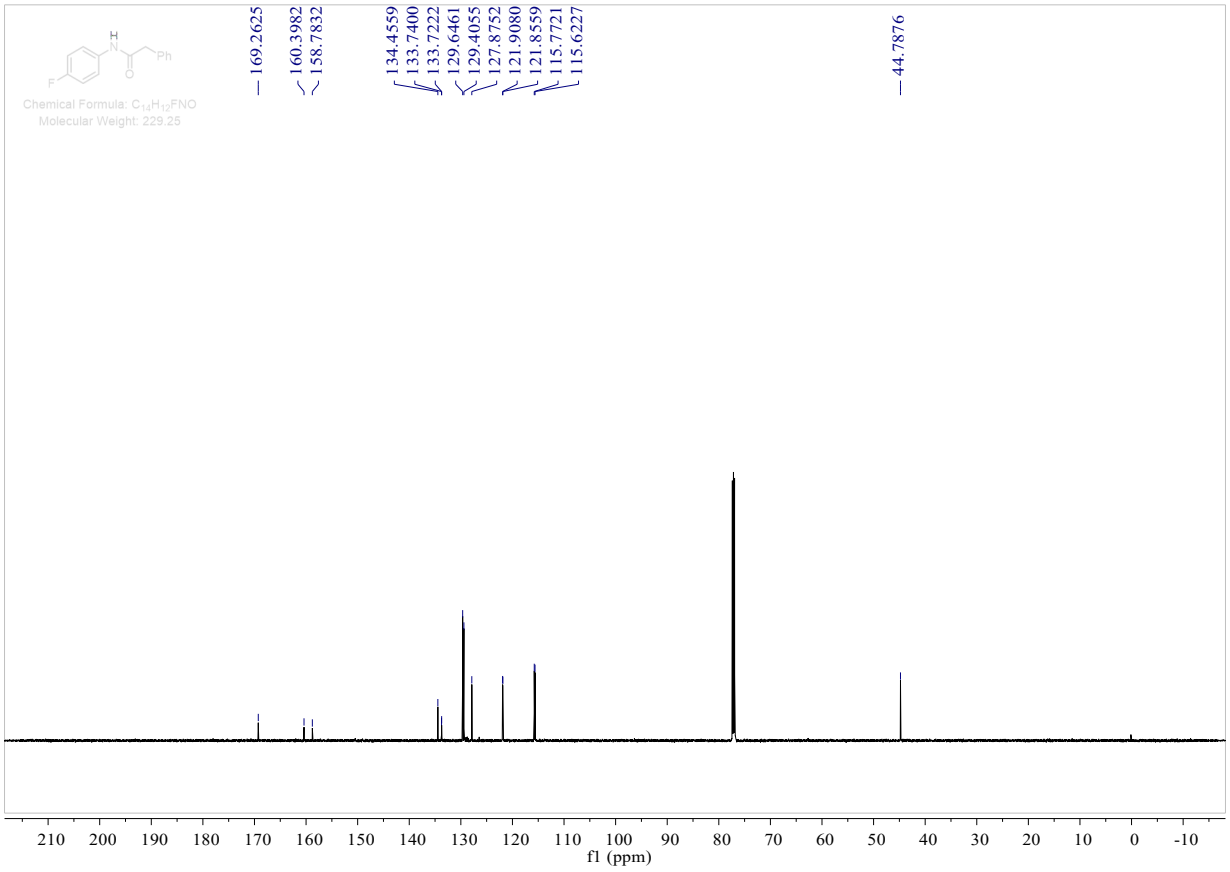
-117.7630
-117.7709
-117.7776
-117.7859
1.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


Chemical Formula: C14H12FNO
Molecular Weight: 229.25
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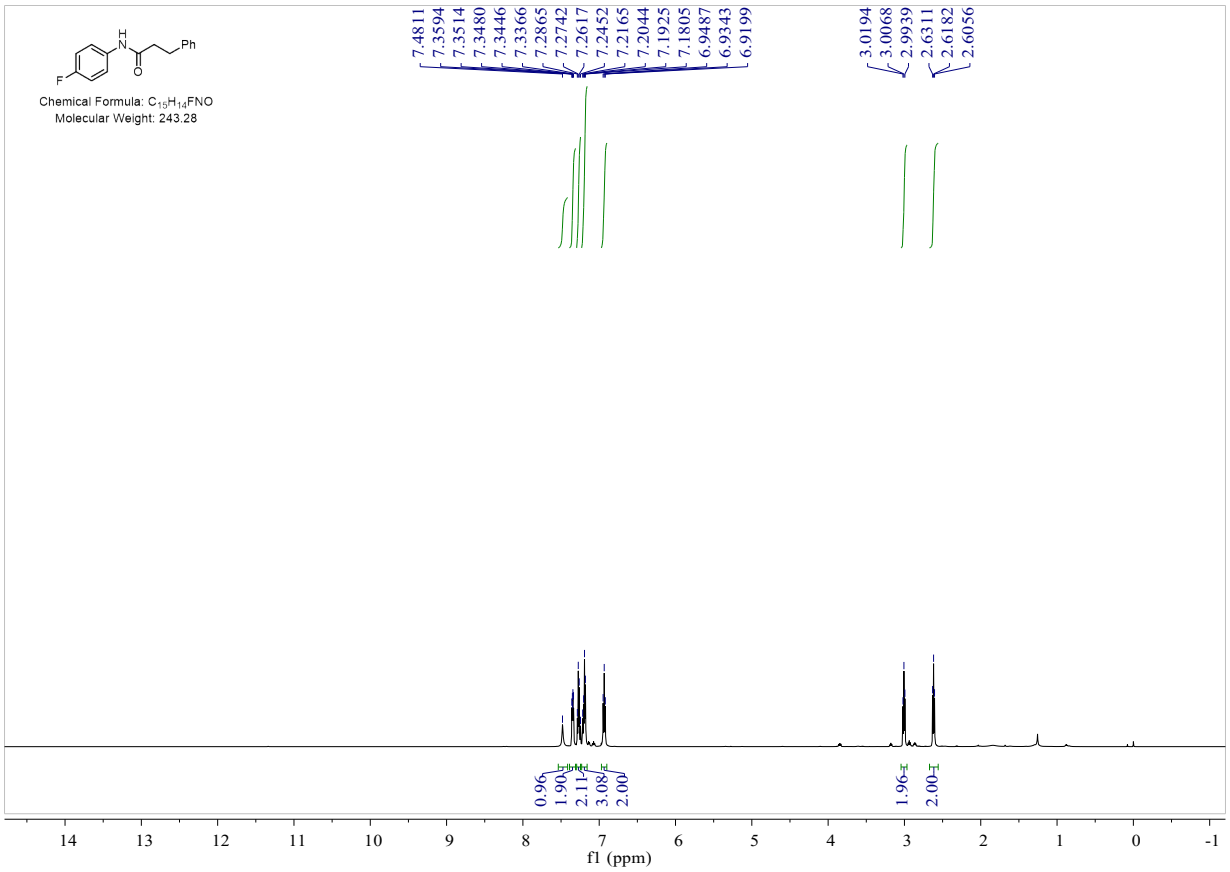
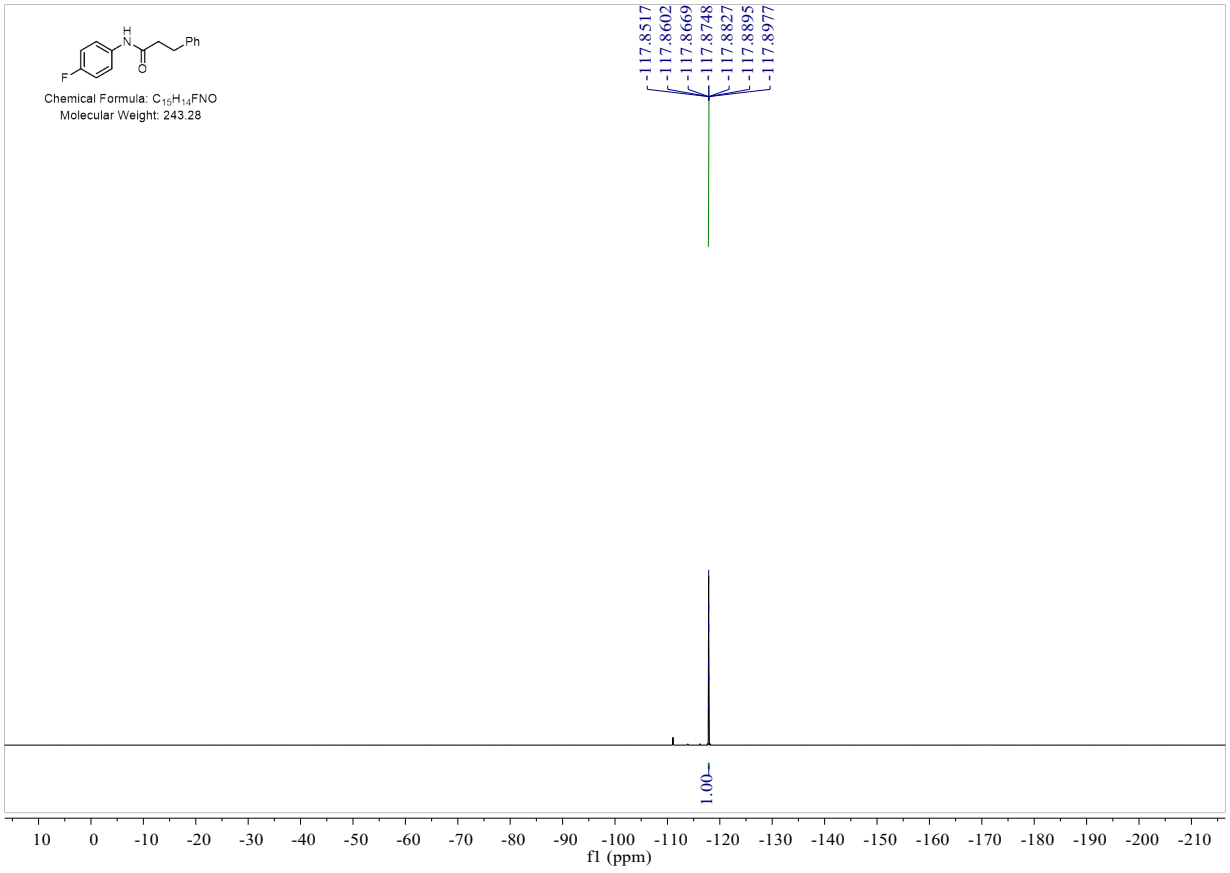
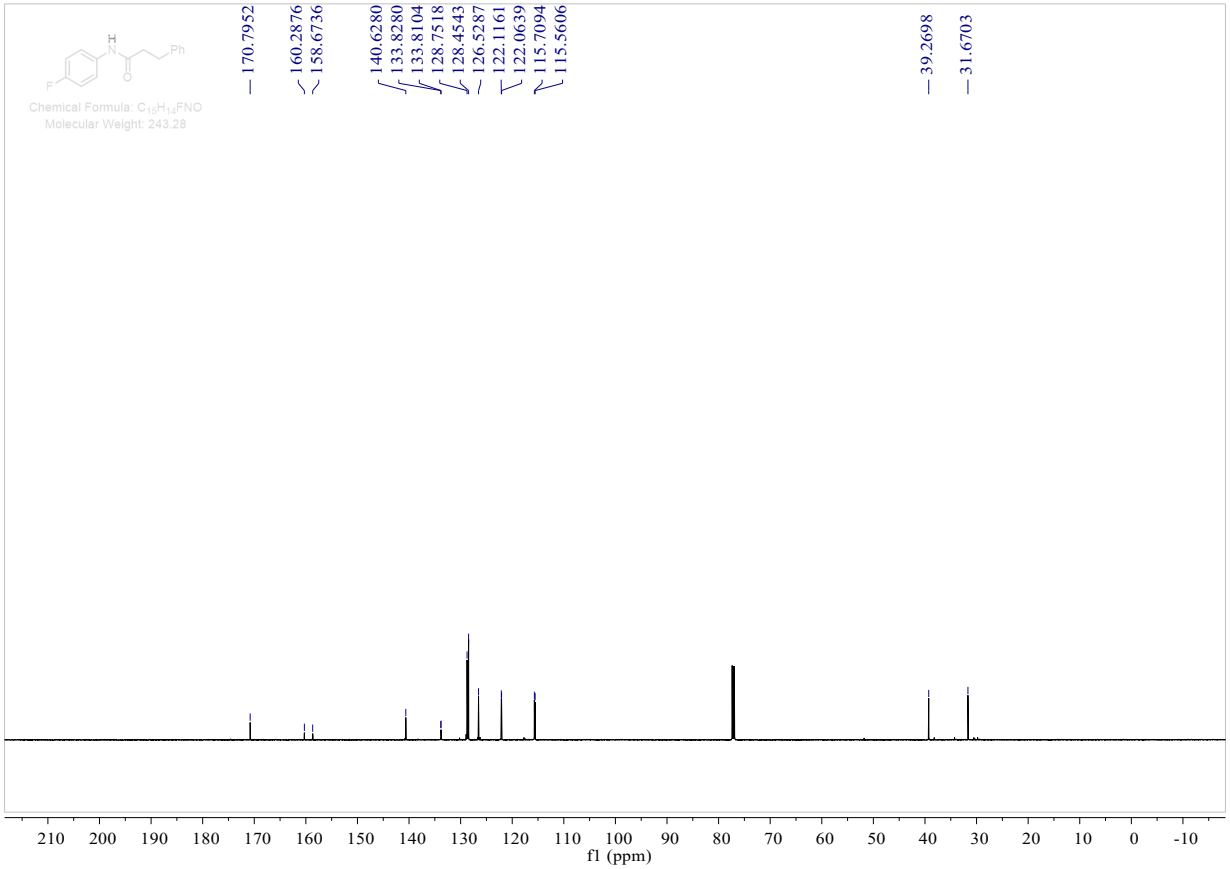
160.3982
158.7832
134.4559
133.7400
133.7222
129.6461
129.4055
127.8752
121.9080
121.8559
115.7721
115.6227
44.7876
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

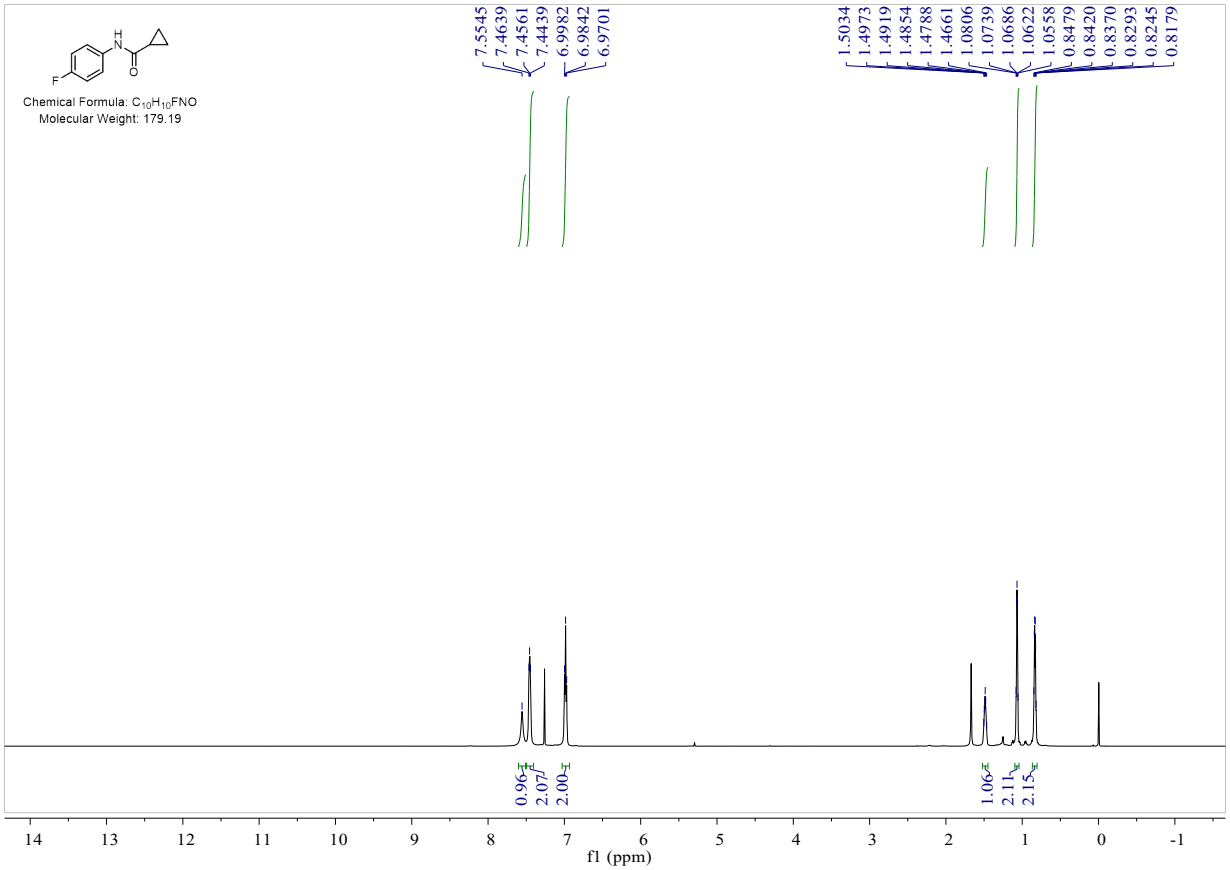
N-(4-fluorophenyl)-3-phenylpropanamide (5l).

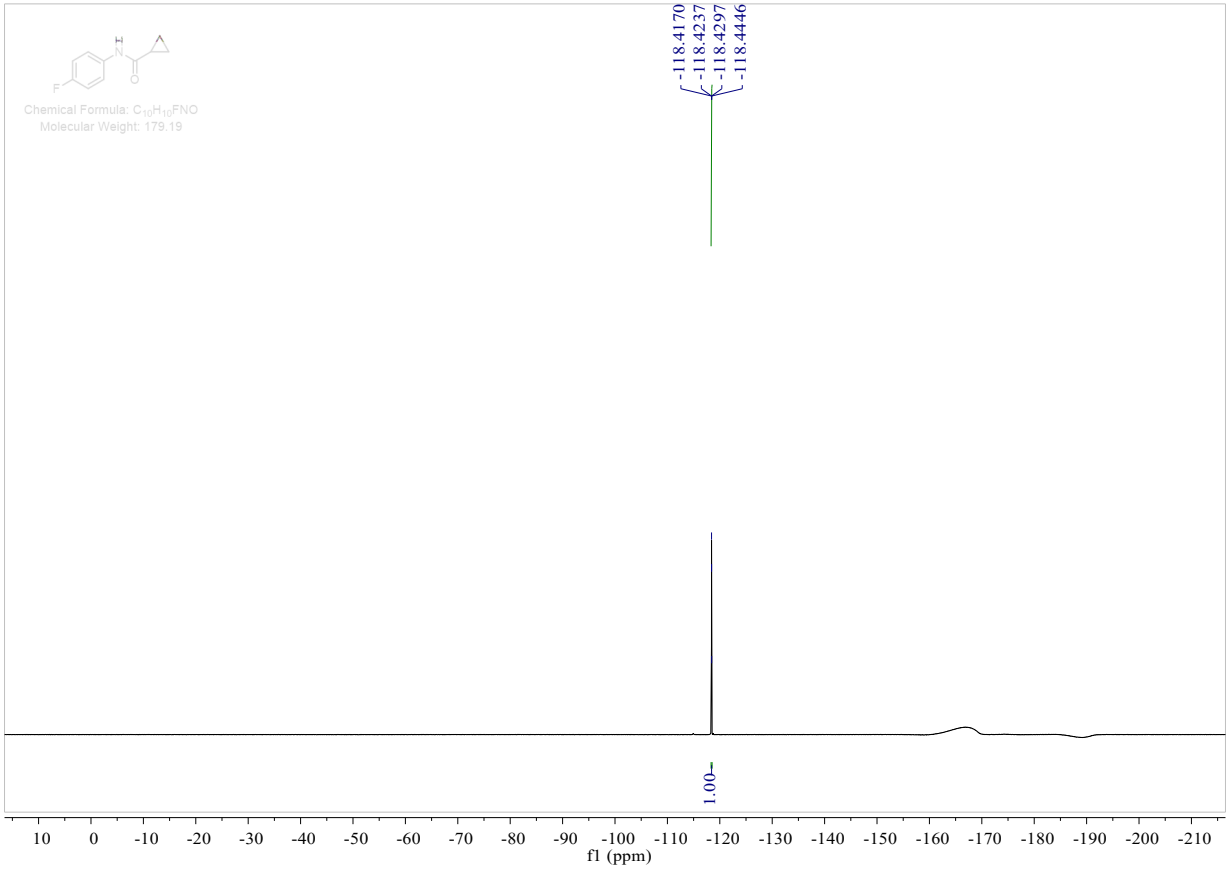


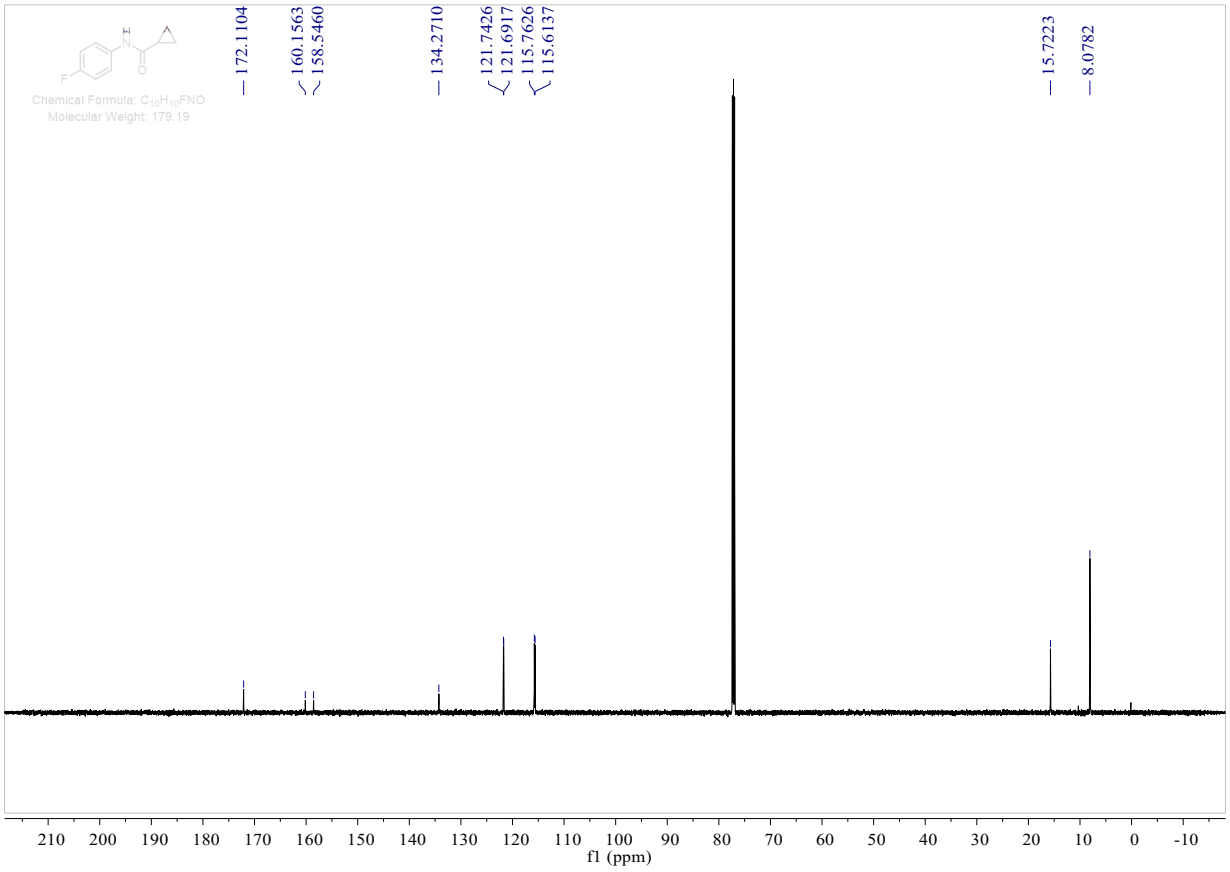




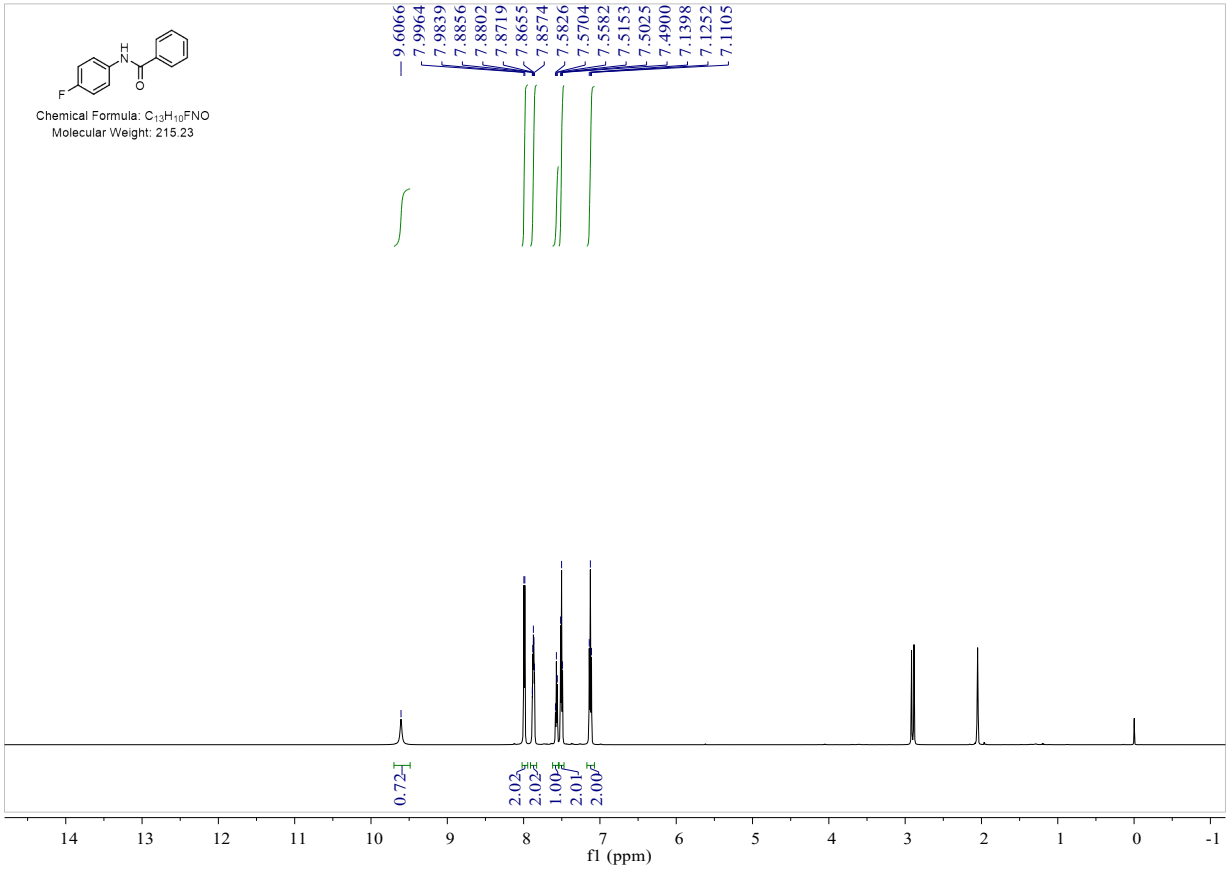
N-(4-fluorophenyl)cyclopropanecarboxamide (5m).







_N_-(4-fluorophenyl)benzamide (5n).


Chemical Formula: C13H10FNO
Molecular Weight: 215.23
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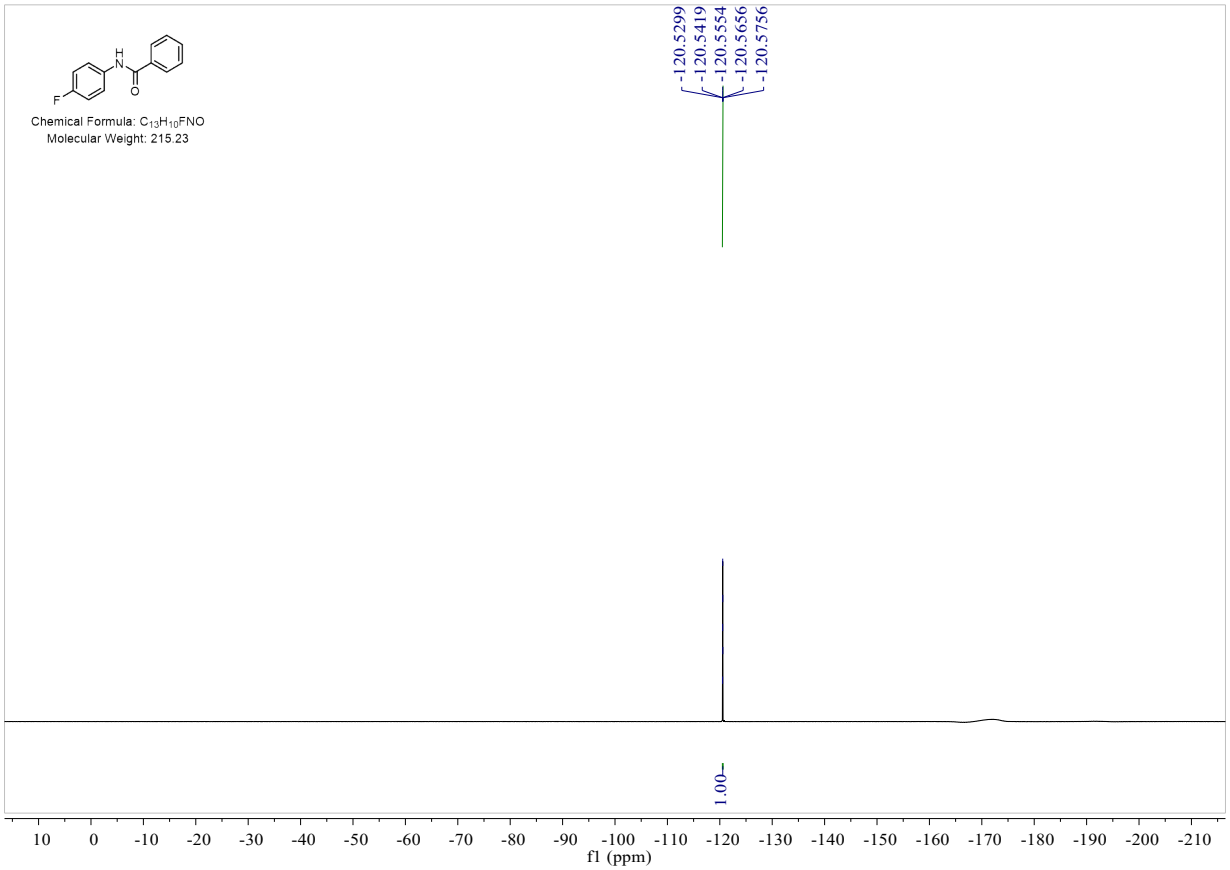
7.9964
7.9839
7.8856
7.8802
7.8719
7.8655
7.8574
7.5826
7.5704
7.5582
7.5153
7.5025
7.4900
7.1398
7.1252
7.1105
0.72
2.02
2.02
1.00
2.01
2.00
f1 (ppm)


Chemical Formula: C13H10FNO
Molecular Weight: 215.23
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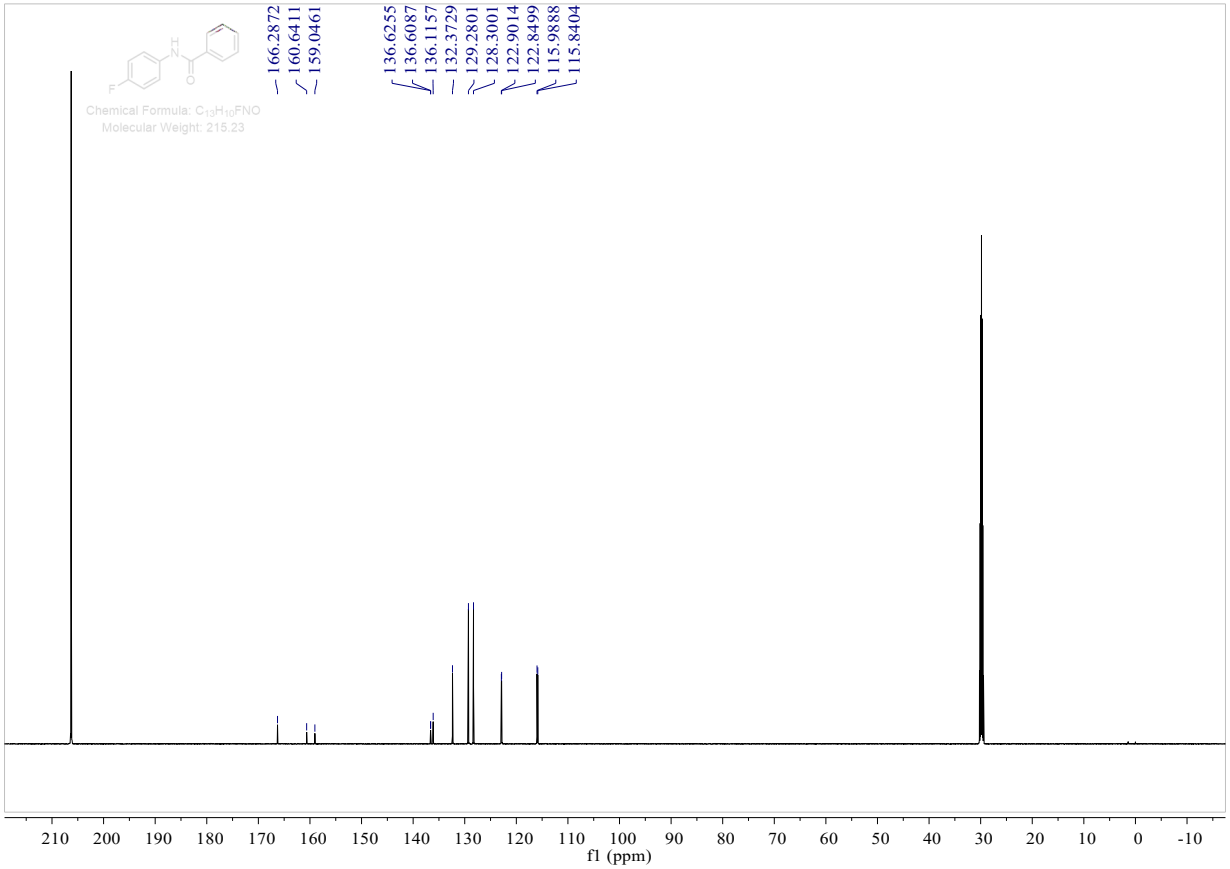
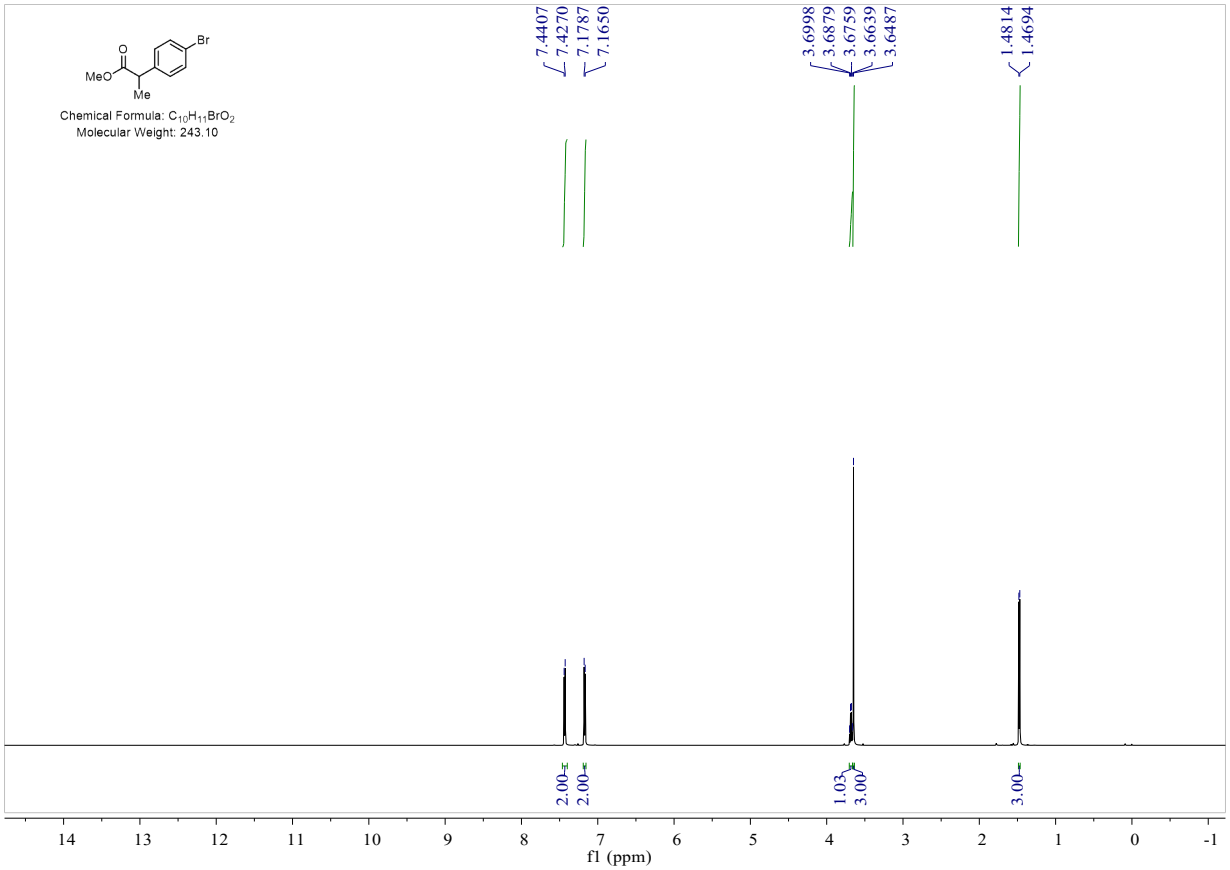
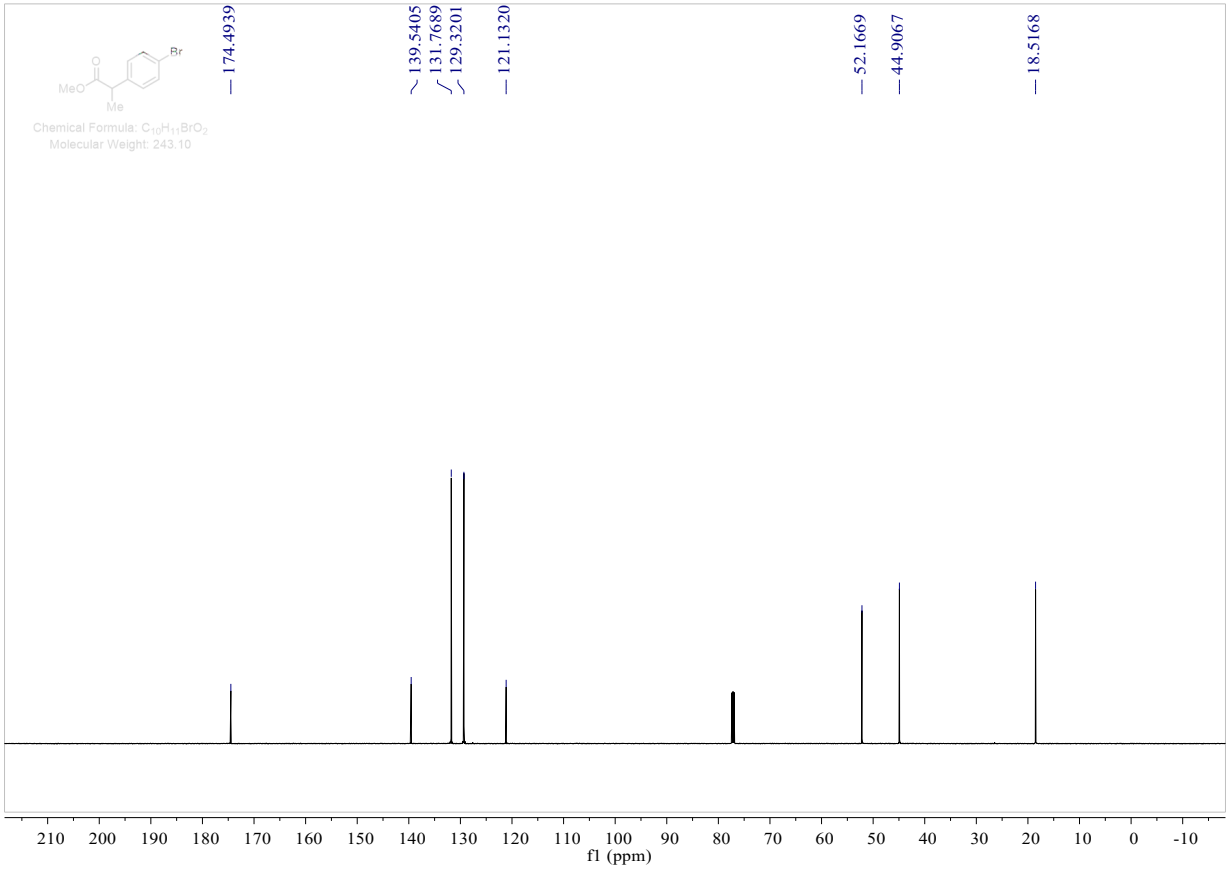
-120.5554
-120.5656
-120.5756
1.00
f1 (ppm)

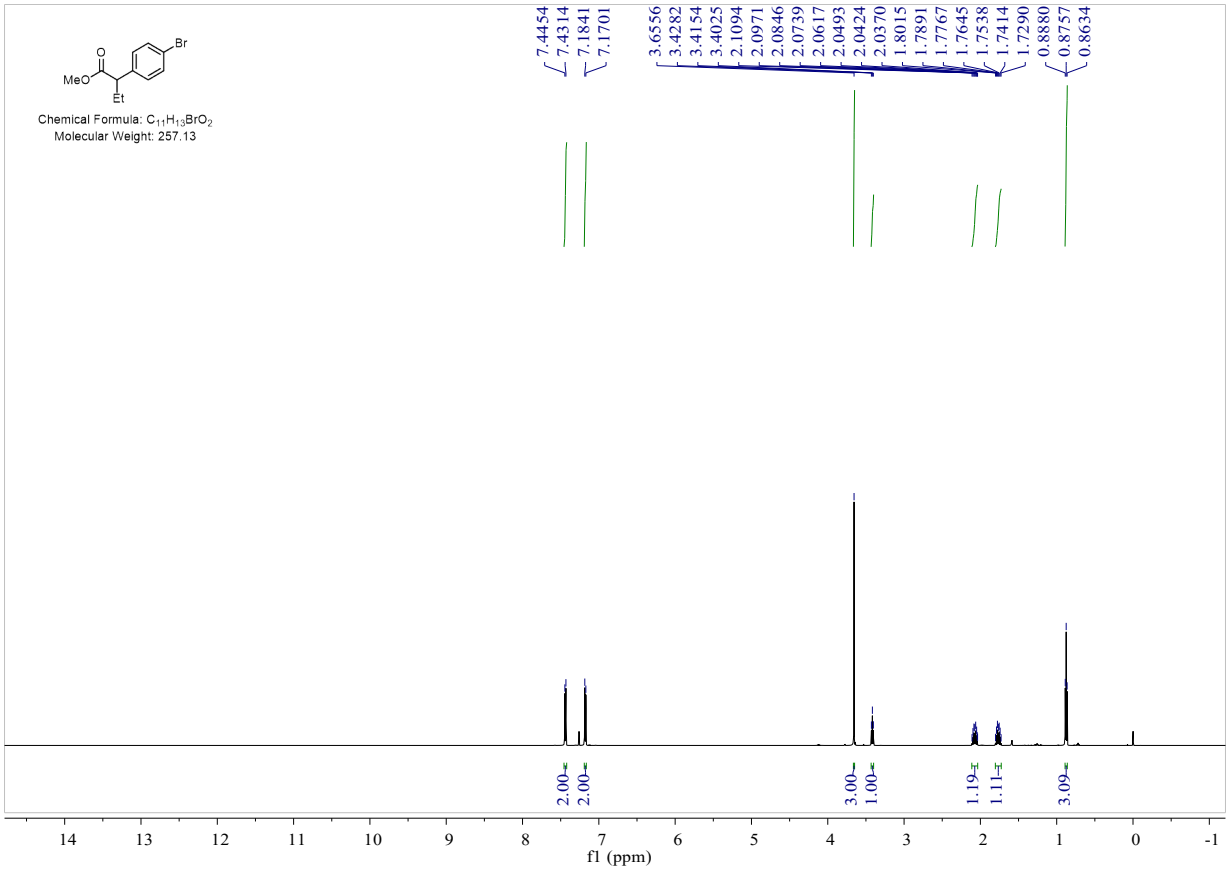


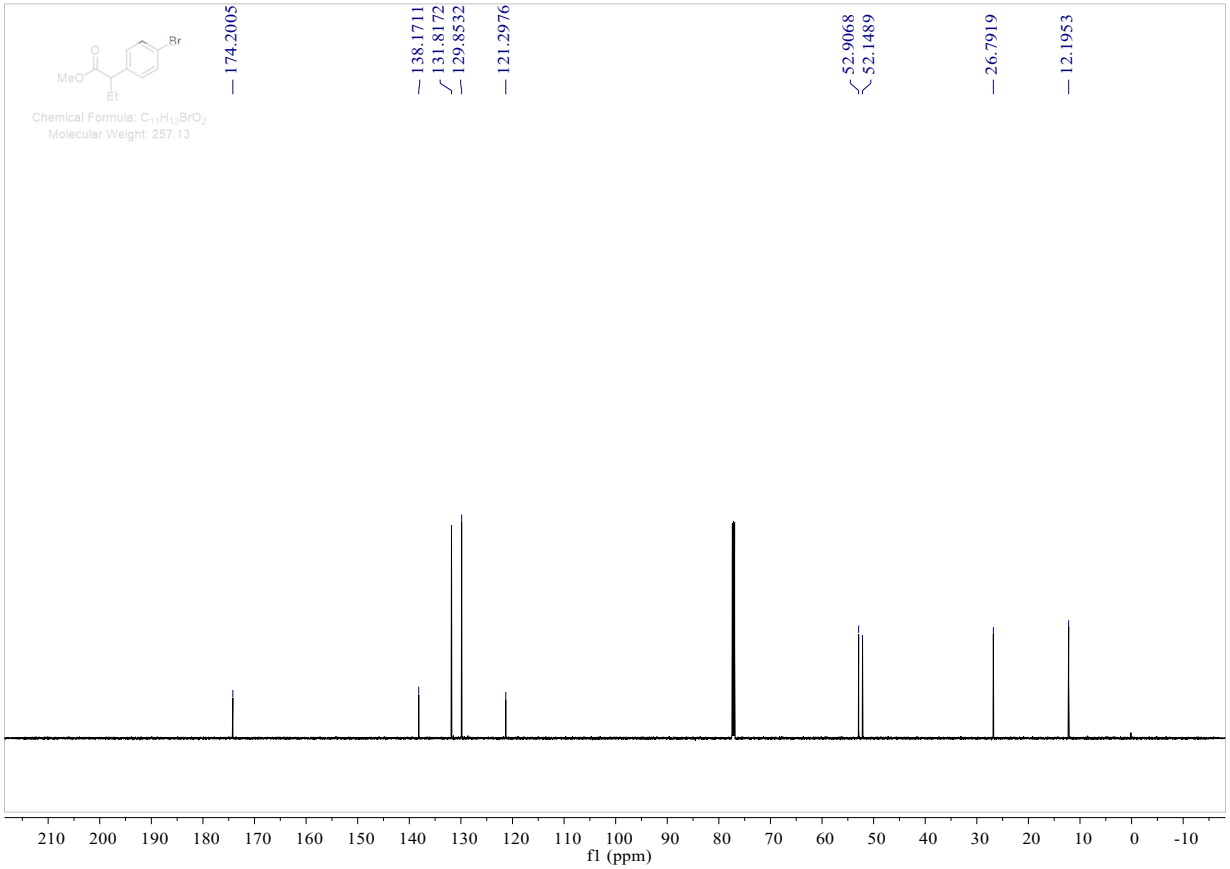
Methyl 2-(4-bromophenyl)propanoate (1za).



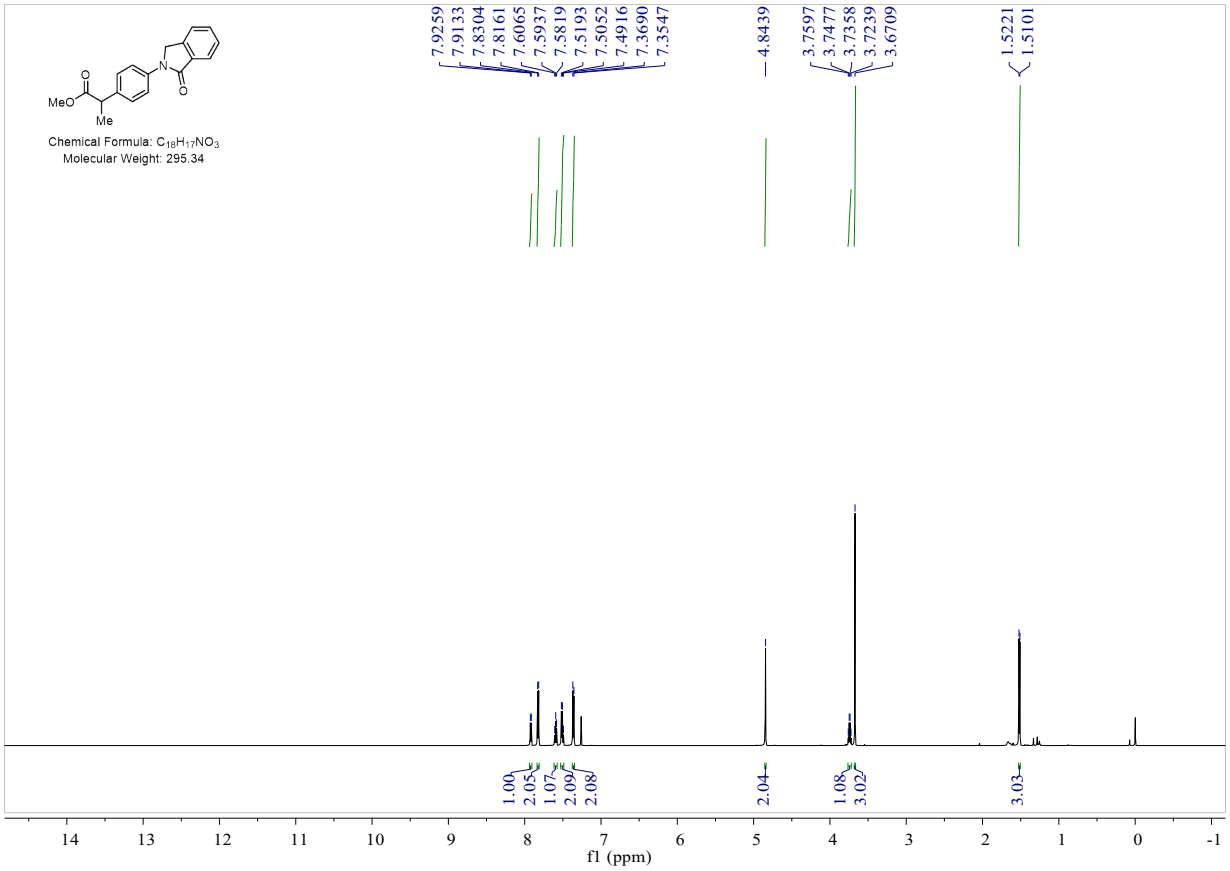


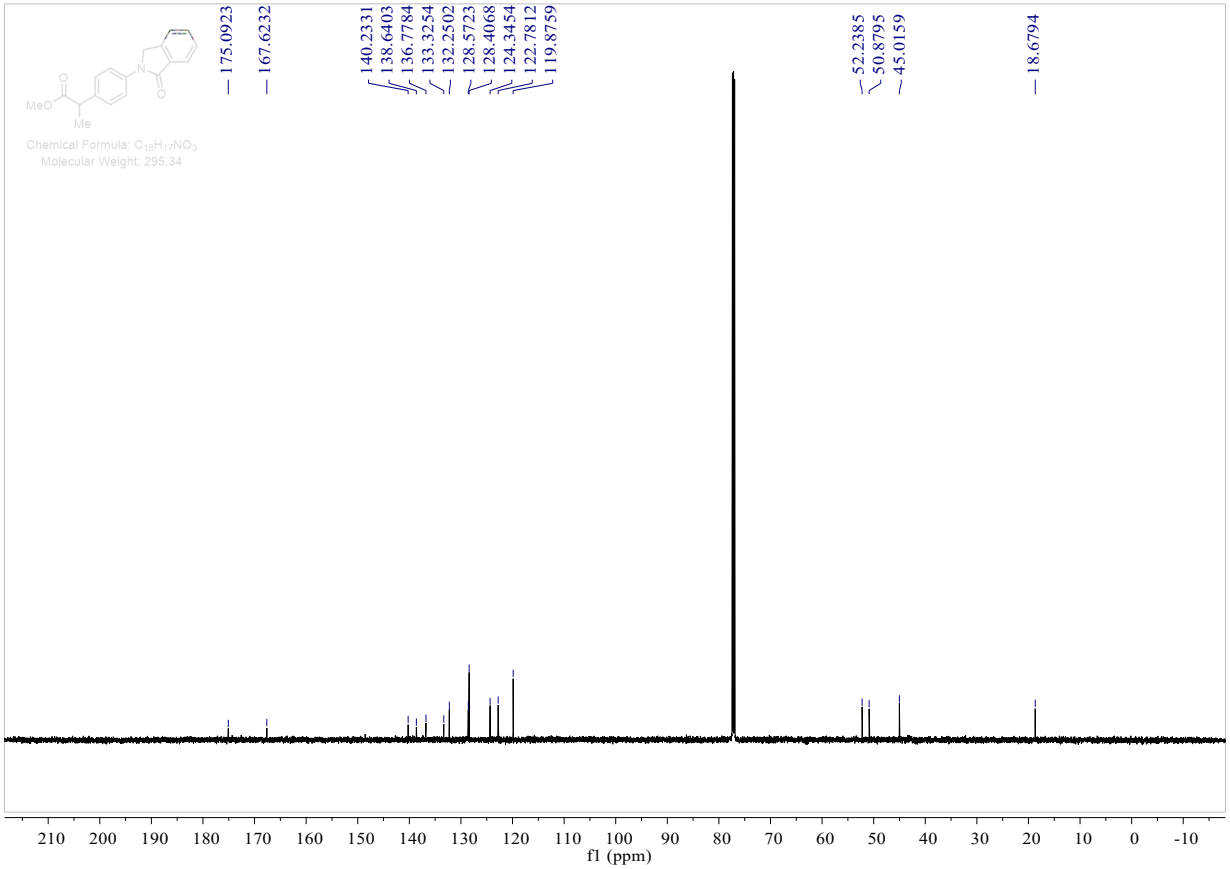
Methyl 2-(4-bromophenyl)butanoate (1zb).



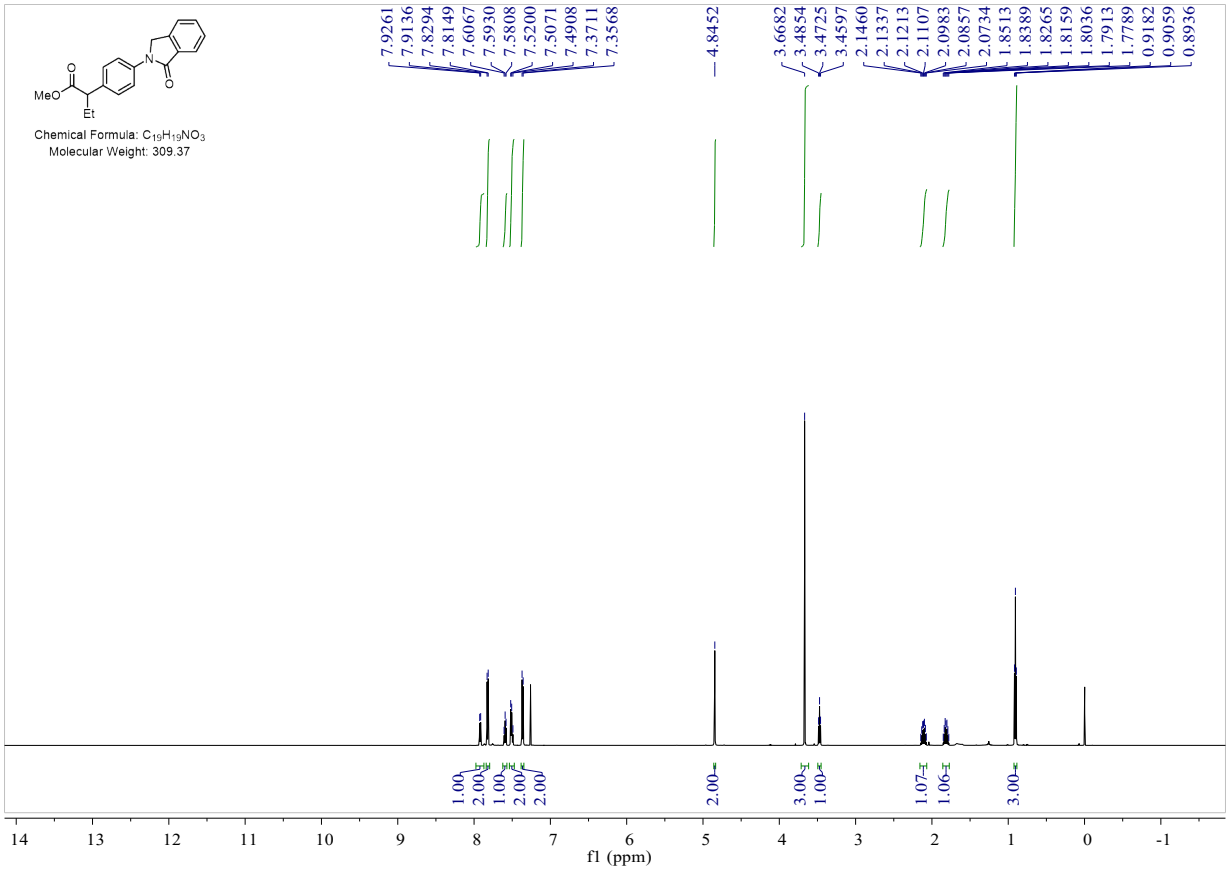


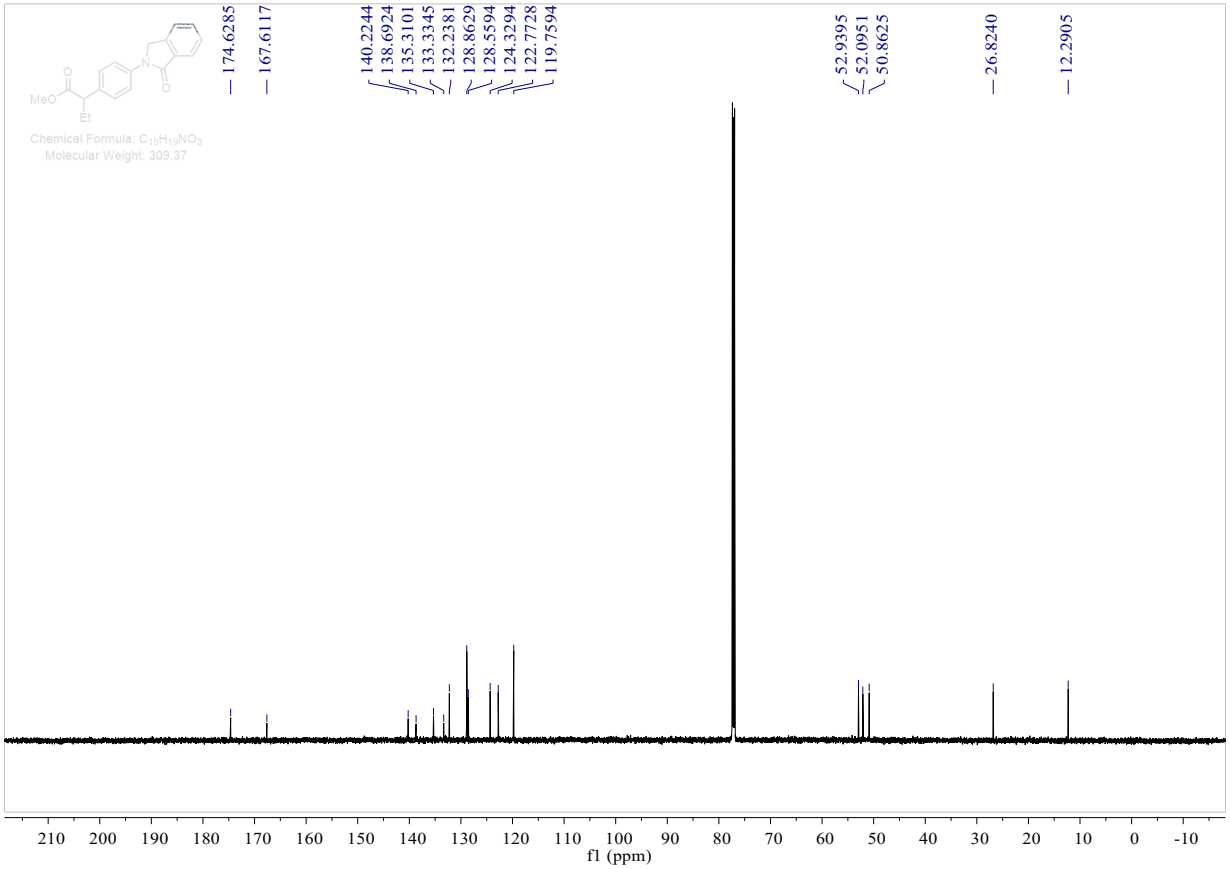
Methyl 2-(4-(1-oxoisoindolin-2-yl)phenyl)propanoate (6a).



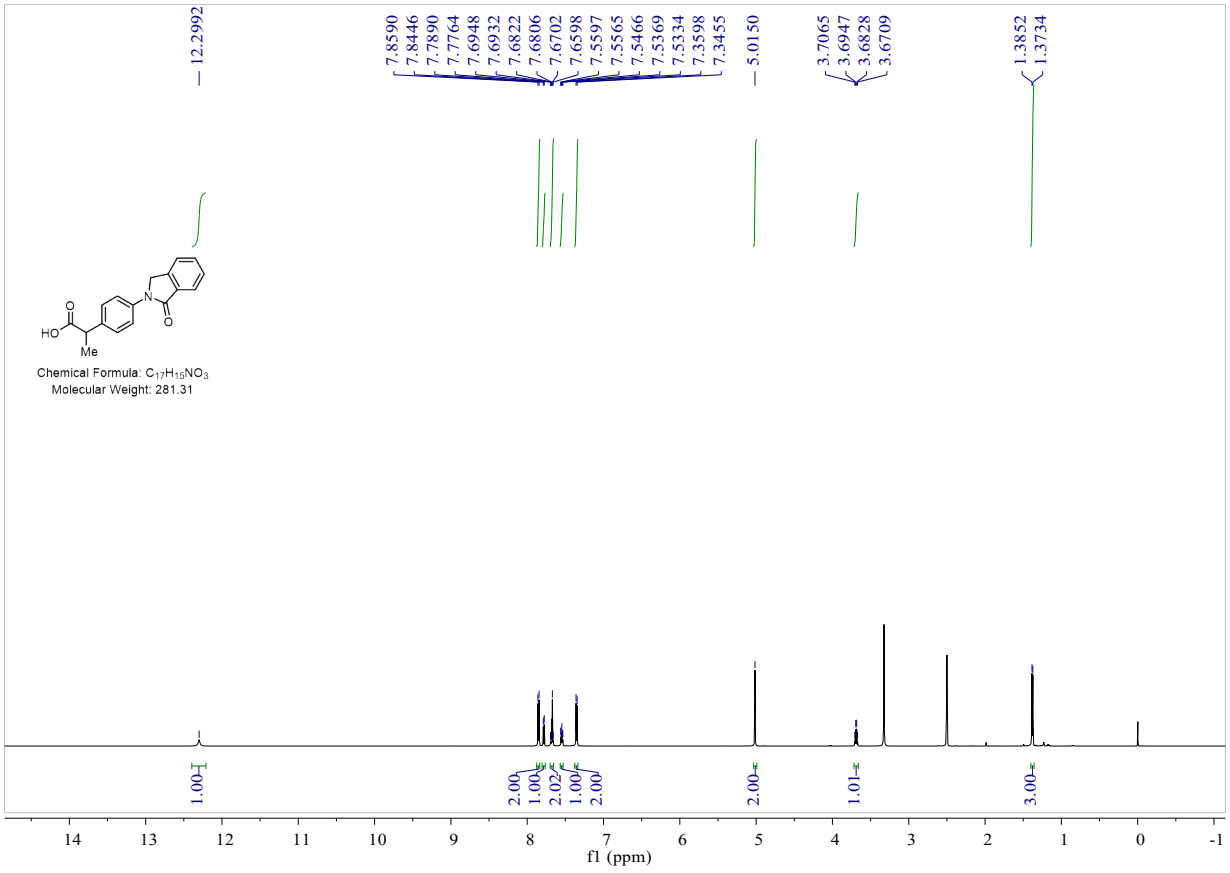


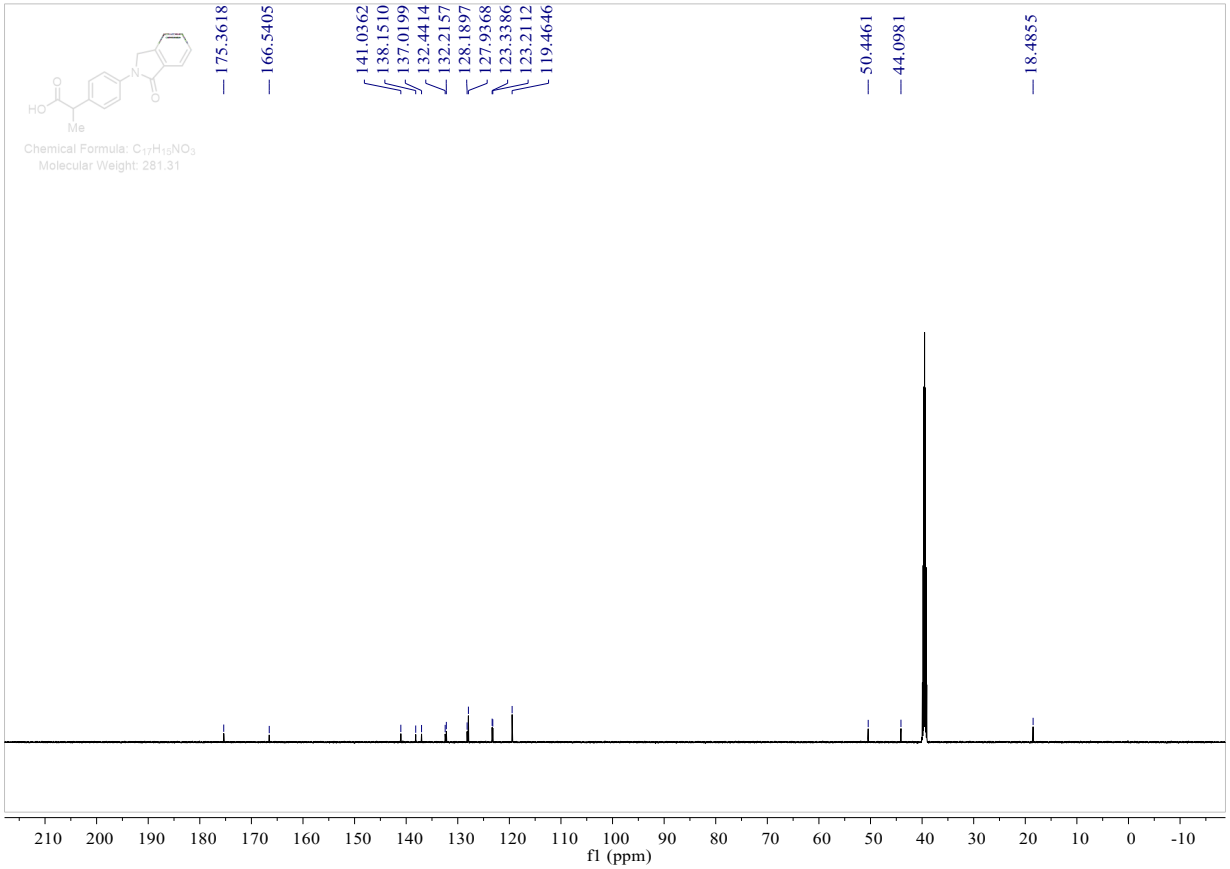
Methyl 2-(4-(1-oxoisoindolin-2-yl)phenyl)butanoate (6b).



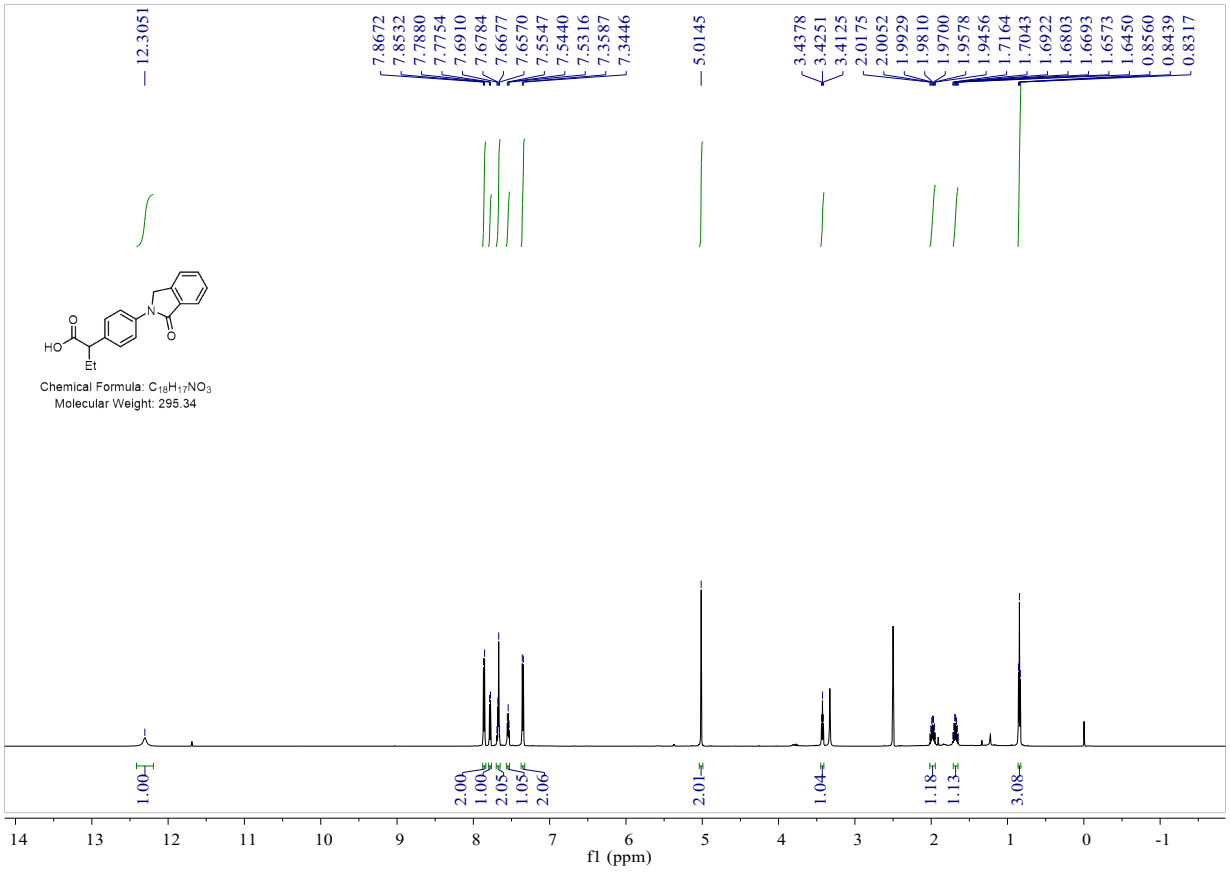


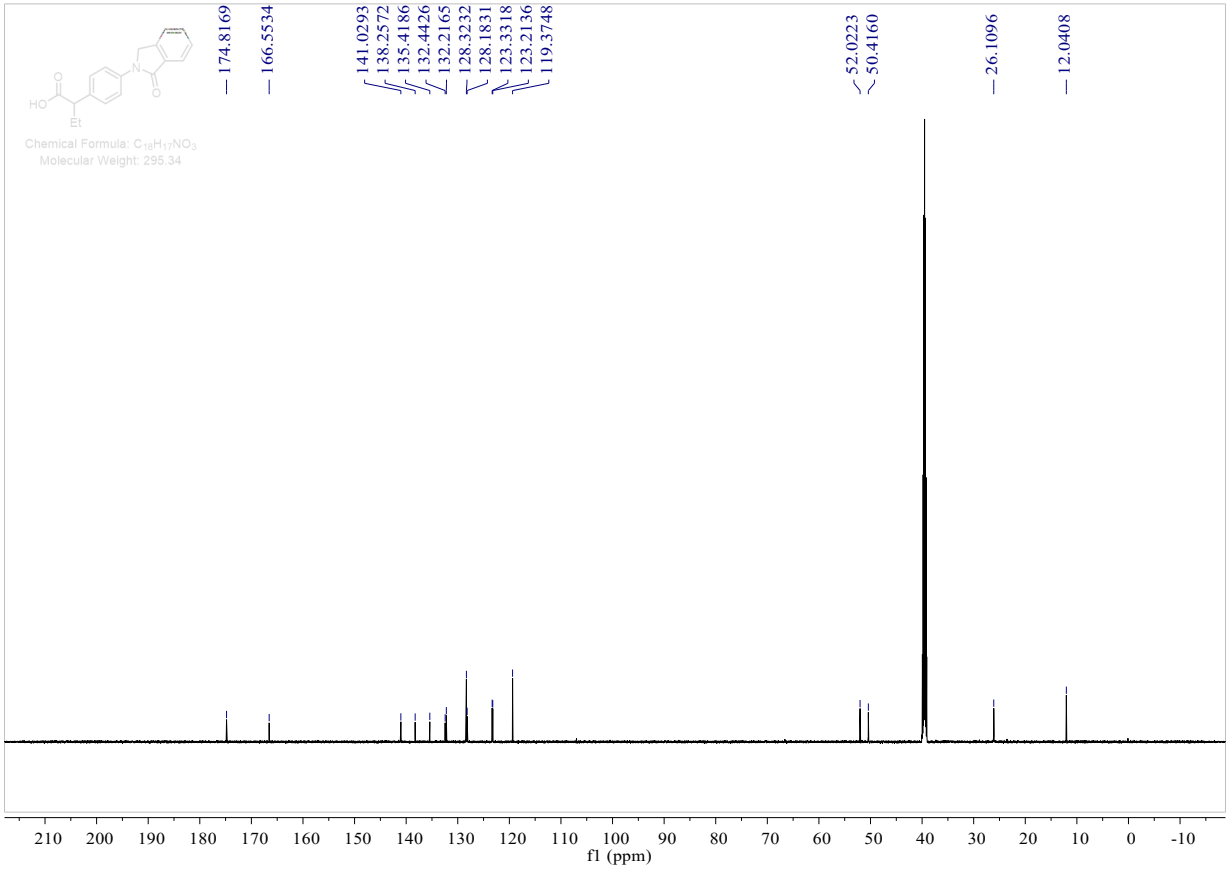
2-(4-(1-Oxoisoindolin-2-yl)phenyl)propanoic acid (7a, Indoprofen).



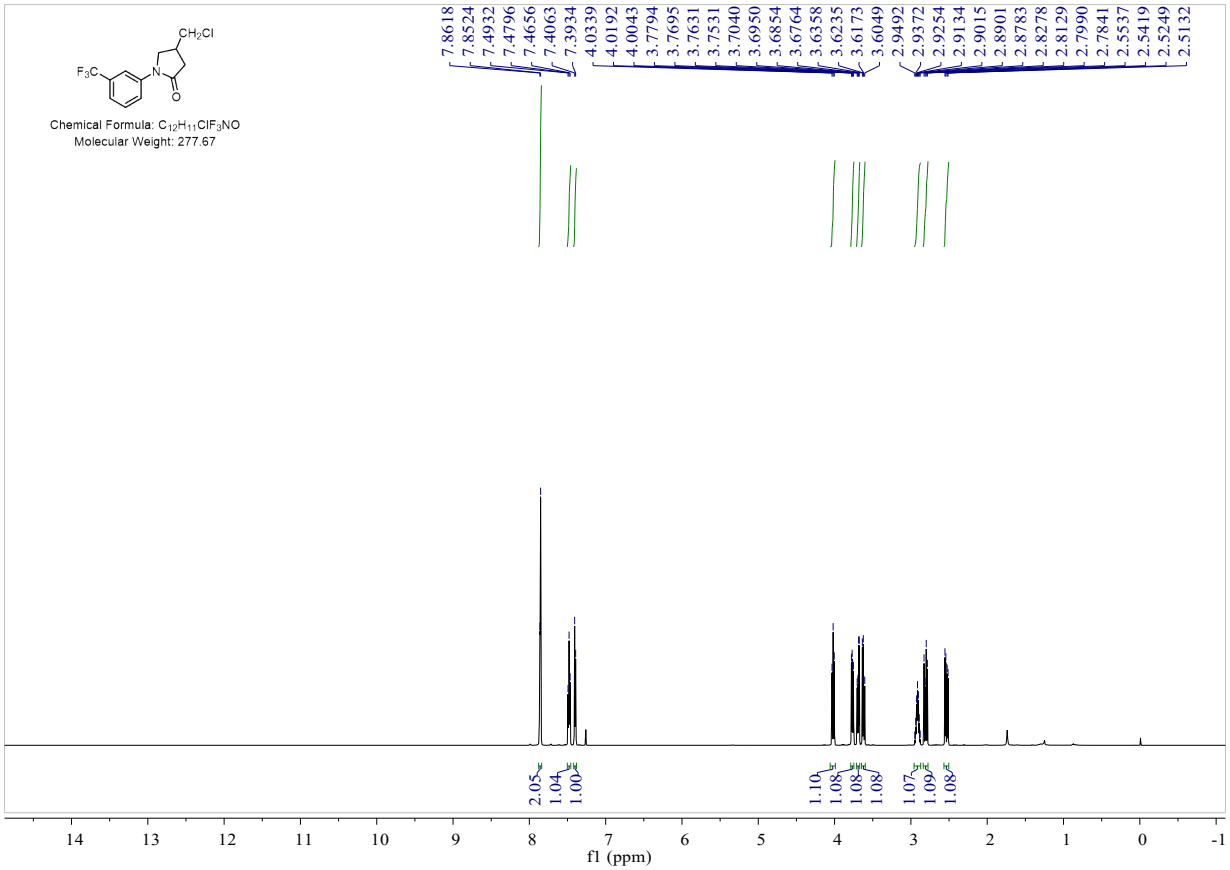


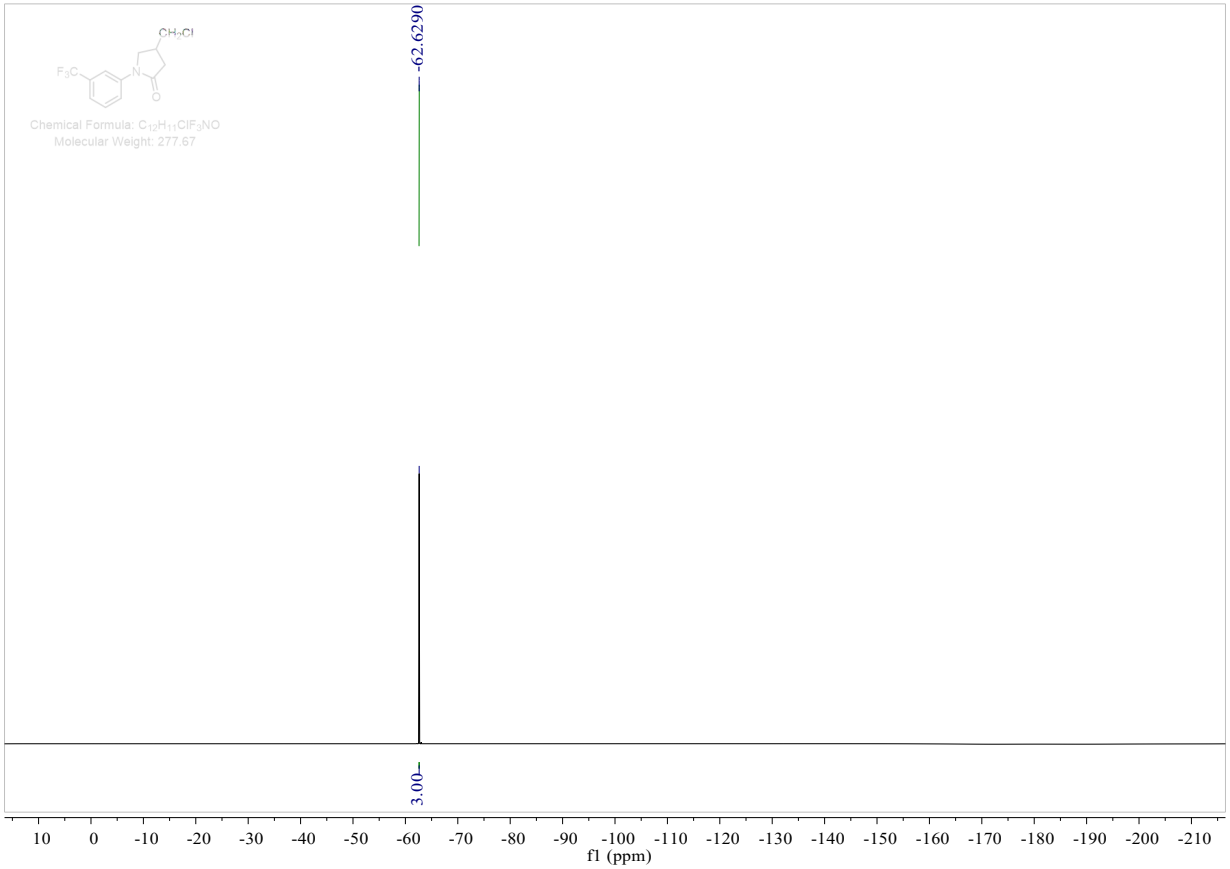
2-(4-(1-Oxoisoindolin-2-yl)phenyl)butanoic acid (7b, Indobufen).





4-(Chloromethyl)-1-(3-(trifluoromethyl)phenyl)pyrrolidin-2-one (8).




CH2Cl
F3C
N
O
Chemical Formula: C12H11ClF3NO
Molecular Weight: 277.67
-62.6290
3.00
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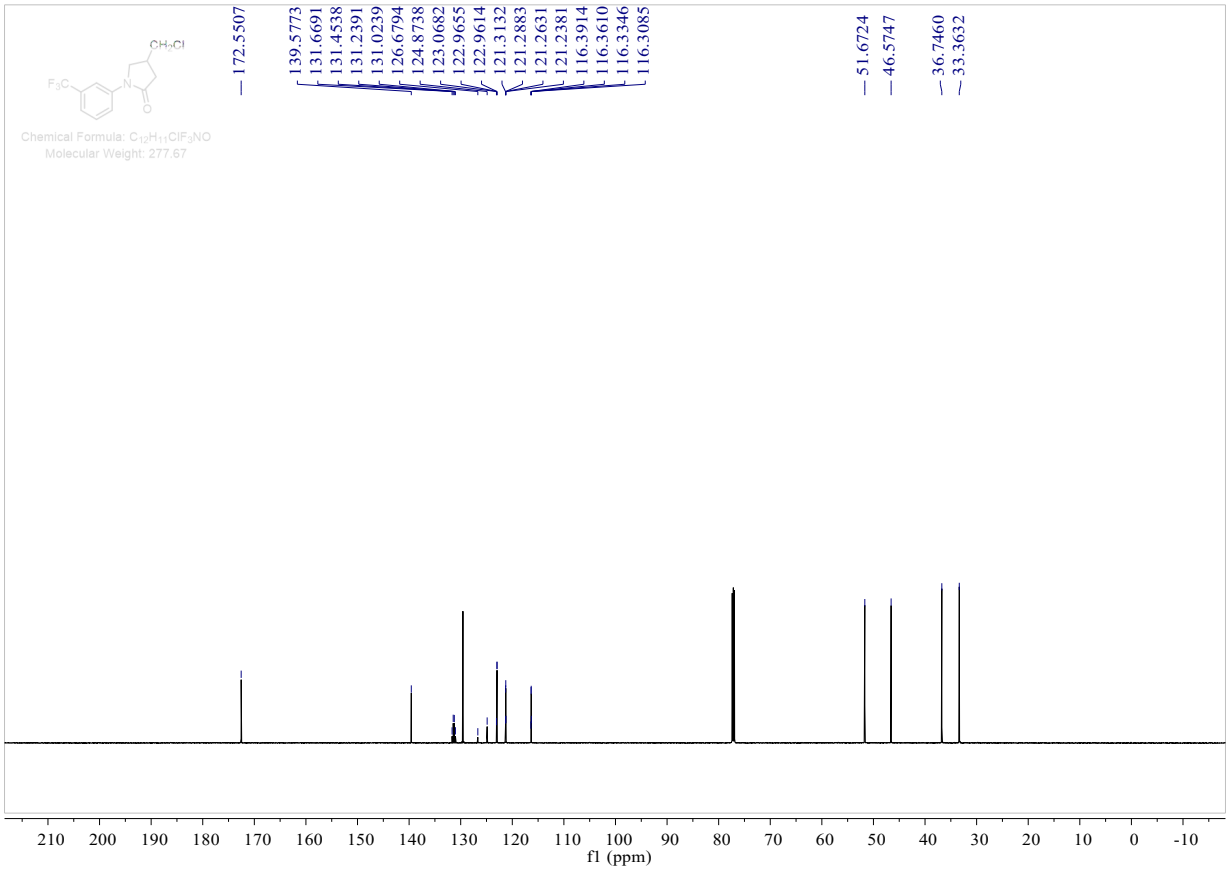
f1 (ppm)


CH2Cl
F3C
N
O
Chemical Formula: C12H11ClF3NO
Molecular Weight: 277.67
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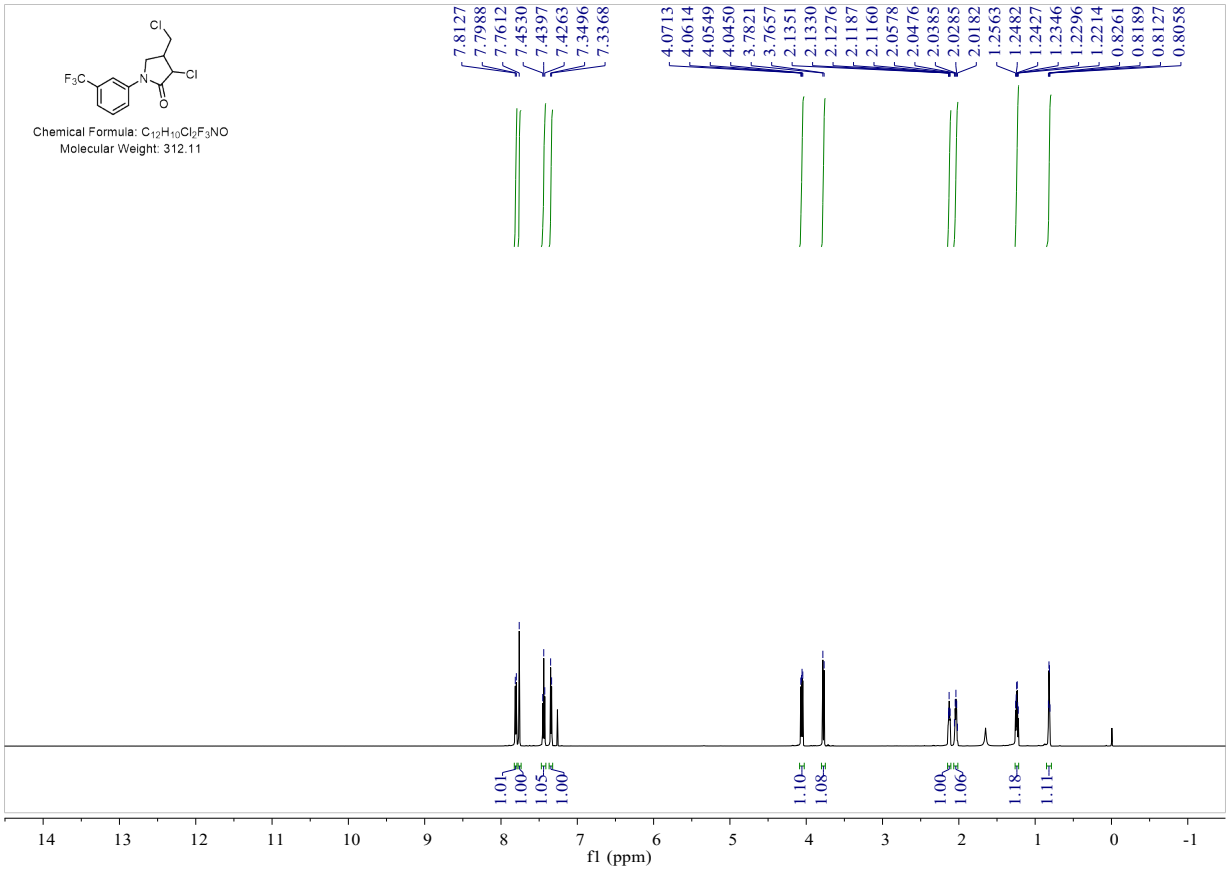
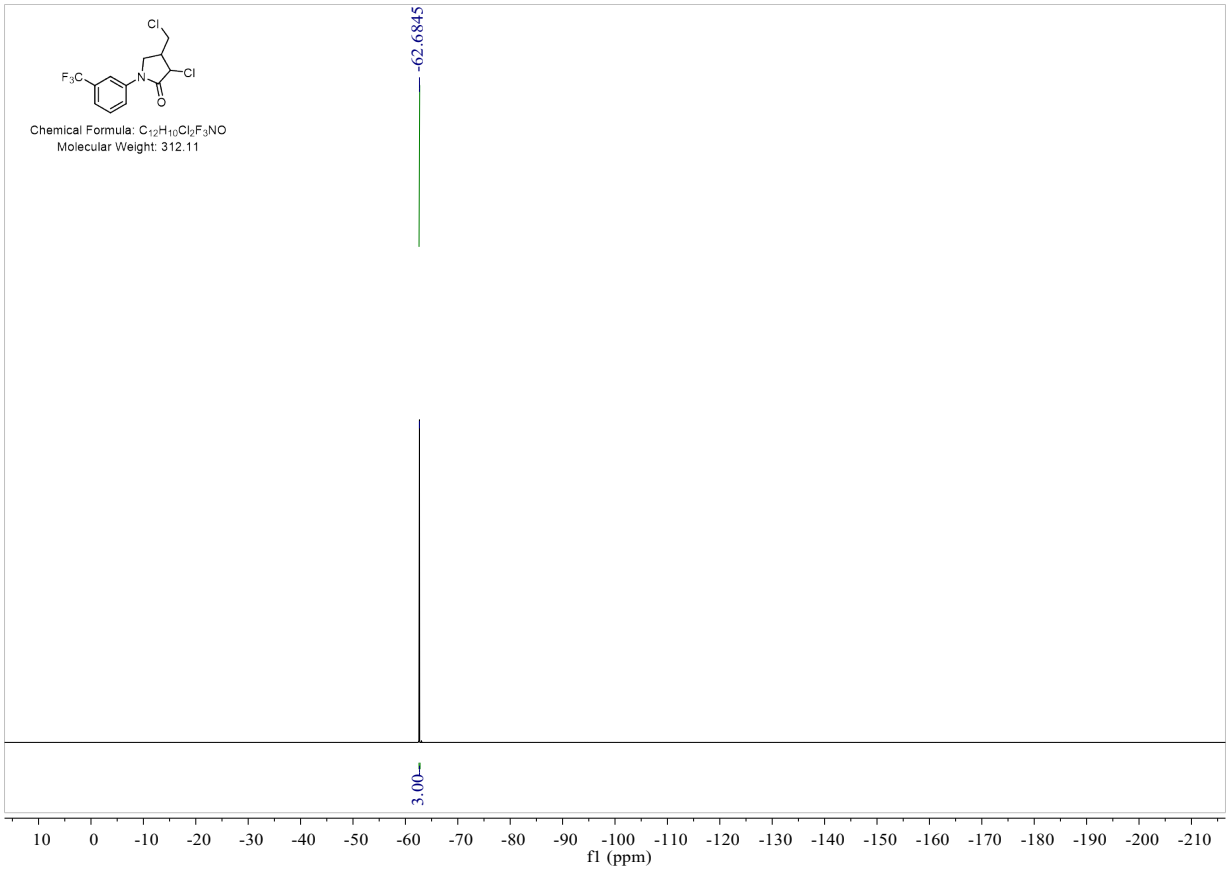
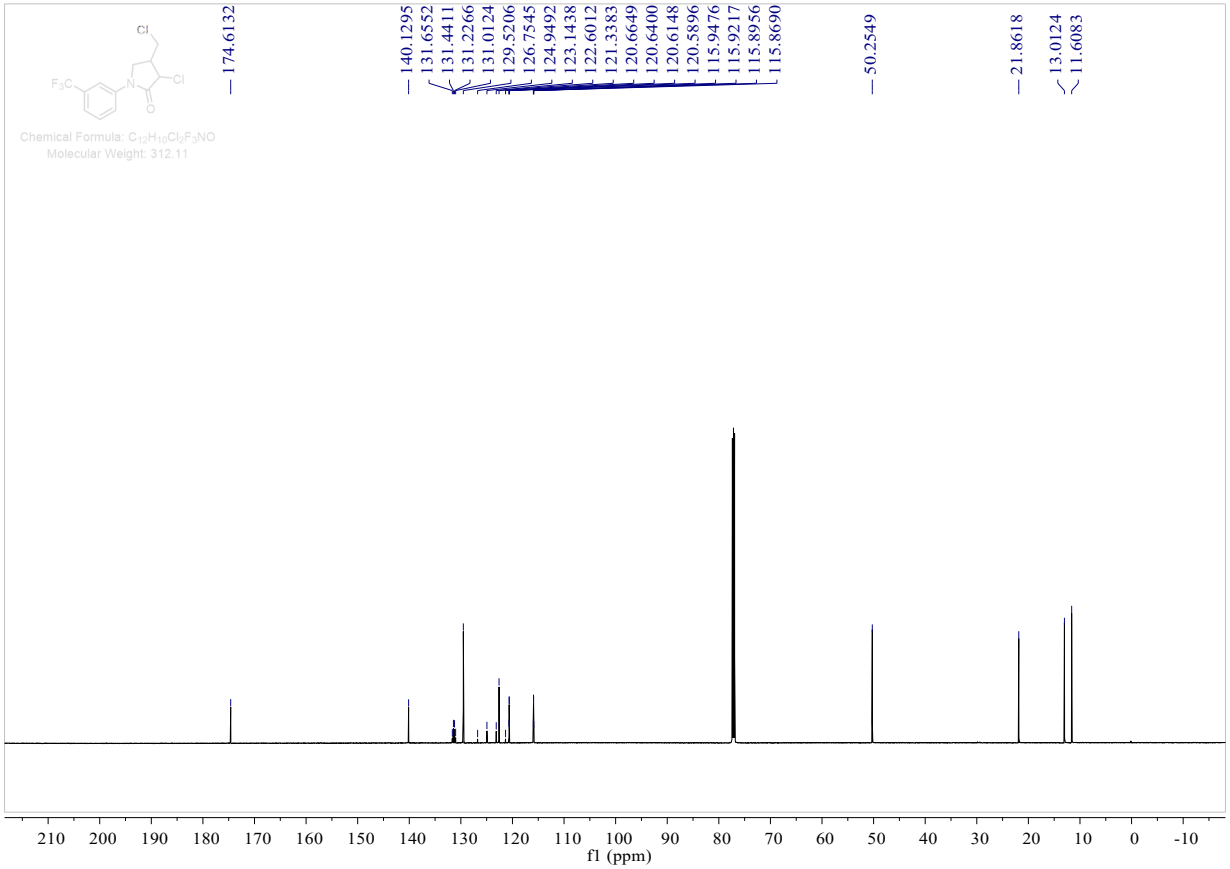
131.4538
131.2391
131.0239
126.6794
124.8738
123.0682
122.9655
122.9614
121.3132
121.2883
121.2631
121.2381
116.3914
116.3610
116.3346
116.3085
51.6724
46.5747
36.7460
33.3632
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3-Chloro-4-(chloromethyl)-1-(3-(trifluoromethyl)phenyl)pyrrolidin-2-one (9, Fluorochloridone).






Chemical Formula: C12H10Cl2F3NO
Molecular Weight: 312.11
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131.0124
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122.6012
121.3383
120.6649
120.6400
120.6148
120.5896
115.9476
115.9217
115.8956
115.8690
50.2549
21.8618
13.0124
11.6083
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)