# Silver- or Iron-Catalyzed Oxidative Fluorination of Cyclopropanols for the Synthesis of *β*-Fluoroketones

*Shichao Ren, Chao Feng,* and Teck-Peng Loh**

*Department of Chemistry, University of Science and Technology of China*

*Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371*

*fengchao@ntu.edu.sg*

*teckpeng@ntu.edu.sg.*

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## General information

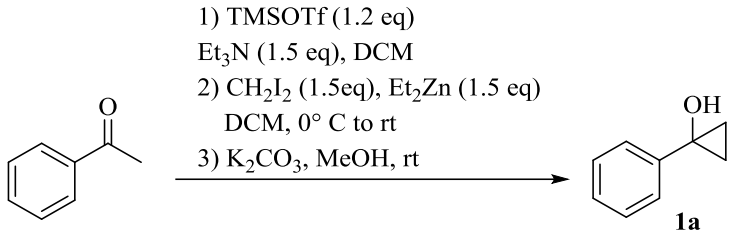
$AgNO_3$, DCM were purchased from commercial suppliers and used as received unless otherwise noted. All reactions were carried out under nitrogen atmosphere. Reactions were monitored through thin layer chromatography [Merck 60 F254 precoated silica gel plate (0.2 mm thickness)]. Subsequent to elution, spots were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible using basic solution of potassium permanganate or acidic solution of ceric molybdate as stain, followed by heating on a hot plate. Flash chromatography was performed using Merck silica gel 60 with distilled solvents. HRMS spectra were recorded on a Waters Q–Tof Permier Spectrometer. $^1$H NMR and $^{13}$C NMR spectra were recorded using Bruker Avance 400 MHz spectrometers. Chemical shifts for $^1$H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of $SiMe_4$ (δ 0.00, singlet). Multiplicities were given as: s (singlet); brs (broad singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet); ddd (doublets of doublets of doublet); td (triplet of doublet); m (multiplets); ddt (doublet of doublet of triplet) and etc. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra ($^{13}$C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 77.00, triplet).

## Experimental section

### Substrate synthesis

Cyclopropanol **1a**, **1e**, **1i**, **1j**, **1k**, **3b**, **3c**, **3d**, **3e** were previously reported. **1k**,[1] **1l**,[1] **3c-3e**[2] were prepared according to the literature.

### General procedure A:




**1a**

**Synthetic procedure:** 1) Acetophenone (0.6 g, 5 mmol, 1.0 eq) was added to a flame dried flask at 0 ℃ under nitrogen. Anhydrous DCM (30 mL) was added to the flask, followed by adding $Et_3N$ (1.0 ml, 7.5 mmol, 1.5 eq). Then TMSOTf (1.1 ml, 6 mmol, 1.2 eq) was added drop wise via syringe over a period of 10 min. The mixture were stirred overnight. The progress of the reaction was monitored by thin-layer chromatography (TLC). Once complete, the reaction was quenched with saturated $NaHCO_3$ aqueous , diluted with DCM and the phases were separated. The aqueous were extracted with DCM (2 x 30 ml ) The combined organic phase was washed with brine, dried using $Na_2SO_4$ and concentrated in vacuo.

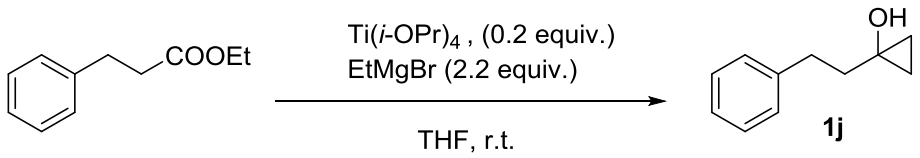
2) The crude ether was transferred to a dry 100 mL round-bottomed flask and placed under an atmosphere of nitrogen. The flask was charged with anhydrous DCM (62 mL) and diiodomethane (2.05 g, 0.61 mL, 7.5 mmol, 1.5 equiv. For **1h**, 4 equiv was used). The resulting solution was cooled to 0 ℃ using an ice bath. Once cold, neat diethyl zinc (7.5 mmol, 7.5 ml, 1M in THF, 1.5 equiv.) was added dropwise to the reaction solution via syringe. After 16 hours the reaction was quenched with a saturated solution of ammonium chloride. The layers were separated and the aqueous layer was extracted once more with

dichloromethane. The combined organic layers were washed with brine and dried using $Na_2SO_4$. Filtration and concentration in vacuo.

3) After evaporation of solvents, the crude materials were dissolved in MeOH (15 mL) followed by addition of $K_2CO_3$ (71 mg, 0.5 mmol). The reaction was stirred for 30 min at room temperature and then quenched by adding pH 9 ammonium buffer, and the organic materials were extracted with ethyl acetate. The organic lay was washed with brine, and dried over $MgSO_4$. After evaporation of solvent, resulting crude materials were purified by flash column chromatography.

Cyclopropanol 1a, 1b, 1c, 1d, 1e, 1f, 1g, 1h, 1k, 1l, 4b were prepared following the procedure A.

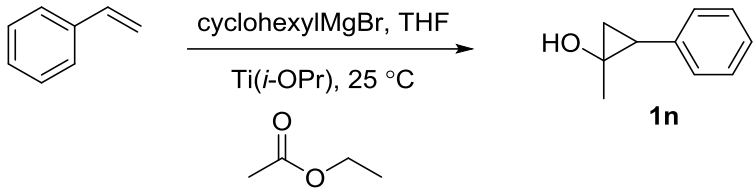
**General reaction scheme for 1j synthesis:**




**Synthetic procedure:** An oven dried 100 mL round-bottomed flask equipped with a stir bar was charged with ethyl 3-phenylpropanoate (1.01 g, 1.76 mL, 10 mmol, 1.0 equiv.), capped with a rubber septum and flushed with nitrogen for 10 minutes. To the flask was added freshly anhydrous tetrahydrofuran (THF, 30 mL). Then neat titanium(IV) isopropoxide (0.568 g, 0.600 mL, 2 mmol, 0.2 equiv.) was added via a syringe. Freshly prepared ethylmagnesium bromide (22.0 mmol, 1.0 M in THF, 2.2 equiv.) was then added dropwise via a cannula over a period of 40 minutes. The progress of the reaction was monitored by thin-layer chromatography (TLC). Once complete, the reaction was quenched with saturated $NH_4Cl$ solution, diluted with EtOAc and the phases were separated. The organic phase was washed with brine, dried using $MgSO_4$ and concentrated in vacuo. The crude product was purified by flash column chromatography.

Cyclopropanol **1i** were prepared according to the same procedure.

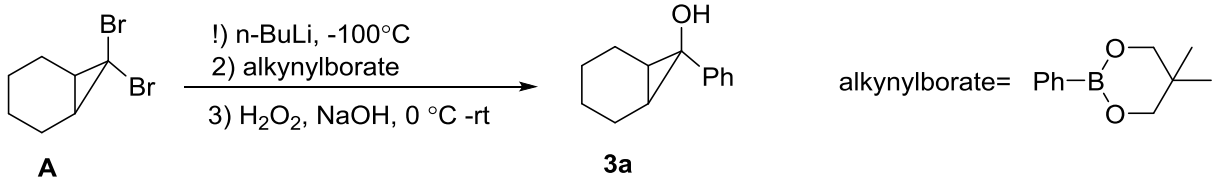
**General reaction scheme for 1n synthesis:**




**Synthetic procedure:** $Ti(i\text{-}OPr)_4$ (1.5 mL, 5 mmol, 1.0 eq) was added to a flame dried flask at room temperature under $N_2$(g). Anhydrous THF (20 mL) was added to the flask, followed by the alkene (0.52 g, 5 mmol, 1.0 eq) and EtOAc (0.73mL, 7.5 mmol, 1.5 eq). Then freshly prepared cyclohexylMgBr (20 mL of a 1.0 M solution in THF, 20 mmol, 4 eq) was added by syringe pump over the period of 1 h at 25 ℃. The reaction was stirred over night at 25 ℃, diluted with EtOAc (50 mL) and poured into $NH_4Cl$ (50 mL). The mixture was stirred vigorously for 0.5 h to break up the emulsion and then filtered through celite. The layers were separated and the aqueous layer was extracted twice with EtOAc (50 mL x2). The organic layers were combined, dried with $Na_2SO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography.

Cyclopropanol **1p** were prepared according to the same procedure.

**General reaction scheme for 3a synthesis:**

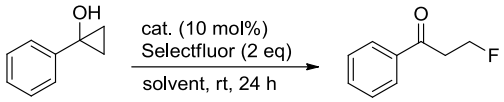



**Synthetic procedure:** To a THF solution (2.5 mL) of a dibromocyclopropane (0.51 g, 2.0 mmol) was added dropwise a 1.65 M hexane solution (1.2 mL, 2.0 mmol) of n-BuLi at -100 ℃, and the mixture was stirred at this temperature for 10 min. Then a THF solution (1.8 mL) of alkynylborate (0.4 g, 2.1 mmol) was added to this mixture at -100 ℃, and the mixture was slowly warmed to room

temperature overnight. Then the mixture was heated to reflux for 10 h. At 0 ℃, 10% aqueous NaOH solution (3 mL) and 30% $H_2O_2$ solution (3 mL) were added successively, and the mixture was further stirred at room temperature overnight. Then the products were extracted with ether three times, and the combined extracts were dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by silica gel column chromatograpy to give the bicyclic alkynylcyclopropanol.

Dibromocyclopropane **A**, [3] alkynylborate [4] were prepared according to the literature.

## Optimization of reaction condition.[a]



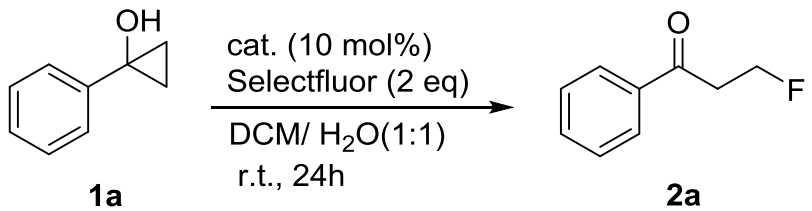

**1a** **2a**

| Entry | Catalyst | Solvent[b] | Yield[c] (%) |
|---|---|---|---|
| 1 | $AgNO_3$ | MeOH/$H_2O$ | 13 |
| 2 | $AgNO_3$ | Toluene/ $H_2O$ | 49 |
| 3 | $AgNO_3$ | Acetone/ $H_2O$ | 32 |
| 4 | $AgNO_3$ | DCM | 0 |
| 5 | $AgNO_3$ | $H_2O$ | 72 |
| 6 | $AgNO_3$ | DCM/$H_2O$ | 92[d] |
| 7 | $AgNO_3$ | DCM/$H_2O$ | 91 |
| 8 | - | DCM/$H_2O$ | 41[d] |
| 9 | $AgNO_3$ | DCM/$H_2O$ | 0[e] |
| 10 | AgOAc | DCM/$H_2O$ | 79 |
| 11 | $FeCl_2$ | DCM/$H_2O$ | 63 |
| 12 | $Fe(OAc)_2$ | DCM/$H_2O$ | 87 |
| 13 | $Fe(acac)_3$ | DCM/$H_2O$ | 96 |
| 14 | CuCl | DCM/$H_2O$ | 0 |
| 15 | CuBr | DCM/$H_2O$ | 9 |
| 16 | - | DCM/$H_2O$ | 8[f] |

[a] Unless otherwise noted, the reactions were carried out at rt using **1a** (0.1 mmol), Selectfluor® (0.2 mmol), catalyst (0.01 mmol) in solvent (0.8 mL) for 24 h. [b] All mixed solvent are in ratio of 1:1 by v:v. [c] Yield was determined by **$^1$H NMR** using mesitylene as internal standard. [d] $K_2S_2O_8$ was used as additional oxidant. [e] NFSI was employed in place of Selectfluor®. [f] No catalyst added

## Silver- or Iron-catalyzed Oxidative Fluorination of Cyclopropanols

## General Procedure B:




**1a** **2a**

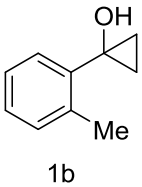
Under nitrogen atmosphere, oven-dried 10mL schlenk tube was charged with 1-phenylcyclopropan-l-ol **1a** (13.4 mg, 0.1 mmol), Selectfluor (70.8 mg, 0.2 mmol), $AgNO_3$ (1.7 mg, 0.01 mmol), in sequence followed by adding DCM (0.4 mL) and $H_2O$ (0.4 mL) through syringe. After stirring at room temperature under dark for 24 hours, diluted with DCM, and the resulting mixture was extracted with DCM (3x15 mL), dried with anhydrous $Na_2SO_4$. Removal of the solvent in vacuo afforded the desired product **2a** (14.6 mg, Yield: 96%).

**Large scale reaction**

**Experiment procedure:** Under nitrogen atmosphere, oven-dried 100mL RBF was successively charged with cyclopropanol **1l** (1g, 1eq), Selectfluor (3.9 g, 9.88 mmol, 2eq), $AgNO_3$ (83.9 mg, 0.494 mmol), in sequence followed by adding DCM (20 mL) and $H_2O$ (20 mL) through syringe. After stirring at room temperature under dark for 24 hours, diluted with DCM, and the resulting mixture was extracted with DCM (3x30 mL), dried with anhydrous $Na_2SO_4$. Removal of the solvent in vacuo afforded the desired product **2l** (0.85 g, Yield: 78%).

**Characterization of unknown substrates and products**

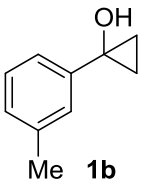
**1-(o-tolyl)cyclopropan-1-ol:**



1b

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.33 – 7.29 (m, 1H), 7.24 – 7.17 (m, 2H), 7.16 – 7.10 (m, 1H), 2.54 (s, 3H), 2.24 (s, 1H), 1.16 – 1.10 (m, 2H), 0.93 – 0.87 (m, 2H). ppm; **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 139.8, 139.0, 130.6, 128.4, 128.1, 125.6, 57.3, 19.1, 13.7. ppm; **HRMS (ESI, m/z):** calcd for $C_{10}H_{11}O$ $[M-H]^-$ 147.0810, found: 147.0813.

**1-(m-tolyl)cyclopropan-1-ol:**

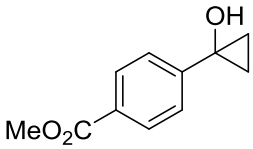


**1b**

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.23 (t, *J* = 7.6 Hz, 1H), 7.15 (s, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 7.4 Hz, 1H), 2.36 (s, 3H), 1.25 (dt, *J* = 5.3, 2.7 Hz, 2H), 1.04 (q, *J* = 5.1 Hz, 2H). ppm; **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 144.2, 137.9, 128.3, 127.2, 125.3, 121.4, 56.6, 21.5, 17.7. ppm; **HRMS (ESI, m/z):** calcd for $C_{10}H_{11}O$

[M-H]$^-$ 147.0810, found: 147.0810.

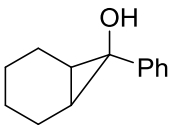
**methyl 4-(1-hydroxycyclopropyl)benzoate:**



**1h**

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.02 – 7.96 (m, 2H), 7.35 – 7.29 (m, 2H), 3.91 (s, 1H), 2.47 (s, 2H), 1.37 (q, *J* = 5.2 Hz, 1H), 1.13 (q, *J* = 5.3 Hz, 2H). ppm; **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 166.98 (s), 150.11 (s), 129.65 (s), 127.94 (s), 123.67 (s), 56.32 (s), 52.03 (s), 19.38 (s). ppm; **HRMS (ESI, m/z):** calcd for $C_{11}H_{12}O_3Na$ [M+Na]$^-$ 215.0684, found: 215.0682.

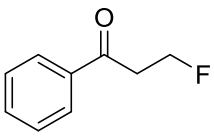
**7-phenylbicyclo[4.1.0]heptan-7-ol:**



**3b**

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.51 – 7.45 (m, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 1.96-1.84 (m, 2H), 1.72 – 1.61 (m, 2H), 1.50 – 1.44 (m, 2H), 1.09 – 0.97 (m, 2H), 0.72 – 0.60 (m, 2H). ppm; **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 138.4, 130.6, 128.9, 127.8, 62.5, 21.8, 21.0, 20.5. ppm; **HRMS (ESI, m/z):** calcd for $C_{13}H_{15}O$ [M-H]$^-$ 187.1123, found: 187.1116.

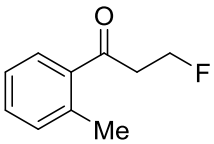
**3-fluoro-1-phenylpropan-1-one:**



**2a**

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.97 (dt, *J* = 8.5, 1.6 Hz, 2H), 7.62 – 7.56 (m, 1H), 7.52 – 7.45 (m, 2H), 4.97 (t, *J* = 6.1 Hz, 1H), 4.85 (t, *J* = 6.1 Hz, 1H), 3.42 (t, *J* = 6.1 Hz, 1H), 3.36 (t, *J* = 6.1 Hz, 1H). ppm; **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 196.7 (d, *J* = 5.6 Hz), 136.6, 133.5, 128.7, 128.1, 79.3 (d, *J* = 165.2 Hz), 38.9 (d, *J* = 21.7 Hz). ppm; **$^{19}$F NMR (376 MHz, CDCl3):** δ -220.88 – -221.38 (m, 1F). ppm; **HRMS (ESI, m/z):** calcd for $C_9H_9OFNa$ [M+Na]$^+$ 175.0535, found: 175.0534.

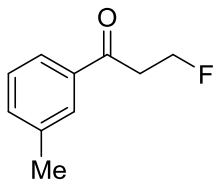
**3-fluoro-1-(o-tolyl)propan-1-one:**



**2b**

**$^1$H NMR (400 MHz, $CDCl_3$):** $^1$H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.64 (m, 1H), 7.40 (m, 1H), 7.32 – 7.24 (m, 2H), 4.93 (t, *J* = 5.9 Hz, 1H), 4.82 (t, *J* = 5.9 Hz, 1H), 3.36 – 3.31 (t, J= 5.9, 1H), 3.28 (t, *J* = 5.9 Hz, 1H), 2.52 (s, 3H). ppm; **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 200.3 (d, *J* = 4.9 Hz), 138.6, 137.2, 132.1, 131.7, 128.7, 125.8, 79.5 (d, *J* = 165.1 Hz), 41.6 (d, *J* = 21.8 Hz), 21.3.ppm; **$^{19}$F NMR (376 MHz, CDCl3):** δ -220.68 (tt, *J* = 46.9, 23.6 Hz). ppm; **HRMS (ESI, m/z):** calcd for $C_{10}H_{11}OFNa$ [M+Na]$^+$ 189.0692, found: 189.0690.

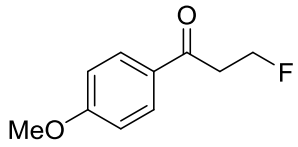
**3-fluoro-1-(m-tolyl)propan-1-one:**




**2c**

**$^{1}$H NMR (400 MHz, $CDCl_3$):** $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.72 (m, 2H), 7.43 – 7.33 (m, 2H), 4.96 (t, *J* = 6.1 Hz, 1H), 4.84 (t, *J* = 6.1 Hz, 1H), 3.40 (t, *J* = 6.1 Hz, 1H), 3.35 (t, *J* = 6.1 Hz, 1H), 2.42 (s, 3H).ppm; **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 195.9 (d, *J* = 5.7 Hz), 137.6, 135.7, 133.2, 127.6, 127.6, 124.3, 78.4 (d, *J* = 165.1 Hz), 37.9 (d, *J* = 21.7 Hz), 20.3. ppm; **$^{19}$F NMR (376 MHz, CDCl3):** δ -220.94 – -221.36 (m, 1F). **HRMS (ESI, m/z):** calcd for $C_{10}H_{11}OFNa$ $[M+Na]^+$ 189.0692, found: 189.0685

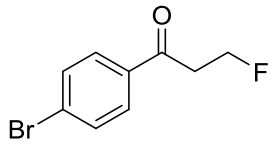
**3-fluoro-1-(4-methoxyphenyl)propan-1-one:**




**2d**

**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 7.98 – 7.91 (m, 2H), 6.97 – 6.92 (m, 2H), 4.95 (t, *J* = 6.1 Hz, 1H), 4.83 (t, *J* = 6.1 Hz, 1H), 3.87 (s, 3H), 3.36 (t, *J* = 6.1 Hz, 1H), 3.30 (t, *J* = 6.1 Hz, 1H). ppm; **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 195.2 (d, *J* = 5.7 Hz), 163.8, 130.4, 129.8, 113.8, 79.5 (d, *J* = 164.9 Hz), 55.5, 38.5 (d, *J* = 21.6 Hz).ppm; **$^{19}$F NMR (376 MHz, CDCl3):** δ -220.76 – -221.16 (m， 1F). **HRMS (ESI, m/z):** calcd for $C_{10}H_{11}O_2FNa$ $[M+Na]^+$ 205.0641, found: 205.0644.

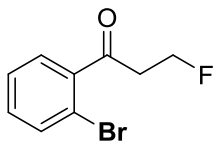
**1-(4-bromophenyl)-3-fluoropropan-1-one:**




**2e**

**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 7.86 – 7.79 (m, 2H), 7.66 – 7.58 (m, 2H), 4.95 (t, *J* = 6.0 Hz, 1H), 4.83 (t, *J* = 6.0 Hz, 1H), 3.37 (t, *J* = 6.0 Hz, 1H), 3.31 (t, *J* = 6.0 Hz, 1H).ppm; **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 195.7 (d, *J* = 5.4 Hz), 135.3, 132.1, 129.6, 128.8, 79.1 (d, *J* = 165.7 Hz), 38.8 (d, *J* = 21.8 Hz). ppm; **$^{19}$F NMR (376 MHz, CDCl3):** δ -220.78 – -221.21 (m). **HRMS (ESI, m/z):** calcd for $C_9H_8OFNaBr$ $[M+Na]^+$ 252.9640, found: 252.9650.

**1-(2-bromophenyl)-3-fluoropropan-1-one:**

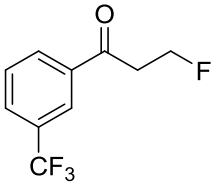



**2f**

**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 7.62 (dt, *J* = 11.2, 5.6 Hz, 1H), 7.44 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.39 (ddd, *J* = 6.8, 5.7, 2.0 Hz, 1H), 7.35 – 7.29 (m, 1H), 4.91 (t, *J* = 5.9 Hz, 1H), 4.80 (t, *J* = 5.9 Hz, 1H), 3.39 (t, *J* = 5.9 Hz, 1H), 3.33 (t, *J* = 5.9 Hz, 1H).ppm; **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 200.5 (d, *J* = 4.8

Hz), 140.9, 133.8, 132.0, 128.8, 127.6, 118.7, 79.0 (d, *J* = 166.2 Hz), 43.0 (d, *J* = 21.8 Hz), 29.7. ppm; **$^{19}$F NMR (376 MHz, CDCl3):** δ -220.22 – -220.65 (m). **HRMS (ESI, m/z):** calcd for $C_9H_8OFNaBr$ $[M+Na]^+$ 252.9640, found: 252.9648.

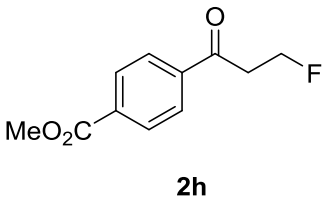
**3-fluoro-1-(3-(trifluoromethyl)phenyl)propan-1-one:**



**2g**

**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 8.22 (s, 1H), 8.15 (d, *J* = 7.9 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.64 (t, *J* = 7.8 Hz, 1H), 4.98 (t, *J* = 5.9 Hz, 1H), 4.86 (t, *J* = 5.9 Hz, 1H), 3.43 (t, *J* = 5.9 Hz, 1H), 3.38 (t, *J* = 5.9 Hz, 1H). ppm; **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 195.4 (d, *J* = 5.2 Hz), 137.1, 131.6, 131.3, 129.9 (q, *J* = 3.6 Hz), 129.5, 125.1 – 124.9 (m), 122.2, 78.9 (d, *J* = 166.0 Hz), 39.0 (d, *J* = 21.9 Hz). ppm; **$^{19}$F NMR (376 MHz, CDCl3)** δ -62.88 (s, 3F), -220.77 – -221.19 (m, 1F). **HRMS (ESI, m/z):** calcd for $C_{10}H8OF_4Na$ $[M+Na]^+$ 243.0409, found: 243.0399

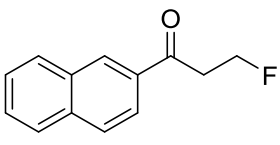
**methyl 4-(3-fluoropropanoyl)benzoate:**



**2h**

**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 8.14 (d, *J* = 8.3 Hz, 2H), 8.01 (d, *J* = 8.3 Hz, 2H), 4.97 (t, *J* = 5.9 Hz, 1H), 4.85 (t, *J* = 5.9 Hz, 1H), 3.95 (s, 3H), 3.43 (t, *J* = 5.9 Hz, 1H), 3.38 (t, *J* = 5.9 Hz, 1H). ppm; **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 195.21 (d, *J* = 5.3 Hz), 165.08 (s), 138.67 (s), 133.22 (s), 128.91 (s), 127.00 (s), 77.98 (d, *J* = 165.6 Hz), 51.49 (s), 38.16 (d, *J* = 21.8 Hz).. ppm; **$^{19}$F NMR (376 MHz, CDCl3)** δ -220.72 – -221.58 (m). **HRMS (ESI, m/z):** calcd for $C_{11}H_{11}O_3FNa$ $[M+Na]^+$ 233.0590, found: 233.0580.

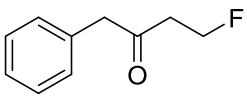
**3-fluoro-1-(naphthalen-2-yl)propan-1-one:**



**2i**

**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 8.48 (s, 1H), 8.04 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.98 (dd, *J* = 8.0, 0.6 Hz, 1H), 7.94 – 7.86 (m, 2H), 7.65 – 7.53 (m, 2H), 5.03 (t, *J* = 6.1 Hz, 1H), 4.91 (t, *J* = 6.1 Hz, 1H), 3.55 (t, *J* = 6.1, 1H), 3.50 (t, *J* = 6.1, 1H). ppm; **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 196.6 (d, *J* = 5.6 Hz), 135.8, 134.0, 132.5, 130.0, 129.6, 128.7, 128.6, 127.8, 126.9, 123.6, 79.4 (d, *J* = 165.3 Hz), 38.9 (d, *J* = 21.7 Hz). ppm; **$^{19}$F NMR (376 MHz, CDCl3)** δ -220.59 – -221.04 (m, 1F). **HRMS (ESI, m/z):** calcd for $C_{13}H_{11}O_2FNa$ $[M+Na]^+$ 225.0692, found: 225.0695.

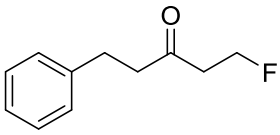
**4-fluoro-1-phenylbutan-2-one:**



**2j**

**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 7.38 – 7.31 (m, 2H), 7.28 (dd, *J* = 12.3, 4.8 Hz, 1H), 7.22 (t, *J* = 6.8 Hz, 2H), 4.74 (t, *J* = 5.9 Hz, 1H), 4.63 (t, *J* = 5.9 Hz, 1H), 3.75 (s, 2H), 2.86 (t, *J* = 5.9 Hz, 1H), 2.80 (t, *J* = 5.9 Hz, 1H).ppm; **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 205.0 (d, J= 3.99), 133.5, 129.4, 128.8, 127.3, 78.9 (d, *J* = 165.3 Hz), 50.7, 42.0 (d, *J* = 21.5 Hz). ppm; **$^{19}$F NMR (376 MHz, CDCl3)** δ -220.51 – -221.04 (m, 1F). ppm; **HRMS (ESI, m/z):** calcd for $C_{10}H_{11}OFNa$ $[M+Na]^+$ 189.0692, found: 189.0697.

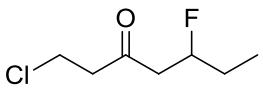
**1-fluoro-5-phenylpentan-3-one:**



**2k**

**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 7.31 – 7.26 (m, 2H), 7.22 – 7.16 (m, 3H), 4.77 (t, *J* = 5.9 Hz, 1H), 4.65 (t, *J* = 5.8 Hz, 1H), 2.96 – 2.89 (m, 2H), 2.84 – 2.78 (m, 3H), 2.75 (t, *J* = 5.8 Hz, 1H).ppm; **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 206.6 – 206.5 (d, *J* = 3.8 Hz ), 140.7, 128.5, 128.3, 126.2, 78.9 (d, *J* = 165.3 Hz), 45.0, 43.1 (d, *J* = 21.5 Hz), 29.4. ppm; **$^{19}$F NMR (376 MHz, CDCl3)** δ -220.15 – -220.61 (m, 1F). ppm; **HRMS (ESI, m/z):** calcd for $C_{11}H_{13}OFNa$ $[M+Na]^+$ 203.0848, found: 203.0848.

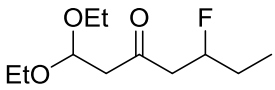
**1-chloro-5-fluoroheptan-3-one:**



**2l**

**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 5.00 – 4.80 (m, 1H), 3.80 – 3.68 (m, 2H), 2.95 (t, *J* = 6.6 Hz, 2H), 2.92 – 2.80 (m, 1H), 2.60 (ddd, *J* = 30.9, 16.3, 4.0 Hz, 1H), 1.75 – 1.60 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).ppm; **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 204.4 (d, *J* = 3.6 Hz), 91.0 (d, *J* = 169.0 Hz), 48.0 (d, *J* = 23.0 Hz), 46.0 (d, *J* = 1.4 Hz), 37.9, 28.1 (d, *J* = 21.1 Hz), 9.1 (d, *J* = 5.6 Hz). ppm; **$^{19}$F NMR (376 MHz, CDCl3)** -180.75 – -181.18 (m,1F). ppm; **HRMS (ESI, m/z):** calcd for $C_7H_{12}OFNaCl$ $[M+Na]^+$ 189.0458, found: 189.0457.

**1,1-diethoxy-5-fluoroheptan-3-one:**

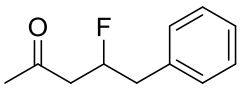


**2m**

**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 5.01 – 4.81 (m, 2H), 3.73 – 3.61 (m, 2H), 3.53 (dq, *J* = 9.3, 7.0 Hz, 2H), 2.89 (ddd, *J* = 16.7, 15.5, 7.8 Hz, 1H), 2.78 (d, *J* = 5.6 Hz, 2H), 2.64 (ddd, *J* = 29.3, 16.9, 4.3 Hz, 1H), 1.73 – 1.60 (m, 2H), 1.19 (td, *J* = 7.0, 1.3 Hz, 6H), 0.98 (t, *J* = 7.4 Hz, 3H).ppm; **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 204.9 – 204.8 (d, *J* =4.35 Hz) 99.8, 90.8 (d, *J* = 168.2 Hz), 62.4 (d, *J* = 19.7

Hz), 48.7 (d, *J* = 22.9 Hz), 48.2, 28.0 (d, *J* = 21.1 Hz), 15.2, 9.1 (d, *J* = 5.5 Hz). ppm; **$^{19}$F NMR (376 MHz, CDCl3)** δ -181.38 – -181.80 (m, 1F). ppm; **HRMS (ESI, m/z):** calcd for $C_{11}H_{21}O_3FNa$ $[M+Na]^+$ 243.1372, found: 243.1368.

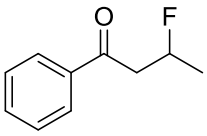
**4-fluoro-5-phenylpentan-2-one:**




**2n**

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.32 (ddd, *J* = 7.5, 4.4, 1.4 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.24 – 7.18 (m, 2H), 5.18 (ddddd, *J* = 47.4, 7.9, 6.6, 5.5, 4.5 Hz, 1H), 3.06 – 2.89 (m, 2H), 2.83 (ddd, *J* = 16.7, 15.1, 7.9 Hz, 1H), 2.59 (ddd, *J* = 29.3, 16.7, 4.4 Hz, 1H), 2.17 (s, 3H).ppm; **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 205.4 (d, *J* = 4.3 Hz), 136.2 (d, *J* = 4.8 Hz), 129.5, 128.5, 126.9, 90.1 (d, *J* = 171.4 Hz), 47.7 (d, *J* = 22.7 Hz), 41.1 (d, *J* = 21.2 Hz), 30.8.ppm; **$^{19}$F NMR (376 MHz, CDCl3)** δ -178.26 – -178.72 (m, 1F). ppm; **HRMS (ESI, m/z):** calcd for $C_{11}H_{13}OFNa$ $[M+Na]^+$ 203.0848, found: 208.0849.

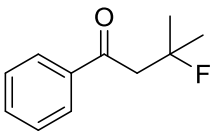
**3-fluoro-1-phenylbutan-1-one:**




**2o**

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.99 – 7.92 (m, 2H), 7.63 – 7.55 (m, 1H), 7.51 – 7.45 (m, 2H), 5.31 (ddq, *J* = 47.5, 12.4, 6.2 Hz, 1H), δ 3.51 (ddd, *J* = 16.7, 15.0, 6.7 Hz, 1H), 3.09 (ddd, *J* = 23.5, 16.7, 5.5 Hz, 1H), 1.48 (dd, *J* = 24.2, 6.2 Hz, 3H).**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 195.9 (d, *J* = 6.6 Hz), 135.8, 132.4, 127.7, 127.2, 86.2 (d, *J* = 165.4 Hz), 44.4 (d, *J* = 23.0 Hz), 20.2 (d, *J* = 22.3 Hz). **$^{19}$F NMR (376 MHz, CDCl3):** δ -172.65 (dpd, *J* = 47.8, 23.9, 14.9 Hz，1F).**HRMS (ESI, m/z):** calcd for $C_{10}H_{11}OFNa$ $[M+Na]^+$ 189.0692, found: 189.0686.

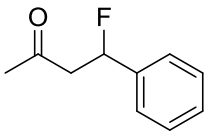
**3-fluoro-3-methyl-1-phenylbutan-1-one:**




**2p**

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.99 – 7.94 (m, 2H), 7.60 – 7.54 (m, 1H), 7.50 – 7.44 (m, 2H), 3.33 (d, *J* = 15.3 Hz, 2H), 1.54 (d, *J* = 22.2 Hz, 6H). ppm; **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 197.2 (d, *J* = 9.0 Hz), 137.4, 133.3, 128.6, 128.4, 94.5 (d, *J* = 166.6 Hz), 49.0 (d, *J* = 24.2 Hz), 27.1 (d, *J* = 23.7 Hz). **$^{19}$F NMR (376 MHz, CDCl3)** δ -128.59 – -129.50 (m，1F). **HRMS (ESI, m/z):** calcd for $C_{11}H_{13}FNa$ $[M+Na]^+$ 203.0848, found: 208.0844.

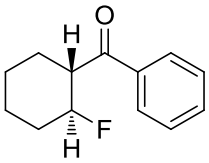
**4-fluoro-4-phenylbutan-2-one:**



2q

**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 7.42 – 7.31 (m, 5H), 5.95 (ddd, *J* = 46.9, 8.8, 4.0 Hz, 1H), 3.21 (ddd, *J* = 16.7, 14.7, 8.8 Hz, 1H), 2.82 (ddd, *J* = 32.1, 16.7, 4.0 Hz, 1H), 2.22 (s, 3H). ppm; **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 204.8 (d, *J* = 3.0 Hz), 139.1 (d, *J* = 19.7 Hz), 128.7 (d, *J* = 2.0 Hz), 128.6, 125.5 (d, *J* = 6.7 Hz), 90.1 (d, *J* = 170.8 Hz), 50.7 (d, *J* = 25.9 Hz), 30.9. ppm; **$^{19}$F NMR (376 MHz, CDCl3)** δ -174.10 (ddd, *J* = 46.8, 32.1, 14.7, 1F). ppm; **HRMS (ESI, m/z):** calcd for $C_{10}H_{11}OFNa$ $[M+Na]^+$ 189.0692, found: 189.0695.

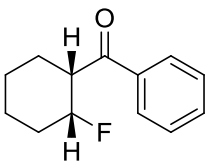
**((1R,2S)-2-fluorocyclohexyl)(phenyl)methanone:**



4a

**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 8.02 – 7.95 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 5.04 – 4.84 (m, 1H), 3.61 – 3.50 (m, 1H), 2.31 – 2.22 (m, 1H), 2.02 – 1.93 (m, 1H), 1.93 – 1.84 (m, 1H), 1.78 – 1.70 (m, 1H), 1.65 – 1.58 (m, 1H), 1.51 – 1.43 (m, 1H), 1.39 – 1.34 (m, 1H), 1.32 – 1.26 (m, 1H). ppm; **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 201.3 (d, *J* = 1.05 Hz), 136.8, 133.2, 128.6, 128.4, 92.3 (d, *J* = 173.6 Hz), 50.7 (d, *J* = 18.8 Hz), 31.8 (d, *J* = 18.1 Hz), 29.0 (d, *J* = 7.8 Hz), 24.6, 23.7 (d, *J* = 11.0 Hz). ppm; **$^{19}$F NMR (376 MHz, CDCl3)** δ -170.84 – -171.14 (m). ppm; **HRMS (ESI, m/z):** calcd for $C_{13}H_{15}OFNa$ $[M+Na]^+$ 229.1005, found: 229.1014.

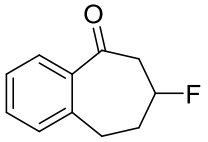
**((1R,2R)-2-fluorocyclohexyl)(phenyl)methanone:**



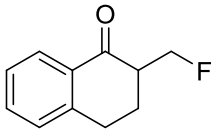
4a'

**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 7.90 – 7.84 (m, 2H), 7.60 – 7.53 (m, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 5.19 – 5.03 (m, 1H), 3.41 (dddd, *J* = 33.6, 11.8, 3.8, 1.9 Hz, 1H), 2.21 – 2.10 (m, 1H), 1.90 (ddd, *J* = 5.5, 4.5, 2.7 Hz, 1H), 1.82 – 1.74 (m, 1H), 1.71 – 1.64 (m, 1H), 1.64 – 1.59 (m, 1H), 1.46 – 1.36 (m, 1H). ppm; **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 200.1, 136.3, 132.8, 128.7, 128.1, 89.2 (d, *J* = 175.8 Hz), 48.7 (d, *J* = 21.4 Hz), 31.0 (d, *J* = 21.2 Hz), 24.3, 22.2 (d, *J* = 2.5 Hz), 19.9 (d, *J* = 1.9 Hz). ppm; **$^{19}$F NMR (376 MHz, CDCl3)** δ -192.90 – -194.31 (m). ppm; **HRMS (ESI, m/z):** calcd for $C_{13}H_{15}OFNa$ $[M+Na]^+$ 229.1005, found: 229.1014.

**4b 7-fluoro-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one, 4b' 2-(fluoromethyl)-3,4-dihydronaphthalen-1(2H)-one：**



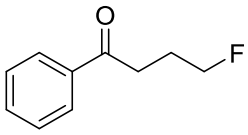
4b



4b'

**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 8.03 (dd, *J* = 7.8, 1.1 Hz, 0.74H), 7.79 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.49 (td, *J* = 7.5, 1.4 Hz, 0.74H), 7.43 (td, *J* = 7.5, 1.5 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1.48H), 7.28 – 7.23 (m, 2H), 5.10 (dddd, *J* = 48.2, 9.8, 7.8, 5.0 Hz, 1H), 4.95 – 4.85 (m, 0.74H), 4.83 – 4.74 (m, 0.74H), 3.34 – 3.13 (m, 3H), 3.10 – 3.00 (m, 1.6H), 2.98 – 2.77 (m, 1.74H), 2.44 – 2.33 (m, 1H), 2.33 – 2.03 (m, 2.7H).ppm; **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 198.4 (d, *J* = 11.4 Hz), 196.6 (d, *J* = 6.6 Hz), 144.1, 142.3, 138.2, 133.7, 132.3, 130.2, 129.0, 128.8, 127.4, 126.8 (d, *J* = 4.6 Hz), 88.1 (d, *J* = 174.0 Hz), 83.1 (d, *J* = 167.4 Hz), 48.4, 48.2, 47.9, 33.7, 33.5, 29.6 (d, *J* = 3.7 Hz), 28.6, 25.8 (d, *J* = 3.8 Hz). ppm; **$^{19}$F NMR (376 MHz, CDCl3)** δ -171.60 – -172.07 (m), -230.09 – -230.49 (m). ppm; **HRMS (ESI, m/z):** calcd for $C_{11}H_{11}OFNa$ $[M+Na]^+$ 201.0692, found: 201.0688.

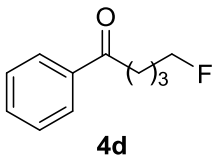
**4-fluoro-1-phenylbutan-1-one：**



4c

**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 7.98 (d, *J* = 7.4 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 4.62 (t, *J* = 5.7 Hz, 1H), 4.50 (t, *J* = 5.7 Hz, 1H), 3.15 (t, *J* = 7.1 Hz, 2H), 2.24 – 2.07 (m, 2H).ppm; **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 199.1, 136.7, 133.2, 128.6, 128.0, 83.3 (d, *J* = 164.4 Hz), 34.0 (d, *J* = 4.1 Hz), 24.8 (d, *J* = 20.0 Hz).ppm; **$^{19}$F NMR (376 MHz, CDCl3)** δ -220.09 (tt, *J* = 47.3, 26.9 Hz, 1F). ppm; **HRMS (ESI, m/z):** calcd for $C_{10}H_{11}OFNa$ $[M+Na]^+$ 189.0692, found: 189.0699.

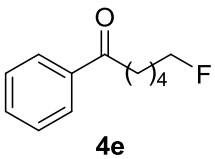
**5-fluoro-1-phenylpentan-1-one：**



4d

**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 8.00 – 7.94 (m, 2H), 7.60 – 7.53 (m, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 4.56 (t, *J* = 5.7 Hz, 1H), 4.44 (t, *J* = 5.9 Hz, 1H), 3.05 (t, *J* = 7.0 Hz, 2H), 1.94 – 1.72 (m, 4H). ppm; **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 199.8, 136.9, 133.1, 128.6, 128.0, 84.0 (d, *J* = 164.7 Hz), 37.9, 29.9 (d, *J* = 19.7 Hz), 20.1 (d, *J* = 5.3 Hz).ppm; **$^{19}$F NMR (376 MHz, CDCl3)** δ -218.46 (dq, *J* = 47.5, 25.2 Hz 1F). ppm; **HRMS (ESI, m/z):** calcd for $C_{11}H_{13}OFNa$ $[M+Na]^+$ 203.0848, found: 203.0845.

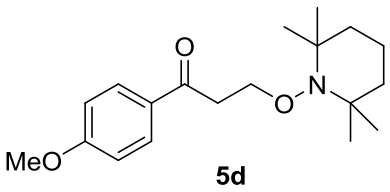
**6-fluoro-1-phenylhexan-1-one：**



**4e**

**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 7.99 – 7.93 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 4.52 (t, *J* = 6.1 Hz, 1H), 4.41 (t, *J* = 6.1 Hz, 1H), 3.00 (t, *J* = 7.3 Hz,2H), 1.84 – 1.68 (m, 4H), 1.54 – 1.45 (m, 2H). ppm; **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 200.11 (s), 136.97 (s), 132.98 (s), 128.58 (s), 128.01 (s), 83.92 (d, *J* = 164.4 Hz), 38.35 (s), 30.30 (d, *J* = 19.6 Hz), 24.99 (d, *J* = 5.3 Hz), 23.81 (s). ppm; **$^{19}$F NMR (376 MHz, CDCl3)** δ -218.38 (tt, *J* = 47.3, 25.2 Hz). ppm; **HRMS (ESI, m/z):** calcd for $C_{12}H_{15}OFNa$ $[M+Na]^+$ 217.1005, found: 217.1006.

**1-(4-methoxyphenyl)-3-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propan-1-one：**



**5d**

**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 8.00 – 7.96 (m, 2H), 6.96 – 6.91 (m, 2H), 4.14 (t, *J* = 6.6 Hz, 2H), 3.87 (s, 3H), 3.11 (t, *J* = 6.6 Hz, 2H), 1.57 – 1.34 (m, 6H), 1.16 (s, 6H), 1.00 (s, 6H). ppm; **HRMS (ESI, m/z):** calcd for $C_{19}H_{29}NO_3Na$ $[M+Na]^+$ 342.2045, found: 342.2050.

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3. Doering，Henderson，*J. Am. Chem. Soc.***1958**, *80*, 5274.
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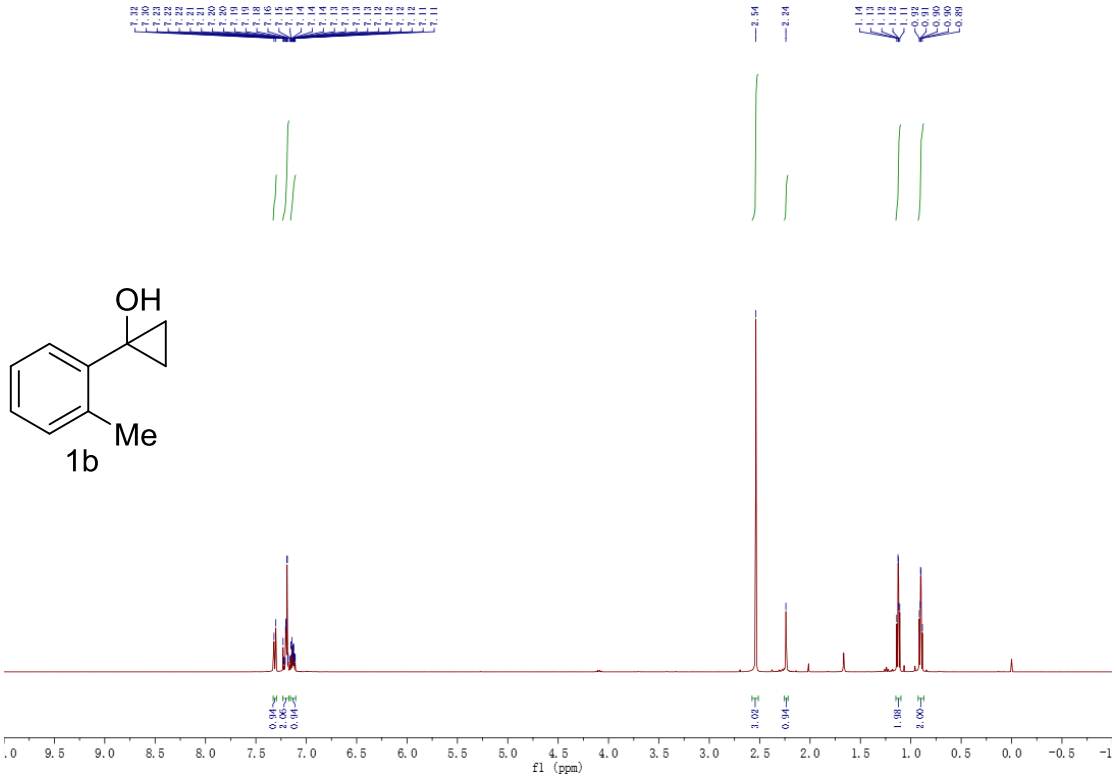
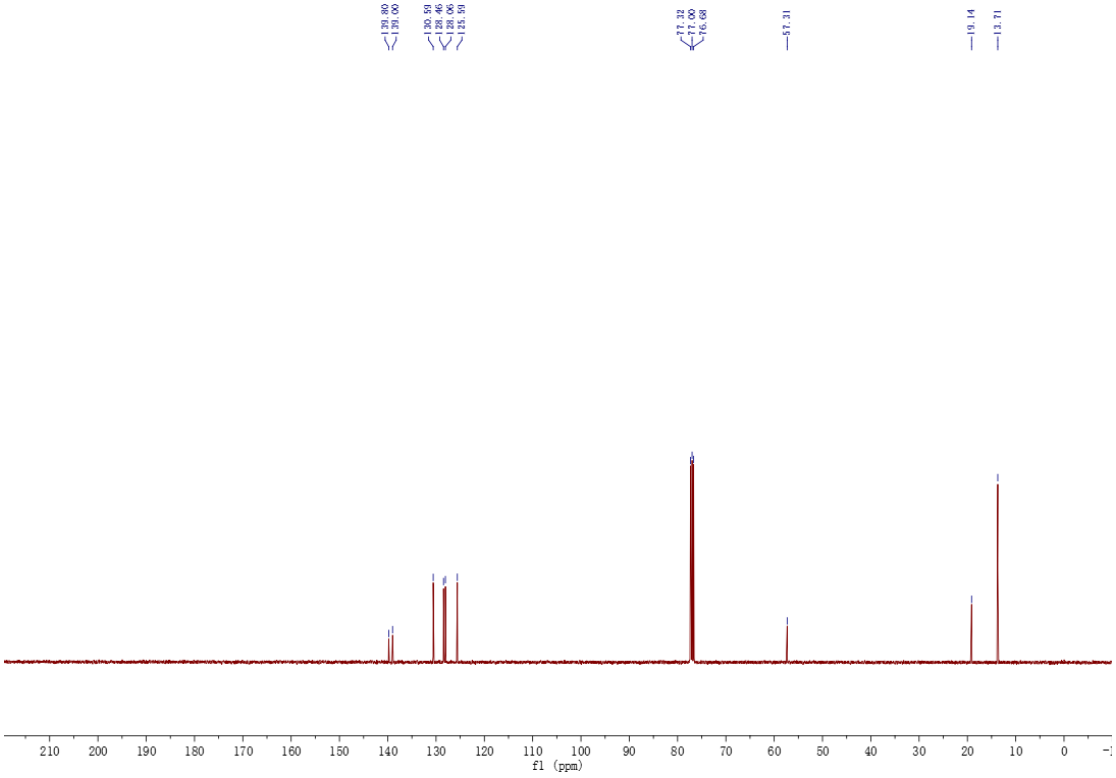
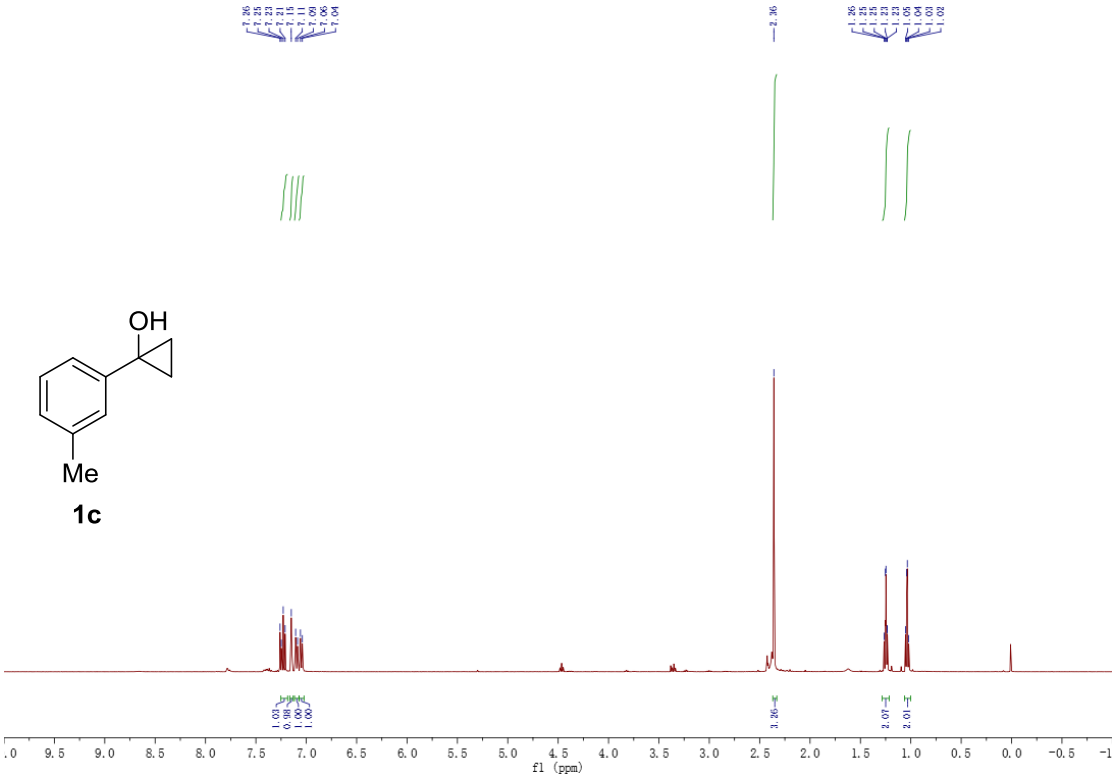
# $^{1}H$ and $^{13}C$ NMR spectra of unknown substrates and products

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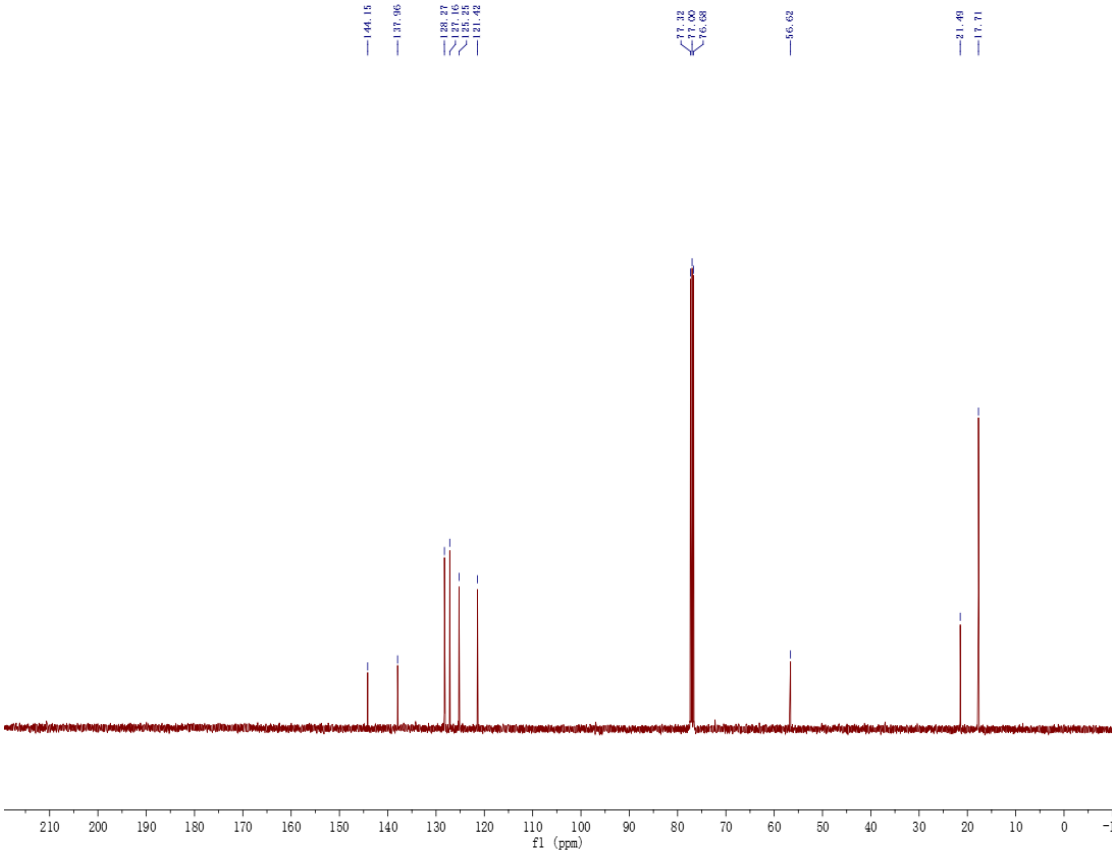
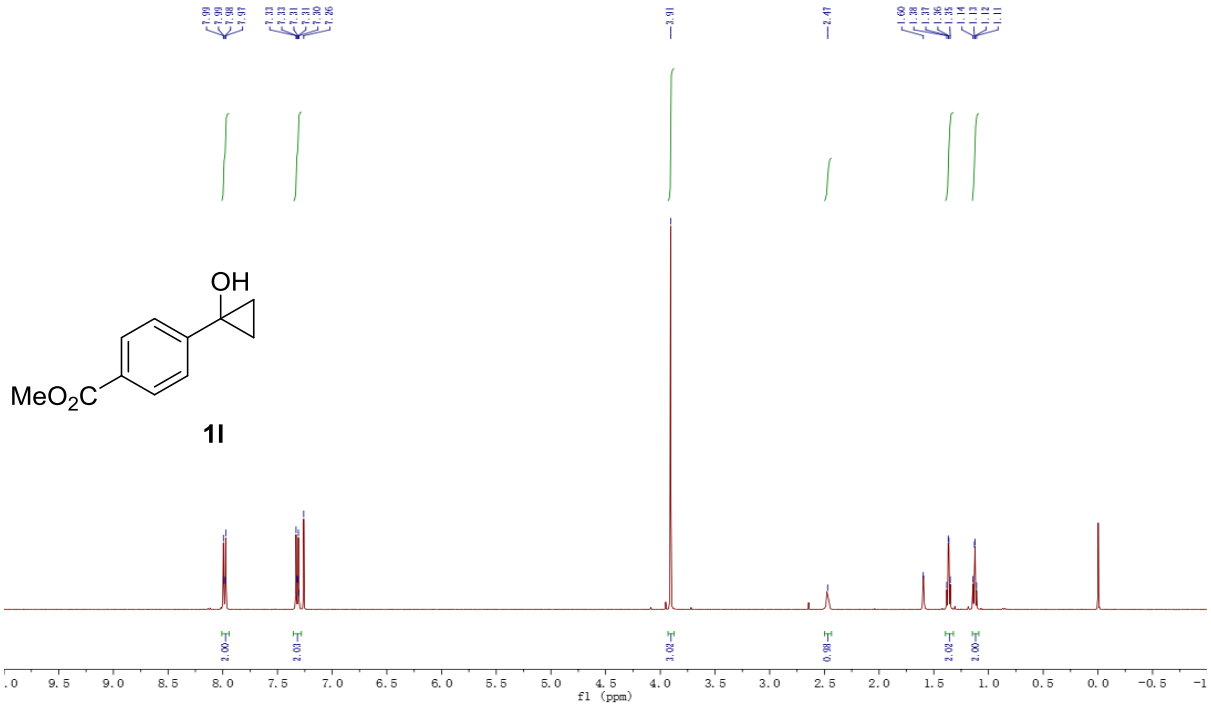
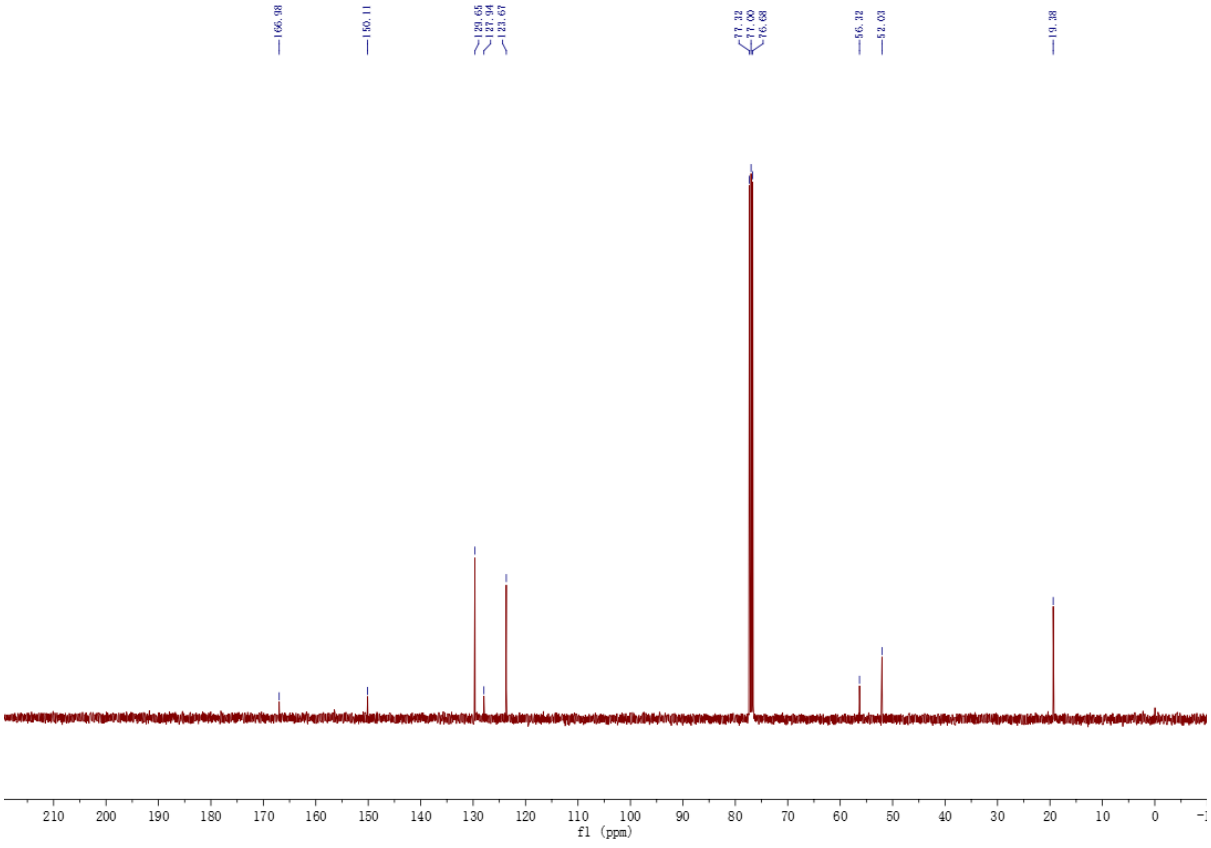
Me
1c
f1 (ppm)


f1 (ppm)


OH
MeO2C
1l
f1 (ppm)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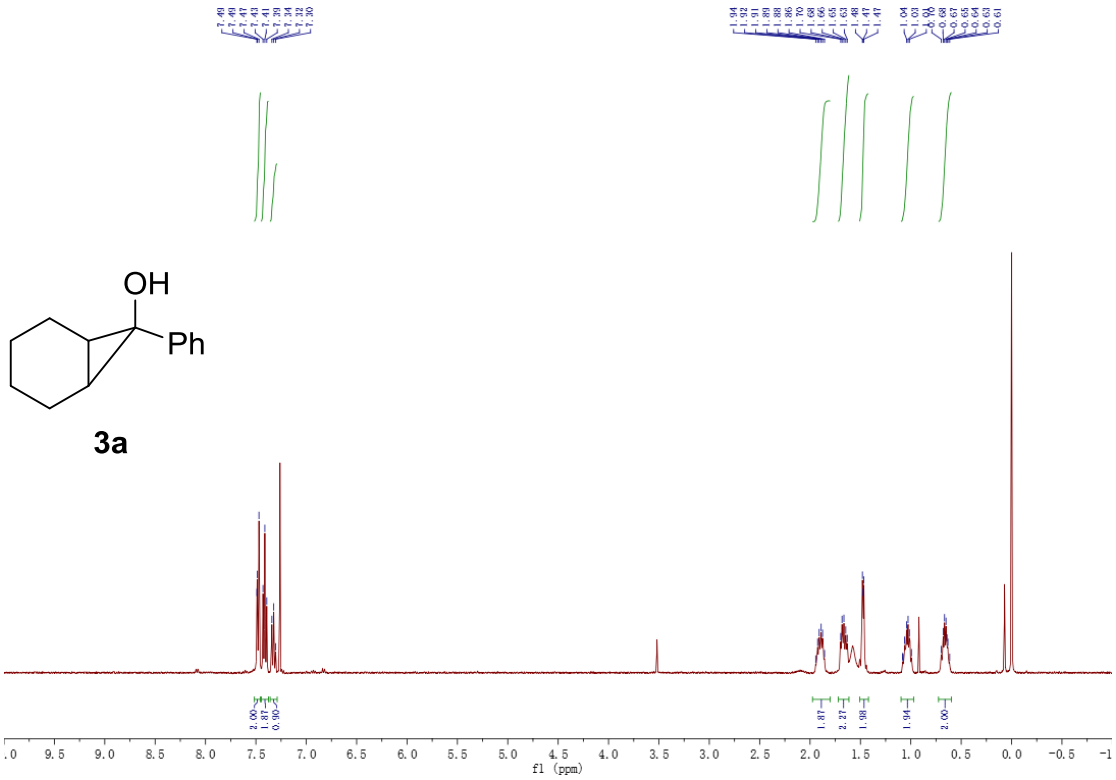
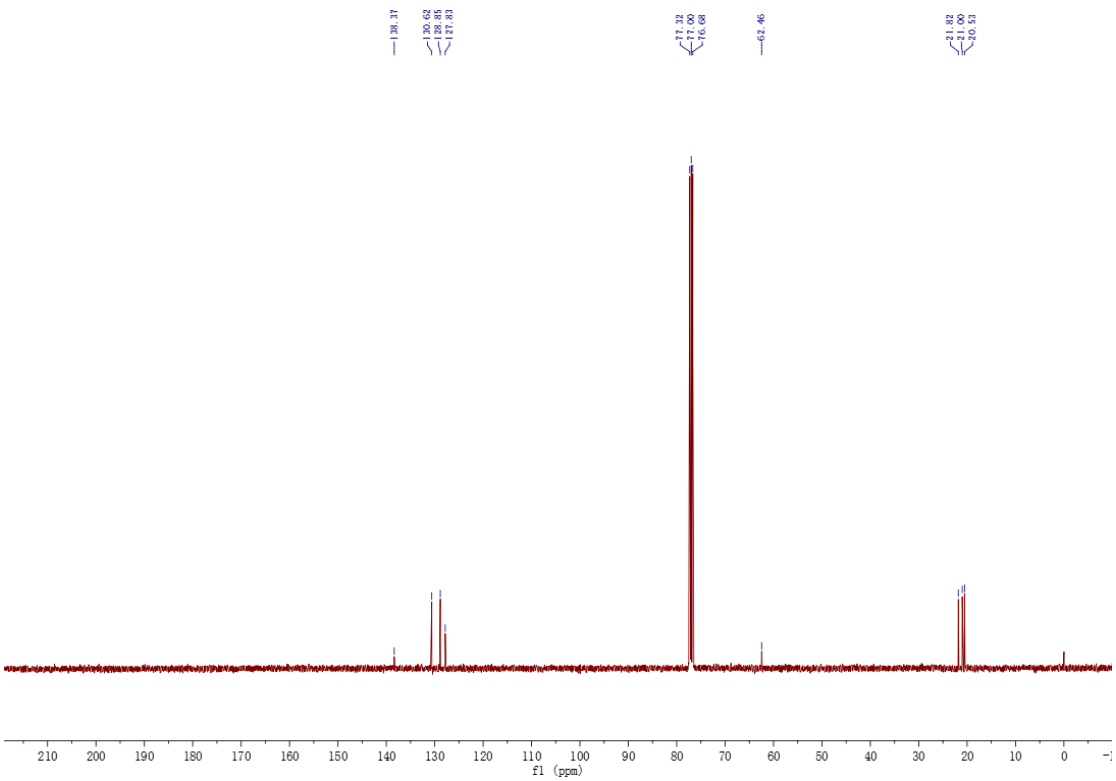
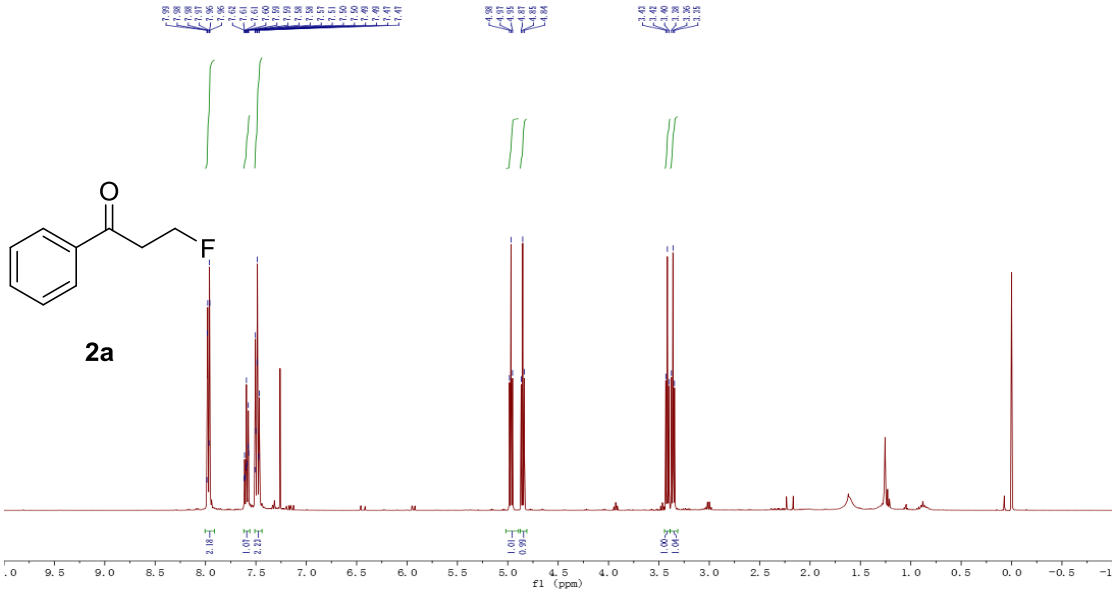
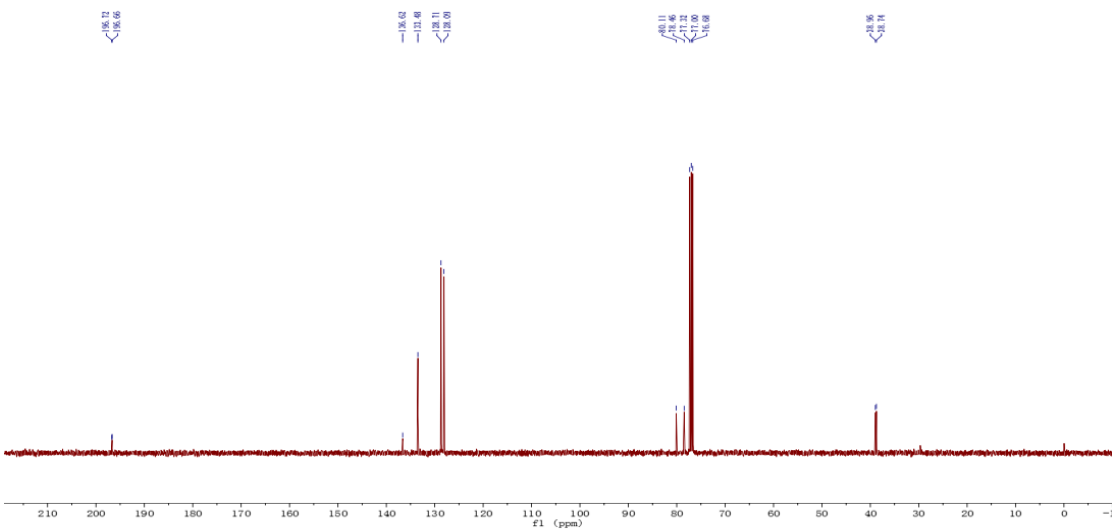



**3a**




O
F
2a
f1 (ppm)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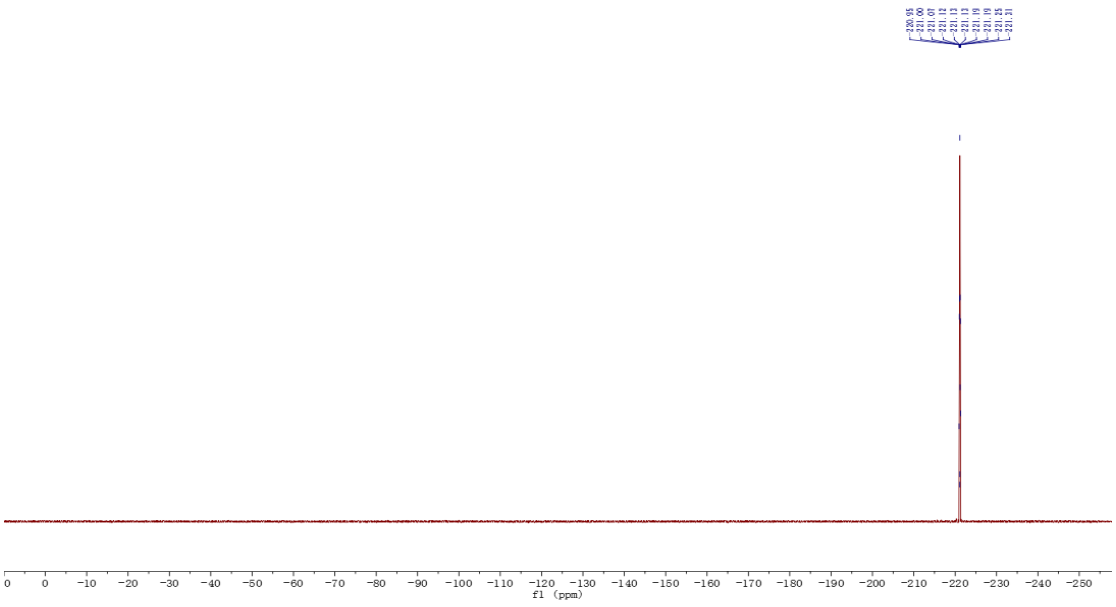
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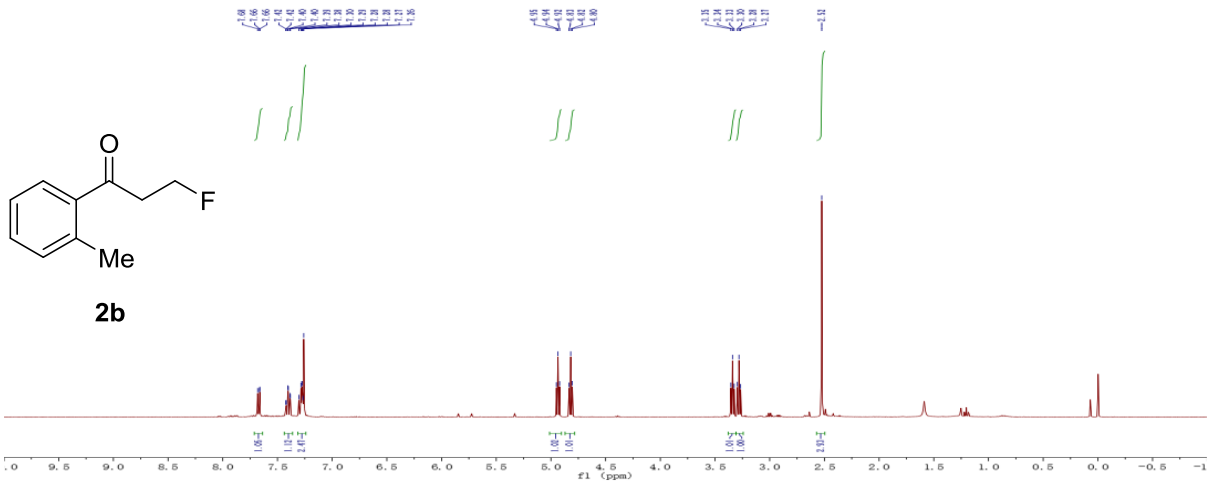
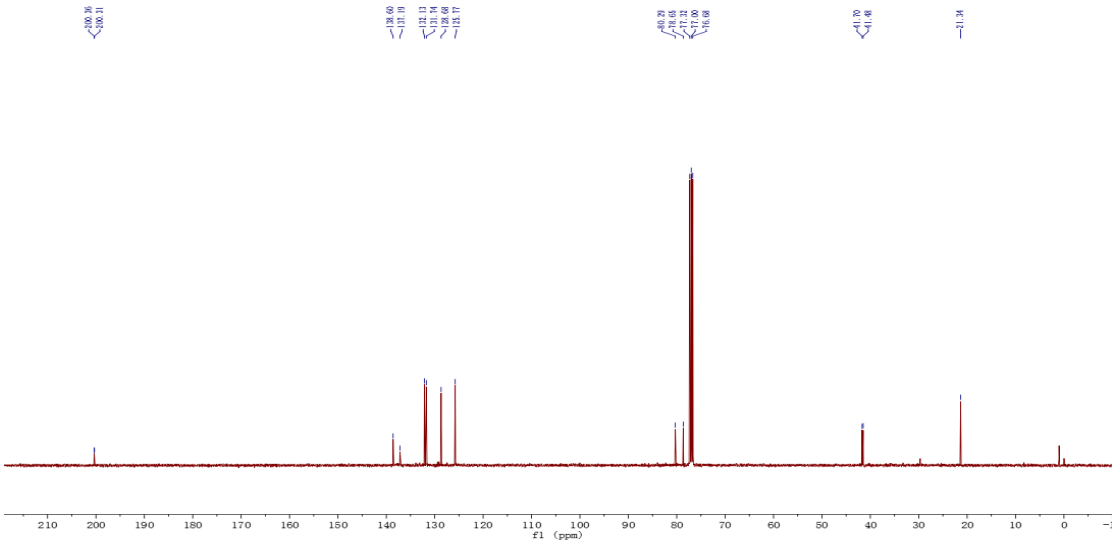
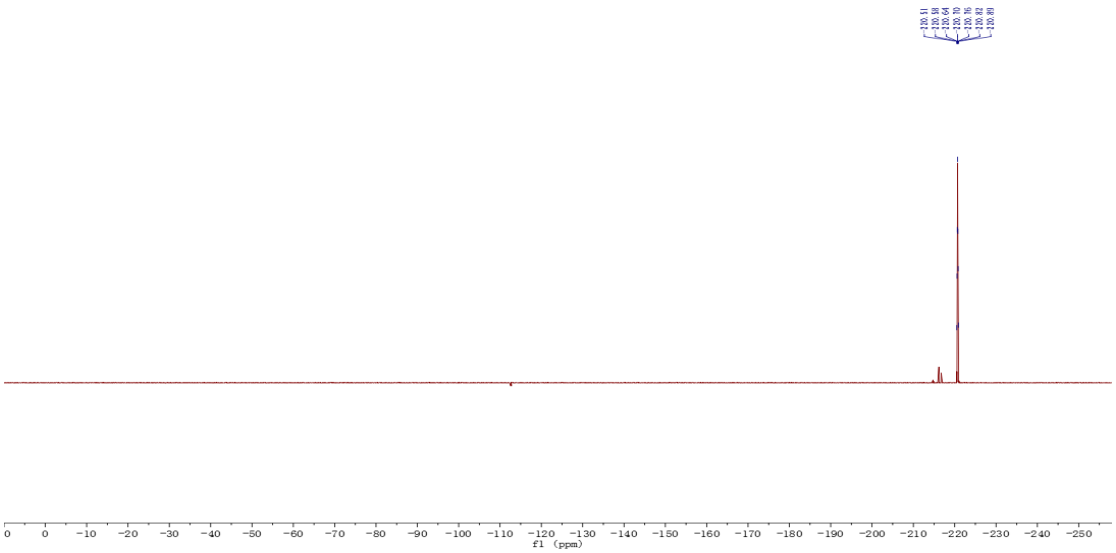
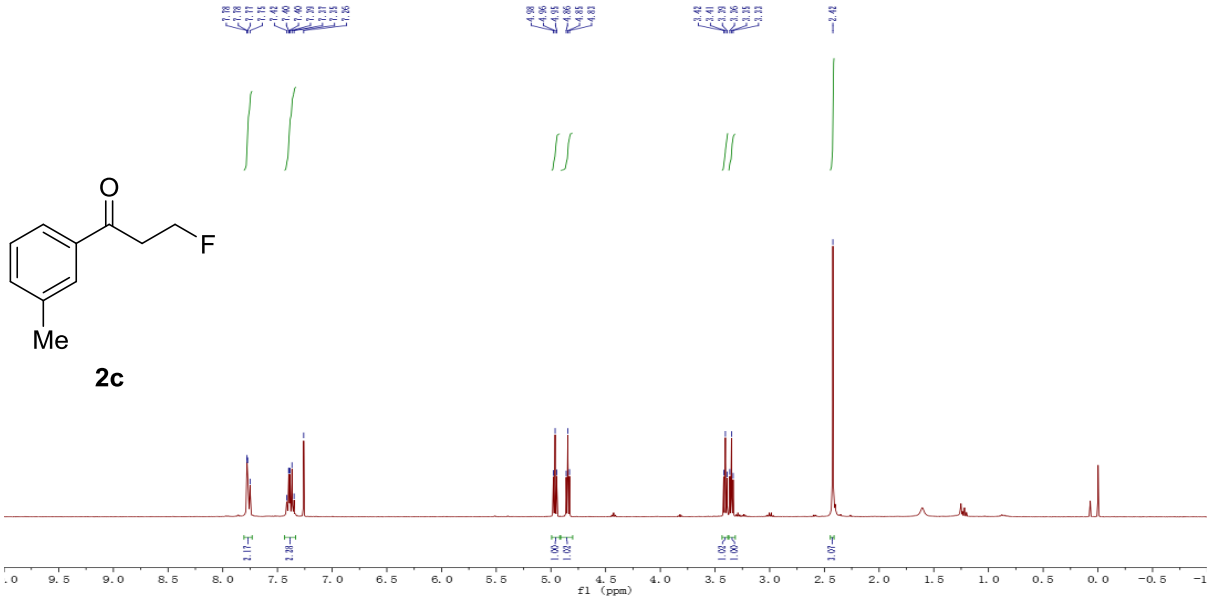


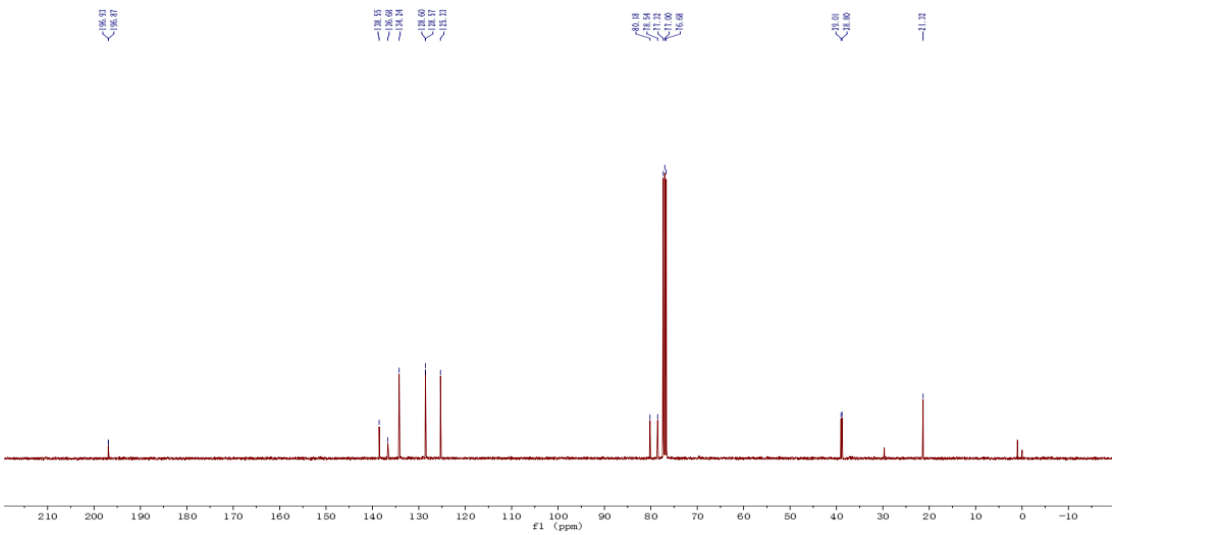

**2b**

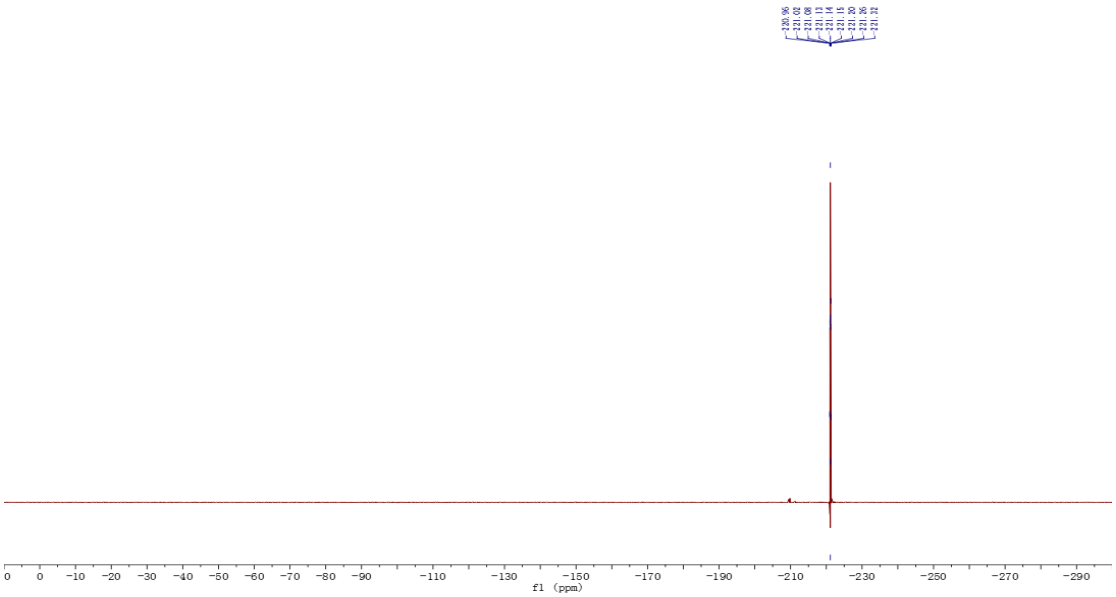


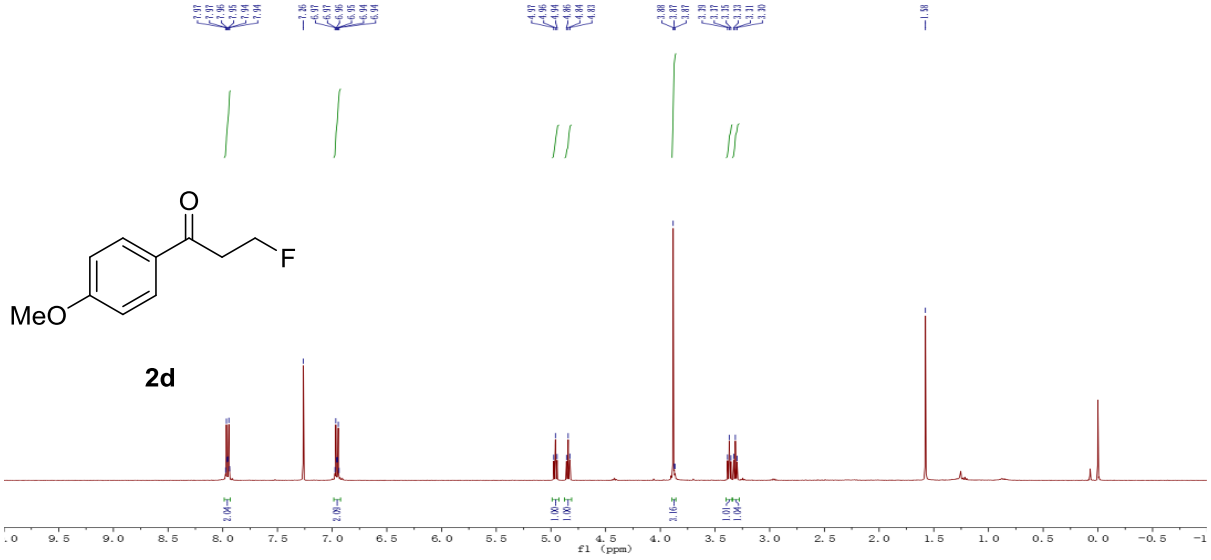





**2c**

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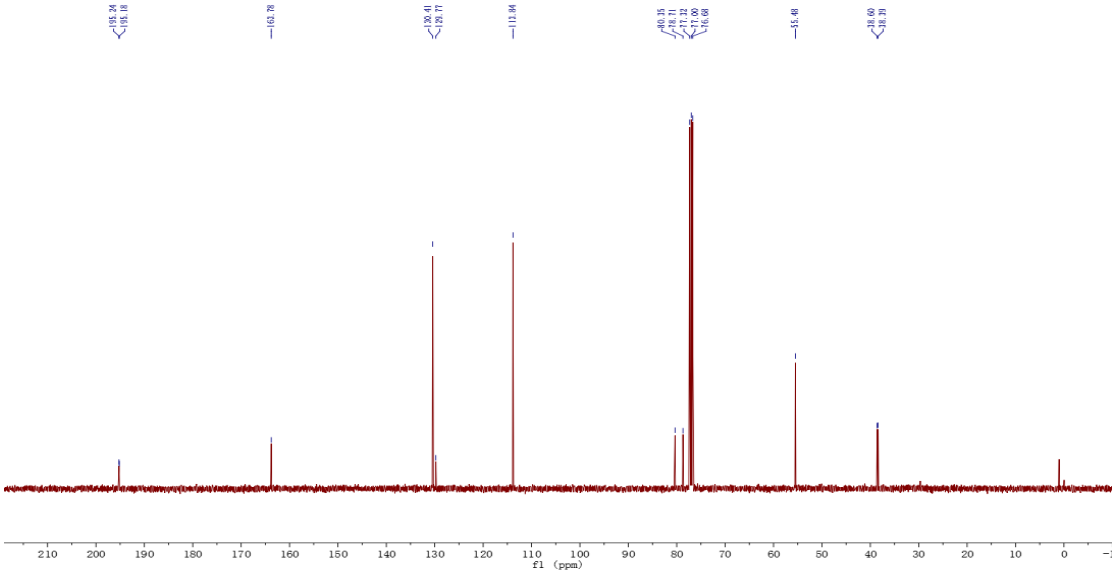
F
MeO
2d
f1 (ppm)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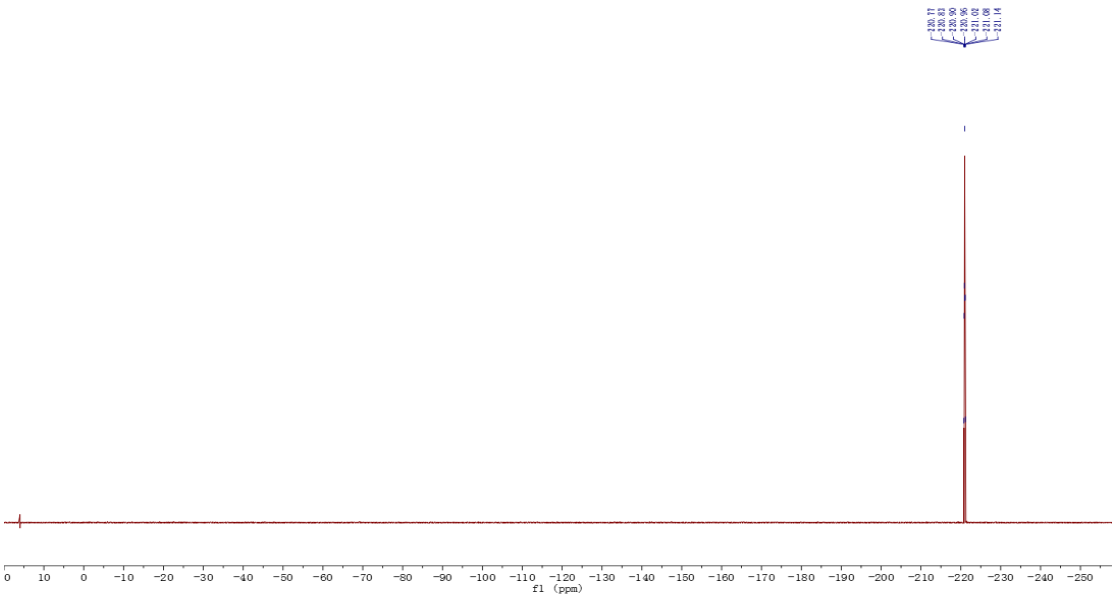
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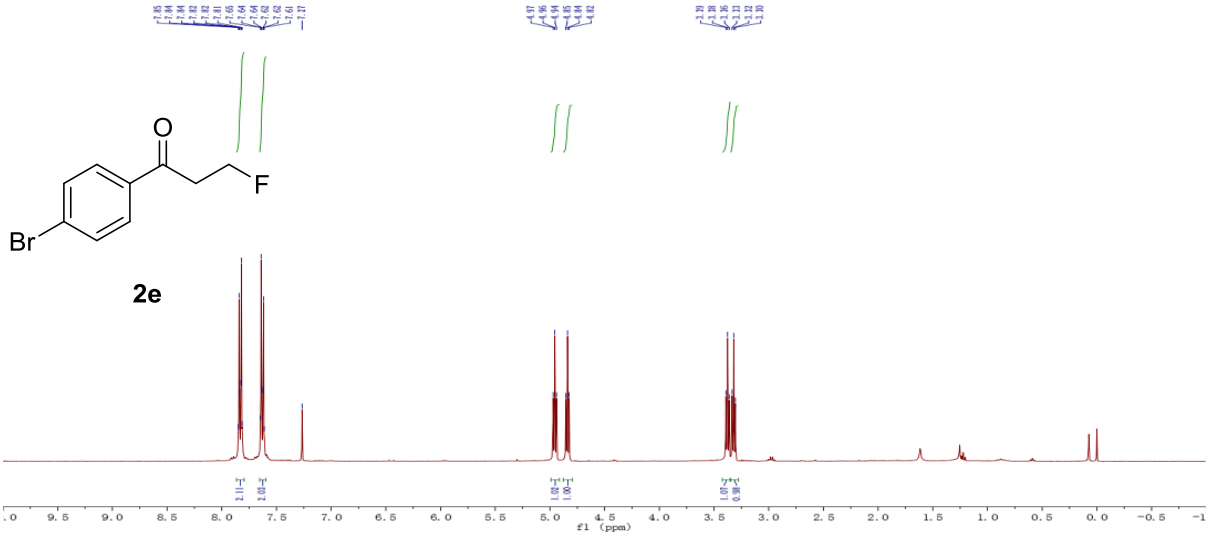
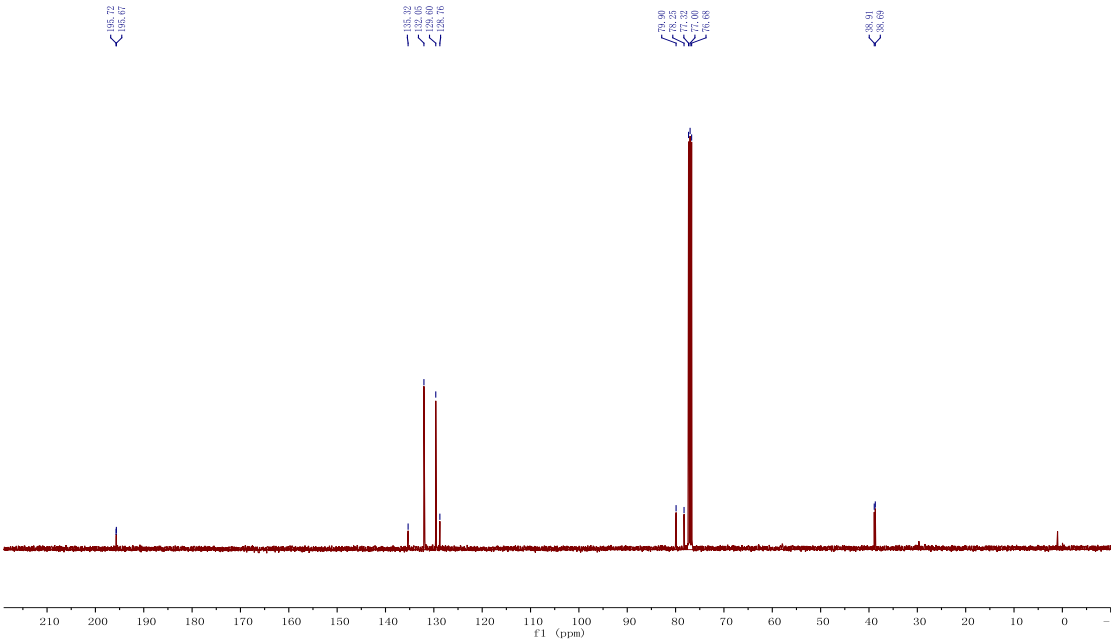
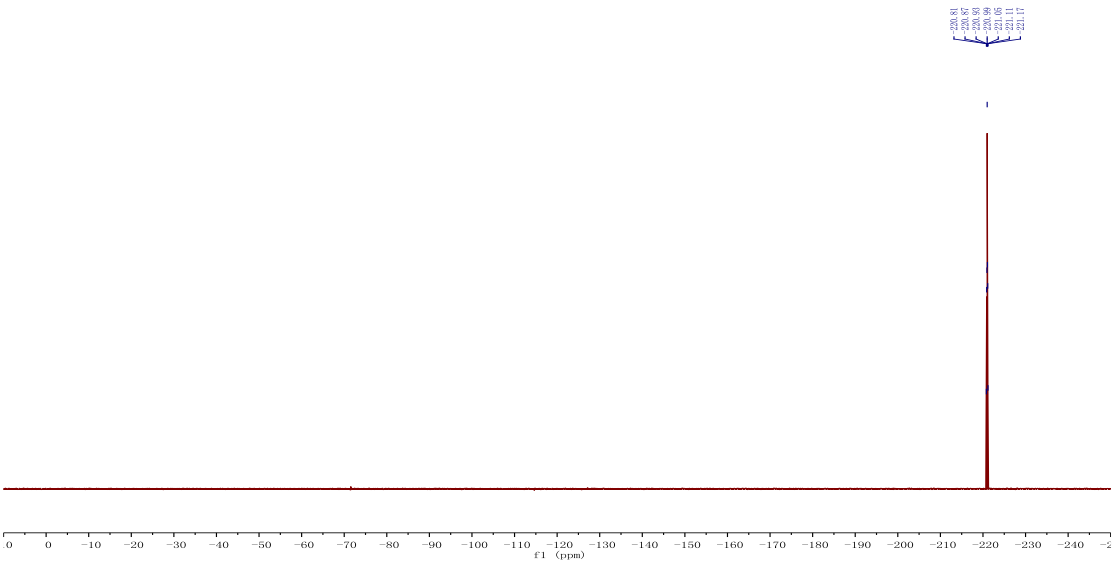
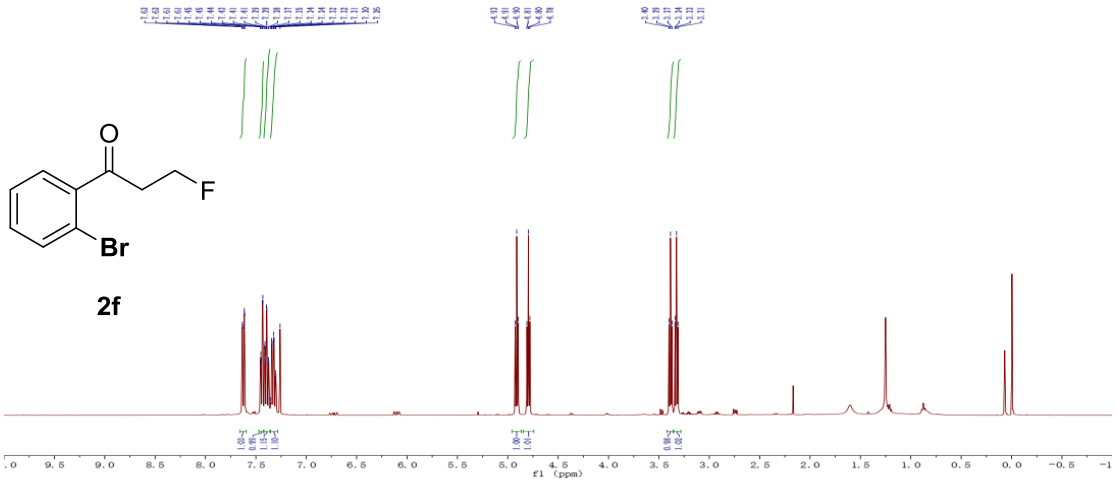



**2e**



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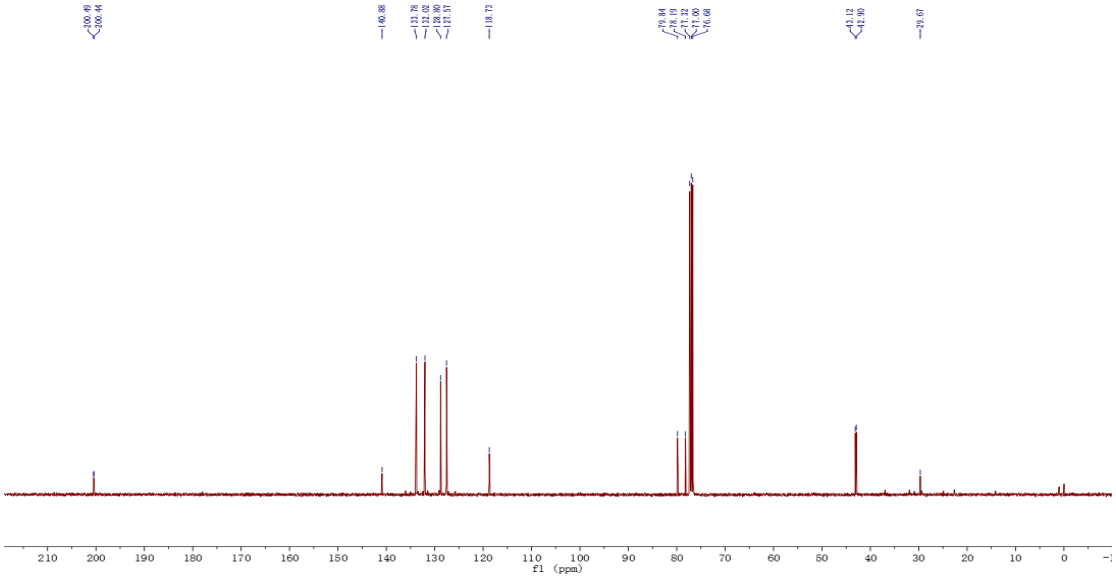
f1 (ppm)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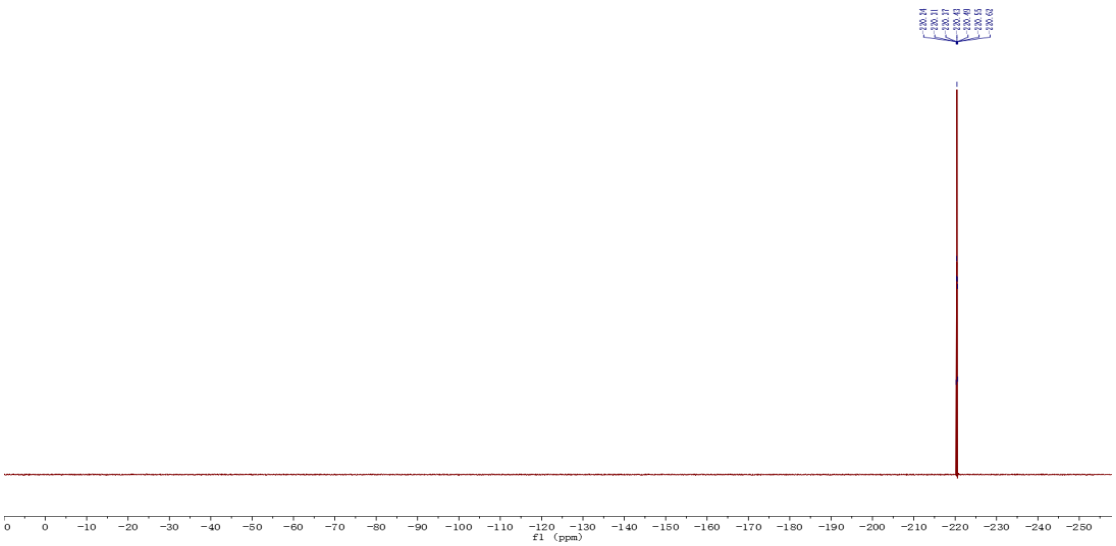
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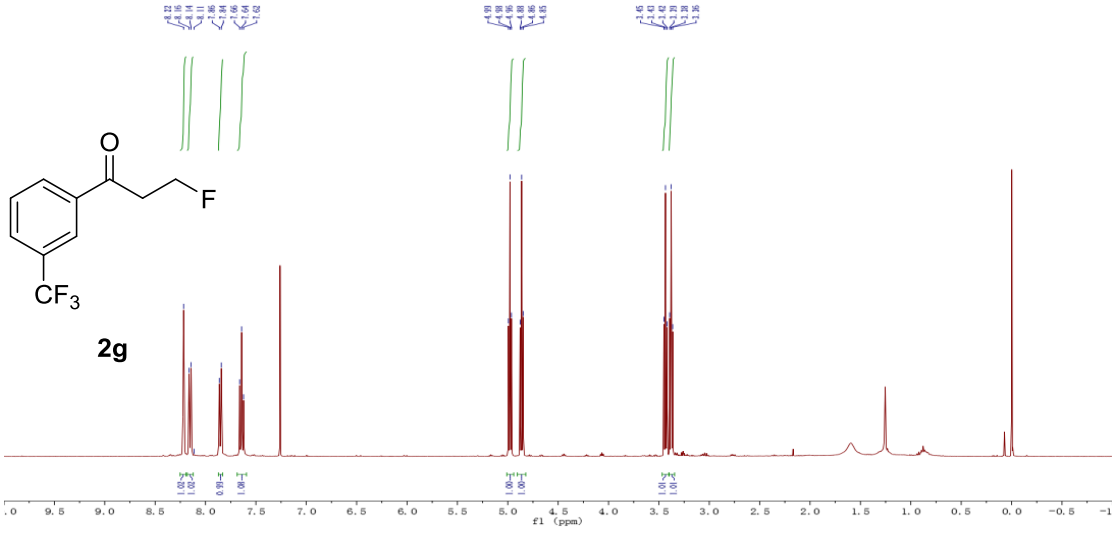
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CF3
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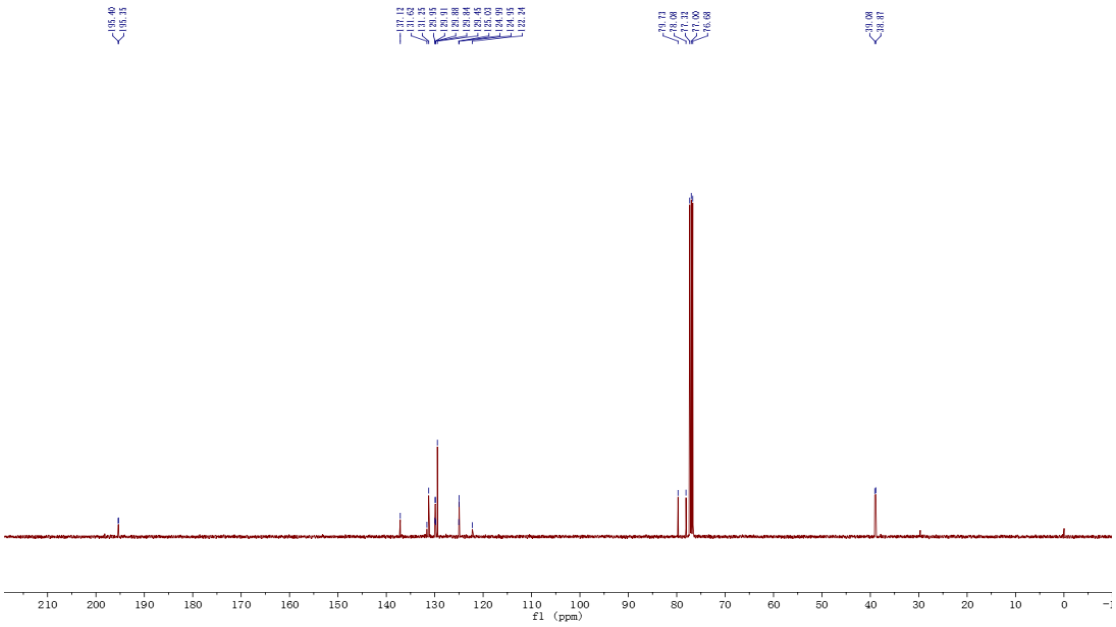
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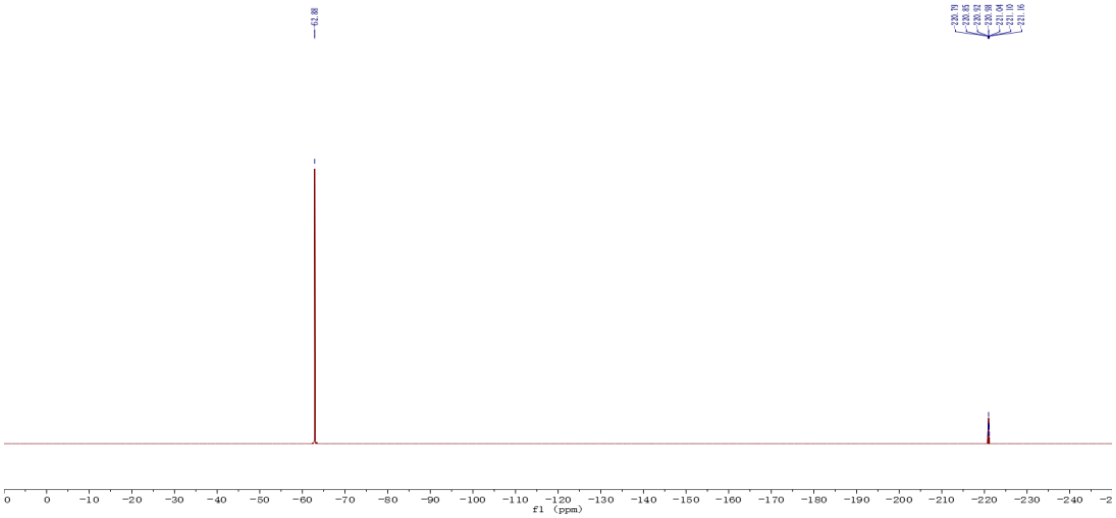
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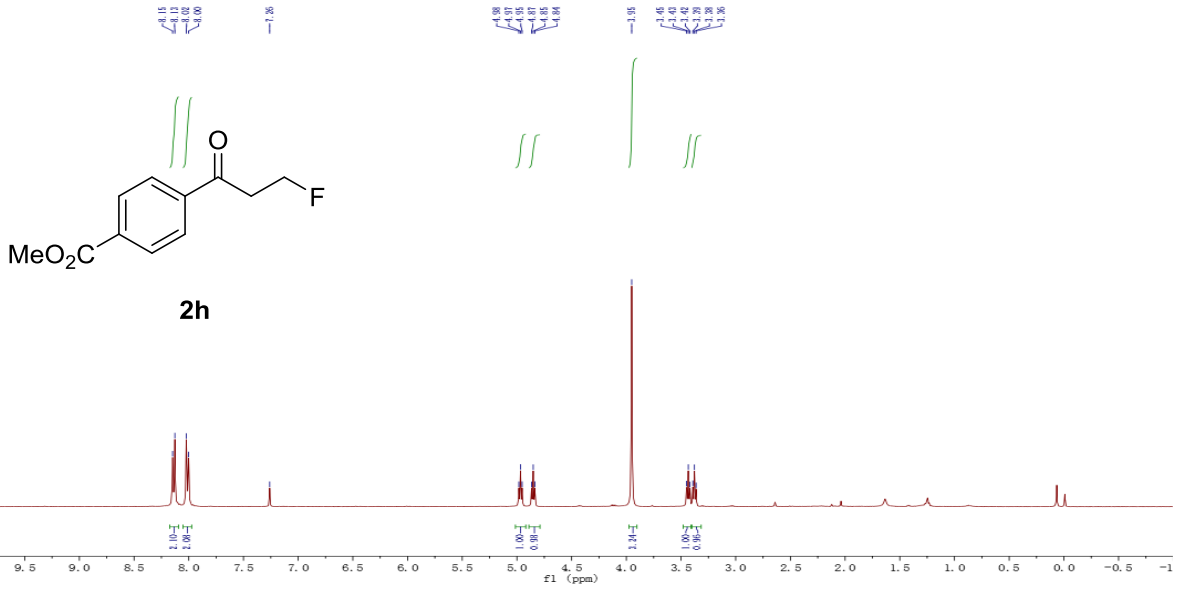


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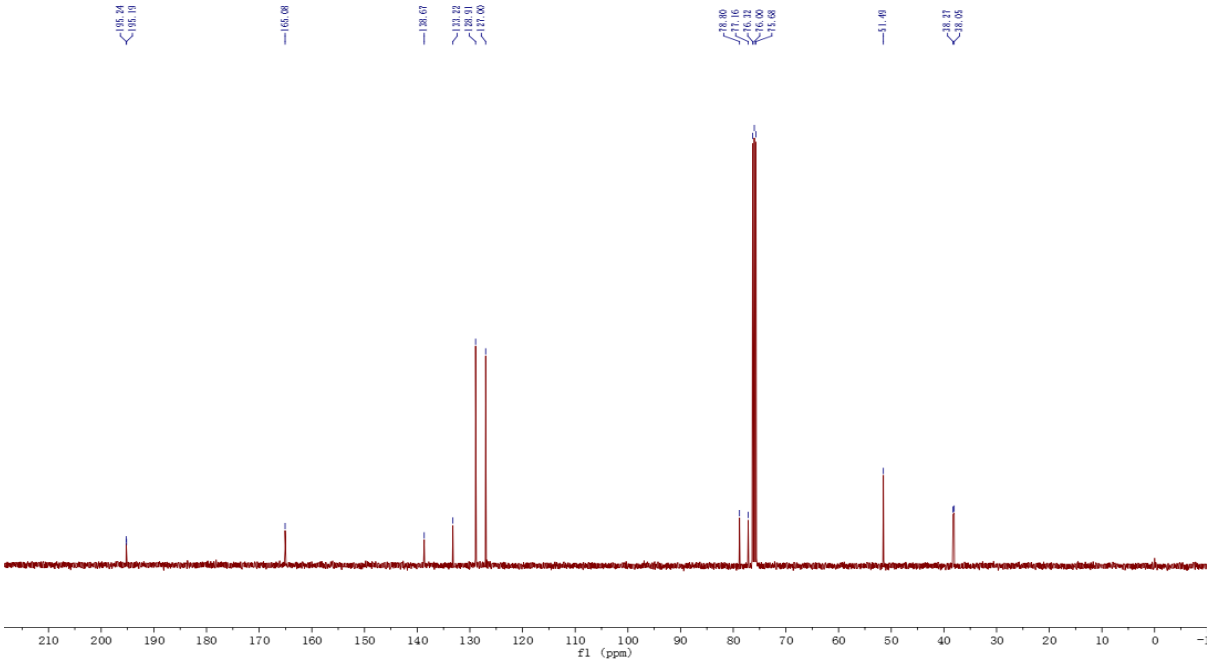
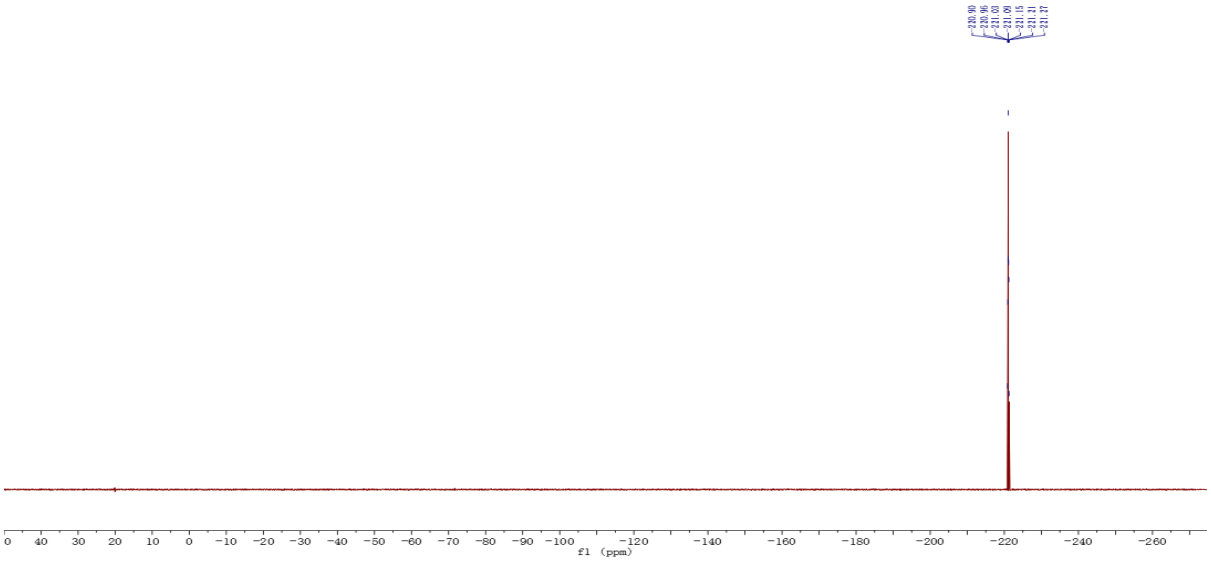
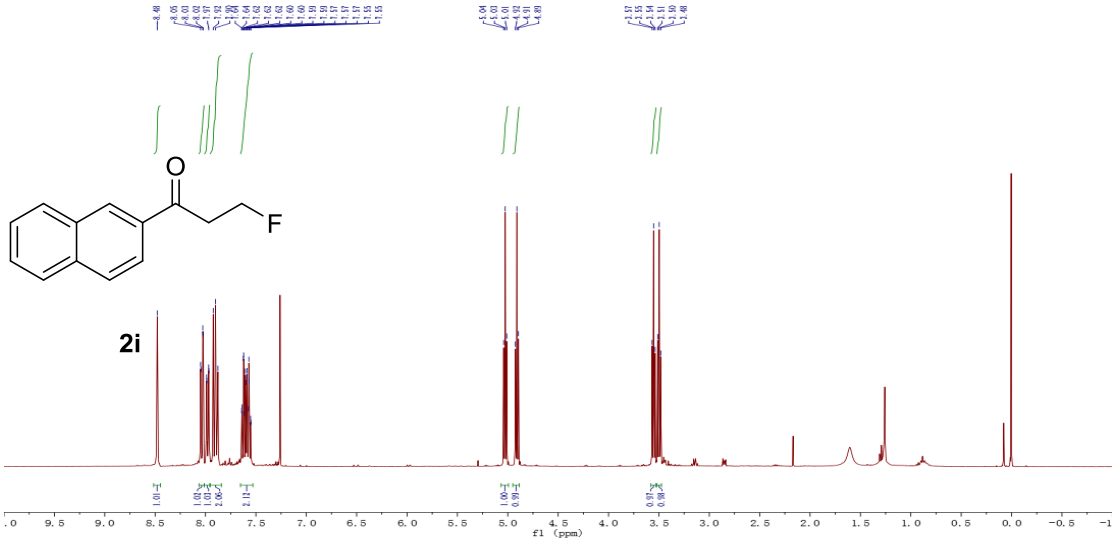
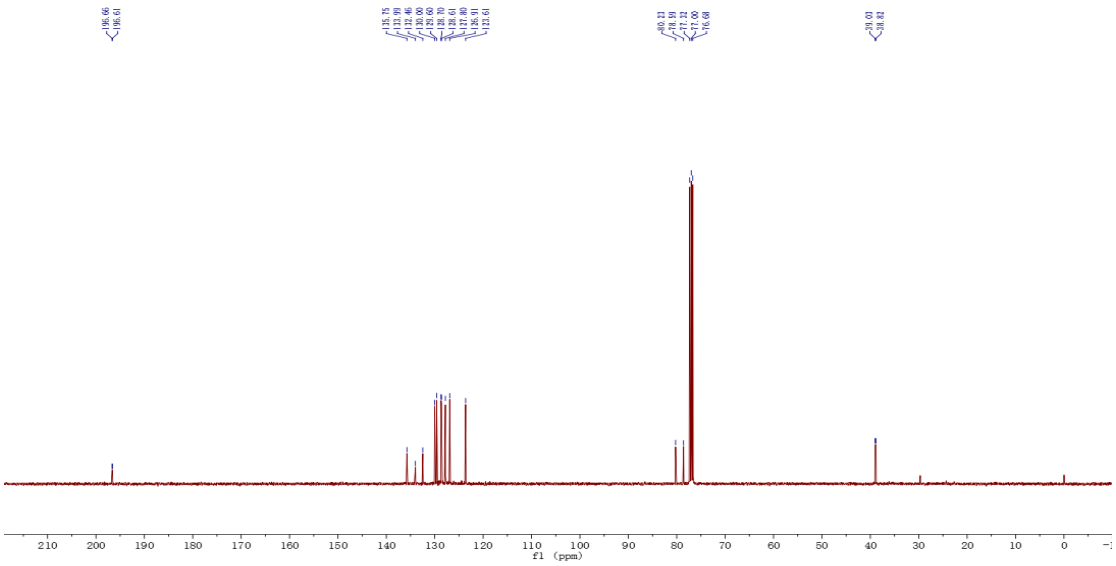









O
F
2i
f1 (ppm)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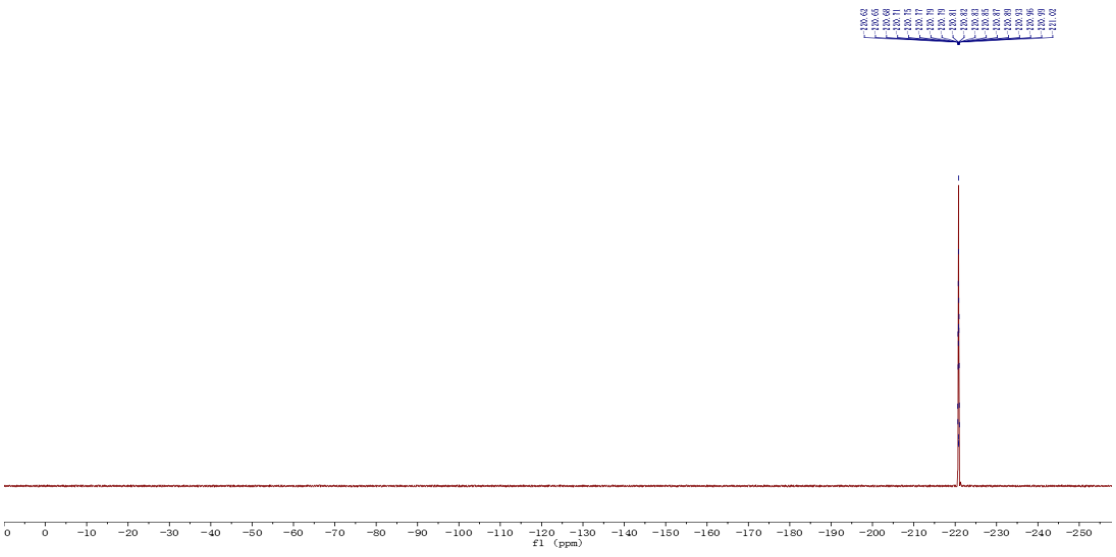
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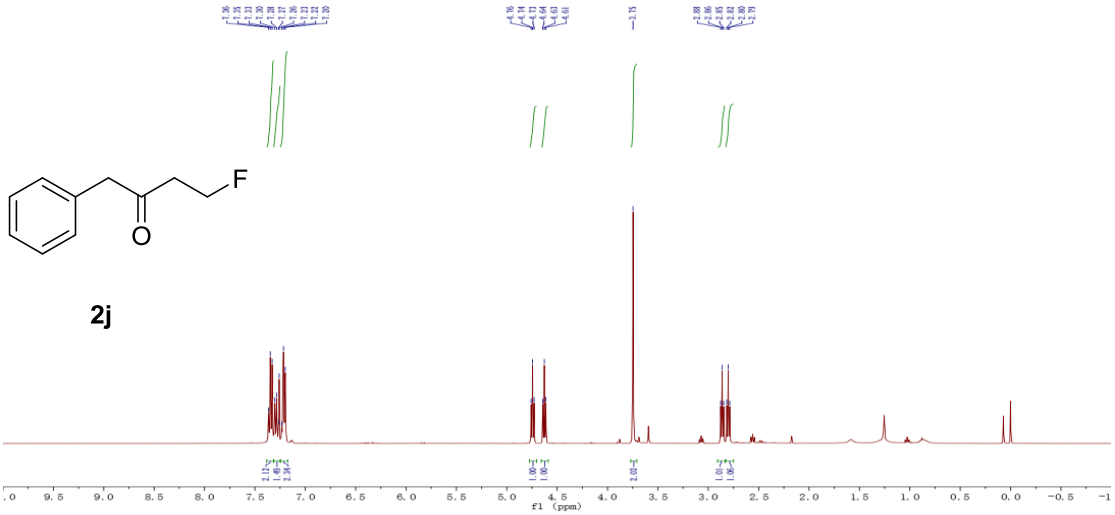
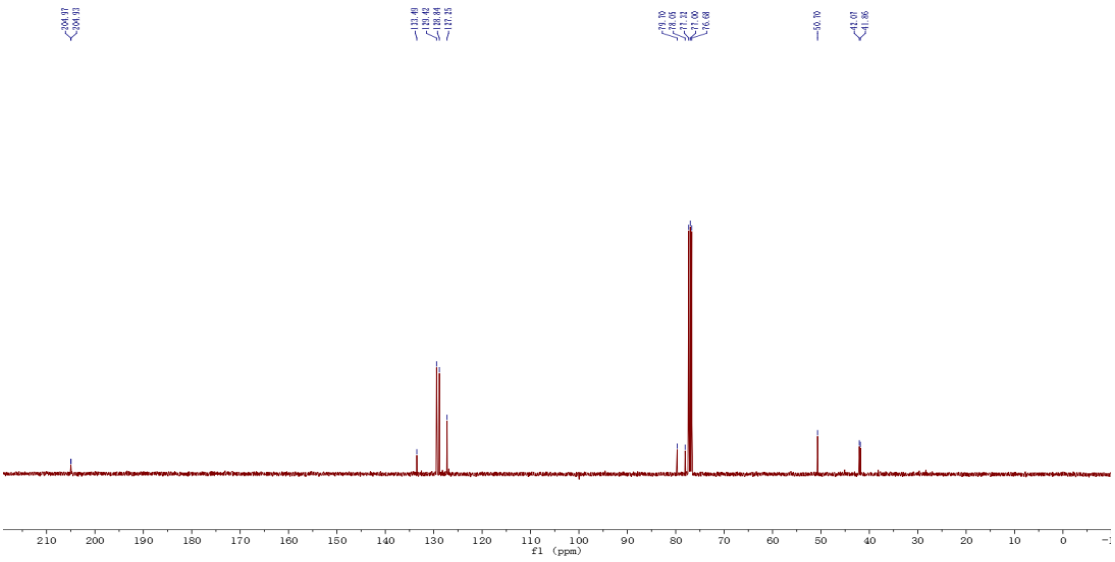
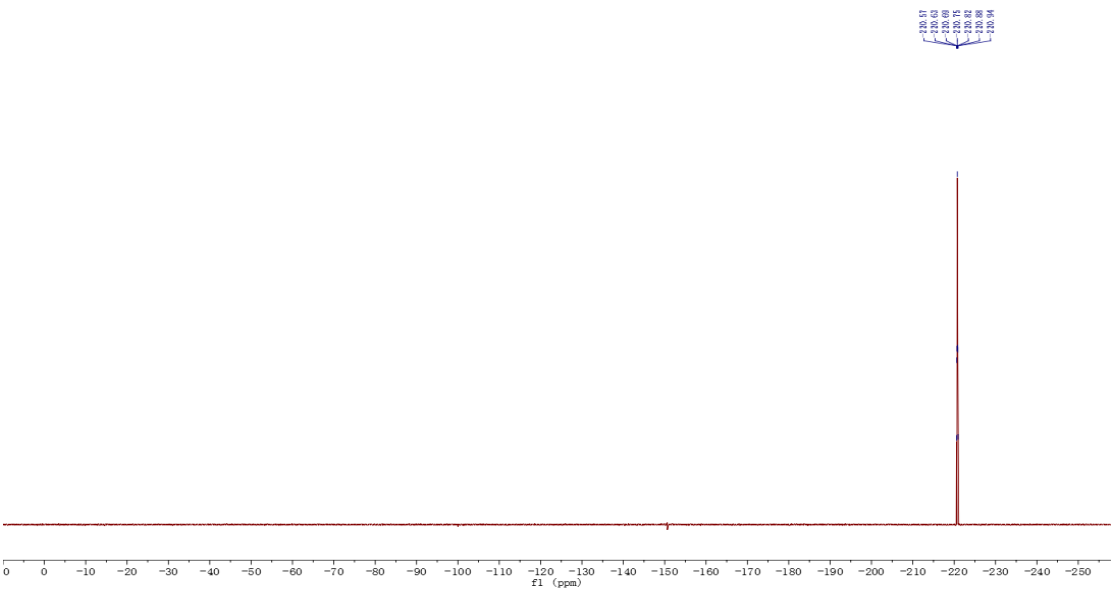
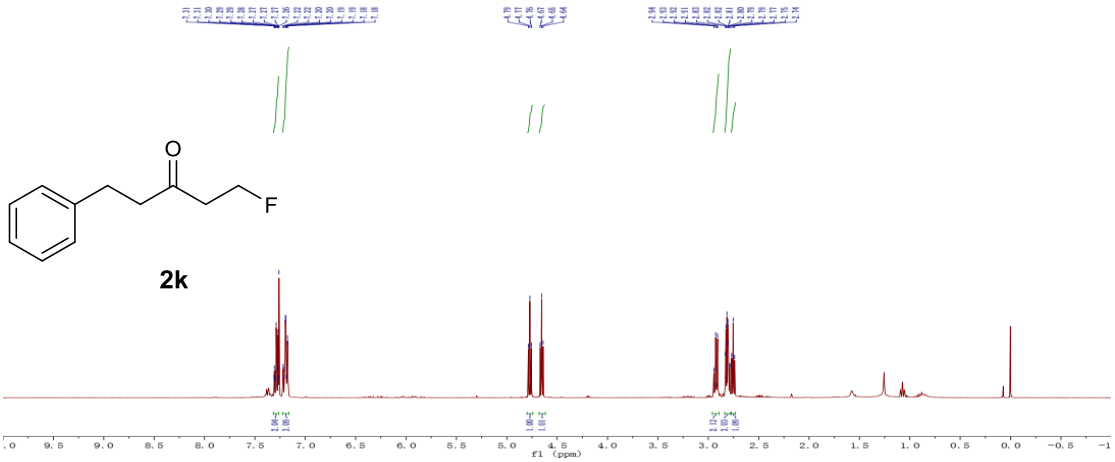


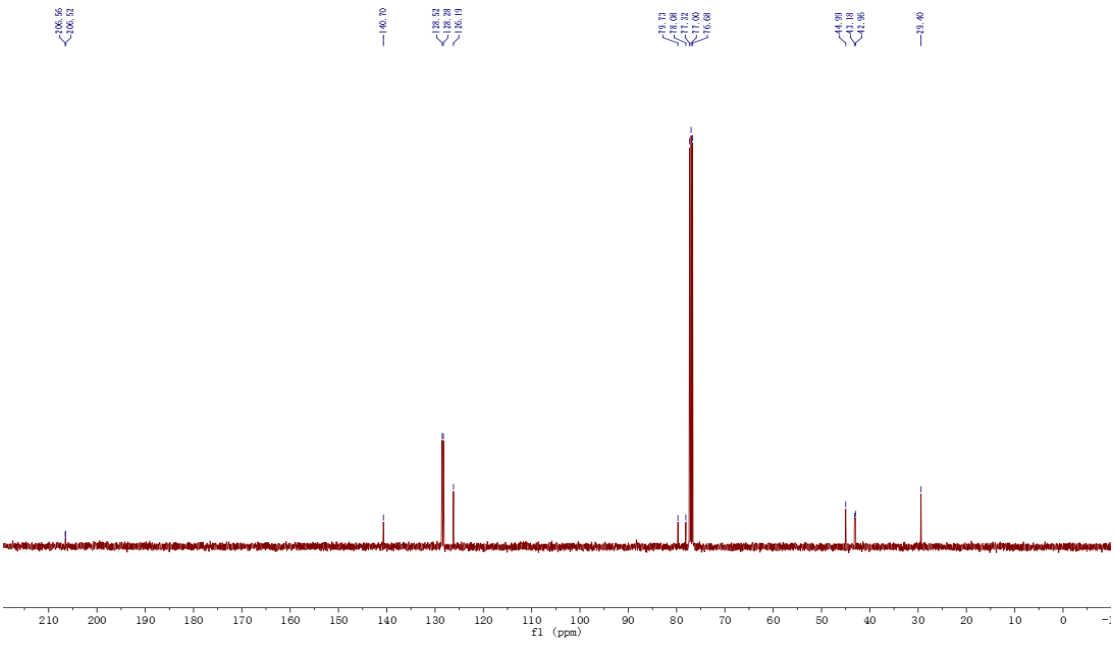

**2j**

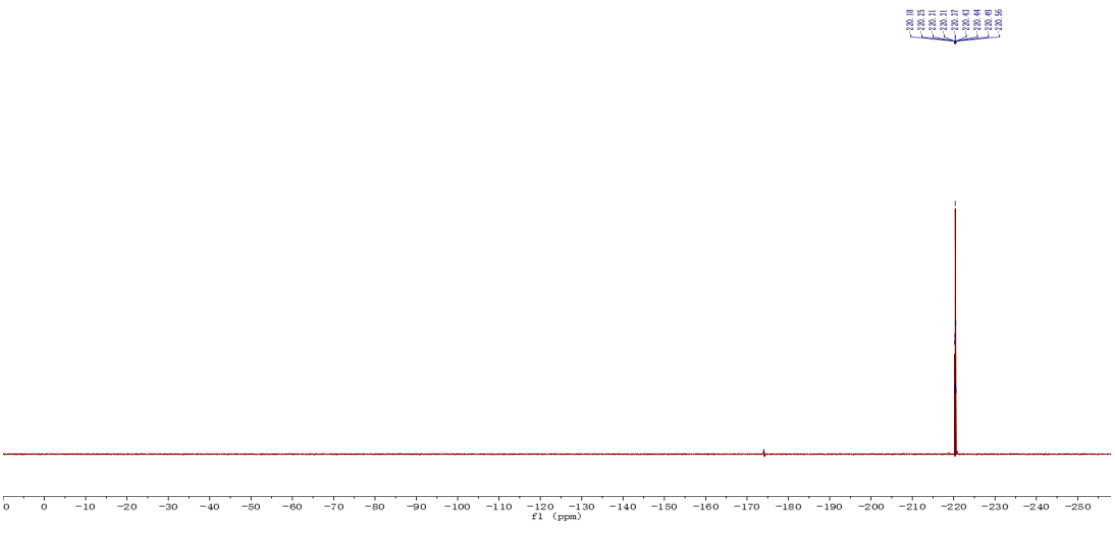


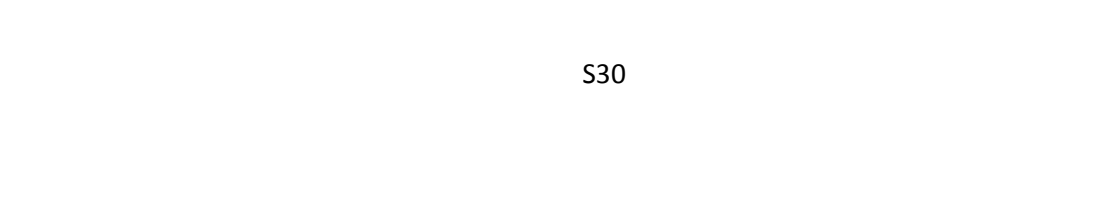


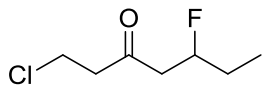



**2k**



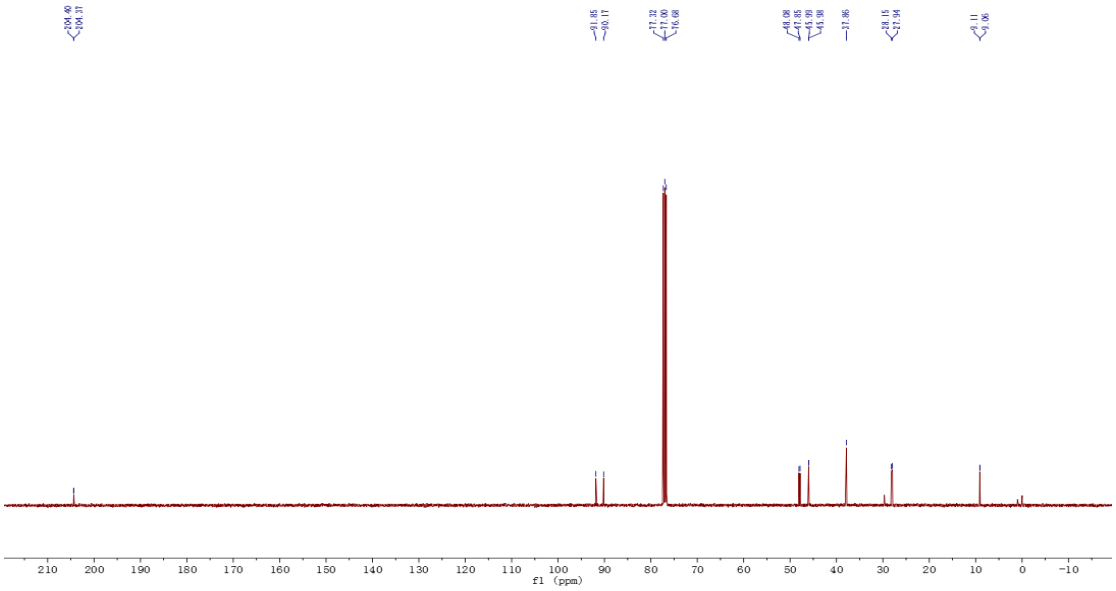


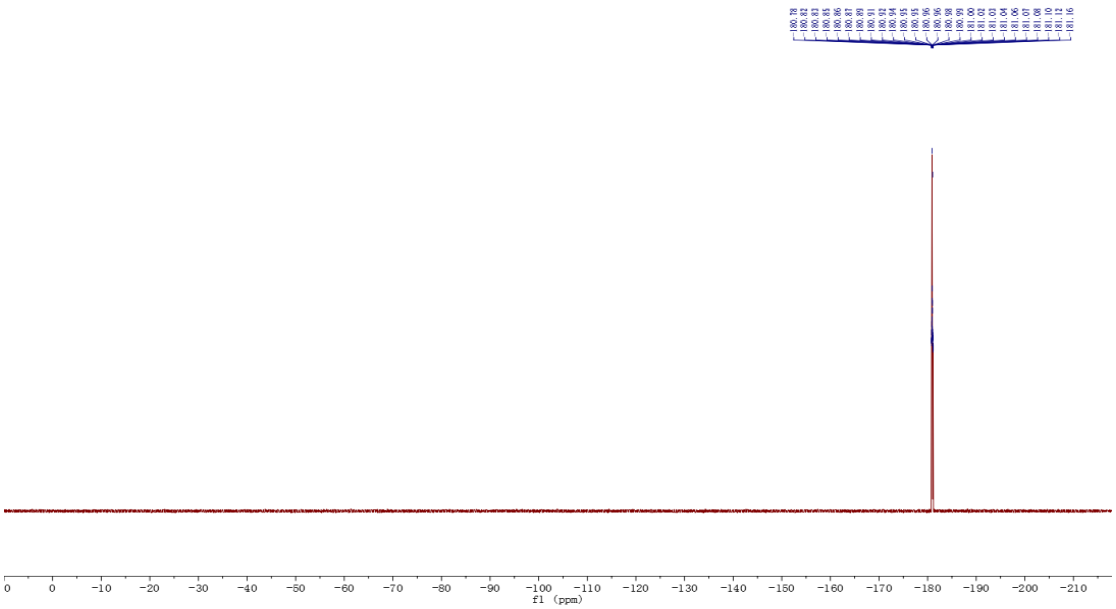


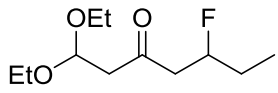



**2l**



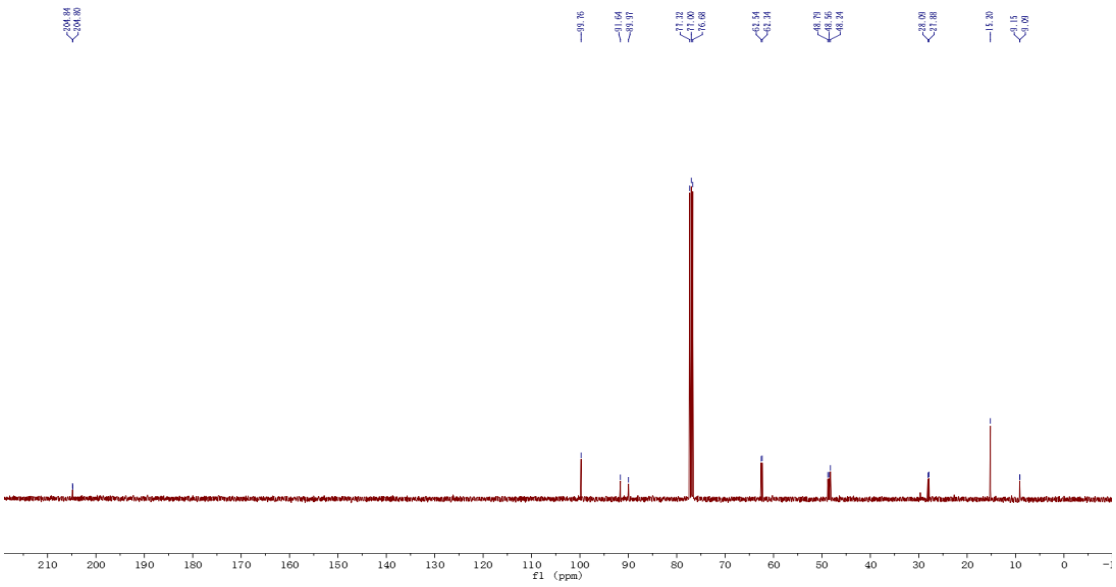



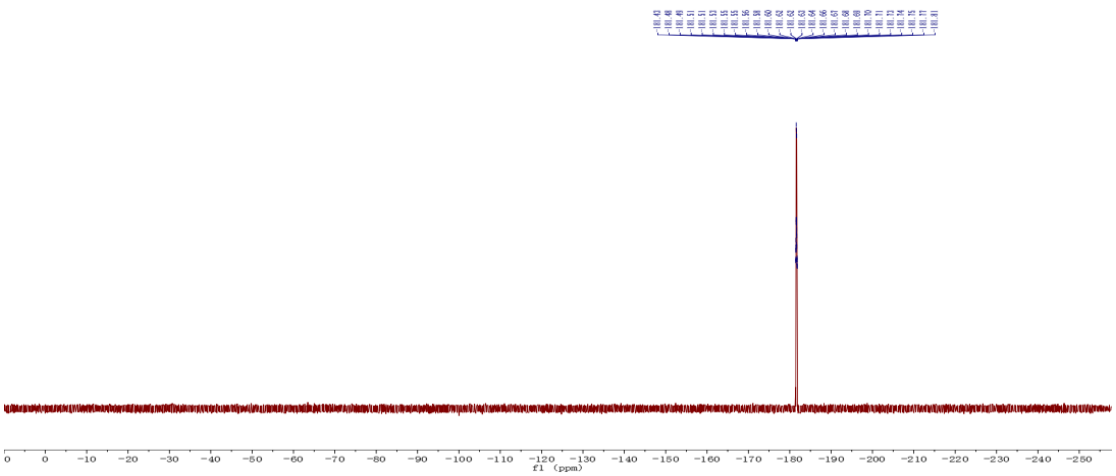



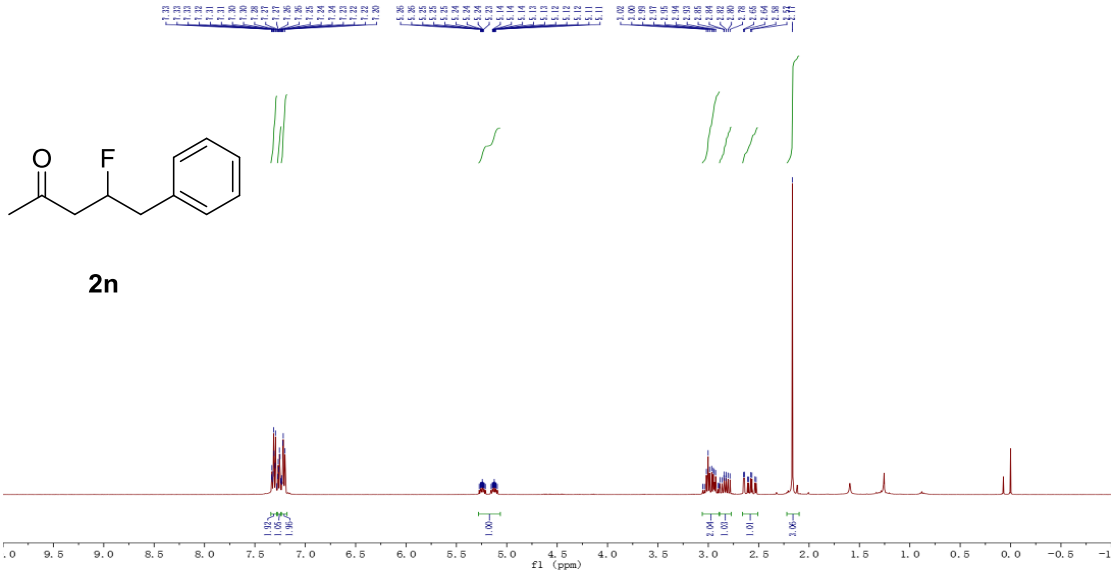



**2m**

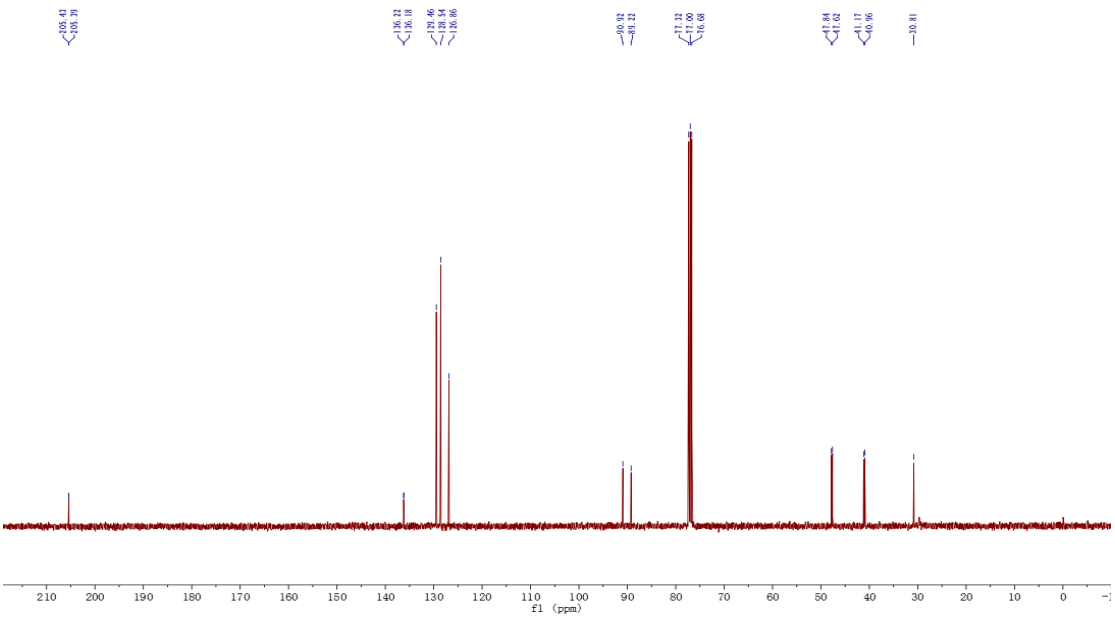


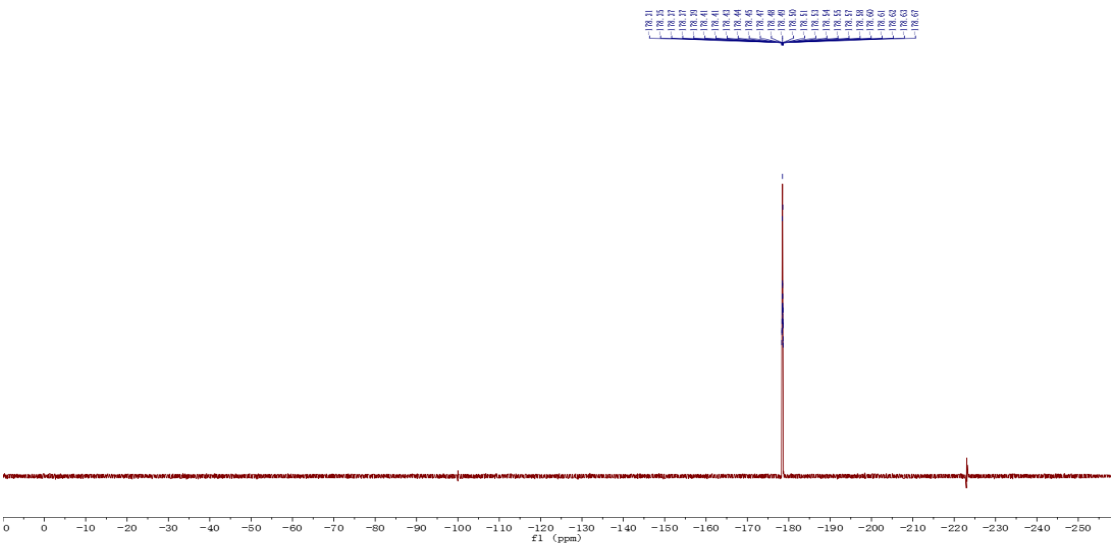



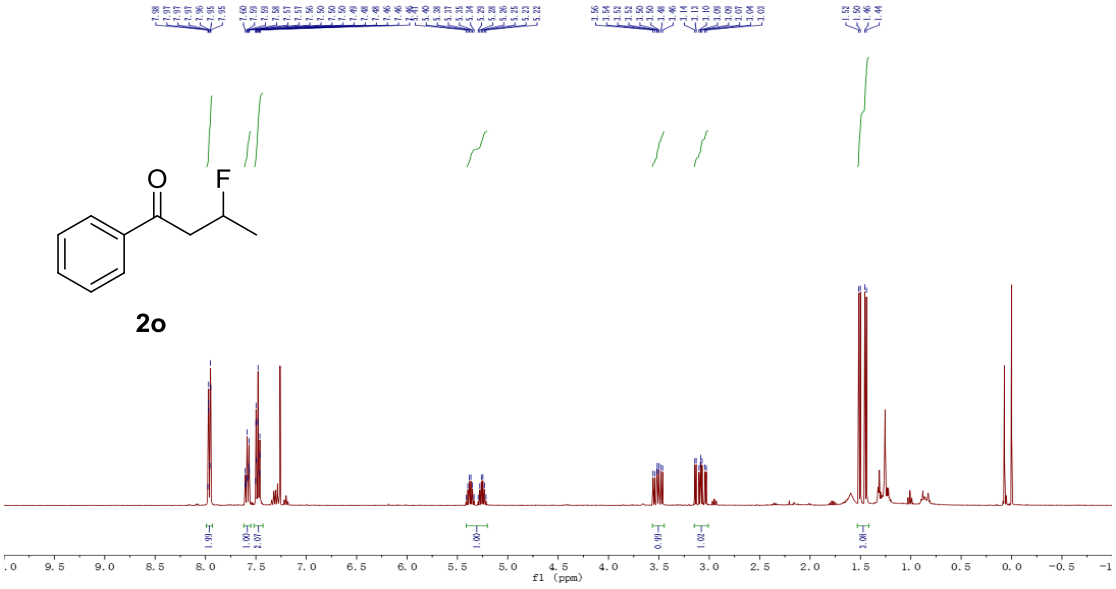





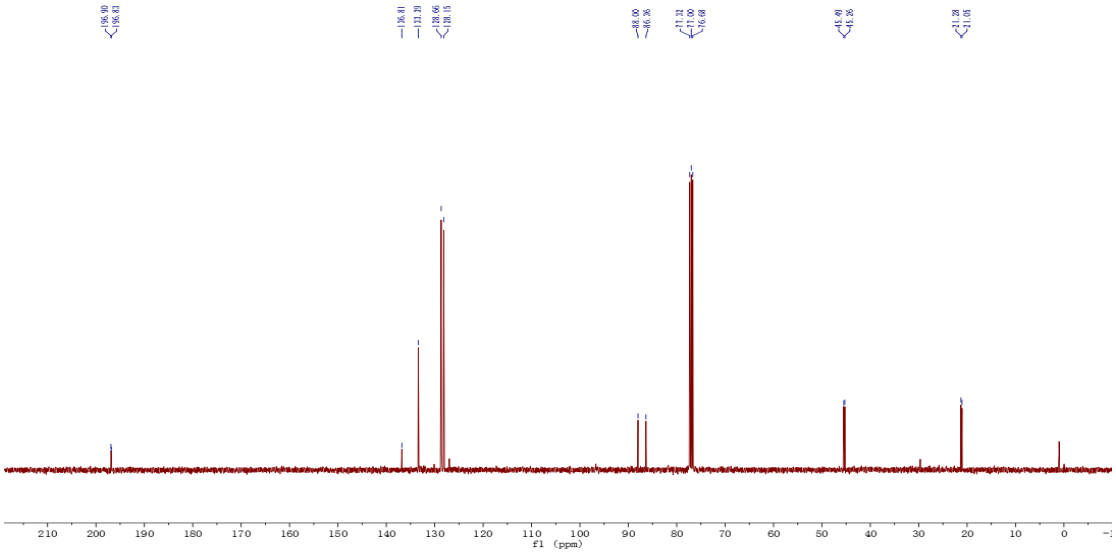

**2n**

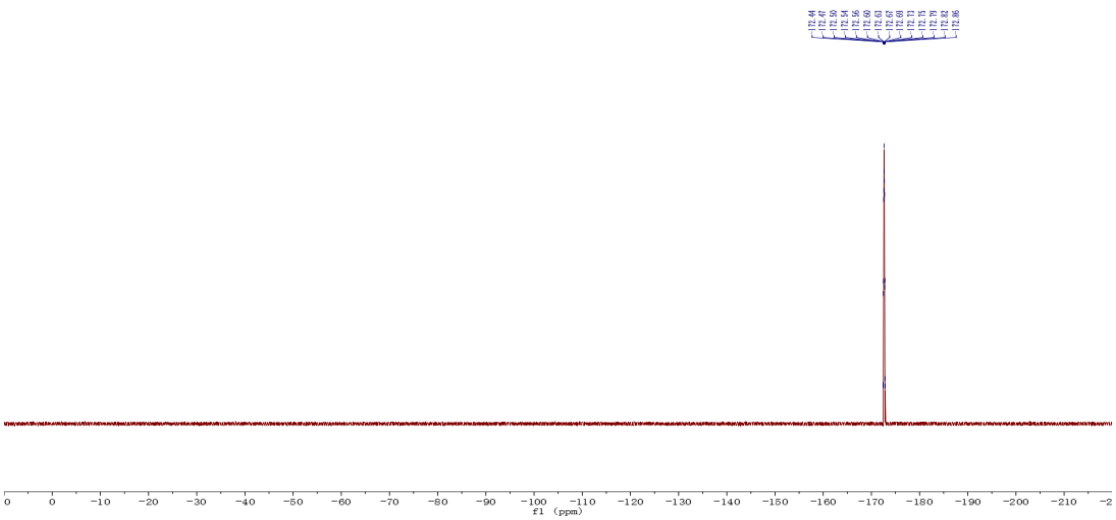


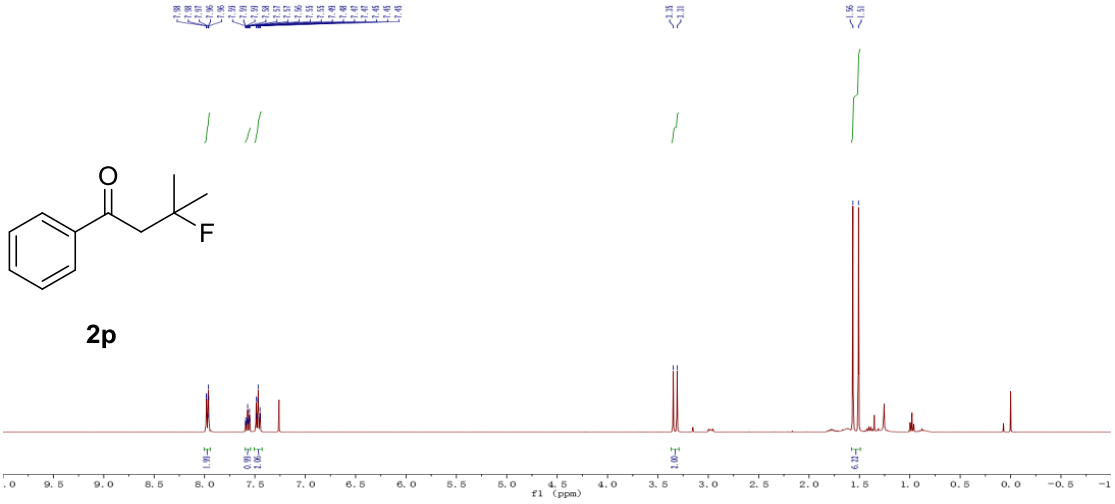




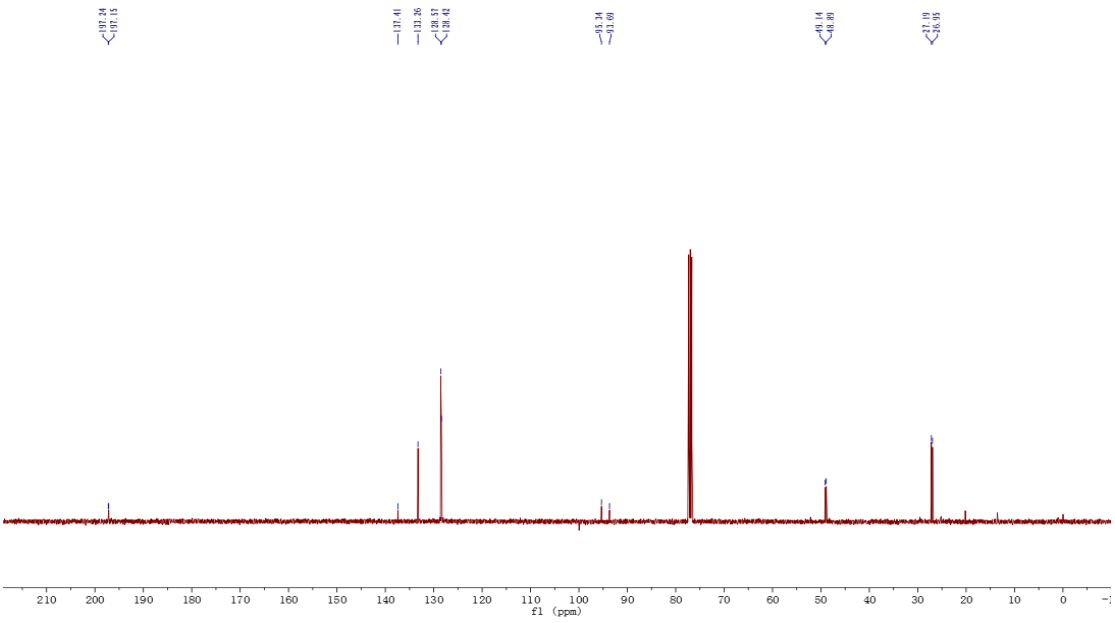

**2o**

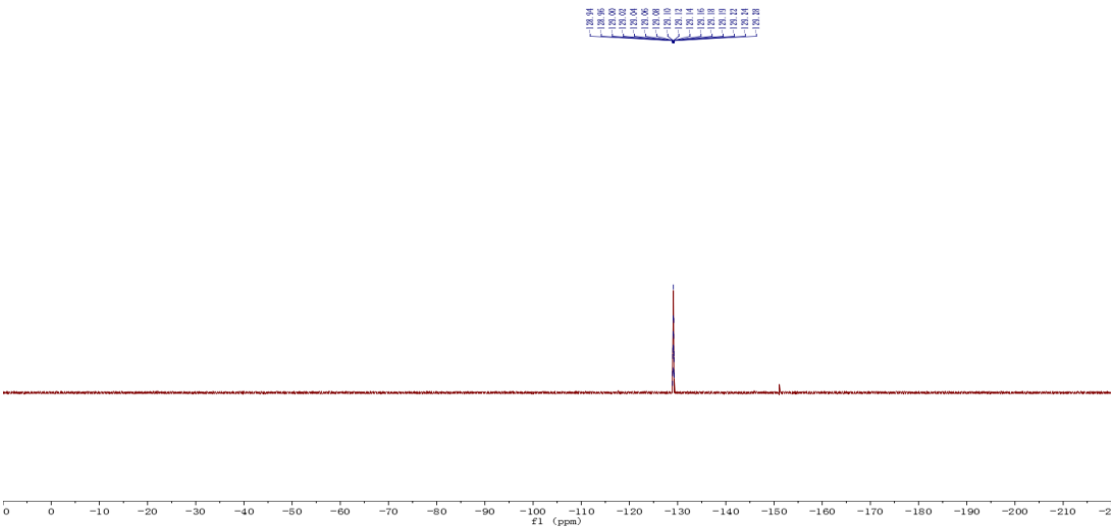


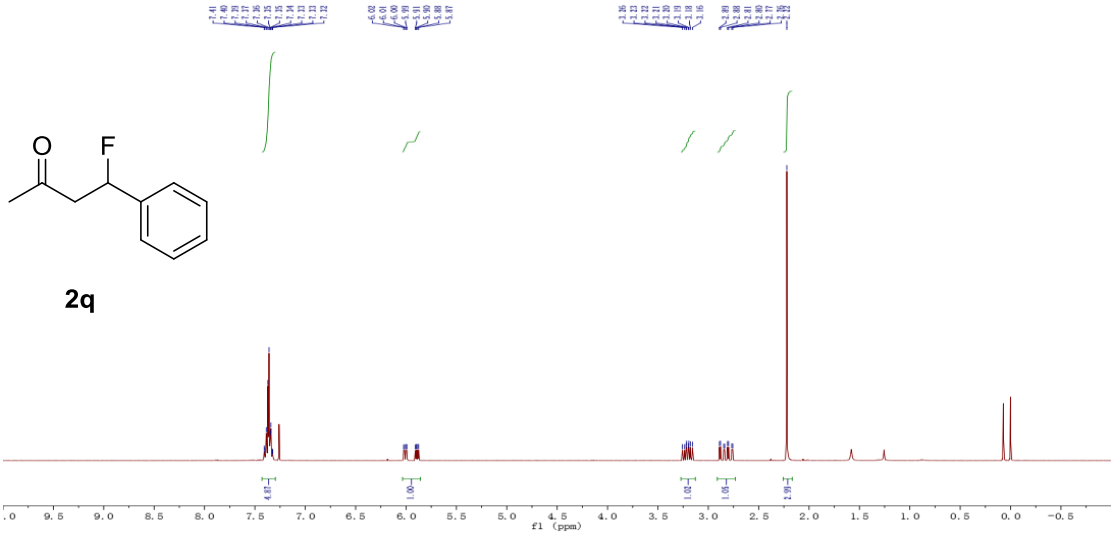




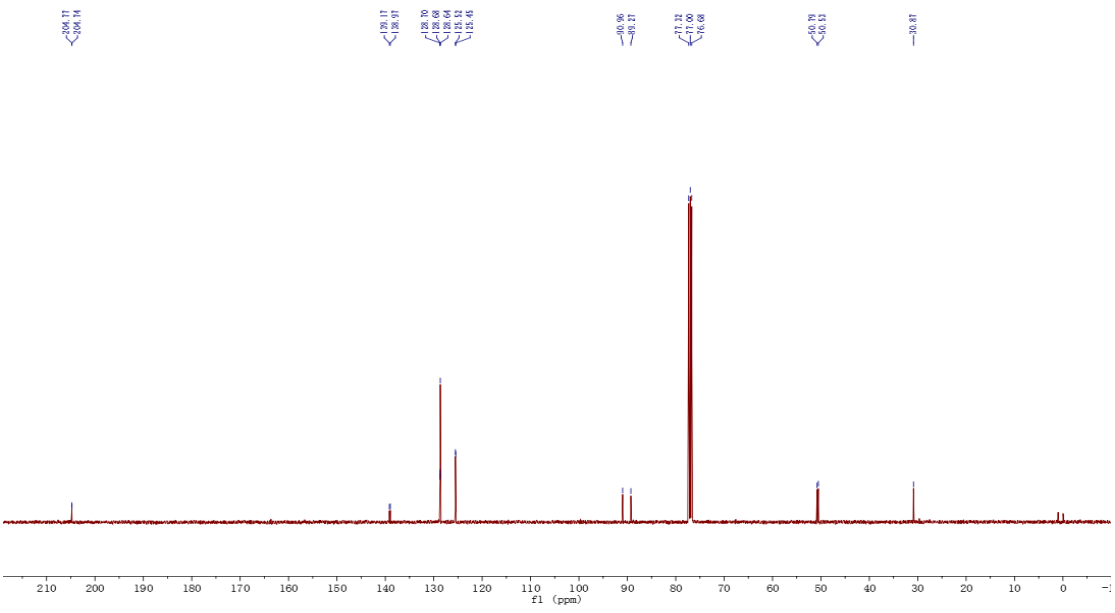

**2p**

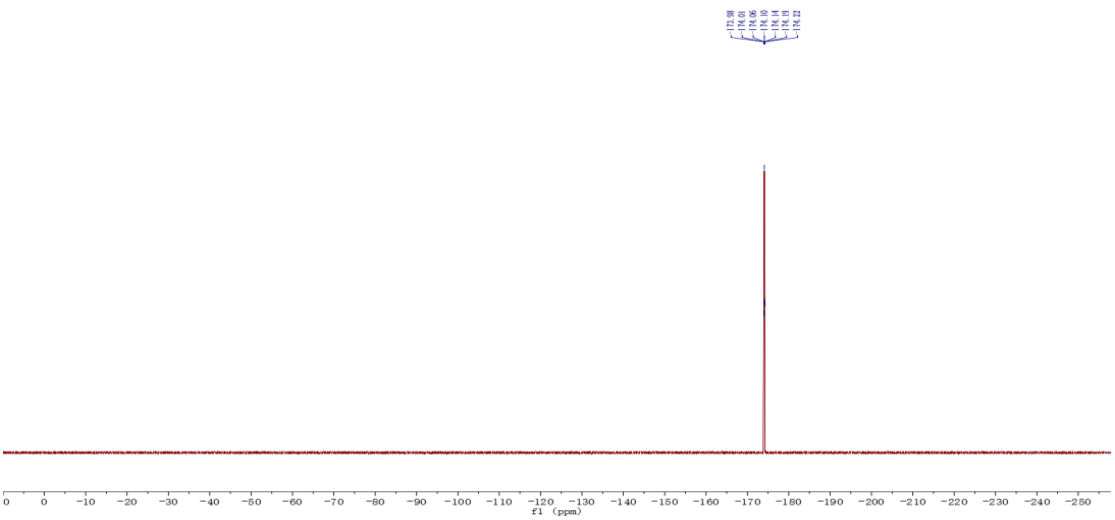


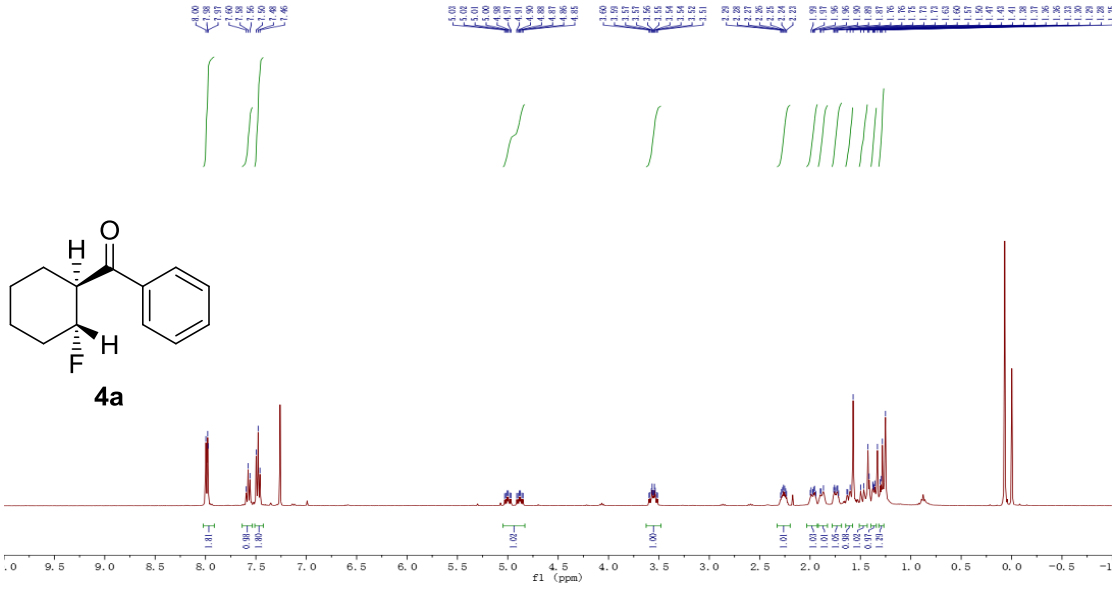




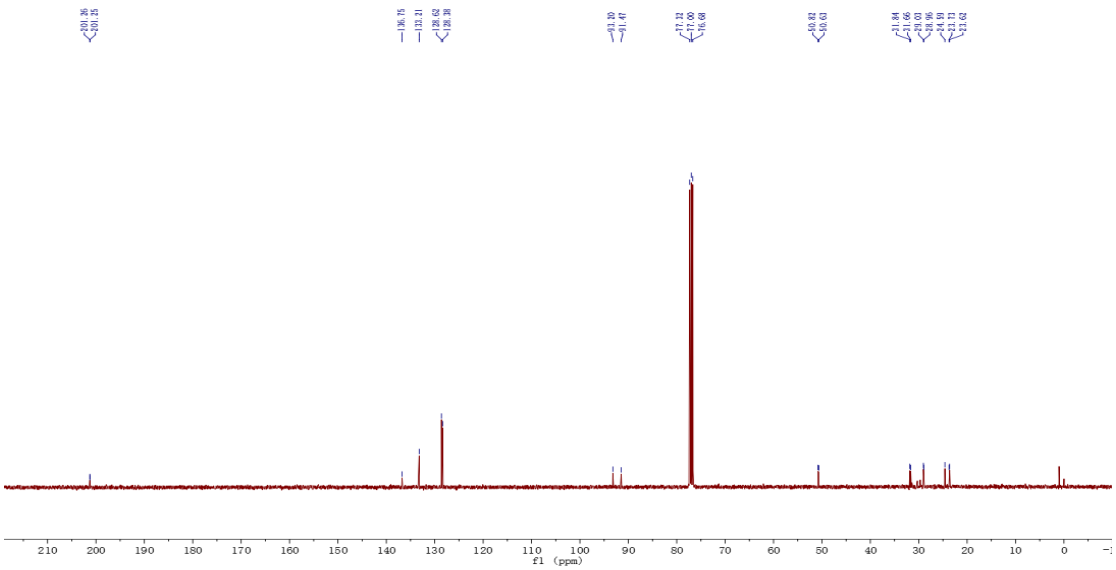

**2q**

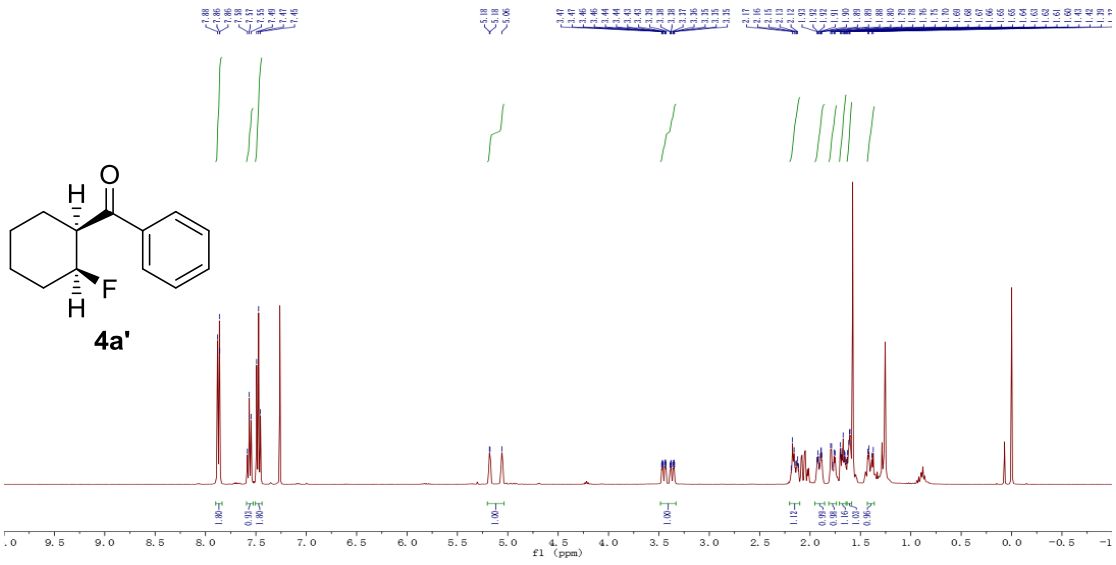






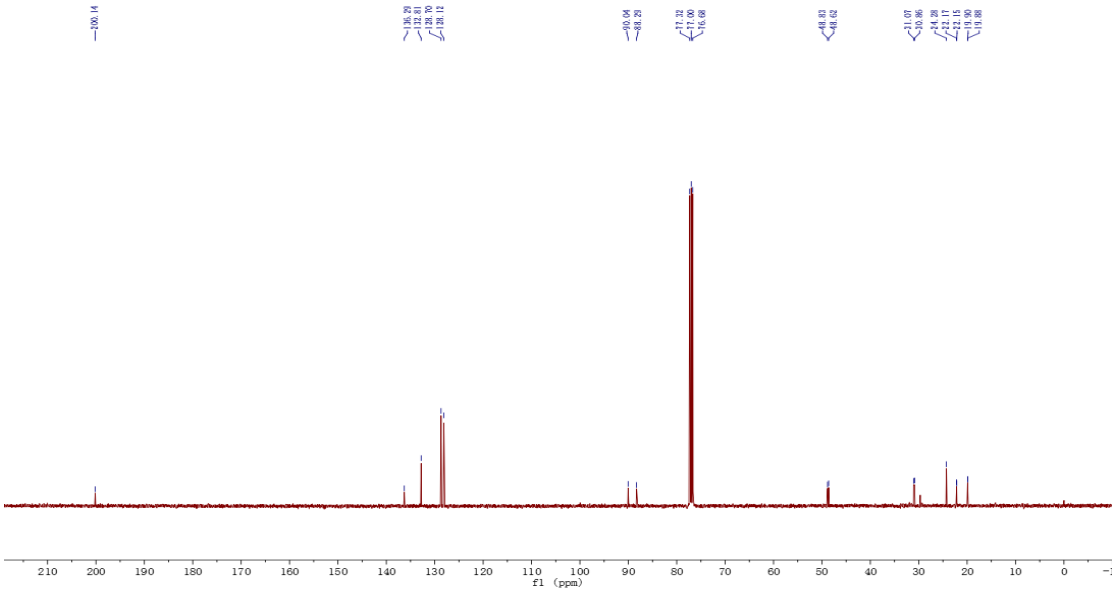

**4a**

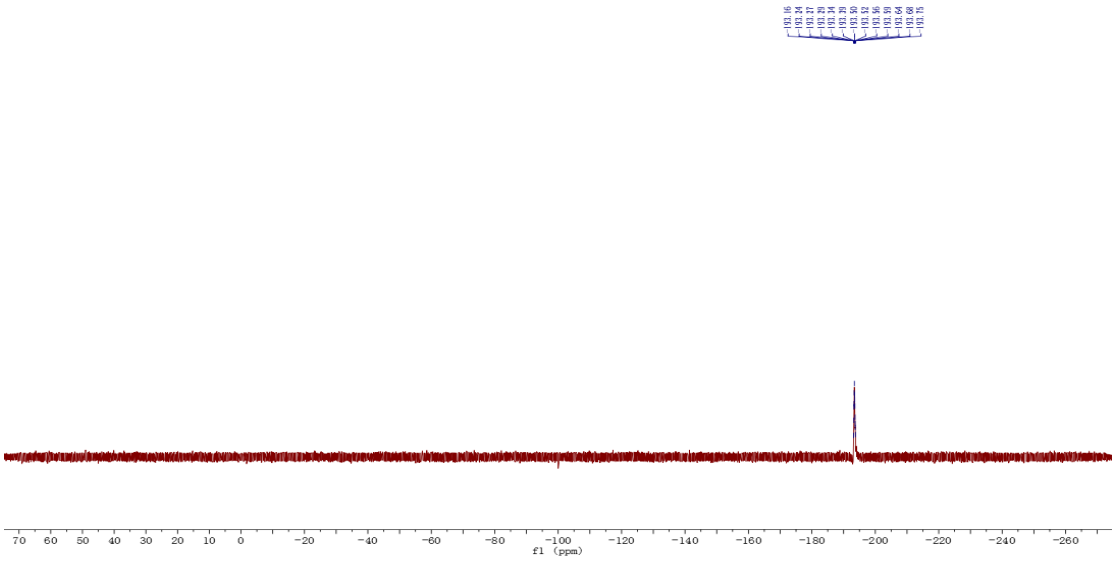


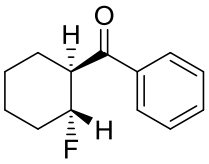



**4a'**



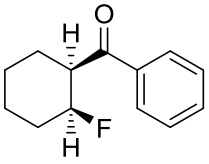





O
H
H
F

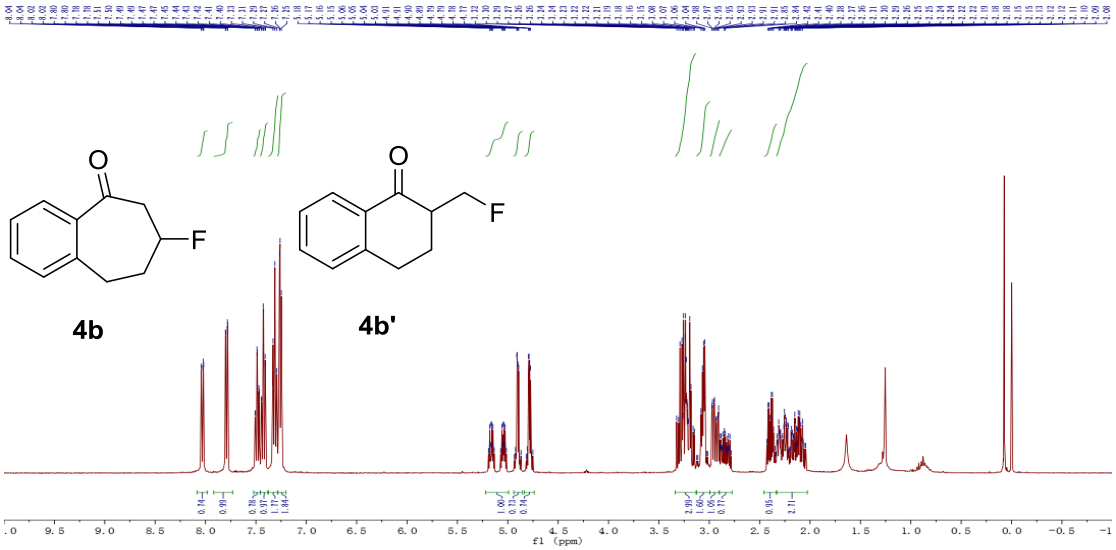
**4a**

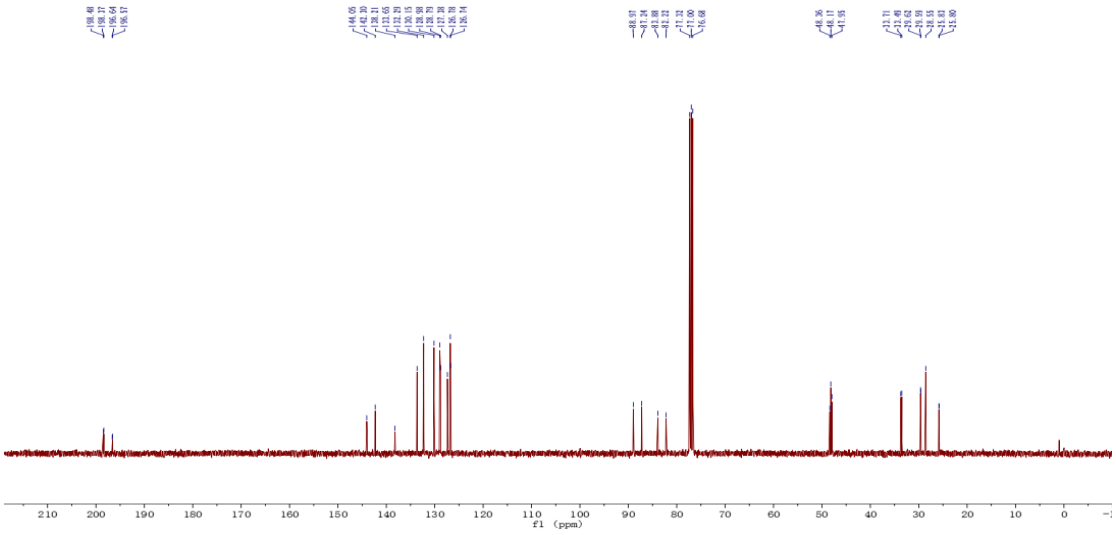

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)
0 1 2 3 4 5 6 7 8 9
f1 (ppm)


O
H
F
H

**4a'**


9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)
0 1 2 3 4 5 6 7 8 9
f1 (ppm)


O
F
4b
O
F
4b'
f1 (ppm)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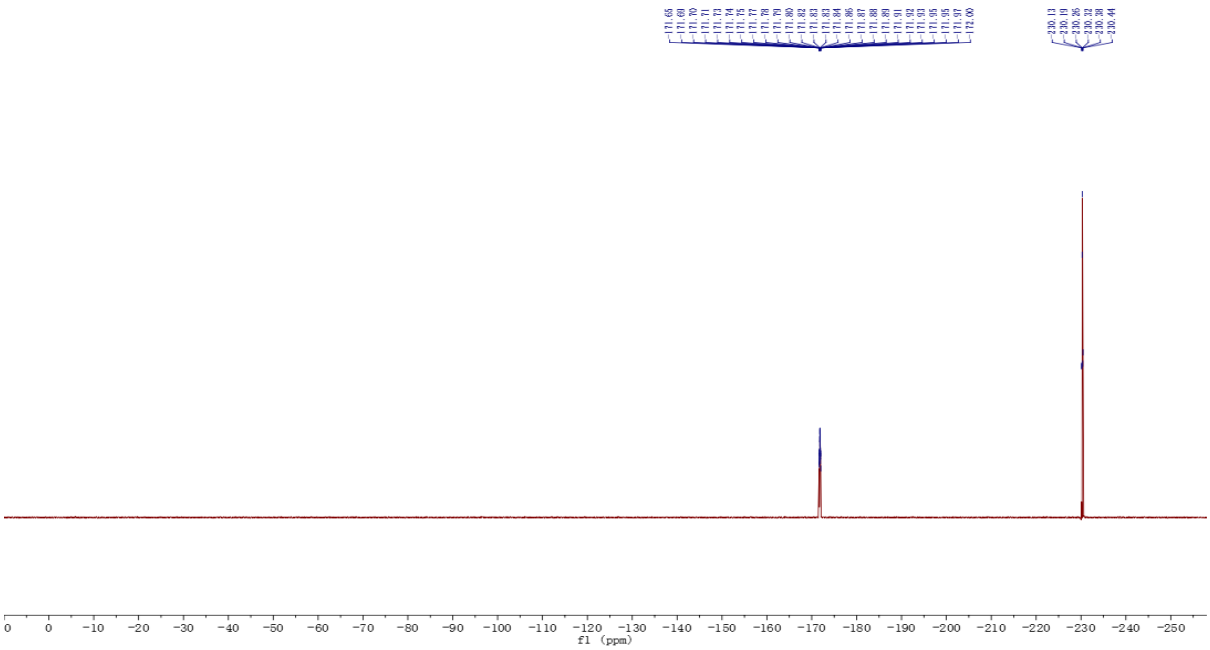
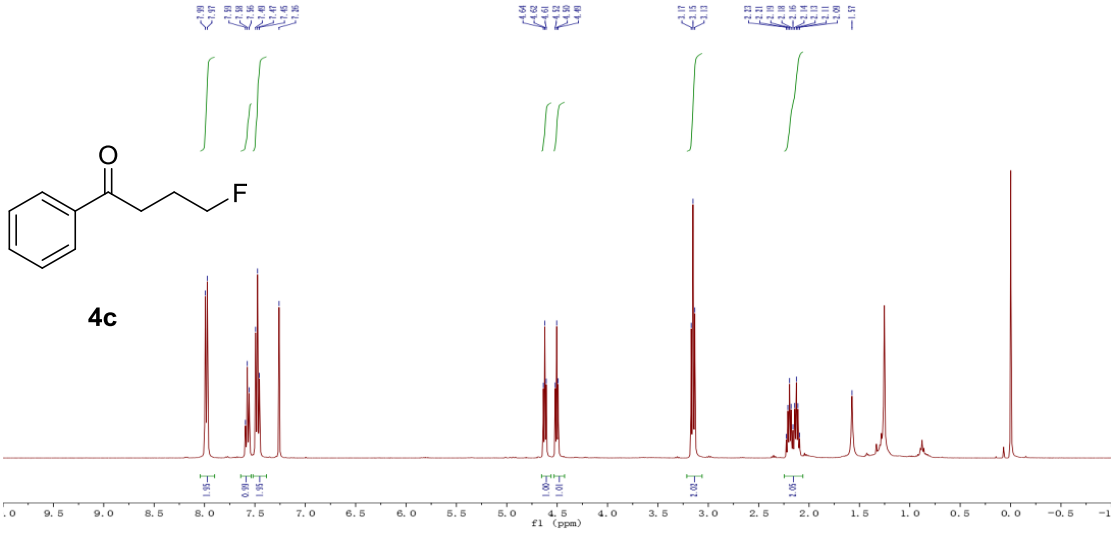
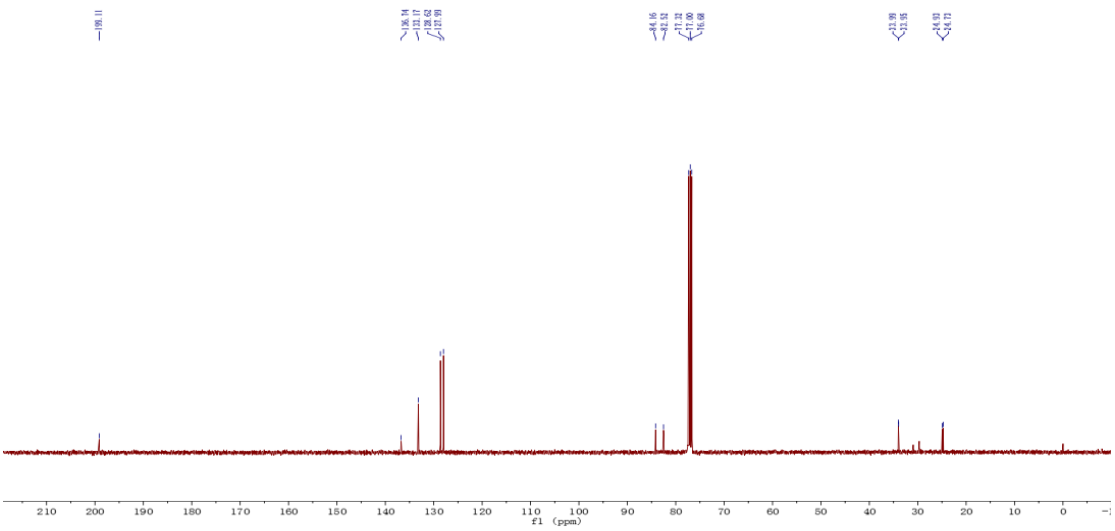
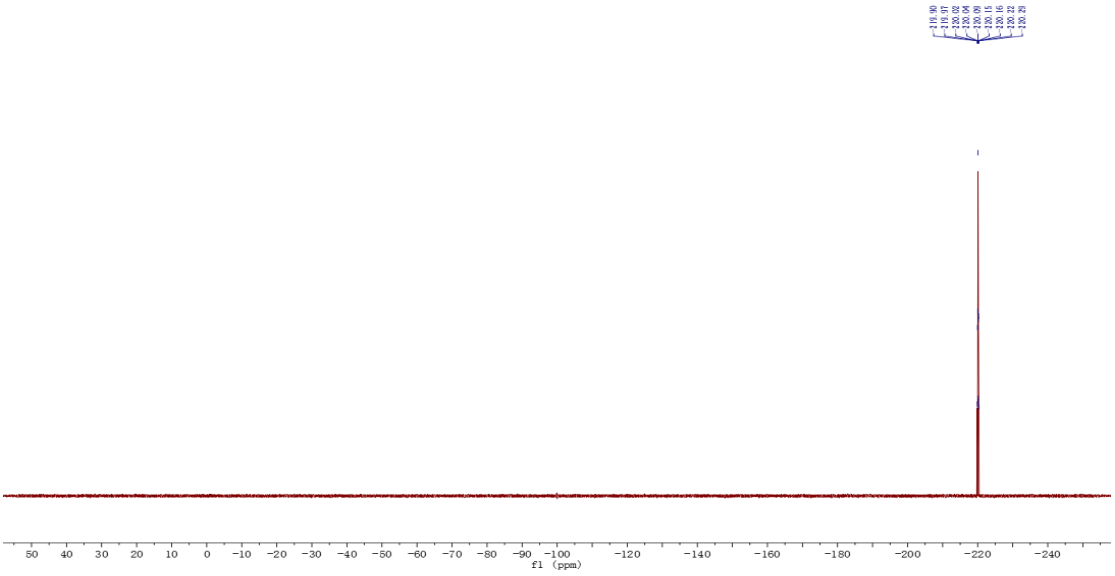

f1 (ppm)


O
F
4c
f1 (ppm)


f1 (ppm)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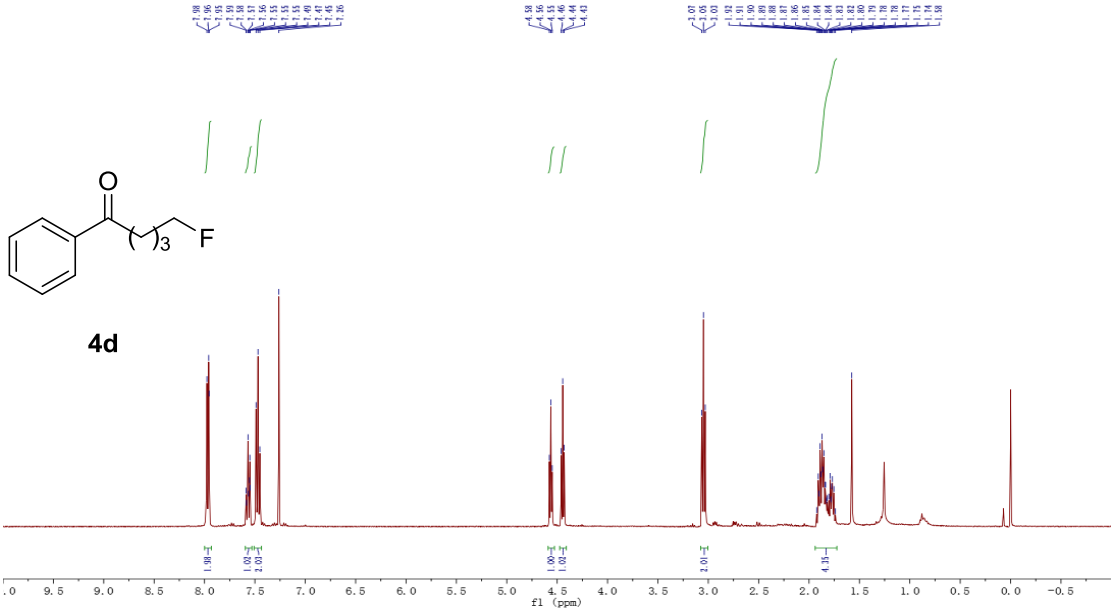
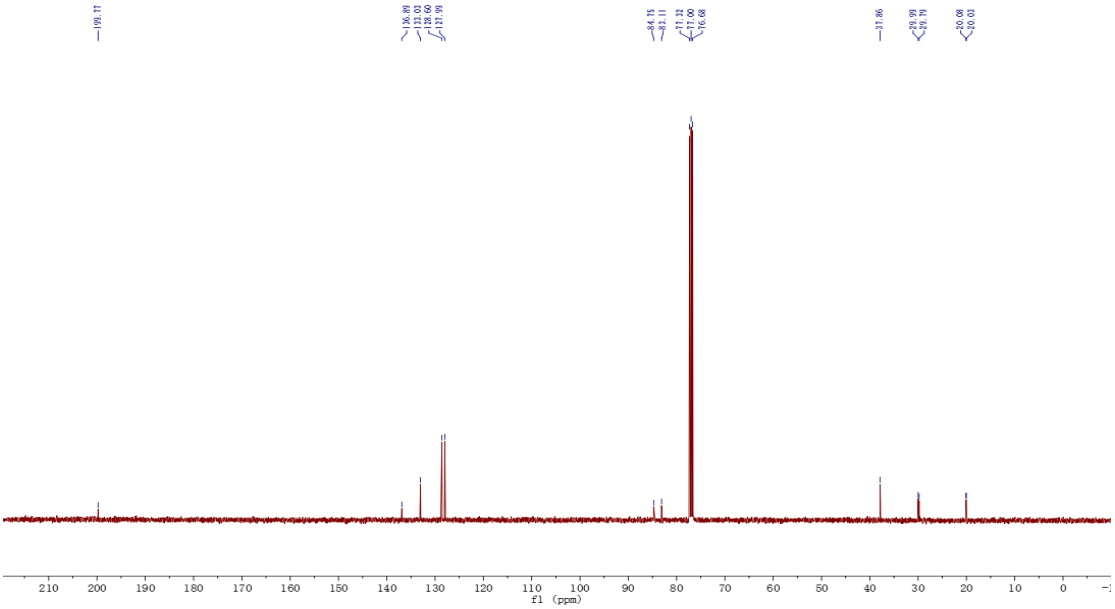
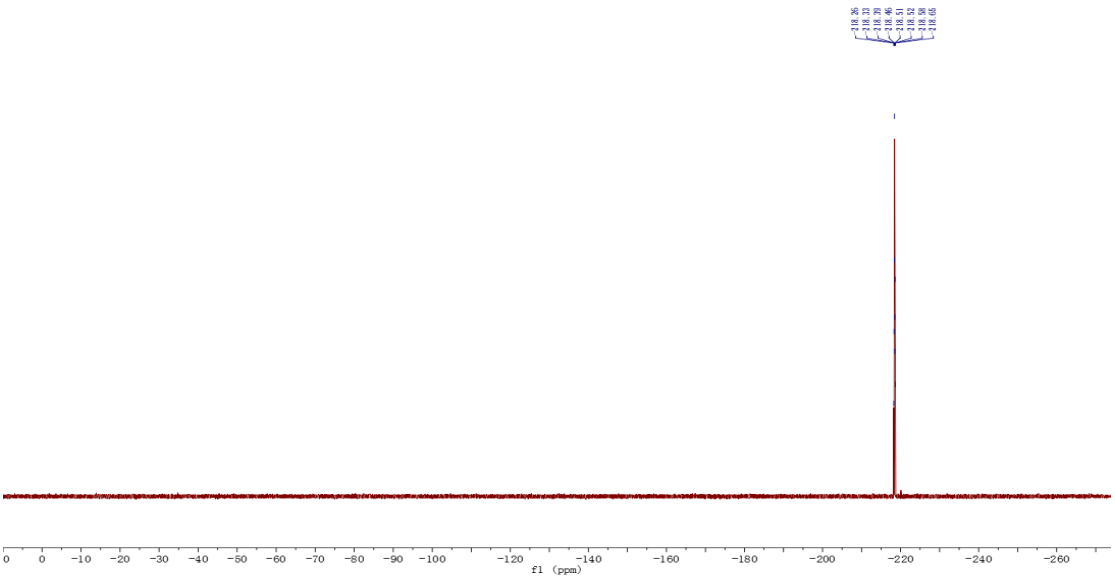
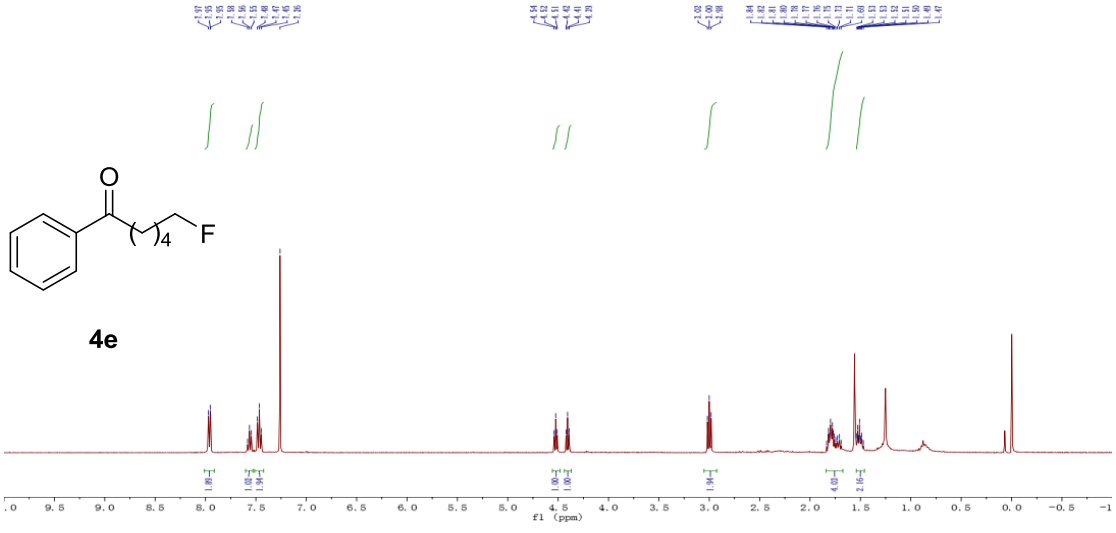
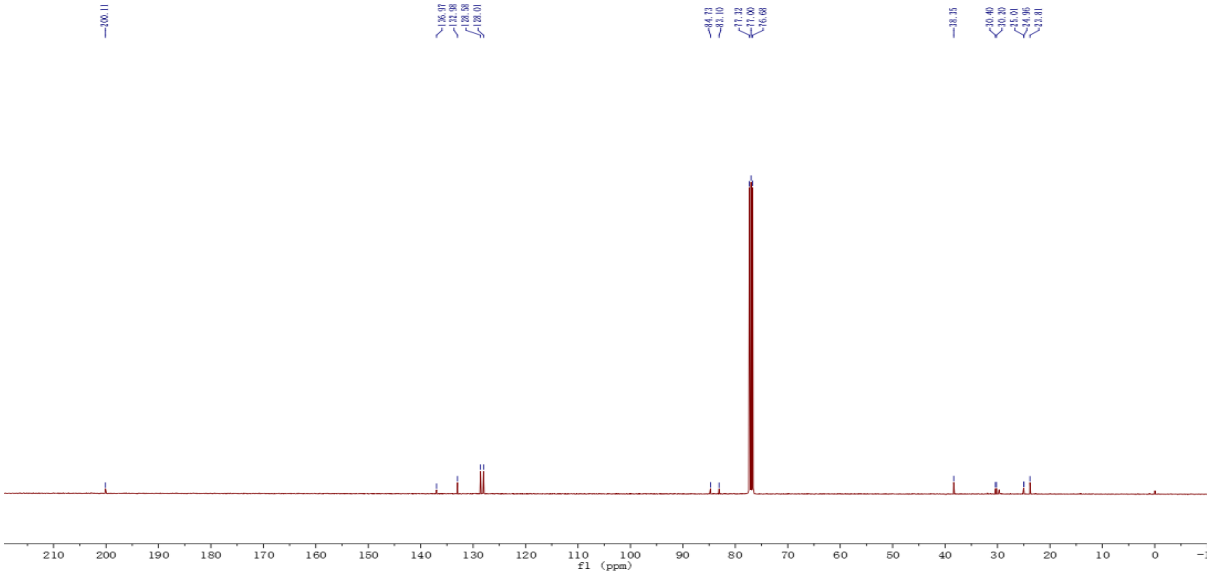
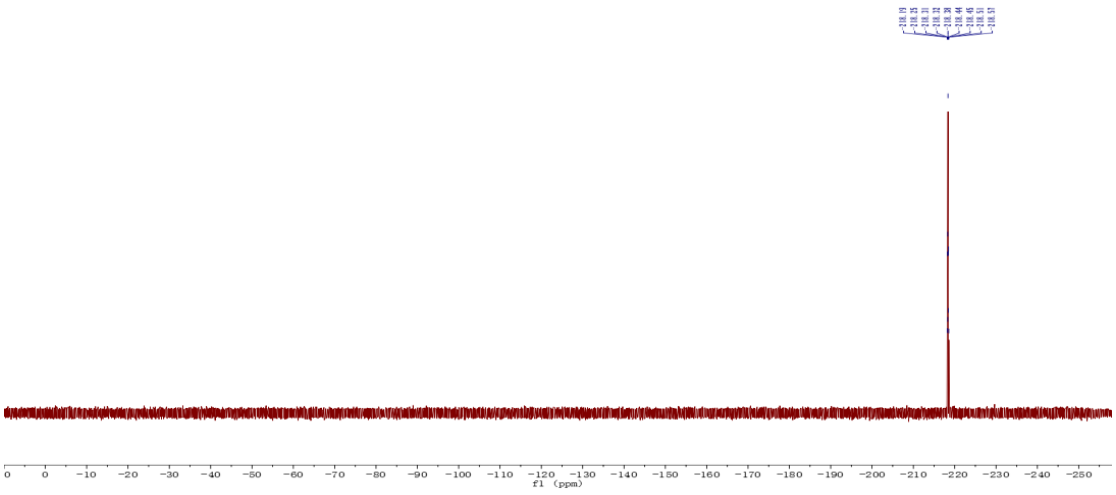

O
3
F
4d
f1 (ppm)

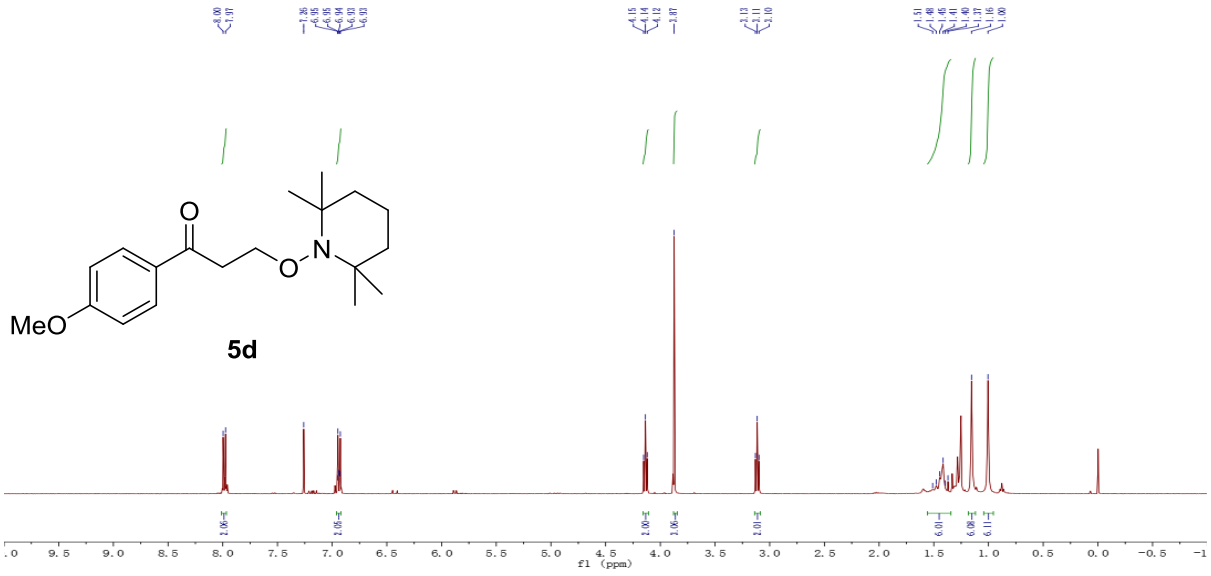

f1 (ppm)


f1 (ppm)


O
4
F
4e
f1 (ppm)


f1 (ppm)


f1 (ppm)


MeO
O
N
O
5d
f1 (ppm)