

## Supporting information

### Silver-Catalyzed Decarboxylative Radical Allylation of $\alpha,\alpha$ -Difluoroarylacetic Acids to the Construction of $\text{CF}_2$ -allyl Bond

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## 1. General information

<sup>1</sup>H NMR spectra were recorded on a 500 MHz. <sup>19</sup>F NMR were recorded on a 470 MHz spectrometer. <sup>13</sup>C NMR spectra were recorded on a 125 MHz spectrometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR chemical shifts were determined relative to internal standard TMS at  $\delta$  0.0 and <sup>19</sup>F NMR chemical shifts were determined relative to CFCl<sub>3</sub> as inter standard. Chemical shifts ( $\delta$ ) 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 <sup>19</sup>F NMR using trifluorotoluene as an internal standard before working up the reaction. Infrared spectra (IR) were recorded on AVATAR 370 FT-IR spectrometer, absorbance frequencies are given at maximum of intensity in cm<sup>-1</sup>. High-resolution mass spectra (HRMS) were measured with JEOL JMX-SX 102A spectrometer (FAB) and electrospray (ESI). Silica gel (200–400 mesh) was used for flash column chromatography.

## 2. Preparation of substrates

### 2.1 General procedure for the synthesis of $\alpha,\alpha$ -difluoroarylacetic acids **1a-1m**



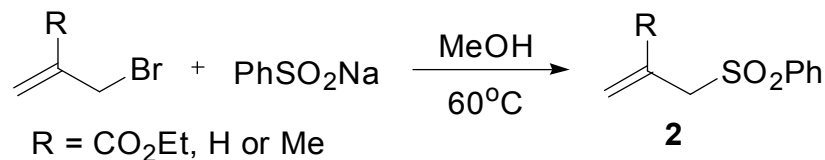
Activation of Cu powder: Copper powder (1.65 g, 26 mmol, 2.6 equiv.) was ground in a mortar with dilute hydrochloric acid (1 N, 10 mL) for 10 minutes. After filtration, the copper powder was washed with water (10 mL), methanol (10 mL) and acetone (10 mL), respectively, to give the pre-activated copper powder.

A 50 mL round bottom flask equipped with a magnetic stir bar was charged with appropriate aryl iodide (10 mmol, 1.0 equiv.), ethyl bromodifluoroacetate (1.28 mL, 10 mmol, 1.0 equiv.), pre-activated copper powder (1.65 g, 26 mmol, 2.6 equiv.), and DMSO (15 mL). The flask was evacuated and backfilled with N<sub>2</sub> (3 times) with the help of a three neck joint. The reaction mixture was stirred at 60 °C under N<sub>2</sub> atmosphere for 12 hours. After cooling down to room temperature, ethyl acetate (30 mL) and water (30 mL) was added. After filtration, the organic phase was separated and the aqueous phase was extracted with ethyl acetate (2 × 15 mL). The combined organic layer was washed with saturated brine (15 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to give the corresponding ethyl  $\alpha,\alpha$ -difluoroaryl acetate.

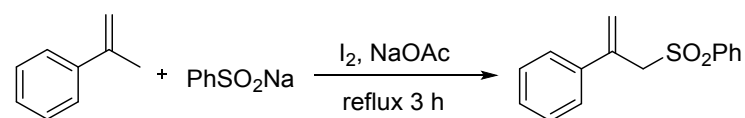
The ethyl  $\alpha,\alpha$ -difluoroaryl acetate were reacted with NaOH (1.0 eq.) in ethanol (95%) for 12 h at room temperature, and the potassium  $\alpha,\alpha$ -difluoroaryl acetate was obtained by removing the ethanol. Ether was then added to remove the residual ethyl  $\alpha,\alpha$ -difluoroaryl acetate. After filtration, the potassium  $\alpha,\alpha$ -difluoroaryl acetate was dissolved in water (20 mL) and concentrated hydrochloric acid was added until pH = 1. The aqueous phase was extracted with ethyl acetate (2 × 20 mL), washed with brine

(10 mL), dried over anhydrous sodium sulfate and concentrated in vacuo to give the corresponding  $\alpha,\alpha$ -difluoroarylacetic acids. (*Org. Lett.* **2013**, *15*, 2648.)

## 2.2 General procedure for the synthesis of allyl sulfones 2a -2d <sup>2-3</sup>

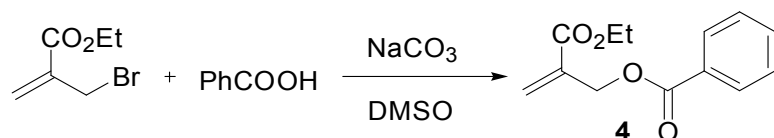


To a solution of allyl bromide (10 mmol) in dry methanol (20 mL) was added sodium phenylsulfinate (15 mmol). After 2 h of reflux, the mixture was concentrated under reduced pressure, the obtained residue was dissolved in EtOAc and the mixture was washed with water, brine, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to give the allyl sulfones. (*Org. Chem. Front.* **2018**, *5*, 3443.)



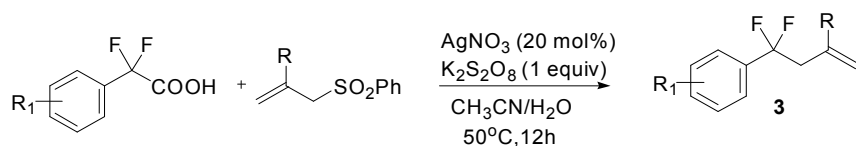
To a suspension of benzenesulfinic acid sodium salt (3.0 equiv) and NaOAc (1.5 equiv) in MeCN (0.25 M) styrene (1.0 equiv) was added followed by iodine (1.5 equiv). The mixture was heated under reflux for 3 h. The reaction mixture was allowed to cool to room temperature and excess iodine was quenched with saturated sodium thiosulfate solution (5 mL). The reaction mixture was basified with saturated aqueous NaHCO<sub>3</sub> (5 mL) and the organic compounds were extracted with EtOAc (3 x 10 mL). The combined organic phases were washed with H<sub>2</sub>O (10 mL), brine (10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified by column chromatography. (*Green Chem.*, **2017**, *19*, 2530-2534.)

## 2.3 General procedure for the synthesis of allyl ester 4 <sup>4</sup>



To carboxylic acid (10mmol) in DMSO (25 mL) was added Na<sub>2</sub>CO<sub>3</sub> (30 mmol) and stirred for 15 min at 60 °C. Allyl bromide (10mmol) was then added and reaction mixture was stirred for 3h at 60 °C. Upon completion (TLC), water (25 mL) was added and product was extracted with EtOAc (3x25ml). The combined organic phases were washed with H<sub>2</sub>O (25 mL), brine (25 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified by column chromatography. (*Bioorg. Med. Chem. Lett.* **2017**, *27*, 776.)

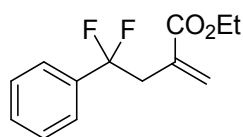
### 3. General procedure for the synthesis of compounds 3



$\alpha,\alpha$ -Difluoroarylacetic acids (0.20 mmol),  $\text{AgNO}_3$  (20 mol%, 0.04 mmol),  $\text{K}_2\text{S}_2\text{O}_8$  (1.0 equiv, 0.20 mmol) and allyl sulfones (3.0 equiv, 0.60 mmol) were placed in a 10 mL round-bottom flask. Solvent  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (v/v=3:7, 2.5ml) were then added under nitrogen atmosphere. The solution was stirred at 50 °C for 12 h. The resulting mixture was cooled down to room temperature and extracted with EA (5 mL  $\times$  4). The combined organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After the removal of solvent under reduced pressure, the crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford pure difluoroallylatedarenes.

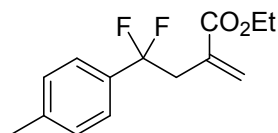
### 4. Data for compounds 3

#### Ethyl 4,4-difluoro-2-methylene-4-phenylbutanoate (3aa)



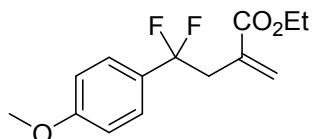
41.9 mg, 87% yield, light yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48-7.43 (m, 2H), 7.42-7.37 (m, 3H), 6.37 (s, 1H), 5.75 (s, 1H), 4.07 (q,  $J = 7.1$  Hz, 2H), 3.22 (t,  $J = 15.9$  Hz, 2H), 1.20 (t,  $J = 7.1$  Hz, 3H).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -95.37 (t,  $J = 15.9$  Hz).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.4, 136.8 (t,  $^2J_{\text{C-F}} = 26.3$  Hz), 132.8 (t,  $^3J_{\text{C-F}} = 3.9$  Hz), 130.4, 129.9, 128.3, 125.3 (t,  $^3J_{\text{C-F}} = 6.2$  Hz), 121.4 (t,  $^1J_{\text{C-F}} = 244.3$  Hz), 61.1, 40.5 (t,  $^2J_{\text{C-F}} = 29.0$  Hz), 14.1. HRMS (ESI) calcd. for  $\text{C}_{13}\text{H}_{14}\text{F}_2\text{NaO}_2$   $[\text{M}+\text{Na}]^+ 263.0854$ , found: 263.0857.

#### Ethyl 4,4-difluoro-2-methylene-4-(p-tolyl)butanoate (3ba)



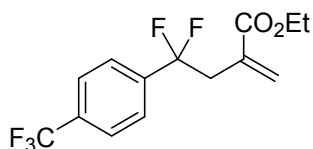
45.7 mg, 90% yield, light yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 (d,  $J = 8.1$  Hz, 2H), 7.20 (d,  $J = 7.9$  Hz, 2H), 6.36 (s, 1H), 5.74 (s, 1H), 4.09 (q,  $J = 7.1$  Hz, 2H), 3.20 (t,  $J = 15.9$  Hz, 2H), 2.36 (s, 3H), 1.21 (t,  $J = 7.1$  Hz, 3H).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -94.75 (t,  $J = 15.9$  Hz).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.5, 139.9, 134.0 (t,  $^2J_{\text{C-F}} = 26.5$  Hz), 132.9 (t,  $^3J_{\text{C-F}} = 3.8$  Hz), 130.3, 129.0, 125.2 (t,  $^3J_{\text{C-F}} = 6.1$  Hz), 121.6 (t,  $^1J_{\text{C-F}} = 244.0$  Hz), 61.1, 40.5 (t,  $^2J_{\text{C-F}} = 29.3$  Hz), 21.4, 14.2. HRMS (ESI) calcd. For  $\text{C}_{14}\text{H}_{16}\text{F}_2\text{NaO}_2$   $[\text{M}+\text{Na}]^+ 277.1010$ , found: 277.1011.

### Ethyl 4,4-difluoro-4-(4-methoxyphenyl)-2-methylenebutanoate (3ca)



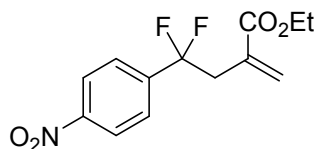
43.1 mg, 81% yield, light yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (d,  $J = 8.8$  Hz, 2H), 6.89 (d,  $J = 8.7$  Hz, 2H), 6.35 (s, 1H), 5.72 (s, 1H), 4.08 (q,  $J = 7.1$  Hz, 2H), 3.80 (s, 3H), 3.19 (t,  $J = 15.7$  Hz, 2H), 1.21 (t,  $J = 7.1$  Hz, 3H).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -93.57 (t,  $J = 15.8$  Hz).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.5, 160.7, 132.9 (t,  $^3J_{\text{C-F}} = 3.8$  Hz), 130.3, 129.0 (t,  $^2J_{\text{C-F}} = 26.9$  Hz), 126.8 (t,  $^3J_{\text{C-F}} = 6.1$  Hz), 121.6 (t,  $^1J_{\text{C-F}} = 243.8$  Hz), 113.6, 61.1, 55.4, 40.5 (t,  $^2J_{\text{C-F}} = 29.7$  Hz), 14.1. HRMS (ESI) calcd. for  $\text{C}_{14}\text{H}_{17}\text{F}_2\text{O}_3$   $[\text{M}+\text{H}]^+$  271.1146, found: 271.1140.

### Ethyl 4,4-difluoro-2-methylene-4-(4-(trifluoromethyl)phenyl)butanoate (3da)



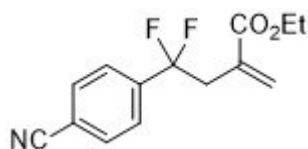
47.6 mg, 77% yield, light yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 (d,  $J = 8.2$  Hz, 2H), 7.58 (d,  $J = 8.2$  Hz, 2H), 6.39 (s, 1H), 5.78 (s, 1H), 4.05 (q,  $J = 7.1$  Hz, 2H), 3.22 (t,  $J = 15.8$  Hz, 2H), 1.17 (t,  $J = 7.1$  Hz, 3H).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.95 (s), -96.03 (t,  $J = 15.8$  Hz).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.0, 140.2 (t,  $^2J_{\text{C-F}} = 26.8$  Hz), 132.2 (t,  $^3J_{\text{C-F}} = 4.2$  Hz), 132.1 (q,  $^2J_{\text{C-F}} = 32.1$  Hz), 130.8, 125.9 (t,  $^3J_{\text{C-F}} = 6.2$  Hz), 125.3 (q,  $^3J_{\text{C-F}} = 3.7$  Hz), 123.7 (q,  $^1J_{\text{C-F}} = 272.3$  Hz), 120.7 (t,  $^1J_{\text{C-F}} = 245.1$  Hz), 61.1, 40.3 (t,  $^2J_{\text{C-F}} = 28.6$  Hz), 14.0. HRMS (ESI) calcd. for  $\text{C}_{14}\text{H}_{14}\text{F}_5\text{O}_2$   $[\text{M}+\text{H}]^+$  309.0914, found: 309.0911.

### Ethyl 4,4-difluoro-2-methylene-4-(4-nitrophenyl)butanoate (3ea)



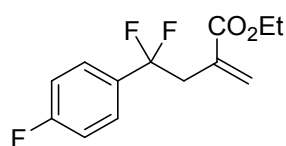
25.8 mg, 45% yield, light yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.26 (d,  $J = 9.0$  Hz, 2H), 7.64 (d,  $J = 9.0$  Hz, 2H), 6.41 (s, 1H), 5.80 (s, 1H), 4.06 (q,  $J = 7.1$  Hz, 2H), 3.23 (t,  $J = 15.9$  Hz, 2H), 1.19 (t,  $J = 7.1$  Hz, 3H).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -95.94 (t,  $J = 15.9$  Hz).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.1, 148.9, 142.9 (t,  $^2J_{\text{C-F}} = 27.0$  Hz), 132.0 (t,  $^3J_{\text{C-F}} = 4.1$  Hz), 131.3, 126.8 (t,  $^3J_{\text{C-F}} = 6.1$  Hz), 123.7, 120.6 (t,  $^1J_{\text{C-F}} = 245.5$  Hz), 61.3, 40.3 (t,  $^2J_{\text{C-F}} = 28.3$  Hz), 14.2. HRMS (ESI) calcd. for  $\text{C}_{13}\text{H}_{14}\text{F}_2\text{NO}_2$   $[\text{M}+\text{H}]^+$  286.0891, found: 286.0895

### Ethyl 4-(4-cyanophenyl)-4,4-difluoro-2-methylenebutanoate (3fa)



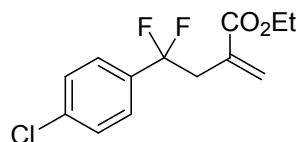
39.3 mg, 74% yield, light yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (d,  $J = 8.3$  Hz, 2H), 7.56 (d,  $J = 8.3$  Hz, 2H), 6.40 (s, 1H), 5.79 (s, 1H), 4.06 (q,  $J = 7.1$  Hz, 2H), 3.20 (t,  $J = 15.8$  Hz, 2H), 1.19 (t,  $J = 7.1$  Hz, 3H).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -96.40 (t,  $J = 15.8$  Hz).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.1, 141.2 (t,  $^2J_{\text{C-F}} = 27.0$  Hz), 132.3, 132.0 (t,  $^3J_{\text{C-F}} = 4.1$  Hz), 131.2, 126.4 (t,  $^3J_{\text{C-F}} = 6.2$  Hz), 120.6 (t,  $^1J_{\text{C-F}} = 245.4$  Hz), 118.1, 114.1 (t,  $^4J_{\text{C-F}} = 1.7$  Hz), 61.3, 40.3 (t,  $^2J_{\text{C-F}} = 28.4$  Hz), 14.2. HRMS (ESI) calcd. for  $\text{C}_{14}\text{H}_{13}\text{F}_2\text{NNaO}_2$   $[\text{M}+\text{Na}]^+$  288.0806, found: 288.0808.

### Ethyl 4,4-difluoro-4-(4-fluorophenyl)-2-methylenebutanoate (3ga)



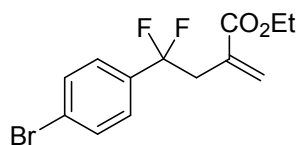
42.7 mg, 83% yield, light yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46-7.41(m, 2H), 7.10-7.04(m, 2H), 6.37 (s, 1H), 5.75 (s, 1H), 4.08 (q,  $J = 7.1$  Hz, 2H), 3.19 (t,  $J = 16.0$  Hz, 2H), 1.21 (t,  $J = 7.1$  Hz, 3H).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -94.28 (t,  $J = 15.7$  Hz), -111.27-111.34 (m).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.3, 163.6 (dt,  $^1J_{\text{C-F}} = 249.1$  Hz,  $^4J_{\text{C-F}} = 1.9$  Hz), 132.8 (td,  $^2J_{\text{C-F}} = 27.1$  Hz,  $^4J_{\text{C-F}} = 3.5$  Hz), 132.7 (t,  $^3J_{\text{C-F}} = 4.1$  Hz), 130.6, 127.5 (dt,  $^3J_{\text{C-F}} = 8.6$  Hz,  $^3J_{\text{C-F}} = 6.2$  Hz), 121.2 (t,  $^1J_{\text{C-F}} = 244.5$  Hz), 115.4 (d,  $^2J_{\text{C-F}} = 21.9$  Hz), 61.2, 40.5 (t,  $^2J_{\text{C-F}} = 29.2$  Hz), 14.2. HRMS (ESI) calcd. for  $\text{C}_{13}\text{H}_{14}\text{F}_3\text{O}_2$   $[\text{M}+\text{H}]^+$  259.0946, found: 259.0943.

### Ethyl 4-(4-chlorophenyl)-4,4-difluoro-2-methylenebutanoate (3ha)



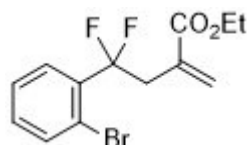
48.5 mg, 88% yield, light yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40-7.34 (m, 4H), 6.37 (s, 1H), 5.75 (s, 1H), 4.08 (q,  $J = 7.1$  Hz, 2H), 3.19 (t,  $J = 15.7$  Hz, 2H), 1.20 (t,  $J = 7.1$  Hz, 3H).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -95.12 (t,  $J = 15.8$  Hz).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.3, 136.1 (t,  $^4J_{\text{C-F}} = 2.0$  Hz), 135.3 (t,  $^2J_{\text{C-F}} = 27.0$  Hz), 132.5 (t,  $^3J_{\text{C-F}} = 4.1$  Hz), 130.7, 128.6, 126.9 (t,  $^3J_{\text{C-F}} = 6.2$  Hz), 121.1 (t,  $^1J_{\text{C-F}} = 244.7$  Hz), 61.2, 40.4 (t,  $^2J_{\text{C-F}} = 29.0$  Hz), 14.2. HRMS (ESI) calcd. for  $\text{C}_{13}\text{H}_{13}\text{ClF}_2\text{NaO}_2$   $[\text{M}+\text{Na}]^+$  297.0464, found: 297.0461.

### Ethyl 4-(4-bromophenyl)-4,4-difluoro-2-methylenebutanoate (3ia)



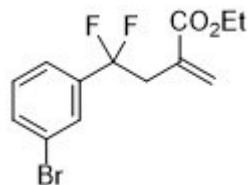
58.2 mg, 91% yield, light yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 (d,  $J = 8.7$  Hz, 2H), 7.32 (d,  $J = 8.7$  Hz, 2H), 6.37 (s, 1H), 5.75 (s, 1H), 4.08 (q,  $J = 7.1$  Hz, 2H), 3.18 (t,  $J = 15.8$  Hz, 2H), 1.20 (t,  $J = 7.1$  Hz, 3H).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -95.33 (t,  $J = 15.8$  Hz).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.3, 135.8 (t,  $^2J_{\text{C-F}} = 27.0$  Hz), 132.5 (t,  $^3J_{\text{C-F}} = 4.0$  Hz), 131.6, 130.7, 127.2 (t,  $^3J_{\text{C-F}} = 6.1$  Hz), 124.3 (t,  $^4J_{\text{C-F}} = 2.1$  Hz), 121.1 (t,  $^1J_{\text{C-F}} = 244.8$  Hz), 61.2, 40.4 (t,  $^2J_{\text{C-F}} = 28.9$  Hz), 14.2. HRMS (ESI) calcd. for  $\text{C}_{13}\text{H}_{13}\text{BrF}_2\text{NaO}_2$   $[\text{M}+\text{Na}]^+$  340.9959, found: 340.9954.

#### Ethyl 4-(2-bromophenyl)-4,4-difluoro-2-methylenebutanoate (3ja)



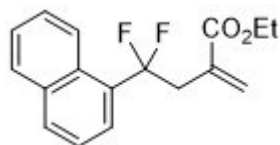
57.3 mg, 90% yield, light yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (d,  $J = 7.9$  Hz, 1H), 7.48 (dd,  $J = 7.8, 1.6$  Hz, 1H), 7.32 (t,  $J = 7.6$  Hz, 1H), 7.28 – 7.23 (m, 1H), 6.36 (s, 1H), 5.75 (s, 1H), 4.06 (q,  $J = 7.1$  Hz, 2H), 3.45 (t,  $J = 16.1$  Hz, 2H), 1.21 (t,  $J = 7.1$  Hz, 3H).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -94.34 (t,  $J = 16.1$  Hz).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.3, 135.5 (t,  $^2J_{\text{C-F}} = 25.6$  Hz), 134.8, 132.6 (t,  $^3J_{\text{C-F}} = 3.8$  Hz), 131.3, 131.0, 128.2 (t,  $^3J_{\text{C-F}} = 9.1$  Hz), 127.3, 120.8 (t,  $^1J_{\text{C-F}} = 246.5$  Hz), 120.1 (t,  $^4J_{\text{C-F}} = 3.7$  Hz), 61.1, 38.4 (t,  $^2J_{\text{C-F}} = 27.1$  Hz), 14.2. HRMS (ESI) calcd. for  $\text{C}_{13}\text{H}_{13}\text{BrF}_2\text{NaO}_2$   $[\text{M}+\text{Na}]^+$  340.9959, found: 340.9956.

#### Ethyl 4-(3-bromophenyl)-4,4-difluoro-2-methylenebutanoate (3ka)



56.4 mg, 88% yield, light yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 (s, 1H), 7.54 (d,  $J = 8.0$  Hz, 1H), 7.38 (d,  $J = 7.8$  Hz, 1H), 7.27 (t,  $J = 7.9$  Hz, 1H), 6.39 (s, 1H), 5.77 (s, 1H), 4.08 (q,  $J = 7.1$  Hz, 2H), 3.18 (t,  $J = 15.9$  Hz, 2H), 1.22 (t,  $J = 7.1$  Hz, 3H).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -95.60 (t,  $J = 15.9$  Hz).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.3, 138.9 (t,  $^2J_{\text{C-F}} = 26.8$  Hz), 133.1 (t,  $^4J_{\text{C-F}} = 1.5$  Hz), 132.4 (t,  $^3J_{\text{C-F}} = 3.9$  Hz), 130.9, 130.1, 128.6 (t,  $^3J_{\text{C-F}} = 6.4$  Hz), 124.1 (t,  $^3J_{\text{C-F}} = 6.1$  Hz), 122.5, 120.6 (t,  $^1J_{\text{C-F}} = 245.3$  Hz), 61.3, 40.5 (t,  $^2J_{\text{C-F}} = 28.6$  Hz), 14.2. HRMS (ESI) calcd. for  $\text{C}_{13}\text{H}_{13}\text{BrF}_2\text{NaO}_2$   $[\text{M}+\text{Na}]^+$  340.9959, found: 340.9953.

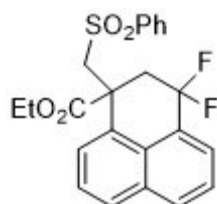
#### Ethyl 4,4-difluoro-2-methylene-4-(naphthalen-1-yl)butanoate (3la)



23.5 mg, 40% yield, light yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.38 (d,  $J = 8.5$  Hz, 1H), 7.94 – 7.87 (m, 2H), 7.66 (d,  $J = 7.1$  Hz, 1H), 7.61 (ddd,  $J = 8.6, 6.8, 1.4$  Hz,

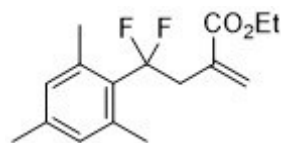
1H), 7.54 (ddd,  $J = 8.0, 6.9, 1.0$  Hz, 1H), 7.46 (t,  $J = 7.8$  Hz, 1H), 6.43 (s, 1H), 5.78 (s, 1H), 4.02 (q,  $J = 7.1$  Hz, 2H), 3.47 (t,  $J = 16.6$  Hz, 2H), 1.13 (t,  $J = 7.1$  Hz, 3H).  $^{19}\text{F}$  NMR (470MHz,  $\text{CDCl}_3$ )  $\delta$  -92.19 (t,  $J = 16.6$  Hz).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.5, 134.2, 132.9 (t,  $^4J_{\text{C-F}} = 3.0$  Hz), 132.3 (t,  $^2J_{\text{C-F}} = 24.1$  Hz), 131.1, 130.9, 129.6 (t,  $^4J_{\text{C-F}} = 2.3$  Hz), 129.0, 127.1, 126.1, 125.0 (t,  $^3J_{\text{C-F}} = 4.4$  Hz), 124.6, 124.5 (t,  $^3J_{\text{C-F}} = 9.3$  Hz), 122.3 (t,  $^1J_{\text{C-F}} = 245.2$  Hz), 61.1, 40.6 (t,  $^2J_{\text{C-F}} = 27.5$  Hz), 14.1. HRMS (ESI) calcd. for  $\text{C}_{17}\text{H}_{17}\text{F}_2\text{O}_2$   $[\text{M}+\text{H}]^+$  291.1196, found: 291.1199.

### Ethyl 3,3-difluoro-1-((phenylsulfonyl)methyl)-2,3-dihydro-1H-phenalene-1-carboxylate (3la')



27.8 mg, 32% yield, white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (d,  $J = 8.2$  Hz, 1H), 7.96-7.92 (m, 3H), 7.84 (d,  $J = 8.2$  Hz, 1H), 7.71 (d,  $J = 7.4$  Hz, 1H), 7.65-7.57 (m, 2H), 7.57-7.50 (m, 2H), 7.50-7.45 (m, 1H), 4.44 (dq,  $J = 10.7, 7.1$  Hz, 1H), 4.35 (dq,  $J = 10.8, 7.1$  Hz, 1H), 4.15 (dd,  $J = 14.7, 1.4$  Hz, 1H), 3.90 (d,  $J = 14.8$  Hz, 1H), 3.64 (ddd,  $J = 15.0, 10.6, 6.6$  Hz, 1H), 3.34 (dddd,  $J = 32.3, 15.0, 5.8, 1.2$  Hz, 1H), 1.37 (t,  $J = 7.1$  Hz, 3H).  $^{19}\text{F}$  NMR (470MHz,  $\text{CDCl}_3$ )  $\delta$  -75.24 (ddd,  $J = 268.3, 32.2, 10.4$  Hz), -93.81 (dt,  $J = 268.1, 5.9$  Hz).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  171.4 (d,  $^4J_{\text{C-F}} = 1.7$  Hz), 142.1, 133.6, 131.3 (d,  $^4J_{\text{C-F}} = 3.0$  Hz), 130.4 (t,  $^3J_{\text{C-F}} = 1.3$  Hz), 129.3, 129.1, 128.3 (dd,  $^2J_{\text{C-F}} = 25.3, 23.4$  Hz), 127.8, 126.9 (d,  $^4J_{\text{C-F}} = 3.6$  Hz), 126.9 (d,  $^4J_{\text{C-F}} = 3.6$  Hz), 126.3, 126.0 (d,  $^4J_{\text{C-F}} = 2.9$  Hz), 125.4, 123.1 (dd,  $^3J_{\text{C-F}} = 6.5, 2.9$  Hz), 118.6 (dd,  $^1J_{\text{C-F}} = 238.4, 234.6$  Hz), 63.4 (d,  $^4J_{\text{C-F}} = 5.0$  Hz), 63.0, 49.6 (d,  $^3J_{\text{C-F}} = 10.4$  Hz), 35.7 (dd,  $^2J_{\text{C-F}} = 26.7, 24.9$  Hz), 14.1. HRMS (ESI) calcd. for  $\text{C}_{23}\text{H}_{21}\text{F}_2\text{O}_4\text{S}$   $[\text{M}+\text{H}]^+$  431.1128, found: 431.1124.

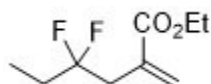
### Ethyl 4,4-difluoro-4-mesityl-2-methylenebutanoate (3ma)



49.2 mg, 87% yield, light yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.86 (s, 2H), 6.43 (s, 1H), 5.82 (s, 1H), 4.15 (q,  $J = 7.1$  Hz, 2H), 3.21 (t,  $J = 16.5$  Hz, 2H), 2.43 (t,  $J = 4.4$  Hz, 6H), 2.27 (s, 3H), 1.26 (t,  $J = 7.1$  Hz, 3H).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -87.4- -87.6 (m).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.6, 138.8, 136.3 (t,  $^3J_{\text{C-F}} = 3.1$  Hz), 132.7 (t,  $^4J_{\text{C-F}} = 2.2$  Hz), 131.0, 130.7 (t,  $^2J_{\text{C-F}} = 23.5$  Hz), 130.5, 123.9 (t,  $^1J_{\text{C-F}} = 246.6$  Hz), 61.0, 39.8 (t,  $^2J_{\text{C-F}} = 27.6$  Hz), 22.1 (t,  $^3J_{\text{C-F}} = 6.6$  Hz), 20.7, 14.1. HRMS (ESI) calcd. for  $\text{C}_{16}\text{H}_{21}\text{F}_2\text{O}_2$   $[\text{M}+\text{H}]^+$  283.1509, found: 283.1516.

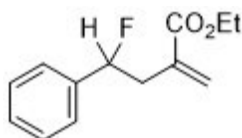


### Ethyl 4,4-difluoro-2-methylenhexanoate (3na)



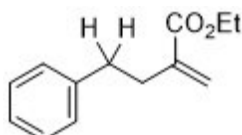
21.3 mg, 55% yield, light yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.39 (s, 1H), 5.81 (s, 1H), 4.23 (q,  $J = 7.1$  Hz, 2H), 2.92 (t,  $J = 16.2$  Hz, 2H), 1.92 – 1.78 (m, 2H), 1.31 (t,  $J = 7.1$  Hz, 3H), 1.03 (t,  $J = 7.5$  Hz, 3H).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -99.62 – -99.79 (m).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.7, 133.1 (t,  $^3J_{\text{C-F}} = 4.3$  Hz), 129.9, 123.9 (t,  $^1J_{\text{C-F}} = 242.3$  Hz), 61.1, 37.3 (t,  $^2J_{\text{C-F}} = 26.6$  Hz), 29.4 (t,  $^2J_{\text{C-F}} = 25.8$  Hz), 14.1, 6.4 (t,  $^3J_{\text{C-F}} = 5.6$  Hz). HRMS (ESI) calcd. for  $\text{C}_9\text{H}_{15}\text{F}_2\text{O}_2$   $[\text{M}+\text{H}]^+$  193.1040, found: 193.1037.

### Ethyl 4-fluoro-2-methylene-4-phenylbutanoate (3oa)



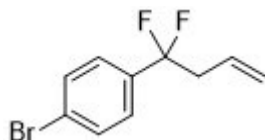
16.5 mg, 37% yield, light yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 – 7.29 (m, 5H), 6.30 (s, 1H), 5.69 (s, 1H), 5.71 – 5.58 (m, 1H), 4.22 (q,  $J = 7.1$  Hz, 2H), 2.91 – 2.89 (m, 1H), 2.89 – 2.81 (m, 1H), 1.31 (t,  $J = 7.1$  Hz, 3H).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -176.27 (m).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.8, 139.9 (d,  $^2J_{\text{C-F}} = 19.8$  Hz), 135.8 (d,  $^3J_{\text{C-F}} = 3.2$  Hz), 128.6, 128.6, 128.5 (d,  $^4J_{\text{C-F}} = 1.8$  Hz), 125.6 (d,  $^3J_{\text{C-F}} = 6.9$  Hz), 92.7 (d,  $^1J_{\text{C-F}} = 173.2$  Hz), 61.1, 40.4 (d,  $^2J_{\text{C-F}} = 25.0$  Hz), 14.3. HRMS (ESI) calcd. for  $\text{C}_{13}\text{H}_{16}\text{FO}_2$   $[\text{M}+\text{H}]^+$  223.1134, found: 223.1139.

### Ethyl 2-methylene-4-phenylbutanoate (3pa)



3.6 mg, 9% yield, light yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 – 7.24 (m, 2H), 7.22 – 7.17 (m, 3H), 6.16 (d,  $J = 1.4$  Hz, 1H), 5.50 (q,  $J = 1.3$  Hz, 1H), 4.22 (q,  $J = 7.1$  Hz, 2H), 2.82 – 2.77 (m, 2H), 2.66 – 2.59 (m, 2H), 1.32 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  167.1, 141.5, 140.2, 128.5, 128.4, 125.9, 125.1, 60.7, 34.9, 33.9, 14.2. HRMS (ESI) calcd. for  $\text{C}_{13}\text{H}_{17}\text{O}_2$   $[\text{M}+\text{H}]^+$  205.1228, found: 205.1233.

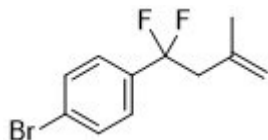
### 1-Bromo-4-(1,1-difluorobut-3-en-1-yl)benzene(3ib)



25.6 mg, 52% yield, colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (d,  $J = 8.6$  Hz, 2H), 7.33 (d,  $J = 8.6$  Hz, 2H), 5.71 (ddt,  $J = 17.3, 10.3, 7.1$  Hz, 1H), 5.24 - 5.10 (m,

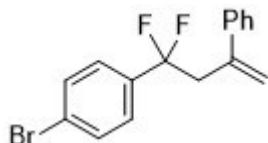
2H), 2.87 (td,  $J = 15.7, 7.1$  Hz, 2H).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -95.06 (t,  $J = 15.7$  Hz).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  136.1 (t,  $^2J_{\text{C-F}} = 27.0$  Hz), 131.7, 128.8 (t,  $^3J_{\text{C-F}} = 5.3$  Hz), 127.0 (t,  $^3J_{\text{C-F}} = 6.2$  Hz), 124.2 (t,  $^4J_{\text{C-F}} = 2.2$  Hz), 121.6 (t,  $^1J_{\text{C-F}} = 243.5$  Hz), 121.0, 43.7 (t,  $^2J_{\text{C-F}} = 28.3$  Hz). HRMS (ESI) calcd. for  $\text{C}_{10}\text{H}_{10}\text{BrF}_2$   $[\text{M}+\text{H}]^+$  246.9934, found: 246.9937.

### 1-Bromo-4-(1,1-difluoro-3-methylbut-3-en-1-yl)benzene(3ic)



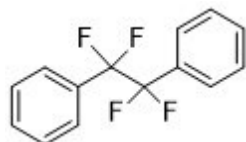
16.9 mg, 32% yield, colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (d,  $J = 8.7$  Hz, 2H), 7.33 (d,  $J = 8.7$  Hz, 2H), 4.91 (s, 1H), 4.71 (s, 1H), 2.82 (t,  $J = 16.3$  Hz, 2H), 1.72 (s, 3H).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -93.48 (t,  $J = 16.3$  Hz).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  137.2 (t,  $^3J_{\text{C-F}} = 3.7$  Hz), 136.3 (t,  $^2J_{\text{C-F}} = 27.1$  Hz), 131.6, 127.0 (t,  $^3J_{\text{C-F}} = 6.2$  Hz), 124.1 (t,  $^4J_{\text{C-F}} = 2.2$  Hz), 122.0 (t,  $^1J_{\text{C-F}} = 244.9$  Hz), 117.5, 47.2 (t,  $^2J_{\text{C-F}} = 27.6$  Hz), 23.6 (t,  $^4J_{\text{C-F}} = 1.7$  Hz). HRMS (ESI) calcd. for  $\text{C}_{11}\text{H}_{12}\text{BrF}_2$   $[\text{M}+\text{H}]^+$  261.0090, found: 261.0097.

### 1-Bromo-4-(1,1-difluoro-3-phenylbut-3-en-1-yl)benzene(3id)



10.8 mg, 17% yield, colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (d,  $J = 8.7$  Hz, 2H), 7.32-7.24 (m, 7H), 5.45 (s, 1H), 5.13 (s, 1H), 3.35 (t,  $J = 15.3$  Hz, 2H).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -93.13 (t,  $J = 15.3$  Hz).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  140.9, 140.2 (t,  $^3J_{\text{C-F}} = 4.2$  Hz), 136.0 (t,  $^2J_{\text{C-F}} = 27.1$  Hz), 131.5, 128.4, 127.7, 127.1 (t,  $^3J_{\text{C-F}} = 6.2$  Hz), 126.4, 124.1 (t,  $^4J_{\text{C-F}} = 2.1$  Hz), 121.8 (t,  $^1J_{\text{C-F}} = 245.2$  Hz), 119.4, 44.8 (t,  $^2J_{\text{C-F}} = 28.3$  Hz). HRMS (ESI) calcd. for  $\text{C}_{16}\text{H}_{14}\text{BrF}_2$   $[\text{M}+\text{H}]^+$  323.0247, found: 323.0244.

### 1,1,2,2-Tetrafluoro-1,2-diphenylethane (5) <sup>5</sup>



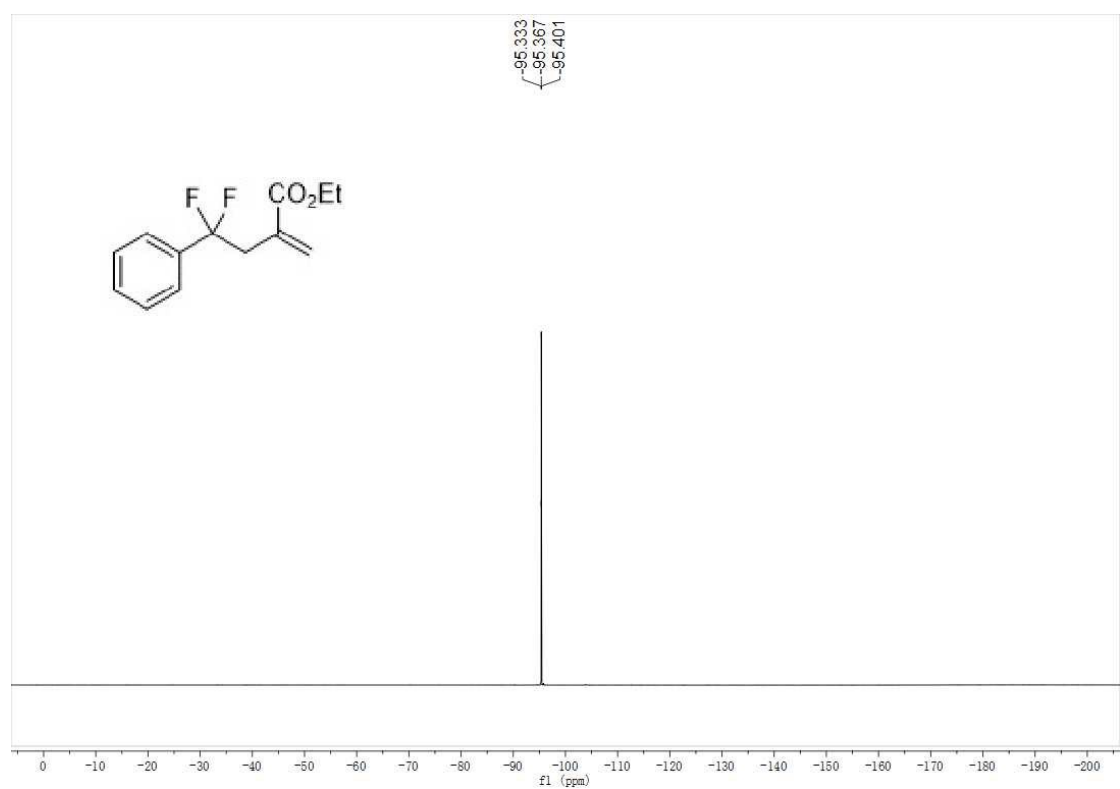
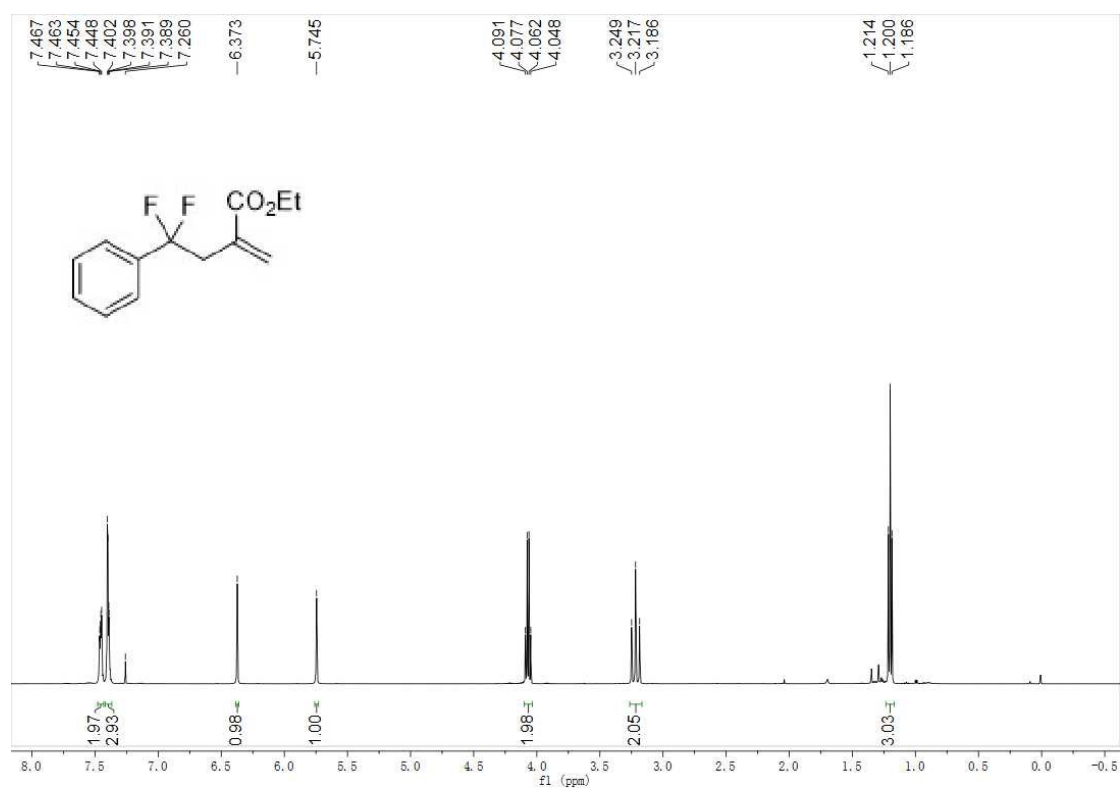
3.6 mg, 14% yield, white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 – 7.46 (m, 2H), 7.47 – 7.39 (m, 8H).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -111.85 (s).

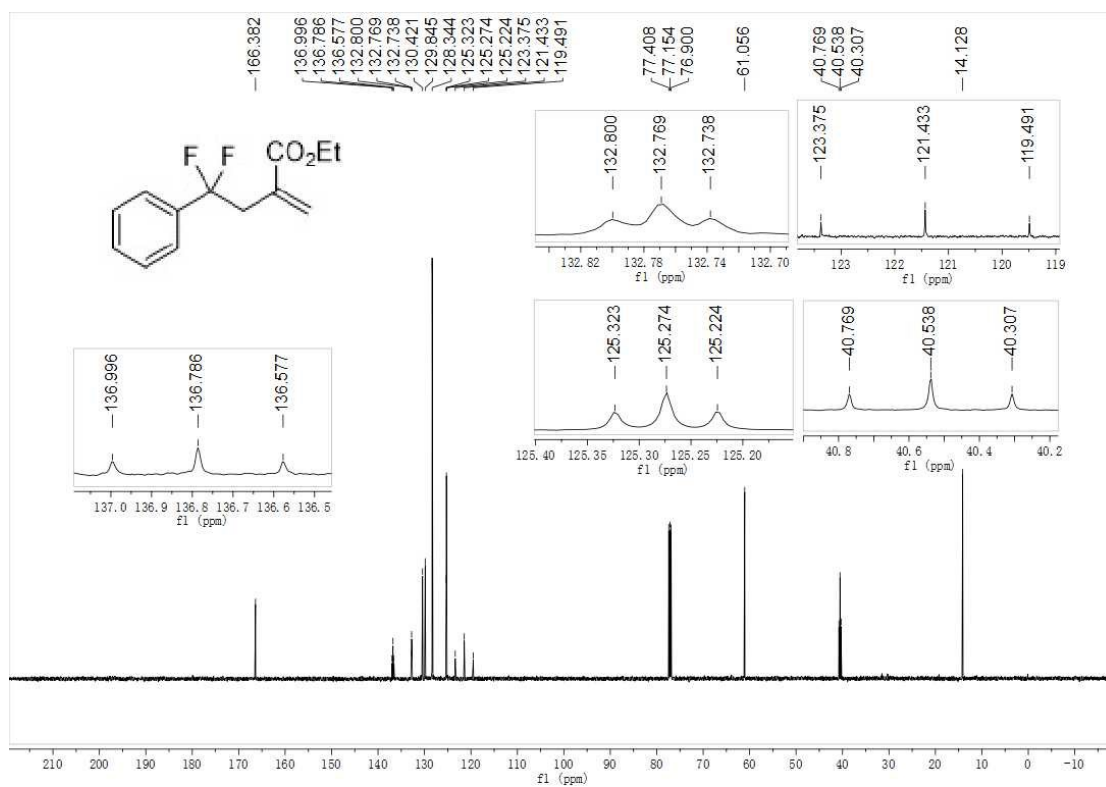
## 5. Reference

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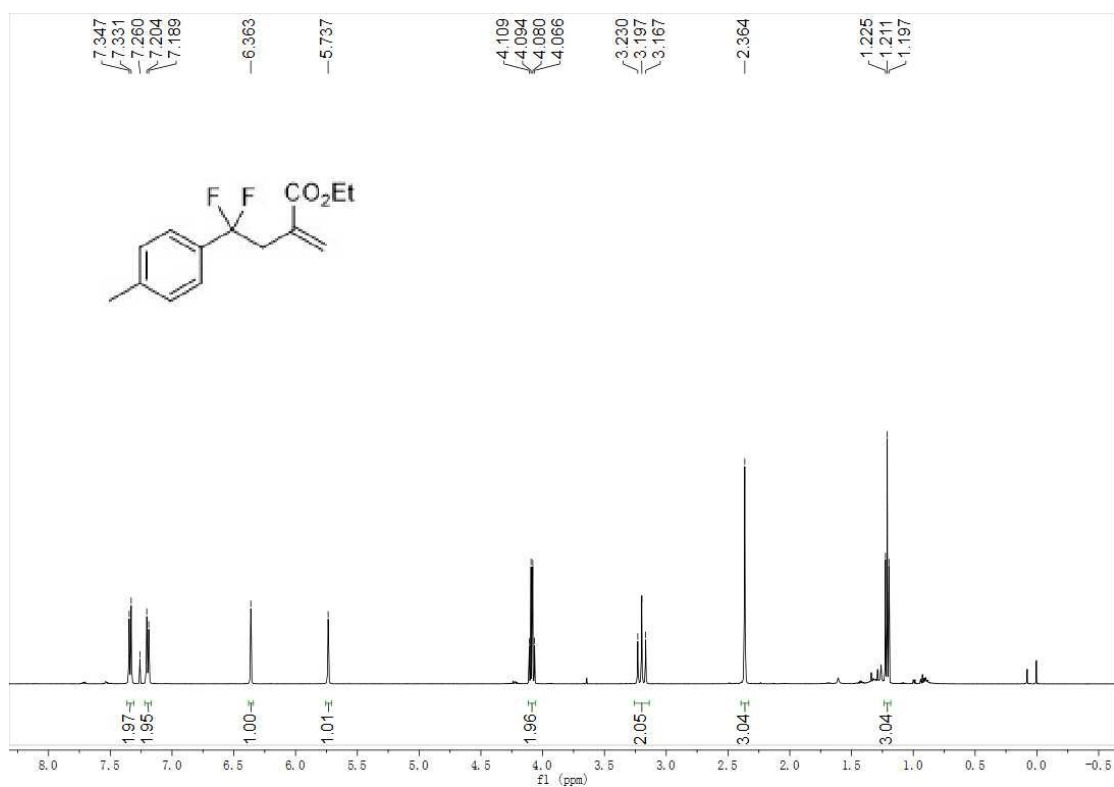
## 6. Copies of $^1\text{H}$ NMR, $^{19}\text{F}$ NMR and $^{13}\text{C}$ NMR Spectra

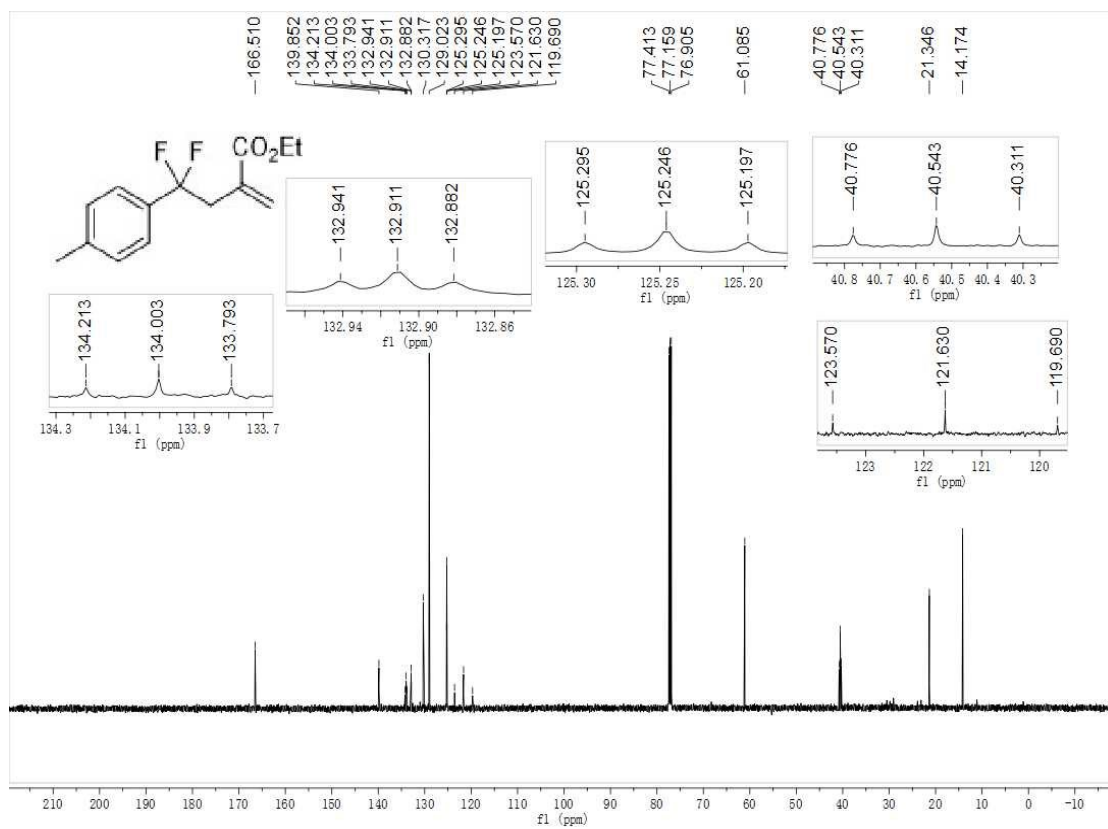
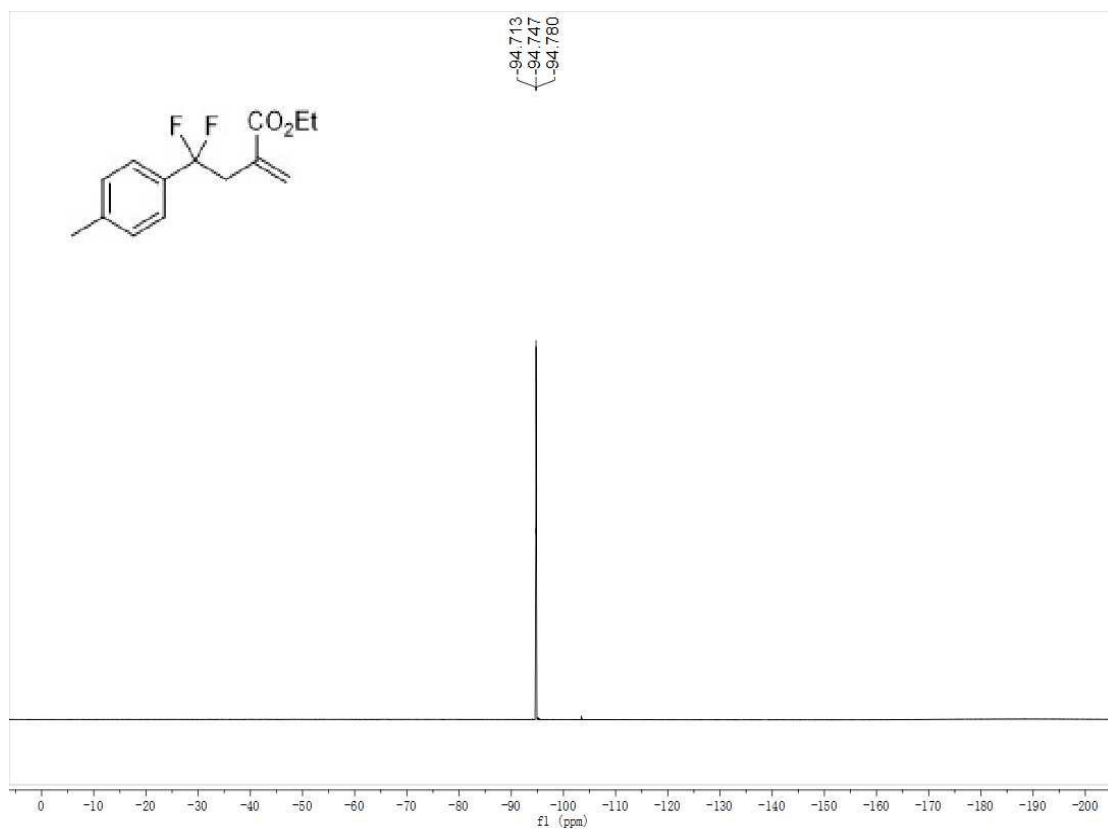
### Ethyl 4,4-difluoro-2-methylene-4-phenylbutanoate (3aa)



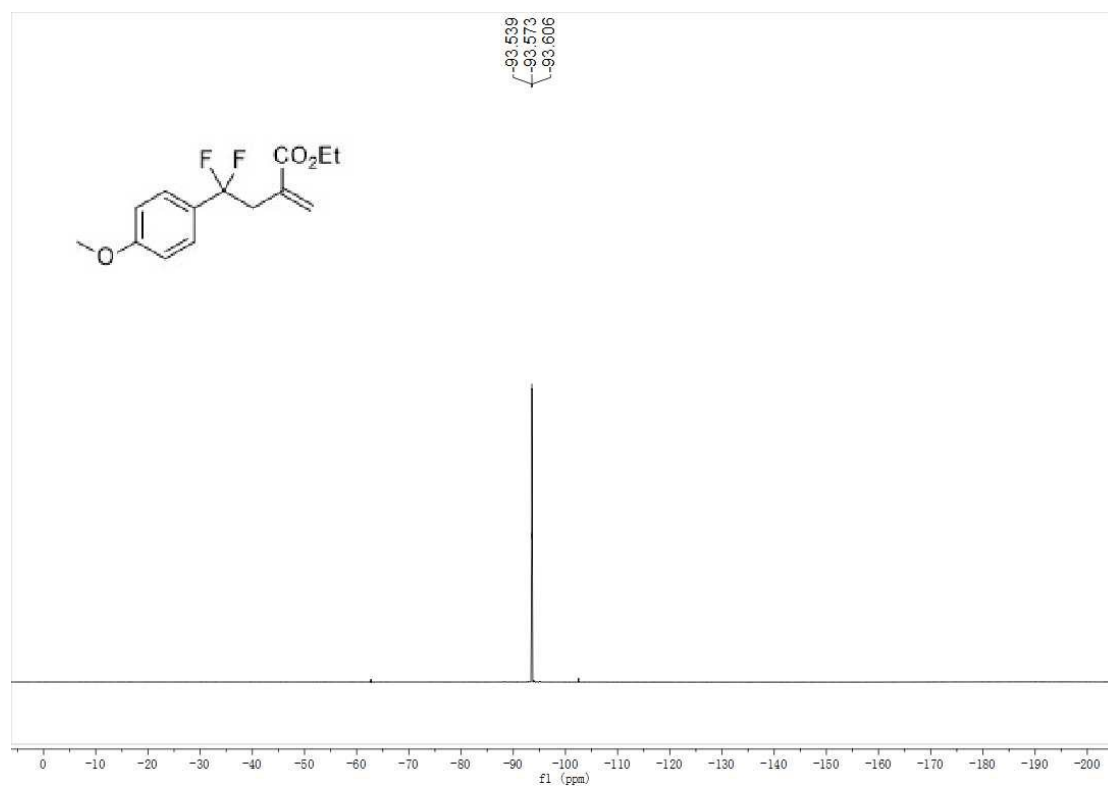
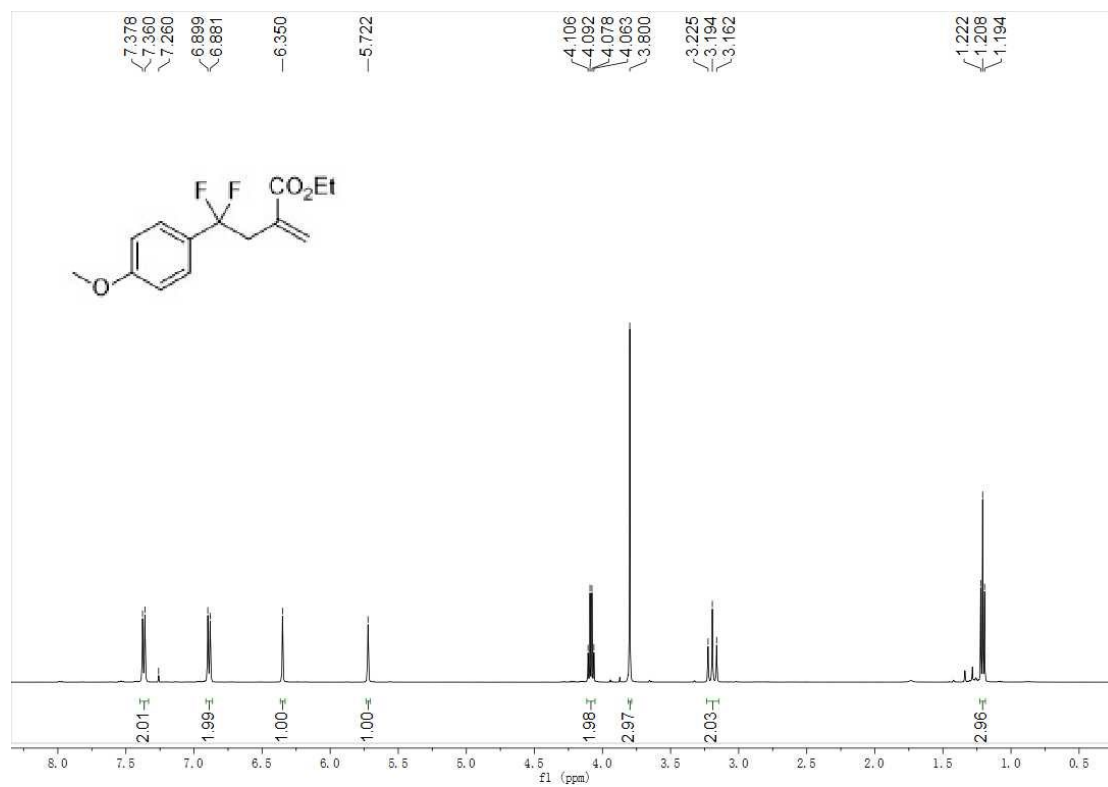


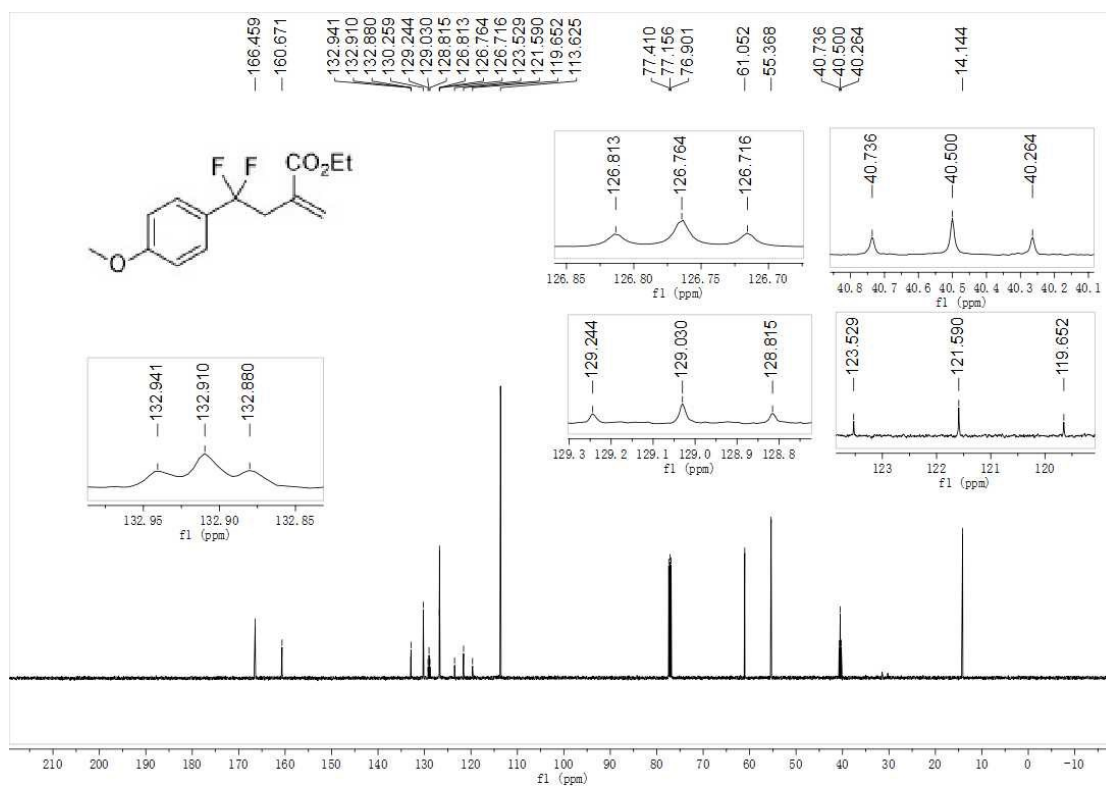
### Ethyl 4,4-difluoro-2-methylene-4-(p-tolyl)butanoate (3ba)



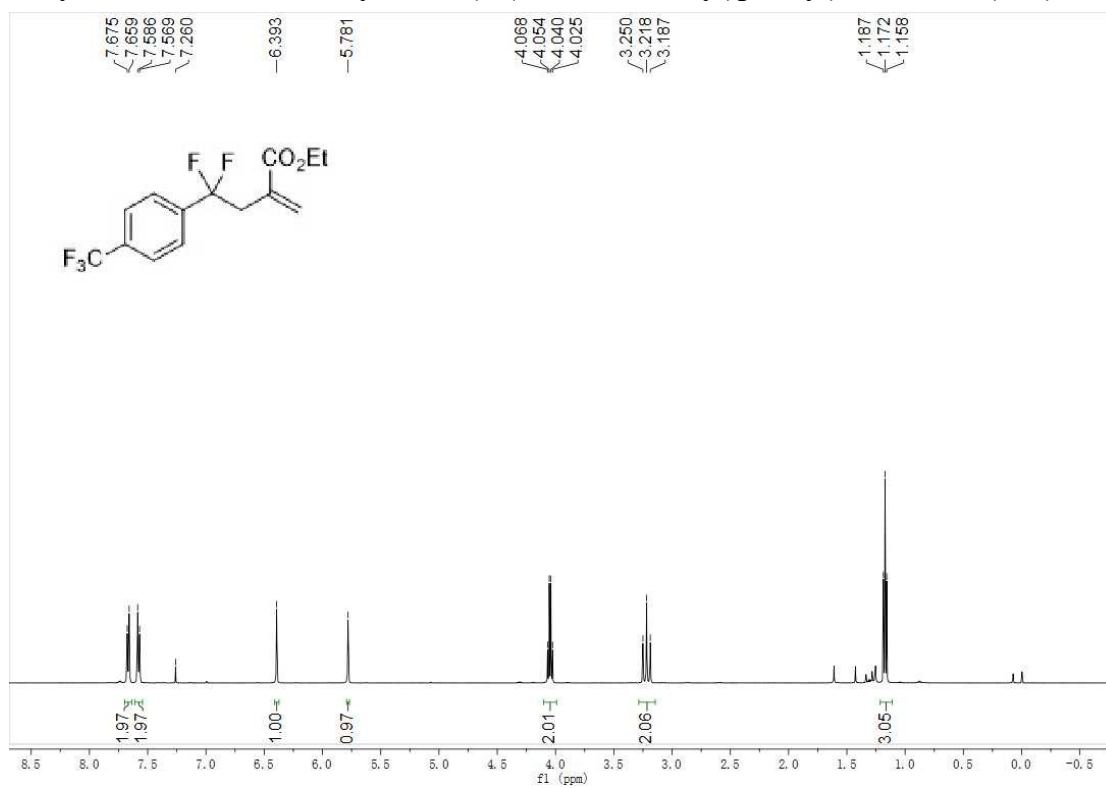


# Ethyl 4,4-difluoro-4-(4-methoxyphenyl)-2-methylenebutanoate (3ca)

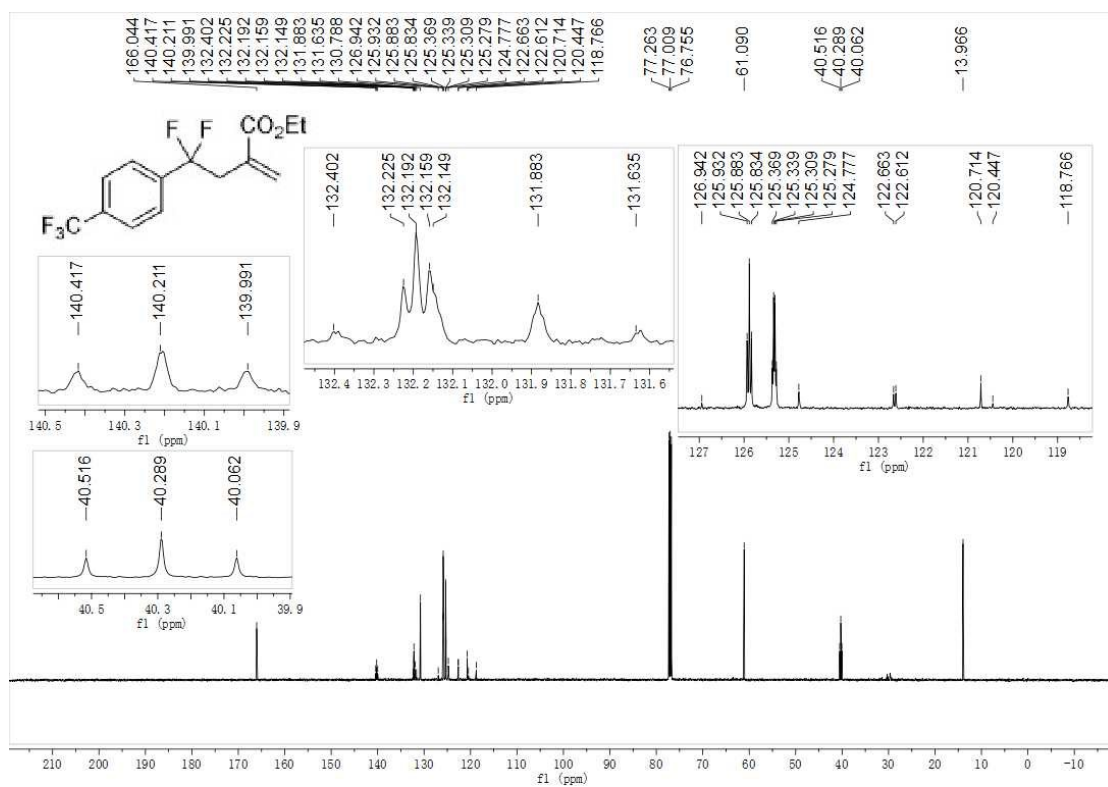
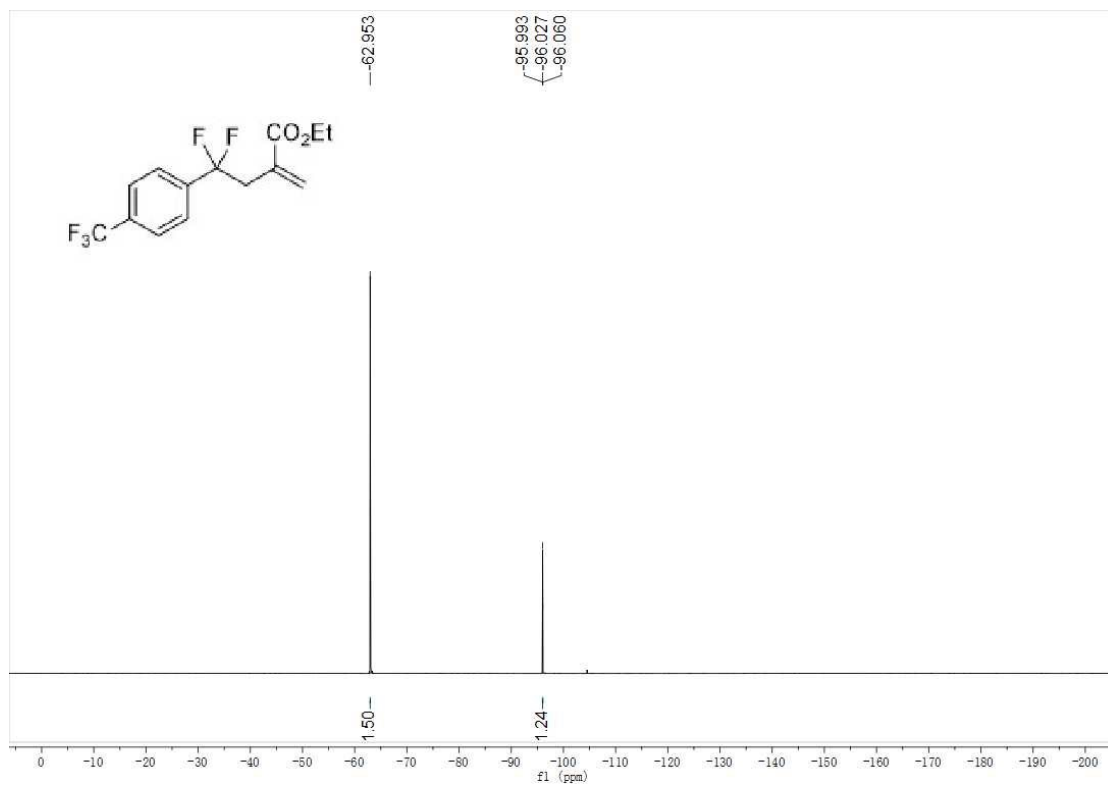




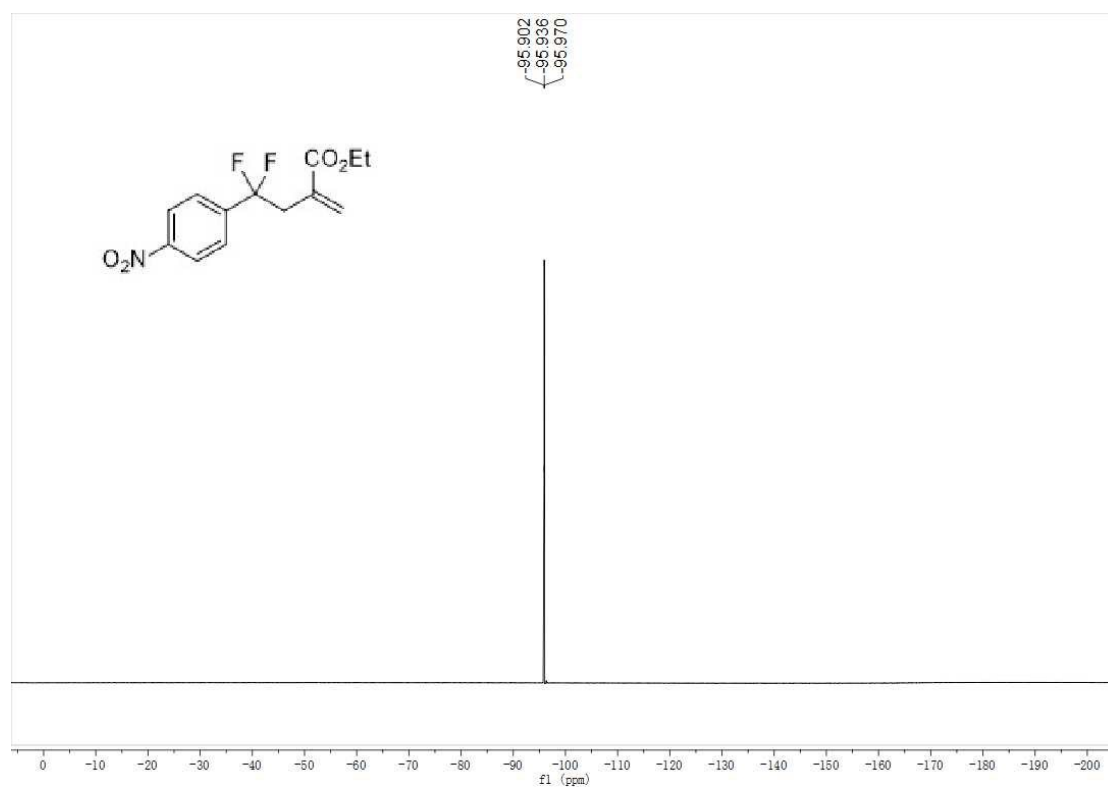
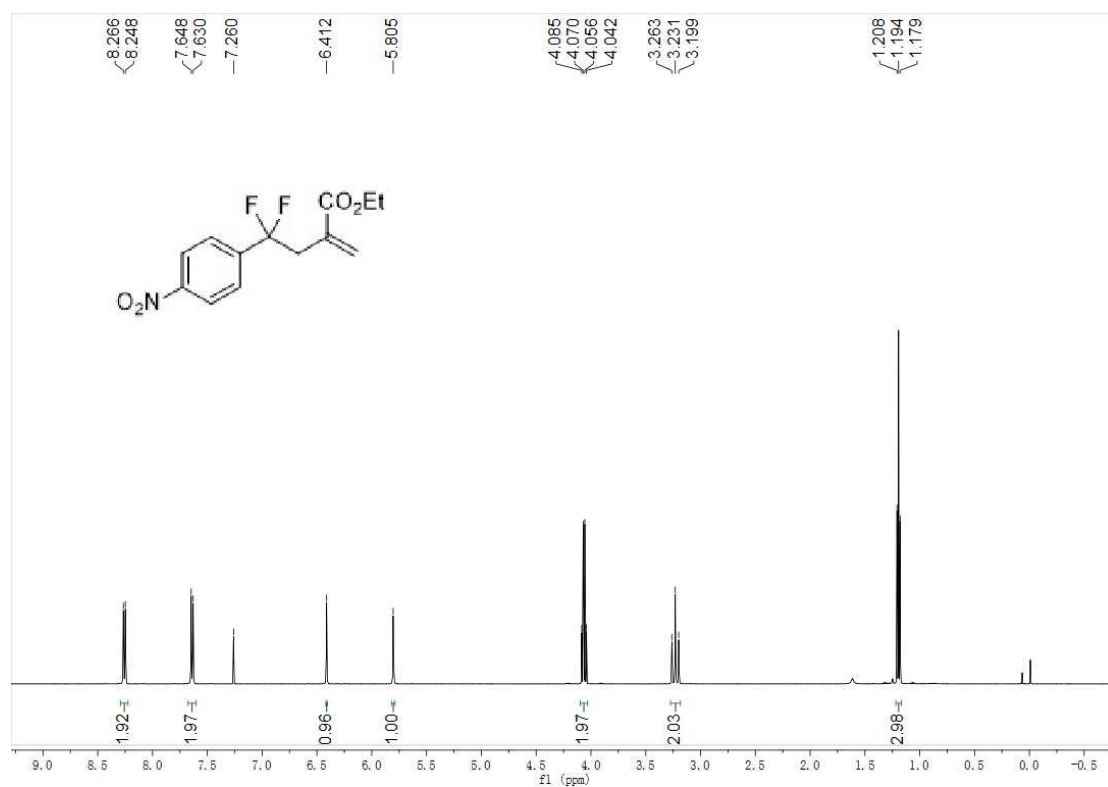
### Ethyl 4,4-difluoro-2-methylene-4-(4-(trifluoromethyl)phenyl)butanoate (3da)

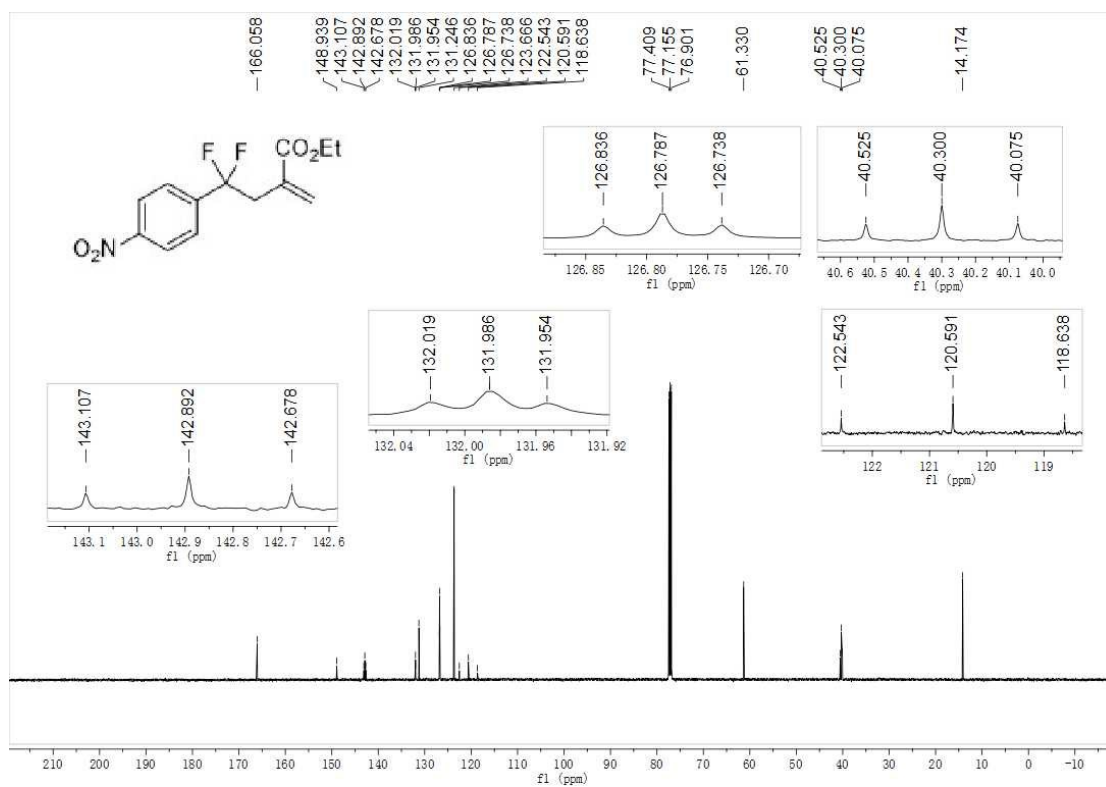




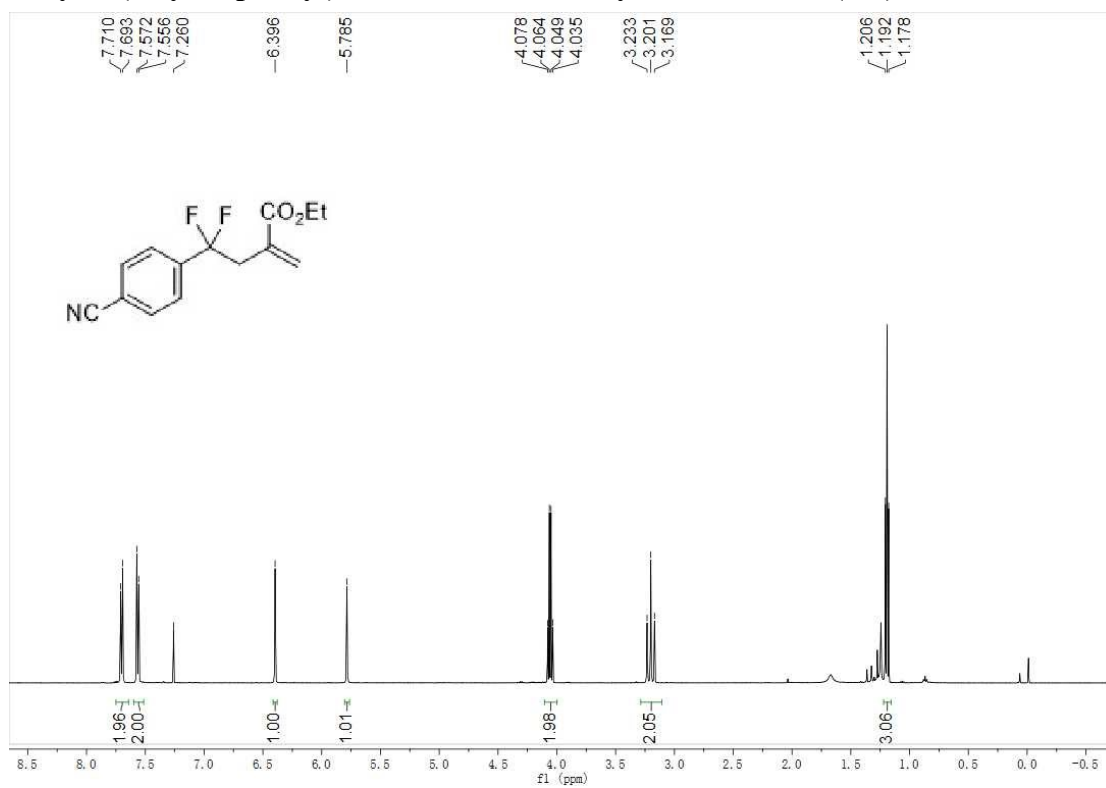


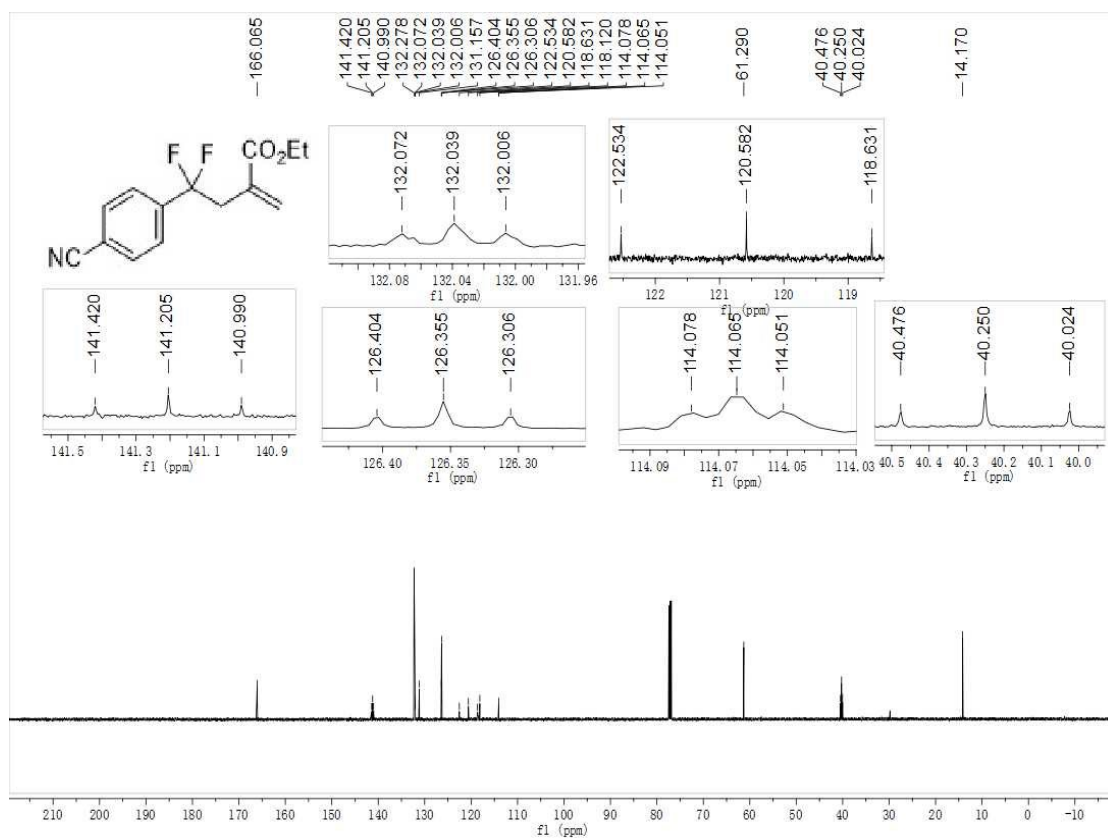
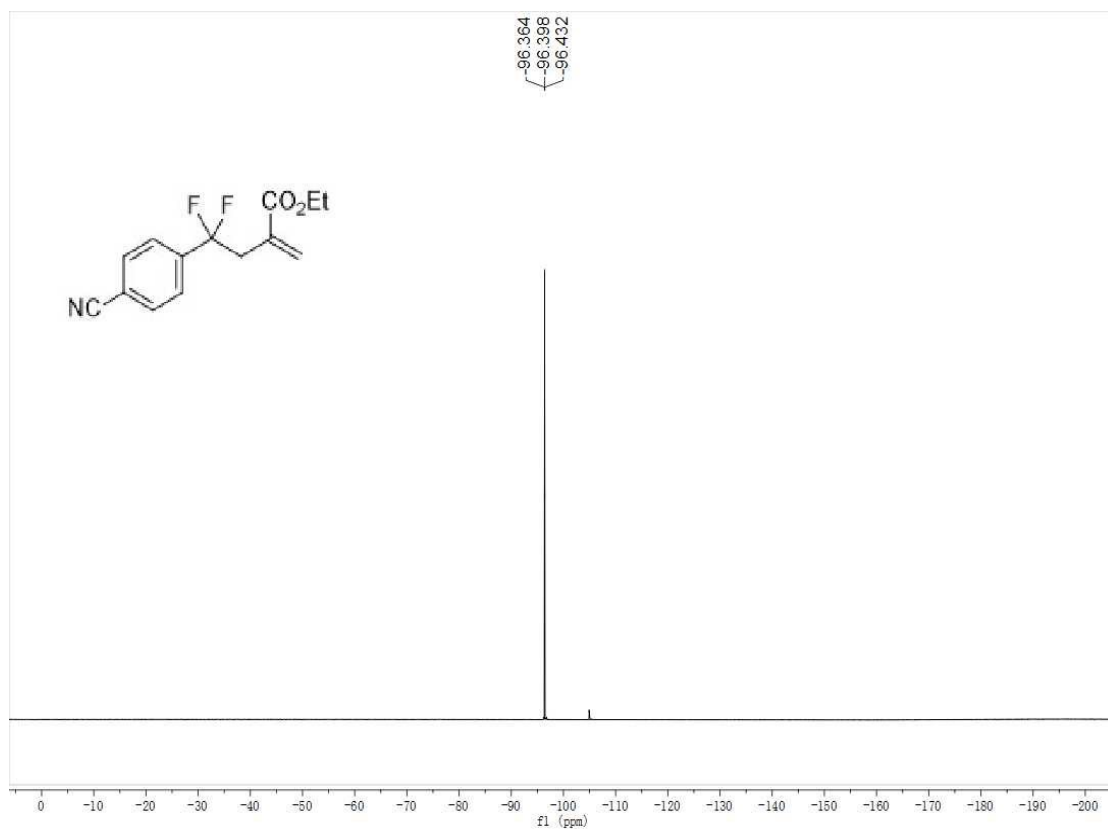
# Ethyl 4,4-difluoro-2-methylene-4-(4-nitrophenyl)butanoate (3ea)



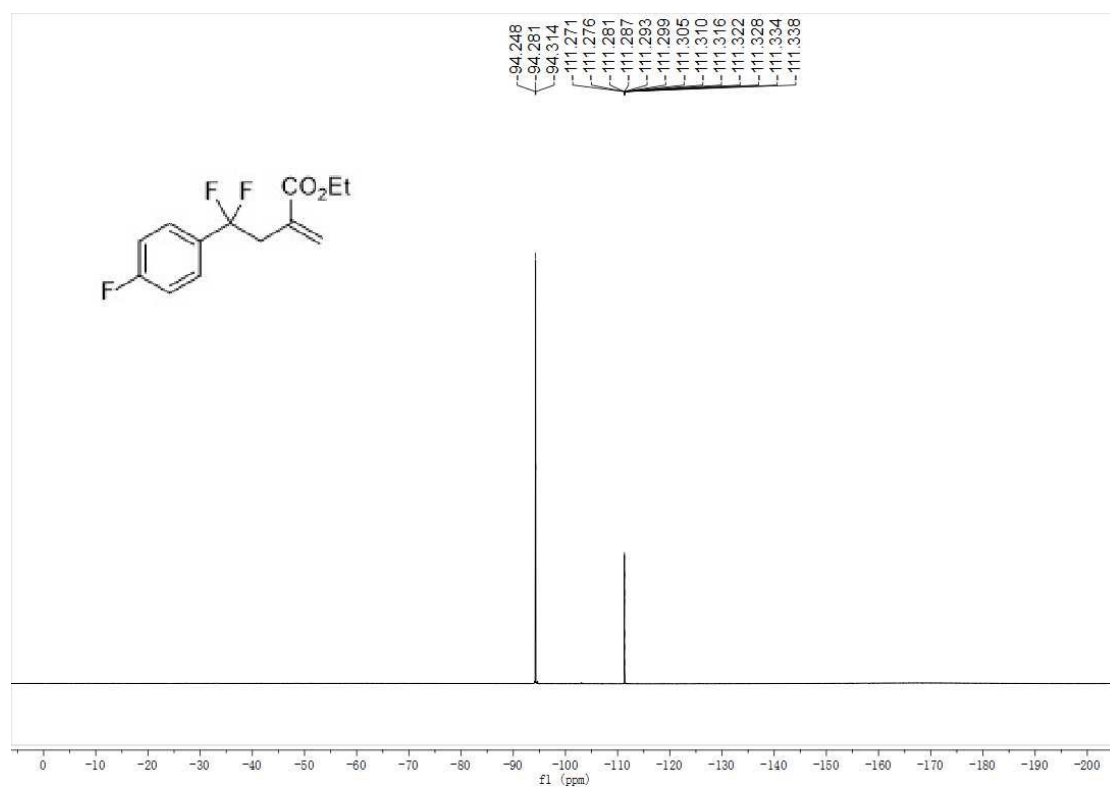
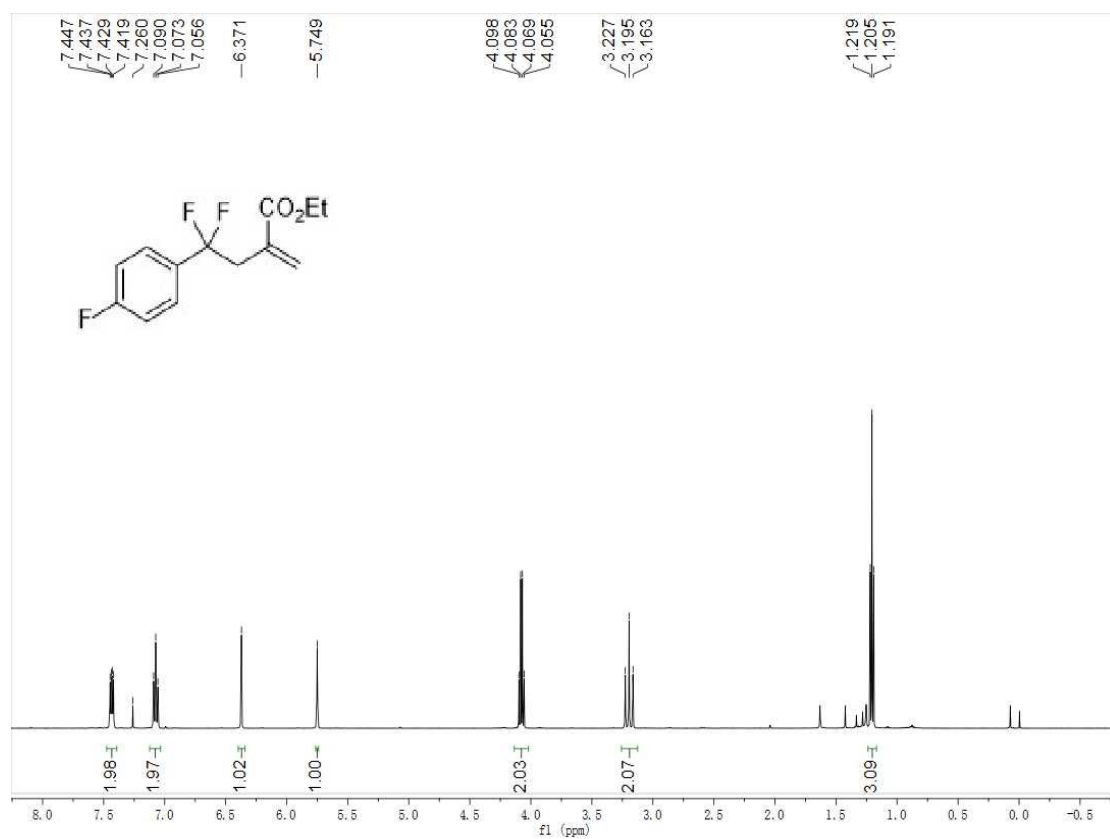


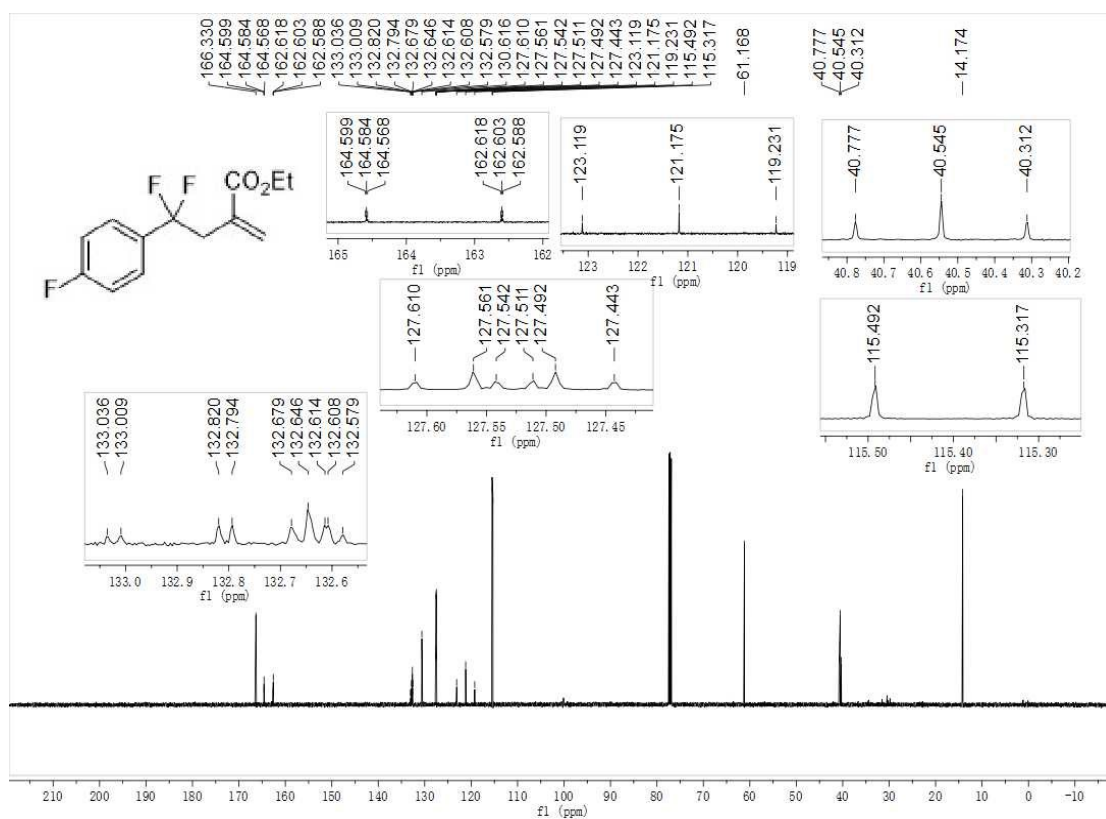
### Ethyl 4-(4-cyanophenyl)-4,4-difluoro-2-methylenebutanoate (3fa)



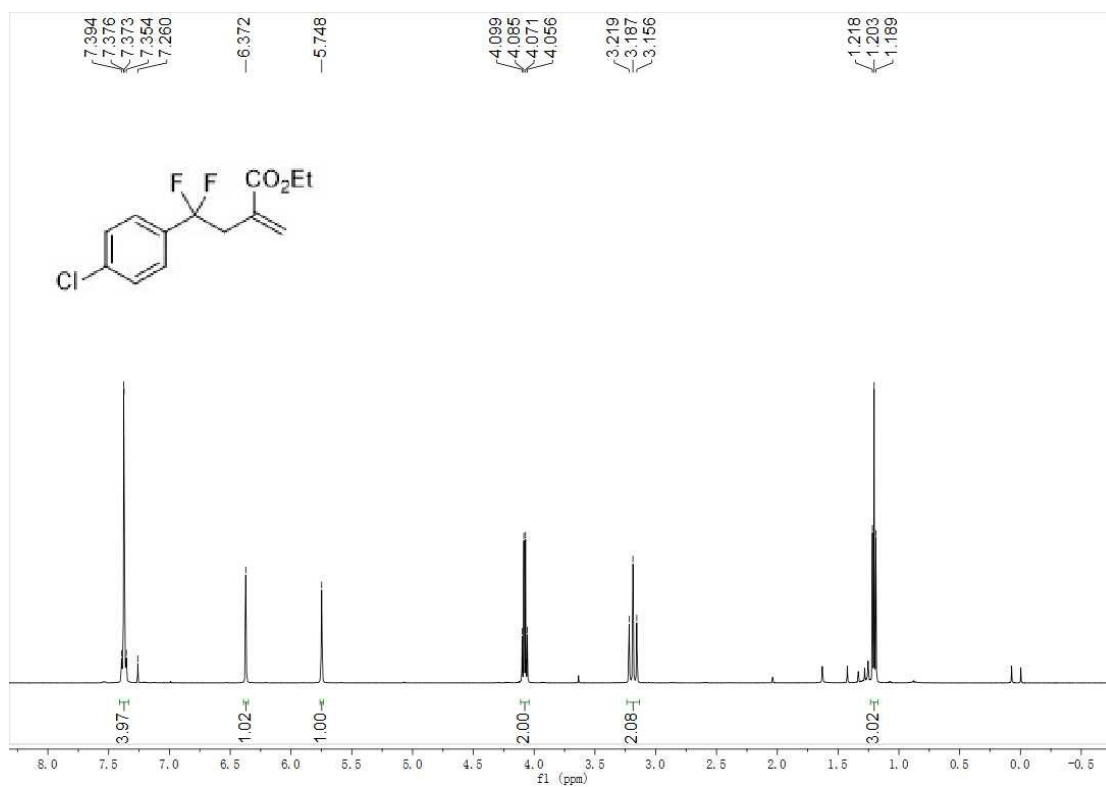


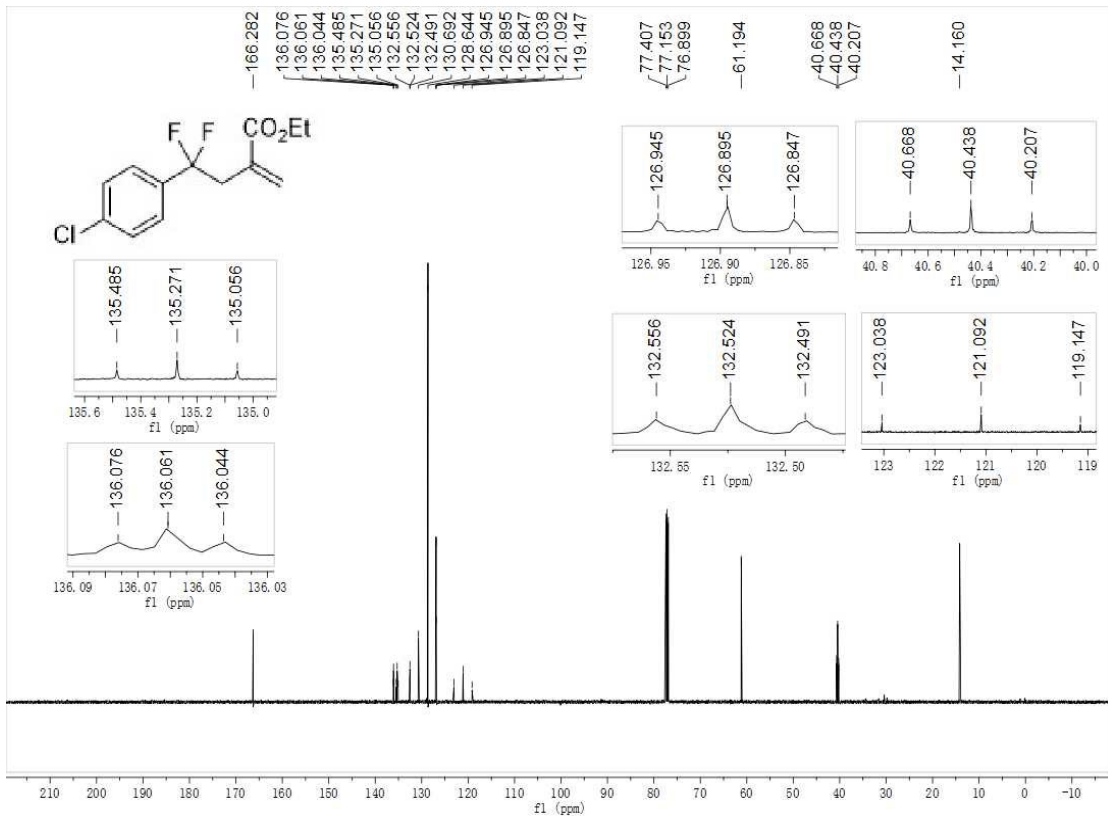
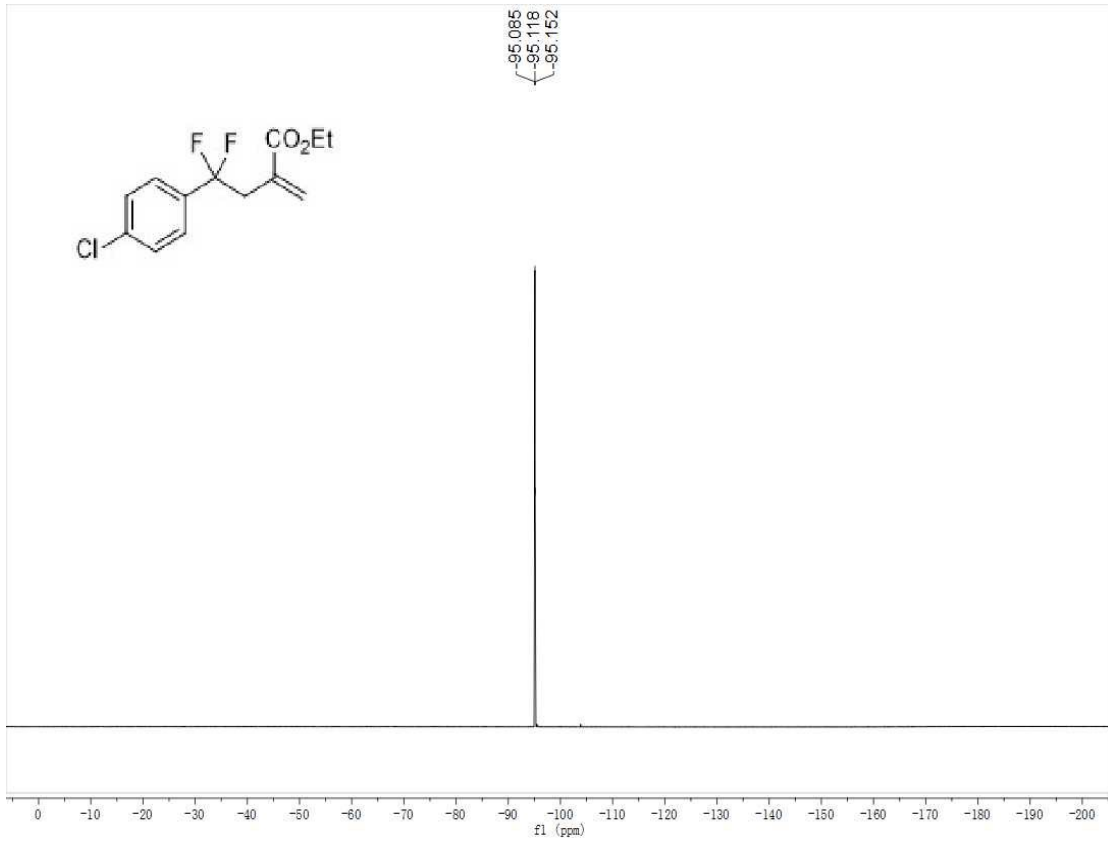
# Ethyl 4,4-difluoro-4-(4-fluorophenyl)-2-methylenebutanoate (3ga)



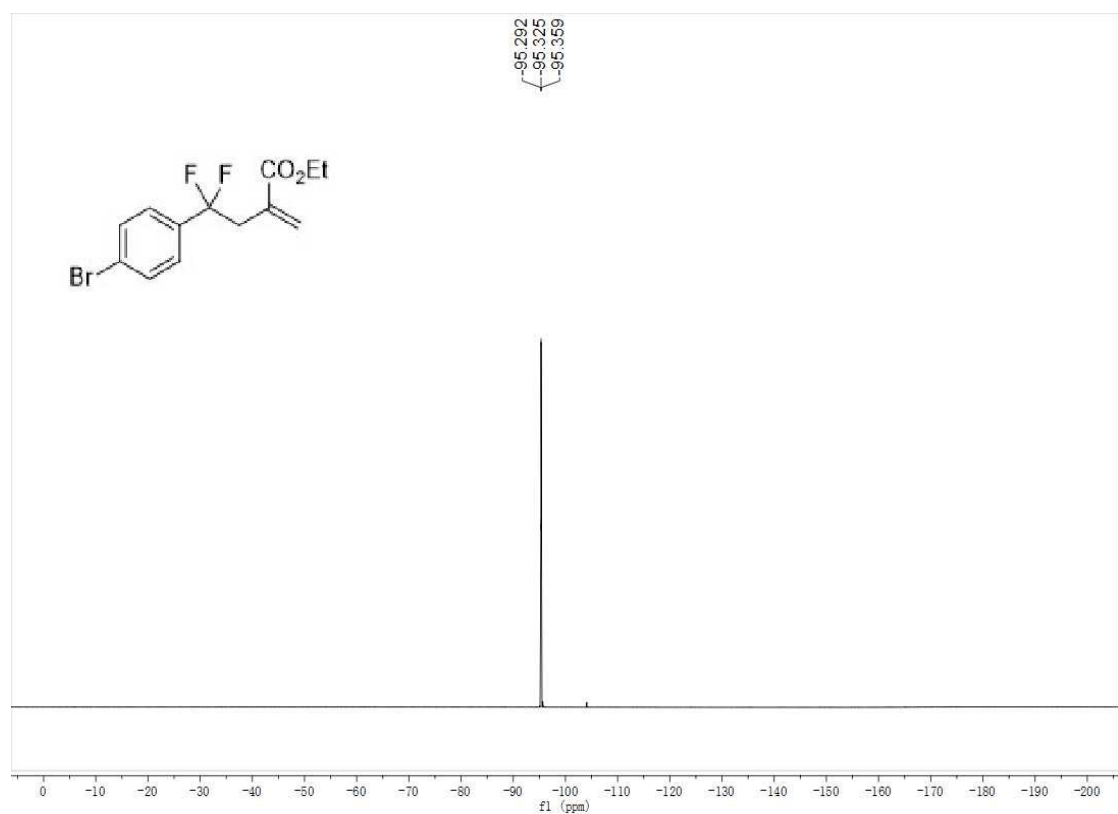
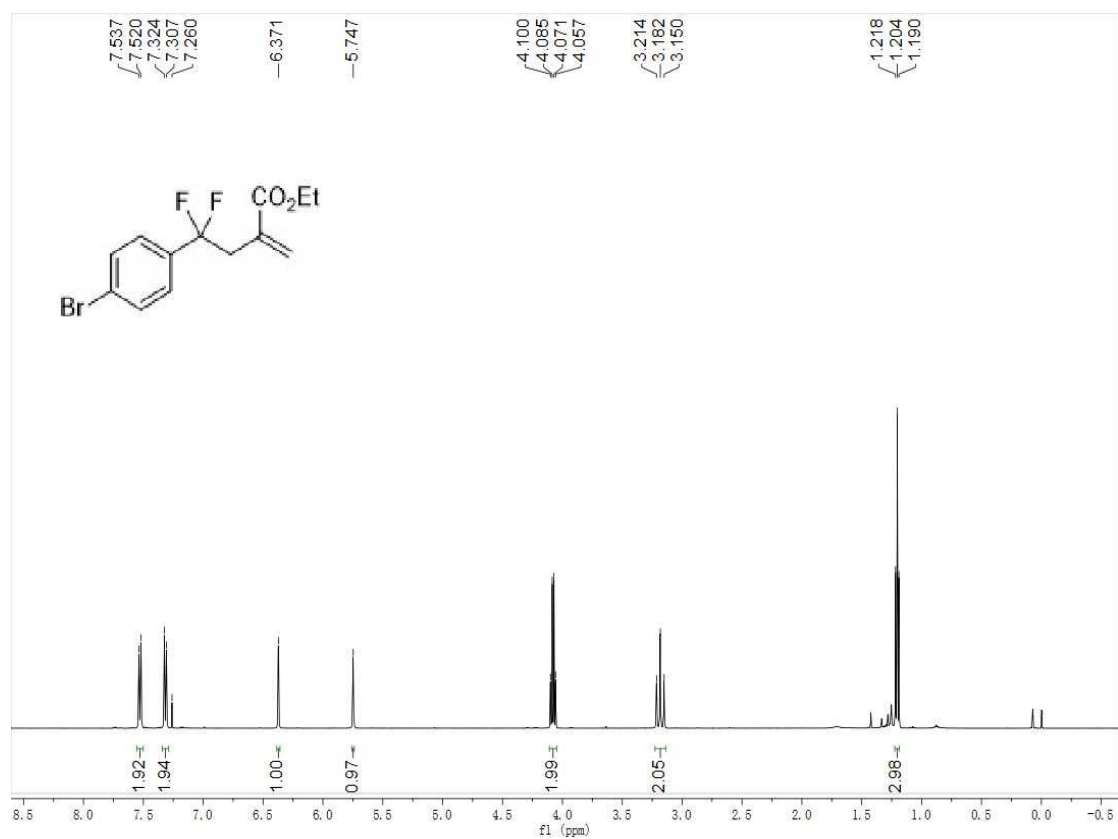


### Ethyl 4-(4-chlorophenyl)-4,4-difluoro-2-methylenebutanoate (3ha)

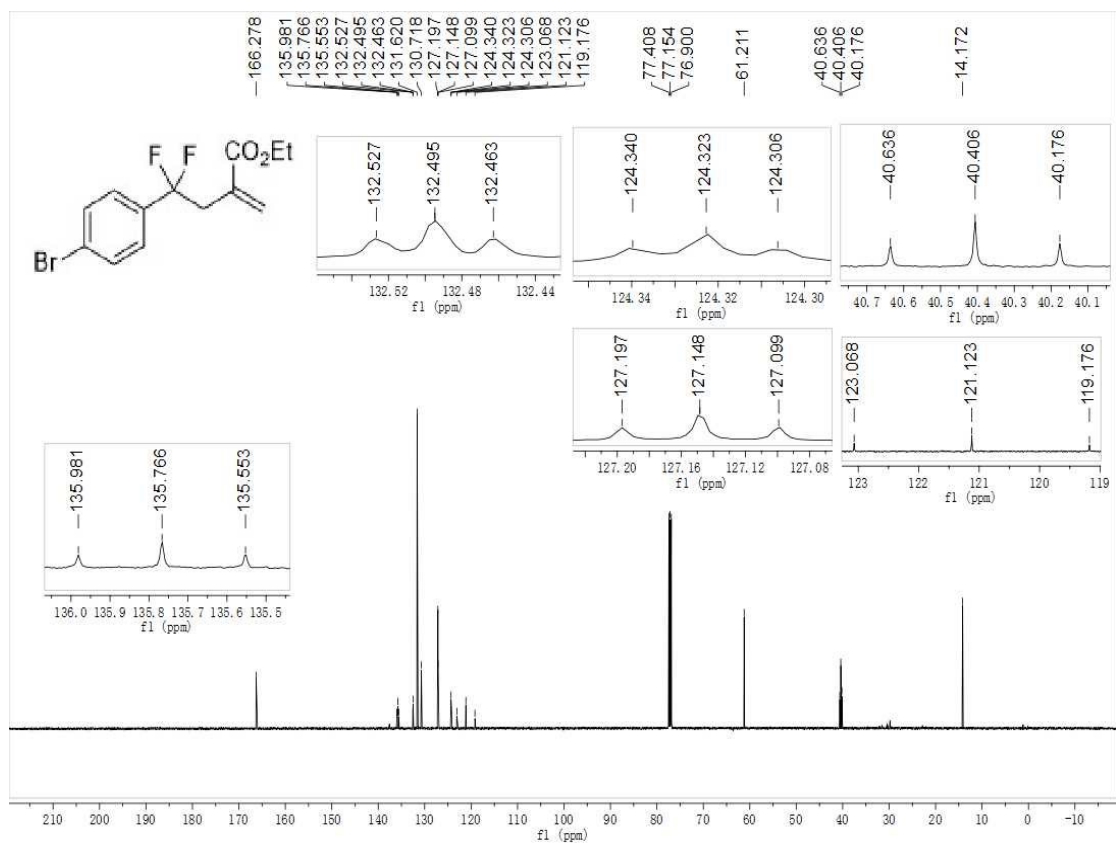




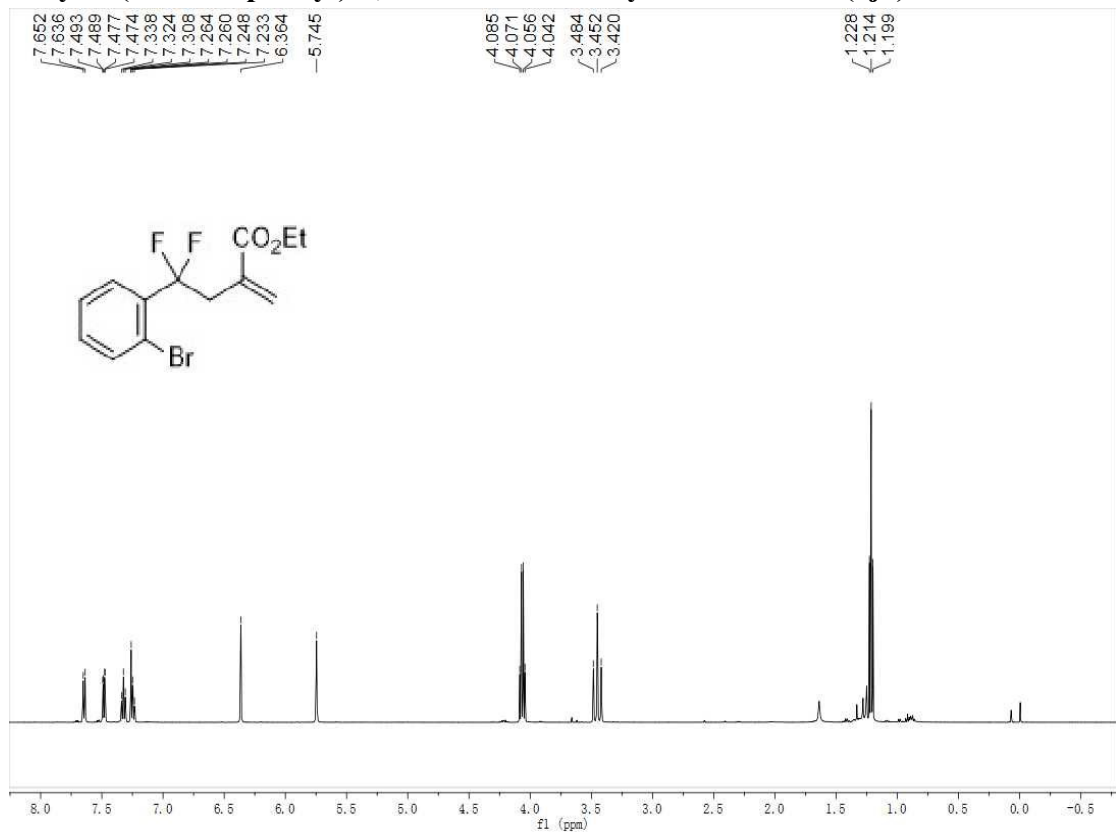
# Ethyl 4-(4-bromophenyl)-4,4-difluoro-2-methylenebutanoate (3ia)

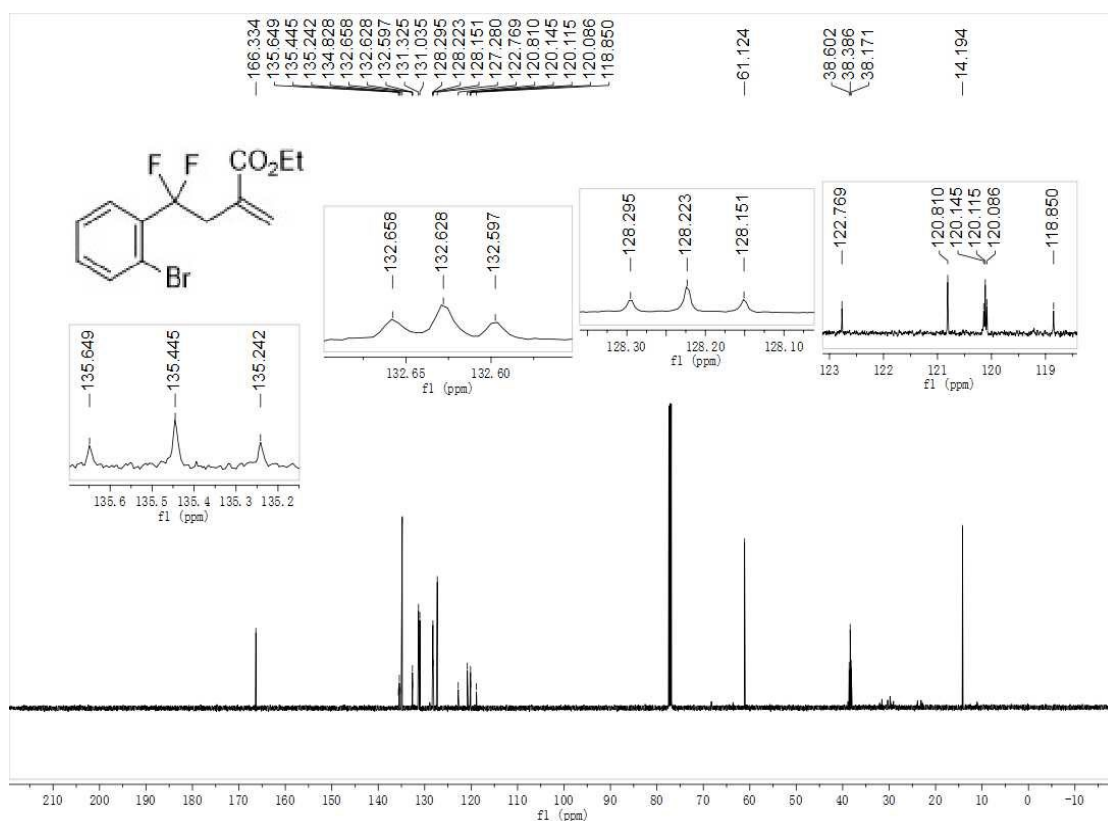
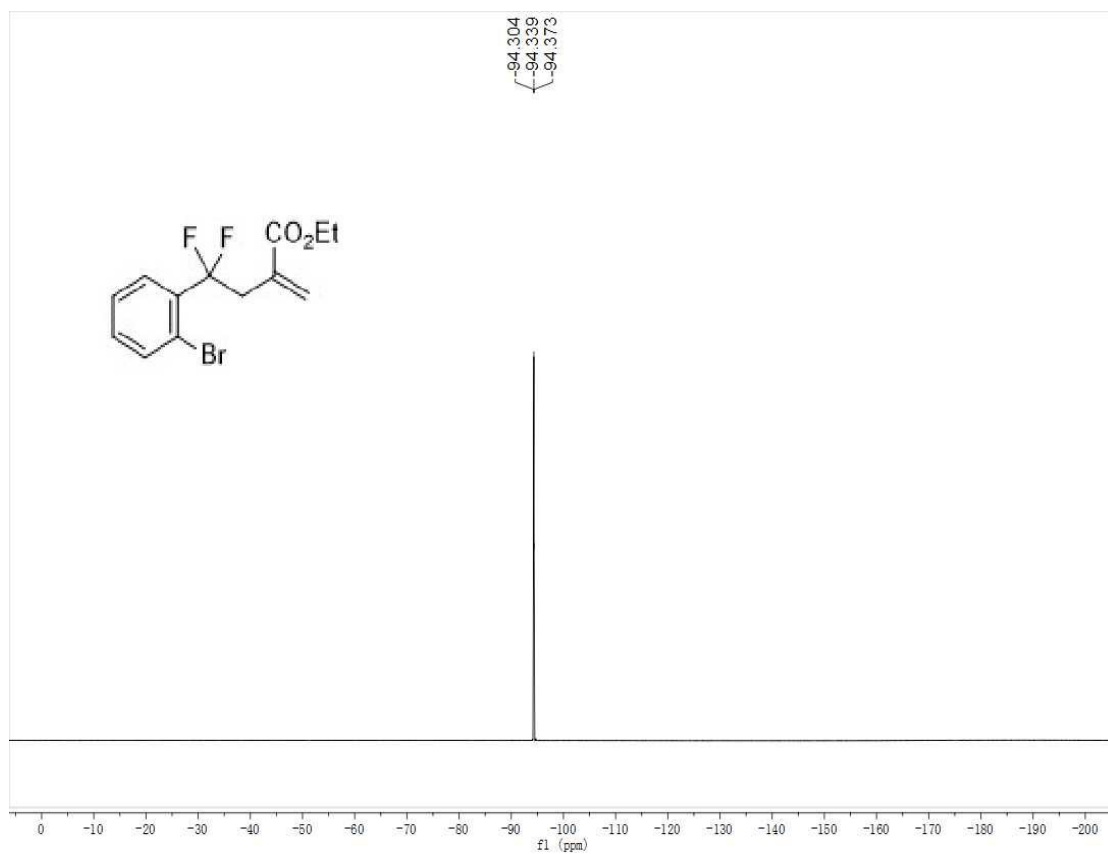




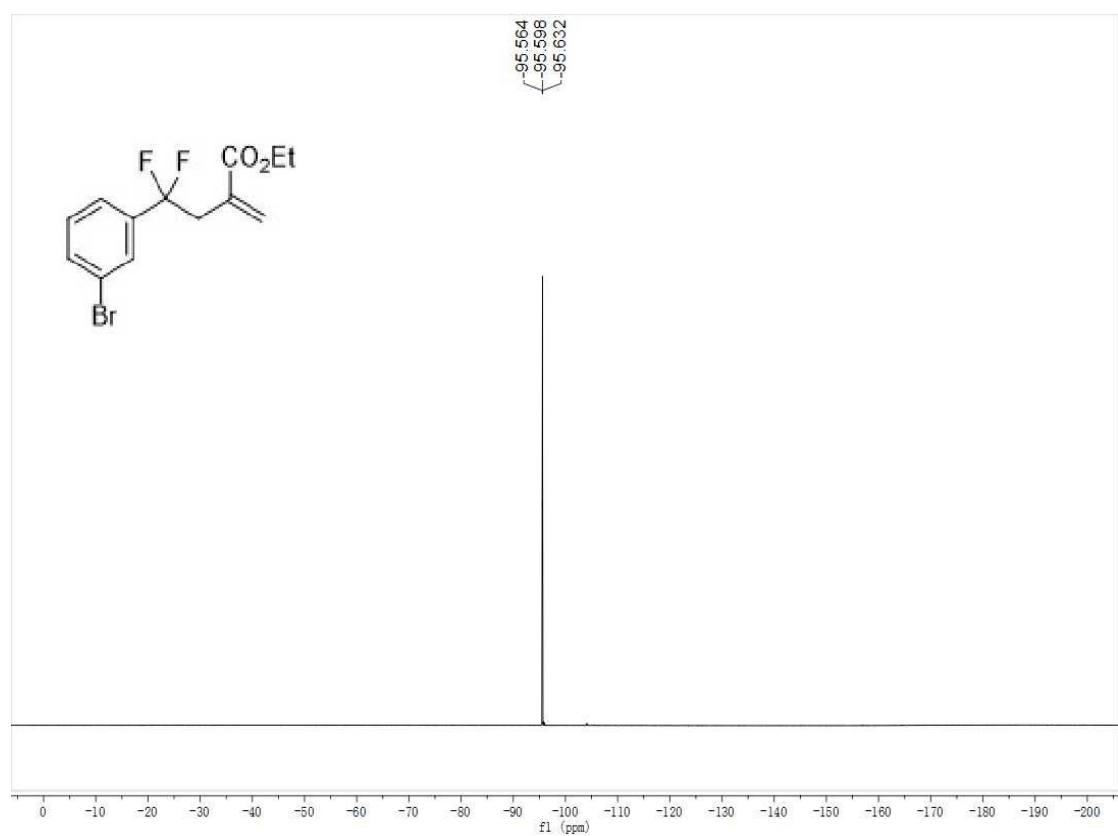
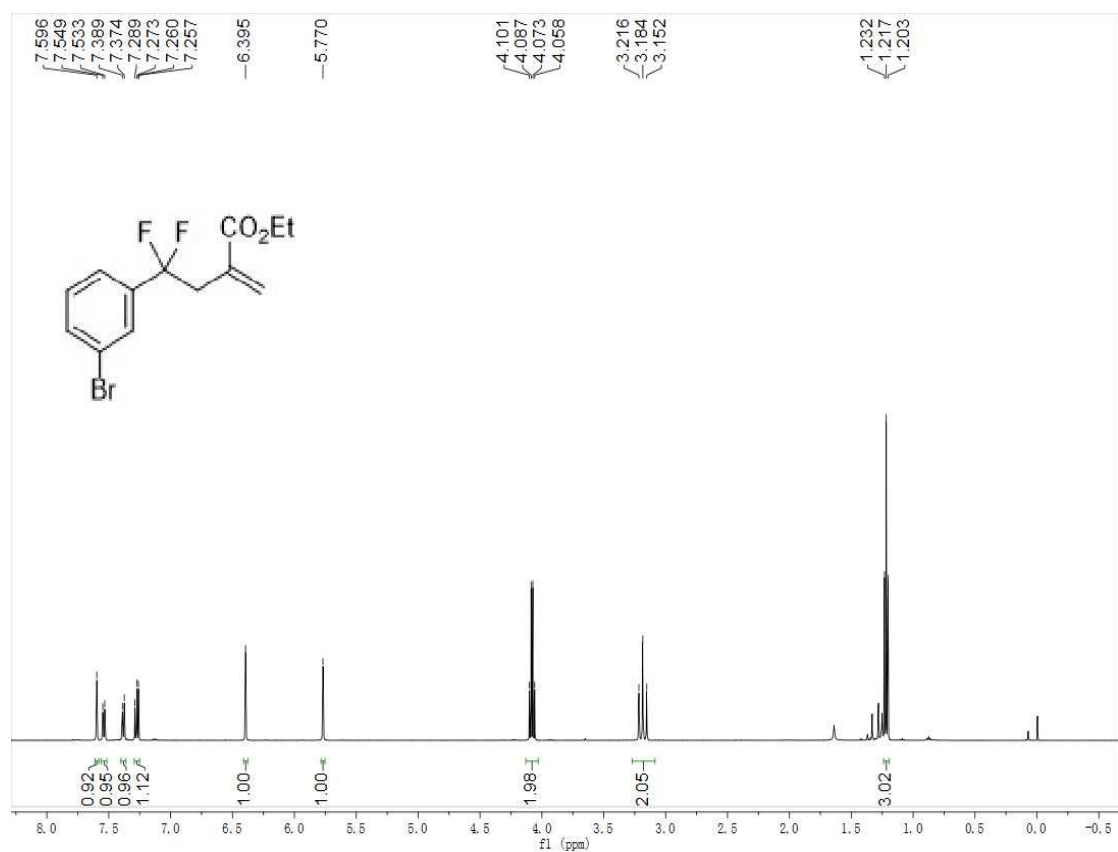


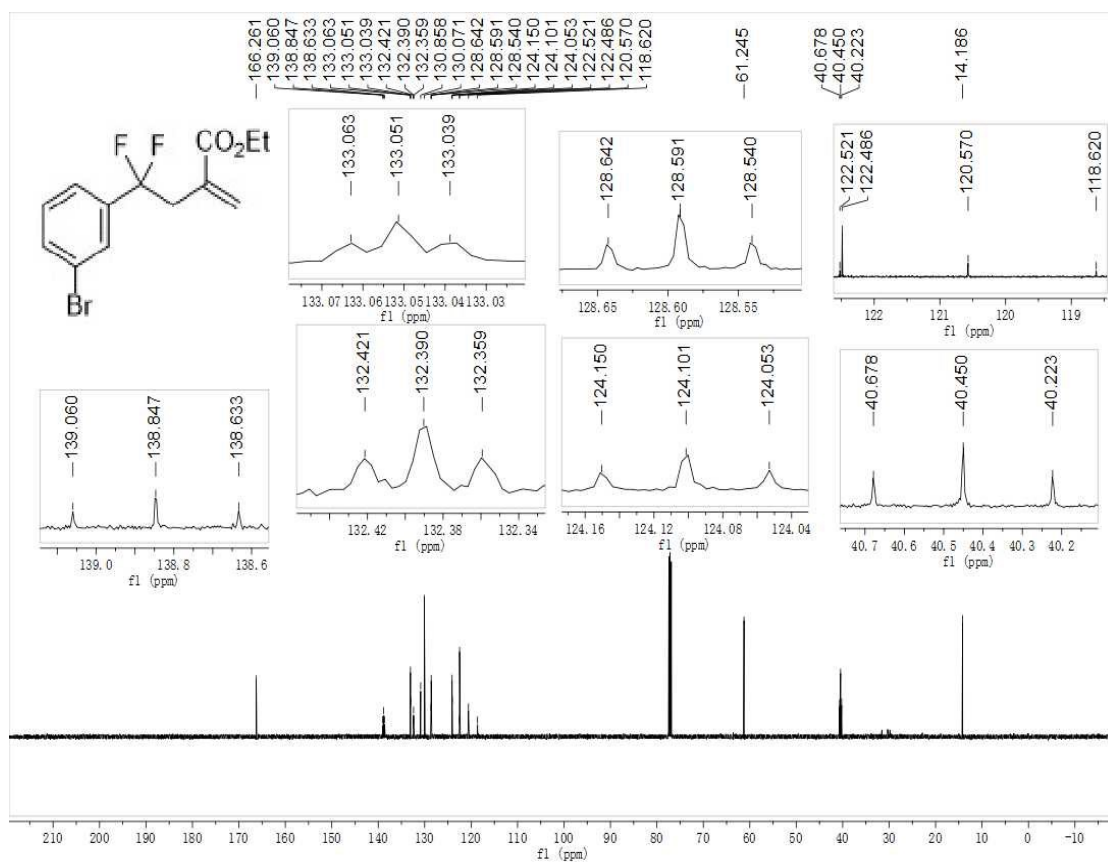
### Ethyl 4-(2-bromophenyl)-4,4-difluoro-2-methylenebutanoate (3ja)



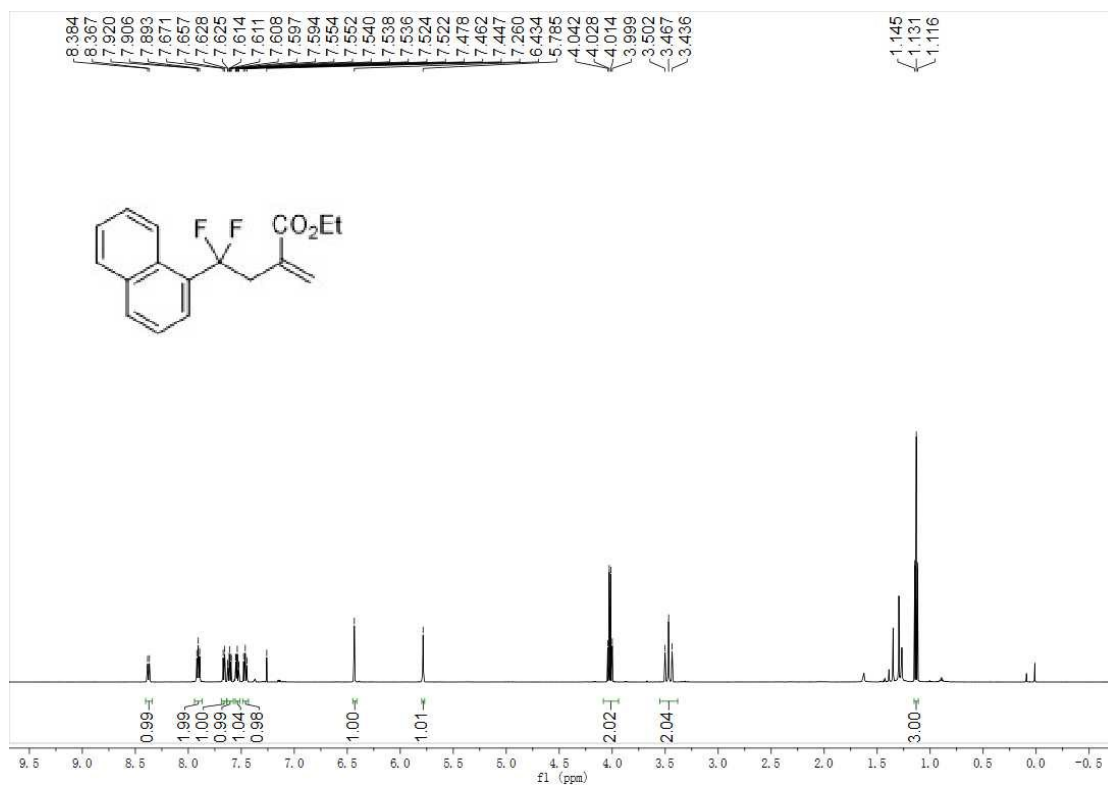


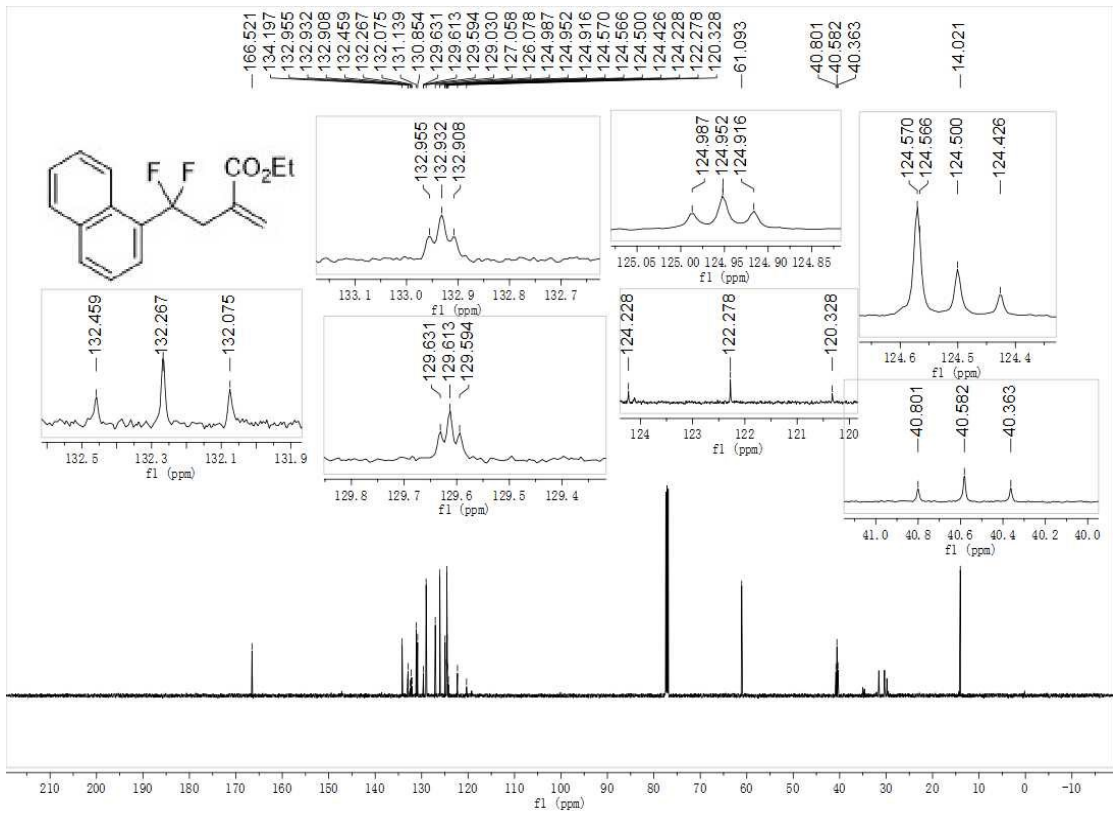
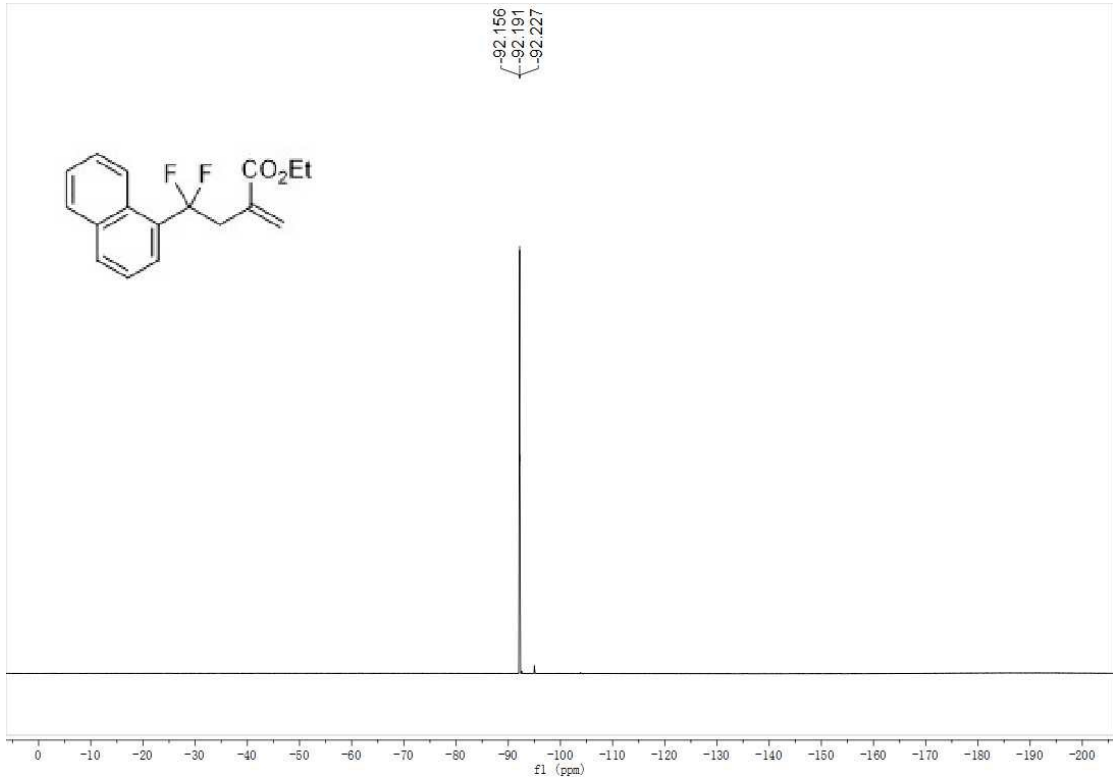
# Ethyl 4-(3-bromophenyl)-4,4-difluoro-2-methylenebutanoate (3ka)



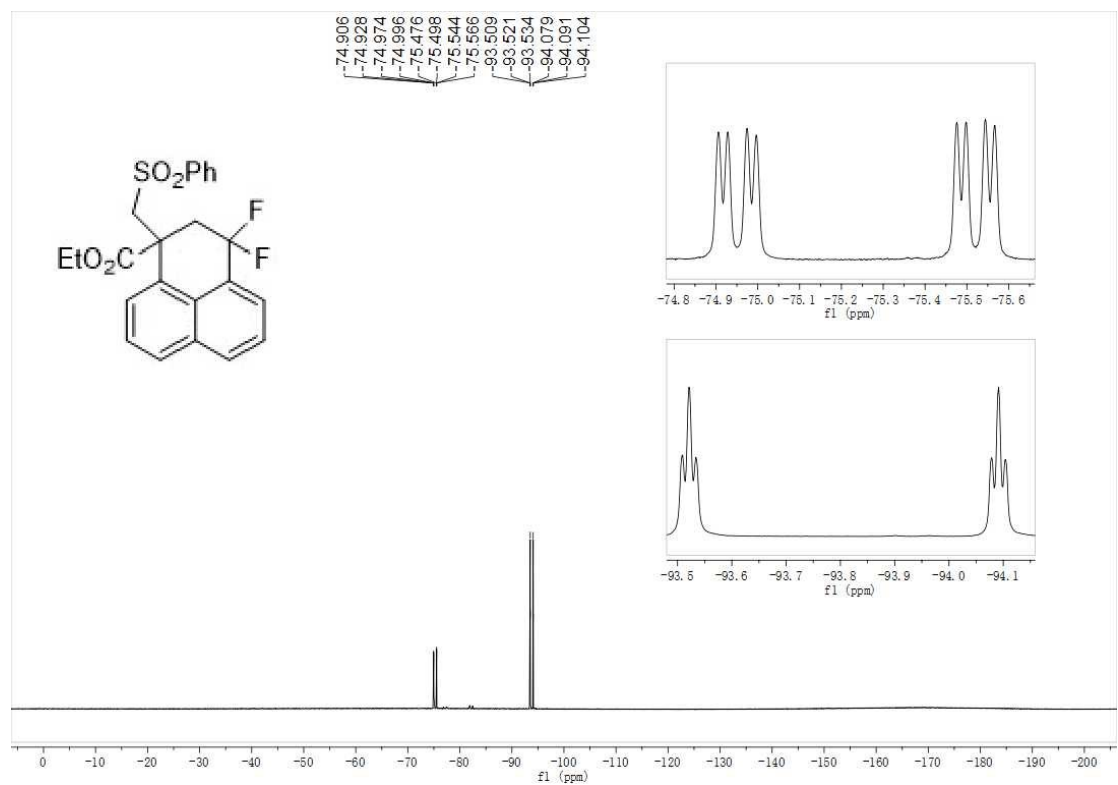
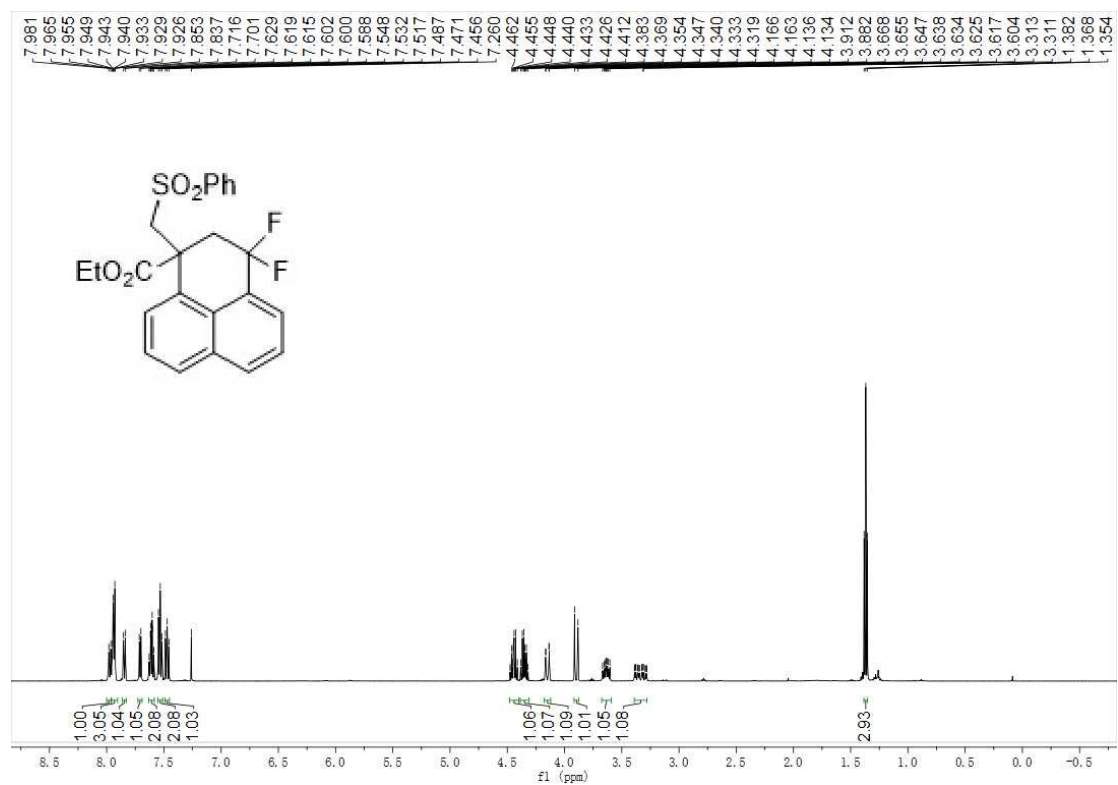


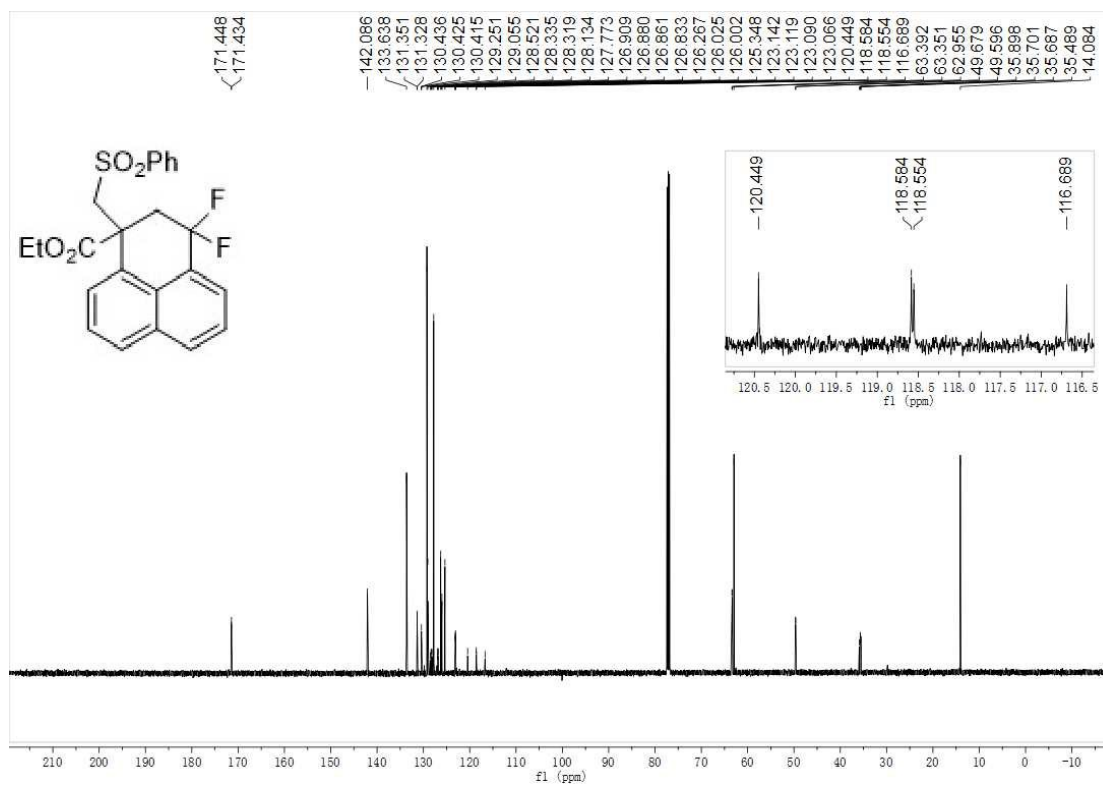
### Ethyl 4,4-difluoro-2-methylene-4-(naphthalen-1-yl)butanoate (31a)



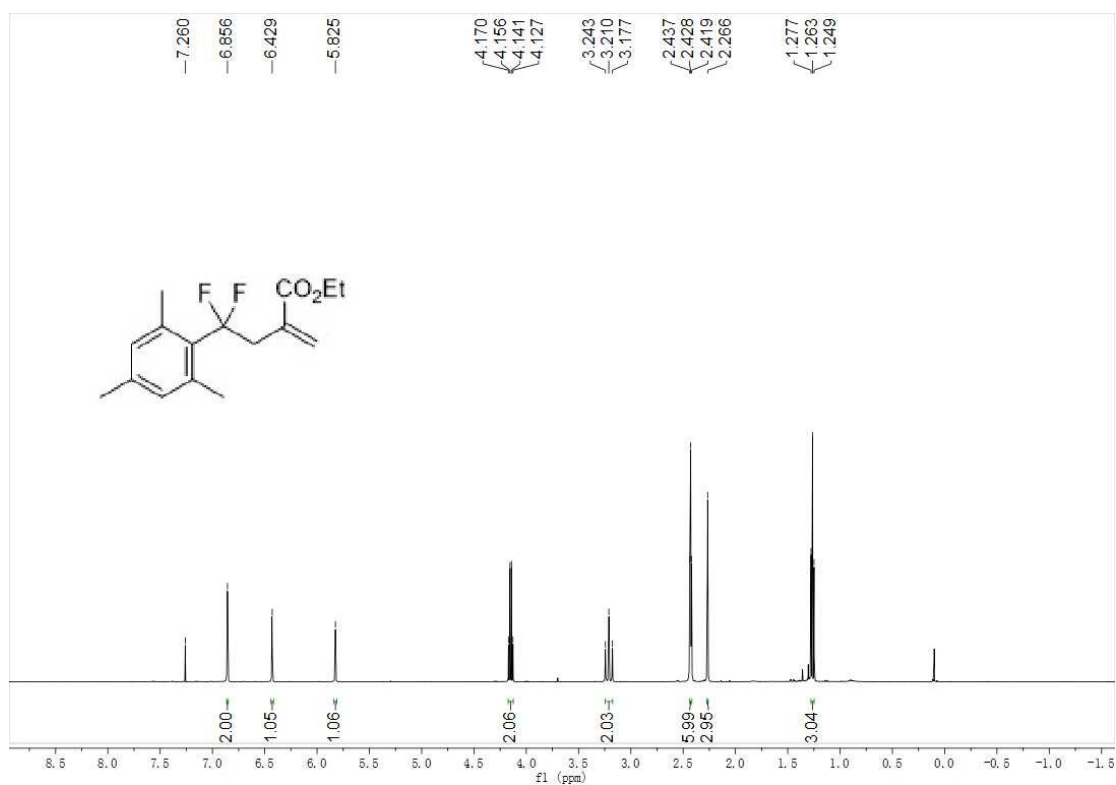


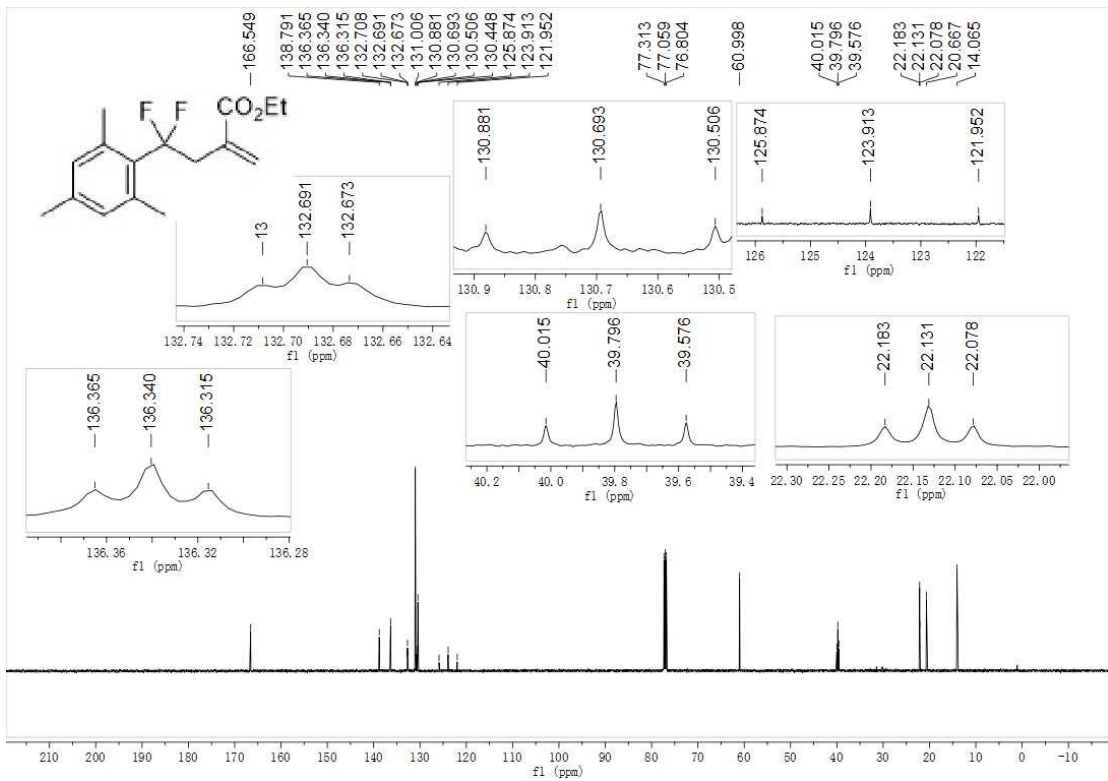
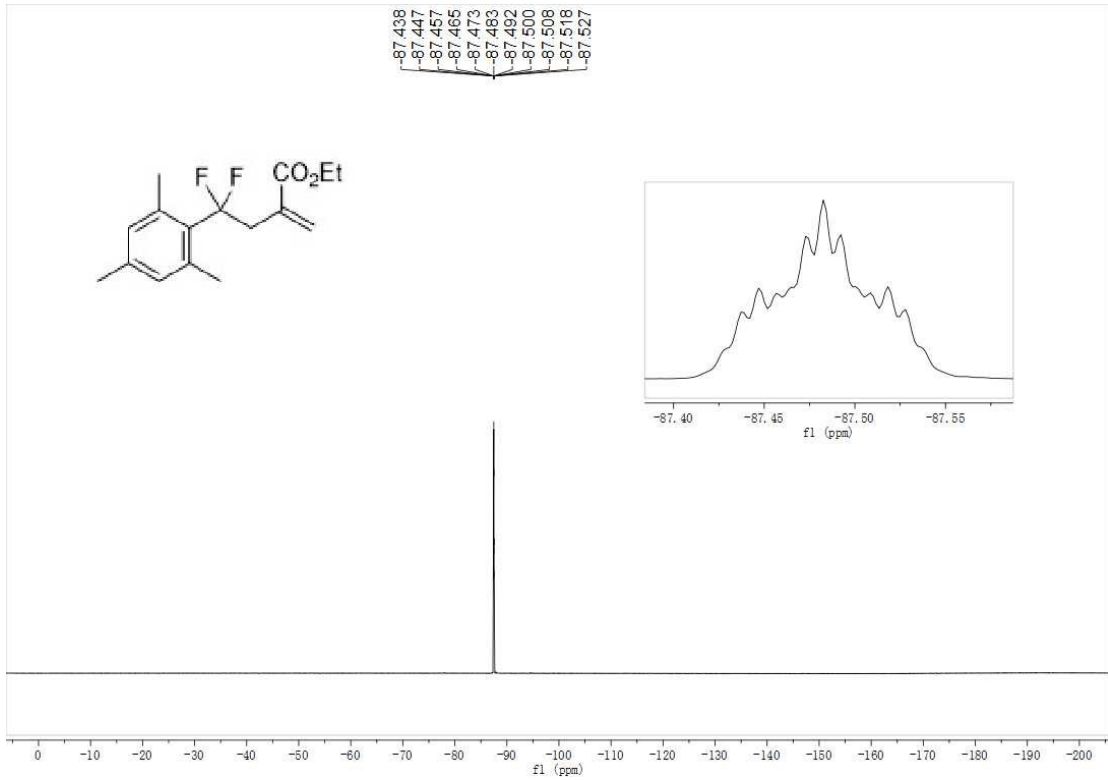
**Ethyl 3,3-difluoro-1-((phenylsulfonyl)methyl)-2,3-dihydro-1H-phenalene-1-carboxylate (3la')**





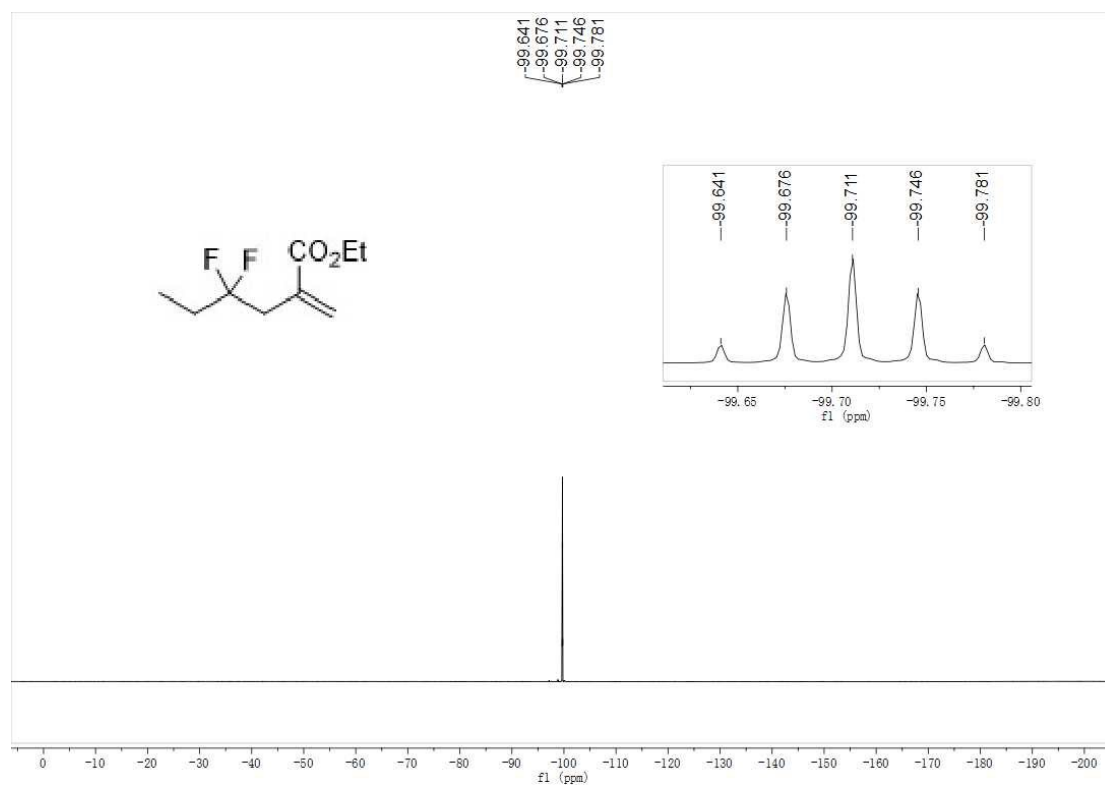
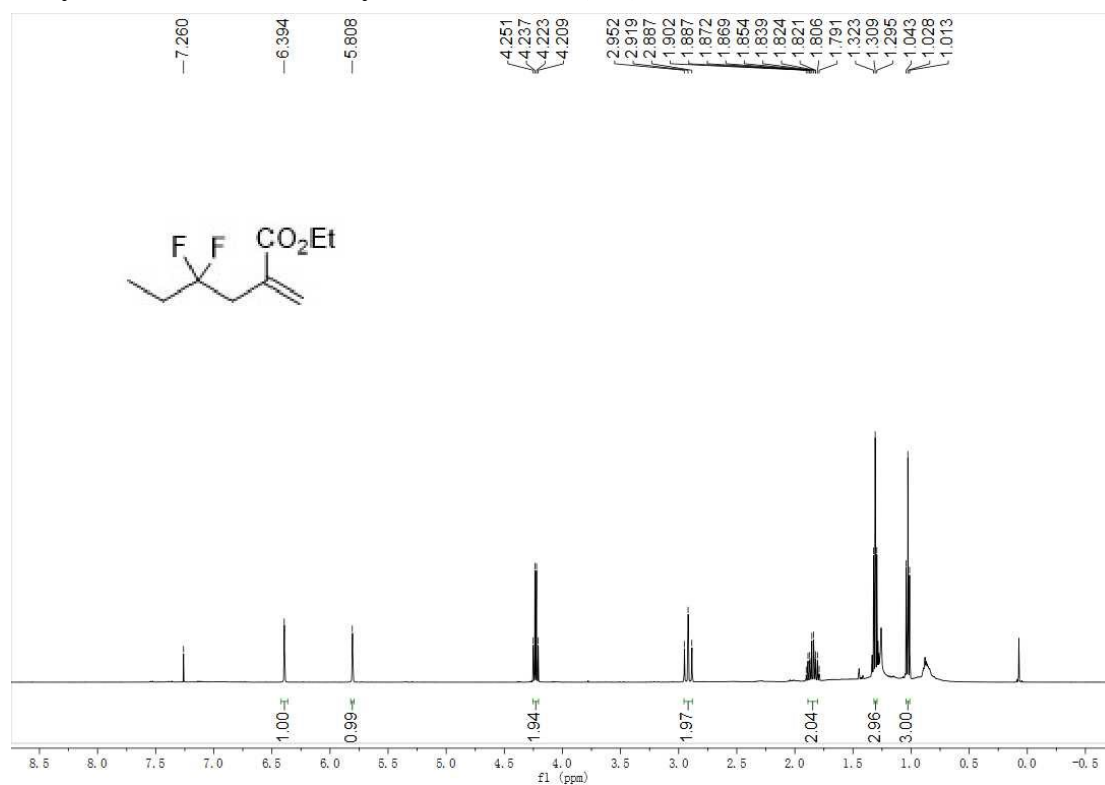
**Ethyl 4,4-difluoro-4-mesityl-2-methylenebutanoate (3ma)**

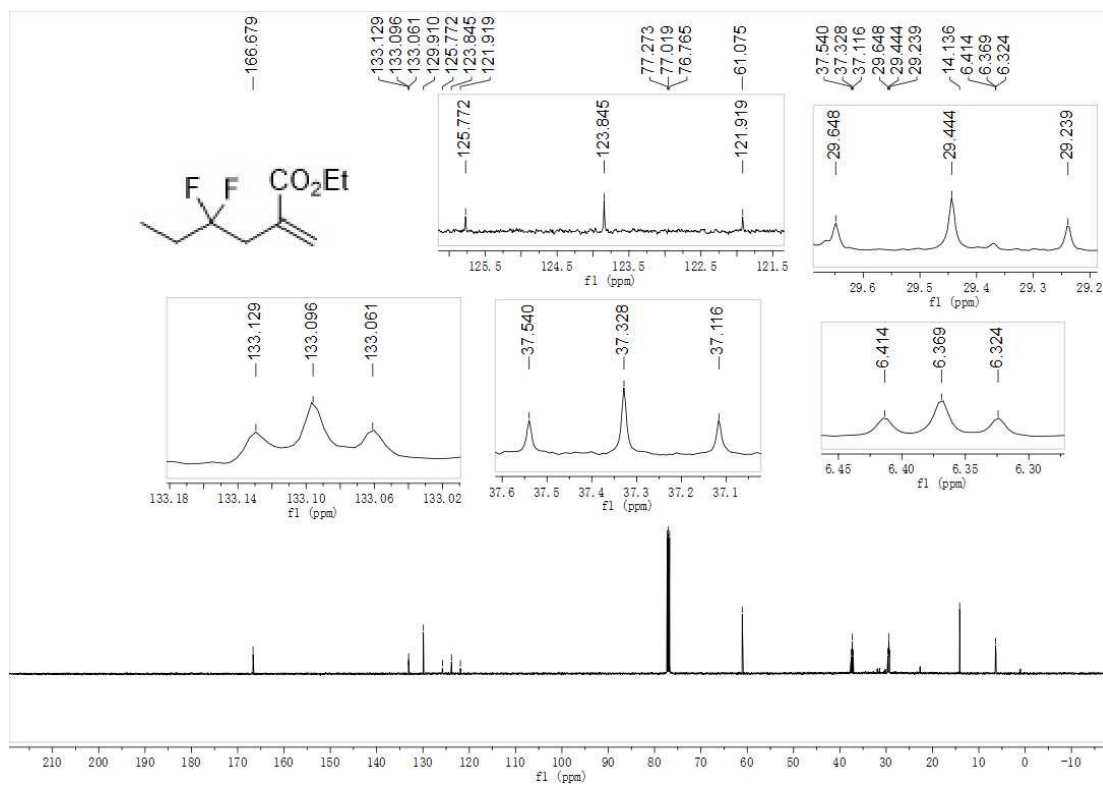




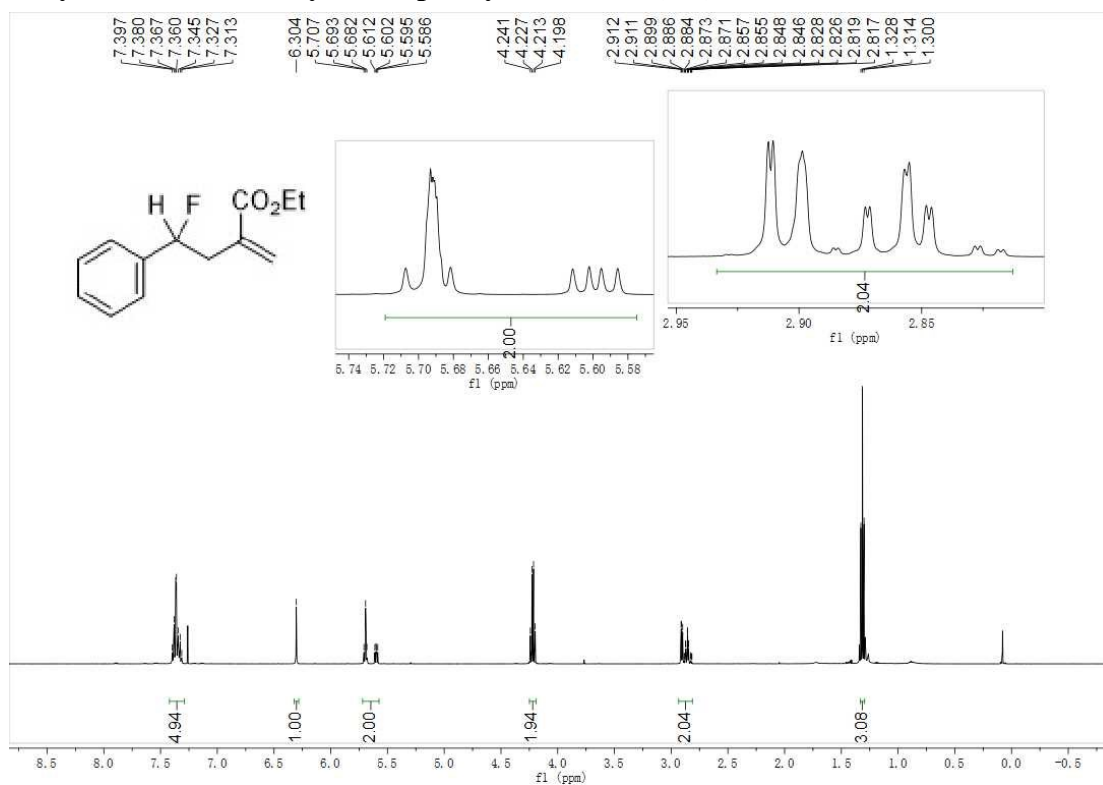


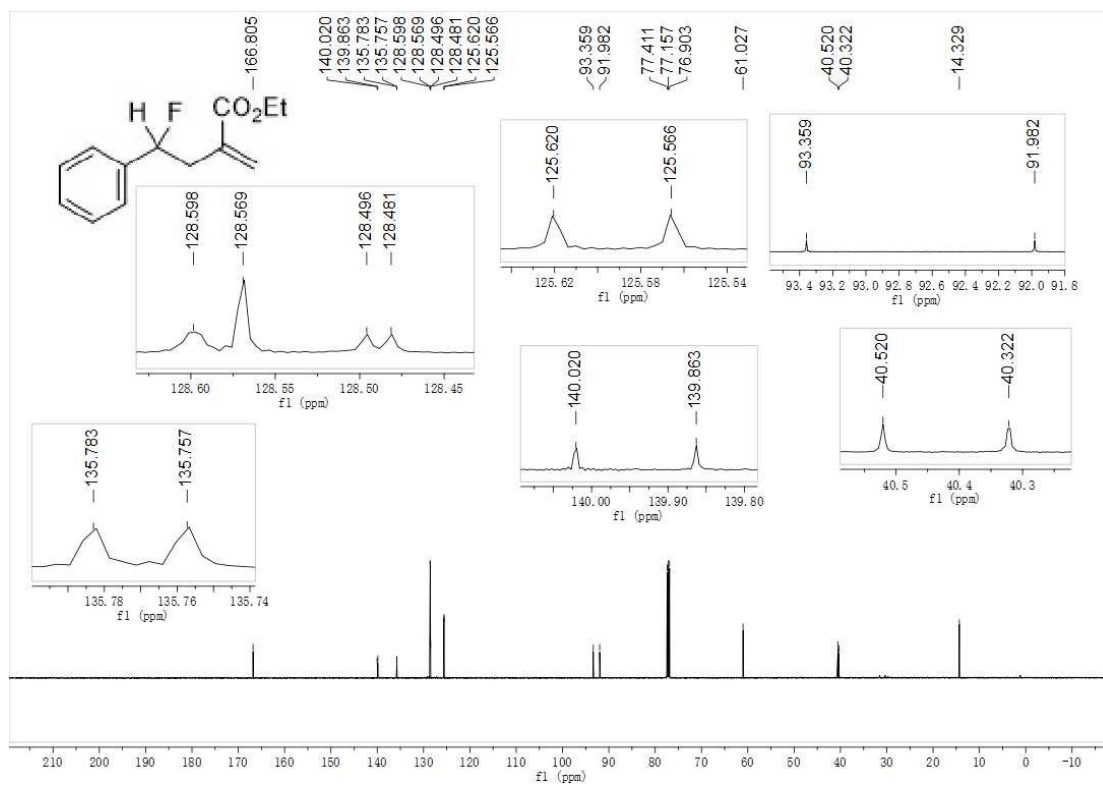
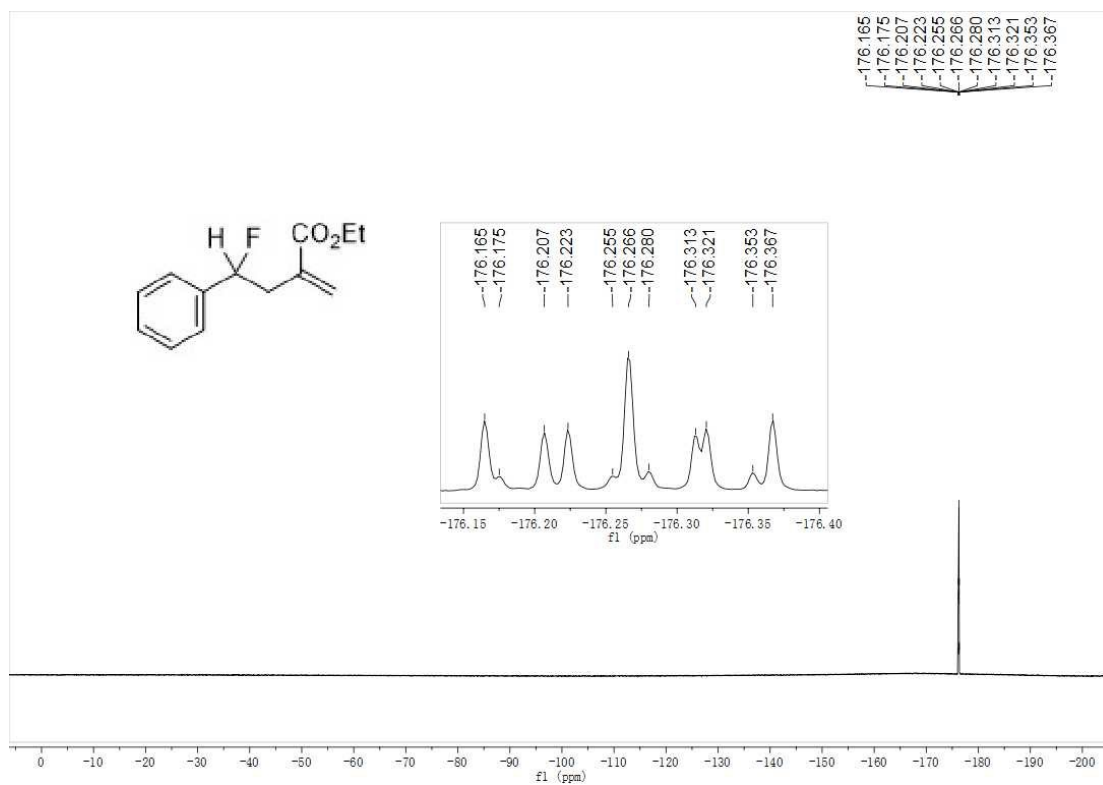
# Ethyl 4,4-difluoro-2-methylenehexanoate (3na)



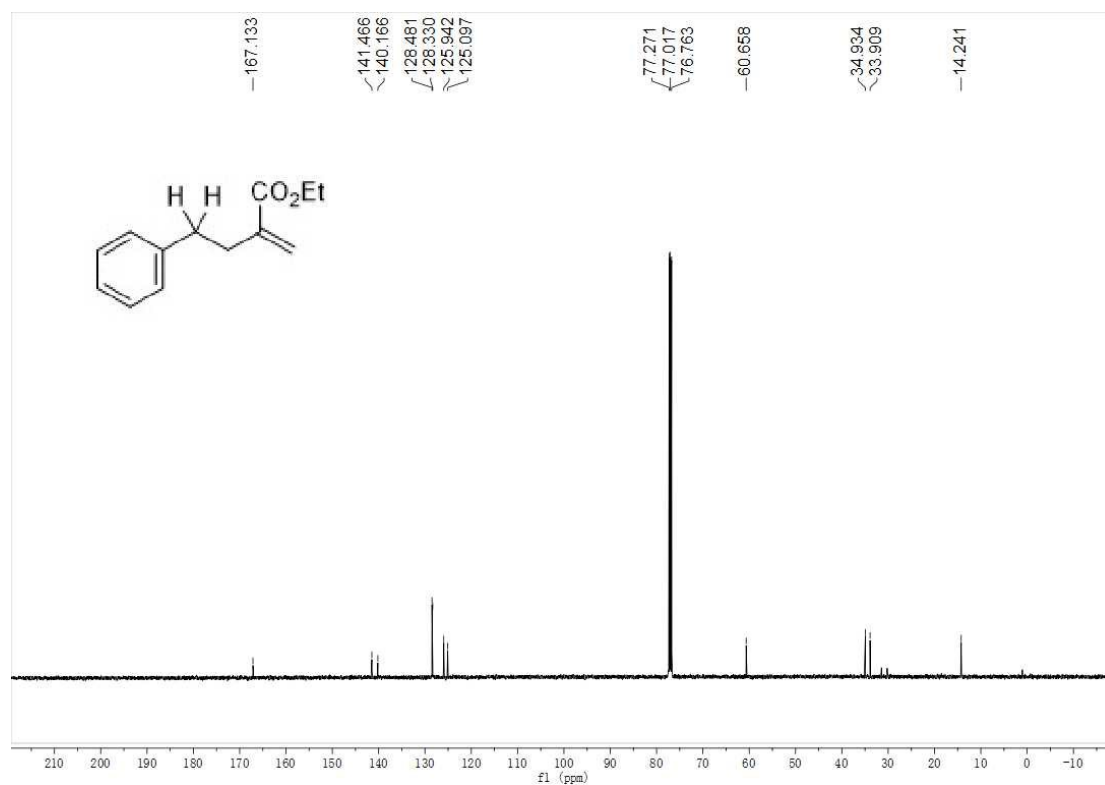
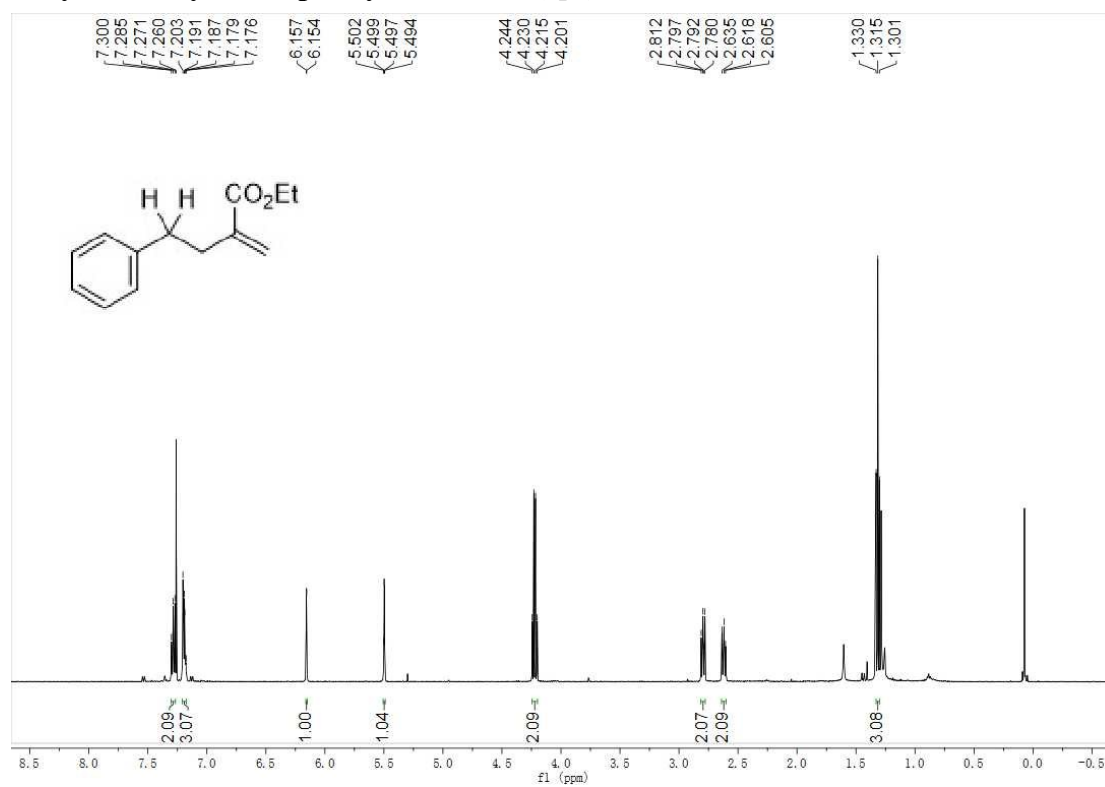


### Ethyl 4-fluoro-2-methylene-4-phenylbutanoate (30a)

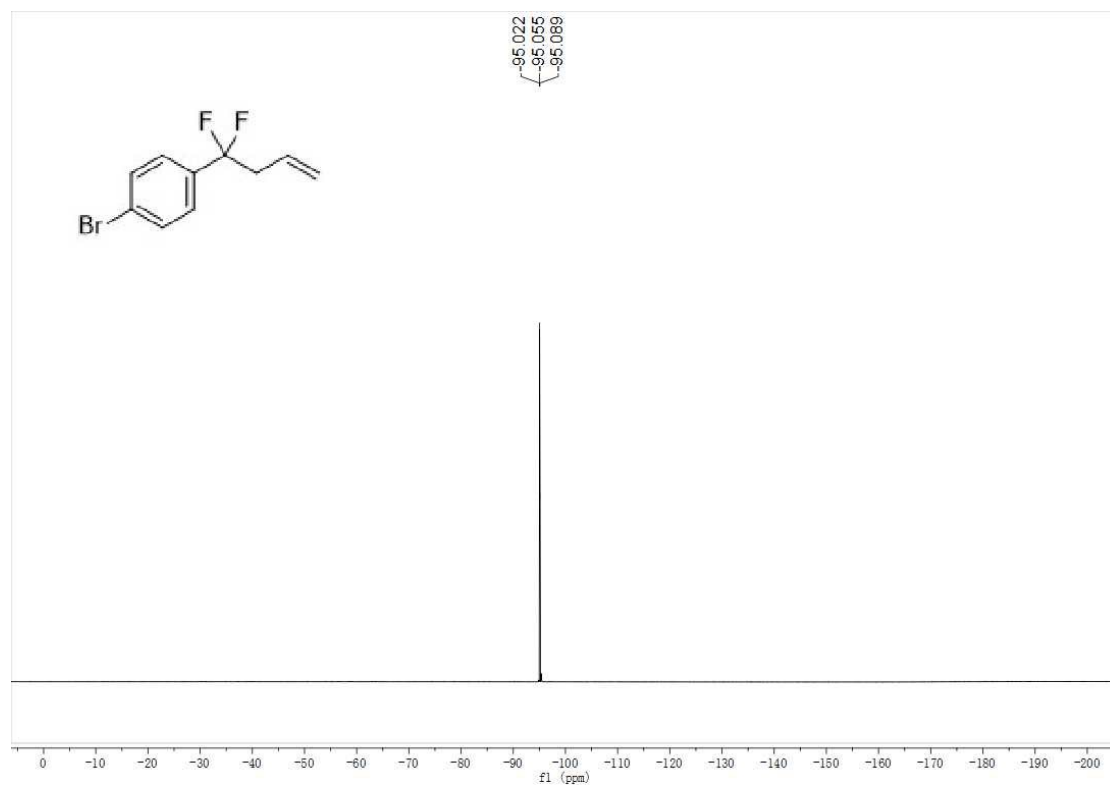
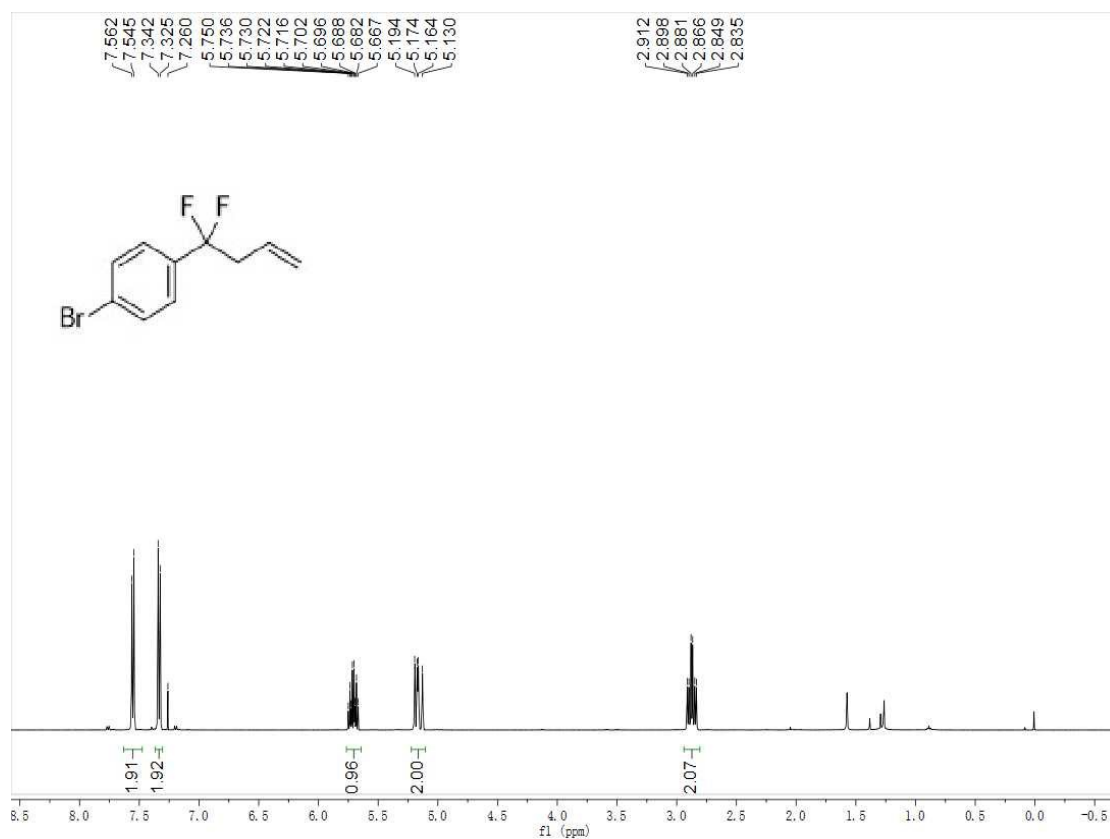


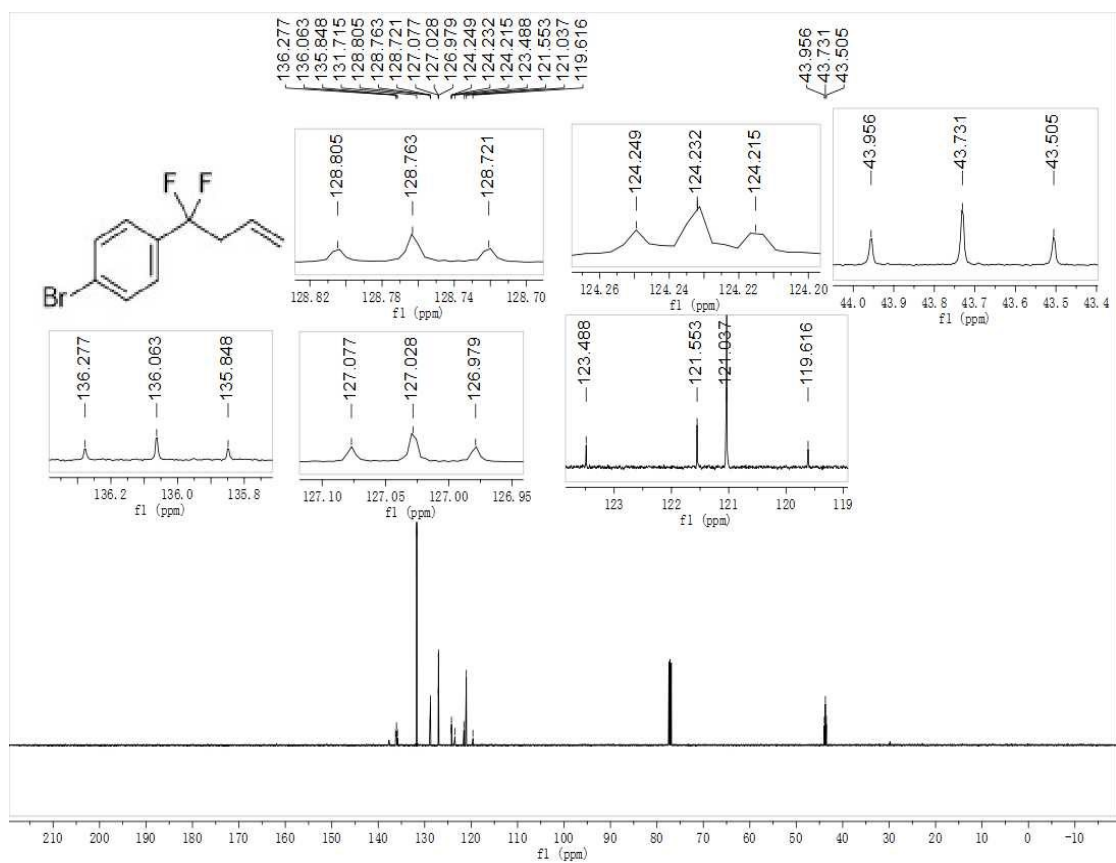


### Ethyl 2-methylene-4-phenylbutanoate (3pa)

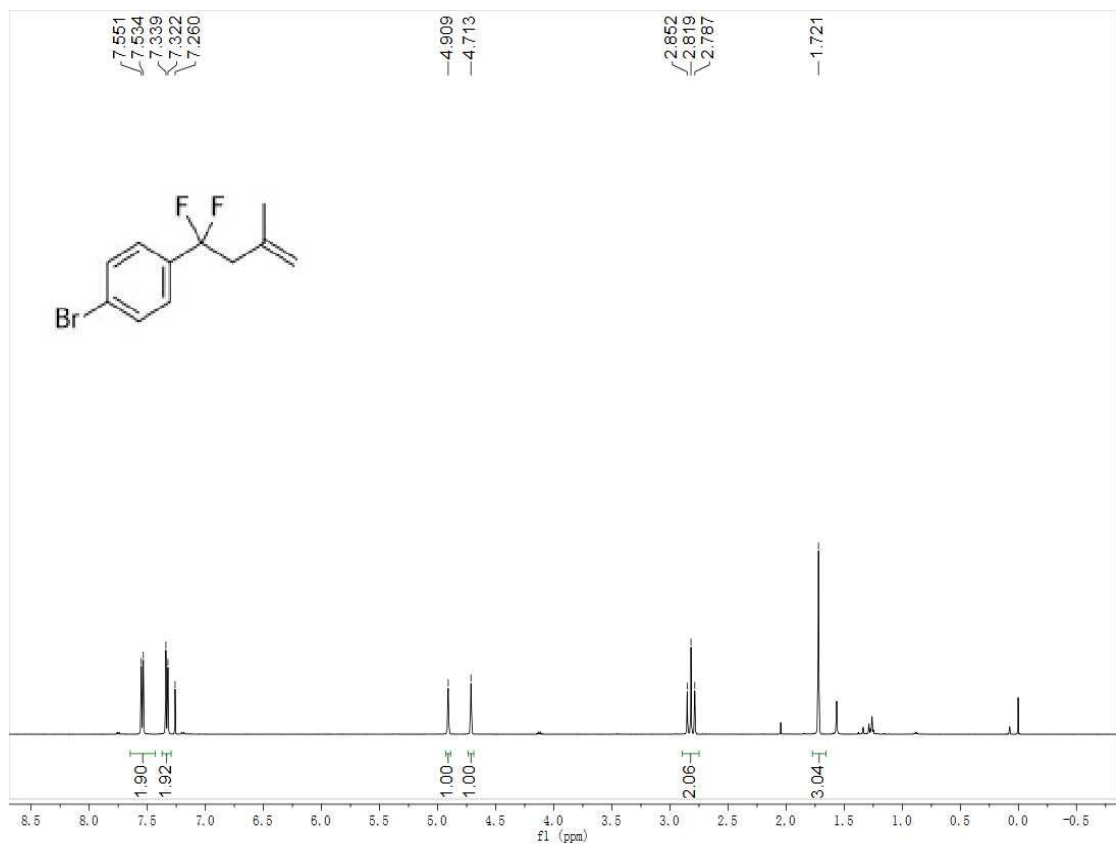


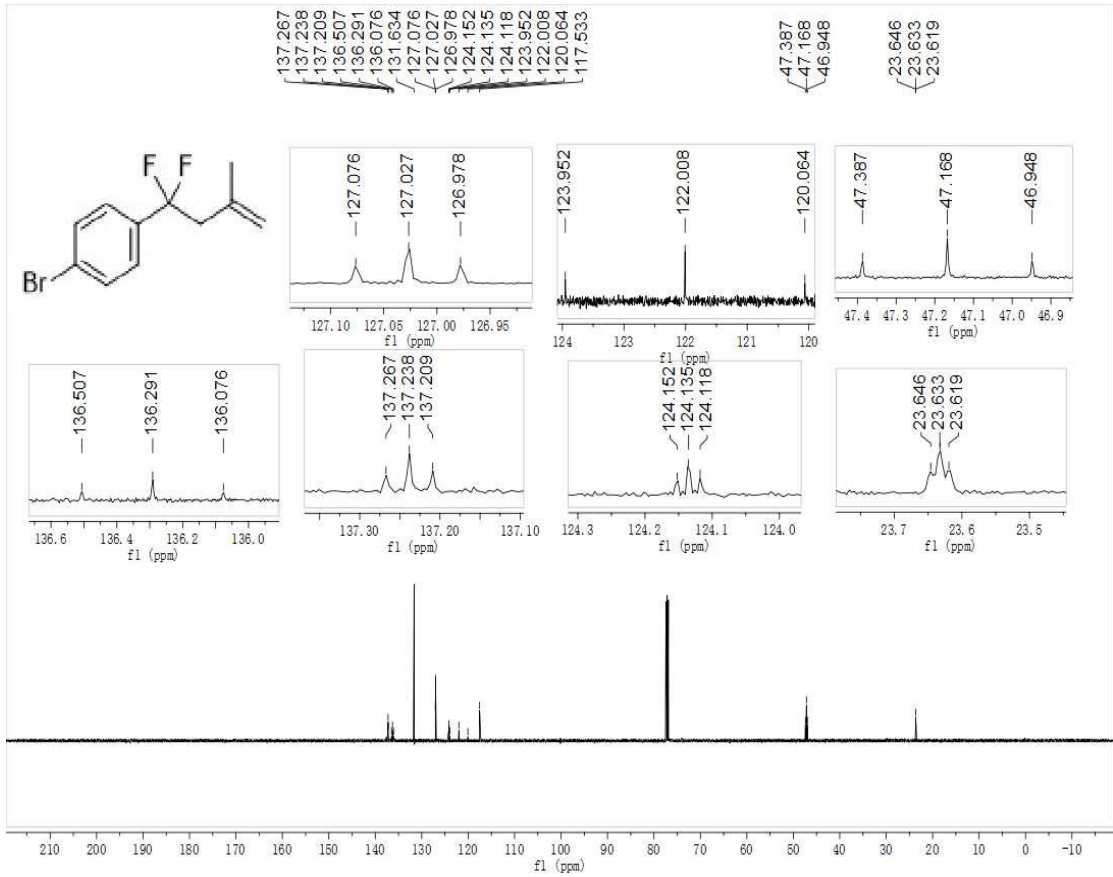
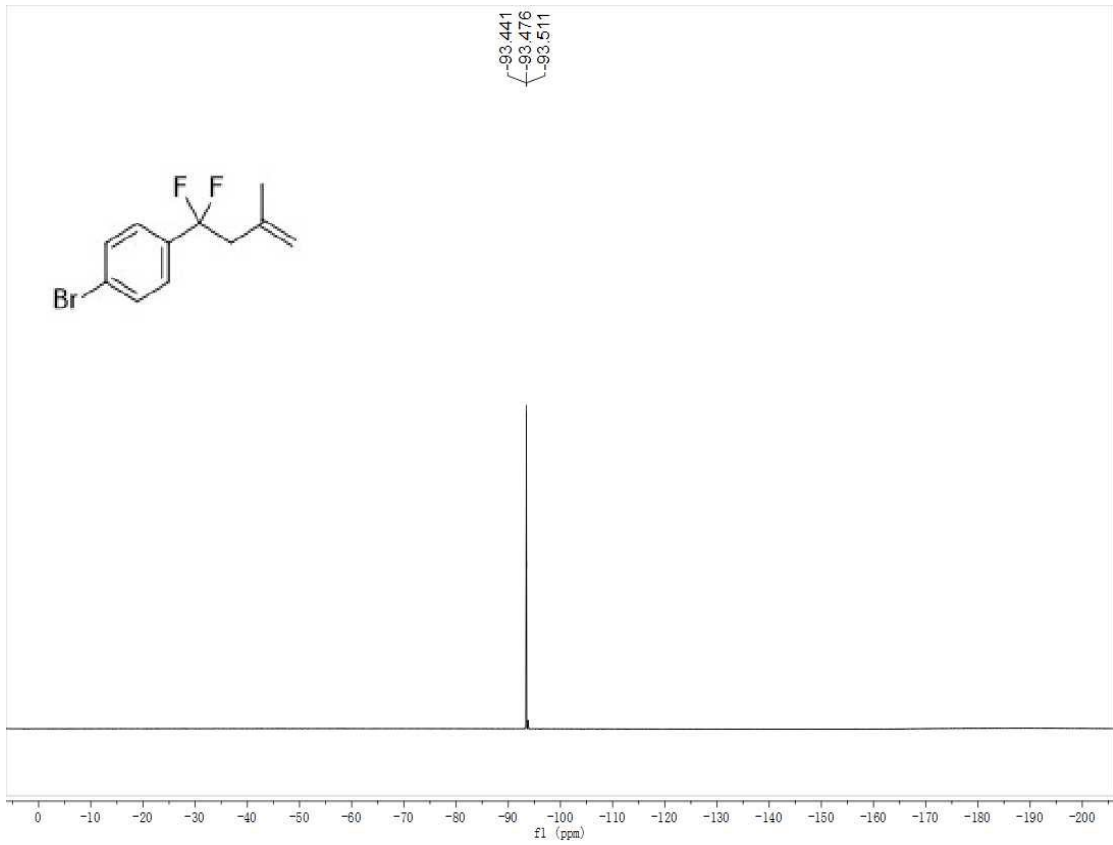
# 1- Bromo-4-(1,1-difluorobut-3-en-1-yl)benzene (3ib)



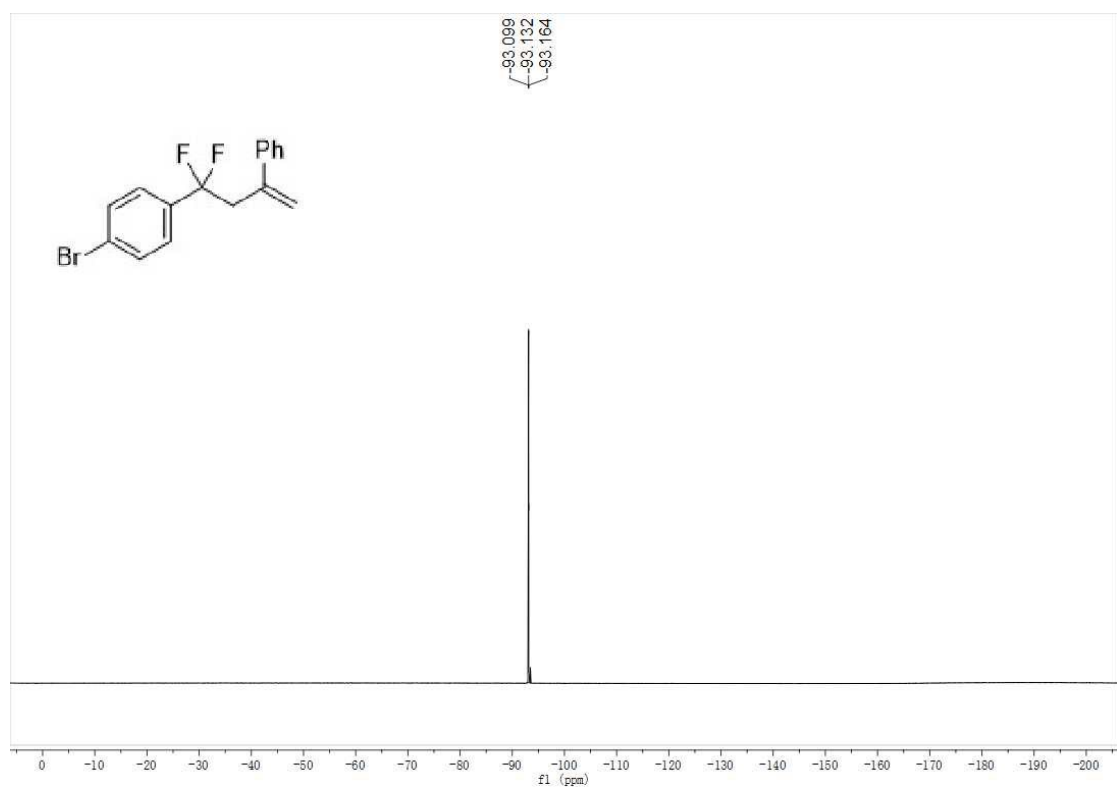
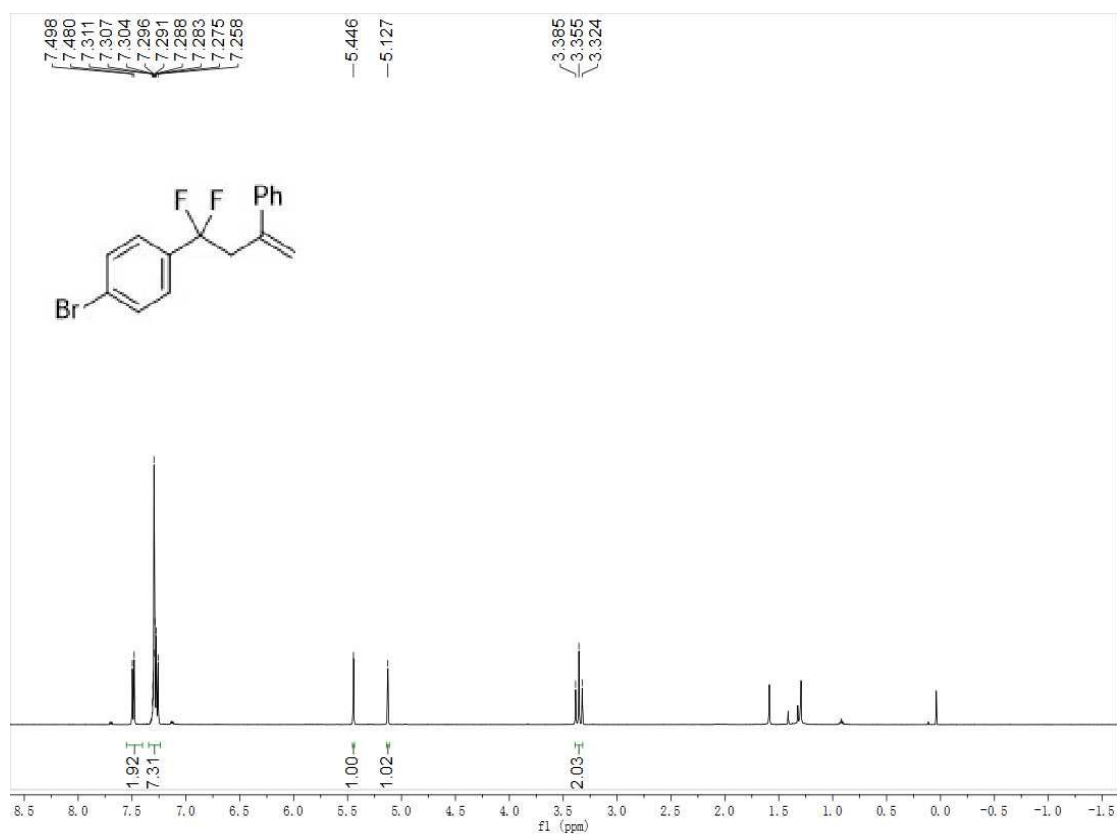


**1-Bromo-4-(1,1-difluoro-3-methylbut-3-en-1-yl)benzene (3ic)**

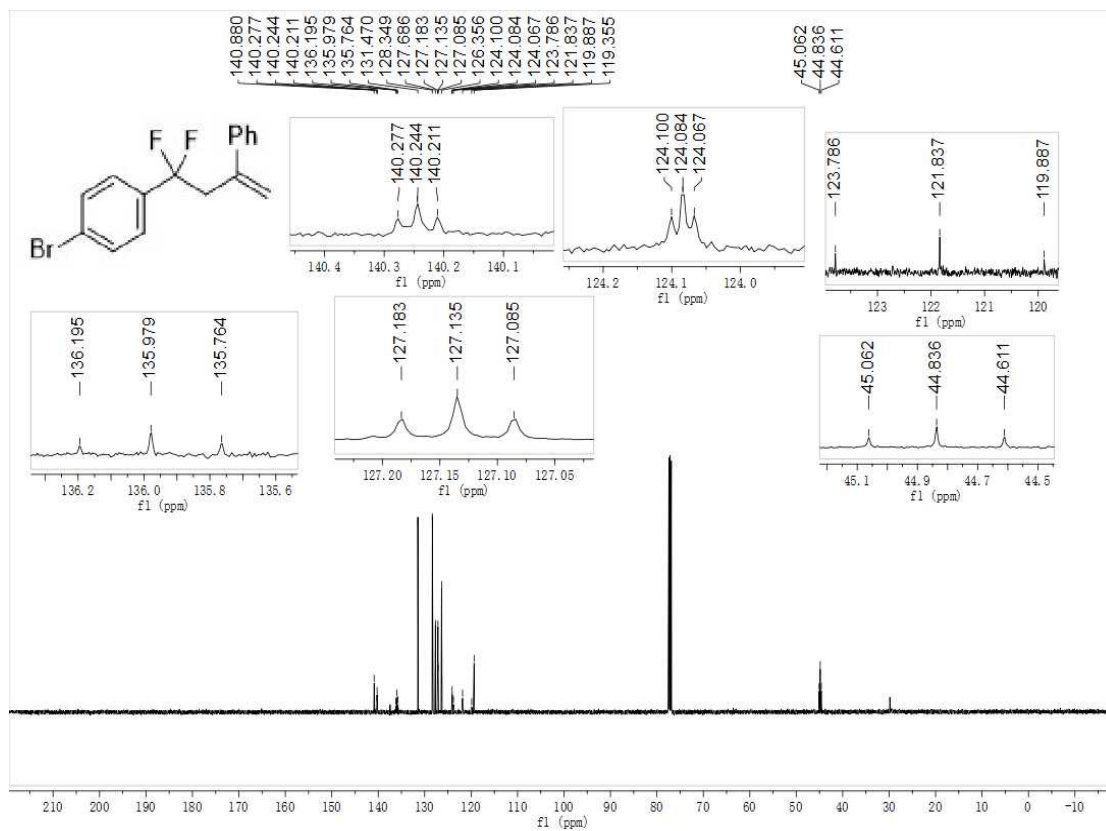




# 1- Bromo-4-(1,1-difluoro-3-phenylbut-3-en-1-yl)benzene (3id)







### 1,1,2,2-tetrafluoro-1,2-diphenylethane (5)

