

Supporting Information

Copper-Catalyzed Carboxylation of C–F Bonds with CO₂

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General Considerations

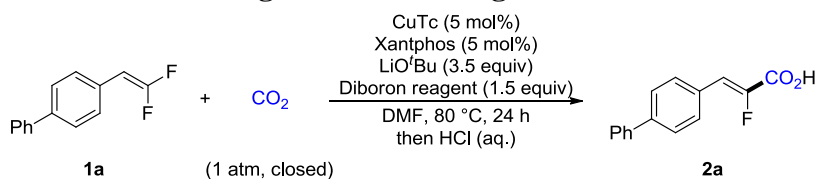
All reactions were set up using standard Schlenk techniques and carried out under a carbon dioxide atmosphere with dry solvents, unless otherwise noted. All commercially available compounds were purchased from J&K, Across, TCI or Adamas and used as received unless otherwise noted. CO₂ (99.99% purity) was commercially available. Xantphos were purchased from Sinocompound. CuTc, B₂pin₂ and LiO^tBu was purchased from Adamas-beta®. Anhydrous DMF and NMP (99.8% purity, with molecular sieves) was purchased from J&K. The substrates were synthesized according to the literature procedure. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.2±0.03 mm using UV light as a visualizing agent.

¹H, ¹⁹F and ¹³C NMR spectra were recorded on a Brüker Advance 400 spectrometer (¹H: 400 MHz, ¹³C: 101 MHz, ¹⁹F: 376 MHz). Chemical shifts (δ) for ¹H and ¹³C NMR spectra are given in ppm relative to TMS, The residual solvent signals were used as references for ¹H and ¹³C NMR spectra and the chemical shifts converted to the TMS scale (CDCl₃: δH = 7.26 ppm, δC = 77.16 ppm, DMSO-*d*₆: δH = 2.50 ppm, δC = 39.52 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad.

GC-MS was obtained using electron ionization (Agilent Technologies 7890B/GC-System and 5977A/MSD). UPLC yields were recorded on waters ACQUITY UPLC M-Class. Exact ESI mass spectra were recorded on a SHIMADZU LCMS-IT-TOF. LRMS were obtained on a Thermo-LTQ. Metal element contents were obtained on a thermo ICP-AES (IRIS Adv.). TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm.

Additional Reaction Optimization Tables

Table S1. Screening of Diboron Reagent^[a]



entry	Diboron reagent	Yield of 2a (%) ^[b]
1	B ₂ pin ₂ (B1)	88
2	B ₂ nep ₂ (B2)	56
3	B3	72
4	B4	37
5	B5	10
6	none	0

[a] Reaction conditions: **1a** (0.4 mmol), 1 atm of CO₂, CuTc (0.02 mmol), Xantphos (0.02 mmol), LiOtBu (1.4 mmol), Diboron reagent (0.6 mmol), DMF (2 mL), 80 °C, 24 h. [b] Yields were determined by UPLC using anisole as an internal standard.

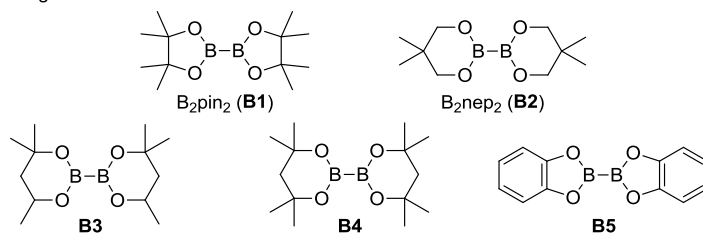
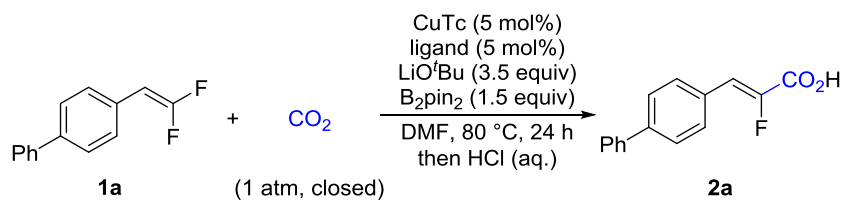


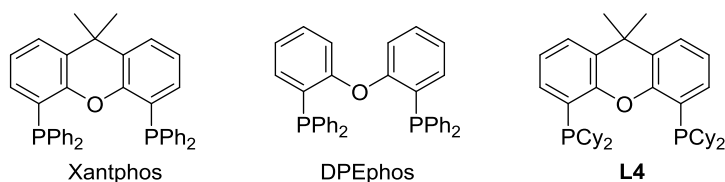
Table S2. Screening of Ligand^[a]



entry	ligand	Yield of 2a (%) ^[b]
1	Xantphos	85
2	DPEphos	31
3	dppp	39
4	L4	17
5	dppf	19

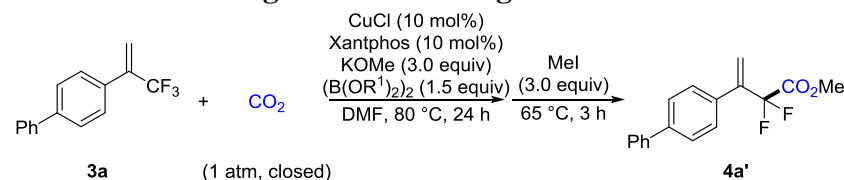
} **1a** remained

[a] Reaction conditions: **1a** (0.4 mmol), 1 atm of CO₂, CuTc (0.02 mmol), ligand (0.02 mmol), LiOtBu (1.4 mmol), B₂pin₂ (0.6 mmol), DMF (2 mL), 80 °C, 24 h. [b] Yields were determined by UPLC using anisole as an internal standard.



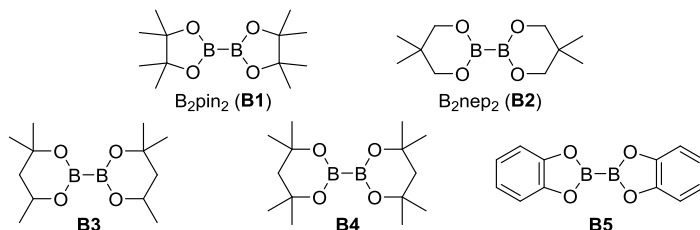
Similar to previous work about Cu-catalyzed stereoselective borylation of *gem*-difluoroalkenes with B₂pin₂, Xantphos shows highest activities in this transformation. The better result provided by Xantphos than other similar diphosphine ligand may arise from the proper nucleophilicity of Xantphos-ligated vinyl copper complex **E** (Please see Figure 5 in the manuscript), which exhibits enhanced reactivity with CO₂. What's more, the Xantphos has a better coordination ability to copper catalyst than DPEphos. The bulky steric hindrance of **L4** may make it difficult to coordinate to copper catalyst.

Table S3. Screening of Diboron Reagent^[a]



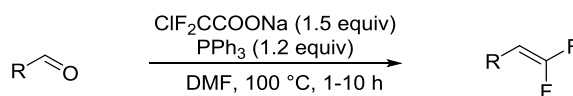
entry	Diboron reagent	Yield of 4a' (%) ^[b]
1	B ₂ pin ₂ (B1)	58
2	B ₂ nep ₂ (B2)	53
3	B3	65
4	B4	50
5	B5	3
6	B3 (NMP as solvent)	72

[a] Reaction conditions: **3a** (0.2 mmol), 1 atm of CO₂, CuCl (0.02 mmol), Xantphos (0.02 mmol), KOMe (0.6 mmol), Diboron reagent (0.3 mmol), DMF (2 mL), 80 °C, 24 h. [b] Yields were determined by GC using *n*-dodecane as an internal standard.



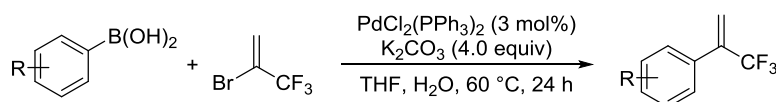
Commercial available bis(hexylene glycolato)diboron (**B3**) turned out to be a better choice for this case with better yields than other diboron reagents. From the result we obtained, we can see that if the diboron reagent has a bulkier steric hindrance, it will give a lower yield. Maybe it is more difficult for bulky fluorinated boronate ester intermediate to react with CO₂ directly in the presence of base. When fluorinated boronate ester **12** made from bis(hexylene glycolato)diboron and **3a** was subjected to the carboxylation reaction, the desired product **4a** was obtained in similar yields with or without copper catalysis. And preliminary kinetic studies indicated that base should dominate the carboxylation of fluorinated boronate ester with CO₂ (Please see control experiments of **12** in SI).

Synthesis of *gem*-Difluoroalkene Substrates^[1]



To a solution of aldehyde (20 mmol, 1.0 equiv) and triphenyl phosphine (24 mmol, 1.2 equiv) in DMF (40 mL) was added sodium chlorodifluoroacetate (30 mmol, 1.5 equiv) and the mixture stirred at 100 °C for 1-10 h (**caution:** During the course of the reaction, vigorous liberation of CO₂ gas was observed). After the aldehyde consumed completely, the mixture was cooled to room temperature. Methyl iodide (2-3 equiv) was added and stirred for 10 min to prevent PPh₃ interference during the column chromatography separation. Then water was added to the reaction slowly and the mixture was extracted with Et₂O. The combined organic layer was dried over Na₂SO₄, filtrated, and concentrated under reduced pressure. The residue was purified by a silica gel flash column chromatography to afford the desired *gem*-difluoroalkenes.

Synthesis of α -Trifluoromethyl Alkene Substrates^[2]



To a Schlenk tube containing a stirring bar were added arylboronic acid (20 mmol, 1.0 equiv), and PdCl₂(PPh₃)₂ (421 mg, 0.6 mmol, 3 mol%). The reaction tube was then evacuated and back-filled with N₂ for 3 times. Subsequently 2-bromo-3,3,3-trifluoropropene (4.15 mL, 40 mmol), aqueous solution of K₂CO₃ (2.0 M, 40 mL) and THF (60 mL) were added via syringes under N₂. The Schlenk tube was sealed, and the resulting solution was stirred at 60 °C for 24 h. After cooling to room temperature, the reaction mixture was quenched with saturated aqueous NH₄Cl, and extracted with Et₂O (3×60 mL). The combined organic layers were dried (Na₂SO₄) and concentrated under reduced pressure. The crude product was purified by flash chromatography using the appropriate gradient of petroleum ether and ethyl acetate.

Experimental Procedures and Characterization Data

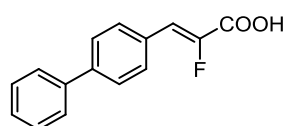
General Procedure A for Synthesis of α -Fluoroacrylic Acids

A flame-dried Schlenk tube (25 mL) containing a stirring bar was charged with bis(pinacolato)diboron (152 mg, 0.6 mmol, 1.5 equiv) and *gem*-difluoroalkenes (0.40 mmol, 1.0 equiv for non-liquid substrates). The reaction tube was transferred to the glovebox and charged with CuTc (3.8 mg, 0.02 mmol, 5 mol%), Xantphos (11.6 mg, 0.02 mmol, 5 mol%) and LiO^tBu (112 mg, 1.4 mmol, 3.5 equiv). The reaction tube was moved out of the glovebox and the tube was then evacuated and back-filled with carbon dioxide for 3 times. Subsequently anhydrous DMF (2 mL), *gem*-difluoroalkenes (0.40 mmol, 1.0 equiv for liquid substrates) were added via syringes under CO₂. Once added, the Schlenk tube was sealed at atmospheric pressure of CO₂ (1 atm). The resulting mixture was stirred for 24 - 36 h at 80 °C (380 r/min). After cooling to room temperature, the resulting mixture was diluted with 2 mL EtOAc and quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (3 x 5 mL) and the combined organic phases were concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (petroleum ether/EtOAc 10/1, then 0.1% AcOH in petroleum ether/EtOAc 8/1~5/1) to give the pure desired product.

General Procedure B for Synthesis of Methyl α -Fluoroacrylates

A flame-dried Schlenk tube (25 mL) containing a stirring bar was charged with bis(pinacolato)diboron (152 mg, 0.6 mmol, 1.5 equiv) and *gem*-difluoroalkenes (0.40 mmol, 1.0 equiv for non-liquid substrates). The reaction tube was transferred to the glovebox and charged with CuTc (3.8 mg, 0.02 mmol, 5 mol%), Xantphos (11.6 mg, 0.02 mmol, 5 mol%) and LiO^tBu (112 mg, 1.4 mmol, 3.5 equiv). The reaction tube was moved out of the glovebox and the tube was then evacuated and back-filled with carbon dioxide for 3 times. Subsequently anhydrous DMF (2 mL), *gem*-difluoroalkenes (0.40 mmol, 1.0 equiv for liquid substrates) were added via syringes under CO₂. Once added, the Schlenk tube was sealed at atmospheric pressure of CO₂ (1 atm). The resulting mixture was stirred for 24 - 36 h at 80 °C (380 r/min). After cooling to room temperature, MeI (75 μ L, 3.0 equiv) was added via syringe and the reaction tube was sealed. The resulting mixture was further stirred for 3 h at 65 °C. After cooling to room temperature, the resulting mixture was diluted with 2 mL EtOAc and quenched by 2 mL H₂O. The reaction mixture was extracted by EtOAc (3 x 5 mL) and the combined organic phases were concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (petroleum ether/EtOAc 30/1~10/1) to give the pure desired product.

(Z)-3-([1,1'-biphenyl]-4-yl)-2-fluoroacrylic acid (2a)



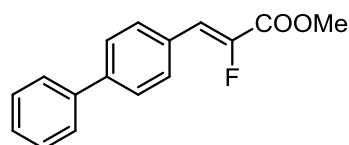
82 mg, 85% yield, white solid; mp 221–223 °C;

R_f (PE/EA 1:1): 0.20;

¹H NMR (400 MHz, DMSO-*d*₆) δ 13.70 (s, 1H), 7.83 – 7.76 (m, 4H), 7.75 – 7.69 (m, 2H), 7.55 – 7.46 (m, 2H), 7.44 – 7.37 (m, 1H), 7.10 (d, *J* = 36.8

Hz, 1H); ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -123.47; ¹³C NMR (101 MHz, DMSO-*d*₆) δ 162.45 (d, *J* = 34.7 Hz), 147.78 (d, *J* = 265.4 Hz), 141.60 (d, *J* = 2.5 Hz), 139.62, 131.16 (d, *J* = 8.0 Hz), 130.55 (d, *J* = 4.0 Hz), 129.49, 128.44, 127.53, 127.17, 116.70 (d, *J* = 4.2 Hz). HRMS (ESI⁻): calcd for C₁₅H₁₀FO₂⁻ [M-H]⁻ 241.0670, found 241.0671.

Methyl (Z)-3-([1,1'-biphenyl]-4-yl)-2-fluoroacrylate (2a^{''})



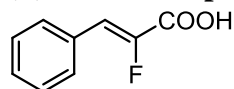
78 mg, 76% yield, white solid; mp 113–114 °C;

R_f (PE/EA 10:1): 0.50;

¹H NMR (400 MHz, CDCl₃) δ 7.73 – 7.69 (m, 2H), 7.66 – 7.59 (m, 4H), 7.49 – 7.42 (m, 2H), 7.42 – 7.33 (m, 1H), 6.97 (d, *J* = 35.3 Hz,

1H), 3.90 (s, 3H); ¹⁹F NMR (376 MHz, CDCl₃) δ -125.44; ¹³C NMR (101 MHz, CDCl₃) δ 161.90 (d, *J* = 34.4 Hz), 146.82 (d, *J* = 267.2 Hz), 142.42 (d, *J* = 2.7 Hz), 140.08, 130.81 (d, *J* = 7.9 Hz), 130.00 (d, *J* = 5.0 Hz), 128.90, 127.86, 127.43, 127.05, 117.47 (d, *J* = 4.1 Hz), 52.69. HRMS (ESI⁺): calcd for C₁₆H₁₃FNao₂⁺ [M+Na]⁺ 279.0792, found 279.0786.

(Z)-2-fluoro-3-phenylacrylic acid (2b)



46 mg, 70% yield, white solid; mp 149–151 °C;

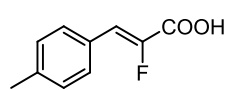
R_f (PE/EA 1:1): 0.20;

¹H NMR (400 MHz, DMSO-*d*₆) δ 13.66 (s, 1H), 7.73 – 7.66 (m, 2H), 7.49 –

7.40 (m, 3H), 7.04 (d, *J* = 36.7 Hz, 1H); ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -123.74; ¹³C NMR (101 MHz, DMSO-*d*₆) δ 162.43 (d, *J* = 34.8 Hz), 147.68 (d, *J* = 264.4 Hz), 131.42 (d, *J* = 4.0 Hz), 130.52 (d, *J* = 7.9 Hz), 130.16 (d, *J* = 2.1 Hz), 129.38, 117.02 (d, *J* = 4.2 Hz). LRMS (ESI⁻): calcd for C₉H₆FO₂⁻ [M-H]⁻ 165.04, found 164.83. The spectroscopic data correspond to those previously reported in the

literature.^[3]

(Z)-2-fluoro-3-(p-tolyl)acrylic acid (2c)

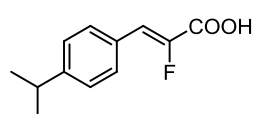


43 mg, 60% yield, white solid; mp 152–153 °C;

R_f (PE/EA 1:1): 0.20;

$^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 13.57 (s, 1H), 7.56 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 37.0 Hz, 1H), 2.30 (s, 3H); $^{19}\text{F NMR}$ (376 MHz, DMSO- d_6) δ -124.73; $^{13}\text{C NMR}$ (101 MHz, DMSO- d_6) δ 162.48 (d, J = 34.3 Hz), 147.12 (d, J = 262.5 Hz), 140.05 (d, J = 2.7 Hz), 130.48 (d, J = 7.9 Hz), 129.96, 128.58 (d, J = 4.1 Hz), 117.05 (d, J = 4.3 Hz), 21.43. **LRMS (ESI-)**: calcd for $\text{C}_{10}\text{H}_8\text{FO}_2^-$ [M-H] $^-$ 179.05, found 178.86. The spectroscopic data correspond to those previously reported in the literature.^[3]

(Z)-2-fluoro-3-(4-isopropylphenyl)acrylic acid (2d)

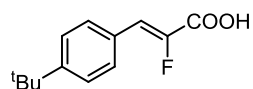


50 mg, 60% yield, white solid; mp 124–125 °C;

R_f (PE/EA 1:1): 0.25;

$^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 7.63 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.01 (d, J = 36.9 Hz, 1H), 2.97 – 2.85 (m, 1H), 1.21 (d, J = 6.9 Hz, 6H); $^{19}\text{F NMR}$ (376 MHz, DMSO- d_6) δ -124.79; $^{13}\text{C NMR}$ (101 MHz, DMSO- d_6) δ 162.55 (d, J = 34.6 Hz), 150.80 (d, J = 2.4 Hz), 147.23 (d, J = 263.7 Hz), 130.65 (d, J = 7.9 Hz), 129.02 (d, J = 4.1 Hz), 127.35, 117.06 (d, J = 4.4 Hz), 33.82, 24.02. **HRMS (ESI-)**: calcd for $\text{C}_{12}\text{H}_{12}\text{FO}_2^-$ [M-H] $^-$ 207.0827, found 207.0825.

(Z)-3-(4-(tert-butyl)phenyl)-2-fluoroacrylic acid (2e)

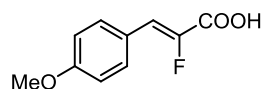


67 mg, 76% yield, white solid; mp 126–127 °C;

R_f (PE/EA 1:1): 0.20;

$^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 7.63 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.01 (d, J = 36.9 Hz, 1H), 1.29 (s, 9H); $^{19}\text{F NMR}$ (376 MHz, DMSO- d_6) δ -124.72; $^{13}\text{C NMR}$ (101 MHz, DMSO- d_6) δ 162.49 (d, J = 34.6 Hz), 152.94 (d, J = 2.4 Hz), 147.28 (d, J = 263.9 Hz), 130.33 (d, J = 7.8 Hz), 128.60 (d, J = 4.0 Hz), 126.14, 116.91 (d, J = 4.5 Hz), 34.96, 31.27. **HRMS (ESI-)**: calcd for $\text{C}_{13}\text{H}_{14}\text{FO}_2^-$ [M-H] $^-$ 221.0983, found 221.0983.

(Z)-2-fluoro-3-(4-methoxyphenyl)acrylic acid (2f)



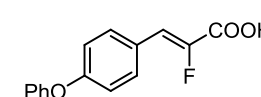
44 mg, 55% yield, white solid; mp 169–170 °C;

R_f (PE/EA 1:1): 0.15;

$^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 13.44 (s, 1H), 7.66 (d, J = 8.7 Hz, 2H), 7.08 – 6.91 (m, 3H), 3.80 (s, 3H); $^{19}\text{F NMR}$ (376 MHz, DMSO- d_6) δ -127.14; $^{13}\text{C NMR}$ (101 MHz, DMSO- d_6) δ 167.34 (d, J = 35.7 Hz), 165.45 (d, J = 3.1 Hz), 151.02 (d, J = 262.8 Hz), 137.04 (d, J = 8.0 Hz), 128.61 (d, J = 4.1 Hz), 121.73 (d, J = 4.4 Hz), 119.61, 60.45. **LRMS (ESI-)**: calcd for $\text{C}_{10}\text{H}_8\text{FO}_3^-$ [M-H] $^-$ 195.05, found 194.83. The spectroscopic data correspond to those previously reported in the literature.^[3]

(Z)-2-fluoro-3-(4-phenoxyphenyl)acrylic acid (2g)

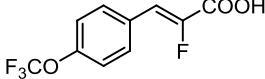
85 mg, 82% yield, white solid; mp 138–140 °C;



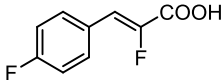
R_f (PE/EA 1:1): 0.18;

¹H NMR (400 MHz, DMSO-*d*₆) δ 13.61 (s, 1H), 7.78 – 7.73 (m, 2H), 7.51 – 7.43 (m, 2H), 7.28 – 7.20 (m, 1H), 7.16 – 6.99 (m, 5H); **¹⁹F NMR** (376 MHz, DMSO-*d*₆) δ -125.64; **¹³C NMR** (101 MHz, DMSO-*d*₆) δ 162.51 (d, *J* = 34.7 Hz), 158.48 (d, *J* = 3.3 Hz), 156.08, 146.98 (d, *J* = 263.8 Hz), 132.59 (d, *J* = 8.1 Hz), 130.68, 126.35 (d, *J* = 4.0 Hz), 124.70, 119.89, 118.72, 116.50 (d, *J* = 4.3 Hz). **HRMS (ESI-)**: calcd for C₁₅H₁₀FO₃⁻ [M-H]⁻ 257.0619, found 257.0618.

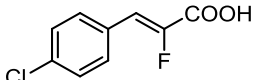
(Z)-2-fluoro-3-(4-(trifluoromethoxy)phenyl)acrylic acid (2h)

 64 mg, 64% yield, white solid; mp 37–38 °C;
R_f (PE/EA 1:1): 0.18;
¹H NMR (400 MHz, DMSO-*d*₆) δ 7.81 – 7.75 (m, 2H), 7.35 – 7.27 (m, 2H), 7.08 (d, *J* = 36.5 Hz, 1H), 7.85 (d, *J* = 8.8 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 36.1 Hz, 1H); **¹⁹F NMR** (376 MHz, DMSO-*d*₆) δ -56.86, -123.14; **¹³C NMR** (101 MHz, DMSO-*d*₆) δ 162.16 (d, *J* = 34.8 Hz), 149.11 (q, *J* = 1.6 Hz), 148.05 (d, *J* = 264.8 Hz), 132.40 (d, *J* = 8.1 Hz), 130.64 (d, *J* = 3.8 Hz), 121.60, 120.39 (q, *J* = 256.9 Hz), 115.43 (d, *J* = 4.2 Hz). **HRMS (ESI-)**: calcd for C₁₀H₅F₄O₃⁻ [M-H]⁻ 249.0180, found 249.0179.

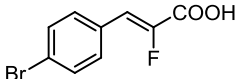
(Z)-2-fluoro-3-(4-fluorophenyl)acrylic acid (2i)

 50 mg, 68% yield, white solid; mp 164–165 °C;
R_f (PE/EA 1:1): 0.22;
¹H NMR (400 MHz, DMSO-*d*₆) δ 7.81 – 7.75 (m, 2H), 7.35 – 7.27 (m, 2H), 7.08 (d, *J* = 36.5 Hz, 1H); **¹⁹F NMR** (376 MHz, DMSO-*d*₆) δ -110.29, -124.87; **¹³C NMR** (101 MHz, DMSO-*d*₆) δ 162.89 (dd, *J* = 248.6, 3.8 Hz), 162.33 (d, *J* = 34.6 Hz), 147.34 (d, *J* = 265.3 Hz), 132.82 (t, *J* = 8.4 Hz), 127.99 (t, *J* = 3.6 Hz), 116.38 (d, *J* = 21.7 Hz), 115.90 (d, *J* = 4.1 Hz). **HRMS (ESI-)**: calcd for C₉H₅F₂O₂⁻ [M-H]⁻ 183.0263, found 183.0270.

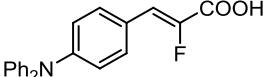
(Z)-3-(4-chlorophenyl)-2-fluoroacrylic acid (2j)

 52 mg, 65% yield, white solid; mp 174–175 °C;
R_f (PE/EA 1:1): 0.25;
¹H NMR (400 MHz, DMSO-*d*₆) δ 7.73 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 36.3 Hz, 1H); **¹⁹F NMR** (376 MHz, DMSO-*d*₆) δ -122.77; **¹³C NMR** (101 MHz, DMSO-*d*₆) δ 162.24 (d, *J* = 34.7 Hz), 148.00 (d, *J* = 266.4 Hz), 134.69 (d, *J* = 3.7 Hz), 132.18 (d, *J* = 8.1 Hz), 130.34 (d, *J* = 4.0 Hz), 129.44, 115.81 (d, *J* = 4.0 Hz). **HRMS (ESI-)**: calcd for C₉H₅ClFO₂⁻ [M-H]⁻ 198.9968, found 198.9970.

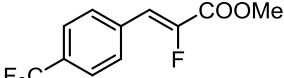
(Z)-3-(4-bromophenyl)-2-fluoroacrylic acid (2k)

 69 mg, 70% yield, white solid; mp 192–193 °C;
R_f (PE/EA 1:1): 0.25;
¹H NMR (400 MHz, DMSO-*d*₆) δ 7.66 (s, 4H), 7.06 (d, *J* = 36.2 Hz, 1H); **¹⁹F NMR** (376 MHz, DMSO-*d*₆) δ -122.41; **¹³C NMR** (101 MHz, DMSO-*d*₆) δ 162.25 (d, *J* = 34.8 Hz), 148.07 (d, *J* = 267.1 Hz), 132.38, 132.37 (d, *J* = 8.0 Hz), 130.66 (d, *J* = 3.9 Hz), 123.51 (d, *J* = 3.7 Hz), 115.89 (d, *J* = 4.0 Hz). **HRMS (ESI-)**: calcd for C₉H₅BrFO₂⁻ [M-H]⁻ 242.9462, found 242.9467.

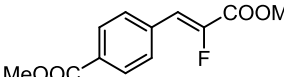
(Z)-3-(4-(diphenylamino)phenyl)-2-fluoroacrylic acid (2l)


 113 mg, 85% yield, yellow solid; mp 172–174 °C;
R_f (PE/EA 1:1): 0.25;
¹H NMR (400 MHz, DMSO-*d*₆) δ 7.57 (d, *J* = 8.9 Hz, 2H), 7.44 – 7.28 (m, 4H), 7.19 – 7.03 (m, 6H), 7.00 – 6.83 (m, 3H); ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -126.67; ¹³C NMR (101 MHz, DMSO-*d*₆) δ 162.65 (d, *J* = 34.3 Hz), 148.97 (d, *J* = 2.9 Hz), 146.80, 146.43 (d, *J* = 261.7 Hz), 131.91 (d, *J* = 8.0 Hz), 130.21, 125.61, 124.66, 124.30 (d, *J* = 4.1 Hz), 121.40, 116.94 (d, *J* = 4.5 Hz). **HRMS (ESI-)**: calcd for C₂₁H₁₅FNO₂⁻ [M-H]⁻ 332.1092, found 332.1087.

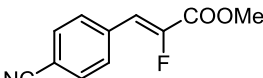
Methyl (Z)-2-fluoro-3-(4-(trifluoromethyl)phenyl)acrylate (2m)


 69 mg, 69% yield, white solid; mp 88–89 °C;
R_f (PE/EA 30:1): 0.30;
¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 6.95 (d, *J* = 34.3 Hz, 1H), 3.92 (s, 3H); ¹⁹F NMR (376 MHz, CDCl₃) δ -62.98, -122.36; ¹³C NMR (101 MHz, CDCl₃) δ 161.37 (d, *J* = 34.5 Hz), 147.95 (d, *J* = 271.5 Hz), 134.37 (dd, *J* = 4.3, 1.4 Hz), 131.18 (qd, *J* = 32.7, 2.9 Hz), 130.36 (d, *J* = 8.3 Hz), 125.70 (q, *J* = 3.7 Hz), 123.74 (q, *J* = 272.2 Hz), 116.08 (d, *J* = 4.3 Hz), 52.89. **GC-MS (EI)**: calcd for C₁₁H₈F₄O₂ *m/z* 248.0, found 248.1. The spectroscopic data correspond to those previously reported in the literature.^[4]

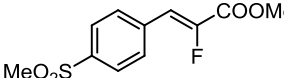
Methyl (Z)-4-(2-fluoro-3-methoxy-3-oxoprop-1-en-1-yl)benzoate (2n)


 72 mg, 75% yield, white solid; mp 104–105 °C;
R_f (PE/EA 30:1): 0.20;
¹H NMR (400 MHz, CDCl₃) δ 8.11 – 8.02 (m, 2H), 7.74 – 7.65 (m, 2H), 6.95 (d, *J* = 34.5 Hz, 1H), 3.93 (s, 3H), 3.91 (s, 3H); ¹⁹F NMR (376 MHz, CDCl₃) δ -122.22; ¹³C NMR (101 MHz, CDCl₃) δ 166.41, 161.49 (d, *J* = 34.5 Hz), 147.87 (d, *J* = 271.5 Hz), 135.29 (d, *J* = 4.5 Hz), 130.80 (d, *J* = 2.8 Hz), 130.12 (d, *J* = 8.3 Hz), 129.95, 116.56 (d, *J* = 4.4 Hz), 52.86, 52.30. **HRMS (ESI+)**: calcd for C₁₂H₁₂FO₄⁺ [M+H]⁺ 239.0714, found 239.0717.

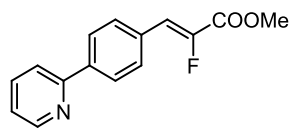
Methyl (Z)-3-(4-cyanophenyl)-2-fluoroacrylate (2o)


 58 mg, 70% yield, white solid; mp 129–130 °C;
R_f (PE/EA 10:1): 0.25;
¹H NMR (400 MHz, CDCl₃) δ 7.71 (q, *J* = 8.3 Hz, 4H), 6.94 (d, *J* = 33.9 Hz, 1H), 3.93 (s, 3H); ¹⁹F NMR (376 MHz, CDCl₃) δ -120.49; ¹³C NMR (101 MHz, CDCl₃) δ 161.13 (d, *J* = 34.5 Hz), 148.44 (d, *J* = 273.7 Hz), 135.34 (d, *J* = 4.4 Hz), 132.49, 130.55 (d, *J* = 8.5 Hz), 118.34, 115.66 (d, *J* = 4.2 Hz), 112.89 (d, *J* = 3.3 Hz), 53.04. **GC-MS (EI)**: calcd for C₁₁H₈FNO₂ *m/z* 205.0 found 205.0. The spectroscopic data correspond to those previously reported in the literature.^[4]

Methyl (Z)-2-fluoro-3-(4-(methylsulfonyl)phenyl)acrylate (2p)


 68 mg, 66% yield, white solid; mp 118–119 °C;
R_f (PE/EA 5:1): 0.30;
¹H NMR (400 MHz, CDCl₃) δ 8.01 – 7.94 (m, 2H), 7.87 – 7.77 (m, 2H), 6.98 (d, *J* = 33.8 Hz, 1H), 3.93 (s, 3H), 3.08 (s, 3H); ¹⁹F NMR (376 MHz, CDCl₃) δ -120.53; ¹³C NMR (101 MHz, CDCl₃) δ 161.11 (d, *J* = 34.5 Hz), 148.53 (d, *J* = 273.6 Hz), 140.88 (d, *J* = 3.0 Hz), 136.23 (d, *J* = 4.4 Hz), 130.81 (d, *J* = 8.3 Hz), 127.82, 115.49 (d, *J* = 4.3 Hz), 53.01, 44.39. **HRMS (ESI+)**: calcd for C₁₁H₁₁FN₂O₄S⁺ [M+Na]⁺ 281.0254, found 281.0257.

Methyl (Z)-2-fluoro-3-(4-(pyridin-2-yl)phenyl)acrylate (2q)



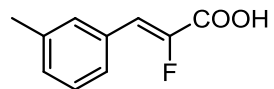
76 mg, 73% yield, white solid; mp 108–109 °C;

R_f (PE/EA 10:1): 0.40;

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.70 (s, 1H), 8.04 (d, $J = 8.0$ Hz, 2H), 7.79 – 7.67 (m, 4H), 7.24 (d, $J = 2.9$ Hz, 1H), 6.97 (d, $J = 35.2$ Hz, 1H), 3.89 (s,

3H); $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -124.56; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 161.76 (d, $J = 34.4$ Hz), 156.20, 149.77, 147.01 (d, $J = 268.2$ Hz), 140.34 (d, $J = 1.7$ Hz), 136.84, 131.54 (d, $J = 4.5$ Hz), 130.71 (d, $J = 8.2$ Hz), 127.15, 122.57, 120.61, 117.33 (d, $J = 4.6$ Hz), 52.67. **HRMS (ESI+)**: calcd for $\text{C}_{15}\text{H}_{13}\text{FNO}_2^+$ $[\text{M}+\text{H}]^+$ 258.0925, found 258.0915.

(Z)-2-fluoro-3-(*m*-tolyl)acrylic acid (2r)

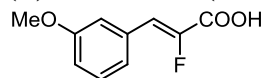


53 mg, 74% yield, white solid; mp 95–97 °C;

R_f (PE/EA 1:1): 0.20;

$^1\text{H NMR}$ (400 MHz, $\text{DMSO}-d_6$) δ 7.53 – 7.46 (m, 2H), 7.37 – 7.32 (m, 1H), 7.26 – 7.22 (m, 1H), 6.99 (d, $J = 36.7$ Hz, 1H), 2.34 (s, 3H); $^{19}\text{F NMR}$ (376 MHz, $\text{DMSO}-d_6$) δ -123.75; $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO}-d_6$) δ 162.45 (d, $J = 33.7$ Hz), 147.60 (d, $J = 266.0$ Hz), 138.56, 131.33 (d, $J = 4.0$ Hz), 131.00 (d, $J = 7.6$ Hz), 130.86 (d, $J = 2.0$ Hz), 129.27, 127.70 (d, $J = 8.0$ Hz), 117.10 (d, $J = 4.2$ Hz), 21.39. **HRMS (ESI-)**: calcd for $\text{C}_{10}\text{H}_8\text{FO}_2^-$ $[\text{M}-\text{H}]^-$ 179.0514, found 179.0523.

(Z)-2-fluoro-3-(3-methoxyphenyl)acrylic acid (2s)

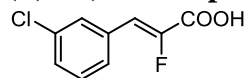


56 mg, 71% yield, white solid; mp 82–83 °C;

R_f (PE/EA 1:1): 0.15;

$^1\text{H NMR}$ (400 MHz, $\text{DMSO}-d_6$) δ 13.65 (s, 1H), 7.37 – 7.32 (m, 1H), 7.28 – 7.21 (m, 2H), 7.06 – 6.93 (m, 2H), 3.74 (s, 3H); $^{19}\text{F NMR}$ (376 MHz, $\text{DMSO}-d_6$) δ -123.00; $^{13}\text{C NMR}$ (101 MHz, $\text{acetone}-d_6$) δ 161.24 (d, $J = 35.0$ Hz), 159.91, 132.45 (d, $J = 4.1$ Hz), 129.86, 122.56 (d, $J = 8.2$ Hz), 117.17 (d, $J = 4.1$ Hz), 115.49 (d, $J = 2.2$ Hz), 115.27 (d, $J = 8.0$ Hz), 54.69. **HRMS (ESI-)**: calcd for $\text{C}_{10}\text{H}_8\text{FO}_3^-$ $[\text{M}-\text{H}]^-$ 195.0463, found 195.0464.

(Z)-3-(3-chlorophenyl)-2-fluoroacrylic acid (2t)

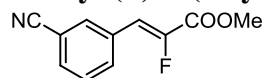


54 mg, 68% yield, white solid; mp 125–126 °C;

R_f (PE/EA 1:1): 0.20;

$^1\text{H NMR}$ (400 MHz, $\text{DMSO}-d_6$) δ 7.75 (s, 1H), 7.71 – 7.64 (m, 1H), 7.54 – 7.44 (m, 2H), 7.08 (d, $J = 36.1$ Hz, 1H); $^{19}\text{F NMR}$ (376 MHz, $\text{DMSO}-d_6$) δ -121.61; $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO}-d_6$) δ 162.09 (d, $J = 34.9$ Hz), 148.39 (d, $J = 266.8$ Hz), 133.94, 133.46 (d, $J = 3.9$ Hz), 131.16, 129.86 (d, $J = 10.2$ Hz), 129.83, 128.96 (d, $J = 8.4$ Hz), 115.54 (d, $J = 3.9$ Hz). **HRMS (ESI-)**: calcd for $\text{C}_9\text{H}_5\text{ClFO}_2^-$ $[\text{M}-\text{H}]^-$ 198.9968, found 198.9967.

Methyl (Z)-3-(3-cyanophenyl)-2-fluoroacrylate (2u)



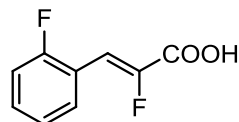
56 mg, 68% yield, white solid; mp 128–129 °C;

R_f (PE/EA 10:1): 0.25;

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.93 (s, 1H), 7.85 (d, $J = 8.0$ Hz, 1H), 7.69 – 7.64 (m, 1H), 7.54 (t, $J = 7.8$ Hz, 1H), 6.91 (d, $J = 33.8$ Hz, 1H), 3.93 (s, 3H); $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -121.86; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 161.15 (d, $J = 34.4$ Hz), 148.10 (d, $J = 272.0$ Hz), 134.10 (d, $J = 8.1$ Hz), 133.38

(d, $J = 8.7$ Hz), 132.75 (d, $J = 2.6$ Hz), 132.22 (d, $J = 4.2$ Hz), 129.74, 118.16, 115.29 (d, $J = 4.3$ Hz), 113.28, 52.99. **GC-MS (EI)**: calcd for $C_{11}H_8FNO_2$ m/z 205.0 found 205.0. The spectroscopic data correspond to those previously reported in the literature.^[4]

(Z)-2-fluoro-3-(2-fluorophenyl)acrylic acid (2v)



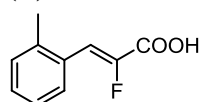
62 mg, 84% yield, white solid; mp 77–78 °C;

R_f (PE/EA 1:1): 0.20;

1H NMR (400 MHz, DMSO- d_6) δ 13.87 (s, 1H), 7.81 (td, $J = 7.7, 1.5$ Hz, 1H), 7.50 – 7.43 (m, 1H), 7.33 – 7.24 (m, 2H), 7.03 (d, $J = 35.4$ Hz, 1H); ^{19}F NMR

(376 MHz, DMSO- d_6) δ -115.01 (d, $J = 7.2$ Hz), -121.35 (d, $J = 7.0$ Hz); ^{13}C NMR (101 MHz, DMSO- d_6) δ 161.93 (d, $J = 34.8$ Hz), 159.97 (dd, $J = 250.5, 1.7$ Hz), 148.75 (d, $J = 268.3$ Hz), 132.33 (dd, $J = 8.8, 1.8$ Hz), 130.93 (dd, $J = 12.5, 1.8$ Hz), 125.48 (d, $J = 3.5$ Hz), 118.90 (dd, $J = 12.1, 4.2$ Hz), 116.21 (d, $J = 21.8$ Hz), 108.04 (dd, $J = 6.8, 4.9$ Hz). **LRMS (ESI-)**: calcd for $C_9H_5F_2O_2^-$ [M-H]⁻ 183.03, found 182.84. The spectroscopic data correspond to those previously reported in the literature.^[5]

(Z)-2-fluoro-3-(*o*-tolyl)acrylic acid (2w)

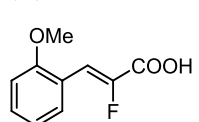


38 mg, 52% yield, white solid; mp 88–89 °C;

R_f (PE/EA 1:1): 0.20;

1H NMR (400 MHz, DMSO- d_6) δ 7.68 (d, $J = 6.8$ Hz, 1H), 7.42 – 7.23 (m, 3H), 7.11 (d, $J = 35.3$ Hz, 1H), 2.35 (s, 3H); ^{19}F NMR (376 MHz, DMSO- d_6) δ -125.59; ^{13}C NMR (101 MHz, acetone- d_6) δ 161.43 (d, $J = 35.7$ Hz), 147.22 (d, $J = 265.2$ Hz), 137.40 (d, $J = 1.2$ Hz), 130.46, 129.71 (d, $J = 11.5$ Hz), 129.71 (d, $J = 3.8$ Hz), 129.46 (d, $J = 1.5$ Hz), 126.19, 114.37 (d, $J = 5.1$ Hz), 19.16. **HRMS (ESI-)**: calcd for $C_{10}H_8FO_2^-$ [M-H]⁻ 179.0514, found 179.0522.

(Z)-2-fluoro-3-(2-methoxyphenyl)acrylic acid (2x)

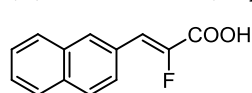


52 mg, 66% yield, white solid; mp 97–98 °C;

R_f (PE/EA 1:1): 0.18;

1H NMR (400 MHz, DMSO- d_6) δ 7.77 (dd, $J = 7.8, 1.7$ Hz, 1H), 7.45 – 7.39 (m, 1H), 7.27 (d, $J = 37.2$ Hz, 1H), 7.11 (d, $J = 8.4$ Hz, 1H), 7.04 (t, $J = 7.6$ Hz, 1H), 3.86 (s, 3H); ^{19}F NMR (376 MHz, DMSO- d_6) δ -125.36; ^{13}C NMR (101 MHz, DMSO- d_6) δ 162.43 (d, $J = 35.7$ Hz), 157.34, 147.61 (d, $J = 263.1$ Hz), 131.83 (d, $J = 1.5$ Hz), 130.51 (d, $J = 13.4$ Hz), 121.17, 119.47 (d, $J = 4.7$ Hz), 111.86, 110.44 (d, $J = 3.5$ Hz), 56.17. **LRMS (ESI-)**: calcd for $C_{10}H_8FO_3^-$ [M-H]⁻ 195.05, found 194.83. The spectroscopic data correspond to those previously reported in the literature.^[5]

(Z)-2-fluoro-3-(naphthalen-2-yl)acrylic acid (2y)



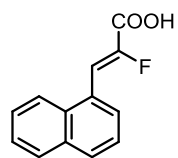
71 mg, 82% yield, white solid; mp 181–182 °C;

R_f (PE/EA 1:1): 0.22;

1H NMR (400 MHz, DMSO- d_6) δ 13.74 (s, 1H), 8.27 (s, 1H), 8.09 – 7.93 (m, 3H), 7.84 (d, $J = 8.6$ Hz, 1H), 7.68 – 7.52 (m, 2H), 7.22 (d, $J = 36.5$ Hz, 1H); ^{19}F NMR (376 MHz, DMSO- d_6) δ -123.41; ^{13}C NMR (101 MHz, DMSO- d_6) δ 162.44 (d, $J = 35.7$ Hz), 147.84 (d, $J = 266.4$ Hz), 133.48 (d, $J = 1.4$ Hz), 133.18, 130.79 (d, $J = 7.8$ Hz), 129.00 (d, $J = 4.2$ Hz), 128.90, 128.87, 128.01, 127.83, 127.19, 127.08 (d, $J = 8.1$ Hz), 117.10 (d, $J = 4.1$ Hz). **LRMS (ESI-)**: calcd for

C₁₃H₈FO₂⁻ [M-H]⁻ 215.05, found 214.85. The spectroscopic data correspond to those previously reported in the literature.^[5]

(Z)-2-fluoro-3-(naphthalen-1-yl)acrylic acid (2z)

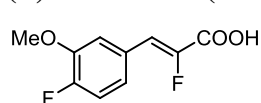


57 mg, 66% yield, white solid; mp 111–112 °C;

R_f (PE/EA 1:1): 0.22;

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.10 (d, *J* = 8.1 Hz, 1H), 8.06 – 7.96 (m, 2H), 7.92 (d, *J* = 7.2 Hz, 1H), 7.77 – 7.56 (m, 4H); ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -123.86; ¹³C NMR (101 MHz, DMSO-*d*₆) δ 162.35 (d, *J* = 35.1 Hz), 148.56 (d, *J* = 265.9 Hz), 133.62, 131.13, 130.26, 129.13, 128.67 (d, *J* = 10.1 Hz), 127.54, 127.30 (d, *J* = 3.3 Hz), 126.74, 125.98, 123.98, 113.52 (d, *J* = 5.9 Hz). HRMS (ESI⁻): calcd for C₁₃H₈FO₂⁻ [M-H]⁻ 215.0514, found 215.0515.

(Z)-2-fluoro-3-(4-fluoro-3-methoxyphenyl)acrylic acid (2aa)

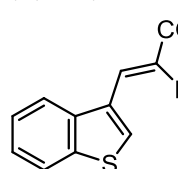


57 mg, 67% yield, white solid; mp 137–138 °C;

R_f (PE/EA 1:1): 0.18;

¹H NMR (400 MHz, DMSO-*d*₆) δ 7.50 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.36 – 7.25 (m, 2H), 7.05 (d, *J* = 36.3 Hz, 1H), 3.88 (s, 3H); ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -124.52, -132.26; ¹³C NMR (101 MHz, DMSO-*d*₆) δ 162.32 (d, *J* = 34.6 Hz), 152.38 (dd, *J* = 249.0, 3.6 Hz), 147.58 (d, *J* = 10.8 Hz), 147.31 (d, *J* = 264.3 Hz), 128.35 (t, *J* = 3.9 Hz), 123.56 (dd, *J* = 9.2, 7.3 Hz), 116.80 (d, *J* = 18.6 Hz), 116.31 (d, *J* = 2.4 Hz), 115.87 (dd, *J* = 7.5, 2.2 Hz), 56.36. HRMS (ESI⁻): calcd for C₁₀H₇F₂O₃⁻ [M-H]⁻ 213.0369, found 213.0365.

(Z)-3-(benzo[*b*]thiophen-3-yl)-2-fluoroacrylic acid (2ab)

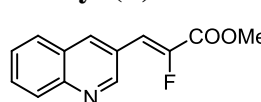


62 mg, 70% yield, light yellow solid; mp 69–71 °C;

R_f (PE/EA 1:1): 0.25;

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.31 (s, 1H), 8.08 (t, *J* = 7.4 Hz, 2H), 7.54 – 7.46 (m, 2H), 7.39 (d, *J* = 35.2 Hz, 1H); ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -120.10; ¹³C NMR (101 MHz, DMSO-*d*₆) δ 162.26 (d, *J* = 34.3 Hz), 148.61 (d, *J* = 265.3 Hz), 139.10, 137.83, 131.36 (d, *J* = 14.9 Hz), 125.83 (d, *J* = 3.3 Hz), 125.49, 125.36, 123.38, 122.00, 108.39 (d, *J* = 7.3 Hz). HRMS (ESI⁻): calcd for C₁₁H₆FO₂S⁻ [M-H]⁻ 221.0078, found 221.0074.

Methyl (Z)-2-fluoro-3-(quinolin-3-yl)acrylate (2ac)

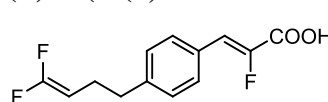


48 mg, 52% yield, light yellow solid; mp 89–90 °C;

R_f (PE/EA 5:1): 0.30;

¹H NMR (400 MHz, CDCl₃) δ 9.05 (d, *J* = 1.5 Hz, 1H), 8.48 (d, *J* = 1.2 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.79 – 7.73 (m, 1H), 7.63 – 7.53 (m, 1H), 7.09 (d, *J* = 35.0 Hz, 1H), 3.94 (s, 3H); ¹⁹F NMR (376 MHz, CDCl₃) δ -121.87; ¹³C NMR (101 MHz, CDCl₃) δ 161.27 (d, *J* = 34.3 Hz), 151.08 (d, *J* = 6.6 Hz), 148.27 (d, *J* = 270.1 Hz), 147.88 (d, *J* = 2.3 Hz), 137.22 (d, *J* = 10.8 Hz), 130.79, 129.29, 128.48, 127.56, 127.36, 124.40 (d, *J* = 5.0 Hz), 114.49 (d, *J* = 5.4 Hz), 52.89. HRMS (ESI⁺): calcd for C₁₃H₁₁FNO₂⁺ [M+H]⁺ 232.0768, found 232.0758.

(Z)-3-(4-(4,4-difluorobut-3-en-1-yl)phenyl)-2-fluoroacrylic acid (2ad)

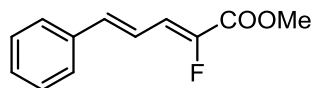


70 mg, 68% yield, white solid; mp 90–91 °C;

R_f (PE/EA 1:1): 0.20;

¹H NMR (400 MHz, DMSO-*d*₆) δ 7.64 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 36.8 Hz, 1H), 4.47 (m, *J* = 26.9, 2.8 Hz, 1H), 2.70 (t, *J* = 7.5 Hz, 2H), 2.27 (q, *J* = 7.7 Hz, 2H); **¹⁹F NMR** (376 MHz, DMSO-*d*₆) δ -89.37 (d, *J* = 49.4 Hz), -91.58 (d, *J* = 49.5 Hz), -124.45; **¹³C NMR** (101 MHz, DMSO-*d*₆) δ 162.45 (d, *J* = 34.7 Hz), 155.78 (dd, *J* = 286.3, 283.5 Hz), 147.30 (d, *J* = 264.0 Hz), 143.22 (d, *J* = 2.5 Hz), 130.55 (d, *J* = 7.9 Hz), 129.42, 129.23 (d, *J* = 4.1 Hz), 116.93 (d, *J* = 4.4 Hz), 78.38 (dd, *J* = 21.5, 19.1 Hz), 34.87 (t, *J* = 2.3 Hz), 23.75 (d, *J* = 4.4 Hz); **HRMS (ESI-)**: calcd for C₁₃H₁₀F₃O₂⁻ [M-H]⁻ 255.0638, found 255.0638.

Methyl (2*Z*,4*E*)-2-fluoro-5-phenylpenta-2,4-dienoate (2ae)

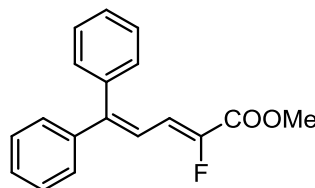


63 mg, 76% yield, light yellow oil;

R_f (PE/EA 30:1): 0.40;

¹H NMR (400 MHz, CDCl₃) δ 7.50 – 7.43 (m, 2H), 7.39 – 7.27 (m, 3H), 7.14 – 7.02 (m, 1H), 6.89 – 6.70 (m, 2H), 3.85 (s, 3H); **¹⁹F NMR** (376 MHz, CDCl₃) δ -128.82; **¹³C NMR** (101 MHz, CDCl₃) δ 161.52 (d, *J* = 33.7 Hz), 146.55 (d, *J* = 264.3 Hz), 139.12 (d, *J* = 4.6 Hz), 136.03 (d, *J* = 1.8 Hz), 129.17, 128.85, 127.28 (d, *J* = 0.9 Hz), 119.20 (d, *J* = 8.8 Hz), 118.76 (d, *J* = 2.0 Hz), 52.47. **GC-MS (EI)**: calcd for C₁₂H₁₁FO₂ *m/z* 206.1 found 206.1. The spectroscopic data correspond to those previously reported in the literature.^[6]

Methyl (Z)-2-fluoro-5,5-diphenylpenta-2,4-dienoate (2af)

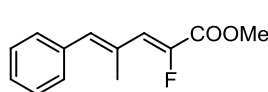


81 mg, 72% yield, light yellow oil;

R_f (PE/EA 30:1): 0.40;

¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.40 (m, 3H), 7.34 – 7.29 (m, 5H), 7.24 – 7.20 (m, 2H), 7.02 (dd, *J* = 11.9, 0.4 Hz, 1H), 6.72 (dd, *J* = 31.1, 11.9 Hz, 1H), 3.79 (s, 3H); **¹⁹F NMR** (376 MHz, CDCl₃) δ -132.82; **¹³C NMR** (101 MHz, CDCl₃) δ 161.56 (d, *J* = 34.1 Hz), 150.13 (d, *J* = 5.2 Hz), 147.32 (d, *J* = 265.0 Hz), 141.20 (d, *J* = 1.3 Hz), 138.41, 130.35, 128.78, 128.45, 128.39, 128.37, 128.21, 117.41 (d, *J* = 1.9 Hz), 116.77 (d, *J* = 7.0 Hz), 52.43. **HRMS (ESI+)**: calcd for C₁₈H₁₆FO₂⁺ [M+H]⁺ 283.1129, found 283.1137.

Methyl (2*Z*,4*E*)-2-fluoro-4-methyl-5-phenylpenta-2,4-dienoate (2ag)

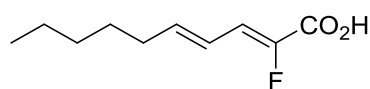


54 mg, 61% yield, light yellow oil;

R_f (PE/EA 30:1): 0.40;

¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.23 (m, 5H), 6.80 (s, 1H), 6.69 (dd, *J* = 35.3, 0.6 Hz, 1H), 3.86 (s, 3H), 2.22 (dd, *J* = 2.8, 1.3 Hz, 3H); **¹⁹F NMR** (376 MHz, CDCl₃) δ -128.08; **¹³C NMR** (101 MHz, CDCl₃) δ 162.18 (d, *J* = 34.6 Hz), 145.60 (d, *J* = 266.3 Hz), 137.51 (d, *J* = 6.4 Hz), 136.44 (d, *J* = 1.5 Hz), 131.34 (d, *J* = 5.9 Hz), 129.37 (d, *J* = 1.0 Hz), 128.30, 127.67, 122.73 (d, *J* = 3.9 Hz), 52.55 (d, *J* = 0.6 Hz), 16.46 (d, *J* = 7.2 Hz). **HRMS (ESI+)**: calcd for C₁₃H₁₃FN₂O₂⁺ [M+Na]⁺ 243.0792, found 243.0790.

(2*Z*,4*E*)-2-Fluorodeca-2,4-dienoic acid (2ah)



33 mg, 45% yield, light yellow solid;

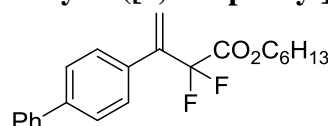
R_f (PE/EA 3:1): 0.15;

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.66 (s, 1H), 6.72 (dd, $J = 31.1, 11.2$ Hz, 1H), 6.40 (dd, $J = 15.4, 11.2$ Hz, 1H), 6.23 – 6.12 (m, 1H), 2.20 (q, $J = 7.2$ Hz, 2H), 1.49 – 1.40 (m, 2H), 1.36 – 1.27 (m, 4H), 0.90 (t, $J = 6.9$ Hz, 3H); $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -132.64.; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.36 (d, $J = 35.0$ Hz), 145.23 (d, $J = 4.2$ Hz), 144.16 (d, $J = 256.9$ Hz), 121.56 (d, $J = 8.6$ Hz), 120.67 (d, $J = 2.2$ Hz), 33.25, 31.32, 28.25, 22.42, 13.95. **HRMS (ESI-)**: calcd for $\text{C}_{10}\text{H}_{14}\text{FO}_2^-$ [$\text{M}-\text{H}$] 185.0983, found 185.1020.

General Procedure C for Synthesis of α,α -Difluorocarboxylates

A flame-dried Schlenk tube (25 mL) containing a stirring bar was charged with bis(hexylene glycolato)diboron (76 mg, 0.3 mmol, 1.5 equiv) and α -trifluoromethyl alkene (0.20 mmol, 1.0 equiv for non-liquid substrates). The reaction tube was transferred to the glovebox and charged with CuCl (2.0 mg, 0.02 mmol, 10 mol%), Xantphos (11.6 mg, 0.02 mmol, 10 mol%) and KOMe (42 mg, 0.6 mmol, 3.0 equiv). The reaction tube was moved out of the glovebox and the tube was then evacuated and back-filled with carbon dioxide for 3 times. Subsequently anhydrous NMP (2 mL), α -trifluoromethyl alkene (0.20 mmol, 1.0 equiv for liquid substrates) were added via syringes under CO_2 . Once added, the Schlenk tube was sealed at atmospheric pressure of CO_2 (1 atm). The resulting mixture was stirred for 24 h at 80 °C (380 r/min). After cooling to room temperature, $^{13}\text{C}_6\text{H}_{13}\text{I}$ (88 μL , 3.0 equiv) was added via syringe and the reaction tube was sealed. The resulting mixture was further stirred for 4 h at 80 °C. After cooling to room temperature, the resulting mixture was diluted with 2 mL EtOAc and quenched by 2 mL H_2O . The reaction mixture was extracted by EtOAc (3 x 5 mL) and the combined organic phases were concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (petroleum ether/EtOAc 100/1~30/1 or petroleum ether/ CH_2Cl_2 30/1~10/1) to give the pure desired product.

Hexyl 3-([1,1'-biphenyl]-4-yl)-2,2-difluorobut-3-enoate (4a)



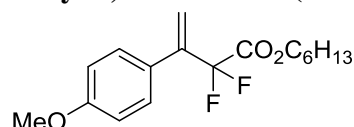
50 mg, 70% yield, light yellow oil;

R_f (PE/EA 30:1): 0.55;

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.61 – 7.55 (m, 4H), 7.52 – 7.40 (m, 4H), 7.37 – 7.34 (m, 1H), 5.92 (t, $J = 1.6$ Hz, 1H), 5.79 (t, $J = 1.6$ Hz, 1H), 4.18 (t, $J = 6.6$ Hz, 2H), 1.57 – 1.49 (m, 2H), 1.26 – 1.17 (m, 6H), 0.83 (t, $J = 6.8$ Hz, 3H); $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -102.01; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 163.73 (t, $J = 33.9$ Hz), 141.49, 140.88 (t, $J = 22.1$ Hz), 140.26, 133.63 (t, $J = 1.3$ Hz), 128.83, 128.08, 127.61, 127.09, 127.01, 119.91 (t, $J = 8.6$ Hz), 113.11 (t, $J = 252.1$ Hz), 67.09, 31.23, 28.16, 25.21, 22.43, 13.93.

HRMS (ESI+): calcd for $\text{C}_{22}\text{H}_{24}\text{F}_2\text{NaO}_2^+$ [$\text{M}+\text{Na}$] $^+$ 381.1637, found 381.1625.

Hexyl 2,2-difluoro-3-(4-methoxyphenyl)but-3-enoate (4b)



35 mg, 56% yield, light yellow oil;

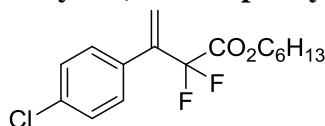
R_f (PE/EA 30:1): 0.45;

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.35 (d, $J = 8.7$ Hz, 2H), 6.86 (d, $J = 8.8$ Hz, 2H), 5.82 (t, $J = 1.6$ Hz, 1H), 5.66 (t, $J = 1.6$ Hz, 1H), 4.16 (t, $J = 6.6$ Hz, 2H), 3.81 (s, 3H), δ 1.58 – 1.48 (m, 2H), 1.29 – 1.16 (m, 6H), 0.87 (t, $J = 6.9$ Hz, 3H); $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -102.26; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 163.80 (t, $J = 33.5$ Hz), 159.89,

140.57 (t, $J = 21.9$ Hz), 128.96, 127.06 (t, $J = 1.3$ Hz), 118.64 (t, $J = 8.6$ Hz), 113.77, 113.16 (t, $J = 251.9$ Hz), 66.99, 55.22, 31.23, 28.16, 25.19, 22.42, 13.96.

HRMS (ESI+): calcd for $C_{17}H_{22}F_2NaO_3^+$ $[M+Na]^+$ 335.1429, found 335.1411.

Hexyl 3-(4-chlorophenyl)-2,2-difluorobut-3-enoate (4c)



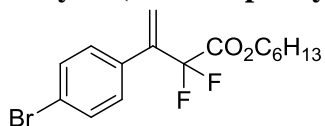
41 mg, 64% yield, light yellow oil;

R_f (PE/EA 30:1): 0.50;

1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 4H), 5.91 (t, $J = 1.6$ Hz, 1H), 5.72 (t, $J = 1.3$ Hz, 1H), 4.17 (t, $J = 6.6$ Hz, 2H), 1.58 – 1.49 (m, 2H), 1.31 – 1.16 (m, 6H), 0.87 (t, $J = 6.9$ Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.37; ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.49 (t, $J = 33.9$ Hz), 140.23 (t, $J = 22.4$ Hz), 134.87, 133.16 (t, $J = 1.4$ Hz), 129.10 (t, $J = 1.2$ Hz), 128.65, 120.60 (t, $J = 8.5$ Hz), 112.83 (t, $J = 252.3$ Hz), 67.17, 31.21, 28.14, 25.20, 22.44, 13.96.

HRMS (ESI+): calcd for $C_{16}H_{19}ClF_2NaO_2^+$ $[M+Na]^+$ 339.0934, found 339.0927.

Hexyl 3-(4-bromophenyl)-2,2-difluorobut-3-enoate (4d)



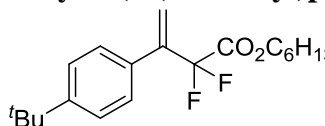
45 mg, 62% yield, light yellow oil;

R_f (PE/EA 30:1): 0.50;

1H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 2H), 7.30 – 7.25 (m, 2H), 5.92 (t, $J = 1.5$ Hz, 1H), 5.73 (t, $J = 1.4$ Hz, 1H), 4.17 (t, $J = 6.6$ Hz, 2H), 1.58 – 1.50 (m, 2H), 1.30 – 1.15 (m, 6H), 0.88 (t, $J = 7.0$ Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.34; ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.47 (t, $J = 33.9$ Hz), 140.30 (t, $J = 22.4$ Hz), 133.64 (t, $J = 1.4$ Hz), 131.61, 129.38 (t, $J = 1.2$ Hz), 123.11, 120.64 (t, $J = 8.5$ Hz), 112.77 (t, $J = 252.3$ Hz), 67.18, 31.21, 28.14, 25.20, 22.44, 13.97.

HRMS (ESI+): calcd for $C_{16}H_{19}BrF_2NaO_2^+$ $[M+Na]^+$ 383.0429, found 383.0421.

Hexyl 3-(4-(tert-butyl)phenyl)-2,2-difluorobut-3-enoate (4e)



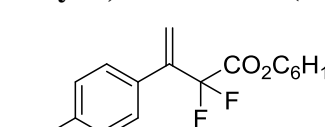
38 mg, 56% yield, light yellow oil;

R_f (PE/EA 30:1): 0.60;

1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 4H), 5.85 (t, $J = 1.6$ Hz, 1H), 5.71 (t, $J = 1.5$ Hz, 1H), 4.16 (t, $J = 6.6$ Hz, 2H), 1.58 – 1.46 (m, 2H), 1.31 (s, 9H), 1.29 – 1.17 (m, 6H), 0.86 (t, $J = 6.9$ Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.12; ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.82 (t, $J = 34.0$ Hz), 151.72, 140.96 (t, $J = 22.1$ Hz), 131.71 (t, $J = 1.4$ Hz), 127.28, 125.35, 119.33 (t, $J = 8.6$ Hz), 113.16 (t, $J = 251.8$ Hz), 66.97, 34.58, 31.20, 28.08, 25.15, 22.42, 13.97.

HRMS (ESI+): calcd for $C_{20}H_{28}F_2NaO_2^+$ $[M+Na]^+$ 361.1950, found 361.1945.

Hexyl 2,2-difluoro-3-(4-(trifluoromethyl)phenyl)but-3-enoate (4f)



35 mg, 51% yield, colourless oil;

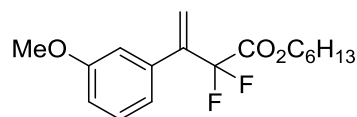
R_f (PE/EA 30:1): 0.58;

1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, $J = 8.3$ Hz, 2H), 7.53 (d, $J = 8.2$ Hz, 2H), 5.99 (t, $J = 1.6$ Hz, 1H), 5.79 (t, $J = 1.5$ Hz, 1H), 4.17 (t, $J = 6.6$ Hz, 2H), 1.57 – 1.49 (m, 2H), 1.28 – 1.17 (m, 6H), 0.86 (t, $J = 6.9$ Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.88, -102.32; ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.34 (t, $J = 33.8$ Hz), 140.35 (t, $J =$

22.8 Hz), 138.32, 130.76 (q, $J = 32.7$ Hz), 128.18 (t, $J = 1.3$ Hz), 125.38 (q, $J = 3.8$ Hz), δ 123.87 (q, $J = 272.1$ Hz), 121.80 (t, $J = 8.4$ Hz), 112.72 (t, $J = 252.4$ Hz), 67.24, 31.14, 28.10, 25.15, 22.37, 13.87.

HRMS (ESI+): calcd for $C_{17}H_{20}F_5O_2^+$ [M+H] $^+$ 351.1378, found 351.1404.

Hexyl 2,2-difluoro-3-(3-methoxyphenyl)but-3-enoate (4g)



33 mg, 52% yield, light yellow oil;

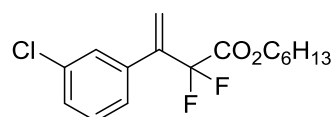
R_f (PE/EA 30:1): 0.45;

1H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, $J = 8.0$ Hz, 1H), 7.00 – 6.96 (m, 1H), 6.95 – 6.93 (m, 1H), 6.91 – 6.86 (m, 1H), 5.90 (t, $J = 1.6$

Hz, 1H), 5.74 (t, $J = 1.5$ Hz, 1H), 4.16 (t, $J = 6.6$ Hz, 2H), 3.80 (s, 3H), 1.58 – 1.48 (m, 2H), 1.31 – 1.14 (m, 6H), 0.87 (t, $J = 6.9$ Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.06; ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.69 (t, $J = 33.9$ Hz), 159.48, 141.16 (t, $J = 22.1$ Hz), 136.10, 129.47, 120.12, 120.12 (t, $J = 8.6$ Hz), 114.22, 113.45, 113.02 (t, $J = 252.0$ Hz), 67.06, 55.22, 31.24, 28.17, 25.20, 22.42, 13.96.

HRMS (ESI+): calcd for $C_{17}H_{22}F_2NaO_3^+$ [M+Na] $^+$ 335.1429, found 335.1418.

Hexyl 3-(3-chlorophenyl)-2,2-difluorobut-3-enoate (4h)



39 mg, 62% yield, light yellow oil;

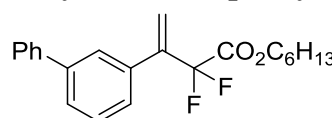
R_f (PE/EA 30:1): 0.50;

1H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.37 – 7.27 (m, 3H), 5.94 (t, $J = 1.6$ Hz, 1H), 5.74 (t, $J = 1.5$ Hz, 1H), 4.18 (t, $J = 6.6$ Hz, 2H),

1.60 – 1.50 (m, 2H), 1.31 – 1.16 (m, 6H), 0.87 (t, $J = 6.9$ Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.31; ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.44 (t, $J = 33.9$ Hz), 140.29 (t, $J = 22.6$ Hz), 136.55 ((t, $J = 1.3$ Hz)), 134.39, 129.70, 128.84, 128.04, 125.99, 121.21 (t, $J = 8.5$ Hz), 112.79 (t, $J = 252.4$ Hz), 67.22, 31.23, 28.17, 25.22, 22.43, 13.96.

HRMS (ESI+): calcd for $C_{16}H_{19}ClF_2NaO_2^+$ [M+Na] $^+$ 339.0934, found 339.0935.

Hexyl 3-([1,1'-biphenyl]-3-yl)-2,2-difluorobut-3-enoate (4i)



49 mg, 68% yield, light yellow oil;

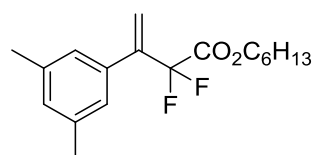
R_f (PE/EA 30:1): 0.55;

1H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.60 – 7.54 (m, 3H), 7.46 – 7.33 (m, 5H), 5.95 (t, $J = 1.7$ Hz, 1H), 5.79 (t, $J = 1.5$ Hz, 1H), 4.16

(t, $J = 6.6$ Hz, 2H), 1.56 – 1.46 (m, 2H), 1.23 – 1.12 (m, 6H), 0.83 (t, $J = 6.8$ Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.99; ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.71 (t, $J = 33.9$ Hz), 141.44, 141.31 (t, $J = 22.2$ Hz), 140.59, 135.29 (t, $J = 1.5$ Hz), 128.86, 128.82, 127.55, 127.46, 127.14, 126.66 – 126.52 (m, 2C), 120.32 (t, $J = 8.5$ Hz), 113.08 (t, $J = 252.1$ Hz), 67.09, 31.20, 28.15, 25.17, 22.38, 13.93.

HRMS (ESI+): calcd for $C_{22}H_{24}F_2NaO_2^+$ [M+Na] $^+$ 381.1637, found 381.1635.

Hexyl 3-(3,5-dimethylphenyl)-2,2-difluorobut-3-enoate (4j)



26 mg, 42% yield, light yellow oil;

R_f (PE/EA 30:1): 0.60;

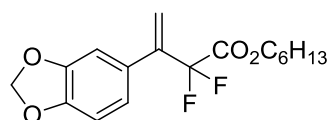
1H NMR (400 MHz, $CDCl_3$) δ 7.01 – 6.97 (m, 3H), 5.86 (t, $J = 1.5$ Hz, 1H), 5.69 (d, $J = 1.5$ Hz, 1H), 4.17 (t, $J = 6.6$ Hz, 2H), 2.31 (s, 6H), 1.58

– 1.50 (m, 2H), 1.30 – 1.17 (m, 6H), 0.87 (t, $J = 6.8$ Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.99;

^{13}C NMR (101 MHz, CDCl_3) δ 163.77 (t, $J = 33.9$ Hz), 141.43 (t, $J = 21.9$ Hz), 137.87, 134.68 (t, $J = 1.5$ Hz), 130.31, 125.50 (t, $J = 1.0$ Hz), 119.64 (t, $J = 8.6$ Hz), 113.11 (t, $J = 252.0$ Hz), 66.95, 31.26, 28.16, 25.19, 22.41, 21.28, 13.95.

HRMS (ESI+): calcd for $\text{C}_{18}\text{H}_{24}\text{F}_2\text{NaO}_2^+ [\text{M}+\text{Na}]^+$ 333.1637, found 333.1624.

Hexyl 3-(benzo[d][1,3]dioxol-5-yl)-2,2-difluorobut-3-enoate (4k)



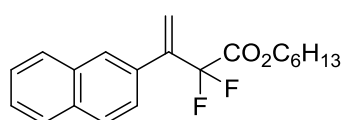
43 mg, 65% yield, light yellow oil;

R_f (PE/EA 30:1): 0.30;

^1H NMR (400 MHz, CDCl_3) δ 6.92 – 6.85 (m, 2H), 6.77 (d, $J = 8.0$ Hz, 1H), 5.97 (s, 2H), 5.83 (t, $J = 1.6$ Hz, 1H), 5.65 (t, $J = 1.6$ Hz, 1H), 4.17 (t, $J = 6.6$ Hz, 2H), 1.59 – 1.51 (m, 2H), 1.30 – 1.16 (m, 6H), 0.87 (t, $J = 6.9$ Hz, 3H); ^{19}F NMR (376 MHz, CDCl_3) δ -102.18; ^{13}C NMR (101 MHz, CDCl_3) δ 163.66 (t, $J = 34.0$ Hz), 148.00, 147.66, 140.69 (t, $J = 22.1$ Hz), 128.58 (t, $J = 1.5$ Hz), 121.70 (t, $J = 1.2$ Hz), 119.33 (t, $J = 8.5$ Hz), 113.01 (t, $J = 252.0$ Hz), 108.28 (t, $J = 1.4$ Hz), 108.17, 101.26, 67.03, 31.23, 28.17, 25.20, 22.41, 13.94.

HRMS (ESI+): calcd for $\text{C}_{17}\text{H}_{20}\text{F}_2\text{NaO}_4^+ [\text{M}+\text{Na}]^+$ 349.1222, found 349.1219.

Hexyl 2,2-difluoro-3-(naphthalen-2-yl)but-3-enoate (4l)



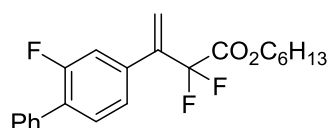
39 mg, 58% yield, light yellow oil;

R_f (PE/EA 30:1): 0.50;

^1H NMR (400 MHz, CDCl_3) δ 7.88 (s, 1H), 7.85 – 7.78 (m, 3H), 7.57 – 7.44 (m, 3H), 6.00 (t, $J = 1.6$ Hz, 1H), 5.86 (t, $J = 1.5$ Hz, 1H), 4.13 (t, $J = 6.6$ Hz, 2H), 1.53 – 1.40 (m, 2H), 1.20 – 1.01 (m, 6H), 0.79 (t, $J = 6.8$ Hz, 3H); ^{19}F NMR (376 MHz, CDCl_3) δ -101.77; ^{13}C NMR (101 MHz, CDCl_3) δ 163.75 (t, $J = 34.1$ Hz), 141.13 (t, $J = 22.0$ Hz), 133.10, 132.97, 132.04, 128.39, 128.14, 127.55, 127.02 (d, $J = 0.8$ Hz), 126.64, 126.45, 125.28 (d, $J = 0.6$ Hz), 120.35 (t, $J = 8.6$ Hz), 113.13 (t, $J = 252.4$ Hz), 67.09, 31.16, 28.14, 25.17, 22.33, 13.94.

HRMS (ESI+): calcd for $\text{C}_{20}\text{H}_{22}\text{F}_2\text{NaO}_2^+ [\text{M}+\text{Na}]^+$ 355.1480, found 355.1460.

Hexyl 2,2-difluoro-3-(2-fluoro-[1,1'-biphenyl]-4-yl)but-3-enoate (4m)



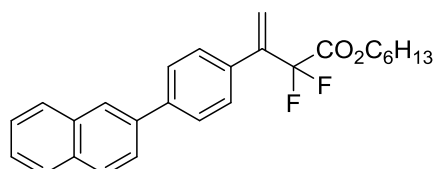
50 mg, 66% yield, light yellow oil;

R_f (PE/EA 30:1): 0.55;

^1H NMR (400 MHz, CDCl_3) δ 7.59 – 7.51 (m, 2H), 7.49 – 7.35 (m, 4H), 7.29 – 7.22 (m, 2H), 5.96 (t, $J = 1.5$ Hz, 1H), 5.81 (t, $J = 1.6$ Hz, 1H), 4.21 (t, $J = 6.6$ Hz, 2H), 1.62 – 1.53 (m, 2H), 1.29 – 1.17 (m, 6H), 0.84 (t, $J = 6.7$ Hz, 3H); ^{19}F NMR (376 MHz, CDCl_3) δ -102.14, -117.35; ^{13}C NMR (101 MHz, CDCl_3) δ 163.52 (t, $J = 33.9$ Hz), 159.38 (d, $J = 248.5$ Hz), 139.93 (td, $J = 22.6, 2.1$ Hz), 135.51 (d, $J = 8.2$ Hz), 135.01 (d, $J = 1.4$ Hz), 130.70 (d, $J = 4.1$ Hz), 129.33 (d, $J = 13.5$ Hz), 128.91 (d, $J = 3.1$ Hz), 128.52, 127.98, 123.65 (d, $J = 3.4$ Hz), 120.85 (t, $J = 8.5$ Hz), 115.72 – 115.39 (m, 1C), 112.85 (t, $J = 252.3$ Hz), 67.24, 31.22, 28.16, 25.22, 22.43, 13.94.

HRMS (ESI+): calcd for $\text{C}_{22}\text{H}_{23}\text{F}_3\text{NaO}_2^+ [\text{M}+\text{Na}]^+$ 399.1542, found 399.1541.

Hexyl 2,2-difluoro-3-(4-(naphthalen-2-yl)phenyl)but-3-enoate (4n)



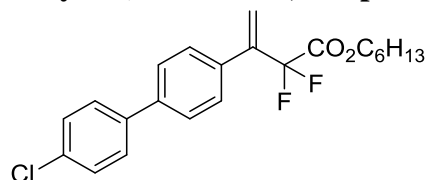
45 mg, 55% yield, light yellow oil;

R_f (PE/EA 30:1): 0.55;

¹H NMR (400 MHz, CDCl₃) δ 8.03 (s, 1H), 7.94 – 7.83 (m, 3H), 7.76 – 7.67 (m, 3H), 7.56 – 7.45 (m, 4H), 5.95 (t, *J* = 1.6 Hz, 1H), 5.81 (t, *J* = 1.5 Hz, 1H), 4.19 (t, *J* = 6.6 Hz, 2H), 1.59 – 1.49 (m, 2H), 1.27 – 1.15 (m, 6H), 0.82 (t, *J* = 6.9 Hz, 3H); **¹⁹F NMR** (376 MHz, CDCl₃) δ -101.97; **¹³C NMR** (101 MHz, CDCl₃) δ 163.76 (t, *J* = 33.9 Hz), 141.38, 140.87 (t, *J* = 22.1 Hz), 137.57, 133.70 (t, *J* = 1.3 Hz), 133.62, 132.75, 128.55, 128.23, 128.18, 127.66, 127.36, 126.41, 126.14, 125.82, 125.25, 119.98 (t, *J* = 8.6 Hz), 113.13 (t, *J* = 252.1 Hz), 67.13, 31.25, 28.18, 25.22, 22.45, 13.96.

HRMS (ESI+): calcd for C₂₆H₂₆F₂NaO₂⁺ [M+Na]⁺ 431.1793, found 431.1783.

Hexyl 3-(4'-chloro-[1,1'-biphenyl]-4-yl)-2,2-difluorobut-3-enoate (4o)



46 mg, 59% yield, light yellow oil;

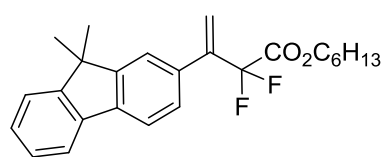
R_f (PE/EA 30:1): 0.55;

¹H NMR (400 MHz, CDCl₃) δ 7.56 – 7.46 (m, 6H), 7.43 – 7.38 (m, 2H), 5.93 (t, *J* = 1.6 Hz, 1H), 5.78 (t, *J* = 1.5 Hz, 1H), 4.18 (t, *J* = 6.6 Hz, 2H), 1.59 – 1.50 (m, 2H), 1.26 –

1.12 (m, 6H), 0.83 (t, *J* = 6.8 Hz, 3H); **¹⁹F NMR** (376 MHz, CDCl₃) δ -102.05; **¹³C NMR** (101 MHz, CDCl₃) δ 163.67 (t, *J* = 33.9 Hz), 140.76 (t, *J* = 22.3 Hz), 140.20, 138.68, 133.98 (t, *J* = 1.3 Hz), 133.74, 128.99, 128.23, 128.21 (t, *J* = 1.1 Hz), 126.91, 120.13 (t, *J* = 8.6 Hz), 113.05 (t, *J* = 252.2 Hz), 67.11, 31.21, 28.15, 25.19, 22.42, 13.92.

HRMS (ESI+): calcd for C₂₂H₂₃ClF₂NaO₂⁺ [M+Na]⁺ 415.1247, found 415.1246.

Hexyl 3-(9,9-dimethyl-9H-fluoren-2-yl)-2,2-difluorobut-3-enoate (4p)



46 mg, 58% yield, light yellow oil;

R_f (PE/EA 30:1): 0.55;

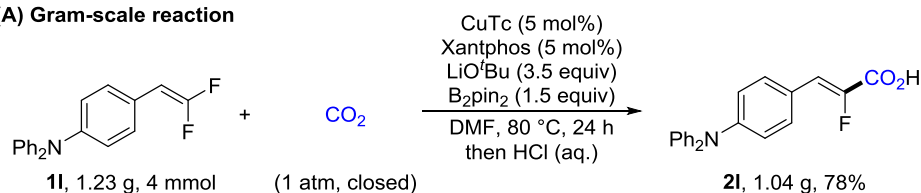
¹H NMR (400 MHz, CDCl₃) δ 7.74 – 7.63 (m, 2H), 7.46 (s, 1H), 7.44 – 7.41 (m, 1H), 7.38 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.36 – 7.28 (m, 2H), 5.93 (t, *J* = 1.6 Hz, 1H), 5.80 (t, *J* = 1.5 Hz, 1H), 4.14 (t,

J = 6.6 Hz, 2H), 1.48 (s, 8H), 1.22 – 1.12 (m, 6H), 0.79 (t, *J* = 6.8 Hz, 3H); **¹⁹F NMR** (376 MHz, CDCl₃) δ -101.62; **¹³C NMR** (101 MHz, CDCl₃) δ 163.79 (t, *J* = 33.9 Hz), 153.88, 153.72, 141.56 (t, *J* = 21.9 Hz), 139.77, 138.42, 133.61 (t, *J* = 1.3 Hz), 127.63, 127.05, 126.70, 122.62, 121.87 (t, *J* = 1.0 Hz), 120.21, 119.89, 119.51 (t, *J* = 8.6 Hz), 113.16 (t, *J* = 252.0 Hz), 67.02, 46.92, 31.20, 28.13, 27.05, 25.16, 22.36, 13.89.

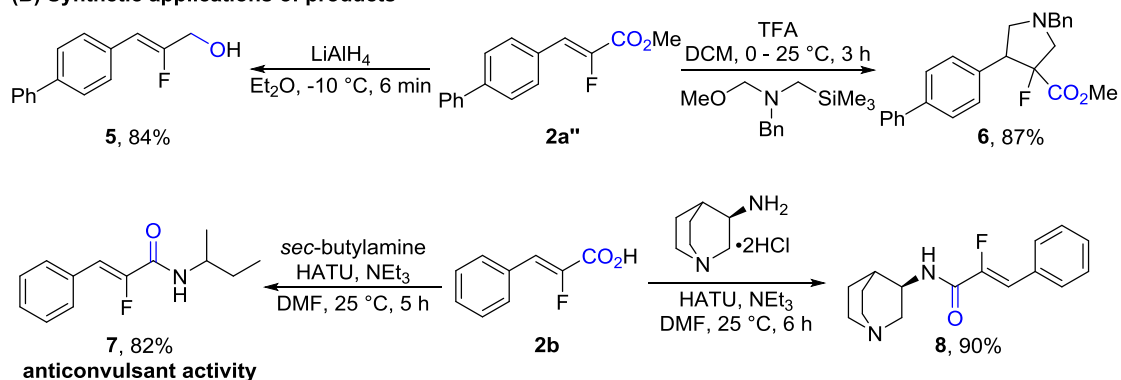
HRMS (ESI+): calcd for C₂₅H₂₈F₂NaO₂⁺ [M+Na]⁺ 421.1950, found 421.1938.

Gram-scale Synthesis and Synthetic Applications of Products

(A) Gram-scale reaction



(B) Synthetic applications of products



Synthesis of 2I in gram scale

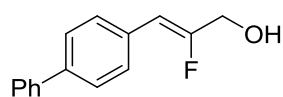
A flame-dried Schlenk flask (250 mL) containing a stirring bar was charged with bis(pinacolato)diboron (1.52 g, 6 mmol, 1.5 equiv) and *gem*-difluoroalkenes **1I** (1.23 g, 4 mmol, 1.0 equiv). The reaction tube was transferred to the glovebox and charged with CuTc (38 mg, 0.2 mmol, 5 mol%), Xantphos (116 mg, 0.2 mmol, 5 mol%) and LiO^tBu (1.12 g, 14 mmol, 3.5 equiv). The reaction tube was moved out of the glovebox and the tube was then evacuated and back-filled with carbon dioxide for 3 times. Subsequently anhydrous DMF (20 mL) were added via syringe under CO₂. Once added, the Schlenk tube was sealed at atmospheric pressure of CO₂ (1 atm). The resulting mixture was stirred for 24 h at 80 °C. After cooling to room temperature, the resulting mixture was diluted with 20 mL EtOAc and quenched by 20 mL 2N HCl. The reaction mixture was extracted by EtOAc (3 x 50 mL) and the combined organic phases were concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (petroleum ether/EtOAc 10/1, then 0.1% AcOH in petroleum ether/EtOAc 8/1~5/1) to give the pure desired product **2I** as a yellow solid (1.04 g, 78% yield).

Synthesis of 5

In a flame-dried Schlenk tube (10 mL) containing a stirring bar, ester **2a''** (51 mg, 0.2 mmol, 1.0 equiv) and lithium aluminium tetrahydride (LiAlH₄, 7.6 mg, 0.2 mmol, 1.0 equiv) were added. The tube was then evacuated and back-filled with N₂ for 3 times. To this mixture was added dried diethyl ether (2 mL) via syringe at -10 °C and left stirred for 6 min. After the completion of the reaction was observed by TLC, the reaction mixture was quenched with water (11 μL), 15% NaOH (11 μL) and water (33 μL) sequentially. The mixture was filtered and then reduced in vacuo. Purification by a silica gel flash column chromatography (petroleum ether/EtOAc 10/1 to 2/1) to give the pure desired product **5** as a white solid (38 mg, 84% yield).

(Z)-3-([1,1'-biphenyl]-4-yl)-2-fluoroprop-2-en-1-ol (**5**)

38 mg, 84% yield, white solid; mp 134–135 °C;



R_f (PE/Ea 3/1): 0.55;

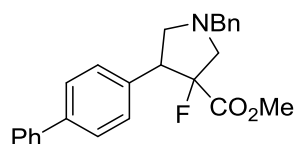
¹H NMR (400 MHz, DMSO-*d*₆) δ 7.72 – 7.66 (m, 4H), 7.61 – 7.57 (m, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.33 (m, 1H), 5.98 (d, *J* = 40.9 Hz, 1H), 5.48 (t, *J* = 5.9 Hz, 1H), 4.14 (dd, *J* = 13.3, 5.9 Hz, 1H); **¹⁹F NMR** (376 MHz, DMSO-*d*₆) δ -110.61; **¹³C NMR** (101 MHz, DMSO-*d*₆) δ 160.73 (d, *J* = 268.1 Hz), 139.97, 139.13 (d, *J* = 2.2 Hz), 132.53 (d, *J* = 2.3 Hz), 129.40, 129.29 (d, *J* = 7.2 Hz), 127.95, 127.24, 126.92, 105.66 (d, *J* = 5.3 Hz), 60.10 (d, *J* = 32.2 Hz).

HRMS (ESI-): calcd for C₁₅H₁₂FO⁻ [M-H]⁻ 227.0878, found 227.0881.

Synthesis of 6

In a flame-dried reaction tube (10 mL) containing a stirring bar, to a solution of **2a** (51 mg, 0.2 mmol, 1.0 equiv), *N*-benzyl-1-methoxy-*N*-((trimethylsilyl)methyl)methanamine (190 mg, 0.8 mmol, 4.0 equiv) in dichloromethane (1 mL) was added TFA (2.3 mg, 0.02 mmol, 10 mol%) at 0 °C. And the resultant mixture was stirred at 25 °C for a further 3 h. The mixture was concentrated to give the crude product. The residue was purified by a silica gel flash column chromatography (petroleum ether/EtOAc 30/1~10/1~7/1) to give the pure desired product **6** as a white solid (68 mg, 87% yield).

Methyl 4-([1,1'-biphenyl]-4-yl)-1-benzyl-3-fluoropyrrolidine-3-carboxylate (6)



68 mg, 87% yield, white solid; mp 132–133 °C;

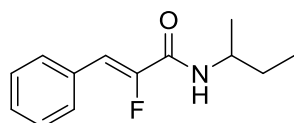
R_f (PE/Ea 10/1): 0.25;

¹H NMR (400 MHz, CDCl₃) δ 7.58 – 7.49 (m, 4H), 7.45 – 7.37 (m, 4H), 7.36 – 7.24 (m, 6H), 4.00 – 3.72 (m, 6H), 3.62 – 3.48 (m, 1H), 3.32 – 3.24 (m, 1H), 3.17 – 2.99 (m, 2H); **¹⁹F NMR** (376 MHz, CDCl₃) δ -160.62; **¹³C NMR** (101 MHz, CDCl₃) δ 170.66 (d, *J* = 28.1 Hz), 140.78, 140.47, 138.43, 133.66 (d, *J* = 3.4 Hz), 129.53 (d, *J* = 1.4 Hz), 128.75, 128.69, 128.44, 127.28, 127.09, 100.08 (d, *J* = 199.7 Hz), 63.97 (d, *J* = 24.6 Hz), 60.20, 57.81, 52.91, 52.29 (d, *J* = 20.1 Hz). **HRMS (ESI+)**: calc. for C₂₅H₂₅FNO₂⁺ [M+H]⁺ 390.1864, found 390.1864.

Synthesis of 7

In a flame-dried Schlenk tube (10 mL) containing a stirring bar, acid **2b** (33 mg, 0.2 mmol) and *o*-(7-Azabenzotriazol-1-yl)-*N,N,N',N'*-tetramethyluronium hexafluorophosphate (HATU, 0.4 mmol, 2 equiv) were added, the tube was then evacuated and back-filled with N₂ for 3 times. Subsequently, *sec*-butylamine (0.3 mmol, 1.5 equiv), NEt₃ (0.6 mmol, 3 equiv) and DMF (2 mL) was added via syringes under N₂. The resulting mixture was stirred for 5 h at 25 °C. The reaction was quenched with H₂O and extracted with ethyl acetate for three times. The combined organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by silica chromatography (PE/EtOAc 10/1) to give the product **7** as a white solid (36 mg, 82% yield).

(Z)-N-(sec-butyl)-2-fluoro-3-phenylacrylamide (7)



36 mg, 82% yield, white solid; mp 84–85 °C;

R_f (PE/Ea 10/1): 0.35;

¹H NMR (400 MHz, CDCl₃) δ 7.64 – 7.55 (m, 2H), 7.44 – 7.30 (m, 3H), 6.93 (d, *J* = 39.5 Hz, 1H), 6.16 (s, 1H), 4.11 – 4.00 (m, 1H), 1.56 (p, *J* = 7.3 Hz, 2H), 1.22 (d, *J* = 6.6 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H); **¹⁹F NMR** (376 MHz, CDCl₃) δ -129.29;

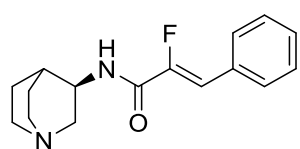
^{13}C NMR (101 MHz, CDCl_3) δ 159.81 (d, $J = 28.7$ Hz), 150.21 (d, $J = 275.7$ Hz), 131.44 (d, $J = 3.5$ Hz), 130.01 (d, $J = 7.6$ Hz), 129.07 (d, $J = 2.6$ Hz), 128.70, 113.27 (d, $J = 4.6$ Hz), 46.91, 29.63, 20.37, 10.37.

HRMS (ESI+): calc. for $\text{C}_{13}\text{H}_{17}\text{FNO}^+$ $[\text{M}+\text{H}]^+$ 222.1289, found 222.1285.

Synthesis of 8

In a flame-dried Schlenk tube (10 mL) containing a stirring bar, acid **2b** (33 mg, 0.2 mmol) and *o*-(7-Azabenzotriazol-1-yl)-*N,N,N',N'*-tetramethyluronium hexafluorophosphate (HATU, 0.4 mmol, 2 equiv) were added, the tube was then evacuated and back-filled with N_2 for 3 times. Subsequently, (*R*)-3-Aminoquinuclidine dihydrochloride (0.2 mmol, 1.0 equiv), NEt_3 (0.8 mmol, 4 equiv) and DMF (2 mL) was added via syringes under N_2 . The resulting mixture was stirred for 6 h at 25 °C. The reaction was quenched by 2 mL 1N aqueous NaOH and extracted with ethyl acetate for three times. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by neutral aluminum oxide chromatography ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ 50/1~30/1) to give the product **7** as a light yellow solid (50 mg, 91% yield).

(*R,Z*)-2-fluoro-3-phenyl-*N*-(quinuclidin-3-yl)acrylamide (**8**)



49 mg, 90% yield, light yellow solid; mp 64–65 °C;

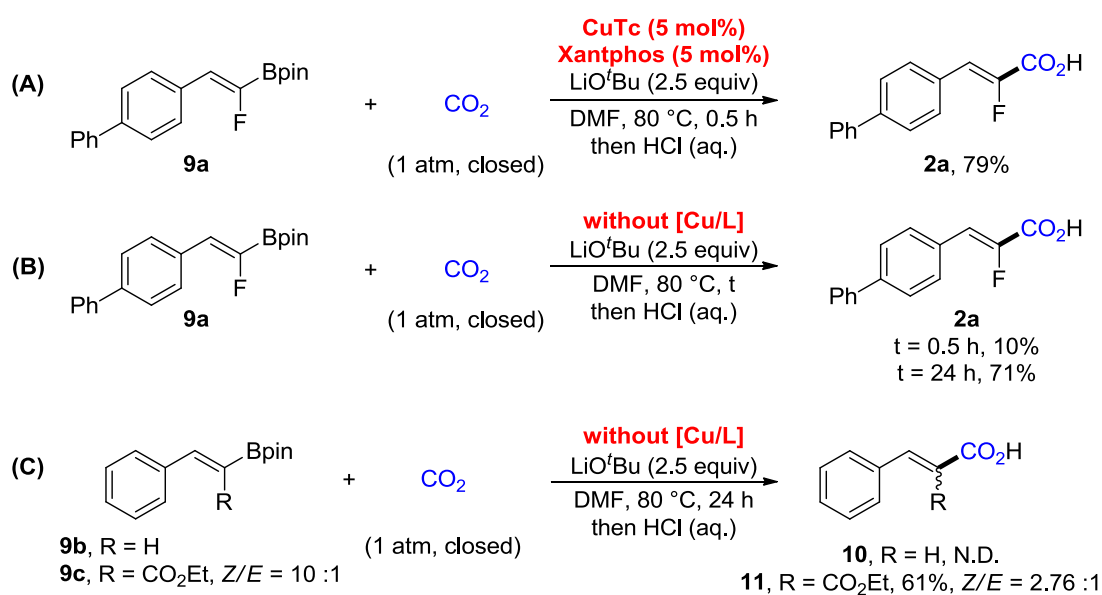
R_f ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ 30/1): 0.45;

^1H NMR (400 MHz, CDCl_3) δ 7.61 – 7.55 (m, 2H), 7.40 – 7.29 (m, 3H), 6.91 (d, $J = 39.5$ Hz, 1H), 6.55 (s, 1H), 4.05 (s, 1H), 3.38 (dd, $J = 14.0$, 9.7 Hz, 1H), 2.96 – 2.74 (m, 4H), 2.57 (dd, $J = 14.2$, 4.3 Hz, 1H), 1.97 (d, $J = 2.8$ Hz, 1H), 1.74 – 1.63 (m, 3H), 1.55 – 1.43 (m, 1H); ^{19}F NMR (376 MHz, CDCl_3) δ -129.36; ^{13}C NMR (101 MHz, CDCl_3) δ 160.33 (d, $J = 29.0$ Hz), 149.95 (d, $J = 275.1$ Hz), 131.28 (d, $J = 3.5$ Hz), 130.05 (d, $J = 7.6$ Hz), 129.21 (d, $J = 2.5$ Hz), 128.73, 113.53 (d, $J = 4.4$ Hz), 55.83, 47.36, 46.82, 46.60, 25.72, 25.65, 20.08.

HRMS (ESI+): calc. for $\text{C}_{16}\text{H}_{20}\text{FN}_2\text{O}^+$ $[\text{M}+\text{H}]^+$ 275.1554, found 275.1549.

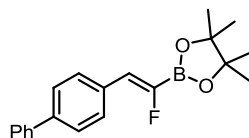
Mechanistic Studies

Control Experiments (Figure 4)



9a, **9b** and **9c** were synthesized according to literatures.^[7]

(Z)-2-(2-([1,1'-biphenyl]-4-yl)-1-fluorovinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9a)



White solid; R_f (PE/EA 10/1): 0.2;

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.70 (d, $J = 8.3$ Hz, 2H), 7.60 (t, $J = 7.3$ Hz, 4H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.35 (t, $J = 7.3$ Hz, 1H), 6.43 (d, $J = 46.8$ Hz, 1H), 1.35 (s, 12H); $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -123.24 (d, $J = 46.7$ Hz);

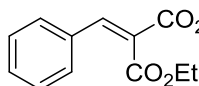
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 141.03 (d, $J = 2.7$ Hz), 140.4, 131.91, 130.32 (d, $J = 8.1$ Hz), 128.81, 127.50, 127.15, 127.00, 123.46, 84.86, 24.75.

The spectroscopic data correspond to those previously reported in the literature.^[7a]

Experimental procedures of Figure 4

A flame-dried Schlenk tube (25 mL) containing a stirring bar was charged with **9** (0.40 mmol, 1.0 equiv for non-liquid substrates). The reaction tube was transferred to the glovebox and charged with LiO^tBu (80 mg, 1.0 mmol, 2.5 equiv) [For Figure 4A, CuTc (3.8 mg, 0.02 mmol, 5 mol%), Xantphos (11.6 mg, 0.02 mmol, 5 mol%) were added]. The reaction tube was moved out of the glovebox and the tube was then evacuated and back-filled with carbon dioxide for 3 times. Subsequently anhydrous DMF (2 mL), **9** (0.40 mmol, 1.0 equiv for liquid substrates) were added via syringes under CO_2 . Once added, the Schlenk tube was sealed at atmospheric pressure of CO_2 (1 atm). The resulting mixture was stirred for the corresponding time at 80 °C (380 r/min). After cooling to room temperature, the resulting mixture was diluted with 2 mL EtOAc and quenched by 2 mL 2N HCl. The reaction mixture was extracted by EtOAc (3 x 5 mL) and the combined organic phases were concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (petroleum ether/EtOAc 10/1, then 0.1% AcOH in petroleum ether/EtOAc 5/1~3/1) to give the desired product.

(Z)-2-(ethoxycarbonyl)-3-phenylacrylic acid (11)



54 mg, 61% yield; light yellow oil; R_f (PE/EA 1/1): 0.2;

$^1\text{H NMR}$ (400 MHz, $\text{DMSO}-d_6$) δ 13.46 (s, 1H), 7.68 (s, 1H), 7.53 – 7.43 (m, 5H), 4.27 (q, $J = 7.1$ Hz, 2H), 1.21 (t, $J = 7.1$ Hz, 3H). The *Z/E* ratio was

determined by $^1\text{H NMR}$ analysis of reaction mixture. (The *Z/E* isomers cannot be separated completely.)

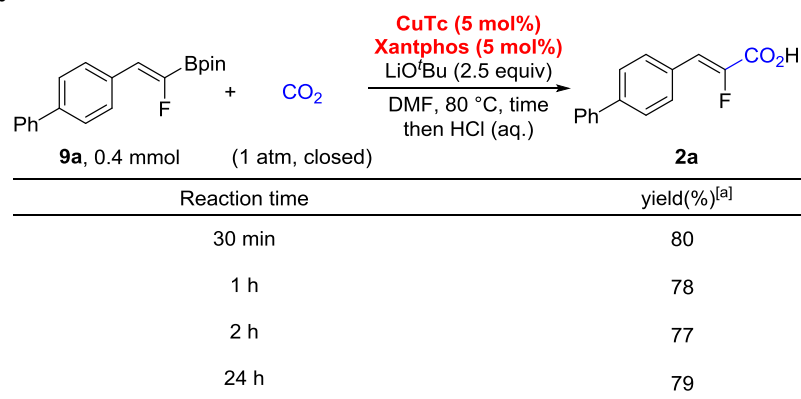
LRMS (ESI-): calcd for $\text{C}_{12}\text{H}_{11}\text{O}_4^-$ [$\text{M}-\text{H}$] 219.07, found 218.74.

The spectroscopic data correspond to those previously reported in the literature.^[8]

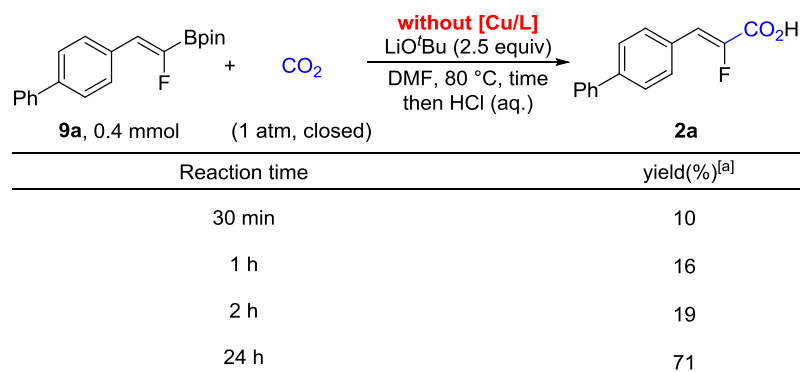
Determination of Metal Element Contents in Figure 4B

Element	Ag3280	Co2388	Cu3247	Fe2599	Mn2576
Units	ppm	ppm	ppm	ppm	ppm
Avg	0.0305	0.0587	0.0059	0.0696	0.0039
Element	Ni2216	Pd3242	Rh3434	Ru2402	Ni2316
Units	ppm	ppm	ppm	ppm	ppm
Avg	0.8482	0.7637	0.0120	0.0707	0.0440

Preliminary Kinetic Studies

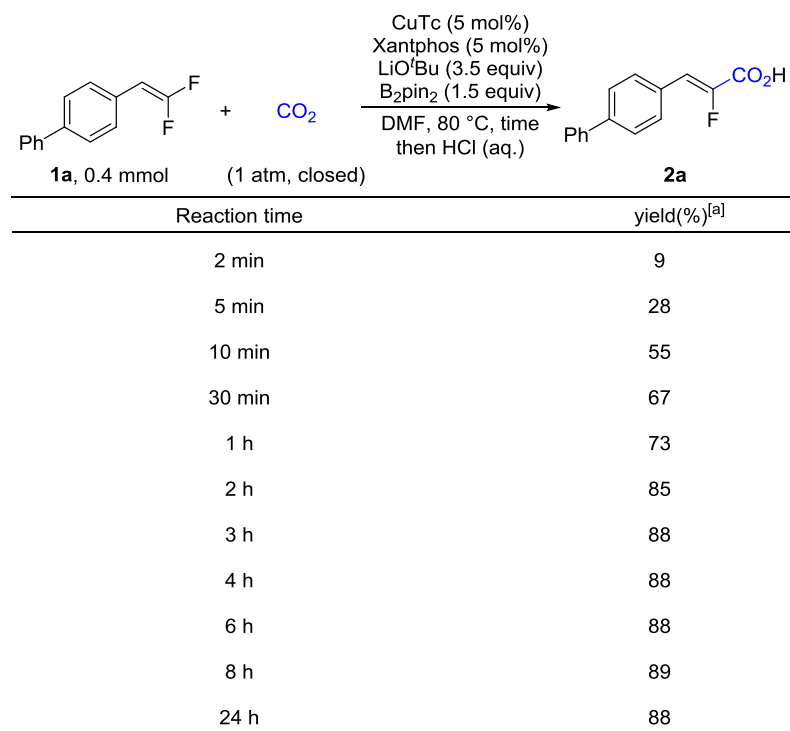


[a] Yields were determined by UPLC using anisole as an internal standard.



[a] Yields were determined by UPLC using anisole as an internal standard.

Figure S1. Preliminary kinetic studies of **9a**.



[a] Yields were determined by UPLC using anisole as an internal standard.

Figure S2. Preliminary kinetic studies of **1a** under standard reaction conditions.

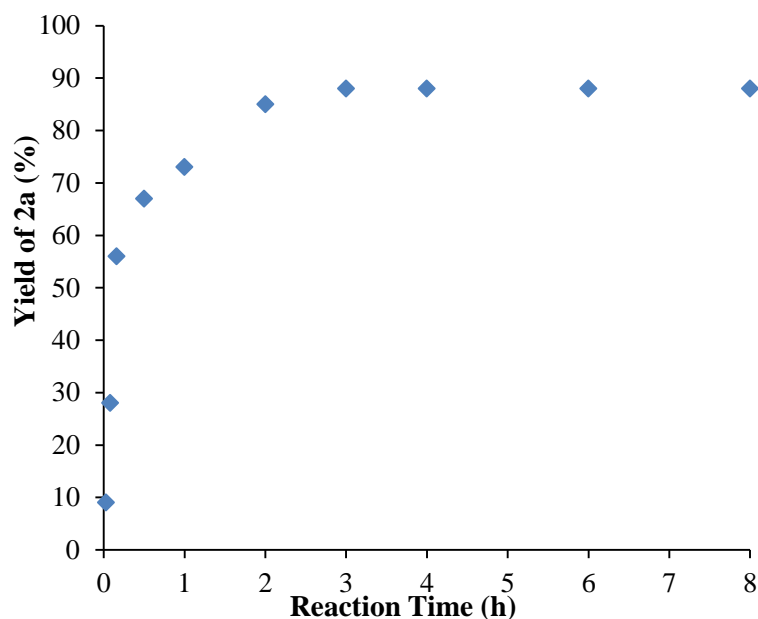
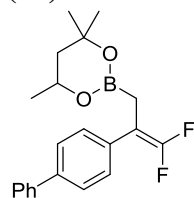


Figure S3. Preliminary kinetic studies of **1a**

Control Experiments of **12**

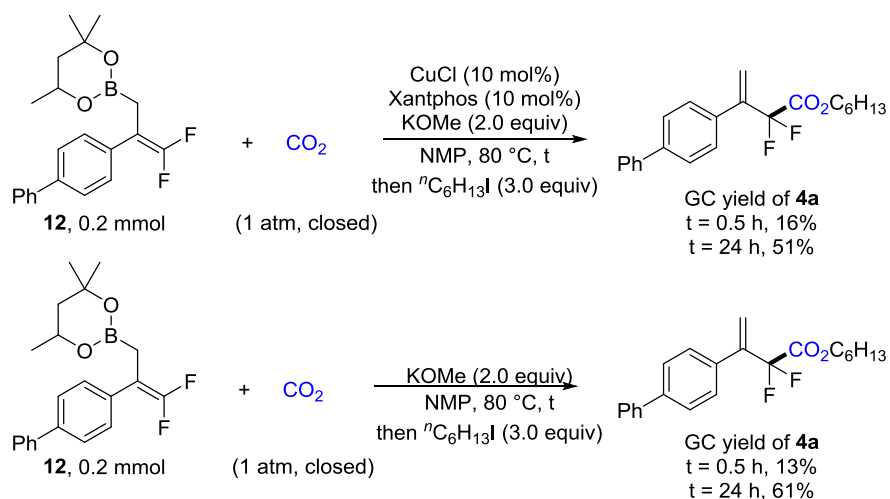
Fluorinated boronate ester **12** were synthesized according to literatures using Bis(hexylene glycolato)diboron instead of B_2pin_2 .^[2]

2-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (**12**)



light yellow oil; R_f (PE/EA 30:1): 0.25;

1H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 4H), 7.47 – 7.40 (m, 4H), 7.36 – 7.30 (m, 1H), 4.12 (dq, $J = 12.2, 6.1, 3.0$ Hz, 1H), 1.84 (t, $J = 2.7$ Hz, 2H), 1.71 (dd, $J = 13.9, 3.0$ Hz, 1H), 1.36 (dd, $J = 13.7, 11.8$ Hz, 1H), 1.19 (s, 6H), 1.17 (d, $J = 6.2$ Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.26 (d, $J = 46.7$ Hz), -92.80 (d, $J = 46.7$ Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.32 (dd, $J = 288.9, 284.3$ Hz), 140.86, 139.37, 135.18 (t, $J = 4.4$ Hz), 128.76, 128.38 (t, $J = 3.7$ Hz), 127.22, 126.99, 126.70, 89.55 (dd, $J = 23.8, 13.7$ Hz), 71.01, 64.97, 45.82, 31.04, 27.84, 23.00. GC-MS (EI): calcd for $C_{21}H_{23}BF_2O_2$ m/z 356.2, found 356.2.

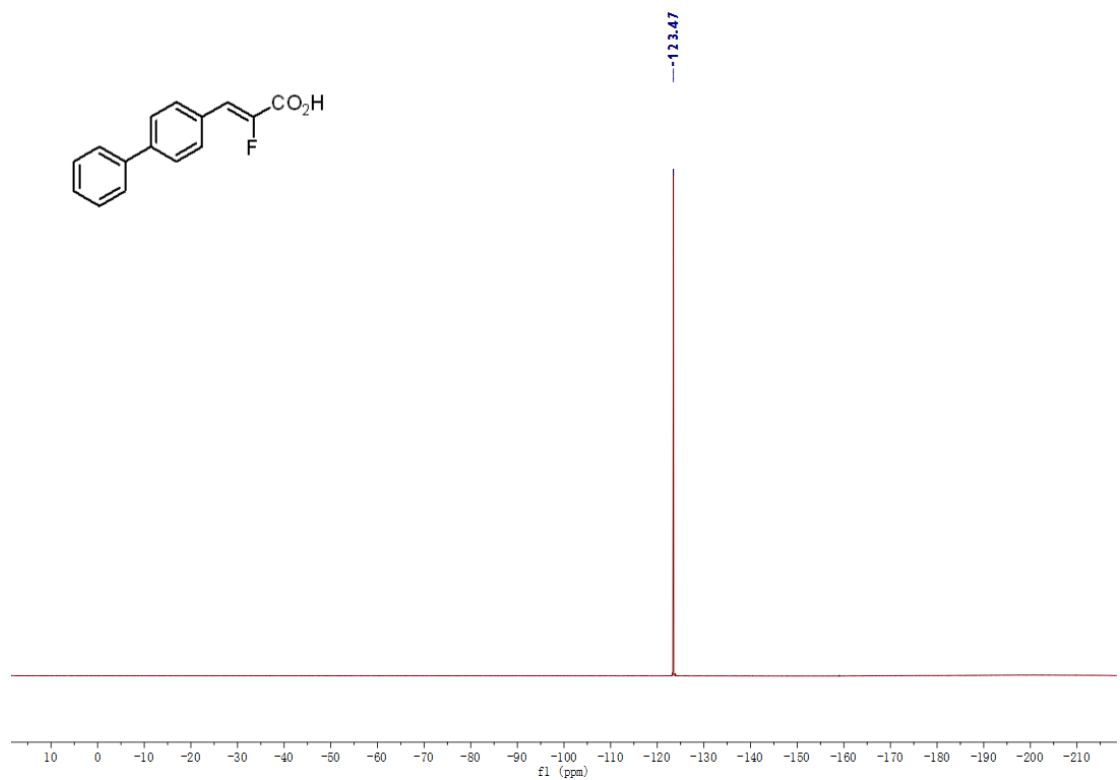
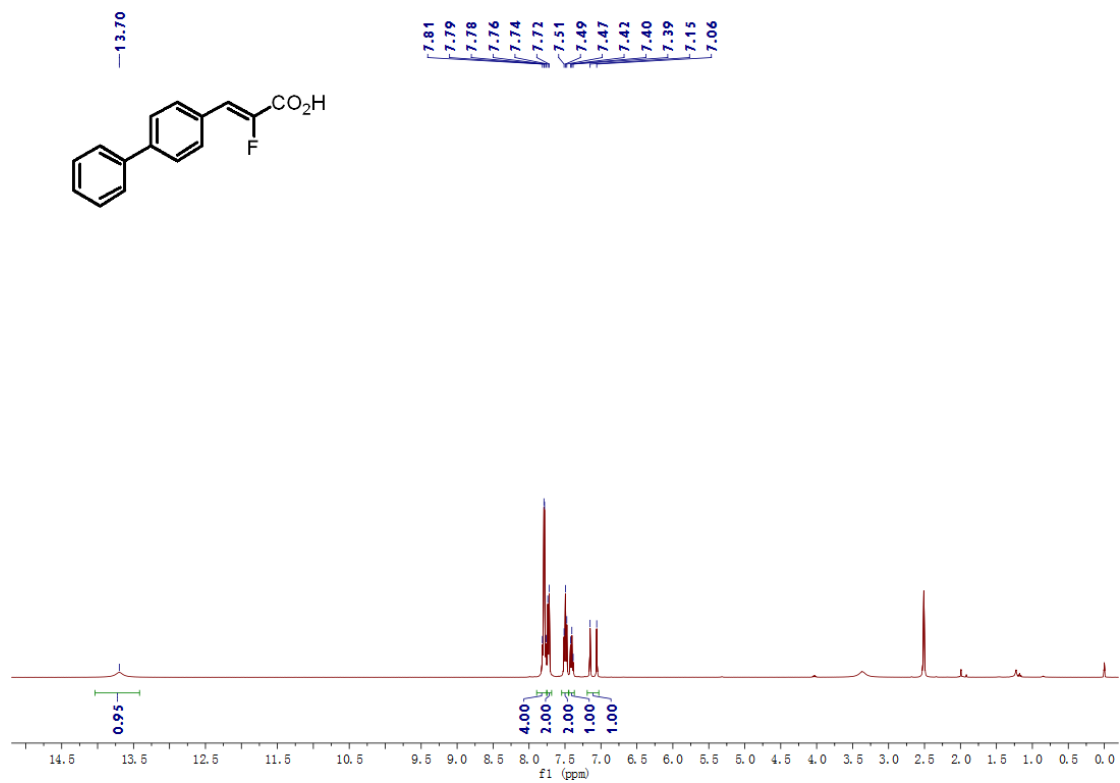


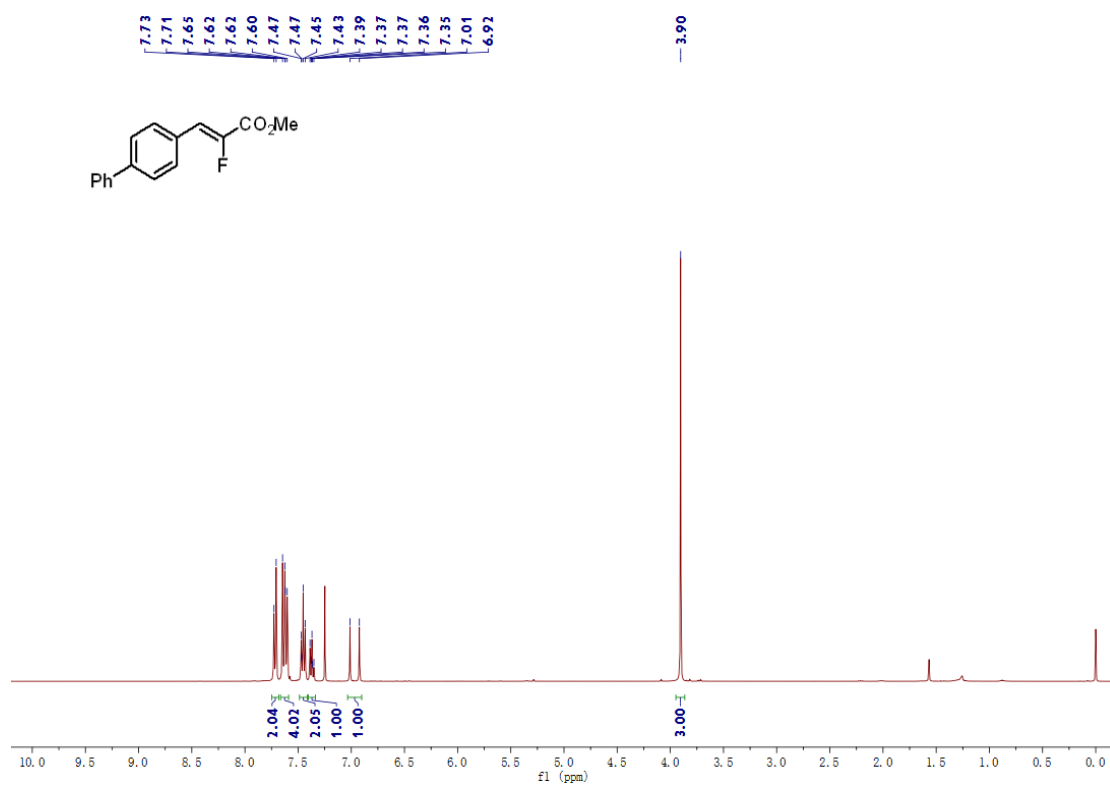
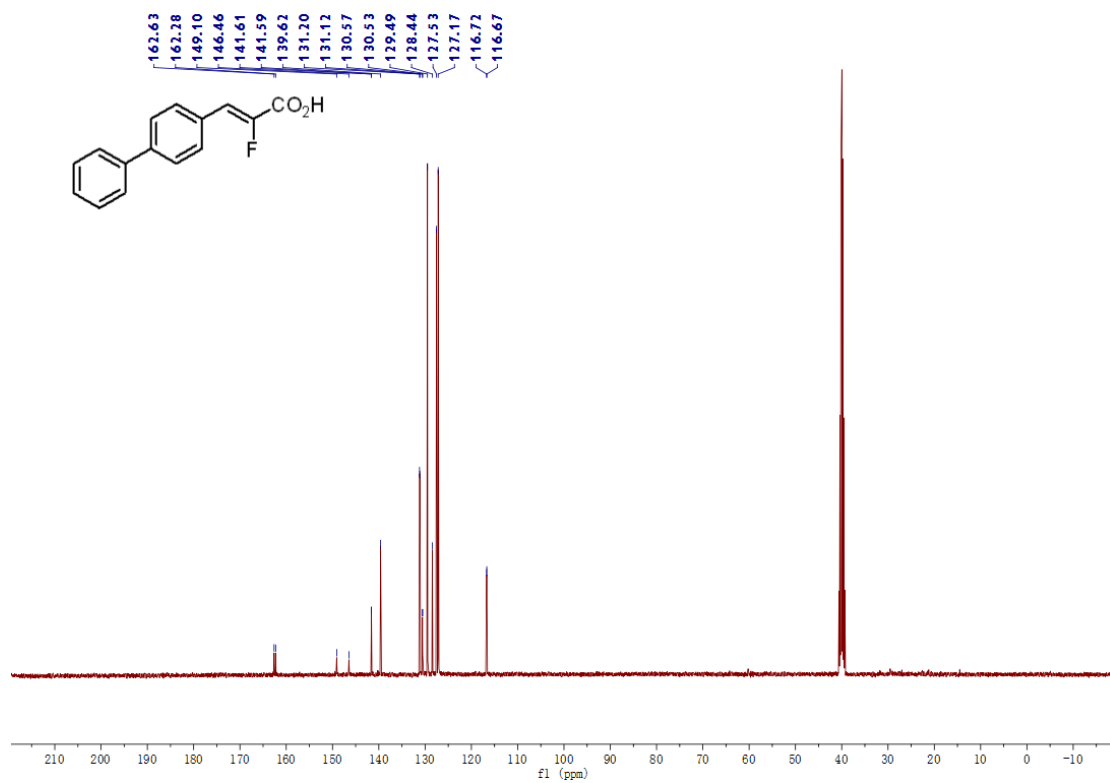
When **12** was subjected to the carboxylation reaction, the desired product **4a** was obtained in similar yields with or without copper catalysis. Moreover, preliminary kinetic studies indicated that base should dominate the carboxylation of fluorinated boronate ester with CO₂.

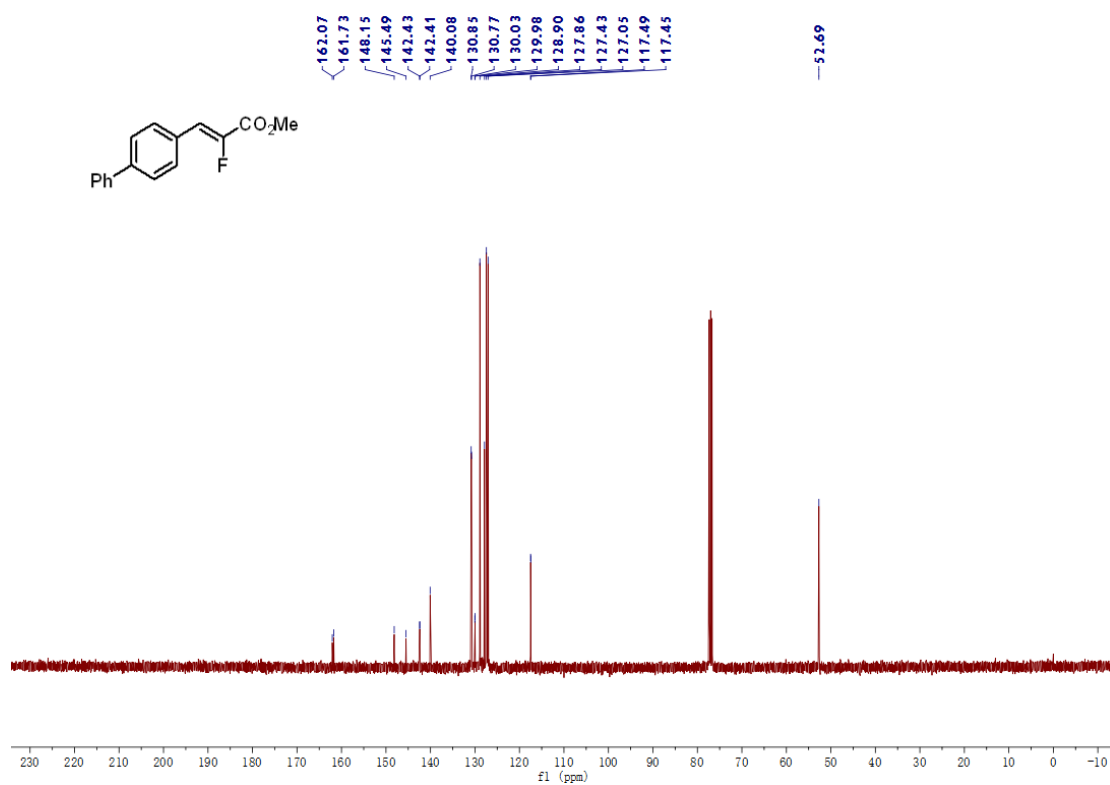
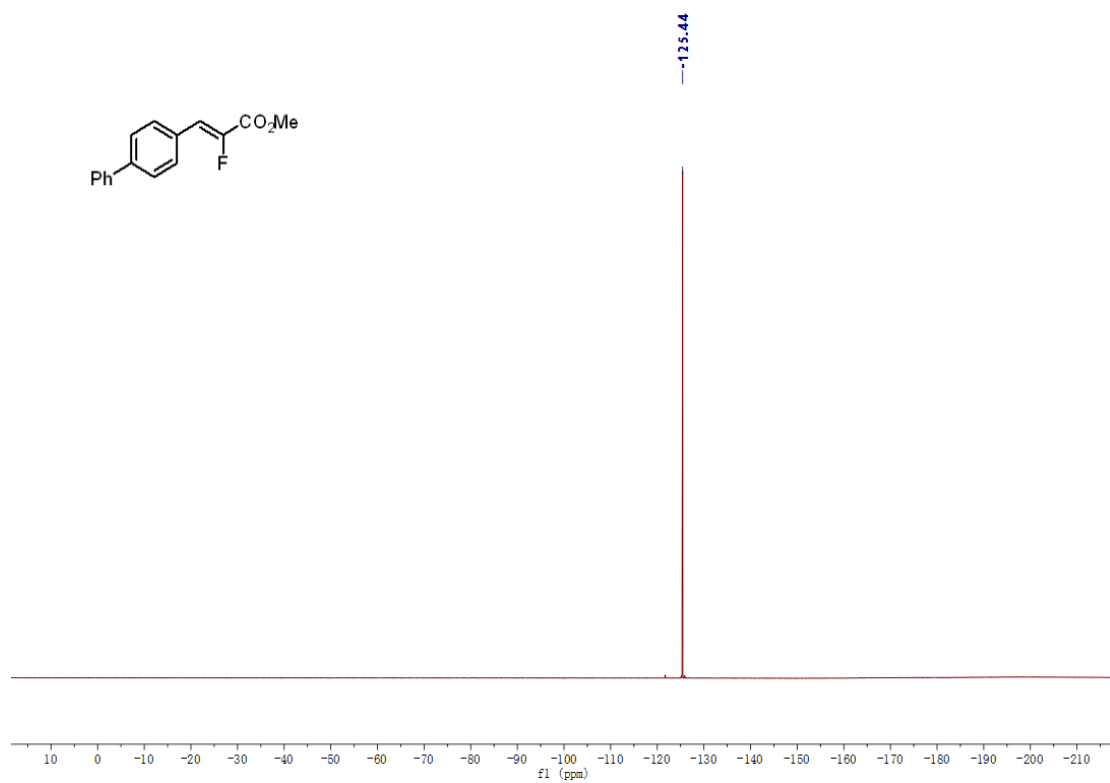
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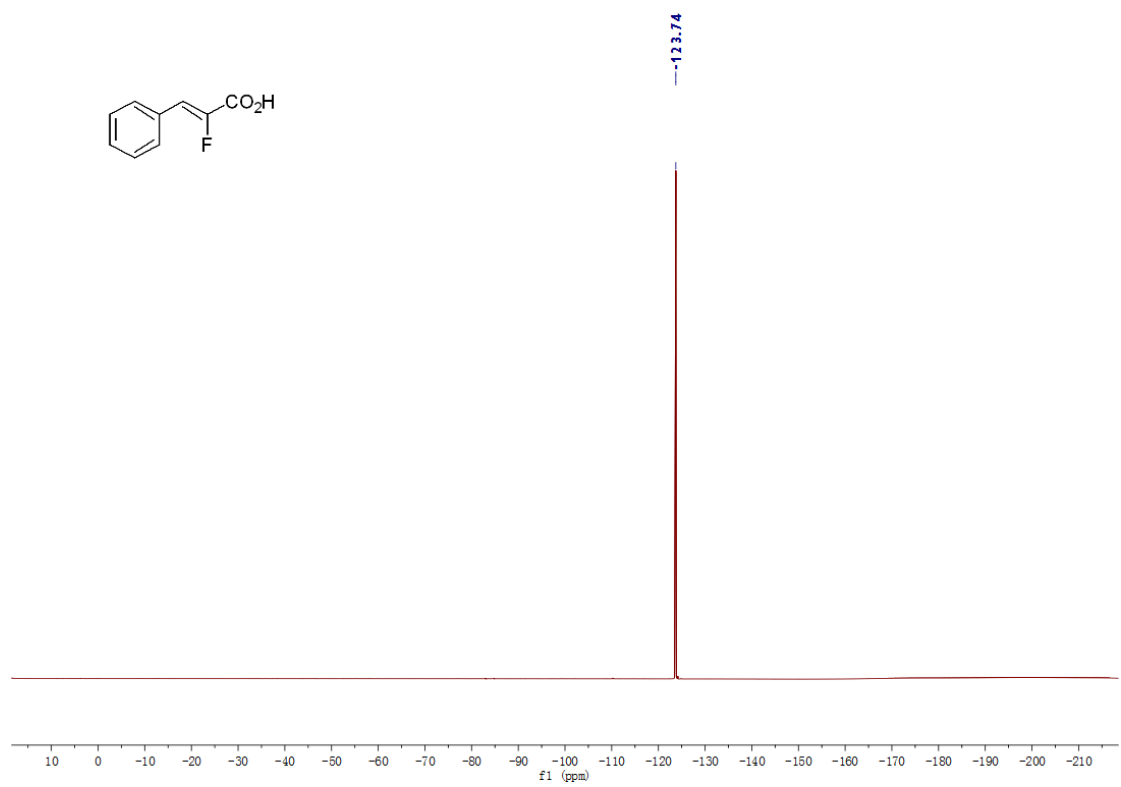
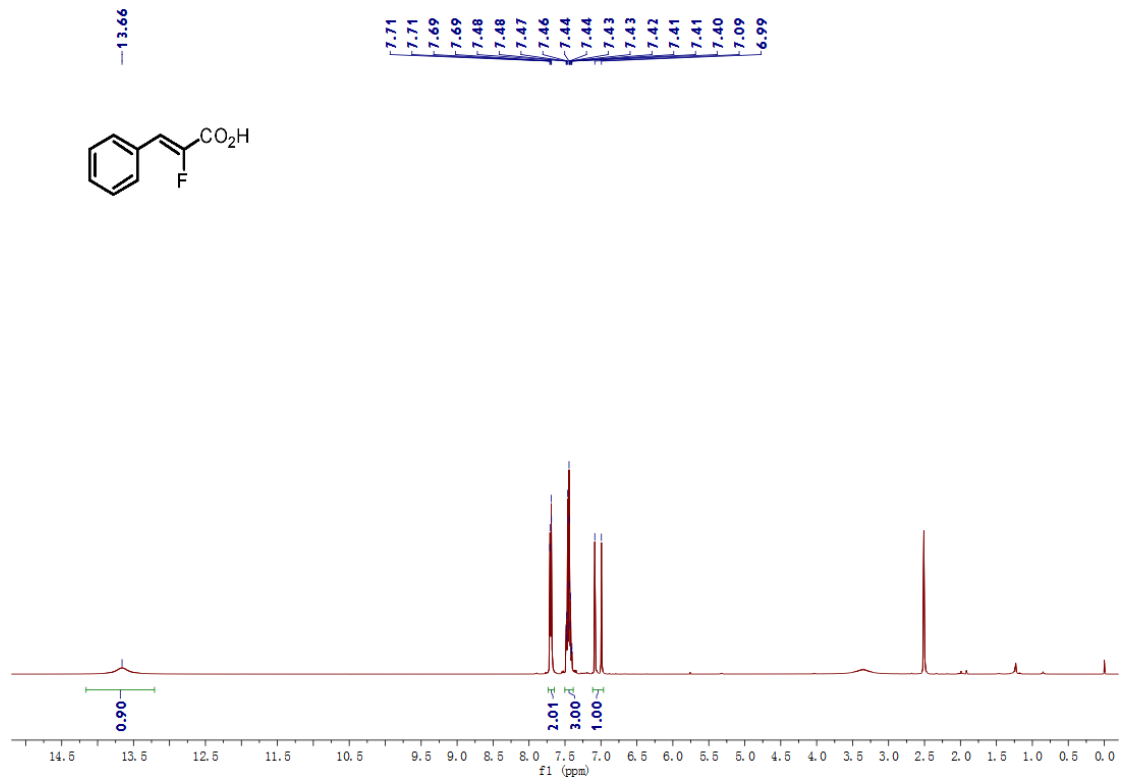
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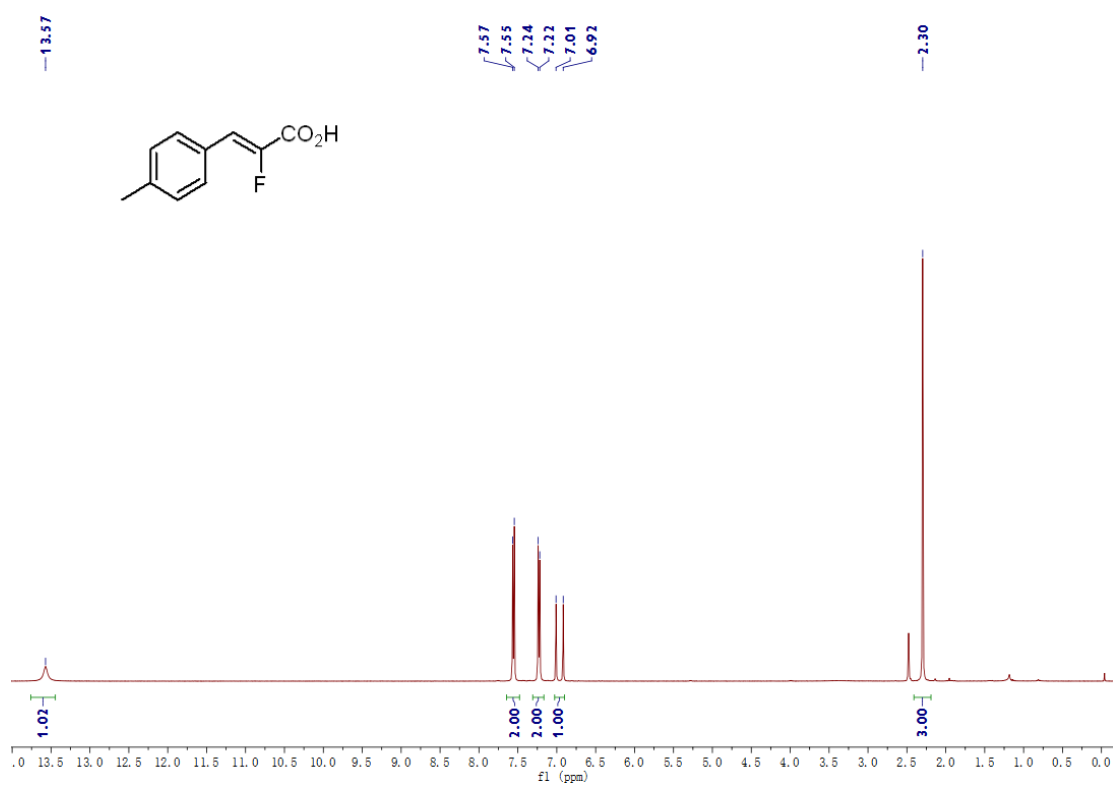
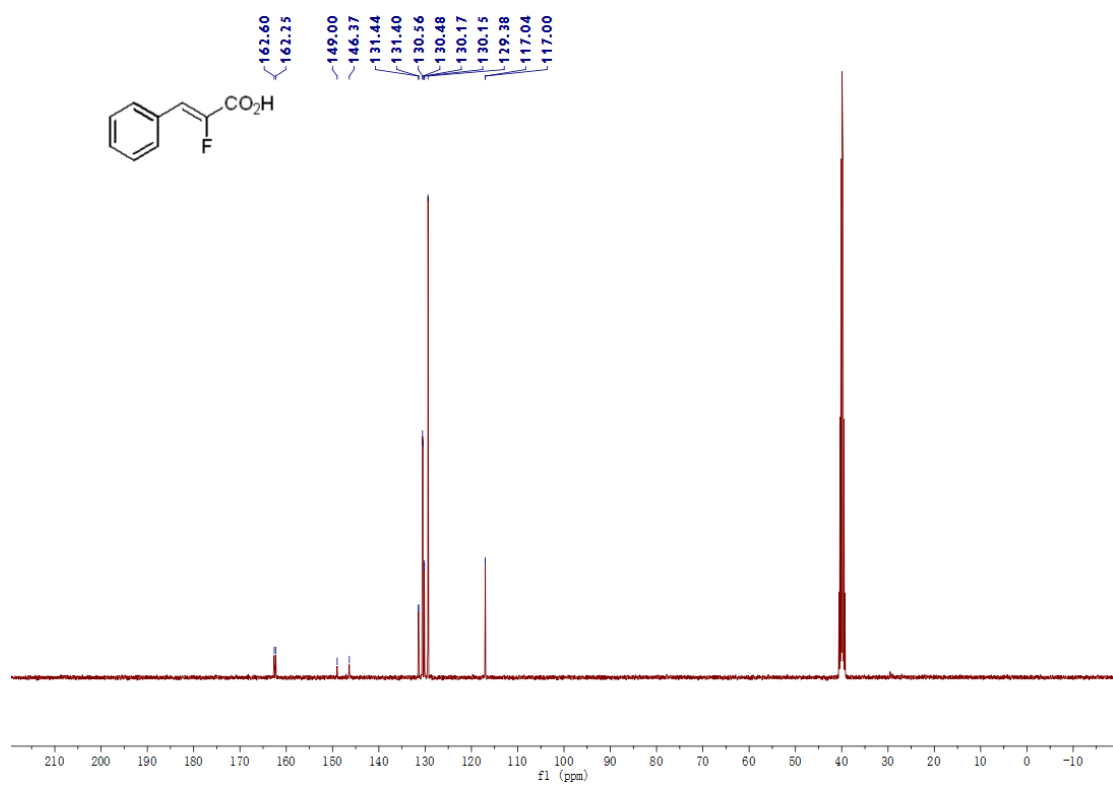
^1H NMR, ^{19}F NMR and ^{13}C NMR Spectra

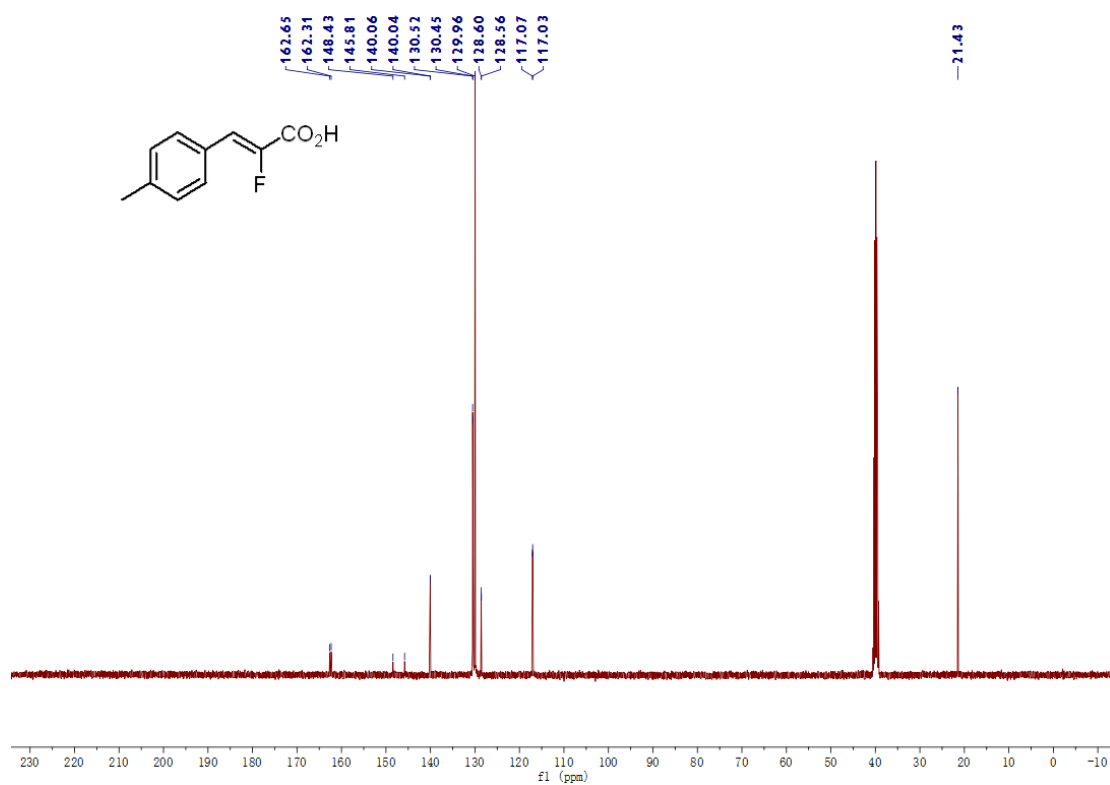
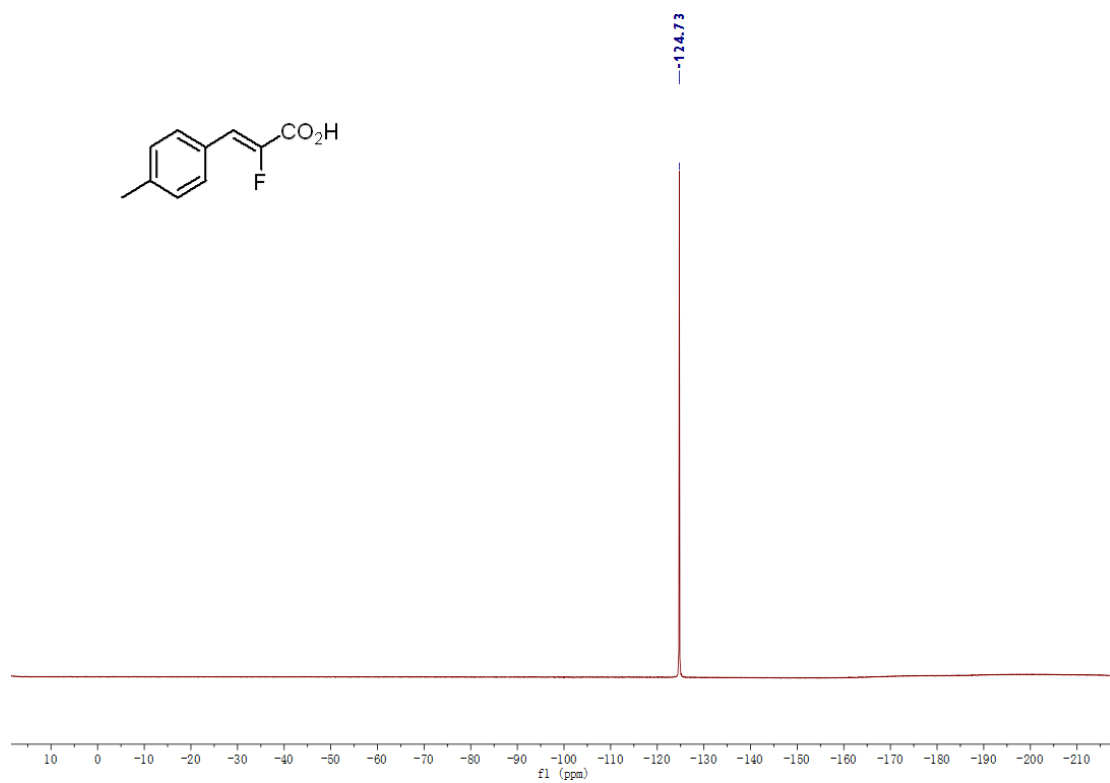


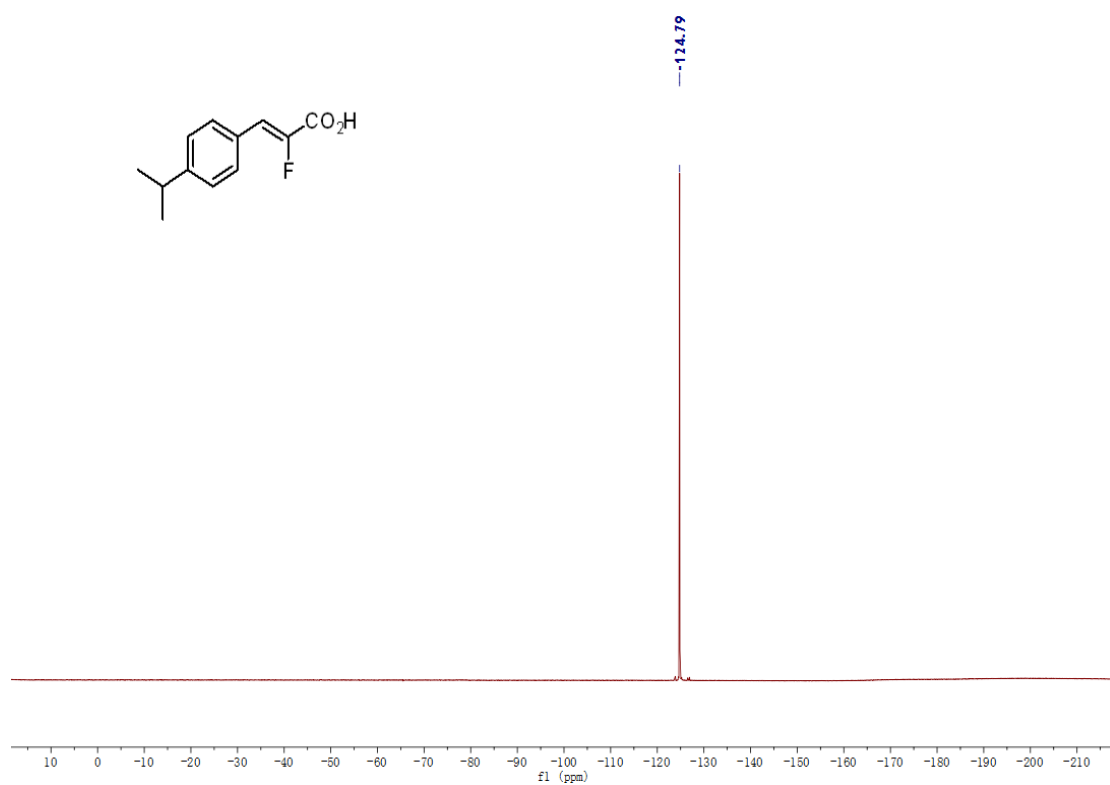
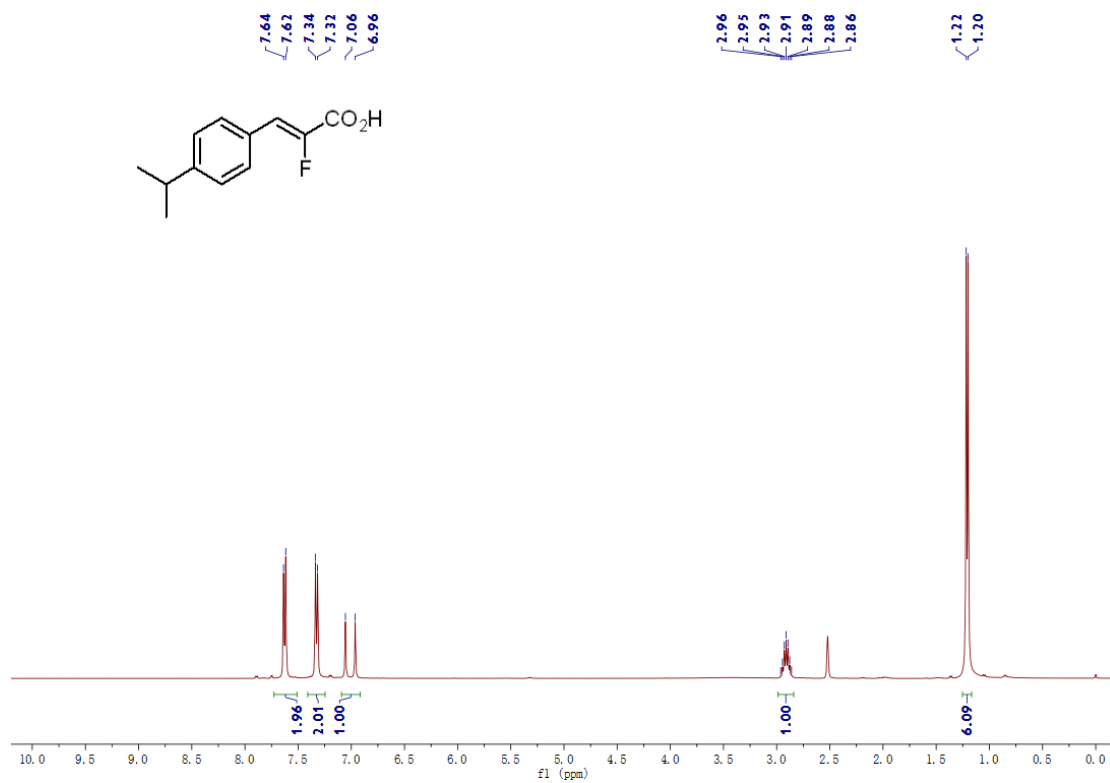


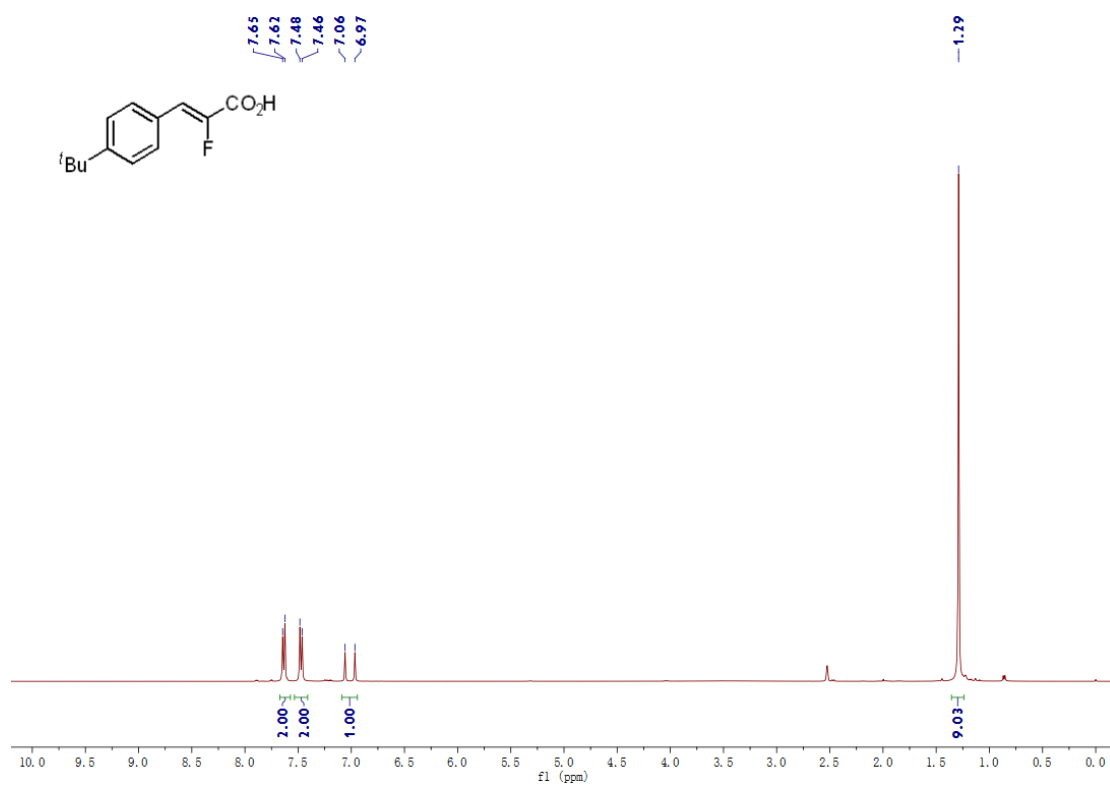
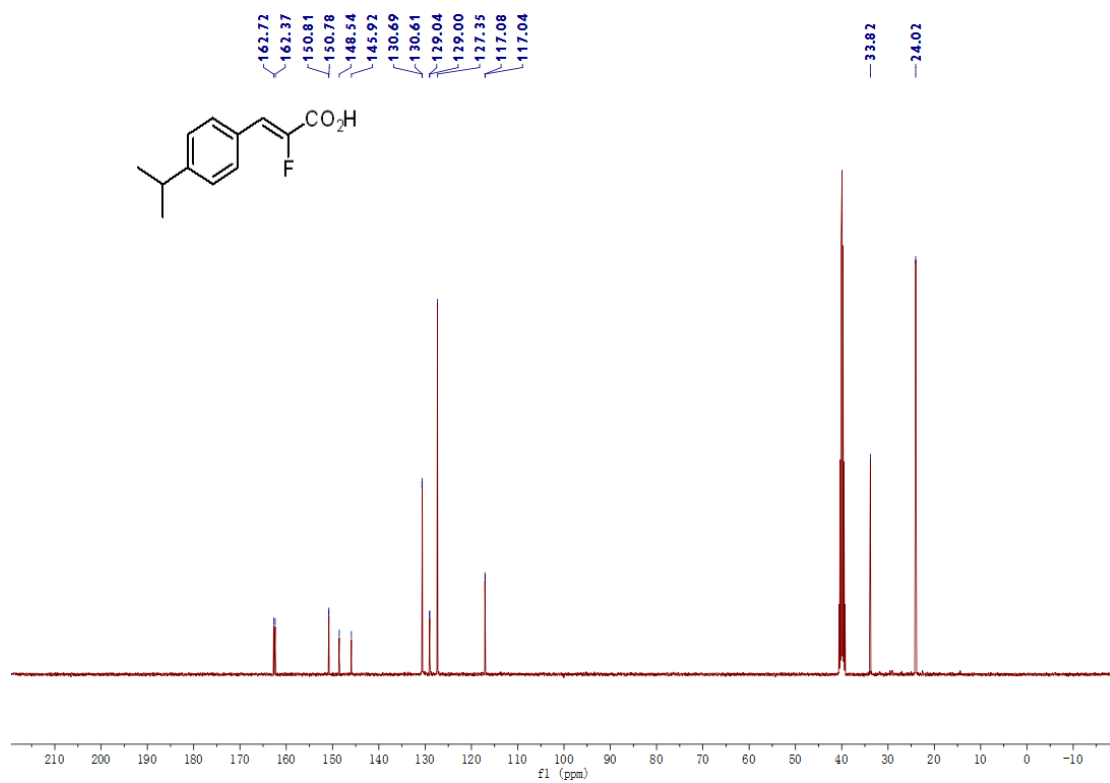


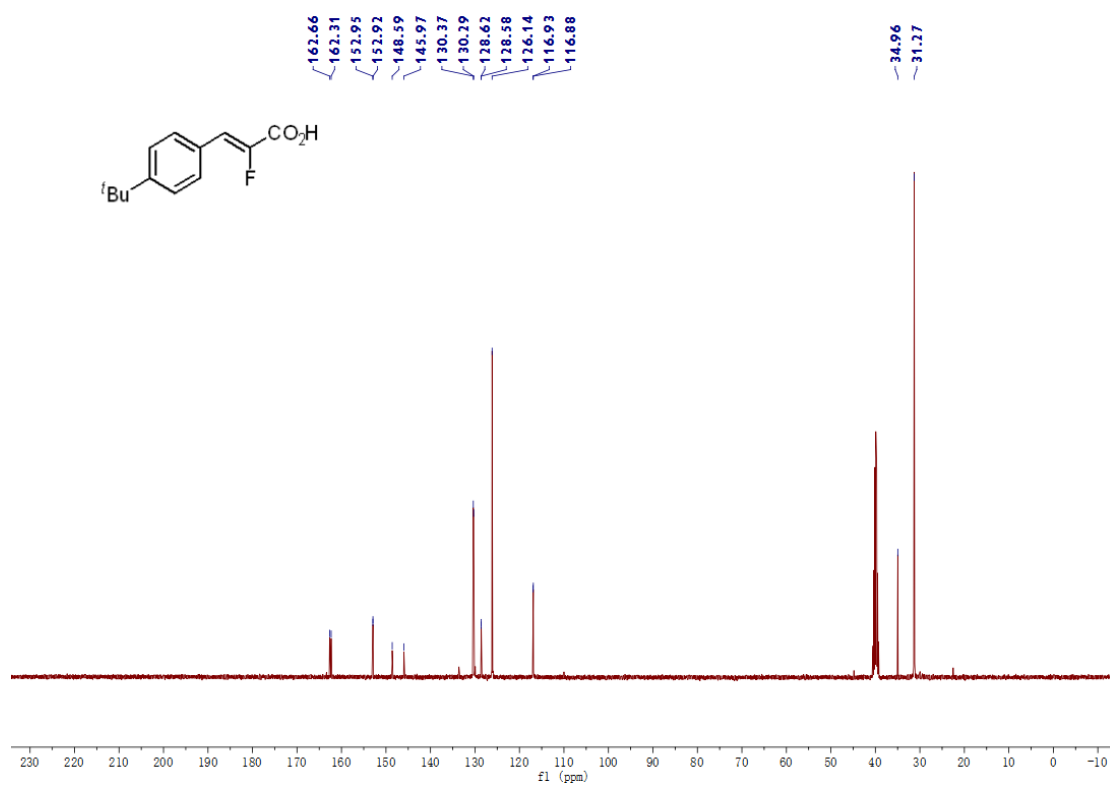
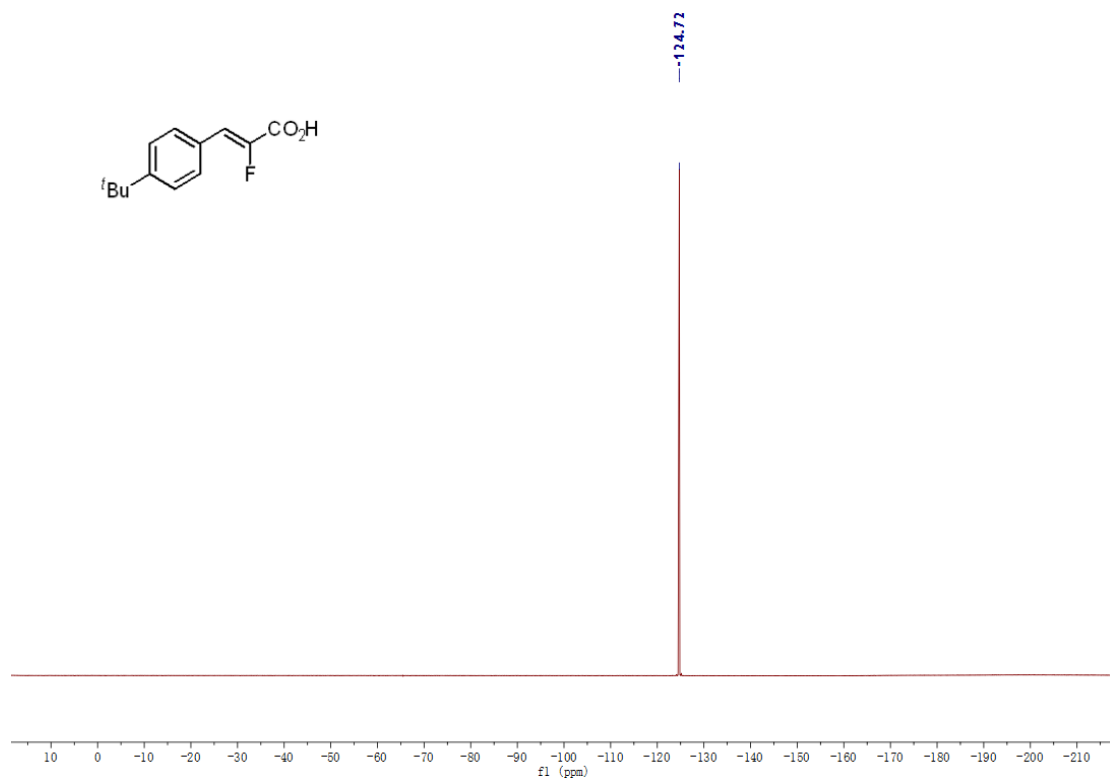


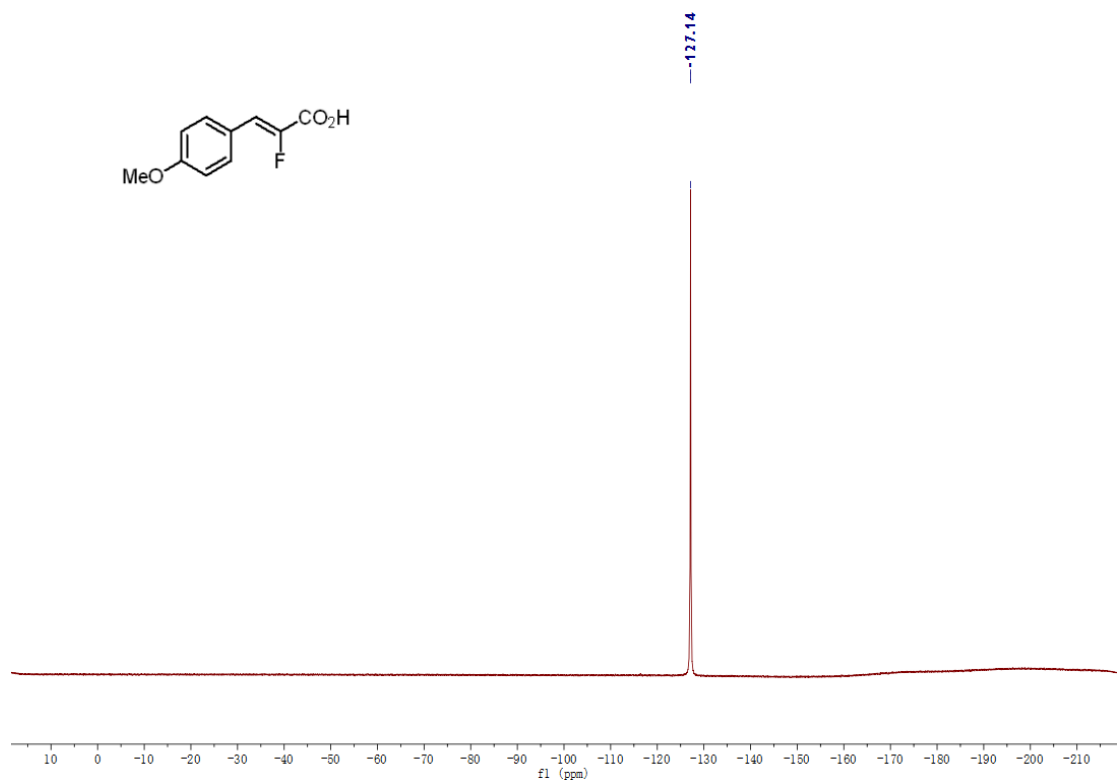
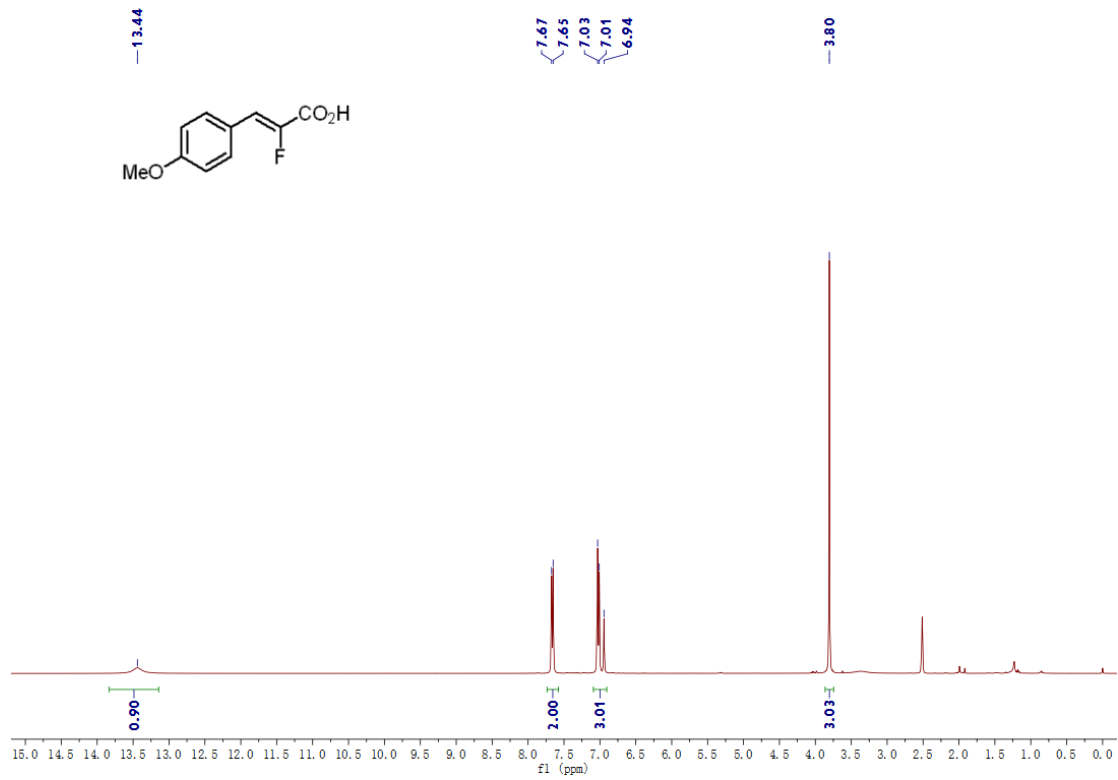


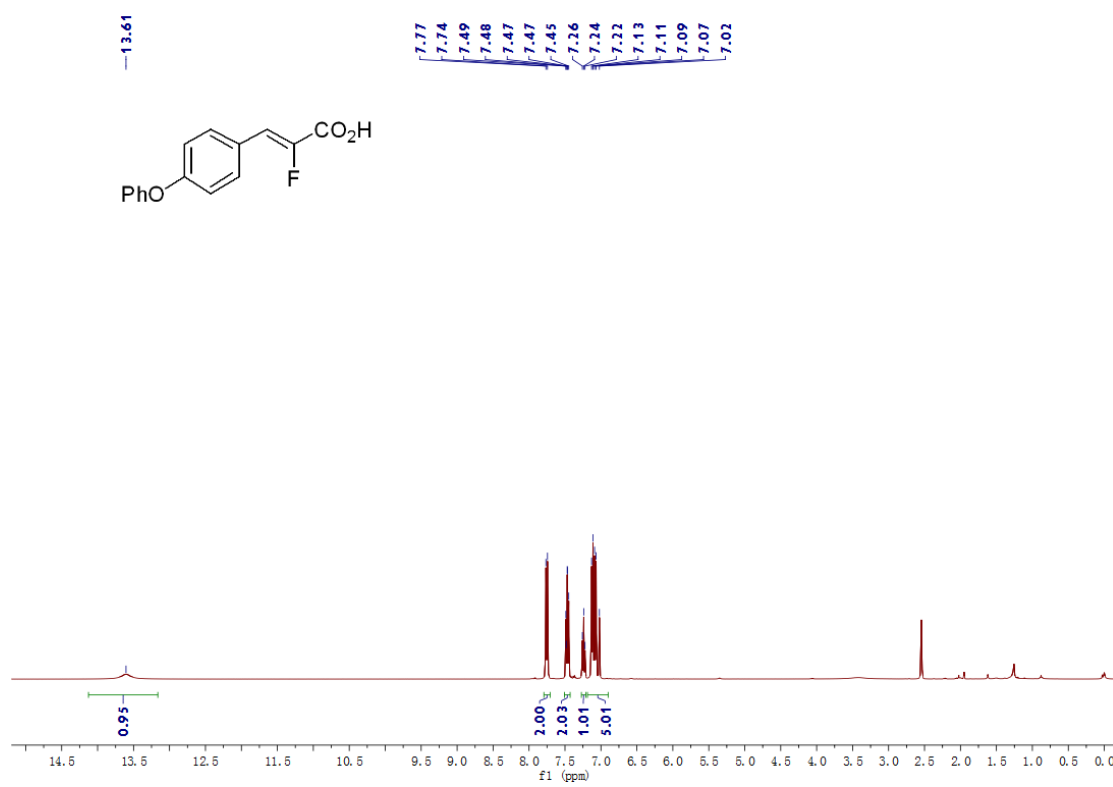
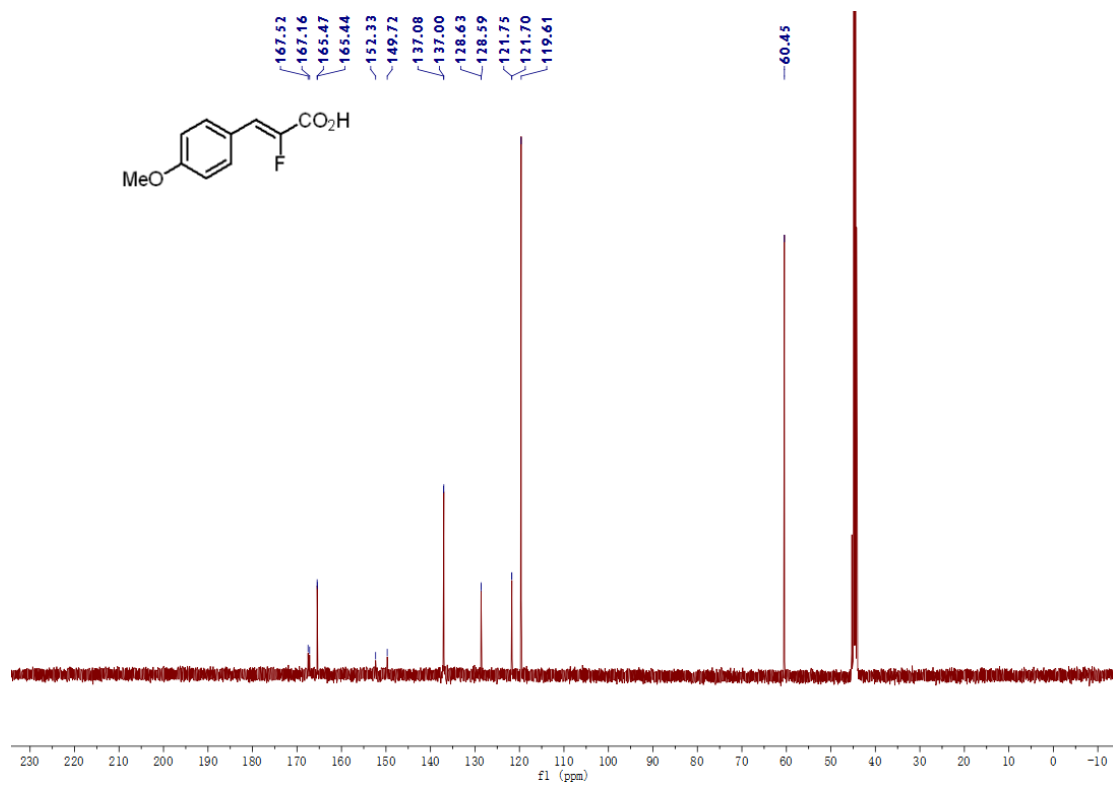


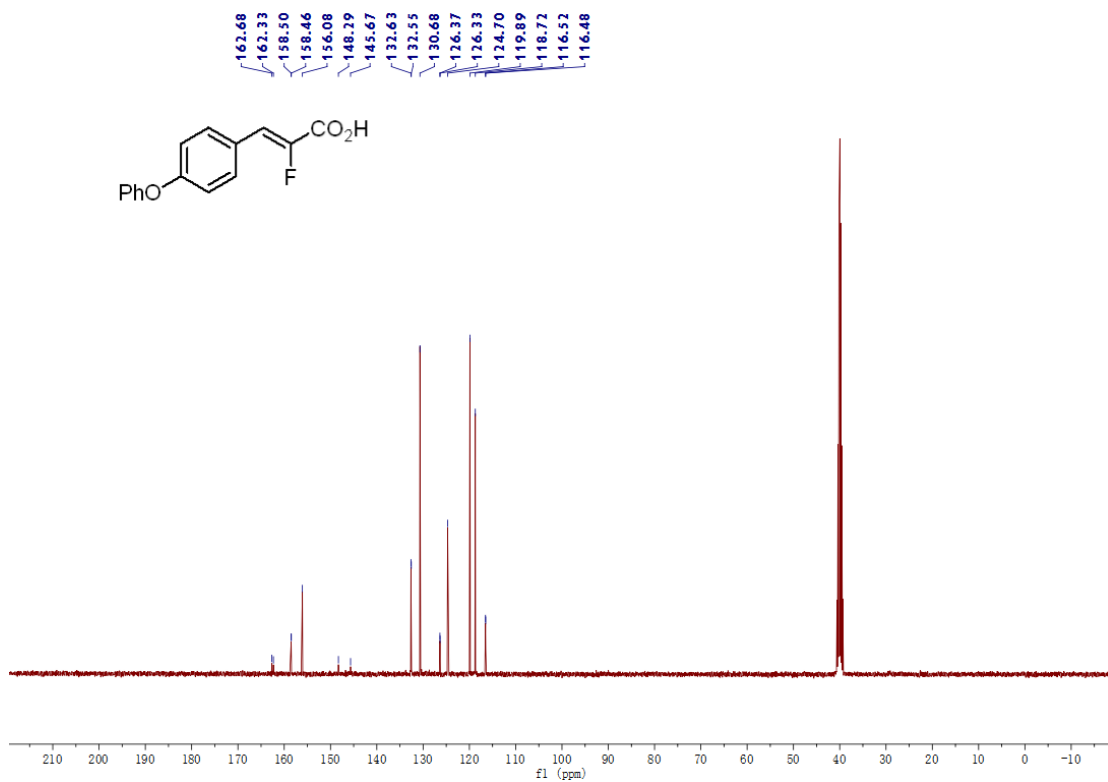
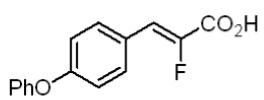
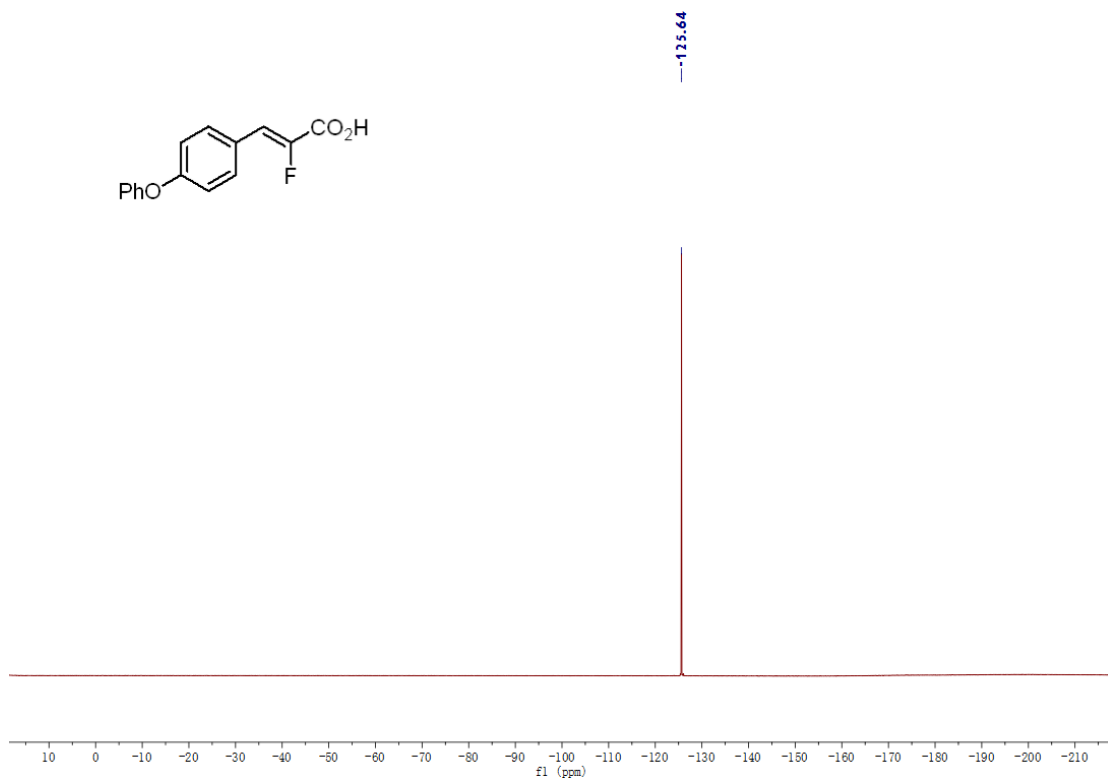
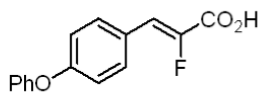


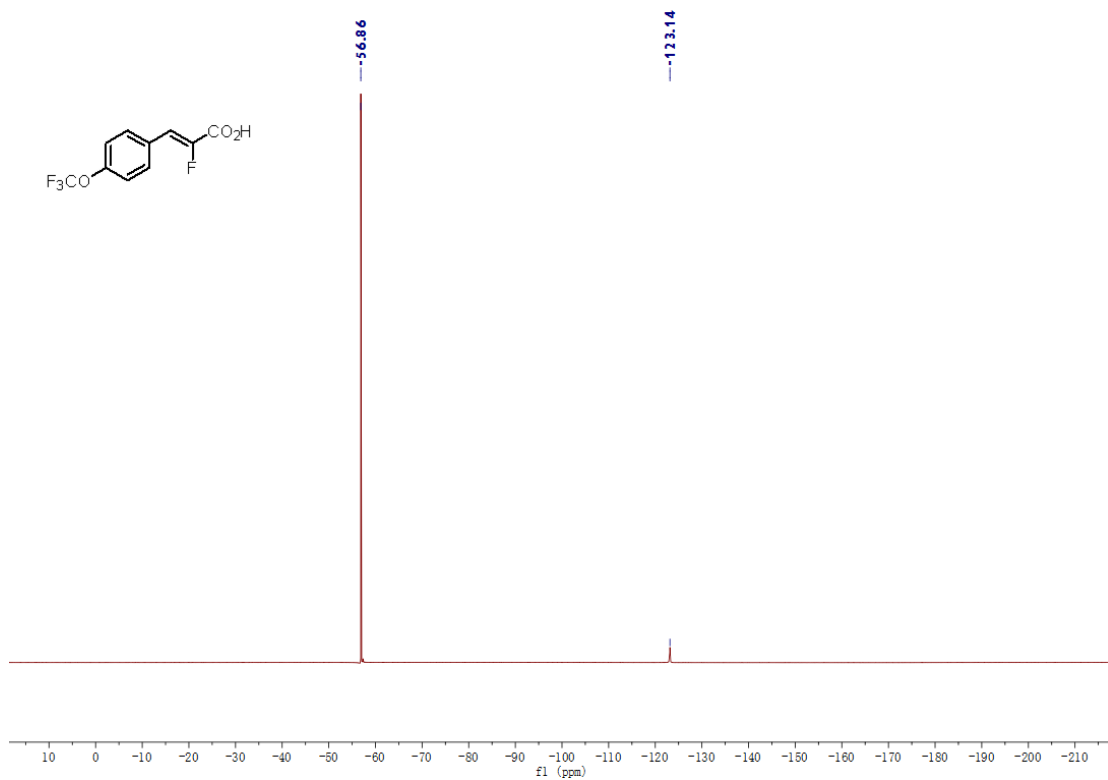
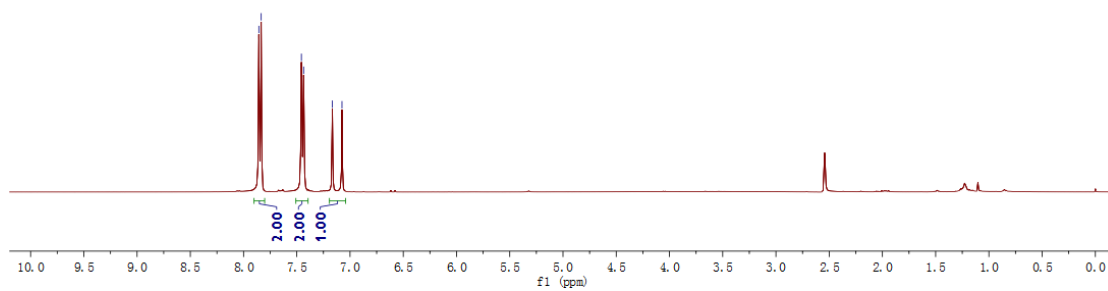
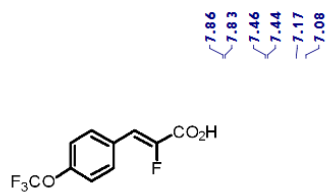


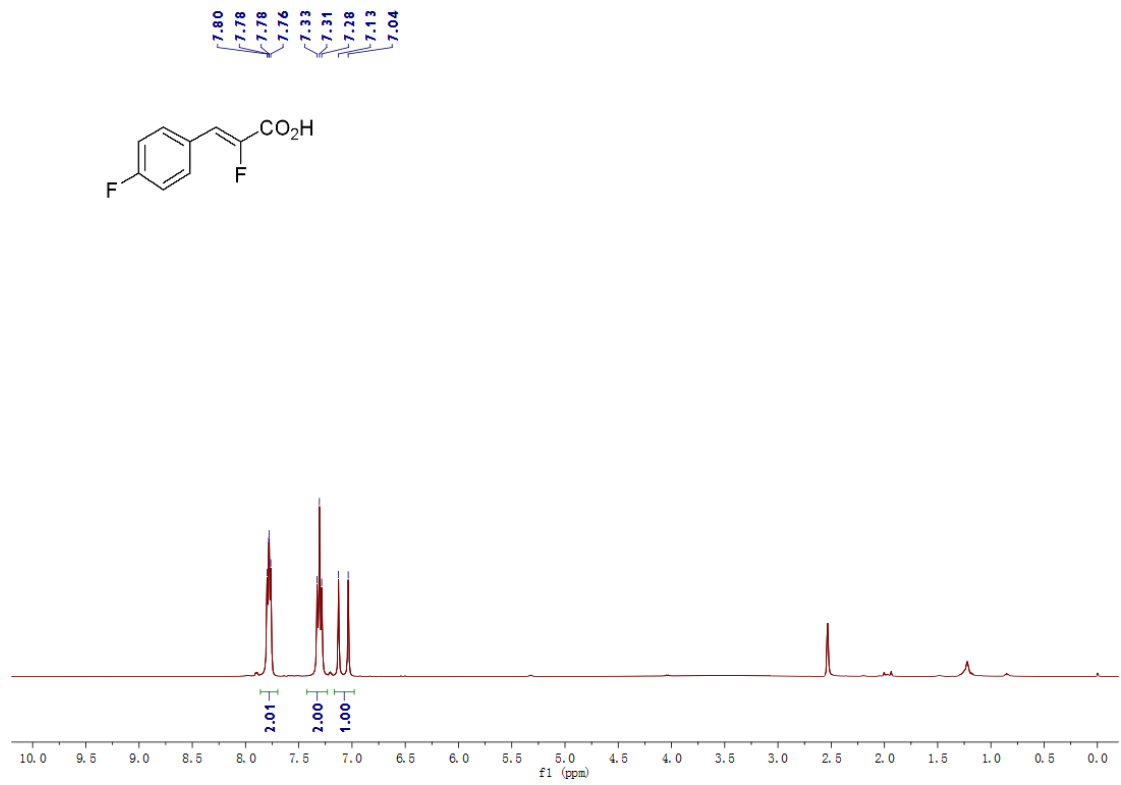
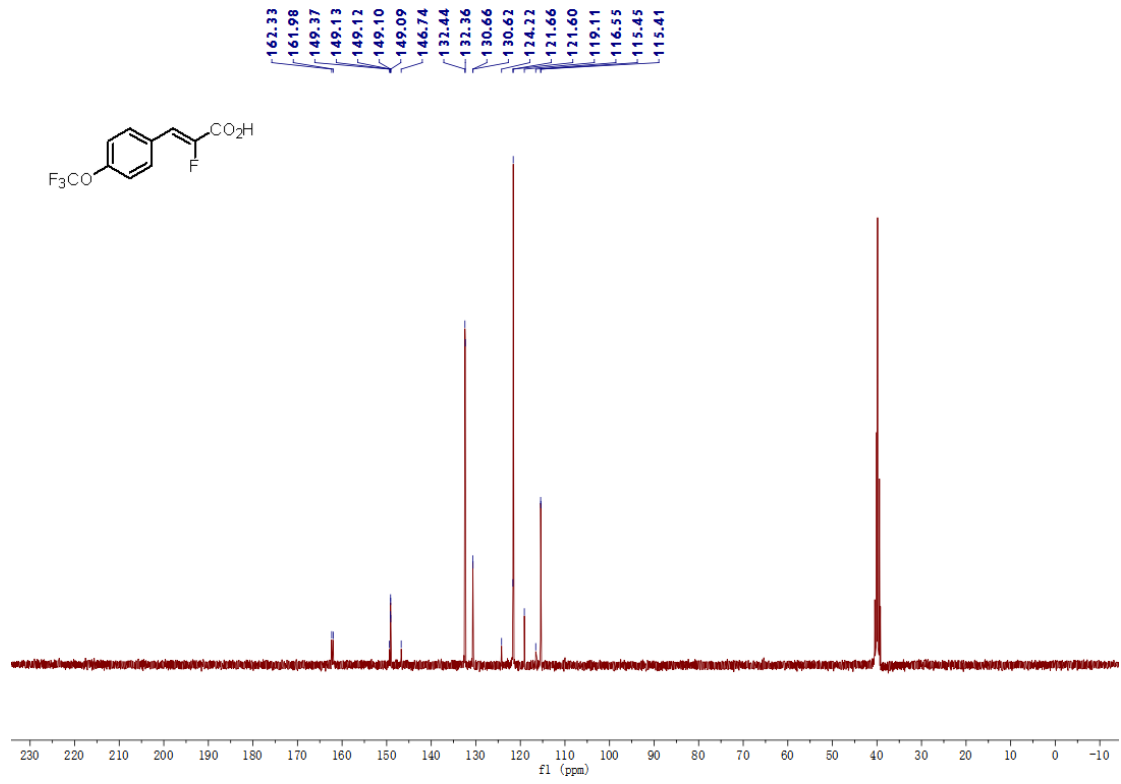


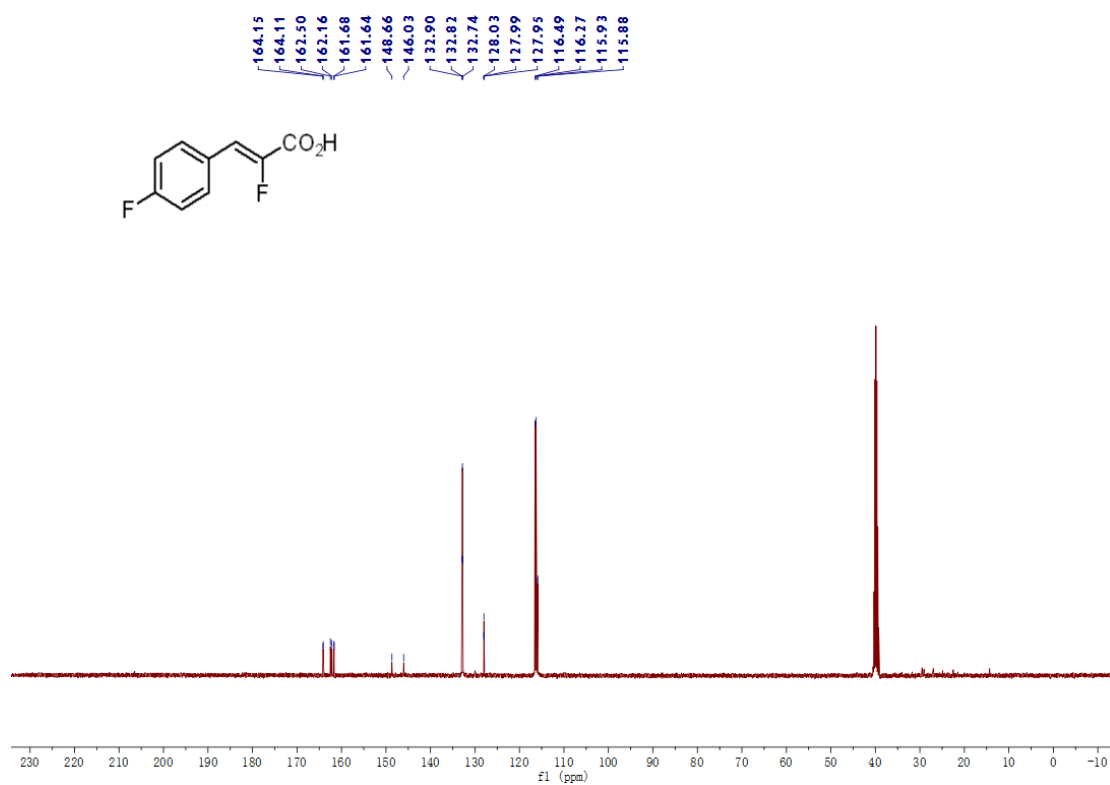
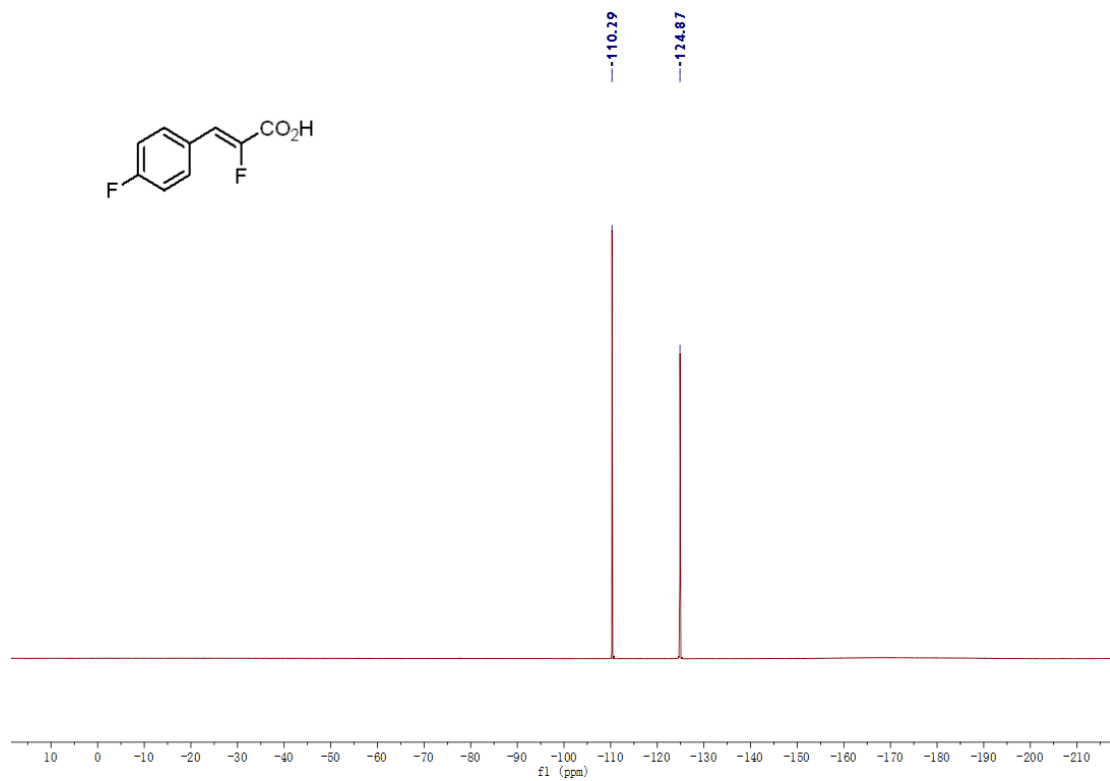


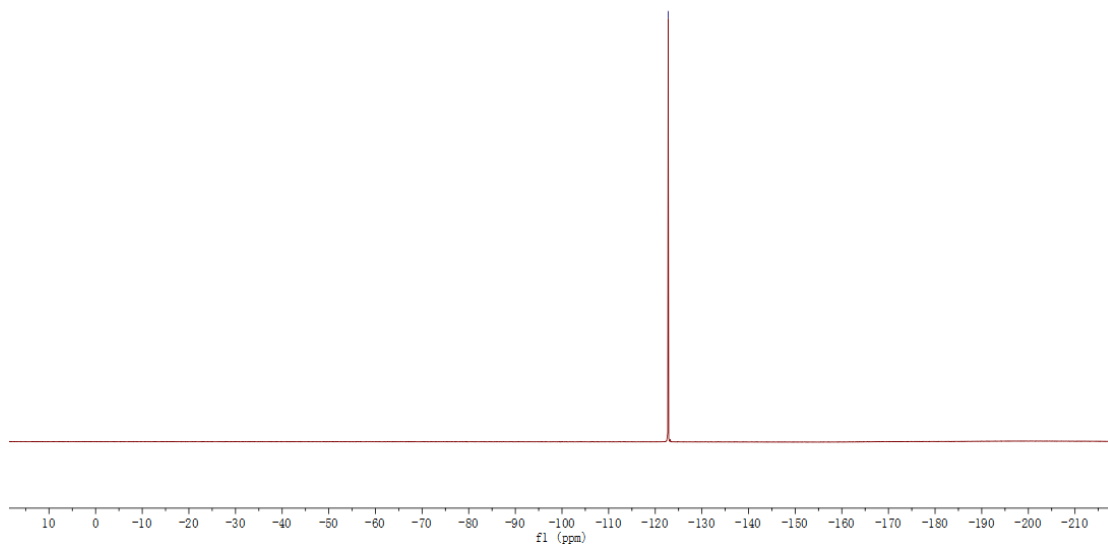
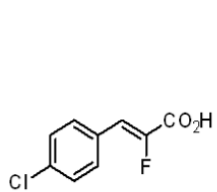
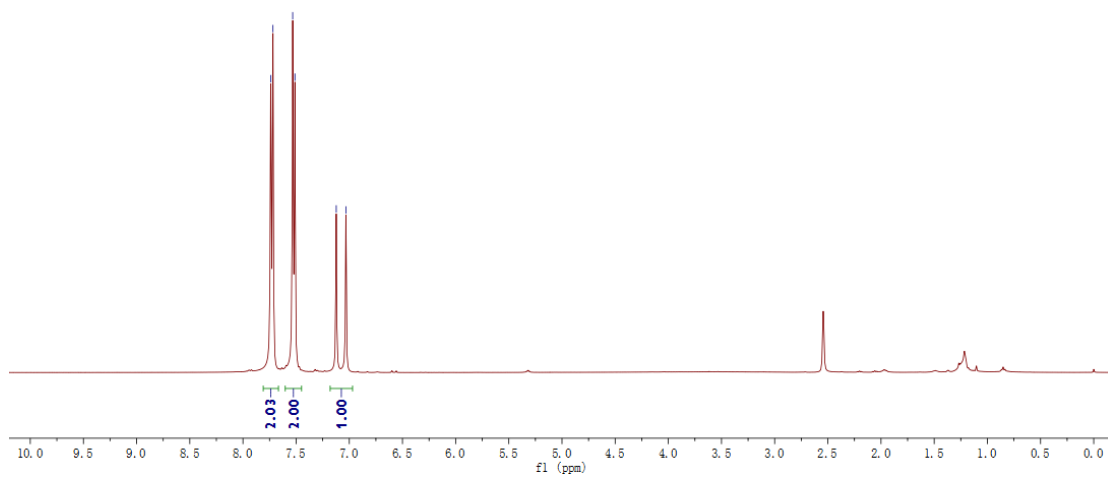
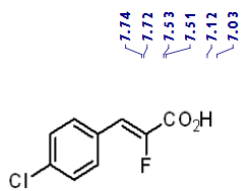


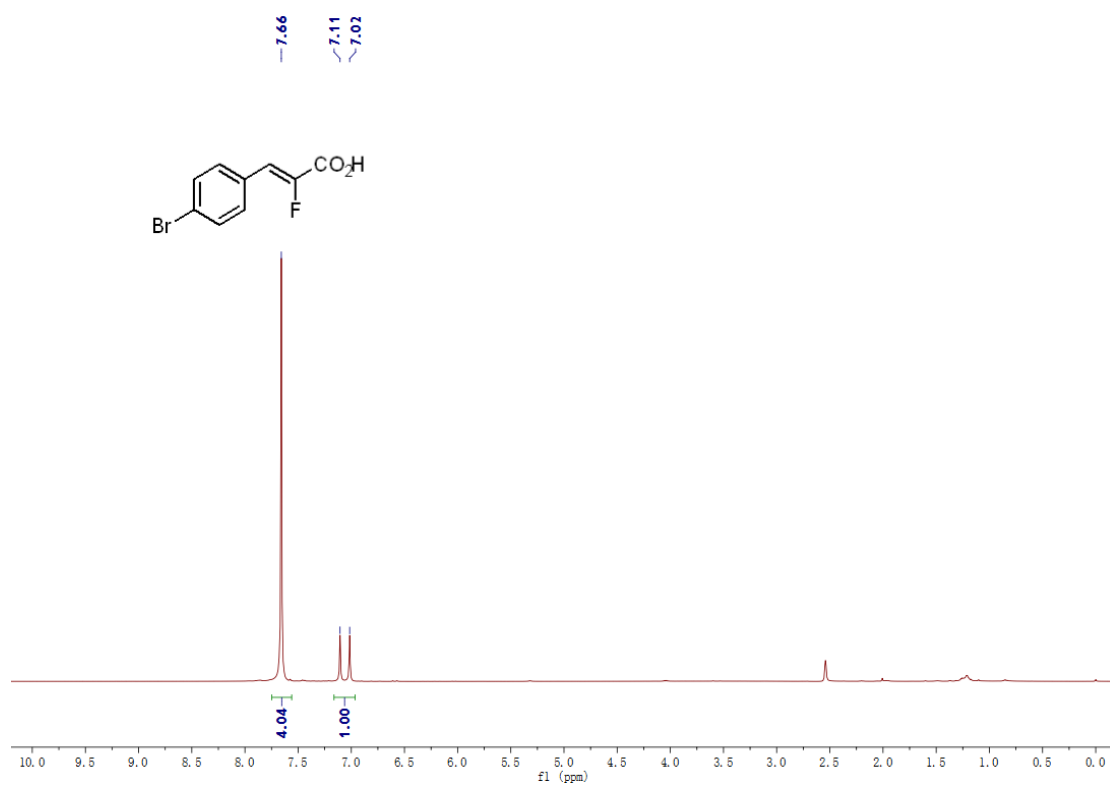
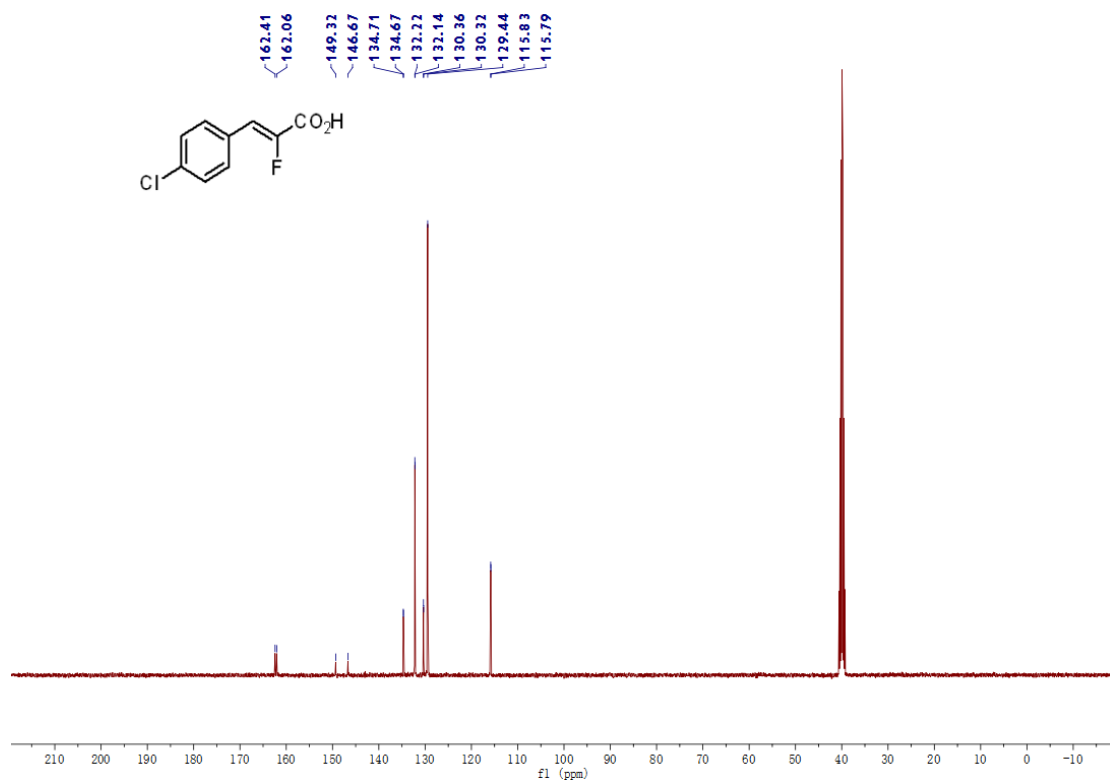


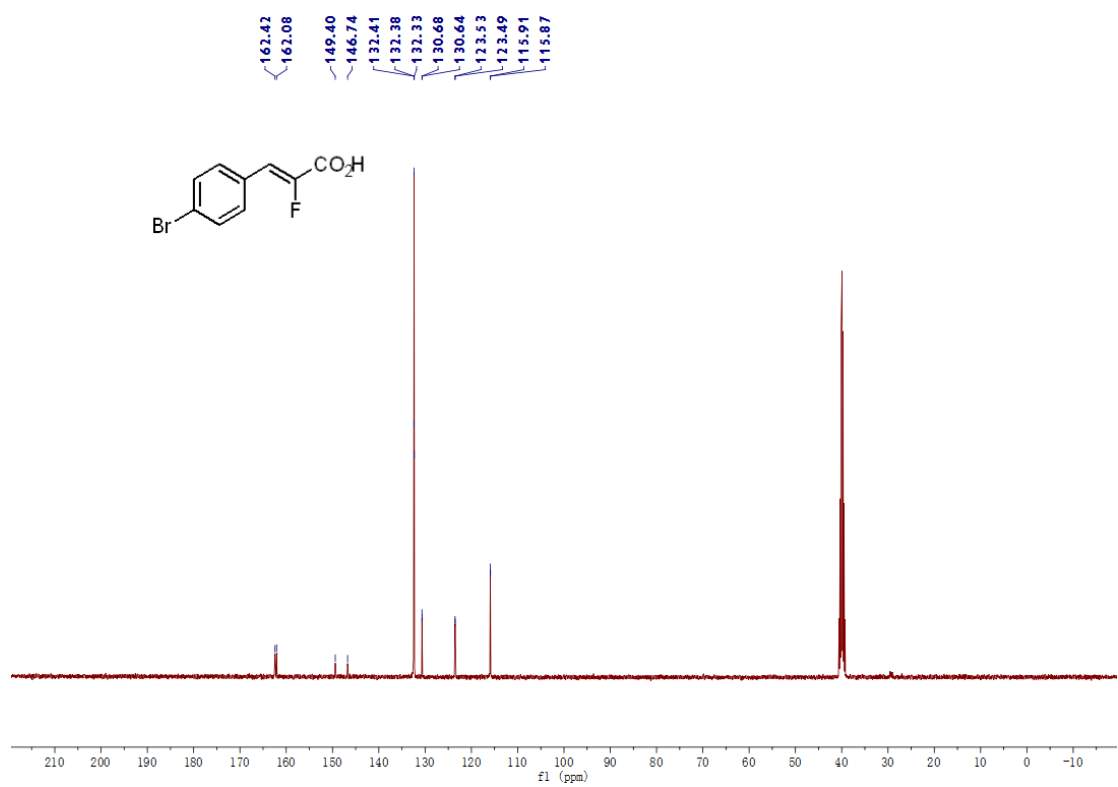
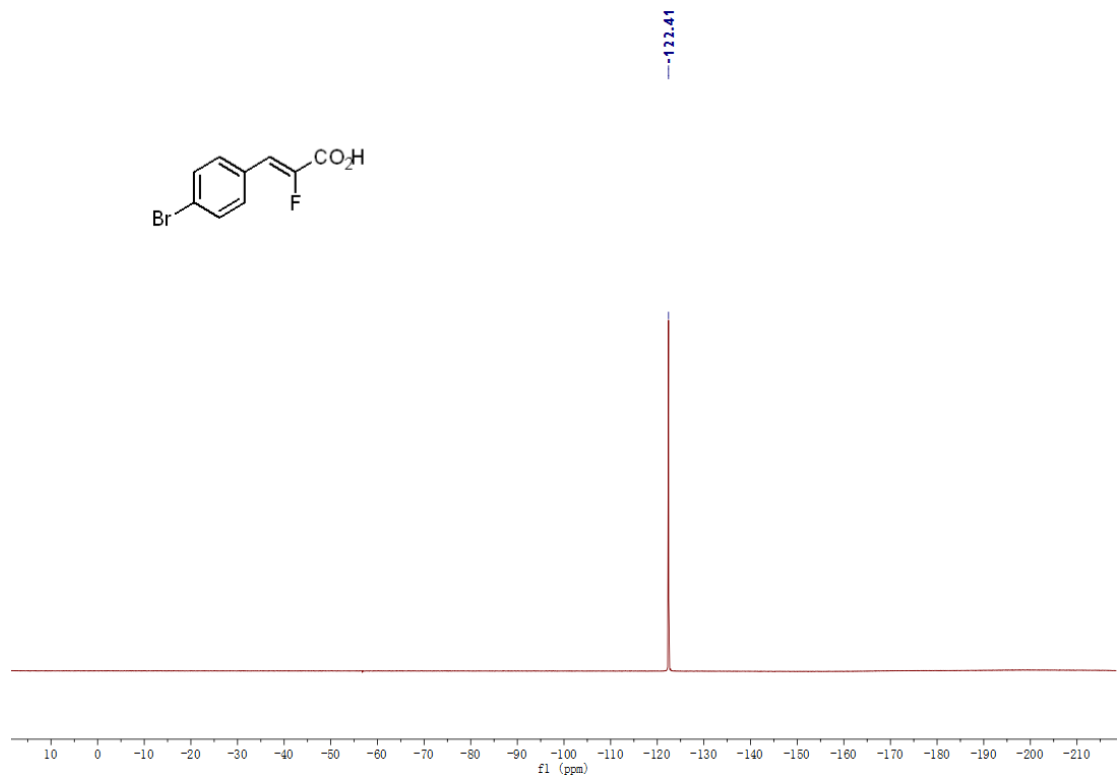




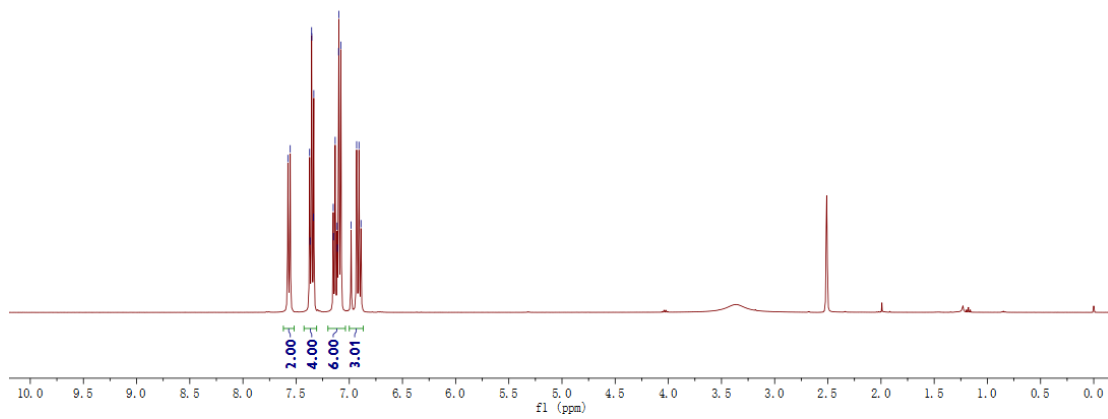
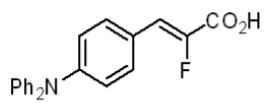




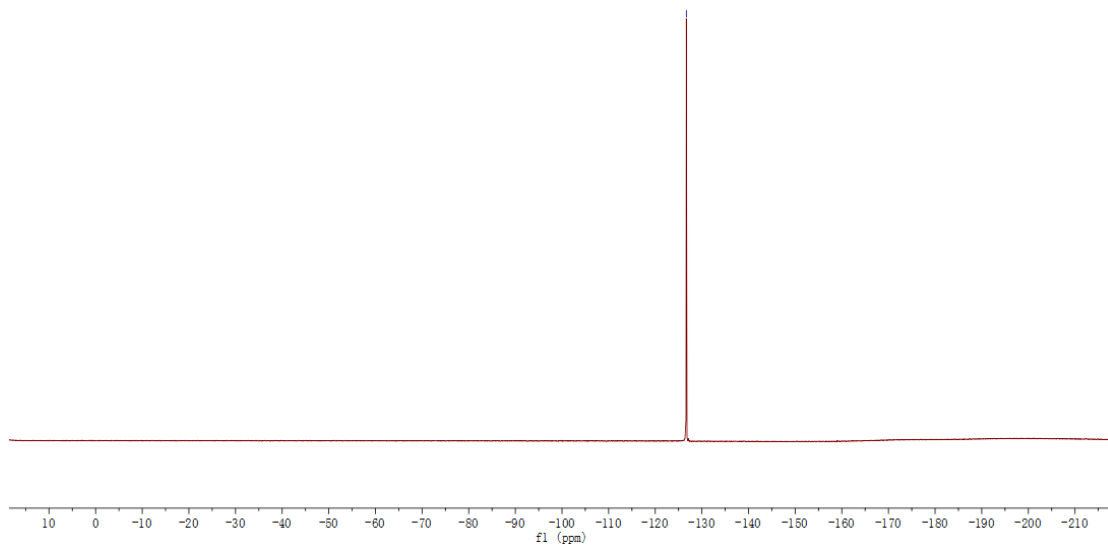
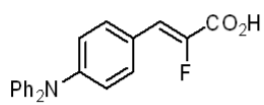


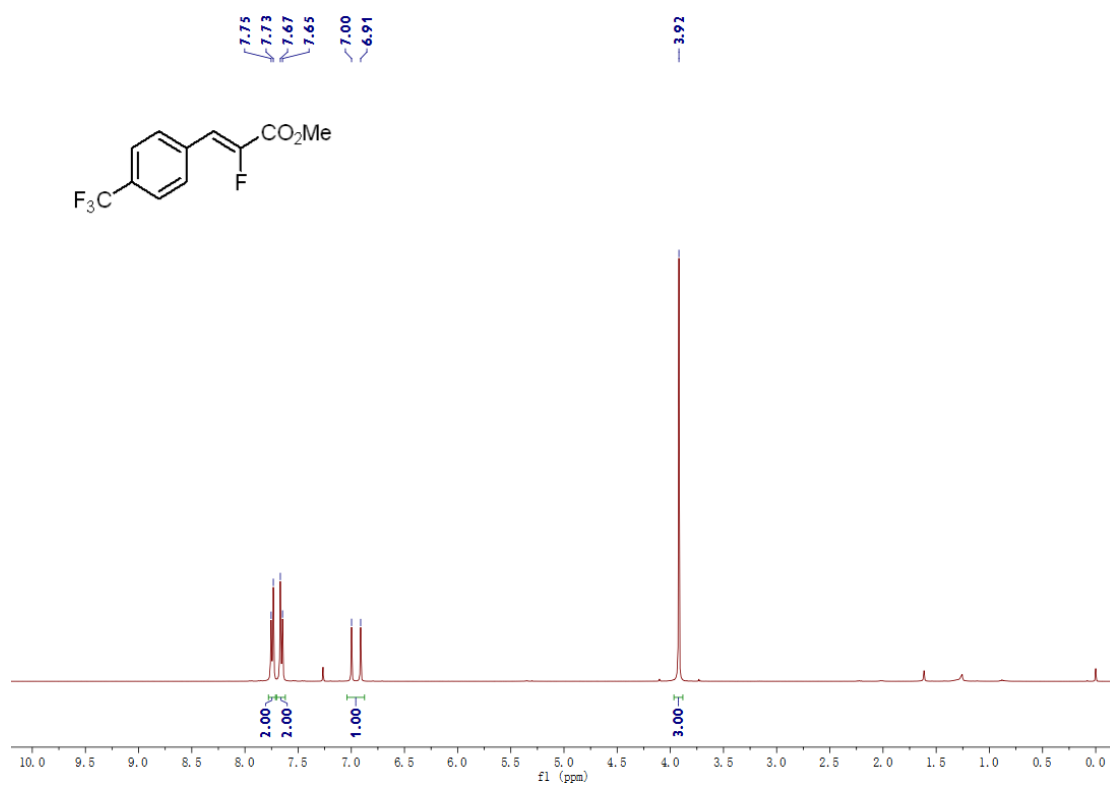
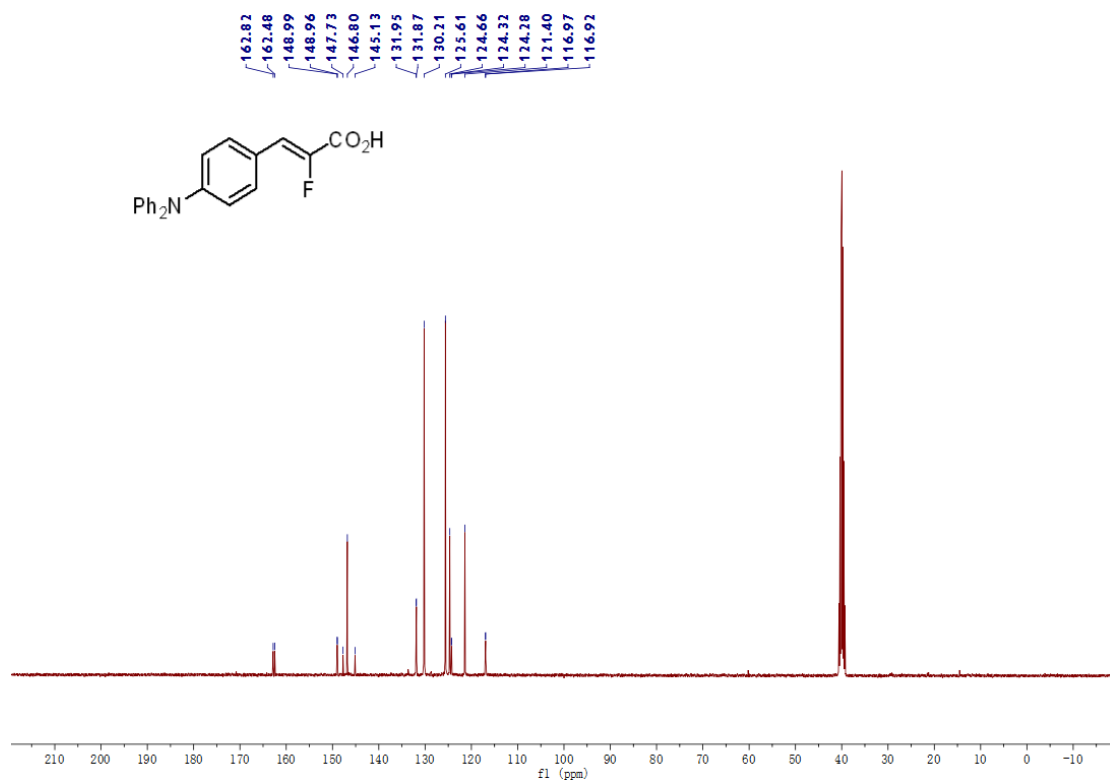


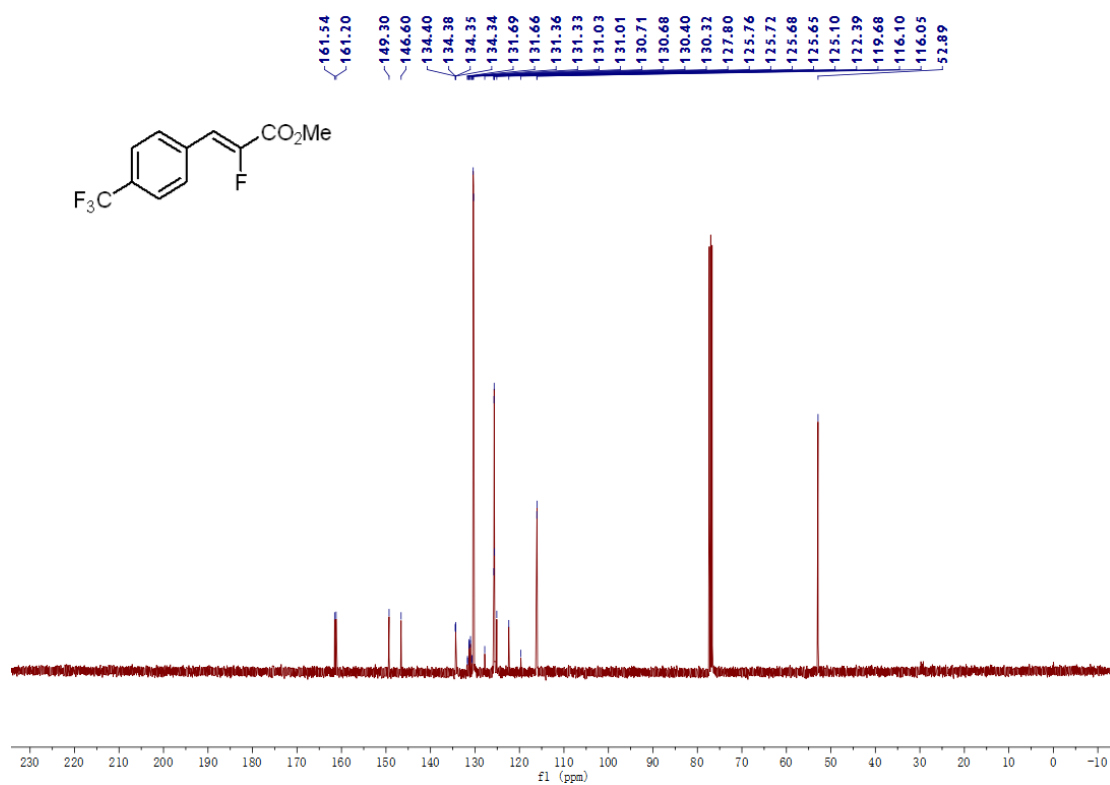
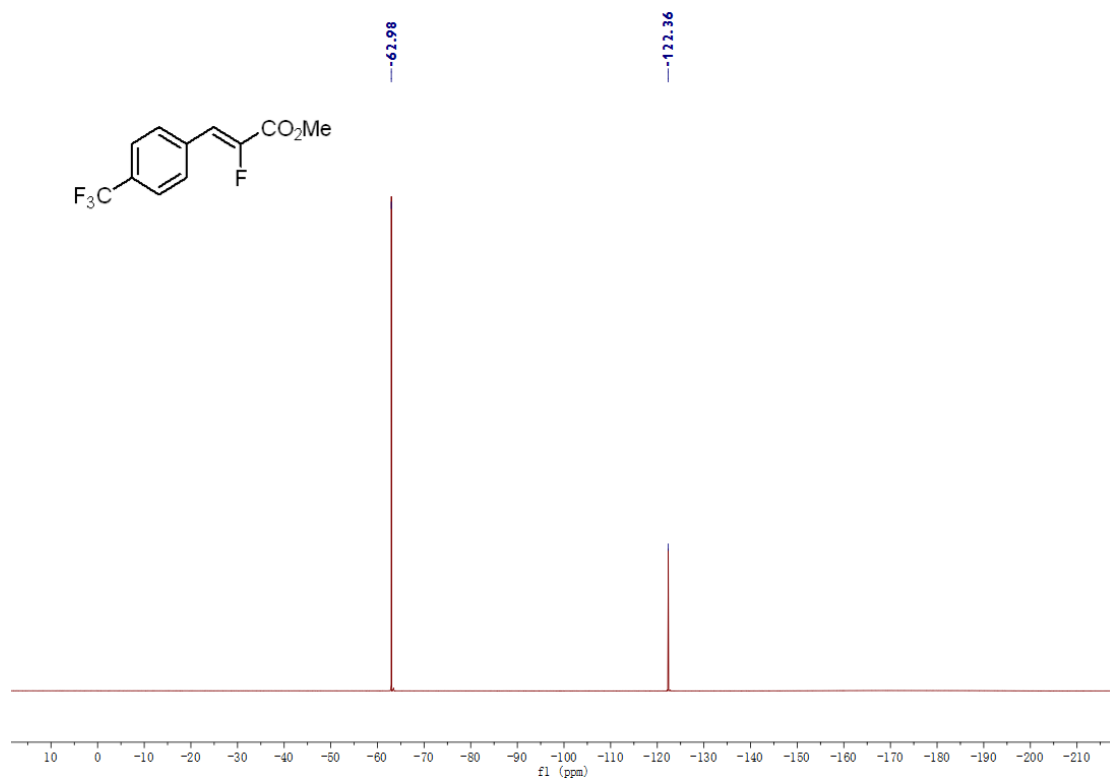
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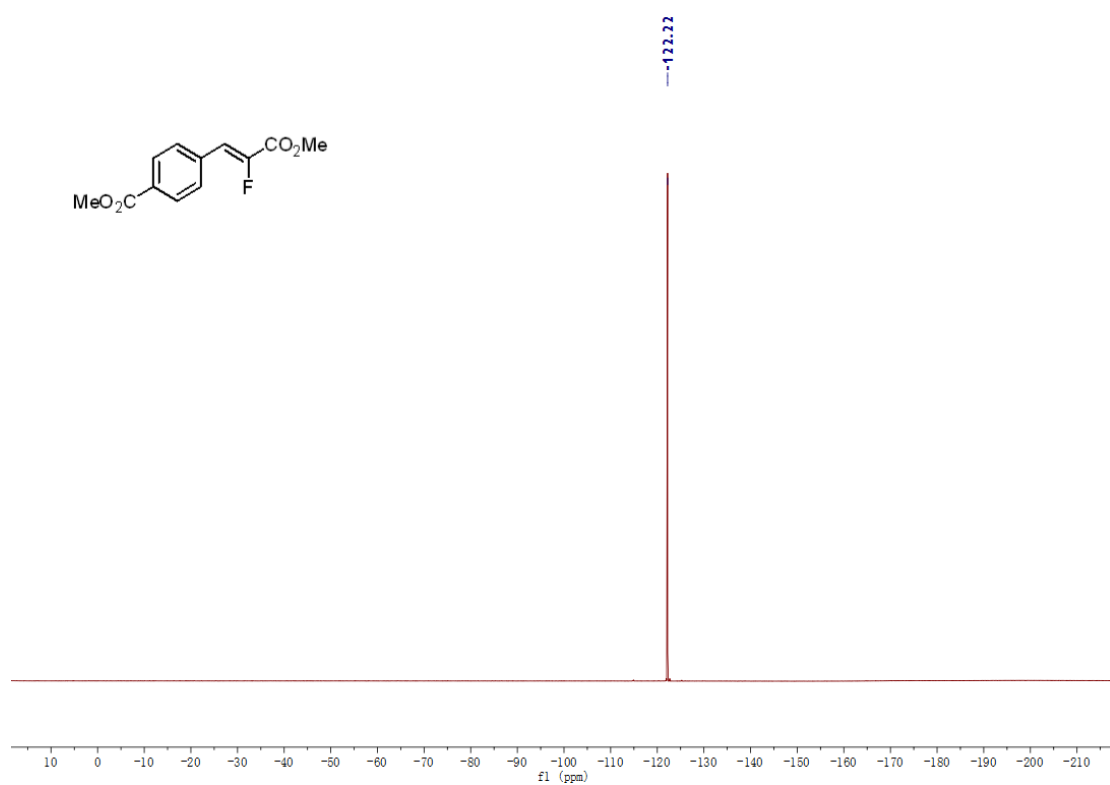
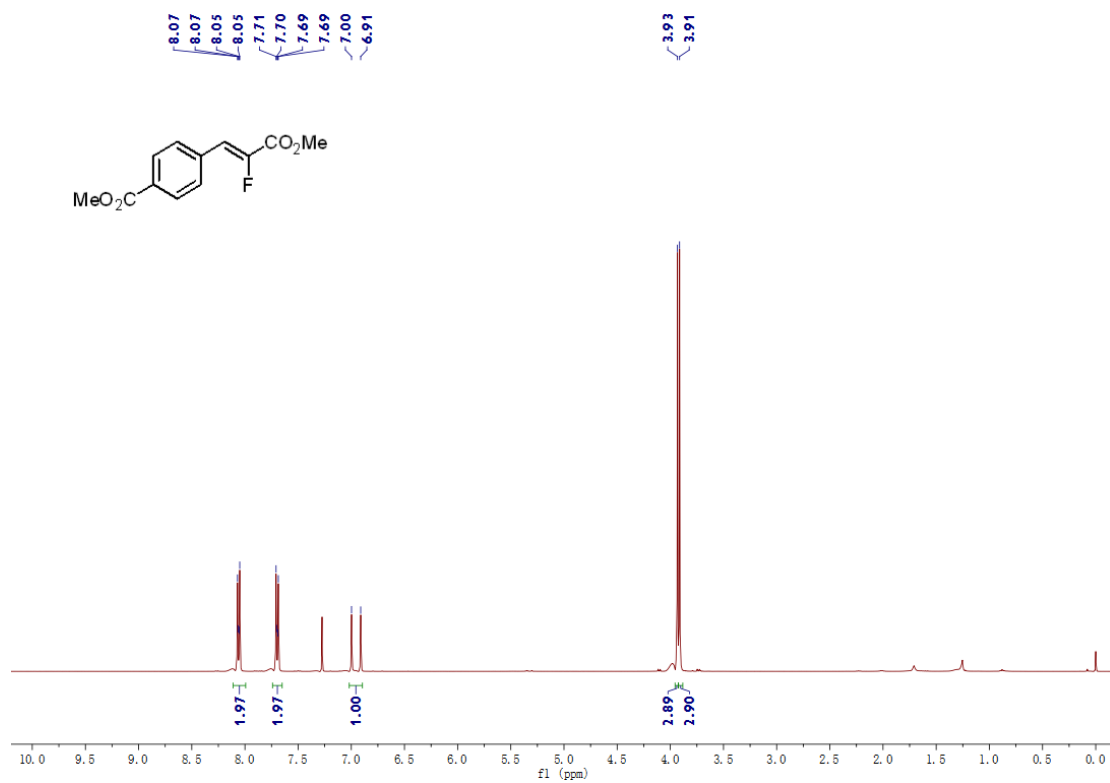


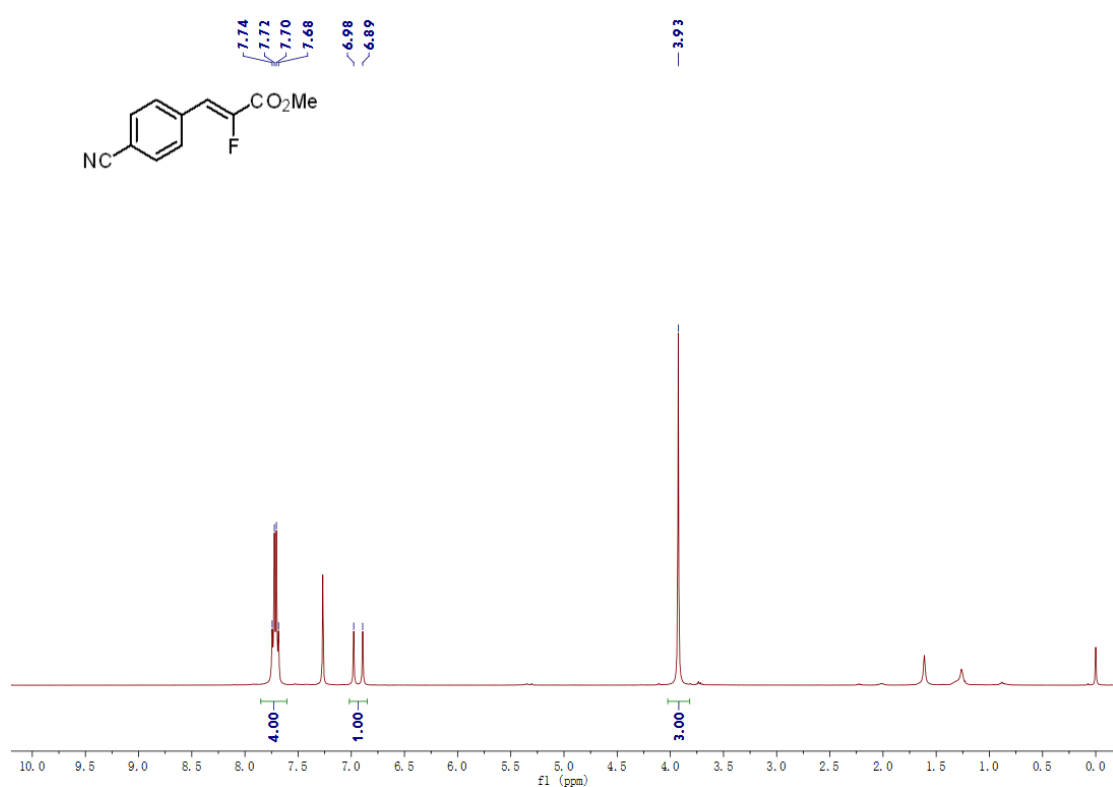
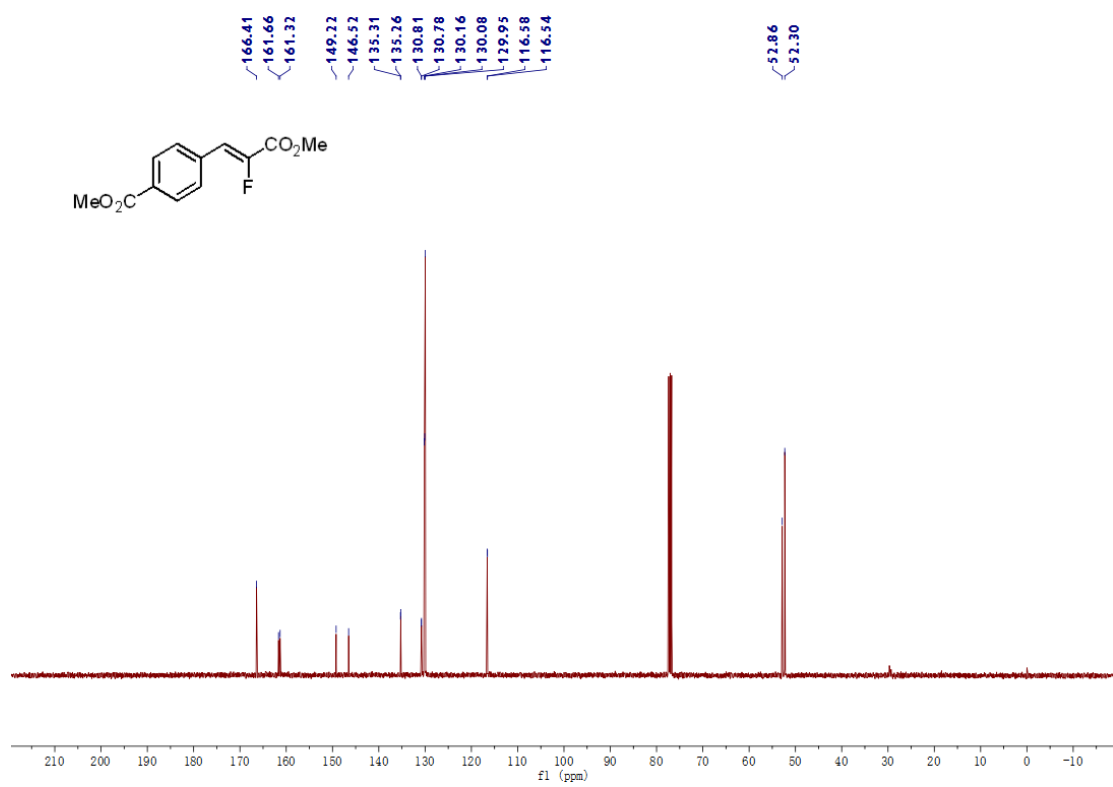
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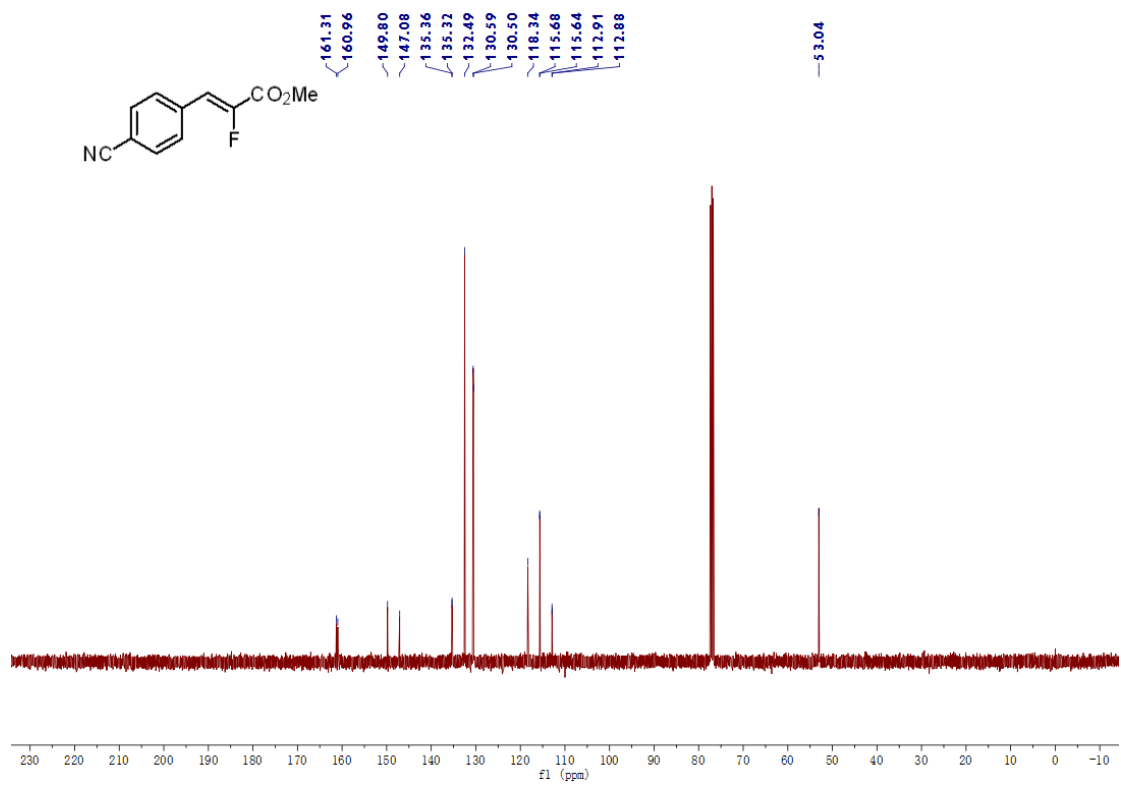
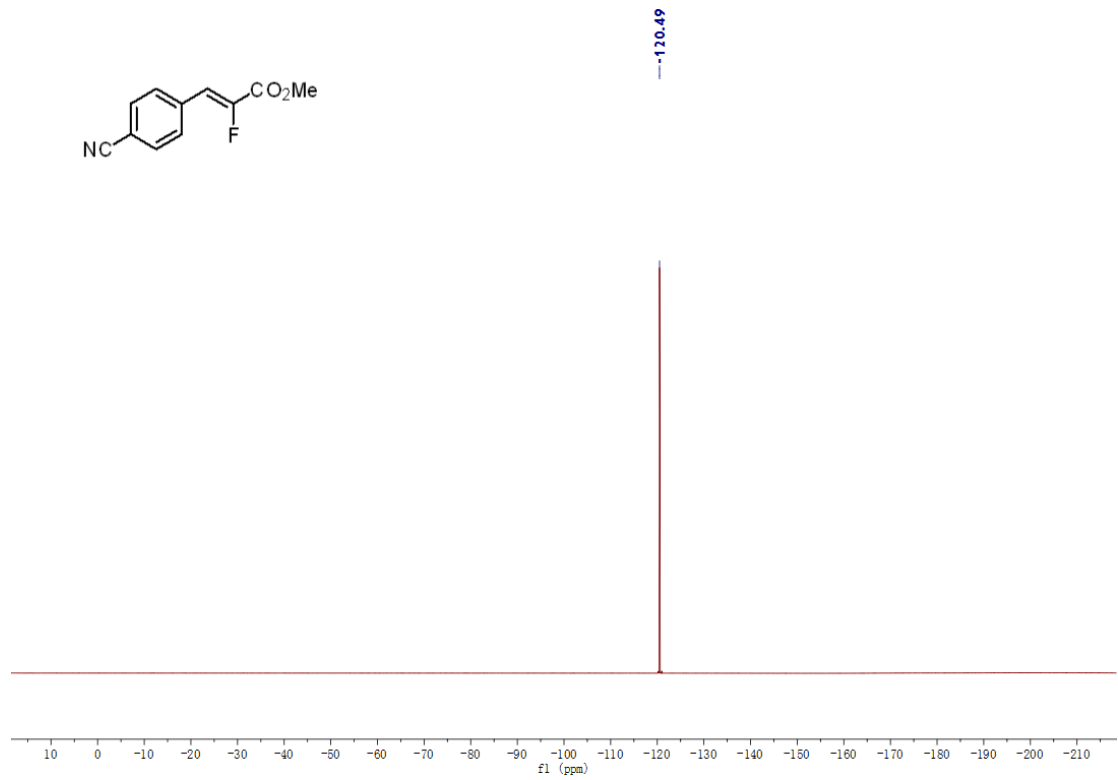


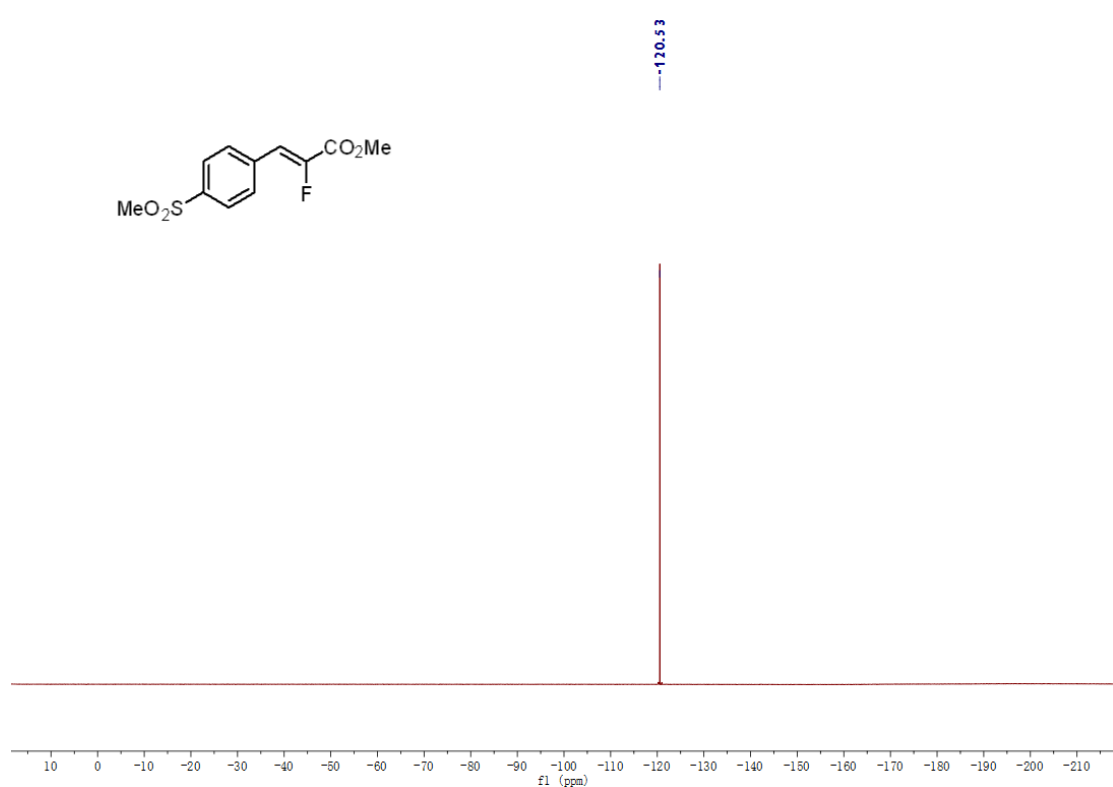
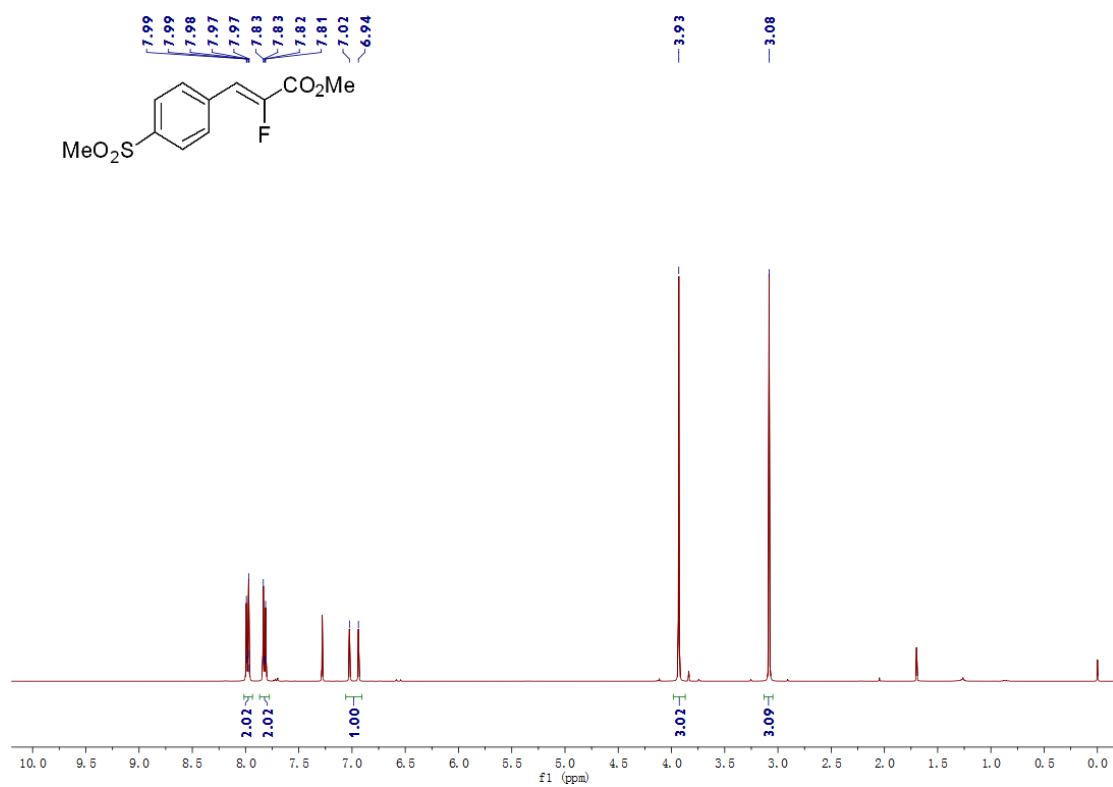


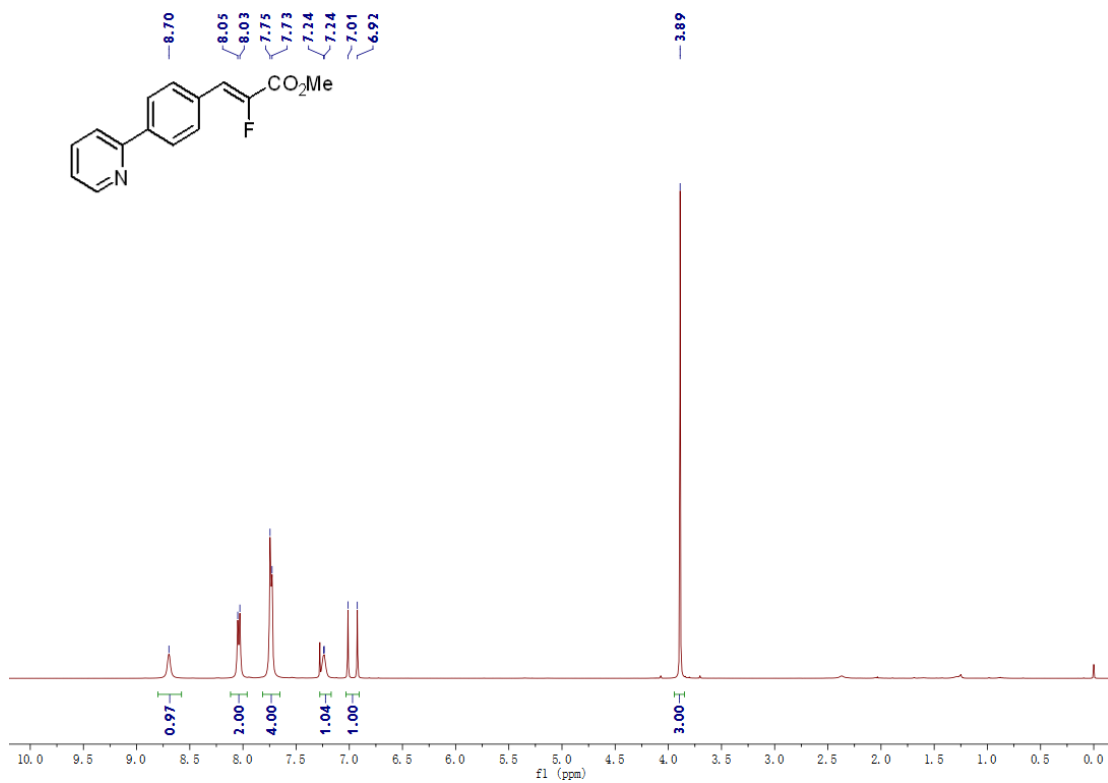
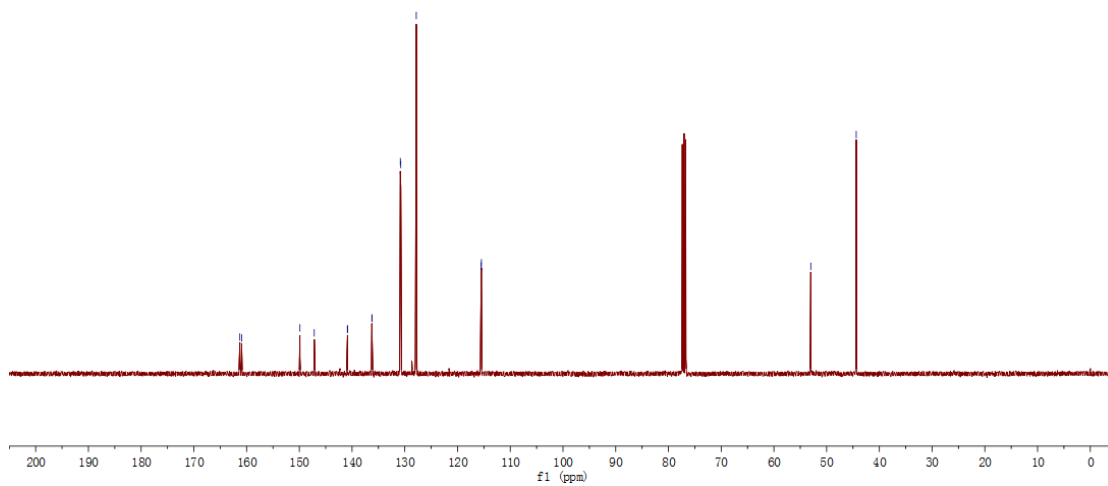
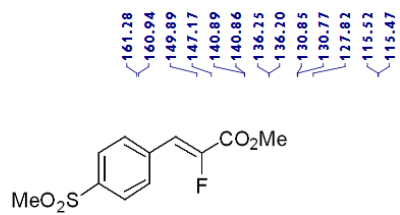


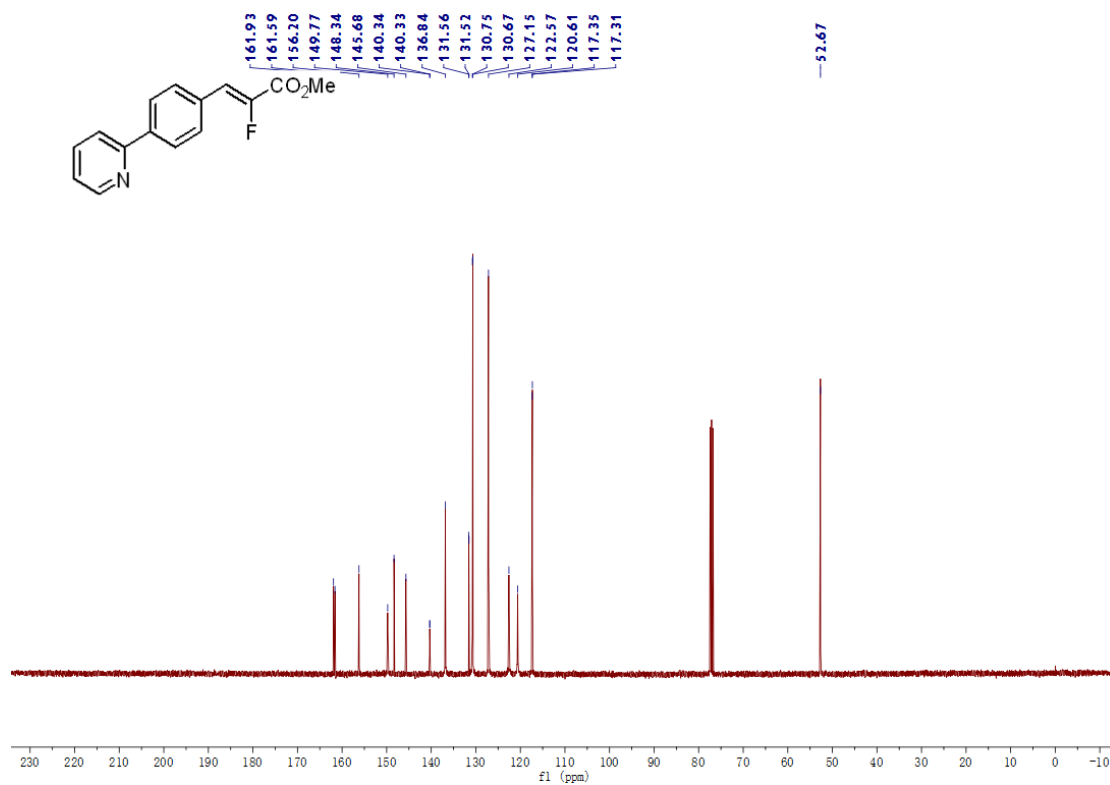
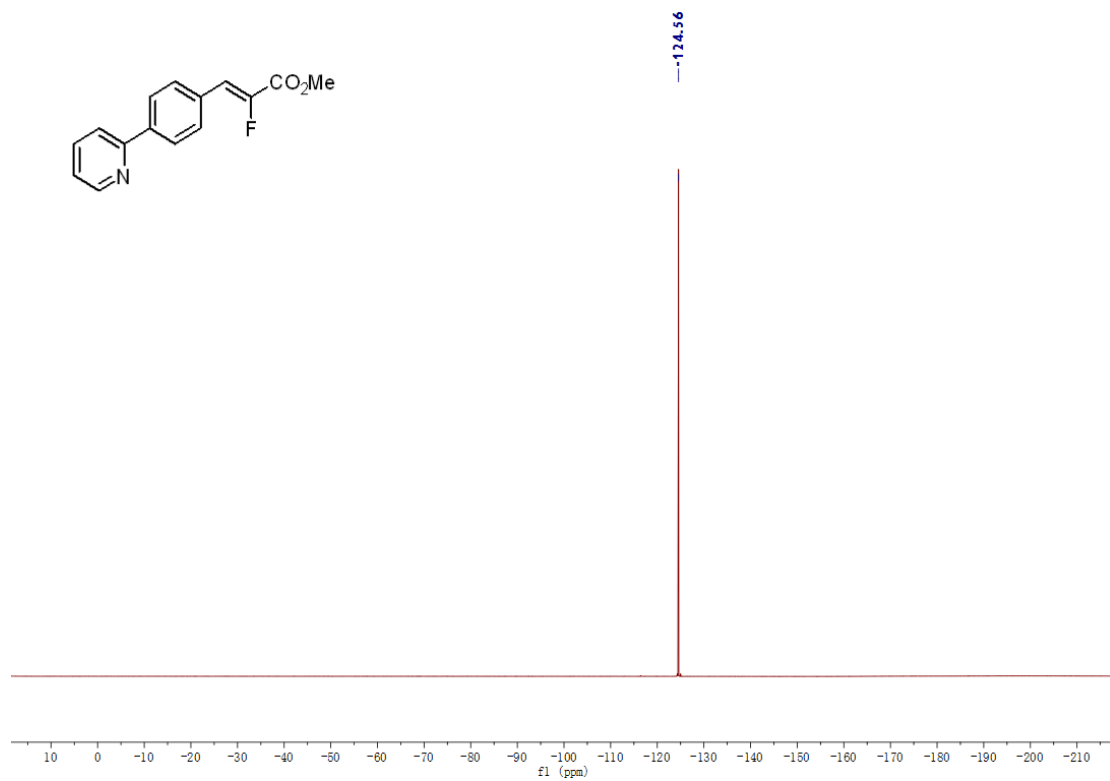


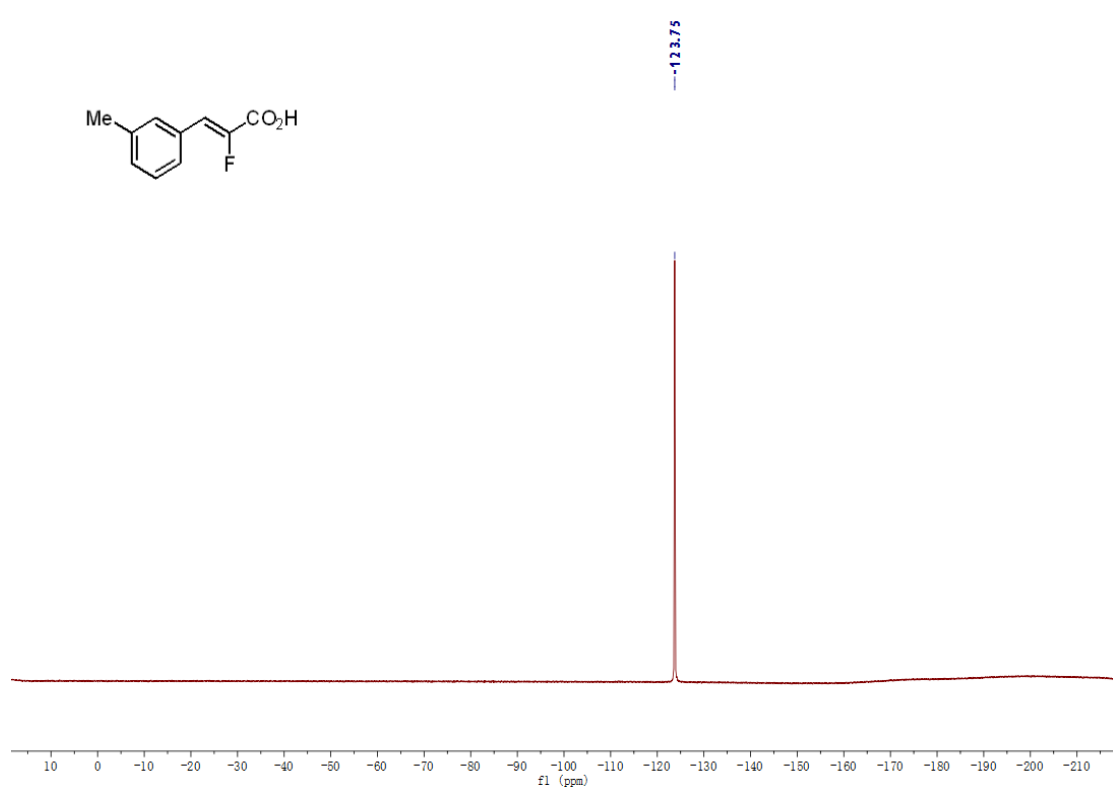
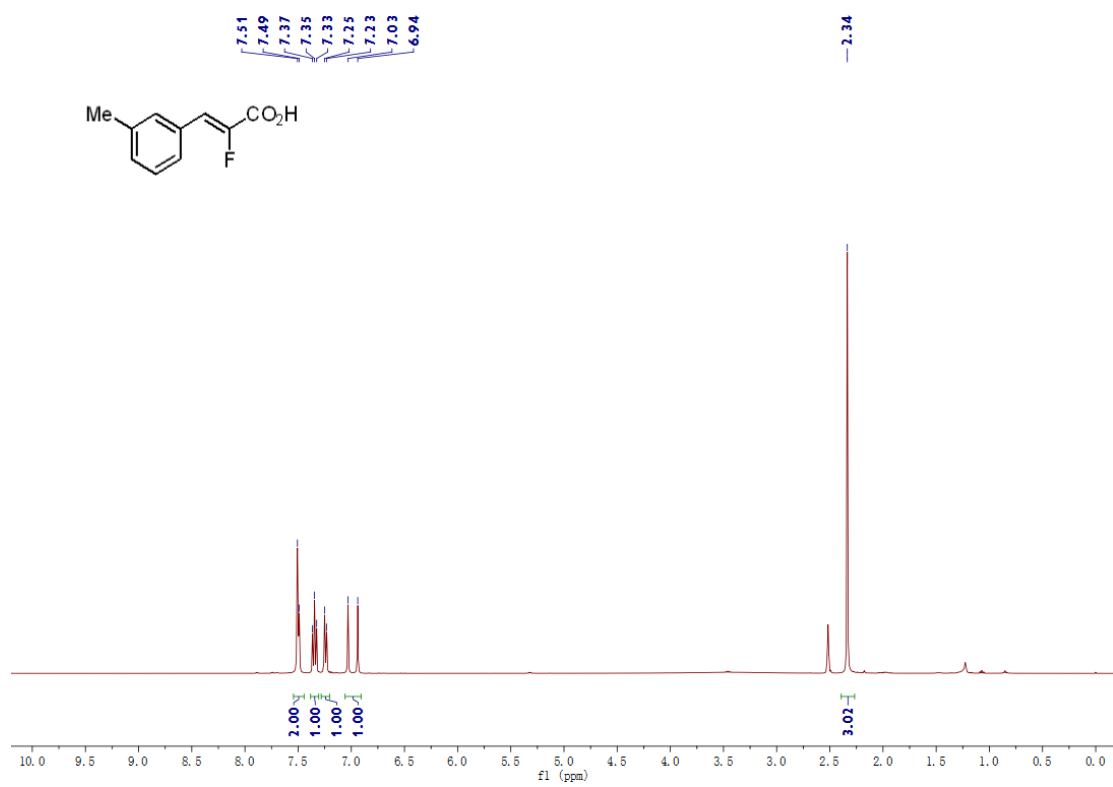


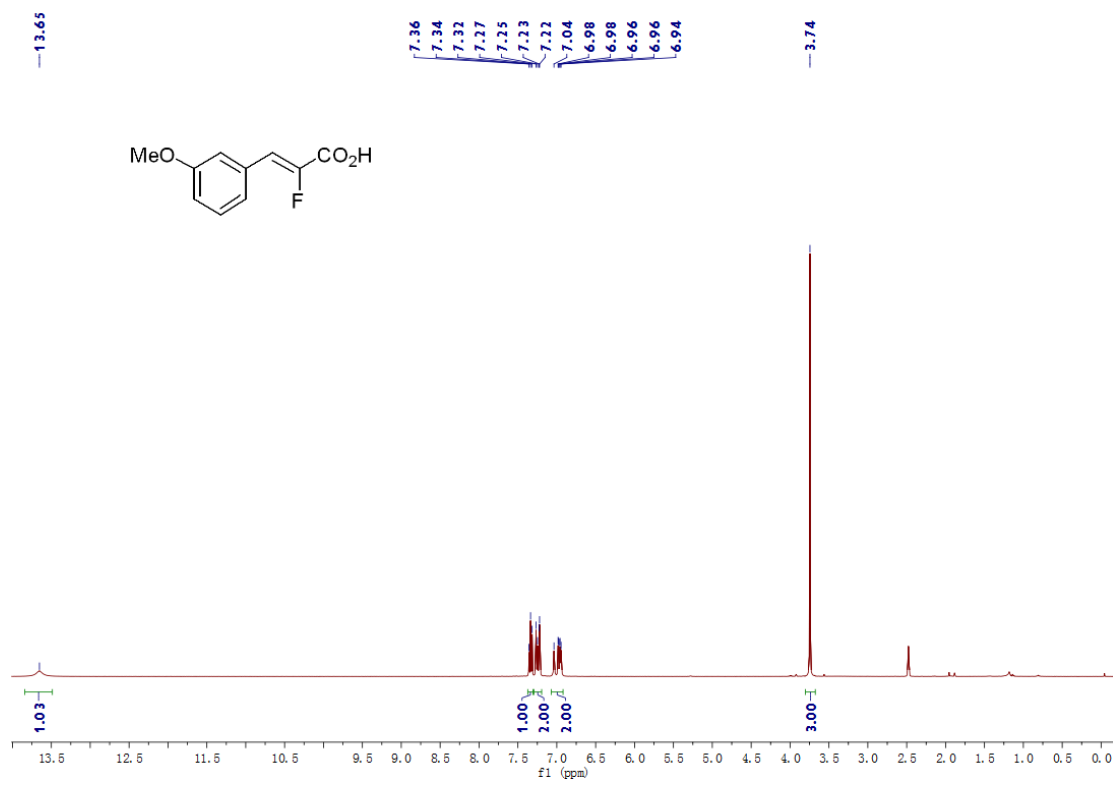
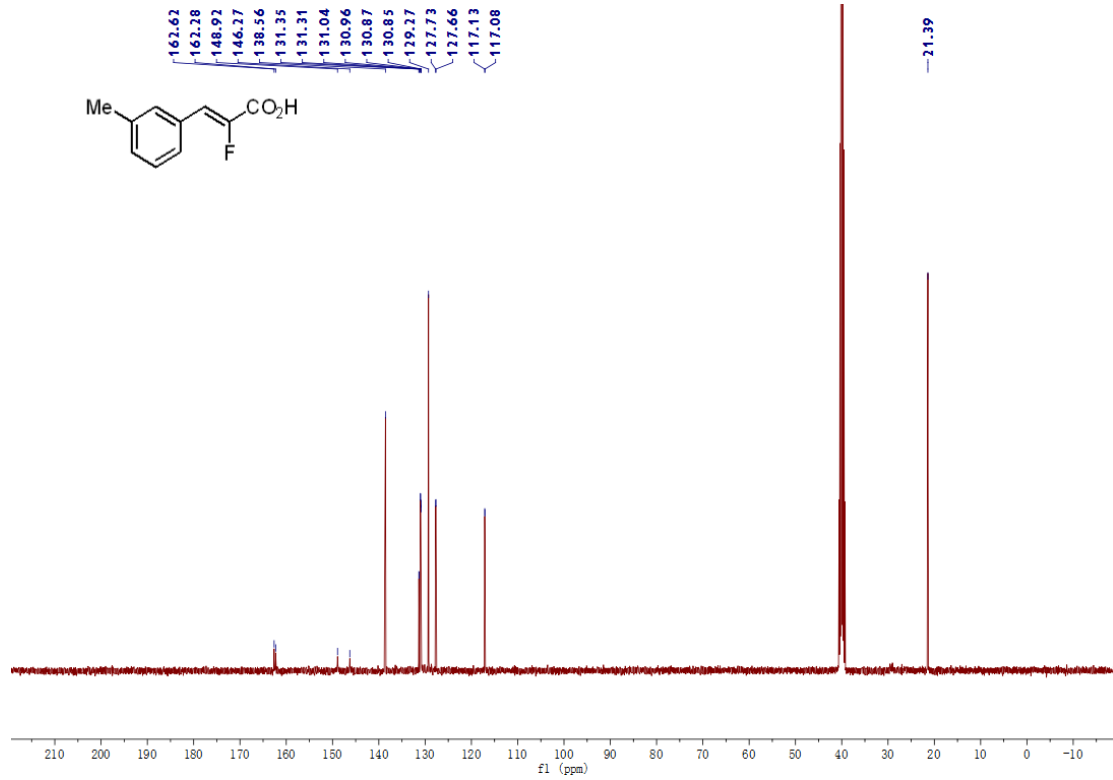


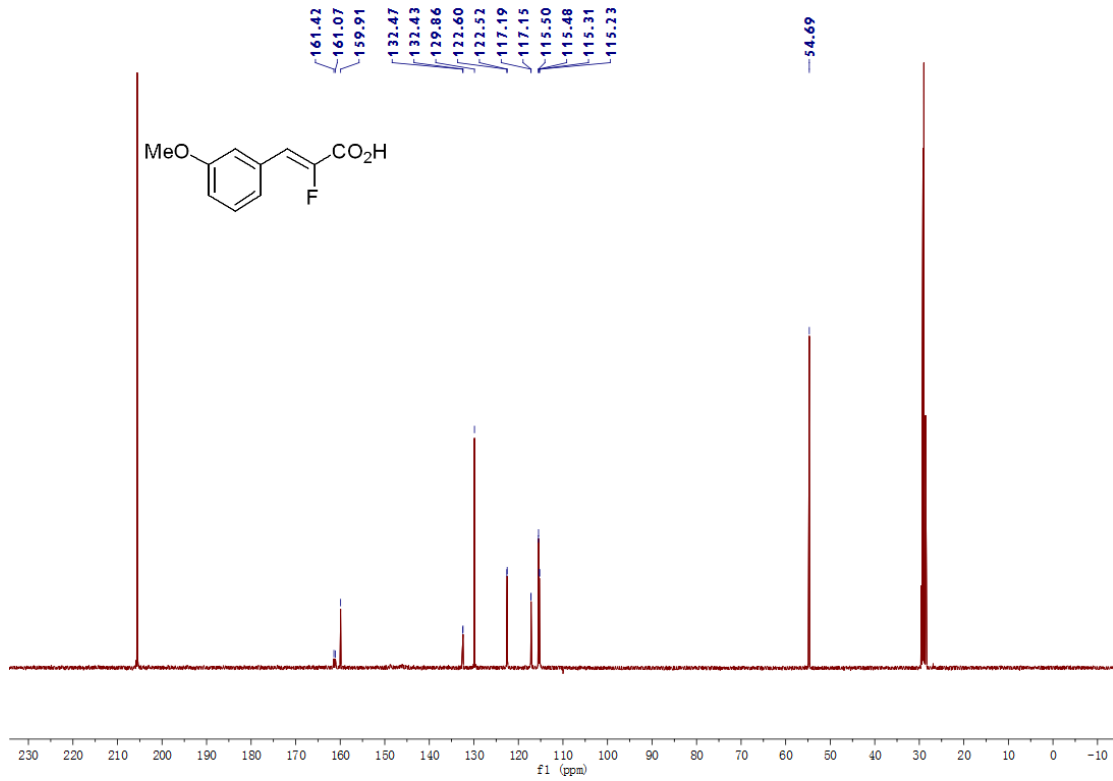
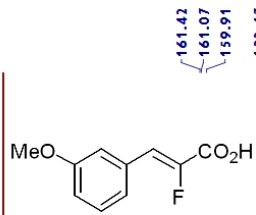
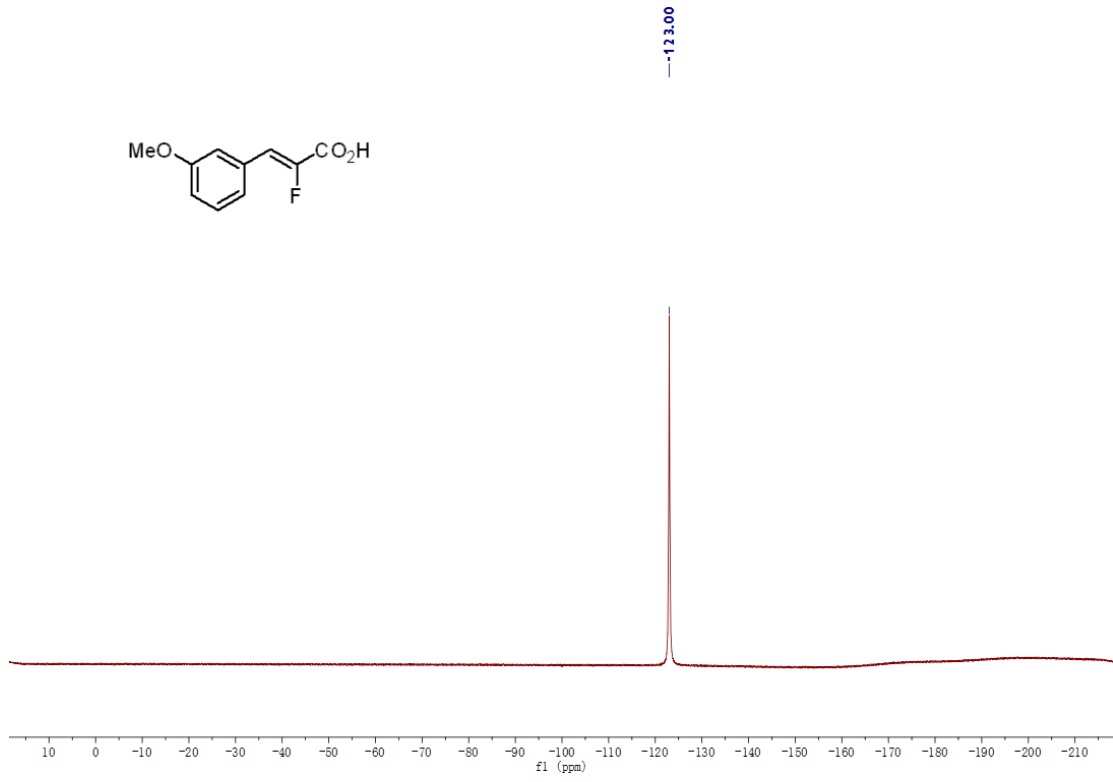
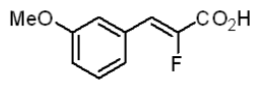


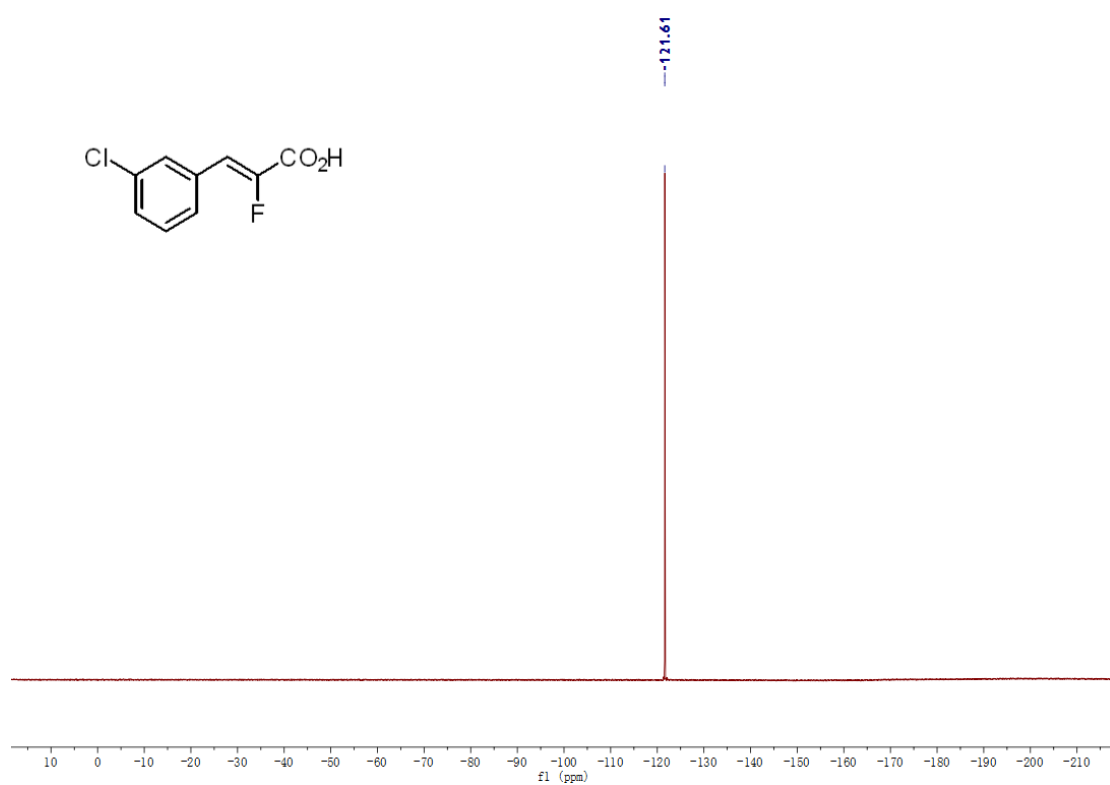
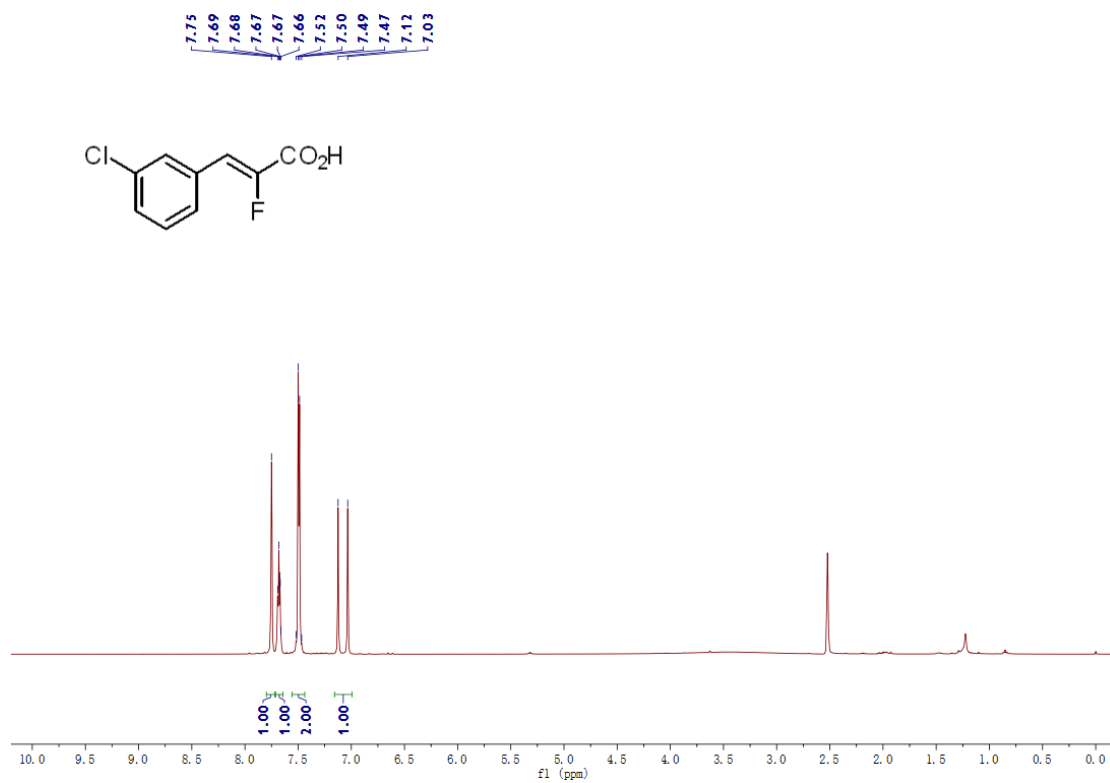


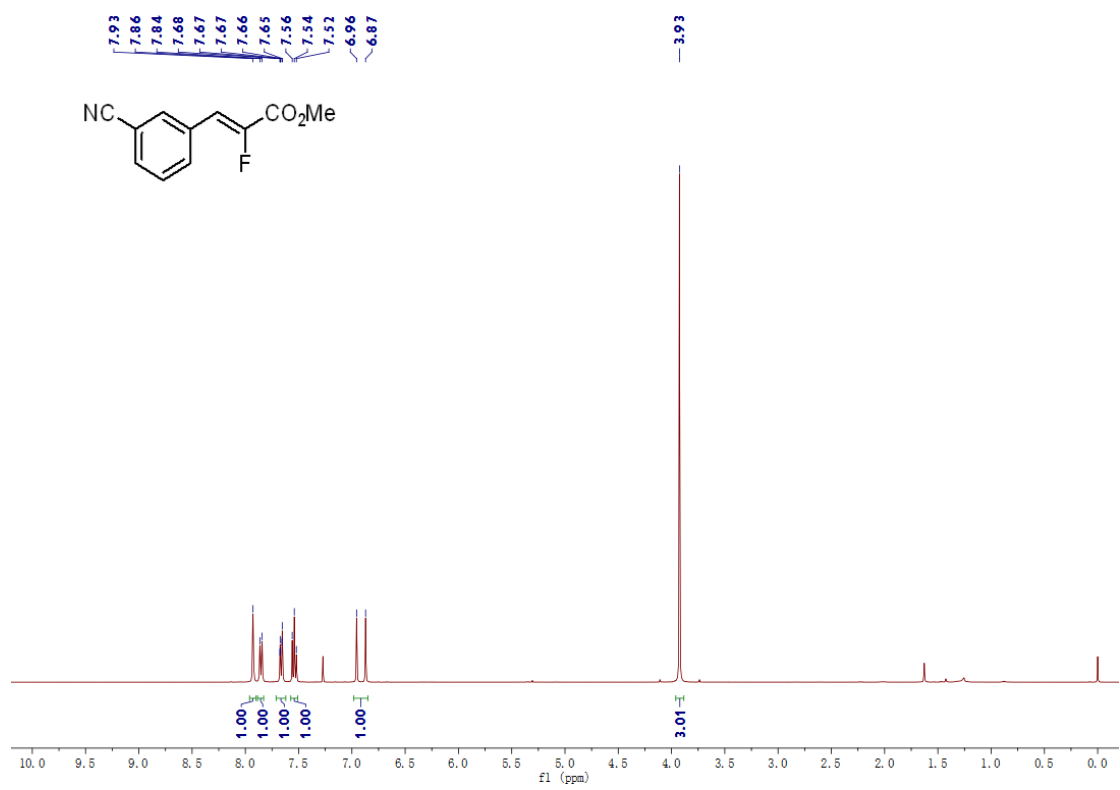
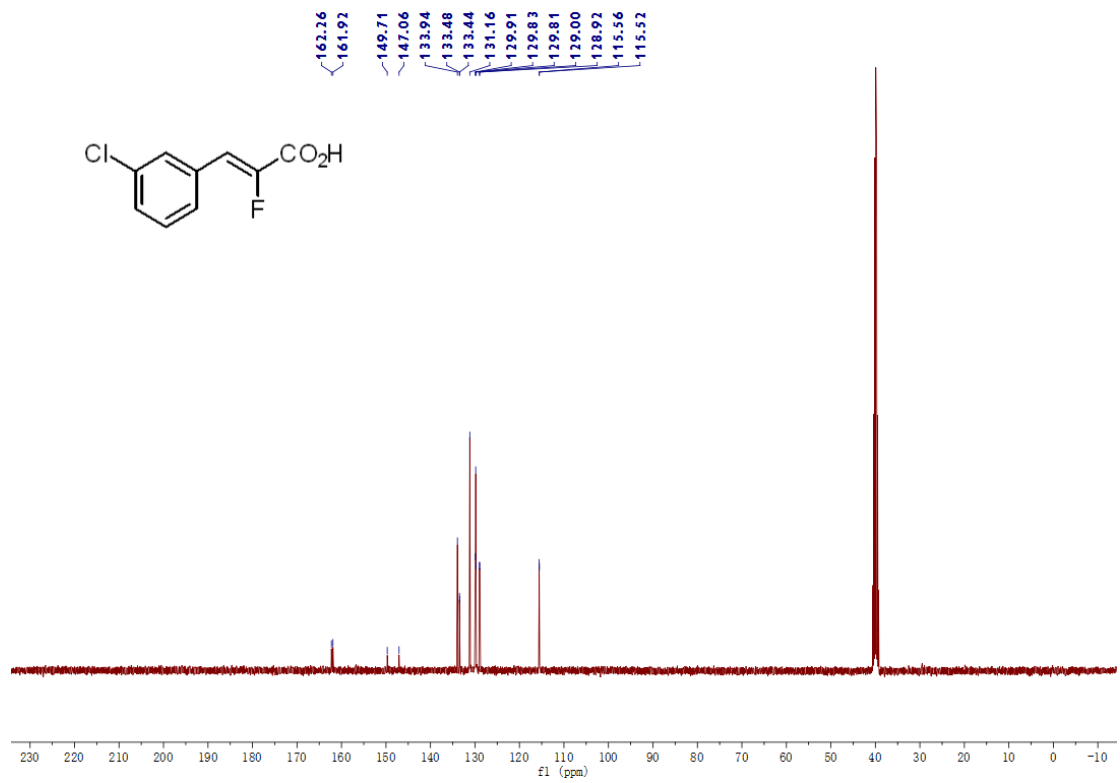


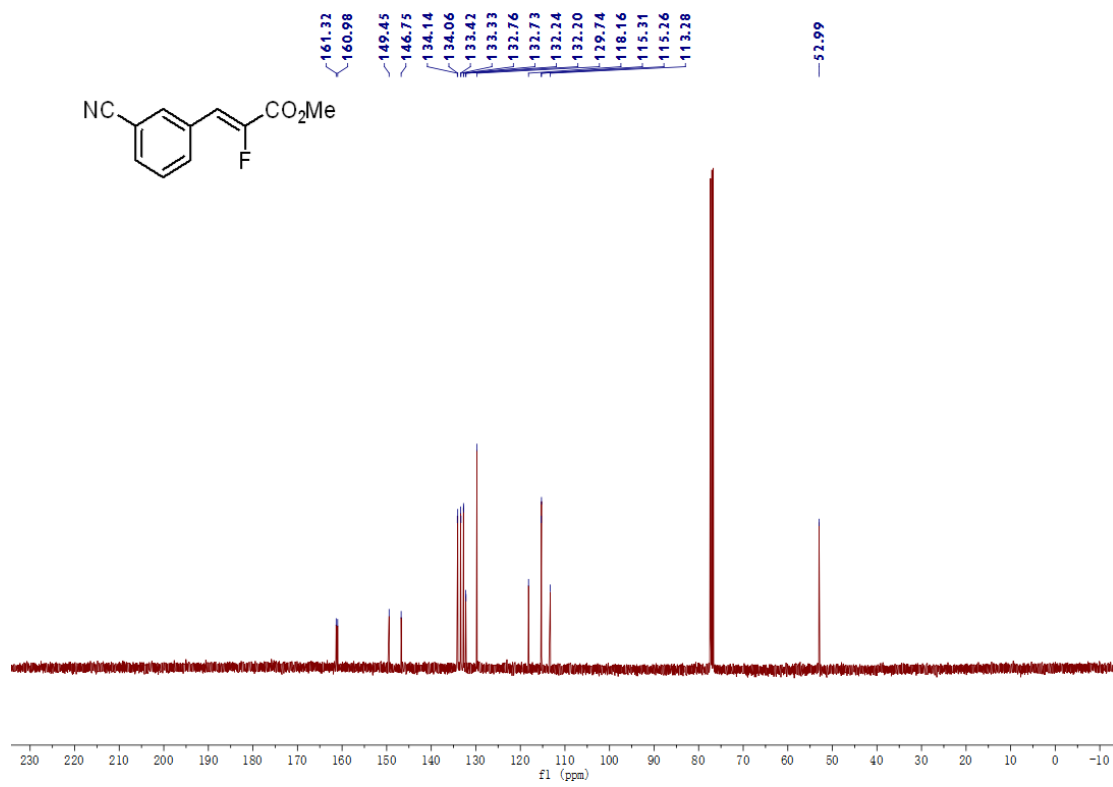
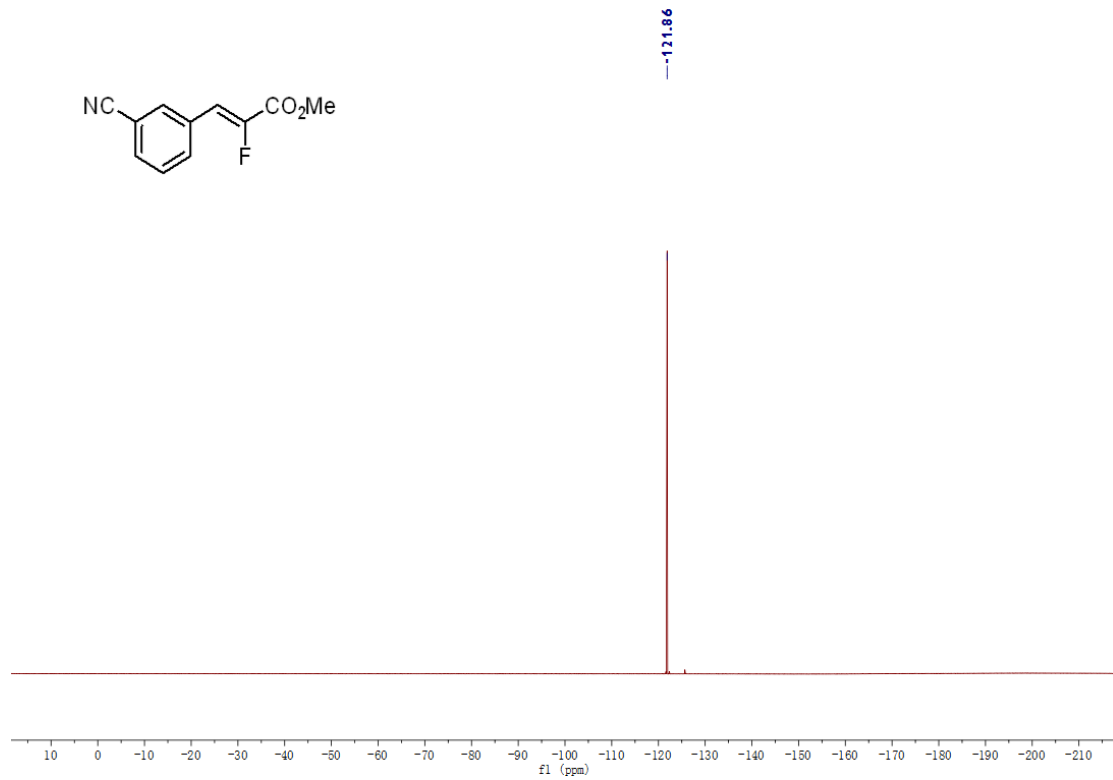


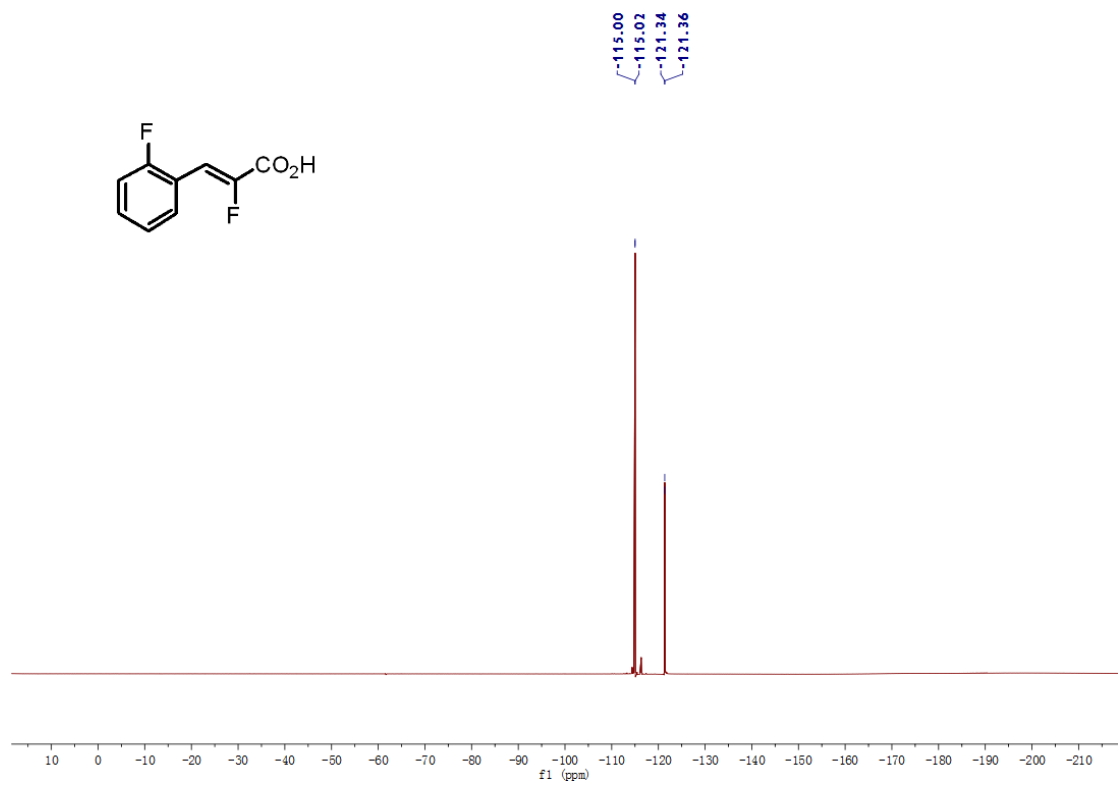
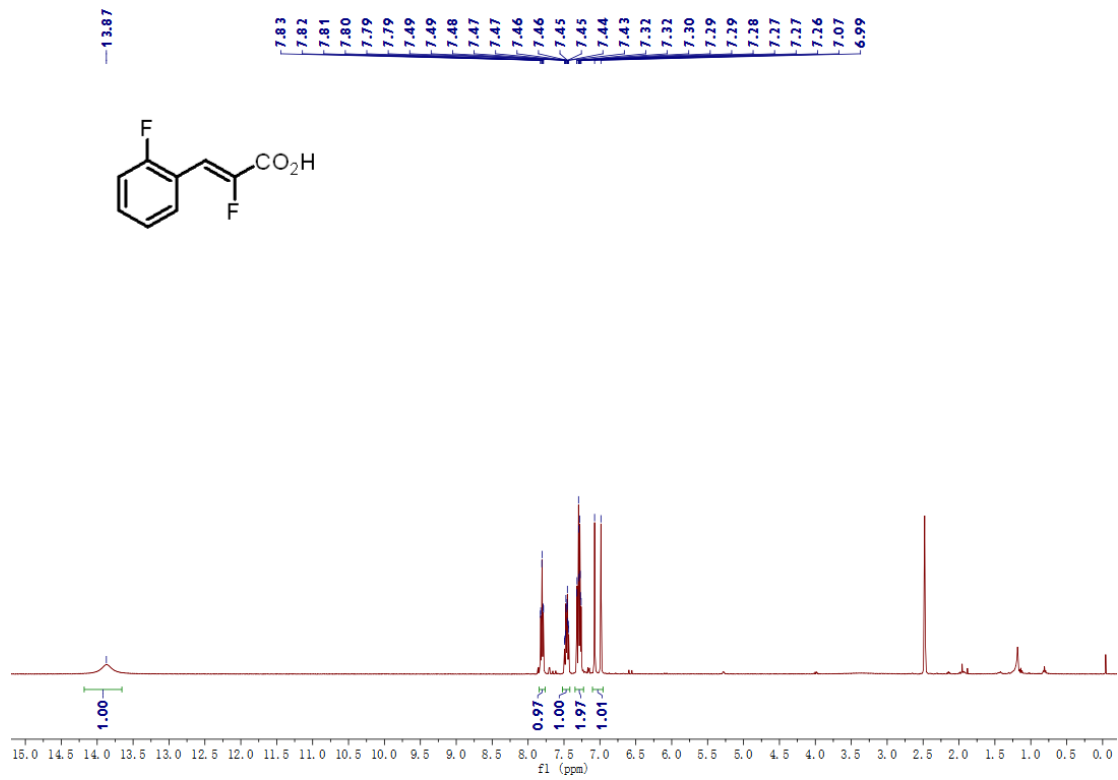


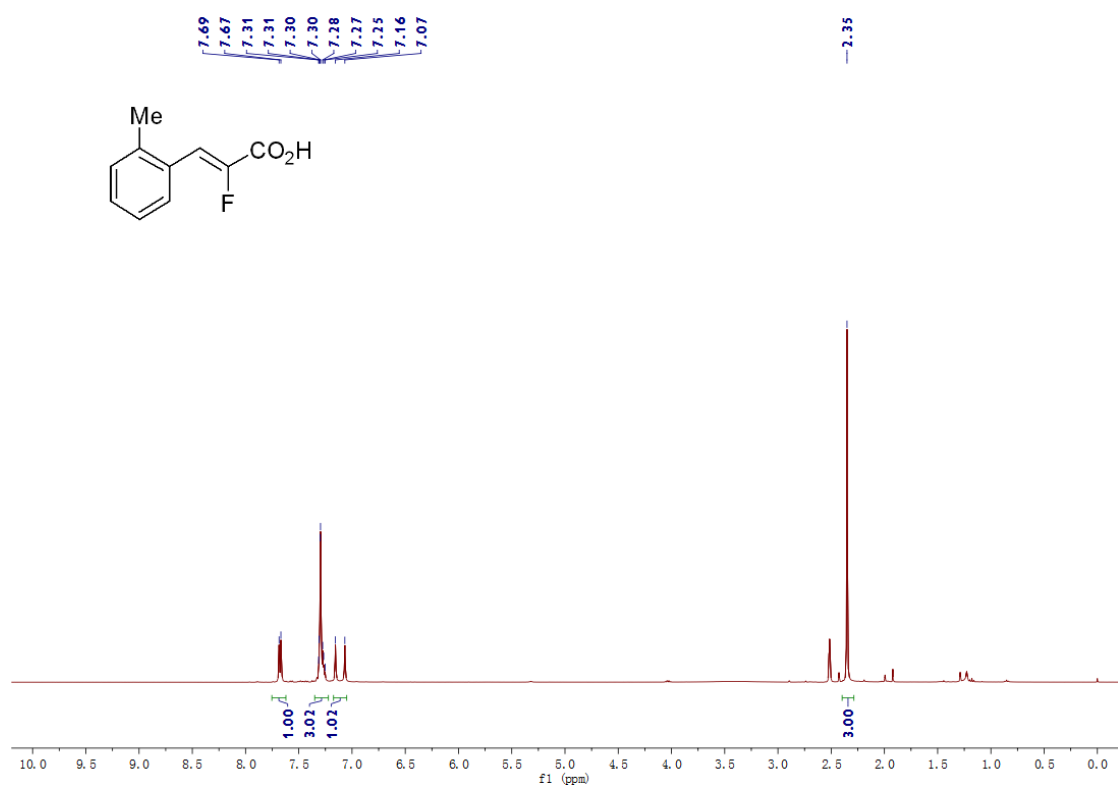
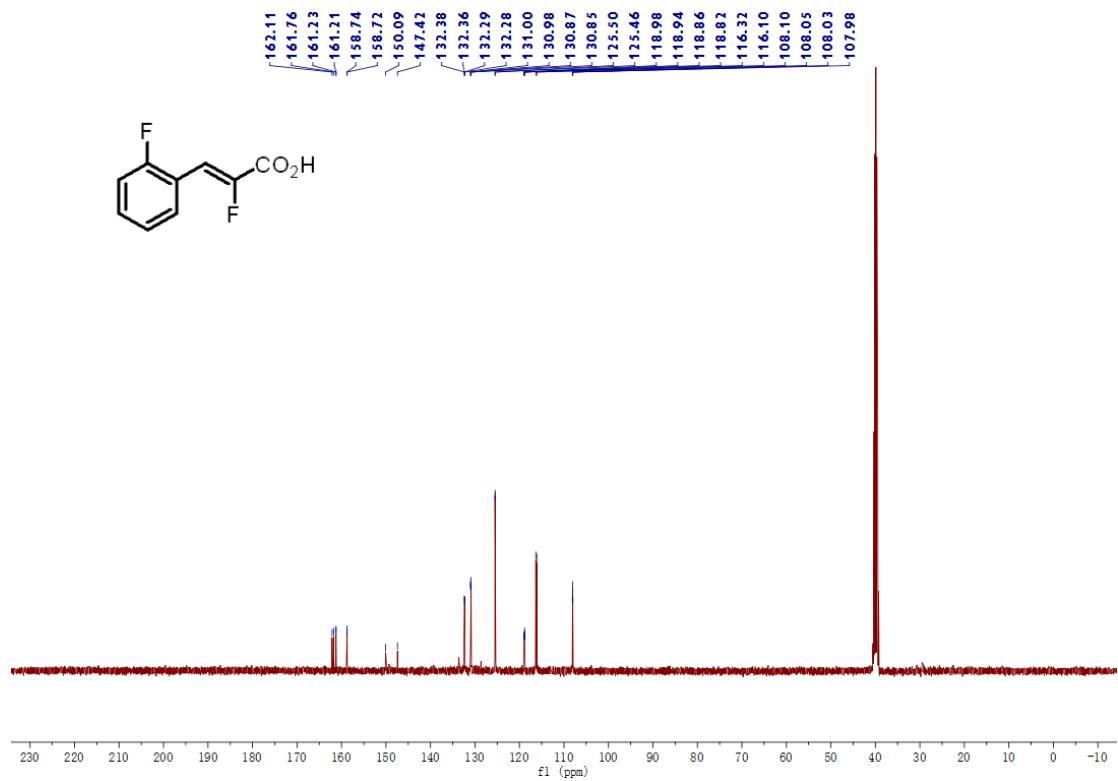


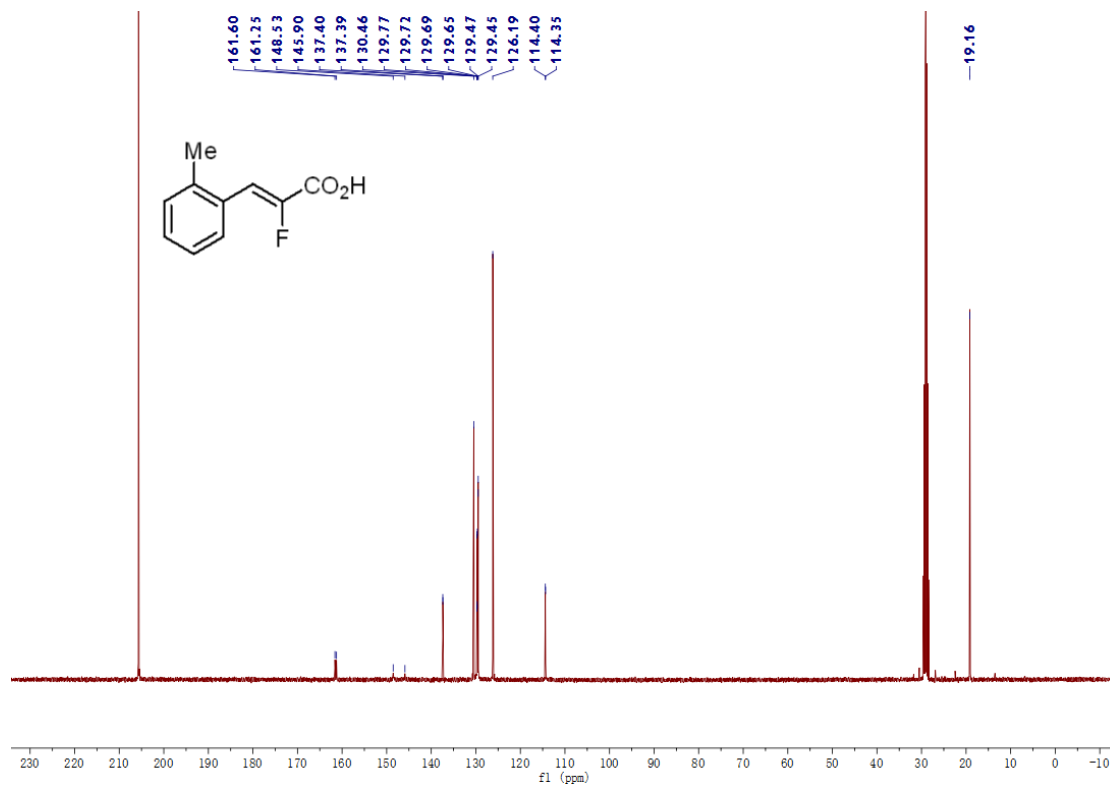
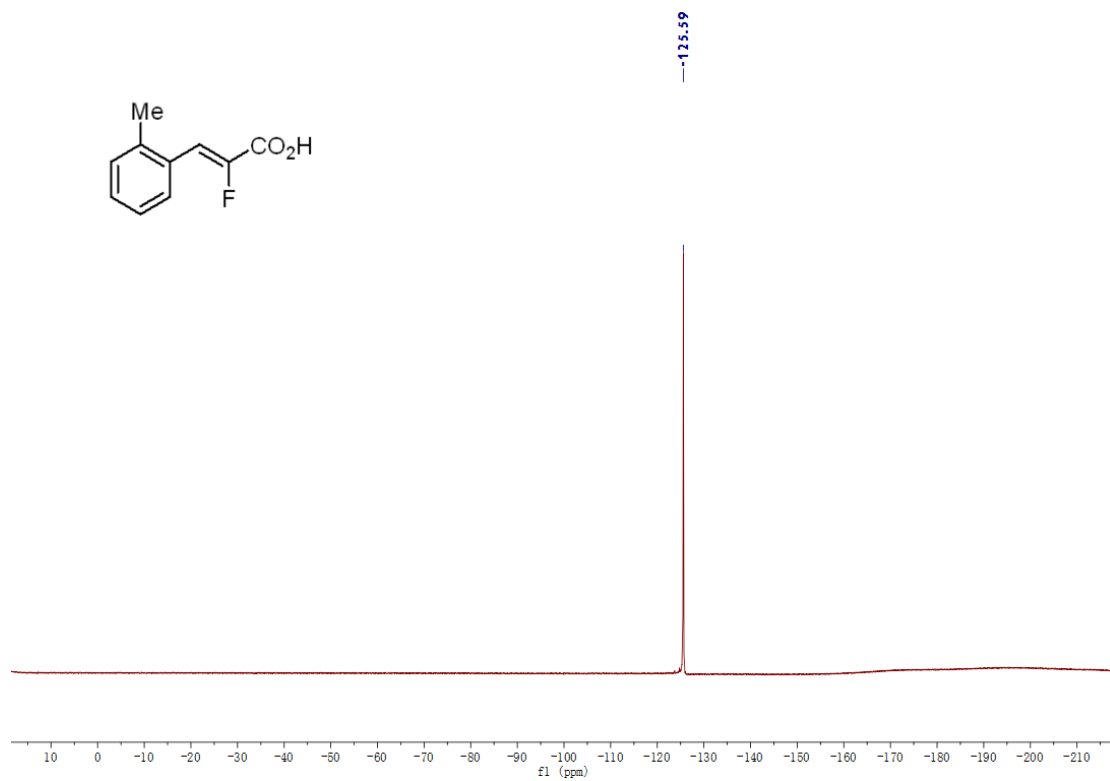


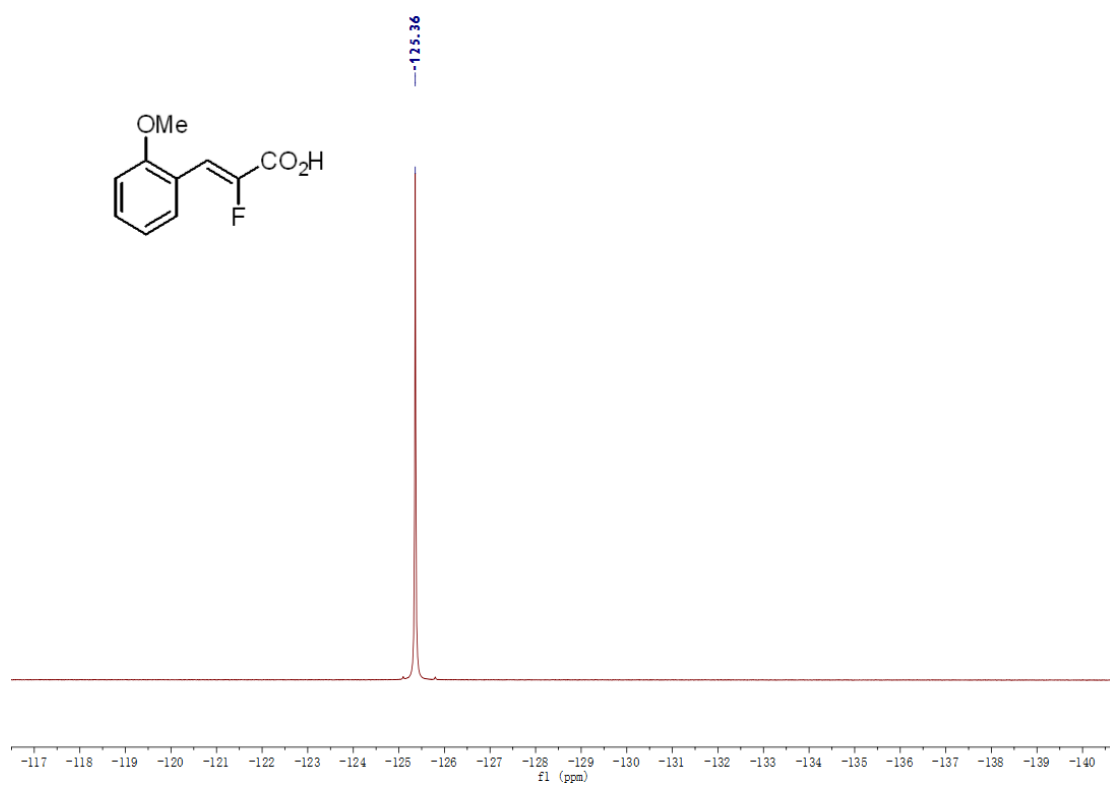
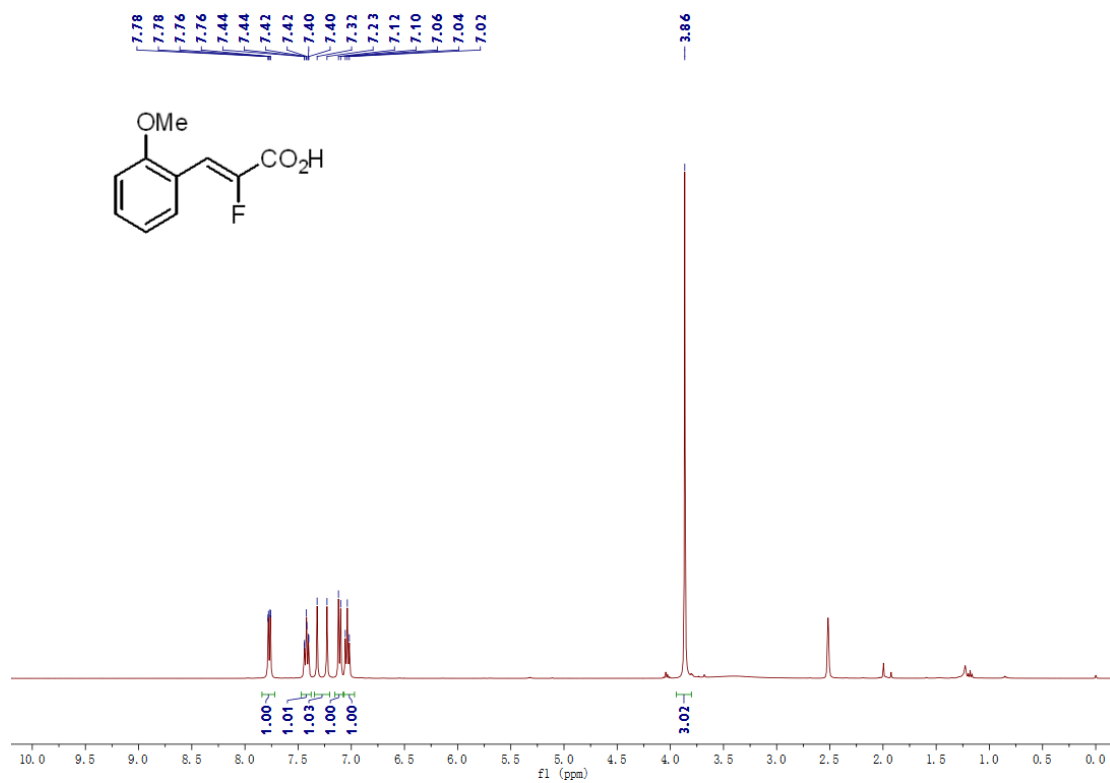


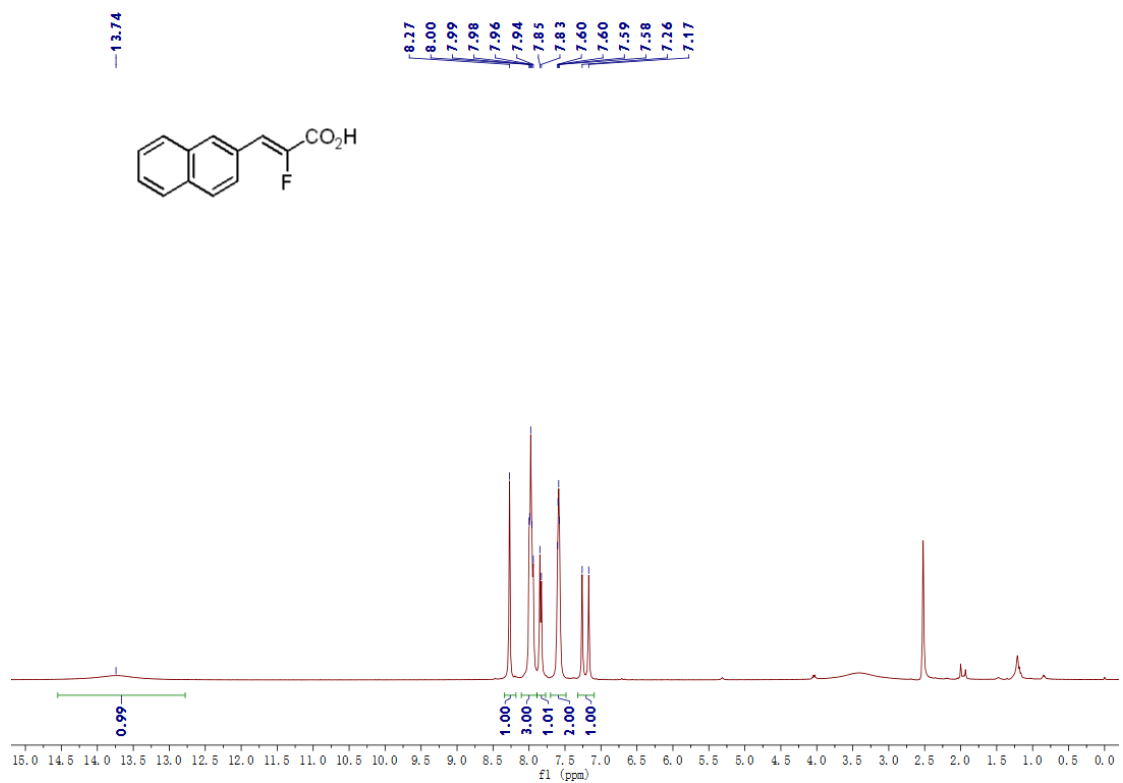
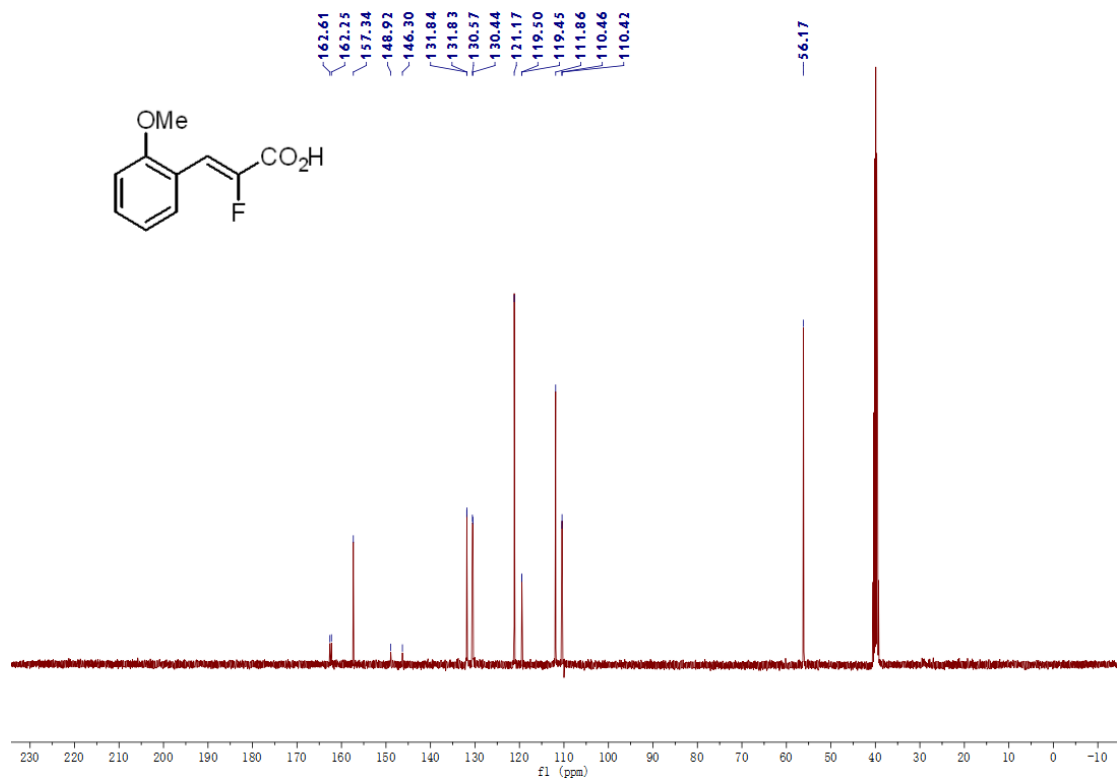


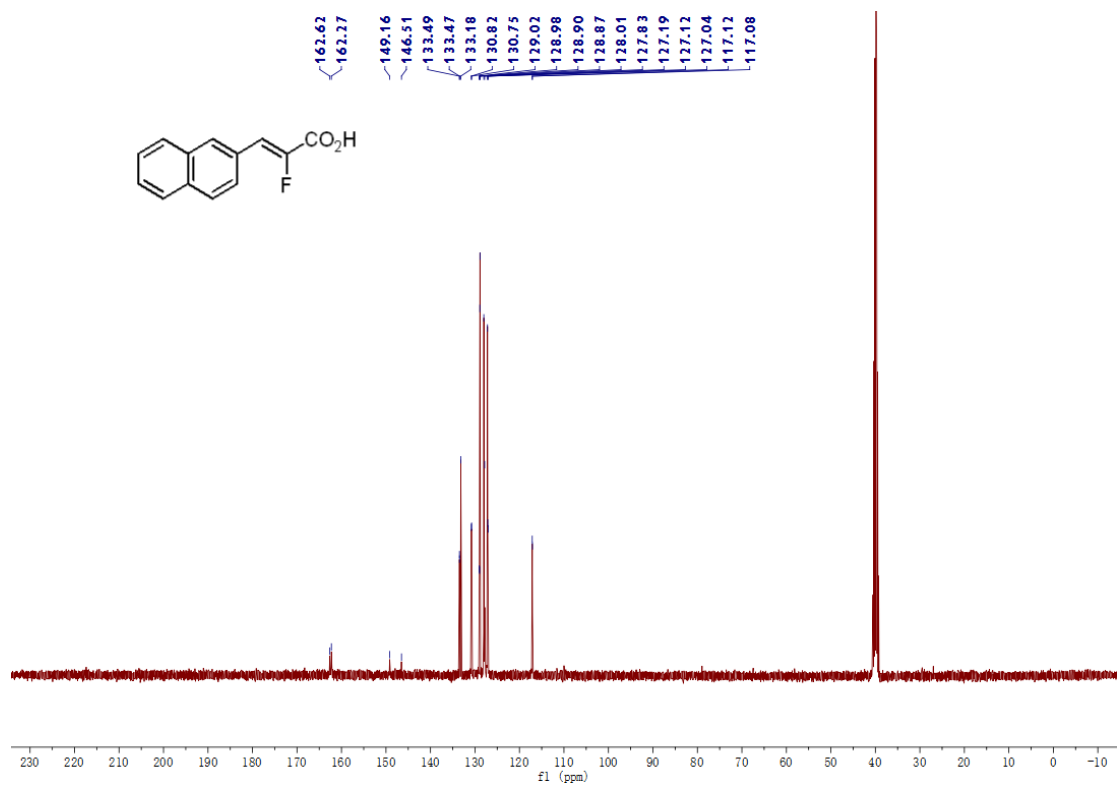
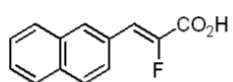
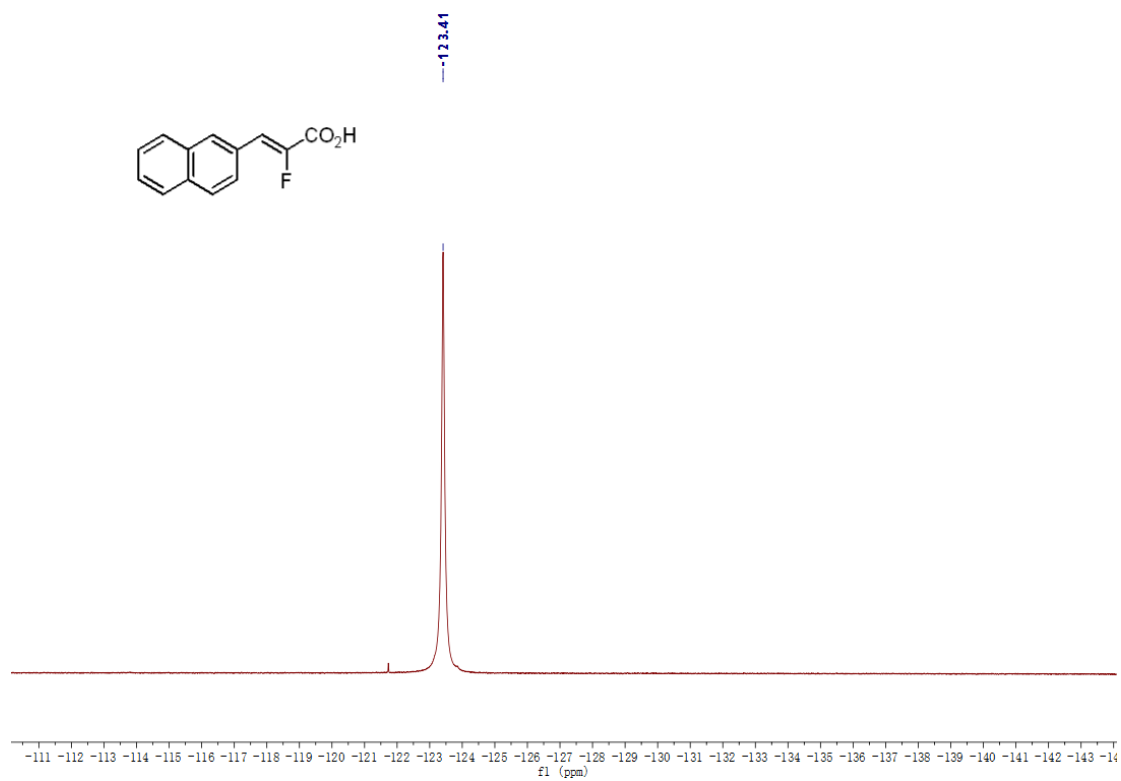
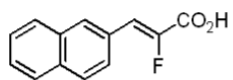


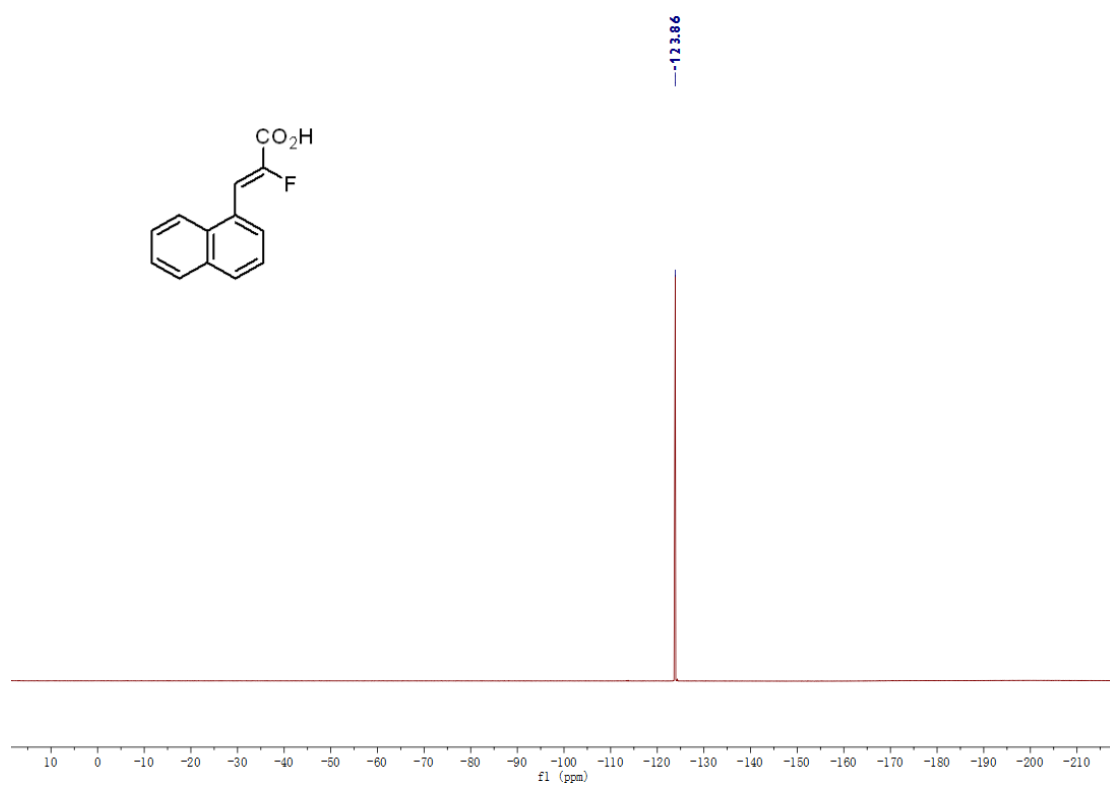
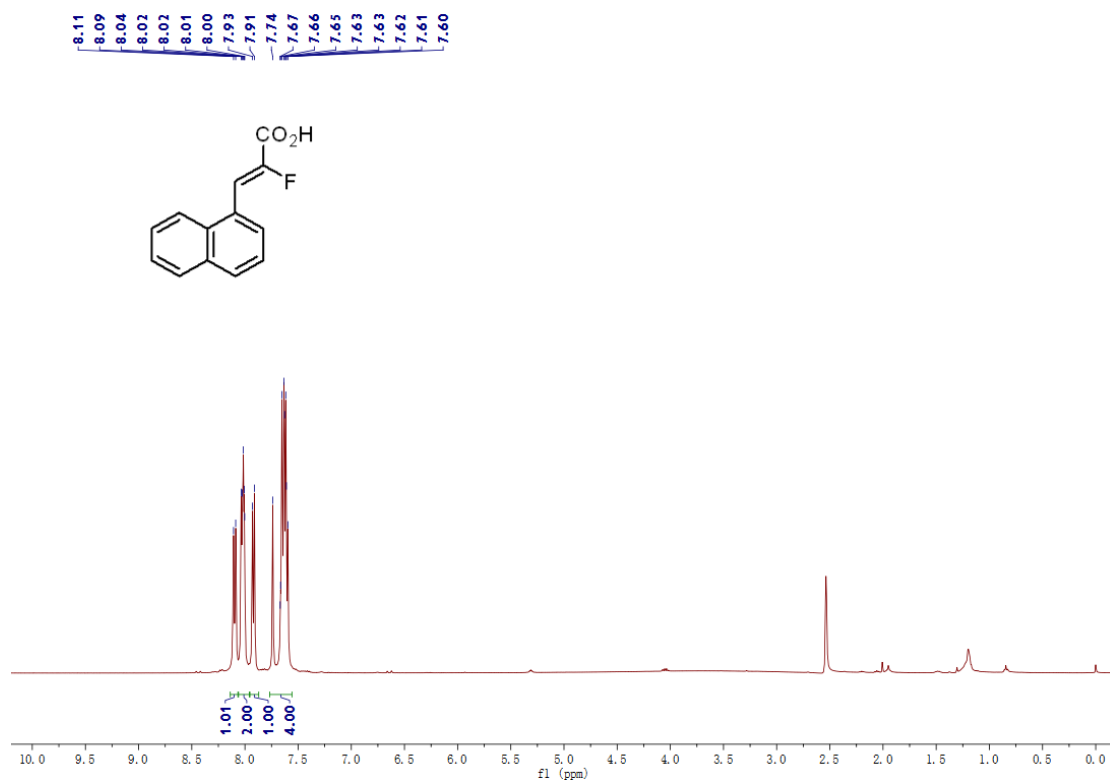


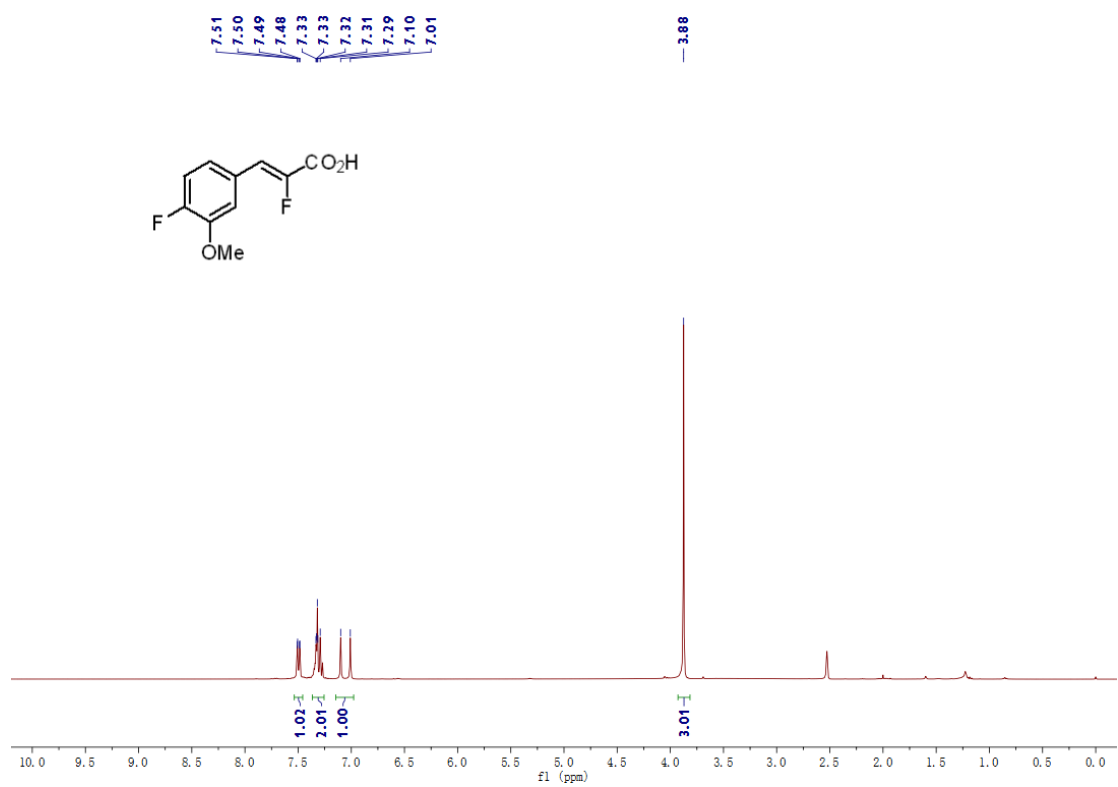
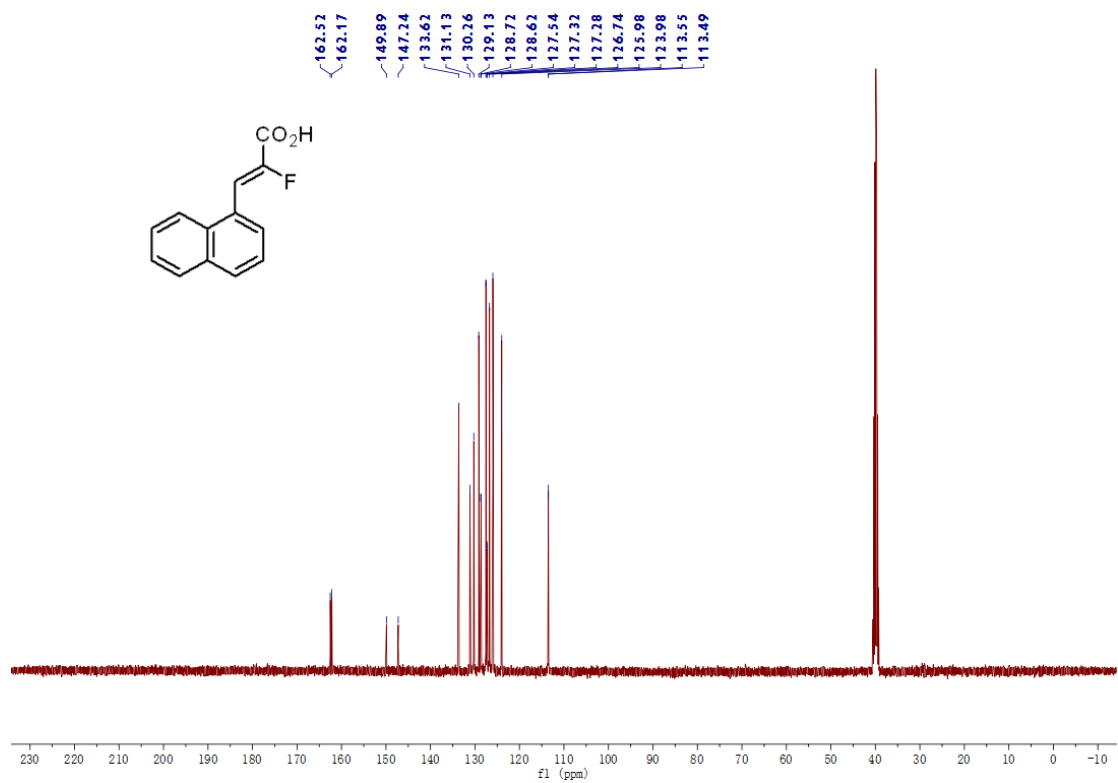


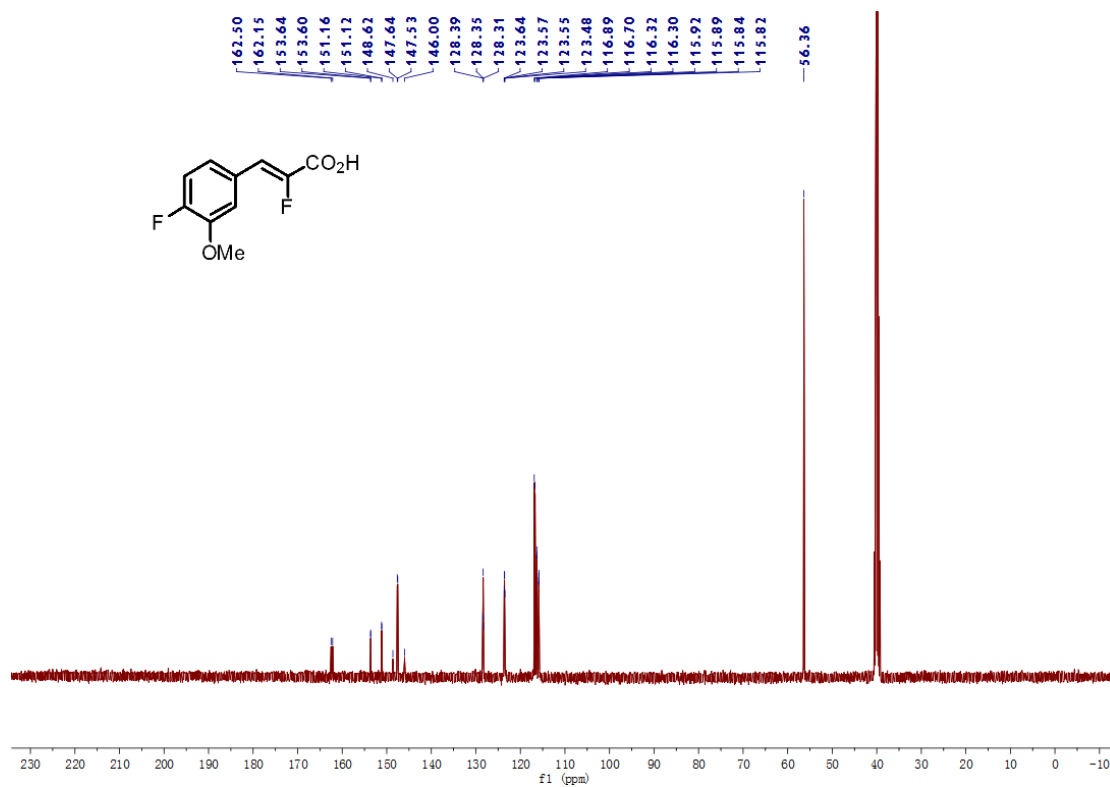
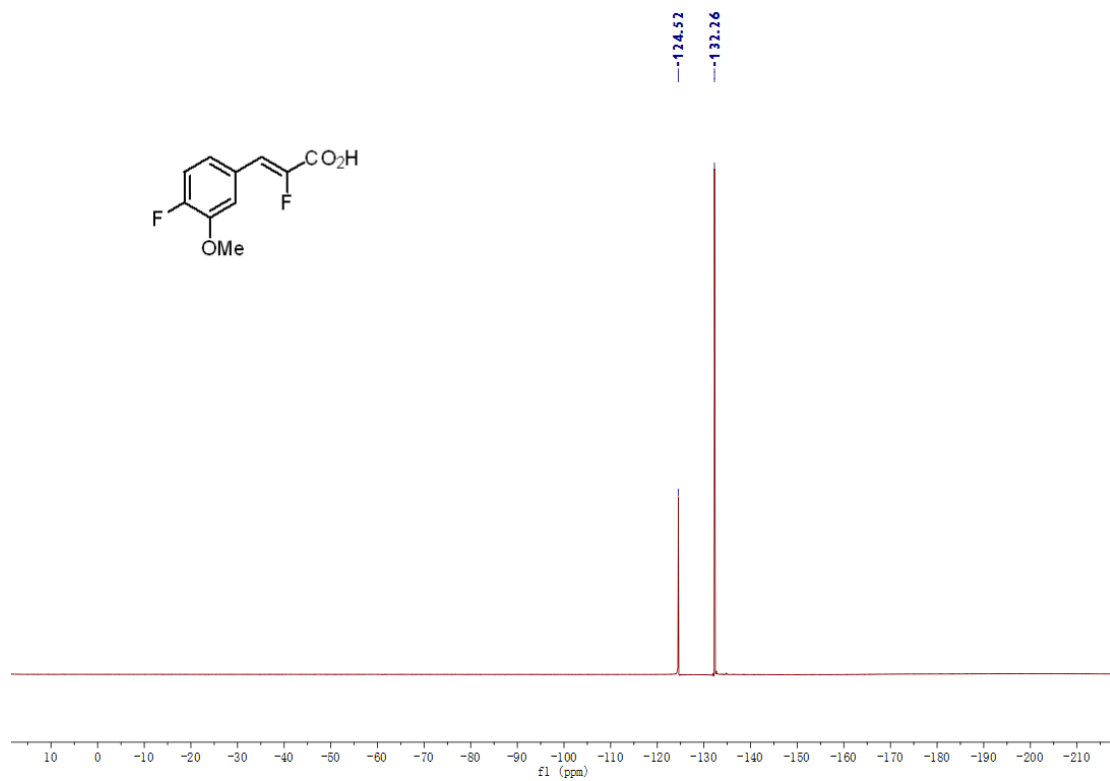




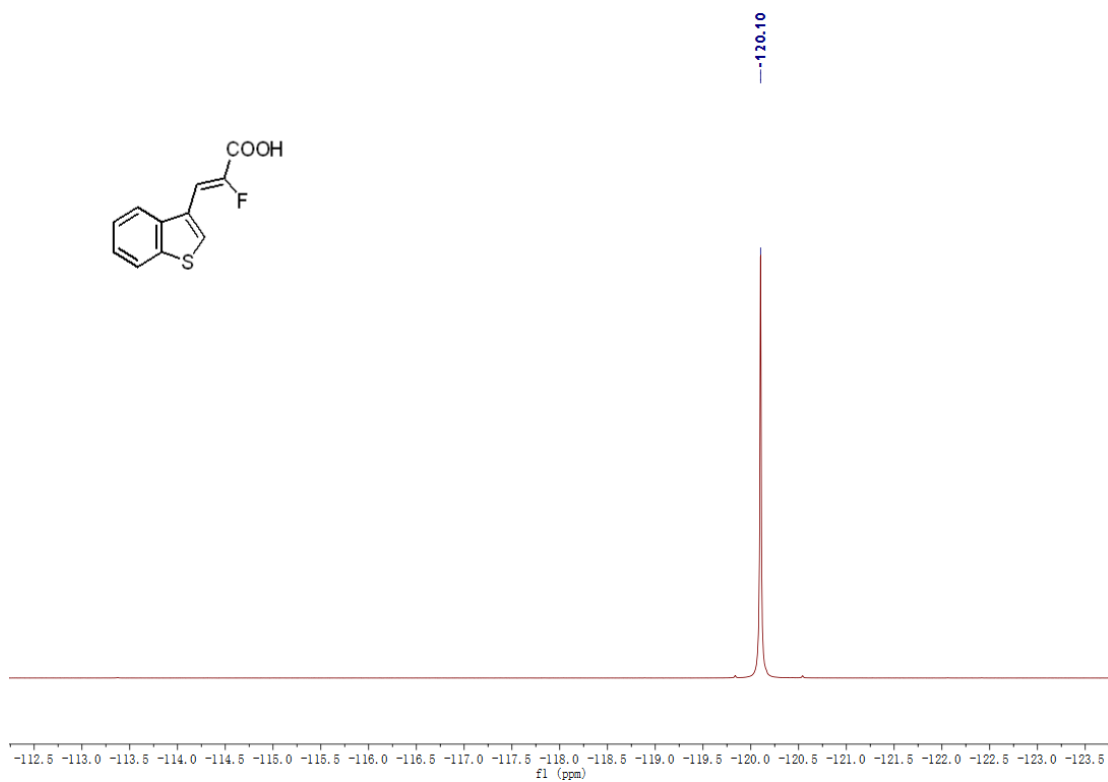
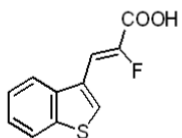
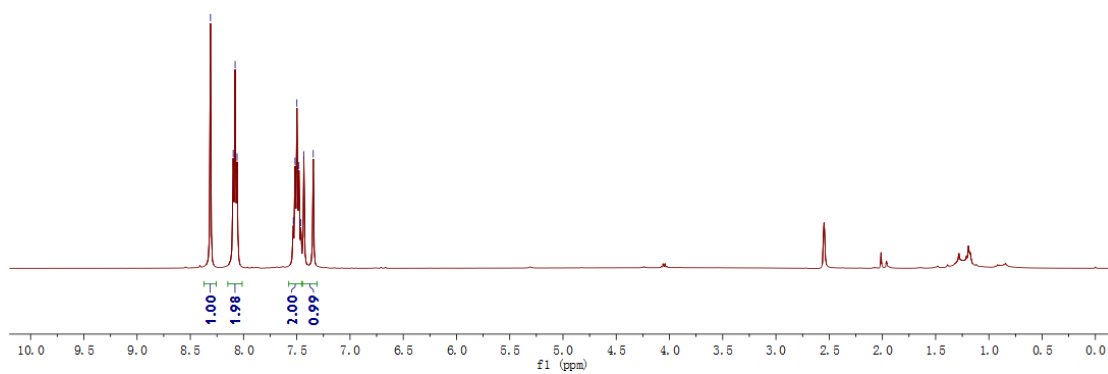
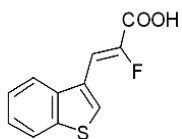


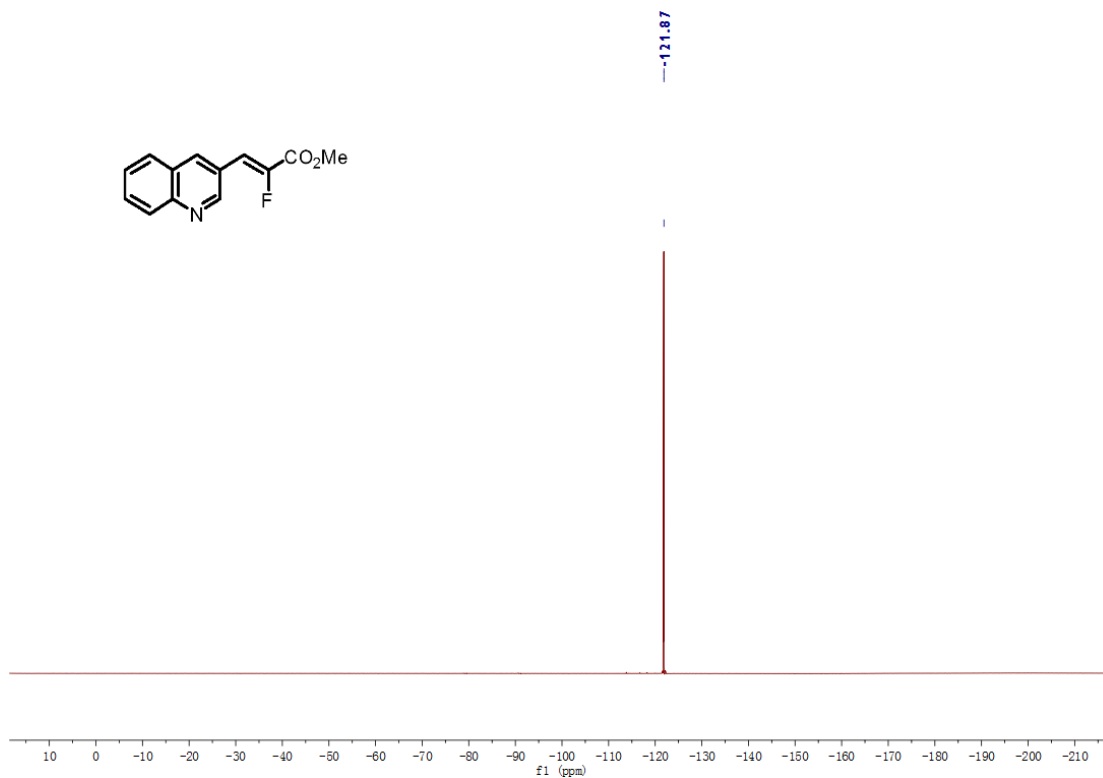
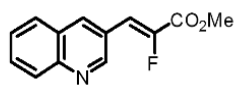






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