

Supporting Information for

Visible Light Promoted Fluoroalkylation of Alkenes and Alkynes Using 2-Bromophenol as a Catalyst

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1. General information.

¹H NMR spectra were recorded on an Agilent NMR system (400 MHz). ¹⁹F NMR was recorded on an Agilent NMR spectrometer (376 MHz, CFC1₃ as outside standard and low field is positive). Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. NMR yield was determined by ¹⁹F NMR using fluorobenzene as an internal standard before working up the reaction.

Materials: All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature. All reagents were weighed and handled in air at room temperature. LEDs with short wavelength (450-455 nm, 460-465 nm, 480-485 nm, 495-500 nm, 510-515 nm, 530-535 nm) were purchased from WATTCASTM, and relevant experiments were performed in a WP-TEC-1020SL parallel reactor from WATTCASTM.

2. General procedure.

2.1 General procedure for visible light promoted fluoroalkylation of alkenes and alkynes using 2-bromophenol as a catalyst. To a 25 mL of Schlenk tube equipped with a Teflon septum were added KOAc (0.6 mmol, 2.0 equiv) under Ar, followed by DCE (2 mL) with stirring. Alkene (**1**)/alkyne (**4**) (0.3 mmol, 1.0 equiv), 2-bromophenol (0.03 mmol, 0.1 equiv), and IR_f (**2**) (0.6 mmol, 2.0 equiv) were added subsequently. The tube was then irradiated with 12 W blue LEDs (430 nm-490 nm). After stirring for 16 h, the solvent was removed and the residue was purified with silica gel chromatography to provide pure product.

2.2 General procedure for visible light promoted fluoroalkylation of allylphenols. (Table 2, 3o-3r). To a 25 mL of Schlenk tube equipped with a Teflon septum were added KOAc (0.6 mmol, 2.0 equiv) under Ar, followed by dioxane (2 mL) with stirring. Allylphenol (**1**) (0.3 mmol, 1.0 equiv) and ICF₂COOEt (**2a**) (0.6 mmol, 2.0 equiv) were added subsequently. The tube was then irradiated with 12 W blue LEDs (430 nm-490 nm). After stirring for 16 h, the solvent was removed and the residue was purified with silica gel chromatography to provide pure product.

2.3 General procedure for the Heck-type reaction of R_fI with alkenes (Table 4, 6a-6h). To a 25

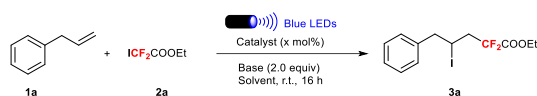
mL of Schlenk tube equipped with a Teflon septum were added K_2CO_3 (0.6 mmol, 2.0 equiv) under Ar, followed by DMSO (2 mL) with stirring. Alkenes (**1**) (0.3 mmol, 1.0 equiv), 2-bromophenol (0.03 mmol, 0.1 equiv), and ICF_2COOEt (**2a**) (0.6 mmol, 2.0 equiv) were added subsequently. The tube was then irradiated with 12 W blue LEDs (430 nm-490 nm). After stirring for 16 h, the residue was diluted with ethyl acetate, washed with H_2O and brine, dried over Na_2SO_4 , filtered and concentrated. The residue was purified with silica gel chromatography to provide pure product.

2.4 General procedure for the Heck-type reaction of R_fI with allylphenols. (Table 4, 6i-6q). To a 25 mL of Schlenk tube equipped with a Teflon septum were added KOAc (0.9 mmol, 3.0 equiv) under Ar, followed by DCM/DMSO (v/v=3:1) (2 mL) with stirring. Allylphenol (**1**) (0.3 mmol, 1.0 equiv) and IR_f (**2**) (0.6 mmol, 2.0 equiv) were added subsequently. The tube was then irradiated with 12 W blue LEDs (430 nm-490 nm). After stirring for 14 h, the residue was diluted with ethyl acetate, washed with H_2O and brine, dried over Na_2SO_4 , filtered and concentrated. The residue was purified with silica gel chromatography to provide pure product.

2.5 General procedure for visible light promoted difluoroalkylation of allylphenols (Table 5, 7a-7e). To a 25 mL of Schlenk tube equipped with a Teflon septum were added K_2CO_3 (0.6 mmol, 2.0 equiv) under Ar, followed by THF (2 mL) with stirring. Allylphenol (**1**) (0.3 mmol, 1.0 equiv) and ICF_2COOEt (**2a**) (0.6 mmol, 2.0 equiv) were added subsequently. The tube was then irradiated with 12 W blue LEDs (430 nm-490 nm). After stirring for 16 h, the solvent was removed and the residue was purified with silica gel chromatography to provide pure product.

3. Optimization.

Reaction optimization table of visible-light promoted difluoroalkylation of allylbenzene (**1a**)

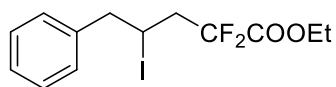


Entry	Wavelength (nm)	Catalyst (x mol%)	Base	Solvent	Yield (%), 3a ^b
1	430-490	----	K ₂ CO ₃	Dioxane	----
2	430-490	PhOH (10)	K ₂ CO ₃	Dioxane	68
3	430-490	PhOH (10)	Cs ₂ CO ₃	Dioxane	64
4	430-490	PhOH (10)	Na ₂ CO ₃	Dioxane	31
5	430-490	PhOH (10)	KOAc	Dioxane	73
6	430-490	PhOH (10)	NaOAc	Dioxane	60
7	430-490	2-Br-C ₆ H ₄ OH (10)	KOAc	Dioxane	85
8	430-490	4-Br-C ₆ H ₄ OH (10)	KOAc	Dioxane	74
9	430-490	2-Cl-C ₆ H ₄ OH (10)	KOAc	Dioxane	65
10	430-490	4-CF ₃ O-C ₆ H ₄ OH (10)	KOAc	Dioxane	20
11	430-490	2-Me-C ₆ H ₄ OH (10)	KOAc	Dioxane	63
12	430-490	Catechol (10)	KOAc	Dioxane	73
13	430-490	2-MeO-C ₆ H ₄ OH (10)	KOAc	Dioxane	72
14	430-490	2-Br-C ₆ H ₄ OH (10)	KOAc	MeCN	65
15	430-490	2-Br-C ₆ H ₄ OH (10)	KOAc	DMSO	----
16	430-490	2-Br-C ₆ H ₄ OH (10)	KOAc	Toluene	12
17	430-490	2-Br-C ₆ H ₄ OH (10)	KOAc	DCE	92 (88)
18	430-490	2-Br-C ₆ H ₄ OH (5)	KOAc	DCE	79
19 ^c	430-490	2-Br-C ₆ H ₄ OH (10)	KOAc	DCE	----
20	430-490	2-Br-C ₆ H ₄ OH (10)	----	DCE	7
21	430-490	----	KOAc	DCE	44
22	450-455	2-Br-C ₆ H ₄ OH (10)	KOAc	DCE	87
23	460-465	2-Br-C ₆ H ₄ OH (10)	KOAc	DCE	83
24	480-485	2-Br-C ₆ H ₄ OH (10)	KOAc	DCE	88
25	495-500	2-Br-C ₆ H ₄ OH (10)	KOAc	DCE	57
26	510-515	2-Br-C ₆ H ₄ OH (10)	KOAc	DCE	14
27	530-535	2-Br-C ₆ H ₄ OH (10)	KOAc	DCE	----

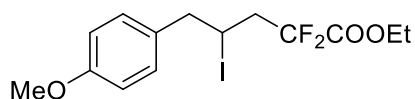
^aReaction conditions (unless otherwise specified): **1a** (0.3 mmol, 1.0 equiv), **2a** (0.6 mmol, 2.0 equiv), catalyst (0.03 mmol, 0.1 equiv), solvent (2.0 mL), 12 W blue LEDs, room temperature, 16 h.

^bNMR yield was determined by ¹⁹F NMR using fluorobenzene as internal standard and number in parentheses is an isolated product yield. ^cThe reaction was performed without light.

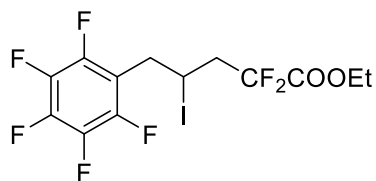
4. Data for compounds 3, 5, 6, 7.



Ethyl 2,2-difluoro-4-iodo-5-phenylpentanoate (3a). This compound is known.¹ The product (97 mg, 88% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 80:1) as colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.30 (m, 3H), 7.20 (d, *J* = 8.0 Hz, 2H), 4.40-4.35 (m, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 3.30-3.18 (m, 2H), 3.05-2.70 (m, 2H), 1.37 (t, *J* = 7.2 Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -101.3 – -102.3 (m, 1F), -106.0 – -106.9 (m, 1F). ¹³C NMR (101 MHz, CDCl₃) δ 163.3 (t, *J* = 32.5 Hz), 138.7, 128.9, 128.5, 127.1, 115.1 (t, *J* = 254.6 Hz), 63.2, 47.1, 44.2 (t, *J* = 23.5 Hz), 21.9 (t, *J* = 3.8 Hz), 13.8.

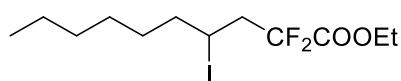


Ethyl 2,2-difluoro-4-iodo-5-(4-methoxyphenyl)pentanoate (3b). The product (85 mg, 71% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 100:1) as pale yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.11 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 4.34 (q, *J* = 7.2 Hz, 2H), 4.29 (m, 1H), 3.80 (s, 3H), 3.17-3.15 (m, 2H), 2.96-2.70 (m, 2H), 1.36 (t, *J* = 7.2 Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -101.3 – -102.1 (m, 1F), -106.1 – -106.9 (m, 1F). ¹³C NMR (101 MHz, CDCl₃) δ 163.4 (t, *J* = 32.5 Hz), 158.6, 130.8, 130.0, 115.2 (t, *J* = 253.7 Hz), 113.9, 63.2, 55.2, 46.3, 44.1 (t, *J* = 23.5 Hz), 22.7 (t, *J* = 3.7 Hz), 13.8. MS (ESI): *m/z* 399 (M+H)⁺. HRMS (ESI): Calculated for C₁₄H₁₈F₂IO₃ (M+H)⁺: 399.0263; Found: 399.0262.

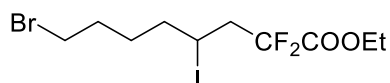


Ethyl 2,2-difluoro-4-iodo-5-(perfluorophenyl)pentanoate (3c). The product (124 mg, 90% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 100:1) as pale yellow

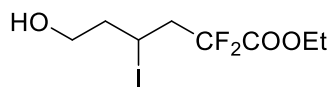
liquid. ^1H NMR (400 MHz, CDCl_3) δ 4.45-4.30 (m, 1H), 4.36 (q, $J = 7.2$ Hz, 2H), 3.45-3.30 (m, 2H), 3.10-2.90 (m, 1H), 2.86-2.73 (m, 1H), 1.38 (t, $J = 7.0$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -101.2 – -102.3 (m, 1F), -106.0 – -106.9 (m, 1F), -142.2 (dd, $J = 21.8$ Hz, 8.3 Hz, 2F), -154.8 (t, $J = 20.3$ Hz, 1F), -161.8 (m, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 163.2 (t, $J = 32.2$ Hz), 145.1 (dm, $J = 251.4$ Hz), 140.5 (dm, $J = 255.3$ Hz), 137.6 (dm, $J = 253.9$ Hz), 114.9 (t, $J = 255.1$ Hz), 113.1 (m), 63.5, 45.1 (t, $J = 23.5$ Hz), 33.8, 16.7, 13.8. MS (EI): m/z (%) 331 (100), (M-I) $^+$, 303, 257. HRMS (EI): Calculated for $\text{C}_{13}\text{H}_{10}\text{F}_7\text{O}_2$ (M-I) $^+$: 331.0569; Found: 331.0566.



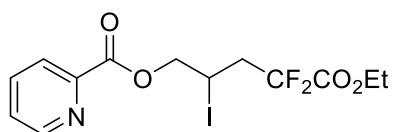
Ethyl 2, 2-difluoro-4-iododecanoate (3d). This compound is known.² The product (102 mg, 94% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 100:1) as colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 4.34 (q, $J = 7.2$ Hz, 2H), 4.25-4.18 (m, 1H), 2.98-2.84 (m, 1H), 2.79-2.66 (m, 1H), 1.85-1.68 (m, 2H), 1.55-1.46 (m, 1H), 1.37 (t, $J = 7.2$ Hz, 3H), 1.36-1.25 (m, 7H), 0.88 (t, $J = 6.8$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -101.5 – -102.6 (m, 1F), -106.4 – -107.3 (m, 1F). ^{13}C NMR (101 MHz, CDCl_3) δ 163.4 (t, $J = 32.7$ Hz), 115.2 (t, $J = 253.4$ Hz), 63.2, 45.3 (t, $J = 23.3$ Hz), 40.4, 31.5, 29.4, 28.2, 23.3 (t, $J = 3.9$ Hz), 22.5, 14.0, 13.9.



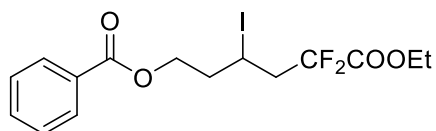
Ethyl 8-bromo-2,2-difluoro-4-iodooctanoate (3e). The product (113 mg, 91% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 50:1) as colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 4.34 (q, $J = 7.2$ Hz, 2H), 4.25-4.19 (m, 1H), 3.41 (t, $J = 6.6$ Hz, 2H), 2.99-2.85 (m, 1H), 2.81-2.67 (m, 1H), 1.96-1.65 (m, 5H), 1.60-1.50 (m, 1H), 1.37 (t, $J = 7.2$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -101.6 – -102.6 (m, 1F), -106.3 – -107.3 (m, 1F). ^{13}C NMR (101 MHz, CDCl_3) δ 163.3 (t, $J = 32.3$ Hz), 115.1 (t, $J = 254.1$ Hz), 63.3, 45.2 (t, $J = 23.2$ Hz), 39.4, 33.1, 31.6, 28.2, 22.2 (t, $J = 3.7$ Hz), 13.9. MS (ESI): m/z 415 (M $^+$ +H), 413 (M+H) $^+$. HRMS (ESI): Calculated for $\text{C}_{10}\text{H}_{17}\text{F}_2\text{O}_2\text{BrI}$ (M+H) $^+$: 412.9419; Found: 412.9419.



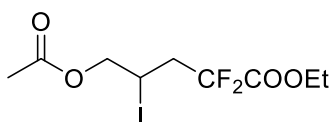
Ethyl 2,2-difluoro-6-hydroxy-4-iodohexanoate (3f). The product (80 mg, 83% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 20:1) as colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 4.42-4.35 (m, 1H), 4.33 (q, $J = 7.2$ Hz, 2H), 3.88-3.68 (m, 2H), 3.05-2.70 (m, 2H), 2.00 (q, $J = 6.1$ Hz, 2H), 1.90 (s, 1H), 1.36 (t, $J = 7.2$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -101.4 – -102.4 (m, 1F), -105.8 – -106.8 (m, 1F). ^{13}C NMR (101 MHz, CDCl_3) δ 163.4 (t, $J = 32.5$ Hz), 115.1 (t, $J = 254.0$ Hz), 63.3, 62.3, 45.4 (t, $J = 23.3$ Hz), 42.4, 19.0 (t, $J = 4.1$ Hz), 13.8. MS (ESI): m/z 323 ($\text{M}+\text{H}$) $^+$, 305. HRMS (ESI): Calculated for $\text{C}_8\text{H}_{14}\text{F}_2\text{O}_3\text{I}$ ($\text{M}+\text{H}$) $^+$: 322.9950; Found: 322.9950.



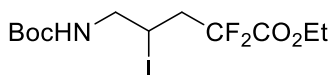
5-Ethoxy-4,4-difluoro-2-iodo-5-oxopentyl picolinate (3g). The product (81 mg, 65% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 8.77 (d, $J = 4.0$, 1H), 8.13 (d, $J = 7.6$ Hz, 1H), 7.86 (m, 1H), 7.51-7.48 (m, 1H), 4.71-4.67 (m, 1H), 4.58-4.46 (m, 2H), 4.32 (q, $J = 7.2$ Hz, 2H), 3.03-2.81 (m, 2H), 1.34 (t, $J = 7.2$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -102.2 – -103.4 (m, 1F), -105.6 – -106.6 (m, 1F). ^{13}C NMR (101 MHz, CDCl_3) δ 164.0, 163.1 (t, $J = 32.3$ Hz), 150.1, 147.2, 137.1, 127.2, 125.4, 114.7 (t, $J = 254.2$ Hz), 69.6, 63.4, 41.6 (t, $J = 23.9$ Hz), 14.2 (t, $J = 4.0$ Hz), 13.8. MS (ESI): m/z 414 ($\text{M}+\text{H}$) $^+$. HRMS (ESI): Calculated for $\text{C}_{13}\text{H}_{15}\text{F}_2\text{O}_4\text{IN}$ ($\text{M}+\text{H}$) $^+$: 414.0008; Found: 414.0007.



6-Ethoxy-5,5-difluoro-3-iodo-6-oxohexyl benzoate (3h). The product (104 mg, 81% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 20:1) as colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 8.02 (d, $J = 7.6$ Hz, 2H), 7.56 (t, $J = 7.2$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 2H), 4.57-4.52 (m, 1H), 4.45-4.35 (m, 2H), 4.32 (q, $J = 7.2$ Hz, 2H), 3.07-2.78 (m, 2H), 2.36-2.18 (m, 2H), 1.34 (t, $J = 7.2$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -101.4 – -102.4 (m, 1F), -106.1 – -107.1 (m, 1F). ^{13}C NMR (101 MHz, CDCl_3) δ 166.1, 163.1 (t, $J = 32.4$ Hz), 133.0, 129.8, 129.5, 128.3, 115.0 (t, $J = 254.3$ Hz), 64.4, 63.2, 45.3 (t, $J = 23.2$ Hz), 38.9, 17.4 (t, $J = 3.9$ Hz), 13.8. MS (ESI): m/z 427 ($\text{M}+\text{H}$) $^+$. HRMS (ESI): Calculated for $\text{C}_{15}\text{H}_{18}\text{F}_2\text{O}_4\text{I}$ ($\text{M}+\text{H}$) $^+$: 427.0212; Found: 427.0212.

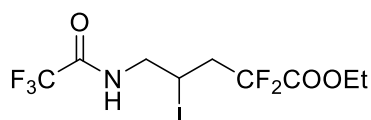


Ethyl 5-acetoxy-2,2-difluoro-4-iodopentanoate (3i). The product (91 mg, 87% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 20:1) as colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 4.37-4.28 (m, 4H), 4.28-4.20 (m, 1H), 2.92-2.72 (m, 2H), 2.10 (s, 3H), 1.36 (t, $J = 7.2$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -102.7 – -103.6 (m, 1F), -105.7 – -106.4 (m, 1F). ^{13}C NMR (101 MHz, CDCl_3) δ 170.0, 163.1 (t, $J = 32.2$ Hz), 114.7 (t, $J = 254.0$ Hz), 68.5, 63.3, 41.7 (t, $J = 23.9$ Hz), 20.7, 14.5 (t, $J = 4.1$ Hz), 13.8. MS (ESI): m/z 368 ($\text{M}+\text{NH}_4$) $^+$. HRMS (ESI): Calculated for $\text{C}_9\text{H}_{17}\text{NF}_2\text{O}_4\text{I}$ ($\text{M}+\text{NH}_4$) $^+$: 368.0165; Found: 368.0163.

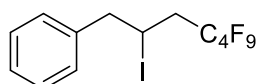


Ethyl 5-((tert-butoxycarbonyl)amino)-2,2-difluoro-4-iodopentanoate (3j). The product (103 mg, 84% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 4.98 (br, 1H), 4.34 (q, $J = 6.8$ Hz, 2H), 4.32-4.24 (m, 1H), 3.60-3.35 (m, 2H), 2.90-2.70 (m, 2H), 1.44 (s, 9H), 1.36 (t, $J = 7.2$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -102.0 – -103.0 (m, 1F), -105.7 – -106.7 (m, 1F). ^{13}C NMR (101 MHz, CDCl_3) δ

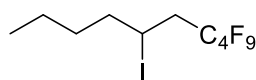
163.2 (t, $J = 32.8$ Hz), 155.5, 114.9 (t, $J = 253.2$ Hz), 80.0, 63.3, 48.9, 42.1 (t, $J = 23.8$ Hz), 28.2, 21.1, 13.8. MS (ESI): m/z 408 (M+H)⁺. HRMS (ESI): Calculated for C₁₂H₂₁NF₂O₄I (M+H)⁺: 408.0478; Found: 408.0477.



Ethyl 2,2-difluoro-4-iodo-5-(2,2,2-trifluoroacetamido)pentanoate (3k). The product (87 mg, 72% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 6.98 (br, 1H), 4.40-4.30 (m, 3H), 3.90-3.50 (m, 2H), 3.00-2.68 (m, 2H), 1.37 (t, $J = 7.0$ Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -75.9 (s, 3F), -102.0 – -103.0 (m, 1F), -105.4 – -106.4 (m, 1F). ¹³C NMR (101 MHz, CDCl₃) δ 163.0 (t, $J = 32.2$ Hz), 157.3 (q, $J = 37.7$ Hz), 115.6 (q, $J = 288.8$ Hz), 114.6 (t, $J = 254.3$ Hz), 63.6, 47.3, 42.6 (t, $J = 23.8$ Hz), 17.6, 13.8. MS (ESI): m/z 404 (M+H)⁺. HRMS (ESI): Calculated for C₉H₁₂NF₅O₃I (M+H)⁺: 403.9777; Found: 403.9778.

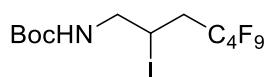


(4,4,5,5,6,6,7,7,7-Nonafluoro-2-iodoheptyl)benzene (3l). This compound is known.³ The product (104 mg, 75% yield) was purified with silica gel chromatography (Petroleum ether (100%)) as colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.28 (m, 3H), 7.22 (d, $J = 6.8$ Hz, 2H), 4.48 (m, 1H), 3.35-3.15 (m, 2H), 2.90 (m, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -81.1 (m, 3F), -113.2 (m, 2F), -124.6 (m, 2F), -126.0 (m, 2F). ¹³C NMR (101 MHz, CDCl₃) δ 138.5, 128.9, 128.6, 127.3, 120.0-104.0 (m), 46.9 (d, $J = 1.8$ Hz), 40.6 (t, $J = 21.0$ Hz), 19.4.

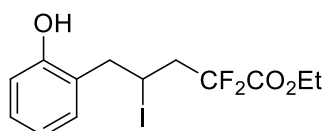


1,1,1,2,2,3,3,4,4-Nonafluoro-6-iododecane (3m). This compound is known.³ The product (112 mg,

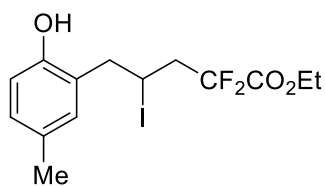
87% yield) was purified with silica gel chromatography (Petroleum ether (100%)) as colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 4.39-4.29 (m, 1H), 3.00-2.70 (m, 2H), 1.90-1.72 (m, 2H), 1.60-1.20 (m, 4H), 0.93 (t, $J = 7.2$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -81.1 (t, $J = 9.6$ Hz, 3F), -113.6 (m, 2F), -124.7 (m, 2F), -126.0 (m, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 122.0-105.0 (m), 41.5 (t, $J = 20.9$ Hz), 40.0 (d, $J = 2.0$ Hz), 31.6, 21.6, 20.8, 13.8.



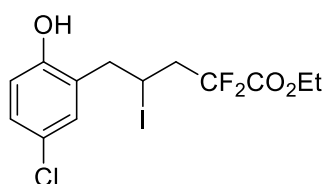
Tert-butyl (4,4,5,5,6,6,7,7,7-nonafluoro-2-iodoheptyl)carbamate (3n). This compound is known.⁴ The product (92 mg, 61% yield) was purified with silica gel chromatography (Petroleum ether /Ethyl acetate = 15:1) as light yellow solid. ^1H NMR (400 MHz, CDCl_3) δ 4.97 (br, 1H), 4.38 (m, 1H), 3.70-3.40 (m, 2H), 2.95-2.65 (m, 2H), 1.45 (s, 9H). ^{19}F NMR (376 MHz, CDCl_3) δ -81.2 (m, 3F), -113.6 (m, 2F), -124.6 (m, 2F), -125.9 (m, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 155.6, 120.0-110.0 (m), 80.2, 48.9, 38.4 (t, $J = 21.3$ Hz), 28.2, 18.7.



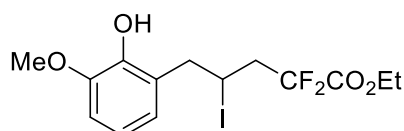
Ethyl 2,2-difluoro-5-(2-hydroxyphenyl)-4-iodopentanoate (3o). The product (98 mg, 85% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.17 (td, $J = 7.8$ Hz, 1.6 Hz, 1H), 7.11 (dd, $J = 7.6$ Hz, 1.2 Hz, 1H), 6.90 (td, $J = 7.4$ Hz, 0.8 Hz, 1H). 6.75 (dd, $J = 8.0$ Hz, 0.8 Hz, 1H), 5.00 (s, 1H), 4.58-4.51 (m, 1H), 4.33 (q, $J = 7.0$ Hz, 2H), 3.33-3.19 (m, 2H), 3.01-2.73 (m, 2H), 1.36 (t, $J = 7.0$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -101.0 – -102.0 (m, 1F), -105.5 – -106.6 (m, 1F). ^{13}C NMR (101 MHz, CDCl_3) δ 163.7 (t, $J = 32.4$ Hz), 153.6, 131.5, 128.6, 125.5, 120.8, 115.5, 115.2 (t, $J = 253.4$ Hz), 63.3, 44.4 (t, $J = 23.7$ Hz), 42.5, 20.9 (t, $J = 4.2$ Hz), 13.8. MS (EI): m/z (%) 384 (M^+), 257 (100), 119. HRMS (EI): Calculated for $\text{C}_{13}\text{H}_{15}\text{F}_2\text{O}_3\text{I}$ (M^+): 384.0034; Found: 384.0030.



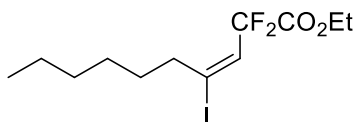
Ethyl 2,2-difluoro-5-(2-hydroxy-5-methylphenyl)-4-iodopentanoate (3p). The product (78 mg, 65% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 6.95 (dd, $J = 7.8$ Hz, 1.6 Hz, 1H), 6.90 (d, $J = 1.6$ Hz, 1H), 6.64 (d, $J = 7.8$ Hz, 1H), 4.81 (s, 1H), 4.56-4.48 (m, 1H), 4.33 (q, $J = 7.0$ Hz, 2H), 3.28-3.17 (m, 2H), 2.99-2.72 (m, 2H), 2.27 (s, 3H), 1.36 (t, $J = 7.2$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -101.0 – -102.0 (m, 1F), -105.8 – -106.8 (m, 1F). ^{13}C NMR (101 MHz, CDCl_3) δ 163.6 (t, $J = 32.6$ Hz), 151.2, 131.9, 130.1, 128.9, 125.3, 115.4, 115.2 (t, $J = 254.5$ Hz), 63.3, 44.3 (t, $J = 23.7$ Hz), 42.5, 20.9 (t, $J = 4.1$ Hz), 20.5, 13.8. MS (EI): m/z (%) 398 (M^+), 271, 133 (100). HRMS (EI): Calculated for $\text{C}_{14}\text{H}_{17}\text{F}_2\text{O}_3\text{I}$ (M^+): 398.0191; Found: 398.0201.



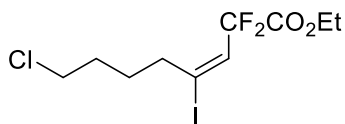
Ethyl 5-(5-chloro-2-hydroxyphenyl)-2,2-difluoro-4-iodopentanoate (3q). The product (72 mg, 57% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.12 (dd, $J = 8.6$ Hz, 2.4 Hz, 1H), 7.10 (d, $J = 2.4$ Hz, 1H), 6.70 (d, $J = 8.4$ Hz, 1H), 5.11 (s, 1H), 4.54-4.47 (m, 1H), 4.35 (q, $J = 7.2$ Hz, 2H), 3.31-3.26 (m, 1H), 3.16-3.10 (m, 1H), 3.02-2.72 (m, 2H), 1.37 (t, $J = 7.2$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -101.0 – -102.0 (m, 1F), -106.0 – -107.0 (m, 1F). ^{13}C NMR (101 MHz, CDCl_3) δ 163.6 (t, $J = 32.4$ Hz), 152.2, 131.1, 128.3, 127.3, 125.4, 116.8, 115.1 (t, $J = 253.7$ Hz), 63.4, 44.6 (t, $J = 23.7$ Hz), 42.1, 20.0 (t, $J = 4.0$ Hz), 13.9. MS (EI): m/z (%) 420 (M^+), 418 (M^+), 291, 153(100). HRMS (EI): Calculated for $\text{C}_{13}\text{H}_{14}\text{F}_2\text{O}_3\text{ClI}$ (M^+): 417.9644; Found: 417.9652.



Ethyl 2,2-difluoro-5-(2-hydroxy-3-methoxyphenyl)-4-iodopentanoate (3r). The product (65 mg, 52% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 6.81 (m, 2H), 6.73 (m, 1H), 5.75 (s, 1H), 4.60-4.50 (m, 1H), 4.33 (q, $J = 7.0$ Hz, 2H), 3.89 (s, 3H), 3.33-3.23 (m, 2H), 3.00-2.70 (m, 2H), 1.36 (t, $J = 7.0$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -101.5 (dt, $J = 264.3, 15.0$ Hz, 1F), 106.4 (dt, $J = 262.8, 16.2$ Hz, 1F). ^{13}C NMR (101 MHz, CDCl_3) δ 163.5 (t, $J = 32.6$ Hz), 146.4, 143.7, 124.8, 123.0, 119.4, 115.2 (t, $J = 253.2$ Hz), 109.5, 63.2, 55.9, 44.2 (t, $J = 23.8$ Hz), 42.3, 20.4 (t, $J = 4.3$ Hz), 13.8. MS (EI): m/z (%) 414 (M^+), 287, 259. HRMS (EI): Calculated for $\text{C}_{14}\text{H}_{17}\text{F}_2\text{O}_4\text{I}$ (M^+): 414.0140; Found: 414.0132.

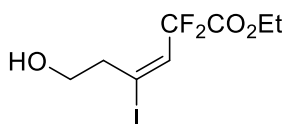


Ethyl (*E*)-2,2-difluoro-4-iododec-3-enoate (5a). This compound is known.⁵ The product (93 mg, 86% yield, $Z:E = 1:5.5$) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 100:1) as colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 6.40 (t, $J = 13.2$ Hz, 1H), 4.33 (q, $J = 7.2$ Hz, 2H), 2.59 (t, $J = 7.2$ Hz, 2H), 1.60-1.48 (m, 2H), 1.35 (t, $J = 7.2$ Hz, 3H), 1.33-1.25 (m, 6H), 0.89 (t, $J = 6.8$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -97.8 (d, $J = 12.4$ Hz, 2F, *E*), -97.9 (d, $J = 12.4$ Hz, 2F, *Z*). ^{13}C NMR (101 MHz, CDCl_3) δ 163.2 (t, $J = 34.4$ Hz), 131.2 (t, $J = 27.2$ Hz), 119.6 (t, $J = 7.7$ Hz), 111.5 (t, $J = 253.6$ Hz), 63.3, 40.7, 31.5, 29.8, 28.0, 22.5, 14.0, 13.9.

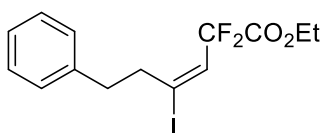


Ethyl (*E*)-8-chloro-2,2-difluoro-4-iodooct-3-enoate (5b). The product (75 mg, 68% yield, $Z:E = 1:6.7$) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 100:1) as colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 6.44 (t, $J = 13.2$ Hz, 1H), 4.34 (q, $J = 7.2$ Hz, 2H), 3.55 (t, $J = 6.4$ Hz, 2H), 2.65 (t, $J = 7.0$ Hz, 2H), 1.82-1.67 (m, 4H), 1.36 (t, $J = 7.2$ Hz, 3H). ^{19}F

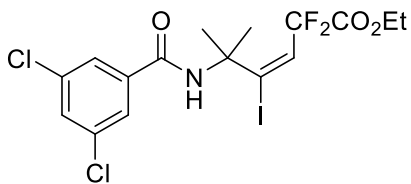
NMR (376 MHz, CDCl₃) δ -97.8 (d, J = 13.5 Hz, 2F, *E*). ¹³C NMR (101 MHz, CDCl₃) δ 163.1 (t, J = 34.4 Hz), 131.9 (t, J = 27.2 Hz), 118.3 (t, J = 7.7 Hz), 111.5 (t, J = 253.8 Hz), 63.4, 44.4, 39.8, 31.0, 27.1, 13.9. MS (ESI): m/z 369 (M⁺+H), 367 (M+H)⁺. HRMS (ESI): Calculated for C₁₀H₁₅F₂O₂ClI (M+H)⁺: 366.9768; Found: 366.9767.



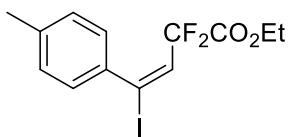
Ethyl (*E*)-2,2-difluoro-6-hydroxy-4-iodohex-3-enoate (5c). The product (67 mg, 70% yield, *Z*:*E* = 1:5.6) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 5:1) as colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 6.56 (t, J = 13.2 Hz, 1H), 4.34 (q, J = 7.2 Hz, 2H), 3.82 (t, J = 6.2 Hz, 2H), 2.92 (m, 2H), 1.59 (s, 1H), 1.36 (t, J = 7.2 Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -97.6 (d, J = 12.4 Hz, 2F, *E*). ¹³C NMR (101 MHz, CDCl₃) δ 163.4 (t, J = 34.3 Hz), 133.8 (t, J = 27.5 Hz), 114.1 (t, J = 7.7 Hz), 111.5 (t, J = 254.0 Hz), 63.6, 61.6, 43.3, 13.9. MS (ESI): m/z , 321 (M+H)⁺. HRMS (ESI): Calculated for C₈H₁₂F₂O₃I (M+H)⁺: 320.9794; Found: 320.9794.



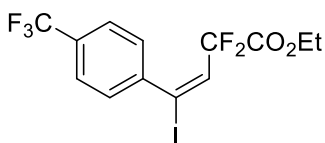
Ethyl (*E*)-2,2-difluoro-4-iodo-6-phenylhex-3-enoate (5d). The product (83 mg, 73% yield, *Z*:*E* = 1:6.0) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 100:1) as colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.35-7.10 (m, 5H), 6.43 (t, J = 13.2 Hz, 1H), 4.29 (q, J = 7.2 Hz, 2H), 3.00-2.80 (m, 4H), 1.32 (t, J = 7.2 Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -98.1 (d, J = 13.5 Hz, 2F, *E*), -98.3 (d, J = 12.0 Hz, 2F, *Z*). ¹³C NMR (101 MHz, CDCl₃) δ 163.0 (t, J = 34.3 Hz), 139.7, 131.8 (t, J = 27.0 Hz), 128.6, 128.5, 126.4, 117.4 (t, J = 7.5 Hz), 111.5 (t, J = 253.6 Hz), 63.4, 43.0 (t, J = 1.9 Hz), 36.0, 13.9. MS (ESI): m/z 398 (M+NH₄)⁺, 381 (M+H)⁺. HRMS (ESI): Calculated for C₁₄H₁₉F₂NO₂I (M+NH₄)⁺: 398.0423; Found: 398.0421.



Ethyl (E)-5-(3,5-dichlorobenzamido)-2,2-difluoro-4-iodo-5-methylhex-3-enoate (5e). The product (105 mg, 69% yield, *Z:E* = 1:69) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 20:1) as colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.58-7.52 (m, 2H), 7.48-7.38 (m, 1H), 6.70-6.62 (m, 1H), 6.33 (br, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 1.69 (s, 6H), 1.36 (t, *J* = 7.2 Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -97.4 – -95.7 (m, 2F, *E*). ¹³C NMR (101 MHz, CDCl₃) δ 164.2, 162.4 (t, *J* = 34.1 Hz), 137.5, 135.1, 131.1, 128.3 (t, *J* = 30.4 Hz), 125.6, 112.4 (t, *J* = 248.9 Hz), 63.3, 59.9, 26.9, 13.8. MS (ESI): *m/z* 508 (M+H)⁺, 506 (M+H)⁺. HRMS (ESI): Calculated for C₁₆H₁₇F₂Cl₂NO₃I (M+H)⁺: 505.9593; Found: 505.9591.

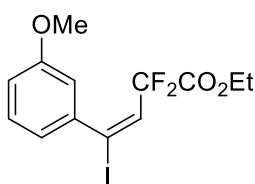


Ethyl (E)-2,2-difluoro-4-iodo-4-(p-tolyl)but-3-enoate (5f). This compound is known.⁶ The product (96 mg, 87% yield, *Z:E* = 1:10) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 100:1) as colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.20 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.69 (t, *J* = 10.8 Hz, 1H), 3.97 (q, *J* = 7.2 Hz, 2H), 2.34 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -93.6 (d, *J* = 10.9 Hz, 2F, *E*). ¹³C NMR (101 MHz, CDCl₃) δ 162.5 (t, *J* = 33.4 Hz), 139.6, 137.8, 132.6 (t, *J* = 28.6 Hz), 128.6, 127.8 (t, *J* = 1.8 Hz), 110.8 (t, *J* = 250.9 Hz), 109.2 (t, *J* = 10.2 Hz), 63.0, 21.3, 13.6.

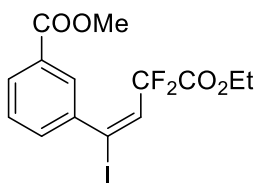


Ethyl (E)-2,2-difluoro-4-iodo-4-(4-(trifluoromethyl)phenyl)but-3-enoate (5g). This compound is known.⁷ The product (115 mg, 91% yield, *Z:E* = 1:8.4) was purified with silica gel chromatography

(Petroleum ether/Ethyl acetate = 100:1) as colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, $J = 8.0$ Hz, 2H), 7.41 (d, $J = 8.0$ Hz, 2H), 6.76 (t, $J = 11.2$ Hz, 1H), 4.09 (q, $J = 7.0$ Hz, 2H), 1.24 (t, $J = 7.0$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -63.0 (s, 3F), -95.3 (d, $J = 10.9$ Hz, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 162.4 (t, $J = 33.4$ Hz), 144.3, 133.8 (t, $J = 27.4$ Hz), 131.2 (q, $J = 33.0$ Hz), 128.0 (t, $J = 2.0$ Hz), 125.1 (q, $J = 3.8$ Hz), 123.6 (q, $J = 273.4$ Hz), 110.8 (t, $J = 253.0$ Hz), 105.9 (t, $J = 8.9$ Hz), 63.4, 13.7.

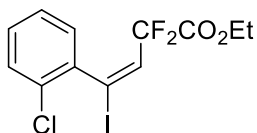


Ethyl (*E*)-2,2-difluoro-4-iodo-4-(3-methoxyphenyl)but-3-enoate (5h). This compound is known.⁷ The product (103 mg, 90% yield, $Z:E = 1:5.6$) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 50:1) as colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.22 (t, $J = 7.8$ Hz, 1H), 6.89 (d, $J = 7.6$ Hz, 1H), 6.86-6.80 (m, 2H), 6.70 (t, $J = 11.0$ Hz, 1H), 3.98 (q, $J = 7.2$ Hz, 2H), 3.80 (s, 3H), 1.20 (t, $J = 7.2$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -93.8 (d, $J = 10.9$ Hz, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 162.4 (t, $J = 33.2$ Hz), 158.8, 141.7, 133.0 (t, $J = 28.7$ Hz), 129.1, 120.2, 115.4, 113.1, 110.8 (t, $J = 251.2$ Hz), 108.3 (t, $J = 10.3$ Hz), 63.1, 55.3, 13.6.

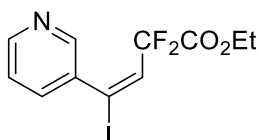


Methyl (*E*)-3-(4-ethoxy-3,3-difluoro-1-iodo-4-oxobut-1-en-1-yl)benzoate (5i). The product (107 mg, 87% yield, $Z:E = 1:25$) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 20:1) as pale yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 7.2$ Hz, 1H), 7.95 (s, 1H), 7.48 (d, $J = 7.2$ Hz, 1H), 7.40 (t, $J = 7.8$ Hz, 1H), 6.74 (t, $J = 11.4$ Hz, 1H), 4.07 (q, $J = 7.2$ Hz, 2H), 3.92 (s, 3H), 1.23 (t, $J = 7.2$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -95.2 (d, $J = 10.9$ Hz, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 166.0, 162.4 (t, $J = 33.5$ Hz), 141.1, 133.6 (t, $J = 27.8$ Hz),

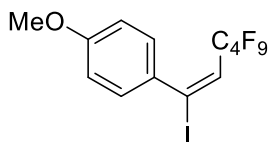
131.8, 130.2, 130.1, 128.6, 128.2, 110.8 (t, $J = 252.2$ Hz), 106.7 (t, $J = 8.9$ Hz), 63.3, 52.3, 13.6. MS (ESI): m/z 411 (M+H)⁺. HRMS (ESI): Calculated for C₁₄H₁₄F₂O₄I (M+H)⁺: 410.9899; Found: 410.9900.



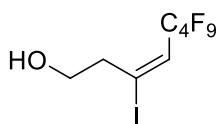
Ethyl (*E*)-4-(2-chlorophenyl)-2,2-difluoro-4-iodobut-3-enoate (5j). This compound is known.⁷ The product (96 mg, 83% yield, $Z:E=1:23$) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 50:1) as pale yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.38-7.34 (m, 1H), 7.29-7.21 (m, 3H), 6.77 (t, $J = 11.2$ Hz, 1H), 4.16-4.09 (m, 2H), (m, 2H), 1.26 (t, $J = 7.0$ Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -98.0 (m, 2F). ¹³C NMR (101 MHz, CDCl₃) δ 162.2 (t, $J = 33.6$ Hz), 138.8, 134.6 (t, $J = 27.6$ Hz), 131.4, 130.4, 129.7, 128.8, 126.5, 110.8 (t, $J = 253.1$ Hz), 103.3 (t, $J = 9.2$ Hz), 63.3, 13.7.



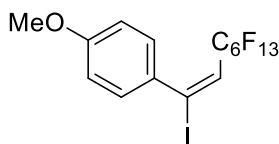
Ethyl (*E*)-2,2-difluoro-4-iodo-4-(pyridin-3-yl)but-3-enoate (5k). This compound is known.⁶ The product (84 mg, 79% yield, $Z:E=1:13$) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 20:1) as pale yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 8.54 (d, $J = 2.0$ Hz, 1H), 8.51 (dd, $J = 4.5$ Hz, 1.4 Hz, 1H), 7.61 (dt, $J = 8.4$ Hz, 2.0 Hz, 1H), 7.25 (dd, $J = 8.0$ Hz, 4.8 Hz, 1H), 6.79 (t, $J = 11.6$ Hz, 1H), 4.11 (q, $J = 7.2$ Hz, 2H), 1.24 (t, $J = 7.2$ Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -95.4 (d, $J = 12.0$ Hz, 2F). ¹³C NMR (101 MHz, CDCl₃) δ 162.4 (t, $J = 33.3$ Hz), 149.9, 147.8, 137.1, 135.1, 134.4 (t, $J = 27.3$ Hz), 122.7, 110.8 (t, $J = 253.3$ Hz), 103.7 (t, $J = 8.8$ Hz), 63.5, 13.7. MS (ESI): m/z 354 (M+H)⁺. HRMS (ESI): Calculated for C₁₁H₁₁F₂NO₂I (M+H)⁺: 353.9797; Found: 353.9796.



(E)-1-Methoxy-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (5l). The product (129 mg, 90% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 150:1) as colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.26 (d, $J = 8.8$ Hz, 1H), 6.83 (d, $J = 8.8$ Hz, 1H), 6.54 (t, $J = 13.6$ Hz, 2H), 3.80 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -81.1 (m, 3F), -105.2 (m, 2F), -123.9 (m, 2F), -125.9 (m, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 160.2, 133.5, 128.8 (t, $J = 2.4$ Hz), 126.2 (t, $J = 21.9$ Hz), 120.0-105.0 (m), 113.3, 55.2. MS (EI): m/z (%) 478 (M^+), 351(100), 132. HRMS (EI): Calculated for $\text{C}_{13}\text{H}_8\text{F}_9\text{OI}$ (M^+): 477.9476; Found: 477.9474.

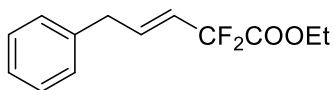


(E)-5,5,6,6,7,7,8,8,8-Nonafluoro-3-iodooct-3-en-1-ol (5m). This compound is known.⁴ The product (77 mg, 62% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as pale yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 6.48 (d, $J = 14.2$ Hz, 1H), 3.86 (t, $J = 6.4$ Hz, 2H), 2.93 (t, $J = 6.0$ Hz, 2H), 1.57 (br, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -81.0 (m, 3F), -105.3 (m, 2F), -124.1 (m, 2F), -125.9 (m, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 128.9 (t, $J = 23.9$ Hz), 117.2 (t, $J = 5.6$ Hz), 120.0-105.0 (m), 61.8, 43.6.

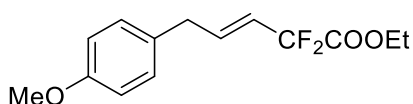


(E)-1-Methyl-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-iodooct-1-en-1-yl)benzene (5n). The product (121.4 mg, 70% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 150:1) as colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.25 (d, $J = 8.6$ Hz, 2H), 6.83 (d, $J = 8.6$ Hz, 2H), 6.53 (t, $J = 13.4$ Hz, 1H), 3.80 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -80.8 (m, 3F), -104.9 (m, 2F), -121.8 (m, 2F), -122.9 (m, 4F), -126.2 (m, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ

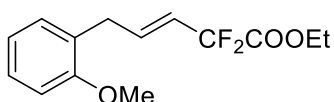
160.2, 133.6, 128.8 (t, $J = 2.4$ Hz), 126.2 (t, $J = 21.9$ Hz), 120.0-105.0 (m), 113.3, 55.3. MS (EI): m/z (%) 578 (M^+), 451 (100), 132. HRMS (EI): Calculated for $C_{15}H_8F_{13}OI$ (M^+): 577.9412; Found: 577.9405.



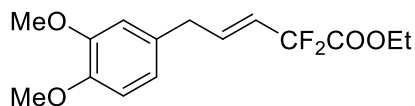
Ethyl (*E*)-2,2-difluoro-5-phenylpent-3-enoate (6a). This compound is known.⁸ The product (50 mg, 70% yield, $Z:E = 1:12$) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 100:1) as colorless liquid. 1H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, $J = 7.2$ Hz, 2H), 7.23 (m, 1H), 7.15 (d, $J = 7.2$ Hz, 2H). 6.43 (m, 1H), 5.69 (dd, $J = 26.0$ Hz, 11.8 Hz, 1H), 4.30 (q, $J = 6.8$ Hz, 2H), 3.47 (s, 2H), 1.32 (t, $J = 6.8$ Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.2 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9 (t, $J = 34.8$ Hz), 138.3 (t, $J = 9.0$ Hz), 137.7, 128.6, 126.6, 126.3, 122.2 (t, $J = 25.2$ Hz), 112.2 (t, $J = 249.1$ Hz), 62.9, 38.0, 13.9.



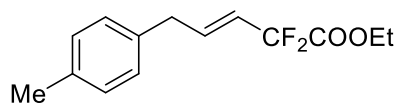
Ethyl (*E*)-2,2-difluoro-5-(4-methoxyphenyl)pent-3-enoate (6b). The product (61 mg, 75% yield, $Z:E = 1:14$) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 200:1) as colorless liquid. 1H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, $J = 8.8$ Hz, 2H), 6.86 (d, $J = 8.8$ Hz, 2H). 6.46-6.35 (m, 1H), 5.75-5.60 (m, 1H), 4.32 (q, $J = 7.2$ Hz, 2H), 3.80 (s, 3H), 3.45-3.38 (m, 2H), 1.34 (t, $J = 7.2$ Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.1 (d, $J = 9.4$ Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0 (t, $J = 34.8$ Hz), 158.3, 138.8 (t, $J = 9.0$ Hz), 129.6, 127.6, 121.8 (t, $J = 25.2$ Hz), 114.0, 112.3 (t, $J = 248.9$ Hz), 62.9, 55.2, 37.2, 13.9. MS (EI): m/z (%) 270 (M^+), 177, 147(100). HRMS (EI): Calculated for $C_{14}H_{16}F_2O_3$ (M^+): 270.1068; Found: 270.1057.



Ethyl (*E*)-2,2-difluoro-5-(2-methoxyphenyl)pent-3-enoate (6c). The product (60 mg, 74% yield, *Z*:*E* = 1:10) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 200:1) as colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.22 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.89 (t, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 1H), 6.50-6.35 (m, 1H), 5.75-5.60 (m, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 3.45 (m, 1H), 1.31 (t, *J* = 7.0 Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -103.1 (d, *J* = 10.9 Hz, 2F). ¹³C NMR (101 MHz, CDCl₃) δ 164.1 (t, *J* = 34.6 Hz), 157.2, 138.0 (t, *J* = 9.0 Hz), 129.9, 128.0, 126.3, 121.5 (t, *J* = 5.0 Hz), 120.5, 112.4 (t, *J* = 246.2 Hz), 110.3, 62.8, 55.2, 32.7, 13.9. MS (EI): *m/z* (%) 270 (M⁺), 177, 147(100). HRMS (EI): Calculated for C₁₄H₁₆F₂O₃ (M⁺): 270.1068; Found: 270.1078.

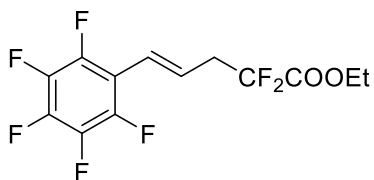


Ethyl (*E*)-5-(3,4-dimethoxyphenyl)-2,2-difluoropent-3-enoate (6d). The product (64 mg, 71% yield, *Z*:*E* = 1:14) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 200:1) as colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 6.81 (d, *J* = 8.2 Hz, 1H), 6.70 (dd, *J* = 8.2 Hz, 1.8 Hz, 1H), 6.66 (d, *J* = 1.8 Hz, 1H), 6.50-6.35 (m, 1H), 5.75-5.60 (m, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 3.87 (s, 6H), 3.46-3.38 (m, 2H), 1.33 (t, *J* = 7.2 Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -103.1 (dd, *J* = 10.9 Hz, 3.1 Hz, 2F). ¹³C NMR (101 MHz, CDCl₃) δ 164.0 (t, *J* = 34.6 Hz), 148.9, 147.7, 138.6 (t, *J* = 8.9 Hz), 130.1, 122.0 (t, *J* = 25.2 Hz), 120.6, 112.2 (t, *J* = 249.1 Hz), 111.8, 111.2, 63.0, 55.9, 55.8, 37.6, 13.9. MS (EI): *m/z* (%) 300 (M⁺), 177 (100). HRMS (EI): Calculated for C₁₅H₁₈F₂O₄ (M⁺): 300.1173; Found: 300.1182.

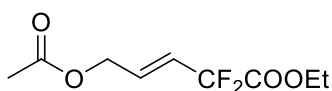


Ethyl (*E*)-2,2-difluoro-5-(*p*-tolyl)pent-3-enoate (6e). The product (55mg, 72% yield, *Z*:*E* = 1:12) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 200:1) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.13 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.50-6.35 (m, 1H), 5.75-5.60 (m, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 3.44 (m, 2H), 2.34 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -103.1 (d, *J* = 10.9 Hz, 2F). ¹³C NMR (101 MHz, CDCl₃) δ

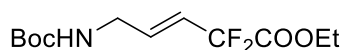
164.0 (t, $J = 34.8$ Hz), 138.6 (t, $J = 9.0$ Hz), 136.2, 134.6, 129.3, 128.5, 122.0 (t, $J = 25.2$ Hz), 112.3 (t, $J = 248.8$ Hz), 62.9, 37.6, 21.0, 13.9. MS (EI): m/z (%) 254 (M^+), 187, 161 (100). HRMS (EI): Calculated for $C_{14}H_{16}F_2O_2$ (M^+): 254.1118; Found: 254.1121.



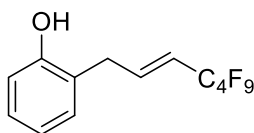
Ethyl (*E*)-2,2-difluoro-5-(perfluorophenyl)pent-4-enoate (6f). The product (35mg, 35% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 200:1) as colorless liquid. 1H NMR (400 MHz, $CDCl_3$) δ 6.55-6.40 (m, 2H), 4.34 (q, $J = 7.2$ Hz, 2H). 3.05 (td, $J = 15.6$ Hz, 5.6 Hz, 2H), 1.35 (t, $J = 7.0$ Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.1 (t, $J = 15.6$ Hz, 2F), -142.9 (dd, $J = 21.8$ Hz, 7.9 Hz, 2F), -155.4 (t, $J = 21.0$ Hz, 1F), -162.7 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5 (t, $J = 32.5$ Hz), 144.7 (dm, $J = 245.0$ Hz), 140.1 (td, $J = 21.4$, 7.5 Hz, 2F), 137.6 (dm, $J = 254.7$ Hz), 128.1 (m), 120.7, 114.7 (t, $J = 253.3$ Hz), 111.1, 63.1, 39.4 (t, $J = 24.4$ Hz), 13.9. MS (EI): m/z (%) 330 (M^+), 310, 282 (100). HRMS (EI): Calculated for $C_{13}H_9F_7O_2$ (M^+): 330.0491; Found: 330.0495.



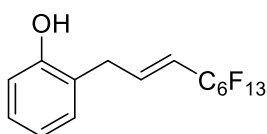
Ethyl (*E*)-5-acetoxy-2,2-difluoropent-3-enoate (6g). The product (34 mg, 51% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 18:1) as colorless liquid. 1H NMR (400 MHz, $CDCl_3$) δ 6.33 (d, $J = 16.0$ Hz, 1H), 5.94 (dd, $J = 26.4$, 11.6 Hz, 1H), 4.67 (br, 2H). 4.32 (q, $J = 7.0$ Hz, 2H), 2.10 (s, 3H), 1.34 (t, $J = 7.0$ Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.5 (d, $J = 10.9$ Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 163.5, 132.8 (t, $J = 9.1$ Hz), 122.6 (t, $J = 25.6$ Hz), 111.8 (t, $J = 249.7$ Hz), 63.1, 62.3, 20.7, 13.9. MS (EI): m/z (%) 222 (M^+), 160, 149, 90 (100). HRMS (EI): Calculated for $C_9H_{12}F_2O_4$ (M^+): 222.0704; Found: 222.0710.



Ethyl (*E*)-5-((*tert*-butoxycarbonyl)amino)-2,2-difluoropent-3-enoate (6h). The product (54 mg, 64% yield, *Z*:*E* = 1:20) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 12:1) as colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 6.26 (d, *J* = 15.6 Hz, 1H), 5.80 (q, *J* = 12.8 Hz, 1H), 4.78 (br, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 3.85 (s, 2H), 1.42 (s, 9H), 1.32 (t, *J* = 7.2 Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -103.6 (d, *J* = 10.2 Hz, 2F). ¹³C NMR (101 MHz, CDCl₃) δ 163.7 (t, *J* = 34.6 Hz), 155.5, 136.1 (t, *J* = 8.7 Hz), 121.4 (t, *J* = 25.4 Hz), 112.1 (t, *J* = 249.3 Hz), 79.8, 63.0, 41.0, 28.2, 13.8. MS (EI): *m/z* (%) 279 (M⁺), 264, 223. HRMS (EI): Calculated for C₁₂H₁₉NF₂O₄ (M⁺): 279.1282; Found: 279.1277.

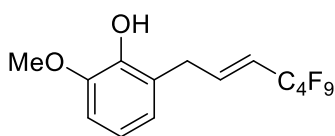


(*E*)-2-(4,4,5,5,6,6,7,7,7-Nonafluorohept-2-en-1-yl)phenol (6i). The product (99 mg, 94% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.16 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.68-6.56 (m, 1H), 5.62 (dd, *J* = 27.2 Hz, 12.8 Hz, 1H), 5.00 (s, 1H), 3.55 (m, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -80.1 (t, *J* = 8.8 Hz, 3F), -110.5 (m, 2F), -123.4 (t, *J* = 13.3 Hz, 2F), -124.8 (t, *J* = 10.2 Hz, 2F). ¹³C NMR (101 MHz, CDCl₃) δ 153.4, 141.0 (t, *J* = 9.0 Hz), 130.6, 128.3, 123.8, 121.2, 121.0-105.0 (m), 117.6 (t, *J* = 23.1 Hz), 115.4, 32.6. MS (EI): *m/z* (%) 352 (M⁺), 133 (100). HRMS (EI): Calculated for C₁₃H₉F₉O (M⁺): 352.0510; Found: 352.0504.

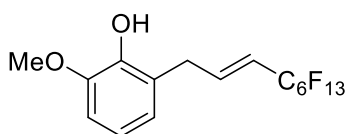


(*E*)-2-(4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluoronon-2-en-1-yl)phenol (6j). The product (99 mg, 73% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as

colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.16 (td, $J = 8.0$ Hz, 1.2 Hz, 1H), 7.09 (d, $J = 7.2$ Hz, 1H), 6.92 (td, $J = 7.2$ Hz, 1.2 Hz, 1H). 6.77 (d, $J = 8.0$ Hz, 1H), 6.65-6.55 (m, 1H), 5.60 (dd, $J = 28.0$ Hz, 12.8 Hz, 1H), 4.74 (s, 1H), 3.54 (m, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -80.1 (t, $J = 9.4$ Hz, 3F), -118.6 (m, 2F), -129.0 (m, 2F), -130.2 (m, 2F), -130.7 (m, 2F), 133.5 (m, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 153.4, 140.9 (t, $J = 9.0$ Hz), 130.6, 128.3, 123.8, 121.2, 121.0-105.0 (m), 117.7 (t, $J = 23.1$ Hz), 115.4, 32.6. MS (EI): m/z (%) 452 (M^+), 133 (100), 105. HRMS (EI): Calculated for $\text{C}_{15}\text{H}_9\text{F}_{13}\text{O}$ (M^+): 452.0446; Found: 452.0445.

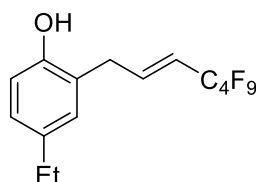


(E)-2-Methoxy-6-(4,4,5,5,6,6,7,7,7-nonafluorohept-2-en-1-yl)phenol (6k). The product (100 mg, 87% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 6.82 (q, $J = 7.9$ Hz, 1H), 6.81 (s, 1H), 6.71 (d, $J = 7.2$ Hz, 1H), 6.65-6.55 (m, 1H), 5.75 (s, 1H), 5.62 (dd, $J = 28.0$ Hz, 12.8 Hz, 1H), 3.90 (s, 3H), 3.55 (m, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -81.2 (t, $J = 9.6$ Hz, 3F), -111.6 (m, 2F), -124.4 (m, 2F), -125.9 (m, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 146.5, 143.6, 141.1 (t, $J = 9.0$ Hz), 123.1, 122.2, 122.0-105.0 (m), 119.7, 117.4 (t, $J = 23.1$ Hz), 109.3, 55.9, 32.2. MS (EI): m/z (%) 382 (100) (M^+), 161, 131. HRMS: Calculated for $\text{C}_{14}\text{H}_{11}\text{F}_9\text{O}_2$ (M^+): 382.0615; Found: 382.0617.

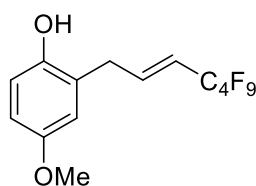


(E)-2-Methoxy-6-(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoronon-2-en-1-yl)phenol (6l). The product (127 mg, 88% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 12:1) as white solid. ^1H NMR (400 MHz, CDCl_3) δ 6.85-6.75 (m, 2H), 6.71 (d, $J = 7.2$ Hz, 1H), 6.65-6.63 (m, 1H), 5.74 (s, 1H), 5.62 (dd, $J = 26.8$ Hz, 12.8 Hz, 1H), 3.90 (s, 3H), 3.55 (m, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -80.9 (m, 3F), -111.4 (m, 2F), -121.8 (m, 2F), -123.0 (m, 2F), -123.5 (m, 2F), 126.3 (m, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 146.5, 143.6, 141.0 (t, $J = 9.1$ Hz), 123.1, 122.1,

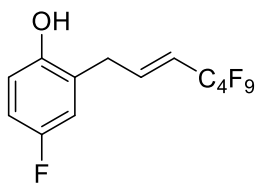
119.7, 120.0-105.0 (m), 117.5 (t, $J = 23.4$ Hz), 109.3, 56.0, 32.2. MS (EI): m/z (%) 482 (M^+), 163, 131(100). HRMS (EI): Calculated for $C_{16}H_{11}F_{13}O_2$ (M^+): 482.0551; Found: 482.0544.



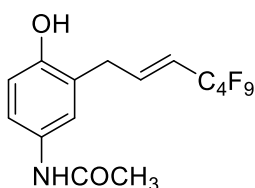
(E)-4-Ethyl-2-(4,4,5,5,6,6,7,7,7-nonafluorohept-2-en-1-yl)phenol (6m). The product (84 mg, 74% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 12:1) as a colorless liquid. 1H NMR (400 MHz, $CDCl_3$) δ 6.98 (dd, $J = 8.2$ Hz, 1.8 Hz, 1H), 6.93 (s, 1H), 6.70 (d, $J = 8.4$ Hz, 1H), 6.65-6.55 (m, 1H), 5.62 (dd, $J = 27.6$ Hz, 12.6 Hz, 1H), 4.79 (s, 1H), 3.52 (m, 2H), 2.58 (q, $J = 7.6$ Hz, 2H), 1.22 (t, $J = 7.6$ Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.2 (m, 3F), -111.6 (m, 2F), -124.4 (m, 2F), -125.8 (t, $J = 10.9$ Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3, 141.2 (t, $J = 9.0$ Hz), 137.0, 129.9, 127.4, 123.5, 121.0-105.0 (m), 117.5 (t, $J = 23.1$ Hz), 115.3, 32.7, 27.9, 15.7. MS (EI): m/z (%) 380 (M^+), 365 (100). HRMS(EI): Calculated for $C_{15}H_{13}F_9O$ (M^+): 380.0823; Found: 380.0830.



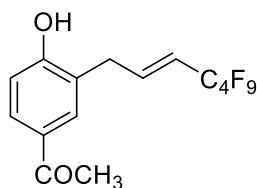
(E)-4-Methoxy-2-(4,4,5,5,6,6,7,7,7-nonafluorohept-2-en-1-yl)phenol (6n). The product (95 mg, 83% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as white solid. 1H NMR (400 MHz, $CDCl_3$) δ 6.70 (m, 2H), 6.66 (s, 1H), 6.59 (m, 1H), 5.62 (dd, $J = 27.2$ Hz, 12.4 Hz, 1H), 4.76 (s, 1H), 3.76 (s, 3H), 3.50 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.2 (m, 3F), -111.6 (m, 2F), -124.4 (m, 2F), -125.9 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 147.4, 140.8 (t, $J = 9.1$ Hz), 124.9, 122.0-105.0 (m), 117.7 (t, $J = 23.1$ Hz), 116.1, 116.0, 113.1, 55.7, 32.8. MS (EI): m/z (%) 382 (100) (M^+), 367, 362. HRMS(EI): Calculated for $C_{14}H_{11}F_9O_2$ (M^+): 382.0615; Found: 382.0621.



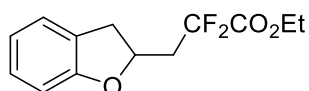
(E)-4-Fluoro-2-(4,4,5,5,6,6,7,7,7-nonafluorohept-2-en-1-yl)phenol (6o). The product (83 mg, 75% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 12:1) as colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 6.90-6.75 (m, 2H), 6.75-6.65 (m, 1H), 6.62-6.50 (m, 1H), 5.62 (dd, $J = 27.2$ Hz, 12.6 Hz, 1H), 4.87 (br, 1H), 3.50 (m, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -81.2 (m, 3F), -111.7 (m, 2F), -123.6 (m, 1F), -124.4 (m, 2F), -125.9 (m, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 157.1 (d, $J = 239.8$ Hz), 149.5 (d, $J = 2.2$ Hz), 140.2 (t, $J = 9.0$ Hz), 125.4 (d, $J = 7.4$ Hz), 120.0-105.0 (m), 118.1 (t, $J = 23.2$ Hz), 116.8 (d, $J = 23.3$ Hz), 116.1 (d, $J = 8.3$ Hz), 114.4 (d, $J = 23.1$ Hz), 32.6. MS (EI): m/z (%) 370 (M^+), 151 (100). HRMS (EI): Calculated for $\text{C}_{13}\text{H}_8\text{F}_{10}\text{O}$ (M^+): 370.0415; Found: 370.0410.



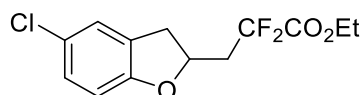
(E)-N-(4-Hydroxy-3-(4,4,5,5,6,6,7,7,7-nonafluorohept-2-en-1-yl)phenyl)acetamide (6p). The product (110 mg, 90% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 2:1) as white solid. ^1H NMR (400 MHz, d^6 -Acetone) δ 8.96 (br, 1H), 8.42 (s, 1H), 7.38 (s, 1H), 7.37 (m, 1H), 6.80 (d, $J = 8.4$ Hz, 1H), 6.75-6.63 (m, 1H), 5.81 (dd, $J = 28.0$ Hz, 13.2 Hz, 1H), 3.55 (m, 2H), 2.02 (s, 3H). ^{19}F NMR (376 MHz, d^6 -Acetone) δ -86.3 (m, 3F), -115.9 (m, 2F), -129.2 (m, 2F), -130.7 (m, 2F). ^{13}C NMR (101 MHz, d^6 -Acetone) δ 168.4, 152.0, 143.6 (t, $J = 9.4$ Hz), 133.1, 124.8, 122.6, 120.4, 120.0-105.0 (m), 117.3 (t, $J = 22.7$ Hz), 115.9, 33.6, 24.1. MS (EI): m/z (%) 409 (M^+), 367 (100). HRMS: Calculated for $\text{C}_{15}\text{H}_{12}\text{F}_9\text{NO}_2$ (M^+): 409.0724; Found: 409.0731.



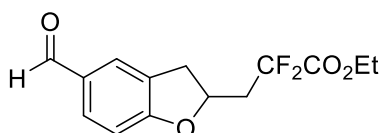
(E)-1-(4-Hydroxy-3-(4,4,5,5,6,6,7,7,7-nonafluorohept-2-en-1-yl)phenyl)ethan-1-one (6q). The product (83 mg, 70% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 12:1) as white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.81 (dd, $J = 8.6$ Hz, 1.8 Hz, 1H), 7.77 (s, 1H), 6.88 (d, $J = 8.4$ Hz, 1H), 6.79 (s, 1H), 6.65-6.53 (m, 1H), 5.62 (dd, $J = 27.2$ Hz, 12.4 Hz, 1H), 3.58 (m, 2H), 2.56 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -80.1 (m, 3F), -110.7 (m, 2F), -123.4 (m, 2F), -124.9 (m, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 197.9, 158.8, 140.3 (t, $J = 9.1$ Hz), 131.5, 130.2, 129.7, 124.2, 120.0-105.0 (m), 118.0 (t, $J = 23.2$ Hz), 115.3, 32.7, 26.2. MS (EI): m/z (%) 394 (M^+), 379 (100), 359. HRMS: Calculated for $\text{C}_{15}\text{H}_{11}\text{F}_9\text{O}_2$ (M^+): 394.0615; Found: 394.0617.



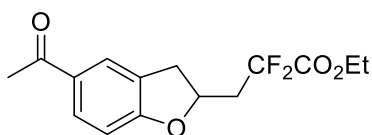
Ethyl 3-(2,3-dihydrobenzofuran-2-yl)-2,2-difluoropropanoate (7a). This compound is known.⁹ The product (31.5 mg, 41% yield) was purified with silica gel chromatography (Petroleum ether /Ethyl acetate = 10:1) as colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.17 (d, $J = 7.2$ Hz, 1H), 7.11 (t, $J = 7.8$ Hz, 1H), 6.86 (t, $J = 7.4$ Hz, 1H), 6.72 (d, $J = 8.0$ Hz, 1H), 5.06-4.99 (m, 1H), 4.40-4.32 (m, 2H), 3.42 (dd, $J = 15.6, 8.8$ Hz, 1H), 2.94 (dd, $J = 15.6, 7.2$ Hz, 1H), 2.80-2.65 (m, 1H), 2.46-2.34 (m, 1H), 1.36 (t, $J = 7.2$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -101.5 – -102.5 (m, 1F), -107.4 – -108.4 (m, 1F). ^{13}C NMR (101 MHz, CDCl_3) δ 163.7 (t, $J = 31.4$ Hz), 158.6, 128.2, 125.7, 124.9, 120.8, 114.7 (t, $J = 249.9$ Hz), 109.6, 76.5 (dd, $J = 7.3, 2.9$ Hz), 63.0, 40.8 (t, $J = 23.1$ Hz), 35.8, 13.9. MS (EI): m/z (%) 256 (M^+), 256, 133 (100), 91. HRMS (EI): Calculated for $\text{C}_{13}\text{H}_{14}\text{F}_2\text{O}_3$ (M^+): 256.0911; Found: 256.0914.



Ethyl 3-(5-chloro-2,3-dihydrobenzofuran-2-yl)-2,2-difluoropropanoate (7b). The product (45 mg, 52% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.12 (s, 1H), 7.06 (dd, $J = 8.2$ Hz, 2.2 Hz, 1H), 6.62 (d, $J = 8.8$ Hz, 1H), 5.08-5.01 (m, 1H), 4.39-4.31 (m, 2H), 3.39 (dd, $J = 15.8$ Hz, 9.0 Hz, 1H), 2.93 (dd, $J = 15.8$ Hz, 7.2 Hz, 1H), 2.78-2.63 (m, 1H), 2.45-2.34 (m, 1H), 1.35 (t, $J = 7.0$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -101.7 – -102.4 (m, 1F), -107.3 – -108.1 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 163.6 (t, $J = 32.2$ Hz), 157.3, 128.1, 127.7, 125.5, 125.0, 114.6 (t, $J = 251.9$ Hz), 110.4, 77.2 (dd, $J = 7.2, 3.2$ Hz), 63.1, 40.6 (t, $J = 23.2$ Hz), 35.6, 13.9. MS (EI): m/z (%) 292 (M^+), 290 (100) (M^+), 167, 125. HRMS (EI): Calculated for $\text{C}_{13}\text{H}_{13}\text{F}_2\text{ClO}_3$ (M^+): 290.0521; Found: 290.0520.

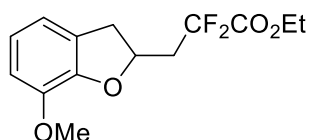


Ethyl 2,2-difluoro-3-(5-formyl-2,3-dihydrobenzofuran-2-yl)propanoate (7c). The product (64 mg, 75% yield) was purified with silica gel chromatography (Petroleum ether /Ethyl acetate = 10:1) as colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 9.82 (s, 1H), 7.73 (s, 1H), 7.67 (d, $J = 8.0$ Hz, 1H), 6.82 (d, $J = 8.4$ Hz, 1H), 5.20-5.10 (m, 1H), 4.35 (q, $J = 6.8$ Hz, 2H), 3.48 (dd, $J = 16.0, 9.2$ Hz, 1H), 3.00 (dd, $J = 15.6, 7.2$ Hz, 1H), 2.82-2.65 (m, 1H), 2.52-2.38 (m, 1H), 1.36 (t, $J = 7.2$ Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -109.1 – -109.9 (m, 1F), -114.2 – -115.0 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 190.5, 164.0, 163.5 (t, $J = 32.2$ Hz), 133.1, 130.8, 127.3, 126.0, 114.4 (t, $J = 252.3$ Hz), 109.8, 78.2 (dd, $J = 6.9, 3.1$ Hz), 63.1, 40.6 (t, $J = 23.3$ Hz), 34.8, 13.9. MS (EI): m/z (%) 284 (M^+), 133, 91 (100). HRMS (EI): Calculated for $\text{C}_{14}\text{H}_{14}\text{F}_2\text{O}_4$ (M^+): 284.0860; Found: 284.0865.



Ethyl 3-(5-acetyl-2,3-dihydrobenzofuran-2-yl)-2,2-difluoropropanoate (7d). This compound is

known.⁹ The product (61 mg, 68% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (s, 1H), 7.80 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 5.17-5.09 (m, 1H), 4.40-4.30 (m, 2H), 3.42 (dd, *J* = 16.0 Hz, 9.2 Hz, 1H), 2.98 (dd, *J* = 15.6 Hz, 6.8 Hz, 1H), 2.80-2.66 (m, 1H), 2.54 (s, 3H), 2.50-2.38 (m, 1H), 1.36 (t, *J* = 7.2 Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -101.5 – -102.8 (m, 1F), -107.0 – -108.2 (m, 1F). ¹³C NMR (101 MHz, CDCl₃) δ 196.6, 163.6 (t, *J* = 31.6 Hz), 162.8, 131.1, 130.6, 126.5, 125.6, 114.5 (t, *J* = 252.1 Hz), 109.2, 78.0 (dd, *J* = 7.0, 3.1 Hz), 63.1, 40.7 (t, *J* = 23.3 Hz), 35.1, 26.4, 13.9. MS (EI): *m/z* (%) 298 (M⁺), 283 (100), 255. HRMS (EI): Calculated for C₁₅H₁₆F₂O₄ (M⁺): 298.1017; Found: 298.1012.



Ethyl 2,2-difluoro-3-(7-methoxy-2,3-dihydrobenzofuran-2-yl)propanoate (7e). This compound is known.⁹ The product (39 mg, 45% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 6.84-6.78 (m, 2H), 6.74 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 5.10-5.03 (m, 1H), 4.40-4.30 (m, 2H), 3.84 (s, 3H), 3.42 (dd, *J* = 15.6 Hz, 9.2 Hz, 1H), 3.00 (dd, *J* = 15.6 Hz, 7.4 Hz, 1H), 2.87-2.73 (m, 1H), 2.50-2.38 (m, 1H), 1.34 (t, *J* = 7.2 Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -101.8 – -102.6 (m, 1F), -107.1 – -108.1 (m, 1F). ¹³C NMR (101 MHz, CDCl₃) δ 163.6 (t, *J* = 32.2 Hz), 146.9, 144.5, 127.1, 121.5, 117.1, 114.7 (t, *J* = 251.7 Hz), 111.4, 77.2 (dd, *J* = 6.9, 3.1 Hz), 63.1, 55.8, 40.6 (t, *J* = 22.9 Hz), 36.2, 13.8. MS (EI): *m/z* (%) 286 (100) (M⁺), 246, 131. HRMS (EI): Calculated for C₁₄H₁₆F₂O₄ (M⁺): 286.1017; Found: 286.1014.

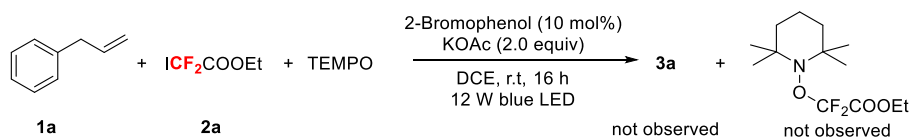
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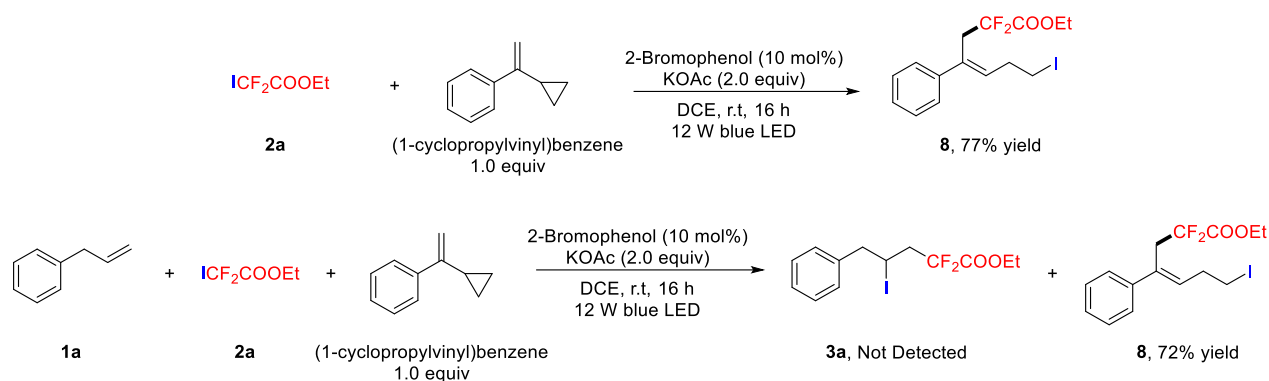
6. Mechanism studies.

6.1 Addition of radical and SET inhibitors:

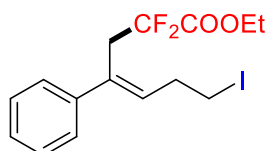


When the radical scavenger TEMPO (2,2,6,6-tetromethyl-1-piperidinyloxy, 1.0 equiv) was added under standard conditions, product **3a** was not observed.

6.2 Radical clock experiments.

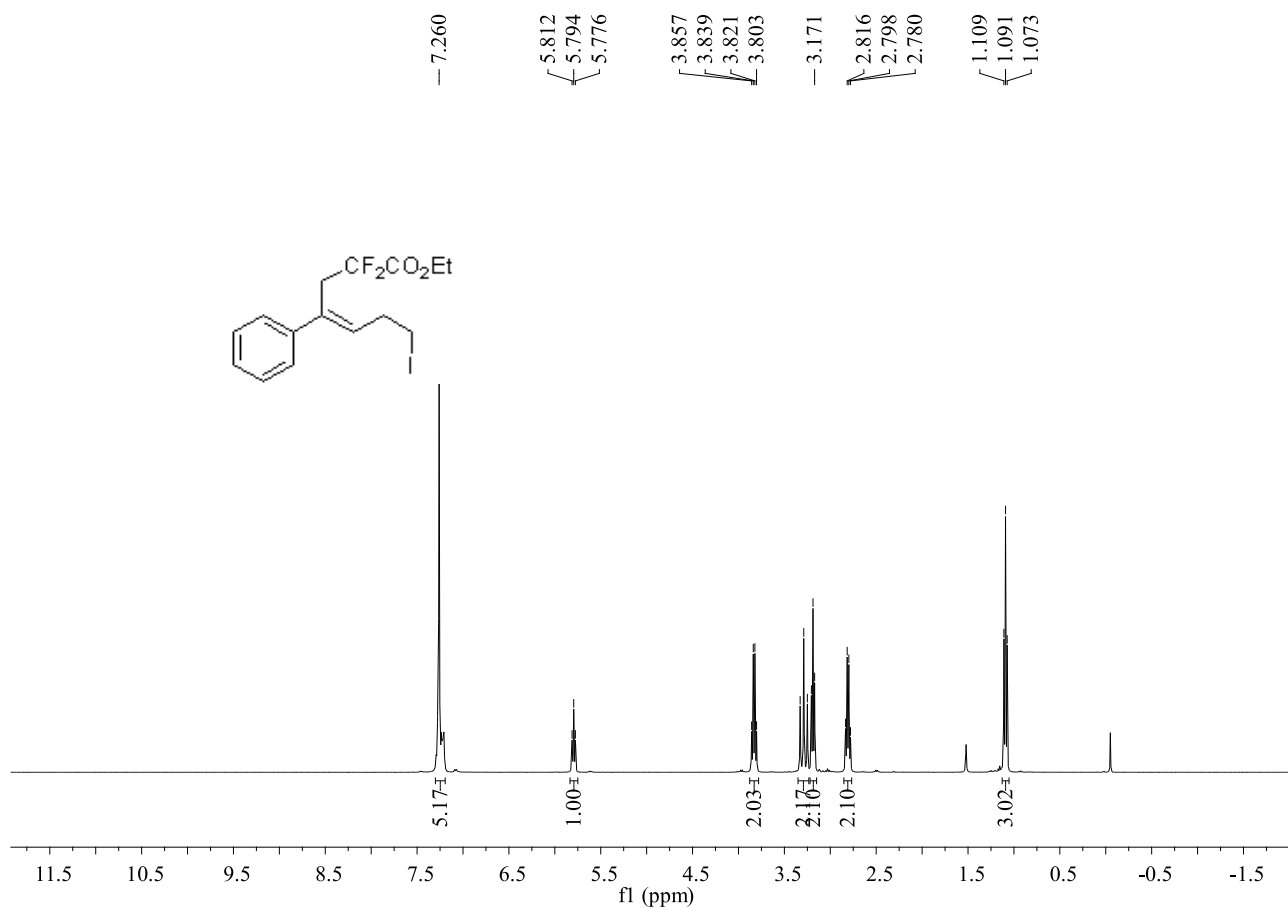


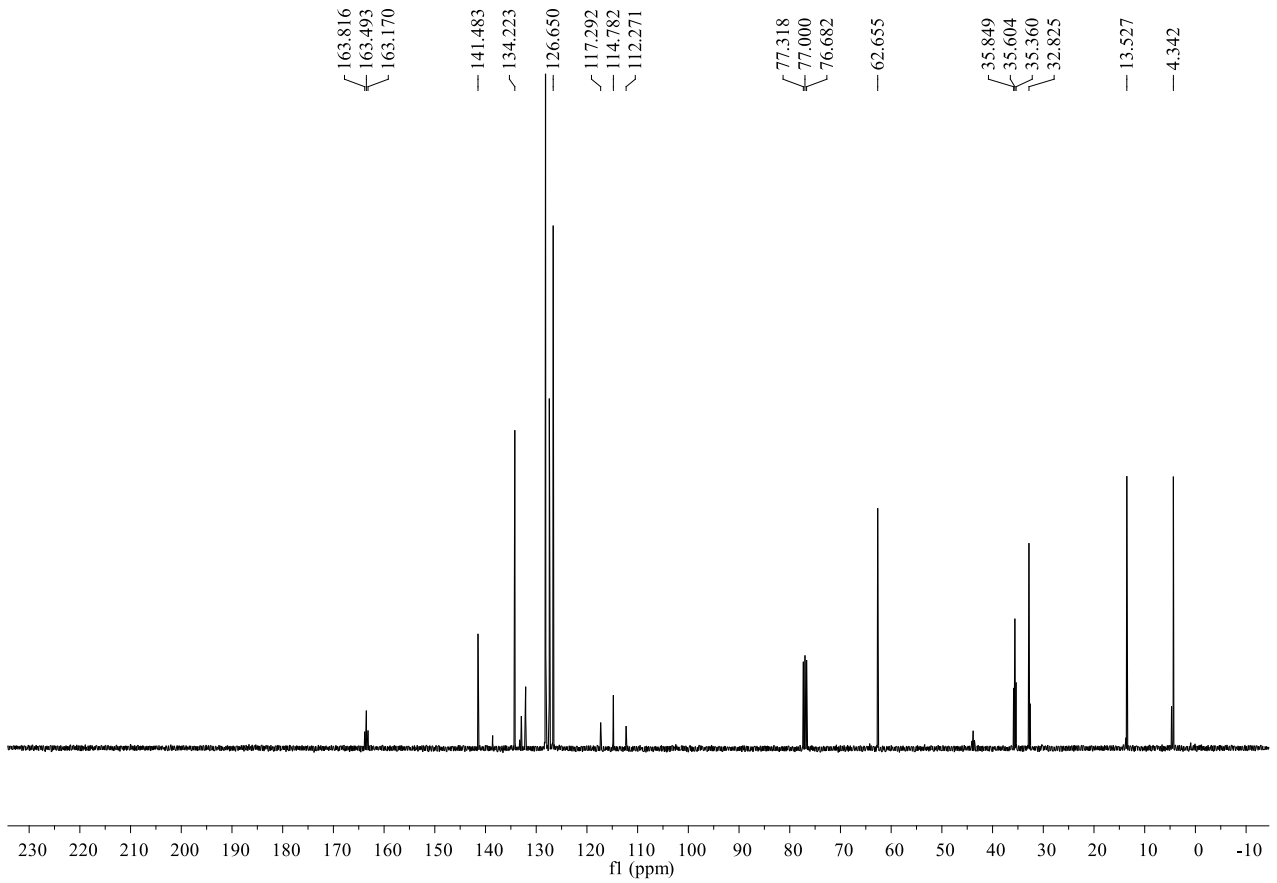
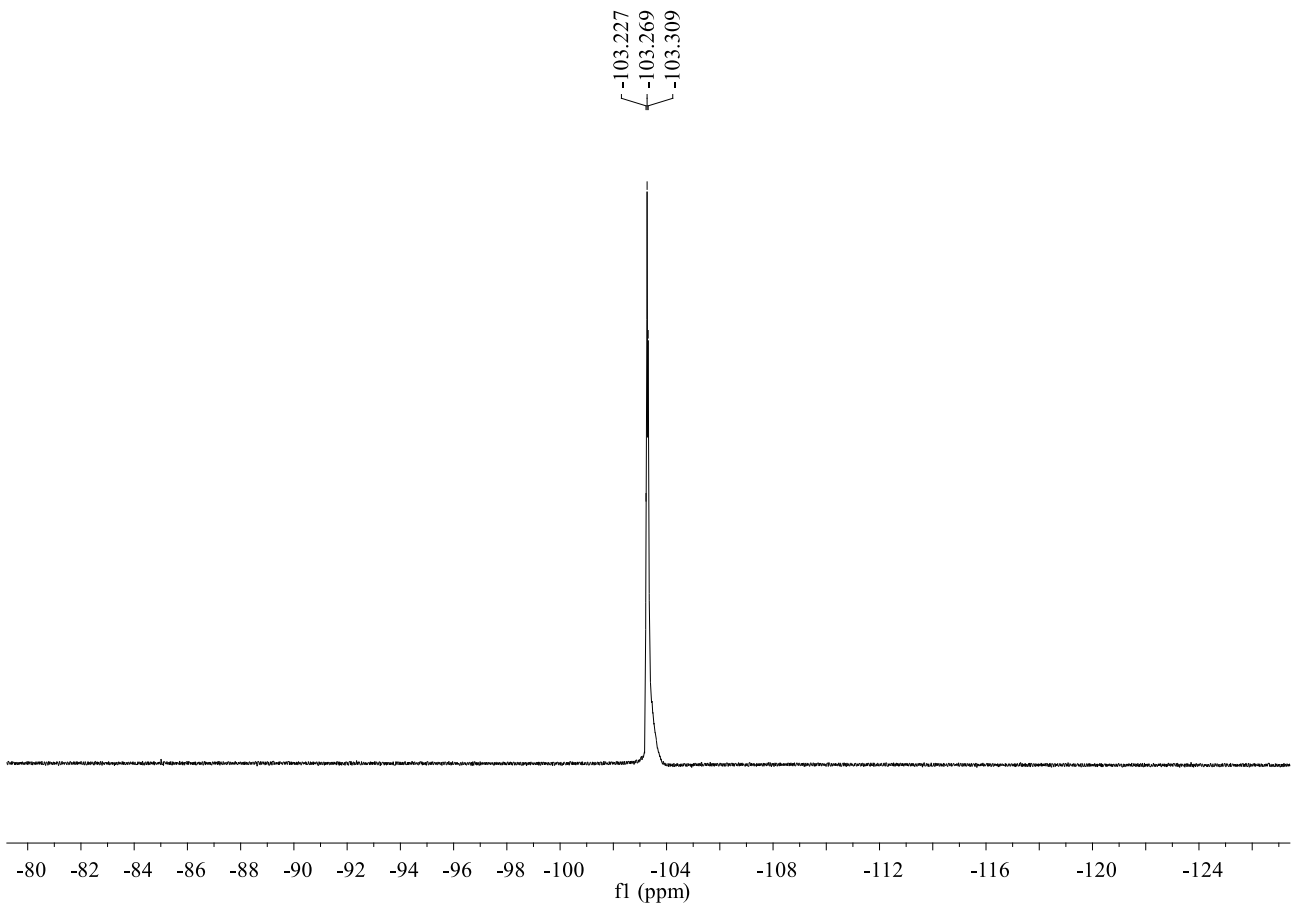
Typical procedure: To a 25 mL of Schlenk tube equipped with a Teflon septum were added KOAc (0.6 mmol, 2.0 equiv) under Ar, followed by DCE (2 mL) with stirring. allylbenzene (**1a**) (0.3 mmol, 1.0 equiv) (or without **1a**), 2-bromophenol (0.03mmol, 0.1 equiv), ICF_2COOEt (**2**) (0.6 mmol, 2.0 equiv) and α -cyclopropylstyrene (0.3 mmol, 1.0 equiv) were added subsequently. After stirring for 16 h, the reaction mixture was diluted with Ethyl acetate, washed with brine, dried over anhydrous Na_2SO_4 , filtered and concentrated. The residue was purified with silica gel chromatography to provide pure product.



Ethyl (E)-2,2-difluoro-7-iodo-4-phenylhept-4-enoate (8). The product (91 mg, 77% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 50:1) as colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.30-7.19 (m, 5H), 5.79 (t, $J = 7.2$ Hz, 1H), 3.83 (q, $J = 7.2$ Hz, 2H),

3.29 (t, $J = 15.6$ Hz, 2H), 3.19 (t, $J = 7.0$ Hz, 2H), 2.81 (q, $J = 7.2$ Hz, 2H), 1.09 (t, $J = 7.2$ Hz, 3H).
 ^{19}F NMR (376 MHz, CDCl_3) δ -103.2 – -103.8 (m, 2F). ^{13}C NMR (101 MHz, CDCl_3) δ 163.6 (t, $J = 32.6$ Hz), 141.5, 134.2, 132.1 (t, $J = 4.2$ Hz), 128.2, 127.4, 126.6, 114.8 (t, $J = 253.6$ Hz), 62.7, 35.6 (t, $J = 24.7$ Hz), 32.8, 13.5, 4.34. MS (EI): m/z (%) 394 (M^+), 267, 129 (100). HRMS (EI):
 Calculated for $\text{C}_{15}\text{H}_{17}\text{F}_2\text{IO}_2$ (M^+): 394.0241; Found: 394.0230.





6.3 UV-vis spectroscopic measurement.

Solution 1: **2a** (176.4 μL , 1.2 mmol), 2-bromophenol (7.0 μL , 0.06 mmol) and KOAc (117.8 mg, 1.2 mmol) was dissolved in DCE (4.0 mL). The mixtures were stirred for 30 seconds, filtered before use.

Solution 2: **2a** (176.4 μL , 1.2 mmol) and 2-bromophenol (7.0 μL , 0.06 mmol) was dissolved in DCE (4.0 mL). The mixtures were stirred for 30 seconds, filtered before use.

Solution 3: **2a** (176.4 μL , 1.2 mmol) and KOAc (117.8 mg, 1.2 mmol) was dissolved in DCE (4.0 mL). The mixtures were stirred for 30 seconds, filtered before use.

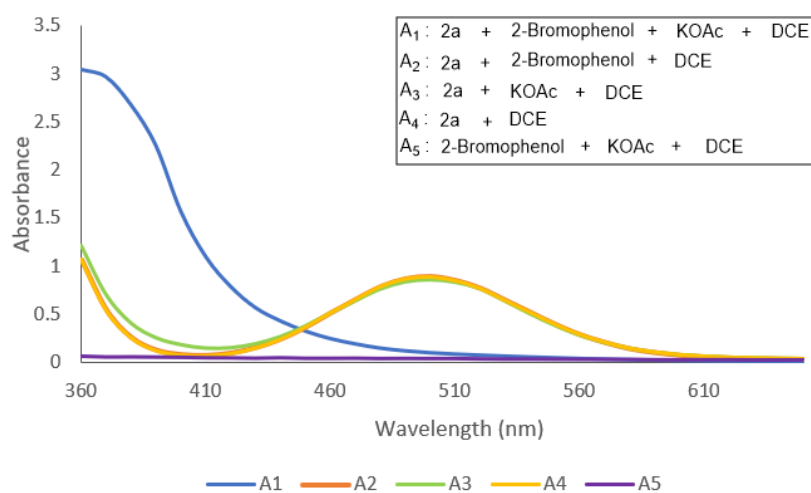
Solution 4: **2a** (176.4 μL , 1.2 mmol) was dissolved in DCE (4.0 mL). The mixtures were stirred for 30 seconds, filtered before use.

Solution 5: 2-bromophenol (11.6 μL 0.1 mmol) and KOAc (117.8 mg, 1.2 mmol) was dissolved in DCE (4.0 mL). The mixtures were stirred for 30 seconds, filtered before use.

Performed on UV visible spectrophotometer, recorded in 1cm path quartz cuvettes using T6 Xinyue visible spectrophotometer (PERSEETM), pure DCE as blank sample.

A λ (nm)	2a + 2-bromophenol + KOAc +DCE A ₁	2a + 2-bromophenol + DCE A ₂	2a + KOAc +DCE A ₃	2a +DCE A ₄	2-bromophenol + KOAc +DCE A ₅
360	3.044	1.069	1.223	1.071	0.061
370	2.967	0.549	0.709	0.548	0.054
380	2.677	0.264	0.411	0.260	0.055
390	2.253	0.133	0.258	0.126	0.053
400	1.570	0.087	0.185	0.078	0.051
410	1.099	0.079	0.149	0.071	0.047
420	0.788	0.103	0.153	0.094	0.046
430	0.568	0.161	0.194	0.153	0.043
440	0.430	0.249	0.270	0.242	0.047
450	0.325	0.373	0.381	0.367	0.042
460	0.247	0.520	0.515	0.515	0.042
470	0.192	0.660	0.644	0.653	0.043
480	0.148	0.792	0.767	0.787	0.040
490	0.120	0.874	0.843	0.868	0.041
500	0.100	0.897	0.865	0.889	0.040
510	0.086	0.857	0.840	0.851	0.040
520	0.075	0.776	0.772	0.771	0.037

530	0.065	0.652	0.644	0.648	0.035
540	0.056	0.527	0.510	0.524	0.035
550	0.048	0.402	0.388	0.401	0.034
560	0.040	0.294	0.285	0.294	0.033
570	0.034	0.213	0.208	0.214	0.033
580	0.028	0.148	0.147	0.150	0.032
590	0.024	0.108	0.108	0.111	0.030
600	0.020	0.080	0.080	0.083	0.029
610	0.017	0.063	0.064	0.067	0.030
620	0.015	0.052	0.053	0.056	0.030
630	0.014	0.046	0.046	0.050	0.028
640	0.013	0.041	0.042	0.045	0.028
650	0.012	0.038	0.038	0.042	0.028



6.4 The reaction of different time periods was examined by HPLC to detect the concentration of 2-bromophenol.

Making a standard curve

The solution A ($c = 0.06$ mmol/mL): mixed 2-bromophenol (69.6 μ L, 0.6 mmol) and DCE (10.0 mL)

The solution B ($c = 0.03$ mmol/mL): mixed phenol (28.2 mg, 0.3 mmol) and DCE (10.0 mL)

Sample 1 (2 mL): mixed the solution A (0.17 mL), the solution B (1.00 mL) and DCE

Sample 2 (2 mL): mixed the solution A (0.33 mL), the solution B (1.00 mL) and DCE

Sample 3 (2 mL): mixed the solution A (0.50 mL), the solution B (1.00 mL) and DCE

Sample 4 (2 mL): mixed the solution A (0.67 mL), the solution B (1.00 mL) and DCE

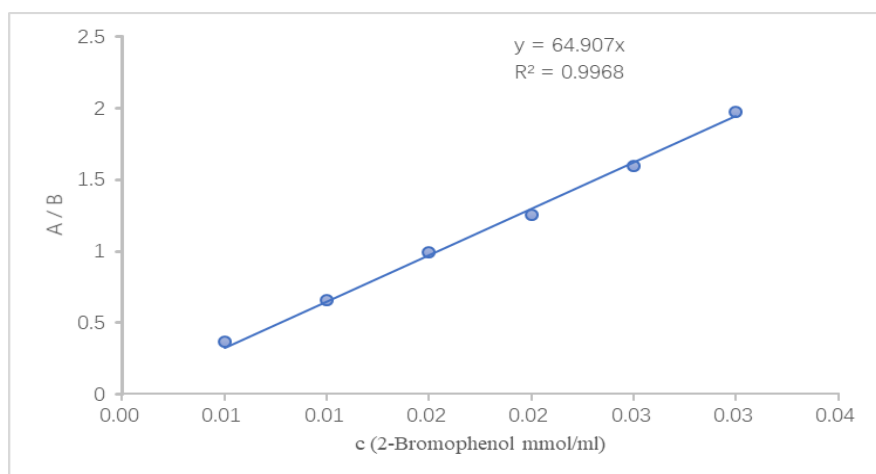
Sample 5 (2 mL): mixed the solution A (0.83 mL), the solution B (1.00 mL) and DCE

Sample 6 (2 mL): mixed the solution A (1.00 mL), the solution B (1.00 mL) and DCE

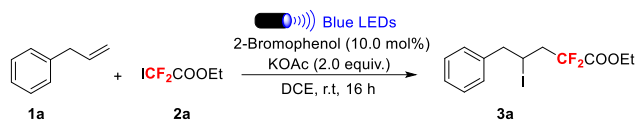
All of the samples were determined by HPLC to measure the content of 2-bromophenol to make a standard curve. A phenol was selected as an internal standard. (V_{H_2O} : V_{MeCN} = 60:40, 1 mL/min, 254 nm, 25 °C, Inj Volume = 20 μ L, Time = 30 min).

To six 25 mL of Schlenk tubes equipped with Teflon septum were added KOAc (0.6 mmol, 2.0 equiv) under argon respectively, followed by DCE (2.0 ml) with stirring. 2-bromophenol (0.03 mmol, 0.1 equiv), allylbenzene (**1a**) (0.3 mmol, 1.0 equiv) and ICF_2COOEt (**2a**) (0.60 mmol, 2.0 equiv) were added subsequently. one Schlenk tube was removed. The remaining five Schlenk tubes were stirred at room temperature under 12w blue LEDs for 3 h, 6 h, 9 h, 12h and 16 h. After each reaction was stopped, 0.5 mL of phenol ($C = 0.075$ mmol/mL) was added as an internal standard, subsequently filtered for HPLC detection.

Entry	2-bromophenol (A)			phenol (B)			A/B
	Ret. Time (min)	Area	C (mmol/mL)	Ret. Time (min)	Area	C (mmol/mL)	
1	8.46	2470.858	0.005	5.581	6770.840	0.015	0.3649
2	8.49	4464.328	0.010	5.602	6742.690	0.015	0.6621
3	8.46	6739.670	0.015	5.581	6807.432	0.015	0.9900
4	8.48	8506.987	0.020	5.573	6782.561	0.015	1.2542
5	8.48	10753.571	0.025	5.590	6732.406	0.015	1.5973
6	8.47	12933.962	0.030	5.588	6537.696	0.015	1.9784

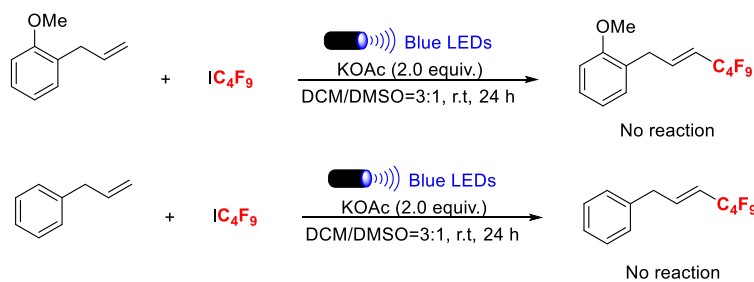


Standard curve of 2-bromophenol using phenol as internal standard

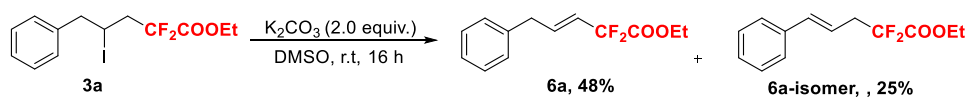


Entry	Area A (2-bromophenol)	Area B (Phenol)	A/B (y)	Calculated concentration A ($y=64.907x$ mmol/mL)	Actual concentration A (mmol/mL)
0 h	5214.82	6276.87	0.8308	0.0128	0.0120
3 h	4636.90	5946.84	0.7797	0.0120	0.0120
6 h	5040.79	6776.42	0.7439	0.0115	0.0120
9 h	4911.38	6566.38	0.7479	0.0115	0.0120
12 h	4594.28	6279.82	0.7316	0.0113	0.0120
16 h	4723.24	6399.03	0.7381	0.0114	0.0120

6.5 No products were observed when phenolic hydroxyl group was protected or in the absence of hydroxyl group.

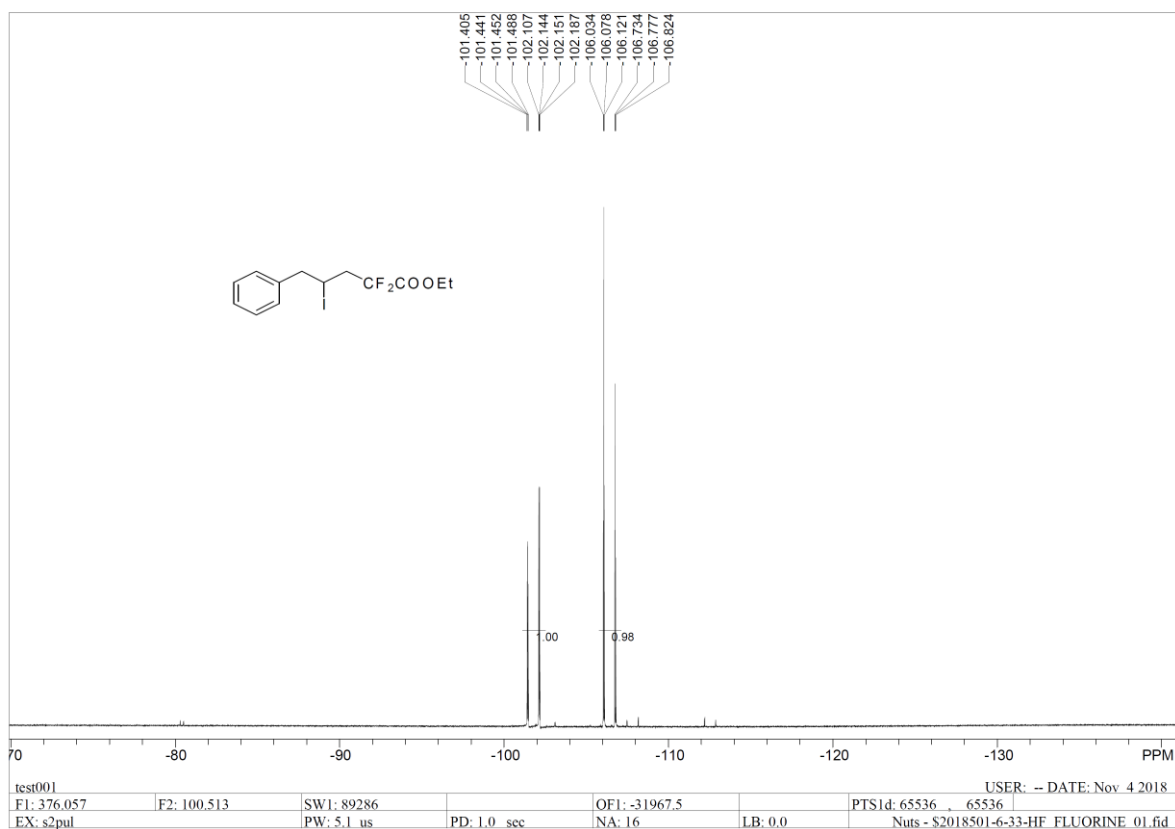
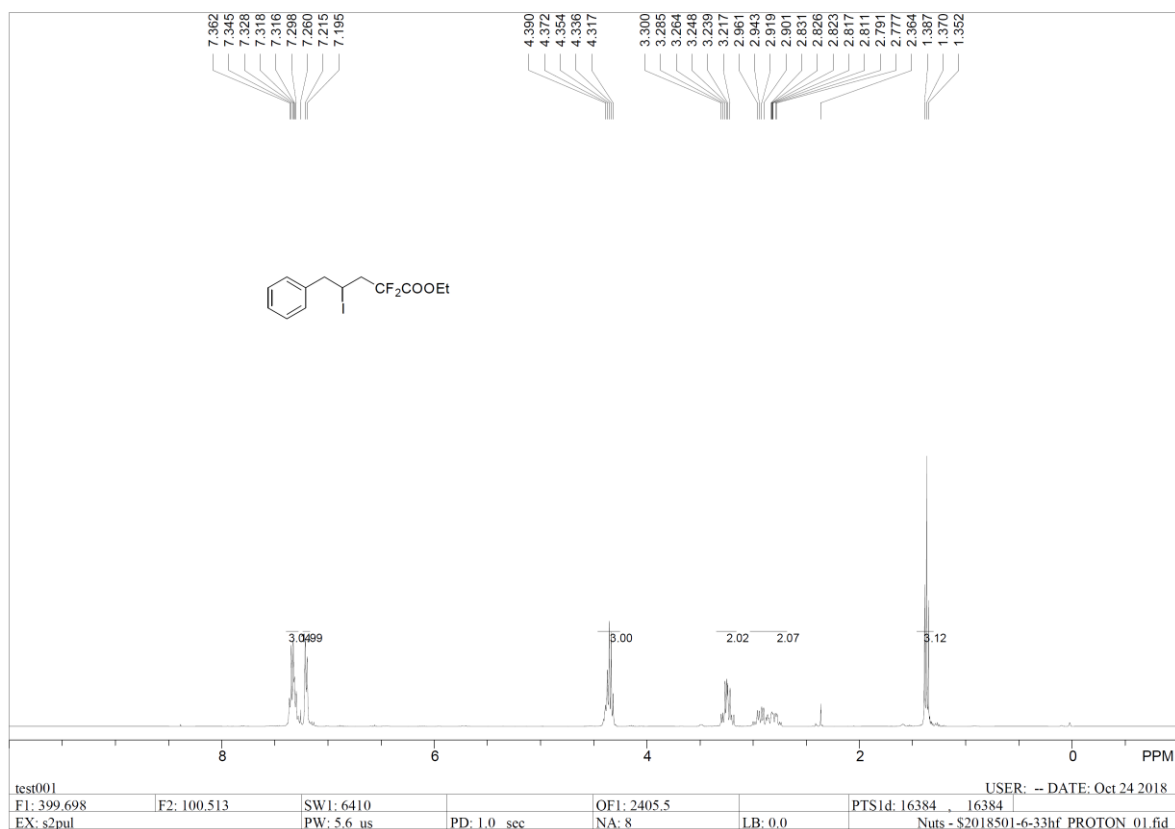


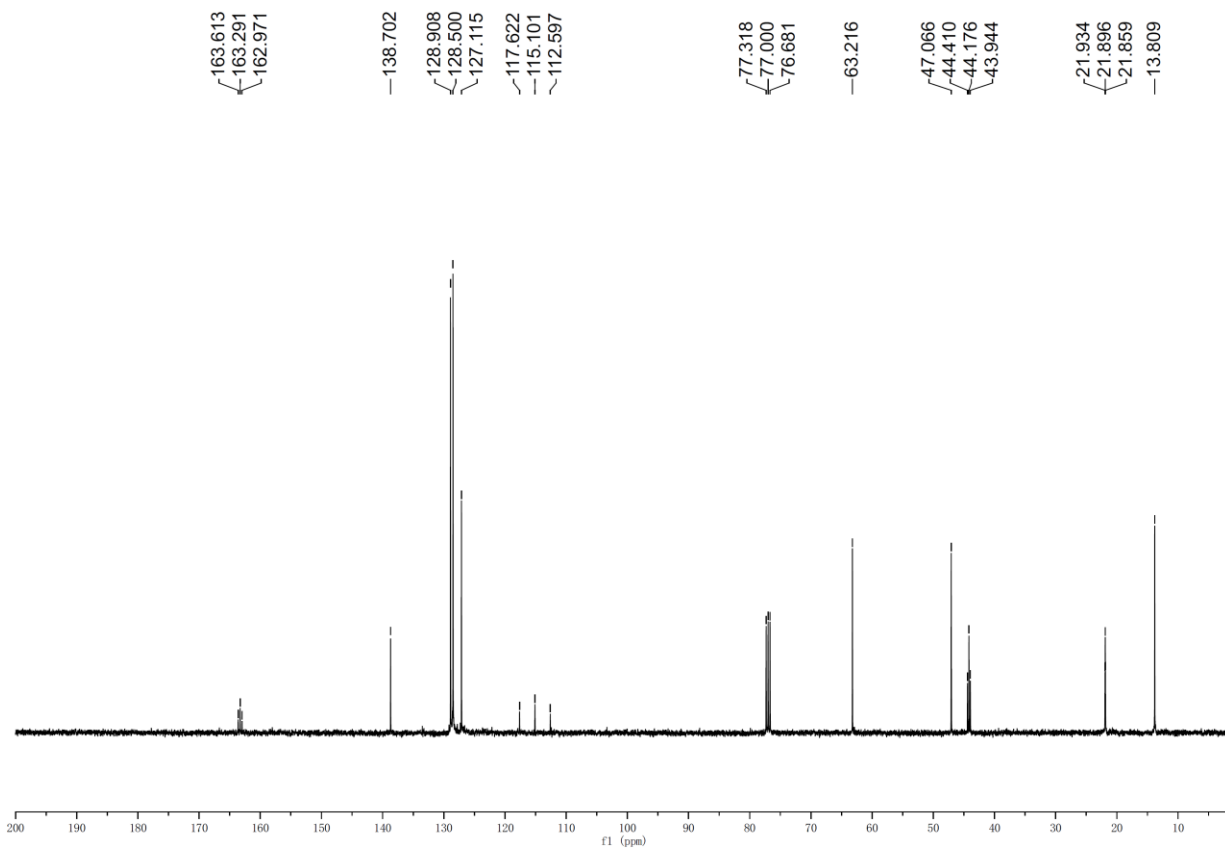
6.6 Transform 3a to 6a in the presence of K_2CO_3 and DMSO.



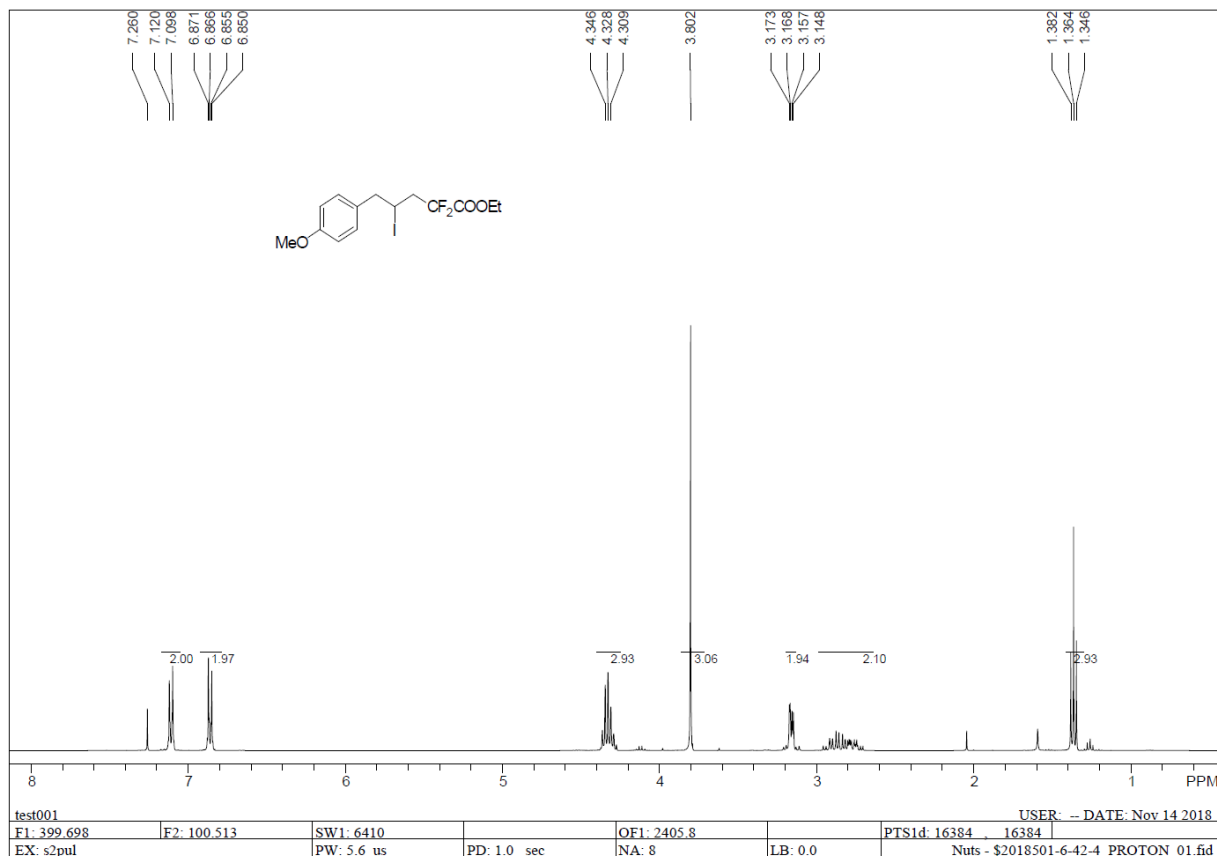
7. Copies of NMR spectra of 3, 5, 6, 7.

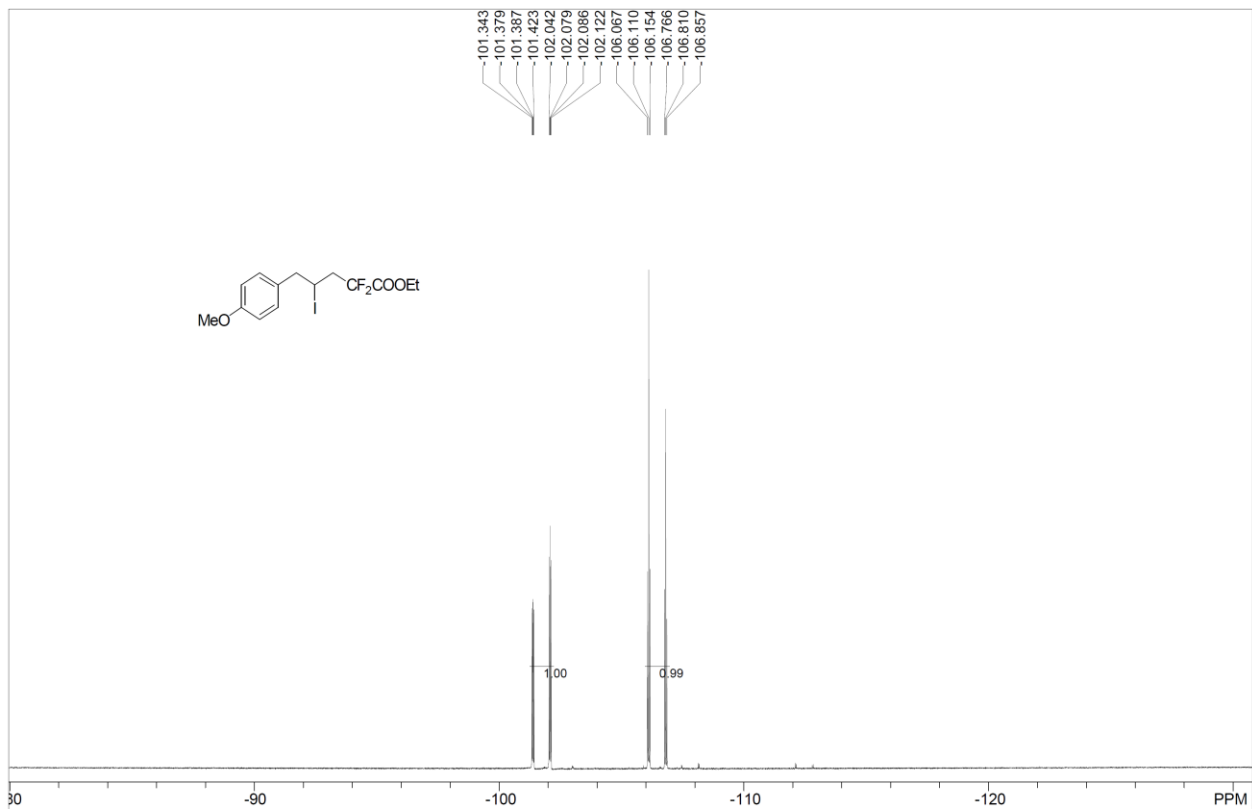
Ethyl 2,2-difluoro-4-iodo-5-phenylpentanoate (3a).



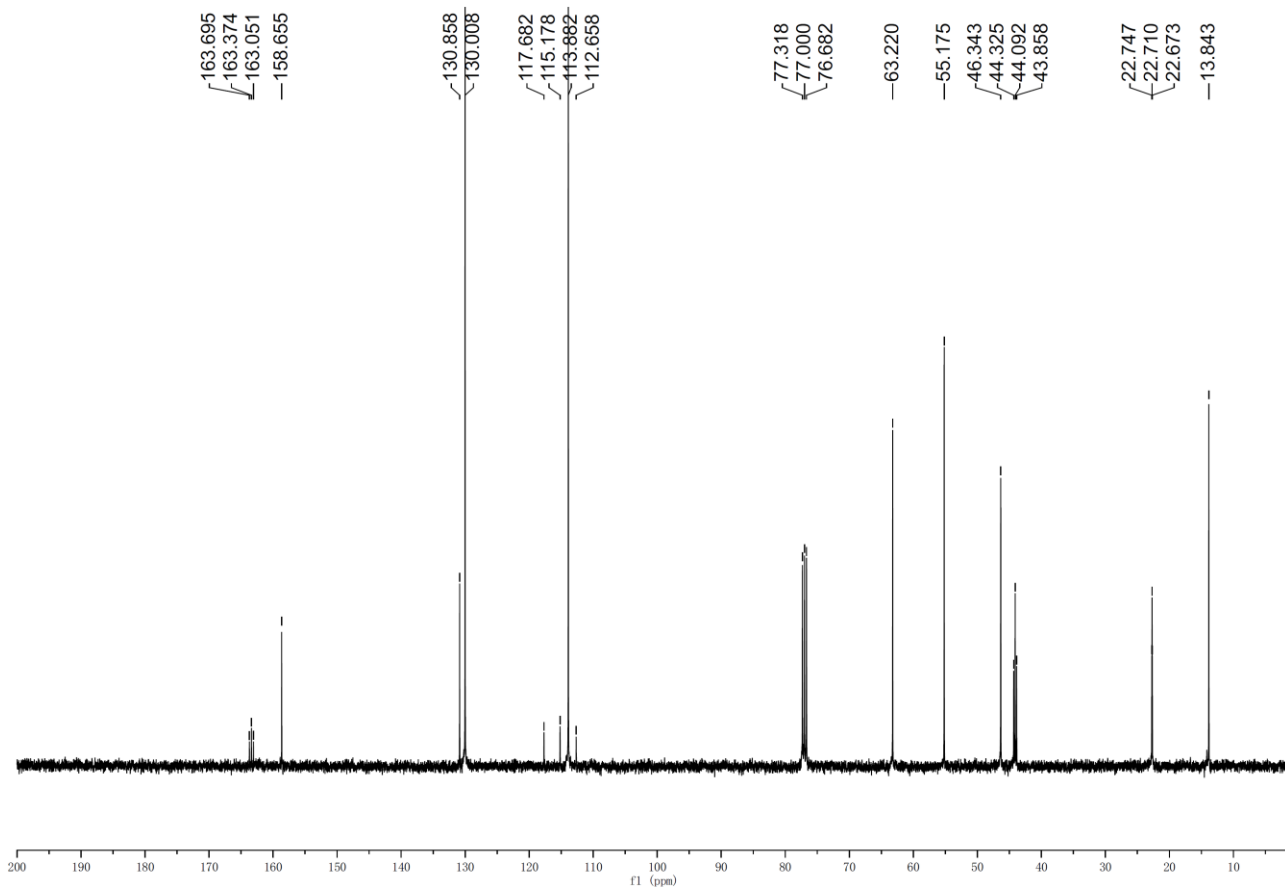


Ethyl 2,2-difluoro-4-iodo-5-(4-methoxyphenyl)pentanoate (3b).

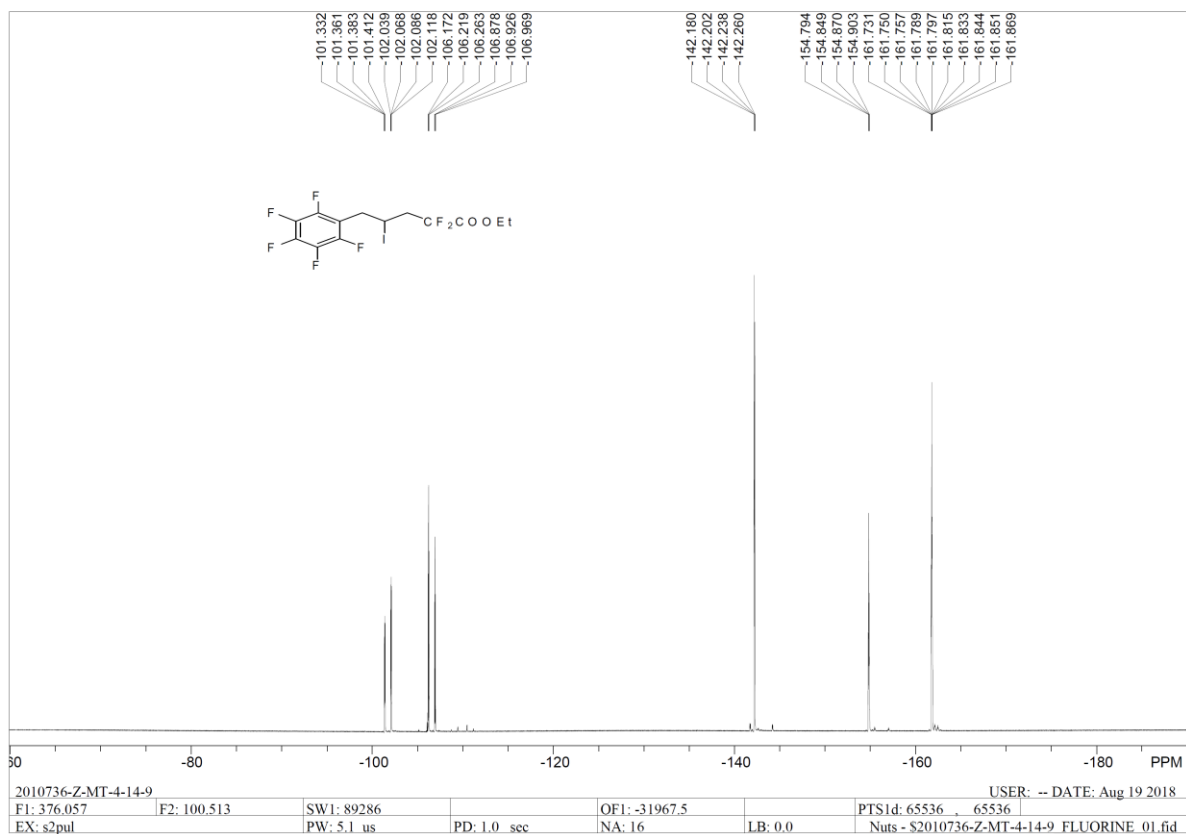
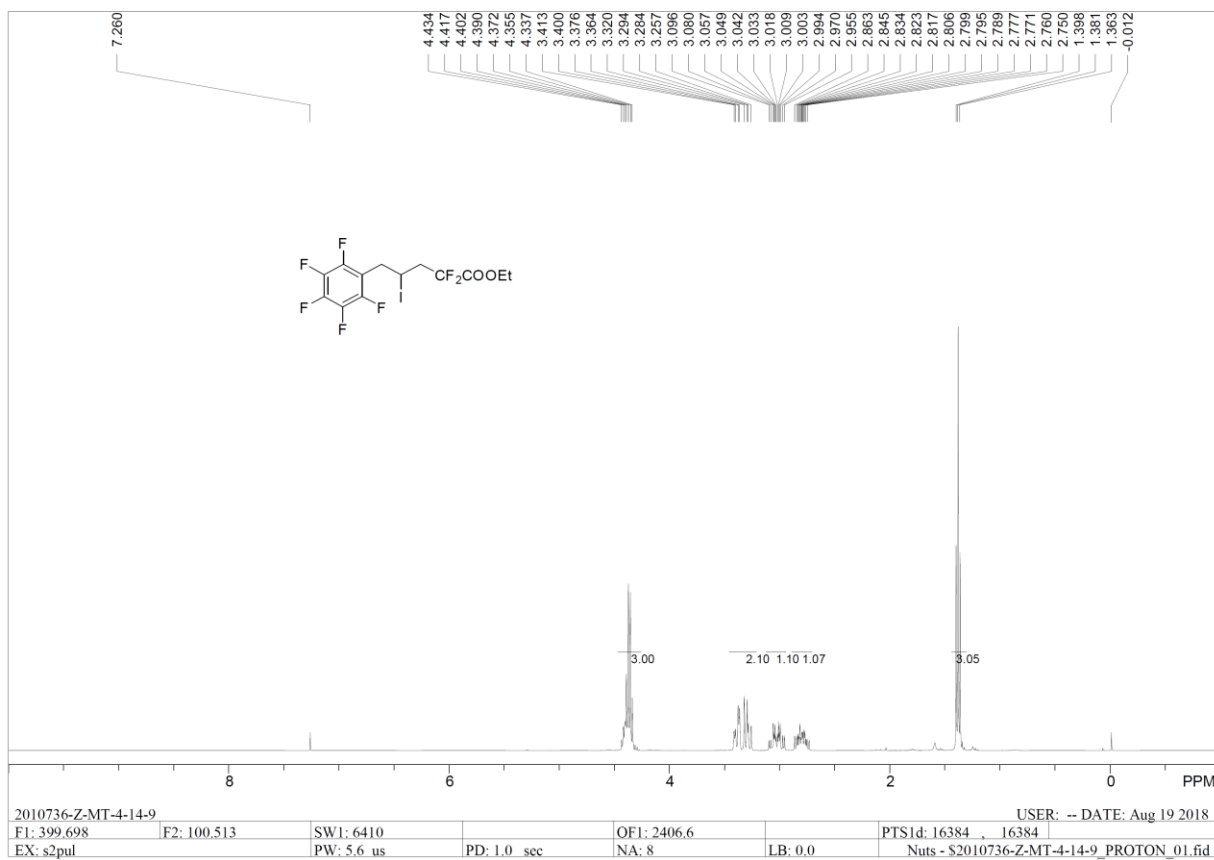


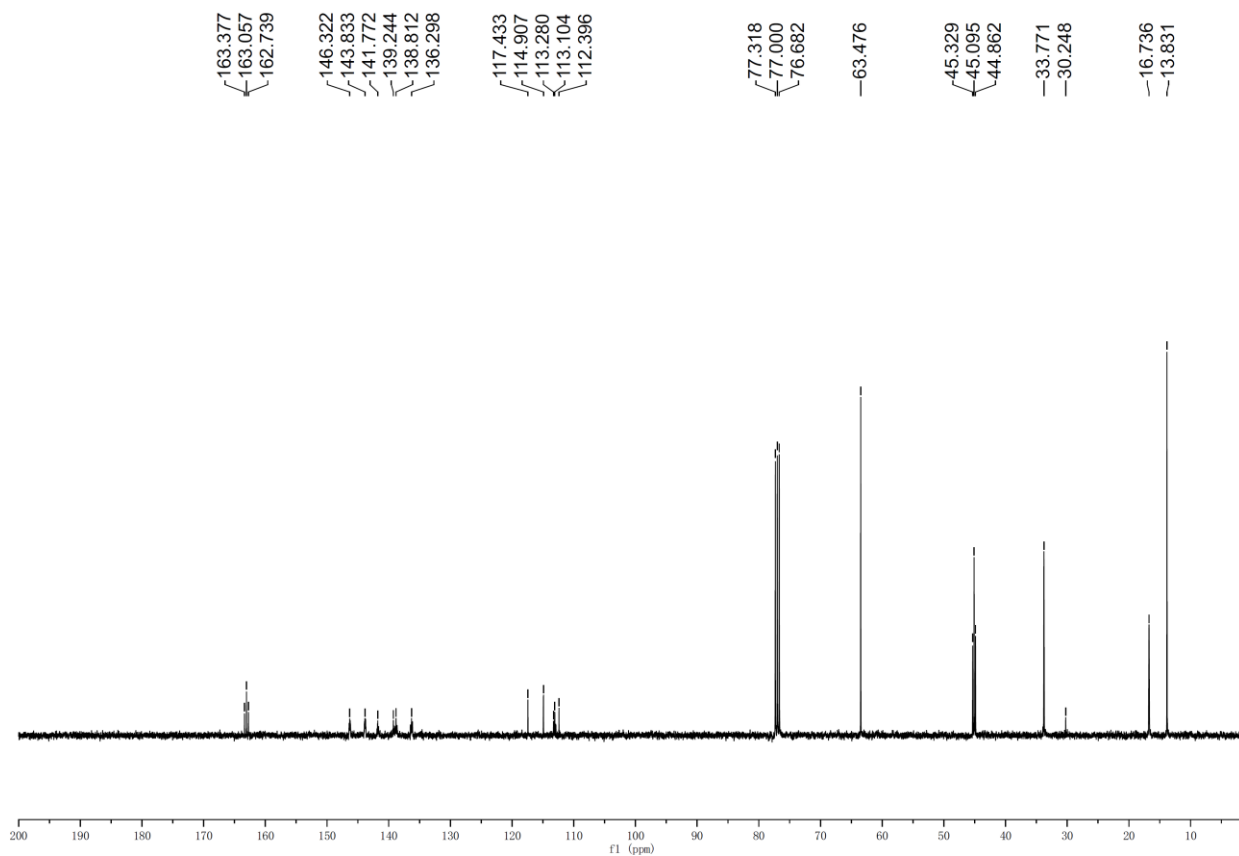


test001
 F1: 376.057 F2: 100.513 SW1: 89286 OF1: -31967.5 PTS1d: 65536 65536 USER: -- DATE: Nov 14 2018
 EX: s2pul PW: 5.1 us PD: 1.0 sec NA: 16 LB: 0.0 Nuts - S2018501-6-42-4_FLUORINE_01.fid

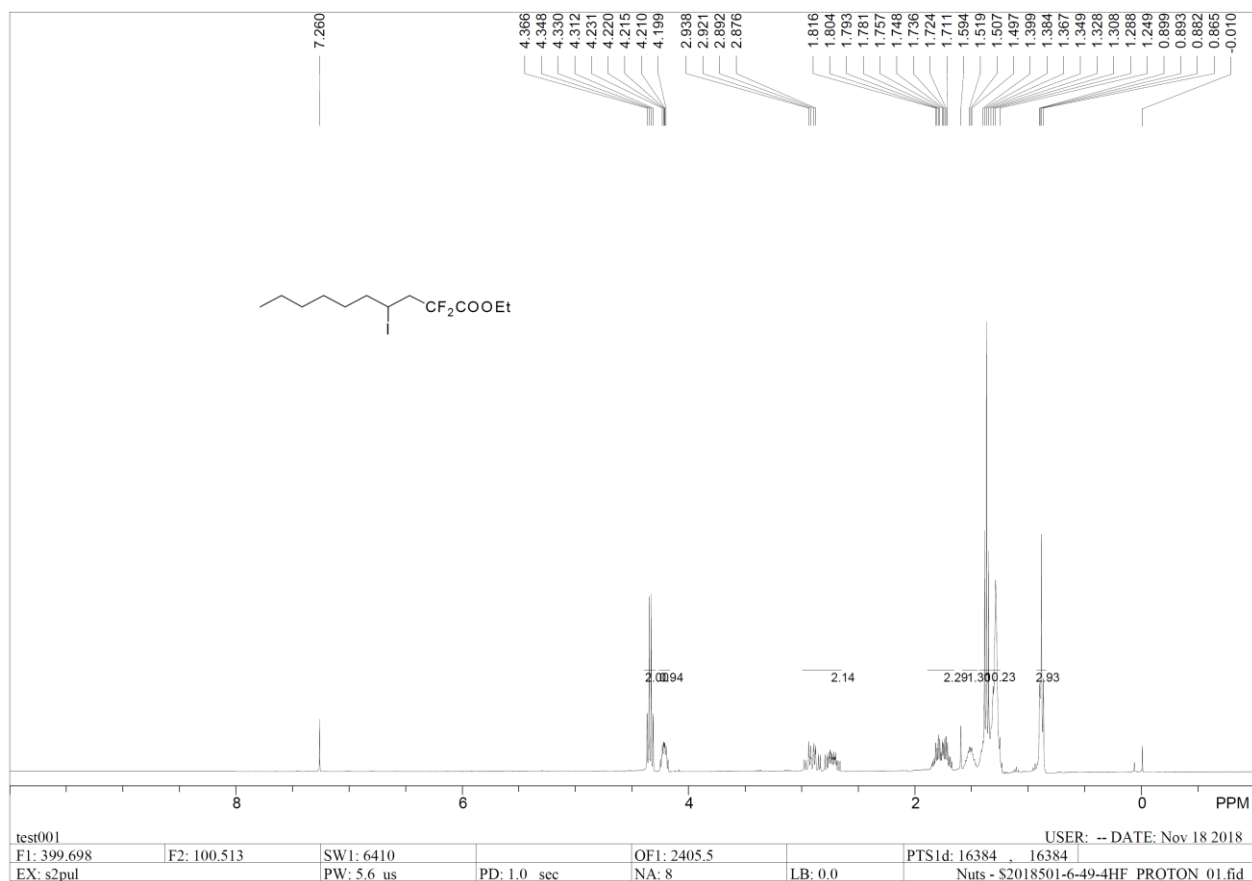


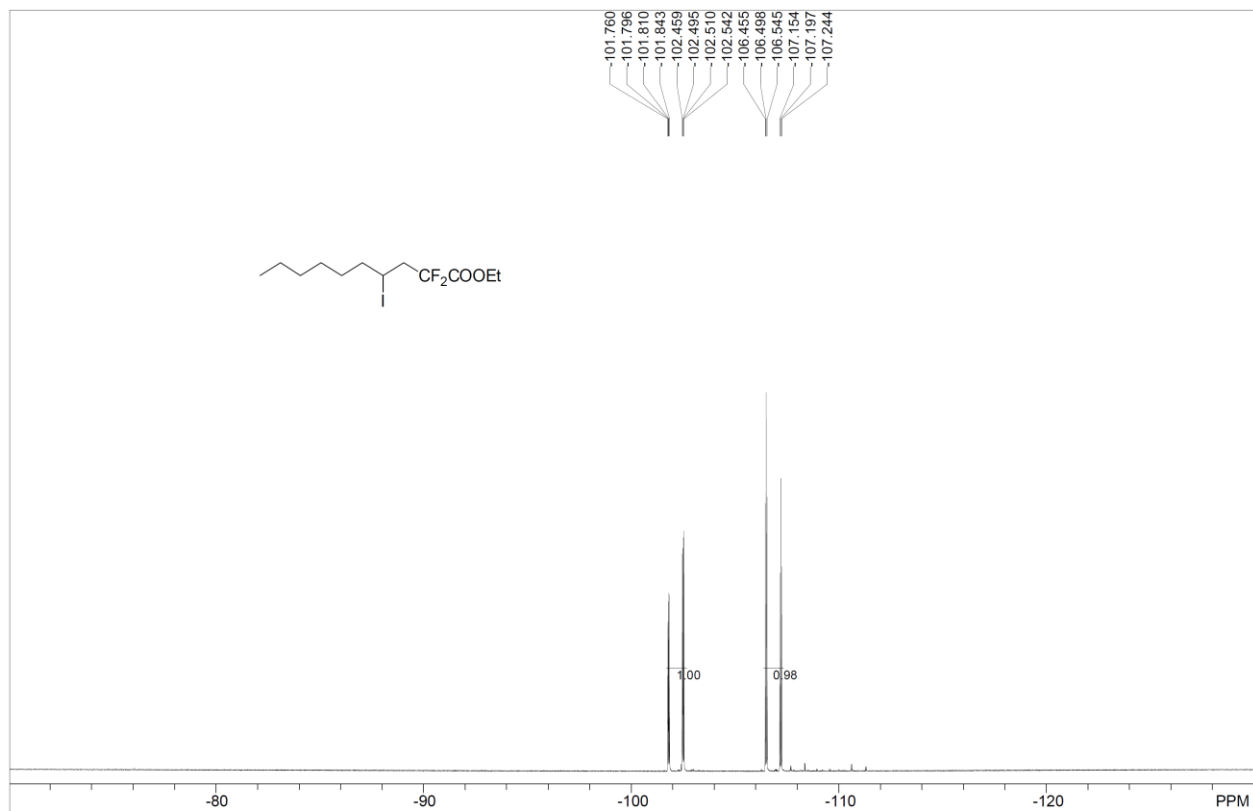
Ethyl 2,2-difluoro-4-iodo-5-(perfluorophenyl)pentanoate (3c).



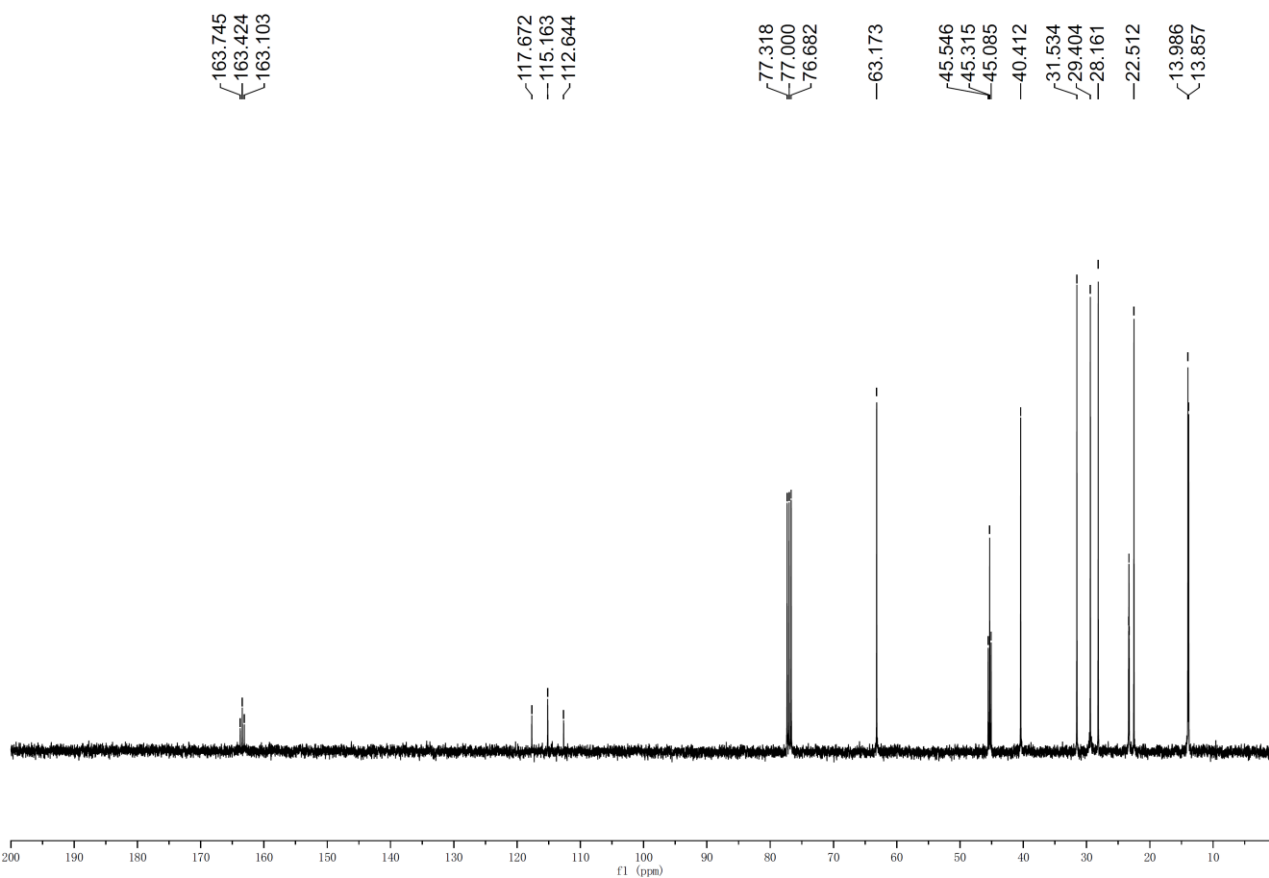


Ethyl 2,2-difluoro-4-iododecanoate (3d).

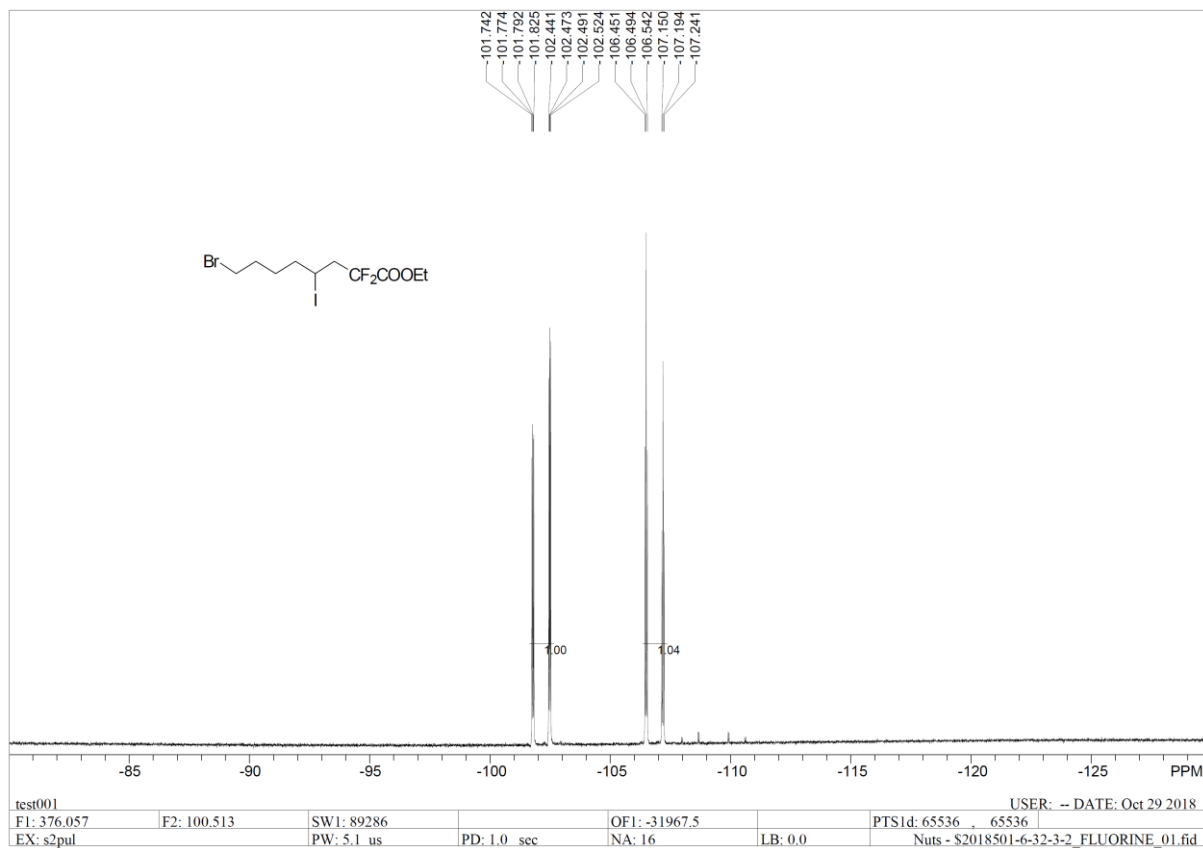
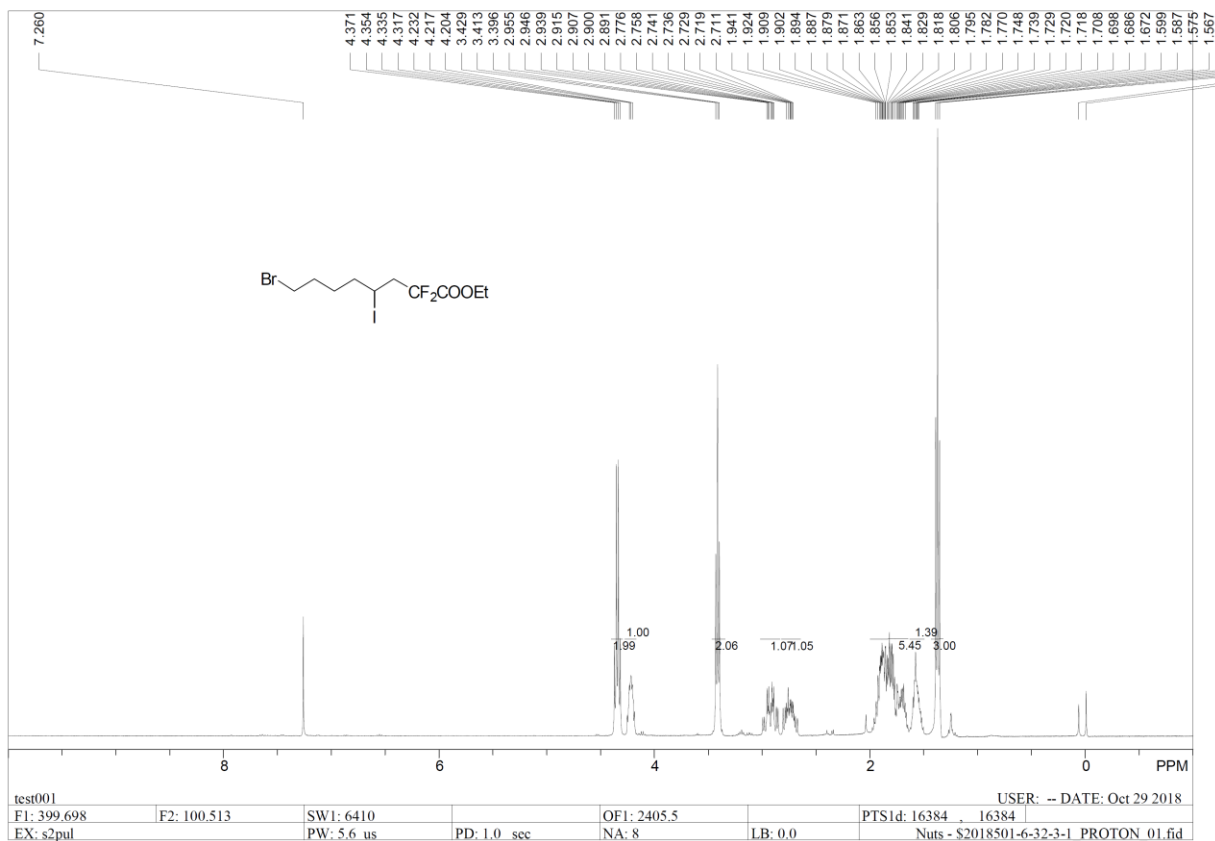


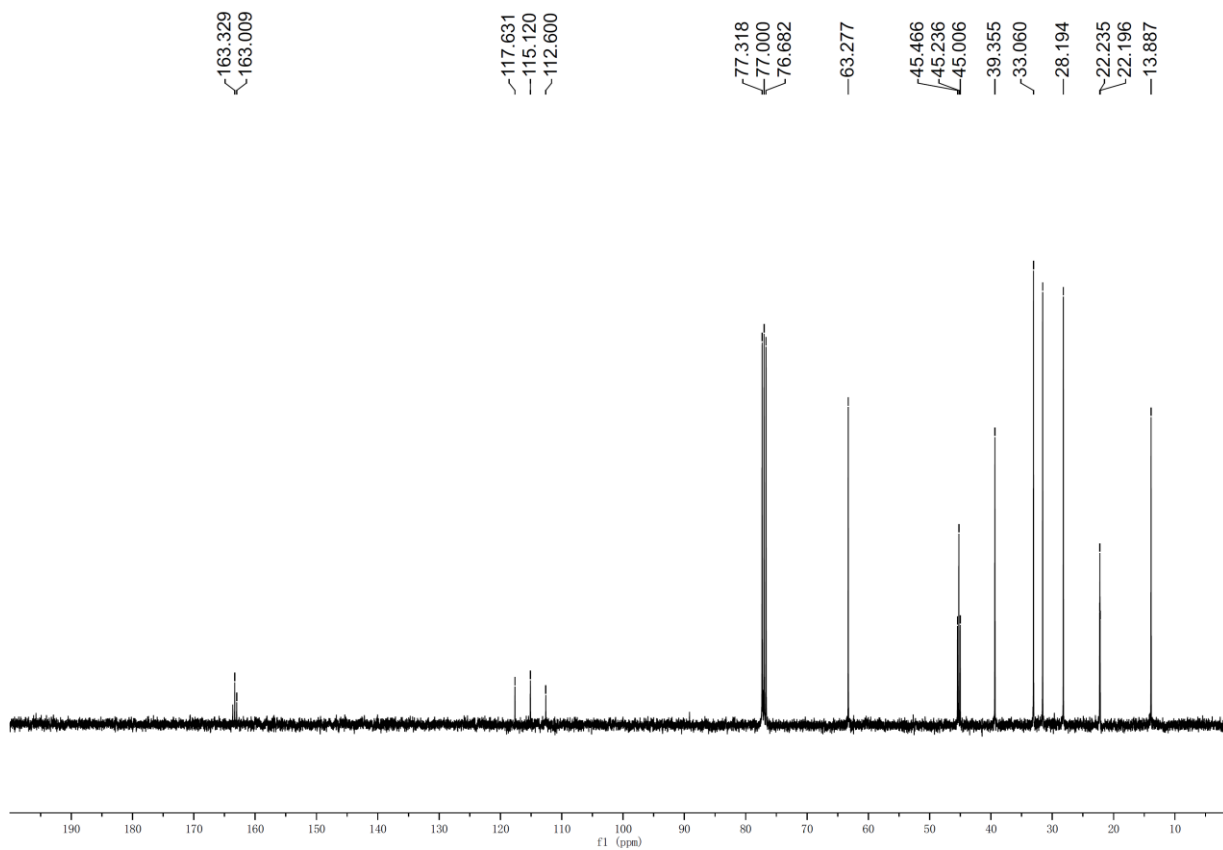


test001
 F1: 376.057 F2: 100.513 SW1: 89286 OF1: -31967.5 PTS1d: 65536 65536 USER: -- DATE: Nov 18 2018
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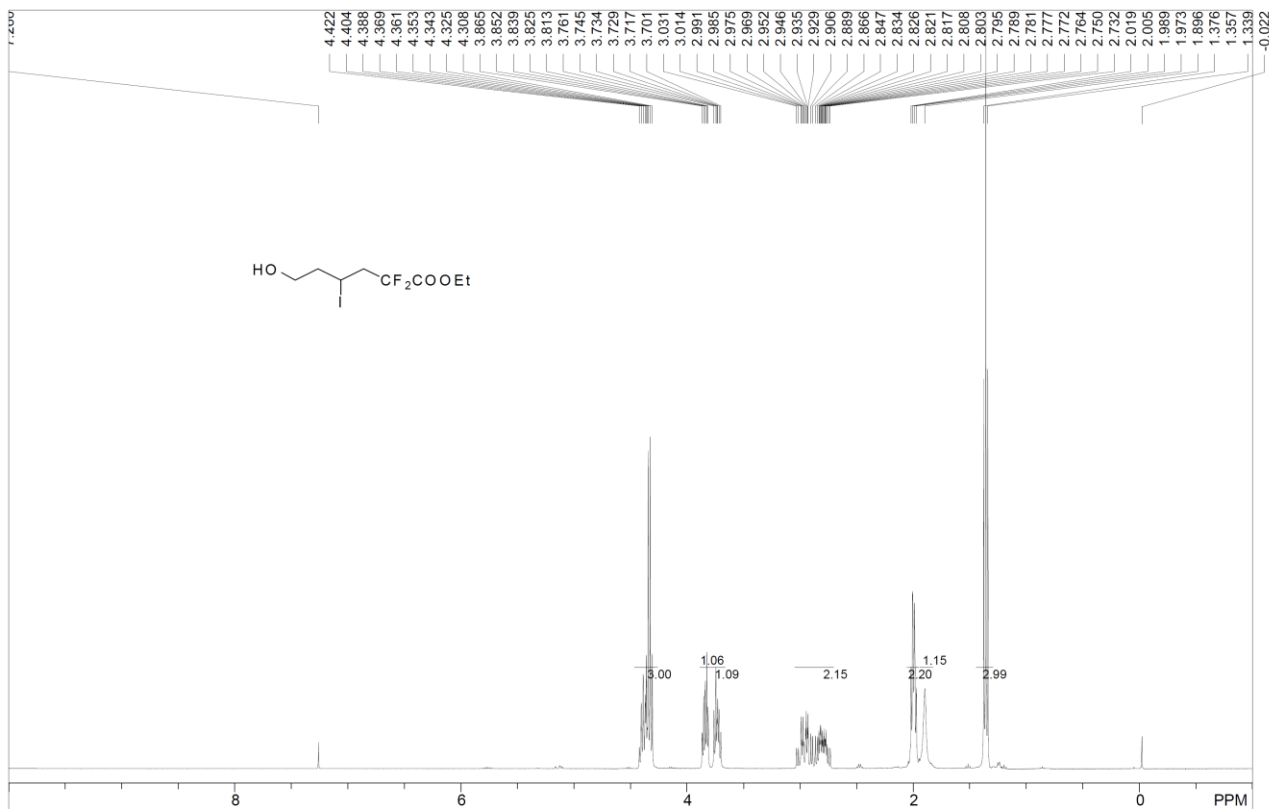


Ethyl 8-bromo-2,2-difluoro-4-iodooctanoate (3e).

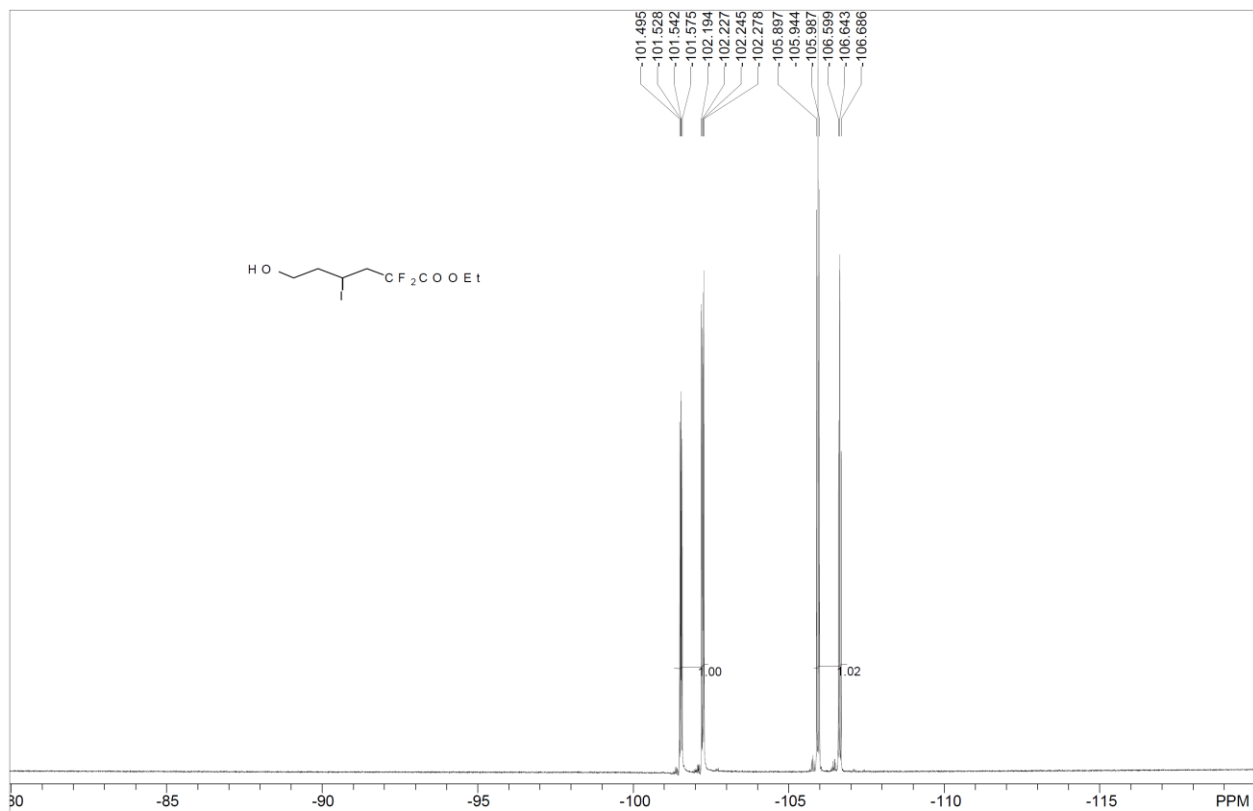




Ethyl 2,2-difluoro-6-hydroxy-4-iodohexanoate (3f).



test001						USER: -- DATE: Oct 29 2018
F1: 399.698	F2: 100.513	SW1: 6410	OF1: 2405.5	PTS1d: 16384	16384	
EX: s2pul	PW: 5.6 us	PD: 1.0 sec	NA: 8	LB: 0.0	Nuts - \$2018501-6-35-1_PROTON_01.fid	



test001 USER: -- DATE: Oct 29 2018
 F1: 376.057 F2: 100.513 SW1: 89286 OF1: -31967.5 PTS1d: 65536 65536
 EX: s2pul PW: 5.1 us PD: 1.0 sec NA: 16 LB: 0.0 Nuts - S2018501-6-35-1_FLUORINE_01.fid

163.753
 163.432
 163.110

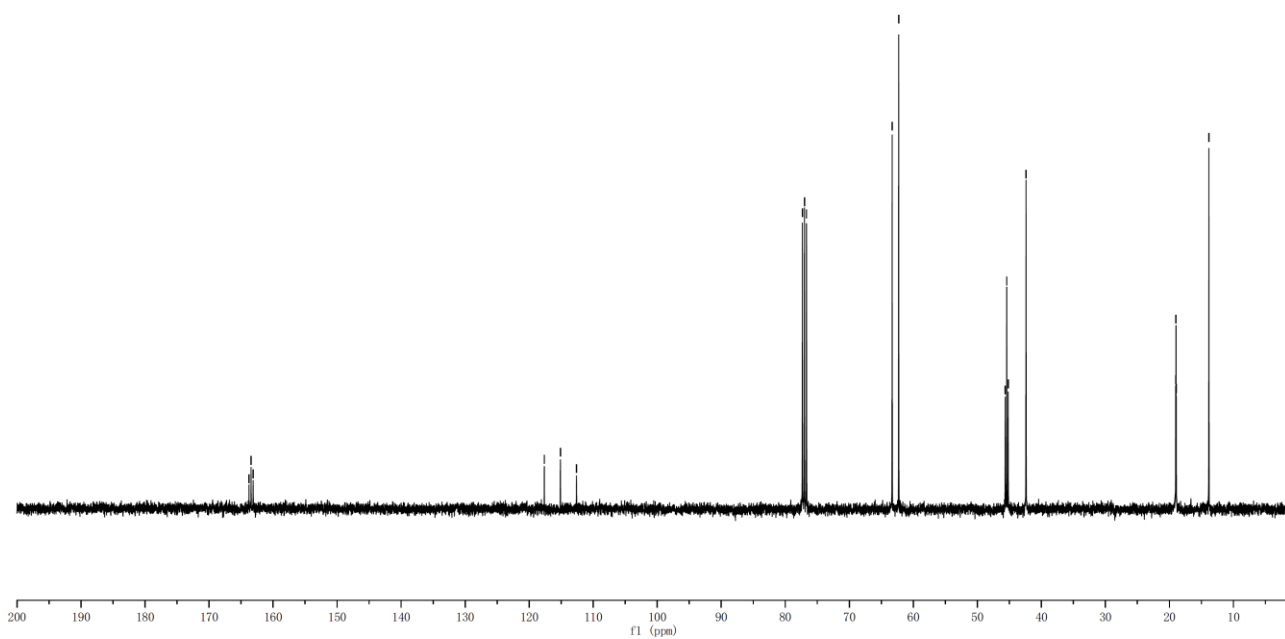
117.637
 115.116
 112.607

77.319
 77.000
 76.682

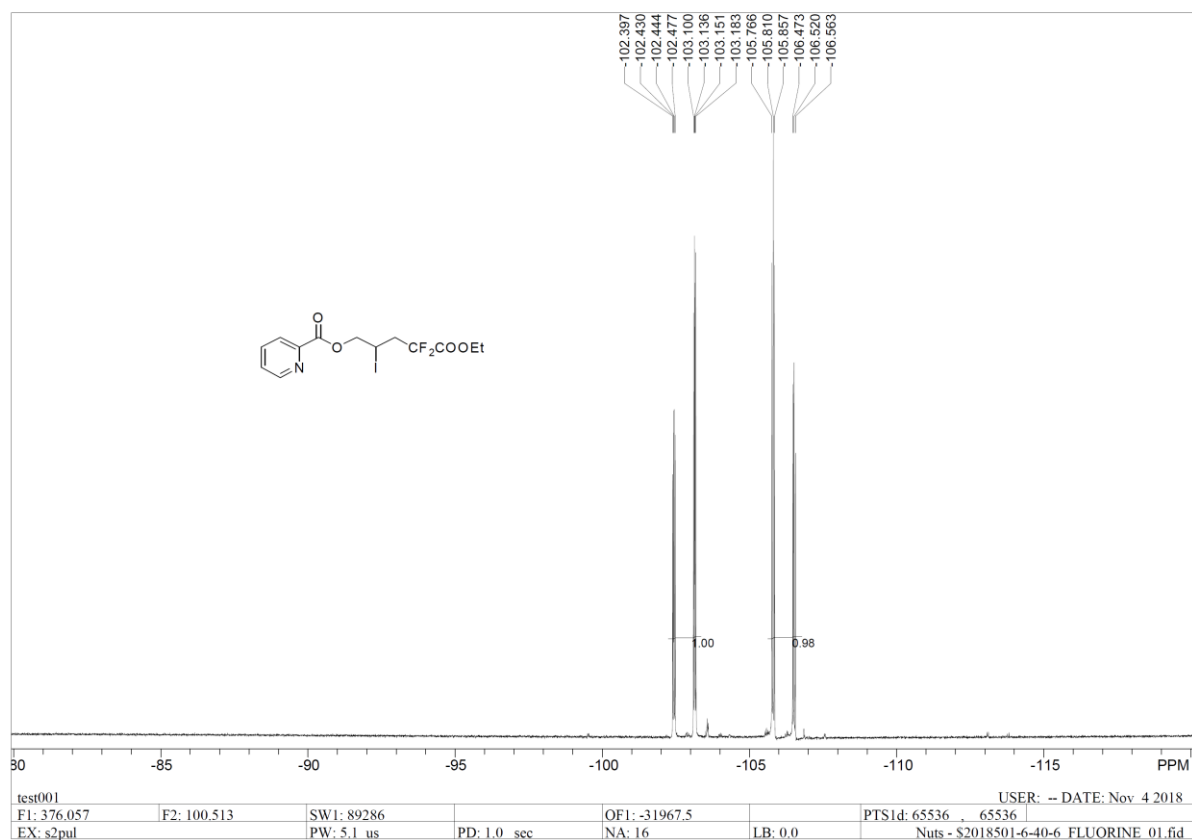
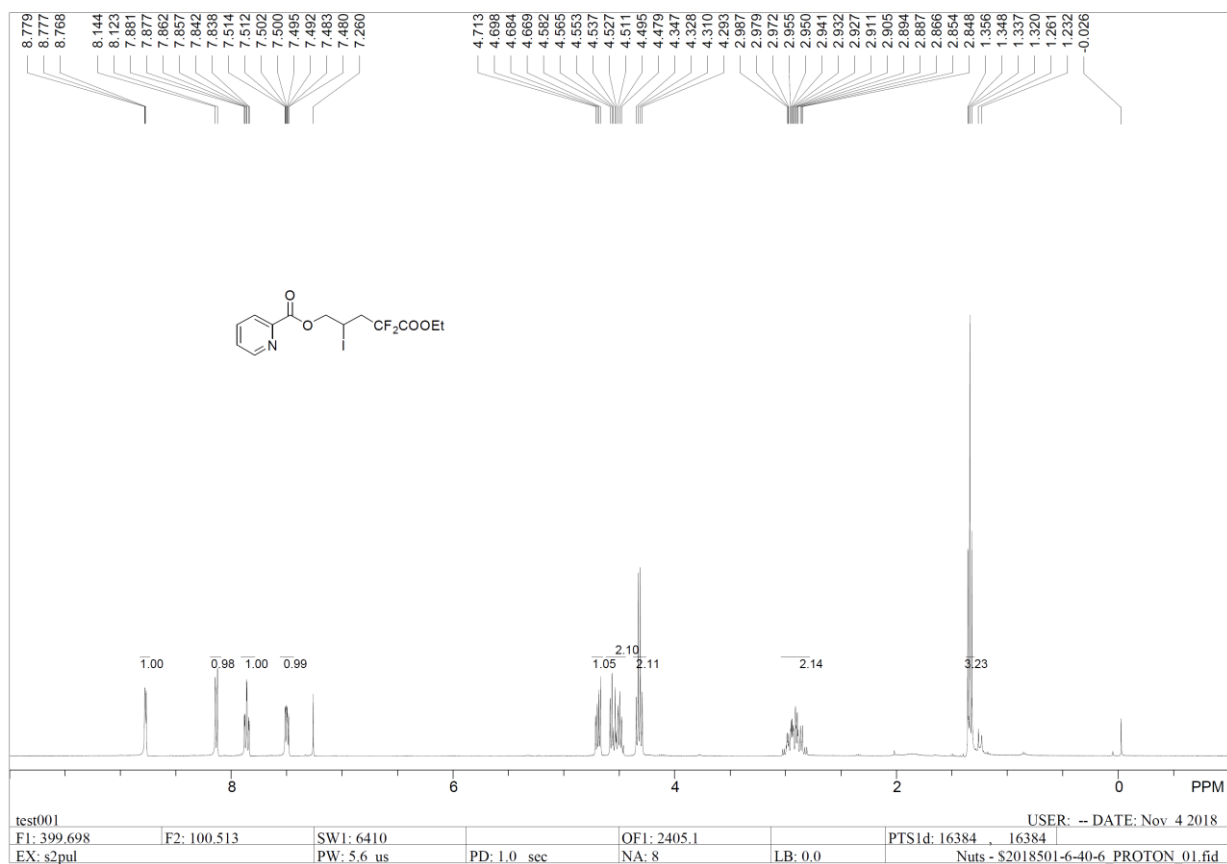
63.304
 62.280

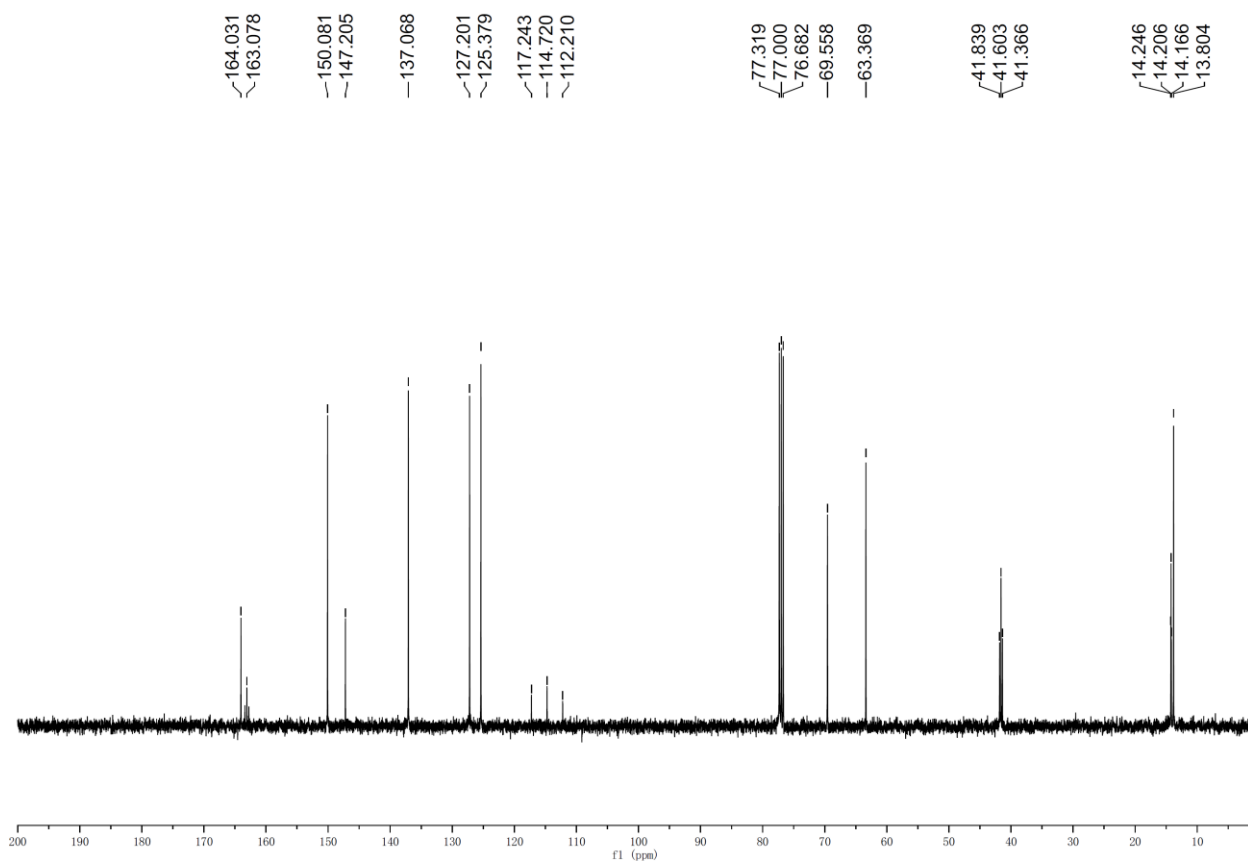
45.641
 45.410
 45.180
 42.390

19.010
 18.970
 18.929
 13.830

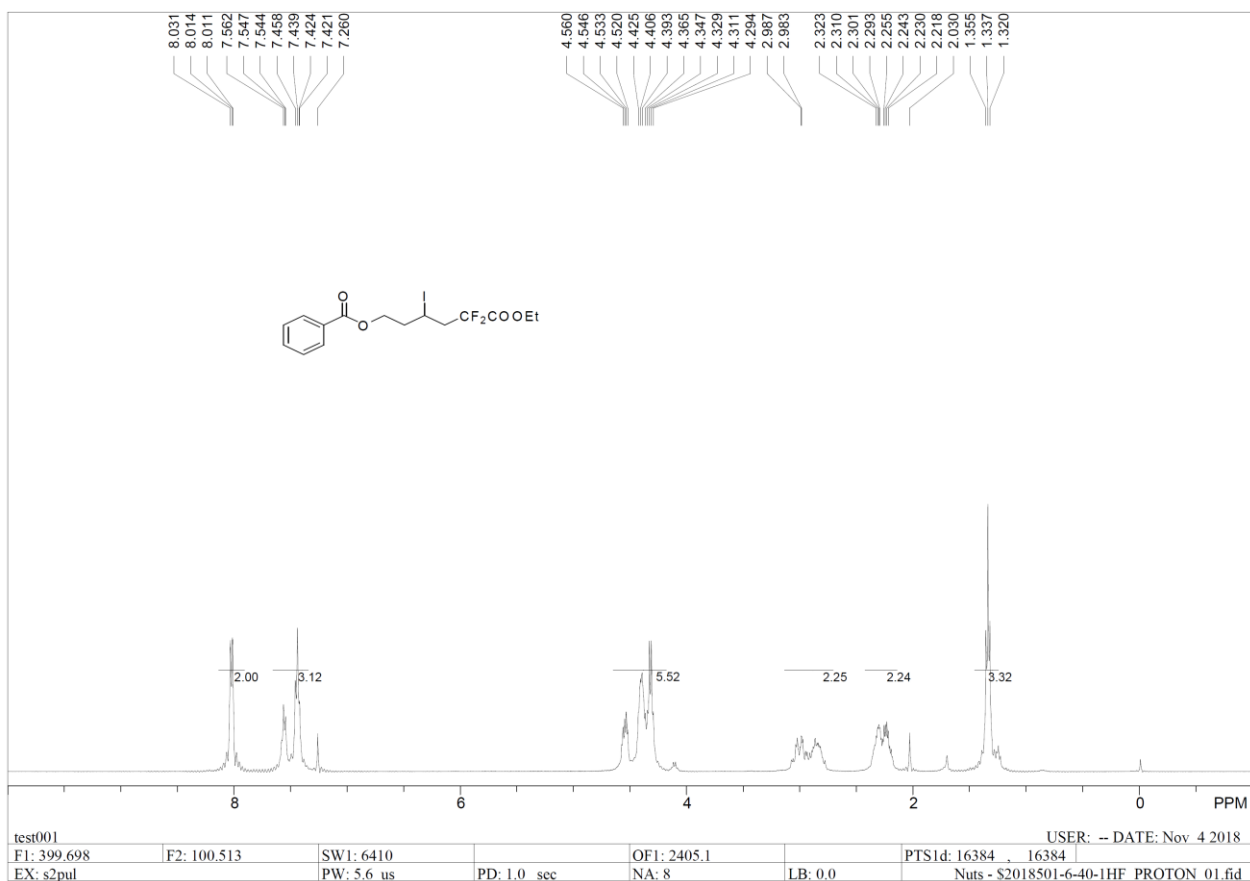


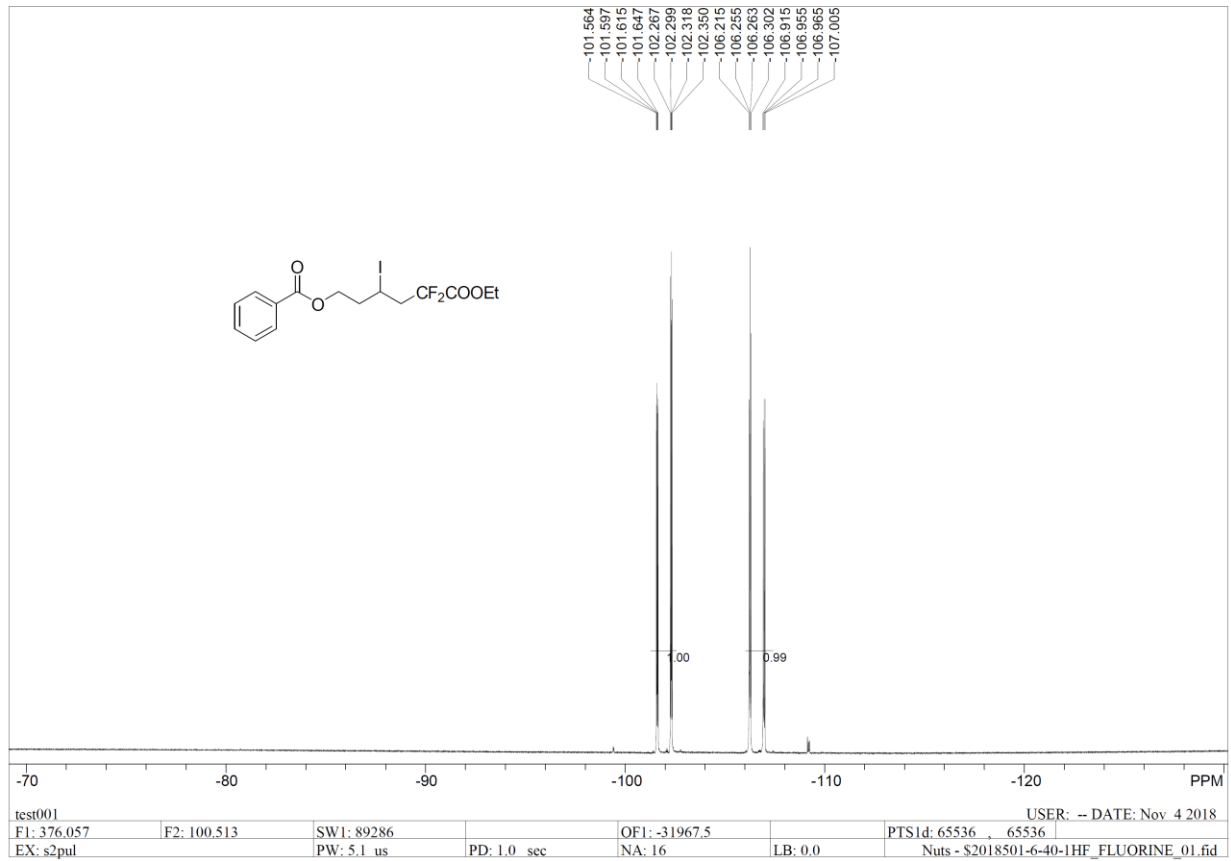
5-Ethoxy-4,4-difluoro-2-iodo-5-oxopentyl picolinate (3g).



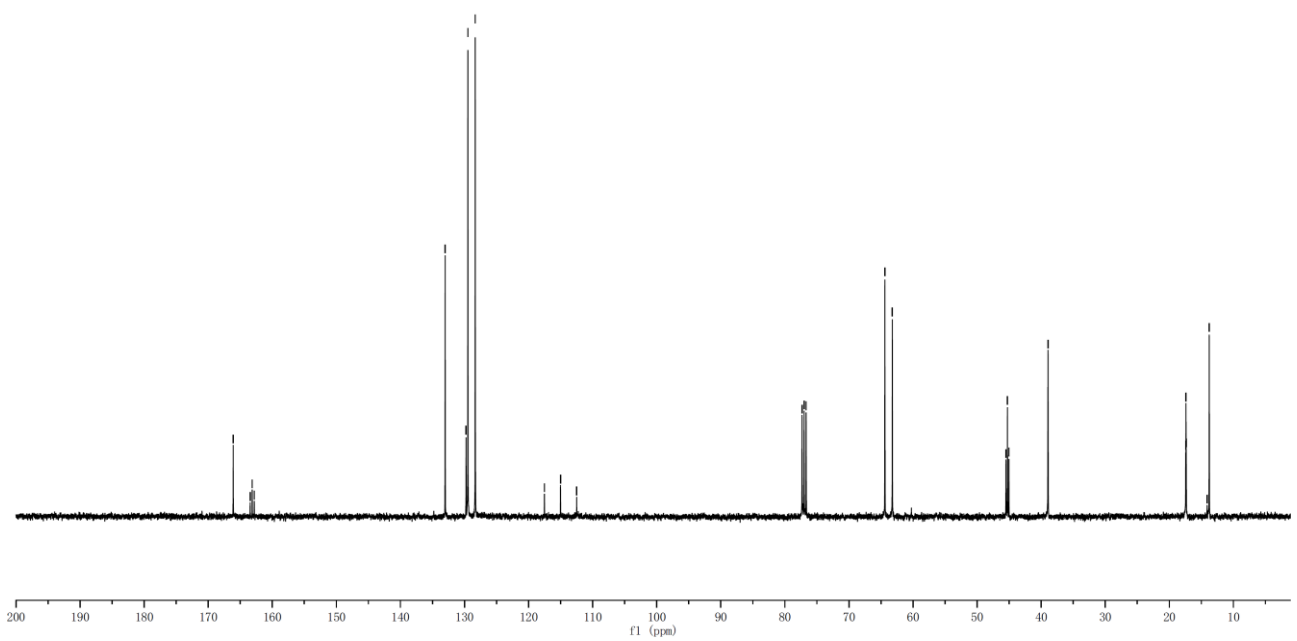


6-Ethoxy-5,5-difluoro-3-iodo-6-oxohexyl benzoate (3h).

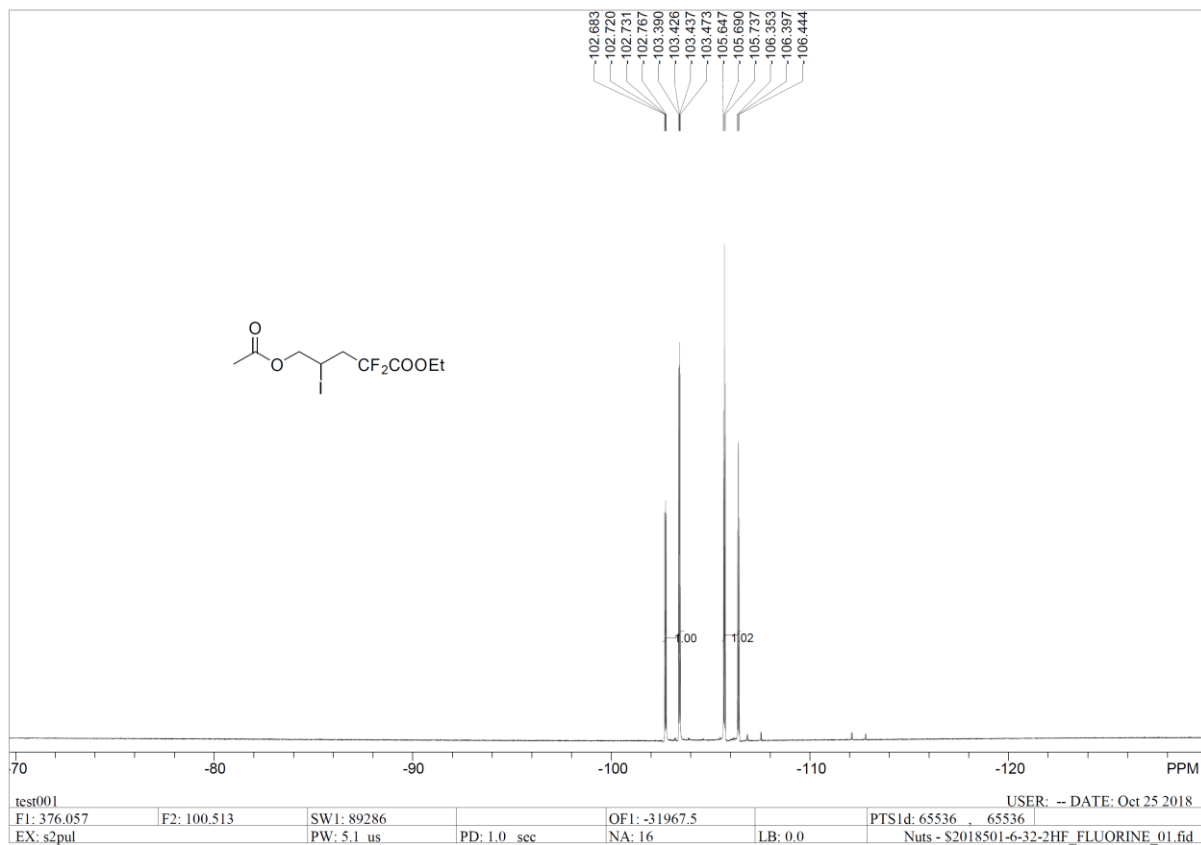
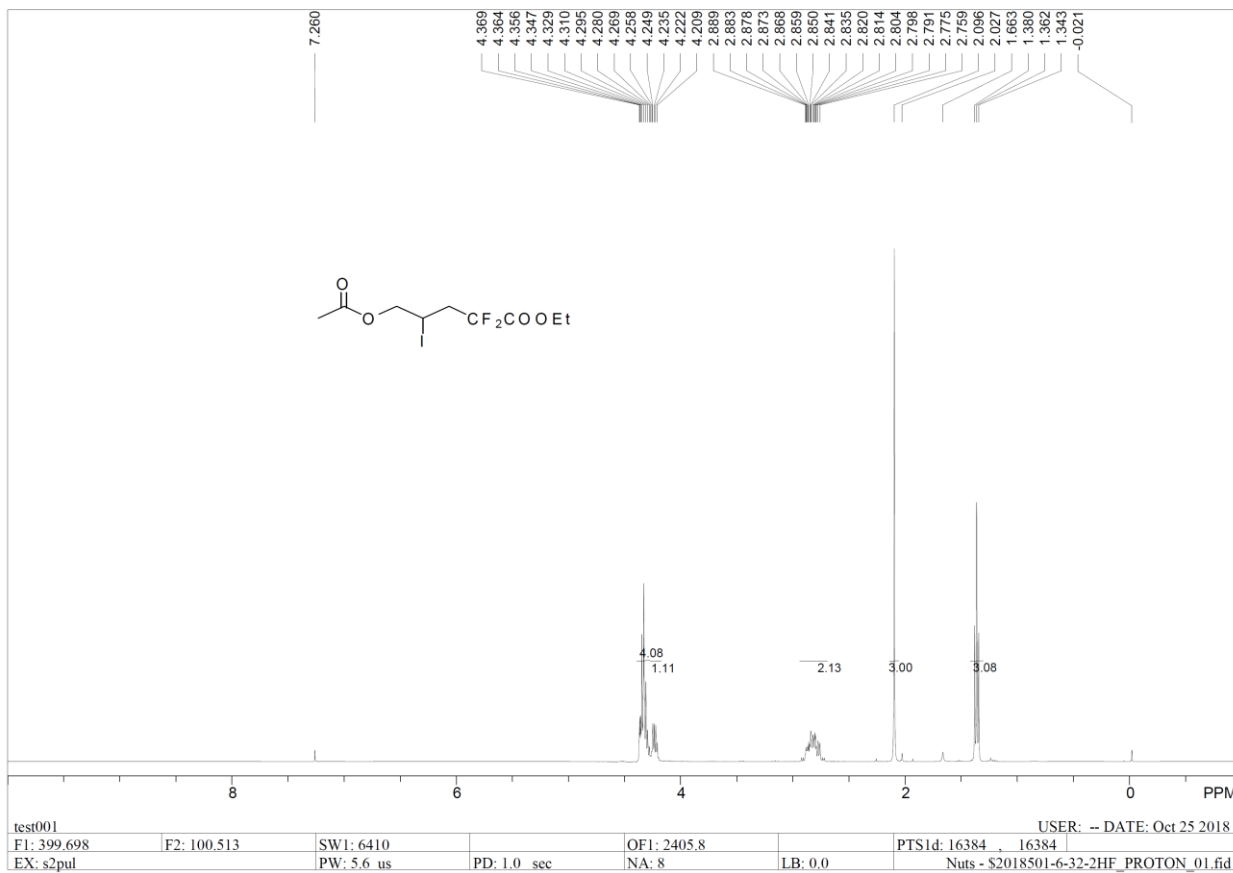


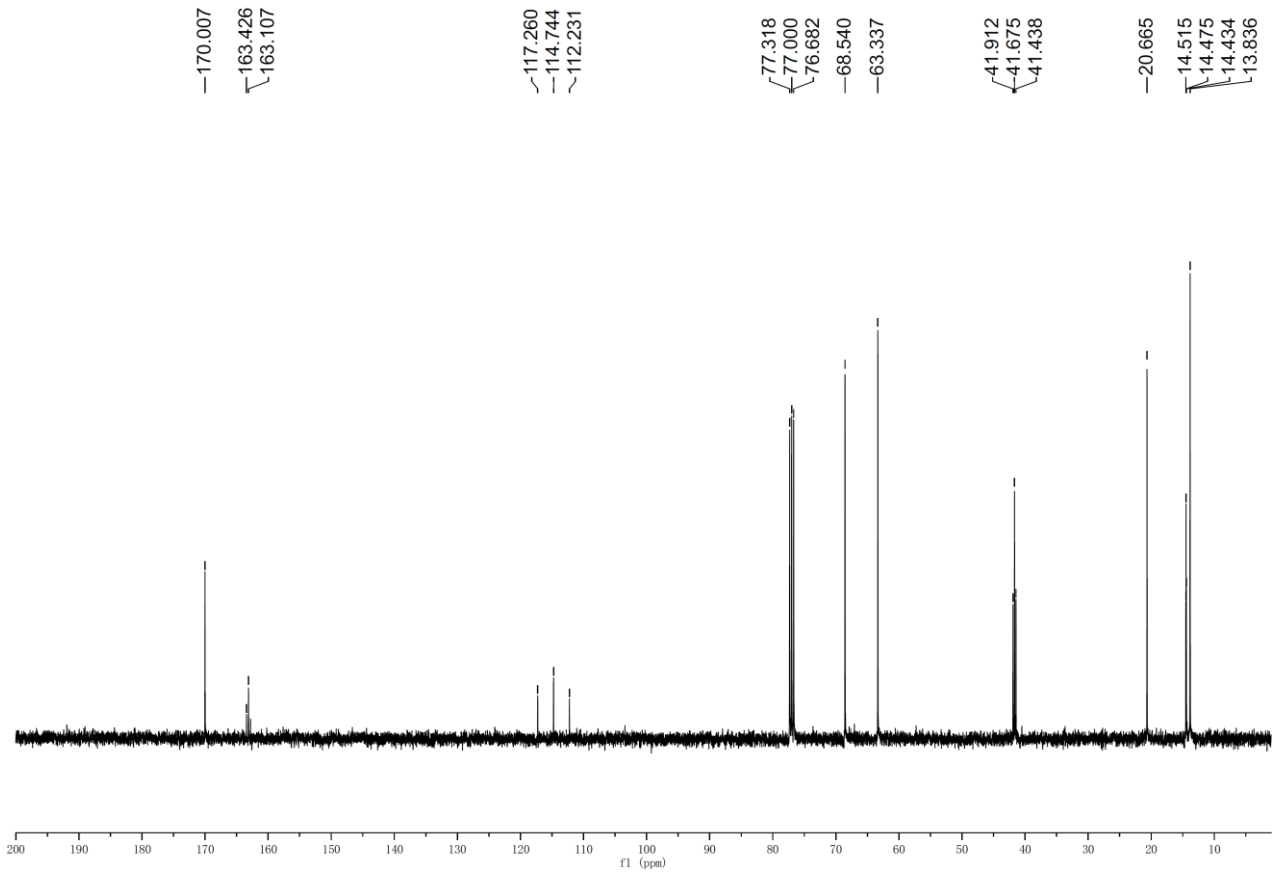


Chemical shifts (PPM): 166.098, 163.450, 163.131, 162.809, 133.016, 129.755, 129.474, 128.323, 117.527, 115.010, 112.492, 77.318, 77.000, 76.681, 64.392, 63.229, 45.495, 45.265, 45.035, 38.927, 17.439, 17.400, 17.361, 14.099, 13.772

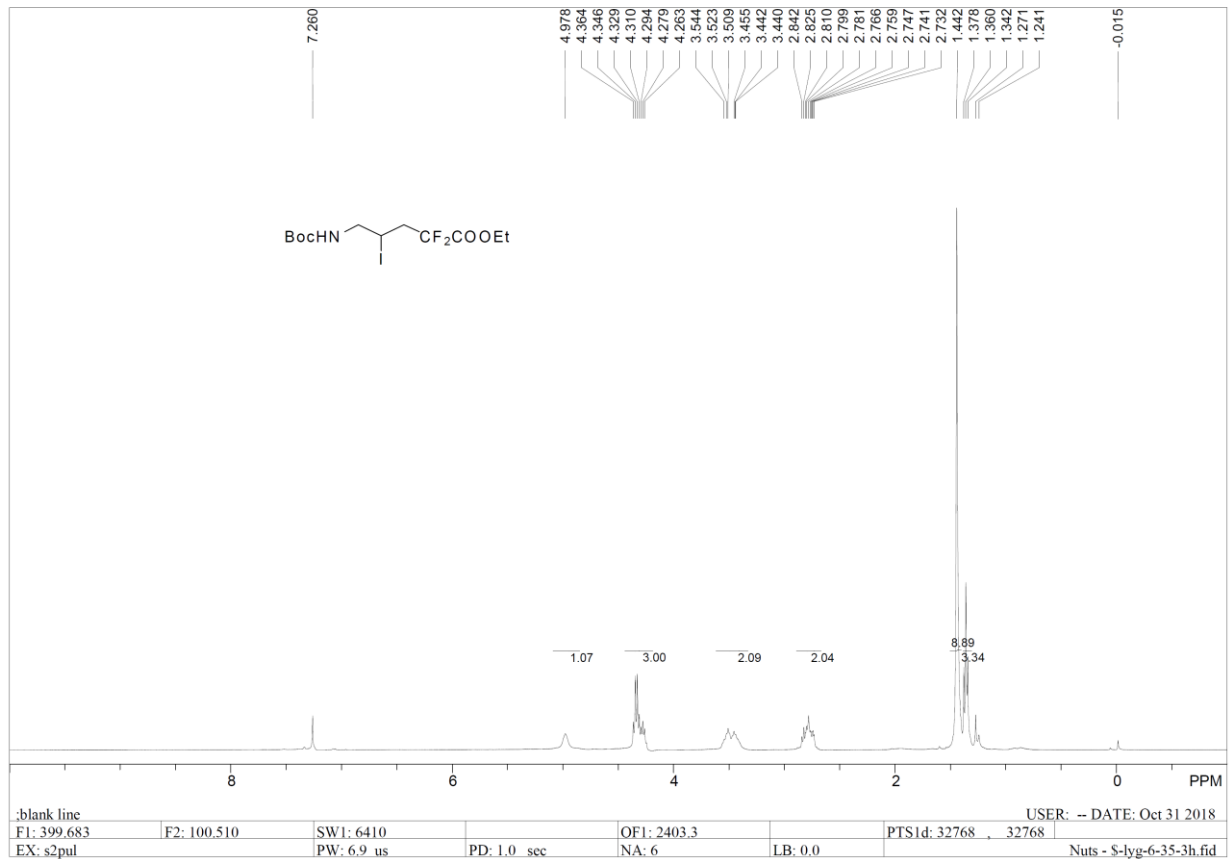


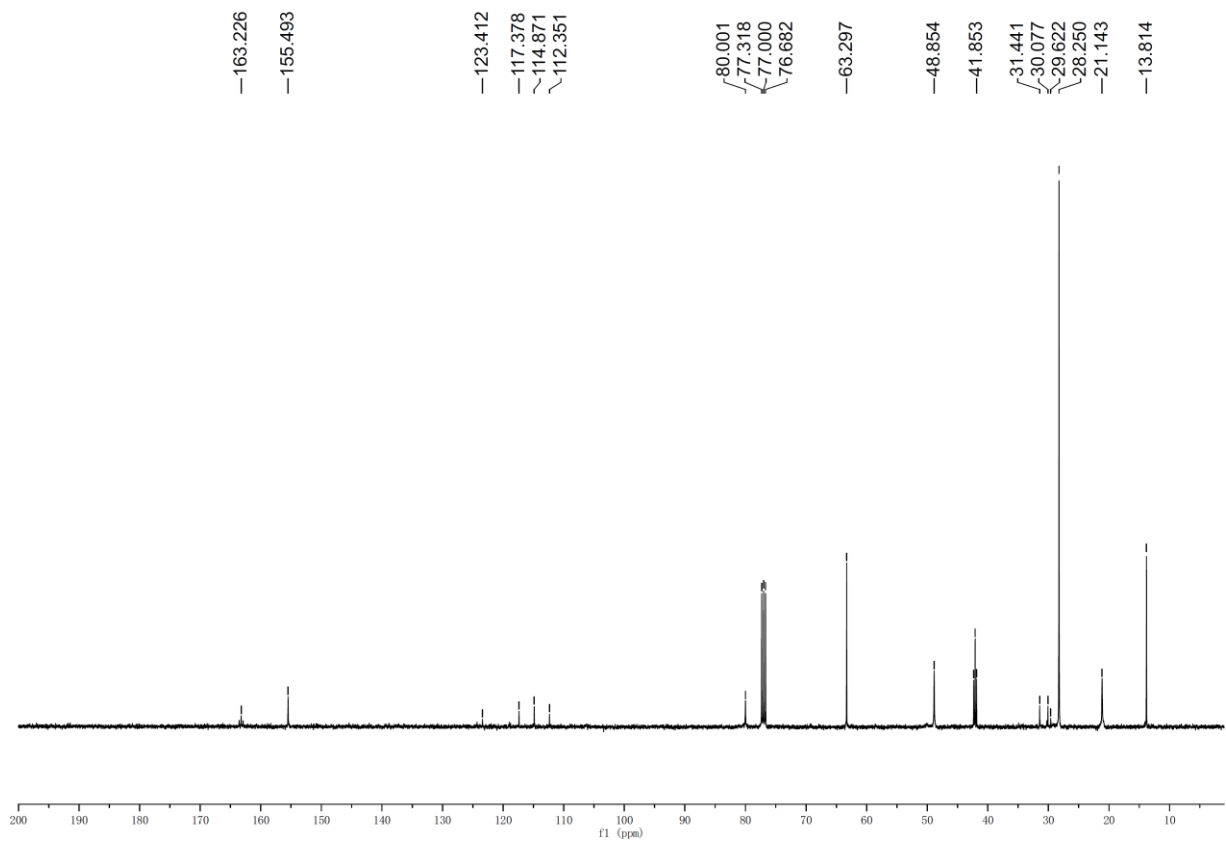
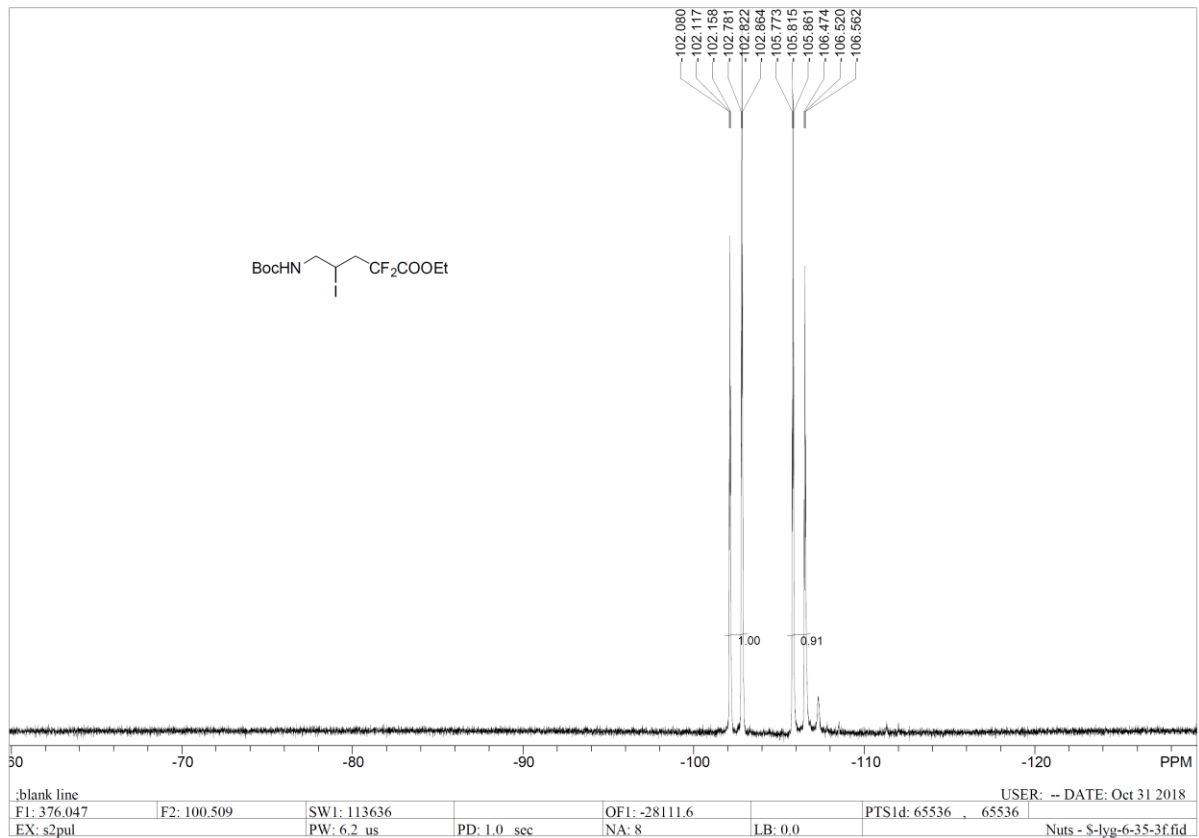
Ethyl 5-acetoxy-2,2-difluoro-4-iodopentanoate (3i).



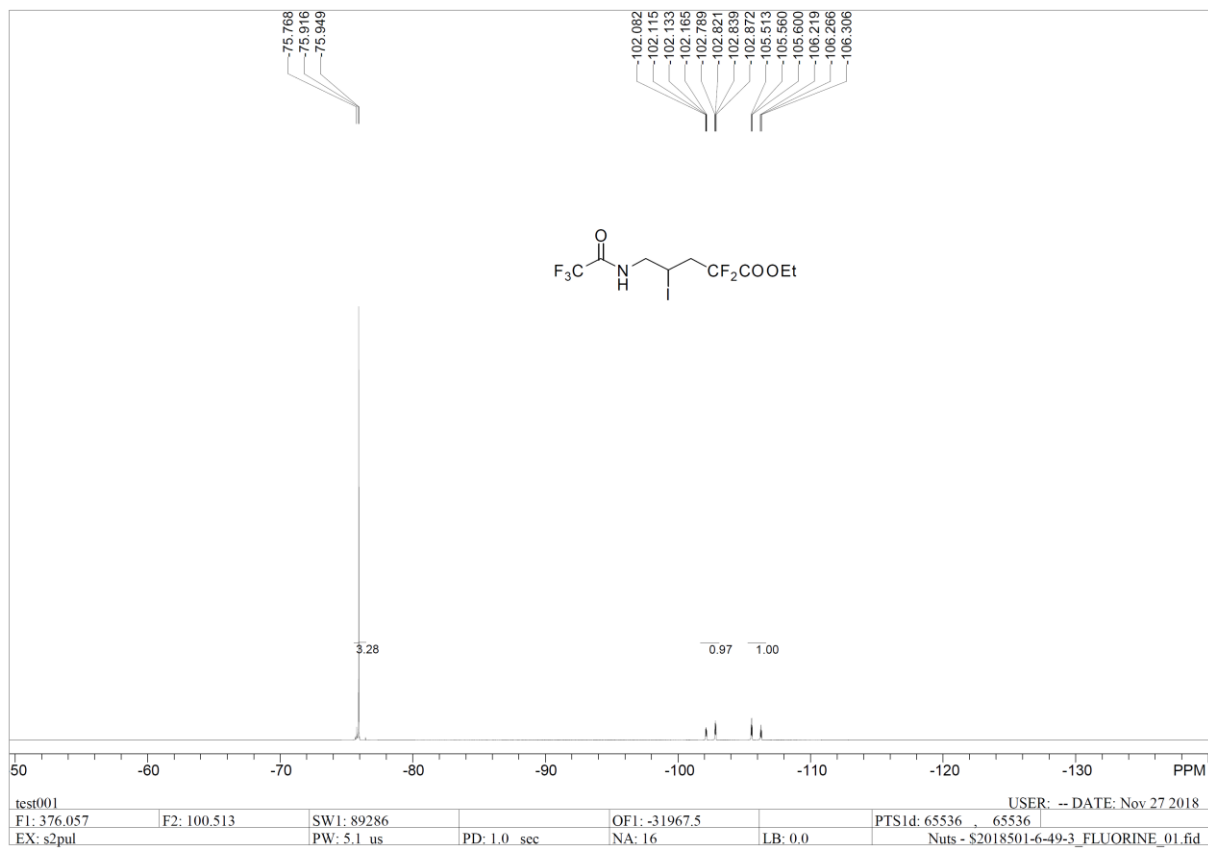
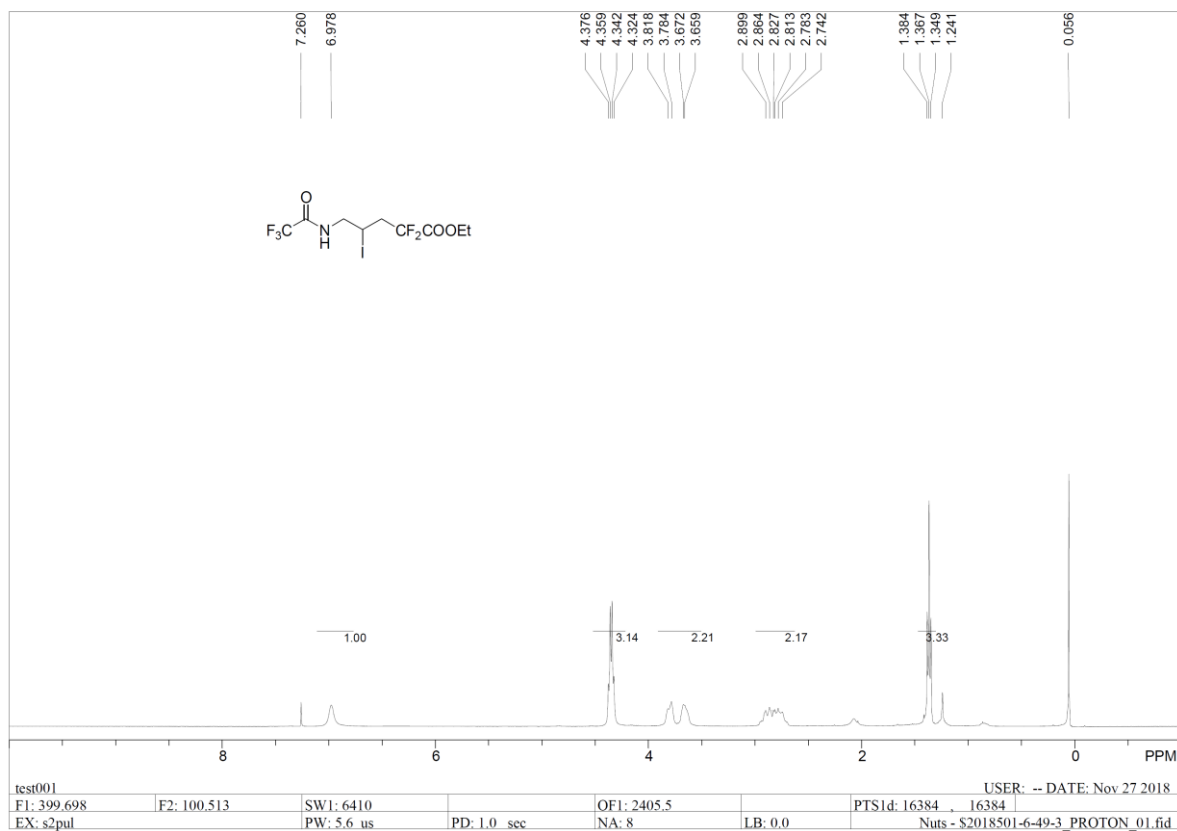


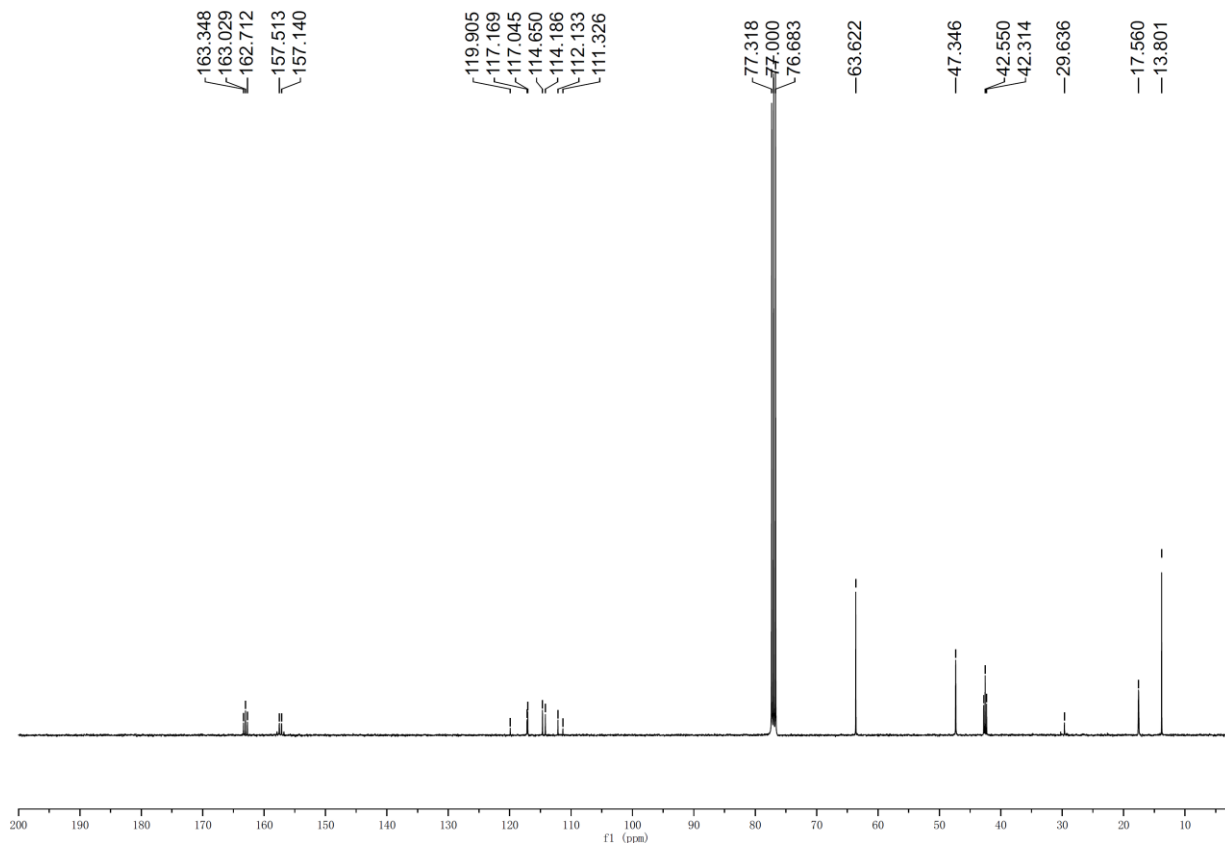
Ethyl 5-((tert-butoxycarbonyl)amino)-2,2-difluoro-4-iodopentanoate (3j).



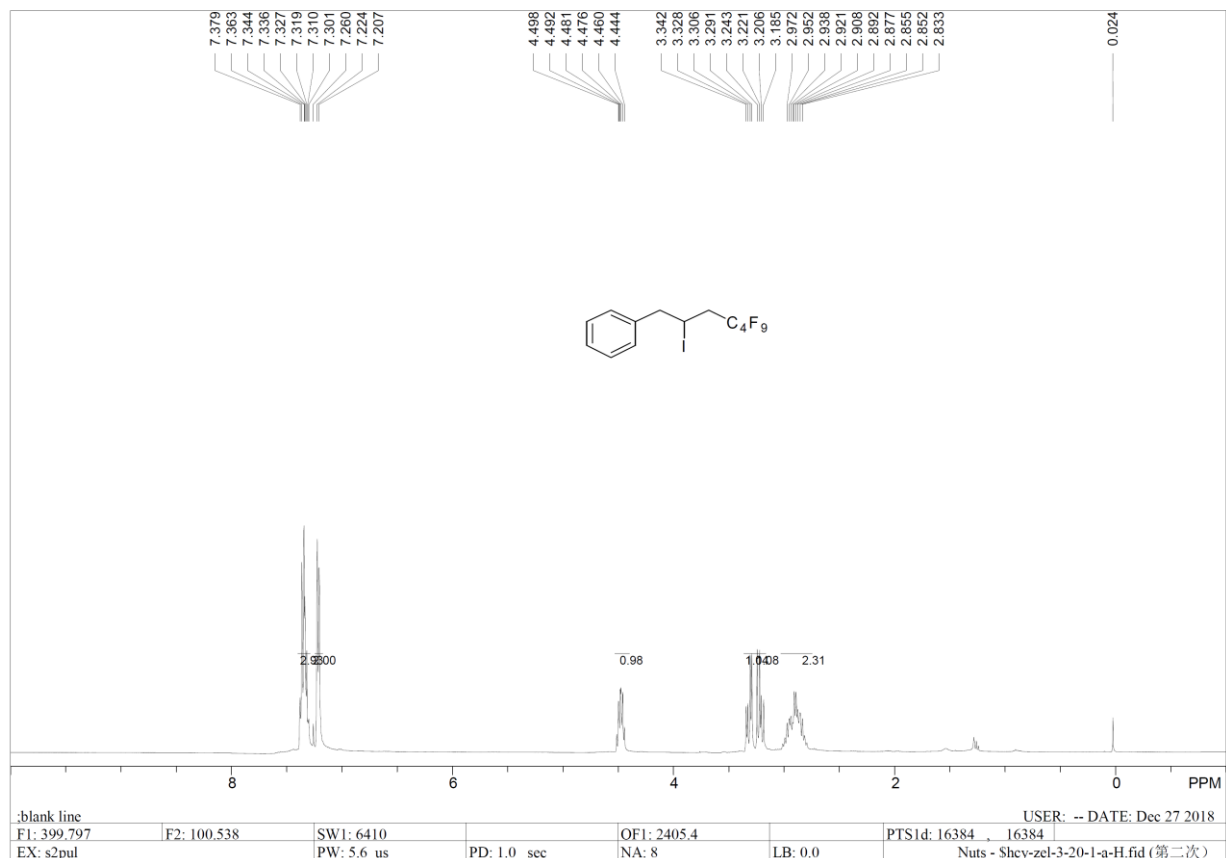


Ethyl 2,2-difluoro-4-iodo-5-(2,2,2-trifluoroacetamido)pentanoate (3k).



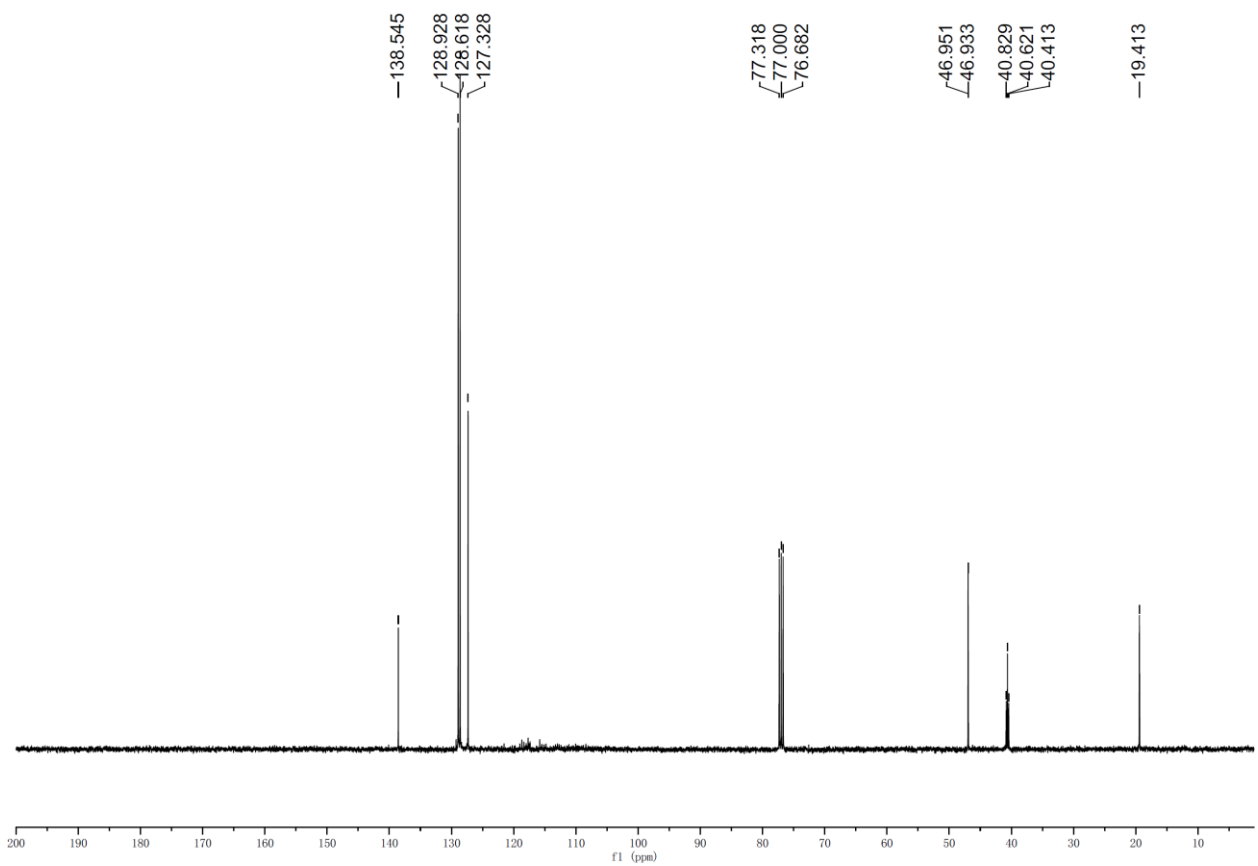


(4,4,5,5,6,6,7,7,7-Nonafluoro-2-iodoheptyl)benzene (3l).

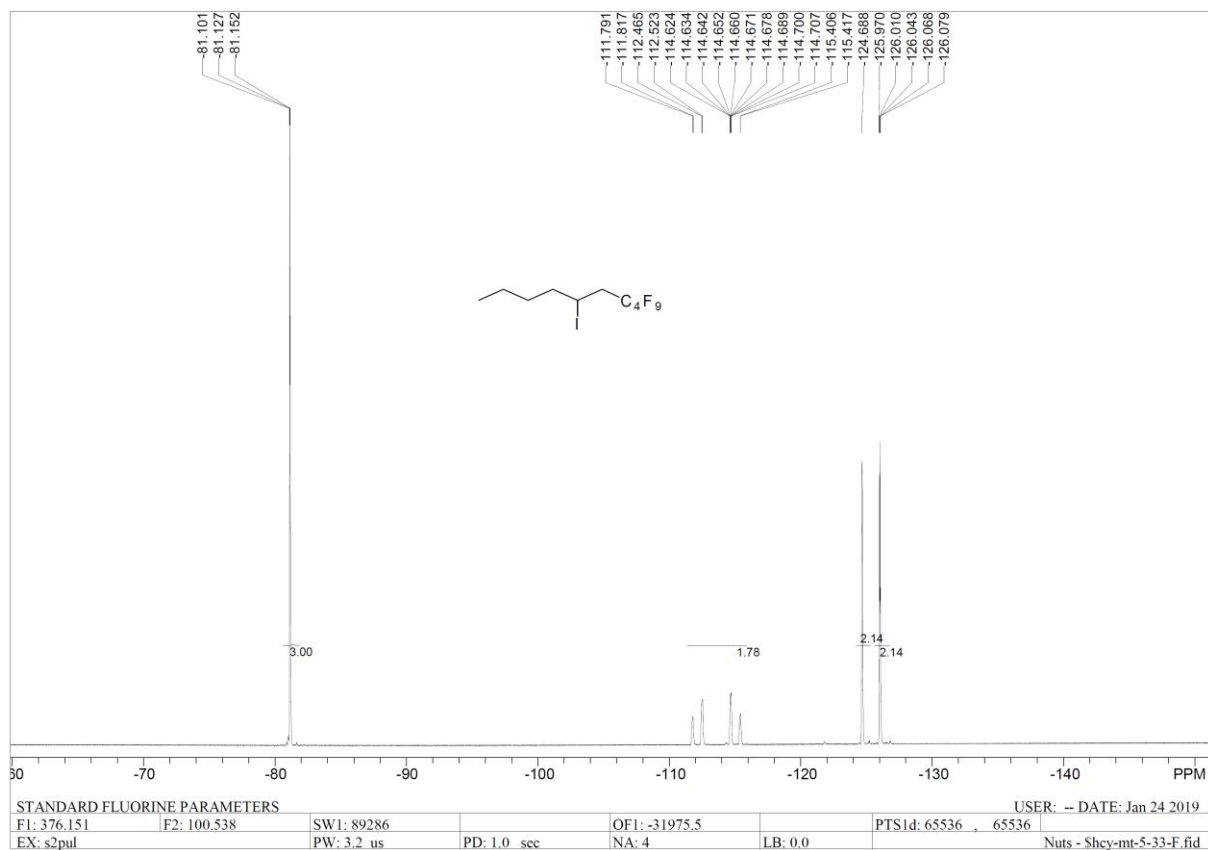
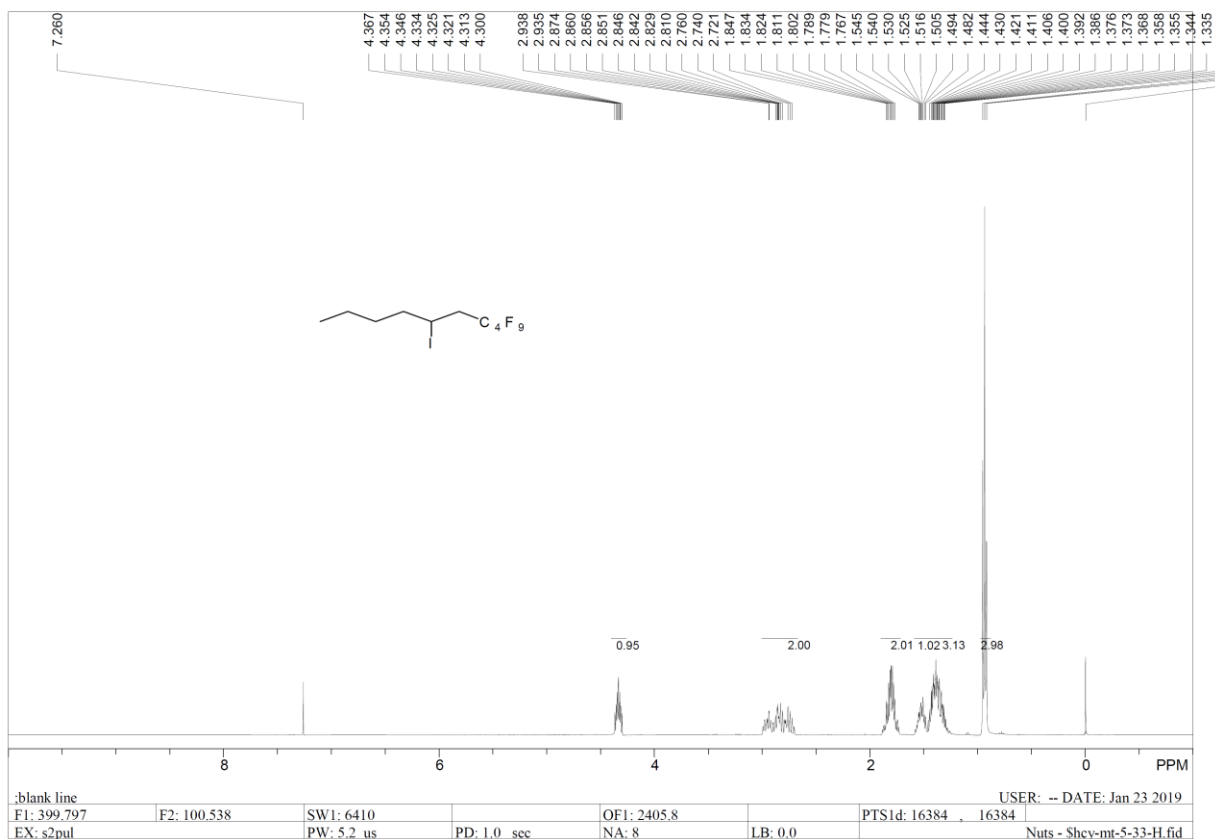


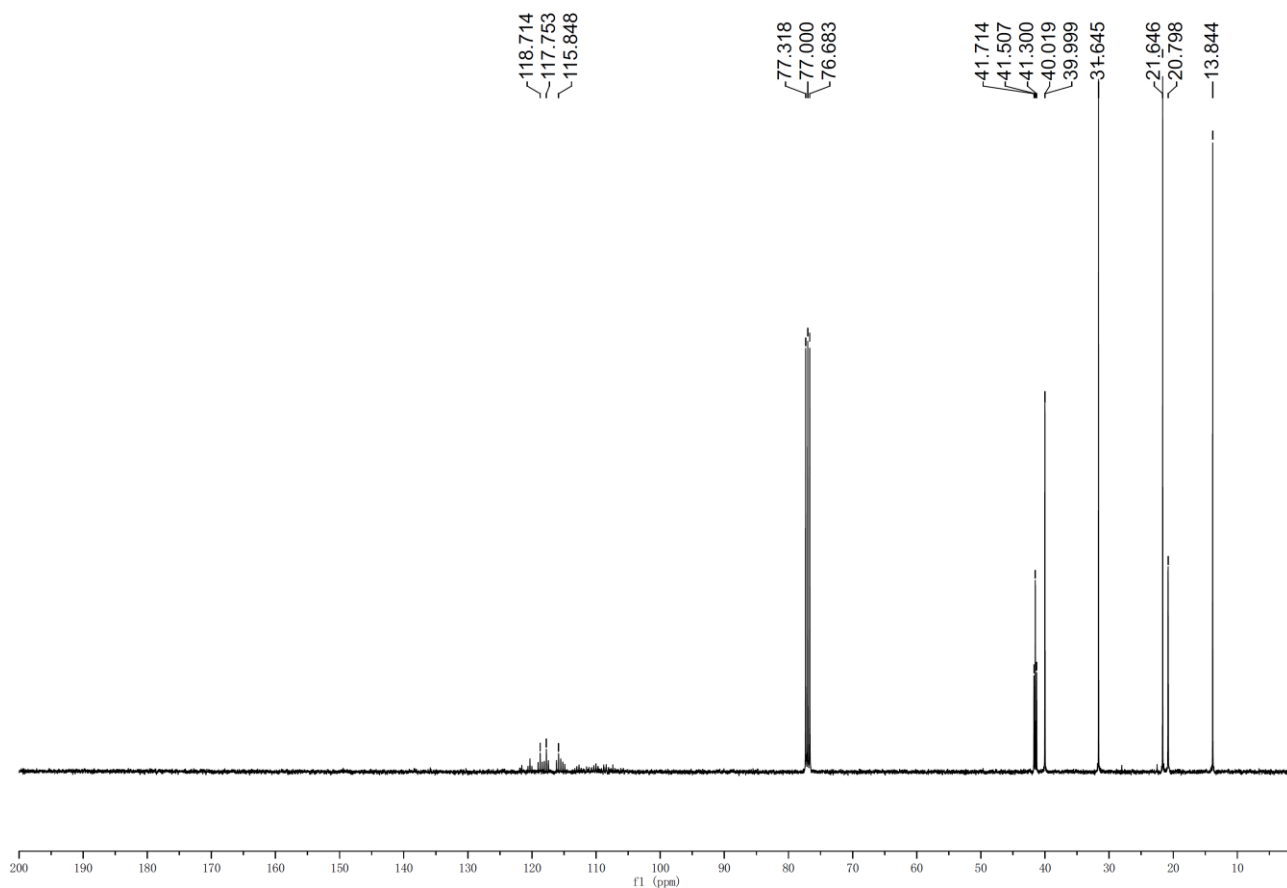


STANDARD FLUORINE PARAMETERS
 F1: 376.151 F2: 100.538 SW1: 89286 OF1: -31975.5 PTS1d: 65536 , 65536 USER: -- DATE: Dec 28 2018
 EX: s2pul PW: 3.2 us PD: 1.0 sec NA: 4 LB: 0.0 Nuts - Shey-zel-3-20-1-a-F.fid

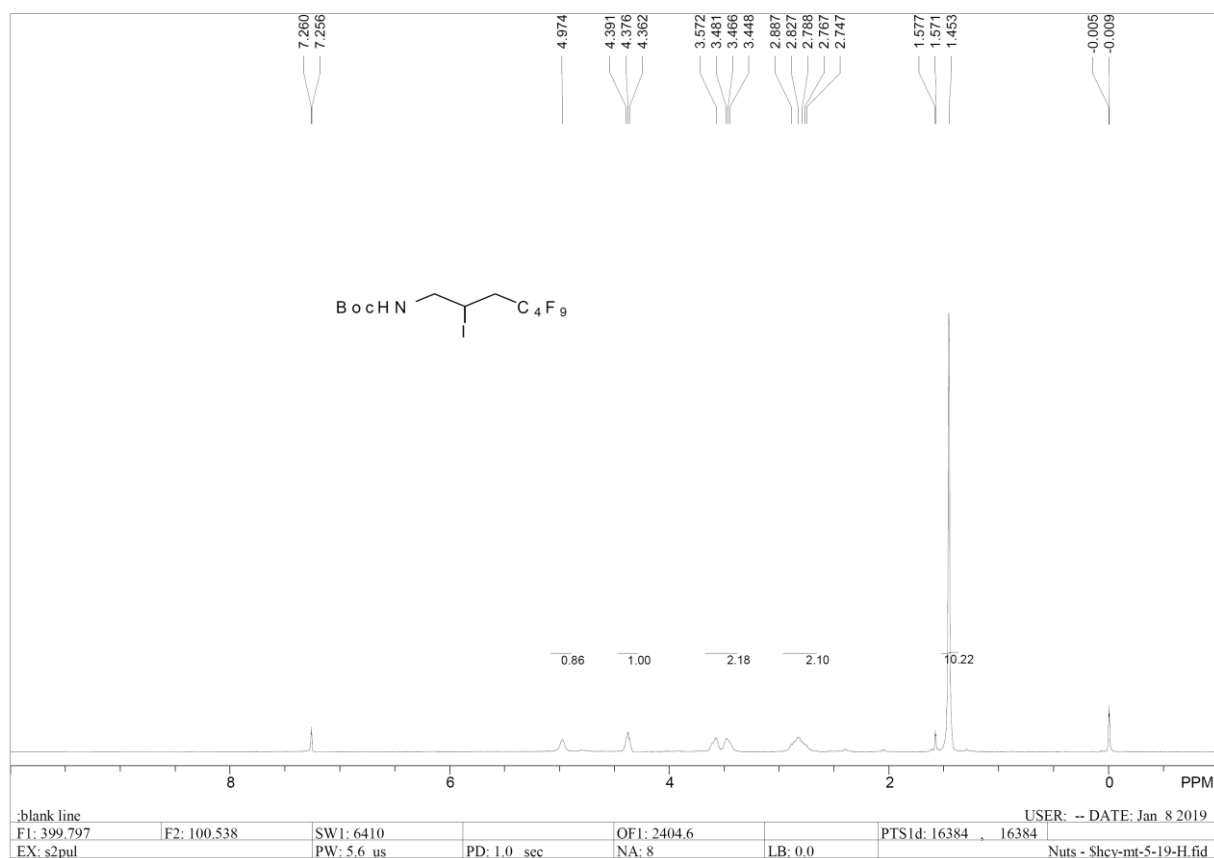


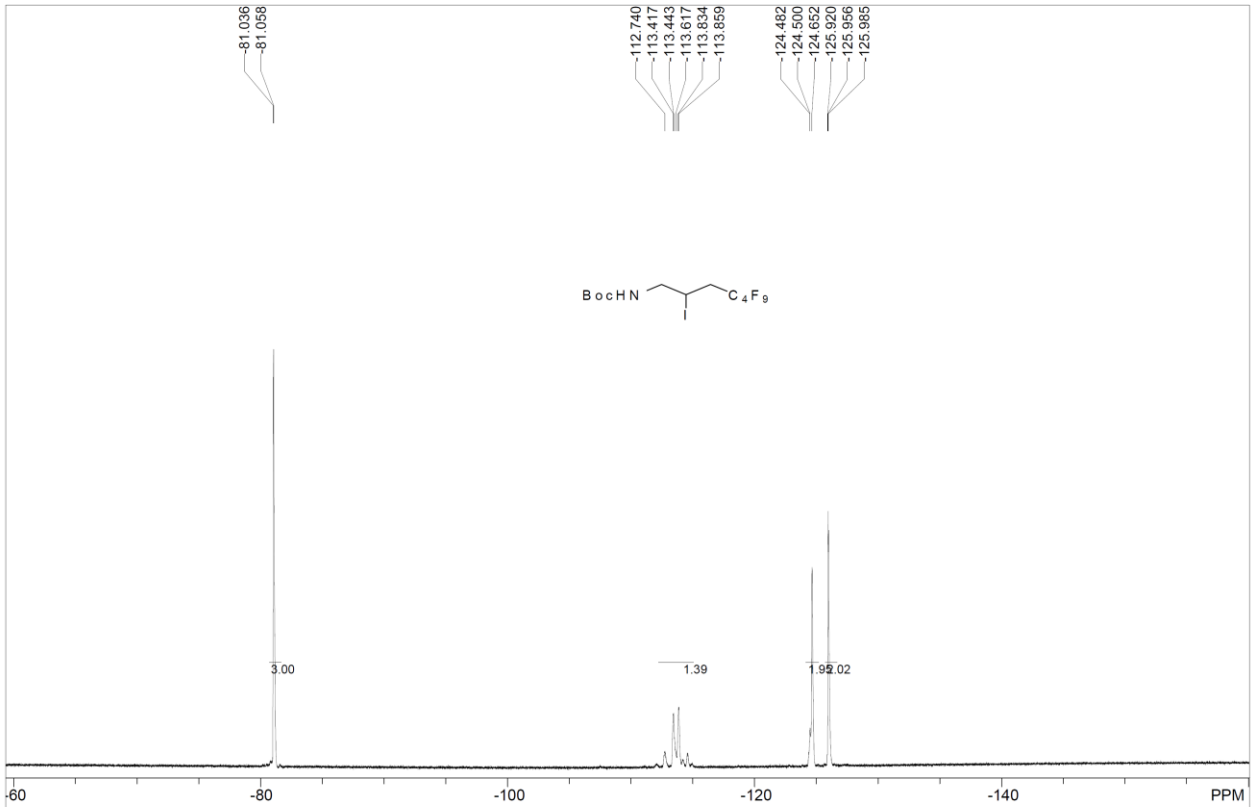
1,1,1,2,2,3,3,4,4-Nonafluoro-6-iododecane (3m).





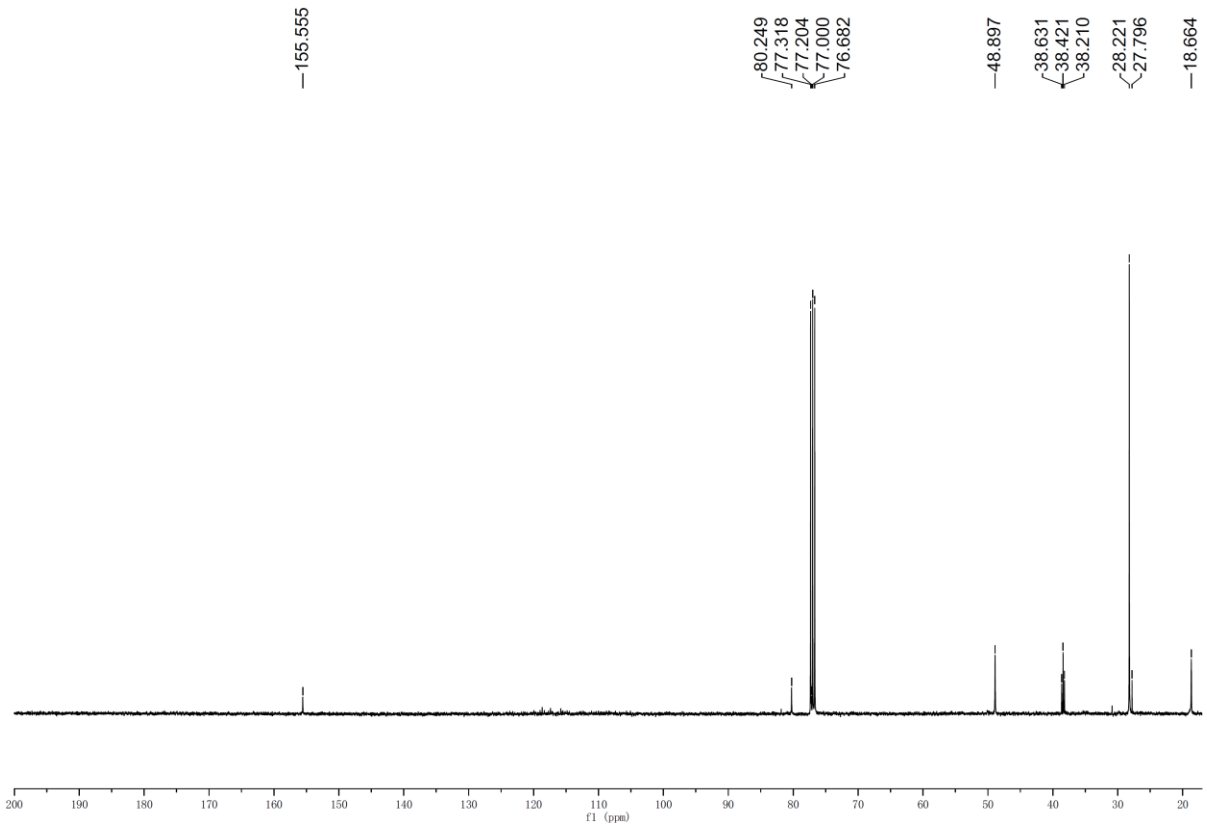
Tert-butyl (4,4,5,5,6,6,7,7,7-nonafluoro-2-iodoheptyl)carbamate (3n).



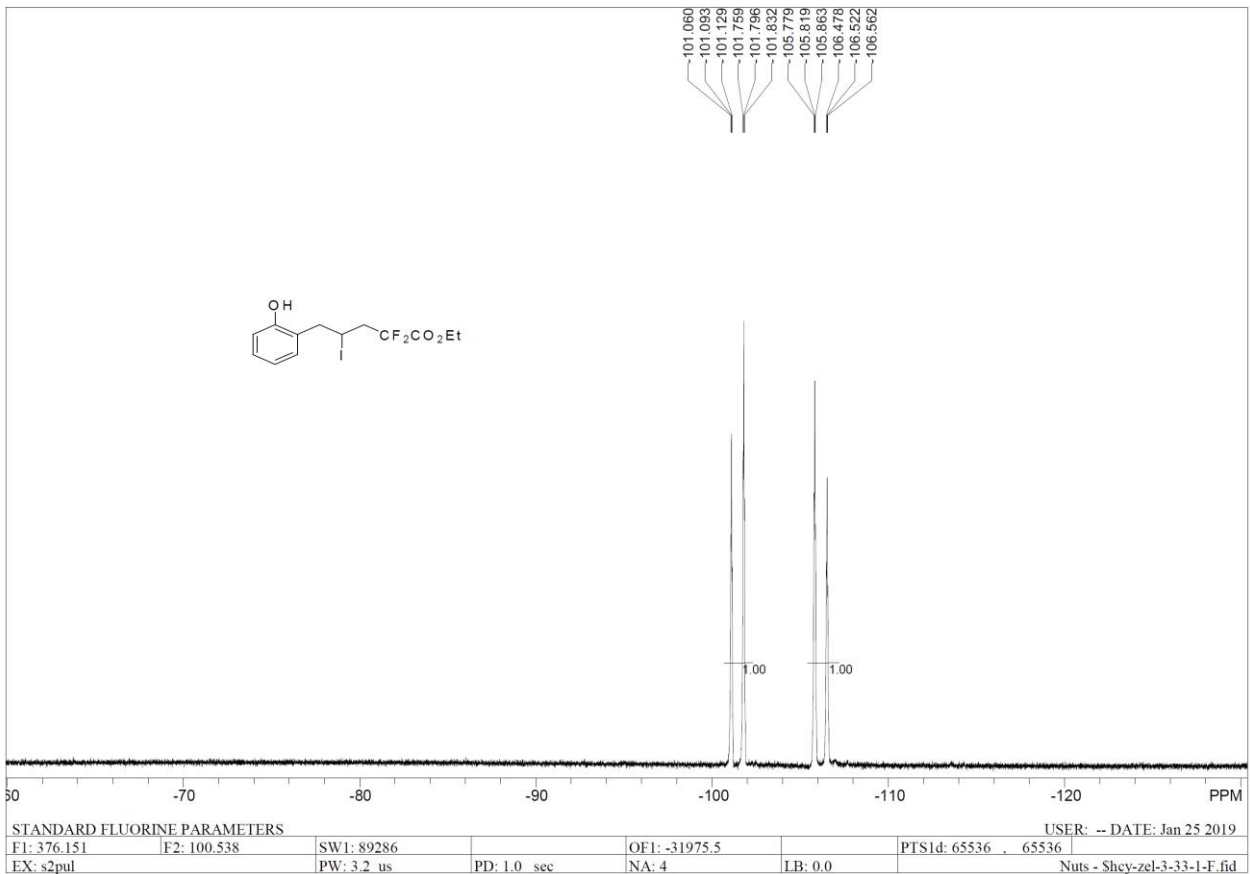
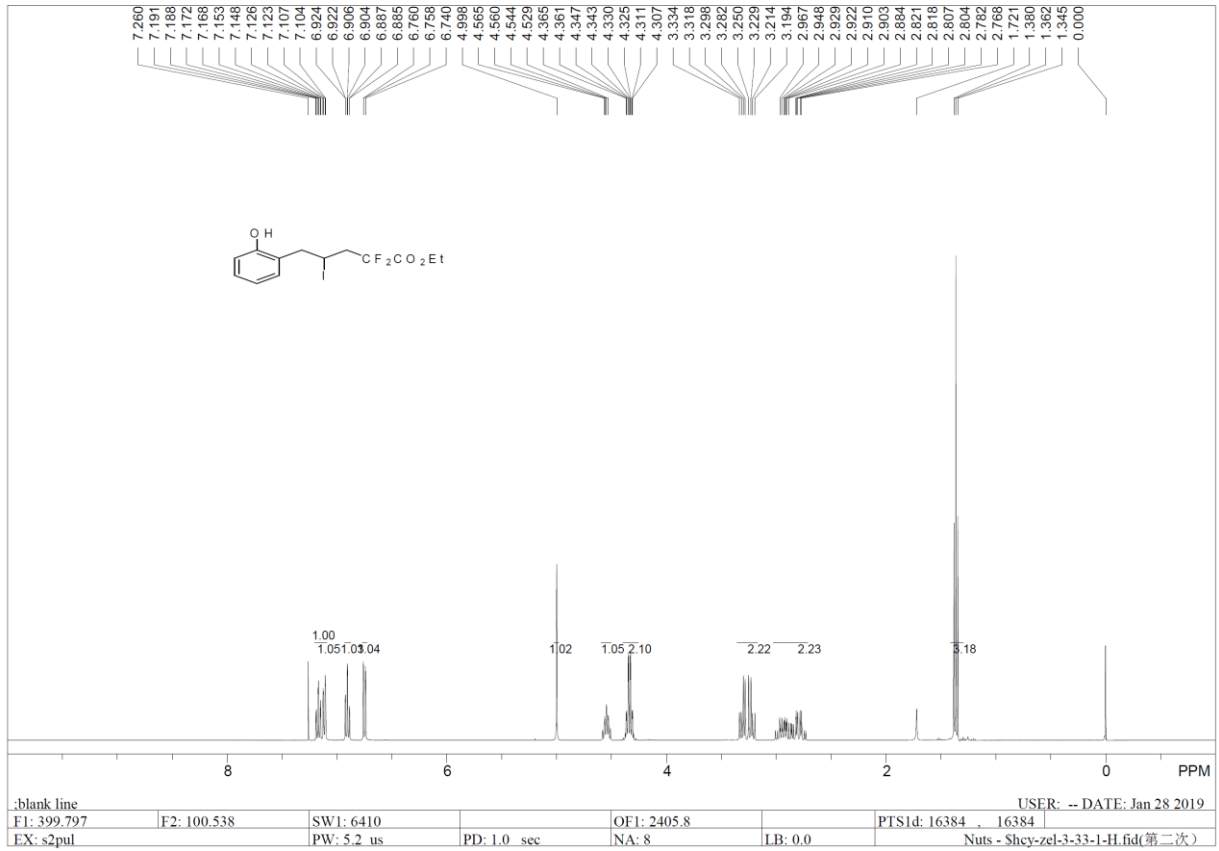


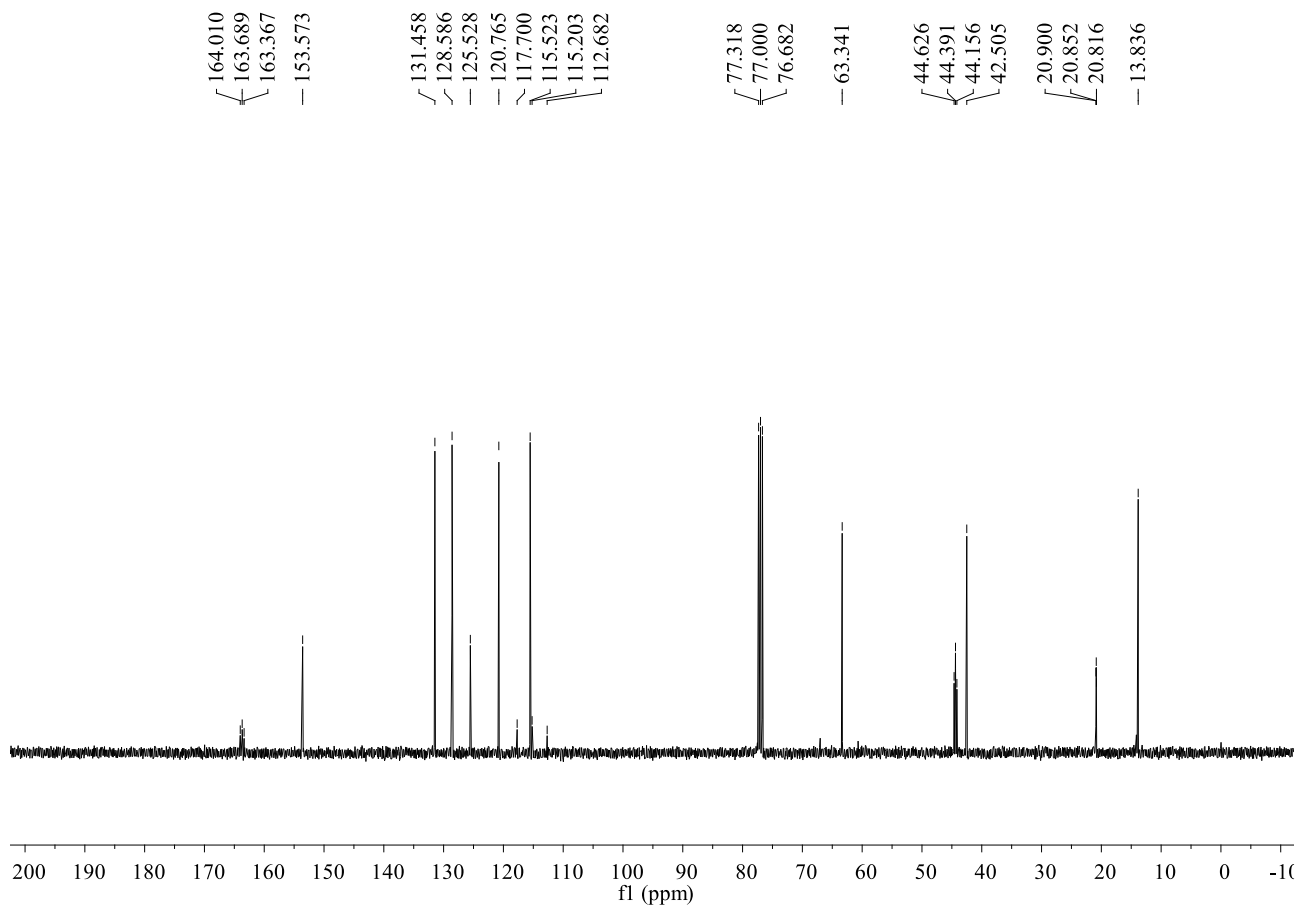
STANDARD FLUORINE PARAMETERS

F1: 376.151	F2: 100.538	SW1: 89286	OFl: -31975.5	PTS1d: 65536	65536	USER: -- DATE: Jan 22 2019
EX: s2pul	PW: 3.2 us	PD: 1.0 sec	NA: 4	LB: 0.0		Nuts - Shcy-mt-5-19-F.fid

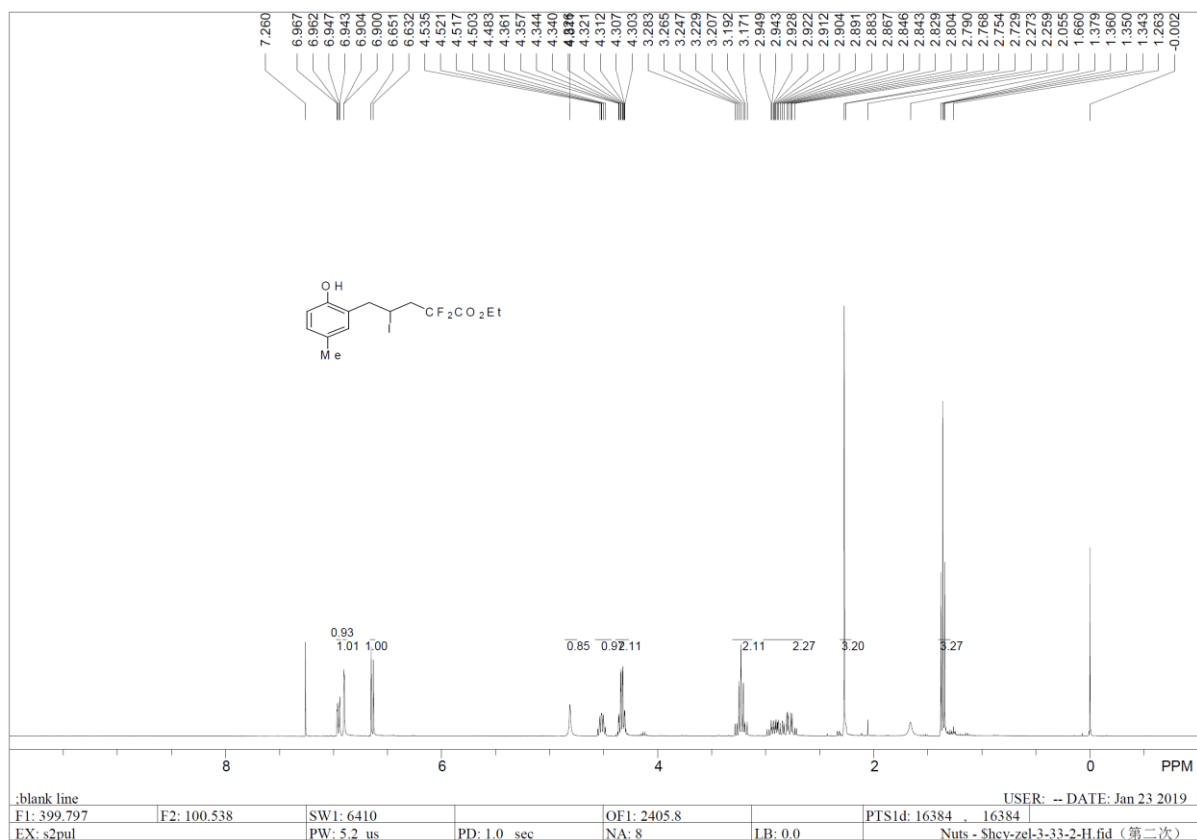


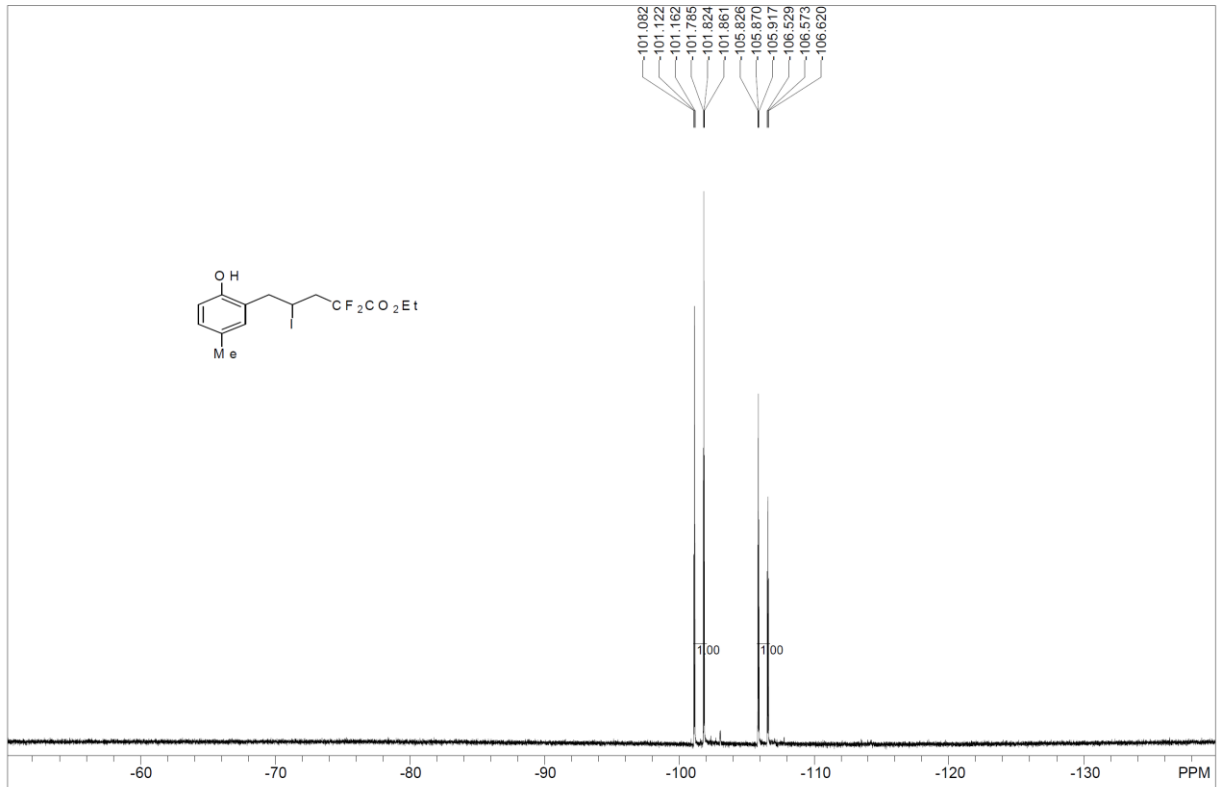
Ethyl 2,2-difluoro-5-(2-hydroxyphenyl)-4-iodopentanoate (3o).



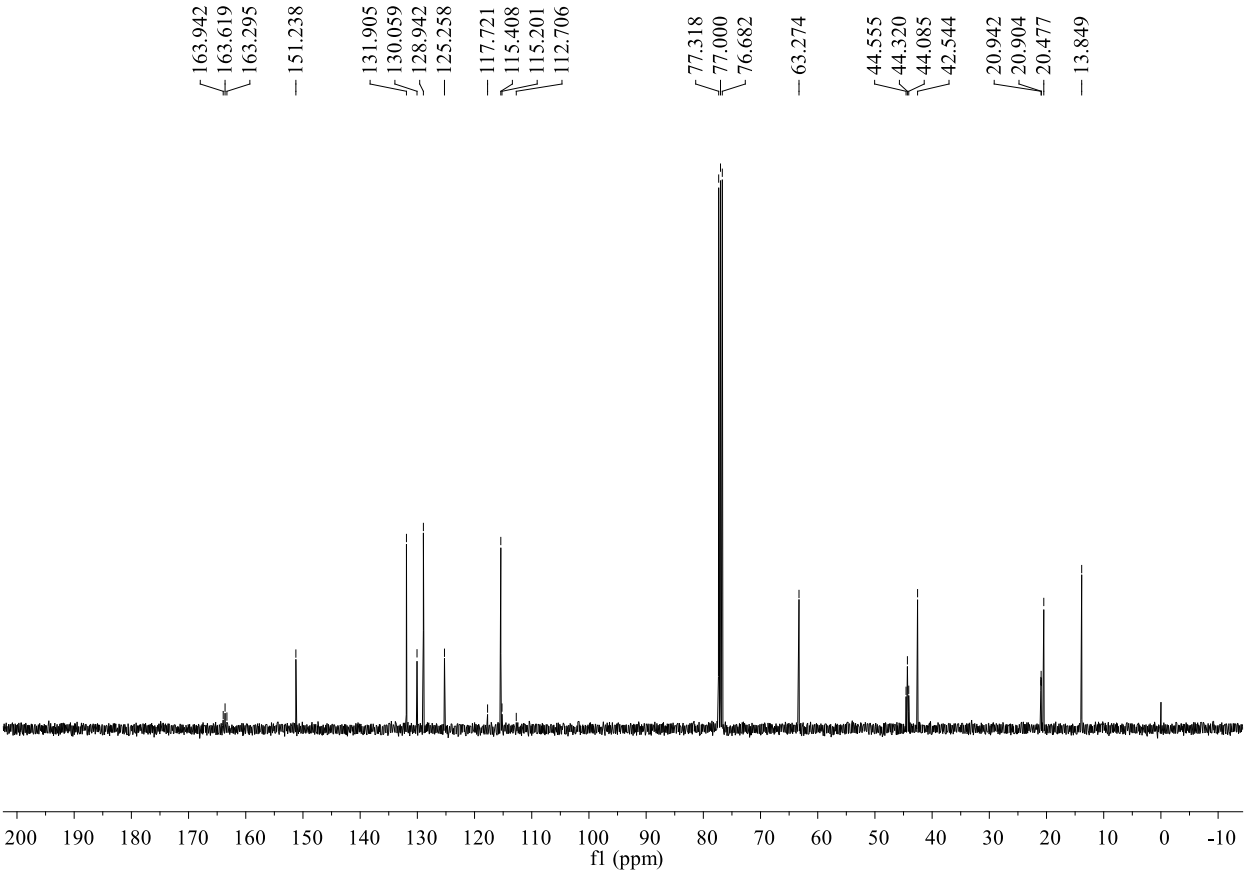


Ethyl 2,2-difluoro-5-(2-hydroxy-5-methylphenyl)-4-iodopentanoate (3p).

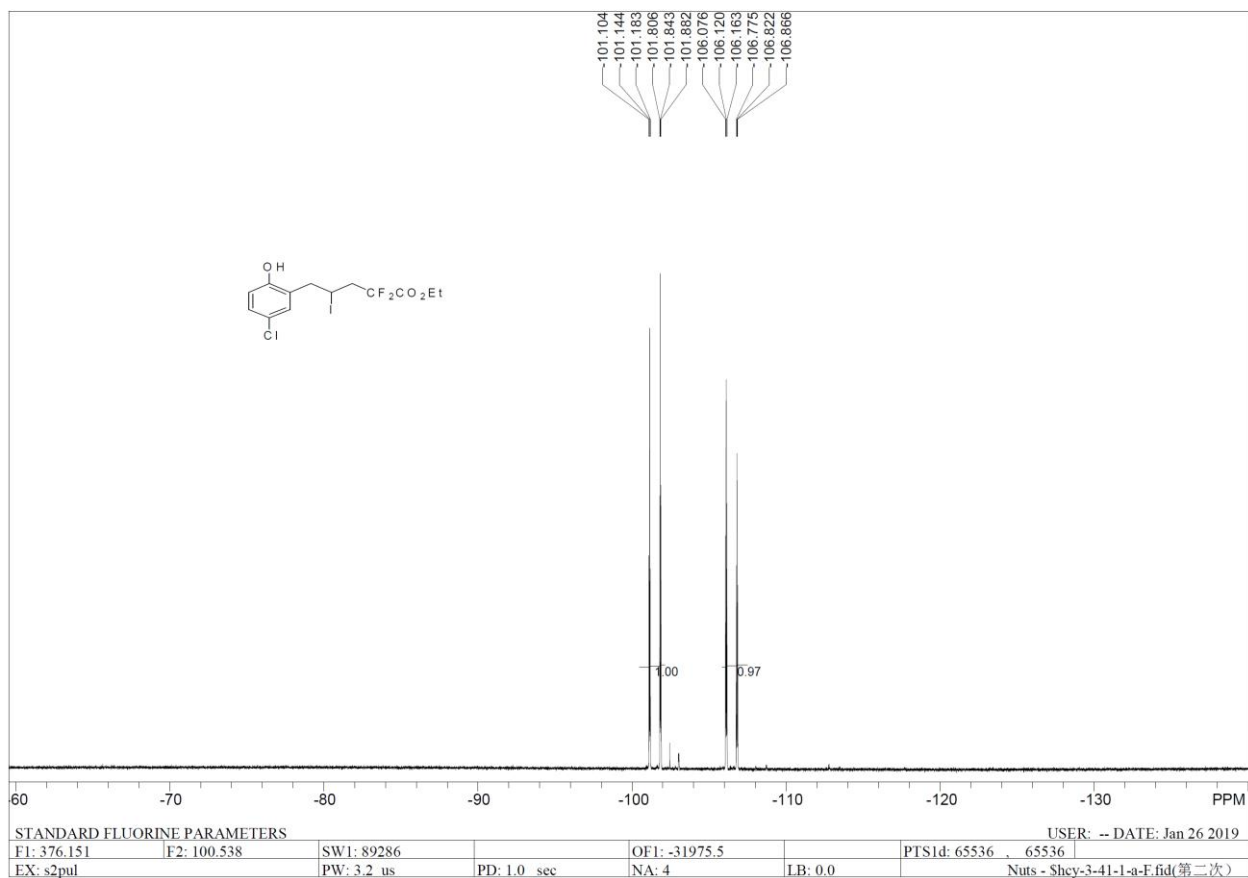
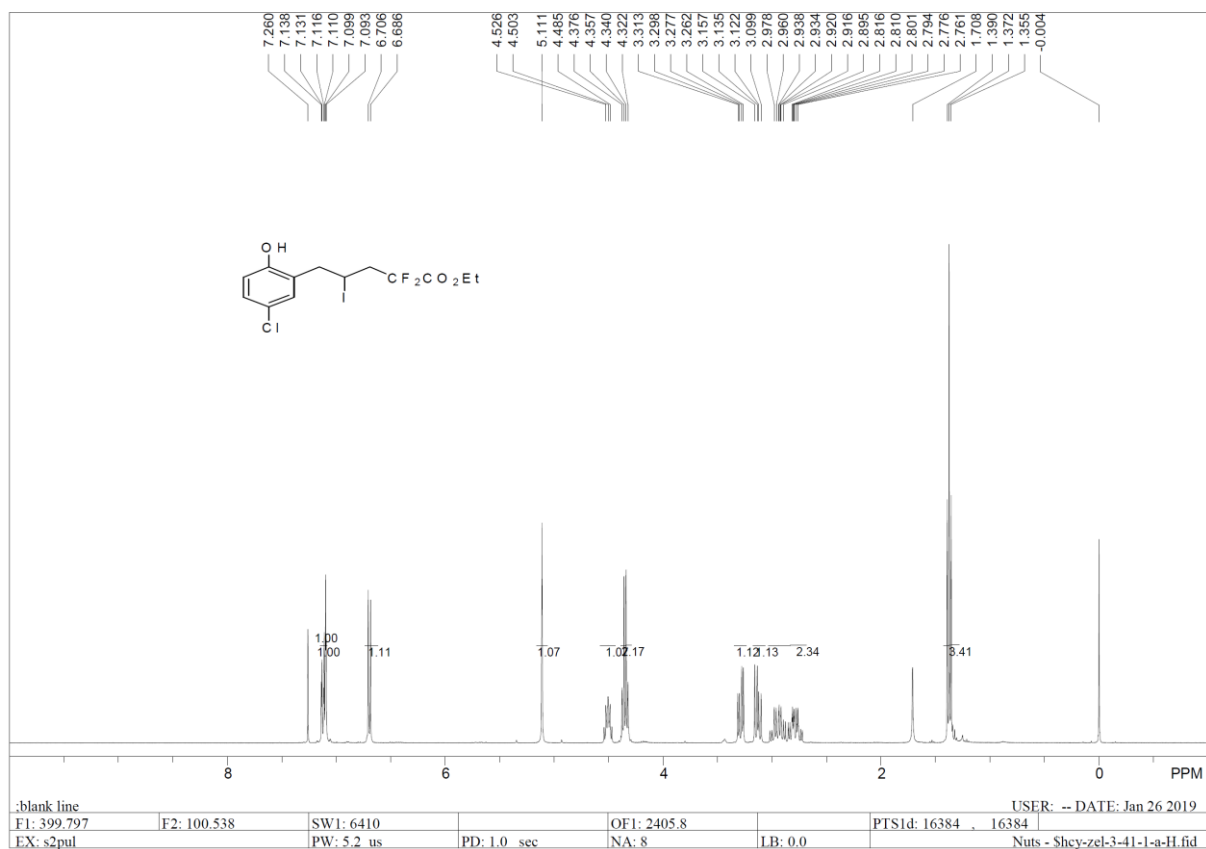


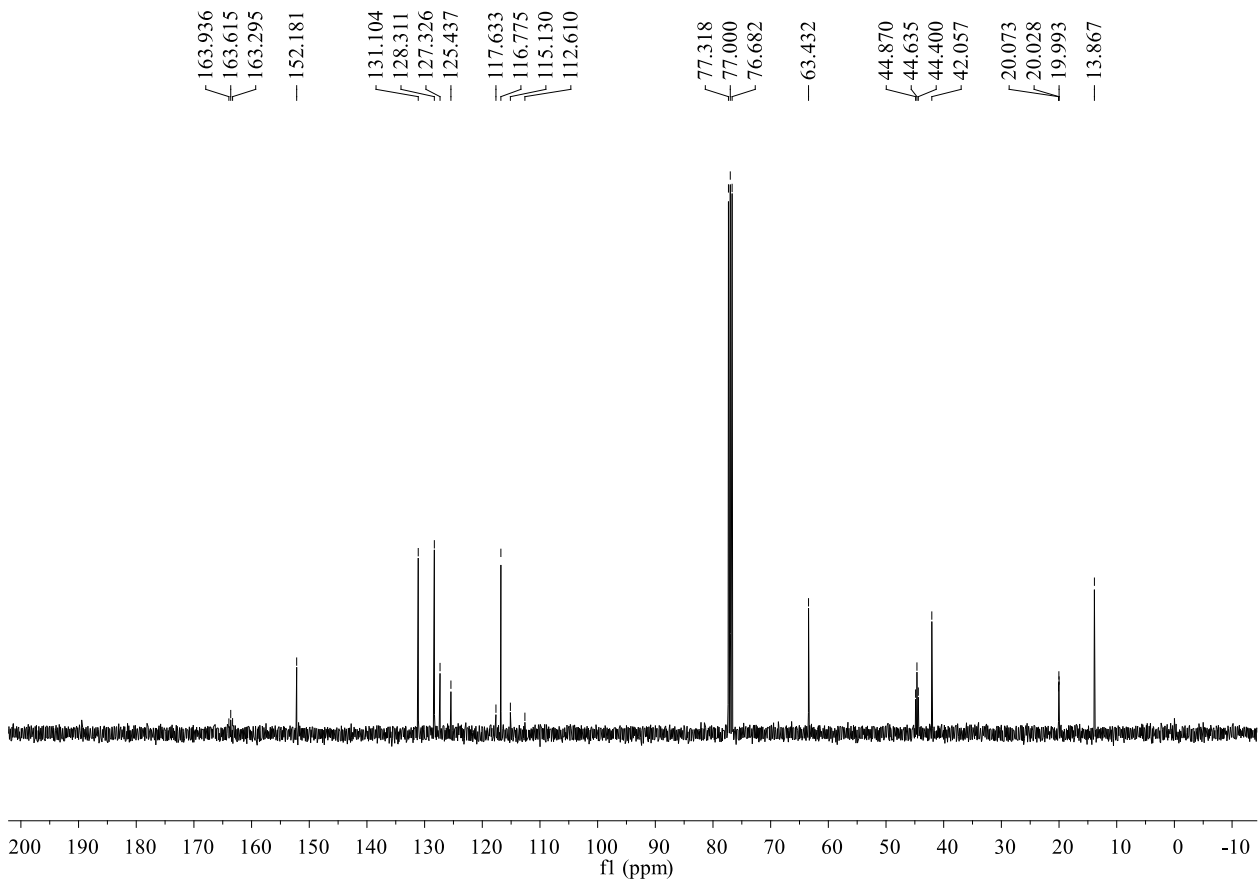


STANDARD FLUORINE PARAMETERS						USER: -- DATE: Jan 22 2019	
F1: 376.151	F2: 100.538	SW1: 89286	OFl: -31975.5	PTS1d: 65536	65536		
EX: s2pul	PW: 3.2 us	PD: 1.0 sec	NA: 4	LB: 0.0	Nuts - Shcy-3-33-2-F.fid		

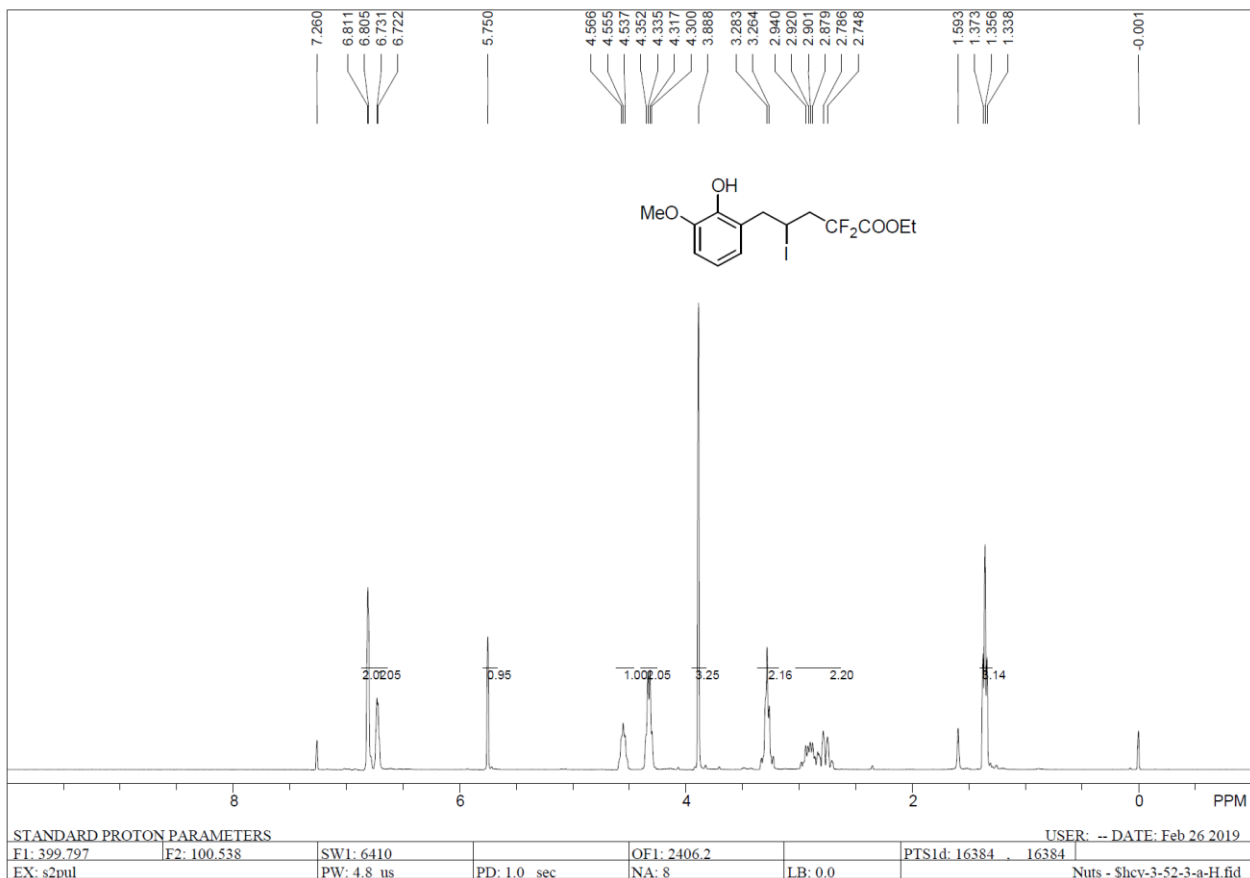


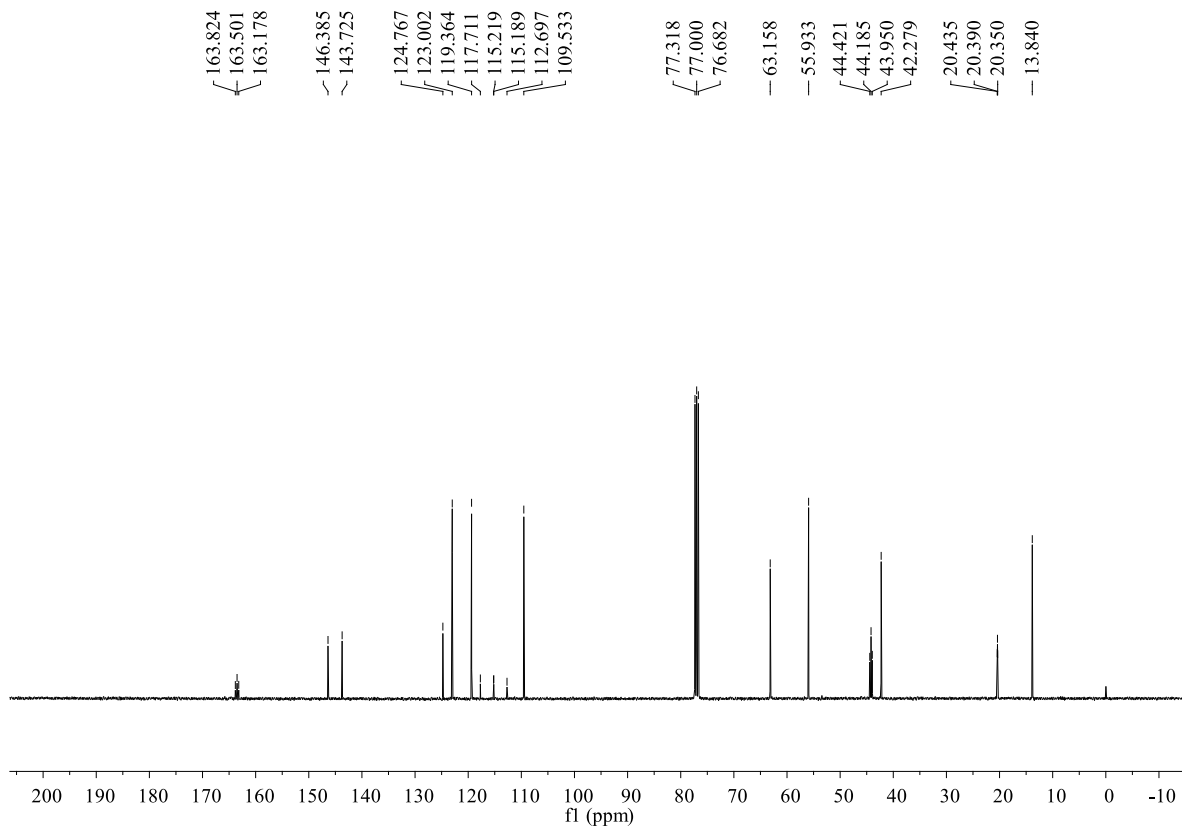
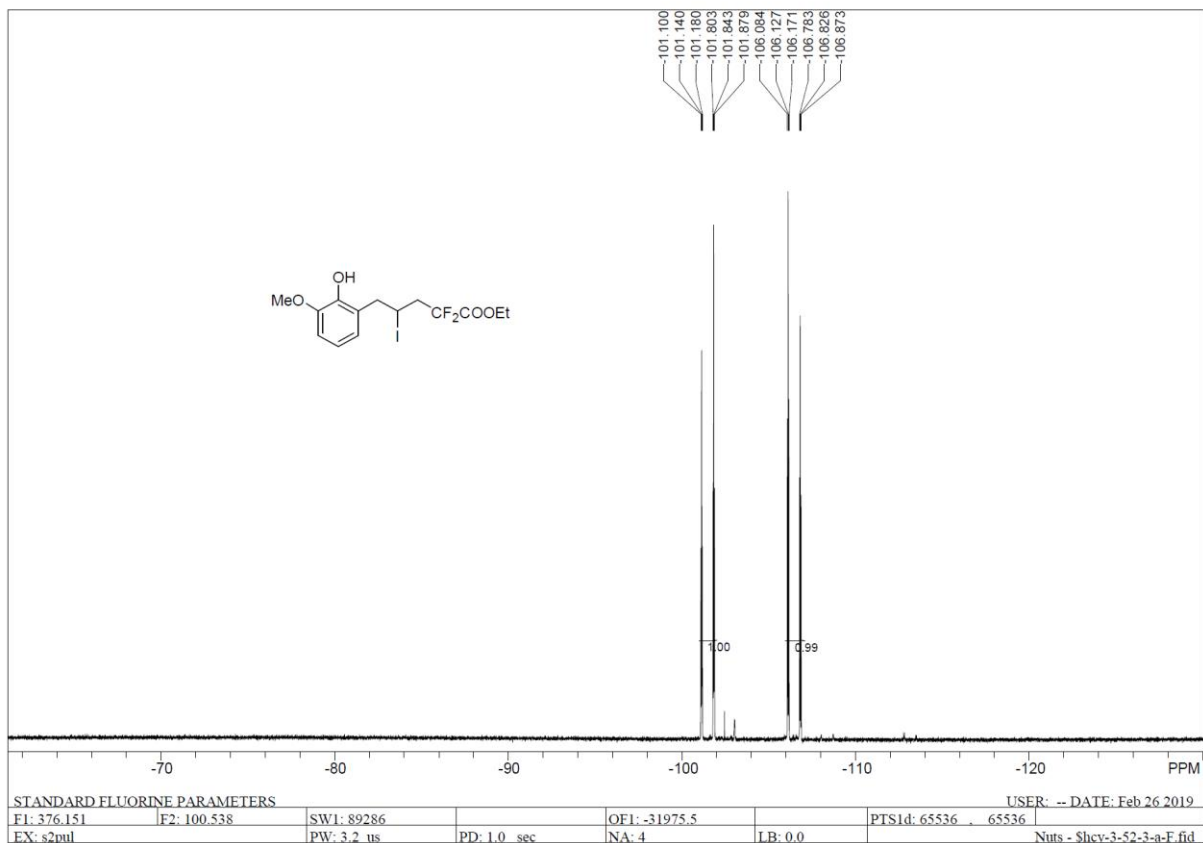
Ethyl 5-(5-chloro-2-hydroxyphenyl)-2,2-difluoro-4-iodopentanoate (3q).



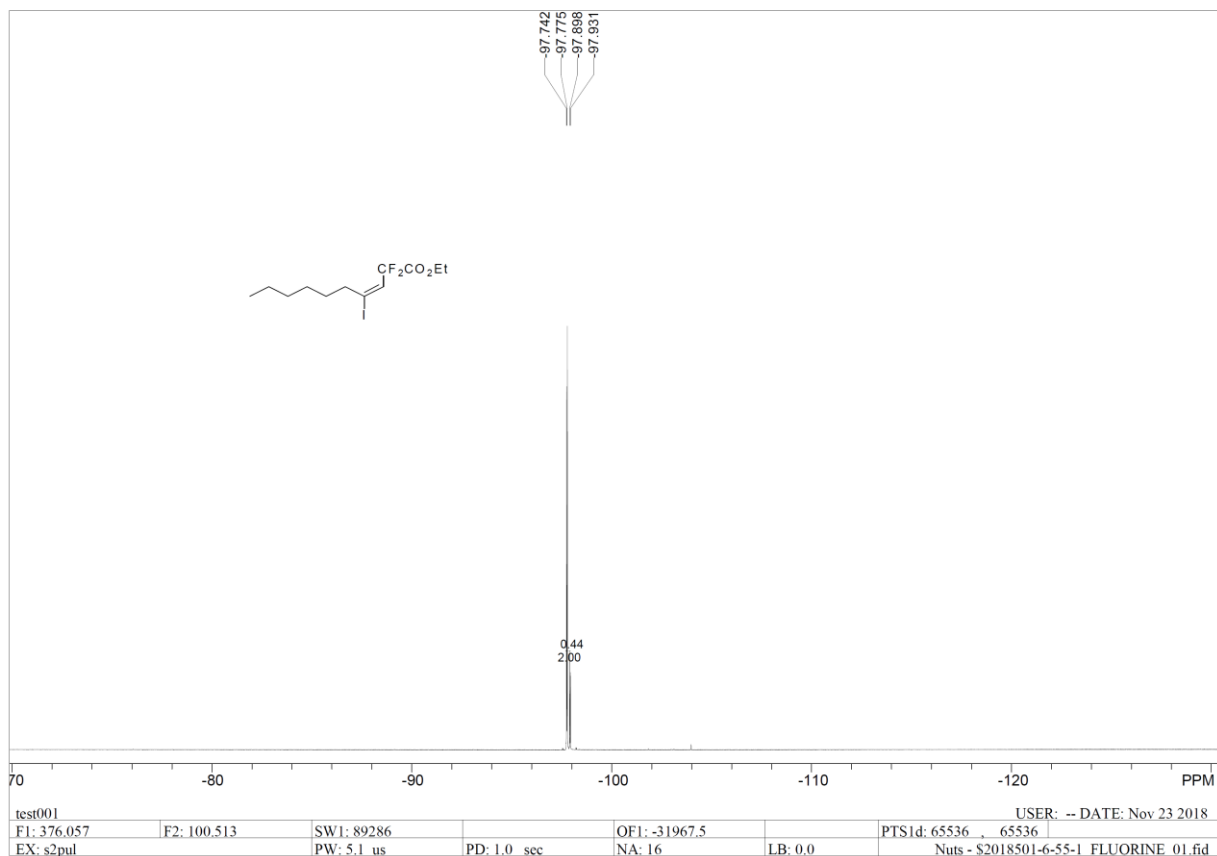
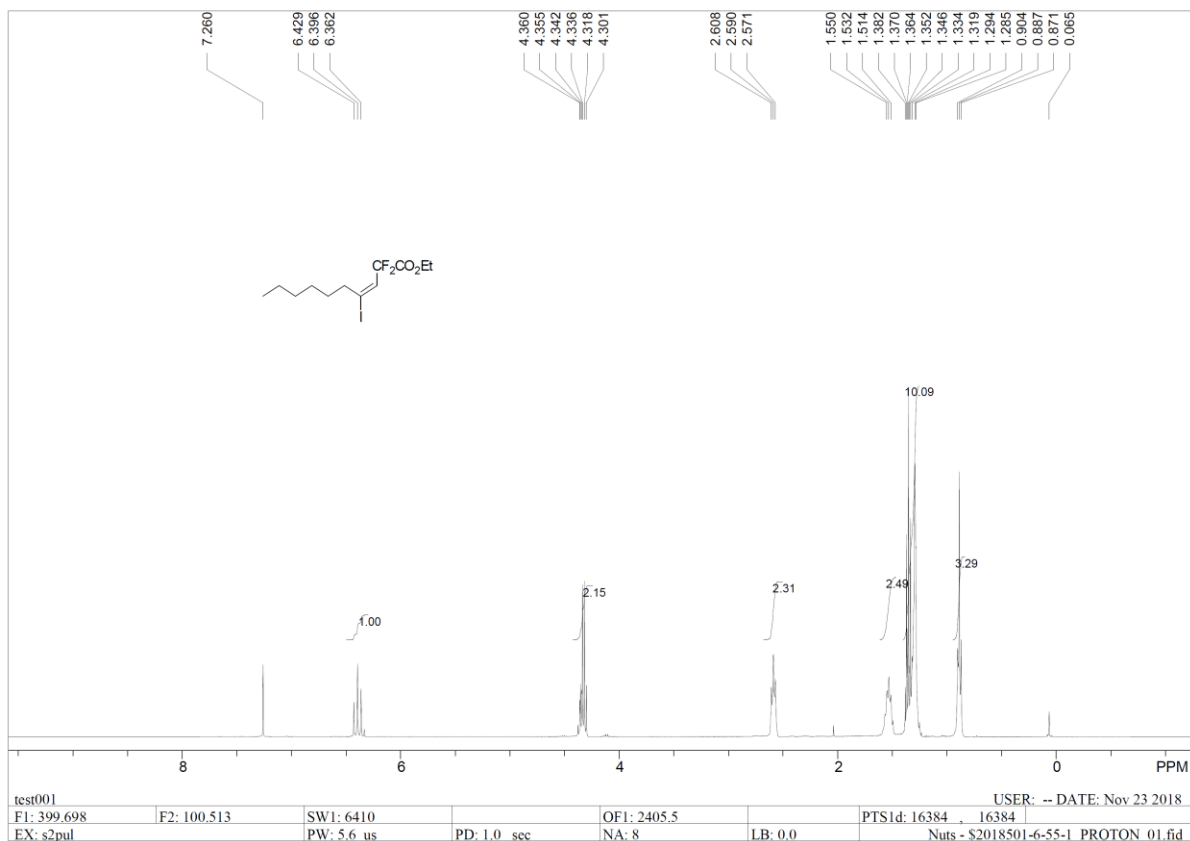


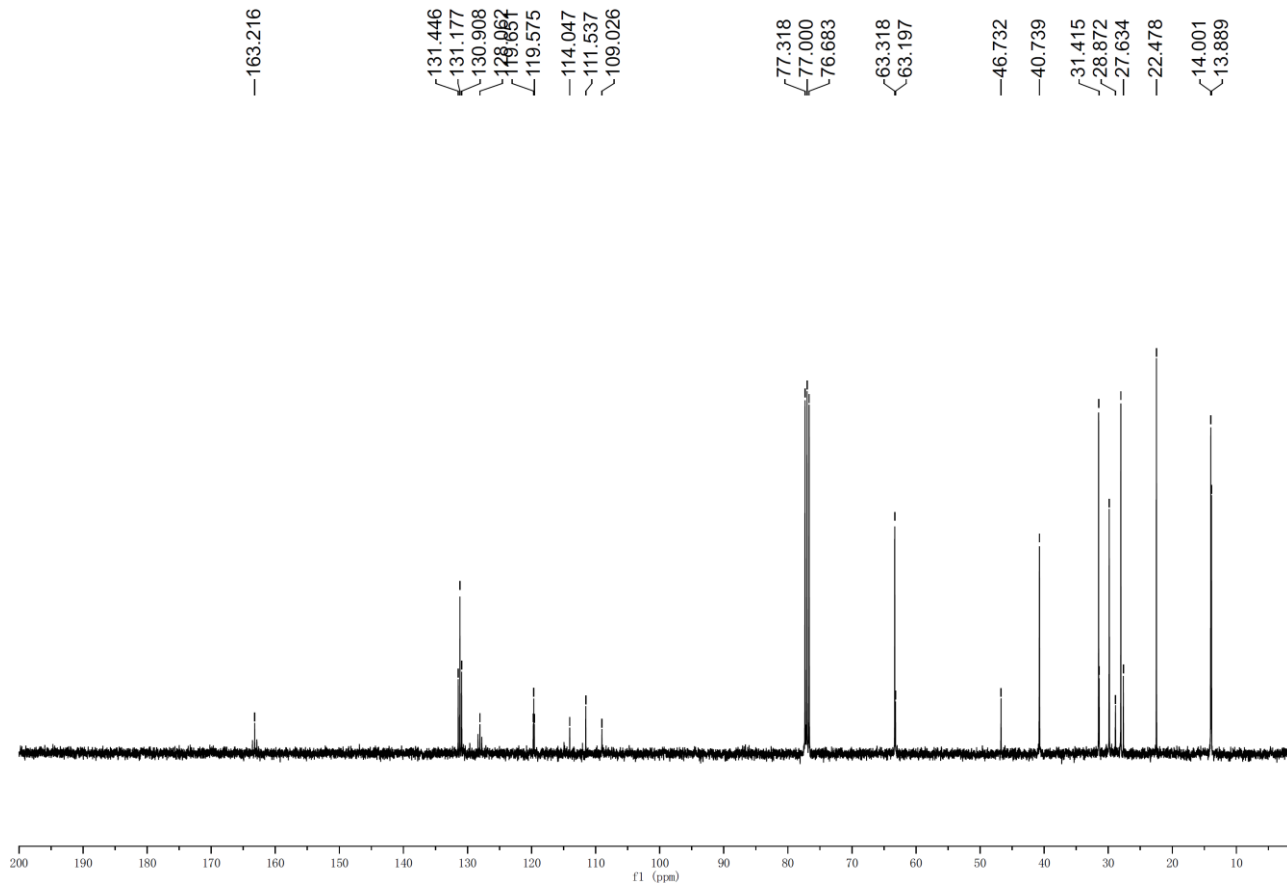
Ethyl 2,2-difluoro-5-(2-hydroxy-3-methoxyphenyl)-4-iodopentanoate (3r).



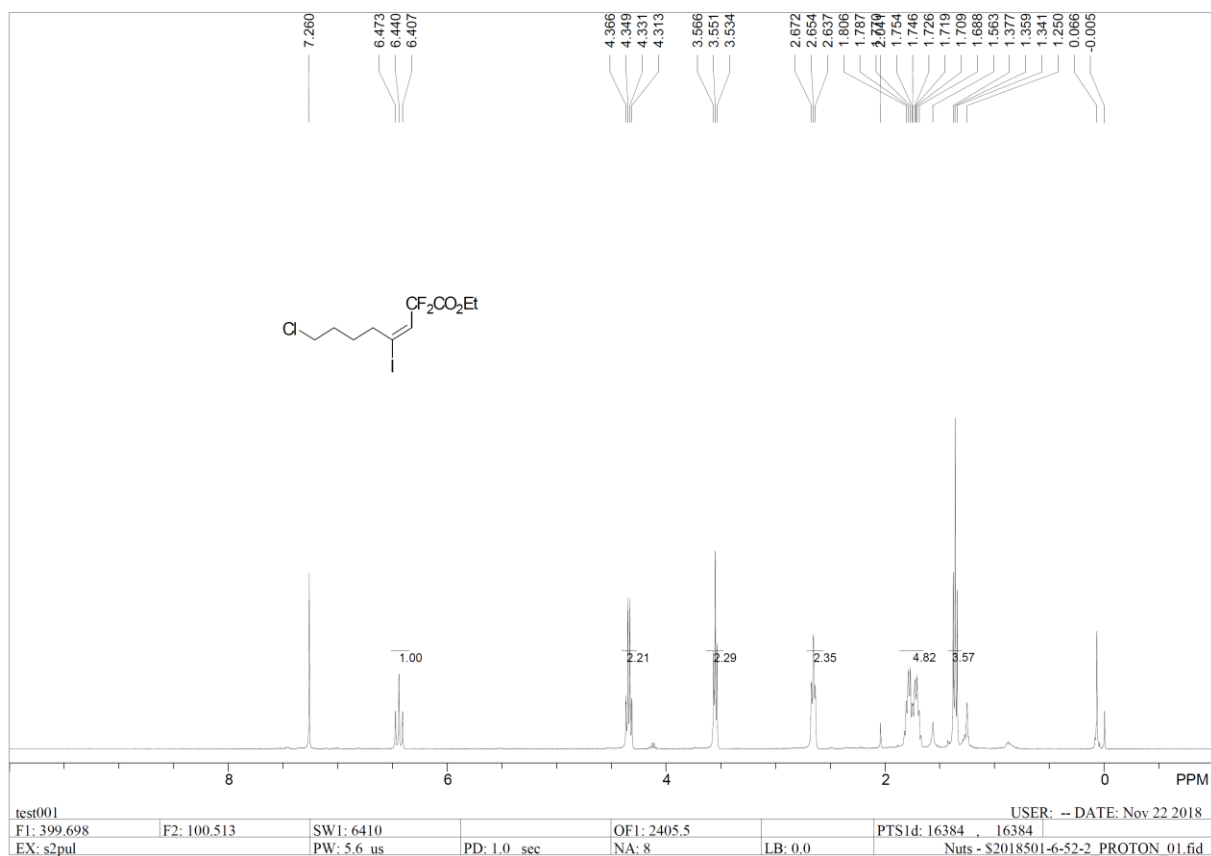


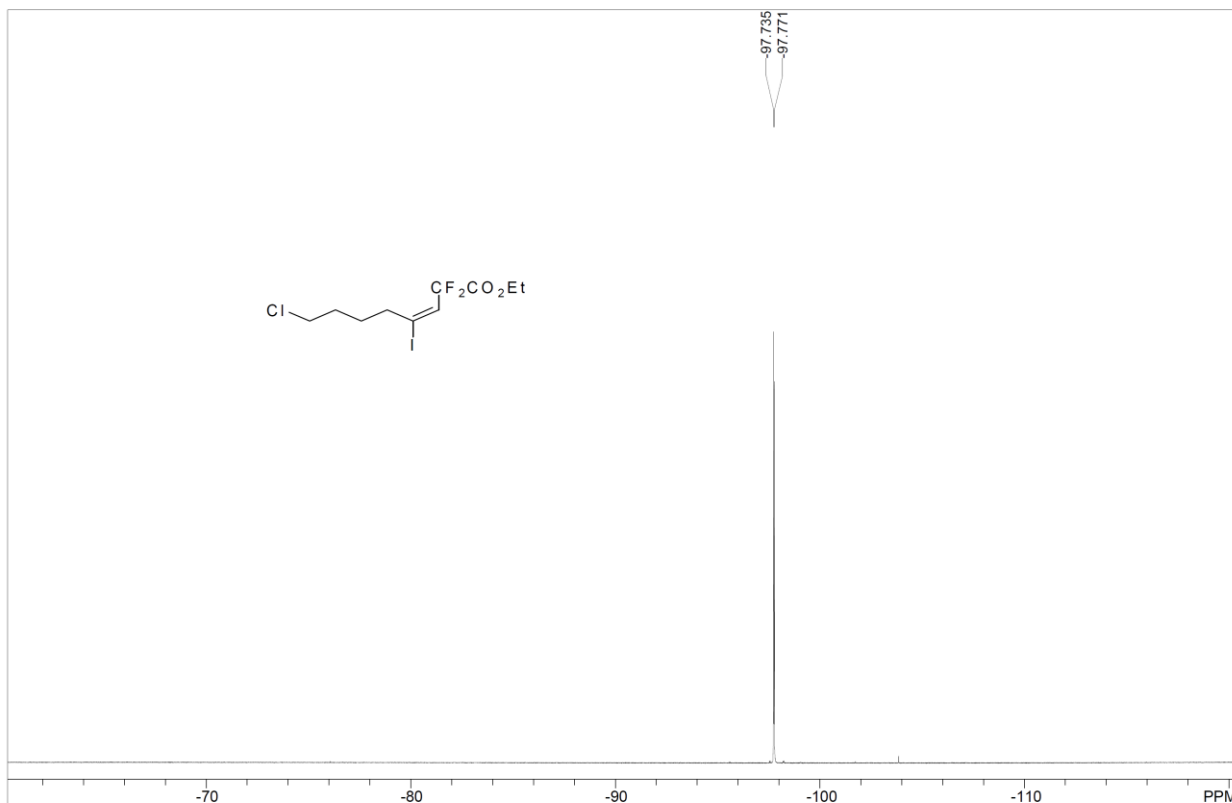
Ethyl (E)-2,2-difluoro-4-iododec-3-enoate (5a).



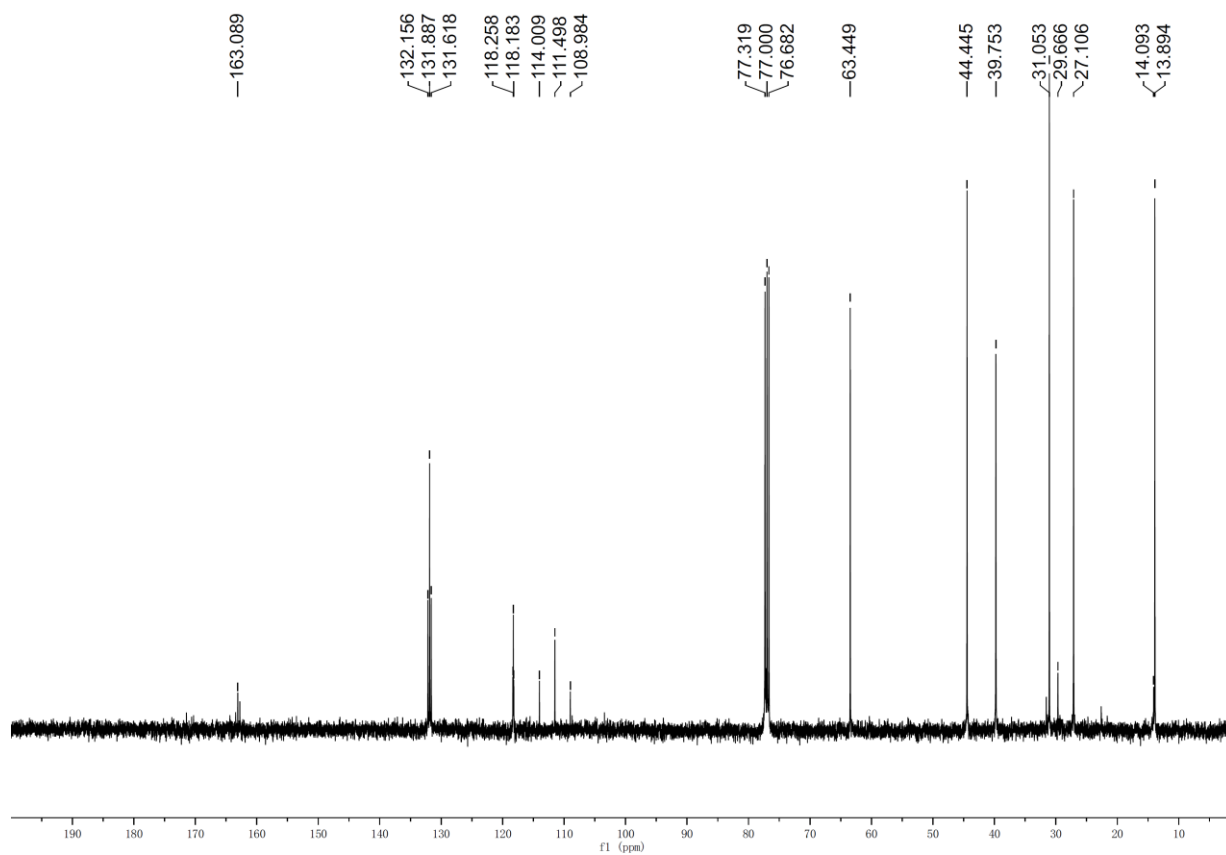


Ethyl (*E*)-8-chloro-2,2-difluoro-4-iodooct-3-enoate (5b).

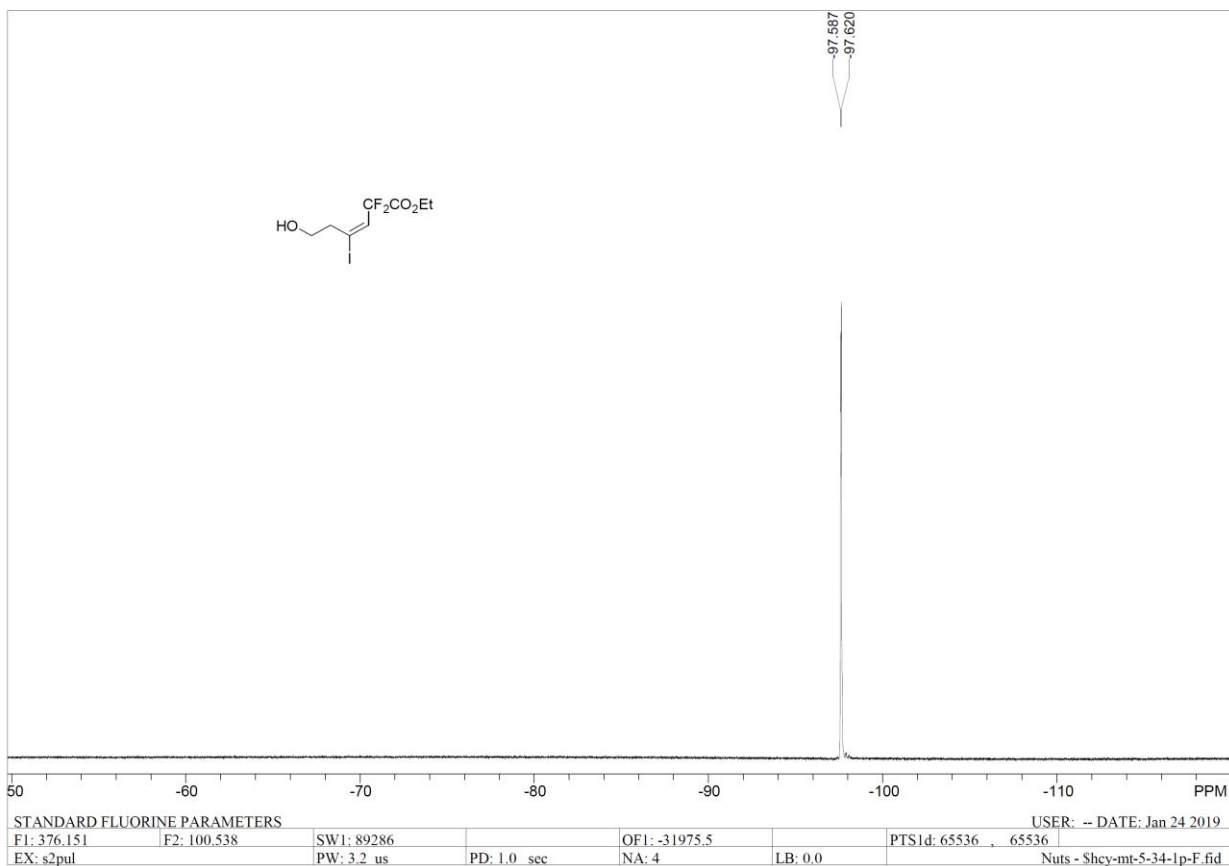
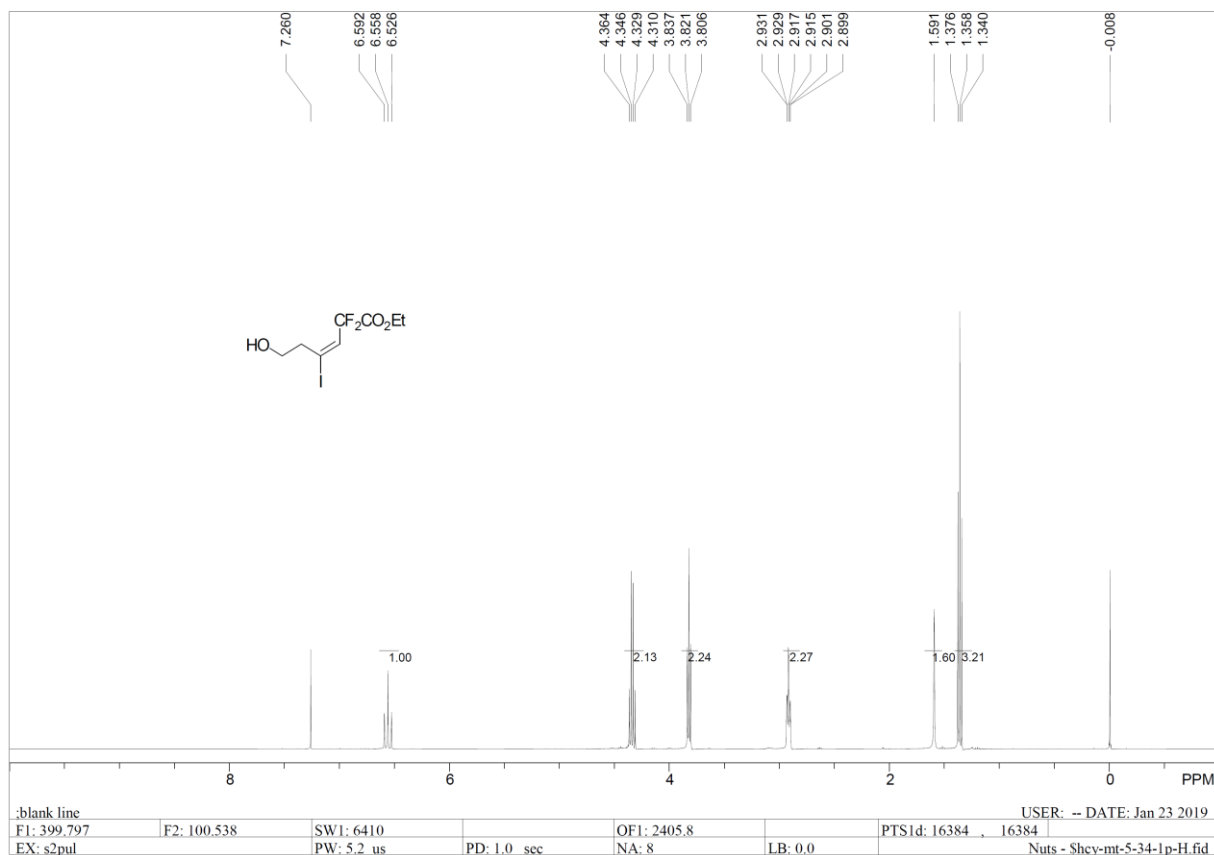


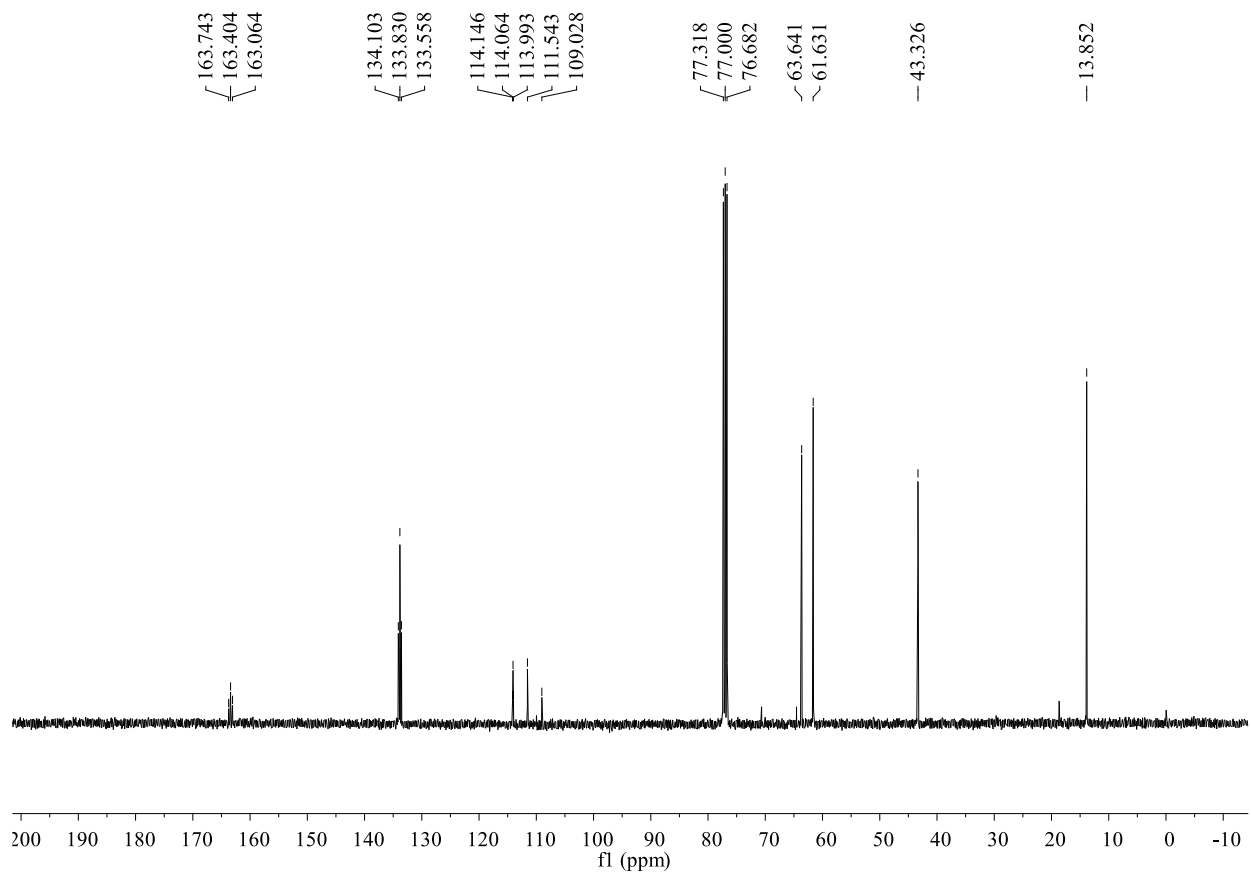


test001						USER: -- DATE: Nov 22 2018	
F1: 376.057	F2: 100.513	SW1: 89286	OF1: -31967.5	PTS1d: 65536	65536		
EX: s2pul	PW: 5.1 us	PD: 1.0 sec	NA: 16	LB: 0.0	Nuts - S2018501-6-52-2_FLUORINE_01.fid		

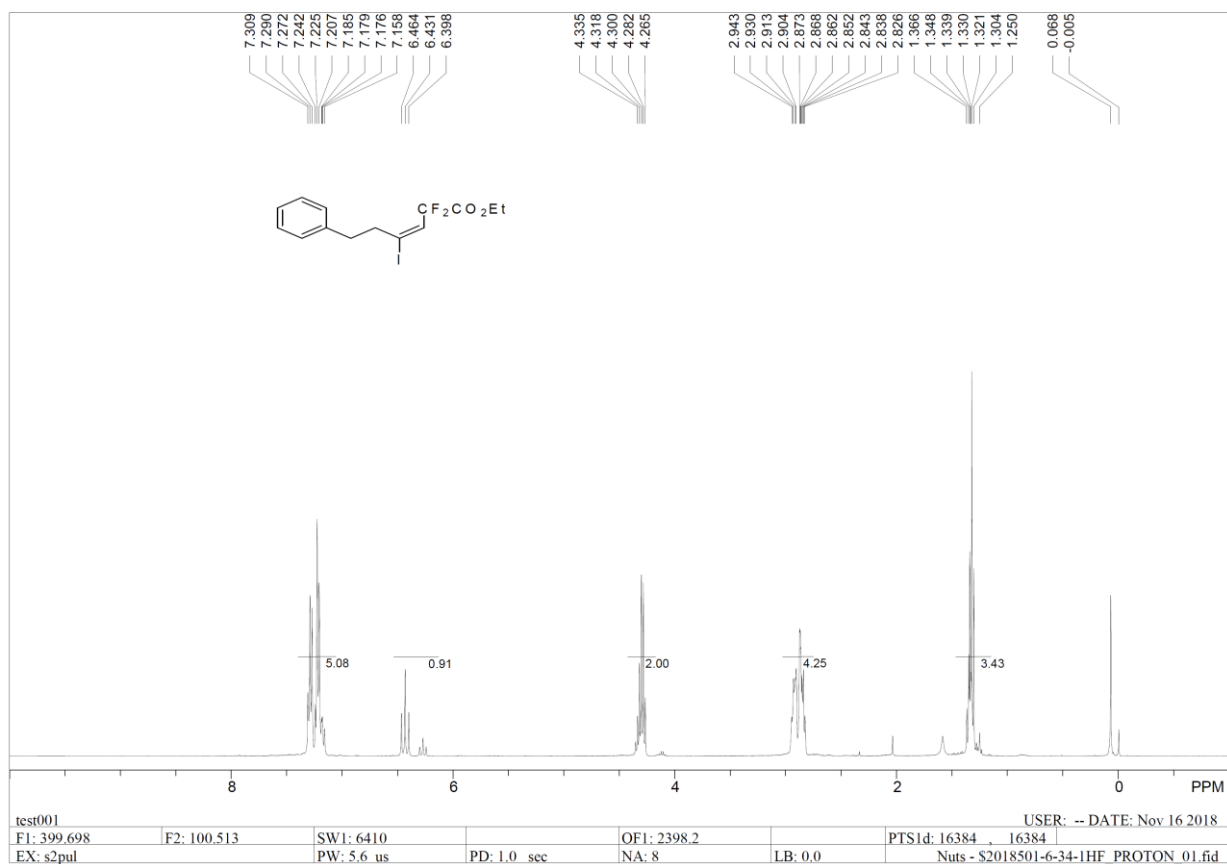


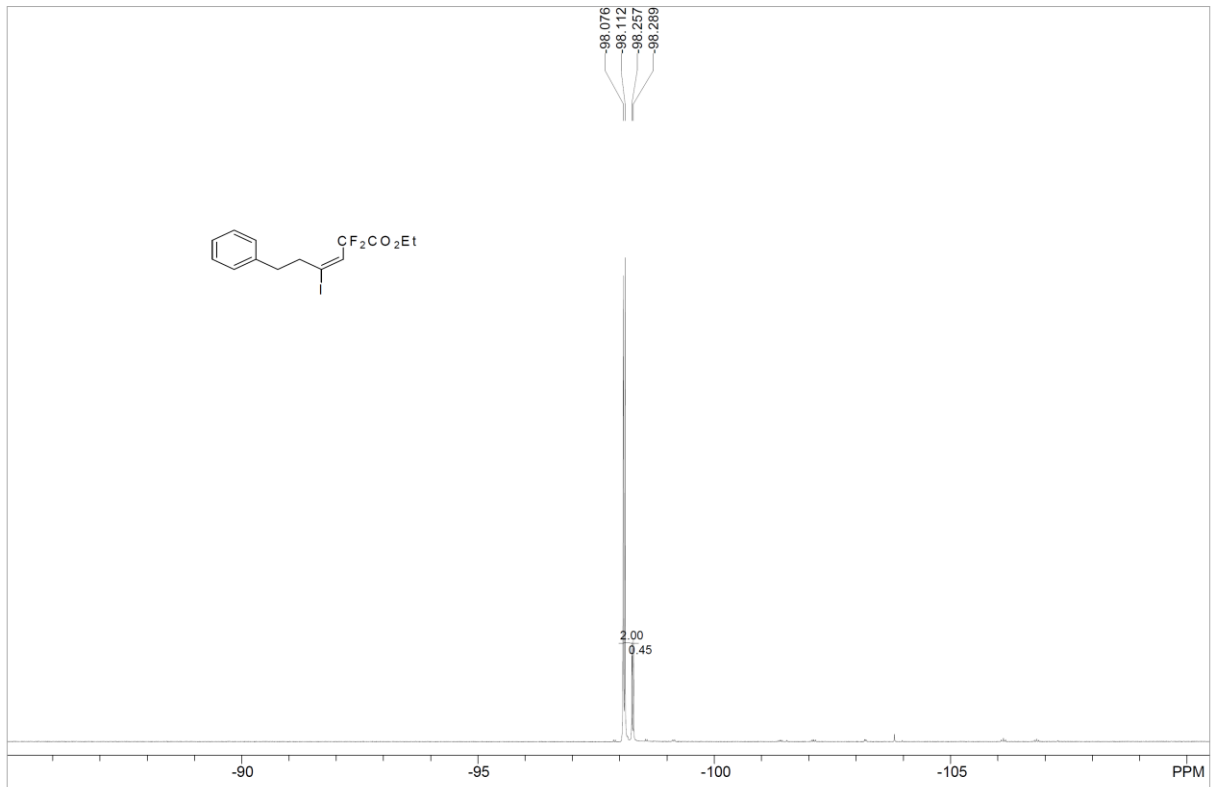
Ethyl (*E*)-2,2-difluoro-6-hydroxy-4-iodohex-3-enoate (5c**).**



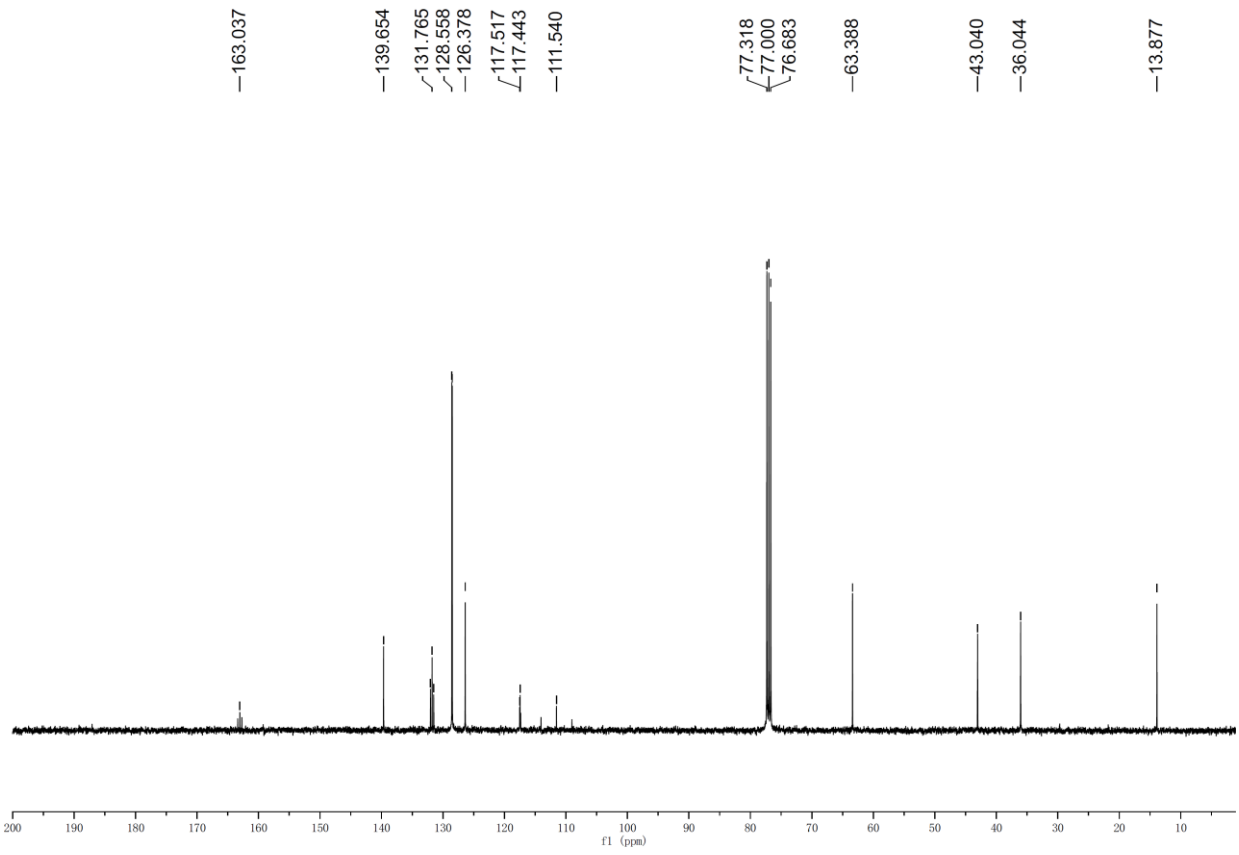


Ethyl (*E*)-2,2-difluoro-4-iodo-6-phenylhex-3-enoate (5d).

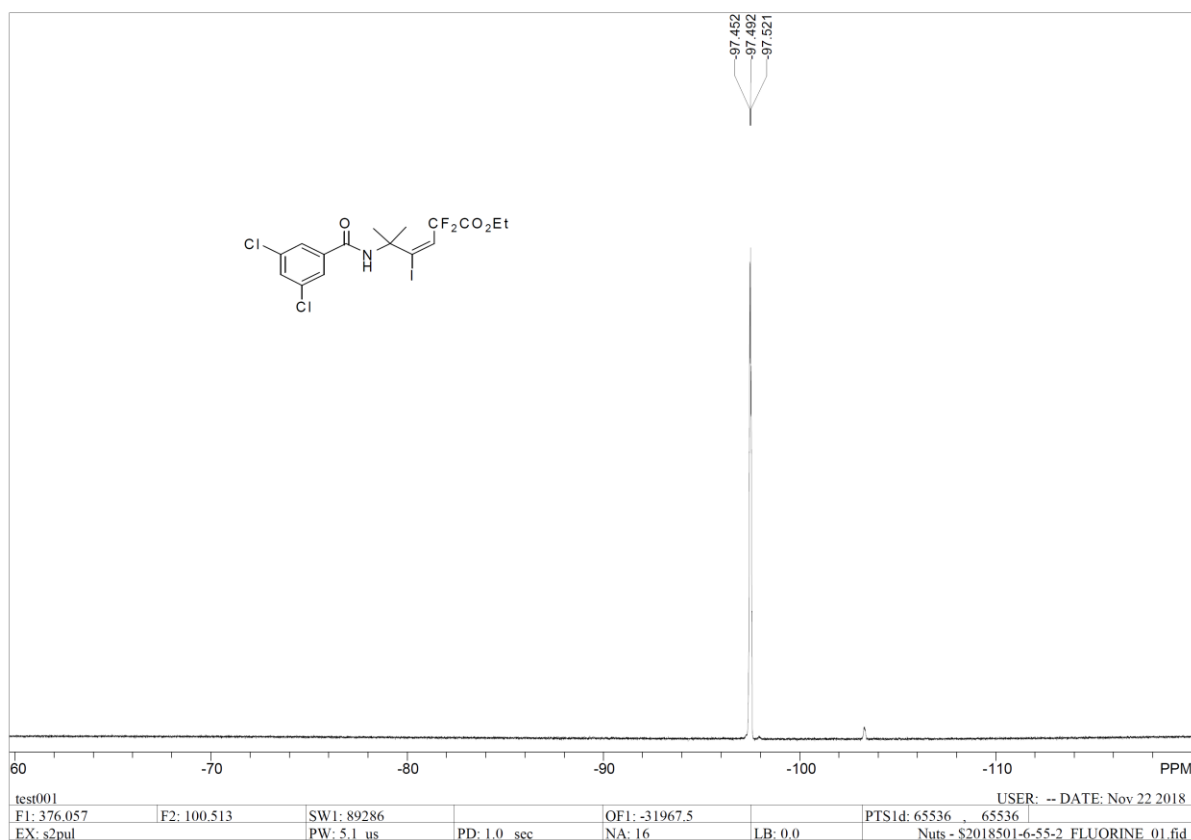
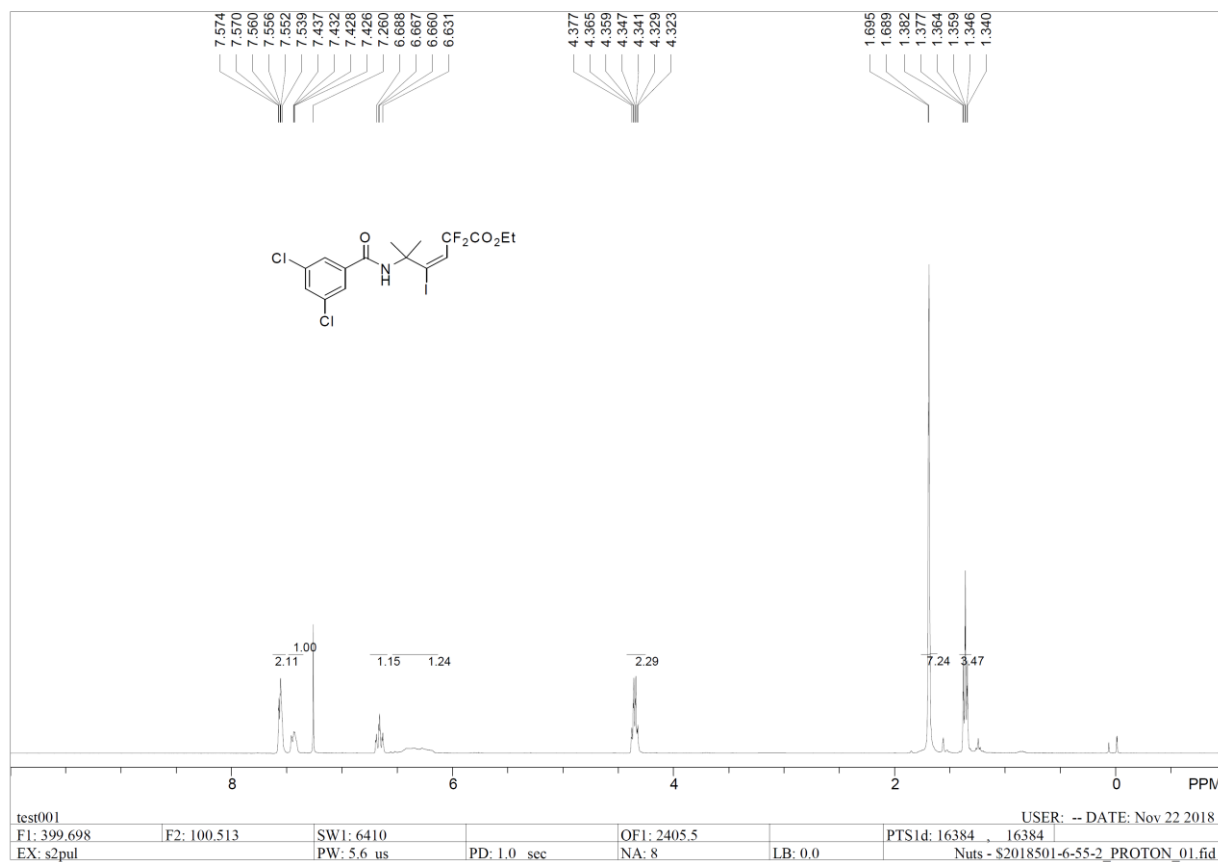


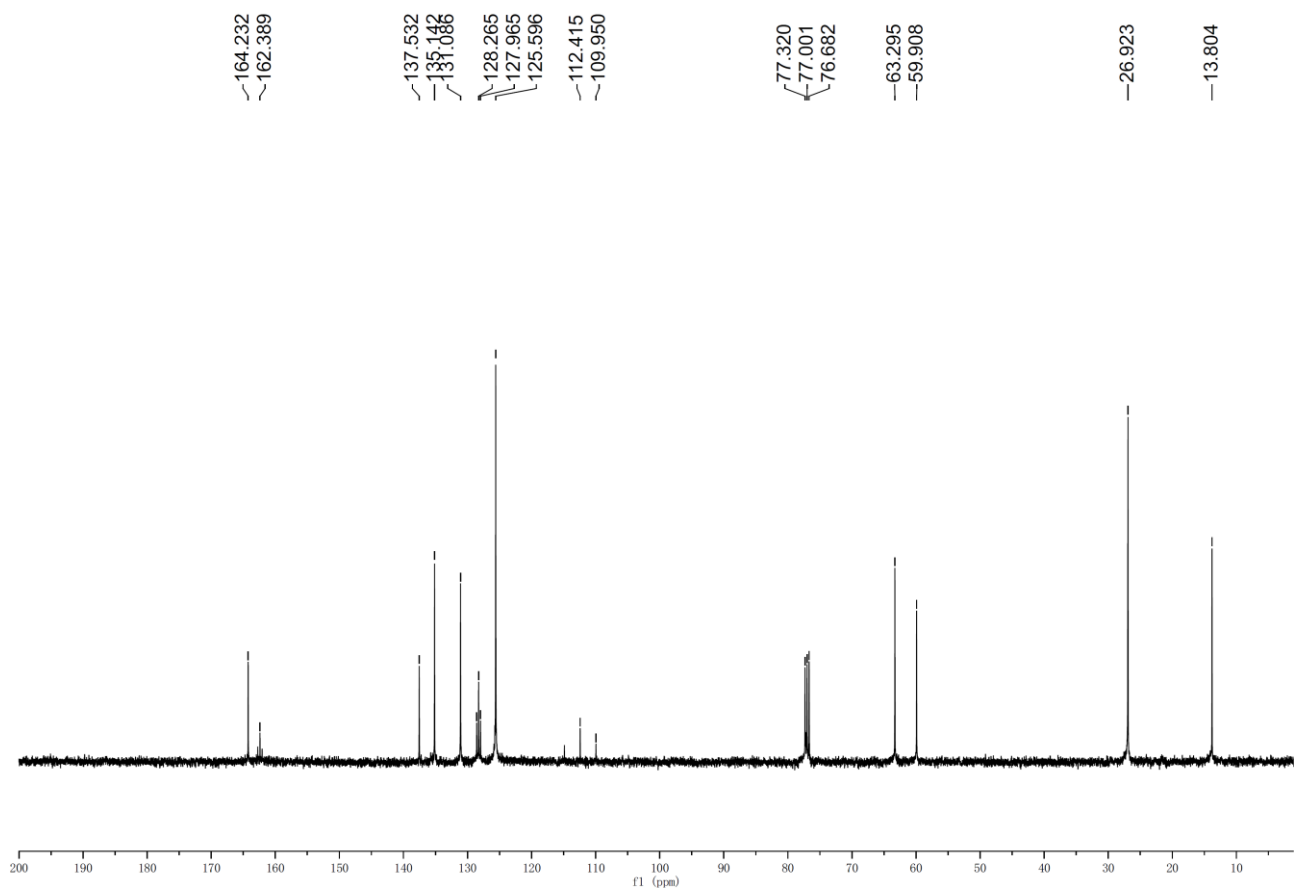


test001
 F1: 376.057 F2: 100.513 SW1: 89286 OF1: -31967.5 PTS1d: 65536 , 65536 USER: -- DATE: Nov 16 2018
 EX: s2pul PW: 5.1 us PD: 1.0 sec NA: 16 LB: 0.0 Nuts - S2018501-6-34-1HF_FLUORINE_01.fid

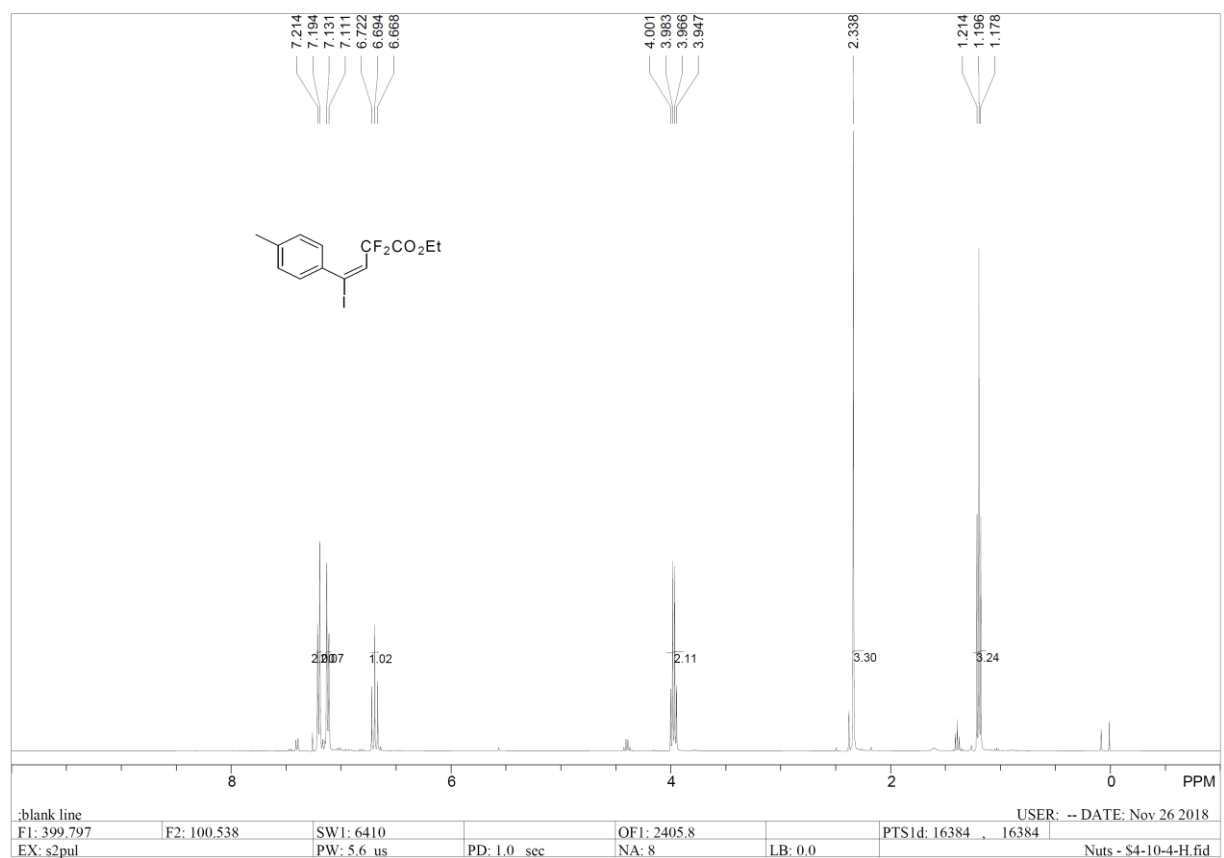


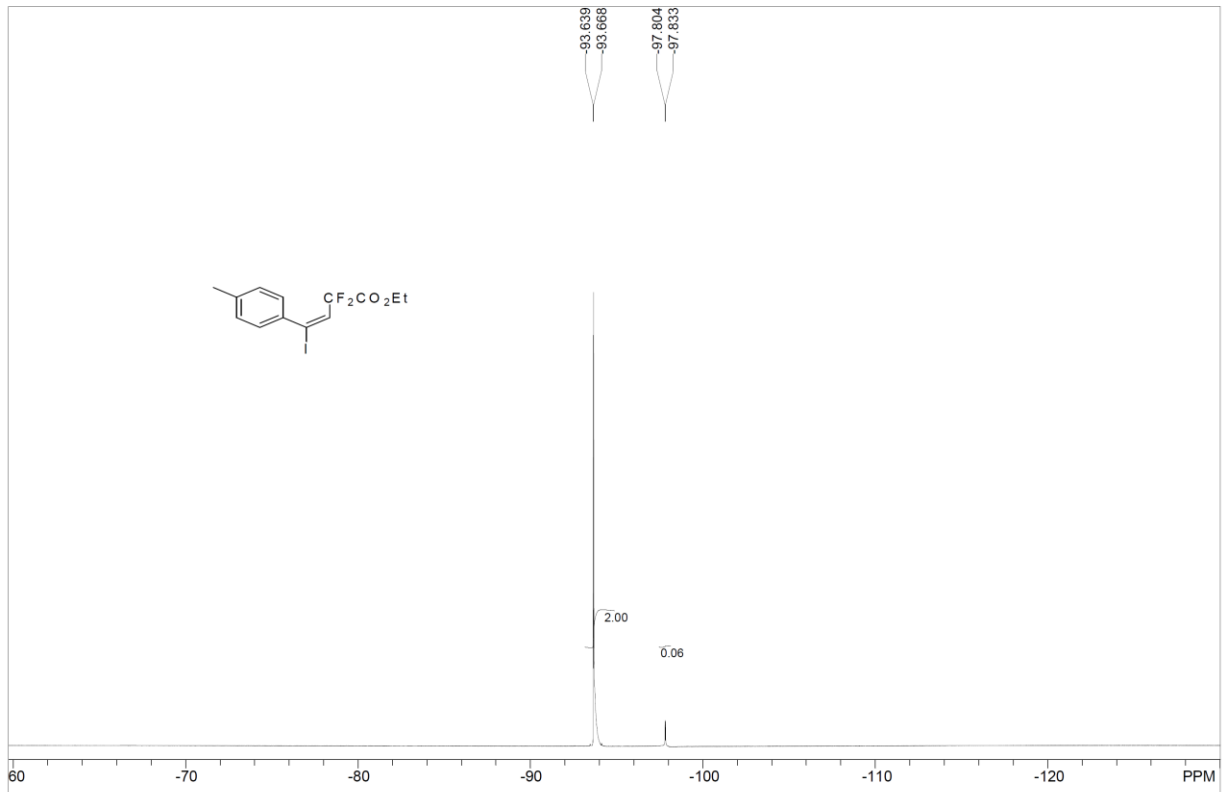
Ethyl (E)-5-(3,5-dichlorobenzamido)-2,2-difluoro-4-iodo-5-methylhex-3-enoate (5e).





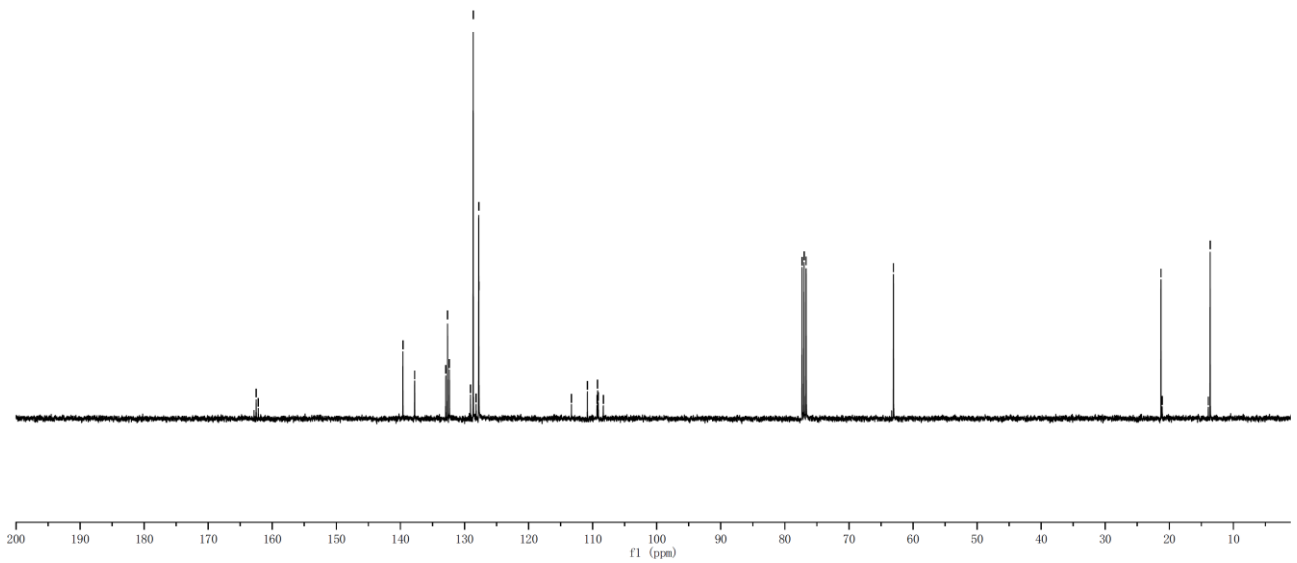
Ethyl (*E*)-2,2-difluoro-4-iodo-4-(*p*-tolyl)but-3-enoate (5f**).**



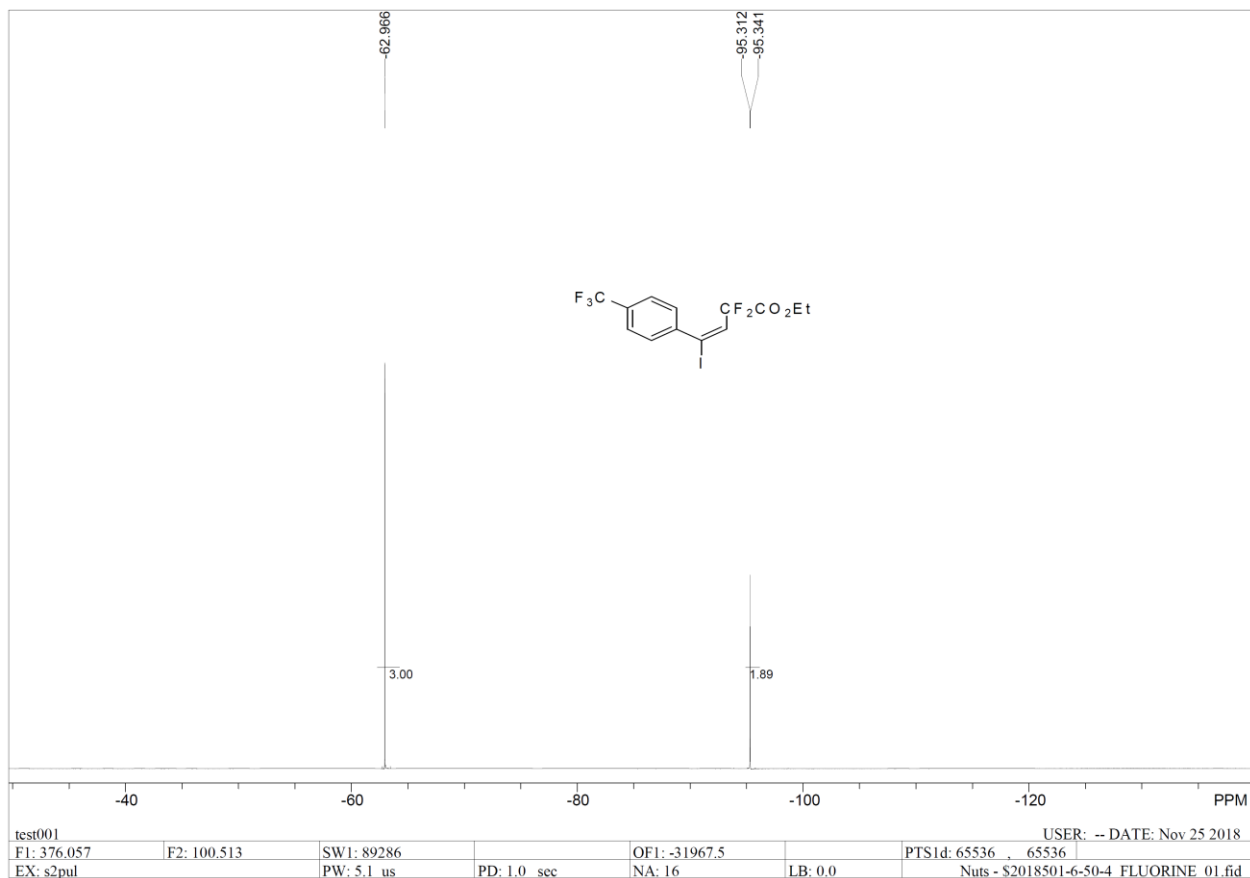
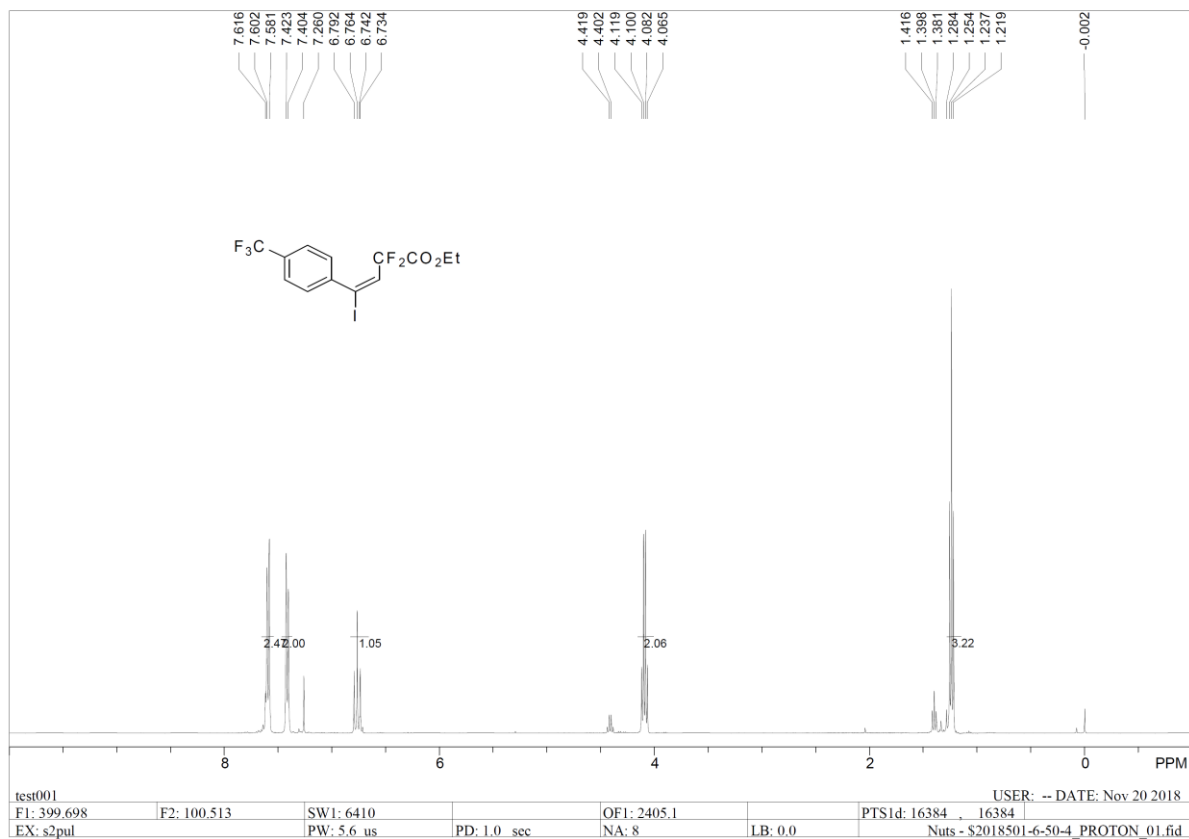


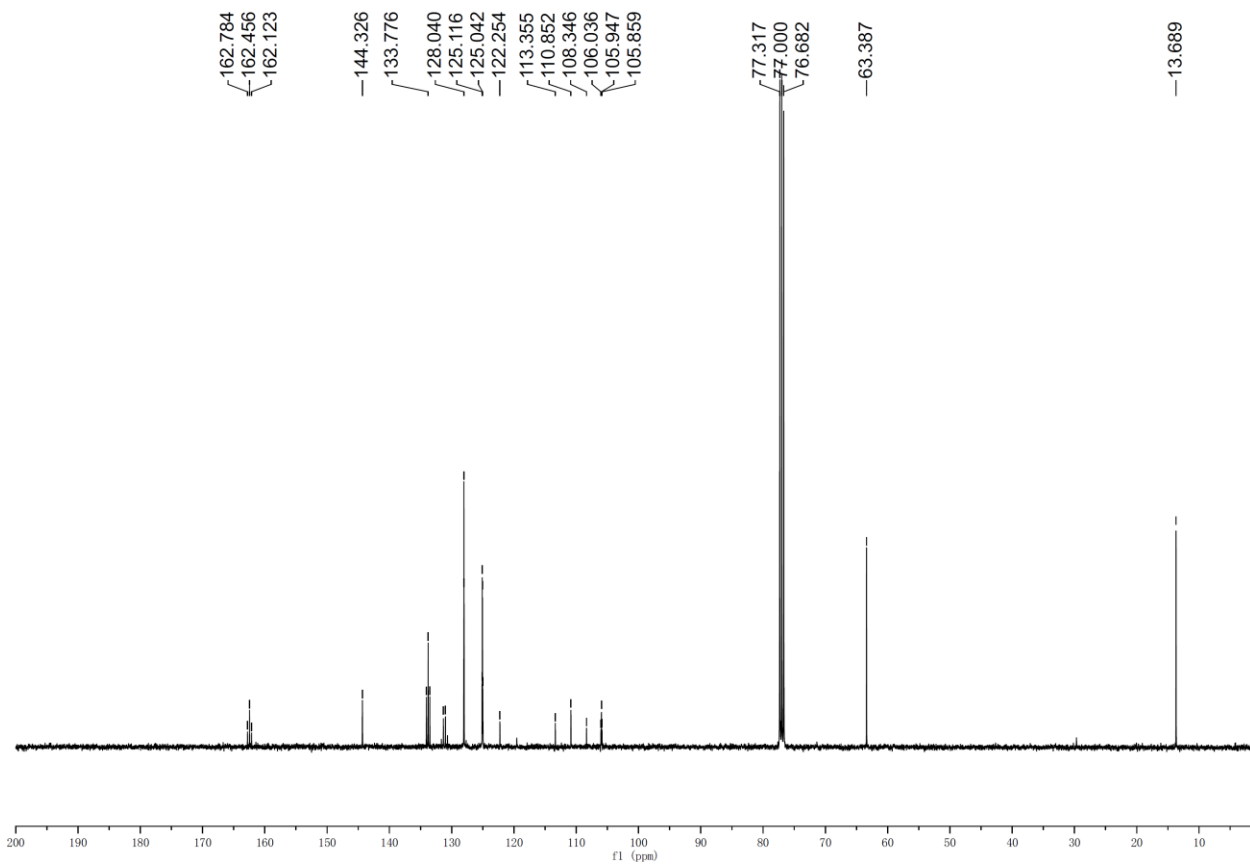
STANDARD FLUORINE PARAMETERS						USER: -- DATE: Nov 28 2018	
F1: 376.151	F2: 100.538	SW1: 89286		OE1: -31975.5		PTS1d: 65536	65536
EX: s2pul		PW: 3.2 us	PD: 1.0 sec	NA: 4	LB: 0.0	Nuts - S4-10-4-F.fid	

- 162.513
- 162.181
- 139.612
- 137.780
- 132.641
- 128.185
- 127.759
- 113.306
- 110.821
- 109.323
- 109.221
- 109.120
- 108.338
- 77.318
- 77.000
- 76.682
- 63.051
- 21.303
- 21.118
- 13.916
- 13.626

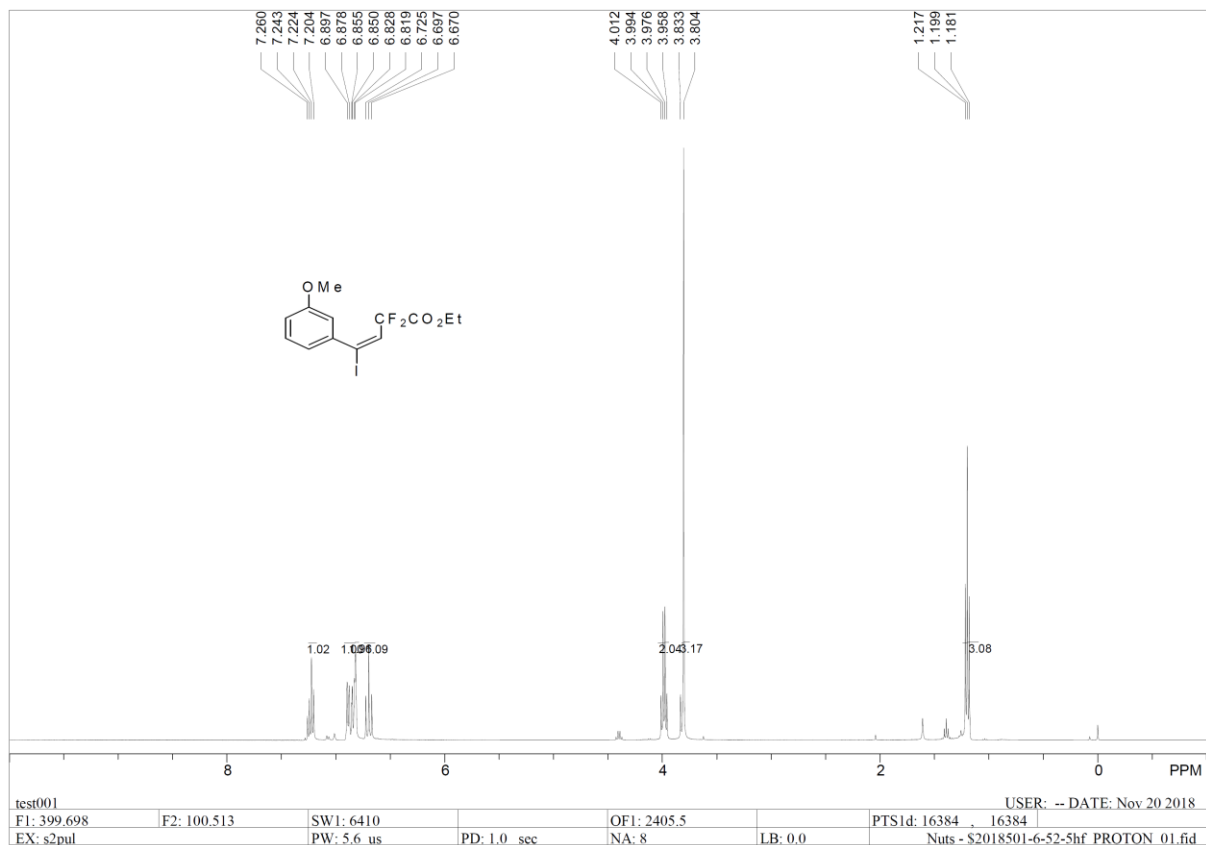


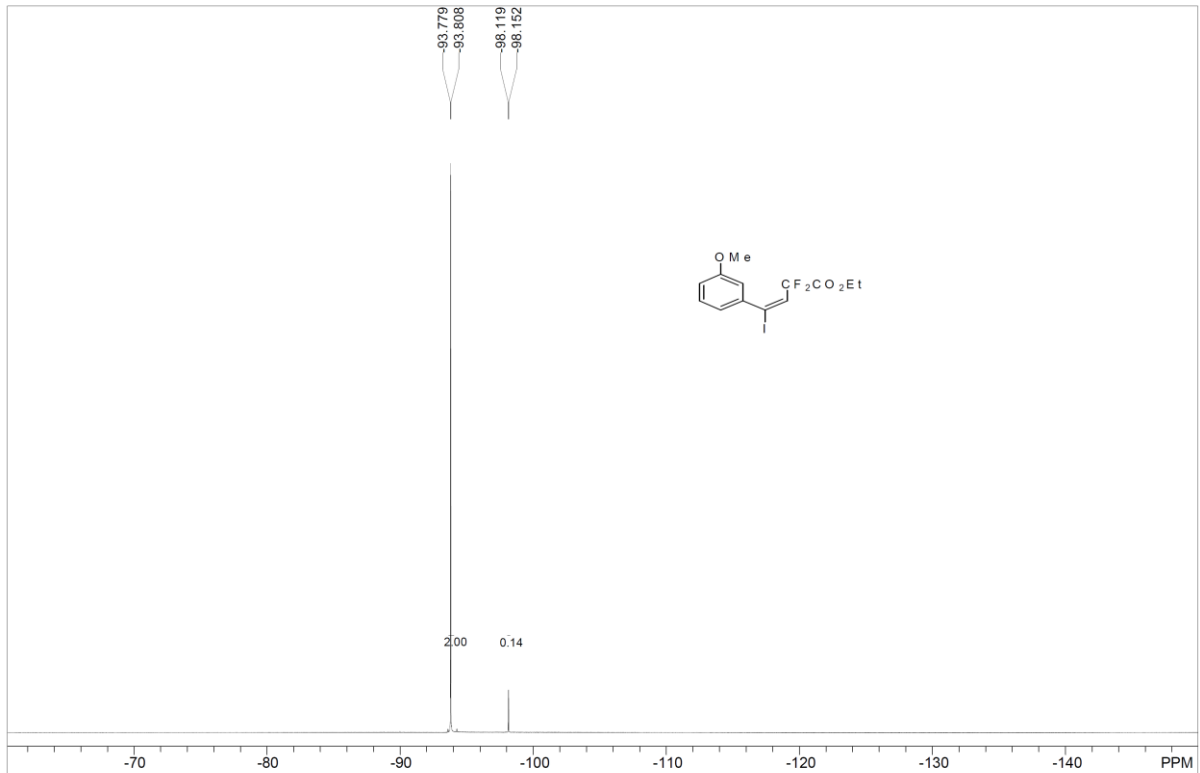
Ethyl (E)-2,2-difluoro-4-iodo-4-(4-(trifluoromethyl)phenyl)but-3-enoate (5g).





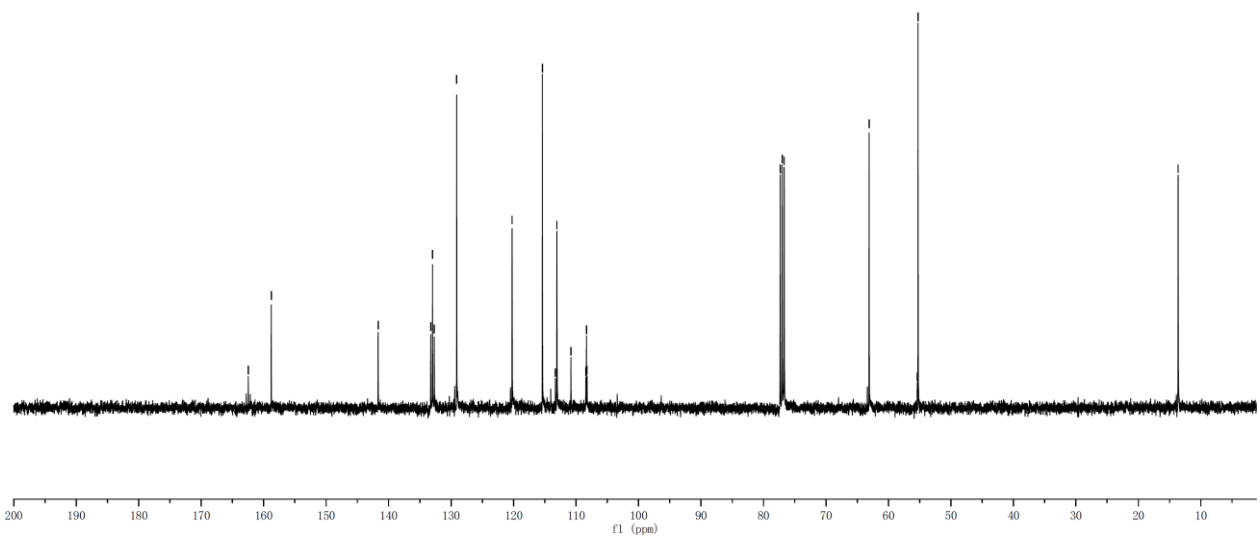
Ethyl (E)-2,2-difluoro-4-iodo-4-(3-methoxyphenyl)but-3-enoate (5h).



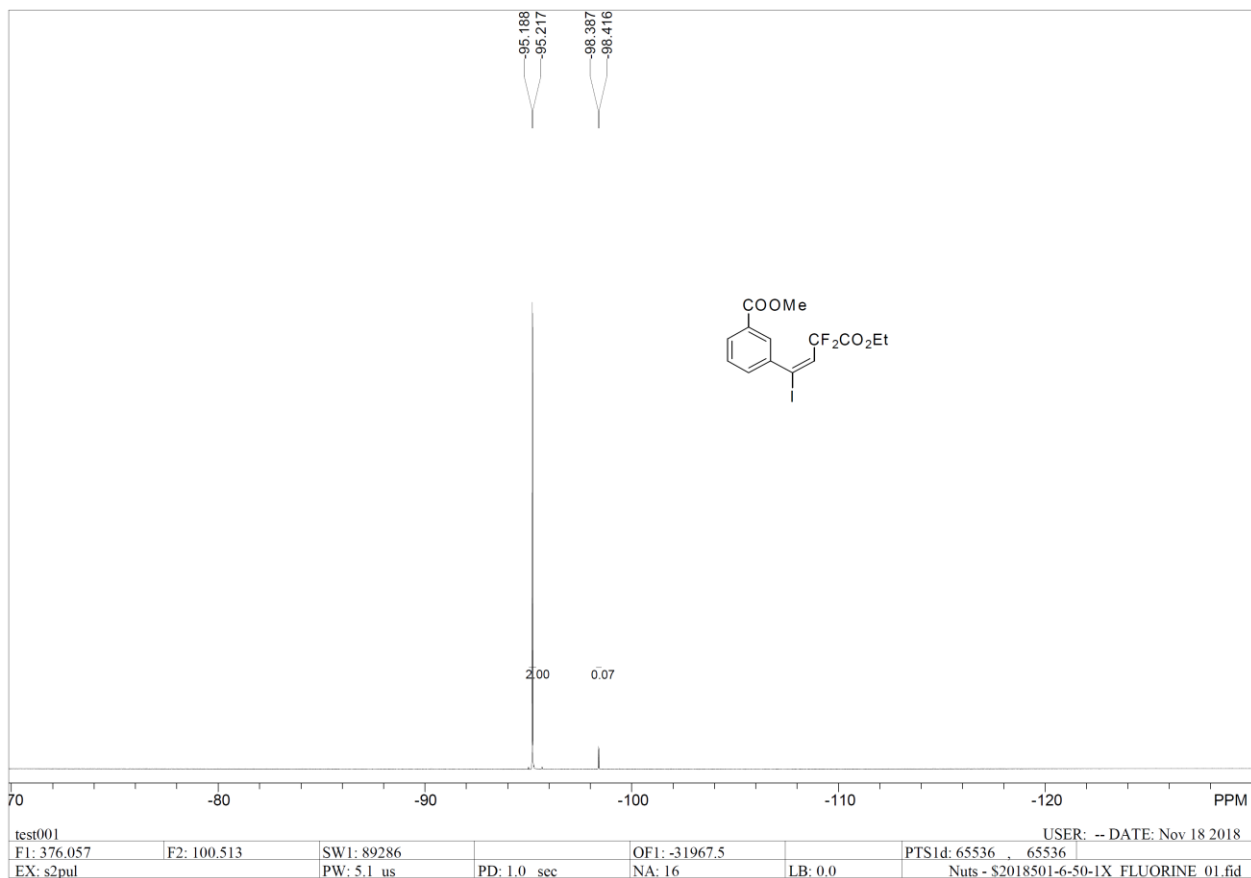
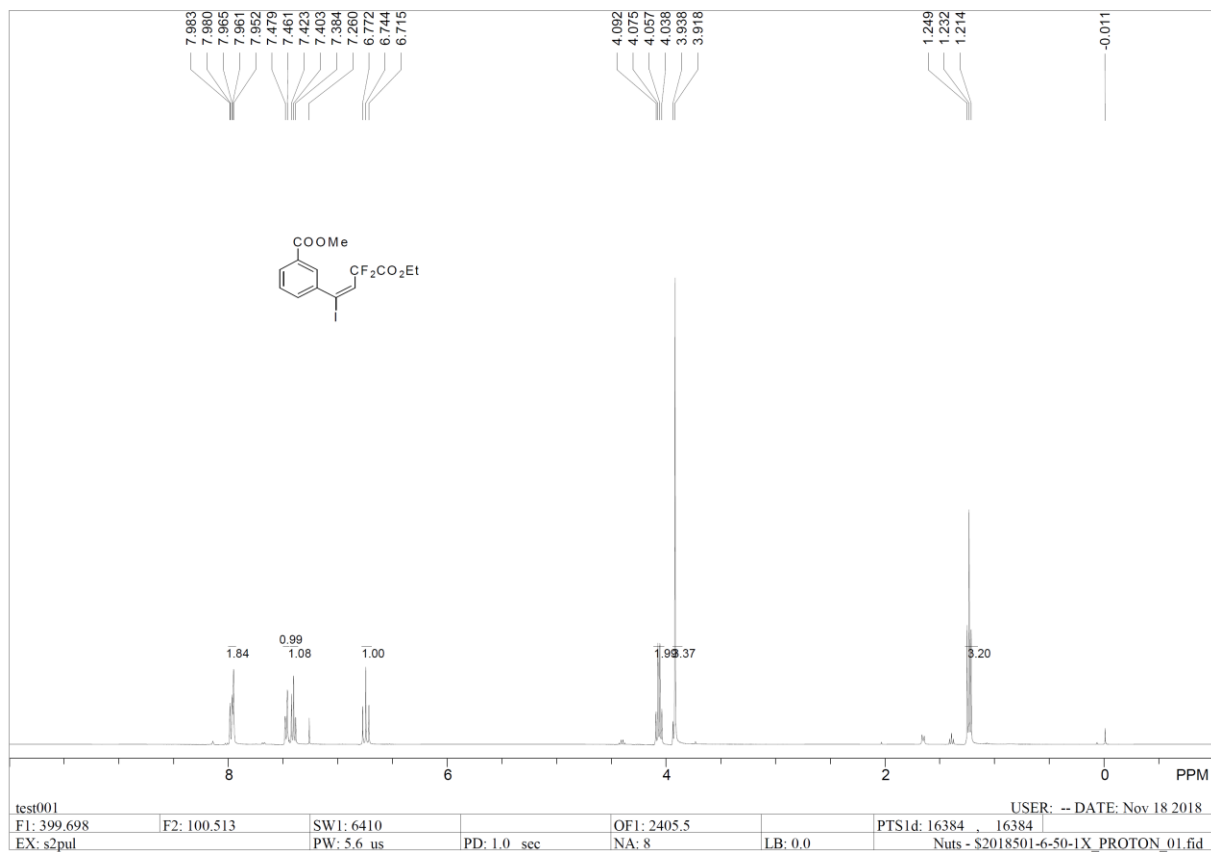


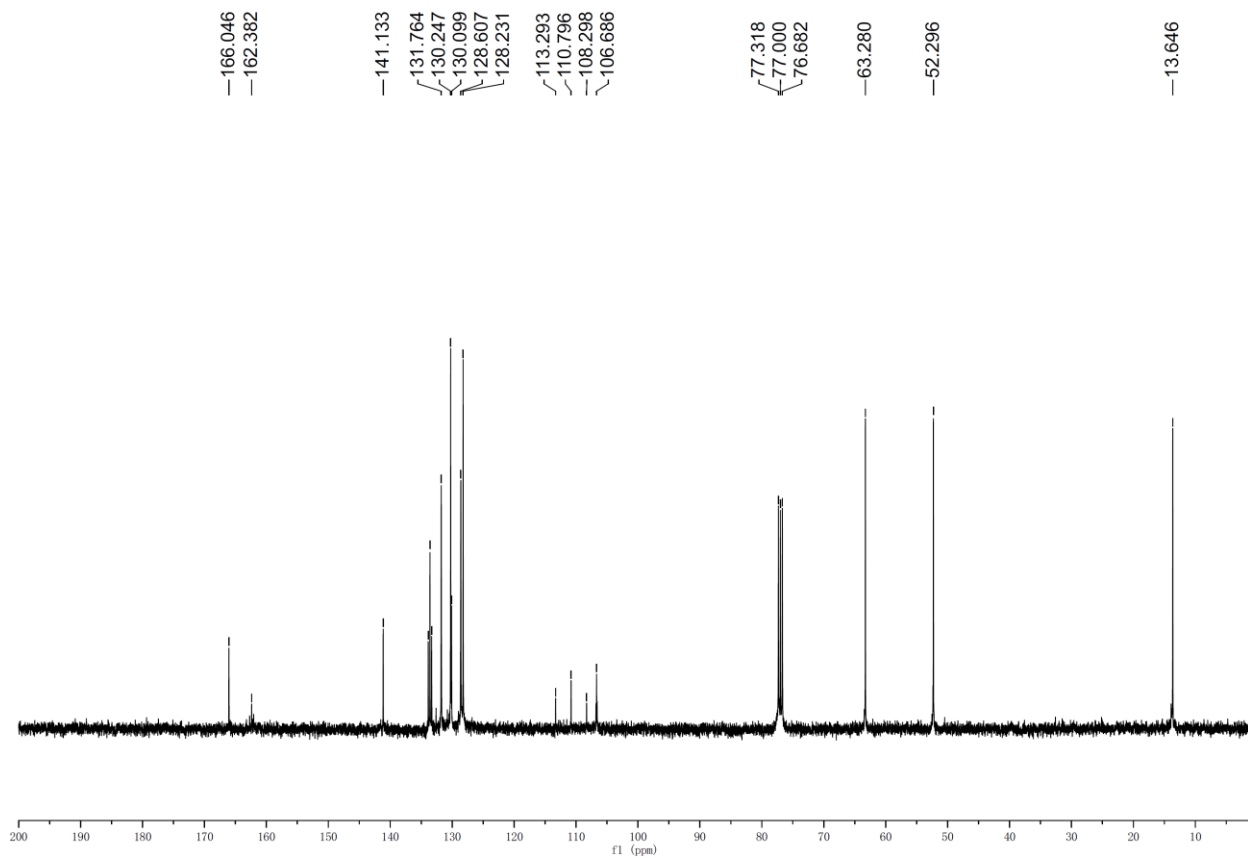
test001						USER: -- DATE: Nov 20 2018	
F1: 376.057	F2: 100.513	SW1: 89286	OF1: -31967.5	PTS1d: 65536	65536		
EX: s2pul	PW: 5.1 us	PD: 1.0 sec	NA: 16	LB: 0.0	Nuts - S2018501-6-52-5hf_FLUORINE_01.fid		

- 162.456
- 158.781
- 141.677
- 132.972
- 132.688
- 129.103
- 120.237
- 115.388
- 113.304
- 113.069
- 110.817
- 108.435
- 108.333
- 108.231
- 77.318
- 77.000
- 76.682
- 63.095
- 55.386
- 55.264
- 13.635

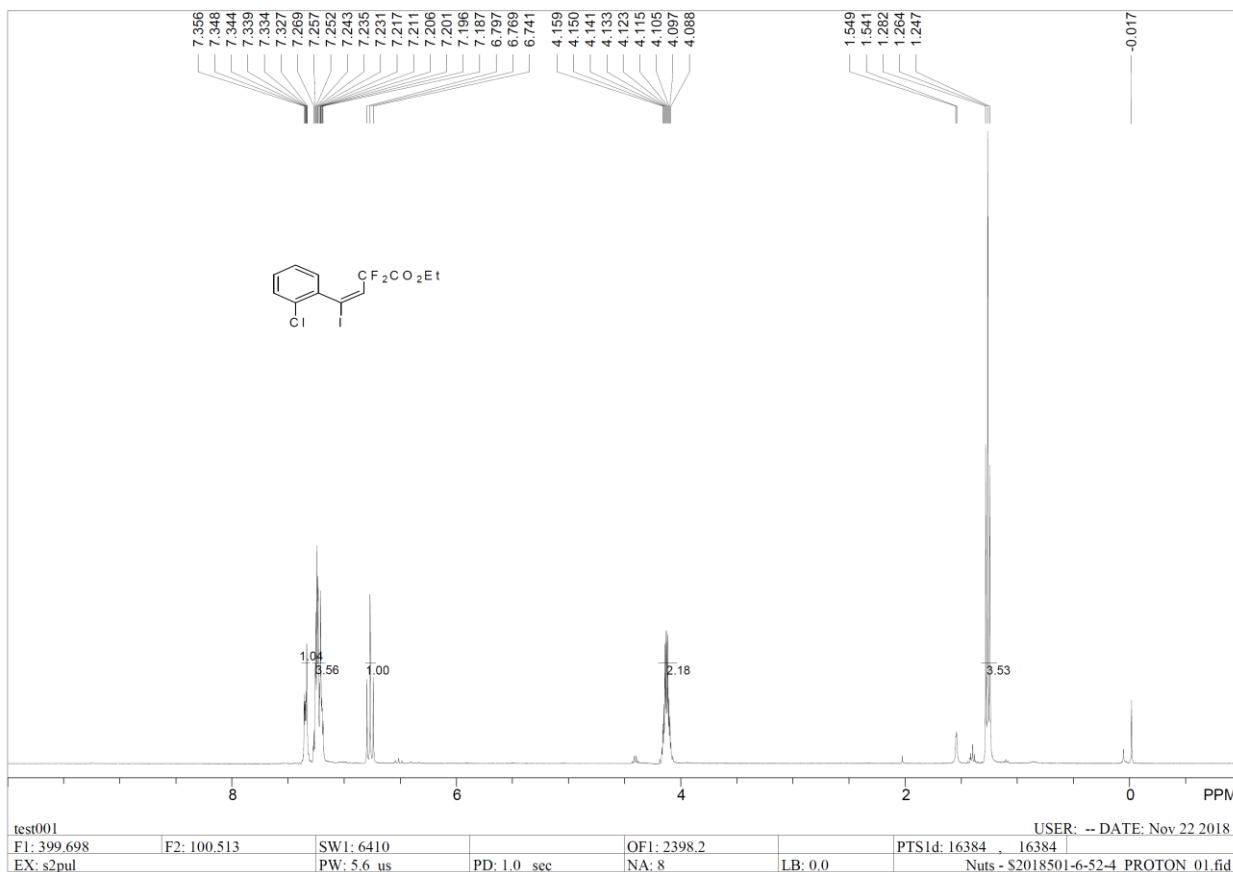


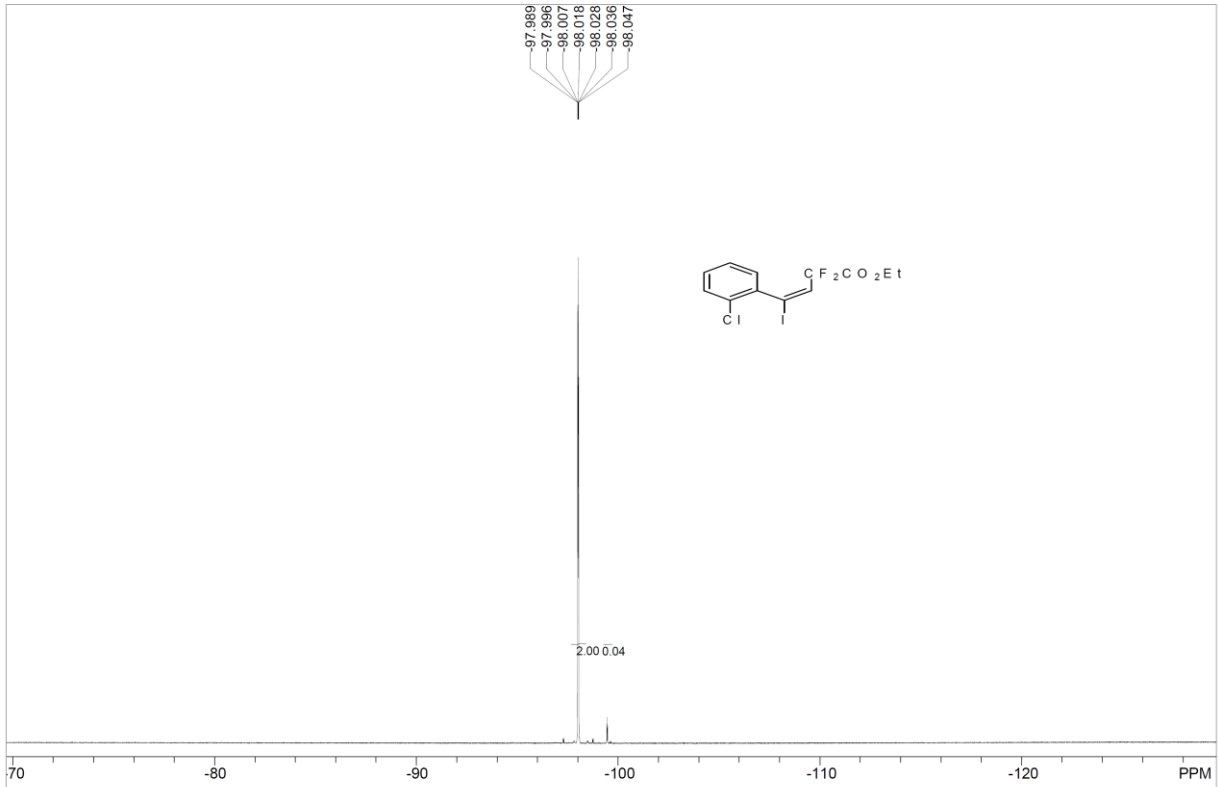
Methyl (*E*)-3-(4-ethoxy-3,3-difluoro-1-iodo-4-oxobut-1-en-1-yl)benzoate (5i).



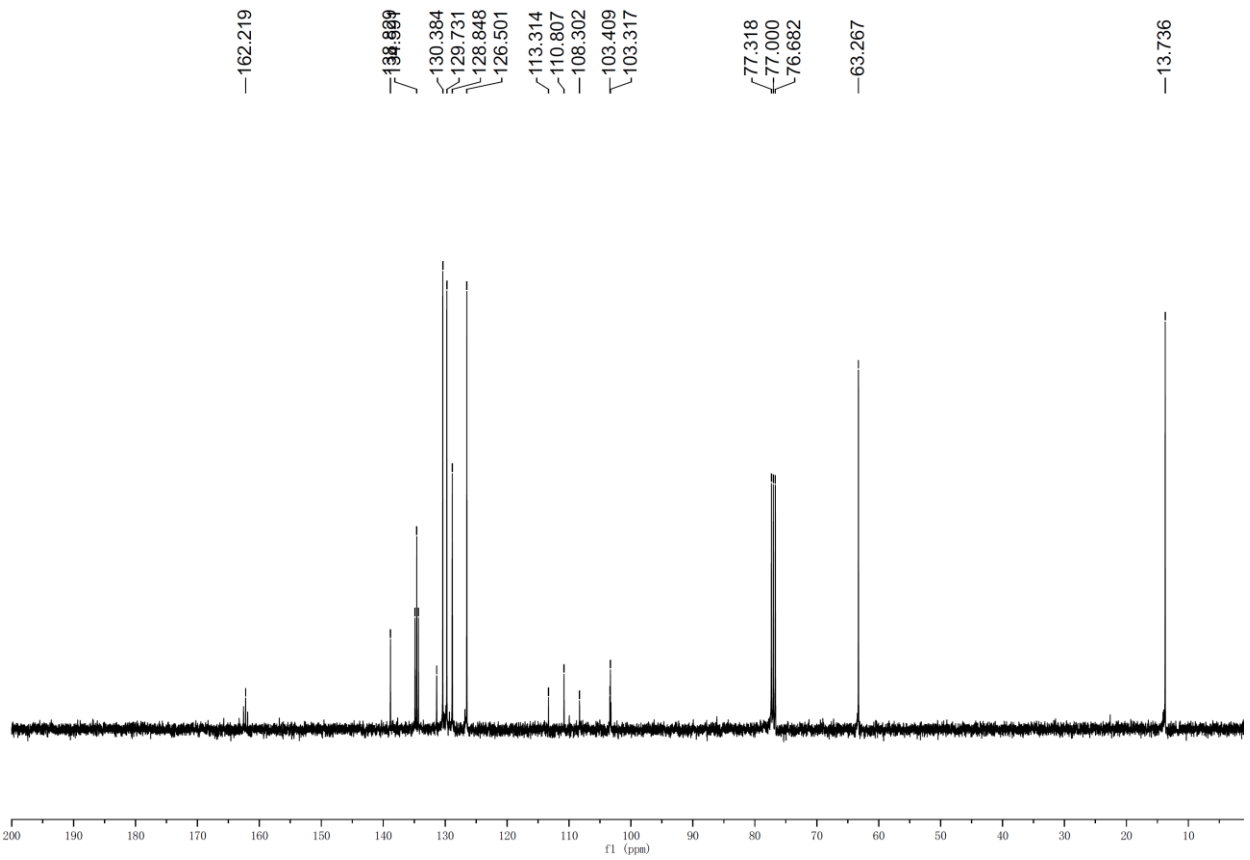


Ethyl (*E*)-4-(2-chlorophenyl)-2,2-difluoro-4-iodobut-3-enoate (5j).

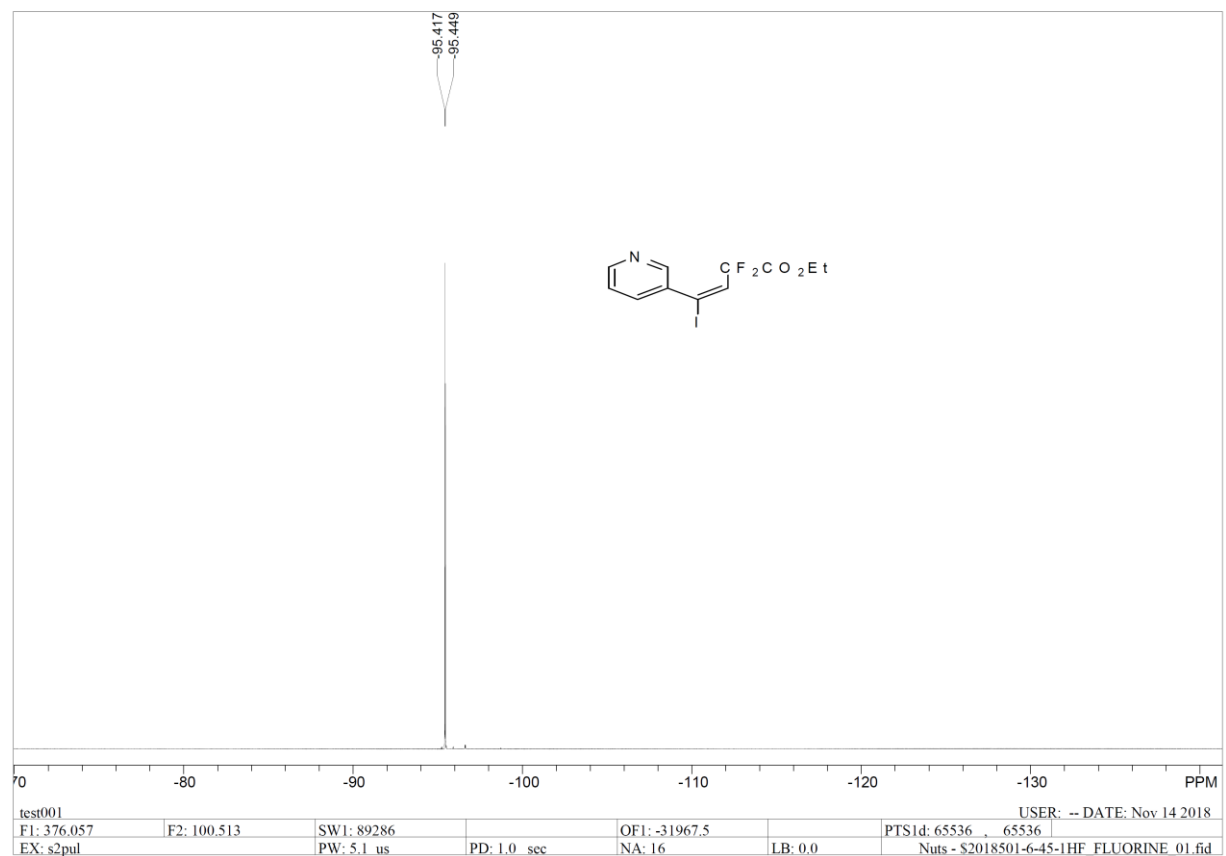
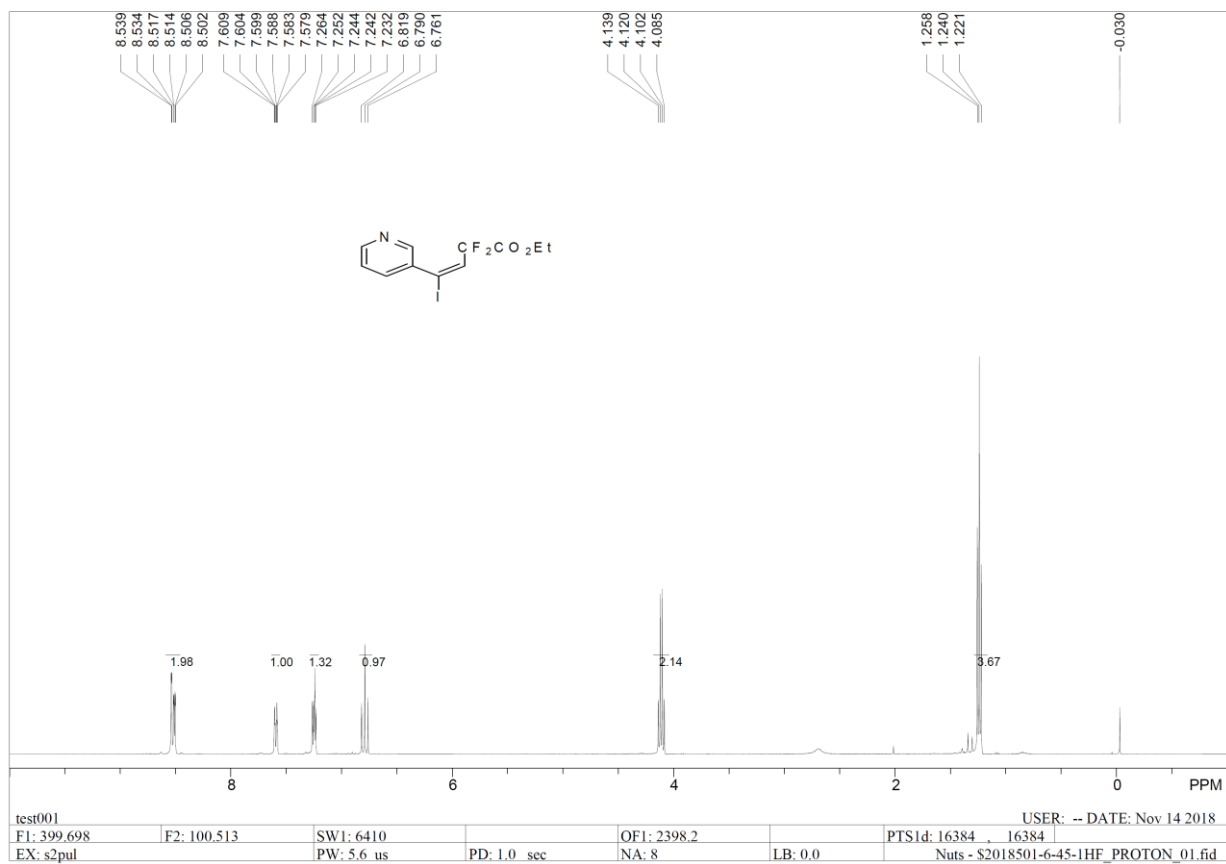


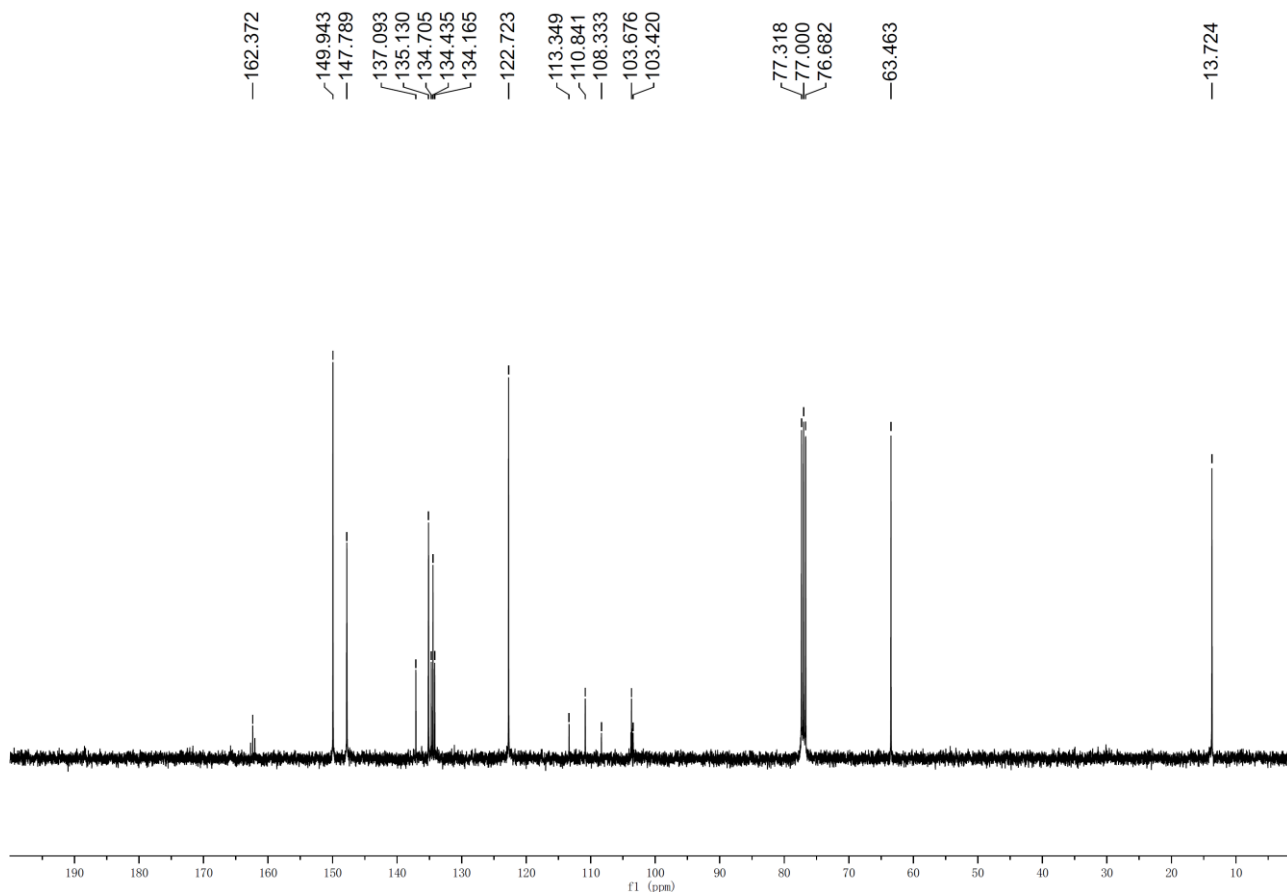


test001
 F1: 376.057 F2: 100.513 SW1: 89286 OF1: -31967.5 PTS1d: 65536 , 65536 USER: -- DATE: Nov 22 2018
 EX: s2pul PW: 5.1 us PD: 1.0 sec NA: 16 LB: 0.0 Nuts - S2018501-6-52-4_FLUORINE_01.fid

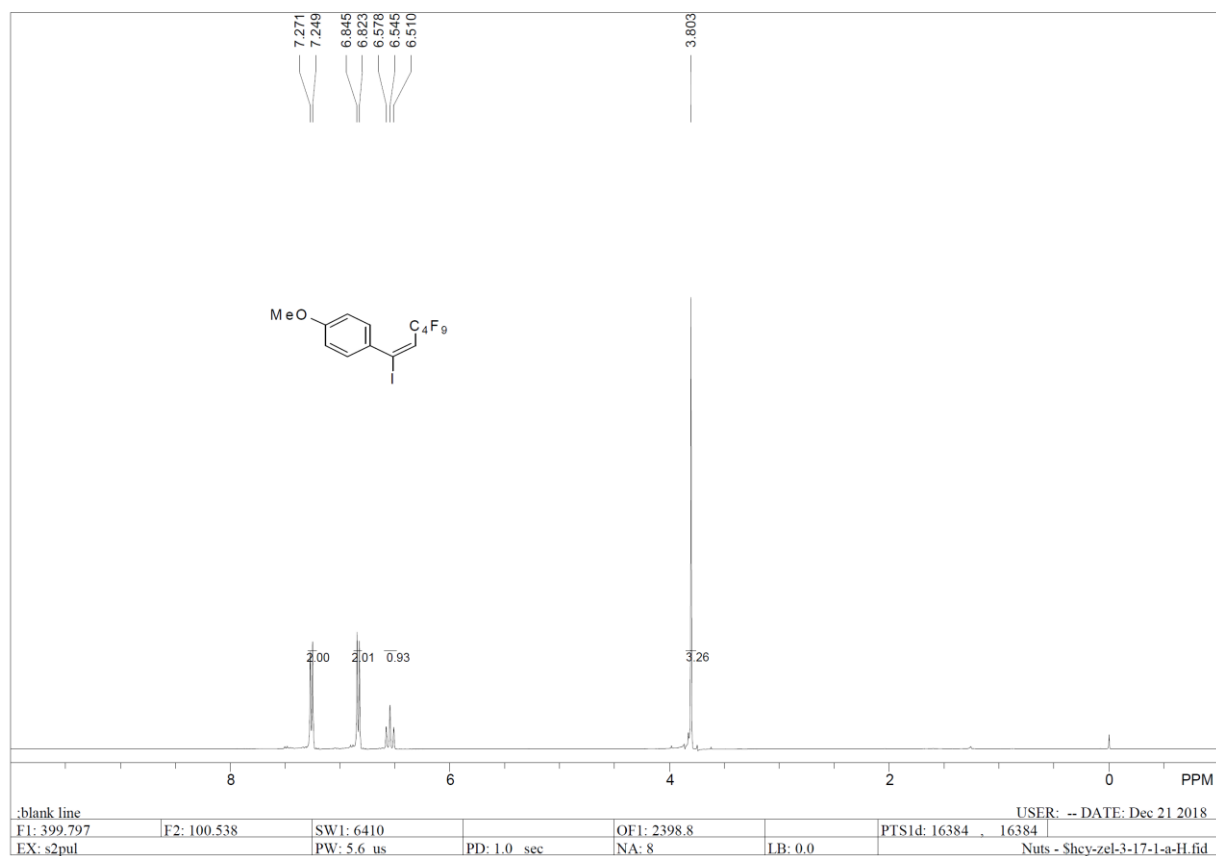


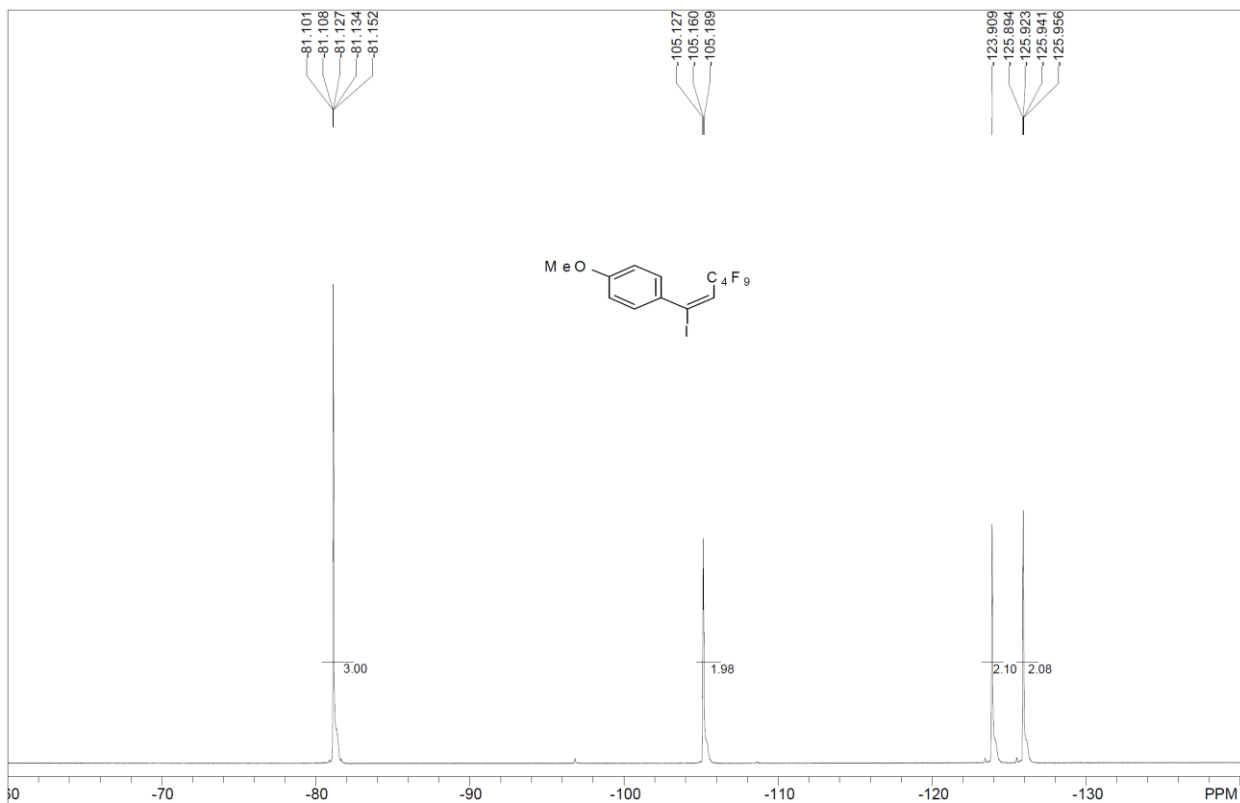
Ethyl (E)-2,2-difluoro-4-iodo-4-(pyridin-3-yl)but-3-enoate (5k).



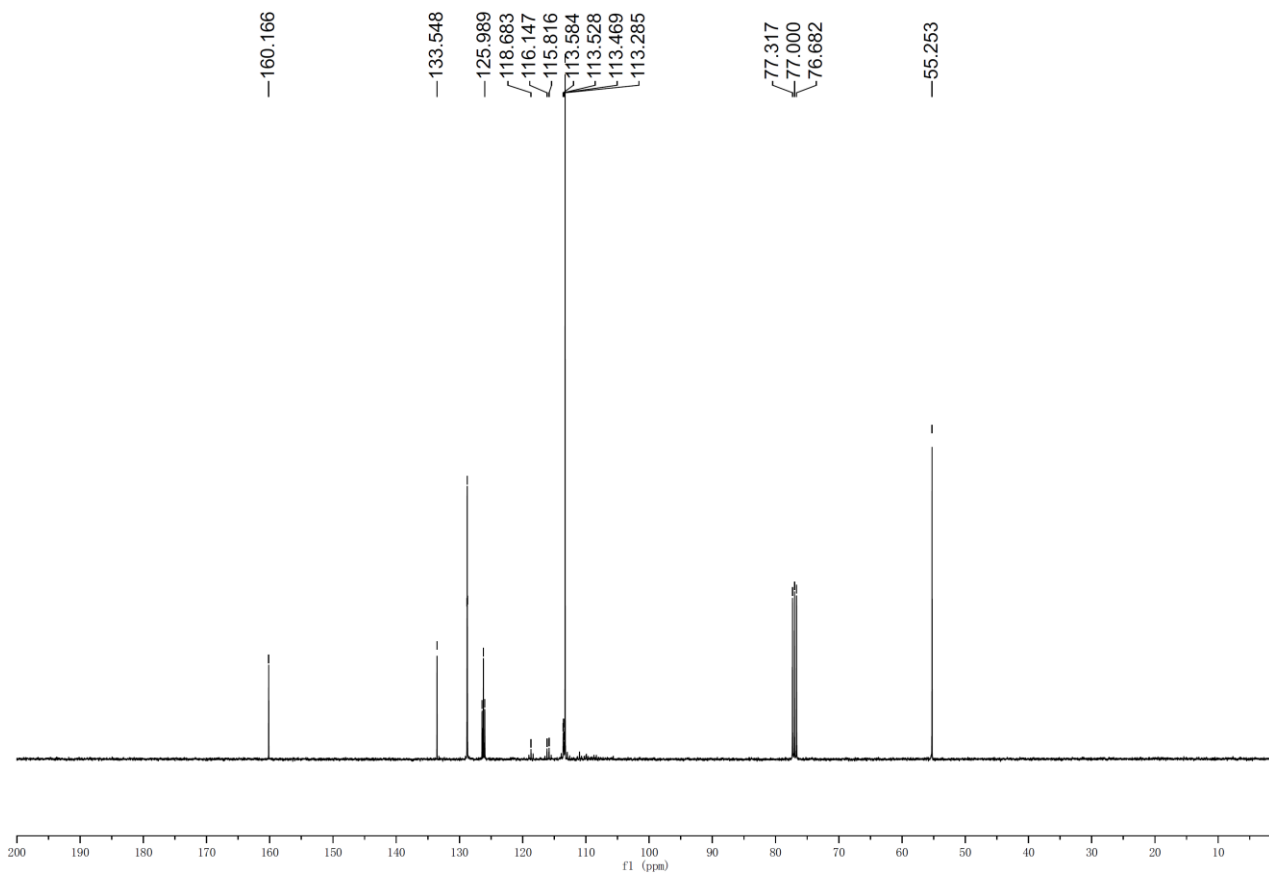


(E)-1-Methoxy-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (5l).

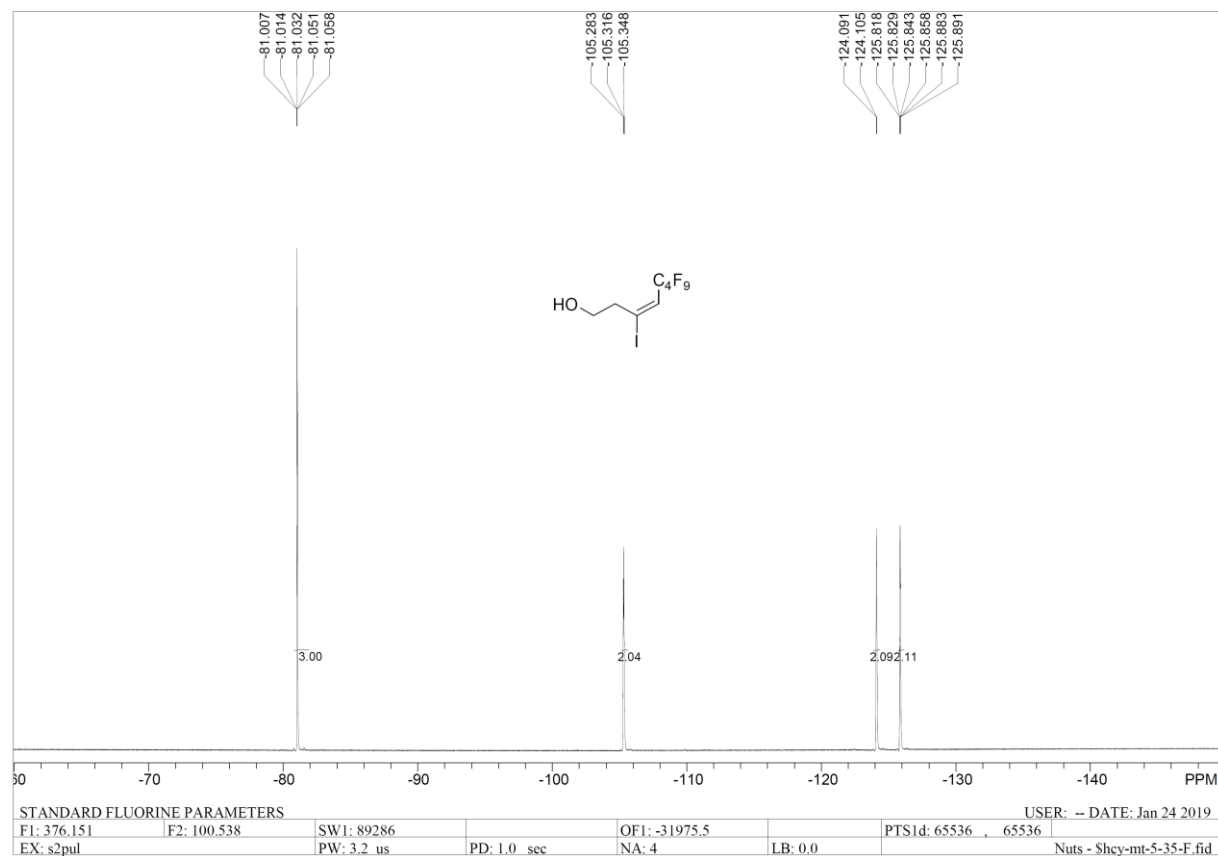
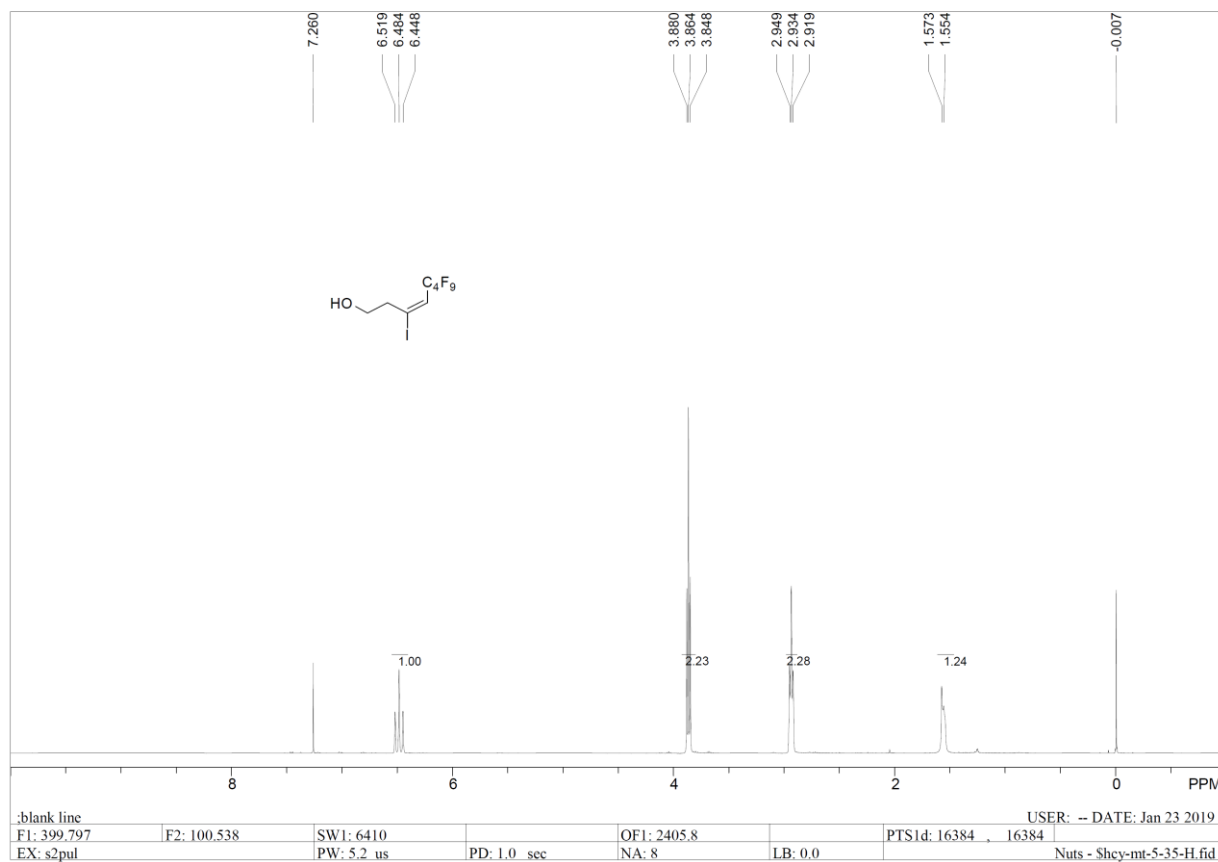


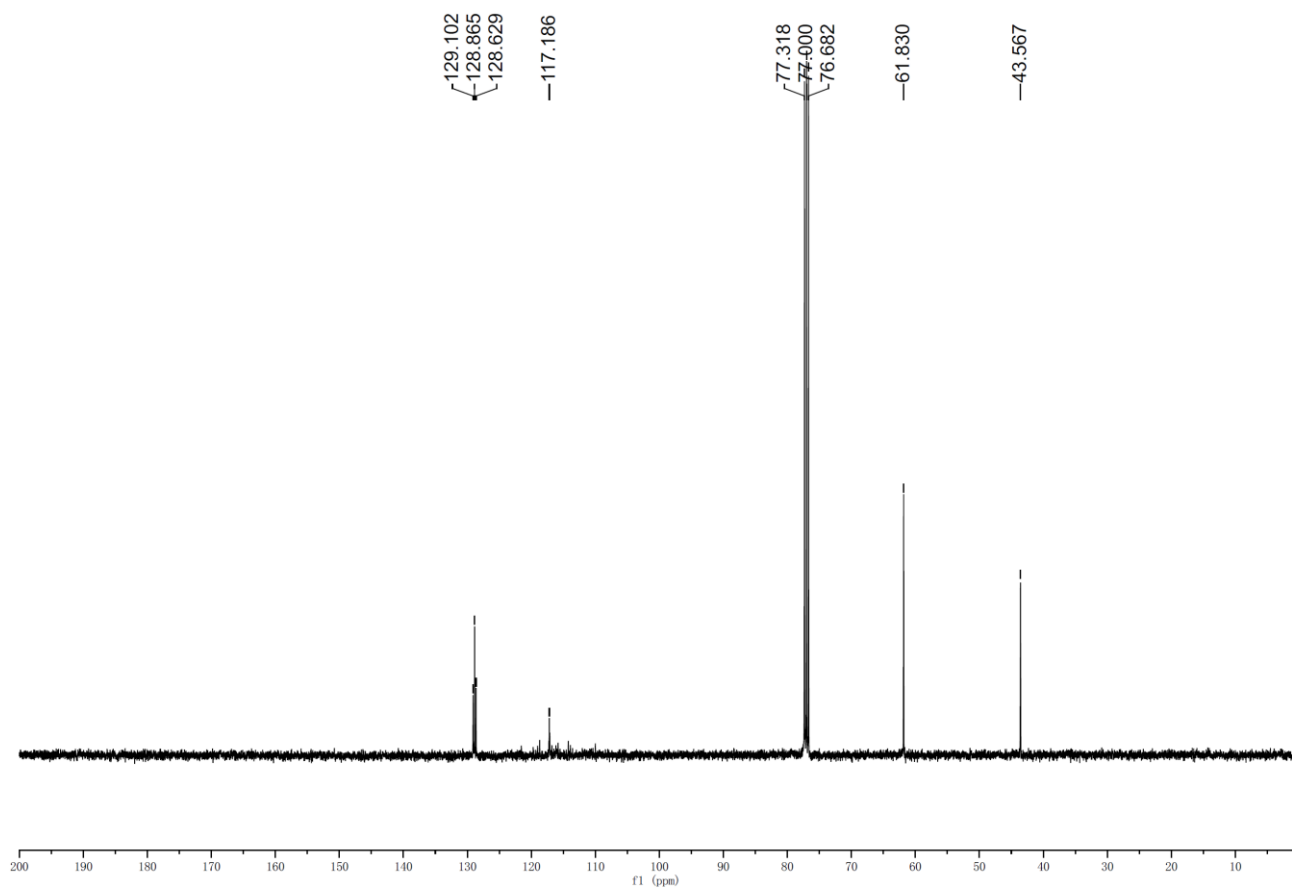


STANDARD FLUORINE PARAMETERS						USER: -- DATE: Dec 24 2018
F1: 376.151	F2: 100.538	SW1: 89286	OF1: -31975.5	PTS1d: 65536	65536	
EX: s2pul	PW: 3.2 us	PD: 1.0 sec	NA: 4	LB: 0.0	Nuts - Shcy-zel-3-17-1-a-F.fid	

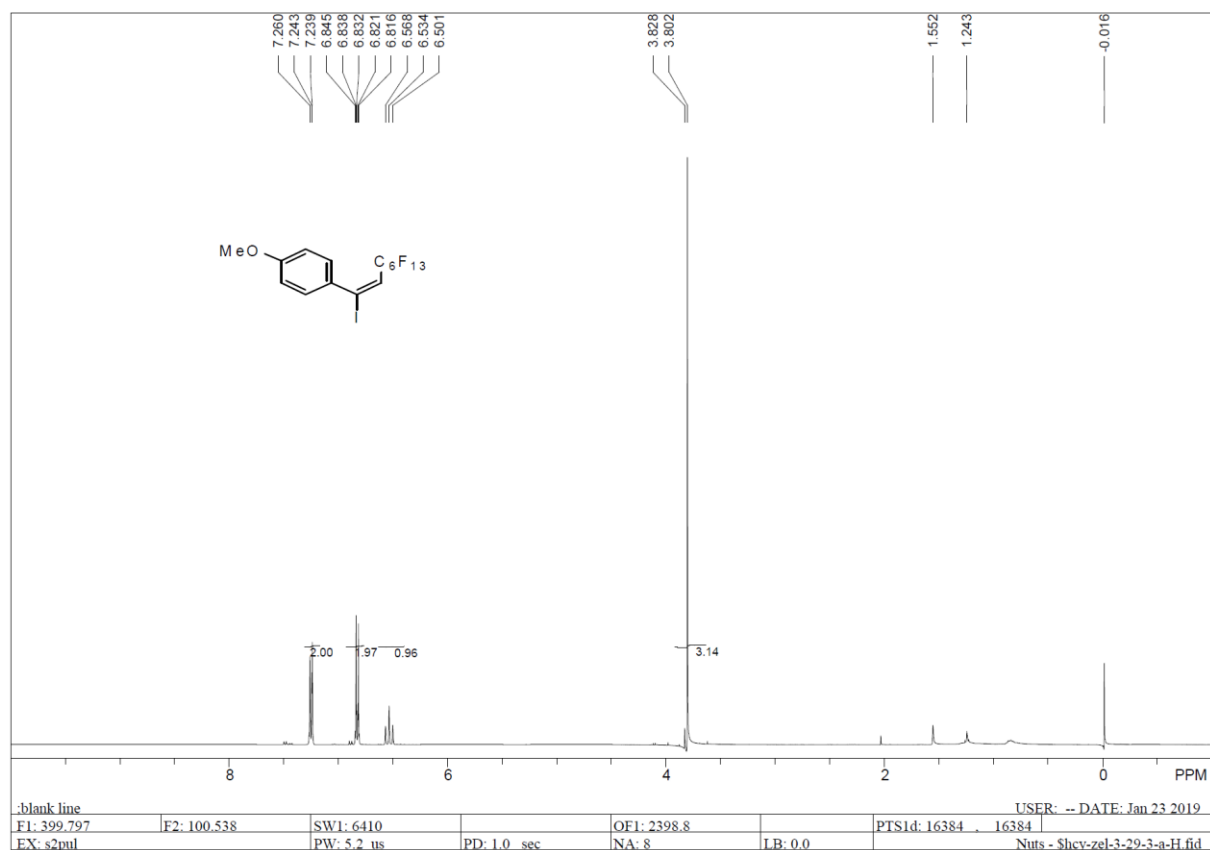


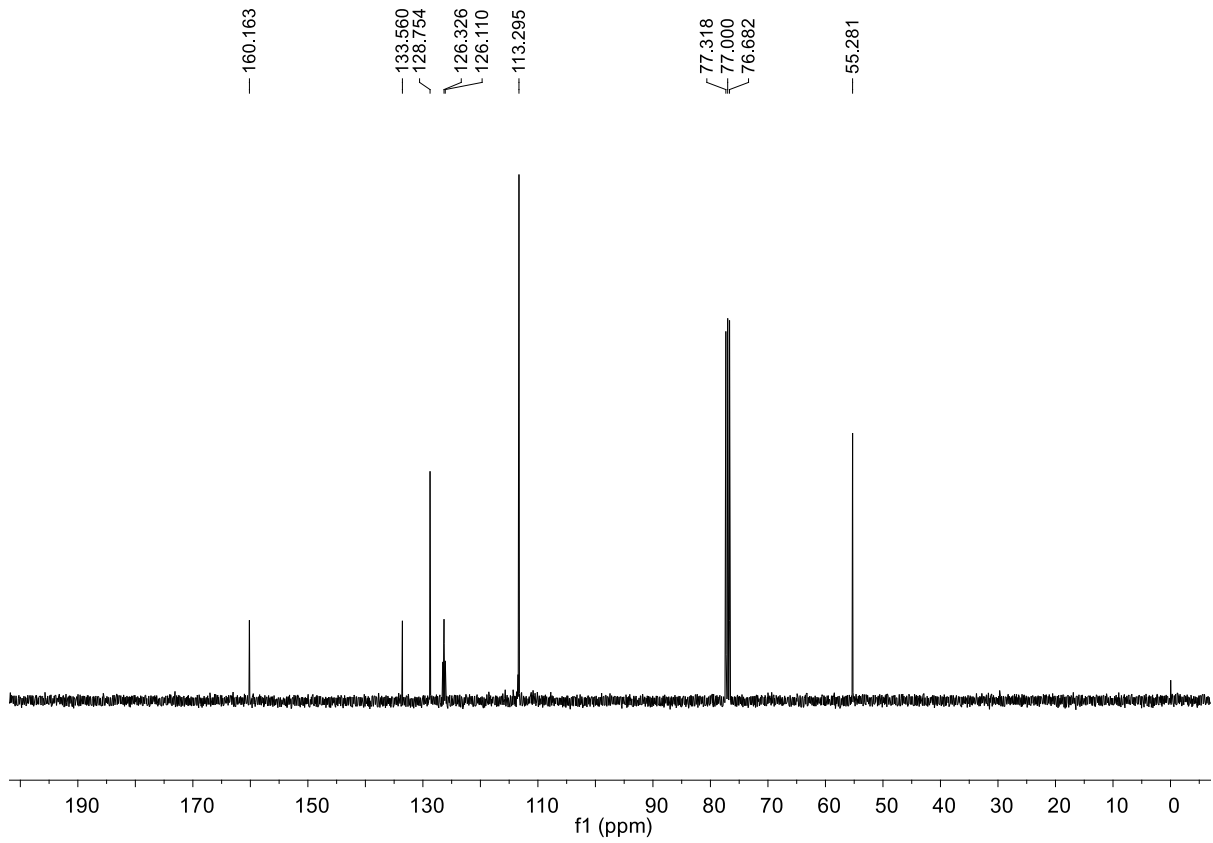
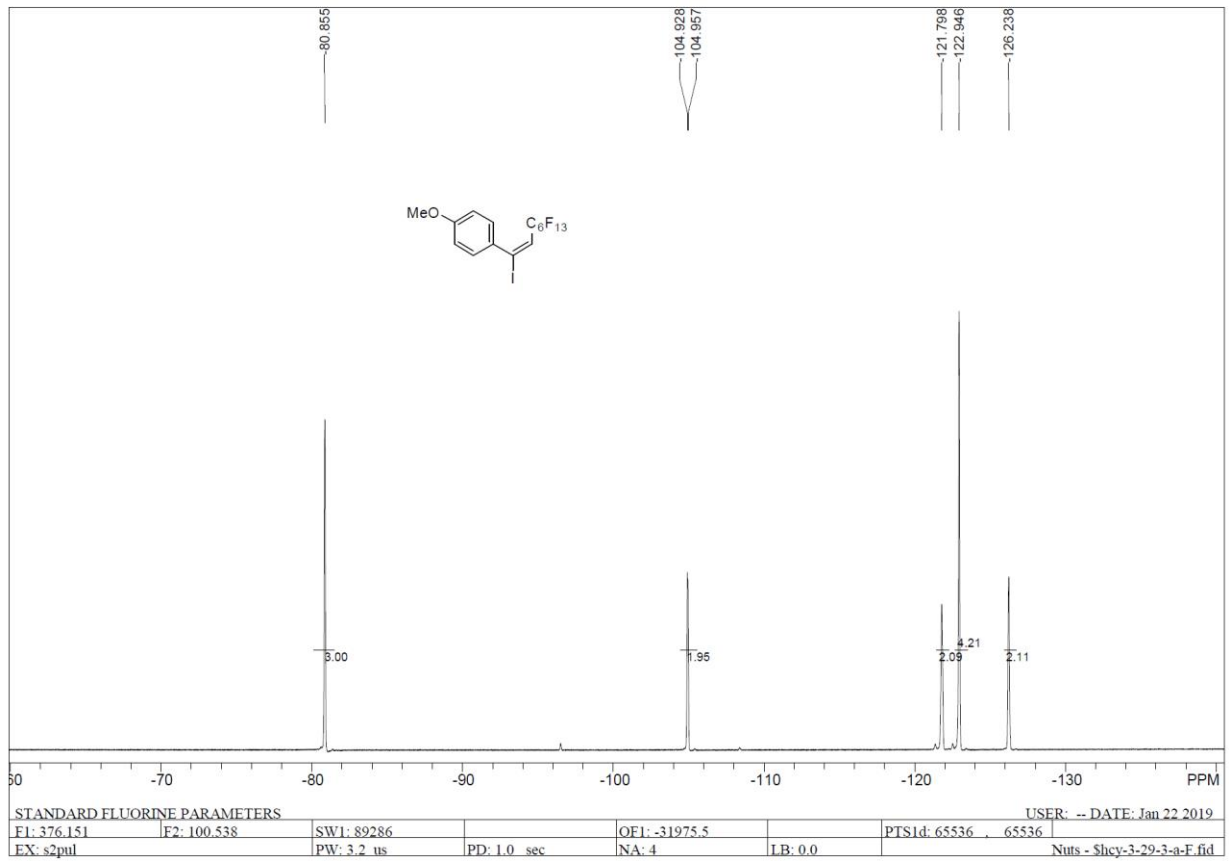
(E)-5,5,6,6,7,7,8,8,8-Nonafluoro-3-iodooct-3-en-1-ol (5m).



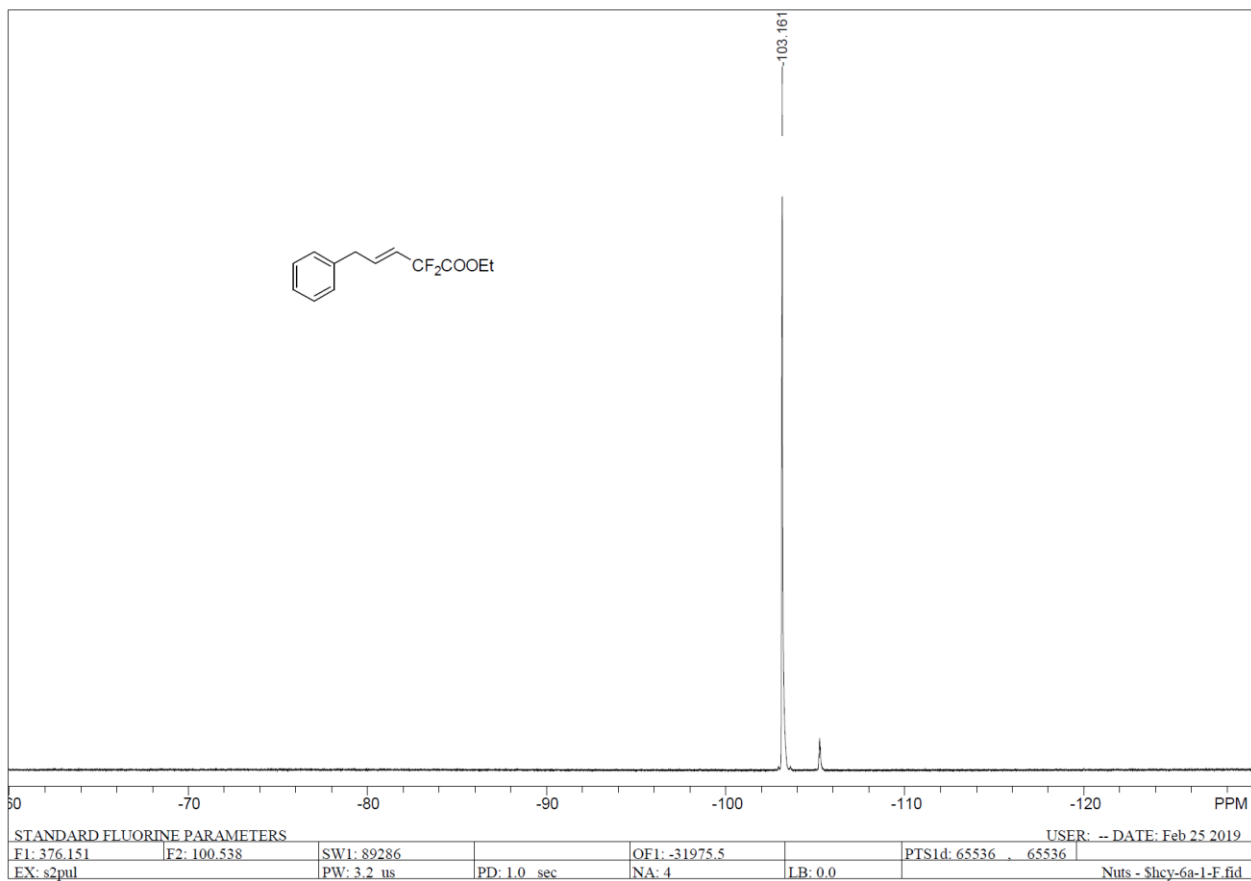
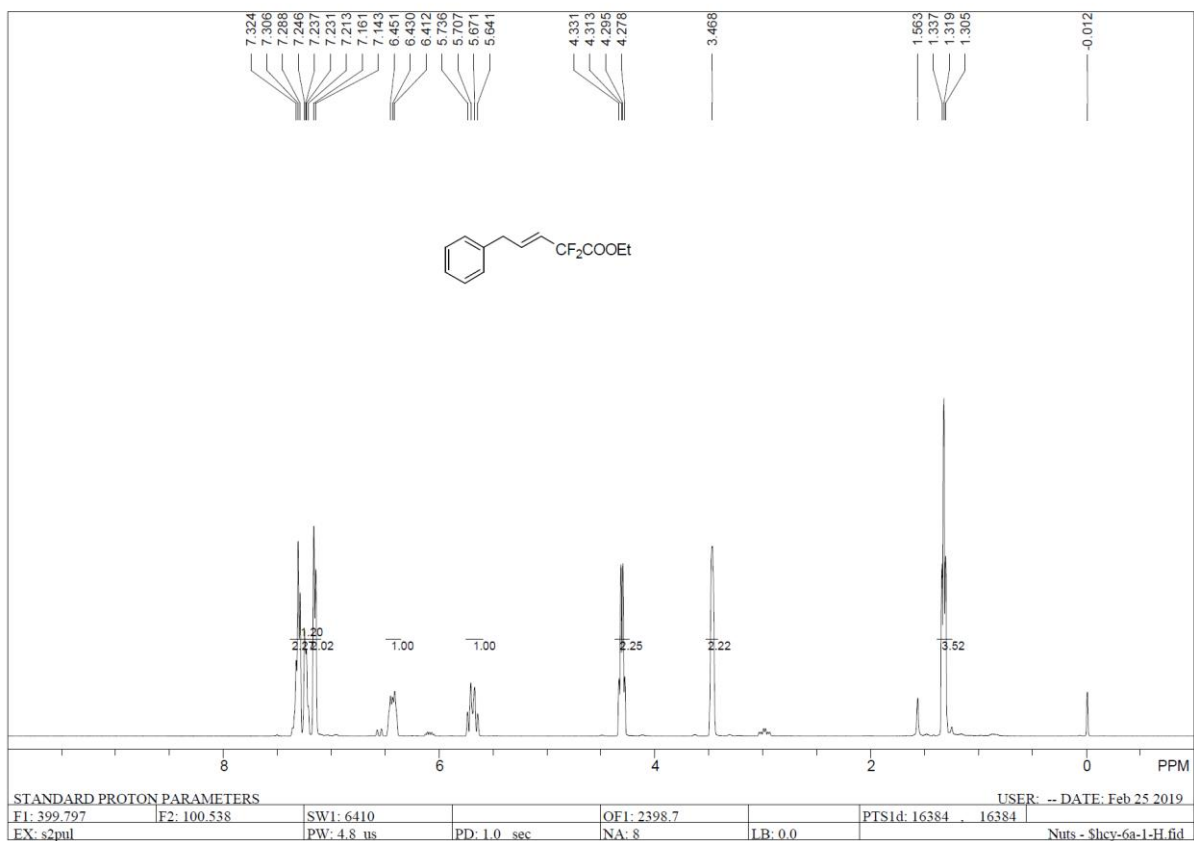


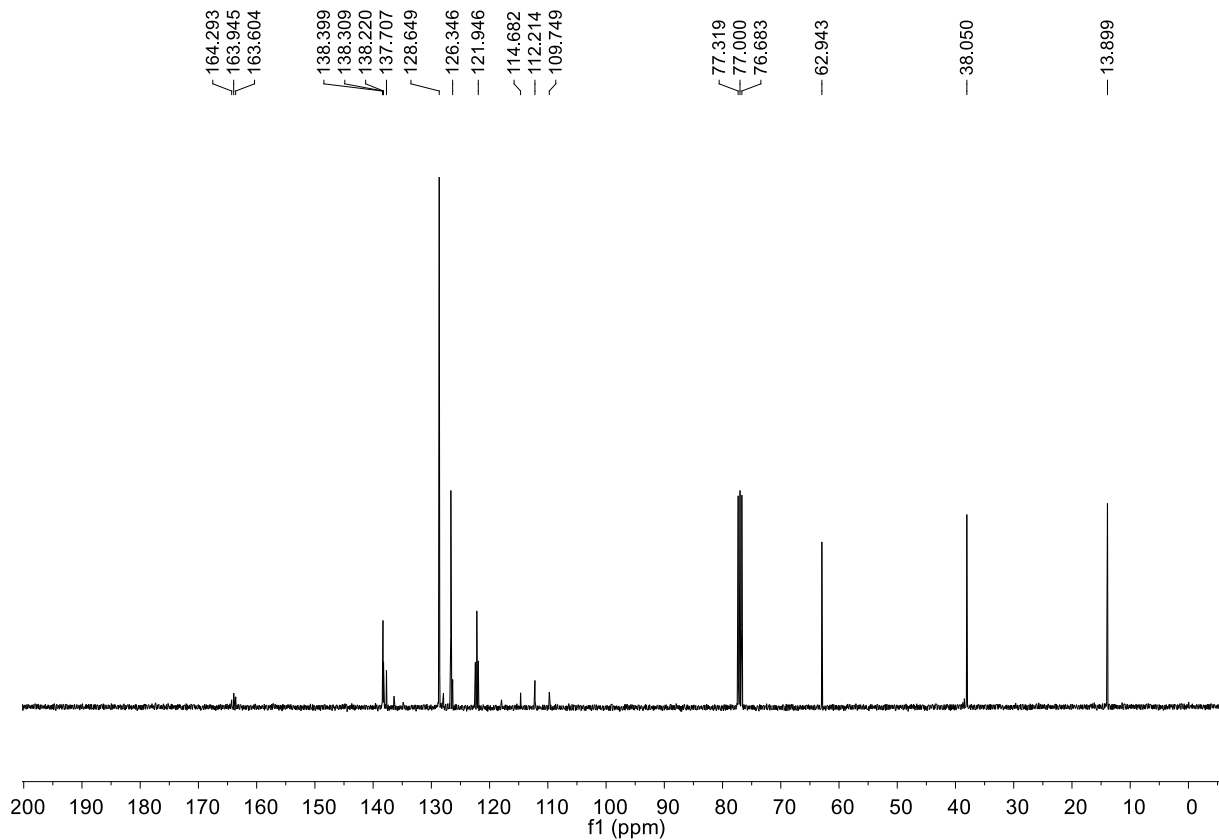
(E)-1-Methyl-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-iodooct-1-en-1-yl)benzene (5n).



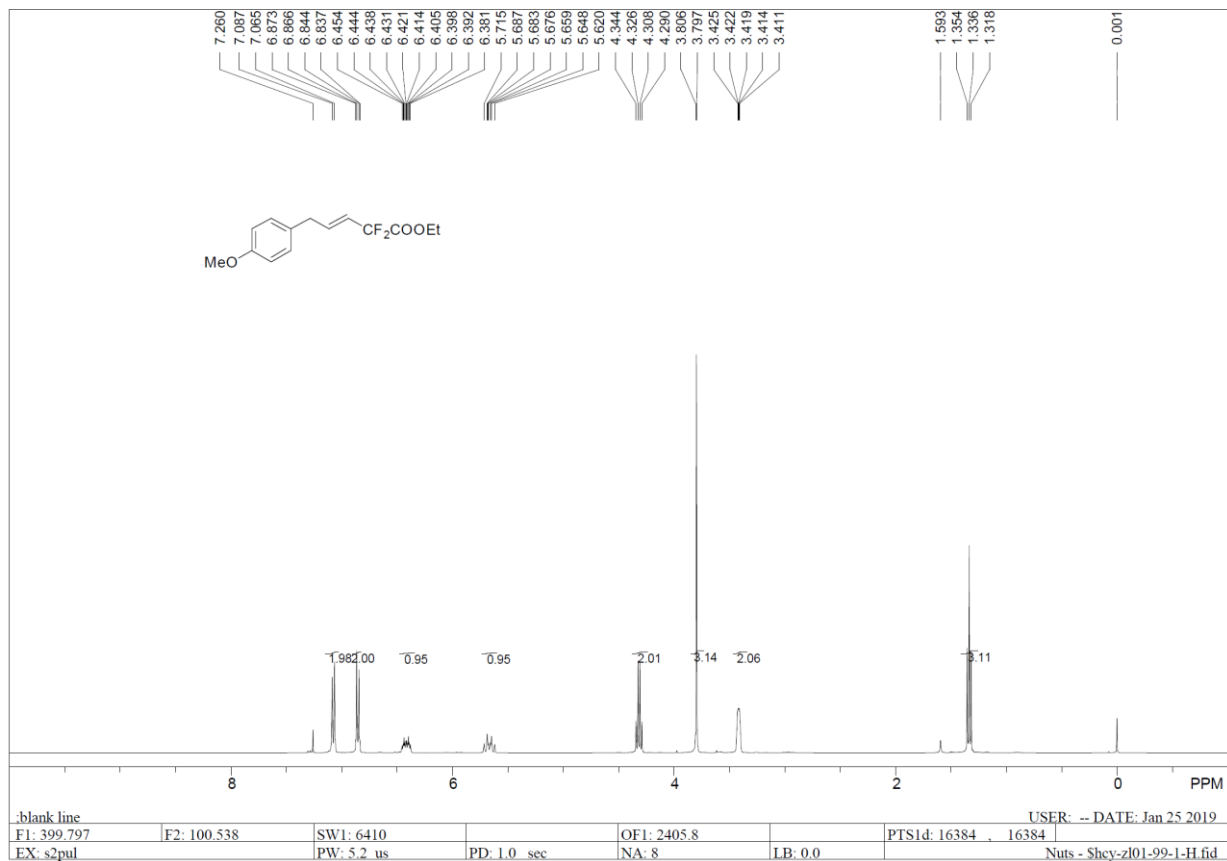


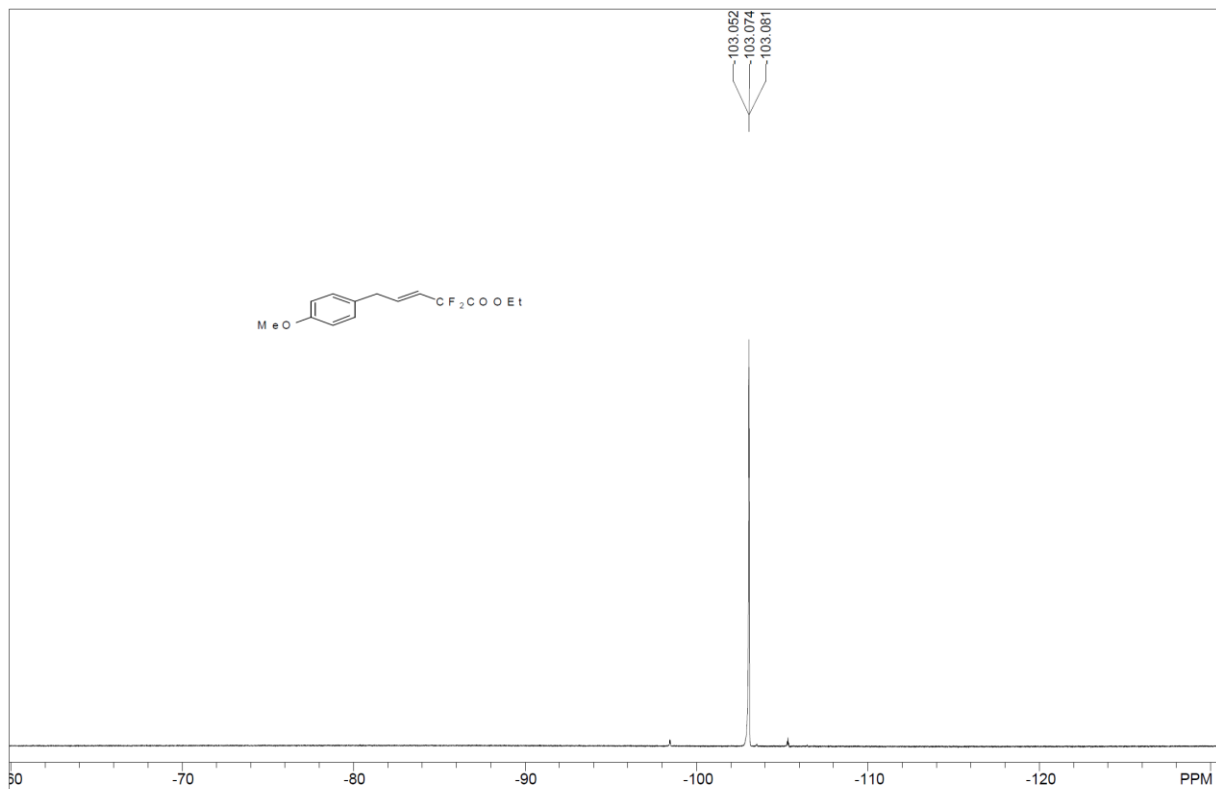
Ethyl (E)-2,2-difluoro-5-phenylpent-3-enoate (6a).



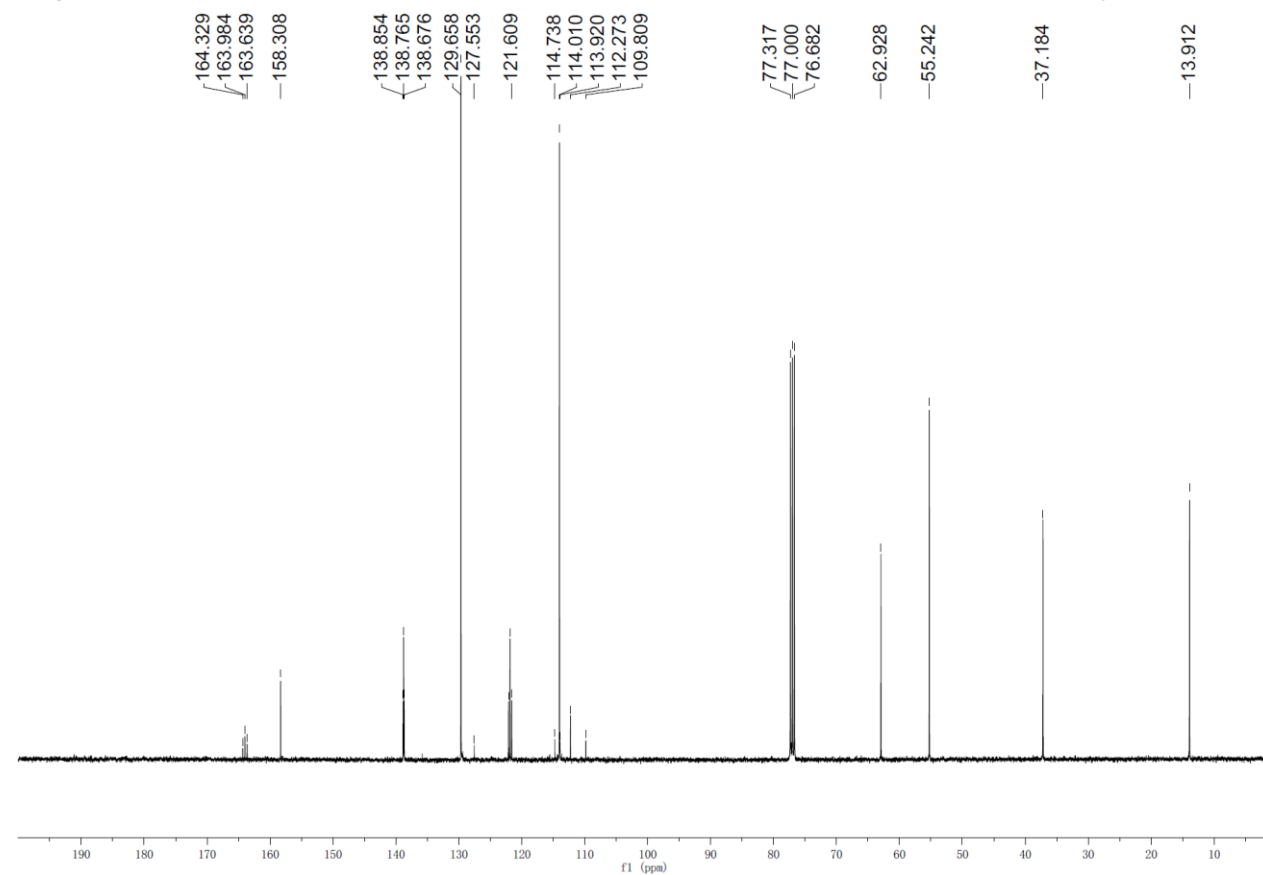


Ethyl (*E*)-2,2-difluoro-5-(4-methoxyphenyl)pent-3-enoate (6b).

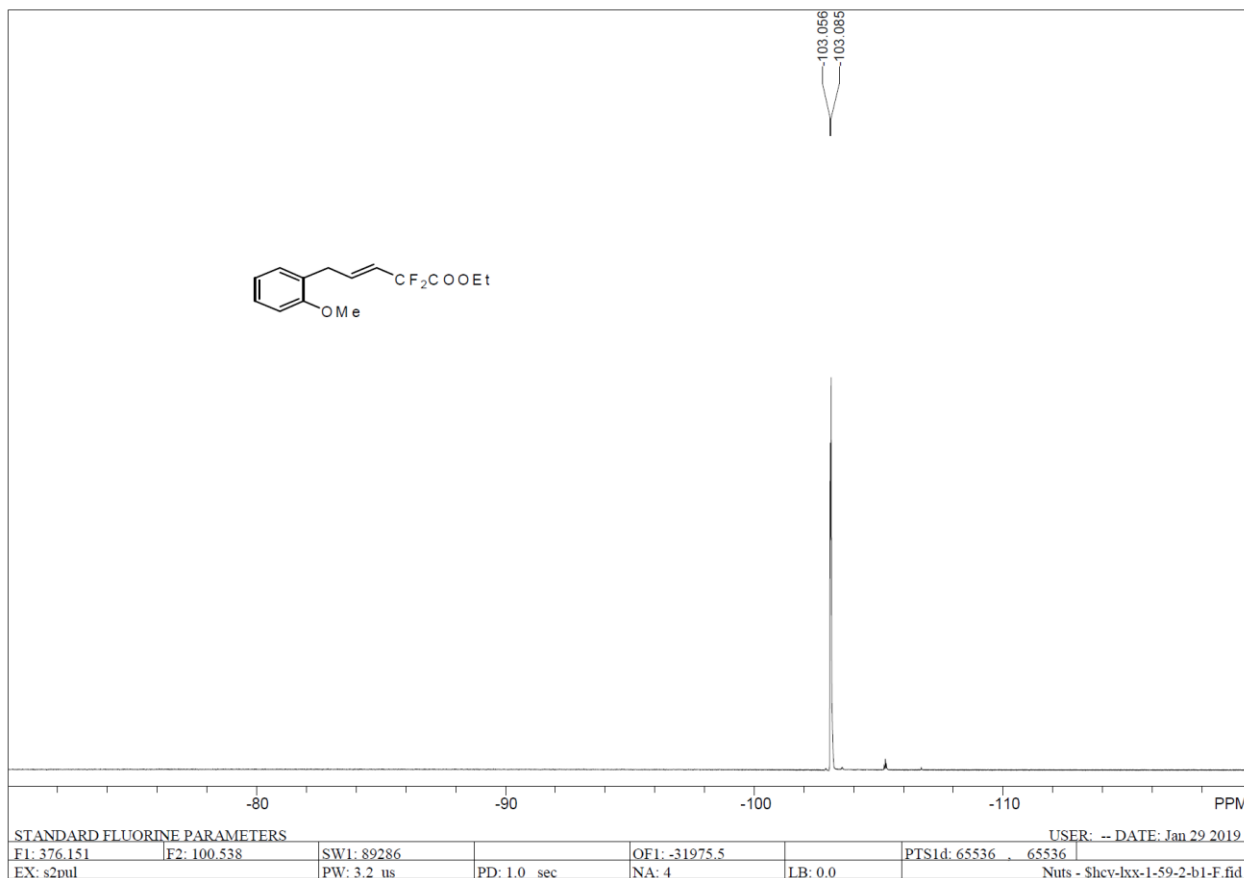
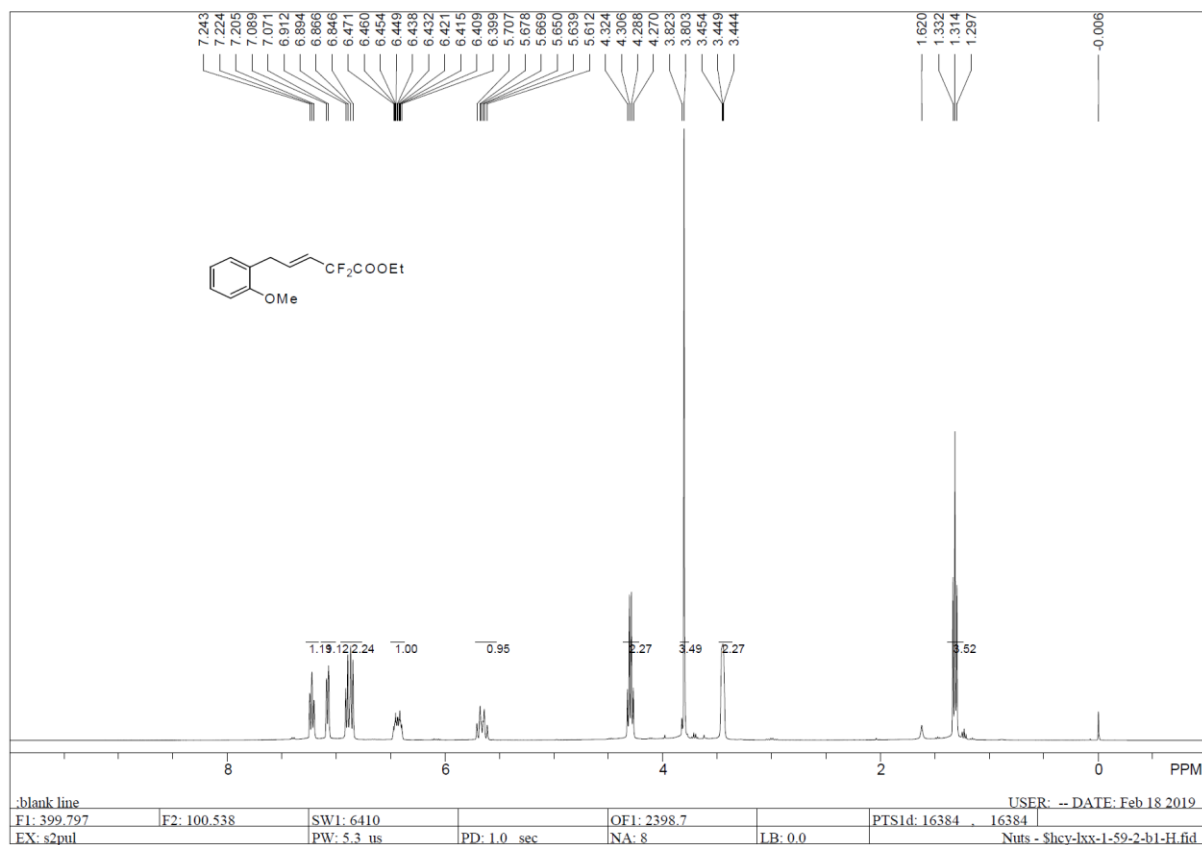


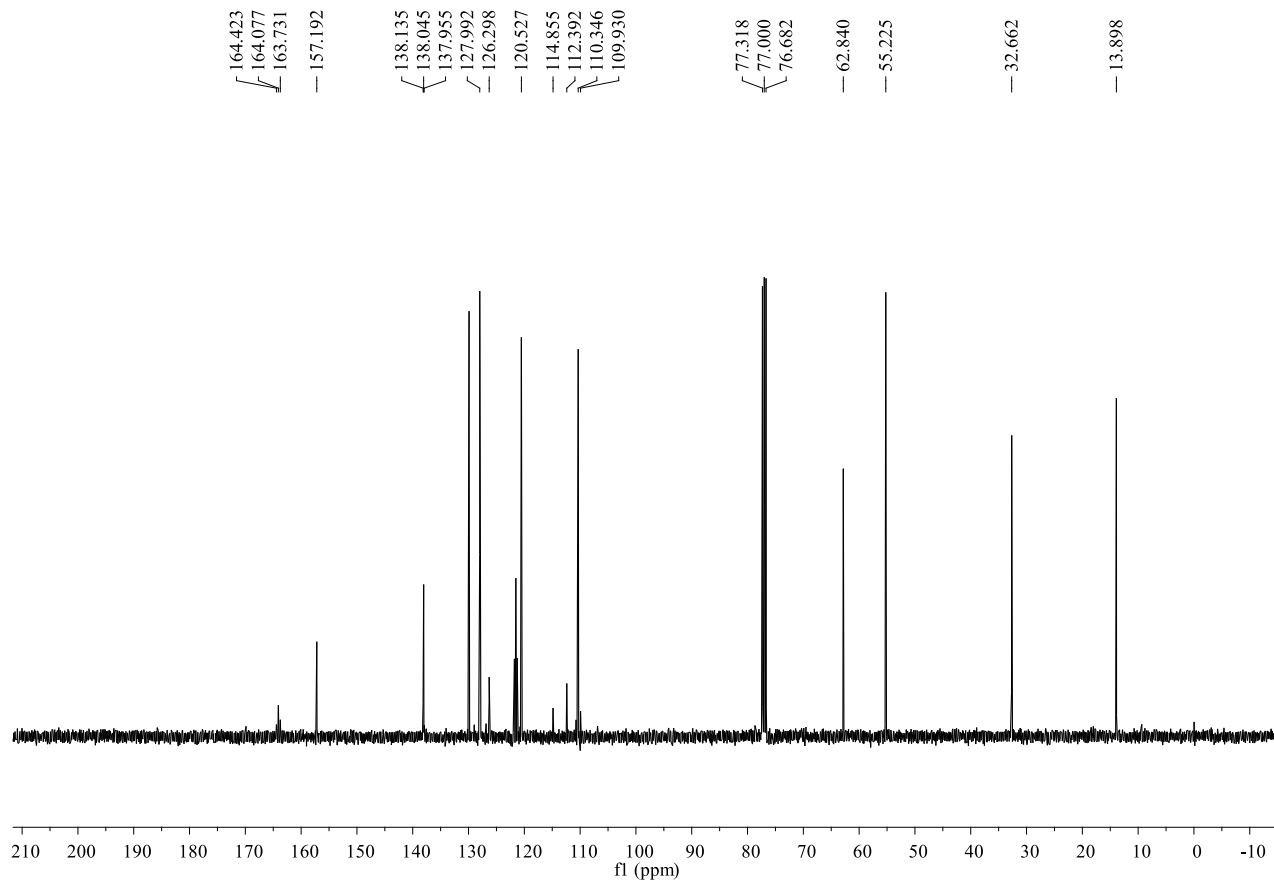


STANDARD FLUORINE PARAMETERS
 F1: 376.151 F2: 100.538 SW1: 89286 OF1: -31975.5 USER: -- DATE: Jan 25 2019
 EX: s2pul PW: 3.2 us PD: 1.0 sec NA: 4 LB: 0.0 PTS1d: 65536 65536
 Nuts - Shcy-zlo1-99-1-F.fid

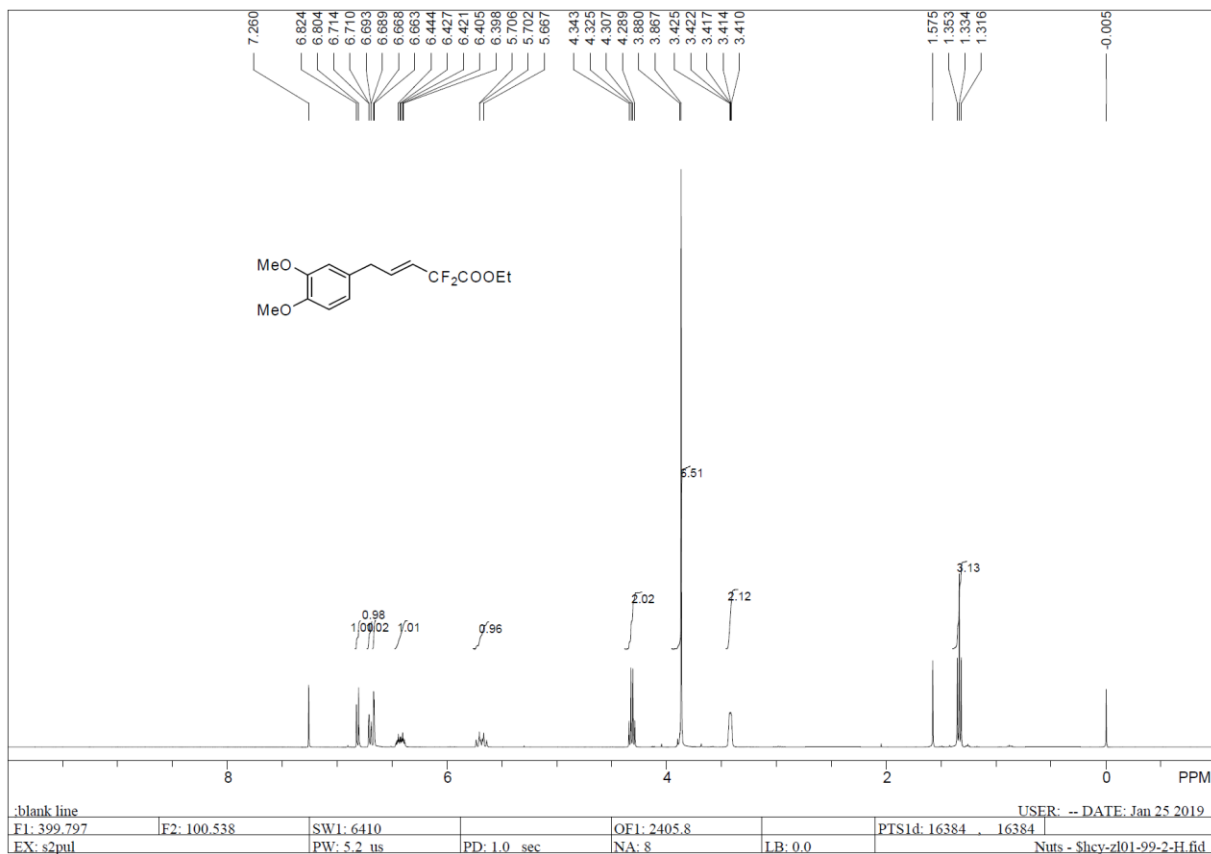


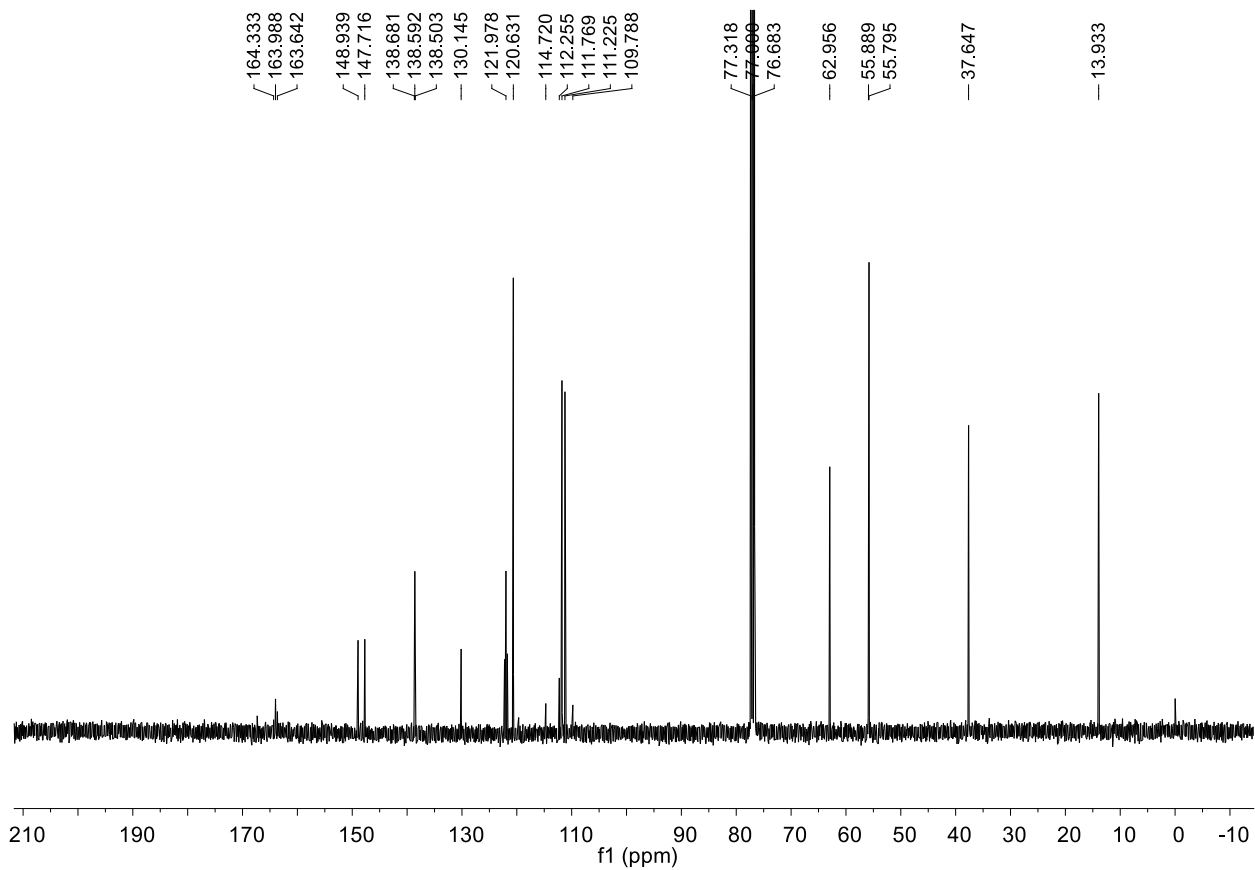
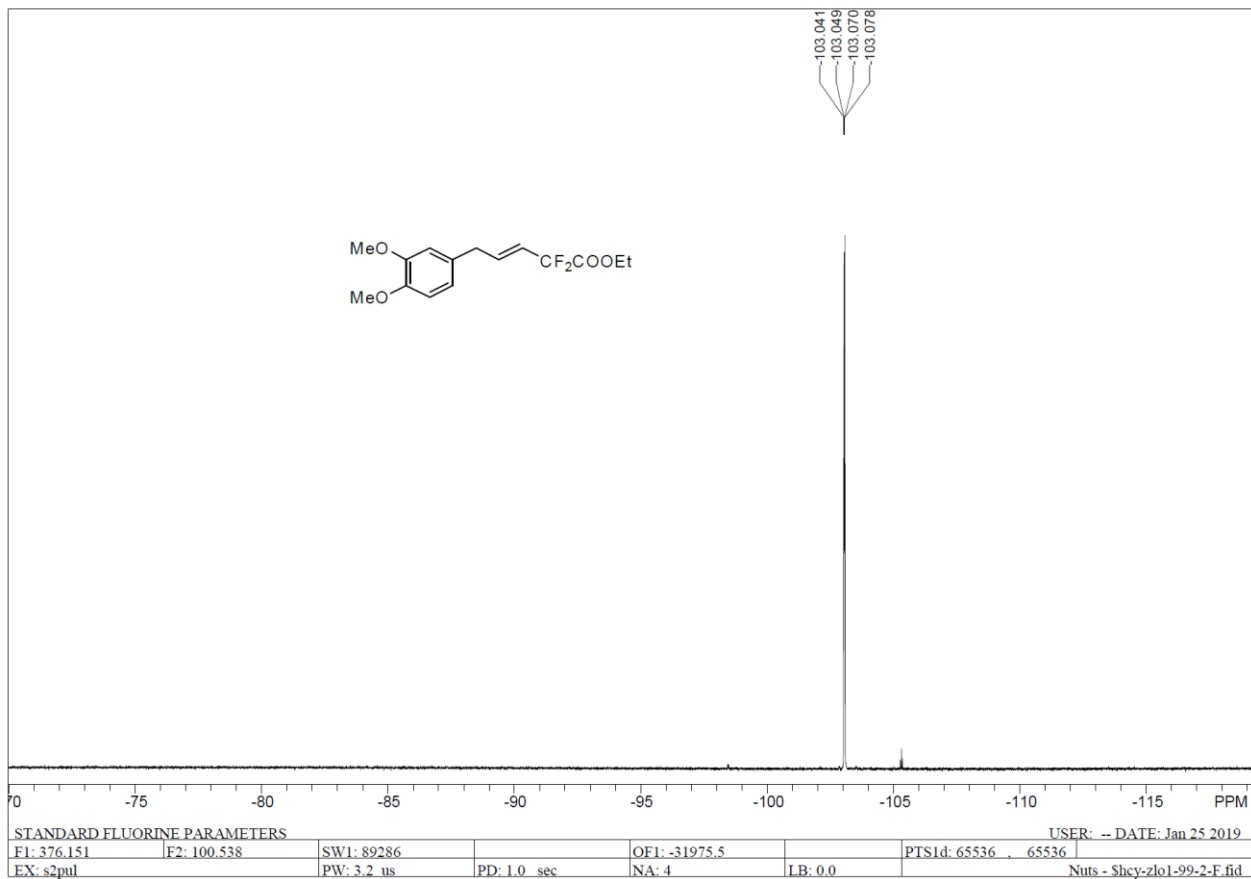
Ethyl (E)-2,2-difluoro-5-(2-methoxyphenyl)pent-3-enoate (6c).



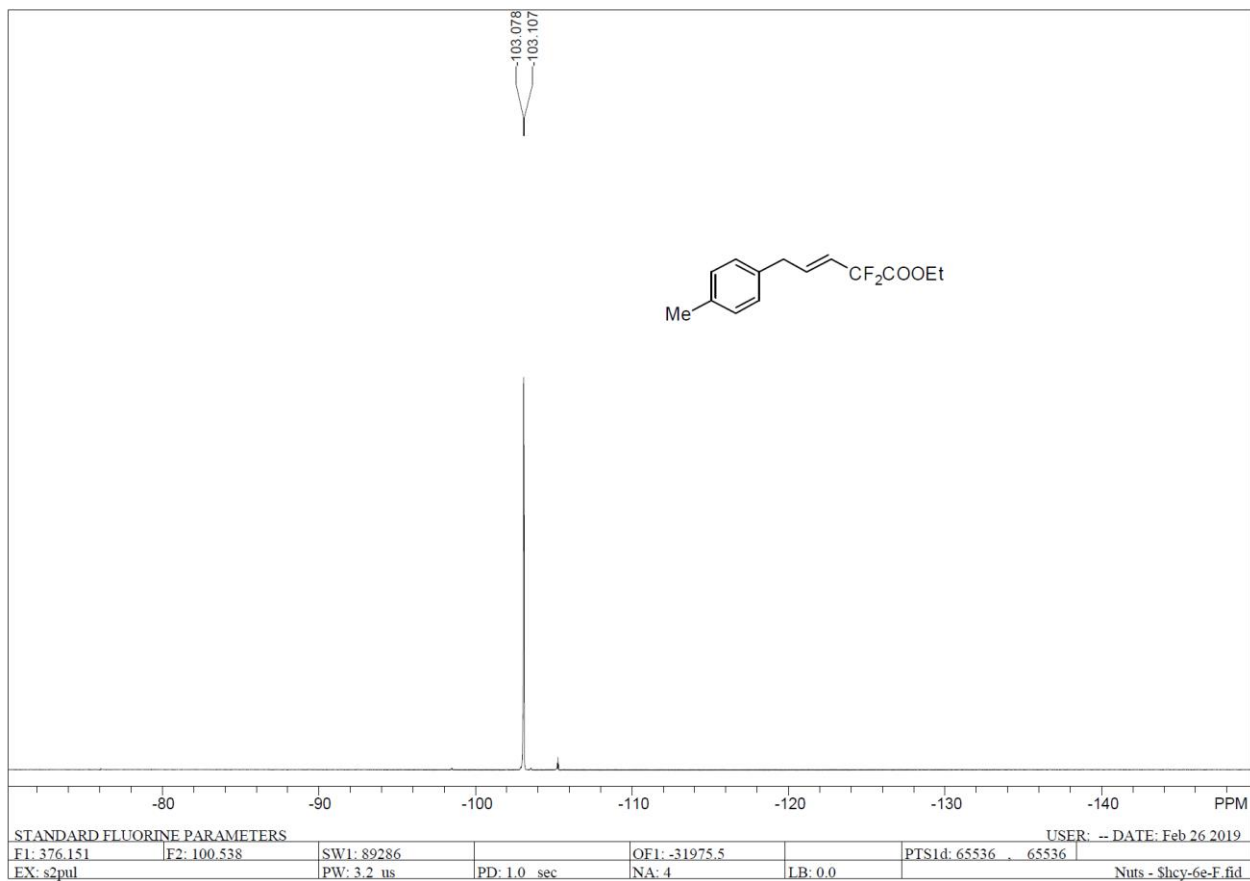
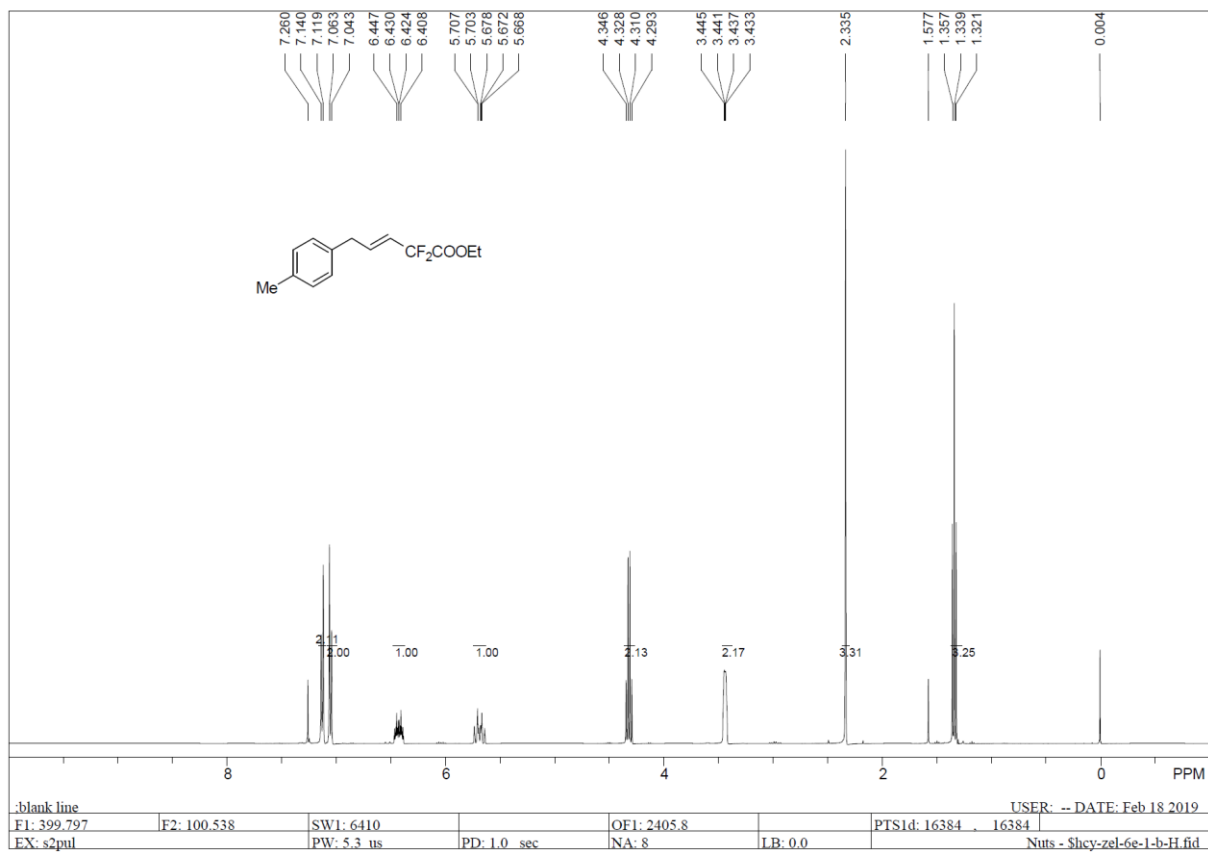


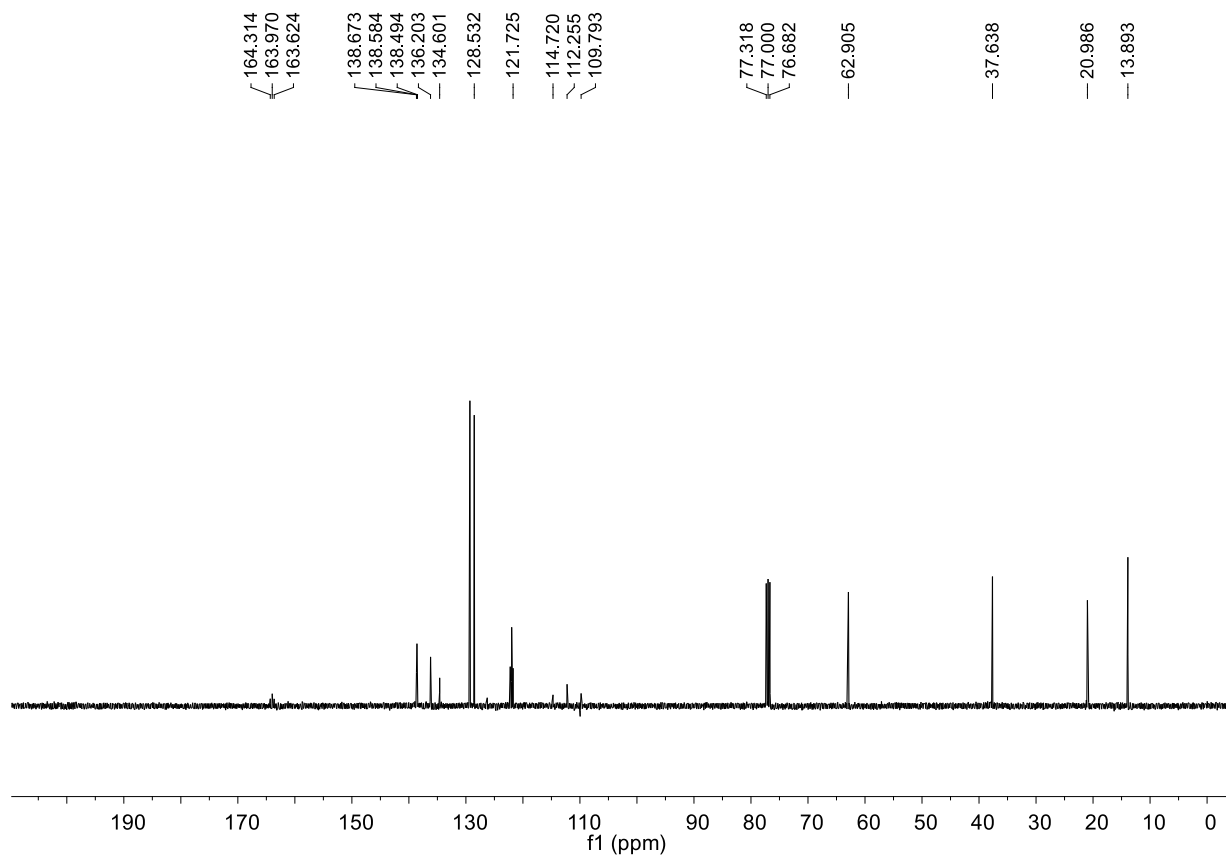
Ethyl (*E*)-5-(3,4-dimethoxyphenyl)-2,2-difluoropent-3-enoate (6d).



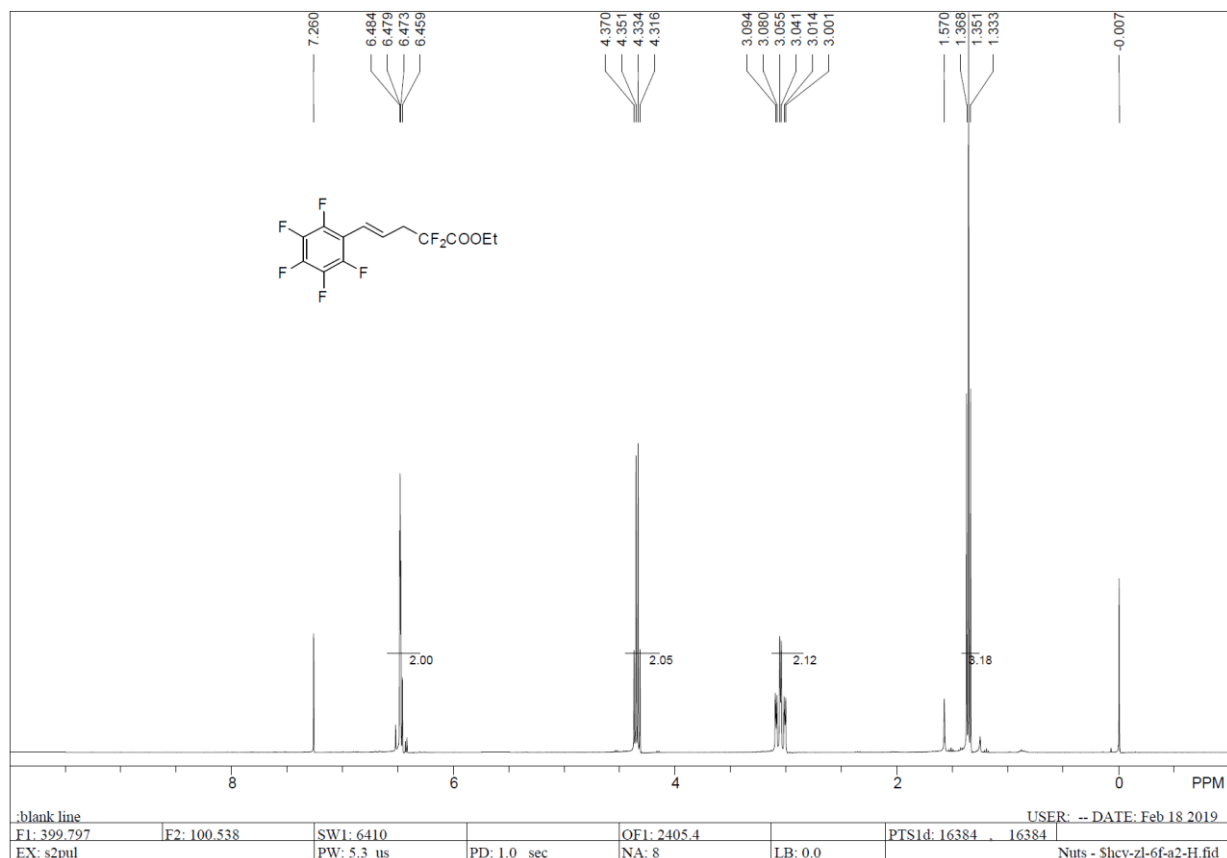


Ethyl (E)-2,2-difluoro-5-(p-tolyl)pent-3-enoate (6e).

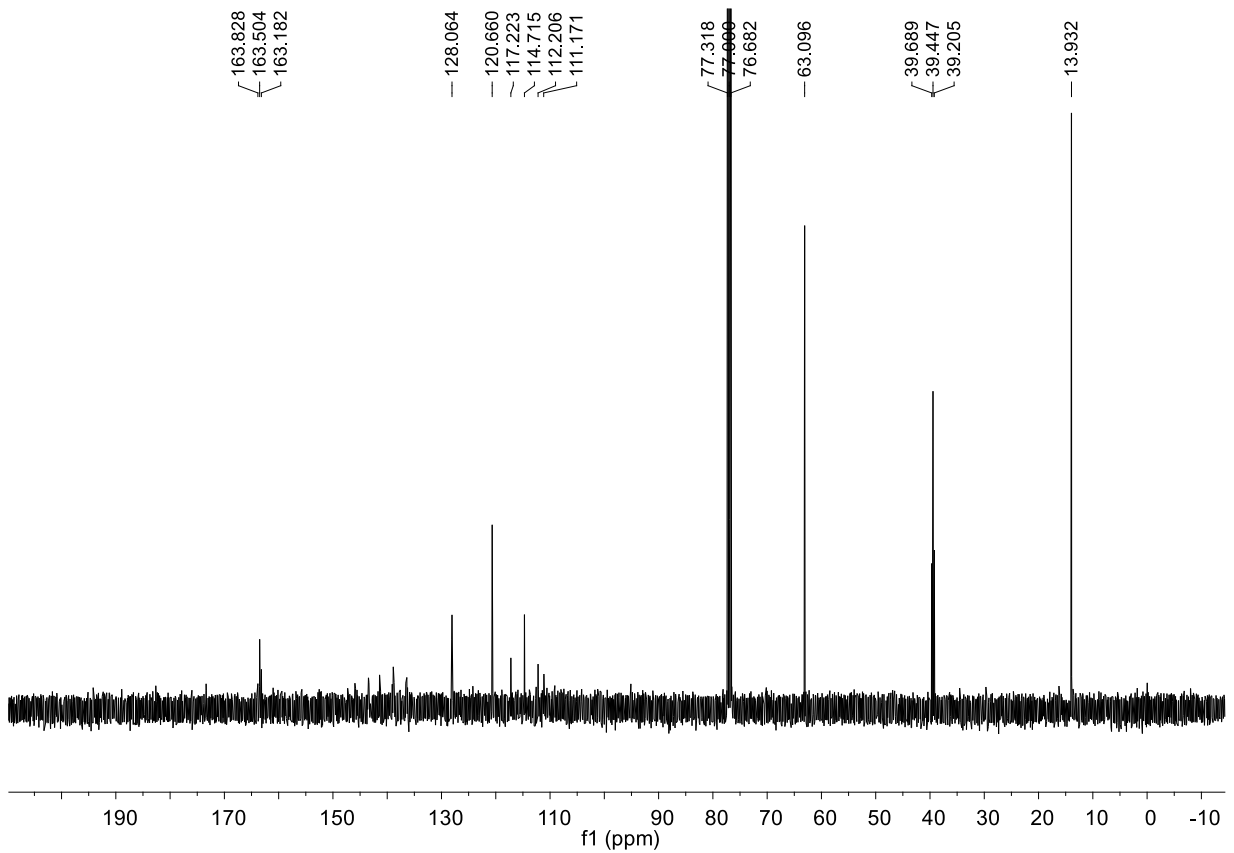
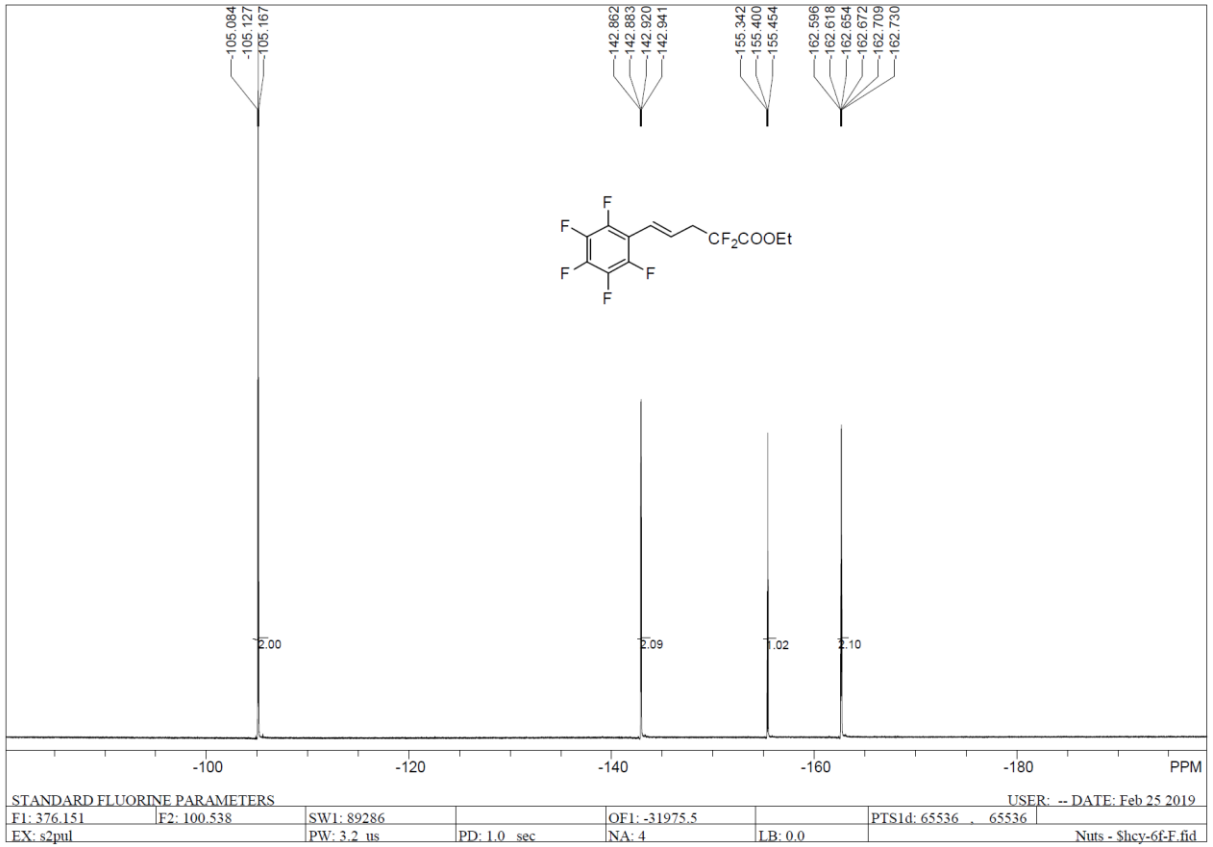




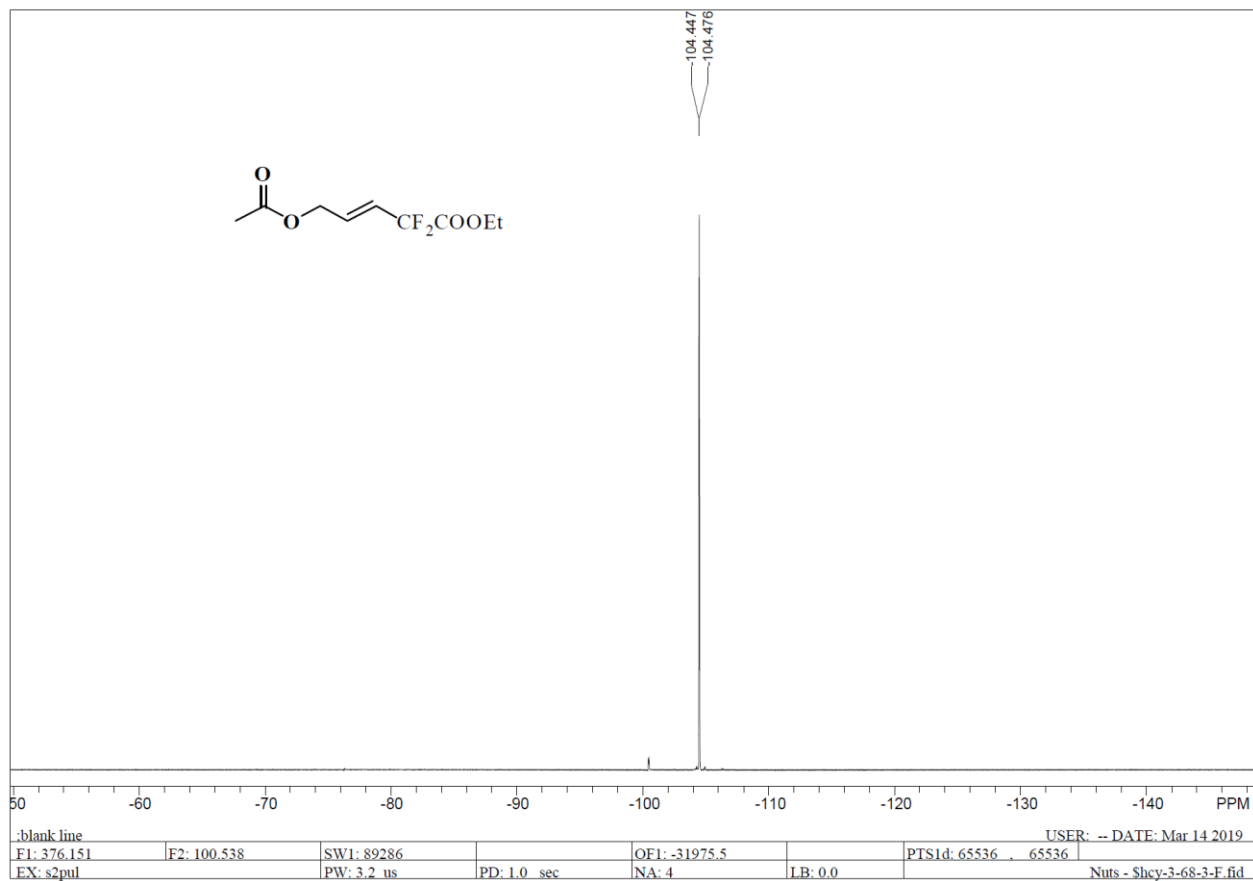
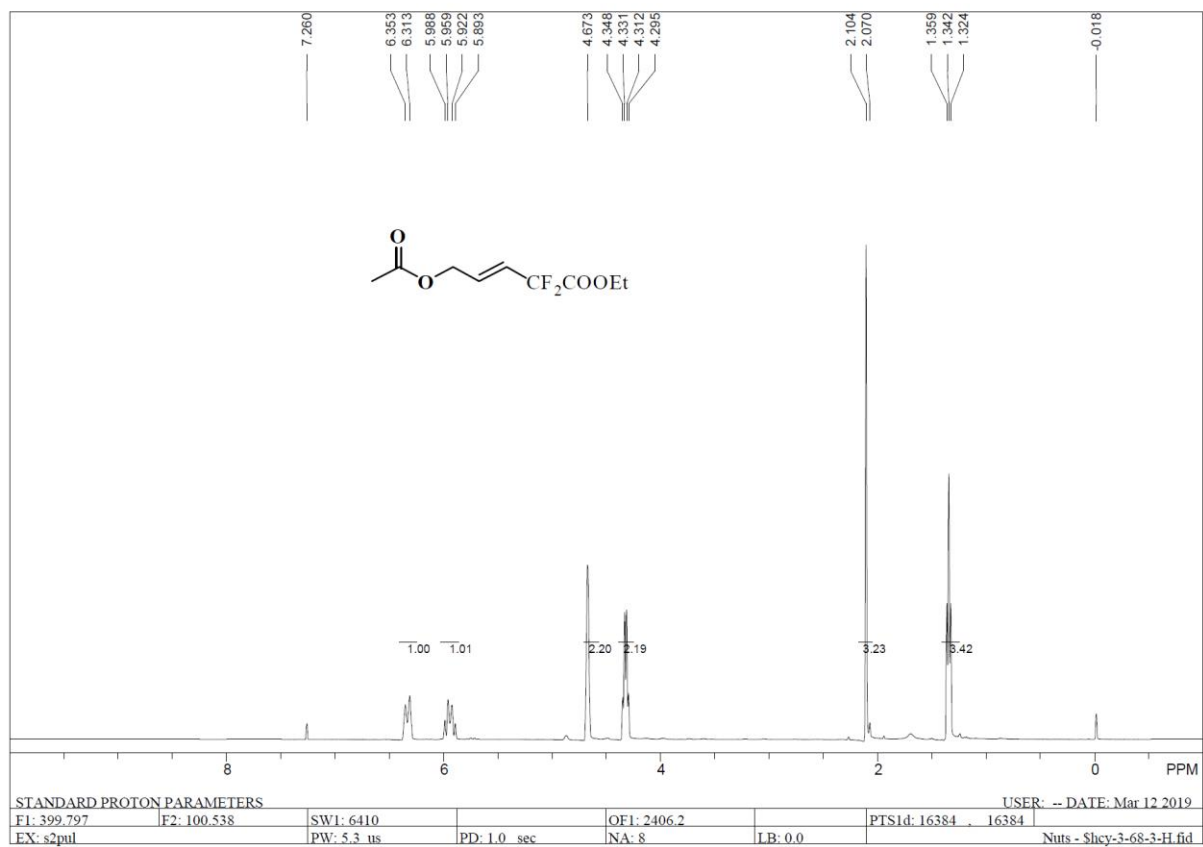
Ethyl (E)-2,2-difluoro-5-(perfluorophenyl)pent-4-enoate (6f).

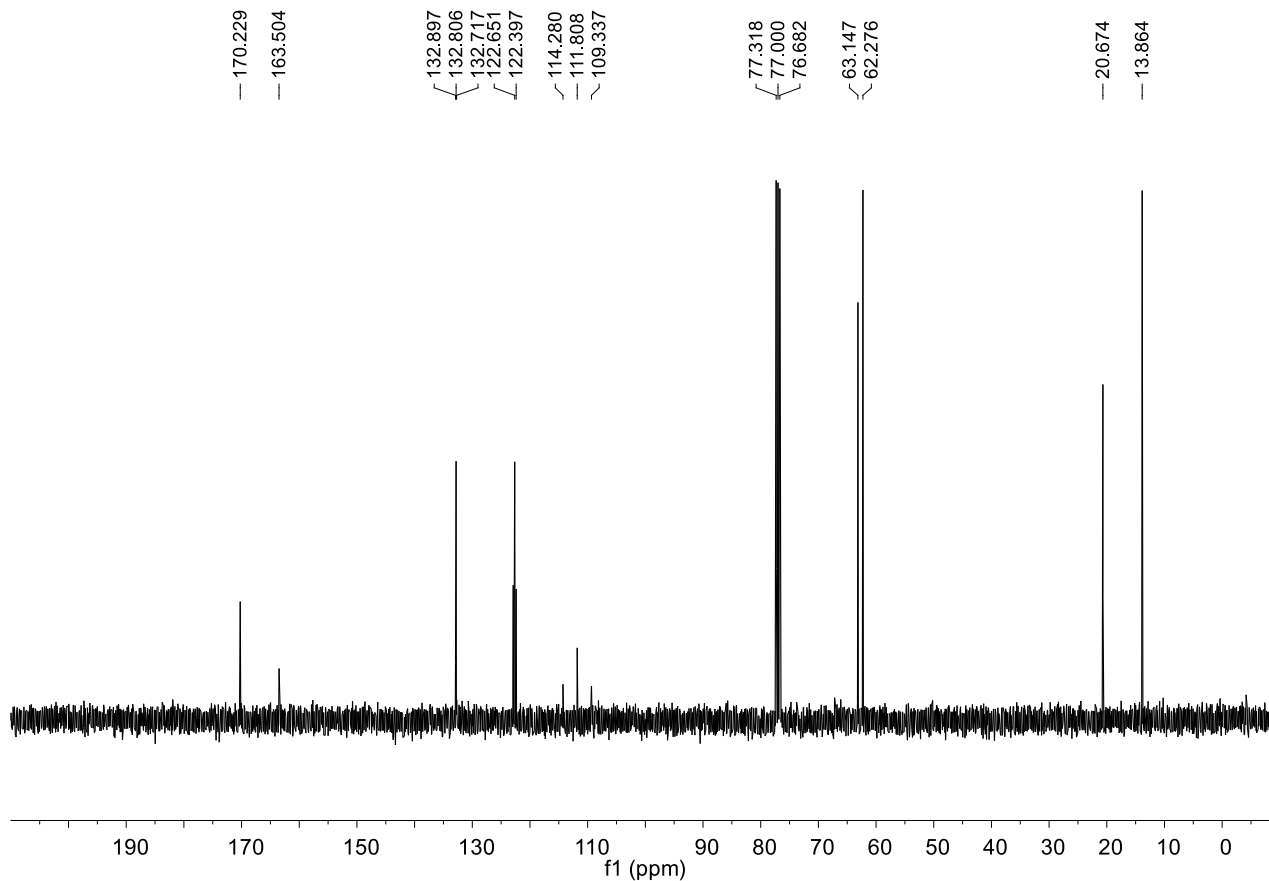


.blank line
 F1: 399.797 E2: 100.538 SW1: 6410 OF1: 2405.4 PTS1d: 16384 . 16384
 EX: s2pul PW: 5.3 us PD: 1.0 sec NA: 8 LB: 0.0 Nuts - Shcy-zl-6f-a2-H.fid
 USER: -- DATE: Feb 18 2019

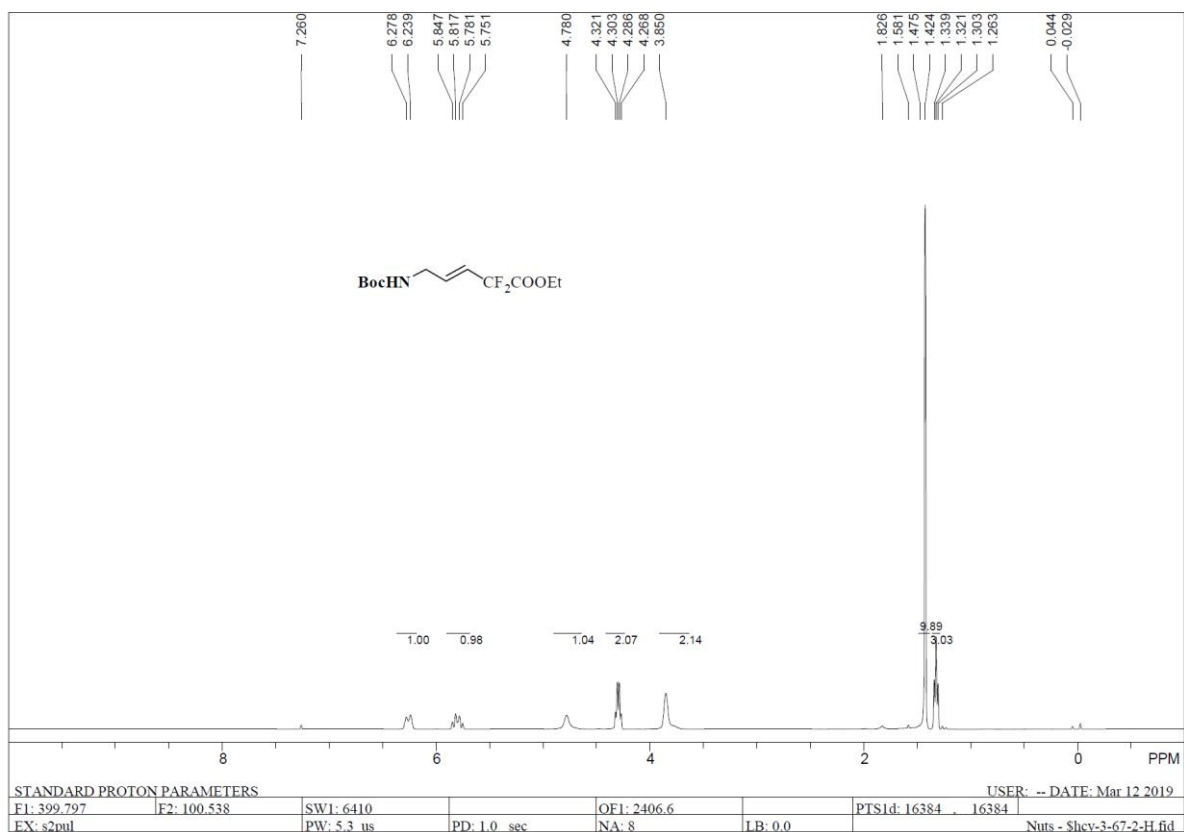


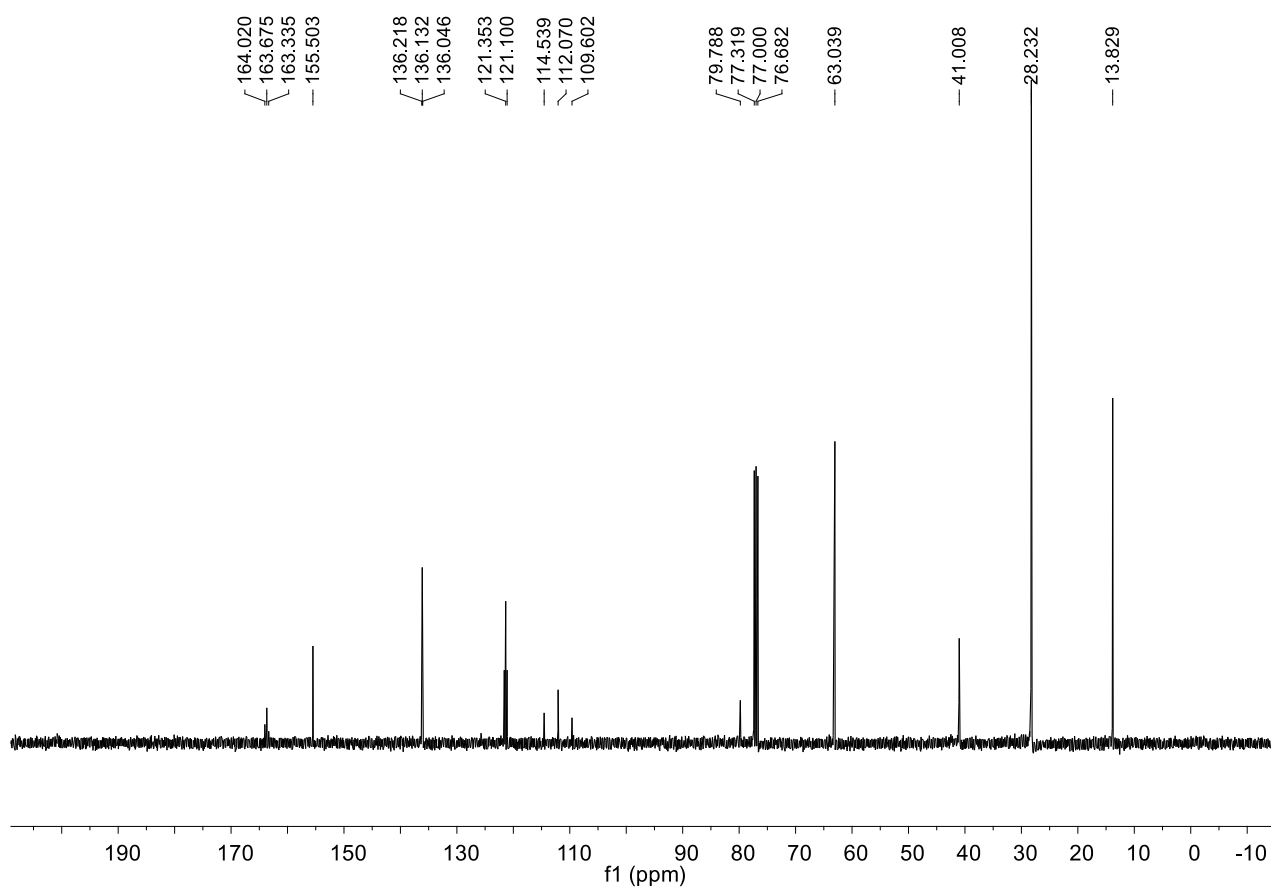
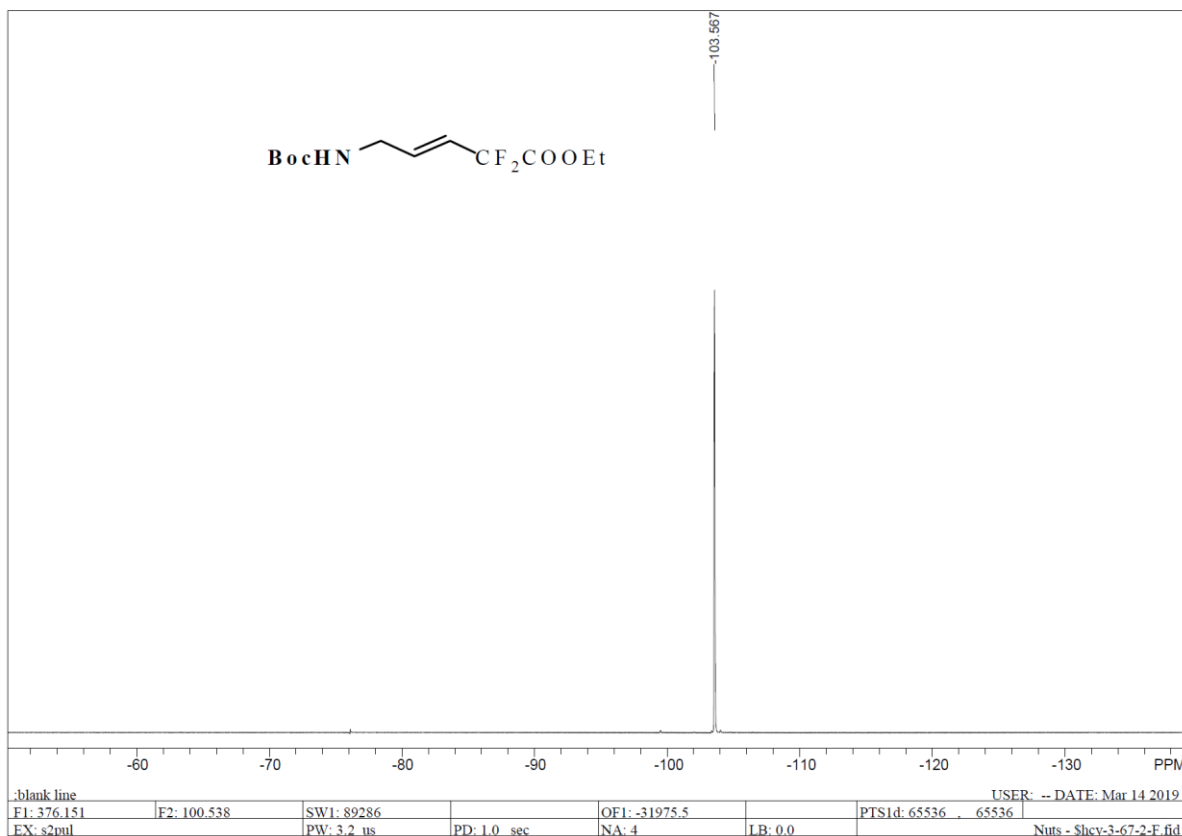
Ethyl (E)-5-acetoxy-2,2-difluoropent-3-enoate (6g).



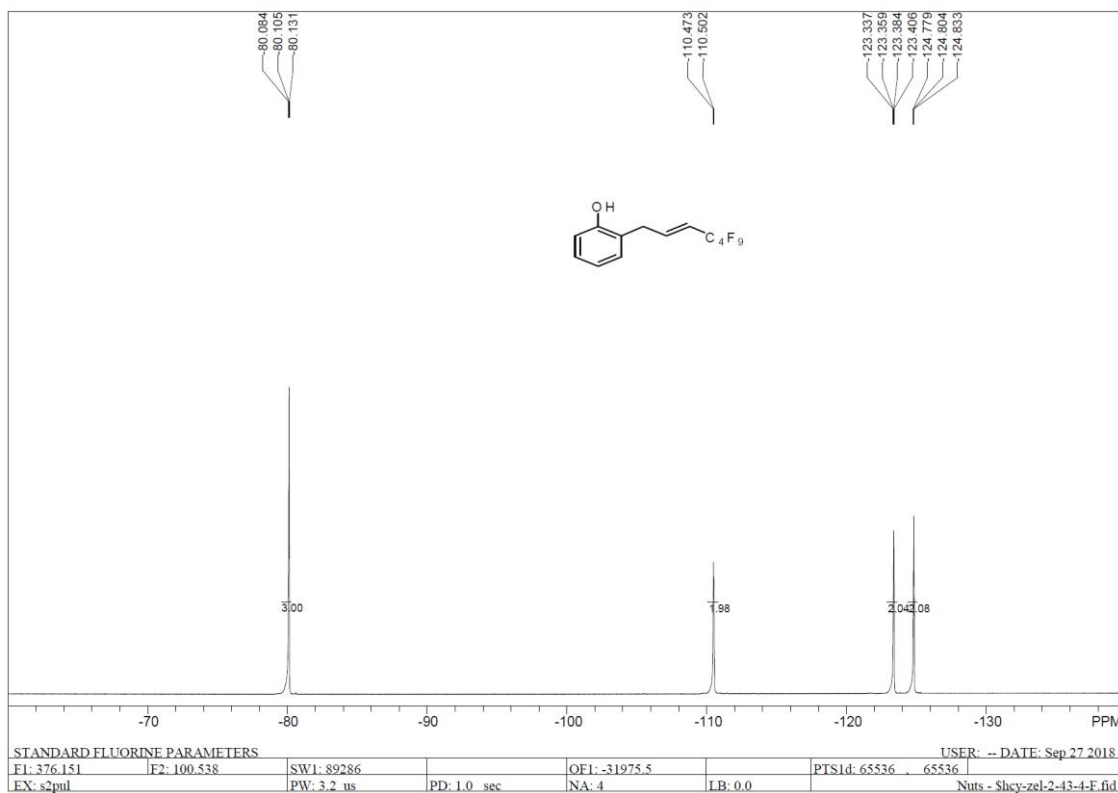
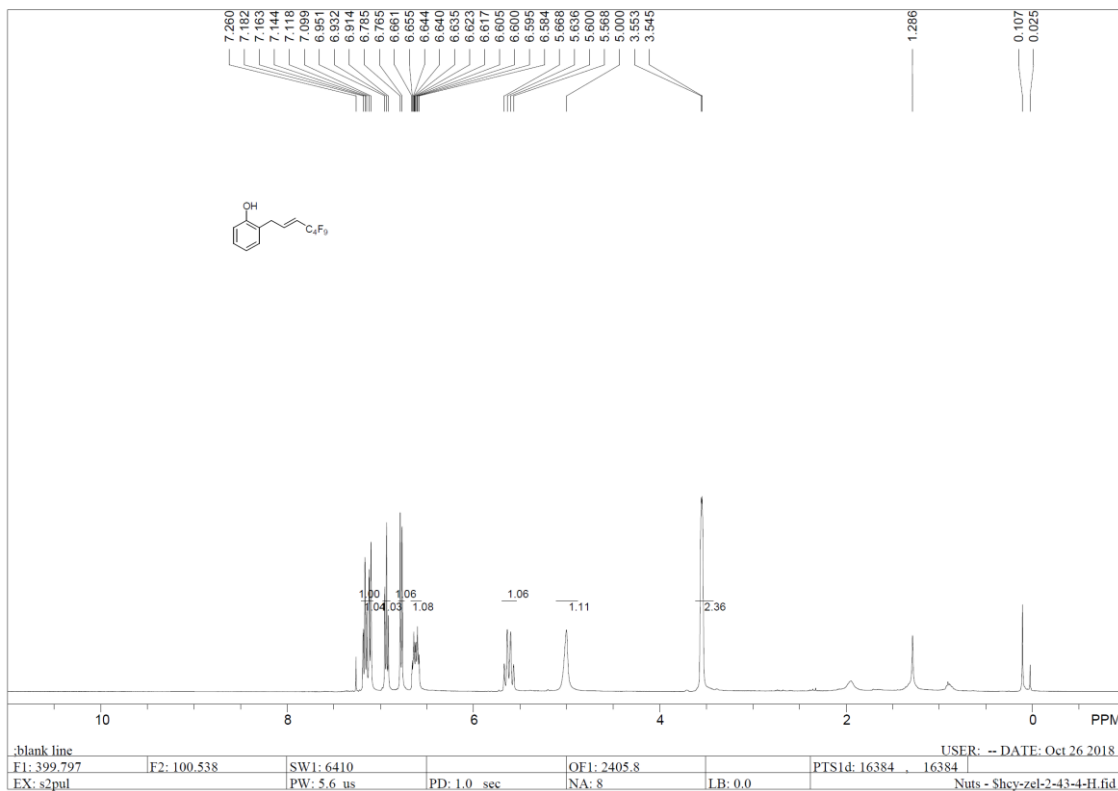


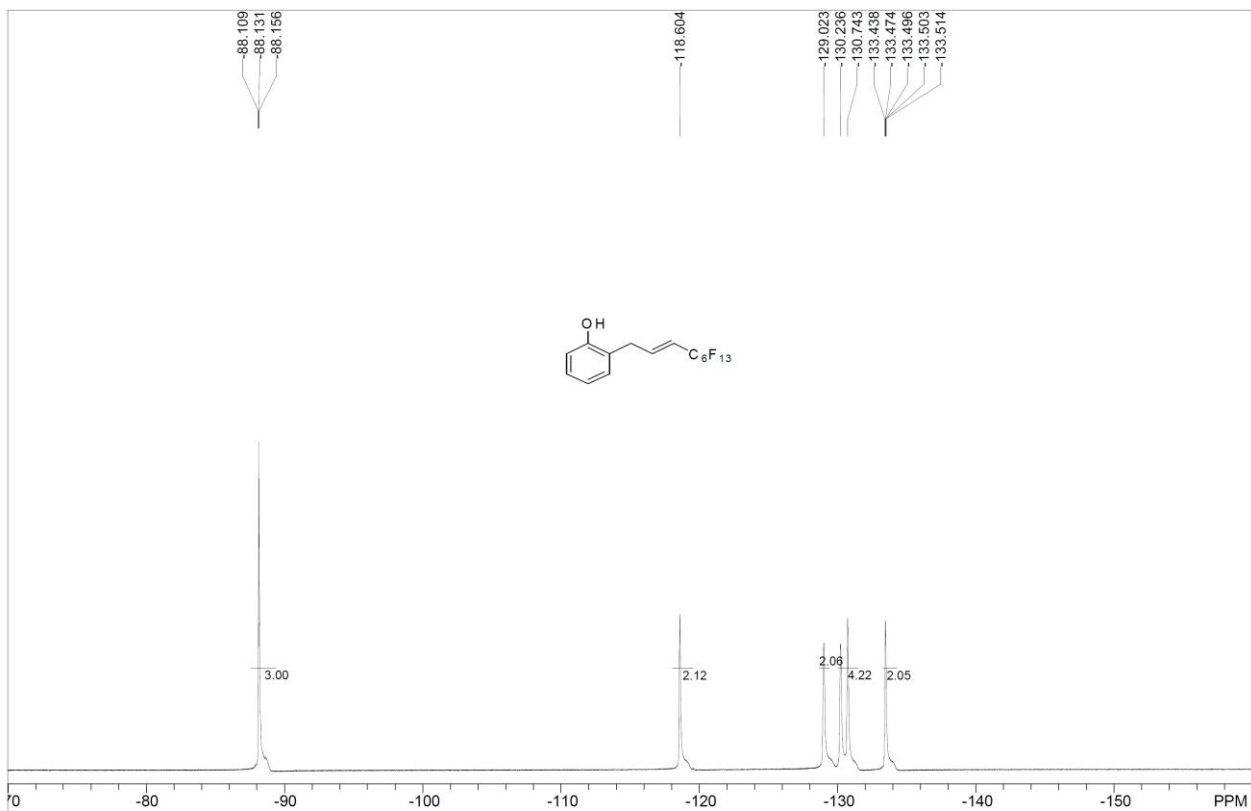
Ethyl (*E*)-5-((*tert*-butoxycarbonyl)amino)-2,2-difluoropent-3-enoate (6h).



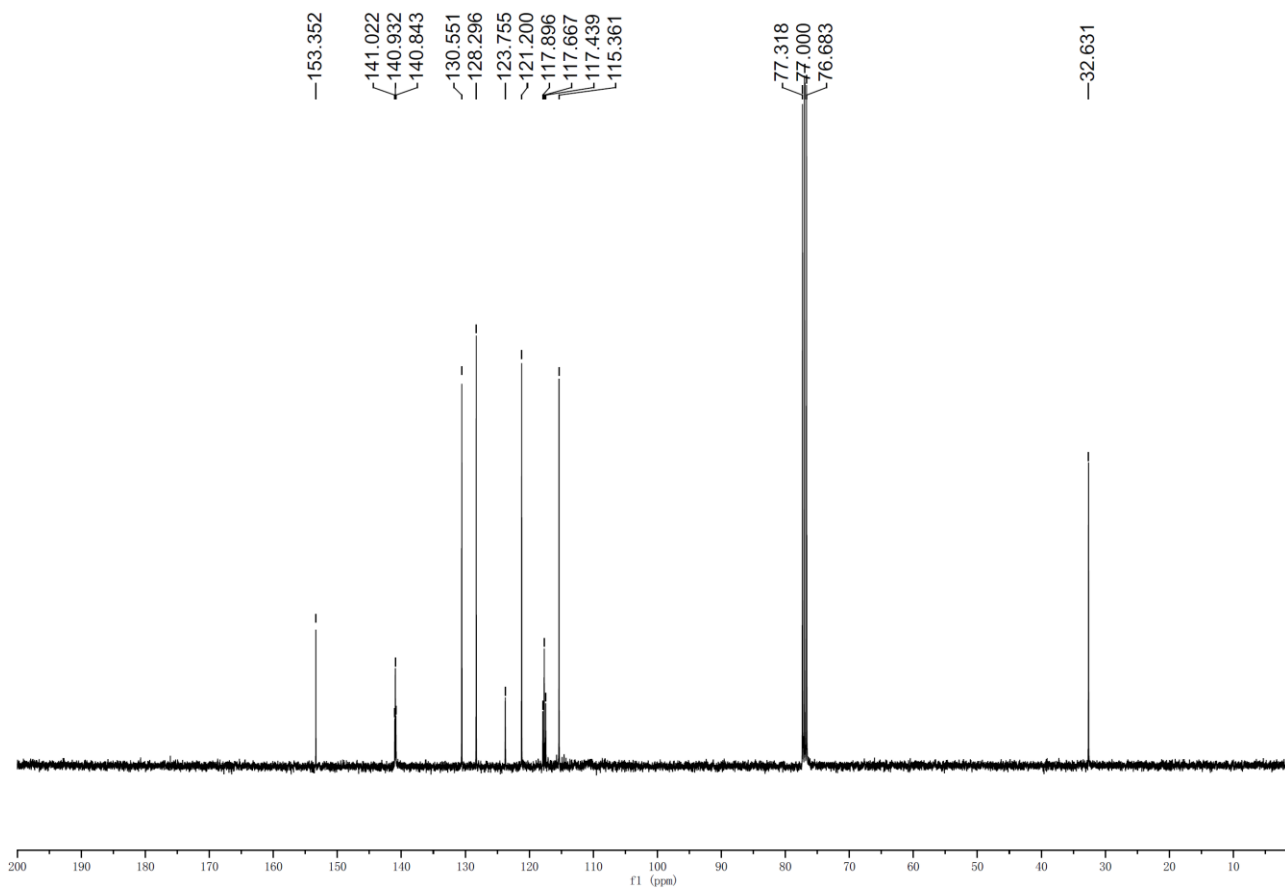


(E)-2-(4,4,5,5,6,6,7,7,7-nonafluorohept-2-en-1-yl)phenol (6i).

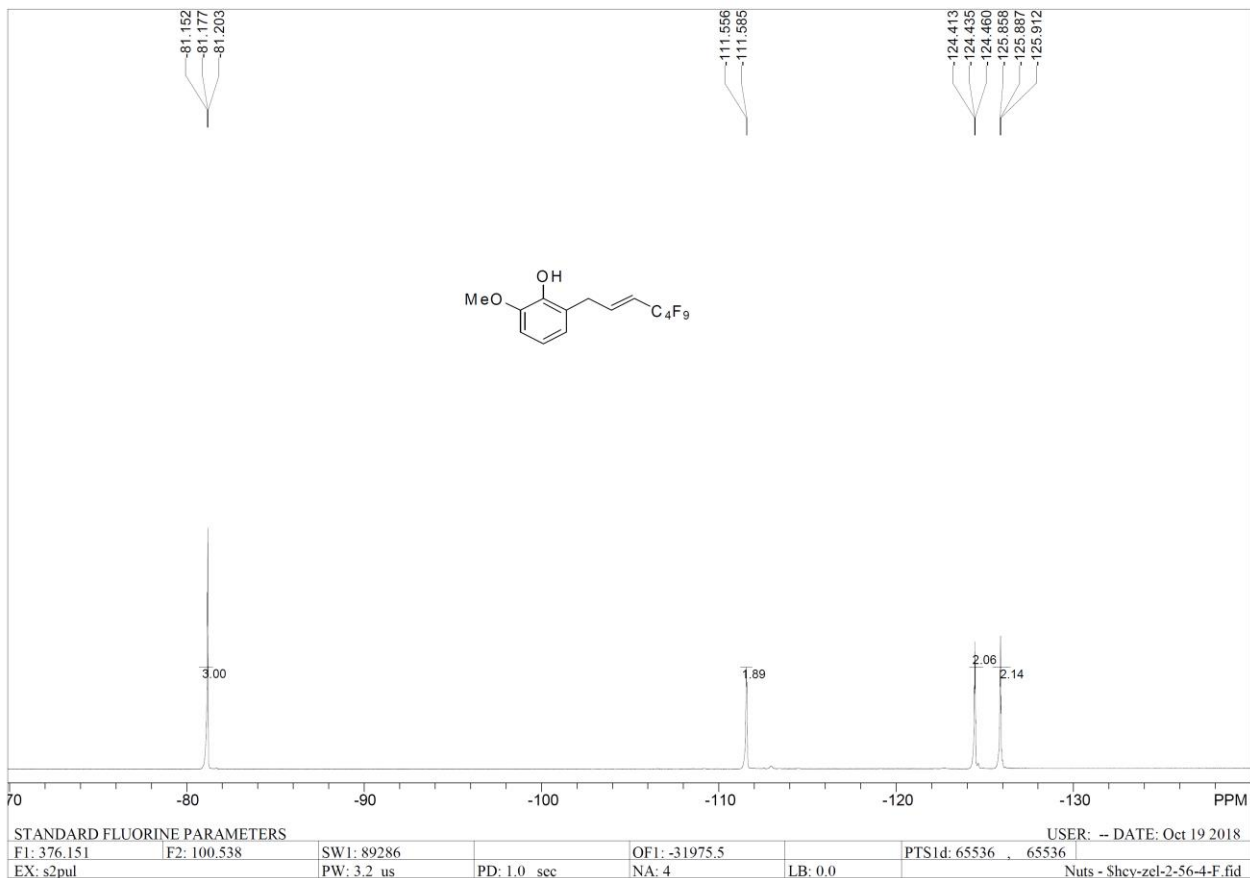
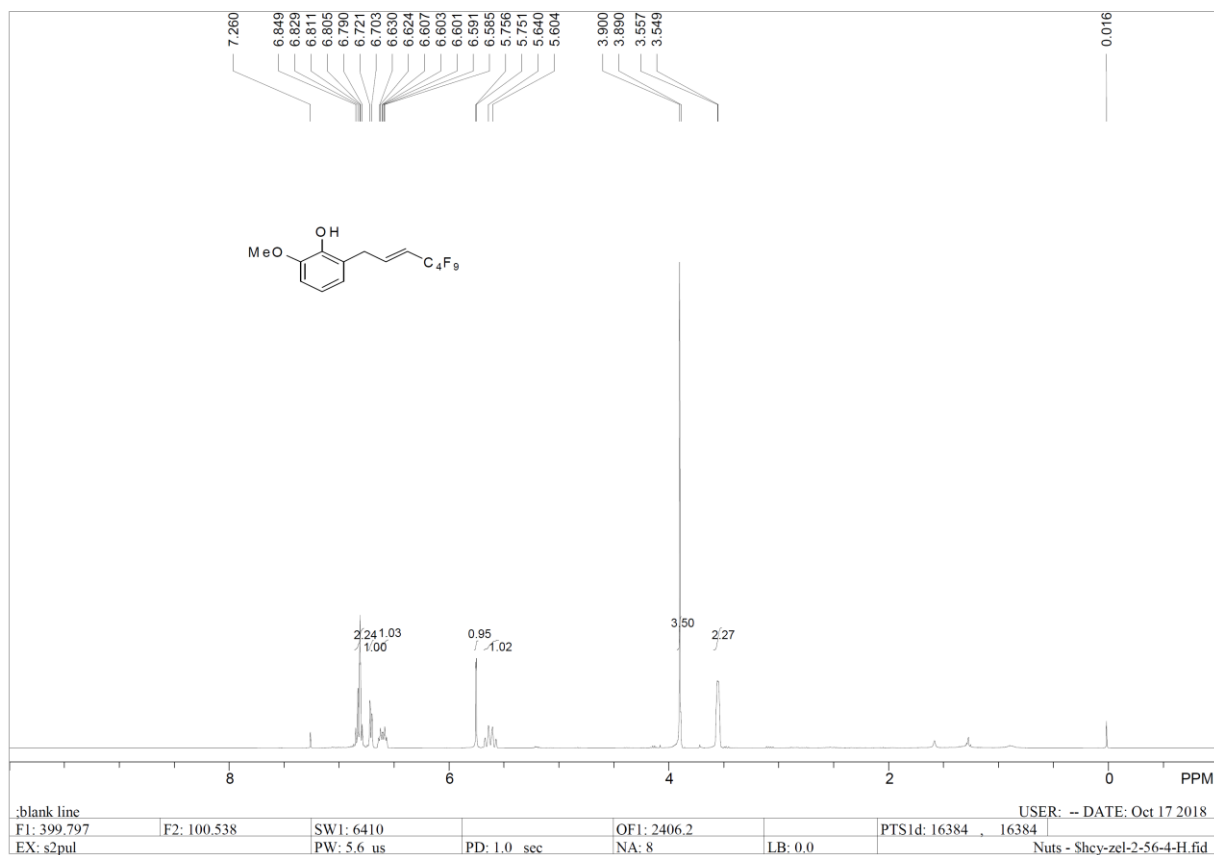


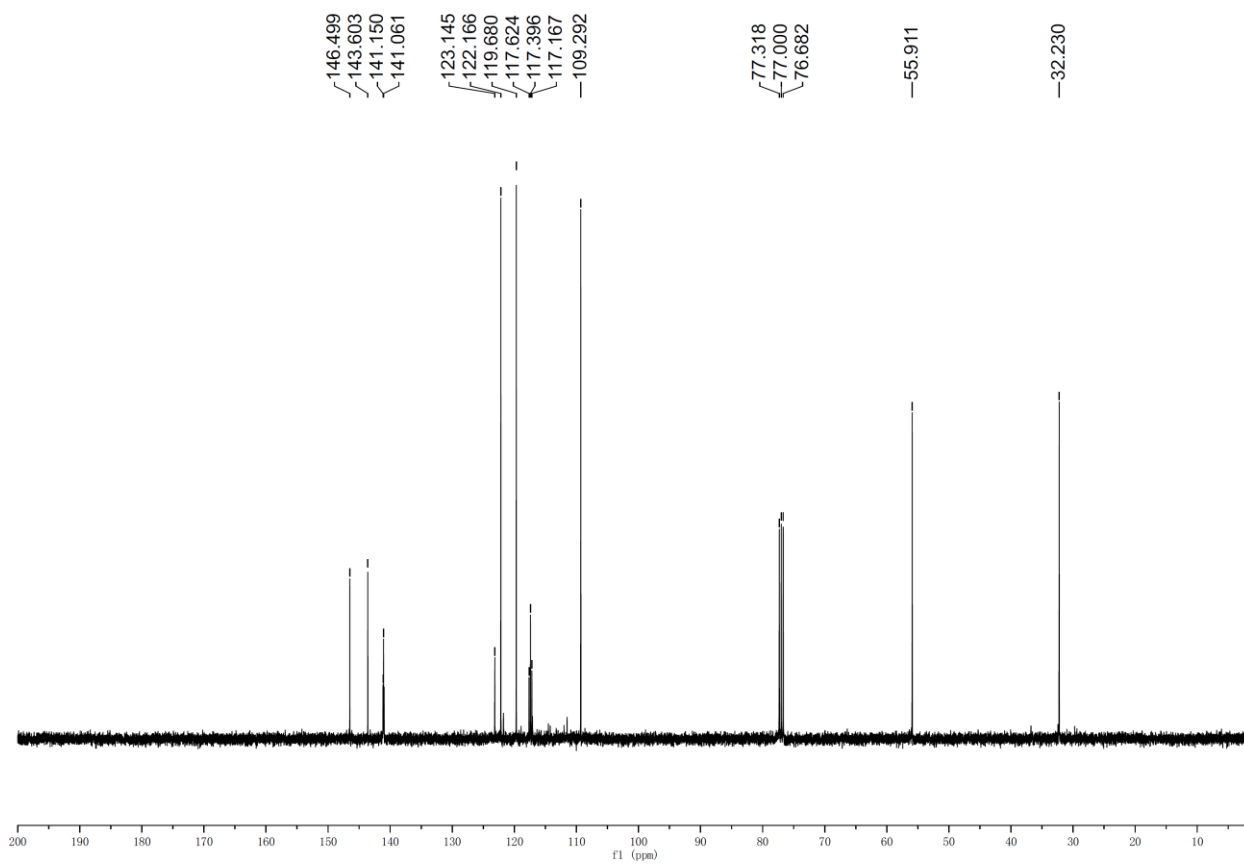


STANDARD FLUORINE PARAMETERS						USER: -- DATE: Jan 4 2019
F1: 376.153	F2: 100.538	SW1: 89286	OF1: -31975.8	PTS1d: 65536	65536	
EX: s2pul	PW: 3.2 us	PD: 1.0 sec	NA: 4	LB: 0.0	Nuts - Shey-zel-3-15-1-a-F.fid	

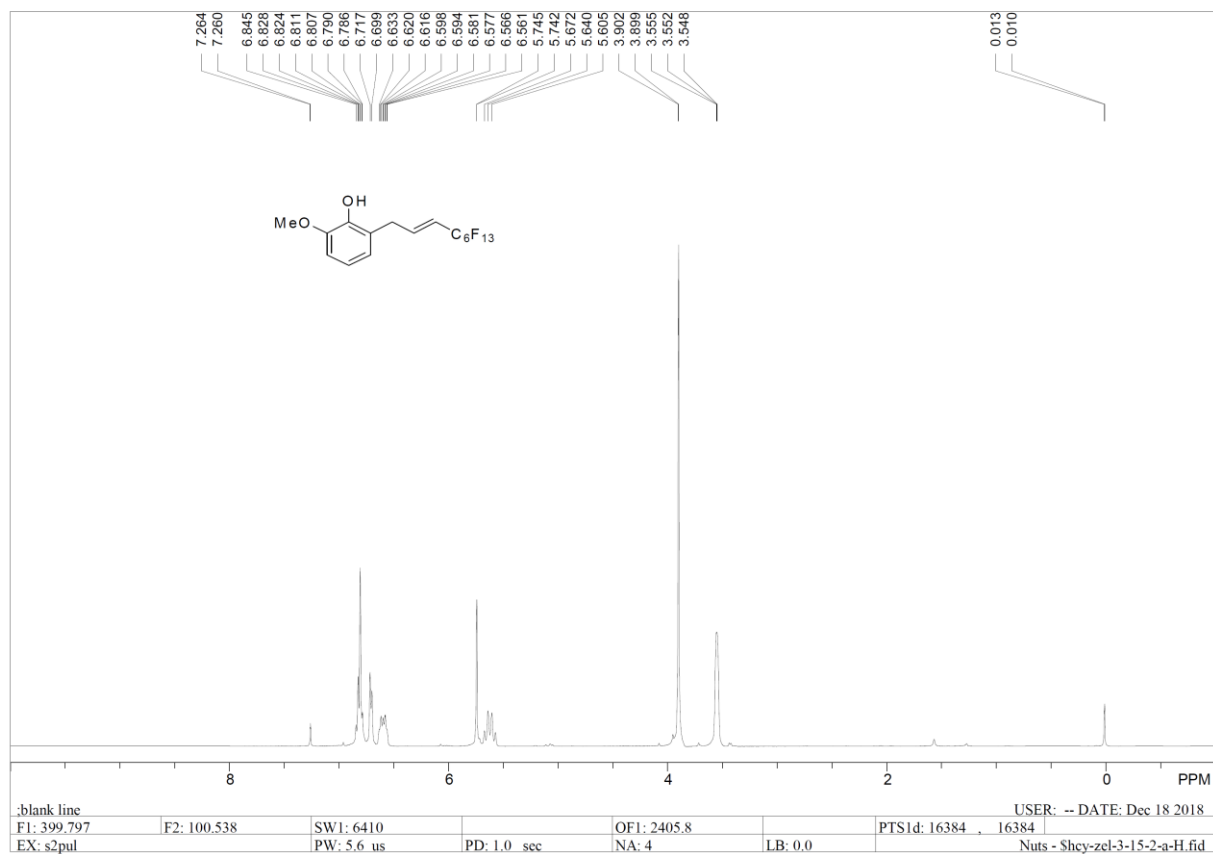


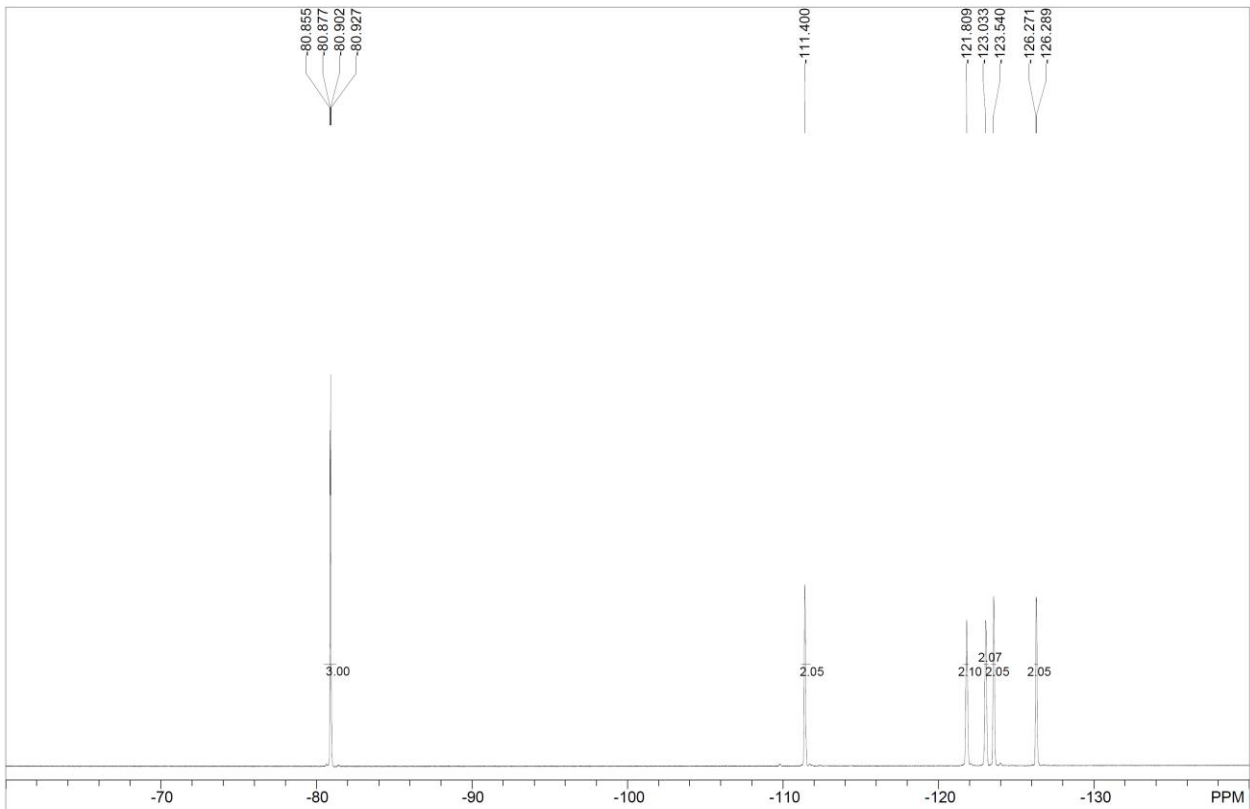
(E)-2-methoxy-6-(4,4,5,5,6,6,7,7,7-nonafluorohept-2-en-1-yl)phenol (6k).





(E)-2-methoxy-6-(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoronon-2-en-1-yl)phenol (6l).

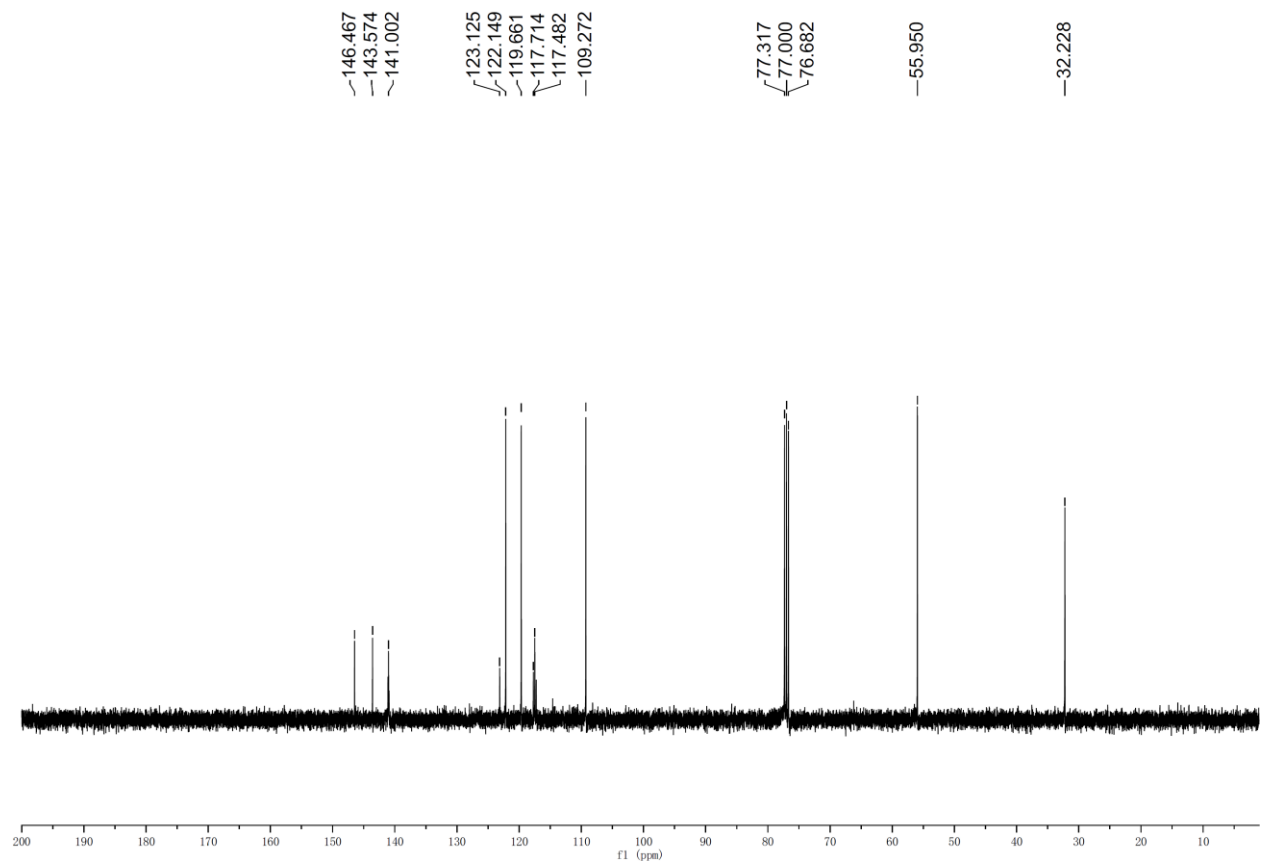




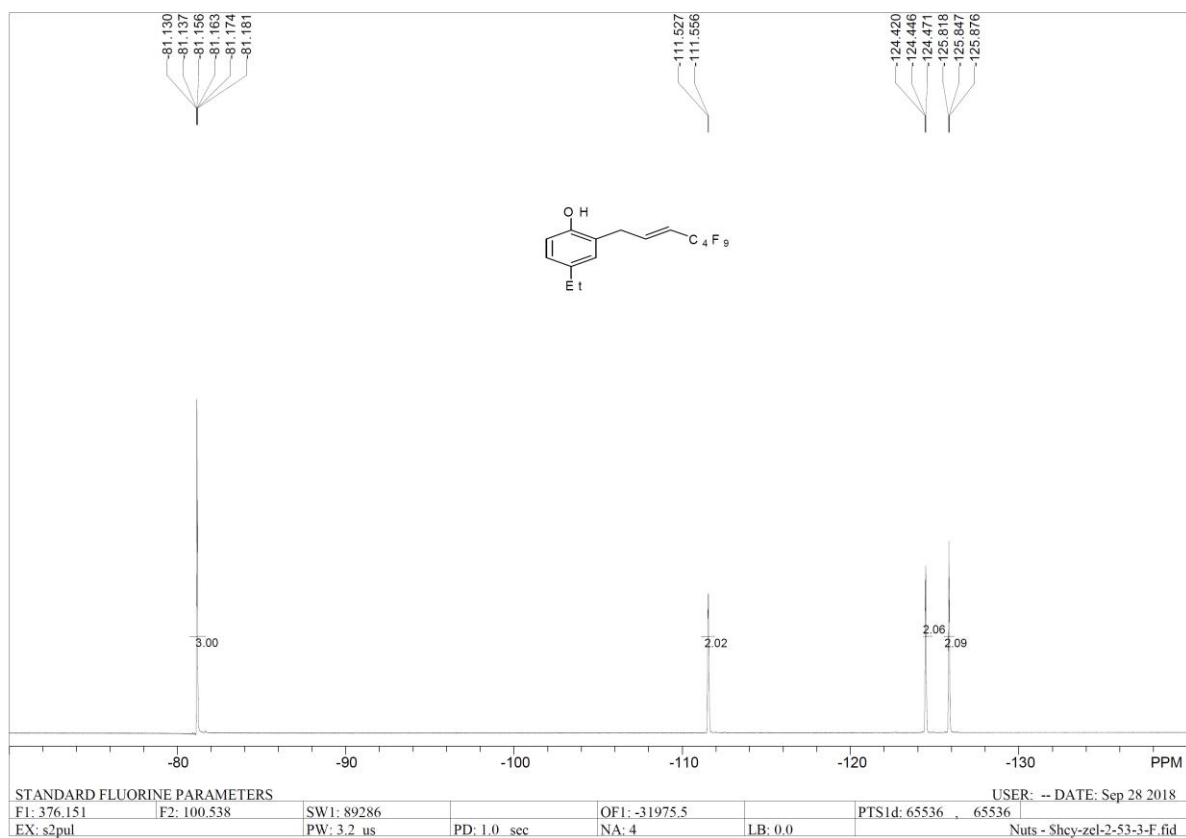
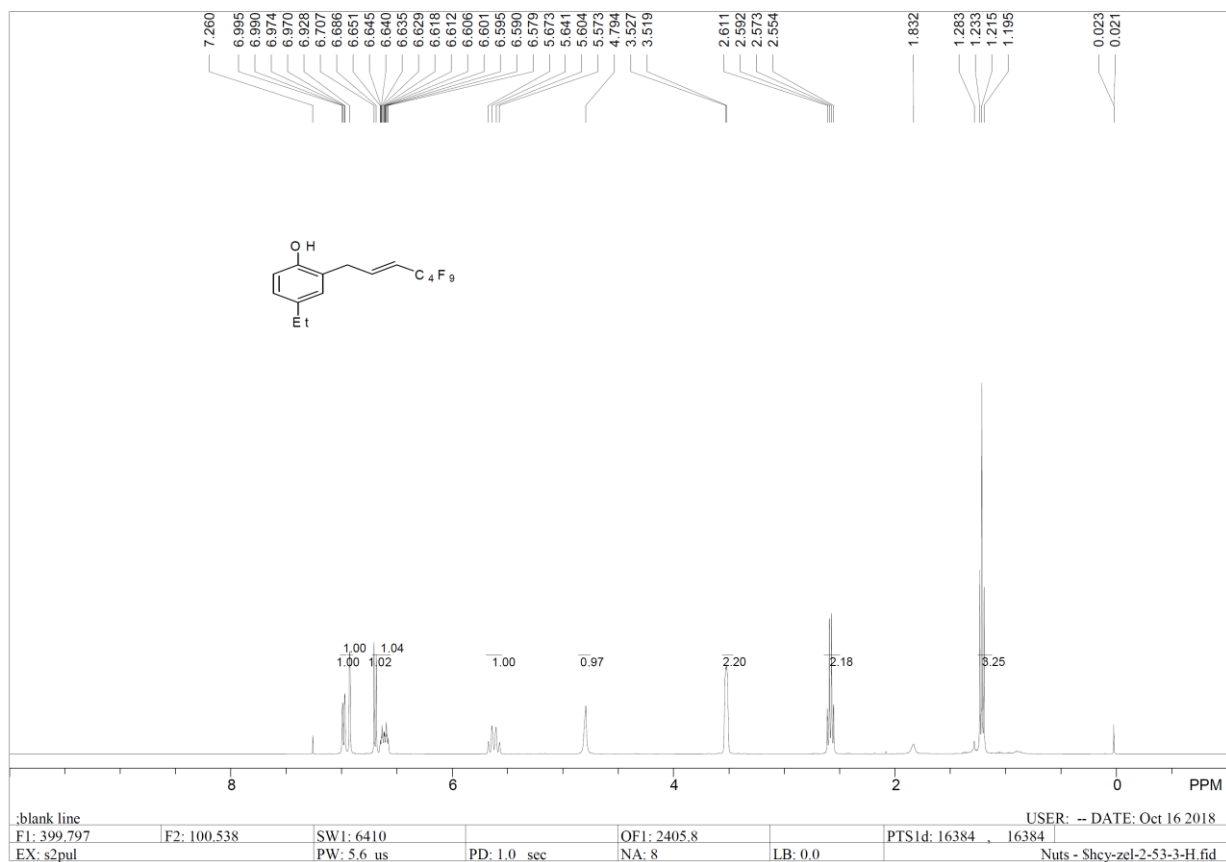
STANDARD FLUORINE PARAMETERS

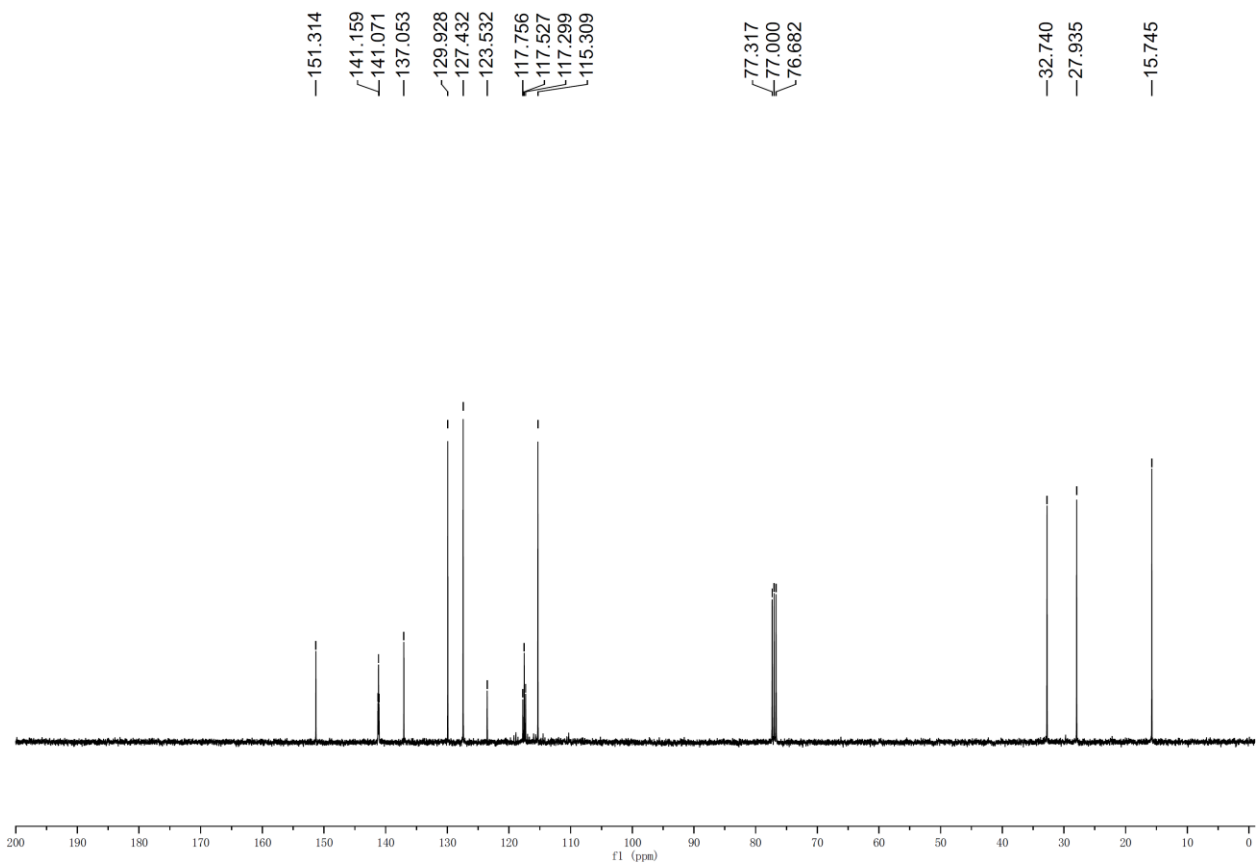
USER: -- DATE: Dec 19 2018

F1: 376.151	F2: 100.538	SW1: 89286	OF1: -31975.5	PTS1d: 65536	65536
EX: s2pul	PW: 3.2 us	PD: 1.0 sec	NA: 4	LB: 0.0	Nuts - Shey-zel-3-15-2-a-F.fid

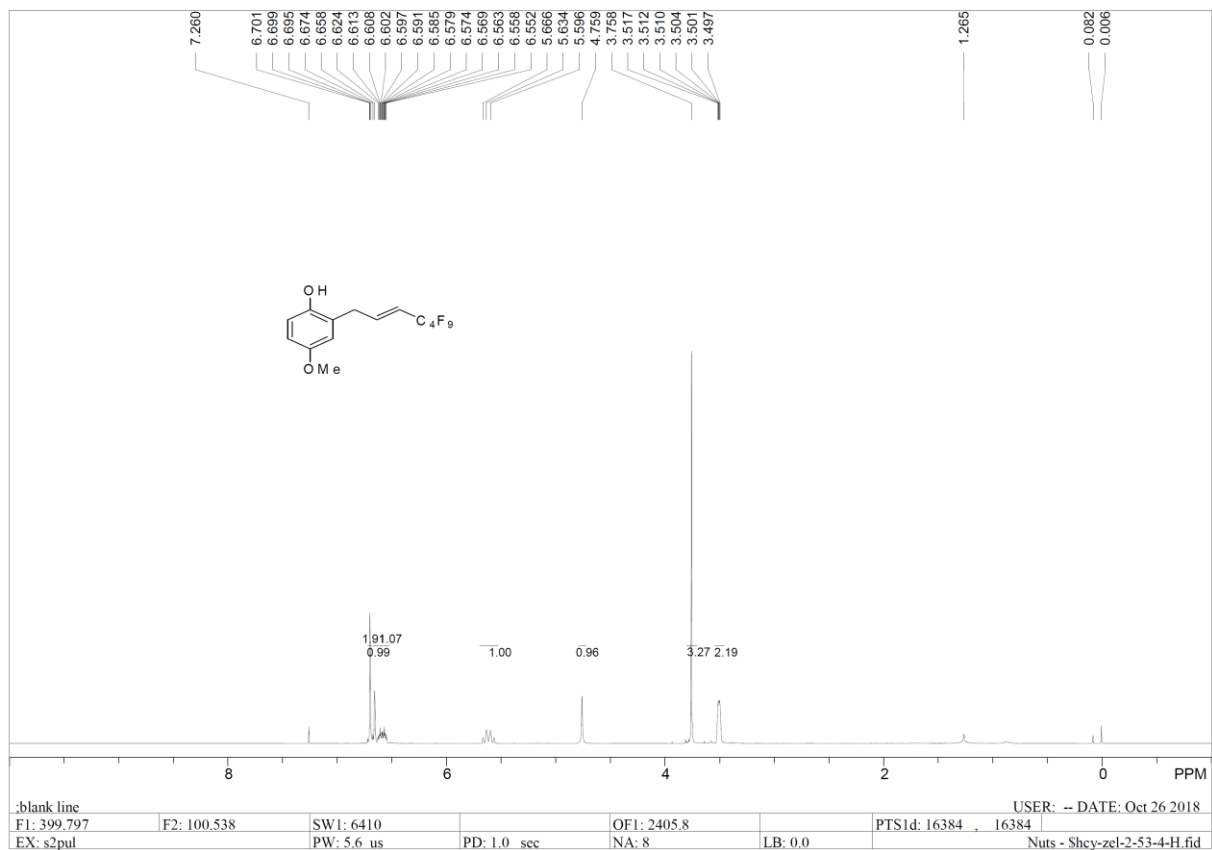


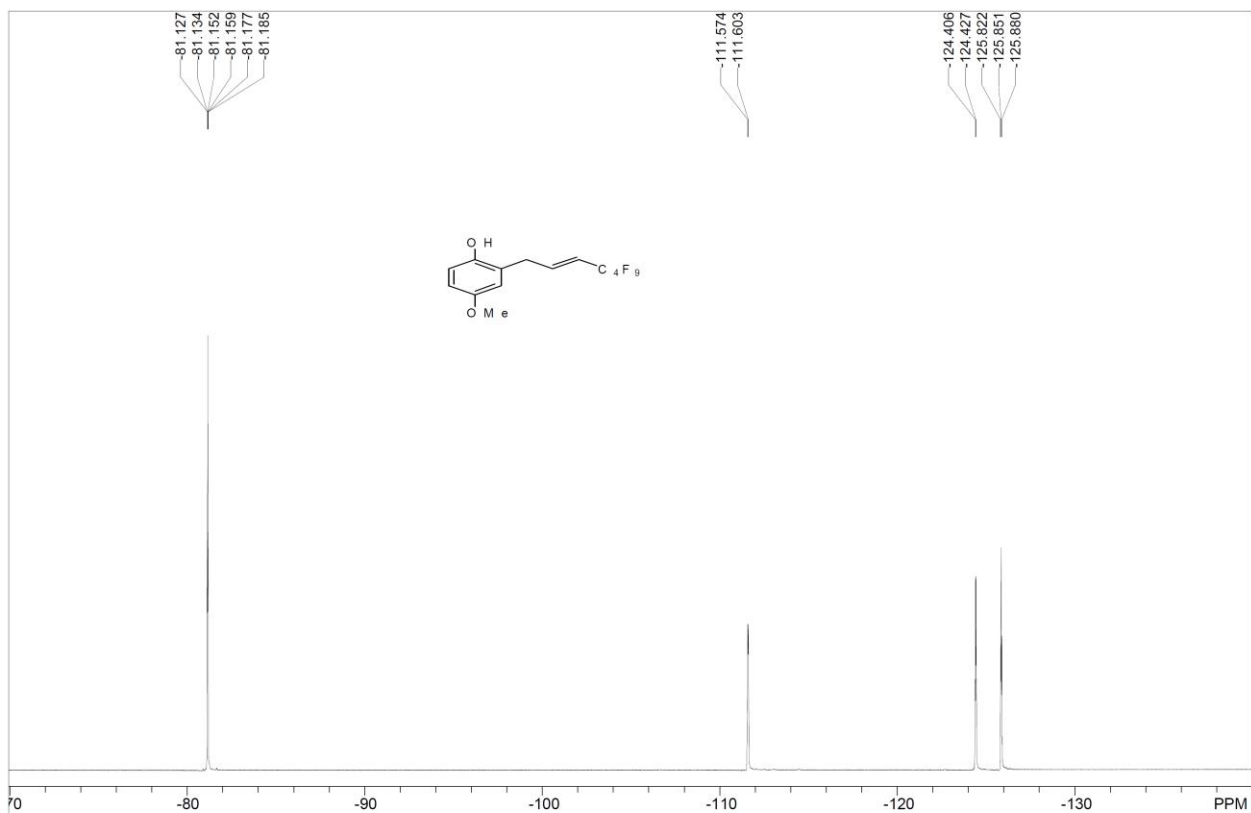
(E)-4-ethyl-2-(4,4,5,5,6,6,7,7,7-nonafluorohept-2-en-1-yl)phenol (6m).



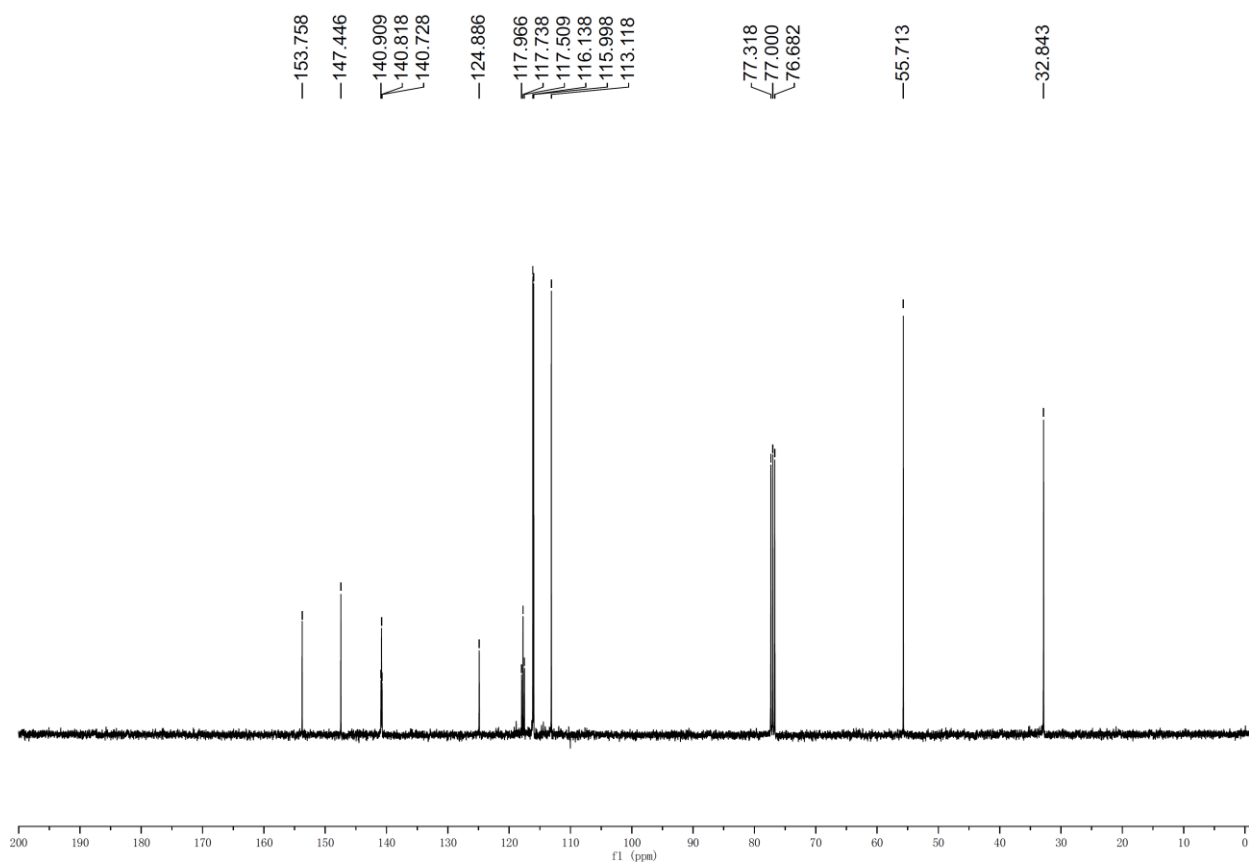


(E)-4-methoxy-2-(4,4,5,5,6,6,7,7,7-nonafluorohept-2-en-1-yl)phenol (6n).

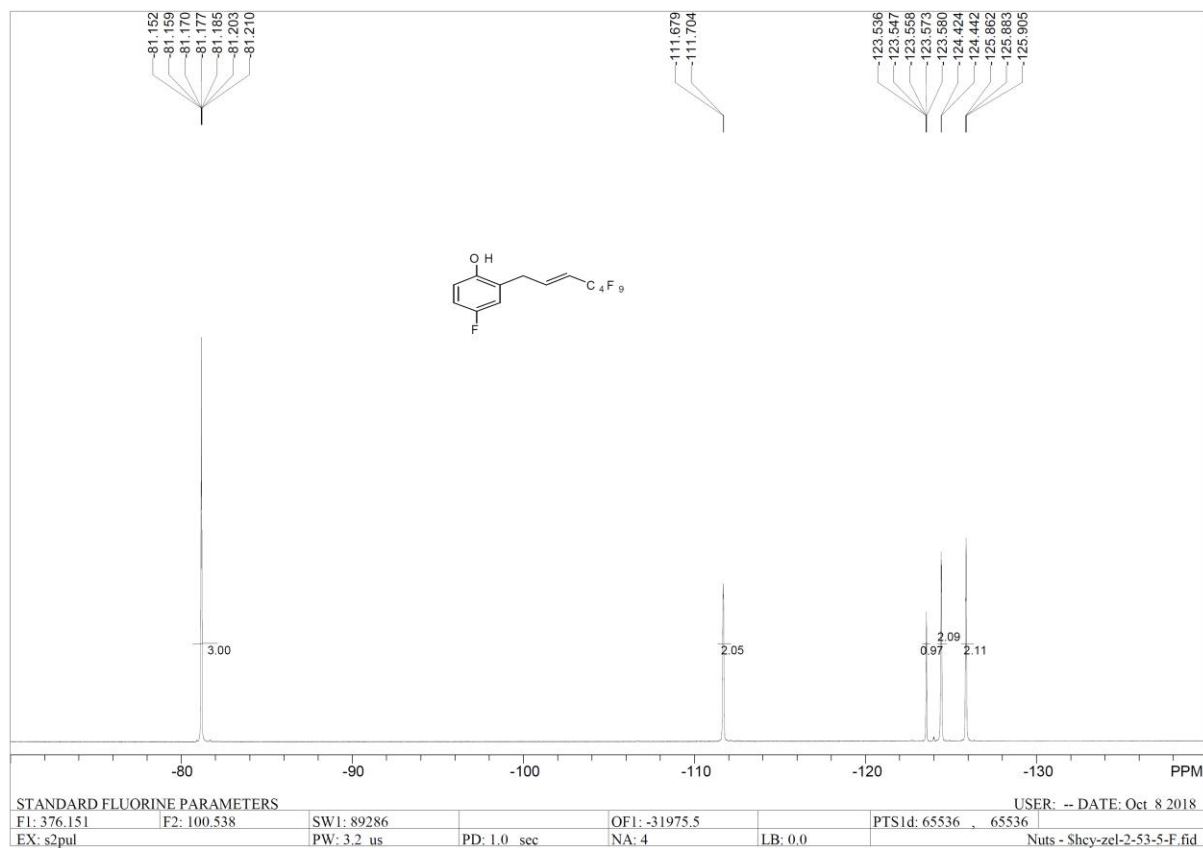
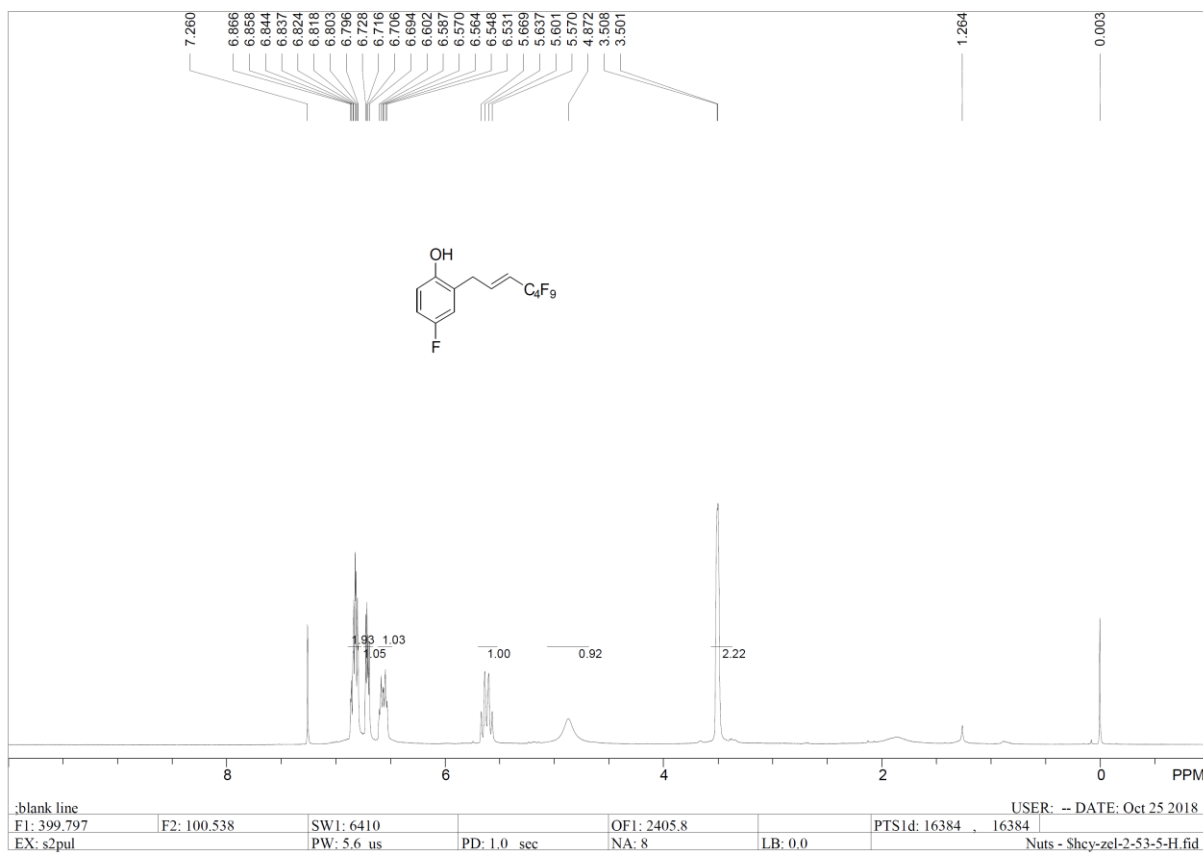


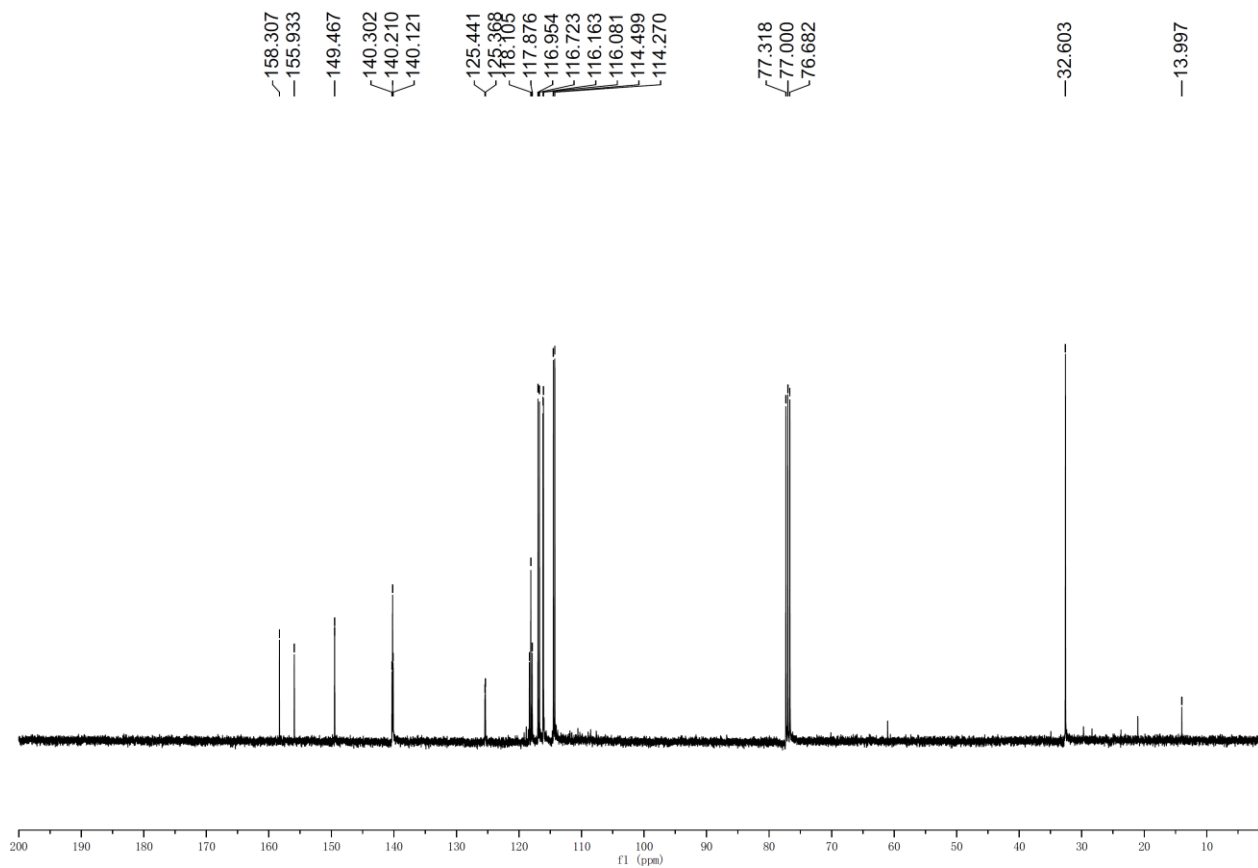


STANDARD FLUORINE PARAMETERS
 F1: 376.151 F2: 100.538 SW1: 89286 OF1: -31975.5 USER: -- DATE: Sep 28 2018
 EX: s2pul PW: 3.2 us PD: 1.0 sec NA: 4 LB: 0.0 PTS1d: 65536 , 65536
 Nuts - Shey-zel-2-53-4-F.fid

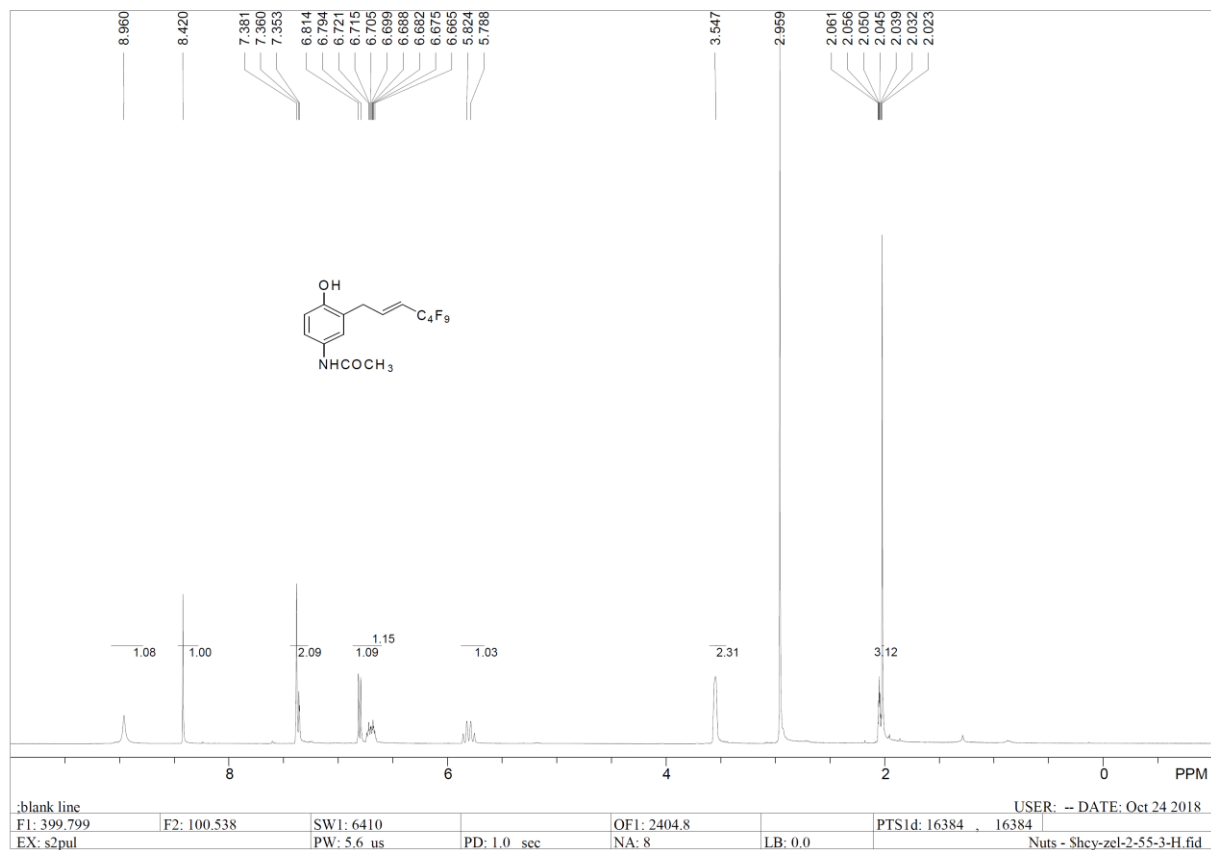


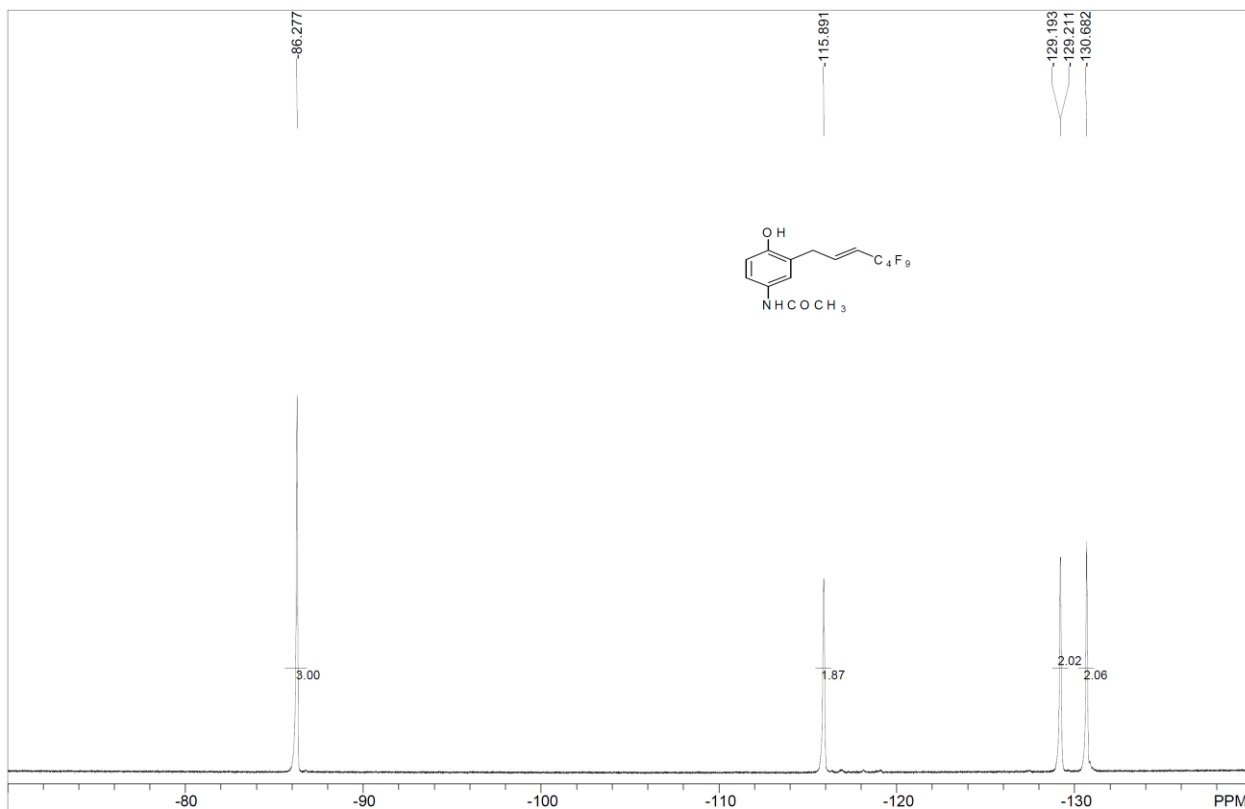
(E)-4-fluoro-2-(4,4,5,5,6,6,7,7,7-nonafluorohept-2-en-1-yl)phenol (6o).



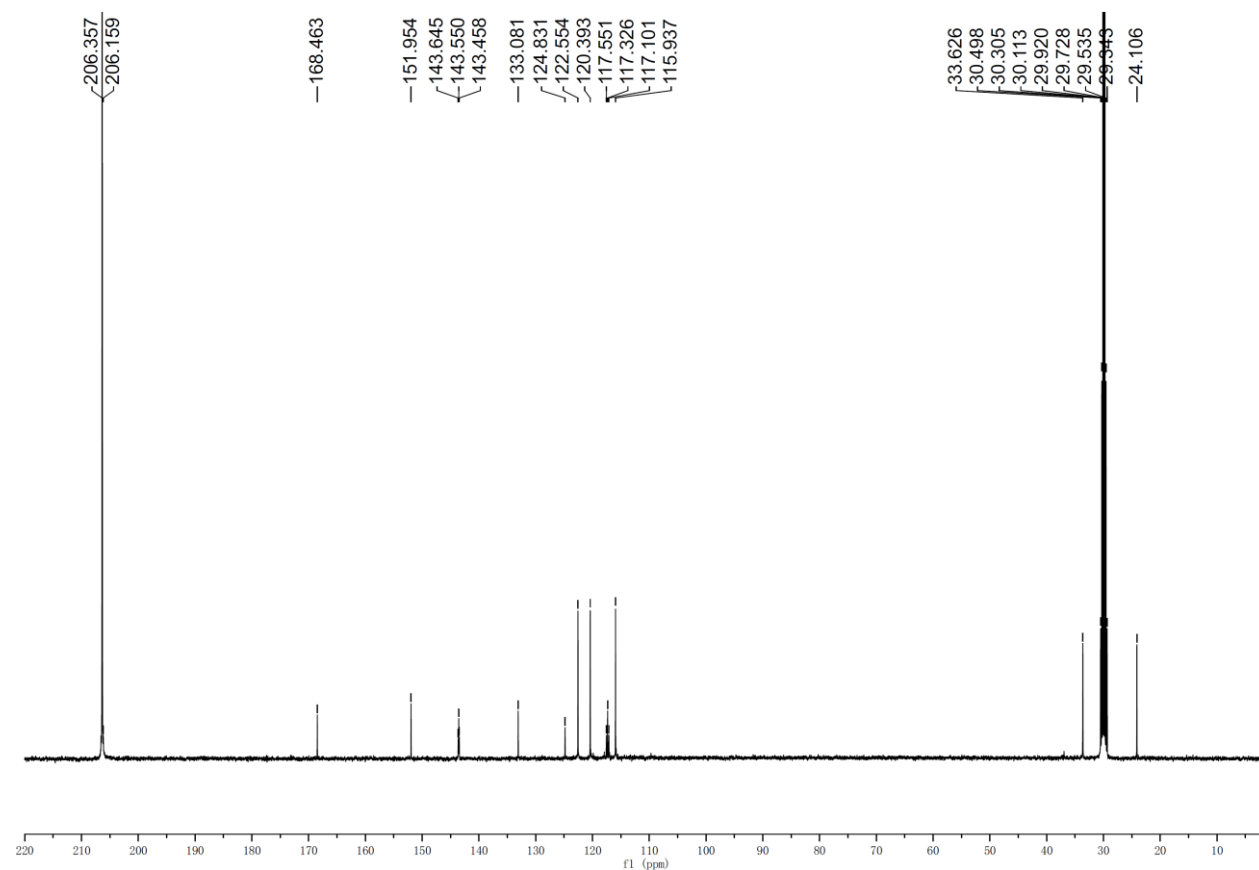


(E)-N-(4-hydroxy-3-(4,4,5,5,6,6,7,7,7-nonafluorohept-2-en-1-yl)phenyl)acetamide (6p).

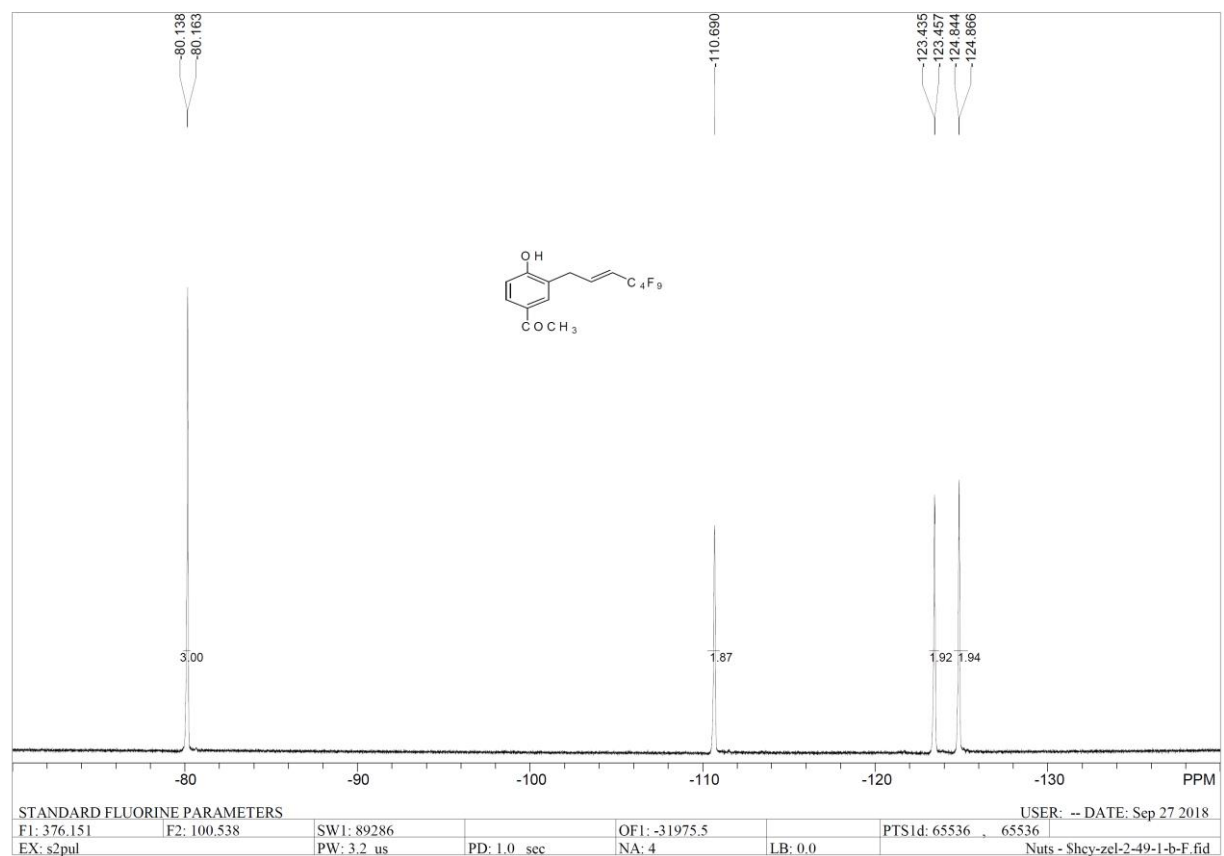
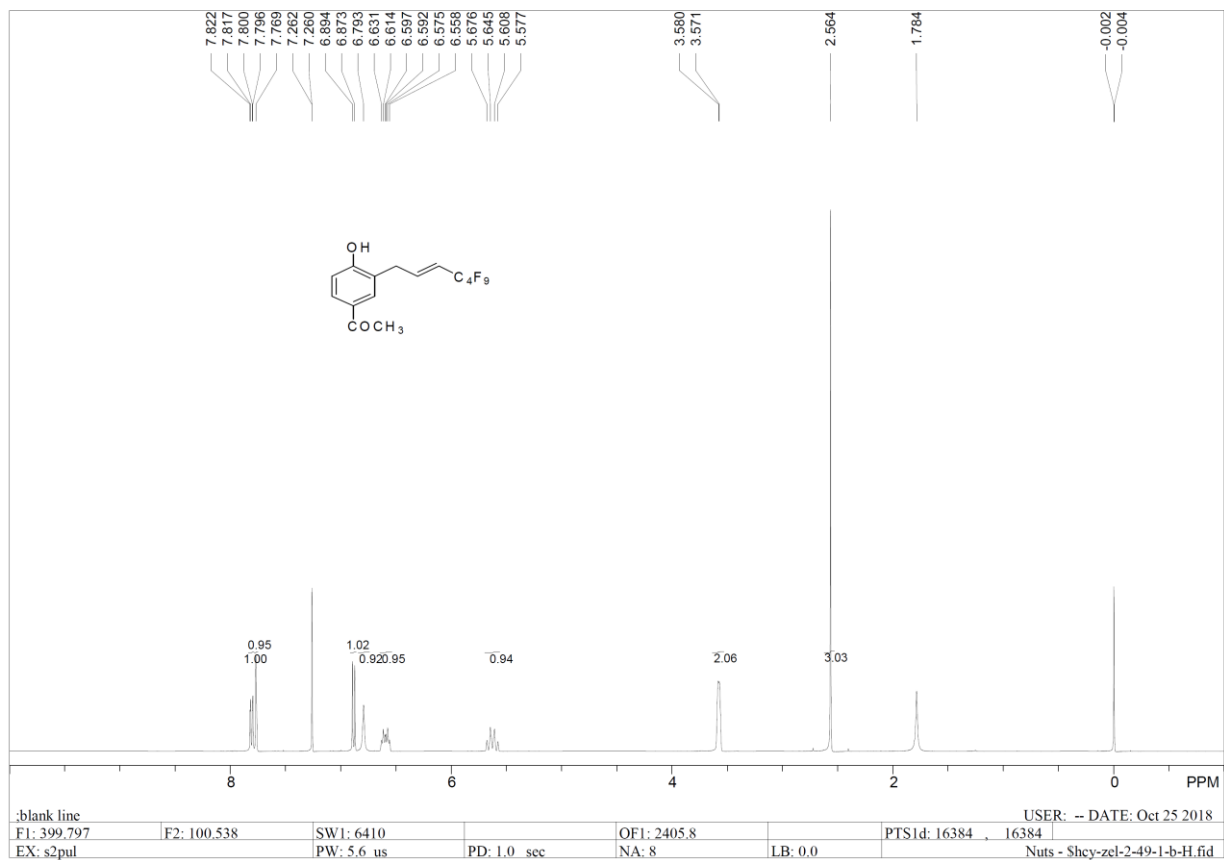


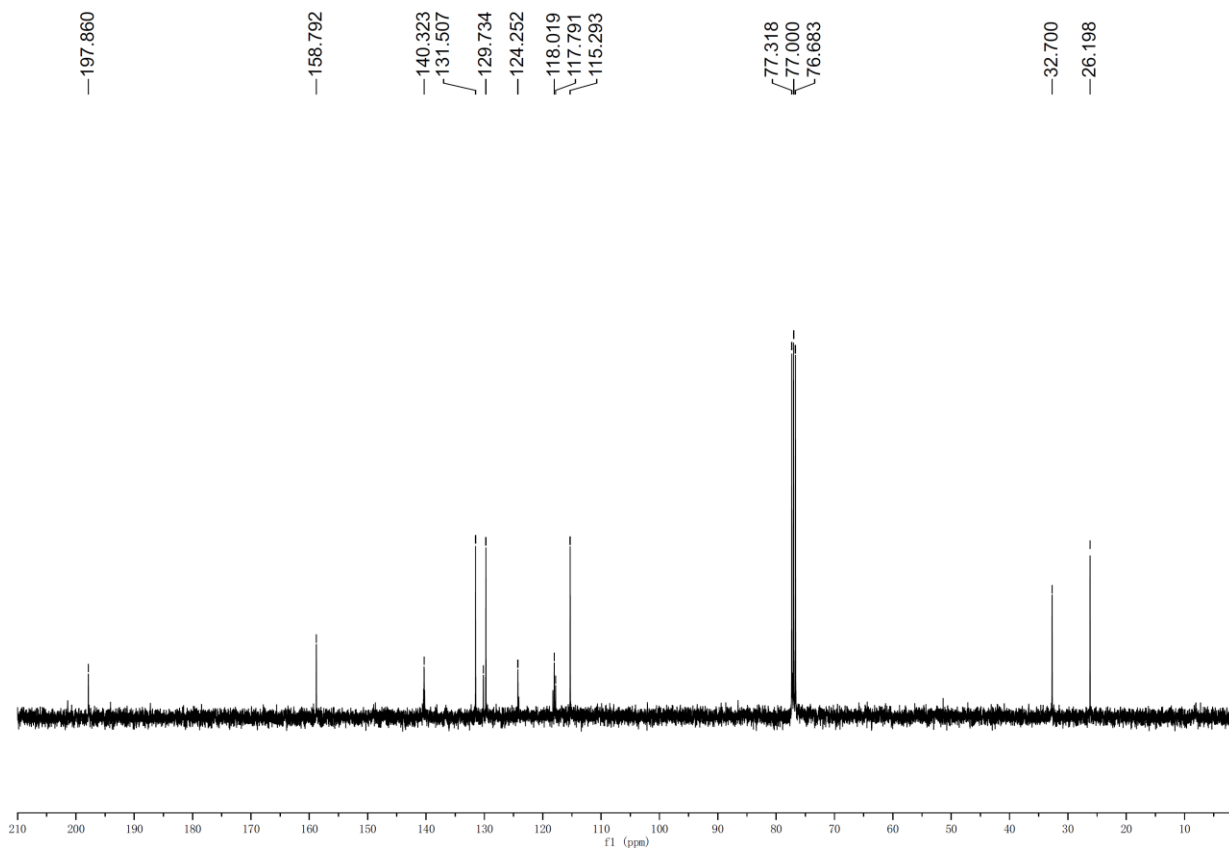


STANDARD FLUORINE PARAMETERS
 F1: 376.152 F2: 100.538 SW1: 89286 OF1: -31975.7 USER: -- DATE: Oct 8 2018
 EX: s2pul PW: 3.2 us PD: 1.0 sec NA: 4 LB: 0.0 PTS1d: 65536 65536
 Nuts - Shey-zel-2-55-3-F.fid

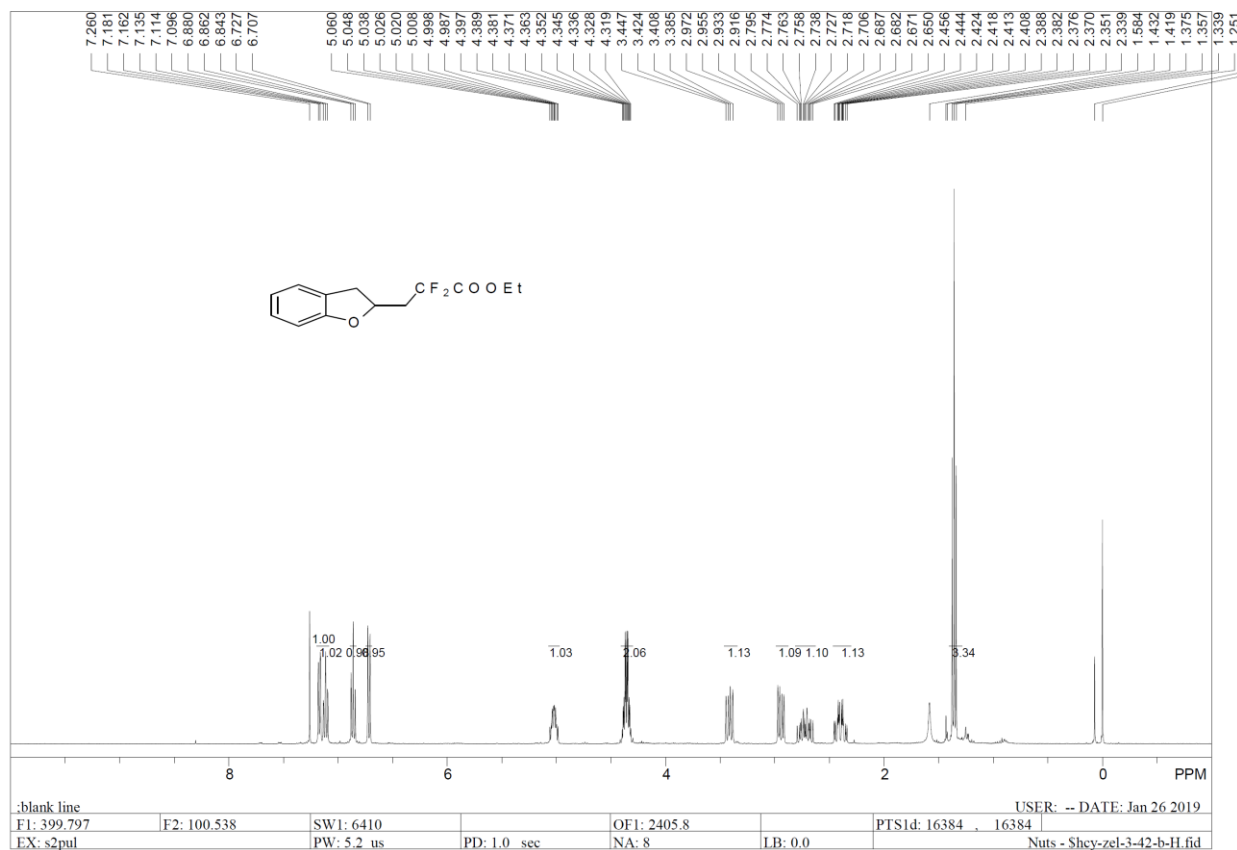


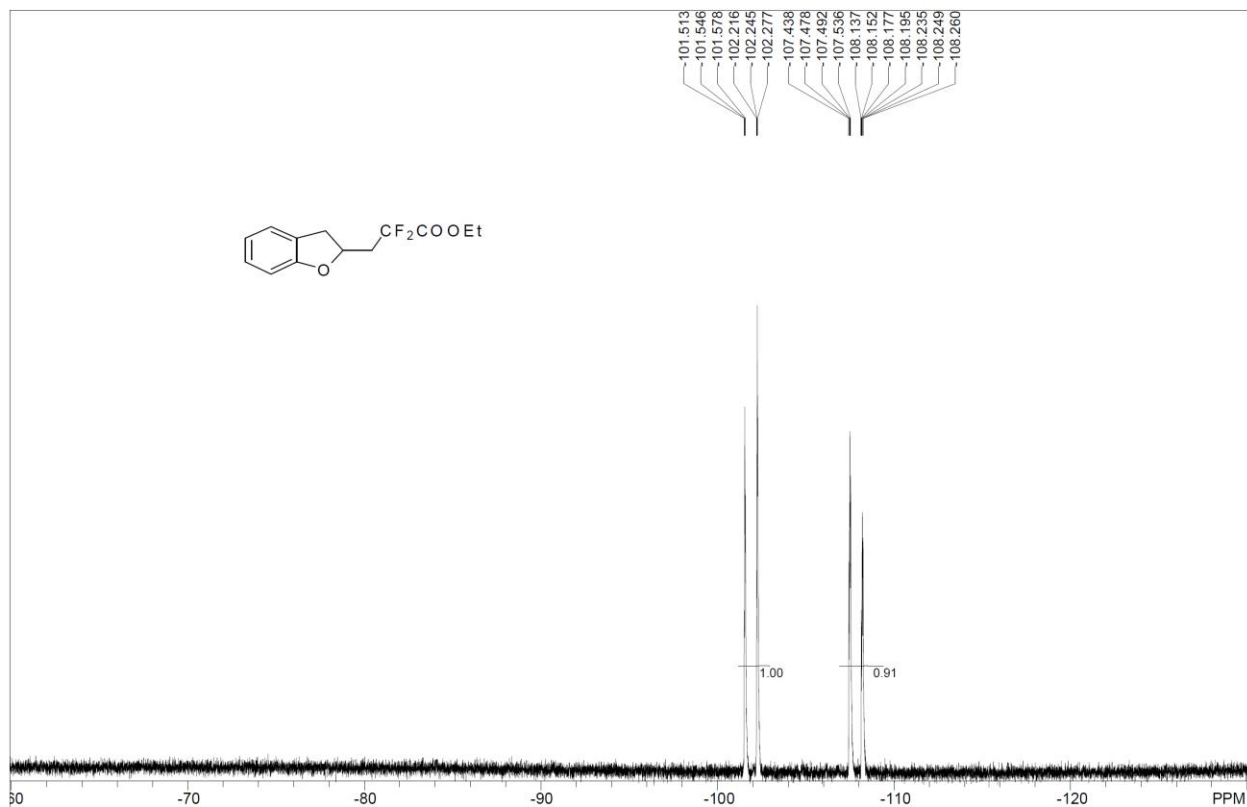
(E)-1-(4-hydroxy-3-(4,4,5,5,6,6,7,7,7-nonafluorohept-2-en-1-yl)phenyl)ethan-1-one (6q).





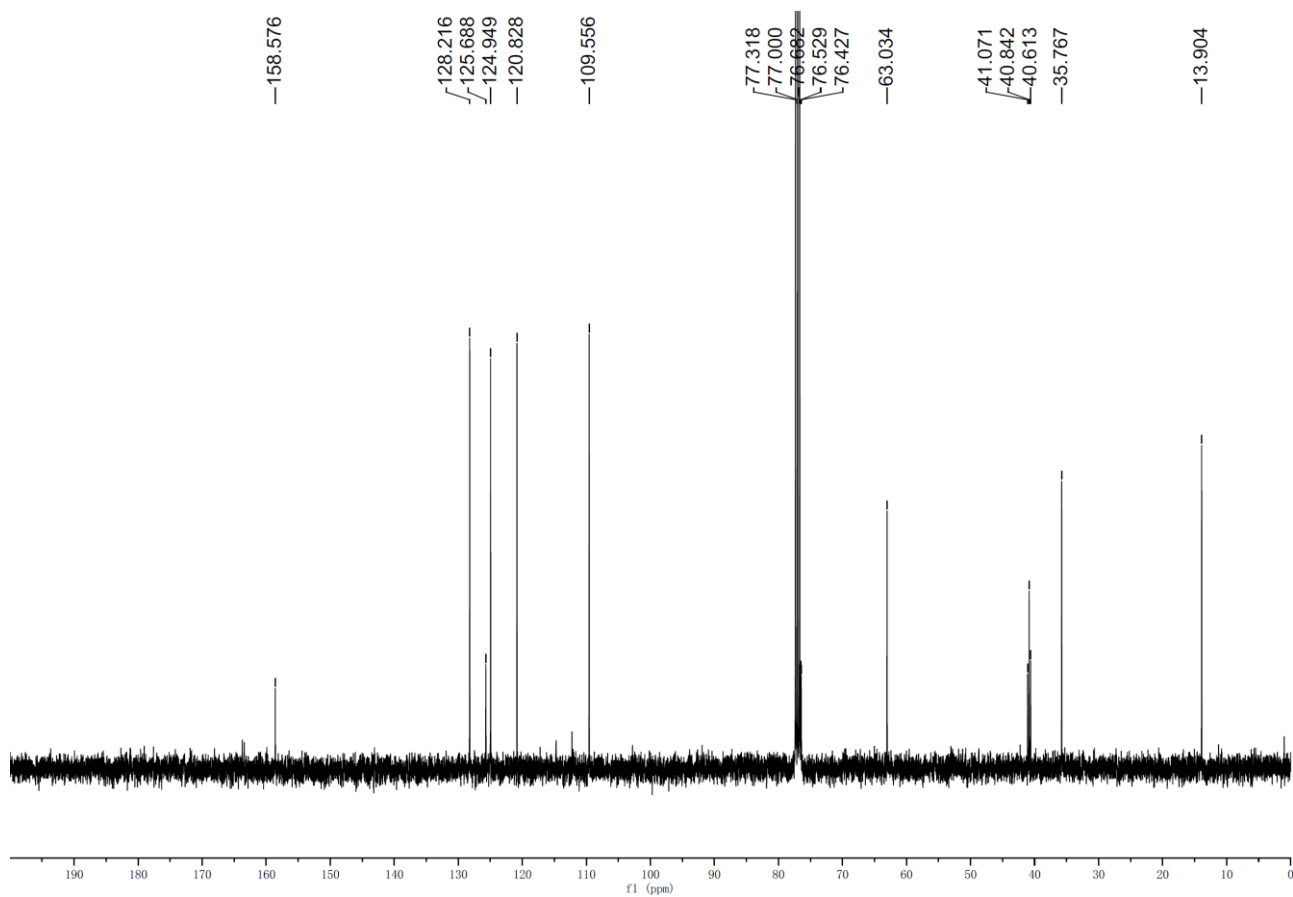
Ethyl 3-(2,3-dihydrobenzofuran-2-yl)-2,2-difluoroacetate (7a).



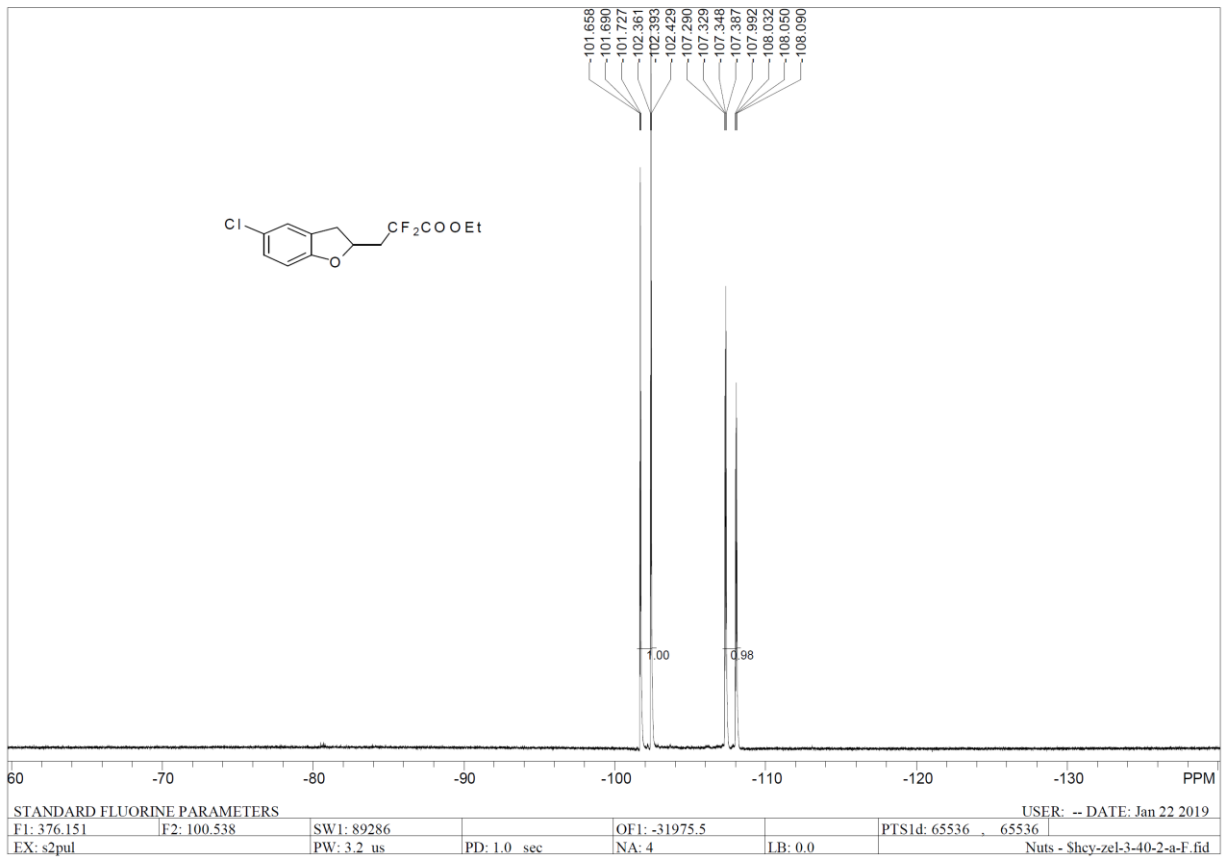
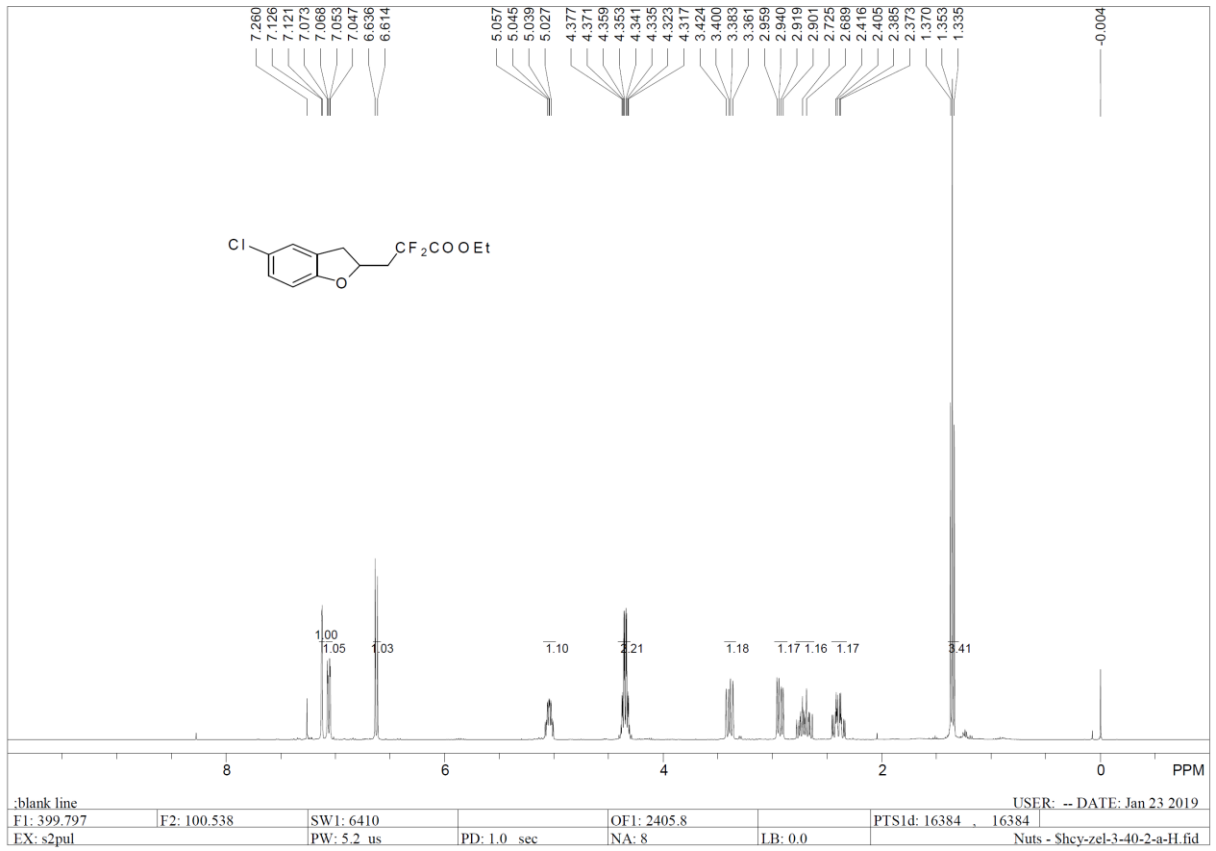


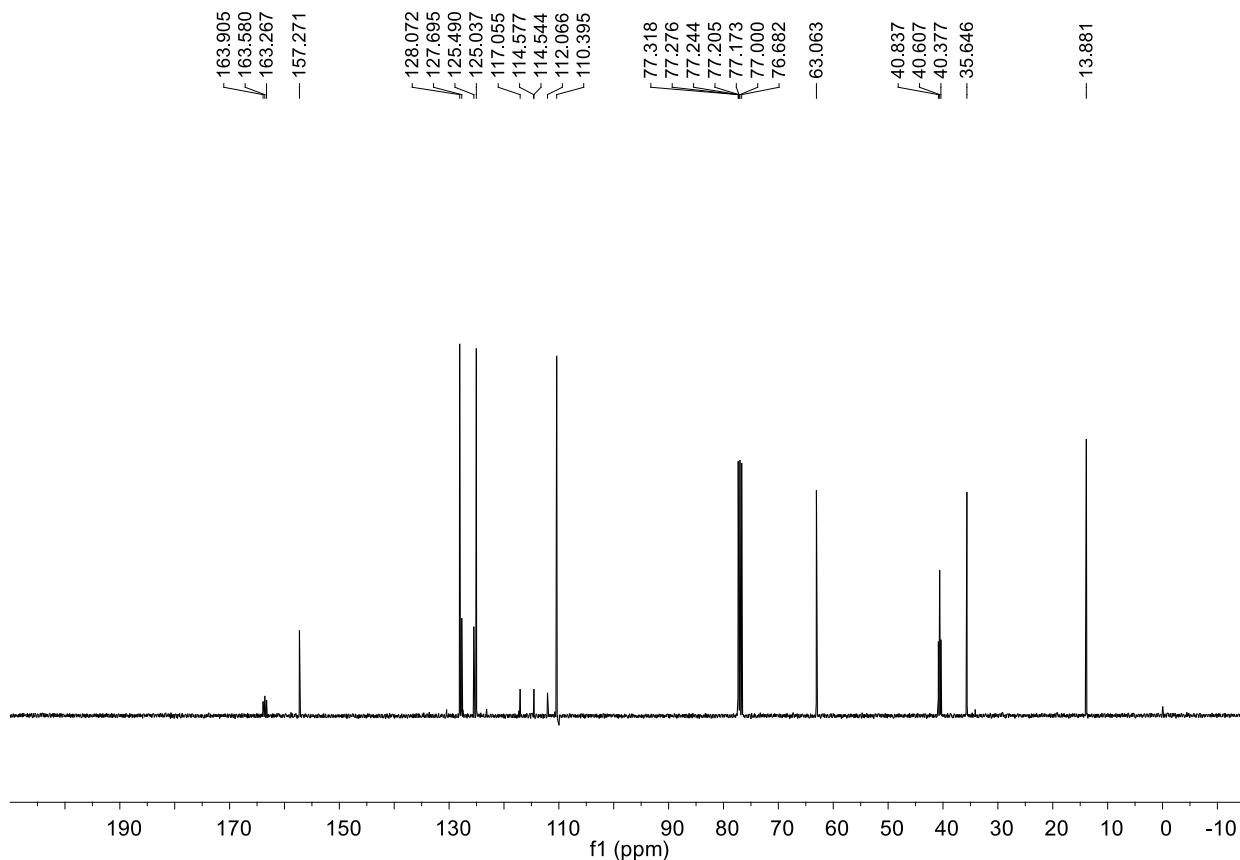
STANDARD FLUORINE PARAMETERS USER: -- DATE: Jan 22 2019

F1: 376.151	F2: 100.538	SW1: 89286	OF1: -31975.5	PTS1d: 65536	65536
EX: s2pul	PW: 3.2 us	PD: 1.0 sec	NA: 4	LB: 0.0	Nuts - Shey-zel-3-42-b-F.fid

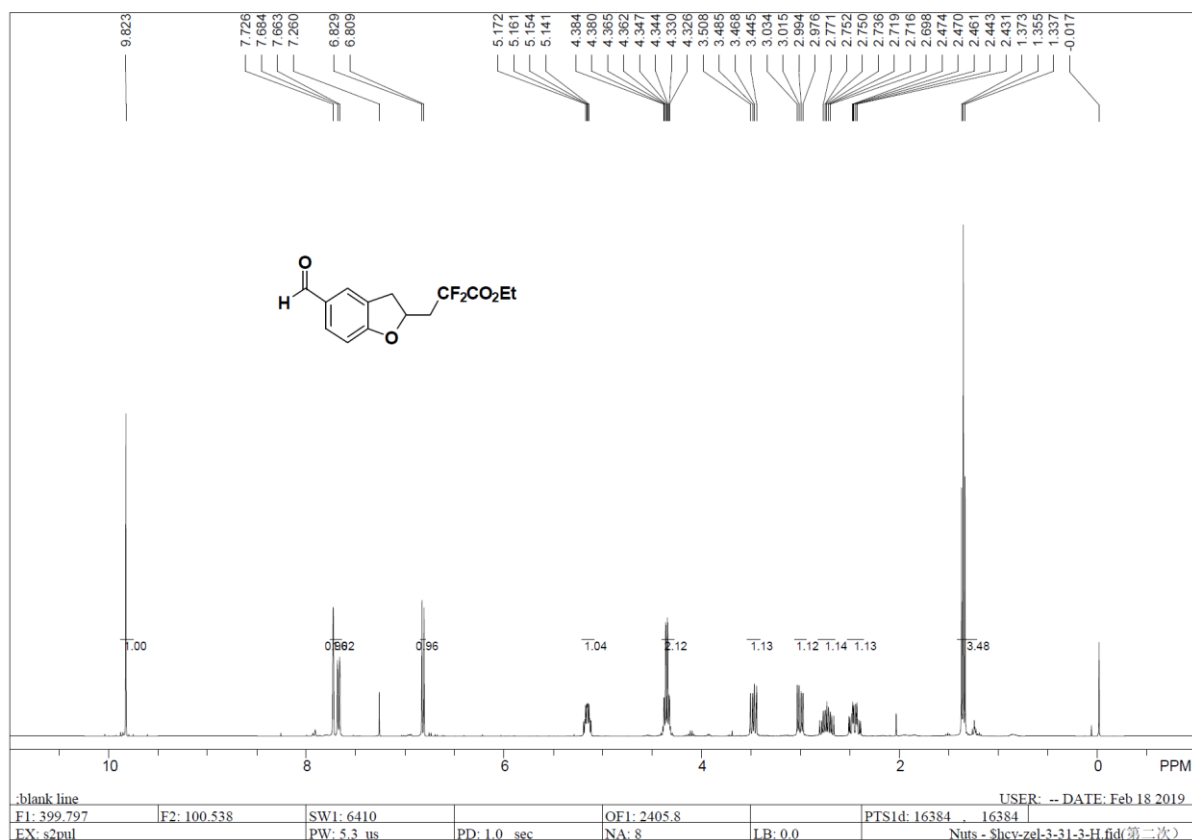


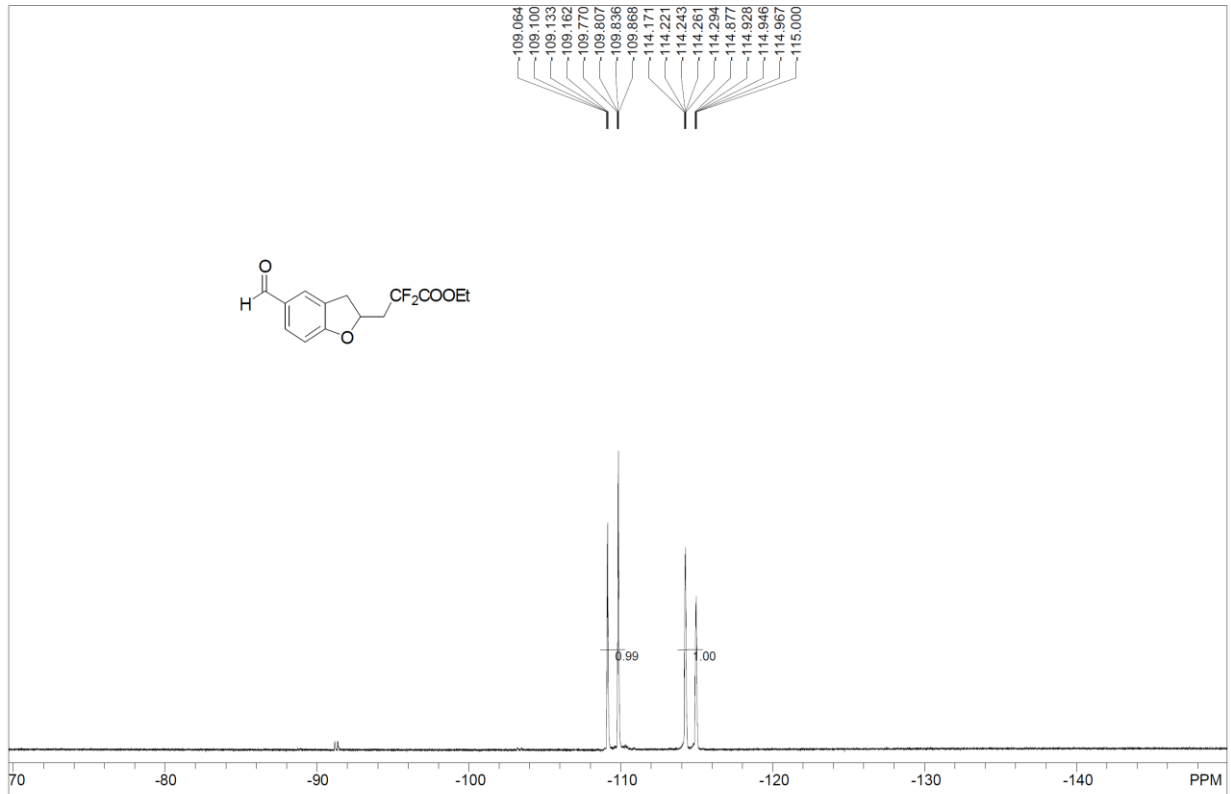
Ethyl 3-(5-chloro-2,3-dihydrobenzofuran-2-yl)-2,2-difluoropropanoate (7b).



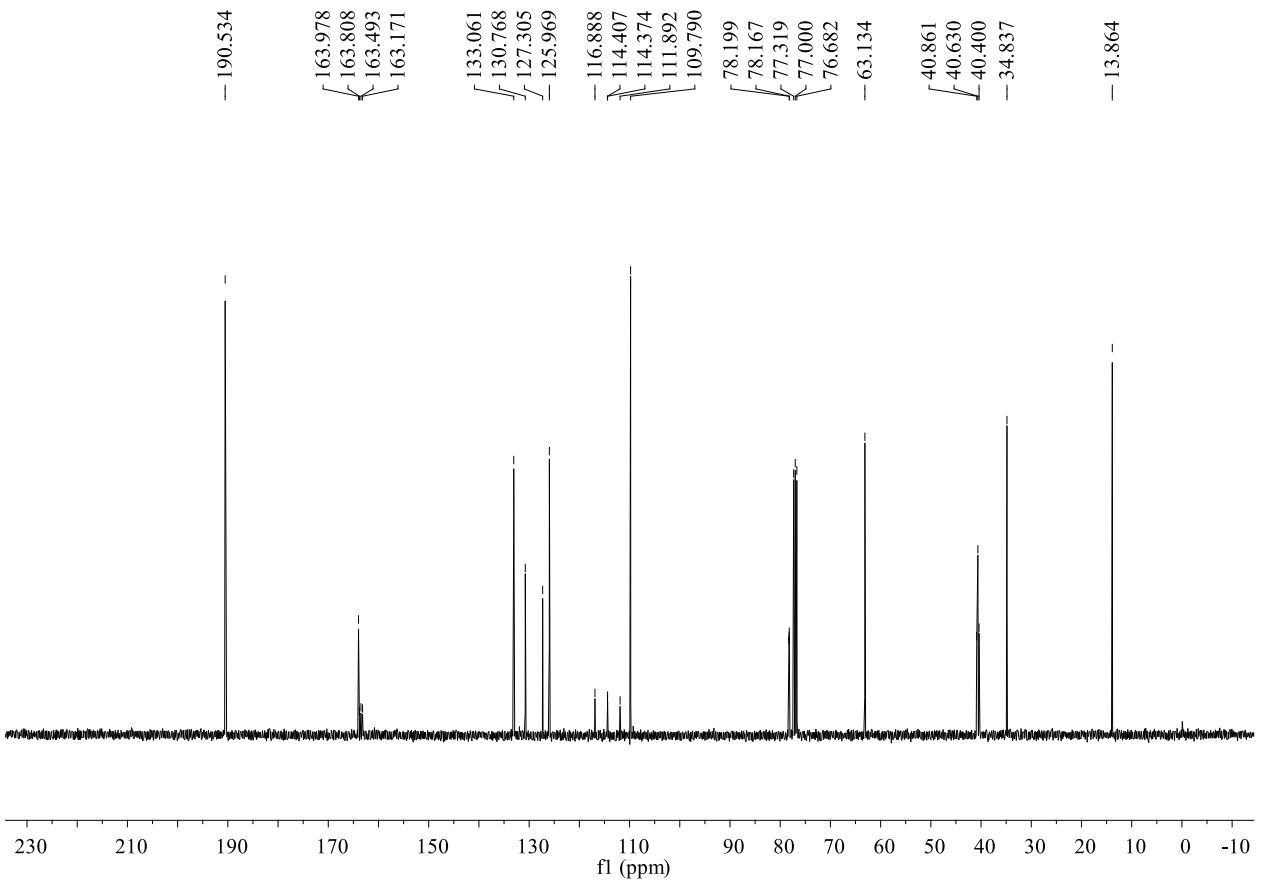


Ethyl 2,2-difluoro-3-(5-formyl-2,3-dihydrobenzofuran-2-yl)propanoate (7c).

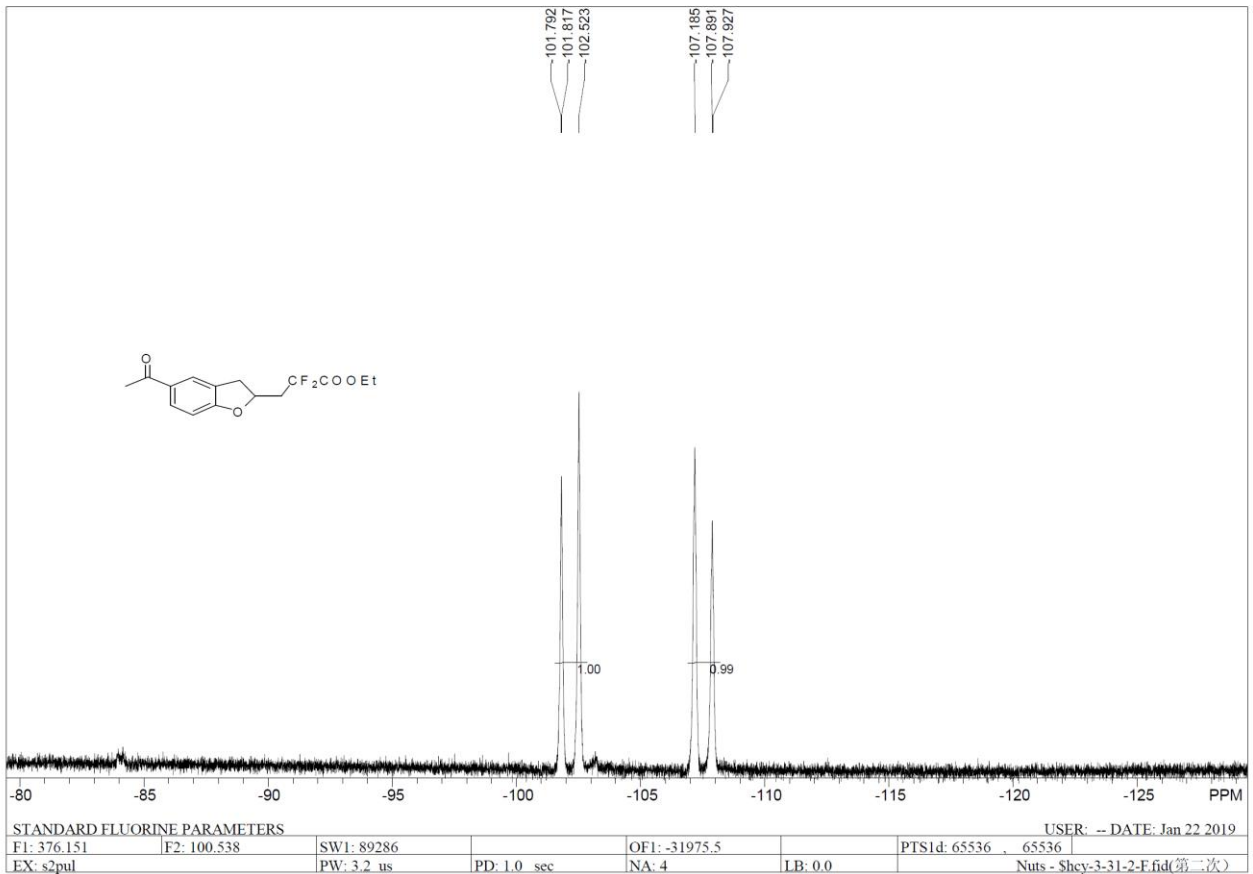
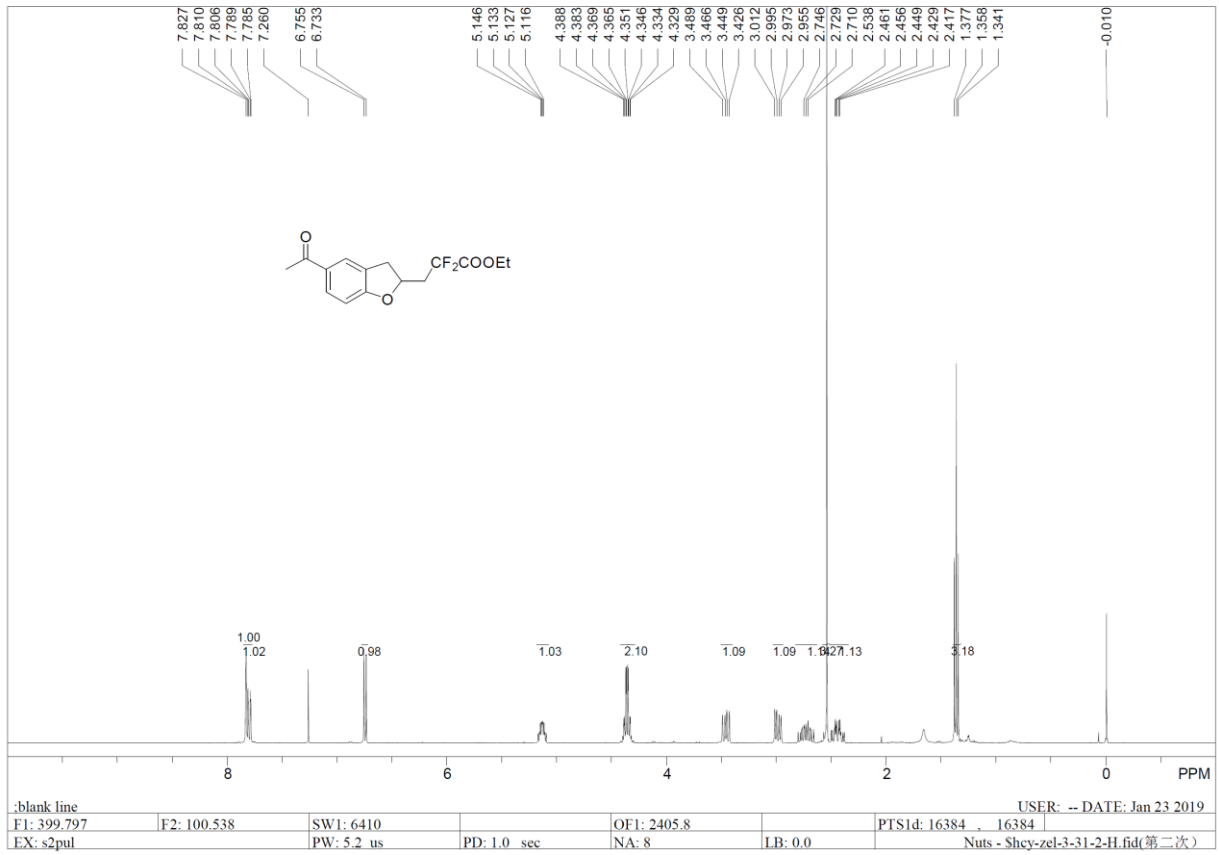


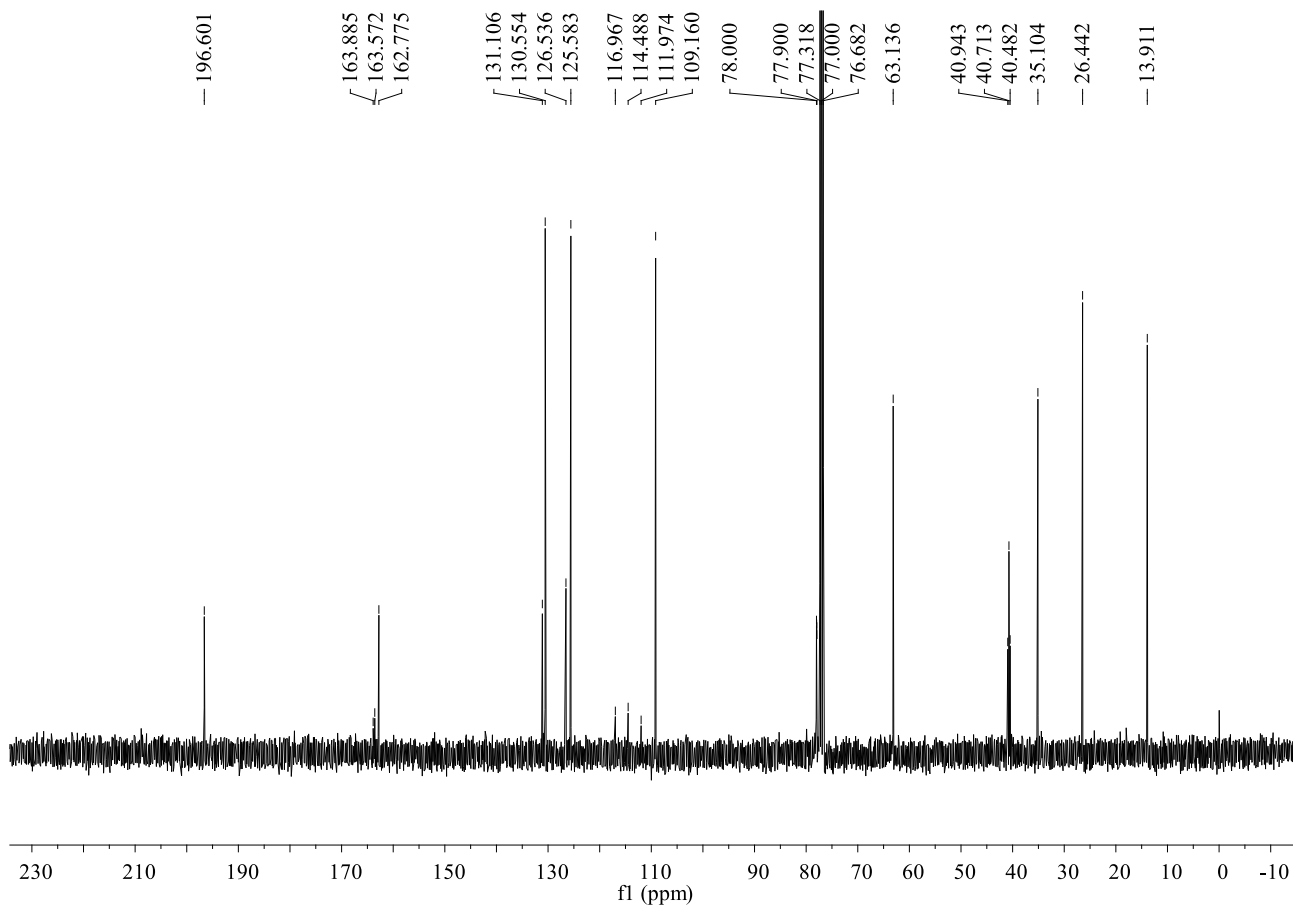


STANDARD FLUORINE PARAMETERS					USER: -- DATE: Jan 4 2019	
F1: 376.153	F2: 100.538	SW1: 89286	PD: 1.0 sec	OF1: -31975.8	PTS1d: 65536	65536
EX: s2pul		PW: 3.2 us		NA: 4	LB: 0.0	Nuts - Shcy-zel-3-31-3-F.fid

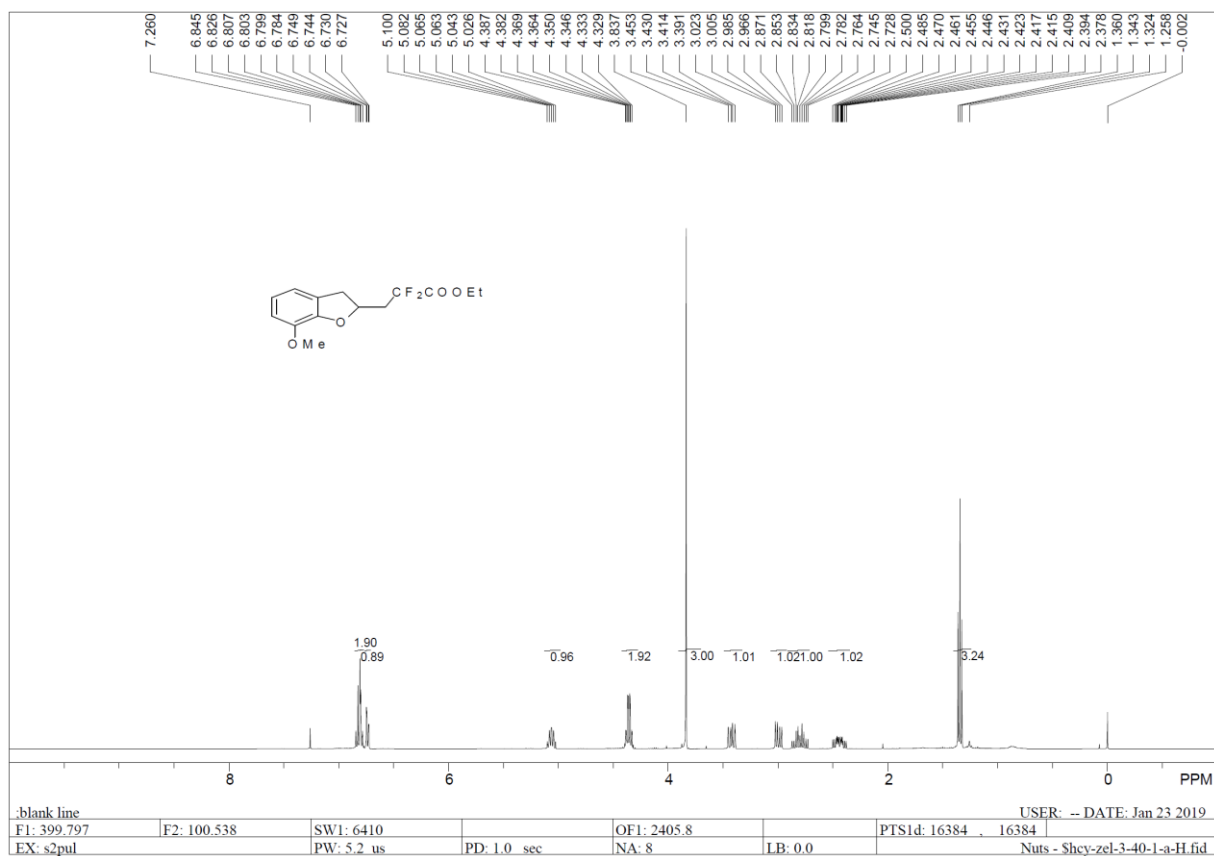


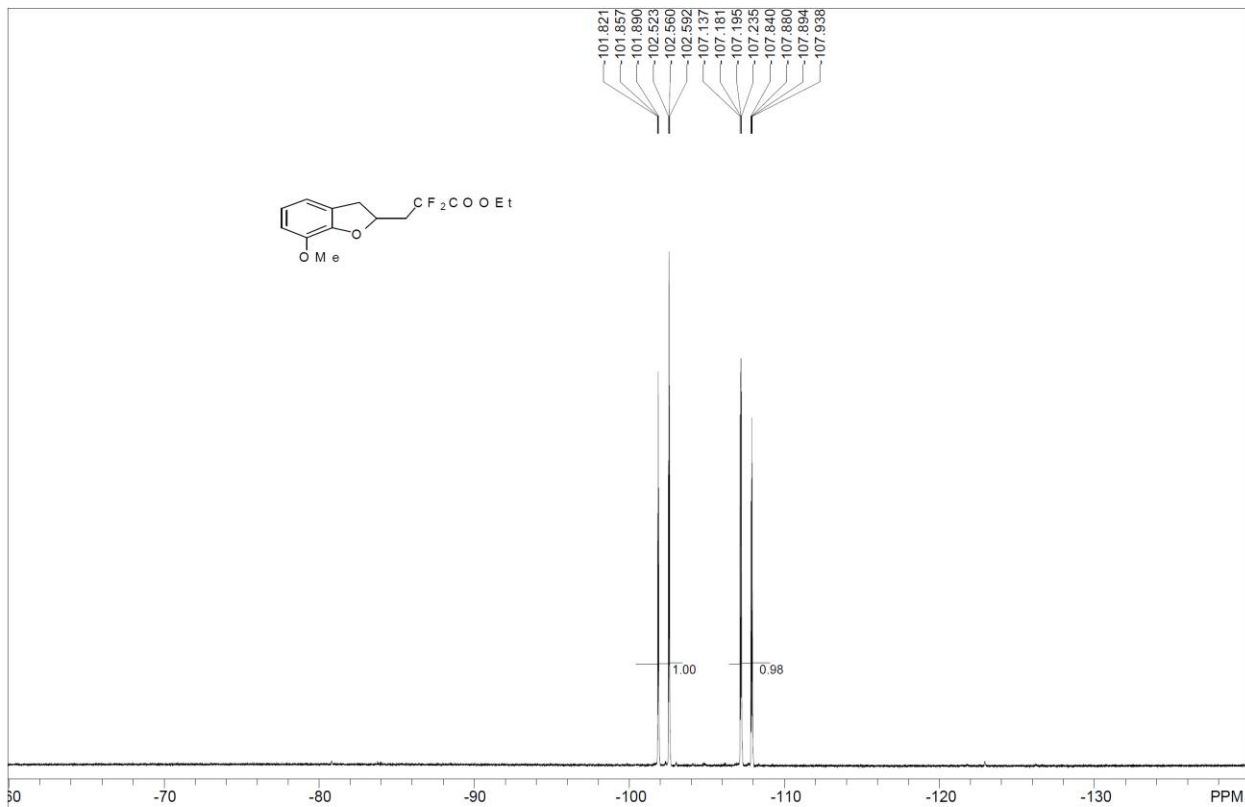
Ethyl 3-(5-acetyl-2,3-dihydrobenzofuran-2-yl)-2,2-difluoropropanoate (7d).





Ethyl 2,2-difluoro-3-(7-methoxy-2,3-dihydrobenzofuran-2-yl)propanoate (7e).





STANDARD FLUORINE PARAMETERS						USER: -- DATE: Jan 22 2019	
F1: 376.151	F2: 100.538	SW1: 89286	OF1: -31975.5	PTS1d: 65536	65536		
EX: s2pul		PW: 3.2 us	PD: 1.0 sec	NA: 4	LB: 0.0	Nuts - Shcy-zel-3-40-1-a-F.fid	

