Supporting Information for

A General and Green Fluoroalkylation Reaction Promoted *via* Noncovalent Interactions between Acetone and Fluoroalkyl Iodides

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List of Contents

1) General information S02

2) General procedure S02

3) Data for compounds **3, 5, 7** S04

4) References S20

5) Mechanism studies S21

6) Copies of NMR spectra of **3, 5, 7** S27

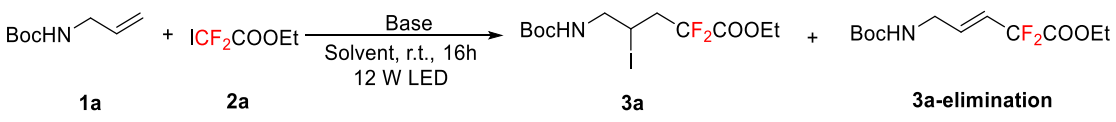
1. General informations

^{1}H NMR spectra and ^{13}C NMR spectra were recorded on an Agilent AM400 spectrometer. ^{19}F NMR was recorded on an Agilent 400MHz NMR spectrometer ($CFCl_3$ 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 ^{19}F NMR using fluorobenzene as an internal standard before working up the reaction.

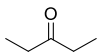
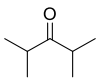
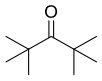
Materials: All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature. All reagents were weighed and handled in air at room temperature. LEDs (430-490 nm) were bought online (Peak Wavelength: 455.0 nm). LEDs with short wavelength (425-430 nm, 450-455 nm, 470-475 nm, 490-495 nm, 510-515 nm, 545-550 nm) were purchased from WATTCAS^{TM}, and relevant experiments were performed in a WP-TEC-1020SL parallel reactor from WATTCAS^{TM}.

2. General procedure

2.1 General procedure for the optimization of the visible-light-promoted difluoroalkylation of allylcarbamate 1a. To a 25 mL of Schlenk tube equipped with a Teflon septum were added Base (1.0-2.0 equiv.) under Ar, followed by solvent (2.0 mL) with stirring. Allylcarbamate **1a** (0.30 mmol, 1.0 equiv.) and ICF_2COOEt (**2a**) (0.45 mmol, 1.5 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.



Entry	Light Source	Base (equiv)	Solvent	3a, Yield (%)	3a-elimination, Yield (%)
1	Blue (430-490)	K_2CO_3 (1)	acetone	74	----
2	Blue (430-490)	KOAc (1)	acetone	64	5
3	Blue (430-490)	K_2CO_3 (2)	acetone	99 (93)	----
4	Blue (430-490)	Na_2CO_3 (2)	acetone	81	----
5	------	K_2CO_3 (2)	acetone	----	----
6	Blue (430-490)	----	acetone	49	----
7	Purple (425-430)	K_2CO_3 (2)	acetone	93	----
8	Blue (450-455)	K_2CO_3 (2)	acetone	93	----
9	Blue (470-475)	K_2CO_3 (2)	acetone	91	----
10	Blue (490-495)	K_2CO_3 (2)	acetone	72	----
11	Green (510-515)	K_2CO_3 (2)	acetone	67	----
12	Green (545-550)	K_2CO_3 (2)	acetone	52	----
13	Blue (430-490)	K_2CO_3 (2)	S-1	82	----
14	Blue (430-490)	K_2CO_3 (2)	S-2	----	----
15	Blue (430-490)	K_2CO_3 (2)	S-3	----	----
16	Blue (430-490)	K_2CO_3 (2)	Dioxane	----	----
17	Blue (430-490)	K_2CO_3 (2)	MeCN	68	----
18	Blue (430-490)	K_2CO_3 (2)	DMA	26	43
19	Blue (430-490)	K_2CO_3 (2)	DMSO	5	30
20	Blue (430-490)	K_2CO_3 (2)	Toluane	----	----

S-1:  S-2:  S-3: 

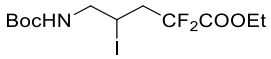
[a] Reaction conditions (unless otherwise specified): **1a** (0.3 mmol, 1.0 equiv), **2a** (0.45 mmol, 1.5 equiv), acetone (2.0 mL), room temperature,16 h. [b] NMR yield determined by ^{19}F NMR using fluorobenzene as internal standard and number in parenthese is yield of isolated product.

2.2 General procedure for the direct fluoroalkylation of alkenes and alkynes. To a 25 mL of Schlenk tube equipped with a Teflon septum were added K_2CO_3 (0.60 mmol, 2.0 equiv) under Ar, followed by acetone (2.0 mL) with stirring. Alkene (**1**)/ alkyne (**4**) (0.30 mmol, 1.0 equiv) and IR_f (**2**) (0.45 mmol, 1.5 equiv) were added subsequently.

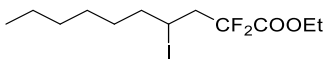
The tube was then irradiated with 12 W blue LEDs (430 nm-490 nm). After stirring for 16 h, the solvent was removed and the residue was purified with silica gel chromatography to provide pure product.

2.3 General procedure for the direct fluoroalkylation of arenes and heteroarenes. To a 25 mL of Schlenk tube equipped with a Teflon septum were added Na_2CO_3 (0.60 mmol, 2.0 equiv) under Ar, followed by Acetone (1.0 mL) + DMF (1.0 mL) with stirring. (Hetero)arene **6** (0.30 mmol, 1.0 equiv) and IR_f (**2**) (0.90 mmol, 3.0 equiv) were added subsequently. The tube was then irradiated with 12 W blue LEDs (430 nm-490 nm). After stirring for 24 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.

3. Data for compounds **3, 5, 7**

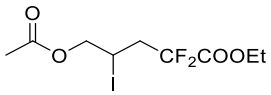


Ethyl 5-((*tert*-butoxycarbonyl)amino)-2,2-difluoro-4-iodopentanoate (3a). The product (114 mg, 93% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 5:1) as pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.01 (br, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 4.31-4.23 (m, 1H), 3.58-3.35 (m, 2H), 2.85-2.70 (m, 2H), 1.43 (s, 9H), 1.35 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.7 (dt, *J* = 264.3 Hz, 15.0 Hz, 1F), -113.4 (dt, *J* = 264.3 Hz, 16.5 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2 (t, *J* = 33.0 Hz), 155.5, 114.8 (t, *J* = 253.8 Hz), 79.9, 63.3, 48.8, 42.0 (t, *J* = 23.8 Hz), 28.2, 21.1, 13.8. HRMS (ESI, m/z): $(M+H)^+$ Calculated for $C_{12}H_{21}NF_2O_4I$: 408.0478; Found: 408.0477.

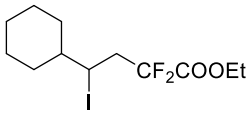


Ethyl 2,2-difluoro-4-iododecanoate (3b). This compound is known.[1] The product (85 mg, 78% yield) was purified with silica gel chromatography (Petroleum ether 100%) as pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.34 (q, *J* = 7.2 Hz, 2H), 4.25-4.19

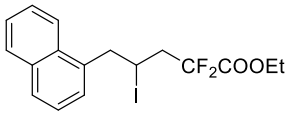
(m, 1H), 2.98-2.67 (m, 2H), 1.86-1.68 (m, 2H), 1.57-1.46 (m, 1H), 1.37 (t, J = 7.2 Hz, 3H), 1.40-1.22 (m, 7H), 0.89 (t, J = 6.6 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.4 (ddd, J = 262.8 Hz, 18.4 Hz, 12.8 Hz, 1F), -114.0 (dt, J = 262.8 Hz, 17.3 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5 (t, J = 32.3 Hz) , 115.2 (t, J = 253.9 Hz), 63.2, 45.3 (t, J = 23.2 Hz), 40.4, 31.6, 29.4, 28.2, 23.3 (t, J = 4.0 Hz), 22.5, 14.0, 13.9.



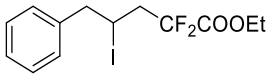
Ethyl 5-acetoxy-2,2-difluoro-4-iodopentanoate (3c). The product (89 mg, 85% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 20:1) as pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.39-4.28 (m, 4H), 4.27-4.20 (m, 1H), 2.92-2.72 (m, 2H), 2.11 (s, 3H), 1.37 (t, J = 7.0 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.3 (ddd, J = 265.5 Hz, 18.0 Hz, 13.2 Hz, 1F), -113.3 (dt, J = 265.8 Hz, 16.9 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 163.1 (t, J = 32.3 Hz), 114.8 (t, J = 254.0 Hz), 68.6, 63.4, 41.7 (t, J = 23.9 Hz), 20.7, 14.5 (t, J = 4.1 Hz) 13.9. MS (ESI, m/z): 368 $(M+NH_4)^+$. HRMS (ESI, m/z): $(M+NH_4)^+$ Calculated for $C_9H_{17}NF_2O_4I$: 368.0165; Found: 368.0163.



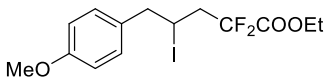
Ethyl 4-cyclohexyl-2,2-difluoro-4-iodobutanoate (3d). The product (104 mg, 96% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 200:1) as pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.34 (q, J = 7.2 Hz, 2H), 4.28-4.19 (m, 1H), 2.93-2.70 (m, 2H), 1.84-1.60 (m, 5H), 1.37 (t, J = 7.0 Hz, 3H), 1.42-1.04 (m, 5H), 0.90-0.80 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.3 (ddd, J = 261.7 Hz, 17.3 Hz, 13.5 Hz, 1F), -107.3 (dt, J = 261.3 Hz, 17.3 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5 (t, J = 32.4 Hz), 115.3 (t, J = 253.5 Hz), 63.2, 44.5, 42.9 (t, J = 23.4 Hz), 33.3, 32.9 (dd, J = 4.2 Hz, 3.1 Hz), 29.9, 26.0, 25.7, 25.6, 13.9. HRMS (ESI, m/z): $(M+Na)^+$ Calculated for $C_{12}H_{19}F_2INaO_2$: 383.0290; Found: 383.0294.



Ethyl 2,2-difluoro-4-iodo-5-(naphthalen-1-yl)pentanoate (3e). The product (91 mg, 73% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 80:1) as pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.86 (m, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.60-7.48 (m, 2H), 7.48-7.40 (m, 1H), 7.39-7.34 (m, 1H), 4.63-4.52 (m, 1H), 4.35-4.20 (m, 2H), 3.75-3.65 (m, 2H), 3.13-2.78 (m, 2H), 1.30 (t, *J* = 7.0 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.1 (dt, *J* = 263.6 Hz, 14.7 Hz, 1F), -113.1 (dt, *J* = 263.6 Hz, 15.0 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3 (t, *J* = 32.5 Hz), 134.9, 134.0, 131.5, 129.1, 128.2, 127.9, 126.5, 125.8, 125.2, 122.9, 115.3 (t, *J* = 253.7 Hz), 63.3, 44.9 (d, *J* = 1.3 Hz), 44.7 (t, *J* = 23.5 Hz), 20.9 (t, *J* = 3.8 Hz), 13.8. HRMS (ESI, m/z): $(M+Na)^+$ Calculated for $C_{17}H_{17}F_2INaO_2$: 441.0134; Found: 441.0140.

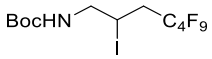


Ethyl 2,2-difluoro-4-iodo-5-phenylpentanoate (3f). This compound is known.[2] The product (93 mg, 84% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 50:1) as pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.27 (m, 3H), 7.20 (d, *J* = 7.2 Hz, 2H), 4.40-4.30 (m, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 3.30-3.16 (m, 2H), 3.00-2.72 (m, 2H), 1.37 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.8 (dt, *J* = 175.6 Hz, 10.5 Hz, 1F), -106.4 (dt, *J* = 175.6 Hz, 11.3 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4 (t, *J* = 32.6 Hz), 138.8, 129.0, 128.5, 127.2, 115.2 (t, *J* = 253.6 Hz), 63.3, 47.1, 44.3 (t, *J* = 23.6 Hz), 21.9 (t, *J* = 3.4 Hz), 13.9.

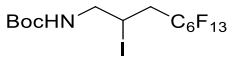


Ethyl 2,2-difluoro-4-iodo-5-(4-methoxyphenyl)pentanoate (3g). The product (108 mg, 91% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 50:1) as pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 4.34 (q, *J* =7.2 Hz, 2H), 4.29 (m, 1H), 3.80 (s, 3H), 3.21-3.11 (m, 2H), 2.96-2.70 (m, 2H), 1.36 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$)

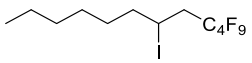
δ -101.7 (ddd, *J* = 263.2 Hz, 16.5 Hz, 13.5 Hz, 1F), -106.5 (dt, *J* = 263.2 Hz, 16.9 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4 (t, *J* = 32.5 Hz), 158.7, 130.9, 130.0, 115.2 (t, *J* = 253.8 Hz), 113.9, 63.2, 55.2, 46.4, 44.1 (t, *J* = 23.6 Hz), 22.7 (t, *J* = 3.7 Hz), 13.9. HRMS (ESI, m/z): $(M+H)^+$ Calculated for $C_{14}H_{18}F_2O_3I$: 399.0263; Found: 399.0262.



***Tert*-butyl (4,4,5,5,6,6,7,7,7-nonafluoro-2-iodoheptyl)carbamate (3h).** This compound is known.[3] The product (109 mg, 72% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.01 (br, 1H), 4.40-4.34 (m, 1H), 3.63-3.40 (m, 2H), 2.95-2.68 (m, 2H), 1.45 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.1 (t, *J* = 6.2 Hz, 3F), -112.7 – -124.5 (m, 2F), -124.6 (m, 2F), -125.9 (t, *J* = 7.7 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 120.0-110.0 (m), 80.2, 48.9, 38.5 (t, *J* = 21.5 Hz), 28.2, 18.6.

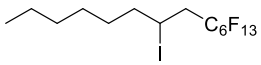


***Tert*-butyl (4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-iodononyl)carbamate (3i).** The product (126 mg, 70% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.98 (br, 1H), 4.41-4.34 (m, 1H), 3.64-3.41 (m, 2H), 2.94-2.70 (m, 2H), 1.45 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.8 (m, 3F), -112.3 – -114.5 (m, 2F), -121.8 (m, 2F), -122.9 (m, 2F). -123.7 (m, 2F), -126.2 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 120.0-110.0 (m), 80.3, 49.0, 38.6 (t, *J* = 21.5 Hz), 28.2, 18.7. HRMS (ESI, m/z): $(M-H)^-$ Calculated for $C_{14}H_{14}F_{13}INO_2$: 601.9867; Found: 601.9877.

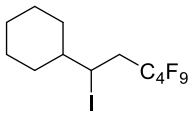


1,1,1,2,2,3,3,4,4-nonafluoro-6-iododododecane (3j). This compound is known.[4] The product (104 mg, 76% yield) was purified with silica gel chromatography (Petroleum ether 100%) as pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.37-4.30 (m, 1H), 3.00-2.66 (m, 2H), 1.89-1.70 (m, 2H), 1.60-1.24 (m, 8H), 0.90 (t, *J* = 6.8 Hz, 3H). ^{19}F

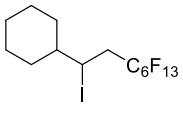
NMR (376 MHz, $CDCl_3$) δ -88.4 (m, 3F), -118.8 – -122.8 (m, 2F), -131.9 (m, 2F), -133.2 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 120.0-110.0 (m), 41.6 (t, *J* = 21.1 Hz), 40.3 (d, *J* = 1.5 Hz), 31.6, 29.5, 28.2, 22.5, 20.8, 14.0.



1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodotetradecane (3k). This compound is known.[5] The product (120 mg, 72% yield) was purified with silica gel chromatography (Petroleum ether 100%) as pale yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 4.37-4.30 (m, 1H), 2.99-2.70 (m, 2H), 1.88-1.72 (m, 2H), 1.60-1.49 (m, 1H), 1.47-1.25 (m, 7H), 0.90 (t, *J* = 6.6 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.8 (m, 3F), -111.6 – -114.9 (m, 2F), -121.8 (m, 2F), -122.9 (m, 2F), -123.7 (m, 2F), -126.2 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 122.0-104.0 (m), 41.7 (t, *J* = 21.0 Hz), 40.4 (d, *J* = 1.9 Hz), 31.6, 29.6, 28.2, 22.6, 20.9, 14.0.

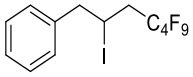


(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)cyclohexane (3l). This compound is known.[6] The product (108 mg, 79% yield) was purified with silica gel chromatography (Petroleum ether 100%) as pale yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 4.35 (td, *J* = 6.8 Hz, 3.2 Hz, 1H), 2.91-2.76 (m, 2H), 1.85-1.76 (m, 2H), 1.75-1.62 (m, 3H), 1.44-1.06 (m, 5H), 0.88-0.78 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.1 (m, 3F), -112.3 – -115.5 (m, 2F), -124.6 (m, 2F), -126.0 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 120.0-110.0 (m), 44.2, 39.0 (t, *J* = 20.9 Hz), 33.7, 30.3, 29.7, 26.0, 25.7, 25.5.

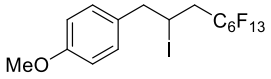


(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-iodooctyl)cyclohexane (3m). The product (132 mg, 79% yield) was purified with silica gel chromatography (Petroleum ether 100%) as pale yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 4.35 (td, *J* = 6.4 Hz, 2.8

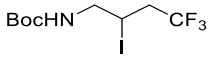
Hz, 1H), 2.93-2.75 (m, 2H), 1.86-1.75 (m, 2H), 1.75-1.61 (m, 3H), 1.44-1.04 (m, 5H), 0.88-0.77 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.0 (m, 3F), -112.4 – -115.2 (m, 2F), -121.9 (m, 2F), -123.0 (m, 2F), -123.7 (m, 2F), -126.3 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 122.0-104.0 (m), 44.2, 39.1 (t, *J* = 20.8 Hz), 33.7, 30.3, 29.7, 26.0, 25.8, 25.5. HRMS (EI): Calculated for $C_{14}H_{14}F_{13}I$: 555.9933; Found: 555.9942.



(4,4,5,5,6,6,7,7,7-nonafluoro-2-iodoheptyl)benzene (3n). This compound is known.[6] The product (117 mg, 84% yield) was purified with silica gel chromatography (Petroleum ether 100%) as pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.29 (m, 3H), 7.21 (d, *J* = 7.6 Hz, 2H), 4.52-4.43 (m, 1H), 3.31 (dd, *J* = 14.4 Hz, 5.6 Hz, 1H), 3.21 (dd, *J* = 14.4 Hz, 8.8 Hz, 1H), 3.02-2.78 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.1 (m, 3F), -111.8 – -114.6 (m, 2F), -124.6 (m, 2F), -126.0 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 128.9, 128.6, 127.3, 122.0-104.0 (m), 47.0 (d, *J* = 1.5 Hz), 40.7 (t, *J* = 21.0 Hz), 19.3.

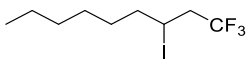


1-methoxy-4-(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-iodononyl)benzene (3o). The product (121 mg, 68% yield) was purified with silica gel chromatography (Petroleum ether 100%) as pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.47-4.38 (m, 1H), 3.81 (s, 3H), 3.22 (dd, *J* = 14.8 Hz, 6.0 Hz, 1H), 3.15 (dd, *J* = 14.8 Hz, 8.8 Hz, 1H), 2.96-2.76 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.8 – -81.0 (m, 3F), -111.8 – -114.1 (m, 2F), -121.8 (m, 2F), -122.9 (m, 2F), -123.7 (m, 2F), -126.2 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 130.6, 130.0, 113.9, 122.0-104.0 (m), 55.2, 46.2, 40.6 (t, *J* = 21.0 Hz), 20.2. HRMS (EI): Calculated for $C_{16}H_{12}F_{13}OI$: 593.9725; Found: 593.9728.

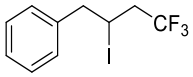


***Tert*-butyl (4,4,4-trifluoro-2-iodobutyl)carbamate (3p).** This compound is known.[3]

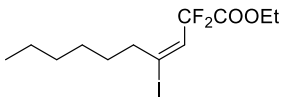
The product (76 mg, 72% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 5:1) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.09 (br, 1H), 4.27-4.18 (m, 1H), 3.55-3.40 (m, 2H), 2.87-2.72 (m, 2H), 1.43 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.0 (t, *J* = 10.0 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 125.4 (q, *J* = 279.4 Hz), 80.1, 48.5, 41.6 (q, *J* = 29.3 Hz), 28.2, 20.0.



1,1,1-trifluoro-3-iodononane (3q). This compound is known.[7] The product (51 mg, 55% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 100:1) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23-4.16 (m, 1H), 2.97-2.71 (m, 2H), 1.85-1.67 (m, 2H), 1.58-1.48 (m, 1H), 1.44-1.24 (m, 7H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.0 (t, *J* = 10.3 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 125.6 (q, *J* = 280.0 Hz), 44.9 (q, *J* = 28.3 Hz), 39.6, 31.6, 29.4, 28.2, 22.5, 21.9 (q, *J* = 2.8 Hz), 14.0.

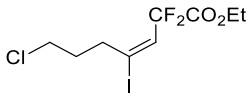


(4,4,4-trifluoro-2-iodobutyl)benzene (3r). This compound is known.[8] The product (39 mg, 41% yield) was purified with silica gel chromatography (Petroleum ether 100%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.29 (m, 3H), 7.20 (d, *J* = 6.8 Hz, 2H), 4.38-4.30 (m, 1H), 3.30-3.18 (m, 2H), 2.95-2.75 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.7 (t, *J* = 10.0 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 128.9, 128.6, 127.3, 125.5 (q, *J* = 279.7 Hz), 46.6, 43.7 (q, *J* = 28.6 Hz), 20.2 (q, *J* = 2.7 Hz).

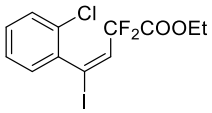


Ethyl (*E*)-2,2-difluoro-4-iododec-3-enoate (5a). This compound is known.[9] The product (94 mg, 87% yield, *Z:E* = 1:4.3) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 100:1) as colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39 (t, *J* = 13.2 Hz, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 2.59 (t, *J* = 7.2 Hz, 2H), 1.60-1.48

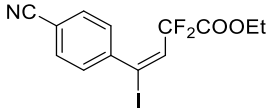
(m, 2H), 1.35 (t, J = 7.2 Hz, 3H), 1.40-1.25 (m, 6H), 0.89 (t, J = 6.4 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.0 (d, J = 6.8 Hz, 2F, *E*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2 (t, J = 34.4 Hz), 131.2 (t, J = 27.2 Hz), 119.6 (t, J = 7.7 Hz), 111.5 (t, J = 253.5 Hz), 63.3, 40.7, 31.5, 29.8, 28.0, 22.5, 14.0, 13.9.



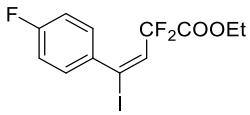
Ethyl (*E*)-7-chloro-2,2-difluoro-4-iodohept-3-enoate (5b). The product (84 mg, 80% yield, *Z:E* = 1:4.3) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 100:1) as colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.45 (t, J = 13.2 Hz, 1H), 4.34 (q, J = 7.2 Hz, 2H), 3.55 (t, J = 6.6 Hz, 2H), 2.79 (t, J = 7.4 Hz, 2H), 2.07-1.99 (m, 2H), 1.35 (t, J = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -97.9 (d, J = 13.2 Hz, 2F, *E*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0 (t, J = 34.3 Hz), 132.3 (t, J = 27.1 Hz), 116.5 (t, J = 7.5 Hz), 111.5 (t, J = 253.9 Hz), 63.5, 43.1, 38.4 (t, J = 2.2 Hz), 32.7, 13.9. HRMS (ESI, m/z): $(M+Na)^+$ Calculated for $C_9H_{12}ClF_2INaO_2$: 374.9431; Found: 374.9444.



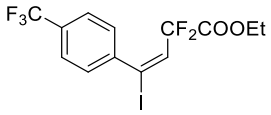
Ethyl (*E*)-4-(2-chlorophenyl)-2,2-difluoro-4-iodobut-3-enoate (5c). This compound is known.[10] The product (94 mg, 81% yield, *Z:E* = 1:33) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 100:1) as colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.34 (m, 1H), 7.30-7.19 (m, 3H), 6.79 (t, J = 11.4 Hz, 1H), 4.19-4.10 (m, 2H), 1.28 (t, J = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.0 (m, 2F, *E*). ^{13}C NMR (101 MHz, $CDCl_3$) 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 (t, J = 2.0 Hz), 126.5, 110.8 (t, J = 253.9 Hz), 103.3 (t, J = 9.1 Hz), 63.3, 13.7.



Ethyl (*E*)-4-(4-cyanophenyl)-2,2-difluoro-4-iodobut-3-enoate (5d). This compound is known.[10] The product (70 mg, 62% yield, *Z:E* = 1:21) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 30:1) as colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 6.75 (t, *J* = 11.8 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -96.0 (d, *J* = 11.7 Hz, 2F, *E*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (t, *J* = 33.3 Hz), 145.3, 133.8 (t, *J* = 27.0 Hz), 131.8, 128.2 (t, *J* = 2.2 Hz), 118.0, 112.9, 110.8 (t, *J* = 253.7 Hz), 105.0 (t, *J* = 8.5 Hz), 63.5, 13.7.

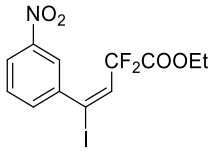


Ethyl (*E*)-2,2-difluoro-4-(4-fluorophenyl)-4-iodobut-3-enoate (5e). This compound is known.[10] The product (94 mg, 85% yield, *Z:E* = 1:20) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 100:1) as colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 8.6 Hz, 5.4 Hz, 2H), 7.01 (t, *J* = 8.6 Hz, 2H), 6.71 (t, *J* = 11.2 Hz, 1H), 4.06 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -94.4 (d, *J* = 7.5 Hz, 2F, *E*), -110.7 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8 (d, *J* = 251.8 Hz), 162.4 (t, *J* = 33.4 Hz), 136.8 (d, *J* = 3.4 Hz), 133.3 (t, *J* = 28.1 Hz), 129.9 (td, *J* = 8.7 Hz, 2.1 Hz), 115.1 (d, *J* = 22.2 Hz), 110.8 (t, *J* = 251.9 Hz), 107.3 (t, *J* = 9.7 Hz), 63.2, 13.7.

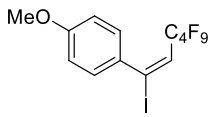


Ethyl (*E*)-2,2-difluoro-4-iodo-4-(4-(trifluoromethyl)phenyl)but-3-enoate (5f). This compound is known.[10] The product (102 mg, 81% yield, *Z:E* = 1:24) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 100:1) as colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 6.76 (t, *J* = 11.4 Hz, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.0 (s, 3F), -95.3 (d, *J* = 11.7 Hz, 2F, *E*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (t, *J* = 33.4 Hz), 144.3, 133.8 (t, *J* = 27.4 Hz), 131.2 (q, *J* = 33.0 Hz), 128.0 (t,

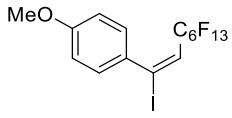
J = 2.0 Hz), 125.1 (q, *J* = 3.8 Hz), 123.6 (q, *J* = 273.4 Hz), 110.8 (t, *J* = 253.0 Hz), 105.9 (t, *J* = 8.9 Hz), 63.4, 13.7.



Ethyl (E)-2,2-difluoro-4-iodo-4-(3-nitrophenyl)but-3-enoateEthyl (5g). The product (83 mg, 70% yield, *Z:E* = 1:32) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 30:1) as colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19-8.14 (m, 2H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 6.79 (t, *J* = 12.0 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -96.4 (d, *J* = 11.7 Hz, 2F, *E*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (t, *J* = 33.4 Hz), 147.5, 142.5, 134.3 (t, *J* = 26.9 Hz), 133.4 (t, *J* = 2.1 Hz), 129.2, 123.9, 122.5 (t, *J* = 2.2 Hz), 110.9 (t, *J* = 253.7 Hz), 104.2 (t, *J* = 8.3 Hz), 63.6, 13.8. HRMS (EI, m/z): Calculated for $C_{12}H_{10}F_2INO_4$: 396.9623; Found: 396.9630.

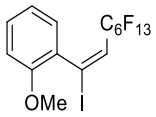


(E)-1-methoxy-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (5h). The product (110 mg, 77% yield) was purified with silica gel chromatography (Petroleum ether 100%) as colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.56 (t, *J* = 13.6 Hz, 1H), 3.82 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.1 (m, 3F), -105.1 (m, 2F), -123.9 (m, 2F), -125.9 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 133.6, 128.8 (t, *J* = 2.2 Hz), 126.3 (t, *J* = 21.8 Hz), 118.0-110.0 (m), 113.5 (t, *J* = 6.3 Hz), 113.3, 55.2. MS (EI): m/z (%) 478 (M^+), 351 (100), 132. HRMS (EI): Calculated for $C_{13}H_8F_9OI$ (M^+): 477.9476; Found: 477.9474.

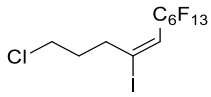


(*E*)-1-methoxy-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-iodooct-1-en-1-yl)

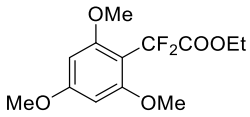
benzene (5i). The product (130 mg, 75% yield) was purified with silica gel chromatography (Petroleum ether 100%) as colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.56 (t, *J* = 13.4 Hz, 1H), 3.82 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.9 (m, 3F), -104.9 (m, 2F), -121.8 (m, 2F), -123.0 (m, 4F), -126.3 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 133.6, 128.8 (t, *J* = 2.1 Hz), 126.4 (t, *J* = 21.9 Hz), 113.5 (t, *J* = 6.3 Hz), 113.3, 110.0-104.0 (m), 55.3. HRMS (EI): Calculated for $C_{15}H_8F_{13}OI$: 577.9412; Found: 577.9419.



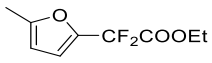
(*E*)-1-methoxy-2-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-iodooct-1-en-1-yl)benzene (5j). The product (128 mg, 74% yield) was purified with silica gel chromatography (Petroleum ether 100%) as colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 6.92 (t, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.60 (t, *J* = 13.2 Hz, 1H), 3.88 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.9 (t, *J* = 9.8 Hz, 3F), -107.9 (q, *J* = 13.2 Hz, 2F), -121.9 (m, 2F), -123.0 (m, 2F), -123.3 (m, 2F), -126.3 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 130.7, 129.9, 128.0 (t, *J* = 22.1 Hz), 127.8, 120.0, 111.0, 108.2 (t, *J* = 6.1 Hz), 110.0-104.0 (m), 55.5. HRMS (EI): Calculated for $C_{15}H_8F_{13}OI$: 577.9412; Found: 577.9416.



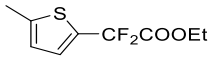
(*E*)-1-chloro-6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluoro-4-iodoundec-4-ene (5k). The product (99 mg, 60% yield) was purified with silica gel chromatography (Petroleum ether 100%) as colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39 (t, *J* = 14.4 Hz, 1H), 3.56 (t, *J* = 6.4 Hz, 2H), 2.83 (t, *J* = 7.4 Hz, 2H), 2.12-2.02 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.0 (t, *J* = 9.8 Hz, 3F), -105.7 (q, *J* = 13.0 Hz, 2F), -121.8 (m, 2F), -123.0 (m, 2F), -123.3 (m, 2F), -126.3 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 127.7 (t, *J* = 24.0 Hz), 119.9 (t, *J* = 6.6 Hz), 110.0-104.0 (m), 43.0, 38.8 (t, *J* = 2.8 Hz), 32.8. HRMS (EI): Calculated for $C_{11}H_7F_{13}ClI$: 547.9073; Found: 547.9068.



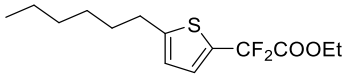
Ethyl 2,2-difluoro-2-(2,4,6-trimethoxyphenyl)acetate (7a). This compound is known.[11] The product (82 mg, 94% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.11 (s, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 3.78 (s, 6H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -96.4 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8 (t, *J* = 33.4 Hz), 163.2, 160.1 (t, *J* = 2.6 Hz), 113.3 (t, *J* = 248.7 Hz), 102.6 (t, *J* = 25.2 Hz), 91.4, 62.3, 56.1, 55.3, 14.0.



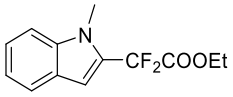
Ethyl 2,2-difluoro-2-(5-methylfuran-2-yl)acetate (7b). This compound is known.[12] The product (36 mg, 59% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 100:1) as colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.63-6.61 (m, 1H), 6.05-6.02 (m, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 2.33-2.31 (m, 3H), 1.36 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.1 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6 (t, *J* = 34.0 Hz), 155.2 (t, *J* = 1.8 Hz), 142.6, 112.6 (t, *J* = 3.8 Hz), 108.7 (t, *J* = 247.9 Hz), 106.9 (t, *J* = 0.9 Hz), 63.4, 13.9, 13.5.



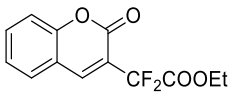
Ethyl 2,2-difluoro-2-(5-methylthiophen-2-yl)acetate (7c). This compound is known.[13] The product (37 mg, 56% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 50:1) as colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.16 (m, 1H), 6.72-6.69 (m, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 2.51-2.49 (m, 3H), 1.35 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -92.9 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4 (t, *J* = 35.5 Hz), 144.2 (t, *J* = 1.8 Hz), 131.1 (t, *J* = 30.3 Hz), 128.5 (t, *J* = 5.8 Hz), 125.3, 111.6 (t, *J* = 251.0 Hz), 63.3, 15.2, 13.9.



Ethyl 2,2-difluoro-2-(5-hexylthiophen-2-yl)acetate (7d). The product (60 mg, 69% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 100:1) as colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.16 (m, 1H), 6.76-6.71 (m, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 2.80 (t, *J* = 7.2 Hz, 2H), 1.71-1.63 (m, 2H), 1.40-1.27 (m, 6H), 1.36 (t, *J* = 7.2 Hz, 3H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -92.7 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5 (t, *J* = 35.8 Hz), 150.4, 130.8 (t, *J* = 30.5 Hz), 128.3 (t, *J* = 5.8 Hz), 124.1, 111.7 (t, *J* = 250.3 Hz), 63.3, 31.5, 31.4, 30.0, 28.7, 22.5, 14.0, 13.9. HRMS (ESI, m/z): $(M+Na)^+$ Calculated for $C_{14}H_{20}F_2NaO_2S$: 313.1044; Found: 313.1052.

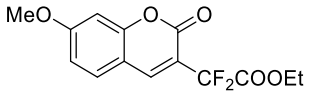


Ethyl 2,2-difluoro-2-(1-methyl-1*H*-indol-2-yl)acetate (7e). This compound is known.[14] The product (34 mg, 45% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 50:1) as colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 1H), 7.39-7.32 (m, 2H), 7.19-7.14 (m, 1H), 6.81 (m, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 3.89 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.4 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2 (t, *J* = 34.3 Hz), 138.8, 129.4 (t, *J* = 28.7 Hz), 126.0, 124.0, 121.9, 120.4, 111.2 (t, *J* = 249.8 Hz), 109.7, 104.7 (t, *J* = 6.3 Hz), 63.5, 31.2, 13.9.

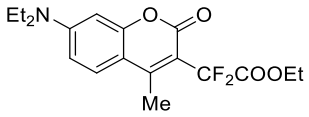


Ethyl 2,2-difluoro-2-(2-oxo-2H-chromen-3-yl)acetate (7f). This compound is known.[15] The product (54 mg, 67% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.68-7.60 (m, 2H), 7.37 (t, *J* = 8.0 Hz, 2H), 4.38 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.2 (s, 2F). ^{13}C NMR (101 MHz,

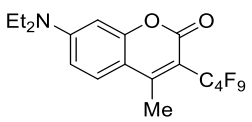
$CDCl_3$) δ 162.2 (t, *J* = 32.9 Hz), 157.9 (t, *J* = 4.4 Hz), 154.1, 141.9 (t, *J* = 7.0 Hz), 133.7, 129.2, 125.2, 121.1 (t, *J* = 25.7 Hz), 117.4, 116.9, 110.4 (t, *J* = 251.9 Hz), 63.5, 13.8.



Ethyl 2,2-difluoro-2-(7-methoxy-2-oxo-2H-chromen-3-yl)acetate (7g). This compound is known.[15] The product (71 mg, 79% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.50 (d, *J* = 8.8 Hz, 1H), 6.91 (dd, *J* = 8.8 Hz, 2.4 Hz, 1H), 6.83 (d, *J* = 2.0 Hz, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 3.89 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.6 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 162.4 (t, *J* = 33.1 Hz), 158.3 (t, *J* = 4.6 Hz), 156.2, 141.9 (t, *J* = 6.9 Hz), 130.2, 117.2 (t, *J* = 26.0 Hz), 113.5, 111.0, 110.7 (t, *J* = 251.3 Hz), 100.7, 63.4, 55.9, 13.8.

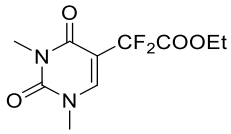


Ethyl 2-(7-(diethylamino)-4-methyl-2-oxo-2H-chromen-3-yl)-2,2-difluoroacetate (7h). This compound is known.[16] The product (100 mg, 95% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 9.2 Hz, 1H), 6.62 (dd, *J* = 9.2 Hz, 2.4 Hz, 1H), 6.39 (m, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 3.40 (q, *J* = 7.2 Hz, 4H), 2.59 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -95.3 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4 (t, *J* = 32.6 Hz), 159.8 (t, *J* = 5.9 Hz), 155.6, 155.5, 151.6, 126.8, 113.5 (t, *J* = 249.7 Hz), 110.6, 109.2, 108.5, 96.7, 62.8, 44.7, 14.8 (t, *J* = 5.9 Hz), 13.7, 12.3.

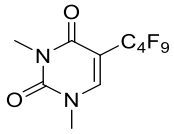


7-(diethylamino)-4-methyl-3-(perfluorobutyl)-2H-chromen-2-one (7i). The product (111 mg, 82% yield) was purified with silica gel chromatography (Petroleum

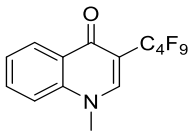
ether/Ethyl acetate = 15:1) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 9.6 Hz, 1H), 6.62 (dd, *J* = 9.2 Hz, 2.4 Hz, 1H), 6.43 (d, *J* = 2.8 Hz, 1H), 3.43 (q, *J* = 7.2 Hz, 4H), 2.52 (t, *J* = 2.6 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.9 (m, 3F), 102.2 (t, *J* = 13.0 Hz, 2F), 121.5 (m, 2F), 126.1 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4 (m), 156.0, 152.1, 127.2, 109.2, 108.3, 108.0-99.0 (m), 96.6, 44.9, 15.9, 12.4. MS (ESI, m/z): 472 (100, M+Na^+), 450 (100, M+H^+). HRMS (ESI, m/z): $(M+H)^+$ Calculated for $C_{18}H_{17}F_9NO_2$: 450.1109; Found: 450.1110.



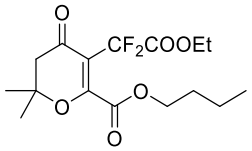
Ethyl 2-(1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-2,2-difluoroacetate (7j). This compound is known.[16] The product (77 mg, 98% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 1:1) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 3.47 (s, 3H), 3.29 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.1 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6 (t, *J* = 33.3 Hz), 160.2 (t, *J* = 4.2 Hz), 151.0, 142.7 (dt, *J* = 8.3 Hz, 3.5 Hz), 111.0 (t, *J* = 250.5 Hz), 106.7 (t, *J* = 25.3 Hz), 63.3, 37.6, 27.7, 13.7.



1,3-Dimethyl-5-(perfluorobutyl)pyrimidine-2,4(1H,3H)-dione (7k). This compound is known.[17] The product (58 mg, 54% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 3:1) as colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 3.51 (s, 3H), 3.36 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.0 (m, 3F), 110.0 (t, *J* = 13.5 Hz, 2F), 122.0 (m, 2F), 126.0 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4 (t, *J* = 2.2 Hz), 150.8, 145.7 (t, *J* = 10.1 Hz), 110.0-104.0 (m), 102.1, 37.9, 28.1.



1-Methyl-3-(perfluorobutyl)quinolin-4(1H)-one (7l). The product (47 mg, 42% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.82 (s, 1H), 7.77-7.71 (m, 1H), 7.50-7.43 (m, 2H), 3.90 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.0 (t, *J* = 10.0 Hz, 3F), 109.9 (t, *J* = 13.5 Hz, 2F), 122.0 (m, 2F), 125.9 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 144.8 (t, *J* = 11.1 Hz), 140.0, 133.2, 127.8, 127.4, 125.3, 115.6, 110.0-104 (m), 41.5. MS (ESI, m/z): 400, 379, 378 (100, M+H)$^+$. HRMS (ESI, m/z): (M+H)$^+$ Calculated for $C_{14}H_9F_9NO$: 378.0534; Found: 378.0535.



Butyl 5-(2-ethoxy-1,1-difluoro-2-oxoethyl)-2,2-dimethyl-4-oxo-3,4-dihydro-2H-pyran-6-carboxylate (7o). This compound is known.[16] The product (56 mg, 54% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1) as colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.31 (q, *J* = 7.2 Hz, 2H), 4.27 (t, *J* = 6.6 Hz, 2H), 2.61 (s, 2H), 1.72-1.64 (m, 2H), 1.52 (s, 6H), 1.45-1.35 (m, 2H), 1.30 (t, *J* = 7.2 Hz, 3H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.5 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.4 (t, *J* = 3.3 Hz), 162.6 (t, *J* = 33.3 Hz), 161.7 (t, *J* = 3.4 Hz), 161.5, 111.1 (t, *J* = 251.3 Hz), 108.5 (t, *J* = 23.0 Hz), 84.9, 66.8, 63.0, 46.7, 30.1, 25.6, 18.8, 13.8, 13.5.

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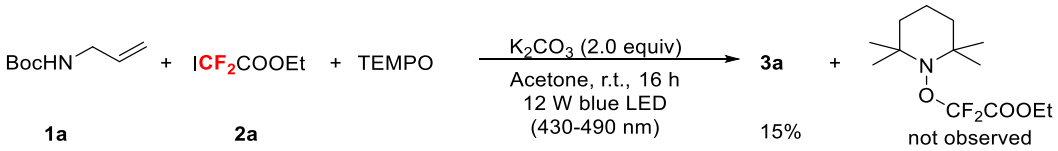
[17] B-H. Zhang, J-J. Kong, Y. Huang, Y-G. Lou, X-F. Li, C-Y. He, *Chin. Chem. Lett.*, **2017**, *28*, 1751.

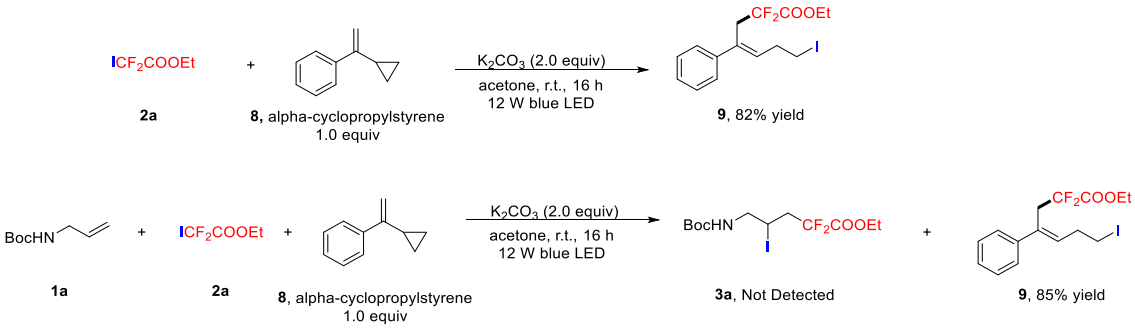
5. Mechanism studies.

5.1 Addition of radical and SET inhibitors:

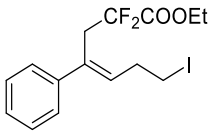


When the radical scavenger TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy, 1.0 equivalent) was added under standard conditions, only 15% of the product **3a** was observed.

5.2 Radical clock experiments.

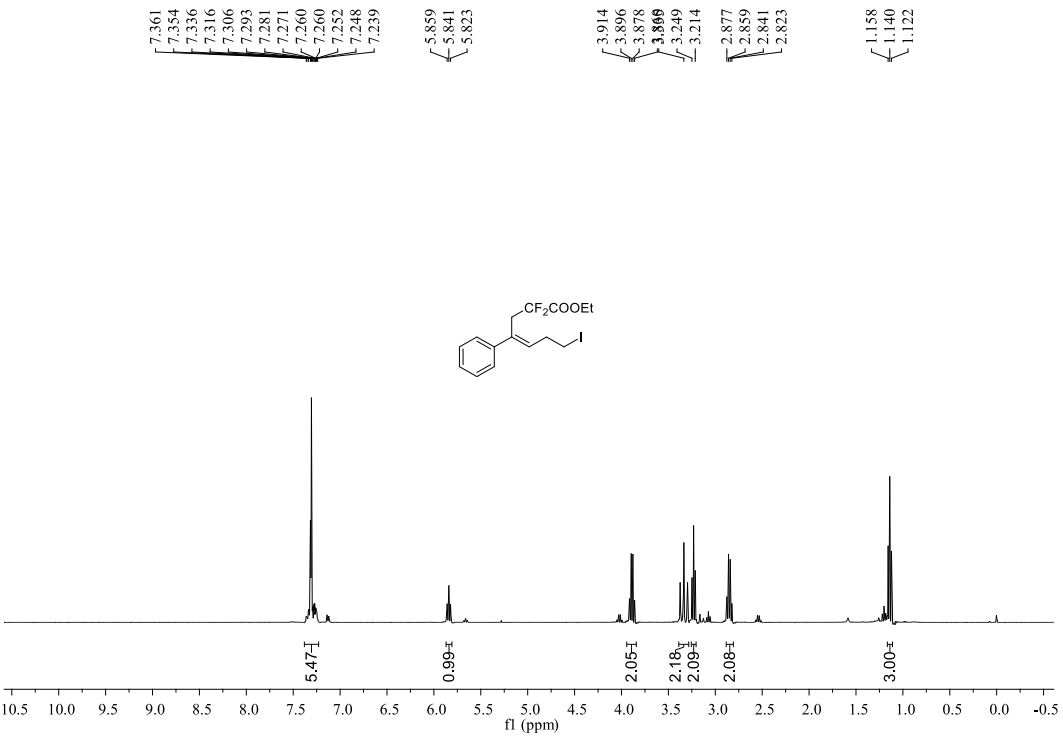


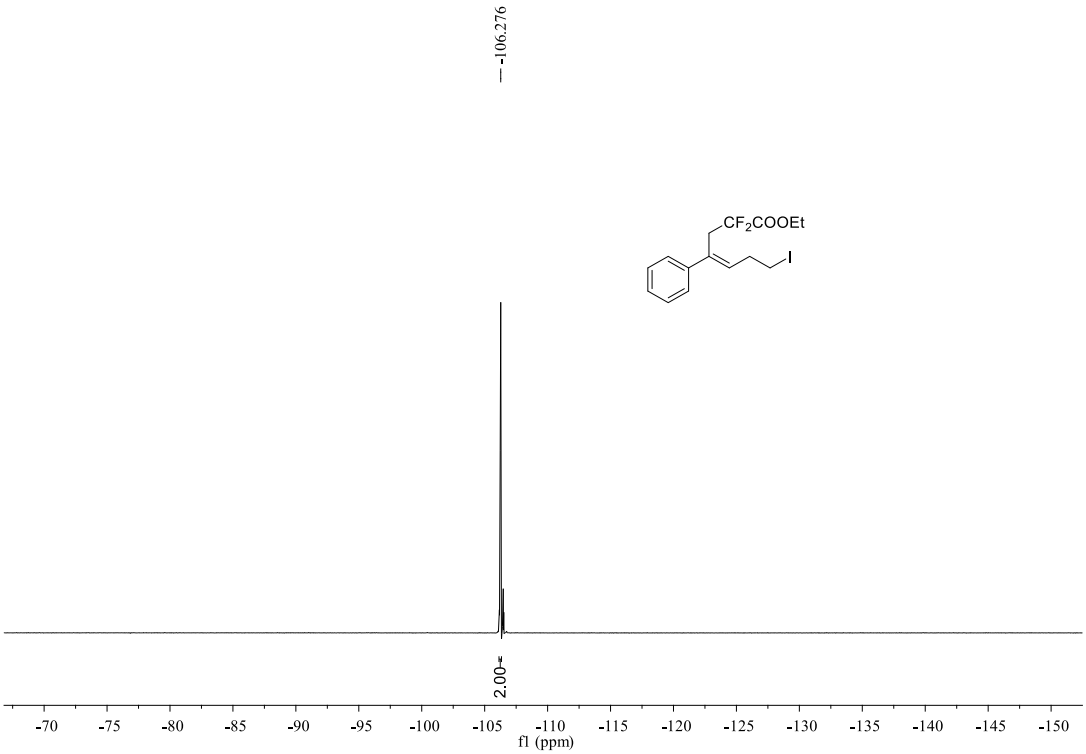
Typical procedure: To a 25 mL of Schlenk tube equipped with a Teflon septum were added **1a** (0.3 mmol, 1.0 equiv) (or without **1a**), K_2CO_3 (0.6 mmol, 2.0 equiv) under Ar, followed by Acetone (2 mL) with stirring, ICF_2COOEt (**2a**) (0.45 mmol, 1.5 equiv) and alpha-cyclopropylstyrene (**8**) (0.3 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.

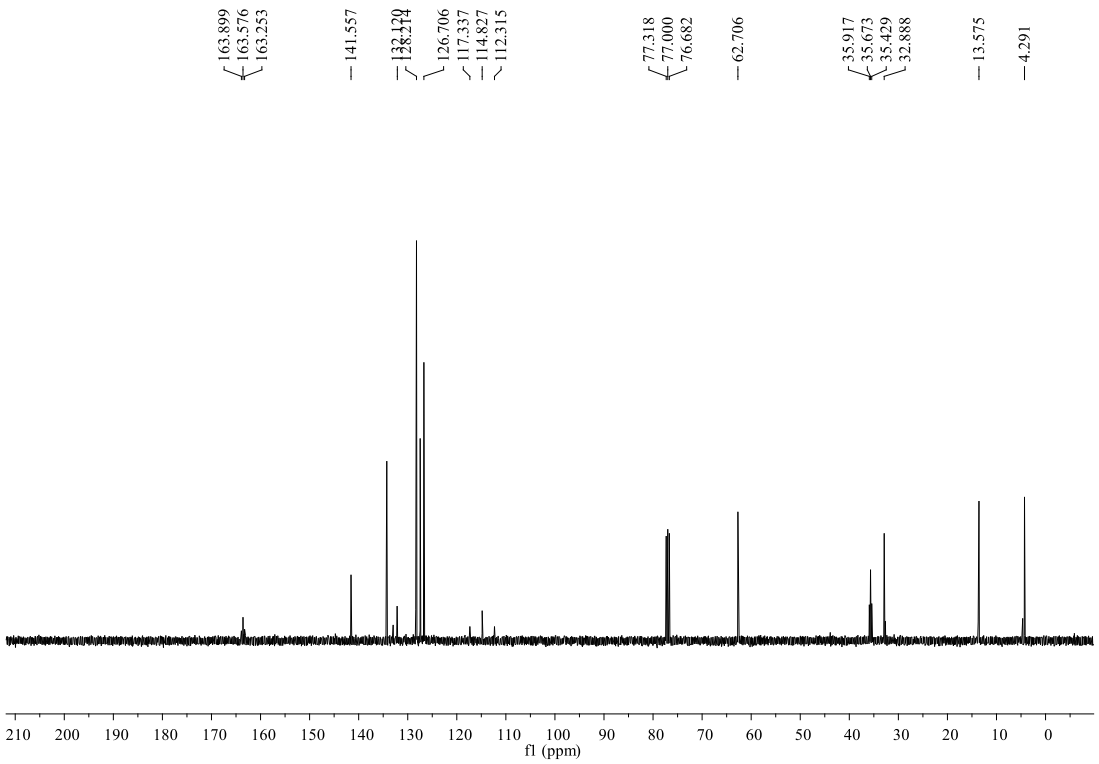


Ethyl (*E*)-2,2-difluoro-7-iodo-4-phenylhept-4-enoate (9). The product (100 mg, 85% yield) was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 50:1) as colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.23 (m, 5H), 5.84 (t, J = 7.2 Hz, 1H), 3.89 (q, J = 7.2 Hz, 2H), 3.33 (t, J = 15.6 Hz, 2H), 3.23 (t, J = 7.0 Hz, 2H),

2.85 (q, J = 7.2 Hz, 2H), 1.14 (t, J = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.2 – -106.3 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6 (t, J = 32.6 Hz), 141.6, 134.3, 132.1 (t, J = 4.2 Hz), 128.2, 127.5, 126.7, 114.8 (t, J = 253.6 Hz), 62.7, 35.7 (t, J = 24.6 Hz), 32.9, 13.6, 4.29. MS (EI): m/z (%) 394 (M^+), 267, 129 (100).







5.3 UV-vis spectroscopic measurement.

Solution 1: **2a** (60 μL, 0.4 mmol), and K_2CO_3 (70 mg, 0.5 mmol) were added in acetone (4.0 mL). The mixture was stirred for 20 minutes and filtered.

Solution 2: **2a** (60 μL, 0.4 mmol) was added in acetone (4.0 mL). The mixture was stirred for 20 minutes and filtered.

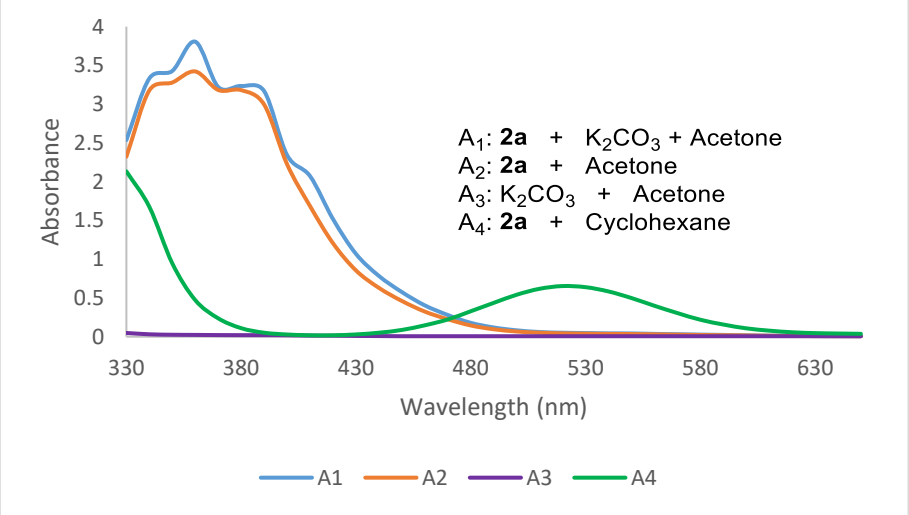
Solution 3: K_2CO_3 (70 mg, 0.5 mmol) was added in acetone (4.0 mL). The mixture was stirred for 20 minutes and filtered.

Solution 4: **2a** (60 μL, 0.4 mmol) was added in cyclohexane (4.0 mL). The mixture was stirred for 20 minutes and filtered.

Performed on UV visible spectrophotometer, recorded in 1cm path quartz cuvettes using T6 Xinyue visible spectrophotometer (PERSEE^{TM}), pure acetone as blank sample.

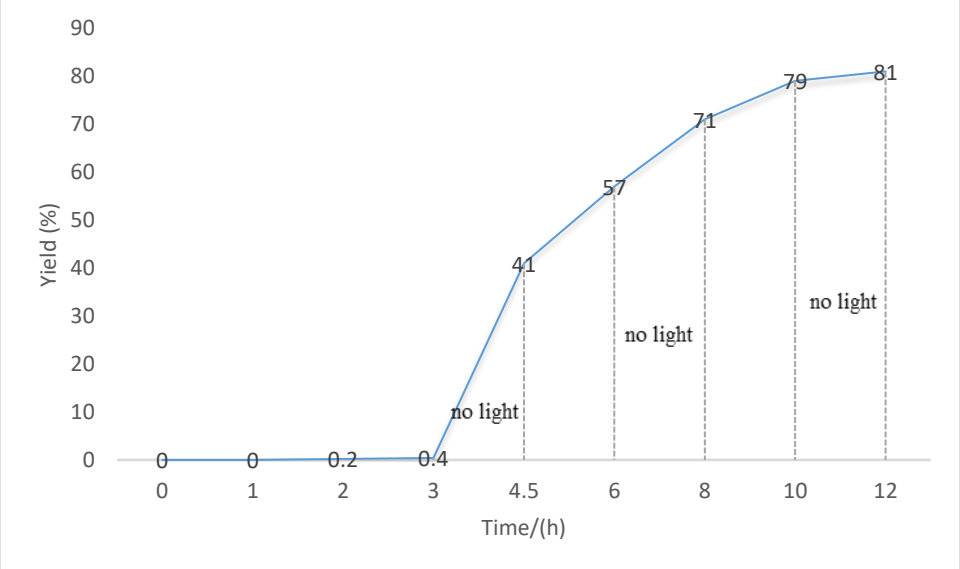
A / λ (nm)	**2a** + K_2CO_3 +Acetone A_1	**2a** +Acetone A_2	K_2CO_3 +Acetone A_3	**2a** +Cyclohexane A_4
330	2.537	2.322	0.048	2.133
340	3.332	3.178	0.031	1.675
350	3.428	3.279	0.025	0.946

360	3.806	3.422	0.023	0.472
370	3.222	3.183	0.021	0.237
380	3.234	3.181	0.02	0.11
390	3.169	2.995	0.02	0.051
400	2.343	2.225	0.018	0.028
410	2.072	1.685	0.014	0.018
420	1.518	1.206	0.013	0.018
430	1.069	0.855	0.01	0.029
440	0.784	0.63	0.008	0.051
450	0.576	0.461	0.006	0.087
460	0.404	0.324	0.006	0.147
470	0.28	0.225	0.006	0.222
480	0.179	0.145	0.006	0.328
490	0.119	0.096	0.006	0.436
500	0.082	0.067	0.006	0.541
510	0.06	0.051	0.006	0.618
520	0.051	0.043	0.006	0.653
530	0.047	0.039	0.006	0.639
540	0.043	0.036	0.006	0.584
550	0.042	0.034	0.006	0.499
560	0.036	0.03	0.006	0.399
570	0.032	0.026	0.006	0.305
580	0.027	0.022	0.006	0.219
590	0.023	0.019	0.006	0.157
600	0.018	0.016	0.006	0.108
610	0.014	0.012	0.006	0.078
620	0.012	0.01	0.006	0.057
630	0.008	0.008	0.006	0.046
640	0.007	0.007	0.006	0.041
650	0.006	0.006	0.006	0.037



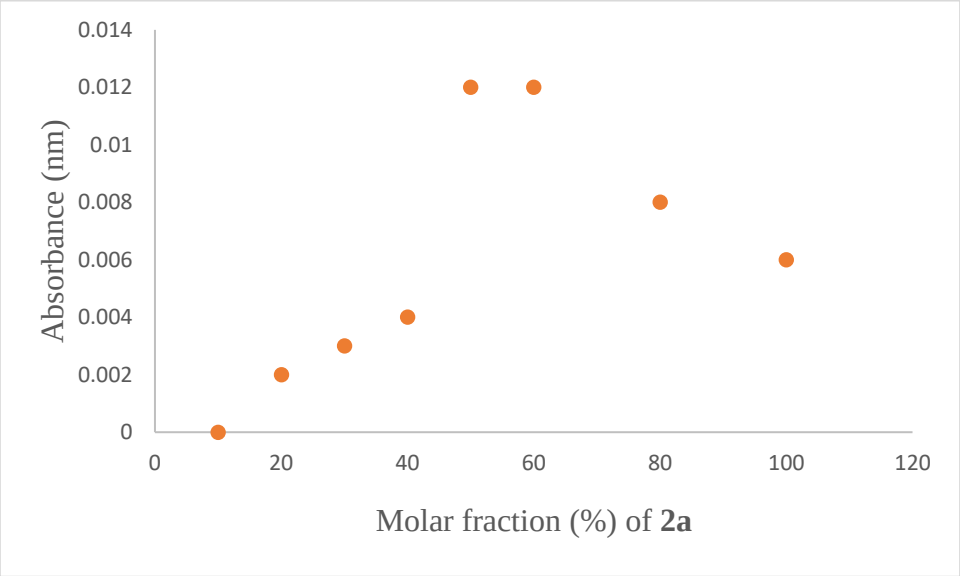
5.4 Light/dark experiments.

six standard reaction mixtures in 25 mL flame-dried thick-walled glass pressure tube equipped with a stir bar was cooled under Ar atmosphere were charged with tert-Butyl N-allylcarbamate (47.2 mg, 0.30 mmol, 1.0 equiv.), ethyl difluoroiodoacetate (112.5 mg, 0.45 mmol, 1.5 equiv.), and K_2CO_3 (82.9 mg, 0.6 mmol, 2.0 equiv.) and acetone (2.0 mL). The reaction mixtures were degassed by Argon sparging for 10 min, then irradiated with 12 W blue LEDs lamps. After 3 h, one tube was removed from the irradiation setup for analysis. The remaining five tubes were stirred in the absence of light for an additional 1.5 h. Then, one tube was removed for analysis, and the lamps were turned back on to irradiate the remaining four reaction mixtures. After an additional 1.5 h of irradiation, the lamps were turned off, and one tube was removed for analysis. The remaining threetubes were stirred in the absence of light for an additional 2 h. Then, a tube was removed for analysis, and the lamps were turned back on to irradiate the remaining two reaction mixtures. After 2 h, the lamp was turned off, and one tube was removed for analysis. The remaining one tube was stirred in the absence light for an additional 2 h. Then it was analyzed. The reaction mixtures were analyzed by ^{19}F NMR with an internal standard.



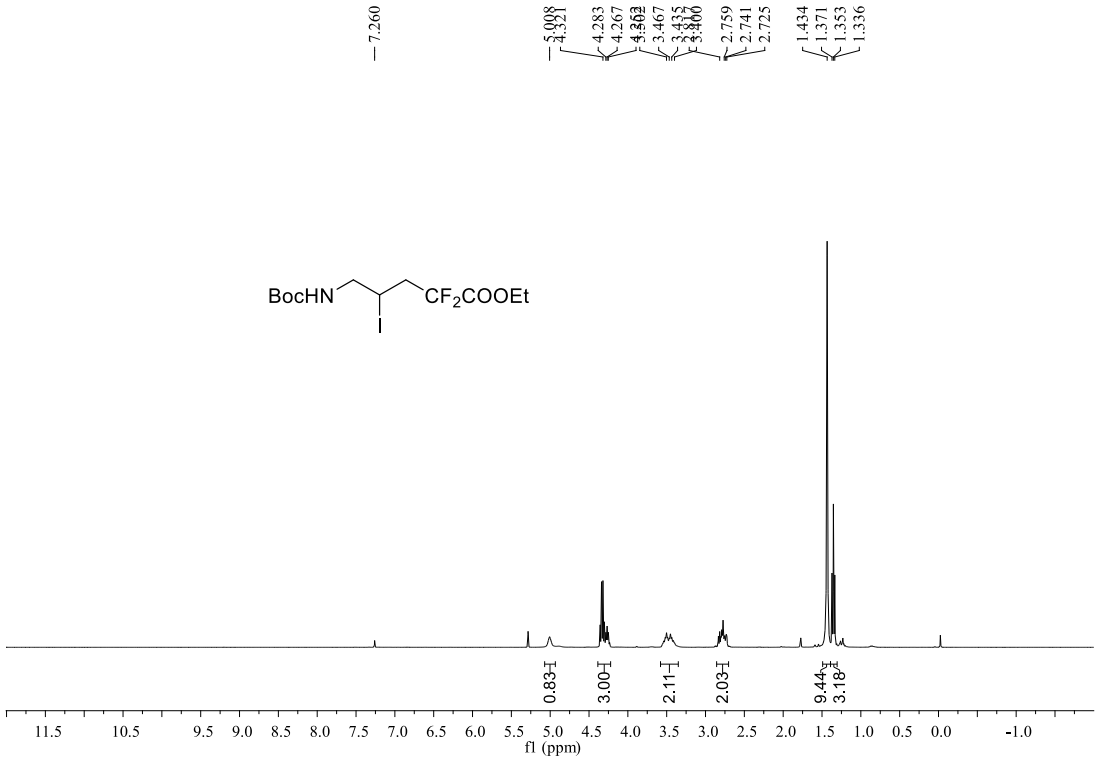
5.5 Stoichiometry of the Weak intermolecular interaction.

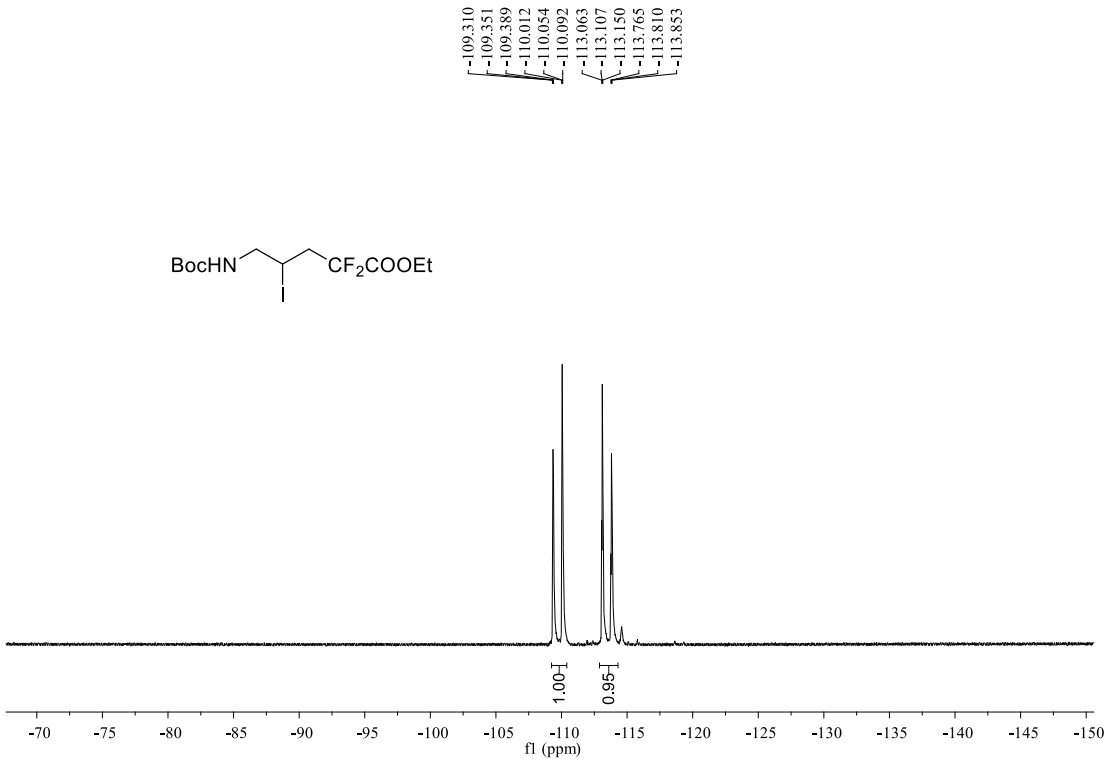
The stoichiometry of weak intermolecular interaction was calculated using the Job´s plot method (P. Job, *Ann. Chim.,* **1928**, *9*, 113.). The Job´s plot of weak intermolecular interaction between Acetone and ethyl difluoroiodoacetate (**2a**) was calculated measuring the absorption of cyclohexane solutions at 420 nm with different donor/acceptor ratios with constant concentration (0.12 M) of the two components. The absorbance values were plotted against the molar fraction (%) of **2a**. The Job´s plot analysis of the weak intermolecular interaction between acetone and **2a** showed a maximal absorbance at 50-60% molar fraction of **2a**.

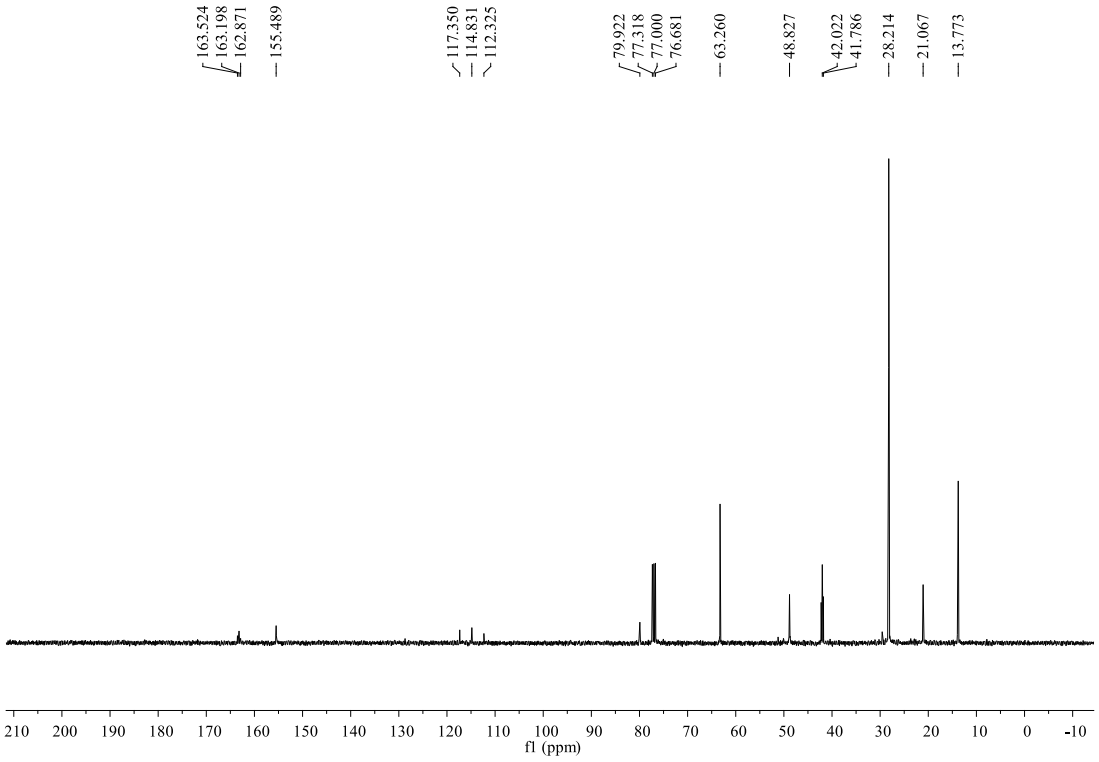


6. Copies of NMR spectra of 3, 5, 7.

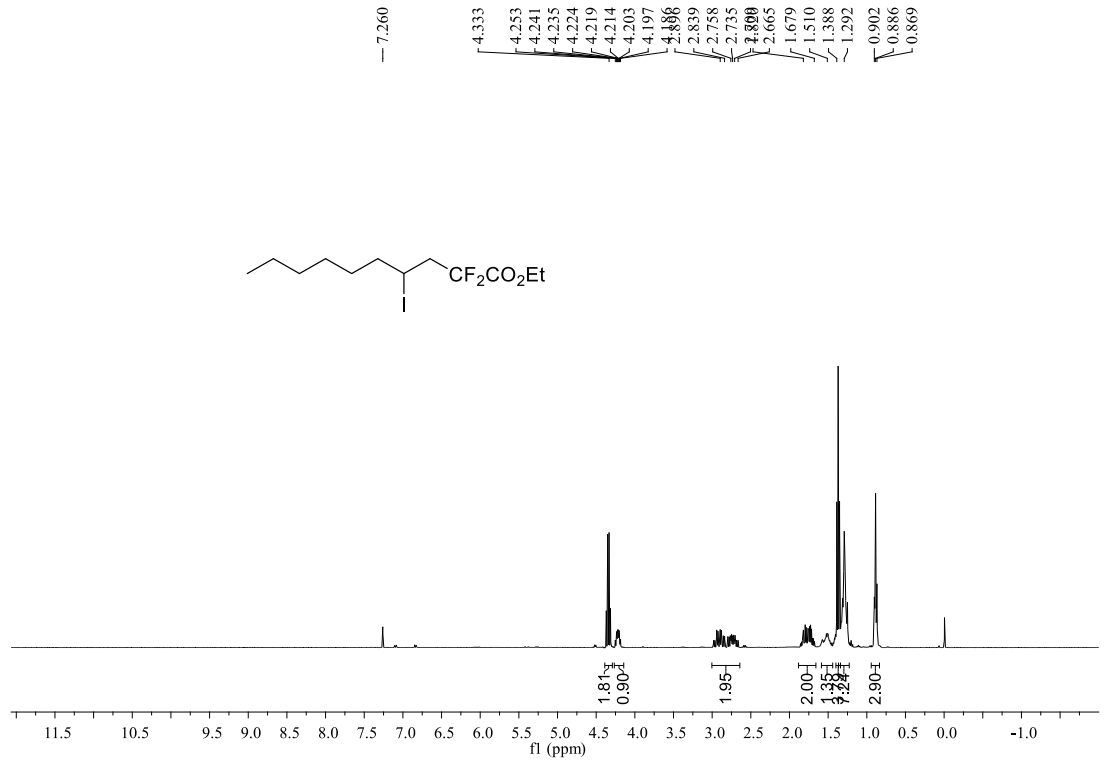
Ethyl 5-((*tert*-butoxycarbonyl)amino)-2,2-difluoro-4-iodopentanoate (3a).

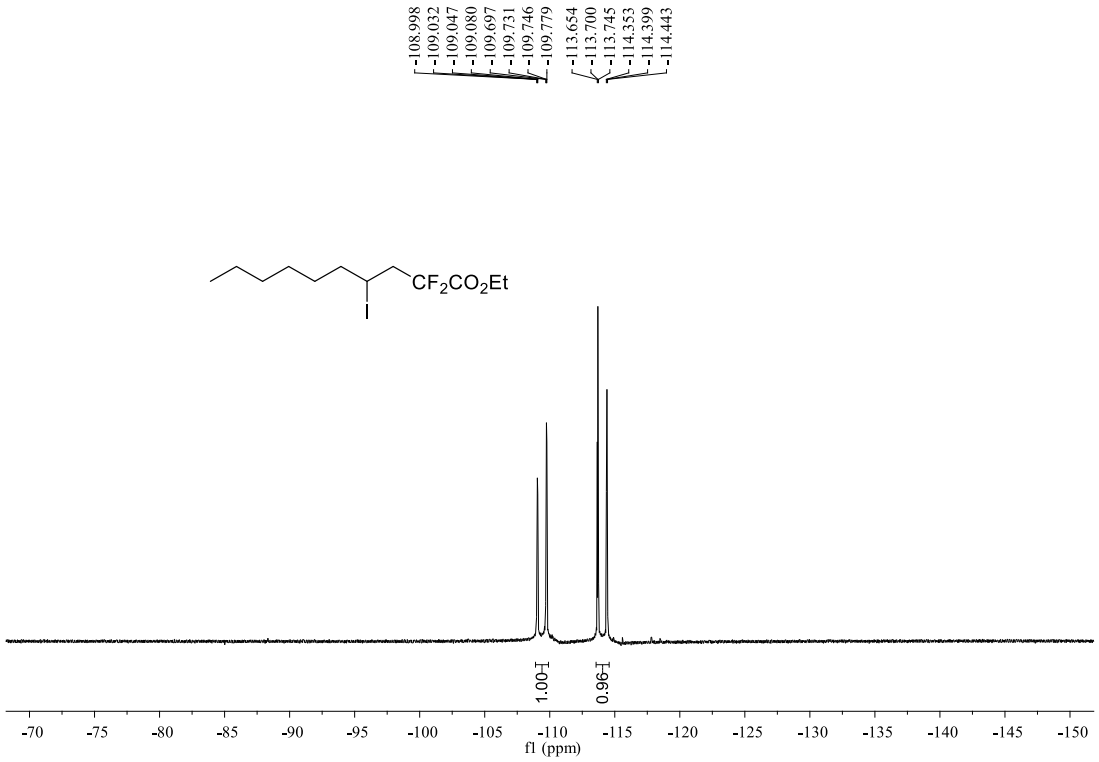


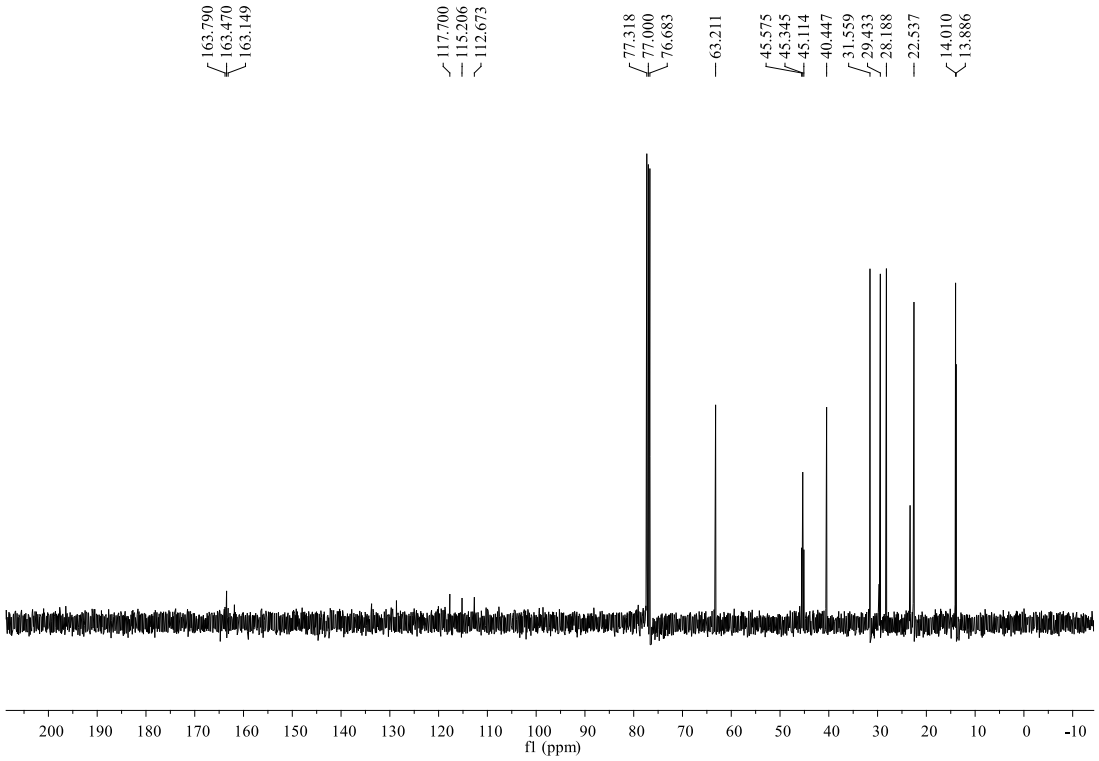




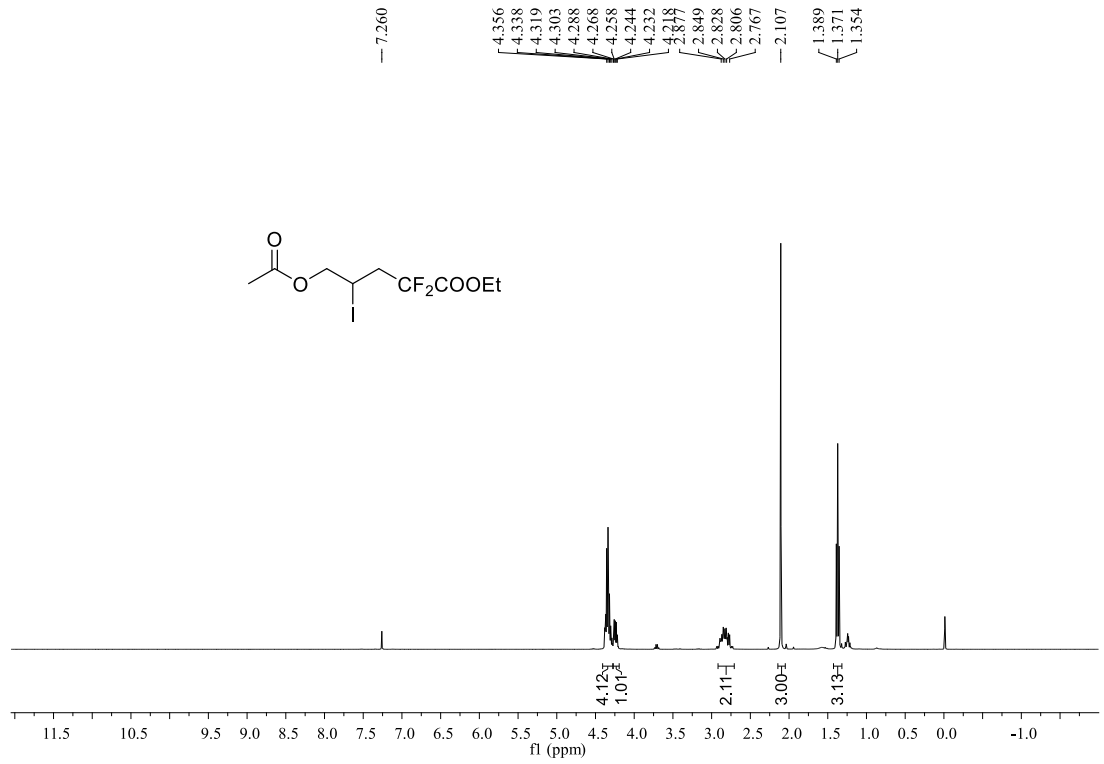
Ethyl 2,2-difluoro-4-iododecanoate (3b).

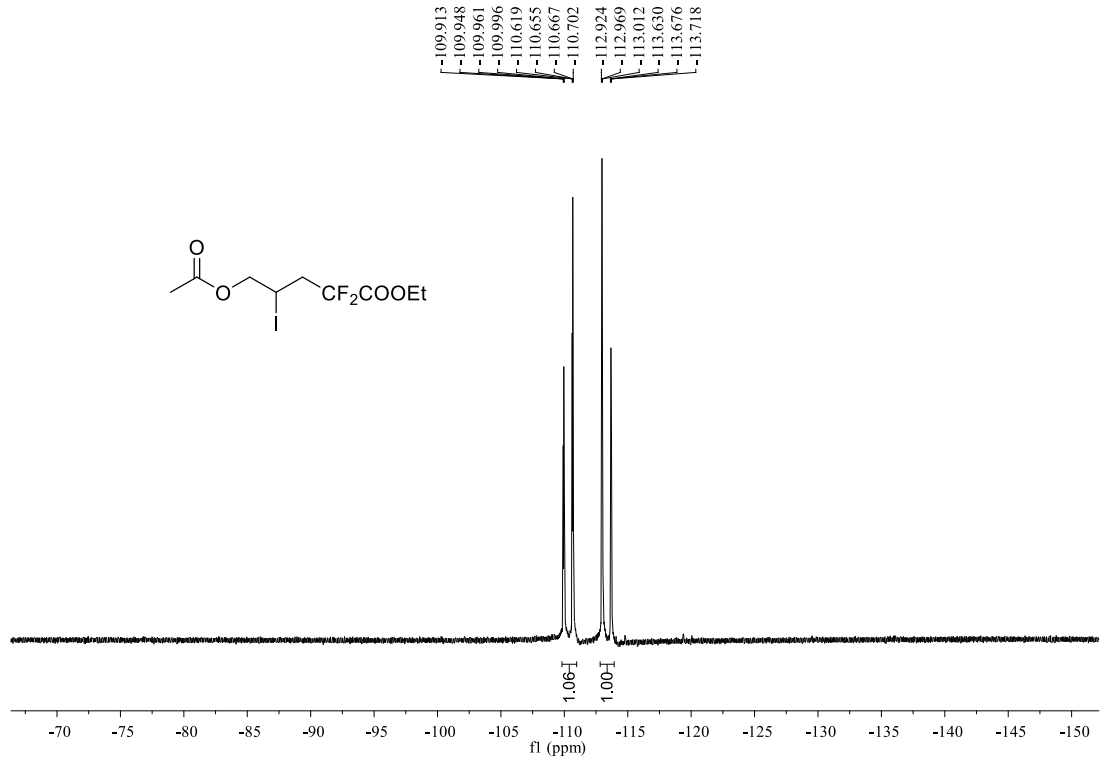


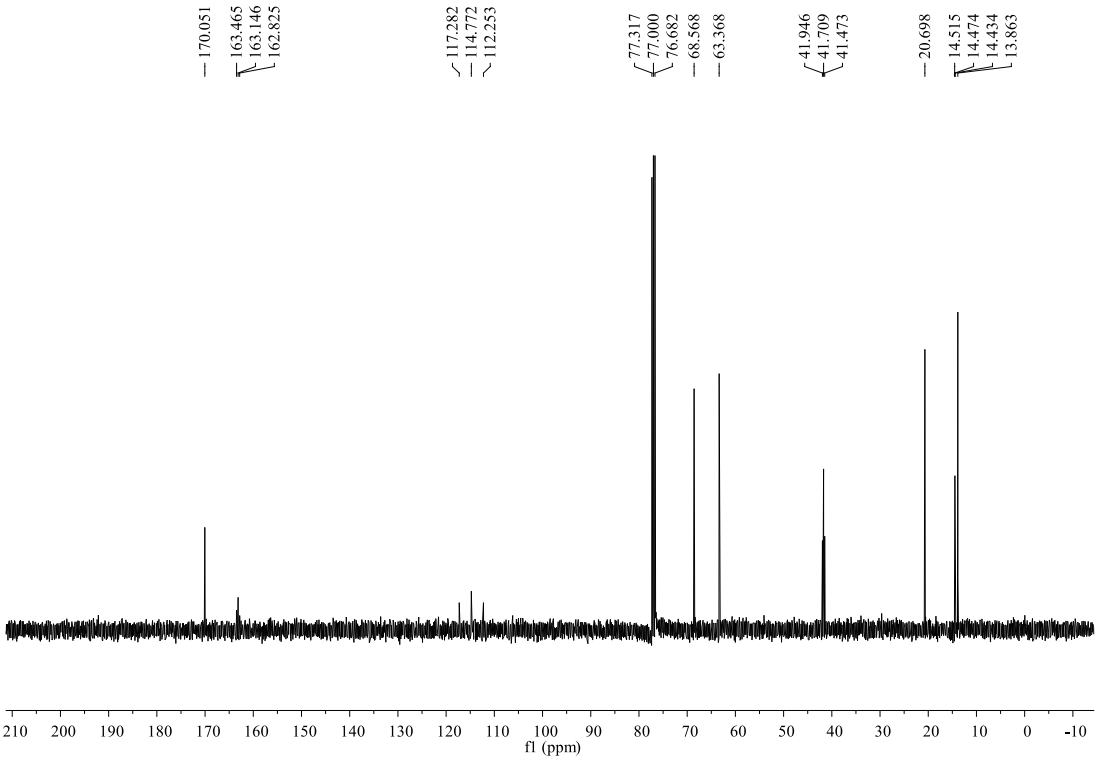

-108.998
-109.032
-109.047
-109.080
-109.697
-109.731
-109.746
-109.779
-113.654
-113.700
-113.745
-114.353
-114.399
-114.443
CF2CO2Et
1.00
0.96
-70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150
f1 (ppm)


163.790
163.470
163.149
117.700
115.206
112.673
77.318
77.000
76.683
63.211
45.575
45.345
45.114
40.447
31.559
29.433
28.188
22.537
14.010
13.886
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

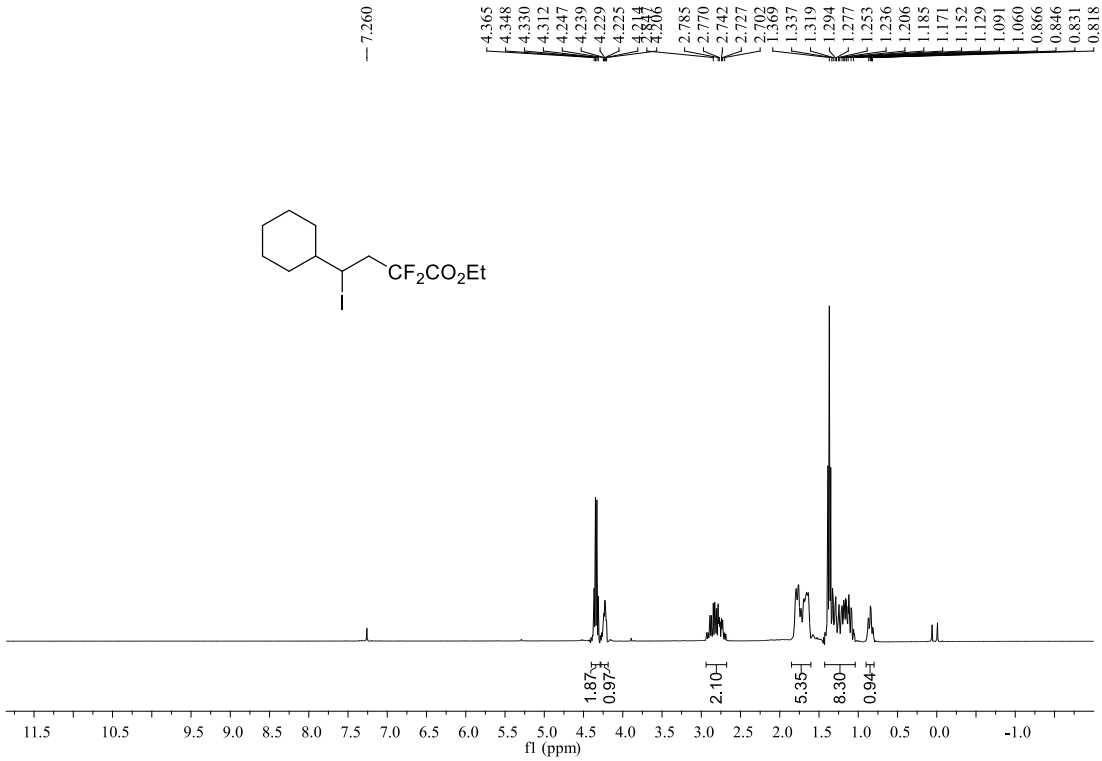
Ethyl 5-acetoxy-2,2-difluoro-4-iodopentanoate (3c).

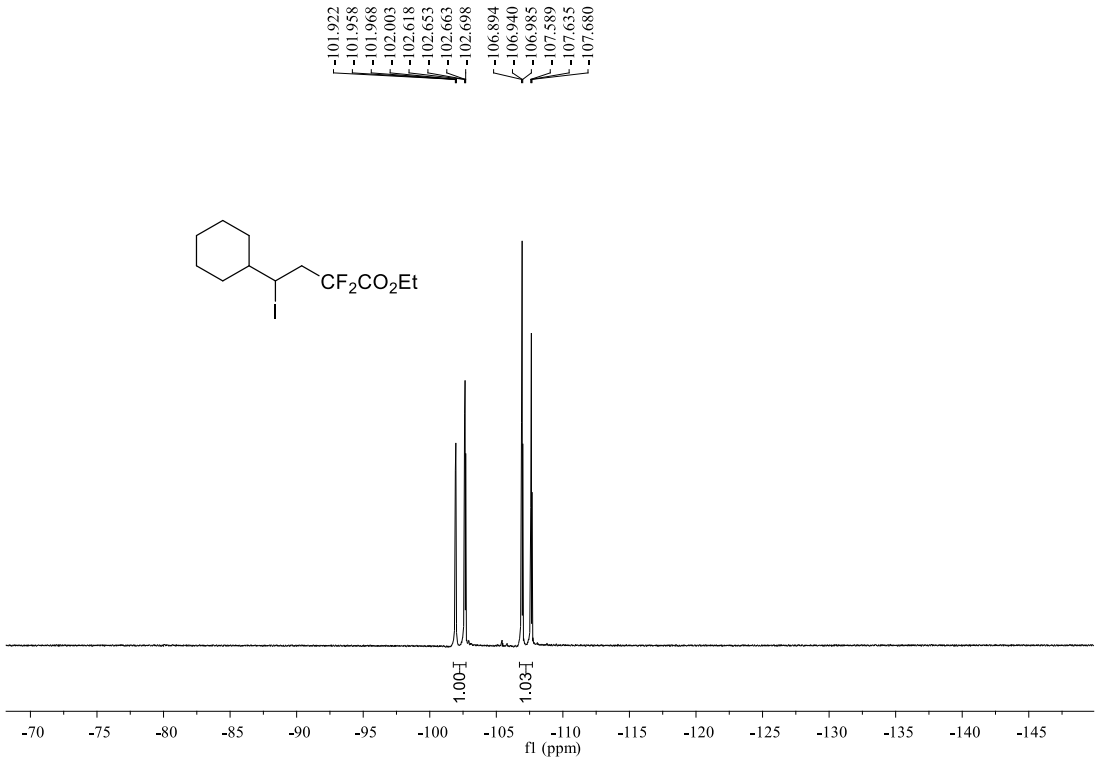


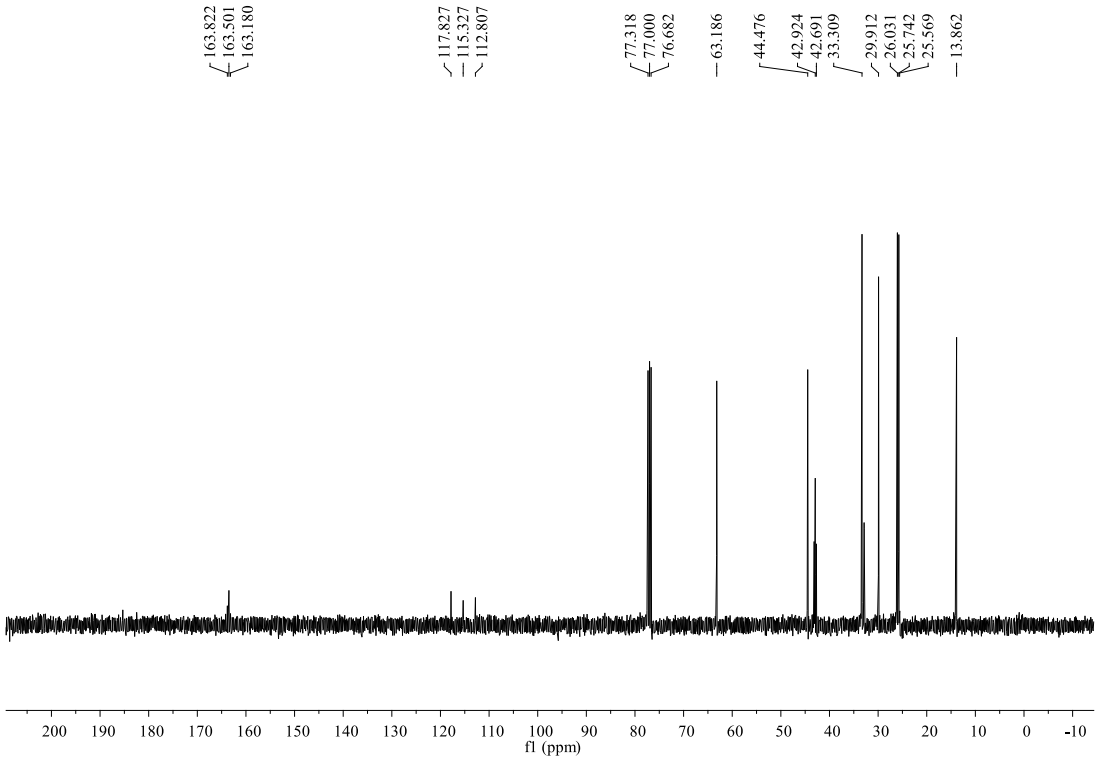




Ethyl 4-cyclohexyl-2,2-difluoro-4-iodobutanoate (3d).




-101.922
-101.958
-101.968
-102.003
-102.618
-102.653
-102.663
-102.698
-106.894
-106.940
-106.985
-107.589
-107.635
-107.680
CF2CO2Et
I
1.00
1.03
-70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145
f1 (ppm)


163.822
163.501
163.180
117.827
115.327
112.807
77.318
77.000
76.682
63.186
44.476
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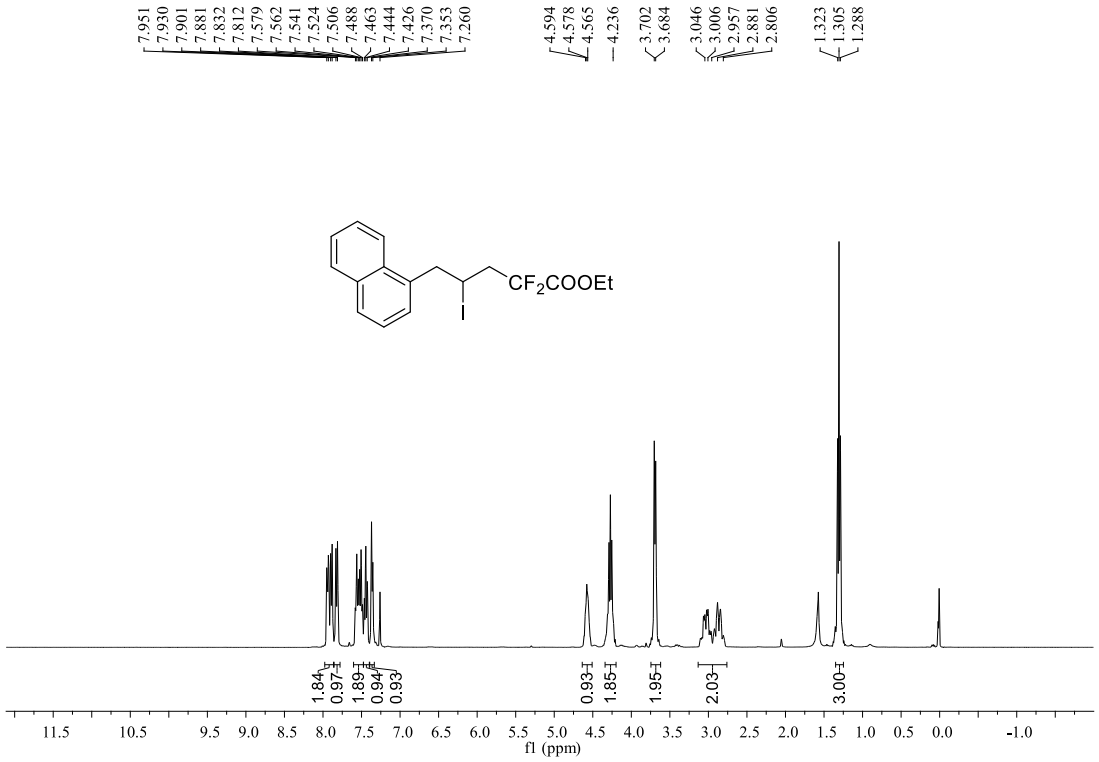
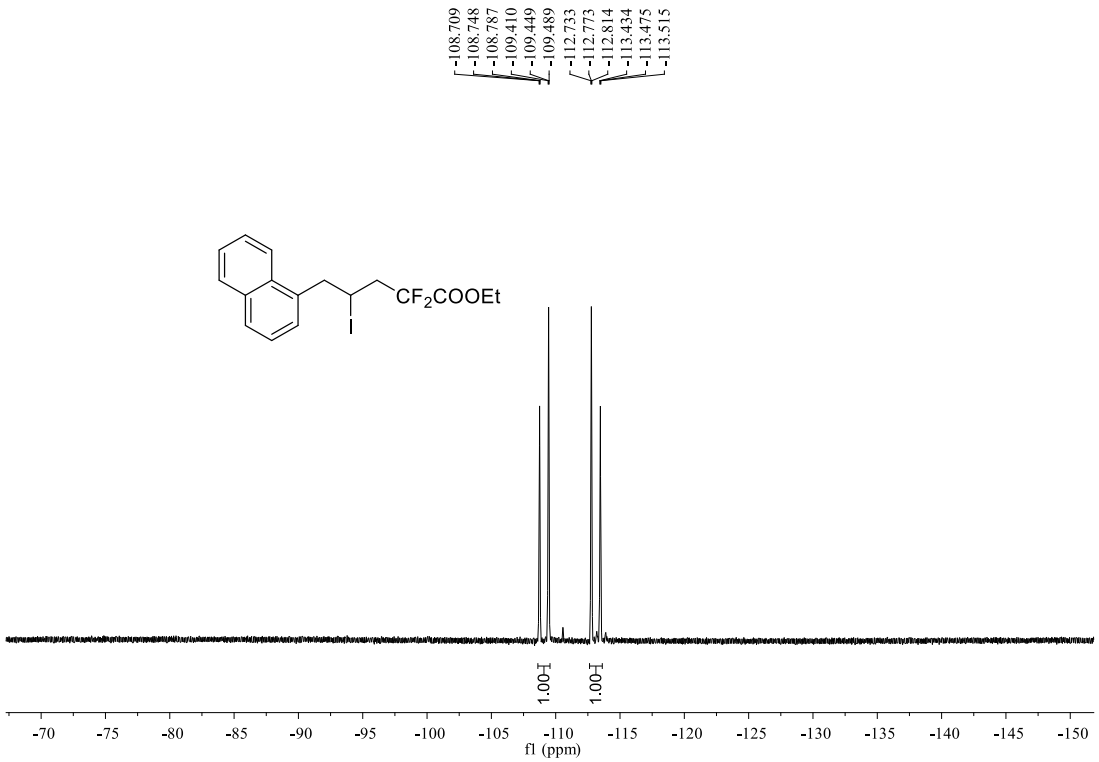
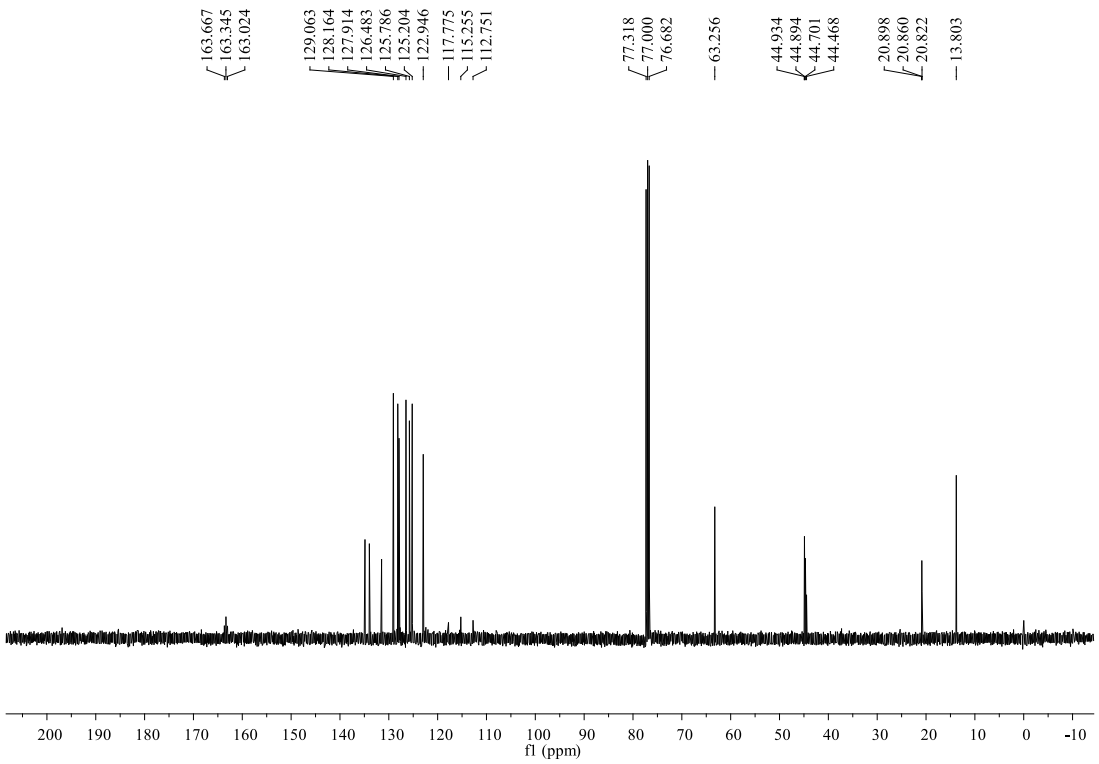
42.691
33.309
29.912
26.031
25.742
25.569
13.862
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

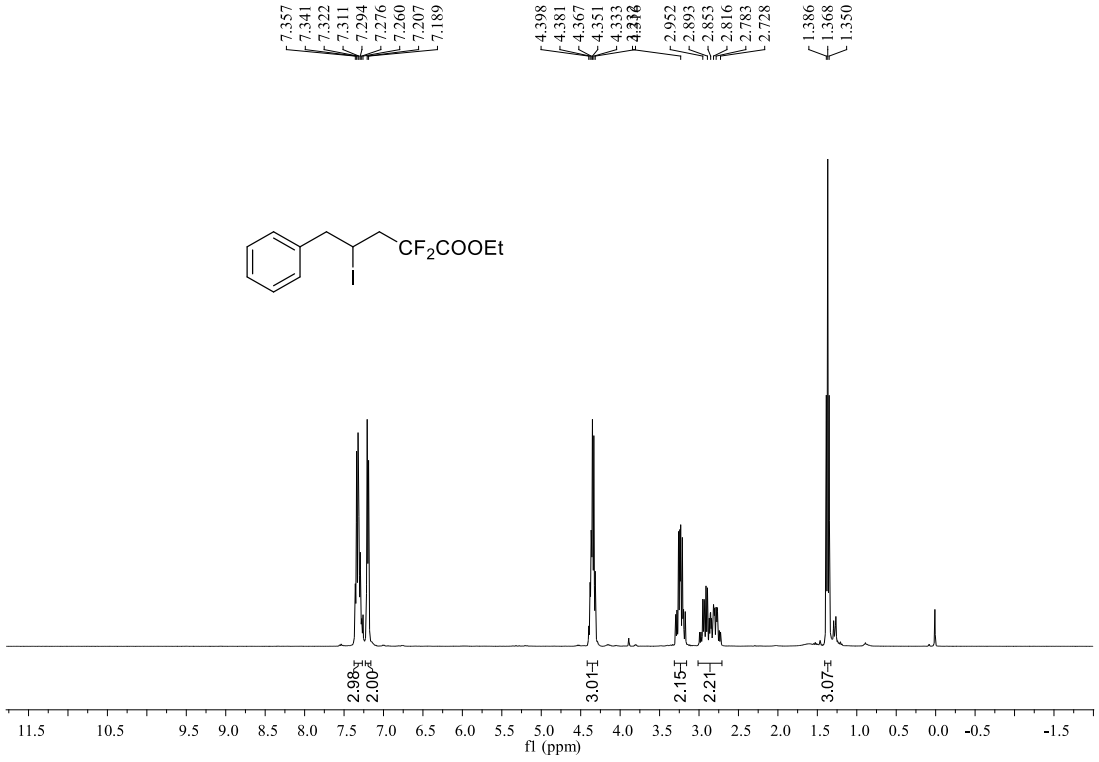
Ethyl 2,2-difluoro-4-iodo-5-(naphthalen-1-yl)pentanoate (3e).

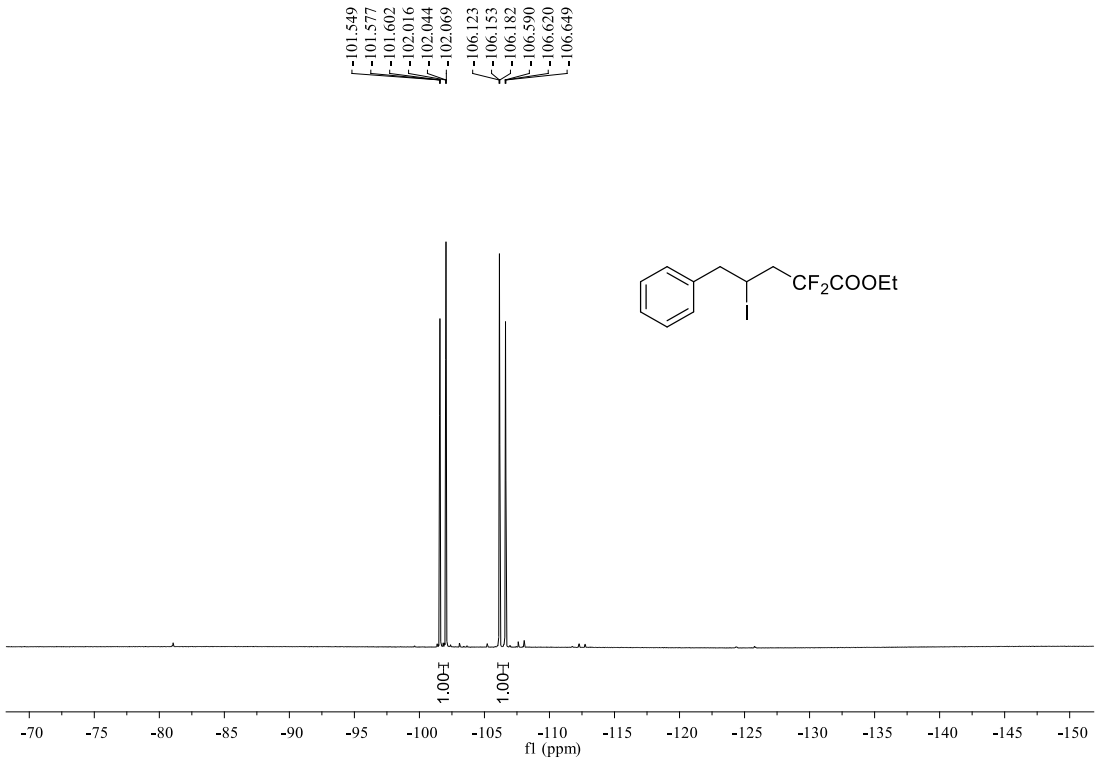


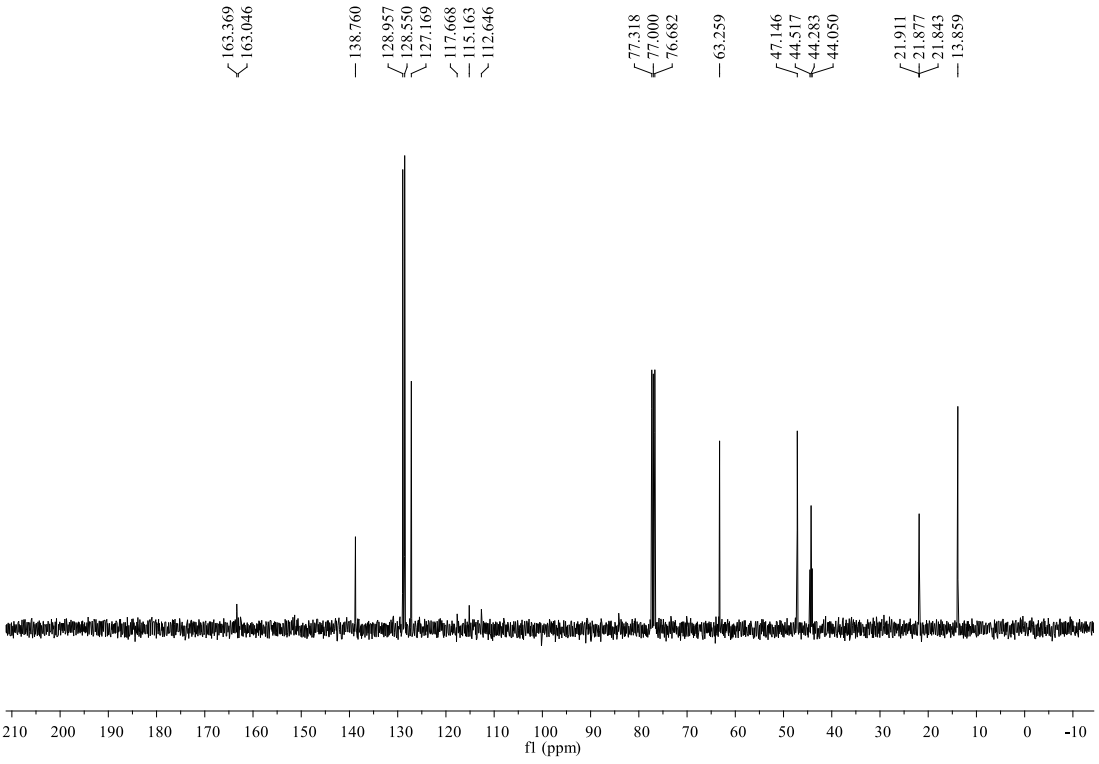




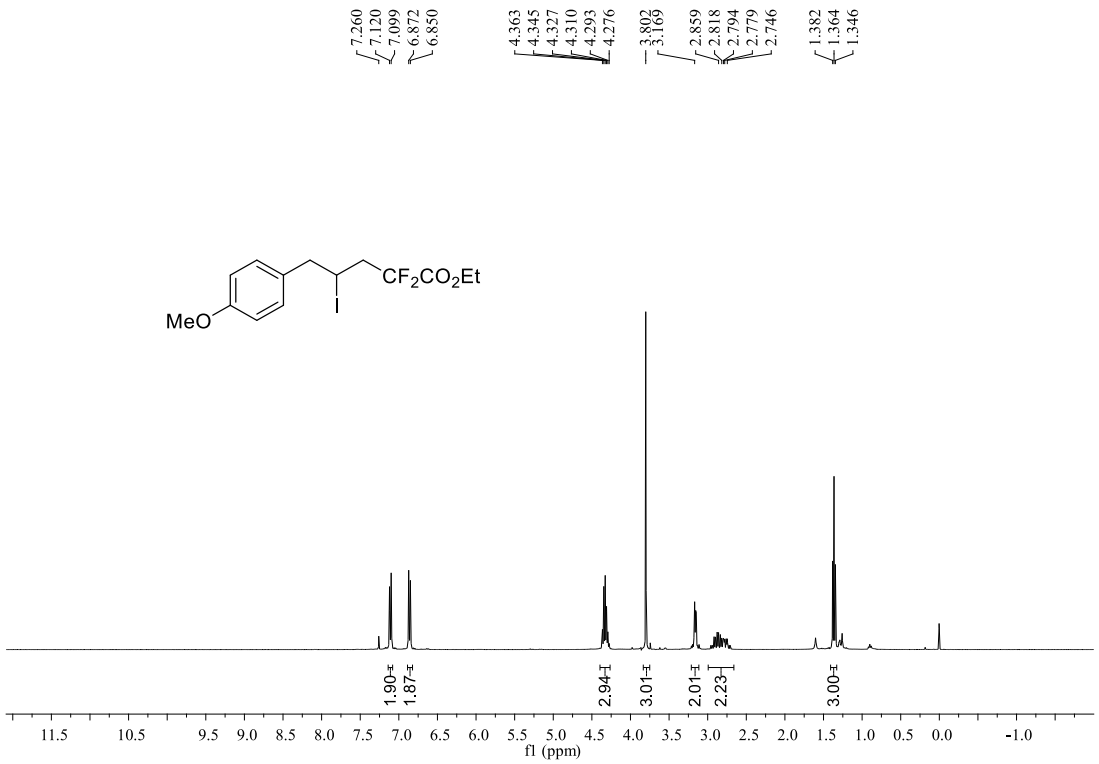
Ethyl 2,2-difluoro-4-iodo-5-phenylpentanoate (3f).

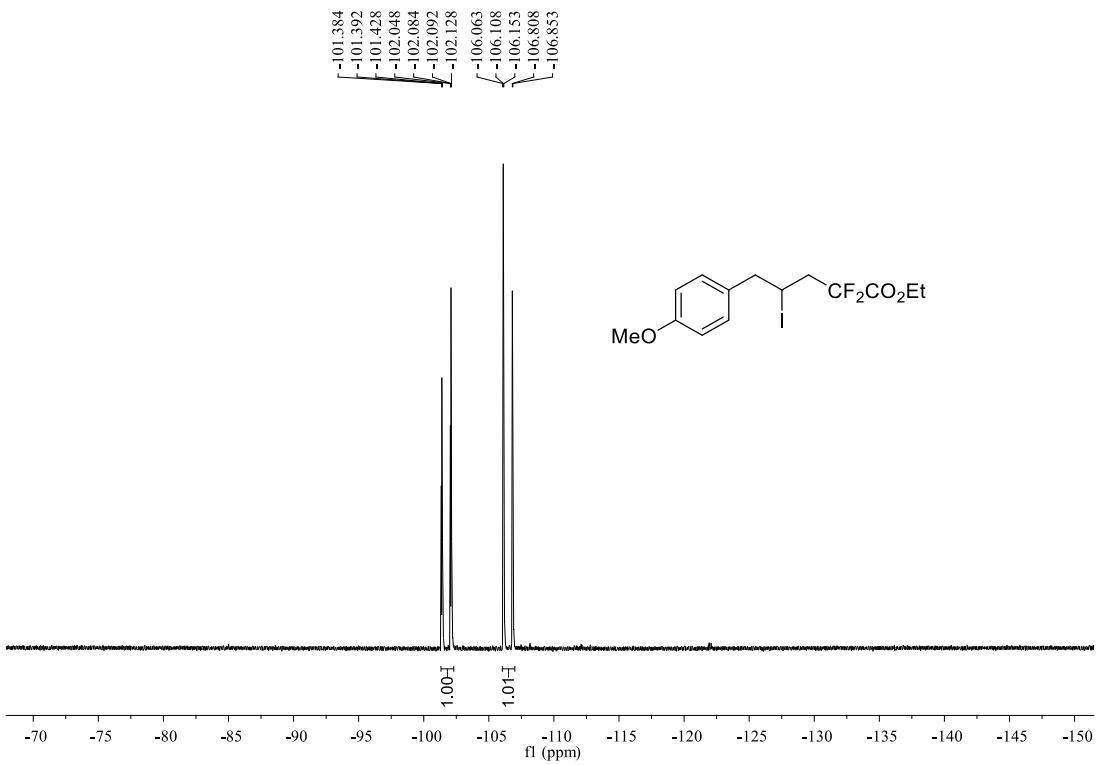


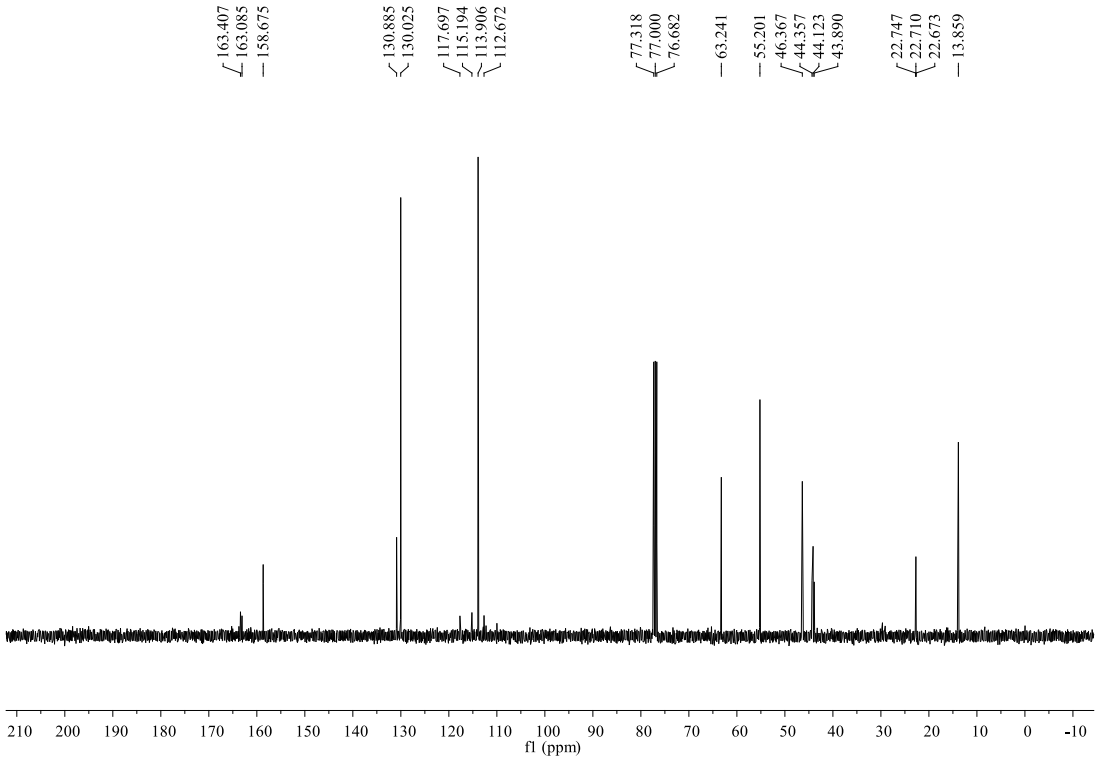

-101.549
-101.577
-101.602
-102.016
-102.044
-102.069
-106.123
-106.153
-106.182
-106.590
-106.620
-106.649
CF2COOEt
I
1.00
1.00
-70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150
f1 (ppm)


163.369
163.046
138.760
128.957
128.550
127.169
117.668
115.163
112.646
77.318
77.000
76.682
63.259
47.146
44.517
44.283
44.050
21.911
21.877
21.843
13.859
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

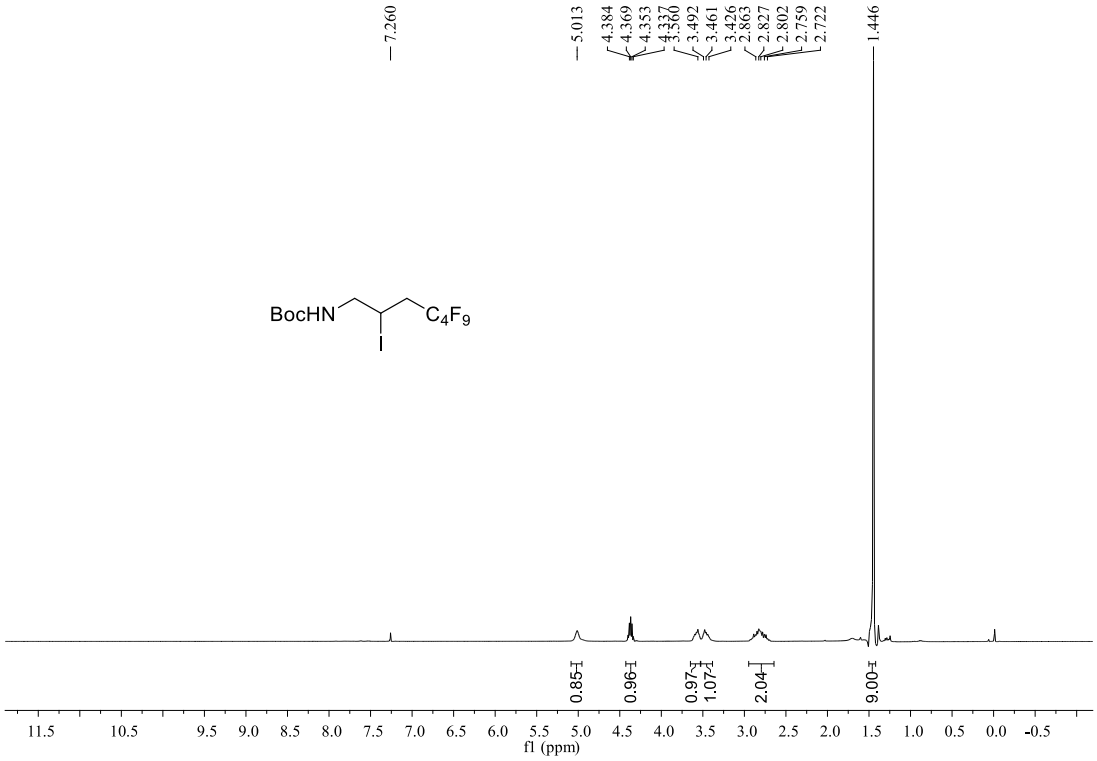
Ethyl 2,2-difluoro-4-iodo-5-(4-methoxyphenyl)pentanoate (3g).

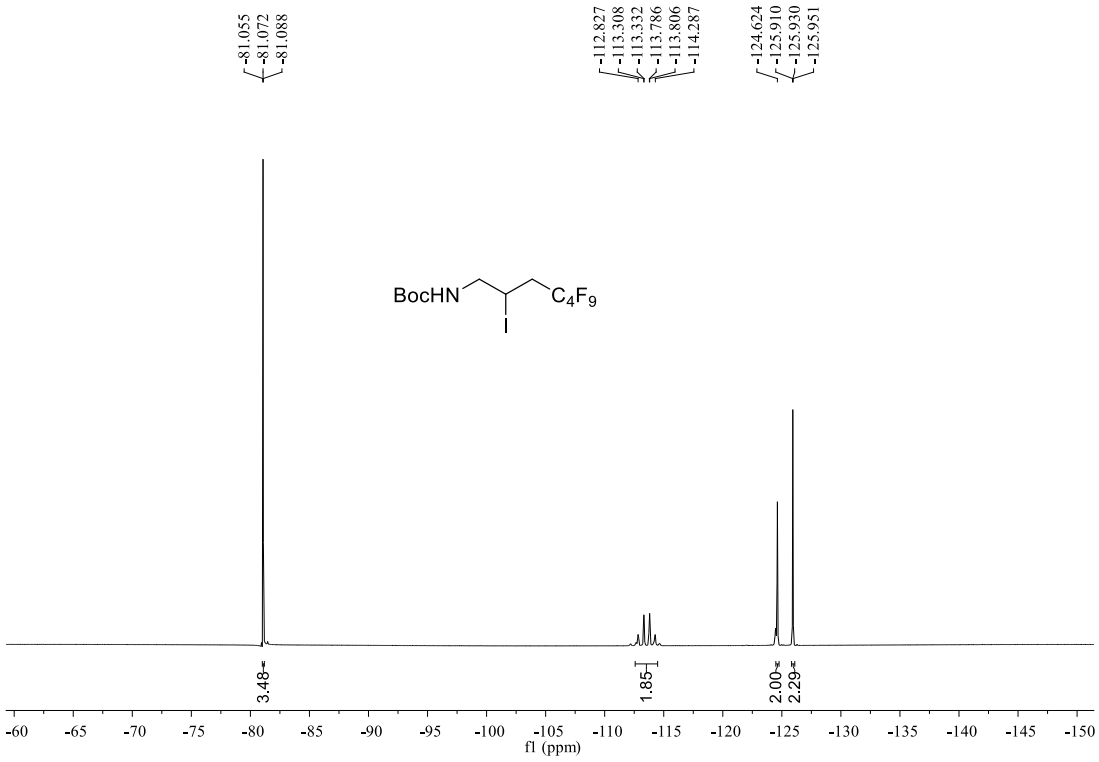


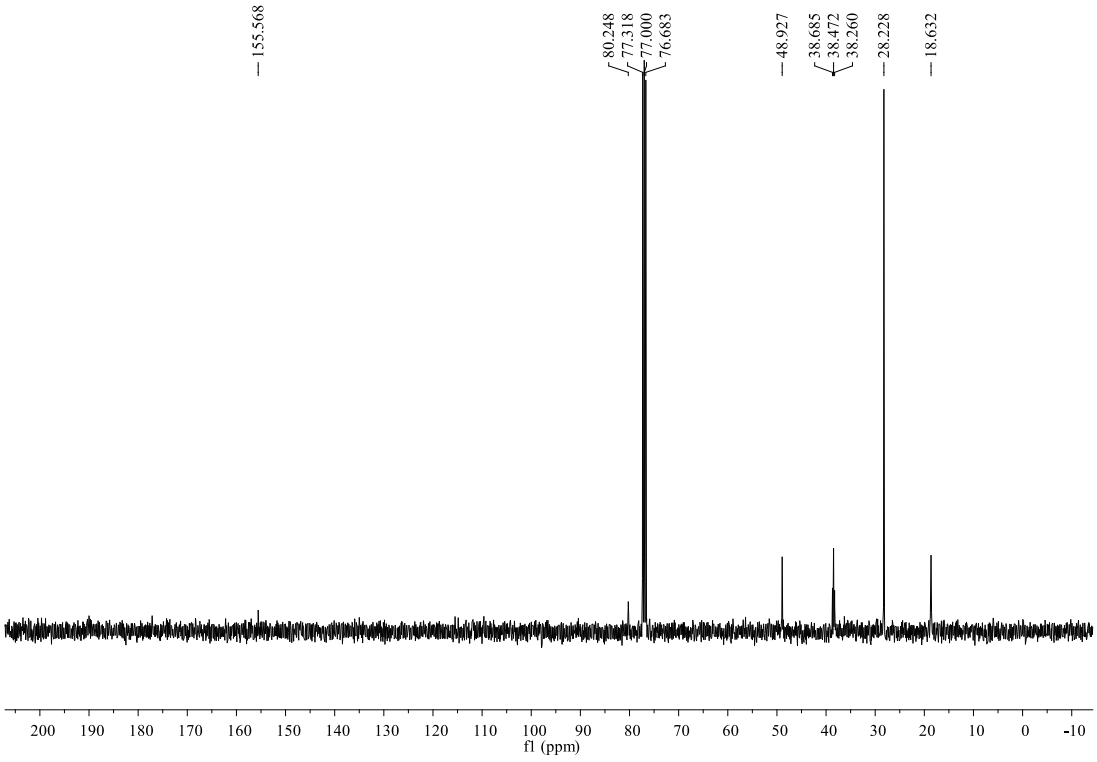




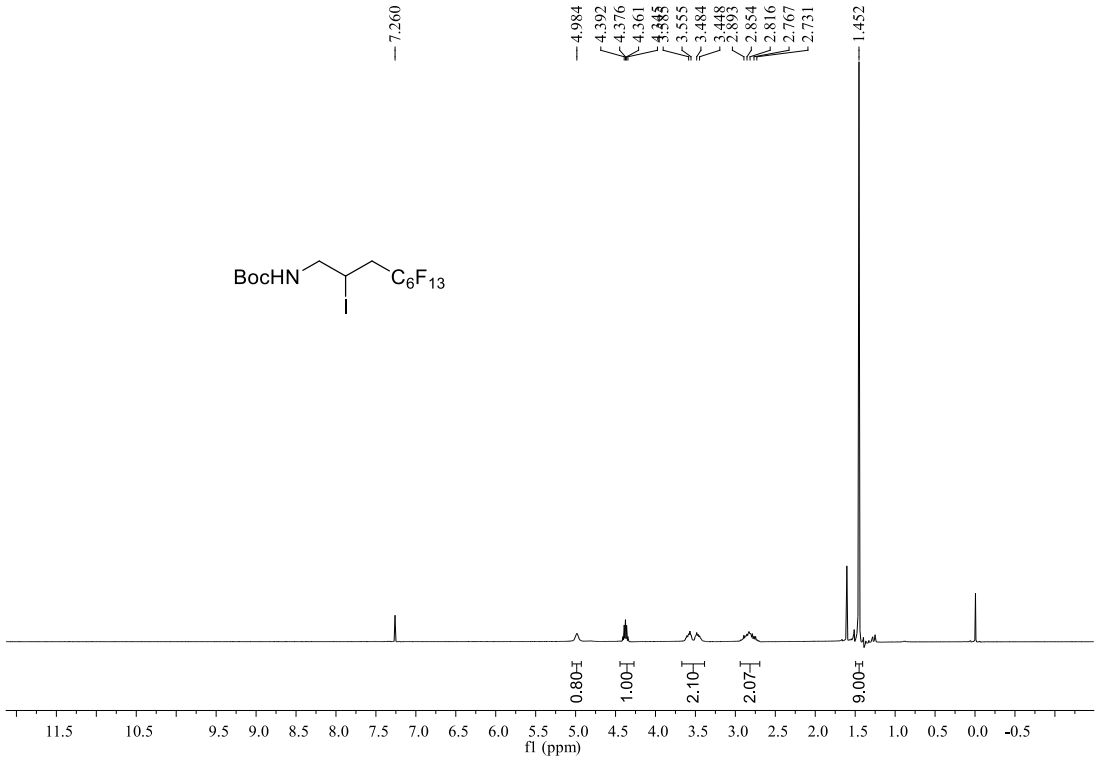
***Tert*-butyl (4,4,5,5,6,6,7,7,7-nonafluoro-2-iodoheptyl)carbamate (3h).**

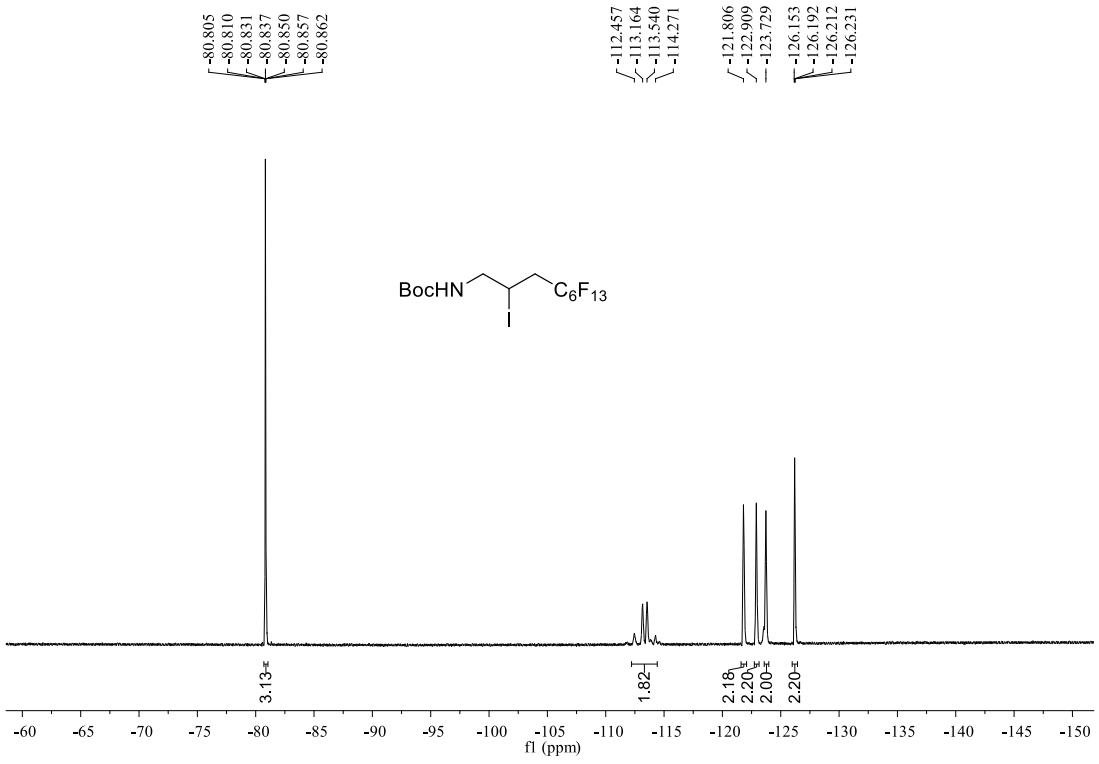


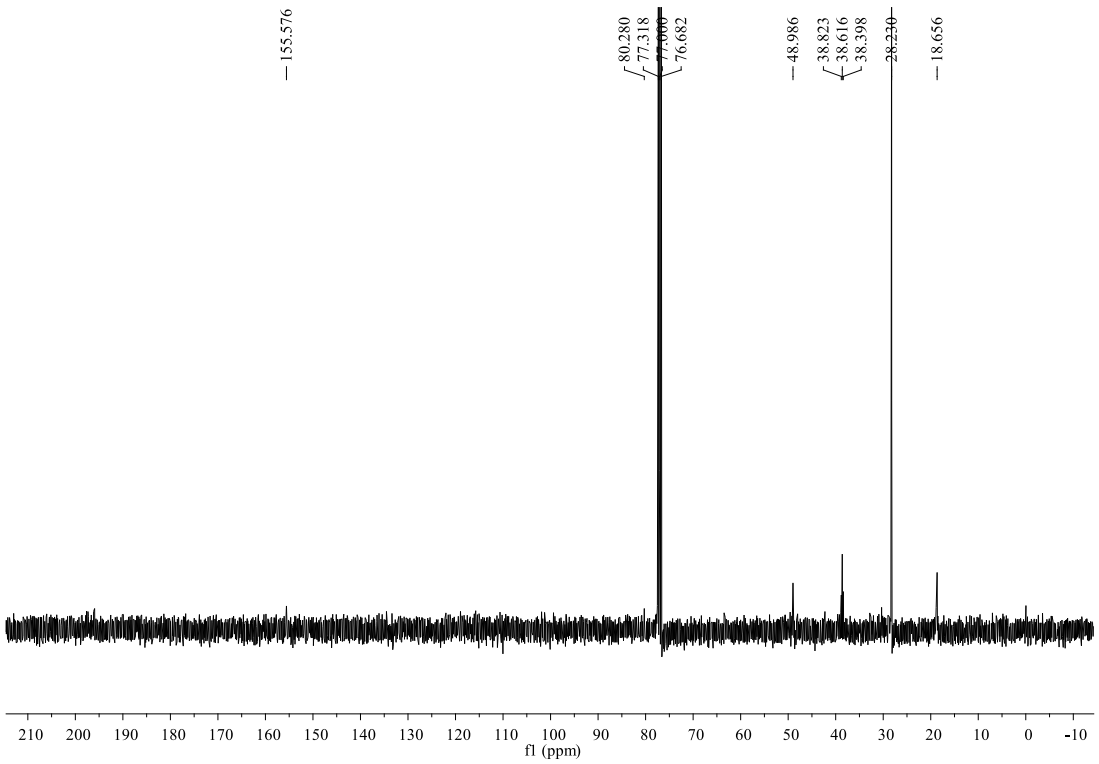

-81.055
-81.072
-81.088
-112.827
-113.308
-113.332
-113.786
-113.806
-114.287
-124.624
-125.910
-125.930
-125.951
BocHN
C4F9
I
3.48
1.85
2.00
2.29
-60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150
f1 (ppm)


155.568
80.248
77.318
77.000
76.683
48.927
38.685
38.472
38.260
28.228
18.632
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

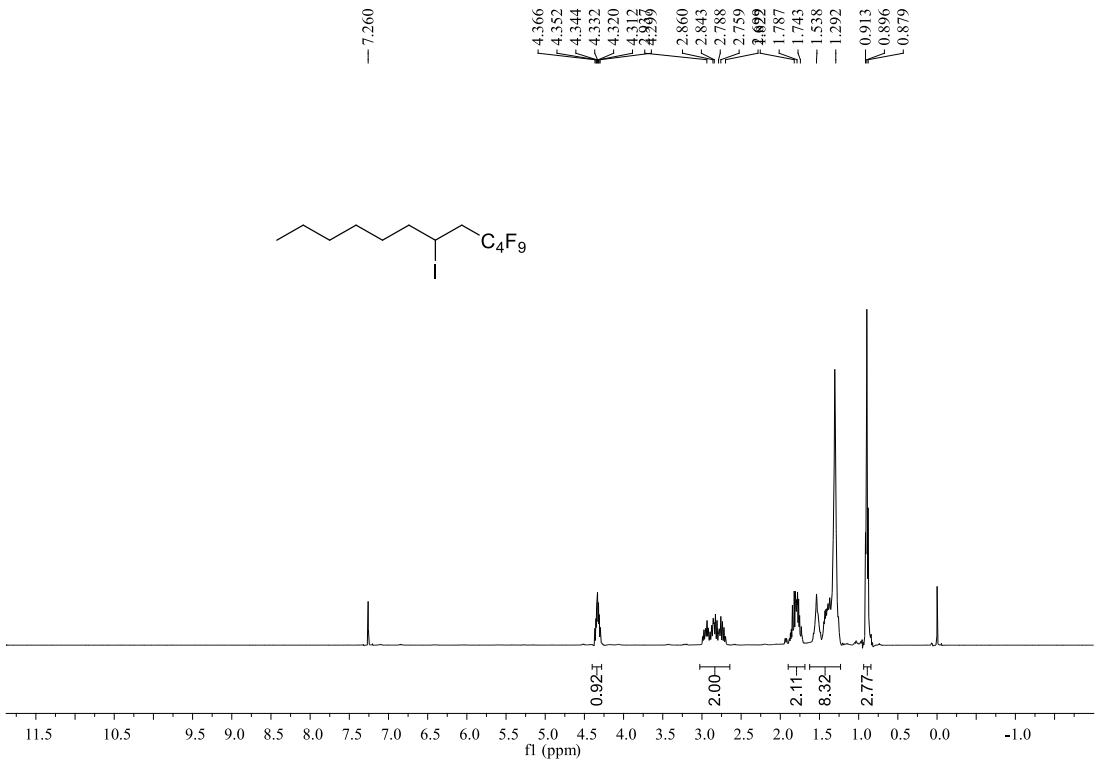
***Tert*-butyl (4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-iodononyl)carbamate (3i).**

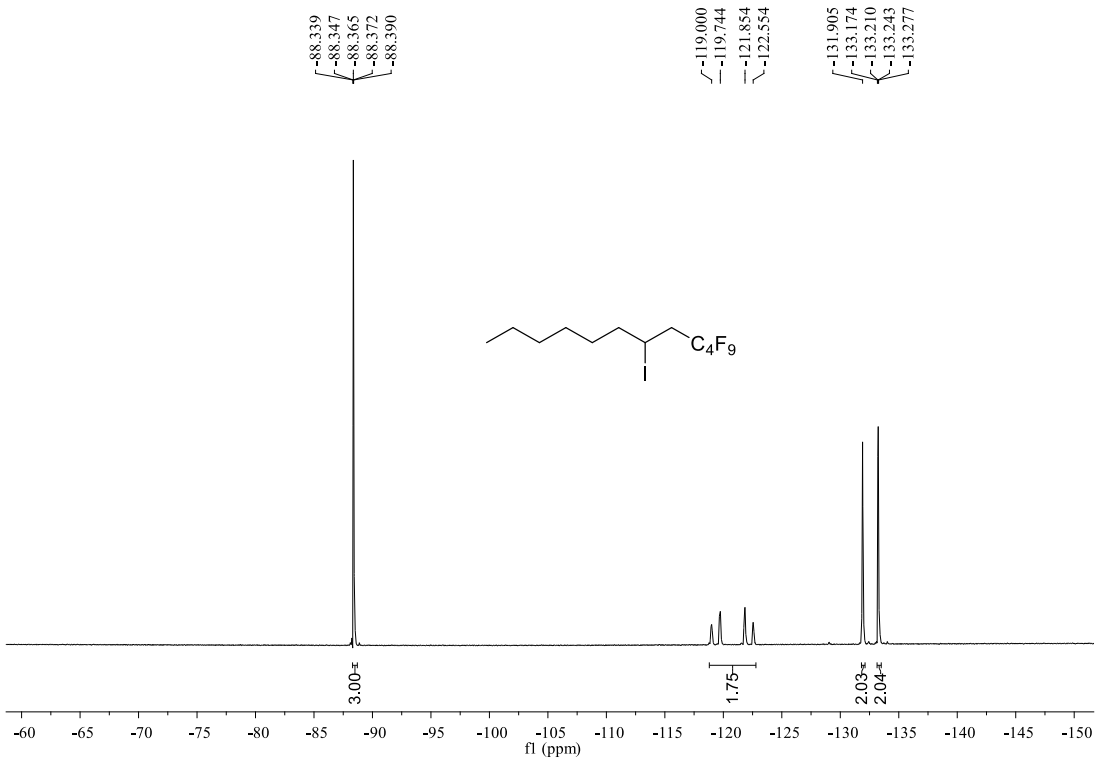


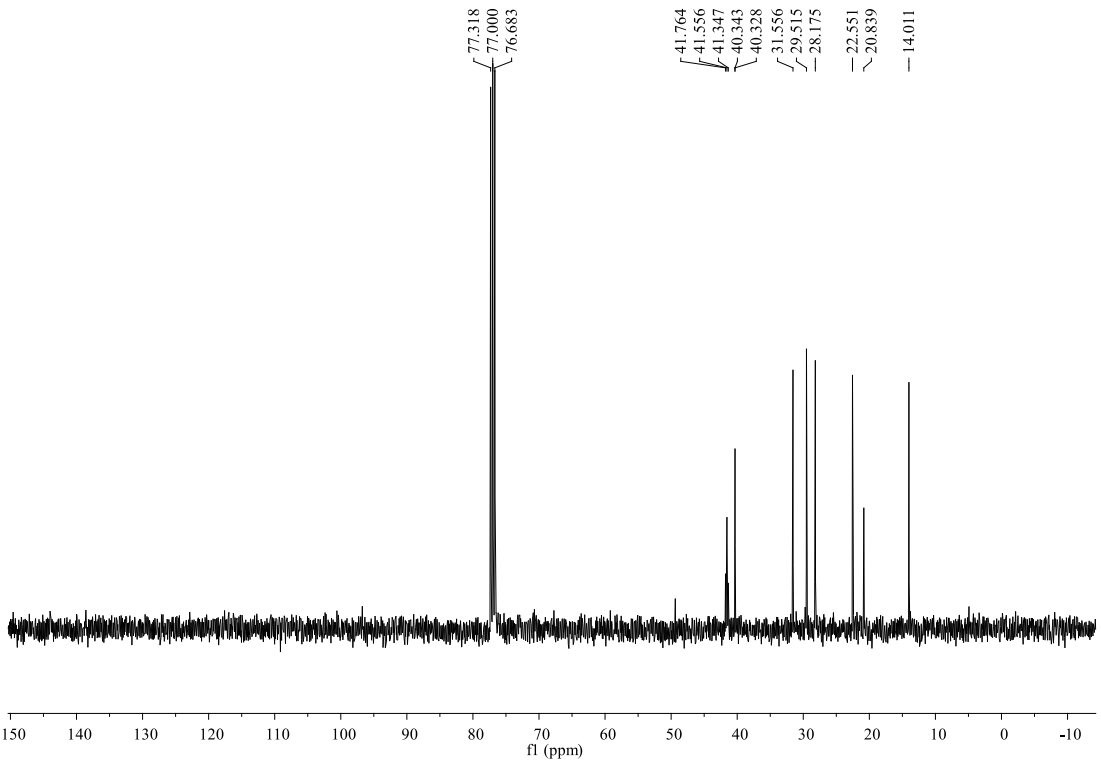




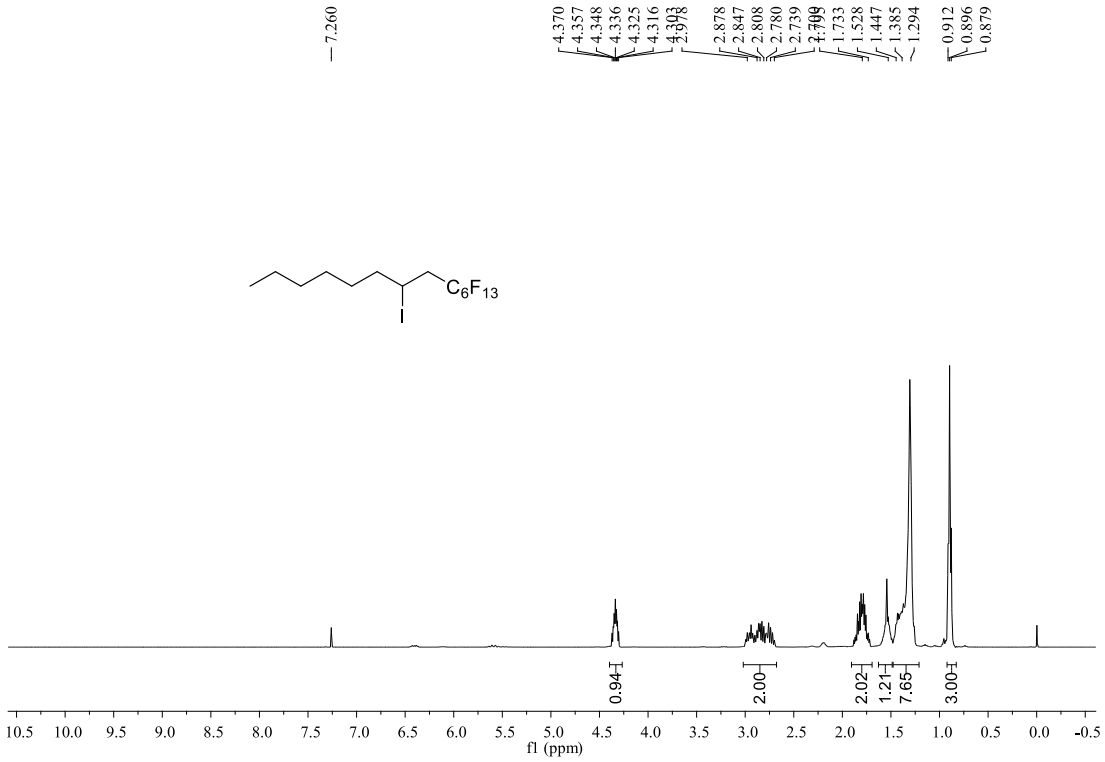
1,1,1,2,2,3,3,4,4-nonafluoro-6-iododododecane (3j).

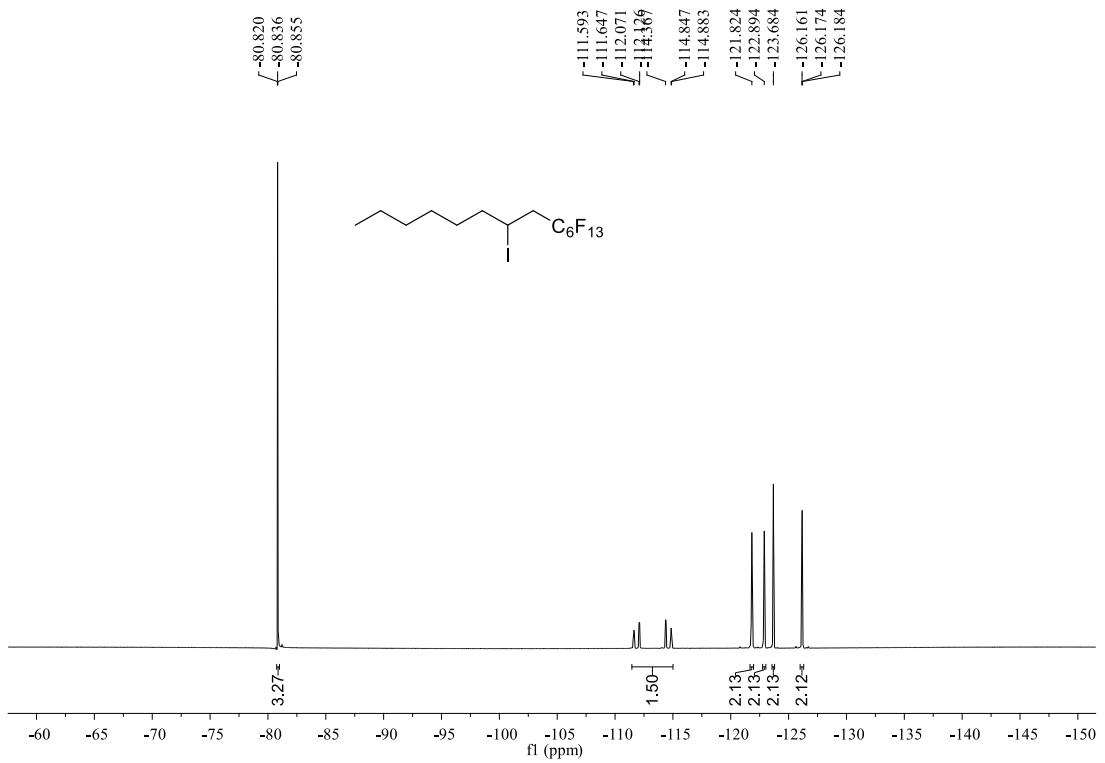


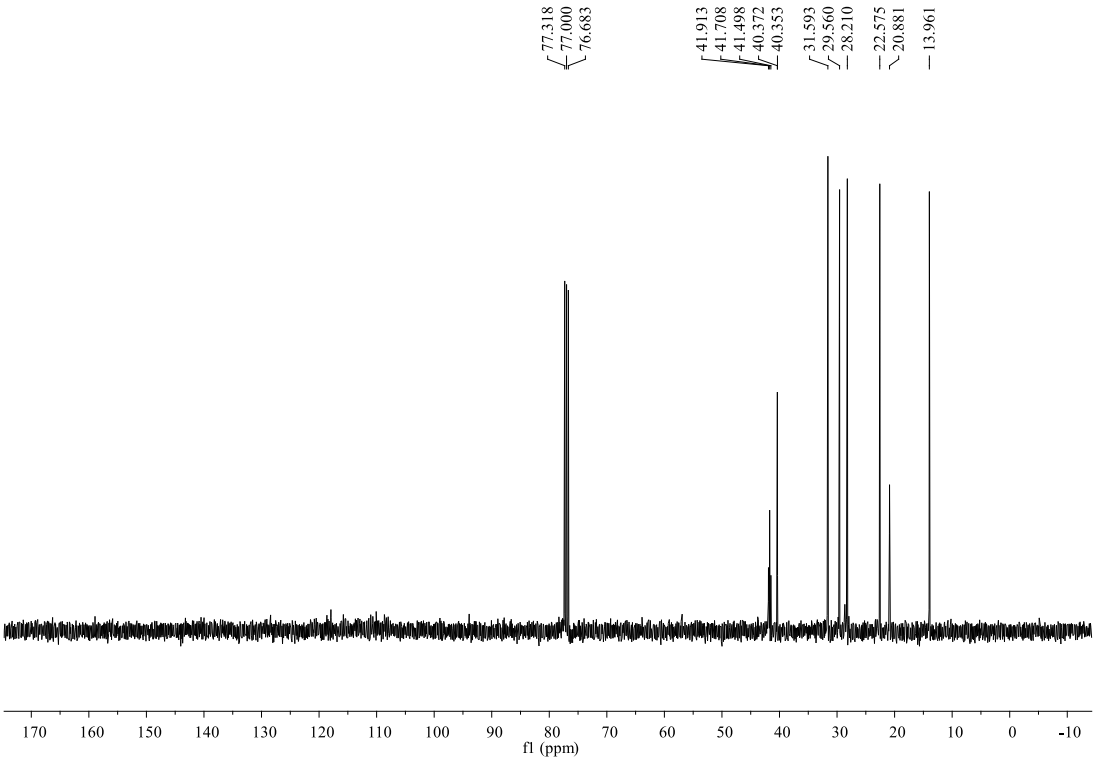

-88.339
-88.347
-88.365
-88.372
-88.390
-119.000
-119.744
-121.854
-122.554
-131.905
-133.174
-133.210
-133.243
-133.277
C4F9
I
3.00
1.75
2.03
2.04
-60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150
f1 (ppm)


77.318
77.000
76.683
41.764
41.556
41.347
40.343
40.328
31.556
29.515
28.175
22.551
20.839
14.011
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

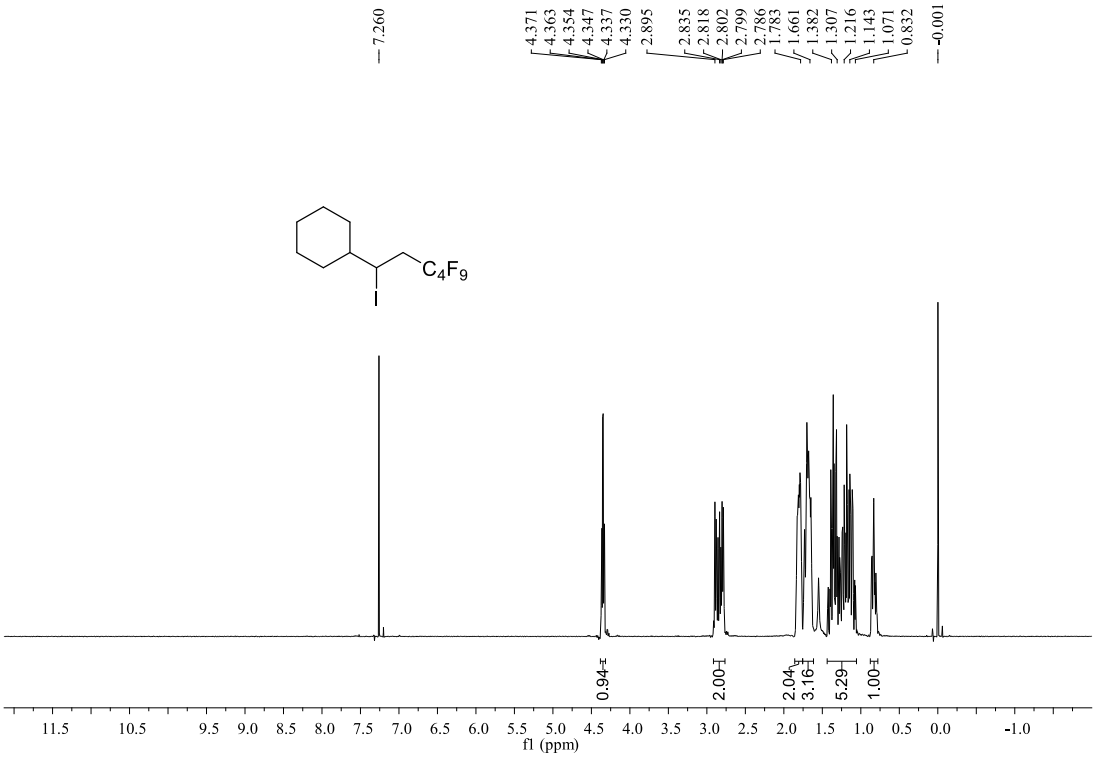
1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodotetradecane (3k).

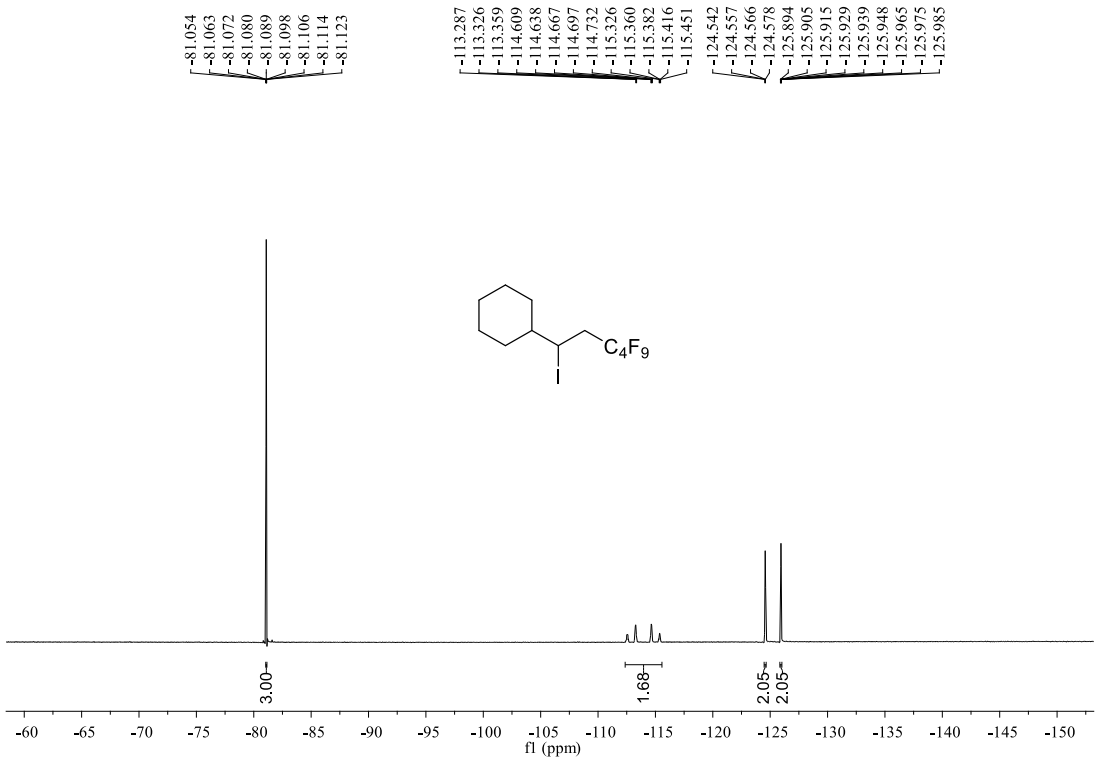


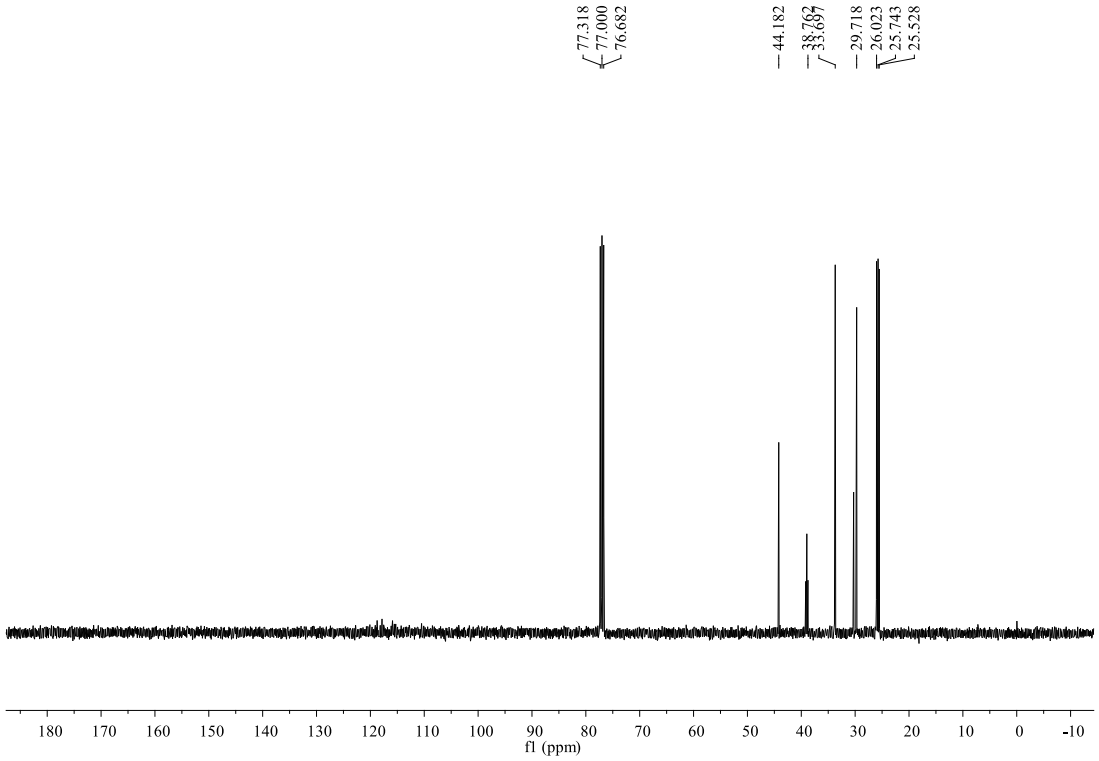




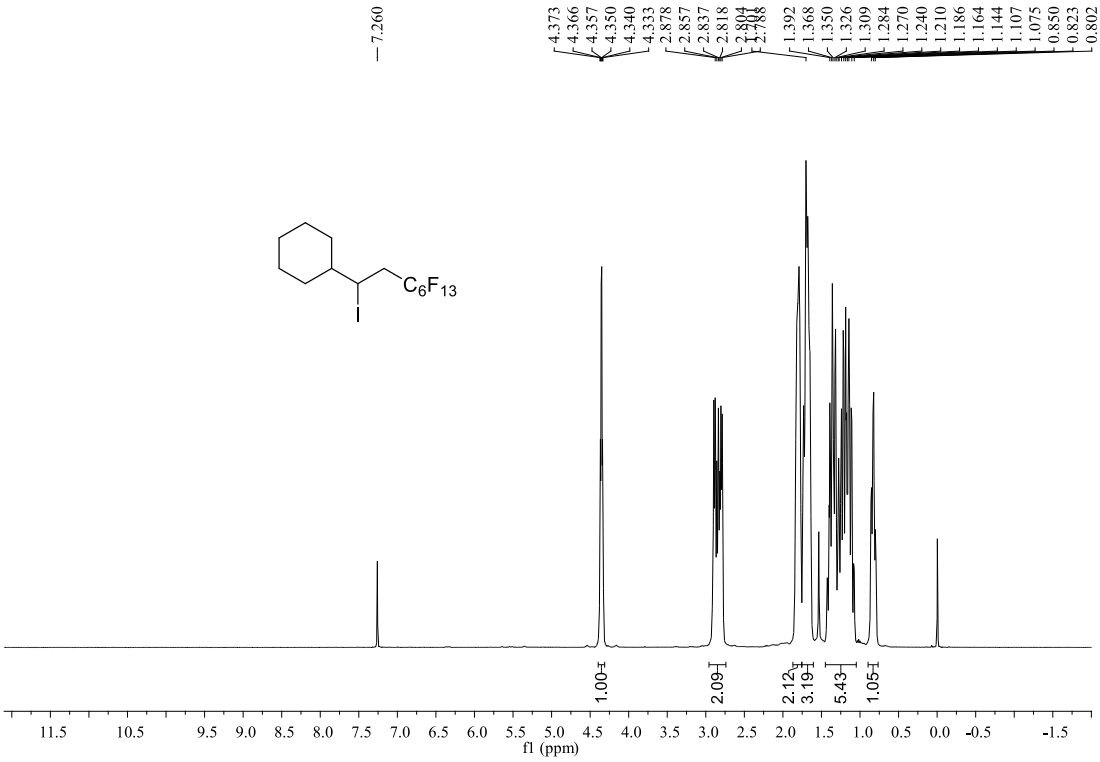
(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)cyclohexane (3l).

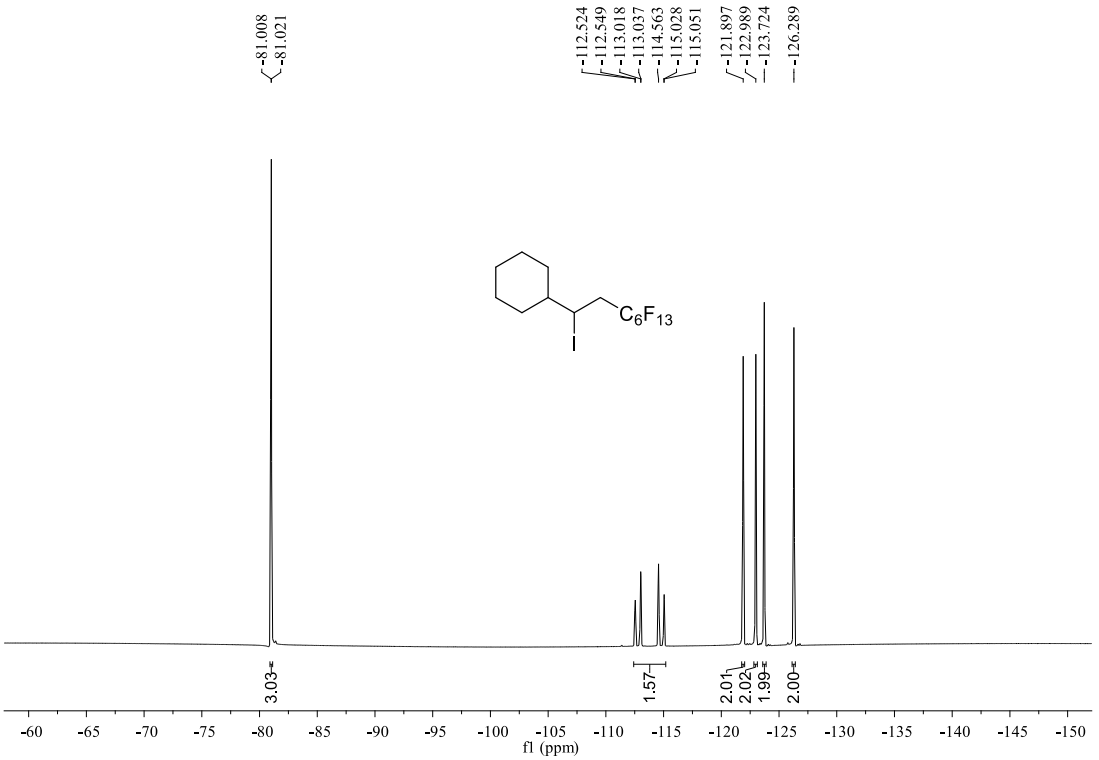


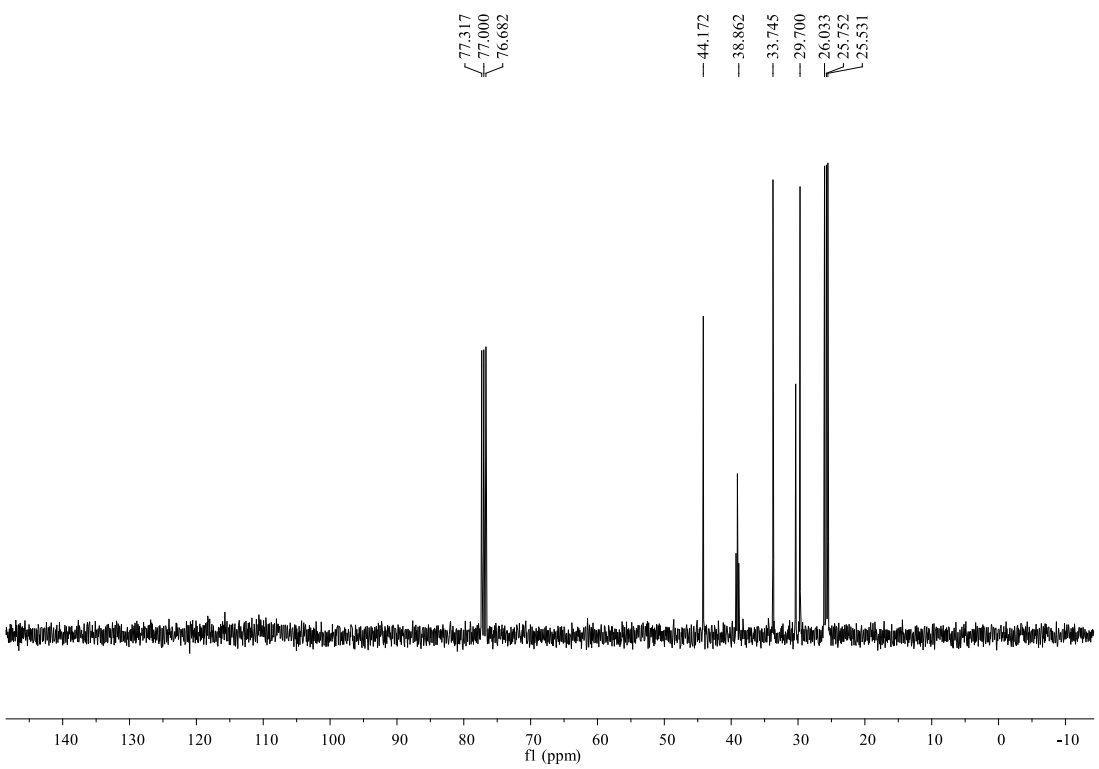

-81.054
-81.063
-81.072
-81.080
-81.089
-81.098
-81.106
-81.114
-81.123
-113.287
-113.326
-113.359
-114.609
-114.638
-114.667
-114.697
-114.732
-115.326
-115.360
-115.382
-115.416
-115.451
-124.542
-124.557
-124.566
-124.578
-125.894
-125.905
-125.915
-125.929
-125.939
-125.948
-125.965
-125.975
-125.985
C_4F_9
I
3.00
1.68
2.05
2.05
-60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150
f1 (ppm)


77.318
77.000
76.682
44.182
38.762
38.697
29.718
26.023
25.743
25.528
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

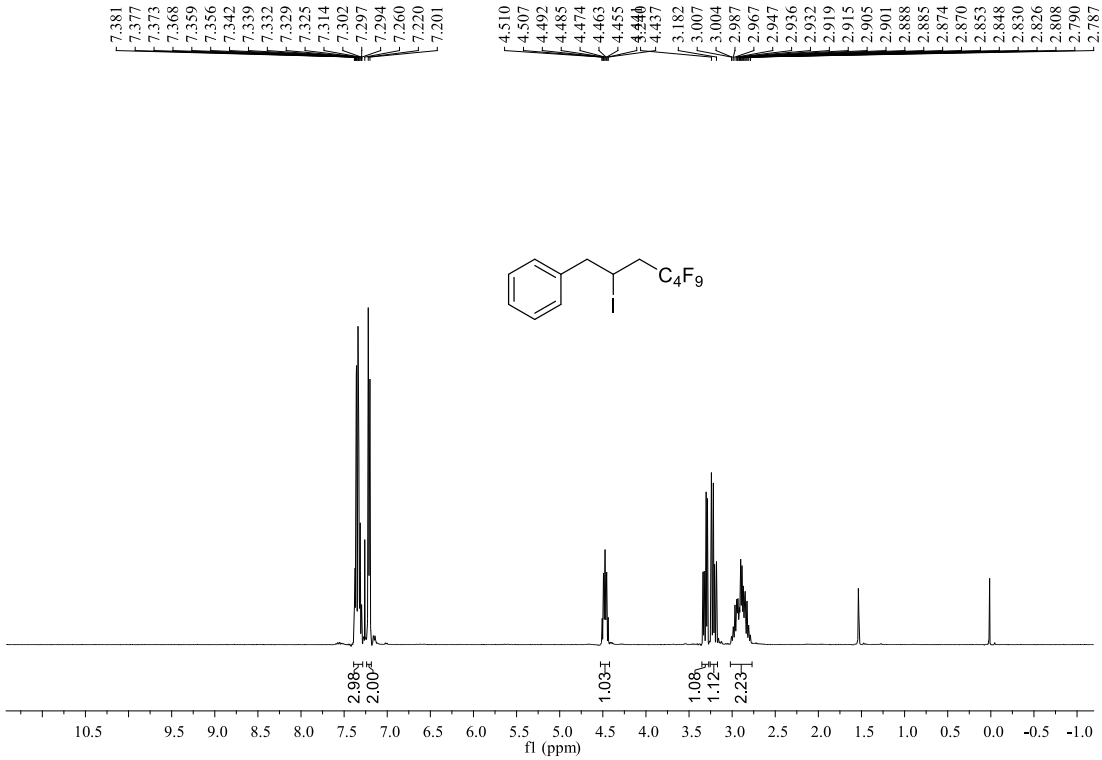
(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-iodooctyl)cyclohexane (3m).

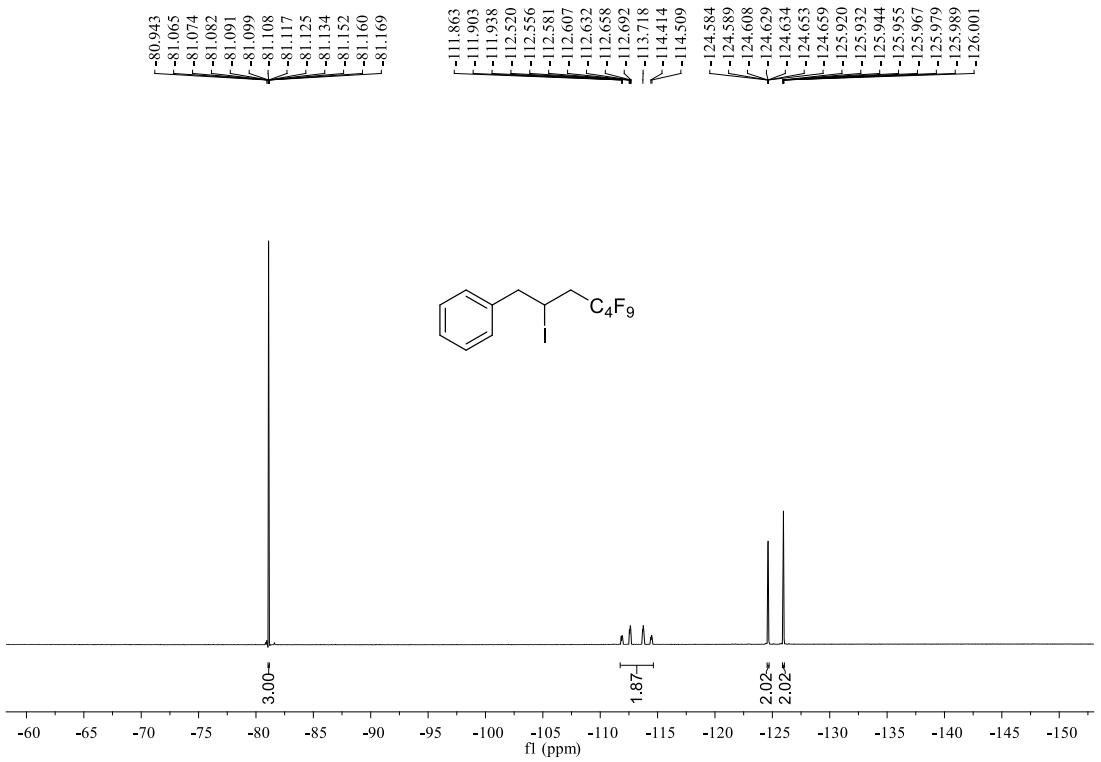


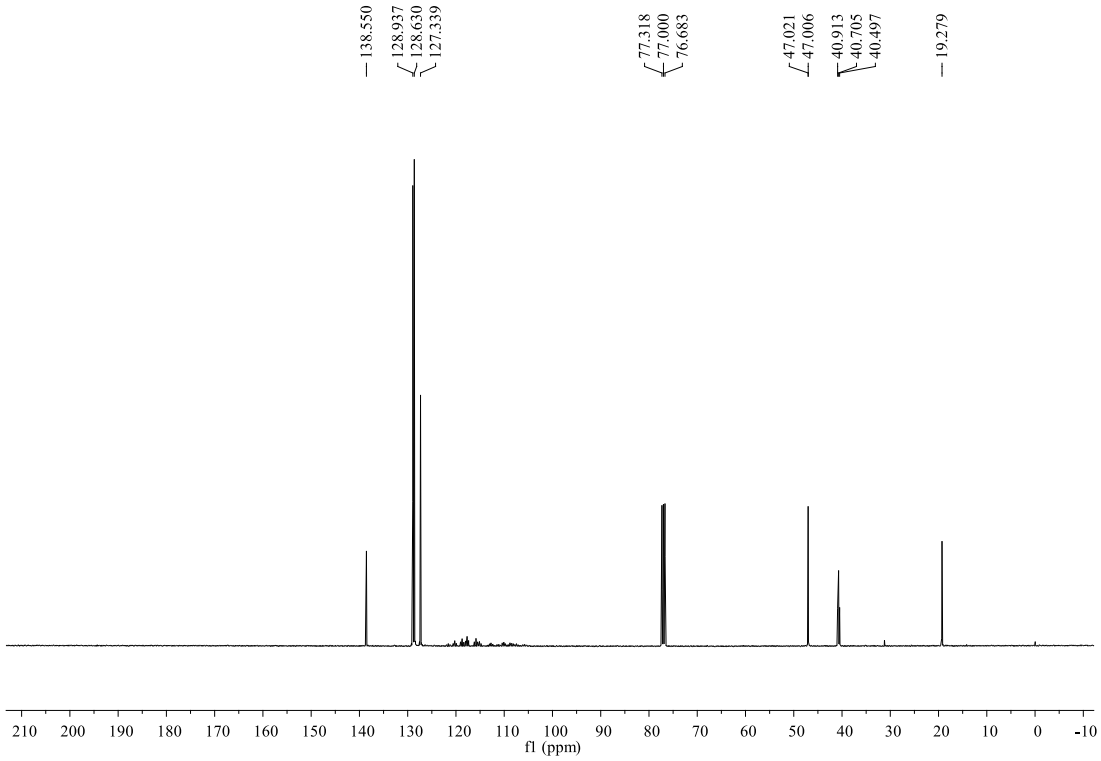




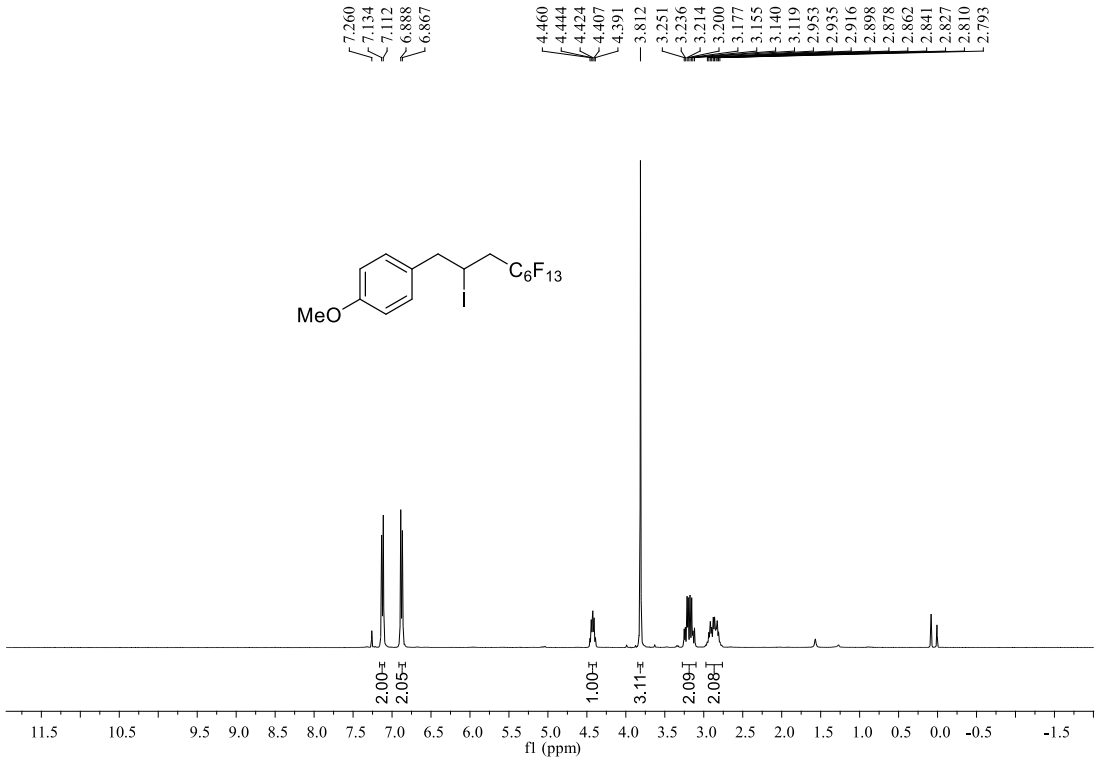
(4,4,5,5,6,6,7,7,7-nonafluoro-2-iodoheptyl)benzene (3n).

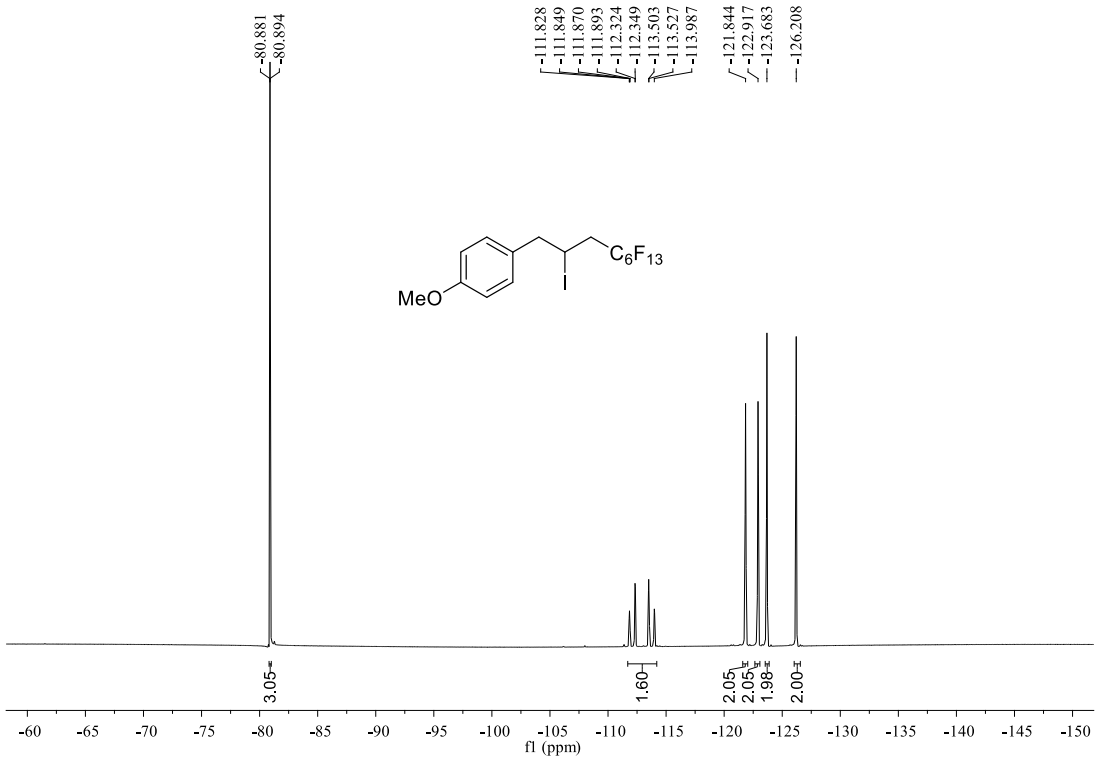


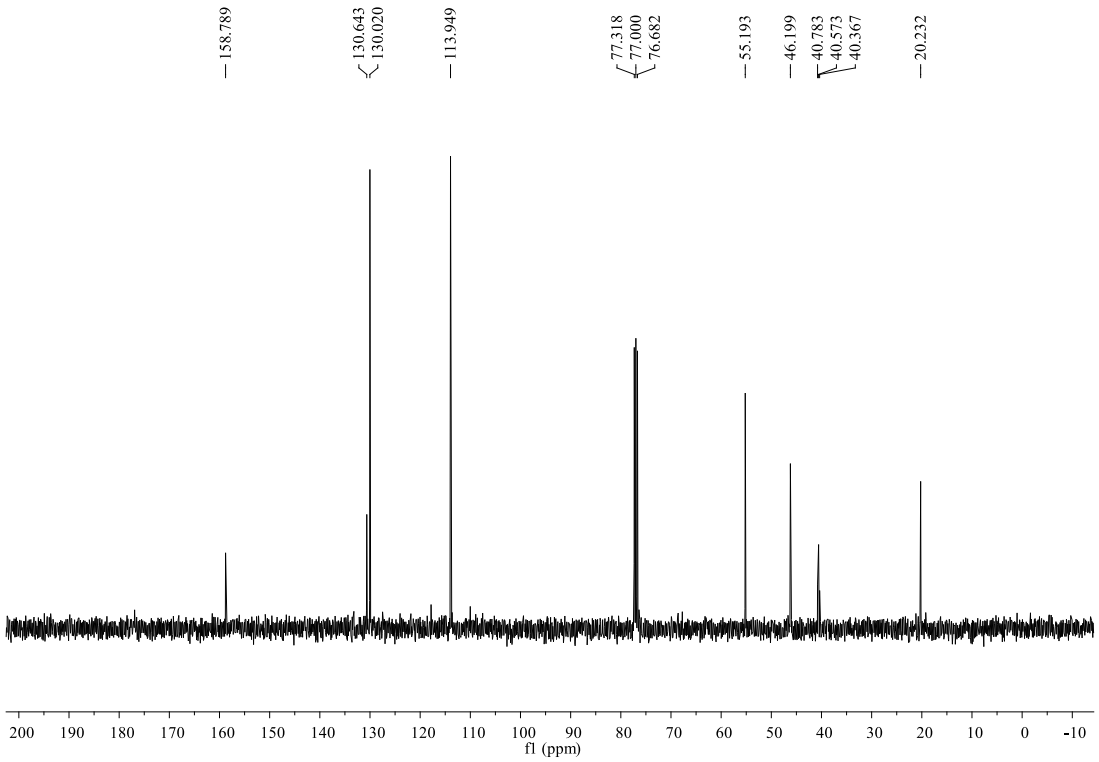

-80.943
-81.065
-81.074
-81.082
-81.091
-81.099
-81.108
-81.117
-81.125
-81.134
-81.152
-81.160
-81.169
-111.863
-111.903
-111.938
-112.520
-112.556
-112.581
-112.607
-112.632
-112.658
-112.692
-113.718
-114.414
-114.509
-124.584
-124.589
-124.608
-124.629
-124.634
-124.653
-124.659
-125.920
-125.932
-125.944
-125.955
-125.967
-125.979
-125.989
-126.001
C4F9
I
3.00
1.87
2.02
2.02
-60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150
f1 (ppm)


138.550
128.937
128.630
127.339
77.318
77.000
76.683
47.021
47.006
40.913
40.705
40.497
19.279
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

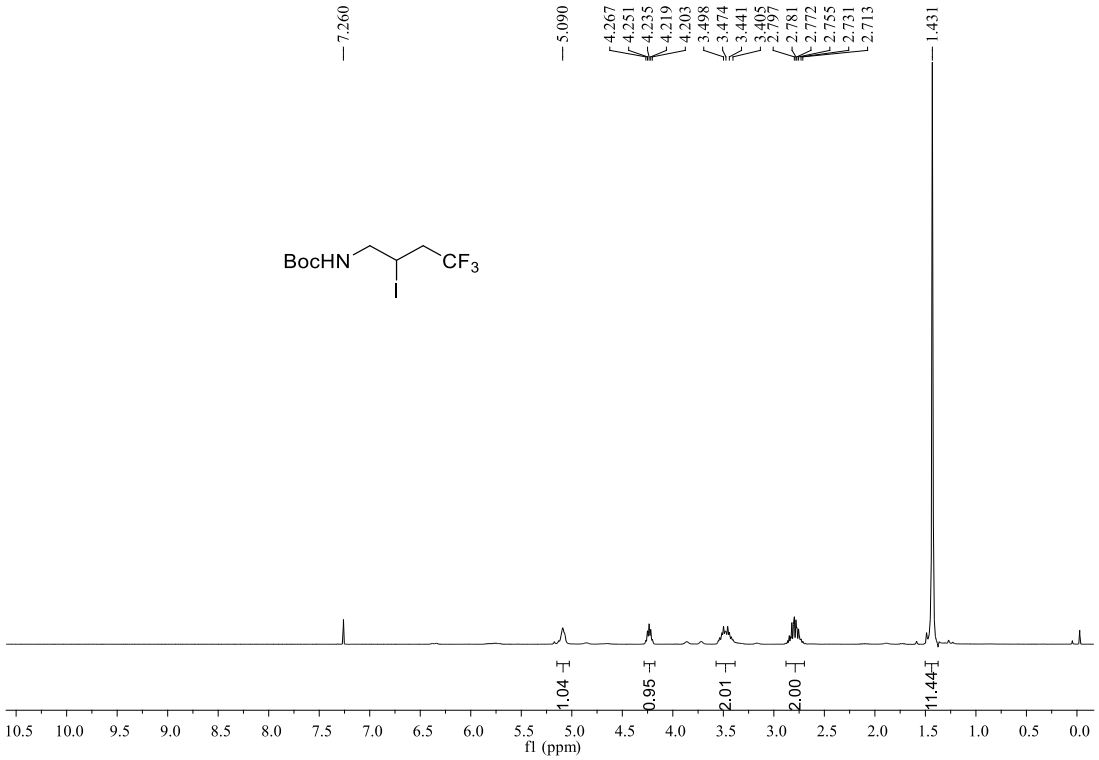
1-methoxy-4-(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-iodononyl)benzene (3o).

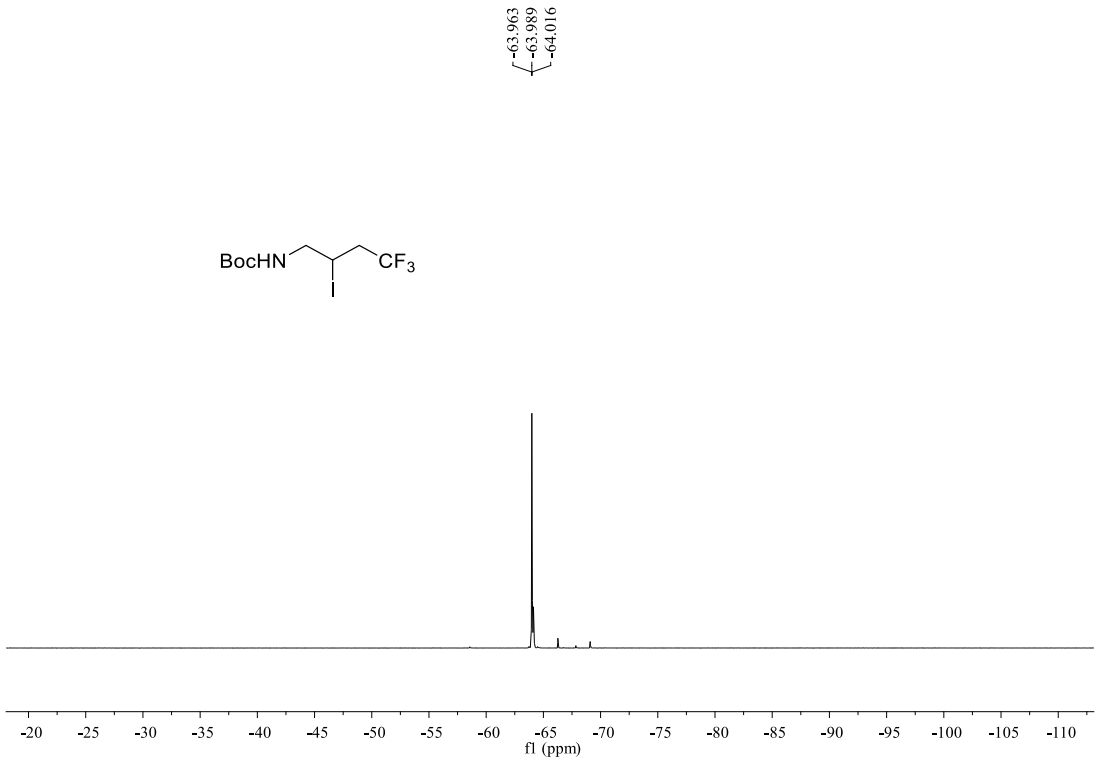


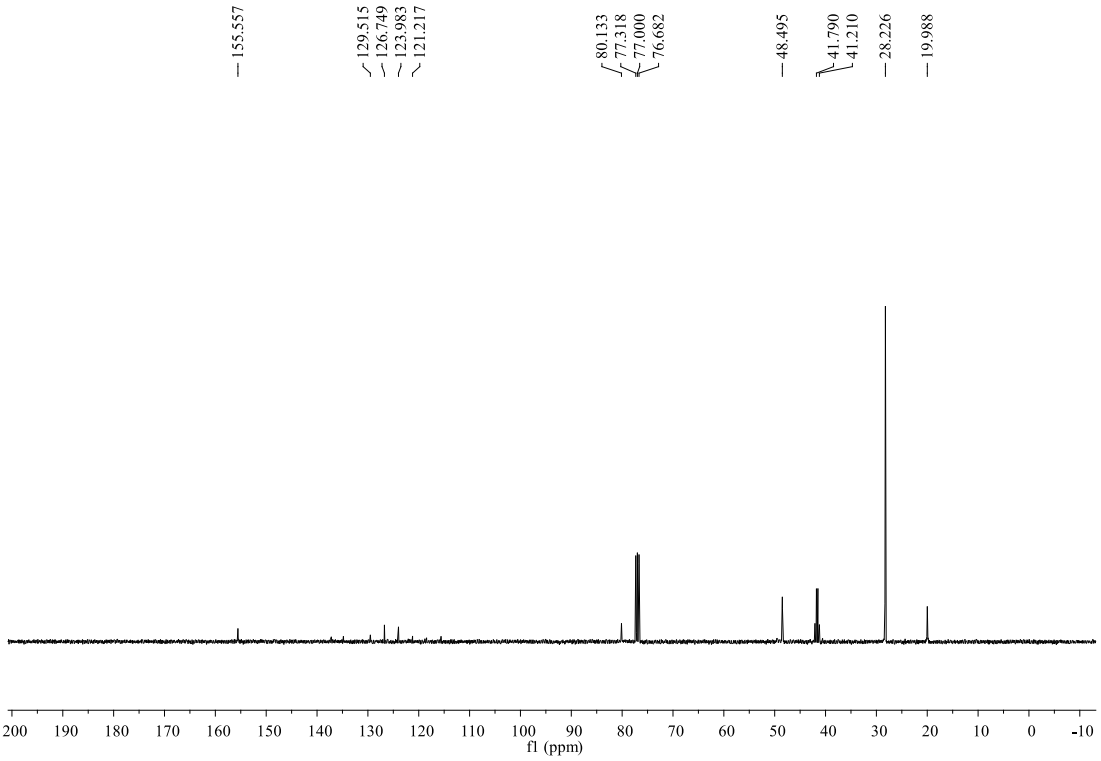




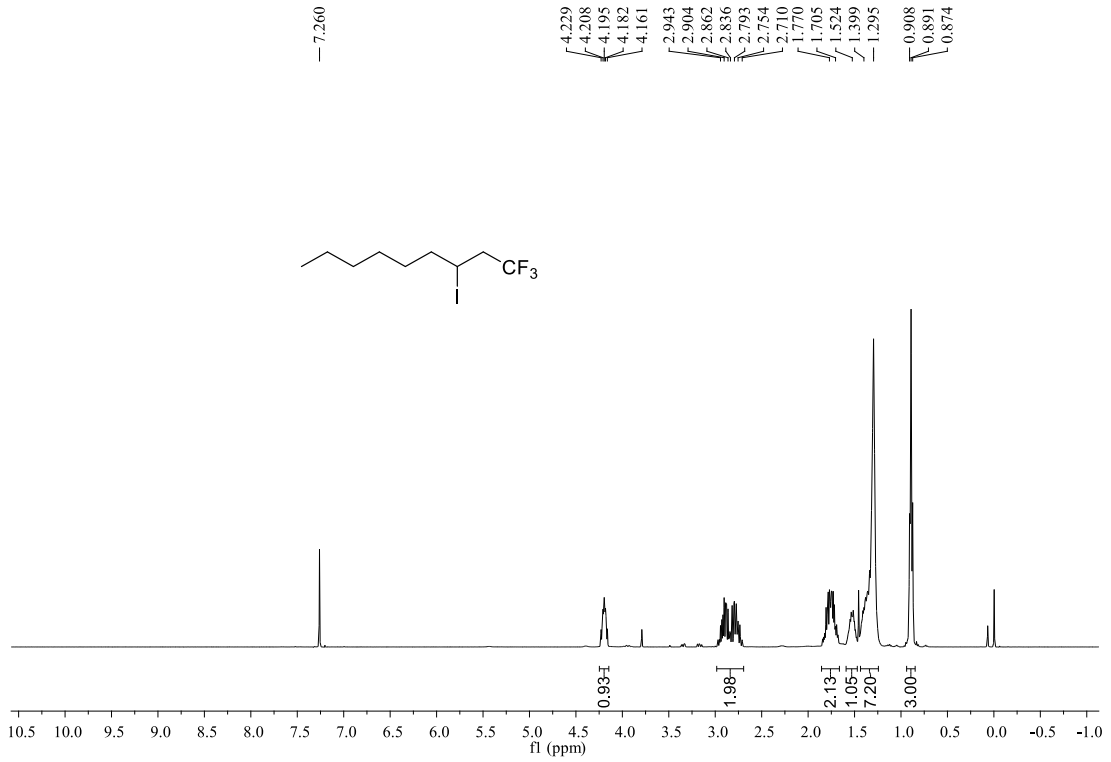
***Tert*-butyl (4,4,4-trifluoro-2-iodobutyl)carbamate (3p).**

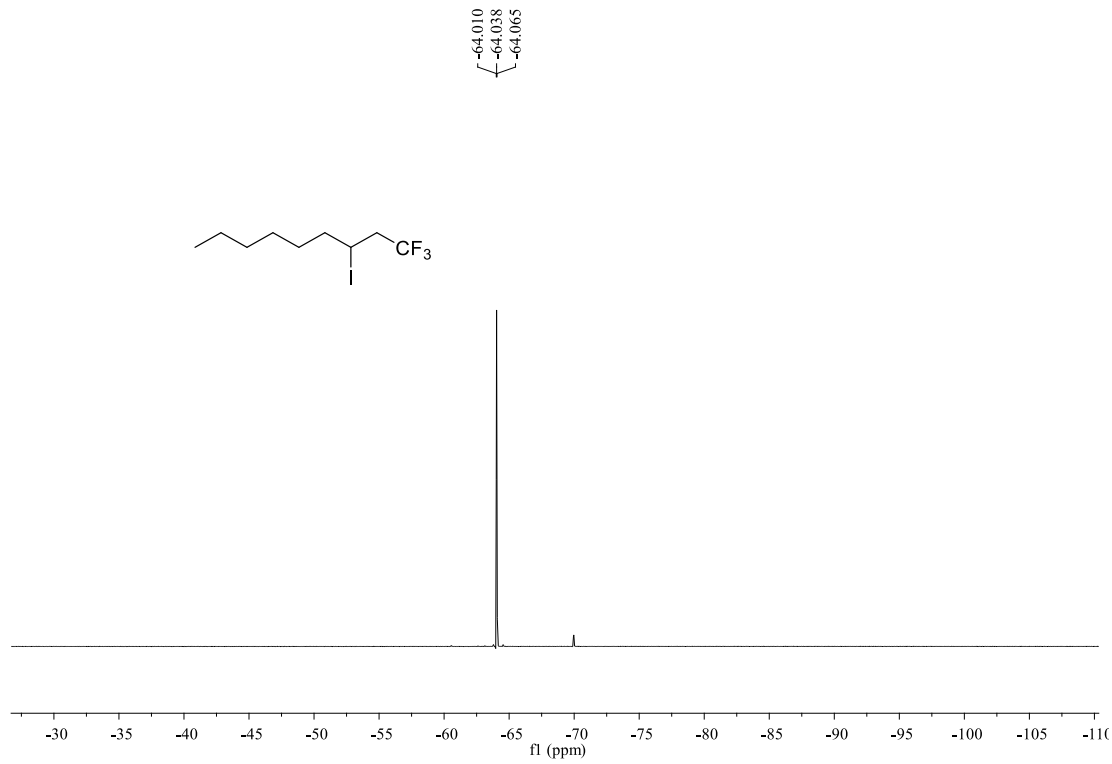


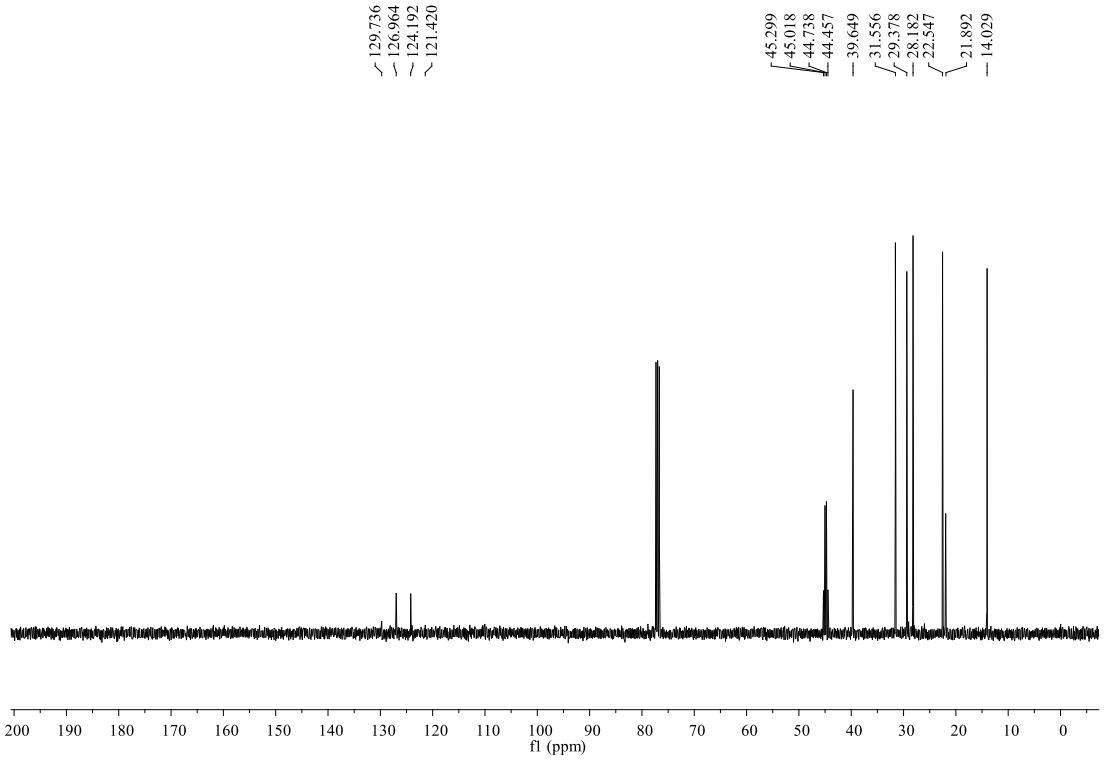

-63.963
-63.989
-64.016
BocHN
CF3
I
-20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110
f1 (ppm)


155.557
129.515
126.749
123.983
121.217
80.133
77.318
77.000
76.682
48.495
41.790
41.210
28.226
19.988
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

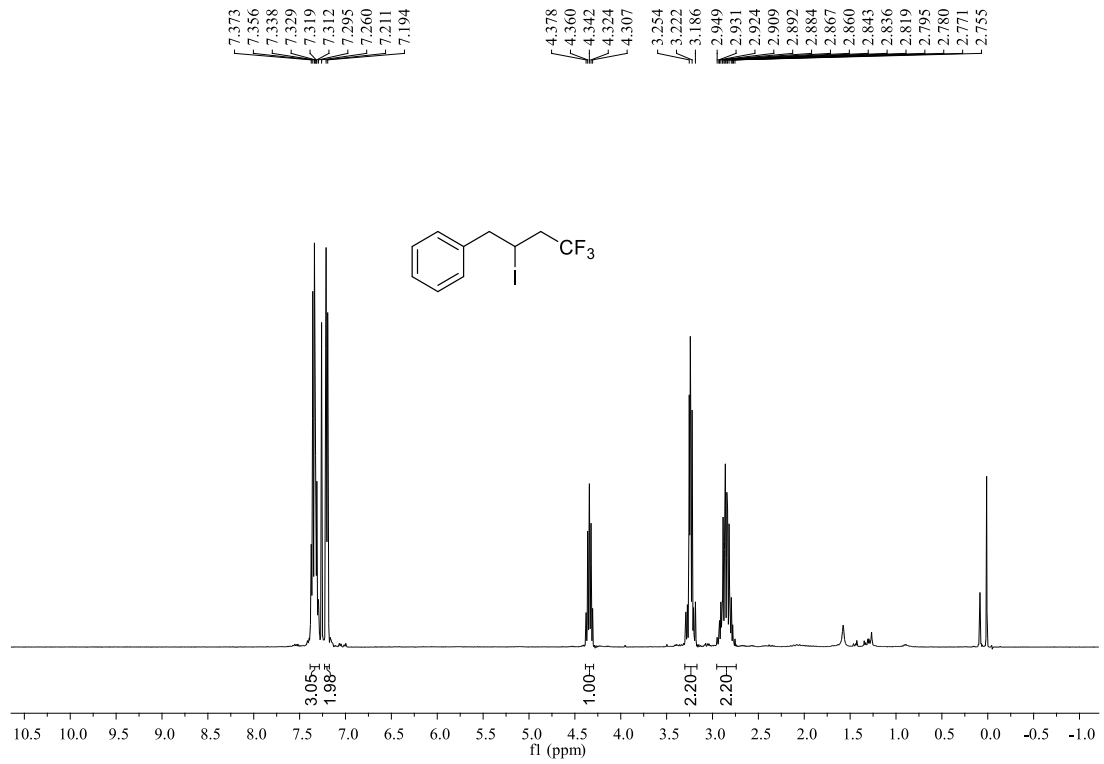
1,1,1-trifluoro-3-iodononane (3q).

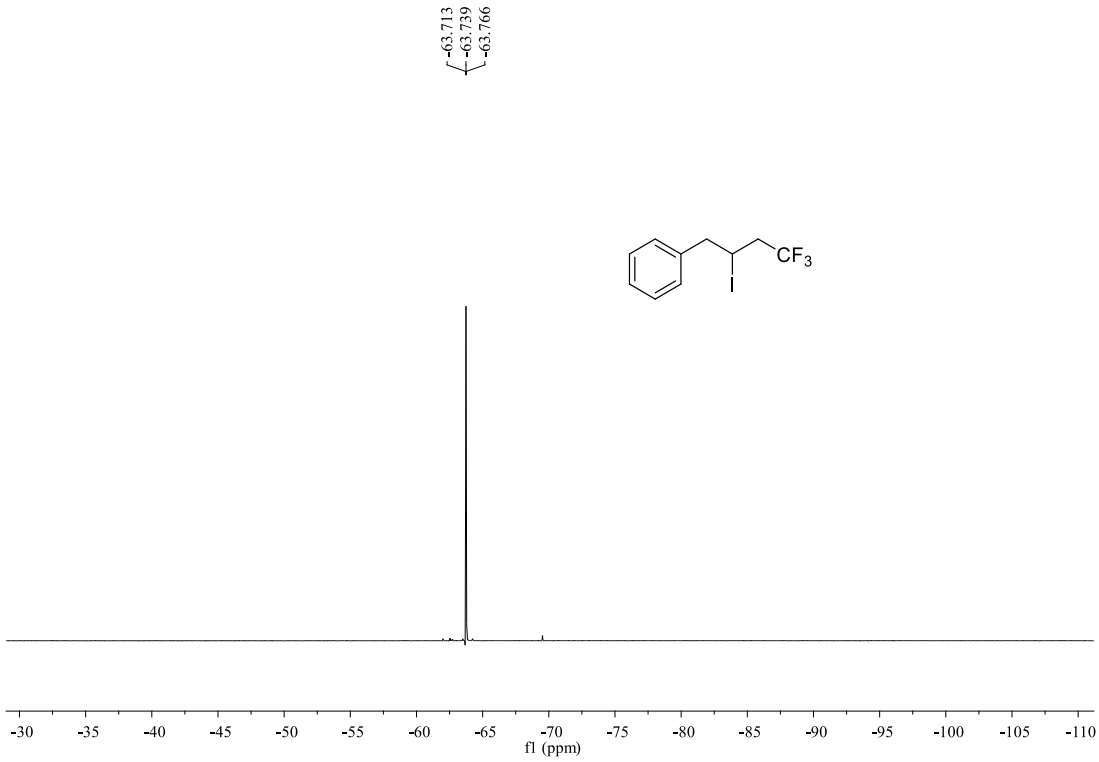


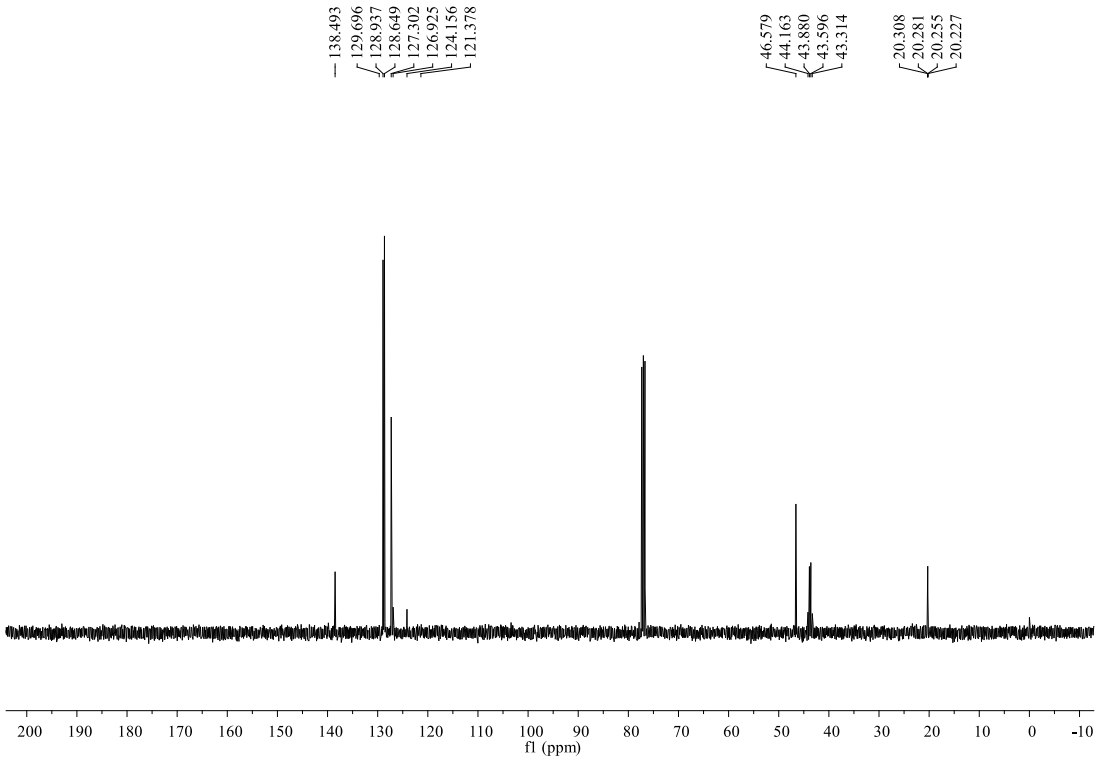




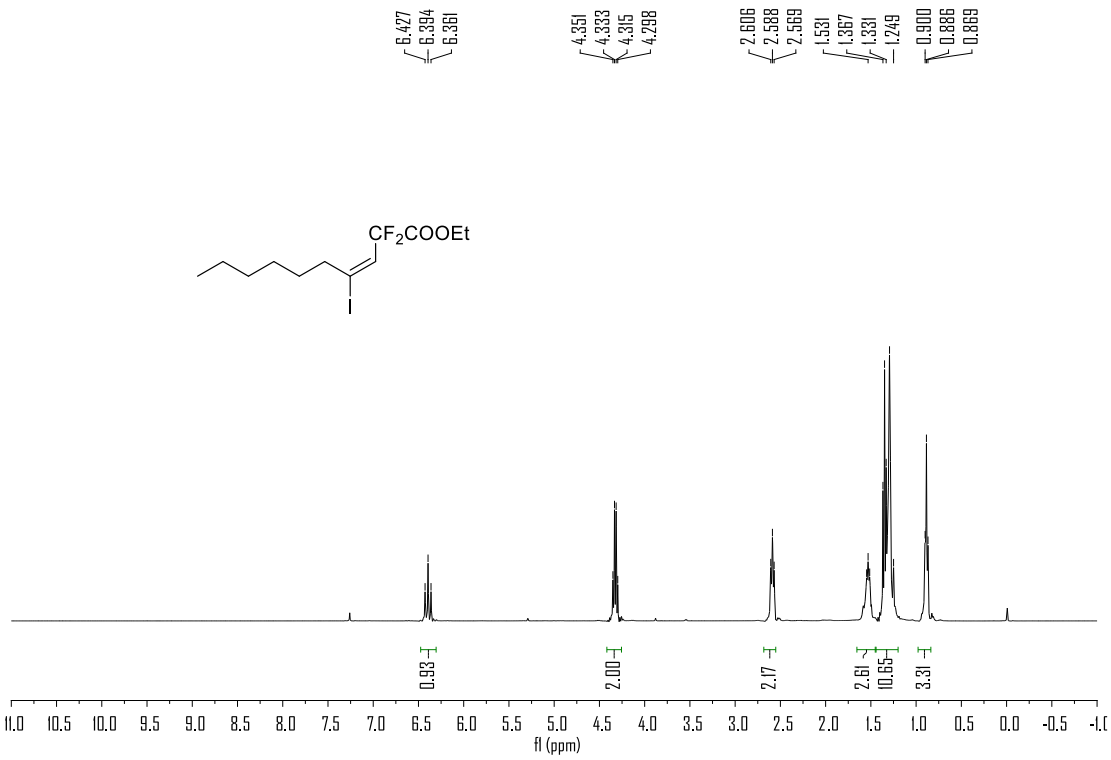
(4,4,4-trifluoro-2-iodobutyl)benzene (3r).

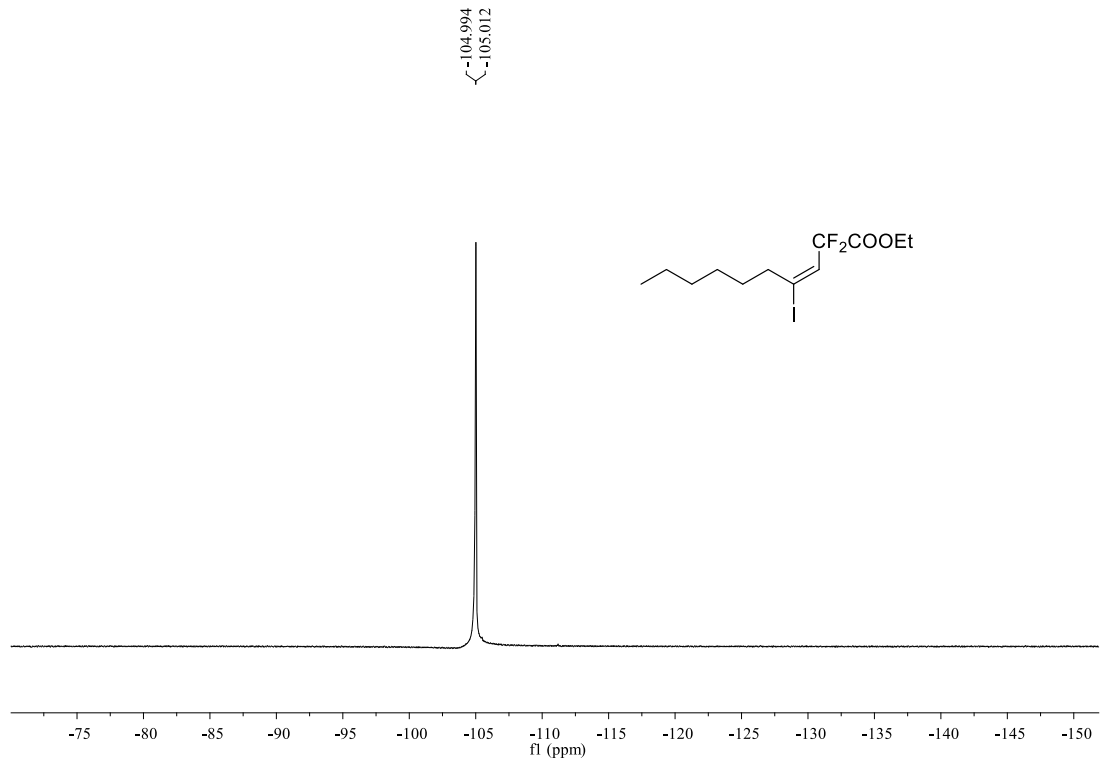


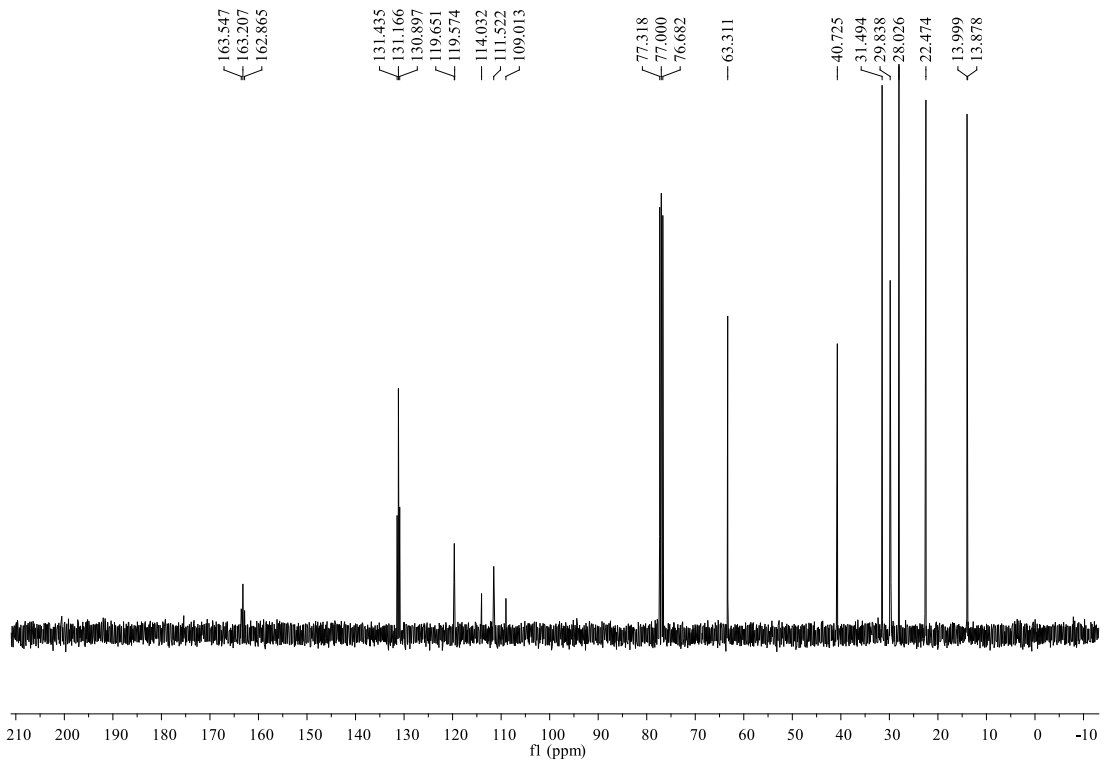

-63.713
-63.739
-63.766
CF3
I
-30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110
f1 (ppm)


138.493
129.696
128.937
128.649
127.302
126.925
124.156
121.378
46.579
44.163
43.880
43.596
43.314
20.308
20.281
20.255
20.227
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

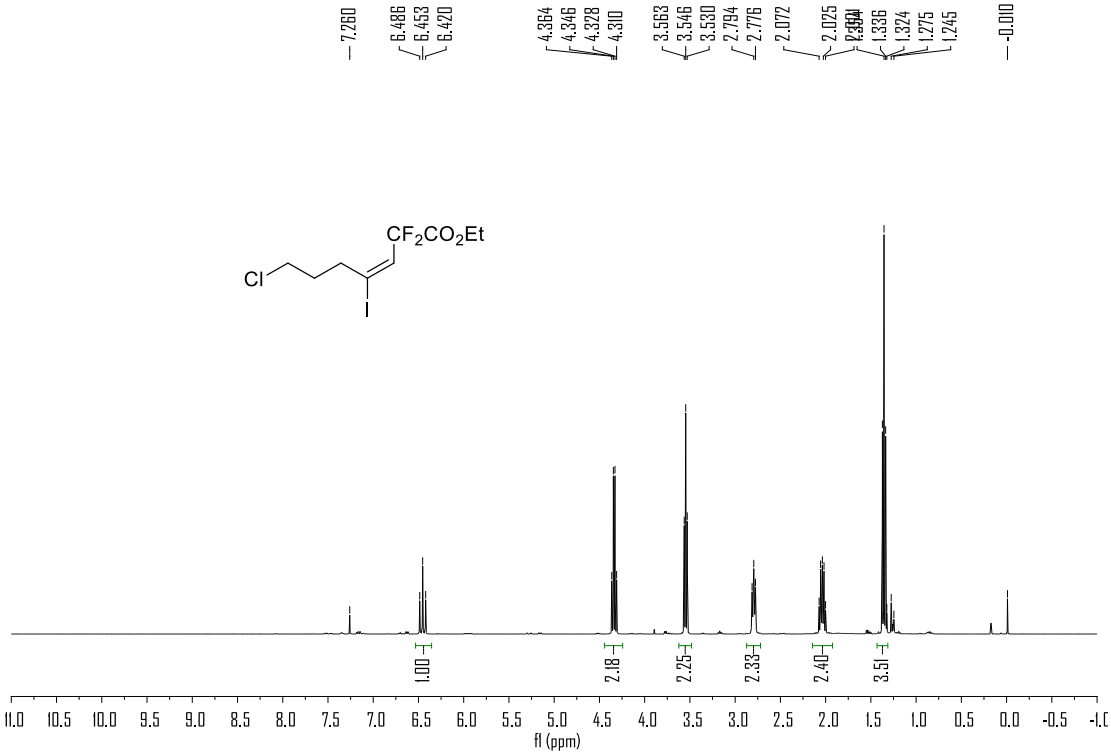
Ethyl (*E*)-2,2-difluoro-4-iododec-3-enoate (5a).

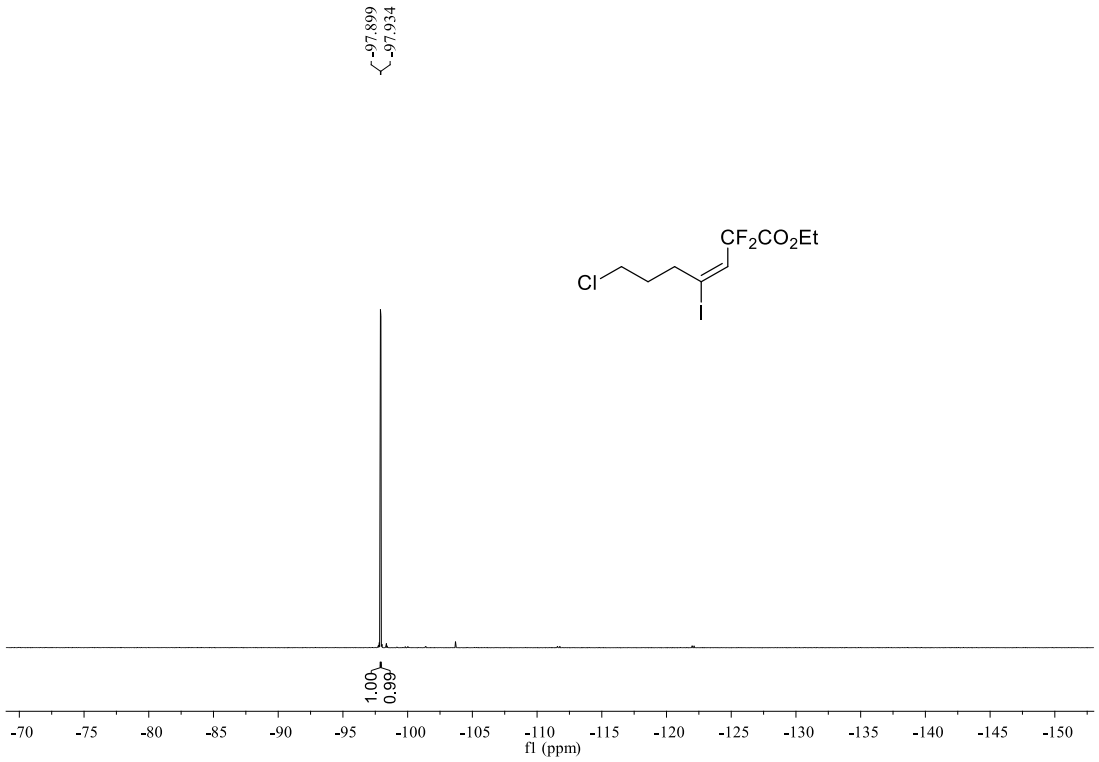


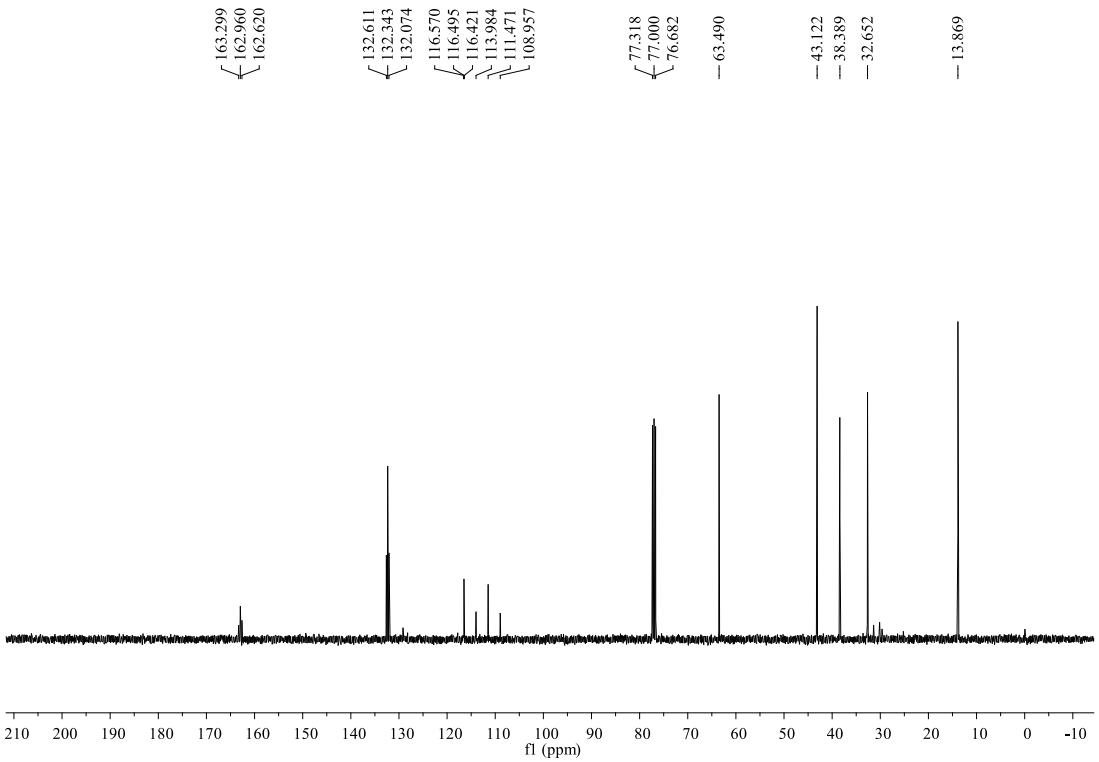




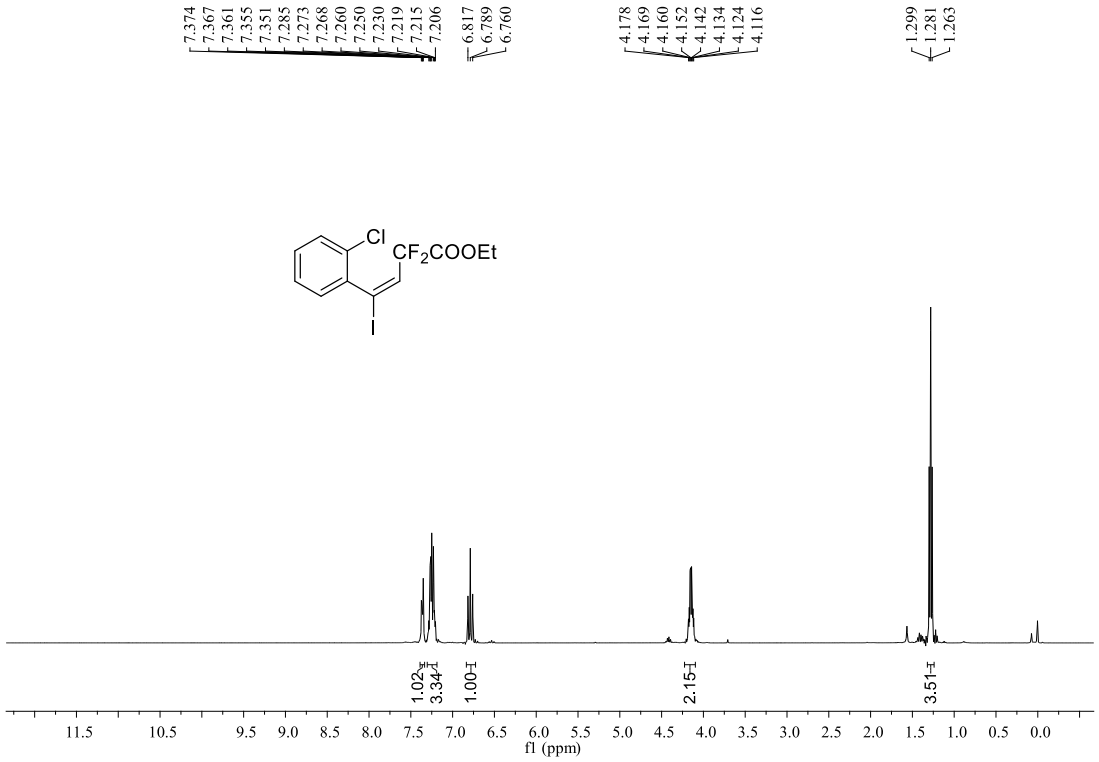
Ethyl (*E*)-7-chloro-2,2-difluoro-4-iodohept-3-enoate (5b).

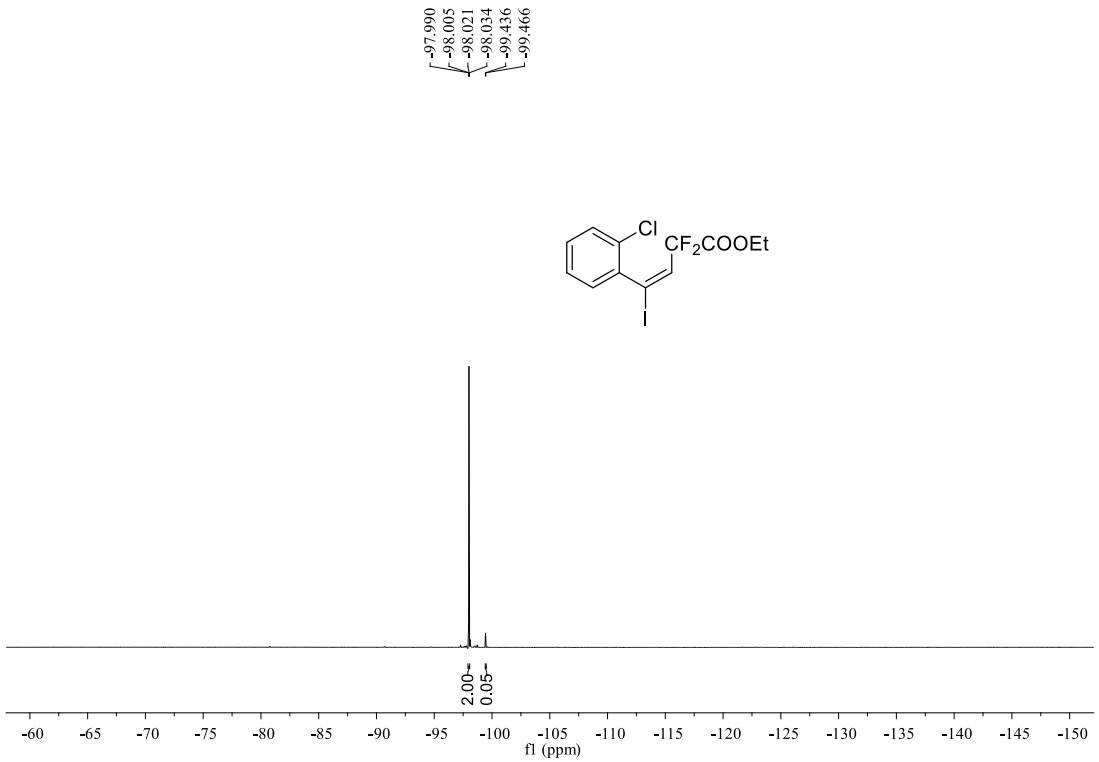


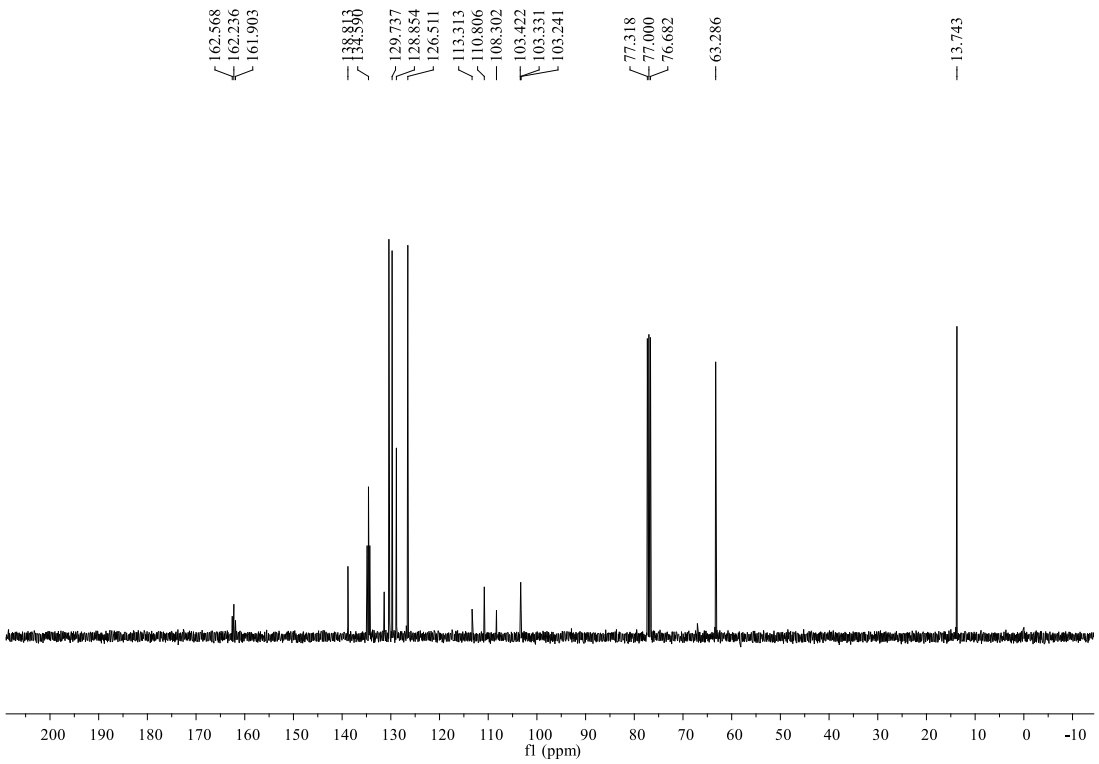

-97.899
-97.934
CF2CO2Et
Cl
1.00
0.99
-70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150
f1 (ppm)


163.299
162.960
162.620
132.611
132.343
132.074
116.570
116.495
116.421
113.984
111.471
108.957
77.318
77.000
76.682
63.490
43.122
38.389
32.652
13.869
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

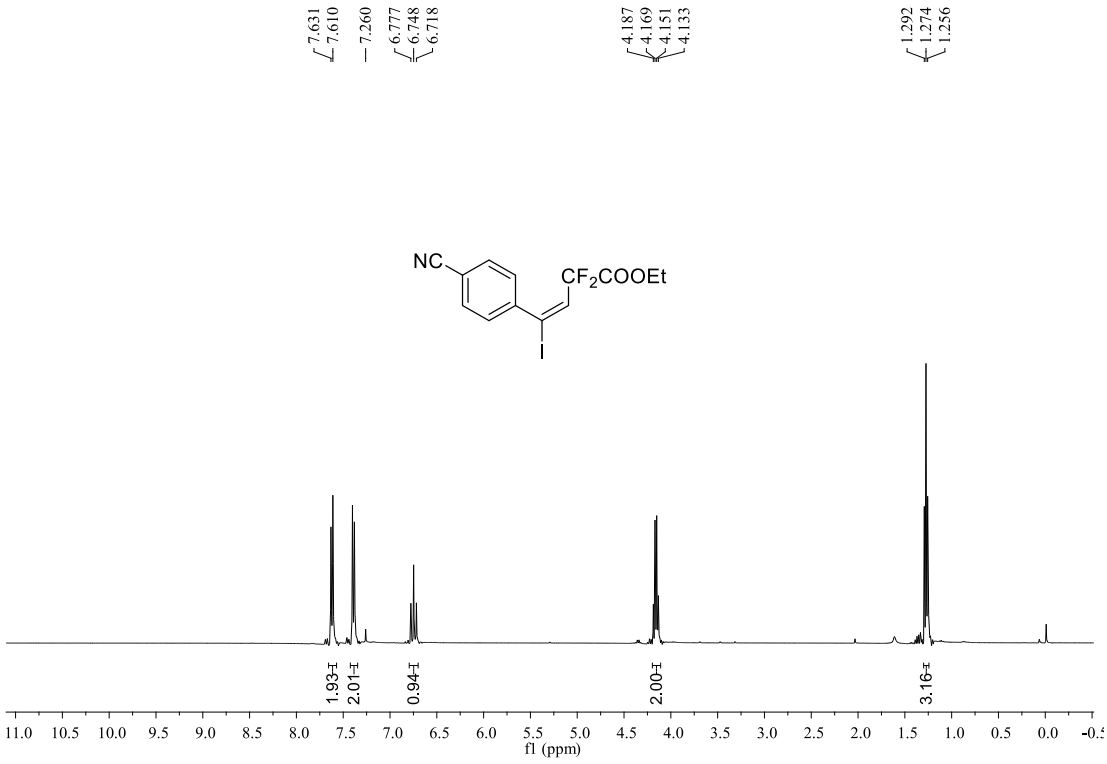
Ethyl (*E*)-4-(2-chlorophenyl)-2,2-difluoro-4-iodobut-3-enoate (5c).

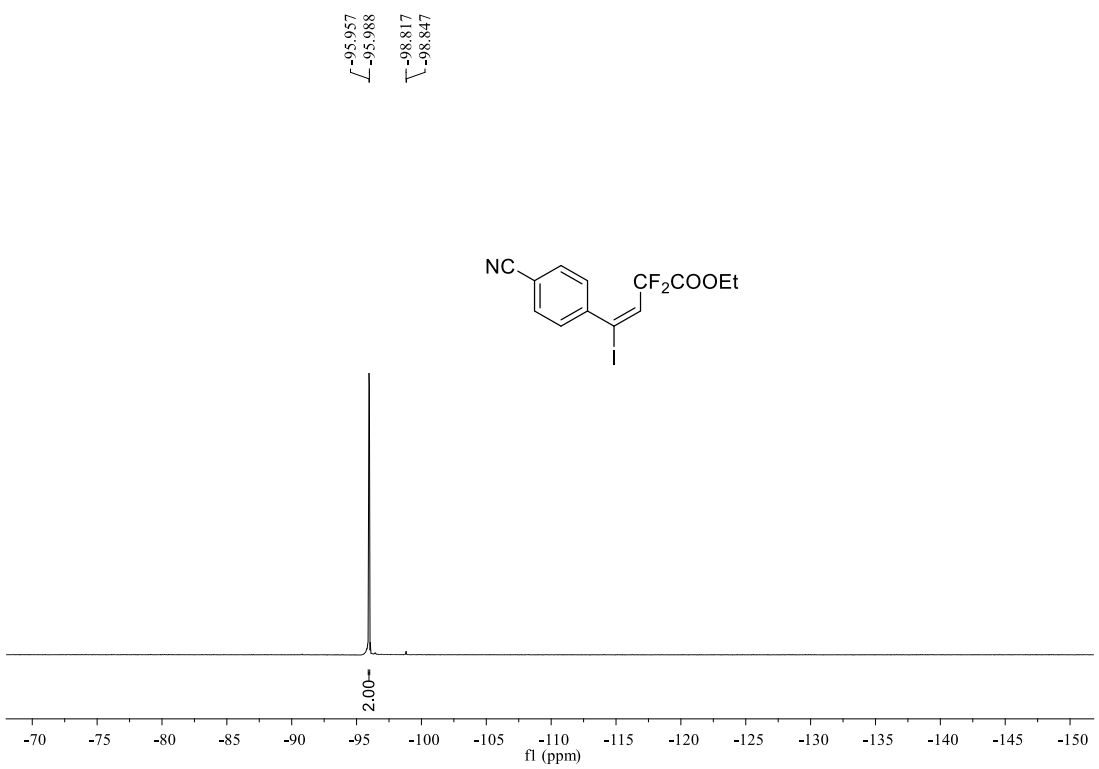


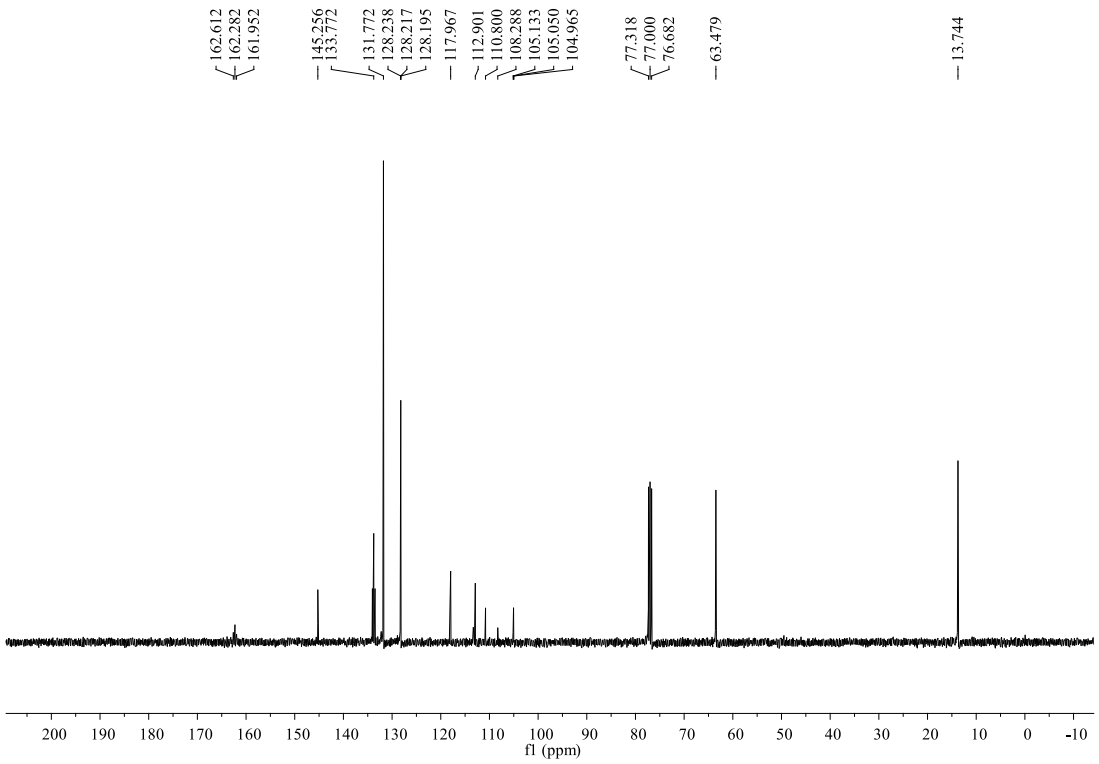




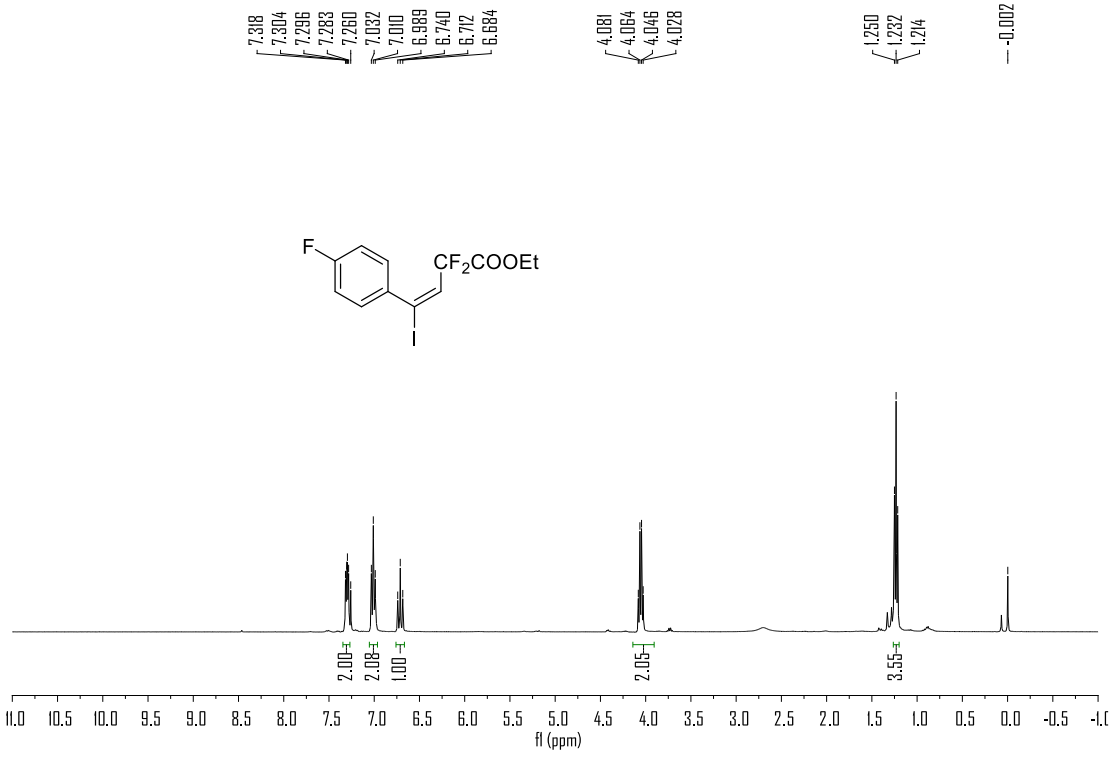
Ethyl (*E*)-4-(4-cyanophenyl)-2,2-difluoro-4-iodobut-3-enoate (5d).

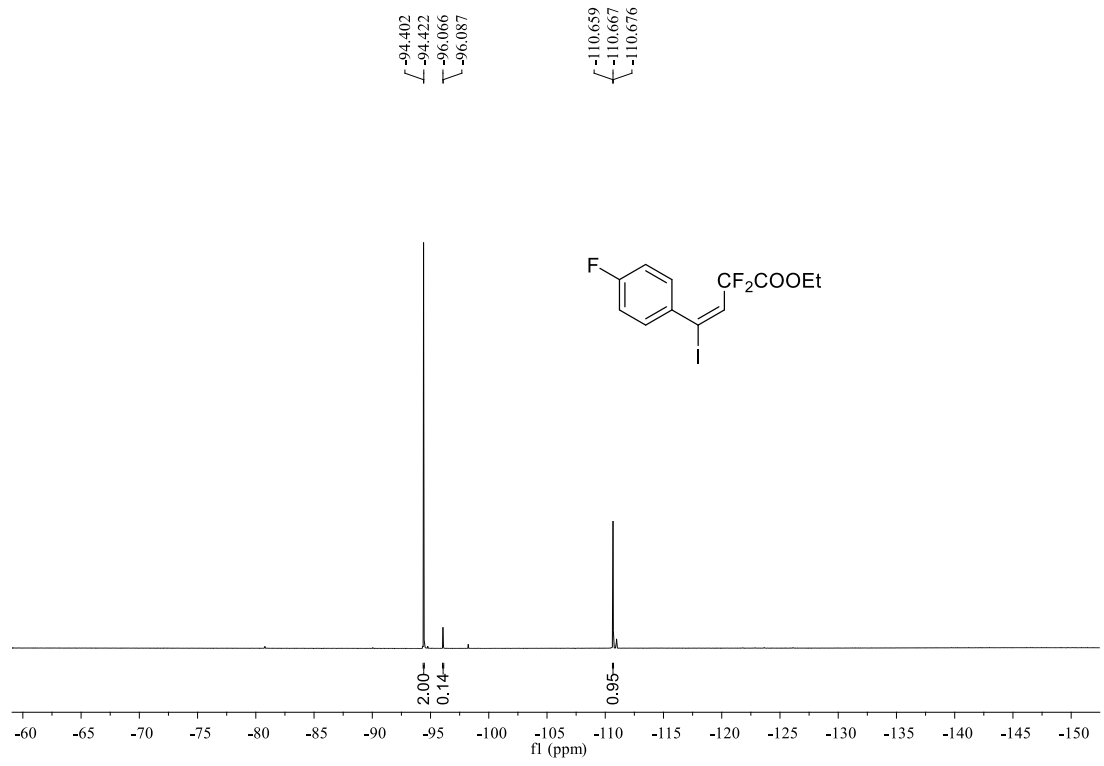


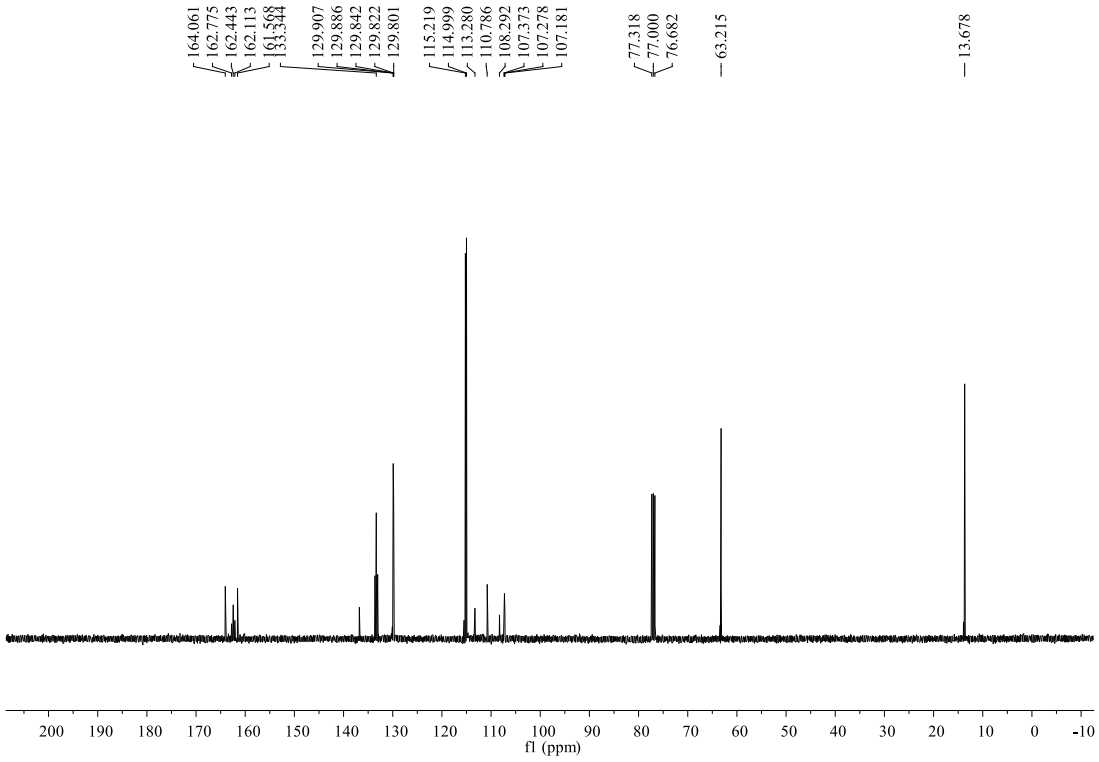

-95.957
-95.988
-98.817
-98.847
NC
CF2COOEt
I
2.00
-70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150
f1 (ppm)


162.612
162.282
161.952
145.256
133.772
131.772
128.238
128.217
128.195
117.967
112.901
110.800
108.288
105.133
105.050
104.965
77.318
77.000
76.682
63.479
13.744
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

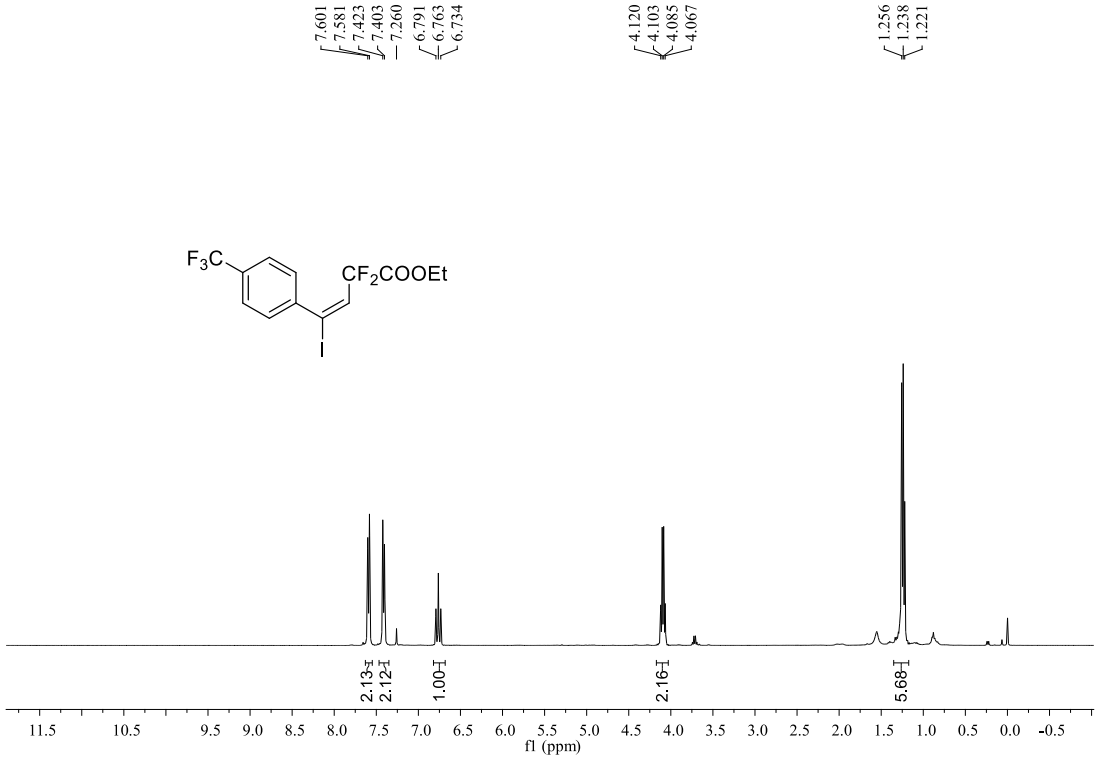
Ethyl (*E*)-2,2-difluoro-4-(4-fluorophenyl)-4-iodobut-3-enoate (5e).

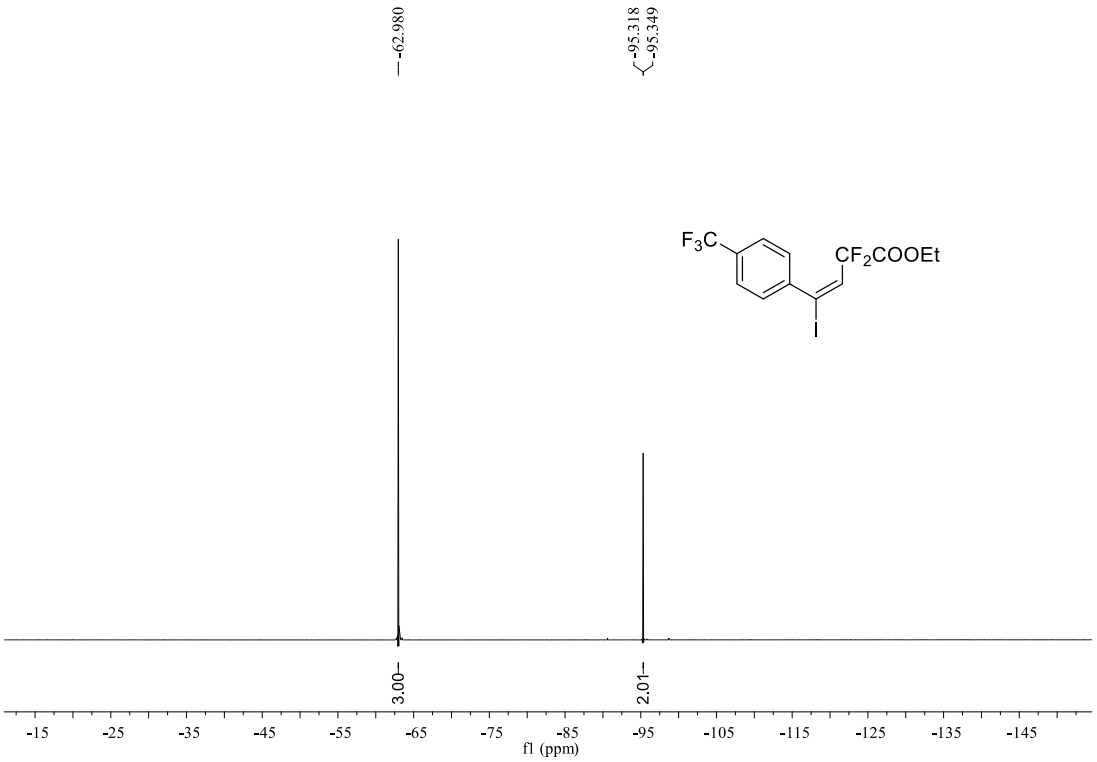


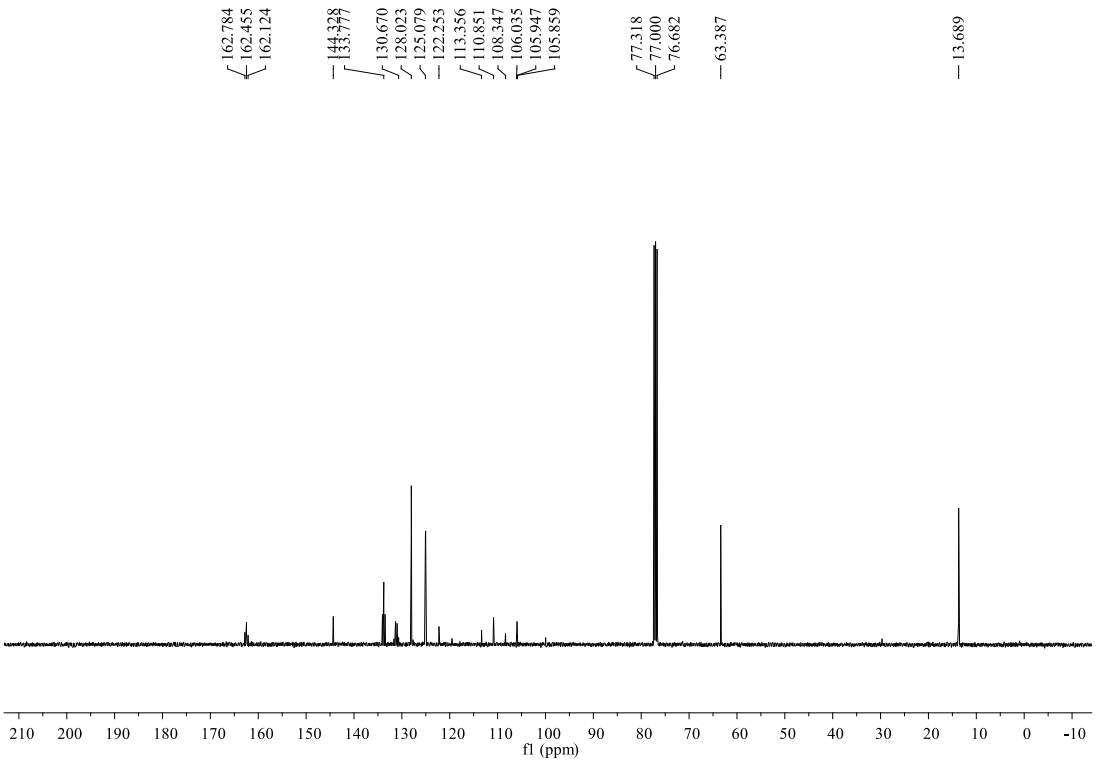




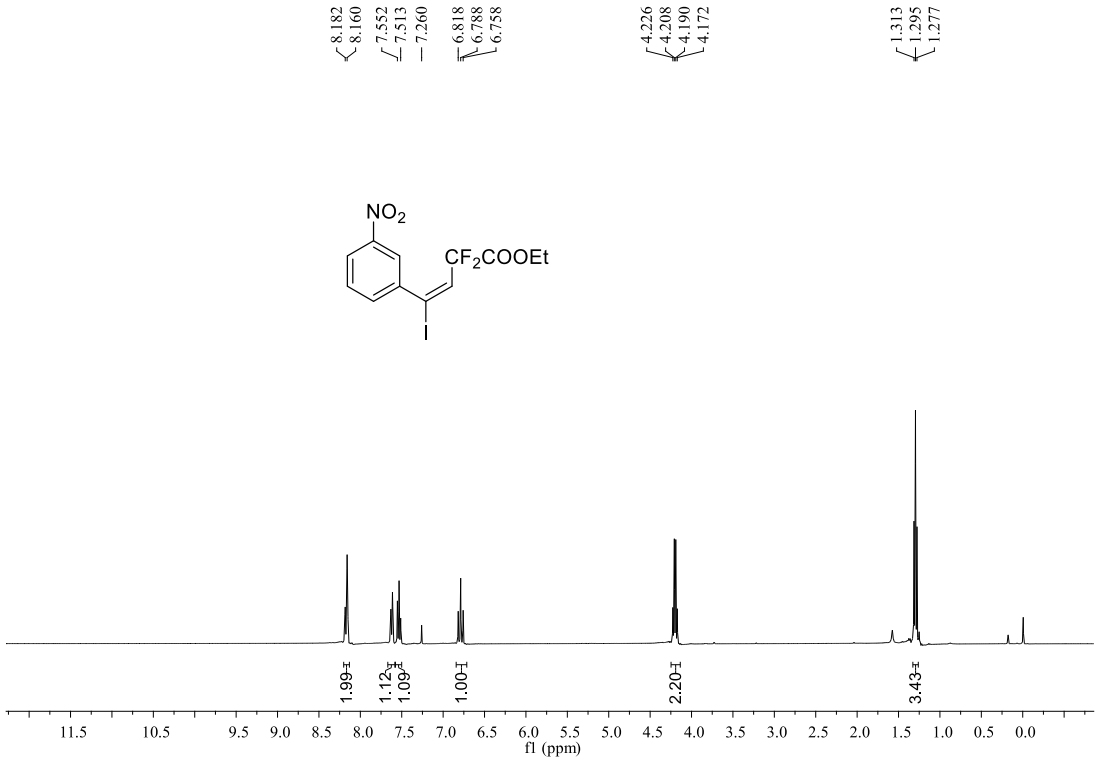
Ethyl (*E*)-2,2-difluoro-4-iodo-4-(4-(trifluoromethyl)phenyl)but-3-enoate (5f).

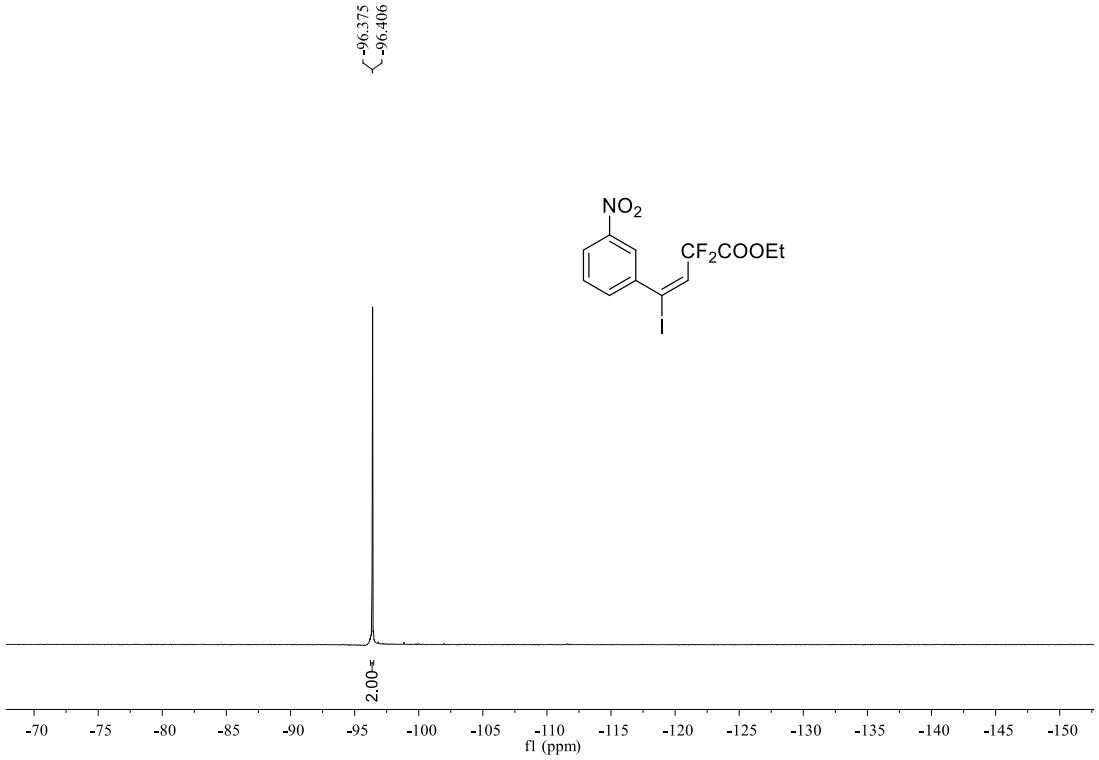


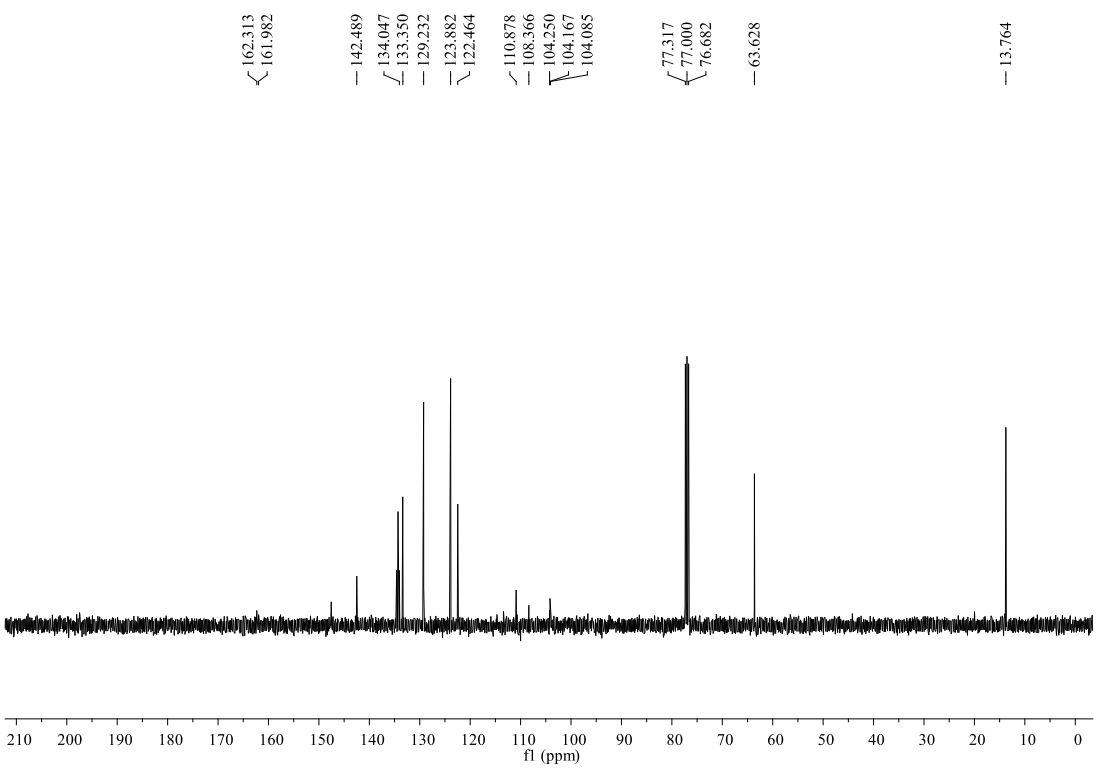

-62.980
-95.318
-95.349
F3C
CF2COOEt
I
3.00
2.01
-15 -25 -35 -45 -55 -65 -75 -85 -95 -105 -115 -125 -135 -145
f1 (ppm)


162.784
162.455
162.124
144.328
133.777
130.670
128.023
125.079
122.253
113.356
110.851
108.347
106.035
105.947
105.859
77.318
77.000
76.682
63.387
13.689
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

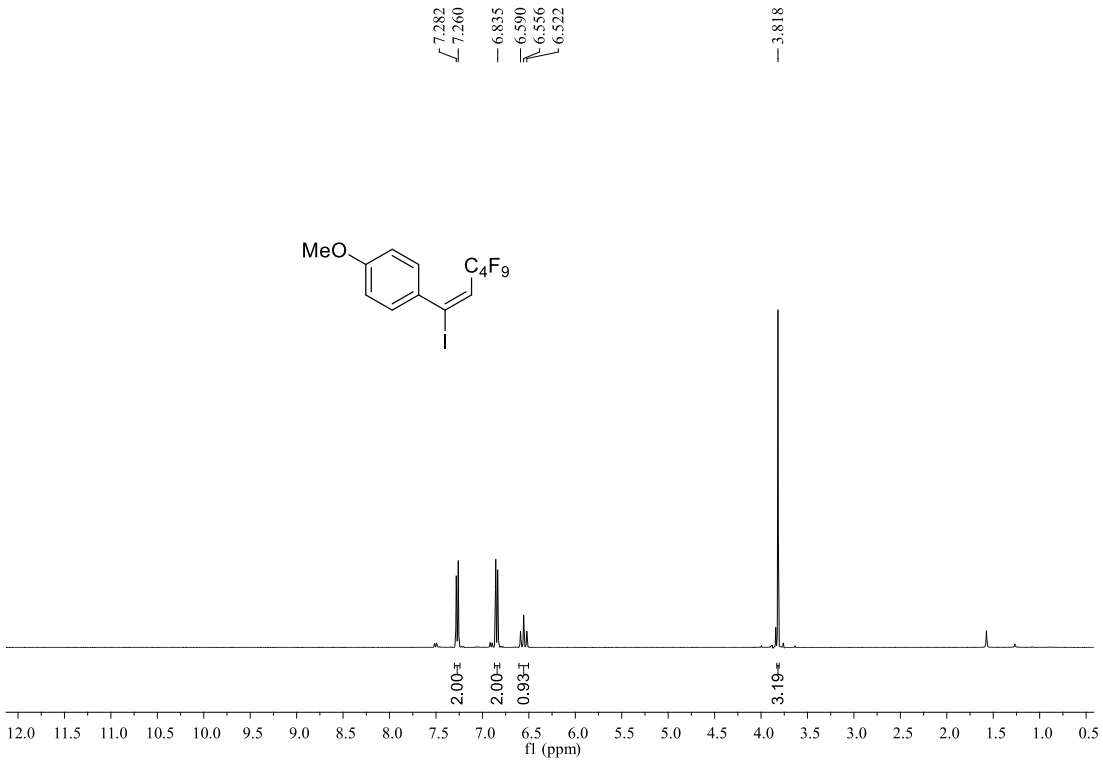
Ethyl (E)-2,2-difluoro-4-iodo-4-(3-nitrophenyl)but-3-enoateEthyl (5g).

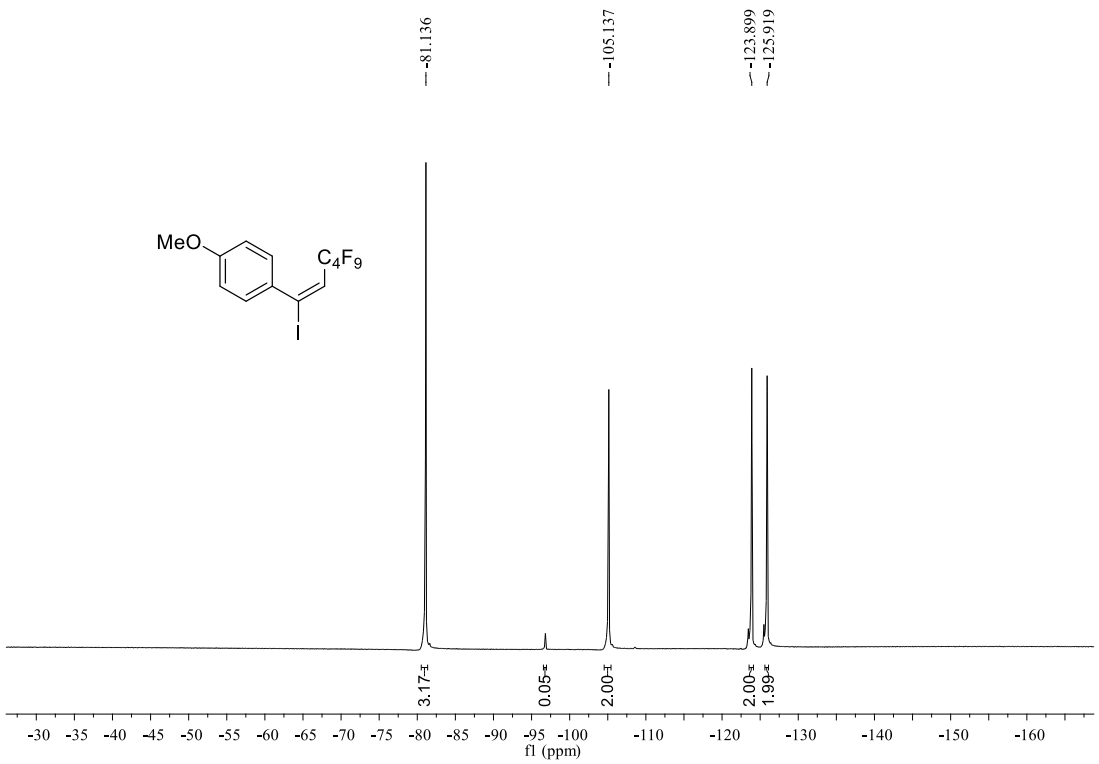


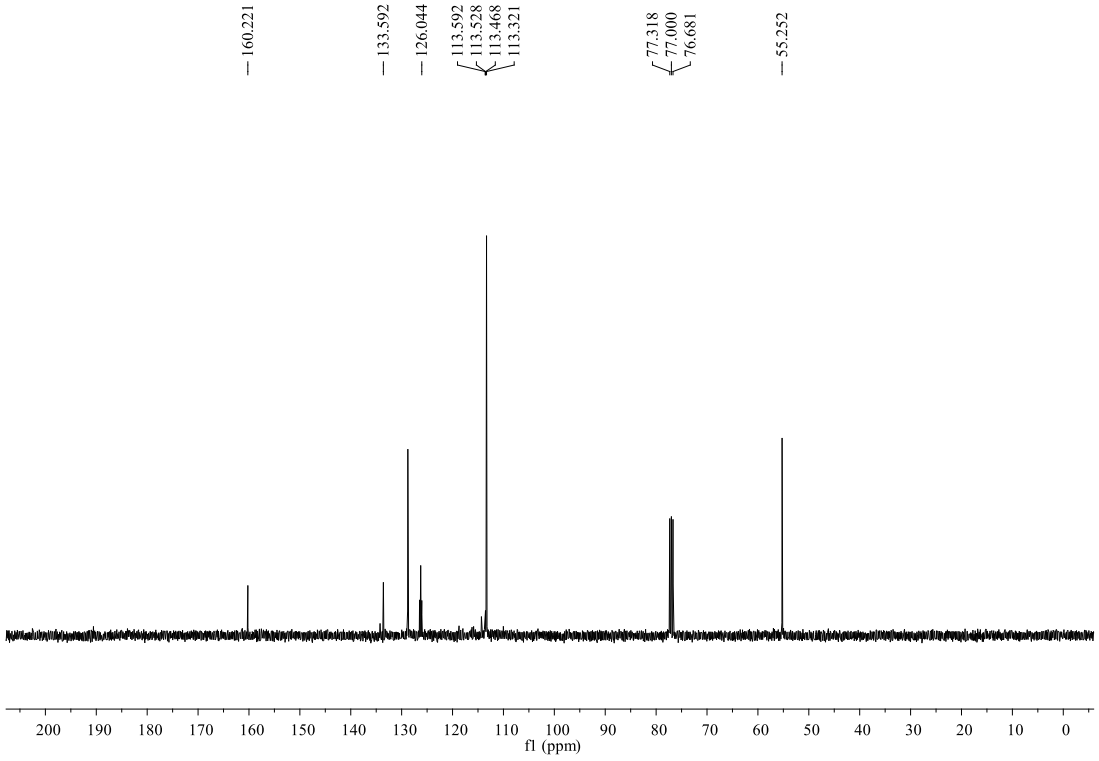




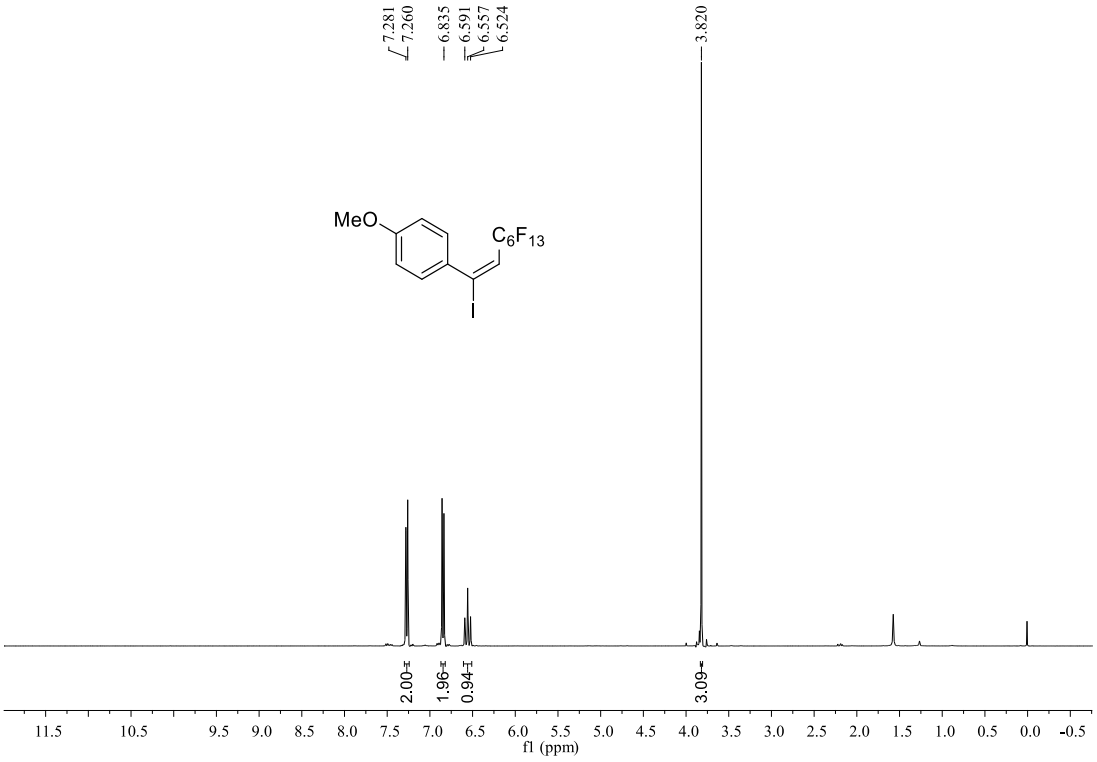
(E)-1-methoxy-4-(3,3,4,4,4,5,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (5h).

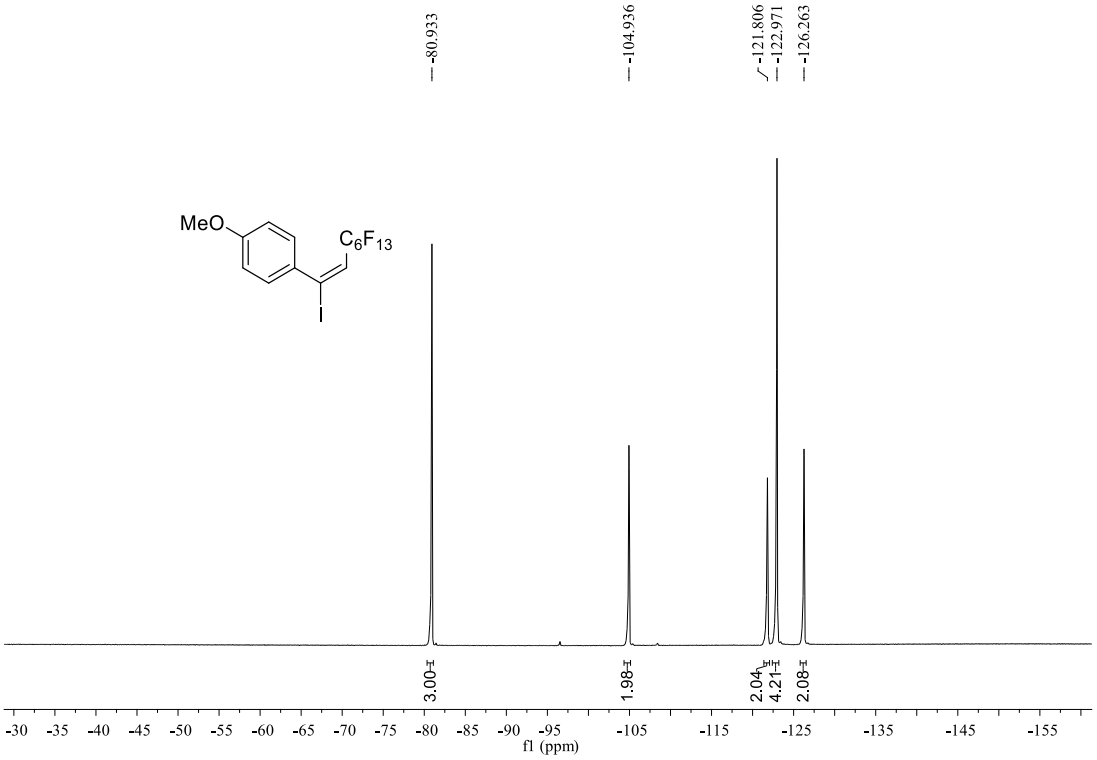


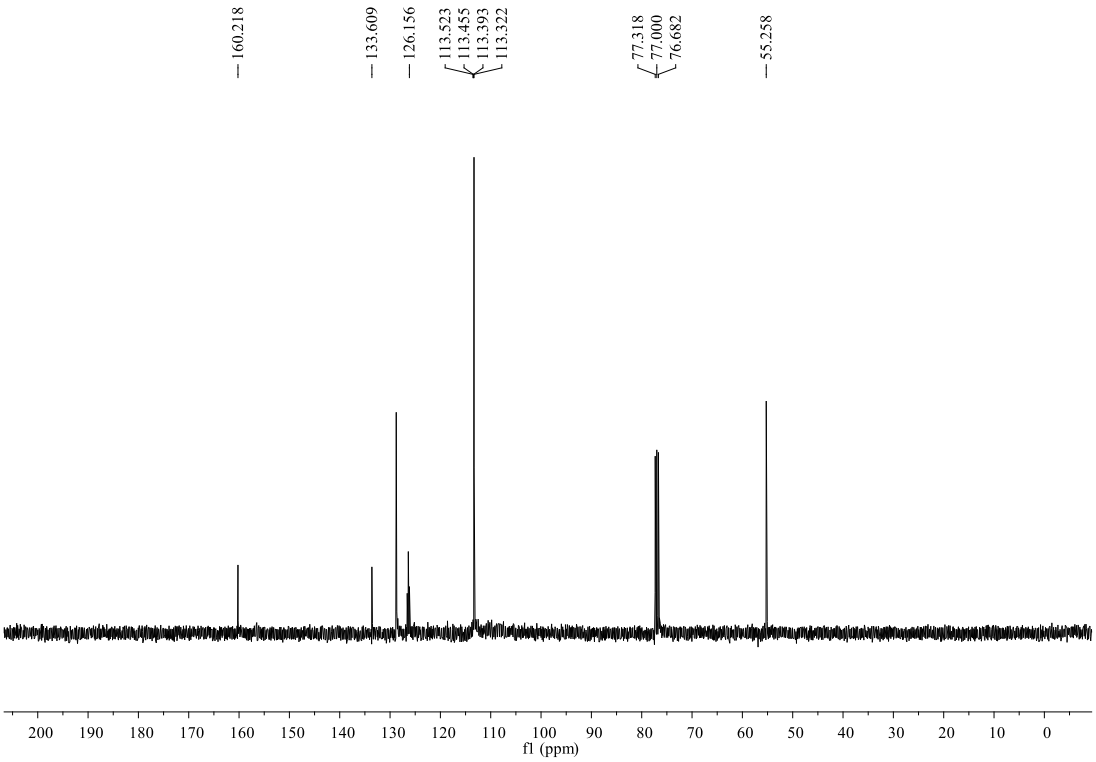

-81.136
-105.137
-123.899
-125.919
MeO
C_4F_9
I
3.17
0.05
2.00
2.00
1.99
-30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)


160.221
133.592
126.044
113.592
113.528
113.468
113.321
77.318
77.000
76.681
55.252
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

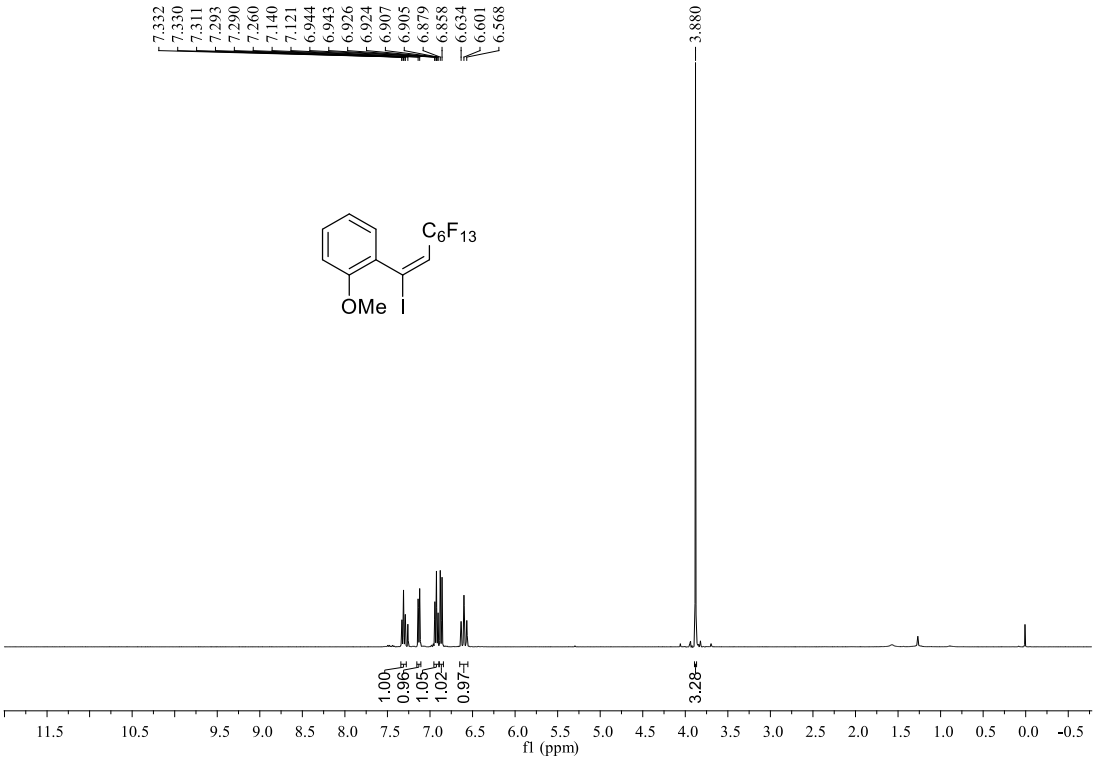
(*E*)-1-methoxy-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-iodooct-1-en-1-yl) benzene (5i).

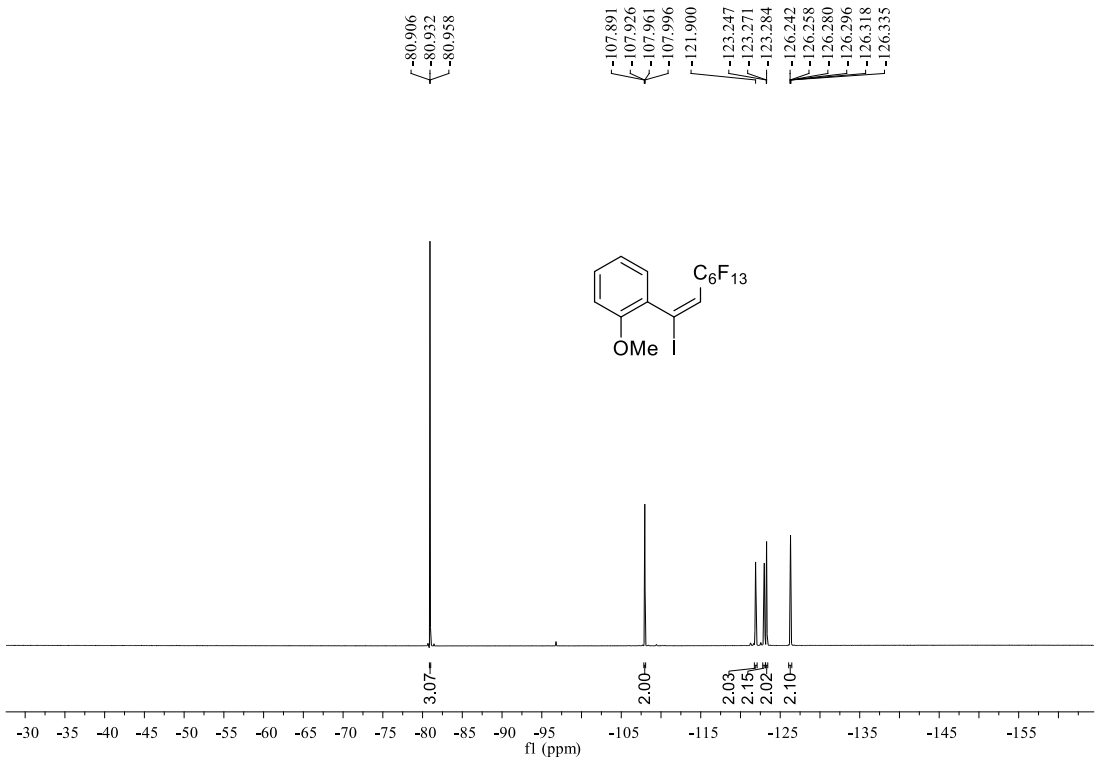


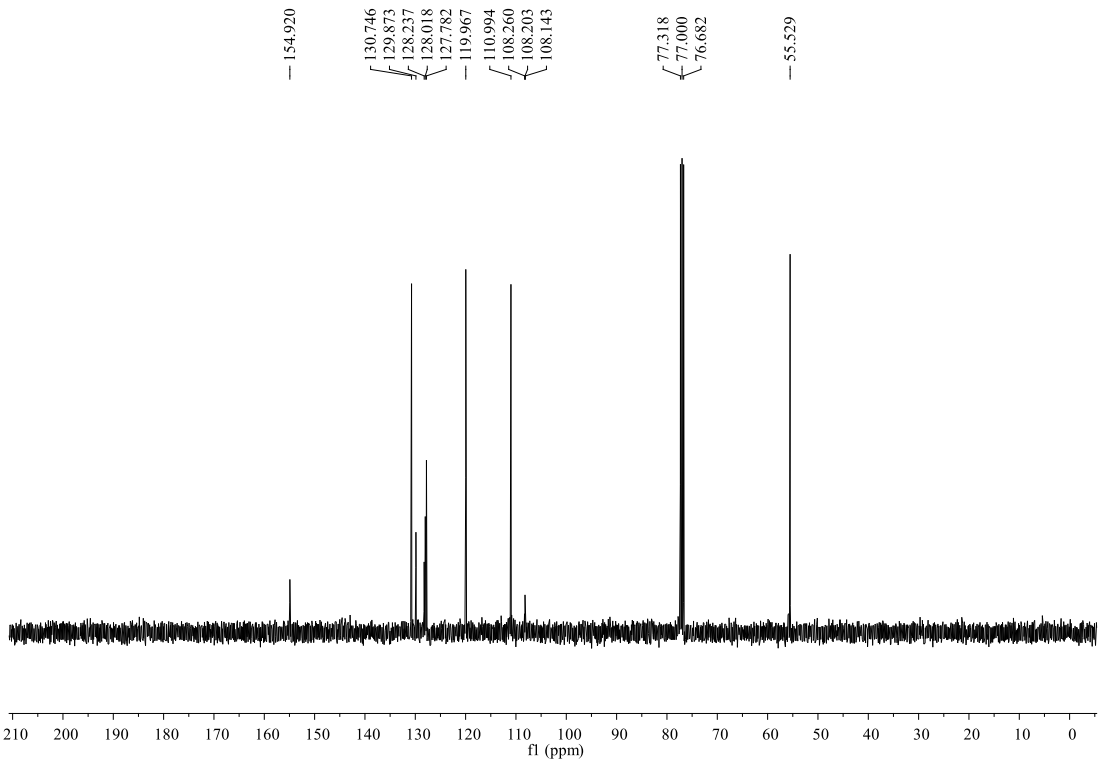




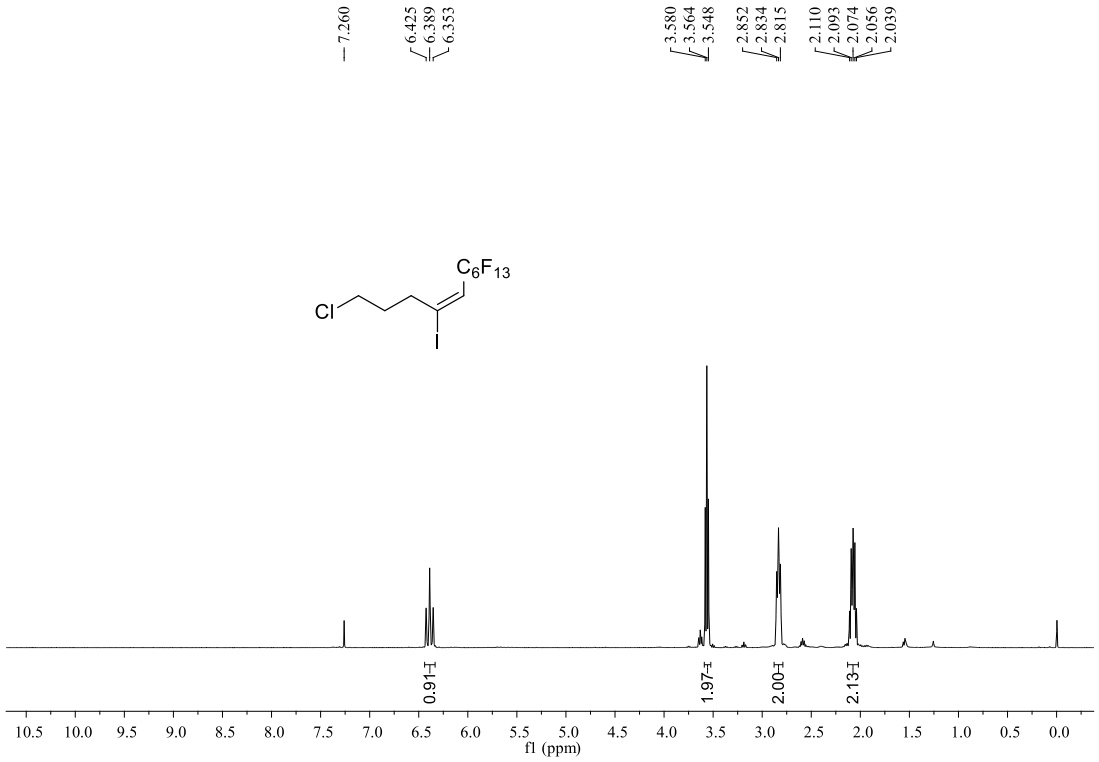
(*E*)-1-methoxy-2-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-iodooct-1-en-1-yl)benzene (5j).

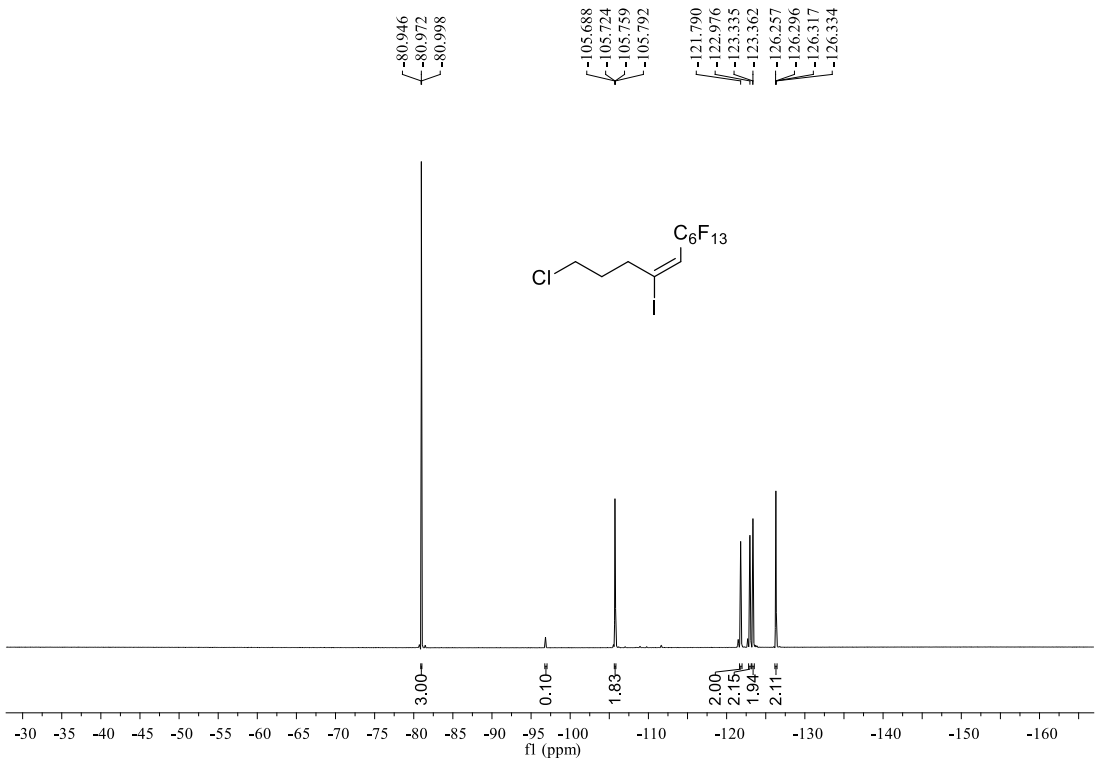


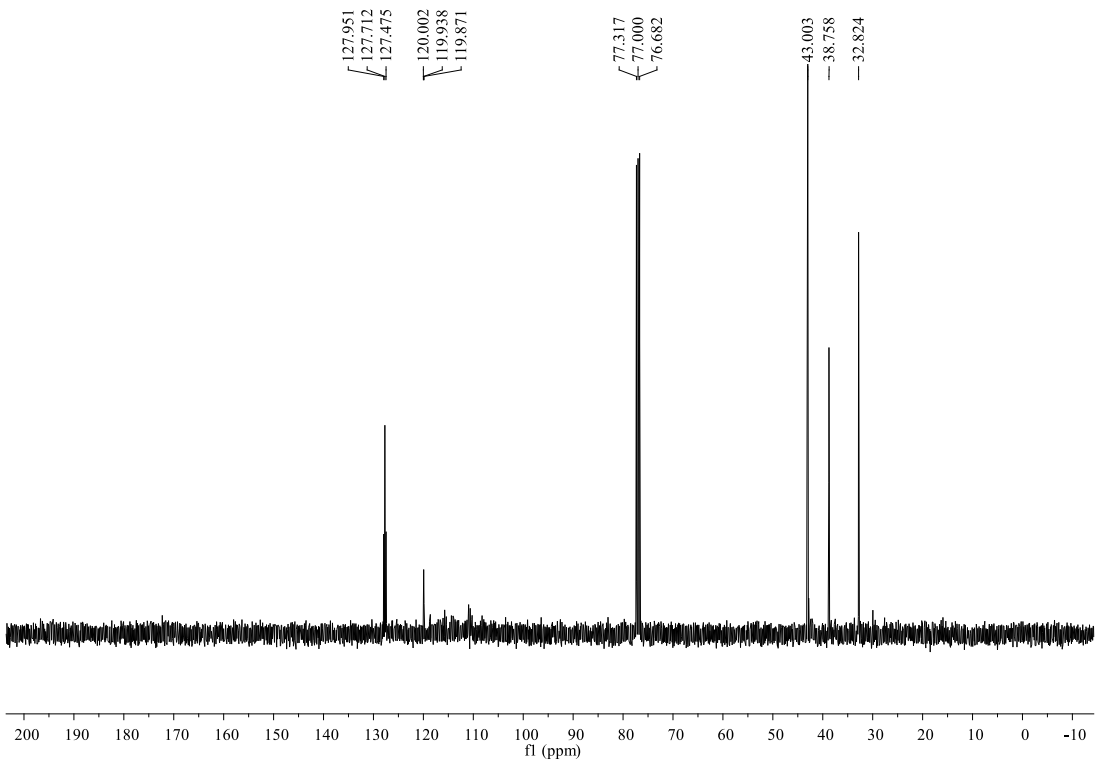

-80.906
-80.932
-80.958
-107.891
-107.926
-107.961
-107.996
-121.900
-123.247
-123.271
-123.284
-126.242
-126.258
-126.280
-126.296
-126.318
-126.335
C6F13
OMe
I
3.07
2.00
2.03
2.15
2.02
2.10
-30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125 -135 -145 -155
f1 (ppm)


154.920
130.746
129.873
128.237
128.018
127.782
119.967
110.994
108.260
108.203
108.143
77.318
77.000
76.682
55.529
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

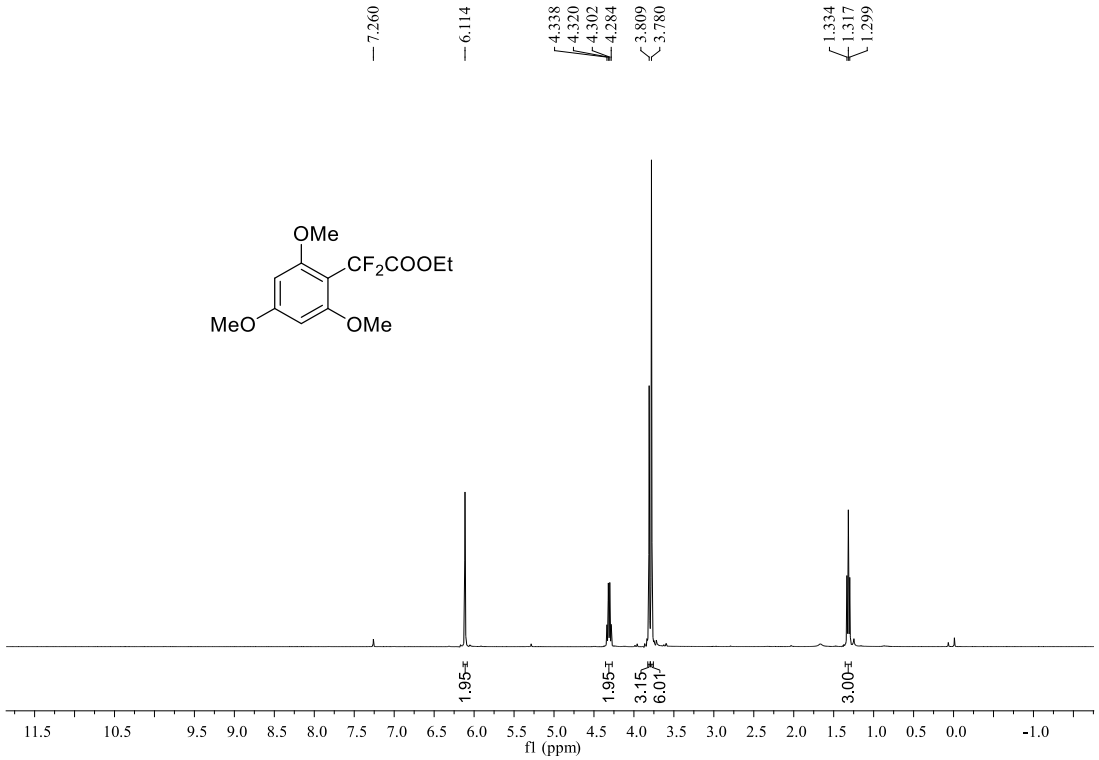
(*E*)-1-chloro-6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluoro-4-iodoundec-4-ene (5k).

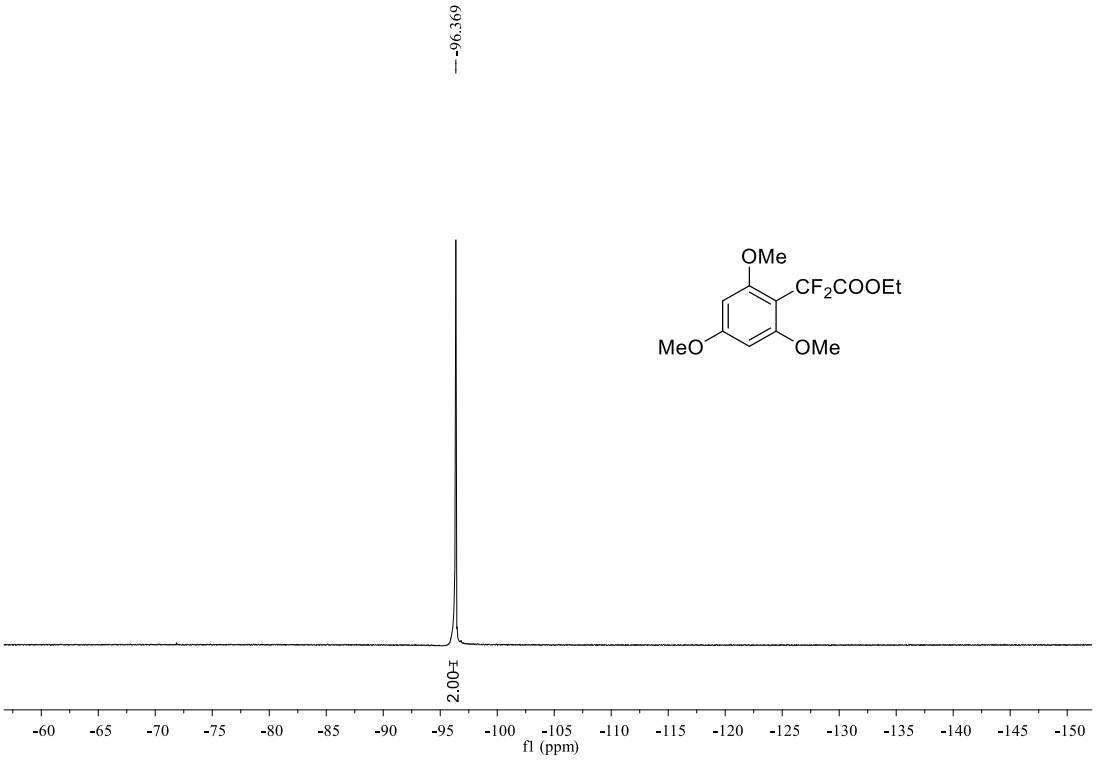


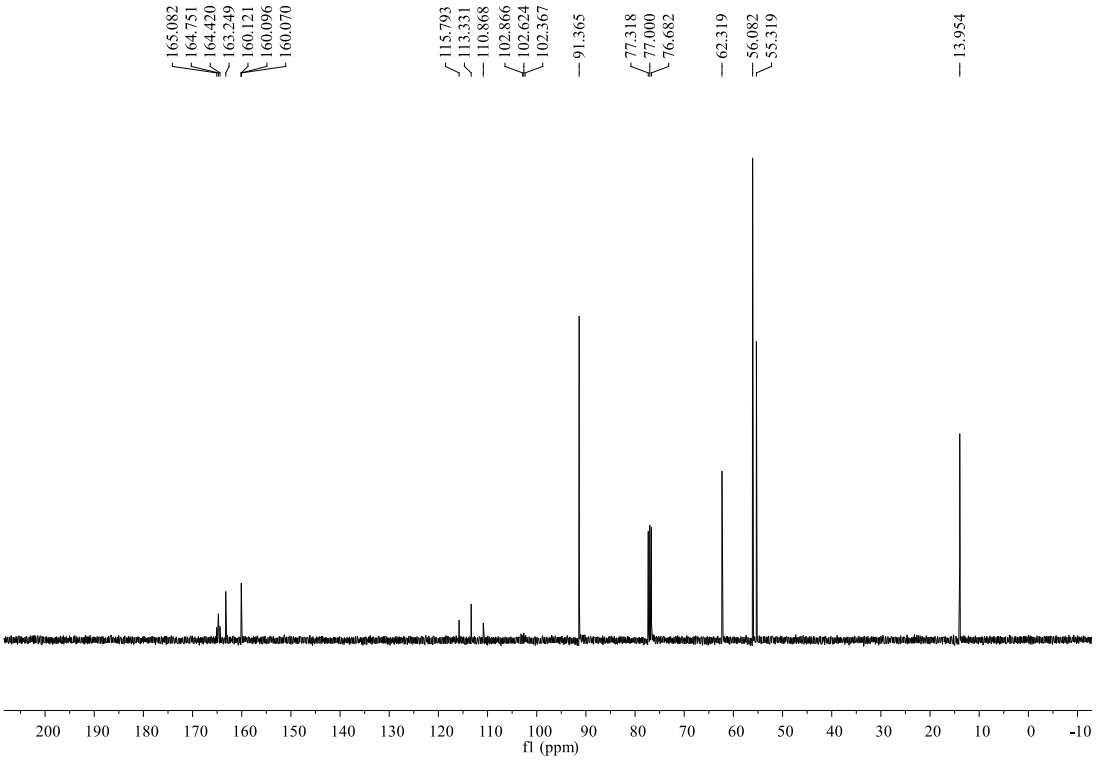




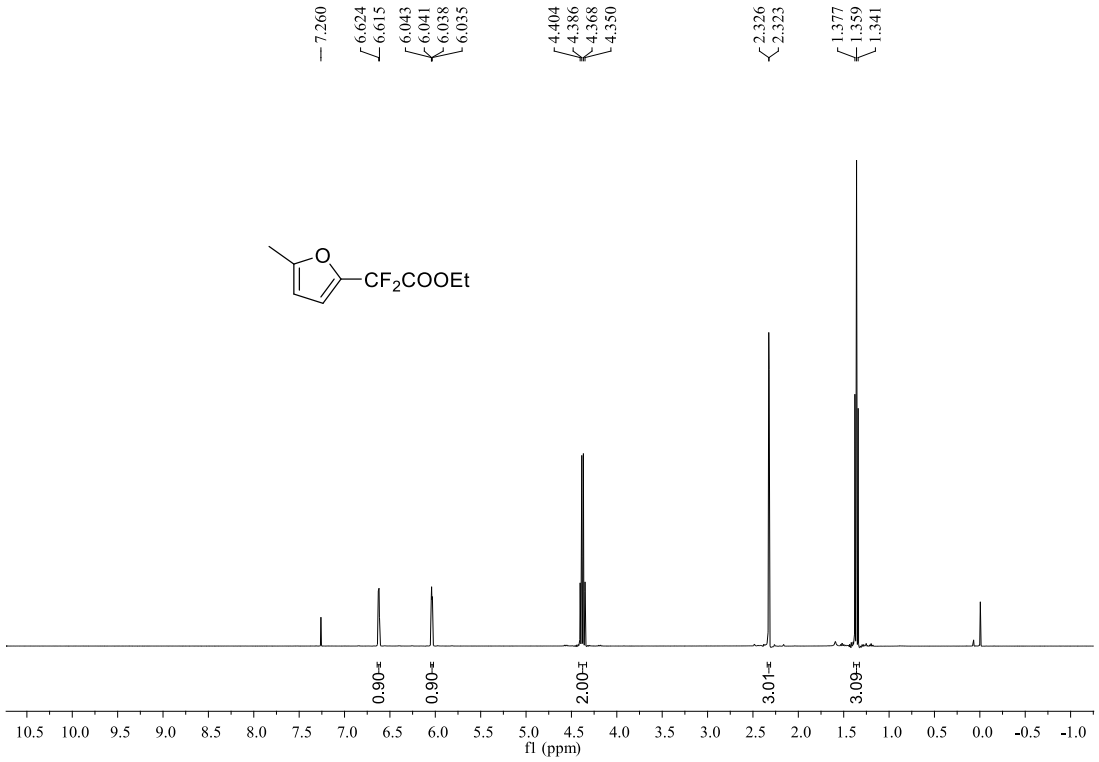
Ethyl 2,2-difluoro-2-(2,4,6-trimethoxyphenyl)acetate (7a).

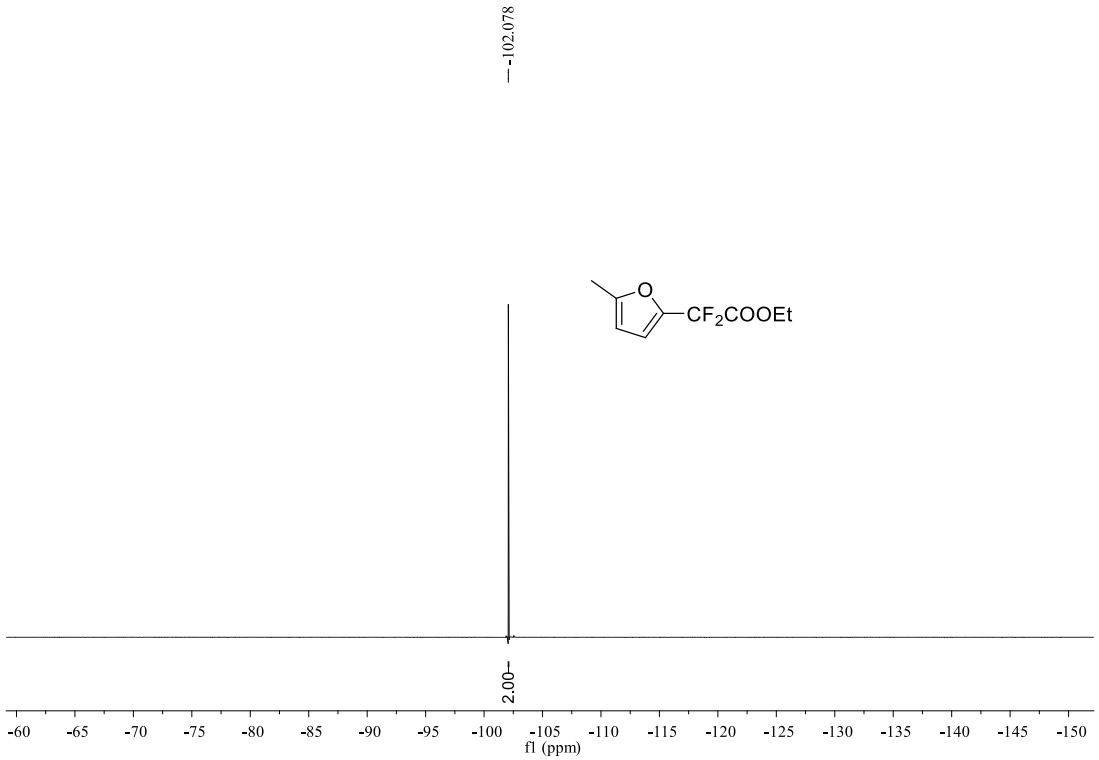


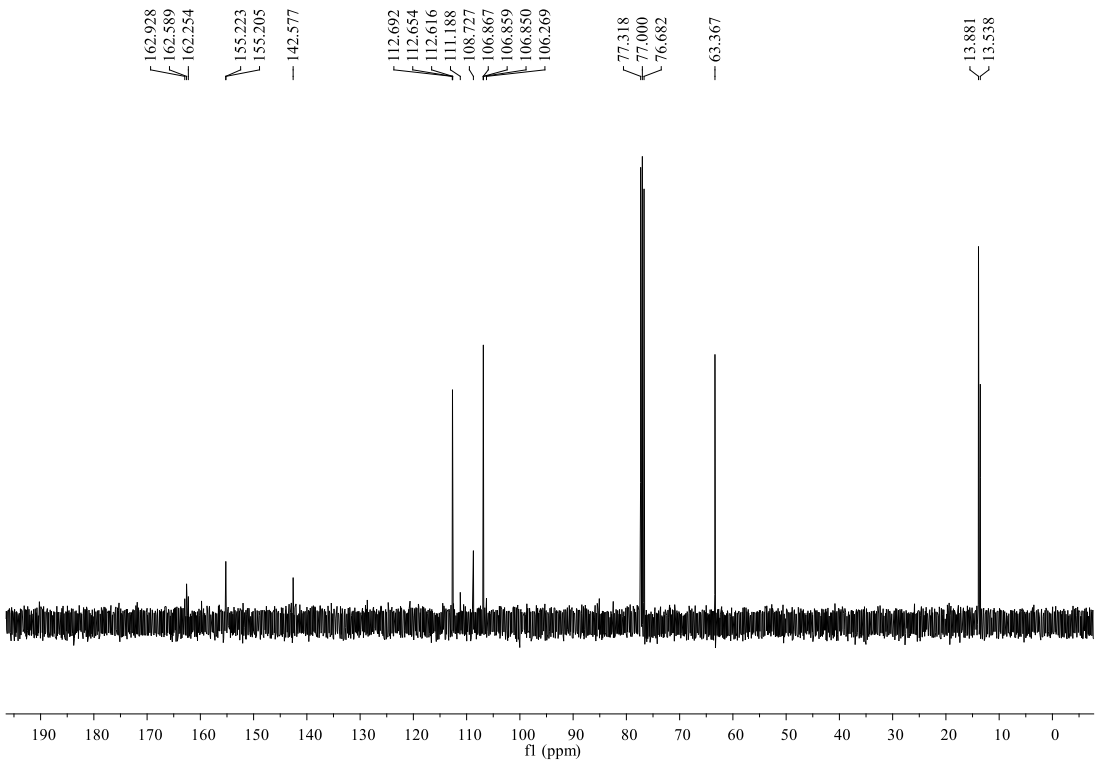

-96.369
OMe
CF2COOEt
MeO
OMe
2.00
-60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150
f1 (ppm)


165.082
164.751
164.420
163.249
160.121
160.096
160.070
115.793
113.331
110.868
102.866
102.624
102.367
91.365
77.318
77.000
76.682
62.319
56.082
55.319
13.954
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

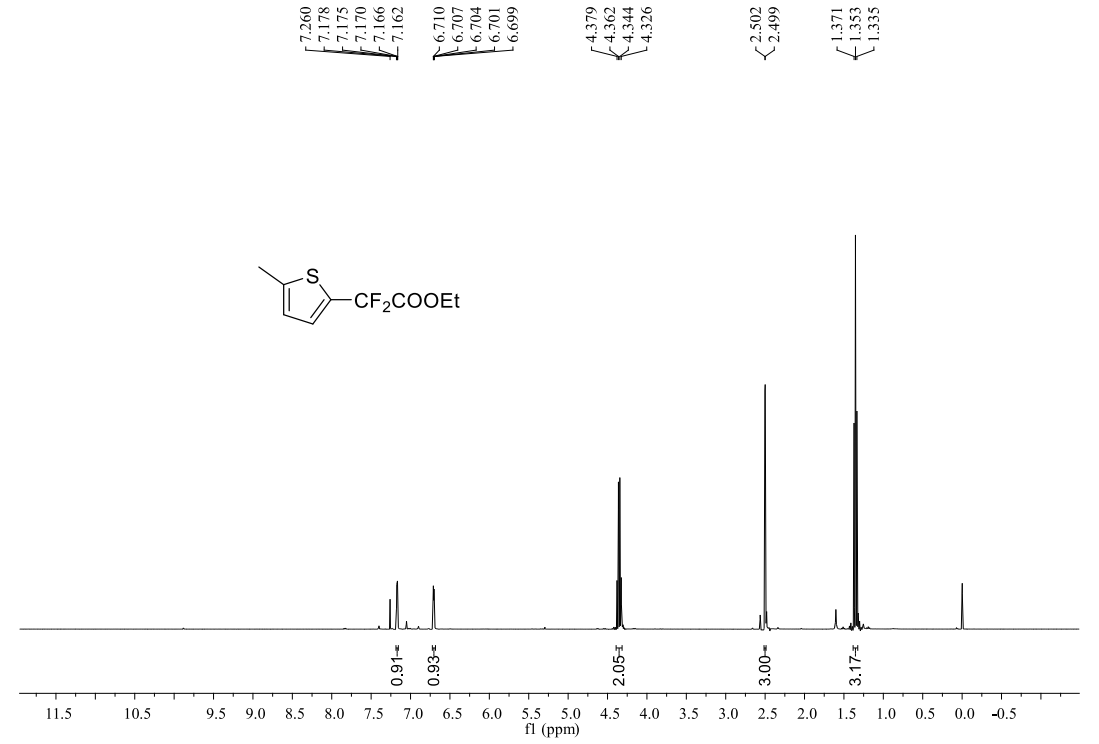
Ethyl 2,2-difluoro-2-(5-methylfuran-2-yl)acetate (7b).

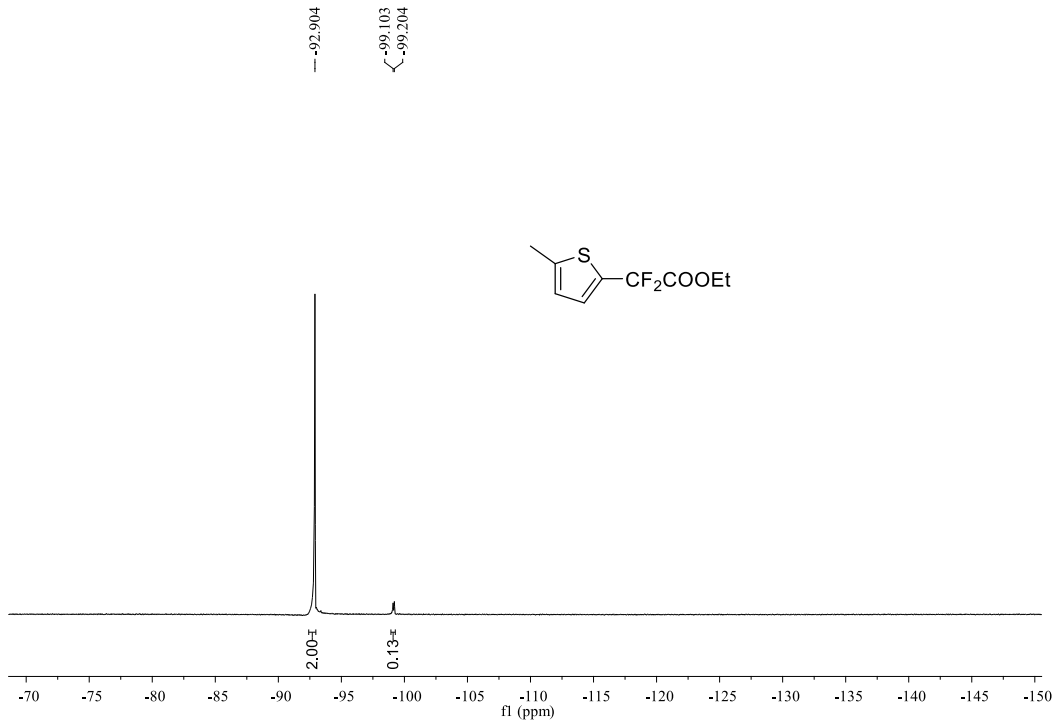


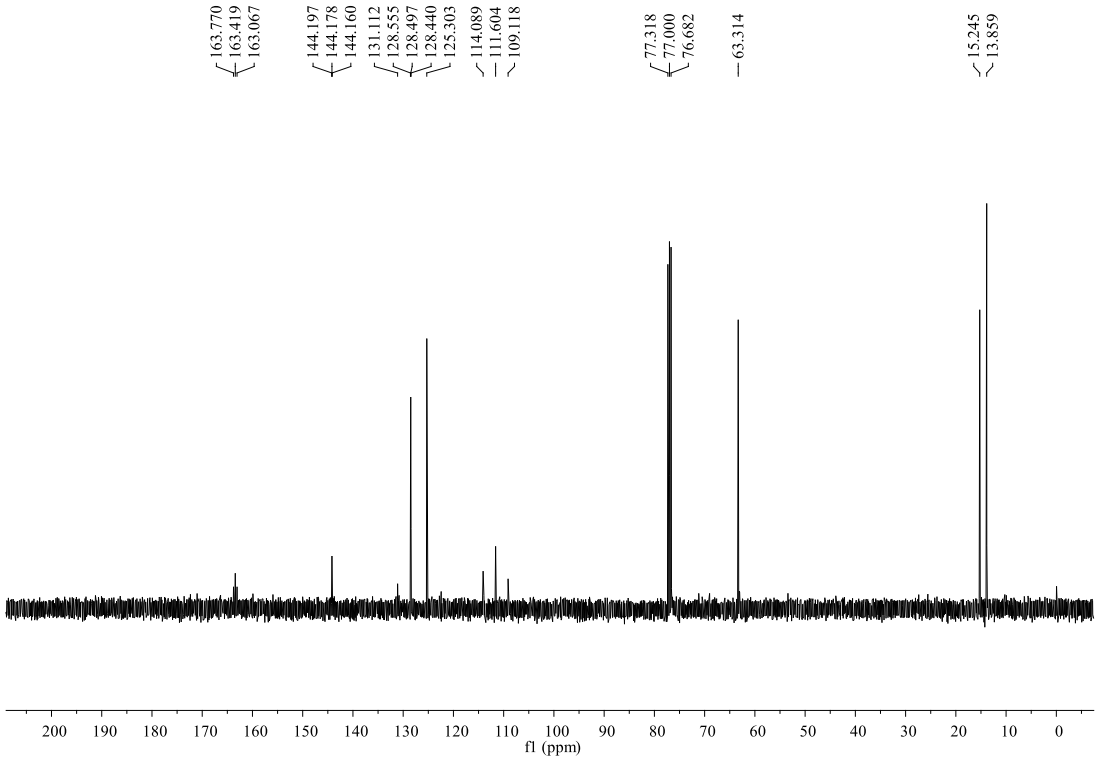




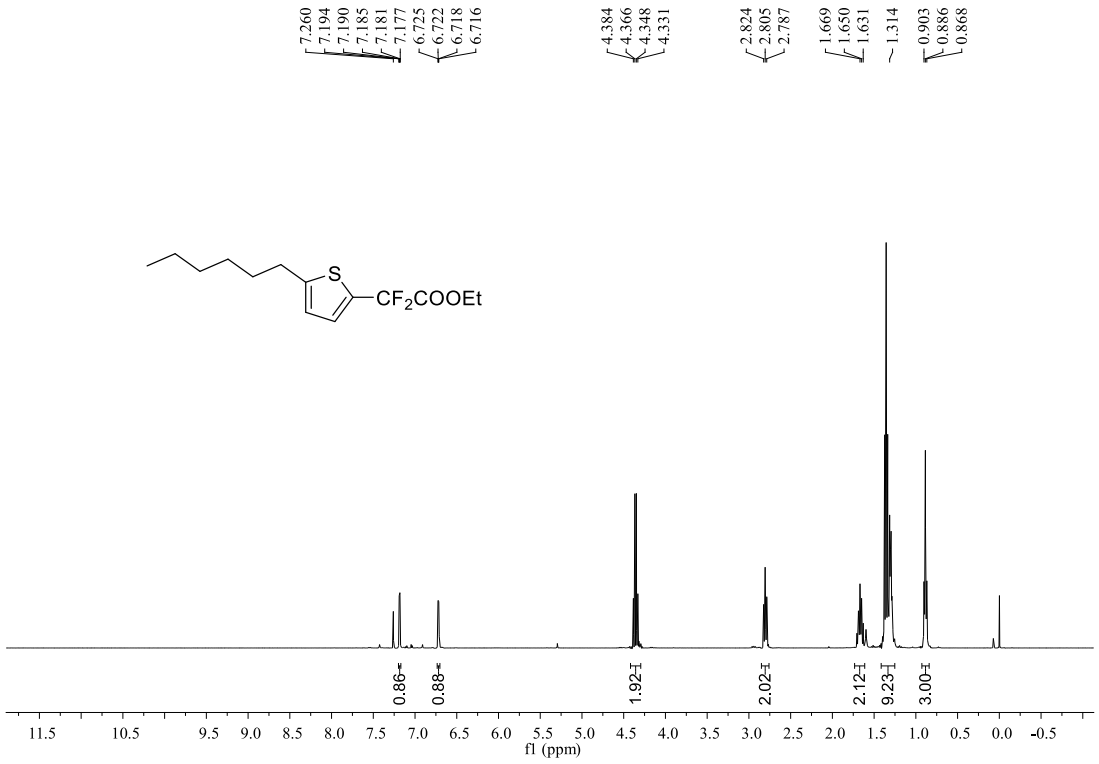
Ethyl 2,2-difluoro-2-(5-methylthiophen-2-yl)acetate (7c).

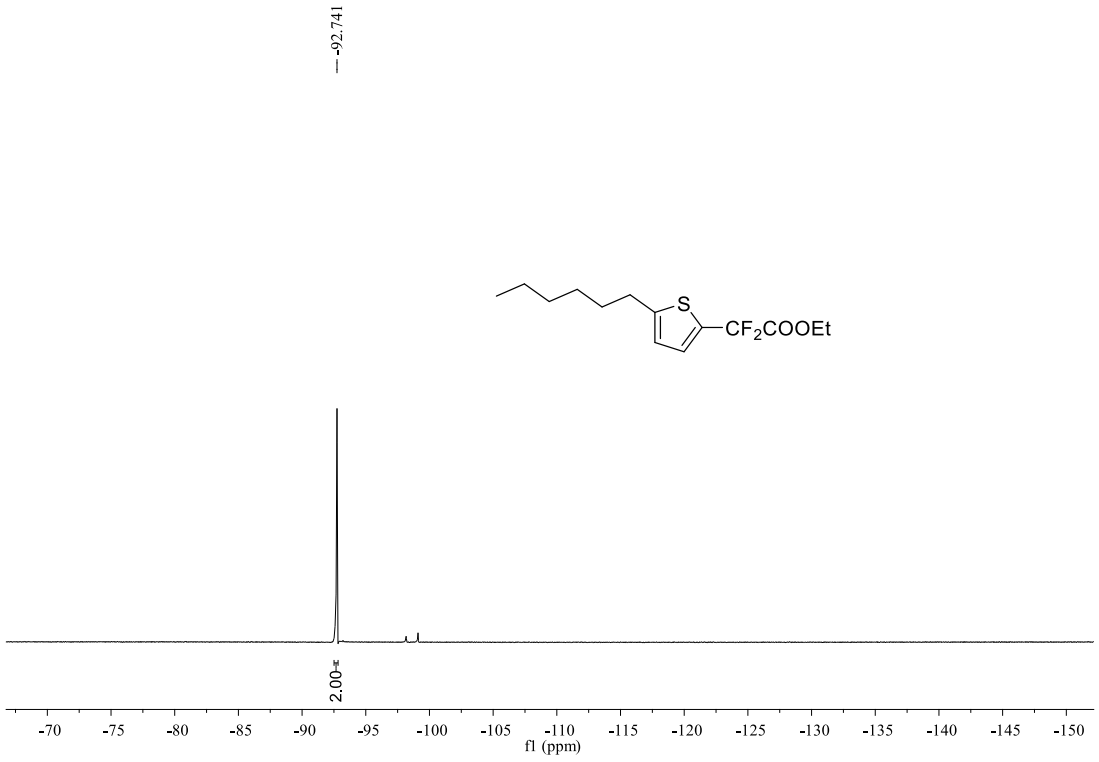


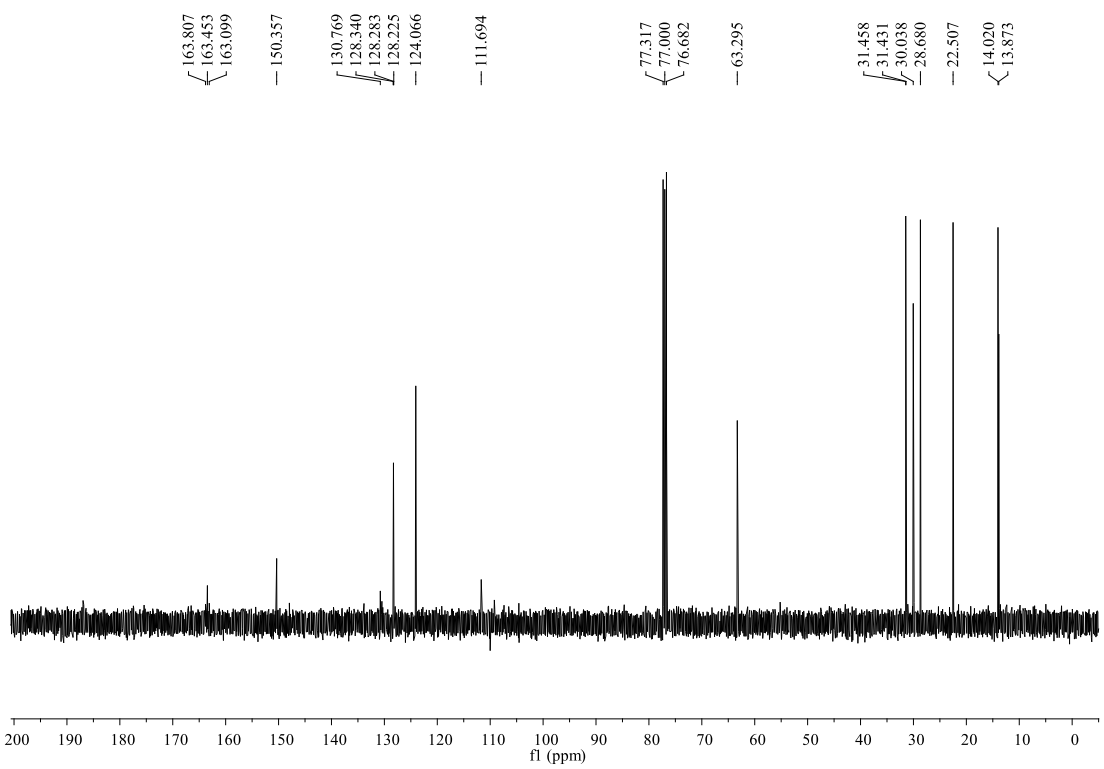

-92.904
-99.103
-99.204
S
CF2COOEt
2.00
0.13
-70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150
f1 (ppm)


163.770
163.419
163.067
144.197
144.178
144.160
131.112
128.555
128.497
128.440
125.303
114.089
111.604
109.118
77.318
77.000
76.682
63.314
15.245
13.859
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

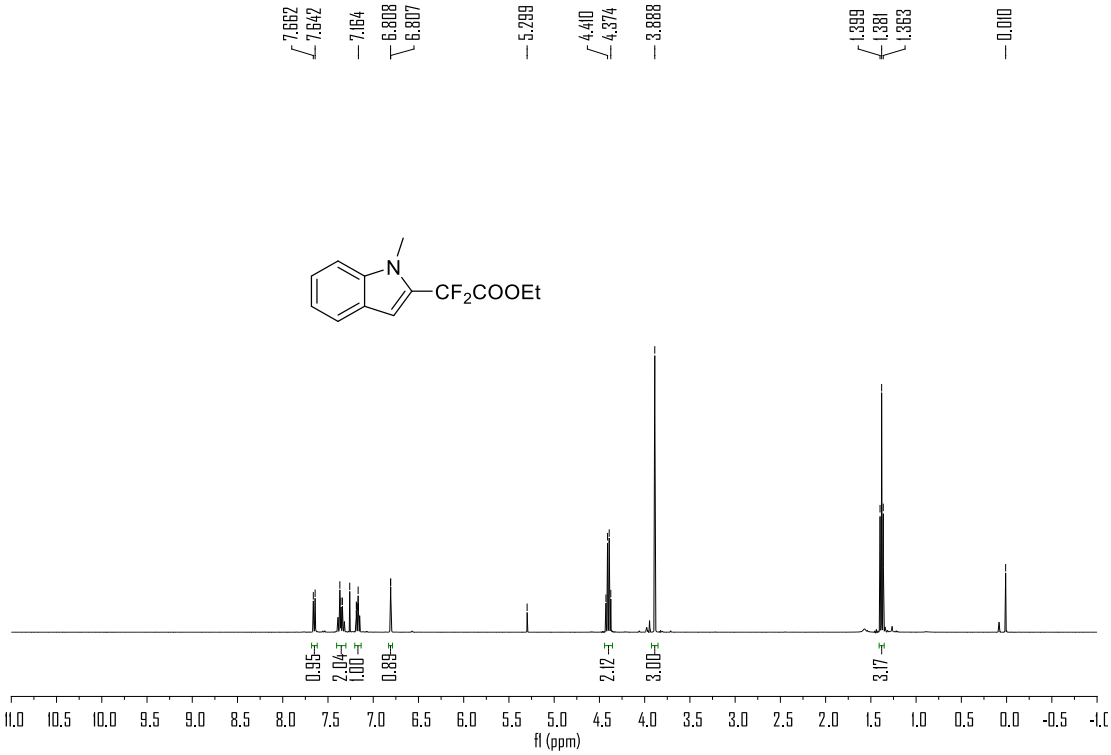
Ethyl 2,2-difluoro-2-(5-hexylthiophen-2-yl)acetate (7d).

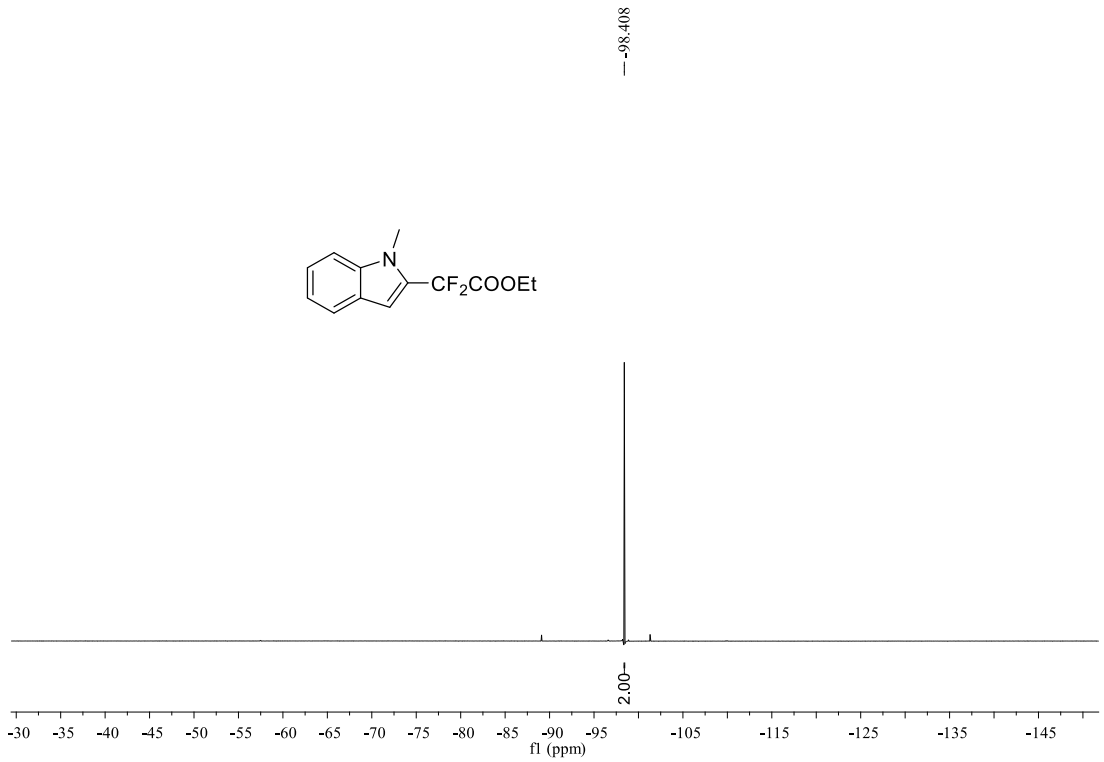


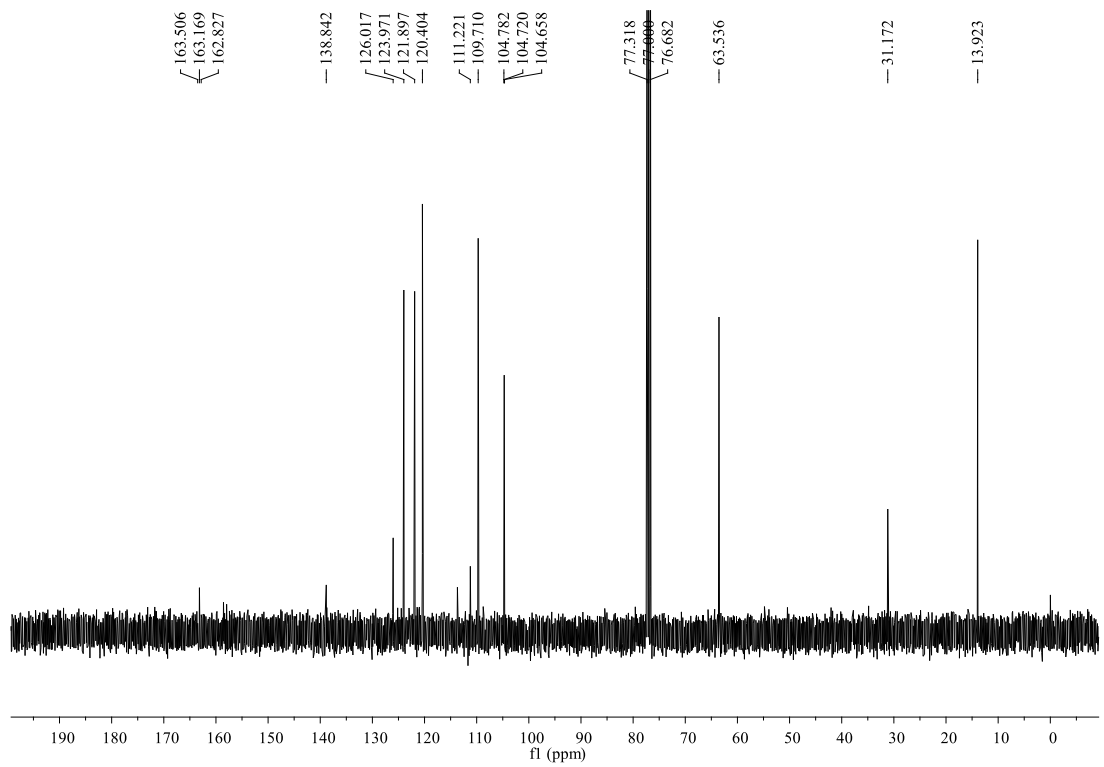




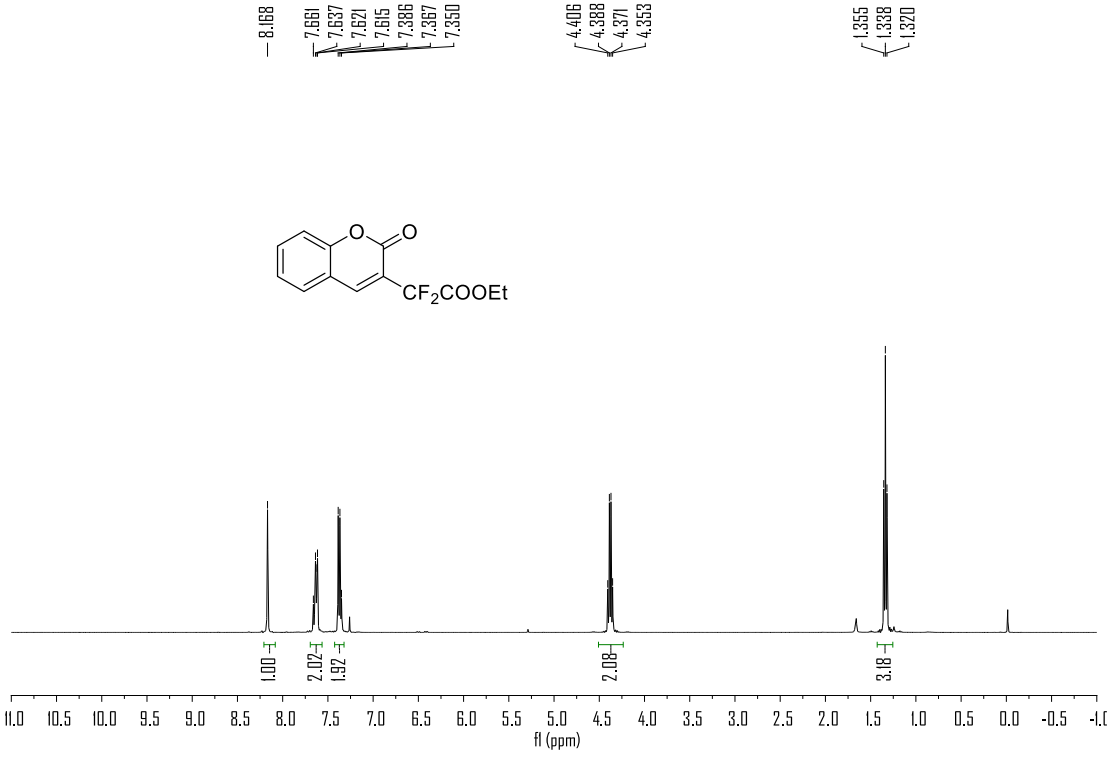
Ethyl 2,2-difluoro-2-(1-methyl-1*H*-indol-2-yl)acetate (7e).

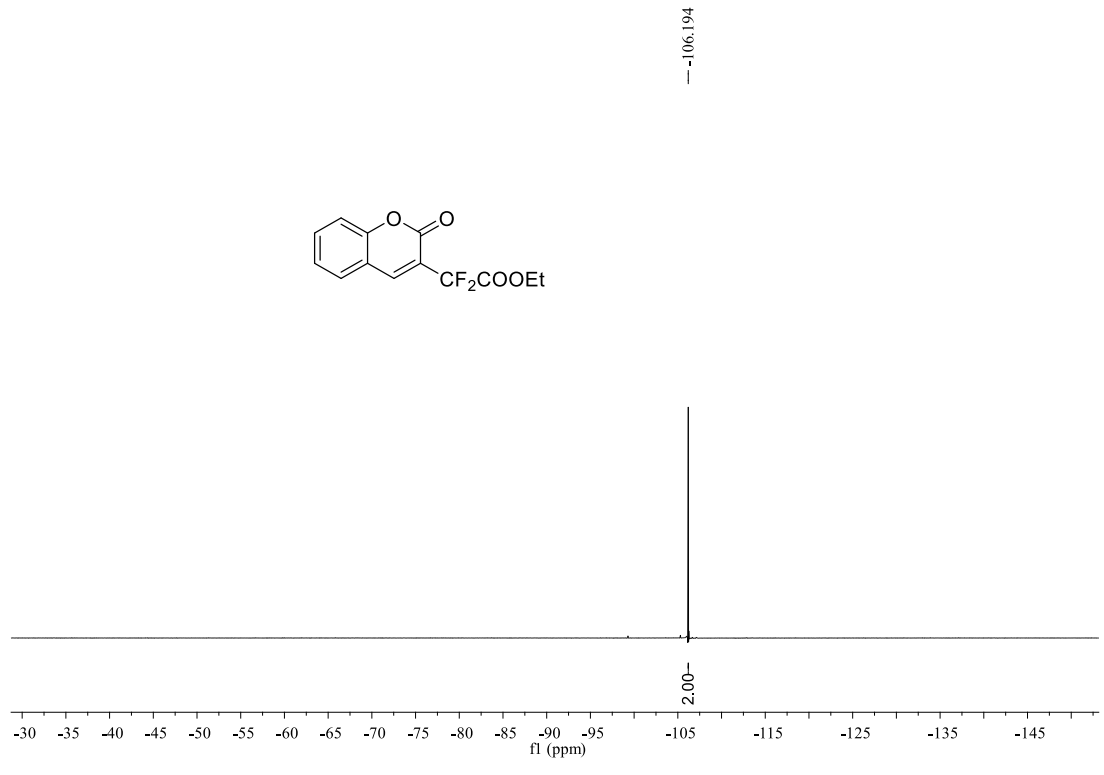


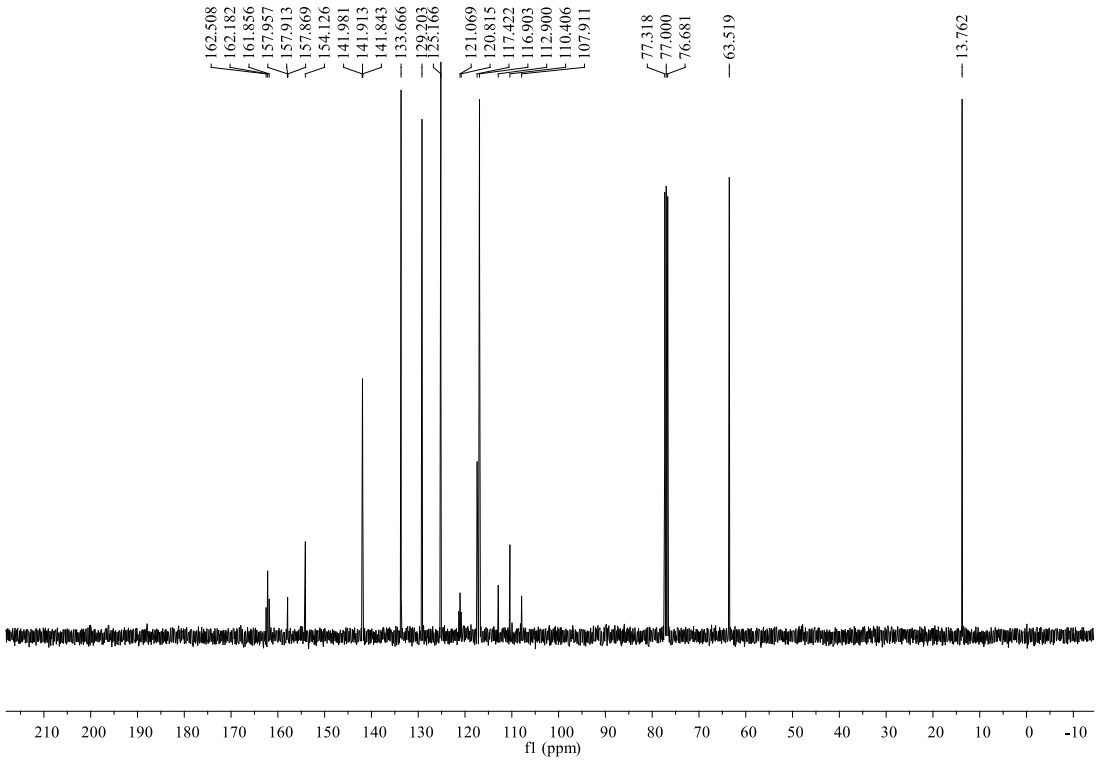

-98.408
N
CF2COOEt
2.00
-30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125 -135 -145
f1 (ppm)


163.506
163.169
162.827
138.842
126.017
123.971
121.897
120.404
111.221
109.710
104.782
104.720
104.658
77.318
77.000
76.682
63.536
31.172
13.923
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

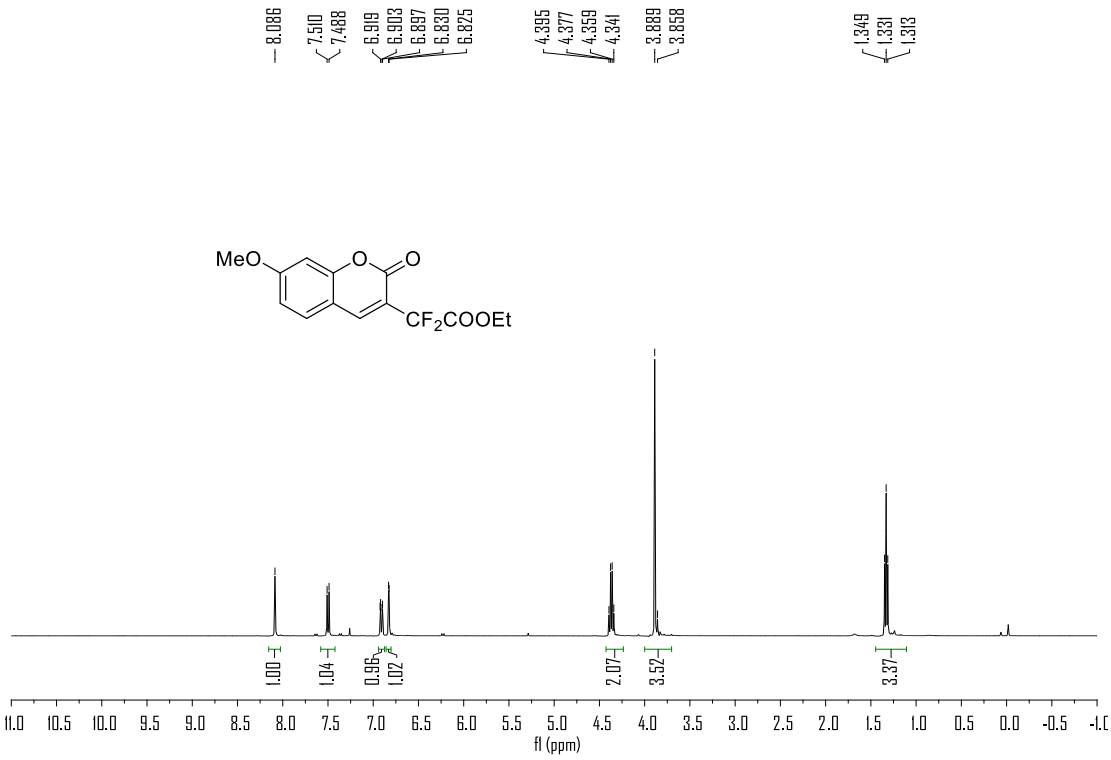
Ethyl 2,2-difluoro-2-(2-oxo-2H-chromen-3-yl)acetate (7f).

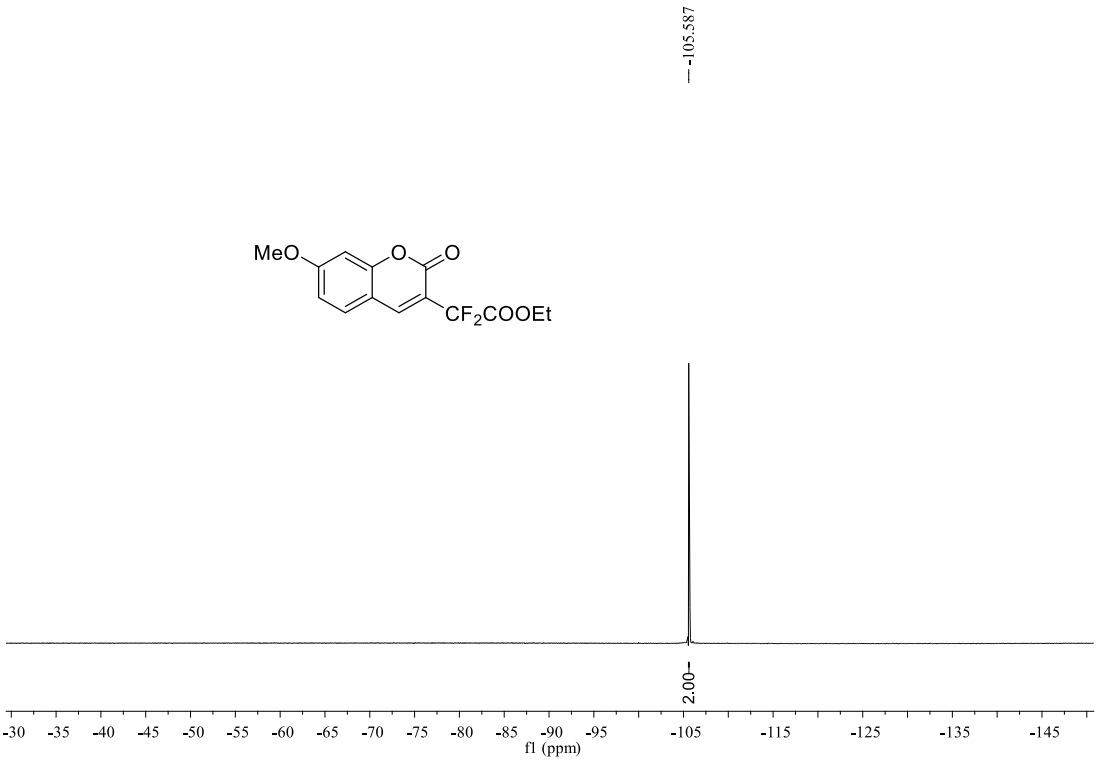


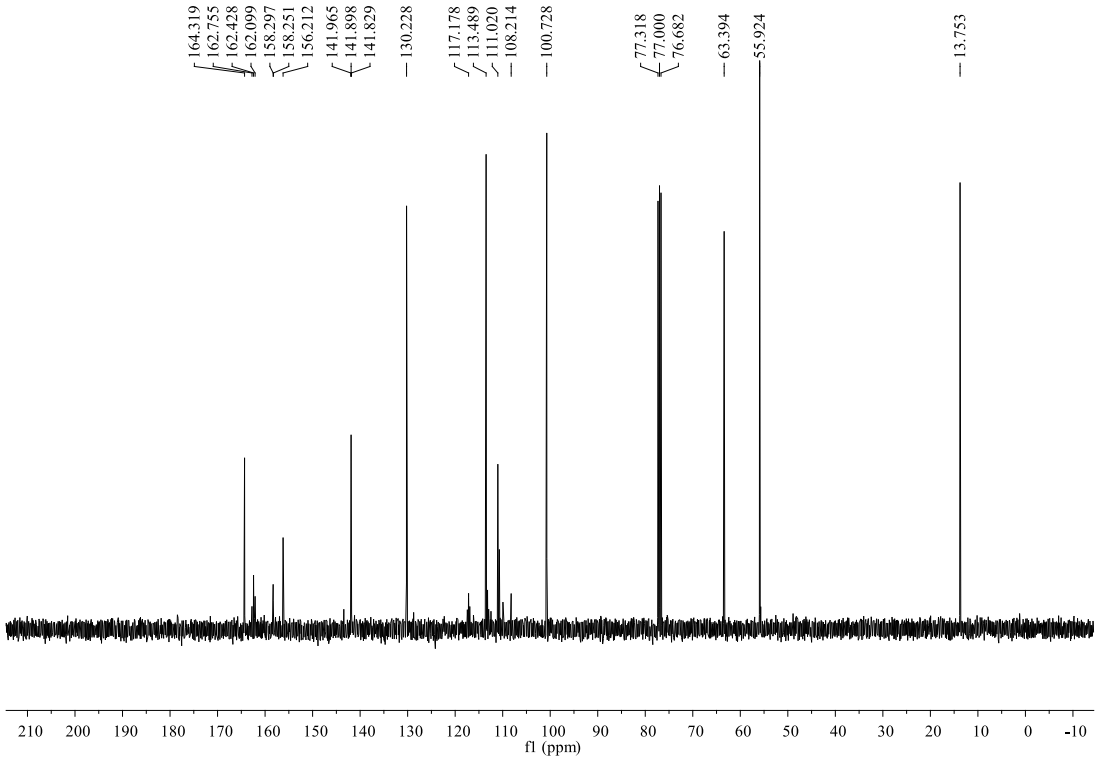




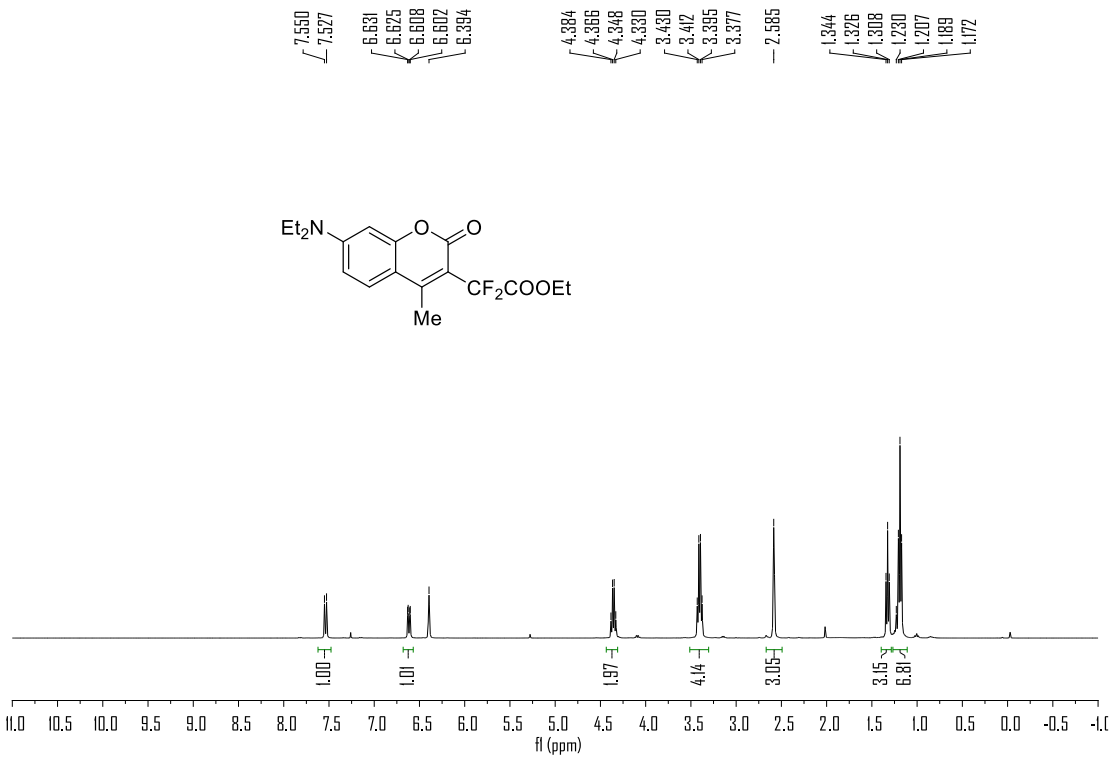
Ethyl 2,2-difluoro-2-(7-methoxy-2-oxo-2H-chromen-3-yl)acetate (7g).

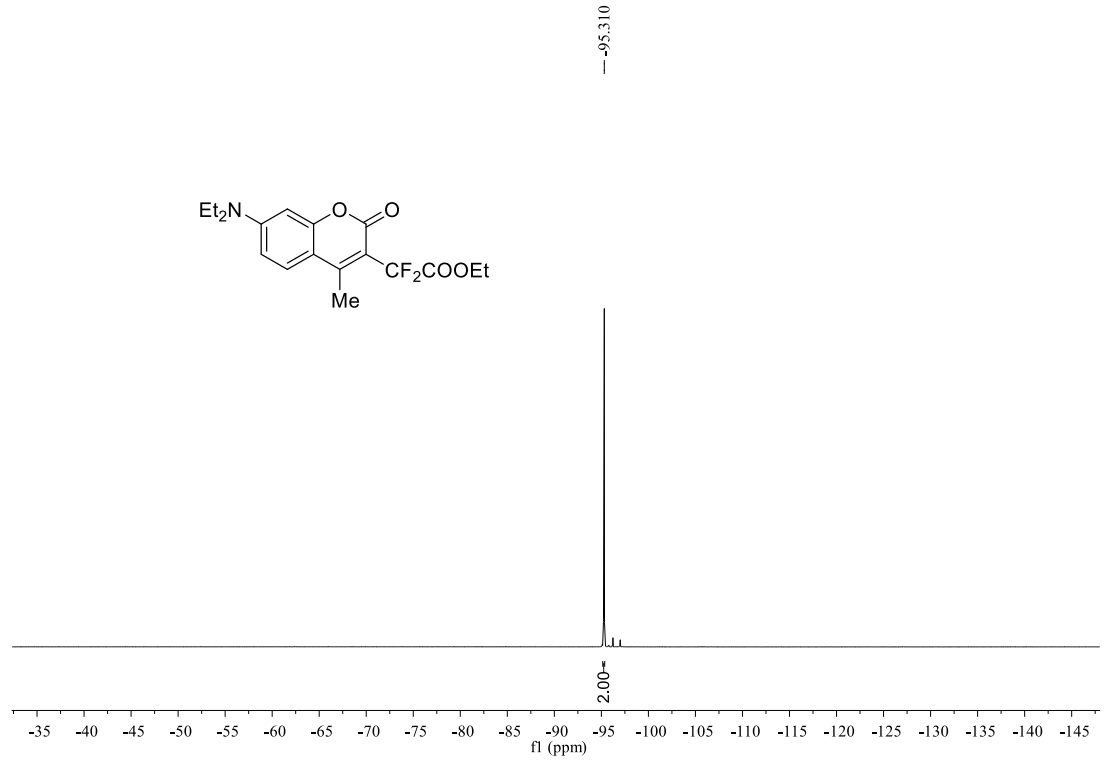


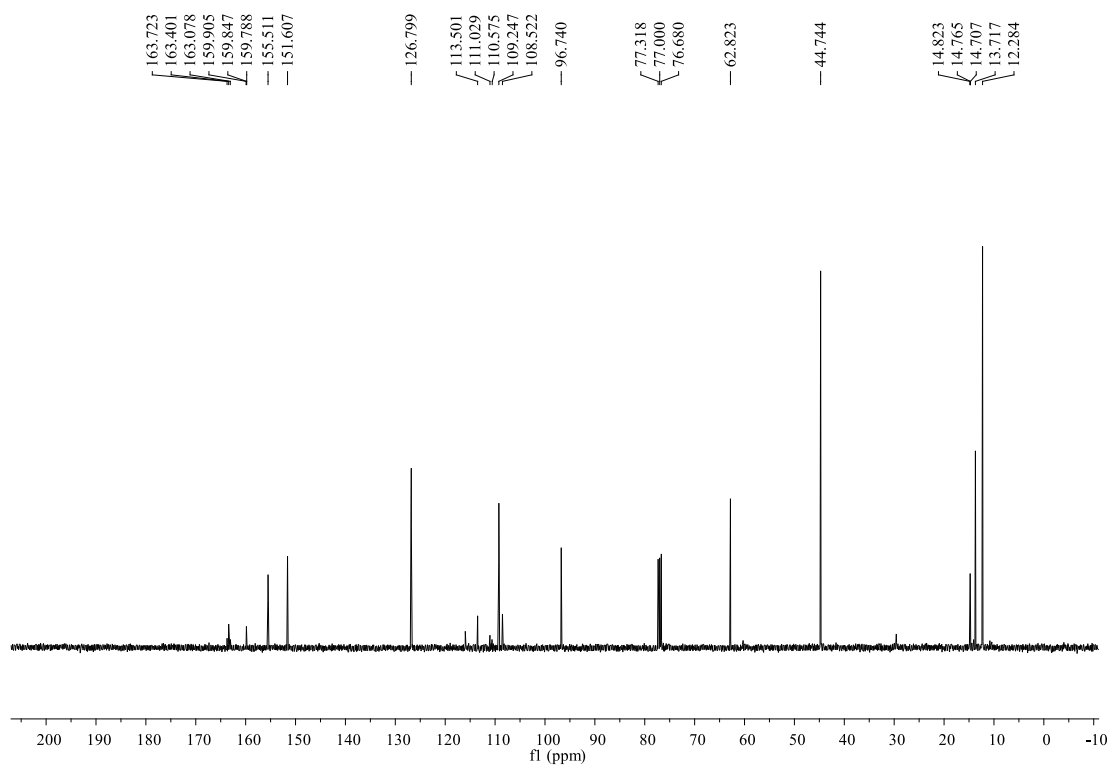

-105.587
MeO
O
O
CF2COOEt
2.00
-30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125 -135 -145
f1 (ppm)


164.319
162.755
162.428
162.099
158.297
158.251
156.212
141.965
141.898
141.829
130.228
117.178
113.489
111.020
108.214
100.728
77.318
77.000
76.682
63.394
55.924
13.753
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

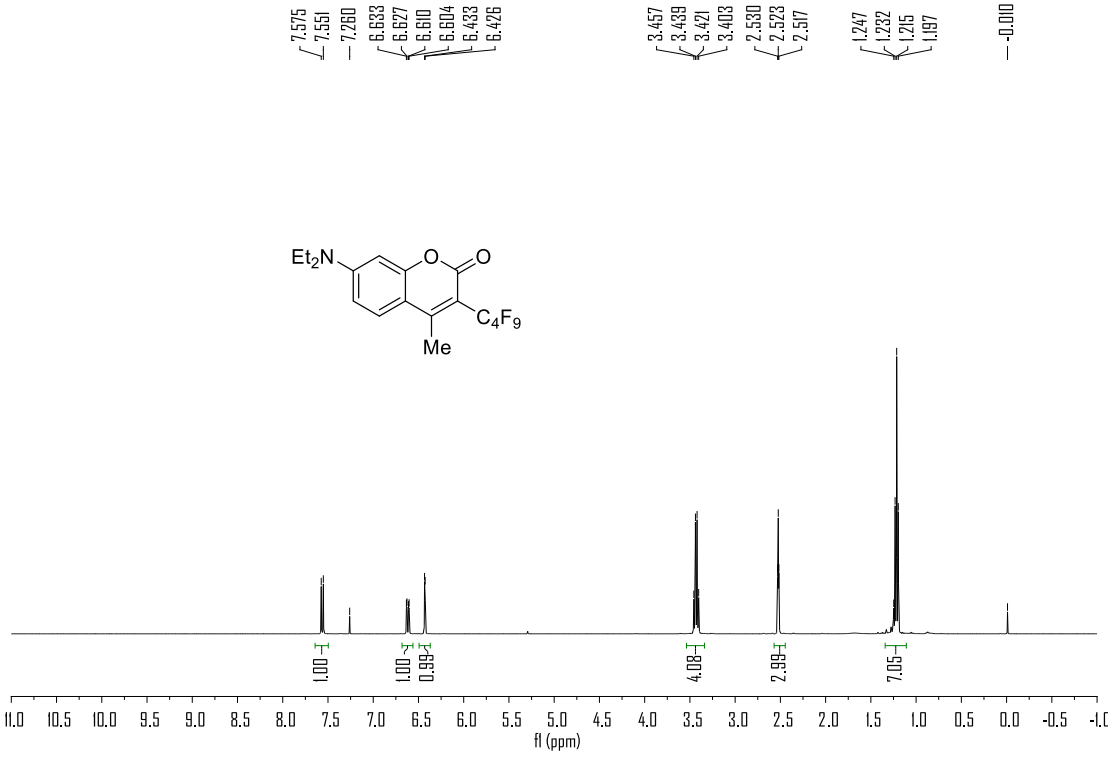
Ethyl 2-(7-(diethylamino)-4-methyl-2-oxo-2H-chromen-3-yl)-2,2-difluoroacetate (7h).

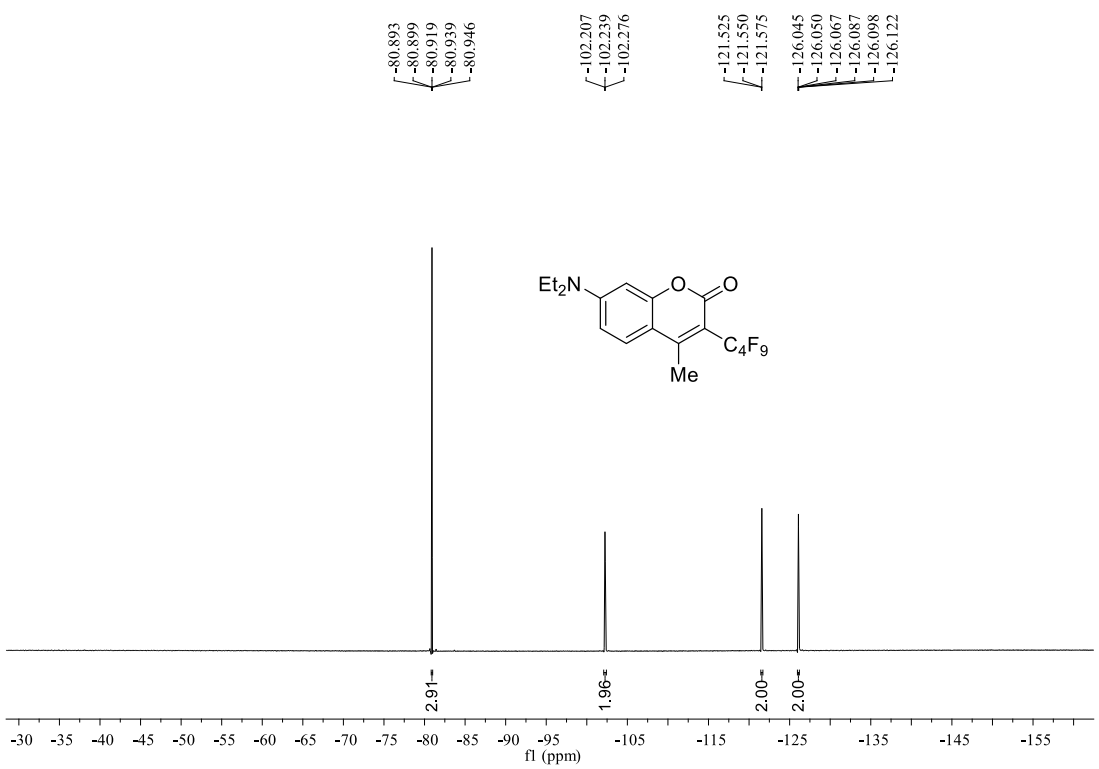


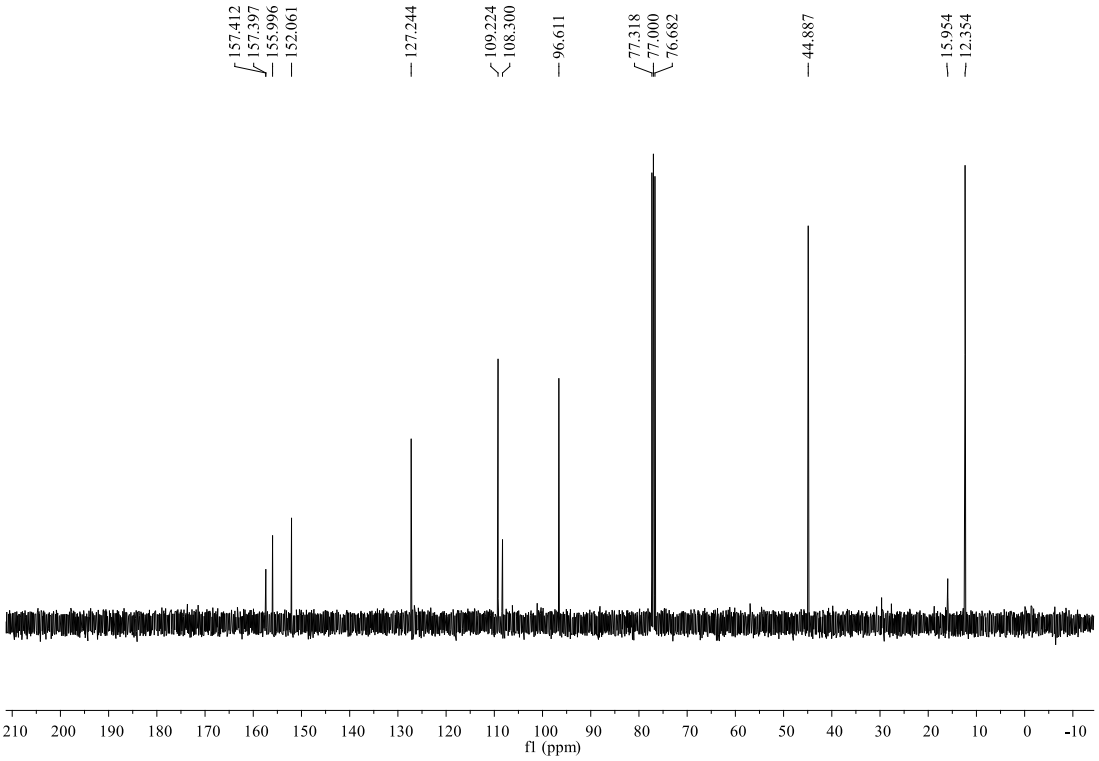




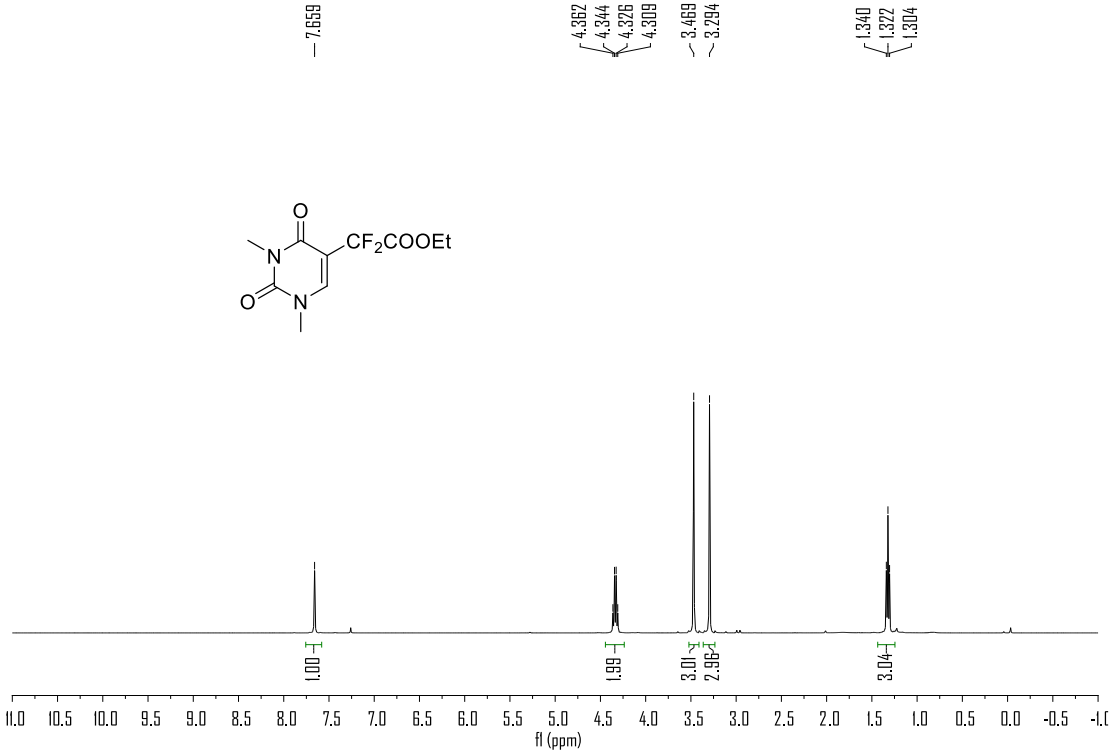
7-(diethylamino)-4-methyl-3-(perfluorobutyl)-2H-chromen-2-one (7i).

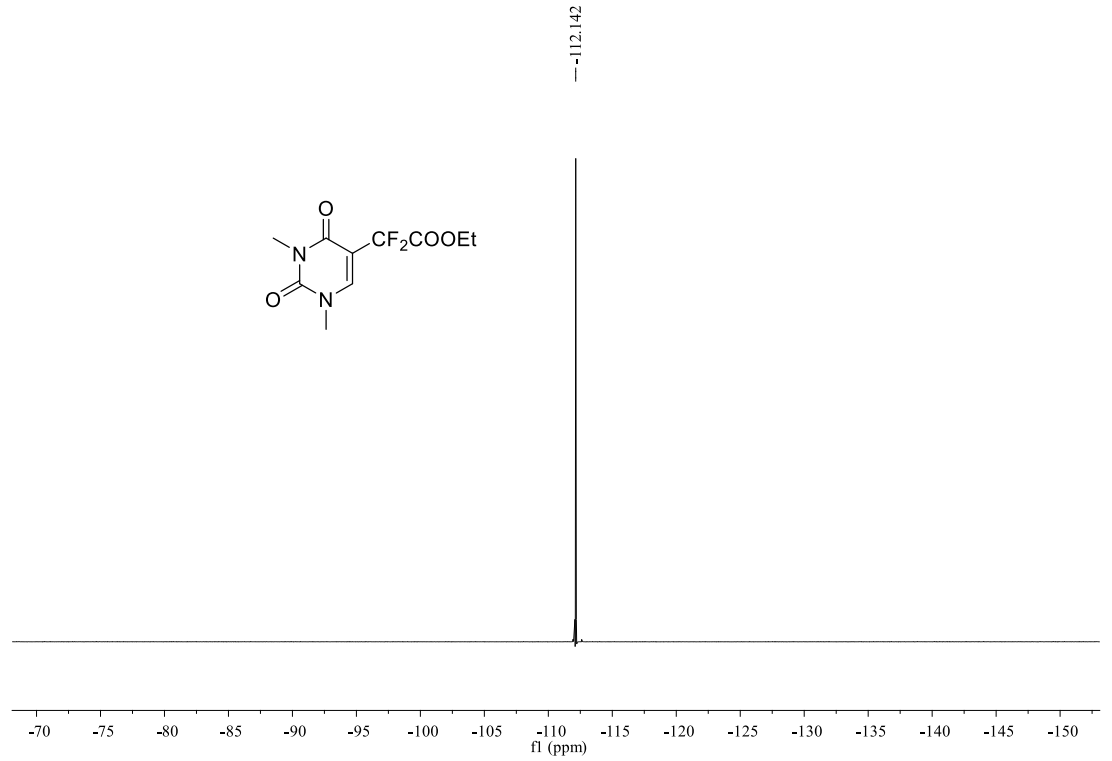


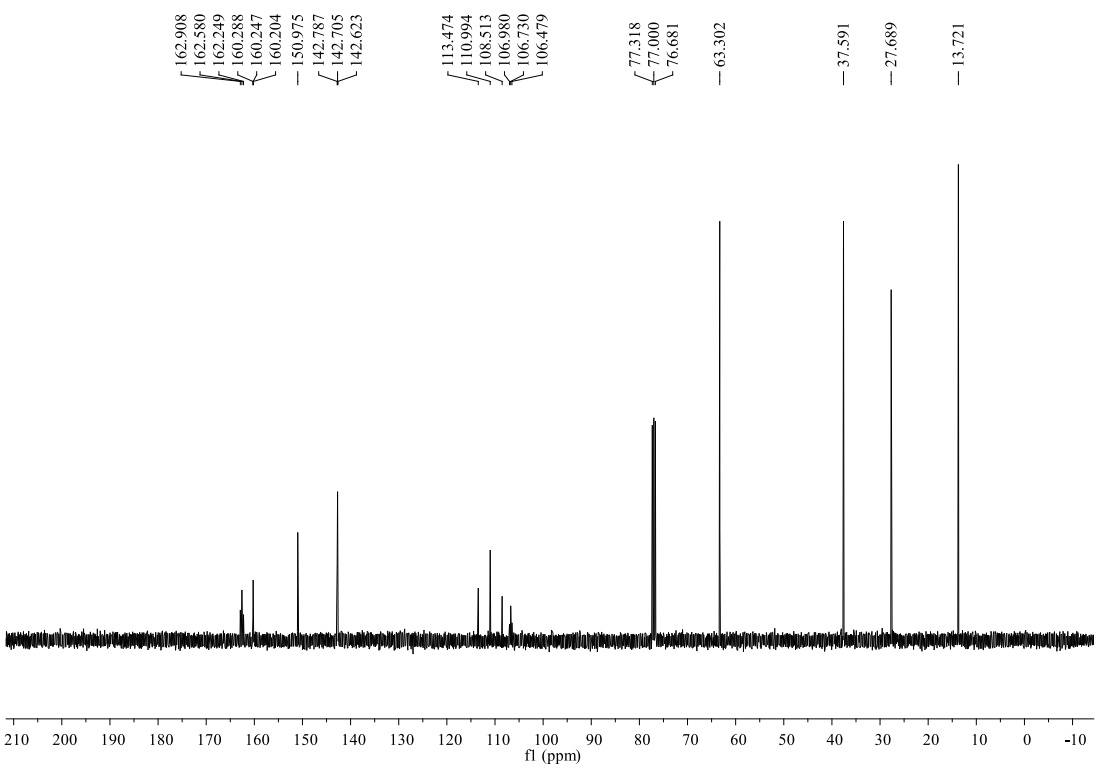

-80.893
-80.899
-80.919
-80.939
-80.946
-102.207
-102.239
-102.276
-121.525
-121.550
-121.575
-126.045
-126.050
-126.067
-126.087
-126.098
-126.122
Et2N
O
O
C4F9
Me
2.91
1.96
2.00
2.00
-30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125 -135 -145 -155
f1 (ppm)


157.412
157.397
155.996
152.061
127.244
109.224
108.300
96.611
77.318
77.000
76.682
44.887
15.954
12.354
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

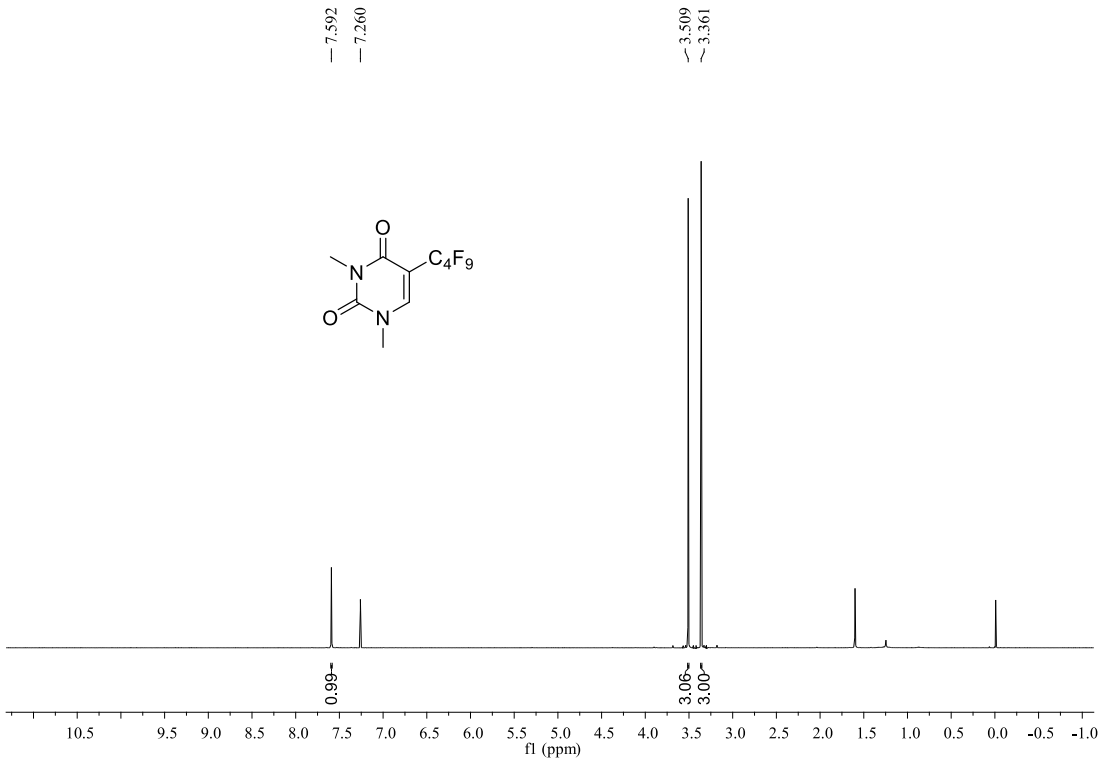
Ethyl 2-(1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-2,2-difluoroacetate (7j).

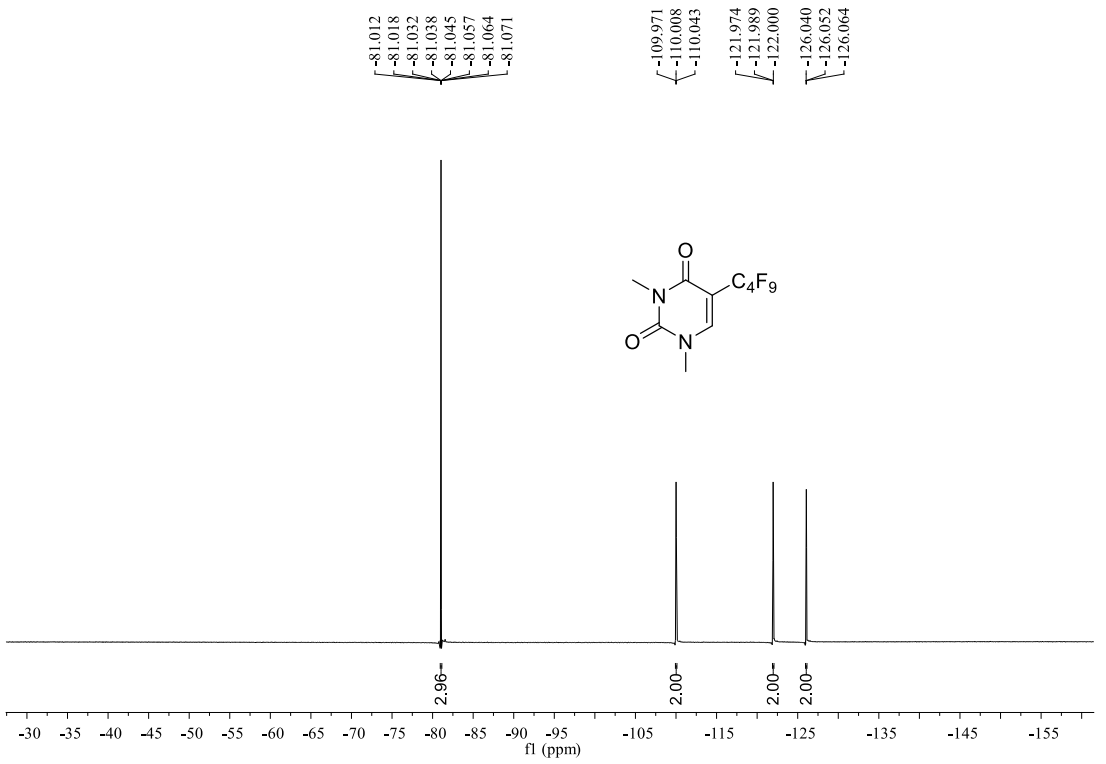


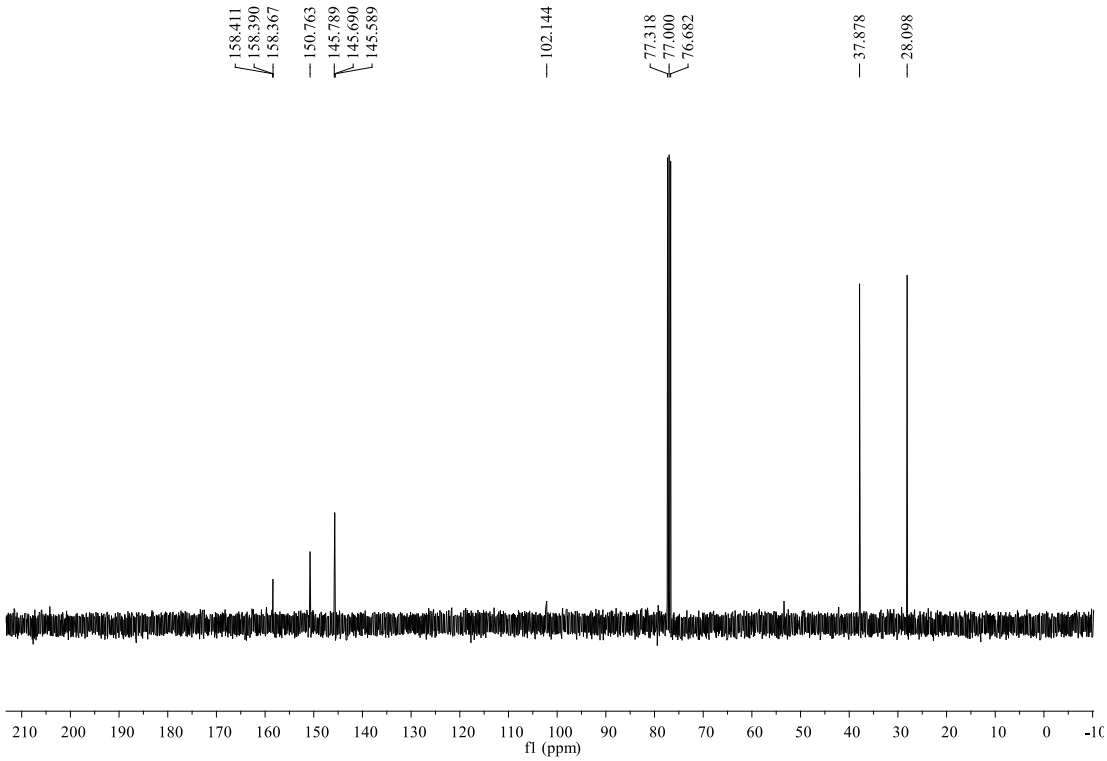




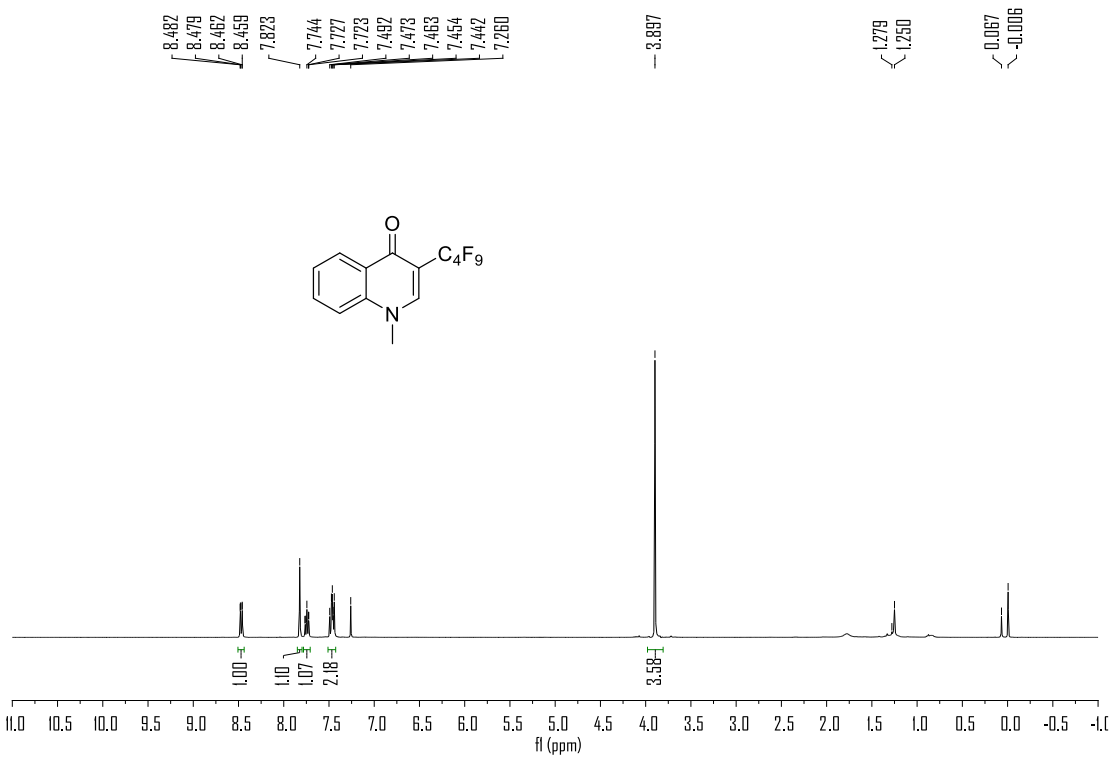
1,3-Dimethyl-5-(perfluorobutyl)pyrimidine-2,4(1H,3H)-dione (7k).

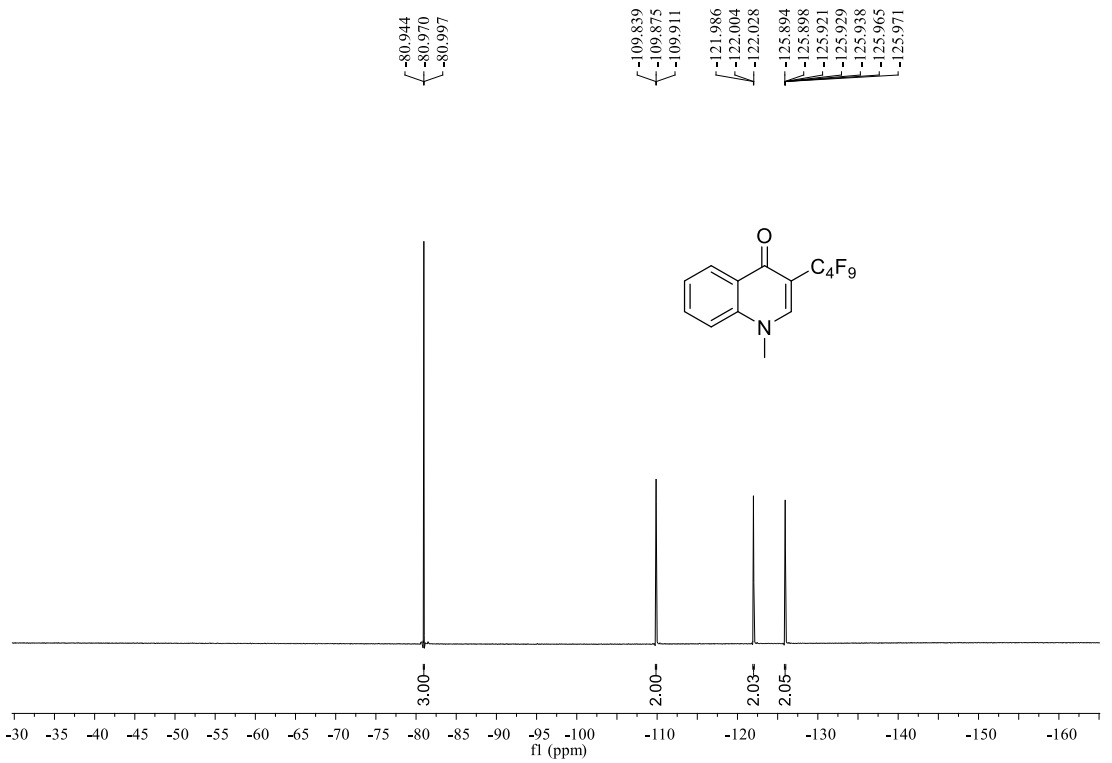


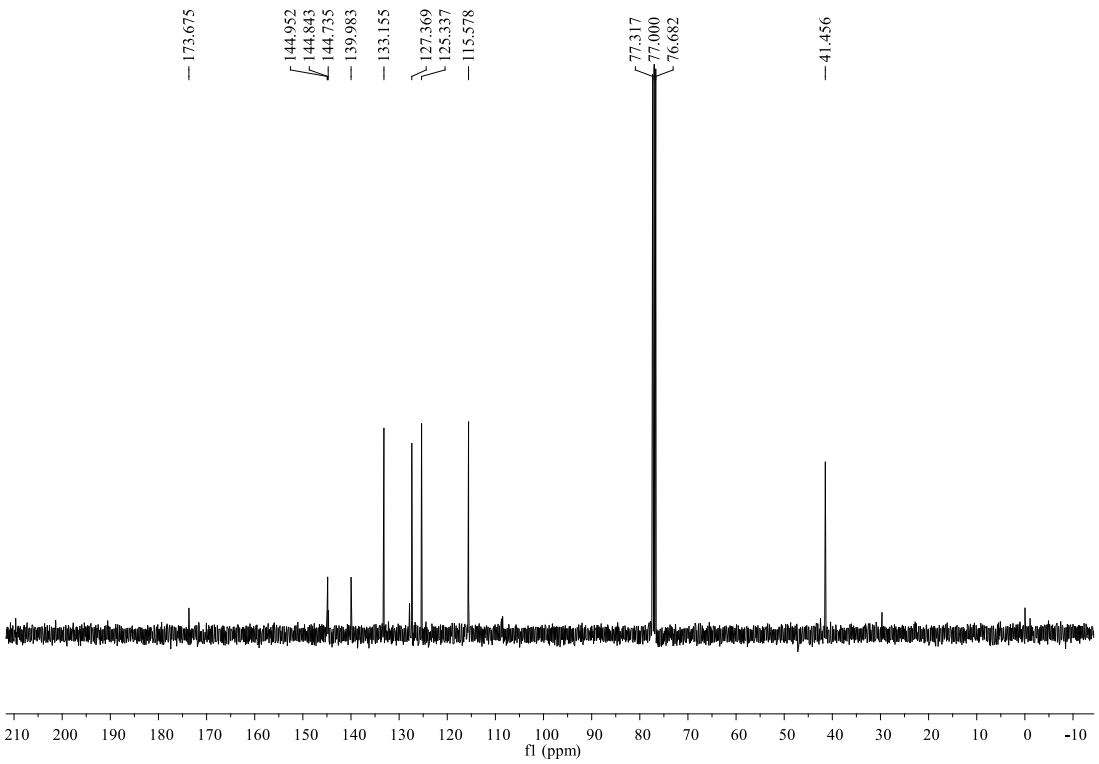

-81.012
-81.018
-81.032
-81.038
-81.045
-81.057
-81.064
-81.071
-109.971
-110.008
-110.043
-121.974
-121.989
-122.000
-126.040
-126.052
-126.064
O
N
C4F9
O
N
2.96
2.00
2.00
2.00
-30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125 -135 -145 -155
f1 (ppm)


158.411
158.390
158.367
150.763
145.789
145.690
145.589
102.144
77.318
77.000
76.682
37.878
28.098
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

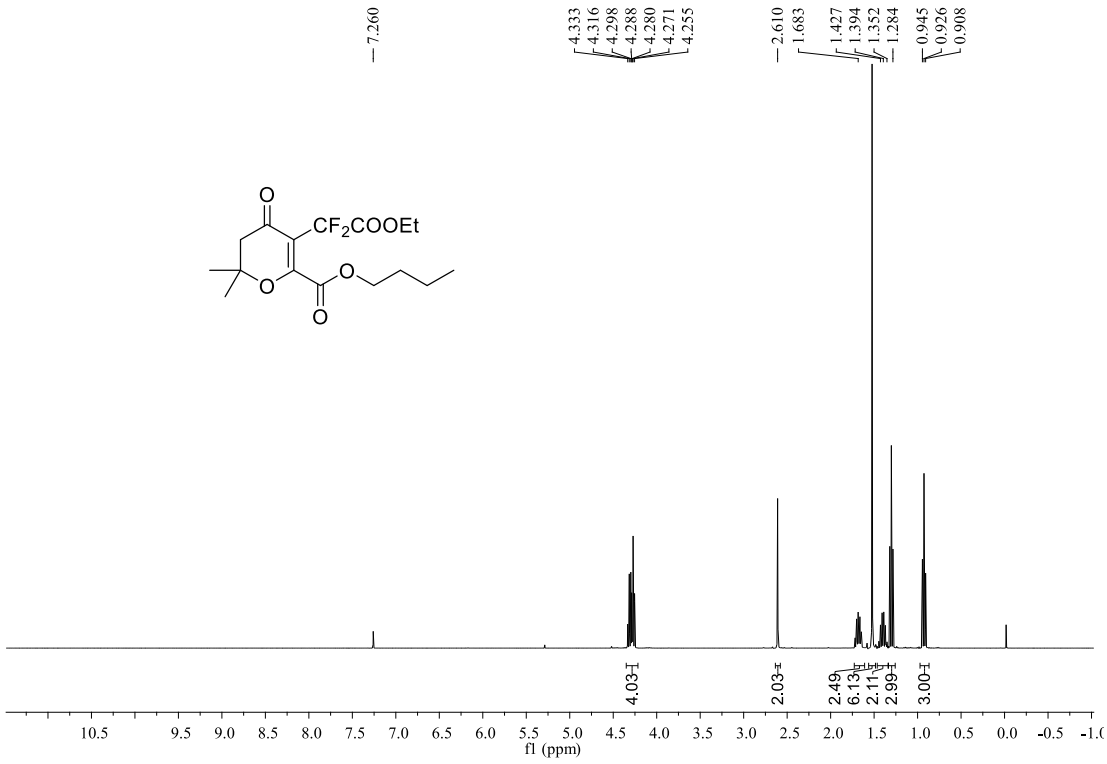
1-Methyl-3-(perfluorobutyl)quinolin-4(1H)-one (7l).

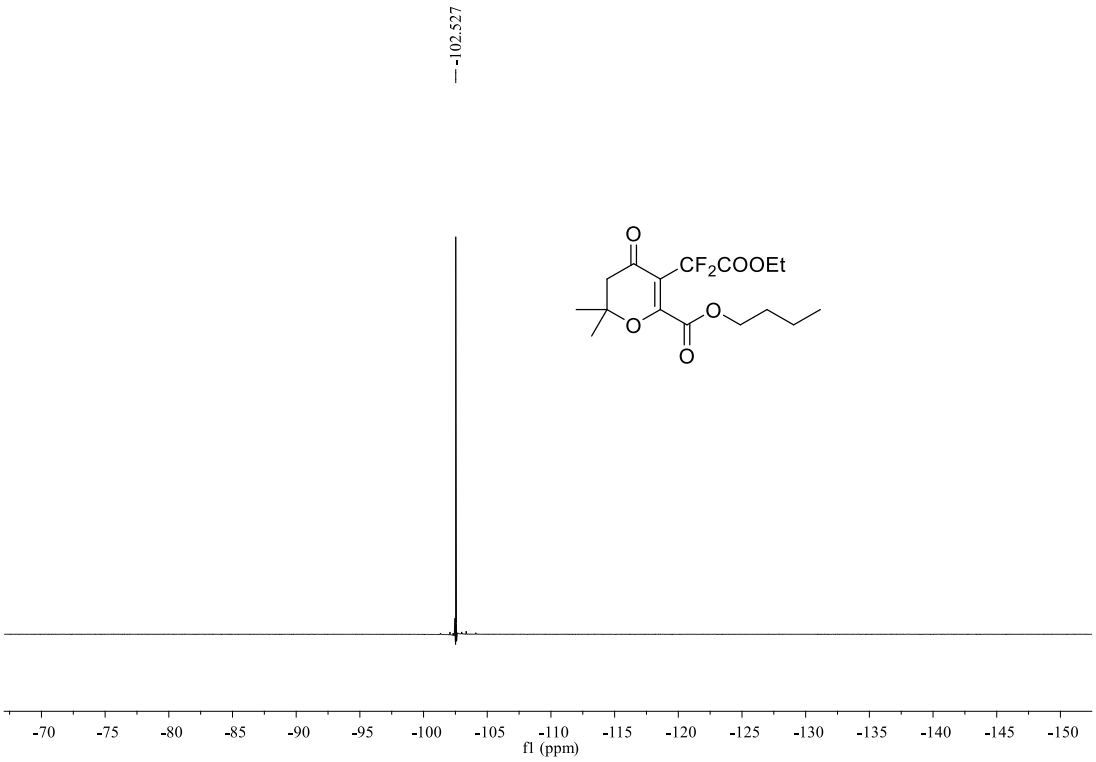


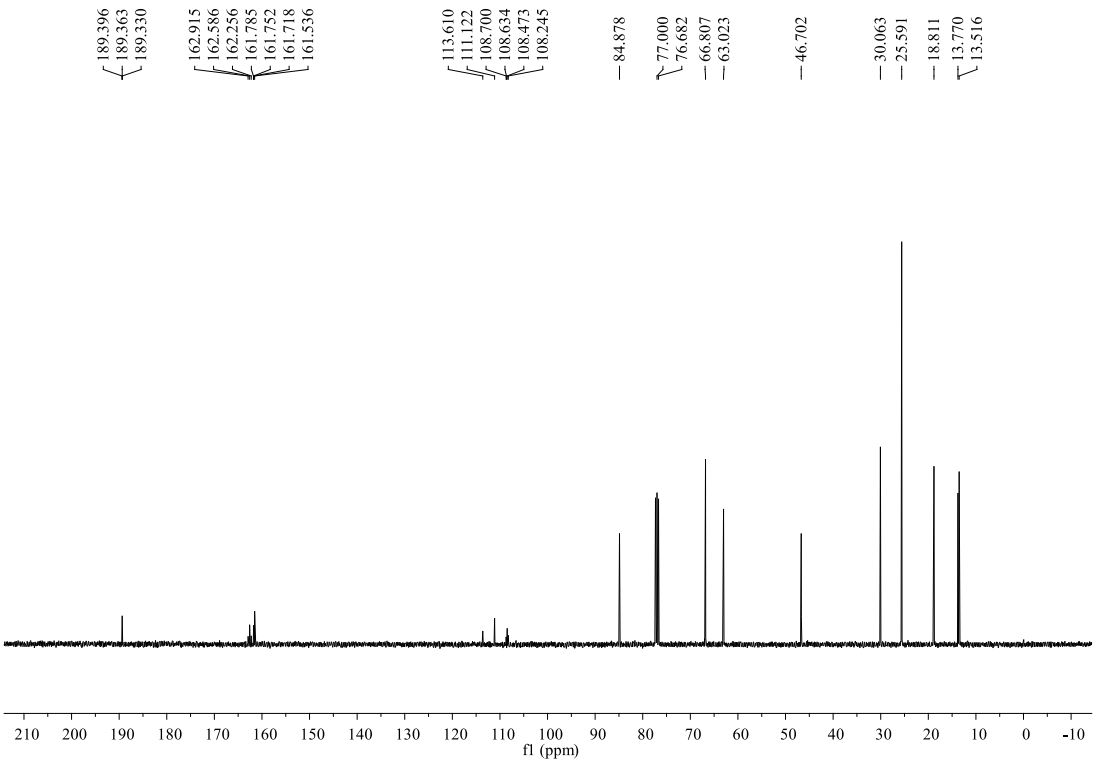




Butyl 5-(2-ethoxy-1,1-difluoro-2-oxoethyl)-2,2-dimethyl-4-oxo-3,4-dihydro-2H-pyran-6-carboxylate (7o).




-102.527
O
CF2COOEt
O
O
O
-70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150
f1 (ppm)


189.396
189.363
189.330
162.915
162.586
162.256
161.785
161.752
161.718
161.536
113.610
111.122
108.700
108.634
108.473
108.245
84.878
77.000
76.682
66.807
63.023
46.702
30.063
25.591
18.811
13.770
13.516
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)