Supporting Information

Synthesis of Remote Fluoroalkenyl Ketones by Photo-induced Ring-opening Addition of Cyclic Alkoxy Radicals to Fluorinated Alkenes

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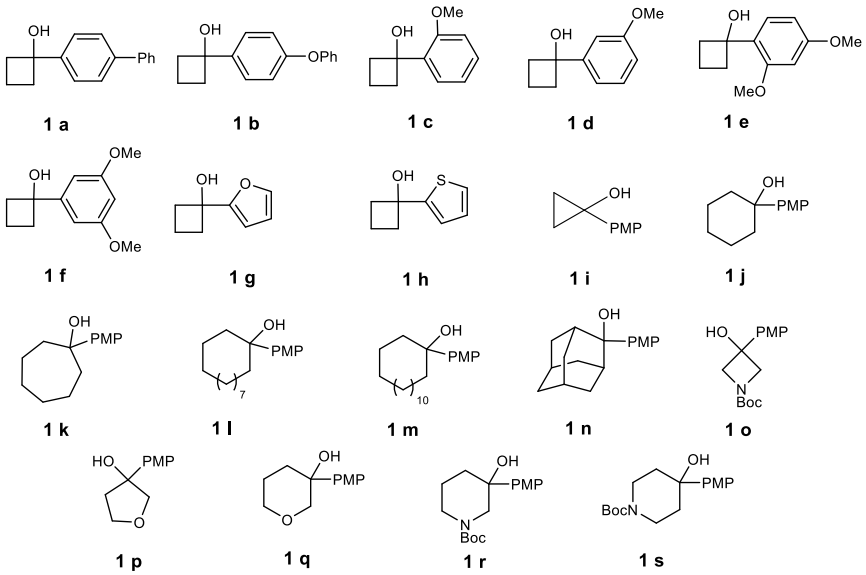
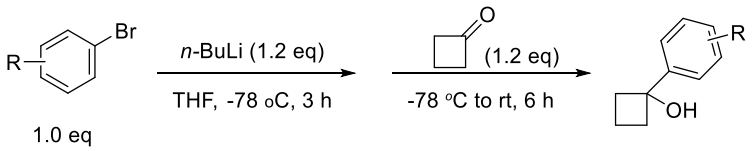
1. General remarks

All preparations and manipulations were carried out using standard Schlenk and Vigor glovebox techniques under an atmosphere of highly pure nitrogen gas. Tetrahydrofuran (THF), 1,2-dichloroethane (DCE), toluene, N,N-dimethylformamide(DMF) and dimethyl sulfoxide(DMSO) were freshly dried over calcium hydride. All chemical reagents were purchased from Shanghai Titan Scientific Co. Ltd, Bide Pharmatech Ltd, Aladdin Chemical Reagent Co. (China) and Sinopharm Chemical Reagent Company. All chemicals were of analytical grade or higher. ^{1}H NMR ^{13}C NMR and ^{19}F NMR spectra were obtained on Bruker Avance II 600MHz NMR spectrometer, Chemical shifts were reported on the form of per million (ppm), and the residual solvent peak was used as an internal reference: ^{1}H (chloroform δ 7.26), ^{13}C (chloroform δ 77.16). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, m = multiplet, etc.), coupling constants (Hz) and integration. High Resolution Mass Spectra was obtained on a Bruker FTMS.Except for special instructions, all reaction conditions were carried out in 20 ml Schlenk at room temperature, and 100 W led was used for light irradiation.

2. General procedure for synthesis of cyclic alcohols



The cyclic alcohols above are prepared in the following manner [1].



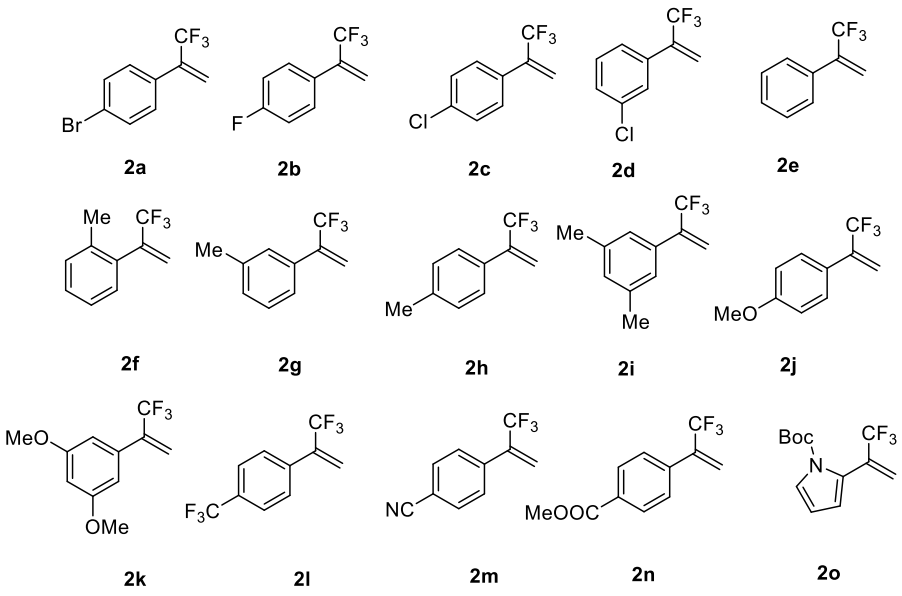
Under nitrogen atmosphere, aryl bromide (1.0 eq) was added to a dry 100 ml round bottom flask with a magnetic stirring, and dissolved in anhydrous THF (0.5M), the resulting solution was cooled to -78 °C. After *n*-BuLi (2.5 M in hexane) was added dropwise into the solution and then it was stirred for an additional 3 h at -78 ºC. Then, a THF solution of Cyclobutanone(1.2 eq, 1 M) was added at same temperature. Then the solution was slowly allowed to warm to room temperature and stirred for 6 h. The reaction was quenched with saturated NH_4Cl (aq.) and extracted with ethyl acetate(× 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and filtered. The organic solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (PE / EA = 6/1 ~ 2/1) to afford the desired product.

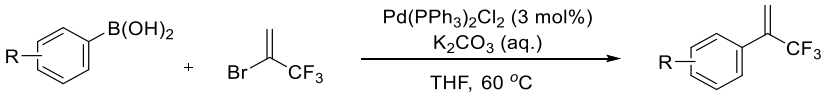
Compound **1i** was synthesized by the following method [2].

To a 250 mL Round bottom flask with stir bar, Ethyl 4-methoxybenzoate (10 mmol, 1.0 equiv)and titanium isopropoxide (14 mmol, 1.4 equiv) were added in N_2 (three times). Add ethylmagnesium bromide (14 mL, 2.8 equiv, 2 M in THF) to the solution dropwise over 30 min at

0°C. Warm the resulting reaction mixture to room temperature and stirred for 12 h. The reaction was quenched with water and extracted with ethyl acetate(× 3). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered. The organic solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (PE / EA = 6/1 ~ 2/1) to afford the desired product.

3. General procedure for the preparation of trifluoromethyl alkenes [3].

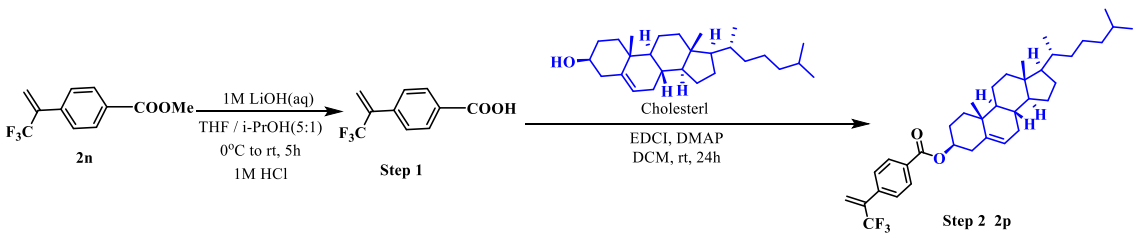




To a Schlenk tube equipped with stir bar, arylboronic acid (1.0 eq) and $Pd(PPh_3)_2Cl_2$ (3 mol%) were added. The vessel was evacuated and filled with N_2 (three times), and then aqueous K_2CO_3 (4.0 eq, 2.0 M) and THF (1:1) were added in. After addition of 2-bromo-3,3,3-trifluoropropene (2.0 eq), the suspension was stirred overnight at 60 °C. The reaction was quenched with saturated NH_4Cl (aq.) and extracted with ethyl acetate(× 3). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered. The solvent was evaporated under reduced pressure and the residue was

purified by column chromatography on silica gel (PE ~ PE / EA=100 ~ 20:1) to afford the corresponding product.

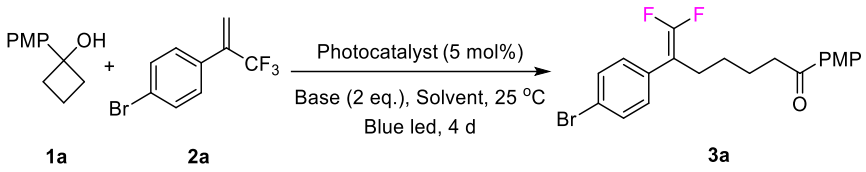
Compound **2p** was synthesized by the following method [4, 5].



Step1: To a 50 mL round bottom flask equipped with a stir bar was added **2n** (1.0 eq) followed by THF (0.5 M). The reaction mixture was cooled to 0 °C in an ice-water bath. After stirring for approximately 10 min, an aq 1 M solution of LiOH (aq. 1.5 eq) was added, followed by i-PrOH ($V_{THF\,/\,i\text{-}PrOH}$ = 5:1). After stirring for 10 min, the ice-bath was removed, and the solution was allowed to stir for 5 h at rt. The solution was concentrated in vacuo, and the resulting residue was dissolved in H_2O. This aqueous solution was transferred to a separatory funnel and washed with Et_2O (× 3). The pH of aq layer was adjusted to ~1.0 with adding HCl (1M) and extracted with EtOAc (× 3). The combined organic layers were then dried over anhyrous Na_2SO_4 and filtered, the filtrate was concentrtated under reduced pressure to afford the desired carboxylic acid as a white solid, which would be directly used in next step without further purification.

Step2: To a solution of the aryl acid (1.0 eq), 4- dimethylaminopyridine (DMAP) (10 mol%) and holesterol (1.1 eq) in DCM (0.3 M), 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDCI) (1.1 eq) was added. The reaction mixture was stirred at room temperature for 12 h. The reaction mixture was quenched by water. The organic layer was then separated, dried over anhydrous Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure to give the residue, which was purified by column chromatography (PE / EA= 4:1) to afford the corresponding product.

4. Detailed optimization of reaction conditions



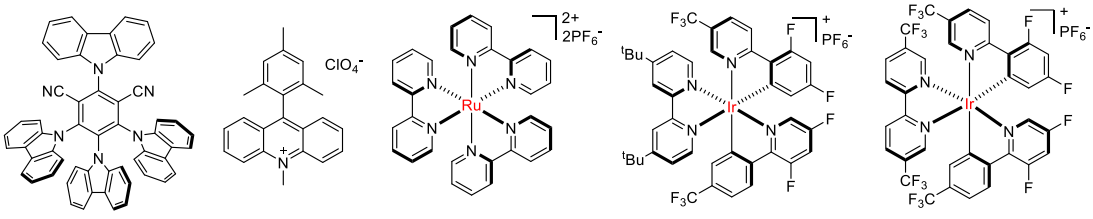
1a **2a** **3a**

Entry	PC	Solvent	Base	Light source	Yield (%) b
1	**PC-1**	DCE	Collidine	456 nm 100 W	88
2	**PC-2**	DCE	Collidine	456 nm 100 W	13
3c	**PC-3**	DCE	Collidine	456 nm 100 W	0
4c	**PC-4**	DCE	Collidine	456 nm 100 W	0
5c	**PC-5**	DCE	Collidine	456 nm 100 W	56
6	**PC-1**	Toluene	Collidine	456 nm 100 W	12
7	**PC-1**	THF	Collidine	456 nm 100 W	5
8	**PC-1**	DMF	Collidine	456 nm 100 W	21
9	**PC-1**	DMSO	Collidine	456 nm 100 W	75
10	**PC-1**	DCE	K2CO3	456 nm 100 W	21
11	**PC-1**	DCE	K2HPO4	456 nm 100 W	15
12	**PC-1**	DCE	Collidine	456 nm 48 W	25
13	**PC-1**	DCE	Collidine	420 nm 100 W	32
14	**PC-1**	DCE	Collidine	365 nm 100 W	19
15	**PC-1**	DCE	Collidine	White Led 100W	20
16	**PC-1**	DCE	Collidine	Dark	0

[a] All reactions were carried out with 0.20 mmol of **1a** and 0.30 mmol of **2a** in 2 mL of solvents under N_2 atmosphere.

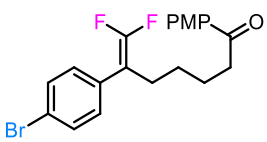
[b] Yields are given as isolated yields.

[c] 2 mol% of photocatalyst was used.

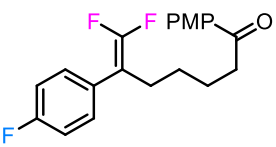


In a glove box filled with nitrogen, **1** (0.2 mmol, 1.0 eq), **2** (0.3 mmol, 1.5 eq), **PC-1** (5% mol) / **PC-5** (2% mol), **2,4,6-collidine**(0.4 mmol, 2 eq) and 2 ml of DCE were successively added to the dry Schlenk tube. Irradiate at room temperature with a 100W Led lamp. Stirred for 4 d, after the reaction is completed, quenched with 2M HCl solution, then was extracted with DCM (× 3). The organic layer was then separated, dried over anhydrous Na_2SO_4 and filtered. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (PE/EA=15:1~ 4:1) to afford the corresponding product.

5. Characterization data of compounds

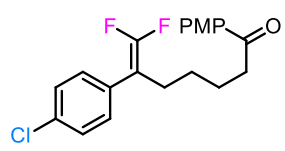


(3a) 6-(4-bromophenyl)-7,7-difluoro-1-(4-methoxyphenyl)hept-6-en-1-one: Colorless oil (72mg, 88%Yield); ^{1}H NMR (600 MHz, Chloroform-d) δ 7.90 (d, *J* = 6.0 Hz, 2H), 7.47 (d, *J* = 6.0 Hz, 2H), 7.17 (d, *J* = 6.0 Hz, 2H), 6.92 (d, *J* = 12.0 Hz, 2H), 3.87 (s, 3H), 2.87 (t, *J* = 6.0 Hz, 2H), 2.44 – 2.41 (m, 2H), 1.74 - 1.69 (m, 2H), 1.45 – 1.39 (m, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 198.68, 163.53, 155.66 (dd, *J* = 289.9, 286.9 Hz), 132.66 (t, *J* =3.0 Hz), 131.76, 130.39, 130.14, 130.02 (t, *J* = 3.0 Hz), 121.32, 113.83, 91.55 (dd, *J* = 22.6, 13.6 Hz), 55.59, 37.87, 27.46, 23.84; ^{19}F NMR (565 MHz, Chloroform-*d*) δ -90.55 (d, *J* = 45.2 Hz), -90.75 (d, *J* = 39.5 Hz). HRMS Calcd. For $[C_{20}H_{20}BrF_2O_2]^+$: 409.0609, found: 409.0611.

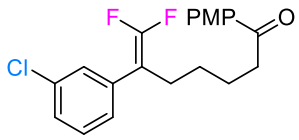


(3b) 6-(4-fluorophenyl)-7,7-difluoro-1-(4-methoxyphenyl)hept-6-en-1-one: Colorless oil (42mg, 61%Yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 6.0 Hz, 2H), 7.26 (dd, *J* = 12.0, 6.0 Hz, 2H), 7.03 (t, *J* = 12.0 Hz, 2H), 6.94 – 6.89 (m, 2H), 3.86 (s, 3H), 2.88 (t, *J* = 6.0 Hz, 2H), 2.44 -

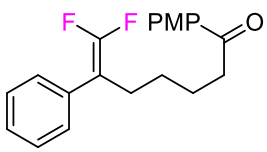
2.42 (m, 2H), 1.74 – 1.70 (m, 2H), 1.45 – 1.40 (m, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 198.71, 163.52, 161.96 (d, *J* = 254.3 Hz), 153.70 (d, *J* = 297.6, 294.8 Hz), 130.39, 130.15, 130.11 – 130.01 (m), 129.57 (q, *J* = 3.1 Hz), 115.55 (d, *J* = 21.8 Hz), 113.82, 91.47 (dd, *J* = 21.8, 14.0 Hz), 55.57, 37.89, 27.74, 27.40, 23.85; ^{19}F NMR (565 MHz, Chloroform-*d*) δ -91.67 (d, *J* = 45.2 Hz), -91.79 (d, *J* = 45.2 Hz), -114.72. HRMS Calcd. For $[C_{20}H_{20}F_3O_2]^+$: 349.1410, found: 349.1409.



(3c) 6-(4-chlorophenyl)-7,7-difluoro-1-(4-methoxyphenyl)hept-6-en-1-one: Colorless oil (65mg, 89%Yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 6.0 Hz, 2H), 7.32 (d, *J* = 6.0 Hz, 2H), 7.23 (d, *J* = 6.0 Hz, 2H), 6.92 (d, *J* = 12.0 Hz, 2H), 3.86 (s, 3H), 2.87 (t, *J* = 6.0 Hz, 2H), 2.44 - 2.41 (m, 2H), 1.74 - 1.69 (m, 2H), 1.45 - 1.40 (m, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 198.69, 163.50, 153.70 (dd, *J* = 289.9, 286.9 Hz), 133.17, 132.1(dd, *J* = 4.5, 3.0 Hz), 130.38, 130.10, 129.68 (t, *J* = 3.0 Hz), 128.79, 113.81, 91.47 (dd, *J* = 22.7, 13.6 Hz), 55.59, 37.87, 27.46 (d, *J* = 9.1 Hz), 23.83; ^{19}F NMR (565 MHz, Chloroform-*d*) δ -90.72 (d, *J* = 45.2 Hz), -90.89 (d, *J* = 45.2 Hz). HRMS Calcd. For $[C_{20}H_{20}ClF_2O_2]^+$: 365.1114, found: 365.1115.

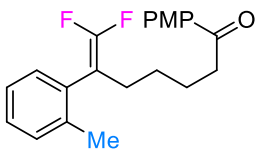


(3d) 6-(3-chlorophenyl)-7,7-difluoro-1-(4-methoxyphenyl) hept-6-en-1-one: Colorless oil (55mg, 75%Yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 6.0 Hz, 2H), 7.32 (d, *J* = 6.0 Hz, 2H), 7.23 (d, *J* = 6.0 Hz, 2H), 6.92 (d, *J* = 6.0 Hz, 2H), 3.86 (s, 3H), 2.87 (t, *J* = 6.0 Hz, 2H), 2.44 - 2.41 (m, 2H), 1.76 - 1.69 (m, 2H), 1.45 - 1.40 (m, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 198.71, 163.51, 153.70 (dd, *J* = 291.4, 288.4 Hz), 133.17, 132.13 (dd, *J* = 4.5, 3.0 Hz), 130.39, 130.10, 129.69 (t, *J* = 3.0 Hz), 129.04, 128.94, 128.79, 113.82, 91.48 (dd, *J* = 21.1, 12.1 Hz), 55.60, 37.88, 27.47 (d, *J* =7.6 Hz), 23.84; ^{19}F NMR (565 MHz, Chloroform-*d*) δ -90.73 (d, *J* = 39.5 Hz), -90.89 (d, *J* = 39.5 Hz). HRMS Calcd. For $[C_{20}H_{20}ClF_2O_2]^+$: 365.1114, found: 365.1115.

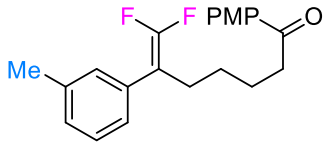


(3e) 6-phenyl-7,7-difluoro-1-(4-methoxyphenyl)hept-6-en-1-one: Colorless oil (46mg, 70%Yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 12.0 Hz, 2H), 7.36-7.34 (m, 2H), 7.30 – 7.26 (m, 3H), 6.92 (d, *J* = 6.0 Hz, 2H), 3.86 (s, 3H), 2.87 (t, *J* = 6.0 Hz, 2H), 2.47 – 2.44 (m, 2H), 1.76-1.71 (m,

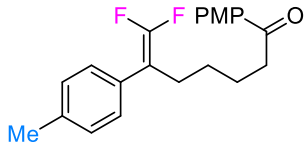
2H), 1.47-1.42 (m, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 198.79, 163.48, 153.72 (dd, *J* = 289.9, 288.4 Hz), 133.73(d, *J* = 1.5 Hz), 130.39, 130.17, 128.56, 128.38 (t, *J* = 3.0 Hz), 127.36, 113.81, 92.25 (dd, *J* = 19.6, 15.1 Hz), 55.57, 37.96, 27.6 (d, *J* =12.1 Hz), 23.95; ^{19}F NMR (565 MHz, Chloroform-*d*) δ -91.63 (d, *J* = 45.2 Hz), -91.74 (d, *J* = 39.5 Hz). HRMS Calcd. For $[C_{20}H_{21}F_2O_2]^+$: 331.1504, found: 331.1503.



(3f) 6-(o-tolyl)-7,7-difluoro-1-(4-methoxyphenyl) hept-6-en-1-one: Colorless oil (57mg, 84%Yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 6.0 Hz, 2H), 7.24 (t, *J* = 6.0 Hz, 1H), 7.11-7.08 (m, 3H), 6.92 (d, *J* = 12.0 Hz, 2H), 3.86 (s, 3H), 2.88 (t, *J* = 6.0 Hz, 2H), 2.45 - 2.42 (m, 2H), 2.35 (s, 3H),1.76 – 1.71 (m, 2H), 1.47-1.41 (m, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 198.87, 163.45, 153.64 (dd, *J* = 289.9, 286.9 Hz), 138.14, 133.61 (dd, *J* = 4.5, 3.0 Hz), 130.40, 130.12, 129.07 (t, *J* = 3.0 Hz), 128.42, 128.16, 125.44(t, *J* = 3.0 Hz), 113.79, 92.24(dd, *J* = 21.1, 13.6 Hz), 55.59, 37.99, 27.61 (d, *J* =18.1 Hz), 23.93, 21.61; ^{19}F NMR (565 MHz, Chloroform-*d*) δ -91.78 (d, *J* = 45.2 Hz), -91.92 (d, *J* = 45.2 Hz). HRMS Calcd. For $[C_{21}H_{23}F_2O_2]^+$: 345.1661, found: 345.1661.

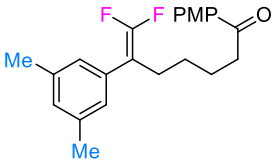


(3g) 6-(m-tolyl)-7,7-difluoro-1-(4-methoxyphenyl) hept-6-en-1-one: Colorless oil (43mg, 62%Yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 6.0 Hz, 2H), 7.22 (d, *J* = 6.0 Hz, 2H), 7.19-7.16 (m, 1H), 7.22 (d, *J* = 6.0 Hz, 1H), 6.93 (d, *J* = 6.0 Hz, 2H), 3.86 (s, 3H), 2.88 (t, *J* = 6.0 Hz, 2H), 2.36-2.34 (m, 2H), 2.27 (s, 3H),1.77 - 1.71 (m, 2H), 1.44 - 1.39 (m, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 198.75, 163.48, 152.67 (dd, *J* =288.4, 286.9 Hz), 136.95, 133.24(dd, *J* =3.0, 1.5 Hz), 130.40, 130.35, 130.16, 129.76(d, *J* =1.5 Hz), 127.89, 125.85, 113.80, 90.96(dd, *J* = 22.7, 18.1 Hz), 55.58, 38.01, 29.00 (d, *J* =1.5 Hz), 27.29 (t, *J* =3.0 Hz), 24.24, 19.61 (d, *J* =1.5 Hz); ^{19}F NMR (565 MHz, Chloroform-*d*) δ -91.78 (d, *J* = 45.2 Hz), -91.93 (d, *J* = 45.2 Hz). HRMS Calcd. For $[C_{21}H_{23}F_2O_2]^+$: 345.1661, found: 345.1660.

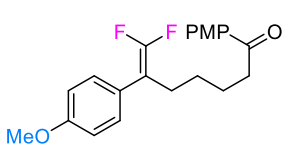


(3h) 6-(p-tolyl)-7,7-difluoro-1-(4-methoxyphenyl) hept-6-en-1-one: Colorless oil (59mg, 86%Yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 6.0 Hz, 2H), 7.20 - 7.15 (m, 4H), 6.92 (d, *J* = 12.0 Hz, 2H), 3.86 (s, 3H), 2.87 (t, *J* = 6.0 Hz, 2H), 2.45 - 2.42 (m, 2H), 2.35 (s, 3H), 1.75 –

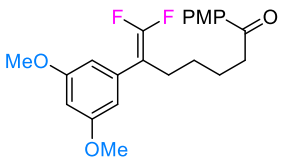
1.70 (m, 2H), 1.47 - 1.42 (m, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 198.84, 163.45, 153.61 (dd, *J* = 288.4, 286.9 Hz), 137.10, 130.64 (d, *J* = 1.5 Hz), 130.39, 130.14, 129.27, 128.21 (t, *J* = 3.0 Hz), 113.78, 92.00 (dd, *J* = 18.1, 16.6 Hz), 55.58, 37.98, 27.56 (d, *J* = 9.1 Hz), 23.93, 21.27; ^{19}F NMR (565 MHz, Chloroform-*d*) δ -92.08. HRMS Calcd. For $[C_{21}H_{23}F_2O_2]^+$: 345.1661, found: 345.1660.



(3i) 6-(3,5-dimethylphenyl)-7,7-difluoro-1-(4-methoxyphenyl) hept-6-en-1-one: Colorless oil (48mg, 67%Yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 12.0 Hz, 2H), 6.94 – 6.89 (m, 5H), 3.87 (s, 3H), 2.88 (t, *J* = 6.0 Hz, 2H), 2.43 - 2.40 (m, 2H), 2.31 (s, 6H), 1.77 – 1.71 (m, 2H), 1.46 – 1.41 (m, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 198.76, 163.37, 153.66 (dd, *J* = 288.4, 286.9 Hz), 137.88, 133.45, 130.29 (dd, *J* = 4.5, 3.0 Hz), 130.09, 129.00, 126.09 (t, *J* = 3.0 Hz), 113.69, 92.16 (dd, *J* = 21.1, 12.1 Hz), 55.46, 37.88, 27.55 (d, *J* = 22.6 Hz), 23.86, 21.34; ^{19}F NMR (565 MHz, Chloroform-*d*) δ -91.82 (d, *J* =45.2 Hz), -92.19 (d, *J* = 45.2 Hz). HRMS Calcd. For $[C_{22}H_{25}F_2O_2]^+$: 359.1817, found: 359.1817.

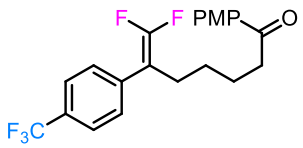


(3j) 6-(4-methoxyphenyl)-7,7-difluoro-1-(4-methoxyphenyl)hept-6-en-1-one: Colorless oil (22mg, 30%Yield); ^{1}H NMR (500 MHz, Chloroform-*d*) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 10.0 Hz, 2H), 7.22 (d, *J* = 10.0 Hz, 2H), 6.92 (d, *J* = 10.0 Hz, 2H), 6.88 (d, *J* = 10.0 Hz, 2H), 3.86 (s, 3H), 3.81 (s, 3H), 2.87 (t, *J* = 5.0 Hz, 2H), 2.43-2.39 (m, 2H), 1.76-1.69 (m, 2H), 1.47 – 1.42 (m, 2H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 198.85, 163.49, 158.78, 153.60 (t, *J* = 345.8 Hz), 130.41, 130.19, 129.49 (t, *J* = 4.5 Hz), 125.83, 114.02, 113.81, 91.67 (t, *J* = 19.6 Hz), 55.59, 55.38, 37.99, 27.69, 27.52 (t, *J* = 10.0 Hz), 23.95; ^{19}F NMR (565 MHz, Chloroform-*d*) δ -92.58. HRMS Calcd. For $[C_{21}H_{23}F_2O_3]^+$: 361.1610, found: 361.1609.

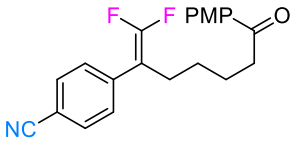


(3k) 6-(3,5-dimethoxyphenyl)-7,7-difluoro-1-(4-methoxyphenyl) hept-6-en-1-one: Colorless oil (58mg, 74%Yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 10.0 Hz, 2H), 6.92 (d, *J* = 10.0 Hz, 2H), 6.45 (s, 2H), 6.38 (t, *J* = 5.0 Hz, 1H), 3.86 (s, 3H), 3.78 (s, 6H), 2.87 (t, *J* = 5.0 Hz, 2H), 2.42 – 2.39 (m, 2H), 1.76 – 1.70 (m, 2H), 1.49 – 1.43 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ

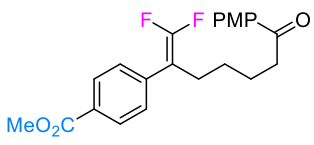
198.81, 163.50, 160.79, 153.71 (dd, *J* = 291.1, 286.3 Hz), 135.74 (dd, *J* = 5.0, 2.6 Hz), 130.41, 130.19, 113.82, 106.78, 99.35, 92.37 (dd, *J* = 22.7, 12.6 Hz), 55.59, 55.47, 37.98, 27.73, 27.55, 23.97. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -90.40 (d, *J* = 42.4 Hz), -91.33 (d, *J* = 42.4 Hz). HRMS Calcd. For $[C_{22}H_{25}F_2O_4]^+$: 391.1715, found: 391.1715.



(31) 6-(4-(trifluoromethyl)phenyl)-7,7-difluoro-1-(4-methoxyphenyl)hept-6-en-1-one: Colorless oil (48mg, 61%Yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 12.0 Hz, 2H), 7.25 (dd, *J* = 12.0, 6.0 Hz, 2H), 7.03 (t, *J* = 12.0 Hz, 2H), 6.92 (d, *J* = 6.0 Hz, 2H), 3.86 (s, 3H), 2.87 (t, *J* = 6.0 Hz, 2H), 2.44 - 2.40 (m, 2H), 1.75 – 1.70 (m, 2H), 1.45 – 1.39 (q, *J* = 7.7 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 197.47, 162.38, 152.82 (dd, *J* = 292.9, 288.4 Hz), 136.39, 129.22, 128.93, 128.26 (q, *J* = 32.5 Hz), 127.51 (t, *J* = 4.5 Hz), 124.37 (q, *J* = 4.5 Hz), 123.01 (q, *J* = 271.8 Hz), 112.66, 90.54 (dd, *J* = 22.7, 12.1 Hz), 54.41, 36.65, 26.29, 26.24, 22.64. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -62.61, -89.43 (d, *J* = 45.2 Hz), -89.89 (d, *J* = 39.6 Hz). HRMS Calcd. For $[C_{21}H_{20}F_5O_2]^+$: 399.1378, found: 399.1378.

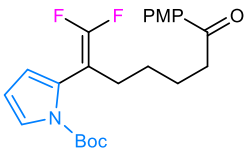


(3m) 4-(1,1-difluoro-7-(4-methoxyphenyl)-7-oxohept-1-en-2-yl) benzonitrile: Colorless oil (56mg, 79%Yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 6.0 Hz, 2H), 7.63 (d, *J* = 12.0 Hz, 2H), 7.42 (d, *J* = 6.0 Hz, 2H), 6.92 (d, *J* = 6.0 Hz, 2H), 3.86 (s, 3H), 2.88 (t, *J* = 6.0 Hz, 2H), 2.47 (t, *J* = 6.0 Hz, 2H), 1.75 – 1.70 (m, 2H), 1.45 – 1.40 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 198.53, 163.55, 154.08 (dd, *J* = 292.9, 288.4 Hz), 138.74 (t, *J* = 4.5 Hz), 132.38, 130.37, 130.02, 128.95 (t, *J* = 3.0 Hz), 118.81, 113.83, 111.01, 91.72 (dd, *J* = 22.7, 10.6 Hz). 55.61, 37.73, 27.50, 27.16, 23.73. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -87.81(d, *J* = 39.5 Hz), -88.43 (d, *J* = 33.9 Hz). HRMS Calcd. For $[C_{21}H_{20}F_2NO_2]^+$: 356.1457, found: 356.1456.

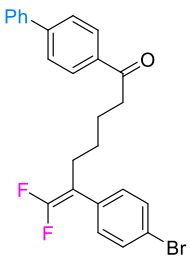


(3n) methyl 4-(1,1-difluoro-7-(4-methoxyphenyl)-7-oxohept-1-en-2-yl)benzoate: Colorless oil (64mg, 83%Yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 6.0 Hz, 2H), 7.89 (d, *J* = 12.0 Hz, 2H), 7.38 (d, *J* = 6.0 Hz, 2H), 6.92 (d, *J* = 6.0 Hz, 2H), 3.91 (s, 3H), 3.86 (s, 3H), 2.87 (t, *J* = 6.0 Hz, 2H), 2.49 – 2.46(m, 2H), 1.75 – 1.70 (m, 2H), 1.46 – 1.41 (m, 2H). ^{13}C NMR (151 MHz,

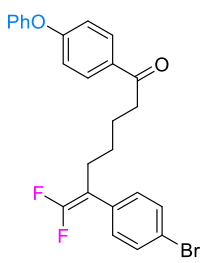
Chloroform-*d*) δ 198.67, 166.86, 163.50, 153.94 (dd, *J* = 292.9, 288.4 Hz), 138.58 (t, *J* = 4.5 Hz), 130.38, 130.08, 129.83, 128.99, 128.27, 113.80, 91.99 (dd, *J* = 22.7, 12.1 Hz), 55.58, 52.28, 37.85, 27.54, 27.30, 23.83. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -89.18 (d, *J* = 39.5 Hz) , -89.46 (d, *J* = 39.5 Hz). HRMS Calcd. For $[C_{22}H_{23}F_2O_4]^+$: 389.1559, found: 389.1561.



(3o) tert-butyl 2-(1,1-difluoro-7-(4-methoxyphenyl)-7-oxohept-1-en-2-yl)-1H-pyrrole-1-carboxylate: light brown oil (52mg, 61%Yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 6.0 Hz, 2H), 7.29 (dd, *J* = 6.0, 3.0 Hz 1H), 6.92 (d, *J* = 12.0 Hz, 2H), 6.15 (t, *J* = 6.0 Hz, 1H), 6.09 (dd, *J* = 3.0, 1.5 Hz, 1H), 3.83 (s, 3H), 2.88 (t, *J* = 6.0 Hz, 2H), 2.29 - 2.27 (m, 2H), 1.74 – 1.69 (m, 2H), 1.56 (s, 9H), 1.44 – 1.38 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 198.90, 163.47, 153.79 (dd, *J* = 292.9, 286.9 Hz), 148.91, 130.43, 130.17, 121.55, 115.45, 110.55, 86.16 (dd, *J* = 27.2, 12.1 Hz), 83.99, 55.61, 38.07, 28.43, 28.01, 27.28, 24.04. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -88.56 (d, *J* = 39.6 Hz), -92.41 (d, *J* = 45.2 Hz). HRMS Calcd. For $[C_{23}H_{28}F_2NO_4]^+$: 420.1981, found: 420.1983.

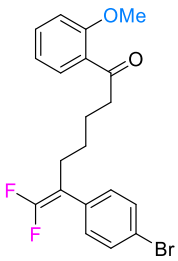


(4a) 1-([1,1'-biphenyl]-4-yl)-6-(4-bromophenyl)-7,7-difluorohept-6-en-1-one: White solide (42mg, 46%Yield); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.00 (d, *J* = 12.0 Hz, 2H), 7.80 (d, *J* = 12.0 Hz, 2H), 7.73 (d, *J* = 12.0 Hz, 2H), 7.58 (d, *J* = 12.0 Hz, 2H), 7.52 – 7.47 (m, 2H), 7.44 – 7.39 (m, 1H), 7.32 (d, *J* = 12.0 Hz, 2H), 3.00 (t, *J* = 12.0 Hz, 2H), 2.49 – 2.36 (m, 2H), 1.68 – 1.53 (m, 2H), 1.40 – 1.25 (m, 2H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 199.40, 144.41, 138.92, 135.42, 131.54, 130.34 (t, *J* = 4.5 Hz), 129.09, 128.60, 128.35, 126.97, 126.86, 120.73, 91.88 (dd, *J* = 31.7, 21.1 Hz), 37.51, 26.64, 23.07; ^{19}F NMR (565 MHz, Chloroform-*d*) δ -90.50 (d, *J* = 39.5 Hz), -90.70 (d, *J* = 39.5 Hz). HRMS Calcd. For $[C_{25}H_{22}BrF_2O]^+$: 455.0817, found: 455.0816.

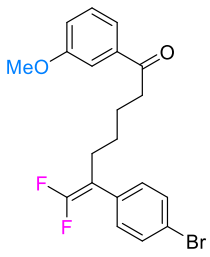


(4b) 6-(4-bromophenyl)-7,7-difluoro-1-(4-phenoxyphenyl)hept-6-en-1-one: Colorless oil(52mg, 55%Yield); ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.94 (d, *J* =12.0 Hz, 2H), 7.58 (d, *J* = 12.0 Hz, 2H), 7.46 (t, *J* =12.0 Hz, 2H), 7.32 (d, *J* = 12.0 Hz, 2H), 7.27 – 7.20 (m, 1H), 7.11 (d, *J* = 12.0 Hz, 2H), 7.02 (d,

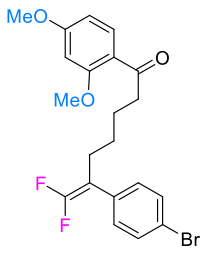
J = 12.0 Hz, 2H), 2.93 (t, *J* = 7.2 Hz, 2H), 2.47 – 2.37 (m, 2H), 1.67 – 1.48 (m, 2H), 1.39 – 1.26 (m, 2H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 198.34, 161.11, 155.03, 131.53, 131.48, 130.42, 130.34, 124.74, 120.72, 119.96, 117.16, 91.88 (dd, *J* = 31.71, 19.6 Hz), 37.25, 26.64, 23.12; ^{19}F NMR (565 MHz, DMSO-d_6) δ -91.47 (d, *J* = 45.2 Hz), -91.62 (d, *J* = 45.2 Hz). HRMS Calcd. For $[C_{25}H_{22}BrF_2O]^+$: 471.0766, found: 471.0764.



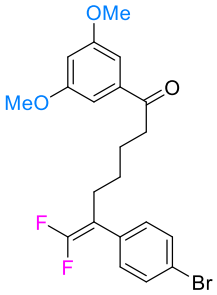
(4c) 6-(4-bromophenyl)-7,7-difluoro-1-(2-methoxyphenyl)hept-6-en-1-one: Colorless oil(57mg, 70%Yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.62 (dd, *J* = 12.0, 6.0 Hz, 1H), 7.50 – 7.42 (m, 3H), 7.16 (d, *J* = 6.0 Hz, 2H), 6.98 (t, *J* = 12.0 Hz, 1H), 6.94 (d, *J* = 12.0 Hz, 1H), 3.86 (s, 3H), 2.93 (t, *J* = 6.0 Hz, 2H), 2.45 – 2.31 (m, 2H), 1.72 – 1.62 (m, 2H), 1.44 – 1.34 (m, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 202.74, 158.45, 153.60 (dd, *J* = 291.4, 288.4 Hz), 133.38, 132.68 (t, *J* = 4.5 Hz), 131.70, 130.25, 129.99, 128.55, 121.22, 120.75, 111.57, 91.59 (dd, *J* = 22.6, 13.5 Hz), 55.54, 43.37, 27.42, 23.71; ^{19}F NMR (565 MHz, Chloroform-*d*) δ -90.63 (d, *J* = 39.5 Hz), -90.84 (d, *J* = 45.2 Hz). HRMS Calcd. For $[C_{20}H_{20}BrF_2O_2]^+$: 409.0609, found: 409.0611.



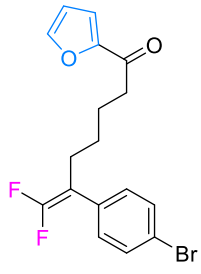
(4d) 6-(4-bromophenyl)-7,7-difluoro-1-(3-methoxyphenyl)hept-6-en-1-one: Colorless oil(42mg, 51%Yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.50 – 7.44 (m, 4H), 7.35 (t, *J* = 12.0 Hz, 1H), 7.17 (d, *J* = 6.0 Hz, 2H), 7.10 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.85 (s, 3H), 2.91 (t, *J* = 6.0 Hz, 2H), 2.44 – 2.41 (m, 2H), 1.80 – 1.66 (m, 2H), 1.48 – 1.39 (m, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 199.90, 159.97, 153.68 (dd, *J* = 289.9, 286.9 Hz), 138.42, 132.63 (dd, *J* = 4.5, 3.0 Hz), 131.77, 130.02 (t, *J* = 3.0 Hz), 129.70, 121.34, 120.76, 119.55, 112.43, 91.52 (dd, *J* = 22.6, 13.5 Hz), 55.57, 38.33, 27.44, 27.38 (t, *J* = 3.0 Hz), 23.68; ^{19}F NMR (565 MHz, Chloroform-*d*) δ -90.54 (d, *J* = 45.2 Hz), -90.71 (d, *J* = 39.5 Hz). HRMS Calcd. For $[C_{20}H_{20}BrF_2O_2]^+$: 409.0609, found: 409.0609.



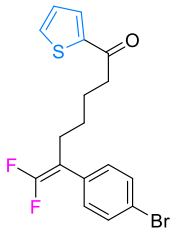
(4e) 6-(4-bromophenyl)-1-(2,4-dimethoxyphenyl)-7,7-difluorohept-6-en-1-one: Colorless oil(81mg, 92%Yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 6.0 Hz, 1H), 7.46 (d, *J* = 12.0 Hz, 2H), 7.16 (d, *J* = 6.0 Hz, 1H), 6.51 (dd, *J* = 12.0, 6.0 Hz, 1H), 6.44 (d, *J* = 6.0 Hz, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 2.89 (t, *J* = 12.0 Hz, 2H), 2.44 – 2.32 (m, 2H), 1.72 – 1.58 (m, 2H), 1.45 – 1.18 (m, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 200.36, 164.40, 160.76, 153.64 (dd, *J* = 291.4, 288.4 Hz), 132.75, 131.71, 130.03 (t, *J* = 3.0 Hz), 121.32, 121.22, 105.17, 98.51, 91.68 (dd, *J* = 22.6, 13.5 Hz), 55.65, 55.54, 43.25, 27.52 (d, *J* = 3.0 Hz), 23.94; ^{19}F NMR (565 MHz, Chloroform-*d*) δ -90.64 (d, *J* = 39.5 Hz), -90.89 (d, *J* = 39.5 Hz). HRMS Calcd. For $[C_{21}H_{22}BrF_2O_3]^+$: 439.0715, found: 439.0715.



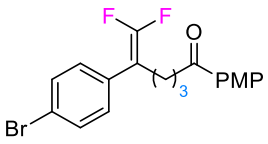
(4f) 6-(4-bromophenyl)-1-(3,5-dimethoxyphenyl)-7,7-difluorohept-6-en-1-one: Colorless oil(50mg, 57%Yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 6.0 Hz, 2H), 7.16 (d, *J* = 6.0 Hz, 2H), 7.04 (d, *J* = 6.0 Hz, 2H), 6.66 – 6.61 (m, 1H), 3.82 (s, 6H), 2.93 – 2.81 (m, 2H), 2.49 – 2.38 (m, 2H), 1.79 – 1.67 (m, 2H), 1.50 – 1.37 (m, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 199.73, 160.98, 153.65 (dd, *J* = 291.4, 288.4 Hz), 138.97, 132.60 (t, *J* = 3.0 Hz), 131.75, 130.02, 130.00, 129.97, 121.32, 105.97, 105.23, 91.51 (dd, *J* = 21.1, 13.5 Hz), 55.68, 38.30, 27.41, 27.34, 23.70; ^{19}F NMR (565 MHz, Chloroform-*d*) δ -90.53 (d, *J* = 33.9 Hz), -90.72 (d, *J* = 39.5 Hz). HRMS Calcd. For $[C_{21}H_{22}BrF_2O_3]^+$: 439.0715, found: 439.0716.



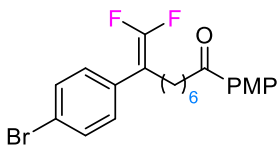
(4g) 6-(4-bromophenyl)-7,7-difluoro-1-(furan-2-yl)hept-6-en-1-one: Color-less oil(55mg, 75%Yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.58 – 7.54 (m, 1H), 7.46 (d, *J* = 6.0 Hz, 2H), 7.18 – 7.14 (m, 3H), 6.56 – 6.46 (m, 1H), 2.77 (t, *J* = 12.0 Hz, 2H), 2.48 – 2.40 (m, 2H), 1.77 – 1.64 (m, 2H), 1.45 – 1.33 (m, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 189.31, 153.67 (dd, *J* = 289.9, 286.9 Hz), 152.84, 146.36, 132.60 (dd, *J* = 4.5, 3.0 Hz), 131.76, 130.00, 121.34, 116.98, 112.30, 91.48 (dd, *J* = 22.6, 13.6 Hz), 38.04, 27.35 (d, *J* = 1.5 Hz), 23.51; ^{19}F NMR (565 MHz, Chloroform-*d*) δ -90.55 (d, *J* = 45.2 Hz), -90.69 (d, *J* = 39.5 Hz). HRMS Calcd. For $[C_{17}H_{16}BrF_2O_2]^+$: 369.0296, found: 369.0296.



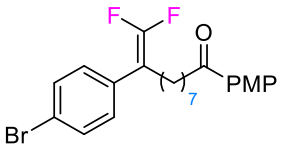
(4h) 6-(4-bromophenyl)-7,7-difluoro-1-(thiophen-2-yl)hept-6-en-1-one: Light brown oil(47mg, 61%Yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.56 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.47 (d, *J* = 5.0 Hz, 2H), 7.16 (d, *J* = 10.0 Hz, 2H), 7.14 (d, *J* = 5.0 Hz, 1H), 6.51 (dd, *J* = 3.6, 1.7 Hz, 1H), 2.78 (t, *J* = 5.0 Hz, 2H), 2.48 – 2.38 (m, 2H), 1.74 – 1.68 (m, 2H), 1.45 – 1.39 (m, 2H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 189.31, 153.68 (dd, *J* = 292.3, 288.5 Hz), 152.86, 146.36, 132.61 (dd, *J* = 3.78, 2.52 Hz), 131.4 (q, *J* = 205.4, Hz), 130.01 (t, *J* = 2.5 Hz), 121.34, 116.98, 112.31, 91.49 (dd, *J* = 21.4, 13.9 Hz), 38.05, 27.36(d, *J* = 5.0 Hz), 23.51; ^{19}F NMR (471 MHz, Chloroform-*d*) δ -90.57(d, *J* = 37.7 Hz), 90.67 (d, *J* = 42.4 Hz). HRMS Calcd. For $[C_{17}H_{16}BrF_2OS]^+$: 385.0068, found: 385.0069.



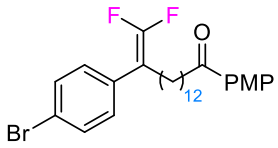
(4i)5-(4-bromophenyl)-6,6-difluoro-1-(4-methoxyphenyl)hex-5-en-1-one: Colorless oil(50mg, 64%Yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 6.0 Hz, 2H), 7.48 (d, *J* = 6.0 Hz, 2H), 7.22 (d, *J* = 12.0 Hz, 2H), 6.91 (d, *J* = 6.0 Hz, 2H), 3.87 (s, 3H), 2.90 (t, *J* = 6.0 Hz, 2H), 2.48 (t, *J* = 6.0 Hz, 2H), 1.80 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 198.07, 163.46, 153.69 (dd, *J* = 291.4, 288.4 Hz), 132.36 – 132.31 (m), 131.71, 130.22, 129.93, 129.86 (t, *J* = 3.0 Hz), 121.28, 113.73, 91.35 (dd, *J* = 22.6, 13.6 Hz), 55.49, 37.03, 26.88, 22.41. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -90.00 (d, *J* = 39.5 Hz), -90.20 (d, *J* = 39.5 Hz). HRMS Calcd. For $[C_{19}H_{18}BrF_2O_2]^+$: 395.0453, found: 395.0455.



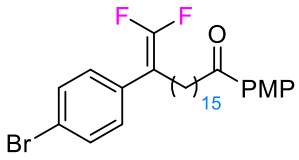
(4j) 8-(4-bromophenyl)-9,9-difluoro-1-(4-methoxyphenyl)non-8-en-1-one: Colorless oil(73mg, 84%Yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92 (d, *J* =6.0 Hz, 2H), 7.46 (d, *J* =6.0 Hz, 2H), 7.16 (d, *J* =6.0 Hz, 2H), 6.92 (d, *J* =6.0 Hz, 2H), 3.86 (s, 3H), 2.88 (t, *J* = 6.0 Hz, 2H), 2.37 – 2.34 (m, 2H), 1.69 – 1.67 (m, 2H), 1.36 – 1.31 (m, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 199.14, 163.47, 153.62 (dd, *J* = 289.9, 286.9 Hz), 132.87 – 132.82 (m), 131.71, 130.41, 130.26, 129.99 (t, *J* = 3.0 Hz), 121.23, 113.79, 91.80 (dd, *J* = 22.7, 12.1 Hz), 55.58, 38.23, 29.12, 28.92, 27.64, 27.49, 24.53. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -90.84 (d, *J* = 39.5 Hz), -91.02 (d, *J* = 39.5 Hz). HRMS Calcd. For $[C_{22}H_{24}BrF_2O_2]^+$: 437.0922, found: 437.0924.



(4k) 9-(4-bromophenyl)-10,10-difluoro-1-(4-methoxyphenyl)dec-9-en-1-one: Colorless oil(74mg, 82%Yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 12.0 Hz, 2H), 7.46 (d, *J* = 6.0 Hz, 2H), 7.16 (d, *J* = 6.0 Hz, 2H), 6.92 (d, *J* = 6.0 Hz, 2H), 3.85 (s, 3H), 2.88 (t, *J* = 6.0 Hz, 2H), 2.44 – 2.25 (m, 2H), 1.68 (m, 2H), 1.41 – 1.10 (m, 8H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 198.04, 162.29, 152.45 (dd, *J* = 291.4, 286.9 Hz), 131.72 (dd, *J* = 4.5, 3.0 Hz), 130.54, 129.26, 129.13, 128.84 (t, *J* = 3.0 Hz), 120.04, 112.64, 90.69 (dd, *J* = 22.7, 12.1Hz), 54.43, 37.15, 28.22, 28.07, 27.74, 26.56, 26.35, 23.43. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -90.87 (d, *J* = 45.2 Hz), -91.02 (d, *J* = 39.5 Hz). HRMS Calcd. For $[C_{23}H_{26}BrF_2O_2]^+$: 451.1079, found: 451.1078

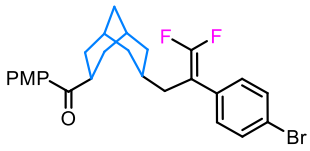


(4l) 14-(4-bromophenyl)-15,15-difluoro-1-(4-methoxyphenyl) pentadec-14-en-1-one: Colorless oil(77mg, 74%Yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 6.0 Hz, 2H), 7.47 (d, *J* = 12.0 Hz, 2H), 7.17 (d, *J* =12.0 Hz, 2H), 6.93 (d, *J* = 6.0 Hz, 2H), 3.87 (s, 3H), 2.90 (t, *J* = 6.0 Hz, 2H), 2.36 – 2.34 (m, 2H), 1.73 – 1.68 (m, 2H), 1.36 – 1.23 (m, 18H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 199.46, 163.41, 153.58 (dd, *J* = 291.4, 286.9 Hz), 133.03 – 132.77 (m), 131.68, 130.45, 130.28, 130.01 (t, *J* = 3.0 Hz), 121.17, 113.77, 91.87 (dd, *J* = 22.7, 13.6 Hz), 55.58, 38.45, 29.69 – 29.56 (m), 29.36, 29.06, 27.76 - 27.73(m), 27.52, 24.75. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -90.93 (d, *J* = 45.2 Hz), -91.14 (d, *J* = 45.2 Hz). HRMS Calcd. For $[C_{28}H_{36}BrF_2O_2]^+$: 521.1861, found: 521.1859

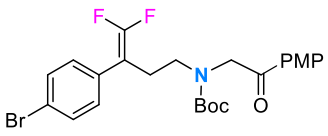


(4m) 17-(4-bromophenyl)-18,18-difluoro-1-(4-methoxyphenyl) octa--dec-17-en-1-one: Colorless oil(98mg, 87%Yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 12.0 Hz, 2H), 7.47 (d, *J* = 6.0 Hz, 2H), 7.17 (d, *J* = 12.0 Hz, 2H), 6.93 (d, *J* = 6.0 Hz, 1H), 3.85 (s, 3H), 2.90 (t, *J* = 6.0 Hz, 2H), 2.40 – 2.33 (m, 2H), 1.72 (m, 2H), 1.41 – 1.18 (m, 24H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 199.33, 162.90, 153.54 (dd, *J* = 282.37, 286.9 Hz), 132.88 – 132.83 (m), 131.65, 130.43, 130.21, 129.98 (t, *J* = 3.0 Hz), 121.14, 113.74, 91.84 (dd, *J* = 22.7, 12.1 Hz), 55.56, 42.21, 38.44, 30.03 – 29.41 (m), 29.37, 29.05, 27.71, 27.48, 26.80 (d, *J* = 7.6 Hz), 26.46, 26.30. ^{19}F NMR (565 MHz,

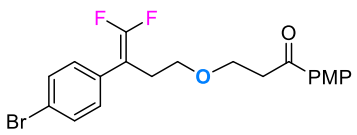
Chloroform-*d*) δ -90.93 (d, *J* = 45.2 Hz), -91.17 (d, *J* = 45.2 Hz). HRMS Calcd. For $[C_{31}H_{42}BrF_2O_2]^+$: 563.2331, found: 563.2330



(4n) ((3r,7r)-7-(2-(4-bromophenyl)-3,3-difluoroallyl)bicyclo [3.3.1]nonan-3-yl)(4-methoxyphenyl)methanone: White solide (52mg, 53%Yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 12.0 Hz, 2H), 7.49 (d, *J* = 6.0 Hz, 2H), 7.17 (d, *J* = 12.0 Hz, 2H), 6.91 (d, *J* = 12.0 Hz, 2H), 3.85 (s, 3H), 3.41 (m, 1H), 2.25 (d, *J* = 6.0 Hz, 2H), 2.14 (d, *J* = 12.0 Hz, 2H), 2.01 – 1.95 (m, 2H), 1.91 – 1.86 (m, 1H), 1.79 (d, *J* = 12.0 Hz, 1H), 1.51 (d, *J* = 12.0 Hz, 2H), 1.32 (t, *J* = 12.0 Hz, 2H), 1.12 (d, *J* = 12.0 Hz, 1H), 1.04 (td, *J* = 12.0, 6.0 Hz, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 202.81, 163.31, 154.01 (dd, *J* = 289.9, 286.9 Hz), 133.32 – 133.27 (m), 131.80, 130.55, 130.00 (t, *J* = 3.0 Hz), 129.77, 121.32, 113.79, 90.48 (dd, *J* = 22.7, 13.6 Hz), 55.57, 40.01, 37.50, 35.41, 29.87, 29.21, 26.01, 25.41; ^{19}F NMR (565 MHz, Chloroform-*d*) δ -89.98 (d, *J* = 39.6 Hz), -90.74 (d, *J* = 39.6 Hz). HRMS Calcd. For $[C_{26}H_{28}BrF_2O_2]^+$: 489.1235, found: 489.1233.

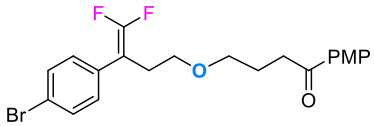


(4o) tert-butyl (3-(4-bromophenyl)-4,4-difluorobut-3-en-1yl)(2-(4-methoxyphenyl)-2-oxoethyl)carbamate: brown oil(84 mg, 82%Yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.90 – 7.87 (m, 2H), 7.46 (d, *J* = 6.0 Hz, 2H), 7.22 (dd, *J* = 12.0, 6.0 Hz, 2H), 6.94 (dd, *J* = 12.0, 6.0 Hz, 2H), 4.55 (s, 1H), 4.43 (s, 1H), 3.86 (d, *J* = 6.0 Hz, 3H), 3.35 (t, *J* = 12.0 Hz, 1H), 3.32 – 3.26 (t, *J* = 6.0 Hz, 1H), 2.68 - 2.66 (m, 2H), 1.46 (s, 6H), 1.34 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 193.87, 163.88, 155.77, 154.131 (dd, *J* = 291.4, 288.4 Hz), 132.25, 132.10, 131.79 (d, *J* = 3.2 Hz), 130.29, 130.06, 129.79, 129.62, 128.13 (d, *J* = 4.5 Hz), 121.39 (d, *J* = 7.6 Hz), 113.98 (d, *J* = 15.1 Hz), 89.34 (ddd, *J* = 51.3, 19.6, 13.6 Hz), 80.55, 55.59 (d, *J* = 6.0 Hz), 54.20, 53.58, 47.38, 47.12, 28.30 (d, *J* = 25.7 Hz), 26.82, 26.54. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -88.69, -89.05 (d, *J* = 39.6 Hz), -89.15 (d, *J* = 39.6 Hz). HRMS Calcd. For $[C_{24}H_{27}BrF_2NO_4]^+$: 510.1086, found: 510.1087.

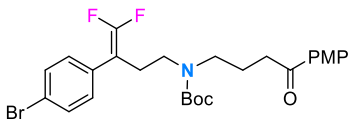


(4p) 3-((3-(4-bromophenyl)-4,4-difluorobut-3-en-1-yl)oxy)-1-(4-methoxyphenyl)propan-1-one: Colorless oil(78mg, 92%

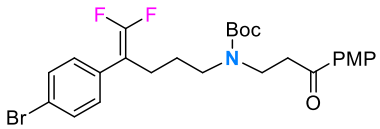
Yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 12.0 Hz, 2H), 7.43 (d, *J* = 12.0 Hz, 2H), 7.15 (d, *J* = 6.0 Hz, 2H), 6.94 (d, *J* = 6.0 Hz, 2H), 3.86 (s, 3H), 3.79 (t, *J* = 6.0 Hz, 2H), 3.44 (t, *J* = 6.0 Hz, 2H), 3.10 (t, *J* = 6.0 Hz, 2H), 2.60 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 197.04, 163.68, 154.04 (dd, *J* = 291.4, 288.6 Hz), 132.65 – 132.48 (m), 131.68, 130.56, 130.28, 130.10 (t, *J* = 3.0 Hz), 121.37, 113.85, 89.22(dd, *J* = 22.6 Hz, 15.1 Hz), 68.59, 66.53, 55.60, 38.44, 28.36; ^{19}F NMR (565 MHz, Chloroform-*d*) δ -89.44 (d, *J* = 39.5 Hz), -89.81 (d, *J* = 39.5 Hz). HRMS Calcd. For $[C_{20}H_{20}BrF_2O_3]^+$: 425.0558, found: 425.0558.



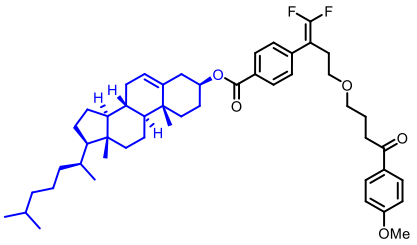
(4q) 4-((3-(4-bromophenyl)-4,4-difluorobut-3-en-1-yl)oxy)-1-(4-methoxyphenyl)butan-1-one: Colorless oil (76mg, 87% Yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 6.0 Hz, 2H), 7.44 (d, *J* =12.0 Hz, 2H), 7.18 (d, *J* = 12.0 Hz, 2H), 6.93 (d, *J* = 6.0 Hz, 2H), 3.86 (s, 3H), 3.44 (t, *J* = 6.0 Hz, 2H), 3.41 (t, *J* = 6.0 Hz, 2H), 2.94 (t, *J* = 12.0 Hz, 2H), 2.62 – 2.59 (m, 2H), 1.97 - 1.93(m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 198.64, 163.51, 154.1 (dd, *J* = 291.4, 288.4 Hz), 132.57 – 132.52 (m), 131.70, 130.39, 130.28, 130.04 (t, *J* = 3.0 Hz), 121.37, 113.84, 89.33 (dd, *J* = 21.1, 13.6 Hz), 70.04, 68.24, 55.56, 34.78, 28.40, 24.50; ^{19}F NMR (565 MHz, Chloroform-*d*) δ -89.41 (d, *J* = 39.5 Hz), -89.60 (d, *J* = 39.5 Hz). HRMS Calcd. For $[C_{21}H_{22}BrF_2O_3]^+$: 439.0715, found: 439.0713.



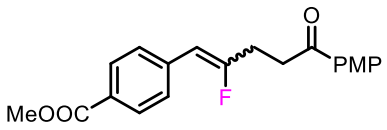
(4r) tert-butyl (3-(4-bromophenyl)-4,4-difluorobut-3-en-1-yl)(4-(4-methoxyphenyl)-4-oxobutyl)carbamate: Light brown oil (100mg, 93%Yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 6.0 Hz, 2H), 7.47 (d, *J* = 12.0 Hz, 2H), 7.22 (d, *J* = 12.0 Hz, 2H), 6.92 (d, *J* = 6.0 Hz, 2H), 3.86 (s, 3H), 3.23 (t, *J* = 6.0 Hz, 2H), 3.20 (t, *J* = 6.0 Hz, 2H), 2.88 (t, *J* = 6.0 Hz, 2H), 2.62 – 2.59 (m, 2H), 1.91 – 1.88 (m, 2H), 1.40 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 198.00 (d, *J* = 52.9 Hz), 163.55, 155.51, 154.22(dd, *J* = 291.4, 288.4 Hz), 132.27, 131.82, 130.34, 130.06 – 129.82 (m), 121.41, 113.82, 89.29 (d, *J* = 33.2 Hz), 79.73 (d, *J* = 19.6 Hz), 55.56, 46.71, 45.72, 35.20, 28.57, 27.00, 26.42 22.87. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -88.50 - -88.58 (m), -88.98 – -89.15 (m). HRMS Calcd. For $[C_{26}H_{31}BrF_2NO_4]^+$: 538.1399, found: 538.1397.



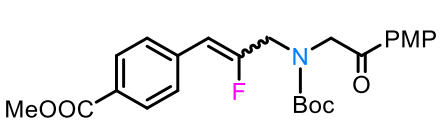
(4s) tert-butyl (4-(4-bromophenyl)-5,5-difluoropent-4-en-1-yl)(3-(4-methoxyphenyl)-3-oxopropyl)carbamate: Light brown oil (103mg, 96%Yield); ^{1}H NMR (600 MHz, Chlorofo -rm-*d*) δ 7.93 (d, *J* = 12.0 Hz, 2H), 7.47 (d, *J* = 6.0 Hz, 2H), 7.17 (d, *J* = 12.0 Hz, 2H), 6.93 (d, *J* = 6.0 Hz, 2H), 3.87 (s, 3H), 3.52 (t, *J* = 12.0 Hz, 2H), 3.27 –3.09 (m, 4H), 2.36 – 2.3 (m, 2H), 1.59 (d, *J* = 12.0 Hz, 2H), 1.42 (d, *J* = 12.0 Hz, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 197.83, 197.36, 164.06, 153.53 (dd, *J* = 288.4, 286.9 Hz), 132.42, 131.79, 130.49 (d, *J* = 13.6 Hz), 129.93 (d, *J* = 16.6 Hz), 121.39, 113.86, 91.25 (dd, *J* = 22.6, 13.6 Hz), 79.79 (d, *J* = 22.6 Hz), 55.60, 47.99, 46.83, 43.52 (d, *J* = 54.4 Hz), 37.57 (d, *J* = 33.2 Hz), 28.52, 26.81 (d, *J* = 87.6 Hz), 24.98; ^{19}F NMR (565 MHz, Chloroform-*d*) δ -90.08 (dd, *J* = 39.6 Hz, 22.6 Hz), -90.26 (d, *J* = 45.2 Hz), -90.48 (d, *J* = 45.2 Hz). HRMS Calcd. For $[C_{26}H_{31}BrF_2NO_4]^+$: 538.1399, found: 538.1401.



(4t) (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((S)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(1,1-difluoro-4-(4-(4-methoxyphenyl)-4-oxobutoxy)but-1-en-2-yl)benzoate: White solide (82mg, 53%Yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 12.0 Hz, 2H), 7.92 (d, *J* = 12.0 Hz, 2H), 7.39 (d, *J* = 12.0 Hz, 2H), 6.92 (d, *J* = 6.0 Hz, 2H), 5.41 (d, *J* = 6.0 Hz, 1H), 4.87 - 4.82 (m, 1H), 3.87 (s, 3H), 3.44 – 3.40 (m, 4H), 2.95 (t, *J* = 6.0 Hz, 2H), 2.68-2.66 (m, 2H), 2.44 (d, *J* = 6.0 Hz, 2H), 2.03 – 1.90 (m, 6H), 1.85 – 1.82 (m, 1H), 1.72 – 1.70 (m, 1H), 1.60 – 1.57 (m, 2H), 1.54 – 1.50 (m, 3H), 1.48 – 1.45 (m, 1H), 1.38 – 1.35 (m, 3H), 1.27 - 1.25 (m, 2H), 1.21 – 1.17 (m, 2H), 1.12 – 1.09 (m, 4H), 1.06 (s, 3H), 1.04 – 0.96 (m, 3H), 0.92 (d, *J* = 6.0 Hz, 3H), 0.86 (d, *J* = 6.0 Hz, 6H), 0.69(s, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 198.69, 165.69, 163.55, 154.37 (dd, *J* = 289.9, 286.9 Hz), 139.73, 138.29, 130.40, 130.16, 129.99, 129.77, 128.22 (t, *J* = 4.5 Hz), 122.95, 113.79, 89.78 (dd, *J* = 22.6, 15.1 Hz), 74.77, 70.08, 56.80, 56.23, 55.59, 53.57, 50.14, 42.43, 39.84, 39.63, 38.31, 37.14, 36.76, 36.30, 35.93, 34.73, 32.02 (d, *J* = 12.1 Hz), 28.37, 28.29, 28.15, 27.98, 24.47 (d, *J* = 16.6 Hz), 23.95, 22.96, 22.70, 21.17, 19.50, 18.84, 11.99; ^{19}F NMR (565 MHz, Chloroform-*d*) δ -88.28 (d, *J* = 33.9 Hz), -88.42 (d, *J* = 33.9 Hz). HRMS Calcd. For $[C_{49}H_{67}F_2O_5]^+$: 773.4951, found: 773.4956.

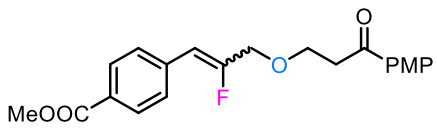


(6a) Methyl 4-(2-fluoro-5-(4-methoxyphenyl)-5-oxopent-1-en-1-yl)benzoate : Colorless oil(43.3mg, 63% Yield, 1:1 Z/E); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.05 – 7.91 (m, 8H), 7.52 (d, *J* = 6.0 Hz, 2H), 7.31 (d, *J* = 12.0 Hz, 2H), 6.94 (t, *J* = 12.0 Hz, 4H), 6.28 (d, *J* = 18.0 Hz, 1H), 5.64 (d, *J* = 42.0 Hz, 1H), 3.90 (s, 6H), 3.87 (s, 6H), 3.29 – 3.23 (q, *J* =6.0 Hz, 4H), 2.94 (dt, *J* = 24.0, 6.0 Hz, 2H), 2.82 (dt, *J* = 24.0, 6.0 Hz, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 196.63, 196.57, 167.04, 166.93, 163.82, 163.80, 163.03 (d, *J* = 93.6 Hz), 161.29 (d, *J* = 108.7 Hz), 138.85 (d, *J* = 13.6 Hz), 138.32 (d, *J* = 1.5 Hz), 130.45, 129.98, 129.85, 129.75, 129.66, 128.51 (d, *J* = 3.0 Hz), 128.32 (d, *J* = 6.0 Hz), 113.98, 113.95, 108.66 (d, *J* = 30.2 Hz), 106.26 (d, *J* = 7.5 Hz), 55.64, 52.25, 52.19, 34.85, 34.47, 28.00 (d, *J* = 25.6 Hz), 24.10 (d, *J* = 25.6 Hz); ^{19}F NMR (565 MHz, Chloroform-*d*) δ -96.41 (q, *J* = 22.6 Hz), -98.35 (dt, *J* = 39.5, 22.6 Hz); HRMS Calcd. For $[C_{20}H_{20}FO_4]^+$: 343.1340, found: 343.1344.

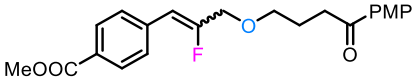


(6b) Methyl 4-(3-((tert-butoxycarbonyl)(2-(4-methoxyphenyl)-2-oxoethyl)amino)-2-fluoroprop-1-en-1-yl)--benzoate: Brown oil (81mg, 89%Yield, 1:1 Z/E) ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.97 (t, *J* = 12.0 Hz, 2H), 7.94 – 7.90 (m, 4H), 7.83 (dd, *J* = 18.0, 12.0 Hz, 2H), 7.52 (t, *J* = 6.0 Hz, 2H), 7.27 (d, *J* = 6.0 Hz, 1H), 7.19 (d, *J* = 12.0 Hz, 1H), 6.95 – 6.89 (m, 4H), 6.39 (dd, *J* = 24.0, 12.0 Hz, 1H), 5.72 (dd, *J* = 54.0, 42.0 Hz, 1H), 4.72 (d, *J* = 42.0 Hz, 2H), 4.58 (d, *J* = 72.0 Hz, 2H), 4.41 (dd, *J* = 30.0, 18.0 Hz, 2H), 4.22 (dd, *J* = 42.0, 18.0 Hz, 2H), 3.89 (s, 6H), 3.85 (s, 6H), 1.44 (d, *J* = 6.0 Hz, 9H), 1.35 (d, *J* = 6.0 Hz, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 193.13 (d, *J* = 9.0 Hz), 192.81 (d, *J* = 13.6 Hz), 166.76 (d, *J* = 6.4 Hz), 166.62 (d, *J* = 13.6 Hz), 163.88 (d, *J* = 13.5 Hz), 159.23 (d, *J* = 43.8 Hz), 158.64, 157.52 (d, *J* = 43.8 Hz), 156.84, 155.46 – 155.42 (m), 137.57 – 137.31 (m), 130.14 (t, *J* = 18.1 Hz), 129.99 (t, *J* = 15.1 Hz), 128.88 (d, *J* = 6.0 Hz), 128.74 (d, *J* = 12.0 Hz), 128.56, 128.42 (d, *J* = 6.0 Hz), 128.09, 128.05 (d, *J* = 4.5 Hz), 113.94 (t, *J* = 15.1 Hz), 111.59 (d, *J* = 27.2 Hz), 110.88 (d, *J* = 28.7 Hz), 107.88 (d, *J* = 6.0 Hz), 107.31 (d, *J* = 6.0 Hz), 81.01 (d, *J* = 18.1 Hz), 80.81 (d, *J* = 19.6 Hz), 55.51 (t, *J* = 4.0 Hz), 52.70, 52.34, 52.23, 52.14 (d, *J* = 3.0 Hz), 52.10, 49.17 (dd, *J* = 34.7, 30.2 Hz), 44.77 (dd, *J* = 25.7, 12.1 Hz), 28.31, 28.15. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -100.73 (q, *J* = 16.9

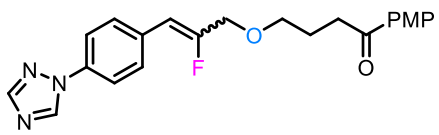
Hz), -102.56 (q, *J* = 22.6 Hz), -104.74 (dt, *J* = 39.5, 16.9 Hz), -105.53 (dt, *J* = 39.5, 16.9 Hz). HRMS Calcd. For $[C_{25}H_{29}FNO_6]^+$: 458.1973, found: 458.1972.



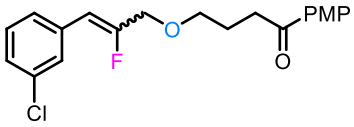
(6c) Methyl 4-(2-fluoro-3-(3-(4-methoxyphenyl)-3-oxopropoxy)prop-1-en-1-yl)benzoate: Colorless oil(68mg, 91% Yield, 1.5:1 Z/E) ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 6.0 Hz, 5H), 7.96 – 7.94 (m, 5H), 7.55 (d, *J* = 6.0 Hz, 3H), 7.31 (d, *J* = 3.0 Hz, 2H), 6.93 (d, *J* = 12.0 Hz, 5H), 6.45 (d, *J* = 18.0 Hz, 1H), 5.82 (d, *J* = 42.0 Hz, 1.5H), 4.24 (s, 1H), 4.20 (s, 2.5H), 4.17 (s, 1.5H), 3.99 (t, *J* = 6.0 Hz, 3H), 3.96 (t, *J* = 6.0 Hz, 2H), 3.90 (s, 7.5H), 3.86 (s, 7.5H), 3.33 – 3.20 (m, 5H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 196.59, 196.49, 166.92, 166.85, 163.76, 163.73, 159.35 (d, *J* = 259.7 Hz), 157.94 (d, *J* = 271.8 Hz), 137.93 (d, *J* = 12.1 Hz), 137.43 (d, *J* = 3.0 Hz), 130.55, 130.54, 130.13, 130.11, 129.92, 129.85, 129.16, 128.88 (d, *J* = 1.5 Hz), 128.74, 128.68, 113.90, 112.67 (d, *J* = 27.2 Hz), 108.00 (d, *J* = 4.5 Hz), 69.46, 66.44 (d, *J* = 28.7 Hz), 55.60, 52.26, 52.21, 38.44, 38.37; ^{19}F NMR (565 MHz, Chloroform-*d*) δ -99.52 (q, *J* = 22.6 Hz), -107.54 (dt, *J* = 39.5, 11.3Hz). HRMS Calcd. For $[C_{21}H_{22}FO_5]^+$: 373.1446, found: 373.1447.



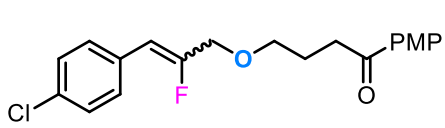
(6d) Methyl 4-(2-fluoro-3-(4-(4-methoxyphenyl)-4-oxobutoxy)prop-1-en-1-yl)benzoate: Colorless oil(66mg, 86% Yield, 1.6:1 Z/E) ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.99 – 7.93 (m, 10.5H), 7.54 (d, *J* = 6.0 Hz, 3.2H), 7.32 (d, *J* = 6.0 Hz, 2H), 6.93 (q, *J* = 6.0 Hz, 5.3H), 6.45 (d, *J* = 18.0 Hz, 1H), 5.79 (d, *J* = 42.0 Hz, 1.6H), 4.17 (d, *J* = 24.0 Hz, 2H), 4.13 (d, *J* = 12.0 Hz, 3.3H), 3.91 (s, 8H), 3.86 (s, 8H), 3.64 (t, *J* = 6.0 Hz, 3.3H), 3.61 (t, *J* = 6.0 Hz, 2H), 3.06 (q, *J* = 6.0 Hz, 5.4H), 2.07 (td, *J* = 12.0, 6.0 Hz, 5.5H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 198.46, 198.44, 166.90, 166.80, 163.54, 159.57 (d, *J* = 259.7 Hz), 159.18 (d, *J* = 271.8 Hz), 137.99 (d, *J* = 12.1 Hz), 137.42 (d, *J* = 3.0 Hz), 130.41, 130.17, 129.90, 129.85, 129.14, 128.87 (d, *J* = 1.5 Hz), 128.66 (dd, *J* = 6.0, 3.0 Hz), 113.81, 112.47 (d, *J* = 27.2 Hz), 107.90 (d, *J* = 4.5 Hz), 70.25, 70.19, 69.21 (d, *J* = 31.7 Hz), 66.08 (d, *J* = 28.7 Hz), 55.56, 52.26, 52.21, 34.56, 24.41; ^{19}F NMR (565 MHz, Chloroform-*d*) δ -99.29 (q, *J* = 22.6 Hz), -107.29 (dt, *J* = 33.9, 11.3 Hz); HRMS Calcd. For $[C_{22}H_{24}FO_5]^+$: 387.1602, found: 387.1603.



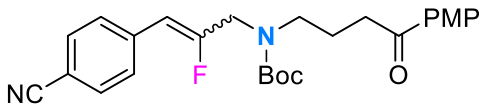
(6e)4-((3-(4-(1H-1,2,4-triazol-1-yl)phenyl)-2-fluoroallyl)oxy)-1-(4-methoxyphenyl)butan-1-one: Brown oil(28mg, 35%Yield, 1.2:1 Z/E) ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.55 (d, *J* = 24.0 Hz, 2.2H), 8.10 (s, 2.2H), 7.95 (dd, *J* = 12.0, 6.0 Hz, 4.4H), 7.64 – 7.59 (m, 6.6H), 7.38 (d, *J* = 12.0 Hz, 2.2H), 6.92 (d, *J* = 6.0 Hz, 4.4H), 6.44 (d, *J* = 18.0 Hz, 1H), 5.78 (d, *J* = 36.0 Hz, 1.2H), 4.18 (s, 1H), 4.14 (s, 2.2H), 4.12 (s, 1.2H), 3.85 (s, 6.6H), 3.63 (dt, *J* = 24.0, 6.0 Hz, 4.6H), 3.08 – 3.03 (m, 4.5H), 2.07 (m, 4.5H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 198.47, 198.39, 163.57, 163.57, 158.34 (t, *J* = 258.2 Hz), 152.75, 140.92, 136.12, 135.81, 133.38 (d, *J* = 12.1 Hz), 132.97 (d, *J* = 3.0 Hz), 130.42, 130.41, 130.17 (d, *J* = 1.5 Hz), 130.13, 130.08, 130.06, 120.15, 120.01, 113.84, 113.82, 112.03 (d, *J* = 27.2 Hz), 107.51 (d, *J* = 6.0 Hz), 70.22, 69.26 (d, *J* = 30.2 Hz), 66.12 (d, *J* = 30.2 Hz), 55.58, 34.58, 24.37; ^{19}F NMR (565 MHz, Chloroform-*d*) δ -100.20 (td, *J* = 22.6, 16.9 Hz), -109.20 (dt, *J* = 39.5, 16.9 Hz); HRMS Calcd. For $[C_{22}H_{23}FN_3O_3]^+$: 396.1718, found: 396.1718.



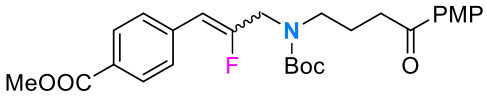
(6f)4-((3-(3-chlorophenyl)-2-fluoroallyl)oxy)-1-(4-methoxyphenyl)butan-1-one: Colorless oil (48mg, 67%Yield, 1.5:1 Z/E) ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 6.0 Hz, 5H), 7.50 (s, 1.5H), 7.35 (d, *J* = 6.0 Hz, 1.5H), 7.28 (d, *J* = 6.0 Hz, 2H), 7.25 -7.22 (m, 3H), 7.14 (t, *J* = 6.0 Hz, 1H), 6.94 (d, *J* = 12.0 Hz, 5H), 6.39 (d, *J* = 18.0 Hz, 1H), 5.70 (d, *J* = 36.0 Hz, 1.5H), 4.16 (d, *J* = 18.0 Hz, 2H), 4.12 (d, *J* = 12.0 Hz, 3H), 3.88 (s, 8H), 3.65 – 3.61 (m, 5H), 3.08 (td, *J* =12.0, 6.0 Hz, 5H), 2.08 (td, *J* = 18.0, 12.0 Hz, 5H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 198.52, 163.56, 163.54, 158.33 (t, *J* = 265.7 Hz), 135.10 (d, *J* = 13.6 Hz), 134.58 (d, *J* = 3.0 Hz), 134.47 (d, *J* = 10.6 Hz), 130.44, 130.21, 129.90, 129.79, 128.75, 128.68, 127.65, 127.60 (d, *J* = 1.5 Hz), 126.96, 126,92 (d, *J* = 1.5 Hz), 113.83, 113.81, 112.02 (d, *J* = 27.2 Hz), 107.58 (d, *J* = 6.0 Hz), 70.27, 70.11, 69.23 (d, *J* = 31.7 Hz), 66.03 (d, *J* = 28.7 Hz), 55.59, 34.72, 34.61, 24.44; ^{19}F NMR (565 MHz, Chloroform-*d*) δ -100.89 (td, *J* = 22.6, 16.9 Hz), -108.76 (dt, *J* = 39.5, 16.9 Hz); HRMS Calcd. For $[C_{20}H_{21}ClFO_3]^+$: 363.1158, found: 363.1159.



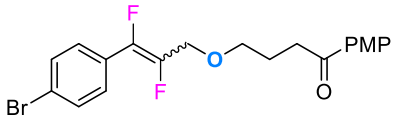
(6g) (Z)-4-((3-(4-chlorophenyl)-2-fluoroallyl)oxy)-1-(4-methoxyphenyl)butan-1-one: Colorless oil (54mg, 74%Yield, 1.3:1 Z/E) ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 12.0 Hz, 4.6H), 7.41 (d, *J* = 6.0 Hz, 2.0H), 7.29 – 7.26 (m, 4.7H), 7.17 (d, *J* = 6.0 Hz, 4.4H), 6.94 – 6.91 (m, 4.6H), 6.38 (d, *J* = 18.0 Hz, 1.3H), 5.70 (d, *J* = 42.0 Hz, 1H), 4.14 (d, *J* = 24.0 Hz, 4.7H), 3.87 (s, 6.9H), 3.63 (t, *J* = 6.0 Hz, 2.0H), 3.60 (t, *J* = 6.0 Hz, 2.6H), 3.06 (q, *J* = 6.0 Hz, 4.6H), 2.09-2.03 (m, 4.6H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 198.53, 198.49, 163.58, 163.56, 158.74 (d, *J* = 277.84 Hz), 158.74 (d, *J* = 288.41 Hz), 133.51, 133.22 (d, *J* = 1.51 Hz), 131.72 (d, *J* = 12.1 Hz), 131.33 (d, *J* = 3.0 Hz), 130.44, 130.21, 130.08 (d, *J* = 7.6 Hz), 130.01 (d, *J* = 3.0 Hz), 128.87, 128.77, 113.85, 113.83, 112.13 (d, *J* = 27.1 Hz), 107.82 (d, *J* = 6.0 Hz), 70.18, 70.07, 69.36 (d, *J* = 30.2 Hz), 66.05 (d, *J* = 28.7 Hz), 55.60, 34.59, 24.88; ^{19}F NMR (565 MHz, Chloroform-*d*) δ -101.52 (td, *J* = 22.6, 16.9 Hz), -110.00 (dt, *J* = 39.6, 16.9 Hz). HRMS Calcd. For $[C_{20}H_{21}ClFO_3]^+$: 363.1158, found: 363.1162.



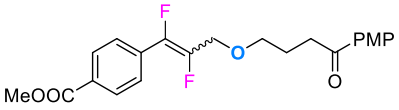
(6h) (Z)-tert-butyl (3-(4-cyanophenyl)-2-fluoroallyl)(4-(4-methoxyphenyl)-4-oxobutyl) carbamate: Brown oil (75mg, 83%Yield, 1.6:1 Z/E) ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 6.0 Hz, 3.2H), 7.89 (d, *J* = 6.0 Hz, 2.0H), 7.61 (d, *J* = 12.0 Hz, 2H), 7.58 (d, *J* = 12.0 Hz, 3.2H), 7.53 (d, *J* = 6.0 Hz, 3.2H), 7.39-7.30(m, 2 H), 6.91 (t, *J* = 6.0 Hz, 5.2H), 6.34 (d, *J* = 24 Hz, 1H), 5.66 (t, *J* = 36.0 Hz, 1.6H), 4.24 (t, *J* = 12.0 Hz, 2H), 4.10 (dd, *J* = 42.0, 12.0 Hz, 3.2H), 3.85 (s, 8H), 3.39 (t, *J* = 6.0 Hz, 3.3H), 3.33 – 3.25 (m, 2H), 2.97 – 2.91 (m, 3.3H), 2.90 – 2.84 (m, 2H), 2.02 – 1.98 (m, 3.4H), 1.90 – 1.86 (m, 2H), 1.42 (s, 24H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 198.14, 197.77, 163.60, 160.12, 158.26, 155.46 (d, *J* = 51.3 Hz), 138.05, 137.62, 132.43, 132.33, 130.32, 129.95, 129.44, 129.08, 118.98, 118.78, 113.83, 110.76 (d, *J* = 52.8 Hz), 106.53 (d, *J* = 96.6 Hz), 80.50 (d, *J* = 13.6 Hz), 55.58, 46.87, 46.68, 44.17 (d, *J* = 25.7 Hz), 34.96 (d, *J* = 34.7 Hz), 28.41, 22.80, 22.47; ^{19}F NMR (565 MHz, Chloroform-*d*) δ -100.59 (d, *J* = 16.9 Hz), -102.14 (d, *J* = 16.9 Hz), -103.38 (dt, *J* = 39.5, 16.9 Hz), -104.09 (dt, *J* = 39.5, 11.3 Hz). HRMS Calcd. For $[C_{26}H_{30}F_2NO_4]^+$: 453.2184, found: 453.2187.



(6i) methyl 4-(3-((tert-butoxycarbonyl)(4-(4-methoxyphenyl)-4-oxobutyl)amino)-2-fluoroprop-1-en-1-yl)benzoate: Brown oil(75mg, 78%Yield, 1:1 Z/E) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.00 -7.96 (m, 4H), 7.91 -7.86 (m, 4H), 7.51 (d, *J* = 10.0 Hz, 2H), 7.27 (d, *J* = 10.0 Hz, 2H), 6.90 (d, *J* = 5.0 Hz, 2H), 6.88 (d, *J* = 5.0 Hz, 2H), 6.37 (d, *J* = 20.0 Hz, 1H), 5.71 (d, *J* = 30.0 Hz, 1H), 4.31 – 4.22 (m, 2H), 4.16 – 4.01 (m, 2H), 3.90 (s, 3H), 3.85 (s, 3H), 3.84 (s, 3H), 3.42 – 3.39 (m, 2H), 3.31 -3.27 (m, 2H), 2.96 – 2.92 (m, 2H), 2.88 – 2.83 (m, 2H),2.03 – 1.99 (m, 2H), 1.90 – 1.82 (m, 2H), 1.87 (s, 18H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 198.08, 166.74 (d, *J* = 15.1 Hz), 163.48, 137.76 (dd, *J* = 10.1, 5.0 Hz), 130.24, 129.78(d, *J* = 11.3 Hz), 128.86, 128.66 (d, *J* = 2.6 Hz), 128.42, 125.95, 113.72, 80.29 (d, *J* = 15.1 Hz), 55.46, 52.11 (d, *J* = 7.6 Hz), 46.57, 34.96 (d, *J* = 29.0 Hz), 28.32, 22.62; ^{19}F NMR (471 MHz, Chloroform-*d*) δ -102.86 (d, *J* = 19.6 Hz), -104.11 (d, *J* = 18.7 Hz), -104.96 (d, *J* = 40.7 Hz), -105.75 (d, *J* = 38.6 Hz). HRMS Calcd. For $[C_{27}H_{33}FNO_6]^+$: 486.2286, found: 486.2294.

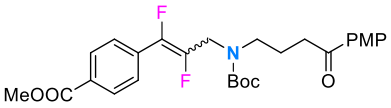


(6j) 4-((3-(4-bromophenyl)-2,3-difluoroallyl)oxy)-1-(4-methoxyphenyl)butan-1-one: Colorless oil(32mg, 37% Yield, 1:2 Z/E) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96 -7.93 (m, 6H), 7.54 – 7.49 (m, 8H), 7.34 (d, *J* = 10.0 Hz, 4H), 6.95 -6.90 (m, 6H), 4.40 (d, *J* = 5.0 Hz, 1H), 4.36 (d, *J* = 5.0 Hz, 1H), 4.14 (d, *J* = 5.0 Hz, 2H), 4.09 (d, *J* = 5.0 Hz, 2H), 3.87 (s, 6H), 3.86 (s, 3H), 3.65 -3.60 (m, 6H),3.08 – 3.04 (m, 6H), 2.10 – 2.03 (m, 6H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 198.40, 163.65, 140.41, 139.98, 131.98, 131.85 (d, *J* = 2.5 Hz), 130.45, 130.21, 129.15 (d, *J* = 3.8 Hz), 127.50 – 127.17 (m), 113.91, 70.18, 66.46, 66.25, 55.63, 34.59, 24.49; ^{19}F NMR (471 MHz, Chloroform-*d*) δ -129.07 (d, *J* = 9.5 Hz), -133.96 (td, *J* = 24.8, 9.5 Hz), -149.93 (dt, *J* = 124.7, 23.5 Hz), -154.80 (dt, *J* = 124.8, 5.9 Hz). HRMS Calcd. For $[C_{20}H_{20}BrF_2O_3]^+$: 425.0558, found: 425.0564.



(6k) methyl 4-(1,2-difluoro-3-(4-(4-methoxyphenyl)-4-oxobutoxy)prop-1-en-1-yl)benzoate: Colorless oil (55mg, 68%Yield, 1:1 Z/E) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 10.0 Hz, 2H), 8.03 (d, *J* = 10.0 Hz, 2H), 7.96 (t, *J* = 5.0 Hz, 2H), 7.94 (t, *J* = 5.0 Hz, 2H), 7.71 (d, *J* =5.0 Hz, 2H), 7.55

(d, *J* = 5.0 Hz, 2H), 6.93 (d, *J* = 10.0, Hz, 2H), 6.91 (d, *J* = 10.0, 2H), 4.42 (d, *J* =5.0 Hz, 1H), 4.38 (d, *J* = 5.0 Hz, 1H), 4.18 (d, *J* = 5.0 Hz, 1H), 4.13 (d, *J* = 5.0 Hz, 1H), 3.93 (s, 6H), 3.88 (s, 3H), 3.85 (s, 3H), 3.67 – 3.59 (m, 4H), 3.06 (m, 4H), 2.10 – 2.06 (m, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 198.50, 166.53, 163.57 (d, *J* = 9.8 Hz), 133.65, 131.41, 130.64, 130.42, 130.23, 129.85, 129.79 (d, *J* = 1.3 Hz), 127.38 (t, *J* = 3.8 Hz), 125.66 (t, *J* = 8.8 Hz), 113.87, 70.25, 66.31 (d, *J* = 27.5 Hz), 64.18 (d, *J* = 24.1 Hz), 55.58, 52.46, 34.56, 24.47; ^{19}F NMR (471 MHz, Chloroform-d) δ -130.29 (d, *J* = 8.8 Hz), -131.91 (td, *J* = 25.1, 8.8 Hz), -147.64 (dt, *J* = 123.5, 23.1 Hz), -155.00 (dt, *J* = 123.5, 6.1 Hz). HRMS Calcd. For $[C_{22}H_{23}F_2O_5]^+$: 405.1508, found: 405.1510.

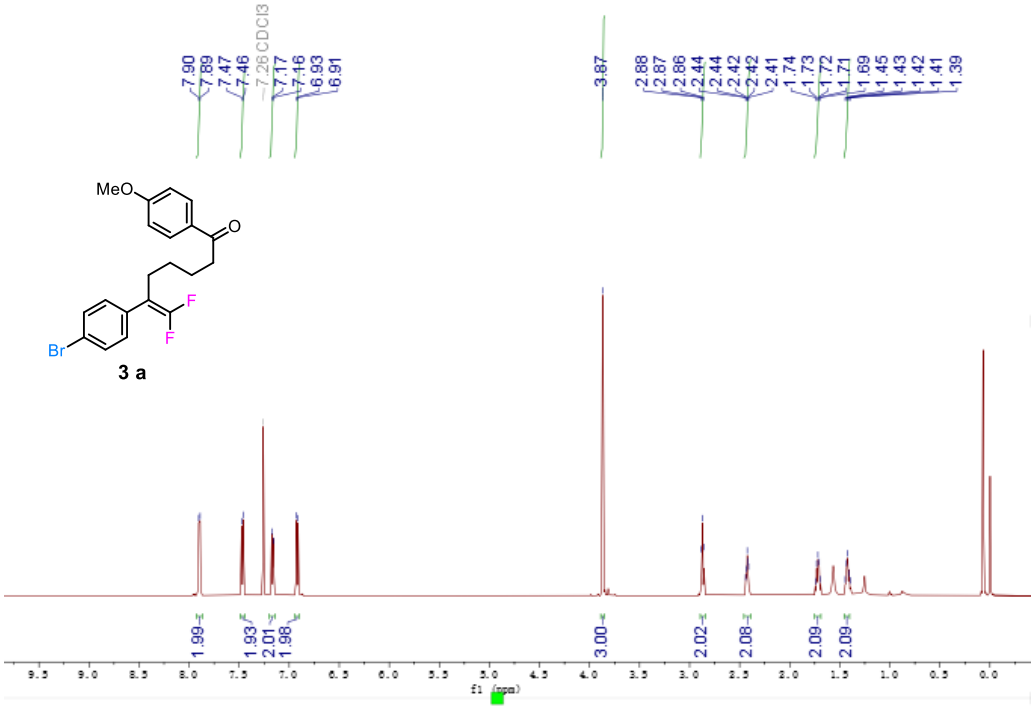


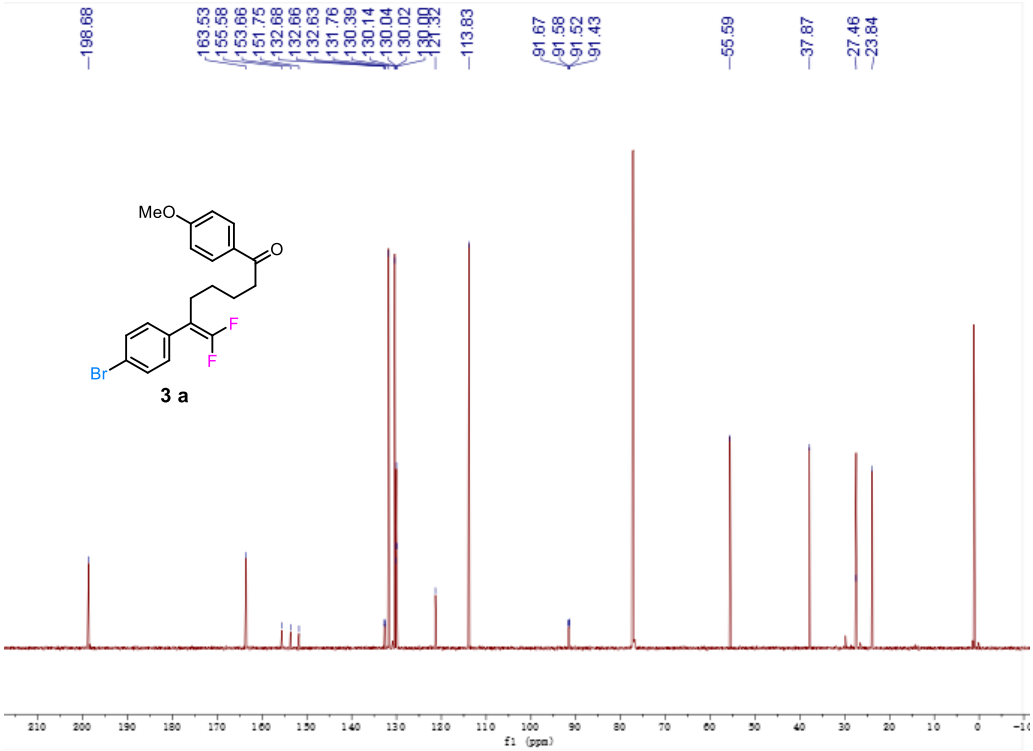
(6l) methyl 4-(3-((tert-butoxycarbonyl)(4-(4-methoxyphenyl)-4-oxobutyl)amino)-1,2-difluoroprop-1-en-1-yl)benzoate: Brown oil (74mg, 74%Yield, 1:2 Z/E) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 5.0 Hz, 6H), 7.92 (d, *J* = 10.0 Hz, 6H), 7.69 (d, *J* = 10.0 Hz, 2H), 7.55(d, *J* = 48.0 Hz, 4H), 6.91 (t, *J* = 10.0 Hz, 6H), 4.39 (d, *J* = 15.0 Hz, 2H), 4.27 (d, *J* = 15.0 Hz, 4H), 3.94 (s, 9H), 3.87 (s, 9H), 3.42-3.39 (m, 2H), 3.35 – 3.32 (m, 4H), 2.95-2,92 (m, 2H), 2.88 – 2.86 (m, 4H), 2.06-2.00 (m, 2H), 1.91 - 1.88 (m, 4H), 1.43 (s,27H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 194.28, 166.41(d, *J* = 34.0 Hz), 165.58, 163.47, 133.22, 131.17, 130.24, 129.82, 129.69, 127.78, 125.25, 113.71, 80.41, 55.47, 52.35, 52.26, 46.44, 28.29, 28.21; ^{19}F NMR (471 MHz, Chloroform-*d*) δ -129.77 (d, *J* = 527.5 Hz), -136.38 (d, *J* = 668.8 Hz), -147.7 (dd, *J* = 301.44, 127.1 Hz), 157.3 (dd, *J* = 241.7, 122.6 Hz). HRMS Calcd. For $[C_{27}H_{32}F_2NO_6]^+$: 504.2198, found: 504.2197;

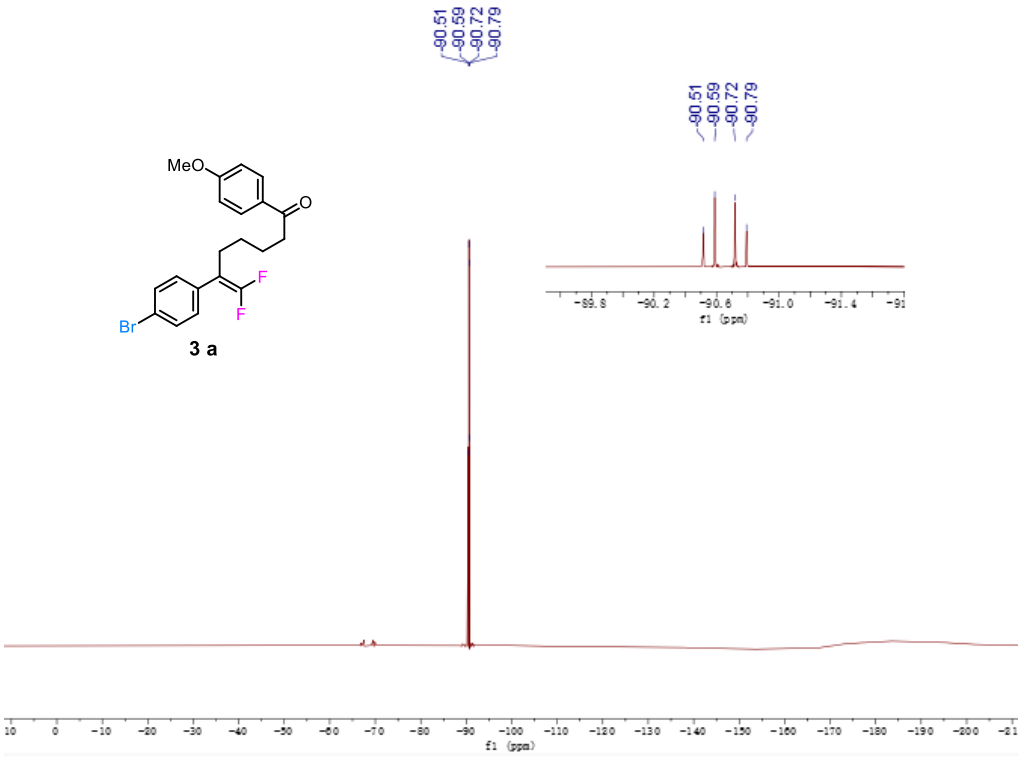
6. References

1. Gan, Y.; Zhang, N.-H.; Huang, S.-X.; Liu, Y.-H*. *Chin. J. Chem.* **2020,** 38, 1686-1690.
2. Zhang Q.; Zhou S.-W.; Shi C.-Y.; Yin L*. Angew. Chem. Int. Ed. **2021**, 60, 26351-26356.
3. Li ,C.-Y.; Ma, Y.; Lei Z.-W.,; Hu X.-G.; *Org. Lett.* **2021,** 23, 8899-8904.
4. Phelan, J. P.; Lang, S. B.; Compton, J. S.; Christopher B. K.; Dykstra R.; Gutierrez, O.; Molander G. A. *J. Am. Chem. Soc.* **2018,** 140, 8037-8047.
5. Xing, W.-L.; Wang, J.-X.; Fu, M.-Ch.*; Fu, Y*. *Chin. J. Chem.* **2021**, 40, 323-328.
6. Gladkov, A. A.; Chernov, G. N.; Levin, V. V.; Kokorekin, V. A.; Dilman, A. D. *Org. Lett.* **2021**, 23, 9645-9648.
7. Zhang, J.-J.; Yang, J.-D.; Cheng, J.-P.; Nat Commun. **2021**, 12, (1), 2835.
8. Xia, G.-D.; He, Y.-Y.; Zhang, J.; Liu, Z.-K.; Gao, Y.; Xiao, Q.-H.; *Chem. Commun.,* **2022**, 58, 6733-6736.

7. NMR spectra [6-8]



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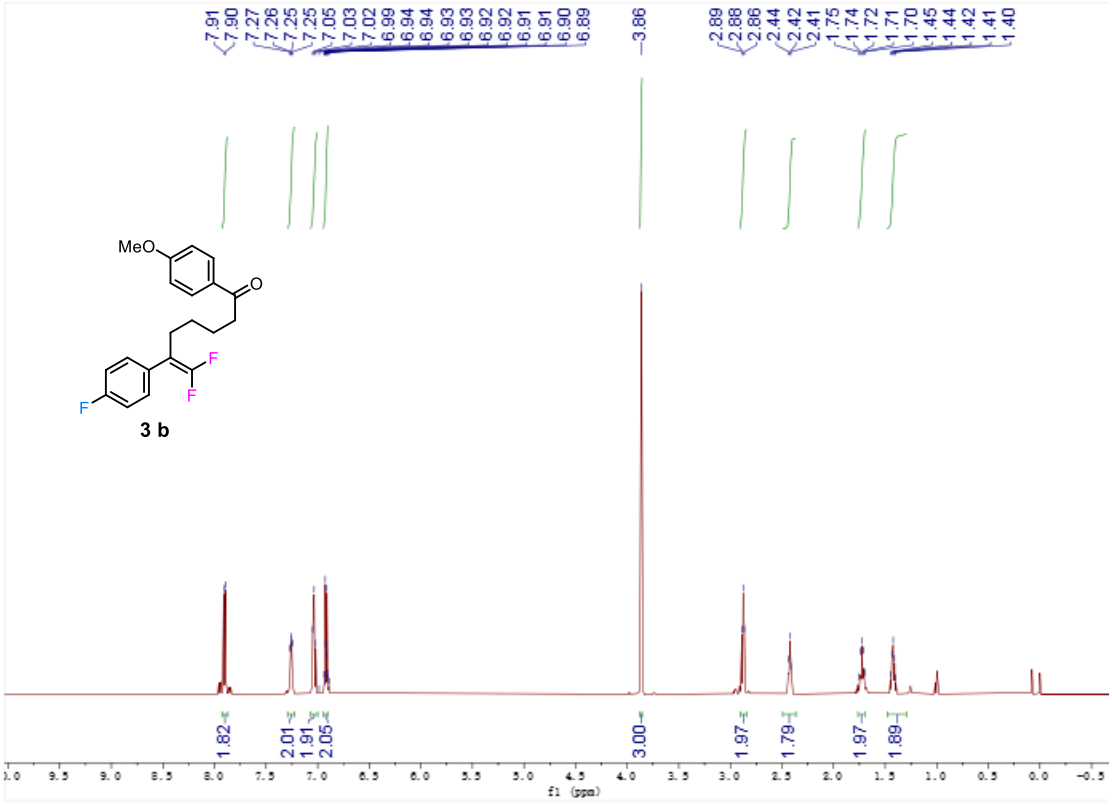
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2.86
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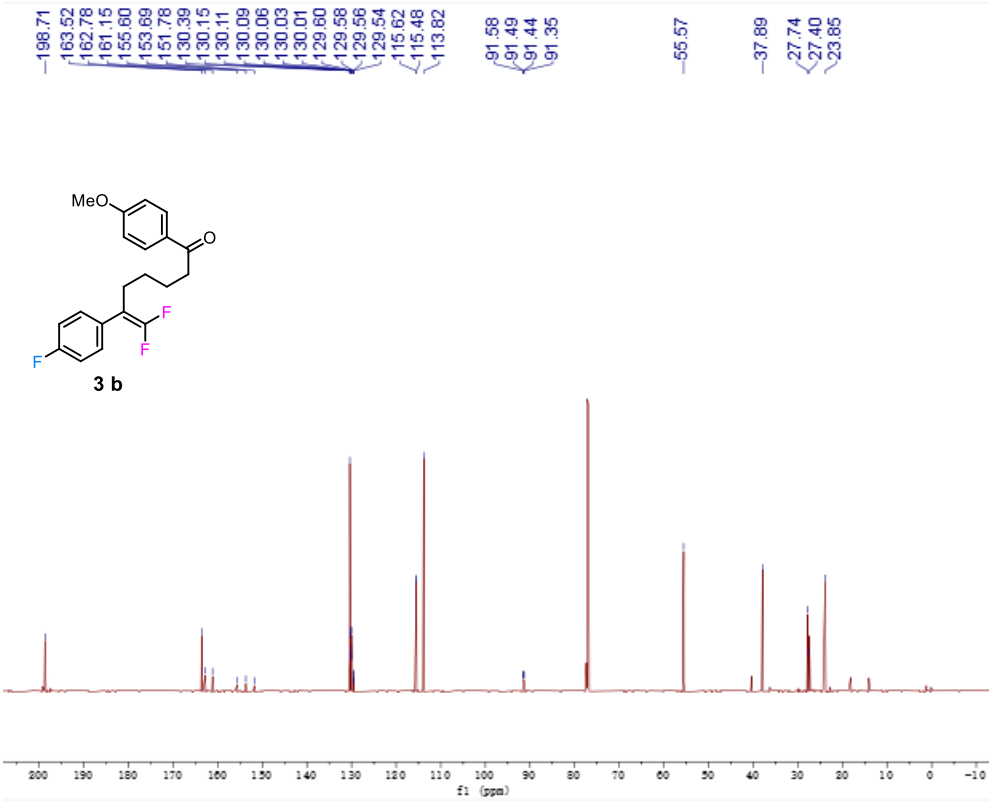
f1 (ppm)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F
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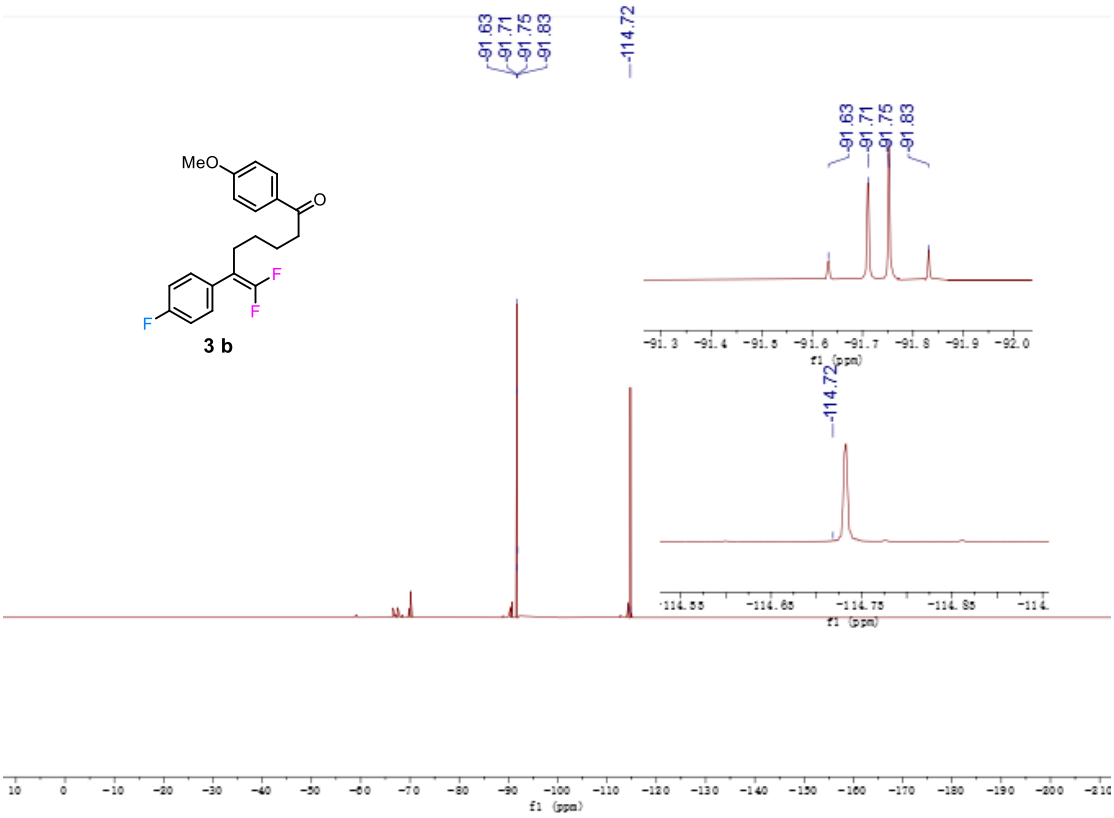
f1 (ppm)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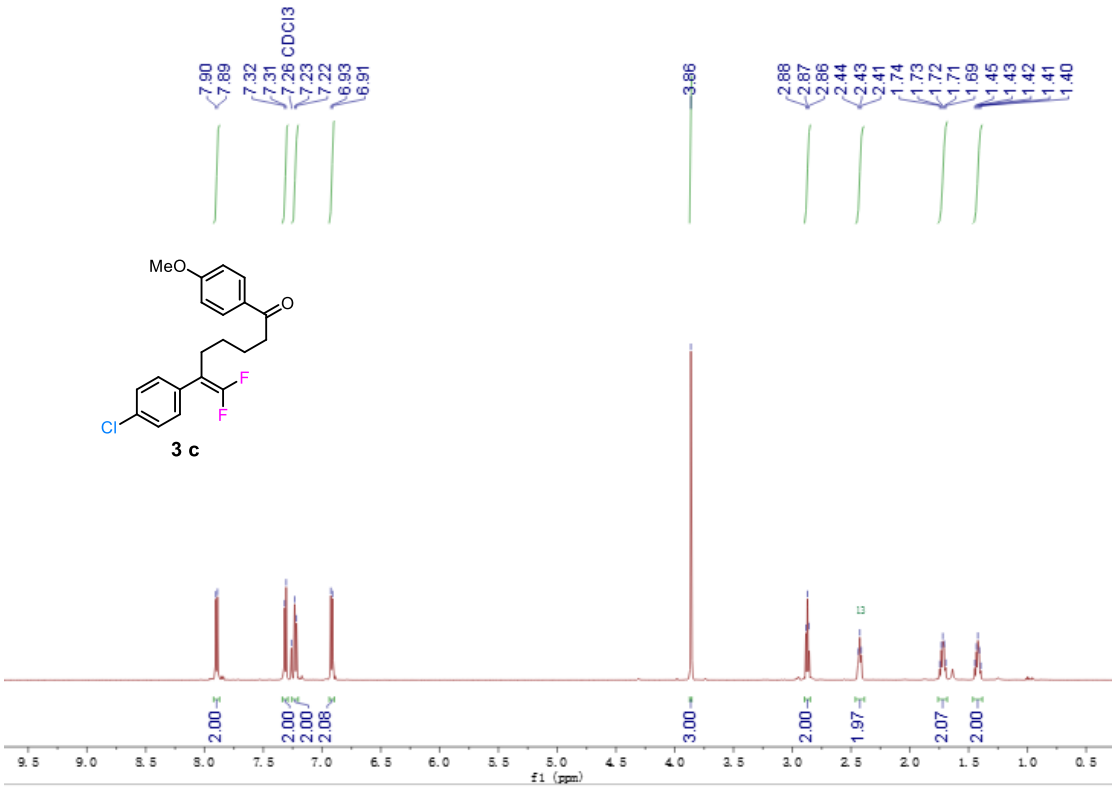
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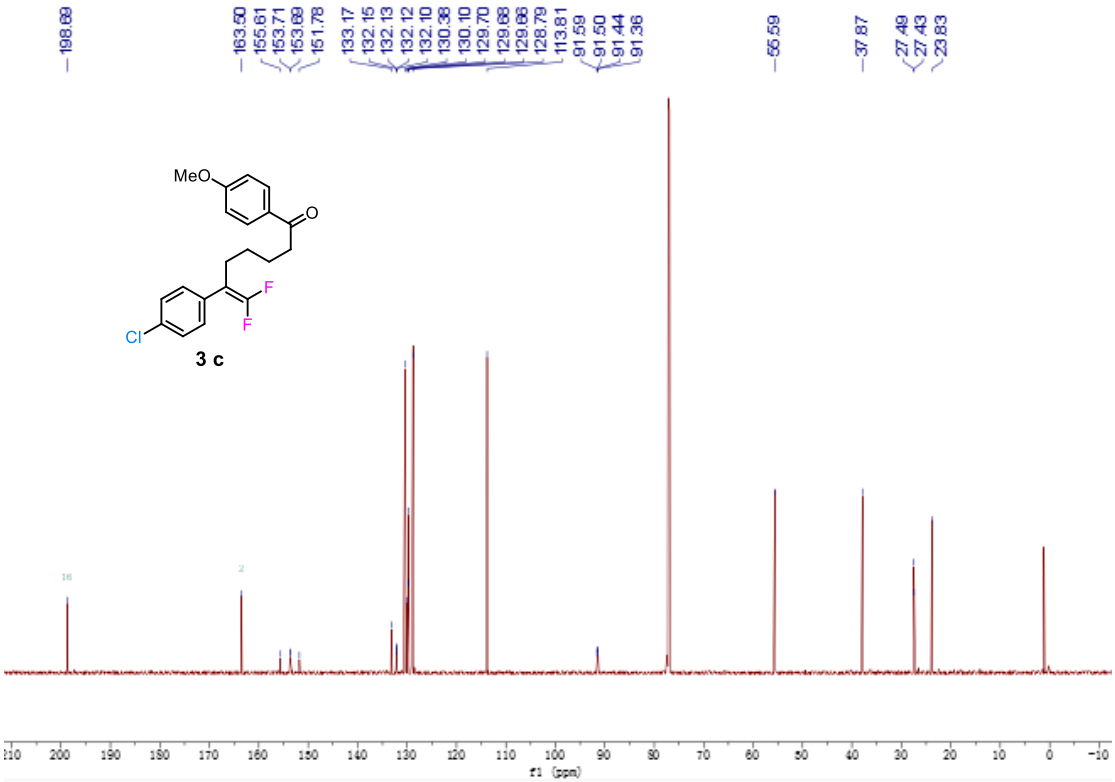
f1 (ppm)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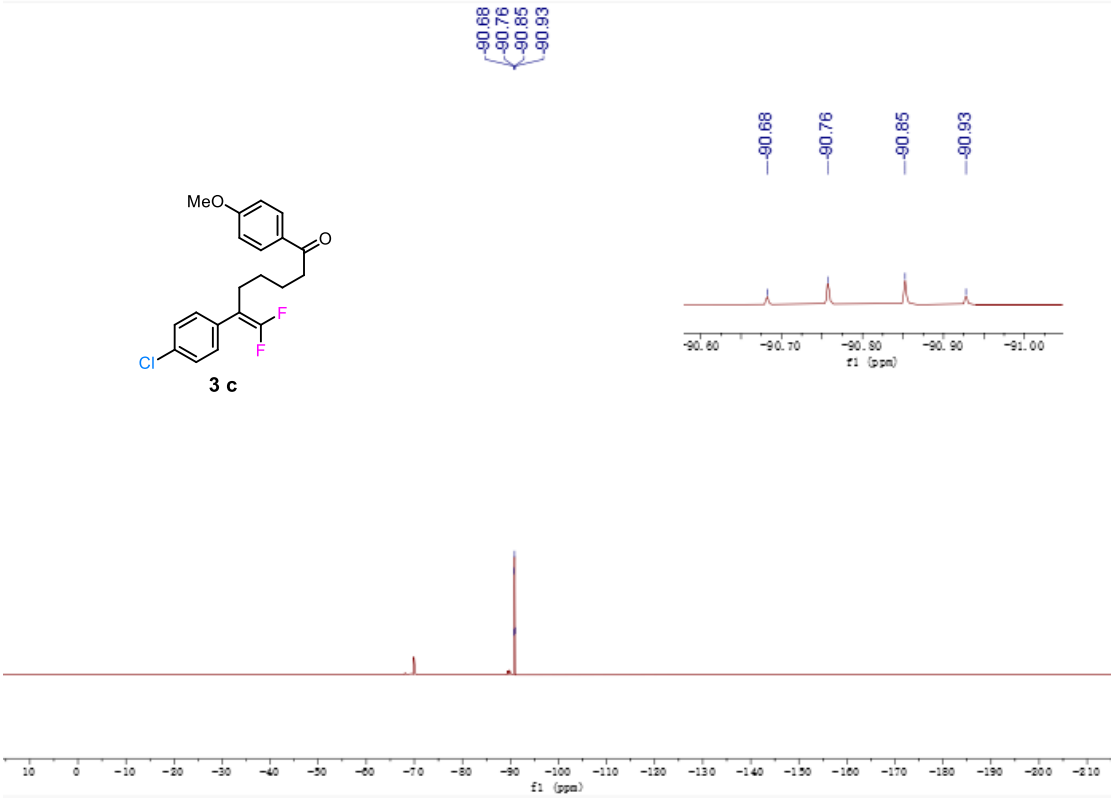
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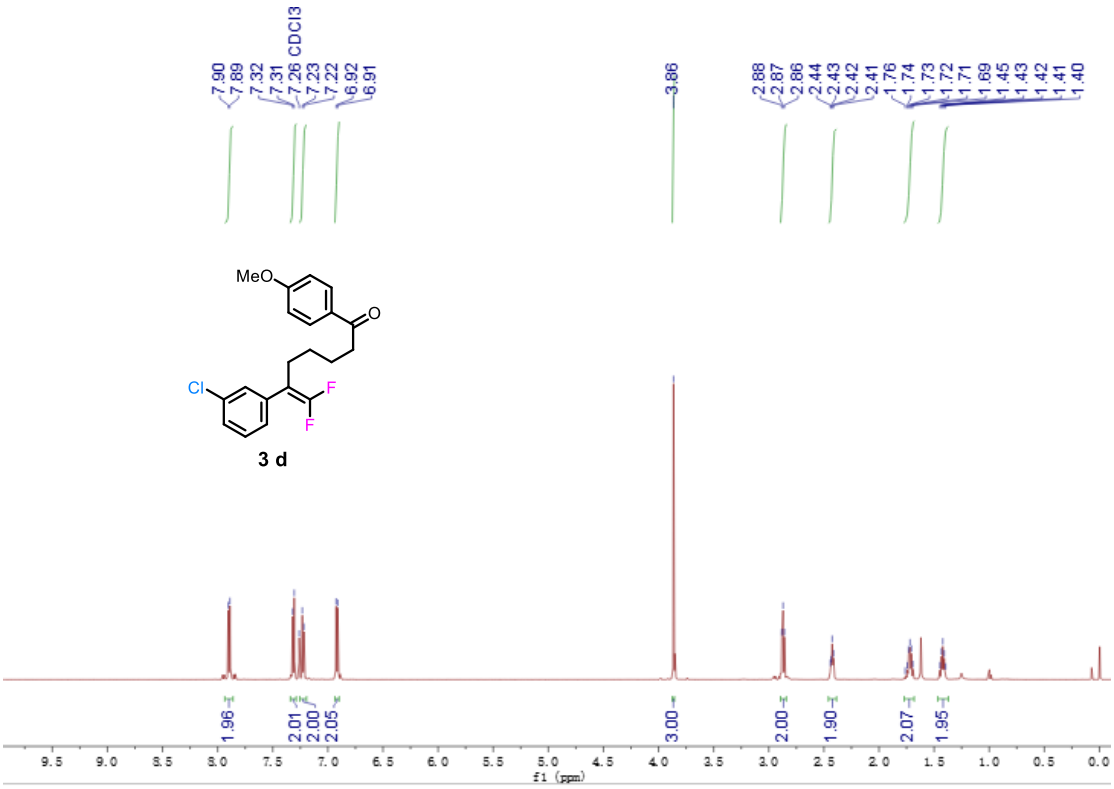
f1 (ppm)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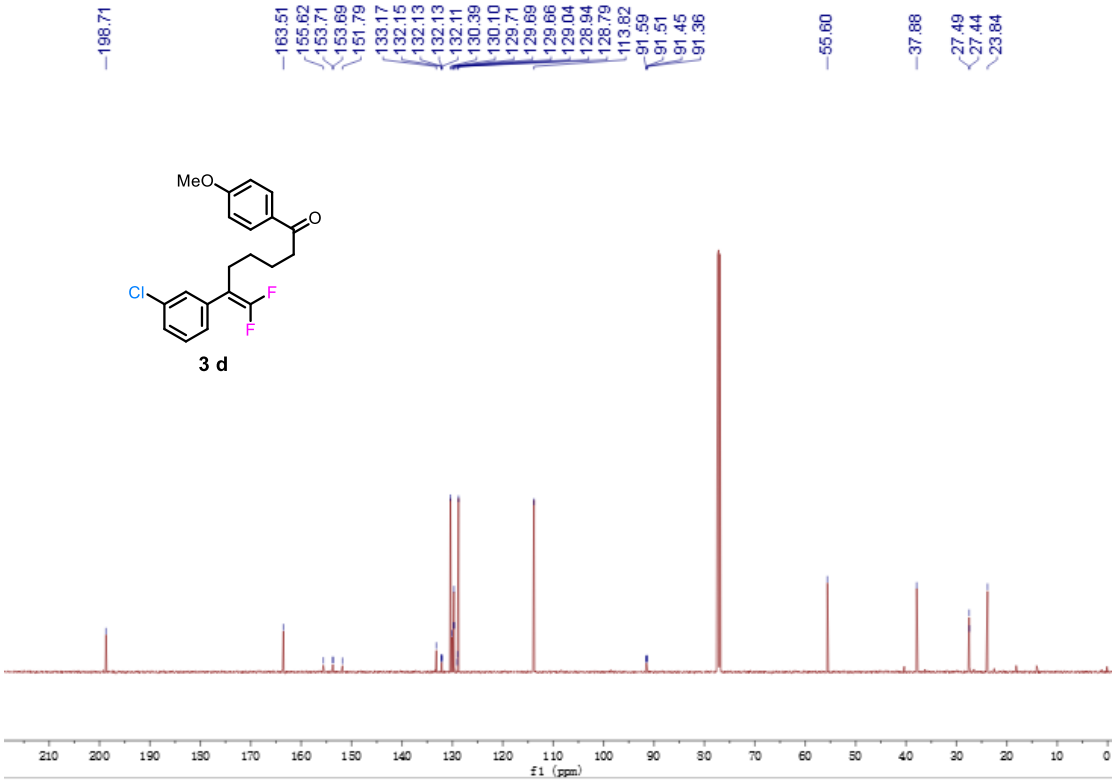
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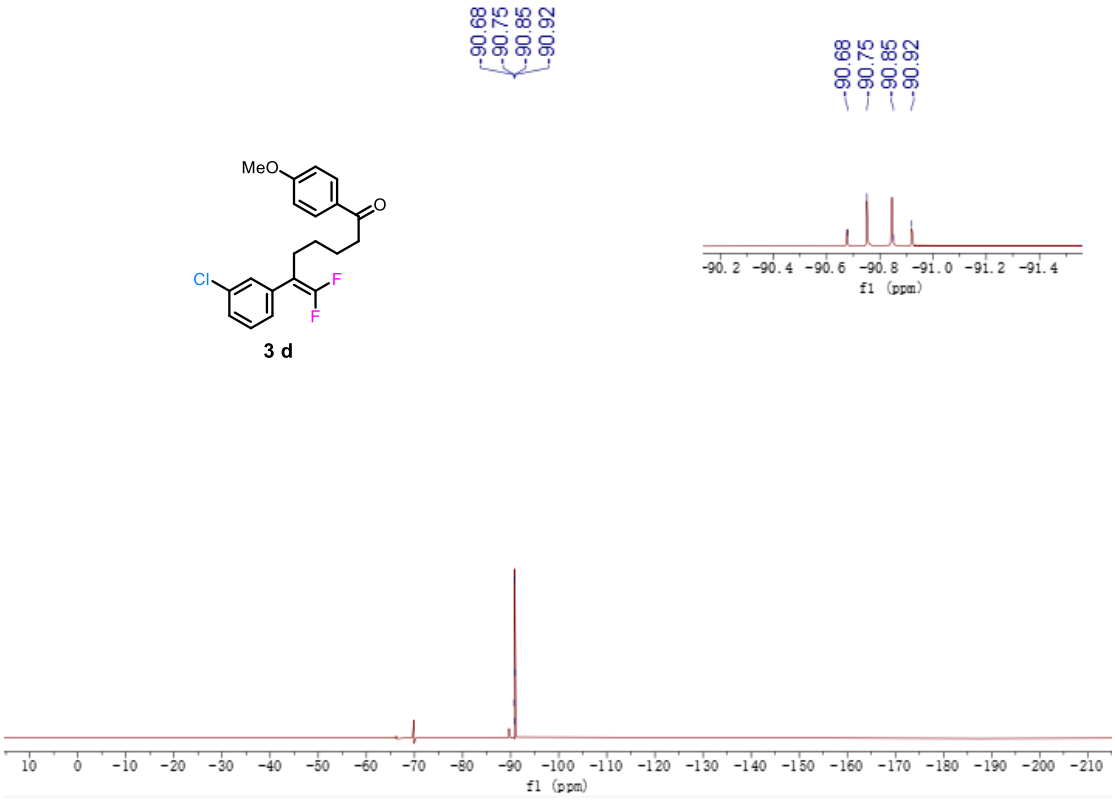
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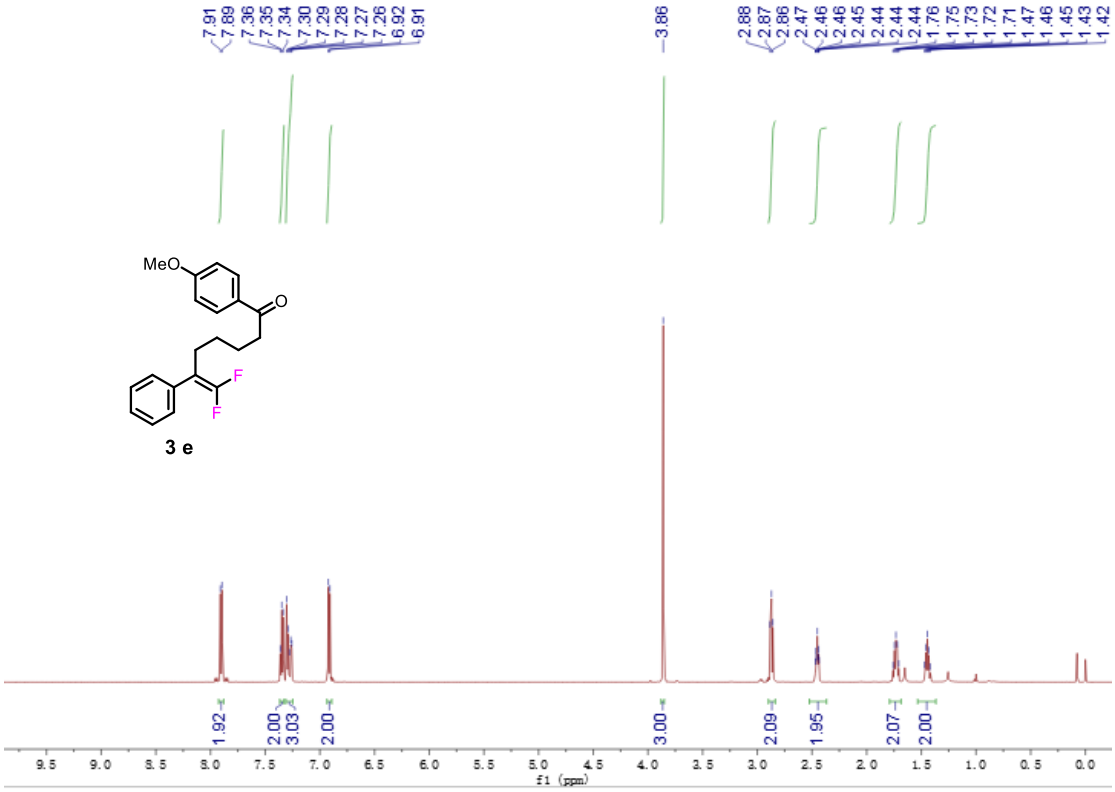
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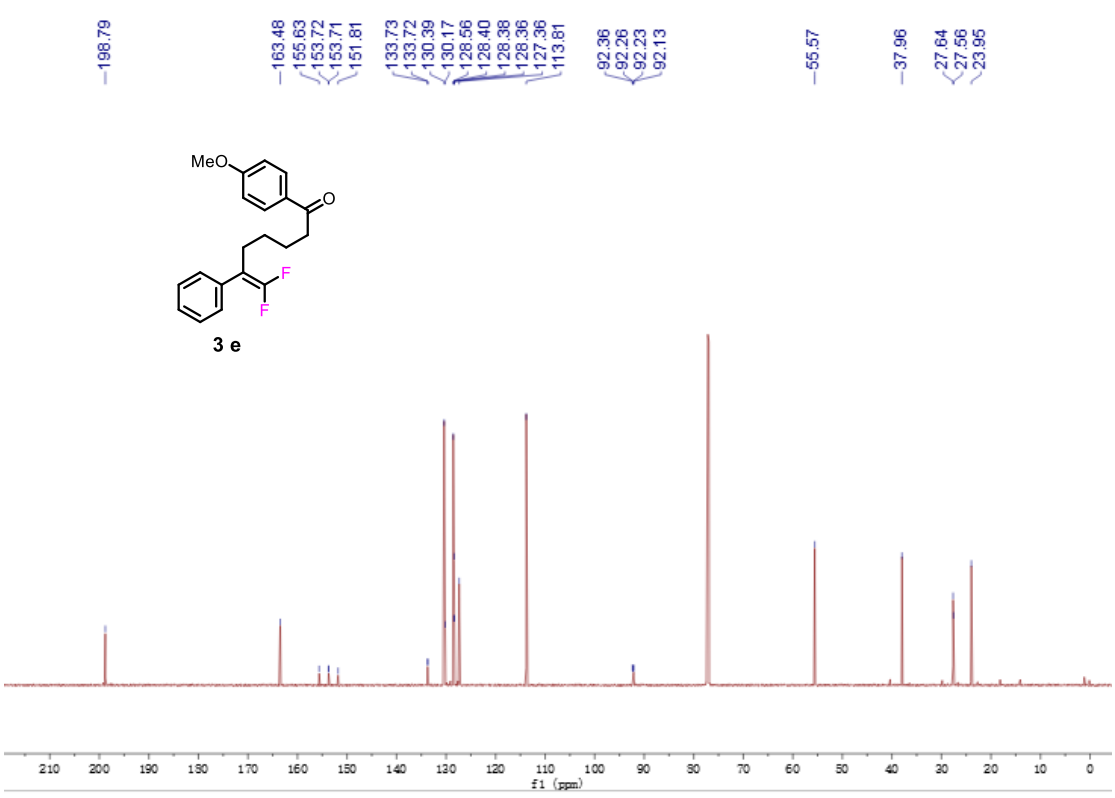
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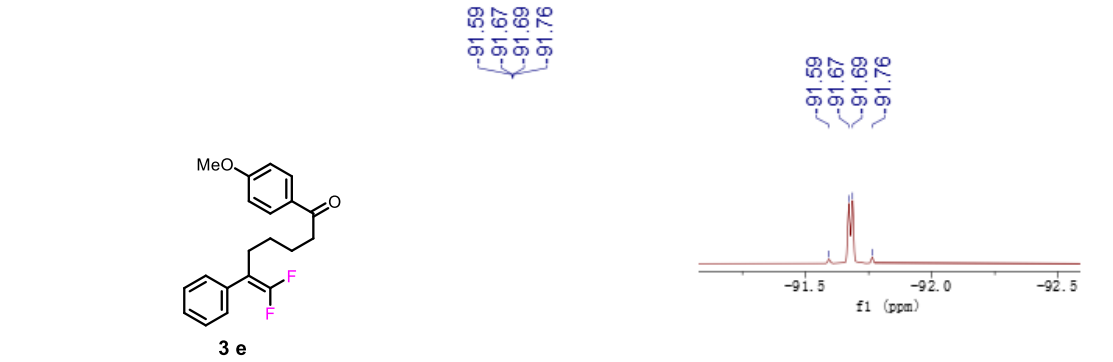
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-91.76
-91.5
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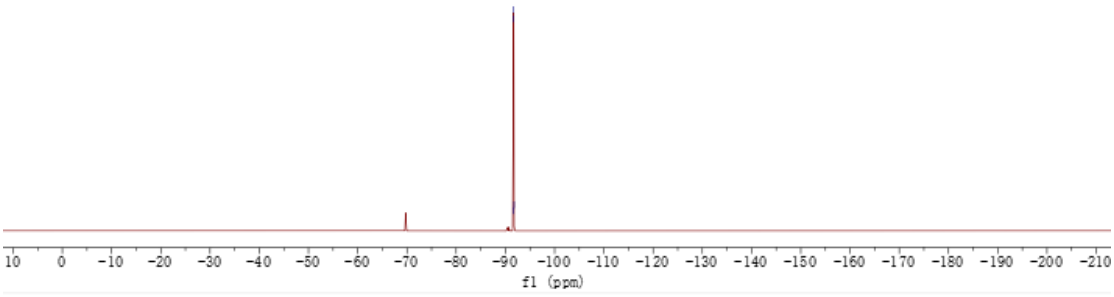
-92.5
f1 (ppm)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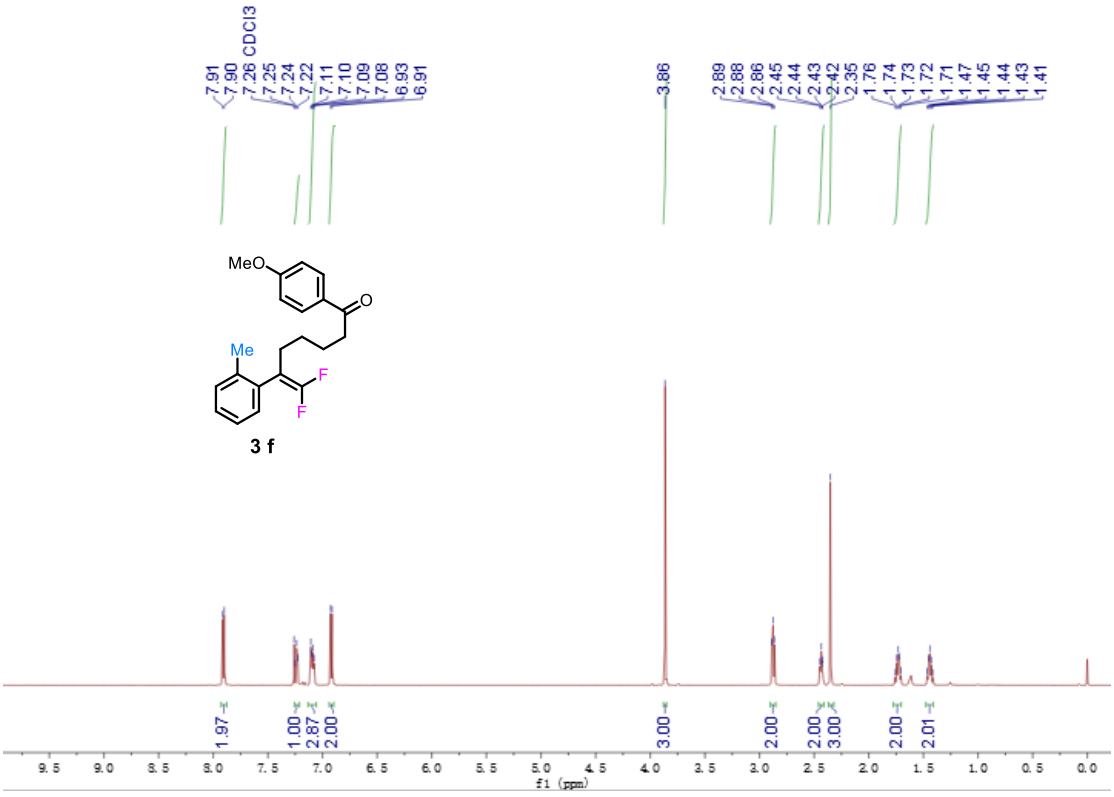
f1 (ppm)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6.91
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2.89
2.88
2.86
2.45
2.44
2.43
2.42
2.35
1.76
1.74
1.73
1.72
1.71
1.47
1.45
1.44
1.43
1.41
MeO
O
Me
F
F
3 f
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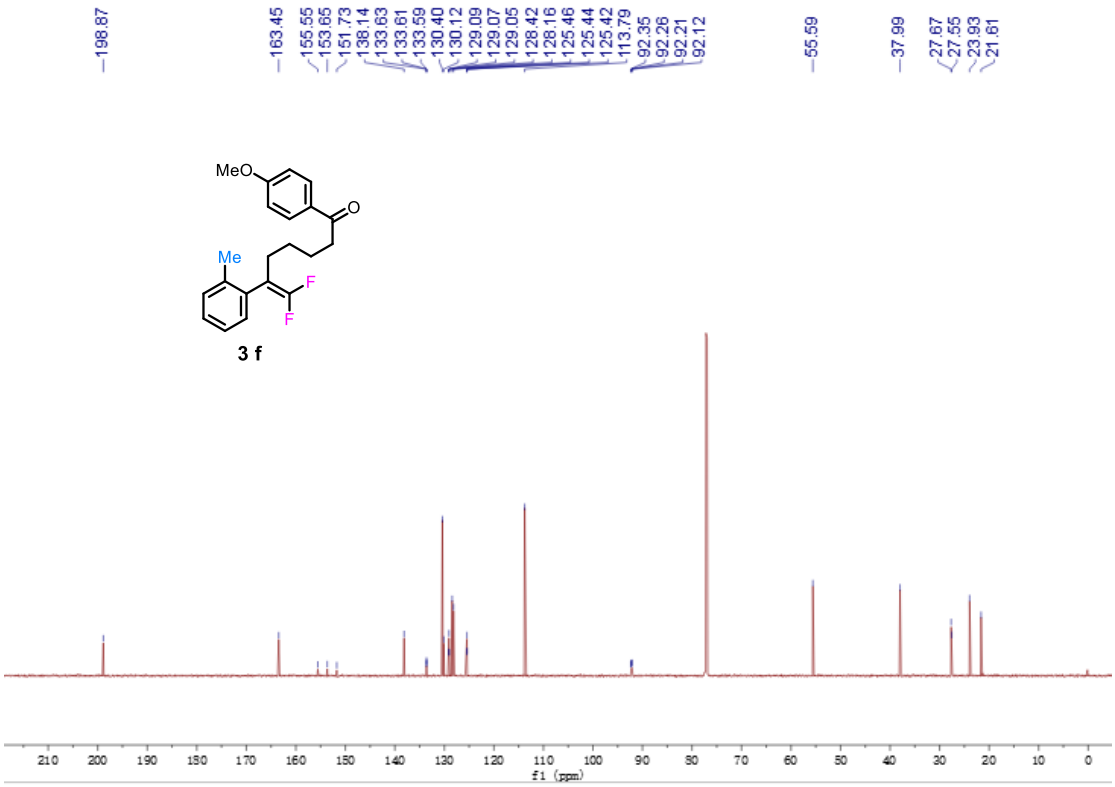
2.87
2.00
3.00
2.00
2.00
3.00
2.00
2.01
f1 (ppm)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125.44
125.42
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92.35
92.26
92.21
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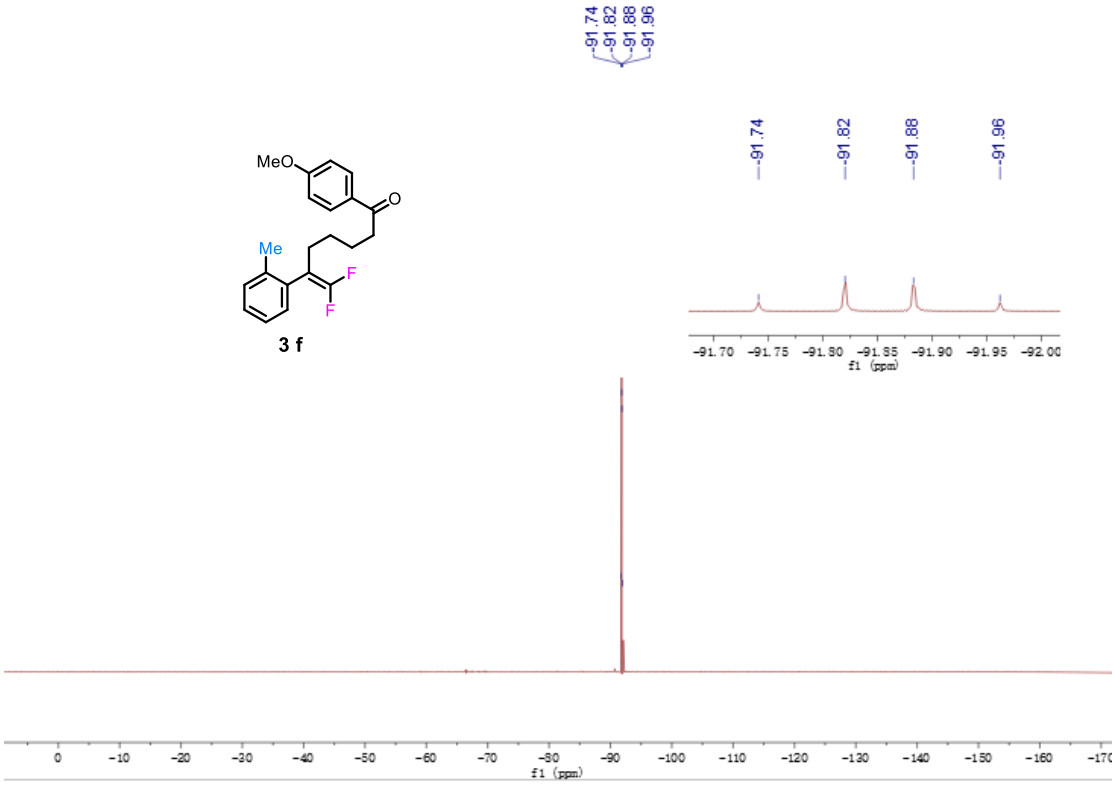
O
Me
F
F
3 f
f1 (ppm)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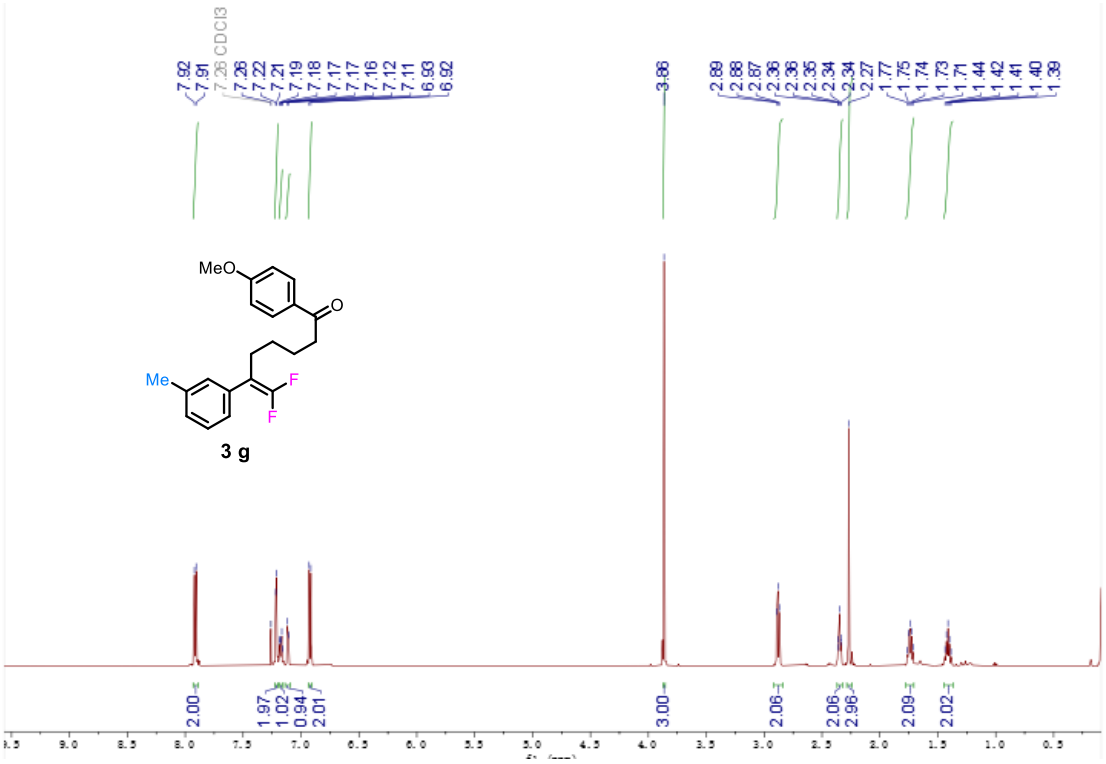
Me
F
F
3 f
f1 (ppm)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7.12
7.11
6.93
6.92
3.86
2.89
2.88
2.87
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2.36
2.35
2.34
2.34
2.27
1.77
1.75
1.74
1.73
1.71
1.44
1.42
1.41
1.40
1.39
MeO
O
Me
F
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2.06
2.06
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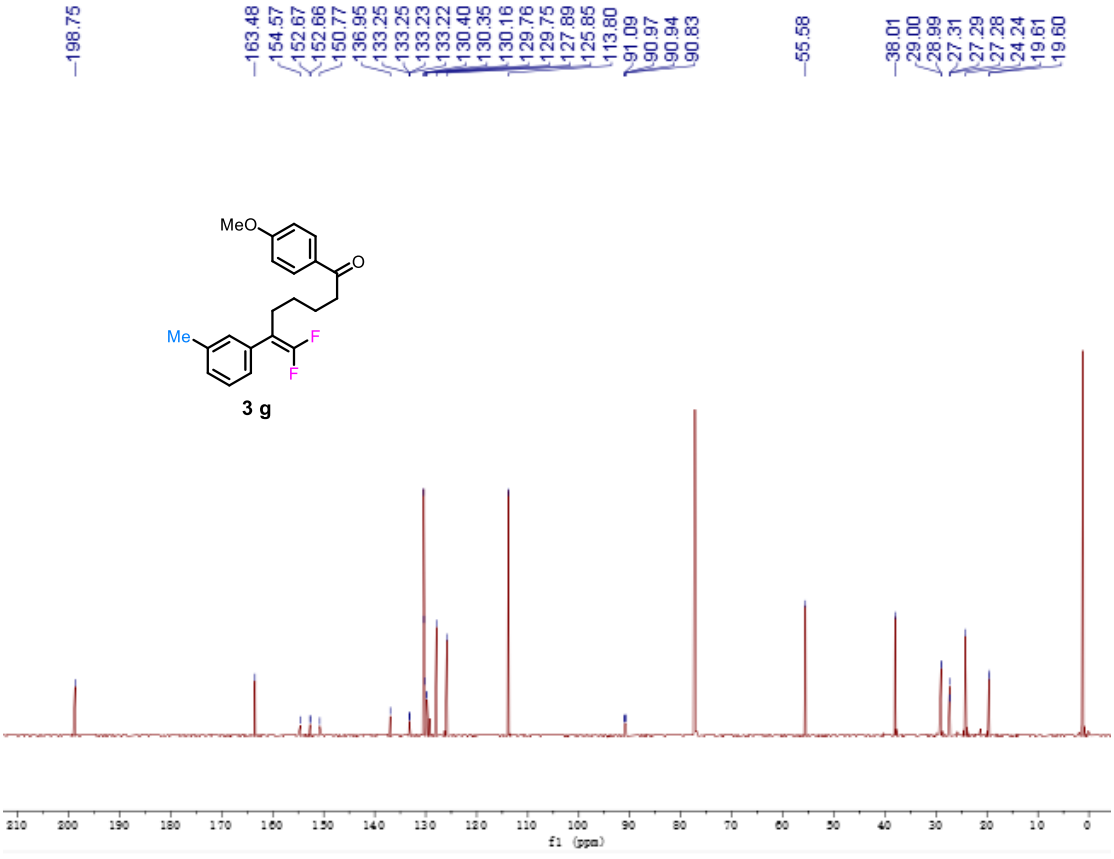
2.02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113.80
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90.97
90.94
90.83
55.58
38.01
29.00
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19.61
19.60
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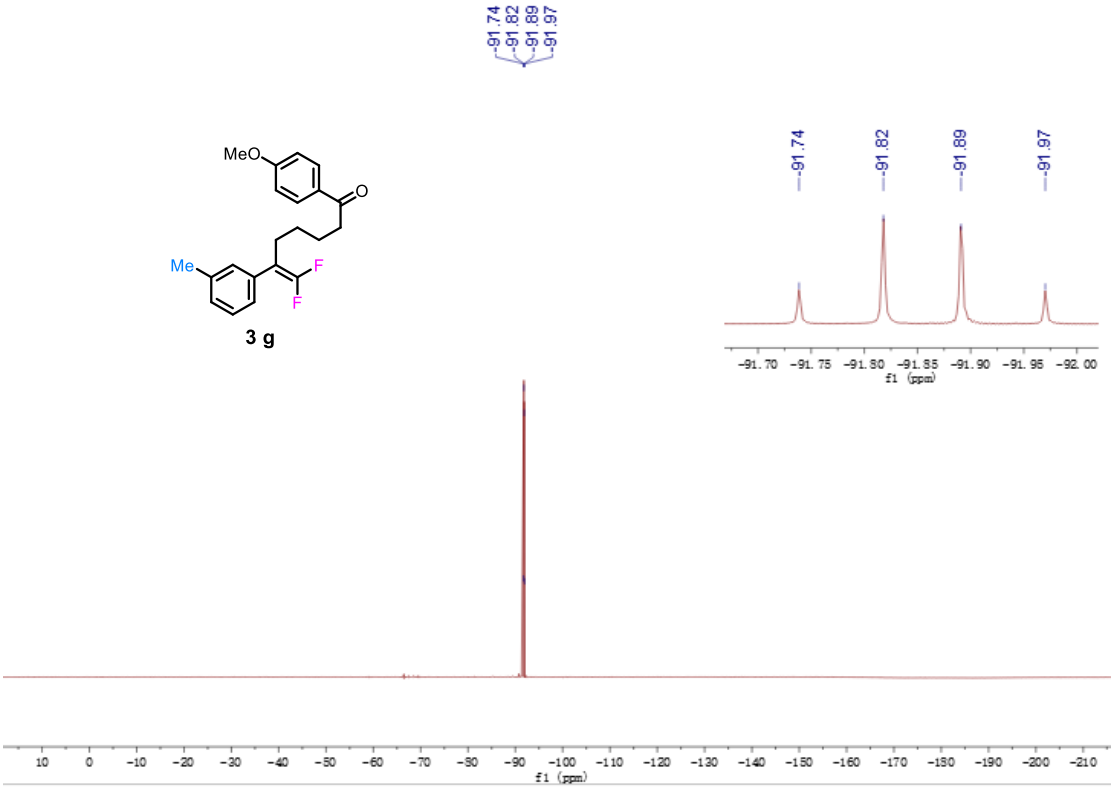
O
Me
F
F
3 g
f1 (ppm)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O
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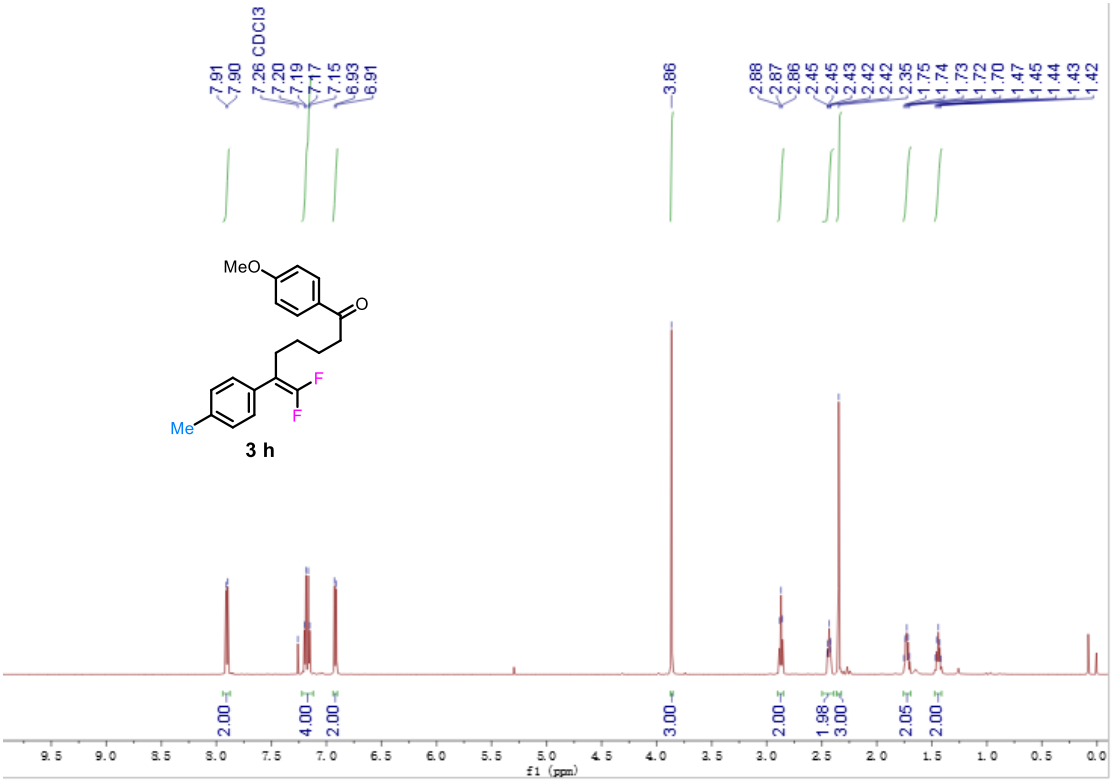
F
3 g
-91.74
-91.82
-91.89
-91.97
-91.70 -91.75 -91.80 -91.85 -91.90 -91.95 -92.00
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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2.86
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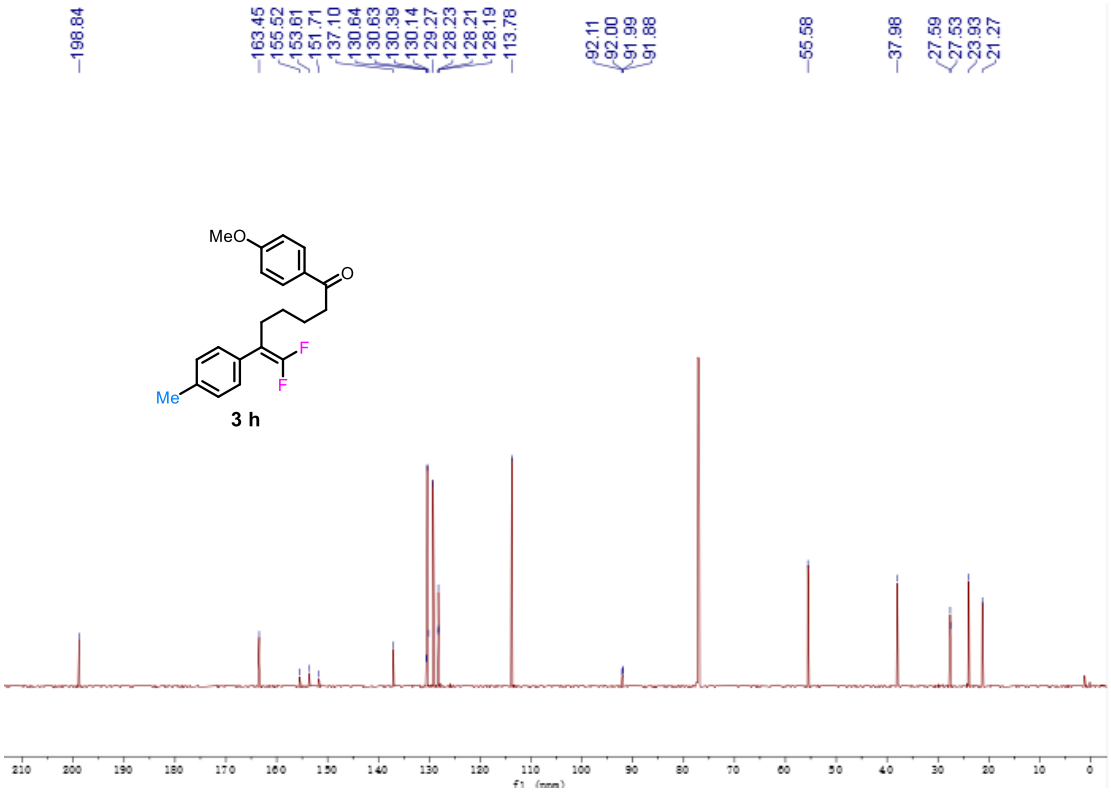
2.42
2.42
2.35
1.75
1.74
1.73
1.72
1.70
1.47
1.45
1.44
1.43
1.42
MeO
O
Me
F
F
3 h
2.00
4.00
2.00
3.00
2.00
1.98
3.00
2.05
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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128.23
128.21
128.19
113.78
92.11
92.00
91.99
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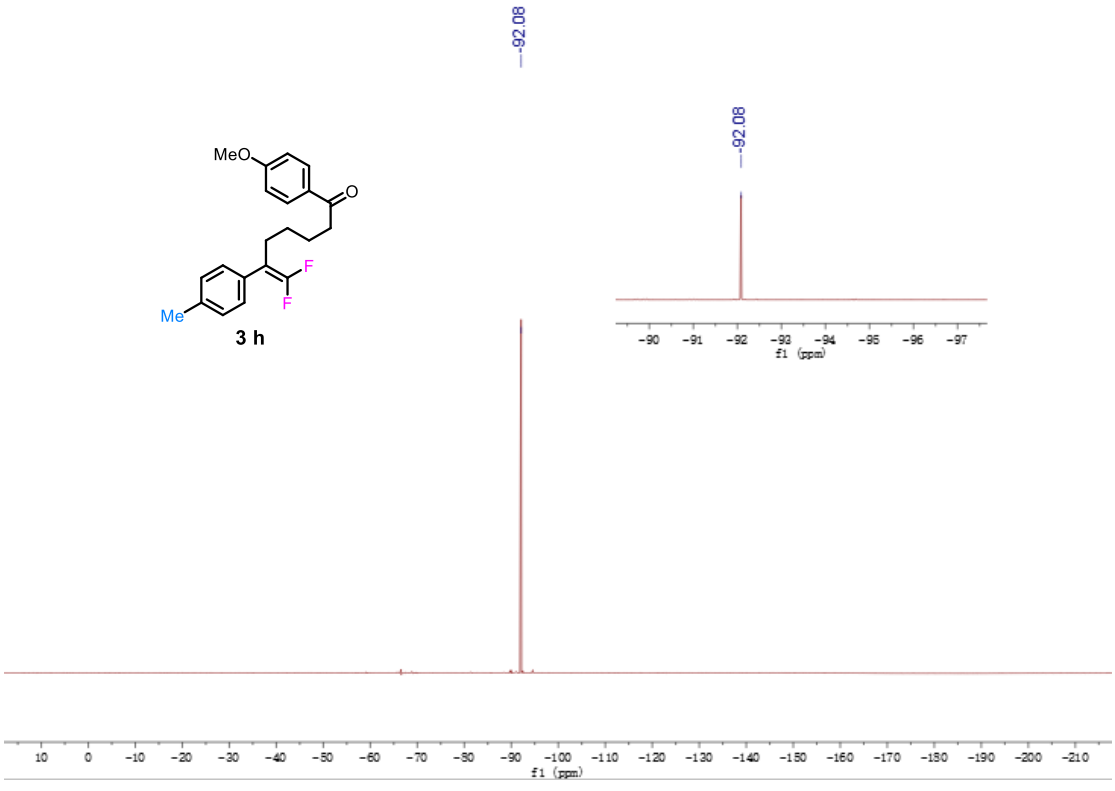
27.59
27.53
23.93
21.27
MeO
O
F
F
Me
3 h
f1 (ppm)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92.08
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O
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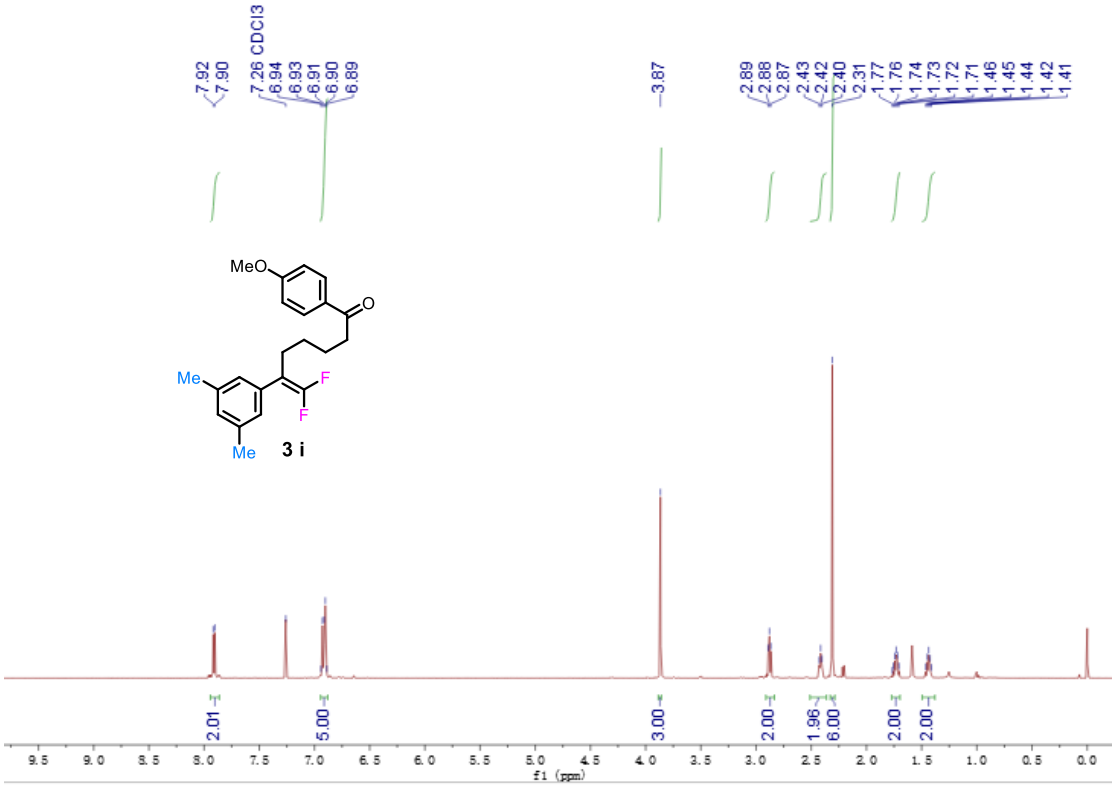
F
Me
3 h
f1 (ppm)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7.90
7.26 CDCl3
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6.90
6.89
3.87
2.89
2.88
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2.40
2.31
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1.76
1.74
1.73
1.72
1.71
1.46
1.45
1.44
1.42
1.41
MeO
O
Me
F
F
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3 i
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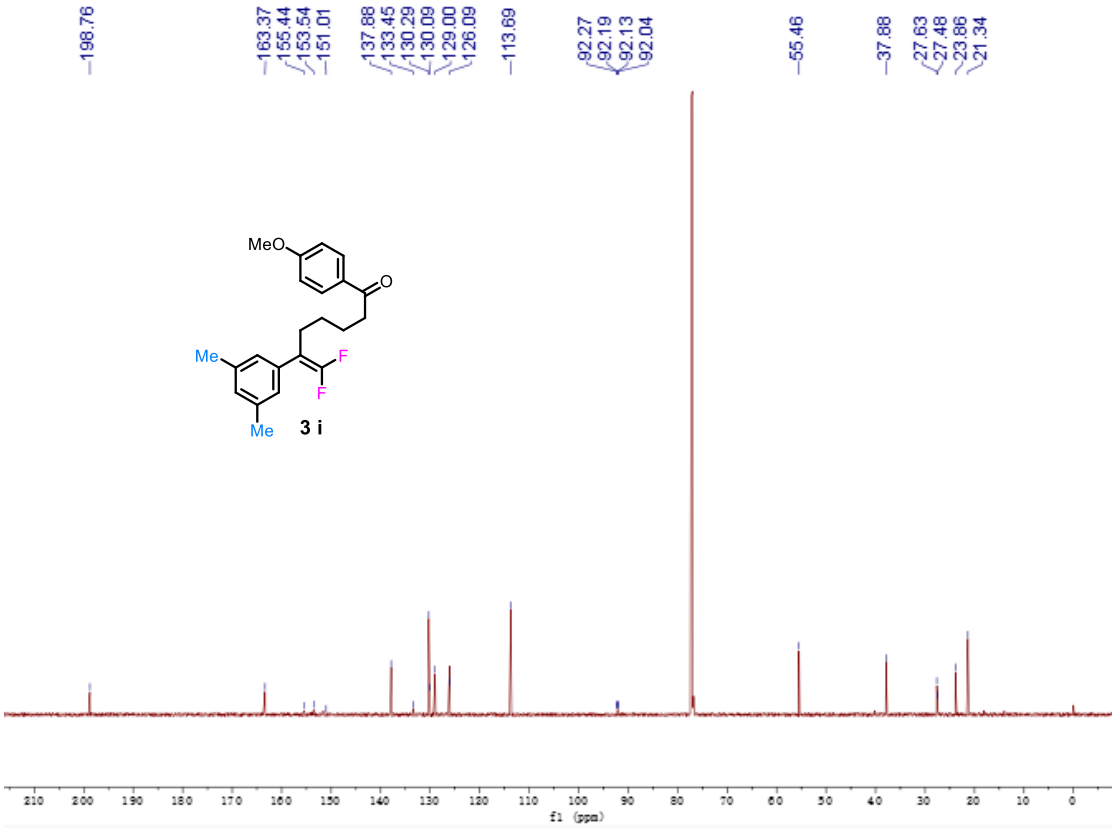
3.00
2.00
1.96
6.00
2.00
2.00
f1 (ppm)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92.19
92.13
92.04
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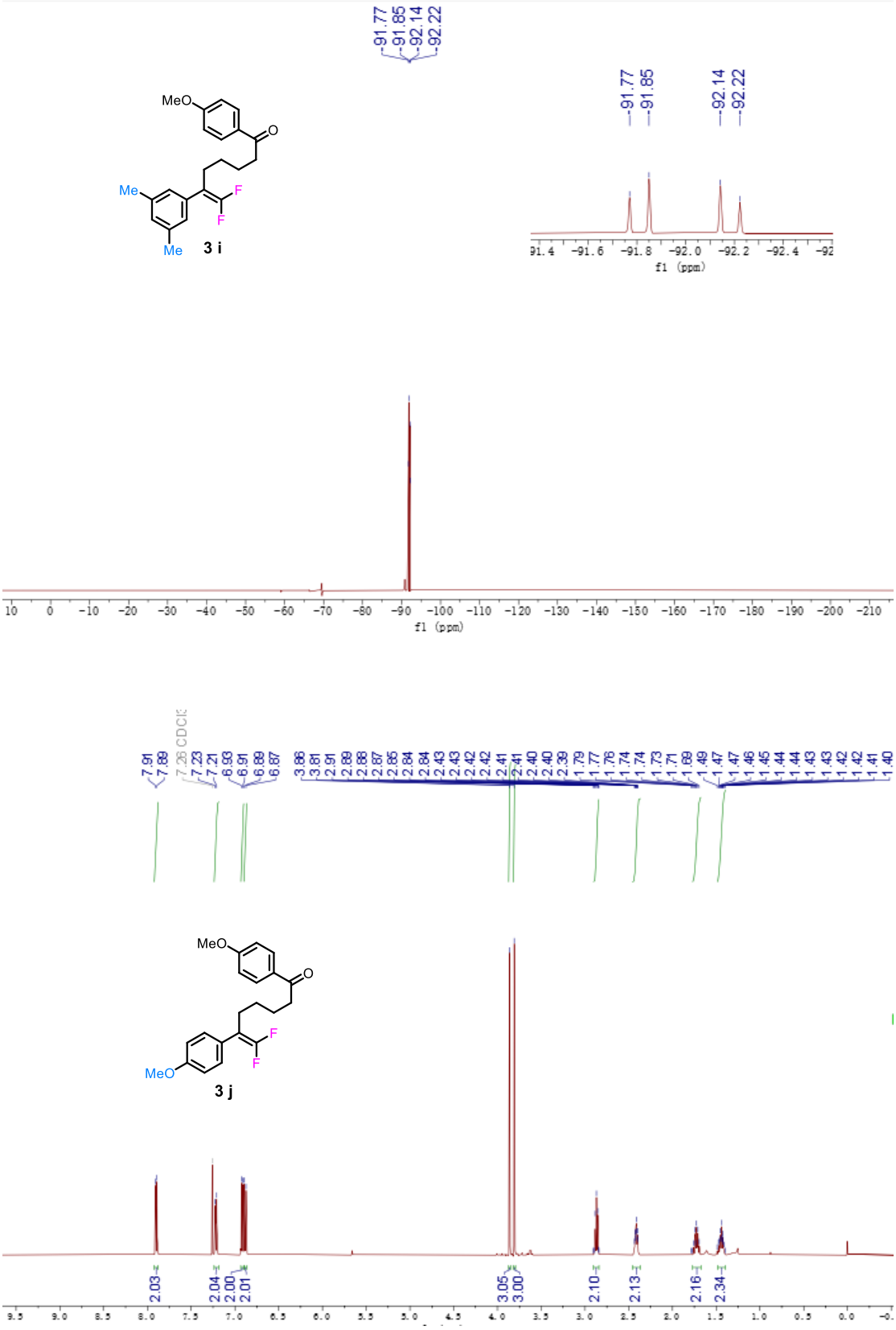
27.48
23.86
21.34
MeO
O
Me
F
F
Me
3 i
f1 (ppm)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-91.85
-92.14
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MeO
O
Me
F
F
Me
3 i
f1 (ppm)
f1 (ppm)
7.91
7.89
7.23
7.21
6.93
6.91
6.89
6.87
3.86
3.81
2.91
2.89
2.88
2.87
2.85
2.84
2.84
2.43
2.43
2.42
2.42
2.41
2.41
2.40
2.40
2.39
1.79
1.77
1.76
1.74
1.74
1.73
1.71
1.69
1.49
1.47
1.47
1.46
1.45
1.44
1.44
1.43
1.43
1.42
1.42
1.41
1.40
MeO
O
F
F
MeO
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2.04
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2.01
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3.00
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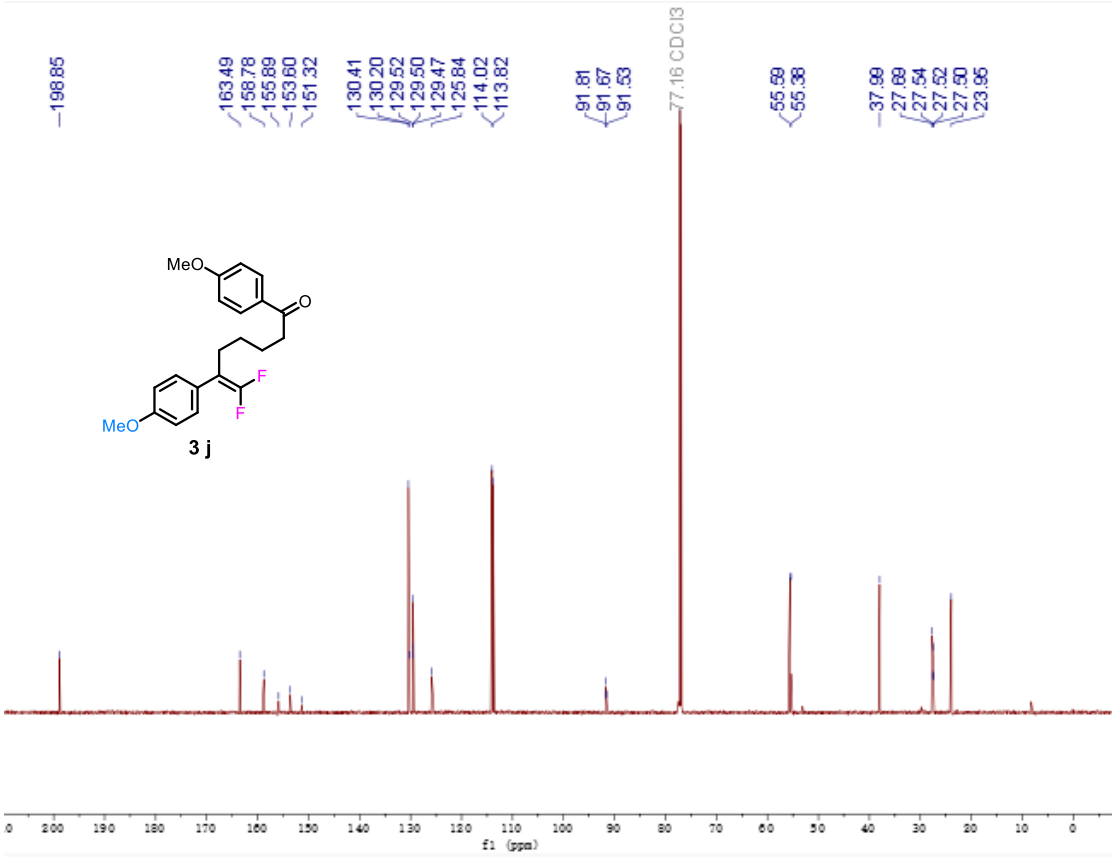
2.16
2.34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114.02
113.82
91.81
91.67
91.53
77.16 CDCl3
55.59
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27.50
23.95
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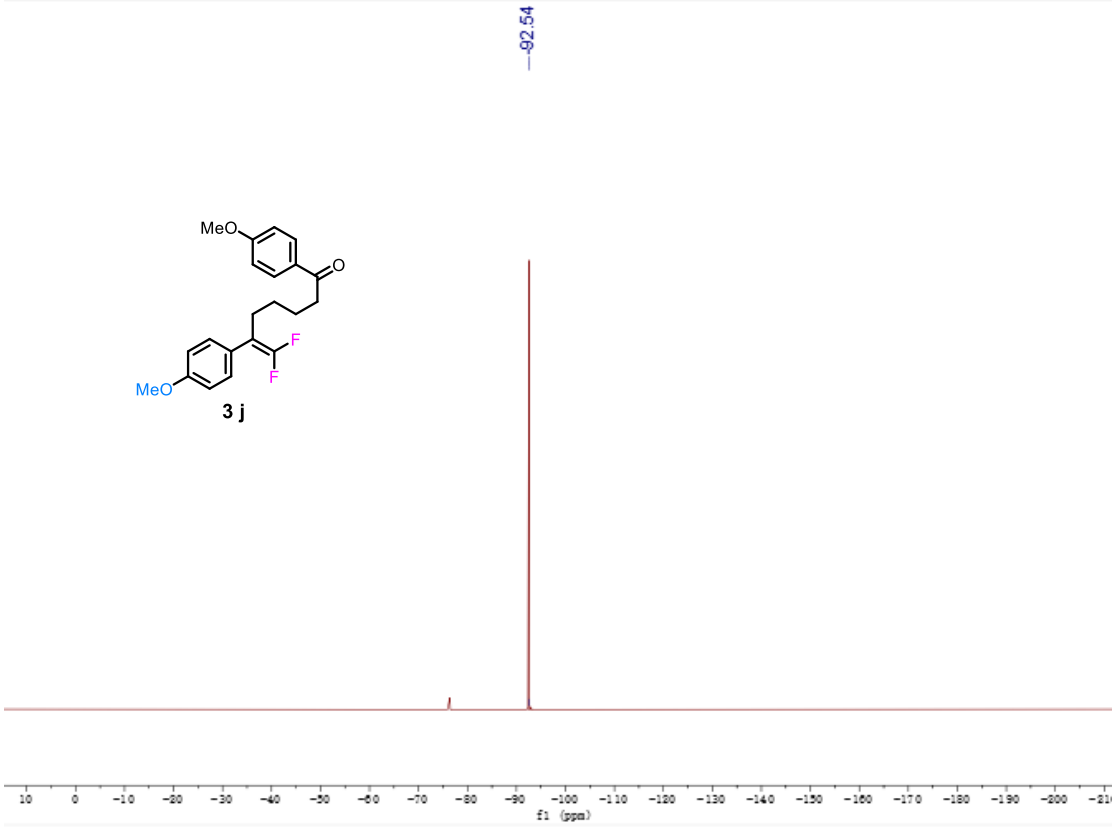
O
F
F
MeO
3 j
f1 (ppm)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MeO
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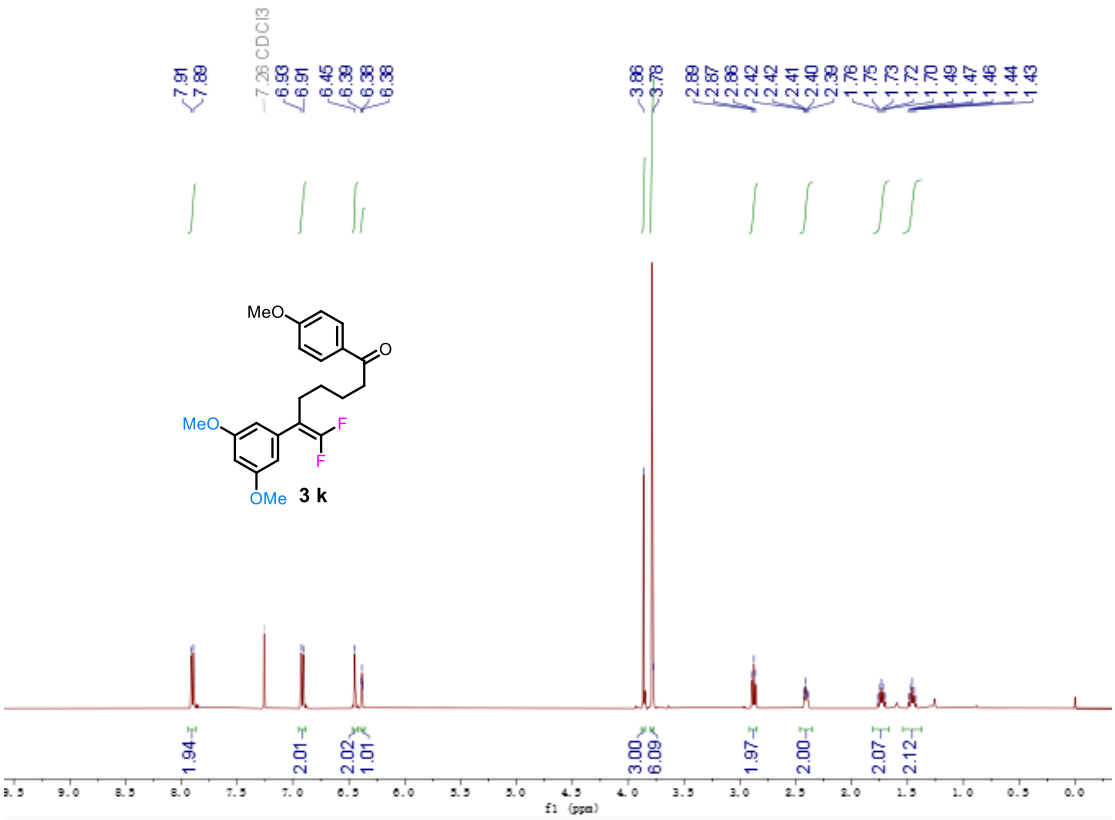
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2.89
2.87
2.86
2.42
2.42
2.41
2.40
2.39
1.76
1.75
1.73
1.72
1.70
1.49
1.47
1.46
1.44
1.43
MeO
O
MeO
F
F
OMe
3 k
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6.09
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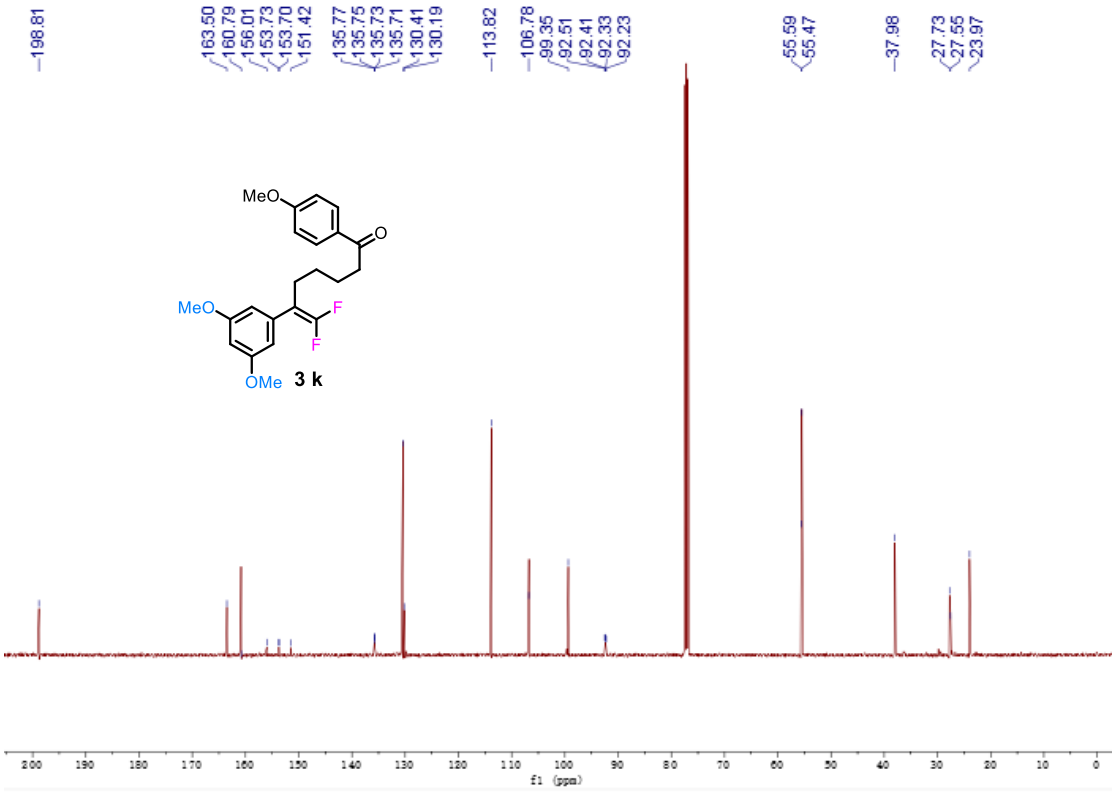
2.00
2.07
2.12
f1 (ppm)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106.78
99.35
92.51
92.41
92.33
92.23
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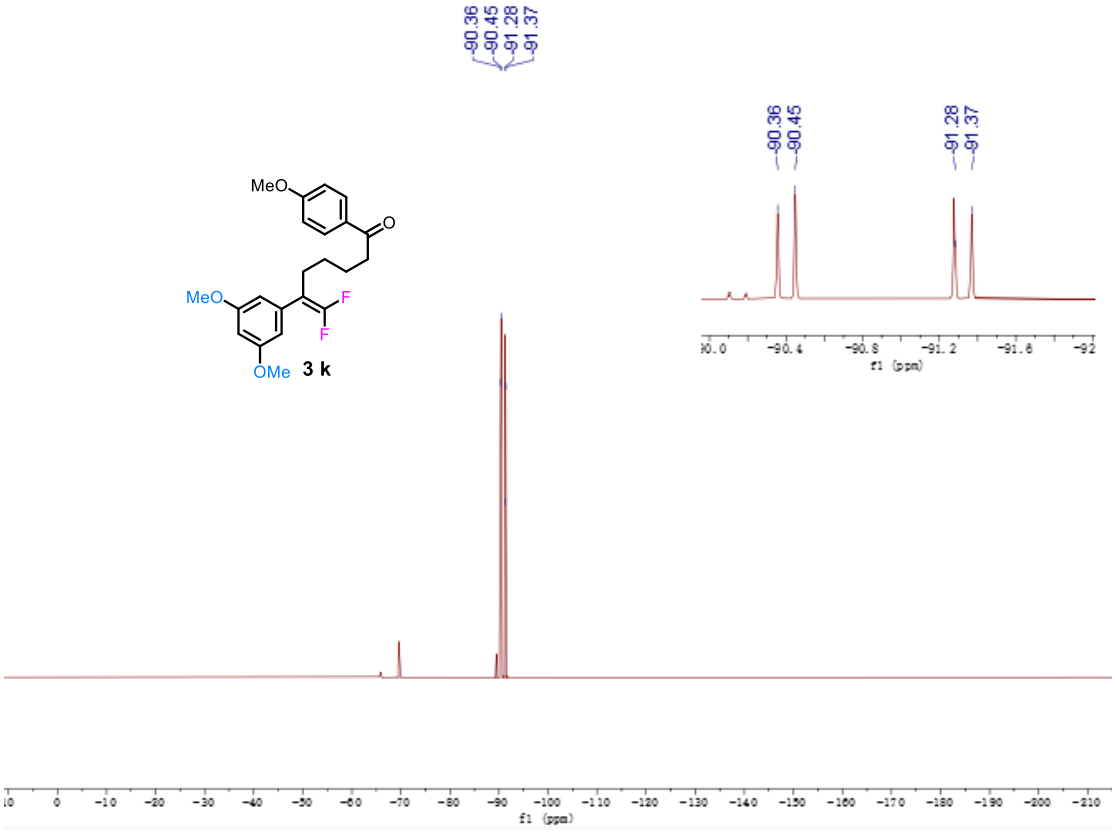
27.73
27.55
23.97
MeO
O
MeO
F
F
OMe
3 k
f1 (ppm)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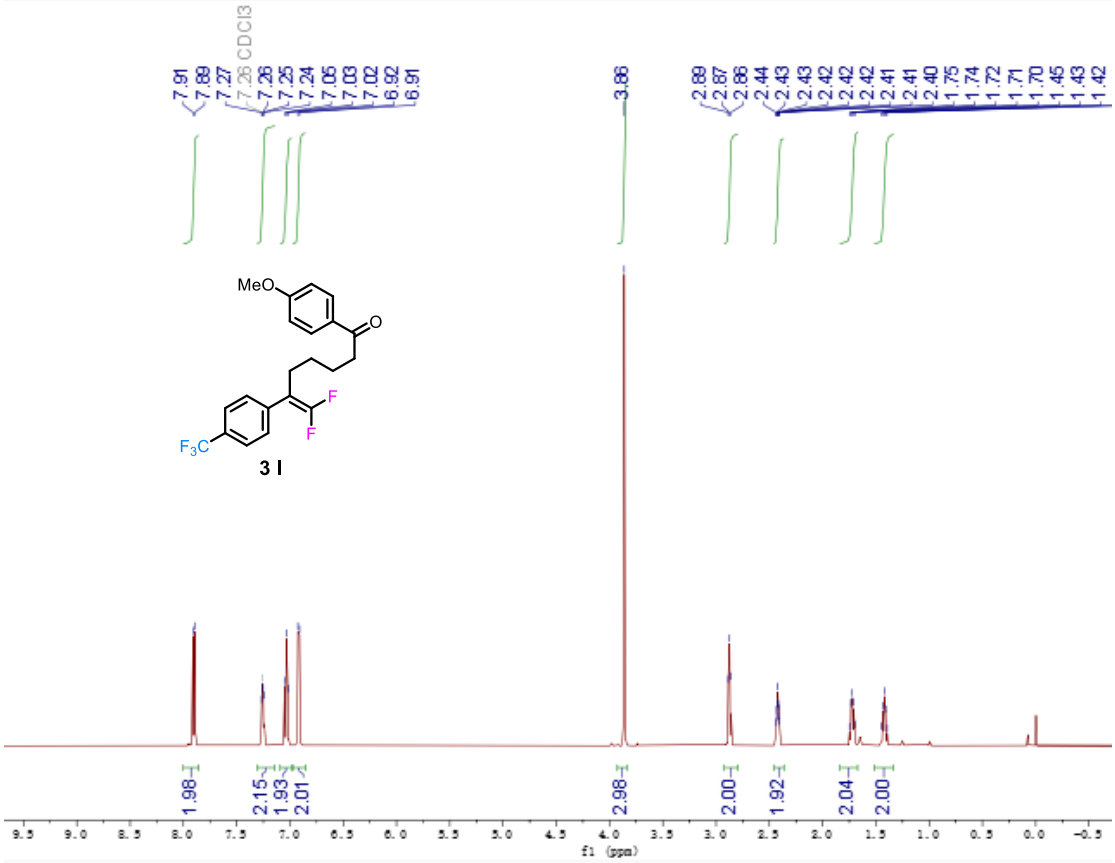
F
F
OMe
3 k
f1 (ppm)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2.87
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2.42
2.42
2.41
2.41
2.40
1.75
1.74
1.72
1.71
1.70
1.45
1.43
1.42
MeO
O
F
F
F3C
3 l
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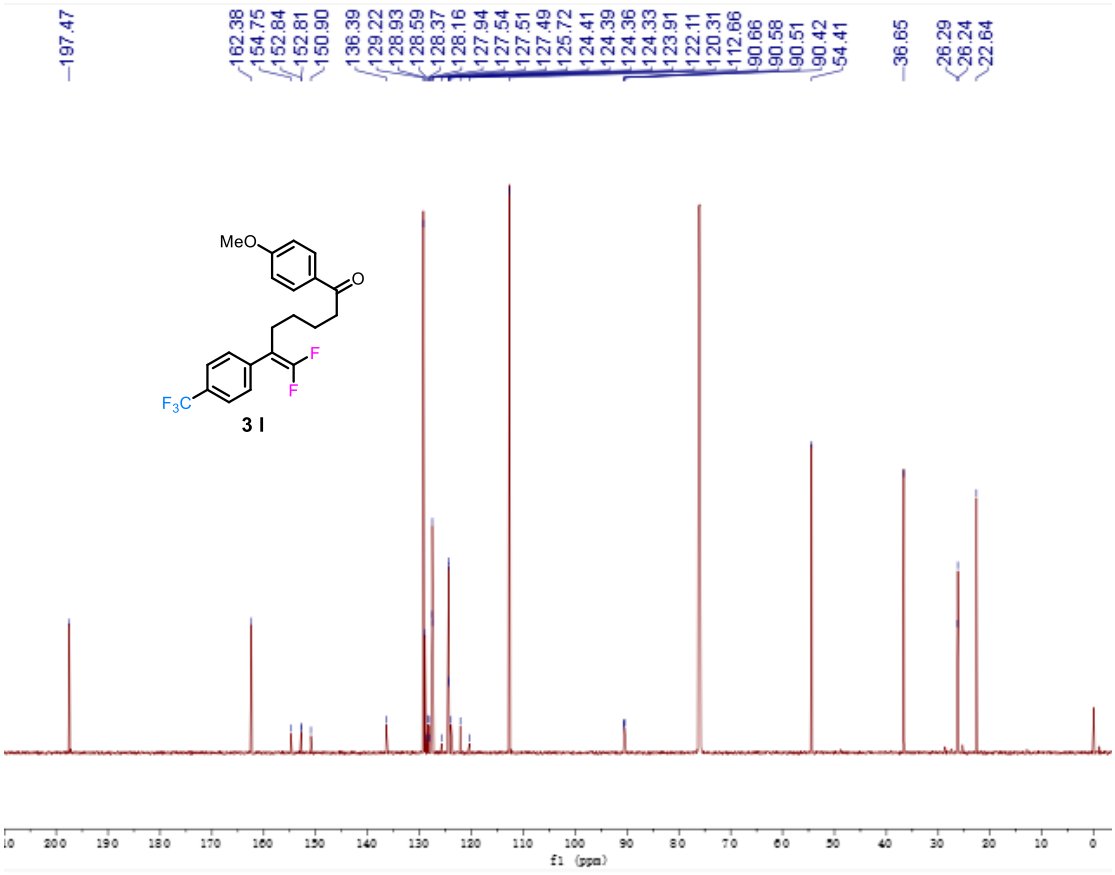
1.93
2.01
2.98
2.00
1.92
2.04
2.00
f1 (ppm)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90.51
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26.29
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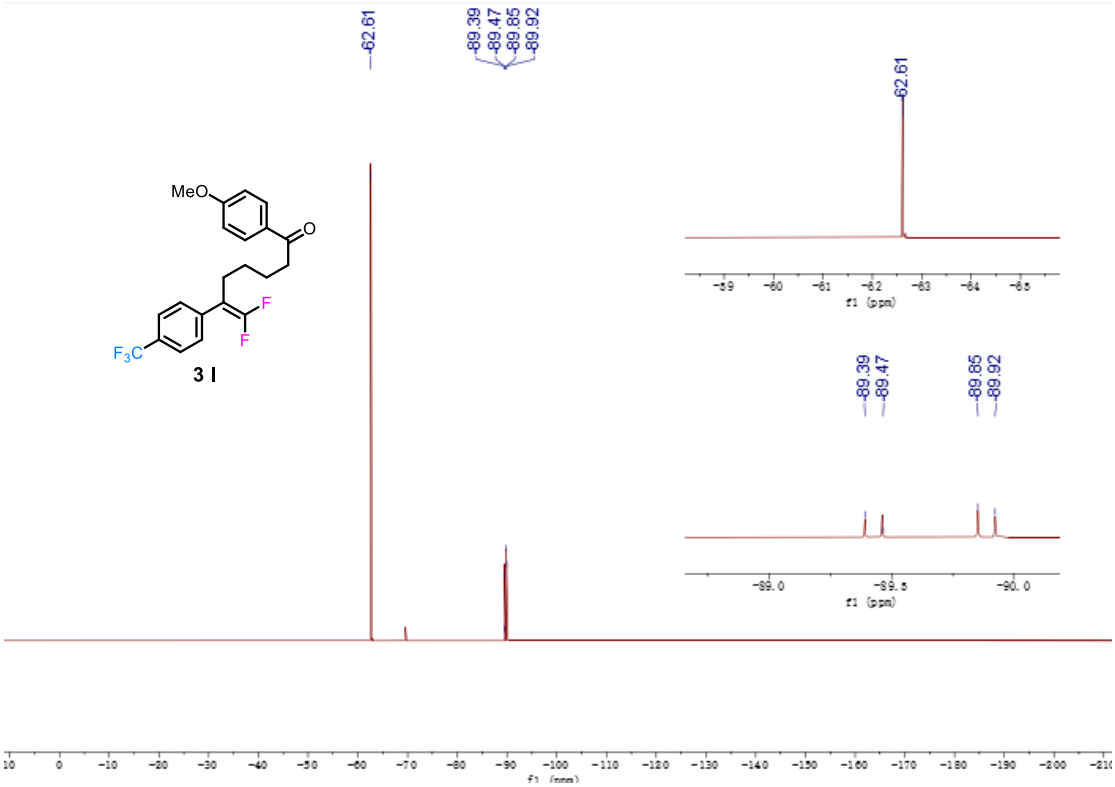
O
F
F
F3C
3 l
f1 (ppm)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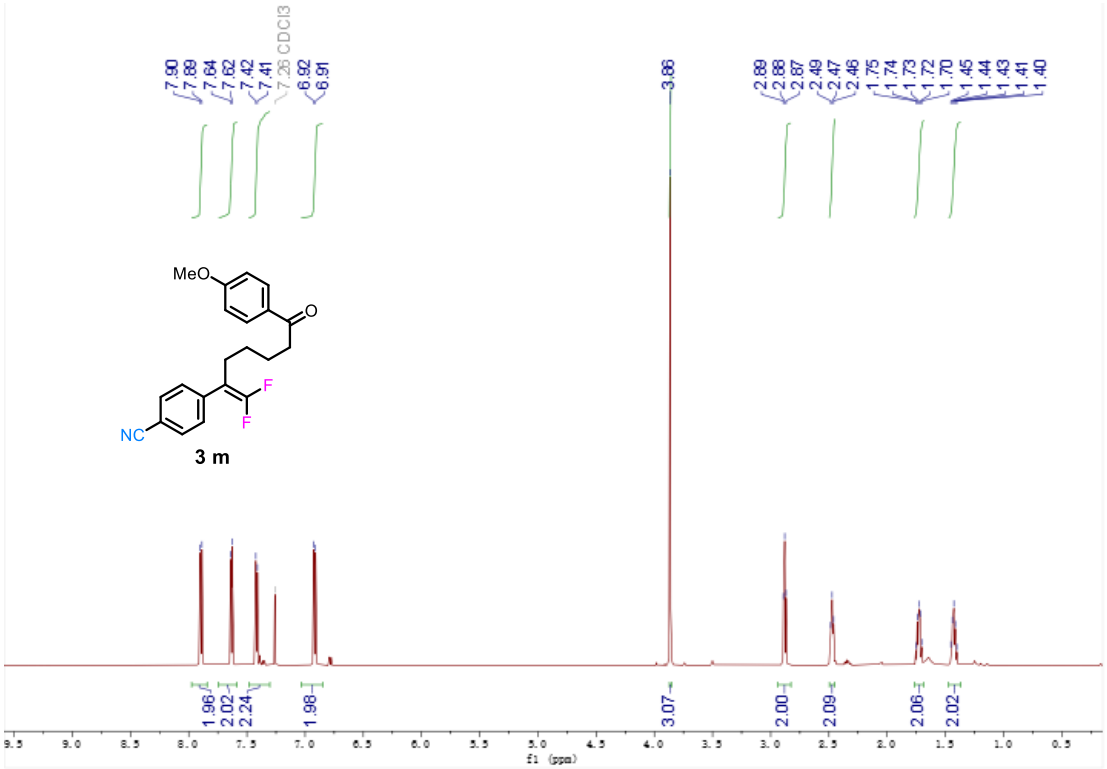
f1 (ppm)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2.87
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2.47
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1.75
1.74
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1.72
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1.45
1.44
1.43
1.41
1.40
MeO
O
F
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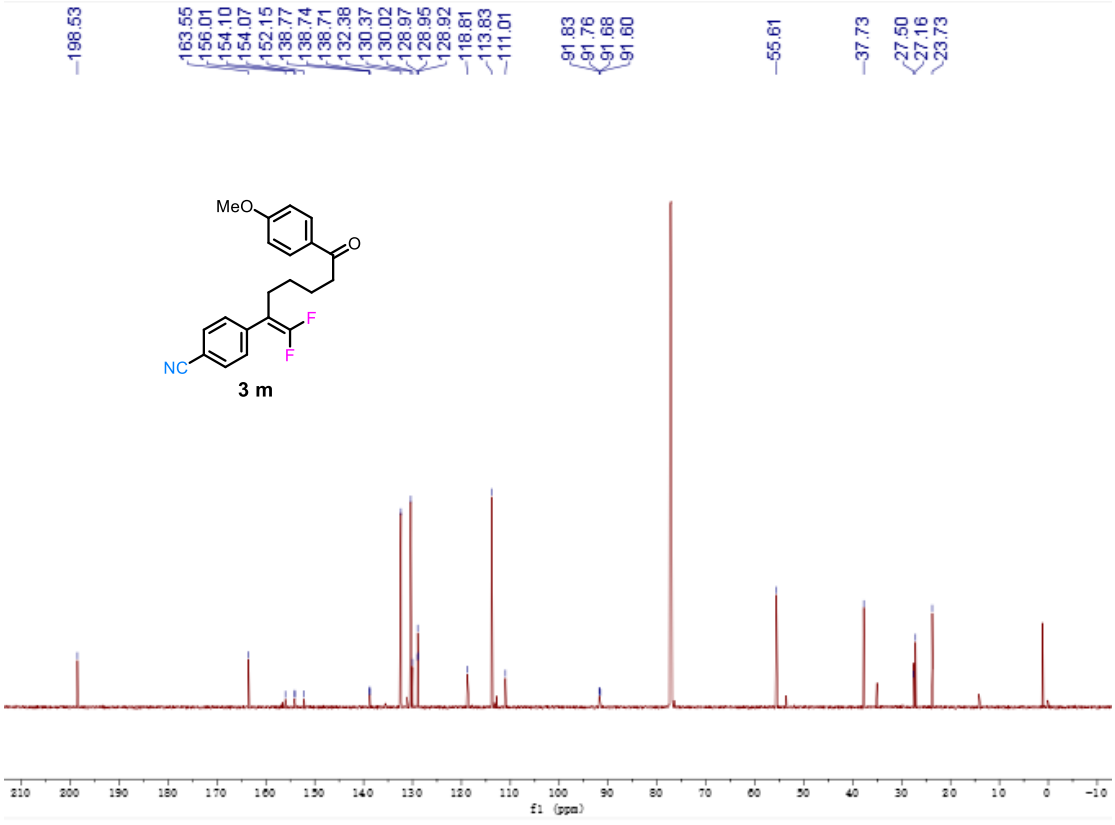
2.02
f1 (ppm)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111.01
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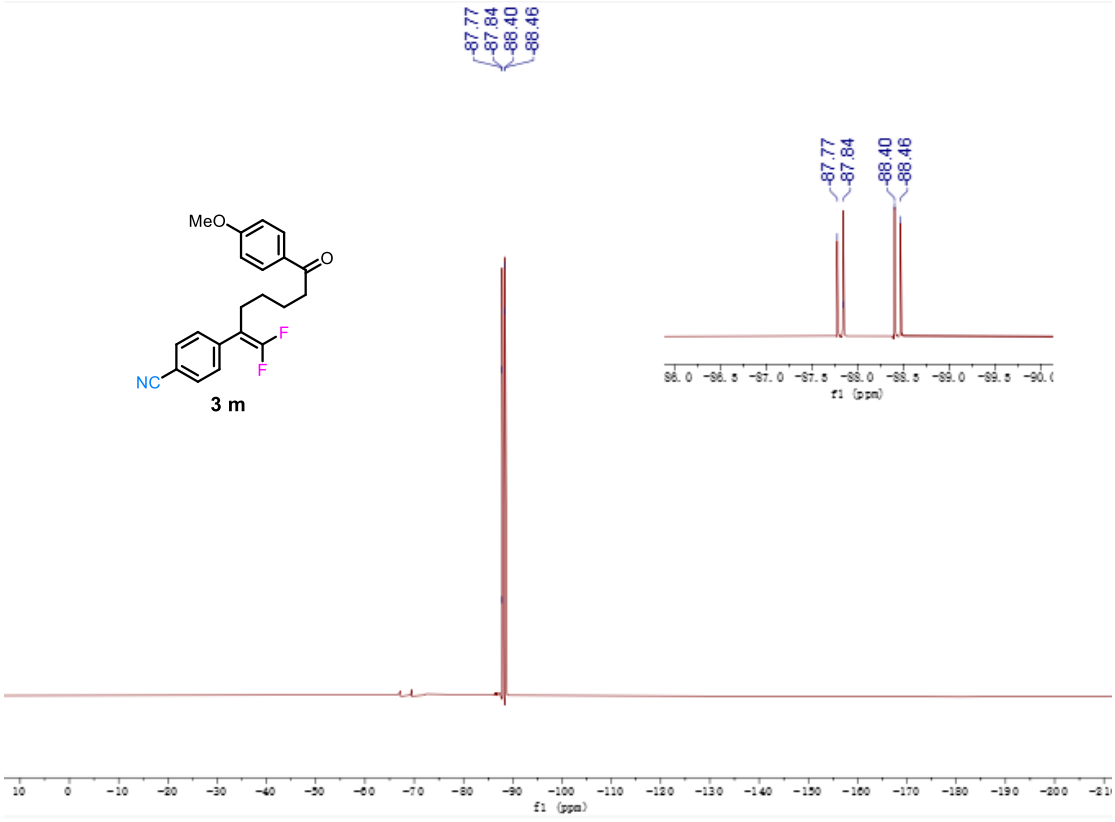
O
F
F
NC
3 m
f1 (ppm)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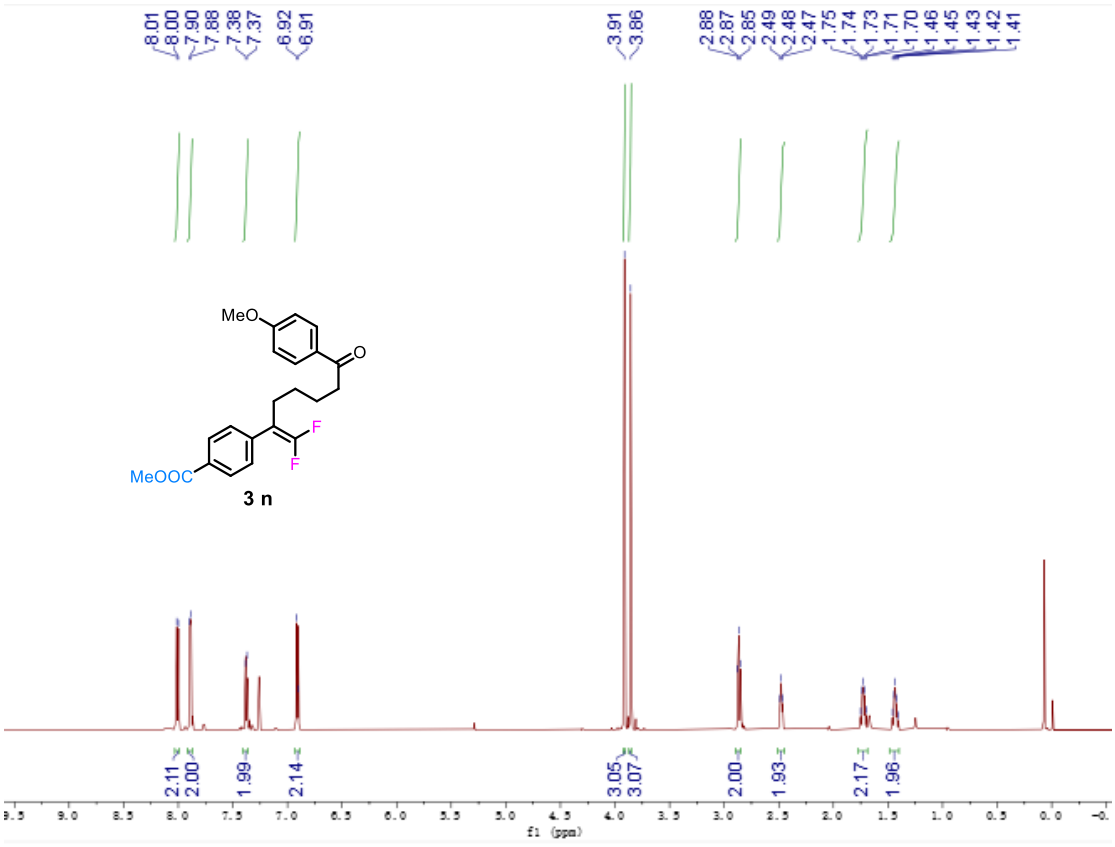
NC
3 m
f1 (ppm)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6.91
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3.86
2.88
2.87
2.85
2.49
2.48
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1.75
1.74
1.73
1.71
1.70
1.46
1.45
1.43
1.42
1.41
MeO
O
F
F
MeOOC
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3.07
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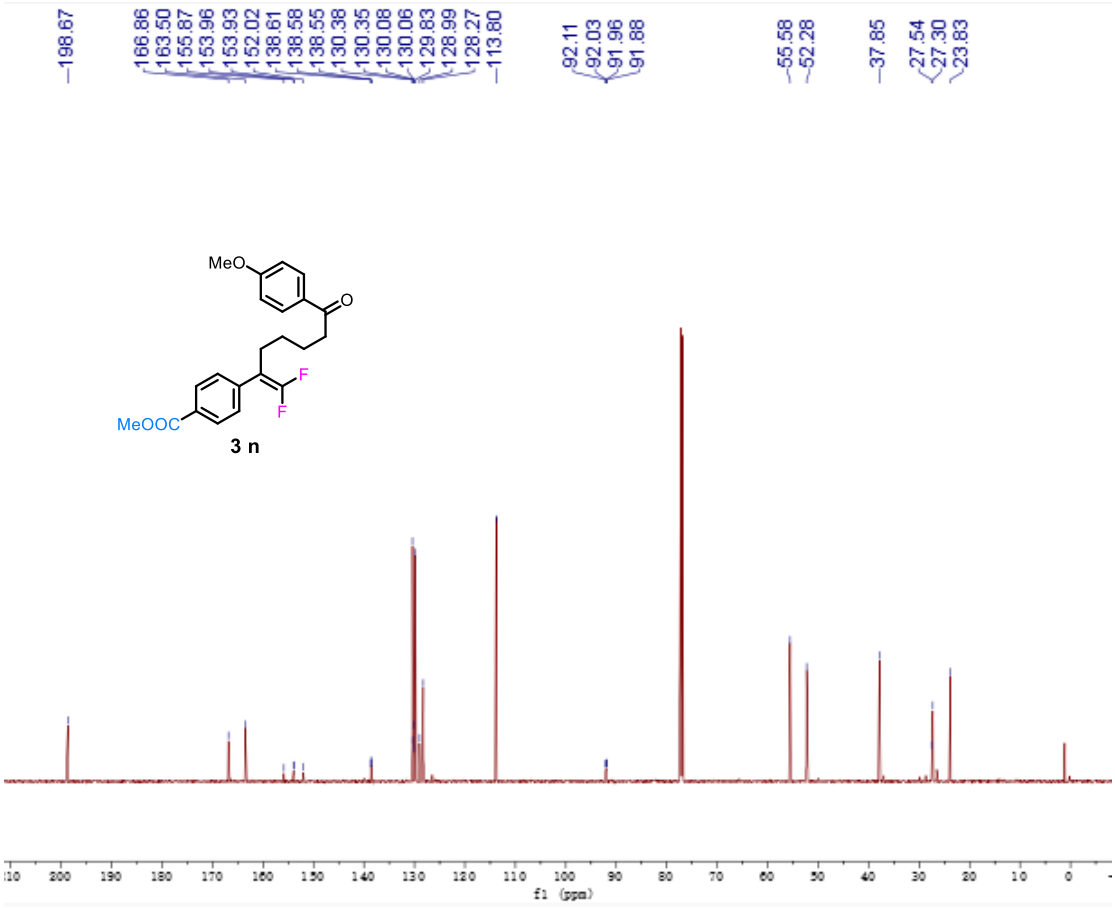
1.96
f1 (ppm)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91.96
91.88
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27.54
27.30
23.83
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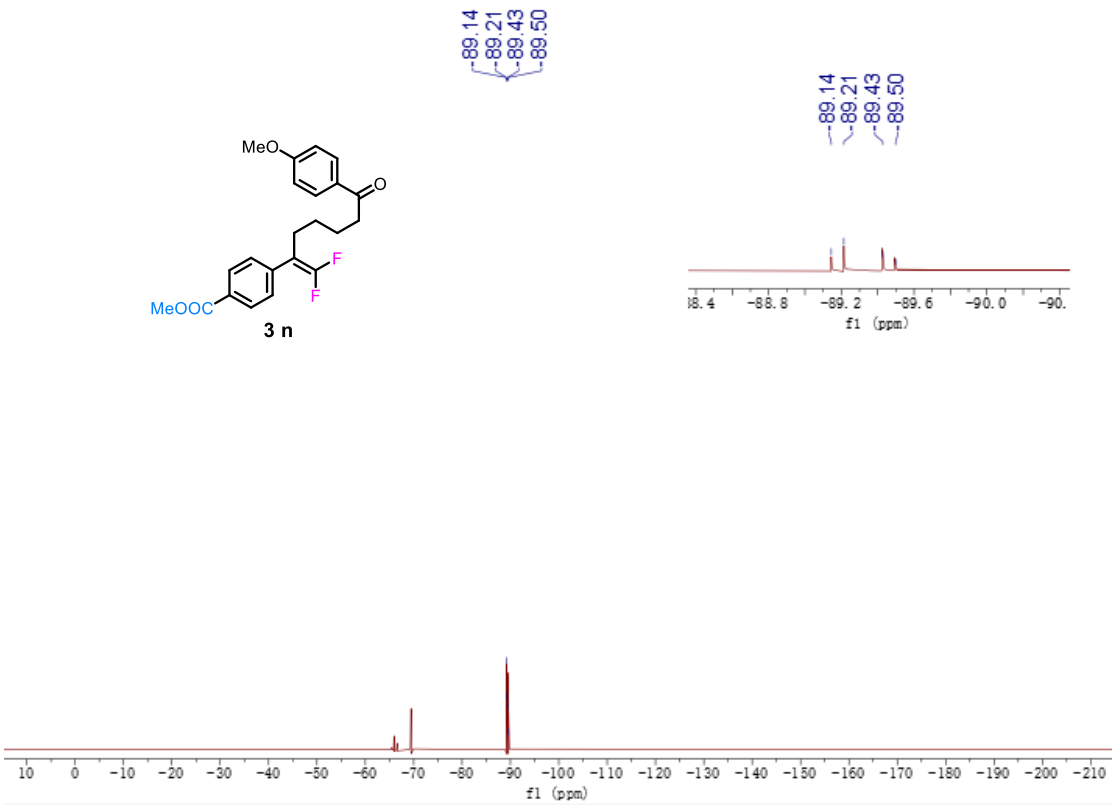
O
F
F
MeOOC
3 n
f1 (ppm)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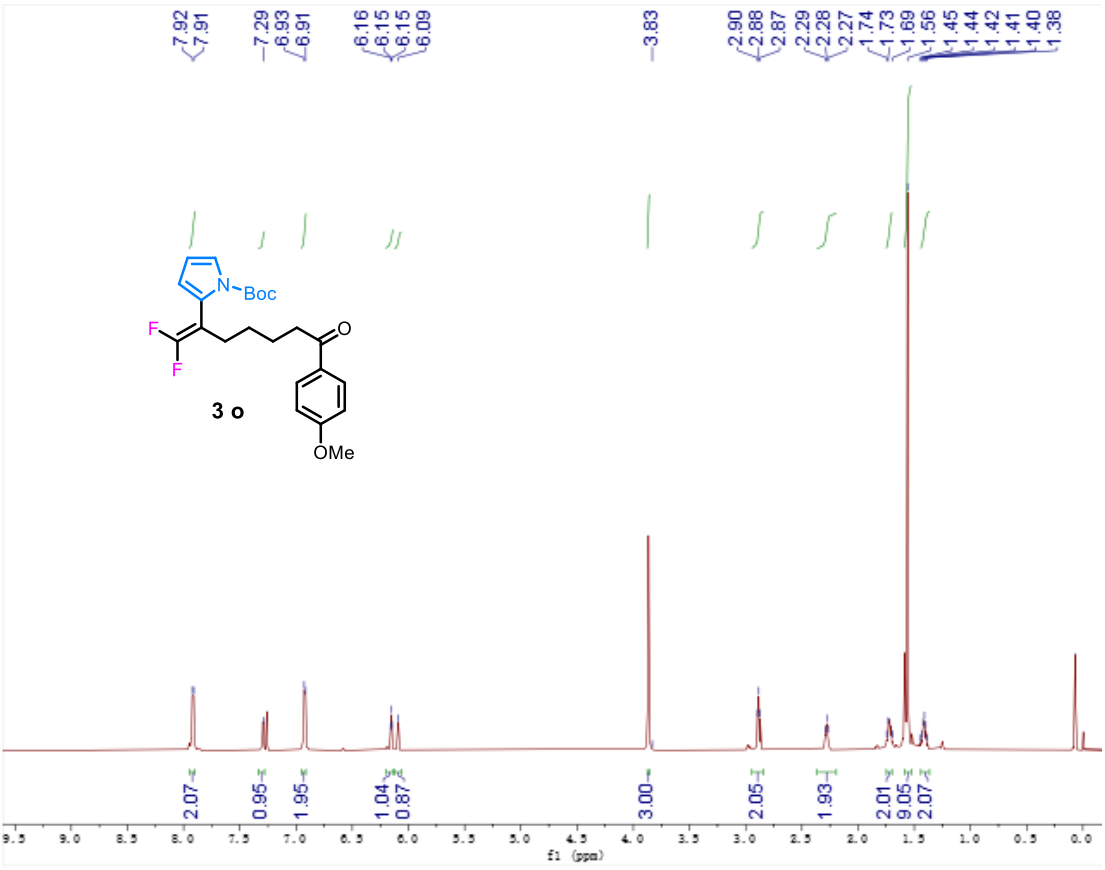
O
F
F
MeOOC
3 n
f1 (ppm)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1.73
1.69
1.56
1.45
1.44
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1.41
1.40
1.38
N
Boc
F
F
O
OMe
3 o
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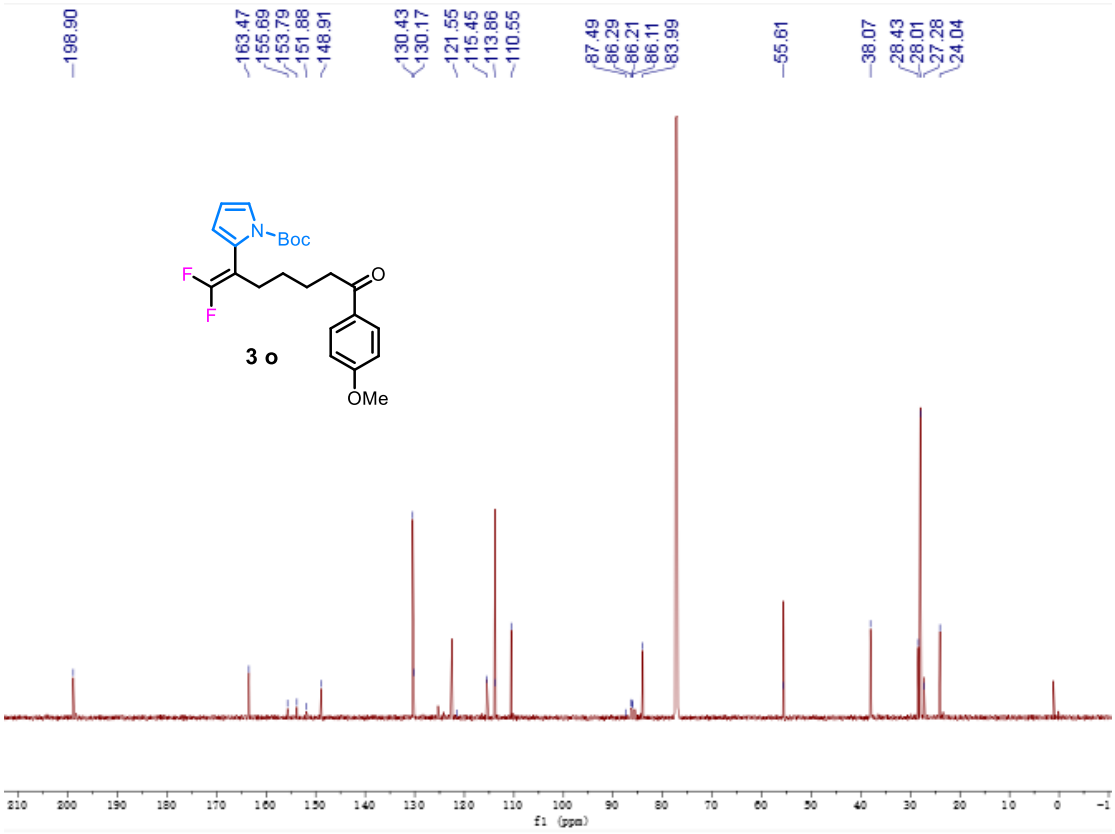
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86.21
86.11
83.99
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24.04
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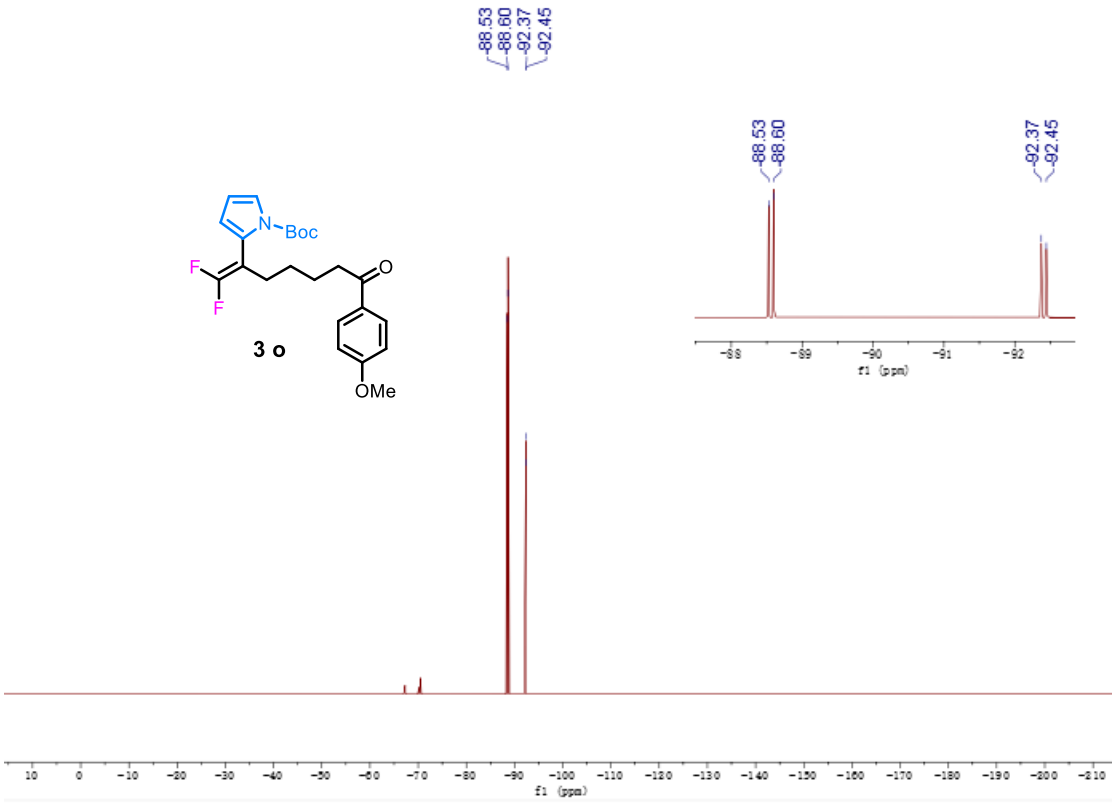
Boc
F
F
O
OMe
3 o
f1 (ppm)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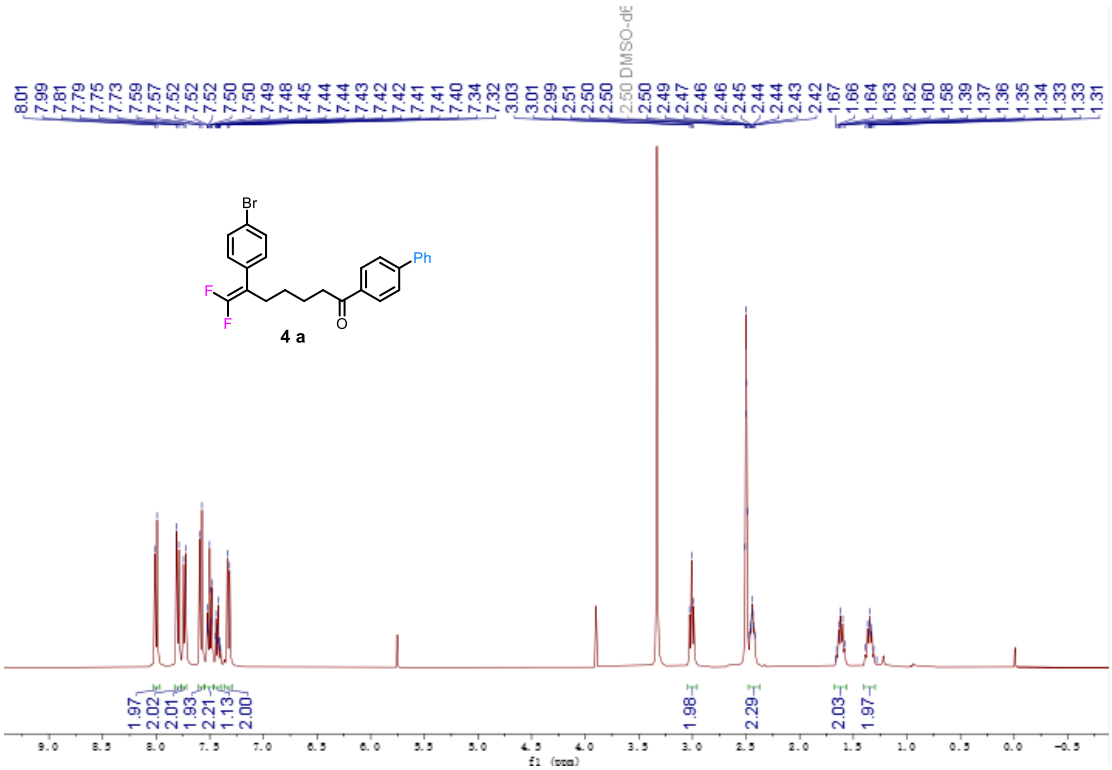
Boc
F
F
O
OMe
3 o
f1 (ppm)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Ph
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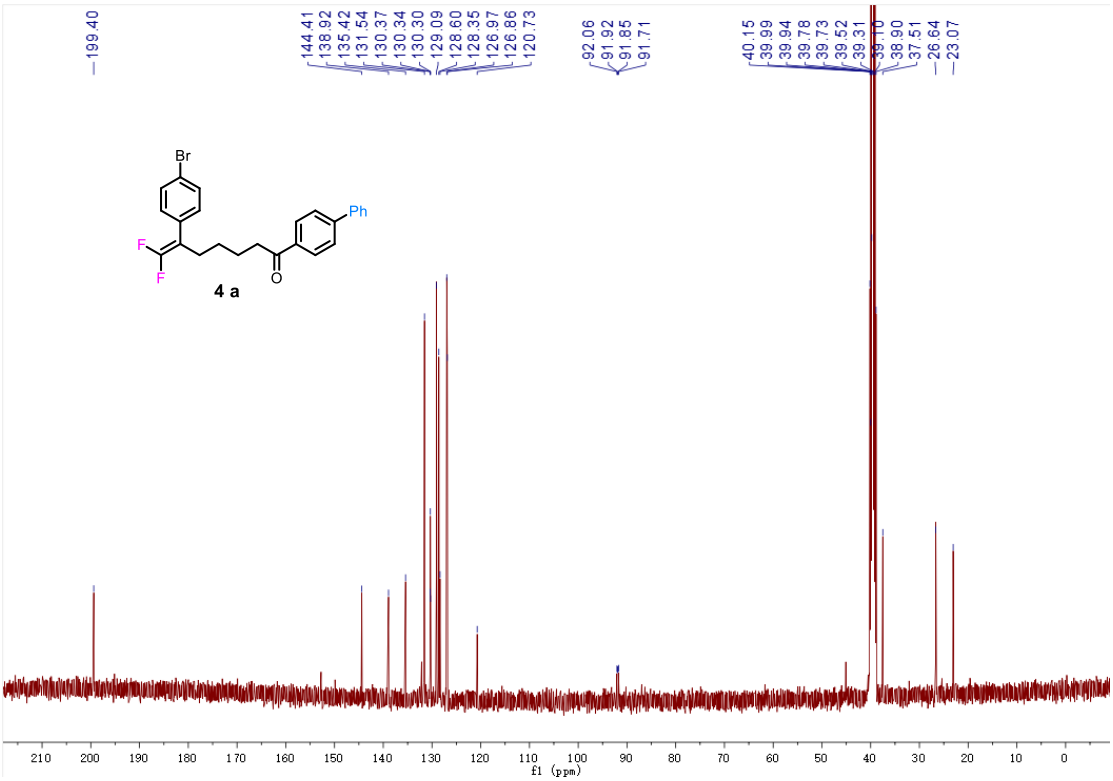
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91.85
91.71
40.15
39.99
39.94
39.78
39.73
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26.64
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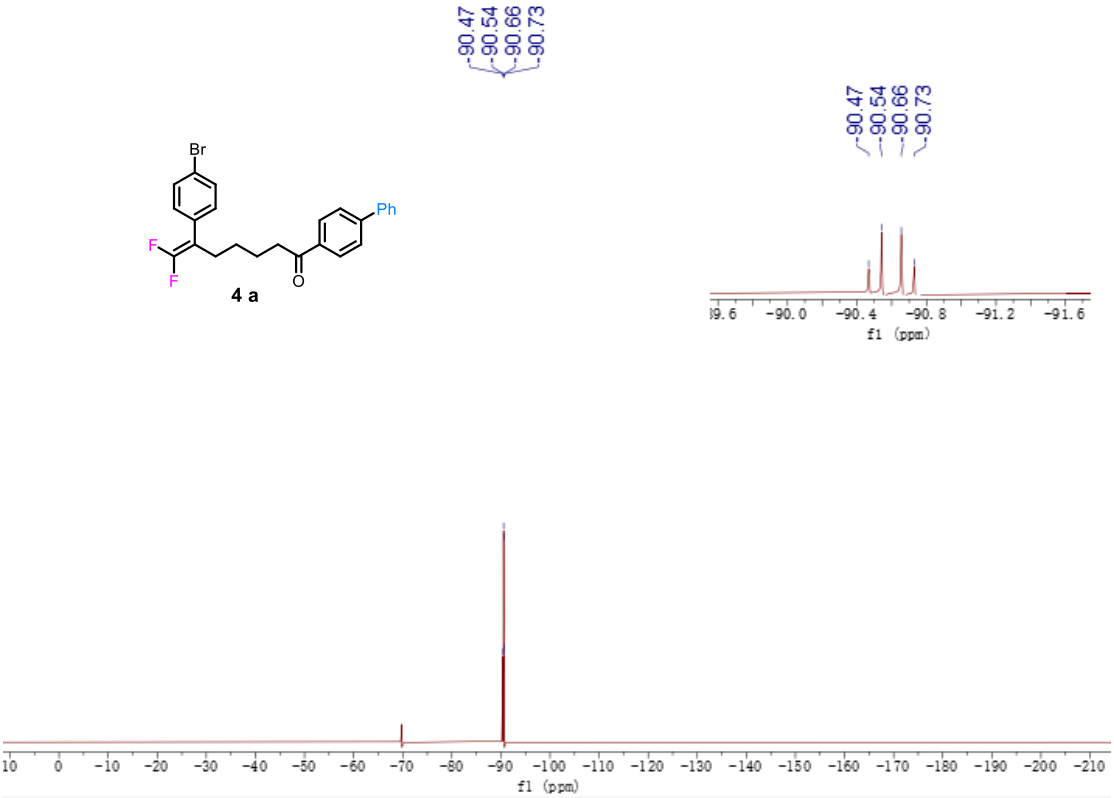
Ph
F
F
O
4 a
f1 (ppm)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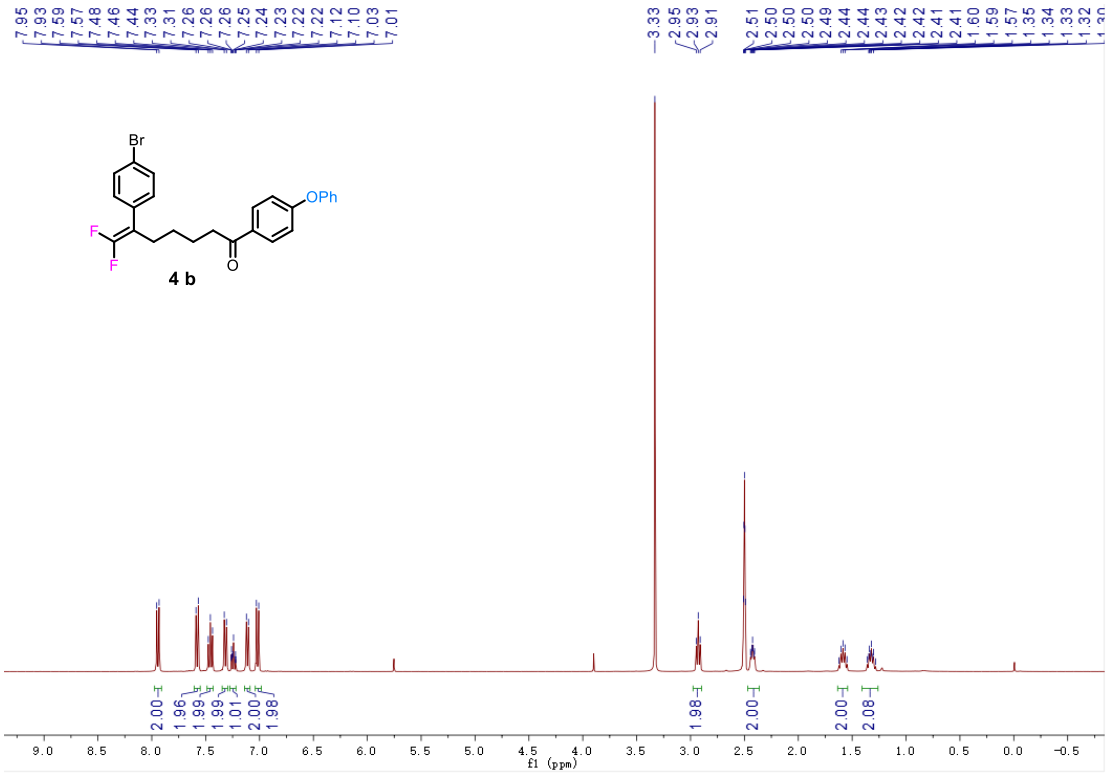
Ph
F
F
O
4 a
f1 (ppm)


Br
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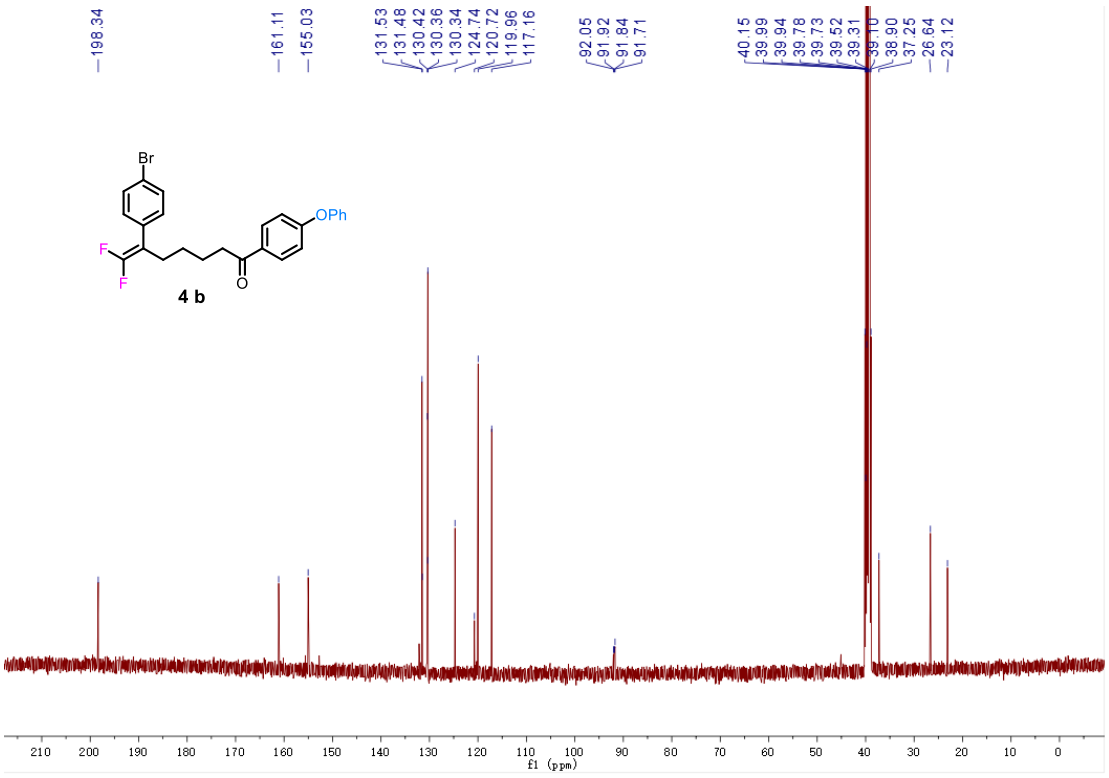
F
F
O
4 b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O
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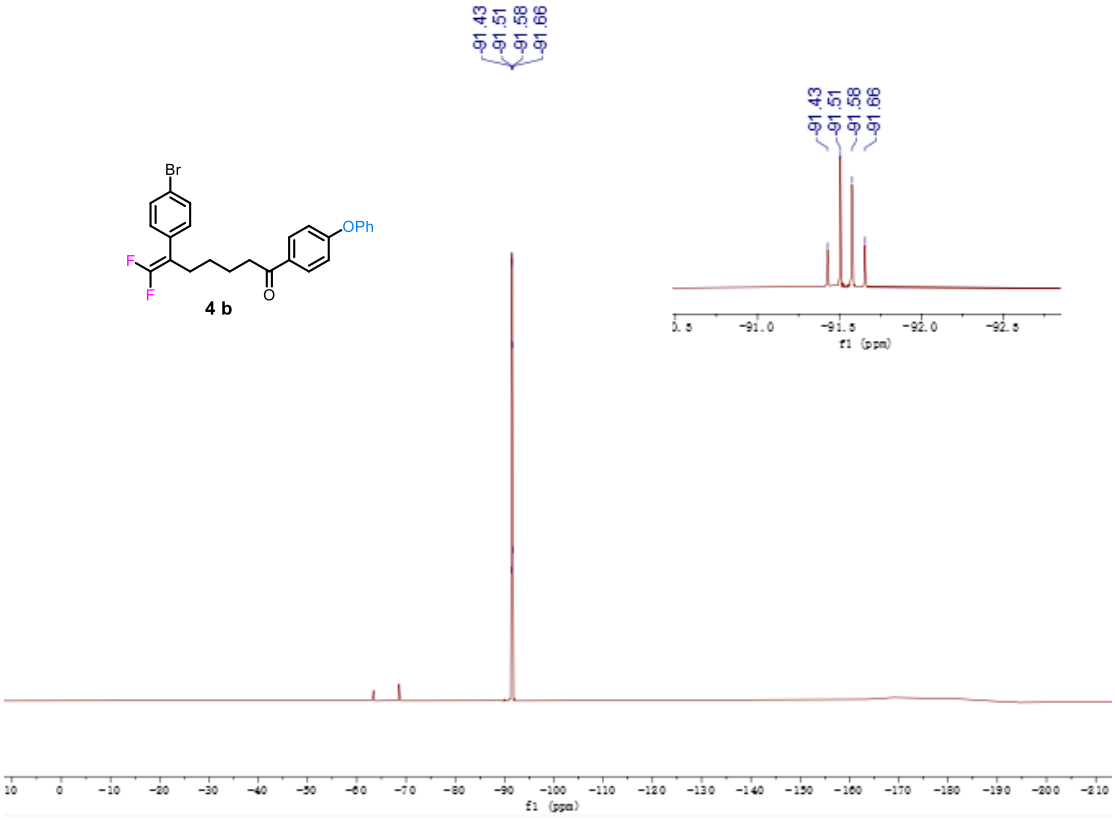
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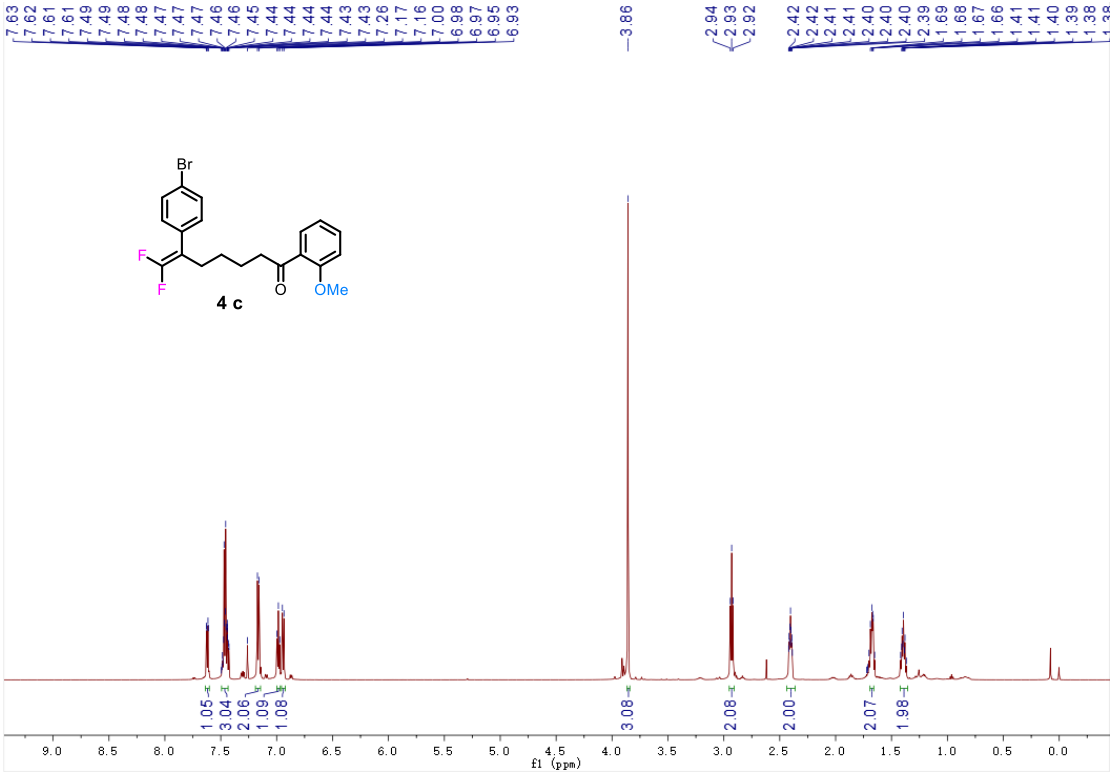
F
F
O
4 b
f1 (ppm)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7.45
7.44
7.44
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7.43
7.26
7.17
7.16
7.00
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6.97
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2.94
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2.40
2.39
1.69
1.68
1.67
1.66
1.41
1.41
1.40
1.39
1.38
Br
F
F
O
OMe
4 c
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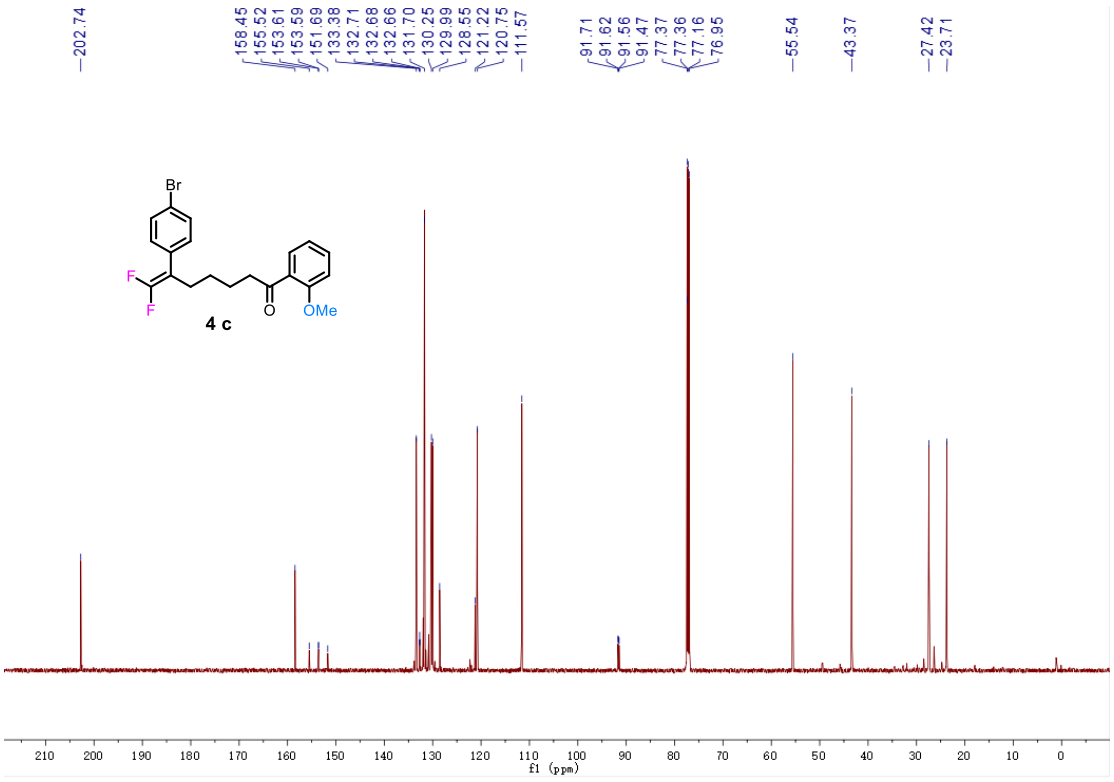
1.98
f1 (ppm)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128.55
121.22
120.75
111.57
91.71
91.62
91.56
91.47
77.37
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27.42
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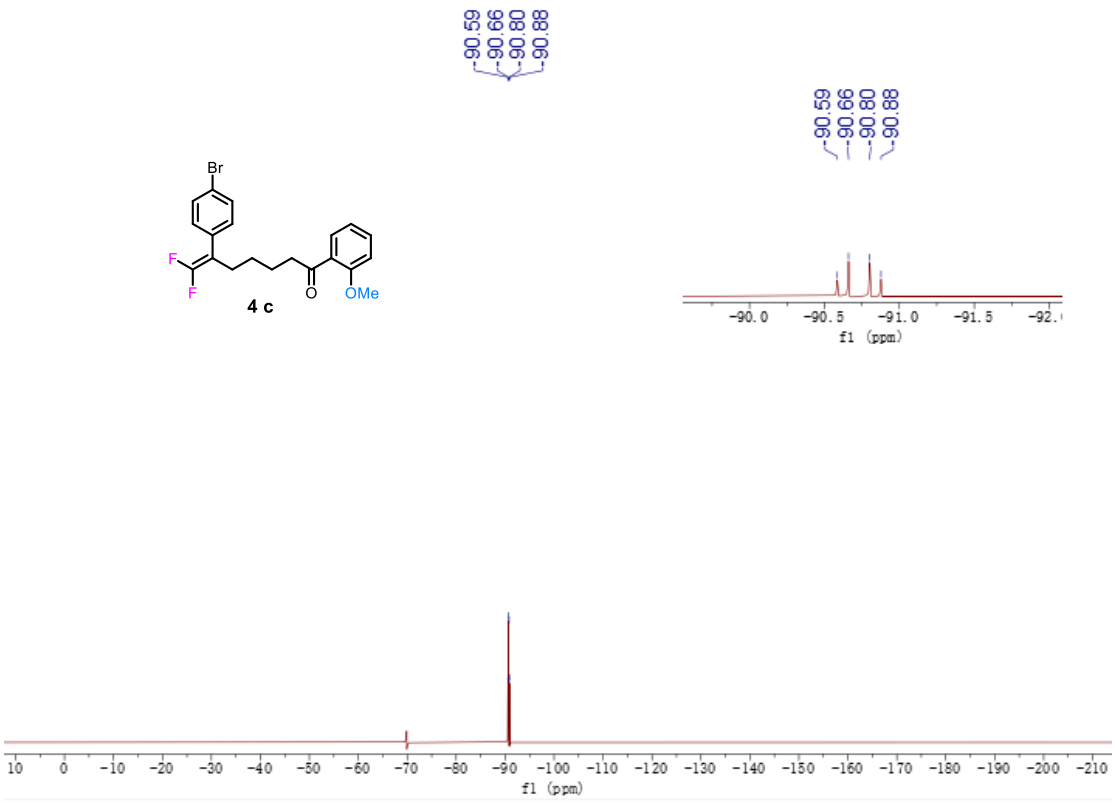
Br
F
F
O
OMe
4 c
f1 (ppm)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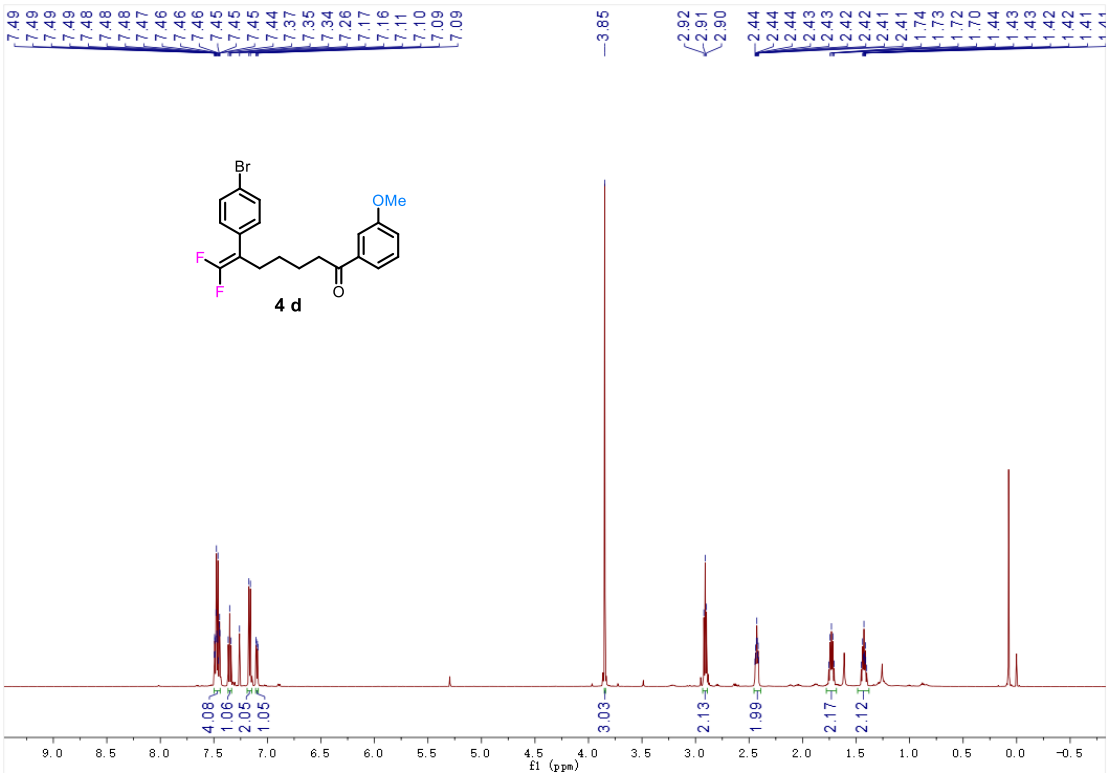
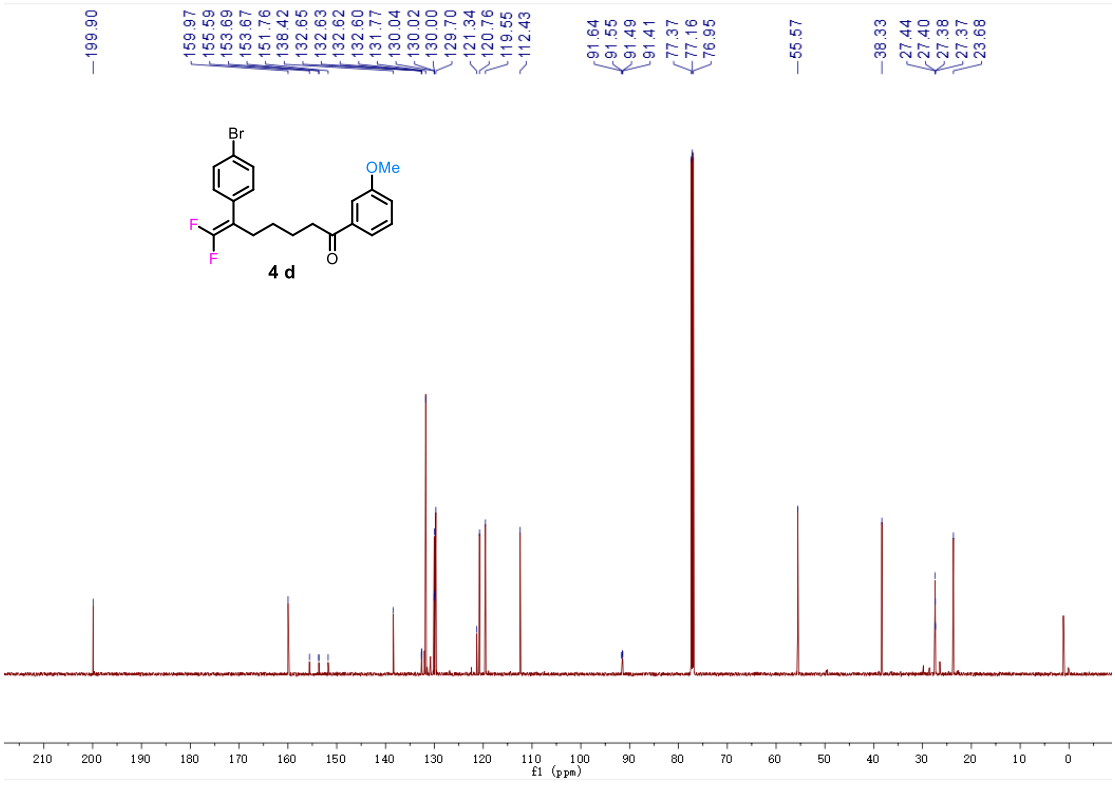
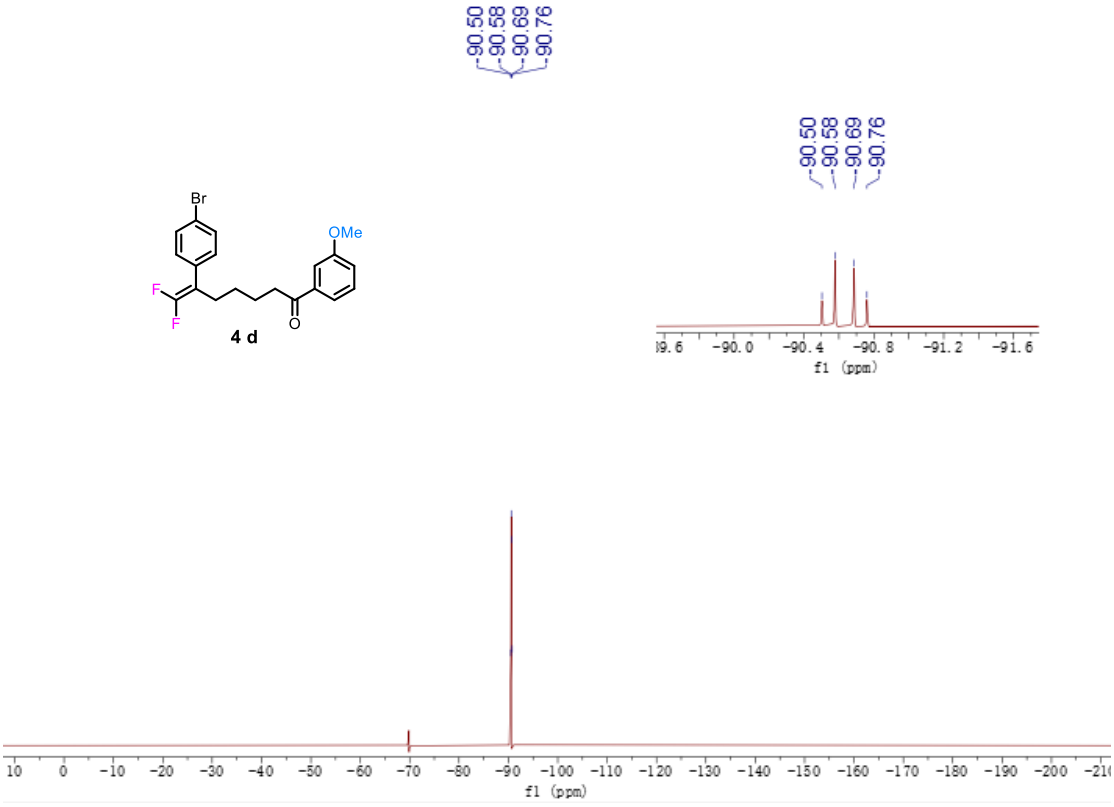
F
F
O
OMe
4 c
f1 (ppm)


Br
OMe
F
F
O
4 d
f1 (ppm)


Br
OMe
F
F
O
4 d
f1 (ppm)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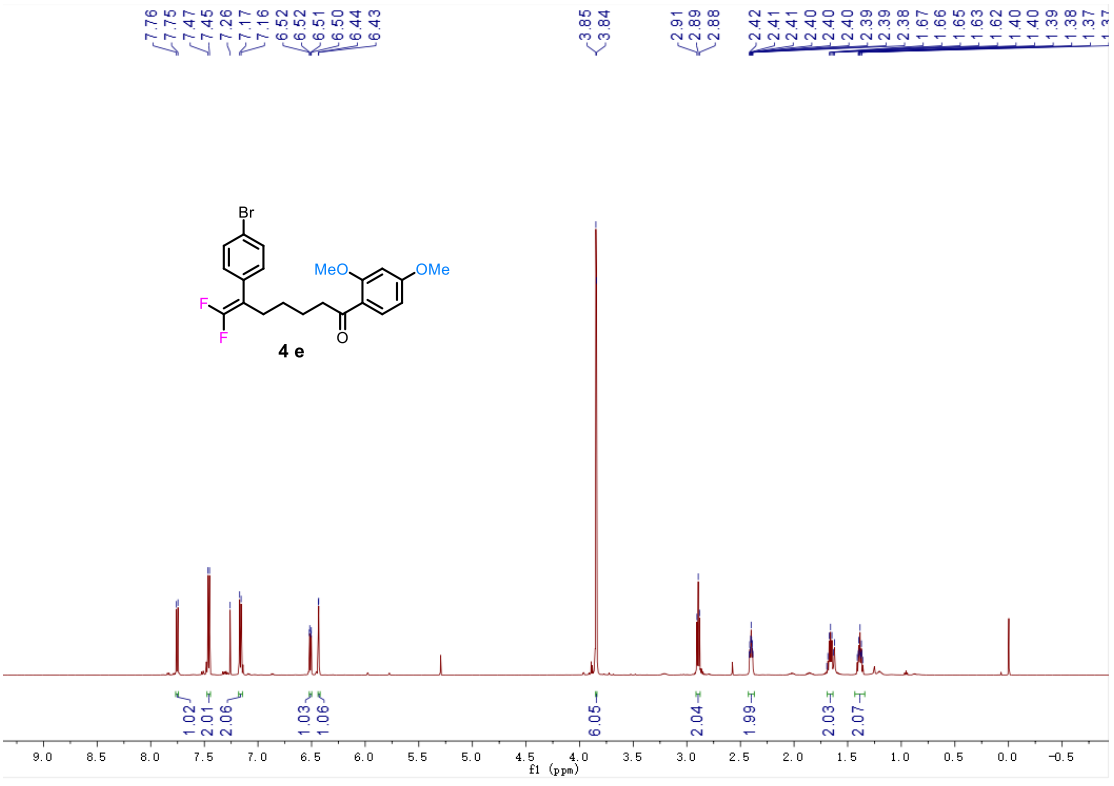
-90.76
Br
OMe
F
F
O
4 d
f1 (ppm)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6.43
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3.84
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2.89
2.88
2.42
2.41
2.40
2.39
2.38
1.67
1.66
1.65
1.63
1.62
1.40
1.39
1.38
Br
MeO
OMe
F
F
O
4 e
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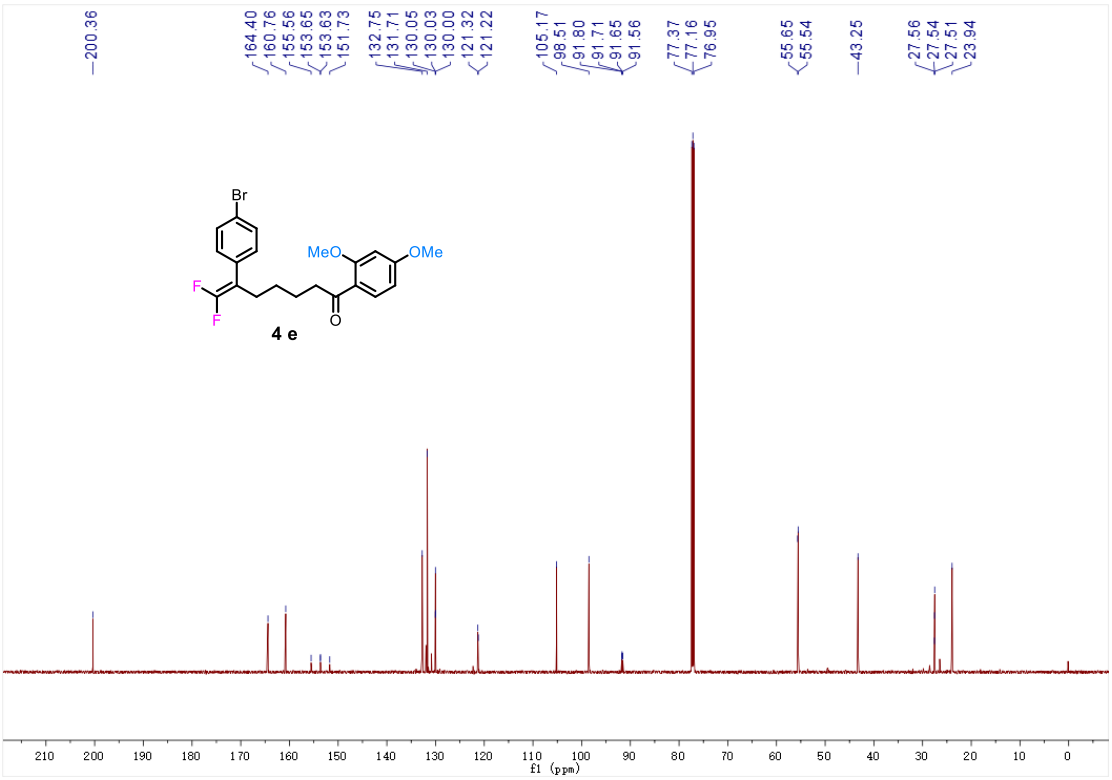
2.06
1.03
1.06
6.05
2.04
1.99
2.03
2.07
f1 (ppm)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121.32
121.22
105.17
98.51
91.80
91.71
91.65
91.56
77.37
77.16
76.95
55.65
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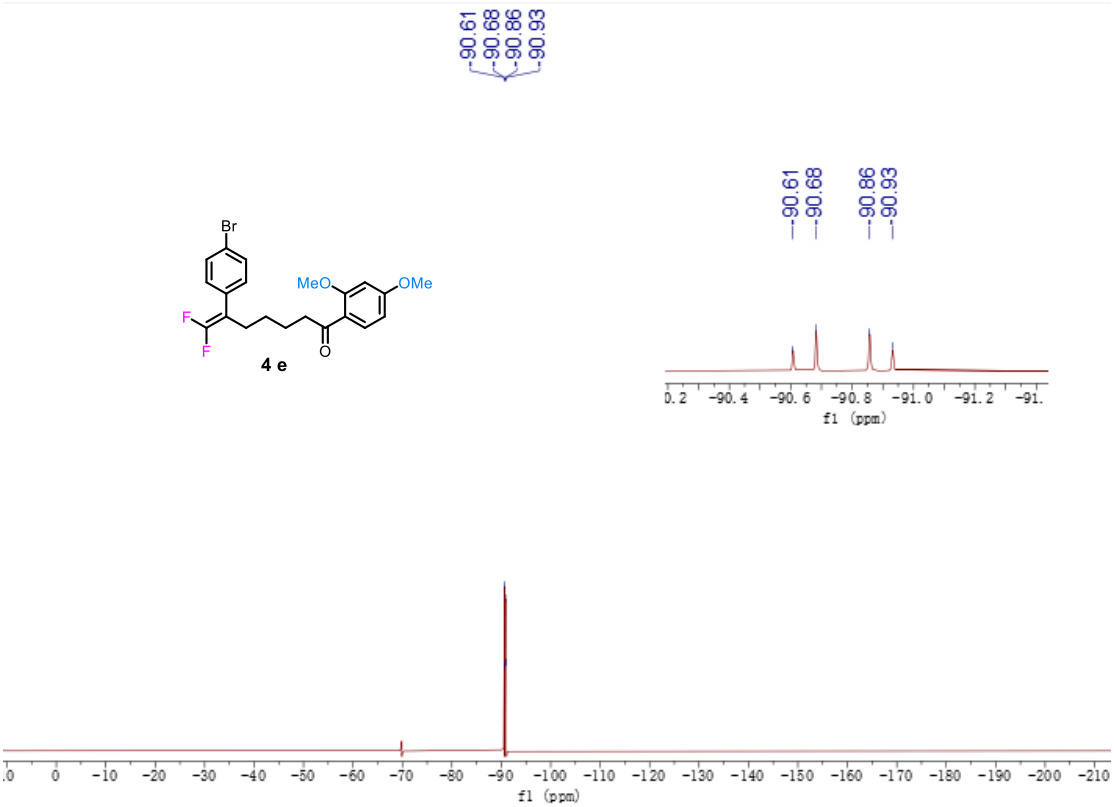
27.54
27.51
23.94
Br
MeO
OMe
F
F
O
4 e
f1 (ppm)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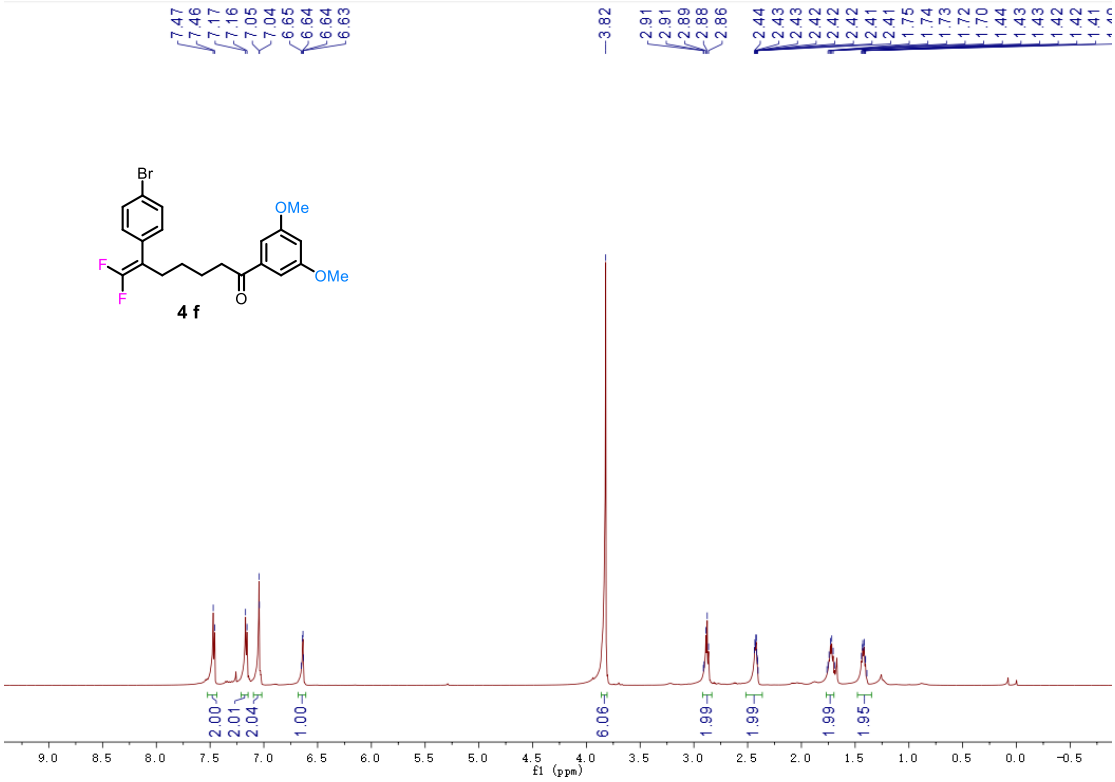
MeO
OMe
F
F
O
4 e
f1 (ppm)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6.63
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2.91
2.89
2.88
2.86
2.44
2.43
2.43
2.42
2.42
2.42
2.41
2.41
1.75
1.74
1.73
1.72
1.70
1.44
1.43
1.43
1.42
1.42
1.41
Br
OMe
OMe
F
F
O
4 f
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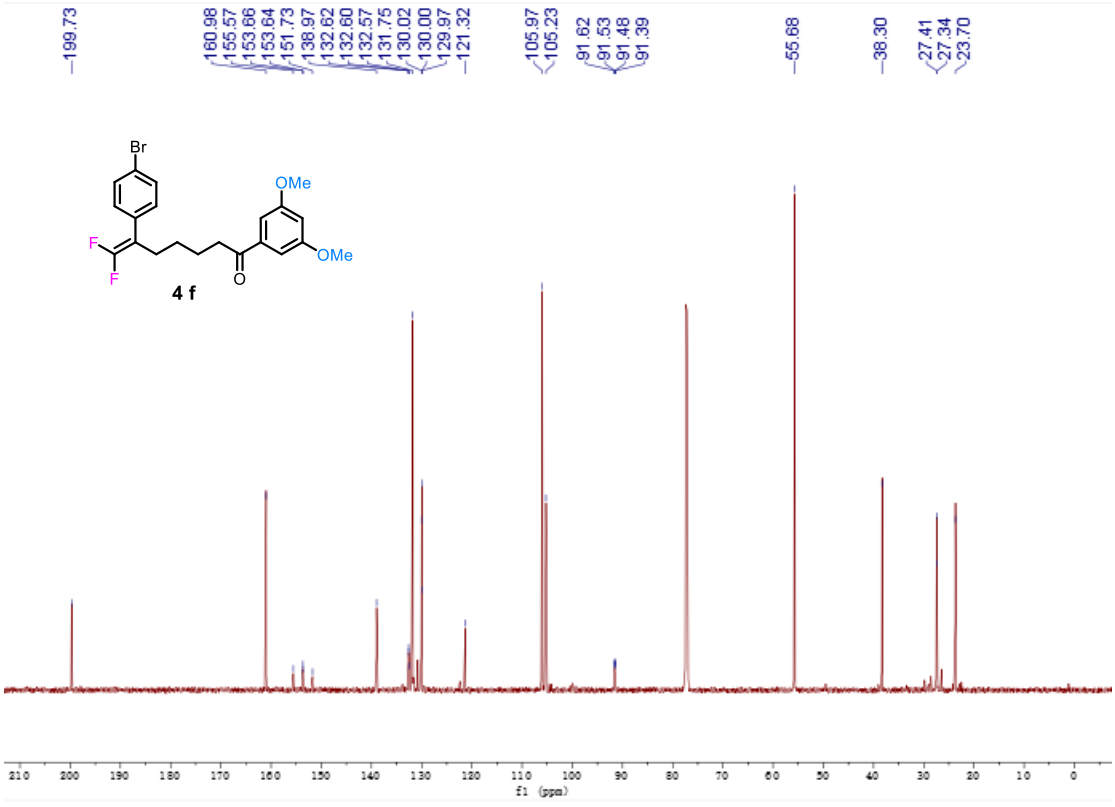
2.01
2.04
1.00
6.06
1.99
1.99
1.99
1.95
f1 (ppm)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121.32
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105.23
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91.53
91.48
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27.41
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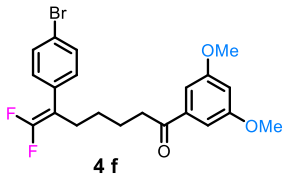
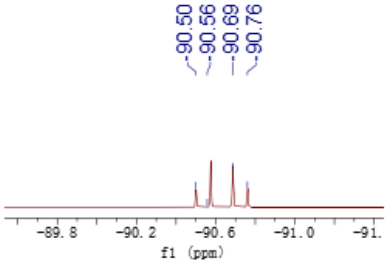
23.70
Br
OMe
OMe
F
F
O
4 f
f1 (ppm)


Br
OMe
OMe
F
F
O

4 f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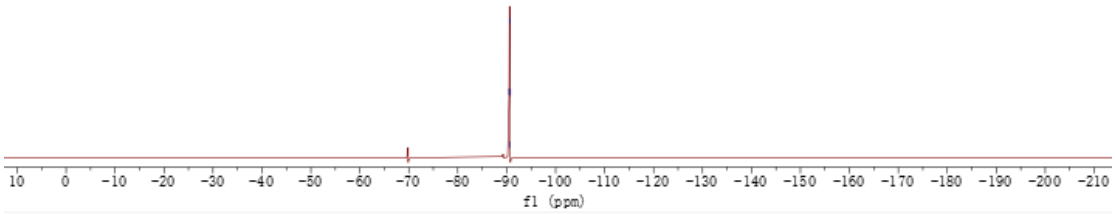
-91.
f1 (ppm)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-130
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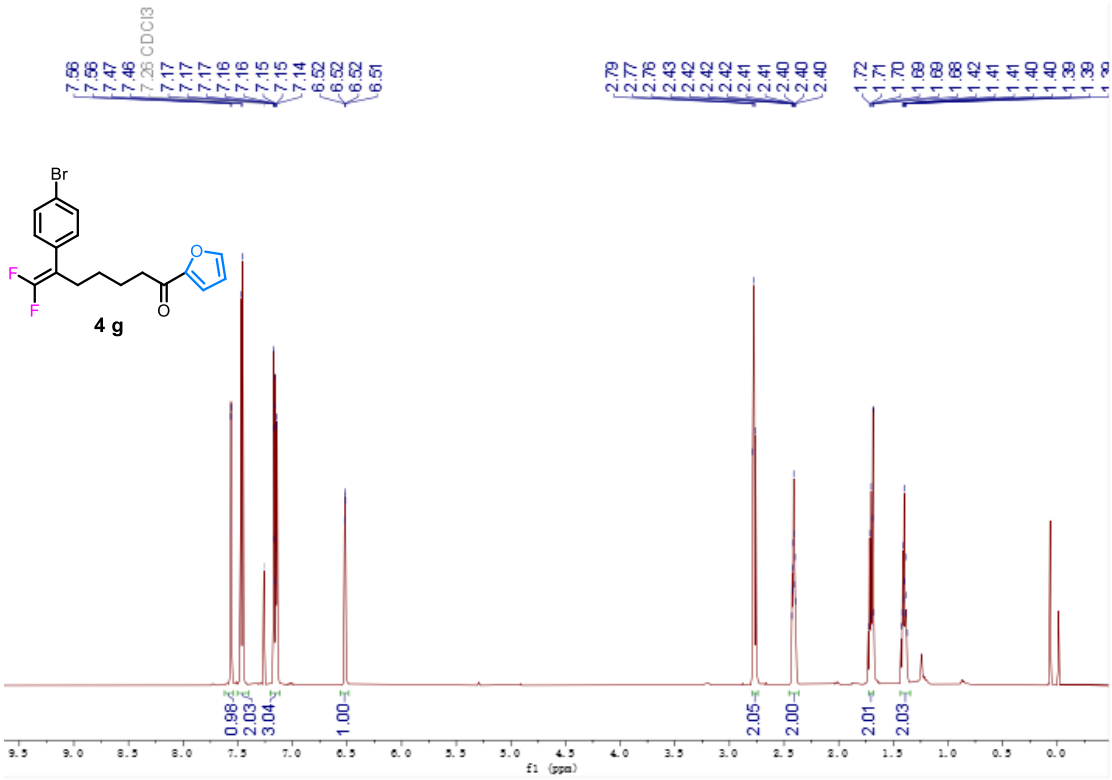
-170
-180
-190
-200
-210
f1 (ppm)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7.15
7.14
6.52
6.52
6.52
6.51
2.79
2.77
2.76
2.43
2.42
2.42
2.42
2.41
2.41
2.40
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2.40
1.72
1.71
1.70
1.69
1.69
1.68
1.42
1.41
1.41
1.40
1.40
1.39
1.39
Br
F
F
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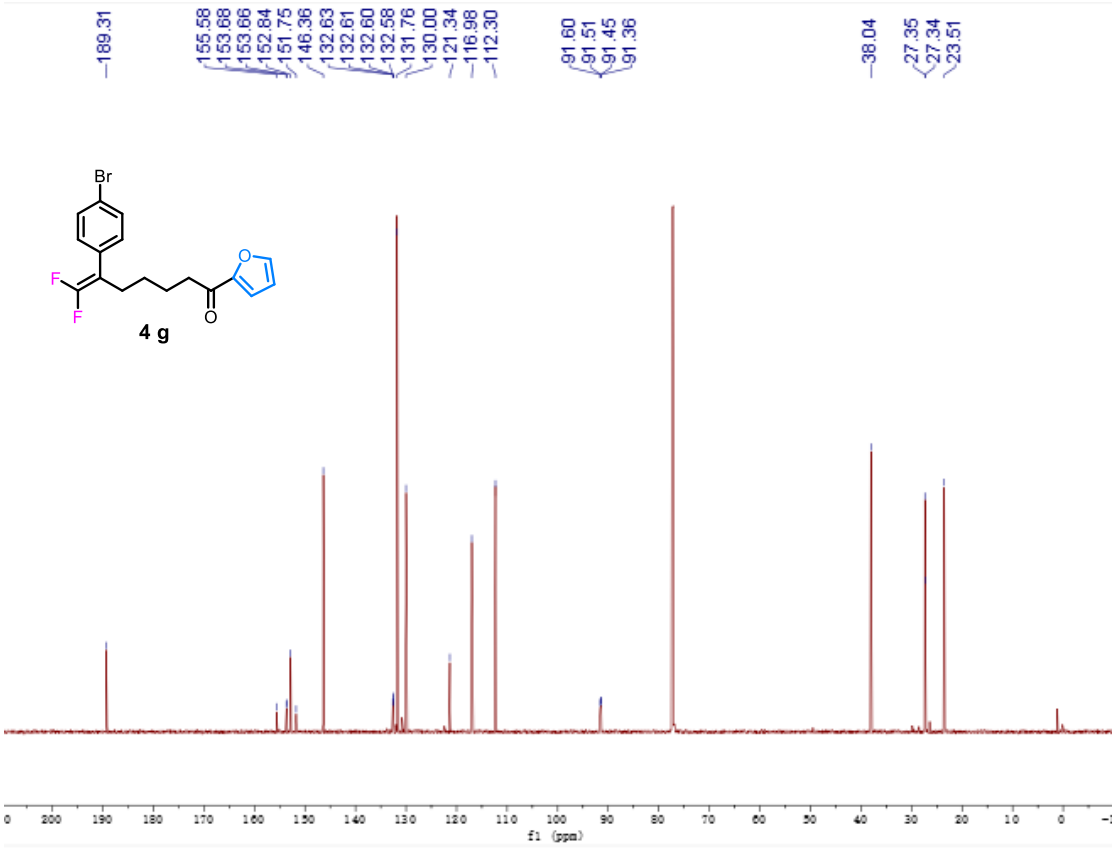
3.04
1.00
2.05
2.00
2.01
2.03
f1 (ppm)

4 g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131.76
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121.34
116.98
112.30
91.60
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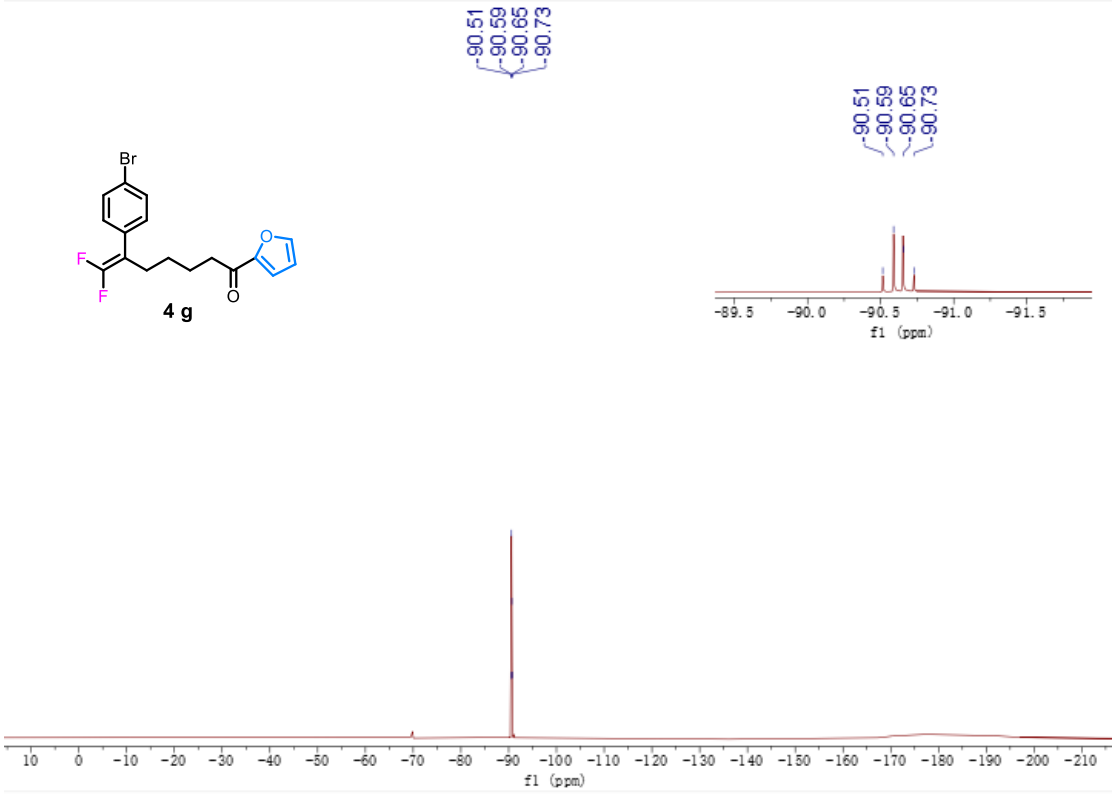
Br
F
F
O
O
4 g
f1 (ppm)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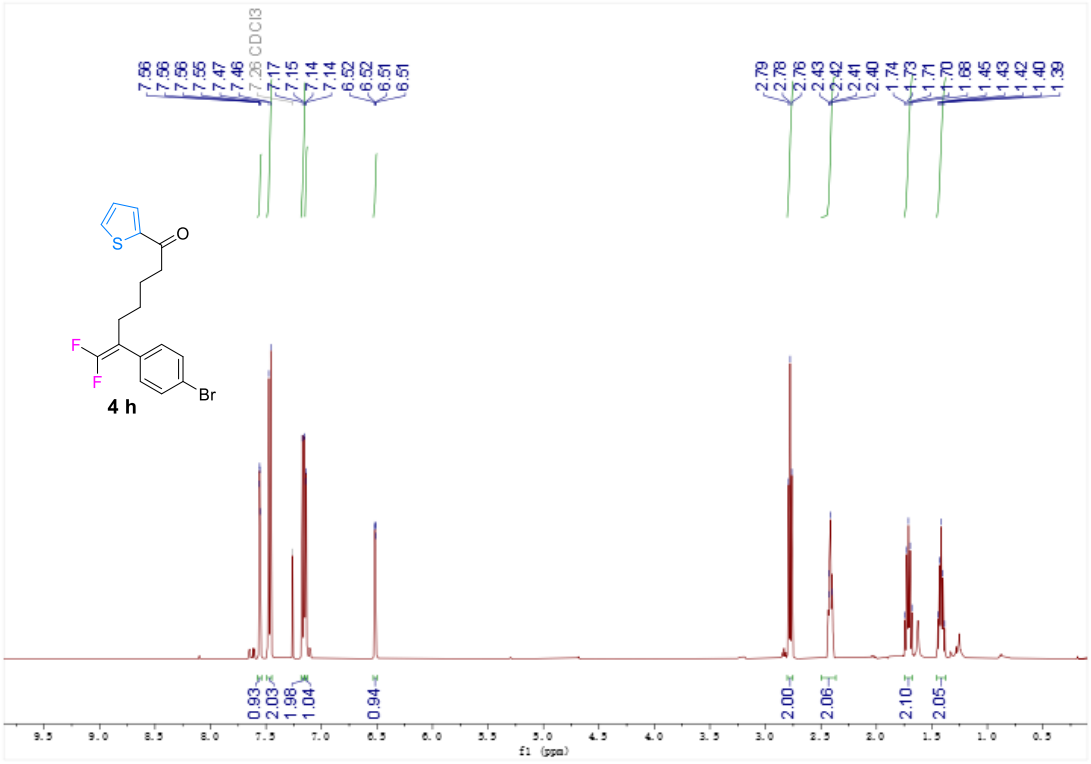
Br
F
F
O
O
4 g
f1 (ppm)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7.14
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6.51
6.51
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2.78
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2.41
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1.71
1.70
1.68
1.45
1.43
1.42
1.40
1.39
O
S
F
F
Br
4 h
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1.04
0.94
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2.06
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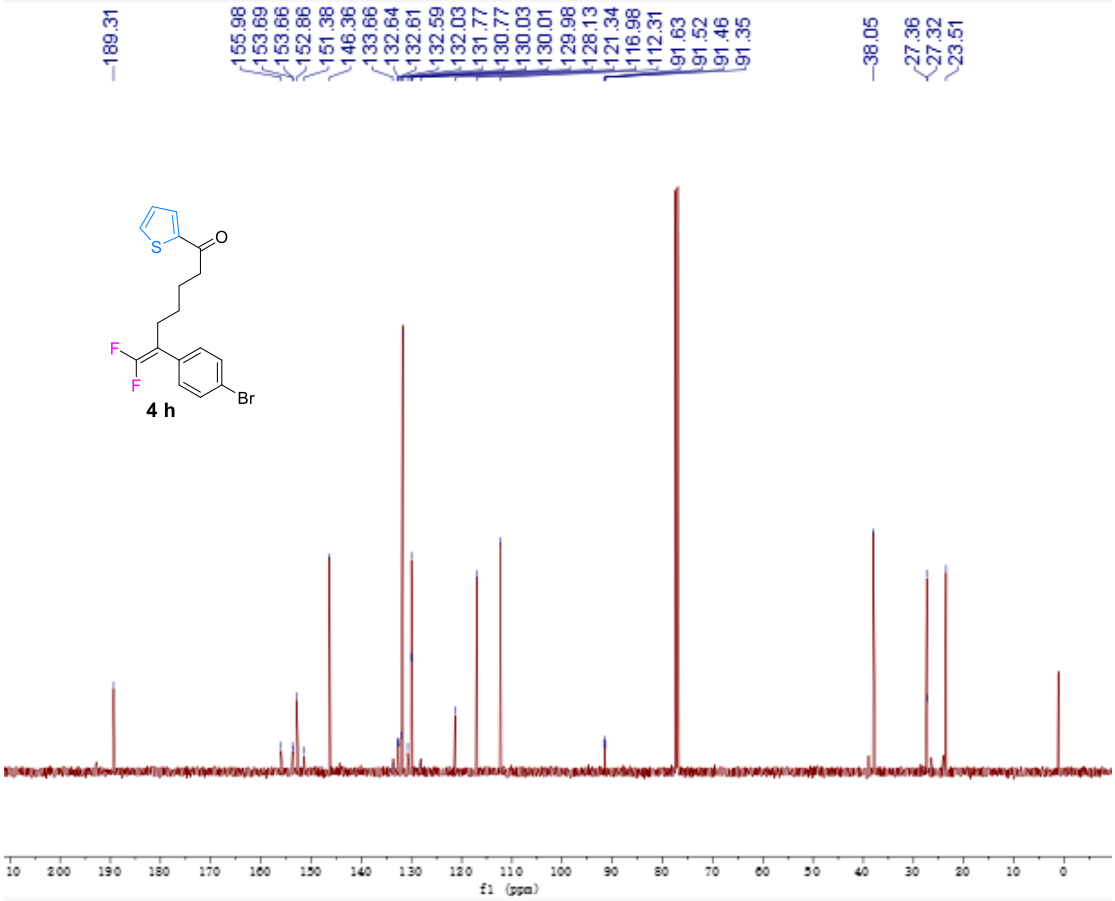
2.05
f1 (ppm)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121.34
116.98
112.31
91.63
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27.32
23.51
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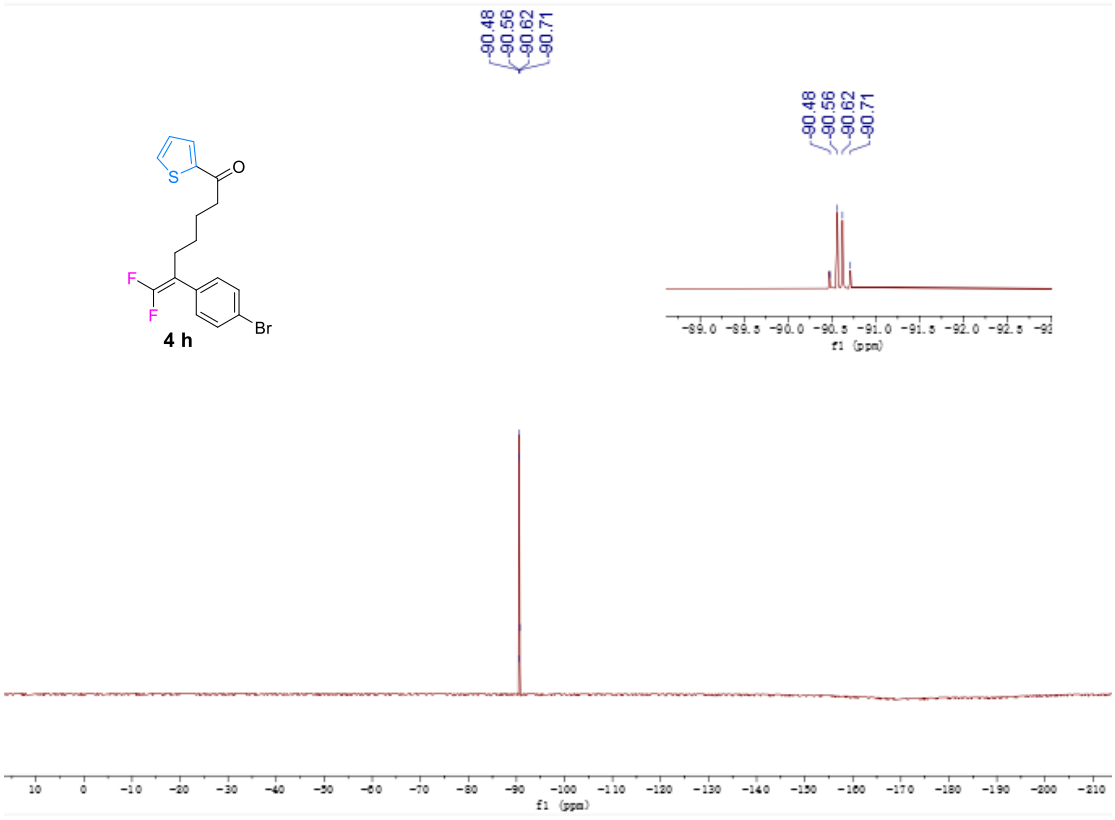
S
F
F
Br
4 h
f1 (ppm)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S
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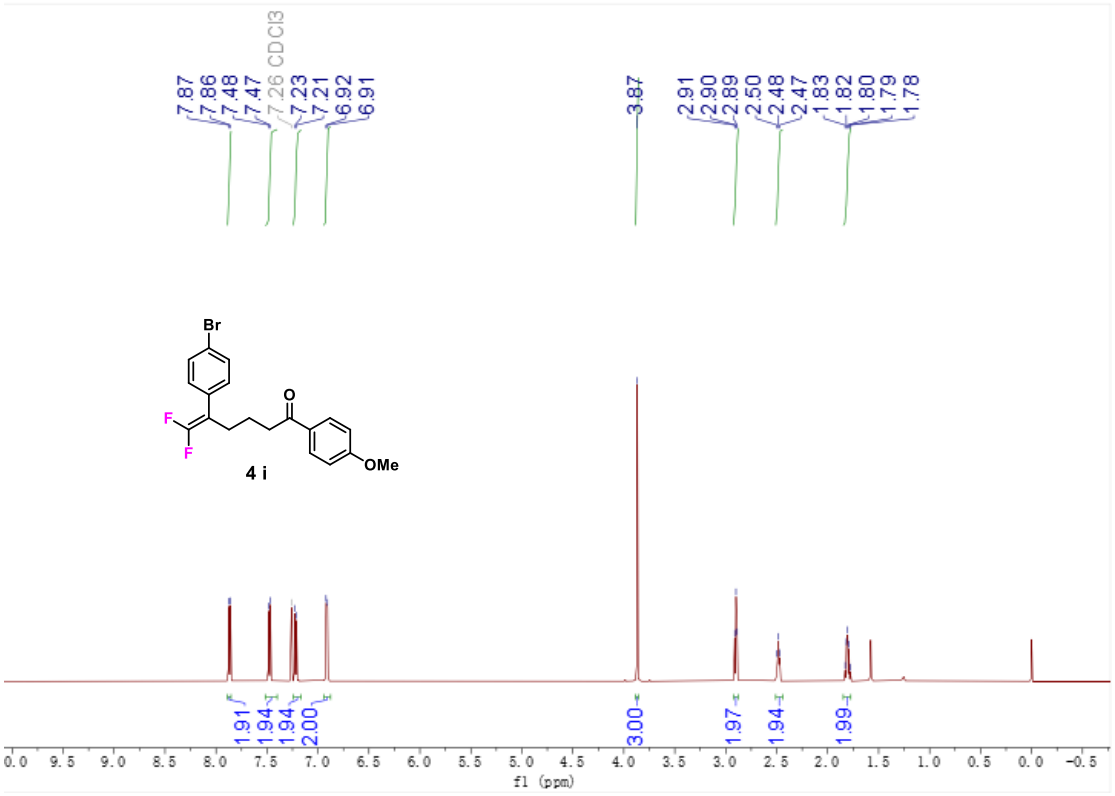
Br
4 h
f1 (ppm)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6.91
3.87
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2.90
2.89
2.50
2.48
2.47
1.83
1.82
1.80
1.79
1.78
Br
O
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F
OMe
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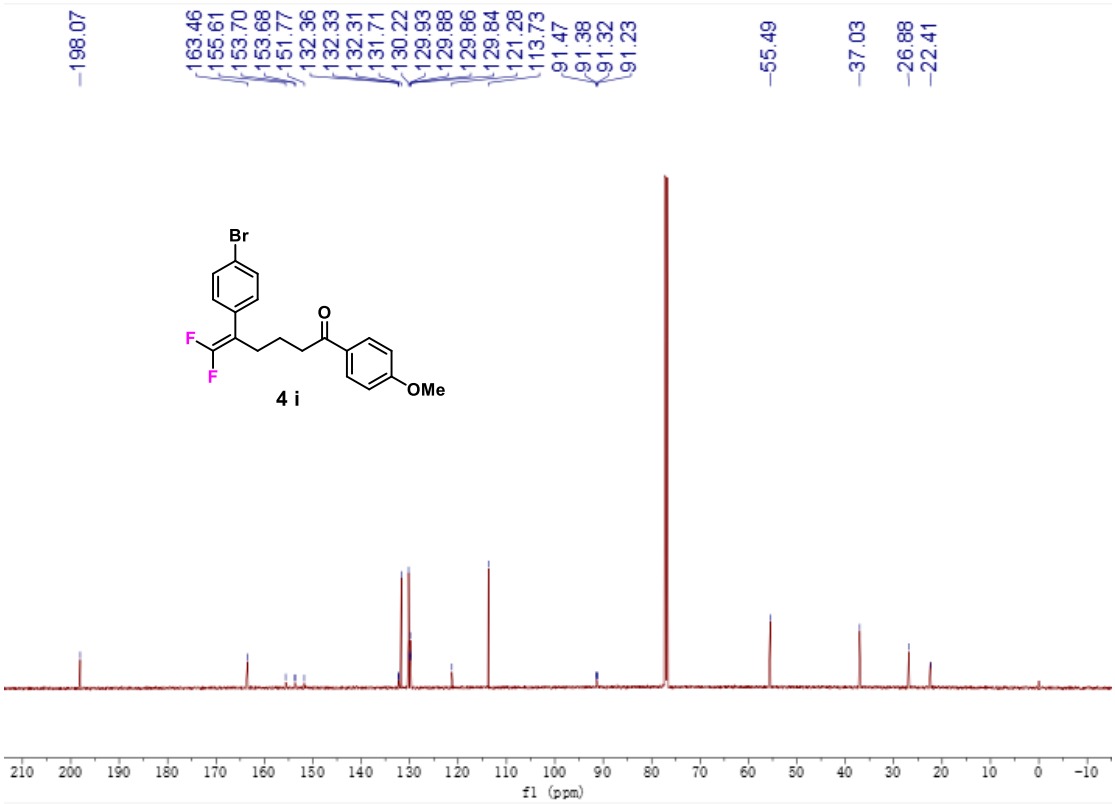
1.94
2.00
3.00
1.97
1.94
1.99
f1 (ppm)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121.28
113.73
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55.49
37.03
26.88
22.41
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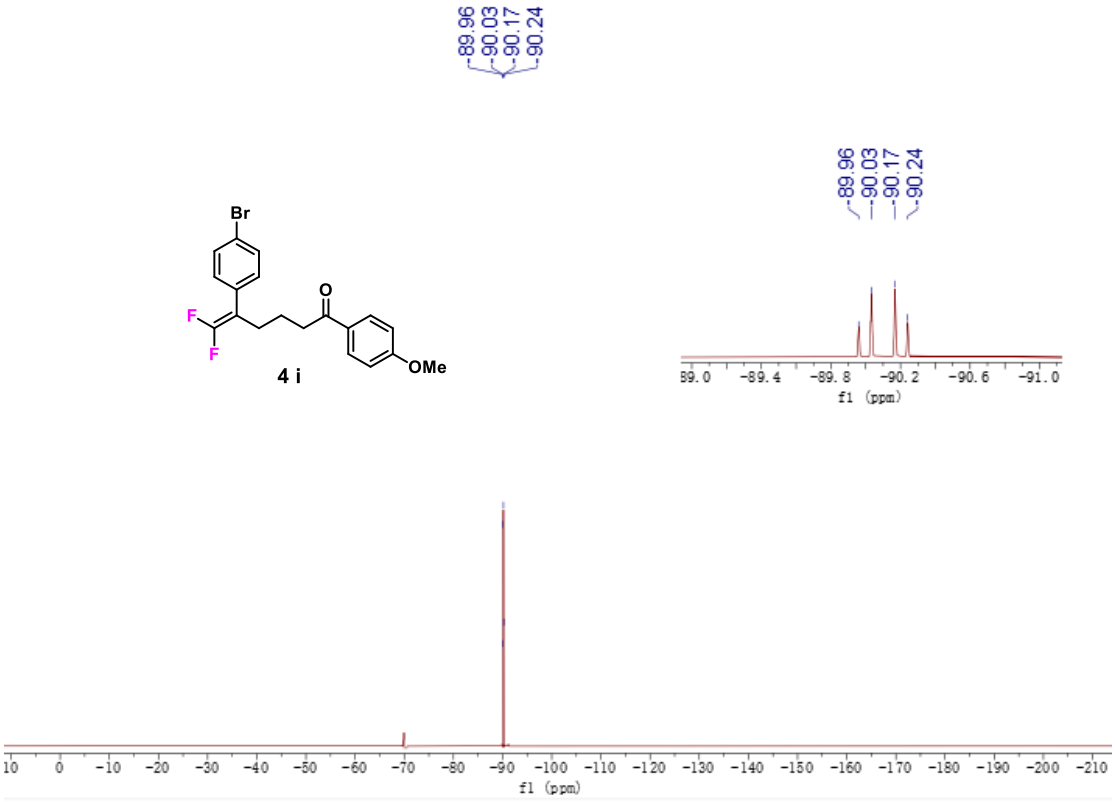
O
F
F
OMe
4 i
f1 (ppm)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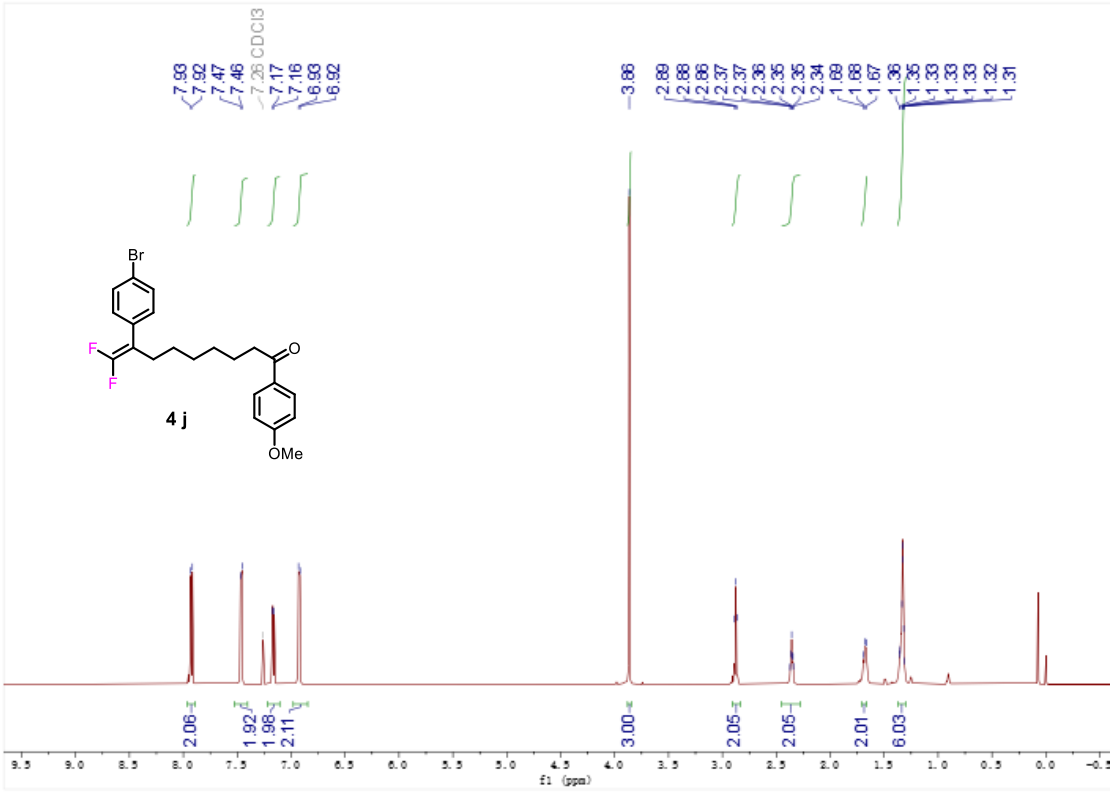
F
F
OMe
4 i
f1 (ppm)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7.46
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6.93
6.92
3.86
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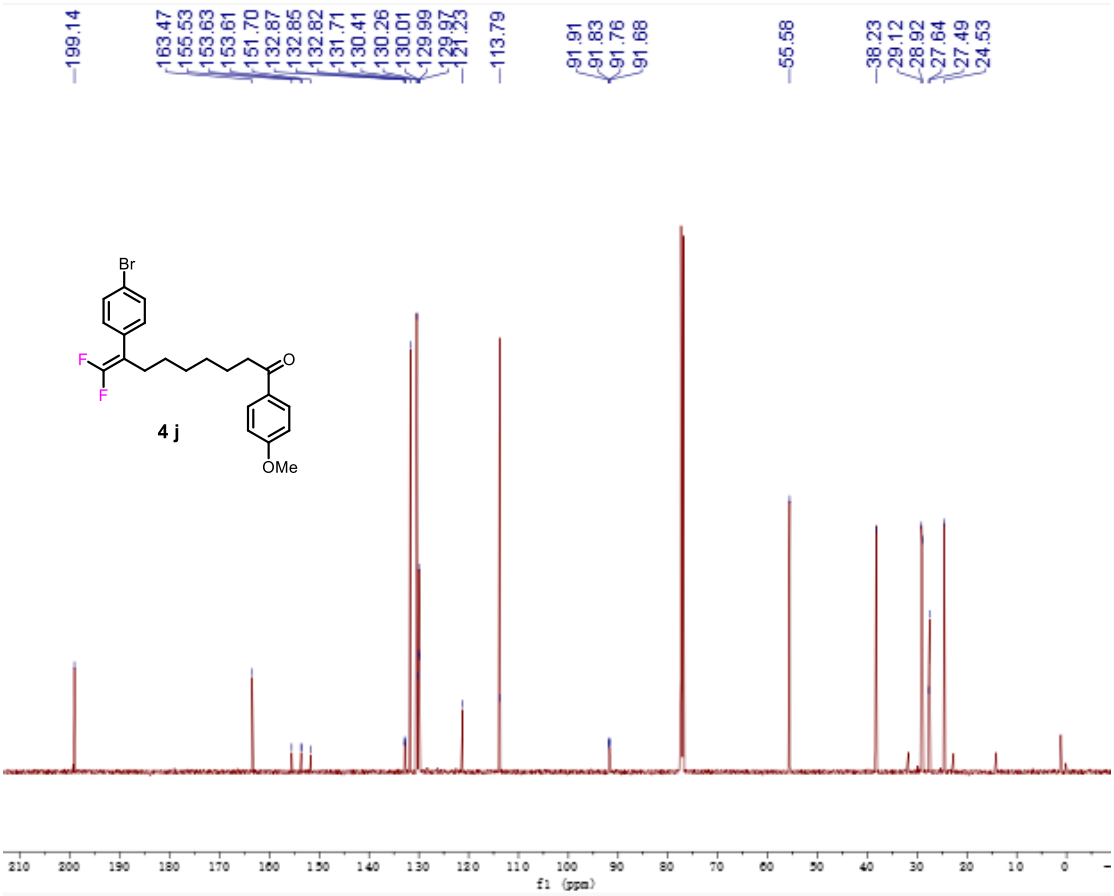
2.37
2.36
2.35
2.34
1.69
1.68
1.67
1.36
1.35
1.33
1.33
1.32
1.31
Br
F
F
O
OMe
4 j
2.06
1.92
1.98
2.11
3.00
2.05
2.05
2.01
6.03
f1 (ppm)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153.61
151.70
132.87
132.85
132.82
131.71
130.41
130.26
130.01
129.99
129.97
121.23
113.79
91.91
91.83
91.76
91.68
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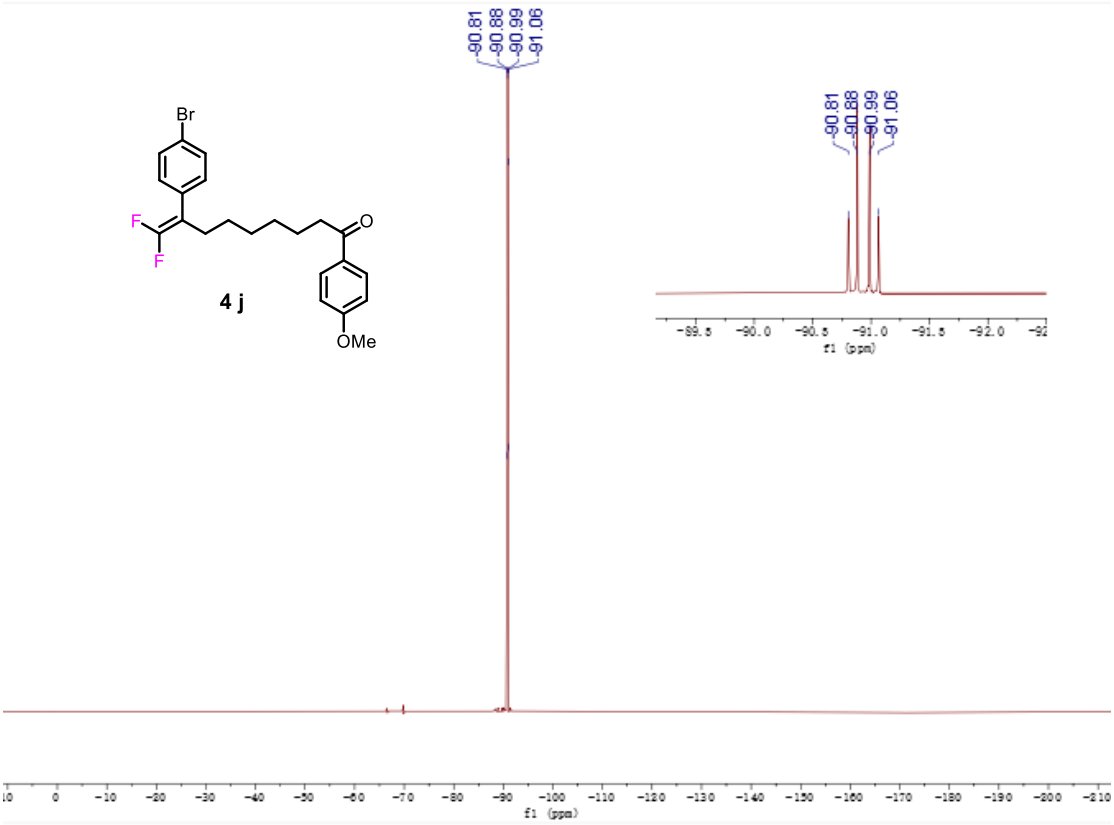
28.92
27.64
27.49
24.53
Br
F
F
O
OMe
4 j
f1 (ppm)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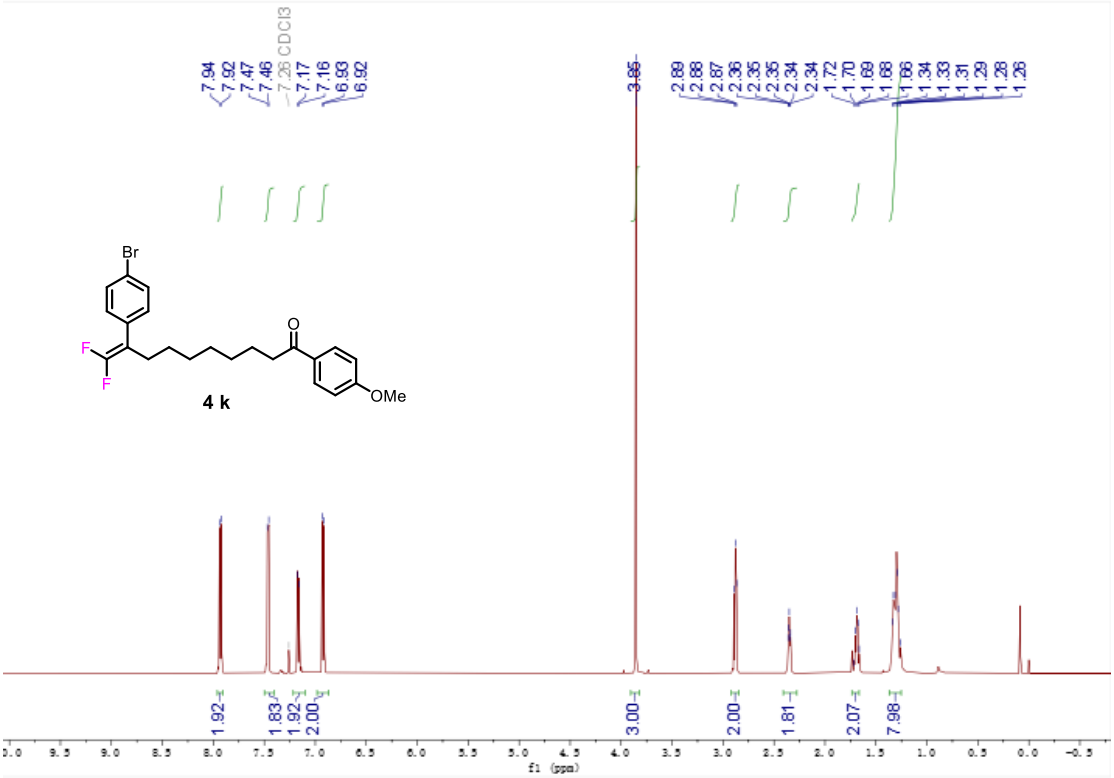
-90.99
-91.06
Br
F
F
O
OMe
4 j
f1 (ppm)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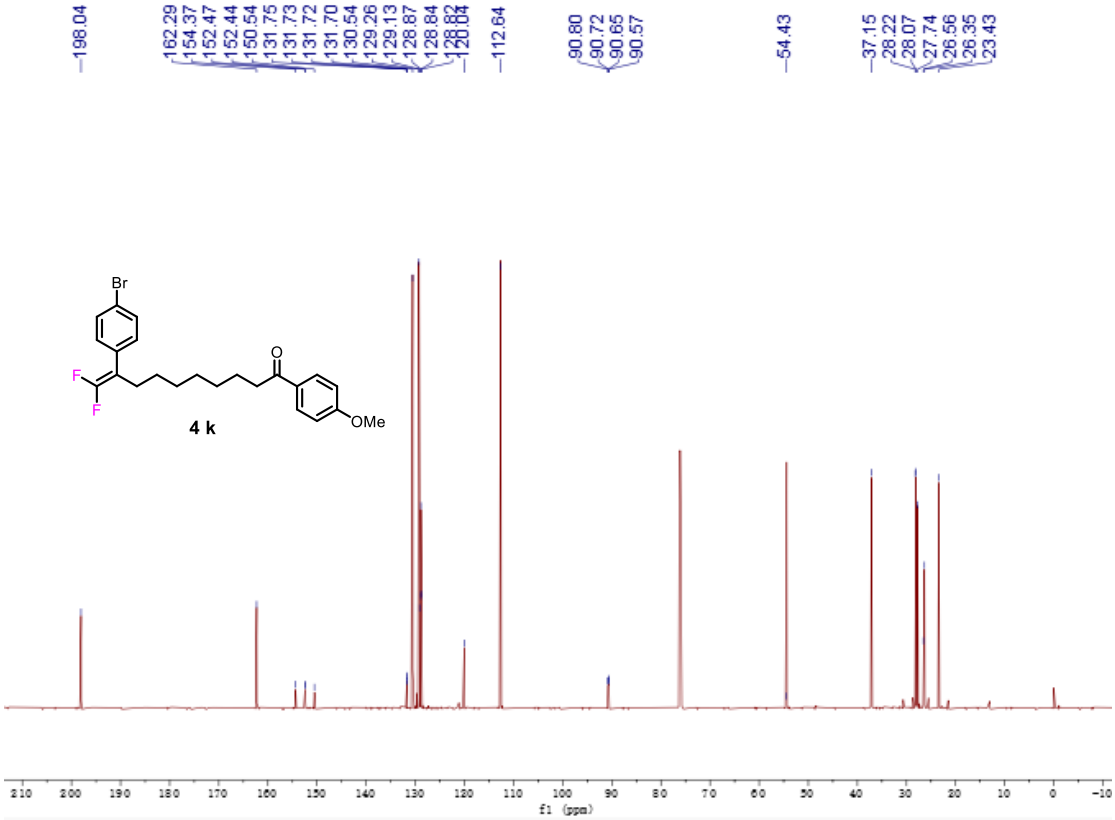
7.92
7.47
7.46
CDCl3
7.17
7.16
6.93
6.92
3.95
2.89
2.88
2.87
2.36
2.35
2.34
2.34
1.72
1.70
1.69
1.68
1.66
1.34
1.33
1.31
1.29
1.28
1.26
Br
F
F
O
OMe
4 k
1.92
1.83
1.92
2.00
3.00
2.00
1.81
2.07
7.98
f1 (ppm)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150.54
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131.73
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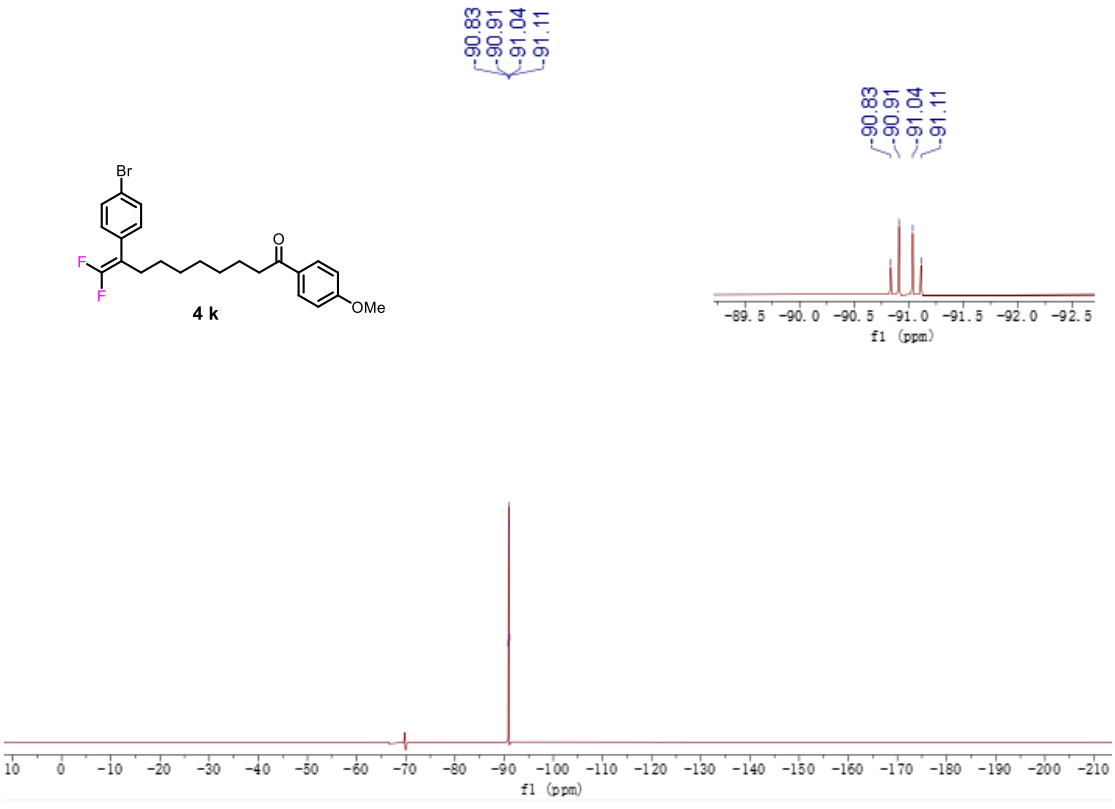
130.54
129.26
129.13
128.87
128.84
112.64
90.80
90.72
90.65
90.57
54.43
37.15
28.22
28.07
27.74
26.56
26.35
23.43
Br
F
F
O
OMe
4 k
f1 (ppm)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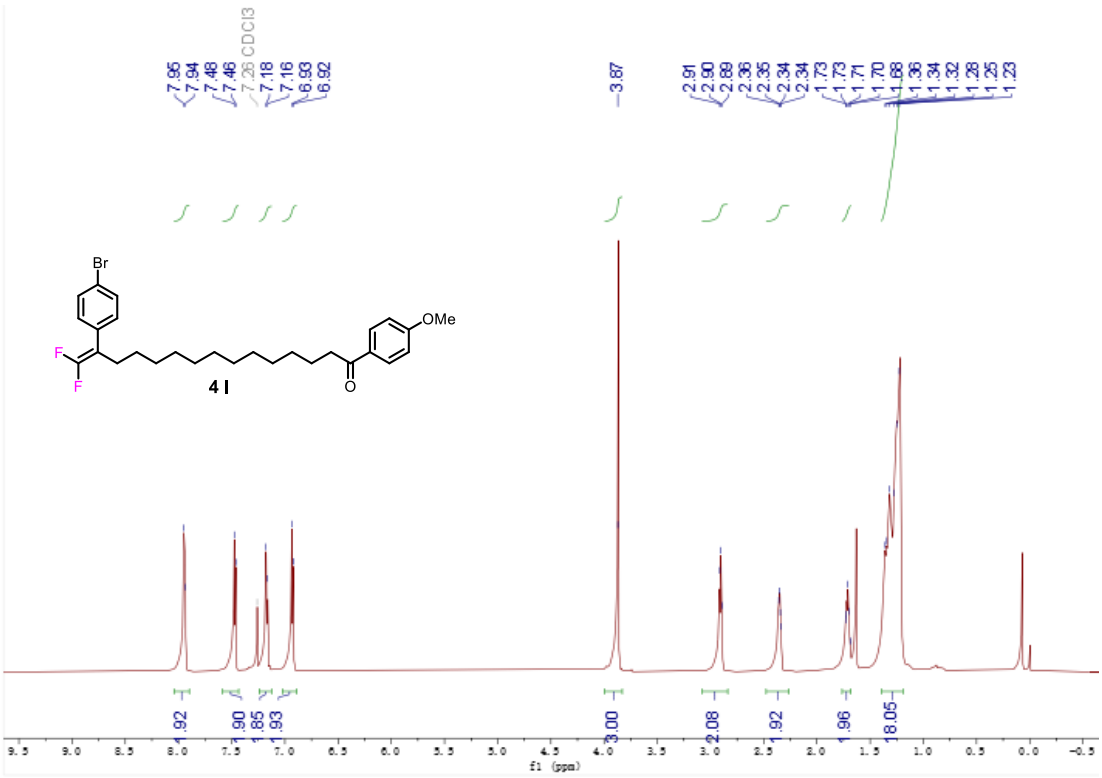
F
O
OMe
4 k
f1 (ppm)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7.94
7.48
7.46
7.26 CDCl3
7.18
7.16
6.93
6.92
3.87
2.91
2.90
2.89
2.36
2.35
2.34
2.34
1.73
1.73
1.71
1.70
1.68
1.36
1.34
1.32
1.28
1.25
1.23
Br
F
F
OMe
O
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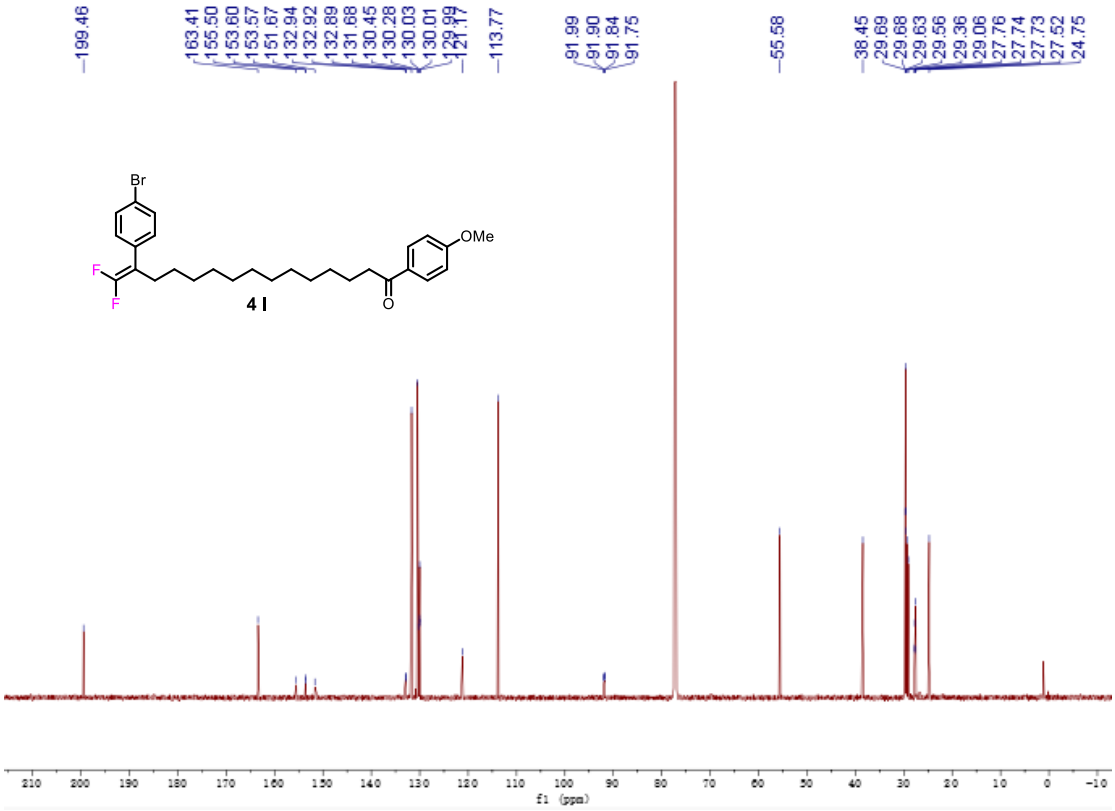
1.92
1.90
1.85
1.93
3.00
2.08
1.92
1.96
18.05
f1 (ppm)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132.92
132.89
131.68
130.45
130.28
130.03
130.01
129.99
121.17
113.77
91.99
91.90
91.84
91.75
55.58
38.45
29.69
29.68
29.63
29.56
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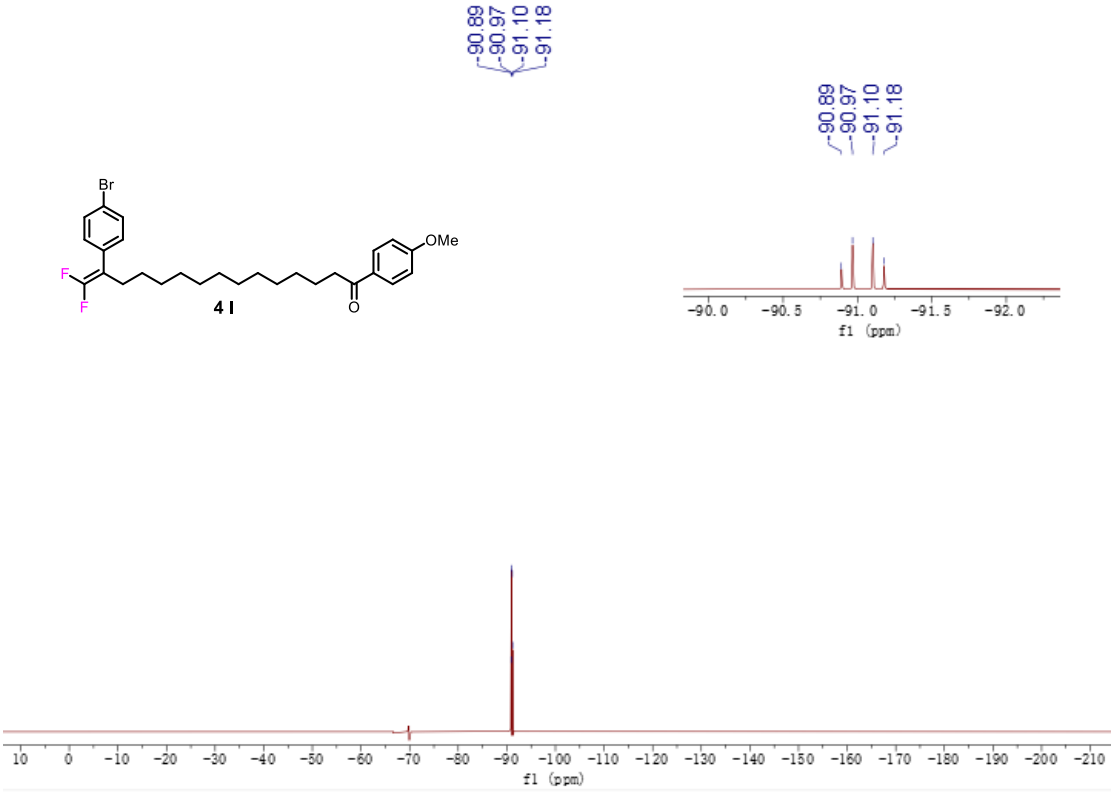
27.74
27.73
27.52
24.75
Br
F
F
OMe
O
4 l
f1 (ppm)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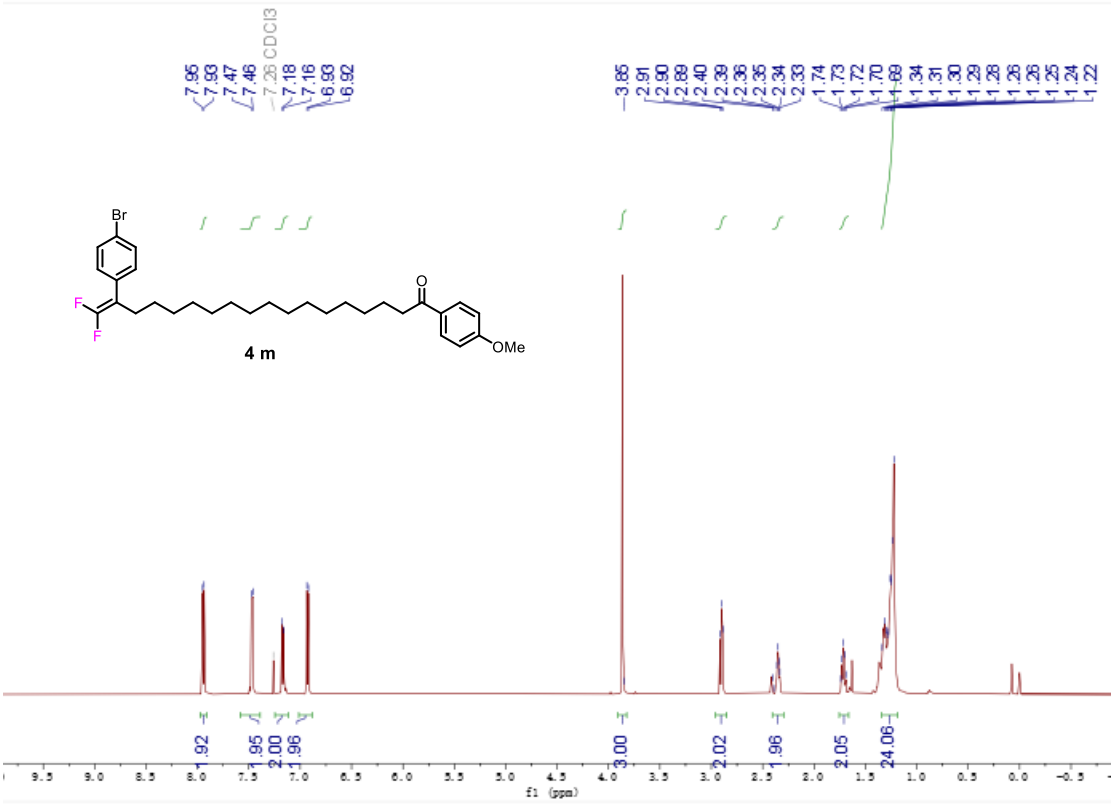
-90.97
-91.10
-91.18
Br
F
F
OMe
O
4 l
-90.89
-90.97
-91.10
-91.18
-90.0
-90.5
-91.0
-91.5
-92.0
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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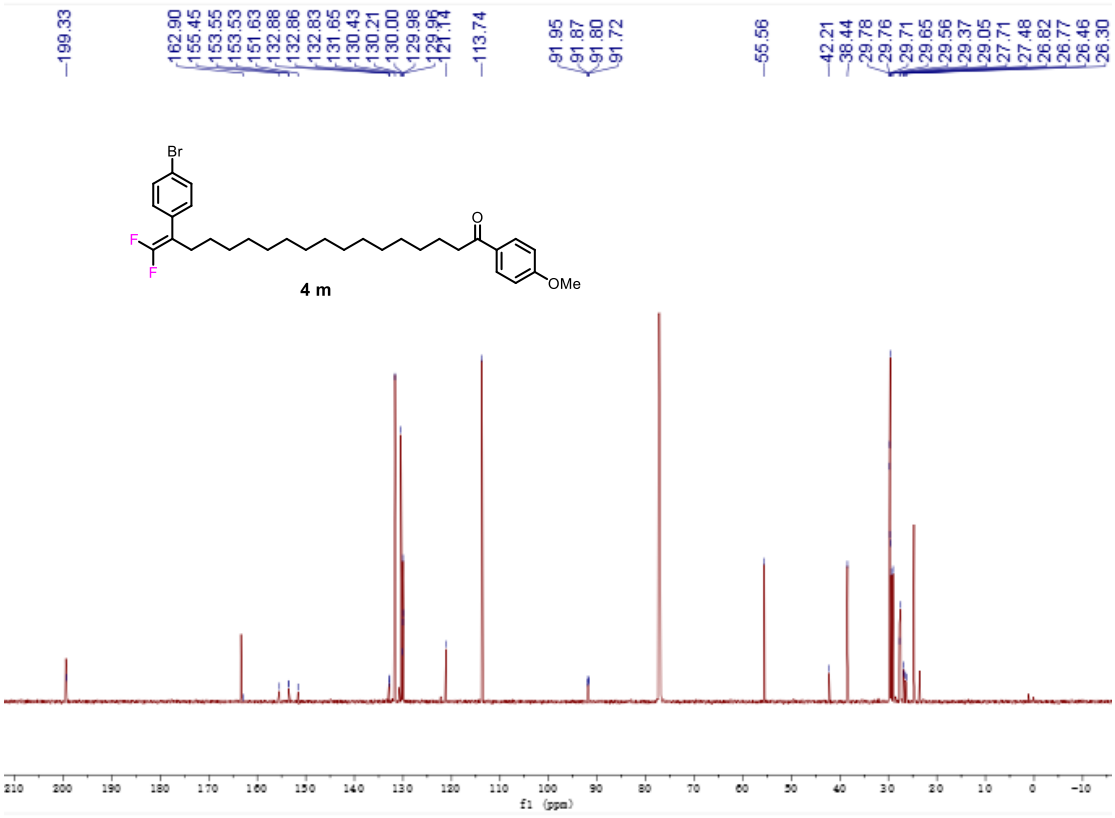
7.93
7.47
7.46
7.26 CDCl3
7.18
7.16
6.93
6.92
3.85
2.91
2.90
2.89
2.40
2.39
2.36
2.35
2.34
2.33
1.74
1.73
1.72
1.70
1.69
1.34
1.31
1.30
1.29
1.28
1.26
1.26
1.25
1.24
1.22
Br
F
F
O
OMe
4 m
1.92
1.95
2.00
1.96
3.00
2.02
1.96
2.05
24.06
f1 (ppm)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153.53
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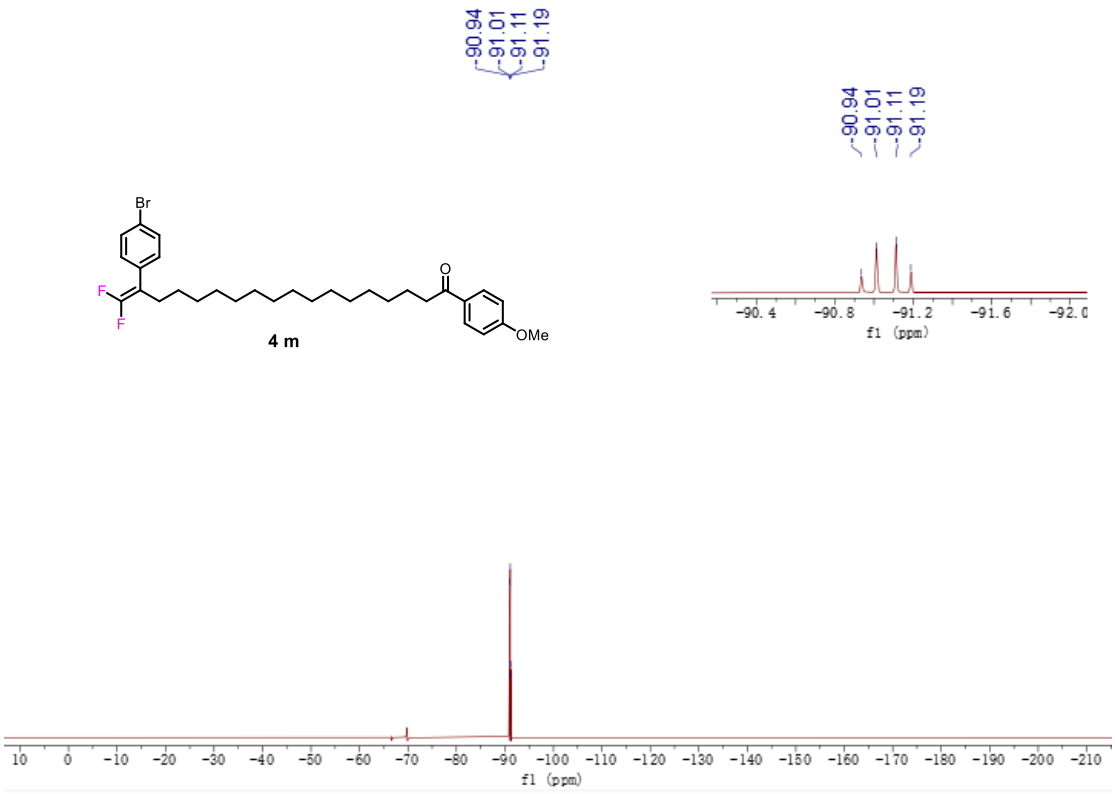
132.88
132.86
132.83
131.65
130.43
130.21
130.00
129.98
129.96
121.14
113.74
91.95
91.87
91.80
91.72
55.56
42.21
38.44
29.78
29.76
29.71
29.65
29.56
29.37
29.05
27.71
27.48
26.82
26.77
26.46
26.30
Br
F
F
O
OMe
4 m
f1 (ppm)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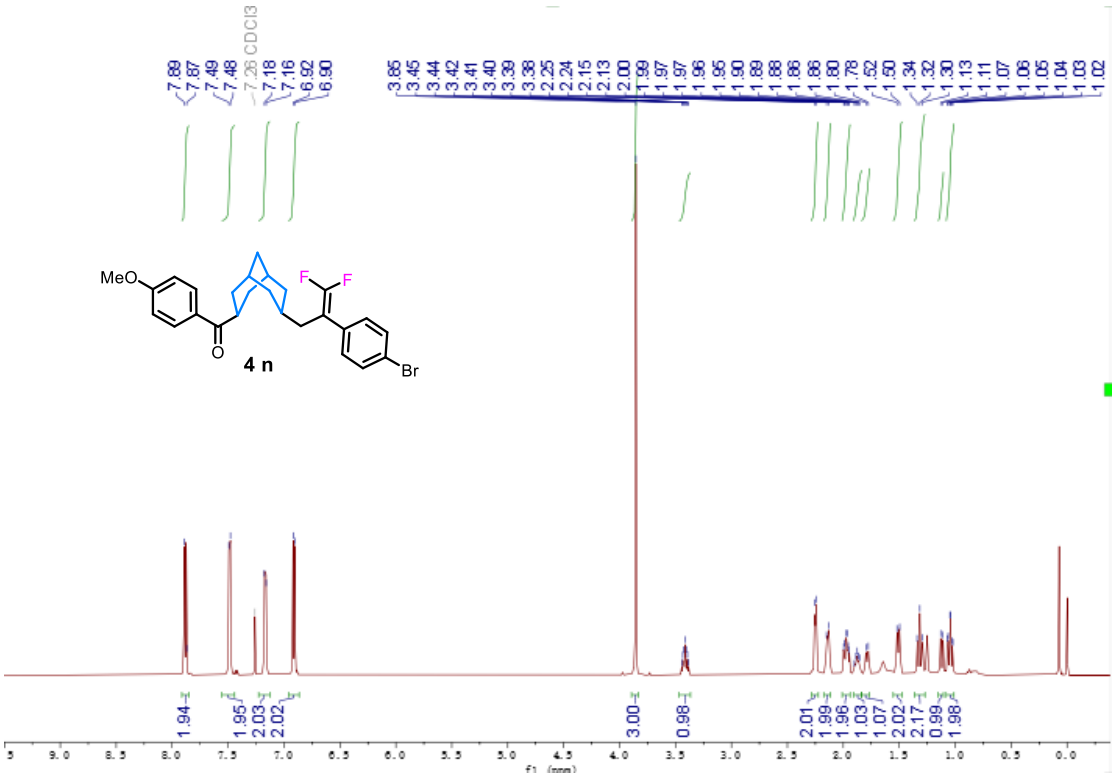
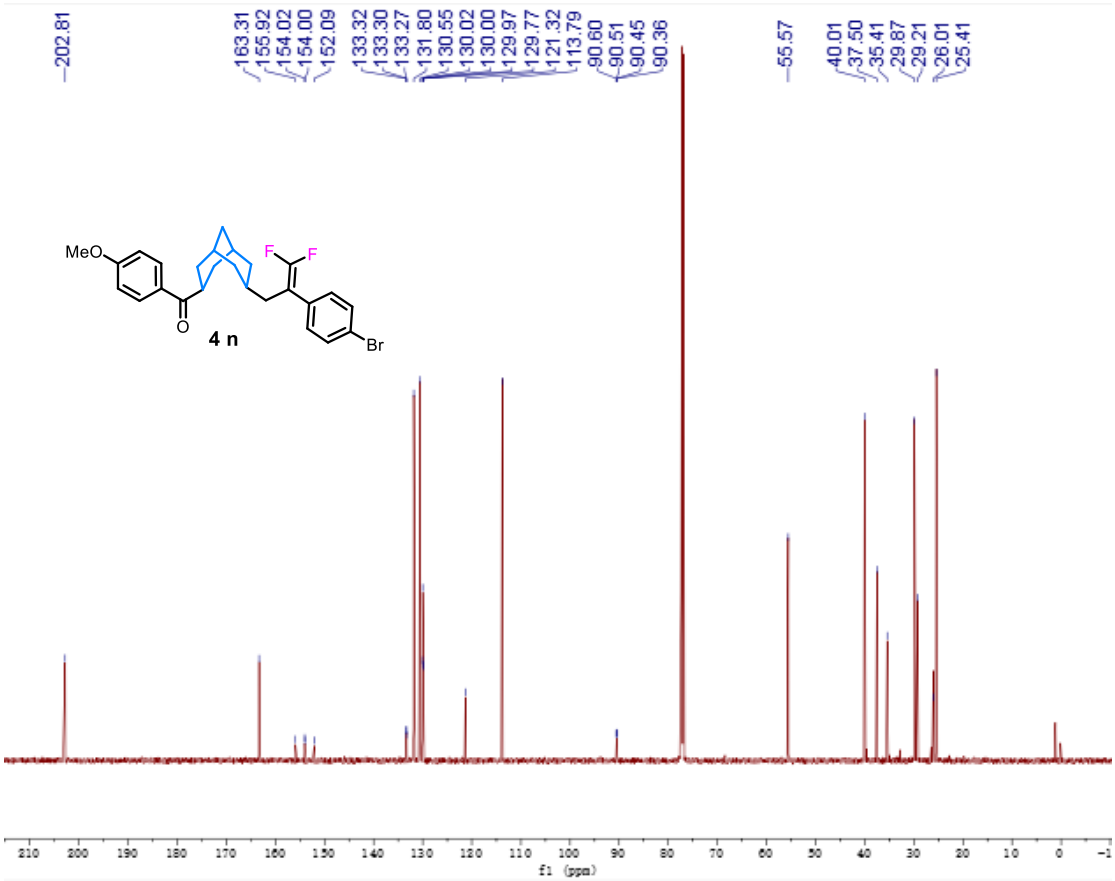
91.01
91.11
91.19
Br
F
F
O
OMe
4 m
f1 (ppm)


7.89
7.87
7.49
7.48
7.26 CDCl3
7.18
7.16
6.92
6.90
3.85
3.45
3.44
3.42
3.41
3.40
3.39
3.38
2.25
2.24
2.15
2.13
2.00
1.99
1.97
1.97
1.96
1.95
1.90
1.89
1.88
1.86
1.86
1.80
1.78
1.62
1.50
1.34
1.32
1.30
1.13
1.11
1.07
1.06
1.05
1.04
1.03
1.02
MeO
O
F
F
Br
4 n
1.94
1.95
2.03
2.02
3.00
0.98
2.01
1.99
1.96
1.03
1.07
2.02
2.17
0.99
1.98
f1 (ppm)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131.80
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130.02
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129.97
129.77
121.32
113.79
90.60
90.51
90.45
90.36
55.57
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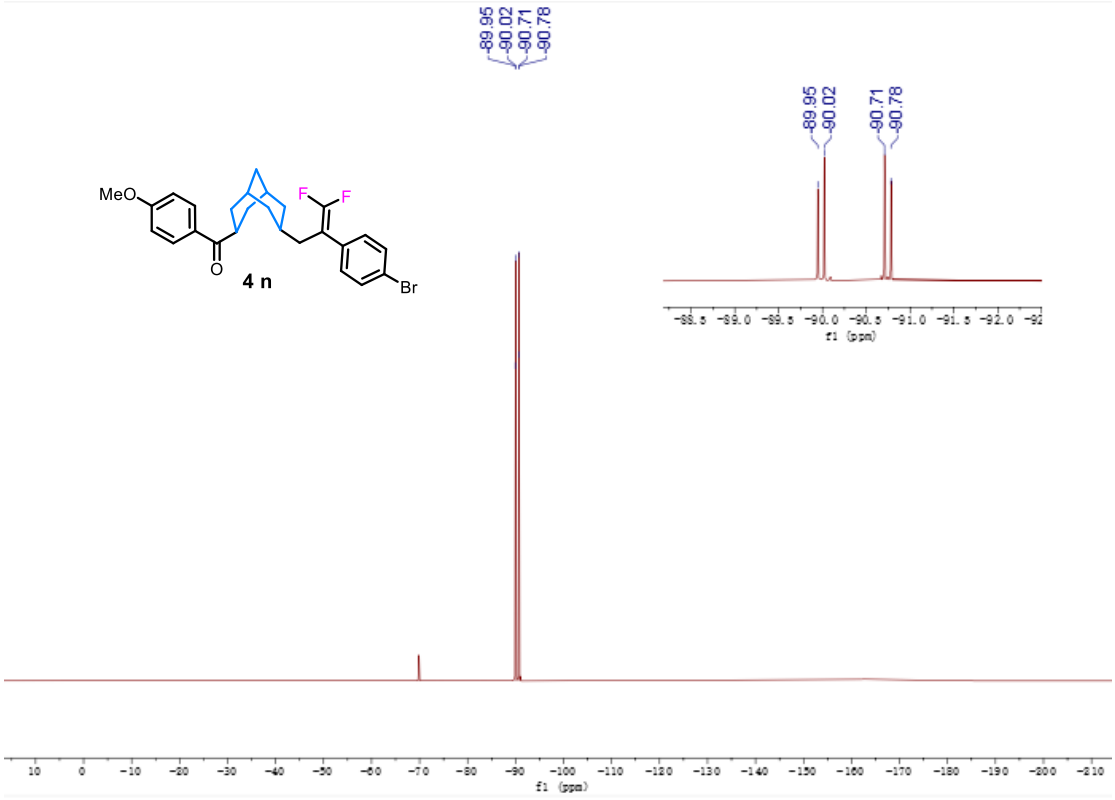
29.87
29.21
26.01
25.41
MeO
O
F
F
Br
4 n
f1 (ppm)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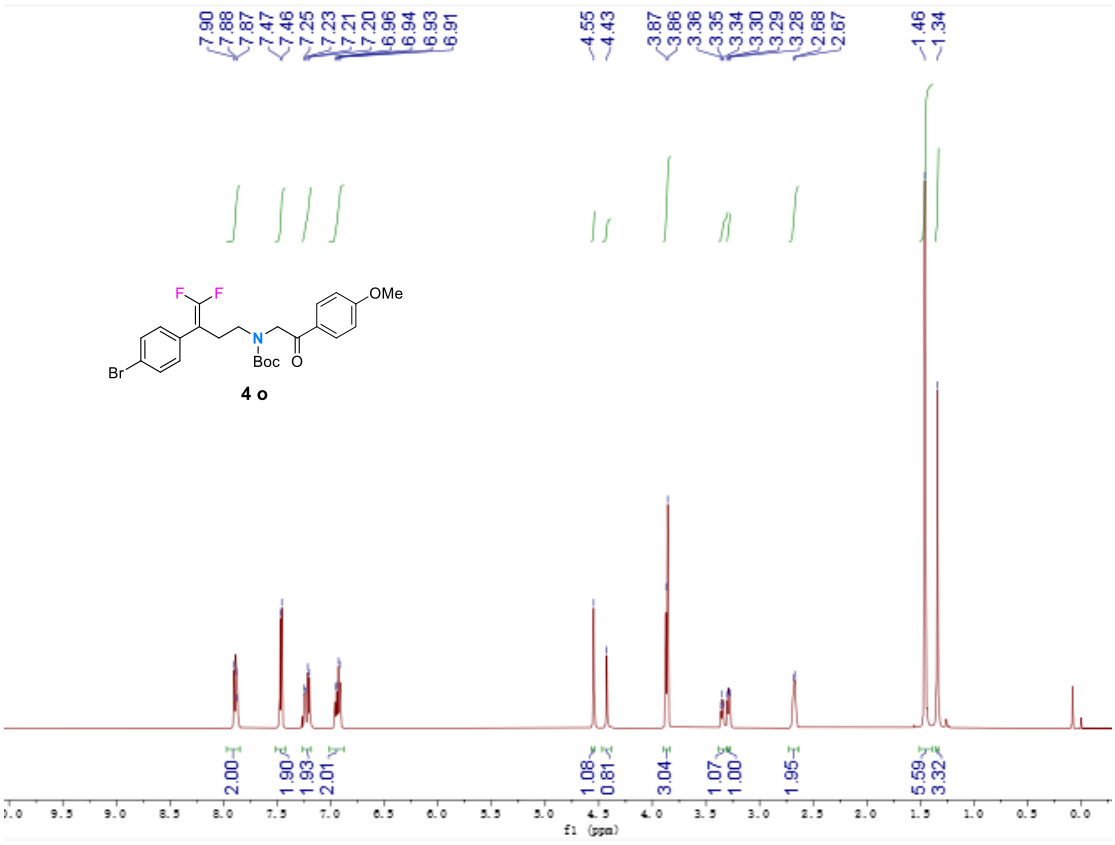
MeO
F
F
O
Br
4 n
f1 (ppm)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7.88
7.87
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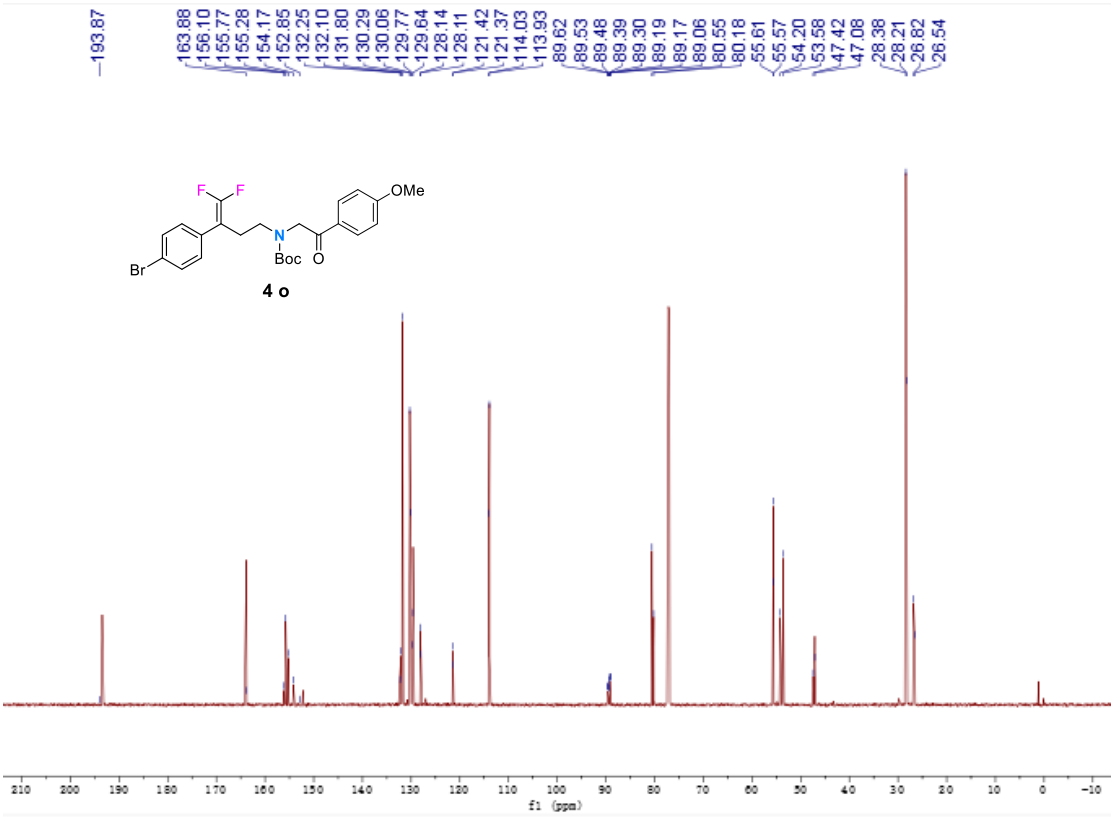
7.46
7.25
7.23
7.21
7.20
6.96
6.94
6.93
6.91
4.55
4.43
3.87
3.86
3.36
3.35
3.34
3.30
3.29
3.28
2.68
2.67
1.46
1.34
F
F
OMe
N
Boc
O
Br
4 o
2.00
1.90
1.93
2.01
1.08
0.81
3.04
1.07
1.00
1.95
5.59
3.32
f1 (ppm)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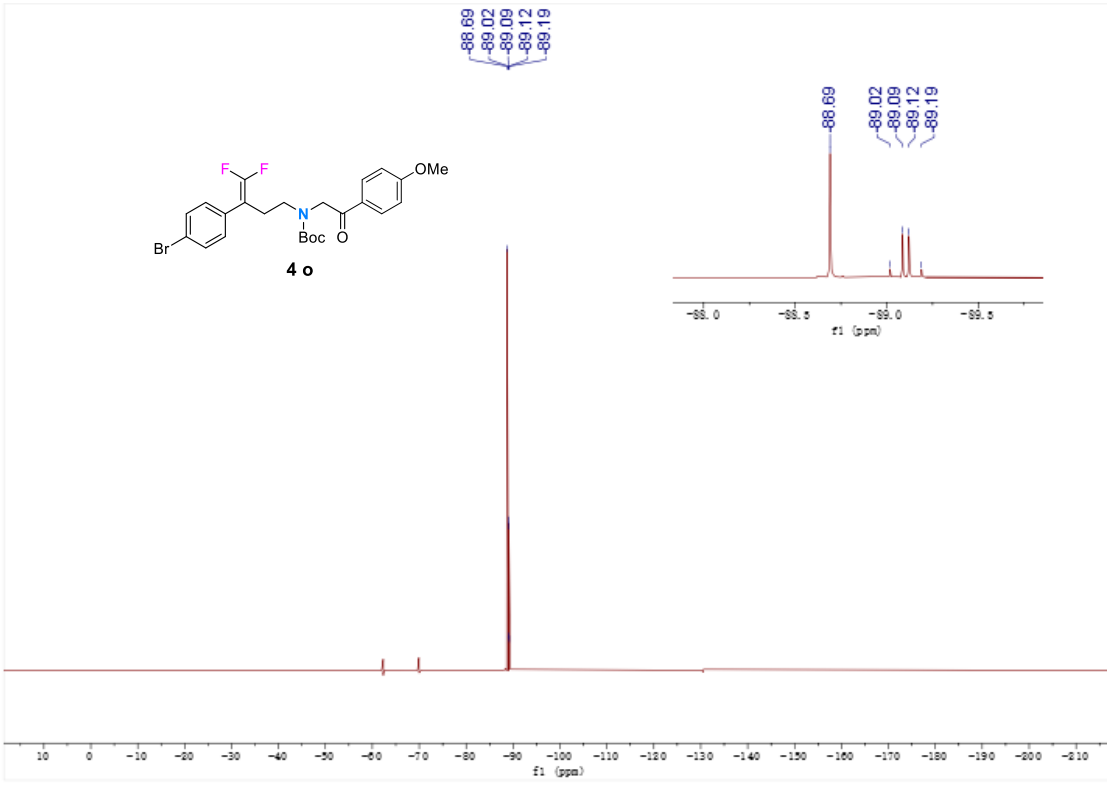
152.85
132.25
132.10
131.80
130.29
130.06
129.77
129.64
128.14
128.11
121.42
121.37
114.03
113.93
89.62
89.53
89.48
89.39
89.30
89.19
89.17
89.06
80.55
80.18
55.61
55.57
54.20
53.58
47.42
47.08
28.38
28.21
26.82
26.54
F
F
OMe
N
Boc
O
Br
4 o
f1 (ppm)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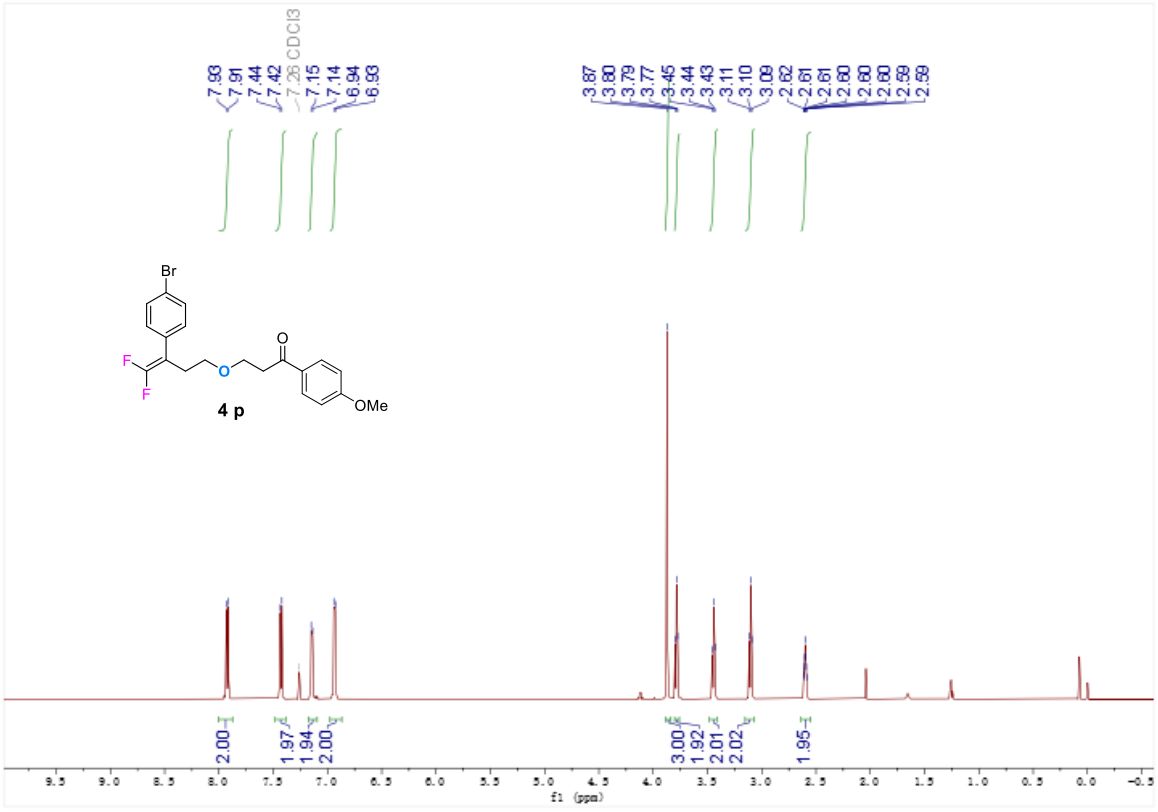
89.12
89.19
F
F
OMe
N
Boc
O
Br
4 o
f1 (ppm)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7.14
6.94
6.93
3.87
3.80
3.79
3.77
3.45
3.44
3.43
3.11
3.10
3.09
2.62
2.61
2.61
2.60
2.60
2.60
2.59
2.59
Br
F
F
O
O
OMe
4 p
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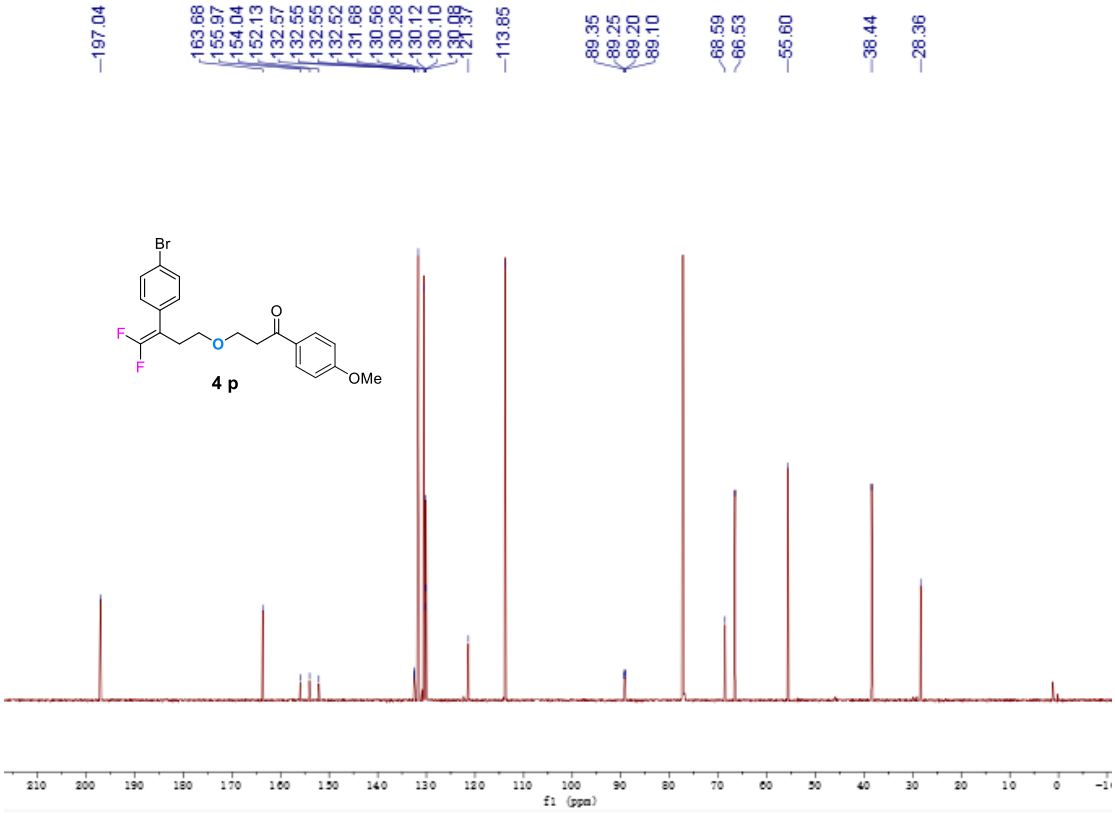
1.97
1.94
2.00
3.00
1.92
2.01
2.02
1.95
f1 (ppm)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132.55
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131.68
130.56
130.28
130.12
130.10
121.37
113.85
89.35
89.25
89.20
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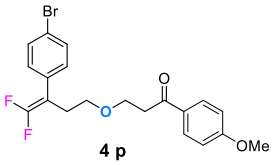
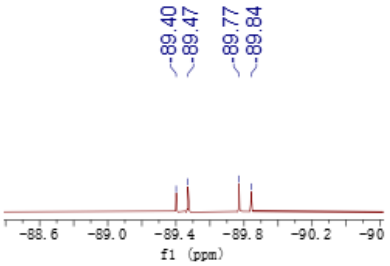
68.59
66.53
55.60
38.44
28.36
Br
F
F
O
O
OMe
4 p
f1 (ppm)


Br
F
F
O
O
OMe

4 p


-89.40
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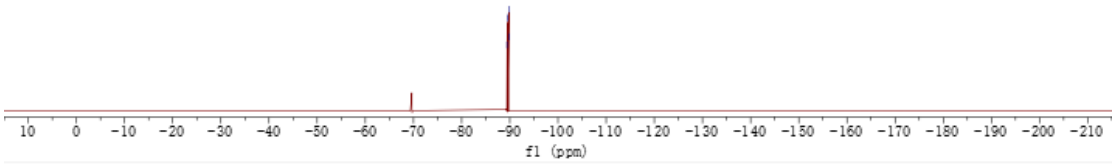
-89.0
-89.4
-89.8
-90.2
-90
f1 (ppm)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0
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-70
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-90
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-120
-130
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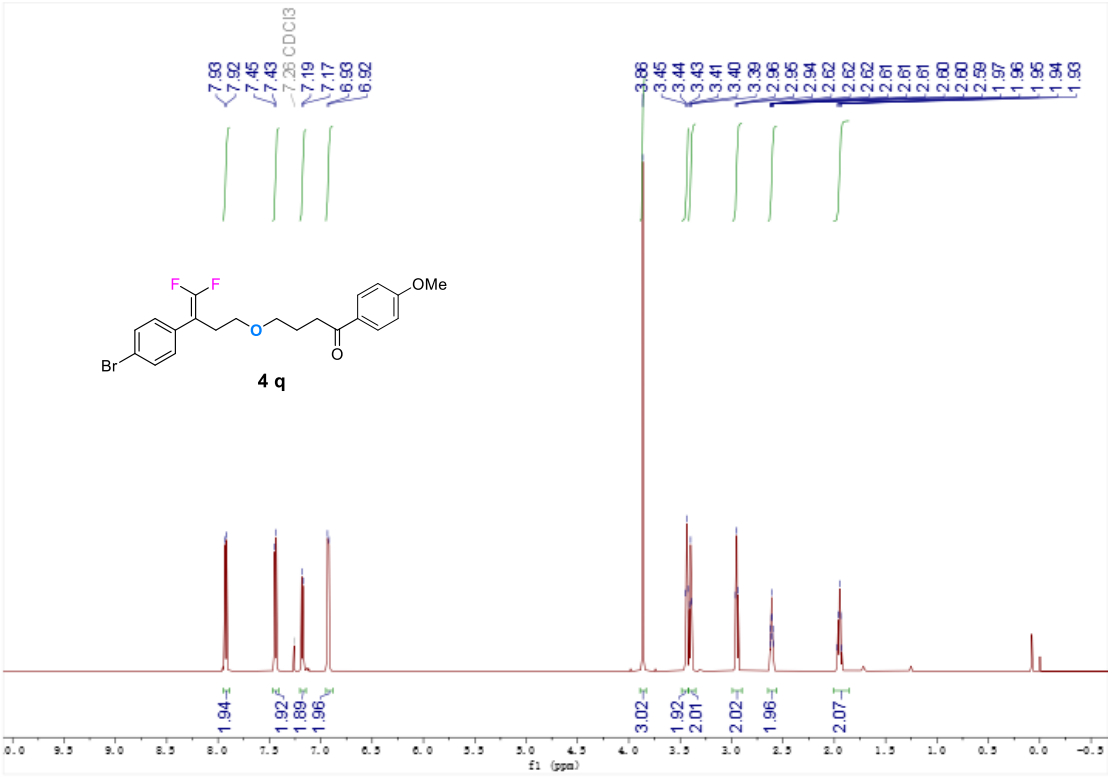
-170
-180
-190
-200
-210
f1 (ppm)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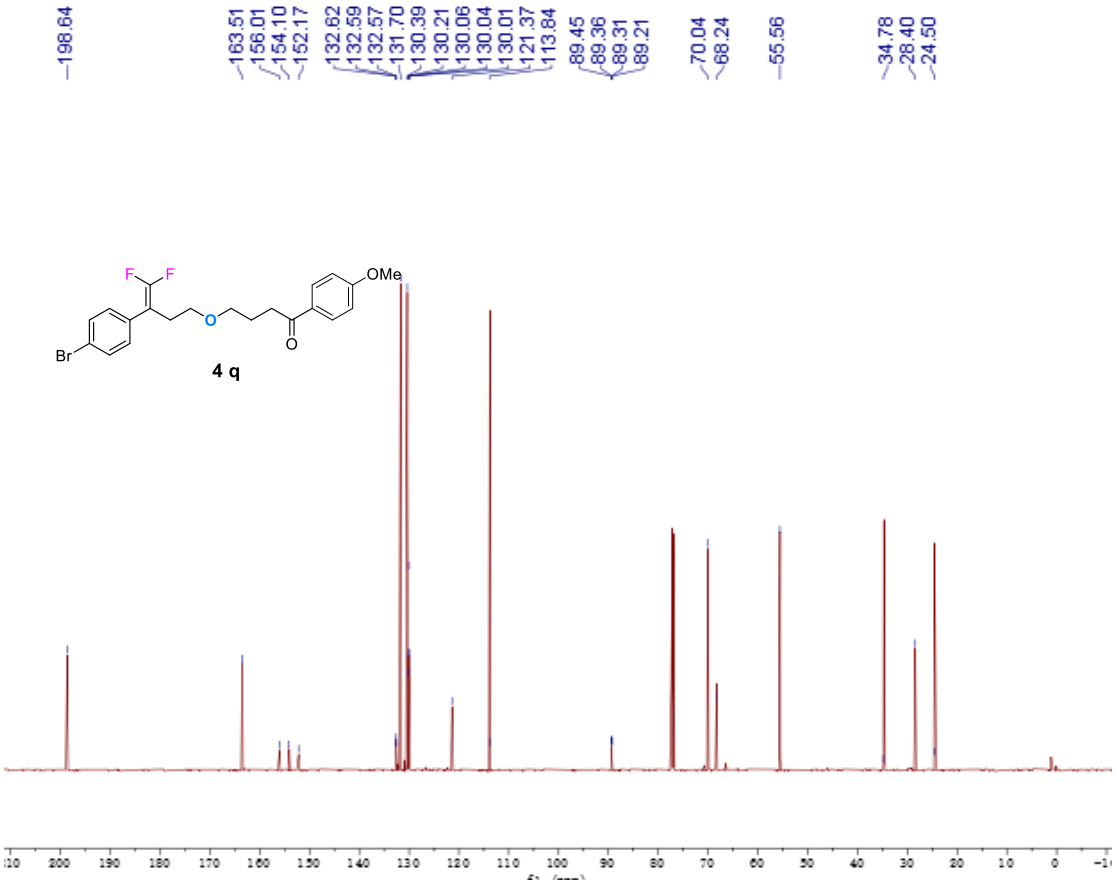
7.92
7.45
7.43
7.26 CDCl3
7.19
7.17
6.93
6.92
3.86
3.45
3.44
3.43
3.41
3.40
3.39
2.96
2.95
2.94
2.62
2.62
2.62
2.61
2.61
2.61
2.60
2.60
2.59
1.97
1.96
1.95
1.94
1.93
F
F
O
O
OMe
Br
1.94
1.92
1.89
1.96
3.02
1.92
2.01
2.02
1.96
2.07
f1 (ppm)

4 q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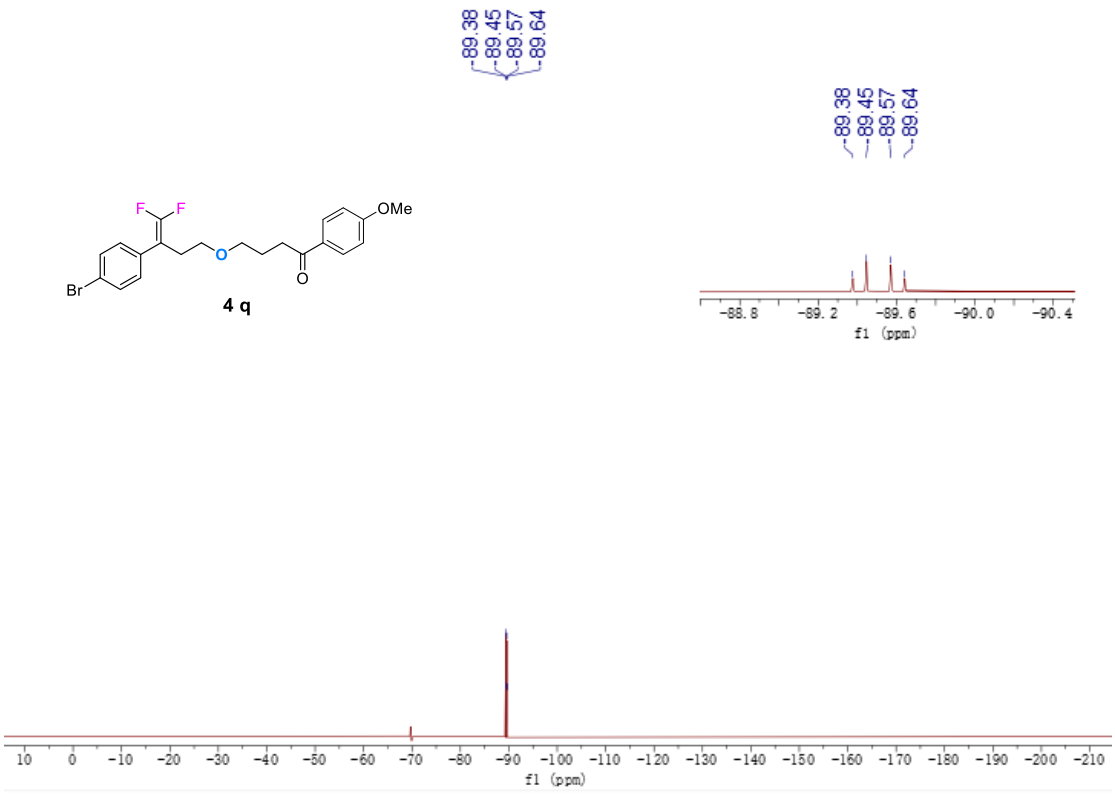
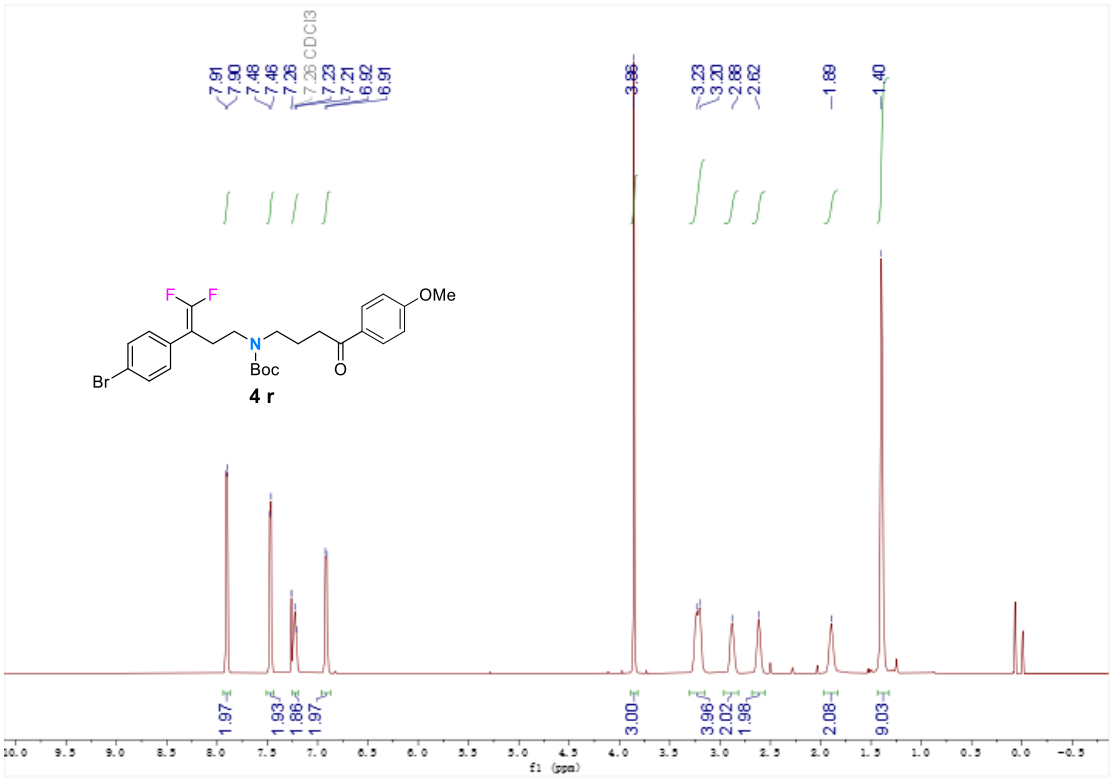
132.59
132.57
131.70
130.39
130.21
130.06
130.04
130.01
121.37
113.84
89.45
89.36
89.31
89.21
70.04
68.24
55.56
34.78
28.40
24.50
F
F
O
OMe
Br
O
4 q


89.38
89.45
89.57
89.64
F
F
O
OMe
Br
O
4 q
89.38
89.45
89.57
89.64
-88.8
-89.2
-89.6
-90.0
-90.4
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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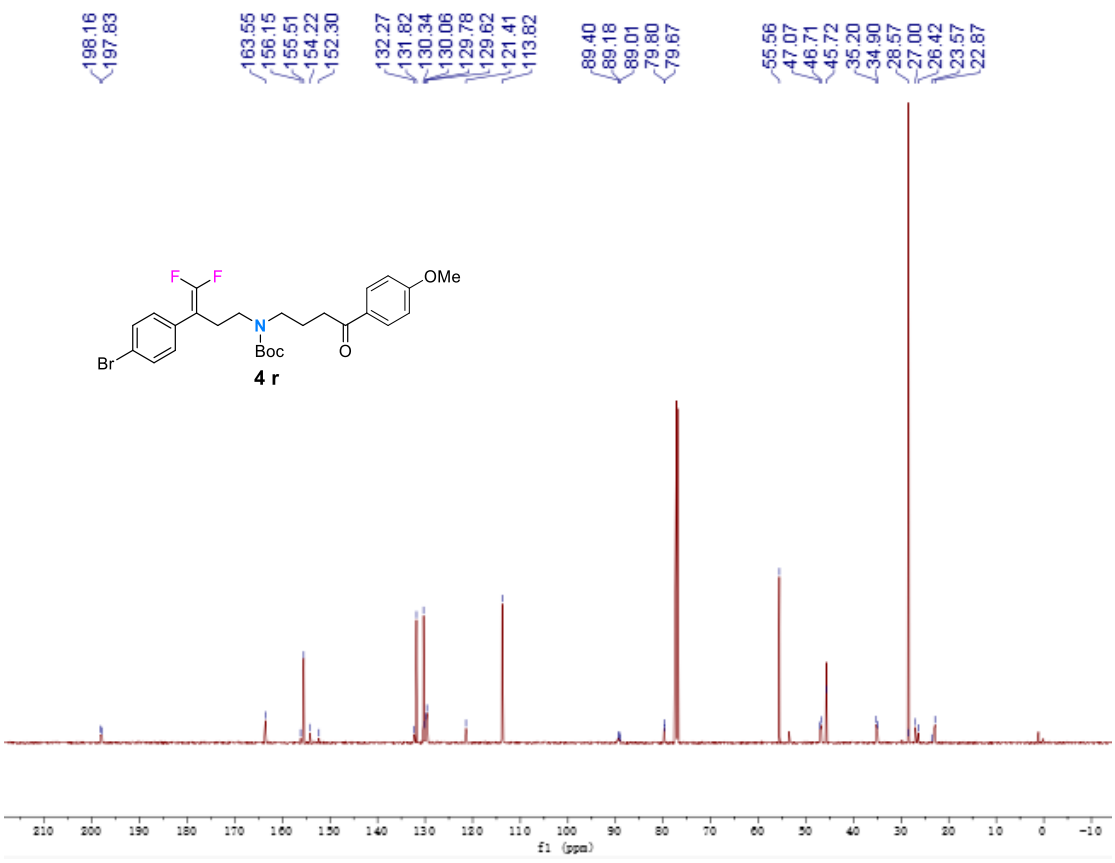
7.46
7.26
7.23
7.21
6.92
6.91
3.86
3.23
3.20
2.88
2.62
1.89
1.40
F
F
N
Boc
O
OMe
Br
4 r
1.97
1.93
1.86
1.97
3.00
3.96
2.02
1.98
2.08
9.03
f1 (ppm)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154.22
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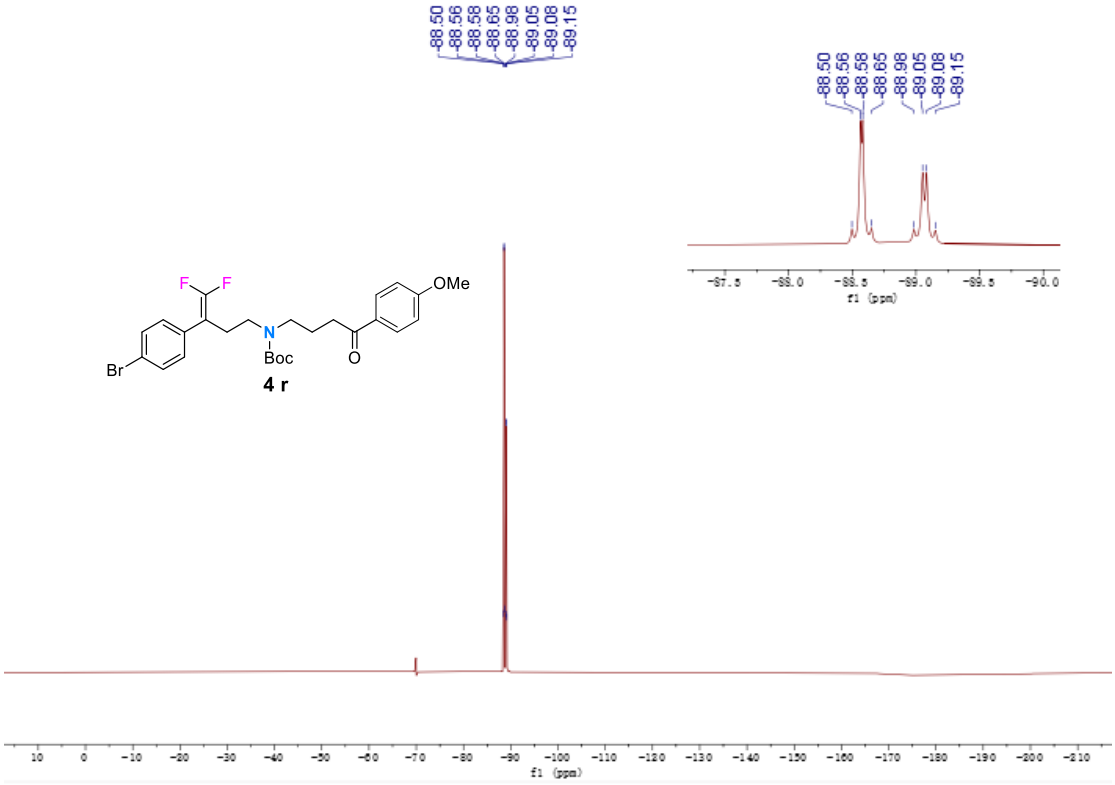
132.27
131.82
130.34
130.06
129.78
129.62
121.41
113.82
89.40
89.18
89.01
79.80
79.67
55.56
47.07
46.71
45.72
35.20
34.90
28.57
27.00
26.42
23.57
22.87
F
F
N
Boc
O
OMe
Br
4 r
f1 (ppm)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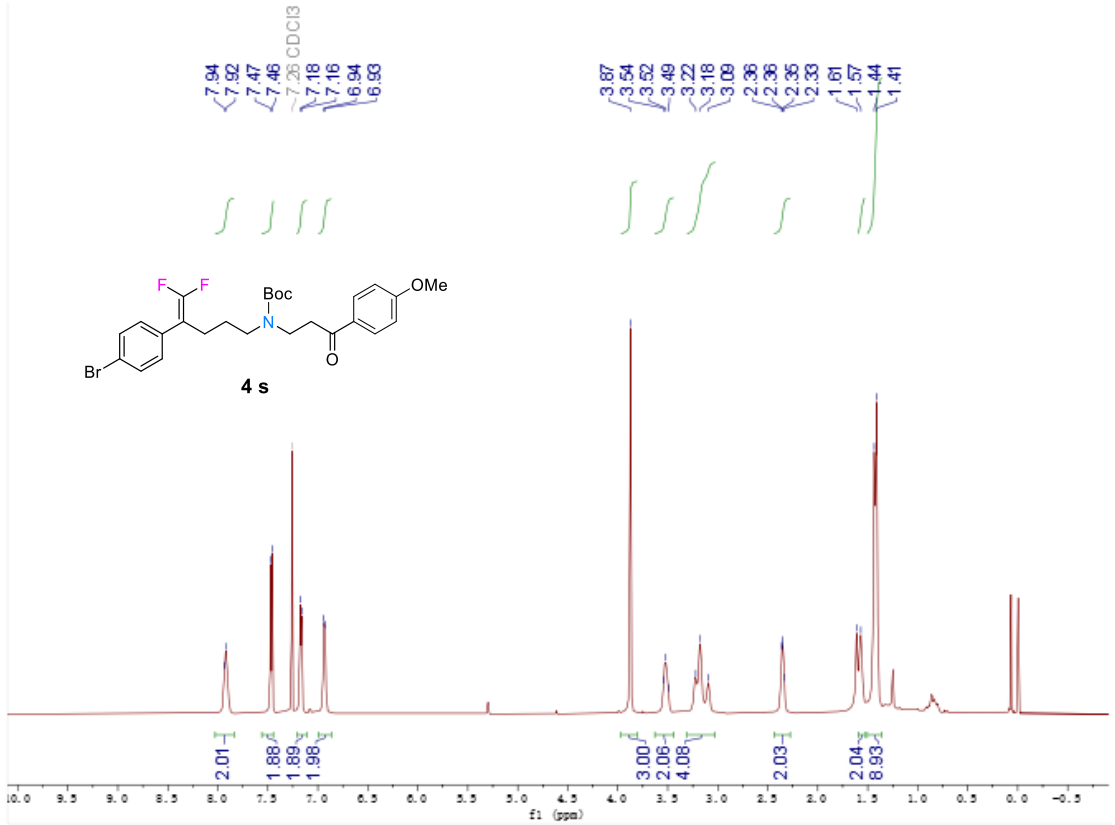
-88.56
-88.58
-88.65
-88.98
-89.05
-89.08
-89.15
F
F
OMe
N
Boc
O
Br
4 r
f1 (ppm)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6.93
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3.54
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3.49
3.22
3.18
3.09
2.36
2.35
2.33
1.61
1.57
1.44
1.41
F
F
Boc
OMe
N
O
Br
4 s
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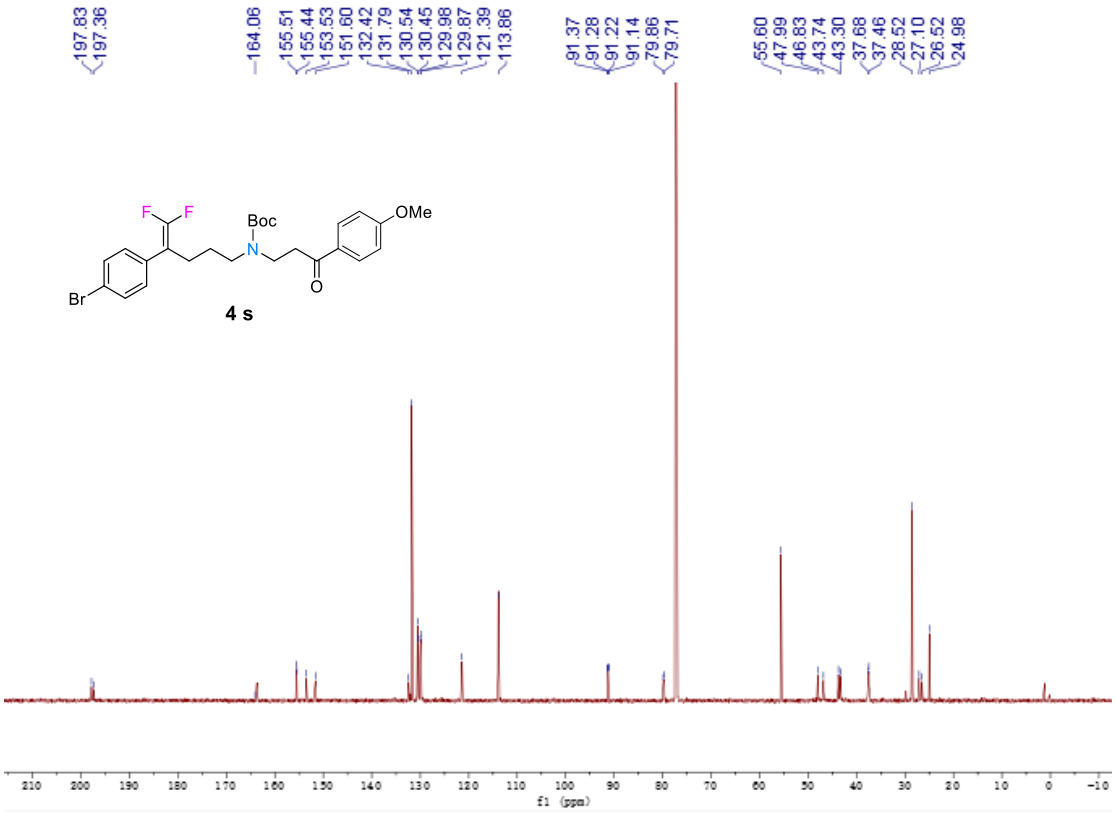
1.89
1.98
3.00
2.06
4.08
2.03
2.04
8.93
f1 (ppm)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113.86
91.37
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91.22
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79.86
79.71
55.60
47.99
46.83
43.74
43.30
37.68
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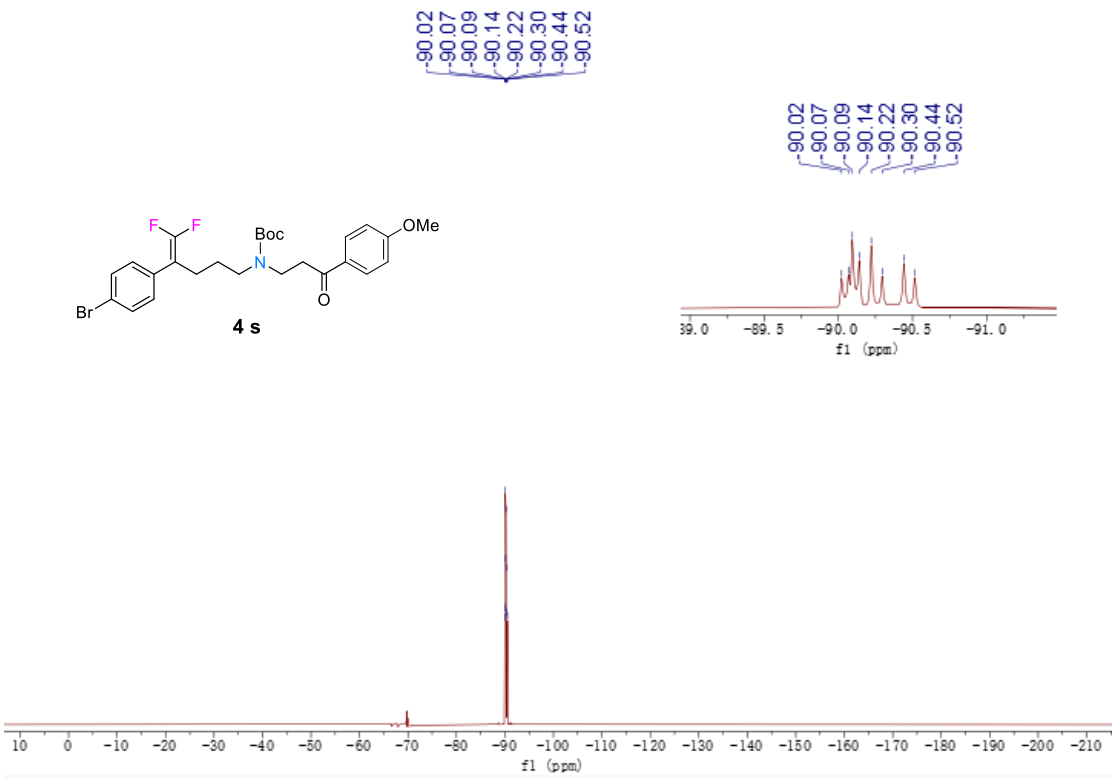
F
Boc
N
OMe
O
Br
4 s
f1 (ppm)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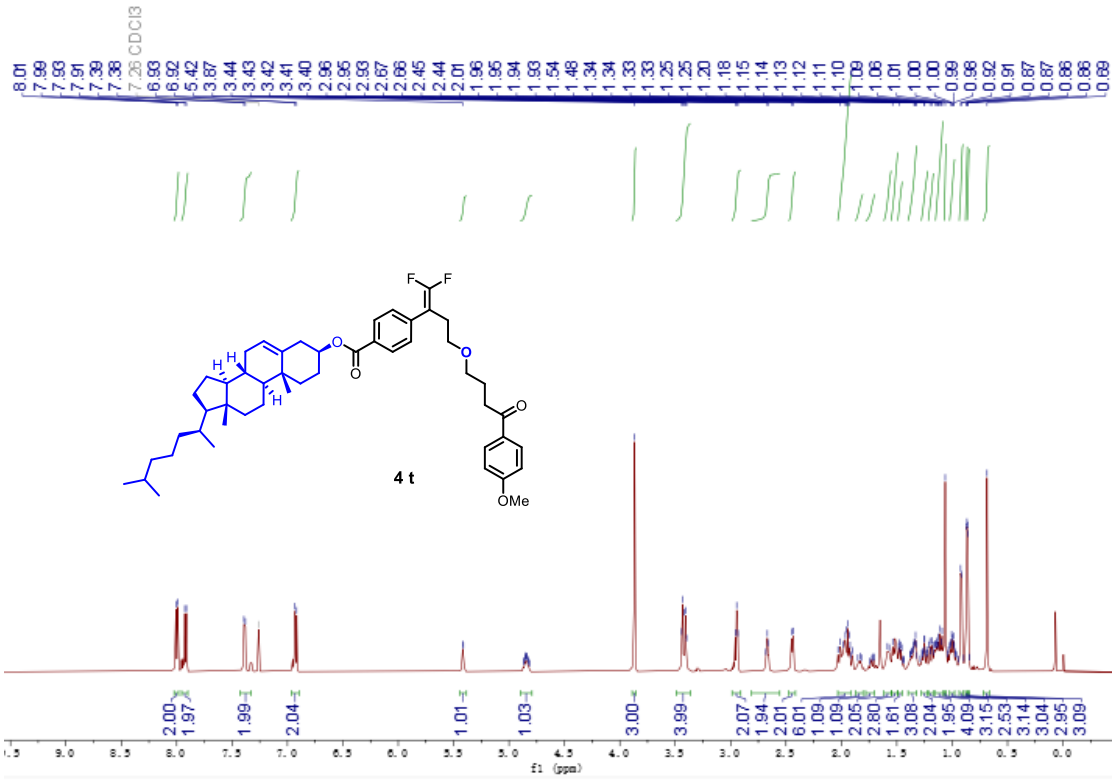
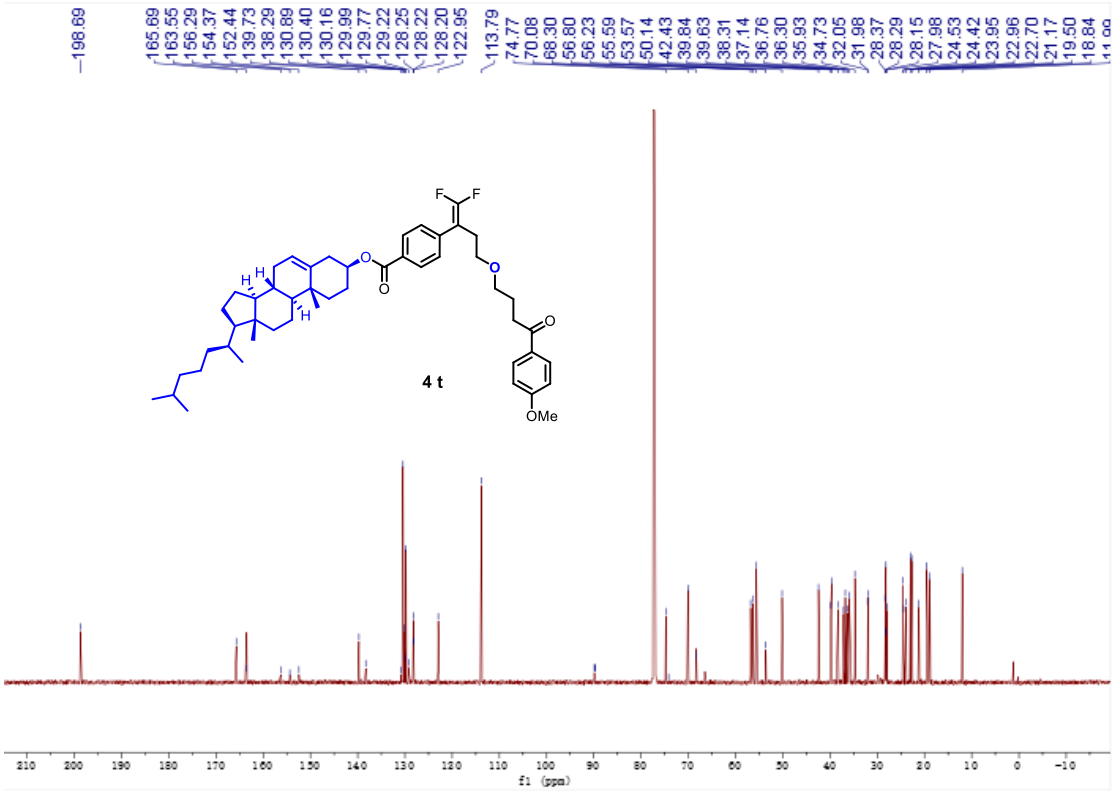
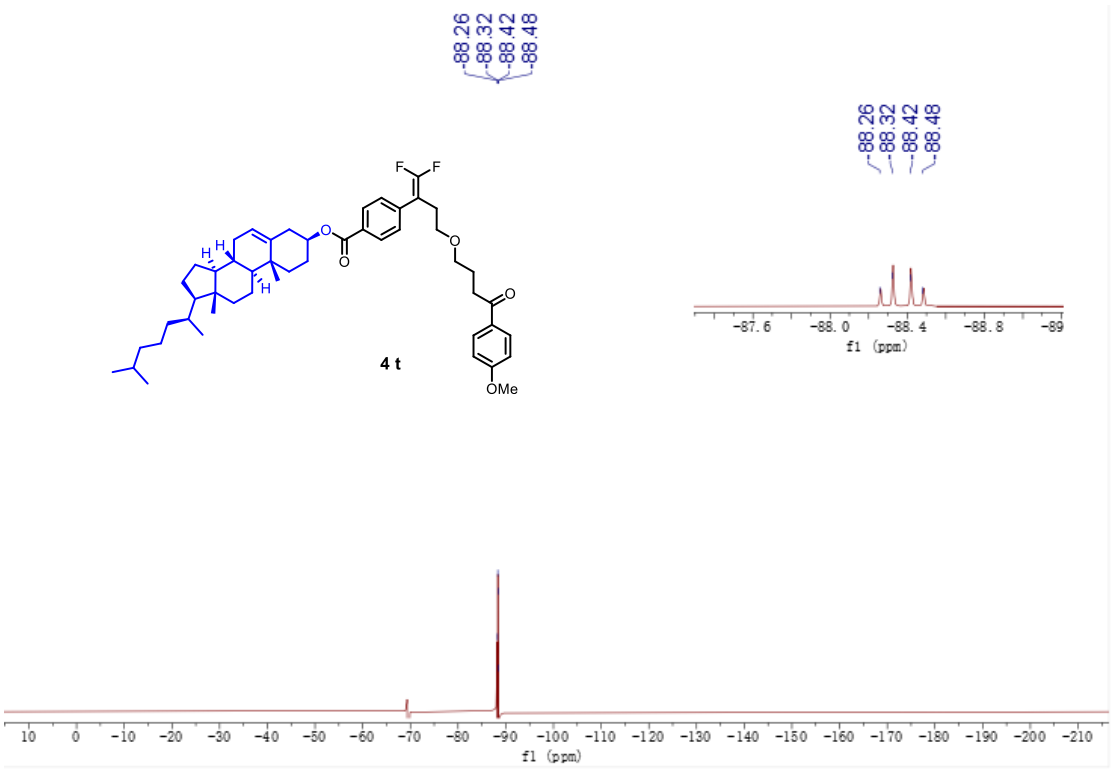
F
Boc
N
OMe
O
Br
4 s
f1 (ppm)


4 t
OMe
f1 (ppm)


4 t
OMe
f1 (ppm)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F
F
O
O
O
O
H
H
H
4 t
OMe
-88.26
-88.32
-88.42
-88.48
-87.6
-88.0
-88.4
-88.8
-89
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
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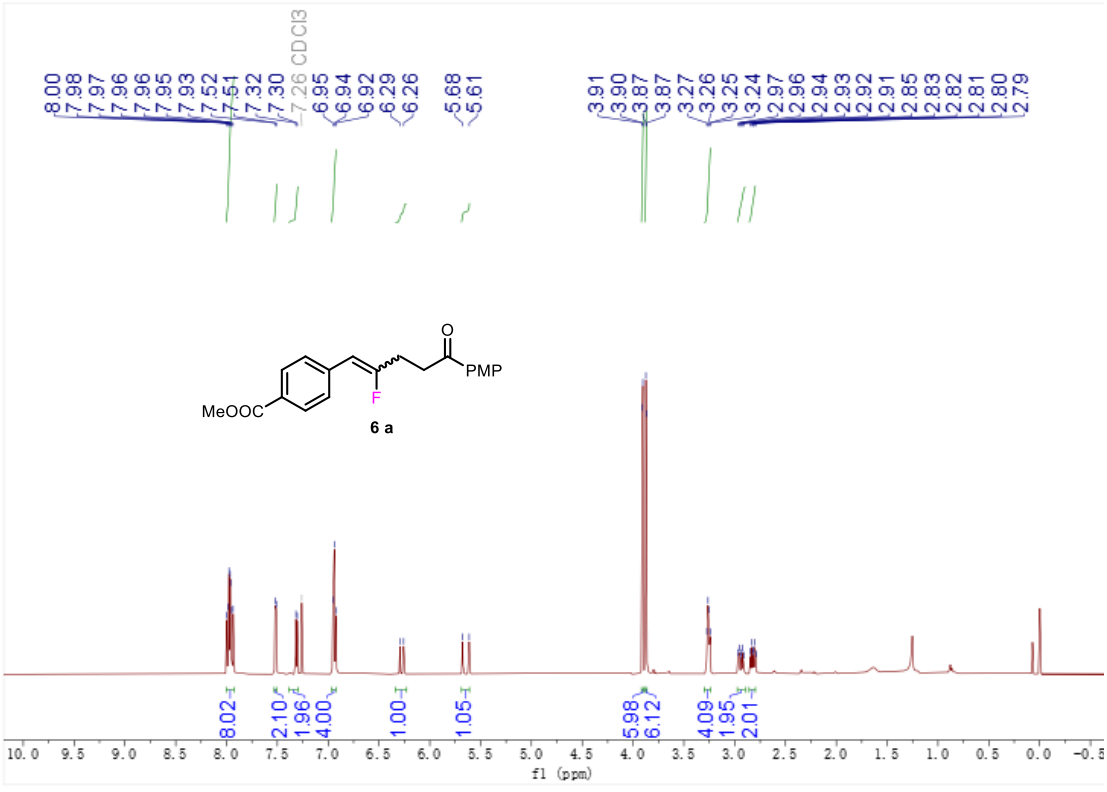
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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6.95
6.94
6.92
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6.26
5.68
5.61
3.91
3.90
3.87
3.87
3.27
3.26
3.25
3.24
2.97
2.96
2.94
2.93
2.92
2.91
2.85
2.83
2.82
2.81
2.80
2.79
O
PMP
F
MeOOC
6 a
8.02
2.10
1.96
4.00
1.00
1.05
5.98
6.12
4.09
1.95
2.01
10.0
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8.5
8.0
7.5
7.0
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6.0
5.5
5.0
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2.0
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0.0
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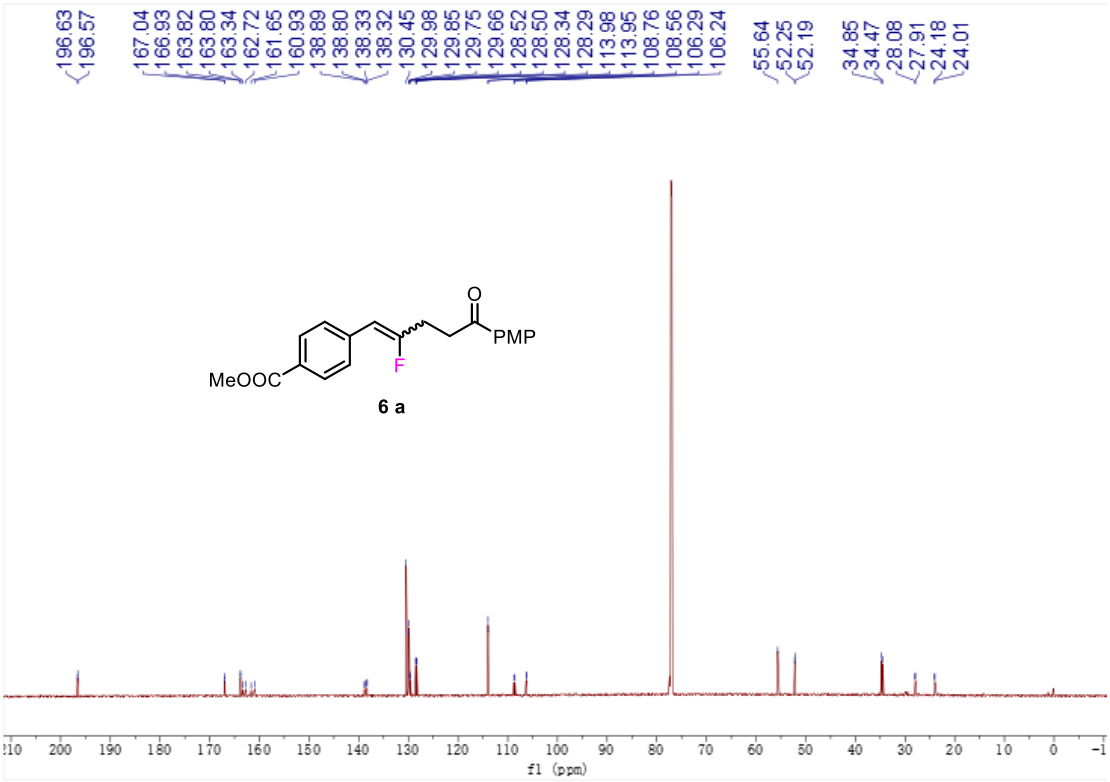
f1 (ppm)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138.33
138.32
130.45
129.98
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129.75
129.66
128.52
128.50
128.34
128.29
113.98
113.95
108.76
108.56
106.29
106.24
55.64
52.25
52.19
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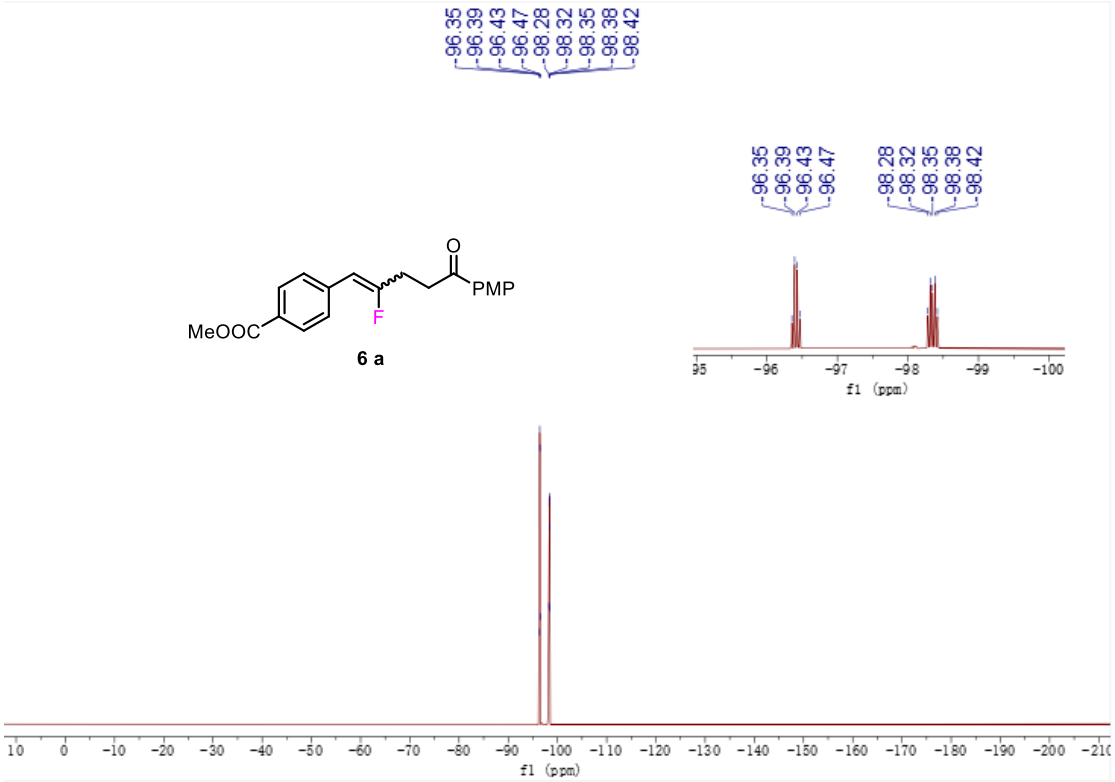
28.08
27.91
24.18
24.01
O
PMP
F
MeOOC
f1 (ppm)

6 a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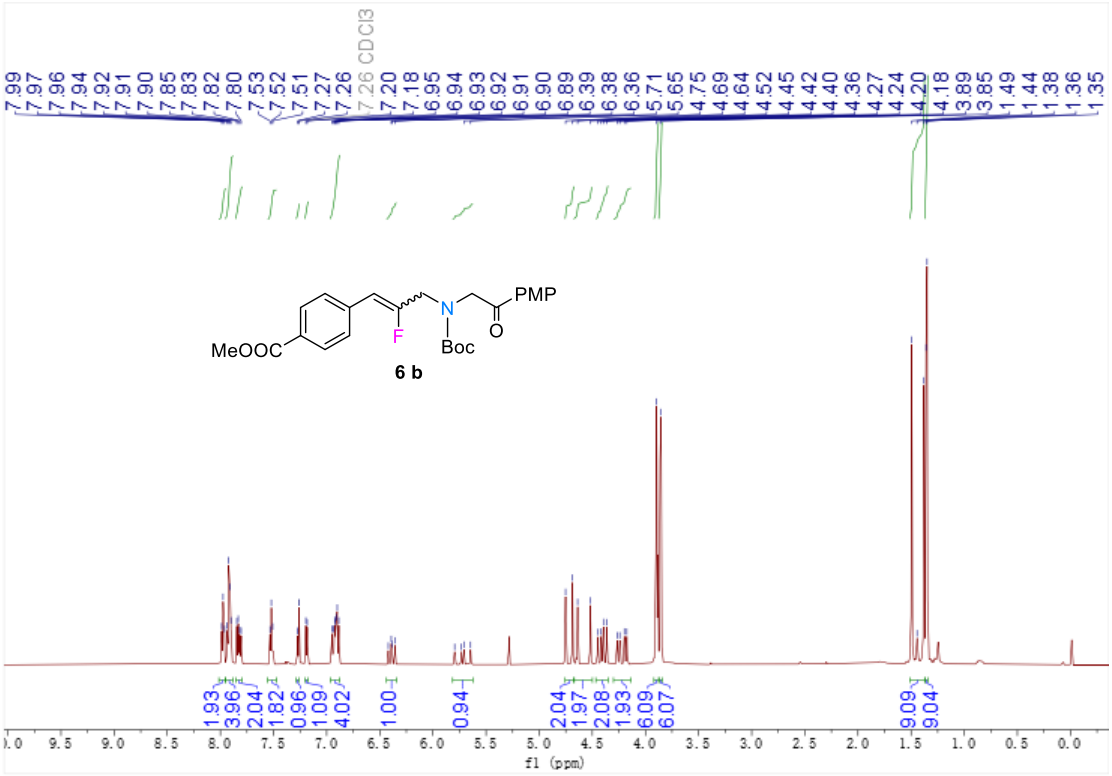
98.38
98.42
O
PMP
F
MeOOC
f1 (ppm)

6 a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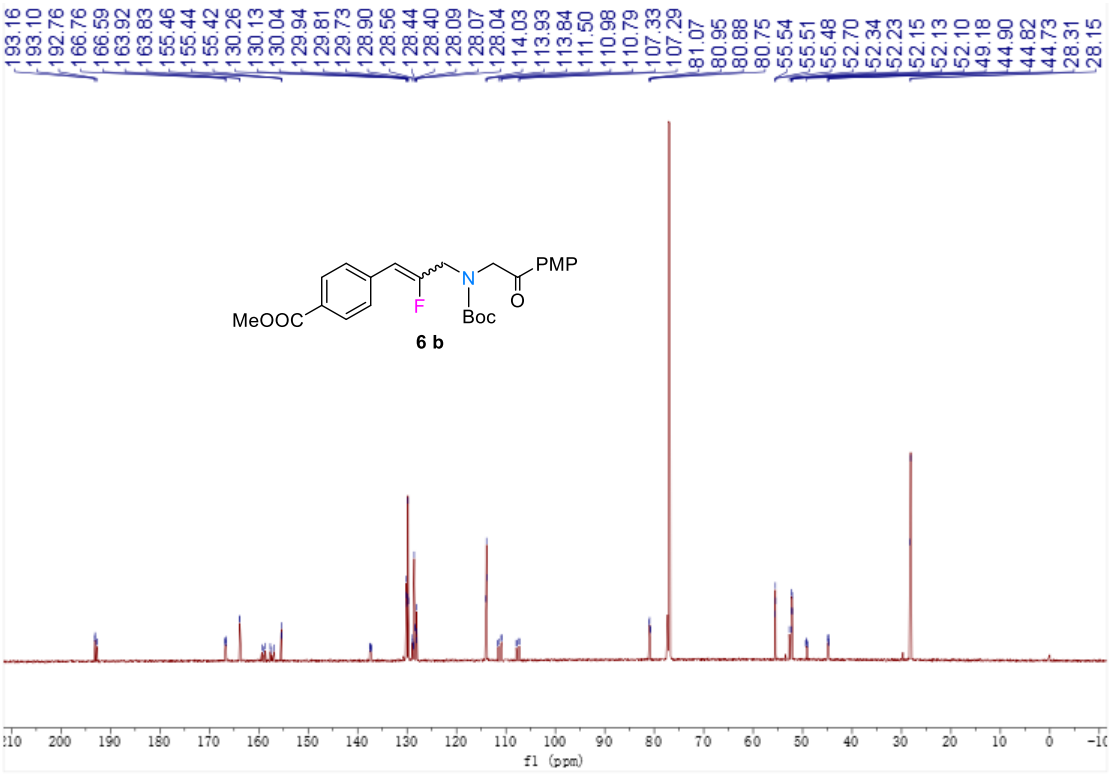
PMP
N
O
F
Boc
MeOOC
6 b
1.93 3.96 2.04 1.82 0.96 1.09 4.02 1.00 0.94 2.04 1.97 2.08 1.93 6.09 6.07 9.09 9.04
f1 (ppm)


193.16 193.10 192.76 166.76 166.59 163.92 163.83 155.46 155.44 155.42 130.26 130.13 130.04 129.94 129.81 129.73 128.90 128.56 128.44 128.40 128.09 128.07 128.04 114.03 113.93 113.84 111.50 110.98 110.79 107.33 107.29 81.07 80.95 80.88 80.75 55.54 55.51 55.48 52.70 52.34 52.23 52.15 52.13 52.10 49.18 44.90 44.82 44.73 28.31 28.15
PMP
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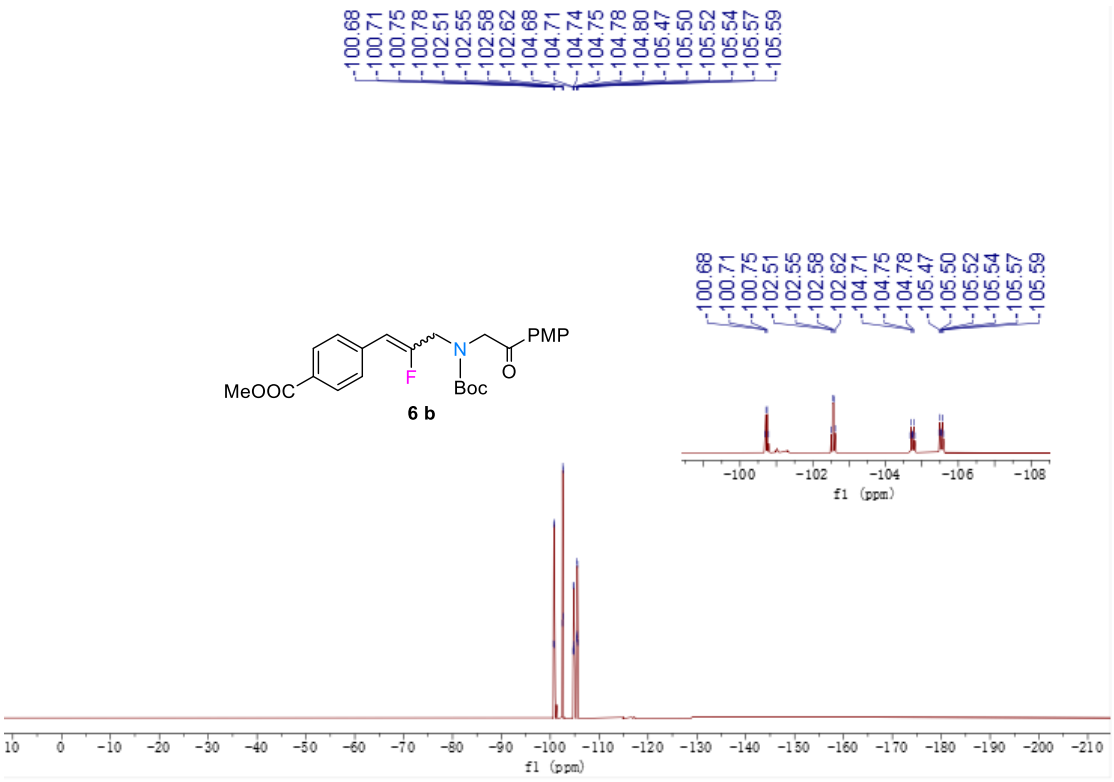
O
F
Boc
MeOOC
6 b
f1 (ppm)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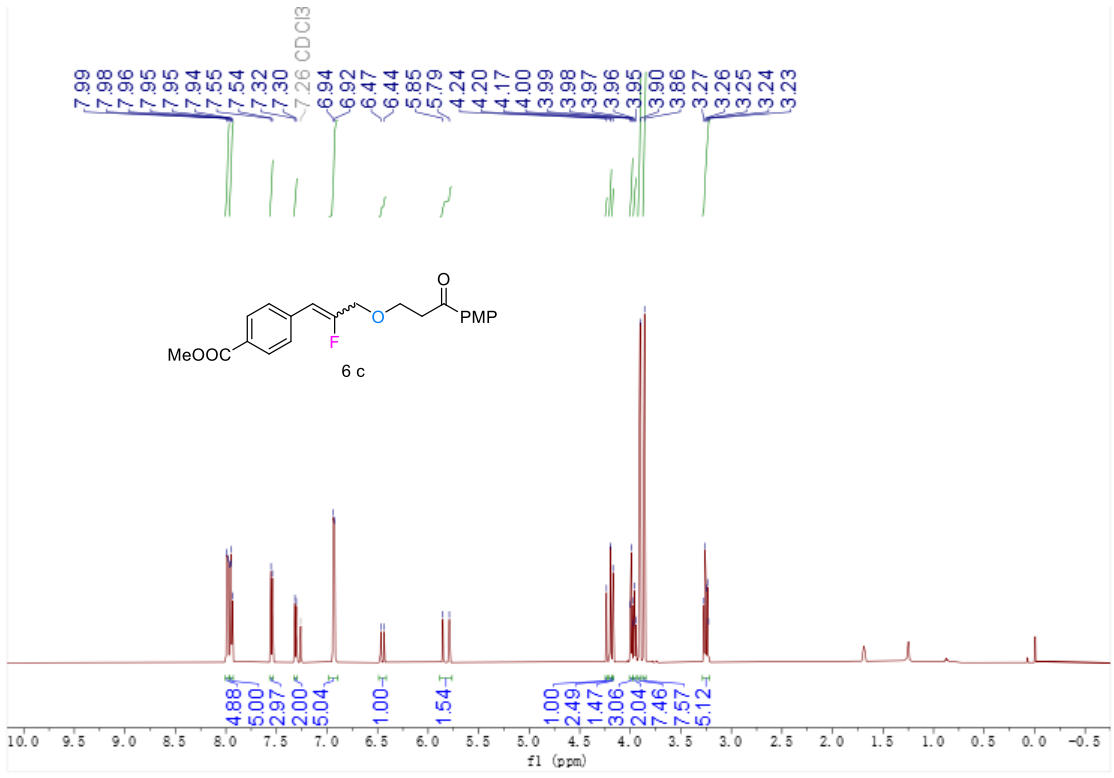
MeOOC
F
N
Boc
PMP
O
6 b
f1 (ppm)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7.55
7.54
7.32
7.30
7.26 CDCl3
6.94
6.92
6.47
6.44
5.85
5.79
4.24
4.20
4.17
4.00
3.99
3.98
3.97
3.96
3.95
3.90
3.86
3.27
3.26
3.25
3.24
3.23
MeOOC
F
O
O
PMP
6 c
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2.97
2.00
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1.00
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2.04
7.46
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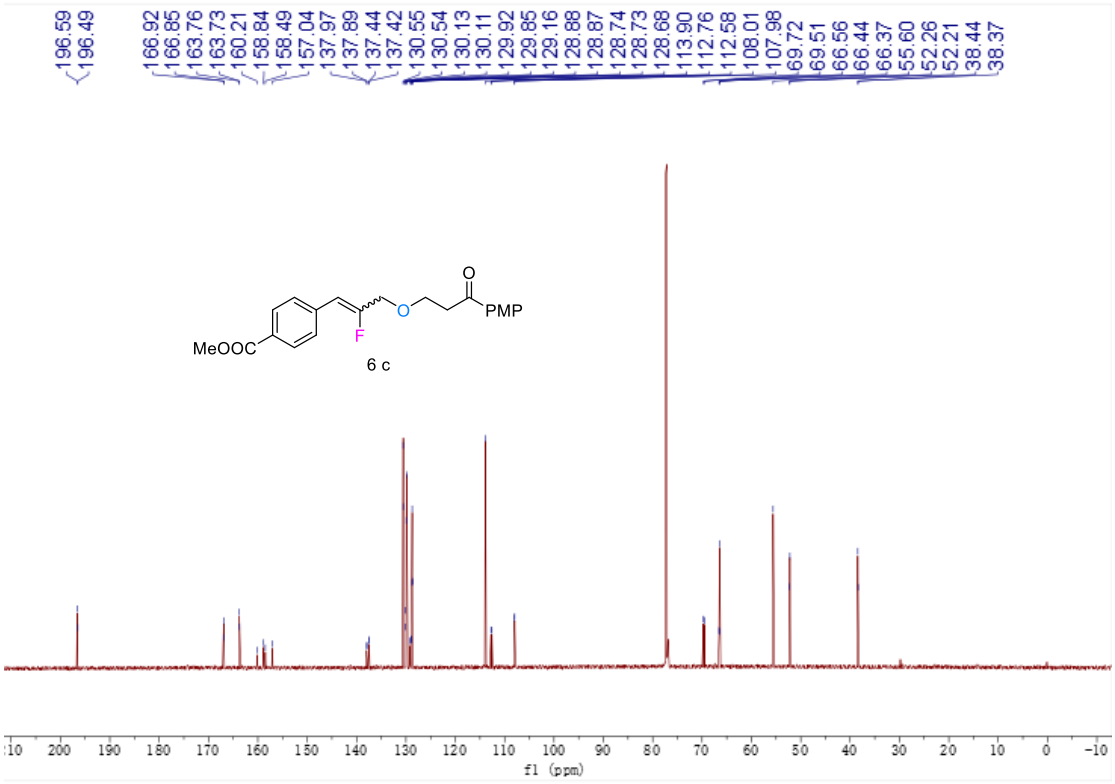
5.12
f1 (ppm)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PMP
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MeOOC
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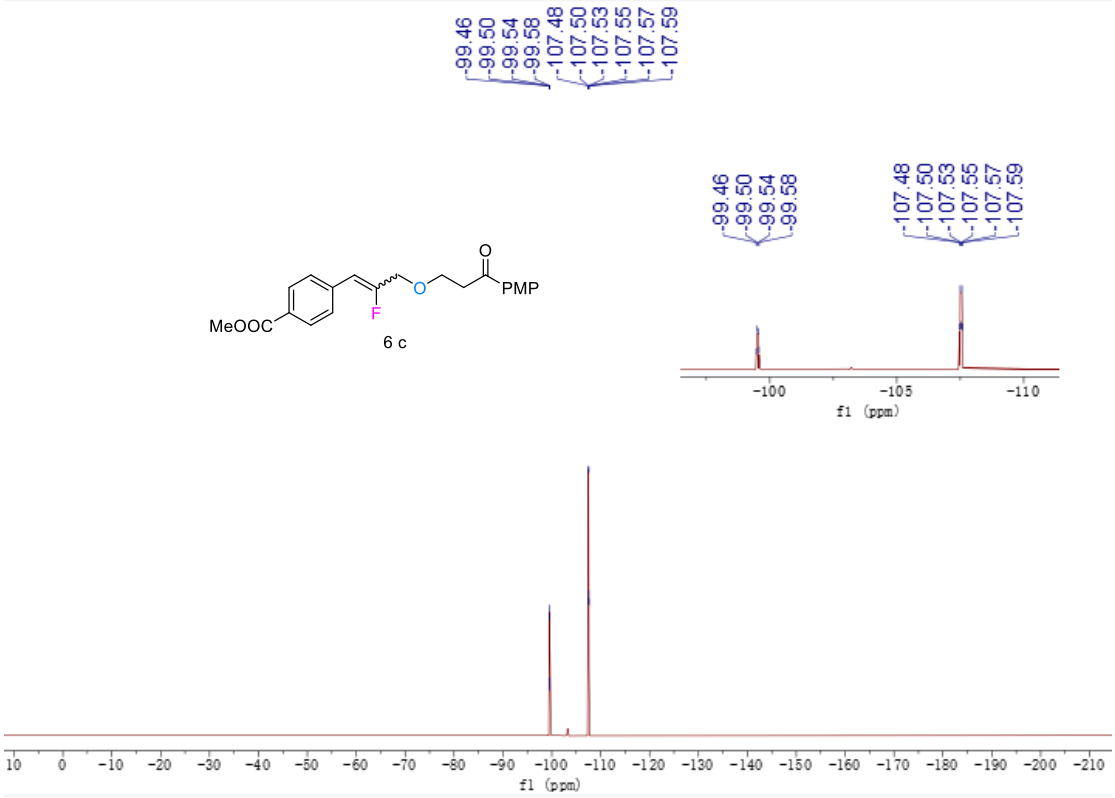
f1 (ppm)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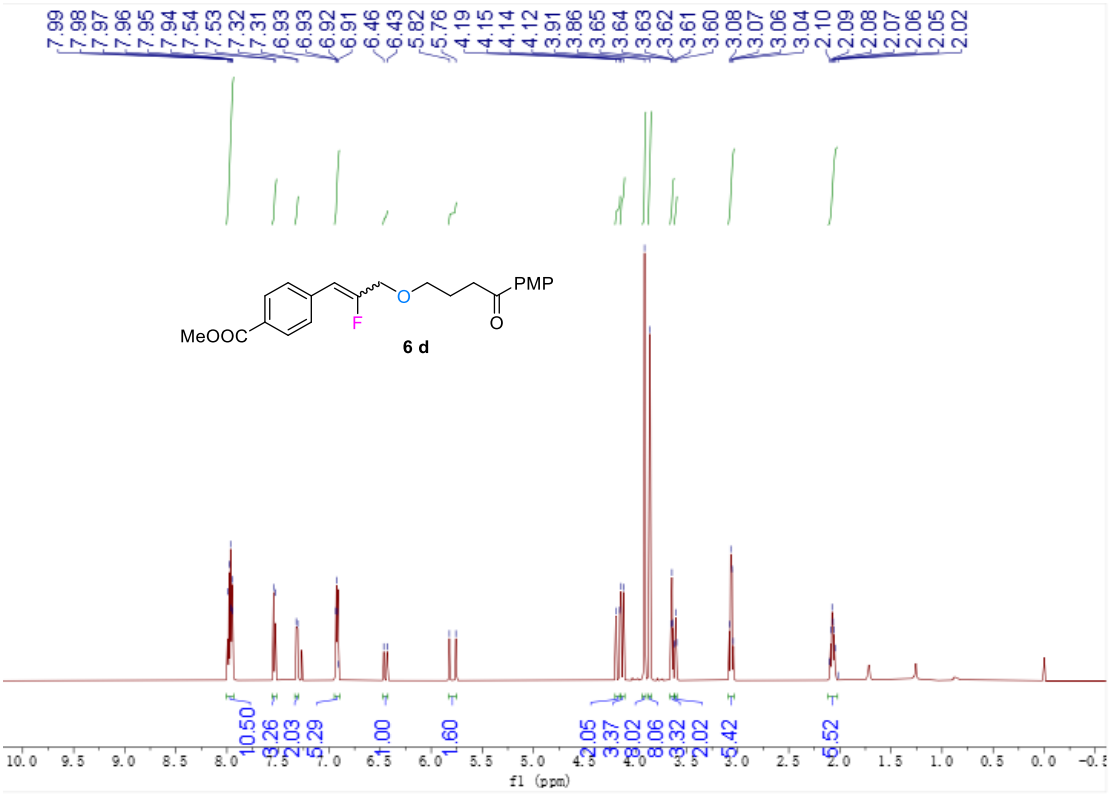
O
PMP
O
F
MeOOC
6 c
f1 (ppm)
f1 (ppm)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6.92
6.91
6.46
6.43
5.82
5.76
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4.15
4.14
4.12
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3.86
3.65
3.64
3.63
3.62
3.61
3.60
3.08
3.07
3.06
3.04
2.10
2.09
2.08
2.07
2.06
2.05
2.02
PMP
O
O
F
MeOOC
6 d
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2.03
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8.06
3.32
2.02
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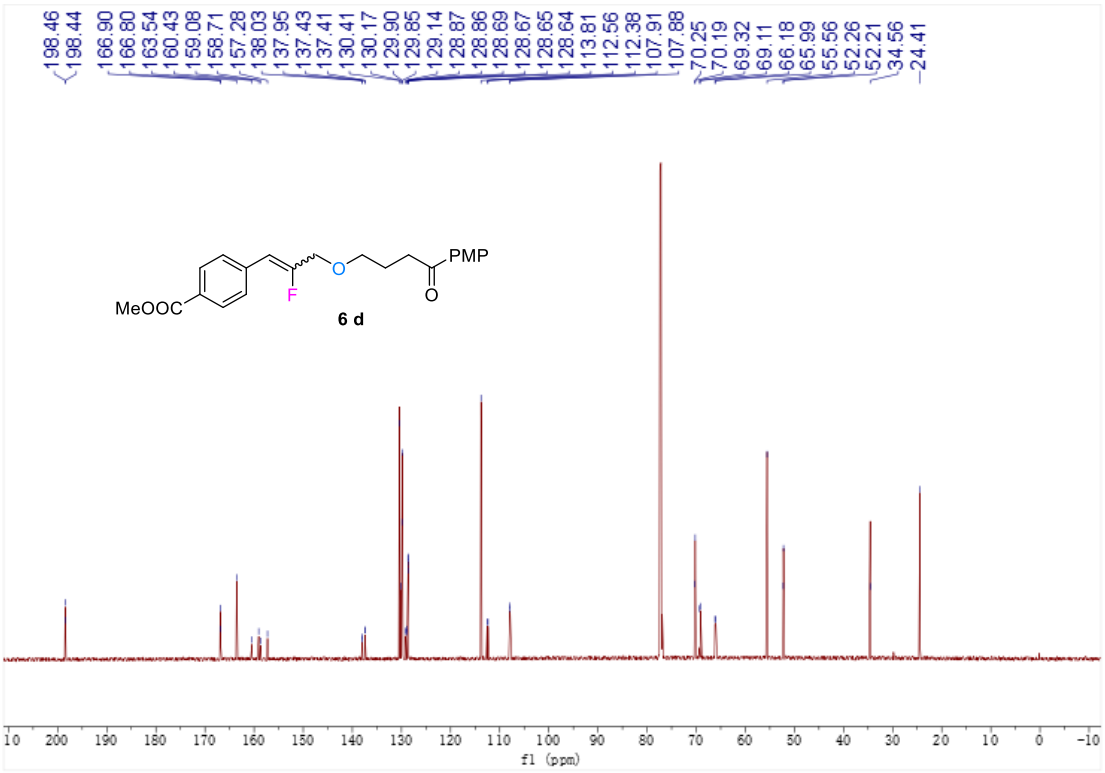
5.52
f1 (ppm)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70.19
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69.11
66.18
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52.21
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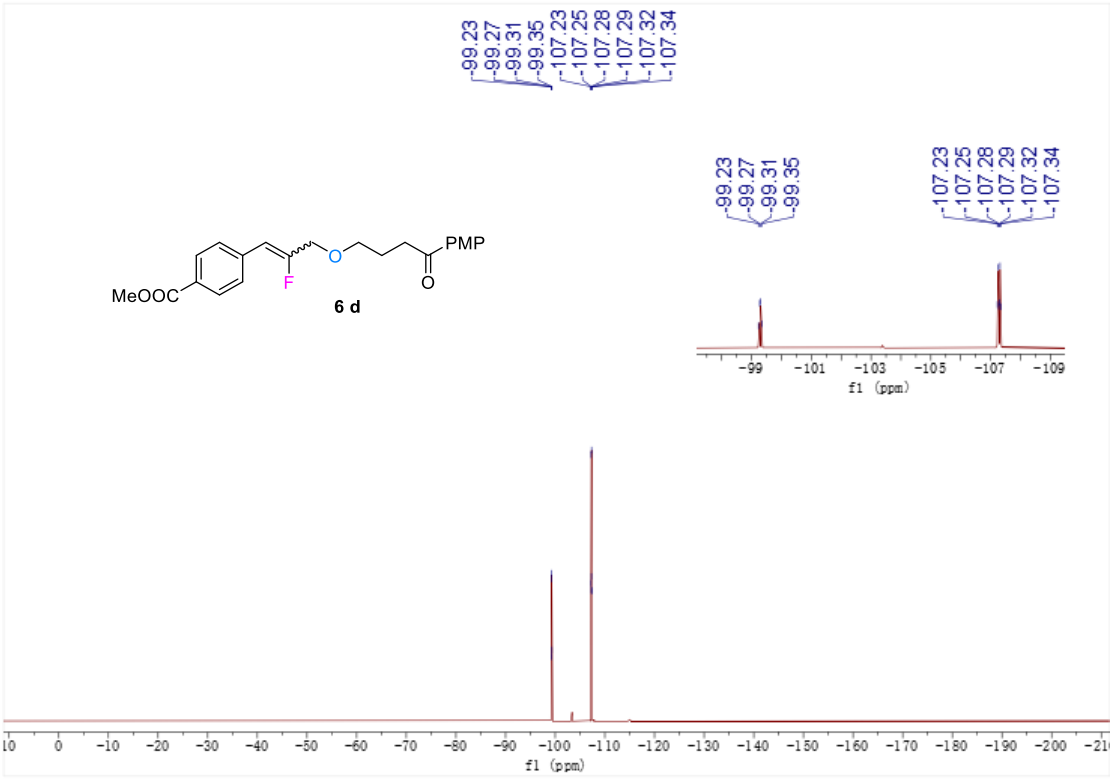
O
O
F
MeOOC
6 d
f1 (ppm)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-107.34
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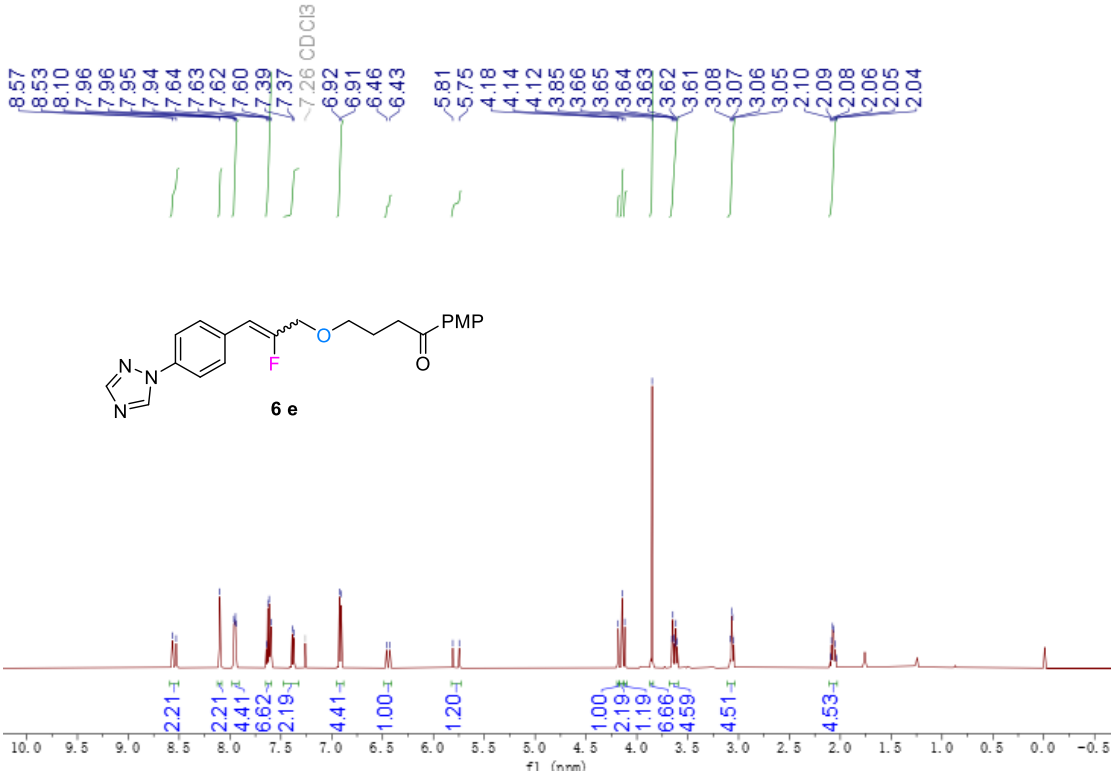
MeOOC
O
F
O
6 d
f1 (ppm)
f1 (ppm)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7.39
7.37
7.26 CDCl3
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6.46
6.43
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4.12
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PMP
N
N
N
O
F
O
6 e
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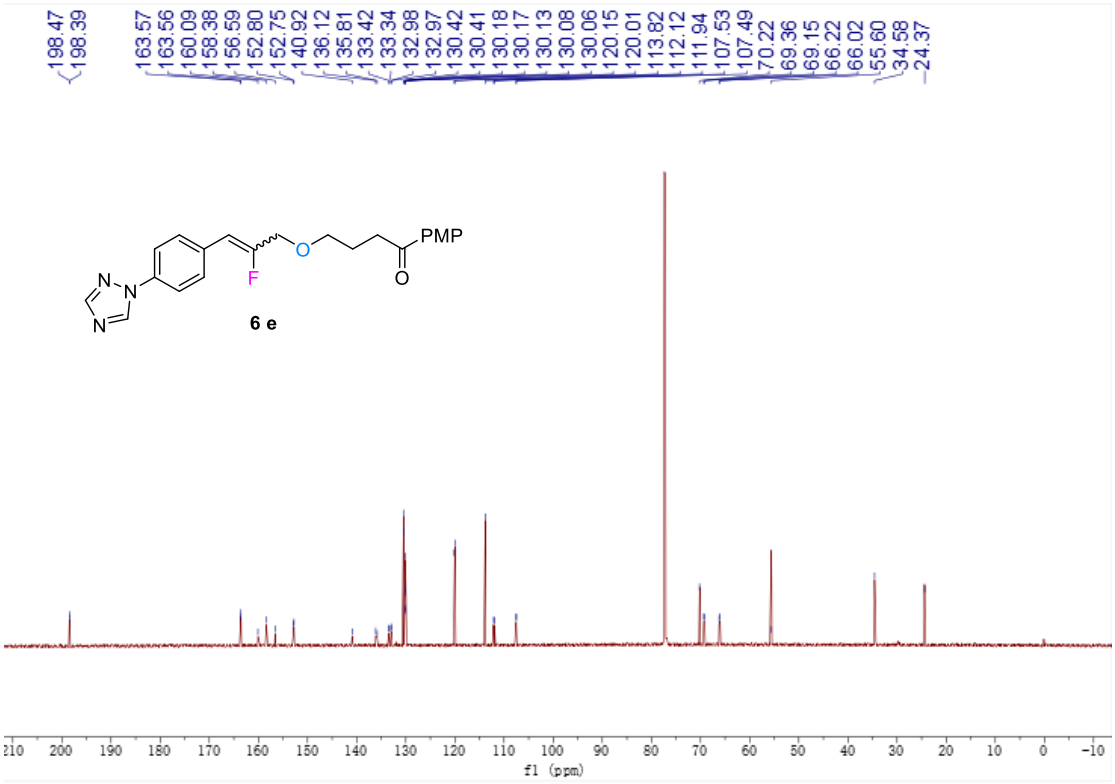
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120.01
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PMP
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F
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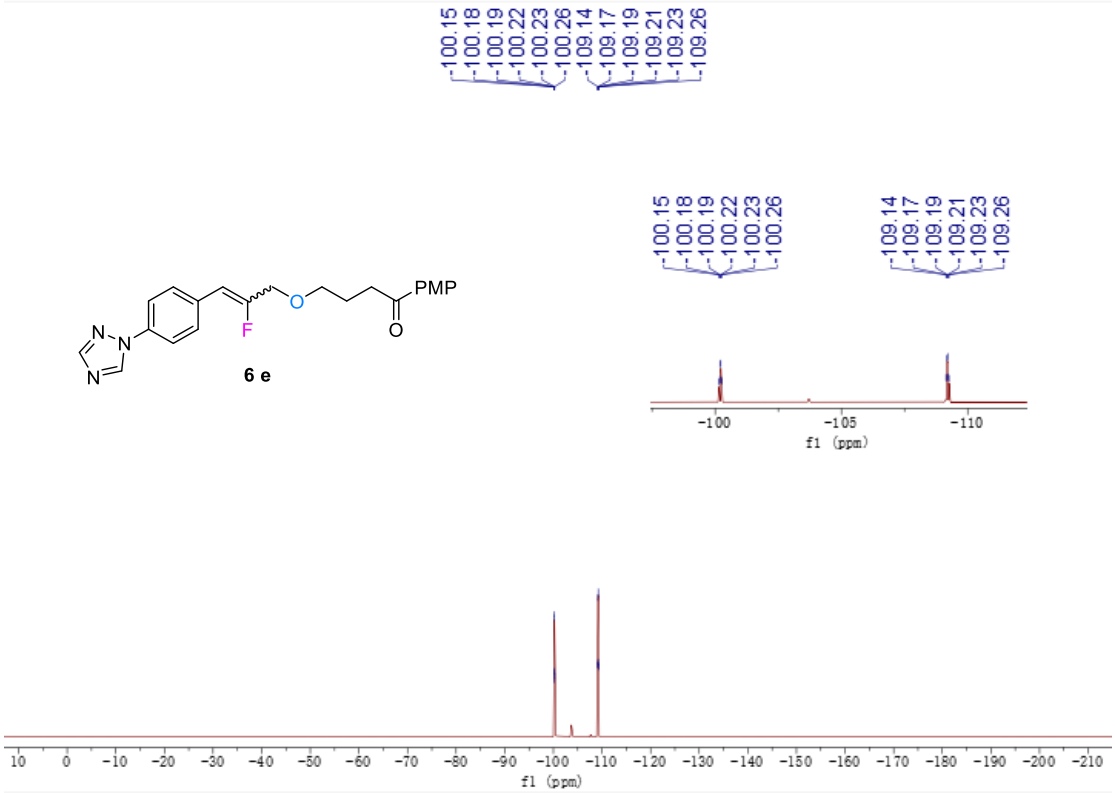
N
6 e
f1 (ppm)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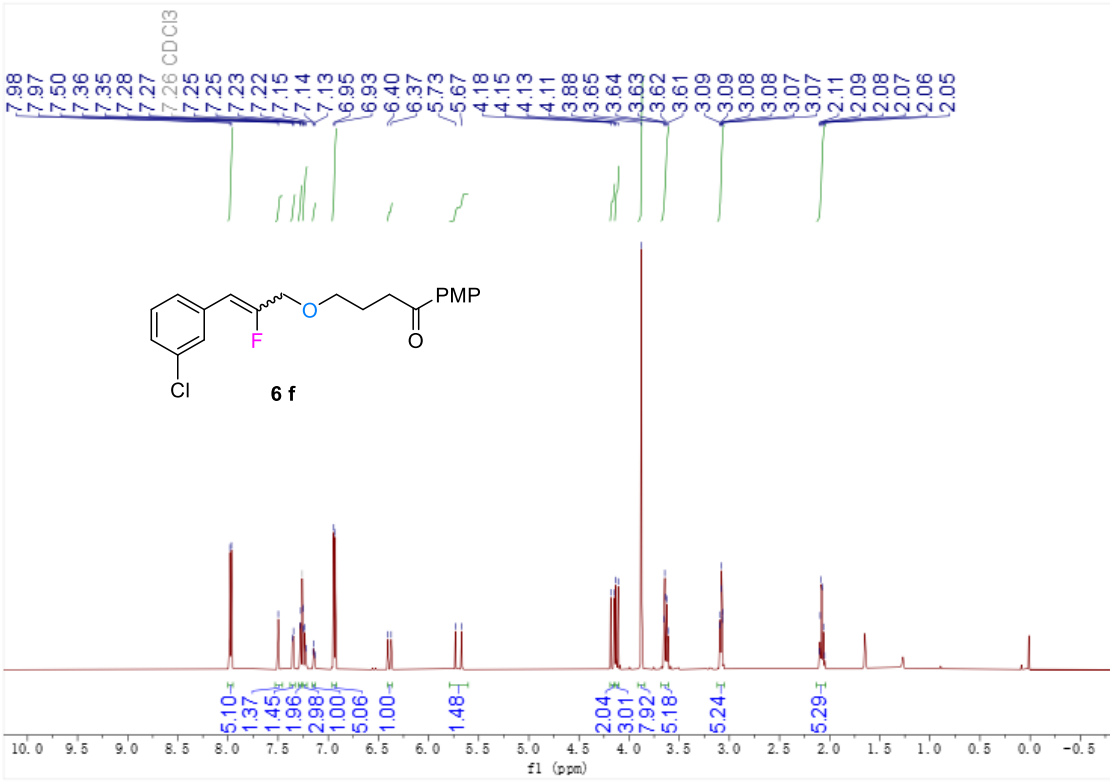
109.26
PMP
O
F
N
N
N
6 e
f1 (ppm)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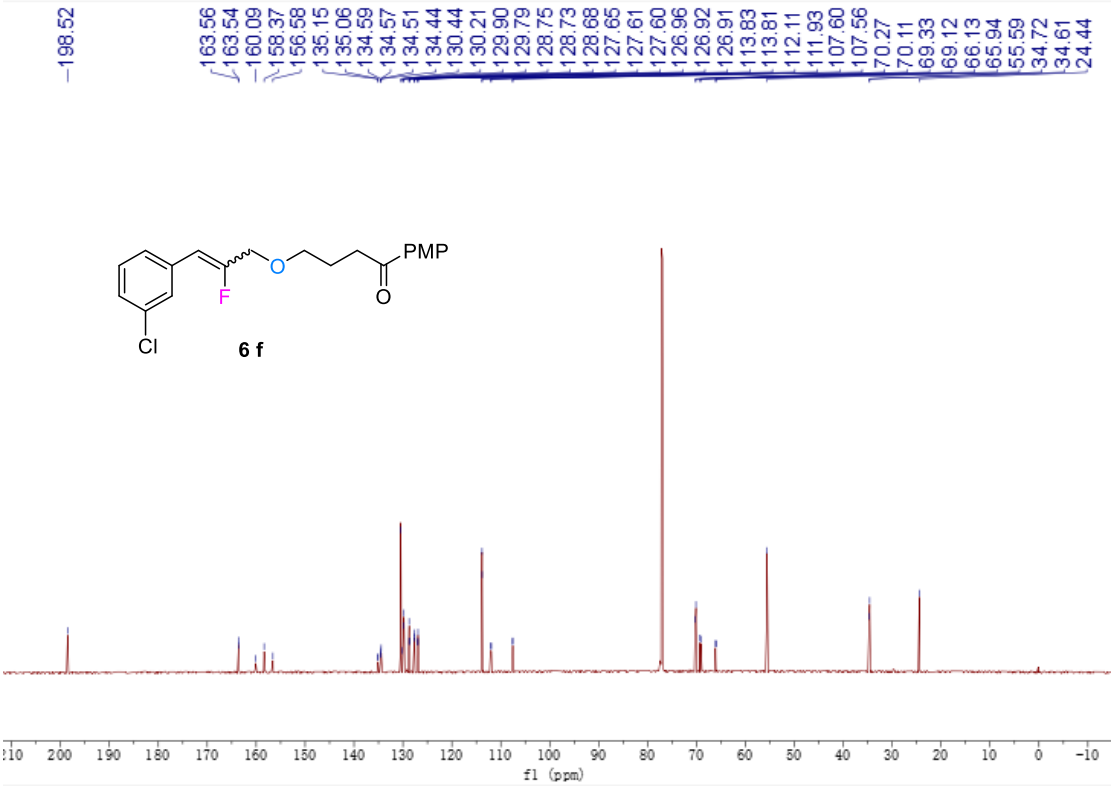
PMP
O
F
O
Cl
6 f
5.10 1.37 1.45 1.96 2.98 1.00 5.06 1.00 1.48 2.04 3.01 7.92 5.18 5.24 5.29
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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O
F
O
Cl
6 f
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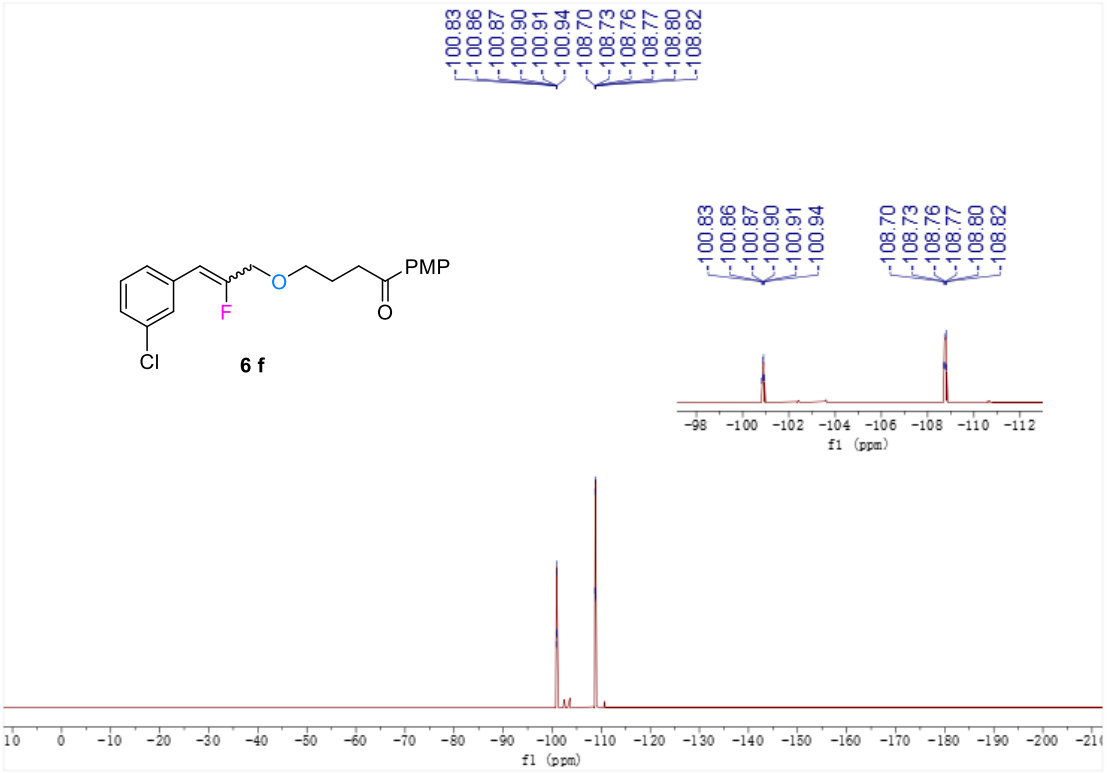
f1 (ppm)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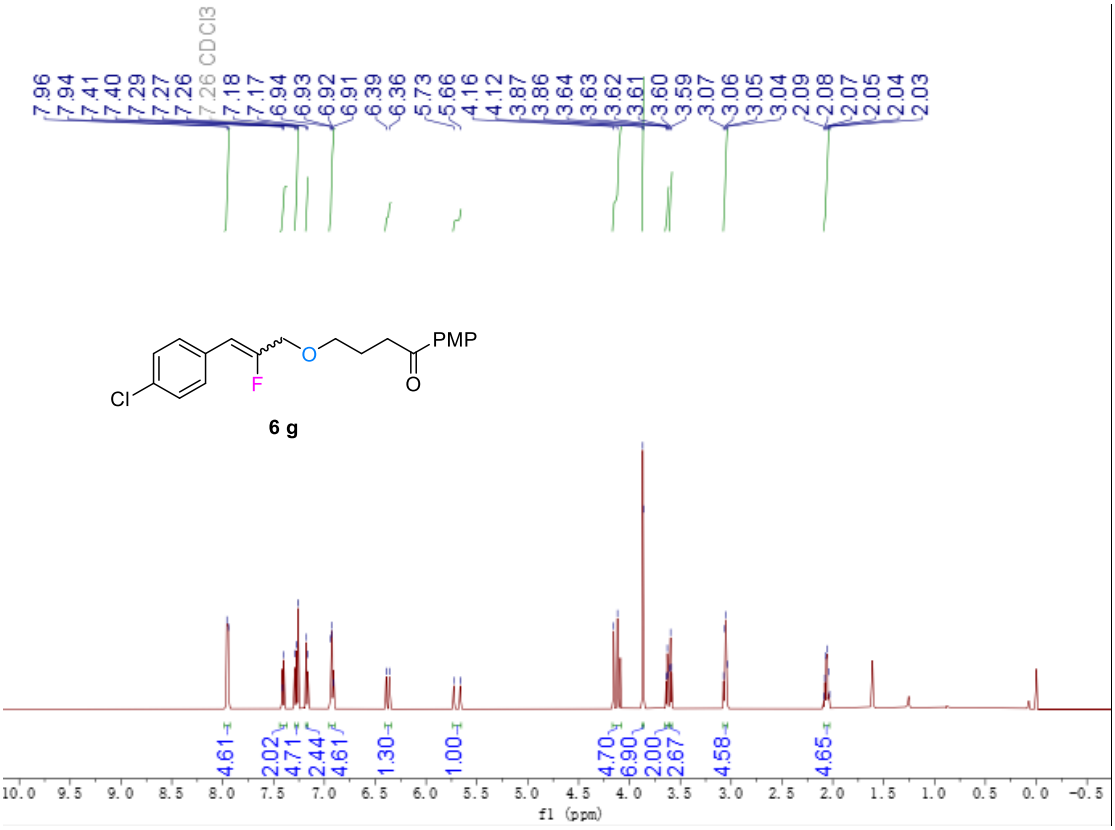
-108.82
PMP
O
F
Cl
6 f
f1 (ppm)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2.04
2.03
PMP
O
F
Cl
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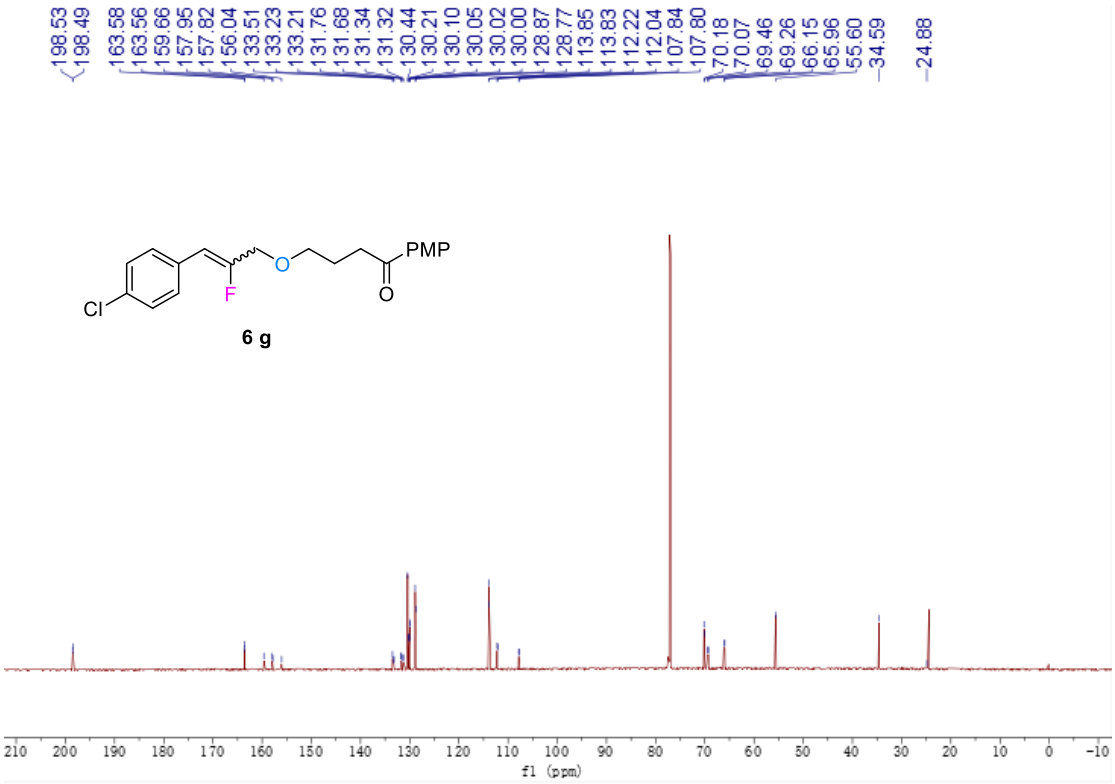
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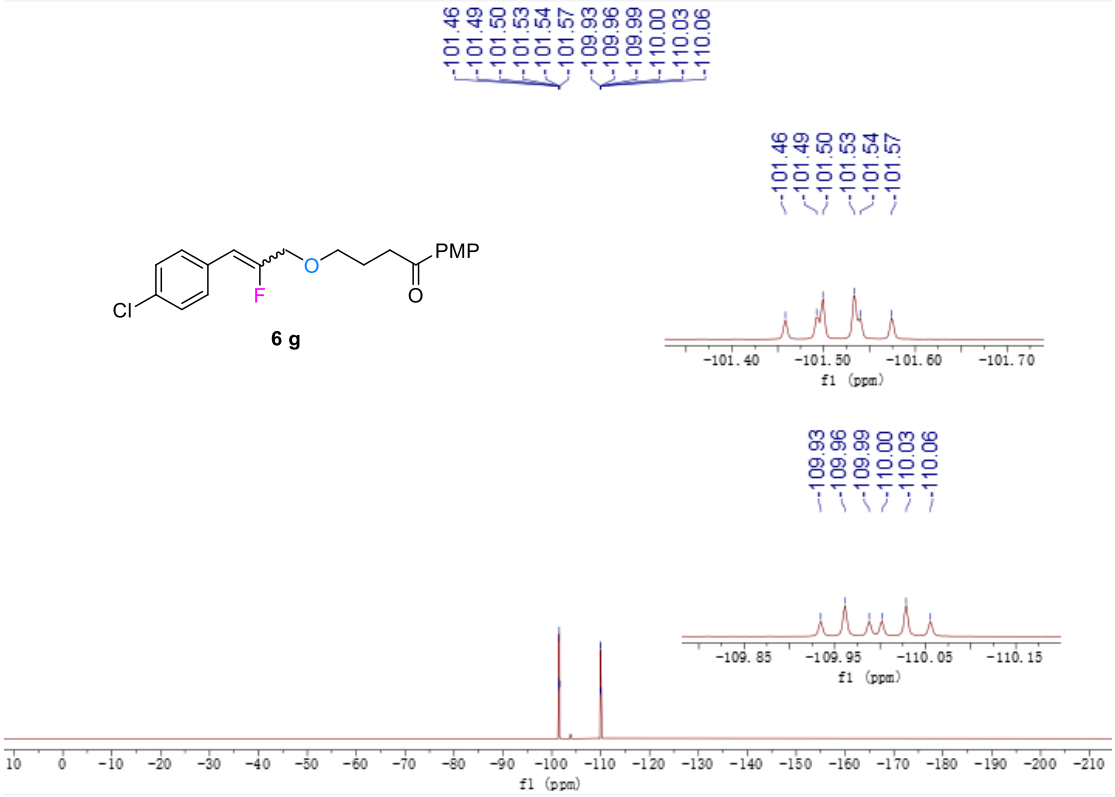
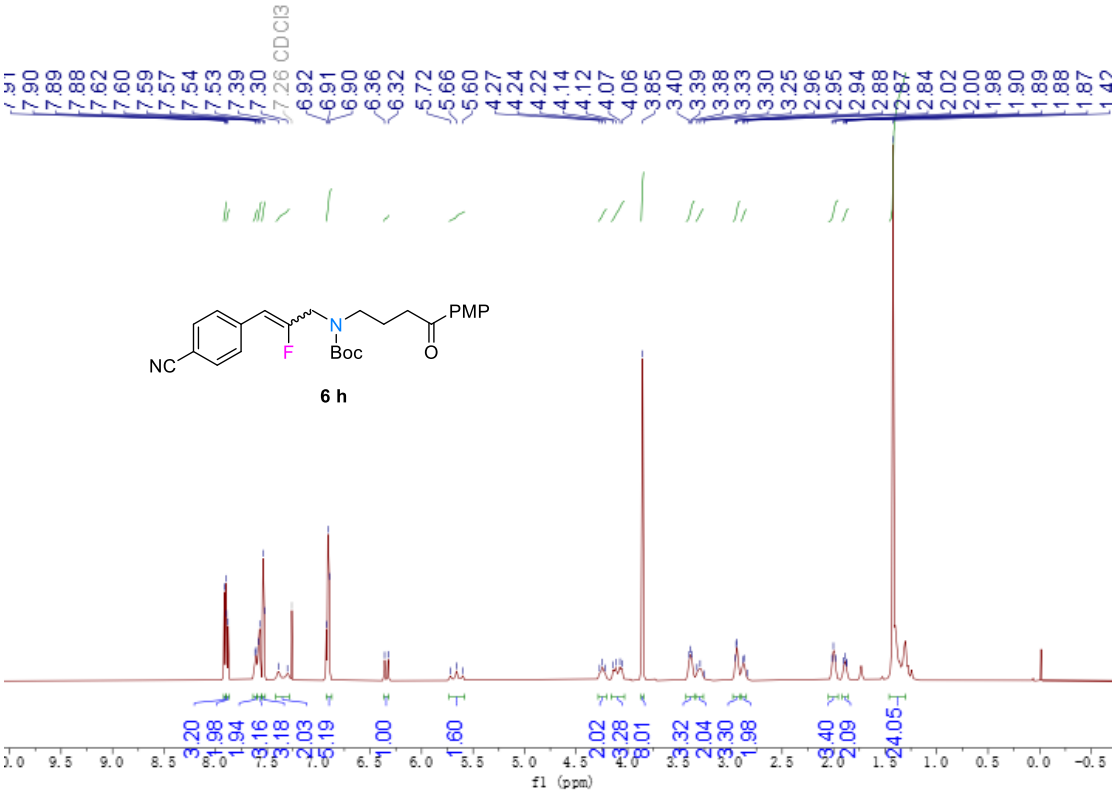
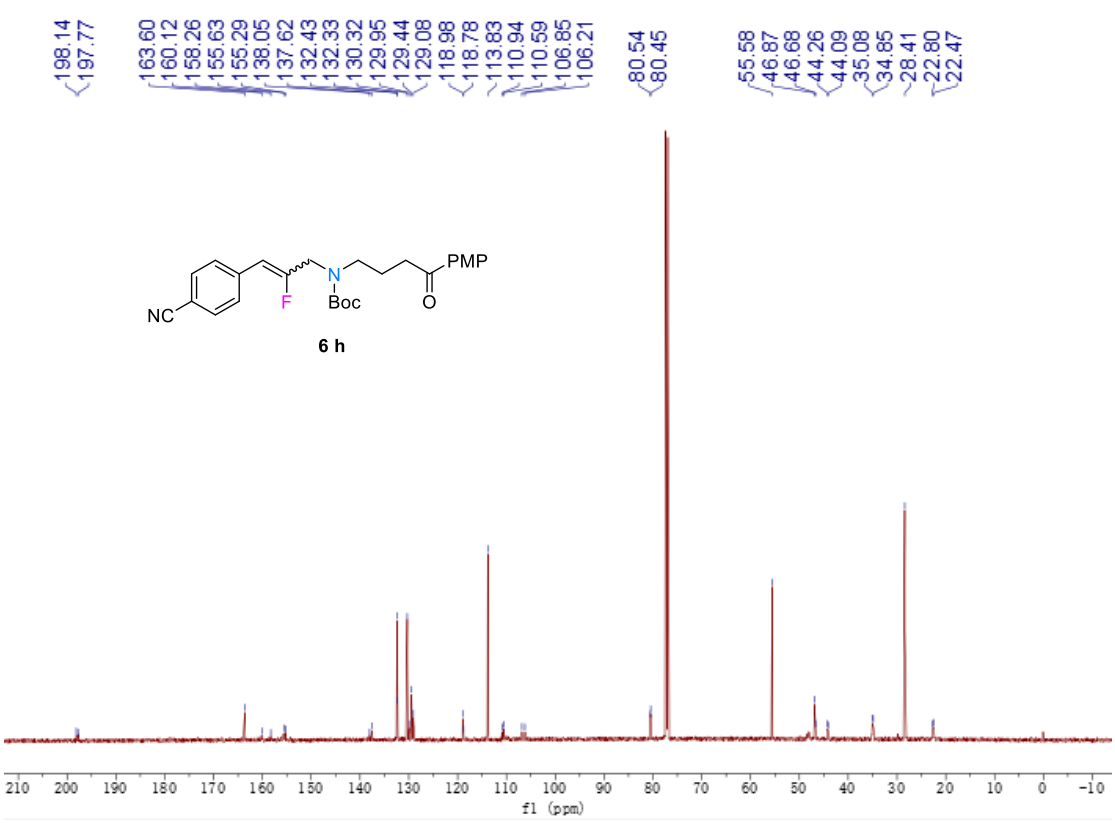
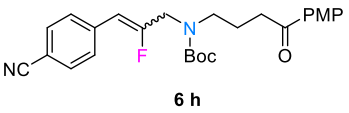
131.32
130.44
130.21
130.10
130.05
130.02
130.00
128.87
128.77
113.85
113.83
112.22
112.04
107.84
107.80
70.18
70.07
69.46
69.26
66.15
65.96
55.60
34.59
24.88
PMP
O
F
Cl
O
6 g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-101.46
-101.49
-101.50
-101.53
-101.54
-101.57
-109.93
-109.96
-109.99
-110.00
-110.03
-110.06
PMP
O
F
Cl
O
6 g
-101.40 -101.50 -101.60 -101.70
f1 (ppm)
-109.85 -109.95 -110.05 -110.15
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

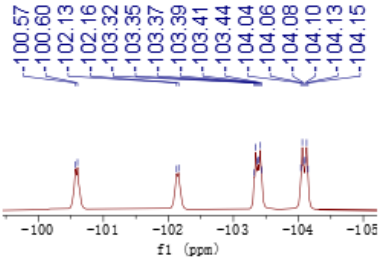

7.26 CDCl3
PMP
N
Boc
F
NC
O
6 h
fl (ppm)


PMP
N
Boc
F
NC
O
6 h
fl (ppm)


-100.57
-100.60
-102.13
-102.16
-103.32
-103.35
-103.37
-103.39
-103.41
-103.44
-104.04
-104.06
-104.08
-104.10
-104.13
-104.15


NC
F
N
Boc
PMP
O

6 h


-100.57
-100.60
-102.13
-102.16
-103.32
-103.35
-103.37
-103.39
-103.41
-103.44
-104.04
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-104.13
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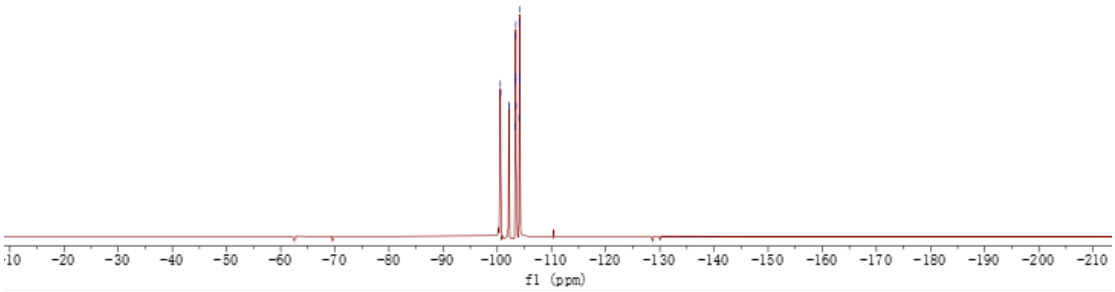
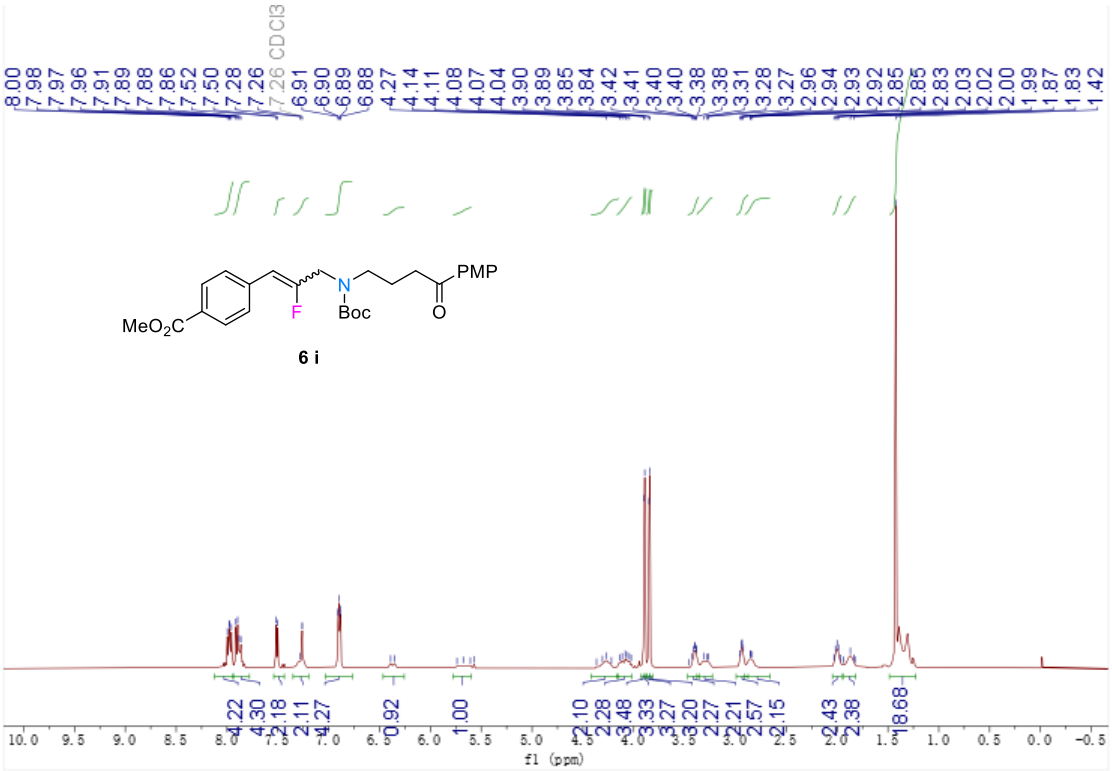
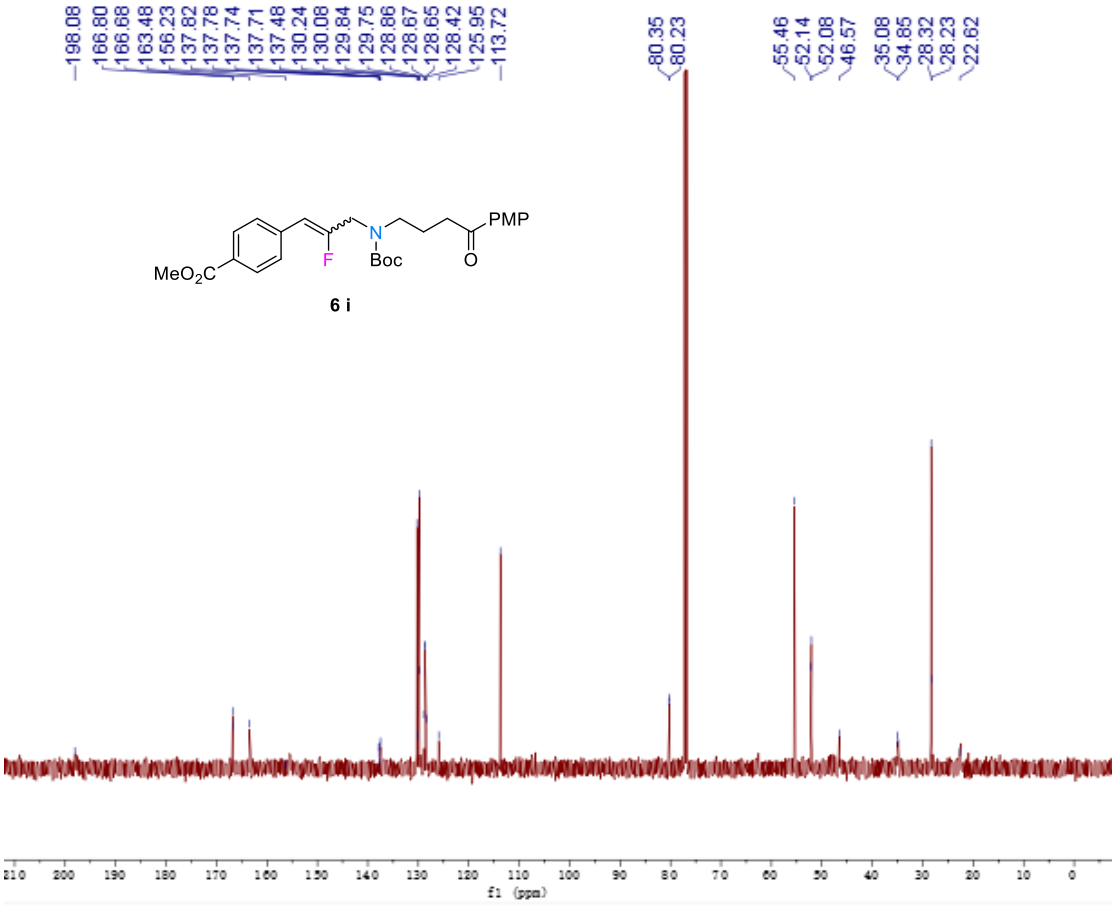
-100
-101
-102
-103
-104
-105
f1 (ppm)

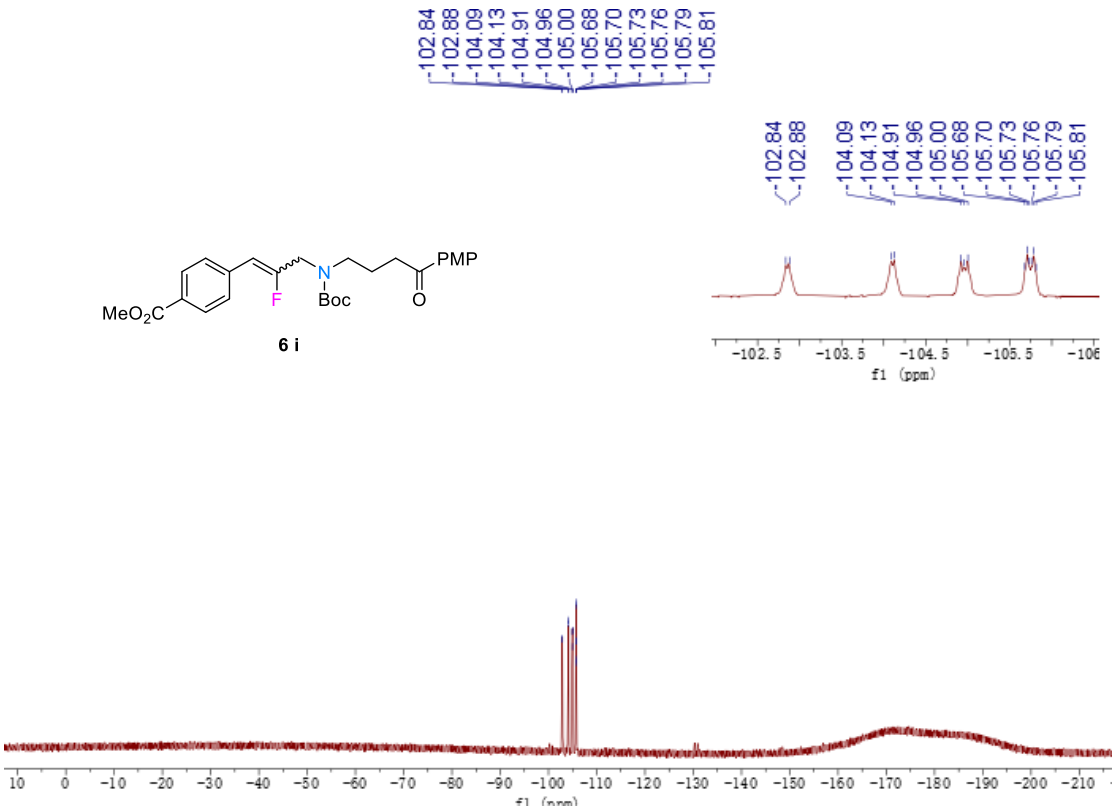

-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


8.00
7.98
7.97
7.96
7.91
7.89
7.88
7.86
7.52
7.50
7.28
7.26
7.26 CDCl3
6.91
6.90
6.89
6.88
4.27
4.14
4.11
4.08
4.07
4.04
3.90
3.89
3.85
3.84
3.42
3.41
3.40
3.40
3.38
3.31
3.28
3.27
2.96
2.94
2.93
2.92
2.85
2.85
2.83
2.03
2.02
2.00
1.99
1.87
1.83
1.42
MeO2C
F
N
Boc
PMP
O
4.22
4.30
2.18
2.11
4.27
0.92
1.00
2.10
2.28
3.48
3.33
3.27
3.20
2.27
2.21
2.57
2.15
2.43
2.38
18.68
f1 (ppm)

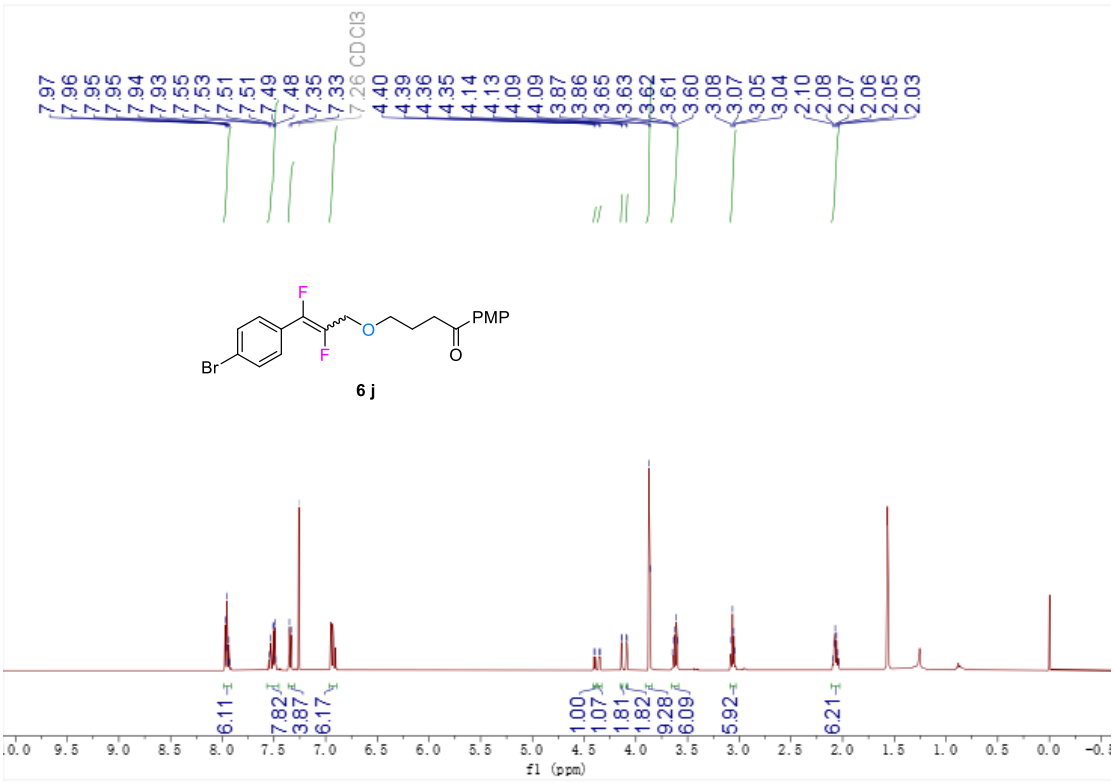
6 i

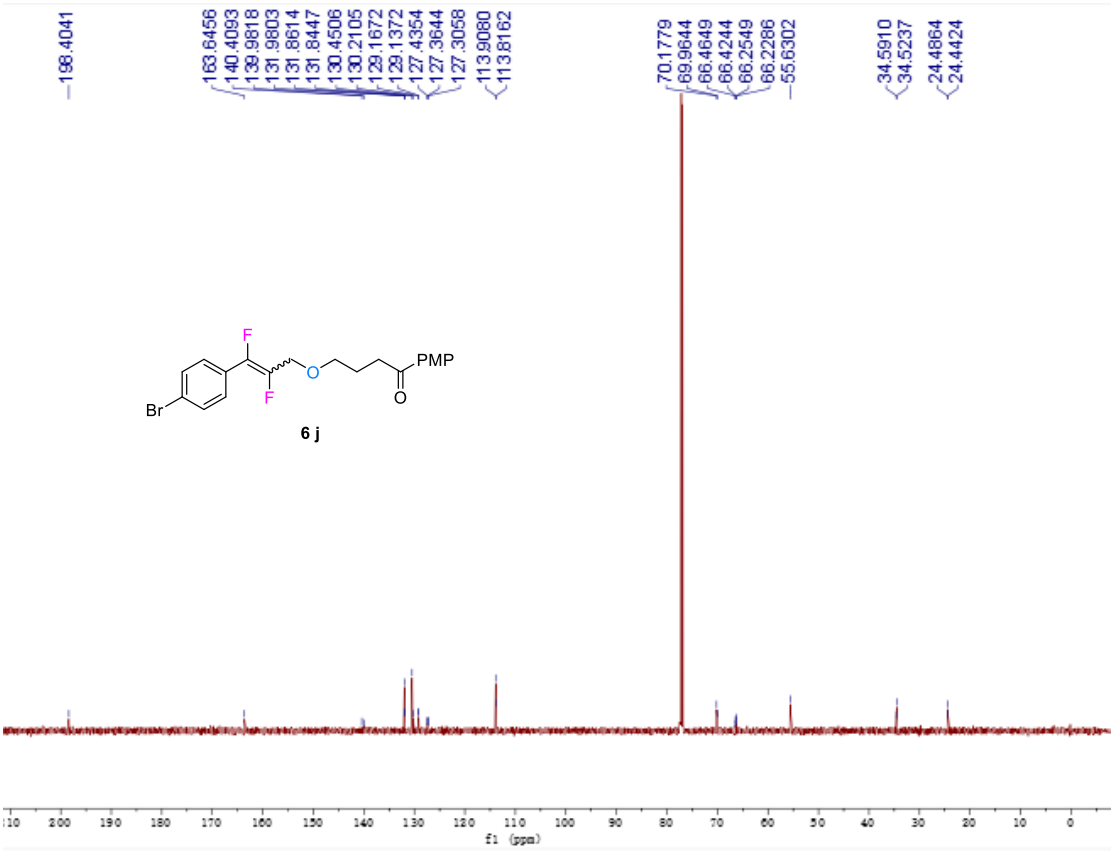

198.08
166.80
166.68
163.48
156.23
137.82
137.78
137.74
137.71
137.48
130.24
130.08
129.84
129.75
128.86
128.67
128.65
128.42
125.95
113.72
80.35
80.23
55.46
52.14
52.08
46.57
35.08
34.85
28.32
28.23
22.62
PMP
N
Boc
O
F
MeO2C
f1 (ppm)

6 i


102.84
102.88
104.09
104.13
104.91
104.96
105.00
105.68
105.70
105.73
105.76
105.79
105.81
PMP
N
Boc
O
F
MeO2C
f1 (ppm)

6 i


7.97
7.96
7.95
7.95
7.94
7.93
7.55
7.53
7.51
7.51
7.49
7.48
7.35
7.33
CDCl3
4.40
4.39
4.36
4.35
4.14
4.13
4.09
4.09
3.87
3.86
3.65
3.63
3.62
3.61
3.60
3.08
3.07
3.05
3.04
2.10
2.08
2.07
2.06
2.05
2.03
F
O
F
PMP
O
Br
6 j
6.11
7.82
3.87
6.17
1.00
1.07
1.81
1.82
9.28
6.09
5.92
6.21
f1 (ppm)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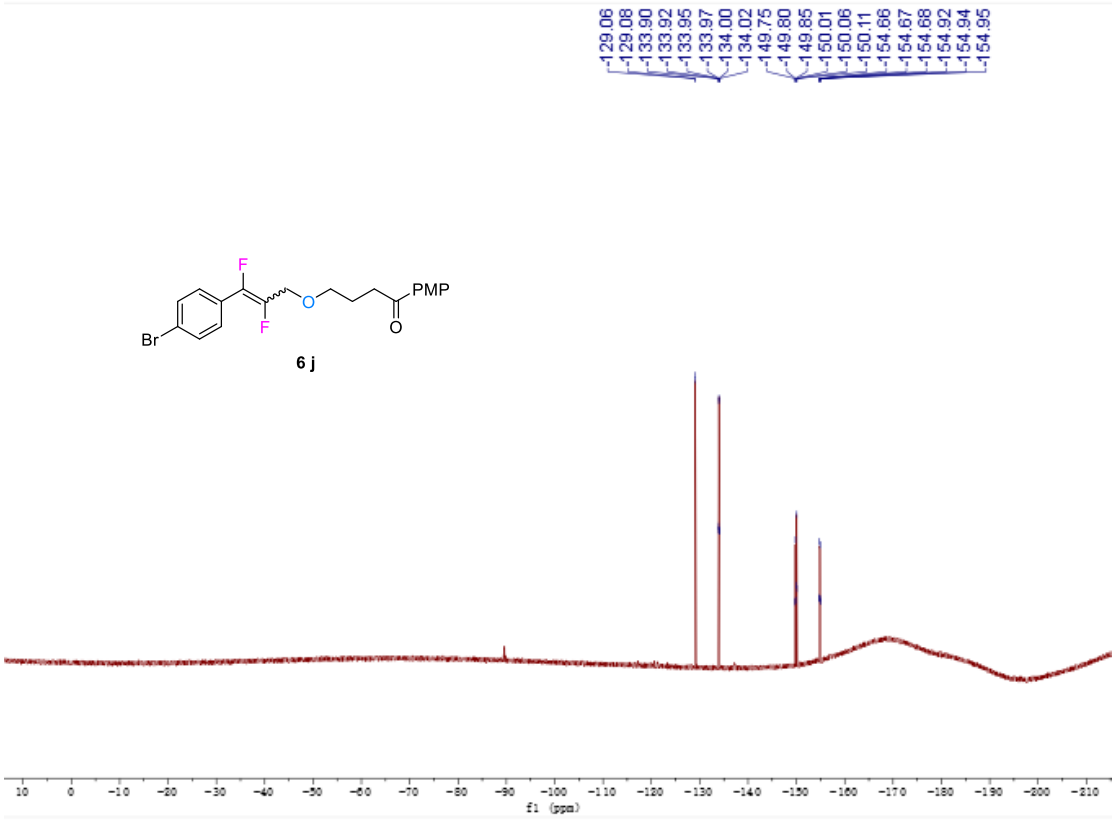
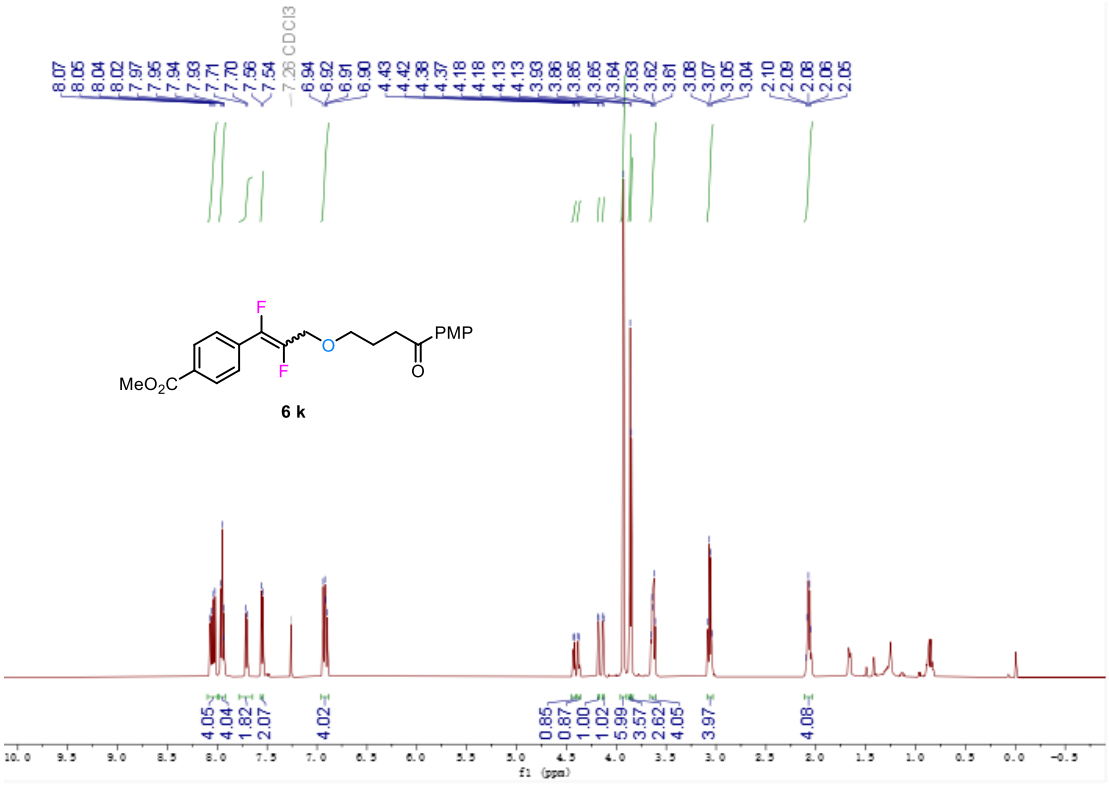
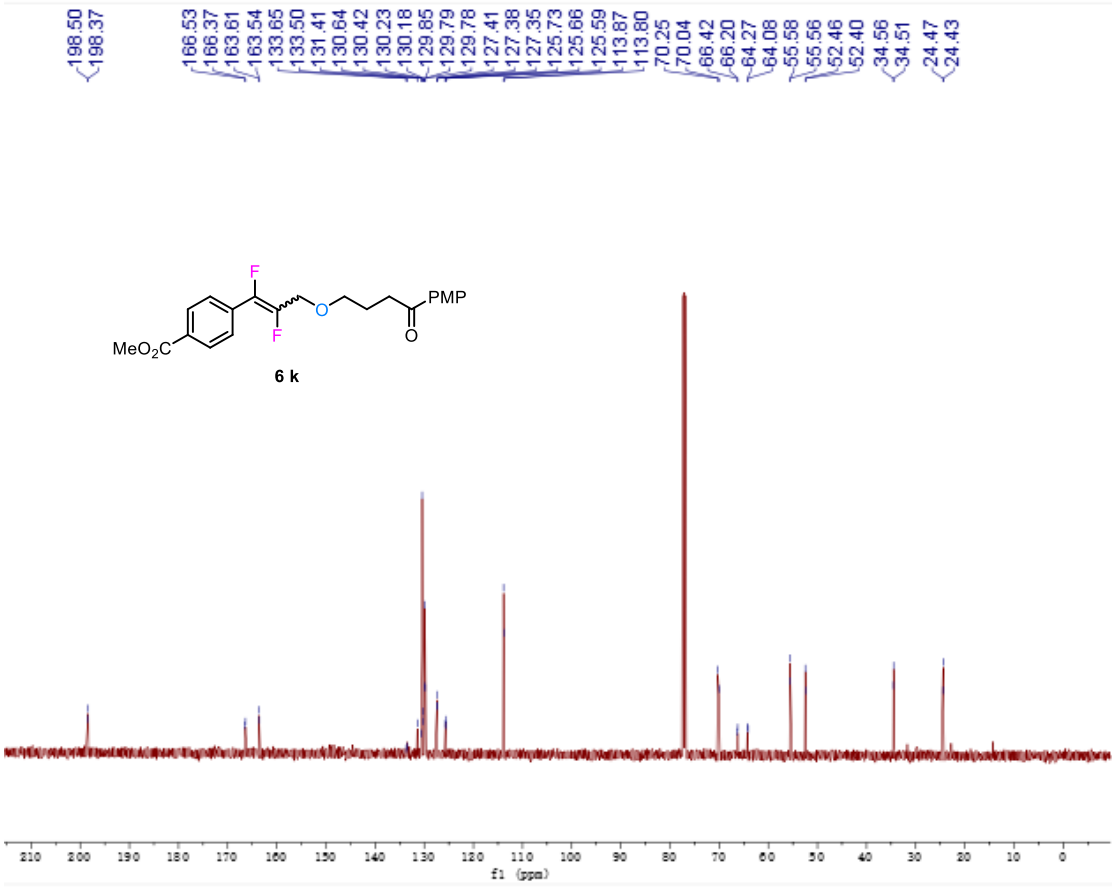
140.4093
139.9818
131.9803
131.8614
131.8447
130.4506
130.2105
129.1672
129.1372
127.4354
127.3644
127.3058
113.9080
113.8162
70.1779
69.9644
66.4649
66.4244
66.2549
66.2286
55.6302
34.5910
34.5237
24.4864
24.4424
F
O
F
PMP
O
Br
6 j
f1 (ppm)

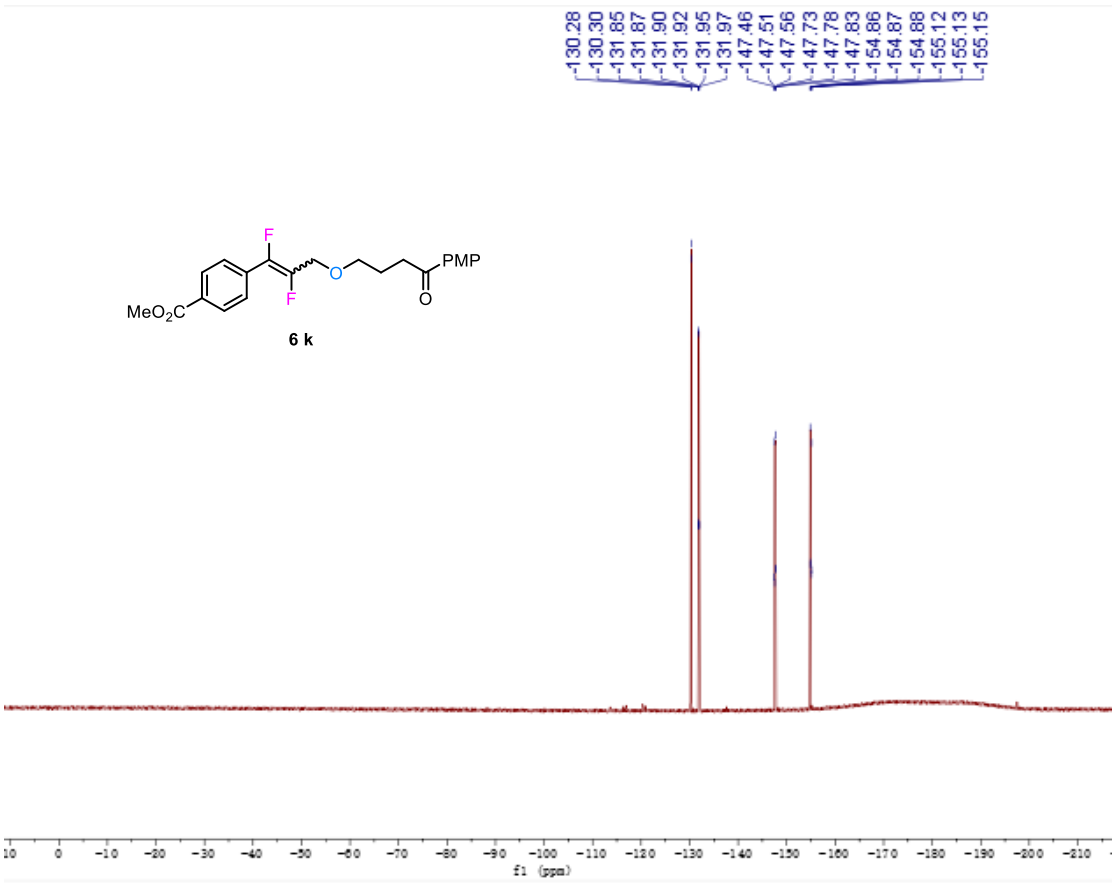

-129.06
-129.08
-133.90
-133.92
-133.95
-133.97
-134.00
-134.02
-149.75
-149.80
-149.85
-150.01
-150.06
-150.11
-154.66
-154.67
-154.68
-154.92
-154.94
-154.95
F
O
F
PMP
O
Br
f1 (ppm)

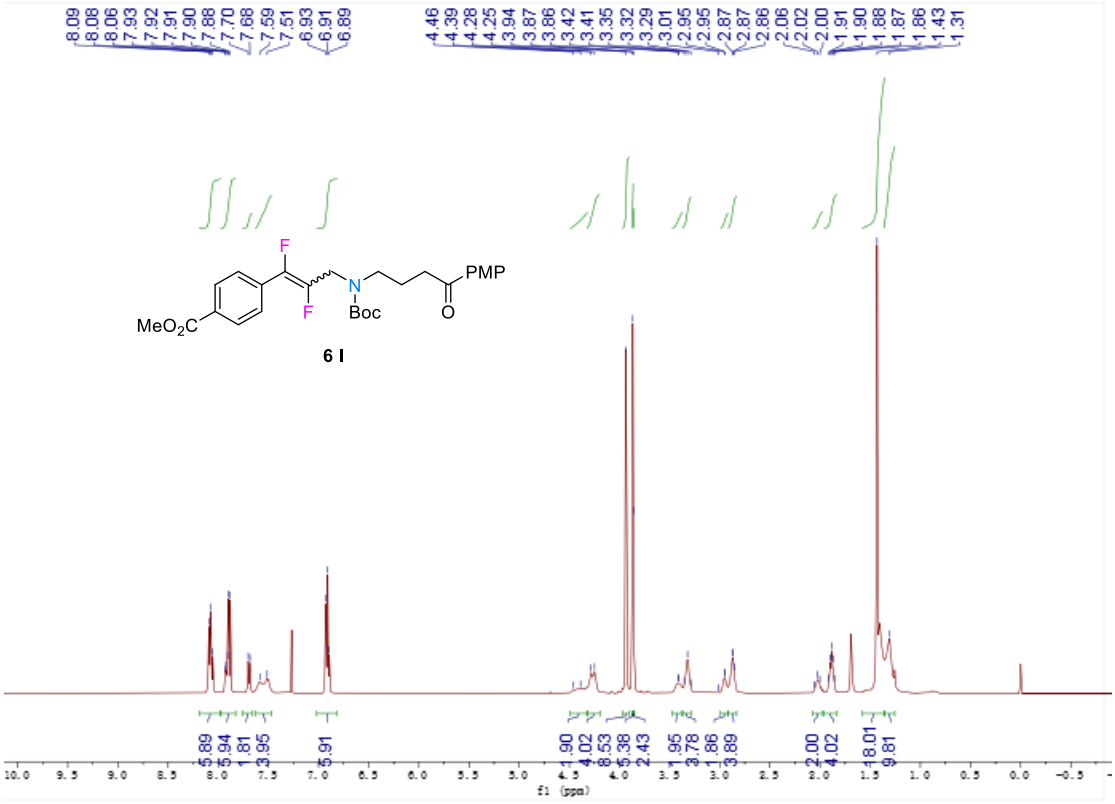
6 j


8.07
8.05
8.04
8.02
7.97
7.95
7.94
7.93
7.71
7.70
7.56
7.54
7.26 CDCl3
6.94
6.92
6.91
6.90
4.43
4.42
4.38
4.37
4.18
4.18
4.13
4.13
3.93
3.86
3.85
3.65
3.64
3.63
3.62
3.61
3.08
3.07
3.05
3.04
2.10
2.09
2.08
2.06
2.05
F
O
F
PMP
O
MeO2C
4.05
4.04
1.82
2.07
4.02
0.85
0.87
1.00
1.02
5.99
3.57
2.62
4.05
3.97
4.08
f1 (ppm)

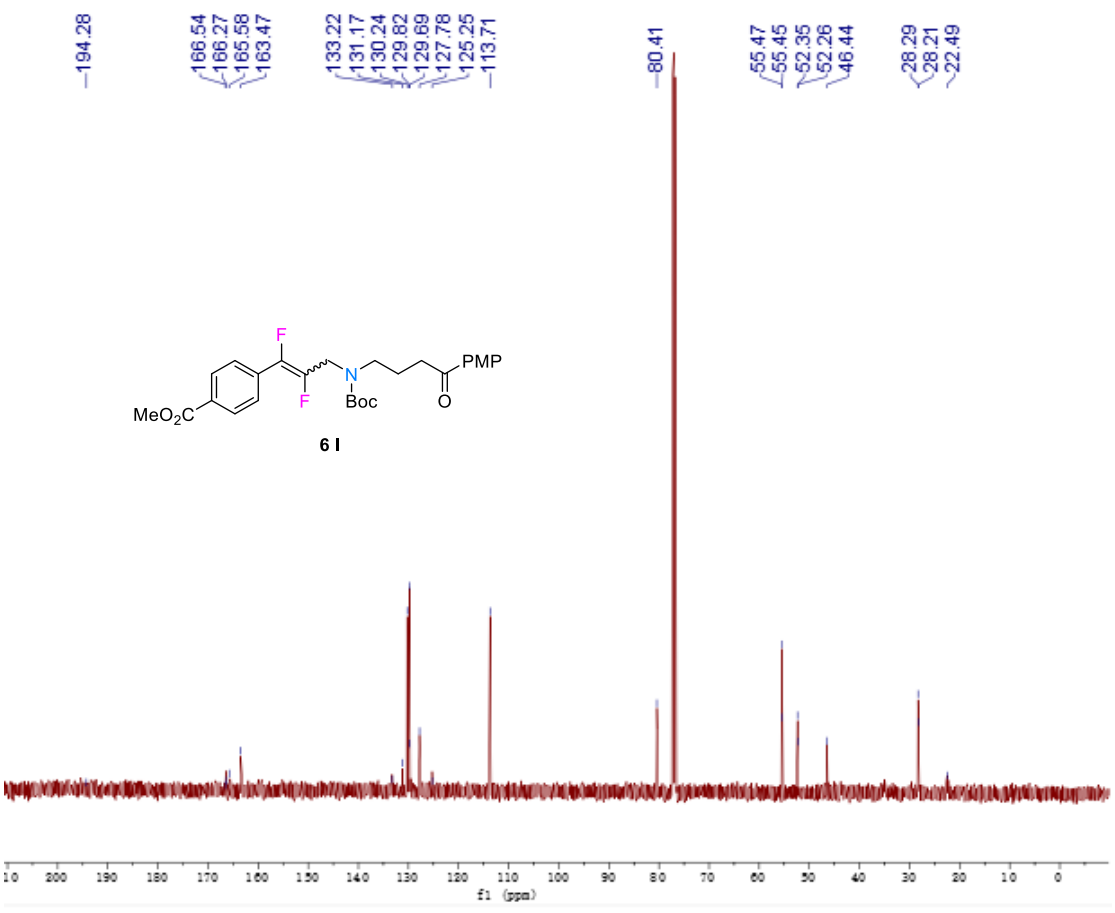
6 k


198.50
198.37
166.53
166.37
163.61
163.54
133.65
133.50
131.41
130.64
130.42
130.23
130.18
129.85
129.79
129.78
127.41
127.38
127.35
125.73
125.66
125.59
113.87
113.80
70.25
70.04
66.42
66.20
64.27
64.08
55.58
55.56
52.46
52.40
34.56
34.51
24.47
24.43
F
O
F
PMP
O
MeO2C
6 k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-130.28
-130.30
-131.85
-131.87
-131.90
-131.92
-131.95
-131.97
-147.46
-147.51
-147.56
-147.73
-147.78
-147.83
-154.86
-154.87
-154.88
-155.12
-155.13
-155.15
F
O
F
PMP
O
MeO2C
6 k
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

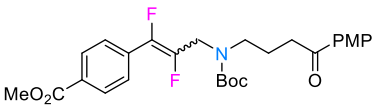


6 l

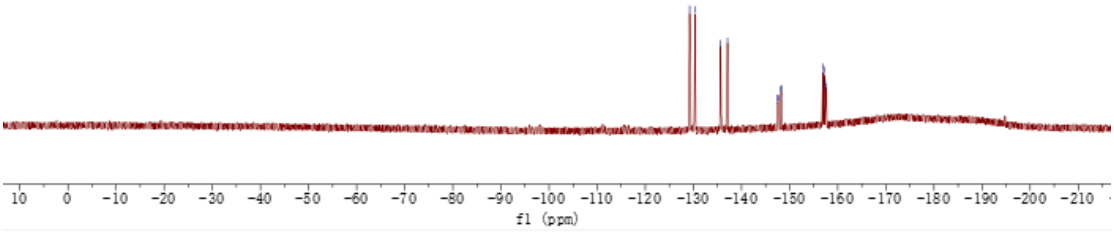


6 l


129.21
130.33
135.67
137.09
147.46
147.73
148.10
148.36
156.89
157.15
157.40
157.66


F
N
PMP
F
Boc
O
MeO2C

6 l


10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)