Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Stereoselective synthesis of fluoroalkylated (*Z*)-alkene via nickel-catalyzed and iron-mediated hydrofluoroalkylation of alkynes

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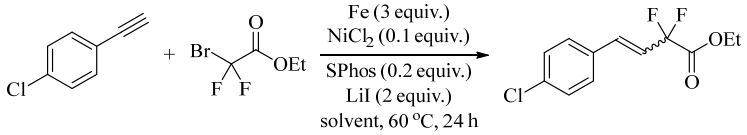
General information

Analytical thin layer chromatography (TLC) was performed using silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm). Flash chromatography was performed using Merck silica gel (200-300 mesh) for column chromatography with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use. IR spectra were recorded on a FT-IR spectrophotometer using KBr optics. ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker Avance or Jeol 400 MHz spectrometers. Tetramethylsilane (TMS) served as internal standard for ^{1}H, ^{19}F, and ^{13}C NMR analysis. High resolution mass spectra (HRMS) were obtained using a commercial apparatus (ESI or EI Source).

Optimization of reaction conditions

Table S1. Optimization of Reaction Conditions by Using Different Solvents[a]

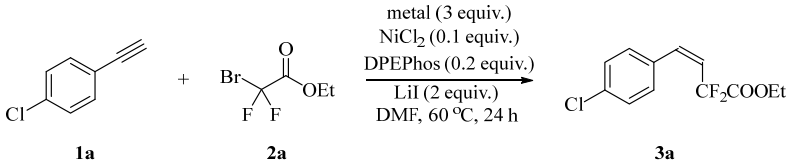


1a **2a** **3a**

entry	solvent	yield (%)[b]
1	MeCN	trace
2	DMA	72[c]
3	Toluene	trace
4	**DMF**	**77[c]**
5	DMSO	46[c]
6	1,4-dioxane	21[c]
7	DCE	15[c]

[a] The reactions were performed at 60 °C for 24 h by using alkyne **1a** (0.5 mmol), ethyl 2-bromo-2,2-difluoroacetate (**2a**, 1.5 mmol), Fe (1.5 mmol), $NiCl_2$ (0.1 equiv.), SPhos (0.2 equiv.), and LiI (2 equiv.) in solvent (2 mL). [b] Yields were determined by NMR analysis of crude reaction mixture after work-up by using 1,4-dimethoxybenzene as an internal standard. [c] *Z*/*E* = 70:30.

Table S2. Optimization of Reaction Conditions by Using Different Metals[a]



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

entry	metal	yield (%)[b]
1	In	10
2	Cr	trace
3	Mn	trace
4	Zn	23
5	Mg	trace
6	**Fe**	**86**

[a] Unless otherwise noted, the reactions were performed at 100 °C for 24 h by using 1-chloro-4-ethynylbenzene (**1a**, 1 mmol), ethyl 2-bromo-2,2-difluoroacetate (**2a**, 3 mmol), metal (3 mmol), $NiCl_2$ (0.1 equiv.), DPEPhos (0.2 equiv.), and LiI (2 equiv.) in DMF (2 mL). [b] Yields were determined by NMR analysis of crude reaction mixture after work-up by using 1,4-dimethoxybenzene as an internal standard.

Tentatively proposed reaction mechanism

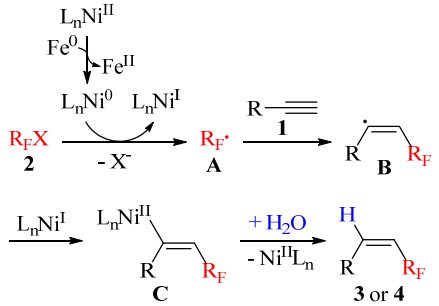
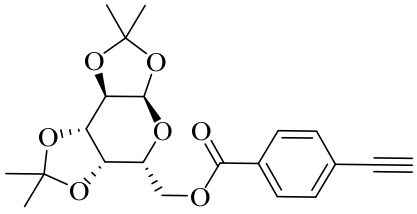
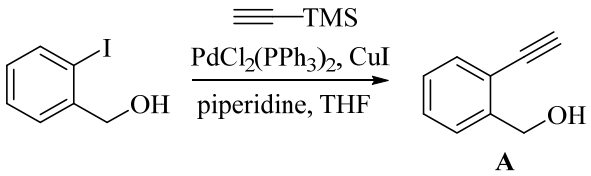


Figure S1. Tentatively proposed preliminary reaction mechanism.

Synthesis of starting materials

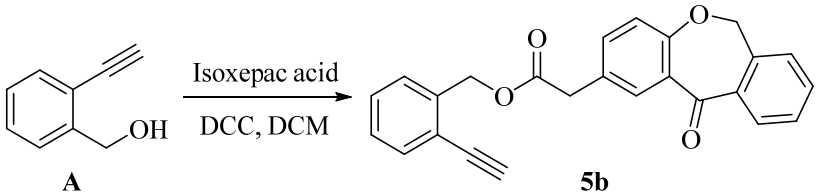


((3*aR*,5*R*,5*aS*,8*aS*,8*bR*)-2,2,7,7-Tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methanol (5a): This compound was synthesized according to the described procedure by using 1,2:3,4-di-*O*-isopropylidene-*D*-galactopyranose (828 mg, 3.18 mmol) and 4-ethynylbenzoic acid (520 mg, 3.56 mmol).[2] White solid, 1.07 g, 87% yield. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.00 (d, *J* = 8.6 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 5.57 (d, *J* = 5.0 Hz, 1H), 4.65 (dd, *J* = 7.9, 2.5 Hz, 1H), 4.53 (dd, *J* = 11.6, 4.8 Hz, 1H), 4.43 (dd, *J* = 11.5, 7.6 Hz, 1H), 4.35 (dd, *J* = 5.0, 2.5 Hz, 1H), 4.32 (dd, *J* = 7.8, 1.9 Hz, 1H), 4.17 (ddd, *J* = 7.1, 4.8, 2.0 Hz, 1H), 3.23 (s, 1H), 1.51 (s, 3H), 1.47 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 165.7, 132.0, 129.9, 129.5, 126.8, 109.7, 108.8, 96.3, 82.8, 80.1, 71.1, 70.6, 70.4, 66.0, 64.1, 26.0, 25.9, 24.9, 24.4 ppm.



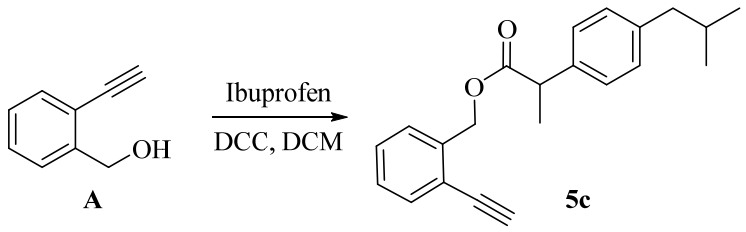
A

(2-Ethynylphenyl)methanol (**A**): This compound was synthesized according to the described procedure by using (2-iodophenyl)methanol and ethynyltrimethylsilane.[3]



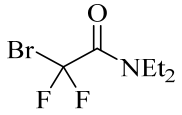
A **5b**

2-Ethynylbenzyl 2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl) acetate (5b): This compound was synthesized according to the described procedure by using Isoxepac acid (805 mg, 3.0 mmol), (2-ethynylphenyl)methanol (396 mg, 3.0 mmol), DCC (929 mg, 4.5 mmol) and DMAP (37 mg, 0.3 mmol) in DCM (10 mL) at rt for 6 h.[4] White solid, 975 mg, 85% yield. **^{1}H NMR (400 MHz, $CDCl_3$):** 8.14 (d, *J* = 2.3 Hz, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.58–7.44 (m, 4H), 7.38–7.34 (m, 3H), 7.33–7.27 (m, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 5.32 (s, 2H), 5.19 (s, 2H), 3.72(s, 2H), 3.31(s, 1H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 190.9, 171.2, 160.5, 140.4, 137.8, 136.4, 135.5, 132.9, 132.8, 132.5, 129.4, 129.3, 129.0, 128.3, 128.1, 127.8, 127.6, 125.1, 121.5, 121.0, 82.3, 80.7, 73.6, 65.0, 40.1 ppm.

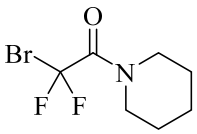


A **5c**

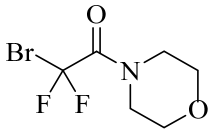
2-Ethynylbenzyl 2-(4-isobutylphenyl) propanoate (5c): This compound was synthesized according to the described procedure by using Ibuprofen acid (619 mg, 3.0 mmol), (2-ethynylphenyl)methanol (396 mg, 3.0 mmol), DCC (929 mg, 4.5 mmol) and DMAP (37 mg, 0.3 mmol) in DCM (10 mL) at rt for 6 h.[4] White solid, 874 mg, 91% yield. **^{1}H NMR (400 MHz, $CDCl_3$):** 7.50–7.46 (m, 1H), 7.26–7.21 (m, 4H), 7.19–7.15 (m, 1H), 7.11–7.08 (m, 2H), 5.28 (s, 2H), 3.79 (q, *J* = 7.2 Hz, 1H), 3.21 (s, 1H), 2.45 (d, *J* = 7.1 Hz, 2H), 1.84 (dt, *J* = 13.6, 6.8 Hz, 1H), 1.53 (d, *J* = 7.1 Hz, 3H), 0.91 (s, 3H), 0.89 (s, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 174.4, 140.6, 138.3, 137.5, 132.7, 129.3, 128.9, 127.7, 127.5, 127.3, 121.0, 82.2, 80.7, 64.6, 45.1, 45.0, 30.2, 22.4, 18.4 ppm.



2-Bromo-*N*,*N*-diethyl-2,2-difluoroacetamide (2b): This compound was synthesized using ethyl 2-bromo-2,2-difluoroacetate and diethylamine according to the described procedure.[5] Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 3.52 (qt, *J* = 7.1, 1.6 Hz, 2H), 3.42 (q, *J* = 7.1 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 158.6 (t, *J* = 26.2 Hz), 111.1 (t, *J* = 314.6 Hz), 42.8 (t, *J* = 3.8 Hz), 42.0, 13.8, 11.8 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -54.33 (s, 2F) ppm.



2-Bromo-2,2-difluoro-1-(piperidin-1-yl)ethan-1-one (2c): This compound was synthesized using ethyl 2-bromo-2,2-difluoroacetate and piperidine according to the described procedure.[5] Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 3.63–3.60 (m, 4H), 1.72–1.61 (m, 6H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 157.8 (t, *J* = 27.3 Hz), 111.3 (t, *J* = 315.1 Hz), 47.9, 47.5 (t, *J* = 4.6 Hz), 26.4 (t, *J* = 1.6 Hz), 23.3 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -53.76 (s, 2F) ppm.



2-Bromo-2,2-difluoro-1-morpholinoethan-1-one (2d): This compound was synthesized using ethyl 2-bromo-2,2-difluoroacetate and morpholine according to the described procedure.[6] Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 3.77–3.68 (m, 8H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 157.6 (t, *J* = 26.4 Hz), 110.2 (t, *J* = 314.6 Hz), 66.3, 65.9, 47.1 (t, *J* = 4.0 Hz), 43.6 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -54.40 (s, 2F) ppm.

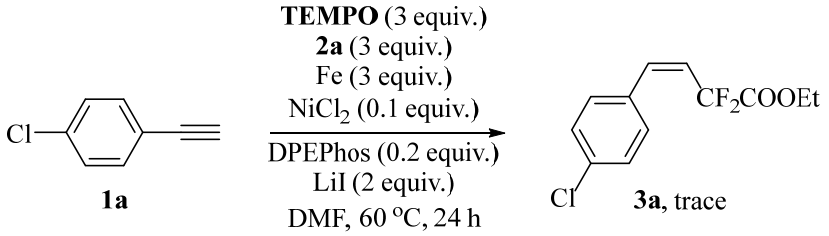
Experimental procedure

Typical procedures for the reaction for the synthesis of fluoroalkylated (*Z*)-alkene compounds

To a 10 mL Schlenk flask was added DMF (2 mL) and iron powder (168 mg, 3.0 mmol), and the iron powder was sequentially activated by using 1,2-dibromoethane (0.15 mmol) and TMSCl (0.15 mmol). After cooling down, alkyne (1.0 mmol), halofluoroacetate (or fluoroalkylated halides) (3.0 mmol), $NiCl_2$ (13 mg, 0.1 mmol), DPEPhos (108 mg, 0.2 mmol), and LiI (266 mg, 2.0 mmol) were added. The reaction mixture was vigorously stirred at 60 °C or 100 °C for 24 h under nitrogen atmosphere, followed by quenching with sat. NH_4Cl solution (20 mL) and extracting with ethyl acetate (20 mL x 3). The combined extracts were washed with brine (20 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Purification by silica gel column chromatography using ethyl acetate/petroleum ether as eluent gave the analytically pure product.

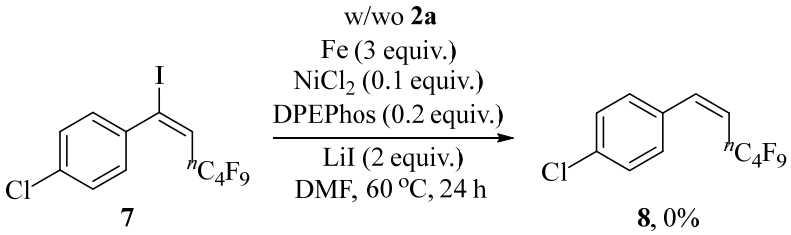
Control experiments

Scheme 4a:



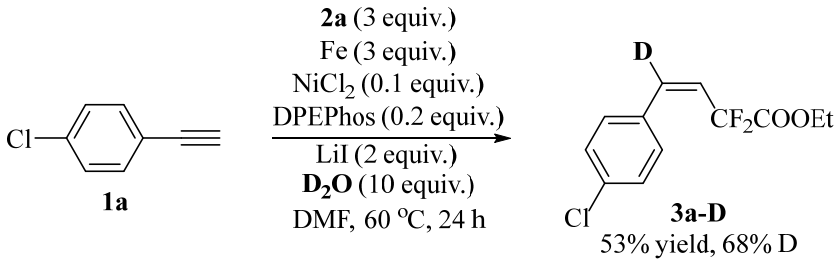
To a 10 mL Schlenk flask was added DMF (2 mL) and iron powder (168 mg, 3.0 mmol), and the iron powder was sequentially activated by using 1,2-dibromoethane (0.15 mmol) and TMSCl (0.15 mmol). After cooling down, alkyne **1a** (137 mg, 1.0 mmol), halofluoroacetate **2a** (609 mg, 3.0 mmol), $NiCl_2$ (13 mg, 0.1 mmol), DPEPhos (108 mg, 0.2 mmol), LiI (266 mg, 2.0 mmol), and TEMPO (469 mg, 3.0 mmol) were added. The reaction mixture was vigorously stirred at 60 °C for 24 h under nitrogen atmosphere, followed by quenching with sat. NH_4Cl solution (20 mL) and extracting with ethyl acetate (20 mL x 3). The combined extracts were washed with brine (20 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. TLC analysis and crude ^1H NMR analysis showed that almost no product **3a** was formed in the reaction.

Scheme 4b:



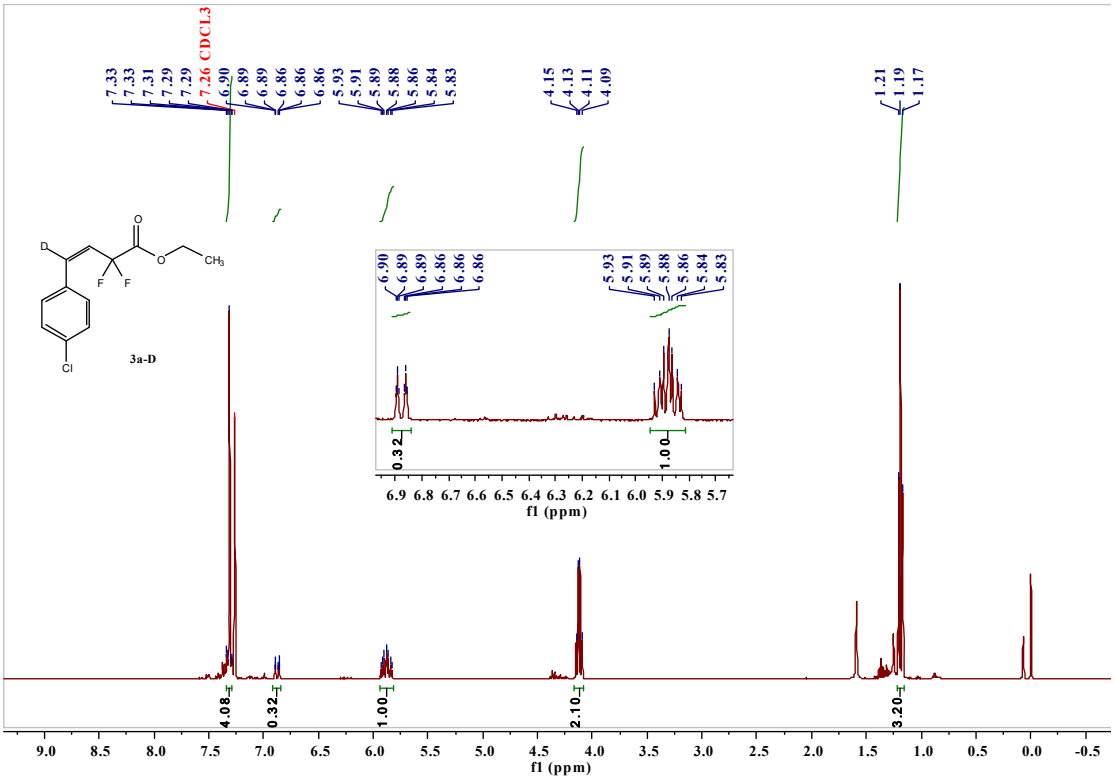
To a 10 mL Schlenk flask was added DMF (2 mL) and iron powder (168 mg, 3.0 mmol), and the iron powder was sequentially activated by using 1,2-dibromoethane (0.15 mmol) and TMSCl (0.15 mmol). After cooling down, alkenyl iodide **7** (483 mg, 1.0 mmol), $NiCl_2$ (13 mg, 0.1 mmol), DPEPhos (108 mg, 0.2 mmol), LiI (266 mg, 2.0 mmol), with or without halofluoroacetate **2a** (609 mg, 3.0 mmol), were added. The reaction mixture was vigorously stirred at 60 °C for 24 h under nitrogen atmosphere, followed by quenching with sat. NH_4Cl solution (20 mL) and extracting with ethyl acetate (20 mL x 3). The combined extracts were washed with brine (20 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Crude ^1H NMR analysis and further purification by silica gel column chromatography using ethyl acetate/petroleum ether as eluent showed that no desired product **8** was formed in the reaction.

Scheme 4c:

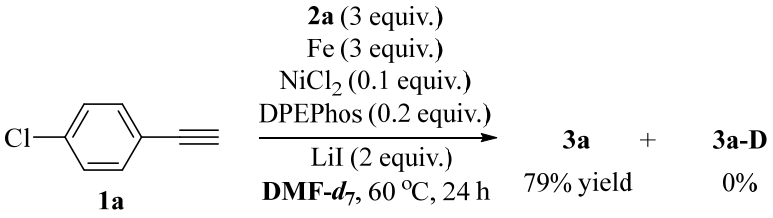


To a 10 mL Schlenk flask was added DMF (2 mL) and iron powder (168 mg, 3.0 mmol), and the iron powder was sequentially activated by using 1,2-dibromoethane (0.15 mmol) and TMSCl (0.15 mmol). After cooling down, alkyne **1a** (137 mg, 1.0 mmol), halofluoroacetate **2a** (609 mg, 3.0 mmol), $NiCl_2$ (13 mg, 0.1 mmol), DPEPhos (108 mg, 0.2 mmol), LiI (266 mg, 2.0 mmol), and D_2O (200 mg, 10.0 mmol) were added. The reaction mixture was vigorously stirred at 60 °C for 24 h under nitrogen atmosphere, followed by quenching with sat. NH_4Cl solution (20 mL) and extracting with ethyl acetate (20 mL x 3). The combined extracts were washed with brine (20 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Purification by silica gel column chromatography using ethyl acetate/petroleum ether as eluent gave the product **3a-D** (138.2 mg, 53% yield) with 68% deuteration.

^1H NMR spectrum of product **3a-D**:

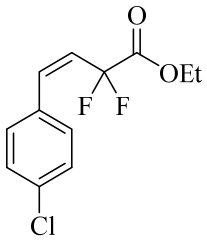


Scheme 4d:

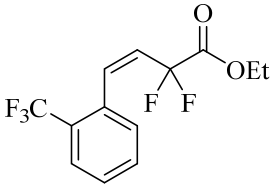


To a 10 mL Schlenk flask was added deuterated DMF-d_7 (2 mL) and iron powder (168 mg, 3.0 mmol), and the iron powder was sequentially activated by using 1,2-dibromoethane (0.15 mmol) and TMSCl (0.15 mmol). After cooling down, alkyne **1a** (137 mg, 1.0 mmol), halofluoroacetate **2a** (609 mg, 3.0 mmol), $NiCl_2$ (13 mg, 0.1 mmol), DPEPhos (108 mg, 0.2 mmol), and LiI (266 mg, 2.0 mmol) were added. The reaction mixture was vigorously stirred at 60 °C for 24 h under nitrogen atmosphere, followed by quenching with sat. NH_4Cl solution (20 mL) and extracting with ethyl acetate (20 mL x 3). The combined extracts were washed with brine (20 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Purification by silica gel column chromatography using ethyl acetate/petroleum ether as eluent gave the analytically pure product **3a** (205.9 mg, 79% yield); no any deuterated product **3a-D** was isolated in the reaction.

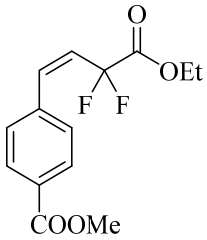
Characterization data of products



Ethyl (*Z*)-4-(4-chlorophenyl)-2,2-difluorobut-3-enoate (3a): 224.2 mg, 86% yield, colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.34–7.28 (m, 4H), 6.88 (dd, *J* = 12.6, 2.1 Hz, 1H), 5.88 (q, *J* = 13.3 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 1.19 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.3 (t, *J* = 33.8 Hz), 137.4 (t, *J* = 8.4 Hz), 134.7, 132.6–132.5 (m), 130.3 (t, *J* = 3.0 Hz), 128.4, 122.3 (t, *J* = 27.6 Hz), 112.1 (t, *J* = 245.6 Hz), 63.1, 13.6 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** *δ* -94.85 (s, 1F), -94.89 (s, 1F) ppm. **IR (KBr):** ν = 3411, 2985, 1768, 1493, 1153, 1094, 844 cm^{-1}. **HRMS (m/z):** calcd for $C_{12}H_{12}ClF_2O_2$ $[M+H]^+$ 261.0488, found: 261.0494.

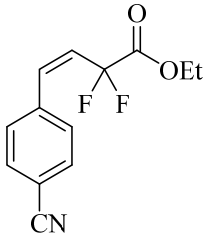


Ethyl (*Z*)-2,2-difluoro-4-(2-(trifluoromethyl)phenyl)but-3-enoate (3b): 203.0 mg, 69% yield, yellow oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.63–7.53 (m, 3H), 7.49 (d, *J* = 7.8 Hz, 1H), 6.96 (dt, *J* = 12.7, 2.1 Hz, 1H), 5.96 (q, *J* = 13.3 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.2 (t, *J* = 33.5 Hz), 137.1 (t, *J* = 8.2 Hz), 135.1 (t, *J* = 1.3 Hz), 132.2 (tt, *J* = 3.2, 1.5 Hz), 130.8, 130.5, 128.7, 125.6 (q, *J* = 4.2 Hz), 125.3 (q, *J* = 4.5 Hz), 123.5 (t, *J* = 27.5 Hz), 112.0 (t, *J* = 247.6 Hz), 63.2, 13.6 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -62.74 (s, 3F), -95.57 (d, *J* = 13.6 Hz, 2F) ppm. **IR (KBr):** ν = 3414, 2989, 1769, 1617, 1331, 1129, 700 cm^{-1}. **HRMS (m/z):** calcd for $C_{13}H_{12}F_5O_2$ $[M+H]^+$ 295.0752, found: 295.0757.

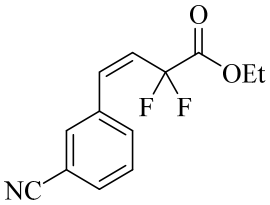


Methyl (*Z*)-3-(4-ethoxy-3,3-difluoro-4-oxobut-1-en-1-yl)benzoate (3c): 213.1 mg, 75% yield, colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.00 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 6.96 (dd, *J* = 12.6, 2.2 Hz, 1H), 5.95 (q, *J* = 13.1 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.91 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 166.5, 163.2 (t, *J* = 33.7 Hz), 138.7 (d, *J* = 1.7 Hz), 137.6 (t, *J* = 8.5 Hz), 130.0, 129.3, 128.8 (t, *J* = 3.1 Hz), 123.4 (t, *J* = 27.7 Hz), 112.0 (t, *J* = 274.1 Hz), 63.1,

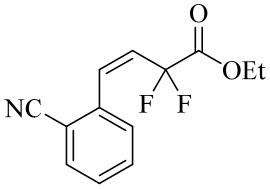
52.2, 13.6 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -94.98 (d, *J* = 1.5 Hz, 1F), -95.01 (d, *J* = 1.8 Hz, 1F) ppm. **IR (KBr):** ν = 3411, 1769, 1724, 1284, 1194, 1074, 777 cm^{-1}. **HRMS (m/z):** calcd for $C_{14}H_{15}F_2O_4$ $[M+H]^+$ 285.0933, found: 285.0938.



Ethyl (*Z*)-4-(4-cyanophenyl)-2,2-difluorobut-3-enoate (3d): 178.4 mg, 71% yield, colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 6.94 (dt, *J* = 12.8, 2.2 Hz, 1H), 5.99 (td, *J* = 13.7, 12.7 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.1 (t, *J* = 33.6 Hz), 138.7 (t, *J* = 1.4 Hz), 136.7 (t, *J* = 7.8 Hz), 131.8, 129.4 (t, *J* = 3.2 Hz), 124.1 (t, *J* = 27.1 Hz), 118.4, 112.1, 111.8 (t, *J* = 248.2 Hz), 63.2, 13.7 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -96.15 (s, 1F), -96.19 (s, 1F) ppm. **IR (KBr):** ν = 3414, 2987, 2230, 1767, 1308, 1075, 849 cm^{-1}. **HRMS (m/z):** calcd for $C_{13}H_{12}F_2NO_2$ $[M+H]^+$ 252.0831, found: 252.0836.

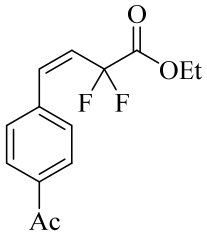


Ethyl (*Z*)-4-(3-cyanophenyl)-2,2-difluorobut-3-enoate (3e): 145.7 mg, 58% yield, colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.66–7.58 (m, 3H), 7.50–7.44 (m, 1H), 6.91 (dt, *J* = 12.6, 2.3 Hz, 1H), 5.97 (td, *J* = 13.8, 12.6 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.1 (t, *J* = 33.6 Hz), 136.2 (t, *J* = 7.5 Hz), 135.4 (t, *J* = 3.1 Hz), 133.1 (t, *J* = 3.1 Hz), 132.2 (t, *J* = 3.1 Hz), 131.9, 129.0, 123.8 (t, *J* = 27.0 Hz), 118.3, 112.3, 111.9 (t, *J* = 248.4 Hz), 63.3, 13.7 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -96.32 (s, 1F), -96.35 (s, 1F) ppm. **IR (KBr):** ν = 3413, 2988, 2232, 1766, 1306, 1075, 791 cm^{-1}. **HRMS (m/z):** calcd for $C_{13}H_{12}F_2NO_2$ $[M+H]^+$ 252.0831, found: 252.0836.

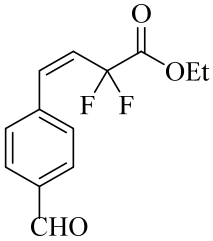


Ethyl (*Z*)-4-(2-cyanophenyl)-2,2-difluorobut-3-enoate (3f): 196.1 mg, 78% yield, colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.67 (d, *J* = 7.7 Hz, 1H), 7.62–7.50 (m, 2H), 7.46–7.40 (m, 1H), 7.12 (dt, *J* = 12.5, 2.2 Hz, 1H), 6.12 (td, *J* = 13.4, 12.5 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 162.9 (t, *J* = 33.6 Hz), 137.8 (t, *J* = 1.1 Hz), 134.5 (t, *J* = 7.7 Hz), 132.4, 132.4, 129.9 (t, *J* = 4.0 Hz), 128.8, 125.6 (t, *J* = 26.8 Hz), 117.2, 111.8 (t, *J* = 1.5 Hz), 111.7 (t, *J* =

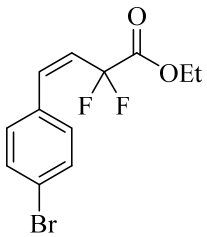
248.3 Hz), 63.3, 13.7 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -96.47 (s, 1F), -96.50 ((s, 1F) ppm. **IR (KBr):** ν = 3412, 2927, 2227, 1770, 1304, 1075, 769 cm^{-1}. **HRMS (m/z):** calcd for $C_{13}H_{12}F_2NO_2$ $[M+H]^+$ 252.0831, found: 252.0836.



Ethyl (*Z*)-4-(4-acetylphenyl)-2,2-difluorobut-3-enoate (3g): 144.8 mg, 54% yield, colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.93 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 6.96 (dd, *J* = 12.6, 2.1 Hz, 1H), 5.96 (td, *J* = 13.6, 12.6 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.60 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** 197.5, 163.2 (t, *J* = 33.7 Hz), 138.9 (t, *J* = 1.4 Hz), 137.5 (t, *J* = 8.3 Hz), 136.6, 129.1 (t, *J* = 3.1 Hz), 128.1, 123.4 (t, *J* = 27.4 Hz), 112.0 (t, *J* = 247.4 Hz), 63.1, 26.6, 13.7 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** -95.30 (s, 1F), -95.34 (s, 1F) ppm. **IR (KBr):** ν = 2986, 1767, 1685, 1268, 1154, 1075, 849 cm^{-1}. **HRMS (m/z):** calcd for $C_{14}H_{15}F_2O_3$ $[M+H]^+$ 269.0984, found: 269.0989.

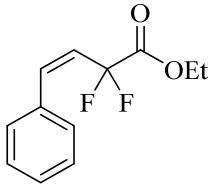


Ethyl (*Z*)-2,2-difluoro-4-(4-formylphenyl)but-3-enoate (3h): 139.4 mg, 55% yield, colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.02 (s, 1H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 6.99 (dd, *J* = 12.7, 2.1 Hz, 1H), 5.99 (q, *J* = 13.3 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 191.6, 163.2 (t, *J* = 33.6 Hz), 140.2, 137.3 (t, *J* = 8.0 Hz), 135.9, 129.5 (t, *J* = 3.0 Hz), 129.4, 123.8 (t, *J* = 27.3 Hz), 111.9 (t, *J* = 247.6 Hz), 63.1, 13.7 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -95.47 (s, 1F), -95.52 (s, 1F) ppm. **IR (KBr):** ν = 3412, 2987, 1768, 1703, 1308, 1074, 843 cm^{-1}. **HRMS (m/z):** calcd for $C_{13}H_{13}F_2O_3$ $[M+H]^+$ 255.0827, found: 255.0833.

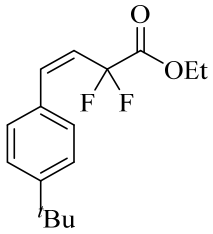


Ethyl (*Z*)-4-(4-bromophenyl)-2,2-difluorobut-3-enoate (3i): 188.5 mg, 62% yield, colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 6.86 (d, *J* = 12.7 Hz, 1H), 5.89 (q, *J* = 13.2 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H),

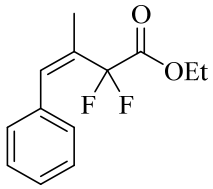
1.19 (t, J = 7.2 Hz, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.3 (t, J = 33.8 Hz), 137.5 (t, J = 8.5 Hz), 133.0 (t, J = 1.5 Hz), 131.3, 130.5 (t, J = 3.2 Hz), 123.0, 122.4 (t, J = 27.6 Hz), 112.1 (t, J = 246.9 Hz), 63.1, 13.7 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -94.93 (s, 1F), -94.96 (s, 1F) ppm. **IR (KBr):** ν = 3409, 2984, 1767, 1488, 1305, 1072, 1011 cm^{-1}. **HRMS (m/z):** calcd for $C_{12}H_{12}BrF_2O_2$ $[M+H]^+$ 304.9983, found: 304.9989.



Ethyl (*Z*)-2,2-difluoro-4-phenylbut-3-enoate (3j): 138.6 mg, 61% yield, colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.37-7.31 (m, 5H), 6.99–6.92 (m, 1H), 5.88 (q, J = 12.8 Hz, 1H), 4.03 (q, J = 7.1 Hz, 2H), 1.13 (t, J = 7.1 Hz, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.4 (t, J = 33.8 Hz), 138.7 (t, J = 9.1 Hz), 134.2 (t, J = 1.5 Hz), 128.9 (t, J = 3.0 Hz), 128.7, 128.2, 121.9 (t, J = 28.0 Hz), 112.2 (t, J = 245.8 Hz), 62.9, 13.6 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -93.75 (s, 1F), -93.79 (s, 1F) ppm. **IR (KBr):** ν = 3413, 2964, 1769, 1617, 1262, 1098, 802 cm^{-1}. **HRMS (m/z):** calcd for $C_{12}H_{13}F_2O_2$ $[M+H]^+$ 227.0878, found: 227.0884.

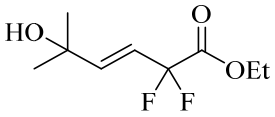


Ethyl (*Z*)-4-(4-(*tert*-butyl)phenyl)-2,2-difluorobut-3-enoate (3k): 231.5 mg, 82% yield, colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.41–7.35 (m, 2 H), 7.32–7.28 (m, 2 H), 6.91 (dt, J = 12.4, 1.9 Hz, 1 H), 5.83 (q, J = 13.1 Hz, 1 H), 4.02 (q, J = 7.2 Hz, 2 H), 1.31 (s, 9 H), 1.09 (t, J = 7.1 Hz, 3 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.5 (t, J = 33.8 Hz), 152.0, 138.6 (t, J = 9.0 Hz), 128.8 (t, J = 2.8 Hz), 127.2, 125.8, 125.1, 121.1 (t, J = 28.1 Hz), 115.4–109.6 (m), 62.9, 34.6, 31.1, 13.5 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -93.57, -93.60 ppm. **IR (KBr):** ν = 2964, 1770, 1365, 1304, 1074, 1018, 843 cm^{-1}. **HRMS (m/z):** calcd for $C_{16}H_{21}F_2O_2$ $[M+H]^+$ 283.1504, found: 283.1510.

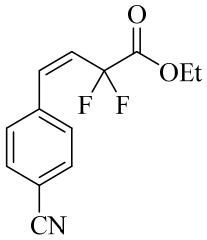


Ethyl (*Z*)-2,2-difluoro-3-methyl-4-phenylbut-3-enoate (3l): 175.3 mg, 73% yield, colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.39–7.27 (m, 3H), 7.22-7.21 (m, 2H), 6.83–6.80 (m, 1H), 3.87 (q, J = 7.1 Hz, 2H), 2.06 (d, J = 1.7 Hz, 3H), 1.11 (t, J = 7.2 Hz, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** 162.8 (t, J = 33.6 Hz), 142.7, 135.4 (t, J = 23.9 Hz), 128.7, 128.3 (t, J = 1.9 Hz), 127.8, 110.6 (t, J = 253.8 Hz), 109.0 (t, J = 7.4 Hz), 62.9, 25.3 (t, J = 4.0 Hz), 13.6 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -96.99 (s,

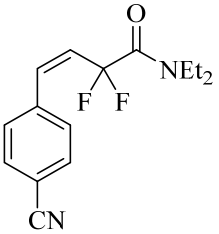
2F), ppm. **IR (KBr):** ν = 2985, 1771, 1371, 1243, 1125, 1051, 698 cm^{-1}. **HRMS (m/z):** calcd for $C_{13}H_{15}F_2O_2$ $[M+H]^+$ 241.1035, found: 241.1040.



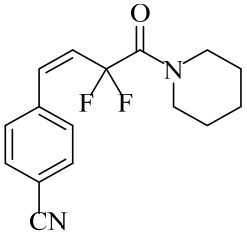
Ethyl (*E*)-2,2-difluoro-5-hydroxy-5-methylhex-3-enoate (3m): 89.5 mg, 43% yield, colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.37 (dt, *J* = 15.8, 2.4 Hz, 1H), 5.92 (dt, *J* = 15.9, 11.4 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.69 (brs, 1H), 1.37–1.33 (m, 9H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.9 (t, *J* = 34.7 Hz), 146.1 (t, *J* = 8.3 Hz), 118.0 (t, *J* = 25.1 Hz), 112.5 (t, *J* = 247.3), 70.6, 63.0, 29.4 (t, *J* = 1.6 Hz), 13.9 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -103.33 (s, 1F), -103.36 (s, 1F) ppm. **IR (KBr):** ν = 2980, 1767, 1374, 1274, 1227, 1081, 971 cm^{-1}. **HRMS (m/z):** calcd for $C_9H_{15}F_2O_3$ $[M+H]^+$ 209.0984, found: 209.0989.



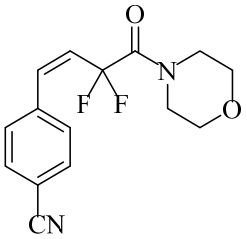
Ethyl (*Z*)-4-(4-cyanophenyl)-2,2-difluorobut-3-enoate (4a): 178.4 mg, 71% yield, colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 6.94 (dt, *J* = 12.8, 2.2 Hz, 1H), 5.99 (td, *J* = 13.7, 12.7 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.1 (t, *J* = 33.6 Hz), 138.7 (t, *J* = 1.4 Hz), 136.7 (t, *J* = 7.8 Hz), 131.8, 129.4 (t, *J* = 3.2 Hz), 124.1 (t, *J* = 27.1 Hz), 118.4, 112.1, 111.8 (t, *J* = 248.2 Hz), 63.2, 13.7 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -96.15 (s, 1F), -96.19 (s, 1F) ppm. **IR (KBr):** ν = 3414, 2987, 2230, 1767, 1308, 1075, 849 cm^{-1}. **HRMS (m/z):** calcd for $C_{13}H_{12}F_2NO_2$ $[M+H]^+$ 252.0831, found: 252.0836.



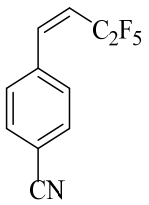
(*Z*)-4-(4-Cyanophenyl)-*N*,*N*-diethyl-2,2-difluorobut-3-enamide (4b): 108.5 mg, 39% yield, colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 6.88 (dt, *J* = 12.6, 2.5 Hz, 1H), 6.14 (td, *J* = 14.0, 12.8 Hz, 1H), 3.39 (q, *J* = 7.1 Hz, 2H), 3.30 (q, *J* = 7.1 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.7 (t, *J* = 29.8 Hz), 139.1 (t, *J* = 1.3 Hz), 135.0 (t, *J* = 7.8 Hz), 131.7, 129.6 (t, *J* = 3.2 Hz), 125.4 (t, *J* = 26.4 Hz), 118.5, 114.4 (t, *J* = 250.4 Hz), 111.8, 41.9 (t, *J* = 4.8 Hz), 41.3, 13.9, 12.0 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -90.57 (s, 1F), -90.62 (s, 1F) ppm. **IR (KBr):** ν = 2973, 2230, 1665, 1464, 1136, 1091, 863 cm^{-1}. **HRMS (m/z):** calcd for $C_{15}H_{17}F_2N_2O$ $[M+H]^+$ 279.1303, found:279.1309.



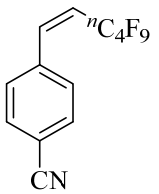
(*Z*)-4-(3,3-Difluoro-4-oxo-4-(piperidin-1-yl)but-1-en-1-yl)benzonitrile (4c): 159.6 mg, 55% yield, colorless oil; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 6.99 (dt, *J* = 16.3, 2.5 Hz, 1H), 6.60 (dt, *J* = 16.3, 11.1 Hz, 1H), 3.65-3.59 (m, 4H), 1.69–1.62 (m, 6H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 160.7 (t, *J* = 29.3 Hz), 139.0 (t, *J* = 1.1 Hz), 135.0 (t, *J* = 7.9 Hz), 131.7, 129.6 (t, *J* = 3.1 Hz), 125.4 (t, *J* = 26.5 Hz), 118.6, 114.3 (t, *J* = 249.7 Hz), 111.9, 46.9 (t, *J* = 4.8 Hz), 44.3, 26.1, 25.4, 24.2 ppm. **^{19}F NMR (376 MHz, CDCl$_3$):** δ -90.09 (s, 1F), -90.13 (s, 1F) ppm. **IR (KBr):** ν = 3032, 2937, 2231, 1664, 1460, 1044, 869 cm^{-1}. **HRMS (m/z):** calcd for $C_{16}H_{17}F_2N_2O$ $[M+H]^+$ 291.1303, found: 291.1309.



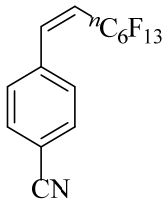
(*Z*)-4-(3,3-Difluoro-4-morpholino-4-oxobut-1-en-1-yl)benzonitrile (4d): 236.6 mg, 81% yield, colorless oil; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.62 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 6.93 (dt, *J* = 12.6, 2.5 Hz, 1H), 6.14 (q, *J* = 13.6 Hz, 1H), 3.65–3.59 (m, 4H), 3.55–3.48 (m, 4H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 161.0 (t, *J* = 30.1 Hz), 138.9 (t, *J* = 1.3 Hz), 135.6 (t, *J* = 7.7 Hz), 131.8, 129.5 (t, *J* = 3.2 Hz), 124.7 (t, *J* = 25.9 Hz), 118.5, 114.2 (t, *J* = 250.1 Hz), 112.1, 66.5, 66.4, 46.5 (t, *J* = 4.9 Hz), 43.3 ppm. **^{19}F NMR (376 MHz, CDCl$_3$):** δ -90.09 (s, 1F), -90.13 (s, 1F) ppm. **IR (KBr):** ν = 3412, 2863, 2230, 1664, 1448, 1109, 855 cm^{-1}. **HRMS (m/z):** calcd for $C_{15}H_{15}F_2N_2O_2$ $[M+H]^+$ 293.1096, found: 293.1102.



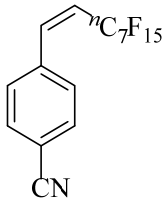
(*Z*)-4-(3,3,4,4,4-Pentafluorobut-1-en-1-yl)benzonitrile (4e): 168.0 mg, 68% yield, colorless oil; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.15 (dt, *J* = 12.8, 2.9 Hz, 1H), 5.87 (td, *J* = 14.9, 12.6 Hz, 1H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 140.1 (t, *J* = 5.0 Hz), 138.5, 131.9, 129.1 (t, *J* = 3.6 Hz), 118.4 (t, *J* = 22.1 Hz), 118.4, 112.4 ppm; carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling. **^{19}F NMR (376 MHz, CDCl$_3$):** δ -85.25 (s, 3F), -108.4 –-111.30 (m, 2F) ppm. **IR (KBr):** ν = 3413, 2232, 1339, 1204, 1109, 880, 582 cm^{-1}. **HRMS (m/z):** calcd for $C_{11}H_7F_5N$ $[M+H]^+$ 248.0493, found: 248.0499.



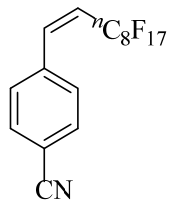
(*Z*)-4-(3,3,4,4,5,5,6,6,6-Nonafluorohex-1-en-1-yl)benzonitrile (4f): 215.1 mg, 62% yield, yellow oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.16 (dt, *J* = 12.8, 3.2 Hz, 1H), 5.91 (q, *J* = 14.6 Hz, 1H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 140.0 (t, *J* = 6.4 Hz), 138.6, 131.9, 129.0 (t, *J* = 4.0 Hz), 118.6 (t, *J* = 22.4 Hz), 118.4, 112.4 ppm; carbons corresponding to the C_4F_9 group cannot be identified due to C-F coupling. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -80.91 (d, *J* = 10.6 Hz, 3F), -105.65–-106.02 (m, 2F), -123.97 (q, *J* = 11.0 Hz, 2F), -125.54–-125.92 (m, 2F) ppm. **IR (KBr):** ν = 3414, 2232, 1617, 1355, 1237, 1134, 872 cm^{-1}. **HRMS (m/z):** calcd for $C_{13}H_7F_9N$ $[M+H]^+$ 348.0429, found: 348.0435.



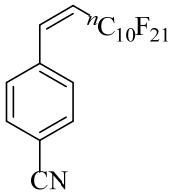
(*Z*)-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooct-1-en-1-yl)benzonitrile (4g): 317.4 mg, 71% yield, white solid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.16 (dt, *J* = 12.8, 3.1 Hz, 1H), 5.91 (q, *J* = 14.8 Hz, 1H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 139.9 (t, *J* = 5.4 Hz), 138.7, 131.9, 129.0 (t, *J* = 3.5 Hz), 118.7 (t, *J* = 22.6 Hz), 118.4, 112.4 ppm. carbons corresponding to the C_6F_{13} group cannot be identified due to C-F coupling. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -80.72 (t, *J* = 9.8 Hz, 3F), -105.64 (q, *J* = 14.3 Hz, 2F), -121.50–-121.64 (m, 2F), -122.76–-122.68 (m, 2F), -123.03–-123.61 (m, 2F), -126.06–-126.17 (m, 2F) ppm. **IR (KBr):** ν = 3063, 2234, 1648, 1368, 1245, 1123, 705 cm^{-1}. **HRMS (m/z):** calcd for $C_{15}H_7F_{13}N$ $[M+H]^+$ 448.0365, found: 448.0371.



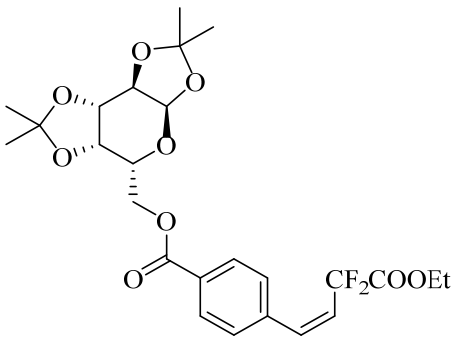
(*Z*)-4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Pentadecafluorononon-1-en-1-yl)benzonitrile (4h): 308.2 mg, 62% yield, white solid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.16 (dt, *J* = 12.7, 3.0 Hz, 1H), 5.91 (td, *J* = 15.5, 13.4 Hz, 1H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** 139.9 (t, *J* = 4.7 Hz), 138.7, 131.9, 129.0 (t, *J* = 3.6 Hz), 118.7 (t, *J* = 22.4 Hz), 118.4, 112.4 ppm; carbons corresponding to the C_7F_{15} group cannot be identified due to C-F coupling. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -80.67 (t, *J* = 9.8 Hz, 3F), -105.62 (q, *J* = 14.3 Hz, 2F), -121.31–-121.47 (m, 2F), -121.97–-122.04 (m, 2F), -122.61–-122.77 (m, 2F), -122.98–-123.08 (m, 2F), -126.04–-126.14 (m, 2F) ppm. **IR (KBr):** ν = 3043, 2235, 1649, 1244, 1147, 1093, 701 cm^{-1}. **HRMS (m/z):** calcd for $C_{16}H_7F_{15}N$ $[M+H]^+$ 498.0333, found: 498.0339.



(*Z*)-4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodec-1-en-1-yl)benzonitrile (4i): 300.9 mg, 55% yield, white solid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.16 (dt, *J* = 12.8, 3.1 Hz, 1H), 5.90 (td, *J* = 15.3, 12.8 Hz, 1H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 139.9 (t, *J* = 6.4 Hz), 138.7, 131.9, 129.0 (t, *J* = 3.9 Hz), 118.7 (t, *J* = 22.5 Hz), 118.4, 112.5 ppm; carbons corresponding to the C_8F_{17} group cannot be identified due to C-F coupling. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -80.80 (t, *J* = 10.2 Hz, 3F), -105.66 (q, *J* = 14.4 Hz, 2F), -121.31–-121.47 (m, 2F), -121.81–-122.01 (m, 4F), -122.65–-122.81 (m, 2F), -123.02–-123.11 (m, 2F), -126.09–-126.18 (m, 2F) ppm. **IR (KBr):** ν = 3063, 2235, 1510, 1220, 1093, 966, 655 cm^{-1}. **HRMS (m/z):** calcd for $C_{17}H_7F_{17}N$ $[M+H]^+$ 548.0302, found: 548.0307.

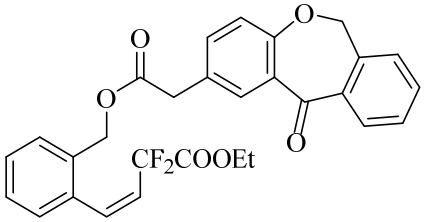


(*Z*)-4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Henicosafluorododec-1-en-1-yl)benzonitrile (4j): 323.5 mg, 50% yield, white solid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.66 (d, *J* = 7.9 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.16 (dt, *J* = 12.8, 3.2 Hz, 1H), 5.91 (q, *J* = 14.8 Hz, 1H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 139.9 (t, *J* = 6.5 Hz), 138.6, 131.9, 129.0 (t, *J* = 3.9 Hz), 118.7 (t, *J* = 22.8 Hz), 118.4, 112.4 ppm; carbons corresponding to the $C_{10}F_{21}$ group cannot be identified due to C-F coupling. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -80.66 (t, *J* = 10.0 Hz, 3F), -105.58 (q, *J* = 13.9 Hz, 2F), -121.29 (s, 2F), -121.52–-121.95 (m, 8F), -122.61 (s, 2F), -122.97 (s, 2F), -125.97–-126.06 (m, 2F) ppm. **IR (KBr):** ν = 2235, 1220, 1150, 1093, 1073, 879, 662 cm^{-1}. **HRMS (m/z):** calcd for $C_{19}H_7F_{21}N$ $[M+H]^+$ 648.0238, found: 648.0234.

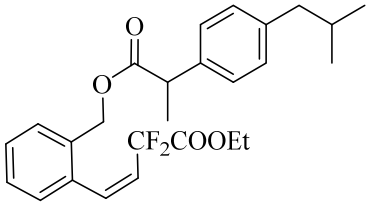


((3*aR*,5*R*,5*aS*,8*aS*,8*bR*)-2,2,7,7-Tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl 4-((*Z*)-4-ethoxy-3,3-difluoro-4-oxobut-1-en-1-yl)benzoate (6a): 276.6 mg, 54% yield, white solid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 6.96 (dt, *J* = 12.8, 2.1 Hz, 1H), 5.95 (td, *J* = 13.4, 12.4 Hz, 1H), 5.56 (d, *J* = 5.0 Hz, 1H), 4.65 (dd, *J* = 7.9, 2.5 Hz, 1H), 4.52 (dd, *J* = 11.5, 4.9 Hz, 1H), 4.43 (dd, *J* = 11.5, 7.5 Hz, 1H), 4.35 (dd, *J* = 4.9, 2.5 Hz,

1H), 4.33 (dd, *J* = 7.9, 1.9 Hz, 1H), 4.17 (ddd, *J* = 7.1, 4.8, 1.9 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 1.52 (s, 3H), 1.48 (s, 3H), 1.36 (s, 3H), 1.33 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 165.9, 163.2 (t, *J* = 33.7 Hz), 138.8 (t, *J* = 1.4 Hz), 137.6 (t, *J* = 8.4 Hz), 129.9, 129.5, 128.8 (t, *J* = 3.1 Hz), 123.4 (t, *J* = 27.6 Hz), 112.0 (t, *J* = 274.1 Hz), 109.7, 108.8, 96.3, 71.1, 70.7, 70.5, 66.1, 64.0, 63.1, 26.0, 26.0, 25.0, 24.5, 13.7 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -95.08 (s, 1F), -95.13 (s, 1F) ppm. **IR (KBr):** ν = 2980, 1770, 1723, 1279, 1212, 1071, 887 cm^{-1}. **HRMS (m/z):** calcd for $C_{25}H_{31}F_2O_9$ $[M+H]^+$ 513.1931, found: 513.1936.



Ethyl (*Z*)-2,2-difluoro-4-(2-((2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)acetoxy)methyl)phenyl)but-3-enoate (6b): 334.1 mg, 66% yield, colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.05 (d, *J* = 2.3 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.49 (td, *J* = 7.5, 1.4 Hz, 1H), 7.40 (td, *J* = 7.6, 1.3 Hz, 1H), 7.35–7.28 (m, 2H), 7.28–7.21 (m, 3H), 7.17 (d, *J* = 5.3 Hz, 1H), 6.99 (dd, *J* = 12.5, 2.1 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 5.90 (q, *J* = 12.1 Hz, 1H), 5.11 (s, 2H), 5.03 (s, 2H), 3.87 (q, *J* = 7.1 Hz, 2H), 3.61 (s, 2H), 1.06 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 190.7, 171.0, 163.2 (t, *J* = 33.3 Hz), 160.5, 140.4, 136.5 (t, *J* = 8.9 Hz), 136.3, 135.5, 134.0, 133.2, 132.8, 132.5, 129.4, 129.2, 128.8, 128.7, 128.2, 127.8, 127.5, 125.1, 124.1 (t, *J* = 27.4 Hz), 121.1, 112.0 (t, *J* = 246.6 Hz), 73.6, 64.6, 62.9, 40.0, 13.6 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -94.55 (s, 1F), -94.60 (s, 1F) ppm. **IR (KBr):** ν = 2925, 1768, 1738, 1491, 1301, 1154, 761 cm^{-1}. **HRMS (m/z):** calcd for $C_{29}H_{25}F_2O_6$ $[M+H]^+$ 507.1614, found: 507.1619.



Ethyl (*Z*)-2,2-difluoro-4-(2-(((2-(4-isobutylphenyl)propanoyl)oxy)methyl)phenyl)but-3-enoate (6c): 239.7 mg, 54% yield, colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.20–7.08 (m, 6H), 7.03–6.99 (m, 2H), 6.75 (dt, *J* = 12.1, 1.6 Hz, 1H), 5.76 (q, *J* = 12.0 Hz, 1H), 4.96 (d, *J* = 2.1 Hz, 2H), 3.82 (q, *J* = 7.2 Hz, 2H), 3.66 (q, *J* = 7.2 Hz, 1H), 2.38 (d, *J* = 7.2 Hz, 2H), 1.82–1.72 (m, 1H), 1.42 (d, *J* = 7.1 Hz, 3H), 1.04 (t, *J* = 7.2 Hz, 3H), 0.83 (d, *J* = 6.6 Hz, 6H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 174.3, 163.2 (t, *J* = 33.5 Hz), 140.7, 137.5, 136.5 (t, *J* = 9.2 Hz), 133.9 (t, *J* = 1.1 Hz), 133.4 (t, *J* = 1.2 Hz), 129.3, 128.6, 128.4, 128.0, 127.2, 123.8 (t, *J* = 27.5 Hz), 112.0 (t, *J* = 246.3 Hz), 64.5, 62.9, 45.0, 45.0, 30.2, 22.4, 22.3, 18.2, 13.6 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -94.53 (d, *J* = 4.9 Hz, 1F), -94.56 (d, *J* = 4.9 Hz, 1F) ppm. **IR (KBr):** ν = 2957, 1771, 1738, 1455, 1318, 1156, 1073 cm^{-1}. **HRMS (m/z):** calcd for $C_{26}H_{31}F_2O_4$ $[M+H]^+$ 445.2185, found: 445.2190.

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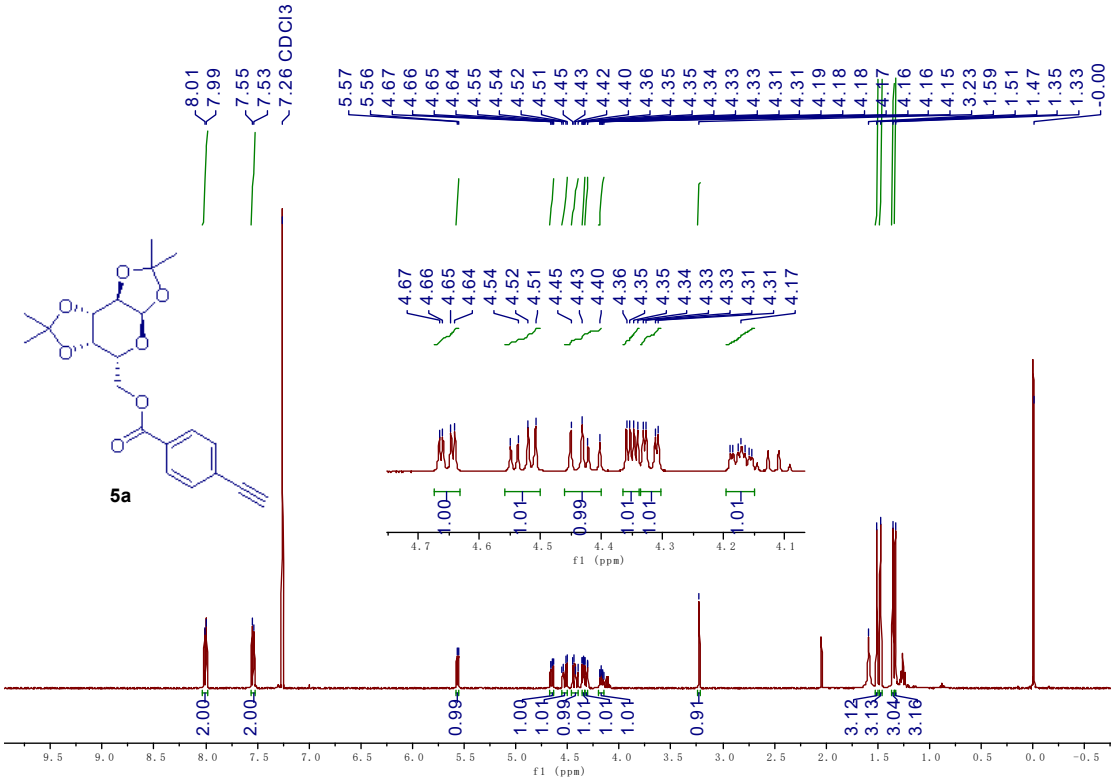
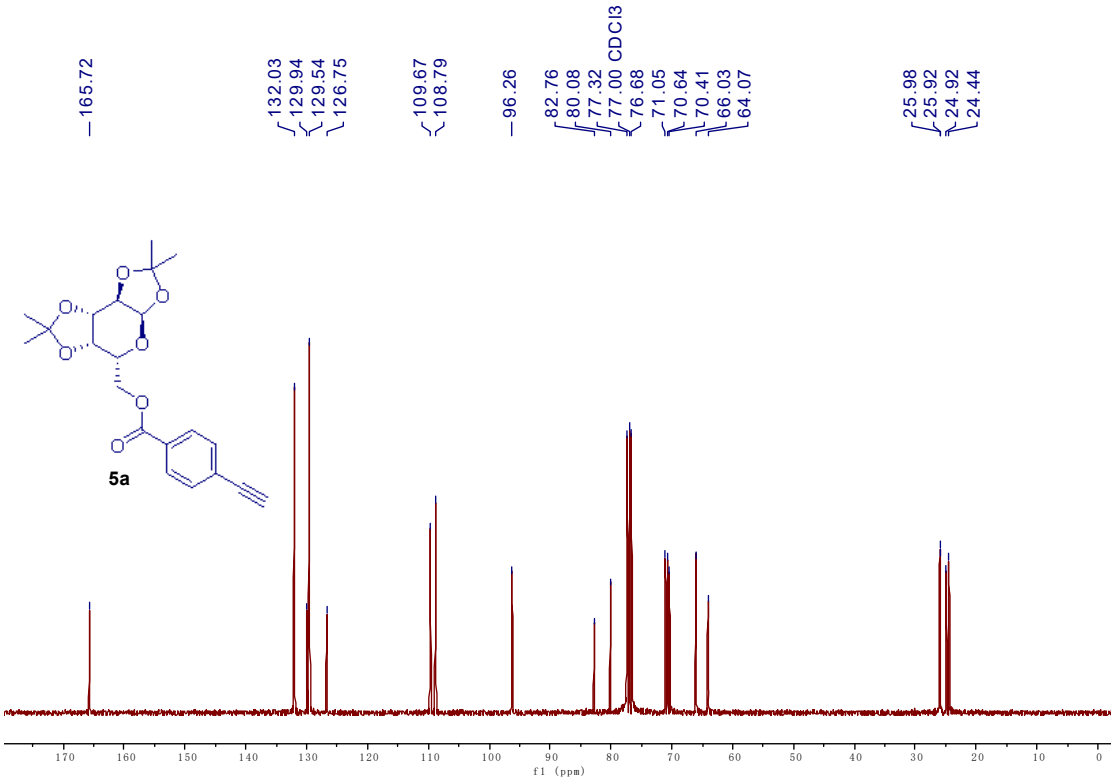
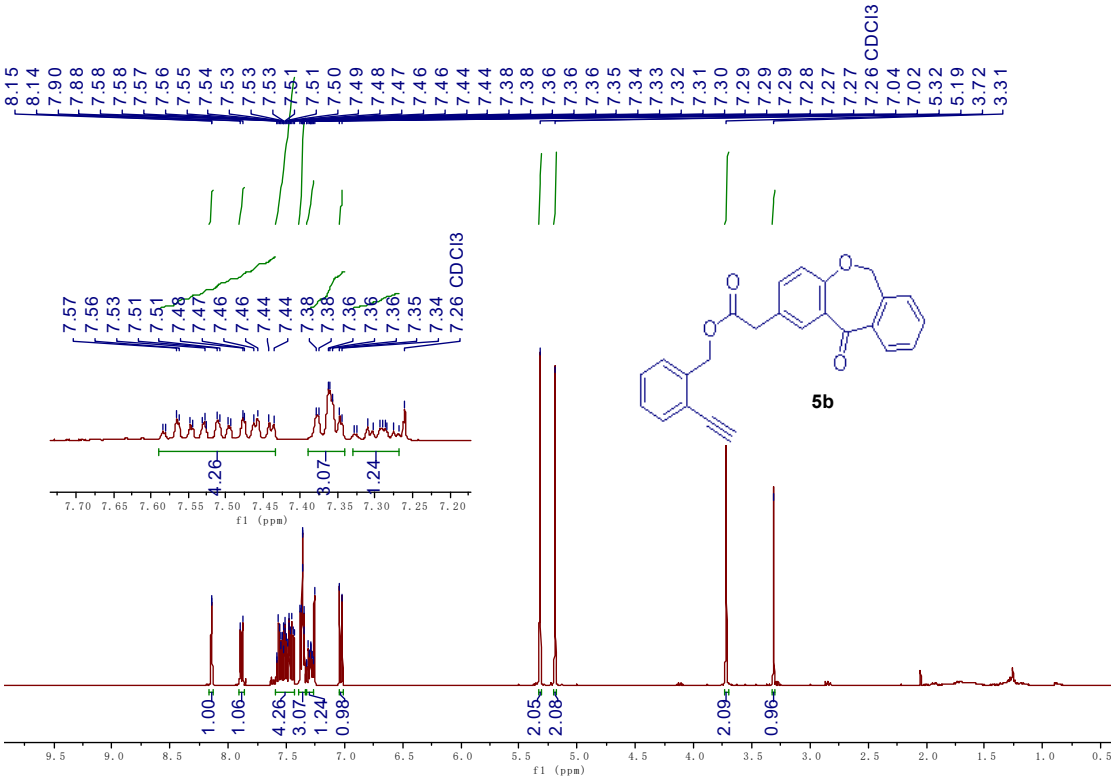
^{1}H, ^{13}C, and ^{19}F NMR spectra of products



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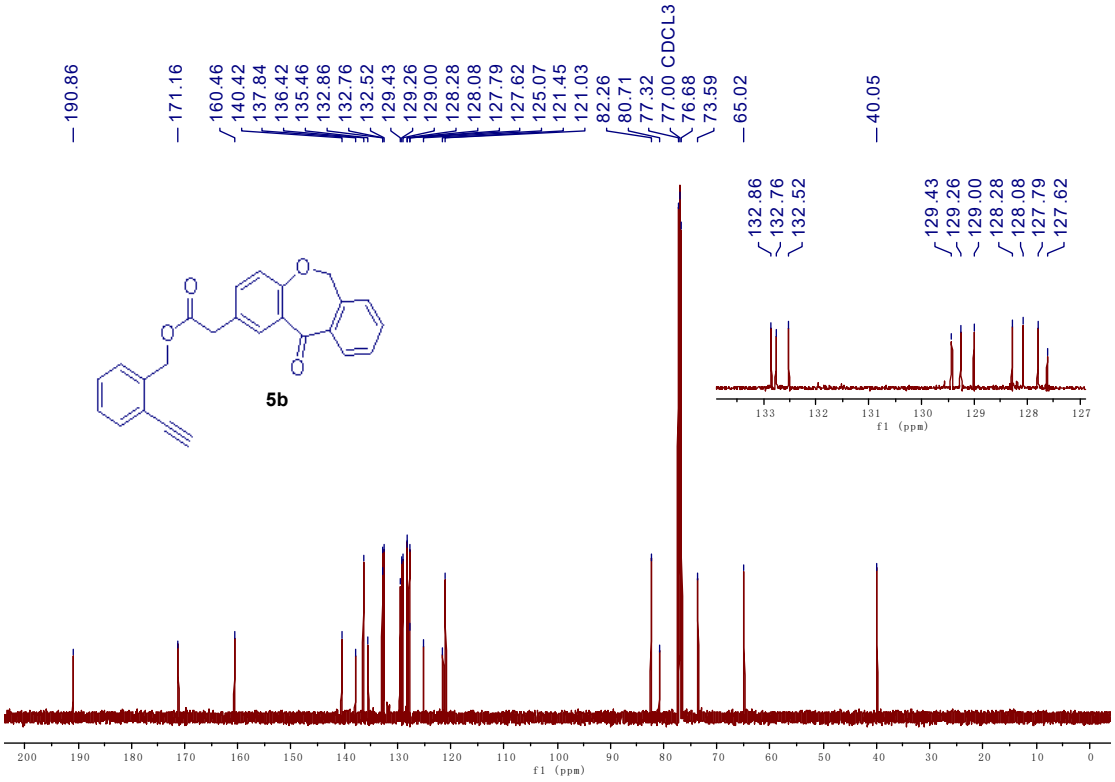
0.96
f1 (ppm)


190.86
171.16
160.46
140.42
137.84
136.42
135.46
132.86
132.76
132.52
129.43
129.26
129.00
128.28
128.08
127.79
127.62
125.07
121.45
121.03
82.26
80.71
77.32
77.00 CDCL3
76.68
73.59
65.02
40.05
132.86
132.76
132.52
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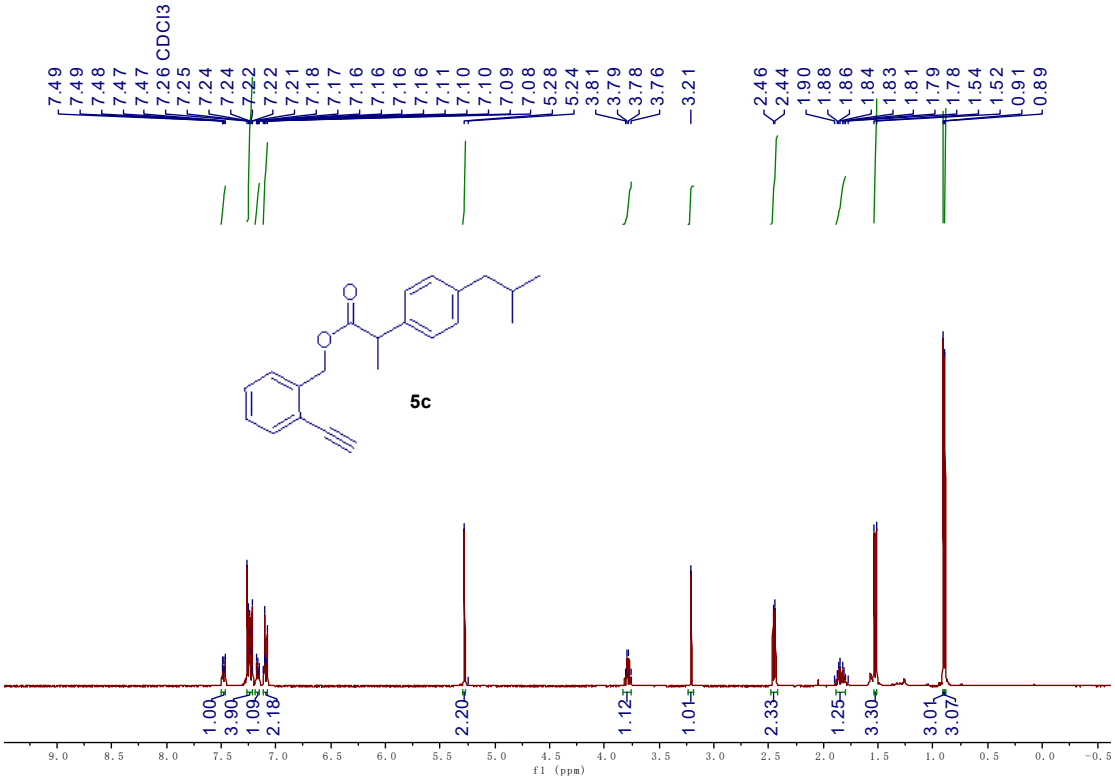
129.26
129.00
128.28
128.08
127.79
127.62
5b
f1 (ppm)
f1 (ppm)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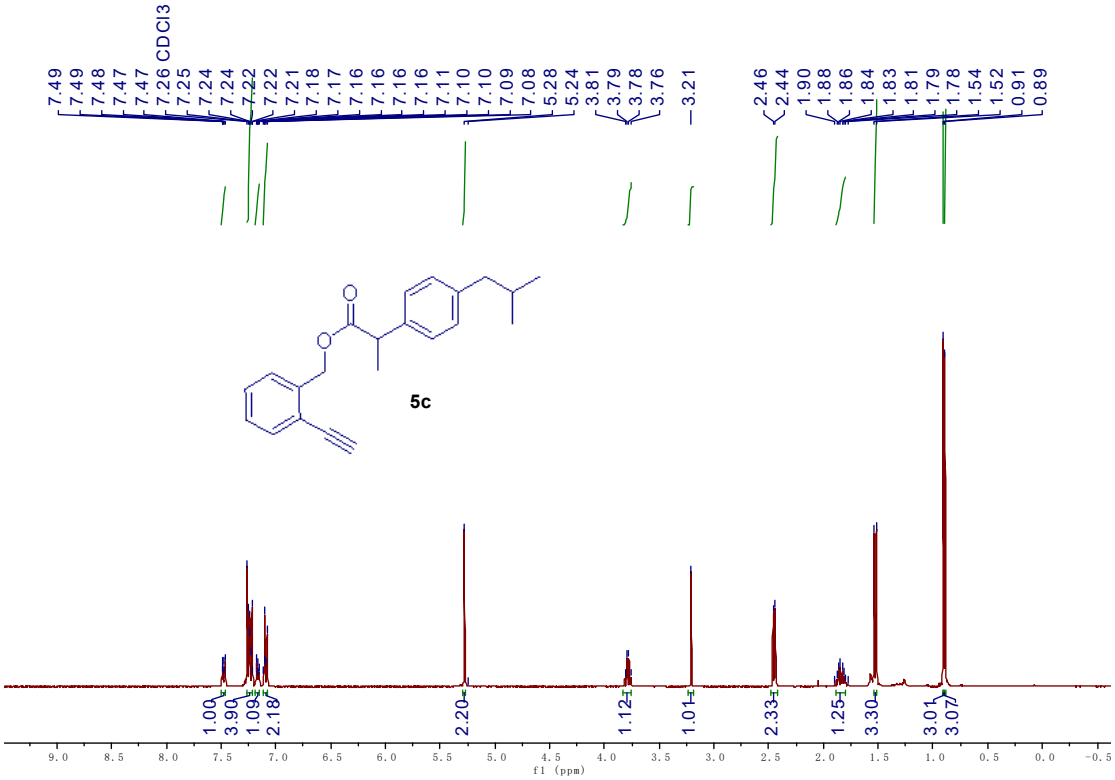
7.47
7.47
7.26 CDCl3
7.25
7.24
7.24
7.22
7.22
7.21
7.18
7.17
7.16
7.16
7.16
7.16
7.11
7.10
7.10
7.09
7.08
5.28
5.24
3.81
3.79
3.78
3.76
3.21
2.46
2.44
1.90
1.88
1.86
1.84
1.83
1.81
1.79
1.78
1.54
1.52
0.91
0.89
5c
1.00
3.90
1.09
2.18
2.20
1.12
1.01
2.33
1.25
3.30
3.01
3.07
f1 (ppm)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7.49
7.48
7.47
7.47
7.26 CDCl3
7.25
7.24
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7.22
7.22
7.21
7.18
7.17
7.16
7.16
7.16
7.16
7.11
7.10
7.10
7.09
7.08
5.28
5.24
3.81
3.79
3.78
3.76
3.21
2.46
2.44
1.90
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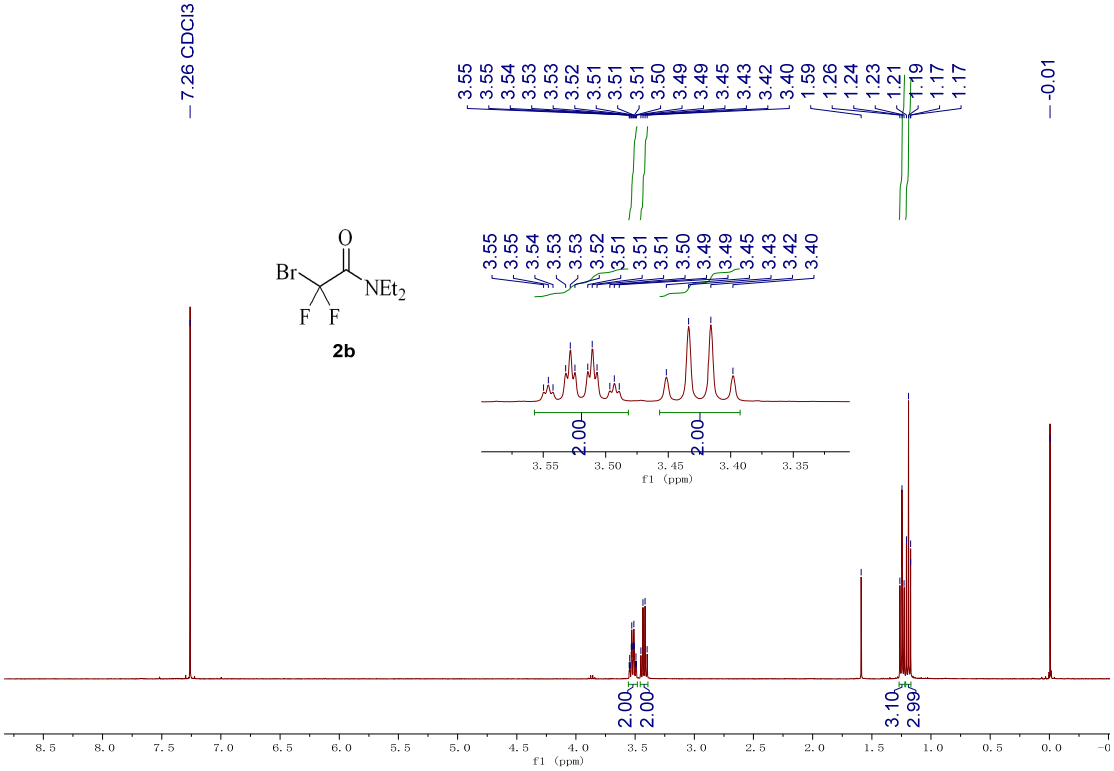
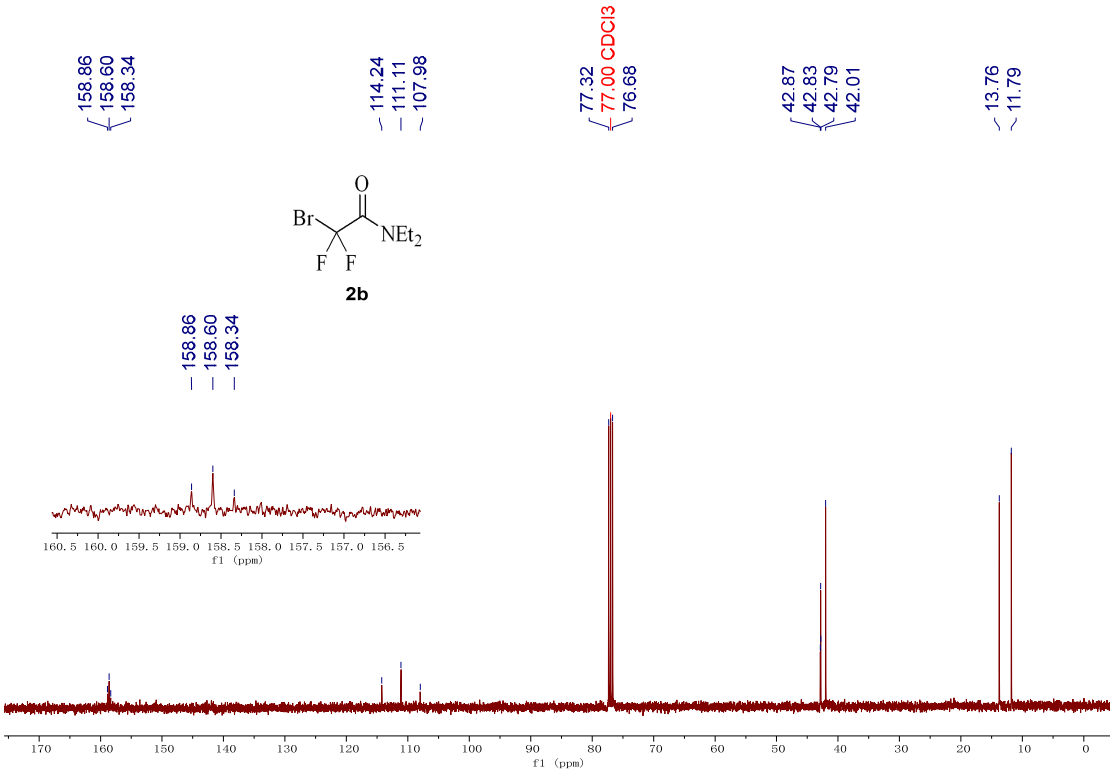
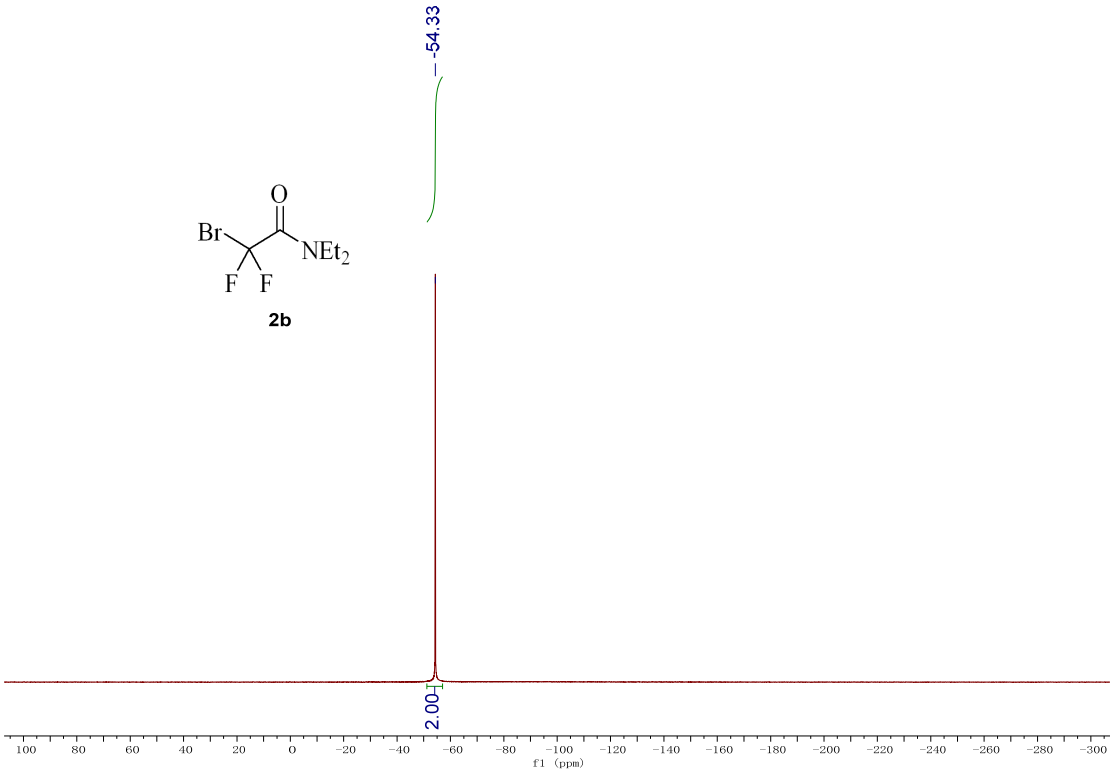
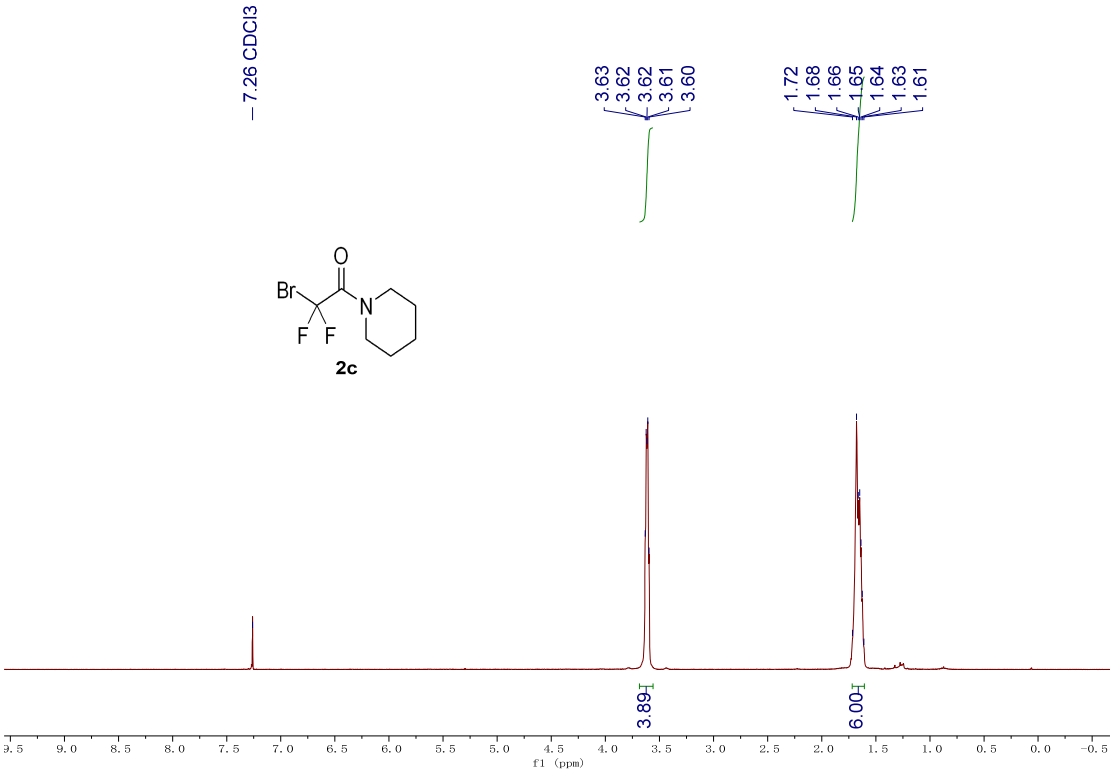
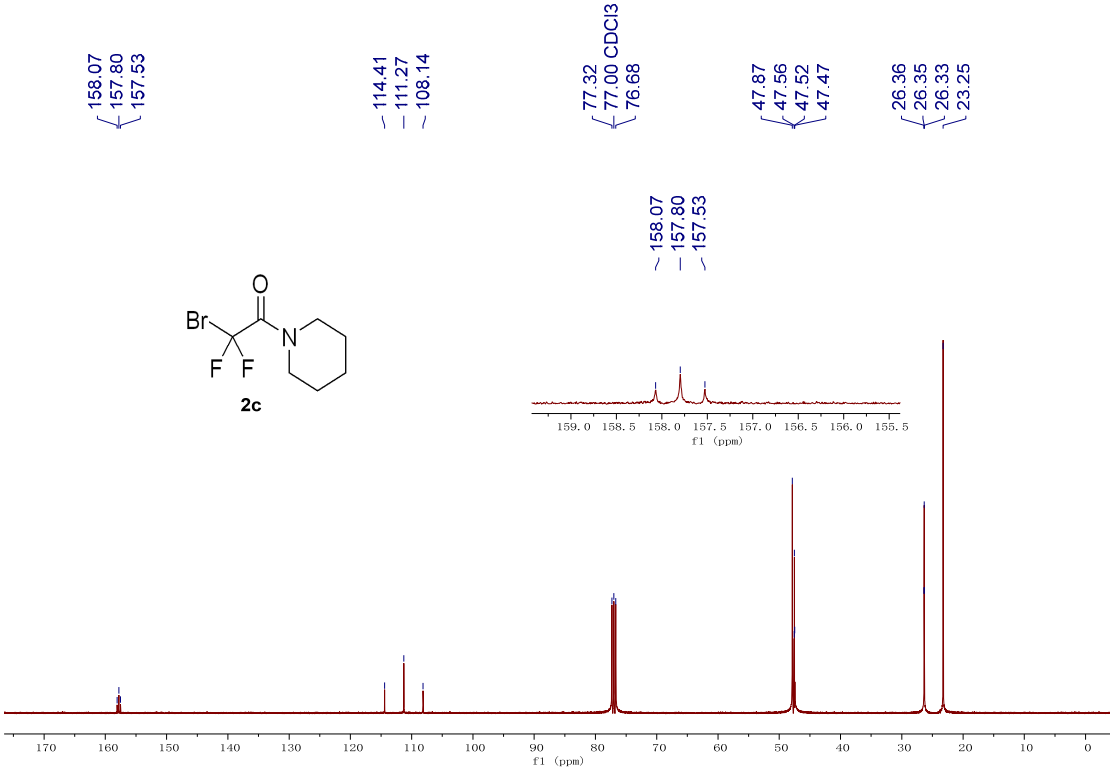
1.83
1.81
1.79
1.78
1.54
1.52
0.91
0.89
5c
1.00
3.90
1.09
2.18
2.20
1.12
1.01
2.33
1.25
3.30
3.01
3.07
f1 (ppm)

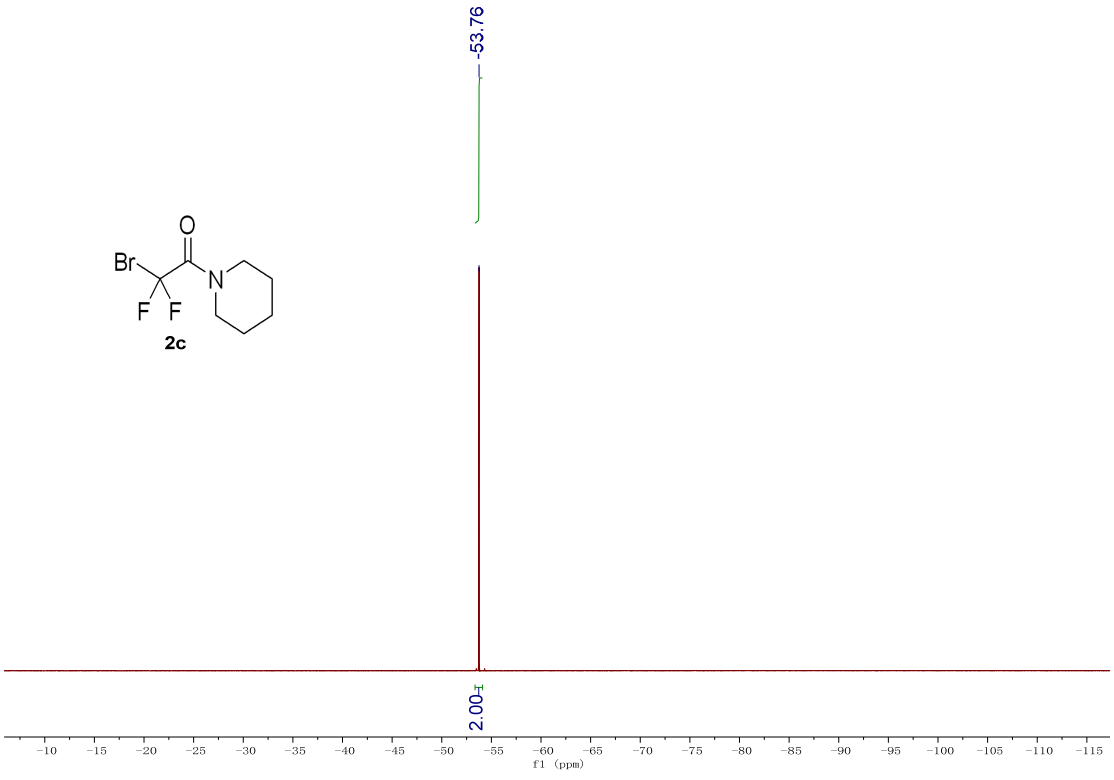

7.26 CDCl3
-0.01
3.55 3.55 3.54 3.53 3.53 3.52 3.51 3.51 3.50 3.49 3.49 3.45 3.43 3.42 3.40
1.59 1.26 1.24 1.23 1.21 1.19 1.17 1.17
Br
O
NEt2
F F
2b
2.00
2.00
3.10
2.99
f1 (ppm)

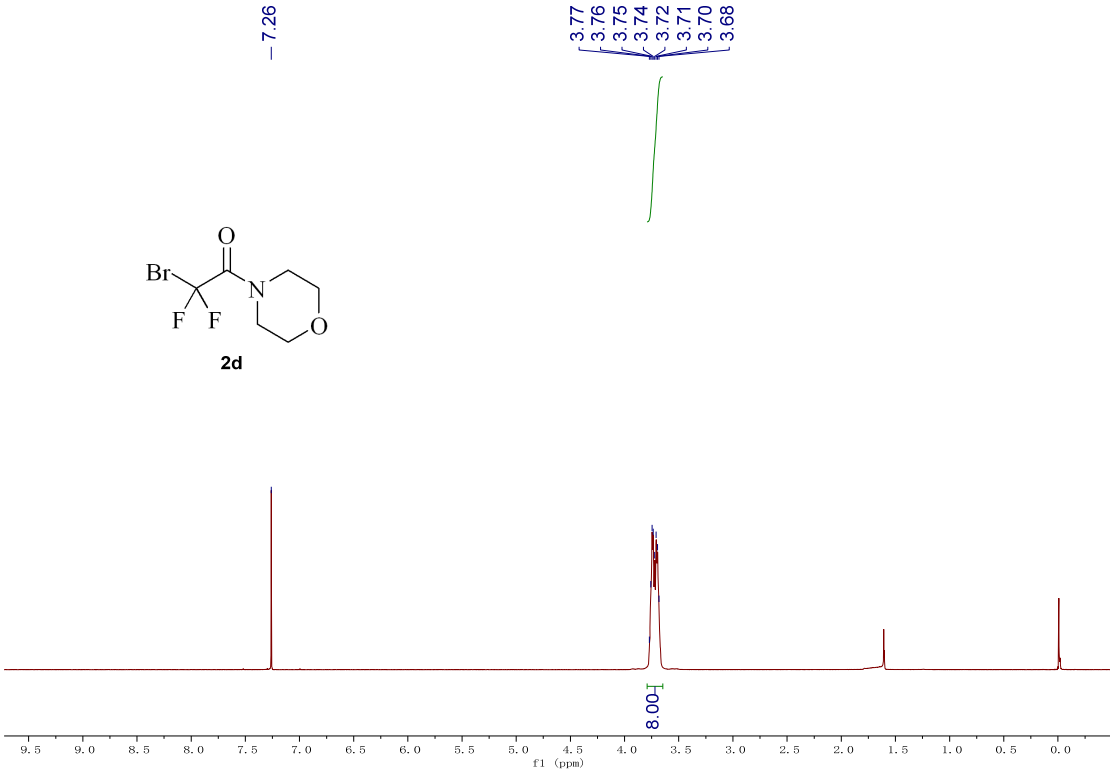

158.86 158.60 158.34
114.24 111.11 107.98
77.32 77.00 CDCl3 76.68
42.87 42.83 42.79 42.01
13.76 11.79
Br
O
NEt2
F F
2b
158.86 158.60 158.34
f1 (ppm)

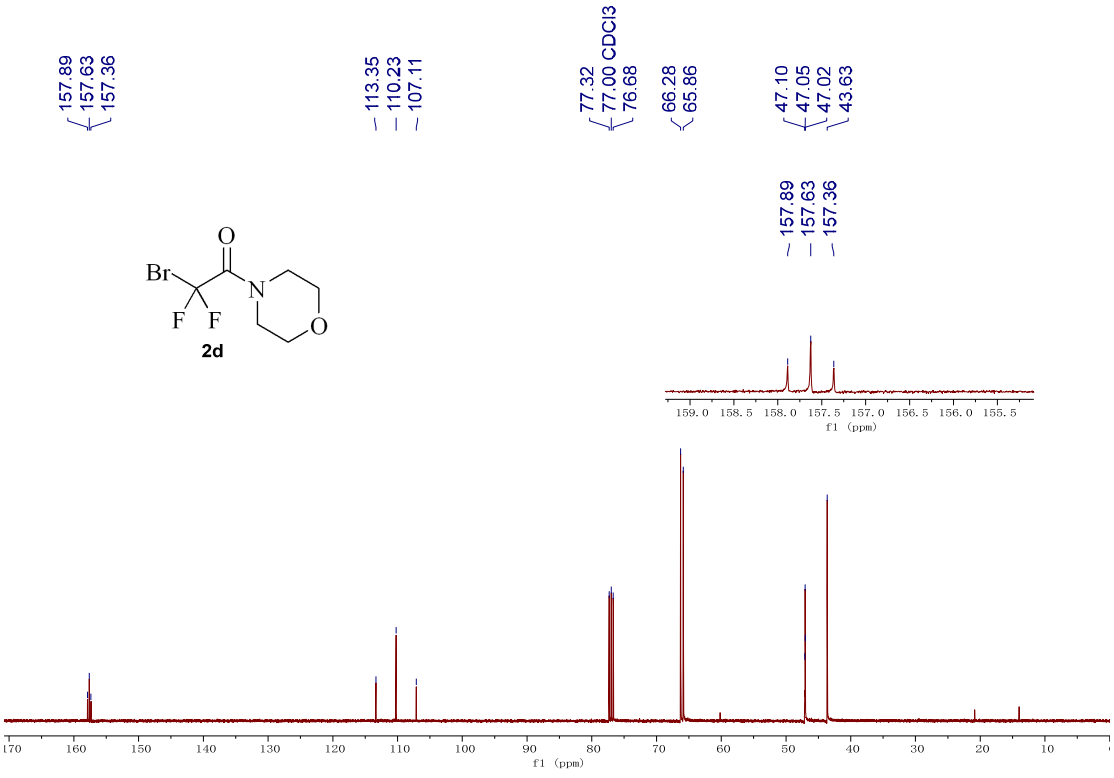

-54.33
O
Br
NEt2
F F
2b
2.00
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)

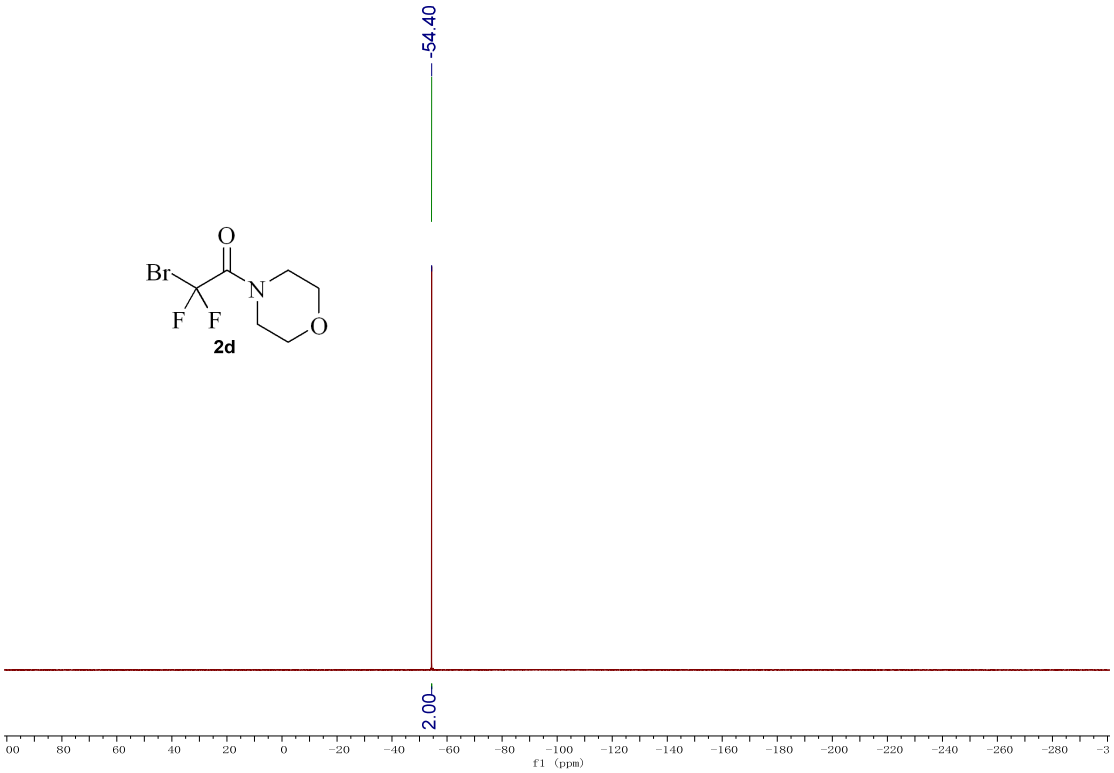

7.26 CDCl3
3.63
3.62
3.62
3.61
3.60
1.72
1.68
1.66
1.65
1.64
1.63
1.61
O
Br
N
F F
2c
3.89
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


158.07
157.80
157.53
114.41
111.27
108.14
77.32
77.00 CDCl3
76.68
47.87
47.56
47.52
47.47
26.36
26.35
26.33
23.25
Br
F F
O
N
2c
f1 (ppm)

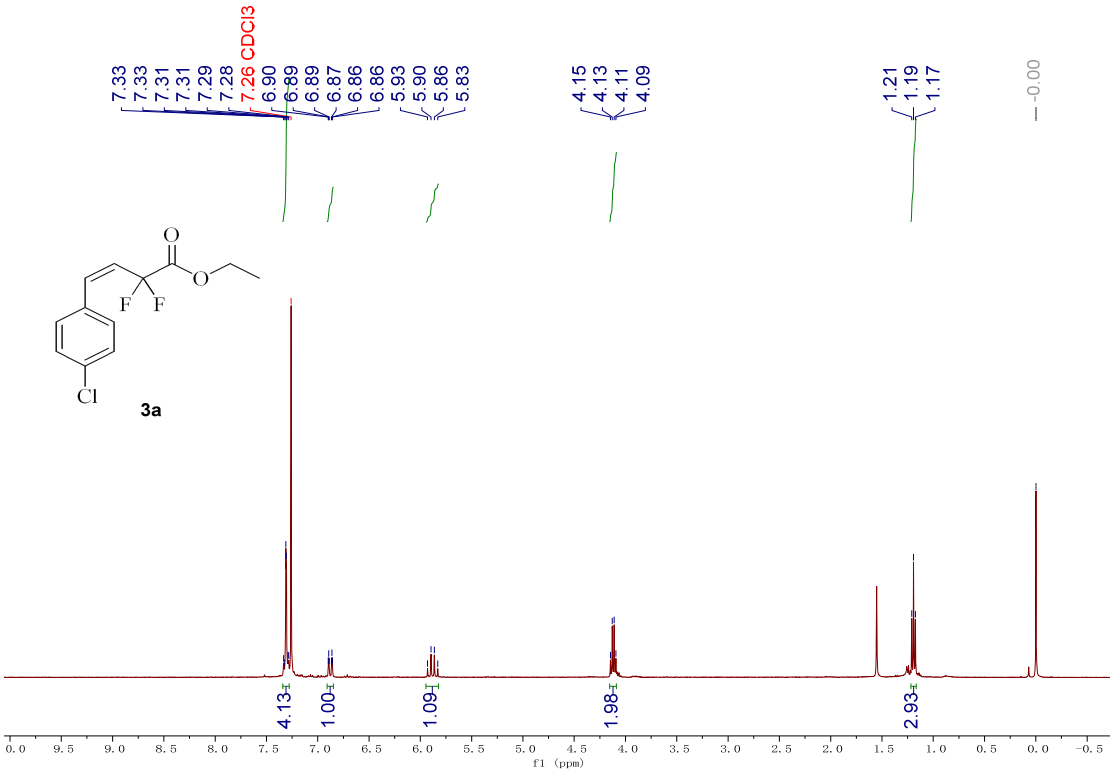

-53.76
2.00
Br
F F
O
N
2c
f1 (ppm)


7.26
3.77
3.76
3.75
3.74
3.72
3.71
3.70
3.68
Br
F
F
O
N
O
2d
8.00
f1 (ppm)

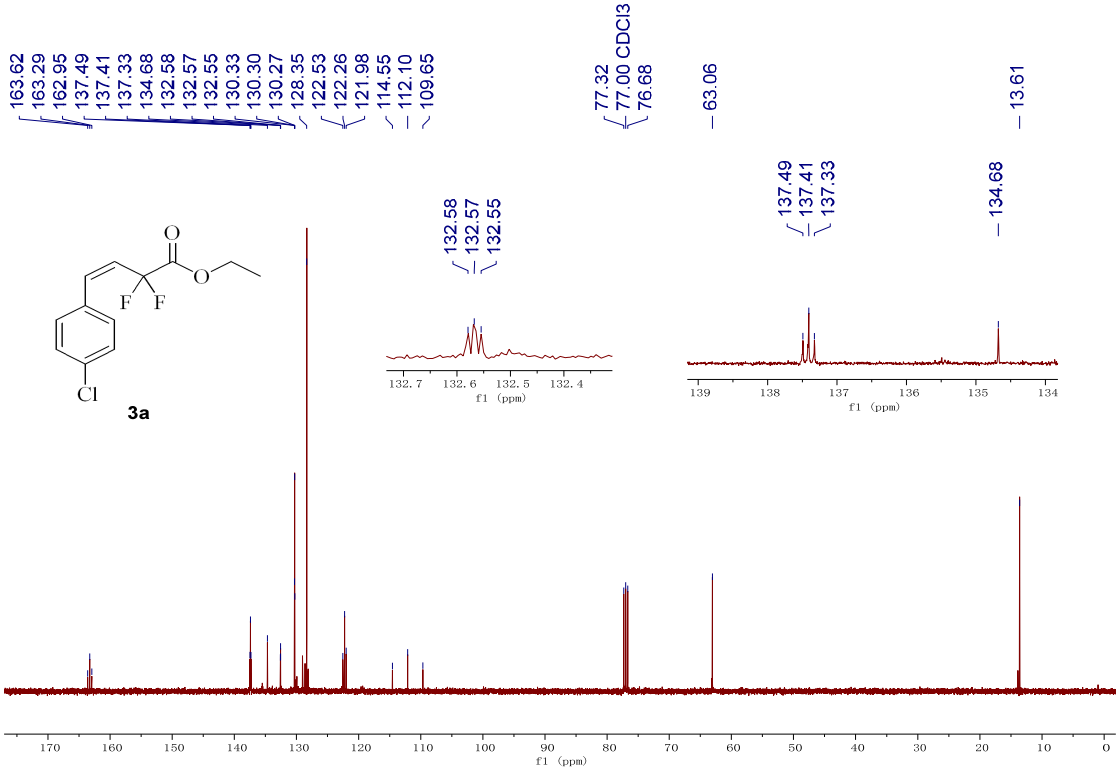

157.89
157.63
157.36
113.35
110.23
107.11
77.32
77.00 CDCl3
76.68
66.28
65.86
47.10
47.05
47.02
43.63
Br
F
F
O
N
O
2d
f1 (ppm)


-54.40
2.00
f1 (ppm)

2d


7.33
7.33
7.31
7.31
7.29
7.28
7.26 CDCl3
6.90
6.89
6.89
6.87
6.86
6.86
5.93
5.90
5.86
5.83
4.15
4.13
4.11
4.09
1.21
1.19
1.17
-0.00
4.13
1.00
1.09
1.98
2.93
f1 (ppm)

3a


163.62
163.29
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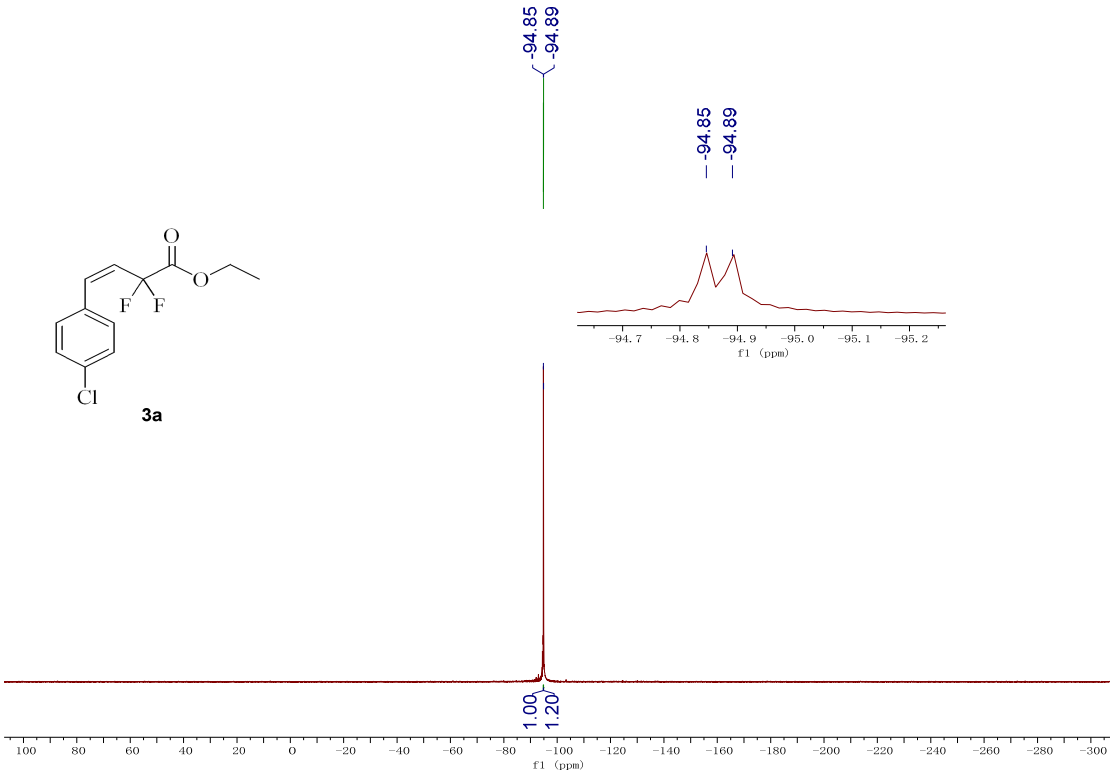
137.33
134.68
132.58
132.57
132.55
130.33
130.30
130.27
128.35
122.53
122.26
121.98
114.55
112.10
109.65
77.32
77.00 CDCl3
76.68
63.06
13.61
137.49
137.41
137.33
134.68
132.58
132.57
132.55
O
O
F
F
Cl
3a
f1 (ppm)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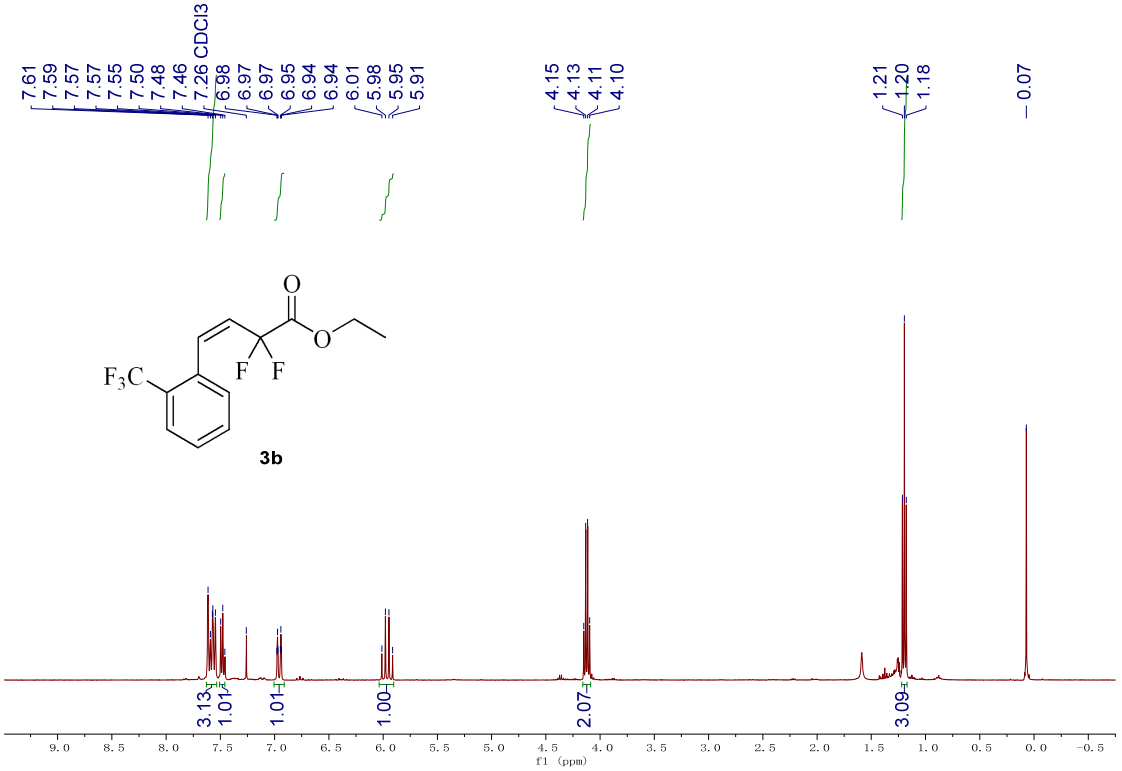
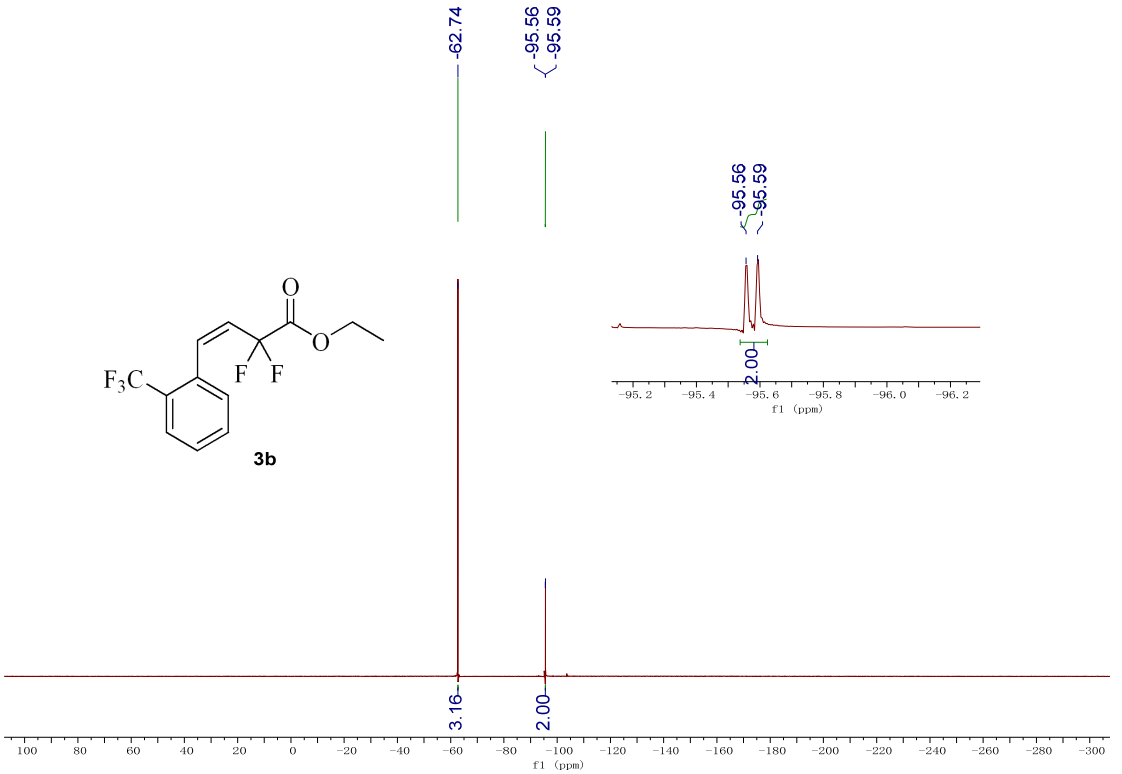
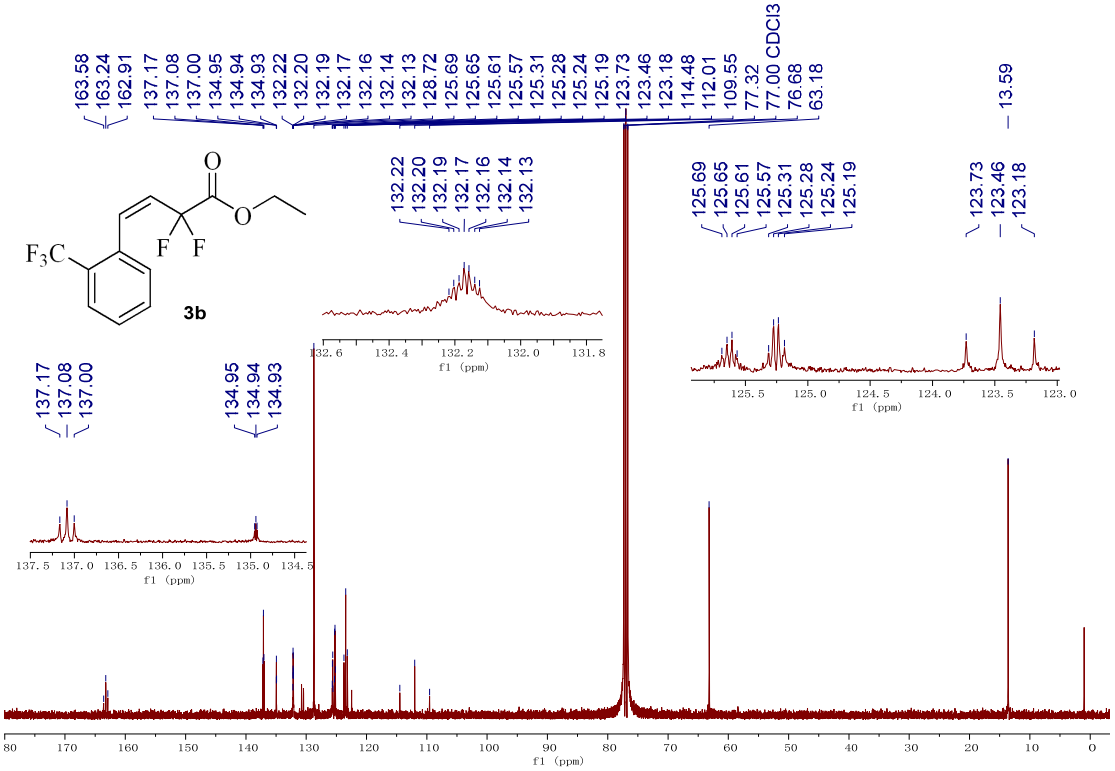
-94.89
-94.85
-94.89
O
O
F
F
Cl
3a
1.00
1.20
f1 (ppm)


7.61
7.59
7.57
7.57
7.55
7.50
7.48
7.46
7.26 CDCl3
6.98
6.97
6.97
6.95
6.94
6.94
6.01
5.98
5.95
5.91
4.15
4.13
4.11
4.10
1.21
1.20
1.18
0.07
O
O
F
F
F3C
3b
3.13
1.01
1.01
1.00
2.07
3.09
f1 (ppm)


-62.74
-95.56
-95.59
-95.56
-95.59
O
O
F
F
F3C
3b
2.00
f1 (ppm)
3.16
2.00
f1 (ppm)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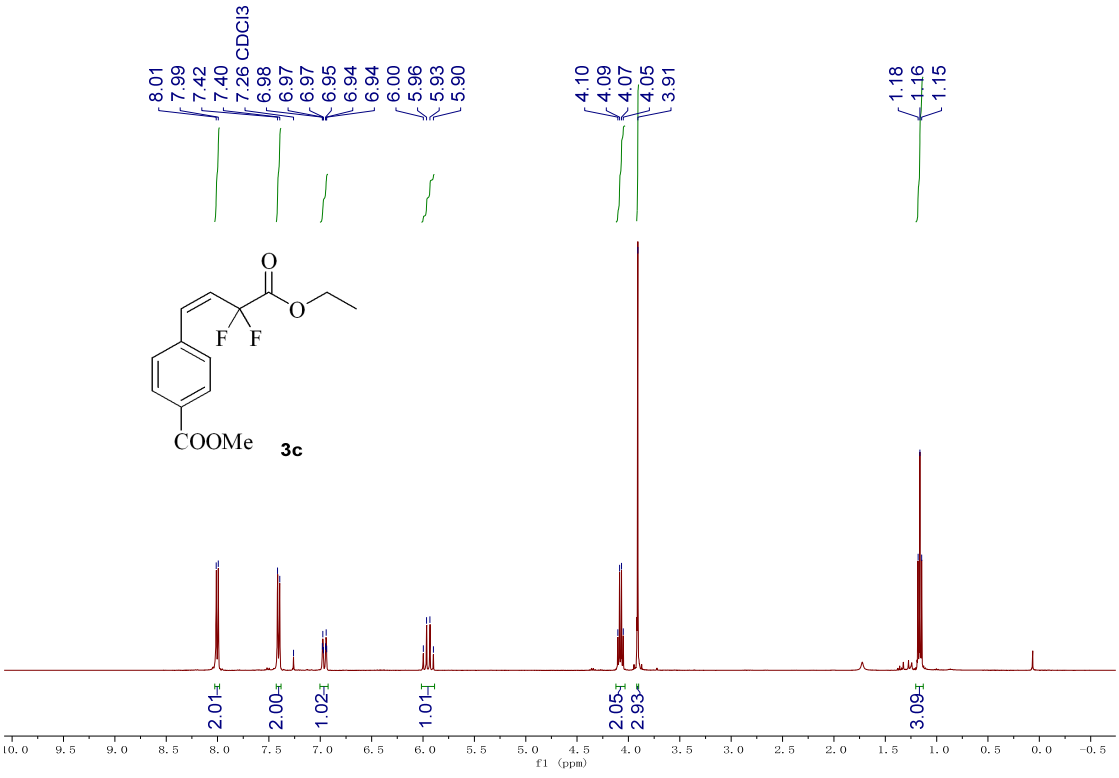
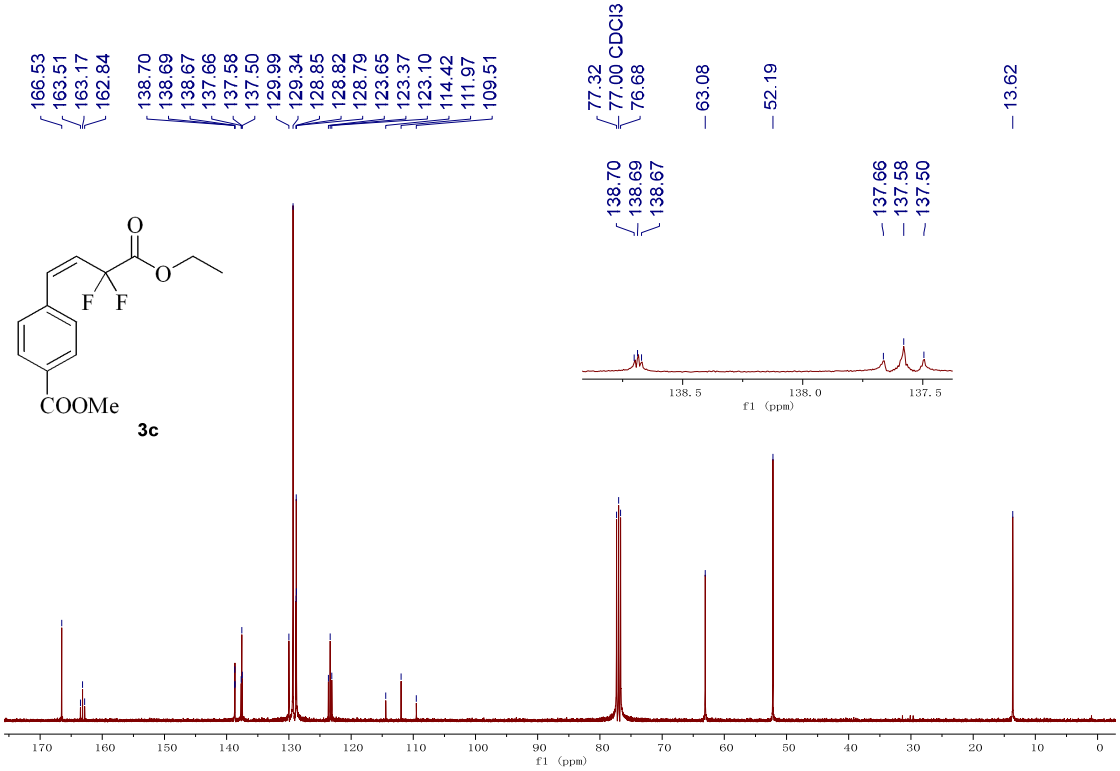
137.17
137.08
137.00
134.95
134.94
134.93
132.22
132.20
132.19
132.17
132.16
132.14
132.13
128.72
125.69
125.65
125.61
125.57
125.31
125.28
125.24
125.19
123.73
123.46
123.18
114.48
112.01
109.55
77.32
77.00 CDCl3
76.68
63.18
13.59
O
O
F F
F3C
3b
f1 (ppm)


8.01
7.99
7.42
7.40
7.26 CDCl3
6.98
6.97
6.97
6.95
6.94
6.94
6.00
5.96
5.93
5.90
4.10
4.09
4.07
4.05
3.91
1.18
1.16
1.15
O
O
F F
COOMe
3c
2.01
2.00
1.02
1.01
2.05
2.93
3.09
f1 (ppm)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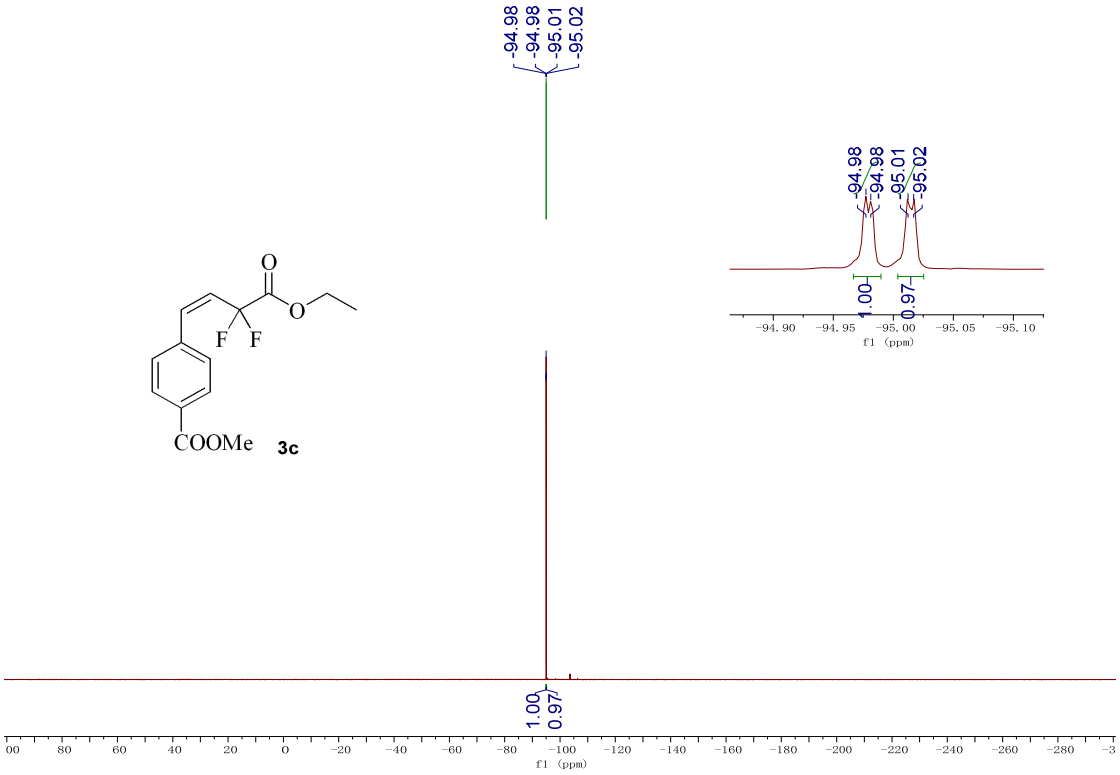
137.50
129.99
129.34
128.85
128.82
128.79
123.65
123.37
123.10
114.42
111.97
109.51
77.32
77.00 CDCl3
76.68
63.08
52.19
13.62
COOMe
3c
f1 (ppm)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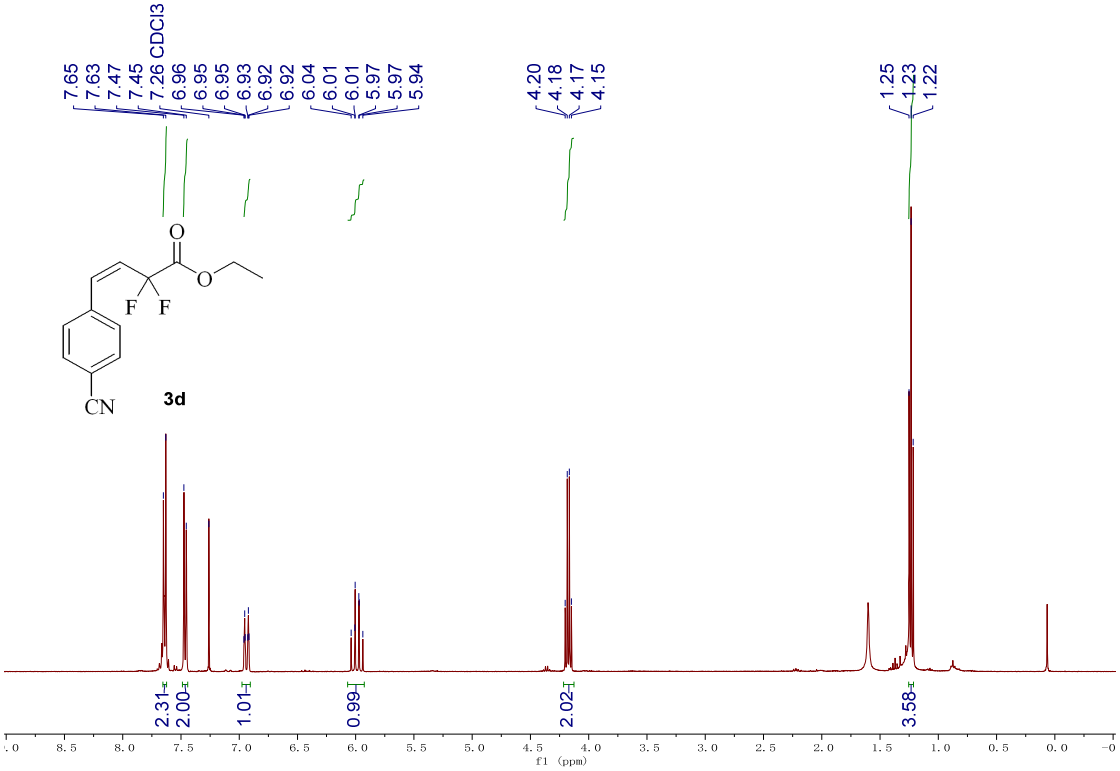
-94.98
-95.01
-95.02
1.00
0.97
COOMe
3c
f1 (ppm)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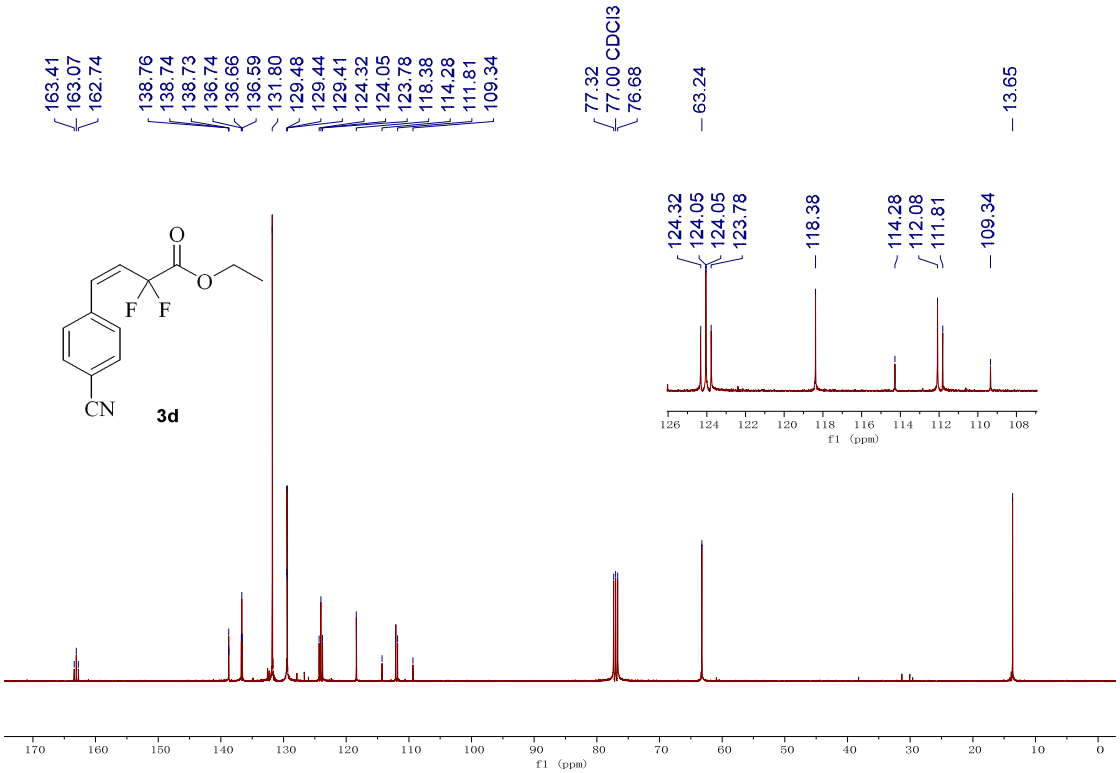
7.63
7.47
7.45
7.26 CDCl3
6.96
6.95
6.95
6.93
6.92
6.92
6.04
6.01
6.01
5.97
5.97
5.94
4.20
4.18
4.17
4.15
1.25
1.23
1.22
O
O
F F
CN
3d
2.31
2.00
1.01
0.99
2.02
3.58
f1 (ppm)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124.32
124.05
123.78
118.38
114.28
111.81
109.34
77.32
77.00 CDCl3
76.68
63.24
13.65
124.32
124.05
124.05
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112.08
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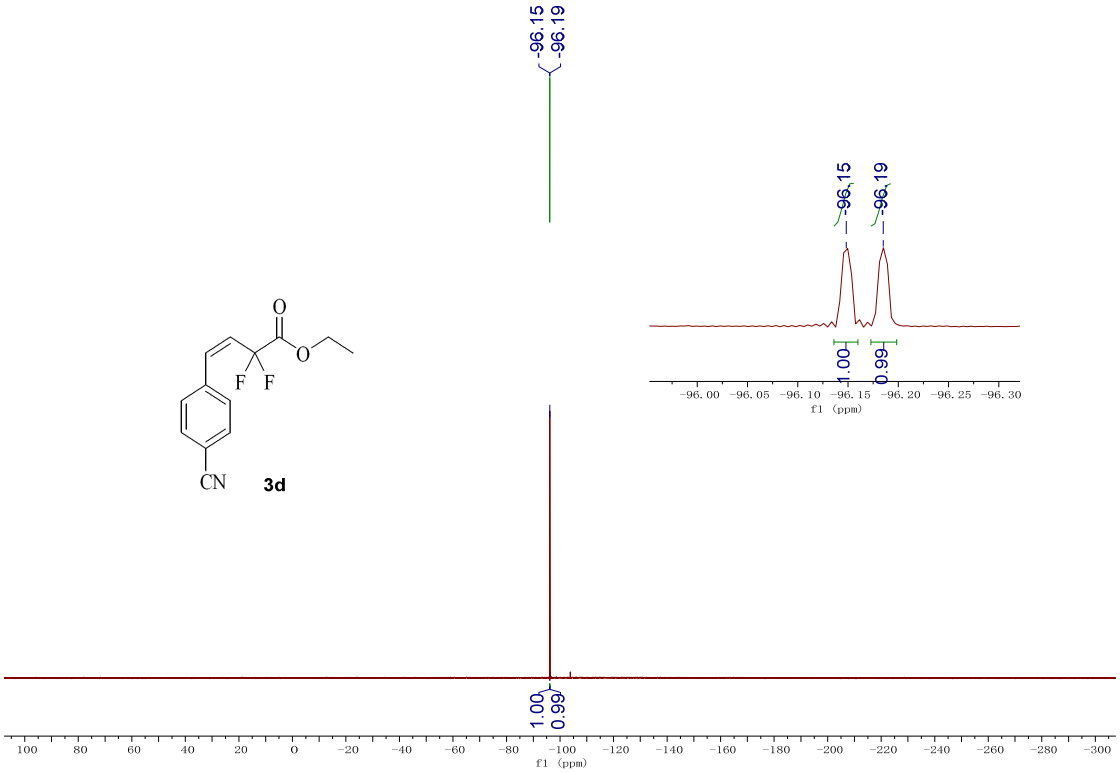
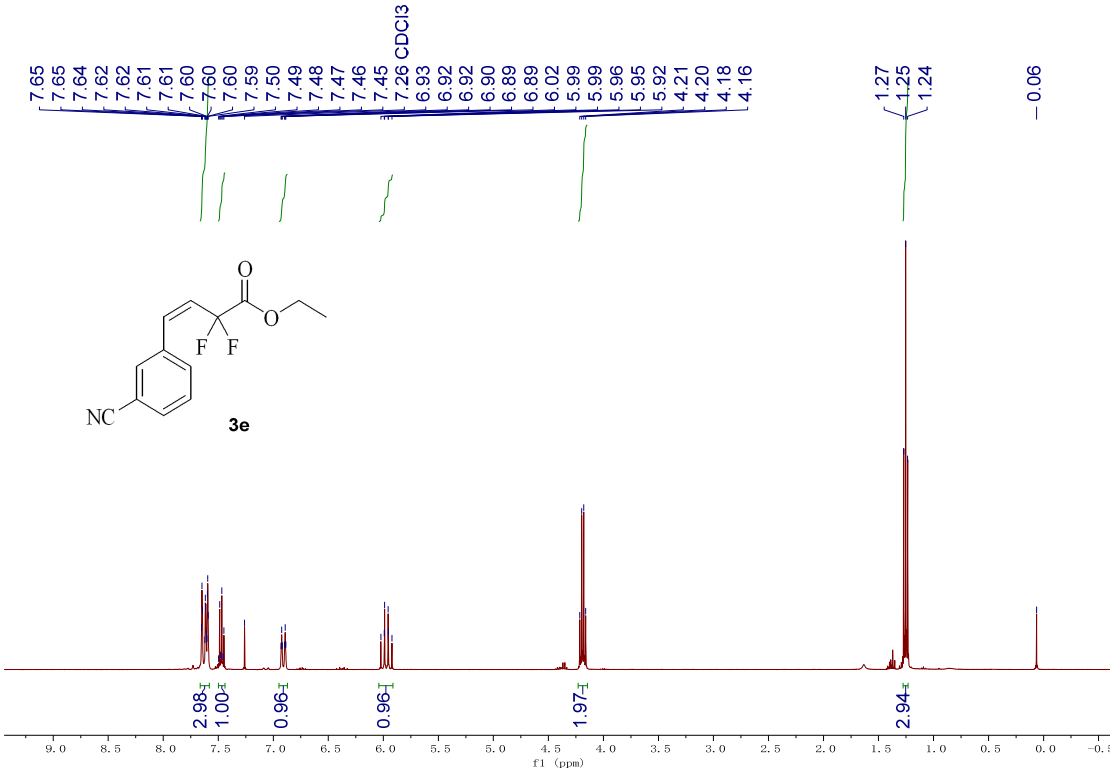
109.34
O
O
F F
CN
3d
f1 (ppm)
f1 (ppm)


-96.15
-96.19
-96.15
-96.19
1.00
0.99
-96.00 -96.05 -96.10 -96.15 -96.20 -96.25 -96.30
f1 (ppm)
O
O
F F
CN
3d
1.00
0.99
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)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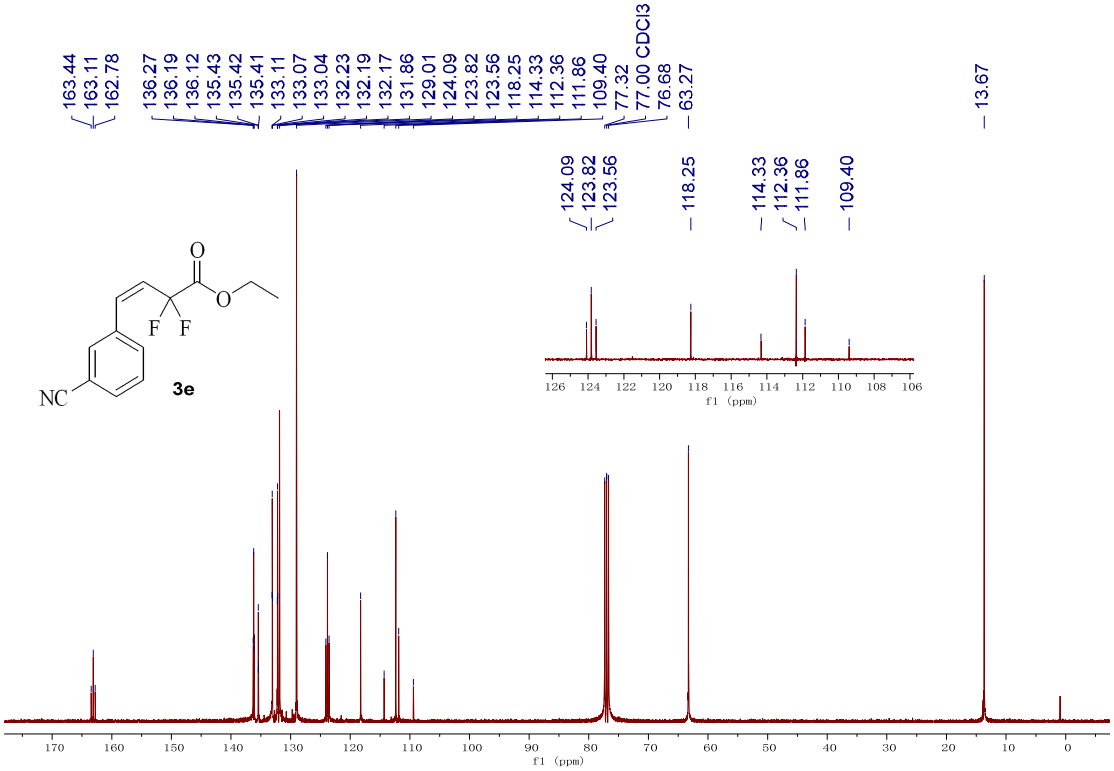
7.62
7.61
7.61
7.60
7.60
7.60
7.59
7.50
7.49
7.48
7.47
7.46
7.45
CDCl3
6.93
6.92
6.92
6.90
6.89
6.89
6.02
5.99
5.99
5.96
5.95
5.92
4.21
4.20
4.18
4.16
1.27
1.25
1.24
0.06
O
O
F F
NC
3e
2.98
1.00
0.96
0.96
1.97
2.94
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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135.43
135.42
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133.11
133.07
133.04
132.23
132.19
132.17
131.86
129.01
124.09
123.82
123.56
118.25
114.33
112.36
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109.40
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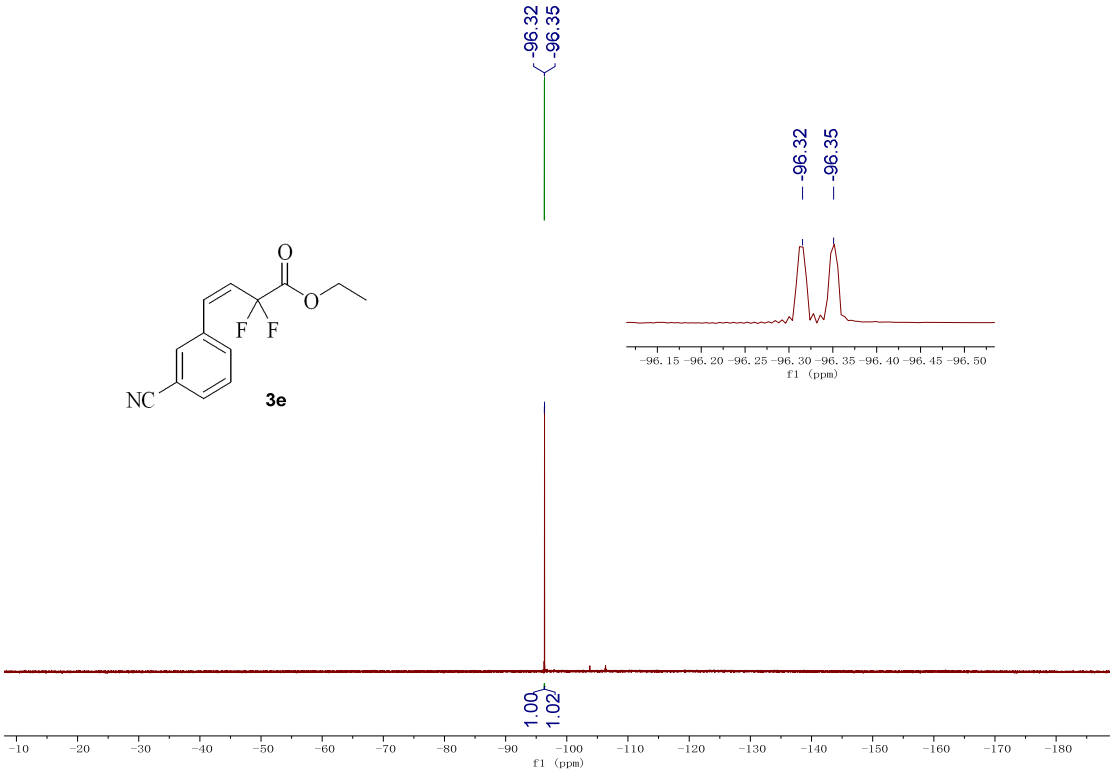
77.00 CDCl3
76.68
63.27
13.67
O
O
F F
NC
3e
f1 (ppm)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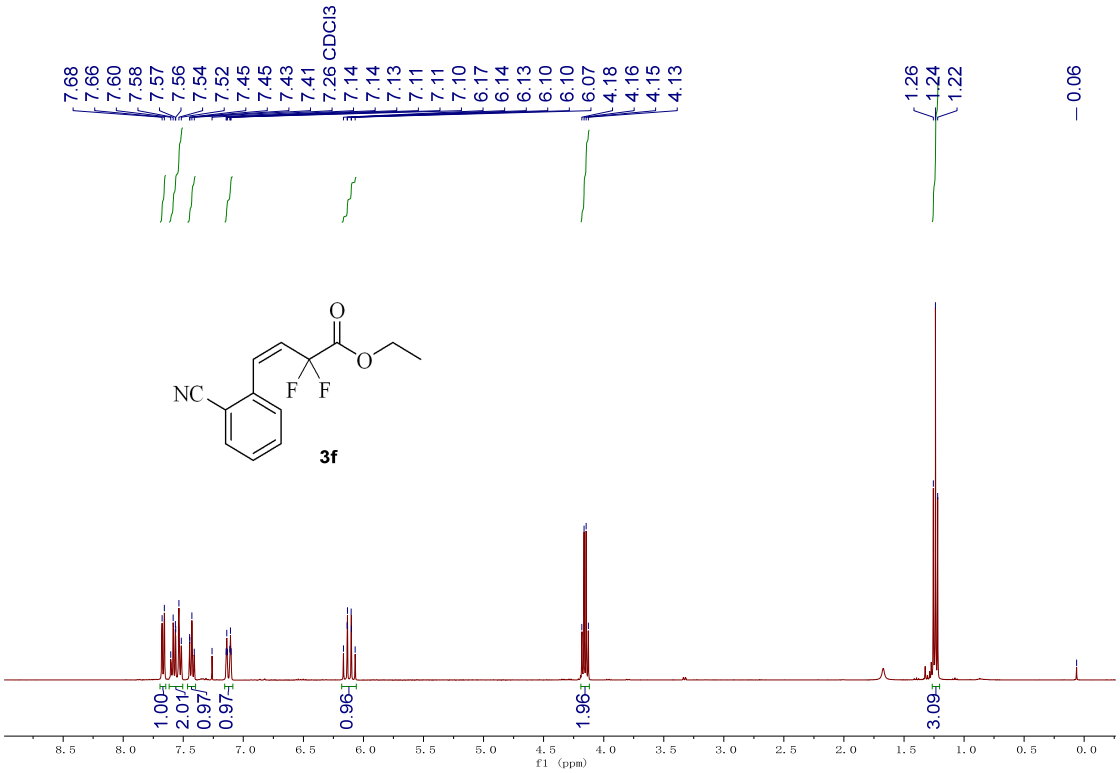
-96.35
O
O
F F
NC
3e
f1 (ppm)
1.00
1.02
f1 (ppm)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7.56
7.54
7.52
7.45
7.45
7.43
7.41
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7.14
7.14
7.13
7.11
7.11
7.10
6.17
6.14
6.13
6.10
6.10
6.07
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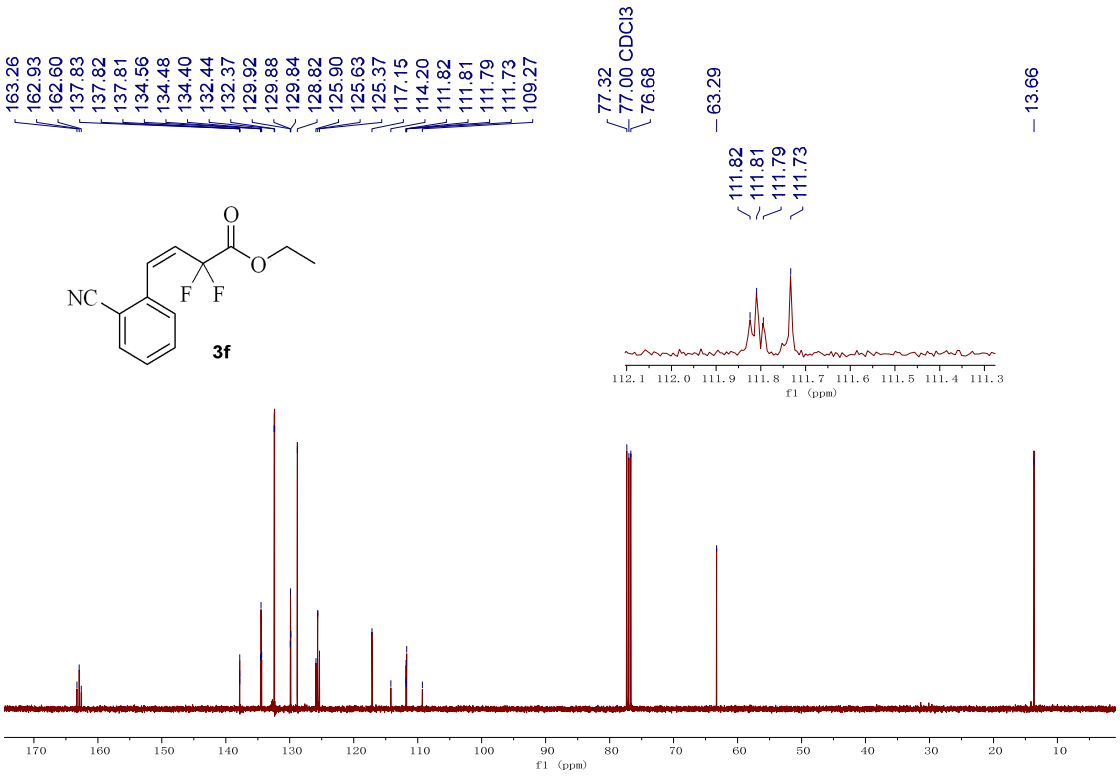
4.16
4.15
4.13
1.26
1.24
1.22
0.06
O
O
NC
F F
3f
1.00
2.01
0.97
0.97
0.96
1.96
3.09
f1 (ppm)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129.88
129.84
128.82
125.90
125.63
125.37
117.15
114.20
111.82
111.81
111.79
111.73
109.27
77.32
77.00 CDCl3
76.68
63.29
13.66
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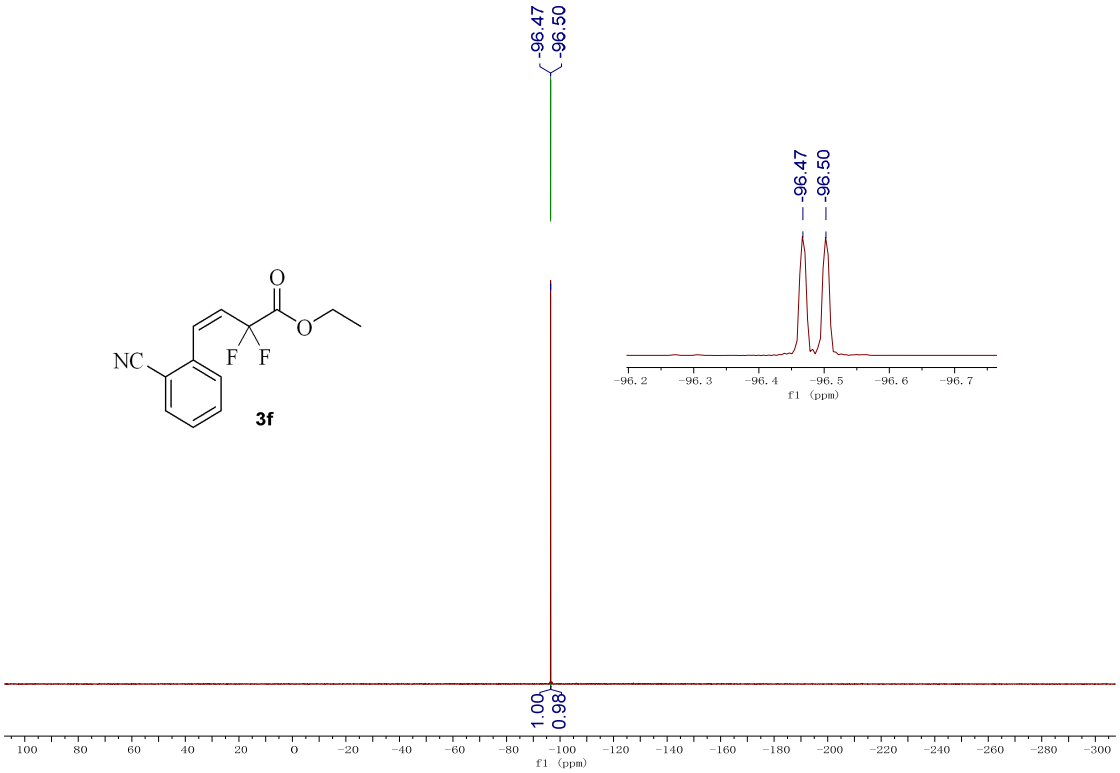
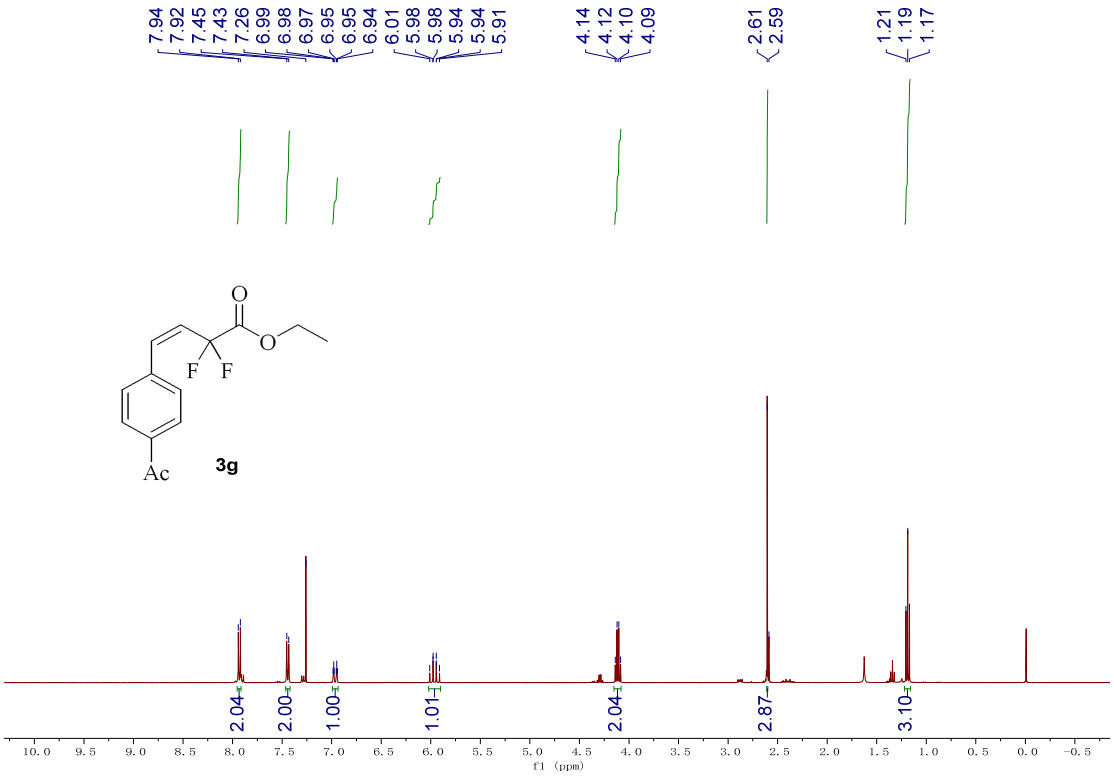
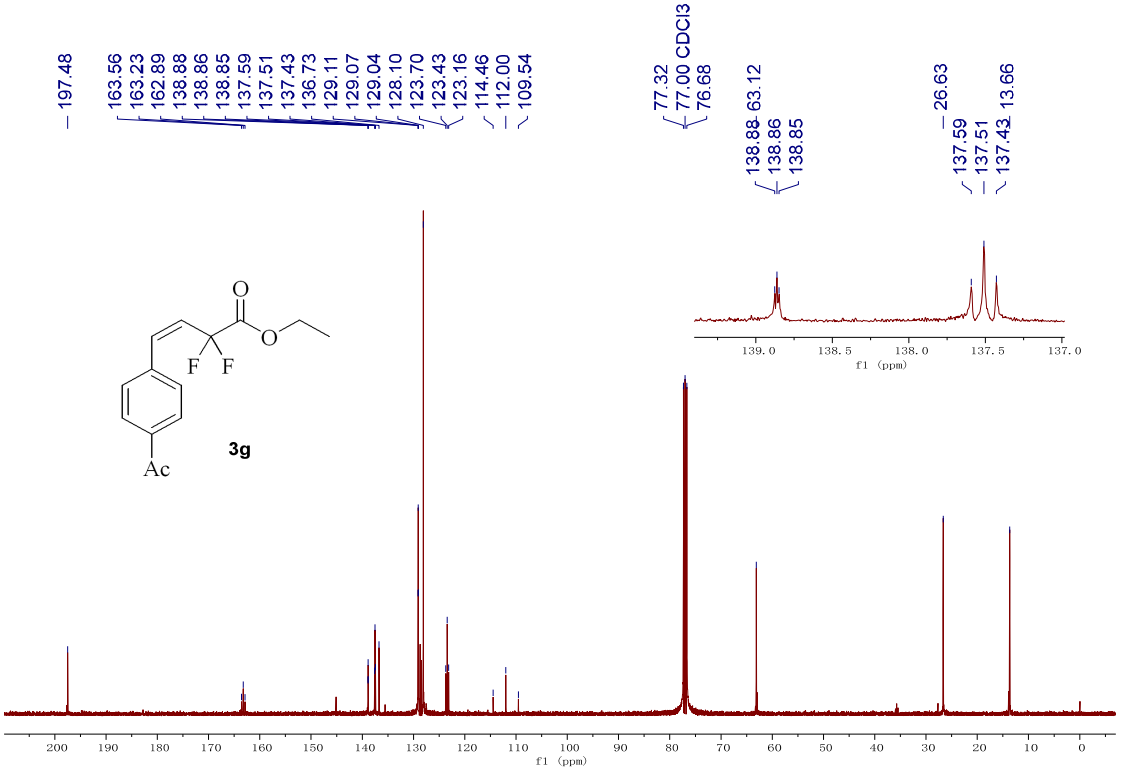
111.81
111.79
111.73
O
O
NC
F F
3f
f1 (ppm)
f1 (ppm)


-96.47
-96.50
O
O
F F
NC
3f
-96.47
-96.50
-96.2 -96.3 -96.4 -96.5 -96.6 -96.7
f1 (ppm)
1.00
0.98
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)


7.94
7.92
7.45
7.43
7.26
6.99
6.98
6.97
6.95
6.95
6.94
6.01
5.98
5.98
5.94
5.94
5.91
4.14
4.12
4.10
4.09
2.61
2.59
1.21
1.19
1.17
O
O
F F
Ac
3g
2.04
2.00
1.00
1.01
2.04
2.87
3.10
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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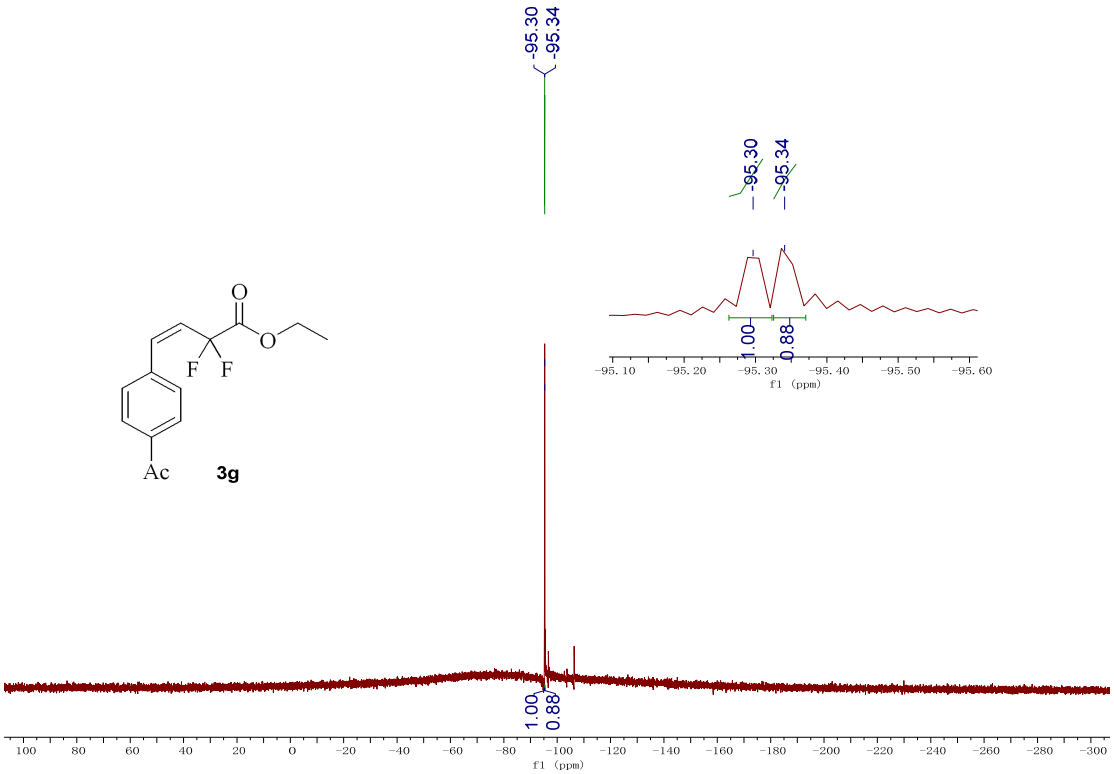
138.86
138.85
137.59
137.51
137.43
136.73
129.11
129.07
129.04
128.10
123.70
123.43
123.16
114.46
112.00
109.54
77.32
77.00 CDCl3
76.68
63.12
138.88
138.86
138.85
26.63
137.59
137.51
137.43
13.66
O
O
F F
Ac
3g
f1 (ppm)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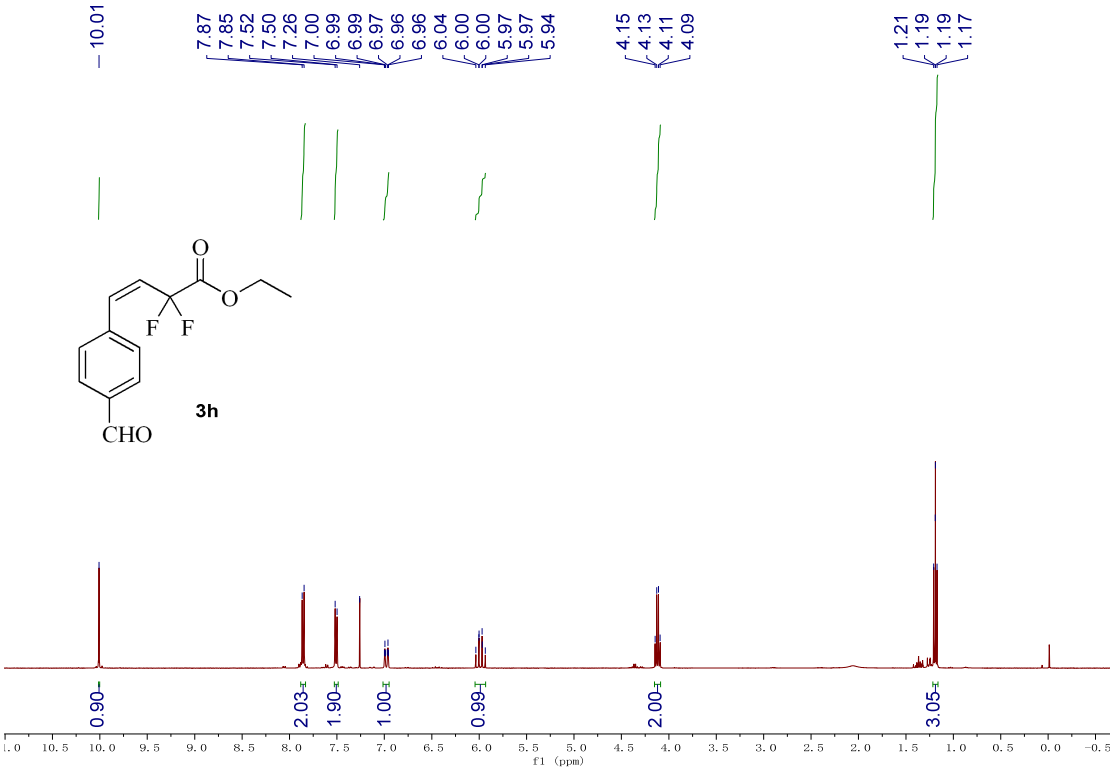
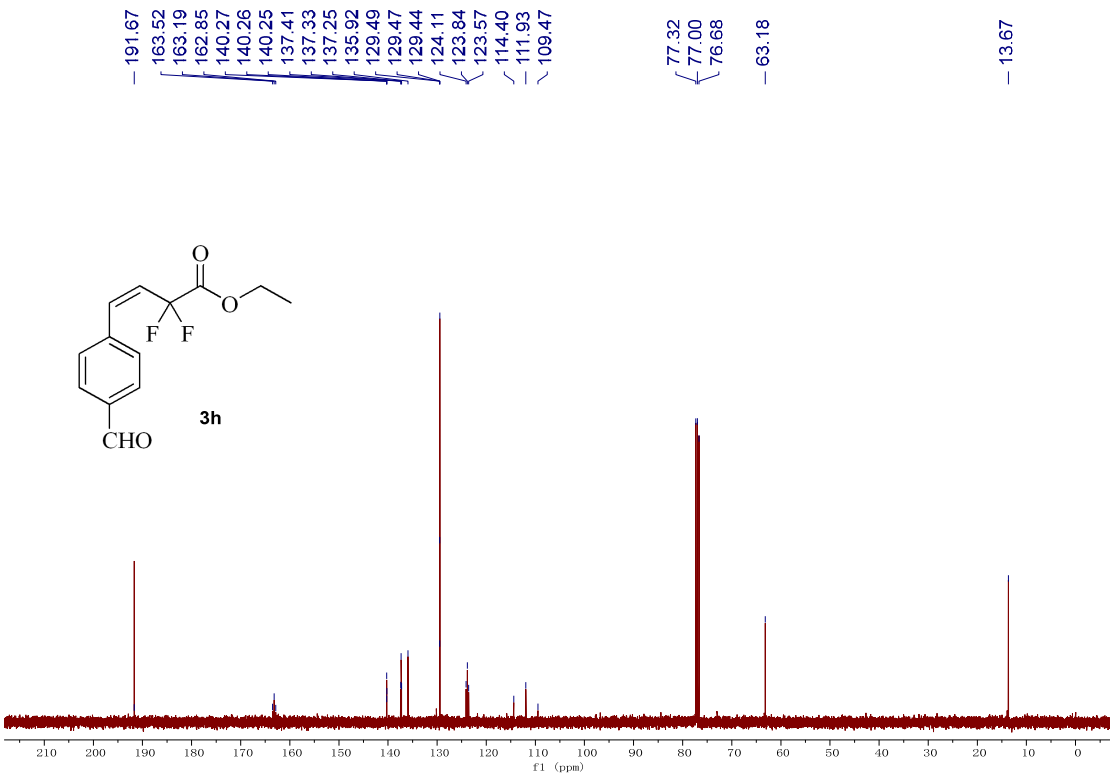
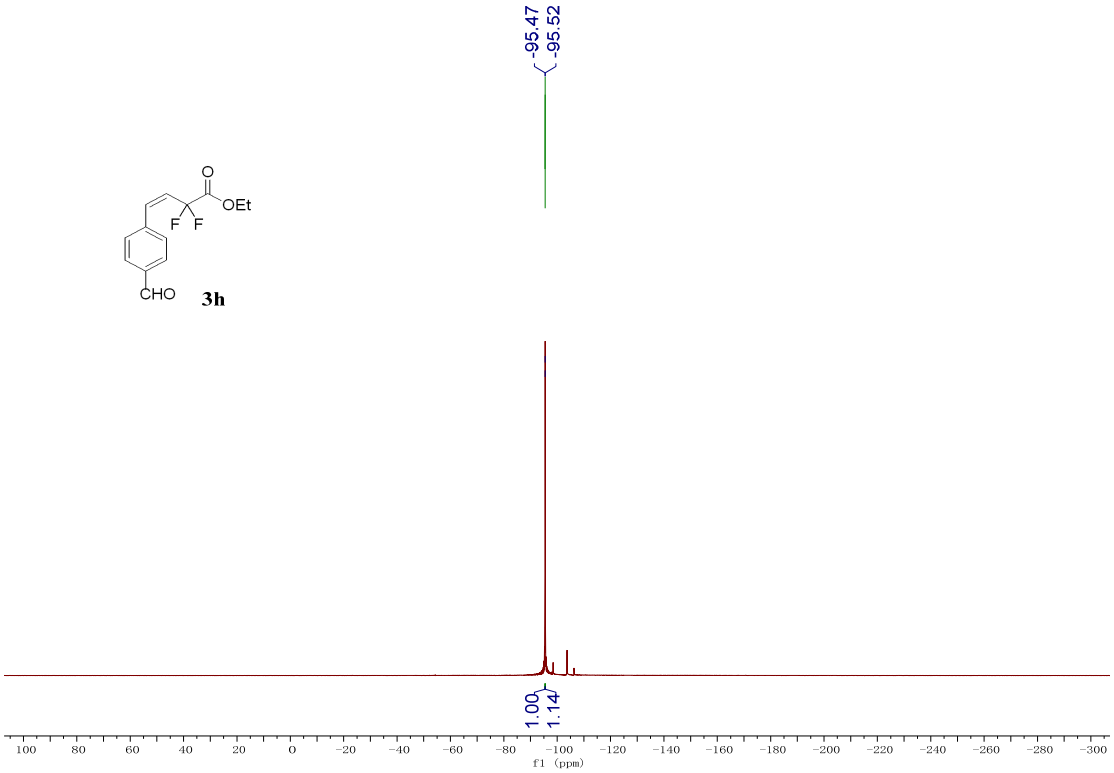
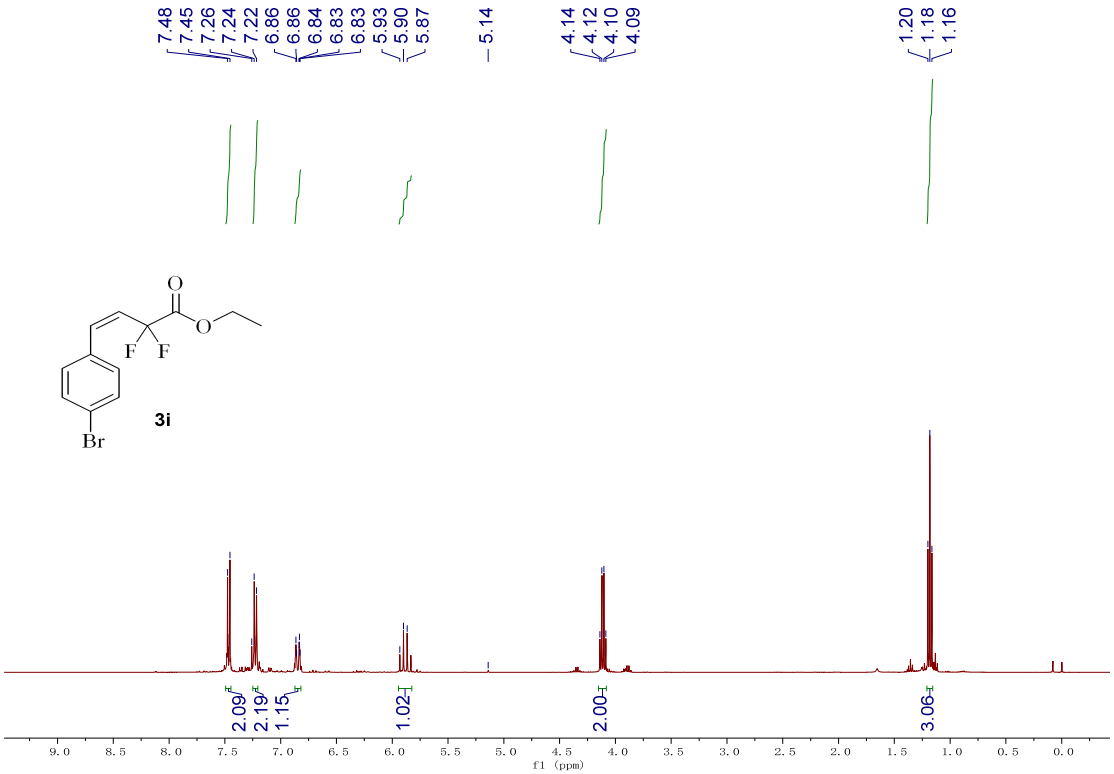
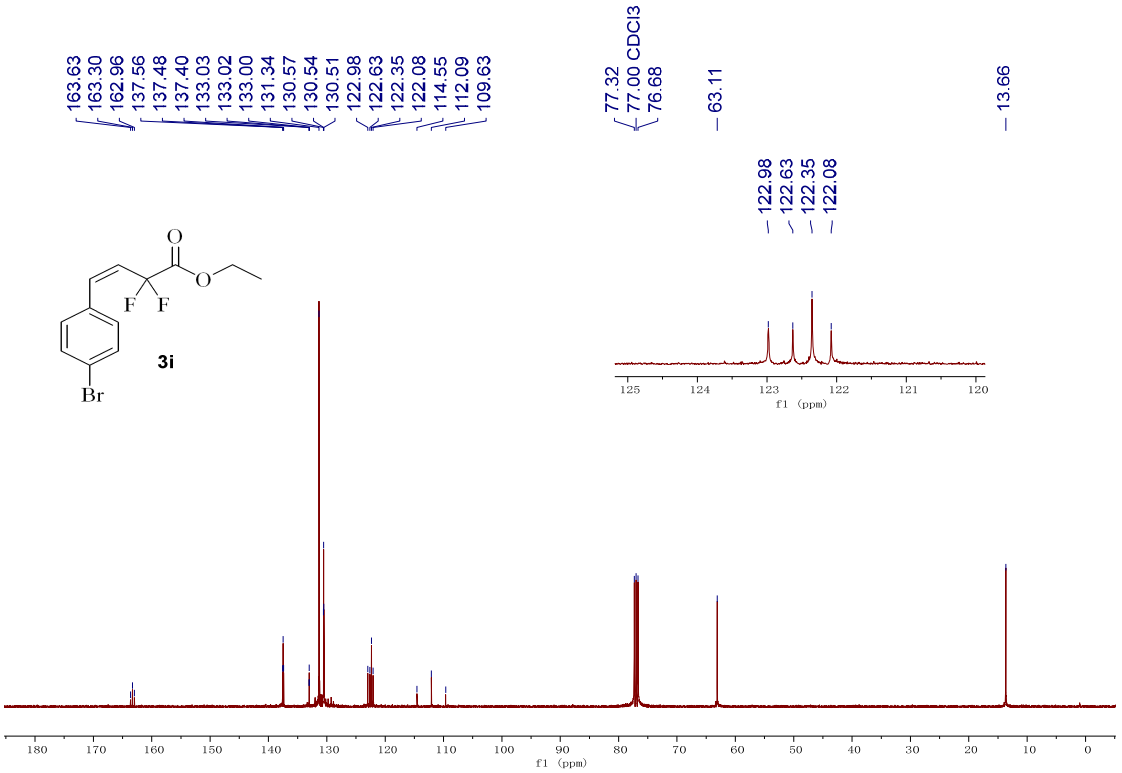
-95.30
-95.34
1.00
0.88
O
O
F F
Ac
3g
f1 (ppm)


10.01
7.87
7.85
7.52
7.50
7.26
7.00
6.99
6.99
6.97
6.96
6.96
6.04
6.00
6.00
5.97
5.97
5.94
4.15
4.13
4.11
4.09
1.21
1.19
1.19
1.17
O
O
F F
CHO
3h
0.90
2.03
1.90
1.00
0.99
2.00
3.05
f1 (ppm)


191.67
163.52
163.19
162.85
140.27
140.26
140.25
137.41
137.33
137.25
135.92
129.49
129.47
129.44
124.11
123.84
123.57
114.40
111.93
109.47
77.32
77.00
76.68
63.18
13.67
O
O
F F
CHO
3h
f1 (ppm)


-95.47
-95.52
O
OEt
F F
CHO
3h
1.00
1.14
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)


7.48
7.45
7.26
7.24
7.22
6.86
6.86
6.84
6.83
6.83
5.93
5.90
5.87
5.14
4.14
4.12
4.10
4.09
1.20
1.18
1.16
O
O
F F
3i
Br
2.09
2.19
1.15
1.02
2.00
3.06
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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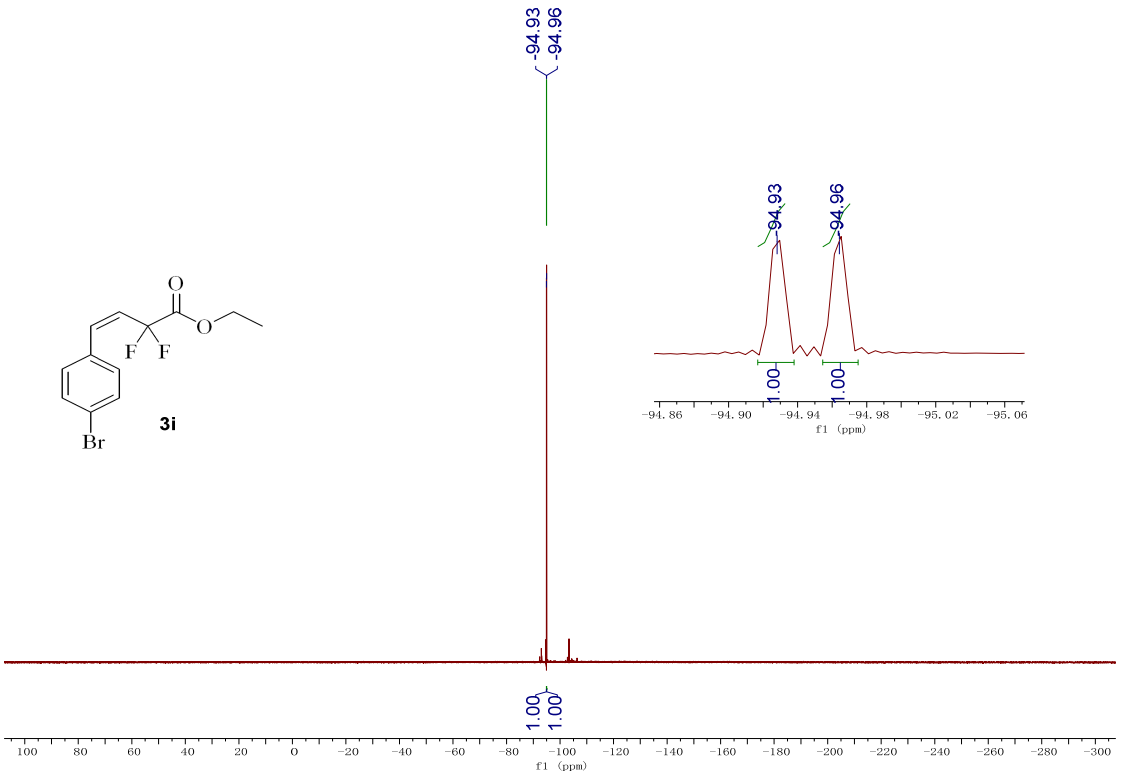
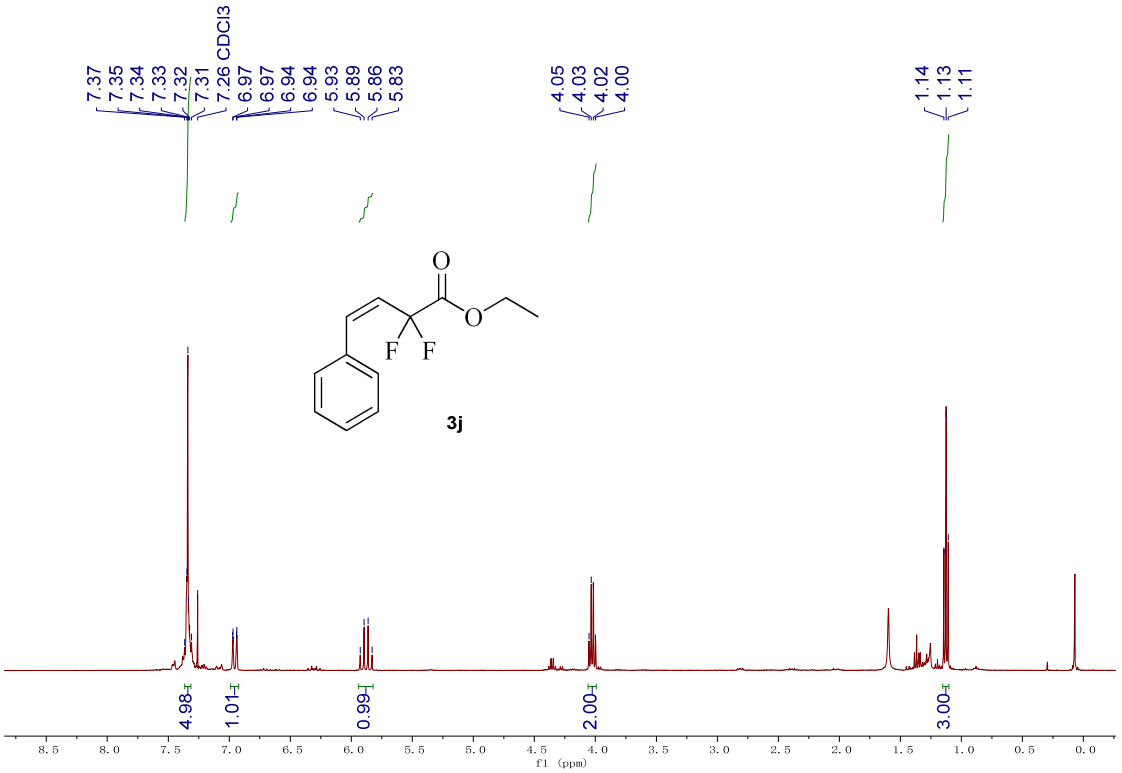
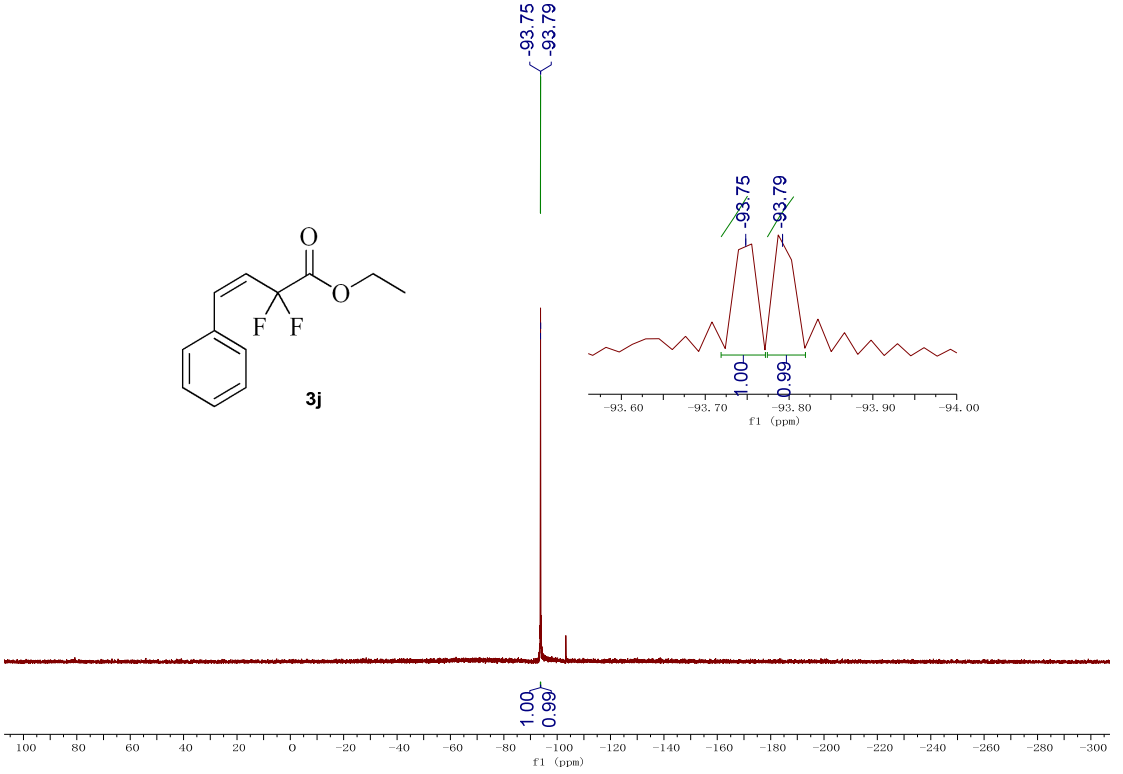
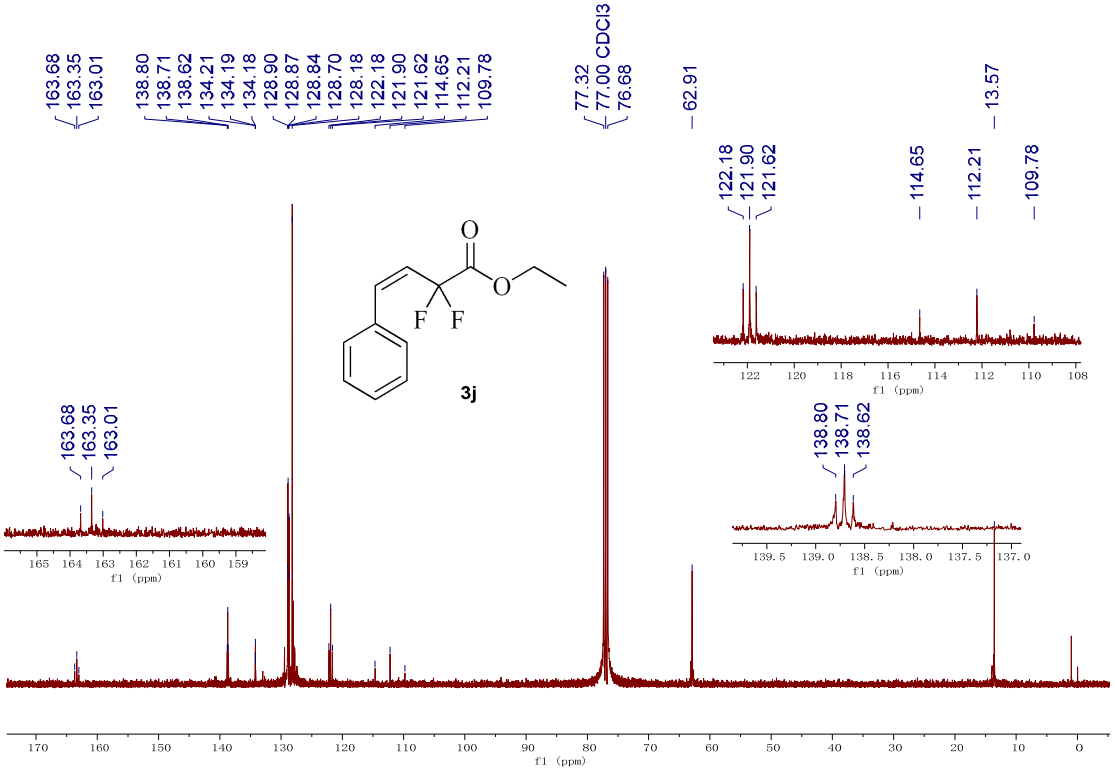
163.30
162.96
137.56
137.48
137.40
133.03
133.02
133.00
131.34
130.57
130.54
130.51
122.98
122.63
122.35
122.08
114.55
112.09
109.63
77.32
77.00 CDCl3
76.68
63.11
13.66
122.98
122.63
122.35
122.08
O
O
F F
Br
3i
f1 (ppm)


-94.93
-94.96
-94.93
-94.96
1.00
1.00
1.00
1.00
O
O
F F
Br
3i
f1 (ppm)


7.37
7.35
7.34
7.33
7.32
7.31
7.26 CDCl3
6.97
6.97
6.94
6.94
5.93
5.89
5.86
5.83
4.05
4.03
4.02
4.00
1.14
1.13
1.11
O
O
F F
3j
4.98
1.01
0.99
2.00
3.00
f1 (ppm)


-93.75
-93.79
O
O
F F
3j
-93.75
-93.79
1.00
0.99
f1 (ppm)
1.00
0.99
f1 (ppm)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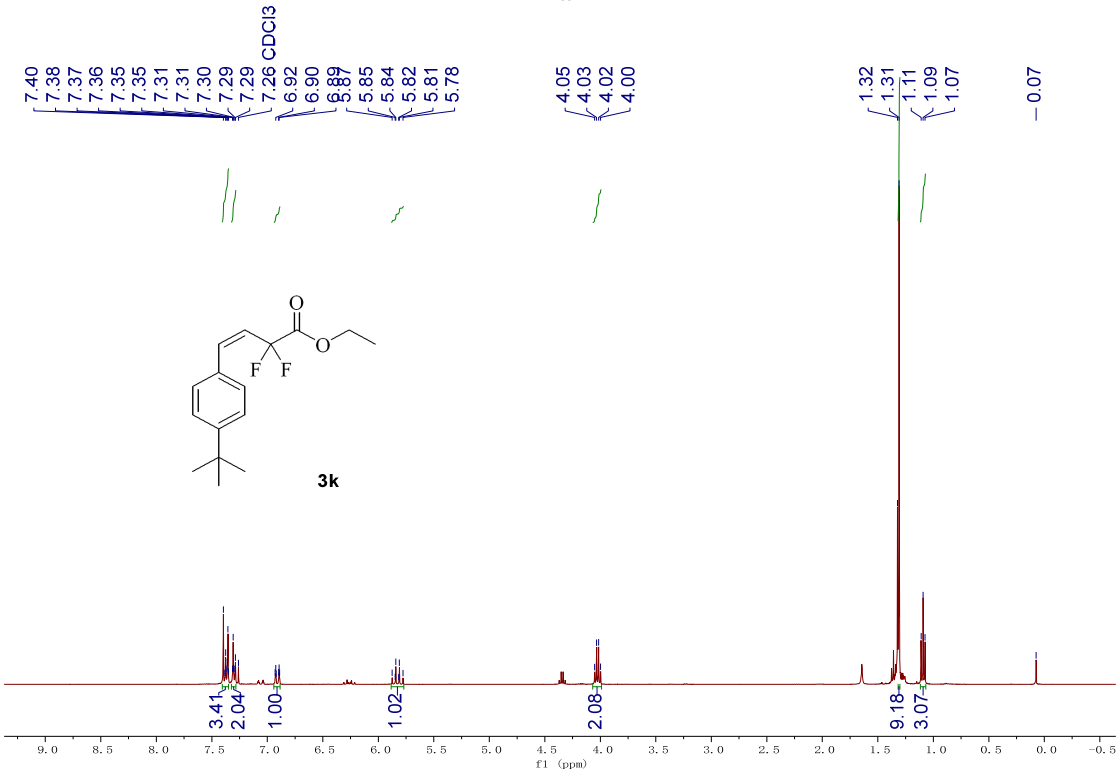
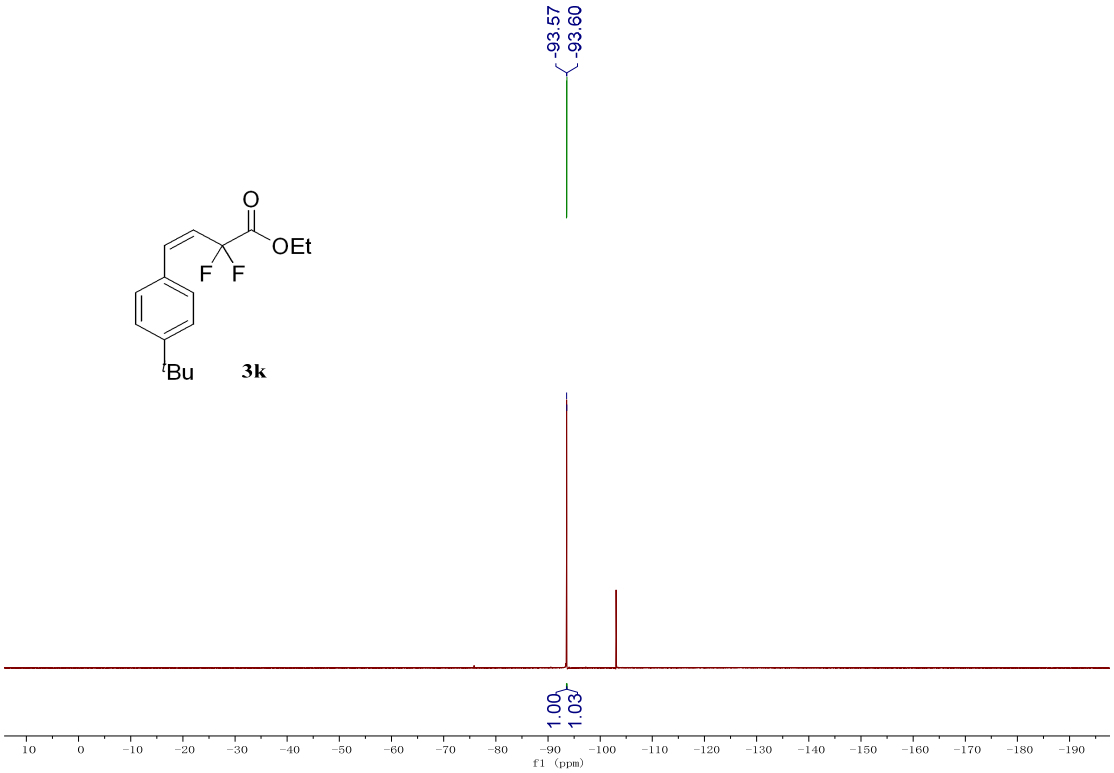
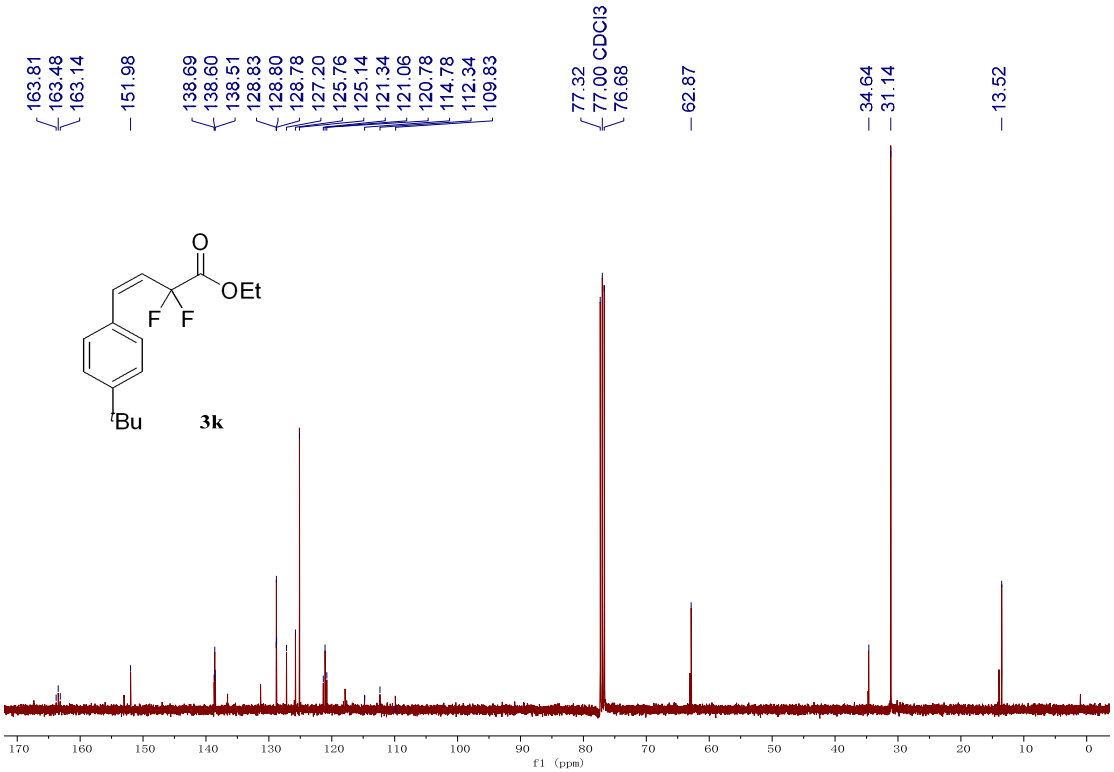
163.35
163.01
138.80
138.71
138.62
134.21
134.19
134.18
128.90
128.87
128.84
128.70
128.18
122.18
121.90
121.62
114.65
112.21
109.78
77.32
77.00 CDCl3
76.68
62.91
13.57
O
O
F F
3j
f1 (ppm)


7.40
7.38
7.37
7.36
7.35
7.35
7.31
7.31
7.30
7.29
7.29
7.26 CDCl3
6.92
6.90
5.85
5.84
5.82
5.81
5.78
4.05
4.03
4.02
4.00
1.32
1.31
1.11
1.09
1.07
0.07
O
O
F F
3k
3.41
2.04
1.00
1.02
2.08
9.18
3.07
f1 (ppm)


-93.57
-93.60
O
OEt
F F
tBu
3k
1.00
1.03
f1 (ppm)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151.98
138.69
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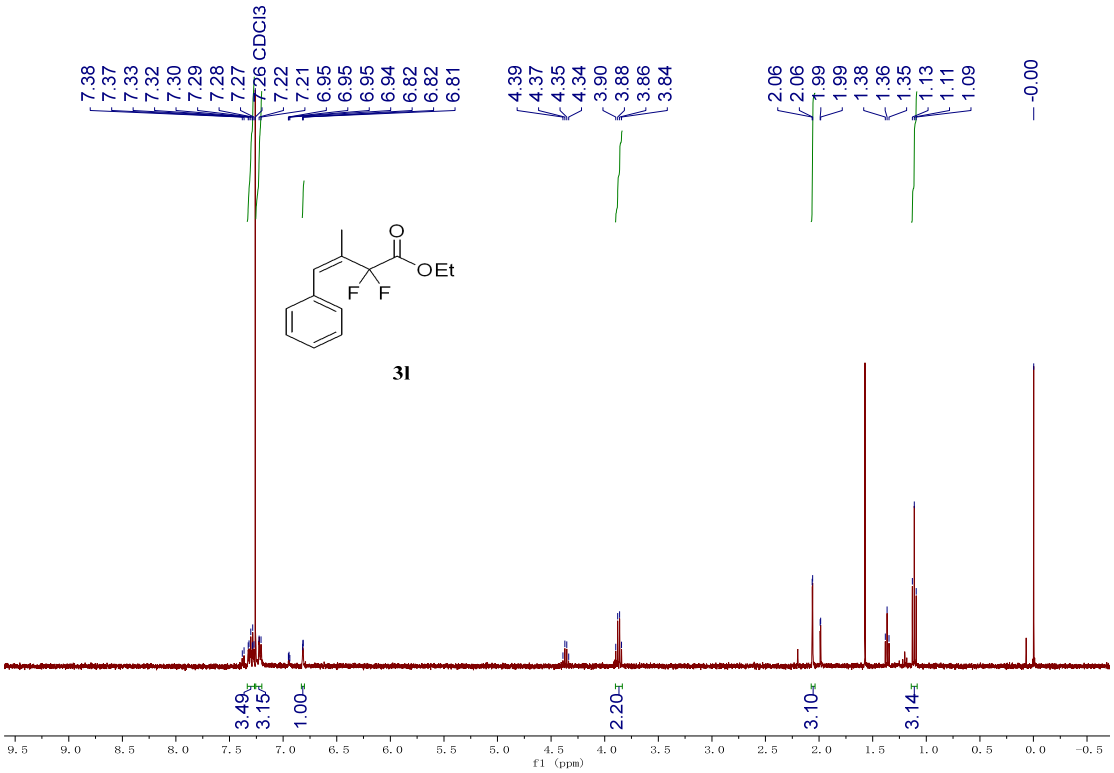
138.51
128.83
128.80
128.78
127.20
125.76
125.14
121.34
121.06
120.78
114.78
112.34
109.83
77.32
77.00 CDCl3
76.68
62.87
34.64
31.14
13.52
O
OEt
F F
tBu
3k
f1 (ppm)


7.38
7.37
7.33
7.32
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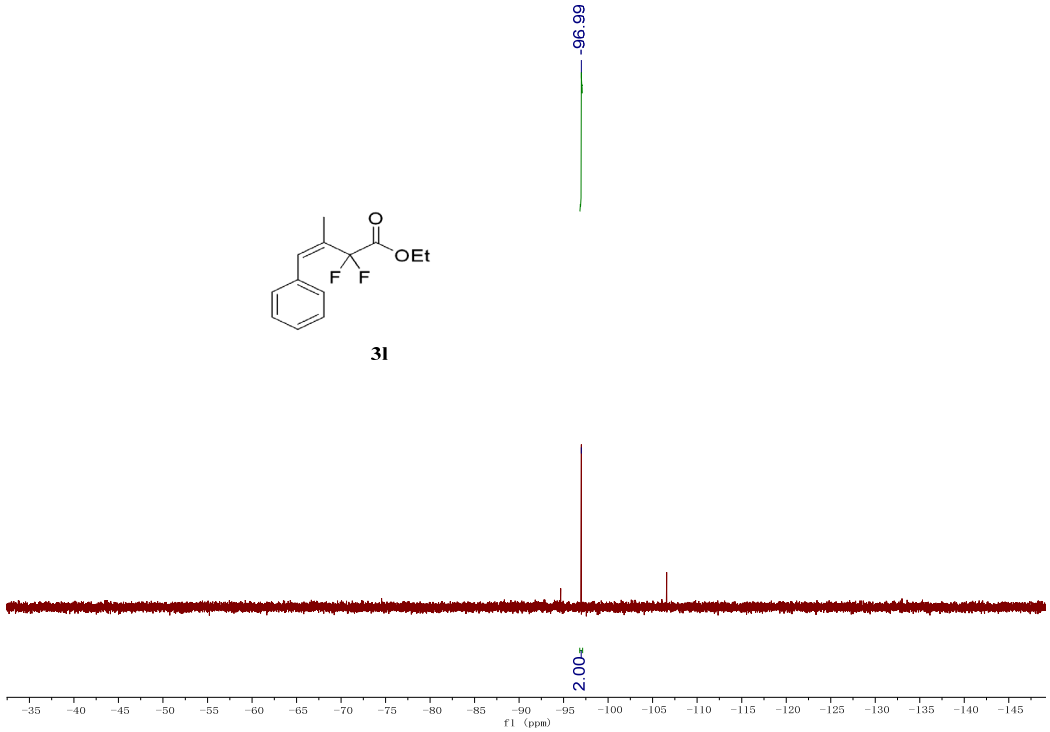
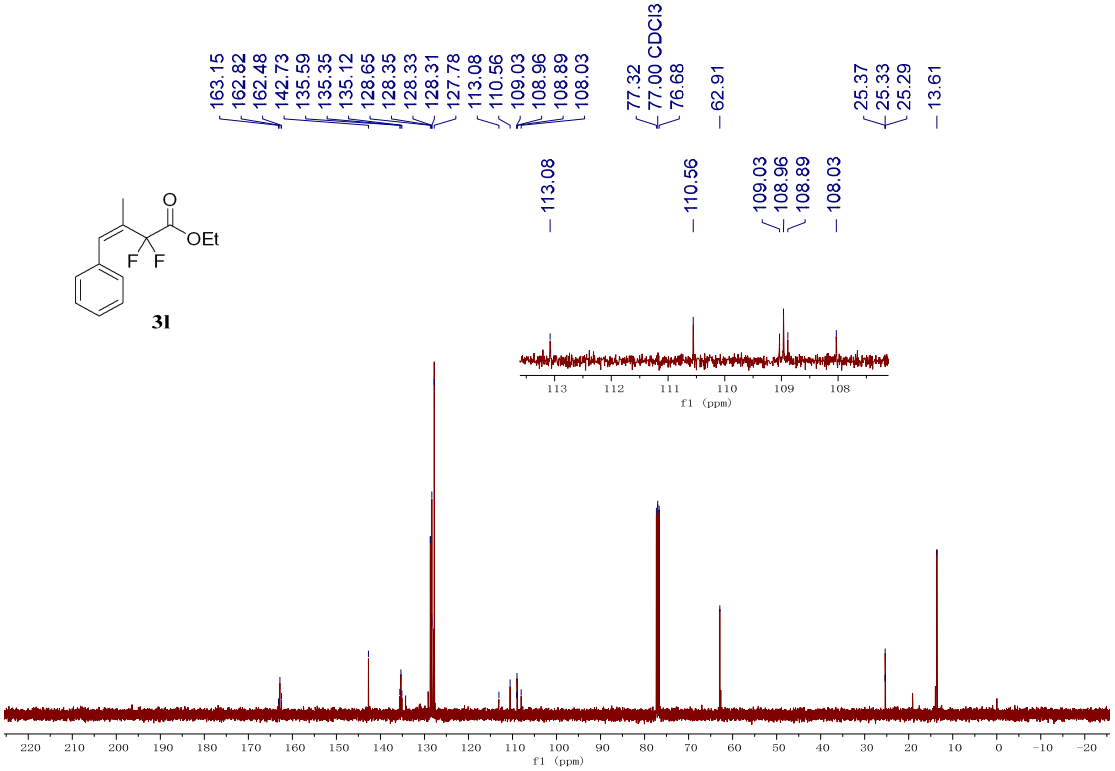
7.29
7.28
7.27
7.26 CDCl3
7.22
7.21
6.95
6.95
6.95
6.94
6.82
6.82
6.81
4.39
4.37
4.35
4.34
3.90
3.88
3.86
3.84
2.06
2.06
1.99
1.99
1.38
1.36
1.35
1.13
1.11
1.09
-0.00
O
OEt
F F
3l
3.49
3.15
1.00
2.20
3.10
3.14
f1 (ppm)


-96.99
O
OEt
F F
3l
2.00
f1 (ppm)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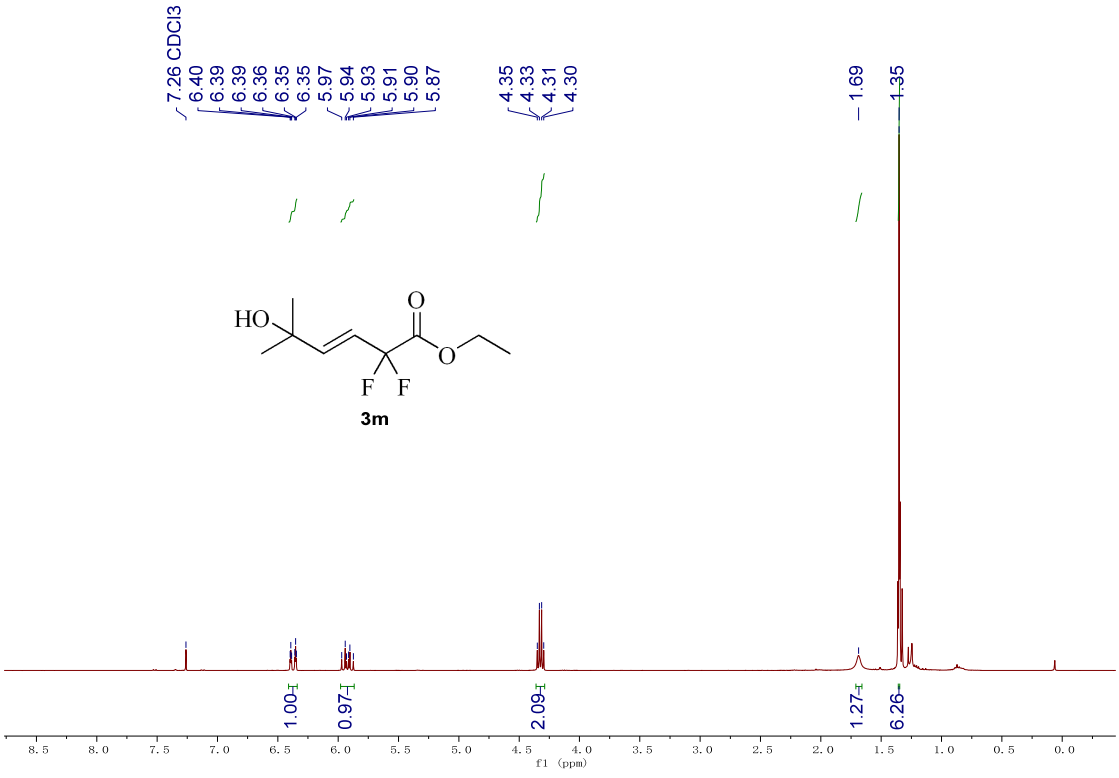
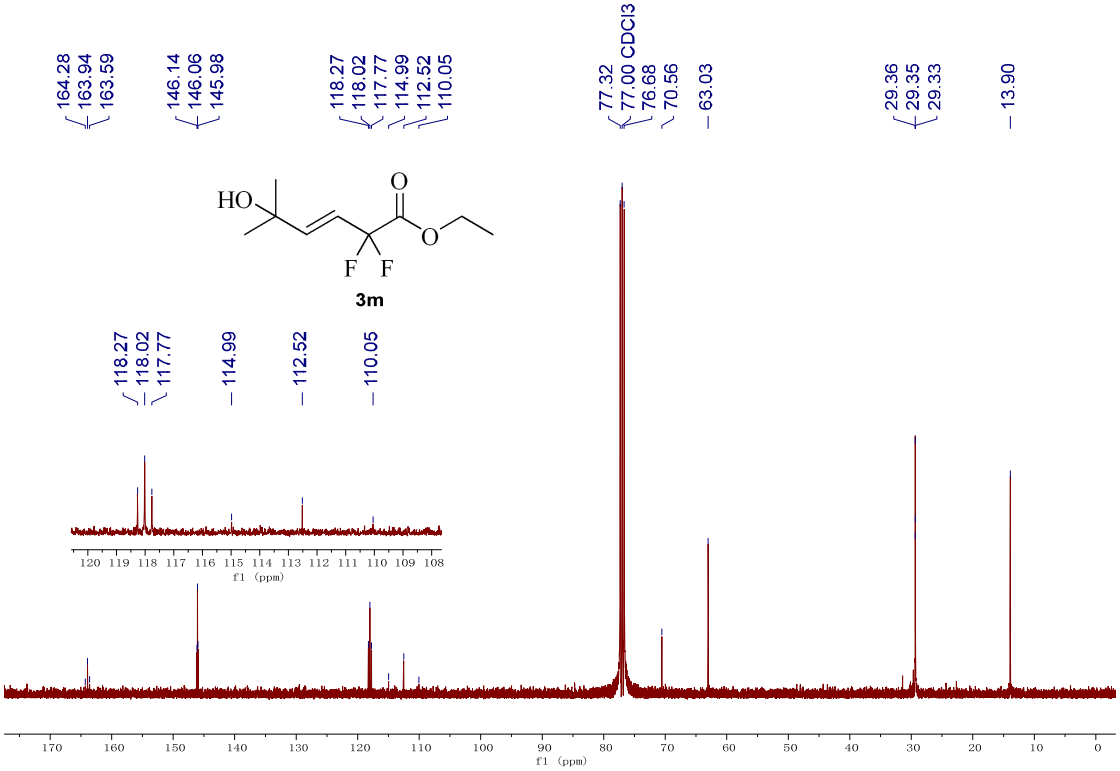
162.82
162.48
142.73
135.59
135.35
135.12
128.65
128.35
128.33
128.31
127.78
113.08
110.56
109.03
108.96
108.89
108.03
77.32
77.00 CDCl3
76.68
62.91
25.37
25.33
25.29
13.61
O
OEt
F F
3l
f1 (ppm)


7.26 CDCl3
6.40
6.39
6.39
6.36
6.35
6.35
5.97
5.94
5.93
5.91
5.90
5.87
4.35
4.33
4.31
4.30
1.69
1.35
HO
O
O
F F
3m
1.00
0.97
2.09
1.27
6.26
f1 (ppm)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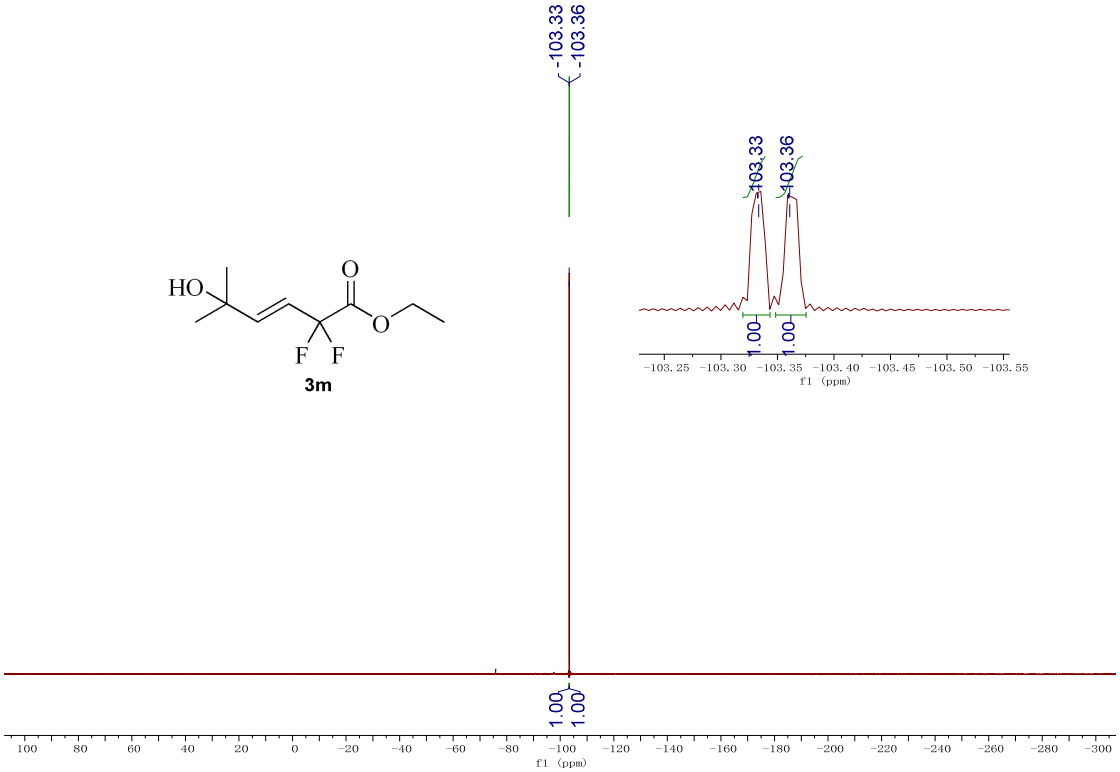
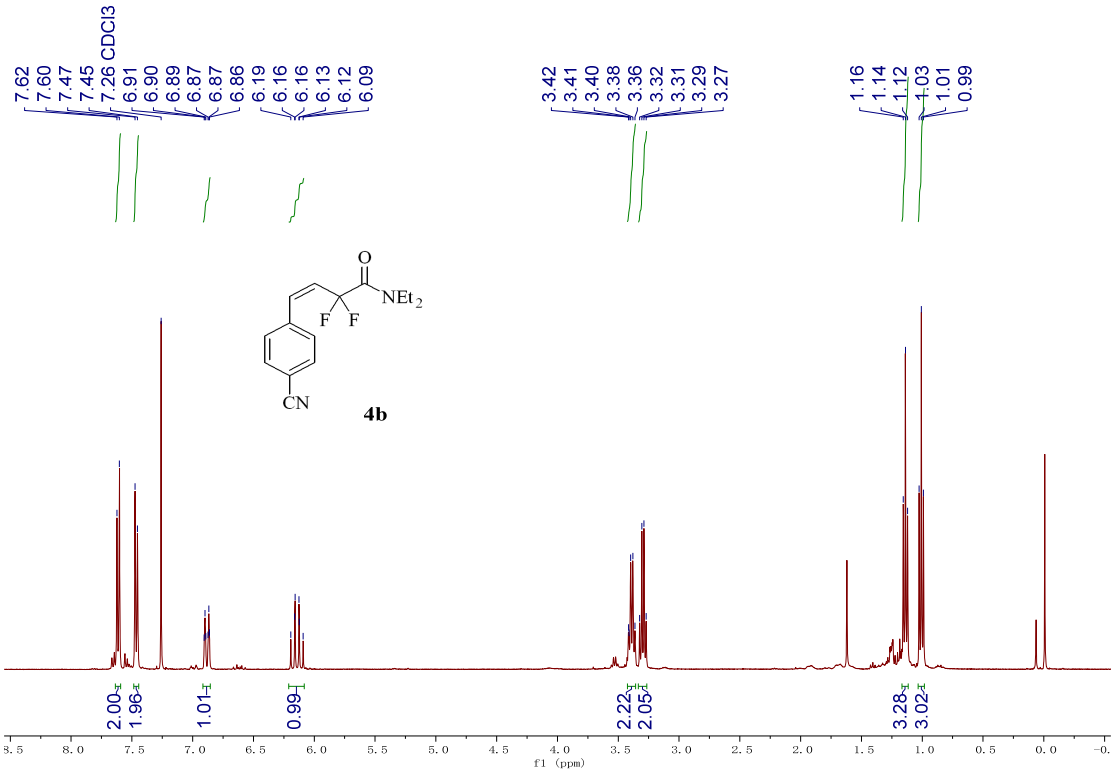
163.94
163.59
146.14
146.06
145.98
118.27
118.02
117.77
114.99
112.52
110.05
77.32
77.00 CDCl3
76.68
70.56
63.03
29.36
29.35
29.33
13.90
HO
O
O
F F
3m
f1 (ppm)


-103.33
-103.36
103.33
103.36
1.00
1.00
HO
O
O
F F
3m
f1 (ppm)


7.62
7.60
7.47
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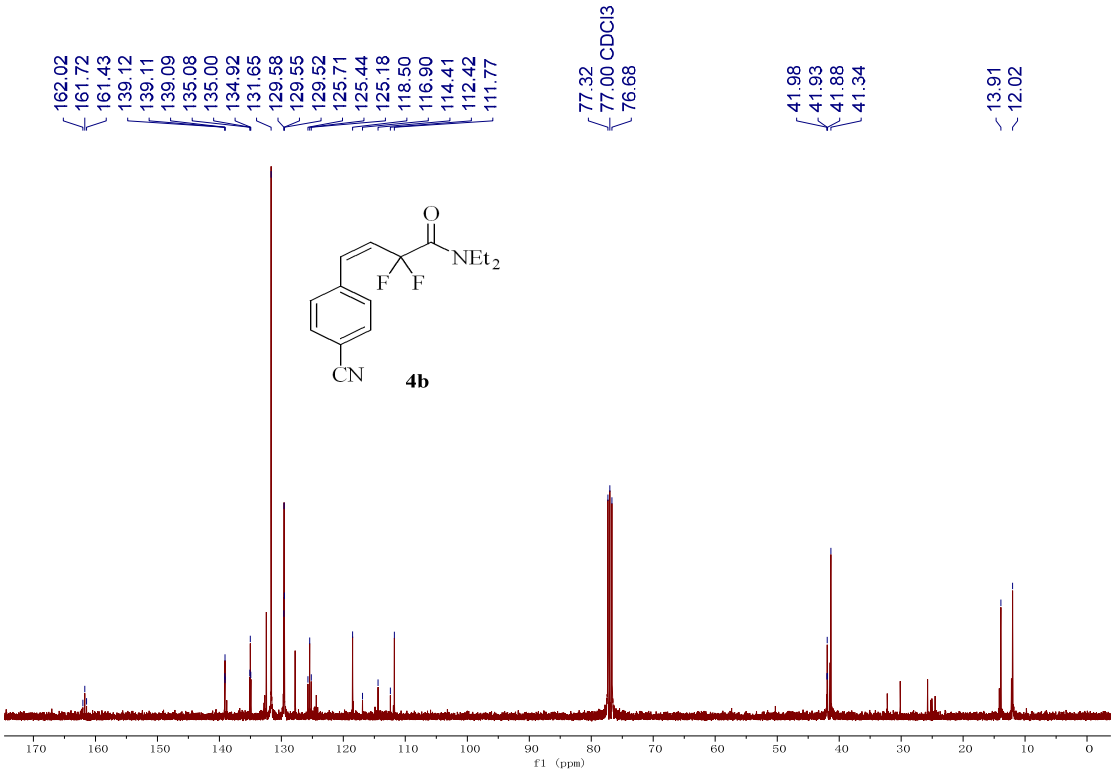
6.91
6.90
6.89
6.87
6.87
6.86
6.19
6.16
6.16
6.13
6.12
6.09
3.42
3.41
3.40
3.38
3.36
3.32
3.31
3.29
3.27
1.16
1.14
1.12
1.03
1.01
0.99
O
NEt2
F F
CN
4b
2.00
1.96
1.01
0.99
2.22
2.05
3.28
3.02
f1 (ppm)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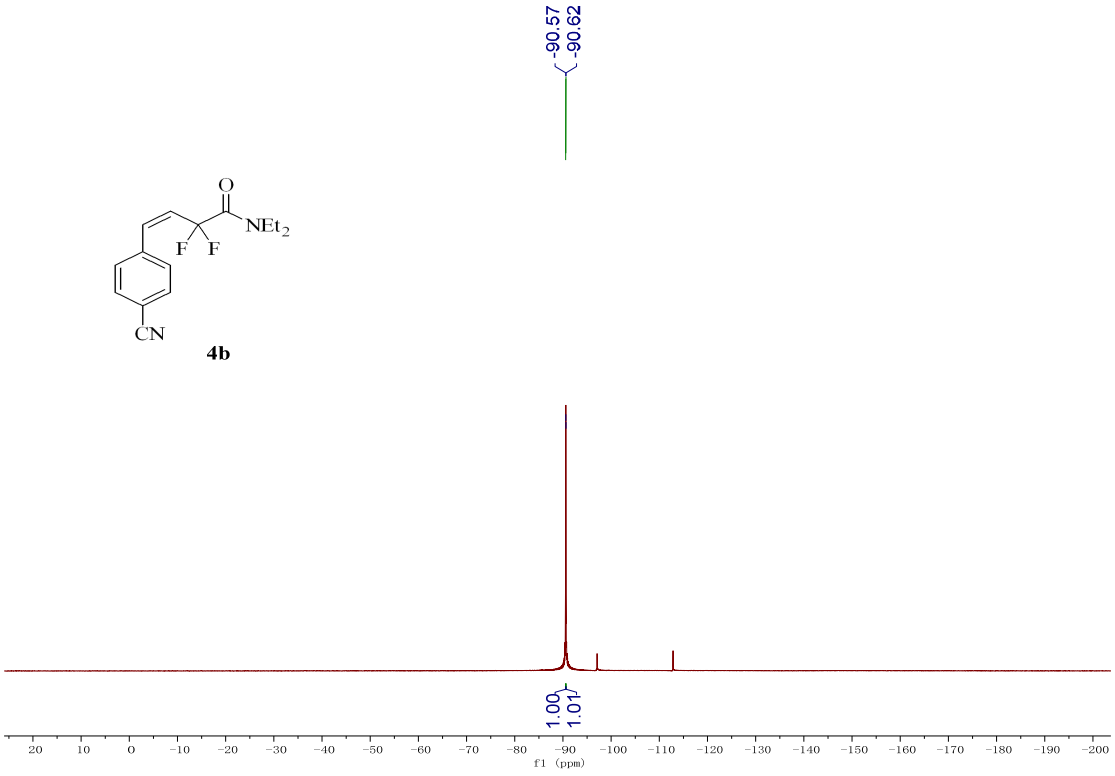
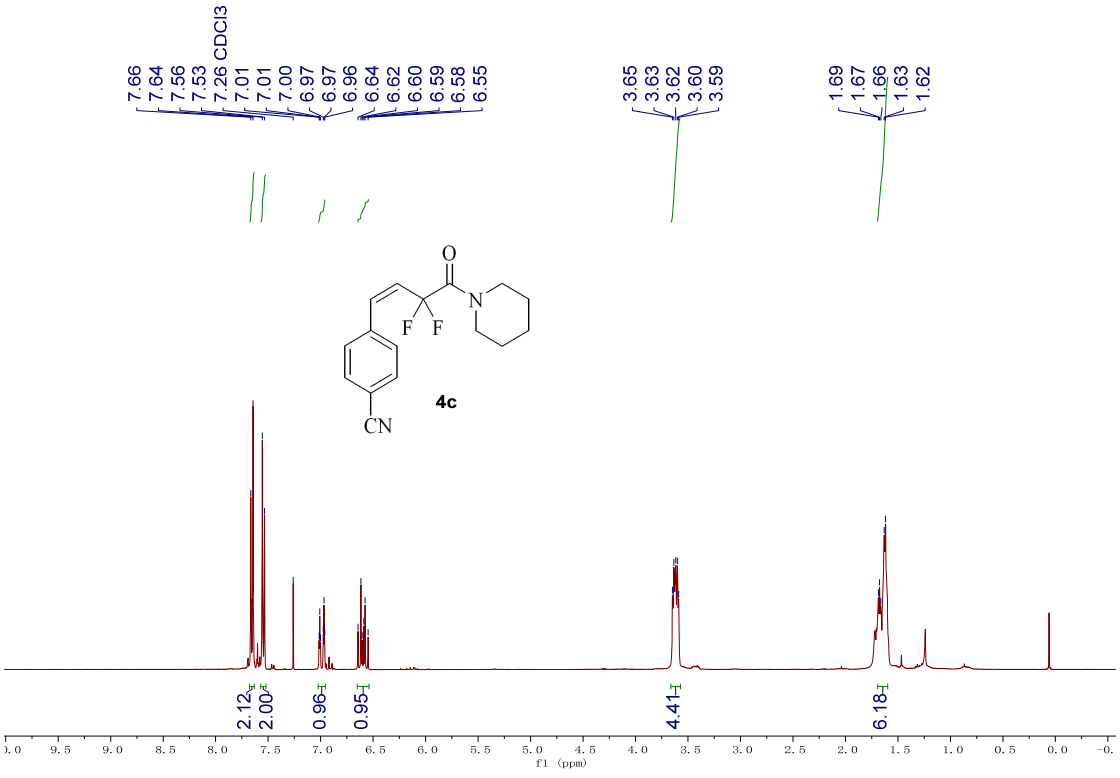
135.00
134.92
131.65
129.58
129.55
129.52
125.71
125.44
125.18
118.50
116.90
114.41
112.42
111.77
77.32
77.00 CDCl3
76.68
41.98
41.93
41.88
41.34
13.91
12.02
O
NEt2
F F
CN
4b
f1 (ppm)


-90.57
-90.62
O
NEt2
F F
CN
4b
1.00
1.01
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)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7.53
7.26 CDCl3
7.01
7.01
7.00
6.97
6.97
6.96
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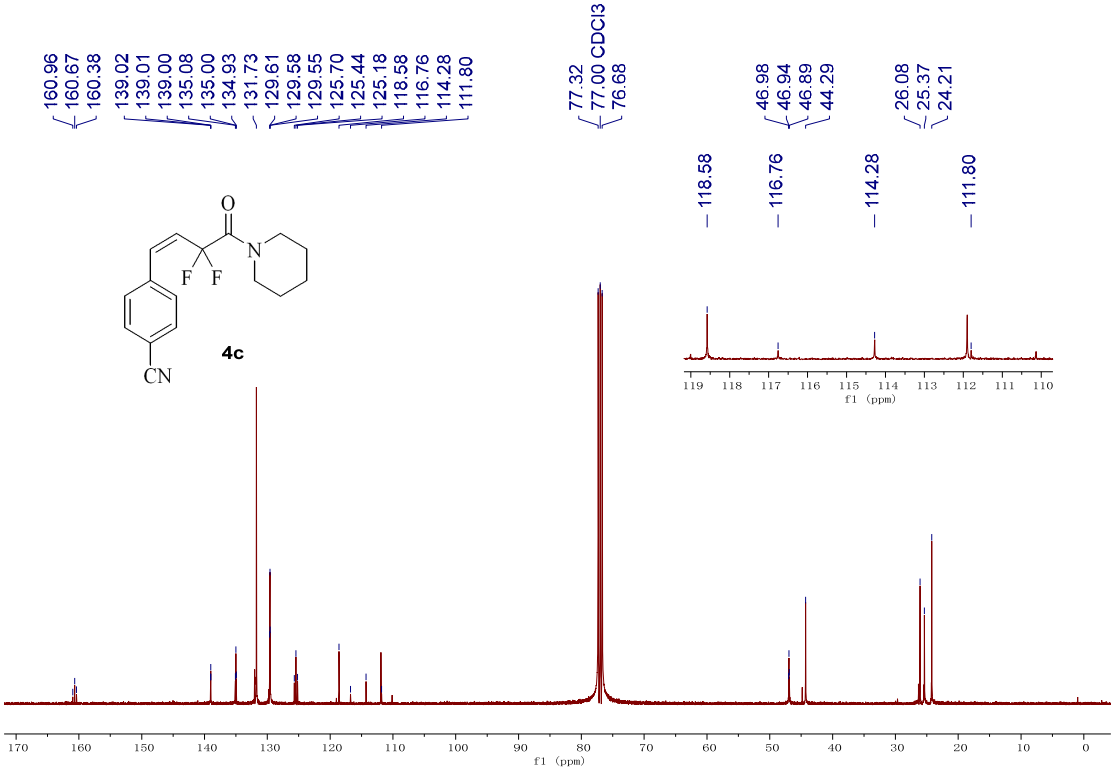
6.62
6.60
6.59
6.58
6.55
3.65
3.63
3.62
3.60
3.59
1.69
1.67
1.66
1.63
1.62
O
N
F F
CN
4c
2.12
2.00
0.96
0.95
4.41
6.18
f1 (ppm)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160.67
160.38
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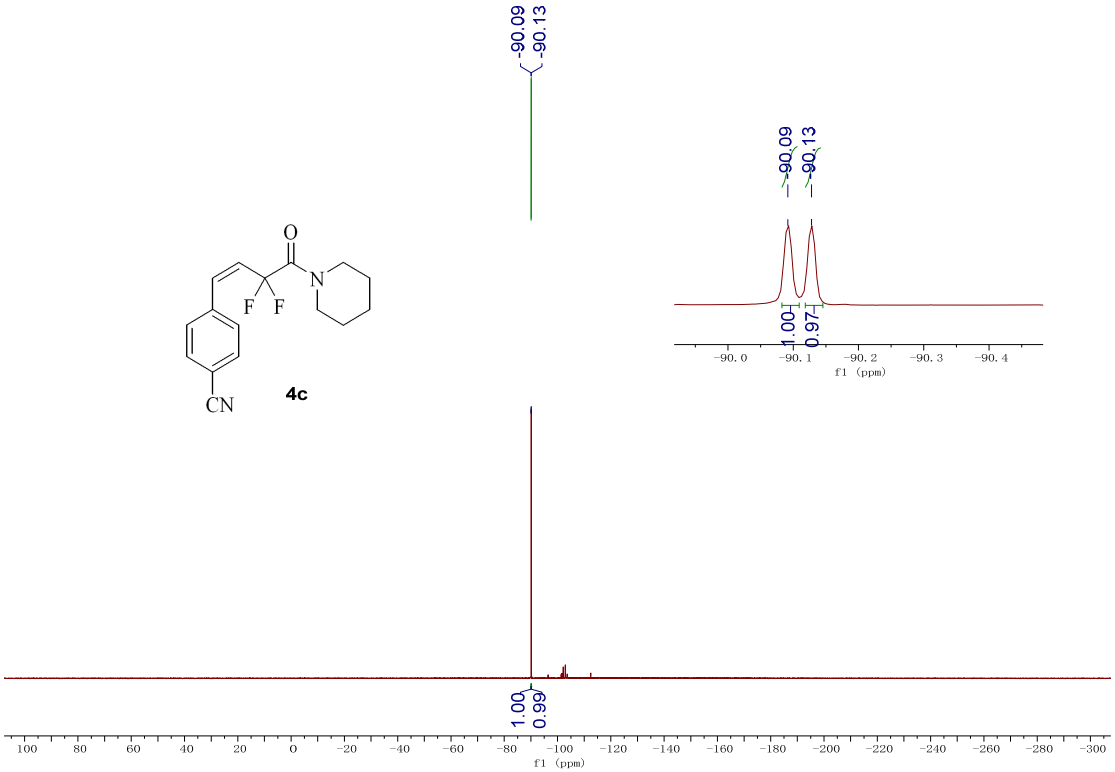
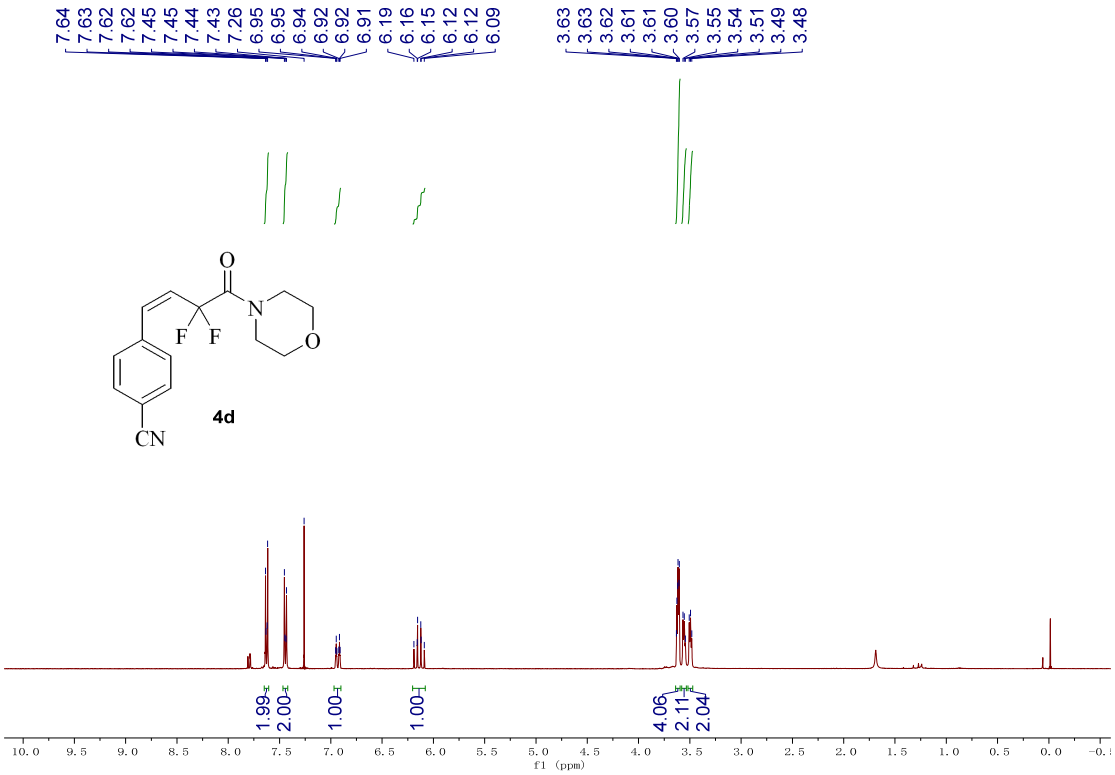
139.01
139.00
135.08
135.00
134.93
131.73
129.61
129.58
129.55
125.70
125.44
125.18
118.58
116.76
114.28
111.80
77.32
77.00 CDCl3
76.68
46.98
46.94
46.89
44.29
26.08
25.37
24.21
118.58
116.76
114.28
111.80
O
N
F F
CN
4c
f1 (ppm)


-90.09
-90.13
-90.09
-90.13
1.00
0.97
O
N
F F
CN
4c
f1 (ppm)
1.00
0.99
f1 (ppm)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7.62
7.62
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7.45
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7.26
6.95
6.95
6.94
6.92
6.92
6.91
6.19
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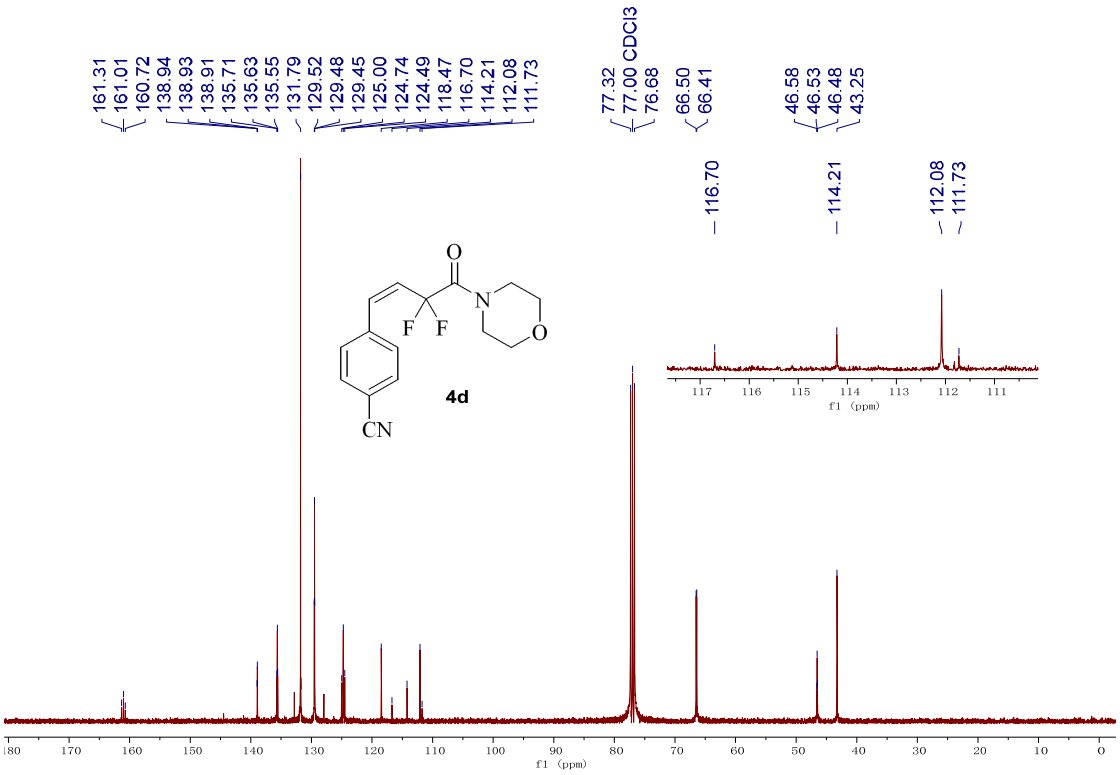
3.48
O
N
F F
O
CN
4d
1.99
2.00
1.00
1.00
4.06
2.11
2.04
f1 (ppm)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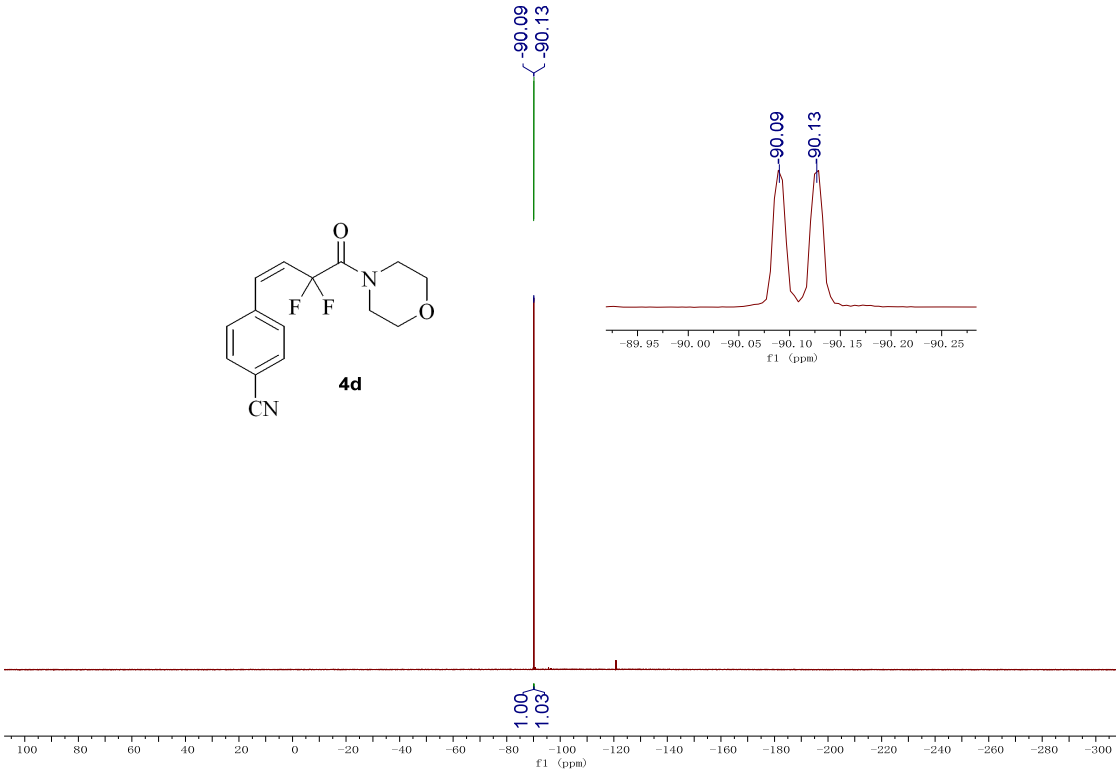
138.91
135.71
135.63
135.55
131.79
129.52
129.48
129.45
125.00
124.74
124.49
118.47
116.70
114.21
112.08
111.73
77.32
77.00 CDCl3
76.68
66.50
66.41
46.58
46.53
46.48
43.25
116.70
114.21
112.08
111.73
O
N
F F
O
CN
4d
f1 (ppm)
f1 (ppm)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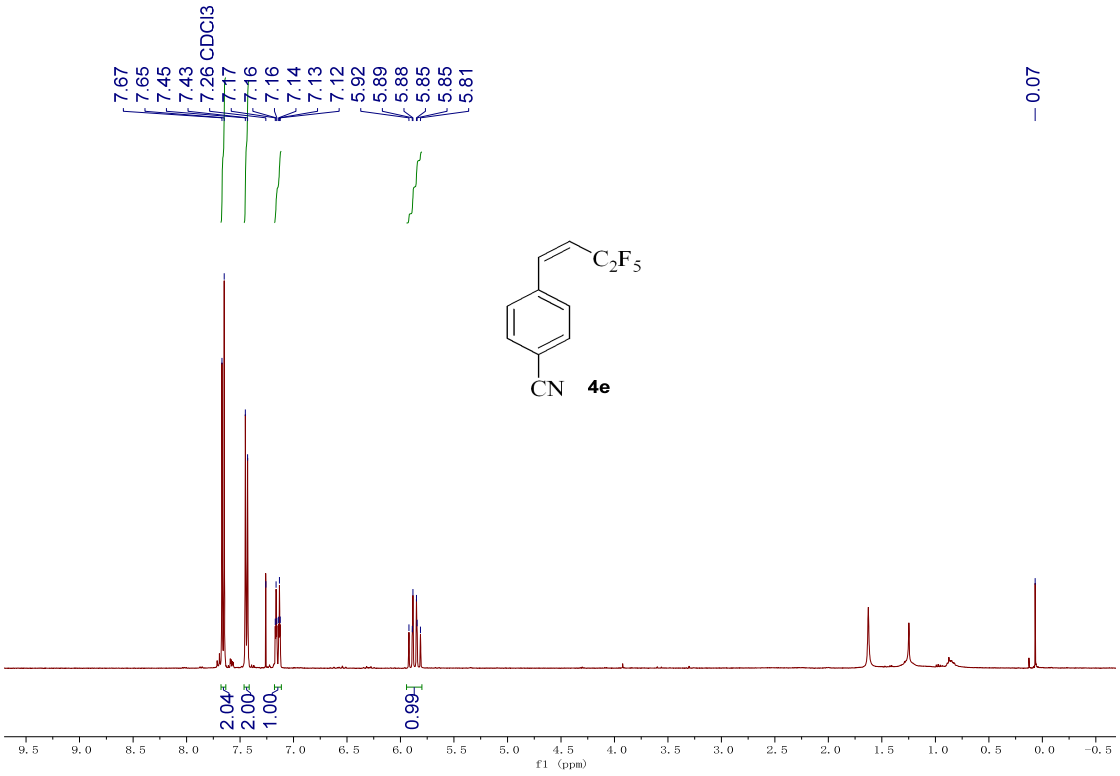
-90.09
-90.13
4d
1.00
1.03
f1 (ppm)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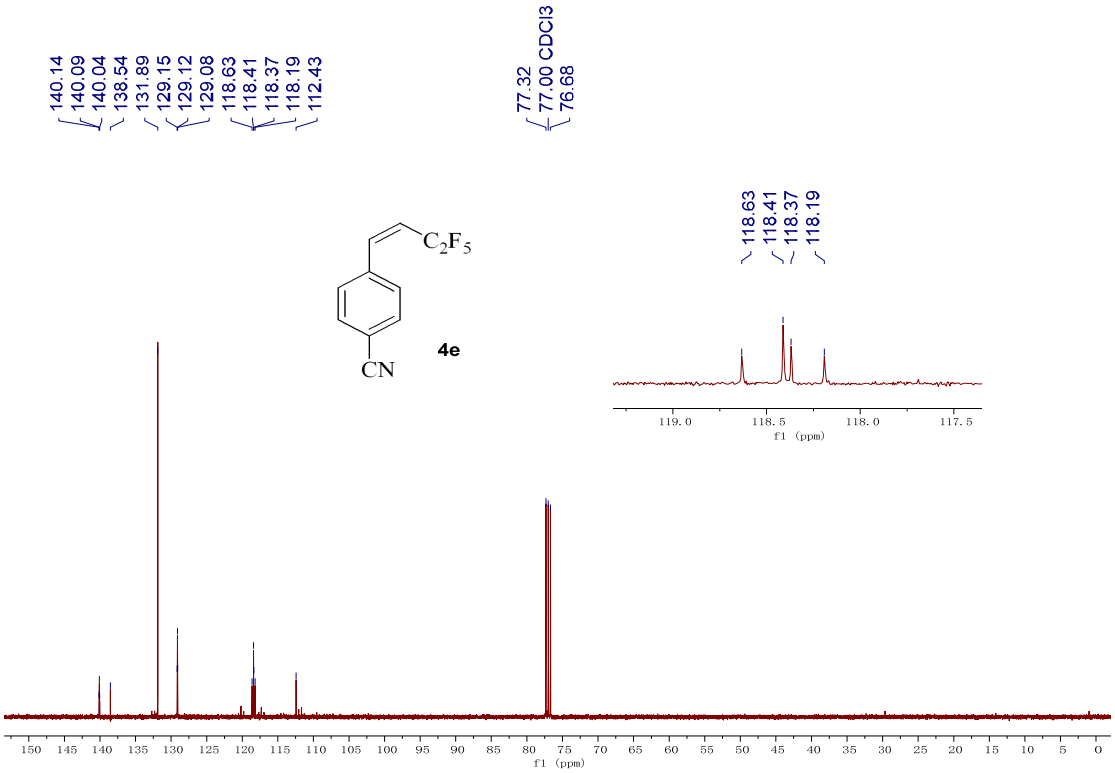
7.65
7.45
7.43
7.26 CDCl3
7.17
7.16
7.16
7.14
7.13
7.12
5.92
5.89
5.88
5.85
5.85
5.81
0.07
4e
2.04
2.00
1.00
0.99
f1 (ppm)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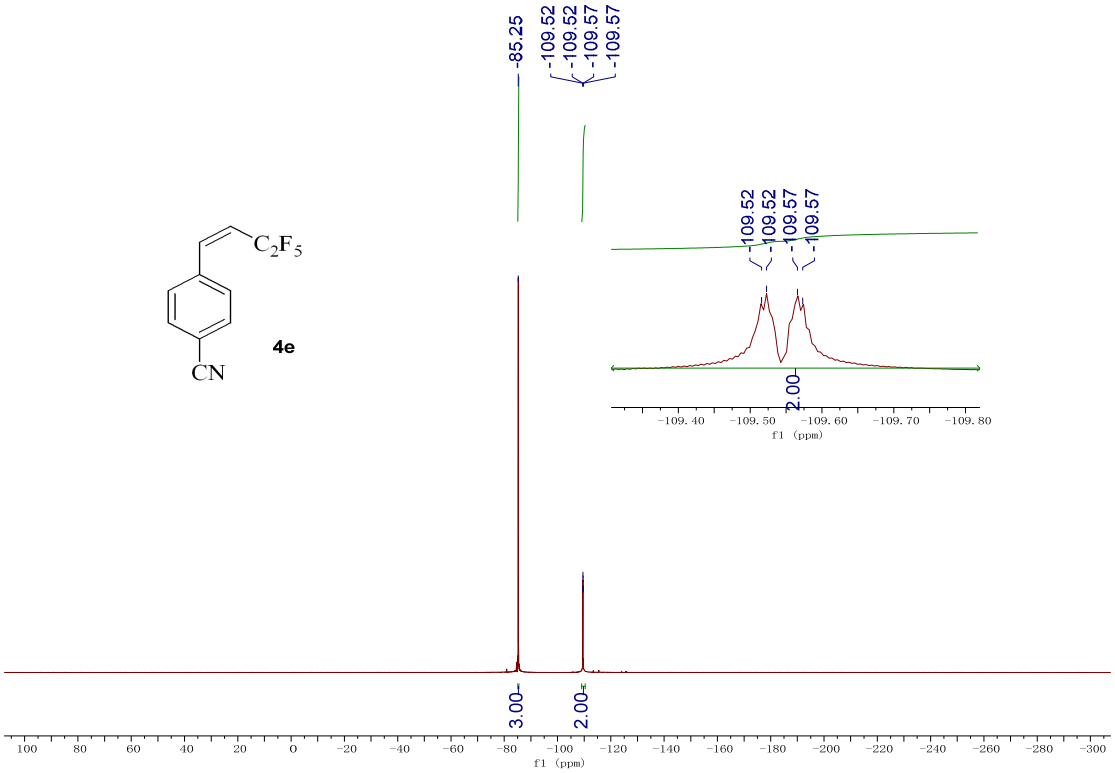
140.09
140.04
138.54
131.89
129.15
129.12
129.08
118.63
118.41
118.37
118.19
112.43
77.32
77.00 CDCl3
76.68
C_2F_5
CN
4e
118.63
118.41
118.37
118.19
119.0
118.5
118.0
117.5
f1 (ppm)
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)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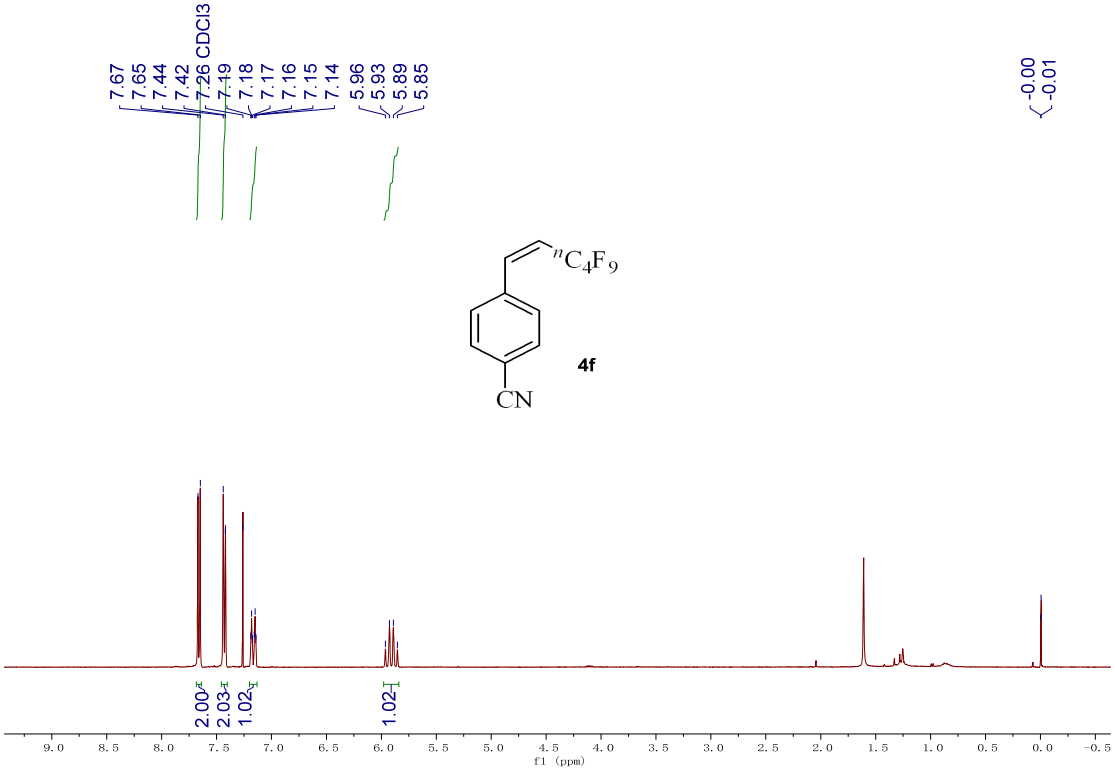
-109.52
-109.57
-109.57
C_2F_5
CN
4e
-109.52
-109.52
-109.57
-109.57
2.00
-109.40
-109.50
-109.60
-109.70
-109.80
f1 (ppm)
3.00
2.00
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)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7.65
7.44
7.42
7.26 CDCl3
7.19
7.18
7.17
7.16
7.15
7.14
5.96
5.93
5.89
5.85
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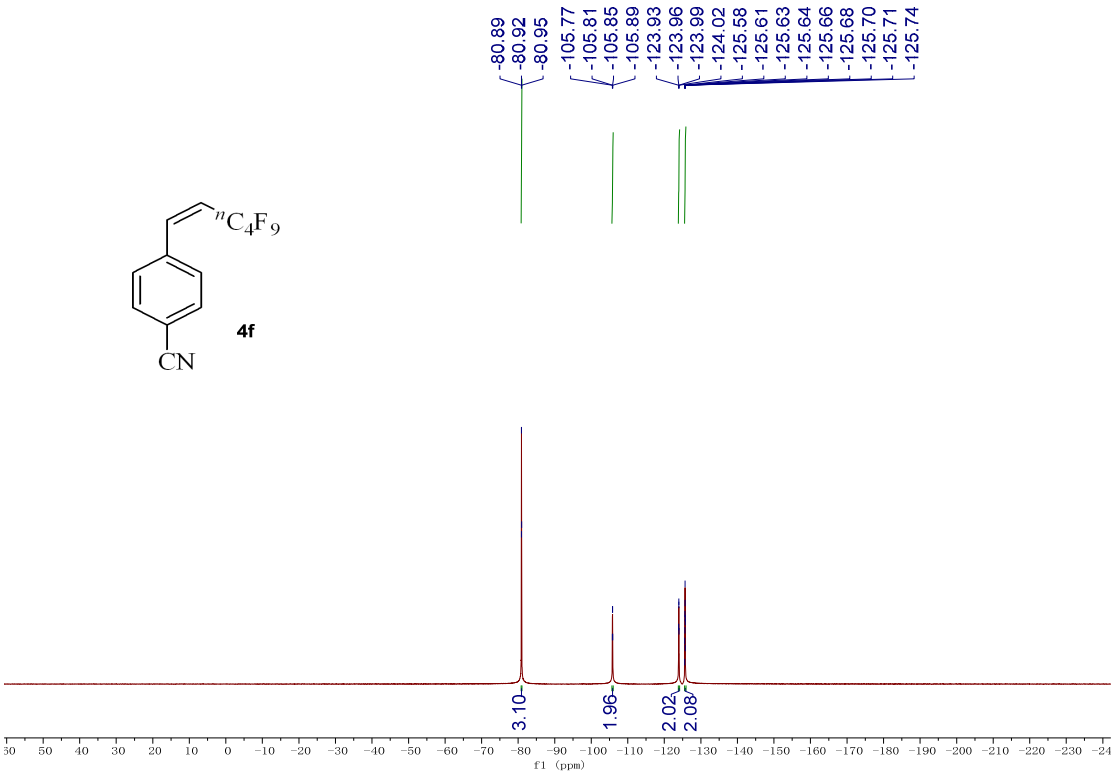
-0.01
$^{n}C_4F_9$
CN
4f
2.00
2.03
1.02
1.02
f1 (ppm)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-80.95
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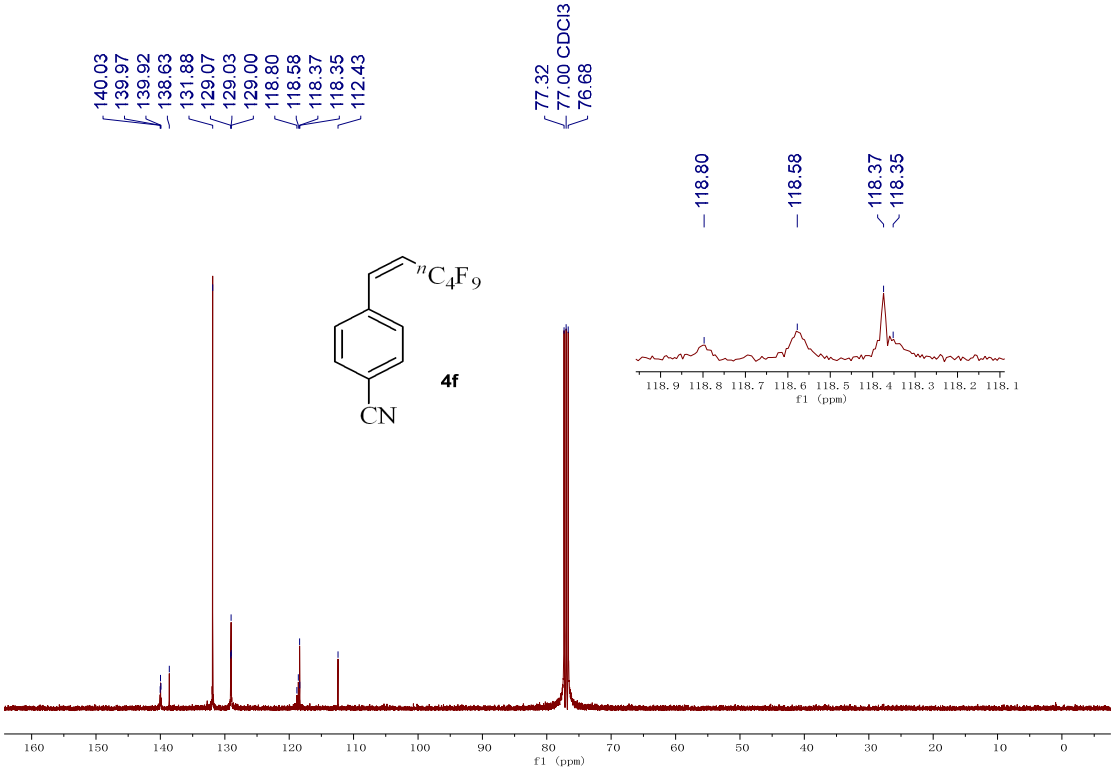
-105.81
-105.85
-105.89
-123.93
-123.96
-123.99
-124.02
-125.58
-125.61
-125.63
-125.64
-125.66
-125.68
-125.70
-125.71
-125.74
$^{n}C_4F_9$
CN
4f
3.10
1.96
2.02
2.08
f1 (ppm)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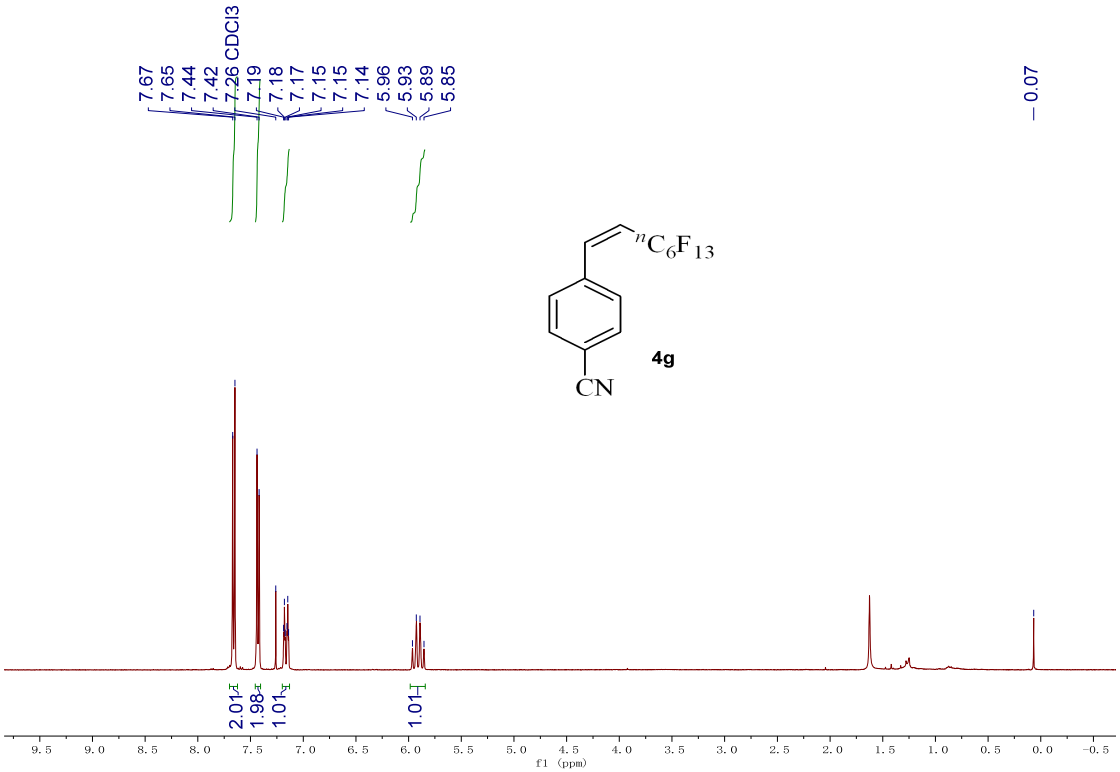
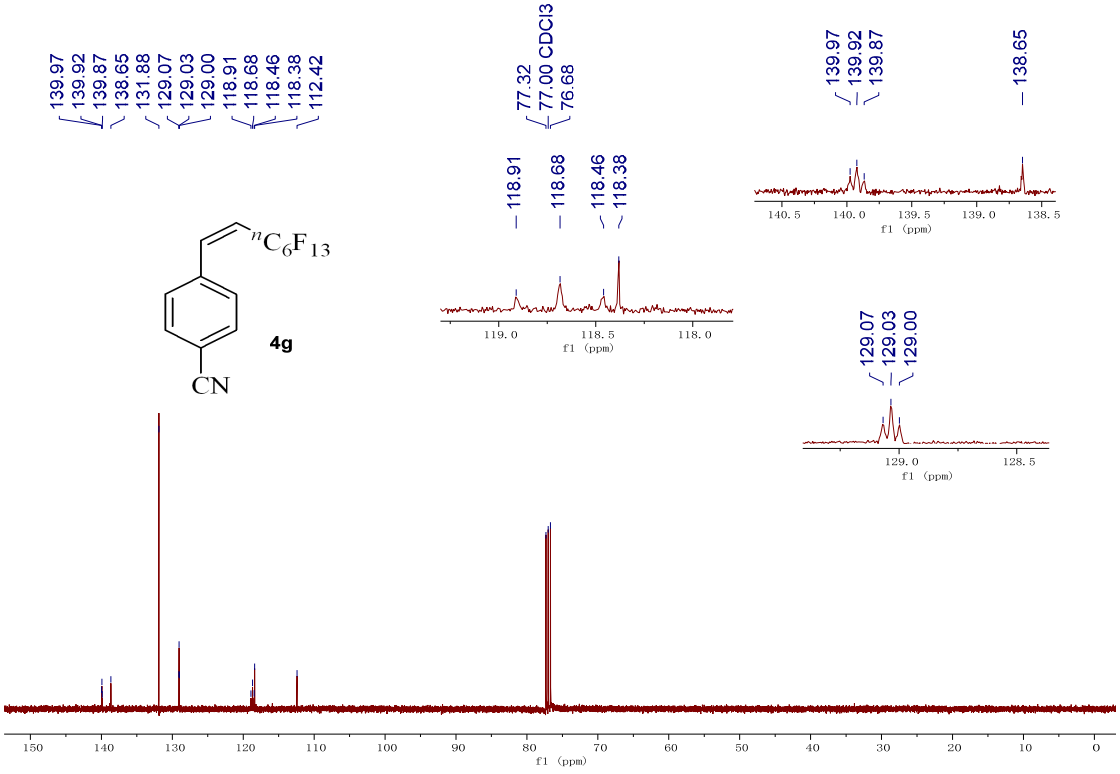
138.63
131.88
129.07
129.03
129.00
118.80
118.58
118.37
118.35
112.43
77.32
77.00 CDCl3
76.68
118.80
118.58
118.37
118.35
$^{n}C_4F_9$
CN
4f
f1 (ppm)


7.67
7.65
7.44
7.42
7.26 CDCl3
7.19
7.18
7.17
7.15
7.15
7.14
5.96
5.93
5.89
5.85
0.07
$^{n}C_6F_{13}$
CN
4g
2.01
1.98
1.01
1.01
f1 (ppm)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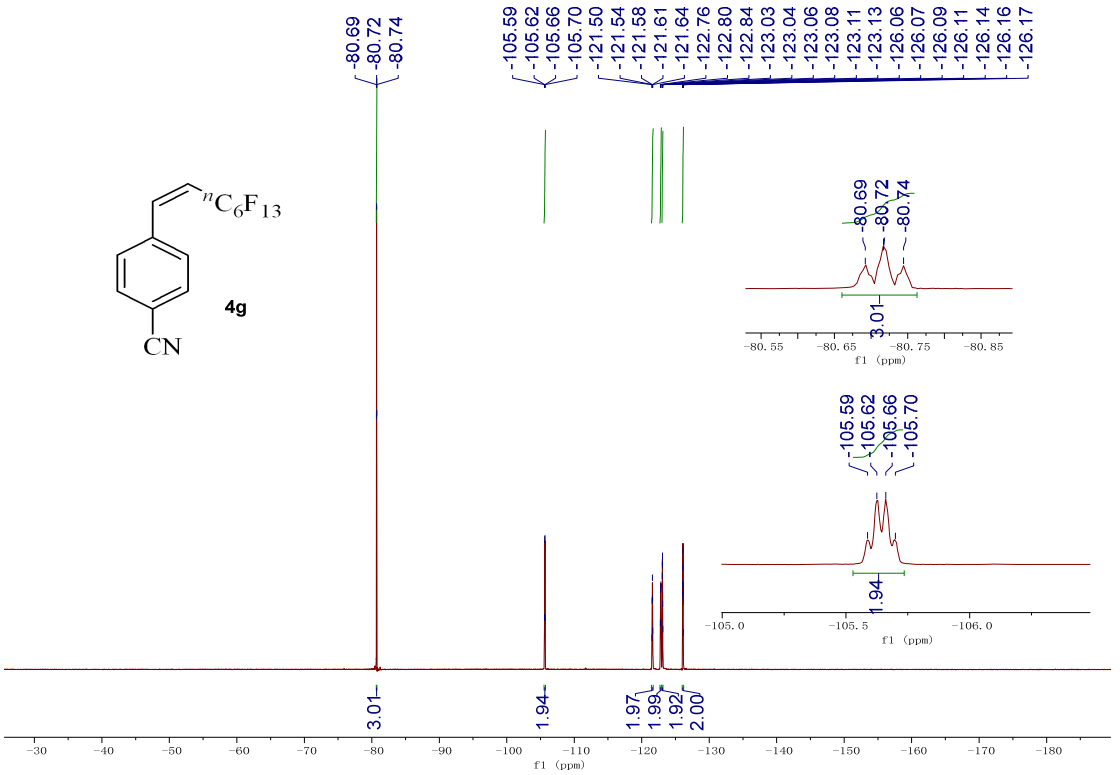
139.92
139.87
138.65
131.88
129.07
129.03
129.00
118.91
118.68
118.46
118.38
112.42
77.32
77.00 CDCl3
76.68
$^{n}C_6F_{13}$
4g
CN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-121.58
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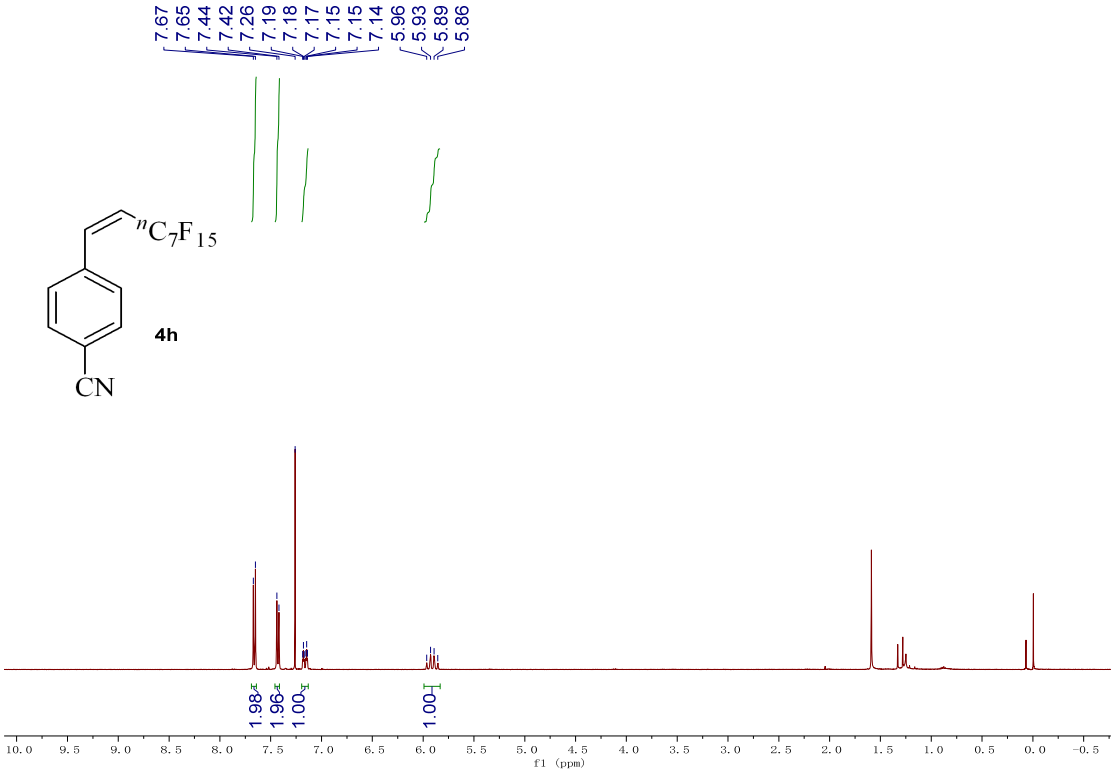
-121.64
-122.76
-122.80
-122.84
-123.03
-123.04
-123.06
-123.08
-123.11
-123.13
-126.06
-126.07
-126.09
-126.11
-126.14
-126.16
-126.17
$^{n}C_6F_{13}$
4g
CN
3.01
1.94
1.97
1.99
1.92
2.00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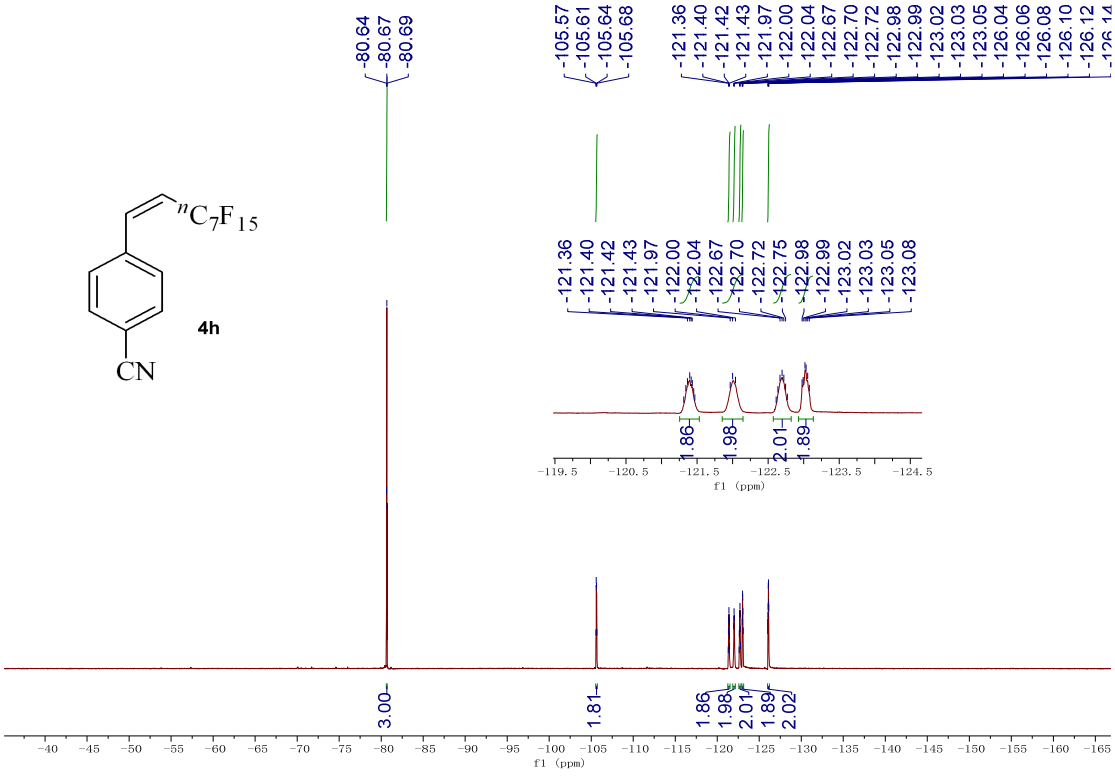
7.65
7.44
7.42
7.26
7.19
7.18
7.17
7.15
7.15
7.14
5.96
5.93
5.89
5.86
$^{n}C_7F_{15}$
4h
CN
1.98
1.96
1.00
1.00
f1 (ppm)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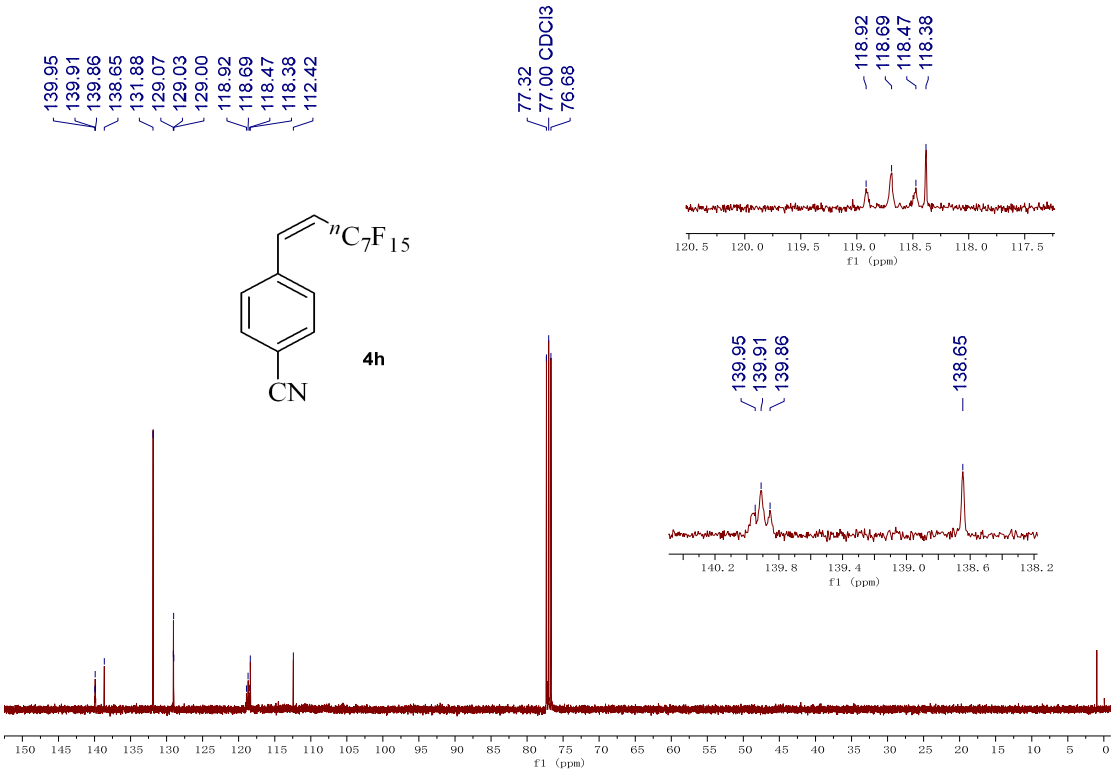
-122.67
-122.70
-122.72
-122.75
-122.98
-122.99
-123.02
-123.03
-123.05
-123.08
$^{n}C_7F_{15}$
4h
CN
1.86
1.98
2.01
1.89
f1 (ppm)
3.00
1.81
1.86
1.98
2.01
1.89
2.02
f1 (ppm)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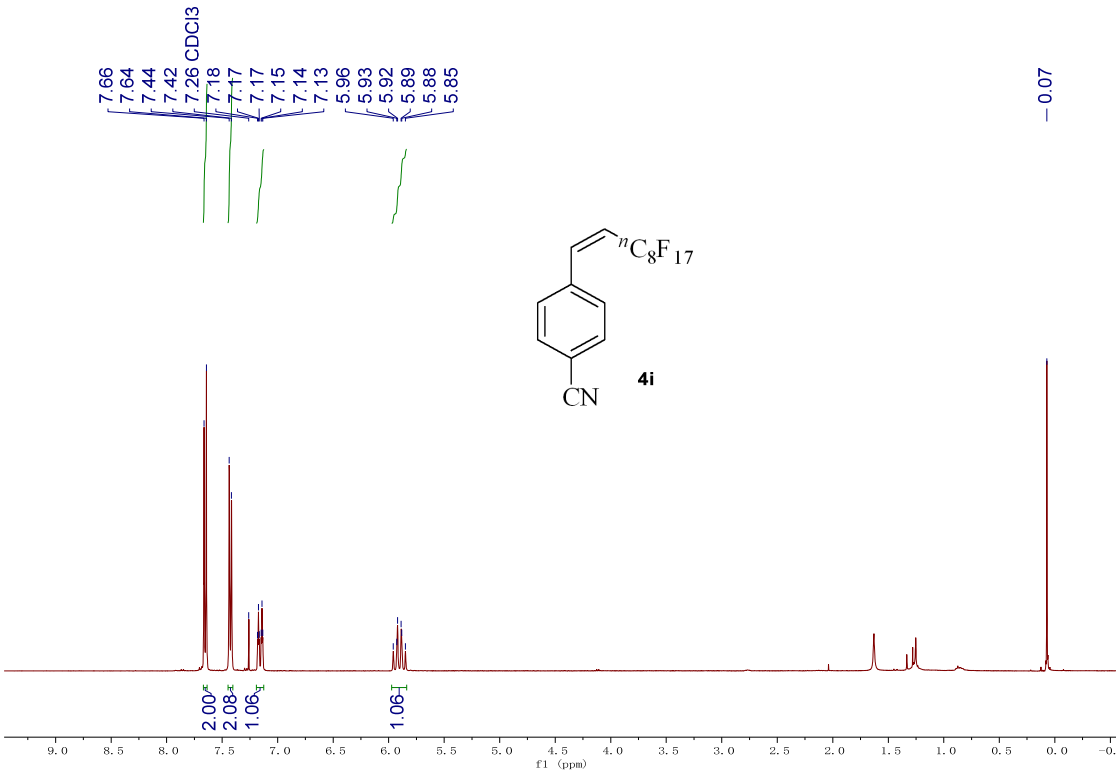
139.91
139.86
138.65
131.88
129.07
129.03
129.00
118.92
118.69
118.47
118.38
112.42
77.32
77.00 CDCl3
76.68
$^{n}C_7F_{15}$
CN
4h
f1 (ppm)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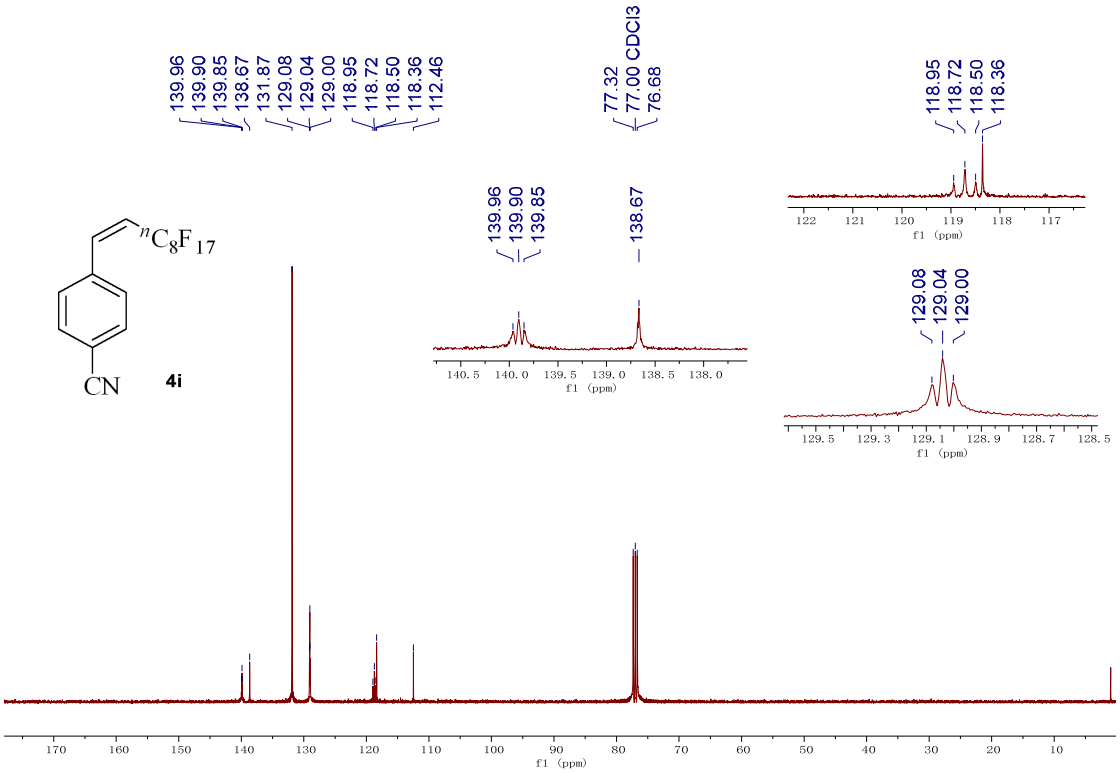
7.64
7.44
7.42
7.26 CDCl3
7.18
7.17
7.17
7.15
7.14
7.13
5.96
5.93
5.92
5.89
5.88
5.85
0.07
$^{n}C_8F_{17}$
CN
4i
2.00
2.08
1.06
1.06
f1 (ppm)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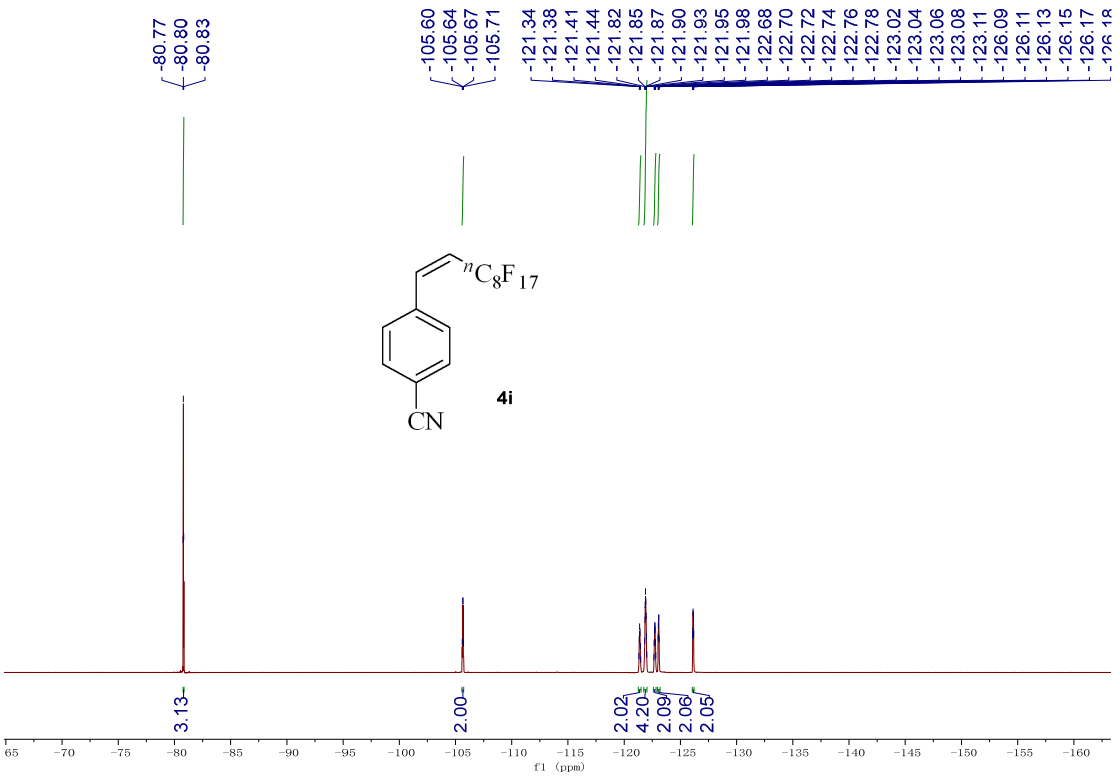
139.90
139.85
138.67
131.87
129.08
129.04
129.00
118.95
118.72
118.50
118.36
112.46
77.32
77.00 CDCl3
76.68
$^{n}C_8F_{17}$
CN
4i
f1 (ppm)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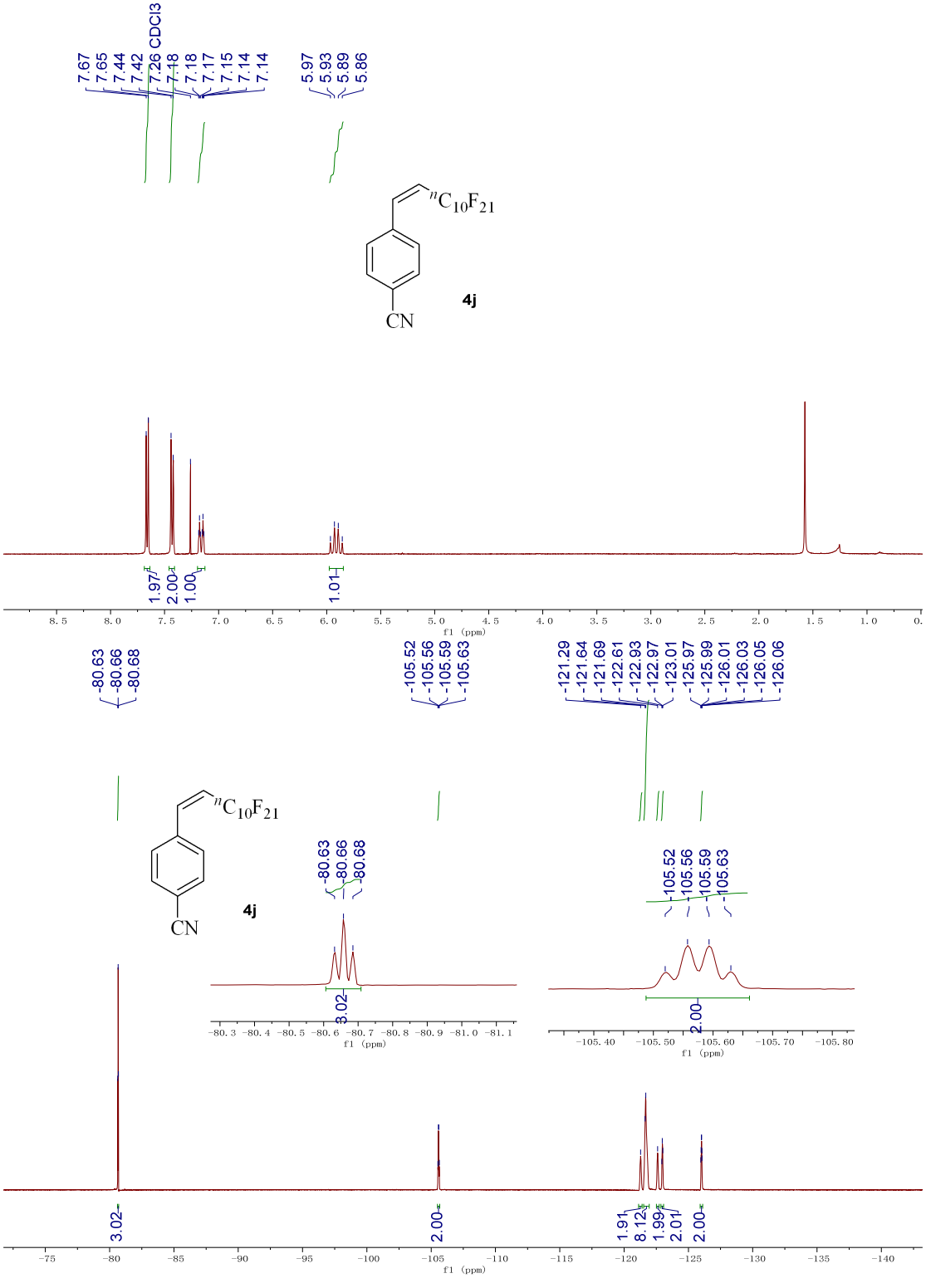
-121.41
-121.44
-121.82
-121.85
-121.87
-121.90
-121.93
-121.95
-121.98
-122.68
-122.70
-122.72
-122.74
-122.76
-122.78
-123.02
-123.04
-123.06
-123.08
-123.11
-126.09
-126.11
-126.13
-126.15
-126.17
$^{n}C_8F_{17}$
CN
4i
3.13
2.00
2.02
4.20
2.09
2.06
2.05
f1 (ppm)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7.44
7.42
7.26 CDCl3
7.18
7.18
7.17
7.15
7.14
7.14
5.97
5.93
5.89
5.86
$^{n}C_{10}F_{21}$
CN
4j
1.97
2.00
1.00
1.01
f1 (ppm)
-80.63
-80.66
-80.68
-105.52
-105.56
-105.59
-105.63
-121.29
-121.64
-121.69
-122.61
-122.93
-122.97
-123.01
-125.97
-125.99
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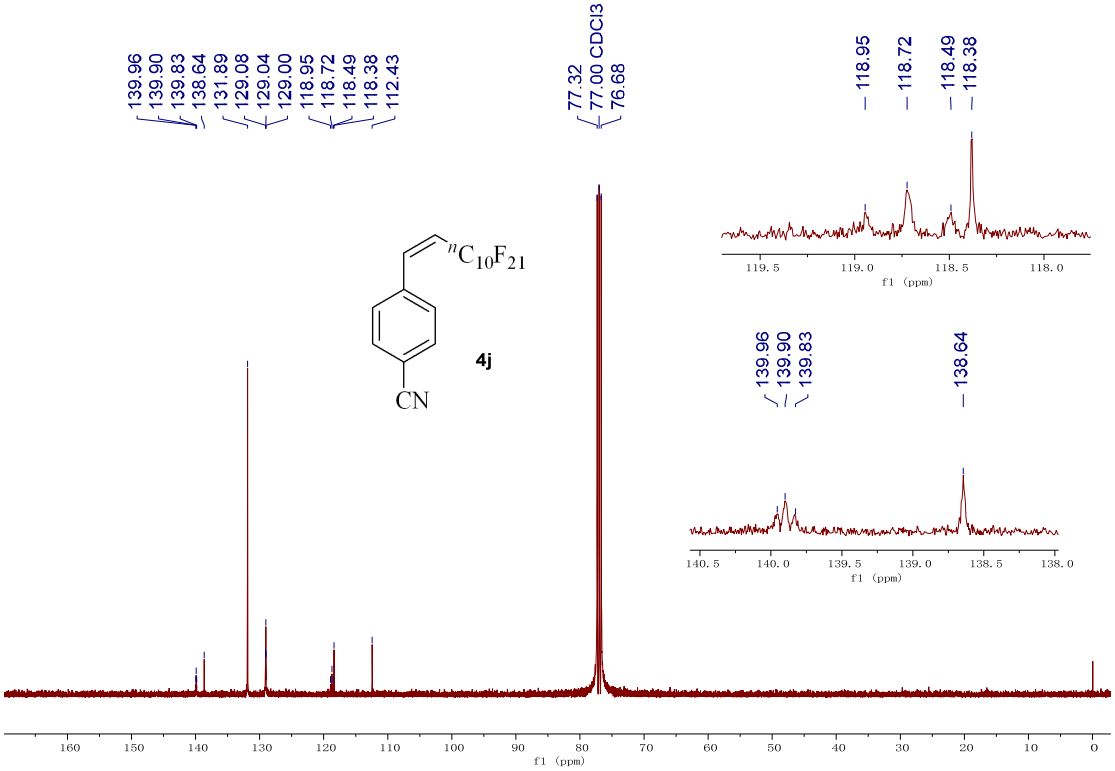
1.91
8.12
1.99
2.01
2.00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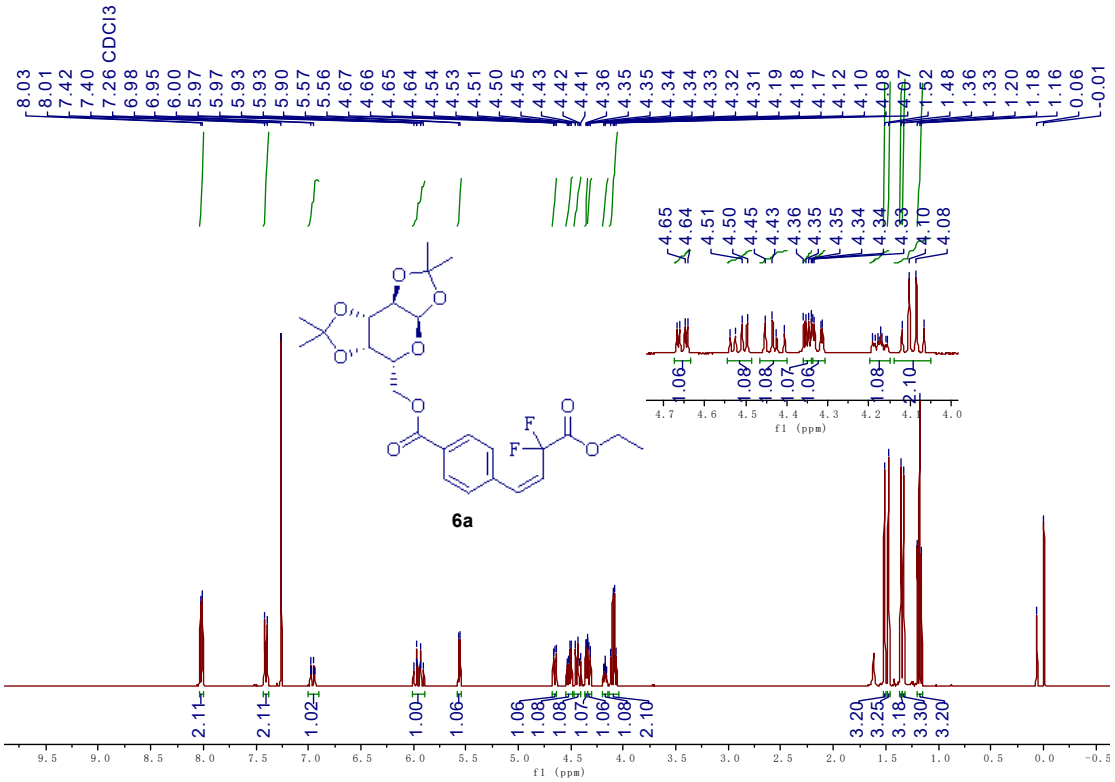
139.90
139.83
138.64
131.89
129.08
129.04
129.00
118.95
118.72
118.49
118.38
112.43
77.32
77.00 CDCl3
76.68
$^{n}C_{10}F_{21}$
CN
4j
f1 (ppm)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8.01
7.42
7.40
7.26 CDCl3
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6.95
6.00
5.97
5.97
5.93
5.93
5.90
5.57
5.56
4.67
4.66
4.65
4.64
4.54
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4.42
4.41
4.36
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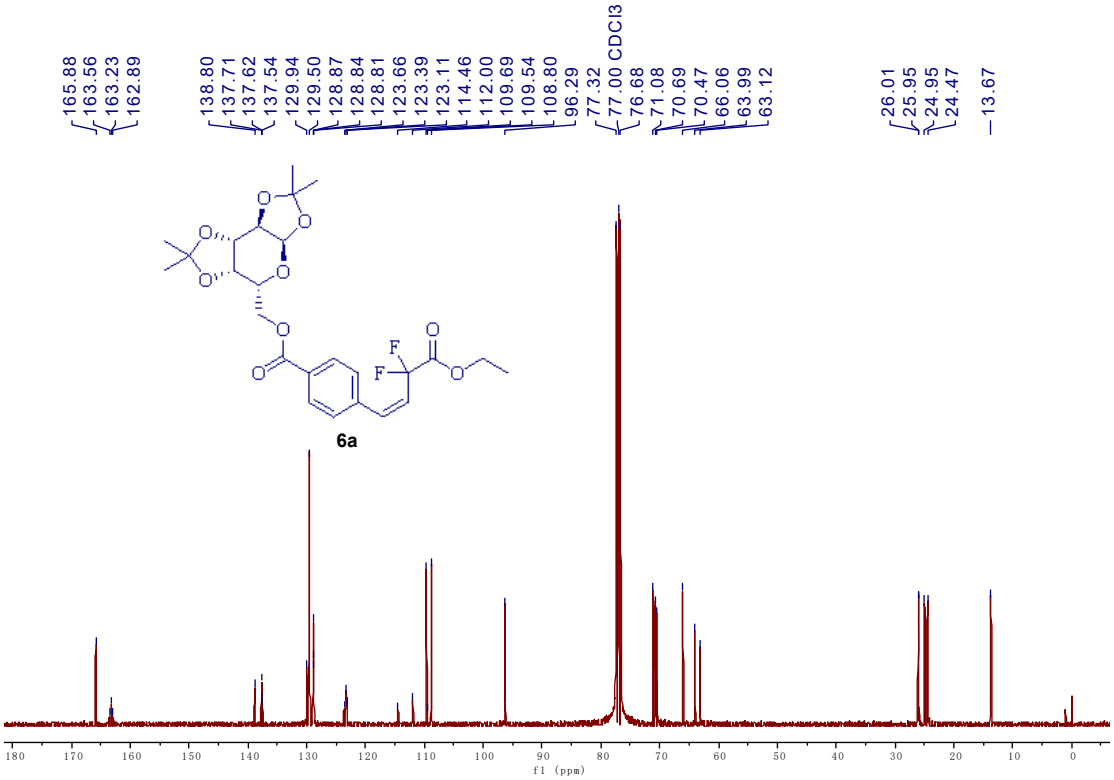
4.35
4.34
4.34
4.33
4.32
4.31
4.19
4.18
4.17
4.12
4.10
4.08
4.07
1.52
1.48
1.36
1.33
1.20
1.18
1.16
0.06
-0.01
6a
f1 (ppm)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137.54
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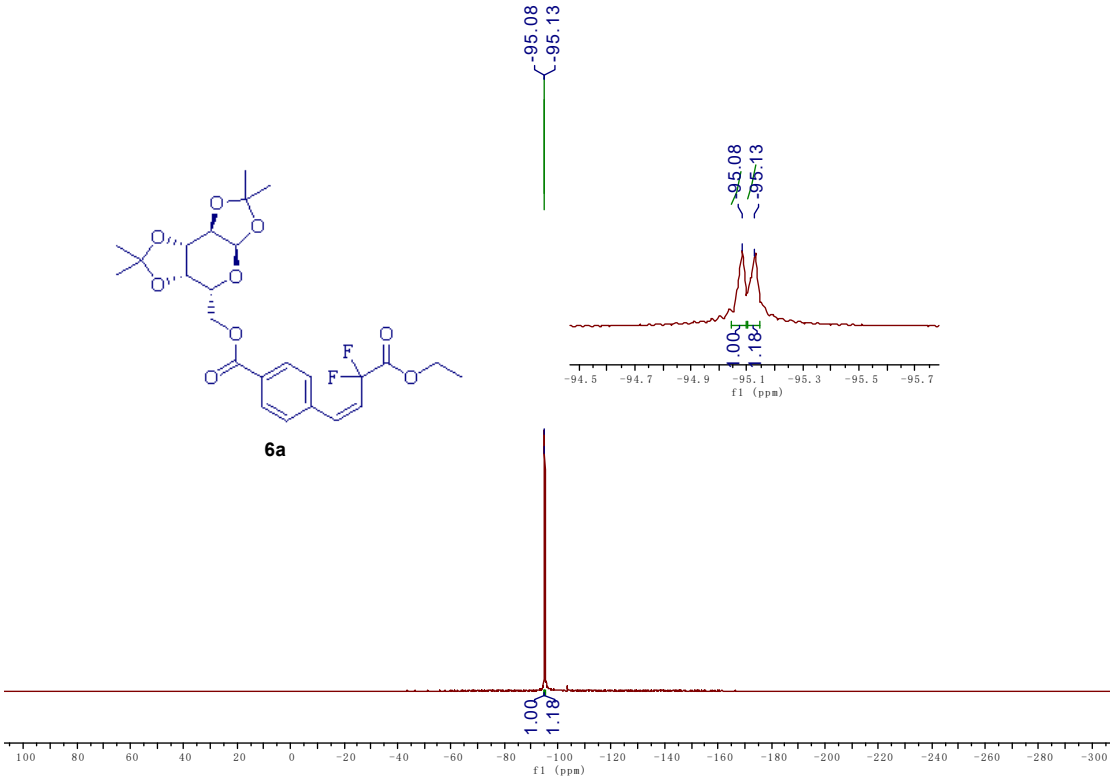
129.50
128.87
128.84
128.81
123.66
123.39
123.11
114.46
112.00
109.69
109.54
108.80
96.29
77.32
77.00 CDCl3
76.68
71.08
70.69
70.47
66.06
63.99
63.12
26.01
25.95
24.95
24.47
13.67
6a
f1 (ppm)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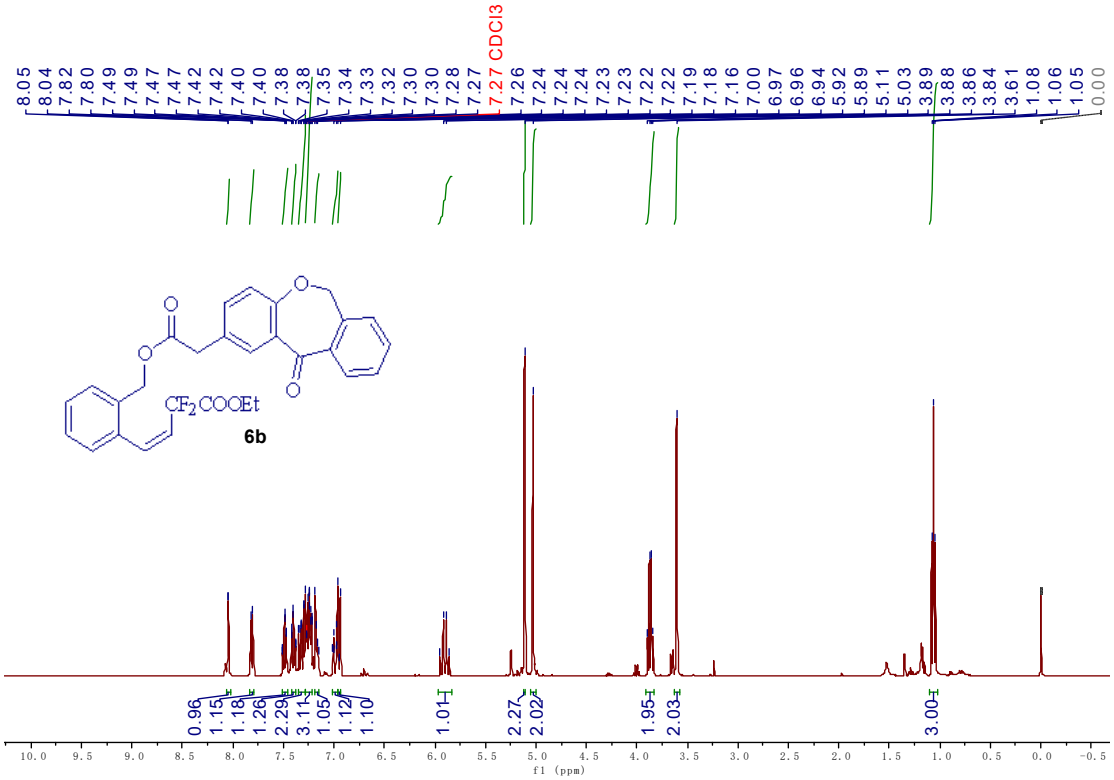
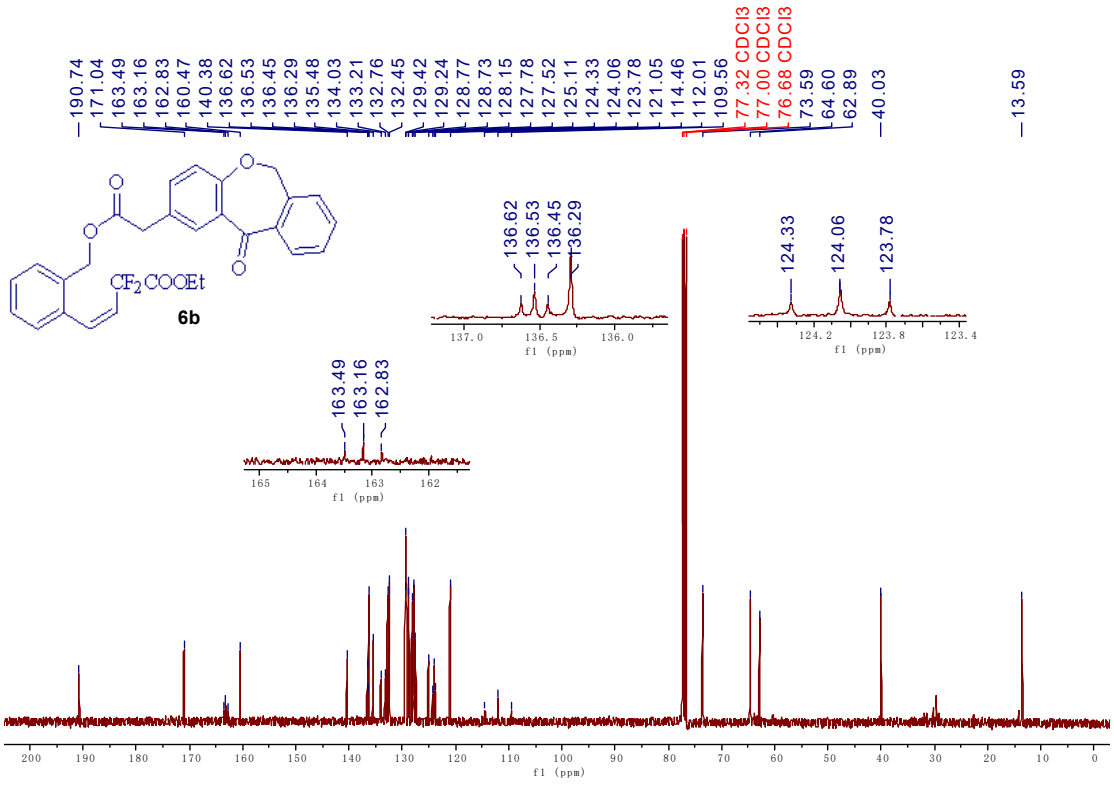
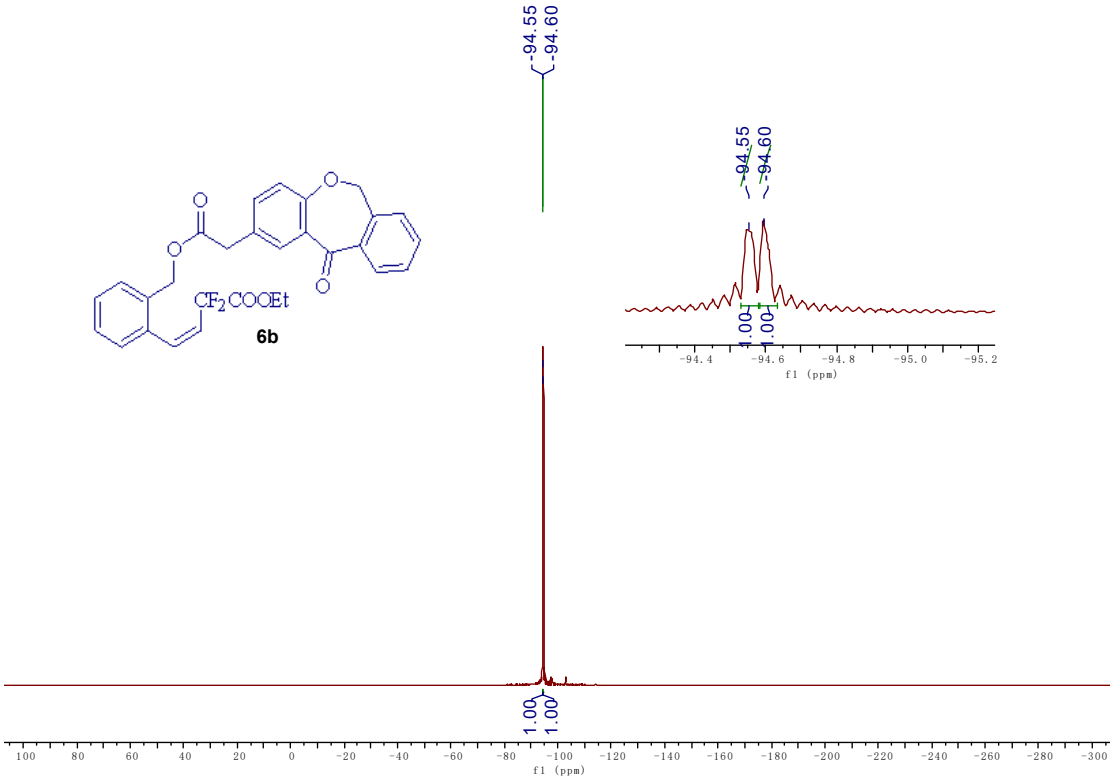
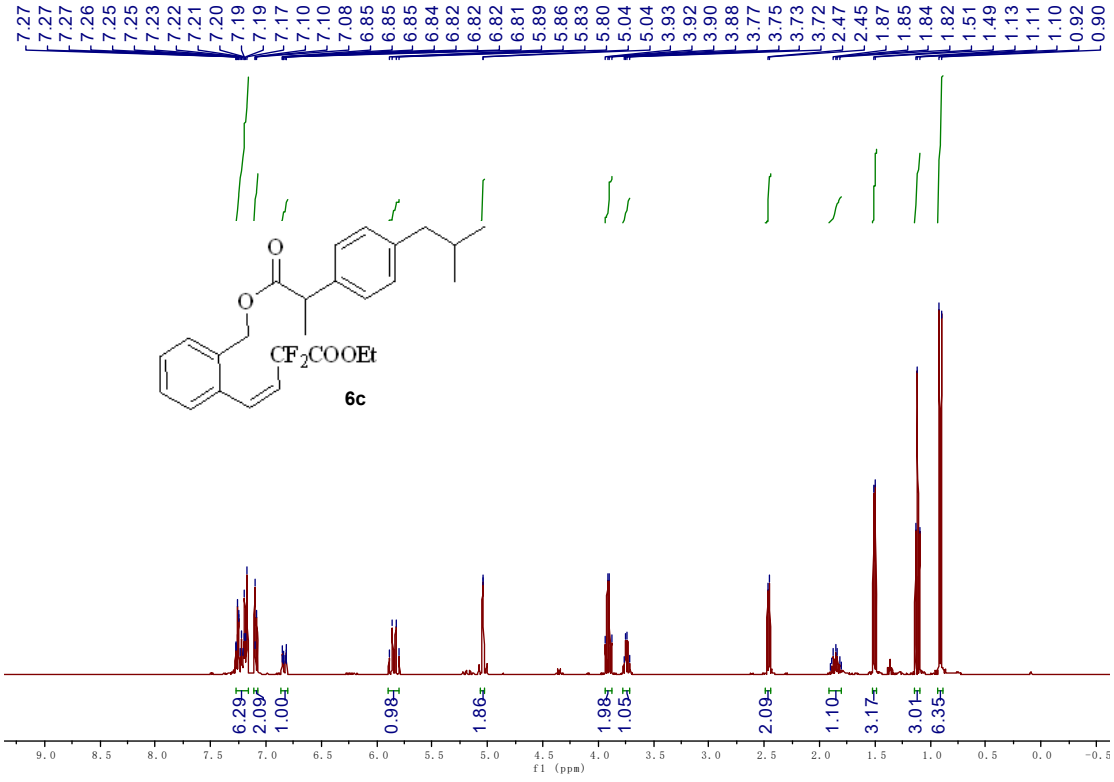
-95.13
1.00
1.18
6a
f1 (ppm)


8.05 8.04 7.82 7.80 7.49 7.49 7.47 7.47 7.42 7.42 7.40 7.40 7.38 7.38 7.35 7.34 7.33 7.32 7.30 7.30 7.28 7.27 7.27 CDCl3 7.26 7.24 7.24 7.24 7.23 7.23 7.22 7.22 7.19 7.18 7.16 7.00 6.97 6.96 6.94 5.92 5.89 5.11 5.03 3.89 3.88 3.86 3.84 3.61 1.08 1.06 1.05 0.00
CF2COOEt
6b
0.96 1.15 1.18 1.26 2.29 3.11 1.05 1.12 1.10 1.01 2.27 2.02 1.95 2.03 3.00
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)


190.74 171.04 163.49 163.16 162.83 160.47 140.38 136.62 136.53 136.45 136.29 135.48 134.03 133.21 132.76 132.45 129.42 129.24 128.77 128.73 128.15 127.78 127.52 125.11 124.33 124.06 123.78 121.05 114.46 112.01 109.56 77.32 CDCl3 77.00 CDCl3 76.68 CDCl3 73.59 64.60 62.89 40.03 13.59
CF2COOEt
6b
136.62 136.53 136.45 136.29
137.0 136.5 136.0
f1 (ppm)
124.33 124.06 123.78
124.2 123.8 123.4
f1 (ppm)
163.49 163.16 162.83
165 164 163 162
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-94.55
-94.60
CF2COOEt
6b
1.00
1.00
f1 (ppm)


7.27
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7.27
7.26
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7.23
7.22
7.21
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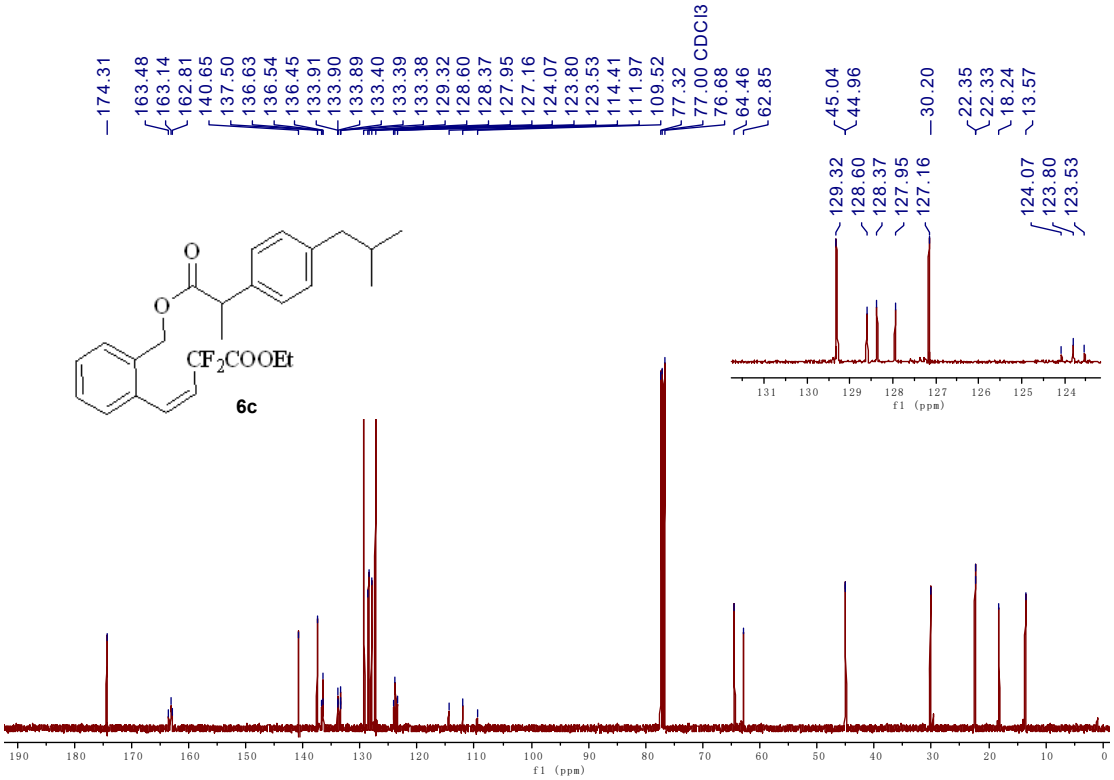
7.19
7.19
7.17
7.10
7.10
7.08
6.85
6.85
6.85
6.84
6.82
6.82
6.82
6.81
5.89
5.86
5.83
5.80
5.04
5.04
3.93
3.92
3.90
3.88
3.77
3.75
3.73
3.72
2.47
2.45
1.87
1.85
1.84
1.82
1.51
1.49
1.13
1.11
1.10
0.92
0.90
O
O
CF2COOEt
6c
6.29
2.09
1.00
0.98
1.86
1.98
1.05
2.09
1.10
3.17
3.01
6.35
f1 (ppm)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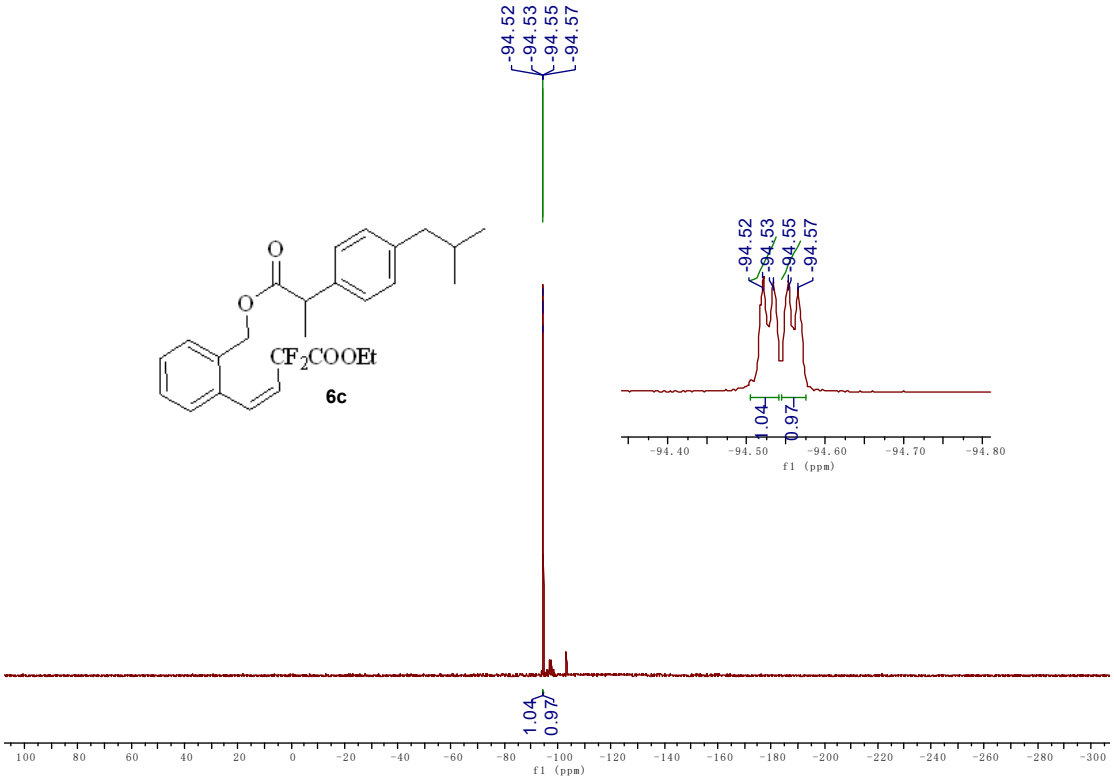
137.50
136.63
136.54
136.45
133.91
133.90
133.89
133.40
133.39
133.38
129.32
128.60
128.37
127.95
127.16
124.07
123.80
123.53
114.41
111.97
109.52
77.32
77.00 CDCl3
76.68
64.46
62.85
45.04
44.96
30.20
22.35
22.33
18.24
13.57
CF2COOEt
6c
f1 (ppm)


-94.52
-94.53
-94.55
-94.57
CF2COOEt
6c
1.04
0.97
f1 (ppm)