Supporting Information

(Fluoro)alkylation of Alkenes Promoted by Photolysis of Alkylzirconocenes

Xiaoxiao Ren,[a] Xing Gao,[b] Qiao-Qiao Min,[b] Shu Zhang,[c] and Xingang Zhang*[ab]

[a]*Green Catalysis Center, and College of Chemistry, Zhengzhou University, Zhengzhou 450001, P. R. China.*

[b]*Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China.*

[c]*The Yangtze Delta Region Institute (Huzhou), University of Electronic Science and Technology of China, Huzhou 313001, China.*

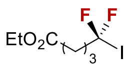
xgzhang@mail.sioc.ac.cn

Table of Contents

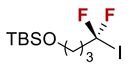
1. General Information and Materials

General Information: ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded on the Agilent MR 400, Bruker MR 500and Bruker MR 600 spectrometer, and are calibrated using residual undeuterated solvent ($CHCl_3$ at 7.26 ppm ^{1}H NMR; 77.0 ppm ^{13}C NMR; $CFCl_3$ as an external standard and low field is positive). Chemical shifts (δ) are reported in ppm and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. NMR yield was determined by ^{19}F NMR using fluorobenzene as an internal standard before working up the reaction. High Resolution Mass spectral data were recorded on Agilent Technologies 7250 GCQTOF spectrometer in EI mode, or on Agilent Technologies 6224 TOF LC MS spectrometer in ESI mode. IR spectra were recorded on a Bruker TENSOR 27 FTIR Spectrometer equipped with a Platinum ATR detector.

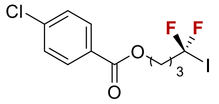
Materials: All reagents were used as received from commercial sources or prepared as described in the literature. The 12 W blue LED strips (GreeThink 12V-5050-60; 1 m×12.5 mm×4.4 mm) was purchased from *Taobao.com*. Compounds **1b-1f**[1], **1g**[2], **1j**[1], **1l**[3], **1m**[4], **1n**[5], **1o**[6] were known compounds. **1p-1u** are commercially available. Compounds **1a**[1], **1h**[7], **1i**[8], **1k**[9] were prepared according to the literature.



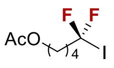
1a



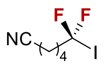
1b



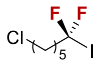
1c



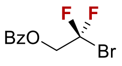
1d



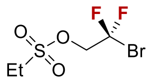
1e



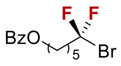
1f



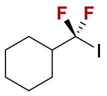
1g



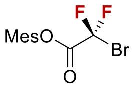
1h



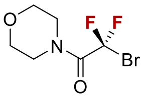
1i



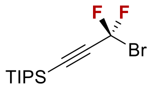
1j



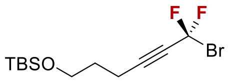
1k



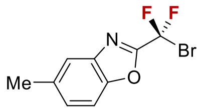
1l



1m



1n



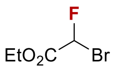
1o

ICF_3

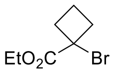
1p

IC_6F_{13}

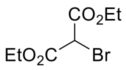
1q



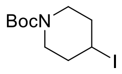
1r



1s



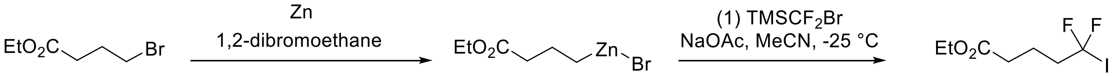
1t



1u

Structures of Difluoroalkyl Iodides and Bromides 1

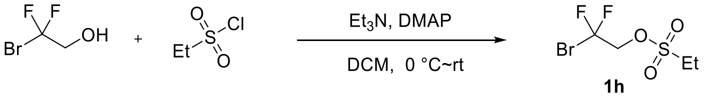
Preparation of compound 1a[1].



1a

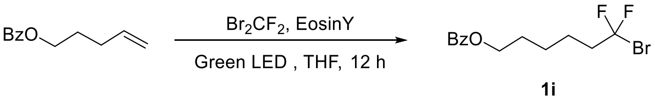
Ethyl 5,5-difluoro-5-iodopentanoate (1a): To a 250 mL round bottle equipped with a Teflon-coated magnetic stir bar were added zinc dust (75 mmol, 1.5 equiv), THF (50 mL), and one drop of 1,2-dibromoethane. The mixture was stirred at 80 ^{o}C and two drops of TMSCl were added. The resulting mixture was then stirred for 15 minutes at 80 ^{o}C. Alkyl bromide (50 mmol, 1.0 equiv) was slowly added. After the resulting mixture was stirred at 80 ^{o}C for 18 h, the unreacted zinc was allowed to settle down. The concentration of organozinc reagent was determined by iodometric titration. A freshly titrated THF solution of organozinc reagent (40 mmol, 1.0 equiv) was concentrated under vacuum until the solid or viscous residue was formed. To the resulting residue were added anhydrous MeCN (40 mL) and NaOAc (48 mmol, 1.2 equiv) at room temperature, the reaction flask was cooled to -25 ^{o}C, and the mixture was stirred for 10 minutes at -25 ^{o}C. Then, $TMSCF_2Br$ (48 mmol, 1.2 equiv) was added dropwise at -25 ^{o}C, and the reaction mixture was stirred at this temperature for 18 h. Iodine (42 mmol, 1.05 equiv) was added at -25 ^{o}C to the reaction mixture. After dissolution of iodine, the cooling bath was removed, the mixture was allowed to warm to room temperature and was stirred for additional 5 hours. The resulting reddish-brown mixture was quenched by addition of aqueous of $Na_2S_2O_3$ until decoloration, diluted with water, and extracted with PE. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The product (9.5 g, 65% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 100:1) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.11 (q, *J* = 7.1 Hz, 2H), 2.42 – 2.29 (m, 4H), 1.92 – 1.80 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -36.1 (t, *J* = 14.9 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.3, 101.4 (t, *J* = 313.6 Hz), 60.5, 47.1 (t, *J* = 19.7 Hz), 32.3, 20.5 (t, *J* = 3.5 Hz), 14.1. IR (thin film) ν_{max} 2982, 1736, 1450 cm^{-1}. MS (EI) m/z (%) 165 $(M-I)^+$, 137 (100), 117, 77. HRMS (FI) calculated for $C_7H_{11}O_2F_2$: 165.0722; Found: 165.0723 $(M-I)^+$.

Preparation of compound 1h[7].



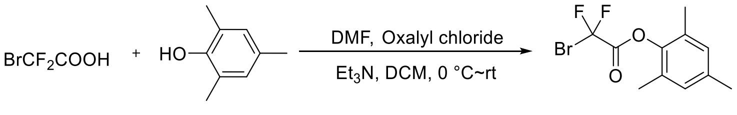
2-Bromo-2,2-difluoroethyl ethanesulfonate (1h): To a 100 mL round bottle equipped with a Teflon-coated magnetic stir bar were added 2-bromo-2,2-difluoroethan-1-ol (10 mmol, 1.0 equiv), CH_2Cl_2 (50 mL), Et_3N (20 mmol, 2.0 equiv), and DMAP (1.0 mmol, 10 mol%). Ethanesulfonyl chloride (15 mmol, 1.5 equiv) was then added at 0 °C. The resulting mixture was stirred at room temperature overnight until the starting material was totally consumed. After the reaction was completed, the reaction mixture was washed with brine and extracted with EA. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The product (1.9 g, 75% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 30:1) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.63 (t, *J* = 11.6 Hz, 2H), 3.26 (q, *J* = 7.4 Hz, 2H), 1.47 (t, *J* = 7.4 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.8 (t, *J* = 11.6 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 116.7 (t, *J* = 306.9 Hz), 70.0 (t, *J* = 27.7 Hz), 46.1, 8.0. IR (thin film) ν_{max} 2987, 2951, 2888, 1458 cm^{-1}. MS (EI) m/z (%) 173 $(M-Br)^+$, 145 (100), 123, 97. HRMS (FI) calculated for $C_4H_7O_3F_2S$: 173.0078; Found: 173.0081 $(M-Br)^+$.

Preparation of compound 1i[8].



6-Bromo-6,6-difluorohexyl benzoate (1i): To a 500 mL of Schlenk tube was added EosinY (2.5 mmol, 5 mol%) in the air. The tube was then evacuated and backfilled with Ar (3 times). Alkene (1.0 equiv, 50 mmol) and anhydrous THF (250 mL) were added under Ar. The resulting mixture was degassed three times by the freeze–pump–thaw procedure. The CF_2Br_2 (6.0 equiv, 300 mmol) was then added to the mixture via a syringe under Ar. The reaction mixture was stirred under irradiation of green LEDs strip for 12 h. The reaction mixture was then cooled to room temperature, filtered and concentrated. The product (8.0 g, 50% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 100:1) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 4.34 (t, *J* = 6.5 Hz, 2H), 2.42 – 2.31 (m, 2H), 1.85 – 1.77 (m, 2H), 1.74 – 1.67 (m, 2H), 1.58 – 1.51 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -43.5 (t, *J* = 13.7 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 132.9, 130.2, 129.5, 128.3, 122.9 (t, *J* = 305.8 Hz), 64.5, 44.1 (t, *J* = 21.4 Hz), 28.4, 25.0, 23.7. IR (thin film) ν_{max} 2949, 1719, 1451 cm^{-1}. MS (EI) m/z (%) 320 (M)$^+$, 123 (100), 105, 77. HRMS (FI) calculated for $C_{13}H_{15}O_2F_2Br$: 320.0218; Found: 320.0223 (M)$^+$.

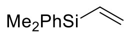
Preparation of compound 1k[9].

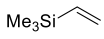


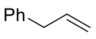
1k

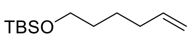
Mesityl 2-bromo-2,2-difluoroacetate (1k): To a 250 mL of round bottle was added $BrCF_2CO_2H$ (36 mmol, 1.2 equiv) and then evacuated and backfilled with Ar (3 times). Anhydrous DCM (50 mL) and DMF (5 mol%, 1.5 mmol) were added under Ar. Oxalyl chloride (1.1 equiv, 33 mmol) was then added to the mixture via a syringe under Ar at 0 °C. After 5 min, the mixture was allowed to warm to rt. After 2 h, the reaction mixture was cooled to 0 °C, and a solution of 2,4,6-trimethylphenol (1.0 equiv, 30 mmol) and Et_3N (2.0 equiv, 60 mmol) in DCM (25 mL) was added. The mixture was stirred for 3 h and then quenched with water, and the aqueous layer was extracted with DCM. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. The product (7.8 g, 90% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 100:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (s, 2H), 2.32 (s, 3H), 2.20 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.4 (s, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.5 (t, *J* = 31.9 Hz), 144.6, 136.7, 129.6, 129.2, 108.4 (t, *J* = 314.5 Hz), 20.7, 15.8. IR (thin film) ν_{max} 2925, 2864, 1789, 1483 cm^{-1}. MS (EI) m/z (%) 292 (M)$^+$, 213, 135 (100), 119, 91. HRMS (FI) calculated for $C_{11}H_{11}O_2F_2Br$: 291.9905; Found: 291.9911 (M)$^+$.

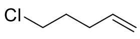
Alkenes **5a-5k** are commercially available. Alkenes **5l**[10]**, 5m**[11]**, 5n**[12]**, 5o**[13]**,** and **5q**[11] were prepared according to the literature. **5p**[14]**, 5r**[14]**,** and **5s**[14] were prepared according to the literature.

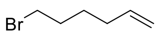

5a

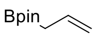

5b


5c

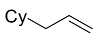

5d

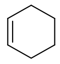

5e

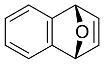

5f

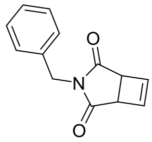

5g

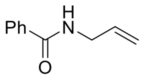

5h

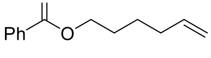

5i

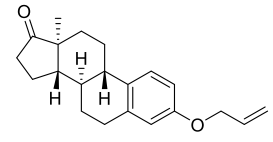

5j

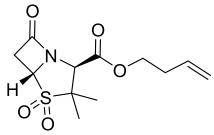

5k

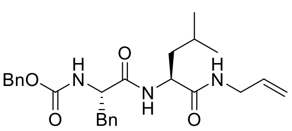

5l

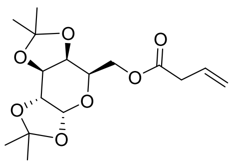

5m

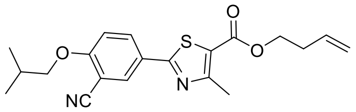

5n


5o


5p


5q


5r

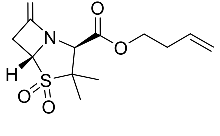

5s

Structures of Alkenes 5

Preparation of compounds 5p, 5r, and 5s.

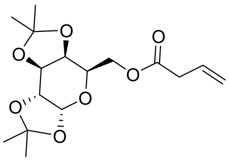
$$R^{1}\text{-OH} + R^{2}CO_2H \xrightarrow[\text{DCM, rt, overnight}]{\text{DMAP, DCC}} R^{2}CO_2R^{1}$$

General Procedure: To a 250 mL round bottle equipped with a Teflon-coated magnetic stir bar were added alcohol (15 mmol, 1.0 equiv), DCM (50 mL), DMAP (0.183 g, 1.5 mmol, 10 mol%) and carboxylic acid (22.5 mmol, 1.5 equiv). DCC (6.18 g, 30 mmol, 2.0 equiv) was then added. The resulting mixture was stirred at room temperature overnight until the starting material was totally consumed. After the reaction was completed, the reaction mixture was washed with brine, dried over Na_2SO_4, filtered and concentrated. The alkene was purified with silica gel chromatography.

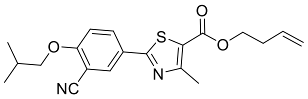


But-3-en-1-yl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate (5p). The product (3.7 g, 87% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 8:1) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 – 5.67 (m, 1H), 5.16 – 5.07 (m, 2H), 4.63 – 4.57 (m, 1H), 4.34 (s, 1H), 4.32 – 4.18 (m, 2H), 3.51 – 3.36 (m, 2H), 2.46 – 2.39 (m, 2H), 1.57 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 166.8, 133.2, 118.0, 65.2, 63.1, 62.6, 61.0, 38.2, 32.7, 20.2, 18.3.

IR (thin film) ν_{max} 2981, 2937, 1797, 1754 cm^{-1}. MS (FI) m/z (%) 288 (M+H)$^+$. HRMS (FI) calculated for $C_{12}H_{18}O_5NS$: 288.0900; Found: 288.0896 (M+H)$^+$.

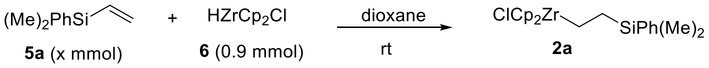


((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-Tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl but-3-enoate (5r). The product (4.3 g, 86% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 10:1) as a yellow solid (m.p. 88 – 90 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.97 – 5.86 (m, 1H), 5.54 (d, *J* = 5.0 Hz, 1H), 5.18 (dd, *J* = 7.7, 1.4 Hz, 1H), 5.15 (s, 1H), 4.62 (dd, *J* = 7.9, 2.5 Hz, 1H), 4.35 – 4.29 (m, 2H), 4.26 – 4.16 (m, 2H), 4.05 – 3.99 (m, 1H), 3.13 (d, *J* = 7.0 Hz, 2H), 1.50 (s, 3H), 1.45 (s, 3H), 1.334 (s, 3H), 1.328 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5, 130.1, 118.6, 109.6, 108.8, 96.3, 71.0, 70.7, 70.4, 66.0, 63.6, 38.9, 26.0, 25.9, 24.9, 24.5. IR (thin film) ν_{max} 3078, 1735 cm^{-1}. MS (DART) m/z (%) 329 (M+H)$^+$. HRMS (DART) calculated for $C_{16}H_{25}O_7$: 329.1595; Found: 329.1593 (M+H)$^+$.



But-3-en-1-yl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (5s). The product (5.0 g, 90% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 5:1) as a white solid (m.p. 98 – 100 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (t, *J* = 2.2 Hz, 1H), 8.05 (dt, *J* = 8.8, 2.2 Hz, 1H), 6.98 (d, *J* = 8.9 Hz, 1H), 5.89 – 5.75 (m, 1H), 5.20 – 5.08 (m, 2H), 4.33 (t, *J* = 6.6 Hz, 2H), 3.88 (d, *J* = 6.4 Hz, 2H), 2.73 (s, 3H), 2.52 – 2.44 (m, 2H), 2.25 – 2.10 (m, 1H), 1.08 (s, 3H), 1.06 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 162.4, 161.7, 161.1, 133.6, 132.4, 131.9, 125.9, 121.7, 117.6, 115.3, 112.5, 102.8, 75.6, 64.2, 33.0, 28.1, 19.0, 17.4. IR (thin film) ν_{max} 3077, 2975, 2232, 1689 cm^{-1}. MS (FI) m/z (%) 370 (M)$^+$, 355, 314, 260 (100), 243. HRMS (FI) calculated for $C_{20}H_{22}O_3N_2S$: 370.1346; Found: 370.1348 (M)$^+$.

Table S1. Preparation of alkylzirconocene 2a by reaction of 5a with 6.[a]



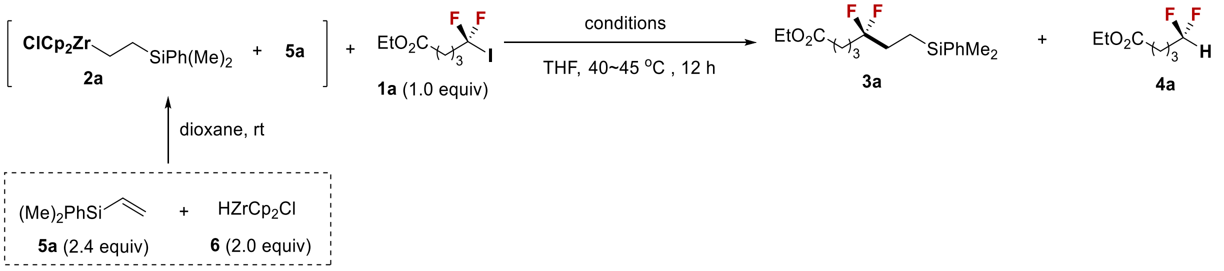
entry	**6:5a**	**Conv 5a** (%)[b]
1	1:1.2	68.2%
2	1:1.1	70.5%
3	1:1.0	75.3%
4	1:0.9	74.4%
5	1:0.8	91.4%
6	1:0.7	98.4%
7	1:0.6	99.5%

[a]Reaction conditions (unless otherwise specified): **6** (0.9 mmol), dioxane (1 mL), 1 h. [b]Determined by GC-MS using established standard curve.

Procedure: To a 25 mL of Schlenk tube was added $ZrCp_2HCl$ (0.9 mmol) in the glovebox. The tube was taken out of the glovebox, and was then evacuated and backfilled with Ar (3 times). **5a** (x mmol) and anhydrous dioxane (1.0 mL) were added under Ar. The reaction mixture was stirred for about 1 h at room temperture. The reaction was quenched with H_2O. The conversion of **5a** was determined by GC-MS using established standard curve.

2. Optimization of the Reaction Conditions

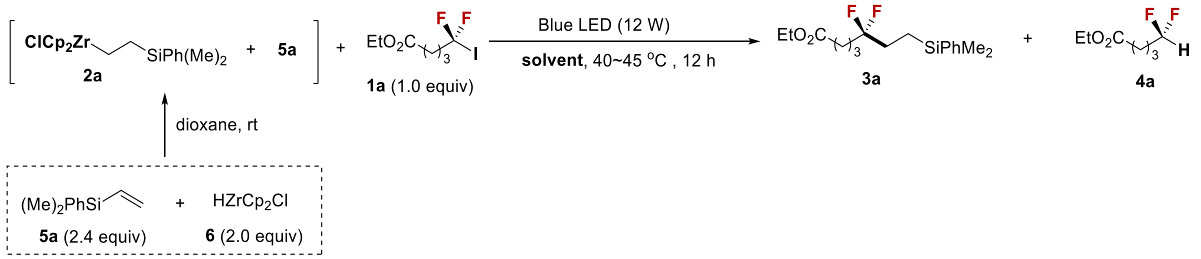
Table S2. Optimization of the reaction conditions[a]



entry	NiBr·DME (10 mol%)	Bpy (10 mol%)	Blue LED	**3a** (%)[b]	**4a** (%)[b]
1	+	+	-	0	5
2	+	+	+	51	27
3	**-**	**-**	**+**	**53**	**33**

[a] Reaction conditions (unless otherwise specified): **1a** (0.3 mmol, 1.0 equiv), **5a** (2.4 equiv), **6** (2.0 equiv), THF (2.0 mL), 40~45 °C, Blue LED (12 W), 12 h. The yield was determined by ^{19}F NMR using fluorobenzene as an internal standard. [b]The yield of **3a** was calculated based on **1a**.

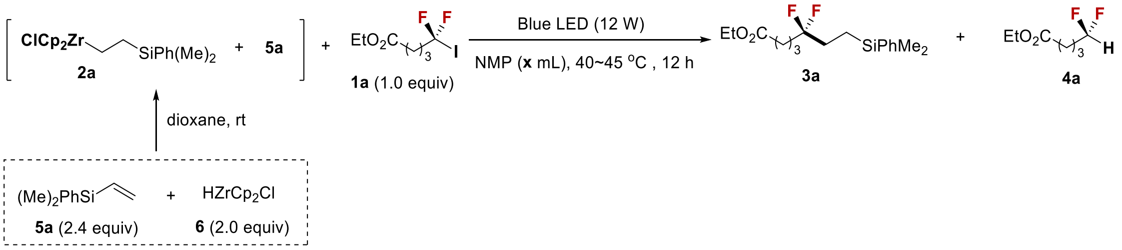
Table S3. Screening of the solvent[a]



entry	solvent	**3a** (%)[b]	**4a** (%)[b]
1	CH_3CN	37	17
2	DCM	29	19
3	DMF	31	16
4	Dioxane	36	23
5	THF	53	33
6	**NMP**	**59**	**34**
7	DME	42	25

[a] Reaction conditions (unless otherwise specified): **1a** (0.3 mmol, 1.0 equiv), **5a** (2.4 equiv), **6** (2.0 equiv), solvent (2.0 mL), 40~45 °C, Blue LED (12 W), 12 h. The yield was determined by ^{19}F NMR using fluorobenzene as an internal standard. [b]The yield of **3a** was calculated based on **1a**.

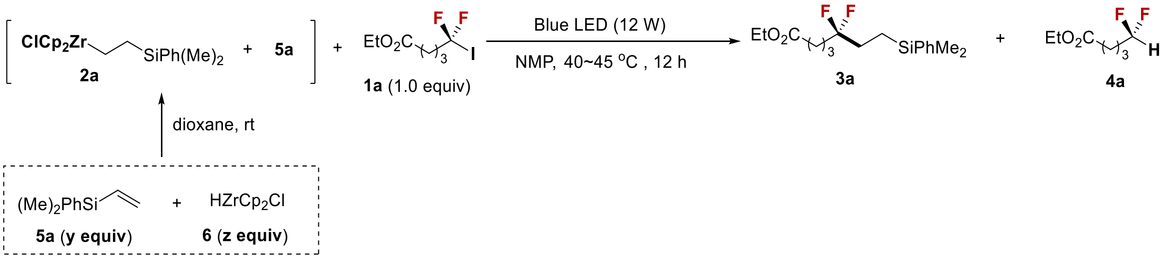
Table S4. Screening of the loading amount of NMP[a]



entry	NMP (x mL)	**3a** (%)[b]	**4a** (%)[b]
1	1.0	51	30
2	2.0	59	34
3	**3.0**	**64**	**31**
5	4.0	60	35

[a]Reaction conditions (unless otherwise specified): **1a** (0.3 mmol, 1.0 equiv), **5a** (2.4 equiv), **6** (2.0 equiv), NMP (x mL), 40~45 °C, Blue LED (12 W), 12 h. The yield was determined by ^{19}F NMR using fluorobenzene as an internal standard. [b]The yield of **3a** was calculated based on **1a**.

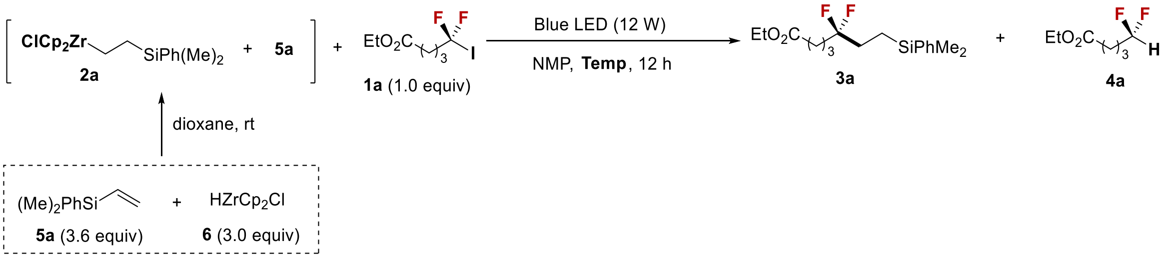
Table S5. Screening of the loading amount of 5a and 6[a]



entry	**5a** (y equiv)	**6** (z equiv)	**3a** (%)[b]	**4a** (%)[b]
1[d]	1.8	1.5	52	38
2	2.4	2.0	64	31
3	3.0	2.5	73	21
4	**3.6**	**3.0**	**81 (62)**	**15**
6	4.2	3.5	82	11

[a]Reaction conditions (unless otherwise specified): **1a** (0.3 mmol, 1.0 equiv), **5a** (y equiv), **6** (z equiv), NMP (3.0 mL), 40~45 °C, Blue LED (12 W), 12 h. The yield was determined by ^{19}F NMR using fluorobenzene as an internal standard. [b]The yield of **3a** was calculated based on **1a**, the number given in parentheses is the isolated yield.

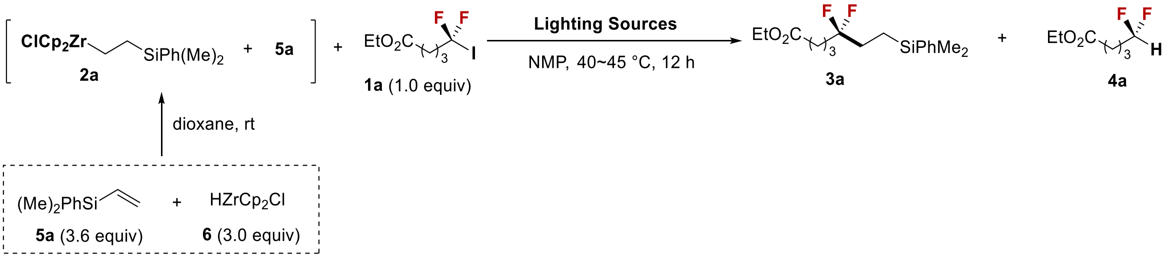
Table S6. Screening of the reaction temperature[a]



entry	Temp (°C)	**3a** (%)[b]	**4a** (%)[b]
1	25	78	18
2	**40~45**	**81**	**15**
3	55	72	23

[a]Reaction conditions (unless otherwise specified): **1a** (0.3 mmol, 1.0 equiv), **5a** (3.6 equiv), **6** (3.0 equiv), NMP (3.0 mL), Blue LED (12 W), 12 h. The yield was determined by ^{19}F NMR using fluorobenzene as an internal standard. [b]The yield of **3a** was calculated based on **1a**.

Table S7. Screening of the lighting sources[a]

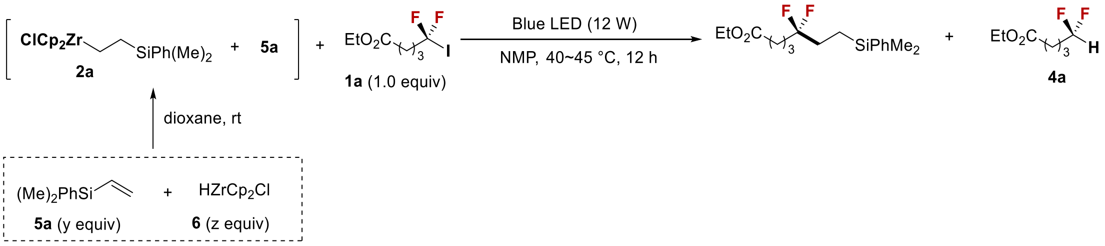


entry	lighting sources	**3a** (%)[b]	**4a** (%)[b]
1	**Blue LED**	**81**	**15**
2	Green LED	79	15
3	White LED	78	17

[a]Reaction conditions (unless otherwise specified): **1a** (0.3 mmol, 1.0 equiv), **5a** (3.6 equiv), **6** (3.0 equiv), NMP (3 mL), 12 h. The yield was determined by ^{19}F NMR using fluorobenzene as an internal standard. [b]The yield of **3a** was calculated based on **1a**.

Re-optimized the reaction conditions

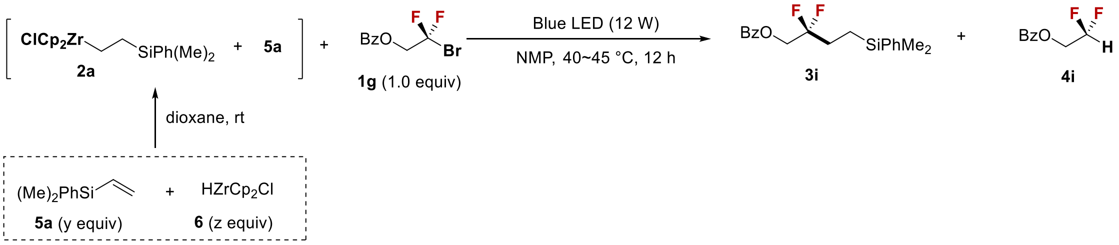
Table S8. Screening of the loading amount of 5a and 6 for the reaction with 1a[a]



entry	**5a** (y equiv)	**6** (z equiv)	**3a** (%)[b]	**4a** (%)[b]
1	2.0	0.1	0	0
2	2.0	0.2	0	2
3	2.0	0.5	36	16
4	2.0	0.75	54	19
5	2.0	1.0	59	19
6	2.0	1.1	68	22
7	2.0	1.2	67	24
8	1.5	1.2	56	36
9	2.2	1.2	73	19
10	**2.5**	**1.2**	**80 (62)**	**14**
11	3.0	1.2	81	12

[a] Reaction conditions (unless otherwise specified): **1a** (0.3 mmol, 1.0 equiv), **5a** (y equiv), **6** (z equiv), NMP (3.0 mL), 40~45 °C, Blue LED (12 W), 12 h. The yield was determined by ^{19}F NMR using fluorobenzene as an internal standard. [b] The yield of **3a** was calculated based on **1a**, the number given in parentheses is the isolated yield.

Table S9. Screening of the loading amount of 5a and 6 for the reaction with 1g[a]

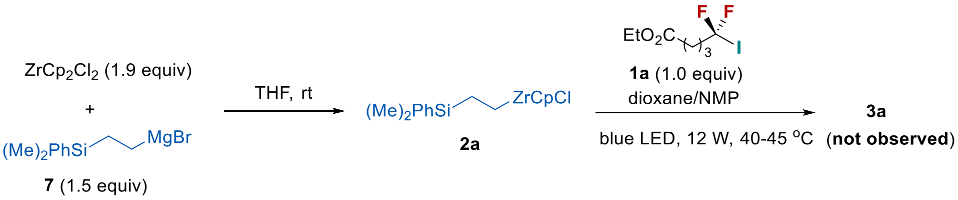


entry	**5a** (y equiv)	**6** (z equiv)	**3i** (%)	**4i** (%)
1	2.5	1.5	42	35
2	2.5	1.8	45	46
3	2.5	2.0	47	48
4	3.0	1.8	54	19
5	**3.5**	**1.8**	**69 (65)**	**19**
6	4.0	1.8	68	22

[a] Reaction conditions (unless otherwise specified): **1g** (0.3 mmol, 1.0 equiv), **5a** (y equiv), **6** (z equiv), NMP (3.0 mL), 40~45 °C, Blue LED (12 W), 12 h. The yield was determined by ^{19}F NMR using fluorobenzene as an internal standard. [b] The yield of **3i** was calculated based on **1g**, the number given in parentheses is the isolated yield.

3. Mechanistic Studies

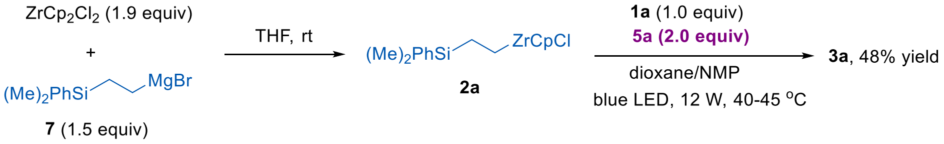
3.1. Preparation of 2a from the reaction of Grignard reagent 7 with ZrCp$_2$Cl$_2$ and using 2a to react with 1a



Procedure: To a 25 mL of Schlenk tube were added ZrCp$_2$Cl$_2$ (0.57 mmol, 1.9 equiv, the loading amount of ZrCp$_2$Cl$_2$ was based on **1a**) and **7**[15] (1.32 mL, 0.34 M, 1.5 equiv, the loading amount of **7** was based on **1a**) under Ar. The mixture was stirred for 3 h at room temperature to afford alkylzirconocene **2a**. (***Note:*** When Grignard reagent **7** was prepared, ~10% of silylalkene **5a** was generated. Alkene **5a** can be trapped by addition of ZrCp$_2$HCl **6** (0.06 mmol) to the resulting solution of **2a**. After the mixture was stirred for 1 h, only trace amount of **5a** was unreacted. This unreacted **5a**

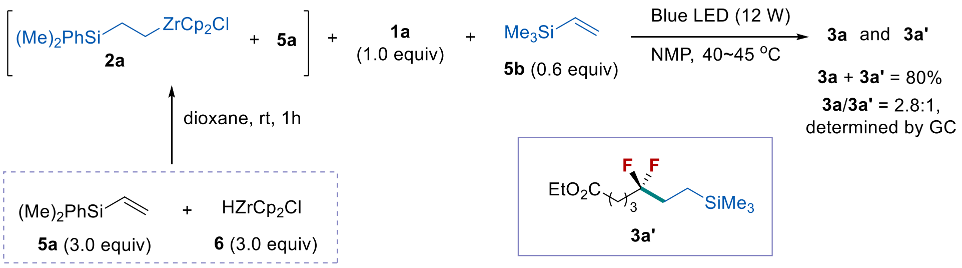
would lead to ≤1% yield of **3a**, after the solution of **2a** was treated with **1a** under the irradiation of blule light.) To another 25 mL of Schlenk tube were added **1a** (0.3 mmol, 1.0 equiv.) and NMP (3.0 mL). The prepared alkylzirconocene **2a** was then transferred to the reaction mixture via syringe under Ar. The resulting reacion mixture was stirred at 40~45 °C for 12 h under irradiation of a 12 W blue LEDs strip. The reaction was cooled to room temperature, and ^{19}F NMR analysis of the reaction showed that essentially, **3a** was not formed during the reaction.

3.2. Preparation of 2a from the reaction of Grignard reagent 7 with ZrCp$_2$Cl$_2$ and using 2a to react with 1a and 5a



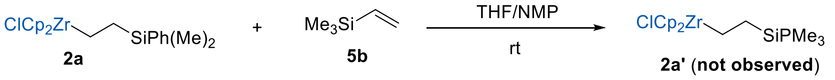
Procedure: To a 25 mL of Schlenk tube were added ZrCp$_2$Cl$_2$ (0.57 mmol, 1.9 equiv, the loading amount of ZrCp$_2$Cl$_2$ was based on **1a**) and **7** (1.32 mL, 0.34 M, 1.5 equiv, the loading amount of **7** was based on **1a**) under Ar. The mixture was stirred for 3 h at room temperature to afford alkylzirconocene **2a**. To another 25 mL of Schlenk tube were added **1a** (0.3 mmol, 1.0 equiv), **5a** (0.6 mmol, 2.0 equiv), and NMP (3.0 mL). The prepared alkylzirconocene **2a** was then transferred to the reaction mixture via syringe under Ar. The resulting reacion mixture was stirred at 40~45 °C for 12 h under irradiation of a 12 W blue LEDs strip. The reaction was cooled to room temperature, and ^{19}F NMR analysis of the reaction showed 48% yield of **3a** was afforded.

3.3. Competetive reactions



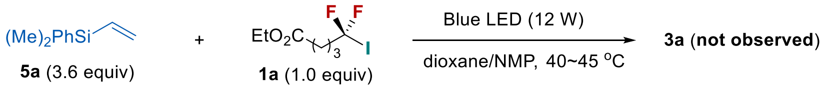
Procedure: To a 25 mL of Schlenk tube was added ZrCp$_2$HCl **6** (3.0 equiv, 0.9 mmol, the loading amount of **6** was based on **1a**) in the glovebox. The tube was then taken out of the glovebox, and was evacuated and backfilled with Ar (3 times). Alkene **5a** (3.0 equiv, 0.9 mmol, the loading amount of **5a** was based on **1a**) and anhydrous dioxane (1.0 mL) were added under Ar. The resulting mixture was stirred at room temperature for 1 h until a clear yellow solution was obtained. To another 25 mL of Schlenk tube were added difluoroalkyl halide **1a** (0.3 mmol, 1.0 equiv), **5b** (0.18 mmol, 0.6 equiv) and NMP (3.0 mL) under Ar. The prepared solution of alkylzirconocene **2a** and alkene **5a** was then added to the mixture via syringe for 1 min under Ar. The resulting mixture was stirred at 40~45 °C under irradiation of a 12 W blue LEDs strip for 12 h. The reaction mixture was then cooled to room temperature. ^{19}F NMR analysis of the reaction showed that 80% yield of **3a** and **3a'** (**3a**/**3a'** = 2.8:1, determined by GC) were afforded.

3.4. Reaction of 2a with silylalkene 5b



Procedure: To a 25 mL of Schlenk tube was added $ZrCp_2HCl$ **6** (5.0 equiv, 0.9 mmol) in the glovebox. The tube was then taken out of the glovebox, and was evacuated and backfilled with Ar (3 times). Alkene **5a** (5.0 equiv, 0.9 mmol) and anhydrous dioxane (1.0 mL) were added under Ar. The resulting mixture was stirred at room temperature for 1 h until a clear yellow solution was obtained. Then **5b** (0.18 mmol, 1.0 equiv) and NPM (3 mL) were added to the reaction mixture under Ar. The resulting mixture was stirred at room temperature for 1 h. GC-MS analysis of the reaction after the reaction was quenched with H_2O.

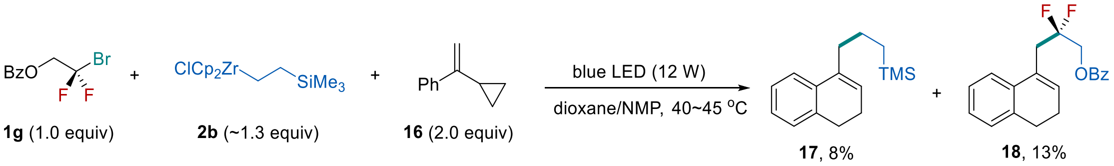
3.5. Reaction of silylalkene 5a with 1a



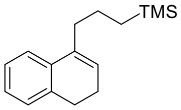
Procedure: To 25 mL of Schlenk tube were added **1a** (0.3 mmol, 1.0 equiv), **5a** (1.08 mmol, 3.6 equiv), dioxane (1.0 mL) and NMP (3.0 mL) under Ar. The resulting reacion mixture was stirred at 40~45 °C for 12 h under irradiation of a 12 W blue LEDs strip. The reaction was cooled to room temperature. ^{19}F NMR analysis of the reaction showed no **3a** was observed.

3.6 Radical clock experiments.

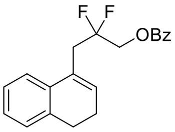
A. Reaction of 1g with 2b and 16



Procedure: To a 25 mL of Schlenk tube was added $ZrCp_2HCl$ (1.8 equiv, 0.54 mmol) in the glovebox. The tube was then taken out of the glove box, and was evacuated and backfilled with Ar (3 times). Silylalkene **5b** (3.5 equiv, 1.05 mmol) and anhydrous dioxane (1.0 mL) were added under Ar. The reaction mixture was stirred for 1 h to provide **2b**. To another 25 mL of Schlenk tube were added **1g** (0.3 mmol, 1.0 equiv), **16** (0.6 mmol, 2.0 equiv) and NMP (3.0 mL). The prepared alkylzirconocene **2b** (~1.3 equiv., ~ 0.38 mmol) was transferred to the reaction via syringe for about 1 min under Ar. The reaction mixture was stirred 12 h at 40~45 °C under irradiation of a 12 W blue LEDs strip. The reaction mixture was then cooled to room temperature. ^{19}F NMR analysis of the reaction showed 13% yield of **18** was provided. The yield of **17** (8% yield) was determined by ^{1}H NMR using mesitylene as the internal standard.

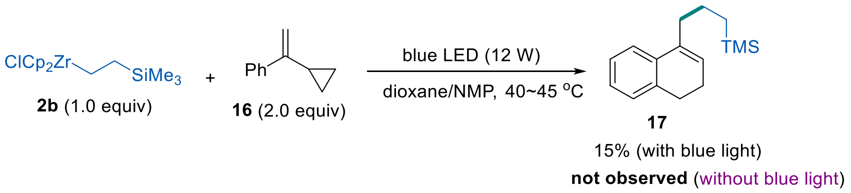


(3-(3,4-Dihydronaphthalen-1-yl)propyl)trimethylsilane (17). The product (8% yield determined by ^{1}H NMR) was purified by flash column chromatography on silica gel (PE) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 7.2 Hz, 1H), 7.21 – 7.06 (m, 3H), 5.92 – 5.77 (m, 1H), 2.73 (t, *J* = 8.0 Hz, 2H), 2.44 (t, *J* = 7.2 Hz, 2H), 2.31 – 2.16 (m, 2H), 1.58 – 1.46 (m, 2H), 0.62 – 0.50 (m, 2H), -0.03 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.7, 136.5, 135.1, 127.5, 126.4, 126.2, 124.7, 122.6, 36.8, 28.5, 23.1, 23.1, 16.8, -1.6. IR (thin film) ν_{max} 2925 cm^{-1}. MS (EI) m/z (%) 244 $(M)^+$, 227, 170, 144 (100), 73. HRMS (FI) calculated for $C_{16}H_{24}Si$: 244.1642; Found: 244.1645 $(M)^+$.



3-(3,4-Dihydronaphthalen-1-yl)-2,2-difluoropropyl benzoate (18). The product (13% determined by ^{19}F NMR) was purified by flash column chromatography on silica gel (PE) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.4 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.39 – 7.28 (m, 1H), 7.21 – 7.06 (m, 3H), 6.20 – 6.01 (m, 1H), 4.47 (t, *J* = 12.4 Hz, 2H), 3.21 (t, *J* = 15.8 Hz, 2H), 2.76 (t, *J* = 8.0 Hz, 2H), 2.35 – 2.20 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.7 – -102.0 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.4, 136.3, 134.0, 133.5, 131.7, 129.8, 129.2, 128.5, 127.7, 127.2, 126.3, 123.1, 121.1 (t, *J* = 244.3 Hz), 63.6 (t, *J* = 33.1 Hz), 37.1 (t, *J* = 24.7 Hz), 28.1 (s), 23.2. IR (thin film) ν_{max} 2934, 2858, 1732, 1351 cm^{-1}. MS (EI) m/z (%) 328 (M$^+$), 222, 186, 141, 105 (100), 77. HRMS (FI) calculated for $C_{20}H_{18}F_2O_2$: 328.1269; Found: 328.1268 (M$^+$).

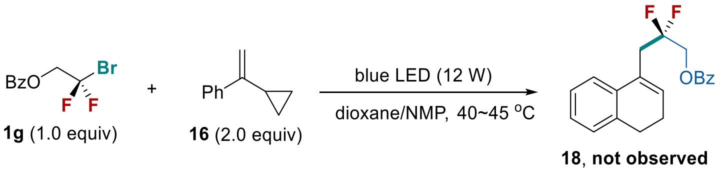
B. Reaction of 2b with 16



2b (1.0 equiv)
16 (2.0 equiv)
17
15% (with blue light)
not observed (without blue light)

Procedure: To a 25 mL of Schlenk tube was added $ZrCp_2HCl$ (0.54 mmol) in the glovebox. The tube was then taken out of the glove box, and was then evacuated and backfilled with Ar (3 times). Silylalkene **5b** (1.05 mmol) and anhydrous dioxane (1.0 mL) were added under Ar. The reaction mixture was stirred for 1 h to provide **2b** (~ 0.38 mmol, 1.0 equiv). To another 25 mL of Schlenk tube were added **16** (0.76 mmol, 2.0 equiv) and NMP (3.0 mL). The prepared alkylzirconocene **2b** was added to the mixture via syringe for about 1 min under Ar. The reaction mixture was stirred 12 h at 40~45 °C under irradiation of a 12 W blue LEDs strip. The reaction mixture was then cooled to room temperature. The yield of **17** (15% yield) was determined by ^{1}H NMR using mesitylene as the internal standard. Under the reaction conditions, the product of **17** was not observed without blue light.

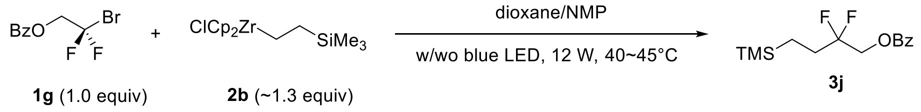
C. Reaction of 1g with 16



1g (1.0 equiv)
16 (2.0 equiv)
18, not observed

Procedure: To a 25 mL of Schlenk tube were added **1g** (0.3 mmol, 1.0 equiv), **16** (0.6 mmol, 2.0 equiv) and NMP (3.0 mL). The reaction mixture was stirred at 40~45 °C for 12 h under irradiation of a 12 W blue LEDs strip. The reaction mixture was then cooled to room temperature. ^{19}F NMR analysis of the reaction showed no **18** was observed.

3.7 Light-dark experiments



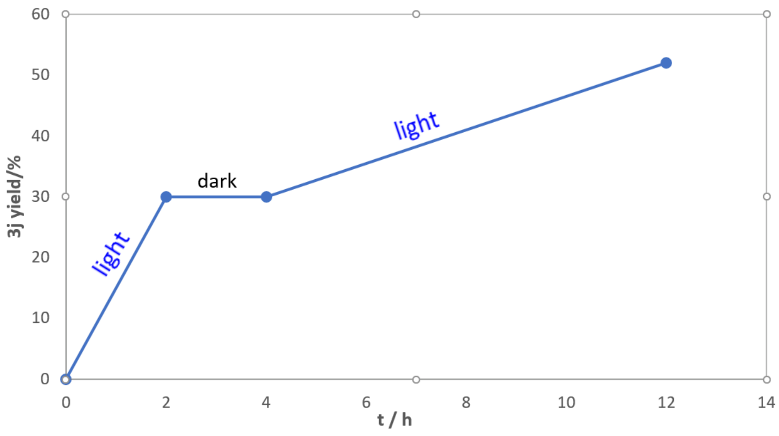
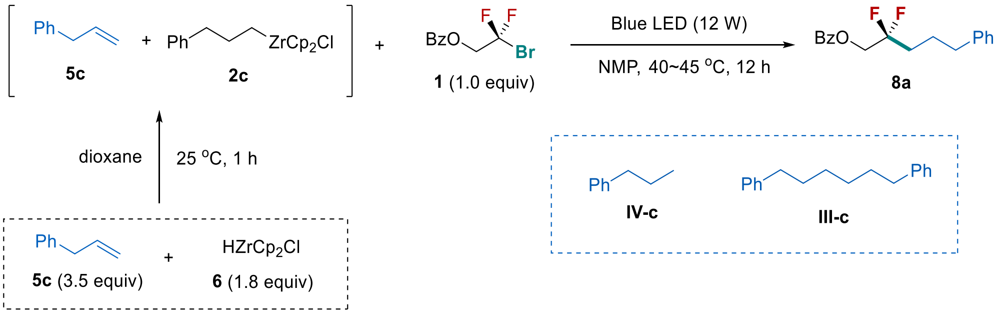


Figure S1. Light -dark experiments for the reaction of 1g with 2b

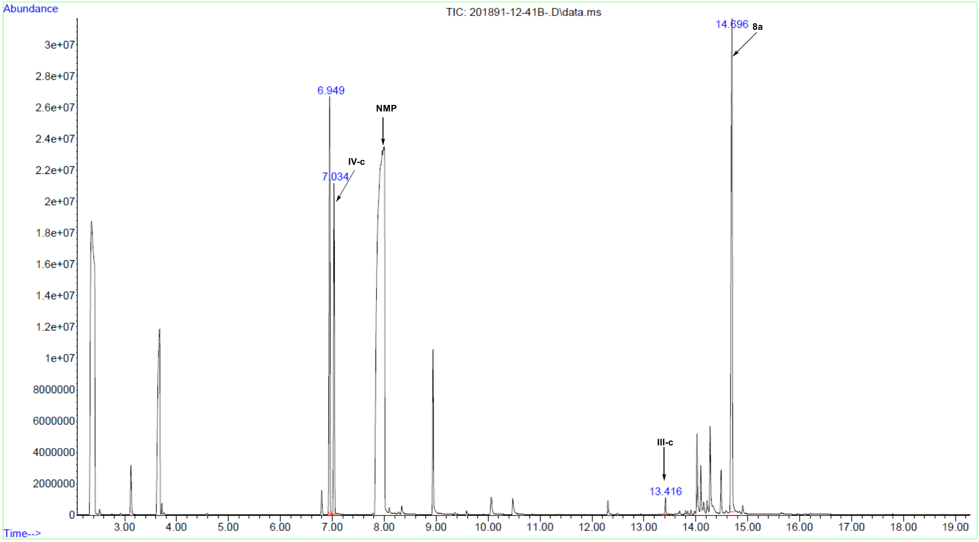
Procedure: To a 25 mL of Schlenk tube was added $ZrCp_2HCl$ (1.8 equiv, 0.54 mmol) in the glovebox. The tube was then taken out of the glovebox, and was evacuated and backfilled with Ar (3 times). Alkene **5b** (3.5 equiv, 1.05 mmol) and anhydrous dioxane (1.0 mL) were added by a syringe under Ar. The mixture was stirred for 1 h until a clear yellow solution was obtained. To another 25 mL of Schlenk tube were added **1g** (0.3 mmol, 1.0 equiv) and NMP (3.0 mL). The prepared solution of alkylzirconocene **2b** (~1.3 equiv, ~ 0.38 mmol) was added to the reaction mixture over 1 min via a syringe under Ar. The reaction mixture was stirred for 2h under irradiation of a 12 W blue LEDs strip at 40~45 ^{o}C. The yield was determined by ^{19}F NMR. Then, the reaction was stirred in dark at 45 ^{o}C for 2 h. The yield was determined by ^{19}F NMR. The reaction mixture was then stirred at the same reaction temperature for 8 h under irradiation of a 12 W blue LEDs strip. The yield was determined by ^{19}F NMR.

3.8 MS analysis of the reaction of 5c with 1g

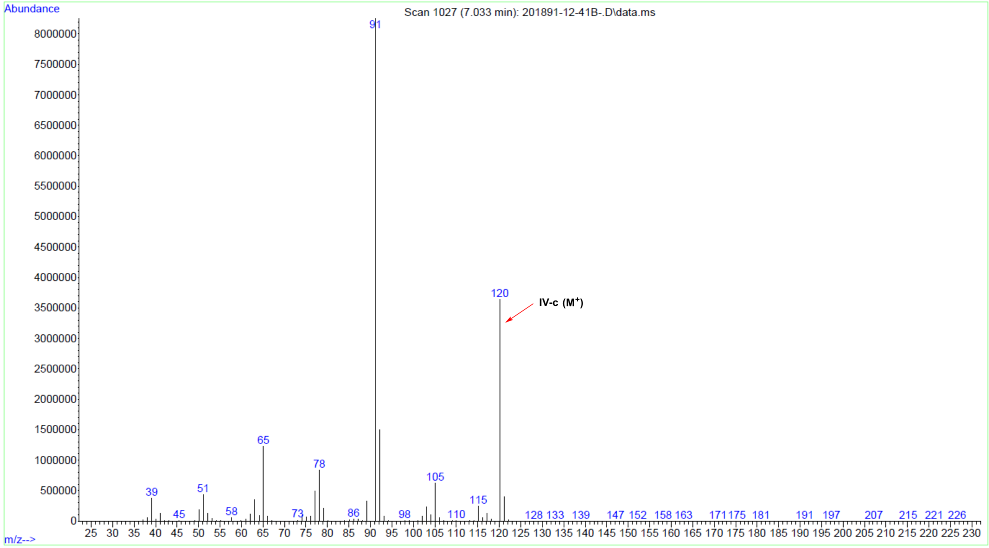


MS analysis of the reaction showed that homo-coupling of **III-c** and a large amount of **IV-c** were formed.

A



B



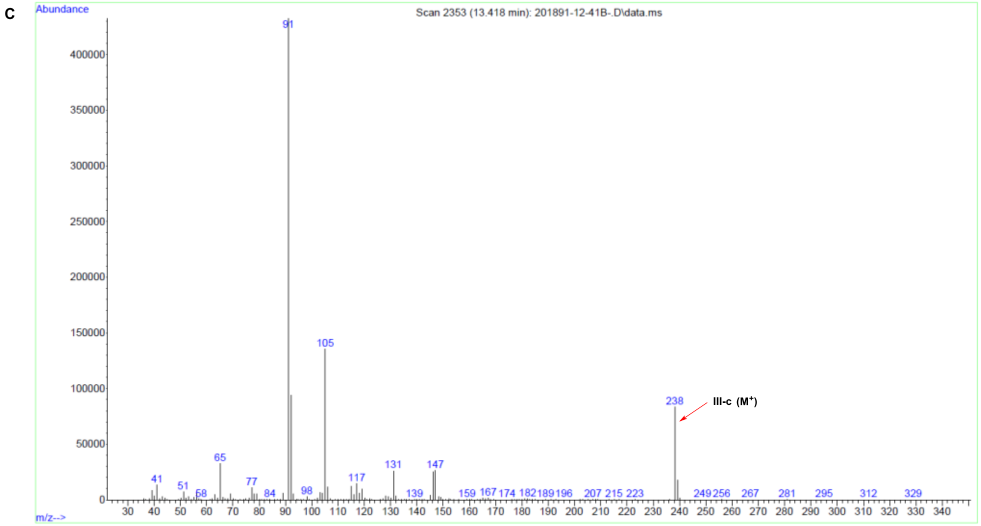
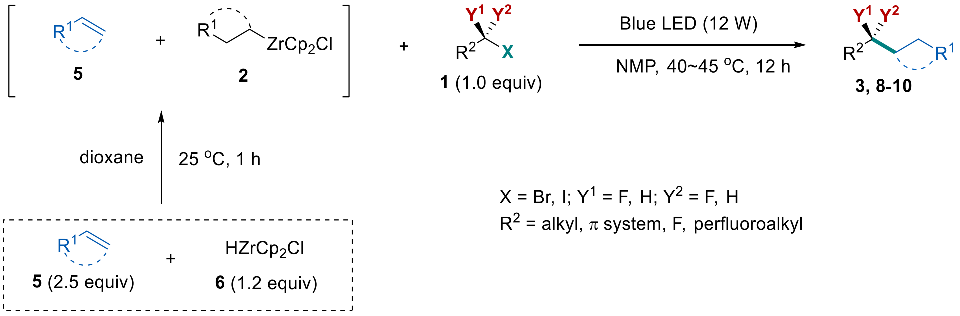


Figure S2. GC-MS analysis of the reaction of 5c with 1g. (A) GC analysis of the reaction; **(B)** MS analysis of **IV-c**; **(C)** MS analysis of **III-c**.

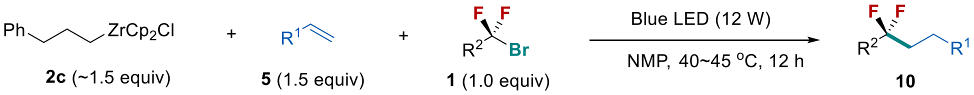
4. (Fluoro)alkylation of Alkenes 5 with (Fluoro)alkylhalides 1 Promoted by Photolysis of Alkylzirconocenes

General Procedure A



To a 25 mL of Schlenk tube was added $ZrCp_2HCl$ (1.2 equiv, 0.36 mmol) in the glovebox. The tube was then taken out of the glovebox, and was evacuated and backfilled with Ar (3 times). Alkene **5** (2.5 equiv, 0.75 mmol) and anhydrous dioxane (1.0 mL) were added under Ar. The resulting mixture was stirred at room temperature for 1 h until a clear yellow solution was obtained. To another 25 mL of Schlenk tube were added difluoroalkyl halide **1** (0.3 mmol, 1.0 equiv) and NMP (3.0 mL) under Ar. The prepared solution of alkylzirconocene and alkene was then added to the mixture via a syringe for 1 min under Ar. The reaction mixture was stirred at 40~45 °C under irradiation of a 12 W blue LEDs strip for 12 h. The reaction mixture was then cooled to room temperature. The reaction mixture was poured into water (50 mL) and extracted with EA (30 mL× 2). The combined organic layers were washed by brine, dried over anhydrous sodium sulfate, filtered, and concentrated. The product was purified with flash column chromatography.

General Procedure B



Preparation of 2c: To a 25 mL of Schlenk tube was added $ZrCp_2HCl$ **6** (2.0 equiv, 0.6 mmol, the loading amount of **6** was calculated based on **1**) in the glovebox. The tube was taken out of the glovebox, and was then evacuated and backfilled with Ar (3 times). Allylbenzene **5c** (1.5 equiv, 0.45 mmol, the loading amount of **5c** was calculated based on **1**) and anhydrous dioxane (1.0 mL) were added under Ar. The mixture was stirred for 1 h at about 40 ^{o}C until a clear yellow solution was obtained.

Reaction of 5 with 1 in the presence of 2c: To a 25 mL of Schlenk tube were added difluoroalkyl **1** (0.3 mmol, 1.0 equiv), alkene **5** (0.45 mmol, 1.5 equiv), and NMP (3.0 mL). The prepared alkylzirconocene **2c** (~1.5 equiv) was then added to the reaction mixture for 1 min under Ar. The reaction was stirred at 40~45 ^{o}C under irradiation of a 12 W blue LEDs strip for 12 h. The reaction mixture was then cooled to room temperature. The reaction mixture was poured into water (50 mL) and extracted with EA (30 mL× 2). The combined organic layers were washed by brine, dried over anhydrous sodium sulfate, filtered, and concentrated. The product was purified by flash column chromatography.

Note: Excessive $ZrCp_2HCl$ **6** used for the preparation of **2c** can be quenched by NMP.[16] Therefore, it cannot influence the reaction.

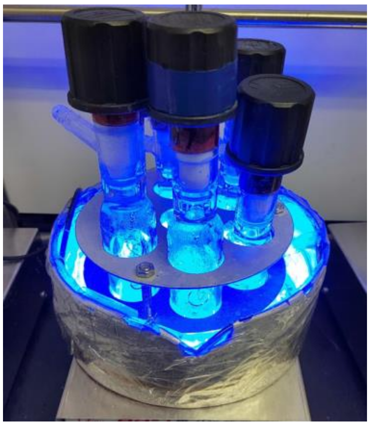
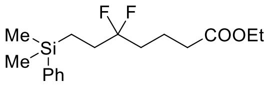
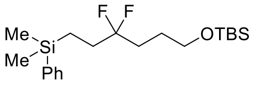


Figure S3. Synthesis of compounds 3, 8-10.

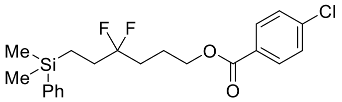
5. Characterization Data for Compounds 3, 8-10.



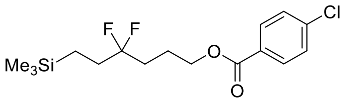
Ethyl 7-(dimethyl(phenyl)silyl)-5,5-difluoroheptanoate (3a). General Procedure A: The product (61 mg, 62% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 80:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.45 (m, 2H), 7.42 – 7.31 (m, 3H), 4.14 (q, J = 7.2 Hz, 2H), 2.34 (t, J = 7.2 Hz, 2H), 1.92 – 1.73 (m, 6H), 1.26 (t, J = 7.2 Hz, 3H), 0.92 – 0.82 (m, 2H), 0.30 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.9 – -100.4 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 138.1, 133.5, 129.1, 127.9, 125.3 (t, J = 241.2 Hz), 60.4, 34.9 (t, J = 25.8 Hz), 33.7, 30.9 (t, J = 26.7 Hz), 17.8 (t, J = 4.8 Hz), 14.2, 7.7 (t, J = 3.4 Hz), -3.4. IR (thin film) ν_{max} 2922, 1731, 1456 cm^{-1}. MS (EI) m/z (%), 313, 235, 135 (100), 81. HRMS (FI) calculated for $C_{17}H_{26}F_2O_2Si$: 328.1665; Found: 328.1671 (M)$^+$.



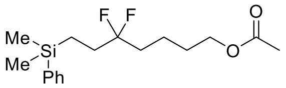
***tert*-Butyl((6-(dimethyl(phenyl)silyl)-4,4-difluorohexyl)oxy)dimethylsilane (3b). General Procedure A:** The product (74 mg, 64% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 100:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.46 (m, 2H), 7.41 – 7.33 (m, 3H), 3.62 (t, J = 6.2 Hz, 2H), 1.95 – 1.70 (m, 4H), 1.68 – 1.56 (m, 2H), 0.94 – 0.83 (m, 11H), 0.29 (s, 6H), 0.04 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.5 – -99.8 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.2, 133.5, 129.1, 127.9, 125.8 (t, J = 241.3 Hz), 62.4, 32.2 (t, J = 25. 8 Hz), 30.9 (t, J = 26.7 Hz), 25.9, 25.7 (t, J = 4.2 Hz), 18.3, 7.8 (t, J = 3.3 Hz), -3.3, -5.4. IR (thin film) ν_{max} 2929, 2857, 1463, 1360 cm^{-1}. MS (EI) m/z (%), 157, 135 (100), 81. HRMS (EI) calculated for $C_{20}H_{36}F_2OSi_2$: 386.2267; Found: 386.2274 (M)$^+$.



6-(Dimethyl(phenyl)silyl)-4,4-difluorohexyl 4-chlorobenzoate (3c). General Procedure A: The product (81 mg, 66% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 80:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.6 Hz, 2H), 7.52 – 7.46 (m, 2H), 7.40 (d, J = 8.6 Hz, 2H), 7.38 – 7.34 (m, 3H), 4.33 (t, J = 5.8 Hz, 2H), 2.03 – 1.88 (m, 4H), 1.87 – 1.72 (m, 2H), 0.94 – 0.86 (m, 2H), 0.29 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -100.5 – -100.7 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6, 139.4, 138.0, 133.5, 130.9, 129.2, 128.7, 128.6, 127.9, 125.1 (t, J = 241.8 Hz), 64.5, 32.4 (t, *J* = 26.2 Hz), 31.1 (t, *J* = 26.6 Hz), 21.8 (t, *J* = 4.5 Hz), 7.8 (t, *J* = 3.2 Hz), -3.4. IR (thin film) ν_{max} 3049, 2870, 1723, 1450 cm^{-1}. MS (DART) m/z (%) 428 $(M+NH_4)^+$. HRMS (DART) calculated for $C_{21}H_{29}F_2O_2NSiCl$: 428.1619; Found: 428.1612 $(M+NH_4)^+$.

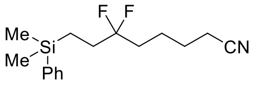


4,4-Difluoro-6-(trimethylsilyl)hexyl 4-chlorobenzoate (3d). General Procedure A, Gram-scale Synthesis: To a 50 mL of Schlenk tube was added $ZrCp_2HCl$ (1.2 equiv, 4.8 mmol) in the glovebox. The tube was then taken out of the glovebox, and was evacuated and backfilled with Ar (3 times). Alkene **5b** (2.5 equiv, 10 mmol) and anhydrous dioxane (13 mL) were added under Ar. The resulting mixture was stirred at room temperature for 1 h until a clear yellow solution was obtained. To another 100 mL of Schlenk tube were added difluoroalkyl halide **1c** (4 mmol, 1.0 equiv) and NMP (40 mL) under Ar. The prepared solution of alkylzirconocene and alkene was then added to the reaction mixture via a syringe for 10 min under Ar. The reaction mixture was stirred at 40~45 ^{o}C under irradiation of a 12 W blue LEDs strip for 12 h. The reaction mixture was then cooled to room temperature. The reaction mixture was poured into water (200 mL) and extracted with EA (150 mL× 2). The combined organic layers were washed by brine, dried over anhydrous sodium sulfate, filtered, and concentrated. The product was purified with flash column chromatography (Petroleum ether: Ethyl acetate = 60:1) to give product **3d** (68%, 0.95 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 4.36 (t, *J* = 5.4 Hz, 2H), 2.08 – 1.91 (m, 4H), 1.89 – 1.70 (m, 2H), 0.70 – 0.56 (m, 2H), 0.01 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -100.1 – -100.6 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 139.4, 130.9, 128.7, 128.6, 125.2 (t, *J* = 242.1 Hz), 64.5, 32.4 (t, *J* = 26.4 Hz), 31.2 (t, *J* = 26.7 Hz), 21.8, 8.6, -2.0. IR (thin film) ν_{max} 2855, 1724, 1450 cm^{-1}. MS (EI) m/z (%) 213, 175, 139 (100), 73. HRMS (FI) calculated for $C_{16}H_{24}F_2O_2SiCl$: 349.1197; Found: 349.1203 $(M+H)^+$.

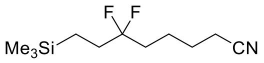


7-(Dimethyl(phenyl)silyl)-5,5-difluoroheptyl acetate (3e). General Procedure A: The product (70 mg, 71% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 80:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.46 (m, 2H), 7.42 – 7.33 (m, 3H), 4.07 (t, *J* = 6.4 Hz, 2H), 2.05 (s, 3H), 1.92 – 1.71 (m, 4H), 1.70 – 1.60 (m, 2H), 1.58 – 1.45 (m, 2H), 0.94 – 0.83 (m, 2H), 0.31 (s, 6H). ^{19}F NMR

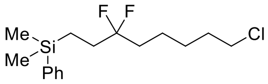
(376 MHz, $CDCl_3$) δ -100.1 – -100.3 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 138.1, 133.5, 129.1, 127.9, 125.3 (t, *J* = 242.8 Hz), 64.0, 35.2 (t, *J* = 25.9 Hz), 30.9 (t, *J* = 26.8 Hz), 28.3, 20.9, 18.8 (t, *J* = 4.7 Hz), 7.8 (t, *J* = 3.2 Hz), -3.4. IR (thin film) ν_{max} 1740, 1461, 1366 cm^{-1}. MS (FI) m/z (%) 251, 179, 135 (100), 95. HRMS (FI) calculated for $C_{17}H_{27}F_2O_2Si$: 329.1743; Found: 329.1741 $(M+H)^+$.



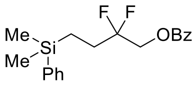
8-(Dimethyl(phenyl)silyl)-6,6-difluorooctanenitrile (3f). General Procedure A: The product (59 mg, 67% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 40:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.42 – 7.34 (m, 3H), 2.35 (t, *J* = 7.0 Hz, 2H), 1.95 – 1.66 (m, 6H), 1.64 – 1.54 (m, 2H), 0.94 – 0.82 (m, 2H), 0.31 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -100.1 – -100.4 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 133.5, 129.1, 127.9, 125.0 (t, *J* = 242.3 Hz), 119.3, 34.8 (t, *J* = 26.2 Hz), 31.1 (t, *J* = 26.8 Hz), 25.1, 21.5 (t, *J* = 4.6 Hz), 17.0, 7.8 (t, *J* = 3.6 Hz), -3.4. IR (thin film) ν_{max} 3069, 3010, 2247, 1464, 1362 cm^{-1}. MS (EI) m/z (%) 295 $(M)^+$, 280, 135 (100), 91. HRMS (EI) calculated for $C_{16}H_{23}F_2NSi$: 295.1562; Found: 295.1567 $(M)^+$.



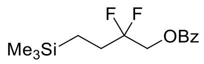
6,6-Difluoro-8-(trimethylsilyl)octanenitrile (3g). **General Procedure A, Gram-scale Synthesis:** To a 100 mL of Schlenk tube was added $ZrCp_2HCl$ (1.2 equiv, 12 mmol) in the glovebox. The tube was then taken out of the glovebox, and was evacuated and backfilled with Ar (3 times). Alkene **5b** (2.5 equiv, 25 mmol) and anhydrous dioxane (33 mL) were added under Ar. The resulting mixture was stirred at room temperature for 1 h until a clear yellow solution was obtained. To another 350 mL of Schlenk tube were added difluoroalkyl halide **1e** (10 mmol, 1.0 equiv) and NMP (130 mL) under Ar. The prepared solution of alkylzirconocene and alkene was then added to the reaction mixture via a syringe for 10 min under Ar. The reaction mixture was stirred at 40~45 °C under irradiation of a 12 W blue LEDs strip for 12 h. The reaction mixture was then cooled to room temperature. The reaction mixture was poured into water (200 mL) and extracted with EA (150 mL× 2). The combined organic layers were washed by brine, dried over anhydrous sodium sulfate, filtered, and concentrated. The product was purified with flash column chromatography (Petroleum ether: Ethyl acetate = 40:1) to give product **3g** (66%, 1.54 g) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.37 (t, *J* = 6.8 Hz, 2H), 1.97 – 1.57 (m, 8H), 0.70 – 0.48 (m, 2H), 0.01 (s, 9H). ^{19}F NMR (376 MHz, CDCl$_3$) δ -99.9 – -100.2 (m, 2F). ^{13}C NMR (101 MHz, CDCl$_3$) δ 125.2 (t, *J* = 242.2 Hz), 119.3, 34.7 (t, *J* = 26.1 Hz), 31.1 (t, *J* = 26.5 Hz), 25.1, 21.5 (t, *J* = 4.5 Hz), 17.0, 8.6, -2.1. IR (thin film) ν_{max} 2898, 2248, 1465, 1361 cm^{-1}. MS (FI) m/z (%) 233 (M)$^+$, 218, 73 (100). HRMS (FI) calculated for $C_{11}H_{21}F_2NSi$: 233.1411; Found: 233.1405 (M)$^+$.



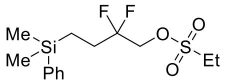
(8-Chloro-3,3-difluorooctyl)dimethyl(phenyl)silane (3h). General Procedure A: The product (69 mg, 72% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 100:1) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.57– 7.50 (m, 2H), 7.43 – 7.38 (m, 3H), 3.55 (t, *J* = 6.6 Hz, 2H), 1.93 – 1.72 (m, 6H), 1.54 – 1.42 (m, 4H), 0.95 – 0.86 (m, 2H), 0.33 (s, 6H). ^{19}F NMR (376 MHz, CDCl$_3$) δ -99.8 – -100.2 (m, 2F). ^{13}C NMR (101 MHz, CDCl$_3$) δ 138.1, 133.5, 129.1, 127.9, 125.4 (t, *J* = 241.5 Hz), 44.7, 35.50 (t, *J* = 25.8 Hz), 32.3, 30.9 (t, *J* = 26.9 Hz), 26.6, 21.5 (t, *J* = 4.7 Hz), -3.4. IR (thin film) ν_{max} 2868, 1670, 1464, 1357 cm^{-1}. MS (EI) m/z (%) 185, 135 (100), 91, 74. HRMS (FI) calculated for $C_{16}H_{25}F_2ClSi$: 318.1377; Found: 318.1380 (M)$^+$.



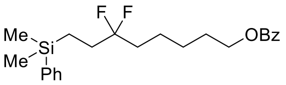
4-(Dimethyl(phenyl)silyl)-2,2-difluorobutyl benzoate (3i). General Procedure A: 3.5 equiv of alkene **5a** and 1.8 equiv of **6** were used. The product (68 mg, 65% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 80:1) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.55 – 7.44 (m, 4H), 7.41 – 7.30 (m, 3H), 4.53 (t, *J* = 12.2 Hz, 2H), 2.19 – 1.82 (m, 2H), 1.13 – 0.88 (m, 2H), 0.34 (s, 6H). ^{19}F NMR (376 MHz, CDCl$_3$) δ -106.7 (tt, *J* = 16.2 Hz, 12.4 Hz, 2F). ^{13}C NMR (101 MHz, CDCl$_3$) δ 165.5, 137.7, 133.44, 133.41, 129.8, 129.1, 128.5, 127.9, 122.2 (t, *J* = 243.4 Hz), 63.5 (t, *J* = 34.4 Hz), 28.6 (t, *J* = 25.1 Hz), 7.33 (t, *J* = 3.0 Hz), -3.4. IR (thin film) ν_{max} 3069, 2956, 1731, 1451 cm^{-1}. MS (EI) m/z (%) 348 (M)$^+$, 333, 135, 105 (100), 77. HRMS (EI) calculated for $C_{19}H_{22}F_2O_2Si$: 348.1352; Found: 348.1347 (M)$^+$.



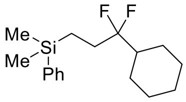
2,2-Difluoro-4-(trimethylsilyl)butyl benzoate (3j). General Procedure A: 3.5 equiv of alkene **5b** and 1.8 equiv of **6** were used. The product (52 mg, 60% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 80:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 7.8 Hz, 2H), 7.60 (t, J = 7.8 Hz, 1H), 7.47 (t, J = 7.8 Hz, 2H), 4.52 (t, J = 12.6 Hz, 2H), 2.06 – 1.84 (m, 2H), 0.79 – 0.61 (m, 2H), 0.03 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.8 (tt, J = 16.5 Hz, 12.4 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 133.4, 129.8, 129.2, 128.5, 122.27 (t, J = 243.2 Hz), 63.6 (t, J = 34.1 Hz), 28.7 (t, J = 25.0 Hz), 8.1, -2.1. IR (thin film) ν_{max} 2954, 1732, 1452, 1354 cm^{-1}. MS (EI) m/z (%) 286 $(M)^+$, 271, 179, 105 (100), 77. HRMS (FI) calculated for $C_{14}H_{20}F_2O_2Si$: 286.1195; Found: 286.1189 $(M)^+$.



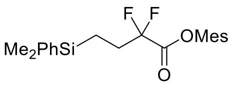
7-(Dimethyl(phenyl)silyl)-5,5-difluoroheptyl acetate (3k). General Procedure A: 3.5 equiv of alkene **5a** and 1.8 equiv of **6** were used. The product (64 mg, 63% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 10:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 2H), 7.42 – 7.35 (m, 3H), 4.30 (t, J = 11.8 Hz, 2H), 3.17 (q, J = 7.4 Hz, 2H), 1.97 – 1.79 (m, 2H), 1.41 (t, J = 7.4 Hz, 3H), 0.95 – 0.86 (m, 2H), 0.32 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.3 (tt, J = 16.2 Hz, 11.9 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 133.5, 129.2, 127.9, 121.2 (t, J = 243.7 Hz), 66.8 (t, J = 35.0 Hz), 45.5, 28.3 (t, J = 24.6 Hz), 8.0, 7.1 (t, J = 3.0 Hz), -3.5. IR (thin film) ν_{max} 1458, 1462, 1170, 1114, 1057, 1018 cm^{-1}. MS (EI) m/z (%) 321, 179, 135 (100), 91. HRMS (EI) calculated for $C_{14}H_{22}F_2O_3SSi$: 336.1021; Found: 336.1024 $(M)^+$.



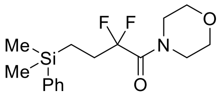
8-(Dimethyl(phenyl)silyl)-6,6-difluorooctyl benzoate (3l). General Procedure A: 3.5 equiv of alkene **5a** and 1.8 equiv of **6** were used. The product (55 mg, 45% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 80:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 7.6 Hz, 2H), 7.56 (t, J = 7.0 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.44 (t, J = 7.4 Hz, 2H), 7.40 – 7.33 (m, 3H), 4.32 (t, J = 6.6 Hz, 2H), 1.93 – 1.68 (m, 6H), 1.58 – 1.42 (m, 4H), 0.94 – 0.82 (m, 2H), 0.30 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.7 – -100.1 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 138.1, 133.5, 132.8, 130.4, 129.5, 129.1, 128.3, 127.9, 125.5 (t, *J* = 241.3 Hz), 64.8, 35.6 (t, *J* = 25.6 Hz), 30.9 (t, *J* = 26.8 Hz), 28.5, 25.9, 21.9 (t, *J* = 4.5 Hz), 7.8 (t, *J* = 3.4 Hz), -3.4. IR (thin film) ν_{max} 2867, 1719, 1451 cm^{-1}. MS (FI) m/z (%) 241, 135, 105 (100), 77. HRMS (EI) calculated for $C_{23}H_{30}F_2O_2Si$: 404.1978; Found: 404.1980 (M)$^+$.



(3-Cyclohexyl-3,3-difluoropropyl)dimethyl(phenyl)silane (3m). General Procedure A: The product (38 mg, 43% yield) was purified by flash column chromatography on silica gel (PE) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 2H), 7.41 – 7.33 (m, 3H), 1.86 – 1.70 (m, 7H), 1.23 – 1.08 (m, 6H), 0.93 – 0.84 (m, 2H), 0.29 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.4 – -107.5 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.3, 133.5, 129.1, 128.2, 126.2 (t, *J* = 243.4 Hz), 43.1 (t, *J* = 23.9 Hz), 28.4 (t, *J* = 27.4 Hz), 26.0, 25.8, 25.7 (t, *J* = 4.5 Hz), 7.10 (t, *J* = 3.7 Hz), -3.3. IR (thin film) ν_{max} 2932, 2855, 1453, 1379 cm^{-1}. MS (EI) m/z (%) 185, 135 (100), 81. HRMS (EI) calculated for $C_{17}H_{26}F_2Si$: 296.1766; Found: 296.1771 (M)$^+$.

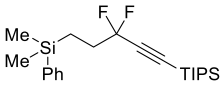


Mesityl 4-(dimethyl(phenyl)silyl)-2,2-difluorobutanoate (3n). General Procedure A: The product (96 mg, 85% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 60:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 2H), 7.46 – 7.39 (m, 3H), 6.93 (s, 2H), 2.32 (s, 3H), 2.30 – 2.16 (m, 2H), 2.14 (s, 6H), 1.10 – 1.03 (m, 2H), 0.40 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.2 (t, *J* = 16.0 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (t, *J* = 34.9 Hz), 144.9, 137.4, 136.1, 133.4, 129.5, 129.3, 129.2, 128.0, 117.0 (t, *J* = 251.9 Hz), 29.5 (t, *J* = 24.2 Hz), 20.7, 16.0, 7.1, -3.4. IR (thin film) ν_{max} 3049, 2925, 2862, 1785, 1437 cm^{-1}. MS (DART) m/z (%) 394 $(M+NH_4)^+$. HRMS (DART) calculated for $C_{21}H_{30}O_2NF_2Si$: 394.2008; Found: 394.2002 $(M+NH_4)^+$.

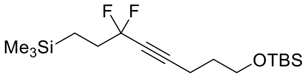


4-(Dimethyl(phenyl)silyl)-2,2-difluoro-1-morpholinobutan-1-one (3o). General Procedure A: The product (80 mg, 82% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 10:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 2H), 7.42 – 7.32 (m, 3H), 3.75 – 3.67 (m, 4H), 3.67 – 3.60

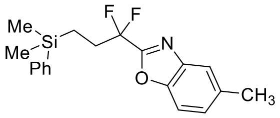
(m, 4H), 2.20 – 2.04 (m, 2H), 1.03 – 0.92 (m, 2H), 0.33 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -100.9 (t, *J* = 17.5 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0 (t, *J* = 30.3 Hz), 137.9, 133.4, 129.0, 127.8, 119.5 (t, *J* = 255.0 Hz), 66.7, 66.6, 46.4 (t, *J* = 6.4 Hz), 43.2, 29.3 (t, *J* = 24.3 Hz), 6.7 (t, *J* = 2.7 Hz), -3.4. IR (thin film) ν_{max} 2923, 2857, 1670, 1435, 1363 cm^{-1}. MS (EI) m/z (%) 312 (100), 250, 135. HRMS (EI) calculated for $C_{16}H_{23}F_2NO_2Si$: 327.1461; Found: 327.1468 $(M)^+$.



(3,3-Difluoro-5-(triisopropylsilyl)pent-4-yn-1-yl)dimethyl(phenyl)silane (3p). General Procedure A: The product (79 mg, 67% yield) was purified by flash column chromatography on silica gel (PE) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 2H), 7.42 – 7.35 (m, 3H), 2.07 – 1.91 (m, 2H), 1.16 – 1.07 (m, 21H), 1.07 – 1.00 (m, 2H), 0.32 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.3 (t, *J* = 13.9 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.9, 133.5, 129.2, 128.0, 115.3 (t, *J* = 233.6 Hz), 99.1 (t, *J* = 39.5 Hz), 89.9 (t, *J* = 5.5 Hz), 34.3 (t, *J* = 27.4 Hz), 18.5, 10.9, 8.8, -3.3. IR (thin film) ν_{max} 2867, 1463, 1367 cm^{-1}. MS (EI) m/z (%) 199, 135 (100), 77. HRMS (EI) calculated for $C_{22}H_{36}F_2Si_2$: 394.2318; Found: 394.2326 $(M)^+$.

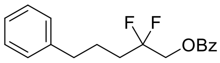


***tert*-Butyl((6,6-Difluoro-8-(trimethylsilyl)oct-4-yn-1-yl)oxy)dimethylsilane (3q). General Procedure A:** The product (71 mg, 68% yield) was purified by flash column chromatography on silica gel (PE) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.69 (t, *J* = 6.0 Hz, 2H), 2.43 – 2.32 (m, 2H), 2.02 – 1.85 (m, 2H), 1.80 – 1.68 (m, 2H), 0.90 (s, 9H), 0.76 – 0.66 (m, 2H), 0.06 (s, 6H), 0.02 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -83.1 (tt, *J* = 14.3, 4.9 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 115.8 (t, *J* = 232.6 Hz), 88.1 (t, *J* = 6.6 Hz), 74.1 (t, *J* = 40.6 Hz), 61.2, 34.4 (t, *J* = 28.0 Hz), 30.9, 25.9, 18.3, 14.8, 9.2, -2.0, -5.4. IR (thin film) ν_{max} 2929, 2858, 2251, 1361 cm^{-1}. MS (EI) m/z (%) 333, 199, 171, 105 (100). HRMS (EI) calculated for $C_{17}H_{34}F_2OSi_2$: 348.2111; Found: 348.2119 $(M)^+$.

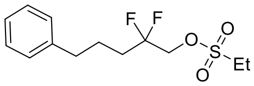


2-(3-(Dimethyl(phenyl)silyl)-1,1-difluoropropyl)-5-methylbenzo[d]oxazole (3r). General Procedure A: The product (65 mg, 63% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate =

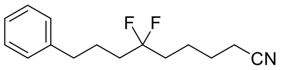
30:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.55 – 7.49 (m, 2H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.42 – 7.32 (m, 3H), 7.26 (d, *J* = 8.2 Hz, 1H), 2.49 (s, 3H), 2.45 – 2.30 (m, 2H), 1.05 – 0.96 (m, 2H), 0.33 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -100.1 (t, *J* = 16.2 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3 (t, *J* = 34.7 Hz), 148.9, 140.2, 137.7, 135.2, 133.5, 129.2, 127.9, 127.8, 120.9, 117.3 (t, *J* = 242.2 Hz), 110.7, 30.9 (t, *J* = 24.8 Hz), 21.4, 7.0, -3.4. IR (thin film) ν_{max} 3022, 2926, 2869, 1458, 1358 cm^{-1}. MS (FI) m/z (%) 330, 268, 191, 135 (100), 77, 91. HRMS (EI) calculated for $C_{19}H_{21}F_2NOSi$: 345.1355; Found: 345.1361 (M)$^+$.



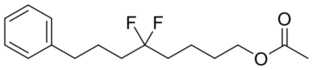
2,2-Difluoro-5-phenylpentyl benzoate (8a). General Procedure A: 3.5 equiv of alkene **5c** and 1.8 equiv of **6** were used. The product (55 mg, 58% yield was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 80:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.14 (m, 3H), 4.47 (t, *J* = 12.4 Hz, 2H), 2.69 (t, *J* = 7.4 Hz, 2H), 2.10 – 1.82 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.3 (tt, *J* = 15.8, 12.8 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 141.1, 133.5, 129.8, 129.1, 128.5, 128.43, 128.37, 126.1, 121.7 (t, *J* = 243.0 Hz), 64.1 (t, *J* = 34.1 Hz), 35.2, 33.34 (t, *J* = 34.2 Hz), 23.3. IR (thin film) ν_{max} 2856, 1731, 1452 cm^{-1}. MS (EI) m/z (%) 304 (M)$^+$, 182, 153, 105 (100), 91, 77. HRMS (EI) calculated for $C_{18}H_{18}F_2O_2$: 304.1269; Found: 304.1268 (M)$^+$.



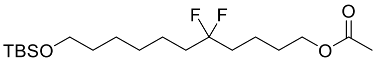
2,2-Difluoro-5-phenylpentyl ethanesulfonate (8b). General Procedure A: 3.5 equiv of alkene **5c** and 1.8 equiv of **6** were used. The product (48 mg, 55% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 10:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.25 – 7.16 (m, 3H), 4.28 (t, *J* = 11.8 Hz, 2H), 3.19 (q, *J* = 7.6 Hz, 2H), 2.69 (t, *J* = 7.2 Hz, 2H), 2.07 – 1.77 (m, 4H), 1.43 (t, *J* = 7.6 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.9 (tt, *J* = 16.5, 12.0 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9, 128.5, 128.3, 126.1, 120.8 (t, *J* = 244.3 Hz), 67.3 (t, *J* = 35.2 Hz), 45.5, 35.1, 32.9 (t, *J* = 23.5 Hz), 23.1 (t, *J* = 3.9 Hz), 8.0. IR (thin film) ν_{max} 2946, 1454, 1362 cm^{-1}. MS (EI) m/z (%) 292 (M)$^+$, 182, 153, 91 (100). HRMS (EI) calculated for $C_{13}H_{18}F_2O_3S$: 292.0939; Found: 292.0942 (M)$^+$.



6,6-Difluoro-9-phenylnonanenitrile (8c). General Procedure A: 3.5 equiv of alkene **5c** and 1.8 equiv of **6** were used. The product (37.0 mg, 49% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 20:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.2 Hz, 2H), 7.23 – 7.15 (m, 3H), 2.66 (t, *J* = 6.4 Hz, 2H), 2.35 (t, *J* = 6.8 Hz, 2H), 1.93 – 1.75 (m, 6H), 1.74 – 1.54 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.3 – -98.6 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 128.4, 128.3, 126.0, 124.6 (t, *J* = 241.9 Hz), 119.2, 35.9 (t, *J* = 25.6 Hz), 35.5 (d, *J* = 26.0 Hz), 35.3, 25.1, 23.9 (t, *J* = 4.5 Hz), 21.5 (t, *J* = 4.7 Hz), 17.0. IR (thin film) ν_{max} 3086, 3027, 2247, 1454 cm^{-1}. MS (EI) m/z (%) 251 (M)$^+$, 104, 91 (100). HRMS (FI) calculated for $C_{15}H_{19}F_2N$: 251.1480; Found: 251.1483 (M)$^+$.

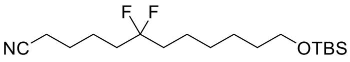


5,5-Difluoro-8-phenyloctyl acetate (8d). General Procedure A: 3.5 equiv of alkene **5c** and 1.8 equiv of **6** were used. The product (41 mg, 48% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 80:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.2 Hz, 2H), 7.22 – 7.14 (m, 3H), 4.06 (t, *J* = 6.6 Hz, 2H), 2.66 (t, *J* = 7.0 Hz, 2H), 2.05 (s, 3H), 1.92 – 1.75 (m, 6H), 1.69 – 1.59 (m, 2H), 1.55 – 1.45 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.2 – -98.5 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.2, 141.5, 128.4, 128.4, 126.0, 125.0 (t, *J* = 241.0 Hz), 64.0, 36.0 (t, *J* = 25.7 Hz), 35.9 (t, *J* = 25.5 Hz), 35.4, 28.3, 24.0 (t, *J* = 4.5 Hz), 21.0, 18.9 (t, *J* = 4.7 Hz). IR (thin film) ν_{max} 2928, 2855, 1730, 1454 cm^{-1}. MS (EI) m/z (%) 284 (M)$^+$, 184, 117, 104 (100), 91. HRMS (FI) calculated for $C_{16}H_{22}F_2O_2$: 284.1582; Found: 284.1579 (M)$^+$.

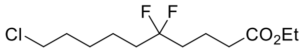


11-((*tert*-Dutyldimethylsilyl)oxy)-5,5-difluoroundecyl acetate (8e). General Procedure A: 3.5 equiv of alkene **5d** and 1.8 equiv of **6** were used. The product (59 mg, 52% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 80:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.07 (t, *J* = 6.4 Hz, 2H), 3.60 (t, *J* = 6.4 Hz, 2H), 2.05 (s, 3H), 1.93 – 1.75 (m, 4H), 1.71 – 1.62 (m, 2H), 1.57 – 1.40 (m, 6H), 1.37 – 1.30 (m, 4H), 0.89 (s, 9H), 0.04 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.1 – -98.4 (m, 2F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.2, 125.1 (t, *J* = 240.4 Hz), 64.0, 63.1, 36.4 (t, *J* =

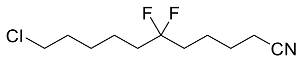
25.1 Hz), 35.9 (t, *J* = 25.7 Hz), 32.6, 29.2, 28.3, 26.0, 25.6, 22.3 (t, *J* = 4.5 Hz), 21.0, 18.9 (t, *J* = 4.6 Hz), -5.3. IR (thin film) ν_{max} 2929, 2856, 1743, 1463 cm^{-1}. MS (EI) m/z (%) 323, 261, 117 (100), 55. HRMS (FI) calculated for $C_{19}H_{39}F_2O_3Si$: 381.2631; Found: 381.2634 $(M+H)^+$.



12-((*tert*-Butyldimethylsilyl)oxy)-6,6-difluorododecanenitrile (8f). General Procedure A: 3.5 equiv of alkene **5d** and 1.8 equiv of **6** were used. The product (52 mg, 50% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 20:1) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.60 (t, *J* = 6.2 Hz, 2H), 2.37 (t, *J* = 6.4 Hz, 2H), 1.93 – 1.60 (m, 8H), 1.55 – 1.39 (m, 4H), 1.39 – 1.24 (m, 4H), 0.89 (s, 9H), 0.04 (s, 6H). ^{19}F NMR (376 MHz, CDCl$_3$) δ -98.2 – -98.6 (m, 2F). ^{13}C NMR (126 MHz, CDCl$_3$) δ 124.8 (t, *J* = 240.6 Hz), 119.3, 63.1, 36.4 (t, *J* = 25.3 Hz), 35.4 (t, *J* = 25.8 Hz), 32.6, 29.1, 25.9, 25.6, 25.1, 22.3 (t, *J* = 4.5 Hz), 21.6 (t, *J* = 4.6 Hz), 18.3, 17.1, -5.3. IR (thin film) ν_{max} 2932, 2857, 2248, 1431 cm^{-1}. MS (EI) m/z (%) 332, 317, 117, 140 (100), 77. HRMS (FI) calculated for $C_{18}H_{36}F_2NOSi$: 348.2529; Found: 348.2535 $(M+H)^+$.

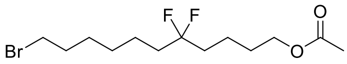


Ethyl 10-chloro-5,5-difluorodecanoate (8g). General Procedure A: 3.5 equiv of alkene **5e** and 1.8 equiv of **6** were used. The product (41 mg, 51% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 80:1) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.14 (q, *J* = 7.2 Hz, 2H), 3.54 (t, *J* = 6.4 Hz, 2H), 2.36 (t, *J* = 6.4 Hz, 2H), 1.91 – 1.72 (m, 8H), 1.50 – 1.42 (m, 4H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, CDCl$_3$) δ -103.5 – -103.9 (m, 2F). ^{13}C NMR (126 MHz, CDCl$_3$) δ 173.0, 124.8 (t, *J* = 240.4 Hz), 60.4, 44.8, 36.2 (t, *J* = 25.4 Hz), 35.6 (t, *J* = 25.7 Hz), 33.6, 32.3, 26.5, 21.5 (t, *J* = 4.6 Hz), 17.8 (t, *J* = 4.9 Hz), 14.2. IR (thin film) ν_{max} 2940, 2870, 1735, 1463 cm^{-1}. MS (EI) m/z (%) 270 $(M)^+$, 160, 102 (100), 55. HRMS (FI) calculated for $C_{12}H_{21}F_2O_2Cl$: 270.1193; Found: 270.1191 $(M)^+$.

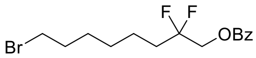


11-Chloro-6,6-difluoroundecanenitrile (8h). General Procedure A: 3.5 equiv of alkene **5e** and 1.8 equiv of **6** were used. The product (35 mg, 49% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate =

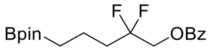
40:1) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.54 (t, *J* = 6.5 Hz, 2H), 2.38 (t, *J* = 6.7 Hz, 2H), 1.91 – 1.76 (m, 6H), 1.76 – 1.69 (m, 2H), 1.68 – 1.61 (m, 2H), 1.52 – 1.47 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.5 – -98.8 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 124.5 (t, *J* = 240.7 Hz), 119.3, 44.7, 36.3 (t, *J* = 25.3 Hz), 35.5 (t, *J* = 25.9 Hz), 32.3, 26.5, 25.1, 21.55 (t, *J* = 3.8 Hz), 21.51 (t, *J* = 3.8 Hz), 17.1. IR (thin film) ν_{max} 2958, 2871, 2247, 1464 cm^{-1}. MS (EI) m/z (%) 236 (M-H)$^+$, 202, 182, 99 (100), 77. HRMS (EI) calculated for $C_{11}H_{17}NClF_2$: 236.1012; Found: 236.1015 (M-H)$^+$.



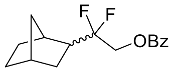
11-Bromo-5,5-difluoroundecyl acetate (8i). General Procedure A: 3.5 equiv of alkene **5f** and 1.8 equiv of **6** were used. The product (51 mg, 52% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 80:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.07 (t, *J* = 6.4 Hz, 2H), 3.41 (t, *J* = 6.8 Hz, 2H), 2.05 (s, 3H), 1.92 – 1.73 (m, 6H), 1.72 – 1.63 (m, 2H), 1.58 – 1.52 (m, 2H), 1.50 – 1.41 (m, 4H), 1.40 – 1.32 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.2 – -98.7 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.2, 124.9 (t, *J* = 240.5 Hz), 64.0, 36.3 (t, *J* = 21.6 Hz), 35.9 (t, *J* = 21.9 Hz), 33.8, 32.5, 28.5, 28.3, 27.9, 22.1 (t, *J* = 4.6 Hz), 21.0, 18.9 (t, *J* = 4.6 Hz). IR (thin film) ν_{max} 2935, 2857, 1739, 1461 cm^{-1}. MS (EI) m/z (%) 309, 248 (100), 167, 149. HRMS (FI) calculated for $C_{13}H_{23}BrF_2O_2$: 328.0844; Found: 328.0846 (M)$^+$.



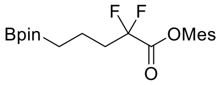
8-Bromo-2,2-difluorooctyl benzoate (8j). General Procedure A: 3.5 equiv of alkene **5f** and 1.8 equiv of **6** were used. The product (60 mg, 57% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 80:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.00 (m, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 4.49 (t, *J* = 12.4 Hz, 2H), 3.40 (t, *J* = 6.8 Hz, 2H), 2.07 – 1.91 (m, 2H), 1.90 – 1.80 (m, 2H), 1.65 – 1.52 (m, 2H), 1.51 – 1.35 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.1 – -105.8 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 133.5, 129.8, 129.0, 128.5, 121.7 (t, *J* = 241.9 Hz), 64.1 (t, *J* = 34.1 Hz), 33.8 (t, *J* = 23.7 Hz), 33.7, 32.4, 28.4, 27.8, 21.5 (t, *J* = 4.4 Hz). IR (thin film) ν_{max} 2935, 2857, 1731, 1452 cm^{-1}. MS (EI) m/z (%) 348 (M)$^+$, 249, 105 (100), 77. HRMS (EI) calculated for $C_{15}H_{19}BrF_2O_2$: 348.0531; Found: 348.0527 (M)$^+$.



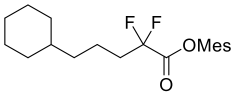
2,2-Difluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl benzoate (8k). General Procedure A: 3.5 equiv of alkene **5g** and 1.8 equiv of **6** were used. The product (61 mg, 60% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 10:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 4.48 (t, *J* = 12.4 Hz, 2H), 2.16 – 1.91 (m, 2H), 1.72 – 1.64 (m, 2H), 1.22 (s, 12H), 0.85 (t, *J* = 7.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.2 (tt, *J* = 16.5, 12.8 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6, 133.4, 129.8, 129.2, 128.5, 121.7 (t, *J* = 242.3 Hz), 83.1, 64.1 (t, *J* = 34.0 Hz), 36.3 (t, *J* = 23.6 Hz), 29.7, 24.8, 16.5. IR (thin film) ν_{max} 2929, 1732, 1452 cm^{-1}. MS (EI) m/z (%) 353 $(M)^+$, 339, 105 (100), 77. HRMS (FI) calculated for $C_{18}H_{25}{}^{10}BF_2O_4$: 353.1845; Found: 353.1851 $(M)^+$.



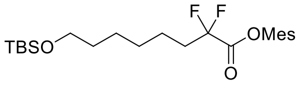
2-((1*S*,4*R*)-Bicyclo[2.2.1]heptan-2-yl)-2,2-difluoroethyl benzoate (8l). General Procedure A: Alkylzirconocene was prepared as following: To a 25 mL of Schlenk tube was added $ZrCp_2HCl$ **6** (1.8 equiv, 0.54 mmol) in the glovebox. The tube was then taken out of the glovebox, and was evacuated and backfilled with Ar (3 times). Alkene **5h** (3.5 equiv, 1.05 mmol) and anhydrous dioxane (1.0 mL) were added under Ar. The resulting mixture was stirred at 50 ^{o}C for 1 h until a clear yellow solution was obtained. The product (64 mg, 76% yield, dr > 20:1) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 100:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.02 (m, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 4.50 (t, *J* = 12.8 Hz, 2H), 2.54 – 2.44 (m, 1H), 2.36 – 2.27 (m, 1H), 2.08 – 1.92 (m, 1H), 1.67 – 1.44 (m, 5H), 1.23 – 1.13 (m, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.7 – -109.6 (m, 1F), -111.4 – -112.8 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 133.4, 129.8, 129.2, 128.5, 122.4 (t, *J* = 245.0 Hz), 63.6 (t, *J* = 33.5 Hz), 45.2 (t, *J* = 22.4 Hz), 37.2, 36.7, 35.8, 32.0, 30.6, 28.1. IR (thin film) ν_{max} 2874, 1731, 1452, 1371 cm^{-1}. MS (EI) m/z (%) 280 $(M)^+$, 138, 105 (100), 77. HRMS (FI) calculated for $C_{16}H_{18}F_2O_2$: 280.1269; Found: 280.1272 $(M)^+$.



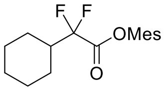
Mesityl 2,2-difluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (8m). General Procedure A: 3.5 equiv of alkene **5g** and 1.8 equiv of **6** were used. The product (75 mg, 65% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 20:1) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.89 (s, 2H), 2.34 – 2.18 (m, 5H), 2.12 (s, 6H), 1.82 – 1.66 (m, 2H), 1.24 (s, 12H), 0.90 (t, *J* = 7.8 Hz, 2H). ^{19}F NMR (376 MHz, CDCl$_3$) δ -105.1 (t, *J* = 16.9 Hz, 2F). ^{13}C NMR (126 MHz, CDCl$_3$) δ 162.4 (t, *J* = 33.1 Hz), 145.0, 136.1, 129.5, 129.3, 116.5 (t, *J* = 250.9 Hz), 83.2, 36.7 (t, *J* = 22.7 Hz), 24.8, 20.7, 16.2 (t, *J* = 4.4 Hz), 16.0. IR (thin film) ν$_{max}$ 1785, 1411, 1380 cm^{-1}. MS (EI) m/z (%) 382 (M)$^+$, 136 (100), 91. HRMS (FI) calculated for $C_{20}H_{29}{}^{10}BF_2O_4$: 381.2158; Found: 381.2155 (M)$^+$.



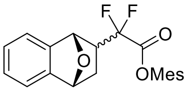
Mesityl 5-cyclohexyl-2,2-difluoropentanoate (8n). General Procedure A: 3.5 equiv of alkene **5i** and 1.8 equiv of **6** were used. The product (69 mg, 68% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 100:1) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.90 (s, 2H), 2.29 (s, 3H), 2.27 – 2.14 (m, 2H), 2.13 (s, 6H), 1.80 – 1.68 (m, 4H), 1.67 – 1.58 (m, 3H), 1.36 – 1.13 (m, 6H), 0.97 – 0.82 (m, 2H). ^{19}F NMR (376 MHz, CDCl$_3$) δ -105.0 (t, *J* = 16.9 Hz, 2F). ^{13}C NMR (101 MHz, CDCl$_3$) δ 162.4 (t, *J* = 34.1 Hz), 145.0, 136.2, 129.5, 129.2, 116.7 (t, *J* = 251.5 Hz), 37.3, 36.9, 34.83 (t, *J* = 23.0 Hz), 33.2, 26.6, 26.3, 20.7, 18.9 (t, *J* = 3.9 Hz), 16.0. IR (thin film) ν$_{max}$ 2924, 2851, 1785, 1448, 1378 cm^{-1}. MS (EI) m/z (%) 338 (M)$^+$, 136 (100), 121. HRMS (EI) calculated for $C_{20}H_{28}F_2O_2$: 338.2052; Found: 338.2053 (M)$^+$.



Mesityl 8-((*tert*-butyldimethylsilyl)oxy)-2,2-difluorooctanoate (8o). General Procedure A: 3.5 equiv of alkene **5d** and 1.8 equiv of **6** were used. The product (96 mg, 75% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 60:1) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.91 (s, 2H), 3.63 (t, *J* = 6.4 Hz, 2H), 2.34 – 2.18 (m, 5H), 2.13 (s, 6H), 1.72 – 1.59 (m, 2H), 1.58 – 1.49 (m, 2H), 1.48 – 1.36 (m, 4H), 0.92 (s, 9H), 0.07 (s, 6H). ^{19}F NMR (376 MHz, CDCl$_3$) δ -105.1 (t, *J* = 16.9 Hz, 2F). ^{13}C NMR (101 MHz, CDCl$_3$) δ 162.3 (t, *J* = 34.5 Hz), 145.0, 136.2, 129.5, 129.2, 116.6 (t, *J* = 251.5 Hz), 63.0, 34.4 (t, *J* = 23.2 Hz), 32.6, 29.0, 25.9, 25.5, 21.5 (t, *J* = 3.9 Hz), 20.7, 18.3, 16.0, -5.3. IR (thin film) ν_{max} 2829, 2857, 1786 cm^{-1}. MS (EI) m/z (%) 371, 137, 121 (100), 107, 77. HRMS (FI) calculated for $C_{23}H_{39}F_2O_3Si$: 429.2631; Found: 429.2634 $(M+H)^+$.

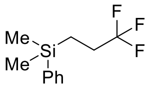


Mesityl 2-cyclohexyl-2,2-difluoroacetate (8p). General Procedure A: Alkylzirconocene was prepared as following: To a 25 mL of Schlenk tube was added $ZrCp_2HCl$ **6** (1.8 equiv, 0.54 mmol) in the glovebox. The tube was then taken out of the glovebox, and was evacuated and backfilled with Ar (3 times). Alkene **5j** (3.5 equiv, 1.05 mmol) and anhydrous dioxane (1.0 mL) were added under Ar. The resulting mixture was stirred at 50 °C for 1 h until a clear yellow solution was obtained. The product (62 mg, 70% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 100:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (s, 2H), 2.35 – 2.33 (m, 4H), 2.14 (s, 6H), 2.02 – 1.82 (m, 4H), 1.80 – 1.70 (m, 1H), 1.50 – 1.13 (m, 5H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.3 (d, *J* = 14.7 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4 (t, *J* = 34.3 Hz), 145.1, 136.1, 129.5, 129.2, 117.6 (t, *J* = 253.5 Hz), 42.1 (t, *J* = 21.7 Hz), 25.8, 25.3, 24.8 (t, *J* = 3.7 Hz), 20.7, 16.1. IR (thin film) ν_{max} 2934, 2858, 1784, 1453, 1378 cm^{-1}. MS (EI) m/z (%) 296 $(M)^+$, 136 (100), 91. HRMS (EI) calculated for $C_{17}H_{22}F_2O_2$: 296.1582; Found: 296.1586 $(M)^+$.

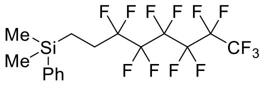


Mesityl 2,2-difluoro-2-((1*S*,2*S*,4*R*)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)acetate (8q). General Procedure A: Alkylzirconocene was prepared as following: To a 25 mL of Schlenk tube was added $ZrCp_2HCl$ **6** (1.8 equiv, 0.54 mmol) in the glovebox. The tube was then taken out of the glovebox, and was evacuated and backfilled with Ar (3 times). Alkene **5k** (3.5 equiv, 1.05 mmol) and anhydrous dioxane (1.0 mL) were added under Ar. The resulting mixture was stirred at 50 °C for 1 h until a clear yellow solution was obtained. The product (65 mg, 60% yield, dr > 20:1) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 40:1) as a white solid (m.p. 80 – 82 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 2H), 7.25 – 7.19 (m, 2H), 6.91 (s, 2H), 5.69 (s, 1H), 5.52 (d, *J* = 4.8 Hz, 1H), 2.70 – 2.56 (m, 1H), 2.39 (dt, *J* = 12.0, 4.8 Hz, 1H), 2.29 (s, 3H), 2.16 (s, 6H), 1.80 (dd, *J* = 12.0, 8.8 Hz, 1H). ^{19}F NMR (376 MHz,

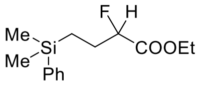
$CDCl_3$) δ -105.6 (dd, *J* = 260.8, 12.8 Hz, 1F), -107.9 (dd, *J* = 260.8, 16.9 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0 (t, *J* = 33.7 Hz), 145.5, 145.1, 144.2, 136.3, 129.5, 129.2, 127.3, 127.0, 119.4, 119.1, 116.5 (t, *J* = 255.7 Hz), 78.7, 78.4 (t, *J* = 3.4 Hz), 45.7 (t, *J* = 22.9 Hz), 29.1, 20.7, 16.1.IR (thin film) ν_{max} 3012, 2958, 1774, 1457, 1365 cm^{-1}. MS (EI) m/z (%) 358 (M)$^+$ 136, 118 (100), 91. HRMS (EI) calculated for $C_{21}H_{20}F_2O_3$: 358.1375; Found: 358.1380 (M)$^+$.



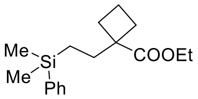
Dimethyl(phenyl)(3,3,3-trifluoropropyl)silane (9a). General Procedure A: The product (49 mg, 70% yield) was purified by flash column chromatography on silica gel (PE) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 2H), 7.46 – 7.35 (m, 3H), 2.14 – 1.92 (m, 2H), 1.07 – 0.95 (m, 2H), 0.35 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.7 (t, *J* = 10.5 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.4, 133.5, 129.4, 128.0, 127.7 (q, *J* = 277.9 Hz), 28.8 (q, *J* = 30.1 Hz), 7.6, -3.5. IR (thin film) ν_{max} 3071, 3012, 1446, 1365 cm^{-1}. MS (EI) m/z (%) 232 (M)$^+$, 154, 135 (100), 91, 77. HRMS (EI) calculated for $C_{11}H_{15}F_3Si$: 232.0890; Found: 232.0896 (M)$^+$.



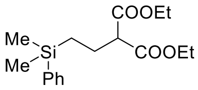
Dimethyl(phenyl)(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane (9b). General Procedure A: The product (95 mg, 66% yield) was purified by flash column chromatography on silica gel (PE) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 2H), 7.44 – 7.38 (m, 3H), 2.13 – 1.92 (m, 2H), 1.06 – 0.96 (m, 2H), 0.35 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.92 (t, *J* = 9.8 Hz, 3F), -115.7 – -116.5 (m, 2F), -121.9 – -122.3 (m, 2F), -122.9 – -123.2 (m, 2F), -123.2 – -123.5 (m, 2F), -126.2 – -126.4 (m, 2F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.3, 133.5, 129.4, 128.1, 118.4, 117.2, 111.3, 111.1, 110.3, 108.5, 25.9, 5.2, -3.5. IR (thin film) ν_{max} 2922, 2112 cm^{-1}. MS (EI) m/z (%) 482 (M)$^+$, 467, 135 (100), 91. HRMS (FI) calculated for $C_{16}H_{15}F_{13}Si$: 482.0730; Found: 482.0726 (M)$^+$.



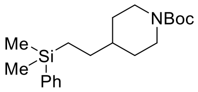
Ethyl 4-(dimethyl(phenyl)silyl)-2-fluorobutanoate (9c). General Procedure A: The product (50 mg, 62% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 80:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.44 (m, 2H), 7.41 – 7.31 (m, 3H), 4.95 – 4.74 (m, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.00 – 1.76 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.97 – 0.78 (m, 2H), 0.29 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -192.5 (dt, *J* = 49.3, 24.4 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8 (d, *J* = 24.5 Hz), 138.2, 133.5, 129.1, 127.9, 90.4 (d, *J* = 185.5 Hz), 61.3, 27.1 (d, *J* = 21.9 Hz), 14.2, 9.8 (d, *J* = 1.7 Hz), -3.3 (d, *J* = 4.7 Hz). IR (thin film) ν_{max} 3069, 2955, 1739, 1427, 1374 cm^{-1}. MS (FI) m/z (%) 268 $(M)^+$, 253, 135 (100), 77. HRMS (EI) calculated for $C_{14}H_{21}FO_2Si$: 268.1289; Found: 268.1294 $(M)^+$.



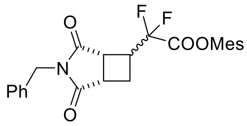
Ethyl 1-(2-(dimethyl(phenyl)silyl)ethyl)cyclobutane-1-carboxylate (9d). General Procedure A: 3.5 equiv of alkene **5a** and 1.8 equiv of **6** were used. The product (57 mg, 65% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 50:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.45 (m, 2H), 7.40 – 7.31 (m, 3H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.45 – 2.27 (m, 2H), 1.92 – 1.78 (m, 4H), 1.78 – 1.69 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.66 – 0.55 (m, 2H), 0.27 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.1, 139.0, 133.5, 128.9, 127.7, 60.1, 49.2, 32.1, 29.4, 15.3, 14.3, 10.2, -3.2. IR (thin film) ν_{max} 2927, 2854, 1727, 1445, 1366 cm^{-1}. MS (EI) m/z (%) 290 $(M)^+$, 275, 247, 213, 135 (100), 105. HRMS (EI) calculated for $C_{17}H_{26}O_2Si$: 290.1697; Found: 290.1695 $(M)^+$.



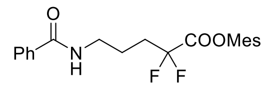
Diethyl 2-(2-(dimethyl(phenyl)silyl)ethyl)malonate (9e). General Procedure A: 3.5 equiv of alkene **5a** and 1.8 equiv of **6** were used. The product (39 mg, 40% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 40:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.45 (m, 2H), 7.40 – 7.31 (m, 3H), 4.25 – 4.09 (m, 4H), 3.28 (t, *J* = 7.4 Hz, 1H), 1.98 – 1.84 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 6H), 0.83 – 0.71 (m, 2H), 0.29 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 138.5, 133.5, 129.0, 127.8, 61.2, 55.0, 23.5, 14.1, 13.5, -3.30. IR (thin film) ν_{max} 3049, 2957, 1732, 1446, 1369 cm^{-1}. MS (EI) m/z (%) 322 $(M)^+$, 307, 245, 161, 135 (100), 105. HRMS (DART) calculated for $C_{17}H_{30}O_4NSi$: 340.1937; Found: 340.1931 $(M+NH_4)^+$.



***tert*-Butyl 4-(2-(dimethyl(phenyl)silyl)ethyl)piperidine-1-carboxylate (9f). General Procedure A:** 3.5 equiv of alkene **5a** and 1.8 equiv of **6** were used. The product (62 mg, 60% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 25:1) as a colorless oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.45 (m, 2H), 7.41 – 7.30 (m, 3H), 4.21 – 3.92 (m, 2H), 2.73 – 2.52 (m, 2H), 1.74 – 1.58 (m, 2H), 1.45 (s, 9H), 1.34 – 1.20 (m, 3H), 1.11 – 0.94 (m, 2H), 0.79 – 0.66 (m, 2H), 0.26 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 139.3, 133.5, 128.8, 127.7, 79.1, 38.9, 31.8, 30.5, 28.5, 12.4, -3.2. IR (thin film) ν_{max} 2916, 2848, 1694, 1449, 1364 cm^{-1}. MS (ESI) m/z (%) 370 $(M+Na)^+$, 348 $(M+H)^+$. HRMS (ESI) calculated for $C_{20}H_{34}NO_2Si$: 348.2356; Found: 348.2355 $(M+H)^+$.

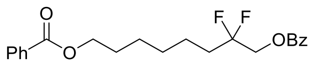


Mesityl 2-(3-benzyl-2,4-dioxo-3-azabicyclo[3.2.0]heptan-6-yl)-2,2-difluoroacetate (10a). General Procedure B: The product (64 mg, 50% yield, dr > 20:1) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 20:1) as a white solid (m.p. 92 – 94 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 6.8 Hz, 2H), 7.36 – 7.28 (m, 3H), 6.90 (s, 2H), 4.72 (s, 2H), 3.58 – 3.51 (m, 1H), 3.40 – 3.32 (m, 1H), 3.28 – 3.13 (m, 1H), 2.91 – 2.80 (m, 1H), 2.44 – 2.34 (m, 1H), 2.28 (s, 3H), 2.11 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.4 (dd, *J* = 267.7, 14.3 Hz, 1F), -115.2 (dd, *J* = 267.7, 17.3 Hz, 1F), ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.8, 176.1, 160.7 (t, *J* = 33.3 Hz), 144.7, 136.5, 135.5, 129.5, 129.0, 128.74, 128.72, 128.1, 114.9 (t, *J* = 252.9 Hz), 42.8, 39.26 (t, *J* = 25.2 Hz), 38.6 (dd, *J* = 5.9, 3.4 Hz), 36.1, 23.1 (dd, *J* = 6.3, 3.1 Hz), 20.7, 16.0. IR (thin film) ν_{max} 3068, 2921, 1772, 1703 cm^{-1}. MS (ESI) m/z (%) 450 $(M+Na)^+$, 428 $(M+H)^+$. HRMS (ESI) calculated for $C_{24}H_{23}NO_4F_2Na$: 450.1487; Found: 450.1482 $(M+Na)^+$.

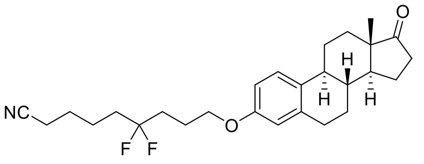


Mesityl 5-benzamido-2,2-difluoropentanoate (10b). General Procedure B: The product (70 mg, 62% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 8:1) as a white solid (m.p. 96 – 98 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.4 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 2H), 6.88 (s, 2H), 6.72 – 6.58 (m, 1H), 3.55 (q, *J* = 6.7 Hz, 2H), 2.41 – 2.28 (m, 2H), 2.27 (s, 3H), 2.10 (s, 6H), 1.99 – 1.90 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.0 (t, *J* = 17.1 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$)

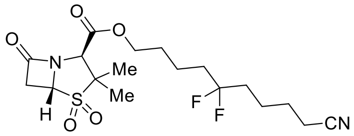
δ 167.8, 162.1 (t, *J* = 33.6 Hz), 144.8, 136.2, 134.2, 131.5, 129.5, 129.1, 128.5, 126.8, 116.2 (t, *J* = 251.2 Hz), 39.1, 31.9 (t, *J* = 23.3 Hz), 21.9 (t, *J* = 3.5 Hz), 20.7, 15.9. IR (thin film) ν$_{max}$ 3256, 3071, 2924, 2863, 1770 cm^{-1}. MS (ESI) m/z (%) 398 (M+Na)$^+$, 376 (M+H)$^+$. HRMS (ESI) calculated for C$_{21}$H$_{23}$NO$_3$F$_2$Na: 398.1538; Found: 398.1529 (M+Na)$^+$.



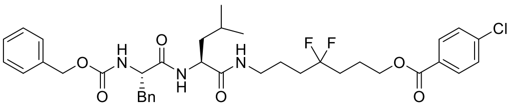
2,2-Difluorooctane-1,8-diyl dibenzoate (10c). General Procedure B: The product (67 mg, 57% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 20:1) as a white solid (m.p. 48 – 50 °C). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.05 (t, *J* = 8.8 Hz, 4H), 7.62 – 7.52 (m, 2H), 7.49 – 7.39 (m, 4H), 4.49 (t, *J* = 12.4 Hz, 2H), 4.32 (t, *J* = 6.6 Hz, 2H), 2.07 – 1.92 (m, 2H), 1.82 – 1.74 (m, 2H), 1.64 – 1.55 (m, 2H), 1.53 – 1.40 (m, 4H). ^{19}F NMR (376 MHz, CDCl$_3$) δ -105.4 (tt, *J* = 16.9, 12.4 Hz, 2F). ^{13}C NMR (126 MHz, CDCl$_3$) δ 166.6, 165.5, 133.5, 132.8, 130.3, 129.8, 129.5, 129.1, 128.5, 128.3, 121.7 (t, *J* = 242.5 Hz), 64.8, 64.1 (t, *J* = 34.1 Hz), 33.9 (t, *J* = 23.8 Hz), 28.9, 28.5, 25.8, 21.6 (t, *J* = 4.4 Hz). IR (thin film) ν$_{max}$ 3064, 2866, 1723 cm^{-1}. MS (EI) m/z (%) 390 (M)$^+$, 248, 105 (100), 77. HRMS (FI) calculated for C$_{22}$H$_{24}$O$_4$F$_2$: 390.1637; Found: 390.1642 (M)$^+$.



6,6-Difluoro-9-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)nonanenitrile (10d). General Procedure B: The product (55 mg, 41% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 4:1) as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.20 (d, *J* = 8.5 Hz, 1H), 6.70 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.64 (d, *J* = 2.3 Hz, 1H), 3.97 (t, *J* = 5.8 Hz, 2H), 2.94 – 2.84 (m, 2H), 2.55 – 2.45 (m, 1H), 2.38 (t, *J* = 7.0 Hz, 3H), 2.29 – 2.20 (m, 1H), 2.18 – 1.82 (m, 10H), 1.76 – 1.38 (m, 10H), 0.91 (s, 3H). ^{19}F NMR (376 MHz, CDCl$_3$) δ -98.9 – -99.2 (m, 2F). ^{13}C NMR (126 MHz, CDCl$_3$) δ 220.9, 156.7, 137.8, 132.2 126.3, 124.5 (t, *J* = 241.3 Hz), 119.3, 114.5, 112.0, 66.9, 50.3, 47.9, 43.9, 38.3, 35.8, 35.7 (t, *J* = 25.8 Hz), 33.20 (t, *J* = 25.7 Hz), 31.5, 29.6, 26.5, 25.9, 25.1, 22.3 (t, *J* = 4.3 Hz), 21.53, 21.51 (t, *J* = 5.0 Hz), 17.0, 13.8. IR (thin film) ν$_{max}$ 2929, 2868, 2246, 1737 cm^{-1}. MS (DART) m/z (%) 444 (M+H)$^+$. HRMS (DART) calculated for $C_{27}H_{36}NO_2F_2$: 444.2709; Found: 444.2706 (M+H)$^+$.

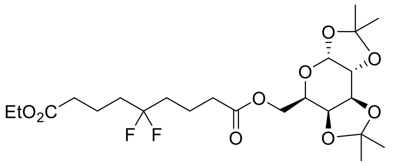


9-Cyano-5,5-difluorononyl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide (10e). General Procedure B: The product (60 mg, 48% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 2:1) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.61 (dd, *J* = 4.2, 19 Hz, 1H), 4.38 (s, 1H), 4.28 – 4.15 (m, 2H), 3.49 (dd, *J* = 16.2, 4.2 Hz, 1H), 3.44 (dd, *J* = 16.2, 1.9 Hz, 1H), 2.38 (t, *J* = 6.8 Hz, 2H), 1.93 – 1.80 (m, 4H), 1.78 – 1.69 (m, 4H), 1.68 – 1.62 (m, 2H), 1.61 (s, 3H), 1.60 – 1.54 (m, 2H), 1.41 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.6 – -99.7 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 166.9, 124.3 (t, *J* = 240.9 Hz), 119.3, 65.9, 63.2, 62.6, 61.0, 38.3, 35.8 (t, *J* = 25.6 Hz), 35.6 (t, *J* = 25.7 Hz), 28.1, 25.0, 21.5 (t, *J* = 4.6 Hz), 20.3, 18.6 (t, *J* = 4.6 Hz), 18.5, 17.1. IR (thin film) ν_{max} 2875, 2246, 1797, 1754 cm^{-1}. MS (ESI) m/z (%) 443 (M+Na)$^+$, 421 (M+H)$^+$. HRMS (ESI) calculated for $C_{18}H_{26}N_2O_5F_2NaS$: 443.1422; Found: 443.1419 (M+Na)$^+$.

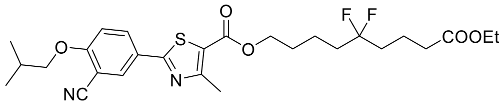


(5*S*,8*S*)-5-Benzyl-14,14-difluoro-8-isobutyl-3,6,9-trioxo-1-phenyl-2-oxa-4,7,10-triazaheptadecan-17-yl 4-chlorobenzoate (10f). General Procedure B: The product (107 mg, 51% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 2:1) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.37 – 7.31 (m, 3H), 7.31 – 7.23 (m, 5H), 7.16 (d, *J* = 7.0 Hz, 2H), 6.42 – 6.31 (m, 1H), 6.24 (d, *J* = 8.0 Hz, 1H), 5.23 (d, *J* = 6.0 Hz, 1H), 5.08 (d, *J* = 12.3 Hz, 1H), 5.05 (d, *J* = 12.3 Hz, 1H), 4.45 – 4.35 (m, 2H), 4.34 (t, *J* = 5.8 Hz, 2H), 3.30 – 3.13 (m, 2H), 3.08 (d, *J* = 6.5 Hz, 2H), 2.04 – 1.92 (m, 4H), 1.91 – 1.80 (m, 2H), 1.72 – 1.64 (m, 3H), 1.51 – 1.34 (m, 2H), 0.88 (d, *J* = 2.5 Hz, 3H), 0.86 (d, *J* = 2.6 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.7 – -99.4 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5, 171.0, 165.7, 156.4, 139.5, 135.8, 131.0, 129.2, 128.9, 128.8, 128.6, 128.5, 128.5, 128.1, 127.4, 124.5 (t, *J* = 241.0 Hz), 67.4, 64.4, 56.5, 51.9, 40.4, 38.9, 33.8 (t, *J* = 25.6 Hz), 33.2 (t, *J* = 26.0 Hz), 29.7, 24.7, 22.9, 22.4 (t, *J* = 4.0 Hz), 21.8 (t, *J* = 4.4 Hz), 21.7. IR (thin film) ν_{max}

3293, 3064, 2851, 1721, 1645 cm^{-1}. MS (ESI) m/z (%) 722 (M+Na)$^+$, 700 (M+H)$^+$,. HRMS (ESI) calculated for $C_{37}H_{44}N_3O_6F_2NaCl$: 722.2778; Found: 722.2769 (M+ Na)$^+$.



1-Ethyl 9-(((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl) 5,5-difluorononanedioate (10g). General Procedure B: The product (76 mg, 51% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 4:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.52 (d, *J* = 5.2 Hz, 1H), 4.64 – 4.57 (m, 1H), 4.36 – 4.26 (m, 2H), 4.25 – 4.07 (m, 4H), 4.05 – 3.97 (m, 1H), 2.40 (t, *J* = 7.0 Hz, 2H), 2.34 (t, *J* = 6.8 Hz, 2H), 1.94 – 1.74 (m, 8H), 1.49 (s, 3H), 1.44 (s, 3H), 1.31 (s, 3H), 1.32 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.6 – -98.9 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.9, 172.8, 124.5 (t, *J* = 241.4 Hz), 109.6, 108.7, 96.3, 71.0, 70.7, 70.4, 65.9, 63.4, 60.4, 35.51 (t, *J* = 25.4 Hz), 35.48 (t, *J* = 25.4 Hz), 33.6, 33.5, 25.92, 25.90, 24.9, 24.4, 17.8, 17.7, 14.2. IR (thin film) ν_{max} 2982, 2935, 1735, 1456 cm^{-1}. MS (DART) m/z (%) 495 (M+H)$^+$. HRMS (DART) calculated for $C_{23}H_{37}O_9F_2$: 495.2400; Found: 495.2396 (M+H)$^+$.

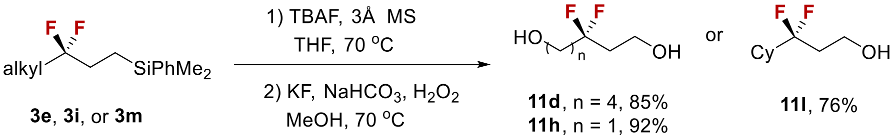


9-Ethoxy-5,5-difluoro-9-oxononyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (10h). General Procedure B: The product (72 mg, 45% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 4:1) as a white solid (m.p. 46 – 48 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 2.0 Hz, 1H), 8.07 (dd, *J* = 8.8 Hz, 1H), 7.00 (d, *J* = 8.8, 2.0 Hz, 1H), 4.30 (t, *J* = 6.4 Hz, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.88 (d, *J* = 6.4 Hz, 2H), 2.74 (s, 3H), 2.35 (t, *J* = 6.8 Hz, 2H), 2.24 – 2.13 (m, 1H), 1.96 – 1.75 (m, 8H), 1.67 – 1.57 (m, 2H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.08 (s, 3H), 1.07 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.5 – -98.8 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.9, 167.2, 162.4, 161.9, 161.2, 132.5, 132.0, 125.9, 124.6 (t, *J* = 241.0 Hz), 121.6, 115.3, 112.6, 102.9, 75.6, 64.8, 60.4, 35.8 (t, *J* = 25.6 Hz), 35.6 (t, *J* = 25.8 Hz), 33.5, 28.3, 28,1, 19.0, 18.8 (t, *J* = 4.5 Hz), 17.8 (t, *J* = 4.9 Hz), 17.4, 14.2. IR (thin film) ν_{max} 2961, 2228, 1733, 1712 cm^{-1}. MS (ESI) m/z (%) 559 (M+Na)$^+$, 537 (M+H)$^+$. HRMS (ESI) calculated for $C_{27}H_{35}N_2O_5F_2S$: 537.2229; Found:

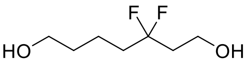
537.2218 $(M+H)^+$.

6. Transformations of Compounds 3

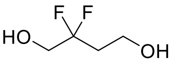
Systhesis of compounds 11d, 11h, and 11l.[17]



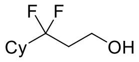
General Procedure: To a 25 mL of Schlenk tube were added TBAF (1.0 mL, 1.0 mmol, 10 equiv, 1M in THF), 3Å molecular sieve (200 mg, 0.2g/mmol). The reaction mixture was stirred at room temperature for 15 min. Subsequently, a solution of compound **3** (0.1 mmol, 1.0 equiv) in THF (1.0 mL) was added. The reaction mixture was stirred at 70 °C for 1.5 h. The reaction mixture was allowed to cool down to room temperature and then KF (20 mg, 0.35 mmol, 3.5 equiv), $NaHCO_3$ (19 mg, 0.23 mmol, 2.3 equiv), MeOH (1.0 mL, 10 mL/ mL THF) and H_2O_2 (0.35 mL, 30% in H_2O) were added. The reaction mixture was stirred at at 70 °C for overnight. The reaction mixture was poured into Na_2SO_3 aqueous (50 mL) and extracted with EA (30 mL× 2). The combined organic solution was washed by brine, dried over anhydrous sodium sulfate, filtered, and concentrated. The product was isolated by flash column chromatography.



3,3-Difluoroheptane-1,7-diol (11d). The product (14 mg, 85% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 2:5) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (t, J = 5.6 Hz, 2H), 3.66 (t, J = 5.6 Hz, 2H), 2.21 – 2.04 (m, 2H), 2.02 – 1.82 (m, 3H), 1.71 (s, 1H), 1.66 – 1.51 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -96.7 – -97.0 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 125.0 (t, J = 241.6 Hz), 62.3, 57.1 (t, J = 5.6 Hz), 38.9 (t, J = 24.5 Hz), 36.6 (t, J = 25.1 Hz), 32.1, 18.6 (t, J = 4.9 Hz). IR (thin film) ν_{max} 3354, 2940, 1462, 1389 cm^{-1}. MS (DART) m/z (%) 169 $(M+H)^+$, 118, 100, 60 (100), 55. HRMS (DART) calculated for $C_7H_{15}F_2O_2$: 169.1035; Found: 169.1035 $(M+H)^+$.

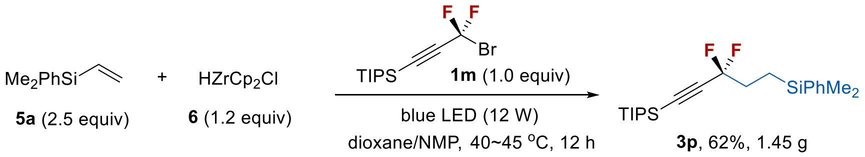


2,2-Difluorobutane-1,4-diol (11h). The product (12 mg, 92% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 2:5) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 – 3.86 (m, 2H), 3.81 (t, *J* = 12.6 Hz, 2H), 2.31 – 2.15 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.9 – -105.2 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 122.9 (t, *J* = 243.1 Hz), 64.3 (t, *J* = 33.4 Hz), 56.8 (t, *J* = 6.6 Hz), 36.9 (t, *J* = 24.6 Hz). IR (thin film) ν_{max} 3370, 2926, 2852, 1427 cm^{-1}. MS (EI) m/z (%) 107, 88, 78 (100), 75. HRMS (FI) calculated for $C_4H_8F_2O_2$: 126.0487; Found: 126.0490 $(M)^+$.



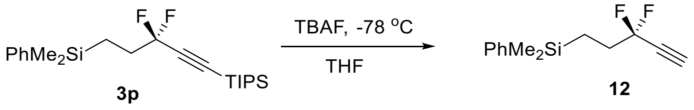
3-Cyclohexyl-3,3-difluoropropan-1-ol (11l). The product (14 mg, 76% yield) was purified by flash column chromatography on silica gel (Petroleum ether: Ethyl acetate = 2:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.89 (t, *J* = 6.0 Hz, 2H), 2.19 – 2.01 (m, 2H), 1.90 – 1.65 (m, 6H), 1.31 – 1.07 (m, 5H).^{19}F NMR (376 MHz, $CDCl_3$) δ -104.4 – -104.7 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 126.3 (t, *J* = 243 Hz), 57.1 (t, *J* = 5.3 Hz), 44.5 (t, *J* = 23.4 Hz), 36.4 (t, *J* = 24.5 Hz), 25.9, 25.8 (t, *J* = 4.6 Hz), 25.6. IR (thin film) ν_{max} 3446, 2924, 2853, 1457, 1377 cm^{-1}. MS (EI) m/z (%) 149, 95, 55 (100). HRMS (DART) calculated for $C_9H_{20}F_2ON$: 196.1507; Found: 196.1507 $(M+NH_4)^+$.

Gram-scale synthesis of 3p



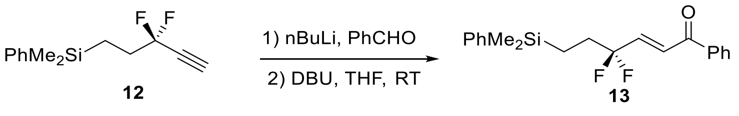
Procedure: To a 10 mL of Schlenk tube was added $ZrCp_2HCl$ (1.2 equiv, 7.2 mmol) in the glovebox. The tube was then taken out of the glovebox, and was evacuated and backfilled with Ar (3 times). Alkene **5a** (2.5 equiv, 15 mmol) and anhydrous dioxane (20 mL) were added under Ar. The resulting mixture was stirred at room temperature for 1 h until a clear yellow solution was obtained. To another 350 mL of Schlenk tube were added difluoroalkyl halide **1m** (6 mmol, 1.0 equiv) and NMP (60 mL) under Ar. The prepared solution of alkylzirconocene and alkene was then added to the reaction mixture via a syringe for 10 min under Ar. The reaction mixture was stirred at 40~45 °C under irradiation of a 12 W blue LEDs strip for 12 h. The reaction mixture was then cooled to room temperature. The reaction mixture was poured into water (200 mL) and extracted with EA (150 mL× 2). The combined organic layers were washed by brine, dried over anhydrous sodium sulfate, filtered, and concentrated. The product was purified with flash column chromatography (Petroleum ether) to give compound **3p** (1.45 g, 62% yeild) as a colorless oil.

Synthesis of copound 12.



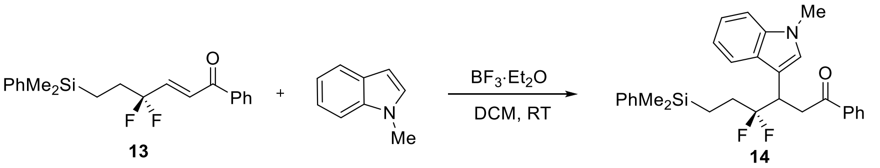
(3,3-Difluoropent-4-yn-1-yl)dimethyl(phenyl)silane (12): To a solution of **3p** (400 mg, 1.0 mmol, 1.0 equiv) in THF (5.0 mL) was added TBAF (1.2 mL, 1.2 equiv, 1.0 M in THF) at -78 °C. The reaction mixture was stirred for 1 h, and was quenched with saturated aq. NH_4Cl. The resulting mixture was extracted with ethyl acetate. The combined organic layers were dried with Na_2SO_4 and concentrated. The residue was purified by flash column chromatography (Petroleum ether: Ethyl acetate = 100:1) to give compound **12** (202 mg, 85% yeild) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.47 (m, 2H), 7.45 – 7.32 (m, 3H), 2.74 (t, J = 4.6 Hz, 1H), 2.09 – 1.91 (m, 2H), 1.09 – 0.93 (m, 2H), 0.33 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.0 (td, J = 14.4, 4.6 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.8, 133.5, 129.2, 127.9, 115.1 (t, J = 233.4 Hz), 76.5 (t, J = 41.2 Hz), 75.1 (t, J = 6.8 Hz), 34.0 (t, J = 26.9 Hz), 8.2, -3.4. IR (thin film) ν_{max} 3303, 2924, 2856, 2133, 1448 cm^{-1}. MS (EI) m/z (%) 238 $(M)^+$, 154, 135 (100), 91. HRMS (EI) calculated for $C_{13}H_{16}F_2Si$: 238.0984; Found: 238.0986 $(M)^+$.

Synthesis of copound 13.



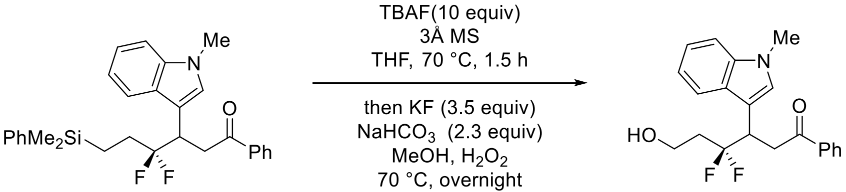
(*E*)-6-(Dimethyl(phenyl)silyl)-4,4-difluoro-1-phenylhex-2-en-1-one (13): To a solution of compound **12** (200 mg, 0.84 mmol, 1.0 equiv) in THF (3 mL) was added *n*-BuLi (1.0 mmol, 1.2 equiv) at -78 °C under Ar. After the mixture was stirred for 1 h at -78 °C, benzaldehyde (133 mg, 1.26 mmol, 1.5 equiv) in THF (1.0 mL) was slowly added. The reaction was warmed to room temperature and stirred for another 8 h. The reaction mixture was concentrated and the residue was redissolved in THF (4 mL), DBU (255 mg, 1.68 mmol, 2.0 equiv) was then added. The resulting mixture was stirred at room temperature overnight. The reaction was quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The combined organic layers were washed with water, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography (Petroleum ether: Ethyl acetate = 40:1) to give copound **13** (150 mg, 52%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.94 (m, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.53 – 7.48 (m, 4H), 7.40 – 7.35 (m, 3H), 7.31 (dt, *J* = 15.5, 1.9 Hz, 1H), 6.85 (dt, *J* = 15.5, 11.6 Hz, 1H), 2.02 – 1.87 (m, 2H), 0.97 – 0.87 (m, 2H), 0.31 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.9 – -100.4 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.3, 138.7 (t, *J* = 27.3 Hz), 137.7, 136.8, 133.6, 133.5, 129.2, 128.8, 128.7, 127.9, 127.6 (t, *J* = 7.3 Hz), 121.6 (t, *J* = 240.3 Hz), 32.0 (t, *J* = 27.3 Hz), 7.7 (t, *J* = 2.5 Hz), -3.4. IR (thin film) ν_{max} 2928, 2899, 1427 cm^{-1}. MS (EI) m/z (%) 201, 135 (100), 77. HRMS (EI) calculated for $C_{20}H_{22}F_2OSi$: 344.1402; Found: 344.1398 $(M)^+$.

Synthesis of compound 14.[18]



To a solution of compound **13** (100 mg, 0.3 mmol, 1.0 equiv) in DCM (2 mL) was added $BF_3{\cdot}Et_2O$ (8.4 mg, 0.06 mmol, 0.2 equiv) at room temperature. After the reaction mixture was stirred for 0.5 h, the 1-methyl-1*H*-indole (78 mg, 0.6 mmol, 2.0 equiv) in DCM (1.0 mL) was added. The mixture was stirred at room temperature until **13** was disappeared. The reaction was then quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography (Petroleum ether: Ethyl acetate = 40:1) to give compound **14** (100 mg, 70%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.2 Hz, 2H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 6.8 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.36 – 7.21 (m, 7H), 7.20 – 7.14 (m, 1H), 6.99 (s, 1H), 4.55 – 4.28 (m, 1H), 3.86 – 3.74 (m, 1H), 3.68 (s, 3H), 3.56 (dd, *J* = 17.2, 8.3 Hz, 1H), 1.94 – 1.65 (m, 2H), 1.08 – 0.86 (m, 2H), 0.16 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.5 (dtd, *J* = 236.4, 19.5, 6.2 Hz, 1F), -103.3 – -104.5 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.8, 138.1, 136.9, 136.7, 133.4, 132.9, 128.8, 128.4, 128.0, 127.78, 127.7, 127.1, 126.8 (t, *J* = 246.7 Hz), 121.6, 119.6 (d, *J* = 2.6 Hz), 119.3, 111.3 (d, *J* = 8.9 Hz), 109.2, 38.7, 37.4 (t, *J* = 25.2 Hz), 32.6, 29.7 (t, *J* = 26.2 Hz), 7.6, -3.2, -3.6. IR (thin film) ν_{max} 2954, 2928, 1688 cm^{-1}. MS (ESI) m/z (%) 476 (M+H)$^+$. HRMS (ESI) calculated for $C_{29}H_{32}NOF_2Si$: 476.2216; Found: 476.2211 (M+H)$^+$.

Synthesis of compound 15.[19]



14 **15**

4,4-Difluoro-6-hydroxy-3-(1-methyl-1H-indol-3-yl)-1-phenylhexan-1-one (15). Compound **15** was prepared according to the procedure of synthesis of compound **11d**. The product **15** (20 mg, 56% yield, 0.1 mmol scale) was purified with silica gel chromatography (Petroleum ether: Ethyl acetate = 3:1) as a white solid (m.p. 121–123 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 6.0 Hz, 2H), 7.88 (d, *J* = 6.8 Hz, 1H), 7.72 – 7.60 (m, 1H), 7.58 – 7.48 (m, 2H), 7.44 – 7.32 (m, 2H), 7.30 – 7.23 (m, 1H), 7.16 (s, 1H), 4.60 - 435 (m, 1H), 4.03 – 3.80 (m, 6H), 3.69 (dd, *J* = 17.0, 7.9 Hz, 1H), 2.39 – 2.07 (m, 2H), 1.78 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -97.8 – -101.0 (m, 1F), -103.3 – 104.5 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.6, 136.8 (d, *J* = 1.5 Hz), 133.0, 128.5, 128.0, 127.1, 126.2 (t, *J* = 246.3 Hz), 121.8, 119.5 (d, *J* = 3.5 Hz), 119.5, 111.0 (d, *J* = 9.2 Hz), 109.3, 57.0 (t, *J* = 5.0 Hz), 39.0 (t, *J* = 24.6 Hz), 38.4 (t, *J* = 2.5 Hz), 37.9 (t, *J* = 23.6 Hz), 32.8. IR (thin film) ν_{max} 3387, 2933, 1683 cm^{-1}. MS (ESI) m/z (%) 380 (M+Na)$^+$. HRMS (ESI) calculated for $C_{21}H_{21}NF_2O_2Na$: 380.1432; Found: 380.1432 (M+Na)$^+$.

7. References

(1) Zhao, H.-Y.; Zhou, M.; Zhang, X. Palladium-Catalyzed Carbonylative Cross-Coupling of Difluoroalkyl Halides with Alkylboranes under 1 Atm of CO. *Org. Lett.* **2021**, *23*, 9106-9111.

(2) Kostromitin, V. S.; Zemtsov, A. A.; Kokorekin, V. A.; Levin, V. V.; Dilman, A. D. Atom-Transfer Radical Addition of Fluoroalkyl Bromides to Alkenes via a Photoredox/Copper Catalytic System. *Chem. Commun.* **2021**, *57*, 5219-5222.

(3) Wang, L.; Wei, X.-J.; Jia, W.-L.; Zhong, J.-J.; Wu, L.-Z.; Liu, Q. Visible-Light-Driven

Difluoroacetamidation of Unactive Arenes and Heteroarenes by Direct C−H Functionalization at Room Temperature. *Org. Lett.* **2014**, *16*, 5842-5845.

(4) Hammond, G. B. Nucleophilic and Electrophilic Substitutions of Difluoropropargyl Bromides. *J. Fluorine Chem.* **2006**, *127*, 476-488.

(5) Xu, C.; Yang, Z.-F.; An, L.; Zhang, X. Nickel-Catalyzed Difluoroalkylation-Alkylation of Enamides. *ACS Catal.* **2019**, *9*, 8224-8229.

(6) Xia, P.-J.; Ye, Z.-P.; Song, D.; Ren, J.-W.; Wu, H.-W.; Xiao, J.-A.; Xiang, H.-Y.; Chen, X.-Q.; Yang, H. Photocatalytic Reductive Radical-Radical Coupling of *N*,*N*′-Cyclicazomethine Imines with Difluorobromo Derivatives. *Chem. Commun.* **2019**, *55*, 2712-2715.

(7) Douglas, J. J.; Albright, H.; Sevrin, M. J.; Cole, K. P.; Stephenson, C. R. J. A Visible-Light-Mediated Radical Smiles Rearrangement and its Application to the Synthesis of a Difluoro-Substituted Spirocyclic ORL-1 Antagonist. *Angew. Chem. Int. Ed.*, **2015**, *54*, 14898 -14902.

(8) Lin, Q.-Y.; Xu, X. H.; Qing, F. L. Visible Light-Induced Selective Hydrobromodifluoromethylation of Alkenes with Dibromodifluoromethane. *Org. Biomol. Chem.* **2015**, *13*, 8740-8749.

(9) Ambler, B. R.; Zhu, L.; Altman, R. A. Copper-Catalyzed Synthesis of Trifluoroethylarenes from Benzylic Bromodifluoroacetates. *J. Org. Chem.* **2015**, *80*, 8449-8457.

(10) Goetzke, F. W.; Hell, A. M. L.; Dijk, L.; Fletcher, S. P. A Catalytic Asymmetric Cross-Coupling Approach to the Synthesis of Cyclobutanes. *Nat. Chem.* **2021**, *13*, 880-886.

(11) Zhou, M.; Zhao, H.-Y.; Zhang, S.; Zhang, Y.; Zhang, X. Nickel-Catalyzed Four-Component Carbocarbonylation of Alkenes under 1 Atm of CO. *J. Am. Chem. Soc.* **2020**, *142*, 18191-18199.

(12) Li, X.; He, S.; Song, Q. Diethylzinc-Mediated Radical 1,2-Addition of Alkenes and Alkynes. *Org. Lett.* **2021**, *23*, 2994-2999.

(13) Fujihara, T.; Semba, K.; Terao, J.; Tsuji, Y. Copper-Catalyzed Hydrosilylation with a Bowl-Shaped Phosphane Ligand: Preferential Reduction of a Bulky Ketone in the Presence of an Aldehyde. *Angew. Chem., Int. Ed.* **2010**, *49*, 1472-1476.

(14) Loesche, A.; Kahnt, M.; Serbian, I.; Brandt, W.; Csuk, R. Triterpene-Based Carboxamides Act as Good Inhibitors of Butyrylcholinesterase. *Molecules*. **2019**, *24*, 948-964.

(15) Zhang, X.; McNally, A. Cobalt-catalyzed Alkylation of Drug-Like Molecules and Pharmaceuticals using Heterocyclic Phosphonium Salts. *ACS Catal.* **2019**, *9*, 4862-4866.

(16) Prince, R. J.; Gao, F.; Pazienza, J. E.; Marx, I. E.; Schulz, J.; Hopkins, B. T. Utilization of Cyclic Amides as Masked Aldehyde Equivalents in Reductive Amination Reactions. *J. Org. Chem*. **2019**, *84*, 7936-7949.

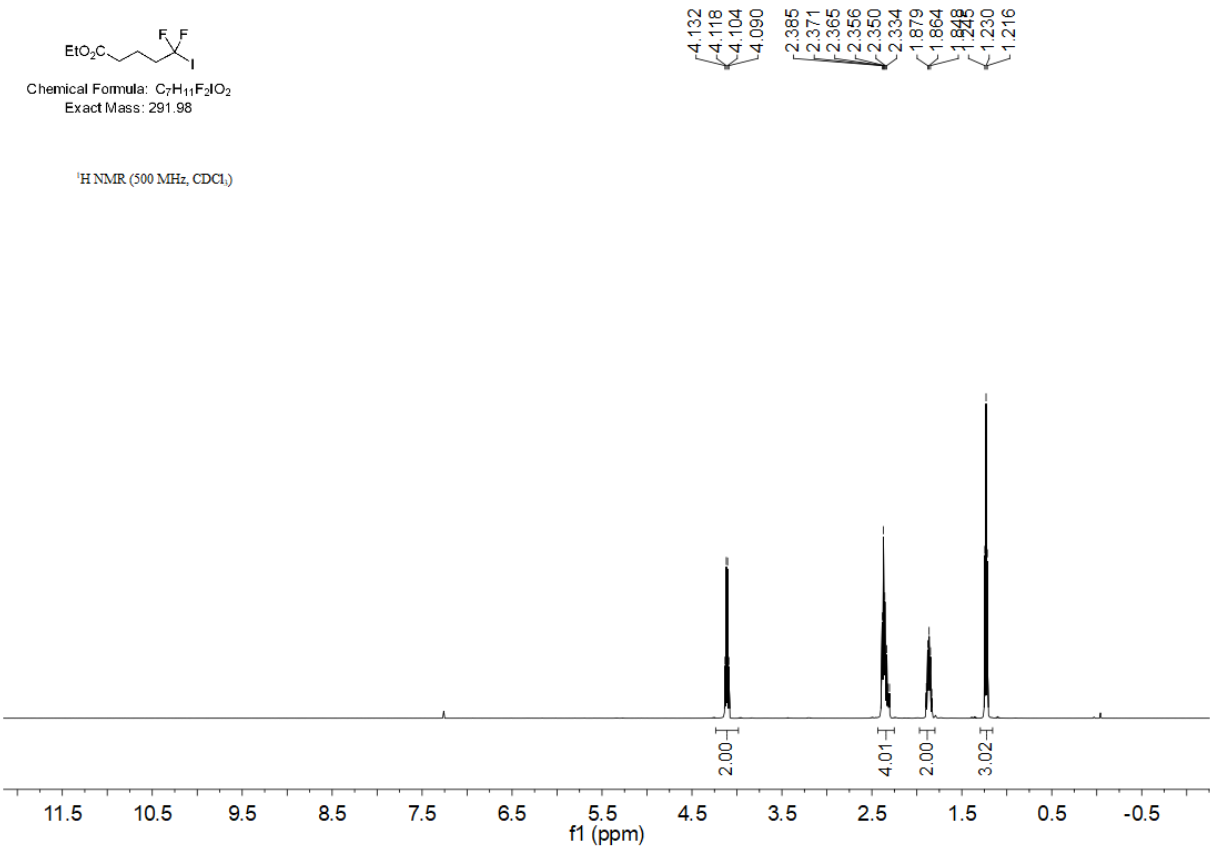
(17) Nelson, B.; Hiller, W.; Pollex, A.; Hiersemann, M. Palladium (II)-Catalyzed Cycloisomerization of Functionalized 1,5-Hexadienes. *Org. Lett*. **2011**, *13*, 4438-4441.

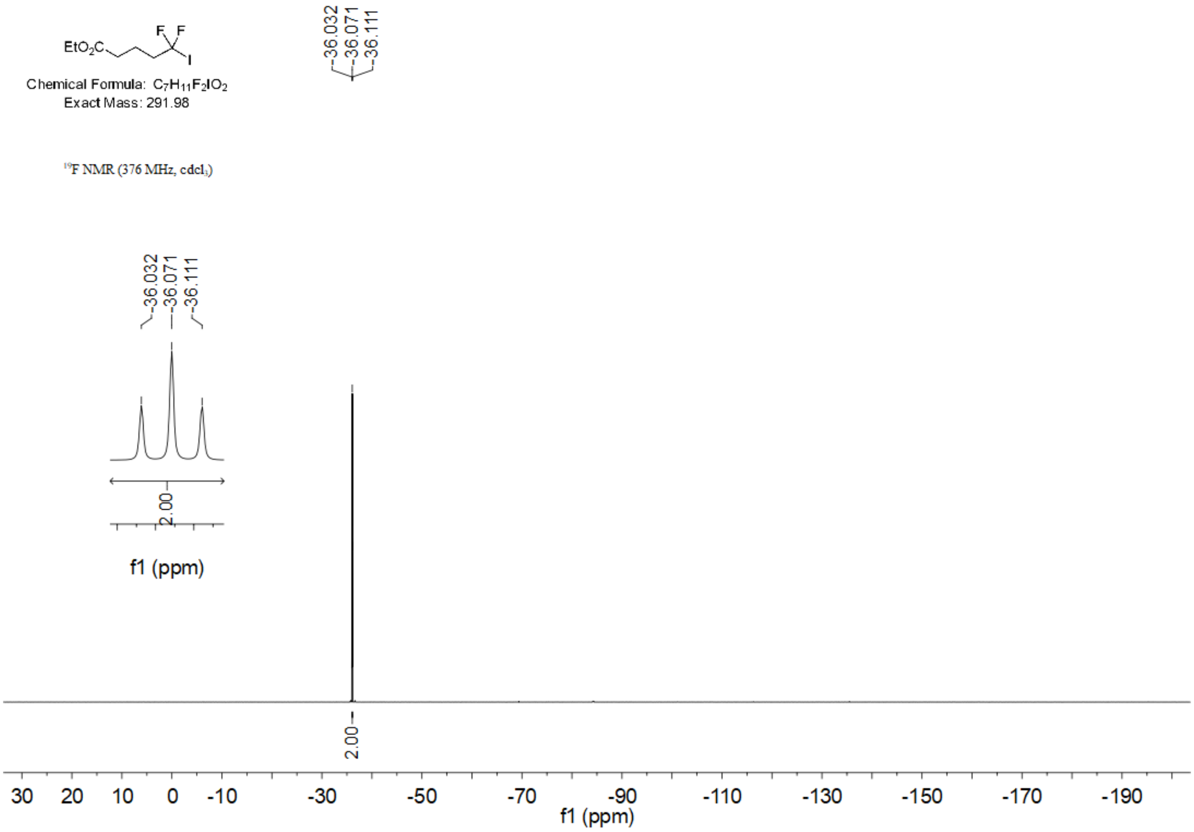
(18) Dine, A. N. E.; Khalaf, A.; Grée, D.; Tasseau, O.; Fares, F.; Jaber, N.; Lesot, P.; Hachem, A.; Grée, R. Synthesis of Enones, Pyrazolines and Pyrrolines with *gem*-Difluoroalkyl Side Chains. *Beilstein J. Org. Chem.* **2013**, *9*, 1943-1948.

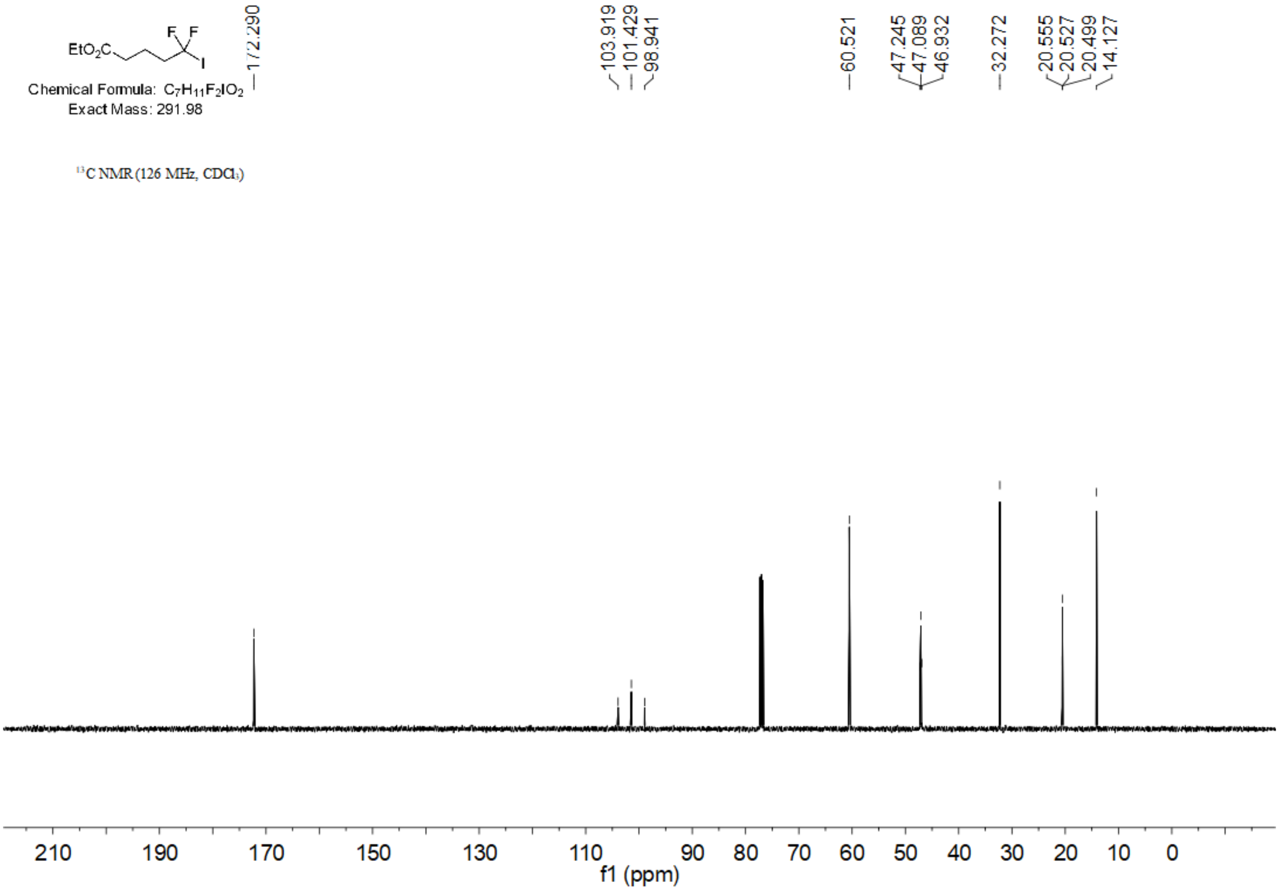
(19) Leuger, J.; Blond, G.; Billard, T.; Haufe, G.; Langlois, B. R. 1,4-Additions of Electron-Rich Heterocycles onto b-Perfluoroalkyl Enones. *J. Fluorine Chem.* **2011**, *132*, 799-803.

8. Copies of ^{1}H NMR, ^{19}F NMR and ^{13}C NMR Spectra of Compounds 1, 3, 5, 8-15

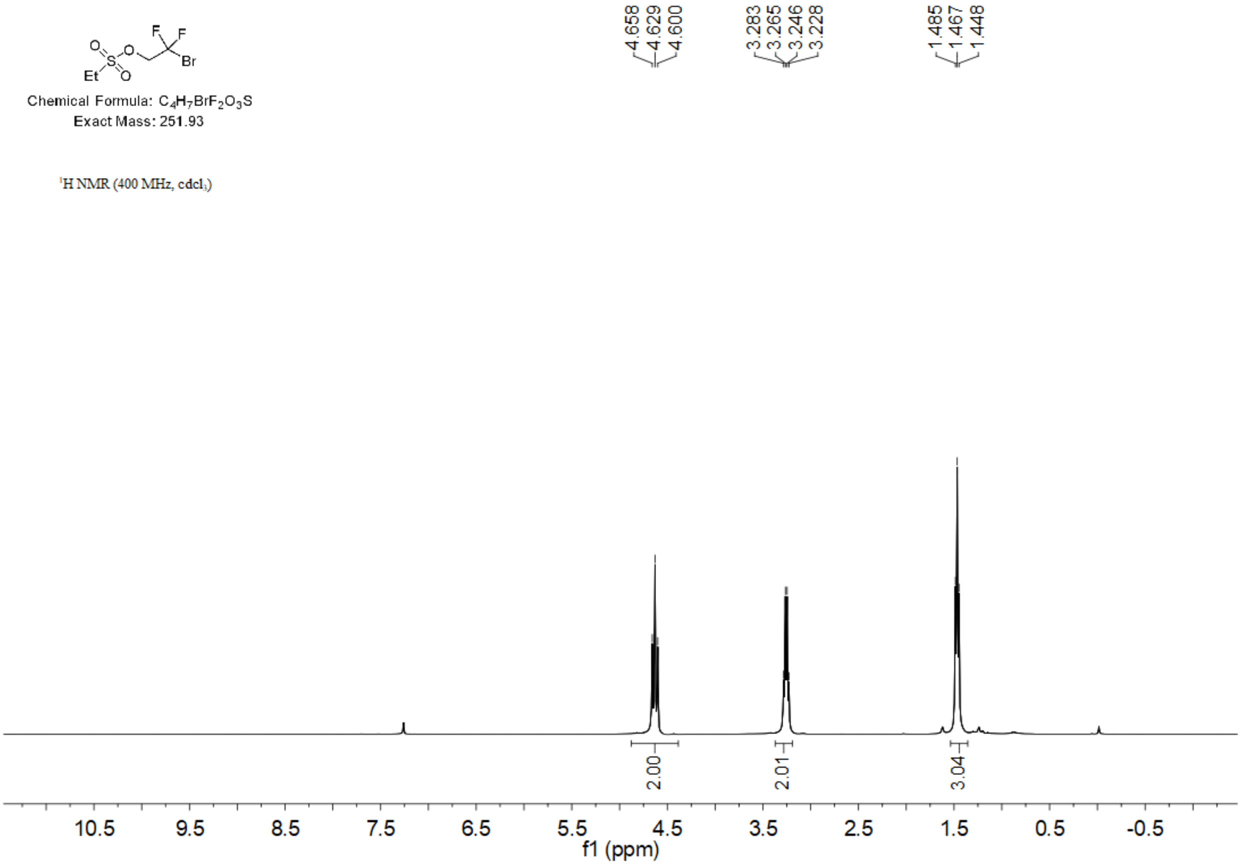
Ethyl 5,5-difluoro-5-iodopentanoate (1a)

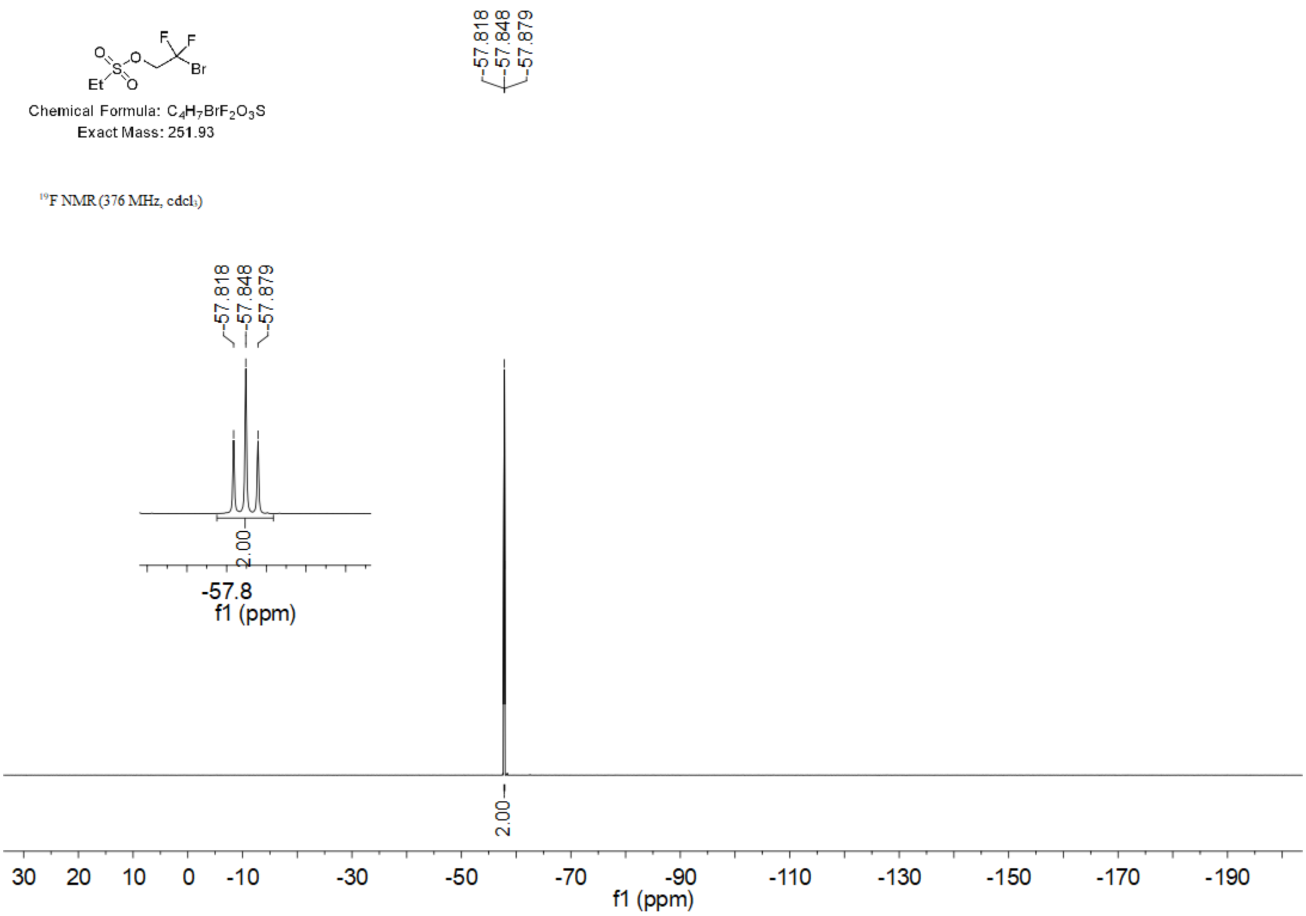




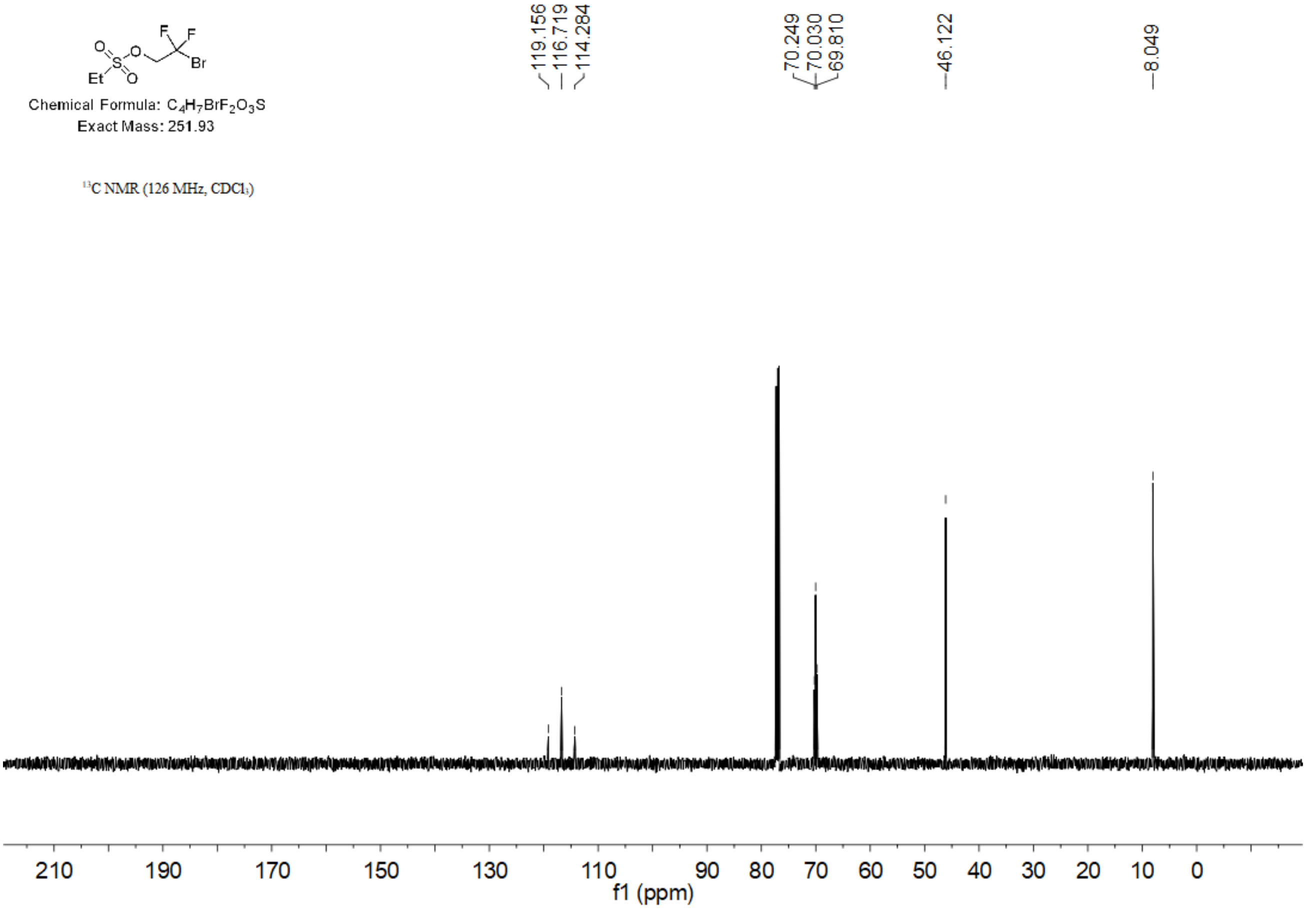


2-Bromo-2,2-difluoroethyl ethanesulfonate (1h)



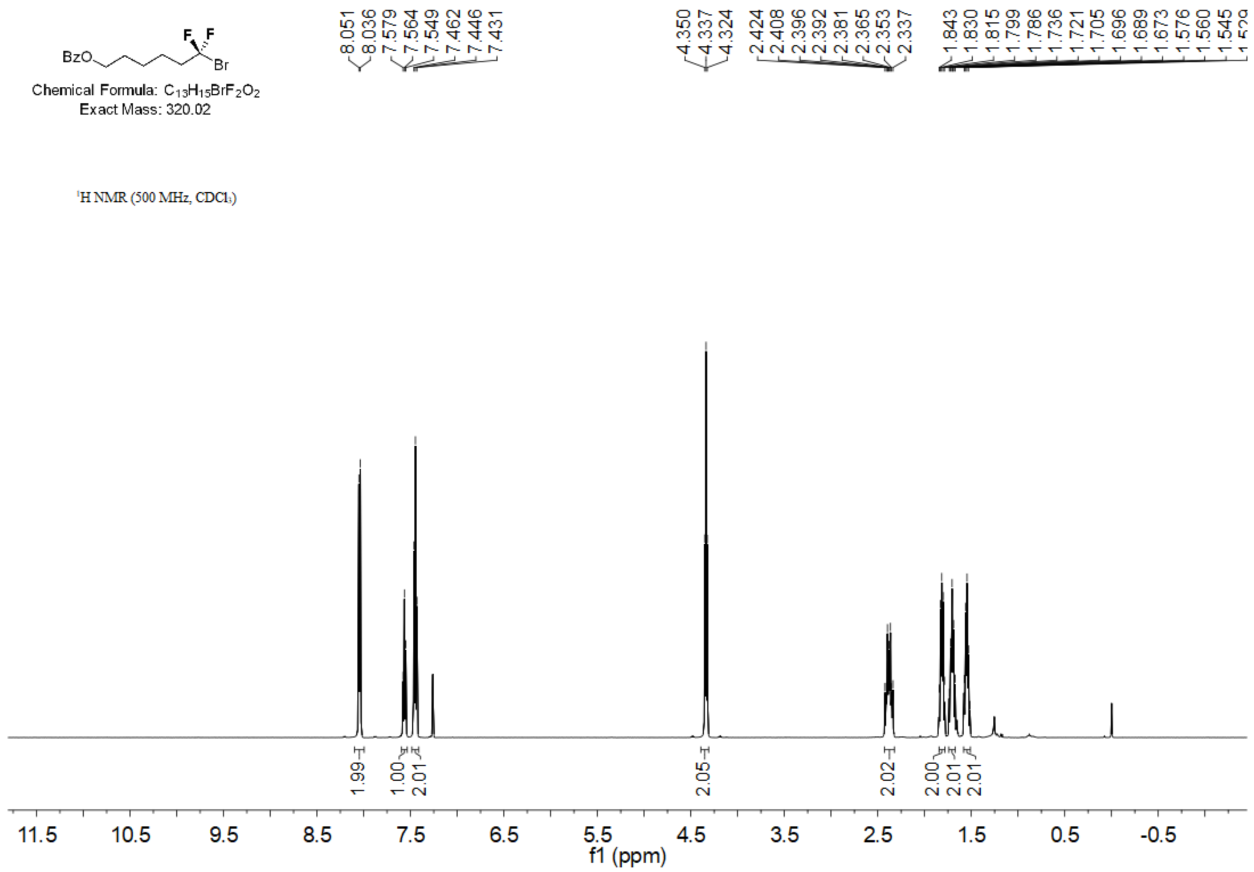

Chemical Formula: $C_4H_7BrF_2O_3S$
Exact Mass: 251.93

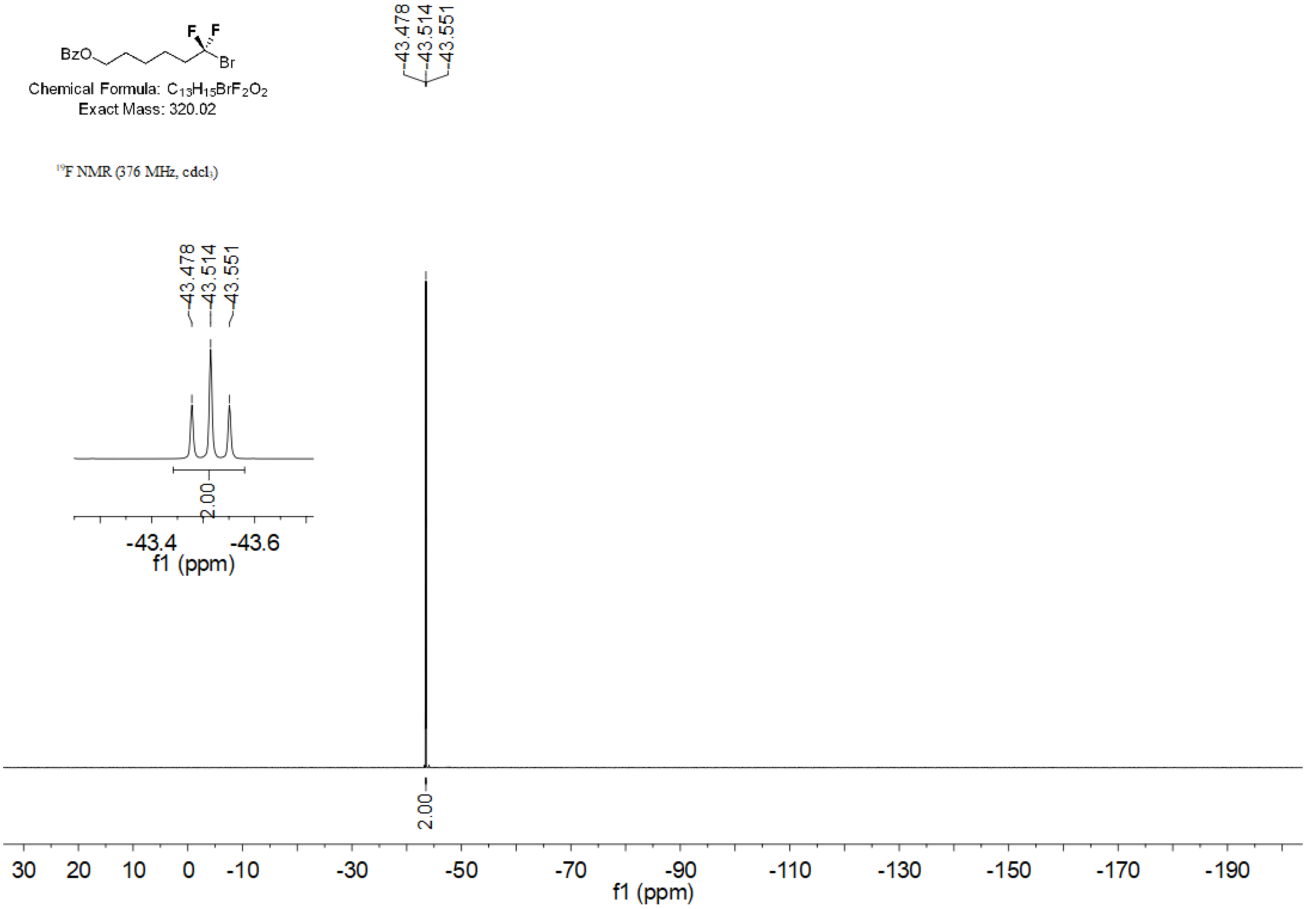
^{19}F NMR (376 MHz, cdcl$_3$)

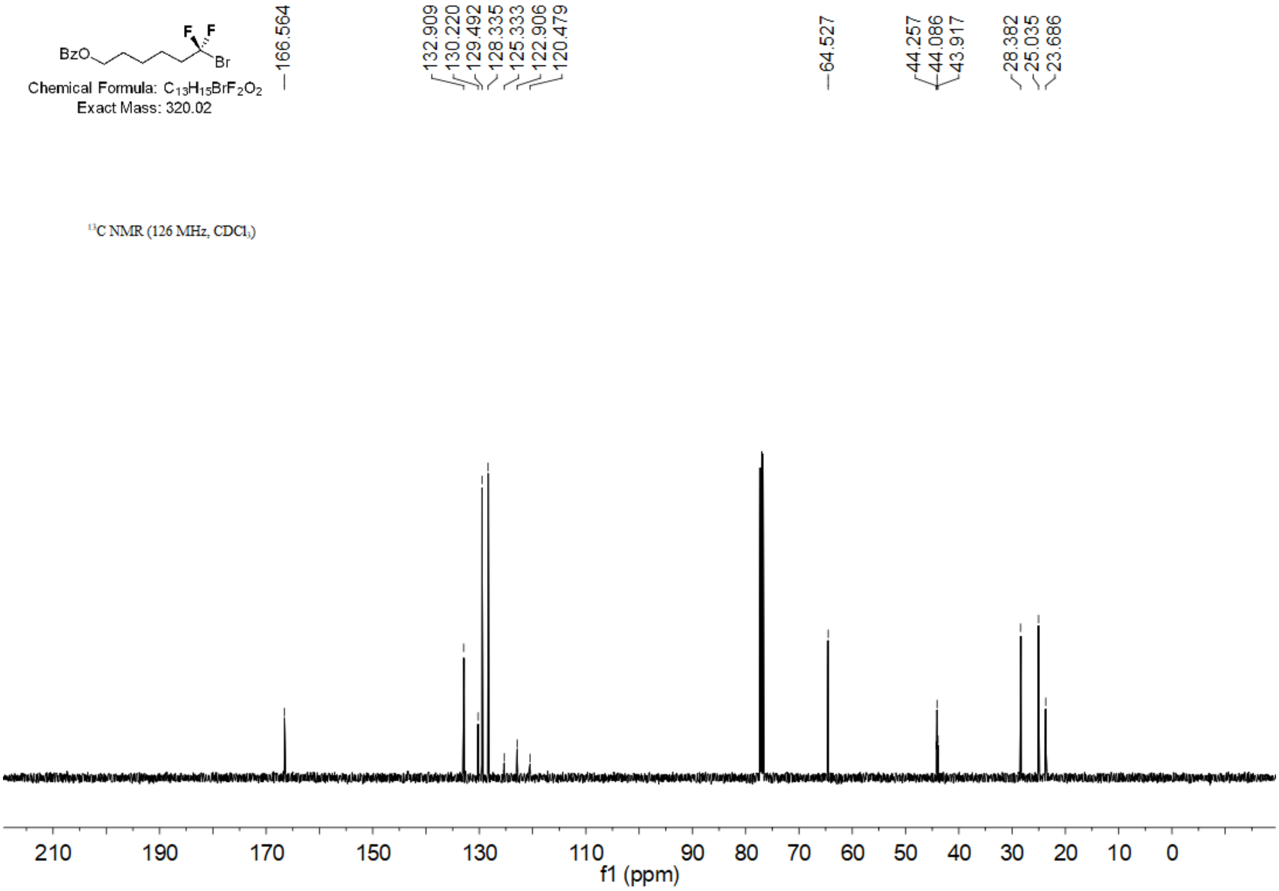

Chemical Formula: $C_4H_7BrF_2O_3S$
Exact Mass: 251.93

^{13}C NMR (126 MHz, CDCl$_3$)

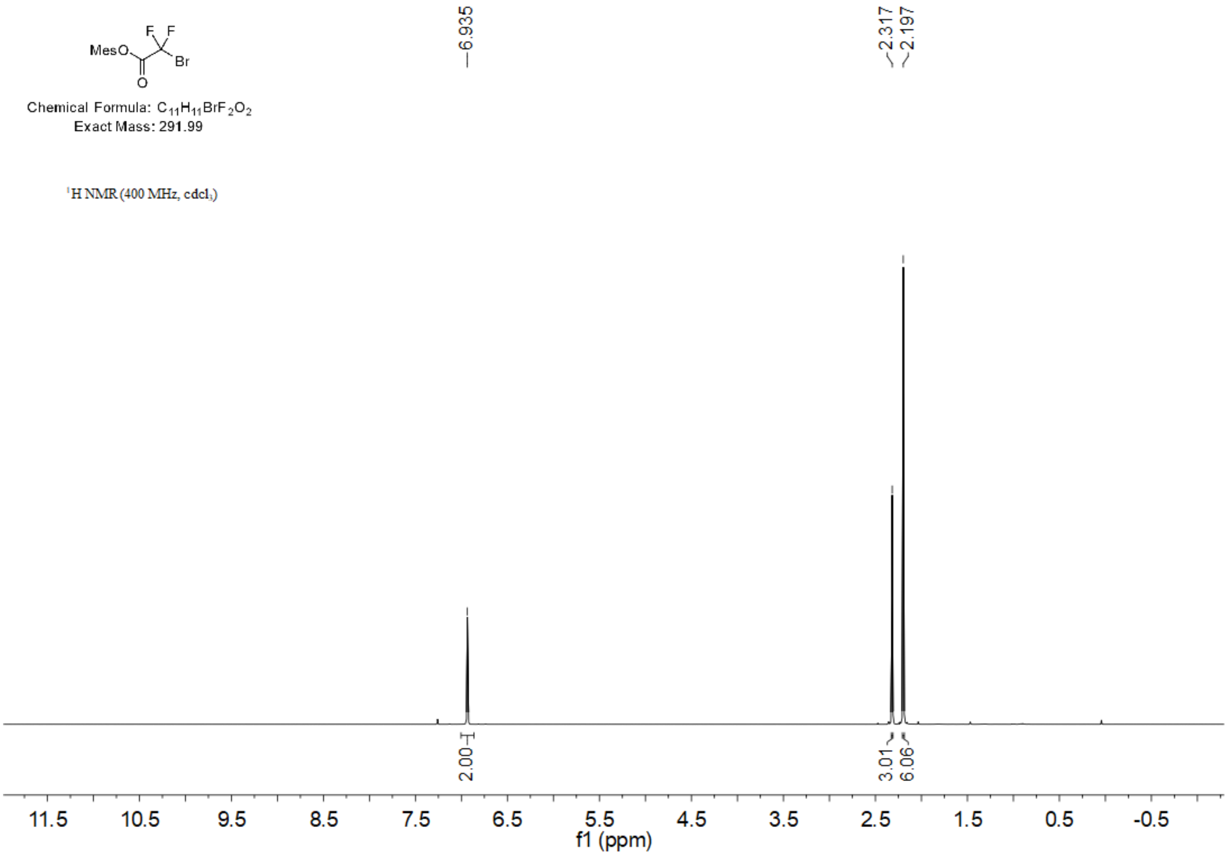
6-Bromo-6,6-difluorohexyl benzoate (1i)

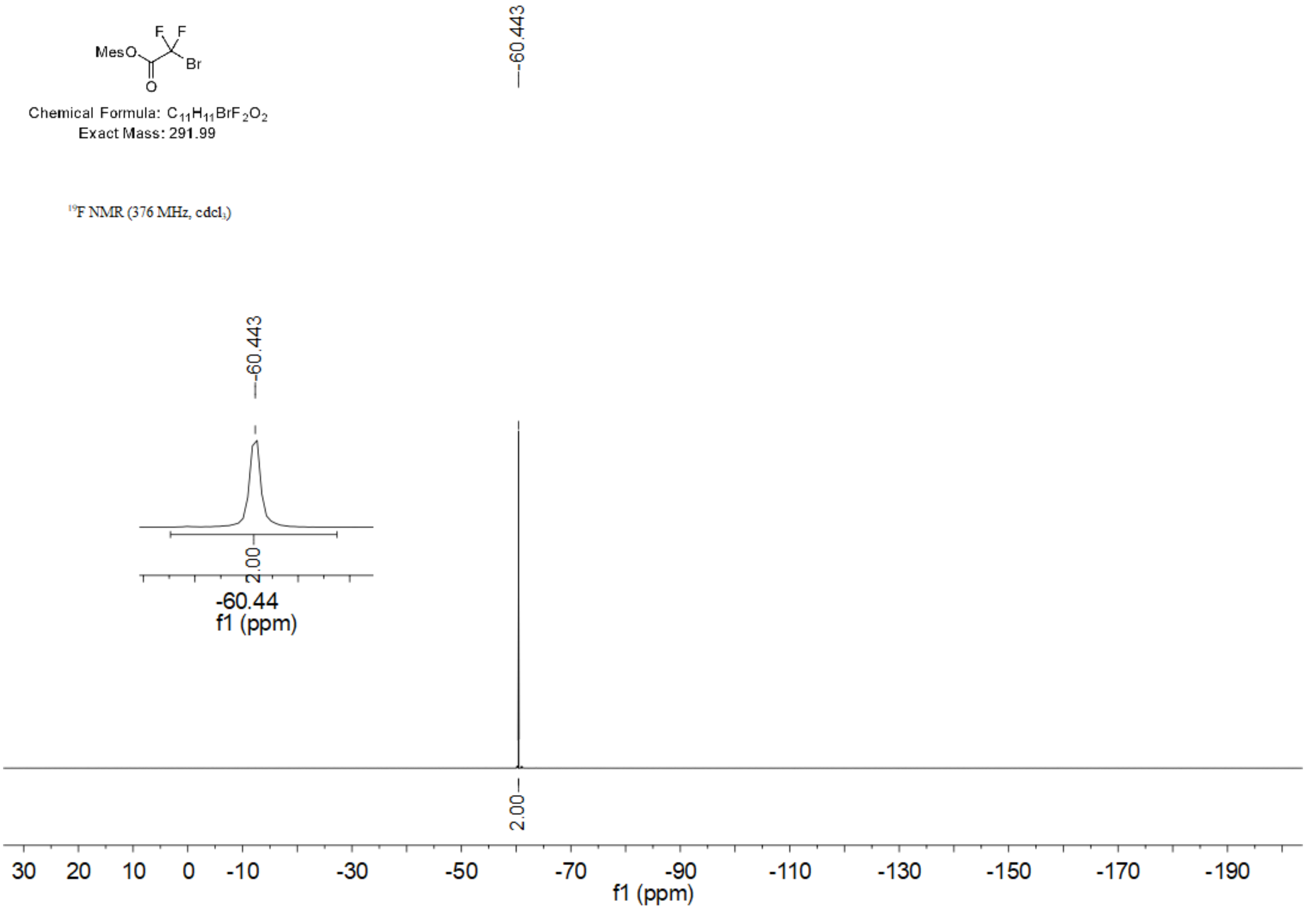






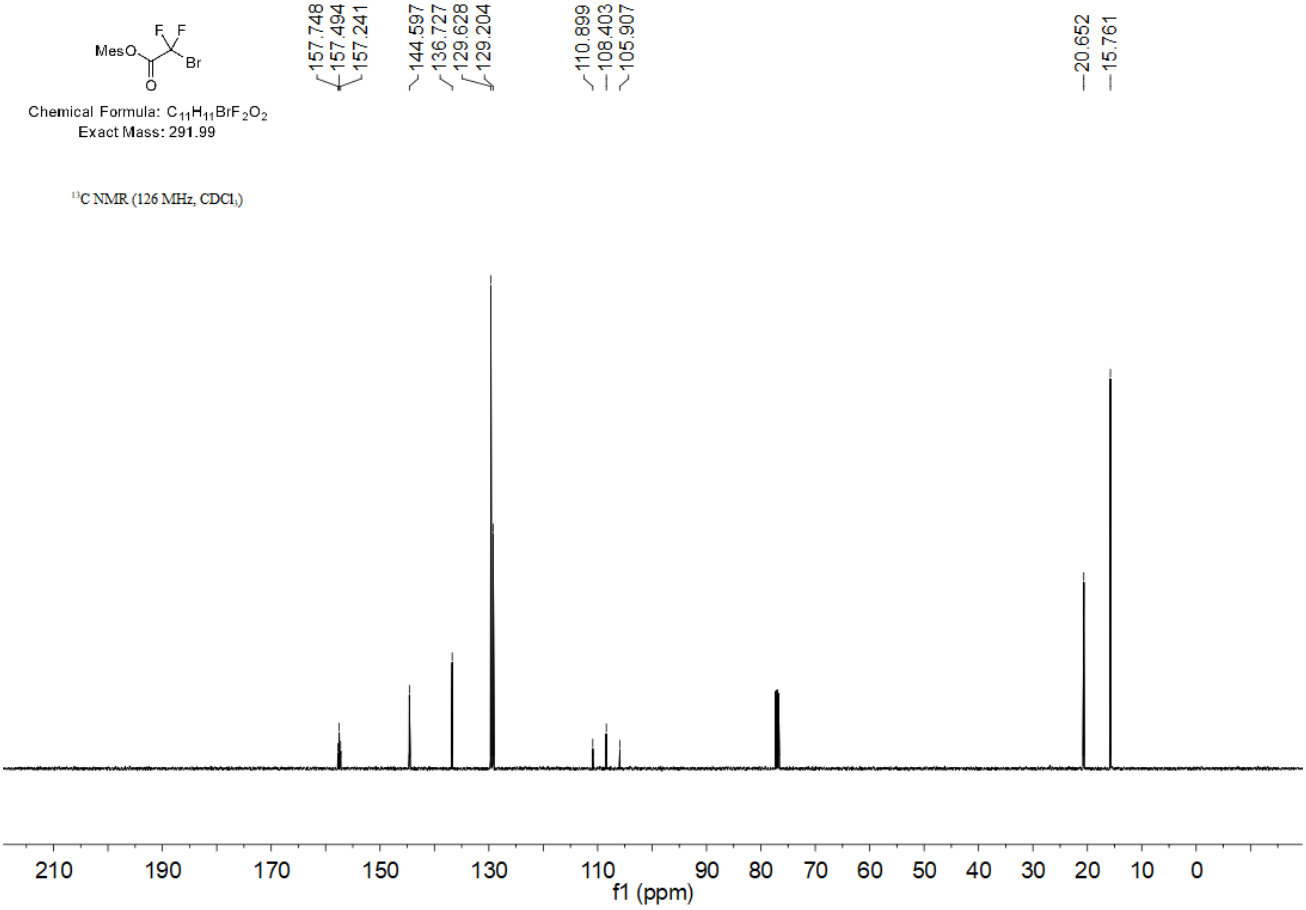
Mesityl 2-bromo-2,2-difluoroacetate (1k)





Chemical Formula: $C_{11}H_{11}BrF_2O_2$
Exact Mass: 291.99

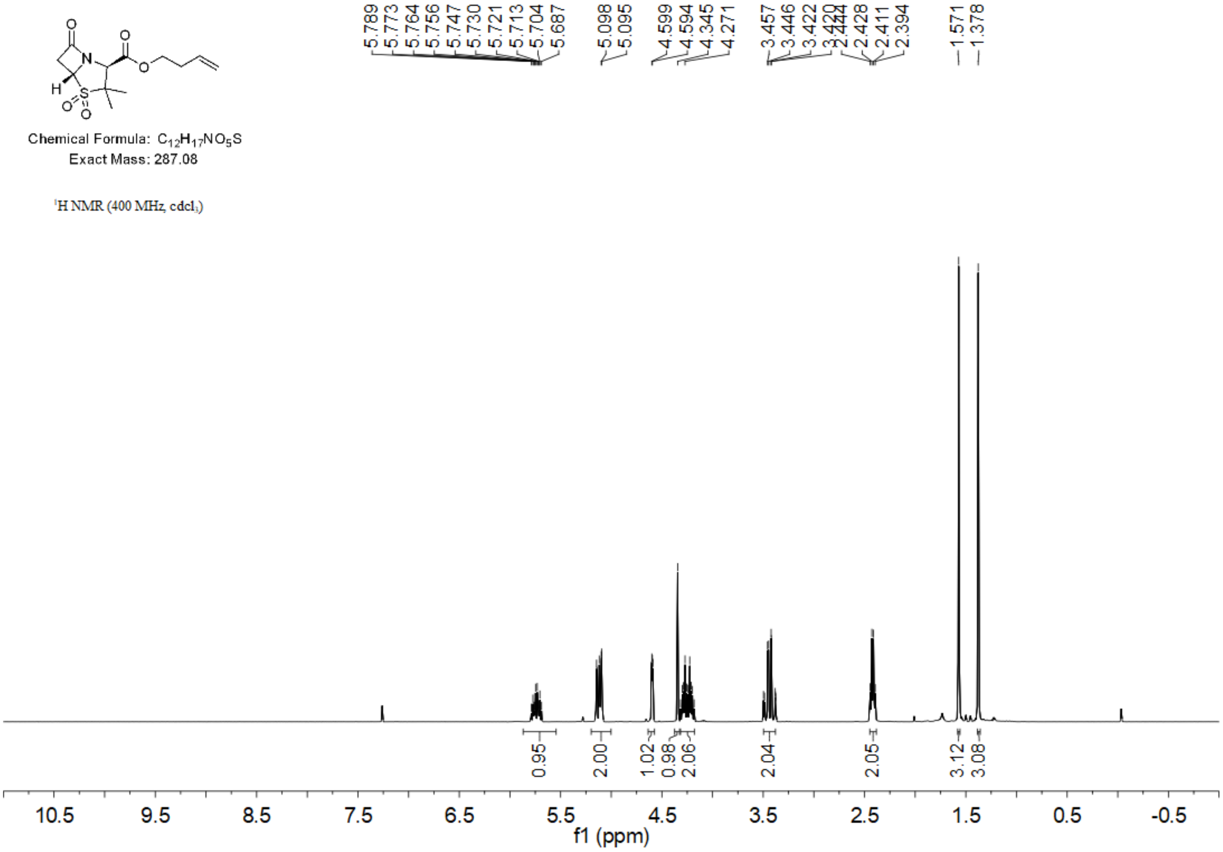
^{19}F NMR (376 MHz, cdcl$_3$)

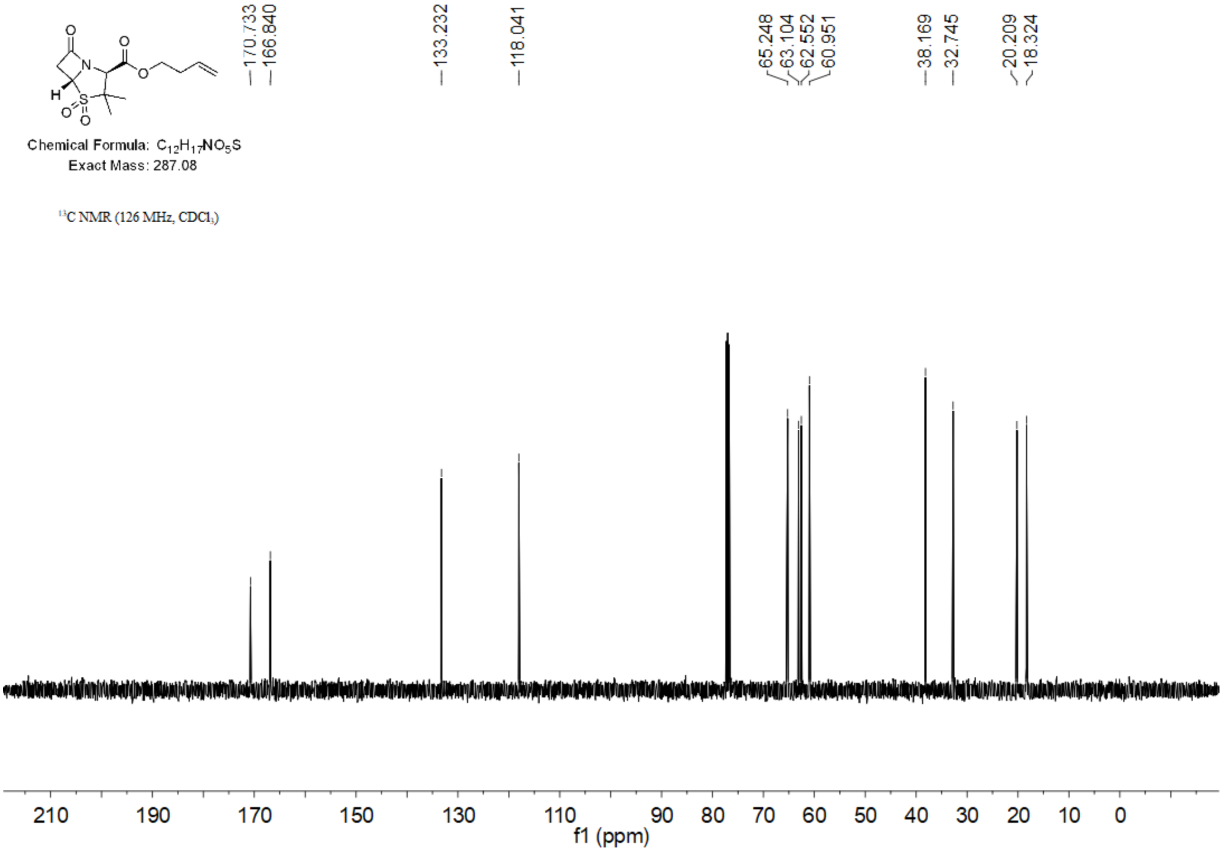


Chemical Formula: $C_{11}H_{11}BrF_2O_2$
Exact Mass: 291.99

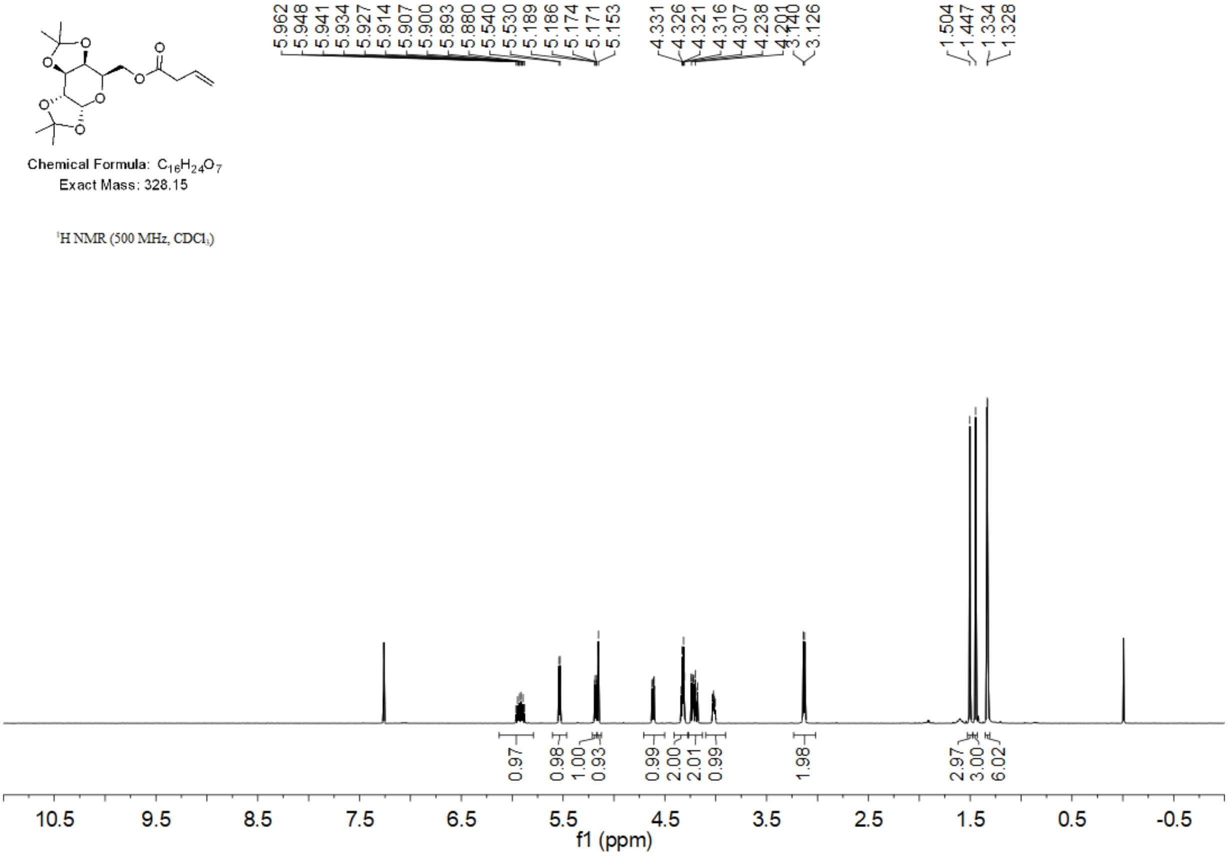
^{13}C NMR (126 MHz, CDCl$_3$)

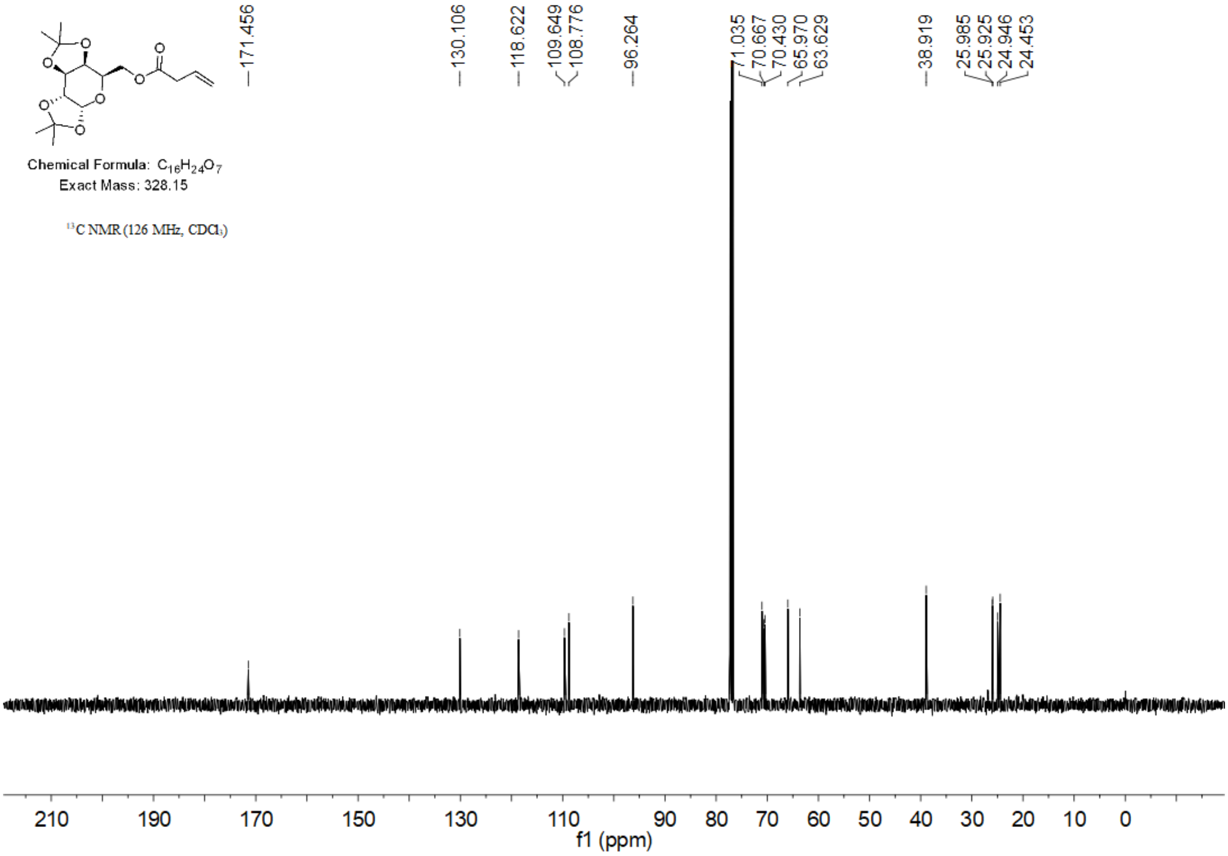
But-3-en-1-yl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate (5p)



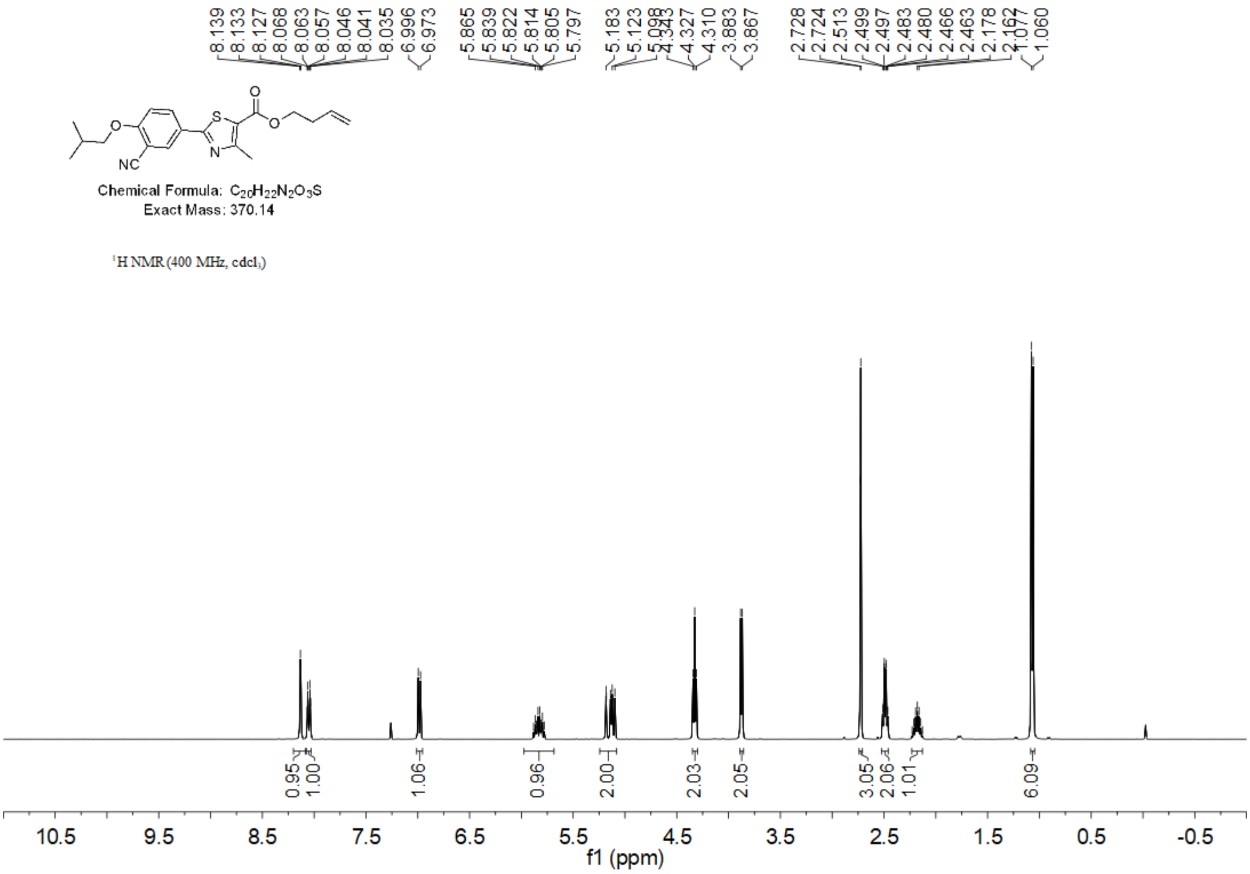


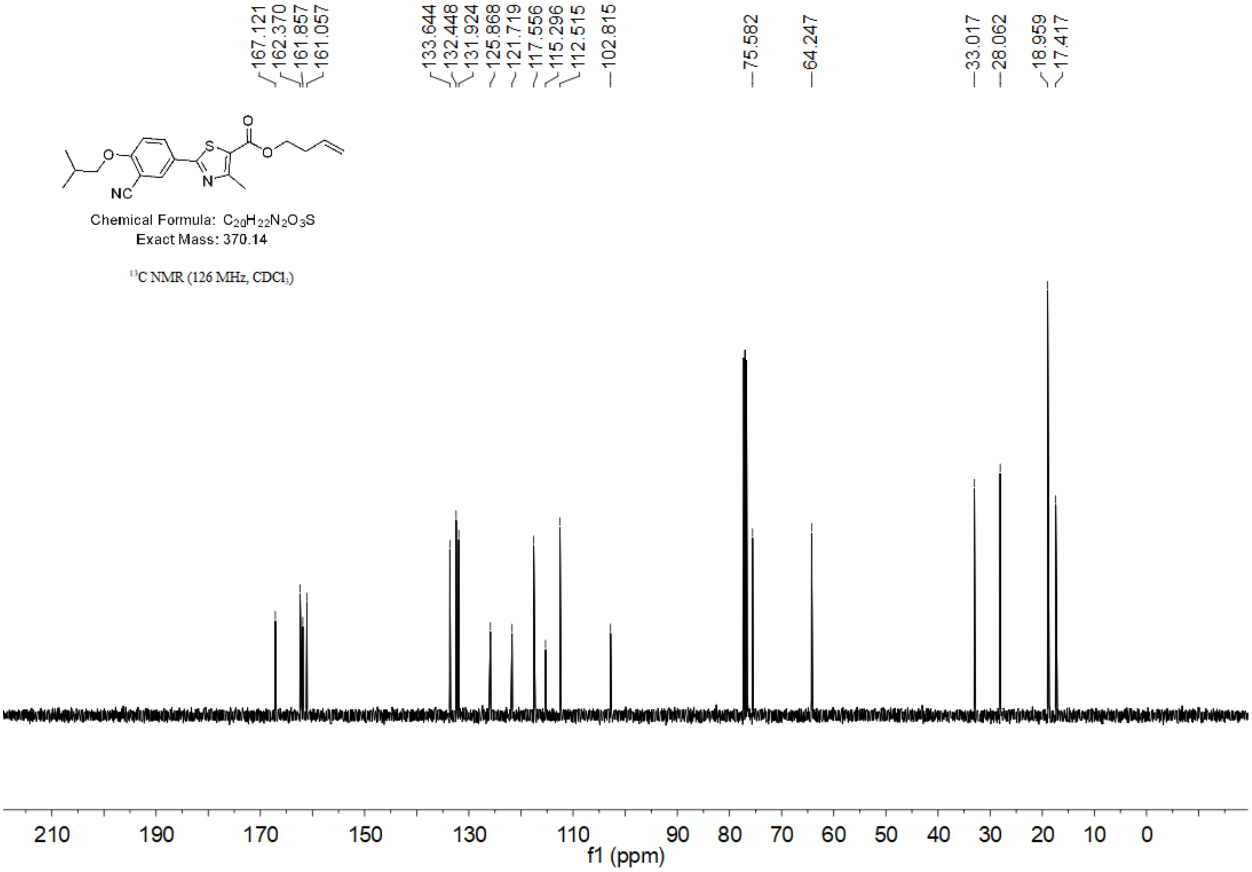
((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-Tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl but-3-enoate (5r)



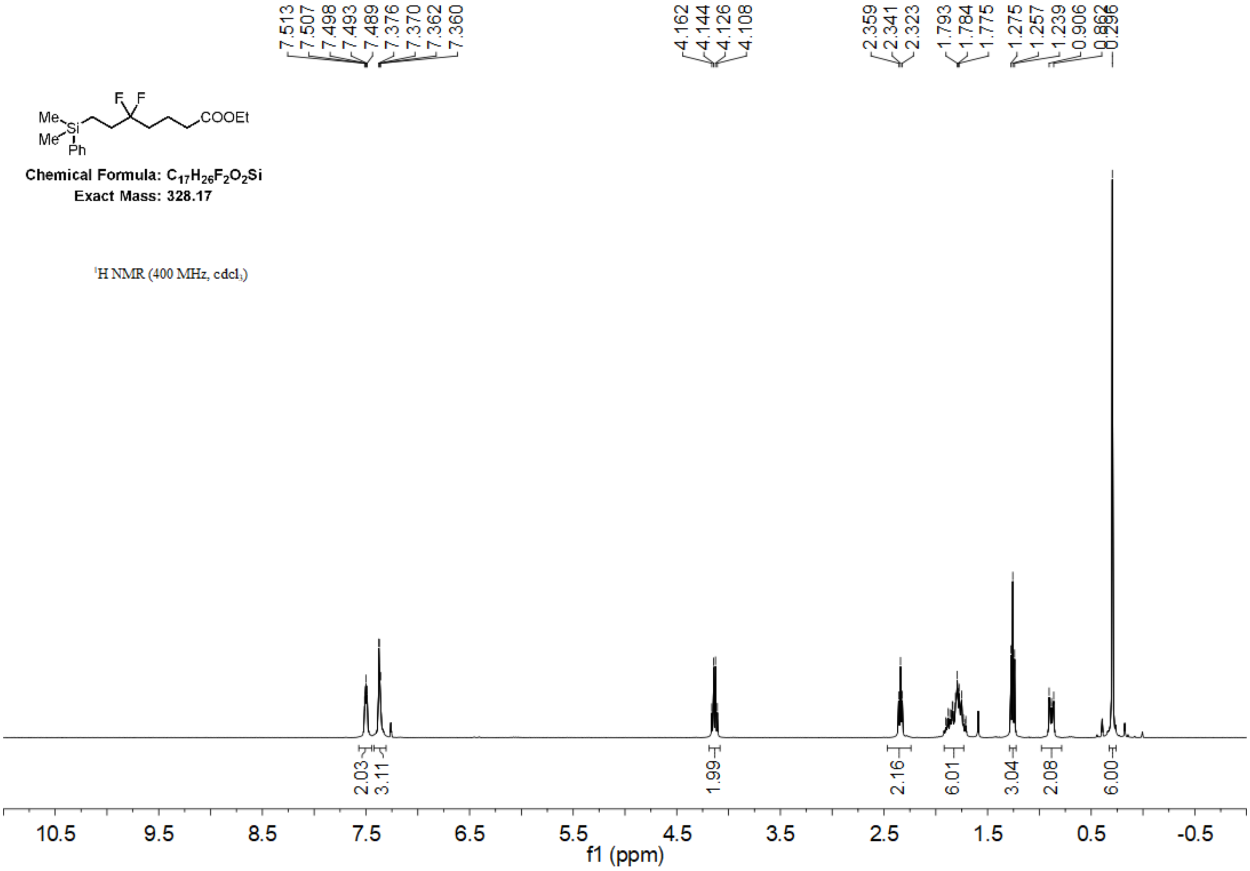


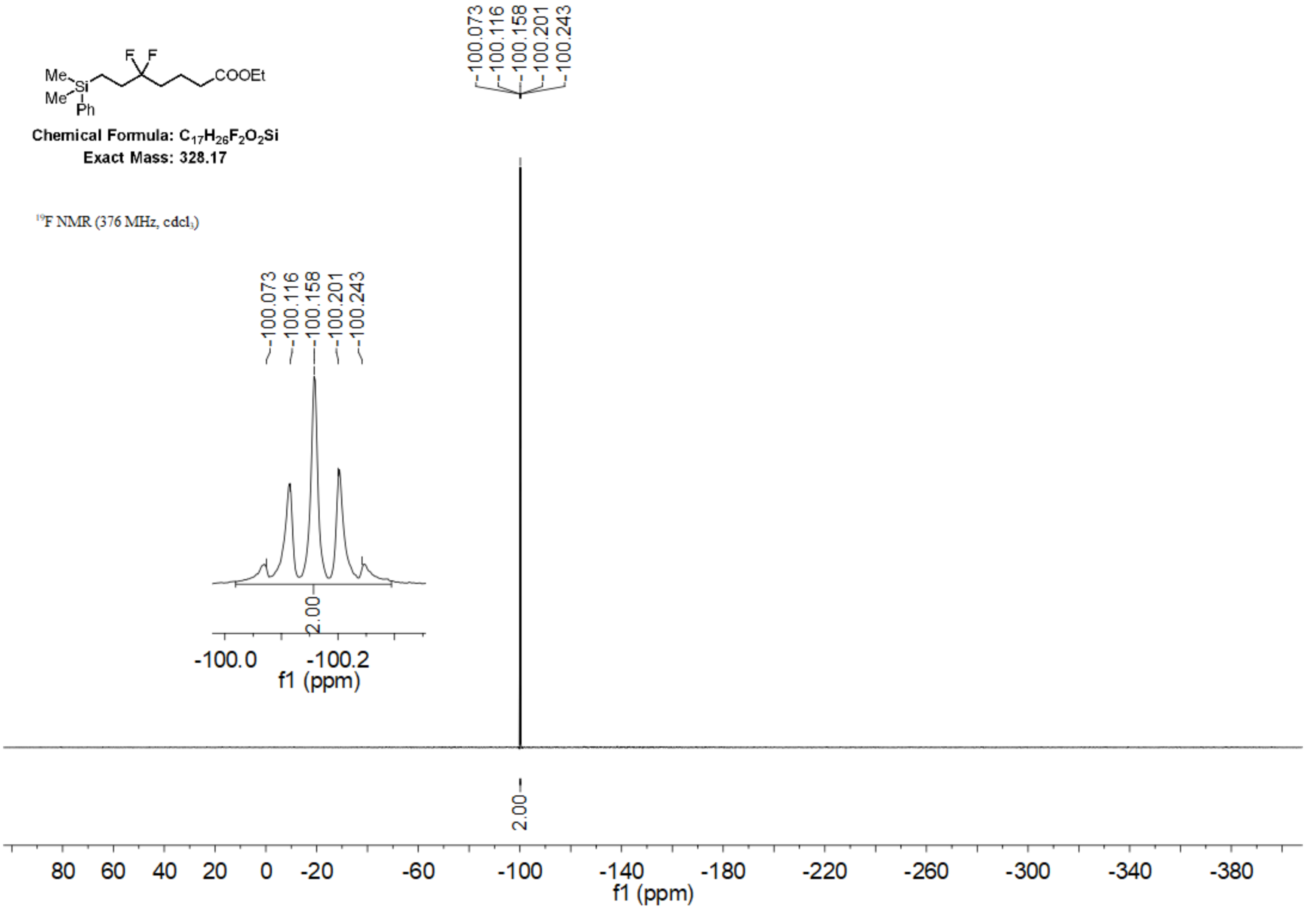
But-3-en-1-yl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (5s)

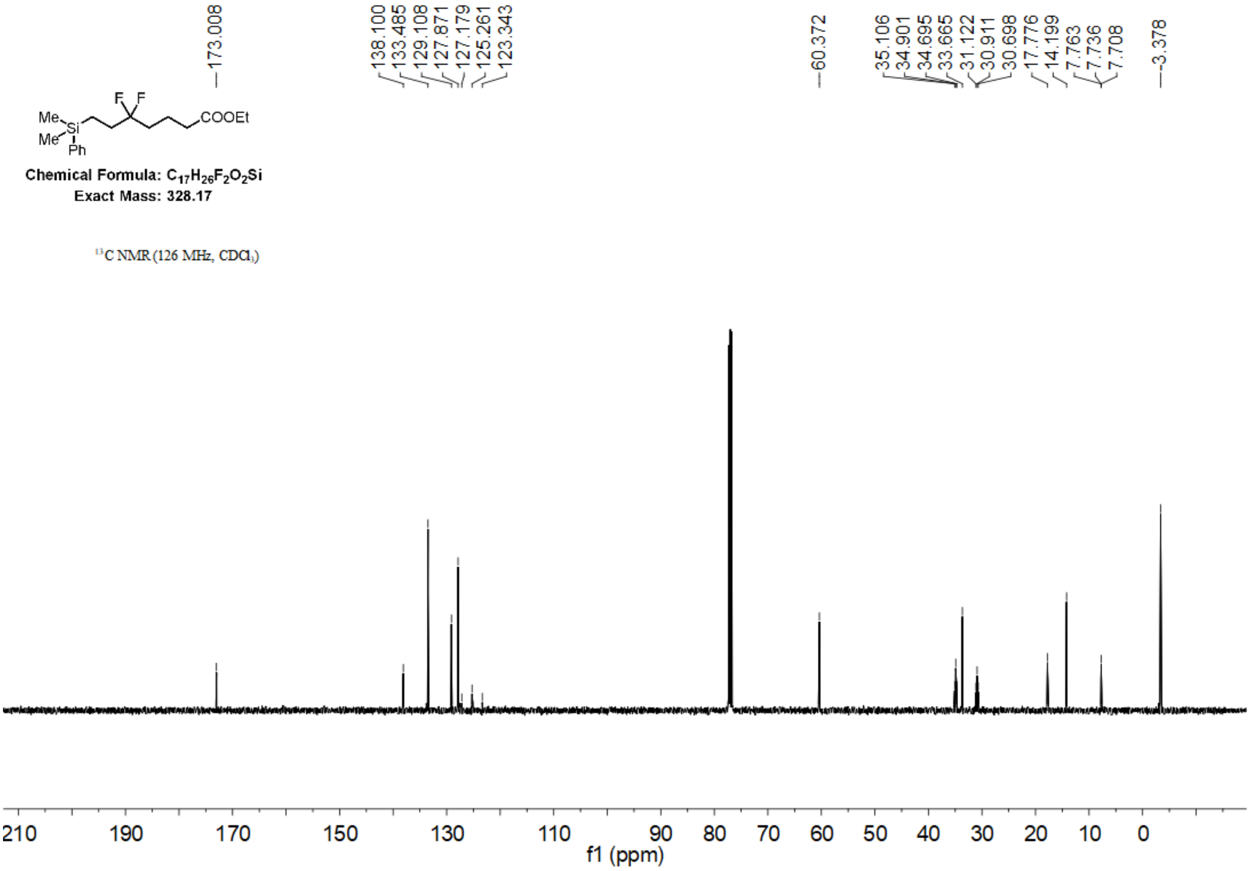




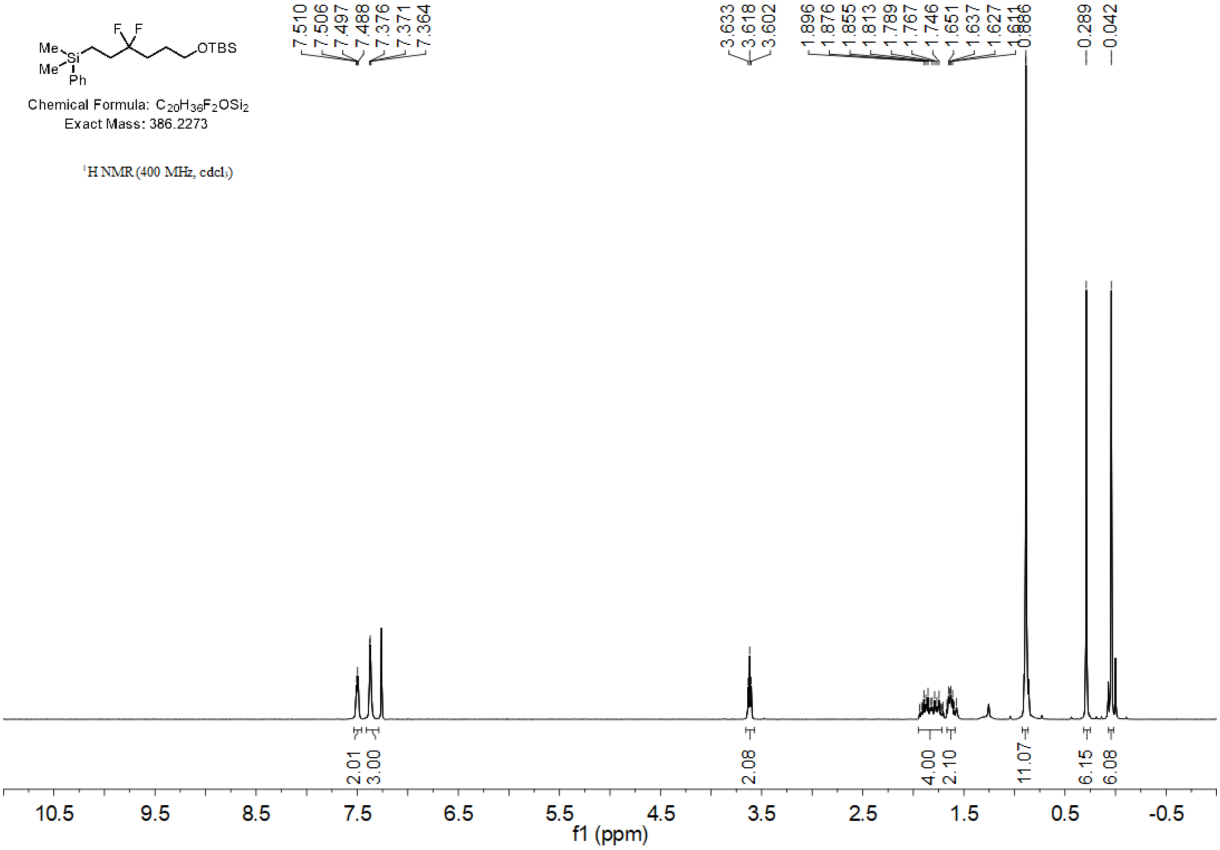
Ethyl 7-(dimethyl(phenyl)silyl)-5,5-difluoroheptanoate (3a)

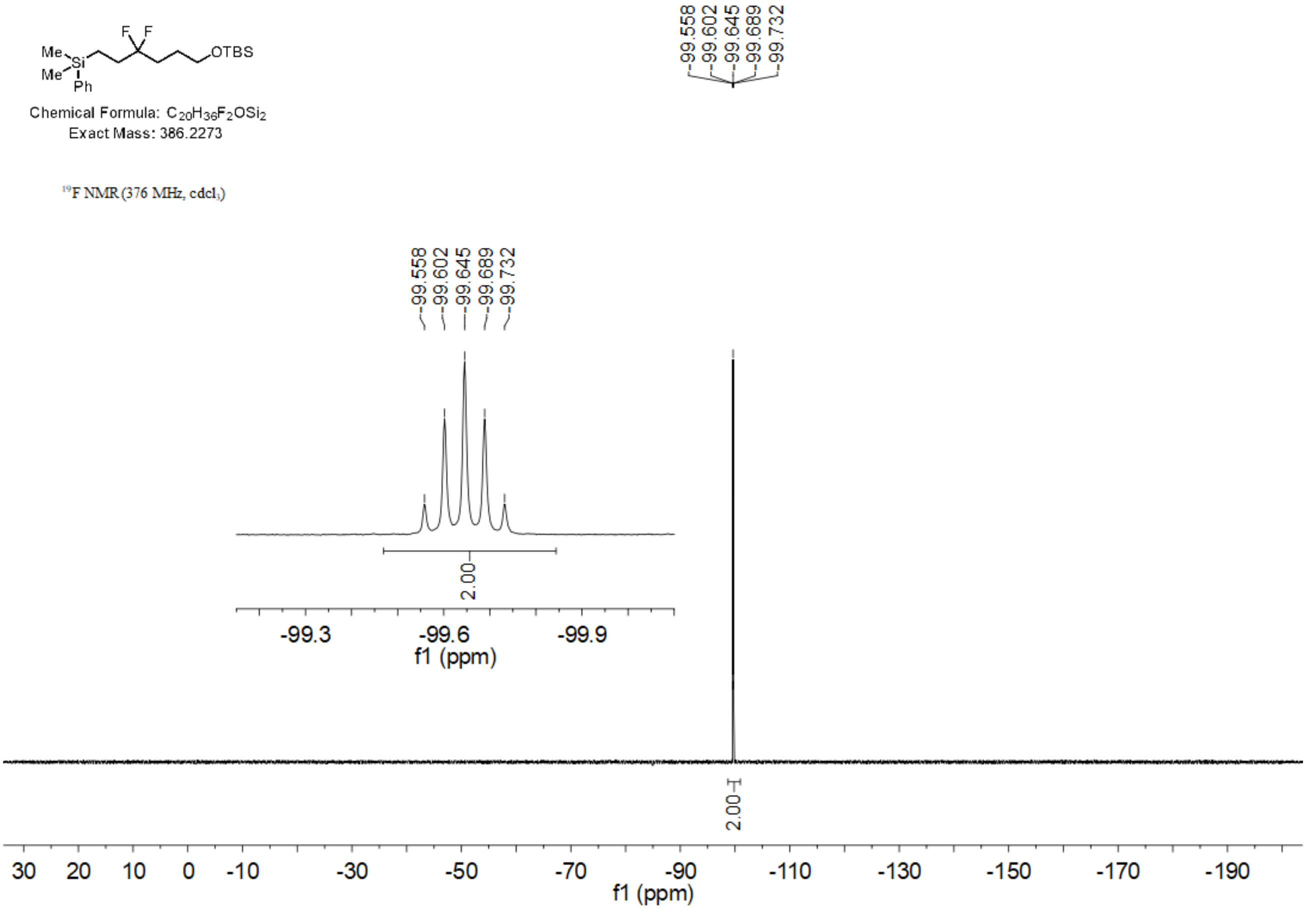






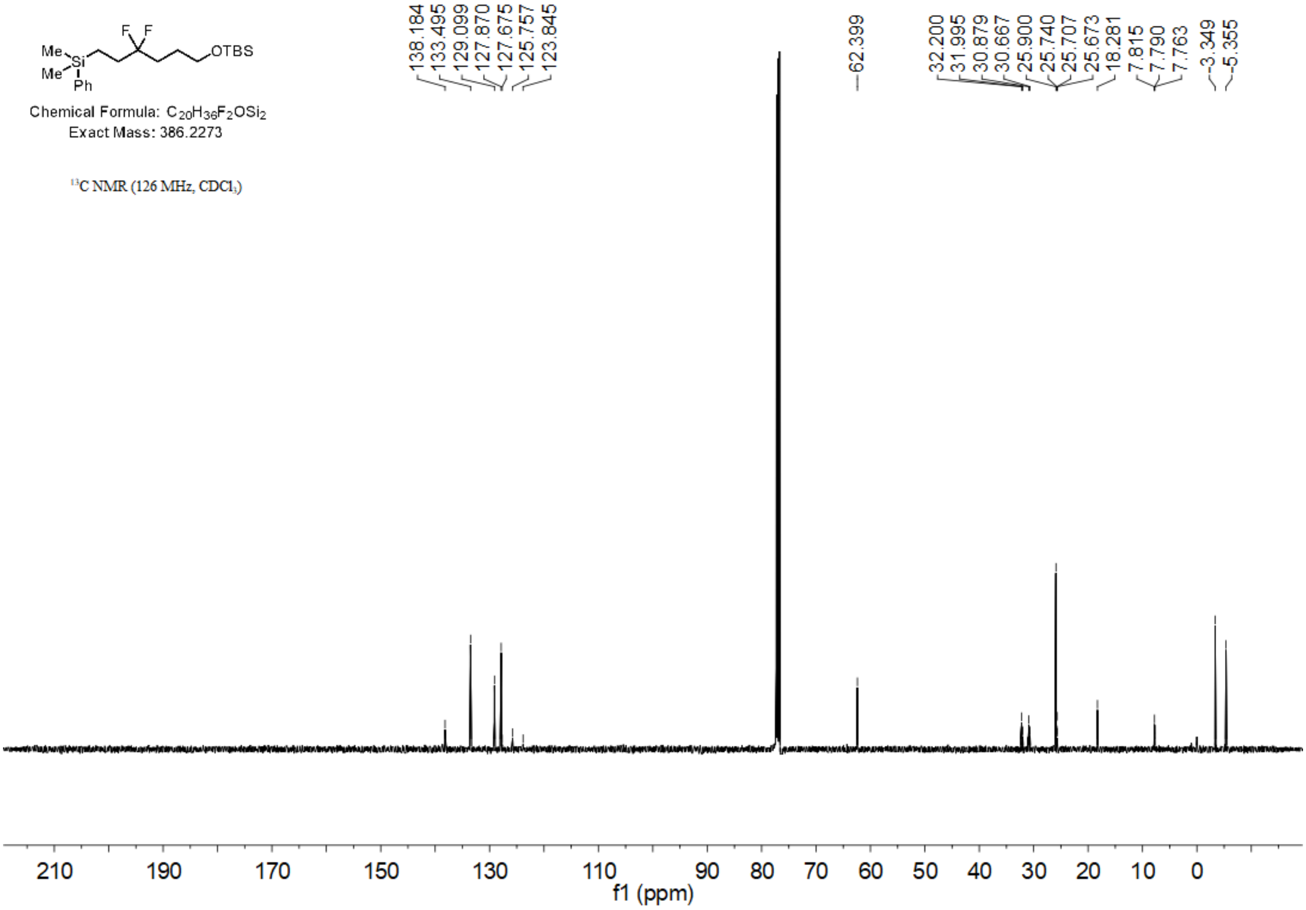
tert-Butyl((6-(dimethyl(phenyl)silyl)-4,4-difluorohexyl)oxy)dimethylsilane (3b)





Chemical Formula: $C_{20}H_{36}F_2OSi_2$
Exact Mass: 386.2273

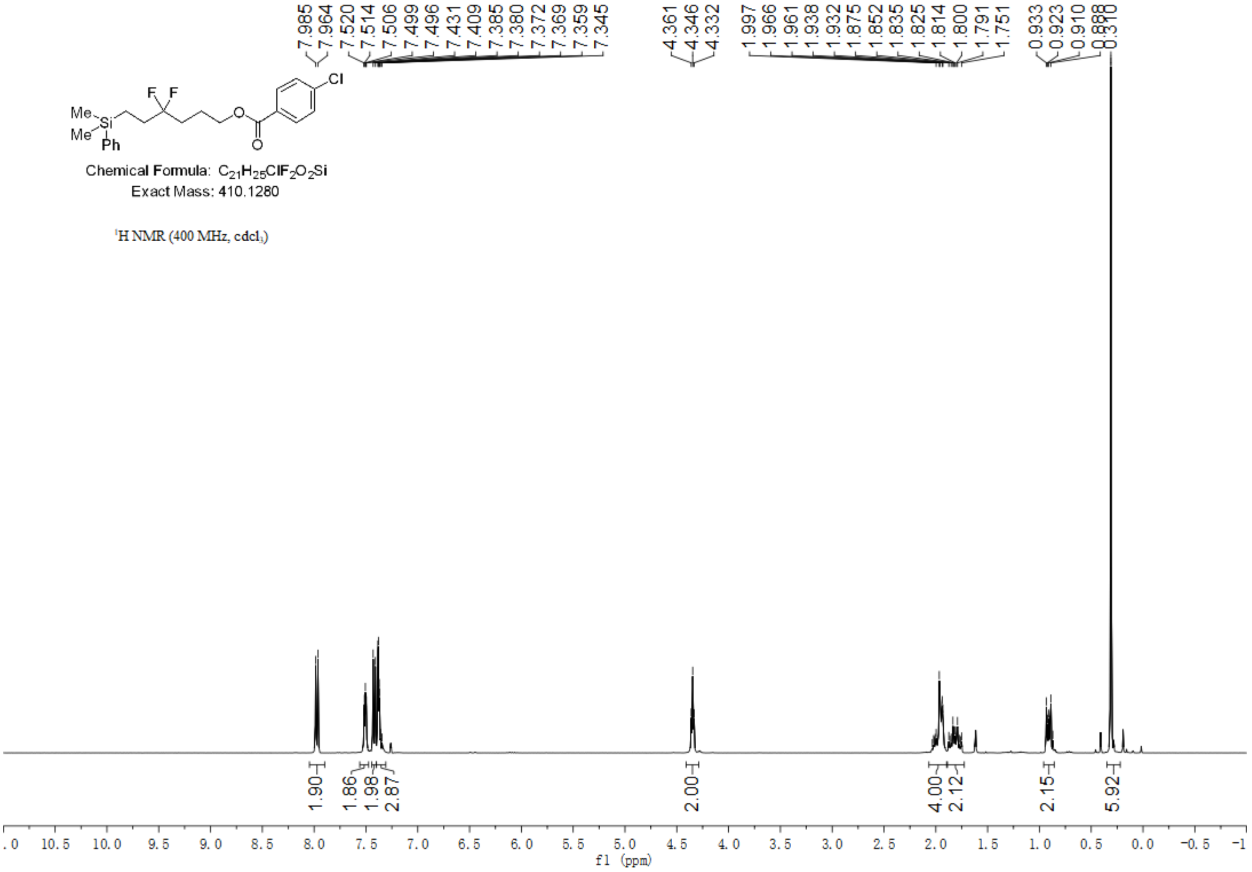
^{19}F NMR (376 MHz, cdcl$_3$)

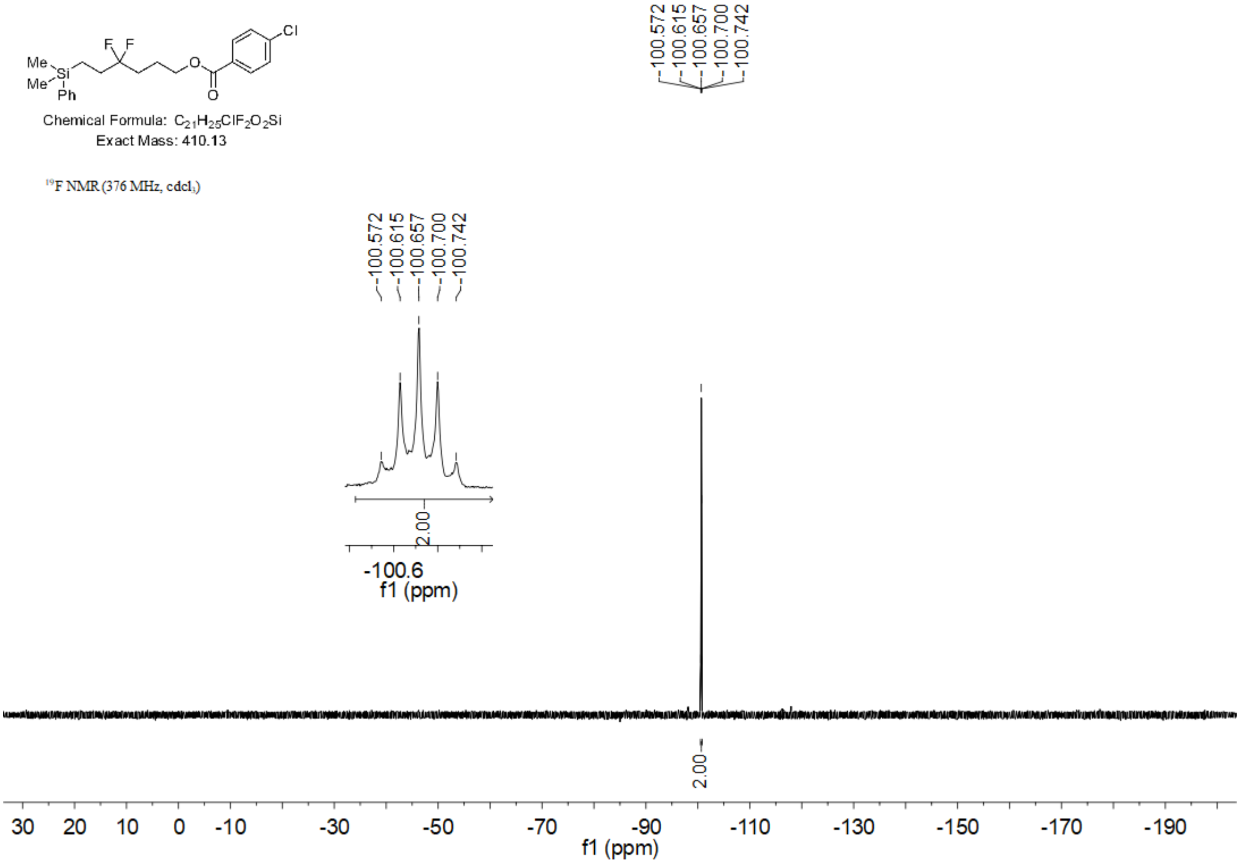


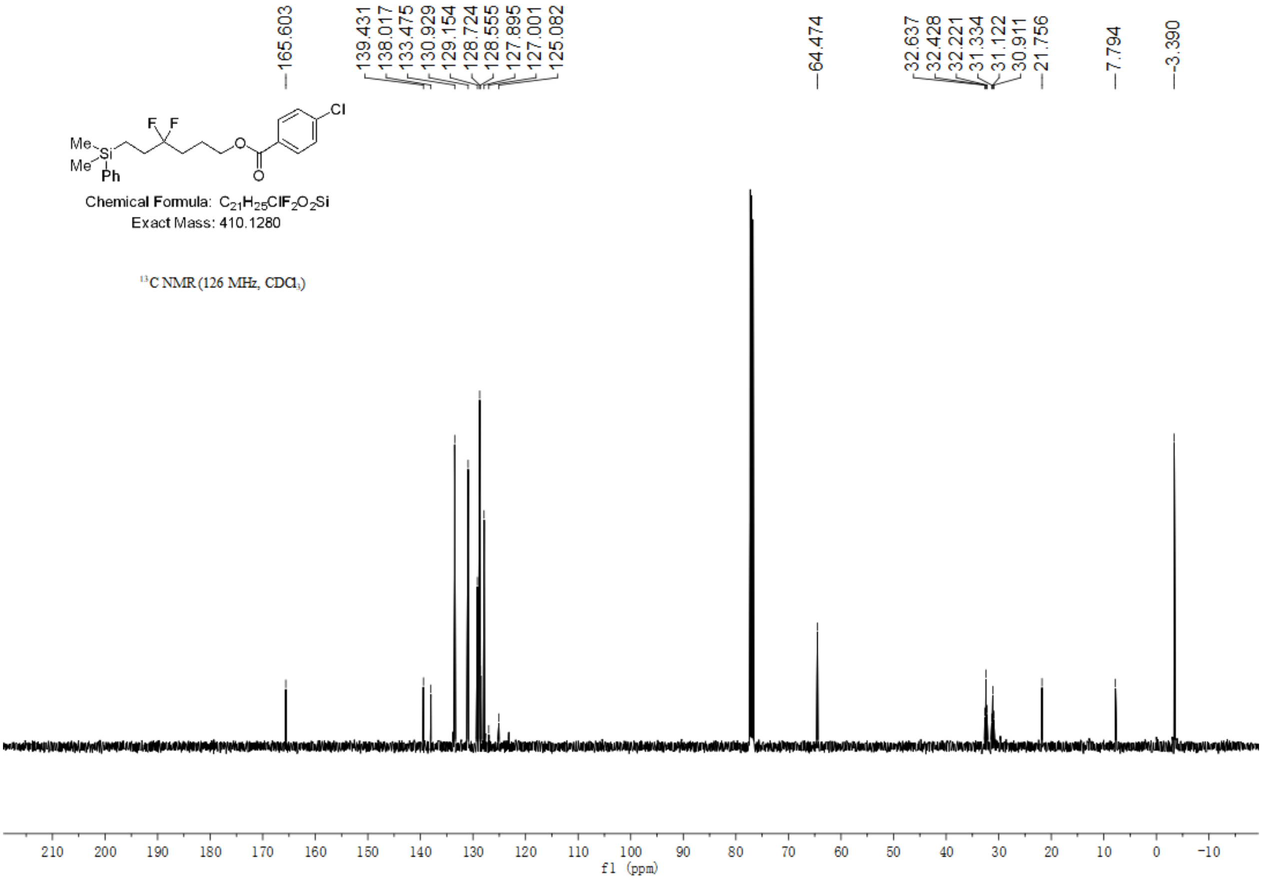
Chemical Formula: $C_{20}H_{36}F_2OSi_2$
Exact Mass: 386.2273

^{13}C NMR (126 MHz, CDCl$_3$)

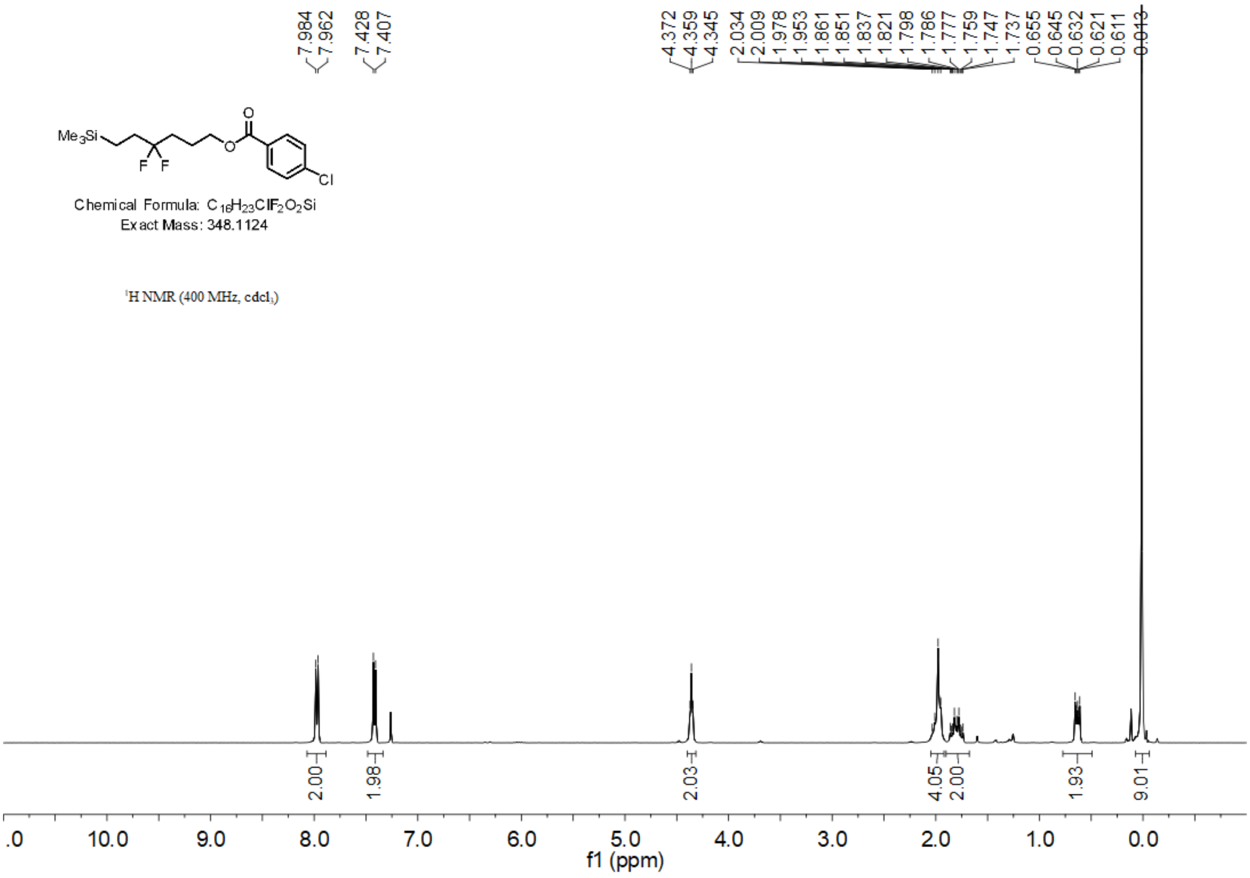
6-(Dimethyl(phenyl)silyl)-4,4-difluorohexyl 4-chlorobenzoate (3c)

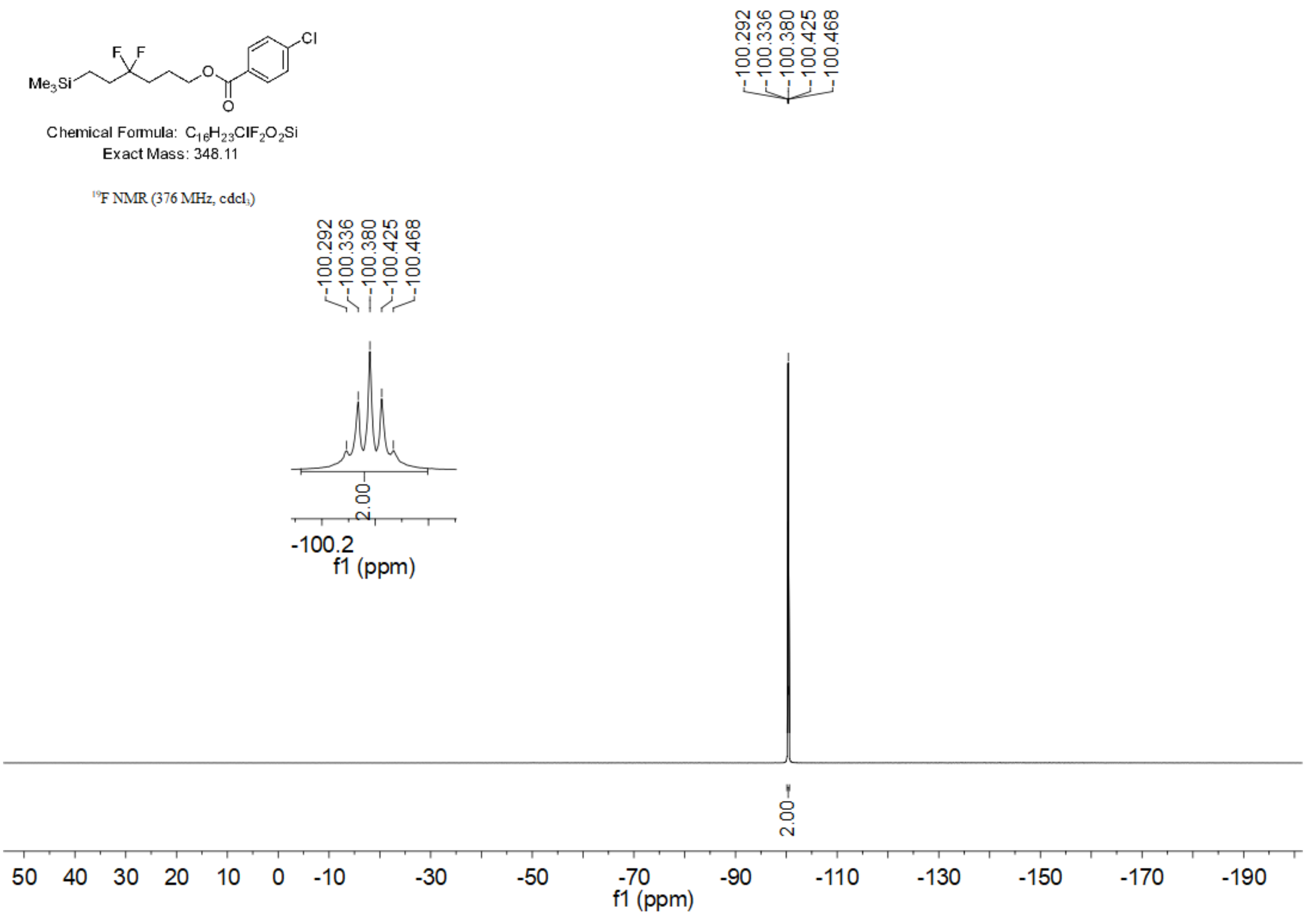






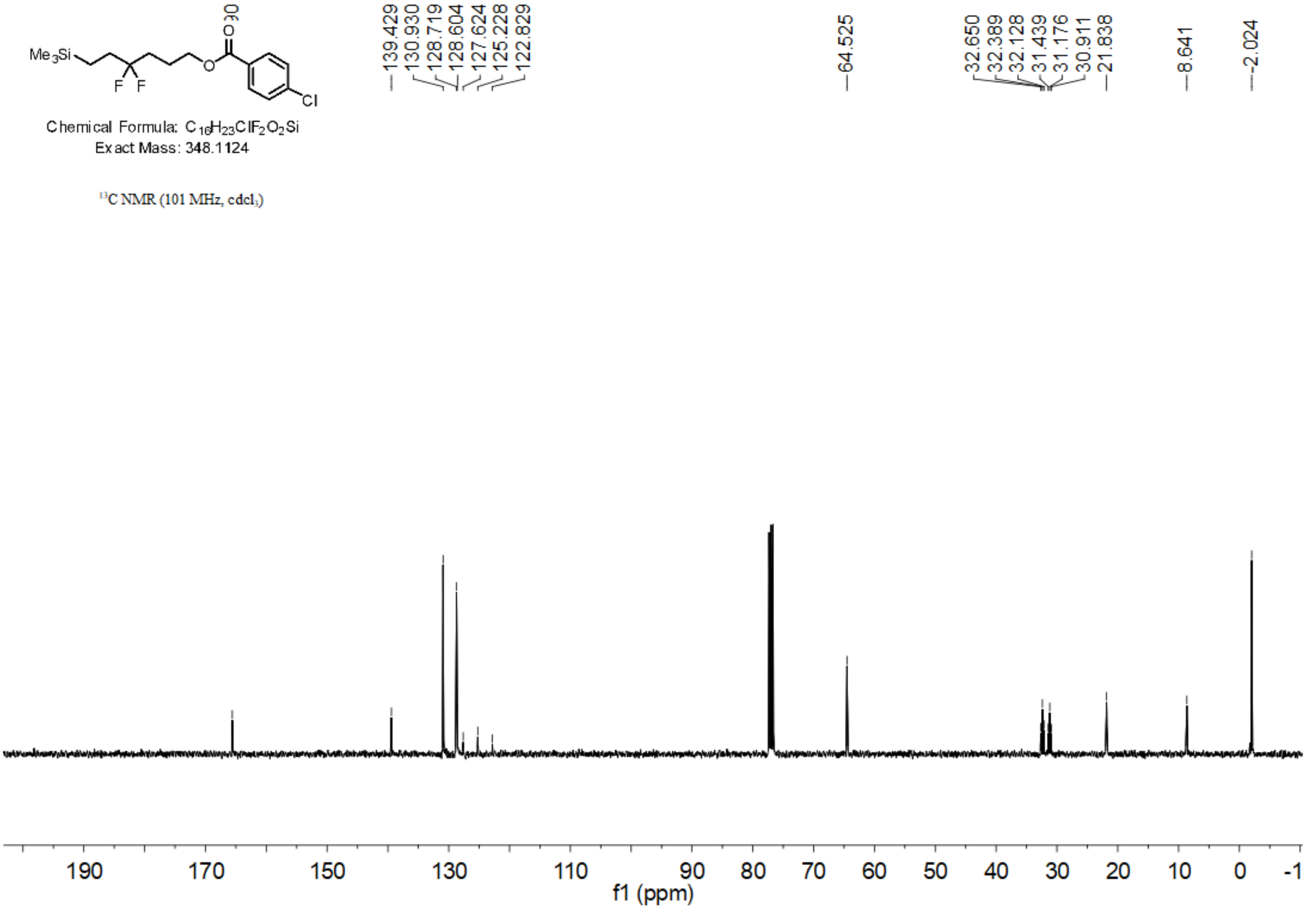
4,4-Difluoro-6-(trimethylsilyl)hexyl 4-chlorobenzoate (3d)





Chemical Formula: $C_{16}H_{23}ClF_2O_2Si$
Exact Mass: 348.11

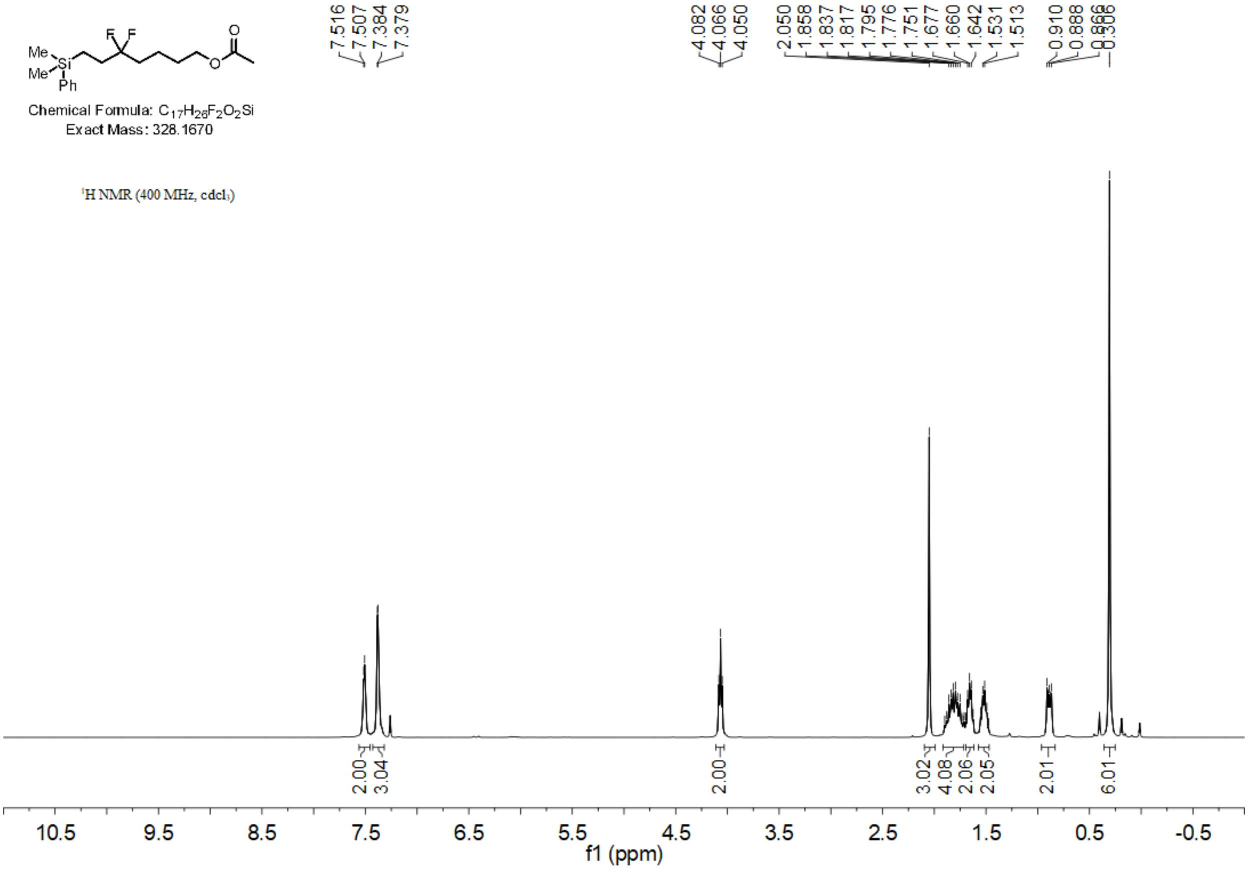
^{19}F NMR (376 MHz, cdcl$_3$)

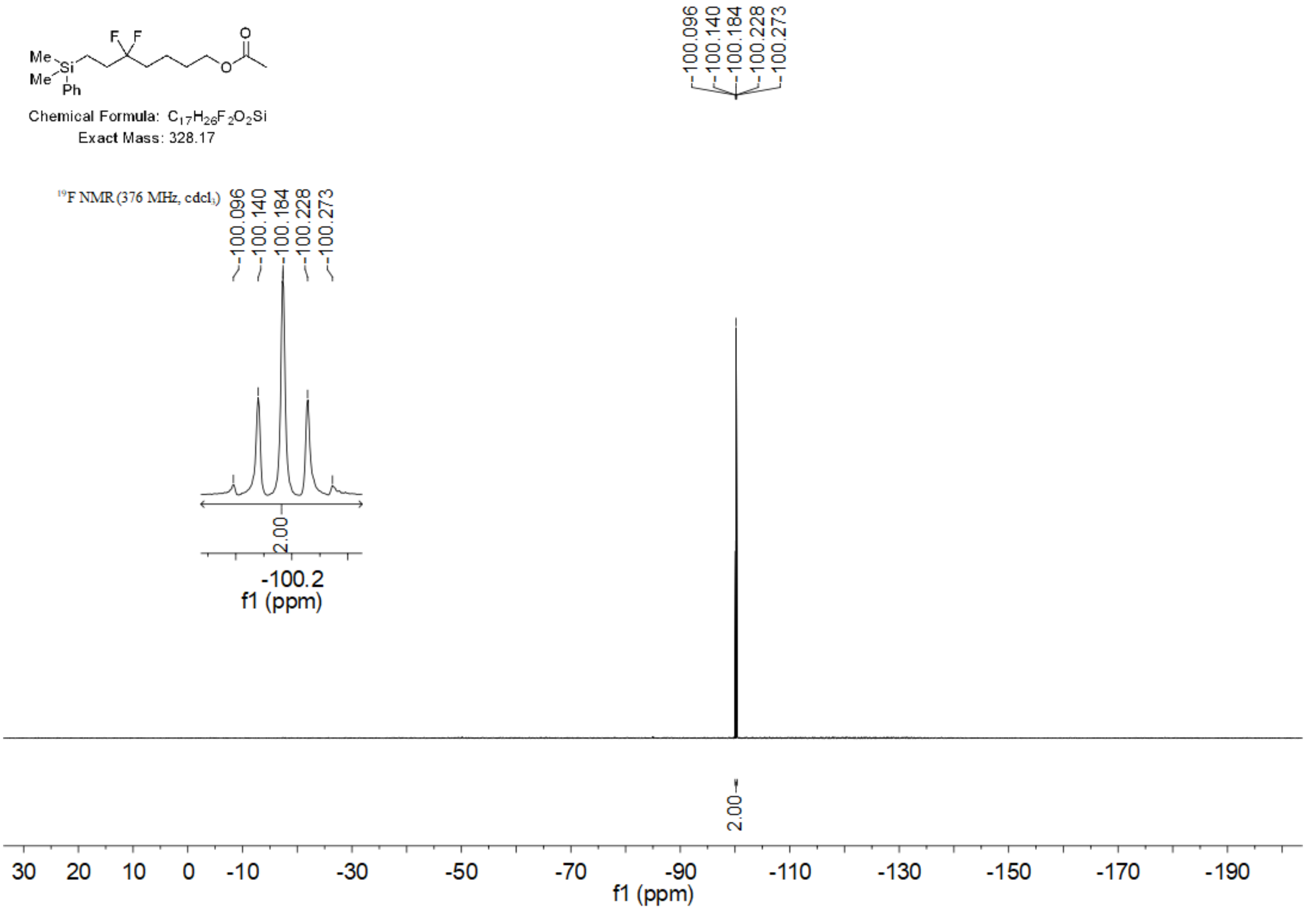


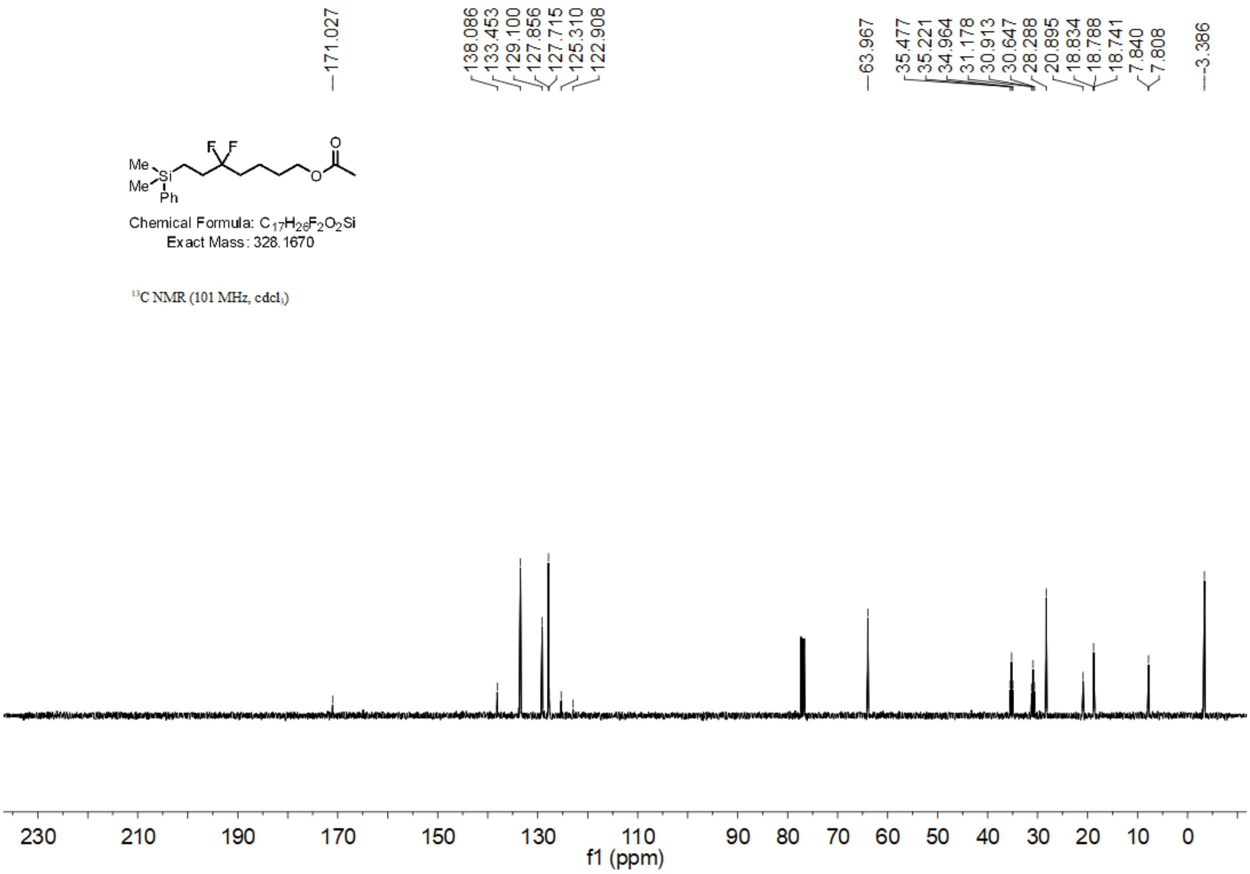
Chemical Formula: $C_{16}H_{23}ClF_2O_2Si$
Exact Mass: 348.1124

^{13}C NMR (101 MHz, cdcl$_3$)

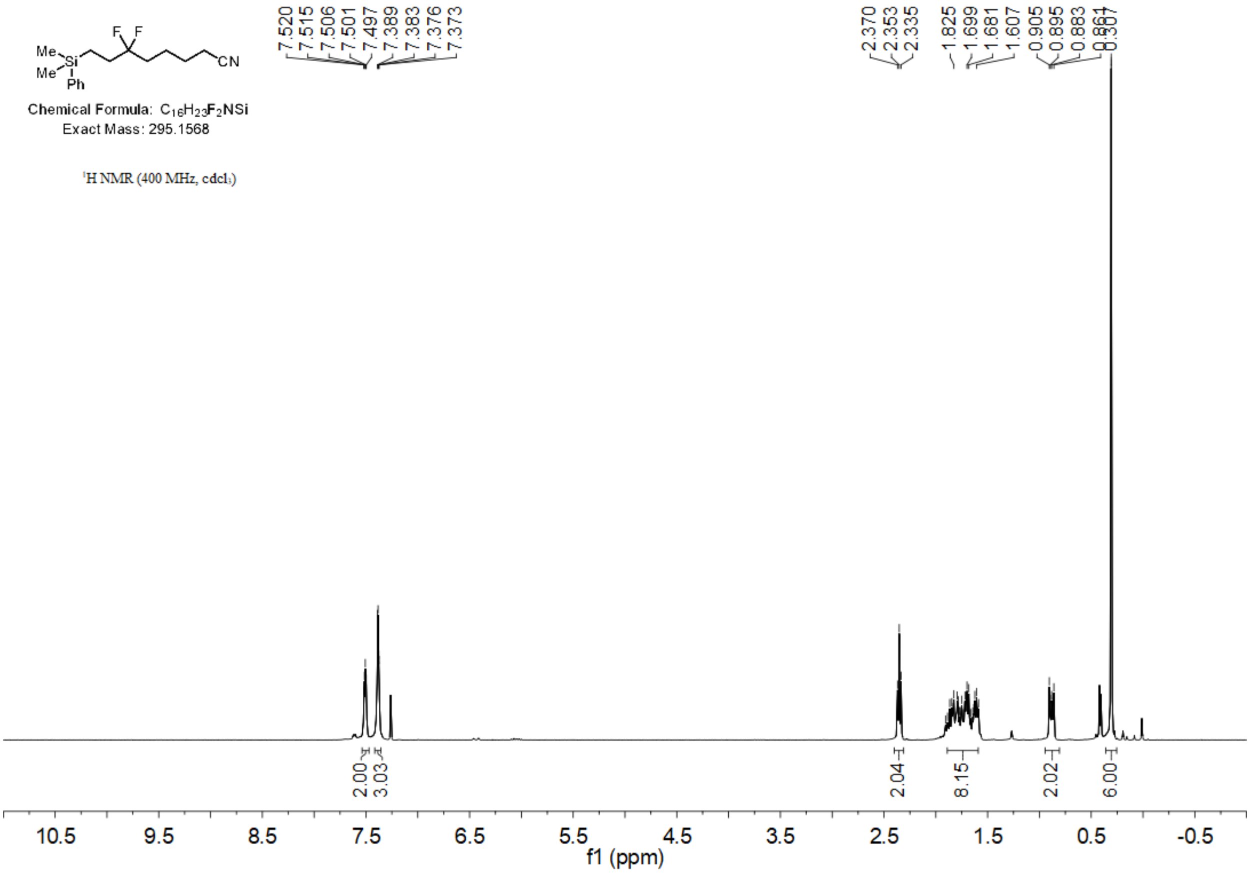
7-(Dimethyl(phenyl)silyl)-5,5-difluoroheptyl acetate (3e)

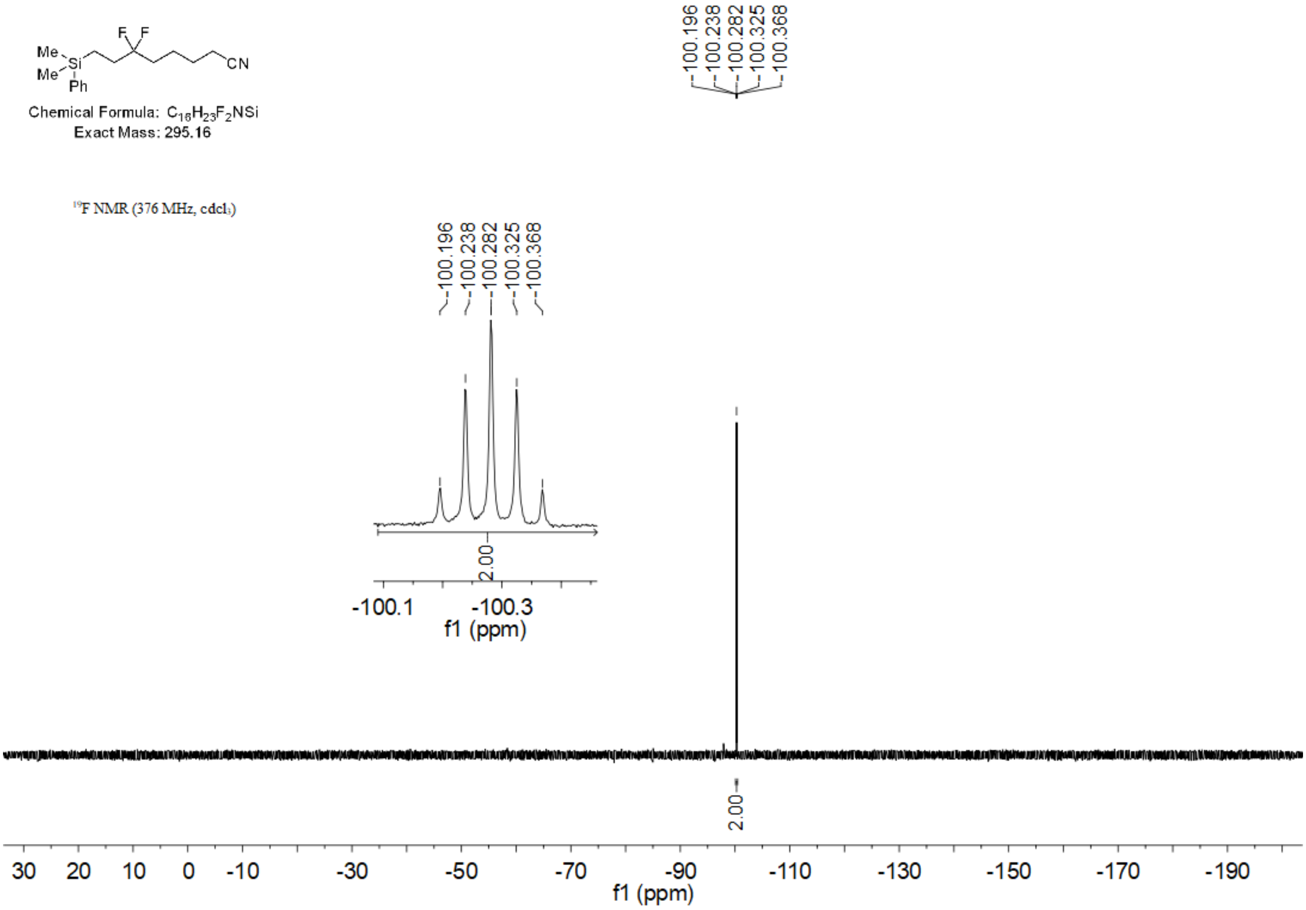


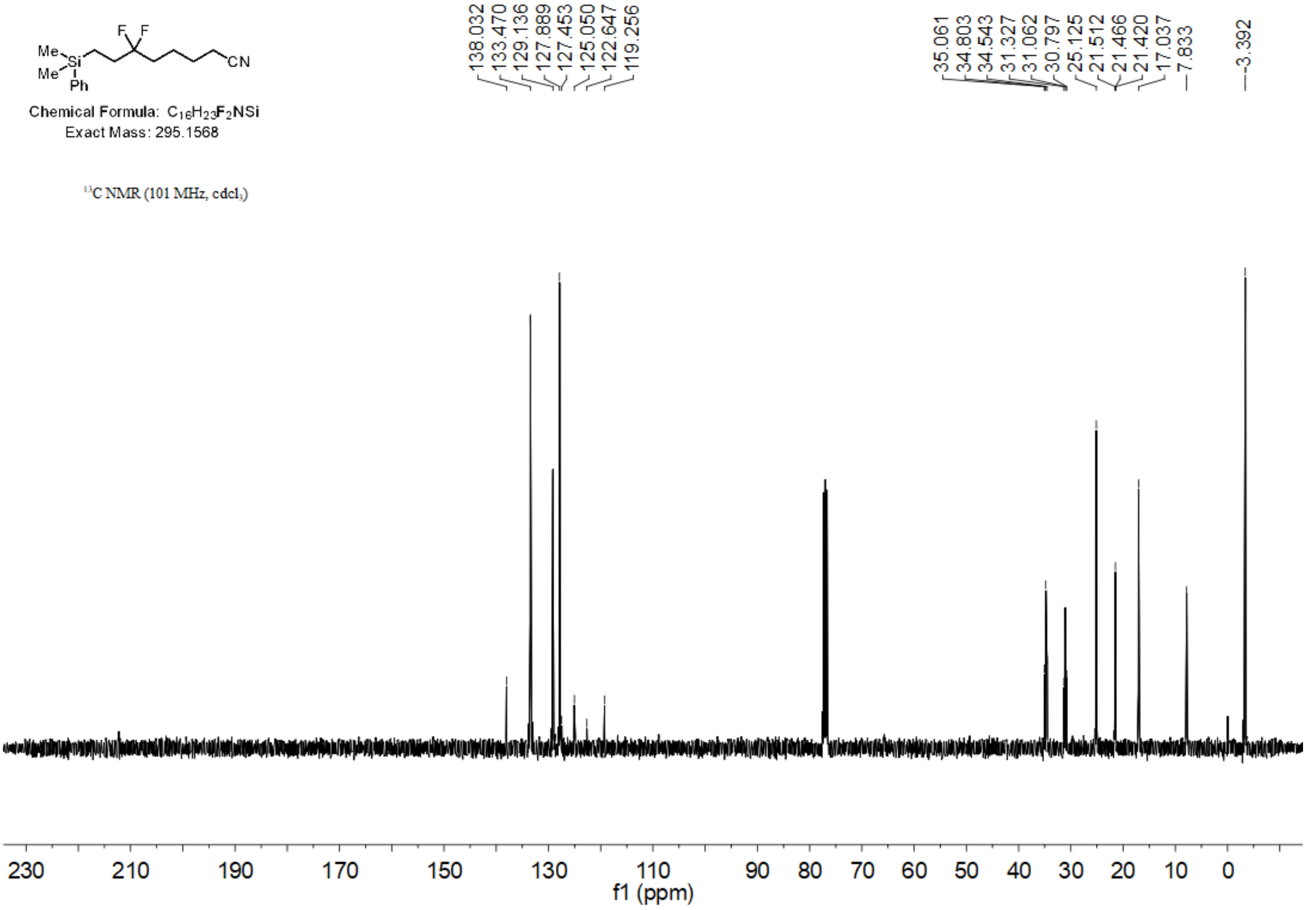




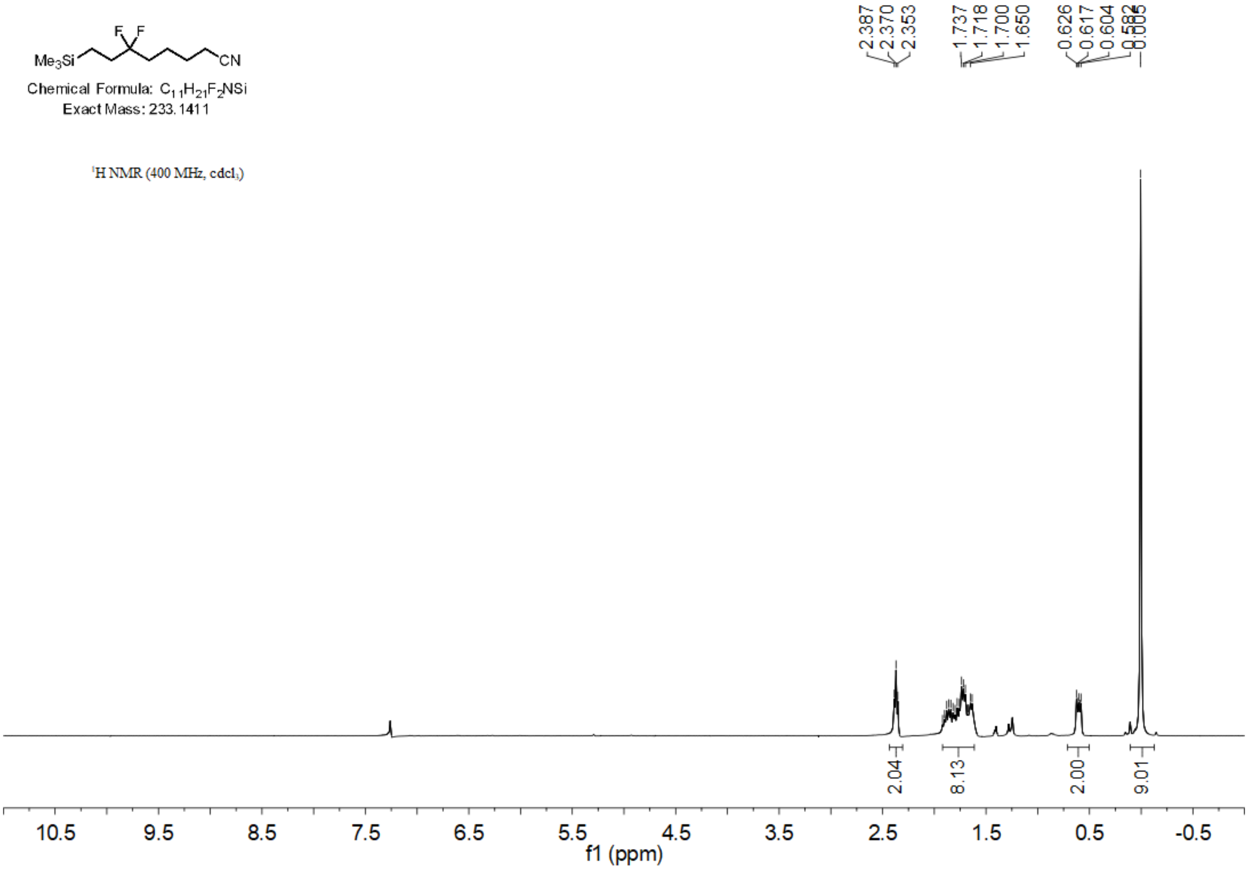
8-(Dimethyl(phenyl)silyl)-6,6-difluorooctanenitrile (3f)

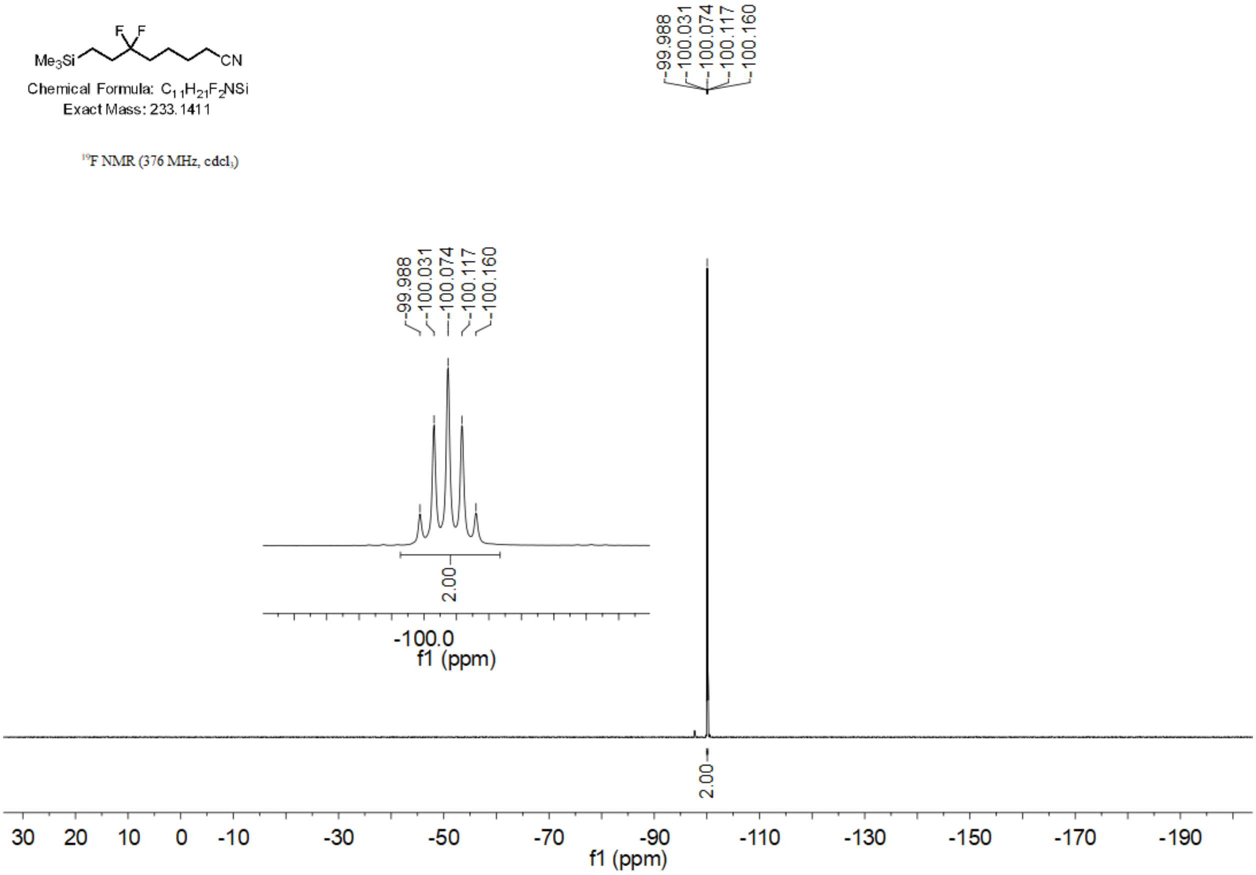


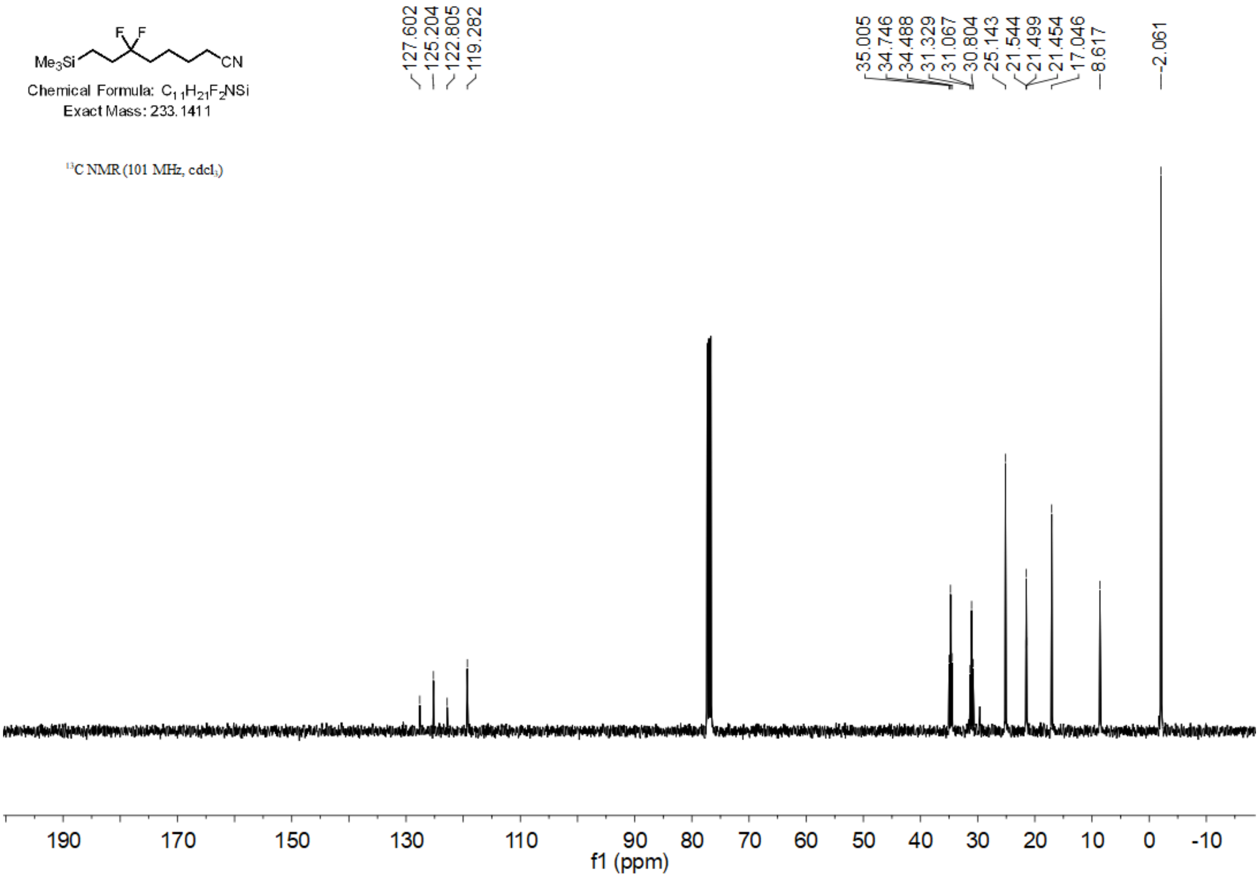

Me
Si
Me
Ph
F F
CN
Chemical Formula: C16H23F2NSi
Exact Mass: 295.16
19F NMR (376 MHz, cdcl3)
-100.196
-100.238
-100.282
-100.325
-100.368
2.00
-100.1
-100.3
f1 (ppm)
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)


Me
Si
Me
Ph
F F
CN
Chemical Formula: C16H23F2NSi
Exact Mass: 295.1568
13C NMR (101 MHz, cdcl3)
138.032
133.470
129.136
127.889
127.453
125.050
122.647
119.256
35.061
34.803
34.543
31.327
31.062
30.797
25.125
21.512
21.466
21.420
17.037
7.833
-3.392
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

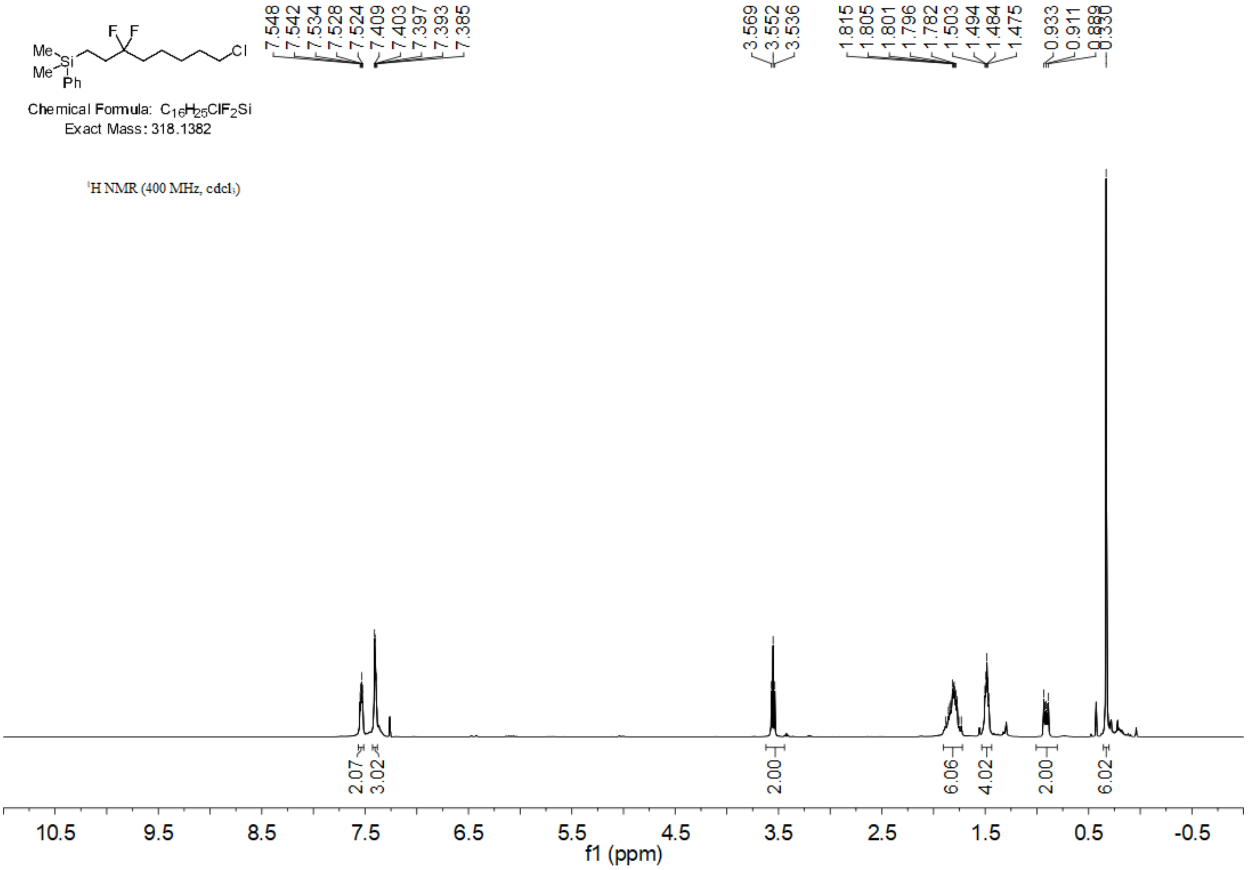
6,6-Difluoro-8-(trimethylsilyl)octanenitrile (3g)

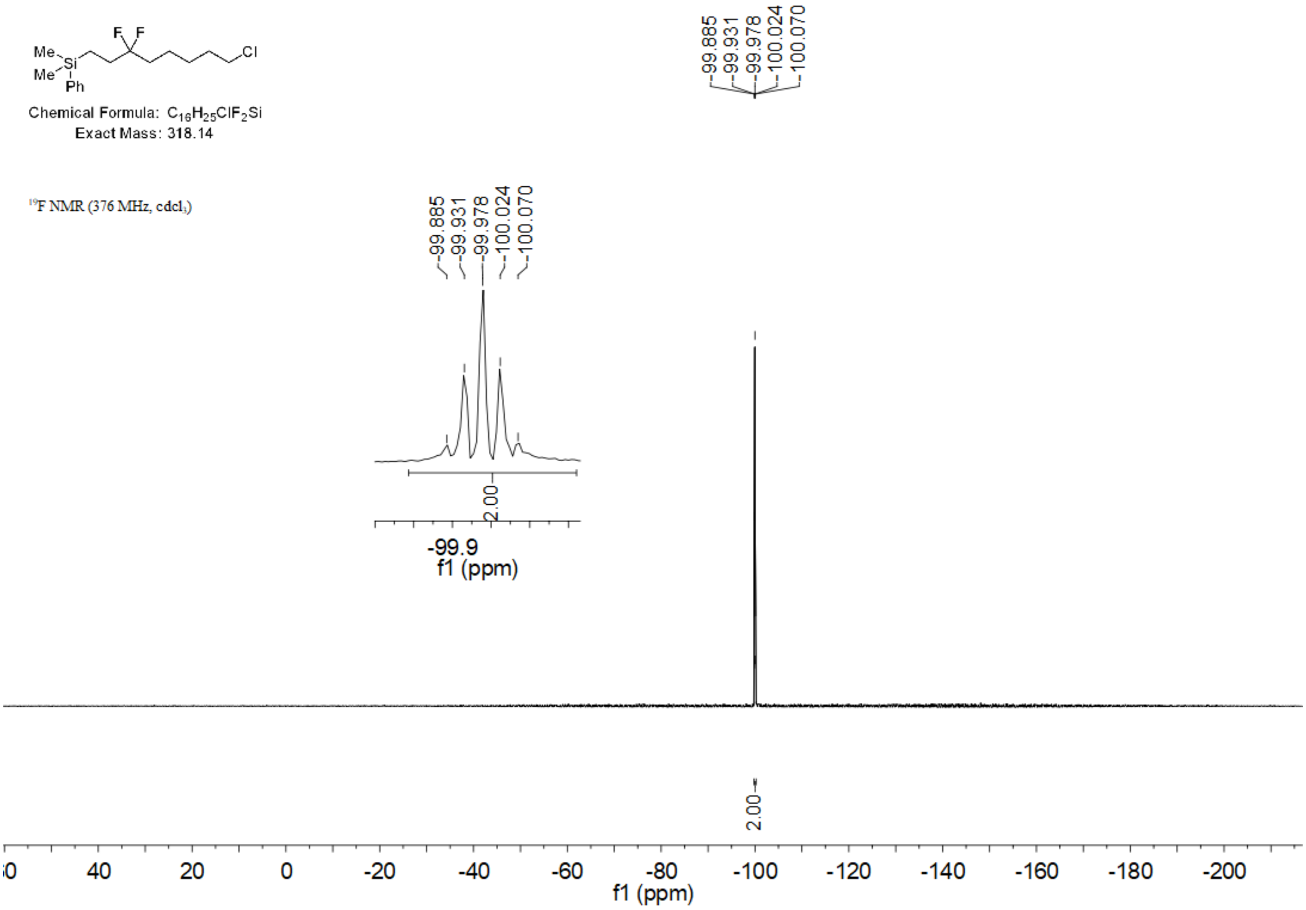


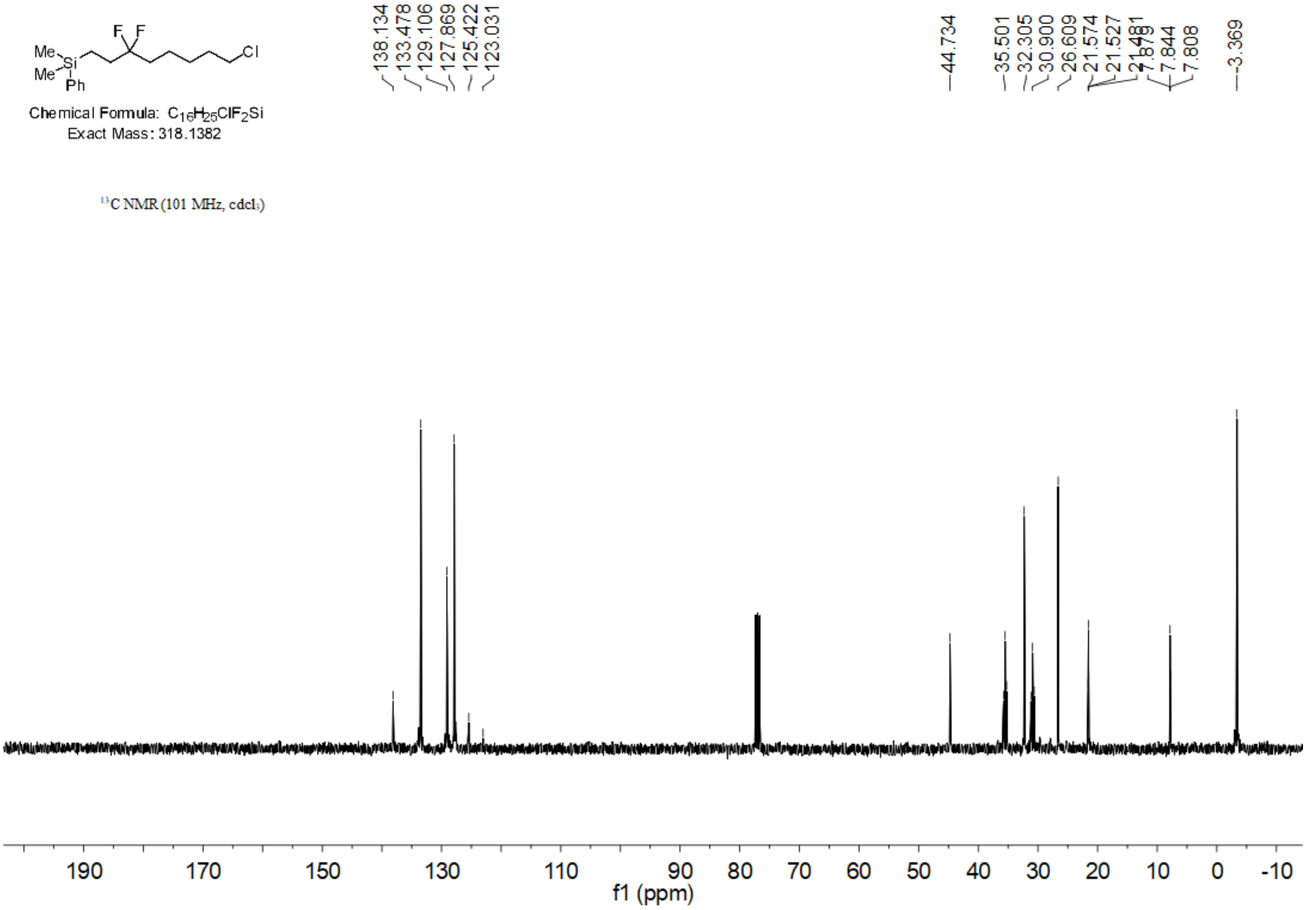




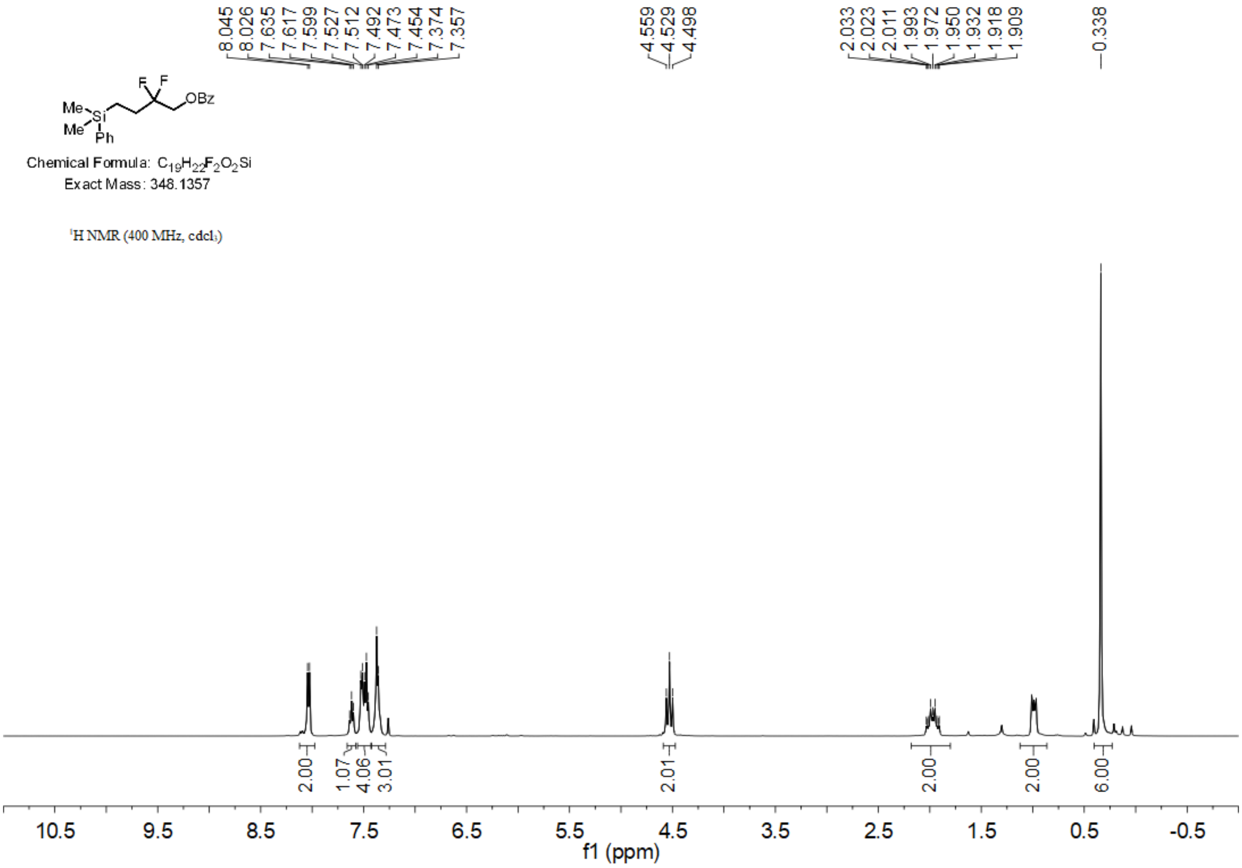
(8-Chloro-3,3-difluorooctyl)dimethyl(phenyl)silane (3h)

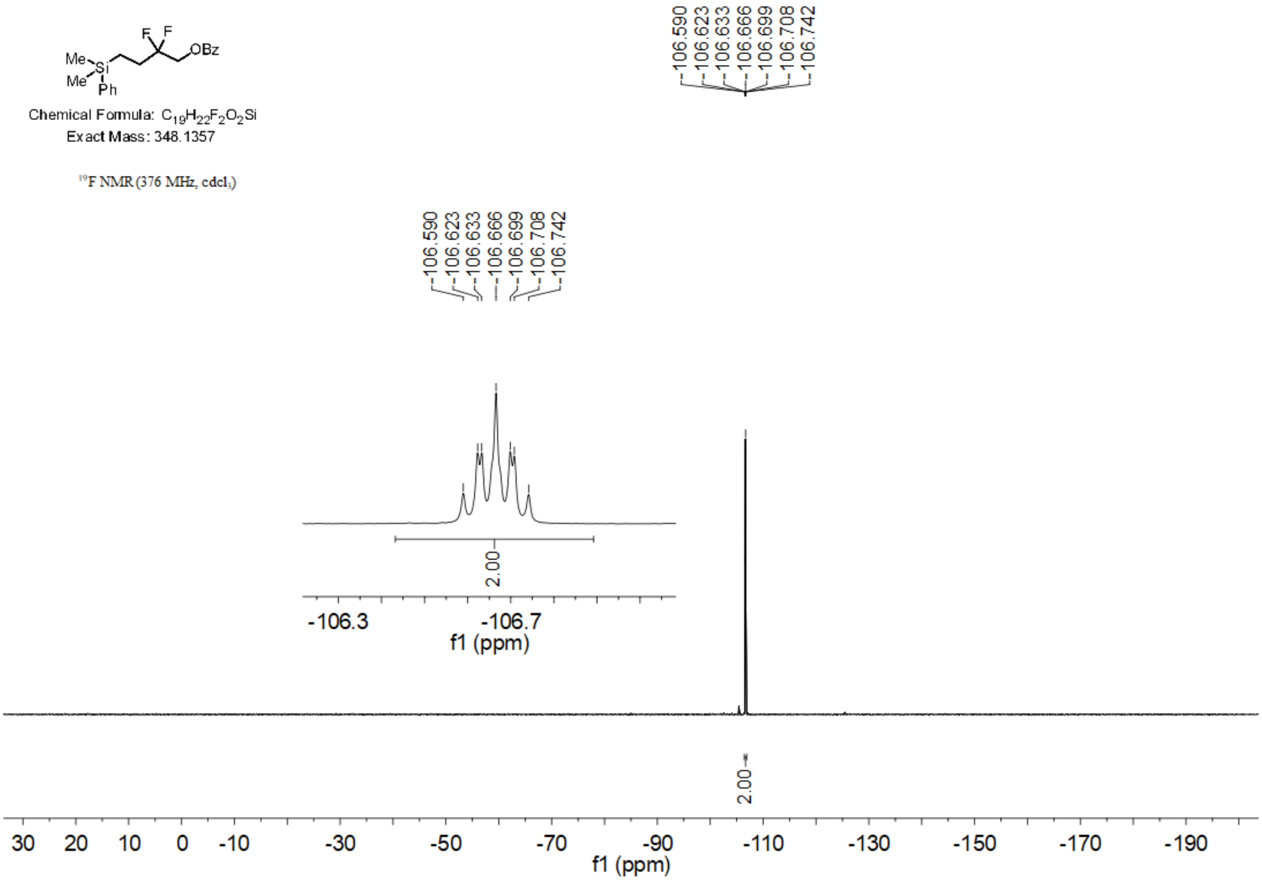


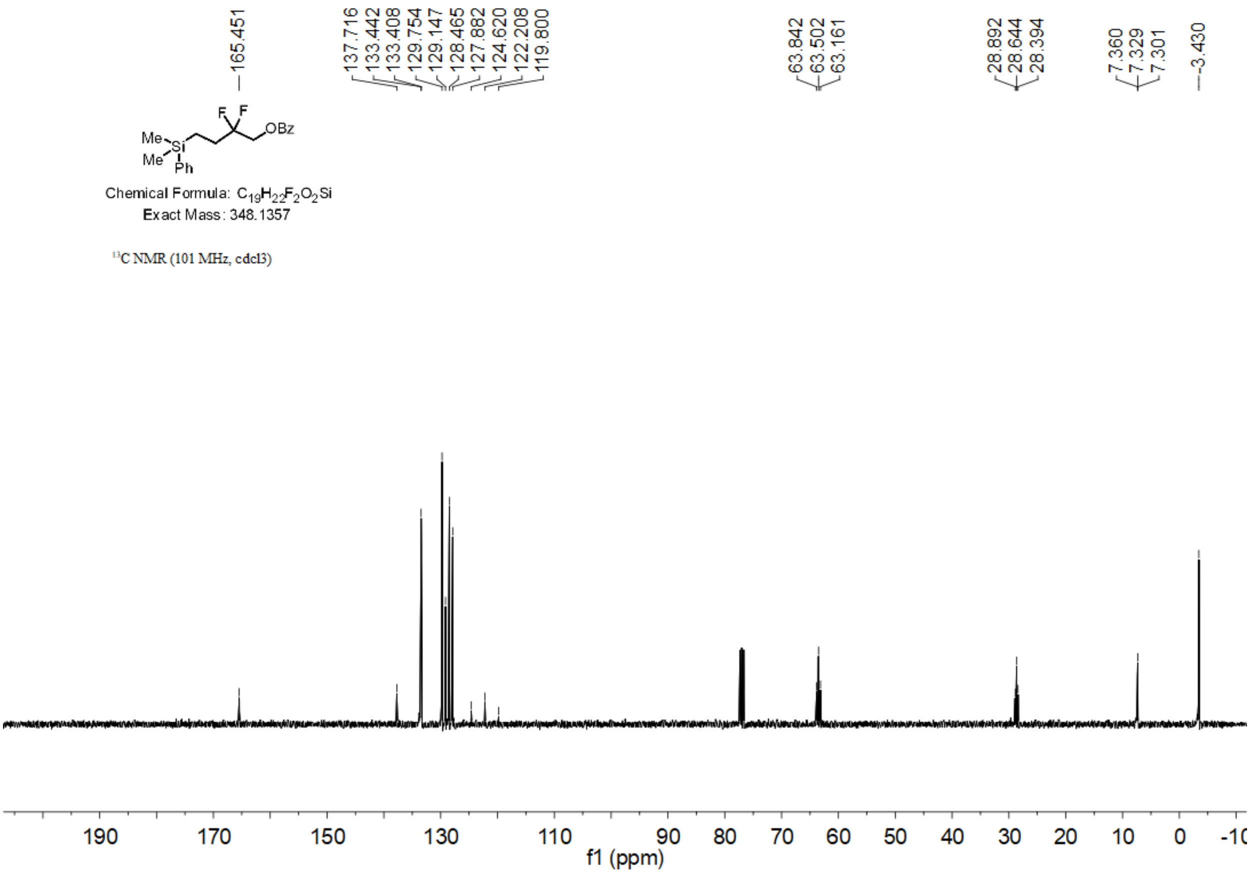

Me
Si
Me
Ph
F
F
Cl
Chemical Formula: C16H25ClF2Si
Exact Mass: 318.14
19F NMR (376 MHz, cdcl3)
-99.885
-99.931
-99.978
-100.024
-100.070
2.00
-99.9
f1 (ppm)
2.00
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)


Me
Si
Me
Ph
F
F
Cl
Chemical Formula: C16H25ClF2Si
Exact Mass: 318.1382
13C NMR (101 MHz, cdcl3)
138.134
133.478
129.106
127.869
125.422
123.031
44.734
35.501
32.305
30.900
26.609
21.574
21.527
21.481
7.879
7.844
7.808
-3.369
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

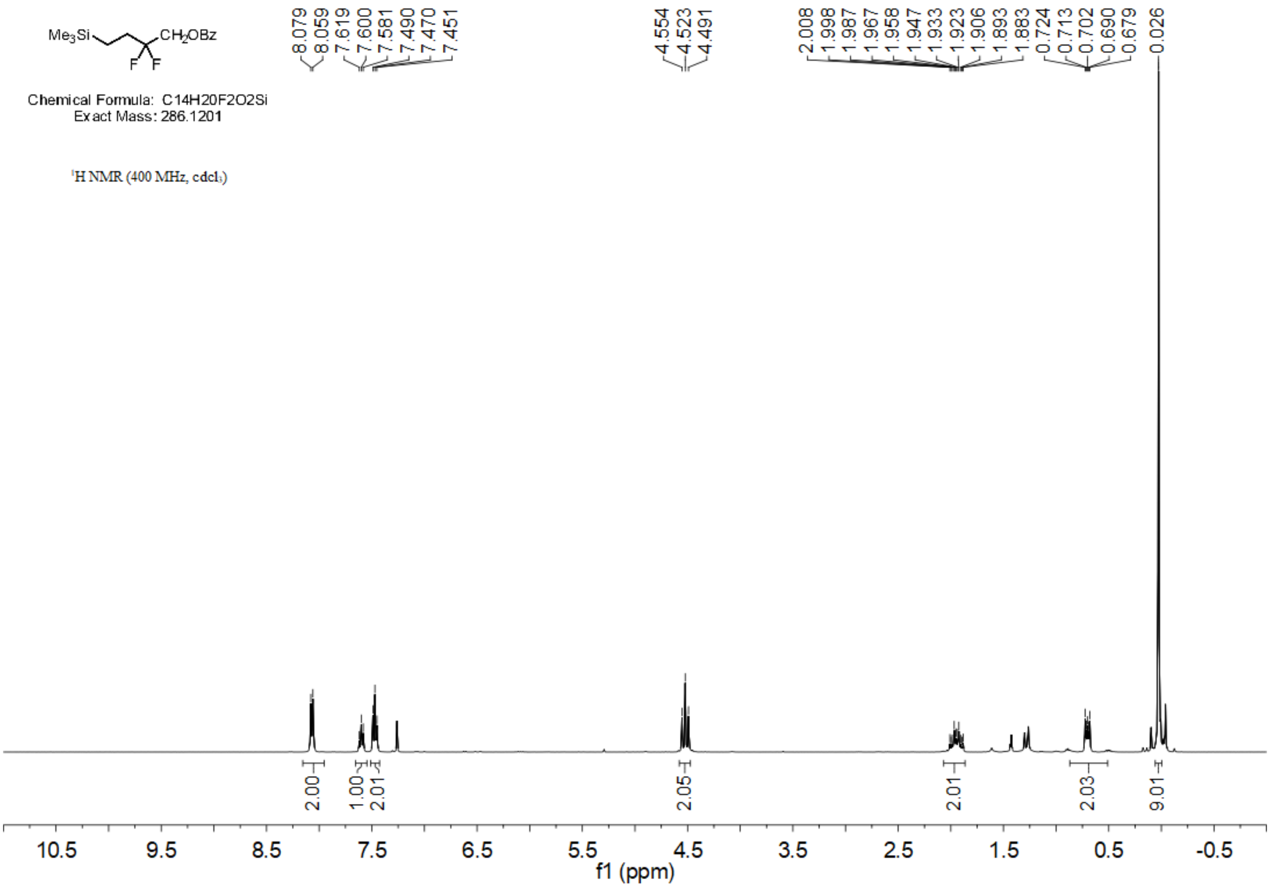
4-(Dimethyl(phenyl)silyl)-2,2-difluorobutyl benzoate (3i)

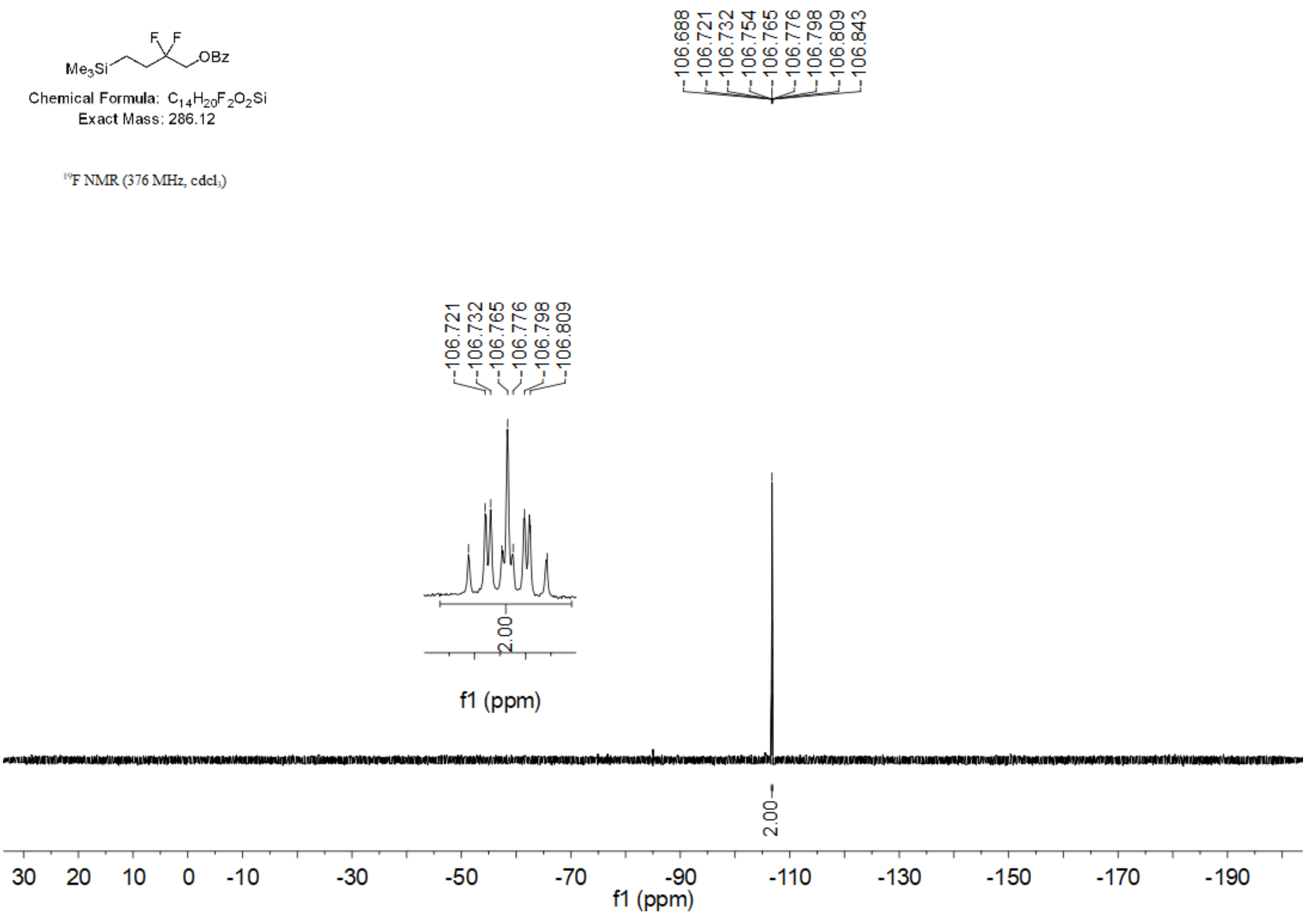


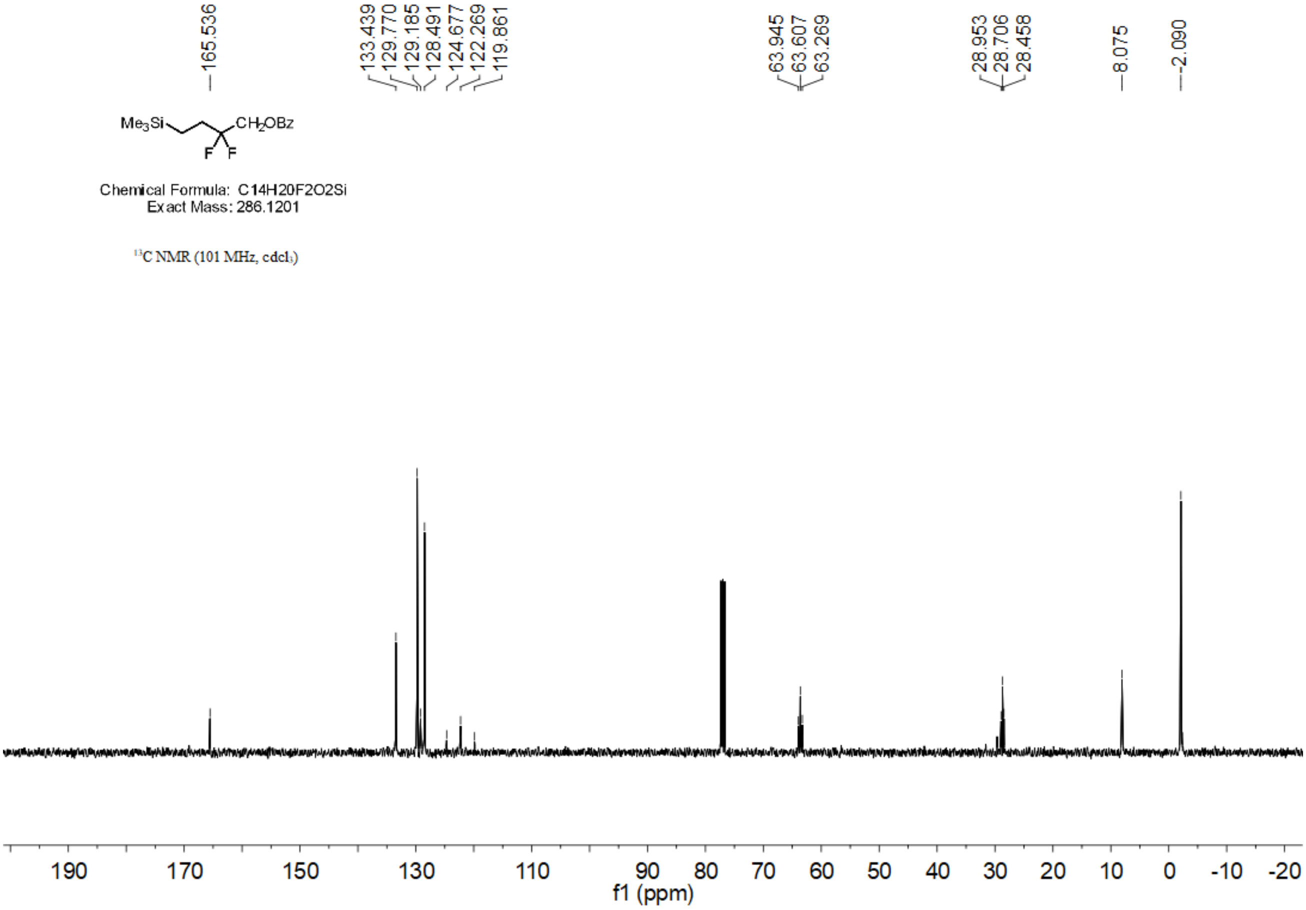




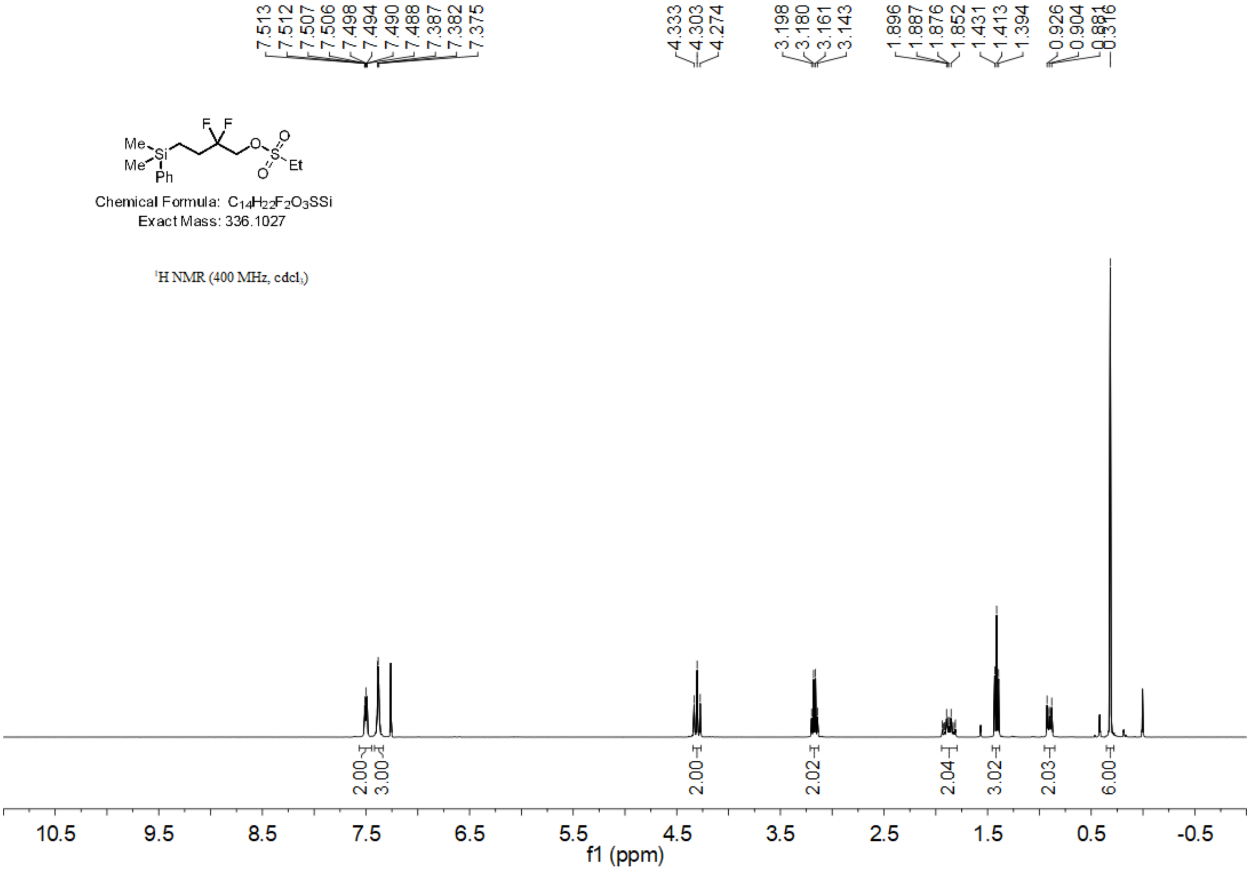
2,2-Difluoro-4-(trimethylsilyl)butyl benzoate (3j)

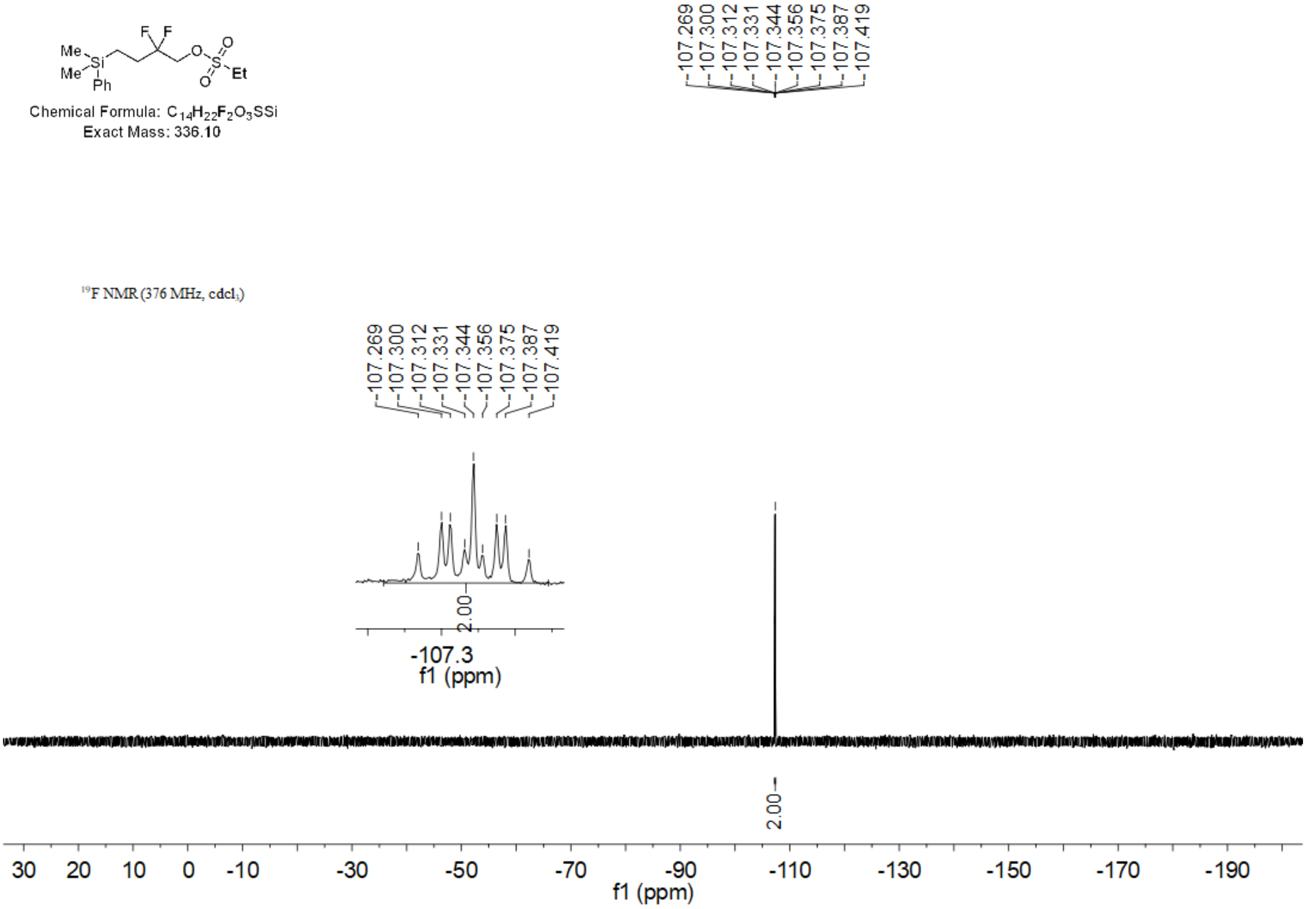


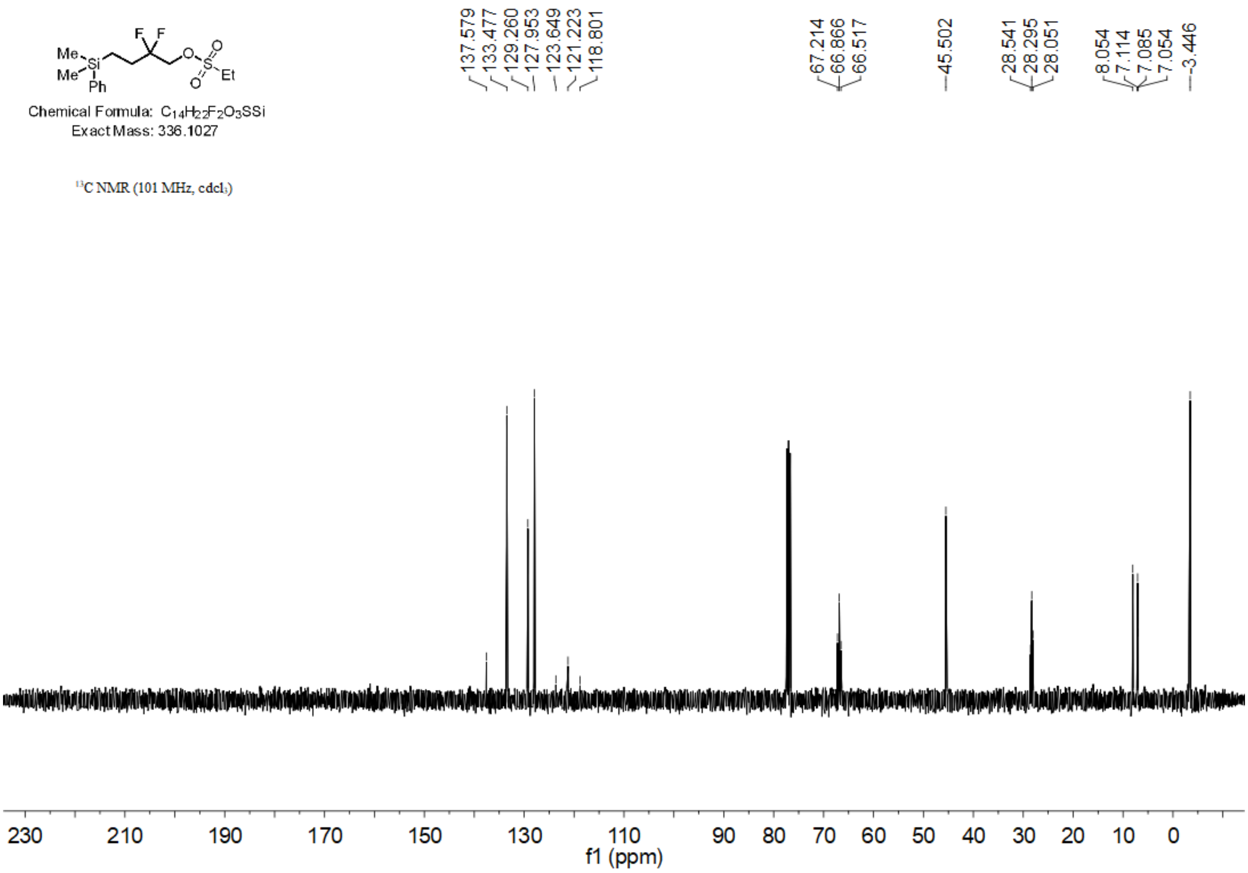

Me3Si
F F
OBz
Chemical Formula: C14H20F2O2Si
Exact Mass: 286.12
19F NMR (376 MHz, cdcl3)
-106.688
-106.721
-106.732
-106.754
-106.765
-106.776
-106.798
-106.809
-106.843
-106.721
-106.732
-106.765
-106.776
-106.798
-106.809
2.00
f1 (ppm)
2.00
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)


165.536
133.439
129.770
129.185
128.491
124.677
122.269
119.861
63.945
63.607
63.269
28.953
28.706
28.458
8.075
-2.090
Me3Si
CH2OBz
F F
Chemical Formula: C14H20F2O2Si
Exact Mass: 286.1201
13C NMR (101 MHz, cdcl3)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

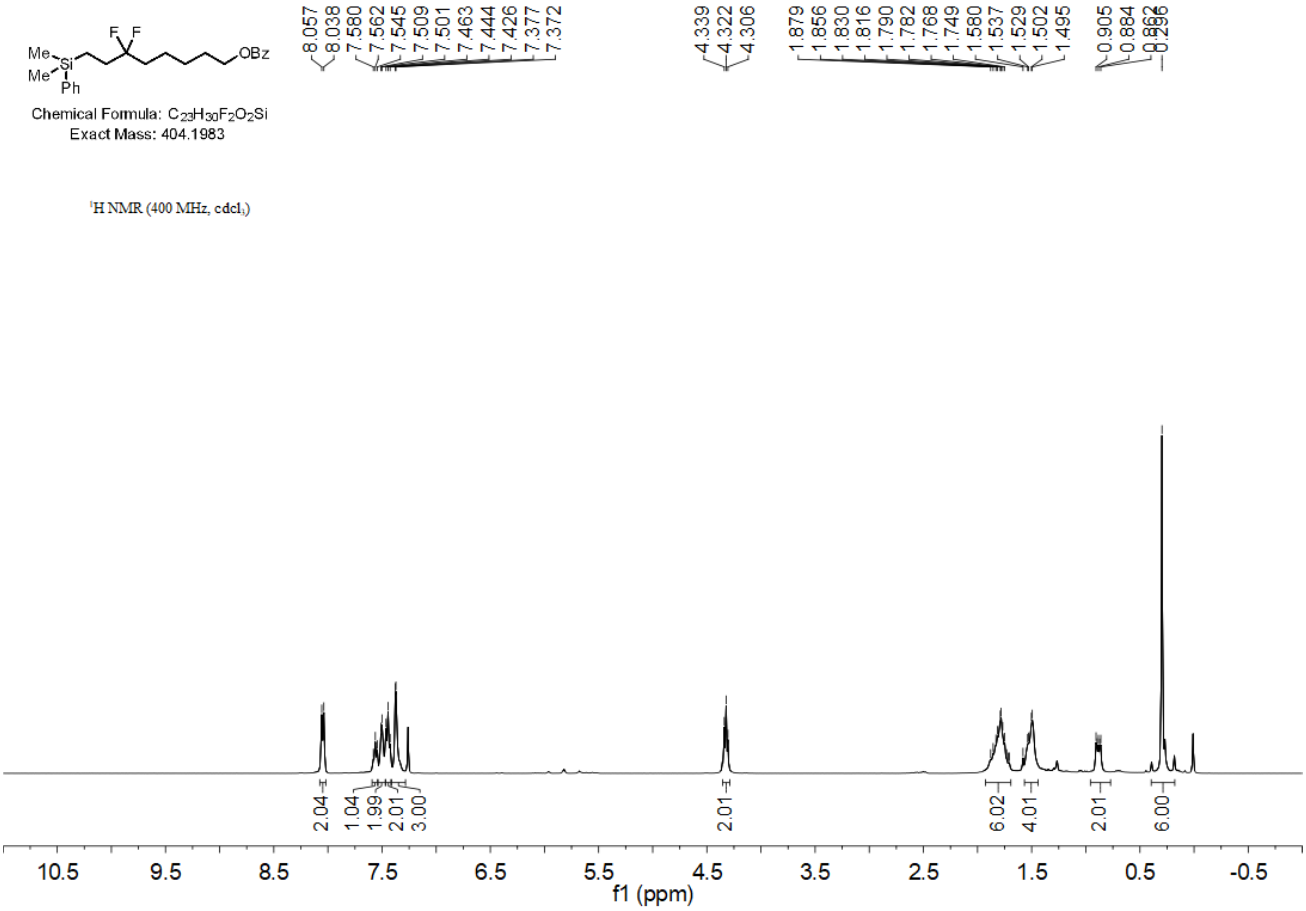
7-(Dimethyl(phenyl)silyl)-5,5-difluoroheptyl acetate (3k)

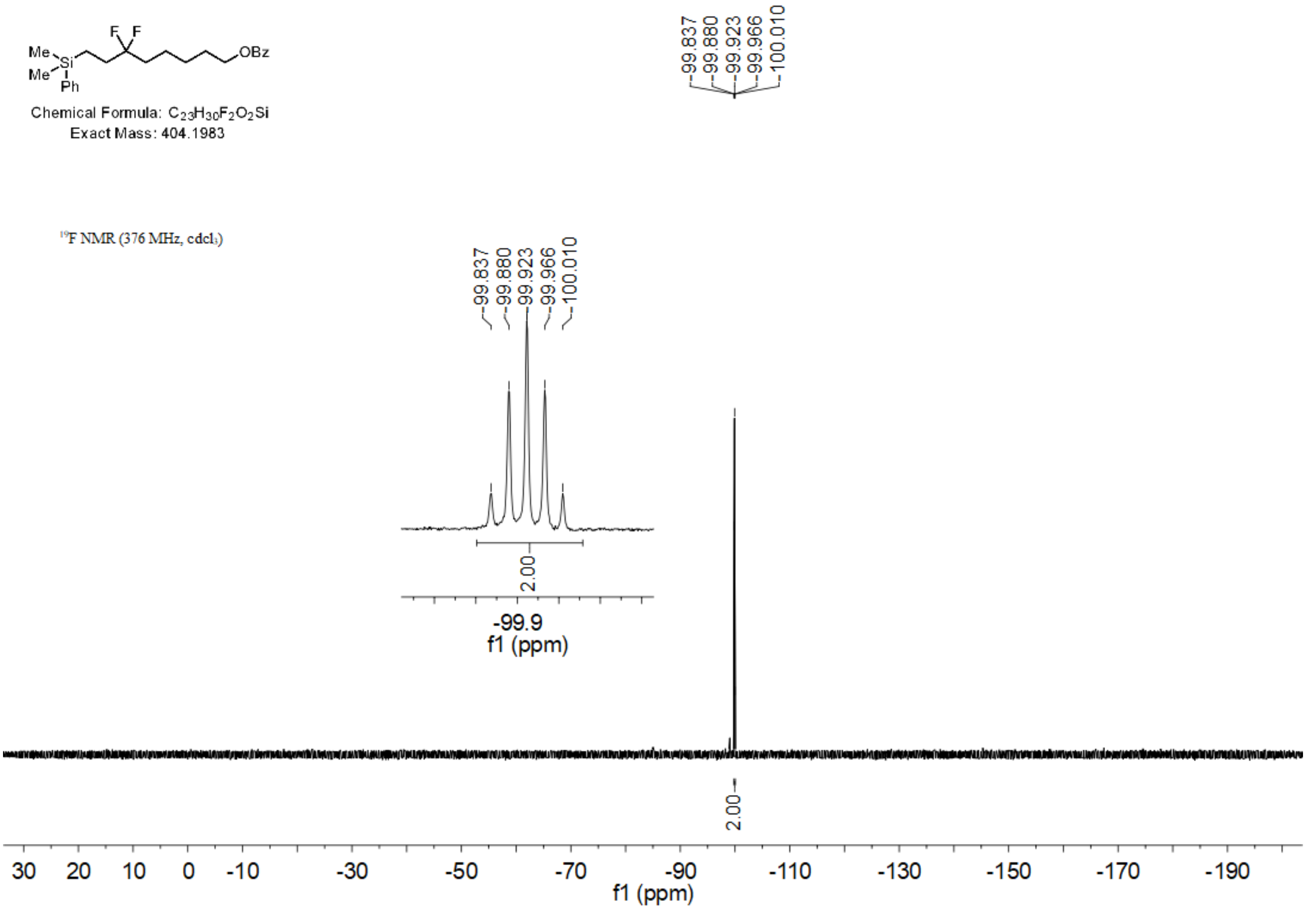






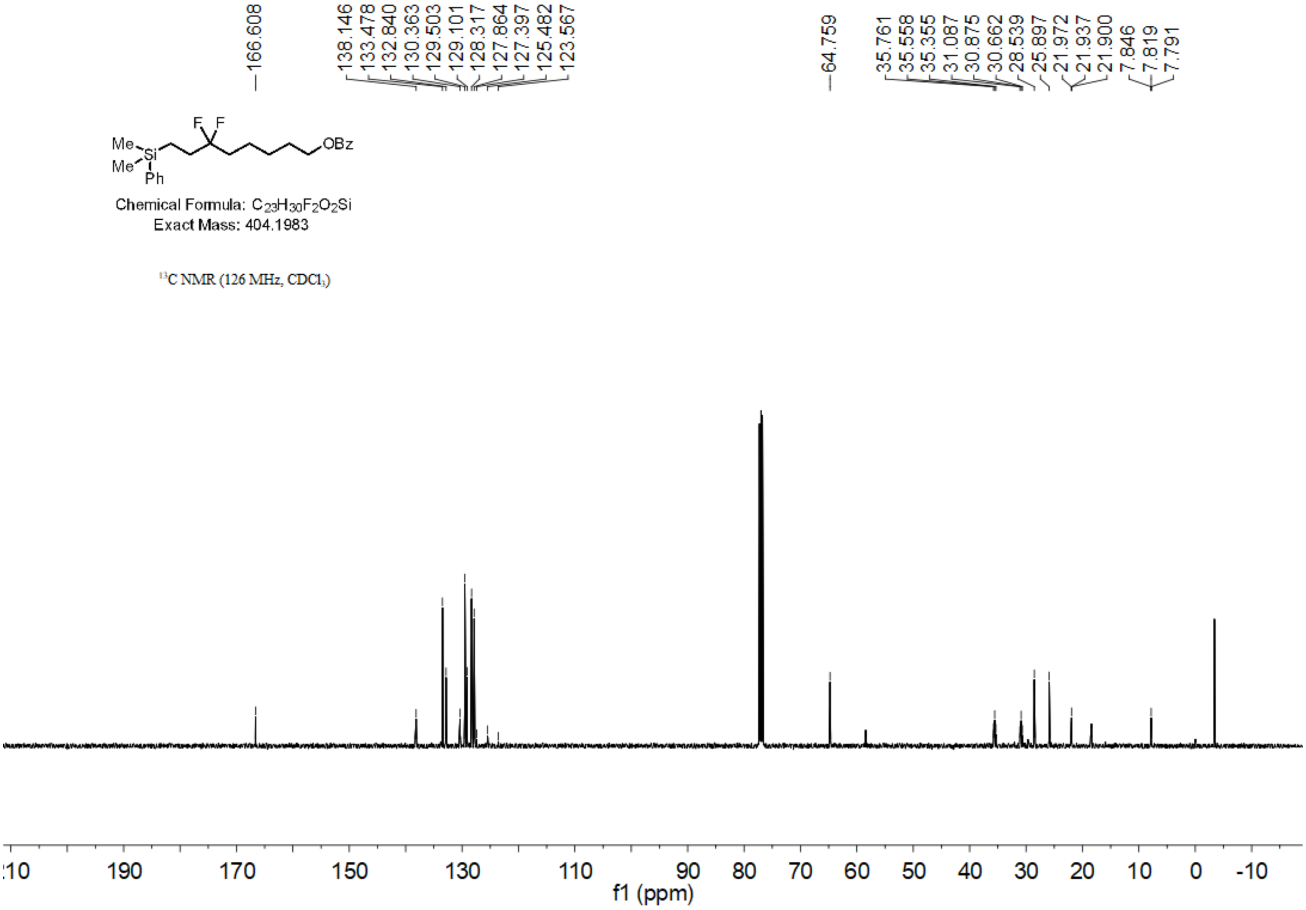
8-(Dimethyl(phenyl)silyl)-6,6-difluorooctyl benzoate (3l)





Chemical Formula: $C_{23}H_{30}F_2O_2Si$
Exact Mass: 404.1983

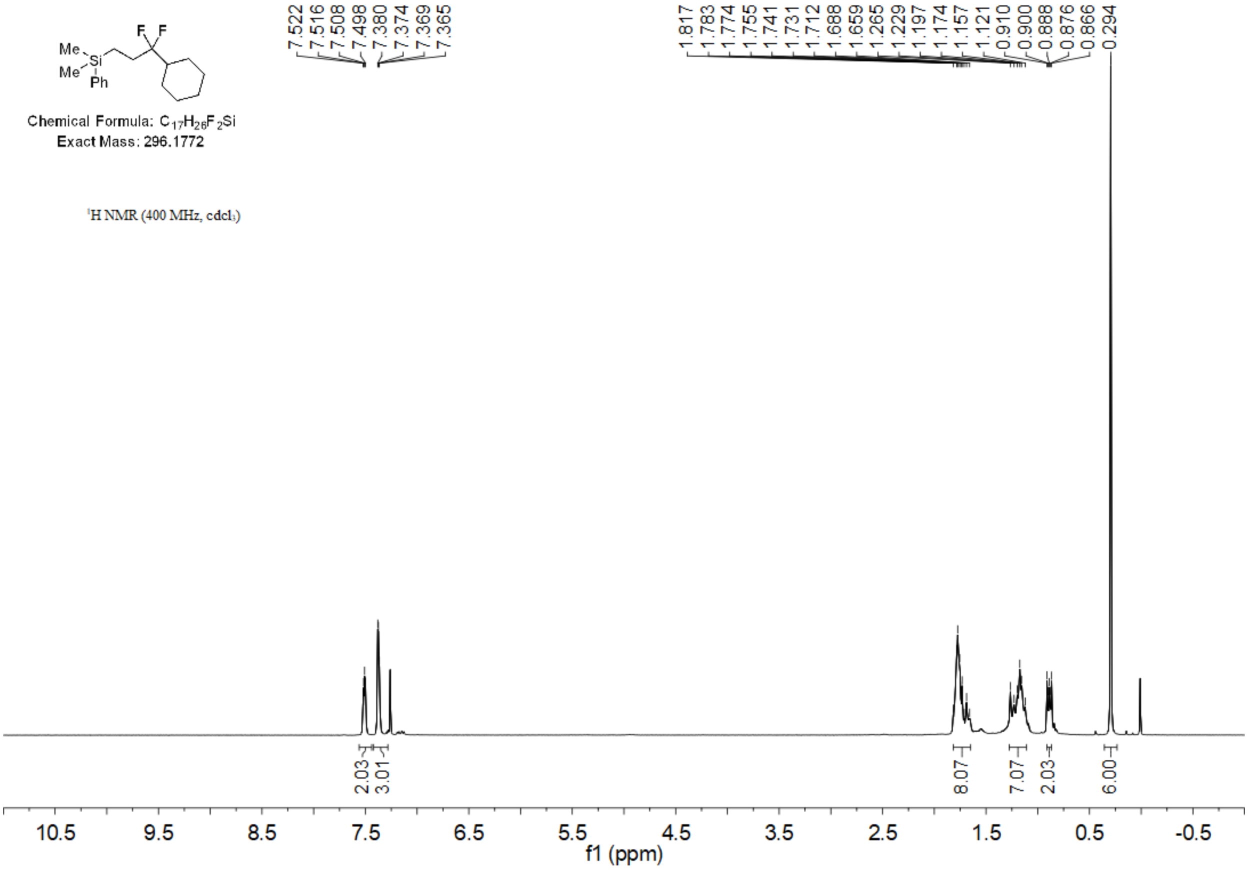
^{19}F NMR (376 MHz, cdcl$_3$)

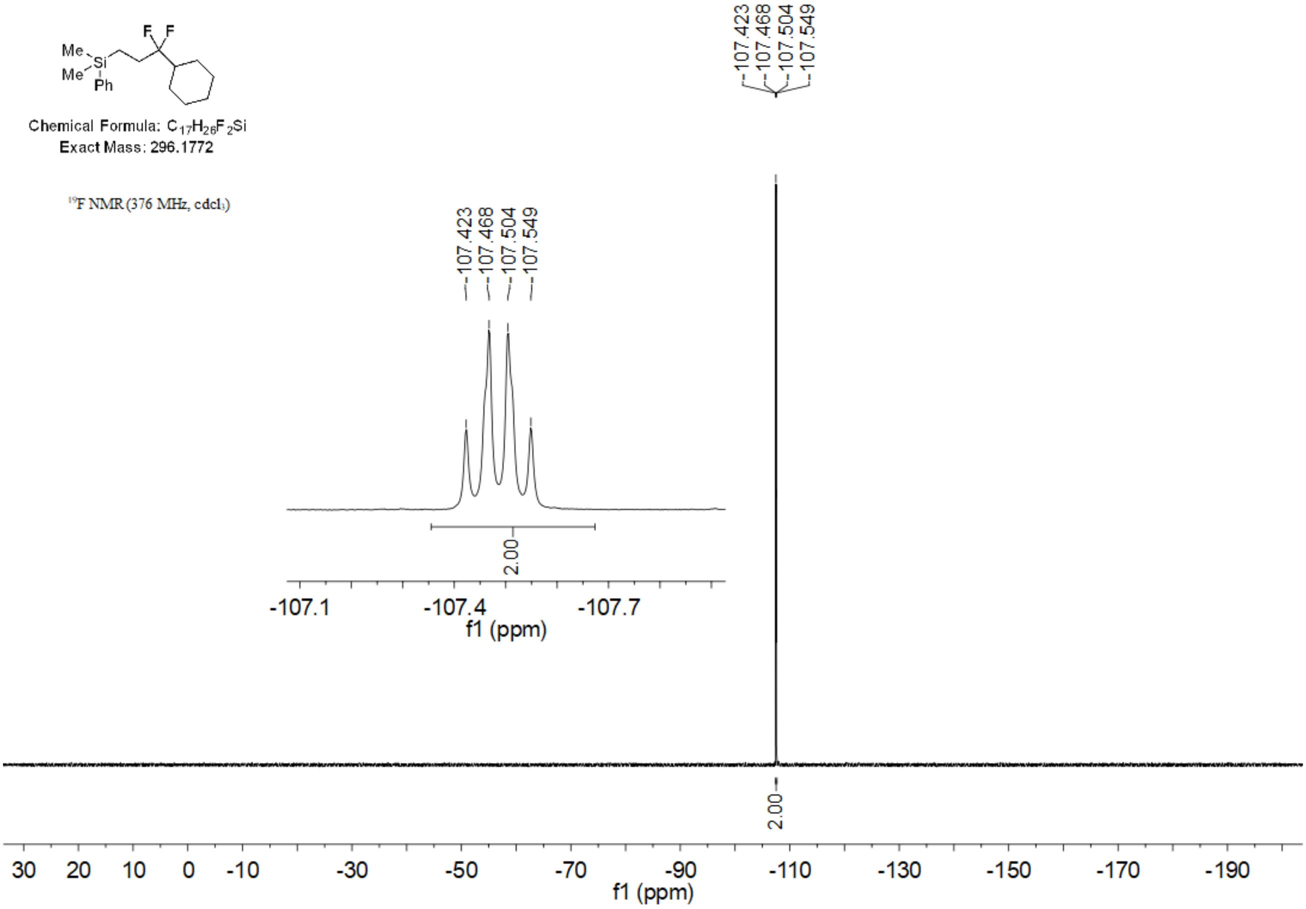


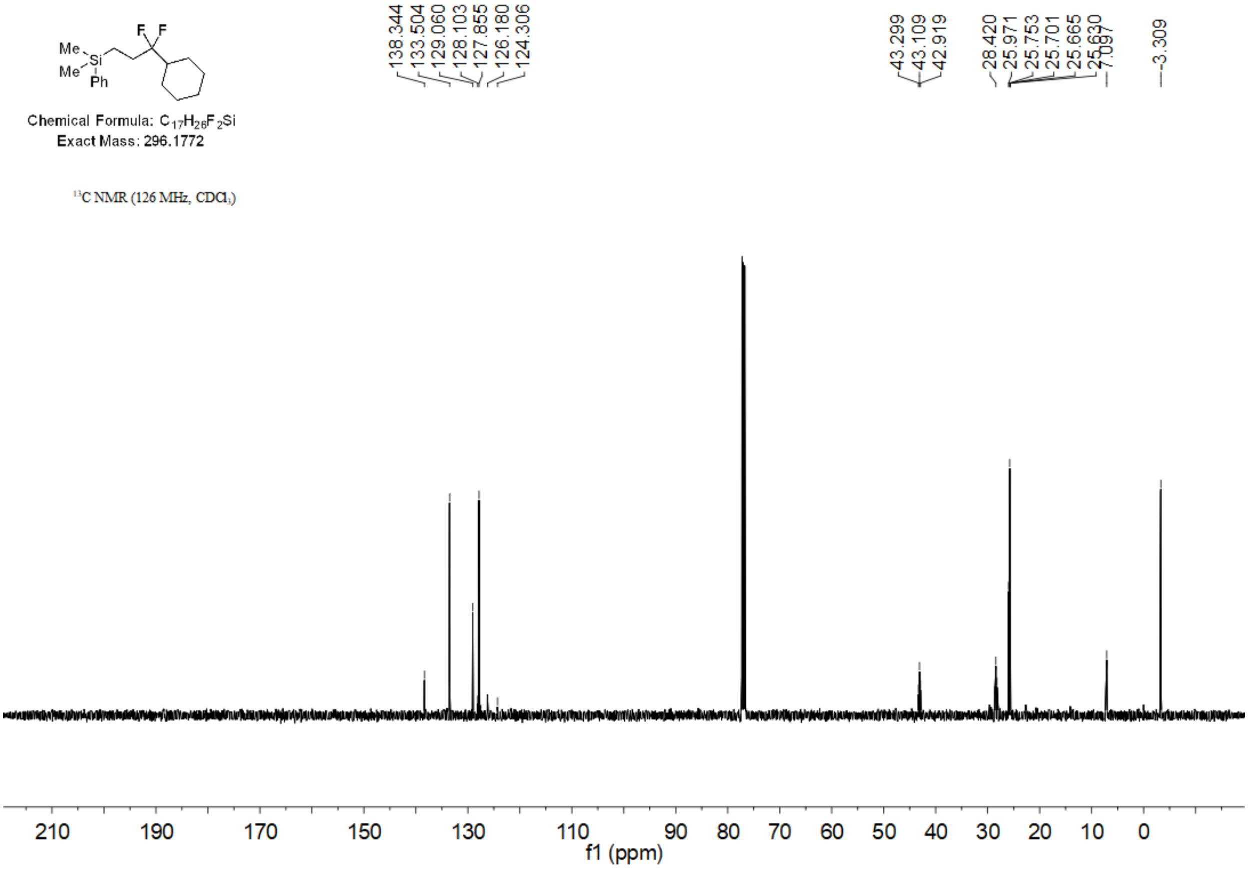
Chemical Formula: $C_{23}H_{30}F_2O_2Si$
Exact Mass: 404.1983

^{13}C NMR (126 MHz, CDCl$_3$)

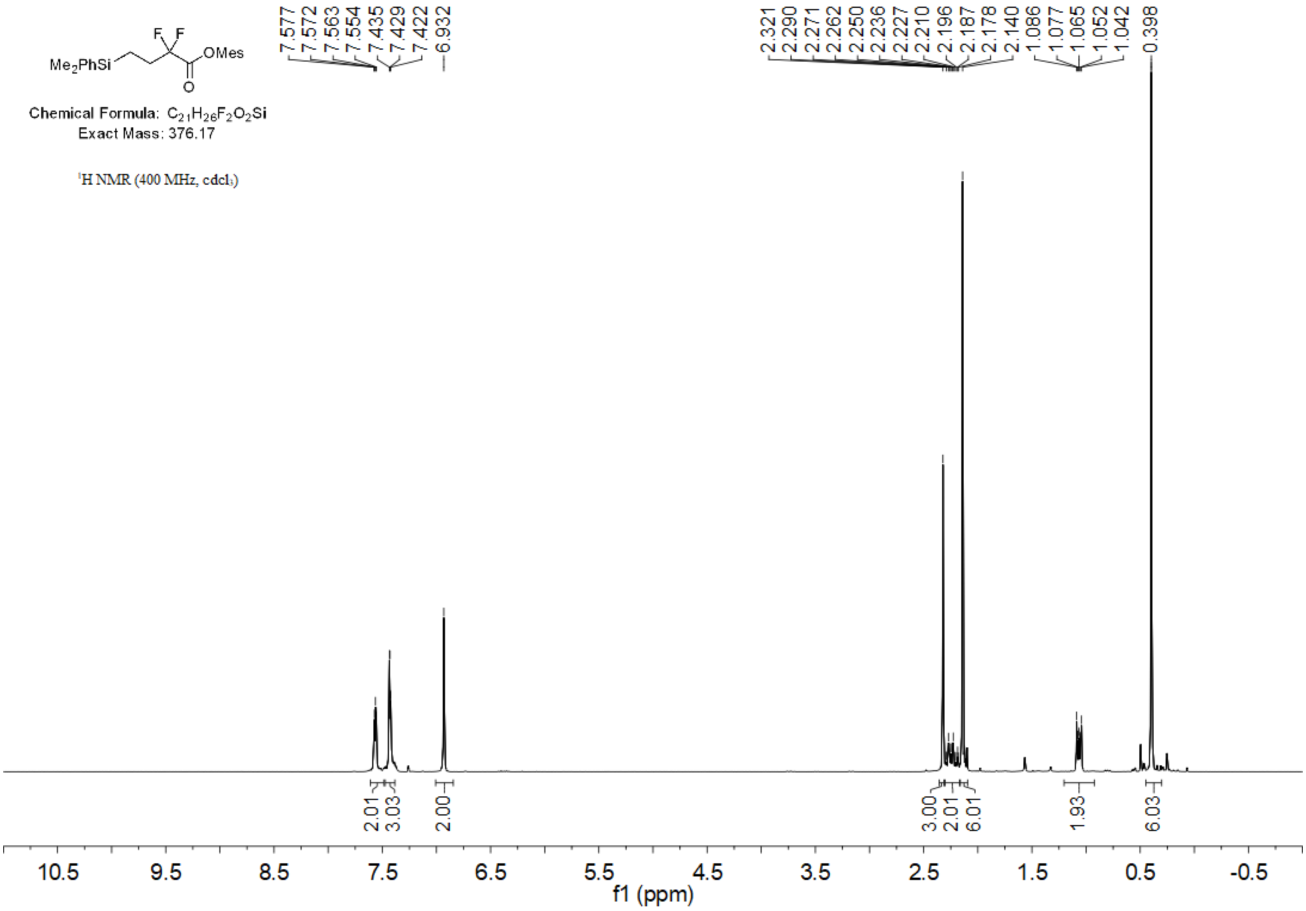
(3-Cyclohexyl-3,3-difluoropropyl)dimethyl(phenyl)silane (3m)

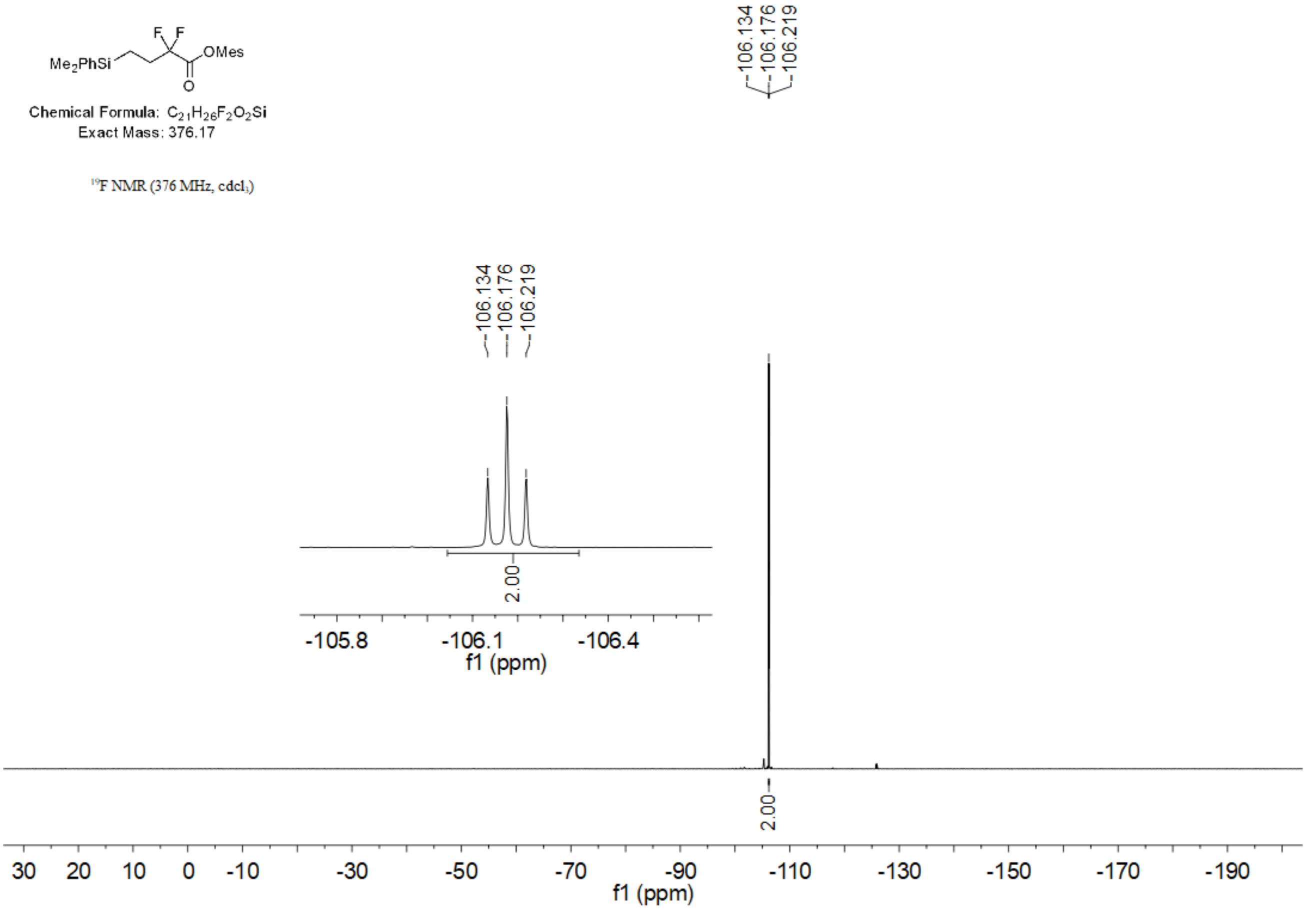






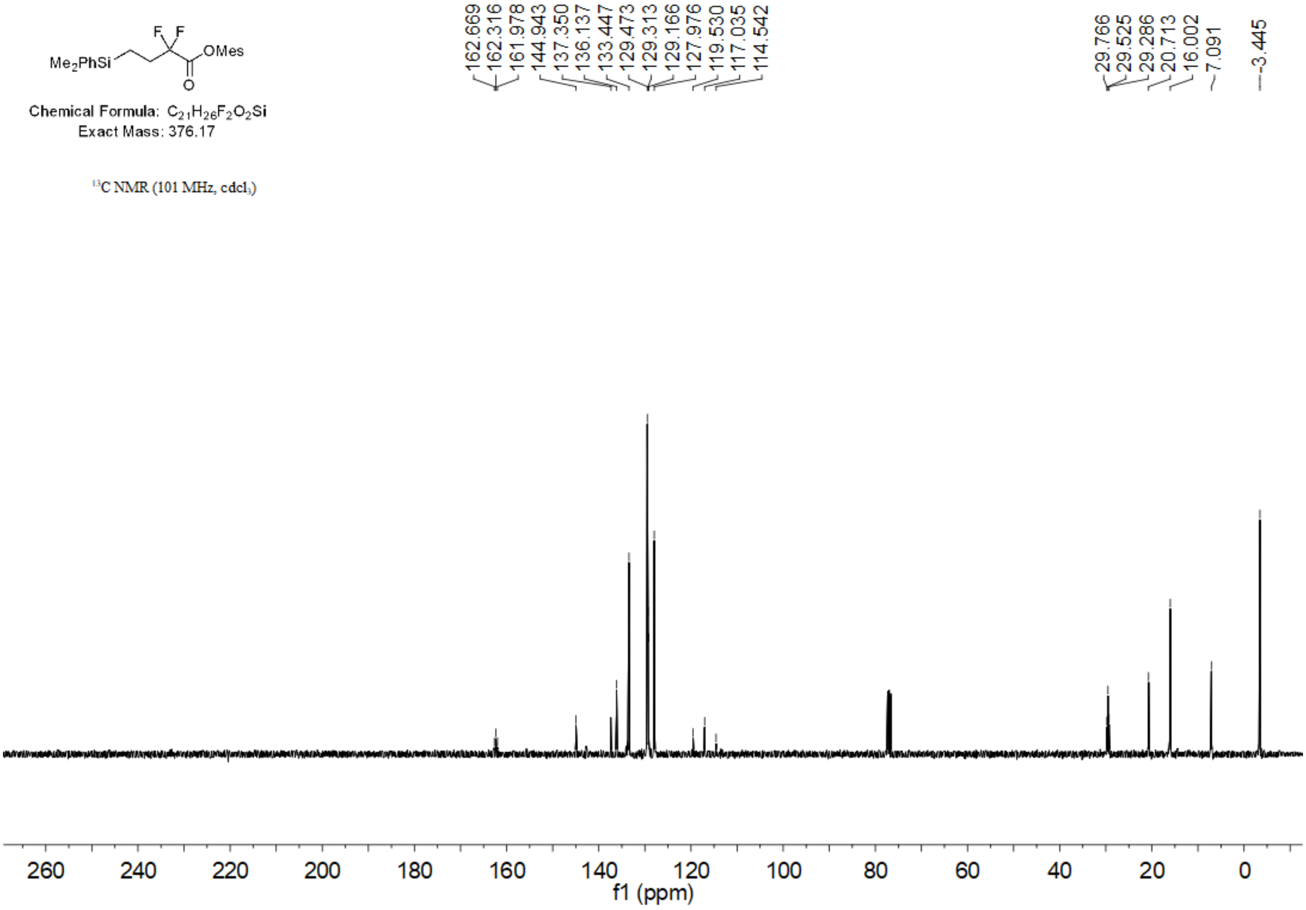
Mesityl 4-(dimethyl(phenyl)silyl)-2,2-difluorobutanoate (3n)





Chemical Formula: $C_{21}H_{26}F_2O_2Si$
Exact Mass: 376.17

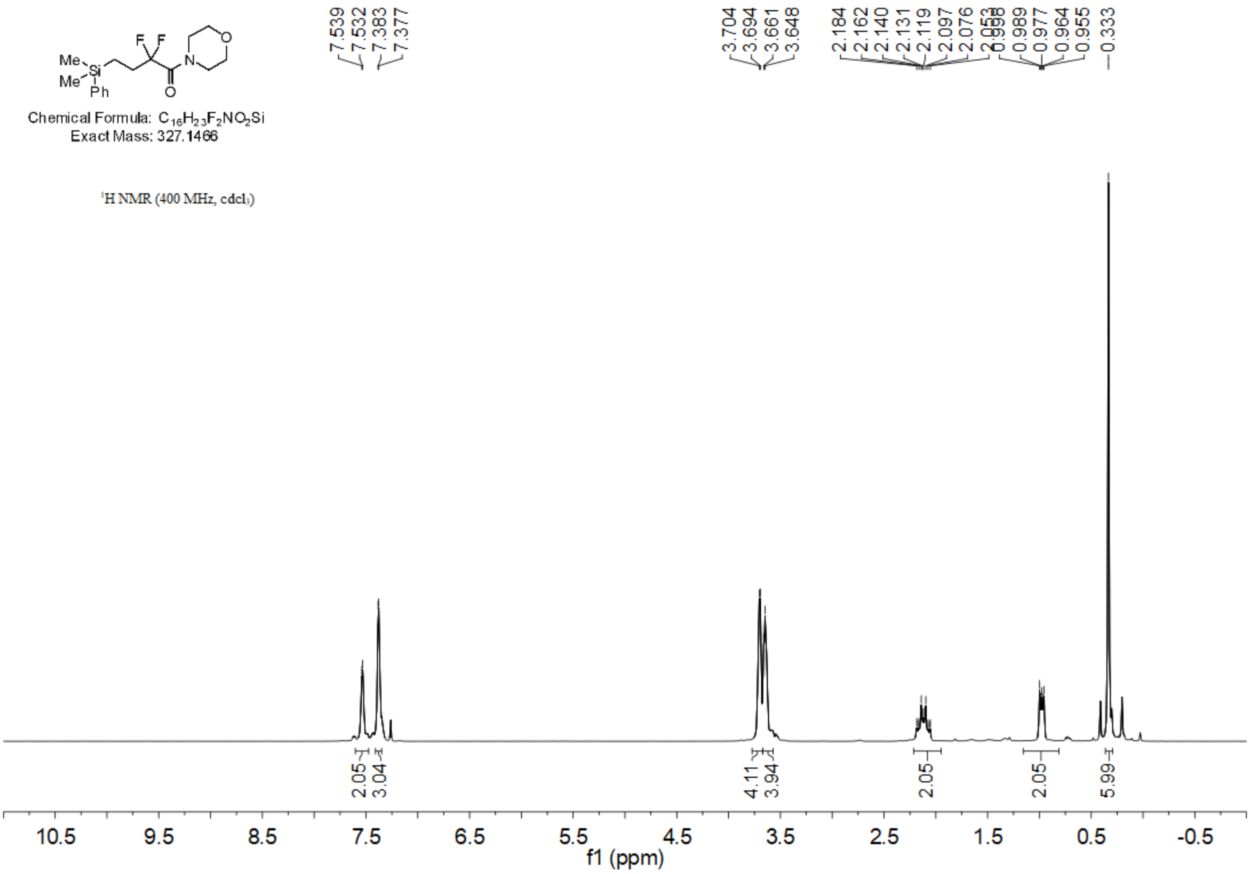
^{19}F NMR (376 MHz, cdcl$_3$)



Chemical Formula: $C_{21}H_{26}F_2O_2Si$
Exact Mass: 376.17

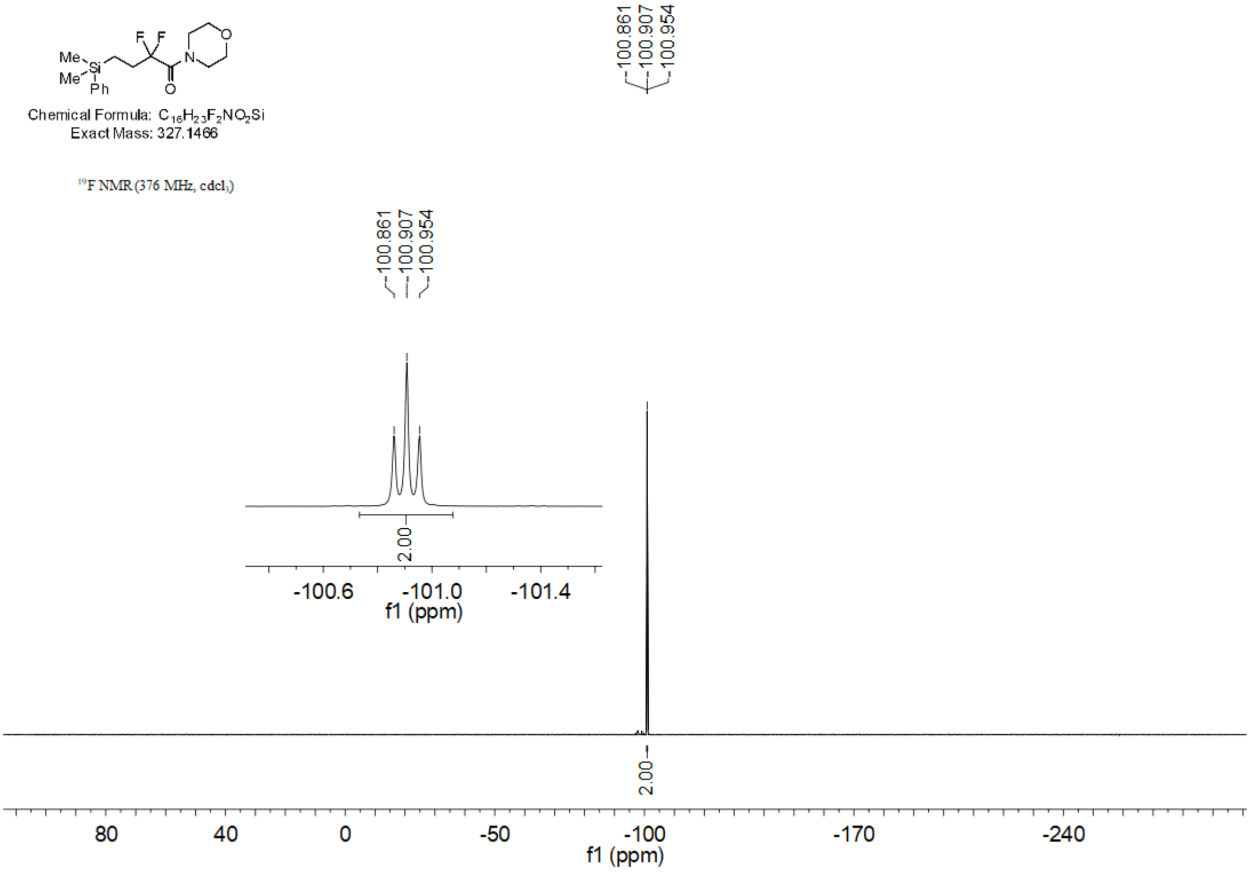
^{13}C NMR (101 MHz, cdcl$_3$)

4-(Dimethyl(phenyl)silyl)-2,2-difluoro-1-morpholinobutan-1-one (3o)



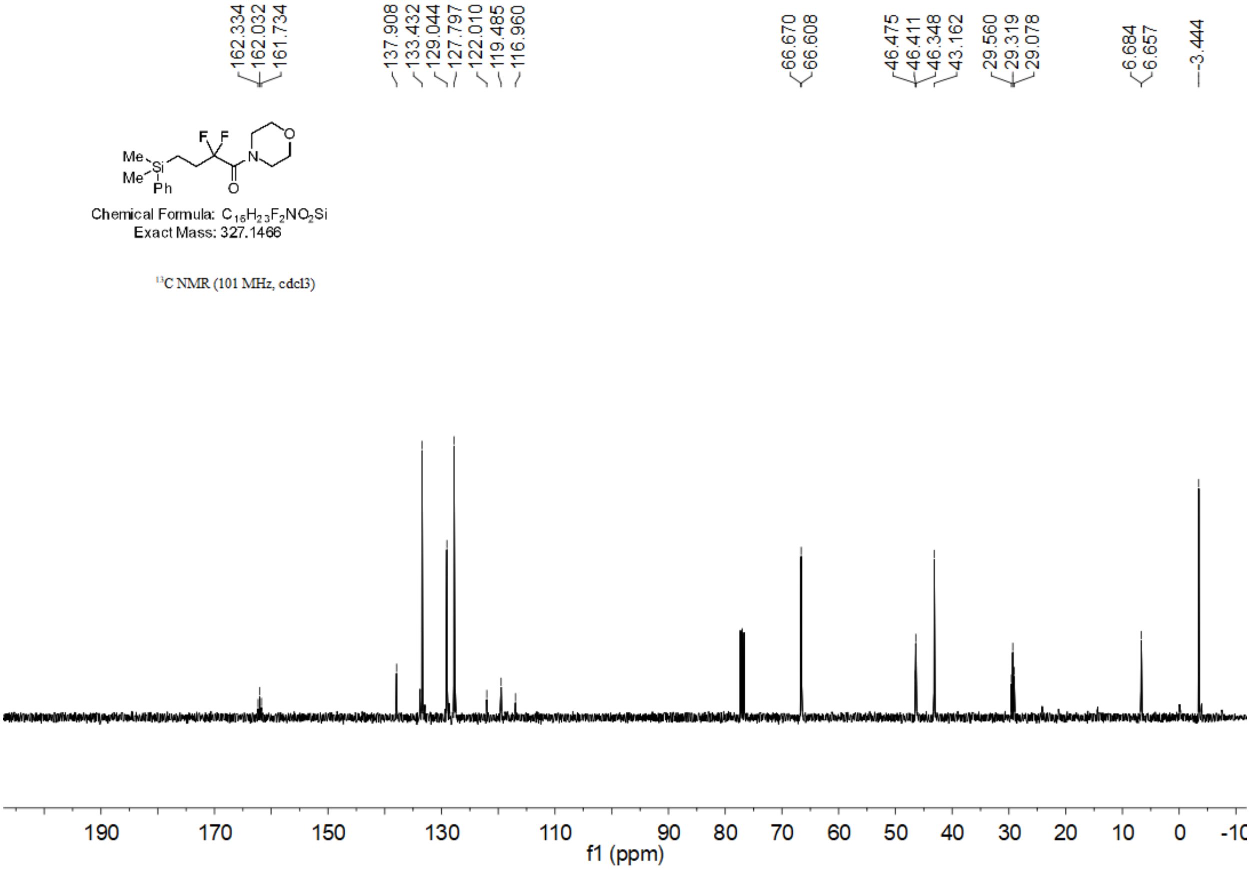
Chemical Formula: $C_{16}H_{23}F_2NO_2Si$
Exact Mass: 327.1466

^{1}H NMR (400 MHz, cdcl$_3$)

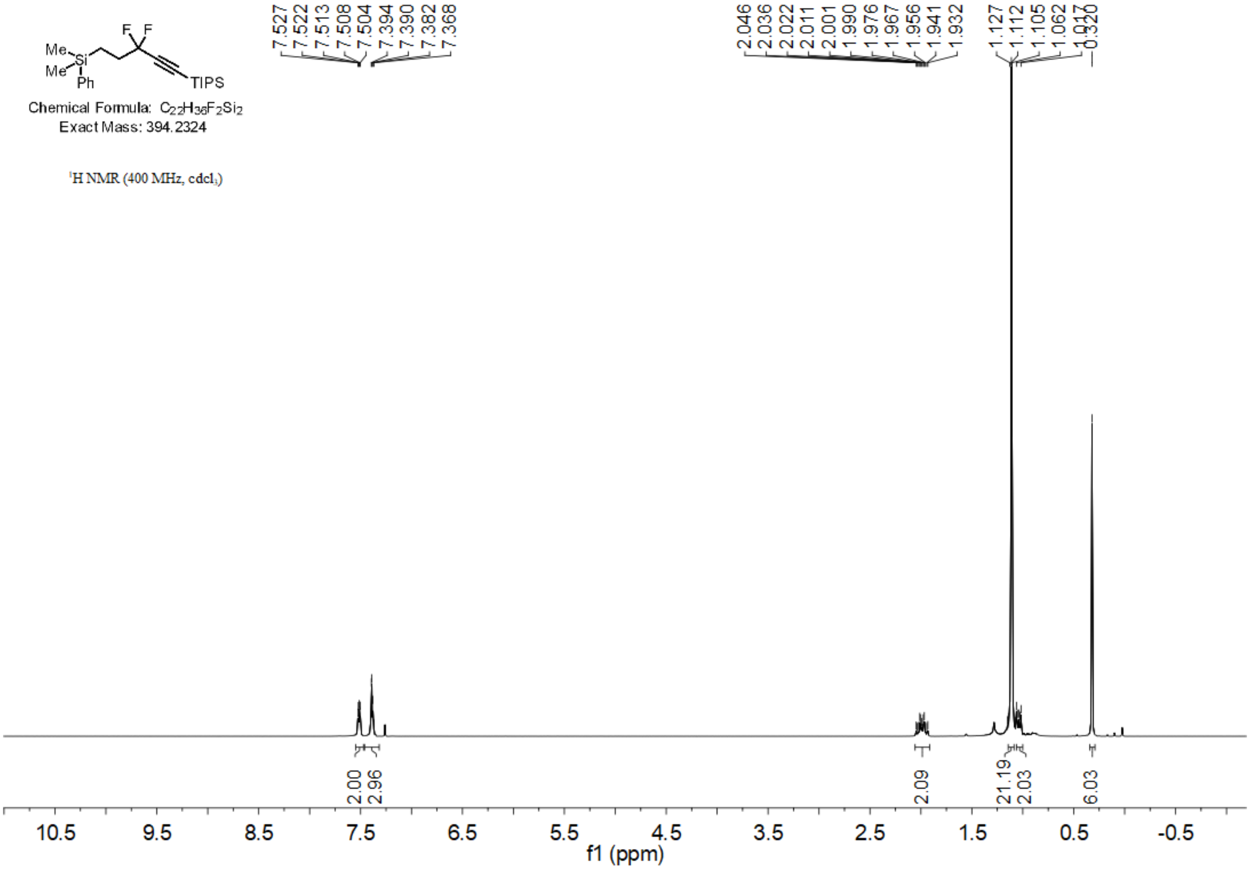


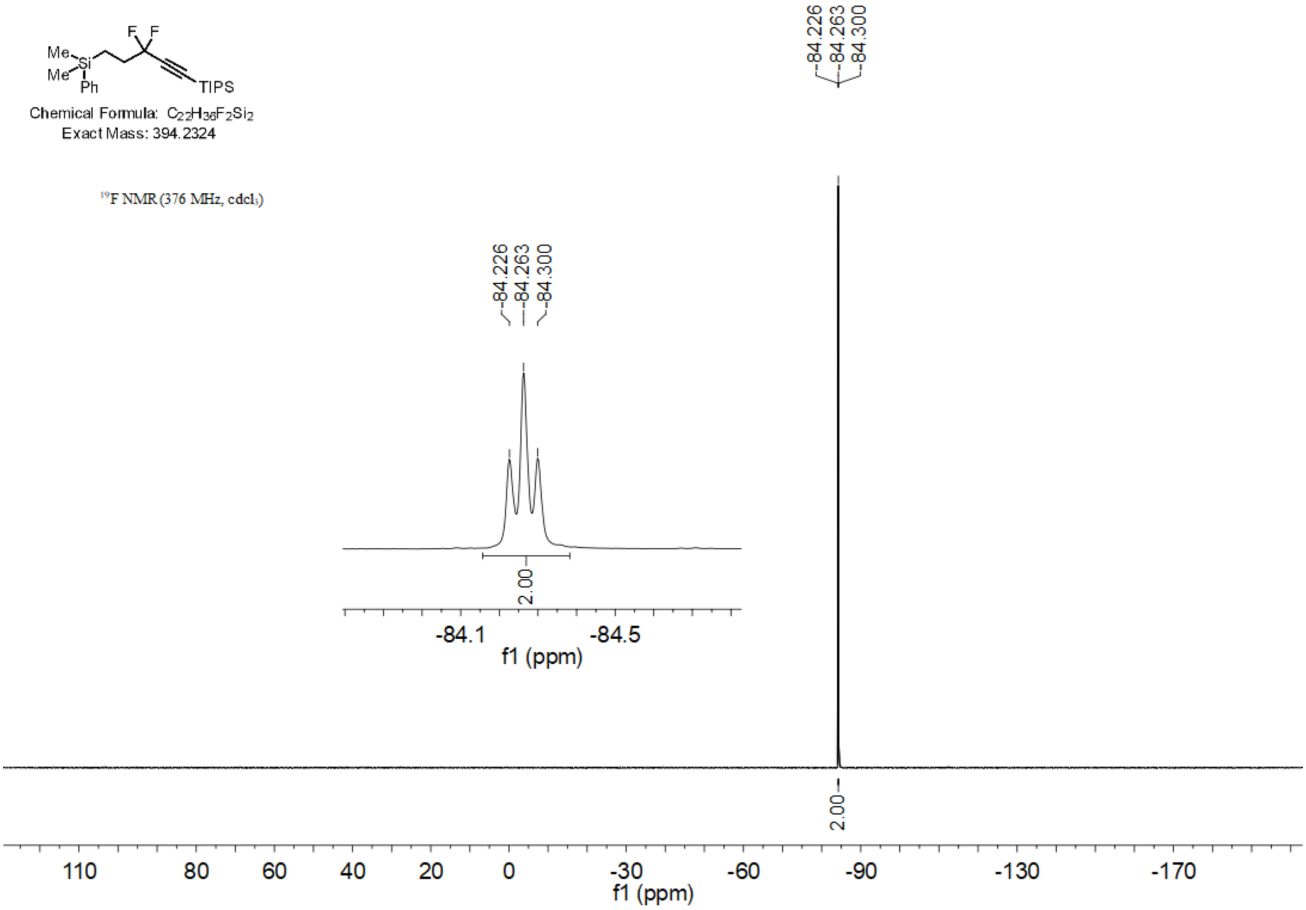
Chemical Formula: $C_{16}H_{23}F_2NO_2Si$
Exact Mass: 327.1466

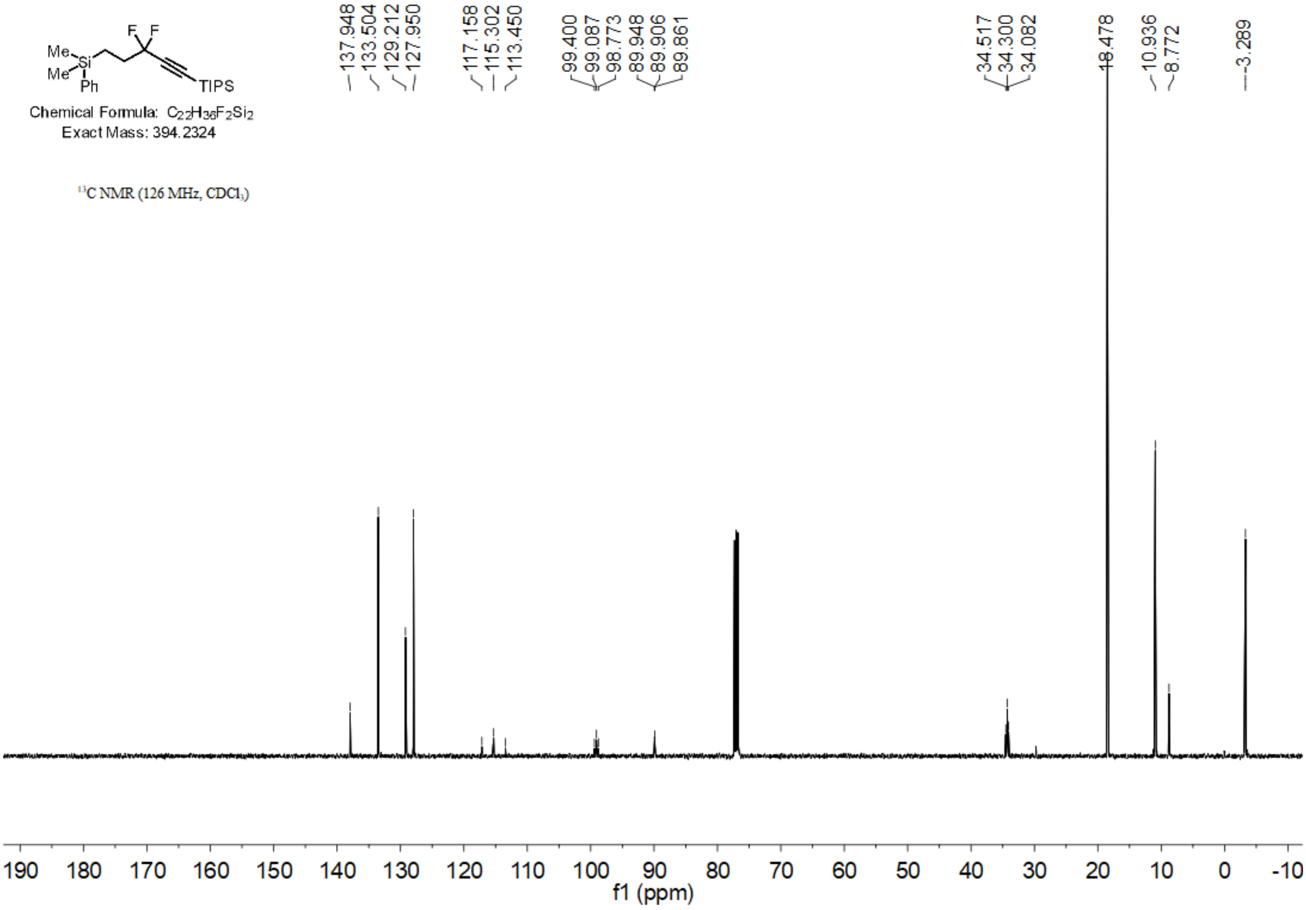
^{19}F NMR (376 MHz, cdcl$_3$)



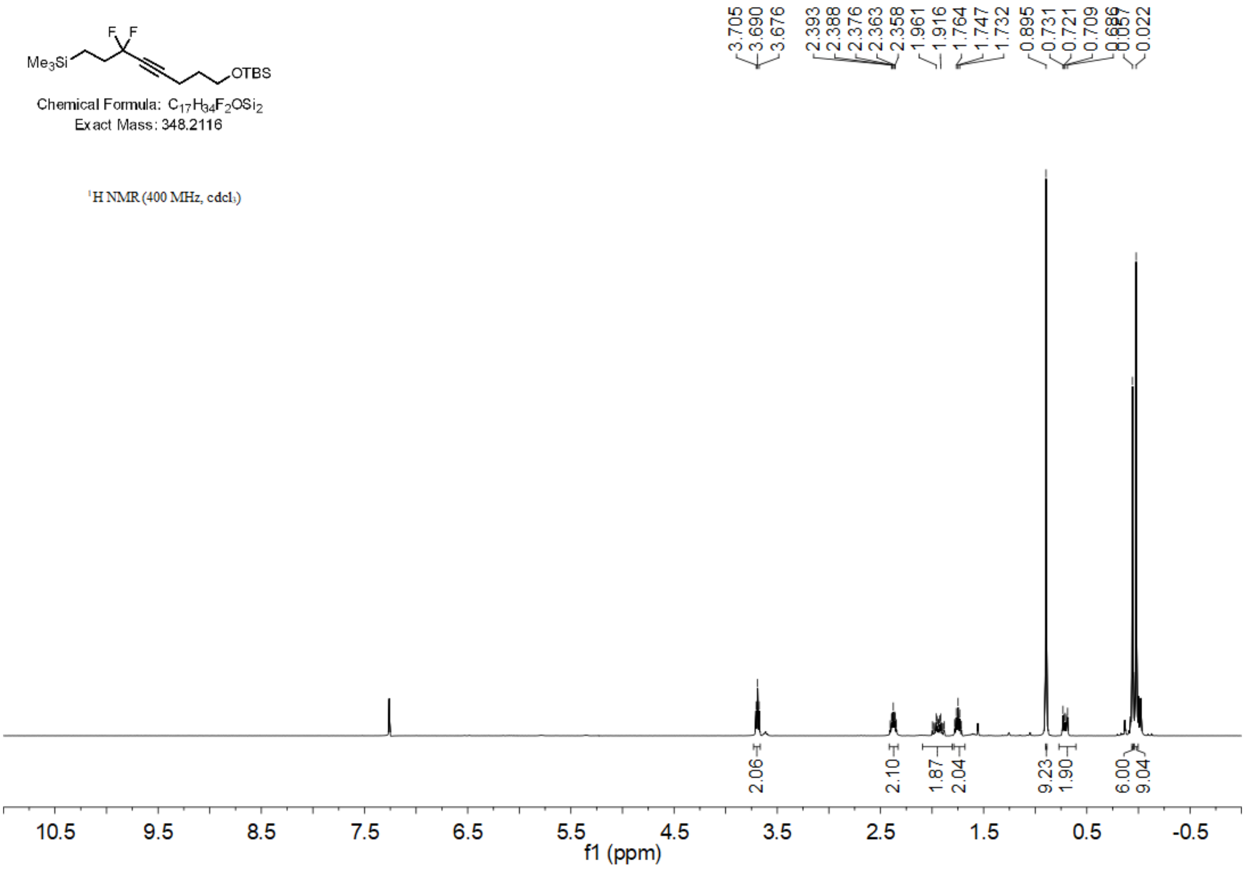
(3,3-Difluoro-5-(triisopropylsilyl)pent-4-yn-1-yl)dimethyl(phenyl)silane (3p)

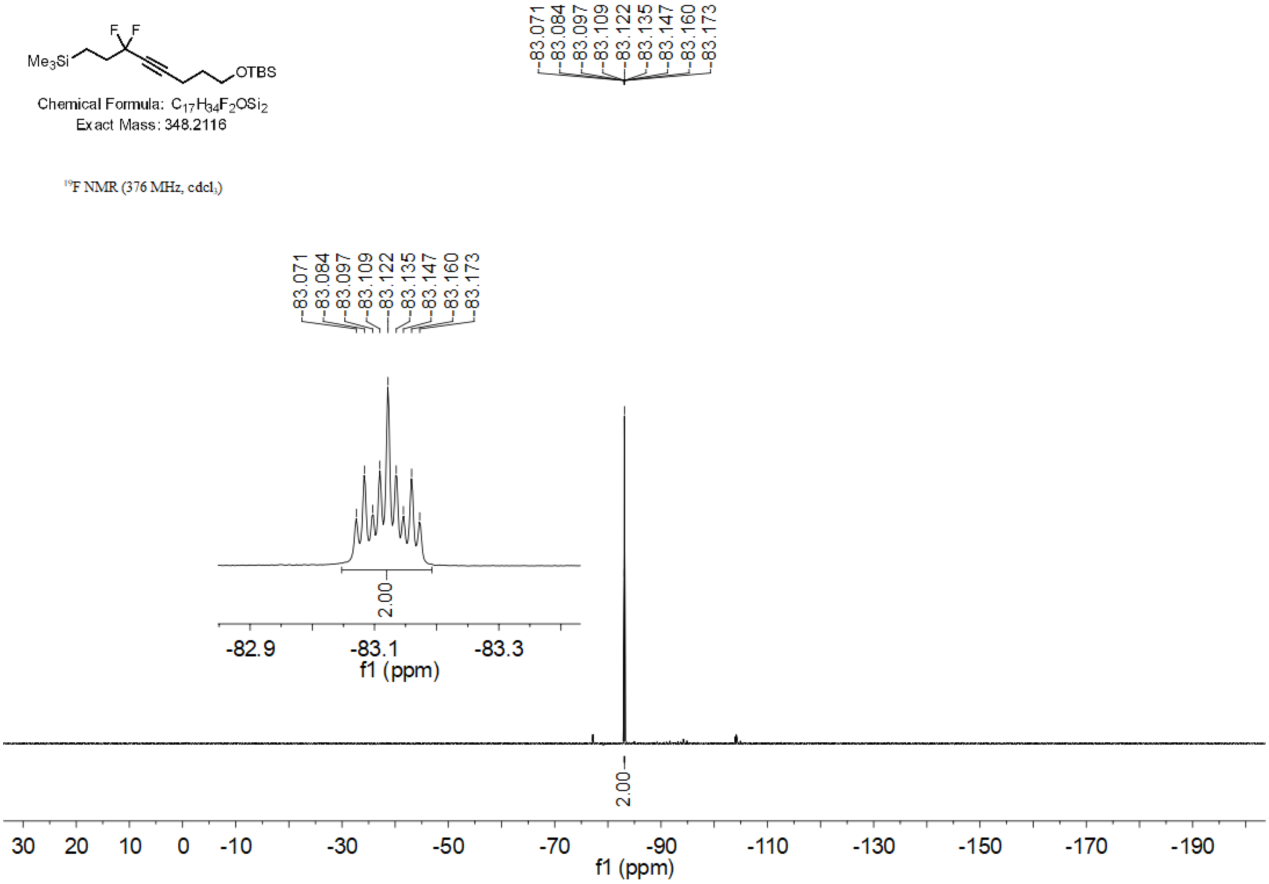


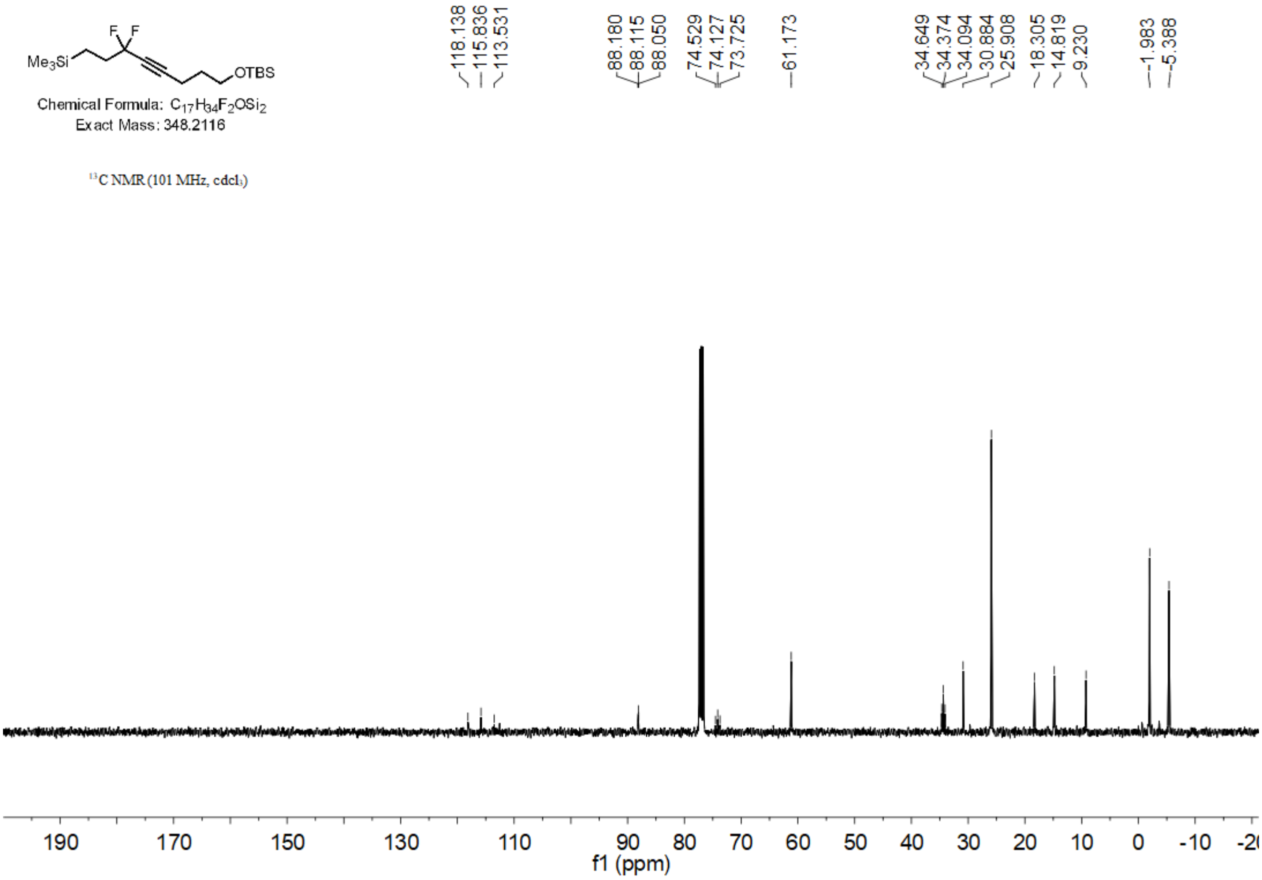

Me
Me
Si
Ph
F F
TIPS
Chemical Formula: C22H36F2Si2
Exact Mass: 394.2324
19F NMR (376 MHz, cdcl3)
-84.226
-84.263
-84.300
-84.226
-84.263
-84.300
2.00
-84.1
-84.5
f1 (ppm)
2.00
110
80
60
40
20
0
-30
-60
-90
-130
-170
f1 (ppm)


Me
Me
Si
Ph
F F
TIPS
Chemical Formula: C22H36F2Si2
Exact Mass: 394.2324
13C NMR (126 MHz, CDCl3)
137.948
133.504
129.212
127.950
117.158
115.302
113.450
99.400
99.087
98.773
89.948
89.906
89.861
34.517
34.300
34.082
18.478
10.936
8.772
-3.289
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

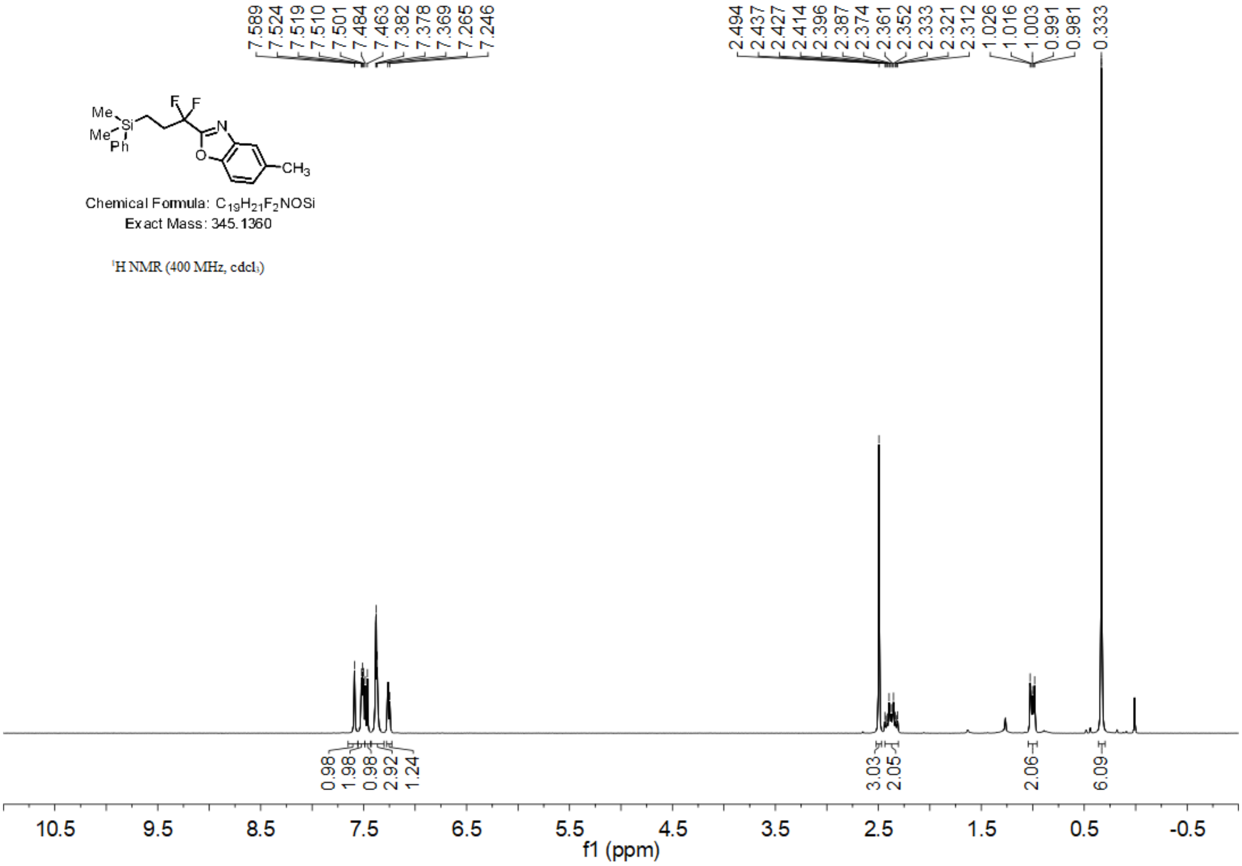
t-Butyl((6,6-difluoro-8-(trimethylsilyl)oct-4-yn-1-yl)oxy)dimethylsilane (3q)

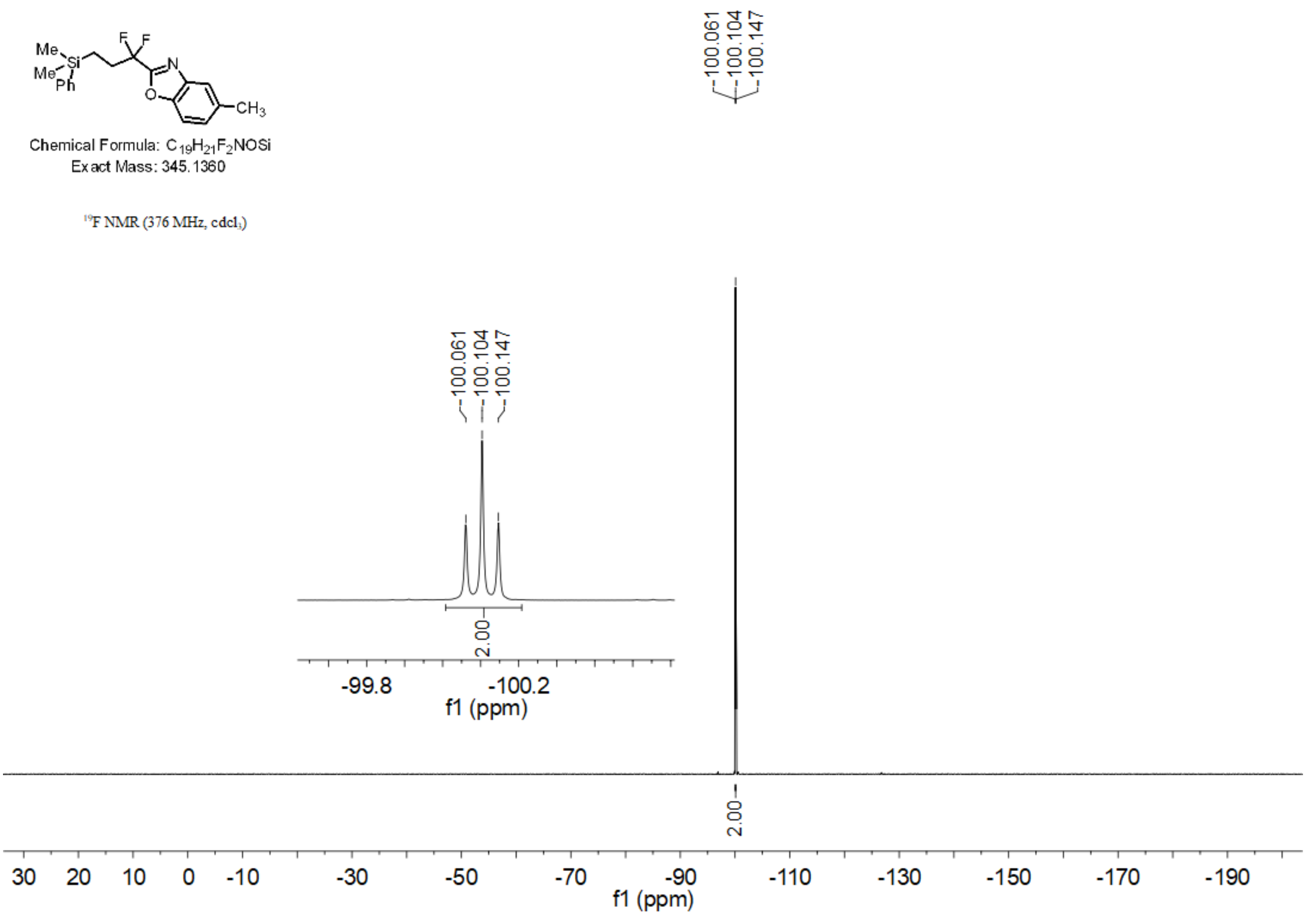




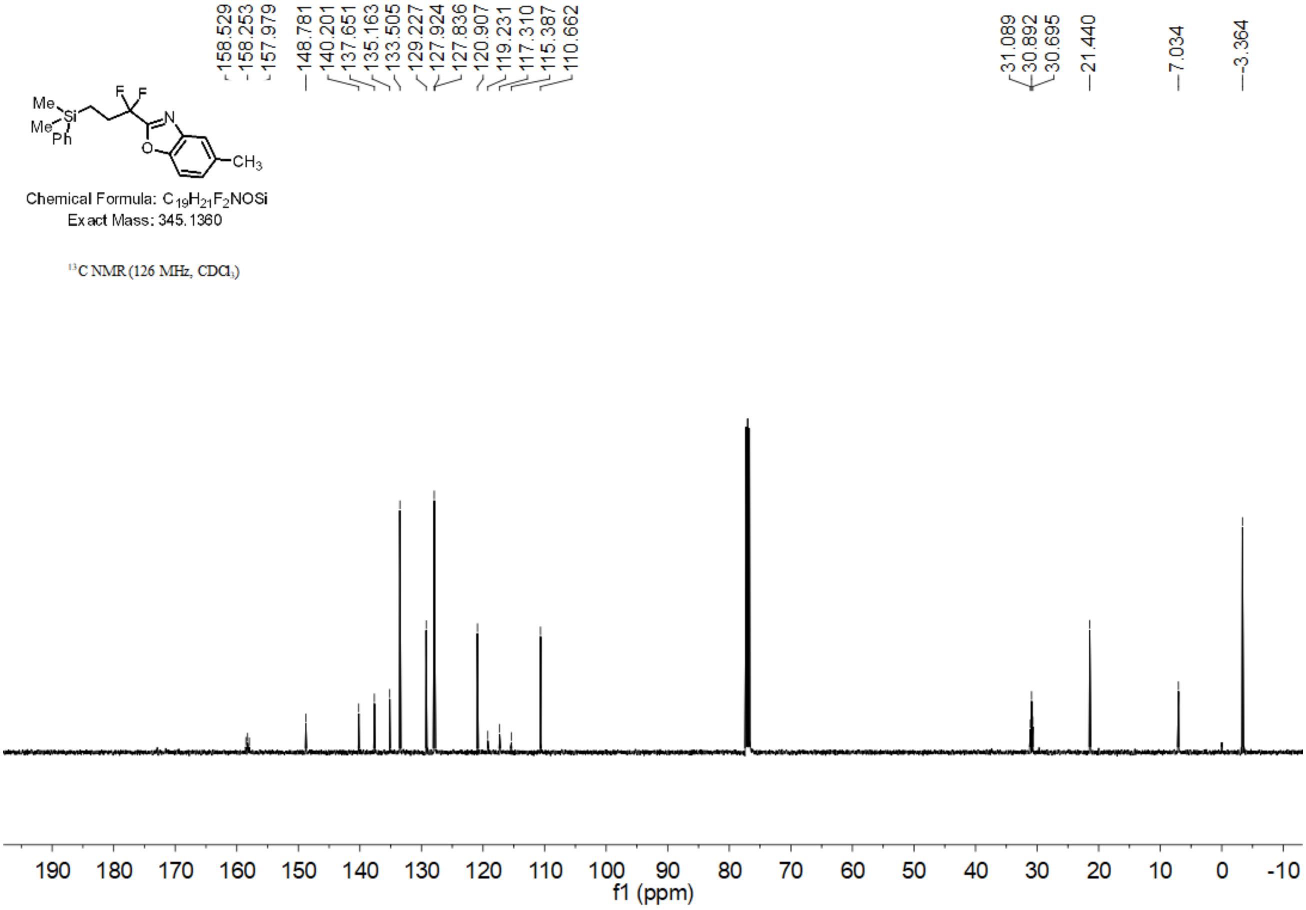


2-(3-(Dimethyl(phenyl)silyl)-1,1-difluoropropyl)-5-methylbenzo[d]oxazole (3r)



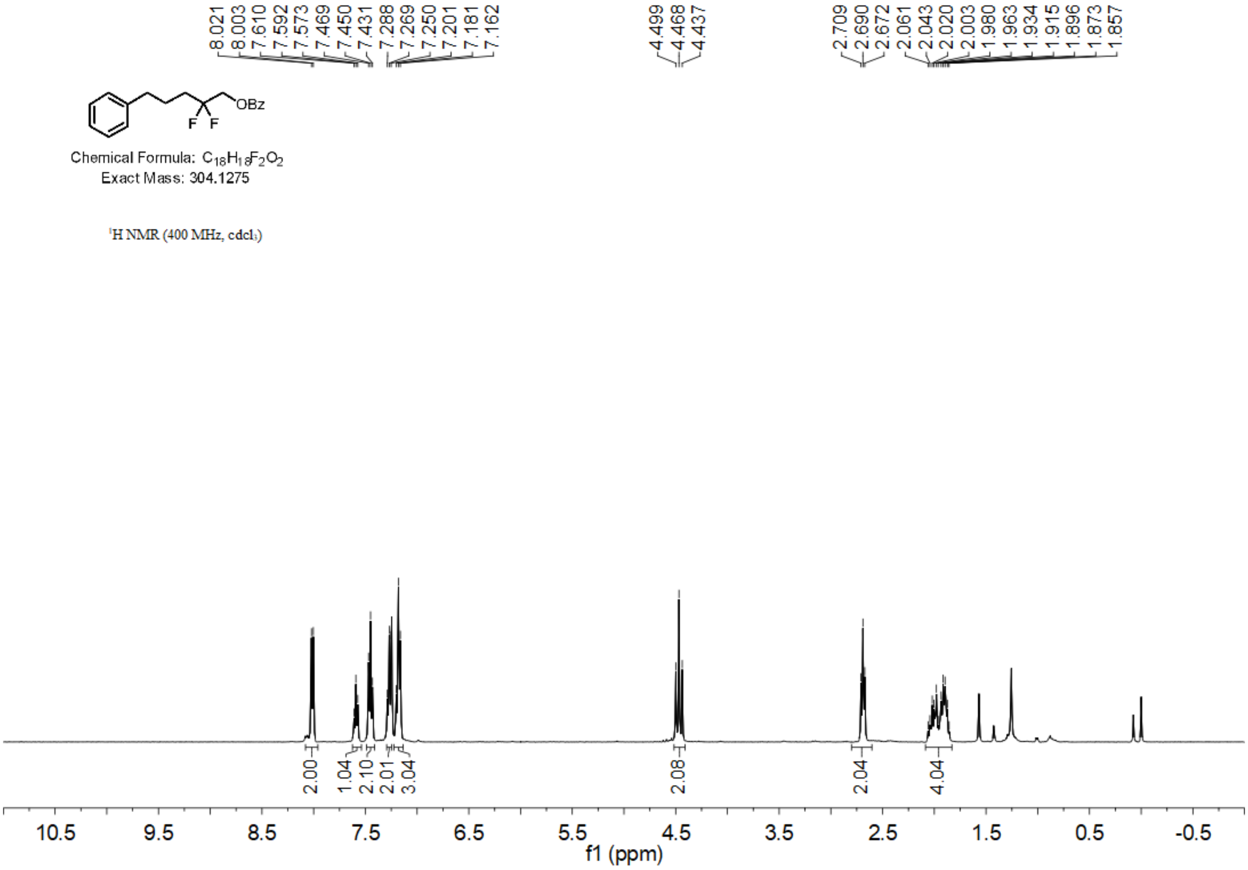

Chemical Formula: $C_{19}H_{21}F_2NOSi$
Exact Mass: 345.1360

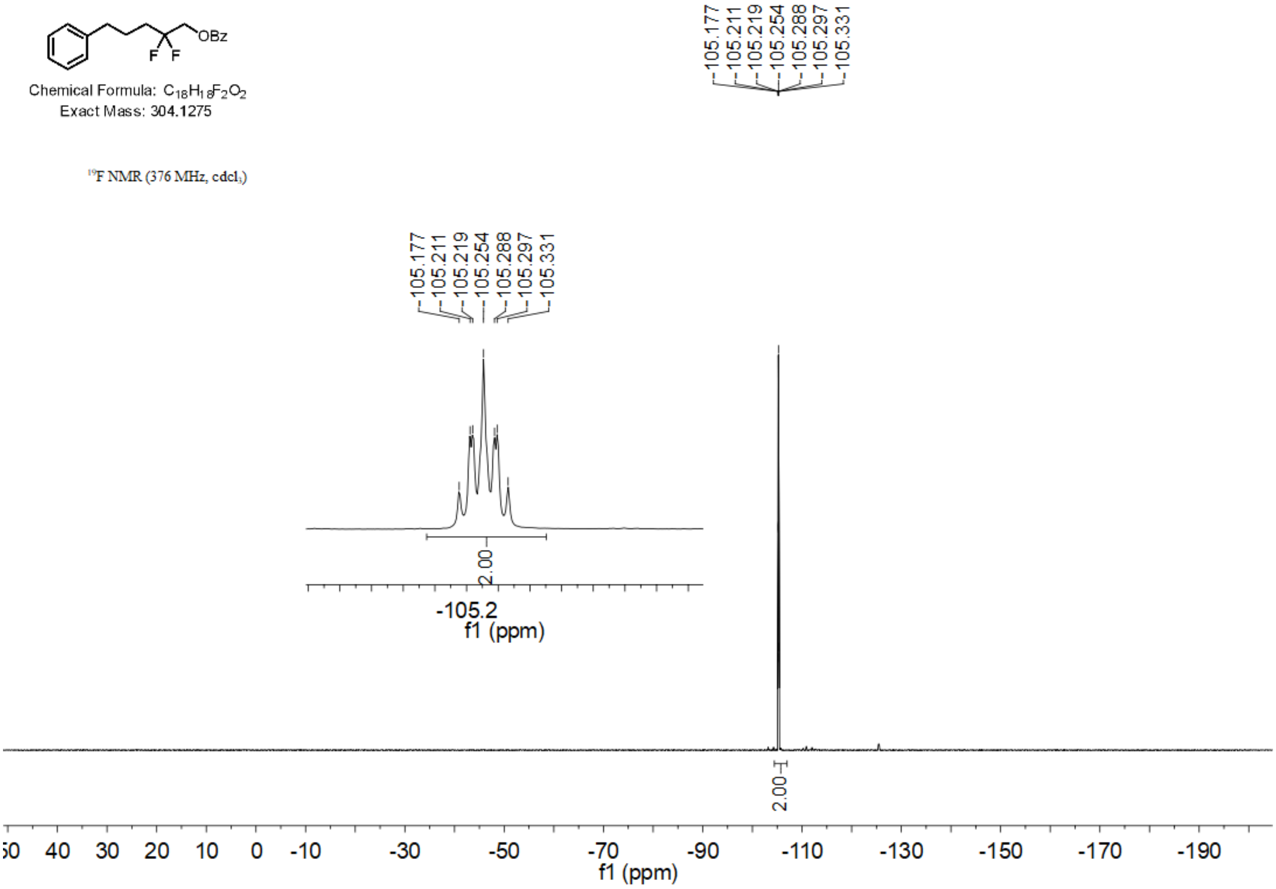
^{19}F NMR (376 MHz, cdcl$_3$)

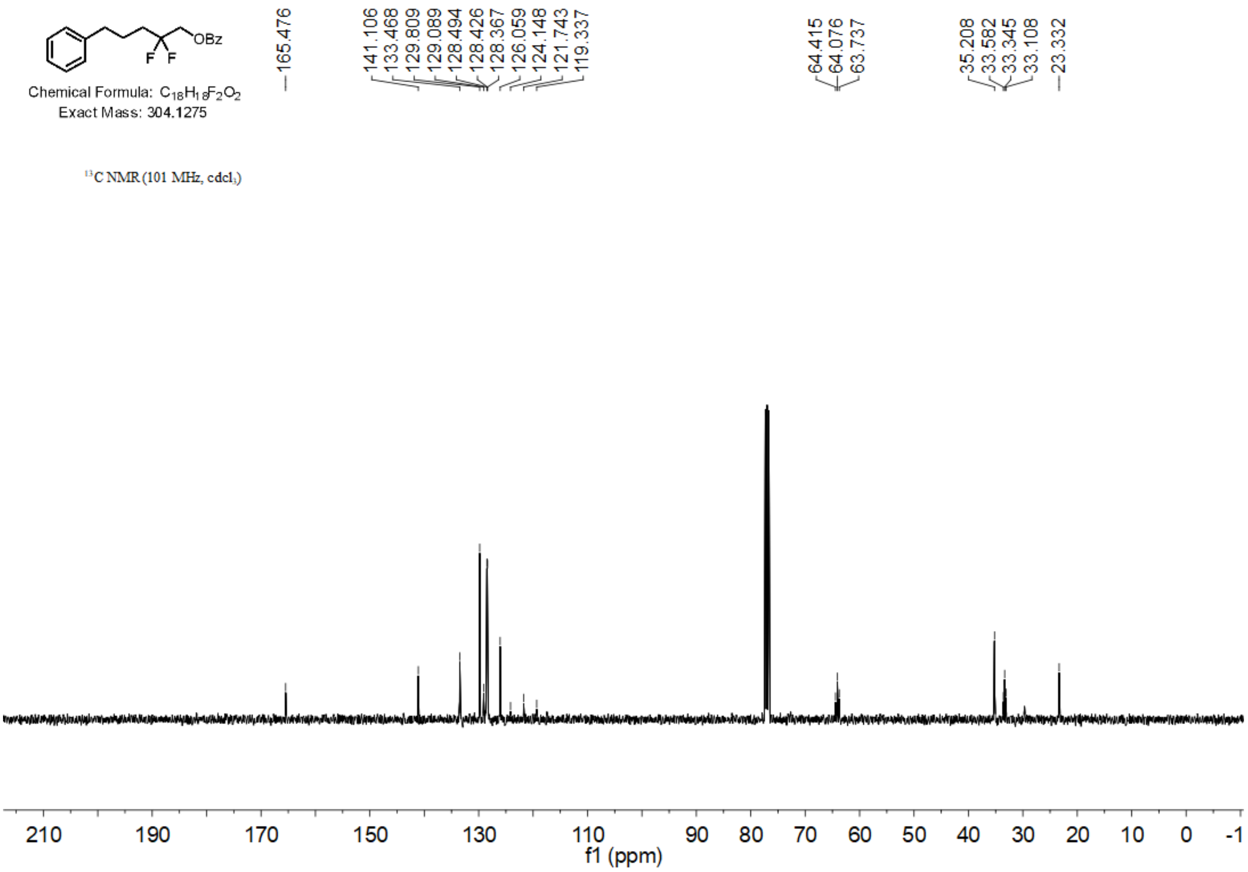

Chemical Formula: $C_{19}H_{21}F_2NOSi$
Exact Mass: 345.1360

^{13}C NMR (126 MHz, CDCl$_3$)

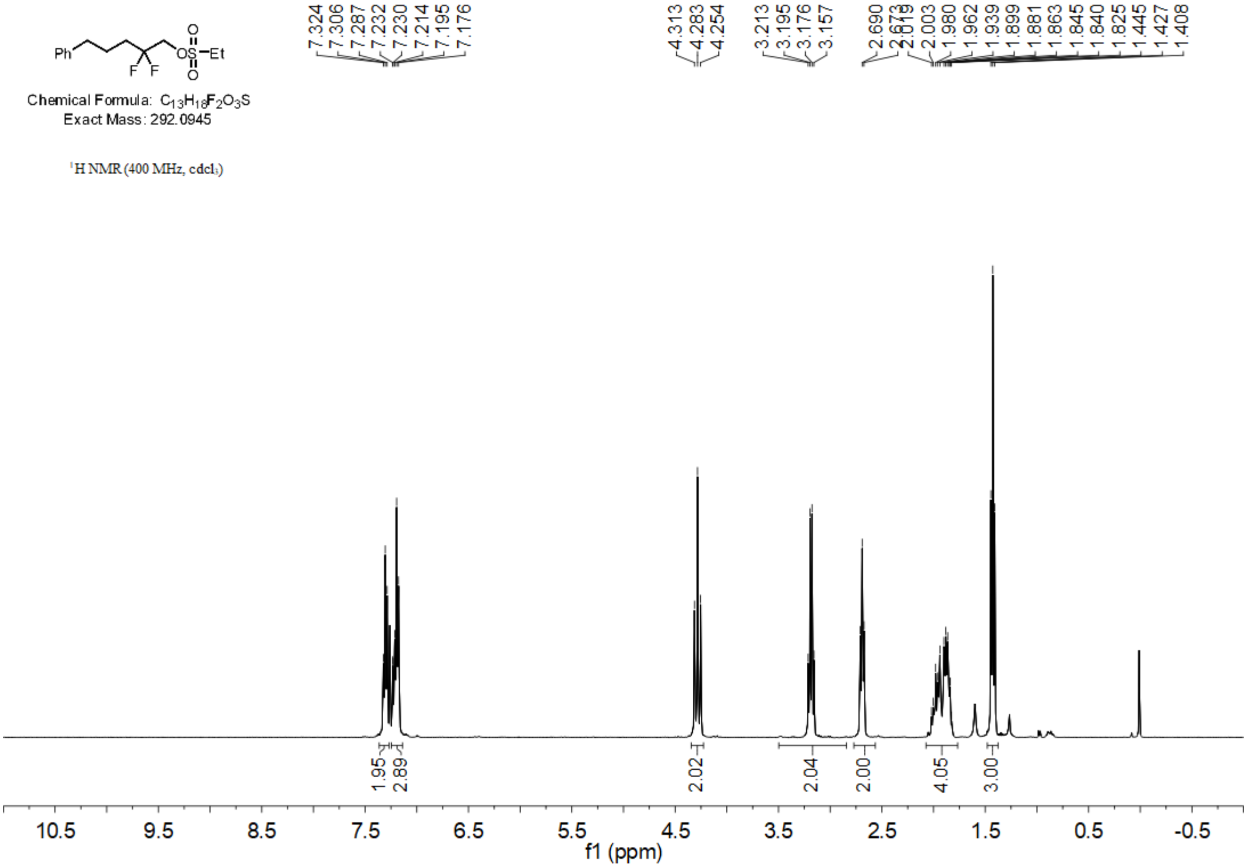
2,2-Difluoro-5-phenylpentyl benzoate (8a)

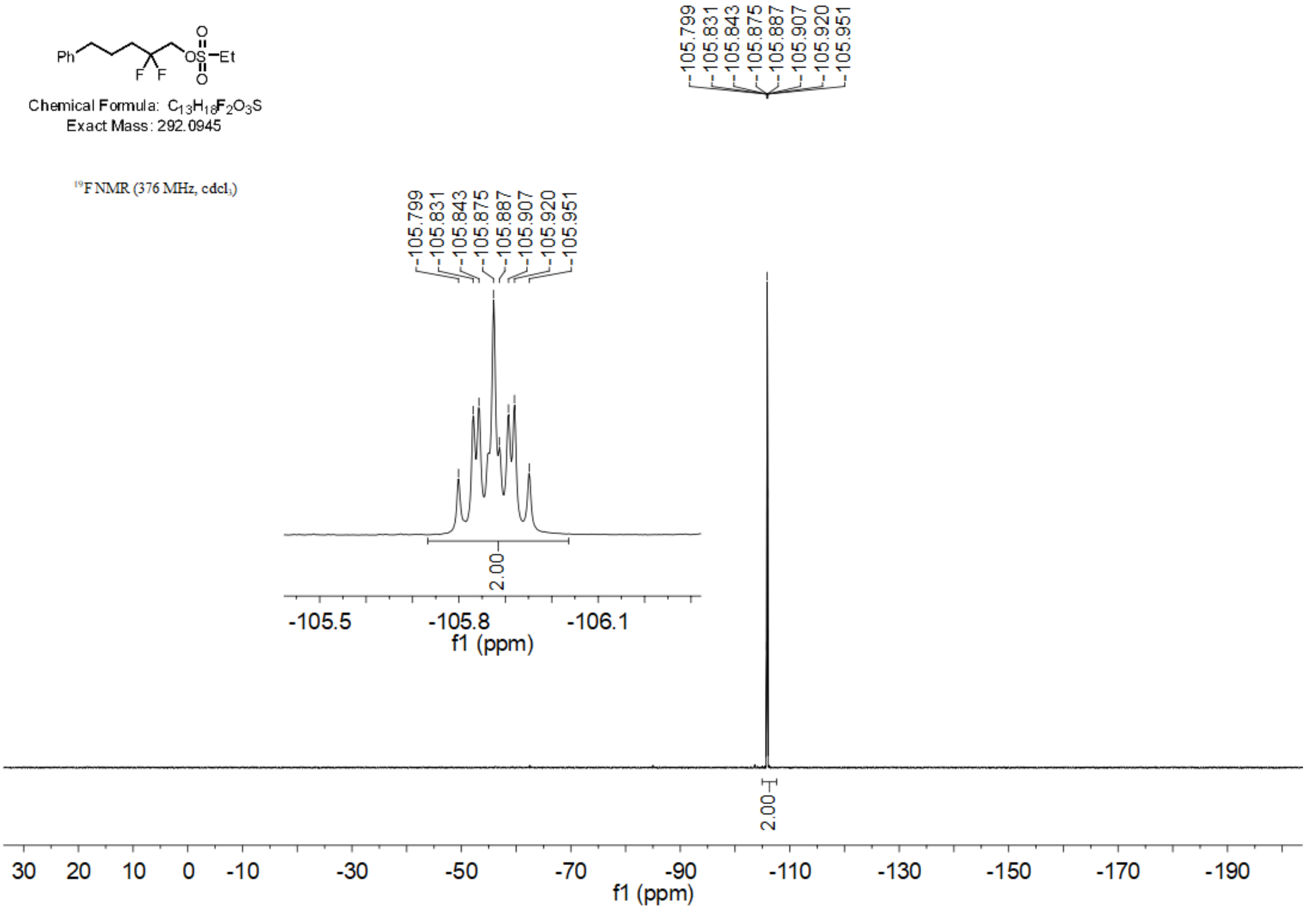


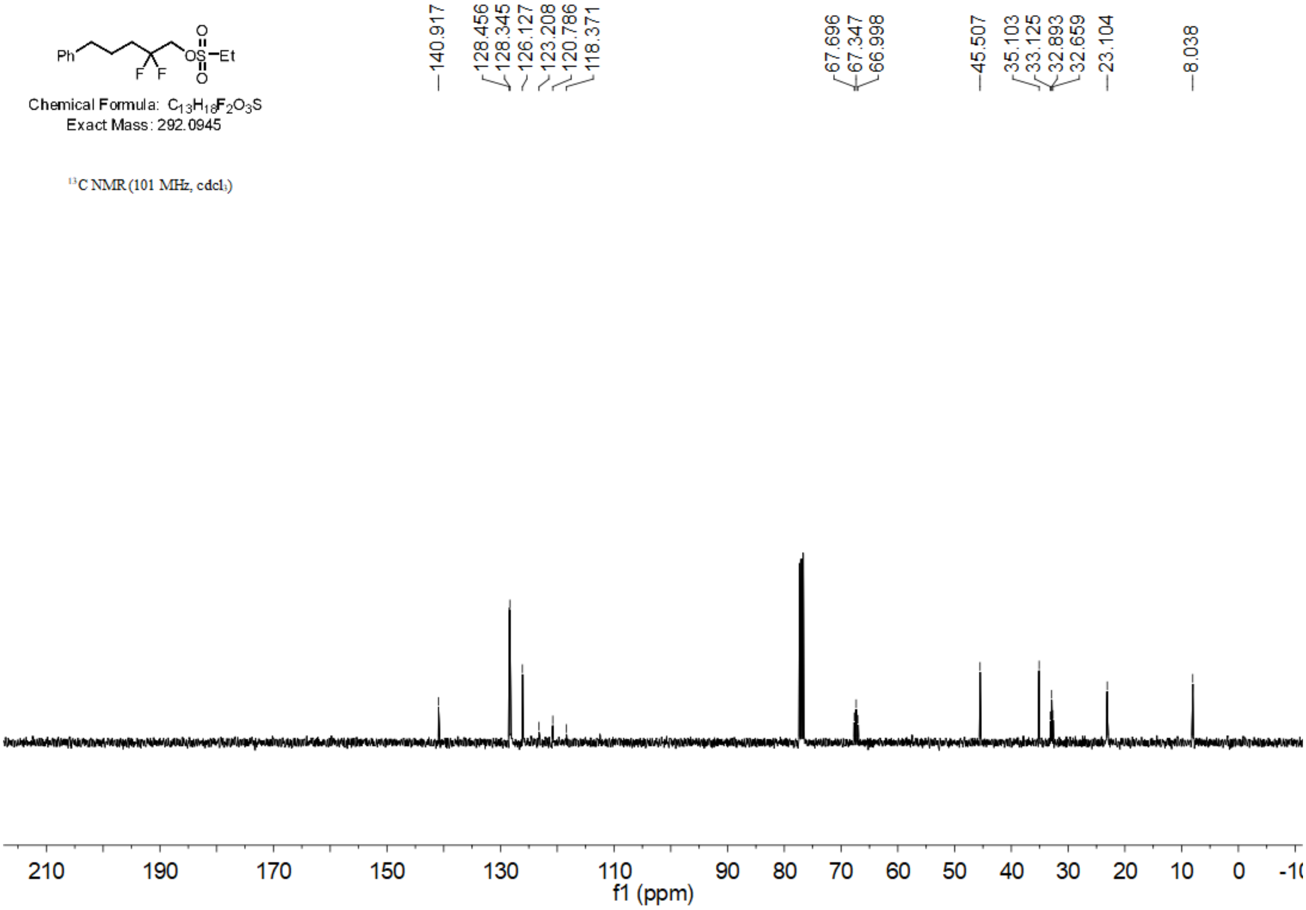




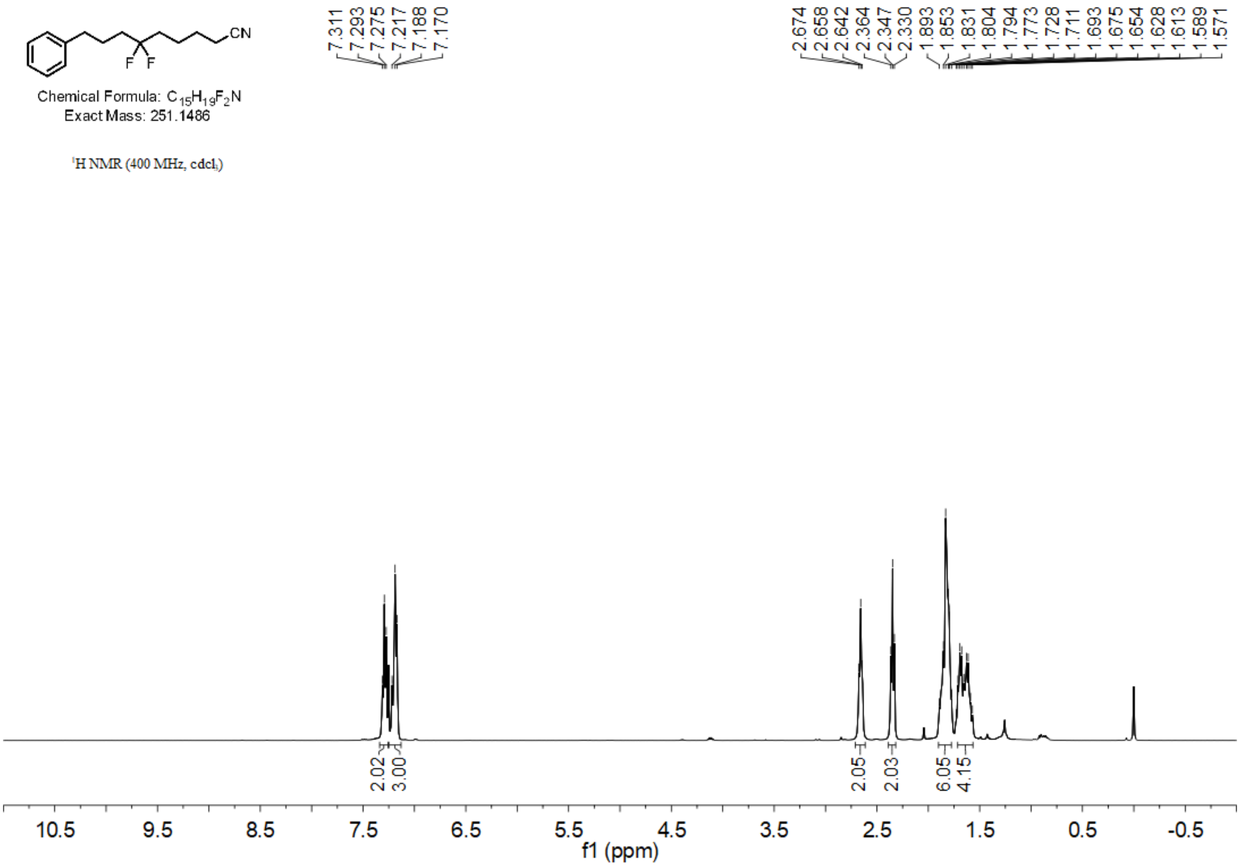
2,2-Difluoro-5-phenylpentyl ethanesulfonate (8b)

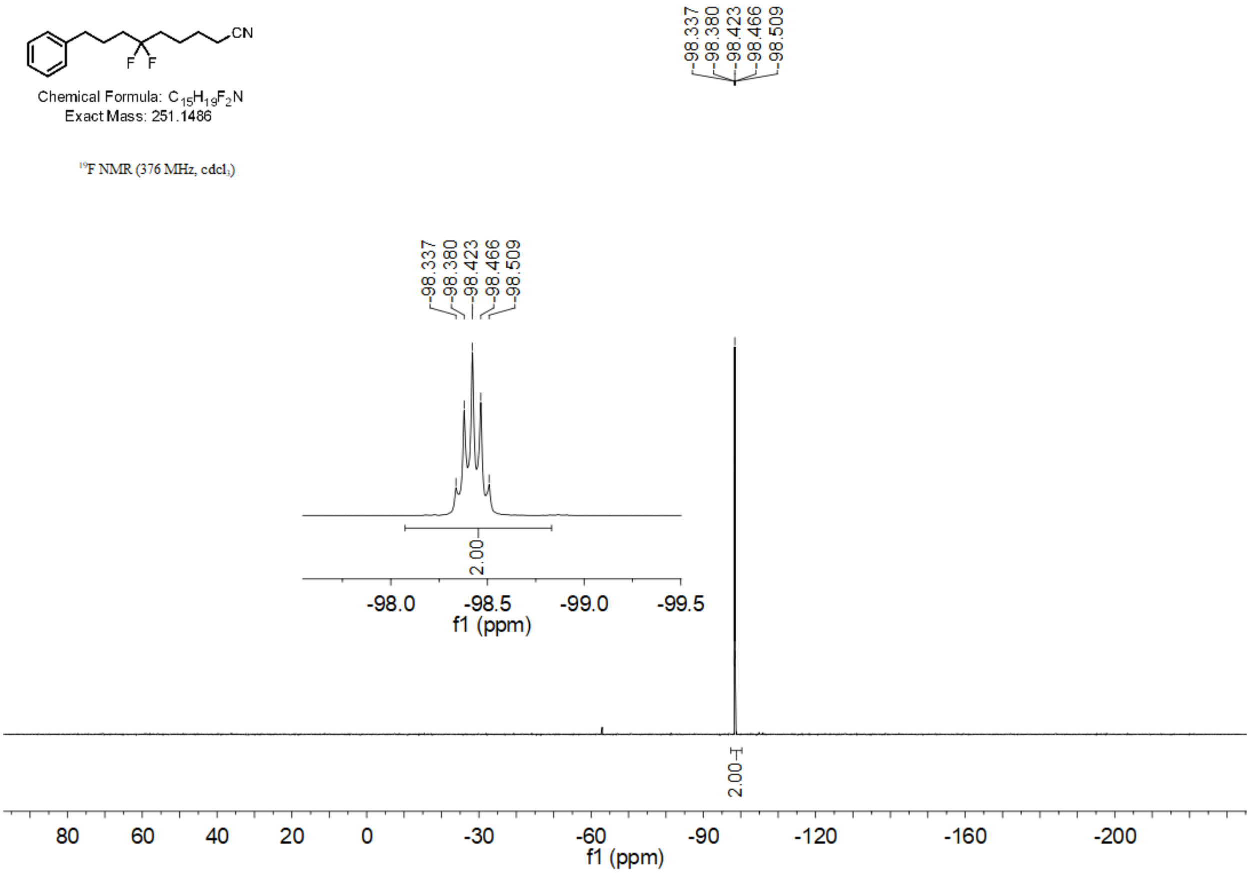


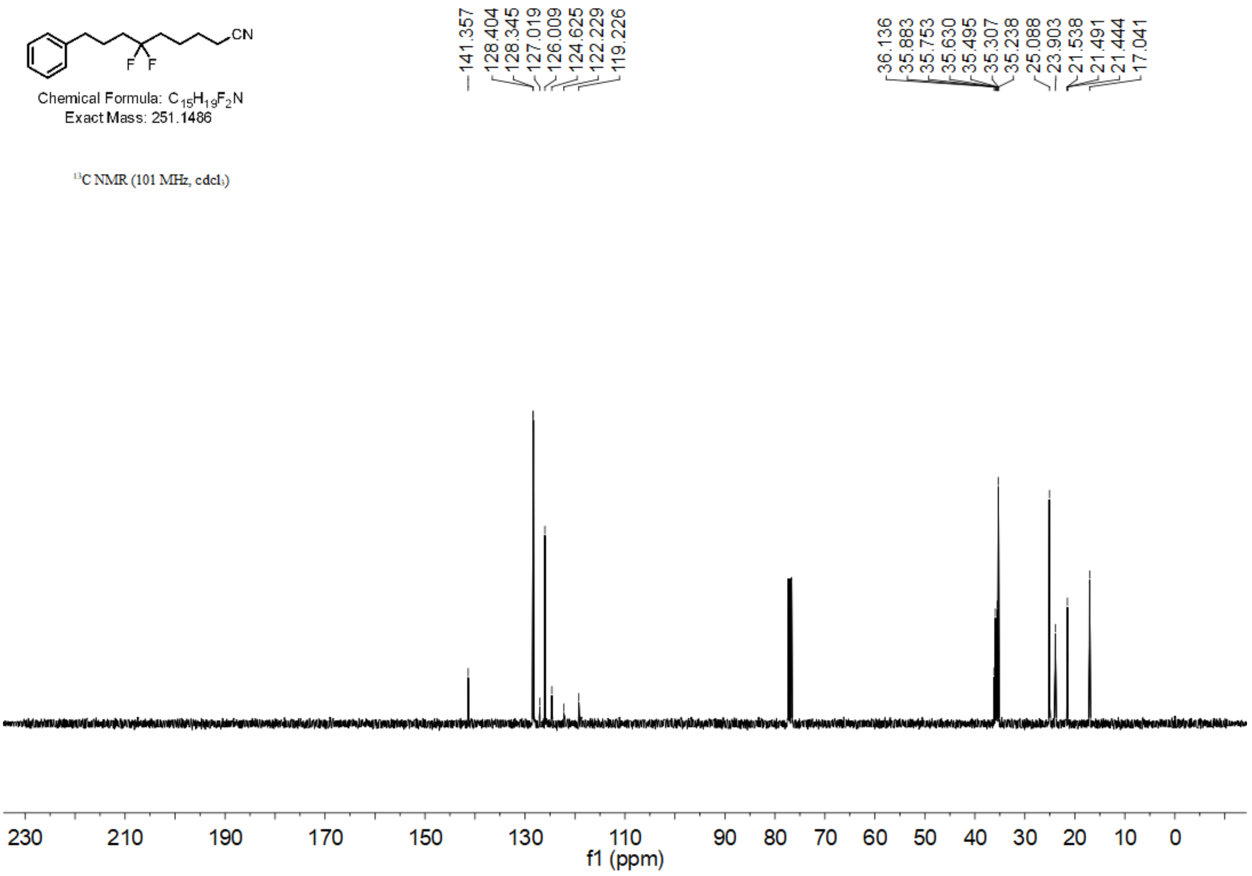

Ph
O
S
O
O
Et
F F
Chemical Formula: $C_{13}H_{18}F_2O_3S$
Exact Mass: 292.0945
^{19}F NMR (376 MHz, cdcl$_3$)
-105.799
-105.831
-105.843
-105.875
-105.887
-105.907
-105.920
-105.951
-105.799
-105.831
-105.843
-105.875
-105.887
-105.907
-105.920
-105.951
2.00
-105.5
-105.8
-106.1
f1 (ppm)
2.00
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)


Ph
O
S
O
O
Et
F F
Chemical Formula: $C_{13}H_{18}F_2O_3S$
Exact Mass: 292.0945
^{13}C NMR (101 MHz, cdcl$_3$)
140.917
128.456
128.345
126.127
123.208
120.786
118.371
67.696
67.347
66.998
45.507
35.103
33.125
32.893
32.659
23.104
8.038
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

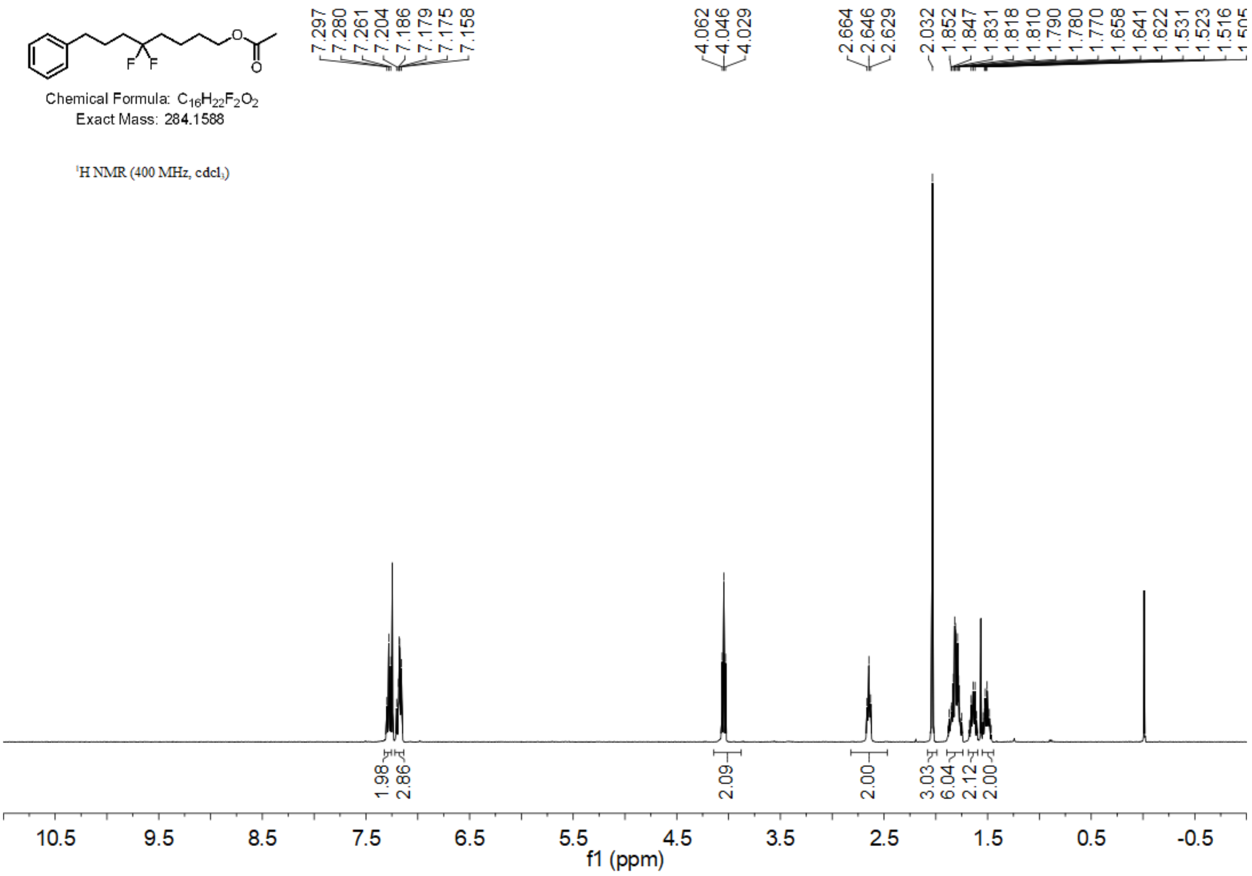
6,6-Difluoro-9-phenylnonanenitrile (8c)

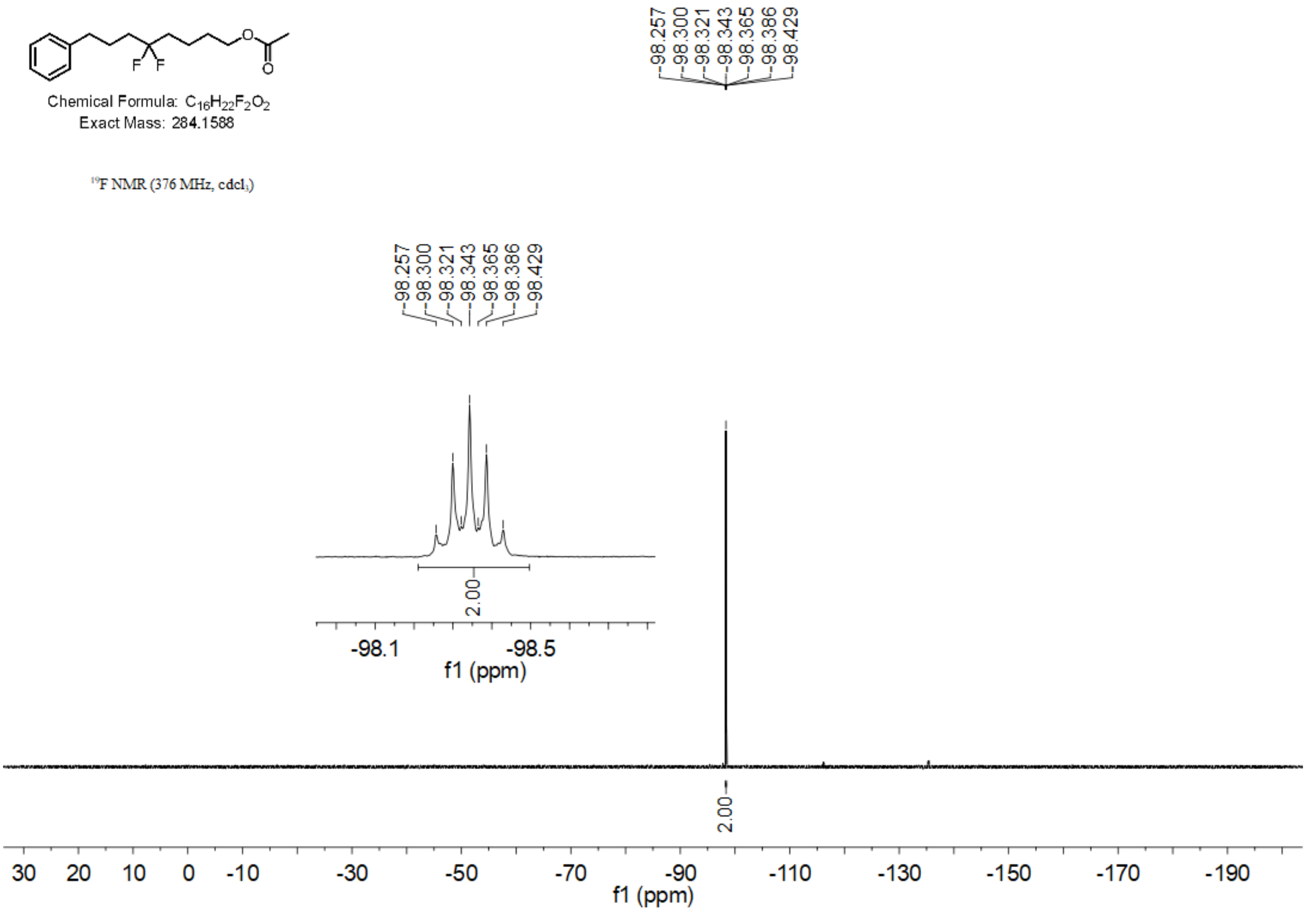






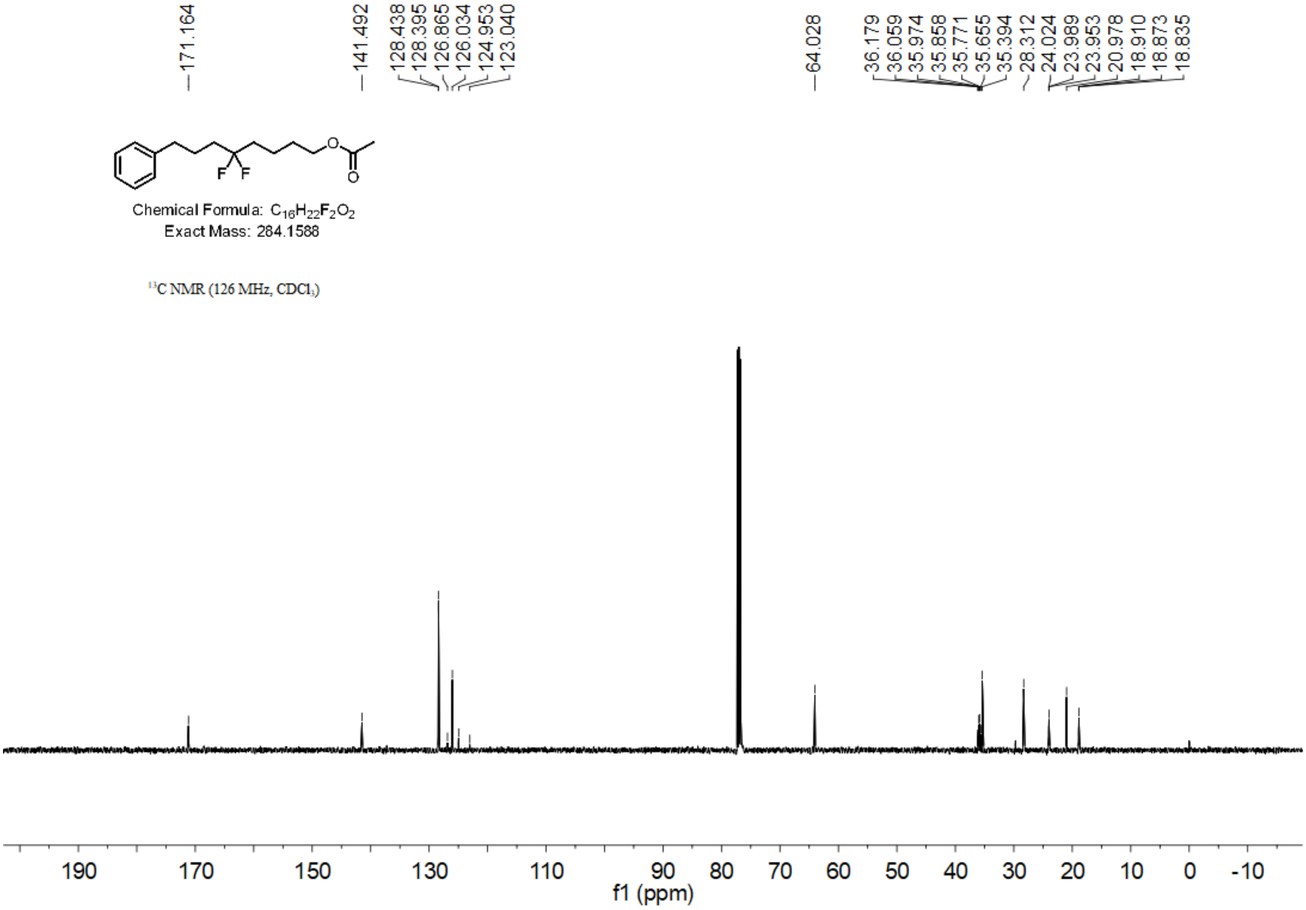
5,5-Difluoro-8-phenyloctyl acetate (8d)





Chemical Formula: $C_{16}H_{22}F_2O_2$
Exact Mass: 284.1588

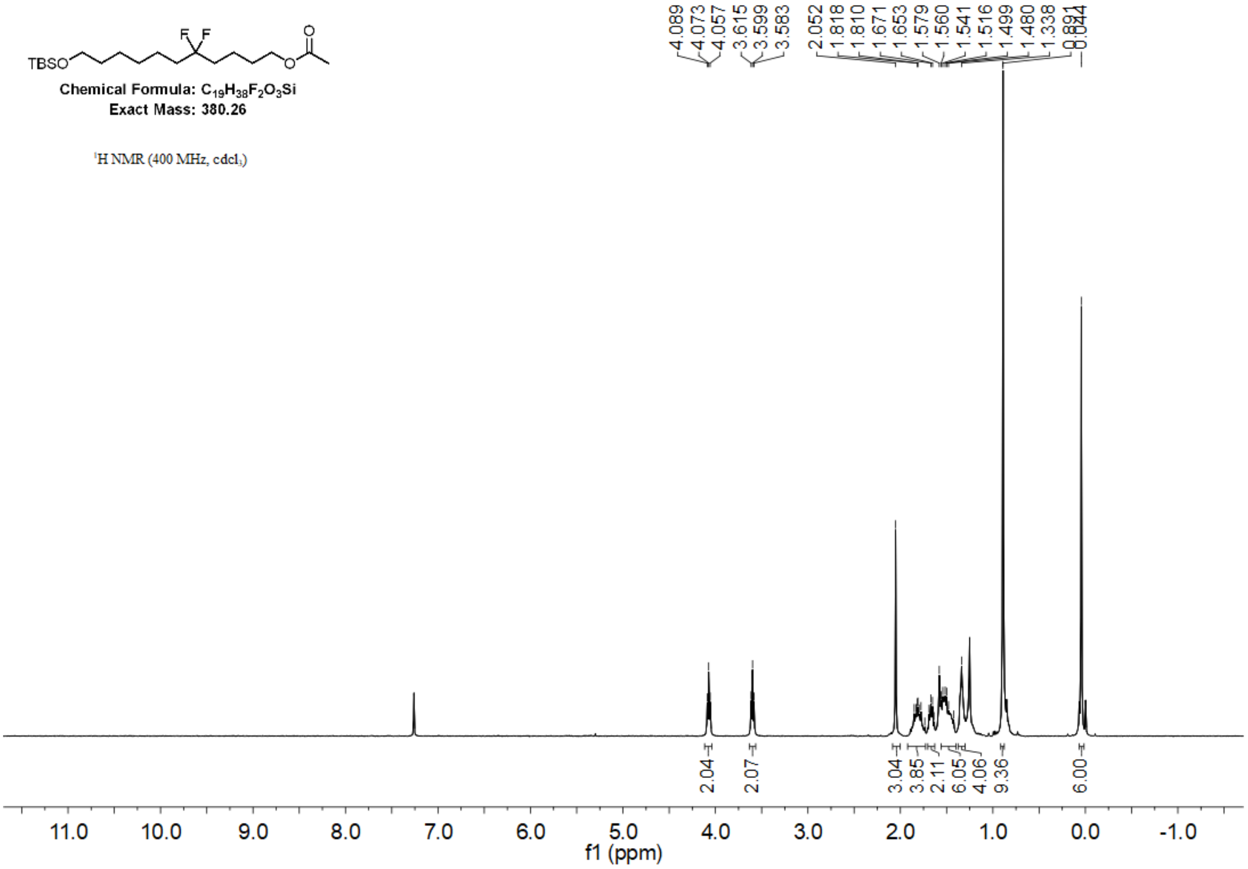
^{19}F NMR (376 MHz, cdcl$_3$)



Chemical Formula: $C_{16}H_{22}F_2O_2$
Exact Mass: 284.1588

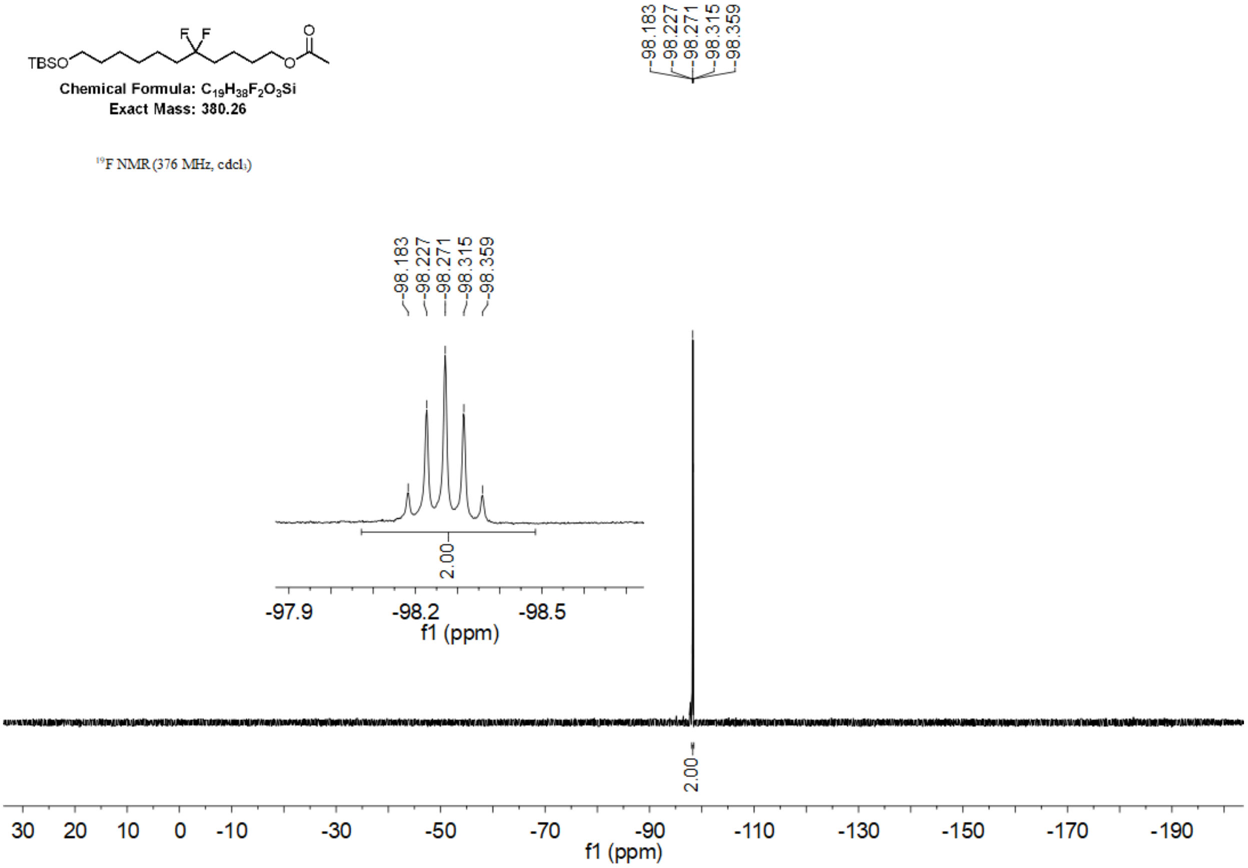
^{13}C NMR (126 MHz, CDCl$_3$)

11-((*tert*-Dutyldimethylsilyl)oxy)-5,5-difluoroundecyl acetate (8e)



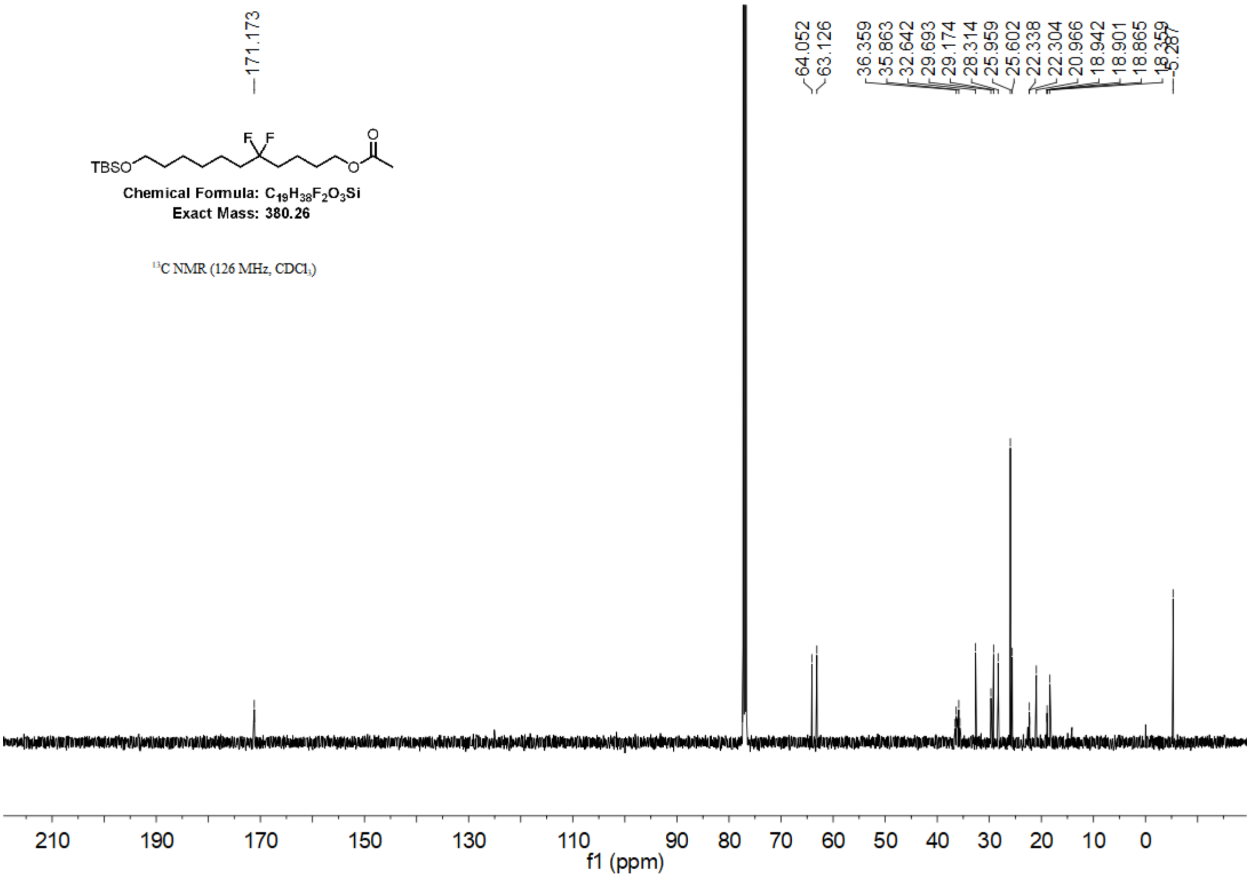
Chemical Formula: $C_{19}H_{38}F_2O_3Si$
Exact Mass: 380.26

^{1}H NMR (400 MHz, cdcl$_3$)

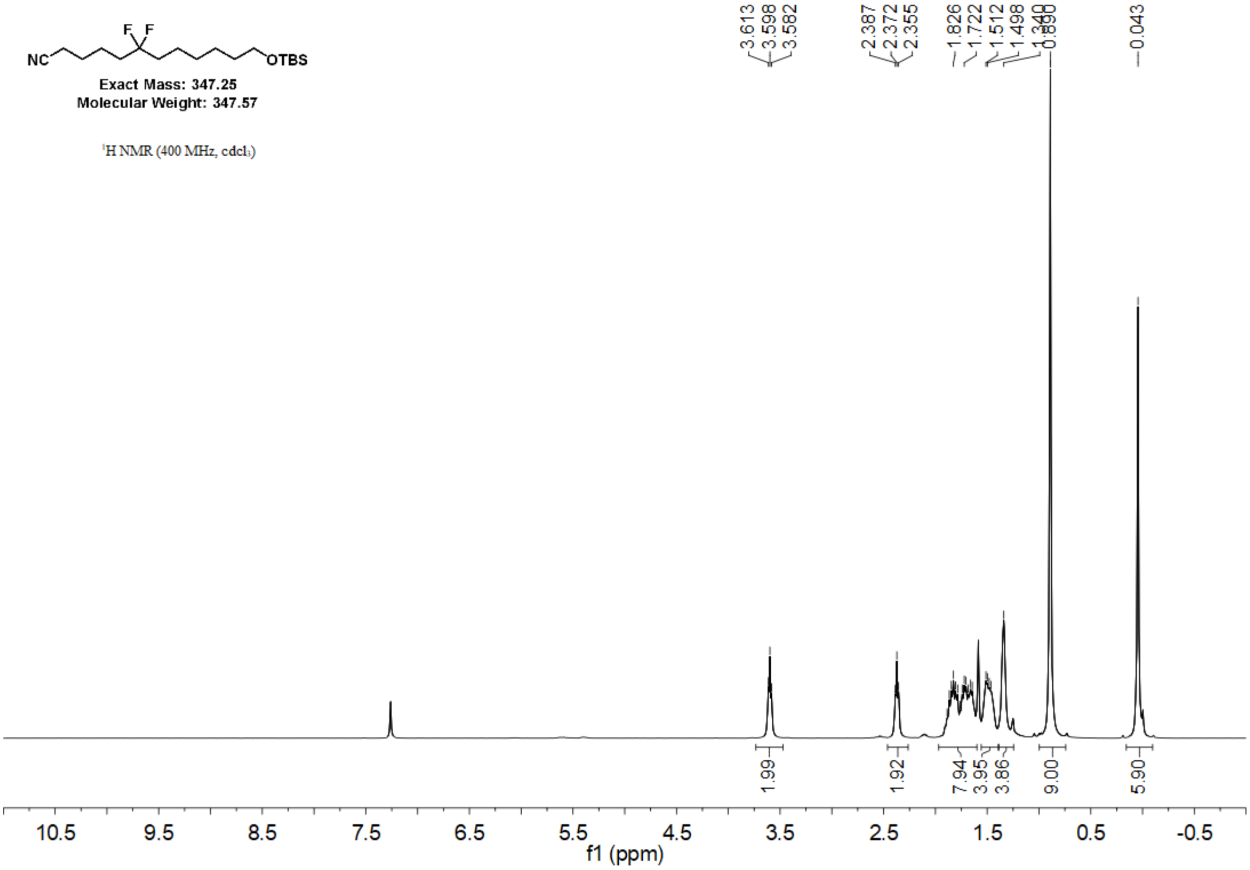


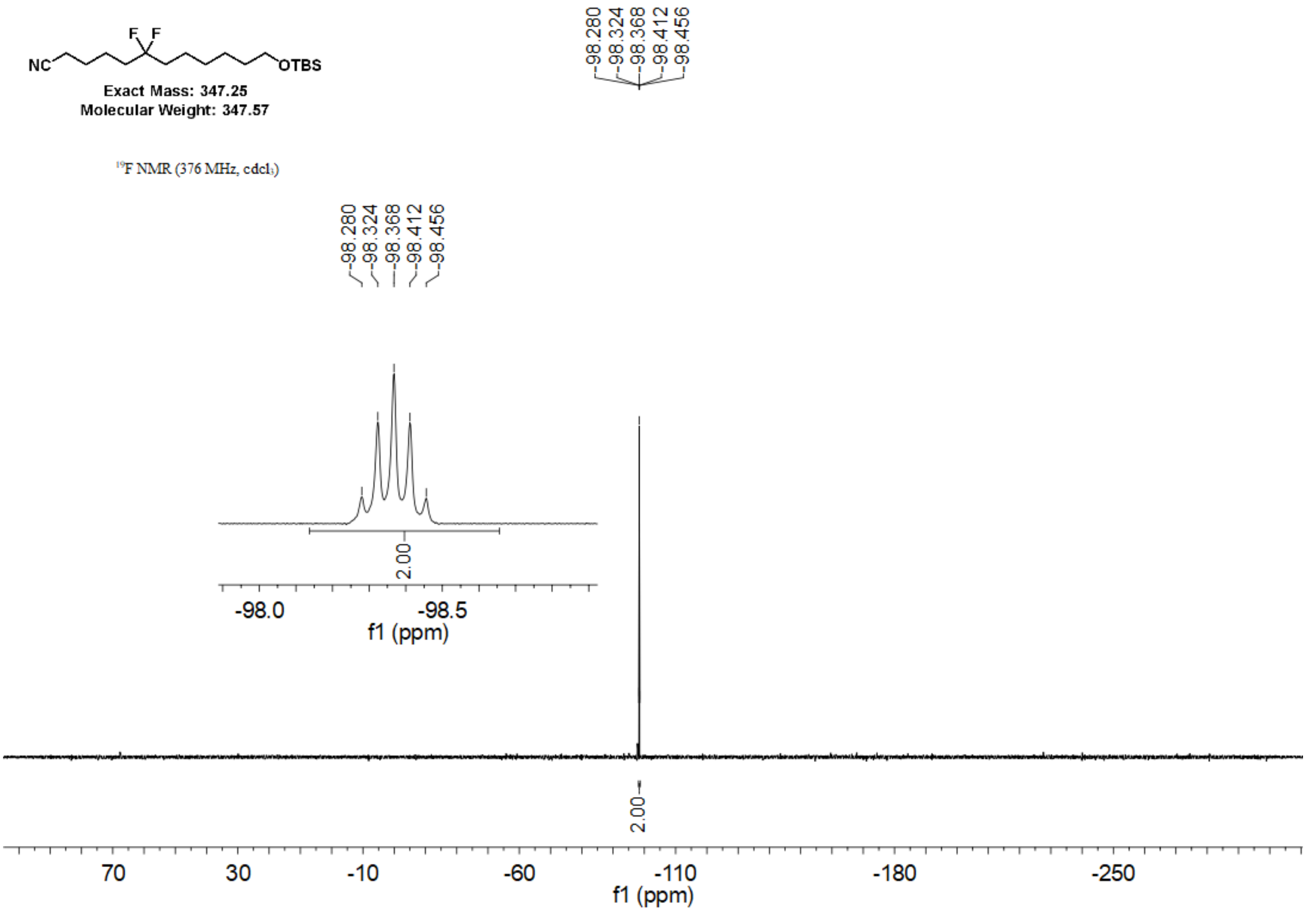
Chemical Formula: $C_{19}H_{38}F_2O_3Si$
Exact Mass: 380.26

^{19}F NMR (376 MHz, cdcl$_3$)



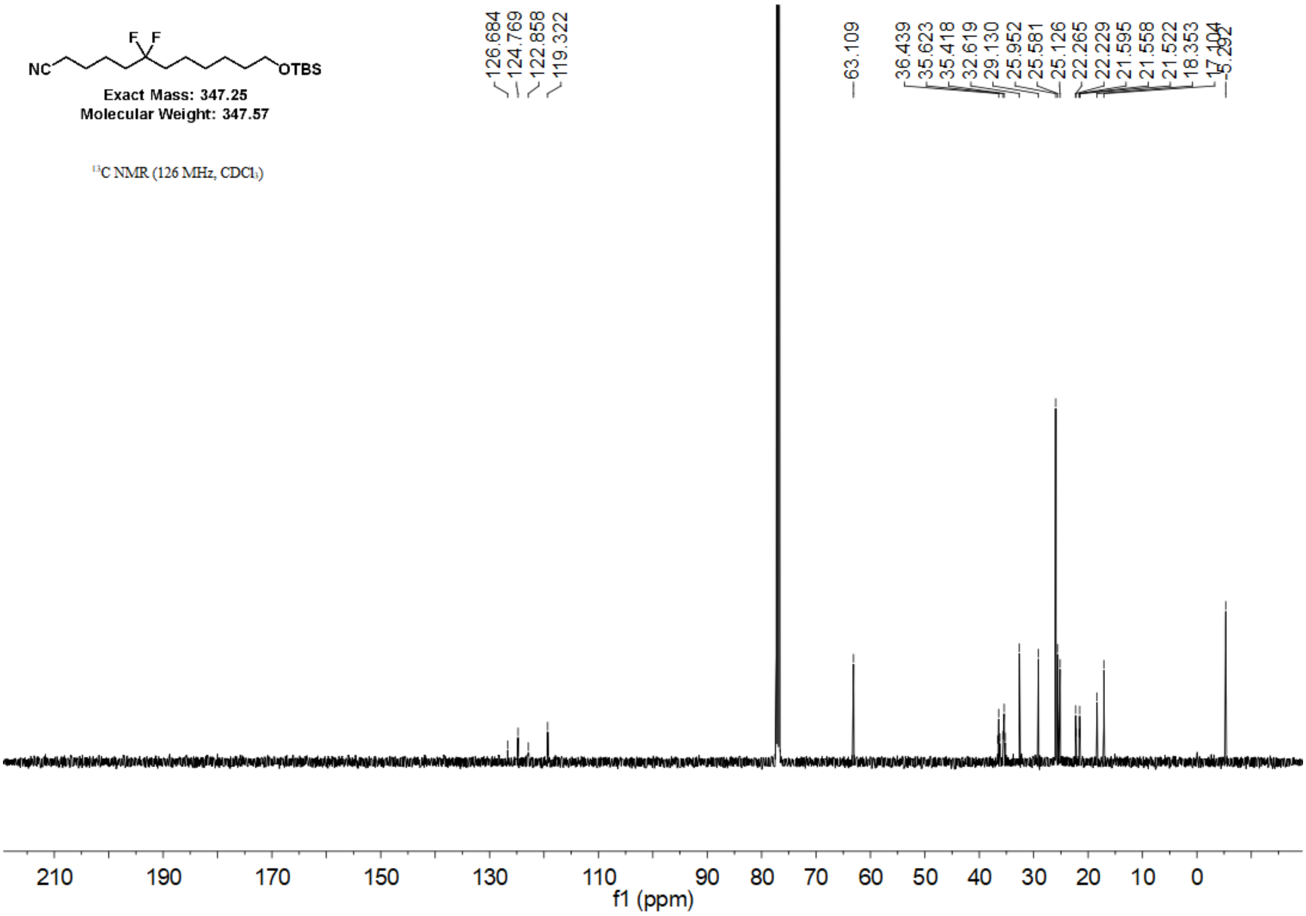
12-((*tert*-Butyldimethylsilyl)oxy)-6,6-difluorododecanenitrile (8f)





Exact Mass: 347.25
Molecular Weight: 347.57

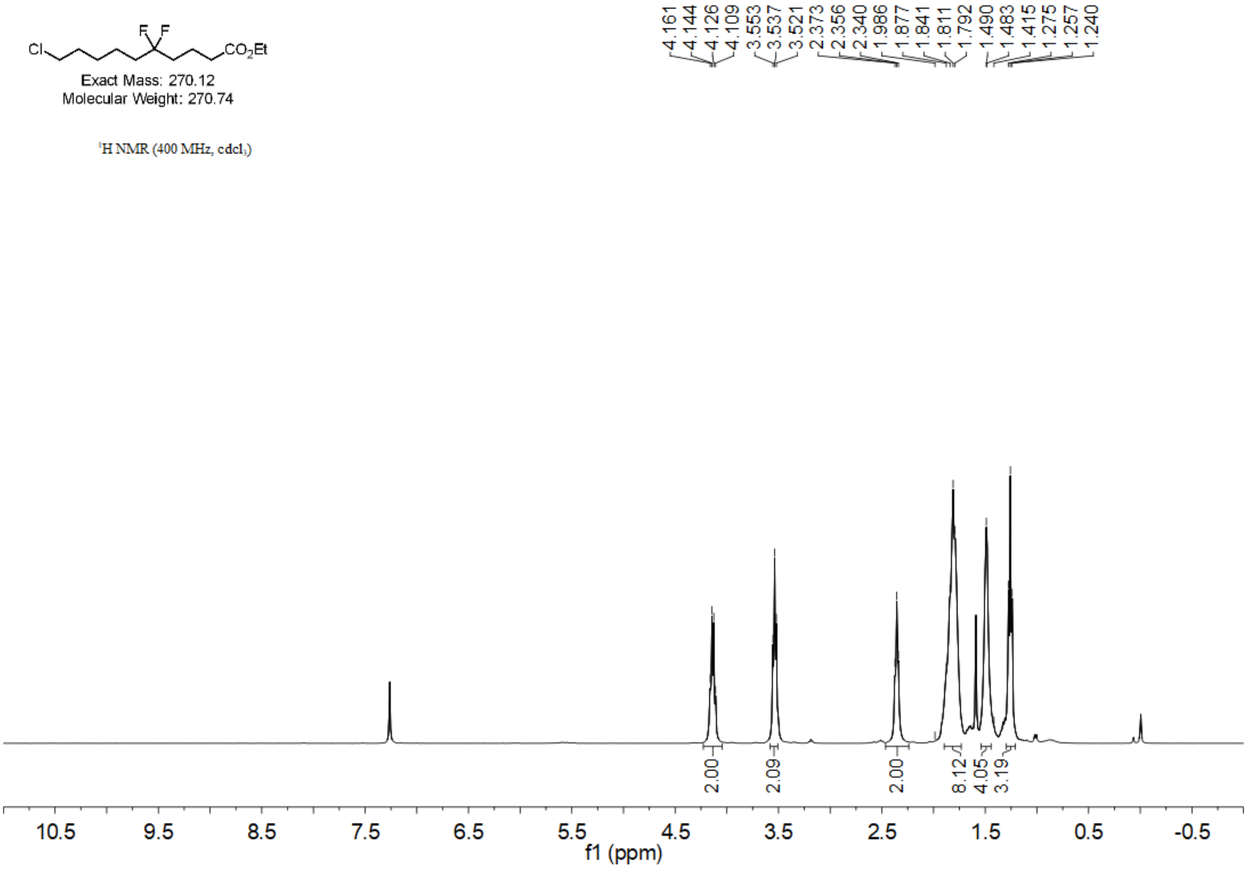
^{19}F NMR (376 MHz, cdcl$_3$)

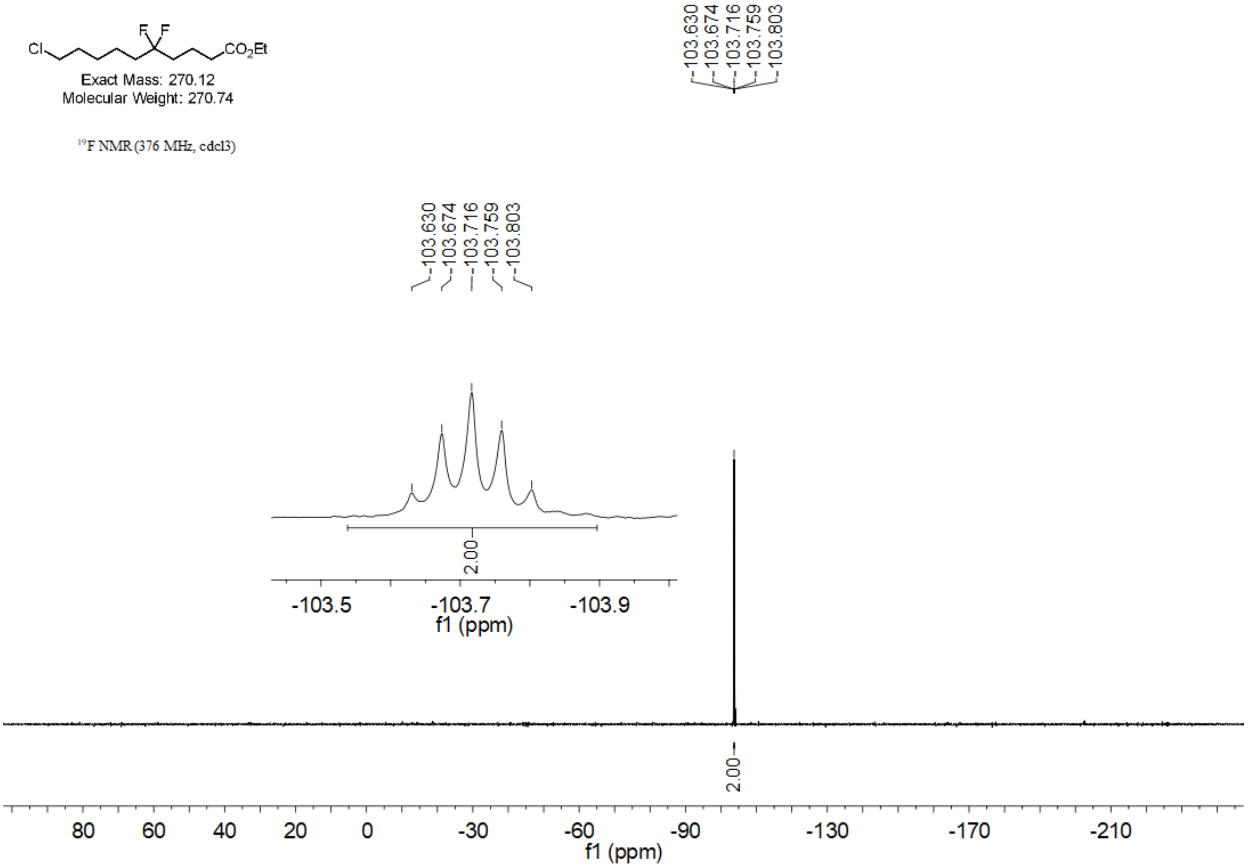


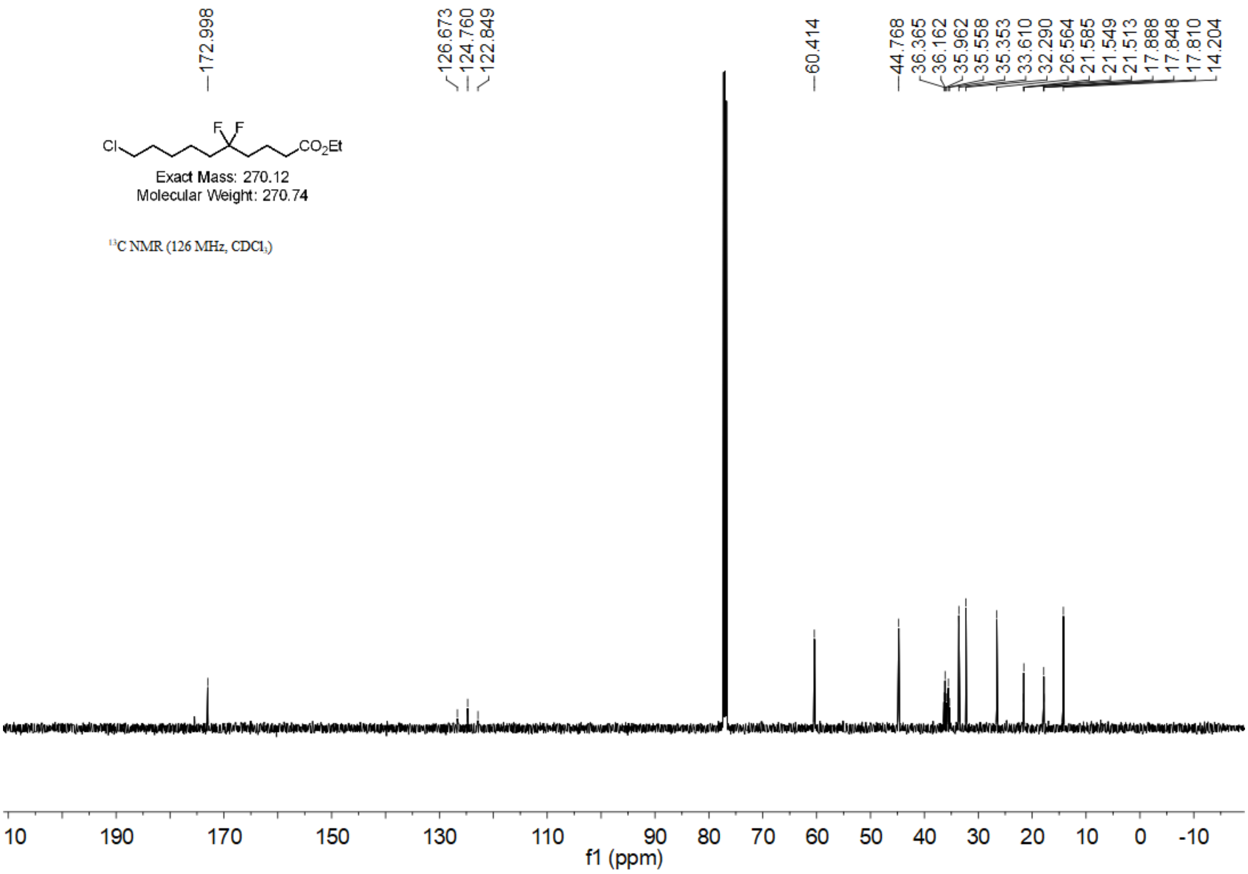
Exact Mass: 347.25
Molecular Weight: 347.57

^{13}C NMR (126 MHz, CDCl$_3$)

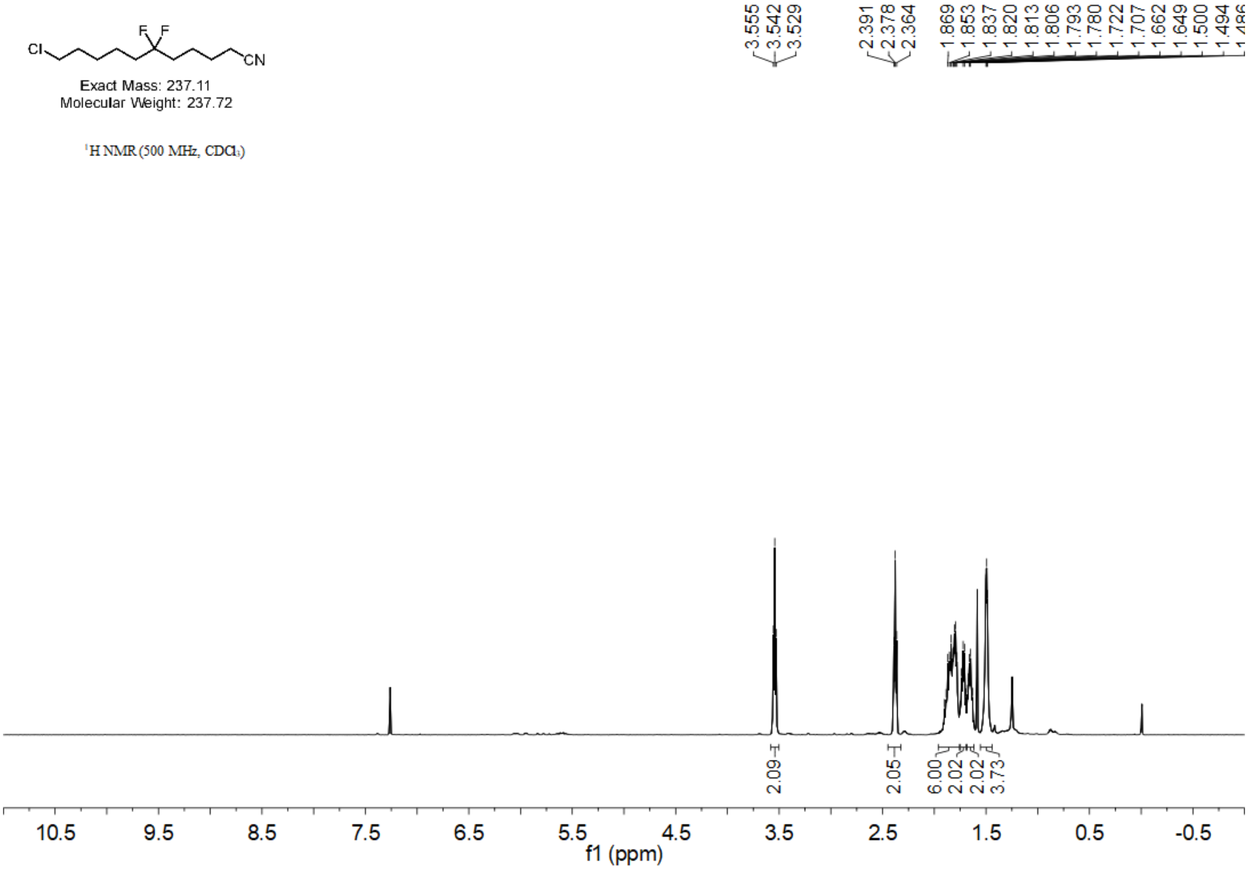
Ethyl 10-chloro-5,5-difluorodecanoate (8g)

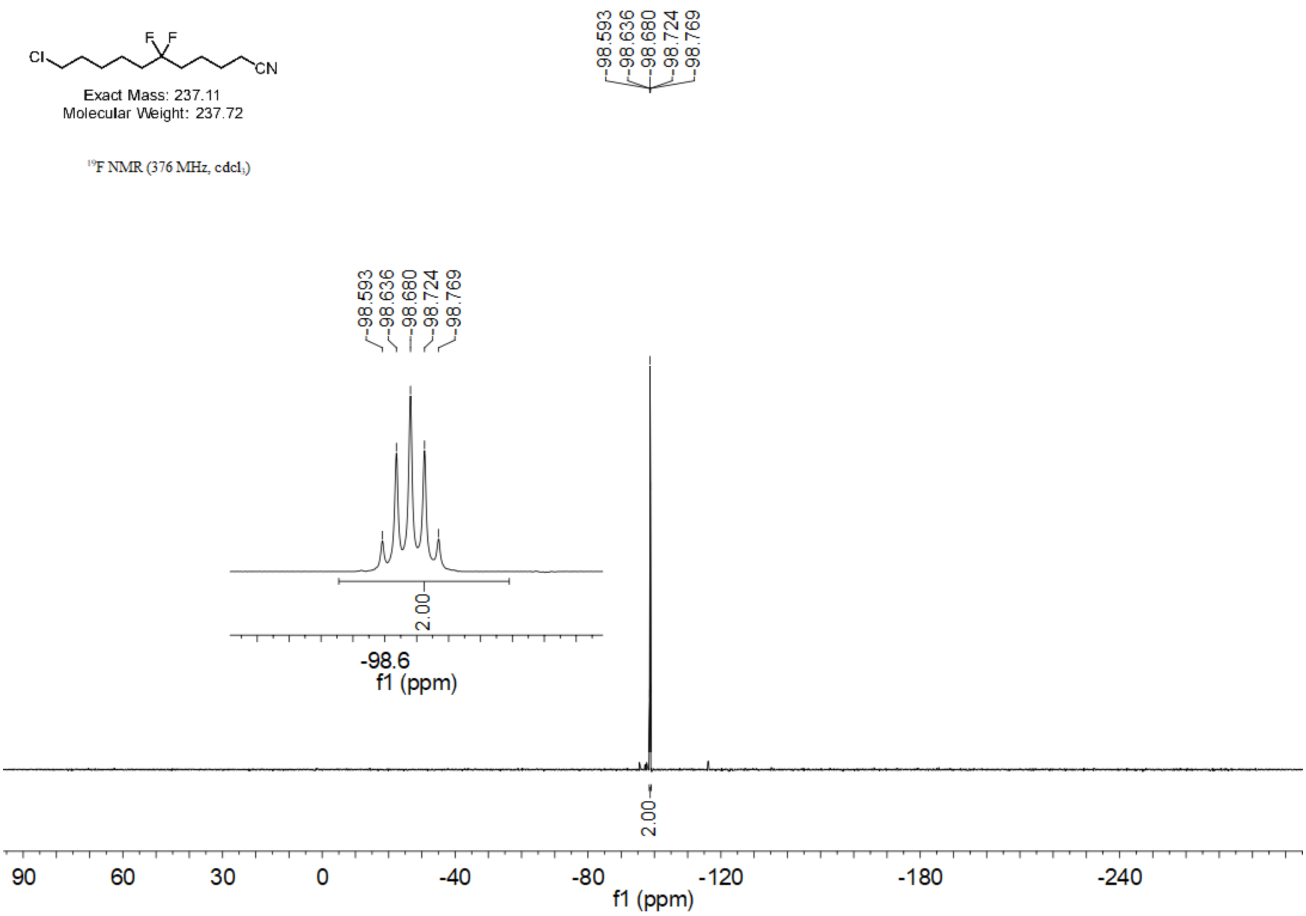


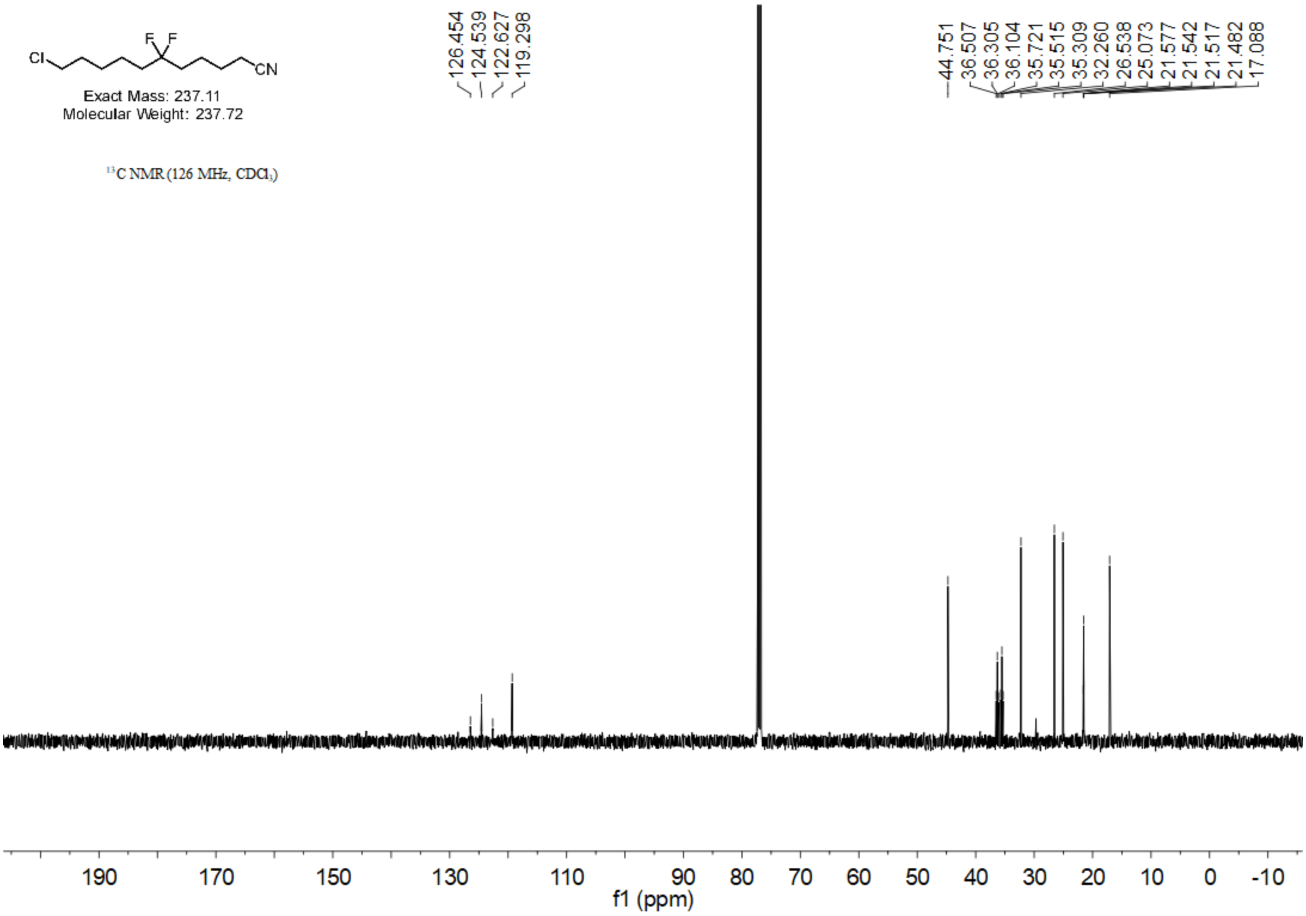




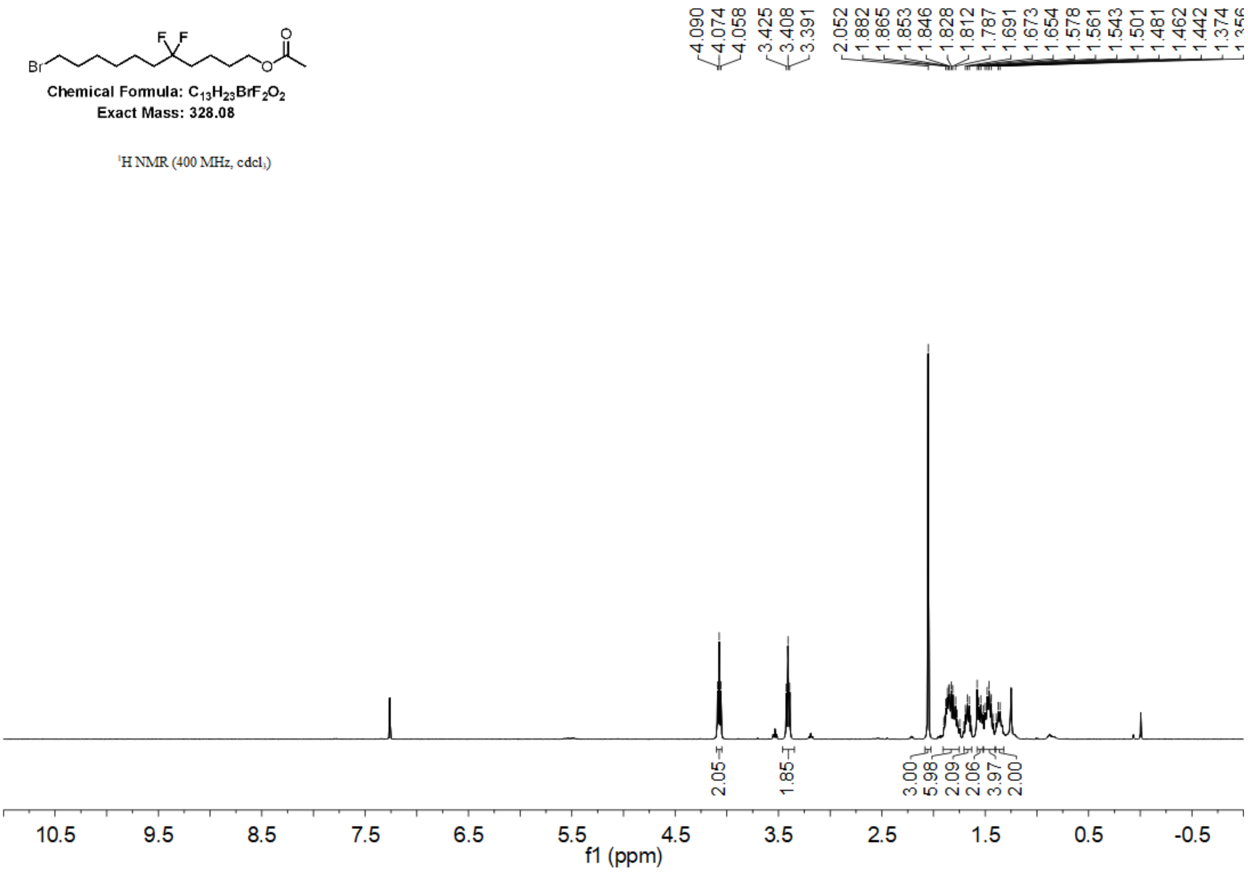
11-Chloro-6,6-difluoroundecanenitrile (8h)




Cl
F F
CN
Exact Mass: 237.11
Molecular Weight: 237.72
^{19}F NMR (376 MHz, cdcl$_3$)
-98.593
-98.636
-98.680
-98.724
-98.769
2.00
-98.6
f1 (ppm)
2.00
90
60
30
0
-40
-80
-120
-180
-240
f1 (ppm)

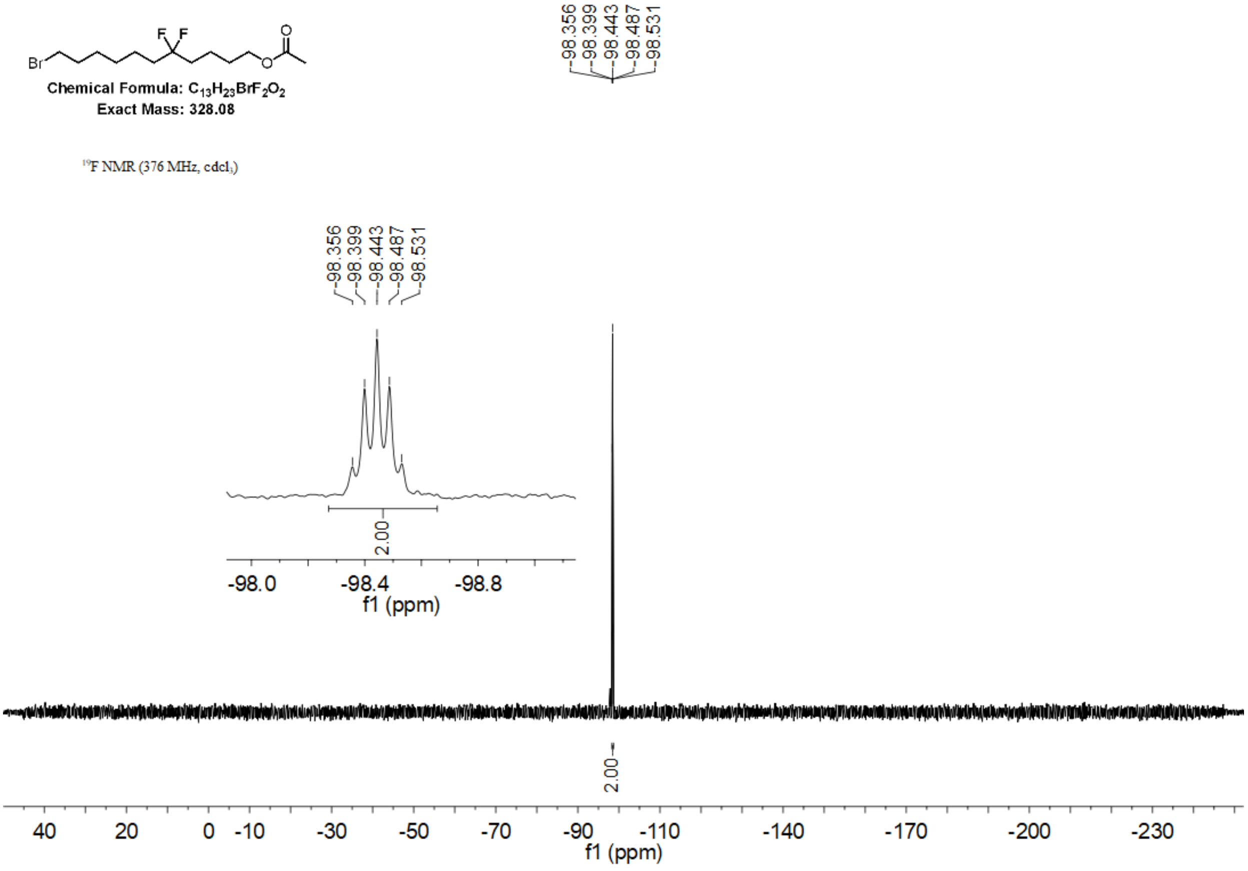

Cl
F F
CN
Exact Mass: 237.11
Molecular Weight: 237.72
^{13}C NMR (126 MHz, CDCl$_3$)
126.454
124.539
122.627
119.298
44.751
36.507
36.305
36.104
35.721
35.515
35.309
32.260
26.538
25.073
21.577
21.542
21.517
21.482
17.088
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

11-Bromo-5,5-difluoroundecyl acetate (8i)



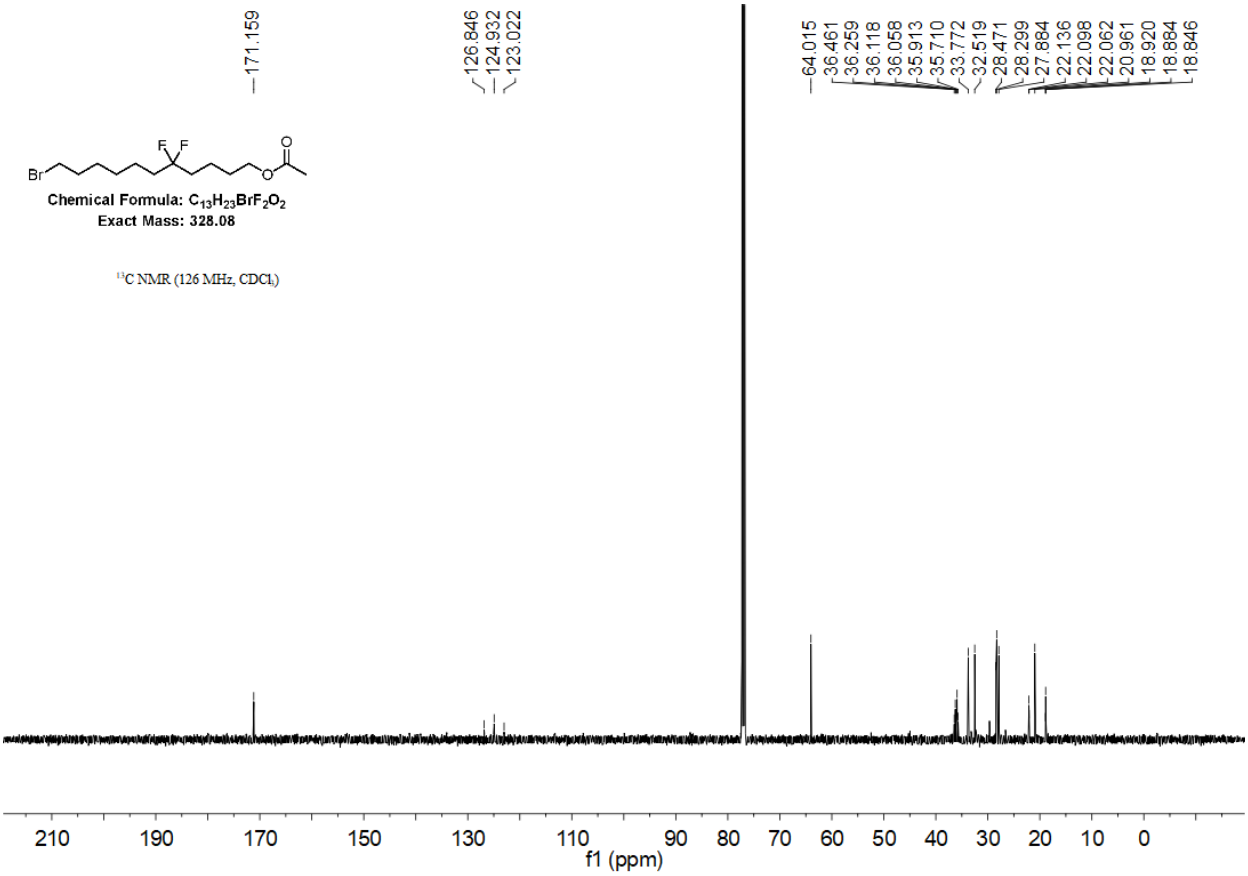
Chemical Formula: $C_{13}H_{23}BrF_2O_2$
Exact Mass: 328.08

^{1}H NMR (400 MHz, cdcl$_3$)

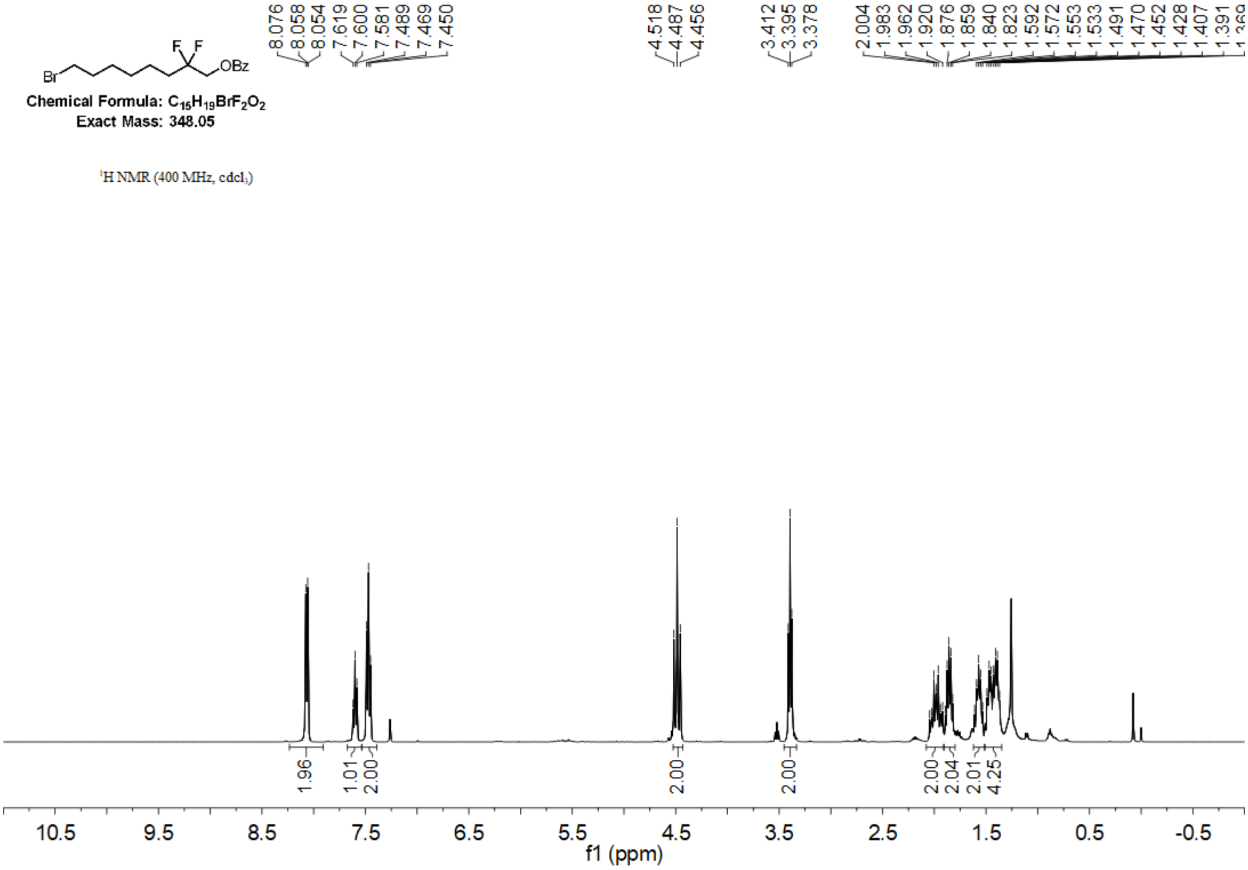


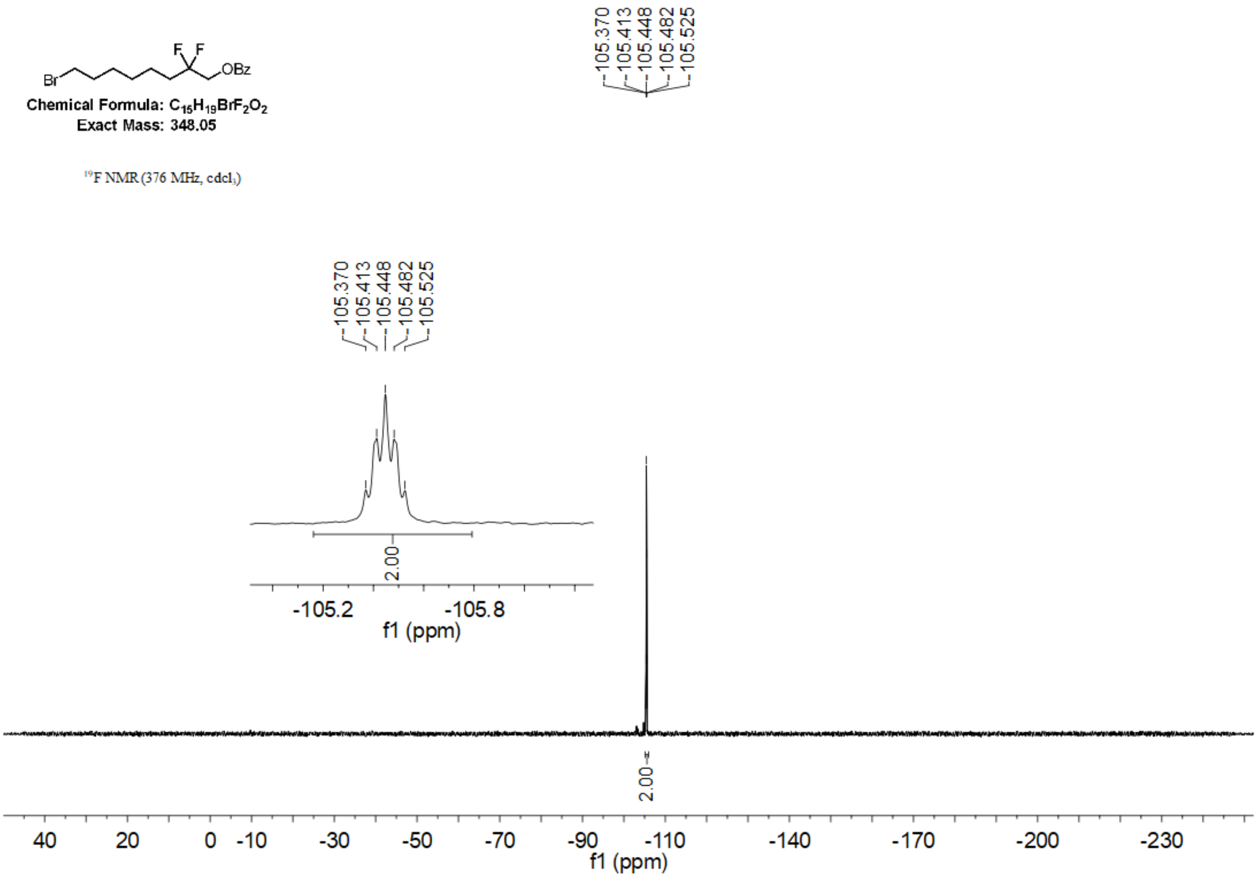
Chemical Formula: $C_{13}H_{23}BrF_2O_2$
Exact Mass: 328.08

^{19}F NMR (376 MHz, cdcl$_3$)



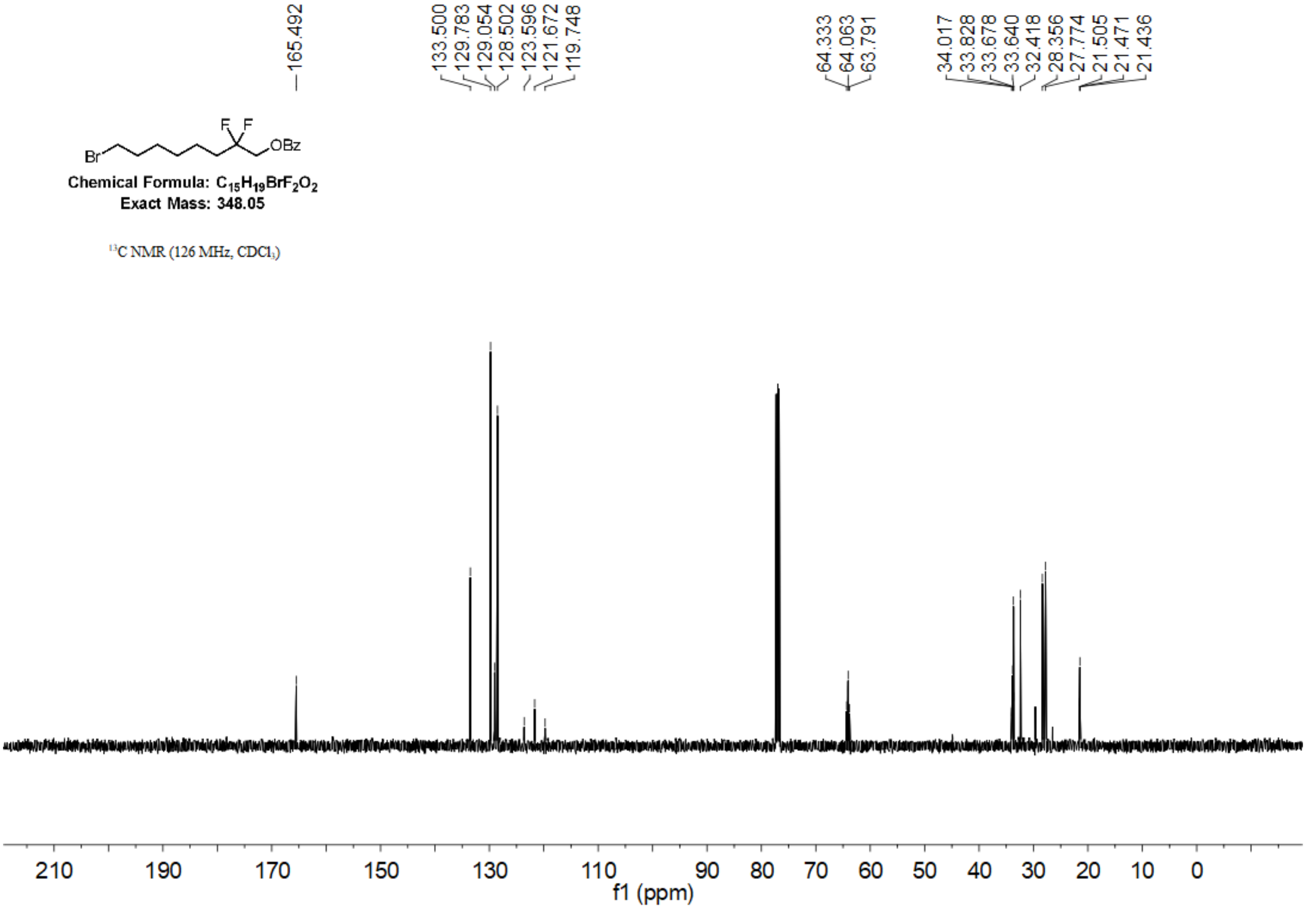
8-Bromo-2,2-difluorooctyl benzoate (8j)





Chemical Formula: $C_{15}H_{19}BrF_2O_2$
Exact Mass: 348.05

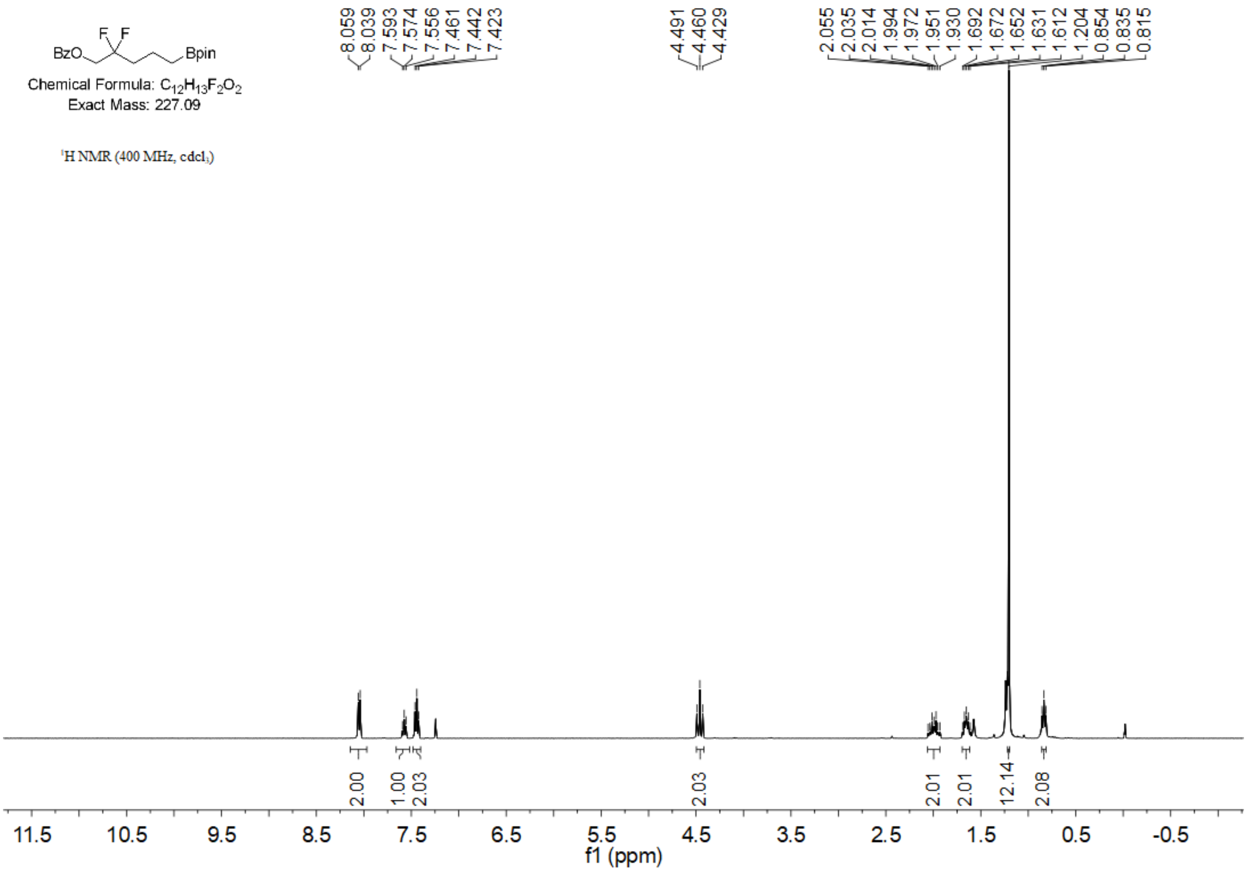
^{19}F NMR (376 MHz, cdcl$_3$)

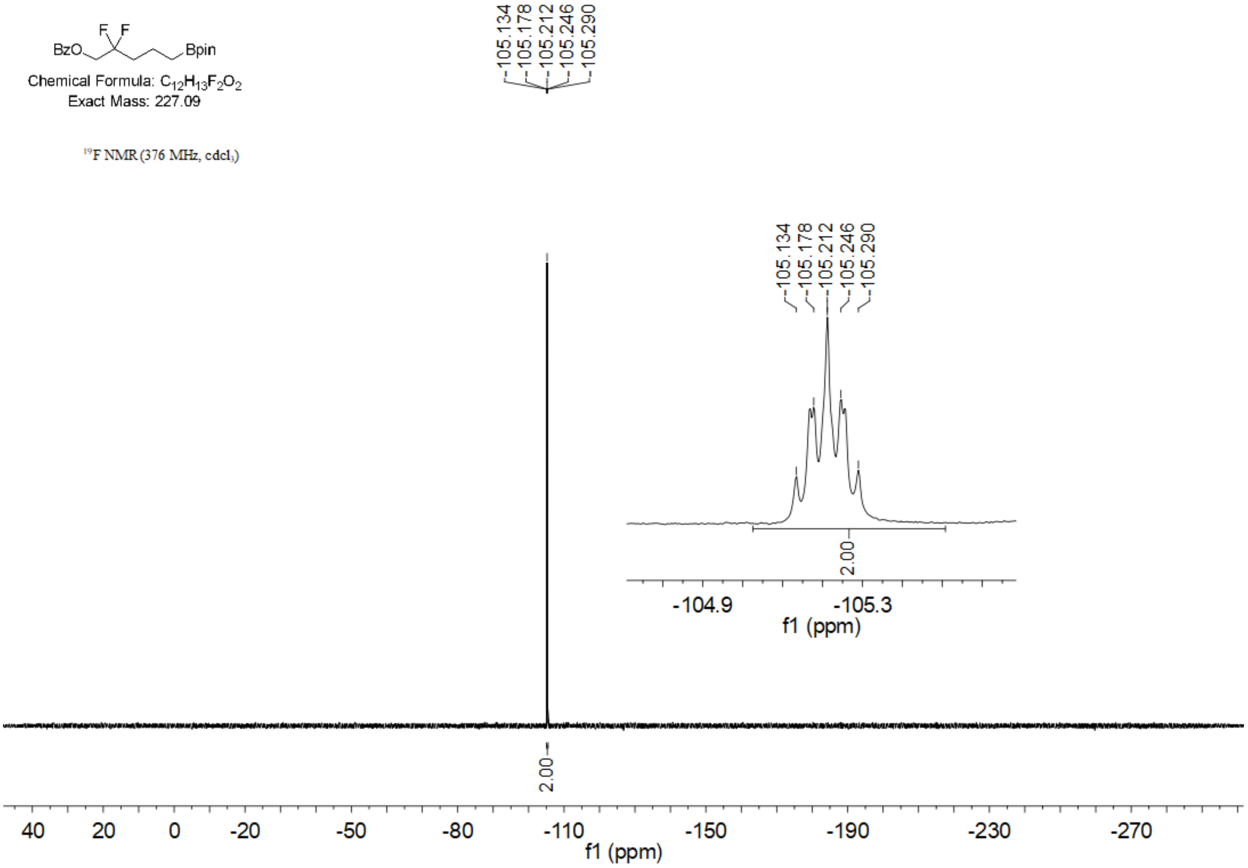


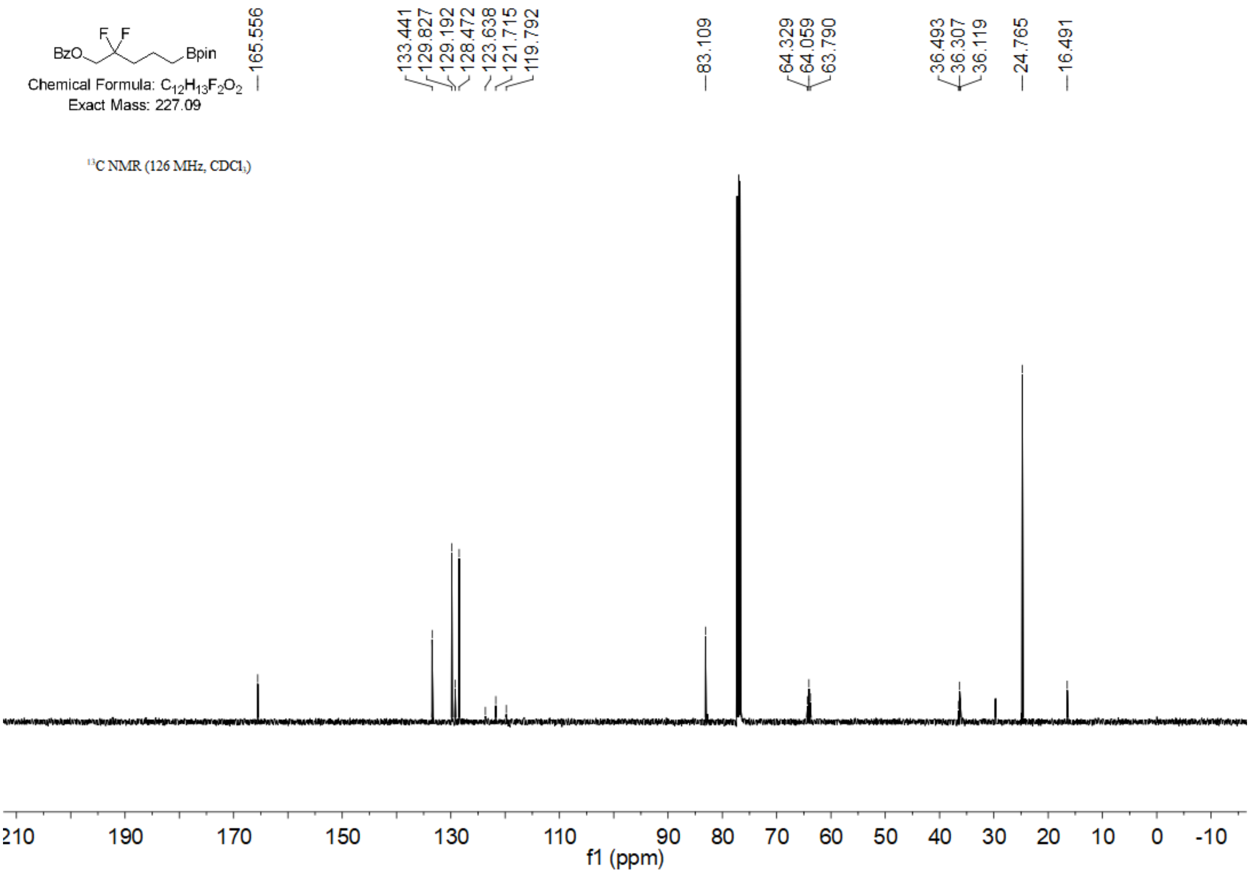
Chemical Formula: $C_{15}H_{19}BrF_2O_2$
Exact Mass: 348.05

^{13}C NMR (126 MHz, CDCl$_3$)

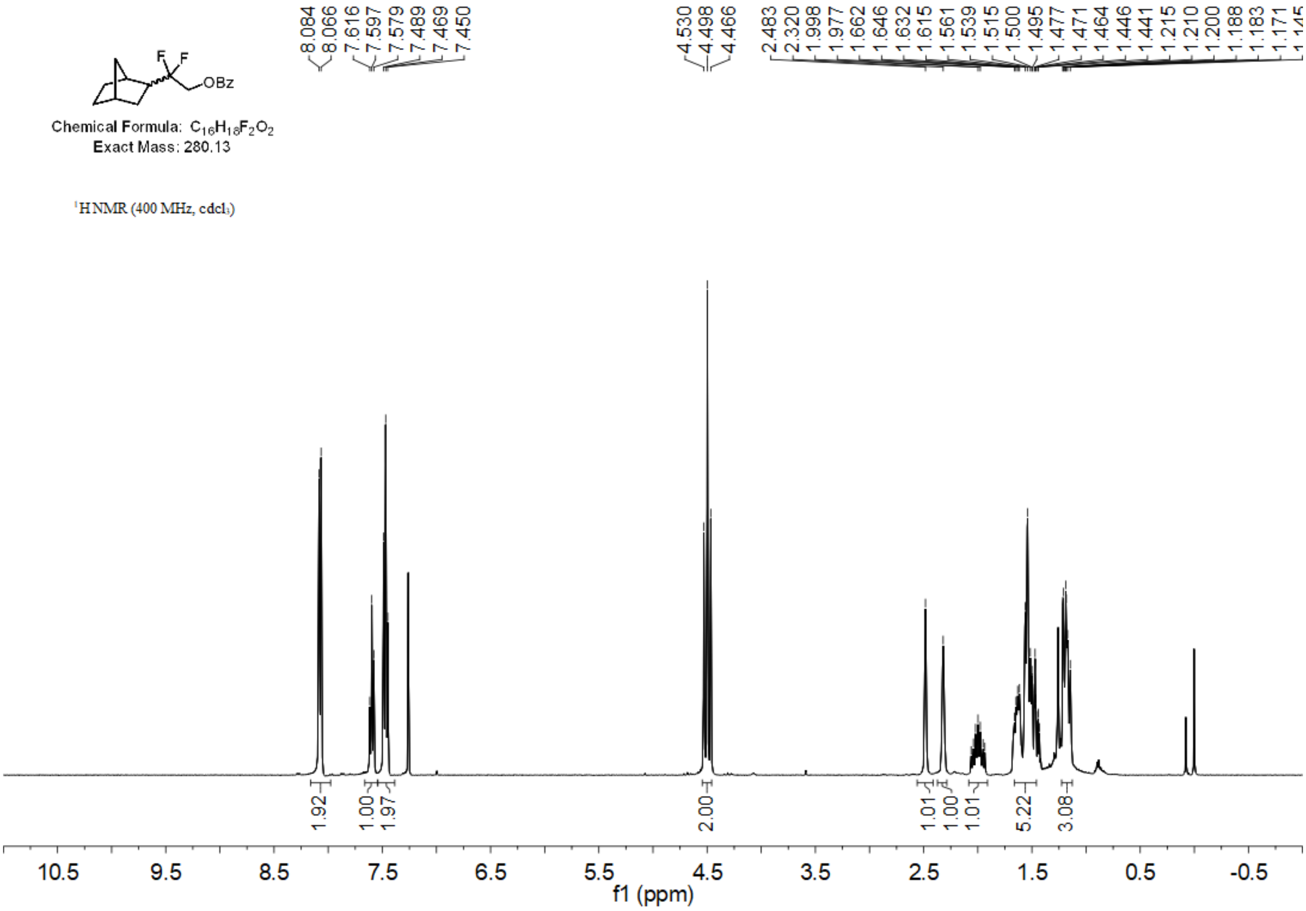
2,2-Difluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl benzoate (8k)

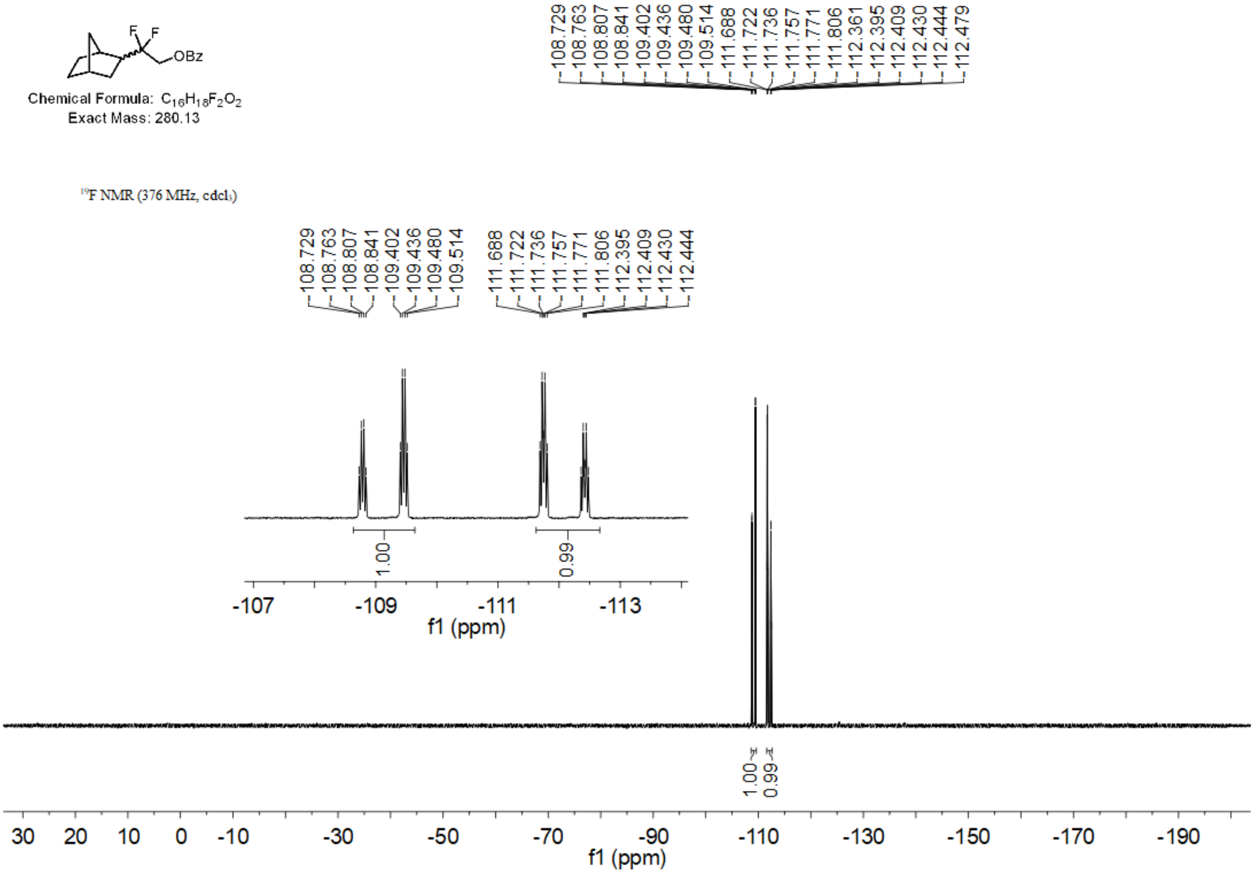






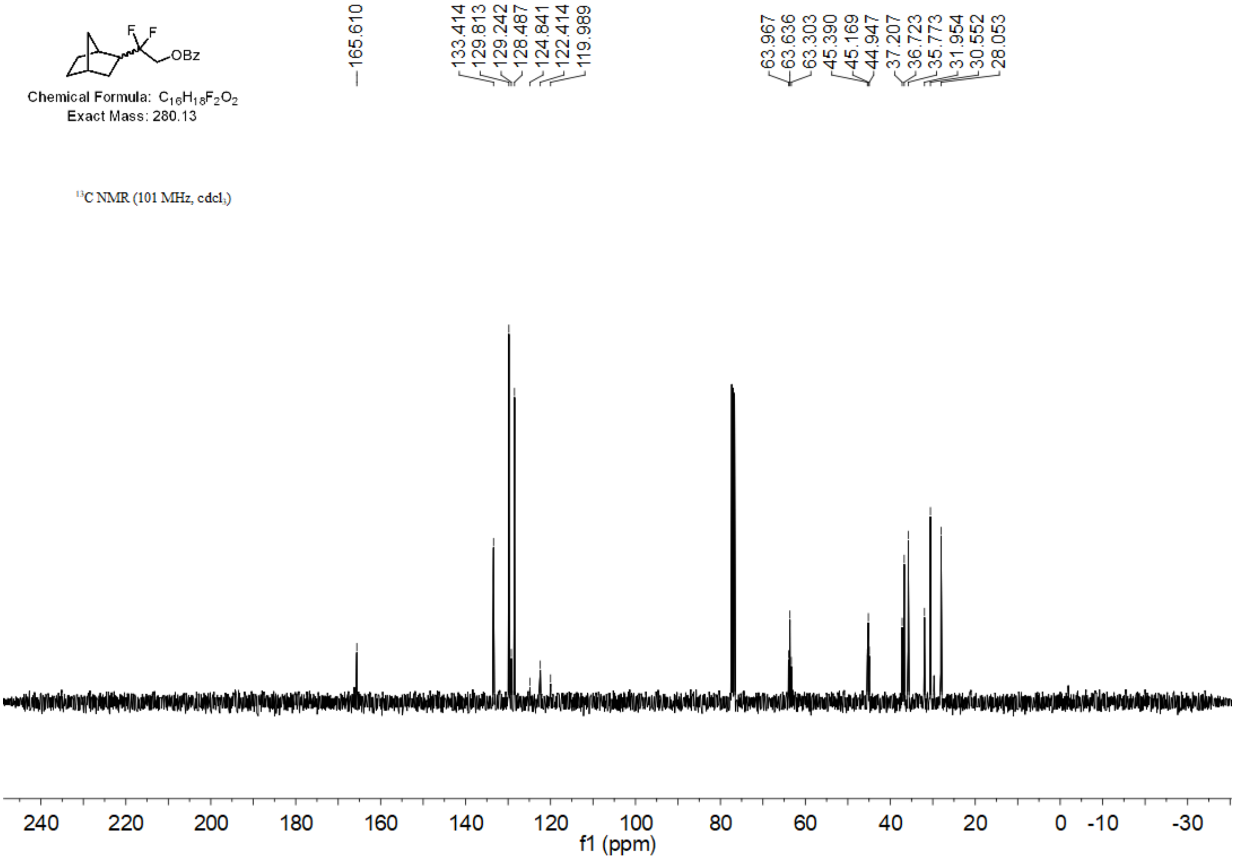
2-((1*S*,4*R*)-Bicyclo[2.2.1]heptan-2-yl)-2,2-difluoroethyl benzoate (8l)





Chemical Formula: $C_{16}H_{18}F_2O_2$
Exact Mass: 280.13

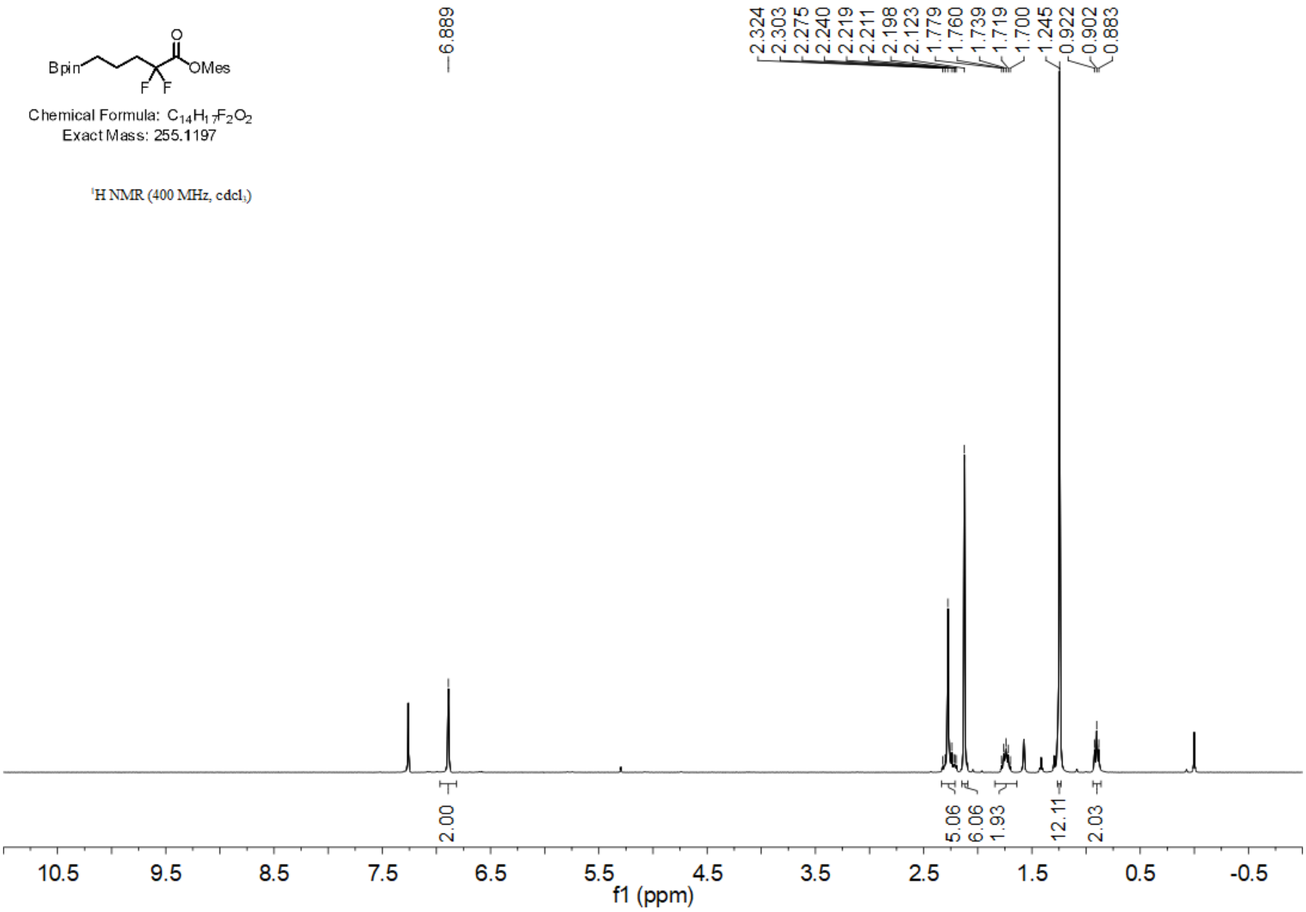
^{19}F NMR (376 MHz, cdcl$_3$)

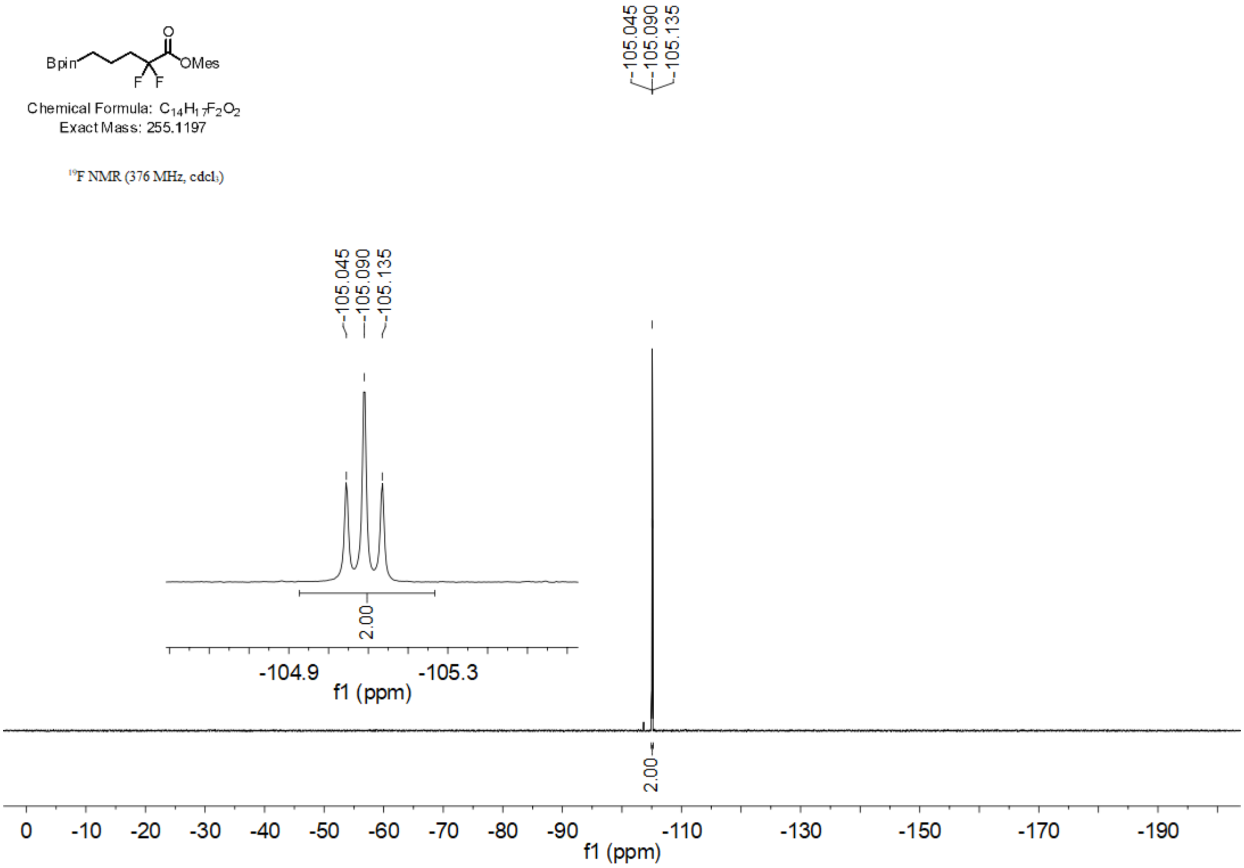


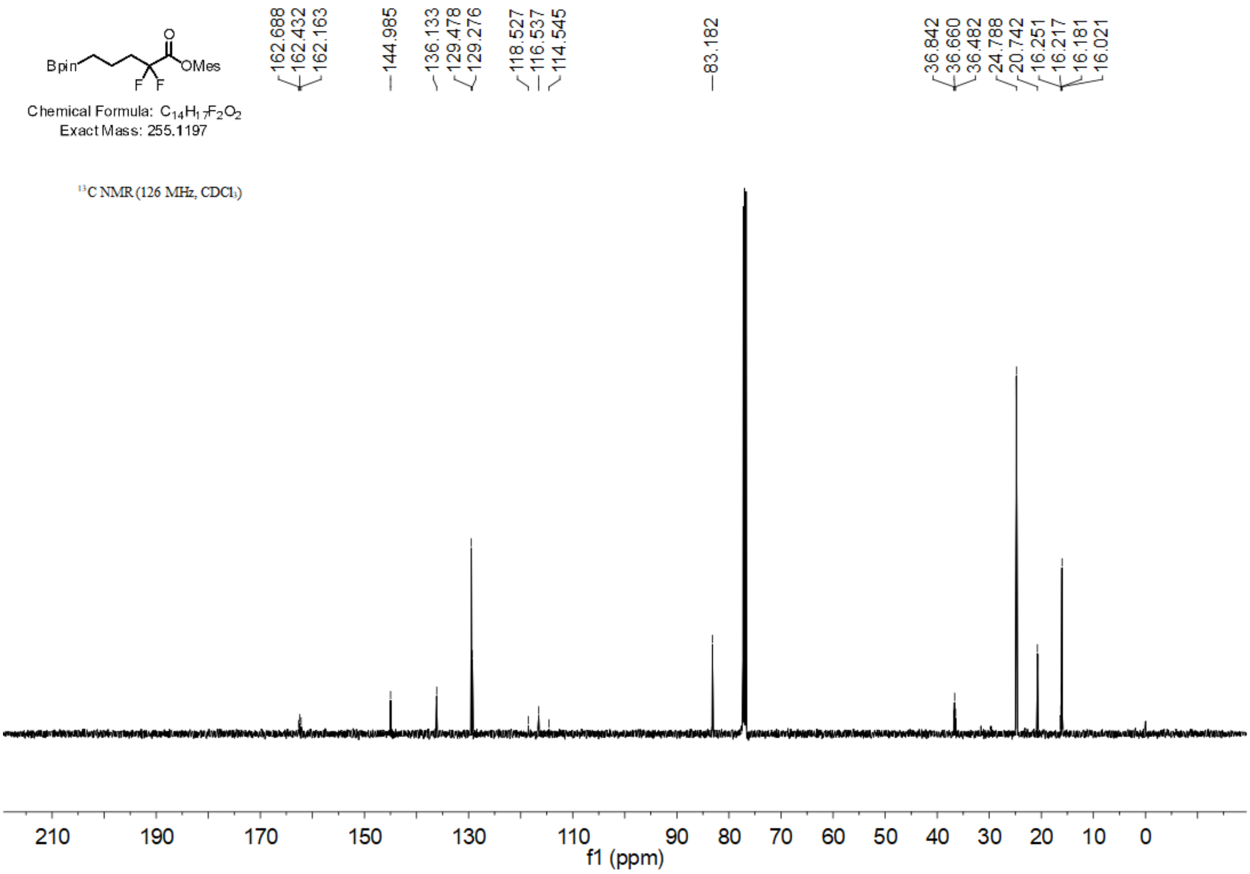
Chemical Formula: $C_{16}H_{18}F_2O_2$
Exact Mass: 280.13

^{13}C NMR (101 MHz, cdcl$_3$)

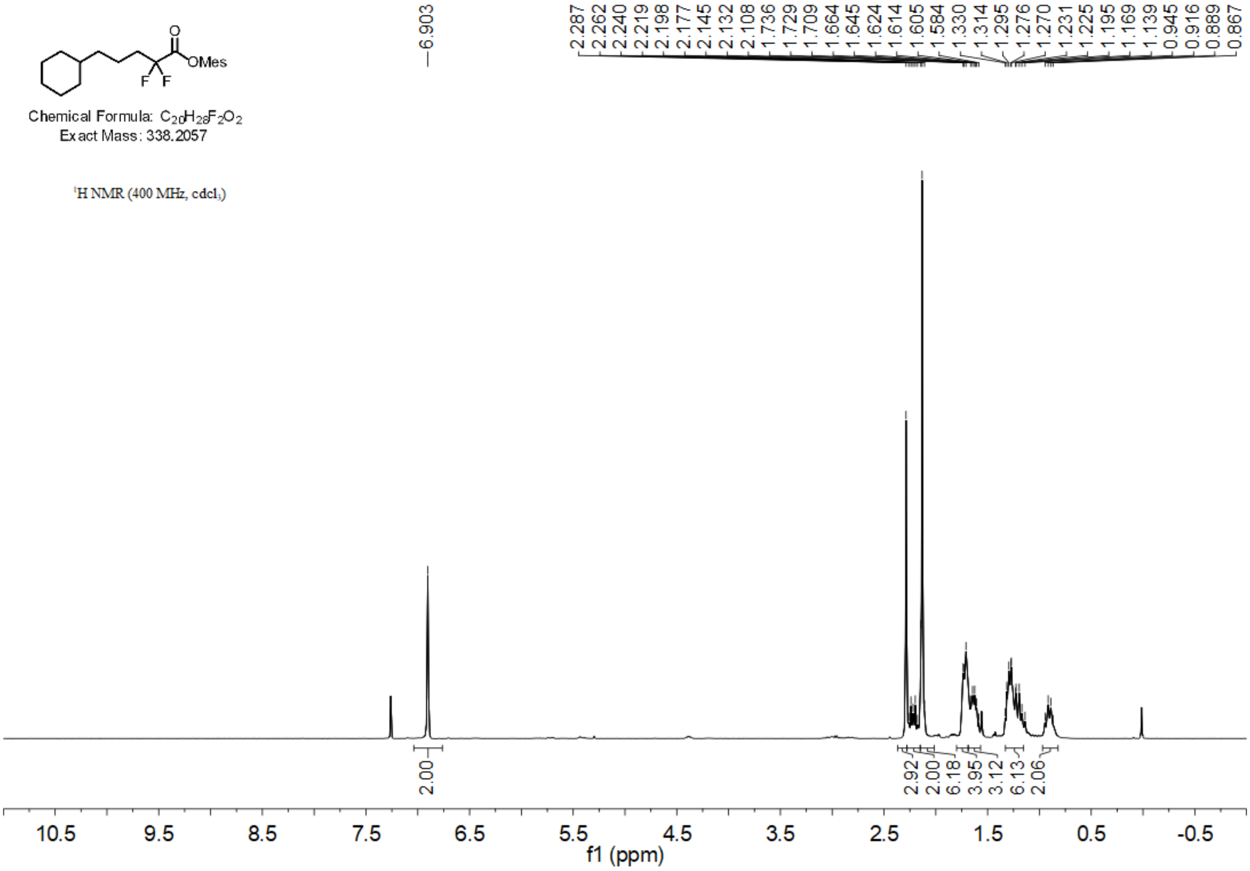
Mesityl 2,2-difluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (8m)

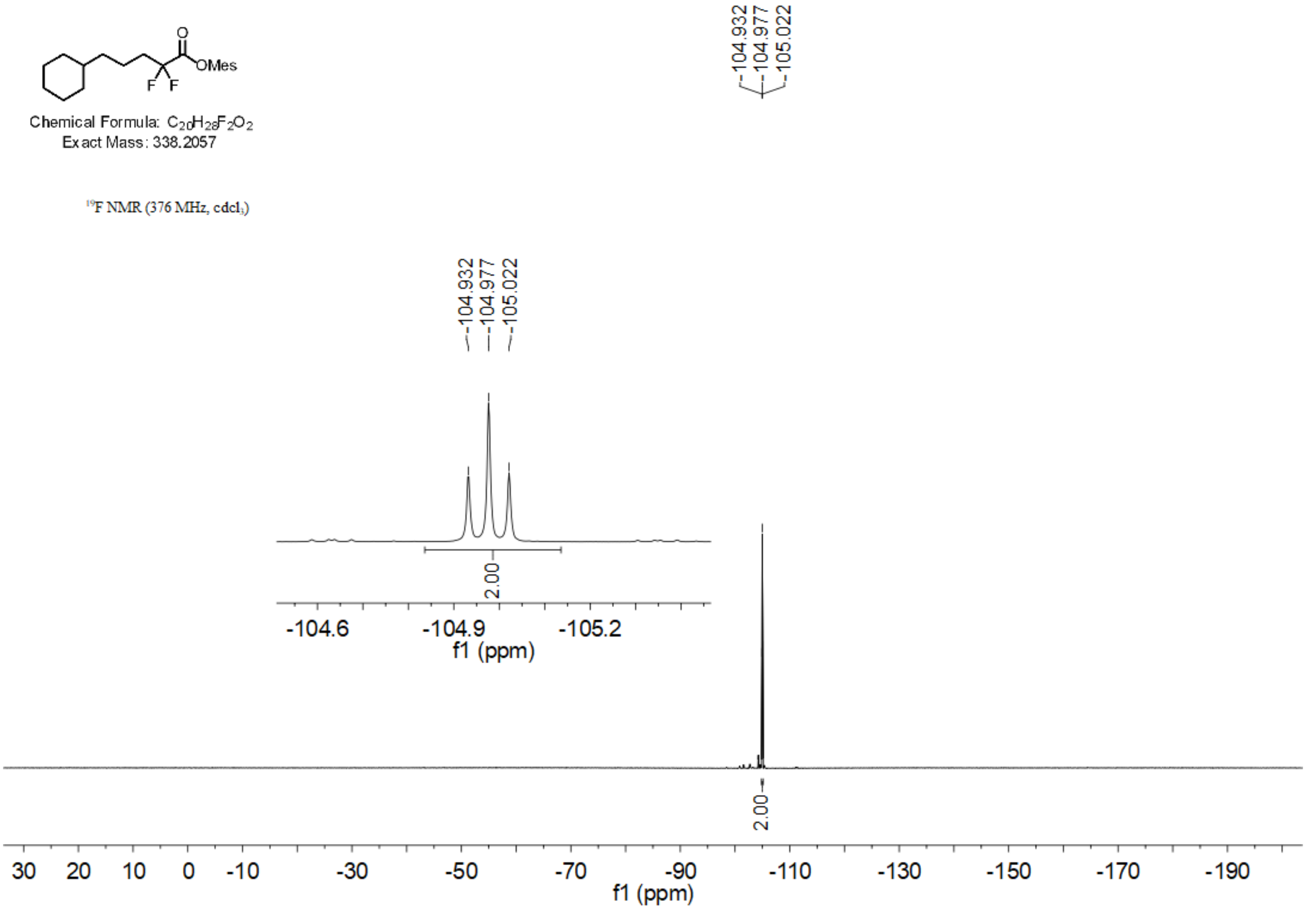






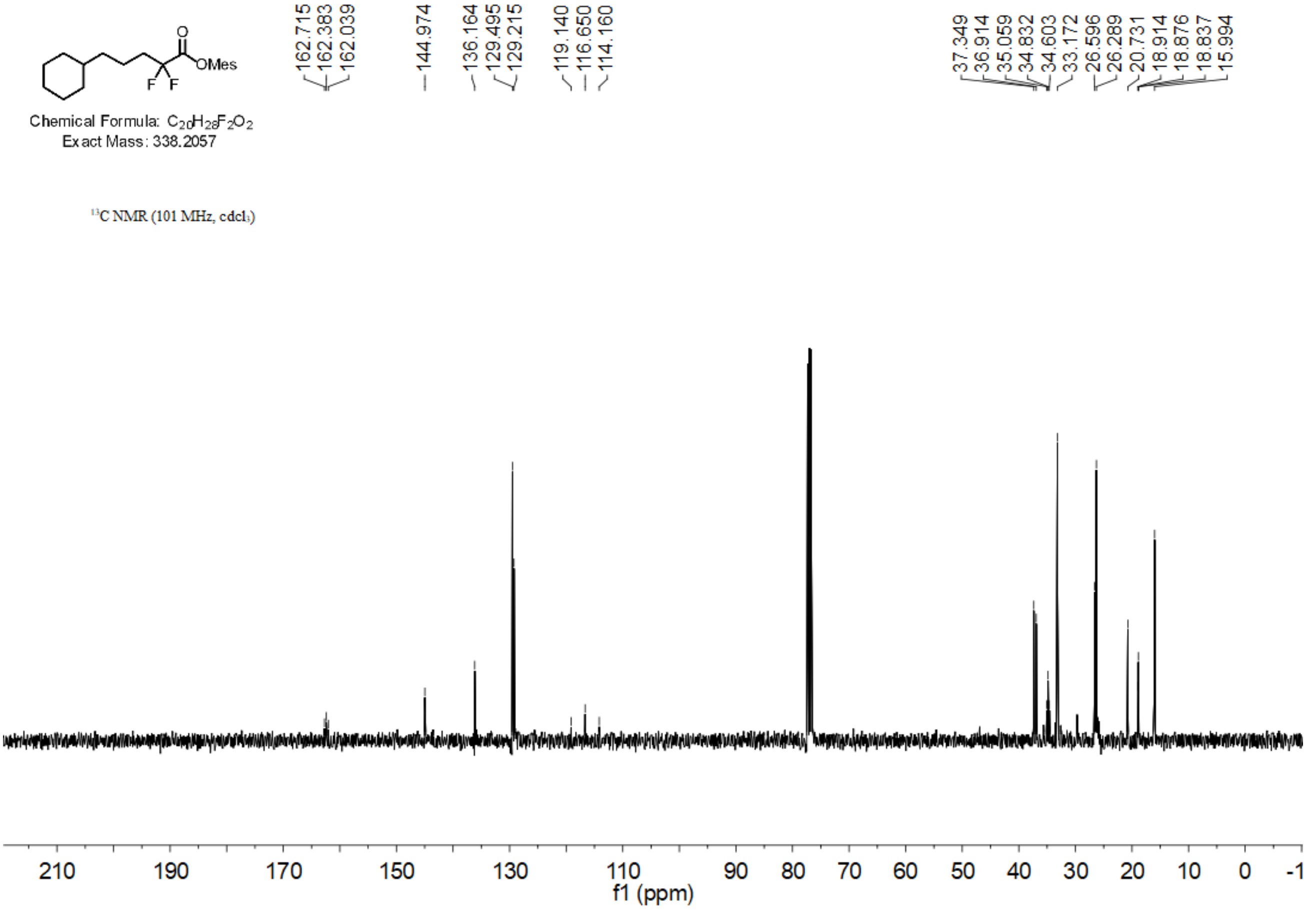
Mesityl 5-cyclohexyl-2,2-difluoropentanoate (8n)





Chemical Formula: $C_{20}H_{28}F_2O_2$
Exact Mass: 338.2057

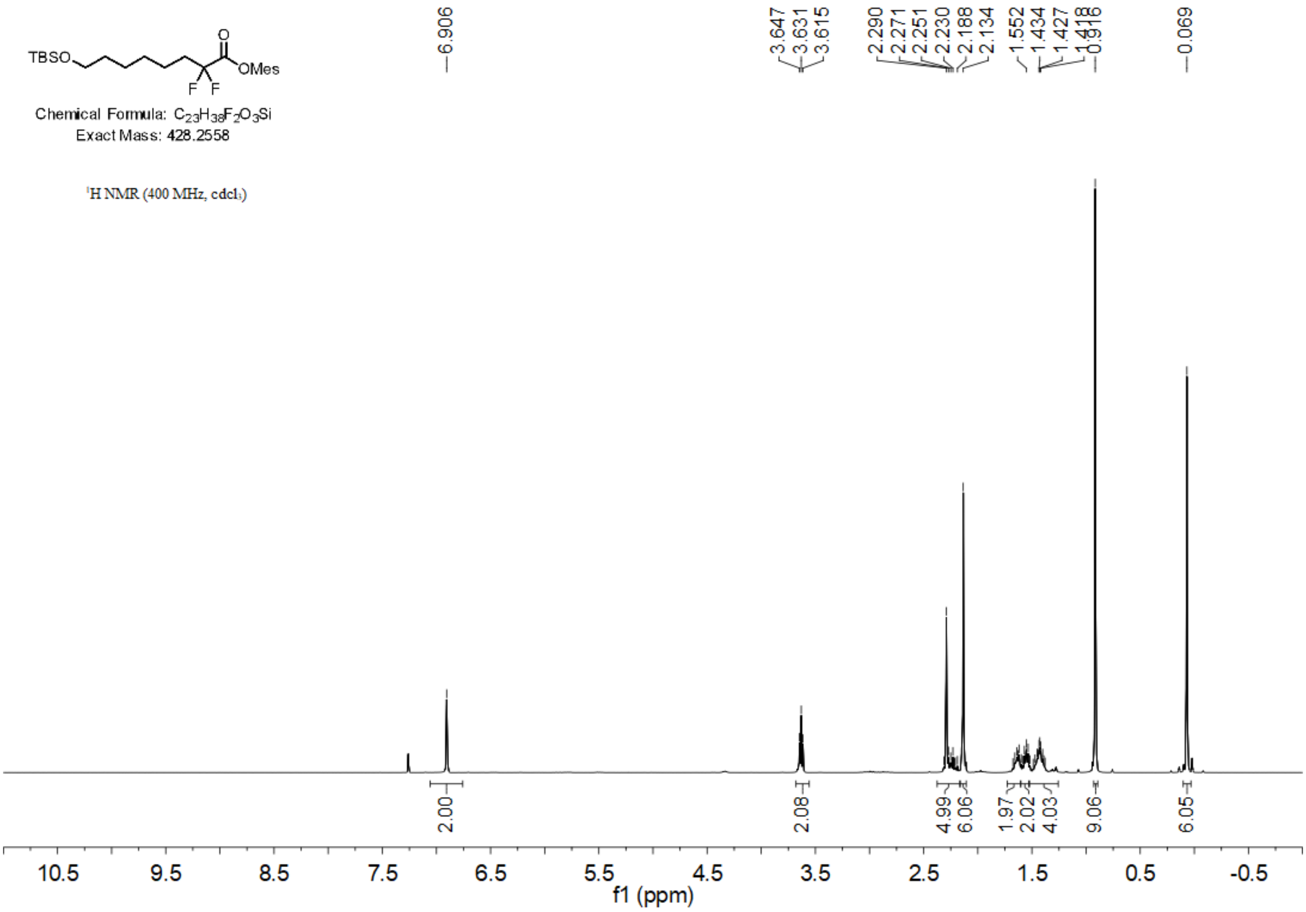
^{19}F NMR (376 MHz, cdcl$_3$)

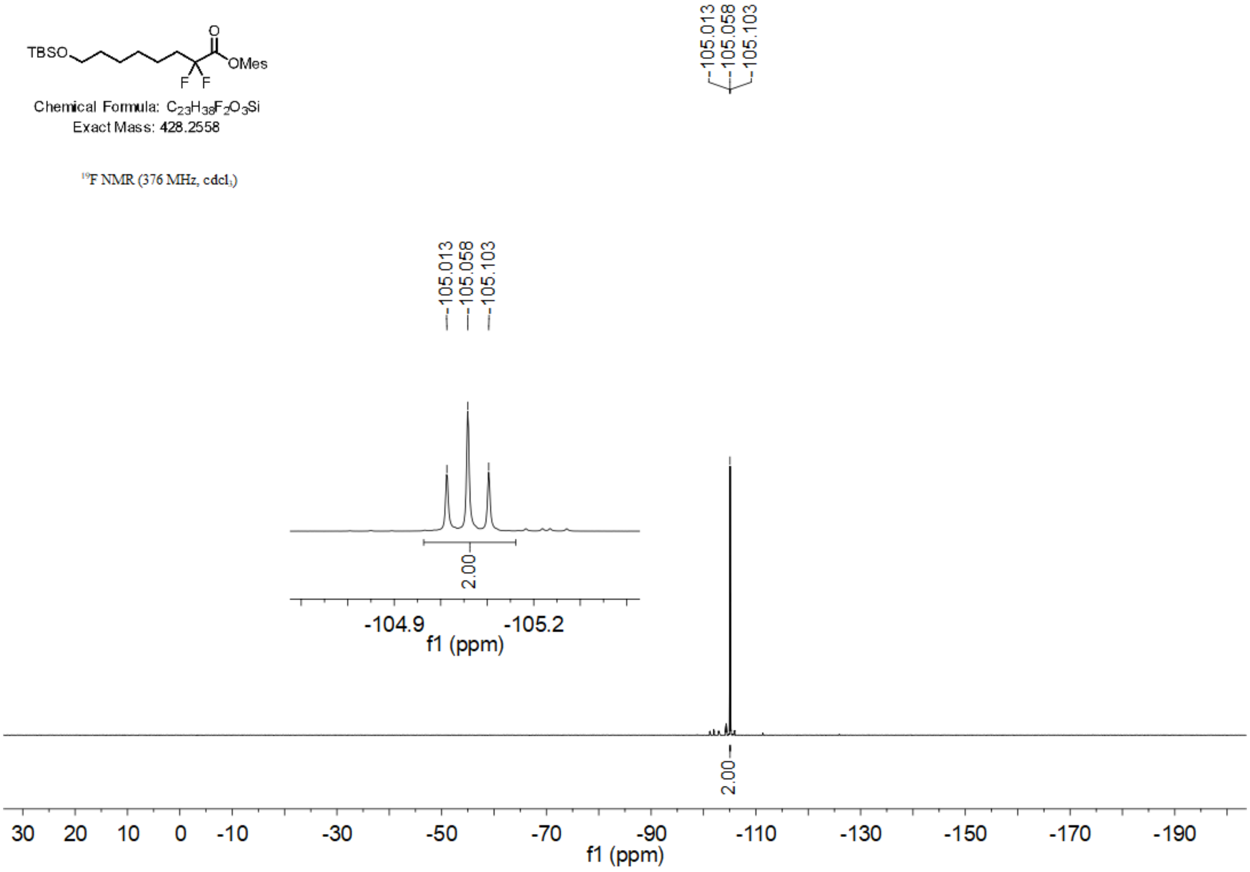


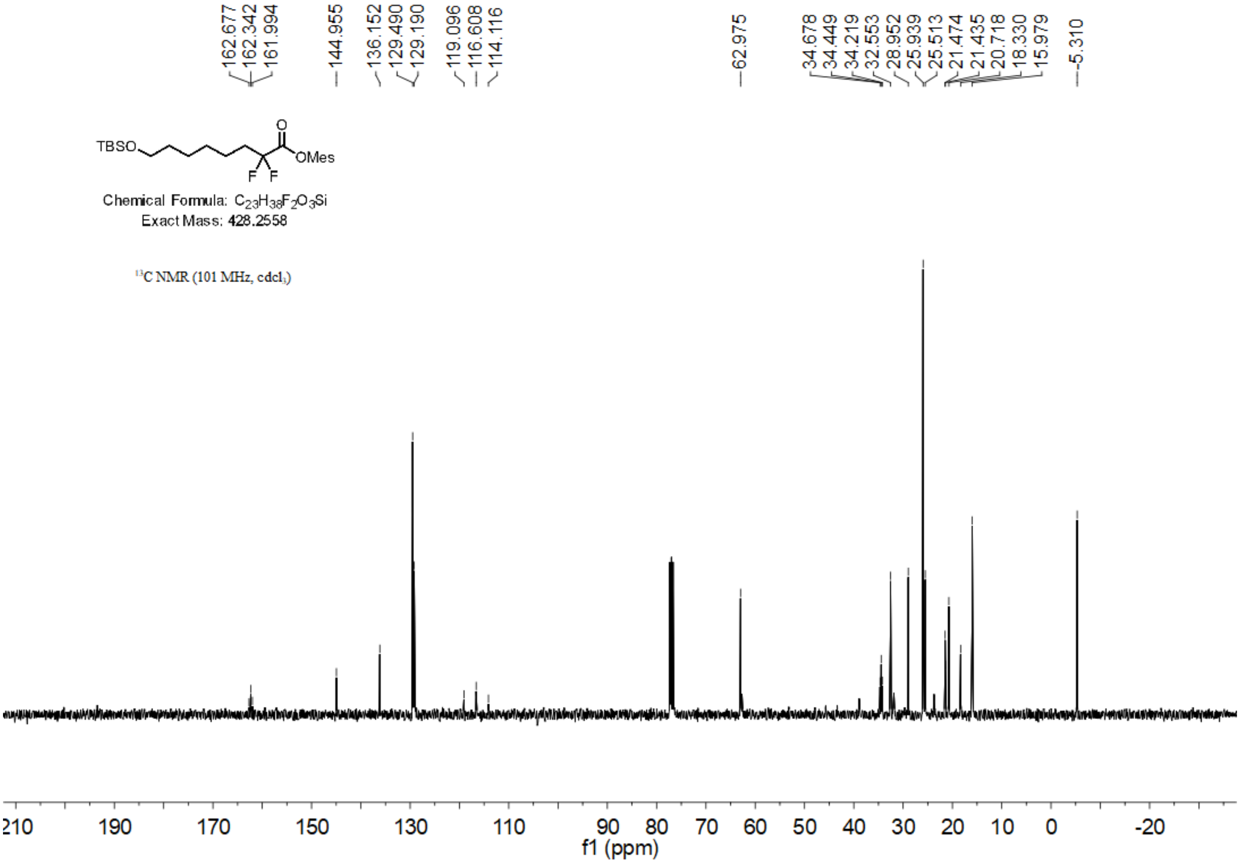
Chemical Formula: $C_{20}H_{28}F_2O_2$
Exact Mass: 338.2057

^{13}C NMR (101 MHz, cdcl$_3$)

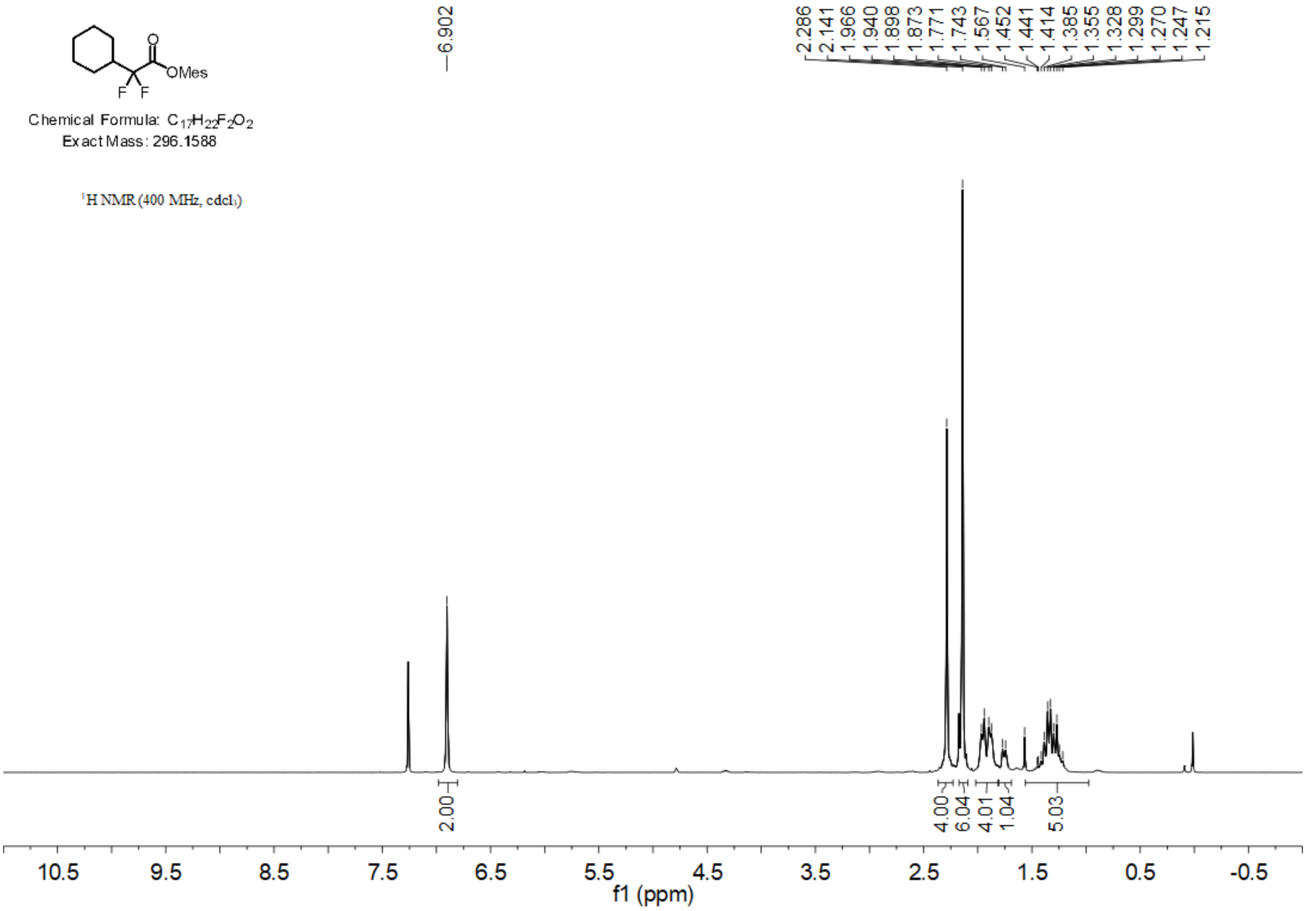
Mesityl 8-((tert-butyldimethylsilyl)oxy)-2,2-difluorooctanoate (8o)

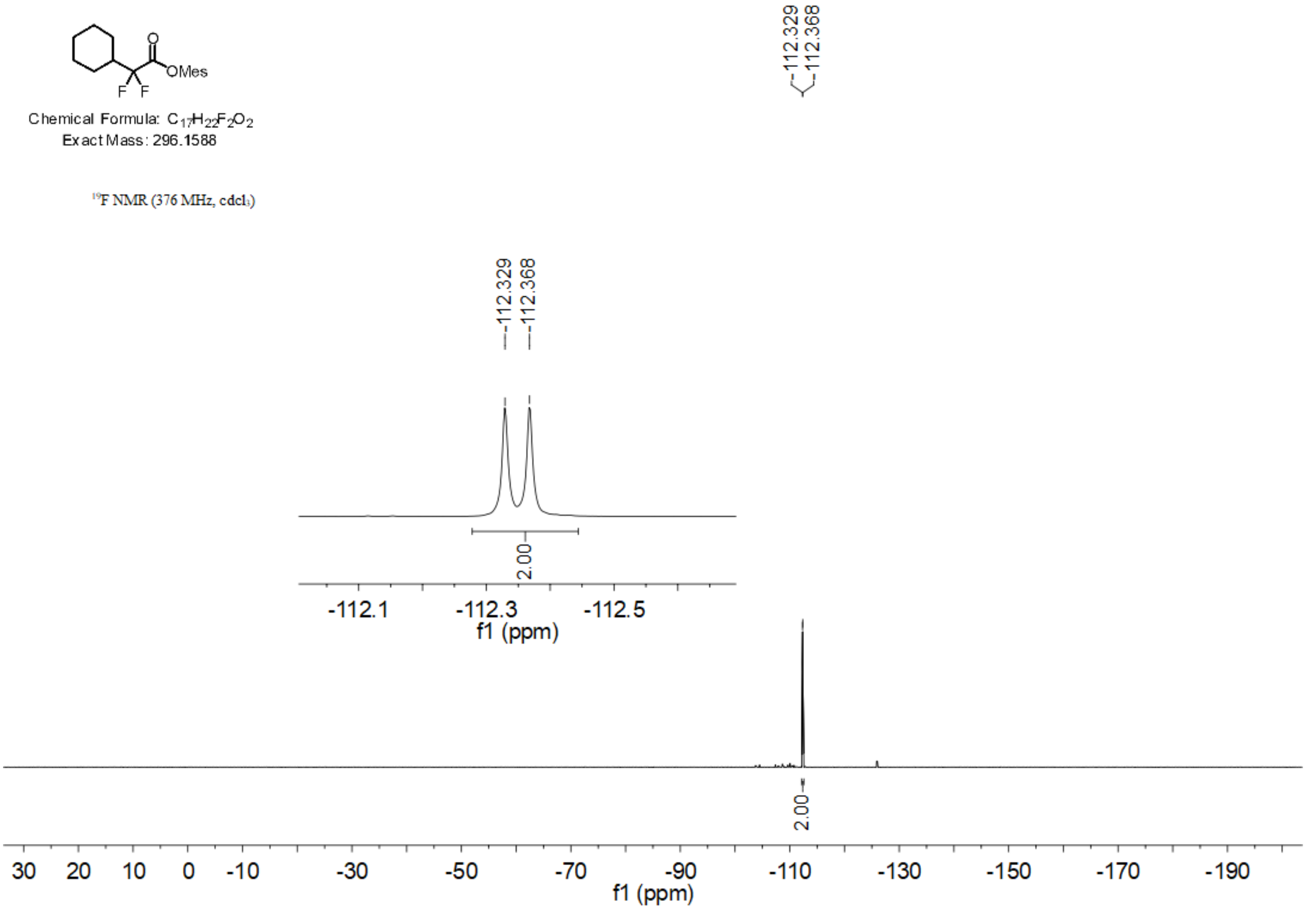






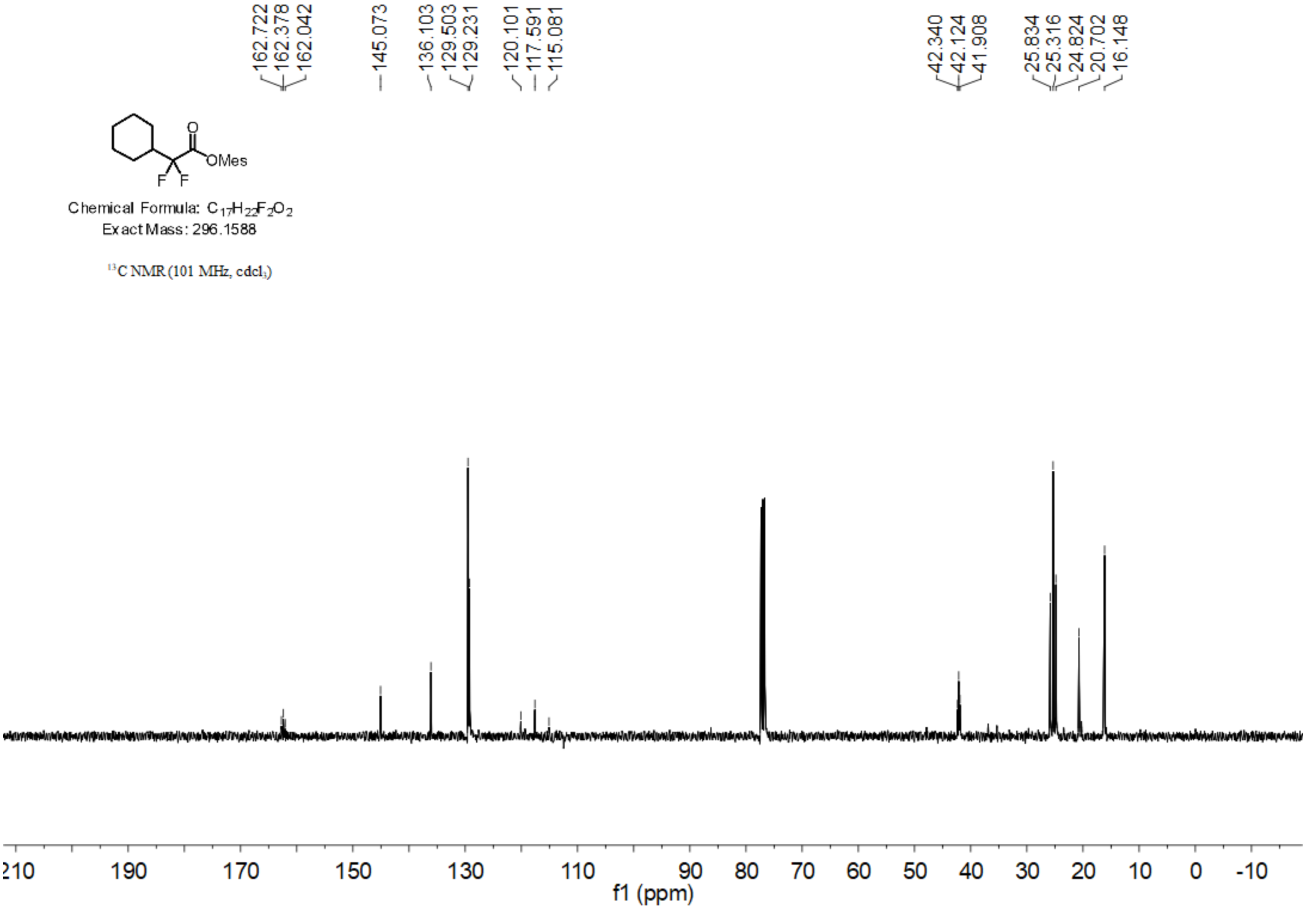
Mesityl 2-cyclohexyl-2,2-difluoroacetate (8p)





Chemical Formula: $C_{17}H_{22}F_2O_2$
Exact Mass: 296.1588

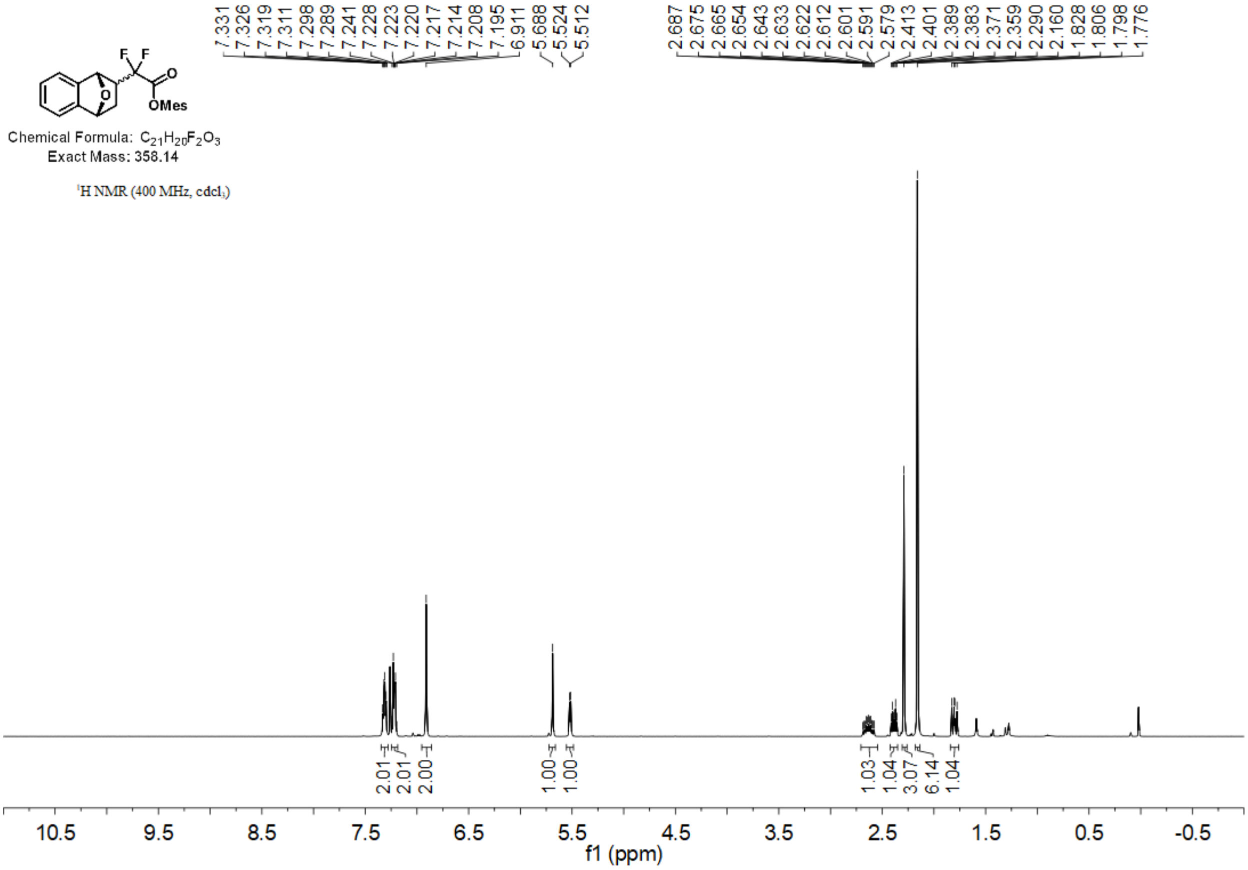
^{19}F NMR (376 MHz, cdcl$_3$)

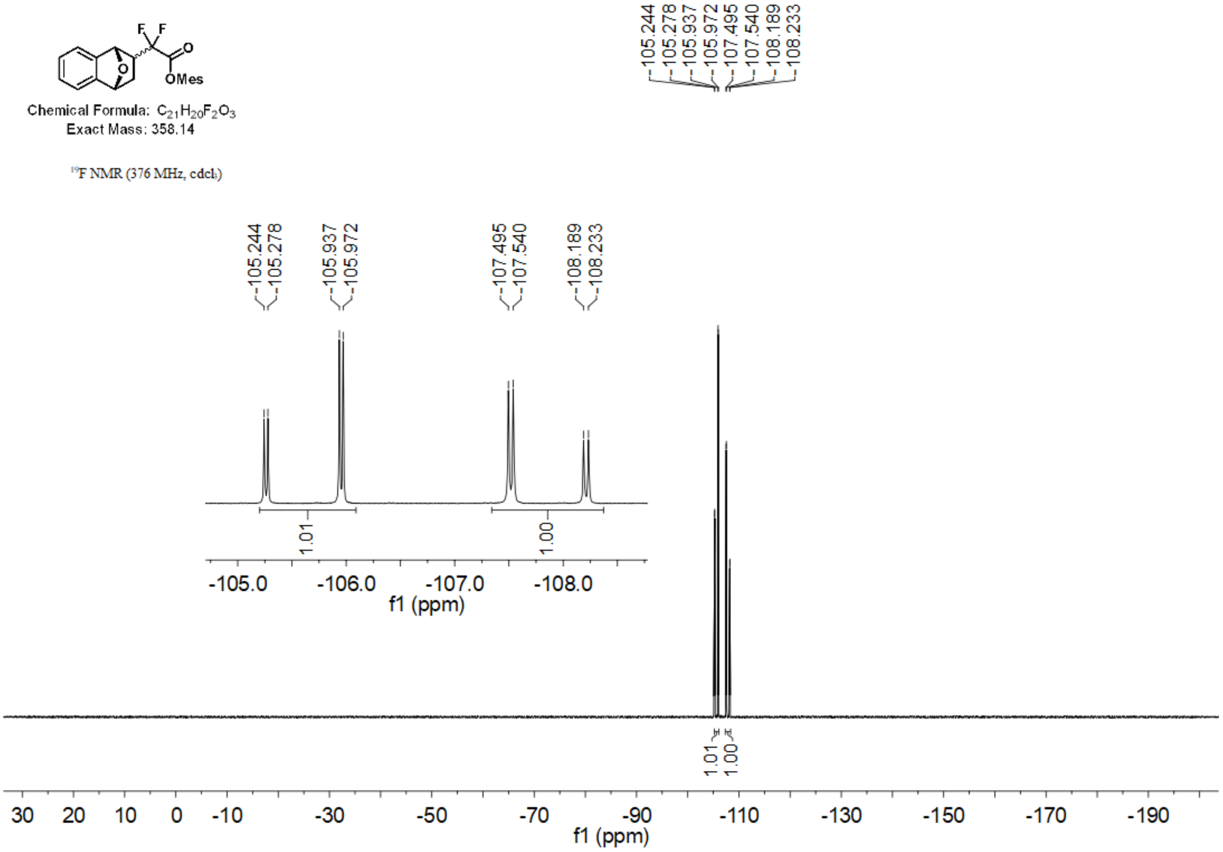


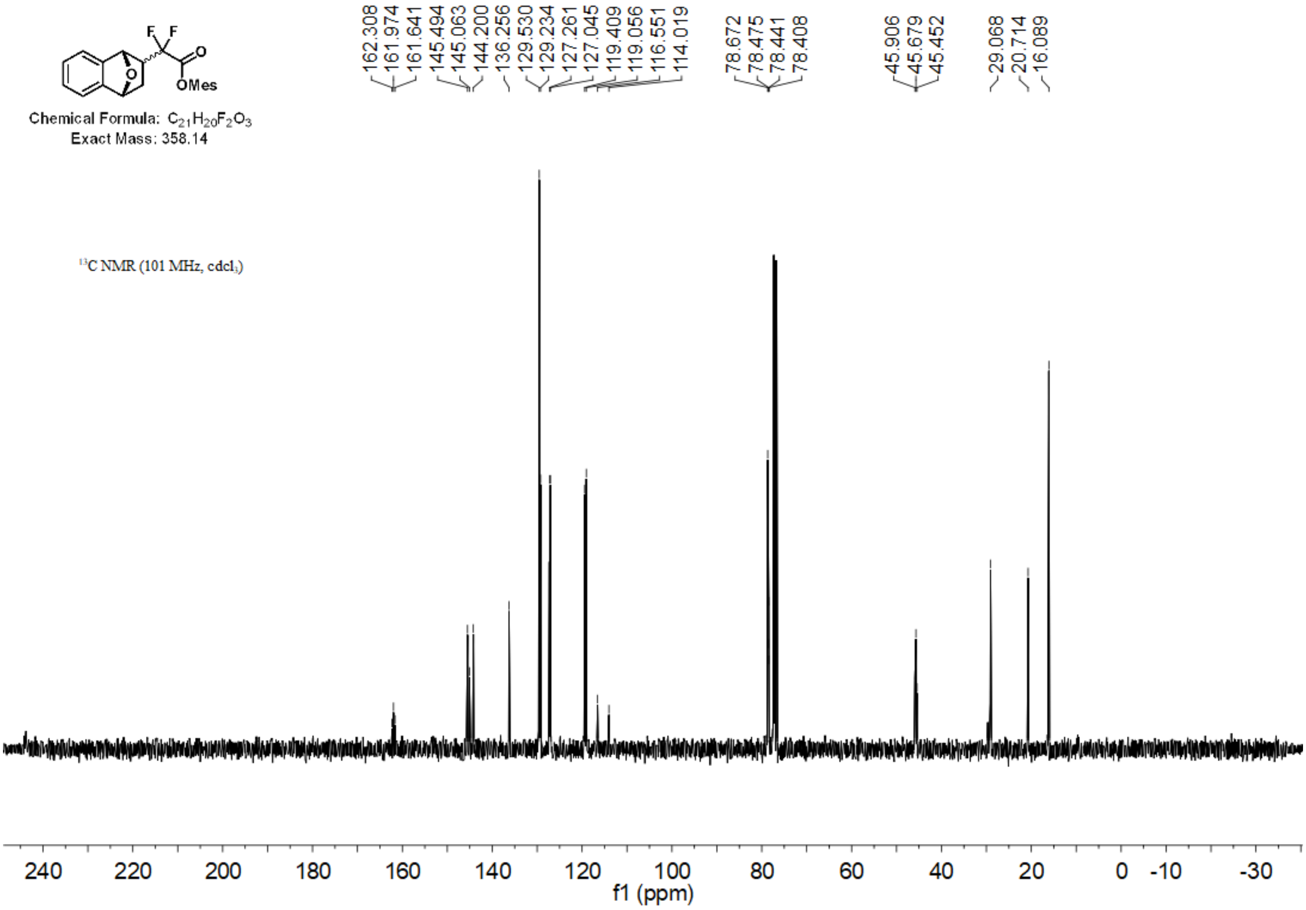
Chemical Formula: $C_{17}H_{22}F_2O_2$
Exact Mass: 296.1588

^{13}C NMR (101 MHz, cdcl$_3$)

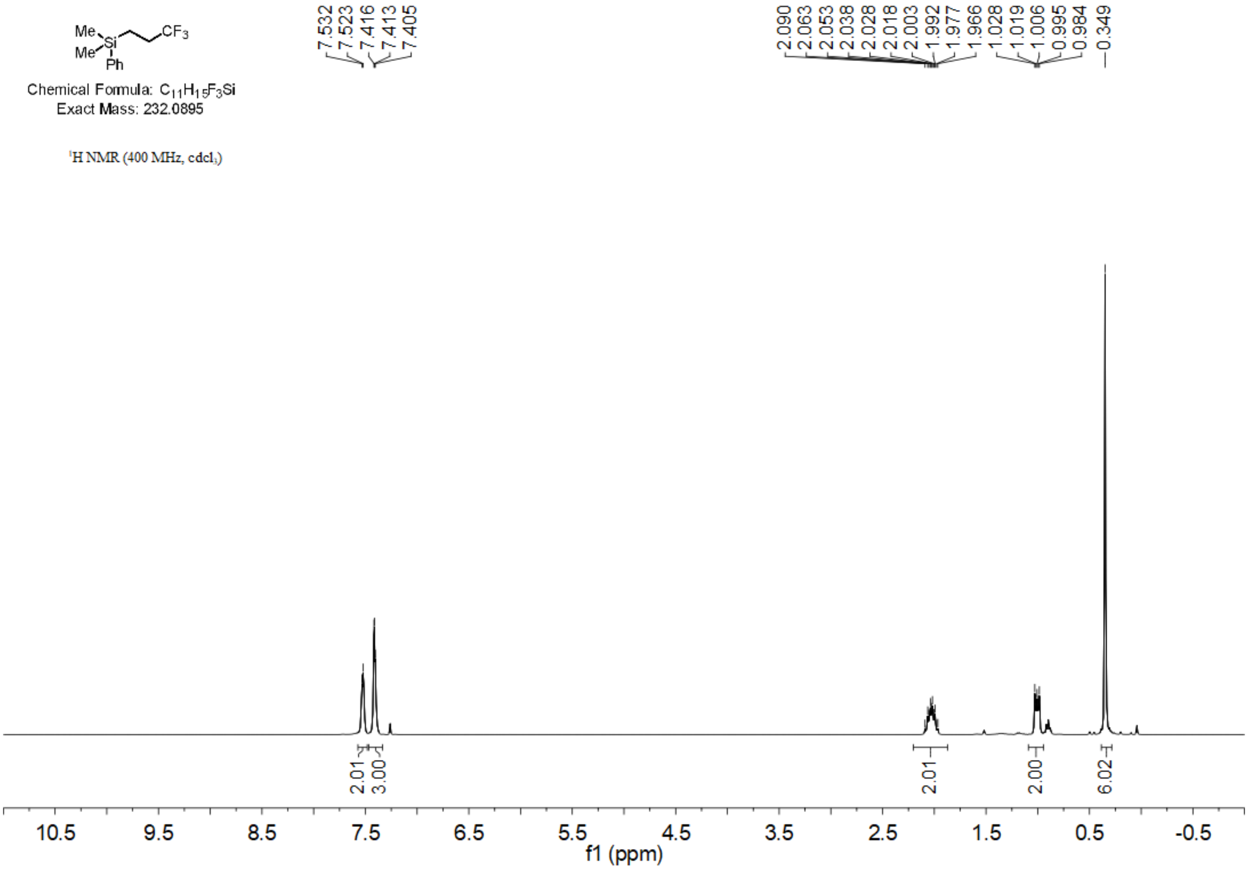
Mesityl 2,2-difluoro-2-((1*S*,4*R*)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)acetate (8q)

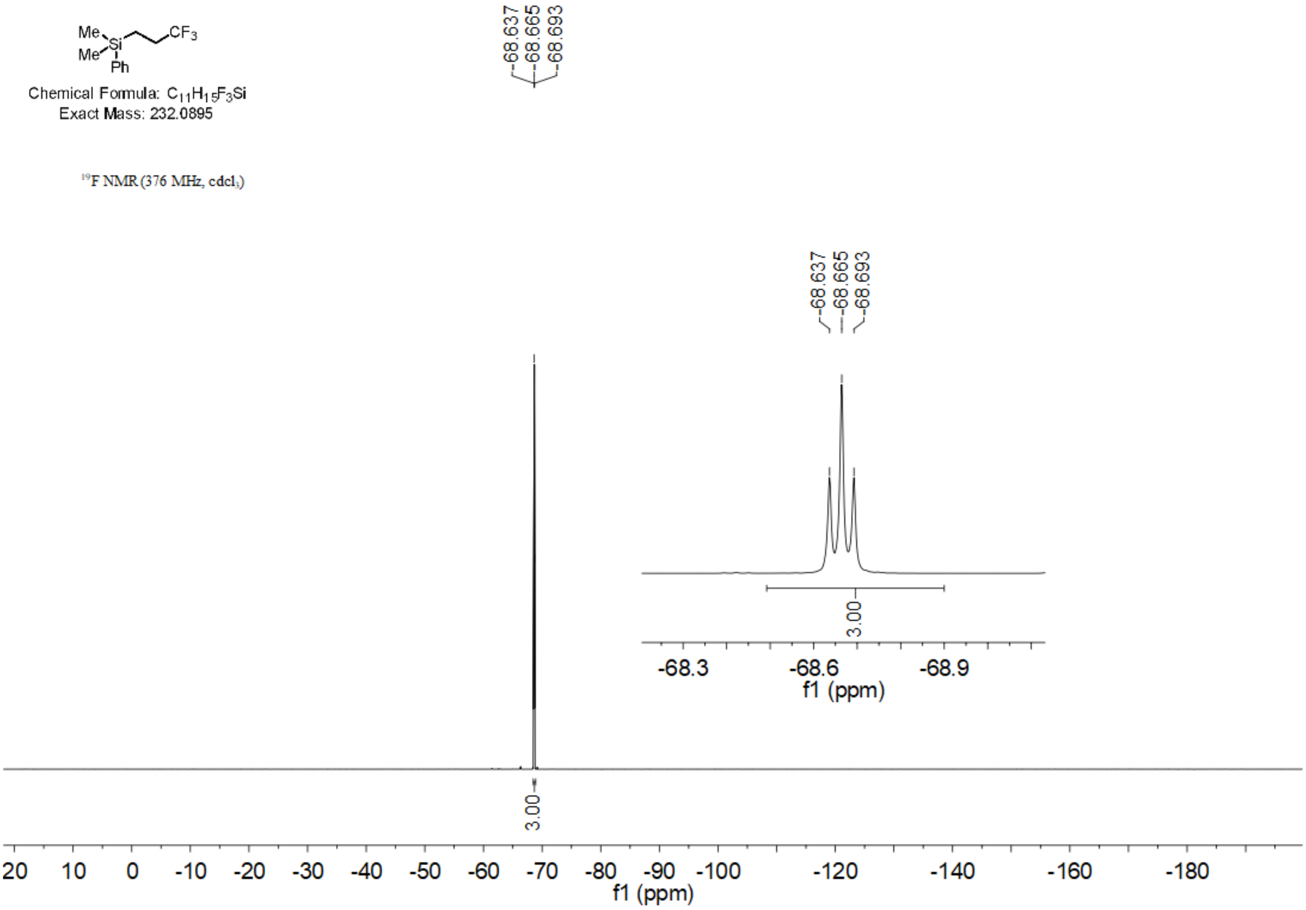






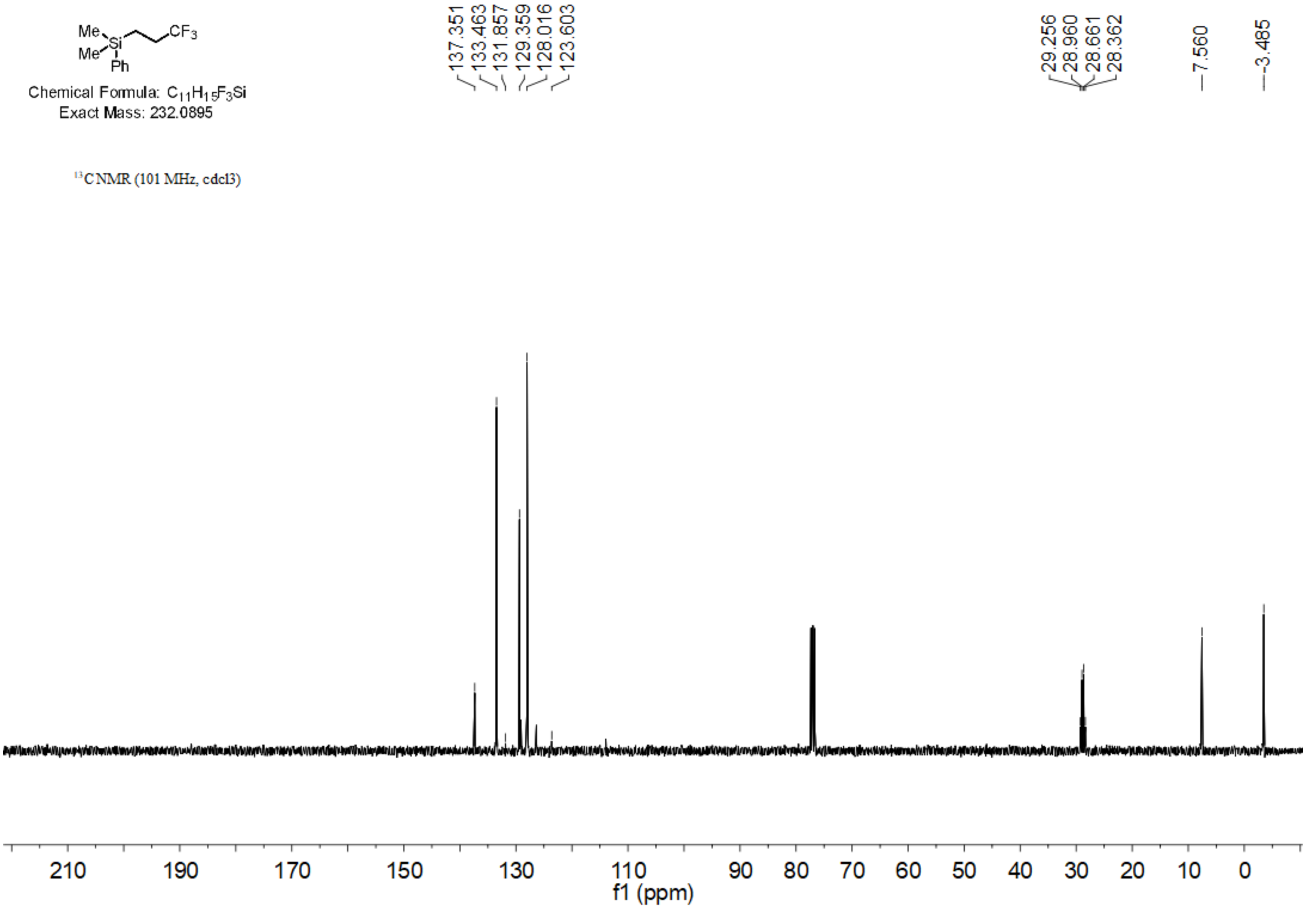
Dimethyl(phenyl)(3,3,3-trifluoropropyl)silane (9a)





Chemical Formula: $C_{11}H_{15}F_3Si$
Exact Mass: 232.0895

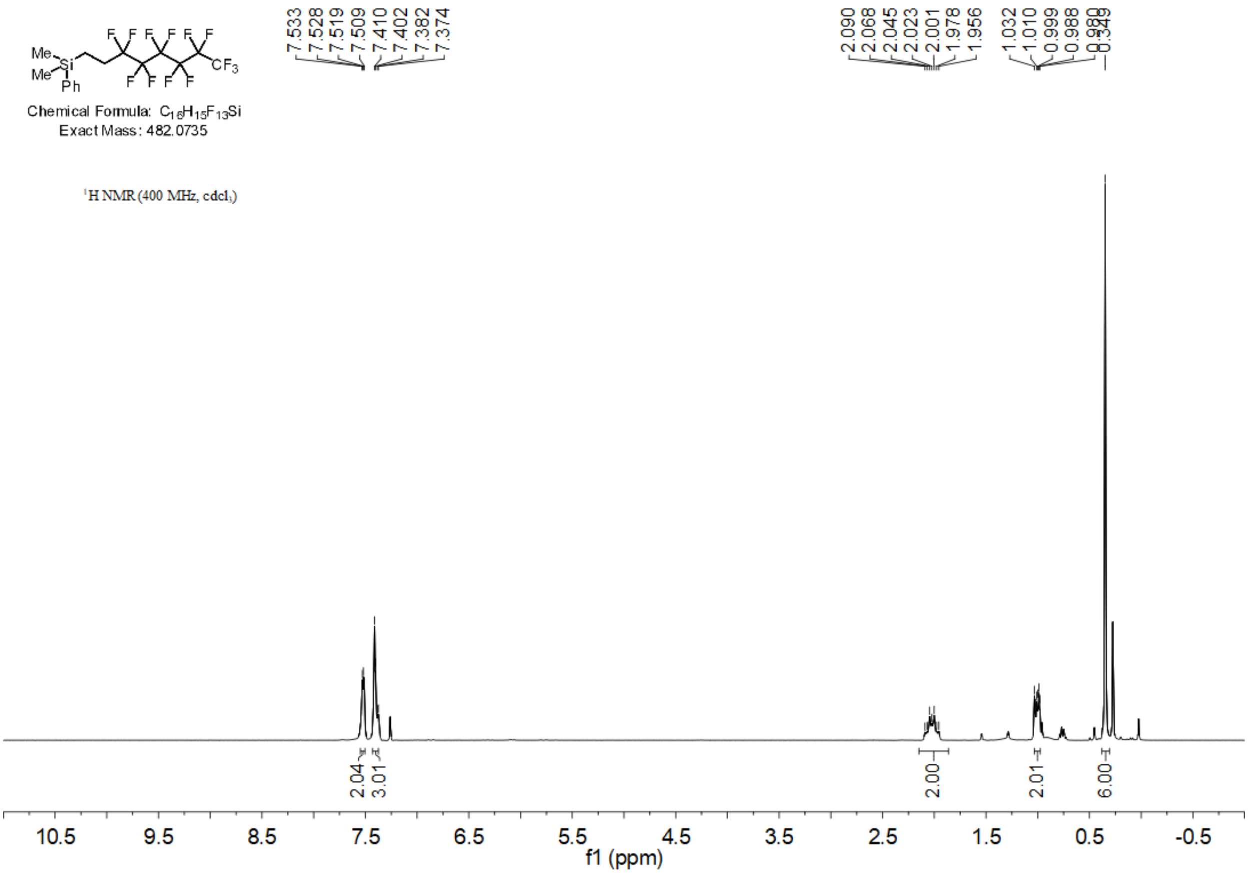
^{19}F NMR (376 MHz, cdcl$_3$)

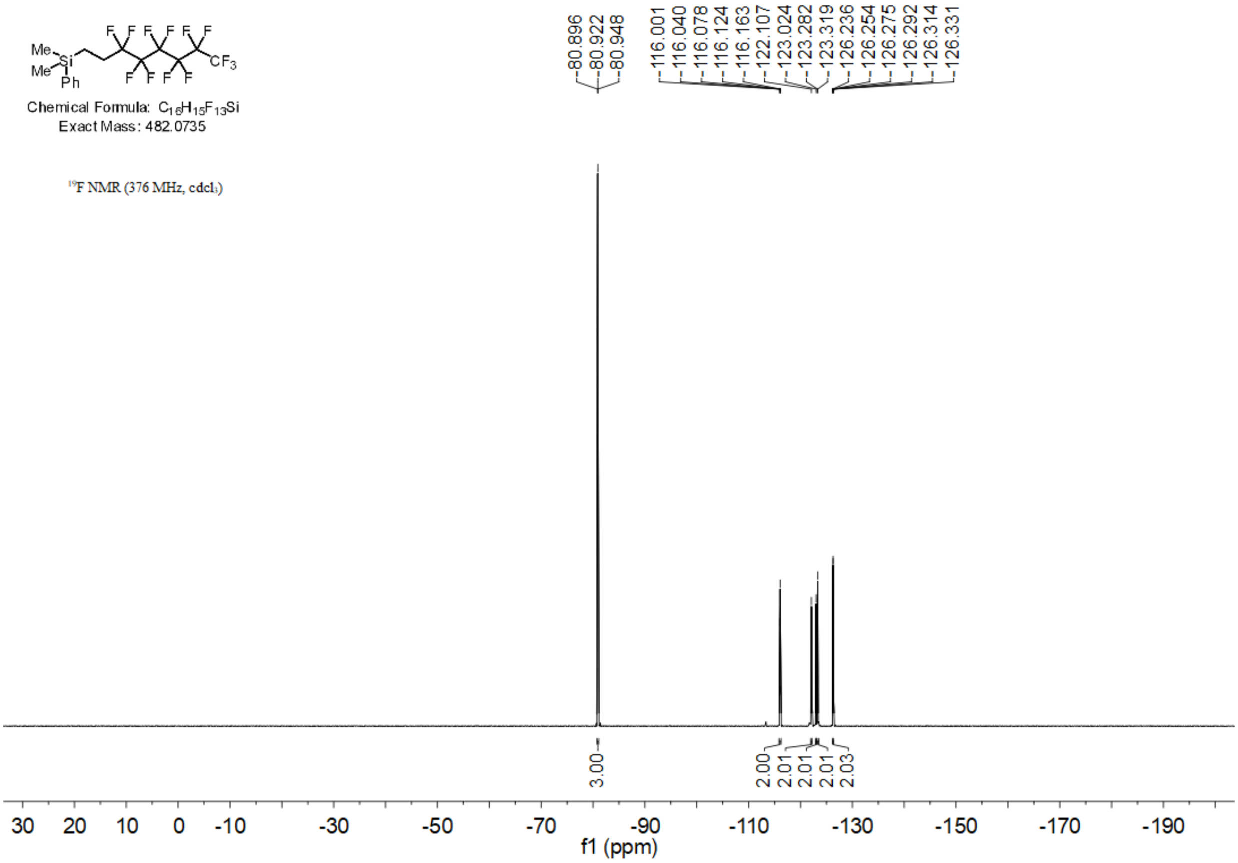


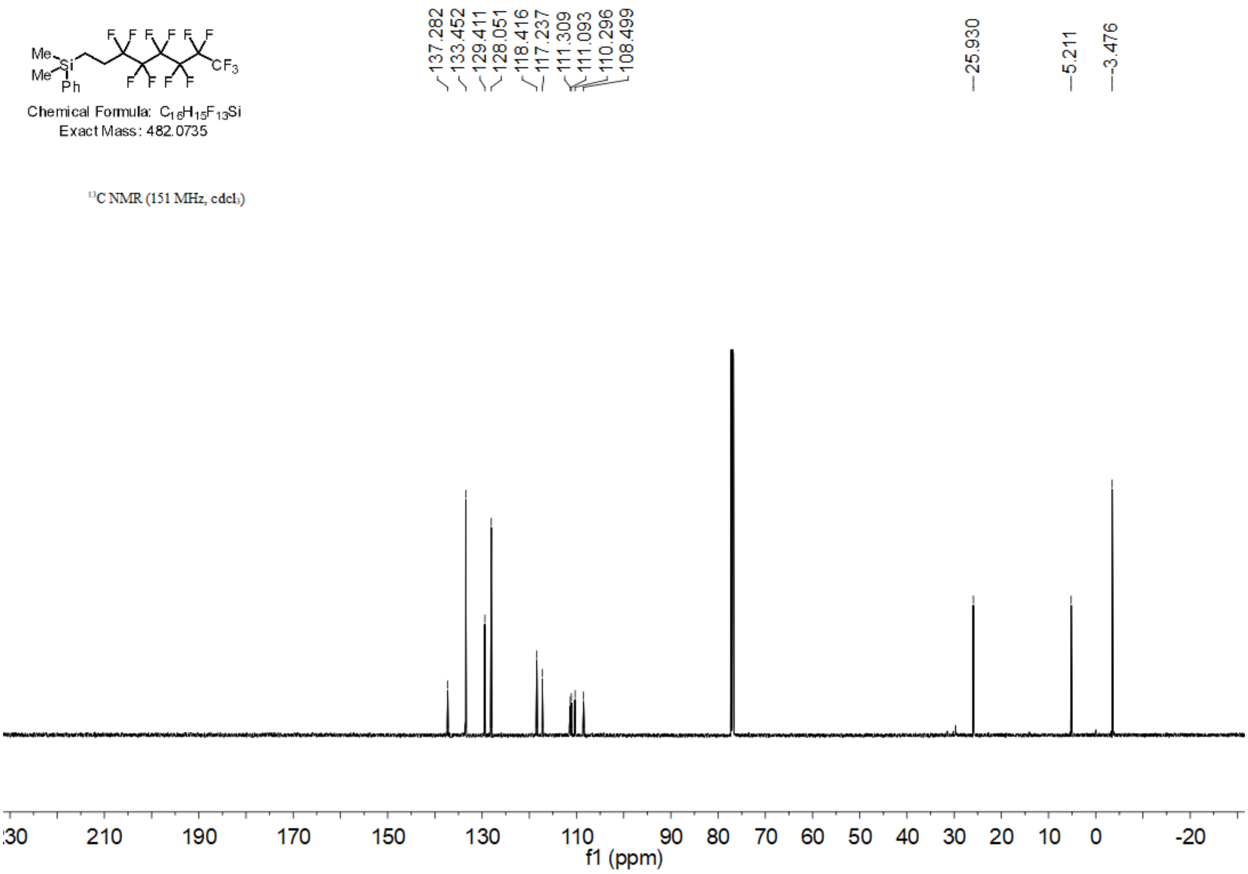
Chemical Formula: $C_{11}H_{15}F_3Si$
Exact Mass: 232.0895

^{13}C NMR (101 MHz, cdcl3)

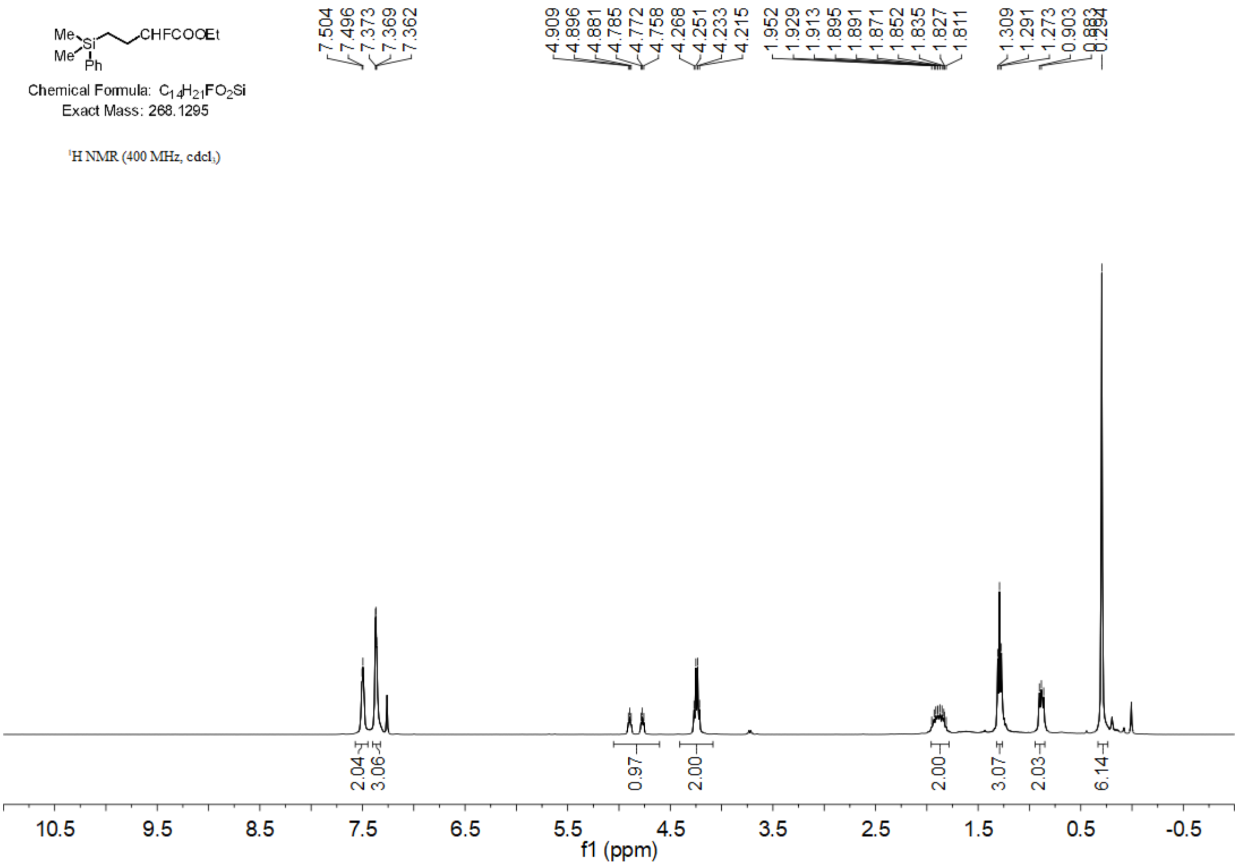
Dimethyl(phenyl)(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane (9b)

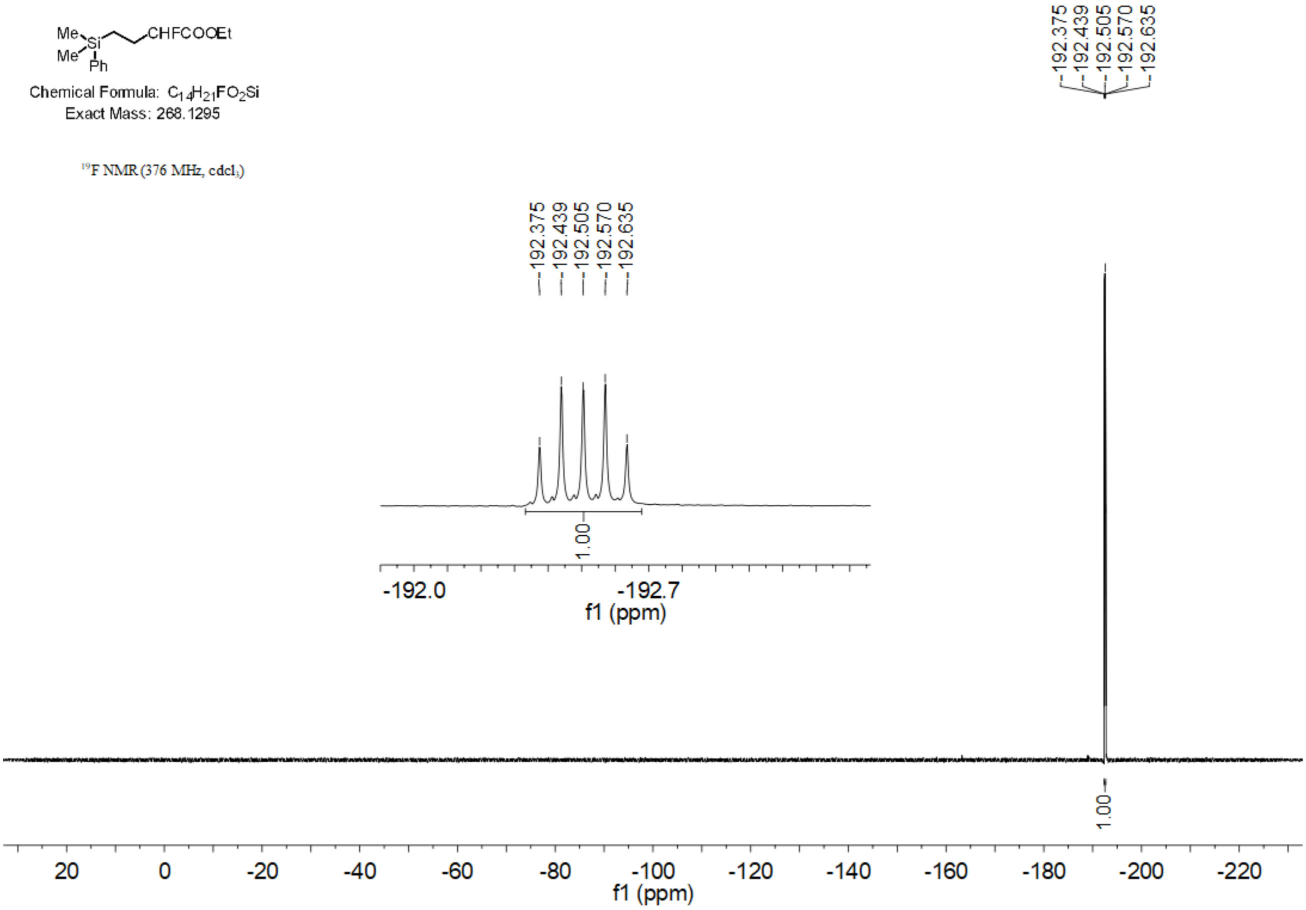






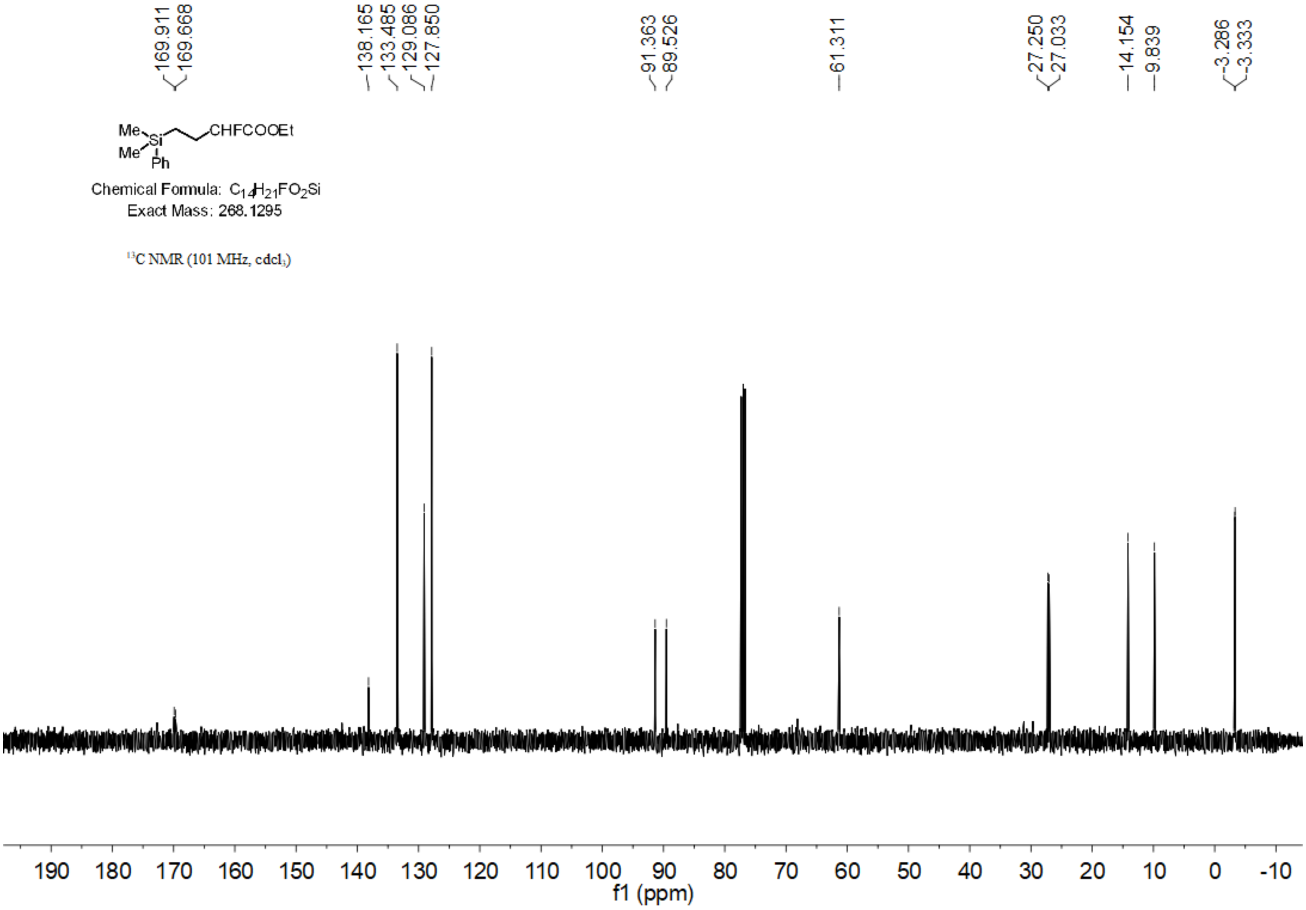
Ethyl 4-(dimethyl(phenyl)silyl)-2-fluorobutanoate (9c)





Chemical Formula: $C_{14}H_{21}FO_2Si$
Exact Mass: 268.1295

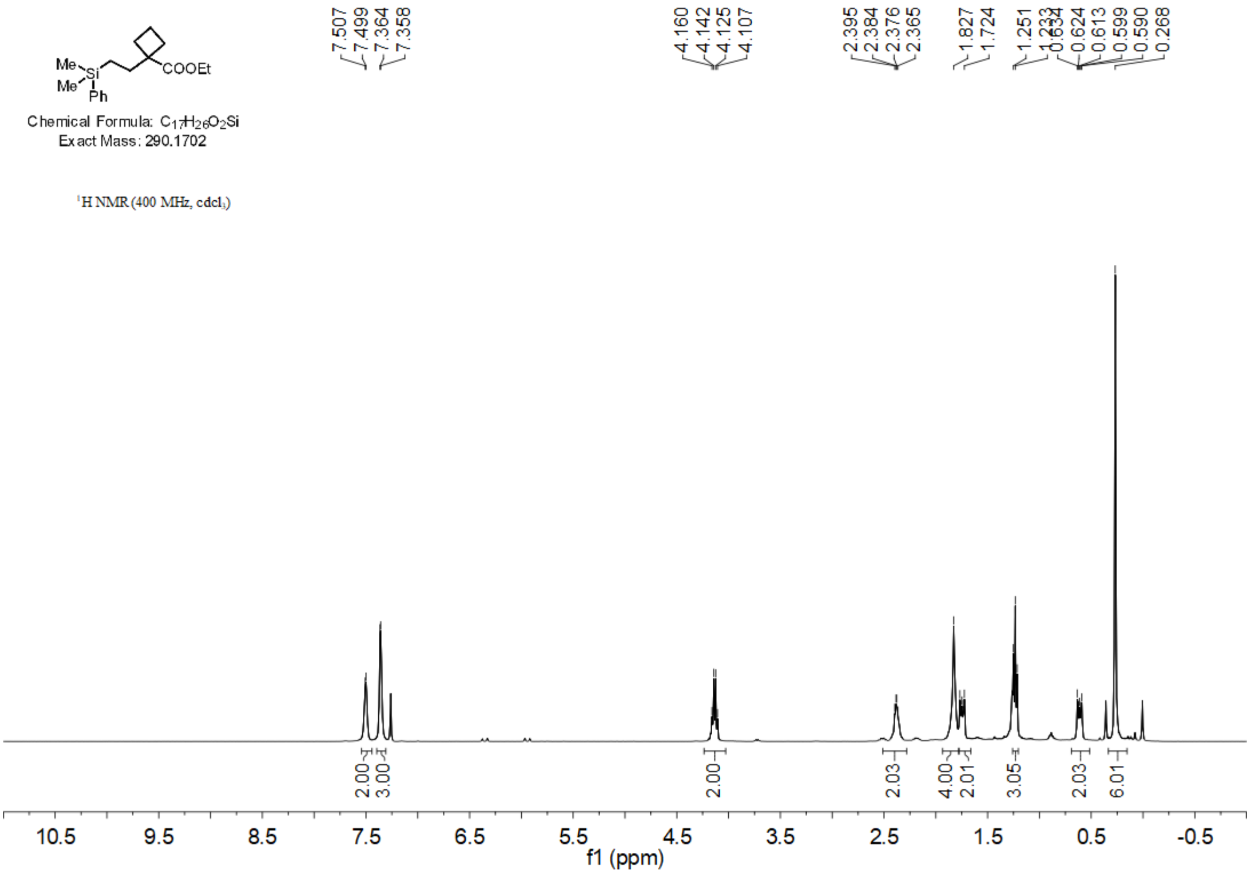
^{19}F NMR (376 MHz, cdcl$_3$)

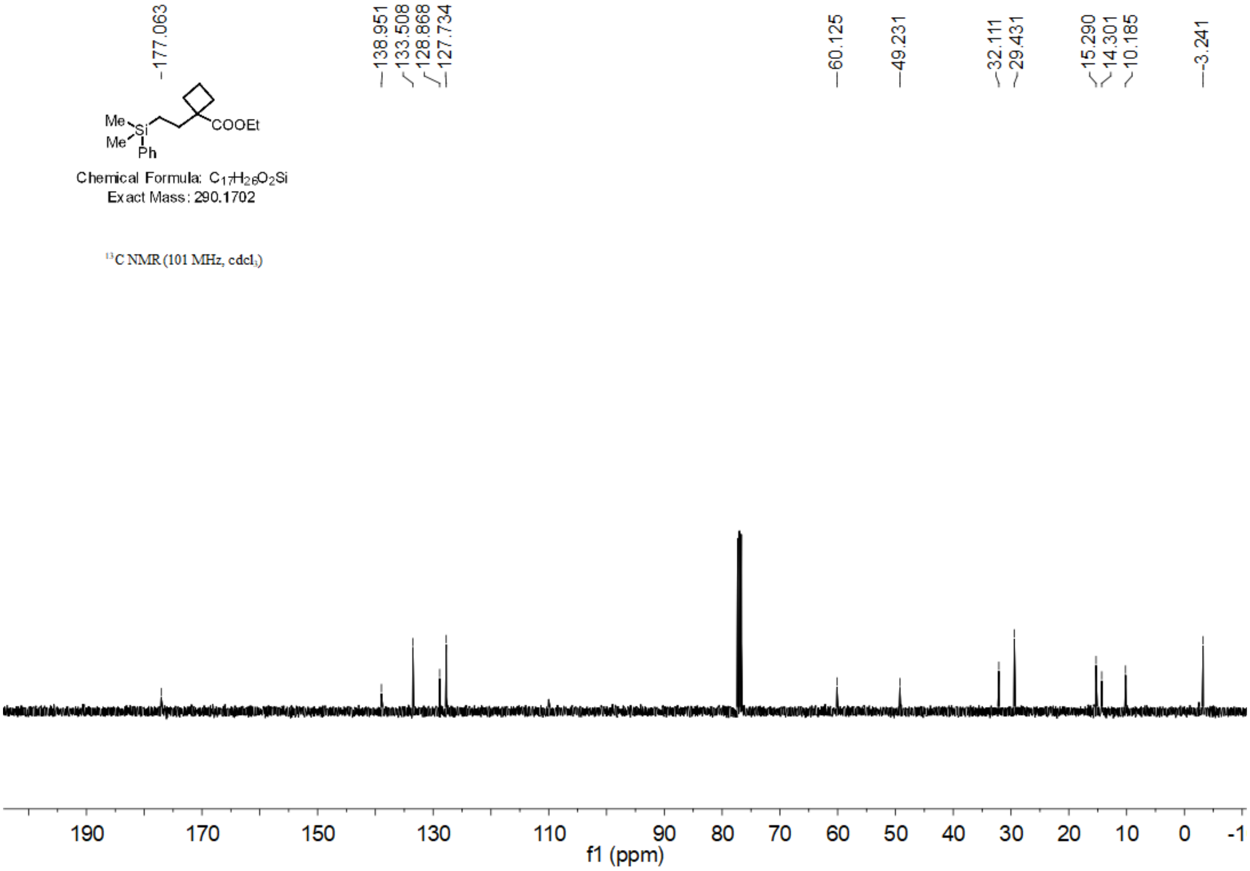


Chemical Formula: $C_{14}H_{21}FO_2Si$
Exact Mass: 268.1295

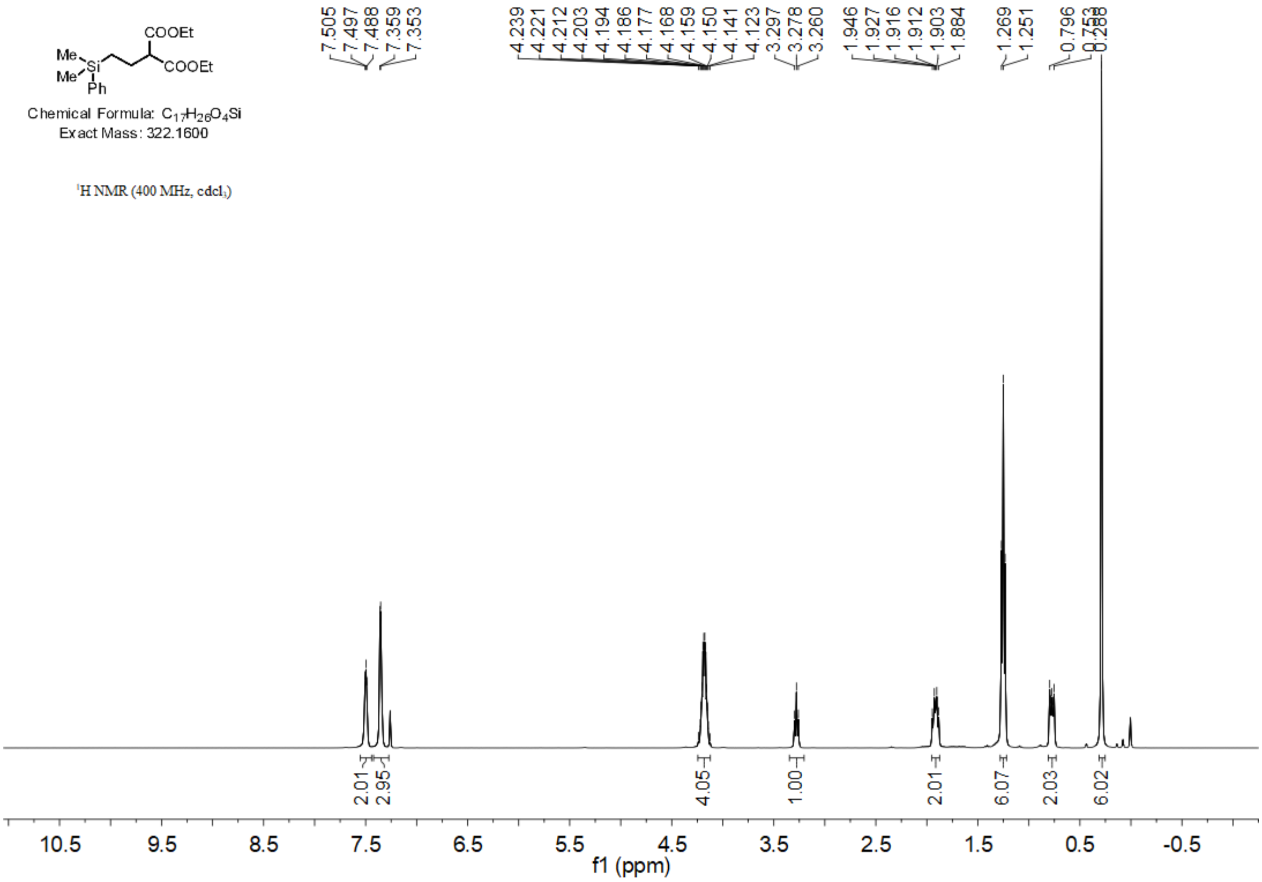
^{13}C NMR (101 MHz, cdcl$_3$)

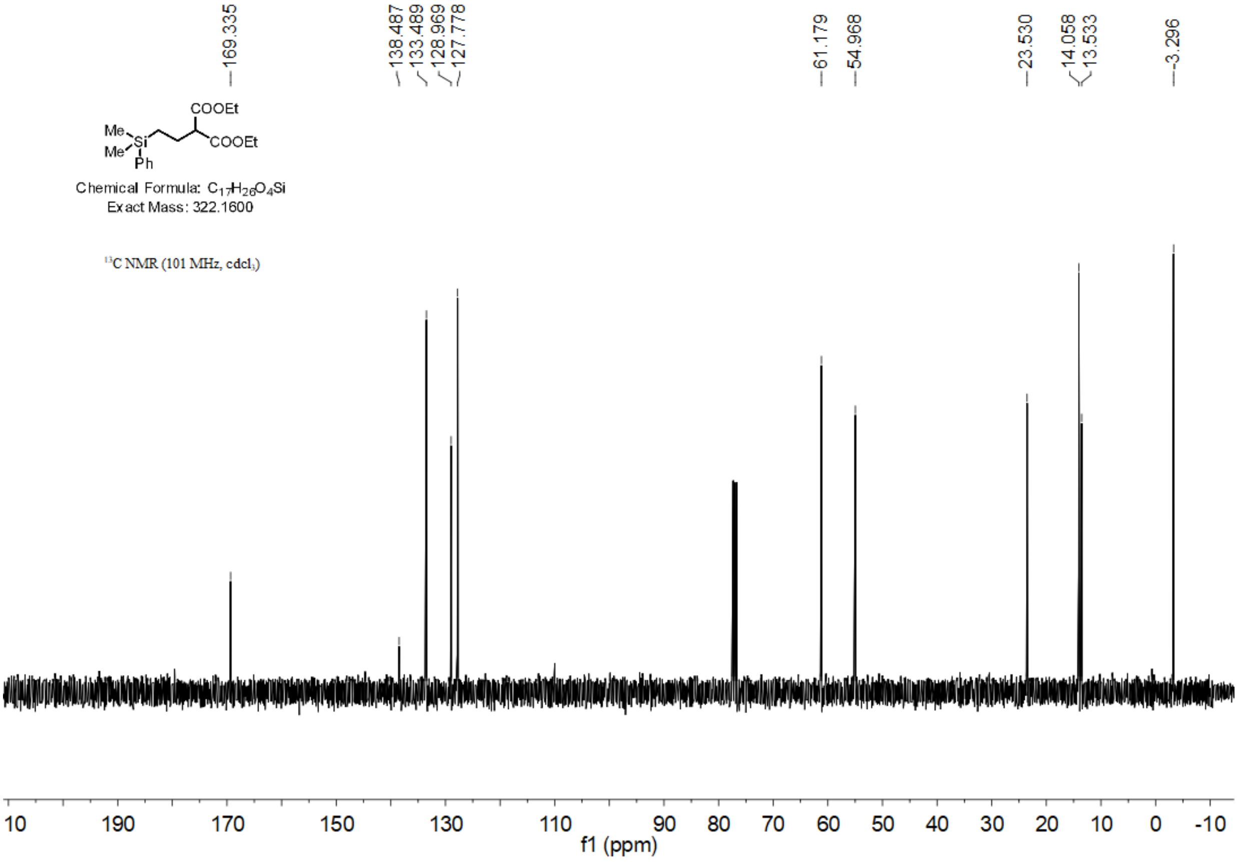
Ethyl 1-(2-(dimethyl(phenyl)silyl)ethyl)cyclobutane-1-carboxylate (9d)



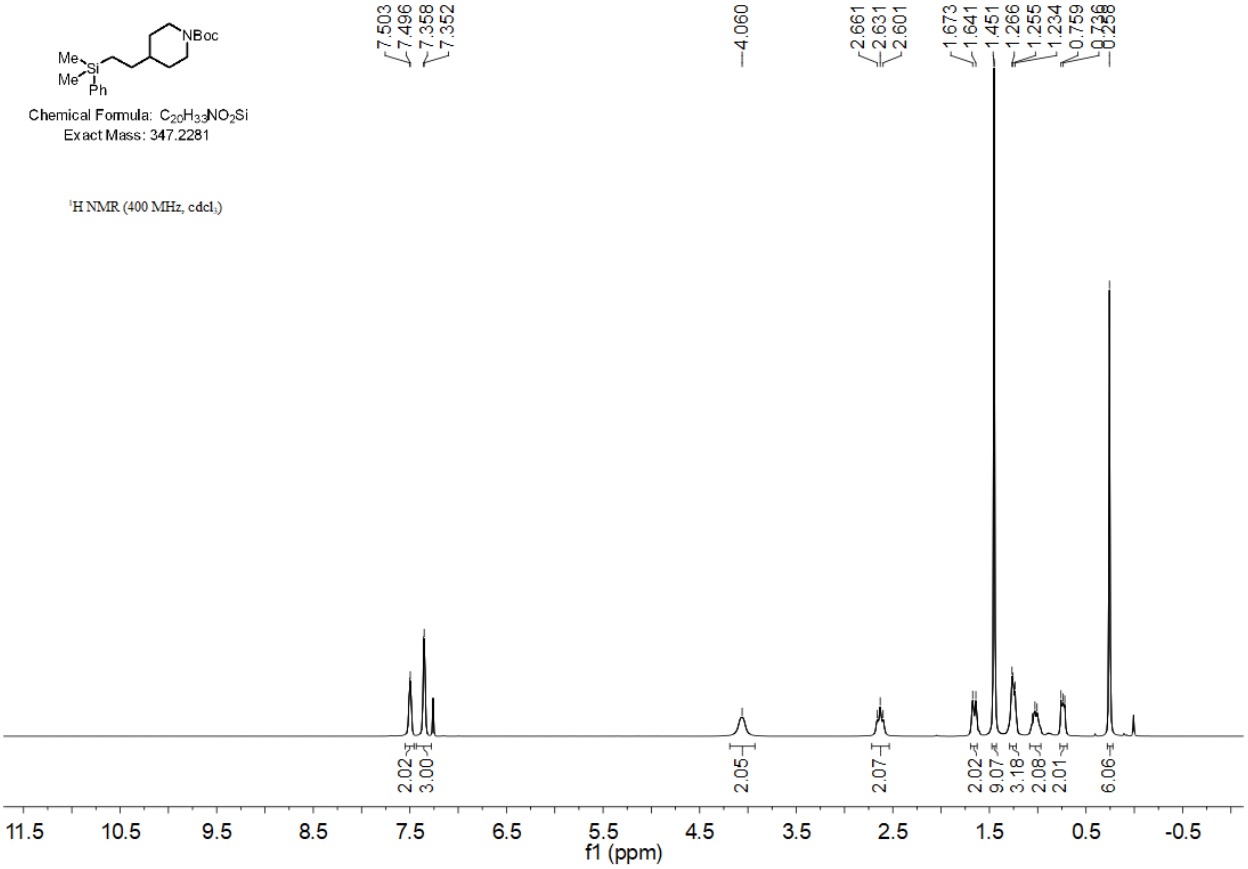


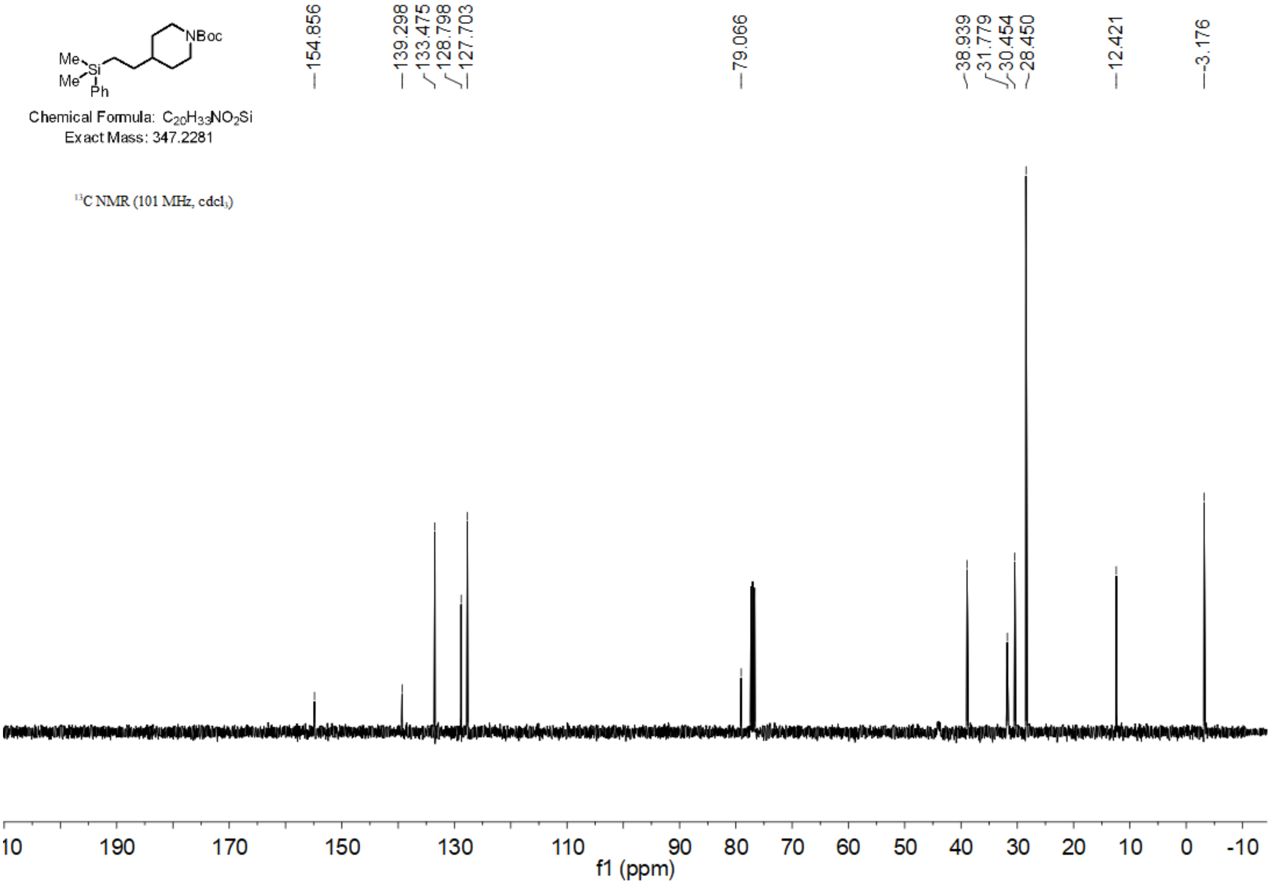
Diethyl 2-(2-(dimethyl(phenyl)silyl)ethyl)malonate (9e)



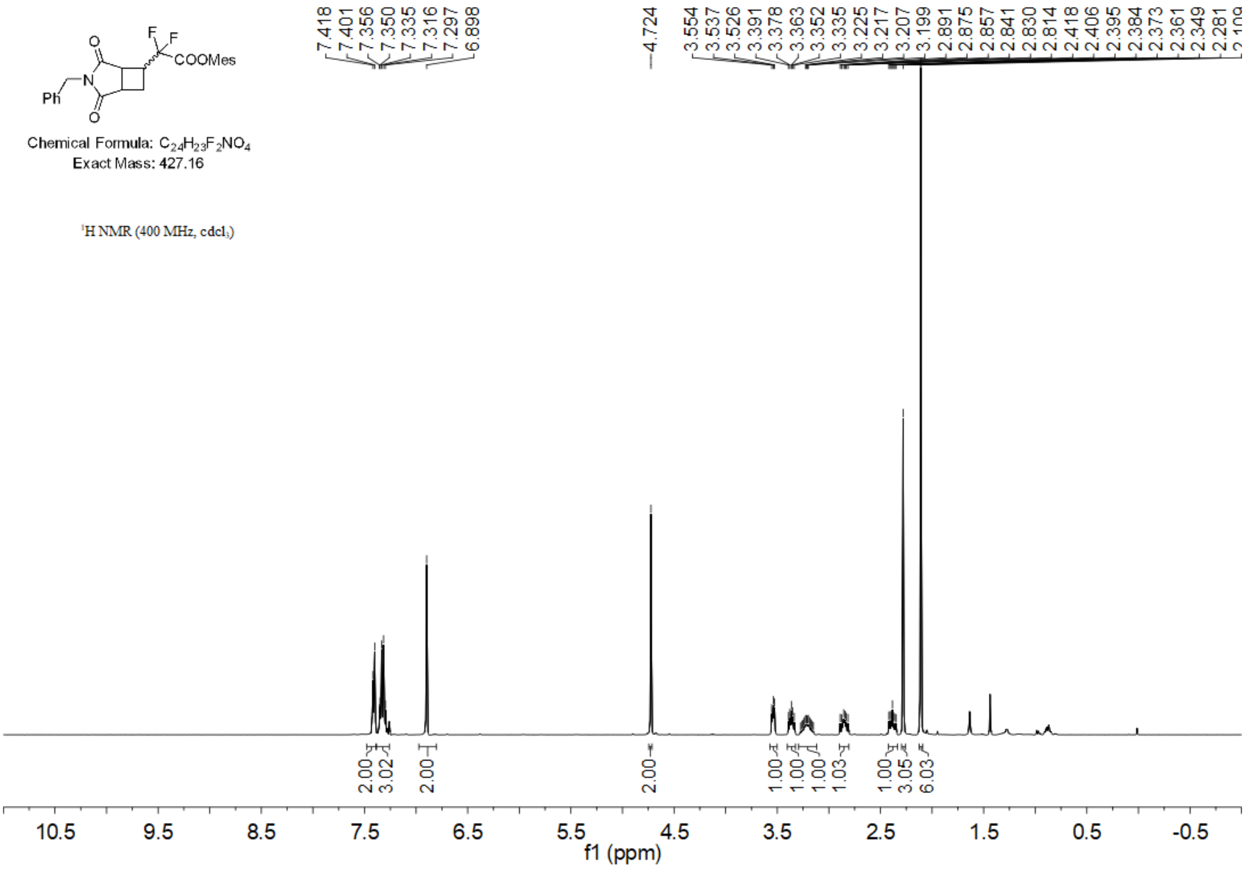


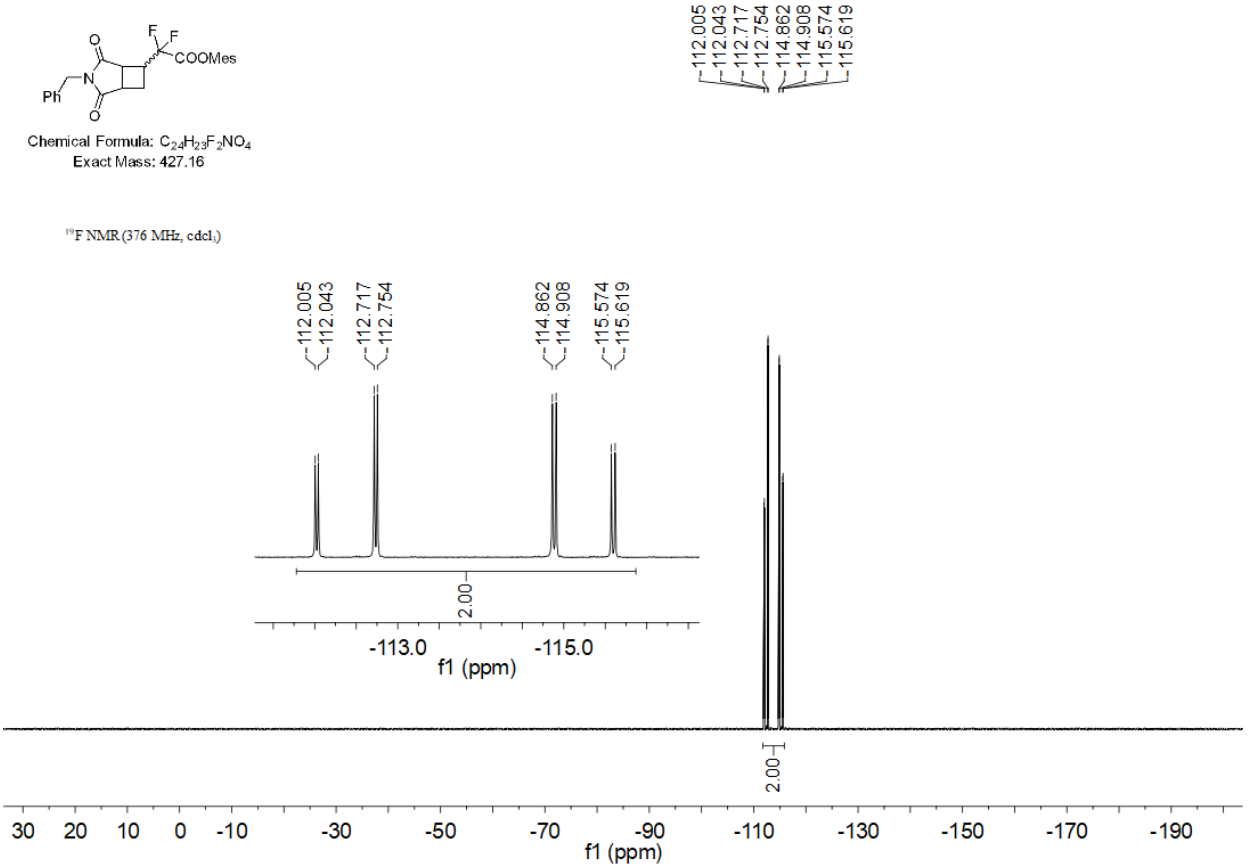
tert-Butyl 4-(2-(dimethyl(phenyl)silyl)ethyl)piperidine-1-carboxylate (9f)

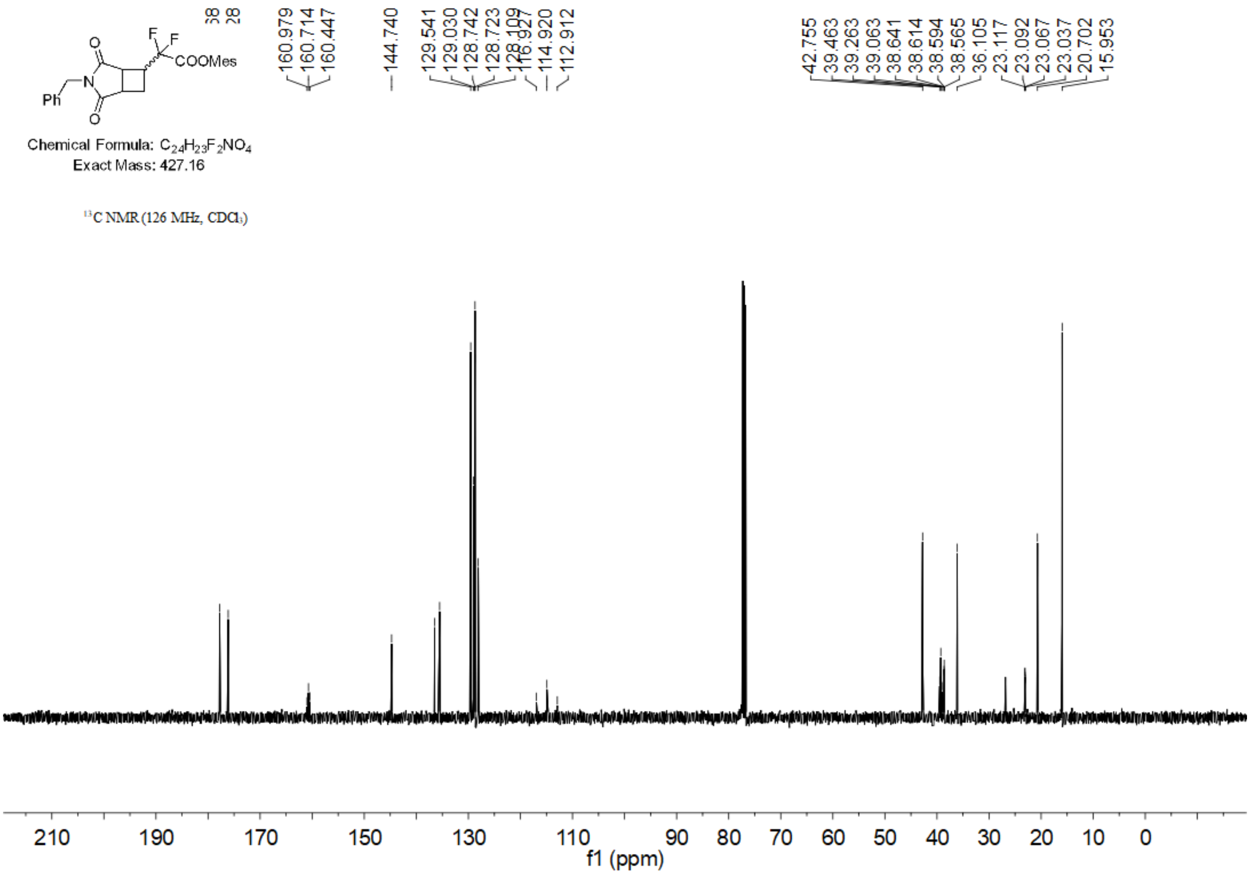




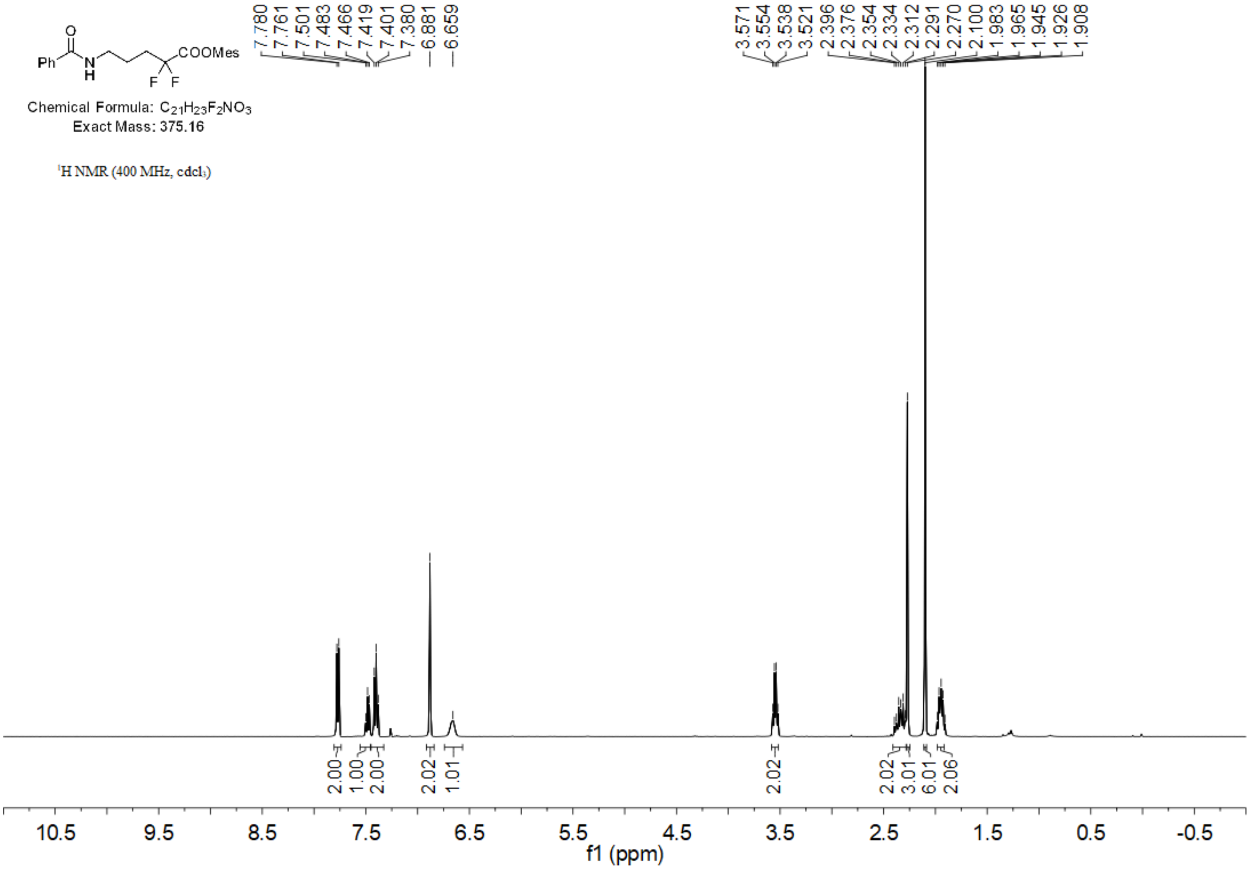
Mesityl 2-(3-benzyl-2,4-dioxo-3-azabicyclo[3.2.0]heptan-6-yl)-2,2-difluoroacetate (10a)

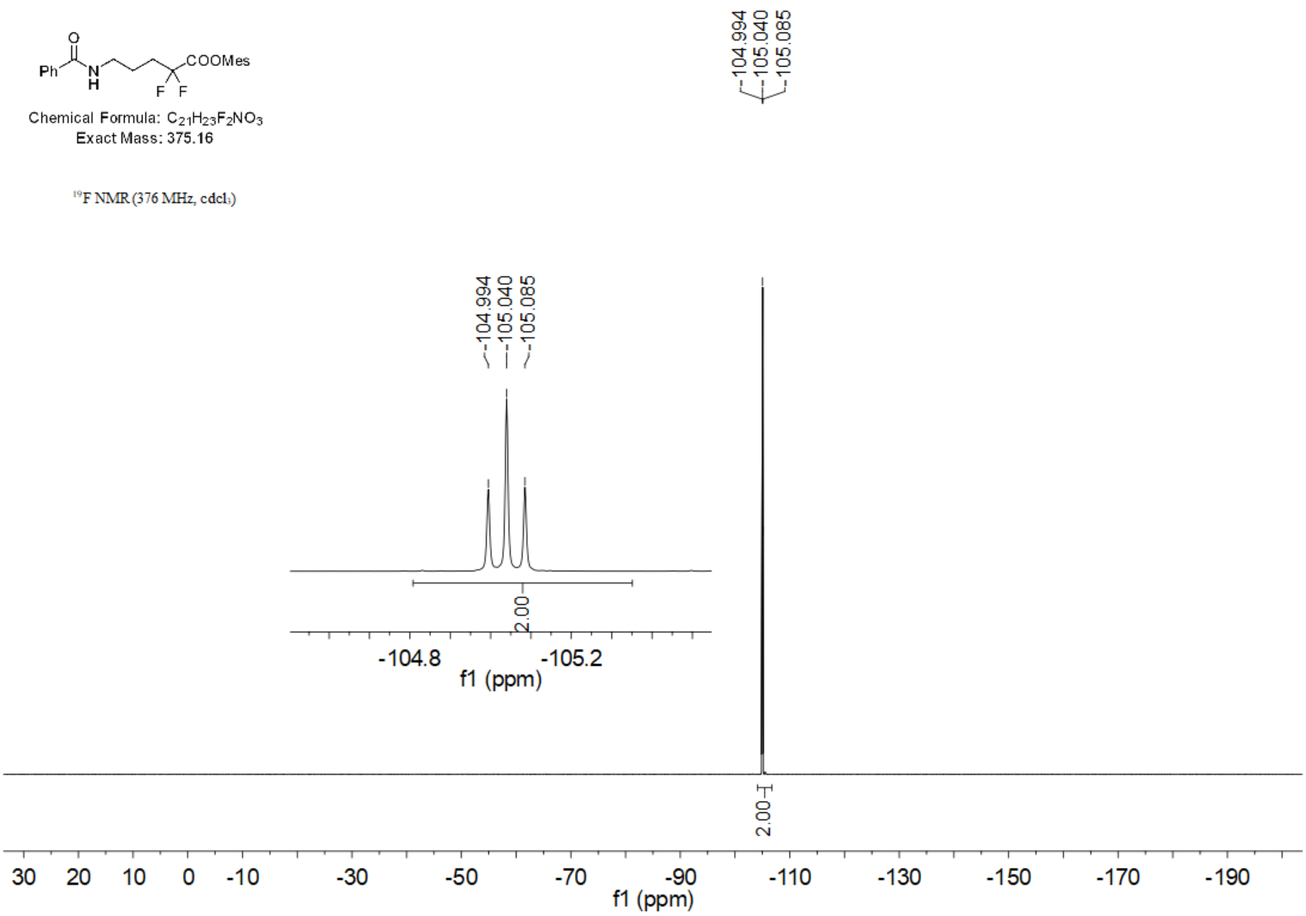






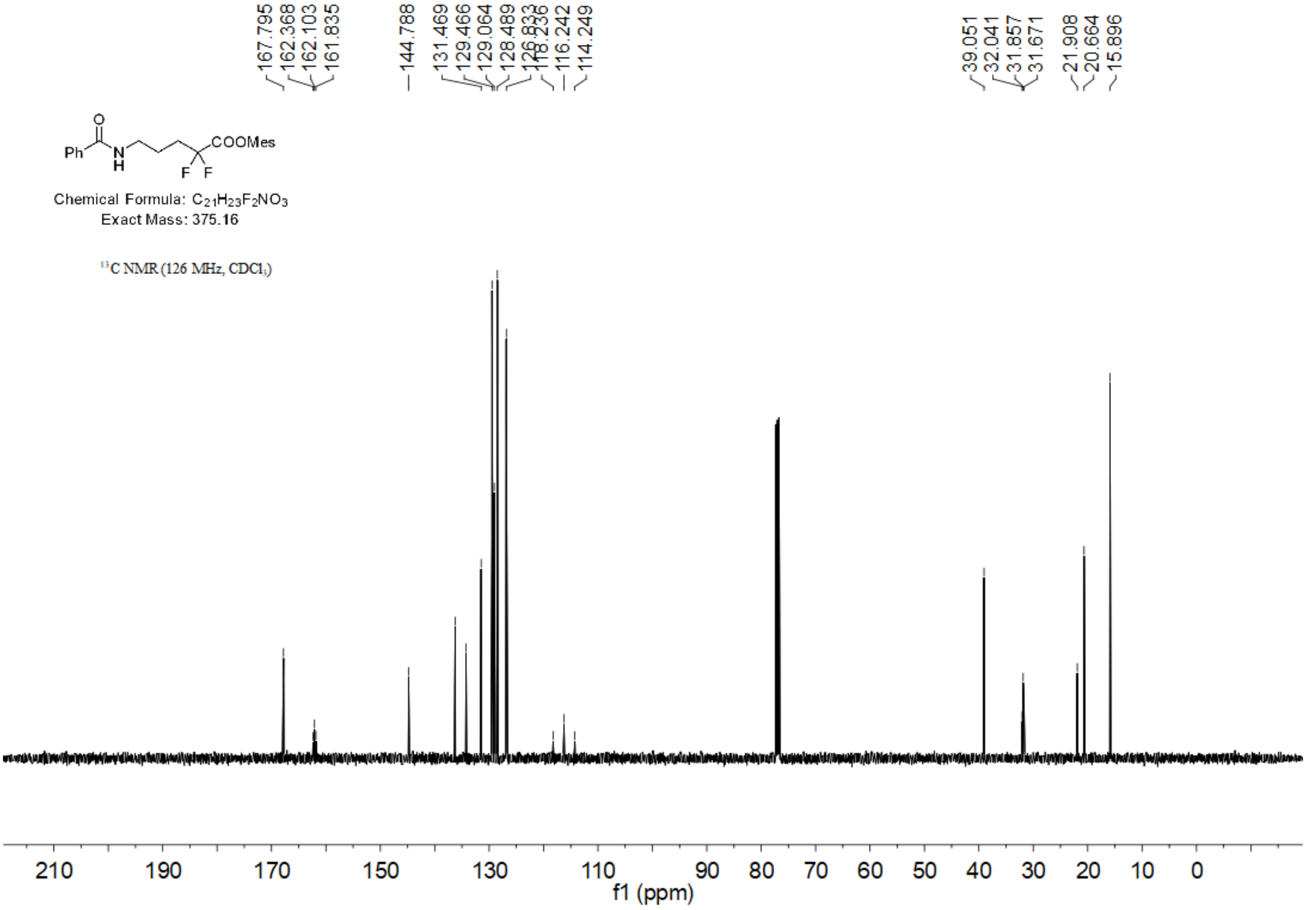
Mesityl 5-benzamido-2,2-difluoropentanoate (10b)





Chemical Formula: $C_{21}H_{23}F_2NO_3$
Exact Mass: 375.16

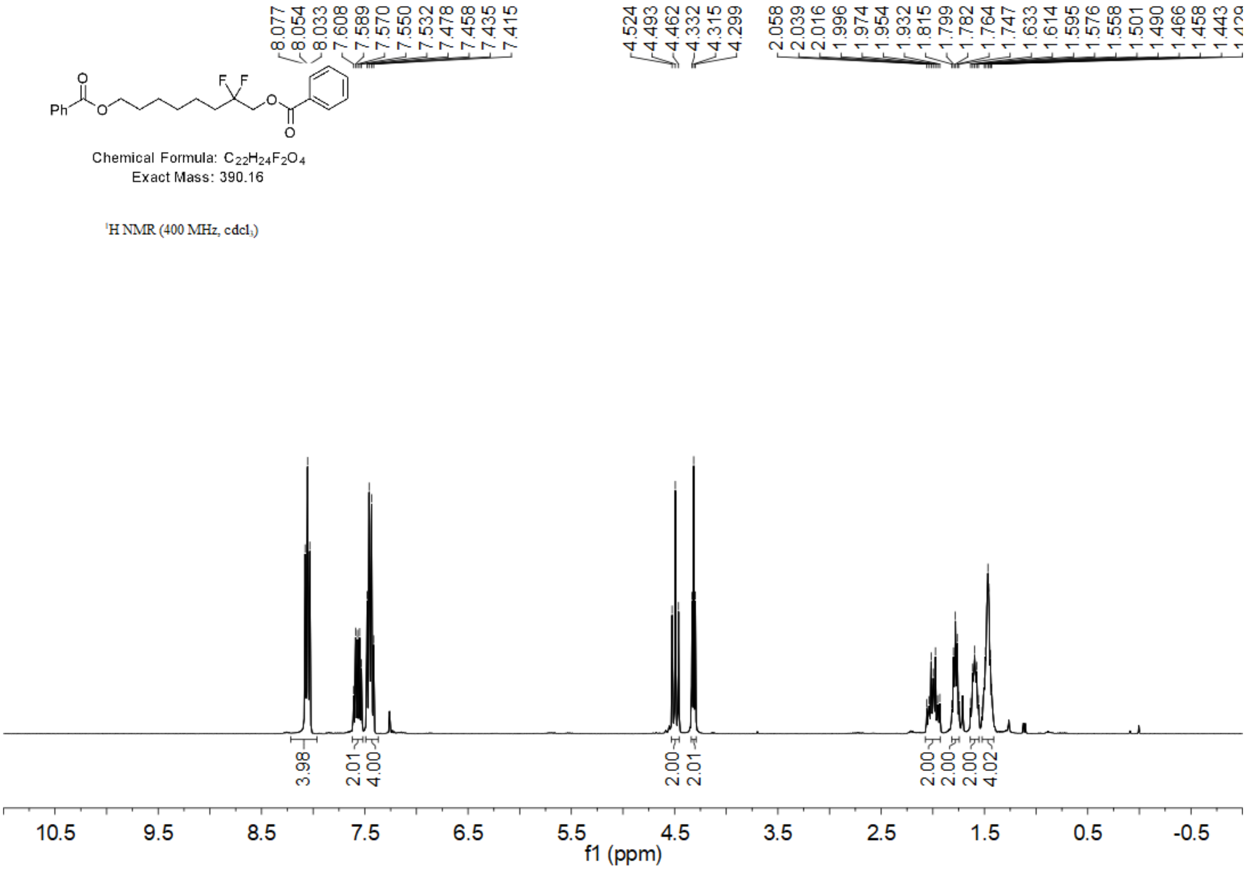
^{19}F NMR (376 MHz, cdcl$_3$)

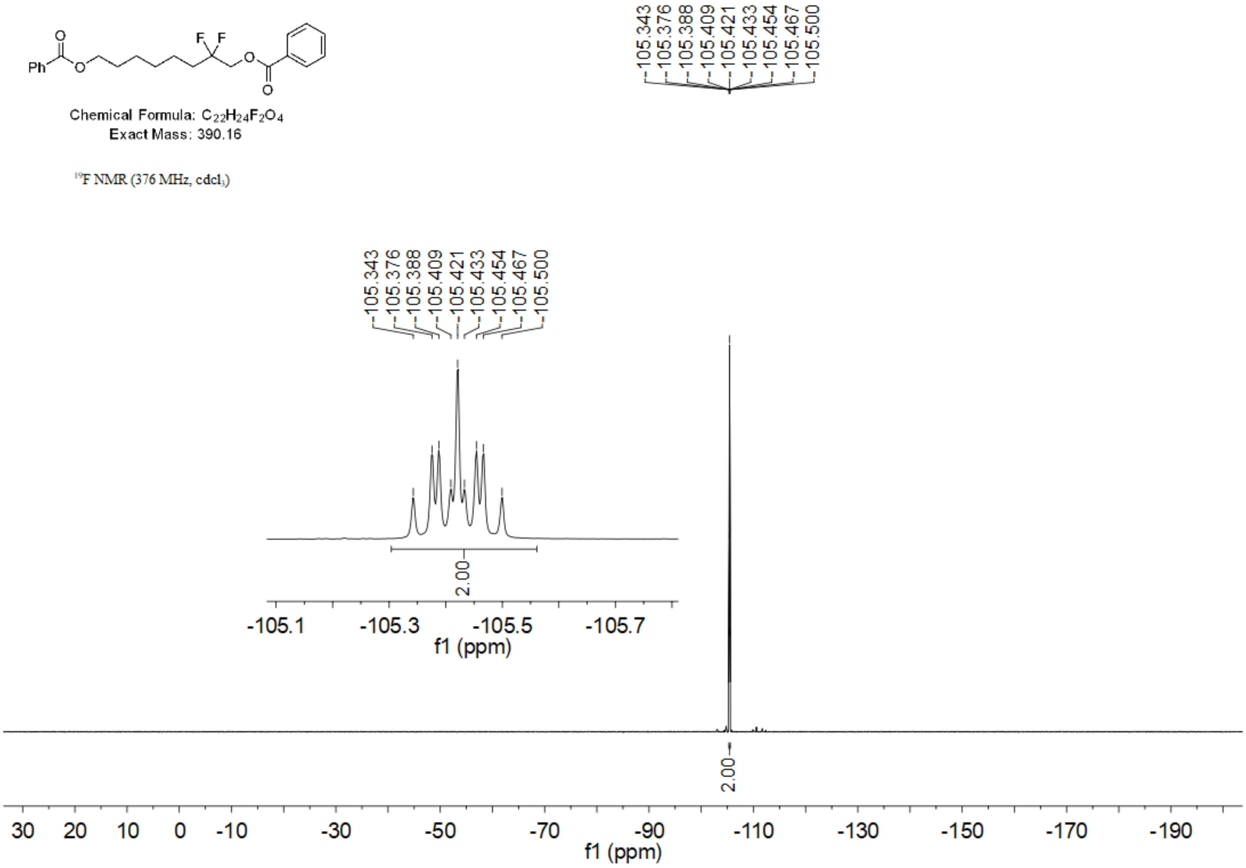


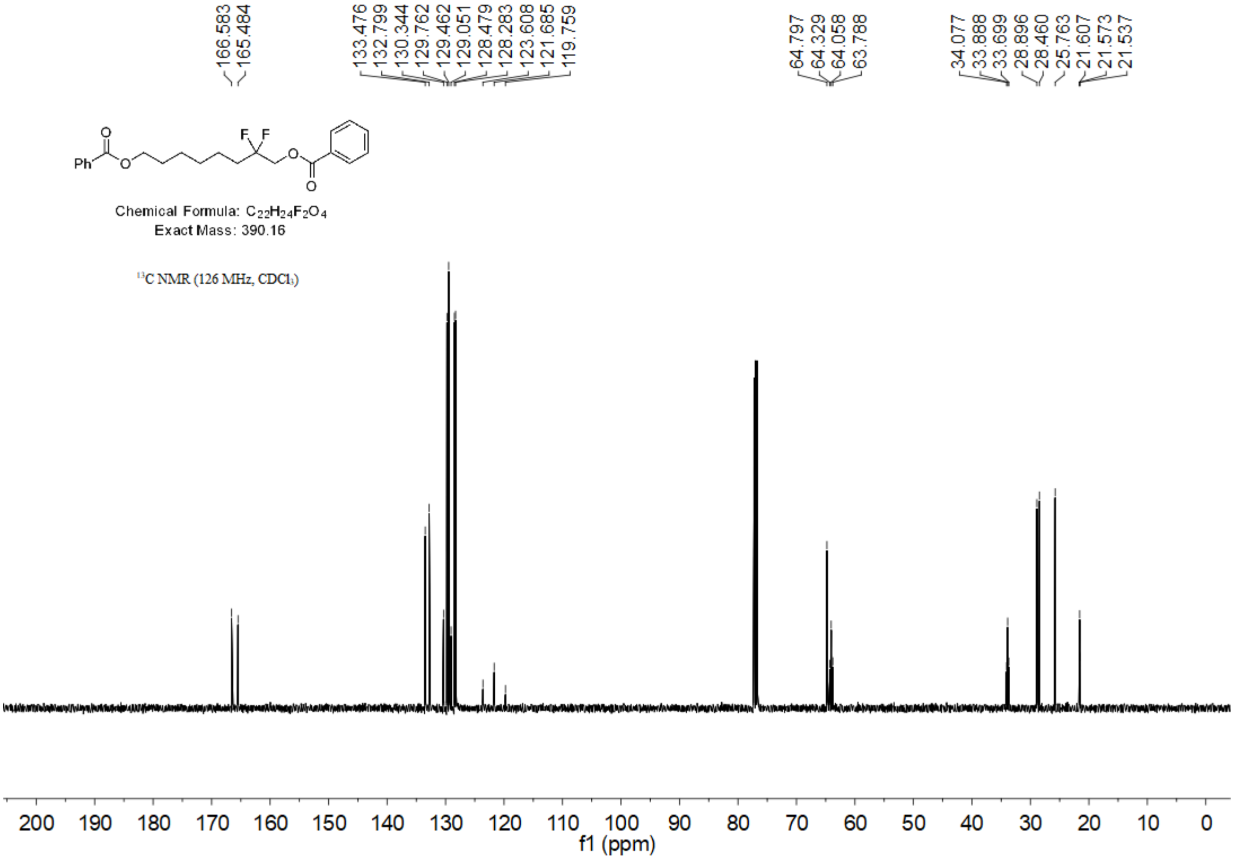
Chemical Formula: $C_{21}H_{23}F_2NO_3$
Exact Mass: 375.16

^{13}C NMR (126 MHz, CDCl$_3$)

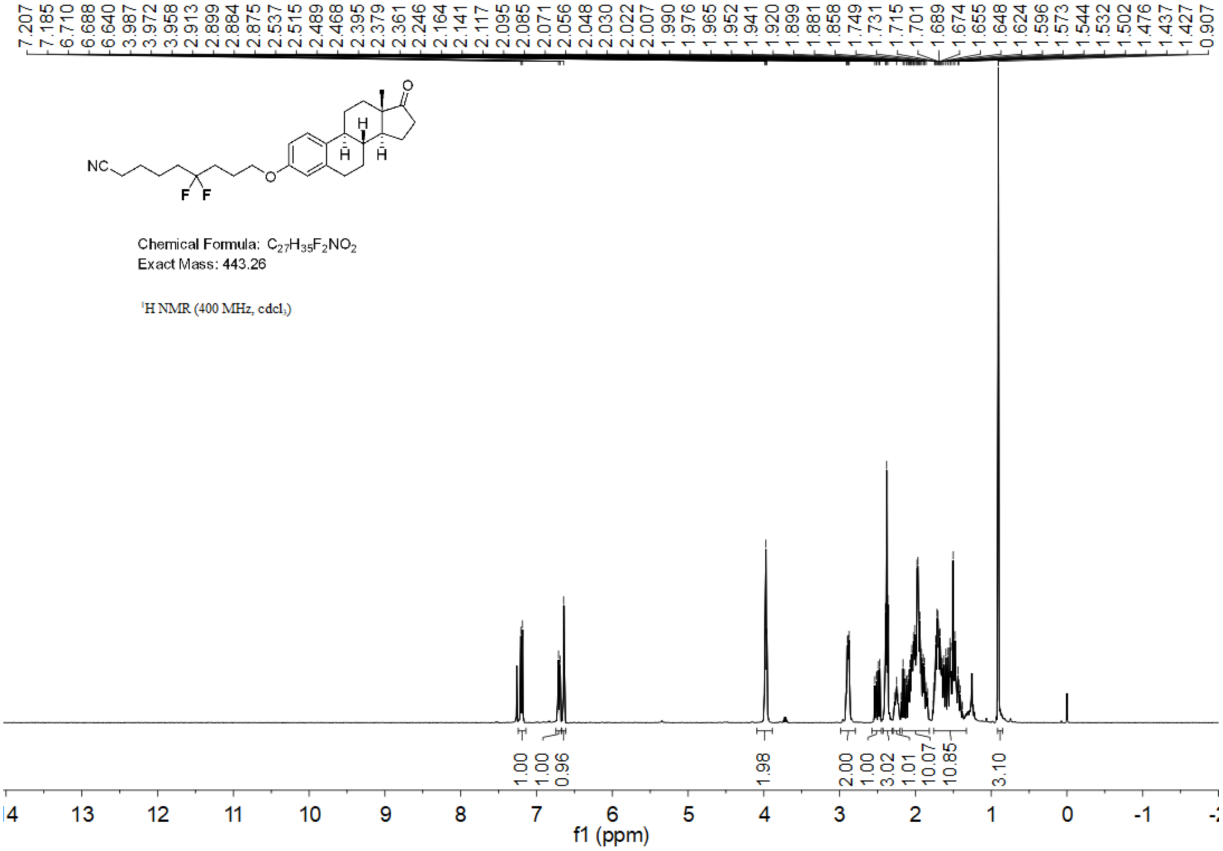
2,2-Difluorooctane-1,8-diyl dibenzoate (10c)

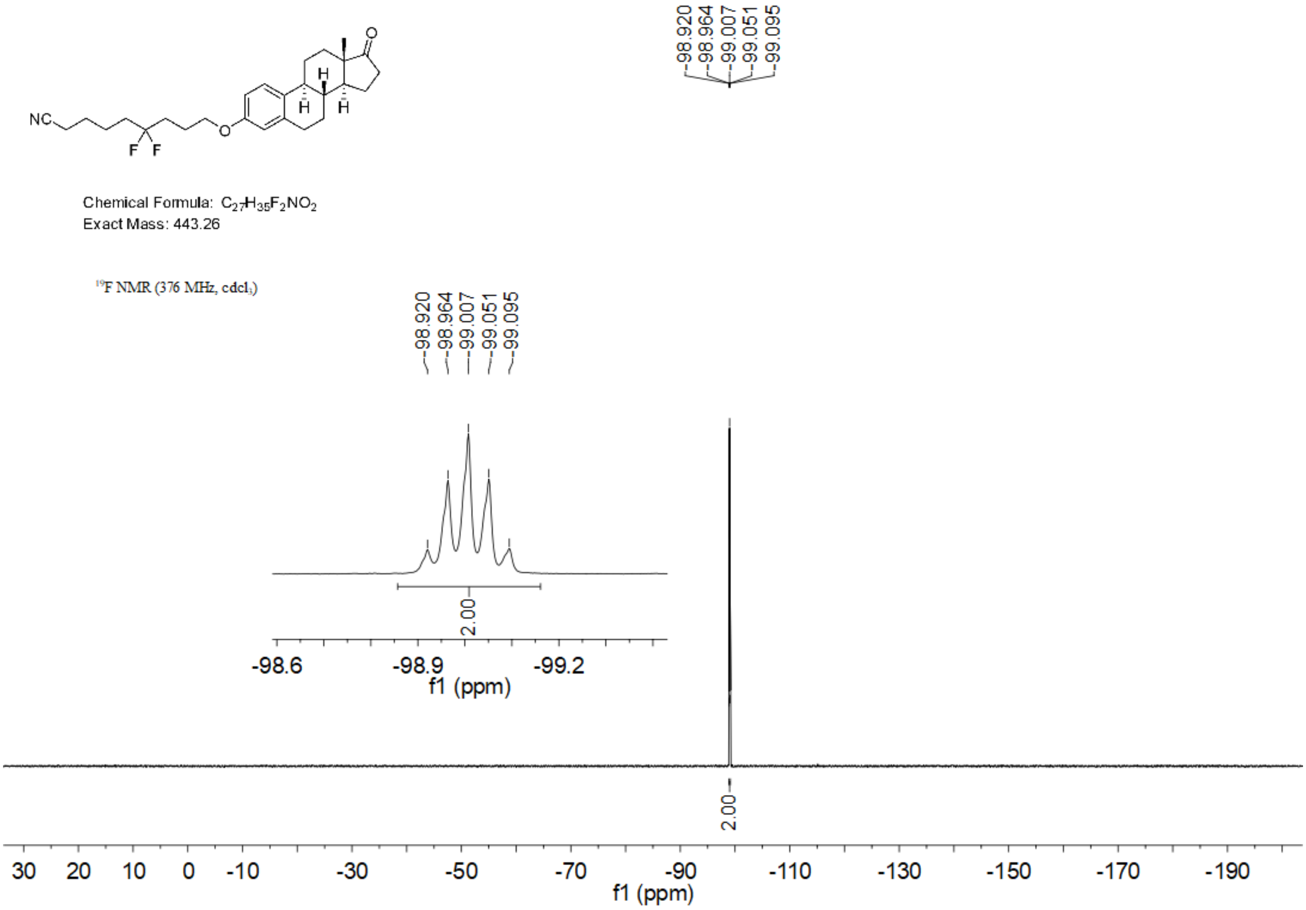


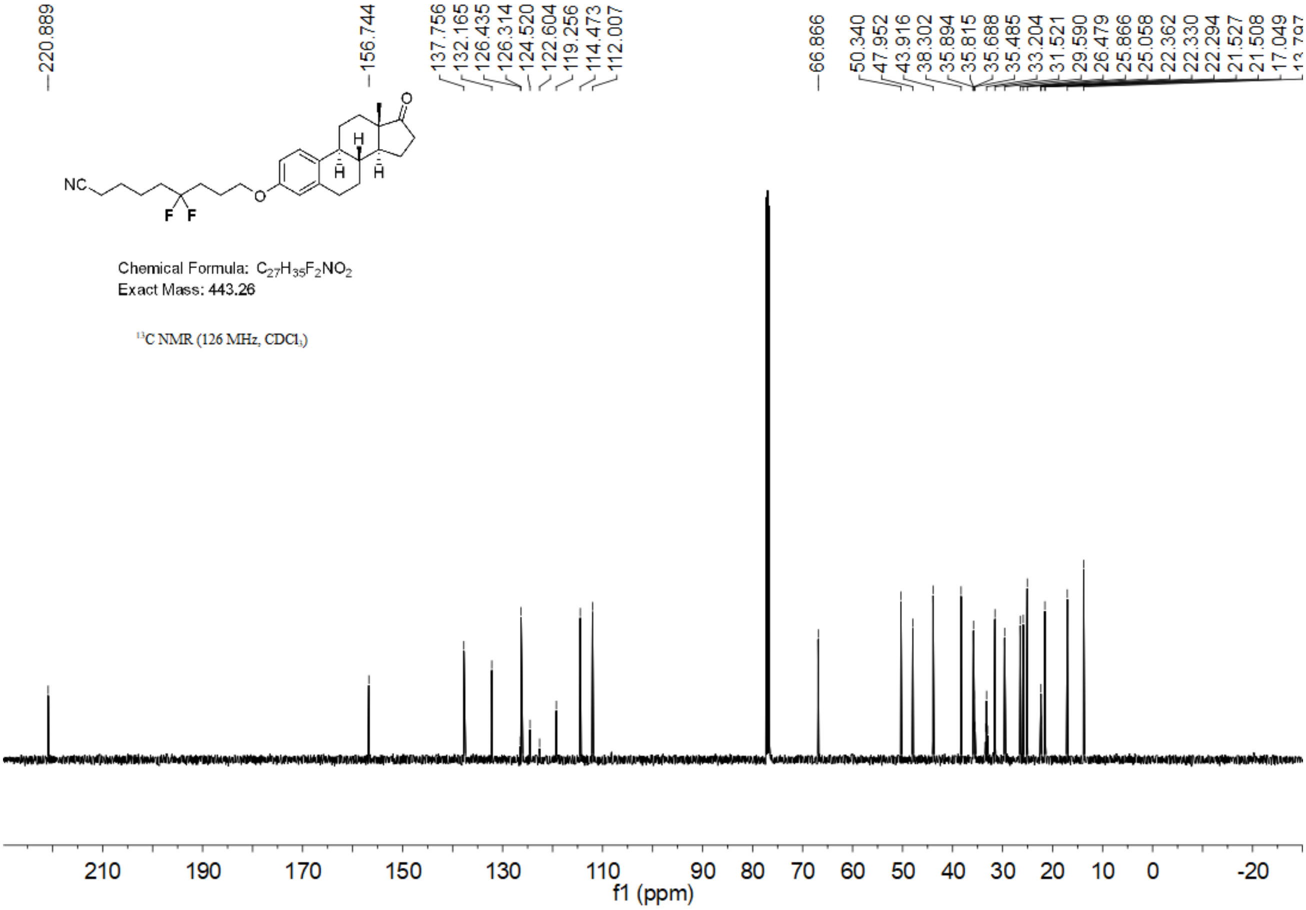




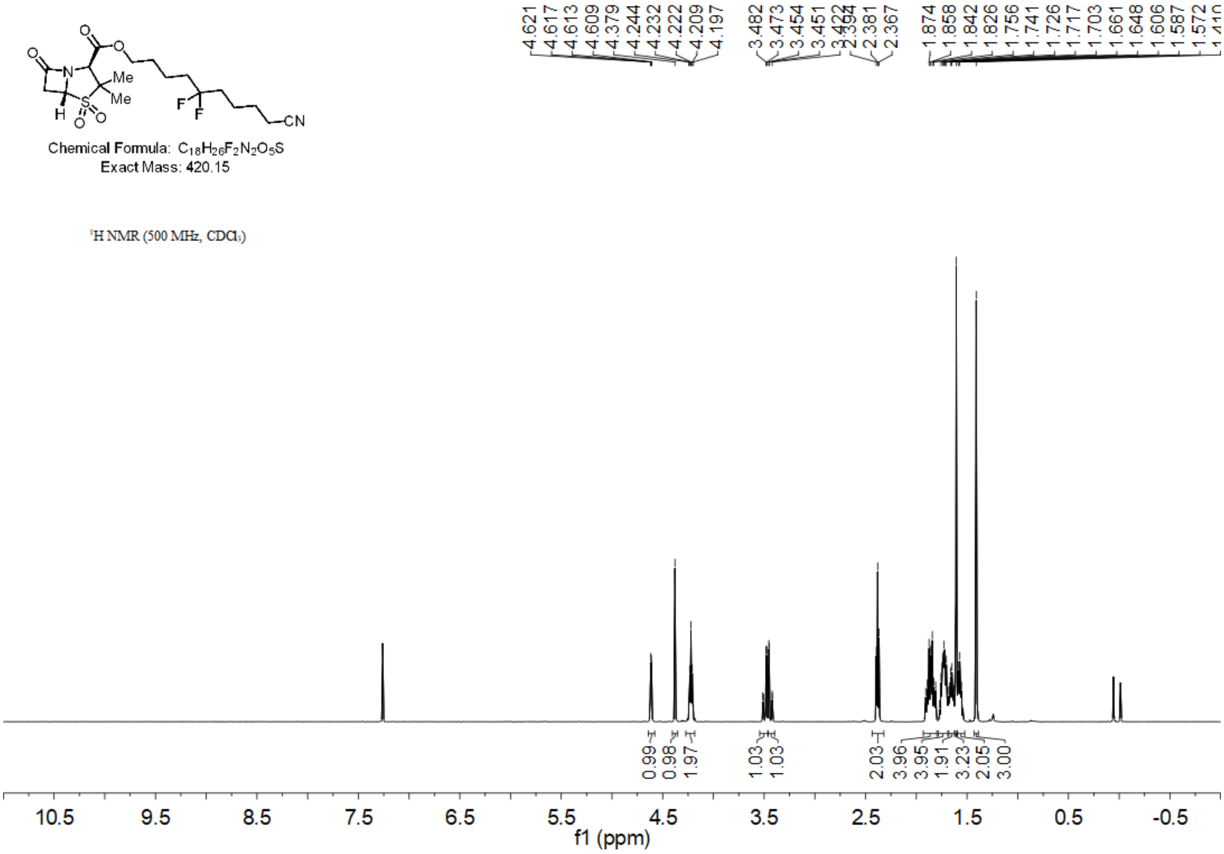
6,6-Difluoro-9-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)nonanenitrile (10d)

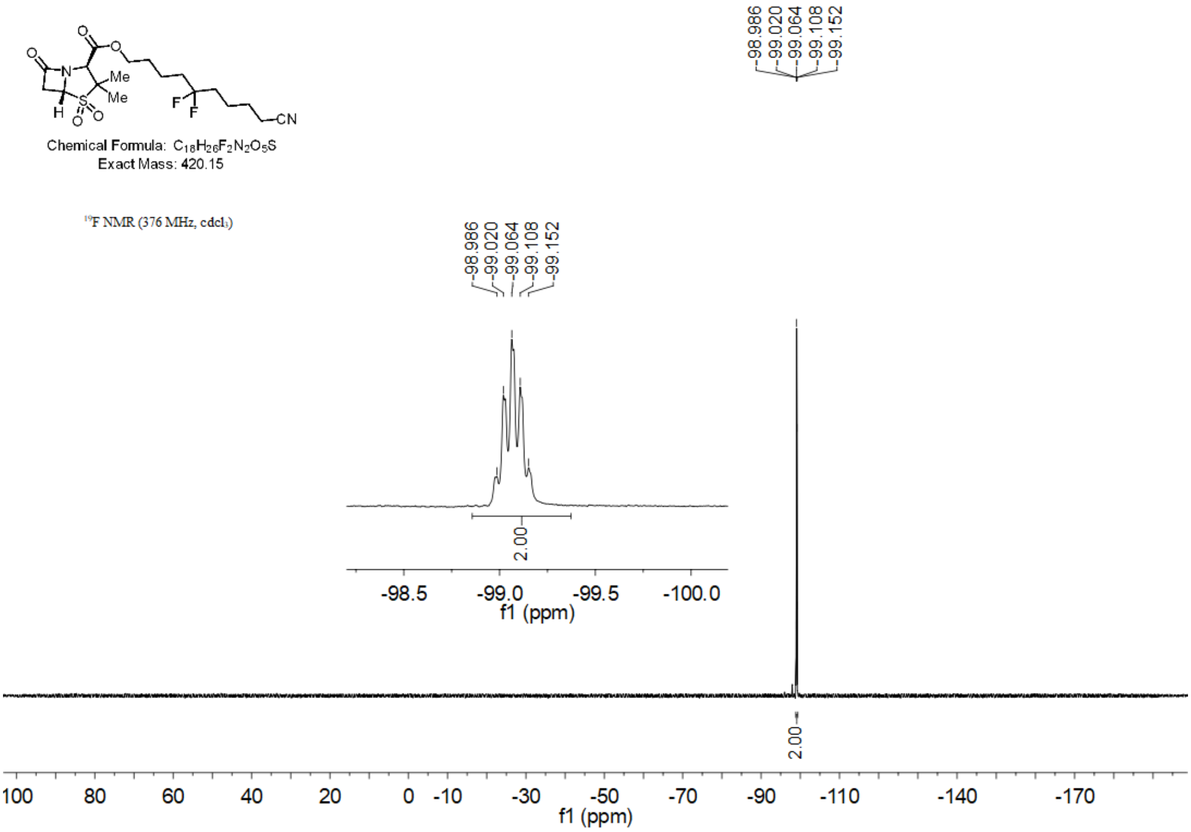


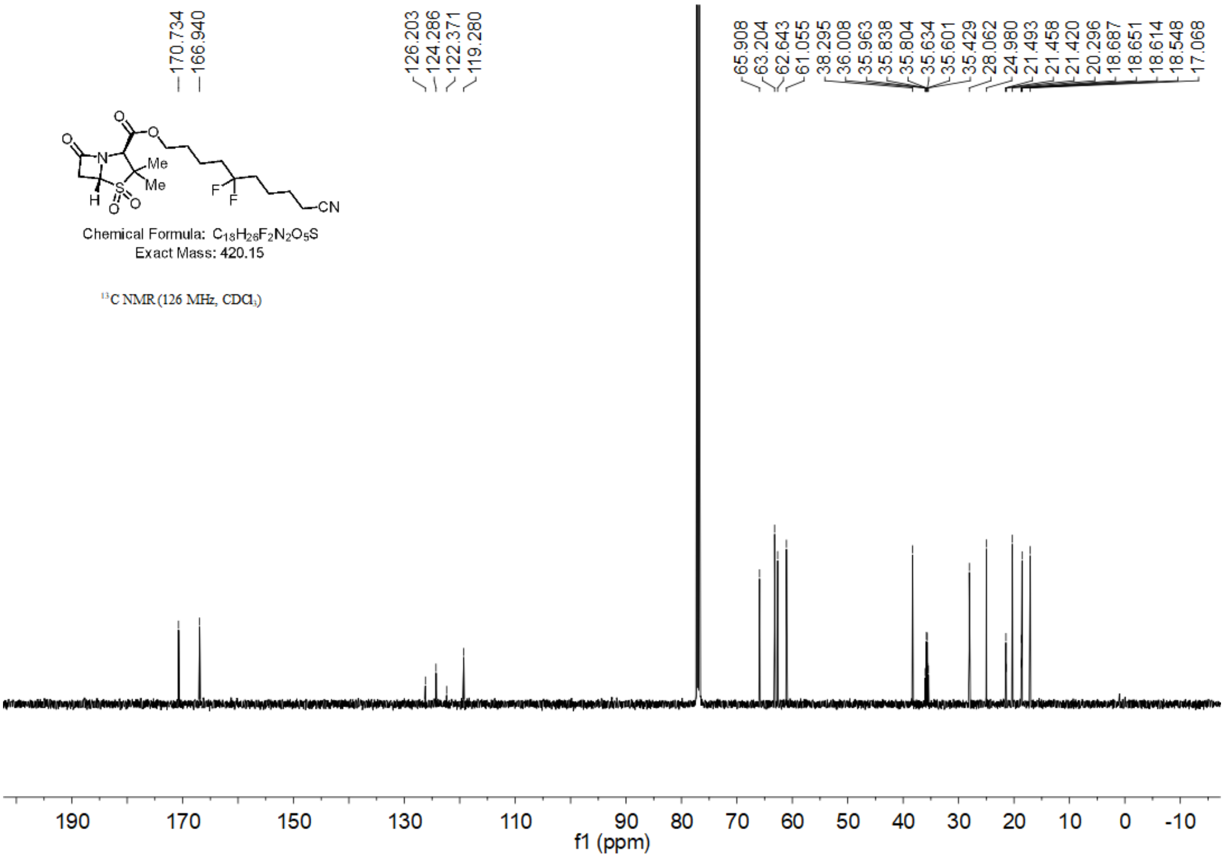

-98.920
-98.964
-99.007
-99.051
-99.095
NC
F F
O
H
H
H
Chemical Formula: $C_{27}H_{35}F_2NO_2$
Exact Mass: 443.26
^{19}F NMR (376 MHz, cdcl$_3$)
-98.920
-98.964
-99.007
-99.051
-99.095
2.00
-98.6
-98.9
-99.2
f1 (ppm)
2.00
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)


220.889
156.744
137.756
132.165
126.435
126.314
124.520
122.604
119.256
114.473
112.007
66.866
50.340
47.952
43.916
38.302
35.894
35.815
35.688
35.485
33.204
31.521
29.590
26.479
25.866
25.058
22.362
22.330
22.294
21.527
21.508
17.049
13.797
NC
F F
O
H
H
H
Chemical Formula: $C_{27}H_{35}F_2NO_2$
Exact Mass: 443.26
^{13}C NMR (126 MHz, CDCl$_3$)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-20
f1 (ppm)

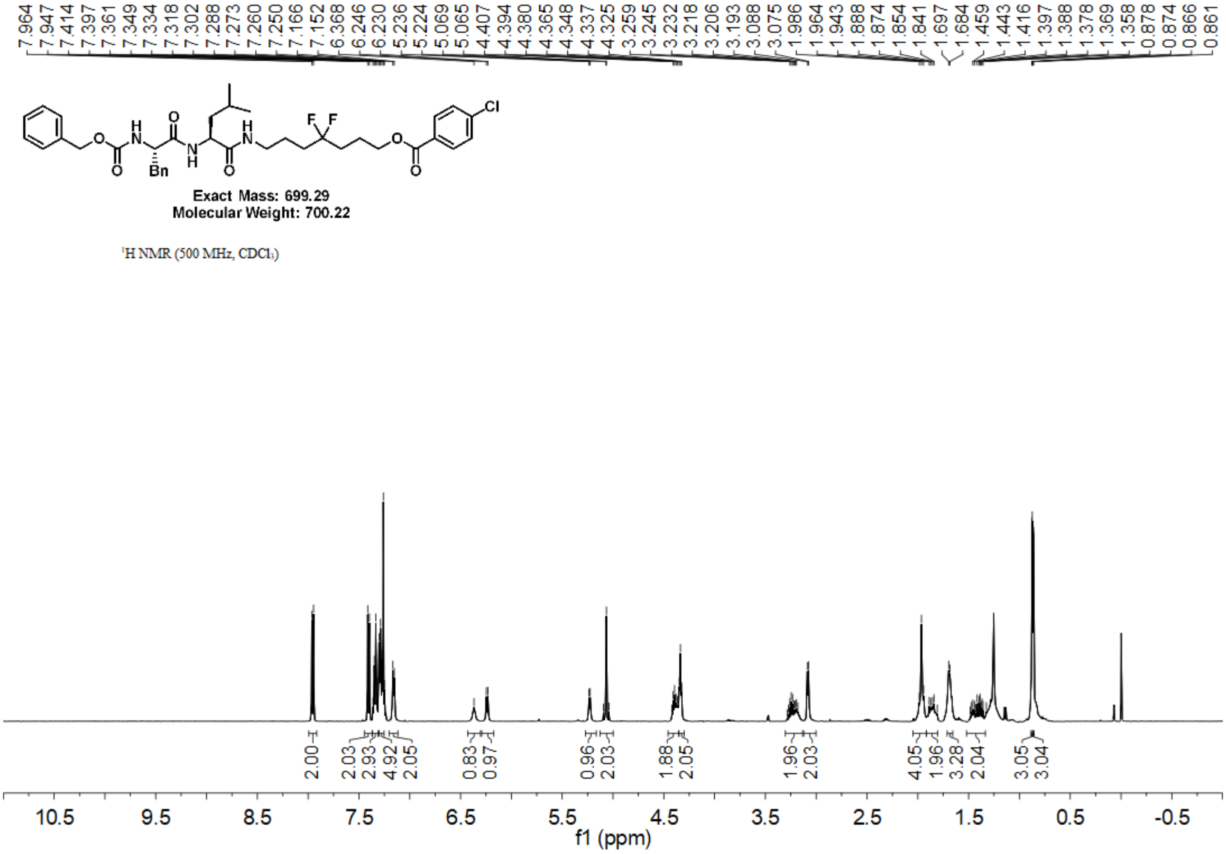
9-Cyano-5,5-difluorononyl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide (10e)

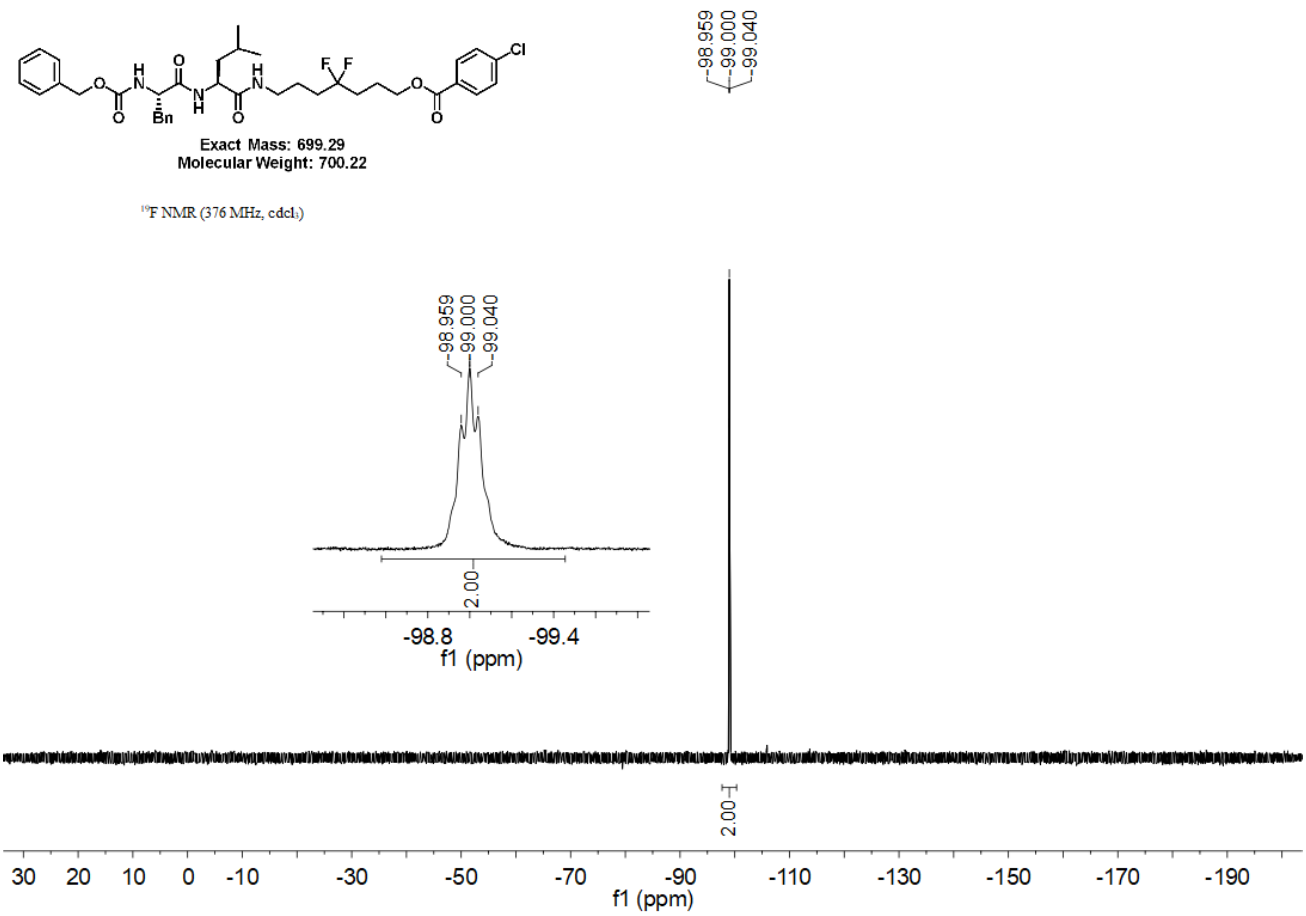




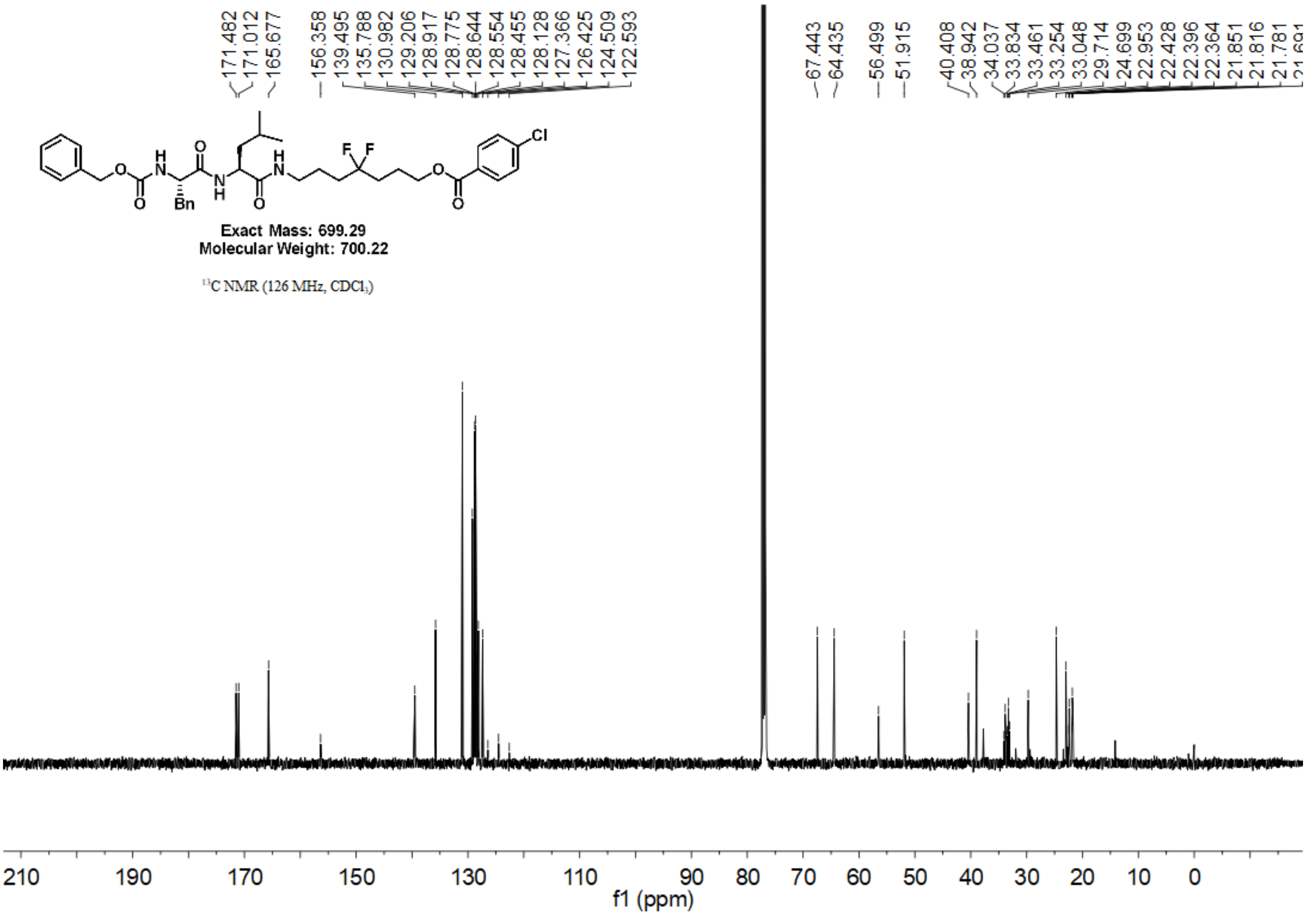


(5*S*,8*S*)-5-Benzyl-14,14-difluoro-8-isobutyl-3,6,9-trioxo-1-phenyl-2-oxa-4,7,10-triazaheptadecan-17-yl 4-chlorobenzoate (10f)



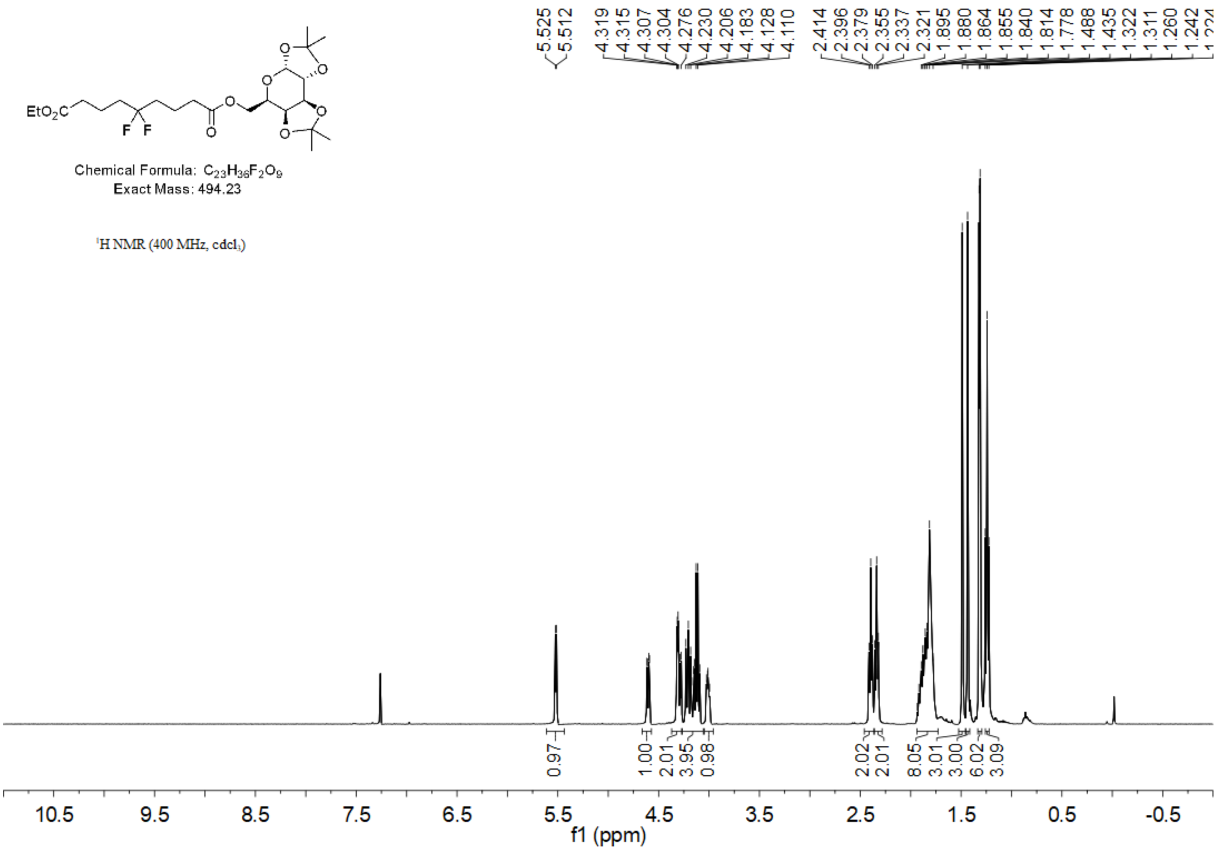


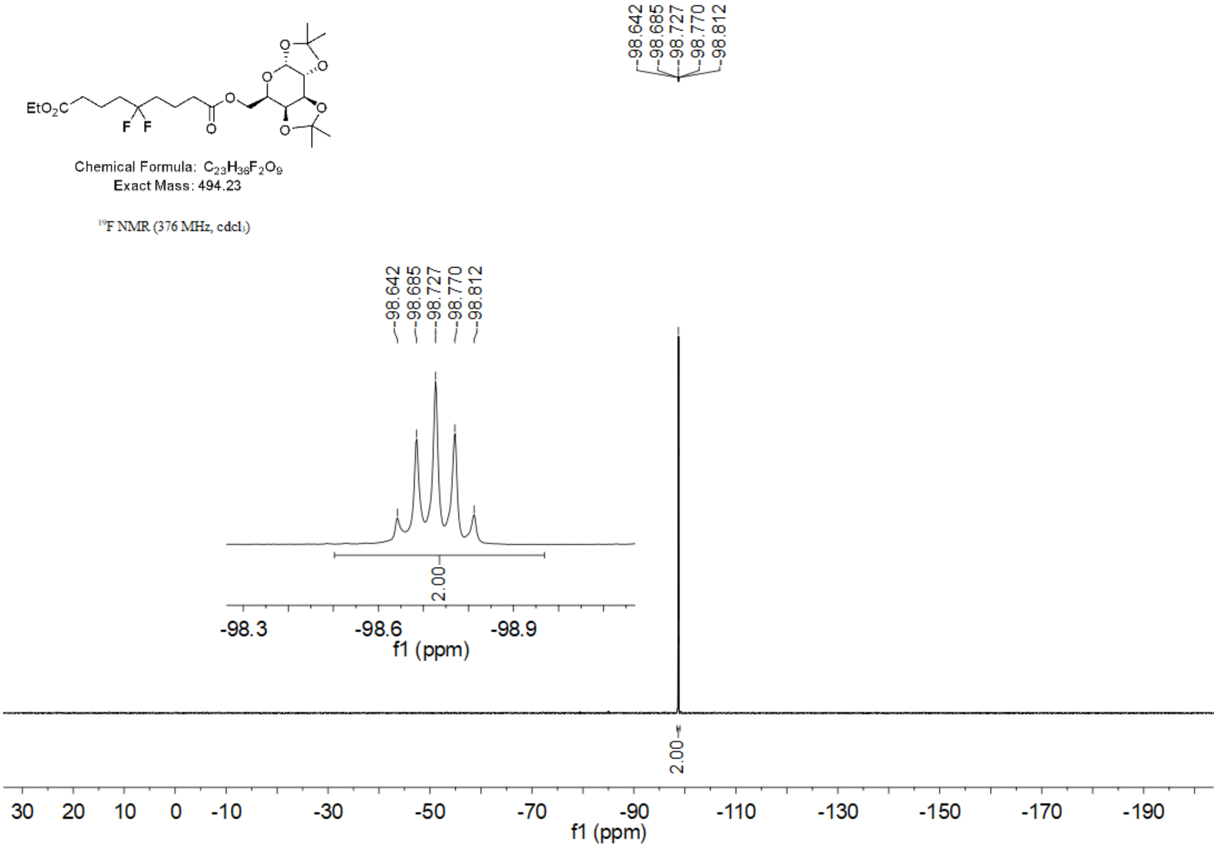
^{19}F NMR (376 MHz, cdcl$_3$)

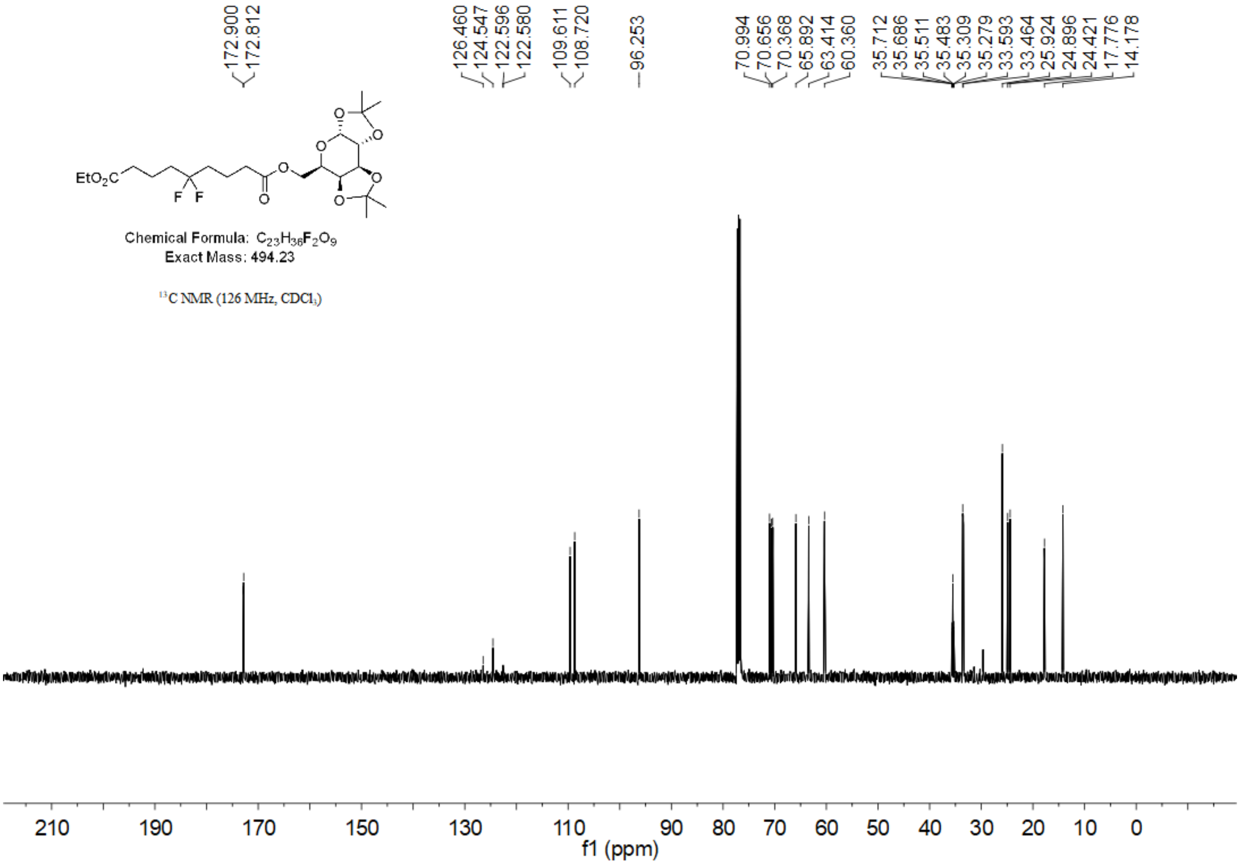


^{13}C NMR (126 MHz, CDCl$_3$)

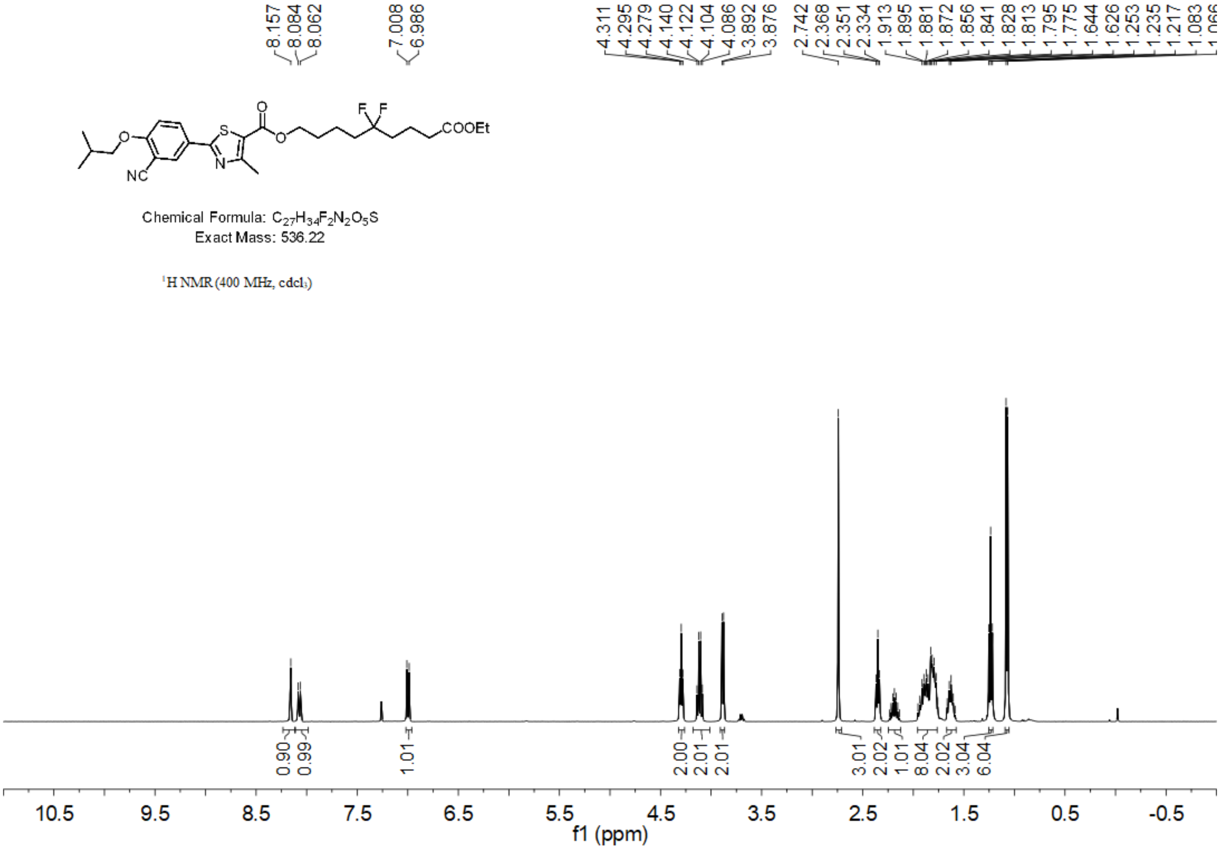
1-Ethyl 9-(((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl) 5,5-difluorononanedioate (10g)

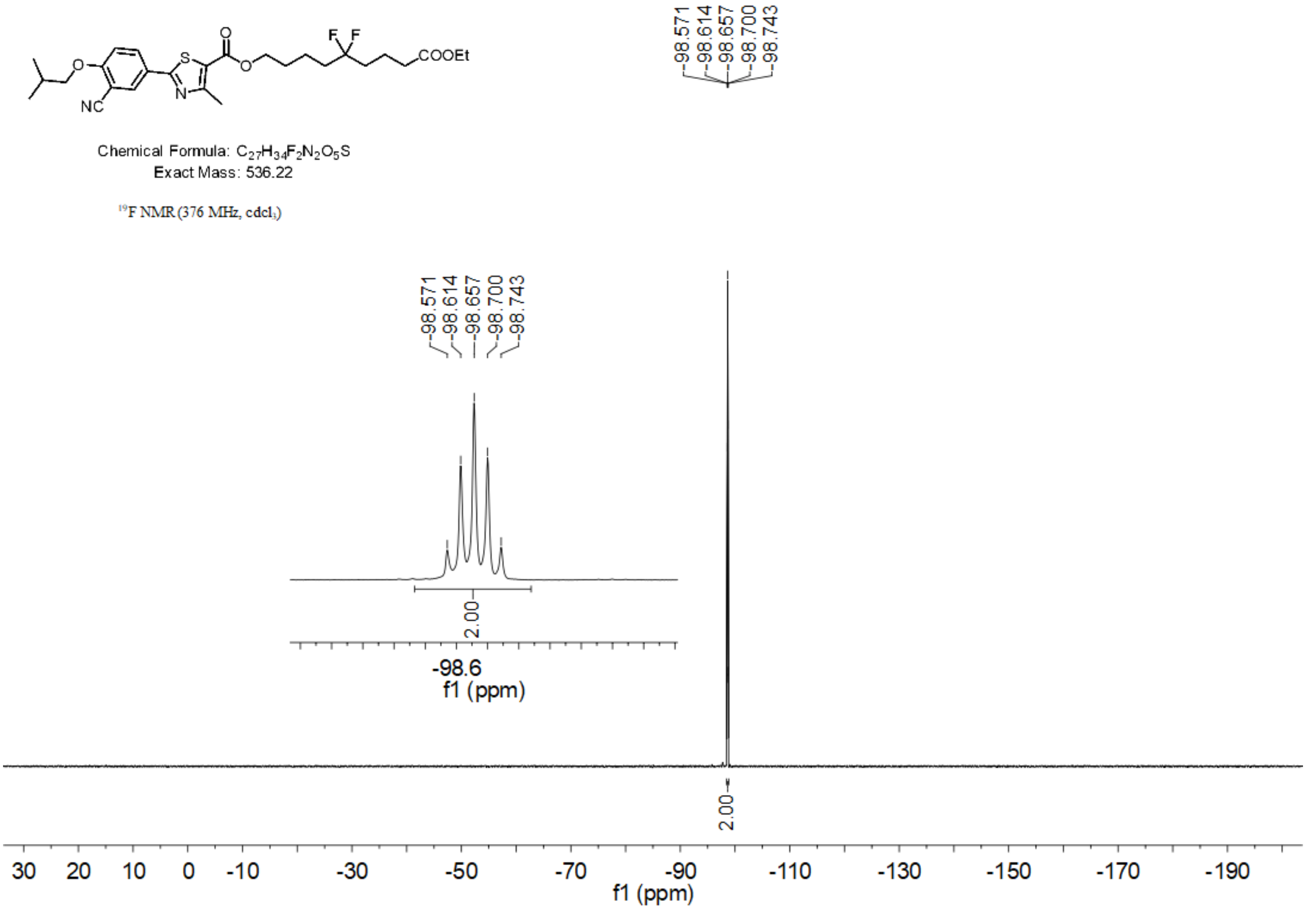


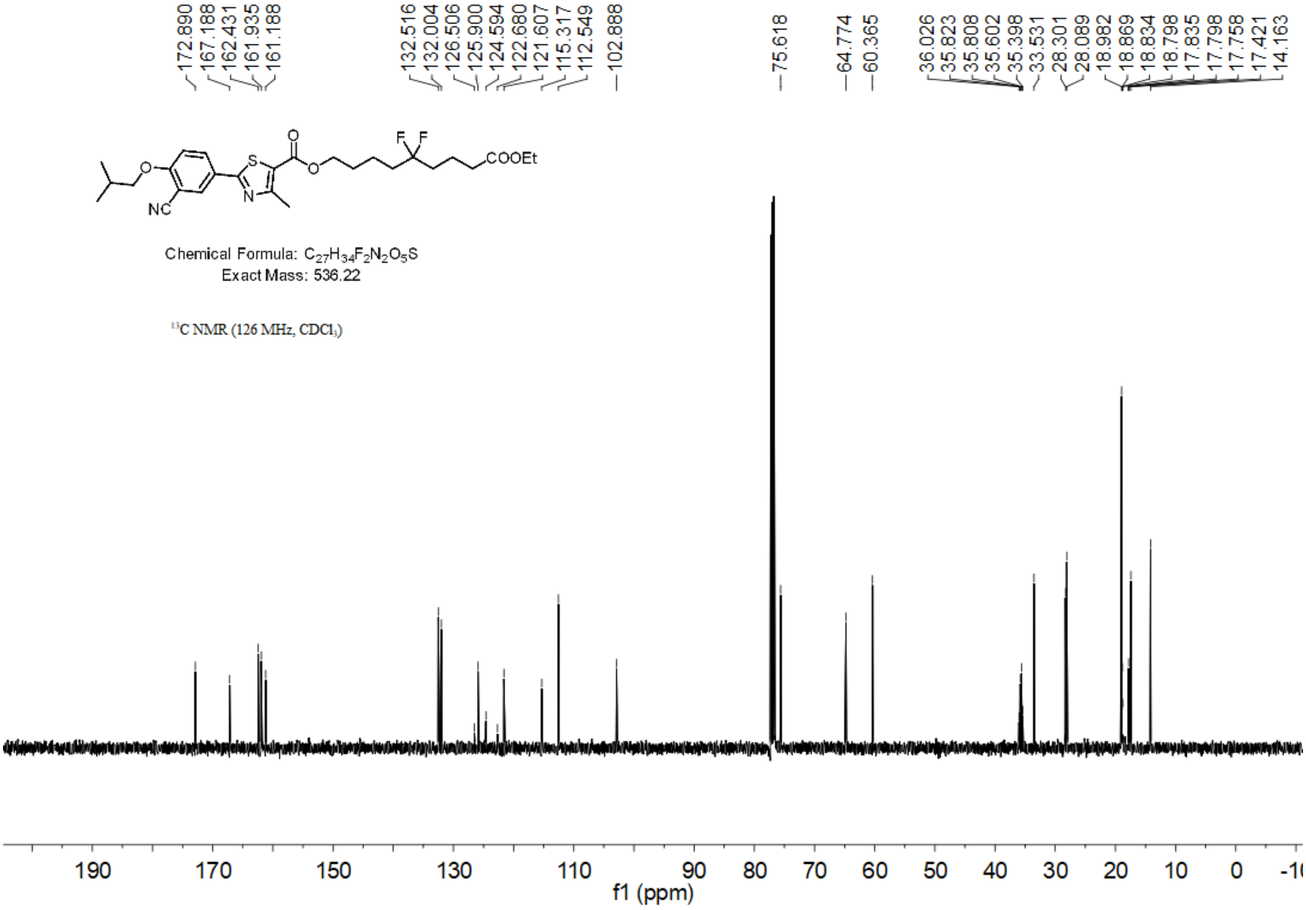




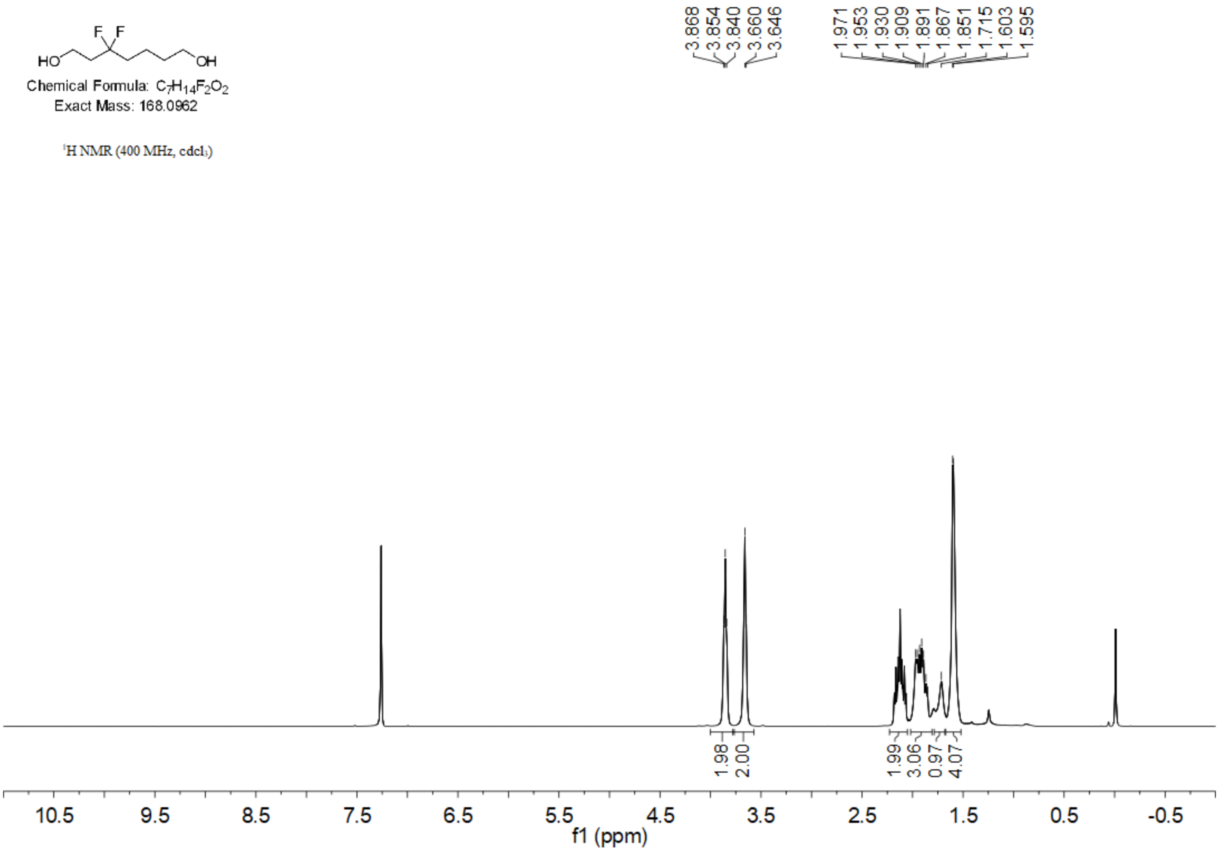
9-Ethoxy-5,5-difluoro-9-oxononyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (10h)

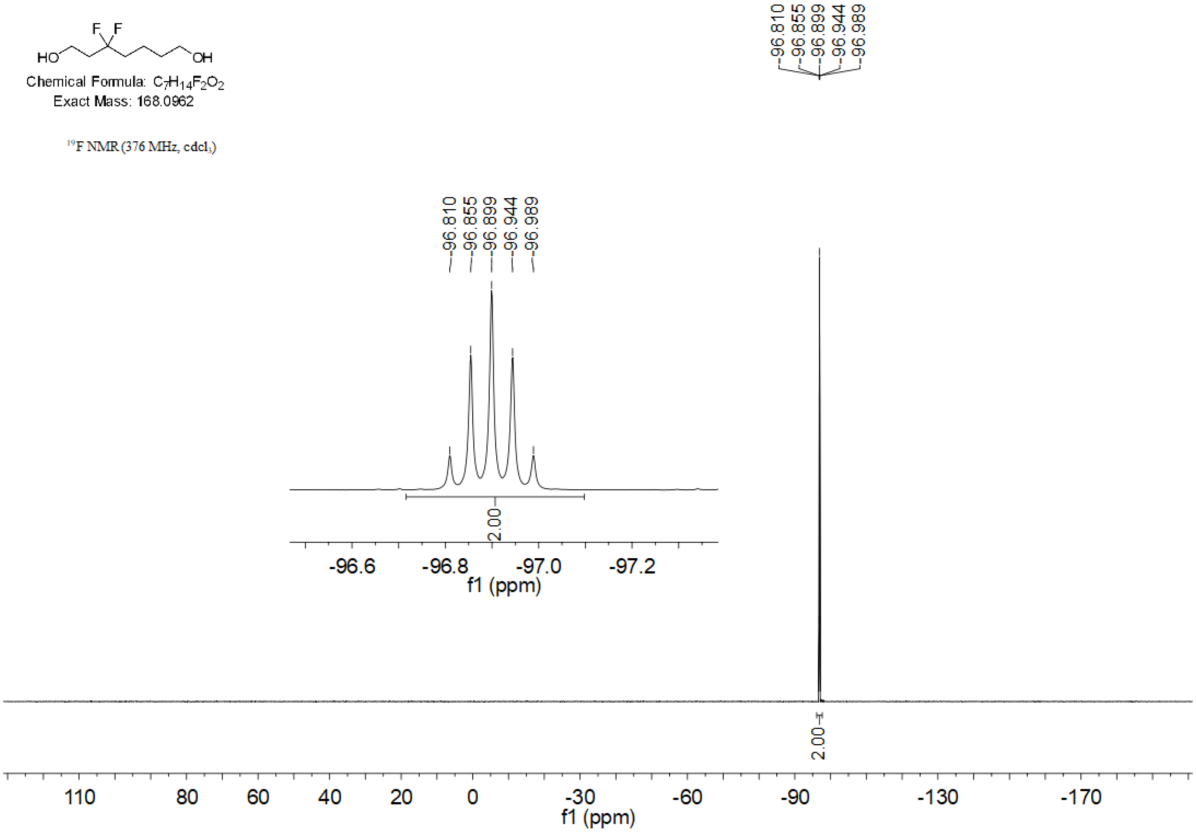


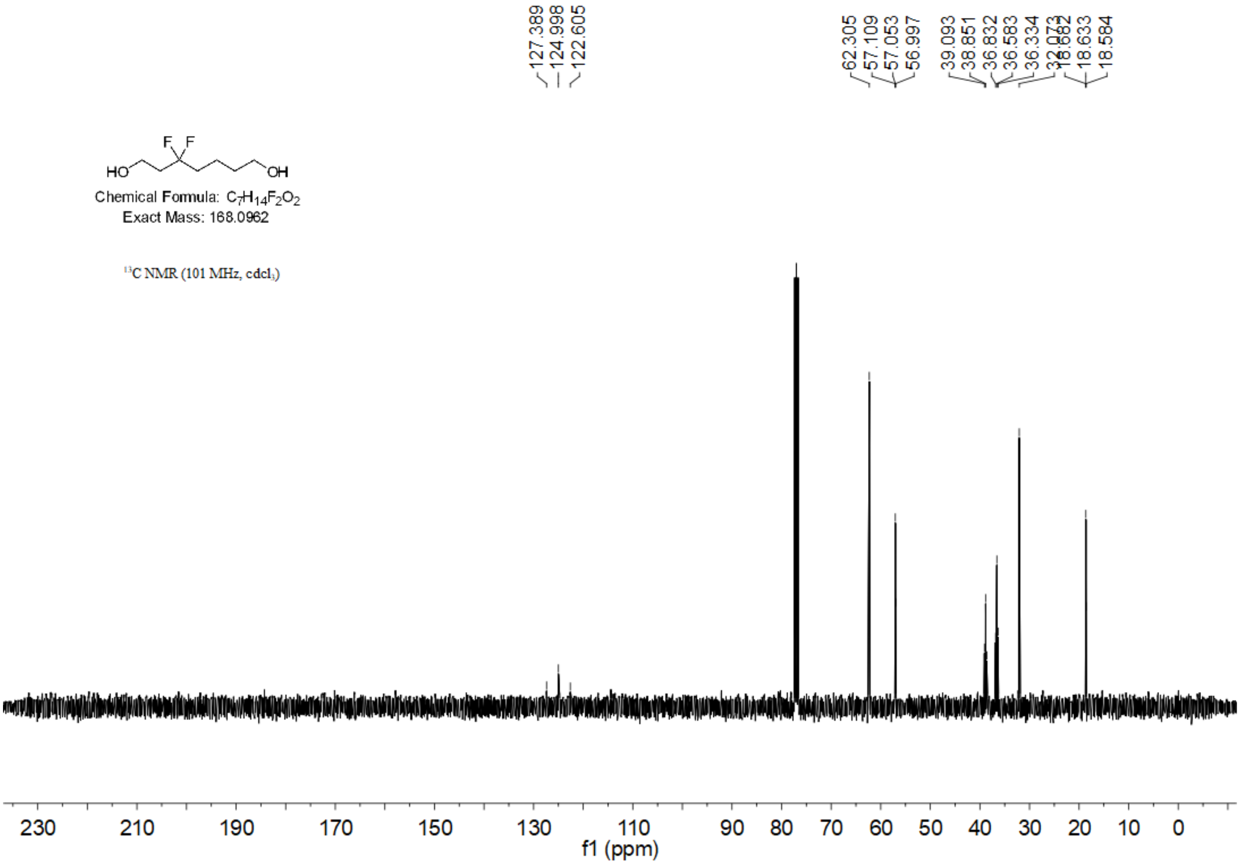

-98.571
-98.614
-98.657
-98.700
-98.743
F F
O
S
N
O
NC
COOEt
Chemical Formula: $C_{27}H_{34}F_2N_2O_5S$
Exact Mass: 536.22
^{19}F NMR (376 MHz, cdcl$_3$)
2.00
-98.6
f1 (ppm)
2.00
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)


172.890
167.188
162.431
161.935
161.188
132.516
132.004
126.506
125.900
124.594
122.680
121.607
115.317
112.549
102.888
75.618
64.774
60.365
36.026
35.823
35.808
35.602
35.398
33.531
28.301
28.089
18.982
18.869
18.834
18.798
17.835
17.798
17.758
17.421
14.163
F F
O
S
N
O
NC
COOEt
Chemical Formula: $C_{27}H_{34}F_2N_2O_5S$
Exact Mass: 536.22
^{13}C NMR (126 MHz, CDCl$_3$)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3,3-Difluoroheptane-1,7-diol (11d)



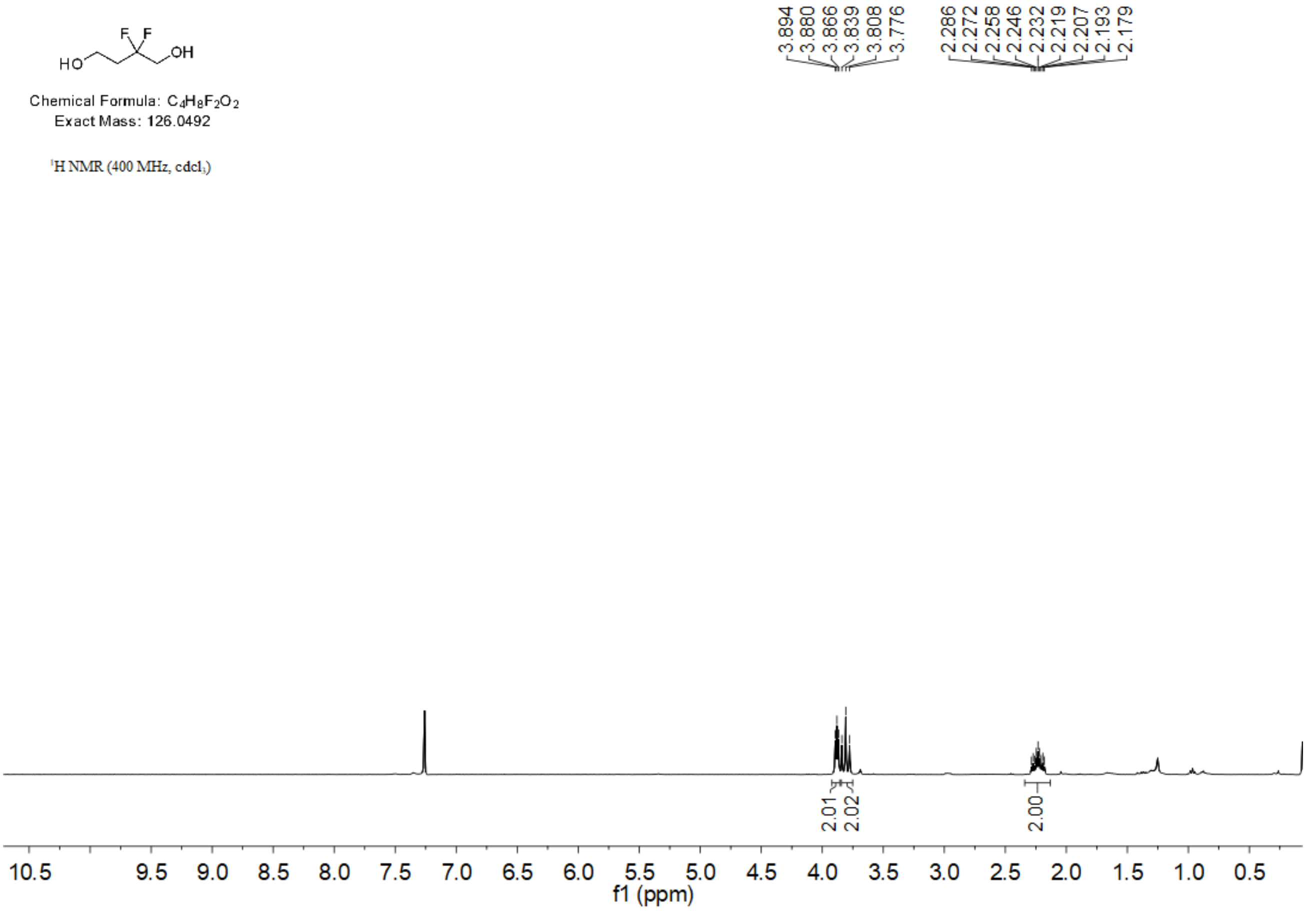




Chemical Formula: $C_7H_{14}F_2O_2$
Exact Mass: 168.0962

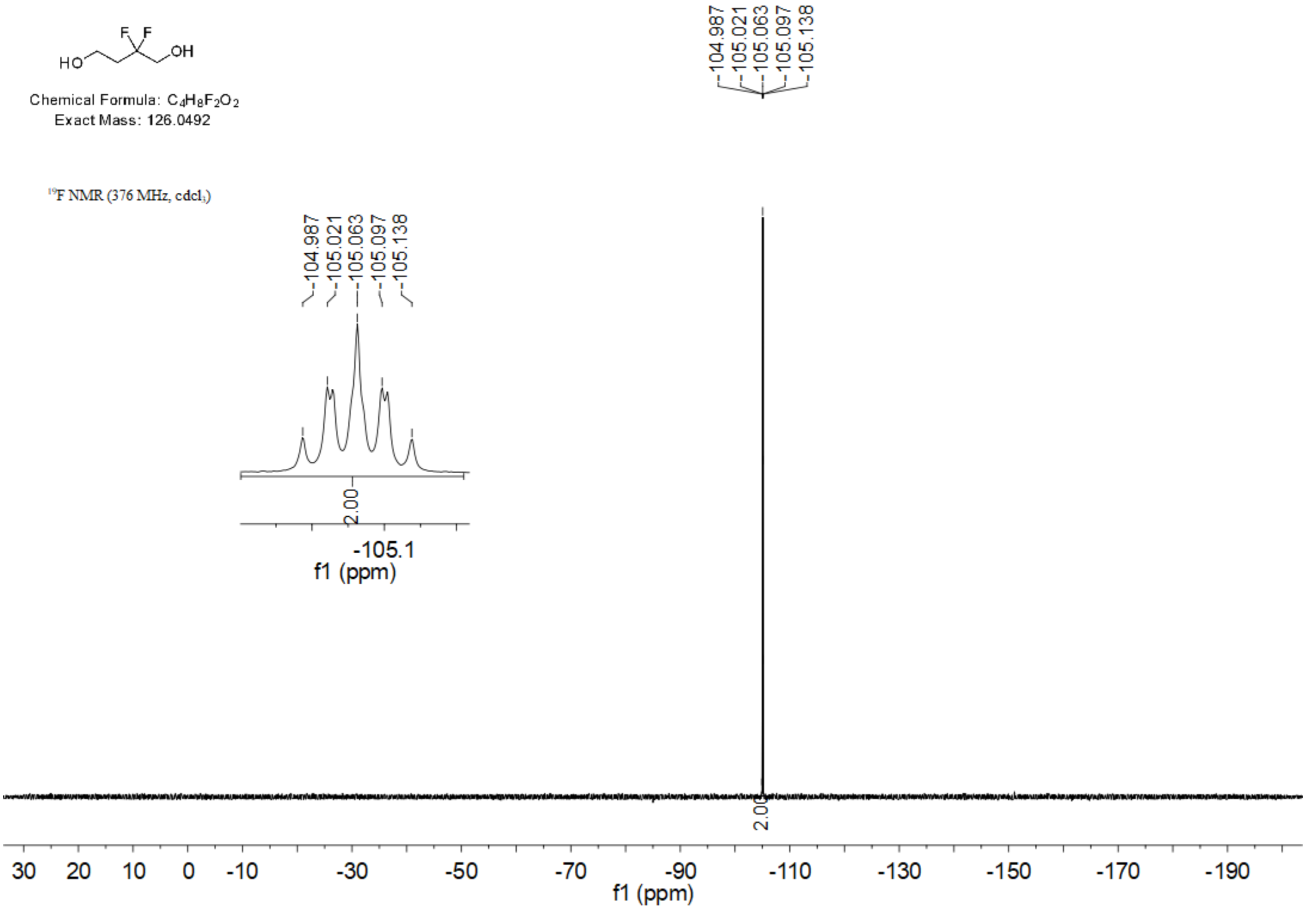
^{13}C NMR (101 MHz, cdcl$_3$)

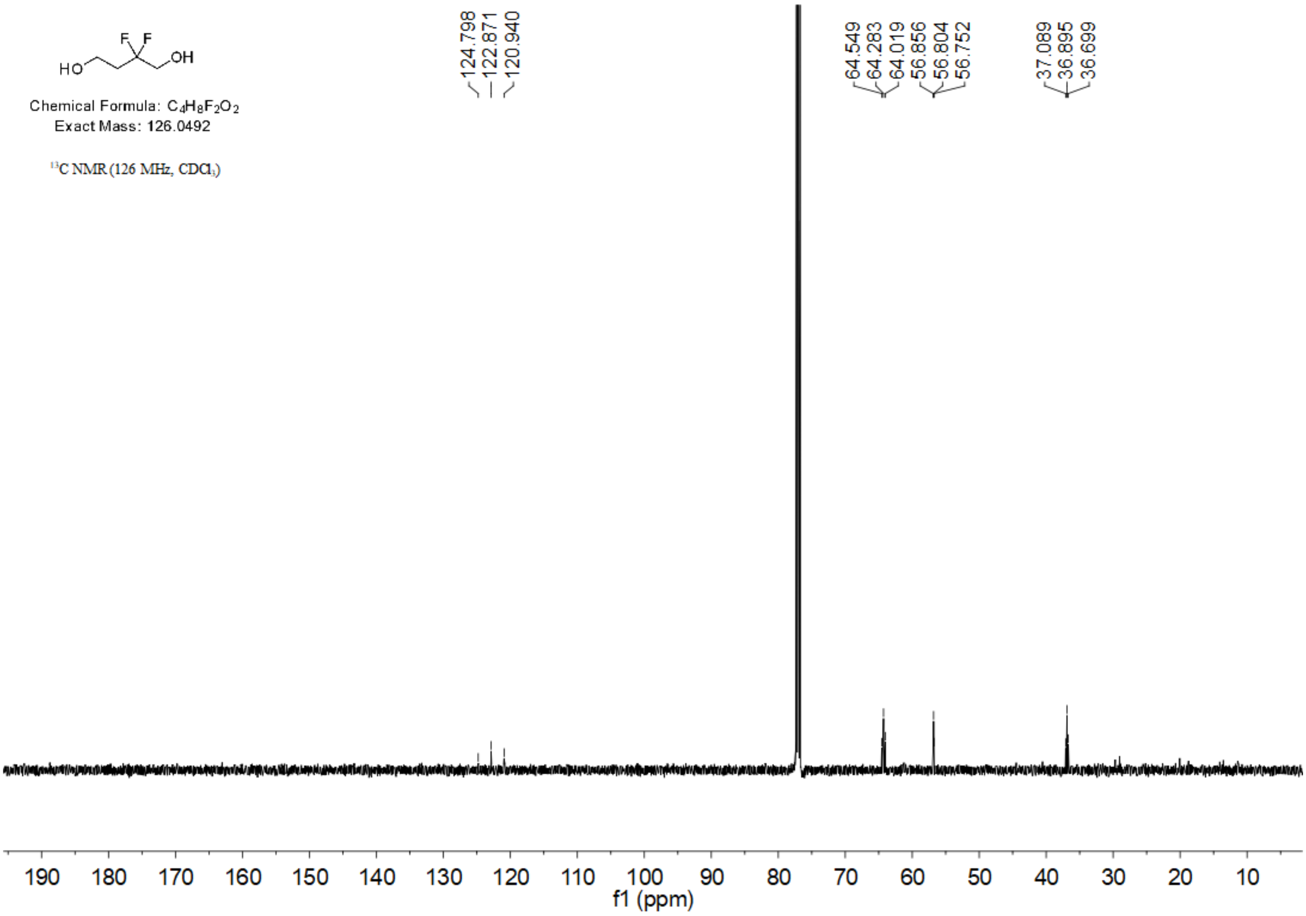
2,2-Difluorobutane-1,4-diol (11h)



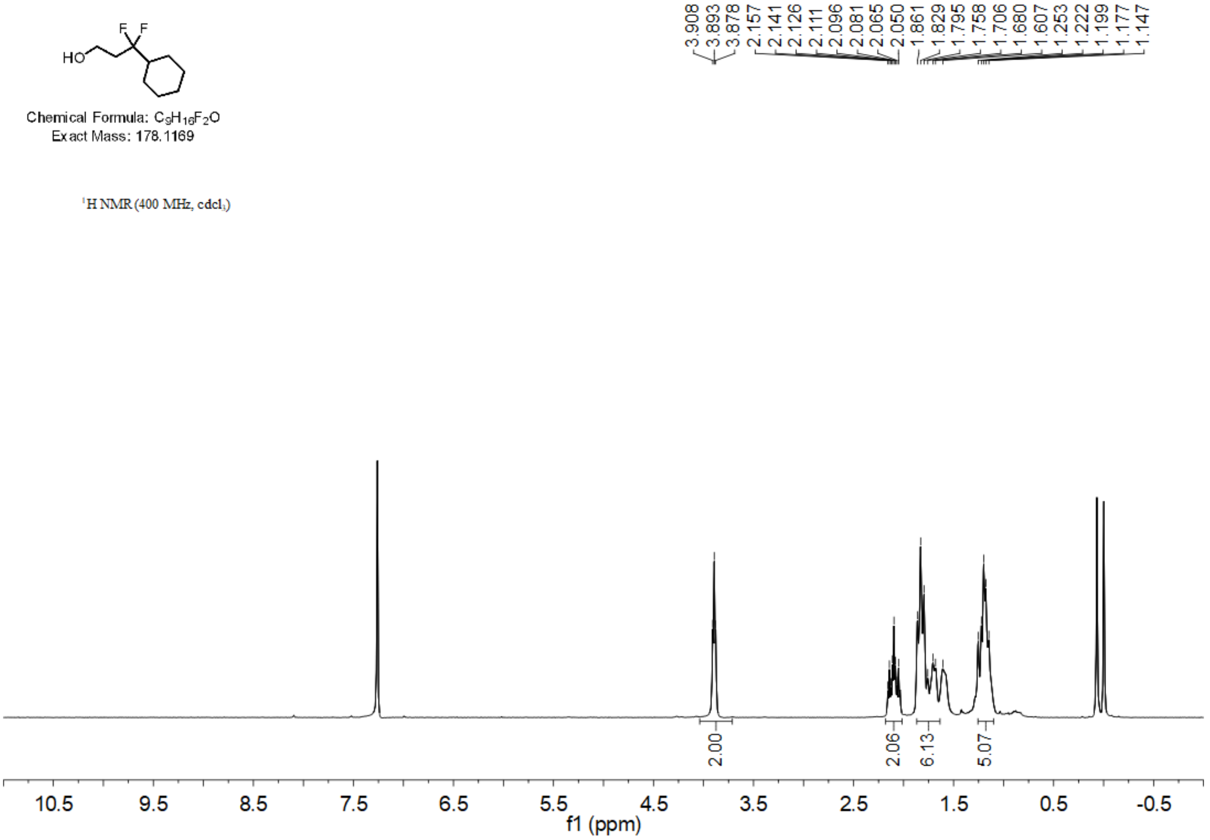
Chemical Formula: $C_4H_8F_2O_2$
Exact Mass: 126.0492

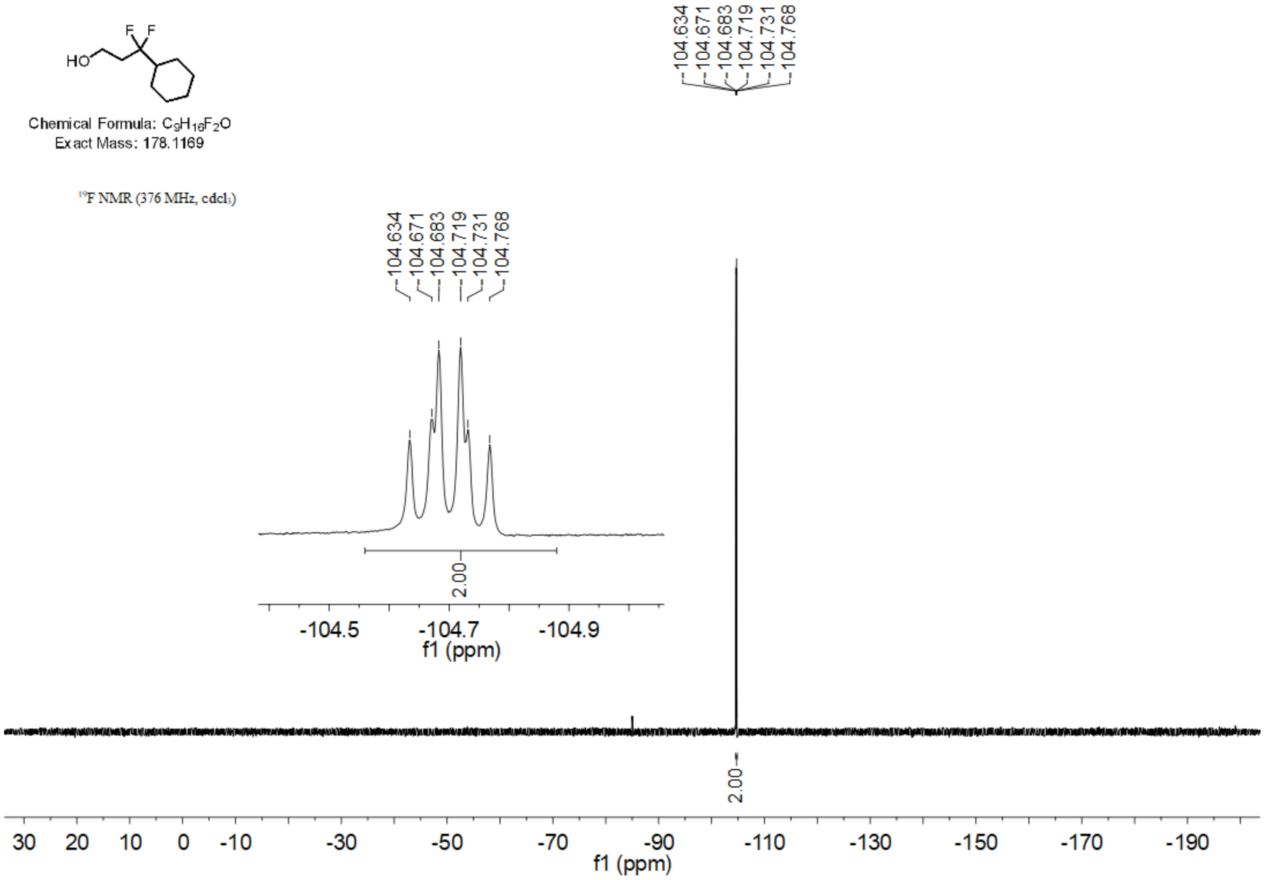
^{1}H NMR (400 MHz, cdcl$_3$)

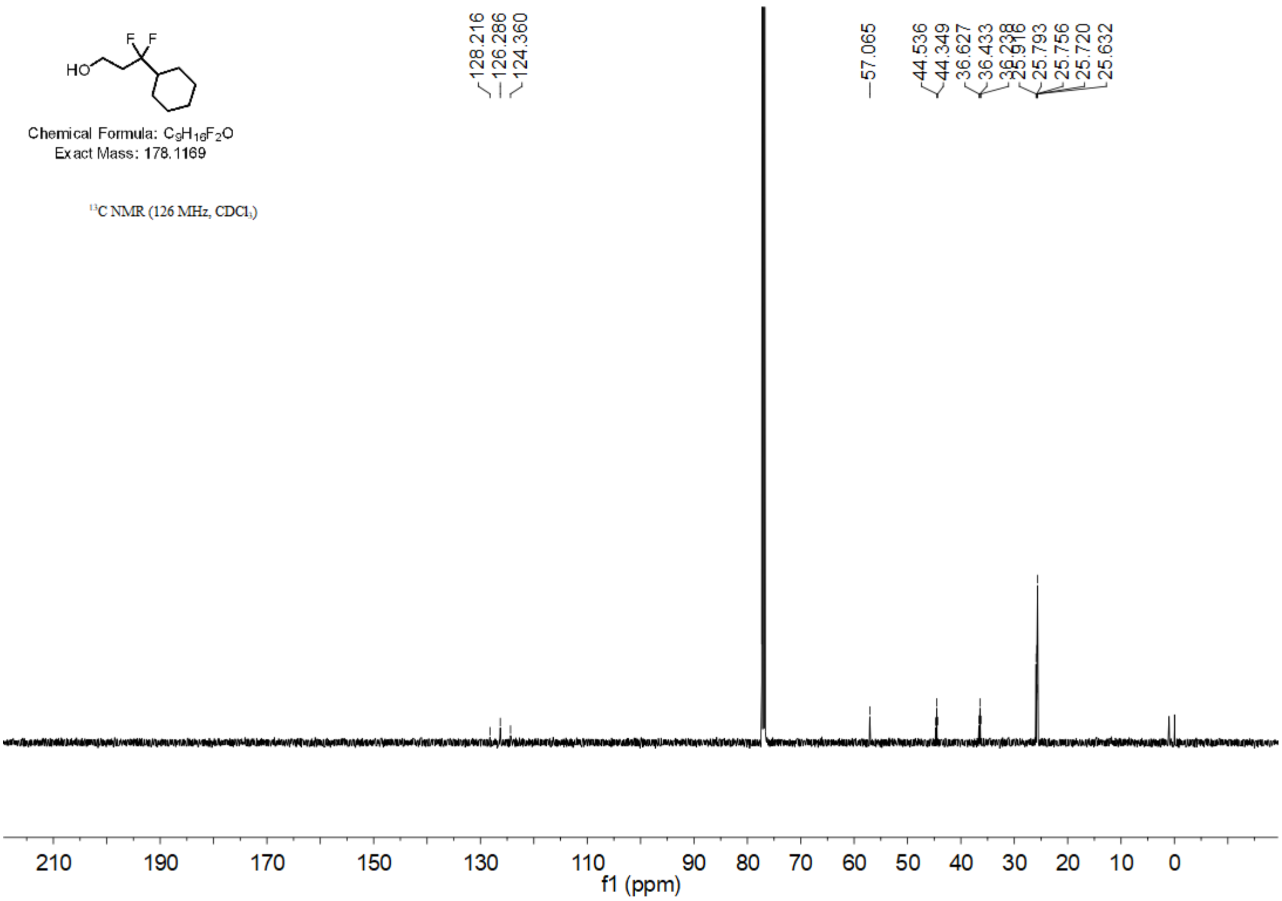

Chemical Formula: $C_4H_8F_2O_2$
Exact Mass: 126.0492
19F NMR (376 MHz, cdcl3)
HO
F
F
OH
-104.987
-105.021
-105.063
-105.097
-105.138
2.00
-105.1
f1 (ppm)
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)


Chemical Formula: $C_4H_8F_2O_2$
Exact Mass: 126.0492
13C NMR (126 MHz, CDCl3)
HO
F
F
OH
124.798
122.871
120.940
64.549
64.283
64.019
56.856
56.804
56.752
37.089
36.895
36.699
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

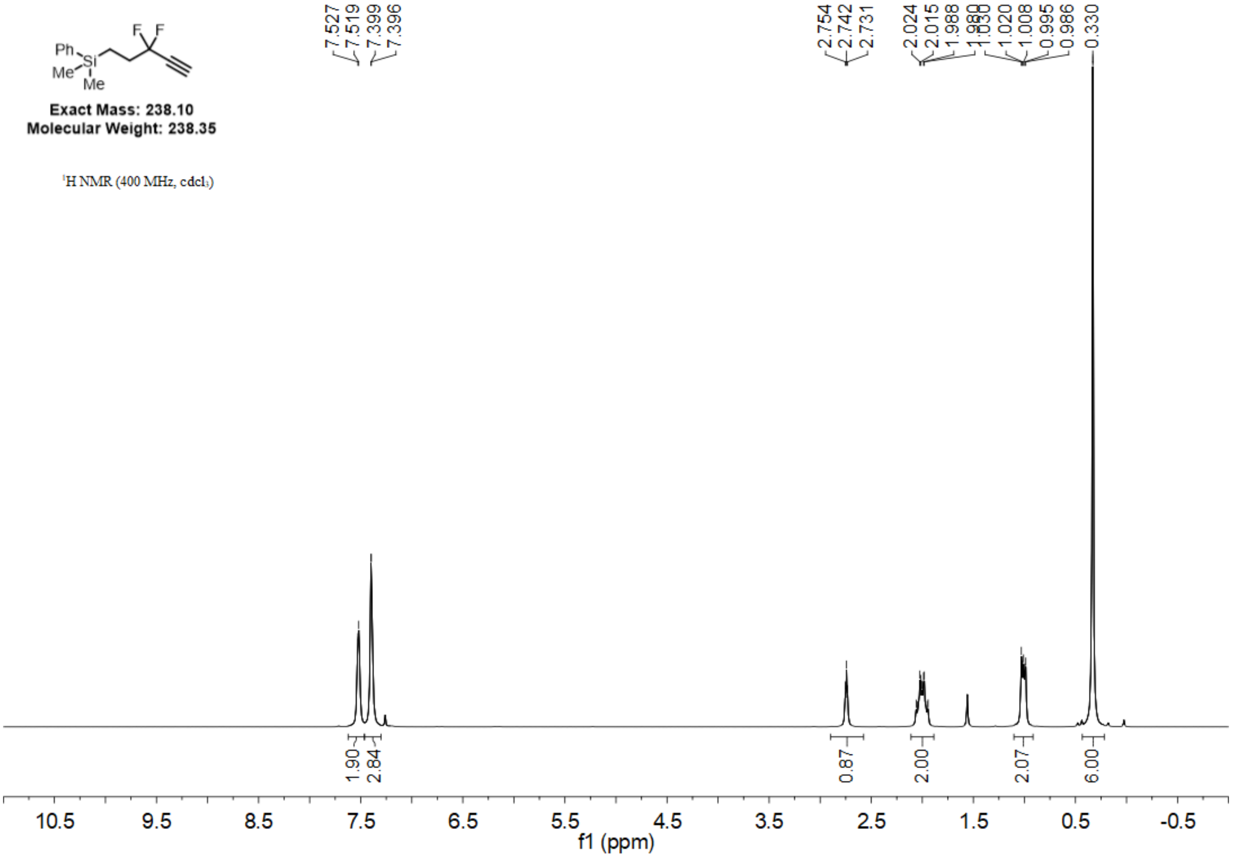
3-Cyclohexyl-3,3-difluoropropan-1-ol (11l)

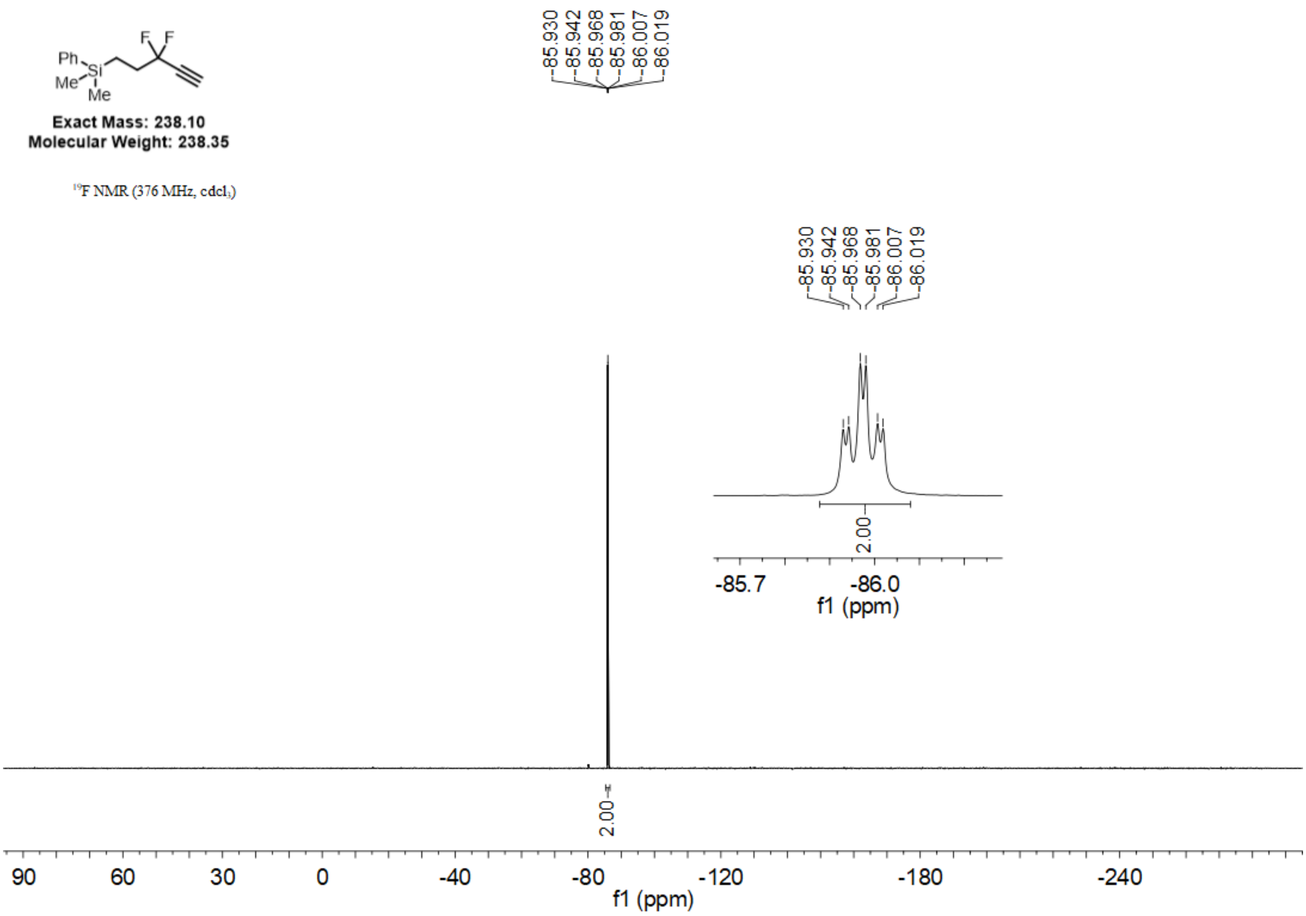






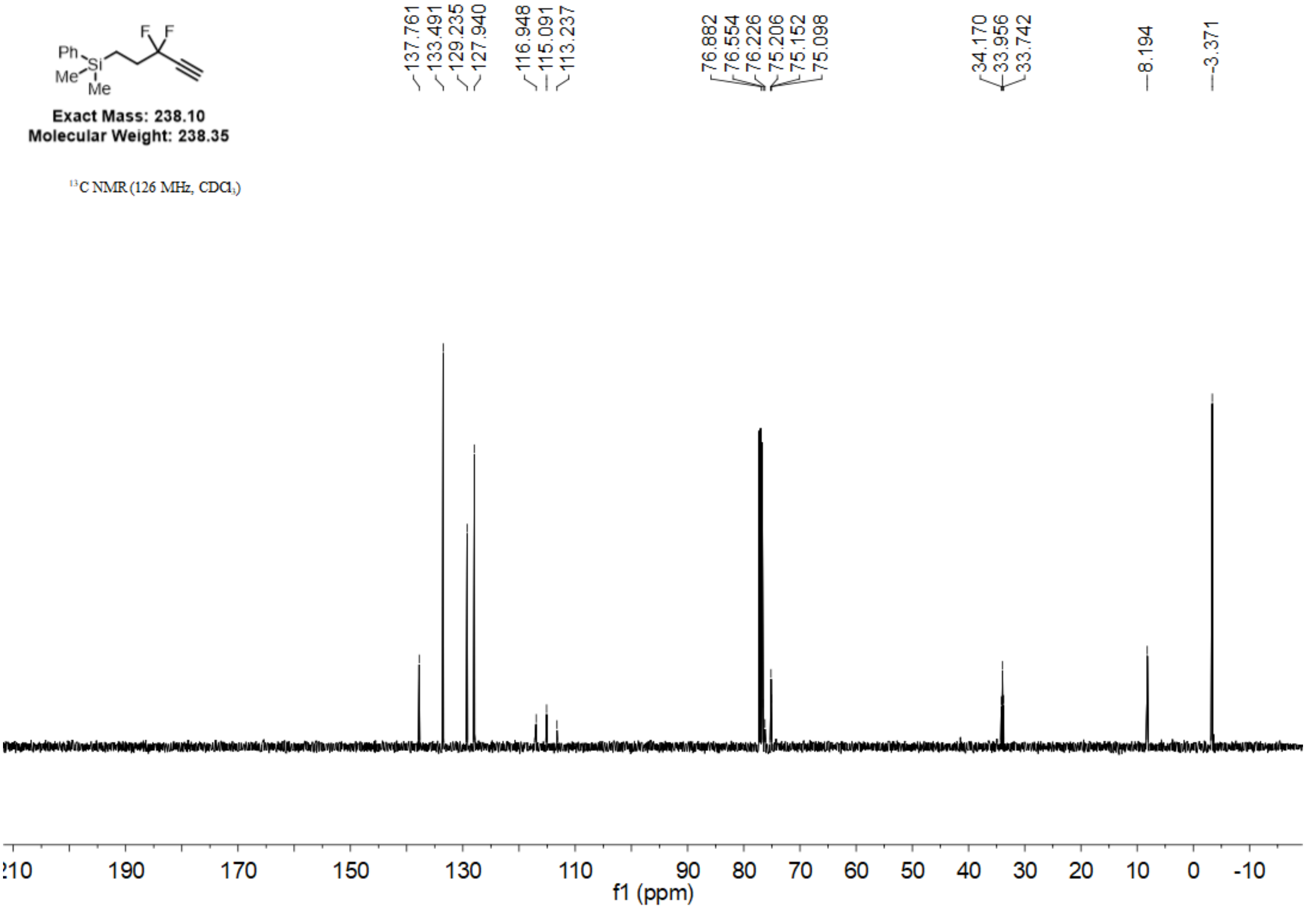
(3,3-difluoropent-4-yn-1-yl) Dimethyl(phenyl)silane (12)





Exact Mass: 238.10
Molecular Weight: 238.35

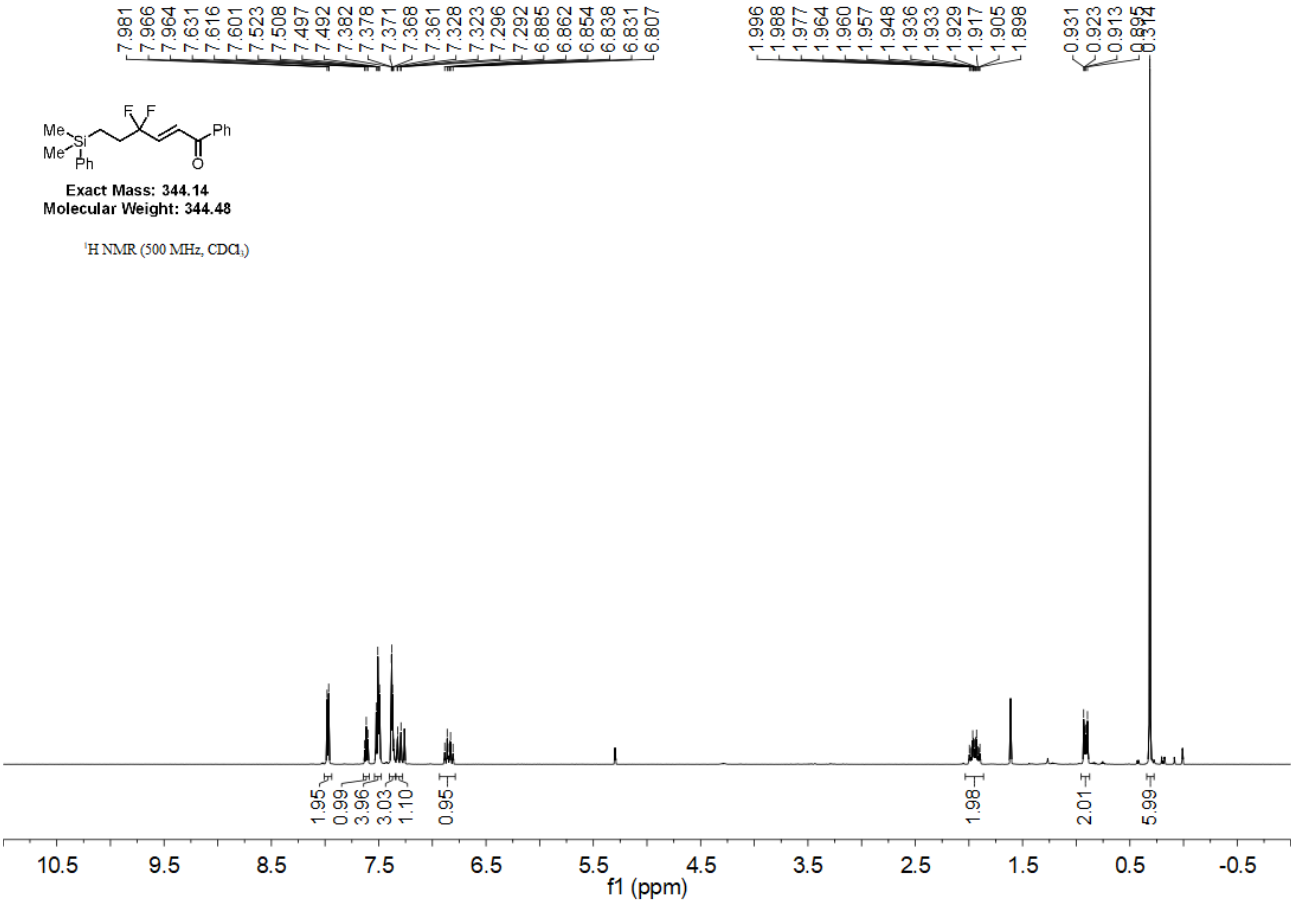
^{19}F NMR (376 MHz, cdcl$_3$)

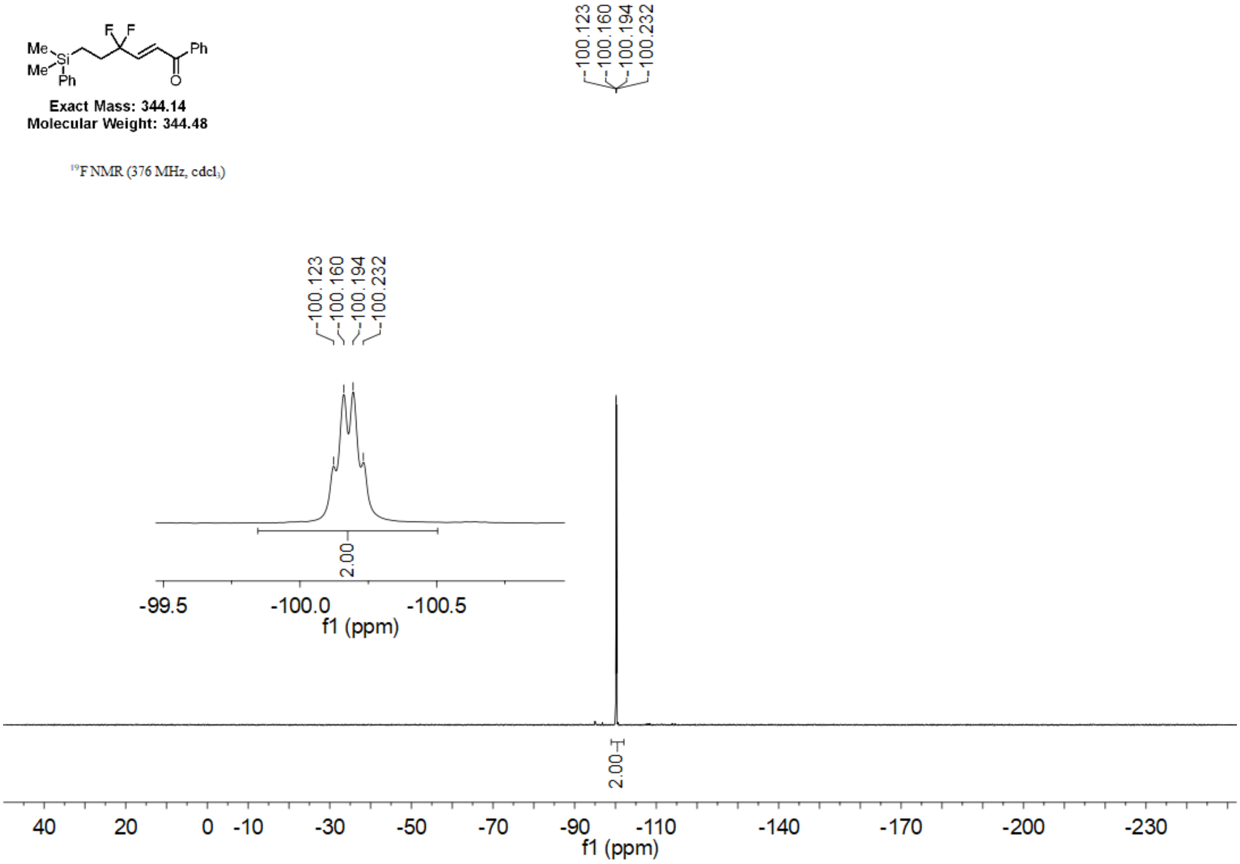


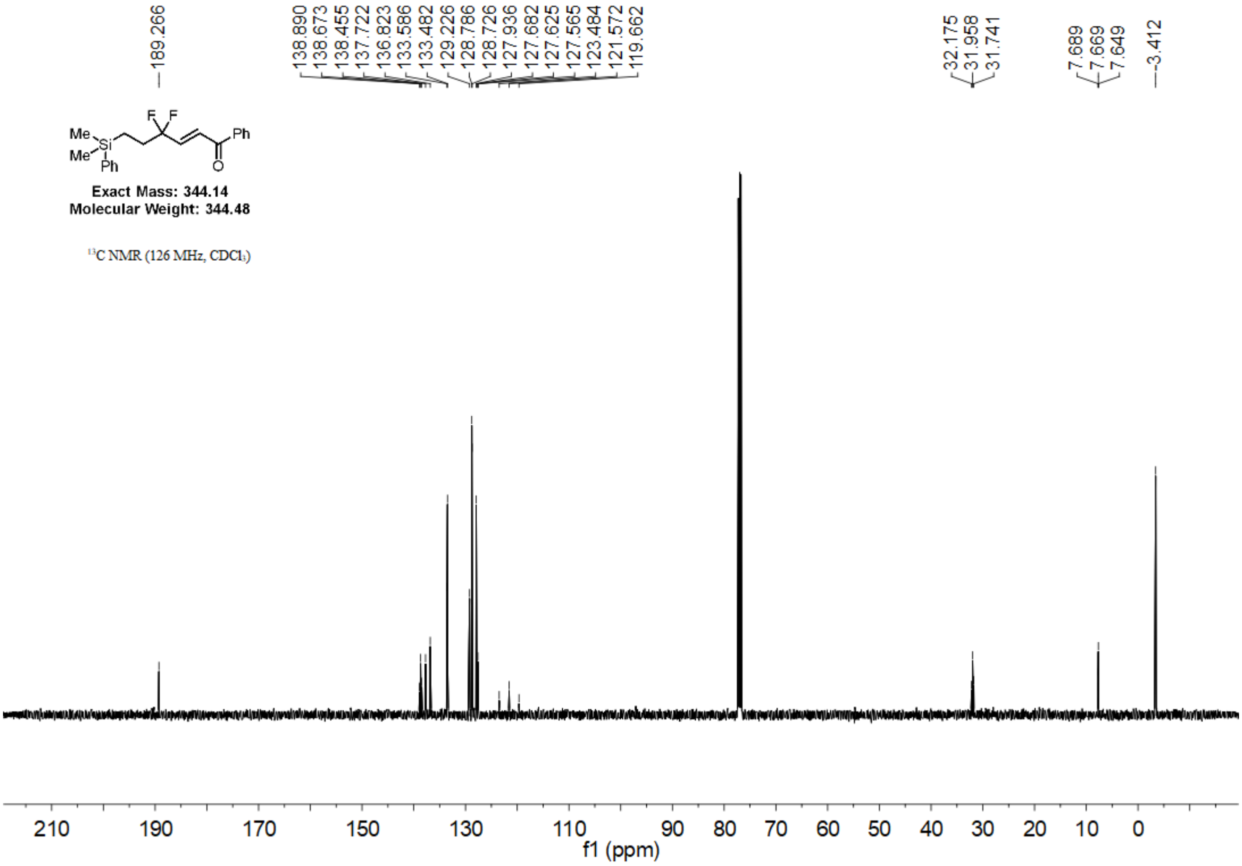
Exact Mass: 238.10
Molecular Weight: 238.35

^{13}C NMR (126 MHz, CDCl$_3$)

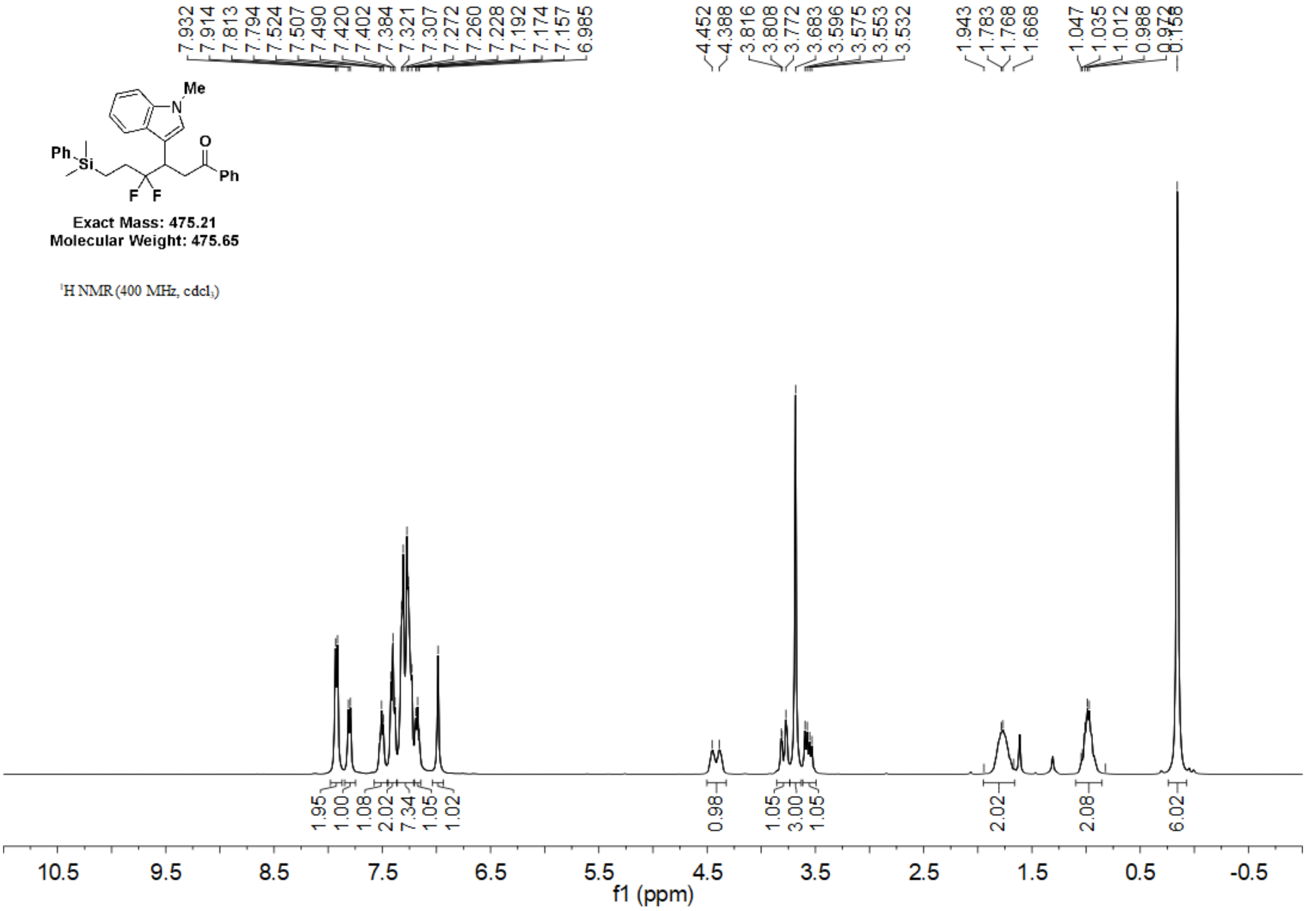
(E)-6-(dimethyl(phenyl)silyl)-4,4-Difluoro-1-phenylhex-2-en-1-one (13)

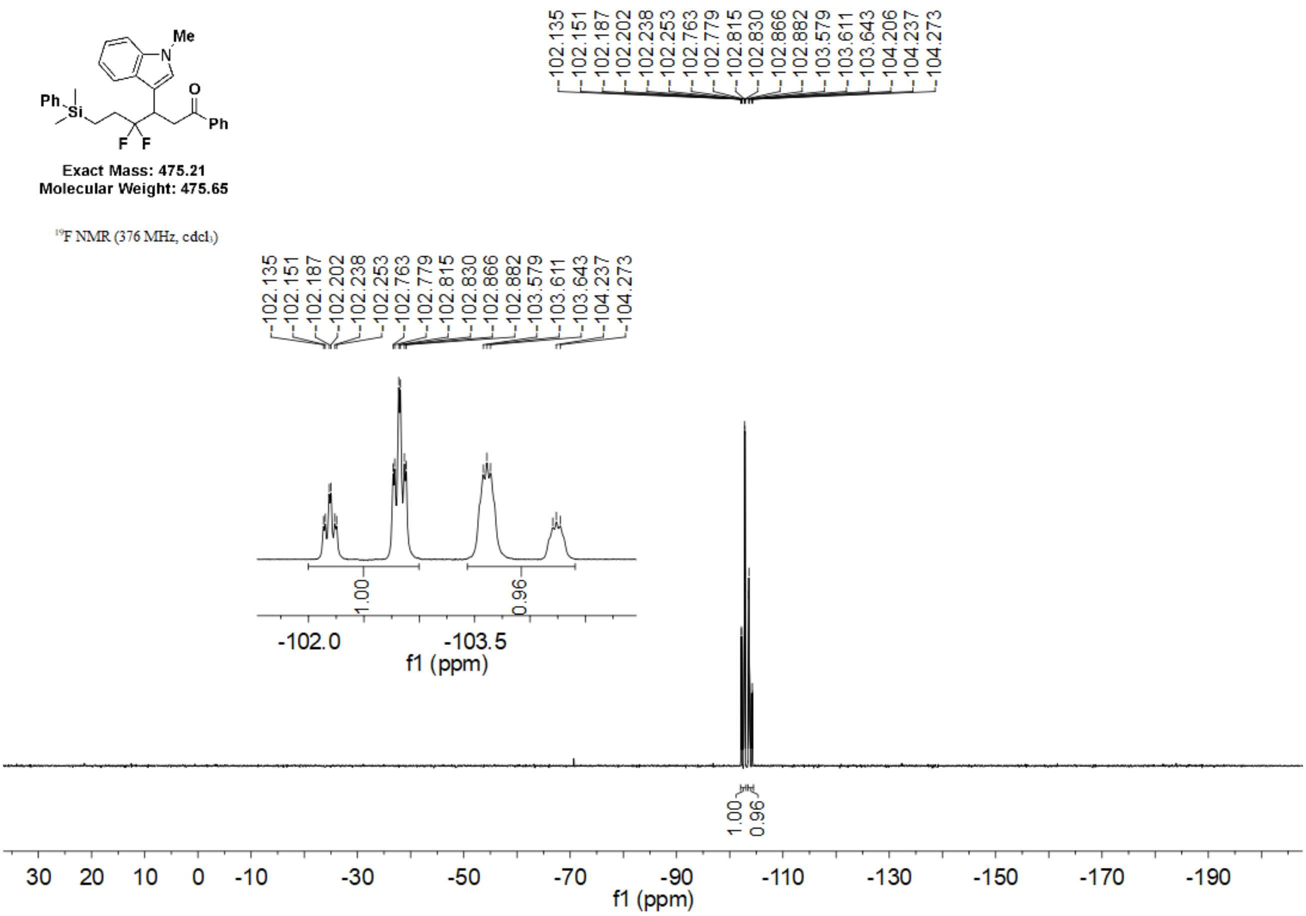


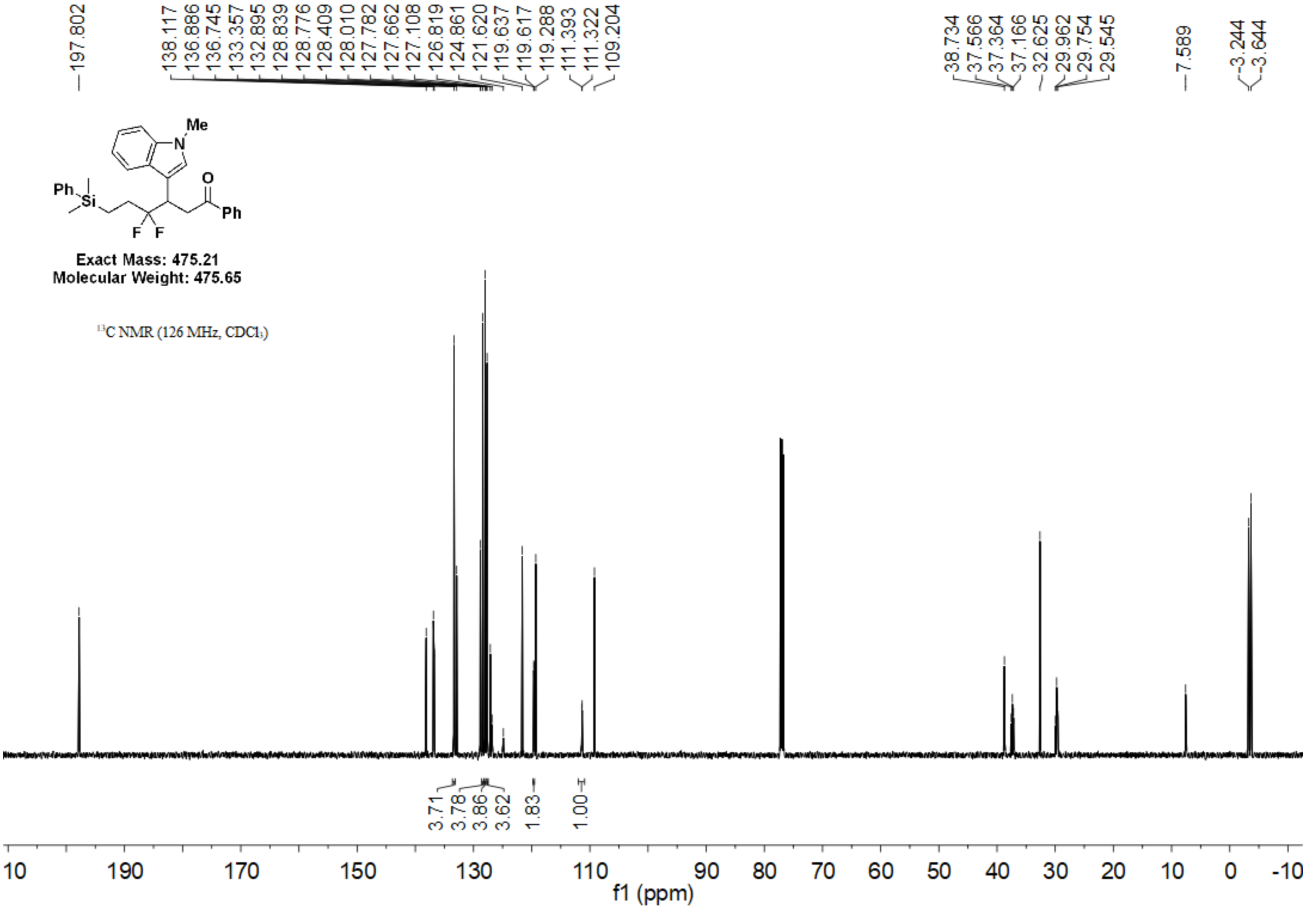




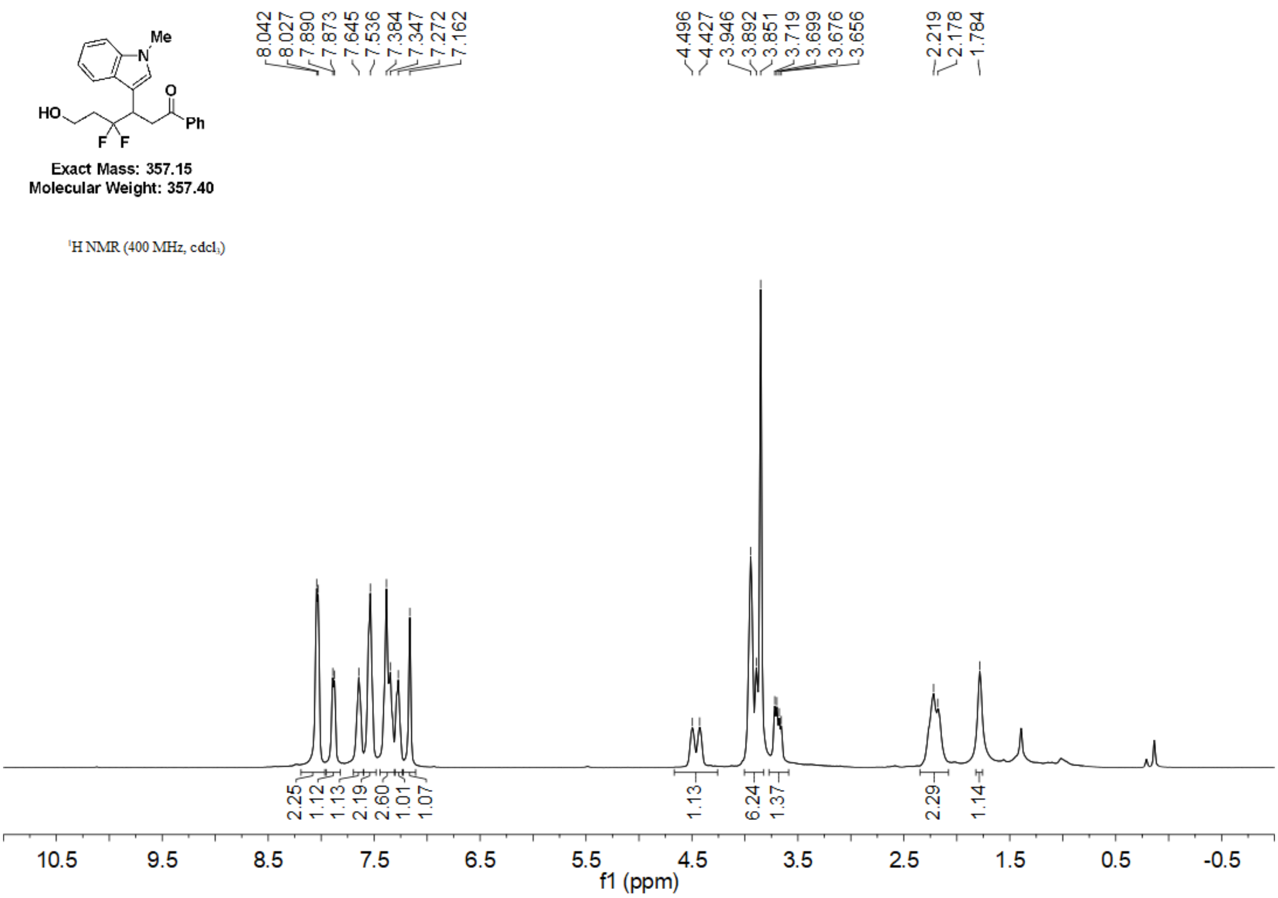
6-(dimethyl(phenyl)silyl)-4,4-Difluoro-3-(1-methyl-1H-indol-3-yl)-1-phenylhexan-1-one (14)

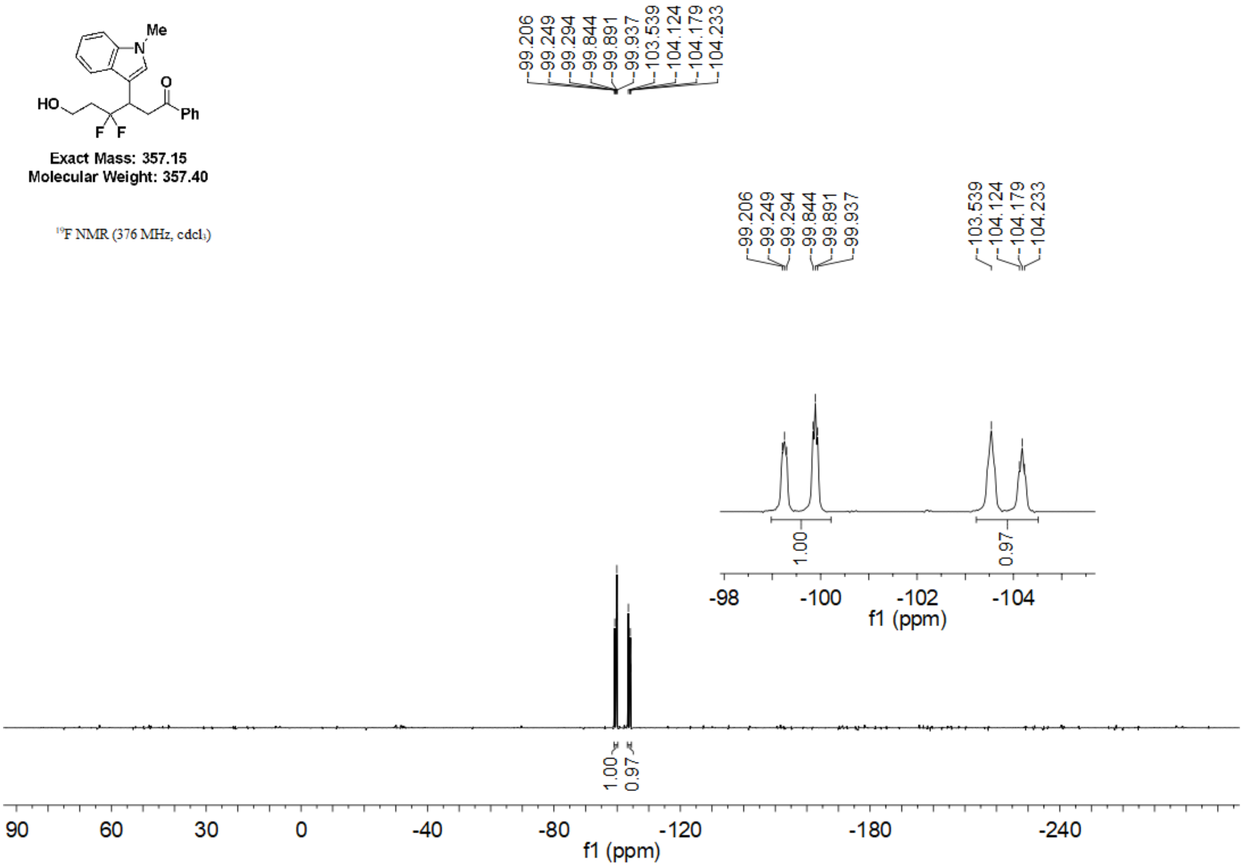


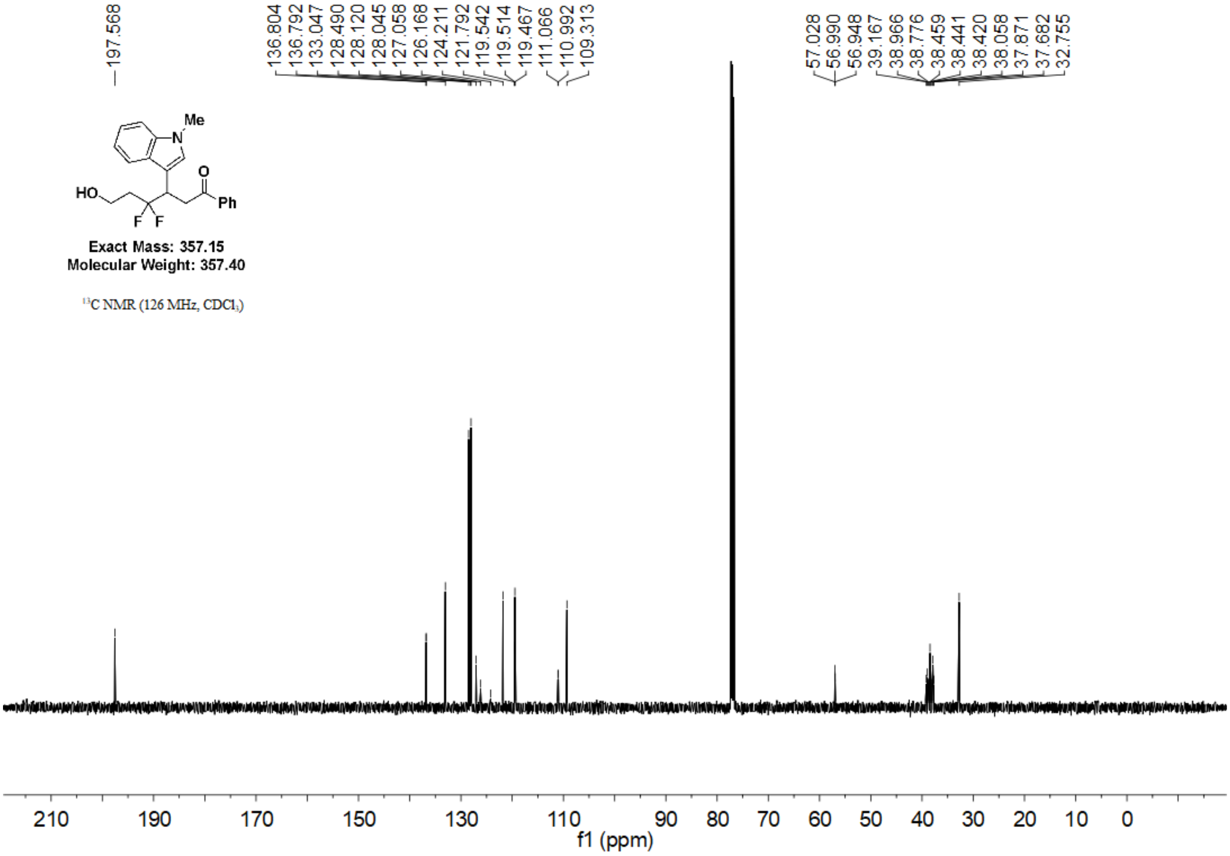

Me
N
Ph
Si
O
Ph
F F
Exact Mass: 475.21
Molecular Weight: 475.65
19F NMR (376 MHz, cdcl3)
-102.135
-102.151
-102.187
-102.202
-102.238
-102.253
-102.763
-102.779
-102.815
-102.830
-102.866
-102.882
-103.579
-103.611
-103.643
-104.206
-104.237
-104.273
1.00
0.96
-102.0
-103.5
f1 (ppm)
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)


197.802
138.117
136.886
136.745
133.357
132.895
128.839
128.776
128.409
128.010
127.782
127.662
127.108
126.819
124.861
121.620
119.637
119.617
119.288
111.393
111.322
109.204
38.734
37.566
37.364
37.166
32.625
29.962
29.754
29.545
7.589
-3.244
-3.644
Me
N
Ph
Si
O
Ph
F F
Exact Mass: 475.21
Molecular Weight: 475.65
13C NMR (126 MHz, CDCl3)
3.71
3.78
3.86
3.62
1.83
1.00
10
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

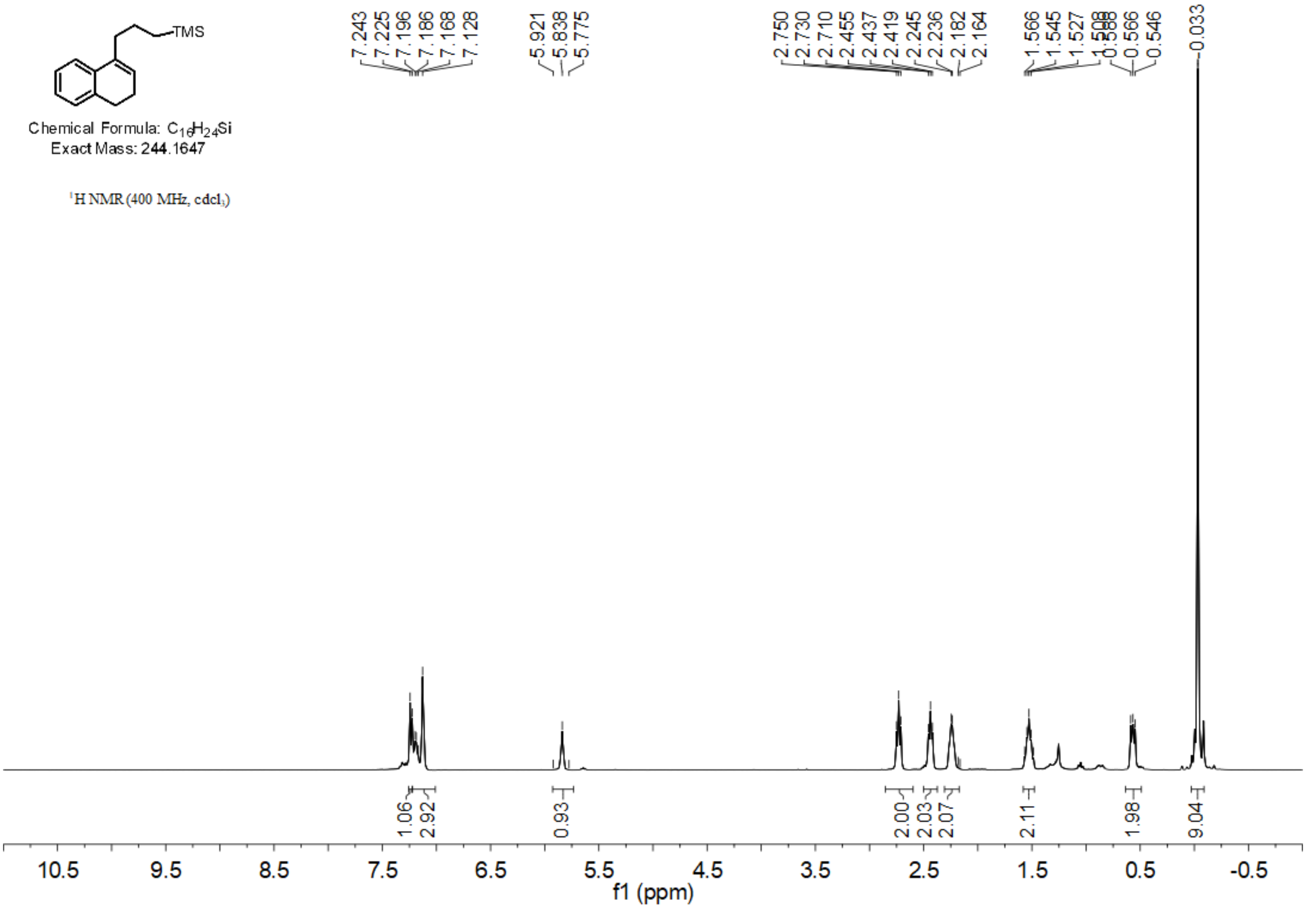
4,4-Difluoro-6-hydroxy-3-(1-methyl-1H-indol-3-yl)-1-phenylhexan-1-one (15)

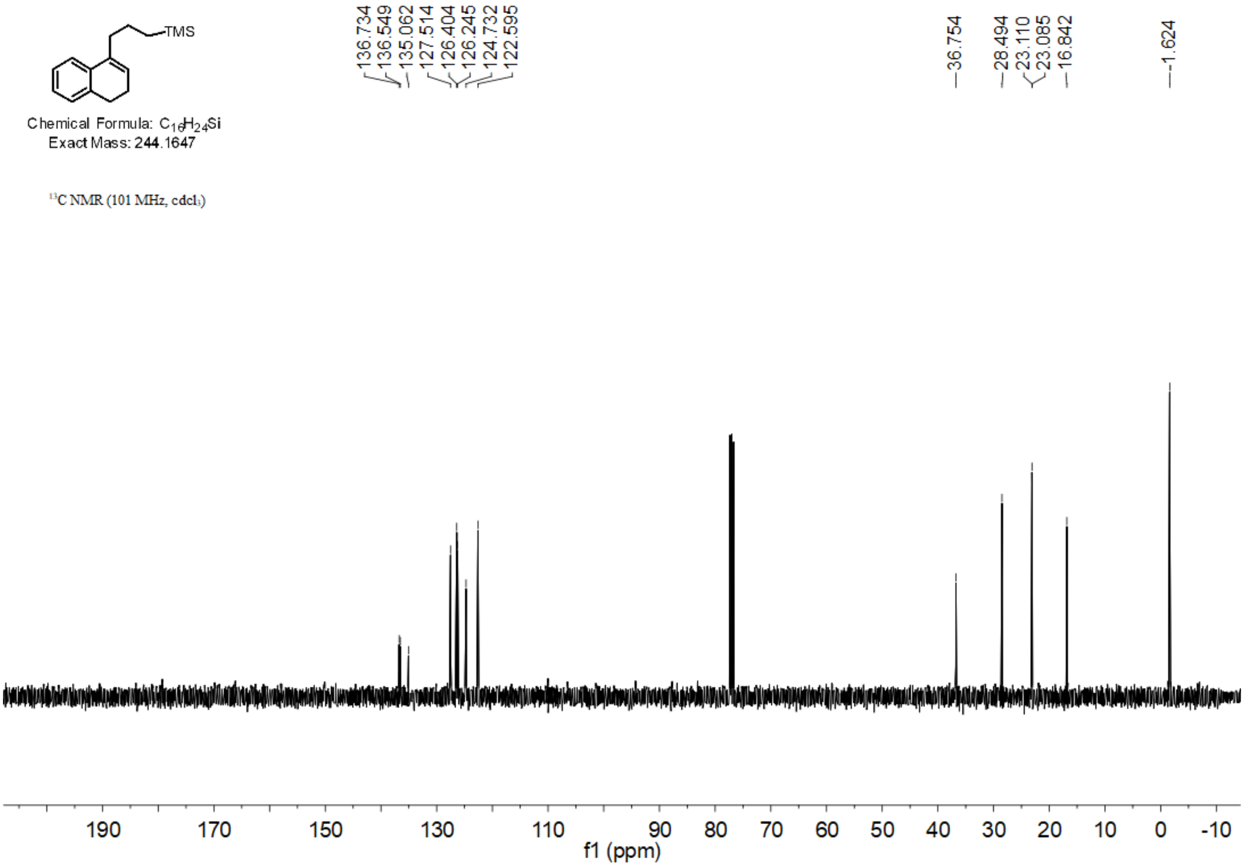




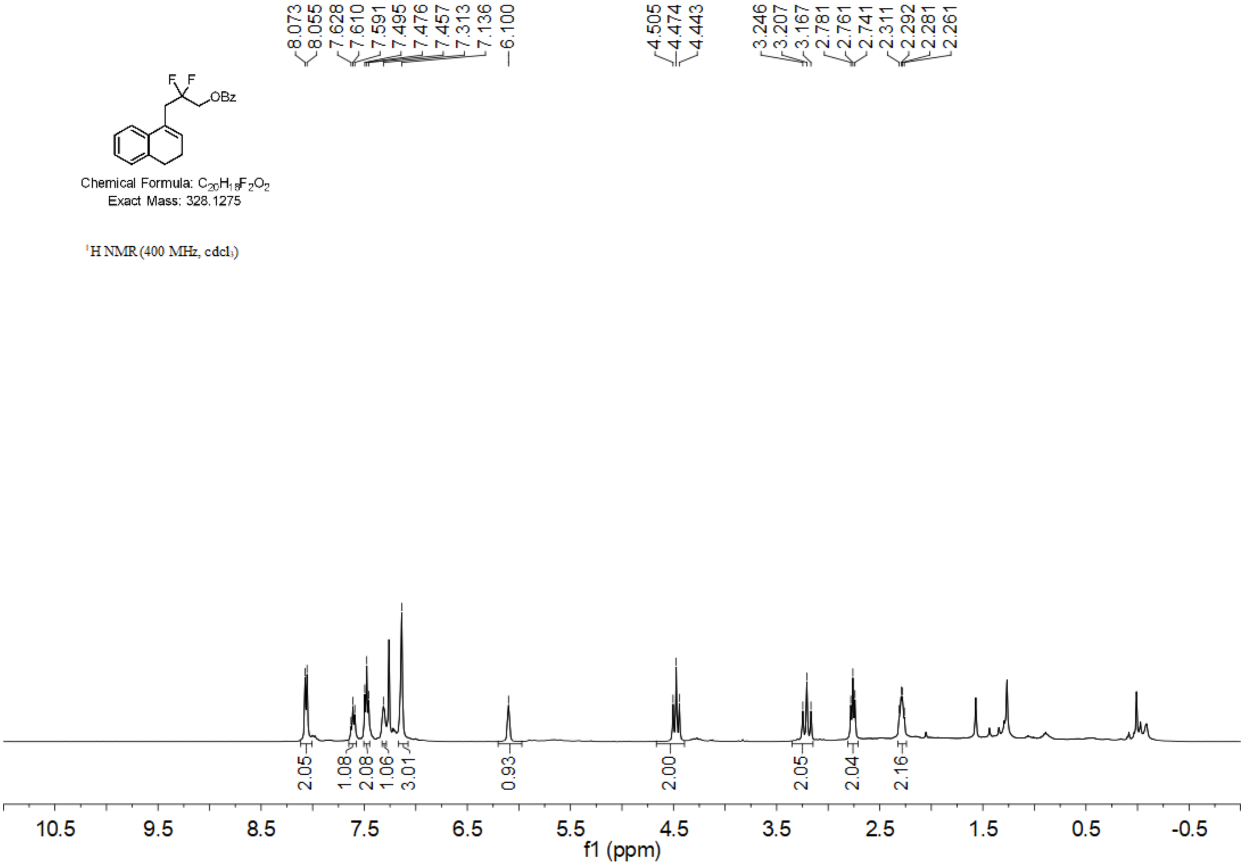


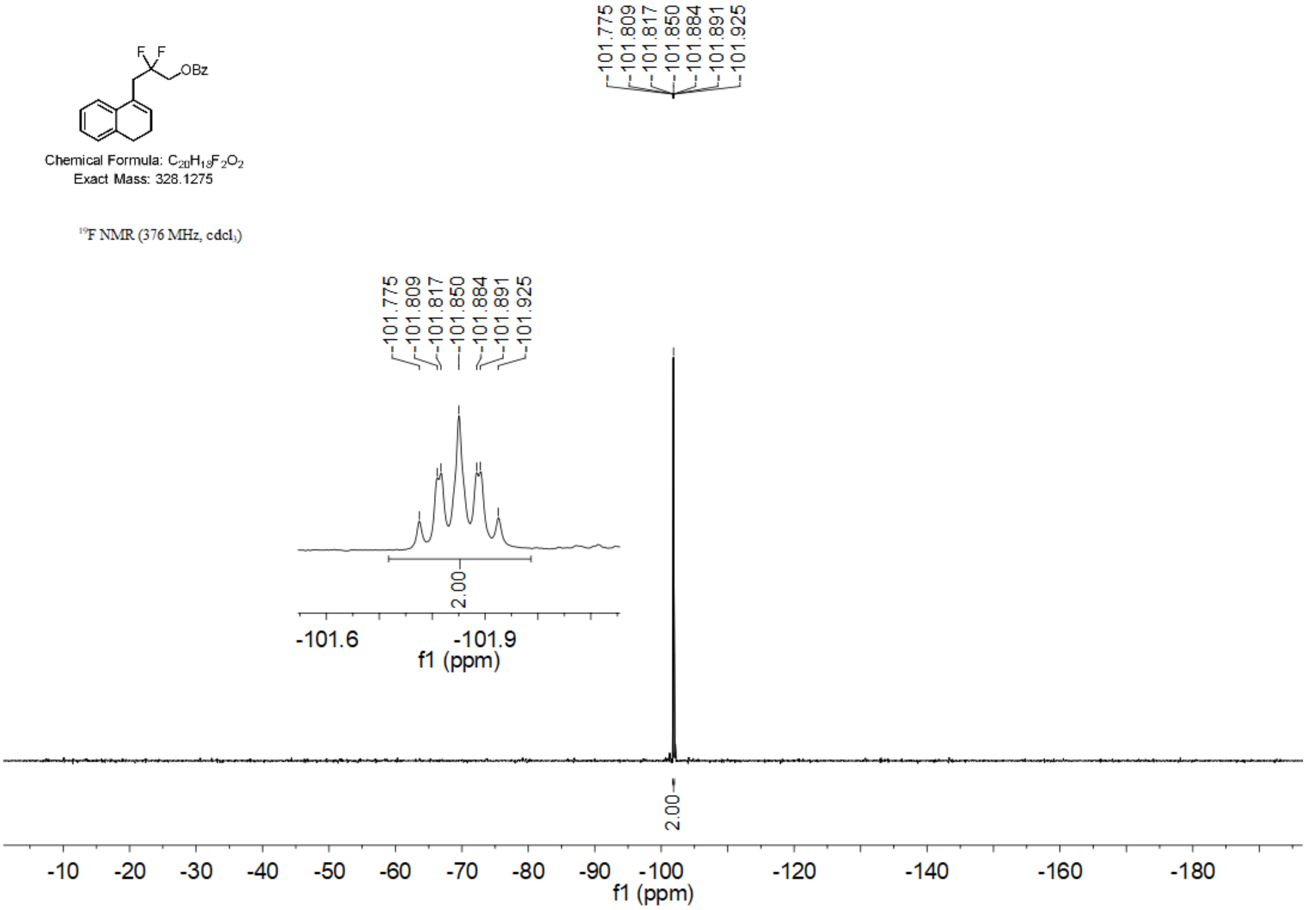
(3-(3,4-Dihydronaphthalen-1-yl)propyl)trimethylsilane (17)

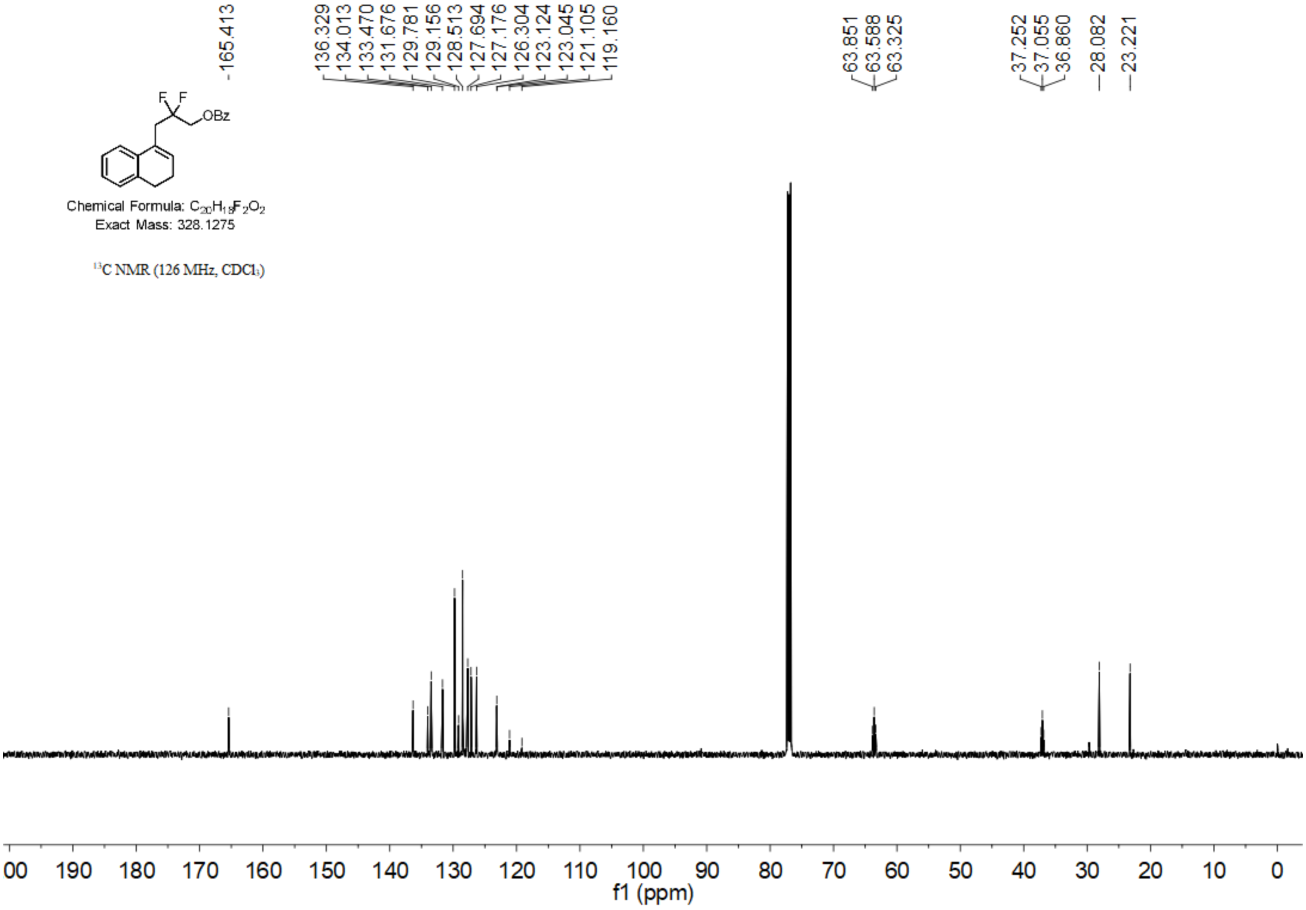




3-(3,4-Dihydronaphthalen-1-yl)-2,2-difluoropropyl benzoate (18)




F F
OBz
Chemical Formula: $C_{20}H_{18}F_2O_2$
Exact Mass: 328.1275
^{19}F NMR (376 MHz, cdcl$_3$)
-101.775
-101.809
-101.817
-101.850
-101.884
-101.891
-101.925
2.00
-101.6
-101.9
f1 (ppm)
2.00
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
f1 (ppm)


165.413
136.329
134.013
133.470
131.676
129.781
129.156
128.513
127.694
127.176
126.304
123.124
123.045
121.105
119.160
63.851
63.588
63.325
37.252
37.055
36.860
28.082
23.221
F F
OBz
Chemical Formula: $C_{20}H_{18}F_2O_2$
Exact Mass: 328.1275
^{13}C NMR (126 MHz, CDCl$_3$)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)