Electronic Supplementary Information

Site-Selective Iodine Atom Transfer in Fluorinated Alkyl Iodides via 1,5-Hydrogen Atom Transfer

Masahiro Abe,* Yuka Yokoi, Aoi Hirta, Yumeno Matsuoka, Tetsutaro Kimachi and Kiyofumi Inamoto*

School of Pharmacy and Pharmaceutical Sciences, Mukogawa Women's University
11-68, 9-Bancho, Koshien, Nishinomiya, Hyogo 663-8179, Japan

e-mail: abe_111@mukogawa-u.ac.jp, inamoto@mukogawa-u.ac.jp

1. General Comments

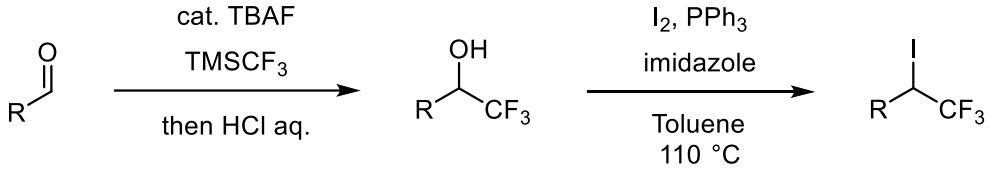
Melting points were measured with a AS ONE Corporation melting temperature measurement device (ATM-02) and uncorrected. IR spectra were recorded on a SHIMADZU IRAffinity-1. NMR data were recorded on either a JEOL JNM-ECP400 spectrometer (400 MHz) or a JEOL ECA500 spectrometer (500 MHz). Chemical shifts are expressed in δ (parts per million, ppm) values and coupling constants are expressed in hertz (Hz). ^{1}H NMR spectra were referenced to $(CH_3)_4Si$ (TMS) as an internal standard or to a residual proton signal in deuterated solvent ($CDCl_3$: 7.26 ppm). ^{13}C NMR spectra were referenced to a residual proton signal in deuterated solvent ($CDCl_3$: 77.16 ppm). ^{19}F NMR spectra were referenced to 4-fluorotoluene as an internal standard (−118.0 ppm). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, dd, = double doublet, dt = double triplet, td = triple doublet, ddd, = double double doublet, m = multiplet, and brs = broad signal. GC data were recorded on GC-2025 (SHIMADZU). Decane was used as an internal standard for GC analysis. Mass spectra and high-resolution mass spectra were measured on a JEOL JMS-700 instrument. Chromatographic separations were achieved on silica gel column (Wakosil® C-200, 64 − 210 μm).

2. Materials

All commercially available materials including benzoyl peroxide (Nacalai tesque, #04422-02) and *t*-BuOH (Sigma–Aldrich Co., #03-4630-5) were purchased from Sigma–Aldrich Co., Nacalai tesque, Tokyo Chemical Industry Co. and Wako Pure Chemical Industries, and were used as received. Test tubes with screws (IWAKI, TST SCR 18-180) were used for the iodine atom transfer reaction. 2-Iodotridecane **1q** was prepared according to the literature.[1]

3. Spectroscopic and Analytical Data

General procedure A: Synthesis of fluorinated alkyl iodides

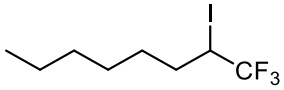


Trifluoromethylation of the aldehyde: 1M solution of TBAF (0.01 equiv) in THF was added dropwise to a solution of an aldehyde (1.0 equiv) and $TMSCF_3$ (1.2 equiv) in THF (2 mL/mmol of aldehyde) at 0 °C. The reaction mixture was warmed to room temperature. After stirring for 3 h, the reaction was quenched with an aqueous solution of 1M HCl (50 mL). The resulting mixture was stirred at room temperature for another 2 h. Then, the reaction mixture was extracted with Et_2O (× 3), and the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was used to the next reaction without any further purification.

Iodination of the alcohol: Iodine (2.7 equiv) was added to a solution of the crude alcohol (1.0 equiv),

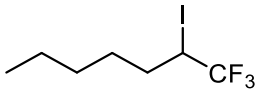
PPh_3 (3.5 equiv) and imidazole (2.7 equiv) in toluene (10 mL/mmol of alcohol). The resulting mixture was stirred at 110 °C for 3 h. After cooling to room temperature, the reaction was quenched with water. The aqueous phase was extracted with hexane (× 3). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. The crude product was purified by flash chromatography on silica gel to give desired fluorinated alkyl iodides.

1,1,1-Trifluoro-2-iodooctane 1a



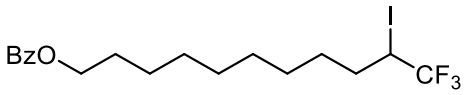
Prepared according to **General procedure A** using heptanal (1.11 mL, 8.0 mmol). Purified by silica gel chromatography (hexane only) and bulb to bulb distillation to afford the desired product **1a** as colorless oil (1.48 g 5.02 mmol, 63%). ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 4.21 – 4.08 (m, 1H), 1.86 (q, *J* = 7.0 Hz, 2H), 1.68 – 1.54 (m, 1H), 1.44 – 1.24 (m, 7H), 0.95 – 0.85 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$/TMS) δ 124.8 (q, *J* = 276.4 Hz), 32.9, 31.6, 29.1, 28.3, 24.6 (q, *J* = 30.9 Hz)., 22.7, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.2 (d, *J* = 8.0 Hz); IR (neat): 2930, 2859 cm^{-1}; LRMS (EI) m/z: 294 $[M]^+$; HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_8H_{14}F_3I$ 294.0092; found 294.0096.

1,1,1-trifluoro-2-iodoheptane 1b



Prepared according to **General procedure A** using hexanal (1.23 mL, 10 mmol). Purified by silica gel chromatography (hexane only) and bulb to bulb distillation to afford the desired product **1b** as colorless oil. (1.70 g 6.06 mmol, 61%). ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 4.21 – 4.07 (m, 1H), 1.90 – 1.81 (m, 2H), 1.70 – 1.54 (m, 1H), 1.46 – 1.22 (m, 5H), 0.92 (t, *J* = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$/TMS) δ 124.8 (q, *J* = 276.4 Hz), 32.9, 30.8, 28.8, 24.56 (q, *J* = 31.0 Hz), 22.5, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.2 (d, *J* = 8.0 Hz); IR (neat): 2959, 2932, 2862 cm^{-1}; LRMS (EI) m/z: 280 $[M]^+$; HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_7H_{12}F_3I$ 279.9936; found 279.9934.

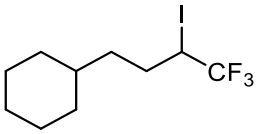
11,11,11-Trifluoro-10-iodoundecyl benzoate 1c



Prepared according to **General procedure A** using 10-oxodecyl benzoate[2] (1.0 g, 3.62 mmol). Purified by silica gel chromatography (hexane/$CHCl_3$: 10:1 to 5:1) to afford the product **1c** as colorless oil. (1.07 g 2.50 mmol, 55%). ^{1}H NMR (500 MHz, $CDCl_3$/TMS): δ 8.07 – 8.02 (m, 2H), 7.58 – 7.52 (m,

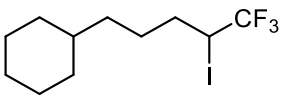
1H), 7.47 – 7.41 (m, 2H), 4.32 (t, *J* = 6.7 Hz, 2H), 4.18 – 4.08 (m, 1H), 1.89 – 1.82 (m, 2H), 1.81 – 1.73 (m, 2H), 1.67 – 1.56 (m, 1H), 1.49 – 1.24 (m, 11H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$/TMS) δ 166.8, 132.9, 130.8, 129.7, 128.5, 124.76 (q, *J* = 276.5 Hz), 65.2, 32.9, 29.5, 29.4, 29.31 (d, *J* = 2.4 Hz), 29.1, 28.9, 28.6, 26.2, 24.51 (q, *J* = 30.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.3 (d, *J* = 8.1 Hz); IR (neat): 2930, 2857, 1719 cm^{-1}; LRMS (EI) m/z: 456 $[M]^+$; HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{18}H_{24}O_2F_3I$ 456.0773; found 456.0773.

(4,4,4-Trifluoro-3-iodobutyl) cyclohexane 1d



Prepared according to **General procedure A** using 3-cyclohexylpropanal[3] (1.6 g, 11.4 mmol). Purified by silica gel chromatography (hexane only) and bulb to bulb distillation to afford the desired product **1d** as colorless oil. (2.12 g 6.61 mmol, 58%). ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 4.18 – 4.03 (m, 1H), 1.96 – 1.77 (m, 2H), 1.76 – 1.61 (m, 5H), 1.54 – 1.42 (m, 1H), 1.35 – 1.09 (m, 5H), 1.02 – 0.84 (m, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$/TMS) δ 124.76 (q, *J* = 276.6 Hz), 37.0, 36.7, 33.7, 32.9, 30.5, 26.7, 26.4, 26.3, 25.0 (q, *J* = 30.8 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -68.2 (d, *J* = 7.3 Hz); IR (neat): 2924, 2853 cm^{-1}; LRMS (EI) m/z: 320 $[M]^+$; HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{10}H_{16}F_3I$ 320.0249; found 320.0248.

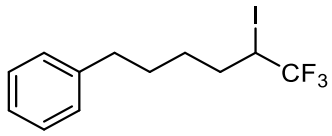
(5,5,5-Trifluoro-4-iodopentyl)cyclohexane 1e



Prepared according to **General procedure A** using 4-cyclohexylbutanal[4] (1.47 g, 9.5 mmol). Purified by silica gel chromatography (hexane only) and bulb to bulb distillation to afford the desired product **1d** as colorless oil. (2.02 g 6.05 mmol, 64%).

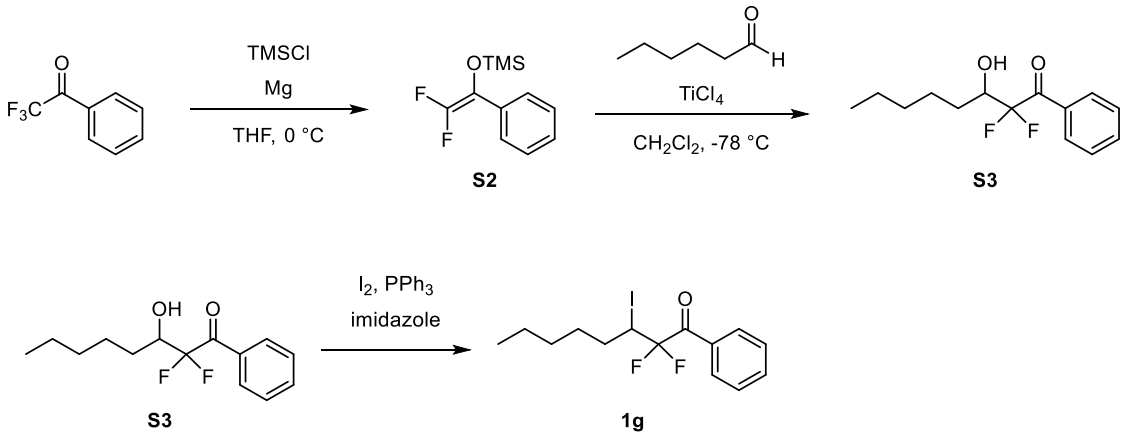
^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 4.21 – 4.06 (m, 1H), 1.86 – 1.77 (m, 2H), 1.76 – 1.56 (m, 6H), 1.46 – 1.30 (m, 1H), 1.30 – 1.07 (m, 6H), 0.98 – 0.78 (m, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$/TMS) δ 124.7 (q, *J* = 276.5 Hz), 37.5, 36.3, 33.6, 33.3, 33.1, 26.8, 26.48, 26.45, 24.8 (q, *J* = 30.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.3 (d, *J* = 8.3 Hz); IR (neat): 2922, 2850, 1449 cm^{-1}; LRMS (EI) m/z: 334 $[M]^+$; HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{11}H_{18}OF_3I$: 334.0405; found 334.0403.

(6,6,6-Trifluoro-5-iodohexyl)benzene 1f



Prepared according to **General procedure A** using 5-phenyl-1-butanol[5] (811.2 mg, 5.0 mmol). Purified by silica gel chromatography (hexane only) and bulb to bulb distillation to afford the desired product **1f** as colorless oil. (629.2 mg, 1.84 mmol, 37%). ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 7.31 – 7.24 (m, 2H), 7.21 – 7.13 (m, 3H), 4.15 – 4.03 (m, 1H), 2.70 – 2.54 (m, 2H), 1.92 – 1.79 (m, 2H), 1.76 – 1.55 (m, 3H), 1.48 – 1.33 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$/TMS) δ 142.0, 128.52, 128.50, 126.0, 124.7 (d, J = 276.5 Hz), 35.7, 32.7, 30.4, 28.7, 24.3 (q, J = 31.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.4 (d, J = 8.1 Hz); IR (neat): 3026, 2938, 2860, 1497 cm^{-1}; LRMS (EI) m/z: 342 $[M]^+$; HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{12}H_{14}F_3I$: 342.0092; found 342.0096.

2,2-Difluoro-3-iodo-1-phenyloctan-1-one 1g

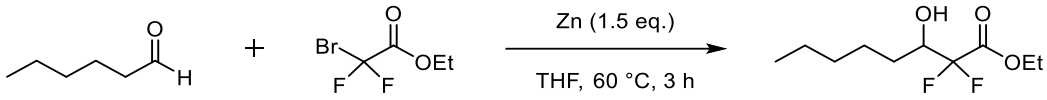


TMSCl (3.05 mL, 24 mmol, 4.0 equiv) was added dropwise to a mixture of Mg (296.1 mg, 12 mmol, 2.0 equiv) and THF (12 mL) at 0 °C under an argon atmosphere. Subsequently, trifluoroacetophenone (0.82 mL, 6 mmol, 1.0 equiv) was added dropwise and the mixture was stirred for 30 min. After evaporation of most of the THF, hexane (20 mL) was added to the residue, and the resulting salt was filtered and the filtrate was concentrated to give crude product **S2**.

To a solution of the crude product **S2** and hexanal (1.47 mL, 12 mmol, 2.0 equiv) in CH_2Cl_2 (10 mL) at -78 °C, a solution of $TiCl_4$ (0.66 mL, 6 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) was added dropwise. After 1 h stirring, the reaction was quenched with sat. NH_4Cl solution, and the organic layer was washed with brine and dried over $MgSO_4$ and concentrated. The crude product was purified by flash chromatography on silica gel (hexane/EtOAc = 10/1) to give the desired alcohol **S3** (34%, 547.3 mg, 2.14 mmol).[6]

Ketone **1g** was prepared from alcohol **S3** (547.3 mg, 2.14 mmol) according to the iodination step in **General procedure A**. Purified by flash chromatography on silica gel (hexane/$CHCl_3$ = 20/1) to afford the product **1g** in 77% yield (603.9 mg, 1.65 mmol) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$/TMS) δ 8.11 – 8.03 (m, 2H), 7.69 – 7.62 (m, 1H), 7.54 – 7.47 (m, 2H), 4.60 – 4.48 (m, 1H), 1.94 – 1.75 (m, 2H), 1.72 – 1.61 (m, 1H), 1.46 – 1.21 (m, 5H) 0.89 (t, *J* = 7.0 Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$/TMS) δ 188.2 (t, *J* = 30.5 Hz), 134.6, 132.4, 130.2 (t, *J* = 3.6 Hz), 129.0, 116.9 (t, *J* = 257.5 Hz), 32.1, 30.8, 30.0 (t, *J* = 24.0 Hz), 29.0, 22.5, 14.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ -94.8 (dd, *J* = 272.4, 13.5 Hz), -99.4 (dd, *J* = 272.4, 15.5 Hz); IR (neat): 2957, 2928, 2859, 1699, 1597 cm^{-1}; LRMS (EI) m/z: 366 [M]$^+$; HRMS (EI-TOF) m/z: [M]$^+$ Calcd for $C_{14}H_{17}OF_2I$ 366.0292; found 366.0291.

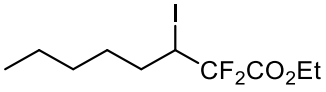
Ethyl 2,2-difluoro-3-hydroxyoctanoate S4[7]



S4

Ethyl bromodifluoroacetate (0.97 mL, 15 mmol, 1.5 equiv) was added to a mixture of zinc dust (0.65 g, 10 mmol, 1.5 equiv) and THF (25 mL) at room temperature under an argon atmosphere. Subsequently, hexanal (0.61 mL, 5 mmol, 1.0 equiv) was added and the mixture was refluxed for 3 h. After cooling down to room temperature, the reaction was quenched with sat. NH_4Cl solution (25 mL). The aqueous layer was extracted with Et_2O (50 mL × 3). The combined organic layer was washed with brine and dried over anhydrous $MgSO_4$. The organic layer was concentrated *in vacuo*, and the residue was purified by column chromatography on silica gel (hexane: EtOAc = 10:1 to 6:1) to give ethyl 2,2-difluoro-3-hydroxy-5-(methylthio) pentanoate **S4** (1.01 g, 4.52 mmol, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 4.35 (q, *J* = 7.1 Hz, 2H), 4.08 – 3.95 (m, 1H), 1.76 – 1.46 (m, 3H), 1.44 – 1.24 (m, 8H), 0.94 – 0.85 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$/TMS) δ 163.9 (t, *J* = 32.0 Hz), 114.8 (dd, *J* = 256.3, 254.6 Hz), 71.9 (dd, *J* = 27.2, 25.0 Hz), 63.2, 31.6, 29.3, 25.0, 22.6, 14.10, 14.08; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.34 (dd, *J* = 264.5, 7.7 Hz), -121.79 (dd, *J* = 264.5, 14.9 Hz); IR (neat): 3335, 2955, 2930, 2862 cm^{-1}; LRMS (EI) m/z: 224 [M]$^+$; HRMS (EI-TOF) m/z: [M]$^+$ Calcd for $C_{10}H_{18}O_3F_2$ 224.1224; found 224.1225.

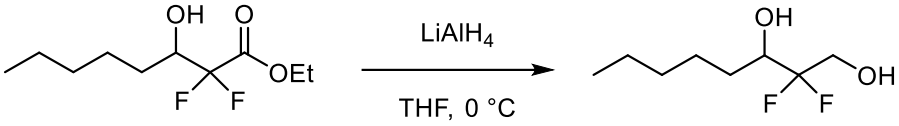
Ethyl 2,2-difluoro-3-iodooctanoate 1h



Prepared according to the iodination step in **General procedure A** using ethyl 2,2-difluoro-3-hydroxyoctanoate **S4** (1.0 g, 4.5 mmol). Purified by silica gel chromatography (hexane only) and bulb

to bulb distillation to afford the product **1h** as colorless oil. (0.80 g 1.96 mmol, 43%). ^{1}H NMR (500 MHz, $CDCl_3$/TMS) δ 4.37 (q, *J* = 7.1 Hz, 2H), 4.36 – 4.25 (m, 1H), 1.90 – 1.74 (m, 2H), 1.70 – 1.52 (m, 1H), 1.44 – 1.22 (m, 8H), 0.91 (t, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$/TMS) δ 162.3 (t, *J* = 33.0 Hz), 114.3 (t, *J* = 254.0 Hz), 63.5, 31.7, 30.8, 29.13 (d, *J* = 24.9 Hz), 28.89, 22.4, 14.0 (2C); ^{19}F NMR (471 MHz, $CDCl_3$) δ -102.35 (dd, *J* = 252.8, 12.2 Hz), -105.52 (dd, *J* = 252.8, 15.5 Hz); IR (neat): 2959, 2932, 2860, 1775, 1759 cm^{-1}; LRMS (EI) m/z 334 $[M]^+$; HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{10}H_{17}O_2F_2I$ 334.0241; found 334.0239.

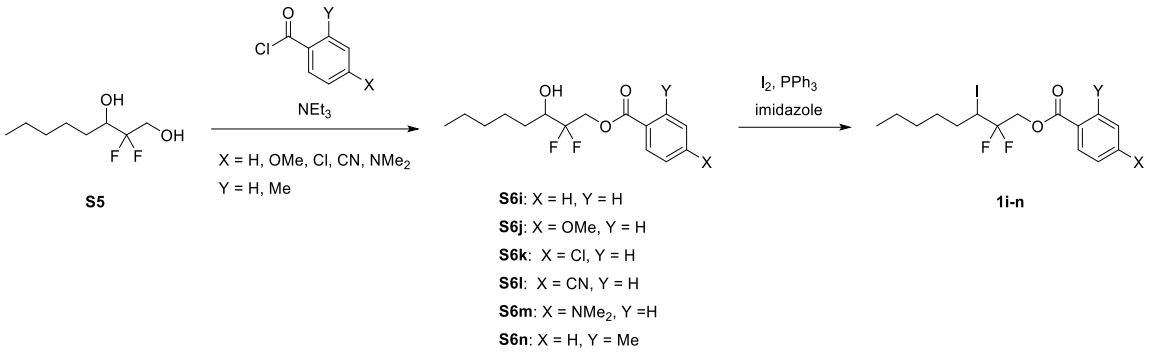
2,2-Difluorooctane-1,3-diol S5



S4 **S5**

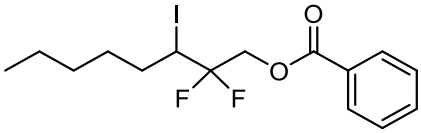
To the solution of ester **S4** (1.91 g, 8.47 mmol, 1.0 equiv) in THF (50 mL) at 0 °C, $LiAlH_4$ (649.9 mg, 16.9 mmol, 2.0 equiv) was added slowly in 4 portions. The reaction was warmed to room temperature and stirred for 16 h. Then, the reaction was quenched with sat. NH_4Cl solution and the mixture was extracted with EtOAc (50 mL × 3). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The colorless oil product **S5** (1.26 g, 6.92 mmol, 82%) was used to the next reaction without any further purification. ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 4.06 – 3.78 (m, 3H), 2.09 (brs, 1H), 2.00 (brs, 1H), 1.76 – 1.66 (m, 1H), 1.60 – 1.47 (m, 2H), 1.44 – 1.24 (m, 5H), 0.90 (t, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$/TMS) δ 121.47 (t, *J* = 246.7 Hz), 71.36 (t, *J* = 27.9 Hz), 62.02 (t, *J* = 31.1 Hz), 31.7, 29.5, 25.3, 22.6, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.0 – -117.10 (m), -123.11 (ddt, *J* = 258.4, 15.8, 10.7 Hz); IR (neat): 3335, 2955, 2930, 2862 cm^{-1}; LRMS (EI) m/z: 183 $[M+1]^+$; HRMS (EI-TOF) m/z: Calcd for $C_8H_{17}O_2F_2$: 183.1197; found 183.1201.

General procedure B: Synthesis of fluorinated alkyl iodides 1i-n



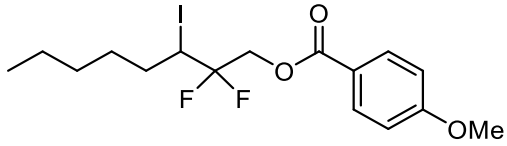
Diol **S5** (1.0 equiv) was dissolved with CH_2Cl_2 (5 mL/mmol of diol) and NEt_3 (1.5 equiv) was added. The solution was cooled to 0 °C and the solution of a corresponding benzoyl chloride (1.1 equiv) in CH_2Cl_2 (5 mL/mmol of diol) was added slowly. After stirring for 3 h at 0 °C, the reaction was quenched with H_2O and the mixture was extracted with EtOAc (× 3). The organic layers were combined, dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel to afford the desired mono-protected diols. The iodination step is the same as in **General procedure A**.

2,2-Difluoro-3-iodooctyl benzoate 1i



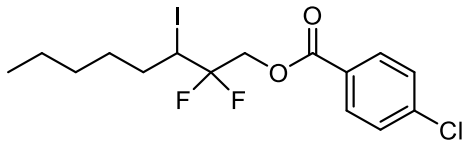
Protected diol **S6i** was prepared according to **General procedure B** using 2,2-difluorooctane-1,3-diol **S5** (868.9 mg, 4.77 mmol) and benzoyl chloride (0.61 mL, 5.25 mmol, 1.1 equiv). The crude was purified by silica chromatography (hexane/EtOAc = 10:1) to afford the corresponding mono-protected diol **S6i** (759.5 mg 2.65 mmol, 56%). The fluorinated alkyl iodide **1i** was prepared according to the iodination step in **General procedure A** using the mono-protected diol **S6i** (695.2 mg, 2.43 mmol). The crude product was purified by silica gel chromatography (hexane/$CHCl_3$ = 10:1 to 5:1) to afford the fluorinated alkyl iodide **1i** (908.8 mg 2.29 mmol, 94%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 8.08 – 8.03 (m, 2H), 7.65 – 7.58 (m, 1H), 7.51 – 7.44 (m, 2H), 4.87 – 4.76 (m, 2H), 4.32 – 4.17 (m, 1H), 1.93 – 1.84 (m, 2H), 1.73 – 1.60 (m, 1H), 1.46 – 1.21 (m, 5H), 0.90 (t, J = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$/TMS) δ 165.36, 133.74, 130.00, 129.13, 128.71, 119.63 (t, J = 246.7 Hz), 63.79 (t, J = 32.7 Hz), 32.58 (t, J = 3.0 Hz), 30.83, 29.95 (t, J = 25.7 Hz), 29.3, 22.5, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.7 (dq, J = 252.6, 12.9 Hz), -104.6 (dq, J = 252.6, 12.0 Hz); IR (neat): 2957, 2930, 2859, 1732 cm^{-1}; LRMS (FAB, NBA) m/z: 397 $[M+1]^+$; HRMS Calcd for $C_{15}H_{20}O_2F_2I$ 397.0476; found 397.0475.

2,2-Difluoro-3-iodooctyl 4-methoxybenzoate 1j



Protected diol **S6j** was prepared according to **General procedure B** using 2,2-difluorooctane-1,3-diol **S5** (364.4 mg, 2.0 mmol) and 4-methoxybenzoyl chloride (375.3 mg, 2.2 mmol, 1.1 equiv). The crude product was purified by silica gel chromatography (hexane/EtOAc = 6:1) to afford the corresponding mono-protected diol **S6j** (571.8 mg 1.81 mmol, 90%). The fluorinated alkyl iodide **1j** was prepared according to the iodination step in **General procedure A** using the mono-protected diol **S6j** (571.8 mg, 1.8 mmol). The crude product was purified by silica gel chromatography (hexane/$CHCl_3$ = 10:1 to 3:1) to afford the desired fluorinated alkyl iodide **1j** (552.5 mg 1.30 mmol, 72%). ^{1}H NMR (500 MHz, $CDCl_3$/TMS) δ 8.04 – 7.97 (m, 2H), 6.98 – 6.90 (m, 2H), 4.78 (t, *J* = 12.6 Hz, 2H), 4.31 – 4.17 (m, 1H), 3.87 (s, 3H), 1.88 (q, *J* = 7.6 Hz, 2H), 1.73 – 1.60 (m, 1H), 1.45 – 1.20 (m, 5H), 0.90 (t, *J* = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$/TMS) δ 165.0, 164.0, 132.1, 121.3, 119.7 (t, *J* = 246.6 Hz), 113.9, 63.4 (t, *J* = 32.7 Hz), 55.6, 32.5 (t, *J* = 2.9 Hz), 30.8, 30.1 (t, *J* = 25.7 Hz), 29.2, 22.4, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.0 (q, *J* = 12.9 Hz); IR (neat): 2957, 2930, 2859, 1722, 1605, 1510 cm^{-1}; LRMS (FAB, NBA) m/z: 426 [M+1]$^+$; HRMS Calcd for $C_{16}H_{21}O_3F_2I$ 426.0504; found 426.0508.

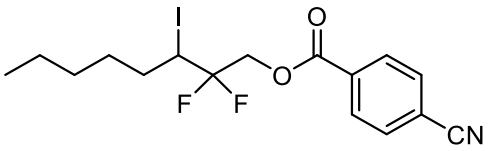
2,2-Difluoro-3-iodooctyl 4-chlorobenzoate 1k



Protected diol **S6k** was prepared according to **General procedure B** using 2,2-difluorooctane-1,3-diol **S5** (364.4 mg, 2.0 mmol) and 4-chlorobenzoyl chloride (0.28 mL, 2.2 mmol, 1.1 equiv). The crude product was purified by silica gel chromatography (hexane/EtOAc = 10:1 to 4:1) to afford the corresponding mono-protected diol **S6k** (383.2 mg 1.19 mmol, 60%). The fluorinated alkyl iodide **1k** was prepared according to the iodination step in **General Procedure A** using the diol **S6k** (383.2 mg, 1.19 mmol). The crude product was purified by silica gel chromatography (hexane/$CHCl_3$ = 20:1 to 5:1) to afford the fluorinated alkyl iodide **1k** (407.6 mg 0.95 mmol, 79%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 8.02 – 7.96 (m, 2H), 7.48 – 7.42 (m, 2H), 4.89 – 4.74 (m, 2H), 4.28 – 4.14 (m, 1H), 1.88 (q, *J* = 7.5 Hz, 2H), 1.73 – 1.60 (m, 1H), 1.45 – 1.20 (m, 5H), 0.90 (t, *J* = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$/TMS) δ 164.6, 140.3, 131.4, 129.1, 127.5, 119.5 (t, *J* = 246.8 Hz), 63.97 (t, *J* = 32.4 Hz), 32.5 (t, *J* = 3.0 Hz), 30.8, 29.8 (t, *J* = 25.7 Hz), 29.2, 22.5, 14.1; ^{19}F NMR (376

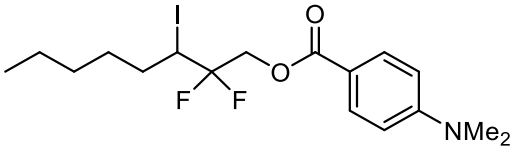
MHz, $CDCl_3$) δ -103.65 (dq, *J* = 262.4, 13.6 Hz), -105.2 (dq, *J* = 262.4, 12.0 Hz); IR (neat): 2957, 2930, 2859, 1732, 1595 cm^{-1}; LRMS (FAB, NBA) m/z: 431 $[M+1]^+$; HRMS Calcd for $C_{15}H_{19}O_2{}^{35}ClF_2I$ 431.0086; found 431.0086.

2,2-Difluoro-3-iodooctyl 4-cyanobenzoate 1l



Protected diol **S6l** was prepared according to **General procedure B** using 2,2-difluorooctane-1,3-diol **S5** (364.4 mg, 2.0 mmol) and 4-cyanobenzoyl chloride (364.3 mg, 2.2 mmol, 1.1 equiv). The crude product was purified by silica gel chromatography (hexane/EtOAc = 6:1 to 4:1) to afford the corresponding mono-protected diol **S6l** (443.2 mg 1.42 mmol, 71%). The fluorinated alkyl iodide **1l** was prepared according to the iodination step in **General procedure A** using the diol **S6l** (443.2 mg, 1.42 mmol). The crude product was purified by silica gel chromatography (hexane/$CHCl_3$ = 6:1 to 1:1) to afford the desired fluorinated alkyl iodide **1l** (445.1 mg 1.15 mmol, 80%) as colorless oil. ^1H NMR (500 MHz, $CDCl_3$/TMS) δ 8.19 – 8.14 (m, 2H), 7.81 – 7.76 (m, 2H), 4.93 – 4.80 (m, 2H), 4.25 – 4.14 (m, 1H), 1.93 – 1.84 (m, 2H), 1.72 – 1.60 (m, 1H), 1.44 – 1.24 (m, 5H), 0.91 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$/TMS) δ 163.8, 132.8, 132.5, 130.5, 119.3(t, *J* = 247.1 Hz), 117.8, 117.2, 64.40 (dd, *J* = 32.7, 30.4 Hz), 32.4 (t, *J* = 3.0 Hz), 30.8, 29.5 (t, *J* = 25.6 Hz), 29.2, 22.4, 14.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ -103.0 – -103.9 (m), -105.6 – -106.5 (m); IR (neat): 2957, 2930, 2859, 2232, 1734 $cm^{-1;}$ LRMS (FAB, NBA) m/z: 422 $[M+1]^+$; HRMS Calcd for $C_{16}H_{19}NO_2F_2I$ 422.0429; found 422.0429.

2,2-Difluoro-3-iodooctyl 4-(dimethylamino)benzoate1m

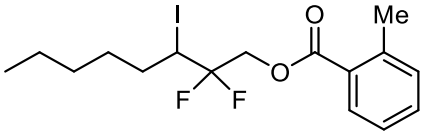


Protected diol **S6m** was prepared according to **General procedure B** using 2,2-difluorooctane-1,3-diol **S5** (364.4 mg, 2.0 mmol) and 4-dimethylamino benzoyl chloride (0.31 mL, 2.2 mmol, 1.1 equiv). The crude product was purified by silica gel chromatography (hexane/EtOAc = 4:1) to afford the corresponding mono-protected diol **S6m** (254.6 mg 0.773 mmol, 39%). The fluorinated alkyl iodide **1m** was prepared according to the iodination step in **General procedure A** using the mono-protected diol **S6m** (432.3 mg, 2.0 mmol). The crude product was purified by silica gel chromatography

(hexane/$CHCl_3$ = 20:1 to 5:1) to afford the desired fluorinated alkyl iodide **1m** (367.9 mg 0.84 mmol, 42%).

^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 7.91 (d, *J* = 9.2 Hz, 2H), 6.65 (d, *J* = 9.2 Hz, 2H), 4.75 (t, *J* = 12.1 Hz, 2H), 4.35 – 4.19 (m, 1H), 3.05 (s, 6H), 1.92 – 1.83 (m, 2H), 1.65 – 1.59 (m, 1H), 1.45 – 1.21 (m, 6H), 0.90 (t, *J* = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$/TMS) δ 165.6, 153.8, 131.8, 122.3, 119.9 (t, *J* = 246.3 Hz), 110.8, 62.9 (t, *J* = 33.2 Hz), 40.1, 32.5, 30.8, 30.5 (t, *J* = 25.7 Hz)., 29.3, 22.5, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.8 (dq, *J* = 252.3, 12.3 Hz), -104.3 (dq, *J* = 252.3, 13.0 Hz); IR (neat): 2955, 2928, 2859 cm^{-1}; LRMS (FAB, NBA) m/z: 439 [M+1]$^+$; HRMS Calcd for $C_{17}H_{24}NO_2F_2I$ 440.0898; found 440.0895.

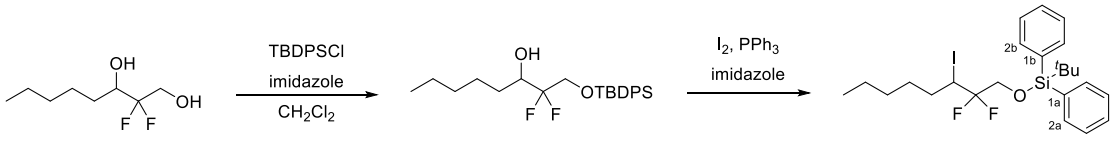
2,2-Difluoro-3-iodooctyl 2-methylbenzoate 1n



Protected diol **S6n** was prepared according to **General procedure B** using 2,2-difluorooctane-1,3-diol **S5** (364.4 mg, 2.0 mmol) and 2-toluoyl chloride (0.29 mL, 2.2 mmol, 1.1 equiv). The crude product was purified by silica gel chromatography (hexane/EtOAc = 8:1) to afford the corresponding mono-protected diol **S6n** (191.7 mg 0.638 mmol, 32%). The fluorinated alkyl iodide **1n** was prepared according to the iodination step in **General procedure A** using the mono-protected diol **S6n** (191.7 mg, 0.638 mmol). The crude product was purified by silica gel chromatography (hexane/$CHCl_3$ = 10:1) to afford the desired fluorinated alkyl iodide **1n** (152.5 mg 0.372 mmol, 58%).

^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 7.93 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.45 (td, *J* = 7.5, 1.5 Hz, 1H), 7.31 – 7.26 (m, 2H), 4.89 – 4.70 (m, 2H), 4.32 – 4.16 (m, 1H), 2.62 (s, 3H), 1.94 – 1.82 (m, 2H), 1.74 – 1.59 (m, 1H), 1.46 – 1.22 (m, 5H), 0.90 (t, *J* = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$/TMS) δ 166.2, 141.0, 132.8, 132.0, 131.0, 128.5, 126.0, 119.7 (t, *J* = 246.7 Hz), 63.7 (t, *J* = 32.2 Hz), 32.6 (t, *J* = 3.0 Hz), 30.9, 30.0 (t, *J* = 25.8 Hz), 29.3, 22.5, 21.9, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.9 (dq, *J* = 252.2, 13.2 Hz), -105.0 (dq, *J* = 252.2, 12.5 Hz); IR (neat): 2957, 2930, 2859, 1728 cm^{-1}; LRMS (FAB, NBA) m/z: 411 [M+1]$^+$; HRMS Calcd for $C_{16}H_{22}O_2F_2I$ 411.0633; found 411.0632.

***tert*-Butyl((2,2-difluoro-3-iodooctyl)oxy)diphenylsilane 1o**

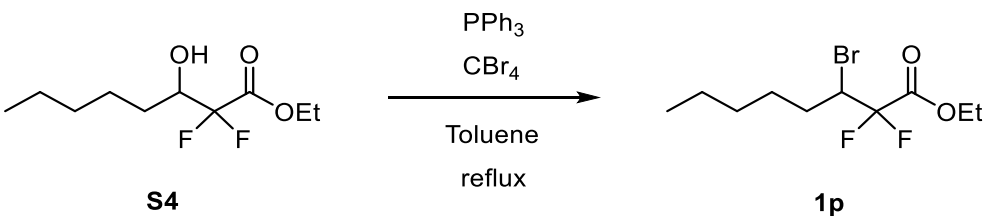


S5 **S6o** **1o**

The solution of diol **S5** (286.5 mg, 1.57 mmol) and imidazole (214.1 mg, 3.15 mmol, 2.0 equiv) in CH_2Cl_2 (10 mL) was cooled to 0 °C. To the solution, TBDPSCl (0.40 mL, 1.57 mmol, 1.0 equiv) was

added slowly. After stirring for 16 h, the reaction was quenched with H_2O and the mixture was extracted with EtOAc (× 3). The organic layers were combined, dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel to afford the corresponding mono-protected diol **S6o** (521.4 mg, 1.24 mmol, 62%). The fluorinated alkyl iodide **1o** was prepared according to the iodination step in **General procedure A** using the mono-protected diol **S6o** (412.6 mg, 0.98 mmol). The crude product was purified by silica gel chromatography (hexane only) to afford the desired fluorinated alkyl iodide **1o** (374.0 mg 0.71 mmol, 72%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 7.75 – 7.65 (m, 4H), 7.52 – 7.38 (m, 6H), 4.55 – 4.39 (m, 1H), 4.23 – 4.08 (m, 1H), 4.05 – 3.92 (m, 1H), 1.94 – 1.81 (m, 2H), 1.77 – 1.62 (m, 1H), 1.49 – 1.24 (m, 5H), 1.13 – 1.07 (m, 9H), 0.98 – 0.91 (m, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$/TMS) δ 135.8 (C_{1a}), 135.7 (C_{1b}), 132.5 (C_{2a}), 132.4 (C_{2b}), 130.2, 128.1, 121.1 (t, *J* = 246.4 Hz), 64.5 (t, *J* = 34.6 Hz), 32.5, δ31.3 (d, *J* = 25.7 Hz), 31.0, 29.4, 26.9, 22.6, 19.4, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.4 (dtd, *J* = 248.7, 14.7, 7.7 Hz), -107.1 (ddt, *J* = 248.7, 17.2, 11.3 Hz); IR (neat): 2955, 2930, 2859 cm^{-1}; LRMS (FAB, NBA) m/z: 531 $[M+1]^+$; HRMS Calcd for $C_{24}H_{34}F_2IOSi$ 531.1392; found 531.1397.

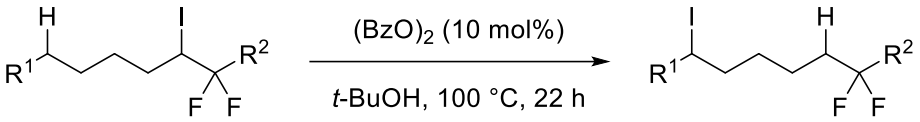
Ethyl 3-bromo-2,2-difluorooctanoate 1p



S4 **1p**

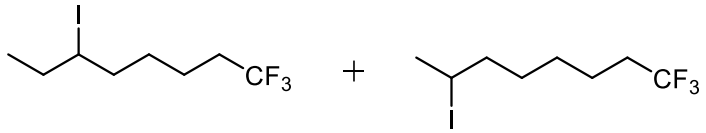
To a solution of alcohol **S4** (455.3 mg, 2.0 mmol) and PPh_3 (1.06 g, 4.0 mmol, 2.0 equiv) in toluene (20 mL), tetrabromomethane (1.33g, 4.0 mmol, 2.0 equiv) was added in one portion. The mixture was refluxed at 110 °C for 3 h. After cooling down to room temperature, the reaction was quenched with H_2O (40 mL). The aqueous phase was extracted with EtOAc (50 mL × 3). The combined organic layers were washed with brine (50 mL), dried over $MgSO_4$ and concentrated. The crude product was purified by flash chromatography on silica gel and bulb to bulb distillation to give the desired alkyl bromide **1p** (67%, 382.7 mg, 1.34 mmol) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 4.38 (q, *J* = 7.1 Hz, 2H), 4.31 – 4.17 (m, 1H), 2.06 – 1.93 (m, 1H), 1.91 – 1.78 (m, 1H), 1.74 – 1.60 (m, 1H), 1.49 – 1.20 (m, 8H), 0.91 (t, *J* = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$/TMS) δ 162.7 (t, *J* = 32.3 Hz), 113.8 (dd, *J* = 257.9, 252.9 Hz), 63.5, 50.4 (dd, *J* = 28.1, 25.4 Hz), 31.0, 30.2 (2C), 26.8, 22.5, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.13 (dd, *J* = 255.6, 8.5 Hz), -114.71 (dd, *J* = 255.6, 16.7 Hz); IR (neat): 2959, 2932, 2862, 1776, 1759 cm^{-1}; LRMS (EI) m/z: 287 $[M+1]^+$; HRMS (EI-TOF) m/z: $[M+1]^+$ Calcd for $C_{10}H_{18}O_2F_2{}^{79}Br$ 287.0458; found 287.0453.

General procedure C: Synthesis of fluorinated alkyl iodides 2a-d, 2g-l, and 2n-o



In a test tube equipped with a stir bar, a fluorinated alkyl iodide (0.2 mmol) and $(BzO)_2$ wetted with ca. 25% H_2O (6.4 mg, 0.02 mmol, 10 mol%) were added. The tube was evacuated and backfilled with Ar three times, and then *t*-BuOH (2.0 mL) was charged. The tube was sealed and heated at 100 °C in an oil bath for 22 h. After cooling to room temperature, the reaction was concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel eluting with hexane/EtOAc to give the corresponding alkyl iodide.

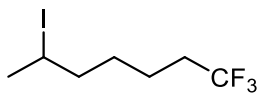
1,1,1-Trifluoro-6-iodooctane 2a and **1,1,1-trifluoro-7-iodooctane 2a'**



2a **2a'**

Prepared according to **General procedure C** using 1,1,1-trifluoro-2-iodooctane **1a** (58.8 mg, 0.2 mmol). Purified by silica gel chromatography (hexane only) to afford the desired product **2a** and **2a'** (53.0 mg 0.18 mmol, 90%) as a mixture in the ratio of 3.7:1 as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 4.22 – 4.12 (m, 0.27H, minor), 4.10 – 4.00 (m, 1H, major), 2.17 – 2.00 (m , 2H+0.54H, major+minor), 1.94 – 1.35 (m, 8 H+2.97H), 1.03 (t, *J* = 7.2 Hz, 3H, major); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$/TMS) δ 127.4 (q, *J* = 276.3 Hz, minor),127.3 (q, *J* = 276.3 Hz, major), 42.7 (minor), 41.2 (major), 39.9 (major), 34.0 (major), 33.80 (d, *J* = 28.3 Hz, major + minor), 30.1 (minor), 29.5 (minor), 29.1 (minor), 28.9 (major), 28.0 (minor), 21.9 (q, *J* = 3.0 Hz, minor), 21.4 (q, *J* = 3.0 Hz, major), 14.2 (major); ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.70 (t, *J* = 11.0 Hz, minor), -65.77 (t, *J* = 10.9 Hz, major); IR (neat): 2968, 2943, 2876 cm^{-1}; LRMS (EI) m/z: 294 $[M]^+$; HRMS (EI-TOF) m/z $[M]^+$ Calcd for $C_8H_{14}F_3I$ 294.0092; found 294.0093.

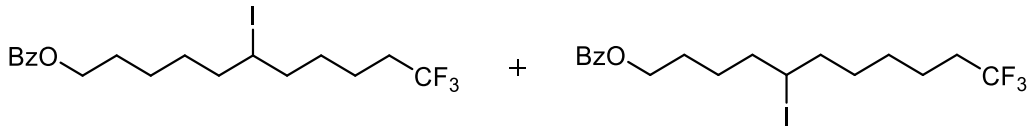
1,1,1-Trifluoro-6-iodoheptane 2b



Prepared according to **General procedure C** using 1,1,1-trifluoro-2-iodoheptane **1b** (56.0 mg, 0.20 mmol). Purified by silica gel chromatography (hexane only) to afford the desired product **2b** (44.6 mg 0.159 mmol, 80%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 4.22 – 4.11 (m, 1H), 2.17 – 2.01 (m, 2H), 1.93 (d, *J* = 6.9 Hz, 3H), 1.90 – 1.79 (m, 1H), 1.69 – 1.39 (m, 5H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$/TMS) δ 127.2 (q, *J* = 276.3 Hz), 42.5, 33.8 (q, *J* = 28.5 Hz), 29.5, 29.1, 29.0, 21.3 (q, *J*

= 3.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.78 (t, *J* = 10.9 Hz); IR (neat): 2945, 2920, 2866 cm^{-1}; LRMS (EI) m/z: 280 $[M]^+$; HRMS (EI-TOF) m/z $[M]^+$ Calcd for $C_7H_{12}F_3I$ 279.9936; found 279.9938.

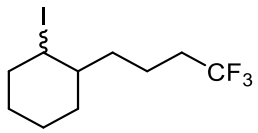
11,11,11-trifluoro-6-iodoundecyl benzoate (major) 2c and **11,11,11-trifluoro-5-iodoundecyl benzoate (minor) 2c'**



2c **2c'**

Prepared according to **General procedure C** using 1,1,1-trifluoro-2-iodooctane **1c** (85.6 mg, 0.2 mmol). Purified by silica gel chromatography (hexane/EtOAc = 20:1) to afford the desired product **2c** and **2c'** (77.1 mg 0.18 mmol, 90%) in the ratio of 2.5:1 as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$/TMS) δ 8.08 – 8.01 (m, 2H), 7.59 – 7.52 (m, 1H), 7.47 – 7.40 (m, 2H), 4.38 – 4.28 (m, 2H), 4.15 – 4.02 (m, 1H), 2.17 – 1.99 (m, 2H), 1.98 – 1.27 (m, 14H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$/TMS) δ 166.73 (major), 166.70 (minor), 133.01 (minor), 132.98 (major), 130.55 (major), 130.49 (minor), 129.7 (major + minor), 128.5 (major + minor), 127.3 (minor, q, *J* = 277.0 Hz), 127.2 (major, q, *J* = 276.5 Hz), 65.0 (major), 64.7 (minor), 40.6 (major), 40.4 (minor), 40.2 (major + minor), 39.1 (minor), 38.8 (major), 33.7 (major + minor, q, *J* = 28.4 Hz), 29.4 (major) , 29.3 (minor), 28.8 (major), 28.7 (major), 28.04 (minor), 28.00 (minor), 26.3 (minor), 25.5 (major), 21.9 (minor, q, *J* = 3.2 Hz), 21.3 (major, q, *J* = 3.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.2 (minor, t, *J* = 10.9 Hz), -66.3 (major, t, *J* = 10.7 Hz); IR (neat): 2940, 2860, 1714 cm^{-1}; LRMS (FAB, NBA) m/z: 457 $[M+1]^+$; HRMS Calcd for $C_{18}H_{24}O_2F_3I$ 457.0851; found 457.0856.

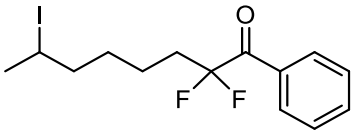
1-Iodo-2-(4,4,4-trifluorobutyl)cyclohexane 2d



Prepared according to **General procedure C** using (4,4,4-trifluoro-3-iodobutyl)cyclohexane **1d** (64.0 mg, 0.2 mmol). Purified by silica gel chromatography (hexane only) to afford the desired product **2d** as the cis/trans mixture (1:1) as colorless oil (50.0 mg 0.156 mmol, 78%). ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 4.72 – 4.64 (m, 1H, *cis*), 3.99 (ddd, *J* = 11.7, 10.5, 4.1 Hz, 1H, *trans*), 2.57 – 2.47 (m, 1H), 2.27 – 1.95 (m, 6H), 1.93 – 1.38 (m, 13H), 1.38 – 1.20 (m, 8H), 1.14 – 1.00 (m, 1H), 0.52 – 0.39(m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$/TMS) δ 127.2 (2C, q, *J* = 276.4 Hz, *cis* and *trans*), 46.9, 46.4, 42.3, 41.7, 41.5, 37.4, 37.2, 36.7, 33.97 (q, *J* = 28.4 Hz), 33.94 (q, *J* = 28.4 Hz), 31.9, 29.1, 29.0, 25.7, 25.5, 22.8, 18.80 (q, *J* = 3.0 Hz), 18.67 (q, *J* = 3.0 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -65.74 (t, *J* = 11.0 Hz), -65.76 (t, *J* = 10.8 Hz); IR (neat): 2932, 2857 cm^{-1}; LRMS (EI) m/z: 320 $[M]^+$; HRMS

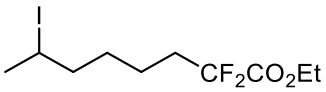
(EI-TOF) m/z: $[M]^+$ Calcd for $C_{10}H_{16}F_3I$ 320.0249; found 320.0241.

2,2-difluoro-7-iodo-1-phenyloctan-1-one 2g



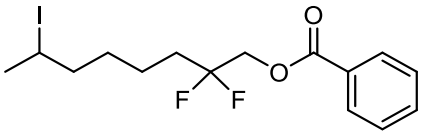
Prepared according to **General procedure C** using 2,2-difluoro-3-iodo-1-phenyloctan-1-one **1g** (73.2 mg, 0.20 mmol). Purified by silica gel chromatography (hexane/$CHCl_3$ = 20:1) to afford the desired product **2g** (33.4 mg, 91.2 μmol, 45%) as colorless oil. ^1H NMR (500 MHz, $CDCl_3$/TMS) δ 8.10 (dd, *J* = 8.4, 1.0 Hz, 2H), 7.67 – 7.59 (m, 1H), 7.53 – 7.46 (m, 2H), 4.22 – 4.11 (m, 1H), 2.28 – 2.12 (m, 2H), 1.92 (d, *J* = 6.8 Hz, 3H), 1.90 – 1.80 (m, 1H), 1.69 – 1.43 (m, 5H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$/TMS) δ 189.6 (t, *J* = 31.3 Hz), 134.4, 132.2 (t, *J* = 2.5 Hz), 130.3 (t, *J* = 3.5 Hz), 128.8, 119.8 (t, *J* = 252.8 Hz), 42.6, 33.9 (t, *J* = 22.9 Hz), 29.9, 29.6, 29.1, 20.8 (t, *J* = 4.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.49 (t, *J* = 17.6 Hz); IR (neat): 2941, 2860, 1701, 1597 cm^{-1}; LRMS (EI) m/z: 366 $[M]^+$; HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{14}H_{17}OF_2I$ 366.0292; found 366.0288.

Ethyl 2,2-difluoro-7-iodooctanoate 2h



Prepared according to **General procedure C** using ethyl 2,2-difluoro-3-iodooctanoate **1h** (66.8 mg, 0.20 mmol). Purified by silica gel chromatography (hexane/EtOAc = 20:1) to afford the desired product **2h** (59.3 mg 0.177 mmol, 89%) as colorless oil. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ 4.32 (q, *J* = 7.1 Hz, 2H), 4.21 – 4.10 (m, 1H), 2.15 – 1.98 (m, 2H), 1.91 (d, *J* = 6.8 Hz, 3H), 1.88 – 1.77 (m, 1H), 1.67 – 1.40 (m, 5H), 1.35 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$/TMS) δ 164.5 (t, *J* = 32.9 Hz), 116.3 (t, *J* = 250.1 Hz), 63.0, 42.5, 34.4 (t, *J* = 23.3 Hz), 29.7, 29.4, 29.1, 20.8 (t, *J* = 4.4 Hz), 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.37 (t, *J* = 16.8 Hz); IR (neat): 2940, 2866, 1761 cm^{-1}; LRMS (EI) m/z: 334 $[M]^+$; HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{10}H_{17}O_2F_2I$ 334.0241; found 334.0234.

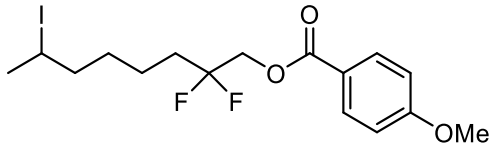
2,2-Difluoro-7-iodooctyl benzoate 2i



Prepared according to **General procedure C** using 2,2-difluoro-3-iodooctyl benzoate **1i** (79.2 mg, 0.2 mmol). Purified by silica gel chromatography (hexane/$CHCl_3$ = 10:1 to 6:1) to afford the desired product **2i** (72.0 mg 0.18 mmol, 90%) as colorless oil. ^1H NMR (400 MHz, $CDCl_3$/TMS) δ 8.10 – 8.03

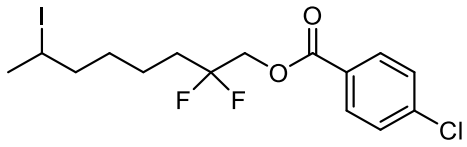
(m, 2H), 7.60 (tt, *J* = 7.4, 1.3 Hz, 1H), 7.50 – 7.44 (m, 2H), 4.49 (t, *J* = 12.4 Hz, 2H), 4.23 – 4.10 (m, 1H), 2.09 – 1.93 (m, 2H), 1.91 (d, *J* = 6.8 Hz, 3H), 1.90 – 1.80 (m, 1H), 1.70 – 1.40 (m, 5H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$/TMS) δ 165.67, 133.67, 129.99, 129.32, 128.70, 121.8 (t, *J* = 242.1 Hz), 64.3 (t, *J* = 34.1 Hz), 42.62, 34.05 (t, *J* = 23.9 Hz), 29.7, 29.6, 29.0, 21.0 (t, *J* = 4.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.8 (tt, *J* = 17.0, 12.4 Hz); IR (neat): 2959, 2938, 2864, 1730, 1450 cm^{-1}; LRMS (EI) m/z: 396 $[M]^+$; HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{15}H_{19}O_2F_2I$ 396.0398; found 396.0399.

2,2-Difluoro-7-iodooctyl 4-methoxybenzoate 2j



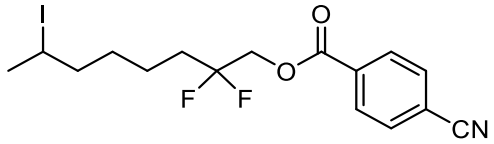
Prepared according to **General procedure C** using 2,2-difluoro-3-iodooctyl 4-methoxybenzoate **1j** (85.2 mg, 0.2 mmol). Purified by silica gel chromatography (hexane/$CHCl_3$ = 6:1 to 4:1) to afford the desired product **2j** (70.1 mg 0.164 mmol, 82%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 8.04 – 7.98 (m, 2H), 6.98 – 6.89 (m, 2H), 4.45 (t, *J* = 12.4 Hz, 2H), 4.21 – 4.11 (m, 1H), 3.86 (s, 3H), 2.06 – 1.78 (m, 6H), 1.68 – 1.40 (m, 5H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$/TMS) δ 165.36, 163.96, 132.06, 123.06 (d, *J* = 242.1 Hz), 121.54, 113.93, 63.98 (t, *J* = 34.0 Hz), 55.60, 42.57, 33.98 (t, *J* = 23.8 Hz), 29.92, 29.57, 29.02, 20.99 (t, *J* = 4.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.7 – -105.0 (m); IR (neat): 2959, 2836, 2860, 1717, 1605, 1508 cm^{-1}; LRMS (EI) m/z: 426 $[M]^+$; HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{16}H_{21}O_3F_2I$ 426.0504; found 426.0504.

2,2-Difluoro-7-iodooctyl 4-chlorobenzoate 2k



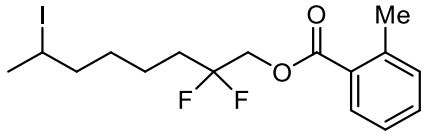
Prepared according to **General procedure C** using 2,2-difluoro-3-iodooctyl 4-chlorobenzoate **1k** (86.1 mg, 0.2 mmol). Purified by silica gel chromatography (hexane/$CHCl_3$ = 6:1) to afford the desired product **2k** (73.4 mg 0.170 mmol, 85%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 8.03 – 7.95 (m, 2H), 7.48 – 7.40 (m, 2H), 4.48 (t, *J* = 12.4 Hz, 2H), 4.21 – 4.11 (m, 1H), 2.05 – 1.78 (m, 6H), 1.68 – 1.40 (m, 5H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$/TMS) δ 164.8, 140.2, 131.4, 129.1, 127.6, 121.6 (t, *J* = 242.2 Hz), 64.4 (t, *J* = 33.7 Hz), 42.6, 34.0 (t, *J* = 23.8 Hz), 29.9, 29.6, 29.0, 21.0 (t, *J* = 4.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.1 (tt, *J* = 17.2, 12.5 Hz); IR (neat): 2959, 2938, 2862, 1730, 1595 cm^{-1}; LRMS (FAB, NBA) m/z: 431 $[M+1]^+$; HRMS Calcd for $C_{15}H_{19}O_2{}^{35}ClF_2I$ 431.0086; found 431.0088.

2,2-Difluoro-7-iodooctyl 4-cyanobenzoate 2l



Prepared according to **General procedure C** using 2,2-difluoro-3-iodooctyl 4-cyanobenzoate **1l** (84.2 mg, 0.2 mmol). Purified by silica gel chromatography (hexane/$CHCl_3$ = 2:1 to 1:1) to afford the desired product **2l** (68.6 mg 0.163 mmol, 81%) as a pale-yellow solid. m.p. = 70–71 °C; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 8.19 – 8.13 (m, 2H), 7.80 – 7.75 (m, 2H), 4.51 (t, *J* = 12.5 Hz, 2H), 4.23 – 4.09 (m, 1H), 2.05 – 1.75 (m, 6H), 1.69 – 1.39 (m, 5H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$/TMS) δ 164.1, 133.0, 132.5, 130.5, 121.4 (t, *J* = 242.4 Hz), 117.9, 117.1, 64.8 (t, *J* = 33.1 Hz), 42.5, 34.0 (t, *J* = 23.7 Hz), 29.8, 29.5, 29.0, 28.7, 20.9 (t, *J* = 4.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.2 – -105.4 (m); IR (neat): 3100, 2957, 2932, 2872, 2859, 2230, 1717 cm^{-1}; LRMS (FAB, NBA) m/z: 422 $[M+1]^+$; HRMS Calcd for $C_{16}H_{19}NO_2F_2I$ 422.0429; found 422.0430.

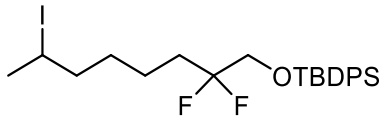
2,2-Difluoro-7-iodooctyl 2-methylbenzoate 2n



Prepared according to **General procedure C** using 2,2-difluoro-3-iodooctyl benzoate **1n** (82.0 mg, 0.2 mmol). Purified by silica gel chromatography (hexane/$CHCl_3$ = 10:1 to 3:1) to afford the desired product **2n** (70.4 mg 0.172 mmol, 86%) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$/TMS) δ 7.98 – 7.92 (m, 1H), 7.47 – 7.40 (m, 1H), 7.30 – 7.25 (m, 2H), 4.47 (t, *J* = 12.5 Hz, 2H), 4.22 – 4.12 (m, 1H), 2.62 (s, 3H), 2.07 – 1.93 (m, 2H), 1.92 (d, *J* = 6.8 Hz, 3H), 1.91 – 1.81 (m, 1H), 1.69 – 1.42 (m, 5H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$/TMS) δ 166.5, 140.9, 132.7, 132.0, 131.0, 128.7, 126.0, 121.8 (t, *J* = 242.1 Hz), 64.1 (t, *J* = 33.7 Hz), 42.7, 34.1 (t, *J* = 23.9 Hz), 29.64, 29.59, 29.1, 21.9, 21.1 (t, *J* = 4.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.7 – -105.0 (m); IR (neat): 2959, 2930, 2859, 1726 cm^{-1}; LRMS (FAB, NBA) m/z: 411 $[M+1]^+$; HRMS m/z: $[M+1]^+$ Calcd for $C_{16}H_{22}O_2F_2I$ 411.0633; found 411.0632.

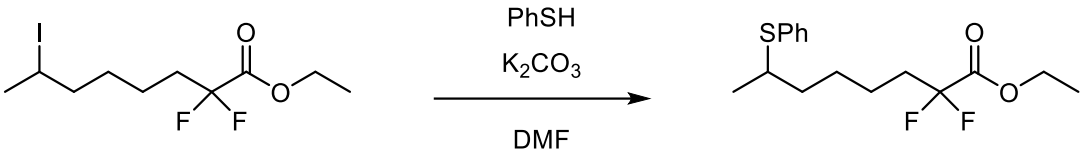
***tert*-Butyl((2,2-difluoro-7-iodooctyl)oxy)diphenylsilane 2o**



Prepared according to **General procedure C** using *tert*-butyl((2,2-difluoro-3-iodooctyl)oxy)diphenylsilane **1o** (106.1 mg, 0.2 mmol). Purified by silica gel chromatography (hexane

only to hexane/EtOAc = 10:1) to afford the desired product **2o** (40.6 mg 0.81 mmol, 41%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 7.70 – 7.65 (m, 4H), 7.49 – 7.37 (m, 6H), 4.25 – 4.12 (m, 1H), 3.75 (t, *J* = 12.1 Hz, 2H), 2.07 – 1.80 (m, 6H), 1.70 – 1.39 (m, 5H), 1.09 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$/TMS) δ 135.75, 132.85, 130.12, 128.00, 123.50 (t, *J* = 242.0 Hz), 65.04 (t, *J* = 35.0 Hz), 42.77, 33.34 (t, *J* = 24.0 Hz), 29.87, 29.67, 29.07, 26.89, 21.21 (t, *J* = 4.8 Hz). 19.42; ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.92 (tt, *J* = 17.0, 12.1 Hz); IR (neat): 2932, 2859 cm^{-1}; LRMS (FAB, NBA) m/z: 531 $[M+1]^+$; HRMS Calcd for $C_{24}H_{34}F_2IOSi$ 531.1392; found 531.1387.

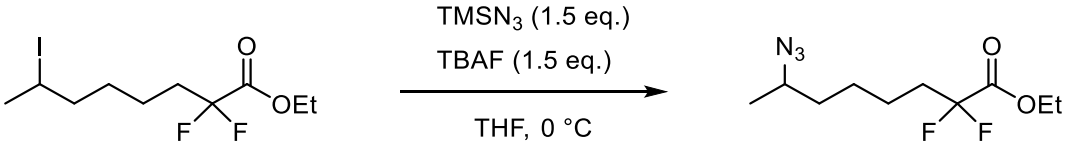
Ethyl 2,2-difluoro-7-(phenylthio)octanoate 3



2h **3**

To a solution of ester **2h** (58.8 mg, 0.2 mmol, 1.0 equiv) and PhSH (30.7 μL, 0.3 mmol, 1.5 equiv) in DMF (1.0 mL) at room temperature, K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv) was added in one portion. After stirring for 4 h, the reaction was quenched with sat. NH_4Cl solution and the aqueous phase was extracted with EtOAc (30 mL × 3). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. The crude product was purified by flash chromatography on silica gel (hexane only to hexane/EtOAc = 20/1) to give the desired sulfide **3** (88%, 43.8 mg, 0.176 mmol) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 7.41 – 7.34 (m, 2H), 7.31 – 7.25 (m, 2H), 7.24 – 7.18 (m, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.18 (h, *J* = 6.7 Hz, 1H), 2.12 – 1.93 (m, 2H), 1.65 – 1.40 (m, 6H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.26 (d, *J* = 6.7 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$/TMS) δ 164.5 (t, *J* = 33.0 Hz), 135.2, 132.2, 129.0, 126.9, 116.4 (t, *J* = 250.0 Hz), 62.9, 43.2, 36.3, 34.5 (t, *J* = 23.2 Hz), 26.6, 21.4 (t, *J* = 4.3 Hz), 21.3, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.3 (t, *J* = 16.8 Hz); IR (neat): 2963, 2940, 2866, 1761 cm^{-1}; LRMS (EI) m/z 316 $[M]^+$; HRMS (EI-TOF) m//z: $[M]^+$ Calcd for $C_{16}H_{22}O_2F_2S$ 316.1309; found 316.1308.

Ethyl 7-azido-2,2-difluorooctanoate 4



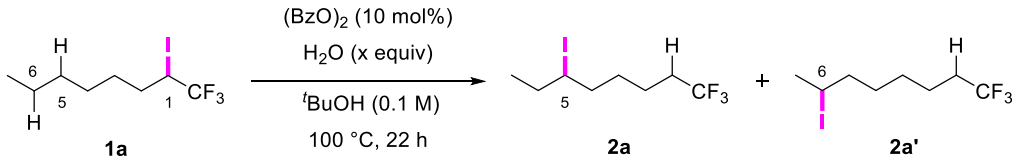
2h **4**

To a solution of ester **2h** (58.8 mg, 0.2 mmol, 1.0 equiv) and $TMSN_3$ (39μL, 0.3 mmol, 1.5 equiv) in THF (2.0 mL) at 0 °C, 1M solution of TBAF in THF (0.3 mL, 0.3 mmol, 1.5 equiv) was added slowly.

After stirring for 16 h, the reaction was quenched with H_2O and the aqueous phase was extracted with EtOAc (30 mL × 3). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. The crude product was purified by flash chromatography on silica gel (hexane/EtOAc = 20/1) to give the desired azide **4** (88%, 43.8 mg, 0.176 mmol) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 4.32 (q, *J* = 7.1 Hz, 2H), 3.40 – 3.36 (m, 1H), 2.15 – 1.95 (m, 2H), 1.56 – 1.36 (m, 6H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.25 (d, *J* = 6.5 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$/TMS) δ 164.5 (t, *J* = 33.0 Hz), 116.3 (t, *J* = 250.1 Hz), 62.9, 57.8, 36.0, 34.5 (t, *J* = 23.2 Hz), 25.7, 21.4 (t, *J* = 4.4 Hz), 19.6, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.3 (t, *J* = 16.8 Hz); IR (neat): 2972, 2941, 2874, 2097, 1761 cm^{-1}; Anal. Calcd. For $C_{10}H_{17}F_2N_3O_2$: C, 48.19; H, 6.87; N, 16.86. Found: C, 48.22; H, 7.12; N, 16.20.

4. Additional Experiments

In a test tube equipped with a stir bar, fluorinated alkyl iodide **1a** (0.2 mmol) and $(BzO)_2$ wetted with ca. 25% H_2O (6.4 mg, 0.02 mmol, 10 mol%) were added. The tube was evacuated and backfilled with Ar three times, and then *t*-BuOH (2.0 mL) and distilled H_2O (3.6 μL or 10.8 μL) were charged. The tube was sealed and heated at 100 °C in an oil bath for 22 h. After cooling to room temperature, the reaction was evaluated by GC analysis using an internal standard (decane) to determine GC yield.



entry	x (equiv)	Yield (2a + 2a') (%)
1	0	94
2	1.0	47
3	3.0	40

GC yields.

5. References

1. A. S. Dudnik and G. C. Fu, *J. Am. Chem. Soc.*, 2012, **134**, 10693–10697.

2. H. Fuse, H. Mitsunuma and M. Kanai, *J. Am. Chem. Soc.*, 2020, **142**, 4493–4499.

3. V. K. Aggarwal, I. Bae and H.-Y. Lee, *Tetrahedron*, 2004, **60**, 9725–9733.

4. M. Stratakis, R. Nencka, C. Rabalakos, W. Adam, O. Krebs, *J. Org. Chem.*, 2002, **67**, 8758–8763.

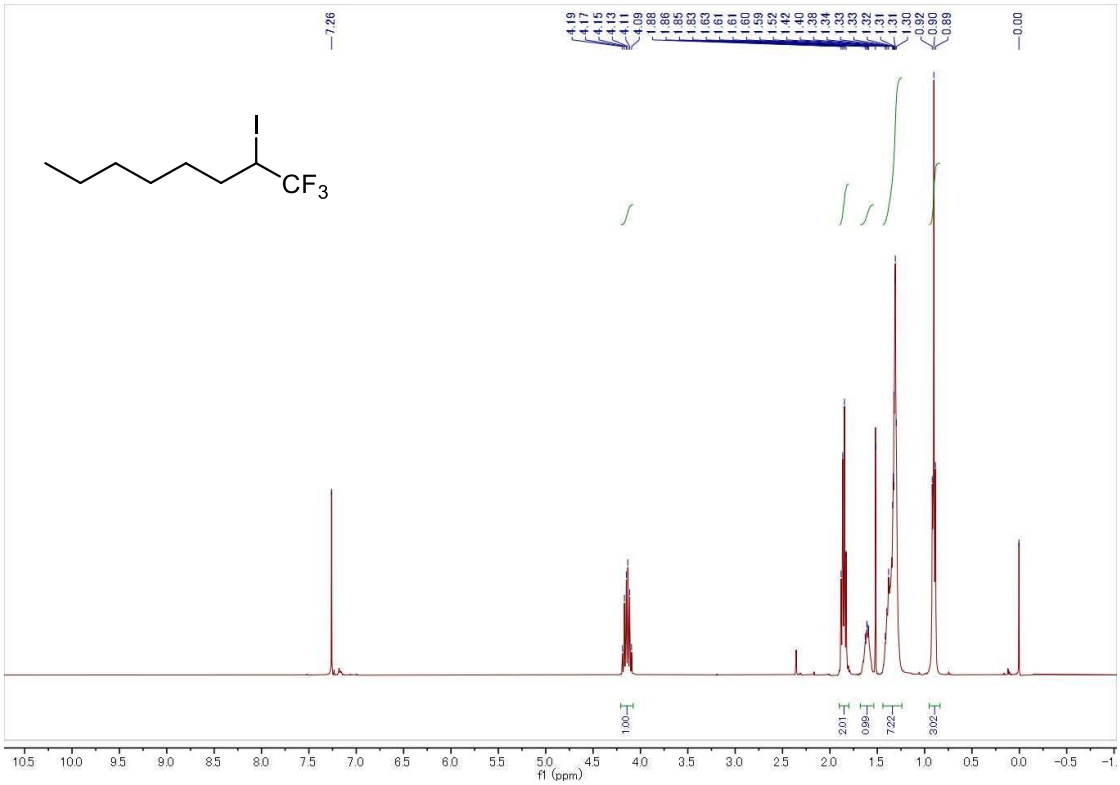
5. S. Munnuri, A. M. Adebesin, M. P. Paudyal, M. Yousufuddin, A. Dalipe, J. R. Falck, *J. Am. Chem. Soc.*, 2017, **139**, 18288−18294.

6. H. Amii, T. Kobayashi, Y. Hatamoto and K. Uneyama, *Chem. Commun.*, 1999, 1323–1324.

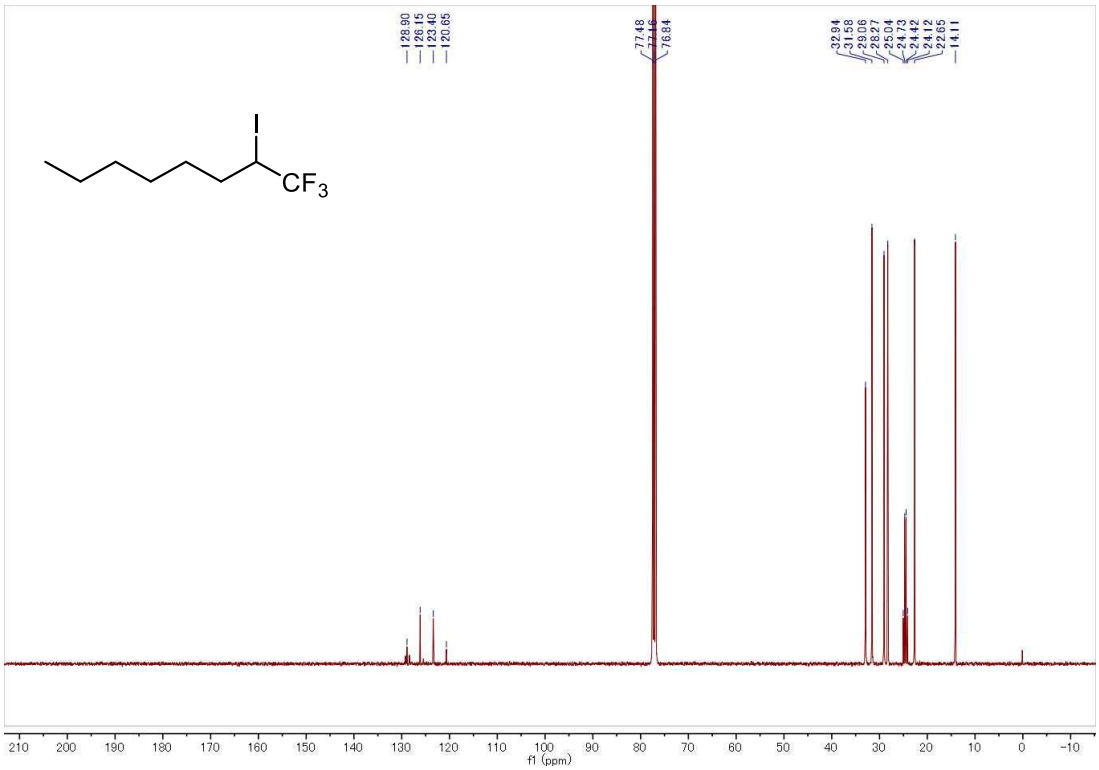
7. F. W. Friese, C. Mück-Lichtenfeld and A. Studer, *Nat. Commun.*, 2018, **9**, 2808.

6. ^{1}H-, ^{13}C- and ^{19}F-NMR Spectra

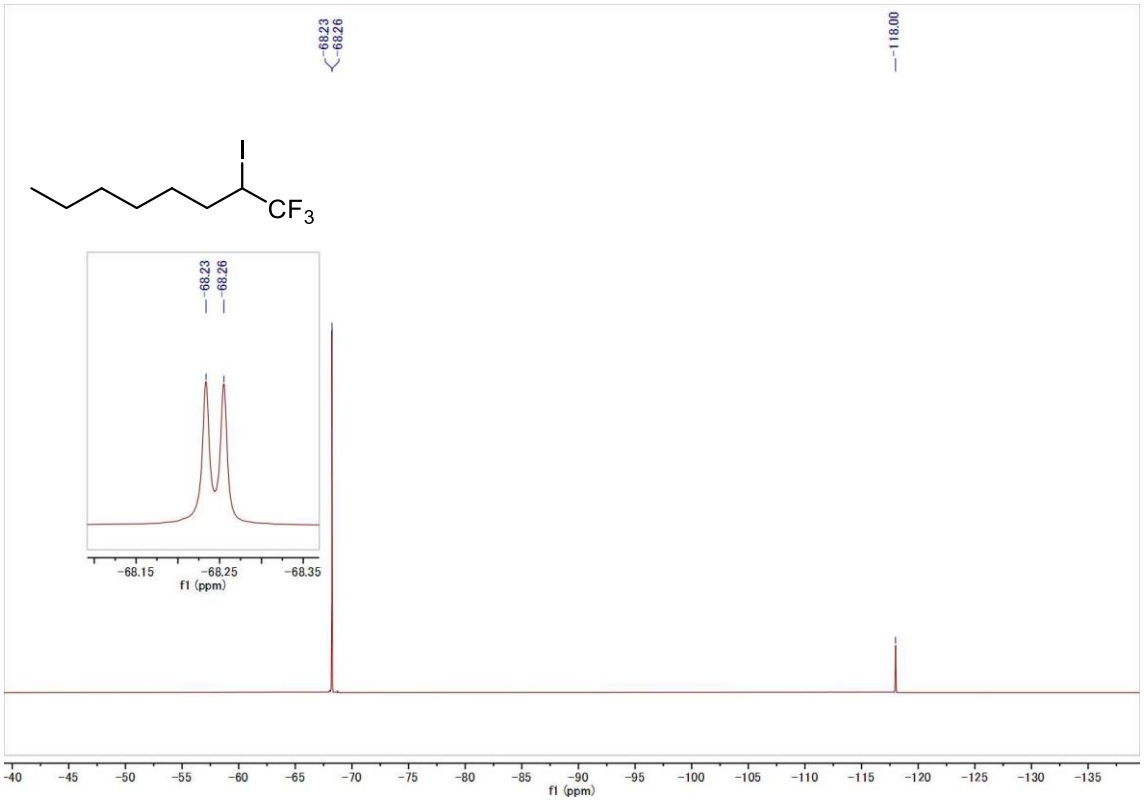
^{1}H NMR (400 MHz, $CDCl_3$) of 1a



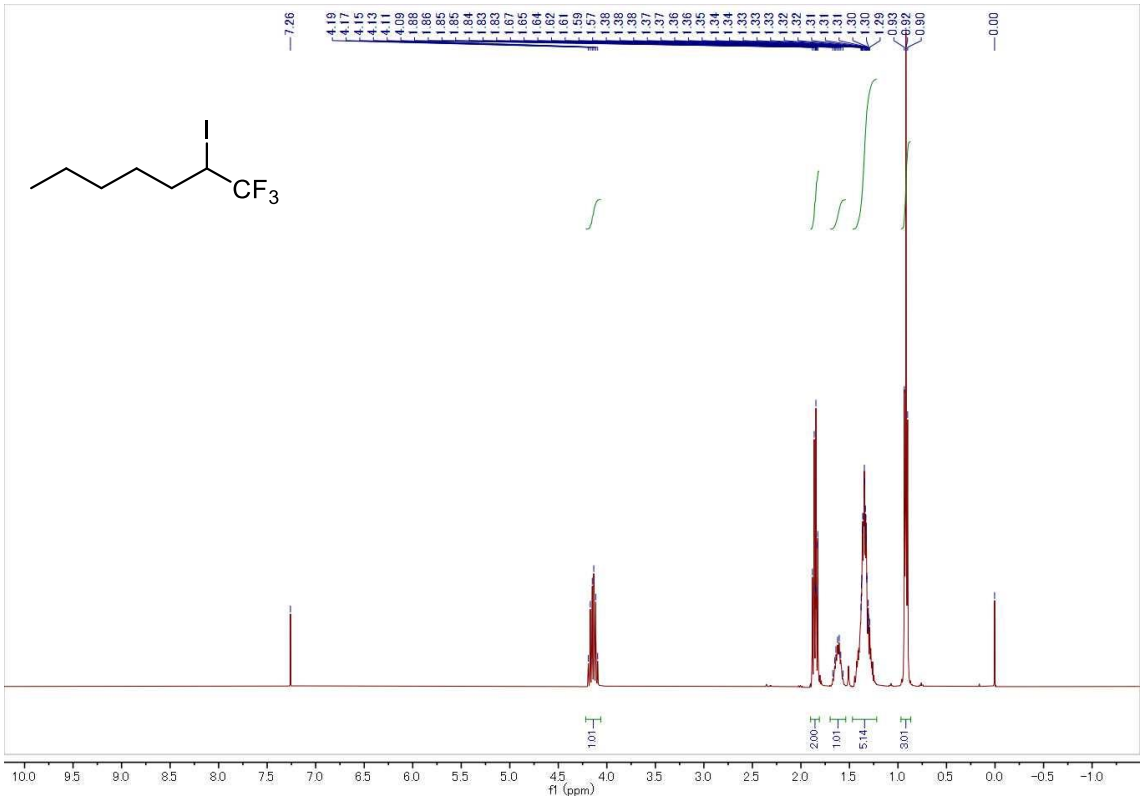
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of 1a



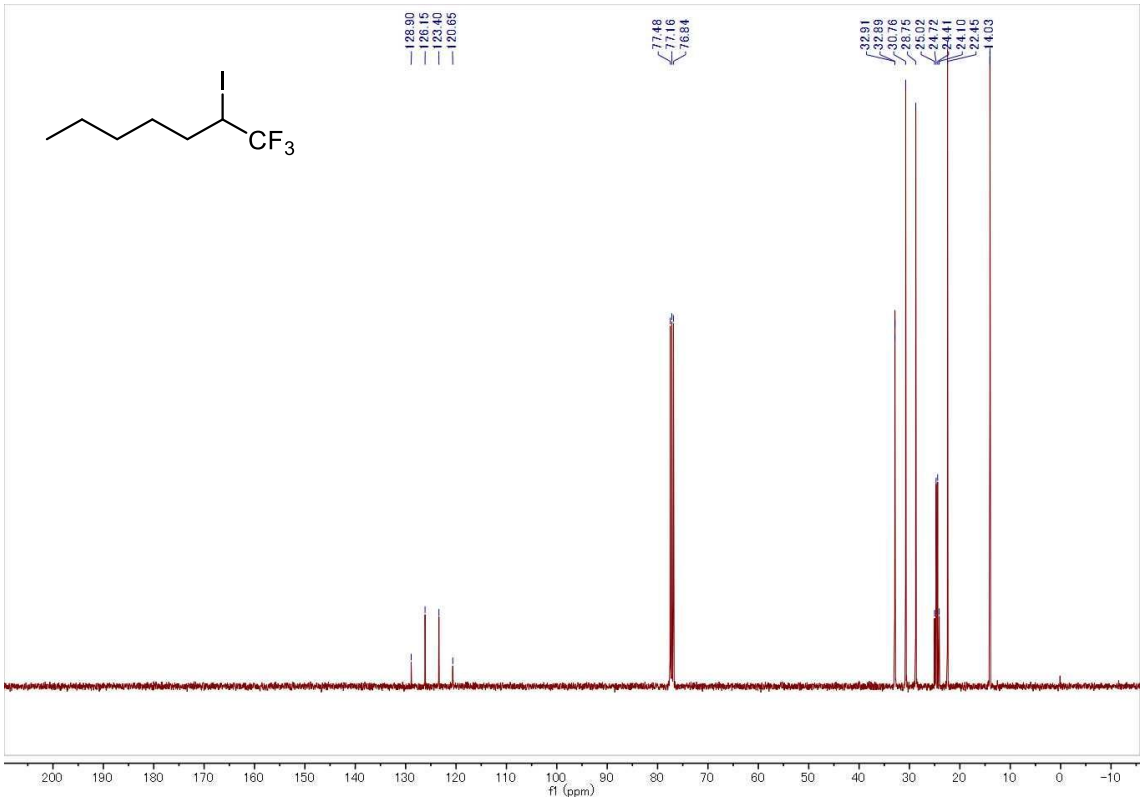
^{19}F NMR (376 MHz, $CDCl_3$) of 1a



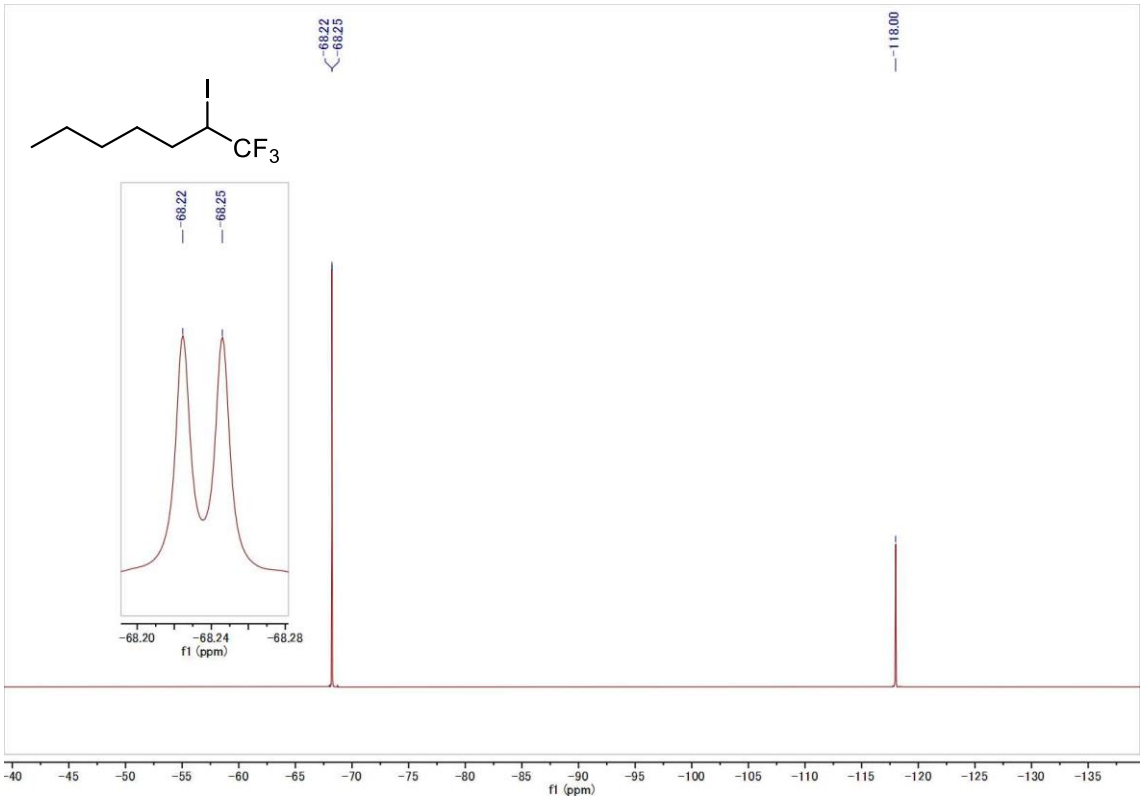
^{1}H NMR (400 MHz, $CDCl_3$) of 1b



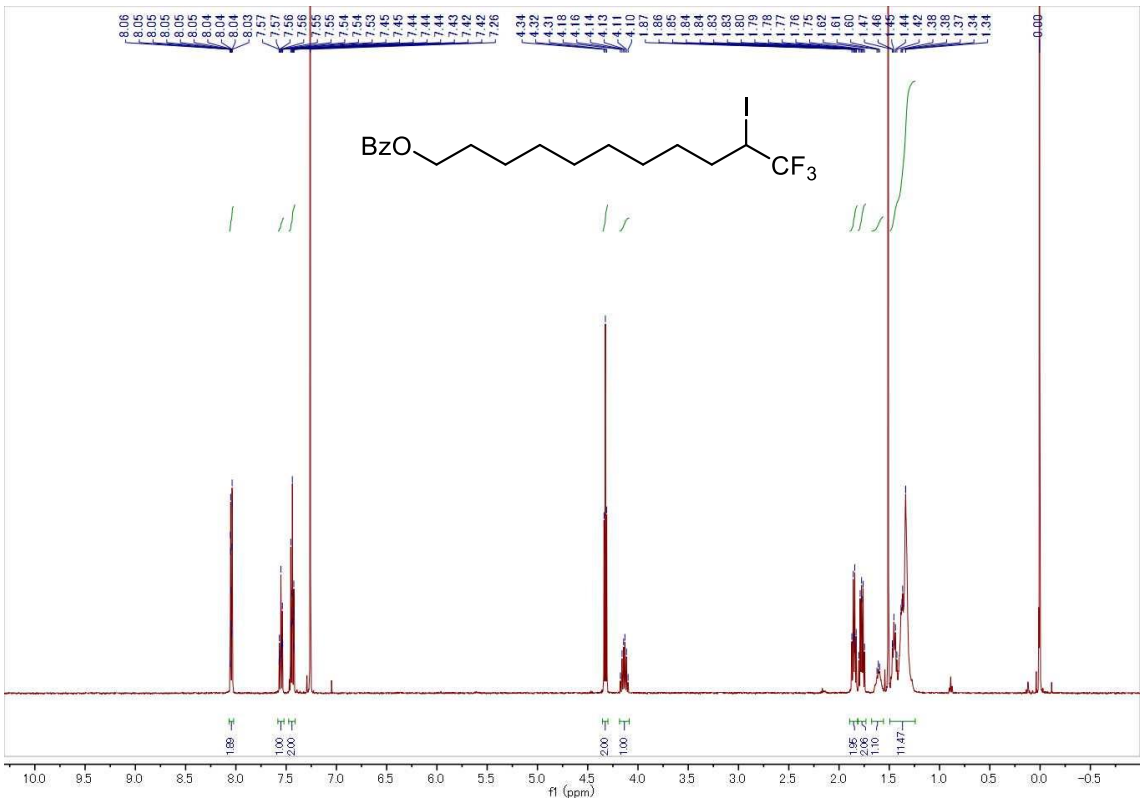
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 1b



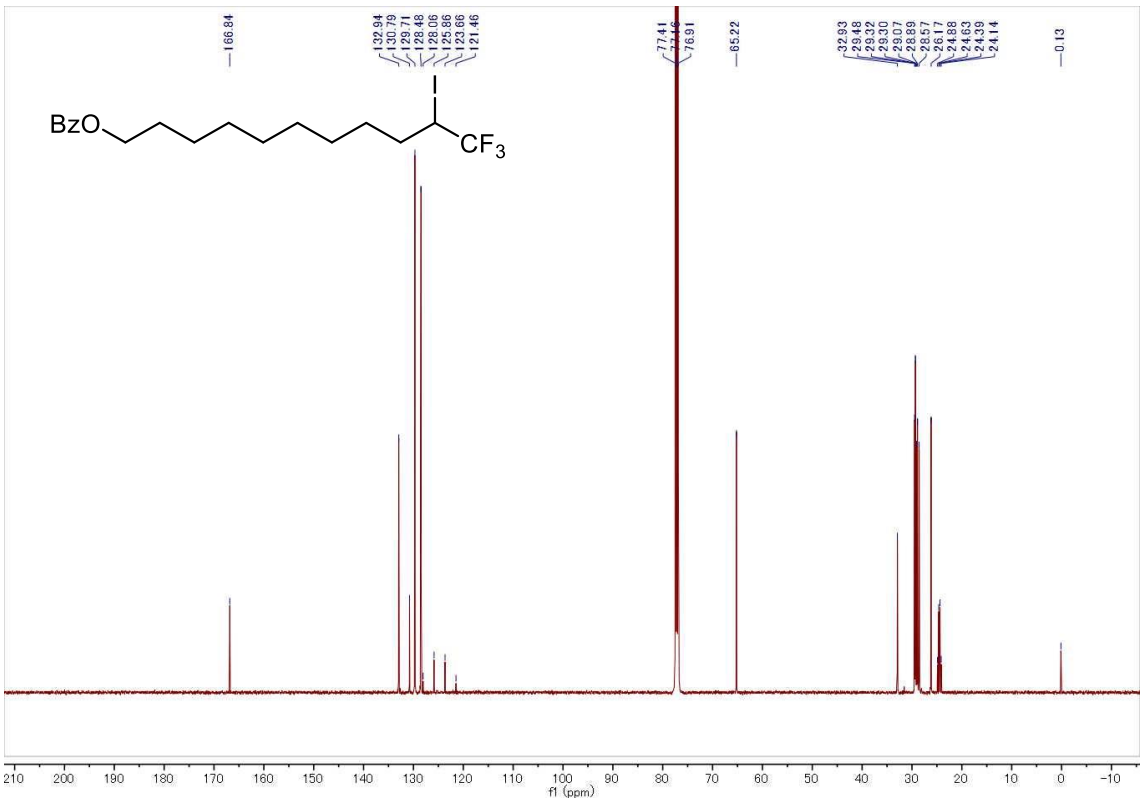
^{19}F NMR (376 MHz, $CDCl_3$) of 1b



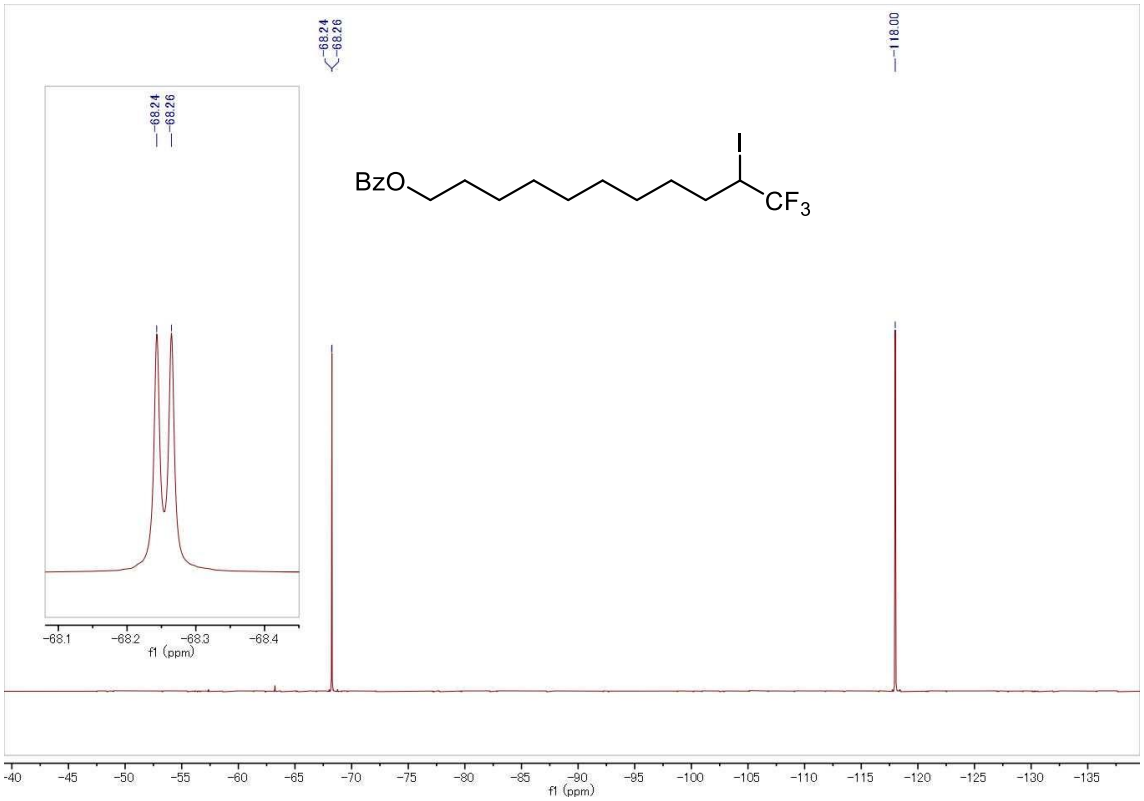
^{1}H NMR (500 MHz, $CDCl_3$) of 1c



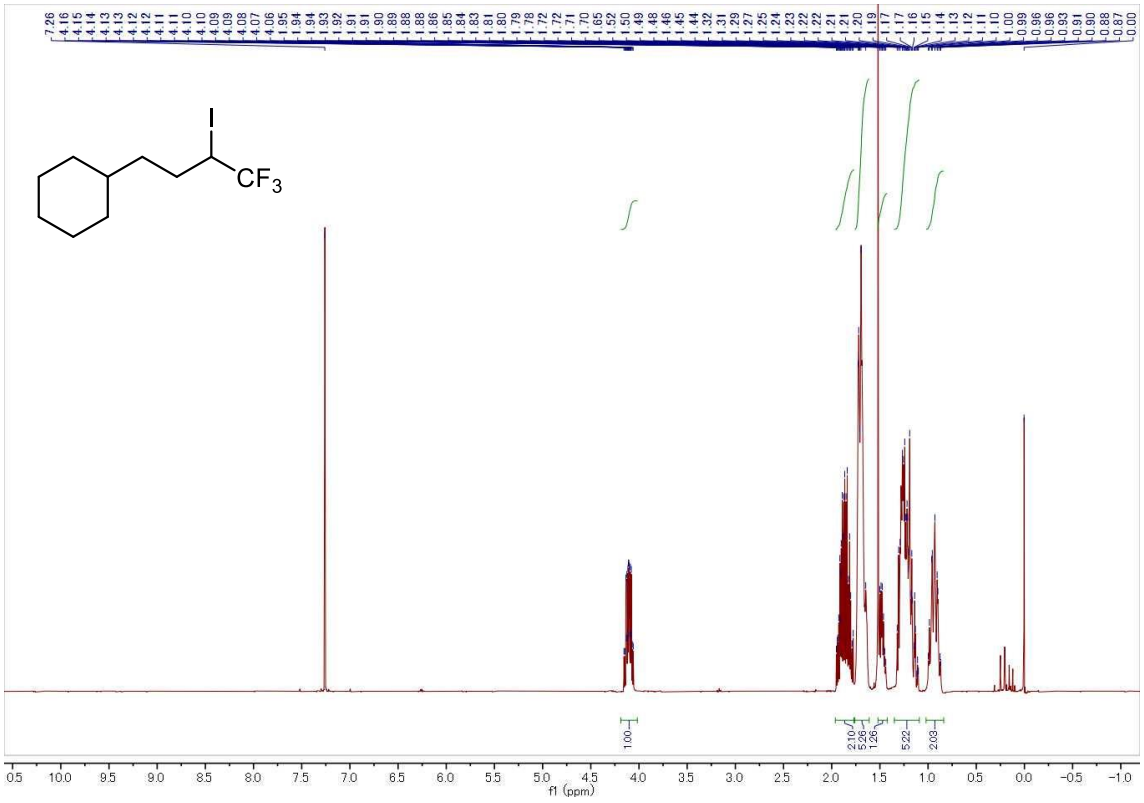
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of 1c



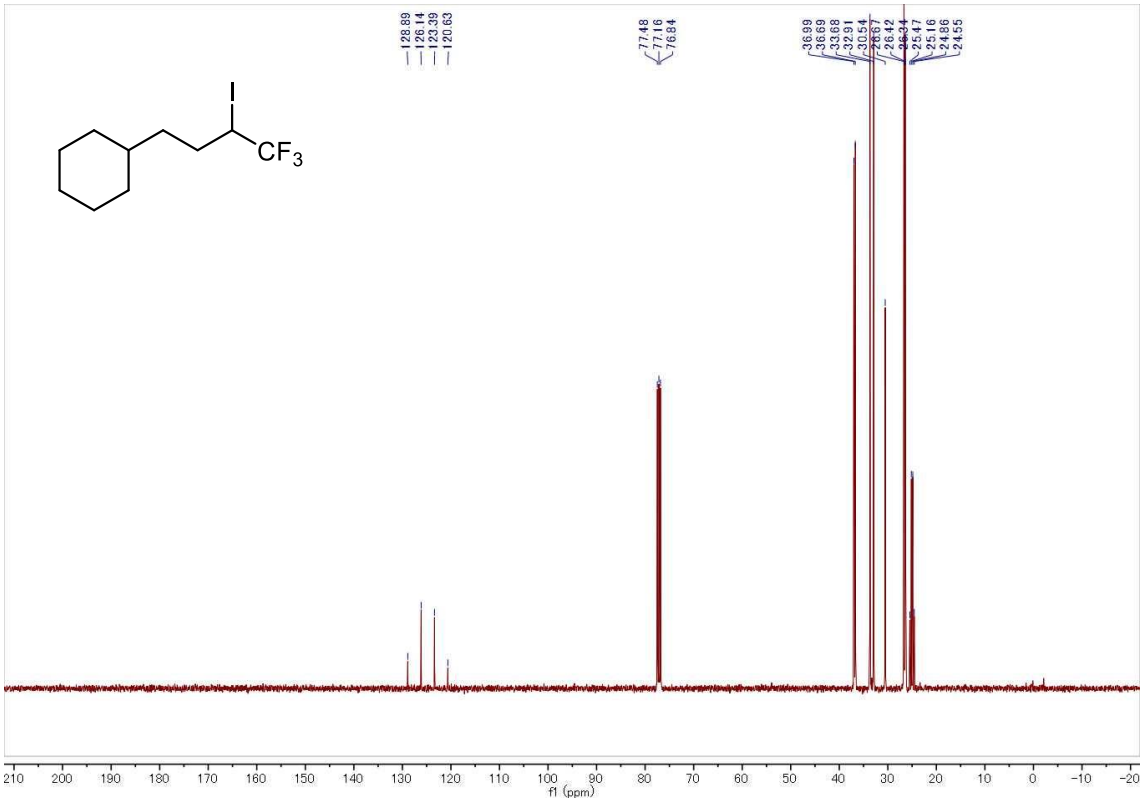
^{19}F NMR (376 MHz, $CDCl_3$) of 1c



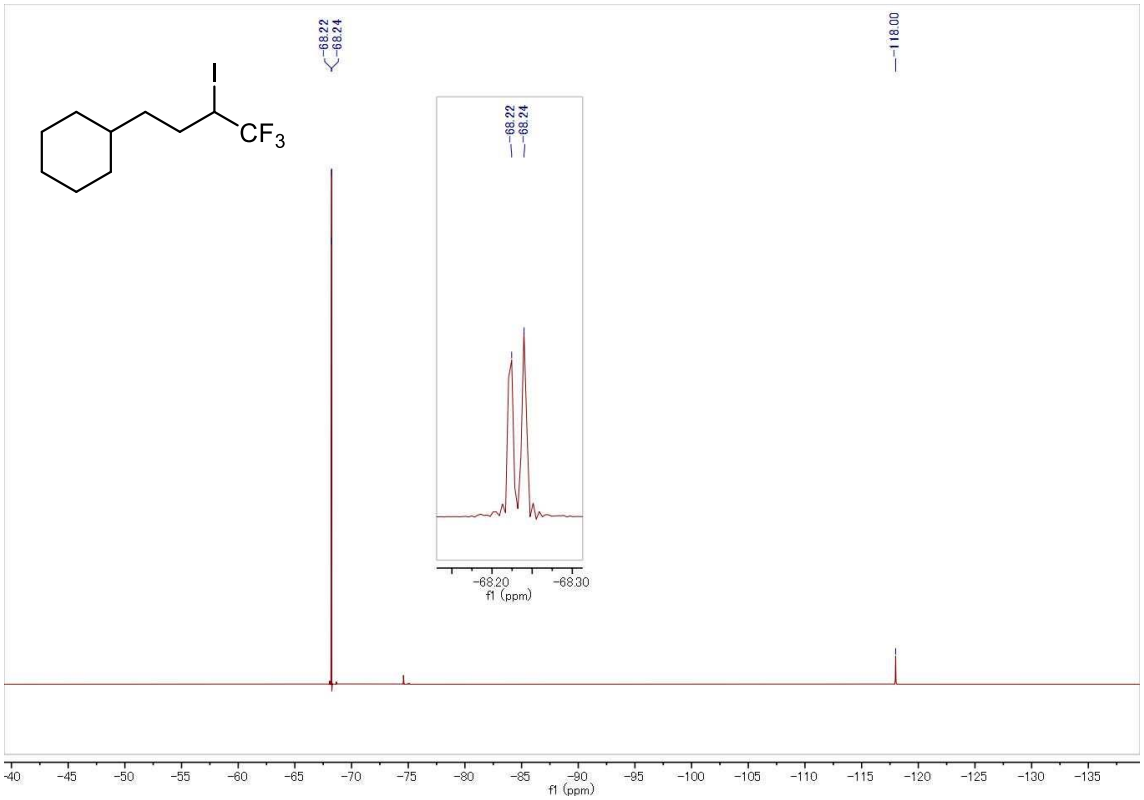
^{1}H NMR (400 MHz, $CDCl_3$) of 1d



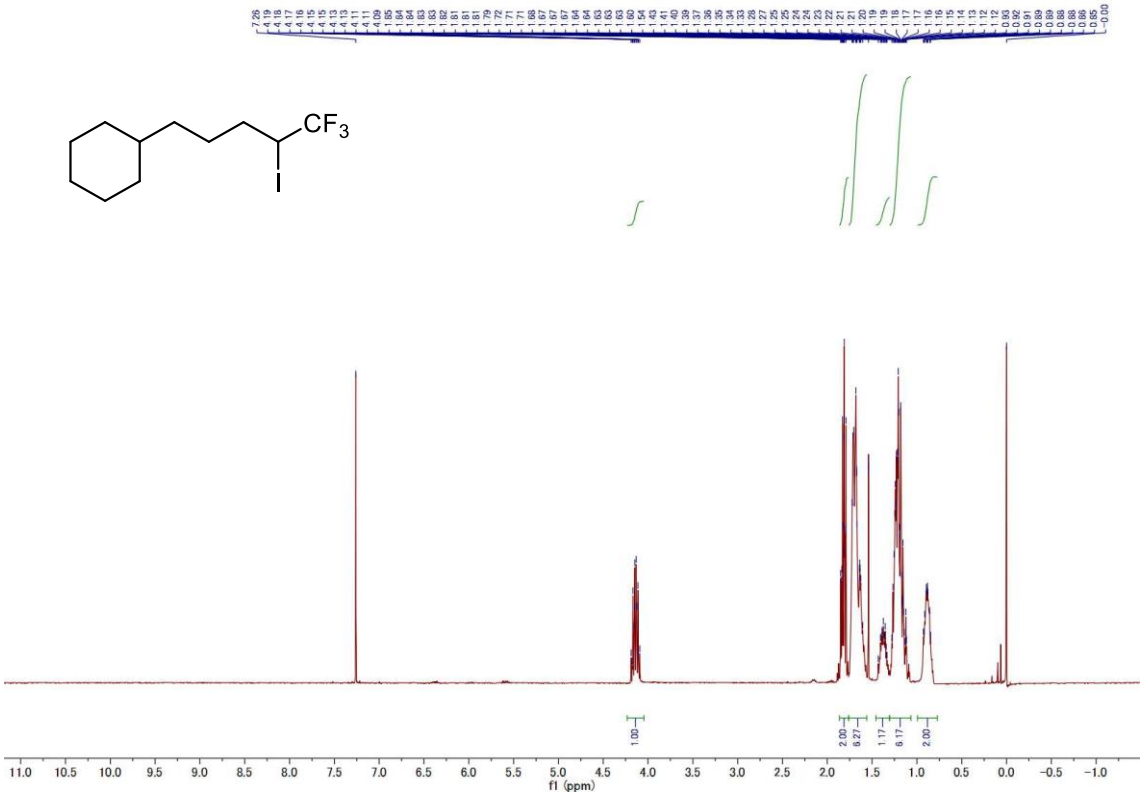
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 1d



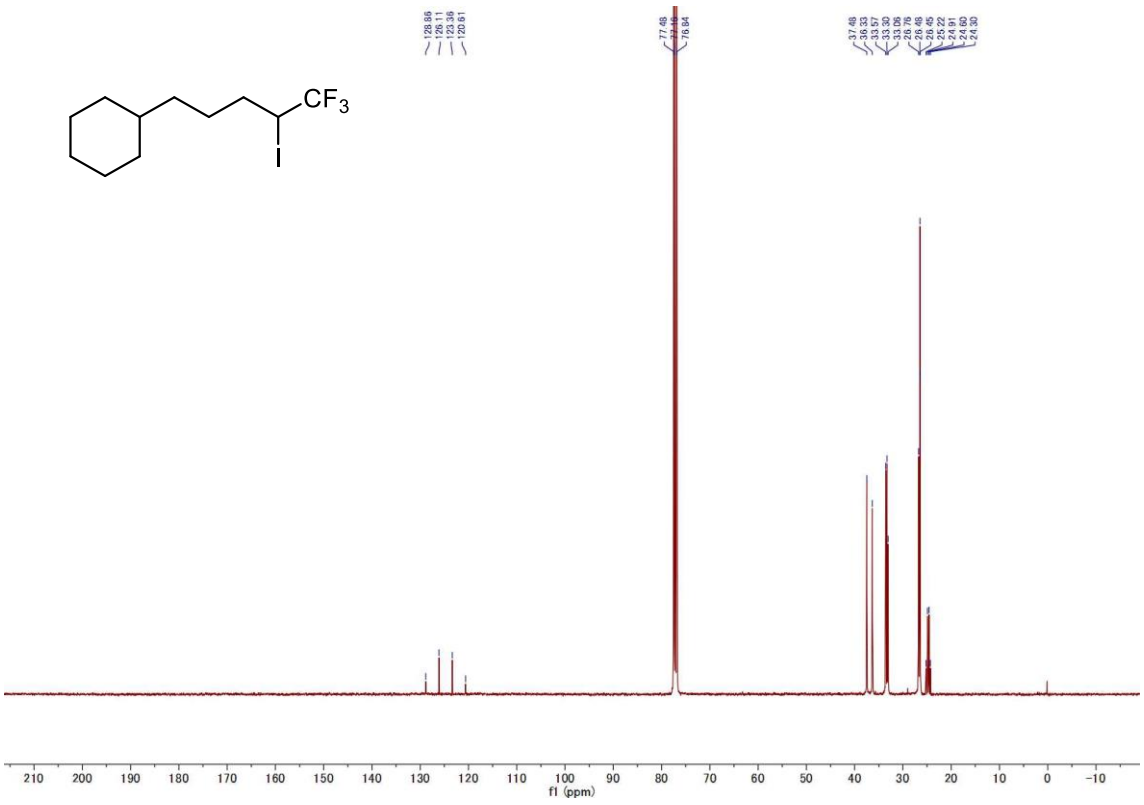
^{19}F NMR (471 MHz, $CDCl_3$) of 1d



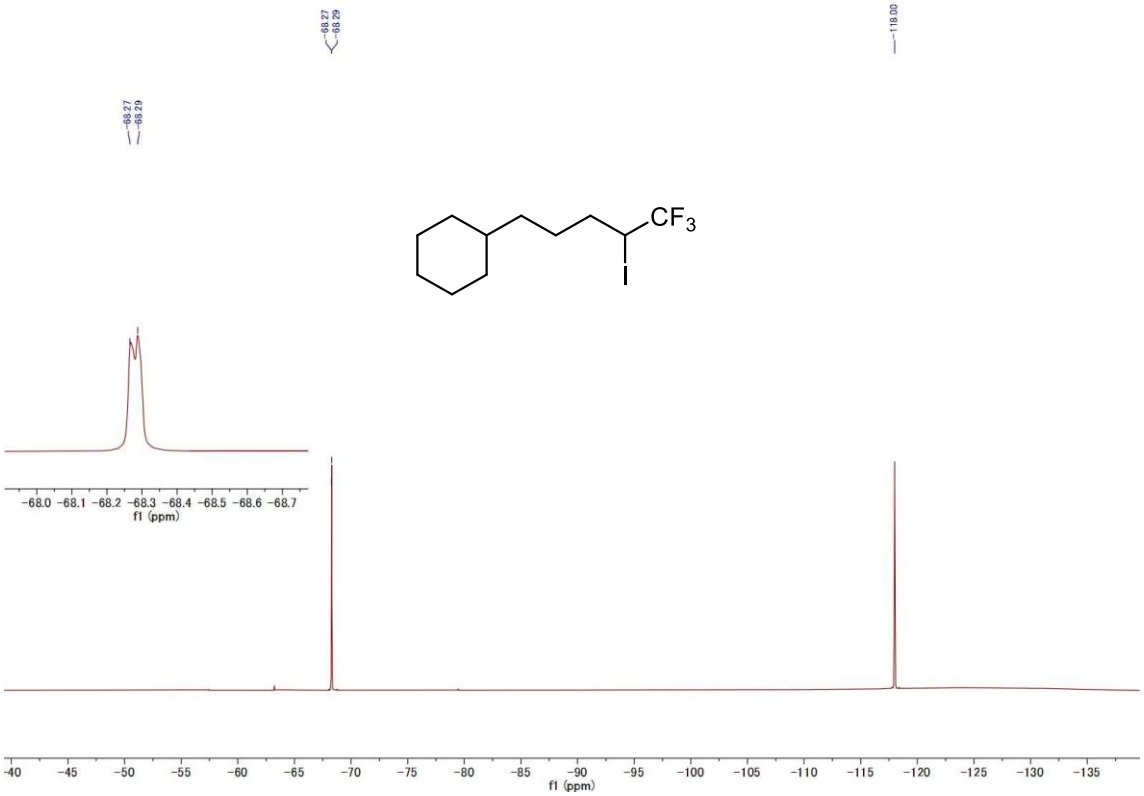
^{1}H NMR (400 MHz, $CDCl_3$) of 1e



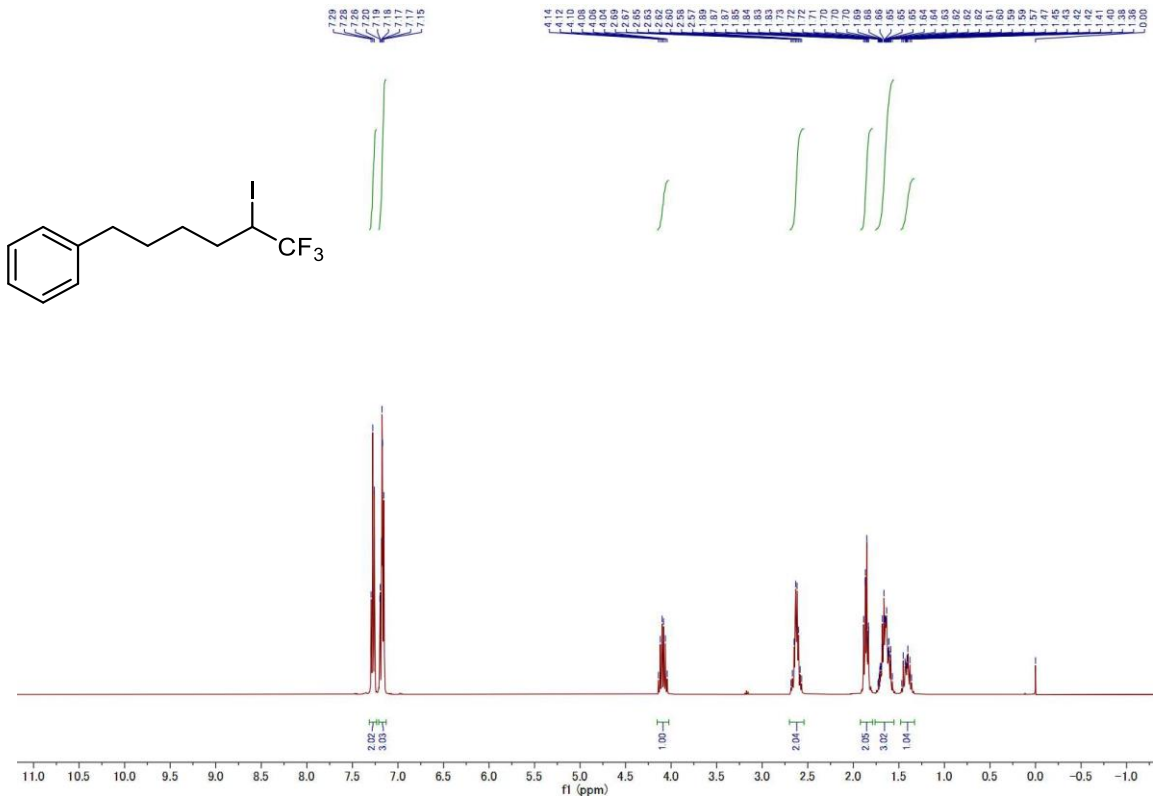
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of 1e



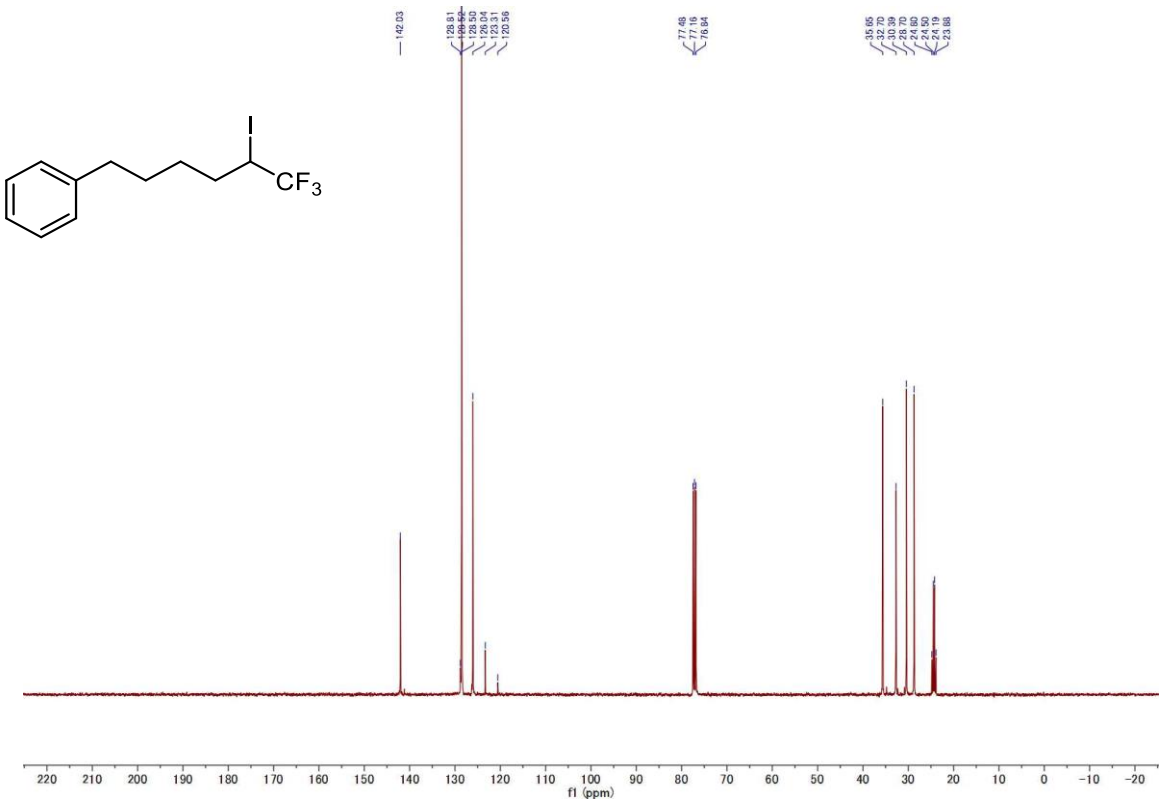
^{19}F NMR (376 MHz, $CDCl_3$) of 1e



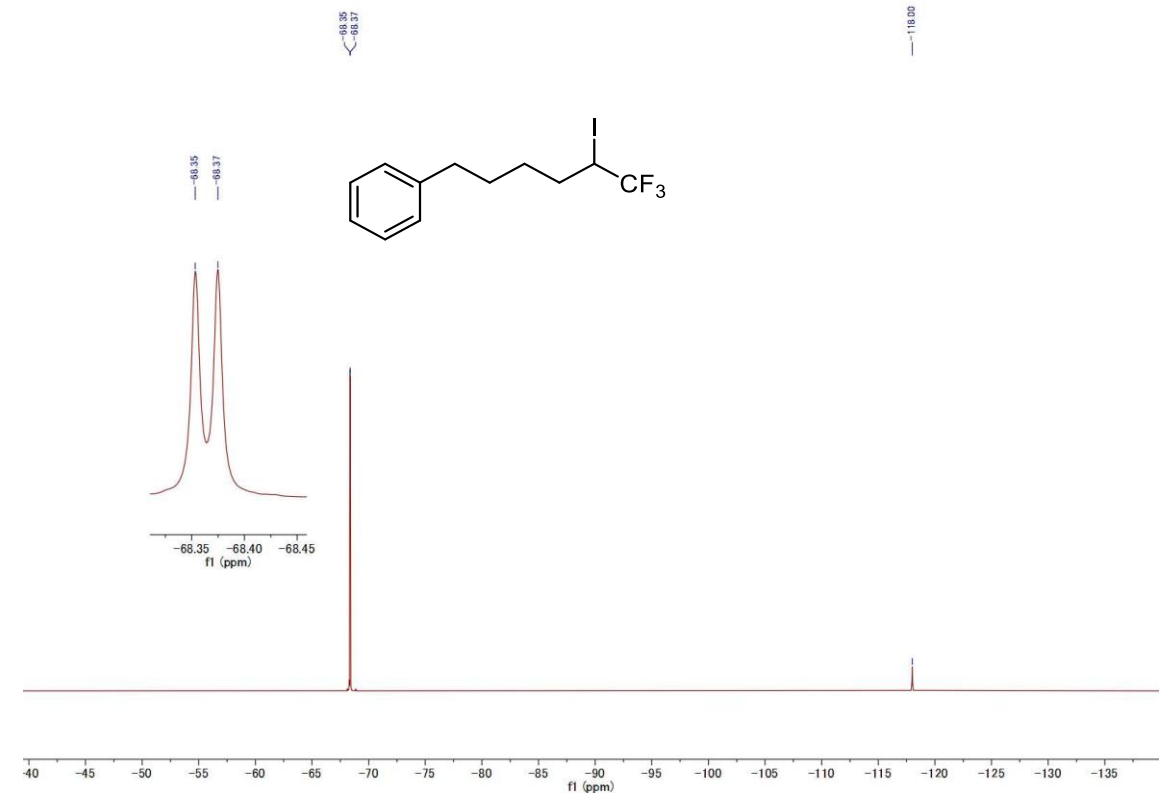
^{1}H NMR (400 MHz, $CDCl_3$) of 1f



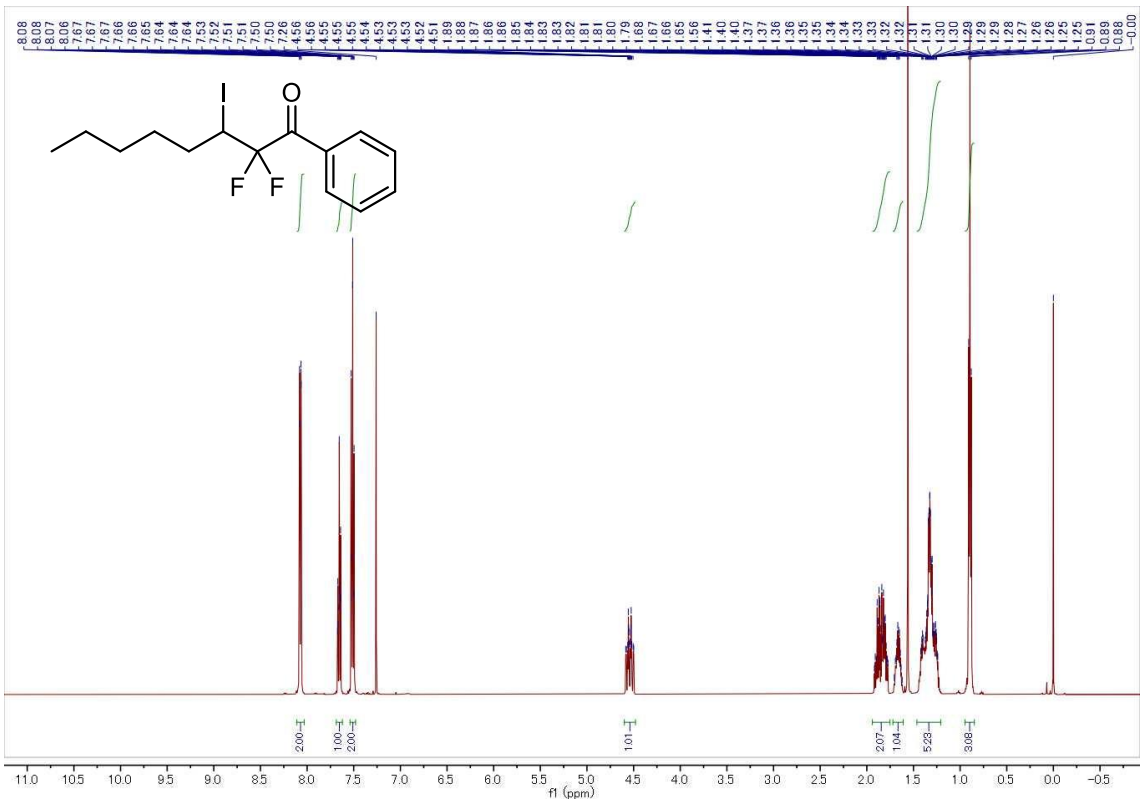
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 1f



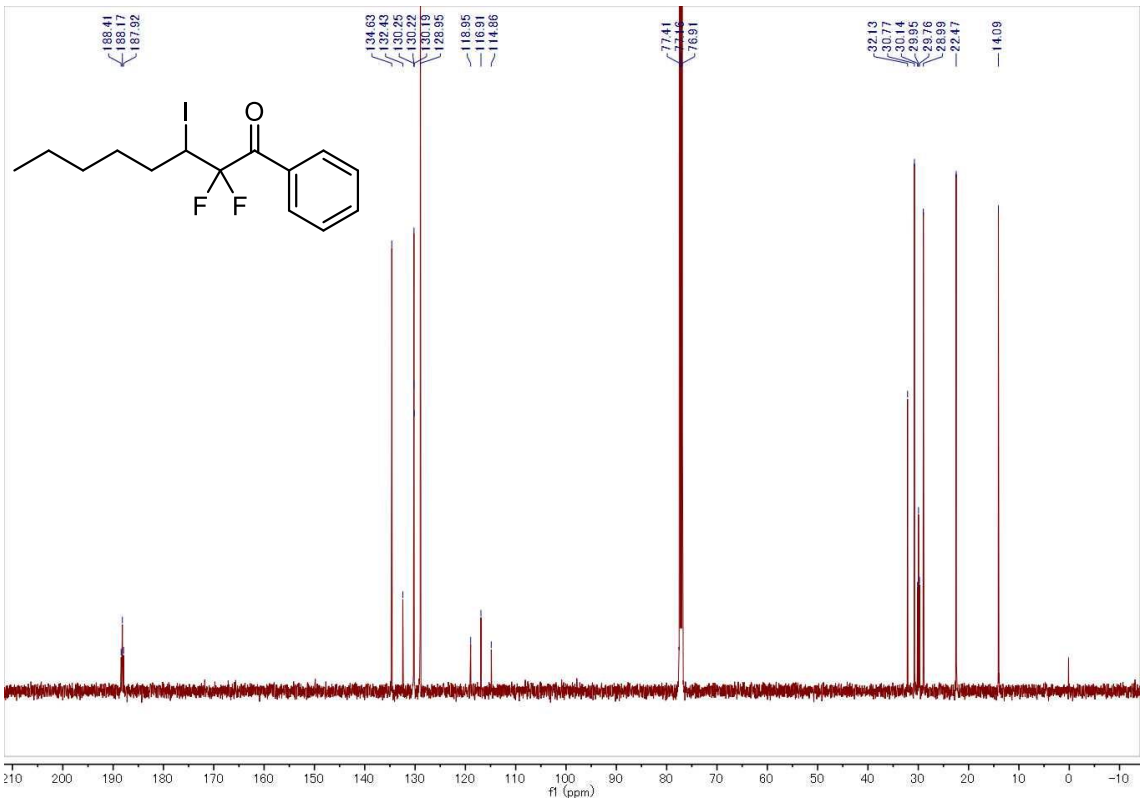
^{19}F NMR (376 MHz, $CDCl_3$) of 1f



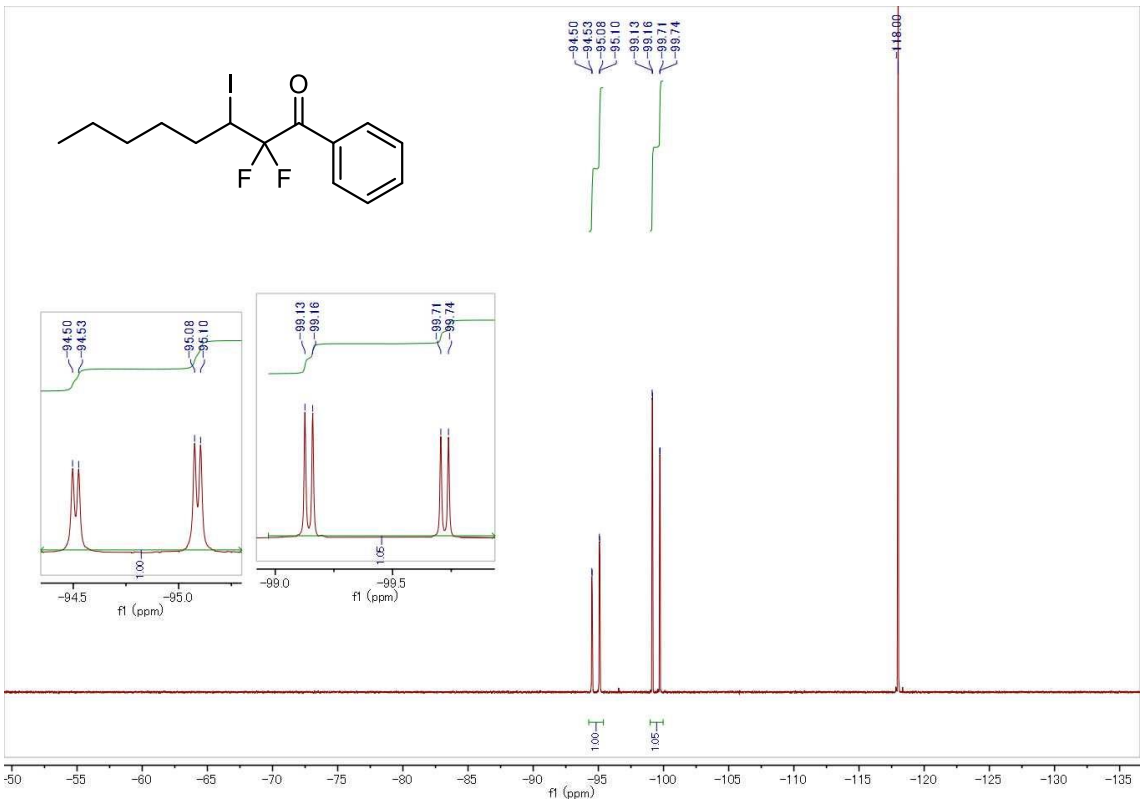
^{1}H NMR (500 MHz, $CDCl_3$) of 1g



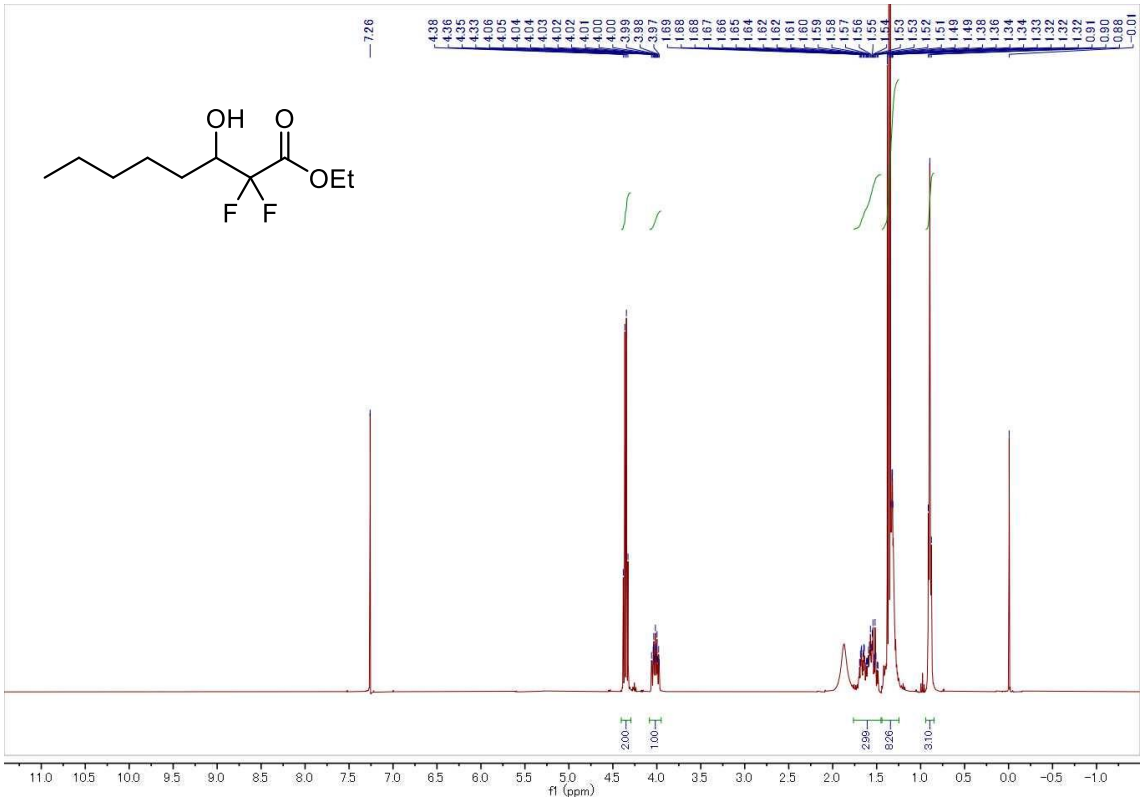
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of 1g



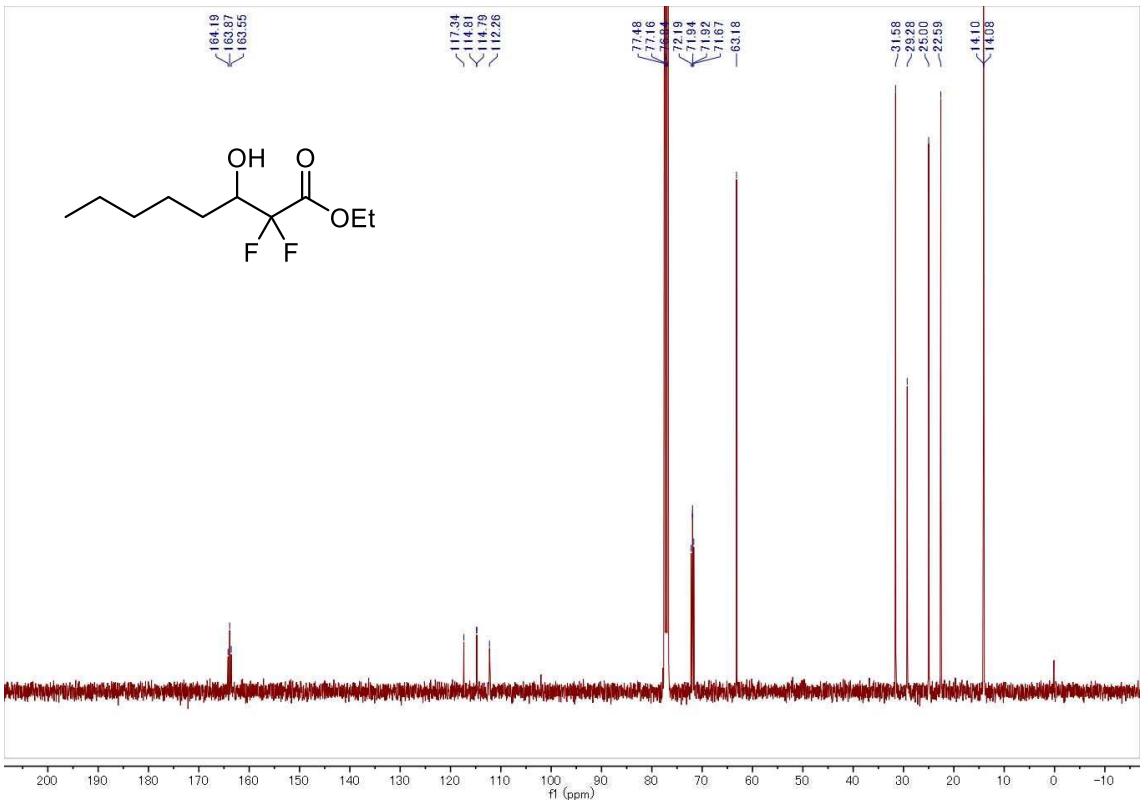
^{19}F NMR (471 MHz, $CDCl_3$) of 1g



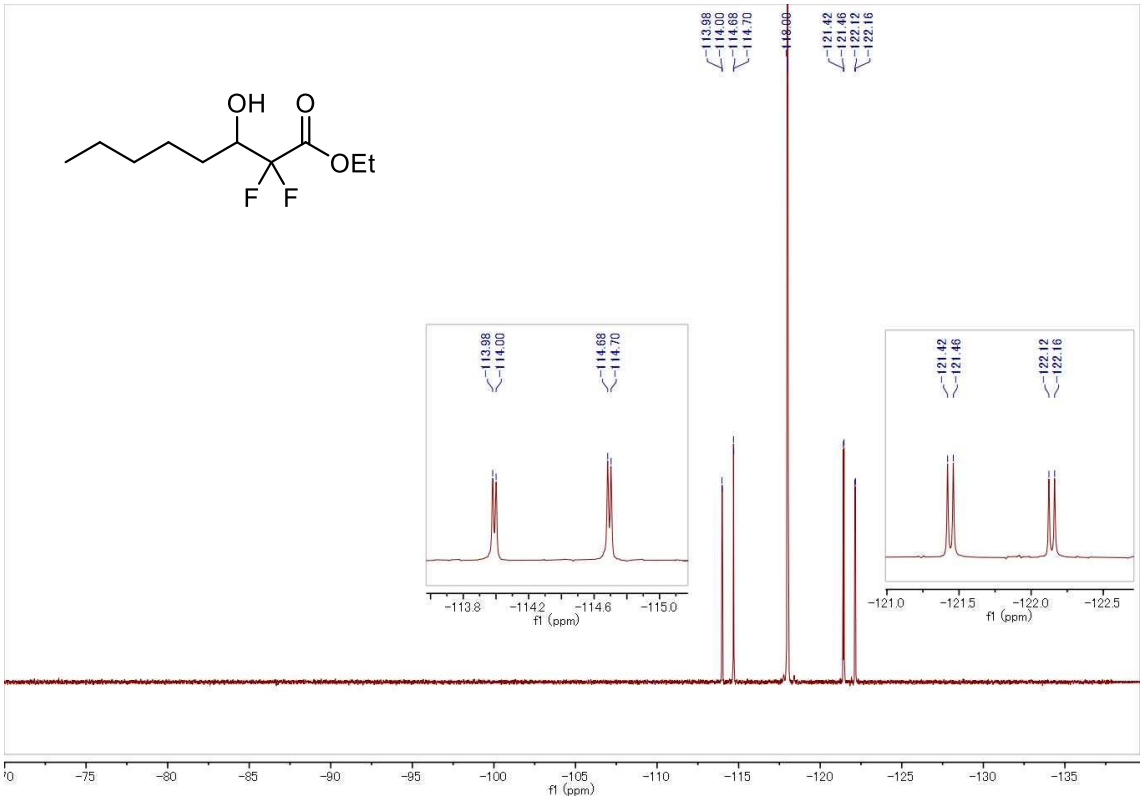
^{1}H NMR (400 MHz, $CDCl_3$) of S4



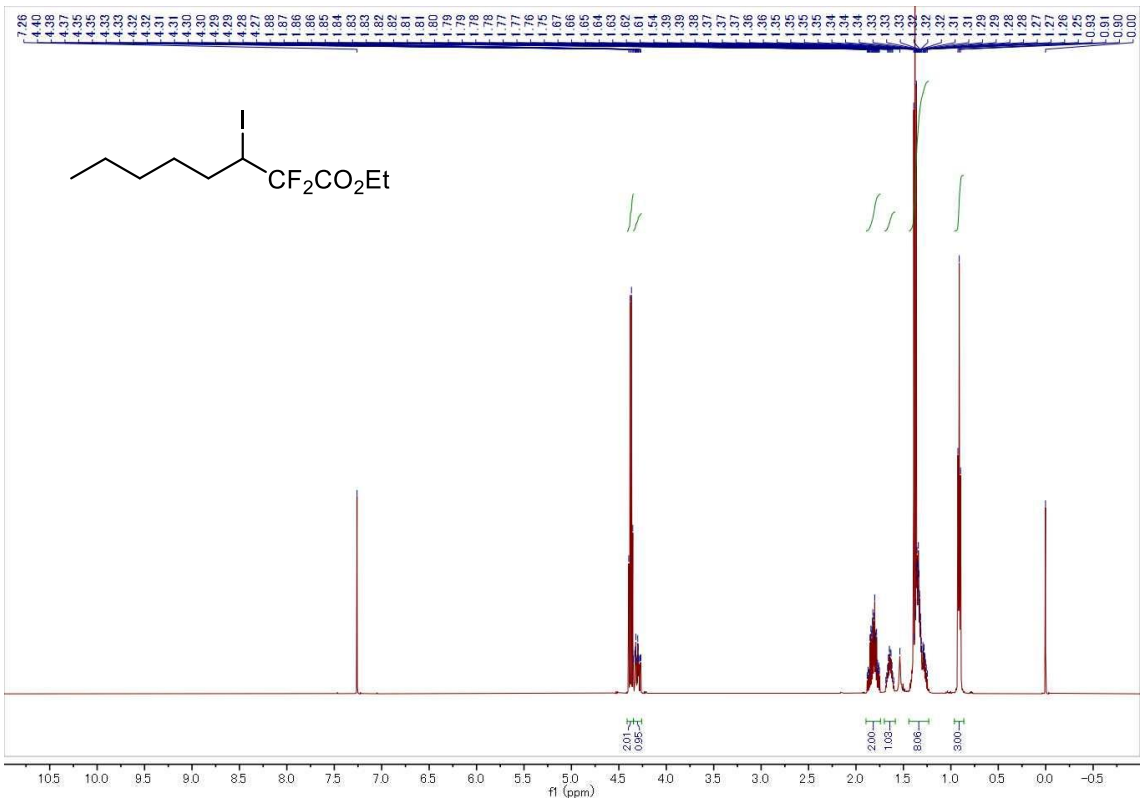
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of S4



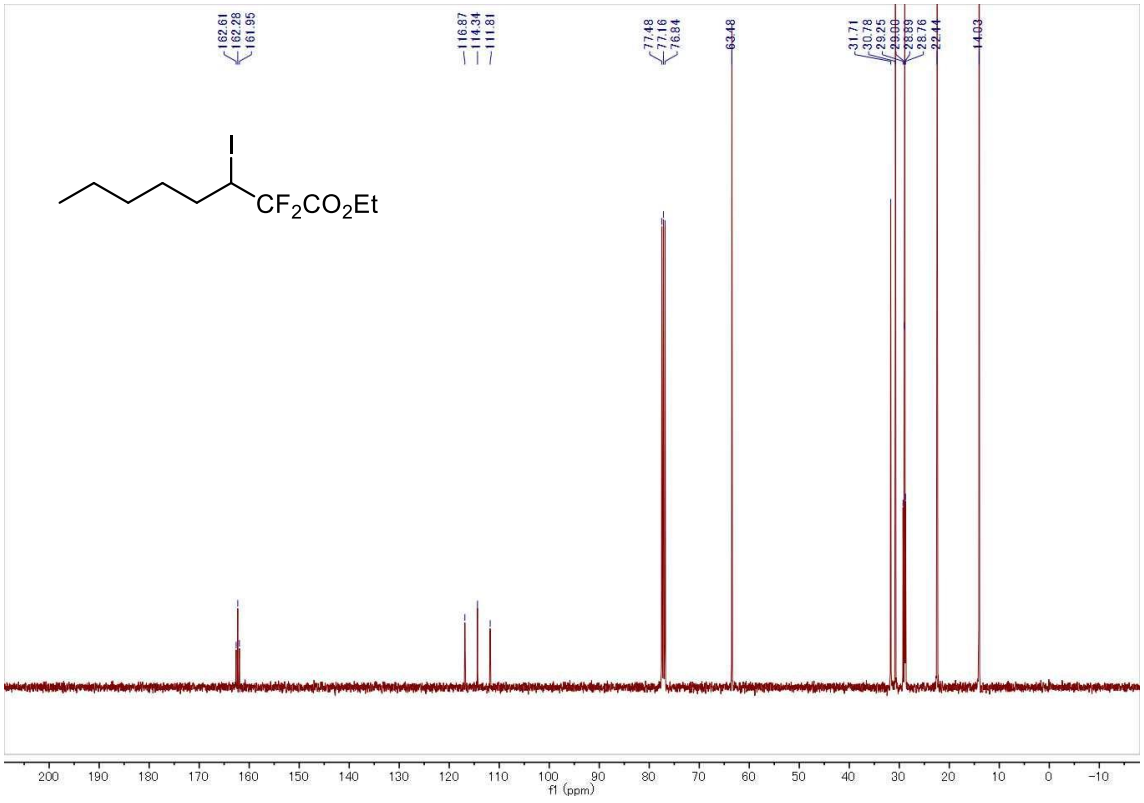
^{19}F NMR (376 MHz, $CDCl_3$) of S4



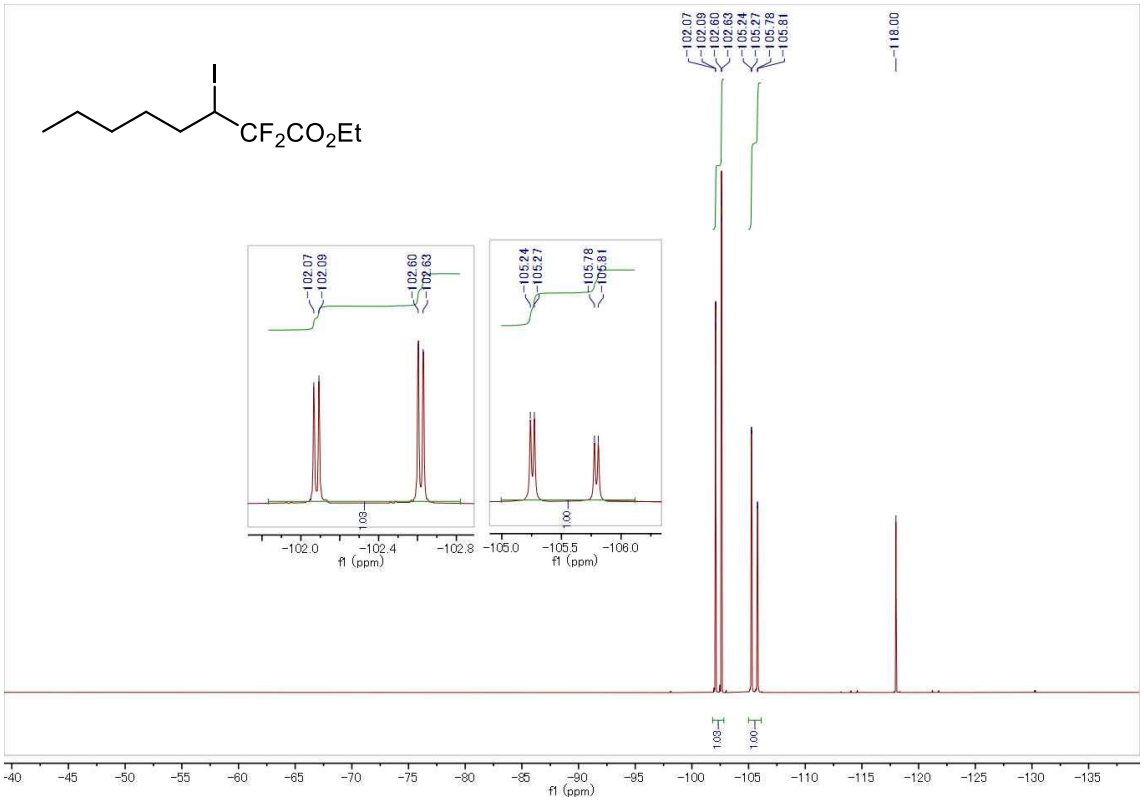
^{1}H NMR (500 MHz, $CDCl_3$) of 1h



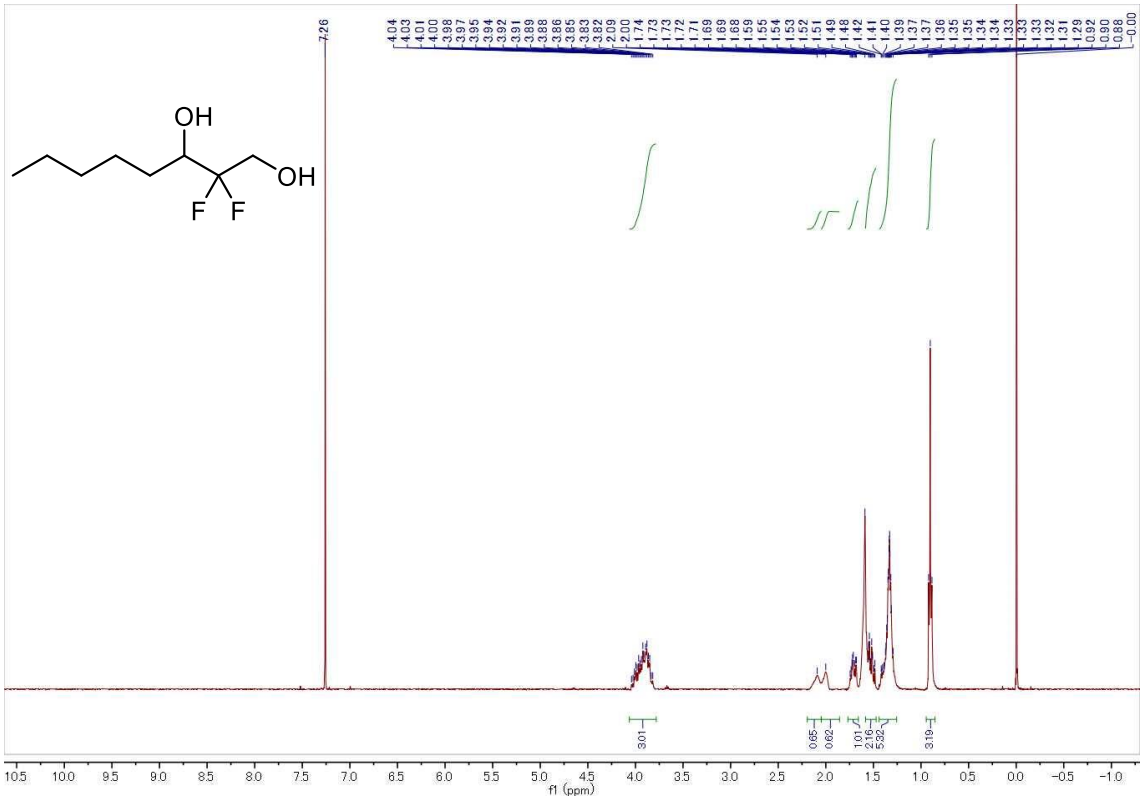
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of 1h



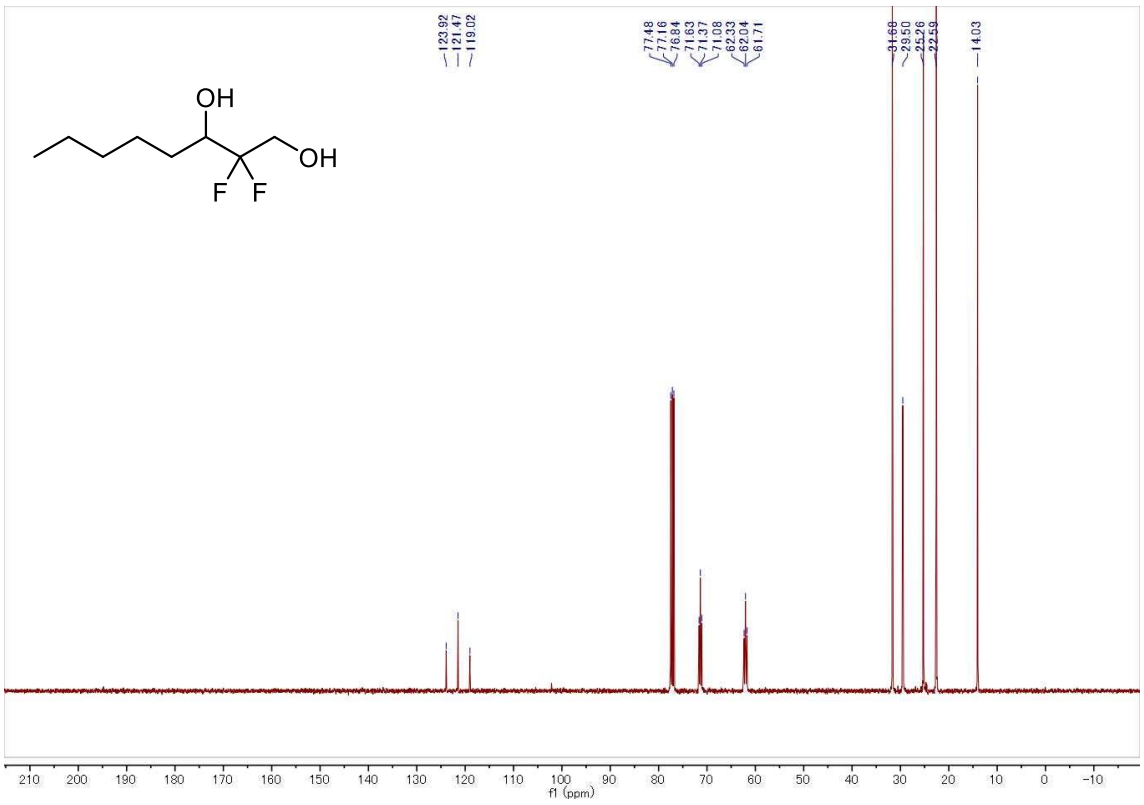
^{19}F NMR (471 MHz, $CDCl_3$) of 1h



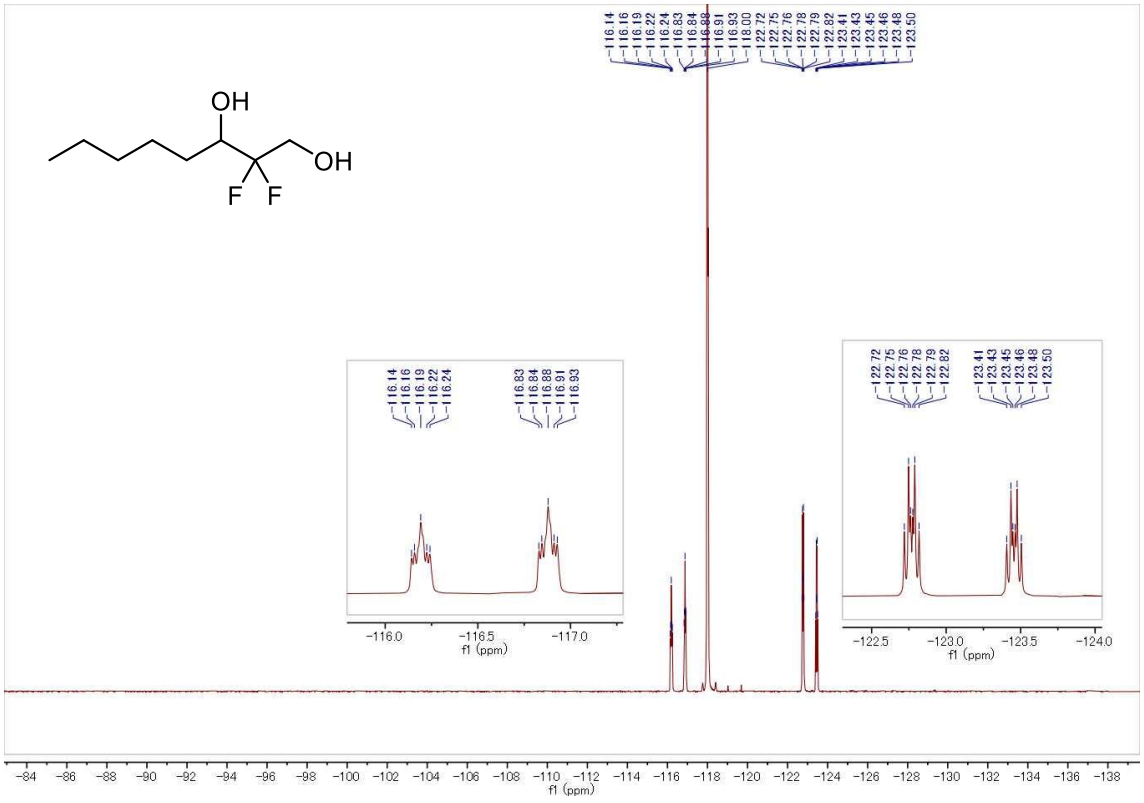
^{1}H NMR (400 MHz, $CDCl_3$) of S5



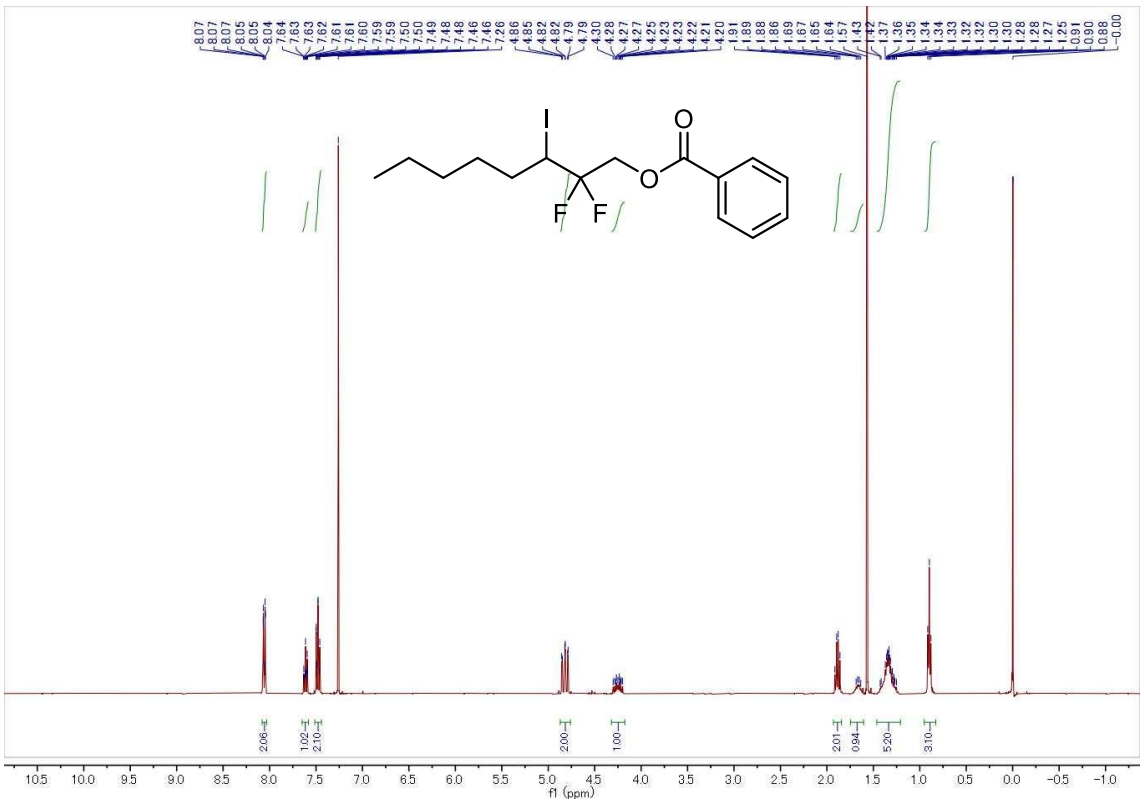
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of S5



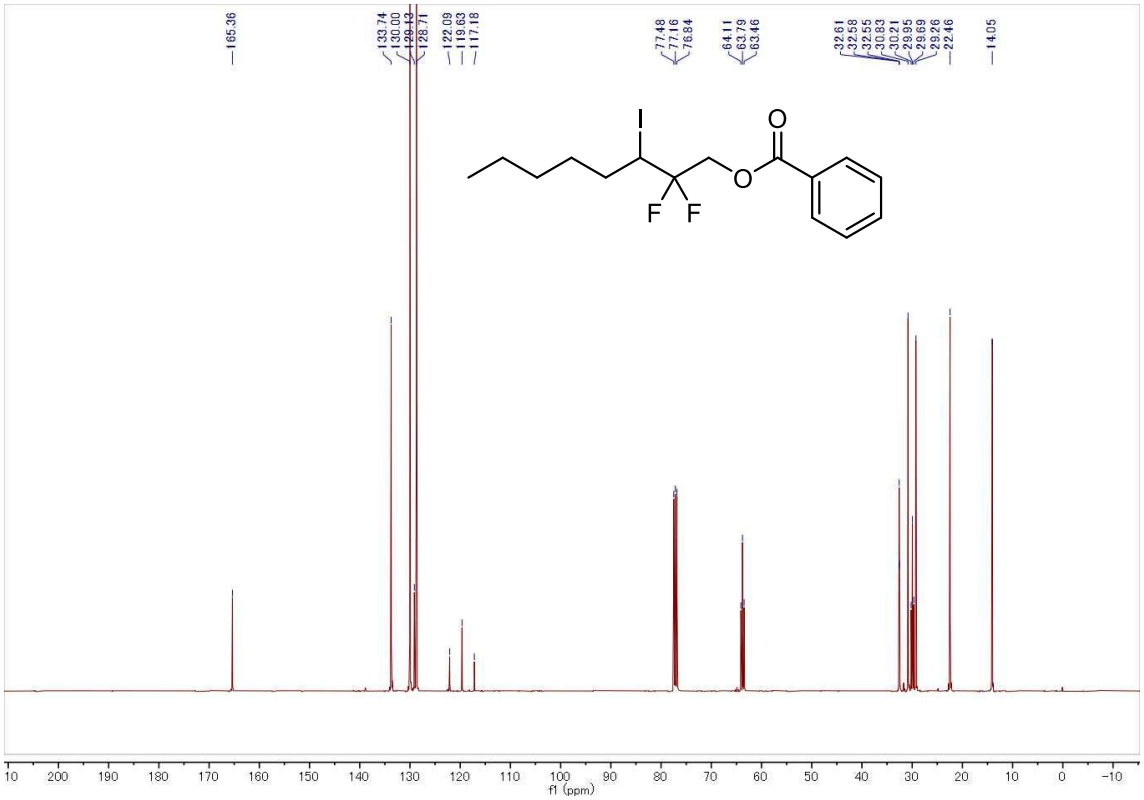
^{19}F NMR (376 MHz, $CDCl_3$) of S5



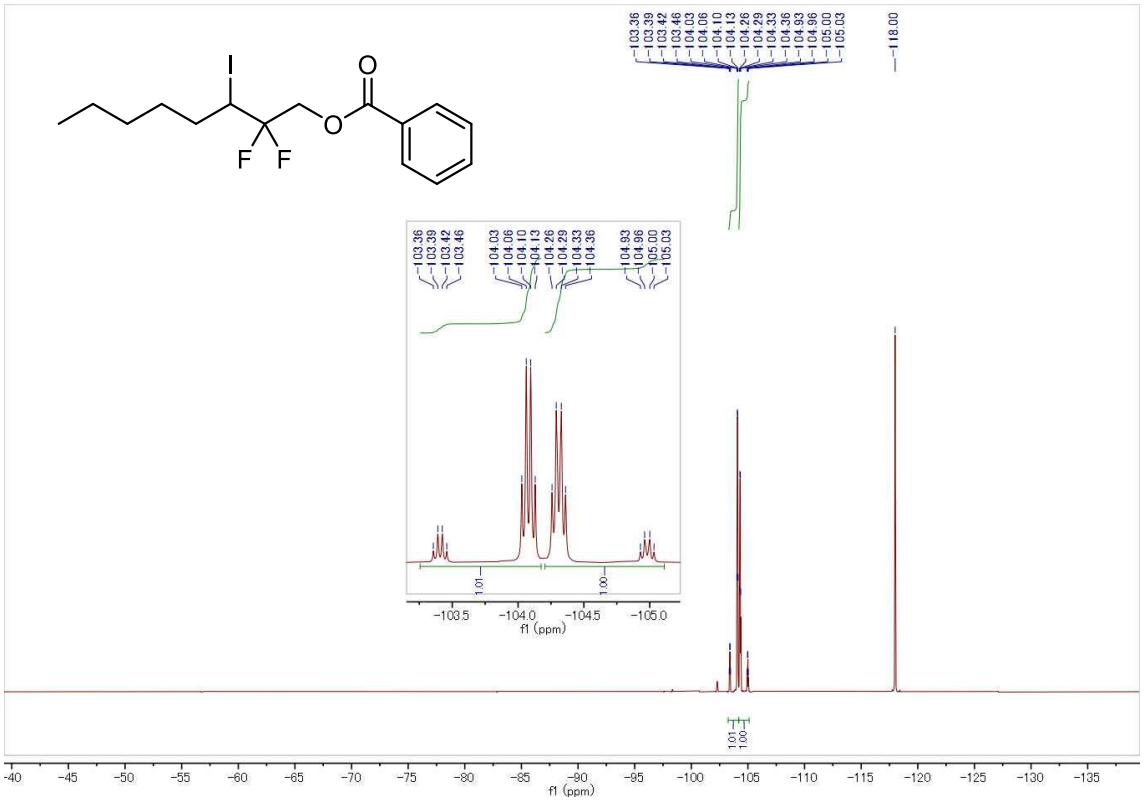
^{1}H NMR (400 MHz, $CDCl_3$) of 1i



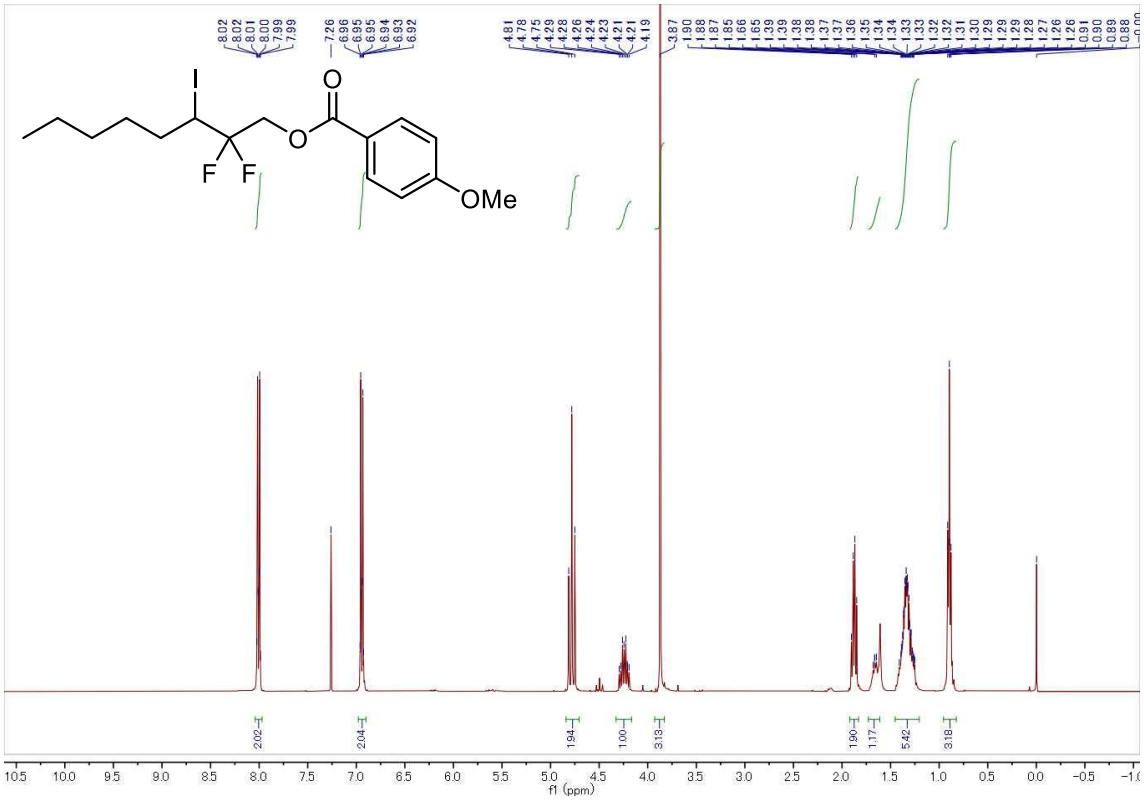
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of 1i



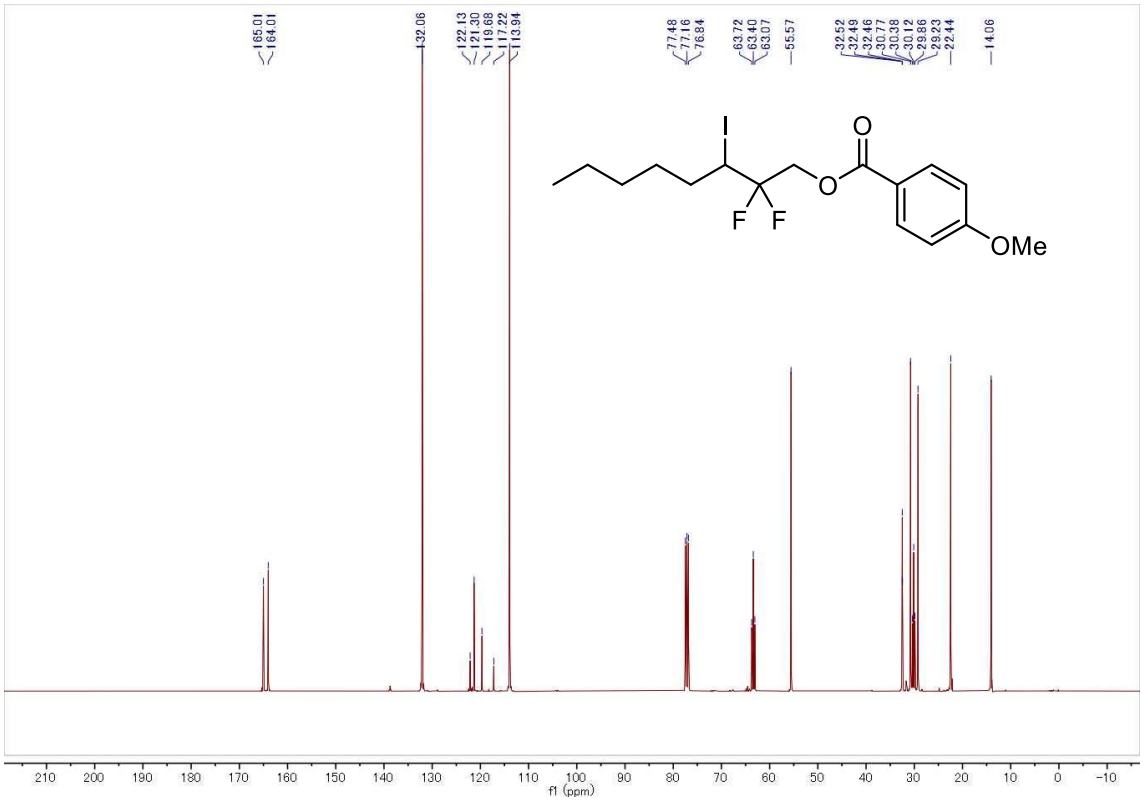
^{19}F NMR (376 MHz, $CDCl_3$) of 1i



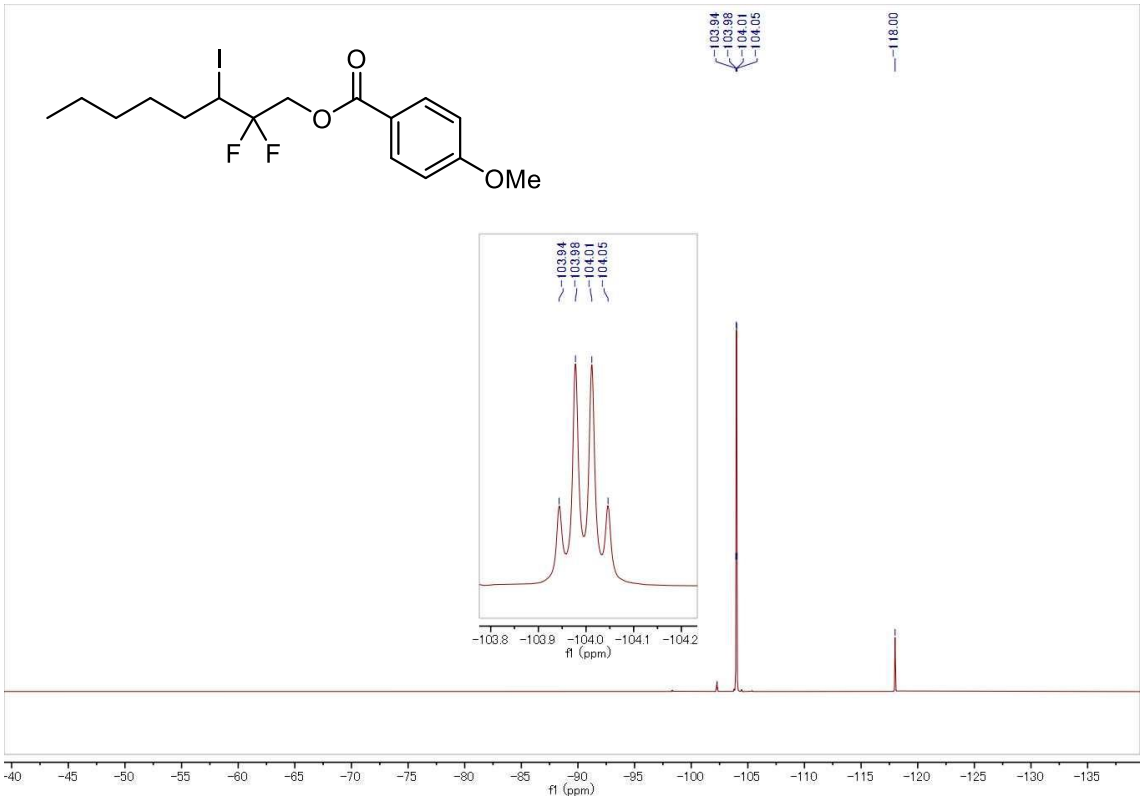
^{1}H NMR (400 MHz, $CDCl_3$) of 1j



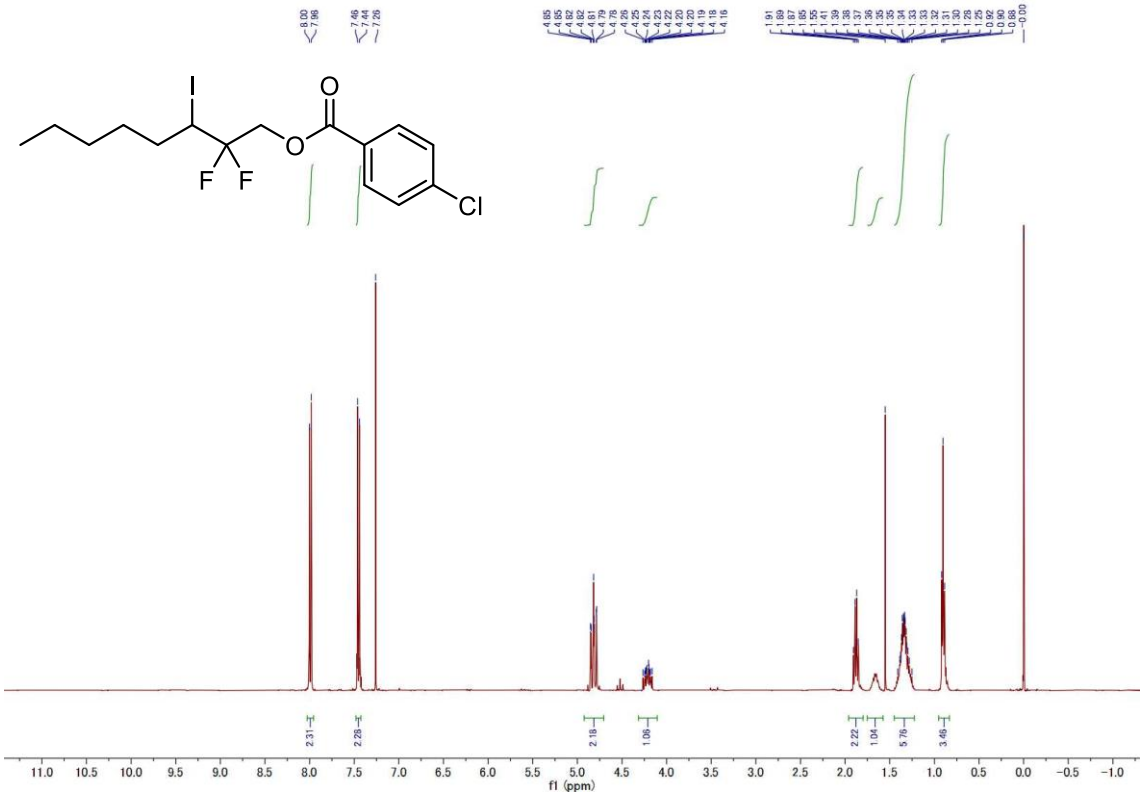
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 1j



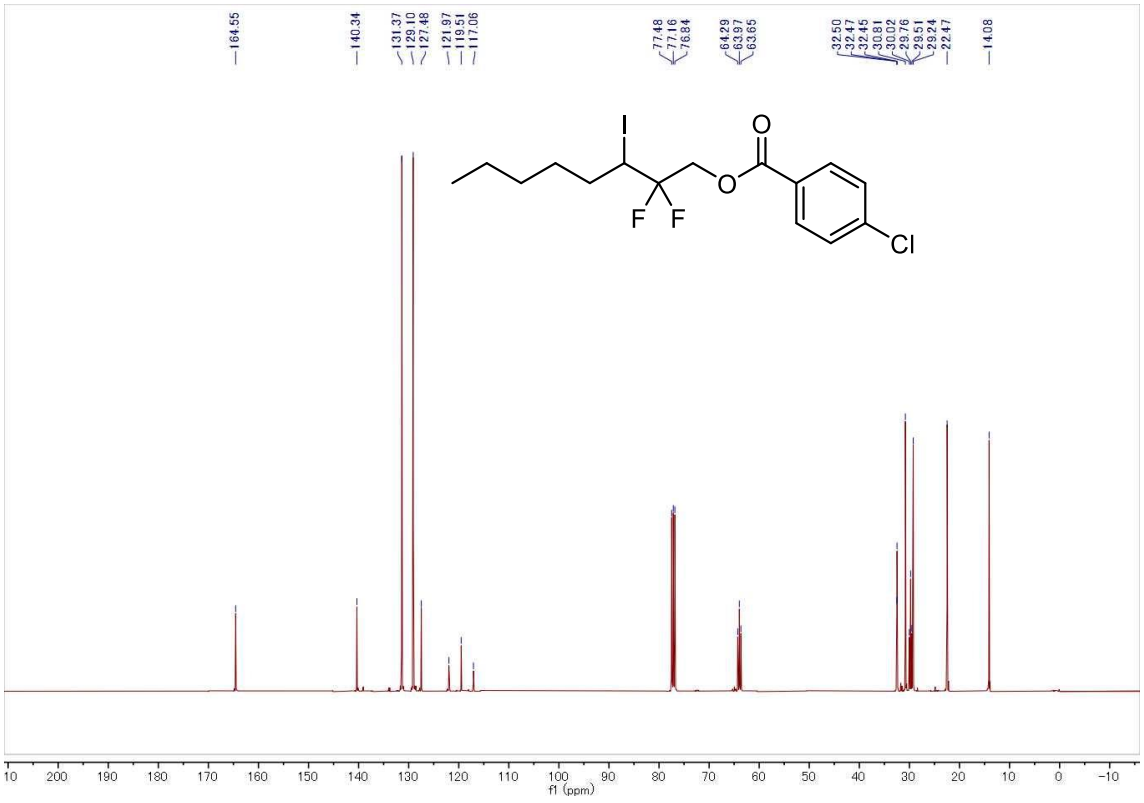
^{19}F NMR (376 MHz, $CDCl_3$) of 1j



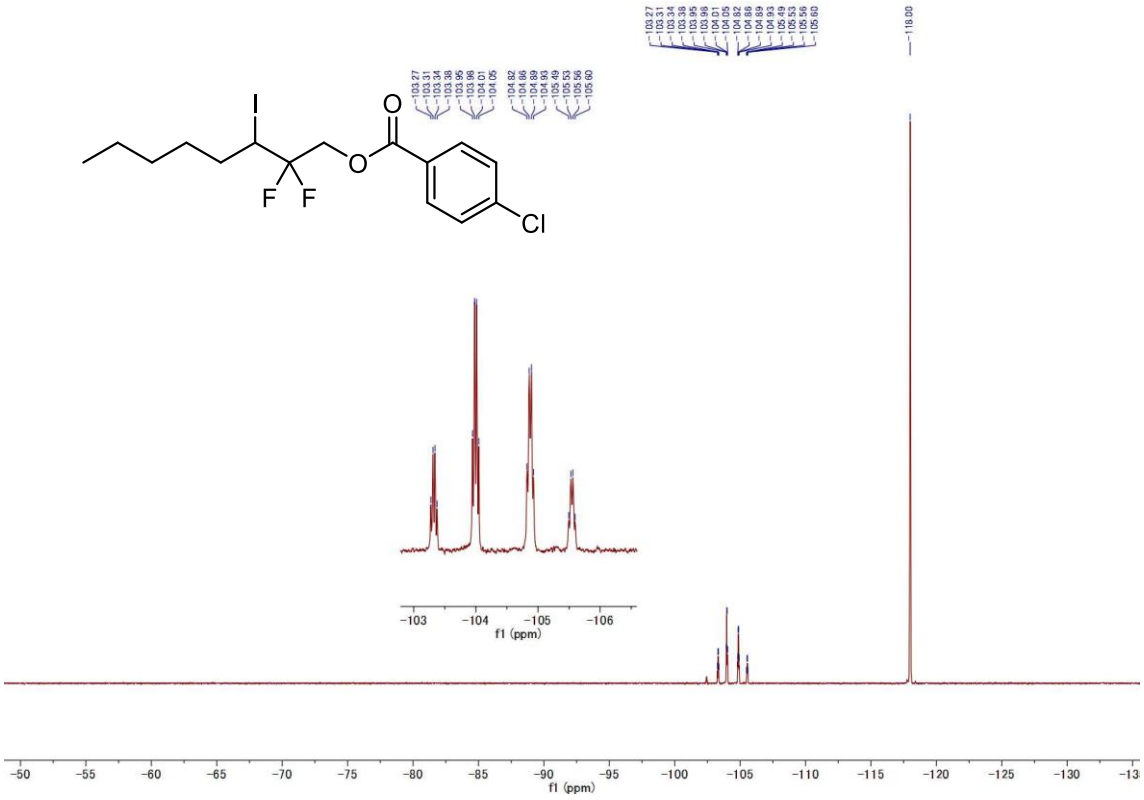
^{1}H NMR (400 MHz, $CDCl_3$) of 1k



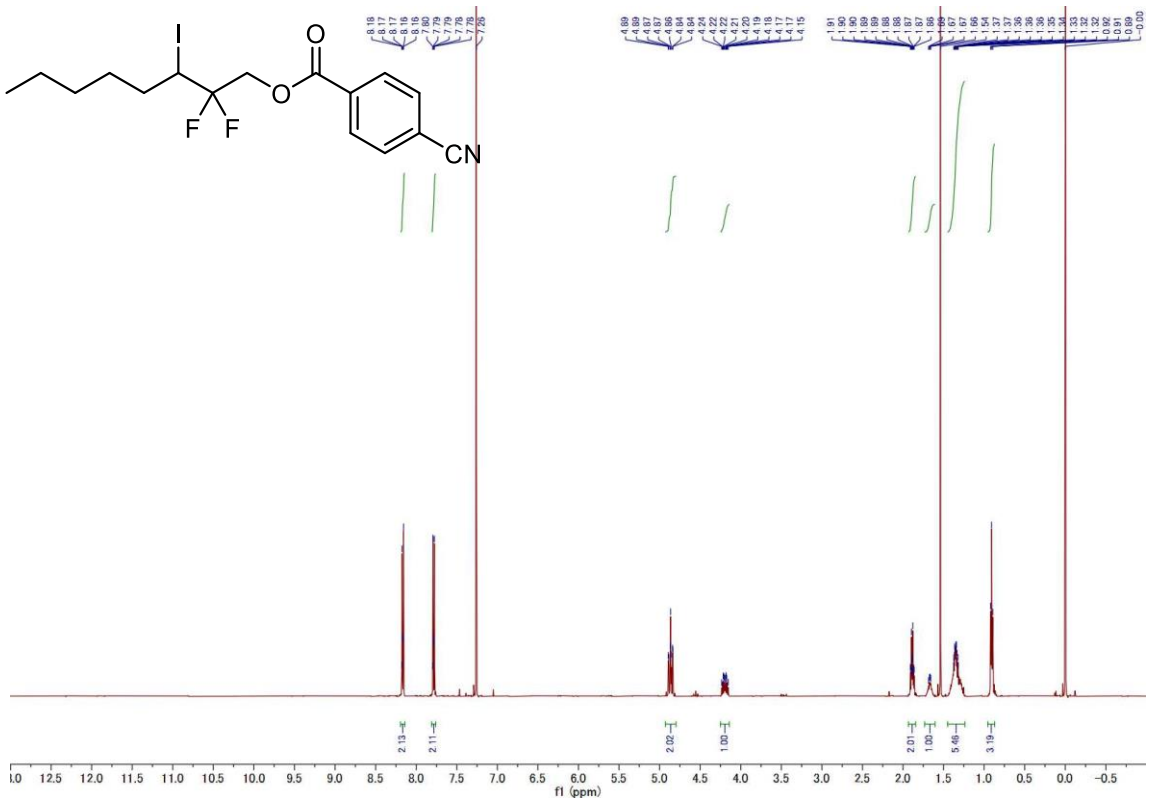
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of 1k



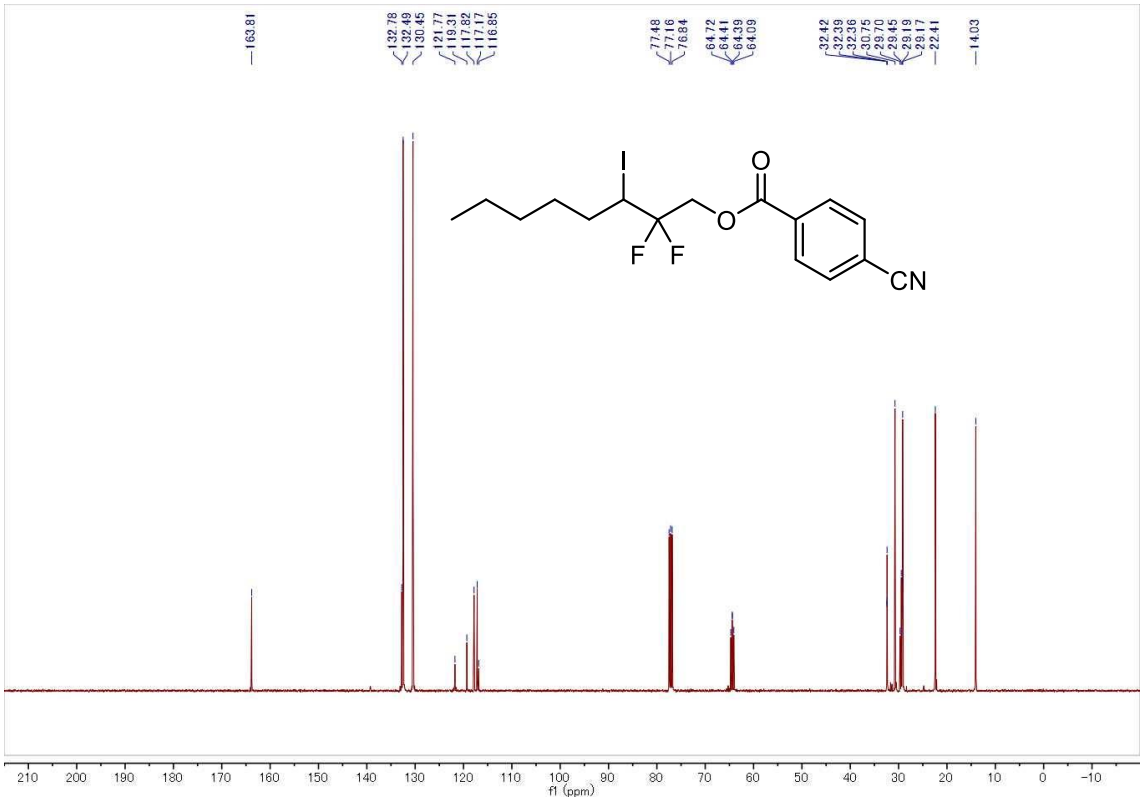
^{19}F NMR (376 MHz, $CDCl_3$) of 1k



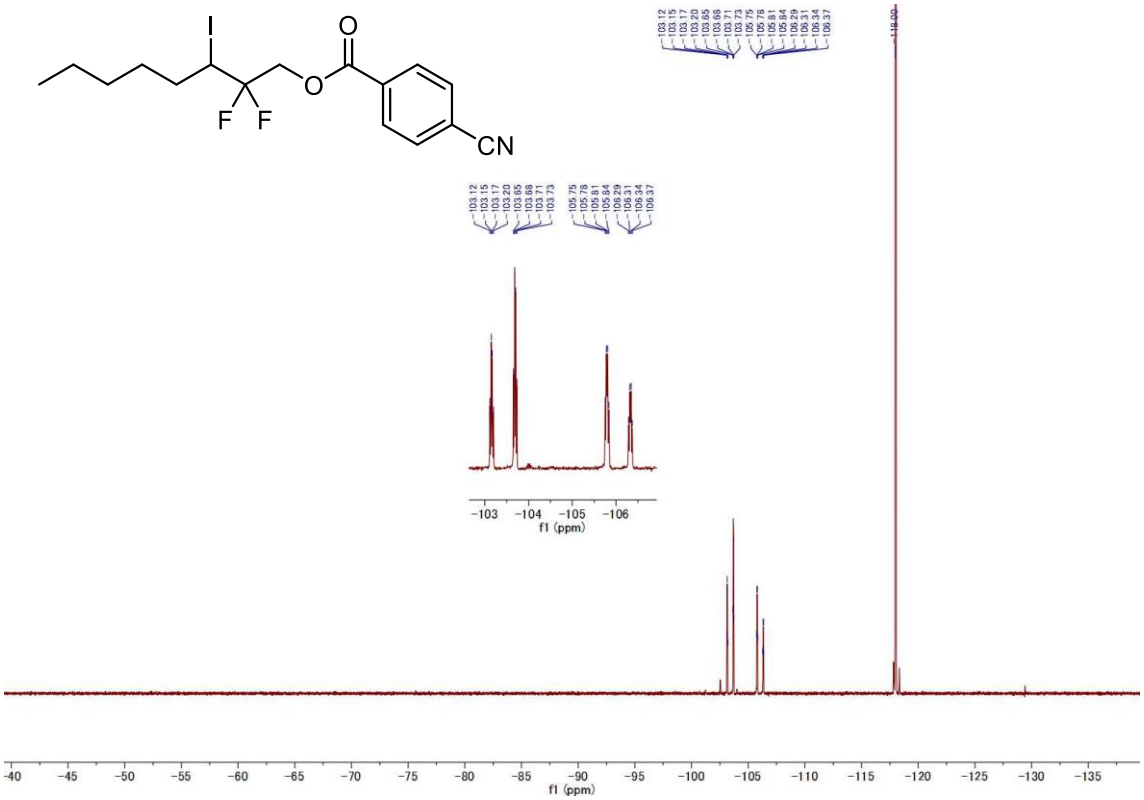
^{1}H NMR (500 MHz, $CDCl_3$) of 1l



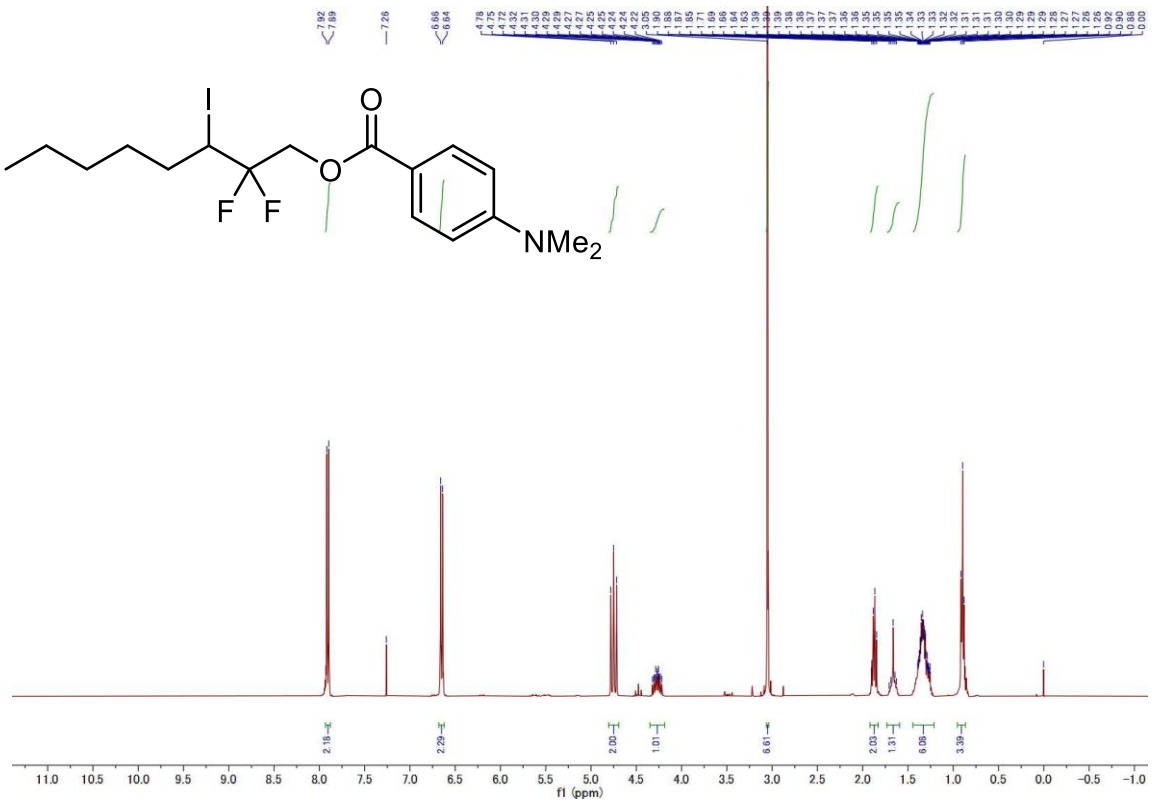
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 1l



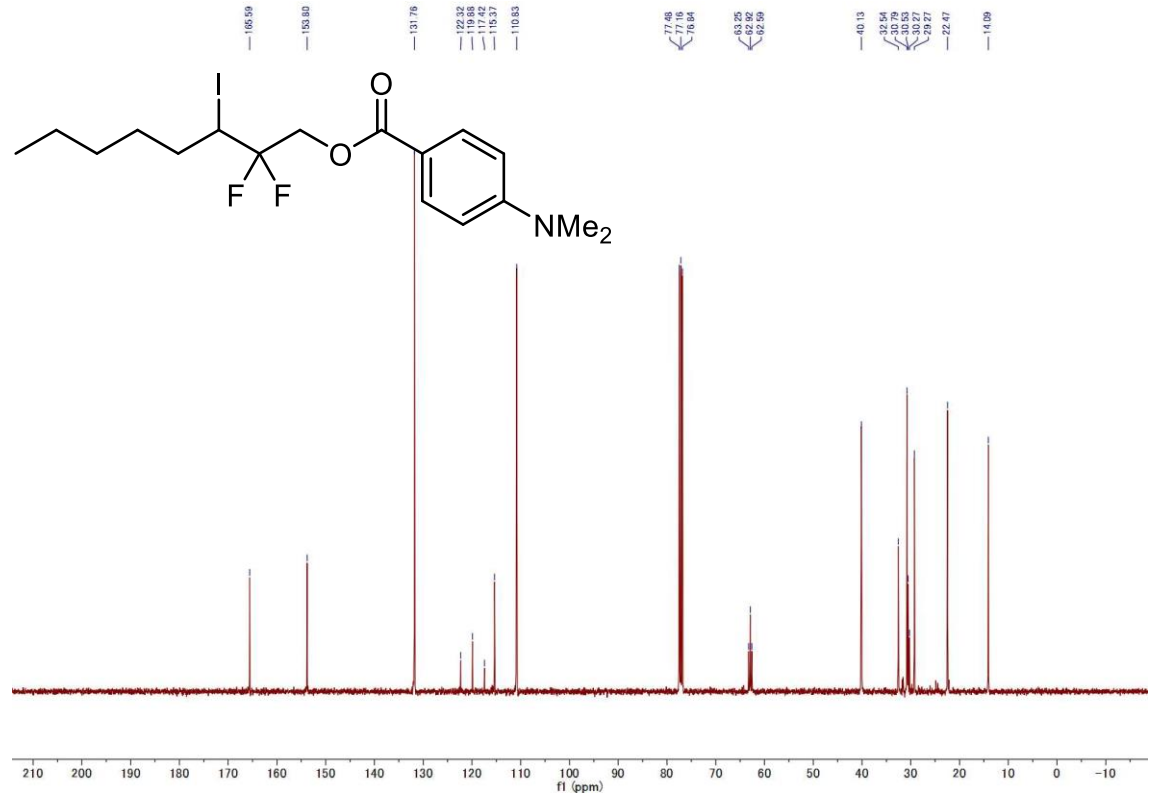
^{19}F NMR (376 MHz, $CDCl_3$) of 1l



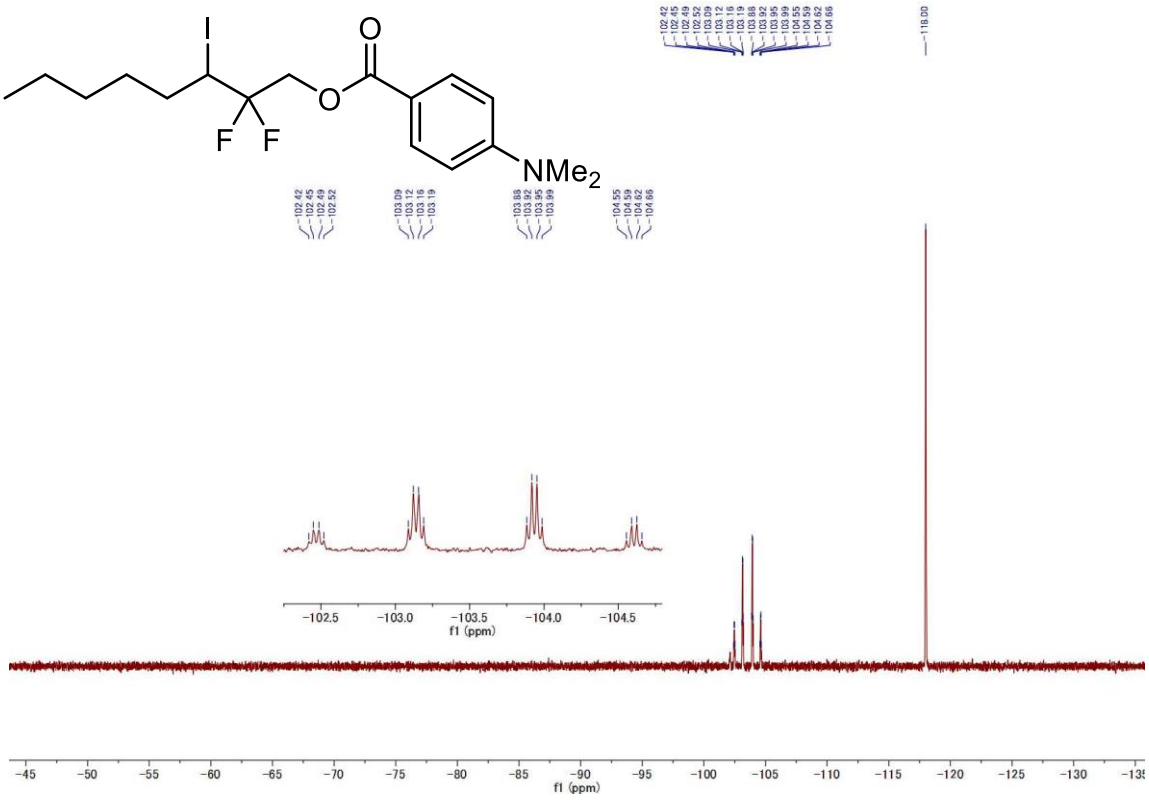
^{1}H NMR (400 MHz, $CDCl_3$) of 1m



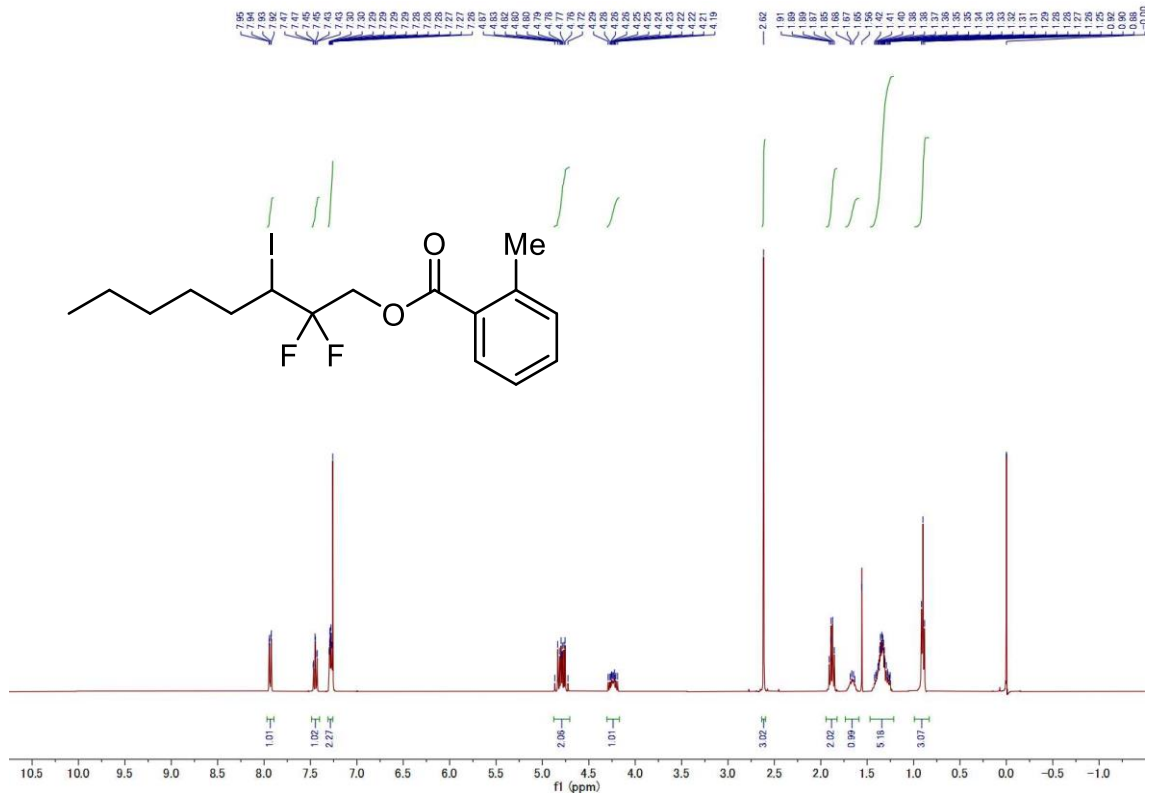
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of 1m



^{19}F NMR (376 MHz, $CDCl_3$) of 1m

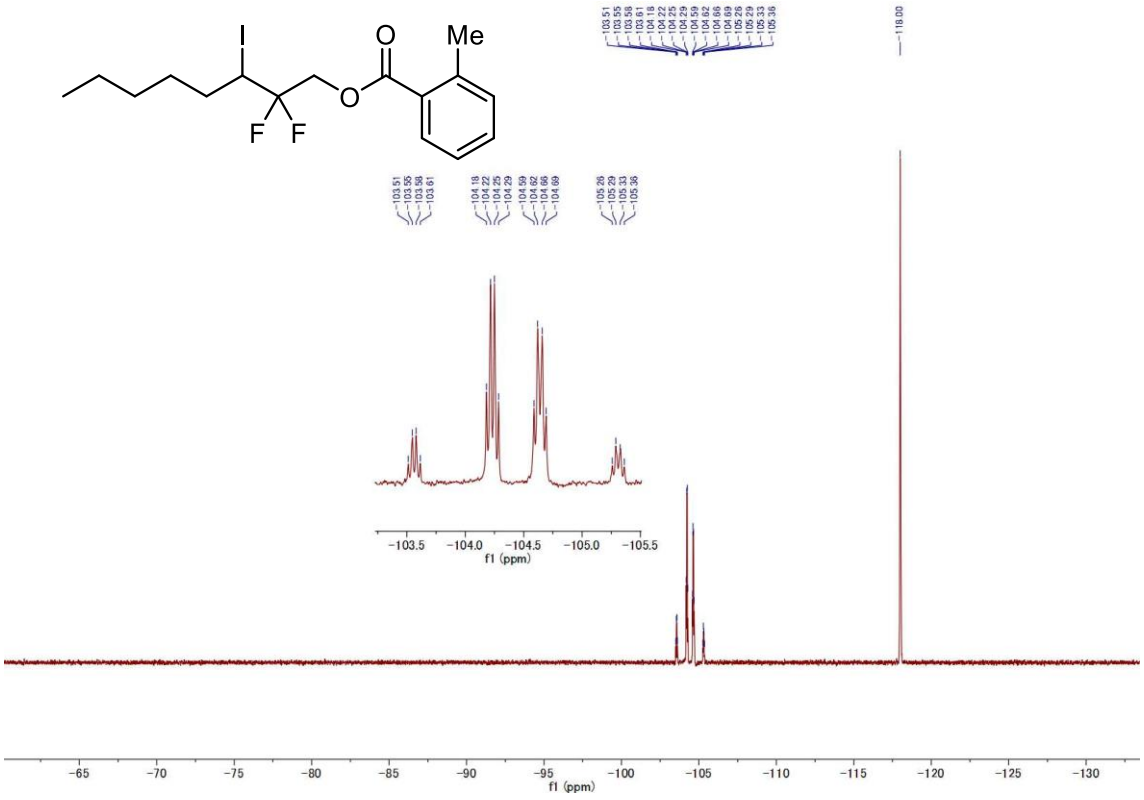


^{1}H NMR (400 MHz, $CDCl_3$) of 1n

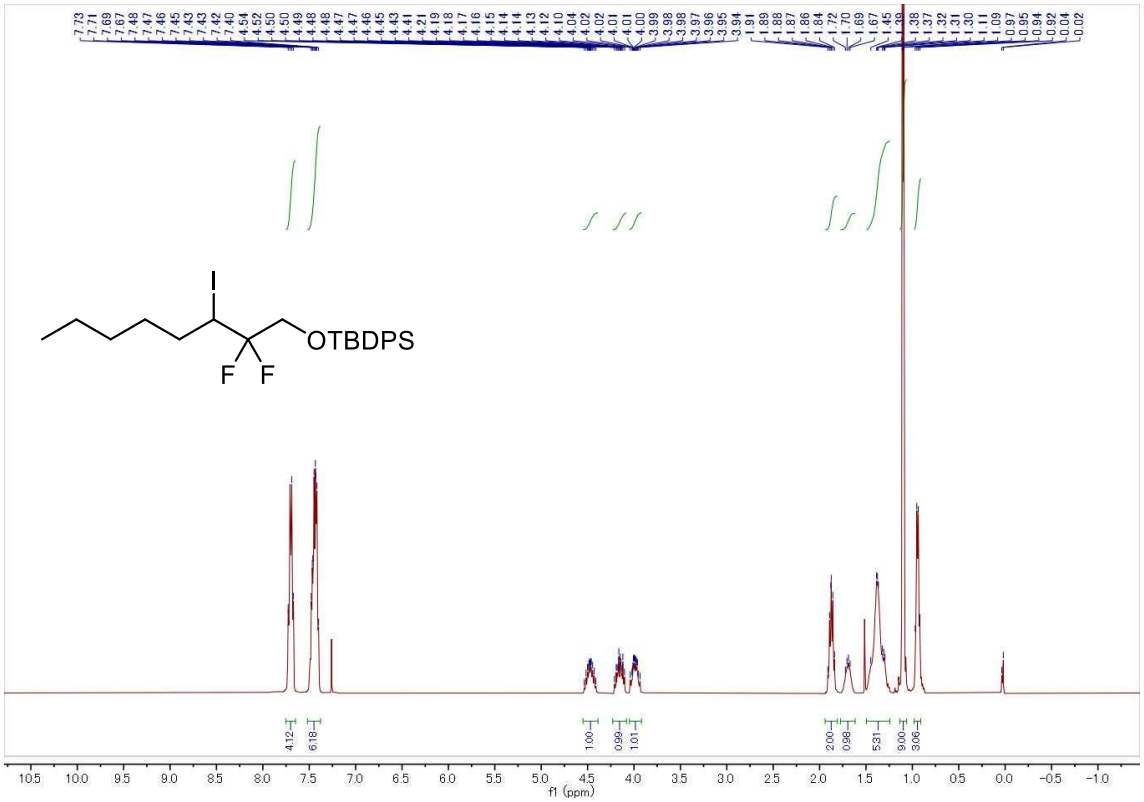


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of 1n

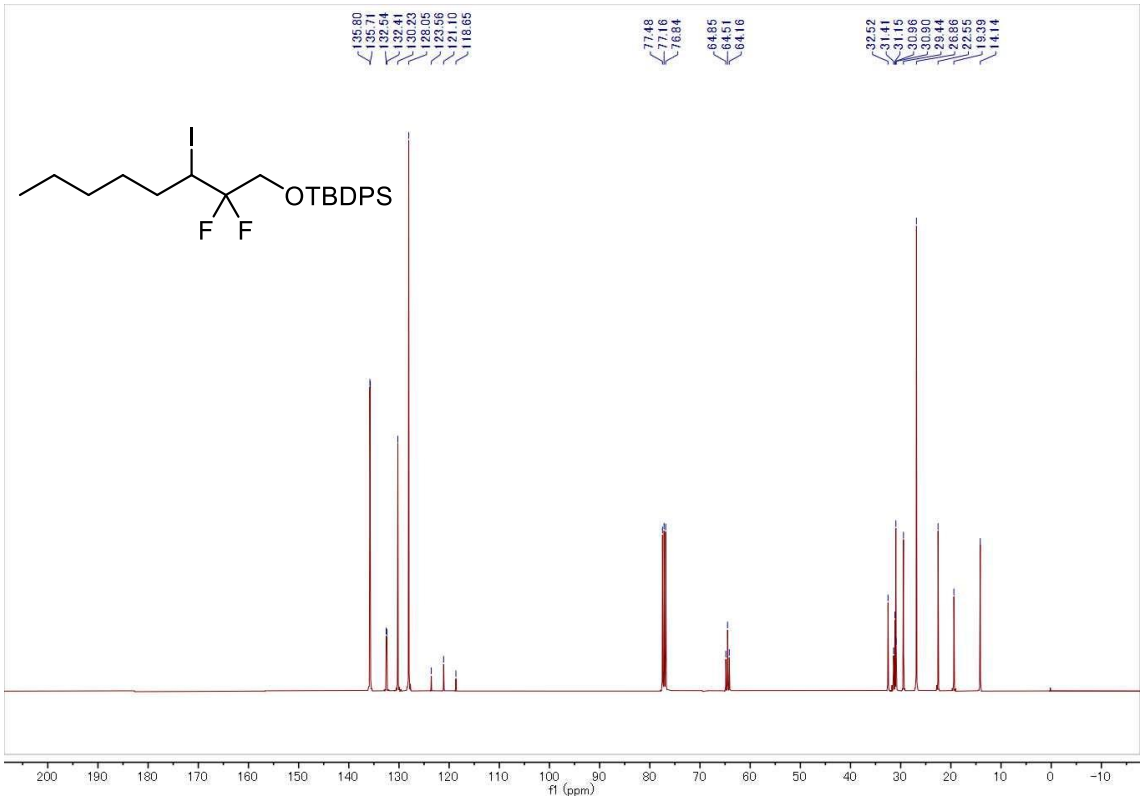
^{19}F NMR (376 MHz, $CDCl_3$) of 1n



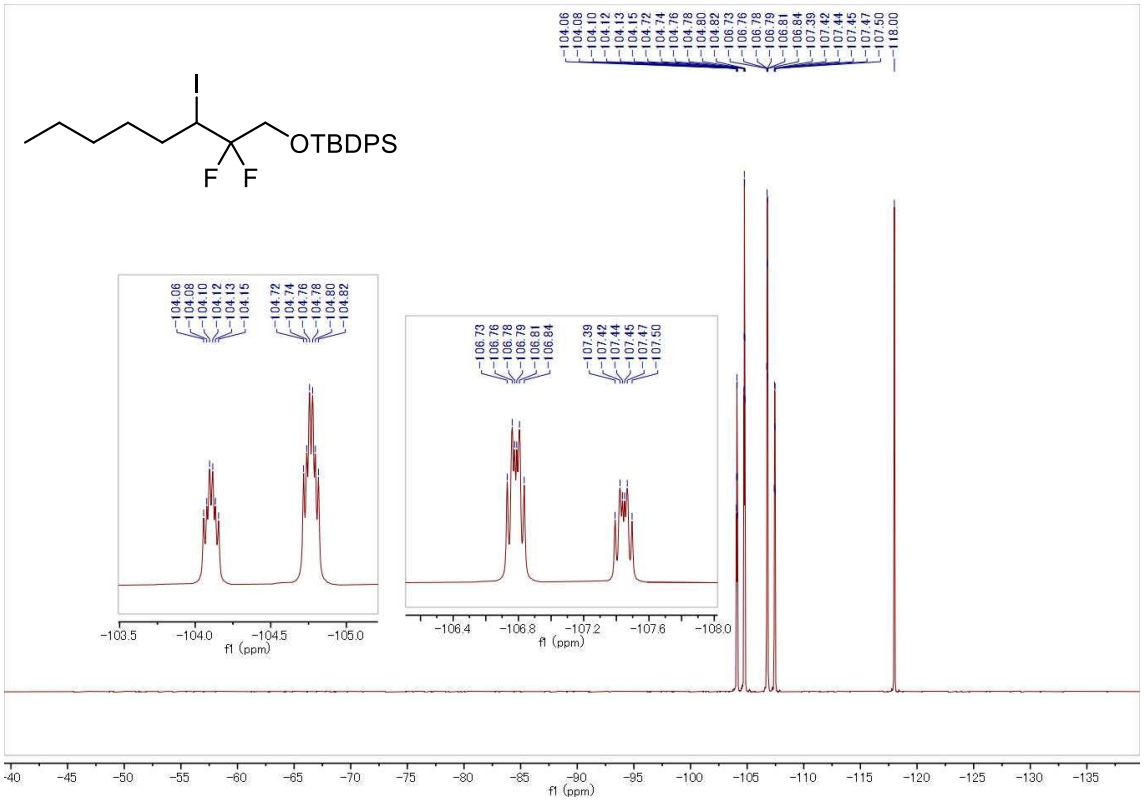
^{1}H NMR (400 MHz, $CDCl_3$) of 1o



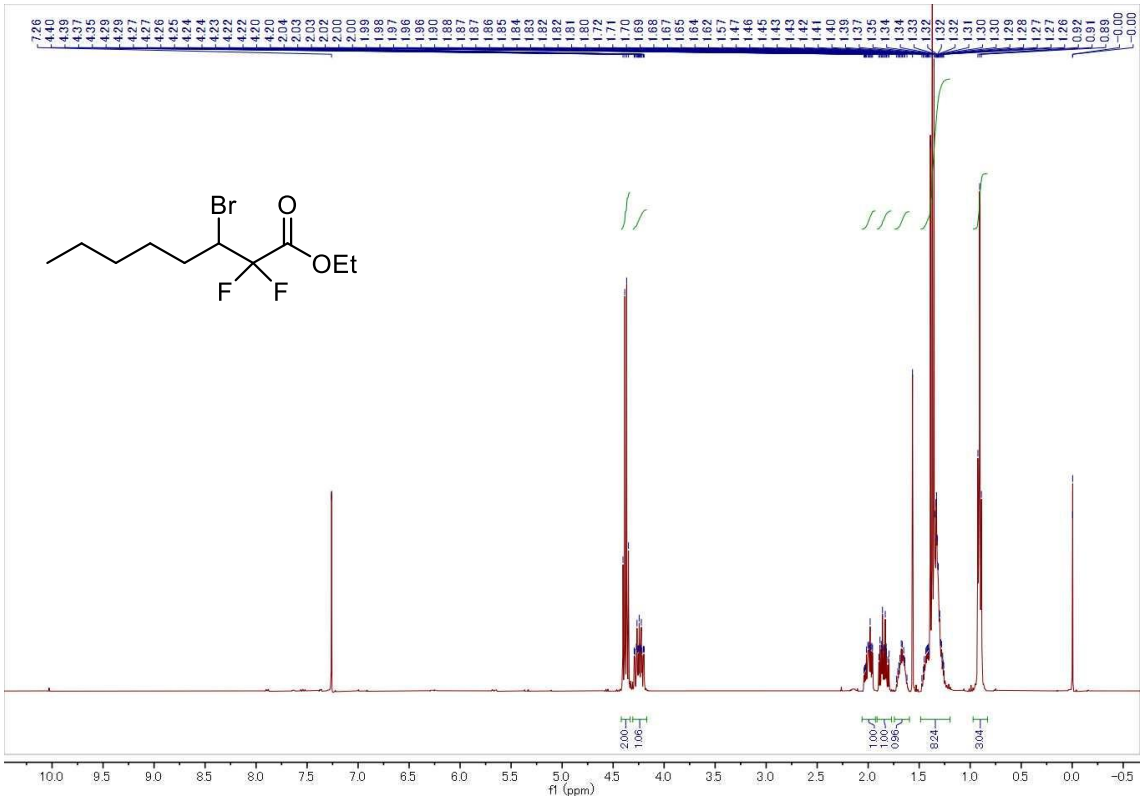
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of 1o



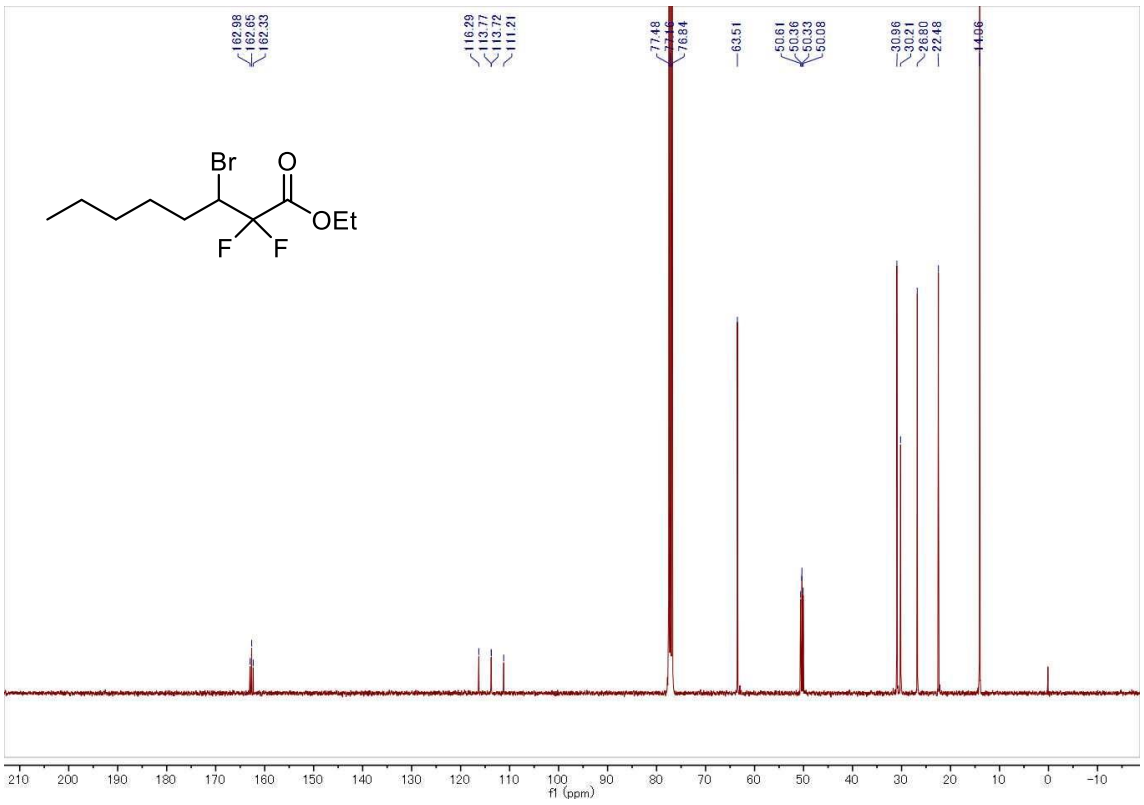
^{19}F NMR (376 MHz, $CDCl_3$) of 1o



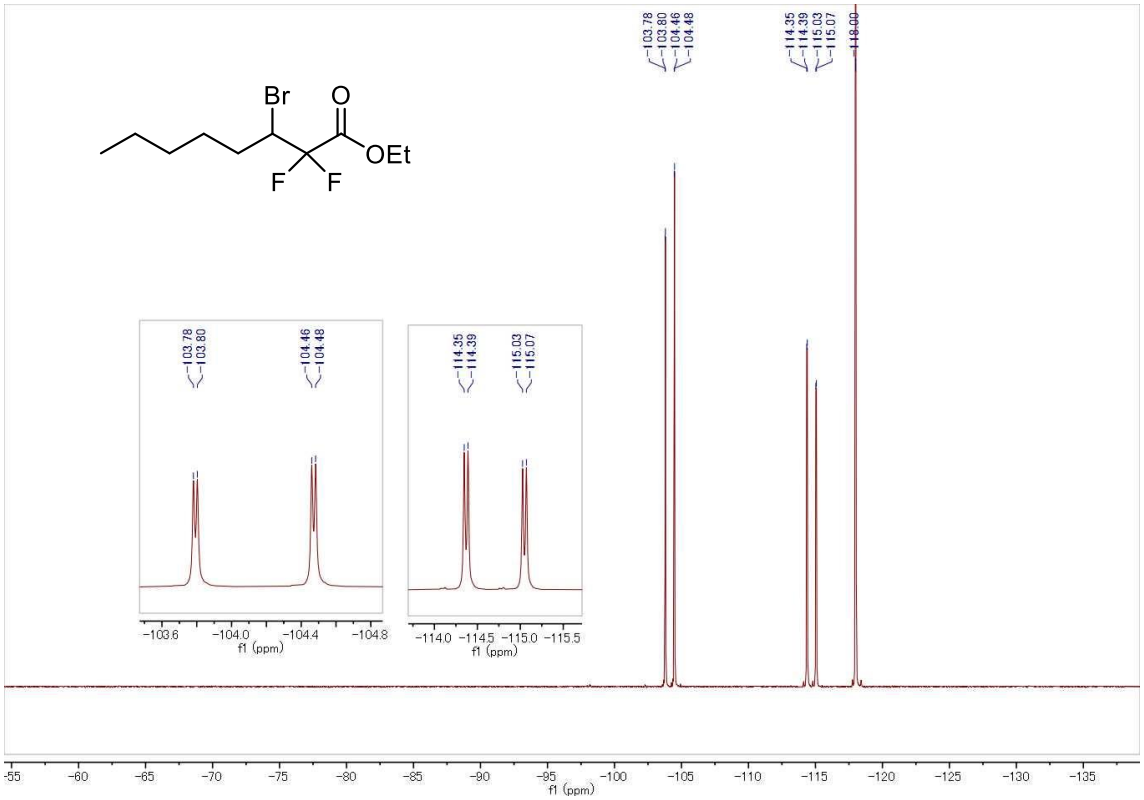
^{1}H NMR (400 MHz, $CDCl_3$) of 1p



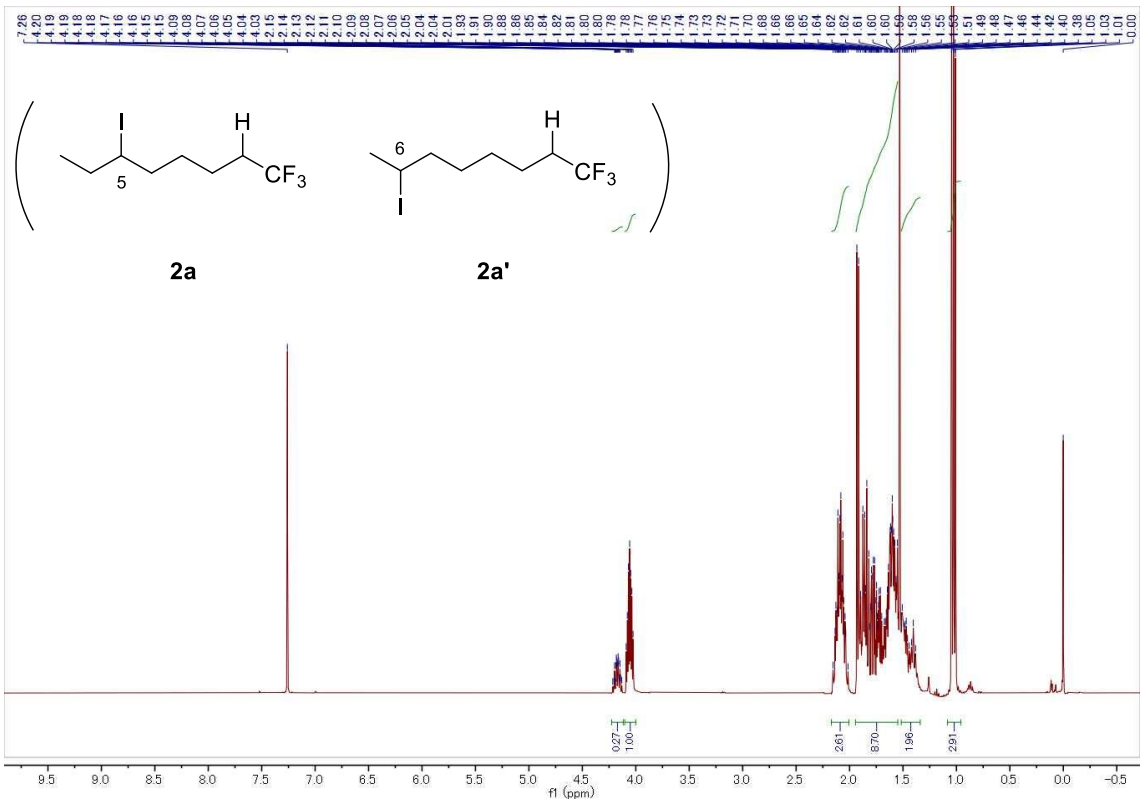
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 1p



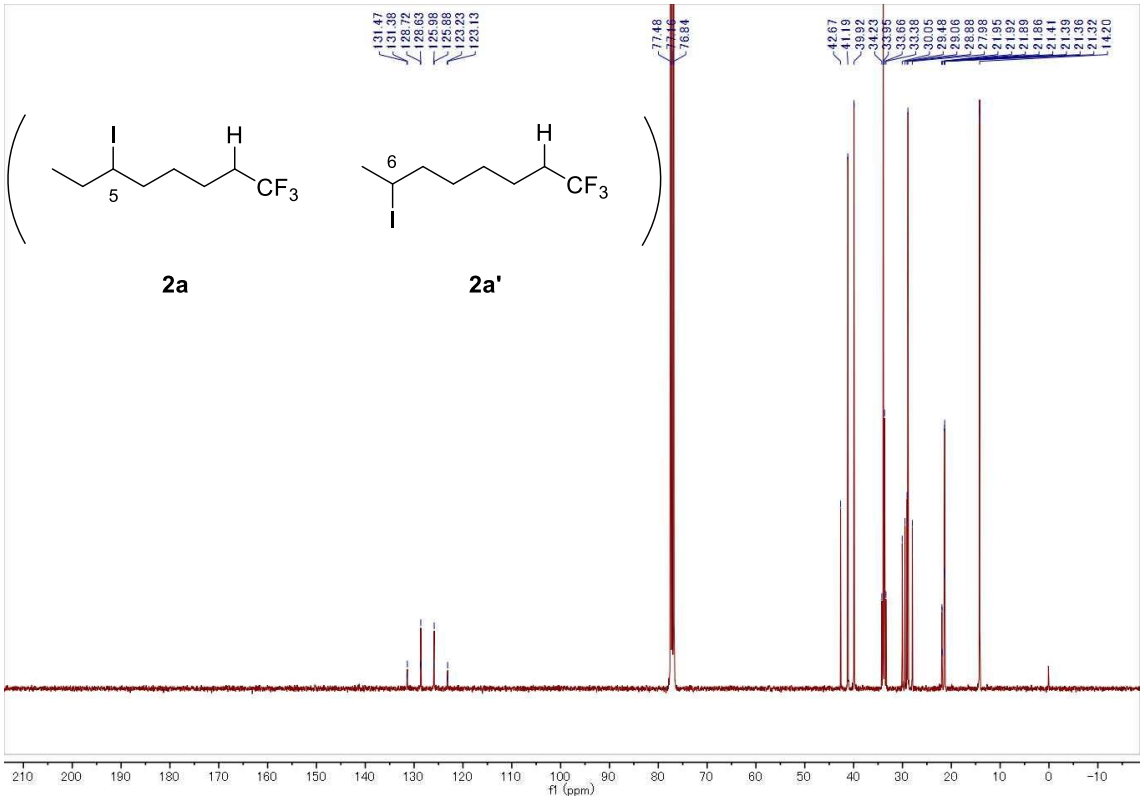
^{19}F NMR (376 MHz, $CDCl_3$) of 1p



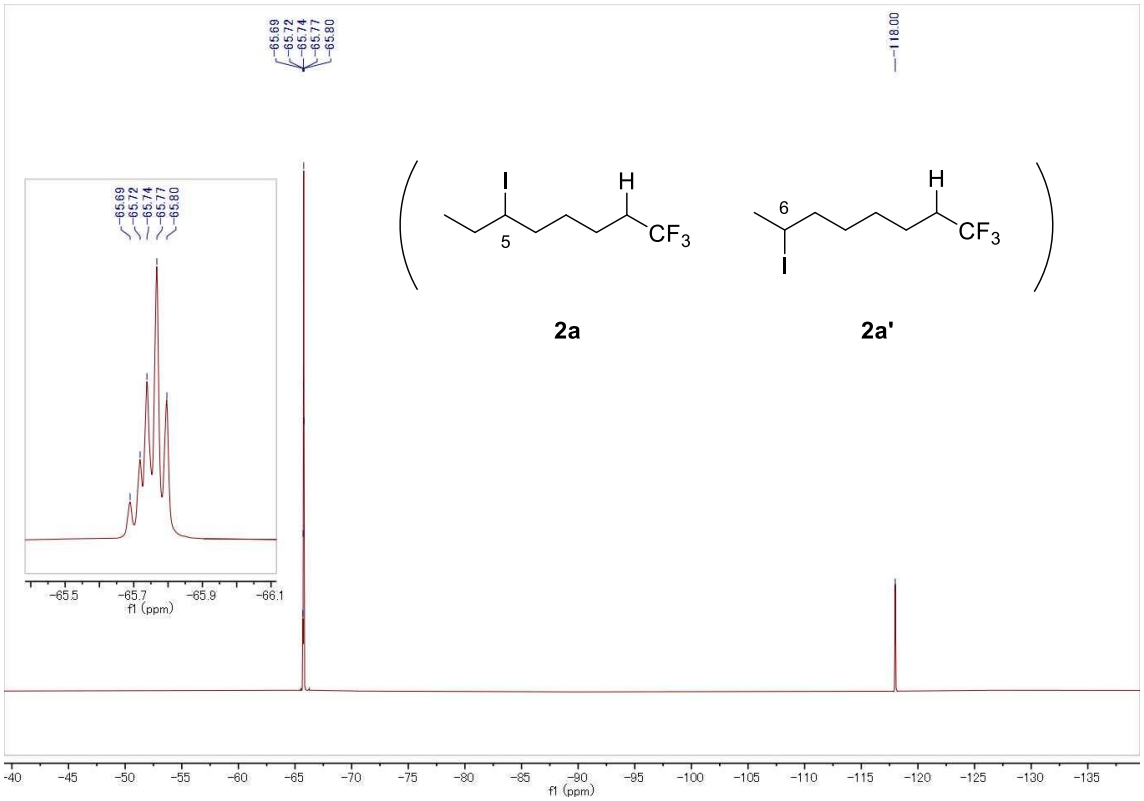
^{1}H NMR (400 MHz, $CDCl_3$) of 2a and 2a'



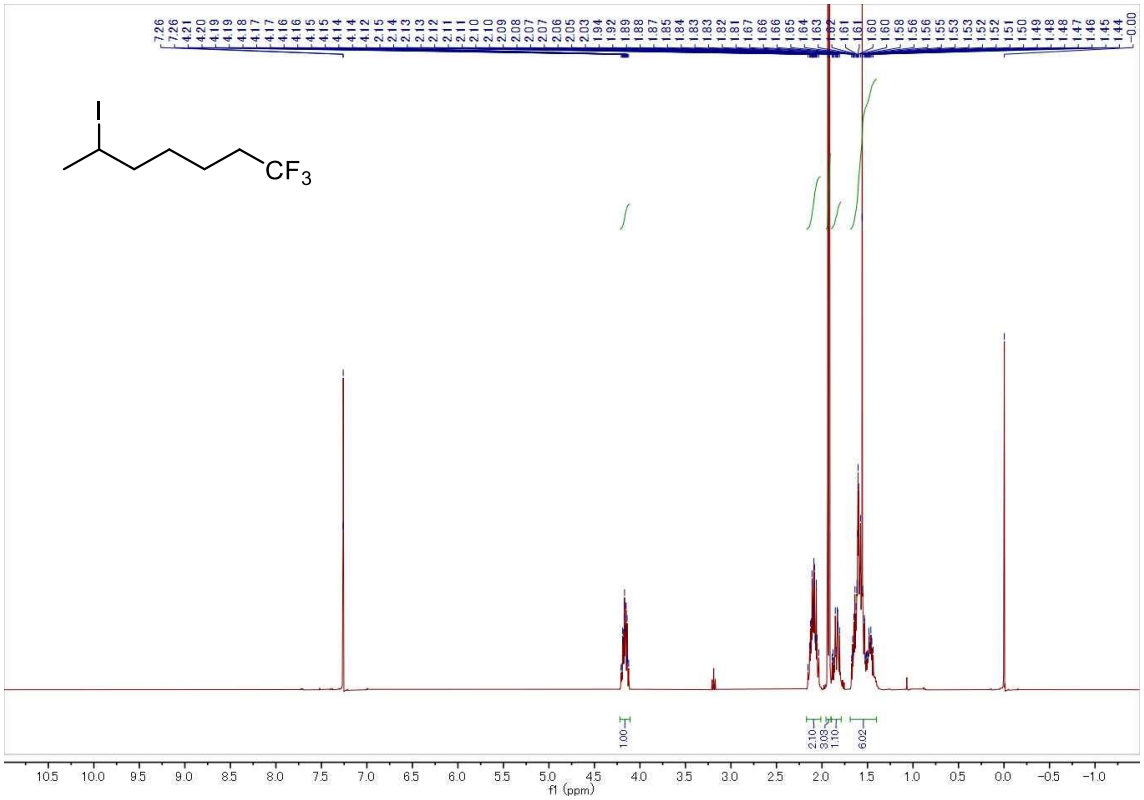
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of 2a and 2a'



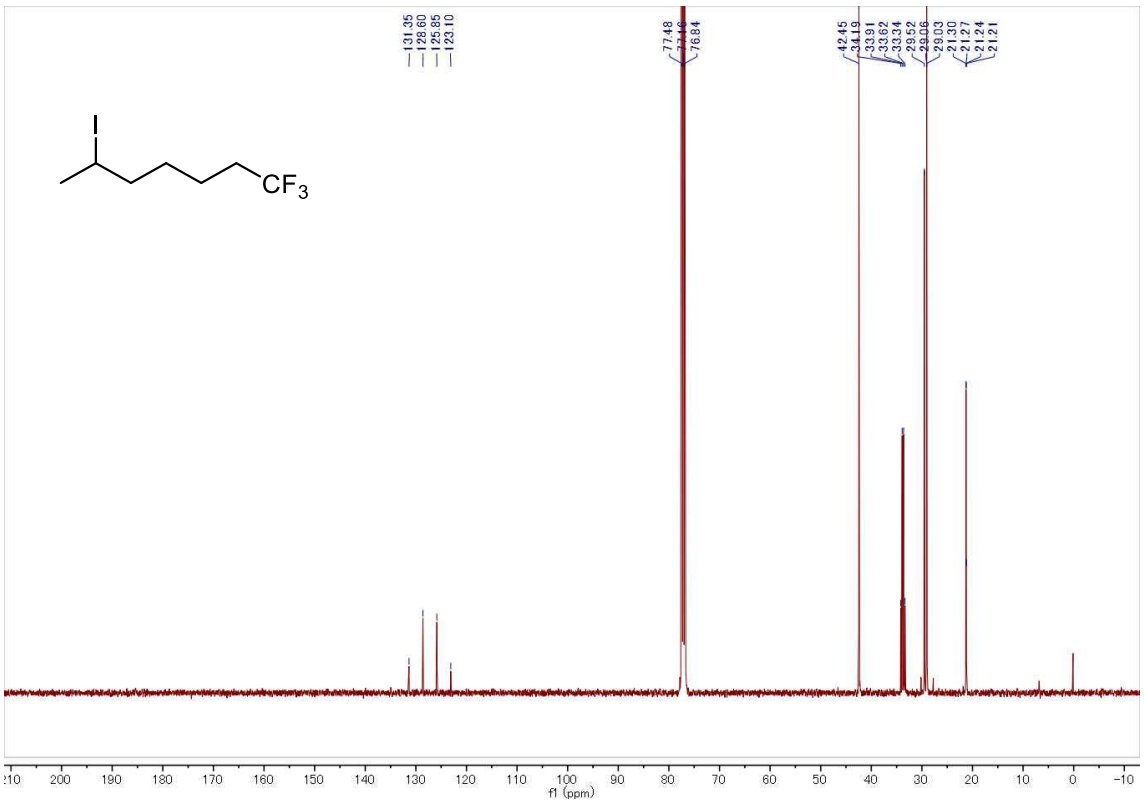
^{19}F NMR (376 MHz, $CDCl_3$) of 2a and 2a'



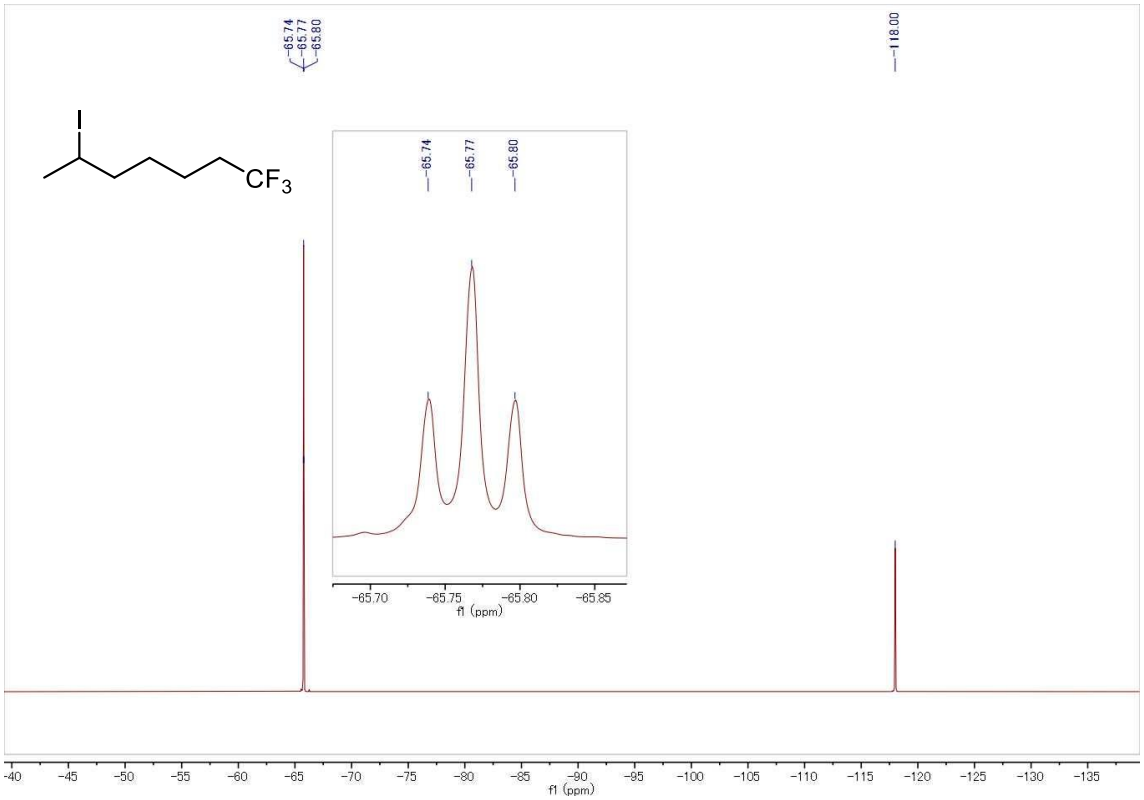
^{1}H NMR (400 MHz, $CDCl_3$) of 2b



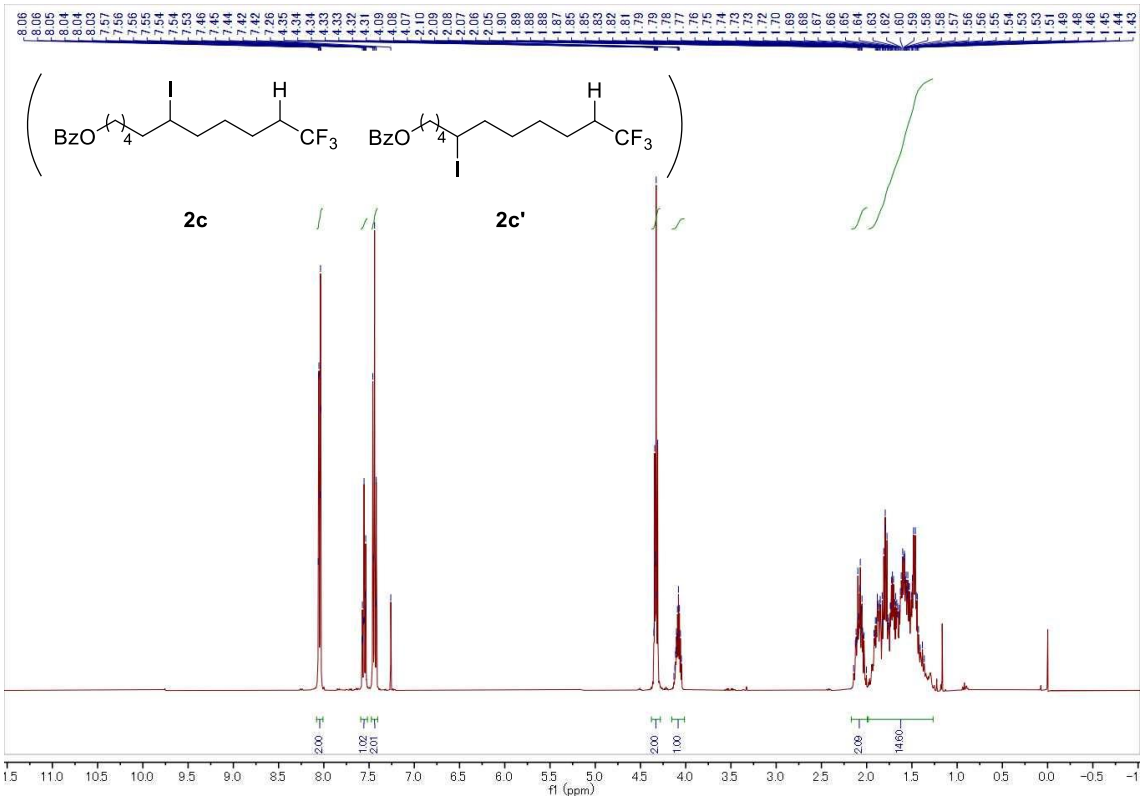
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 2b



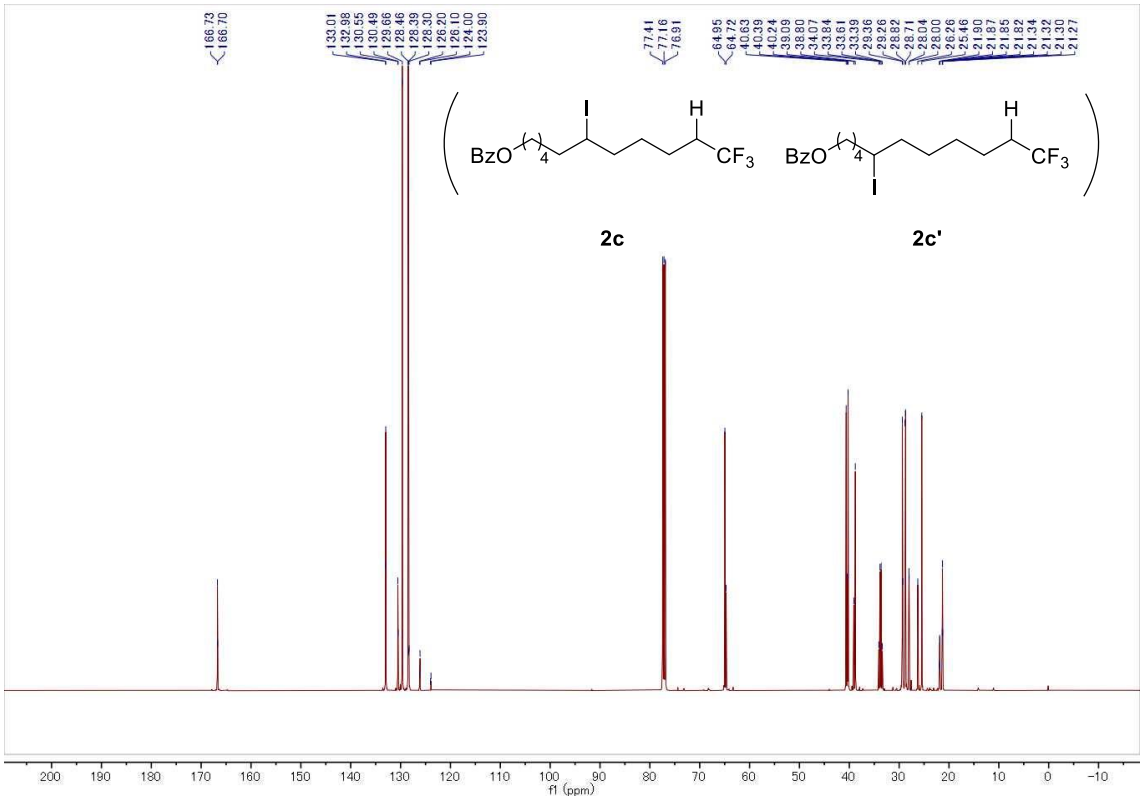
^{19}F NMR (376 MHz, $CDCl_3$) of 2b



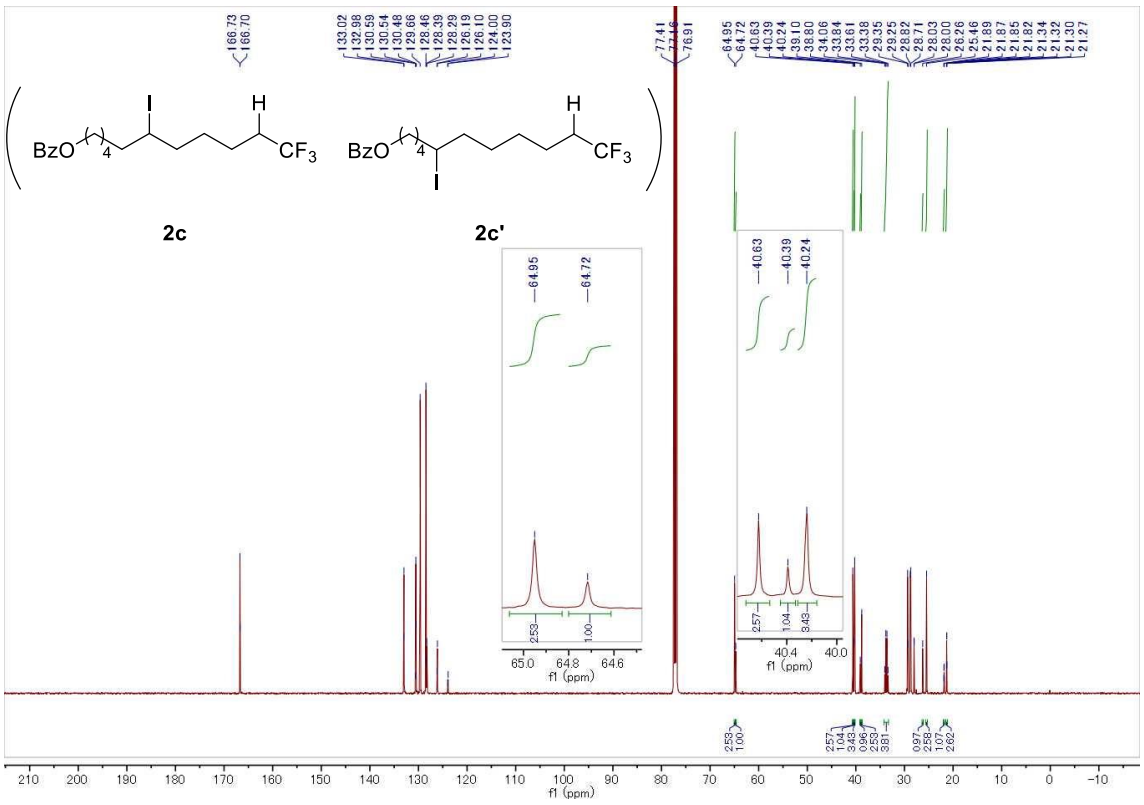
^{1}H NMR (500 MHz, $CDCl_3$) of 2c and 2c'



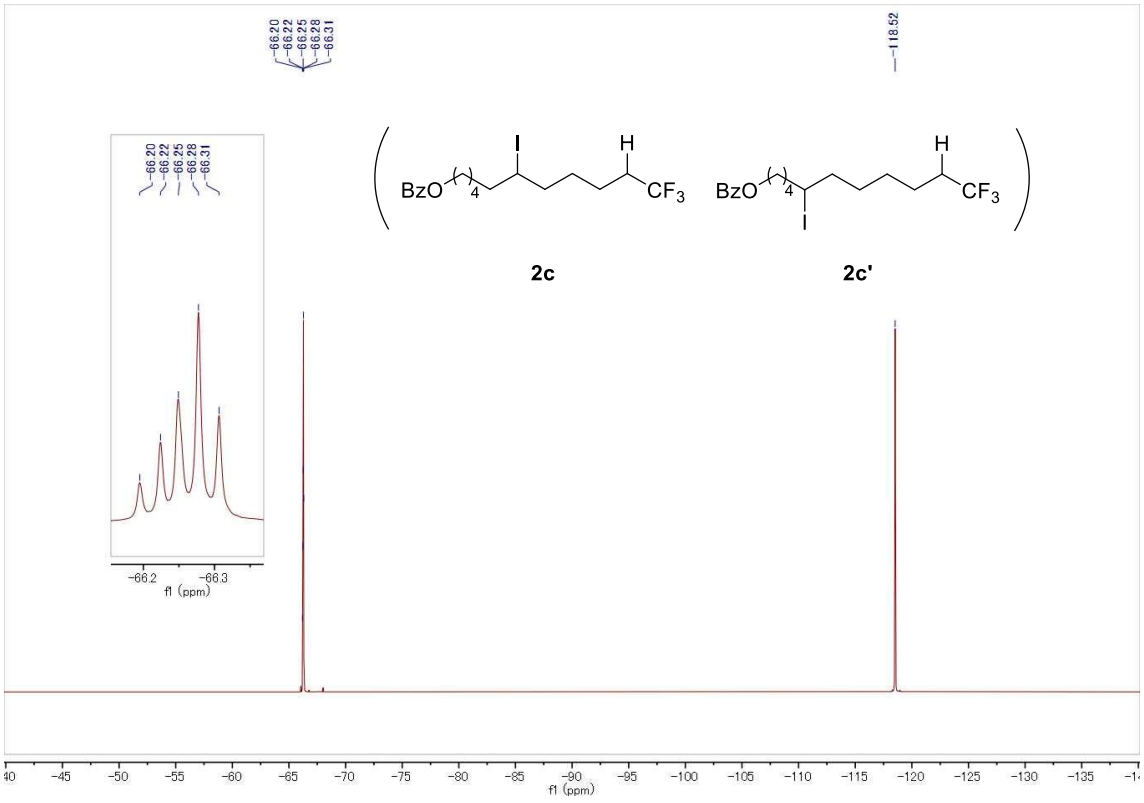
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of 2c and 2c'



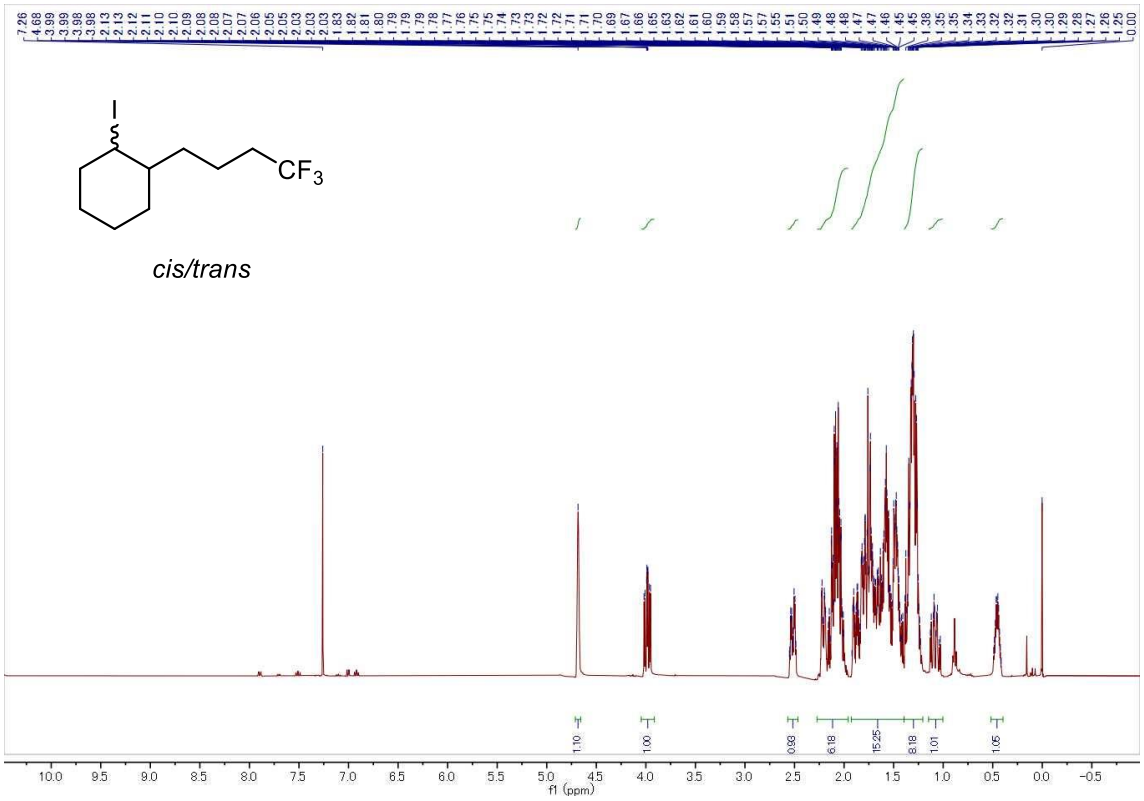
Quantitative ^{13}C NMR with inverse gated ^{1}H-decoupling (126 MHz, $CDCl_3$) of 2c and 2c'



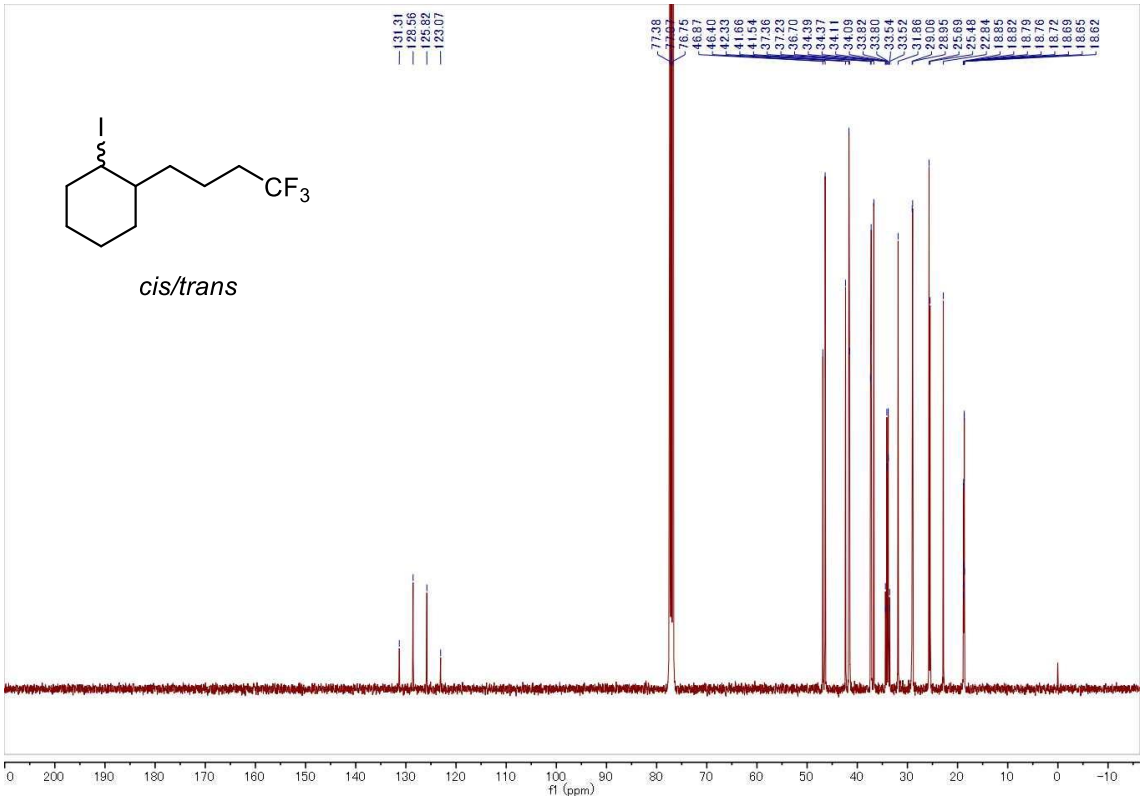
^{19}F NMR (376 MHz, $CDCl_3$) of 2c and 2c'



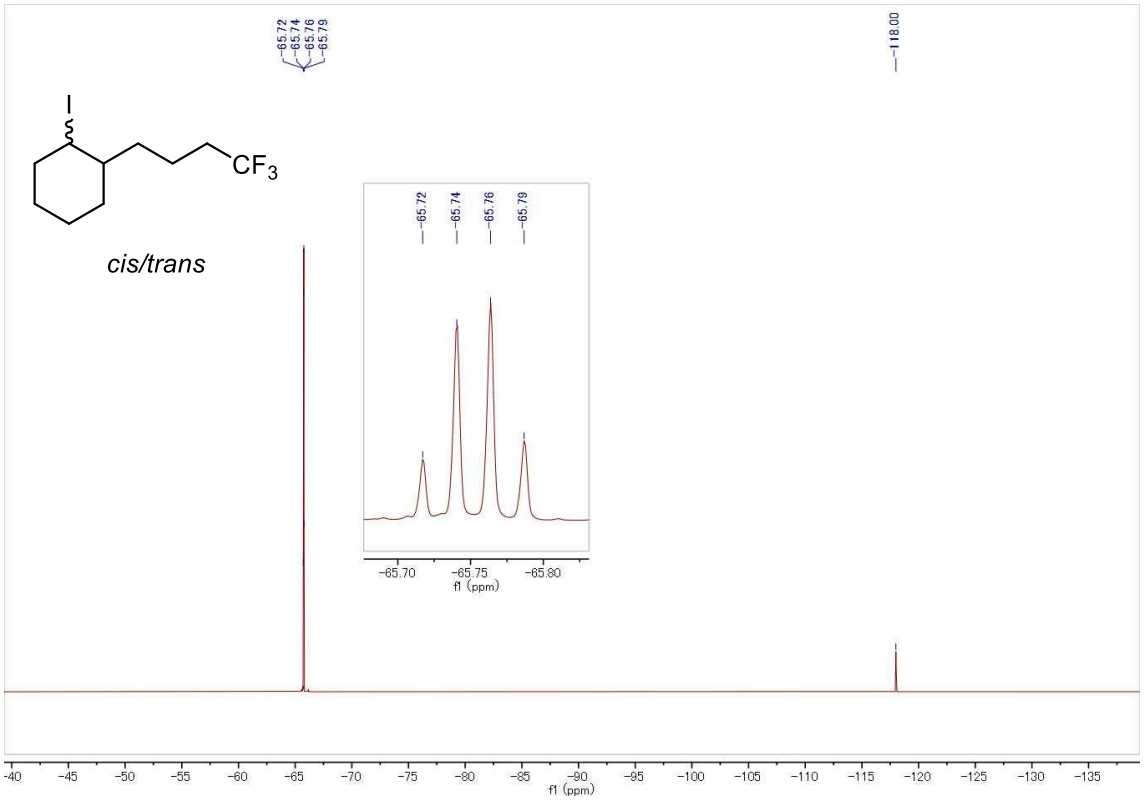
^{1}H NMR (400 MHz, $CDCl_3$) of 2d



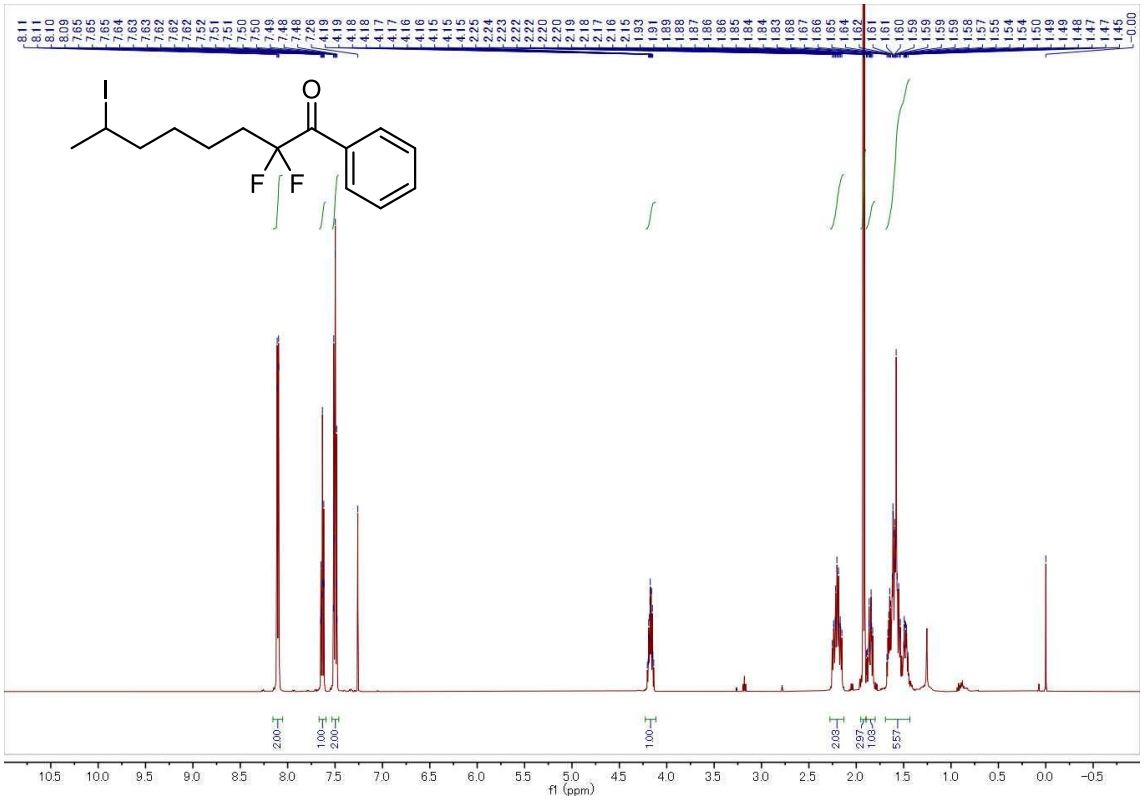
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of 2d



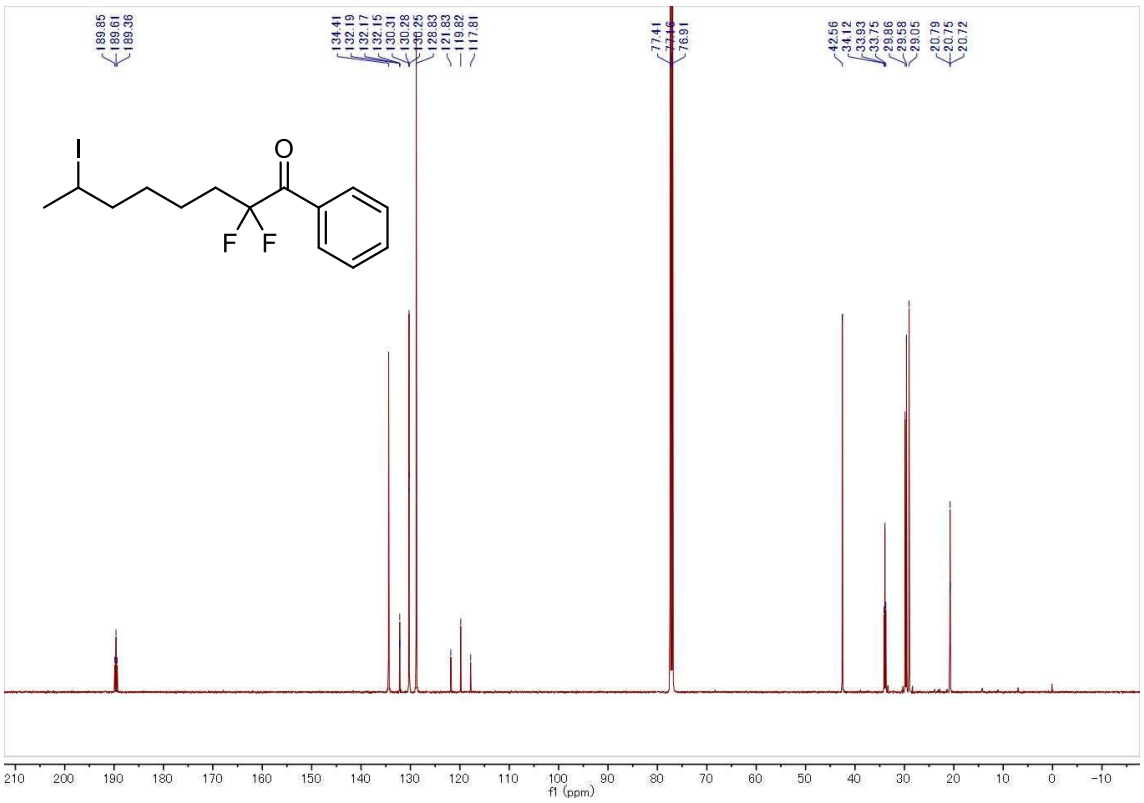
^{19}F NMR (471 MHz, $CDCl_3$) of 2d



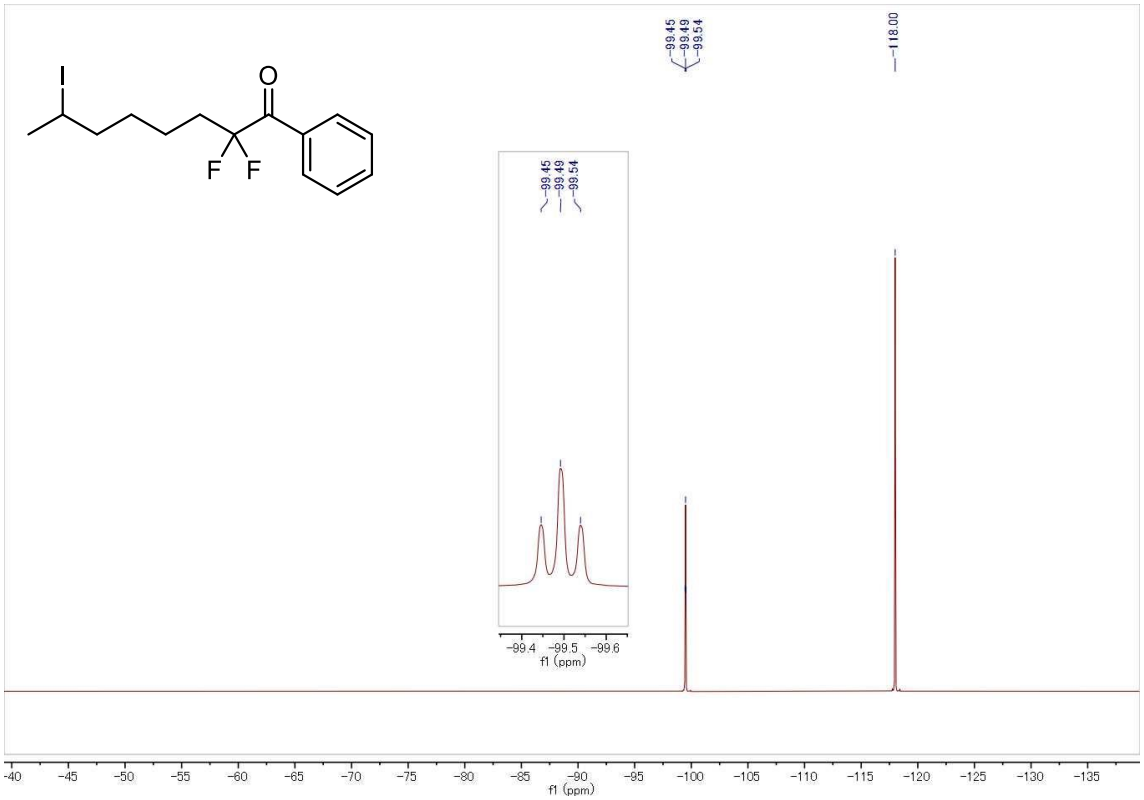
^{1}H NMR (500 MHz, $CDCl_3$) of 2g



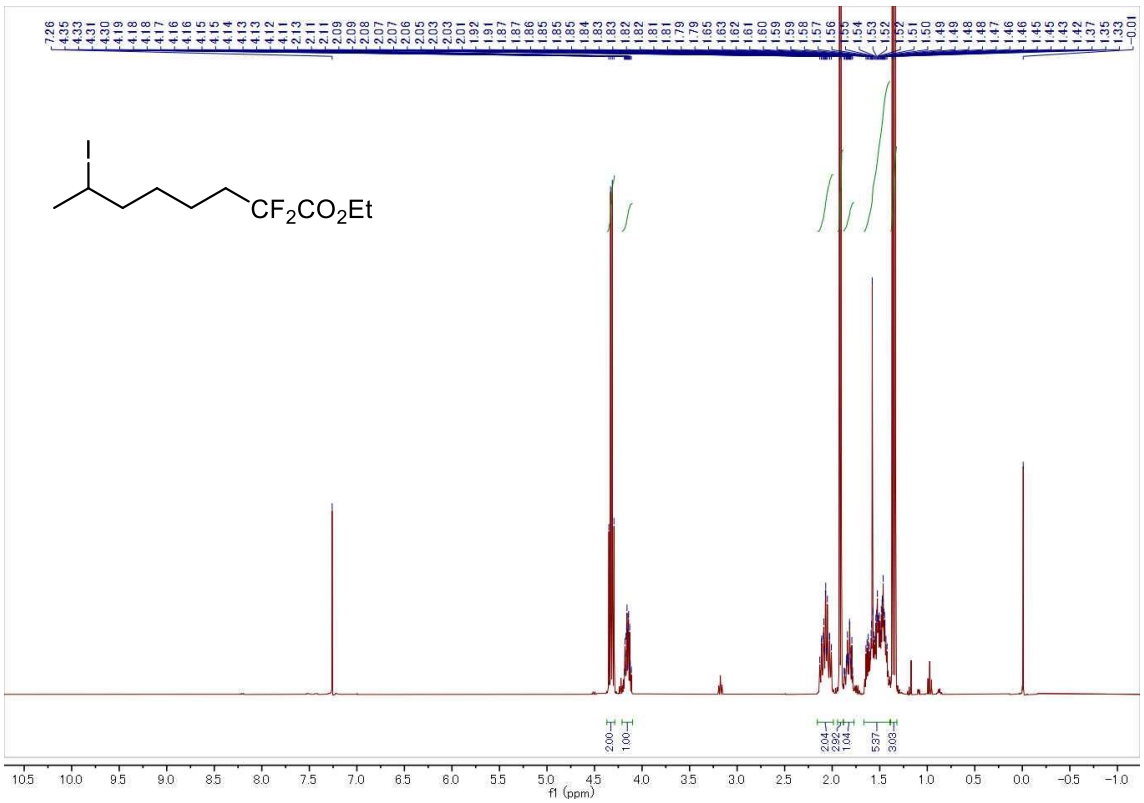
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of 2g



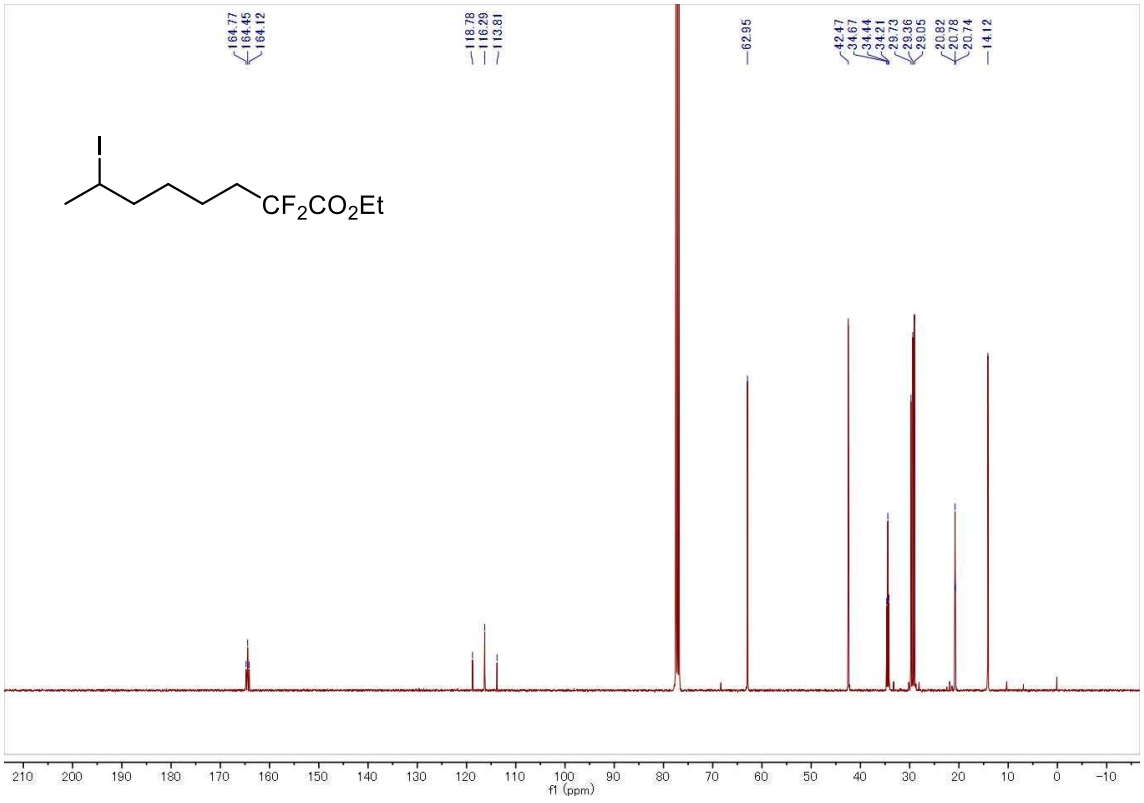
^{19}F NMR (376 MHz, $CDCl_3$) of 2g



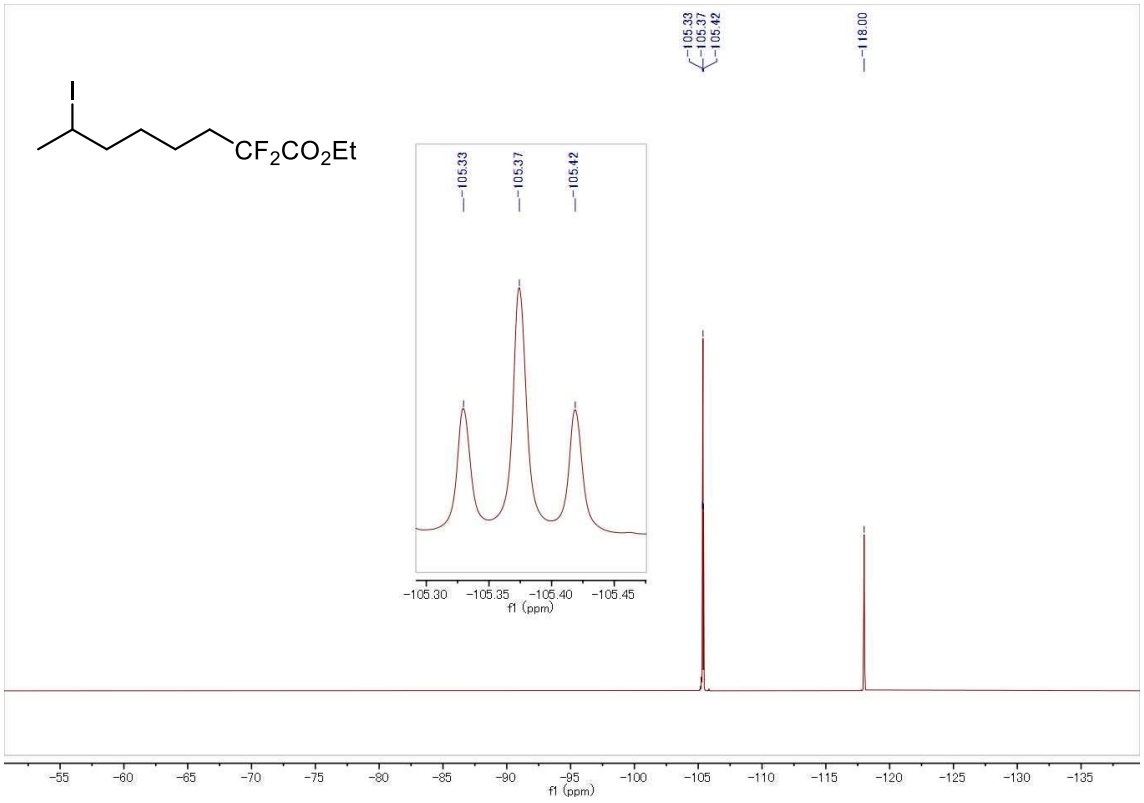
^{1}H NMR (400 MHz, $CDCl_3$) of 2h



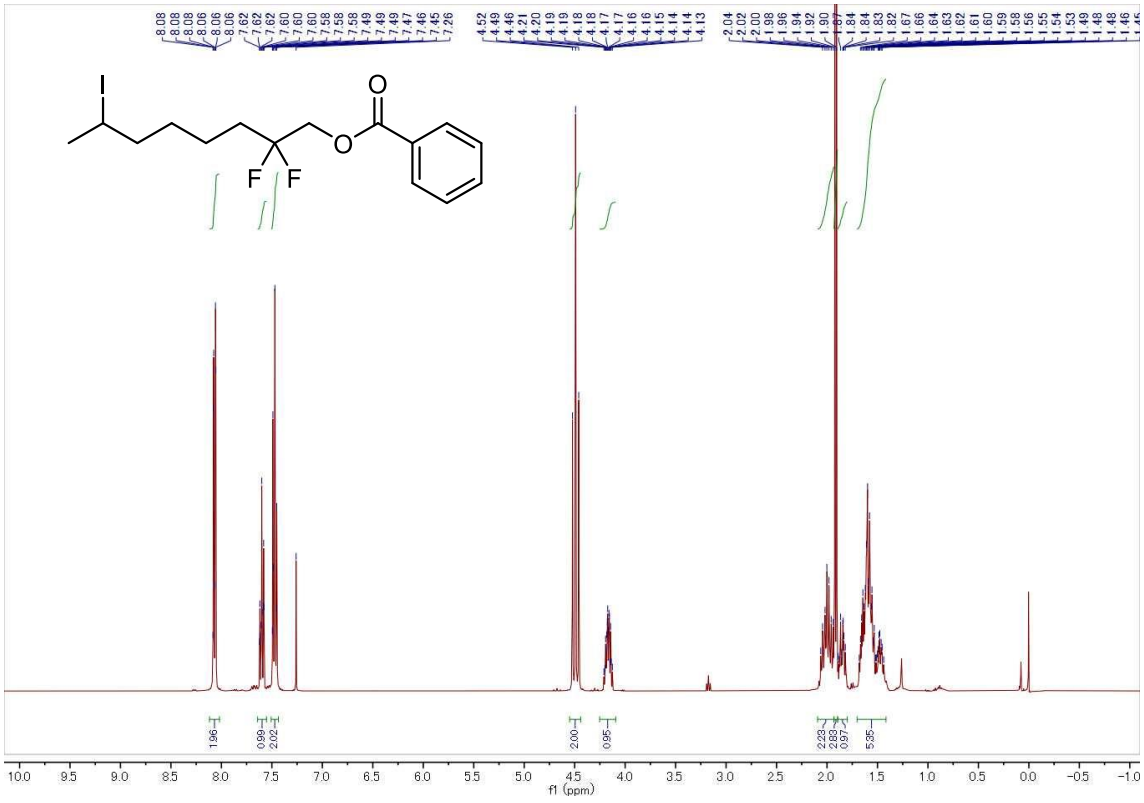
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of 2h



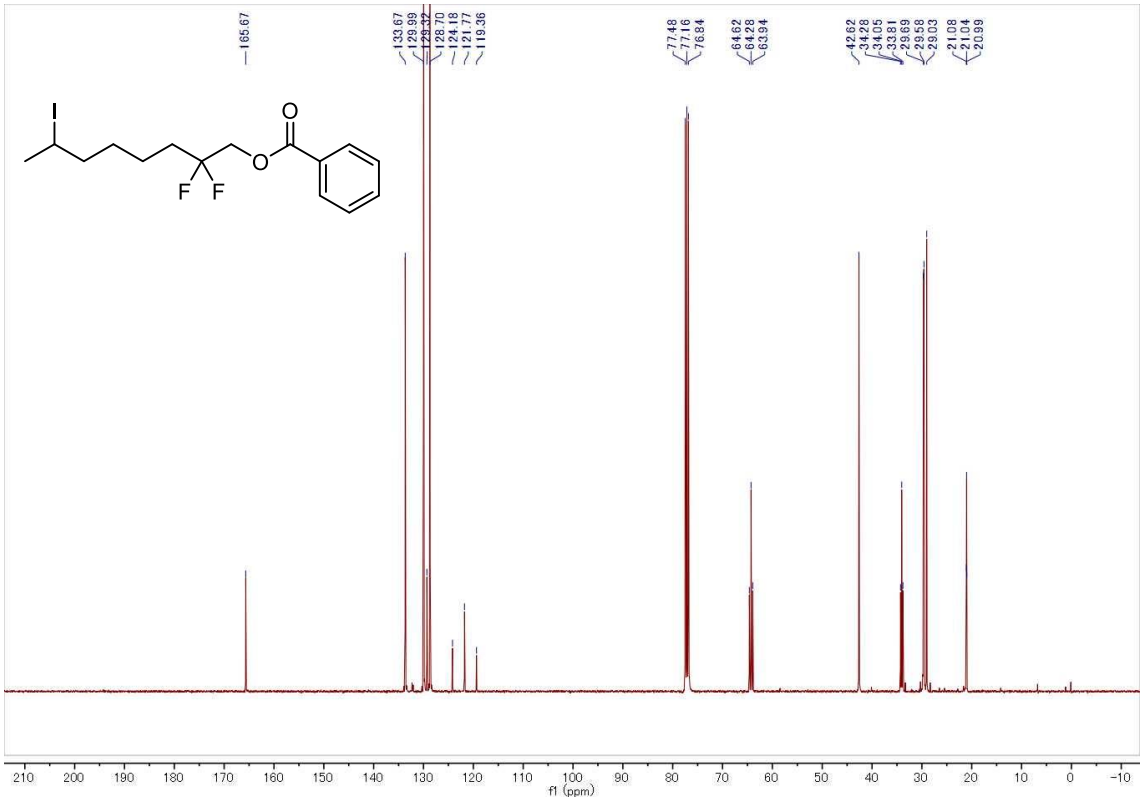
^{19}F NMR (376 MHz, $CDCl_3$) of 2h



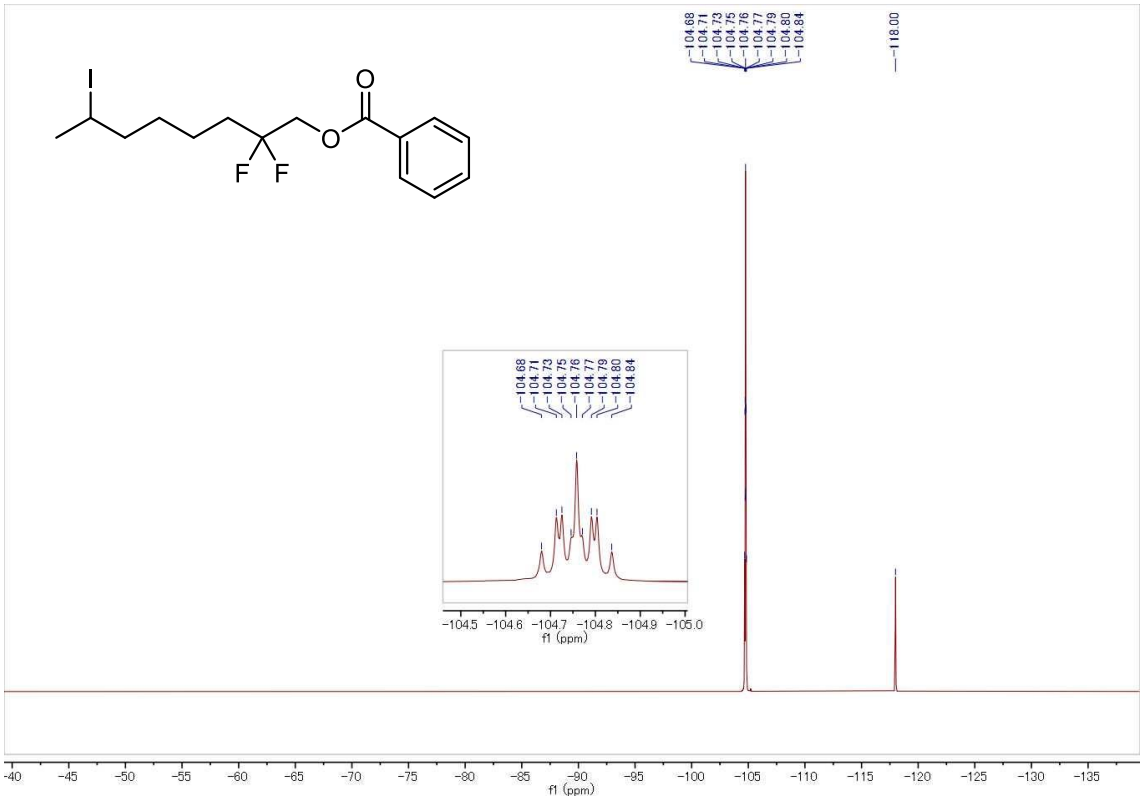
^{1}H NMR (400 MHz, $CDCl_3$) of 2g



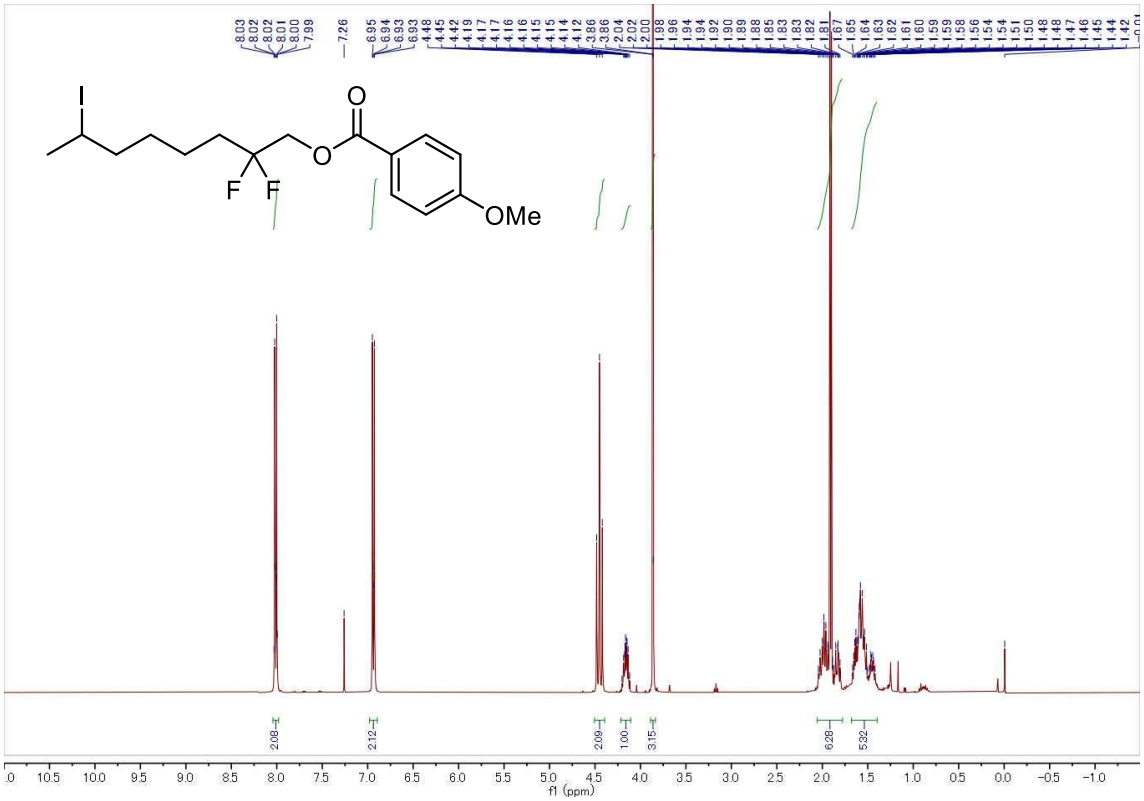
^{13}C NMR (101 MHz, $CDCl_3$) of 2g



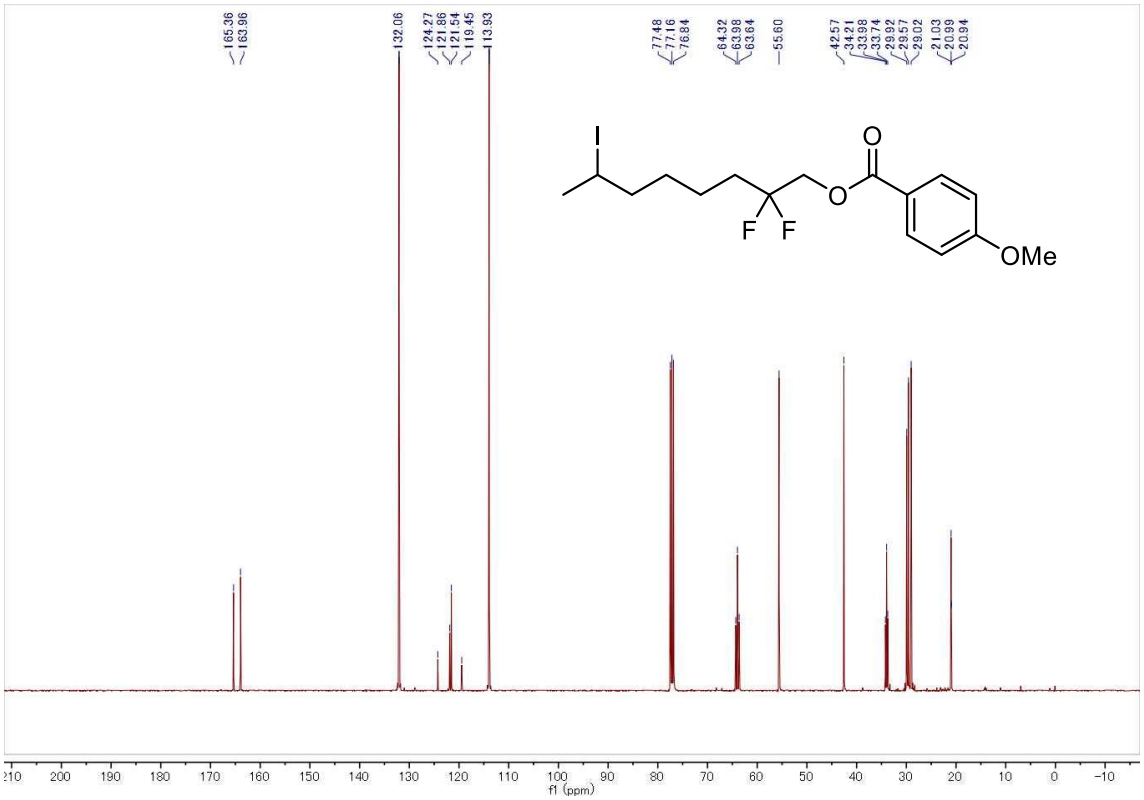
^{19}F NMR (376 MHz, $CDCl_3$) of 2g



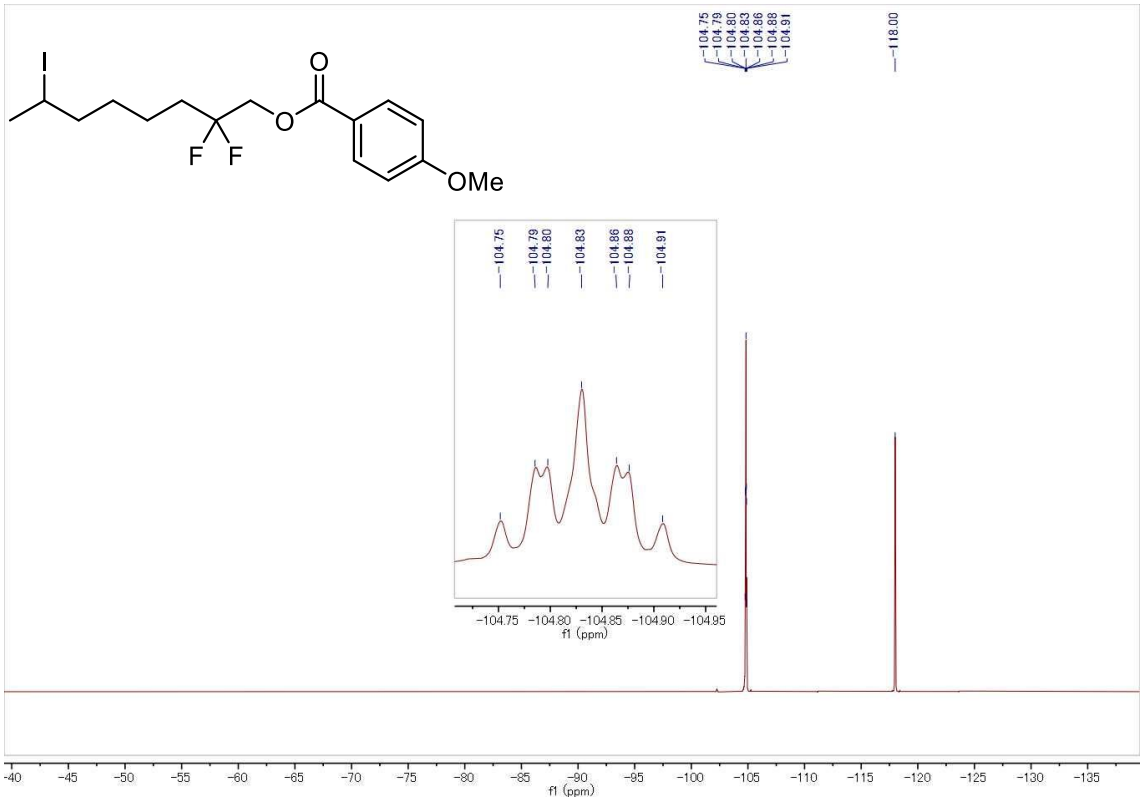
^{1}H NMR (400 MHz, $CDCl_3$) of 2j



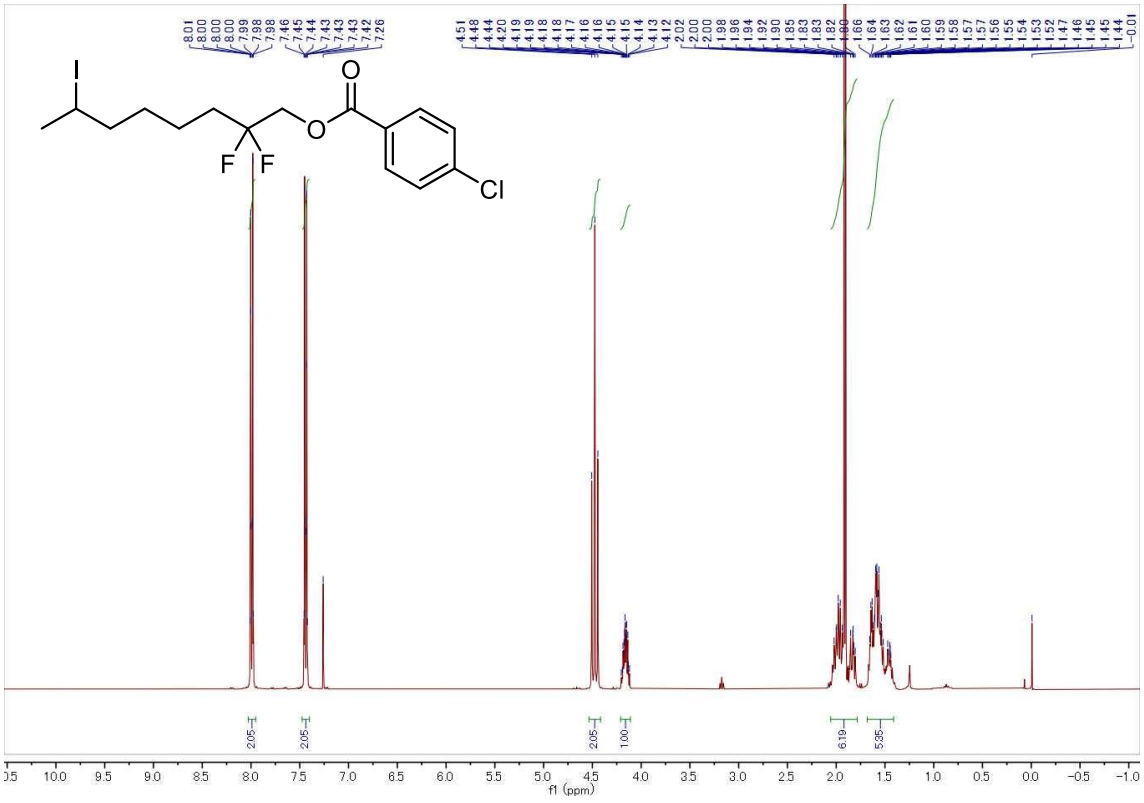
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of 2j



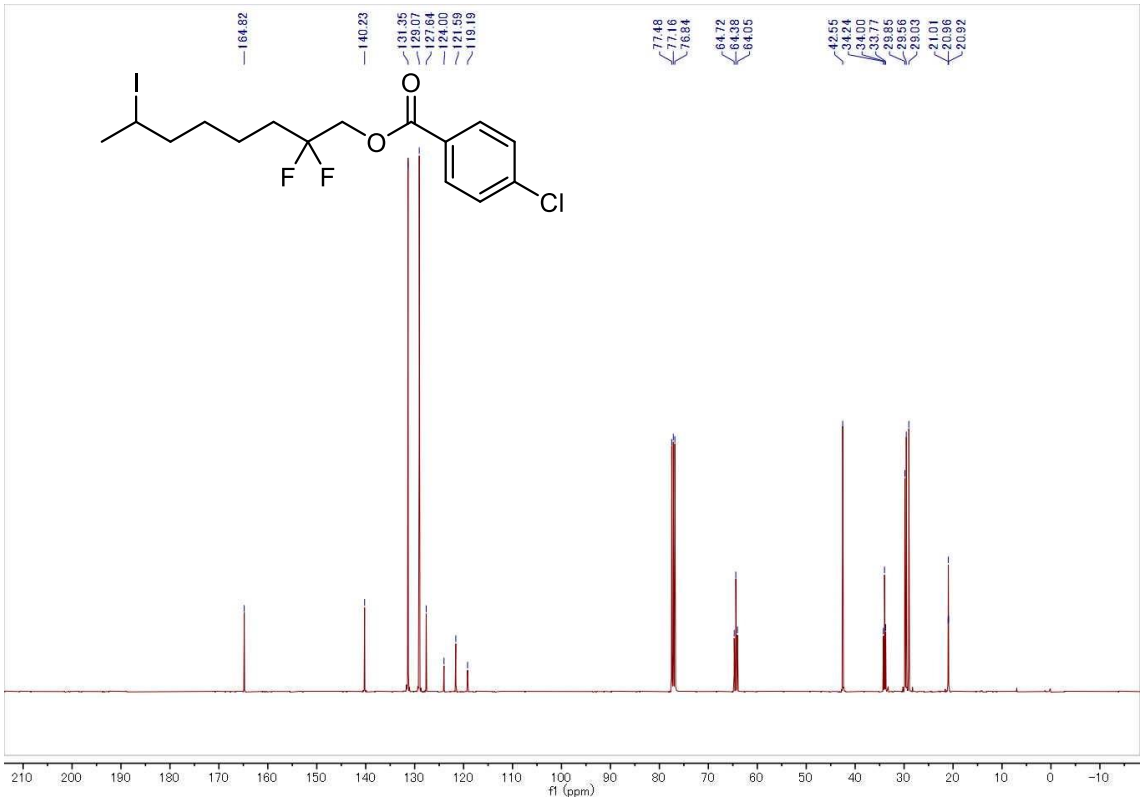
^{19}F NMR (376 MHz, $CDCl_3$) of 2j



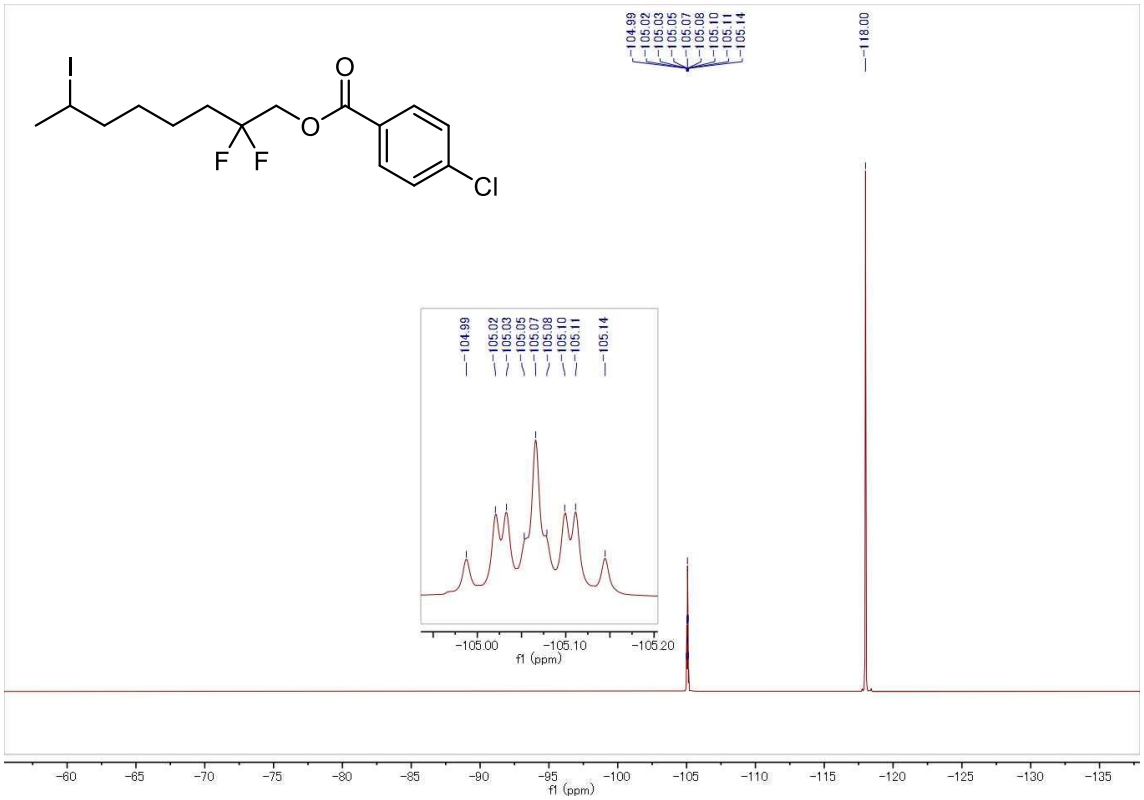
^{1}H NMR (400 MHz, $CDCl_3$) of 2k



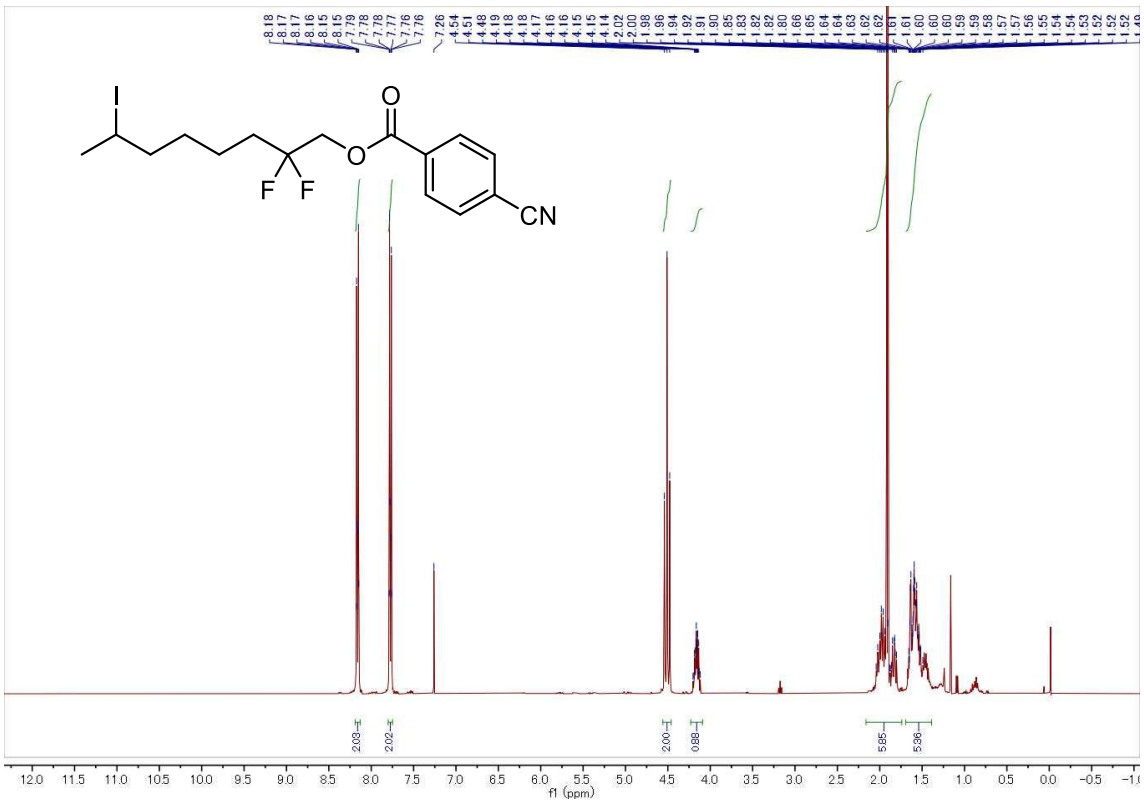
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 2k



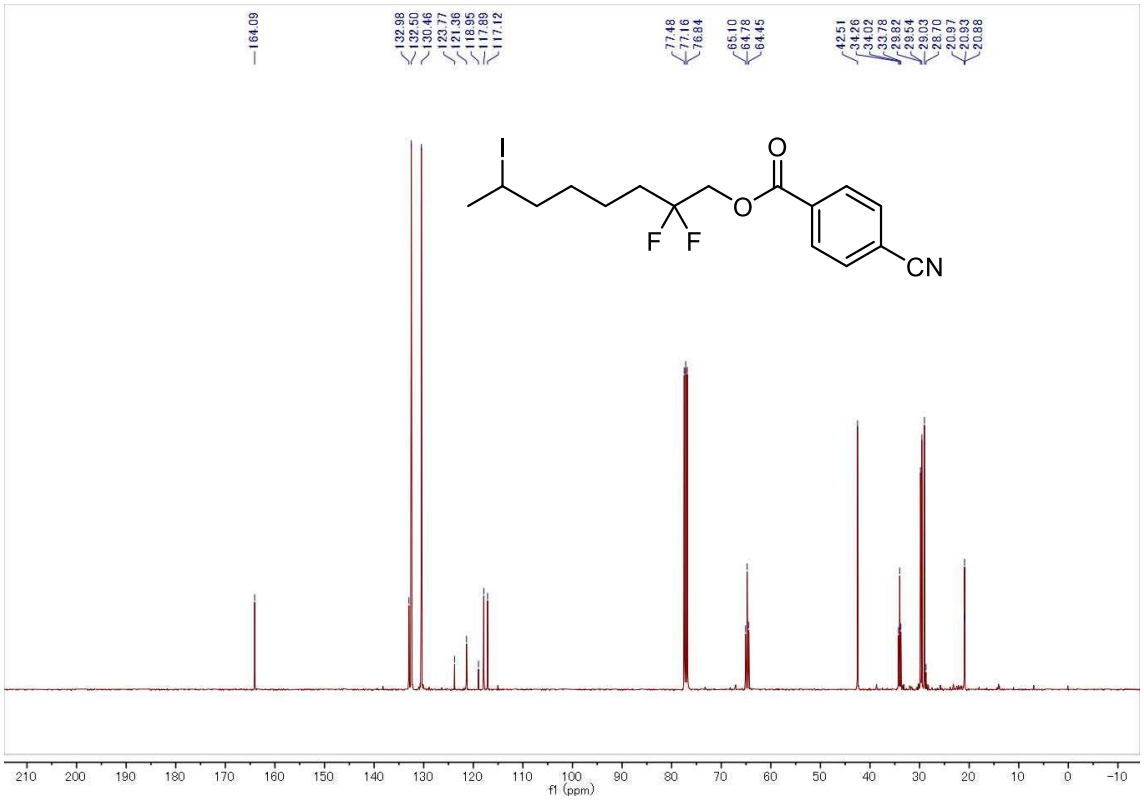
^{19}F NMR (376 MHz, $CDCl_3$) of 2k



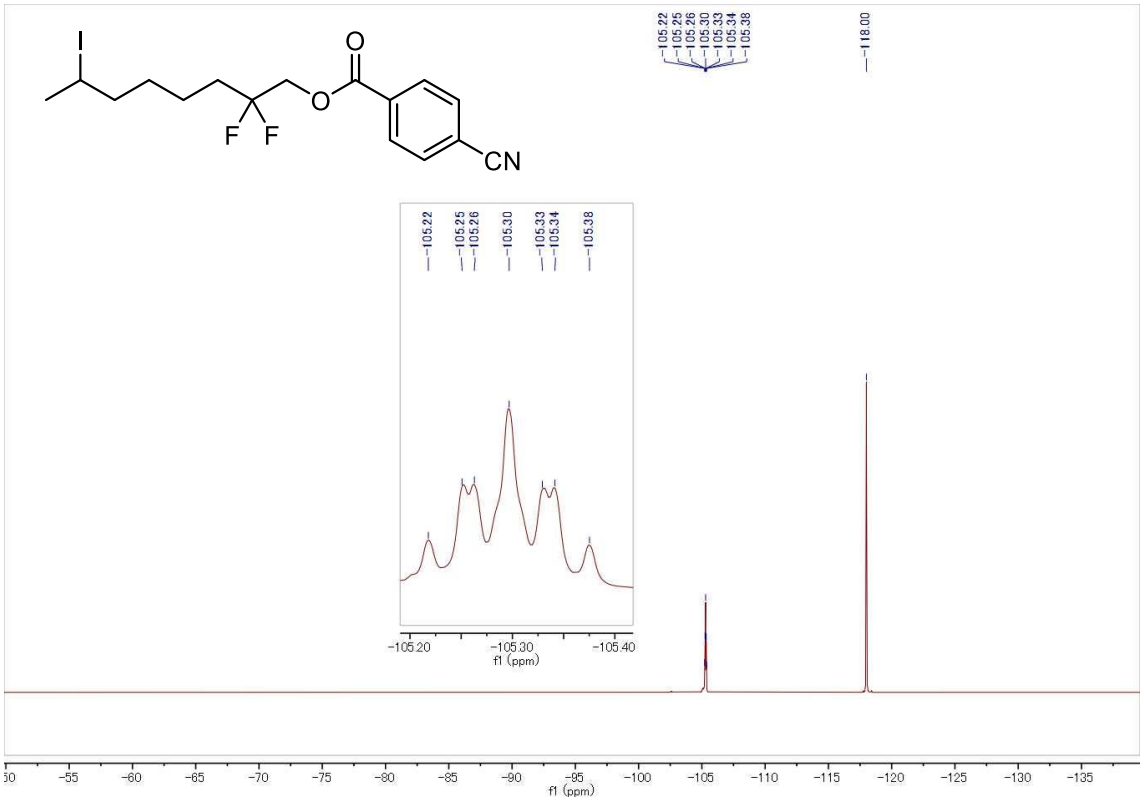
^{1}H NMR (400 MHz, $CDCl_3$) of 2l



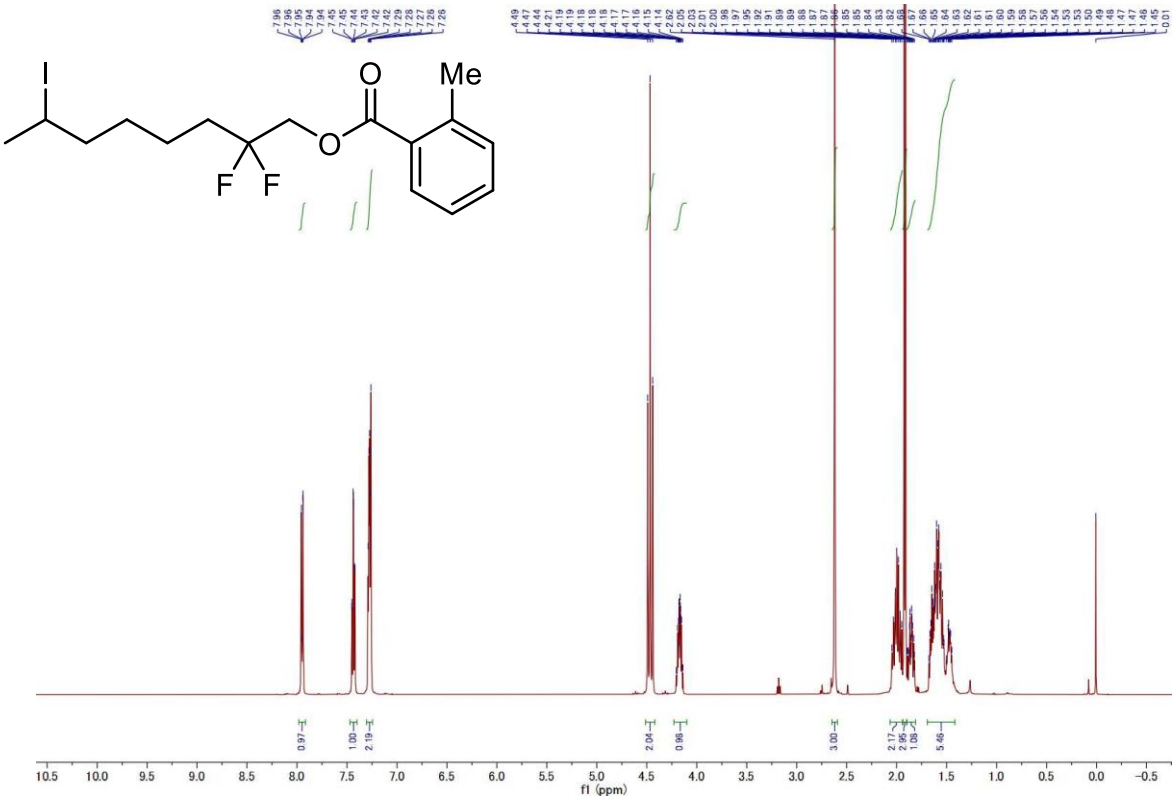
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of 2l



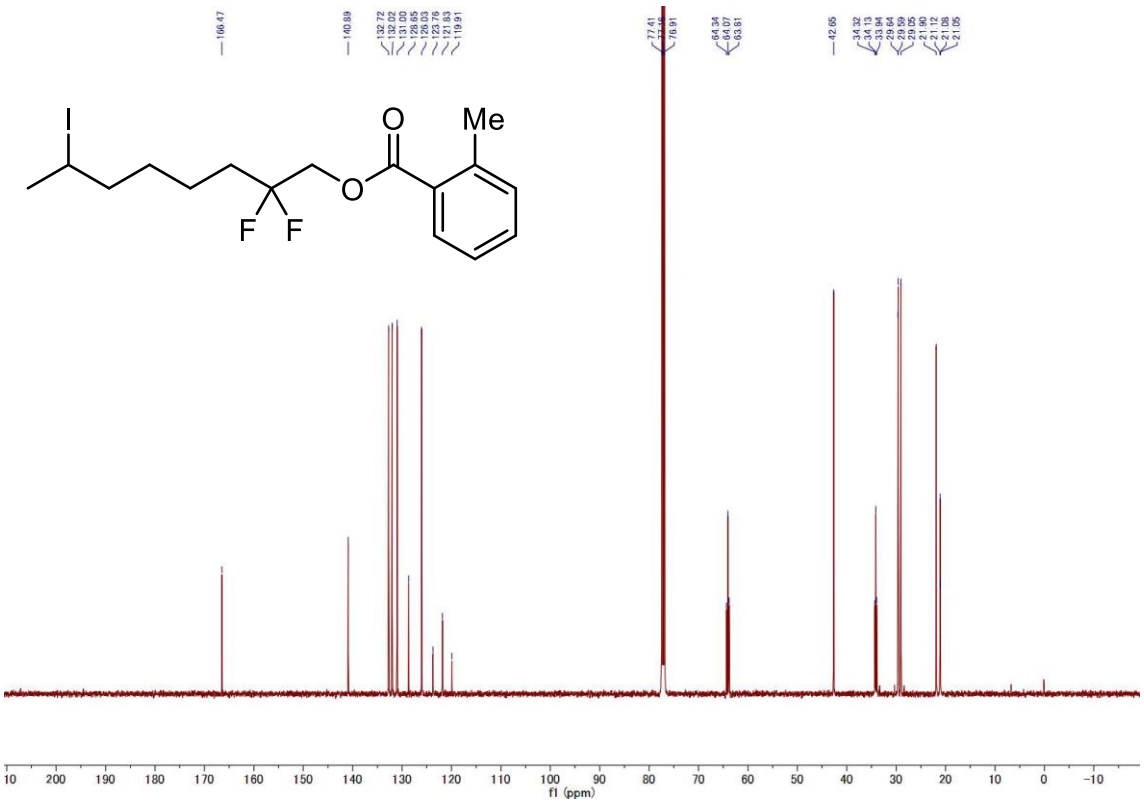
^{19}F NMR (376 MHz, $CDCl_3$) of 2l



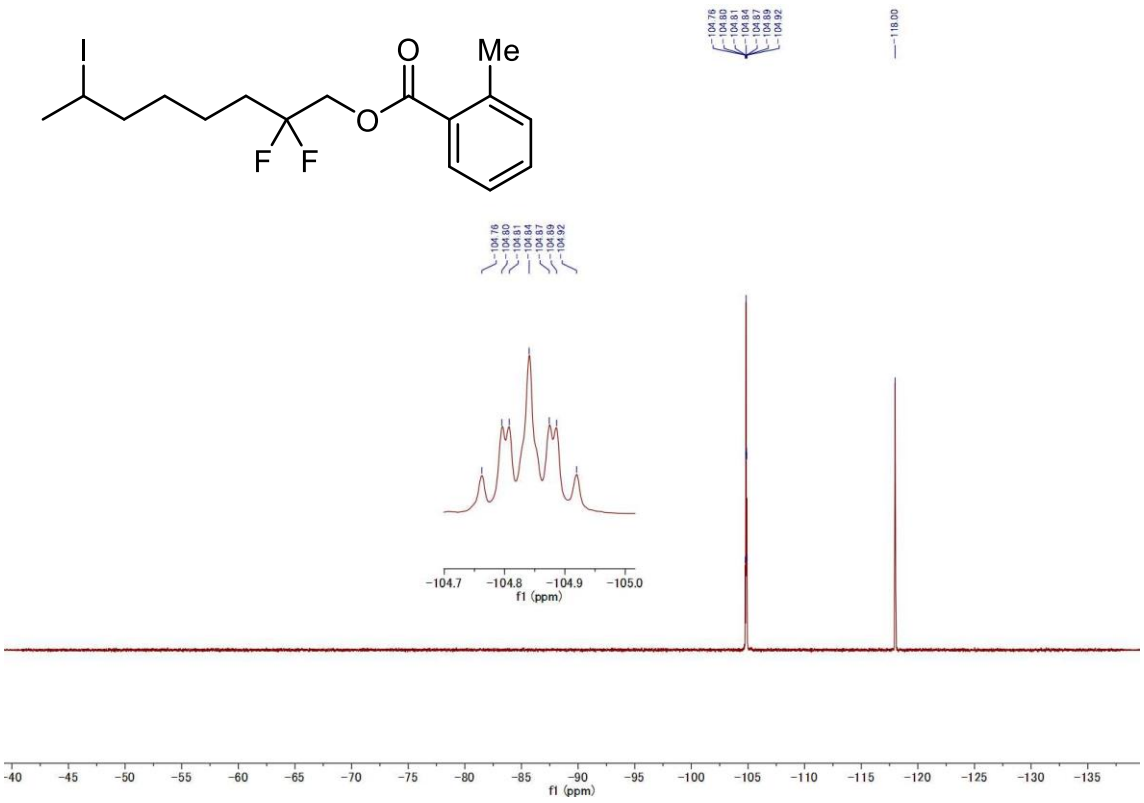
^{1}H NMR (400 MHz, $CDCl_3$) of 2n



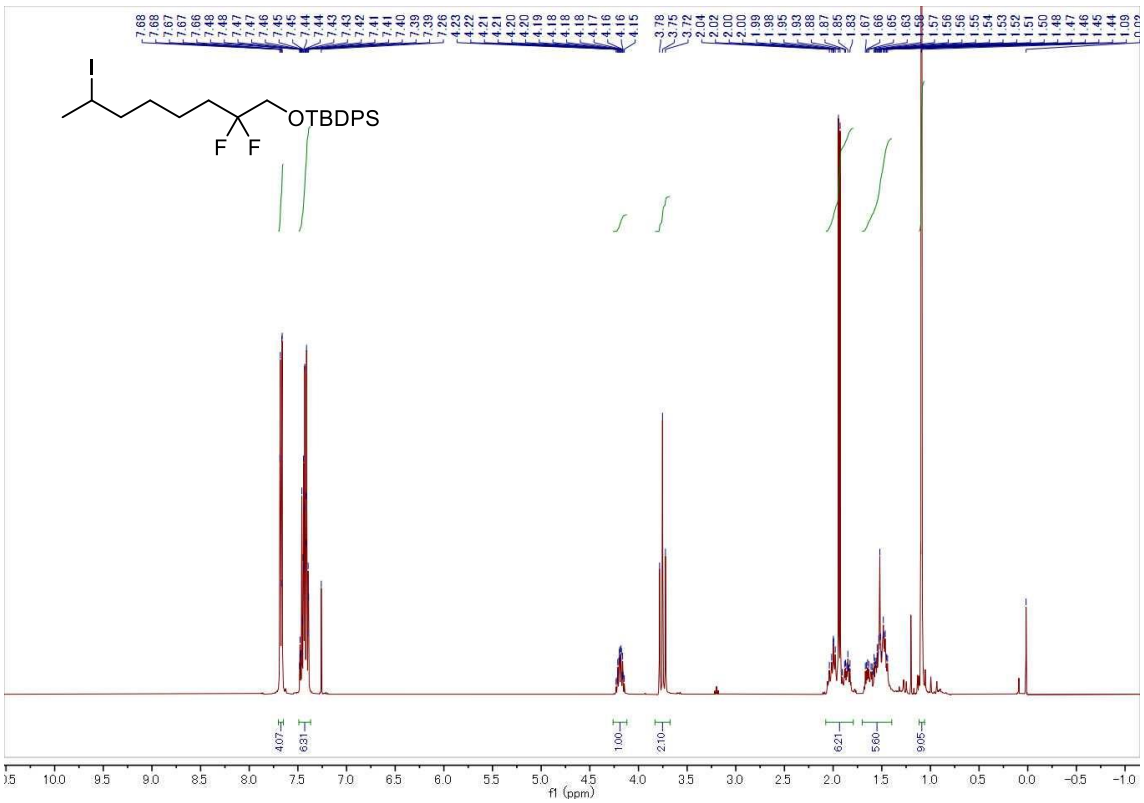
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of 2n



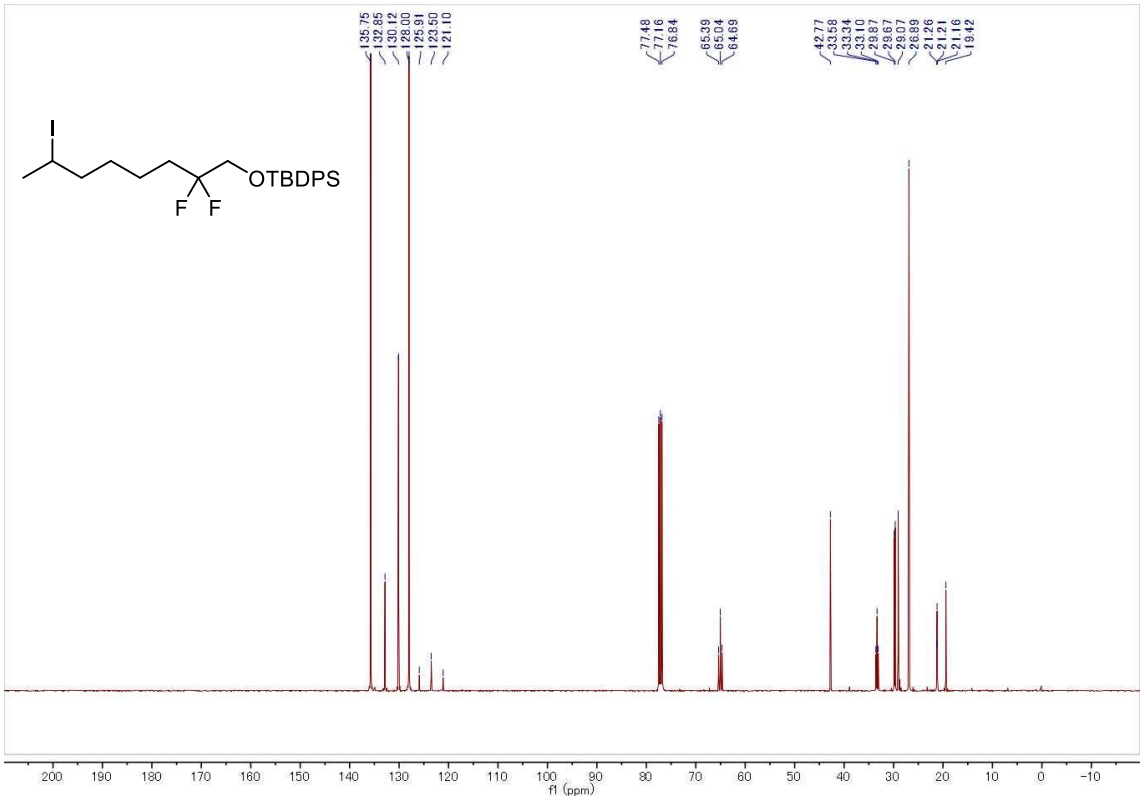
^{19}F NMR (376 MHz, $CDCl_3$) of 2n



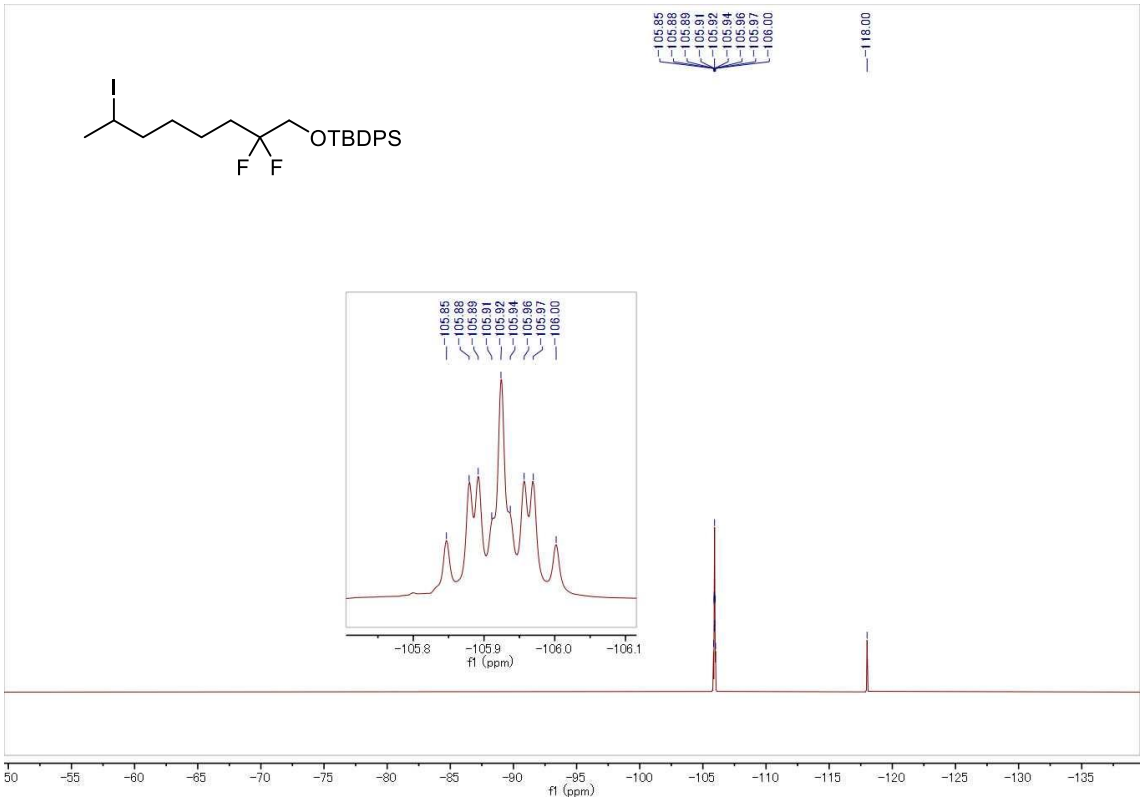
^{1}H NMR (400 MHz, $CDCl_3$) of 2o



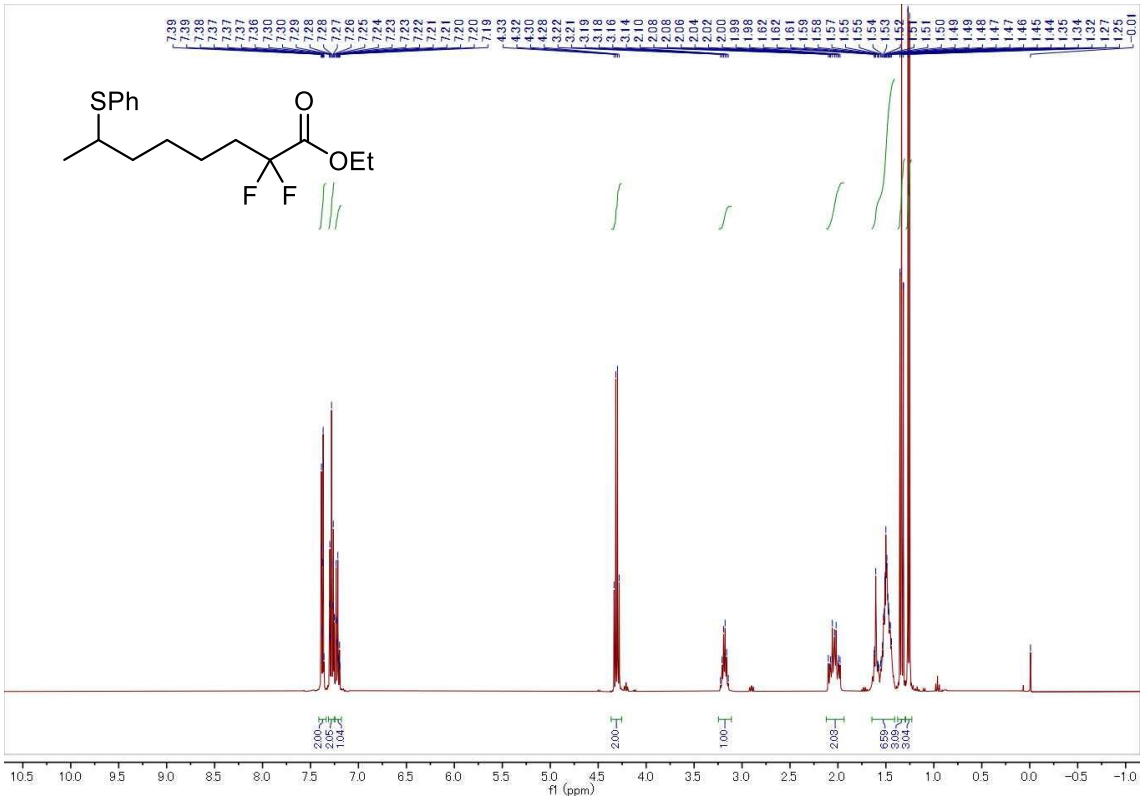
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of 2o



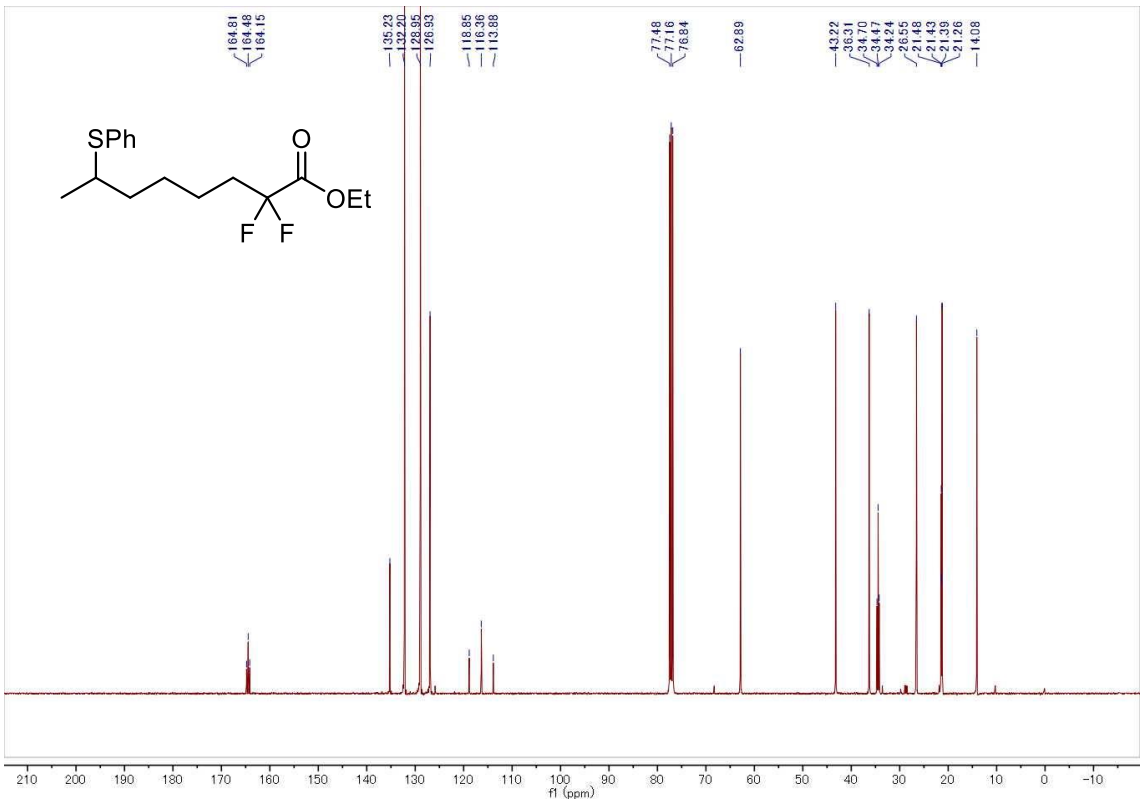
^{19}F NMR (376 MHz, $CDCl_3$) of 2o



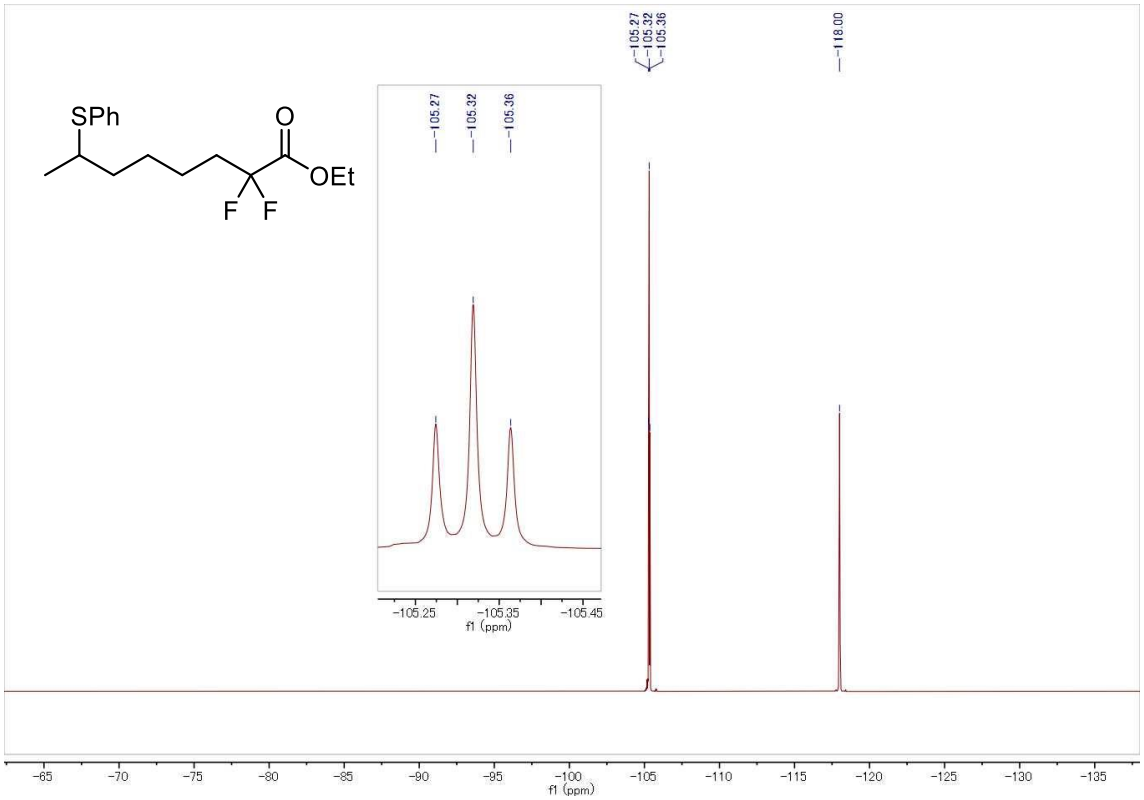
^{1}H NMR (400 MHz, $CDCl_3$) of 3



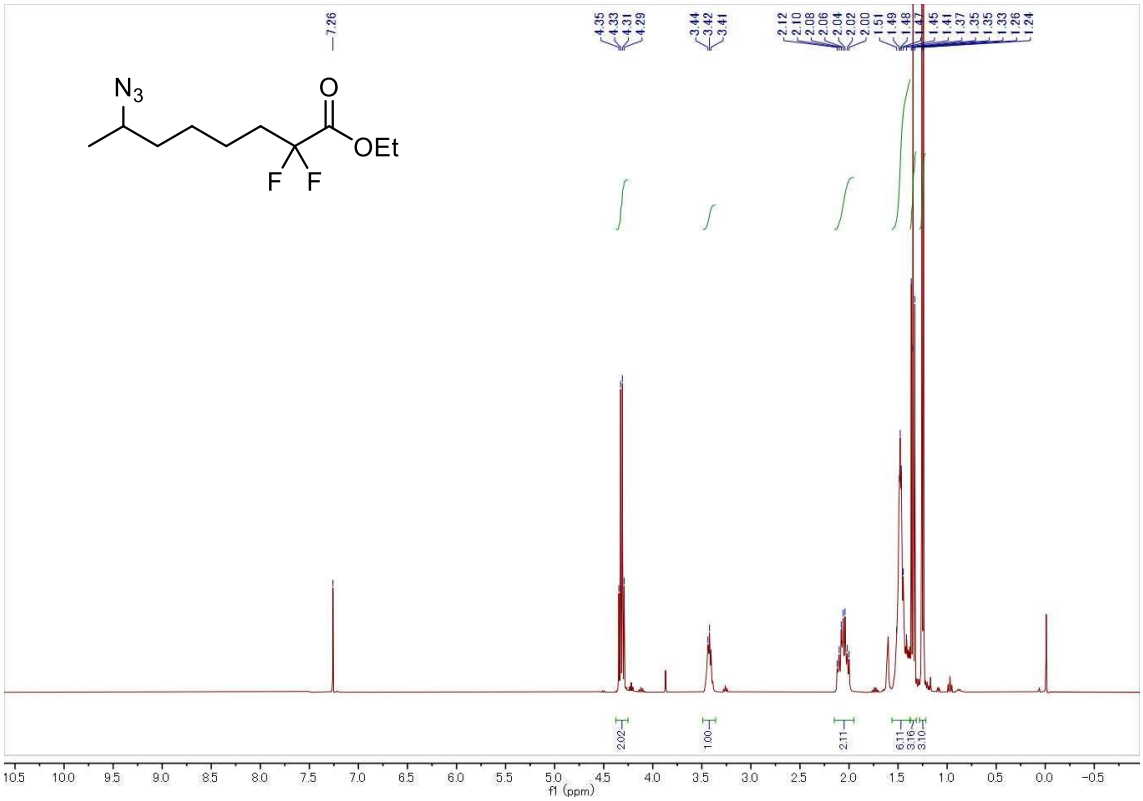
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of 3



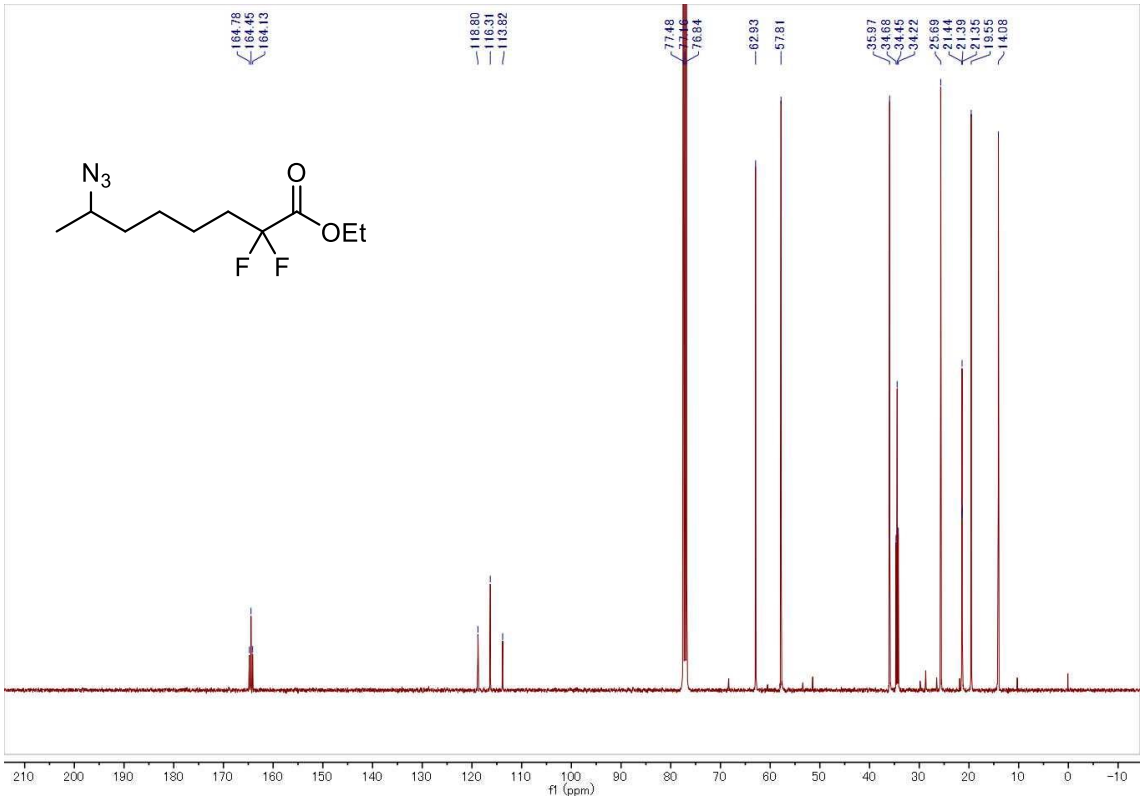
^{19}F NMR (376 MHz, $CDCl_3$) of 3



^{1}H NMR (400 MHz, $CDCl_3$) of 4



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of 4



^{19}F NMR (376 MHz, $CDCl_3$) of 4