Electronic Supplementary Material (ESI) for ChemComm.

Light-Mediated Iodoperfluoroalkylation of Alkenes/Alkynes Catalyzed by Chloride Ions: Role of Halogen Bonding

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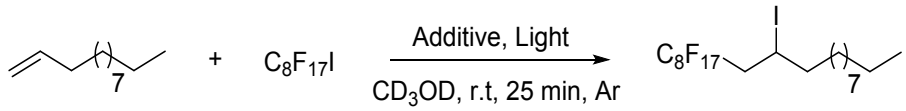
I. General experimental details

All reagents were obtained from commercial sources and used as received. Commercial anhydrous methanol (Sure/Seal, stored on molecular sieves) was used for the ATRA reactions. NMR analyses were carried out on a Bruker avanceII-400 and avanceII-300 (400 MHz and 300 MHz for proton, 101 MHz and 75 MHz for ^{13}C, 282 MHz for ^{19}F) in deuterated chloroform as solvent. The chemical shifts (δ) for carbon and proton resonances are given compared to the residual solvent peak and are expressed in ppm. Mass spectra were recorded by the CESAMO (Bordeaux, France) using electrospray ionisation (ESI) or electron impact ionization (EI). HRMS ESI spectra were obtained on a QStar Elite mass spectrometer (Applied Biosystems) using positive polarity electrospray ionization mode, electron impact ionization (EI) mass spectra were obtained on an ISQ mass spectrometer (Thermo Scientific) and HRMS EI spectra were obtained on a Accutof GCv mass spectrometer (JEOL). Absorption spectra were recorded on a Varian Cary 5000 spectrophotometer in 1 cm pathlength quartz cells. Photoirradiations (320-390 nm) were performed using a portable Fisher Bioblock mercury lamp (type Thin Layer Chromatography "TLC", 6W) set at 365 nm. The transmission spectrum in the UVA region of commercial borosilicate glass of 1 mm thickness can be found at: https://www.sinclairmfg.com/datasheets/optical3.html

Table S1. Optimization of the Reaction Conditions[a]



entry	additive	conversion (%)[b]	yield (%)[c]
1	-	6	4
2	Bu_4NCl (100 mol%)	100	>95
3	Bu_4NCl (10 mol%)	100	>95
4	Bu_4NCl (5 mol%)	83	80
5	Bu_4NCl (1 mol%)	45	41
6	Bu_4NCl (10 mol%)[d]	0	-
7	Bu_4NCl (10 mol%)[e]	0	-
8	Bu_4NCl (10 mol%)[f]	0	-
9	Bu_4NF (10 mol%)	37	32
10	Bu_4NBr (10 mol%)	0	-
11	Bu_4NI (10 mol%)	0	-
12	NaCl (10 mol%)	100	>95

[a] Standard conditions unless otherwise noted: Reactions conducted in NMR tubes in CD_3OD (0.7 mL) on 0.1 mmol of alkene and 0.12 mmol of $C_8F_{17}I$, degassing by Ar bubbling for 20 min, irradiation for 25 min by placing the low pressure Hg Lamp type TLC (set at 365 nm: emitted light ~ 320-390 nm) at ~ 1 cm from the tube. [b] Converted alkene. [c] Isolated yield. [d] Reaction in the dark. [e] Reaction in air. [f] Irradiation with a household CFL bulb (23W).

II. Emission, UV-Vis and NMR spectra.

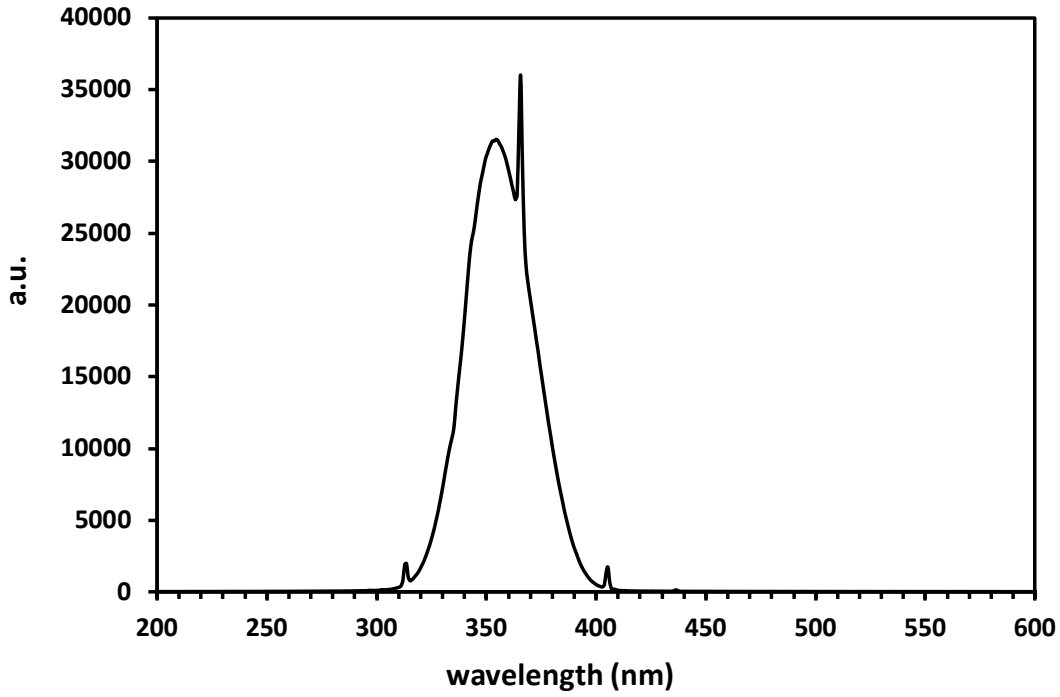


Figure S1: Emission spectrum of the low-pressure Hg lamp used in this study.

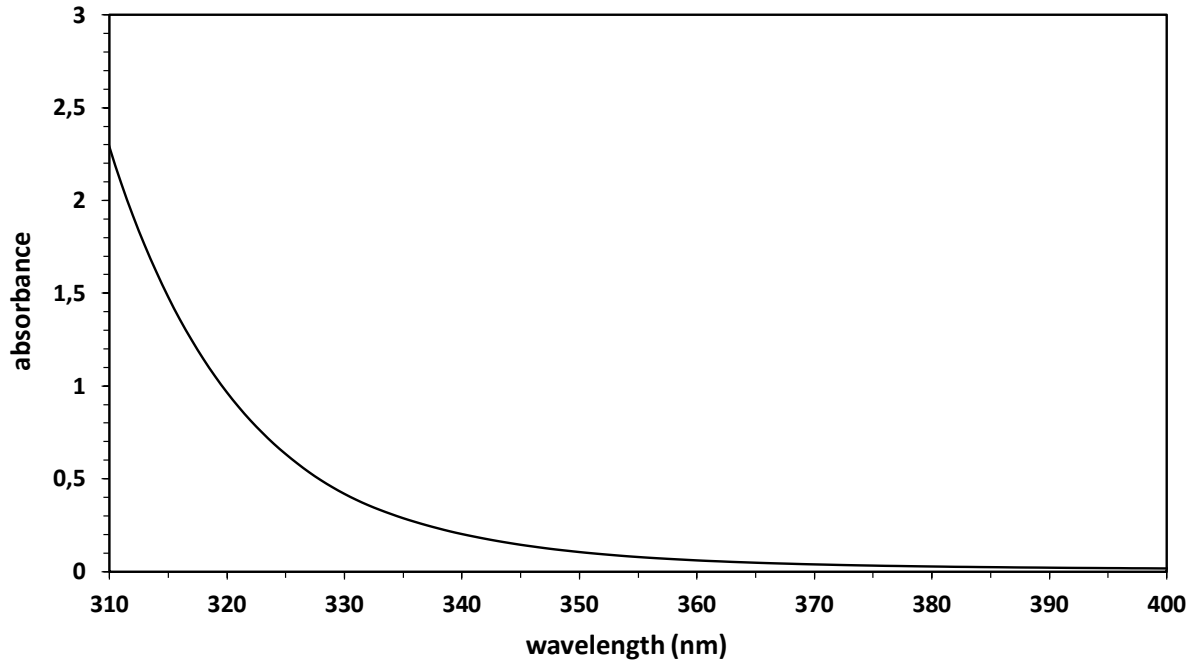


Figure S2: UV light absorption spectrum of a solution of $C_8F_{17}I$ in MeOH (0.15 M, quartz cuvette, path length 10 mm, 3 mL).

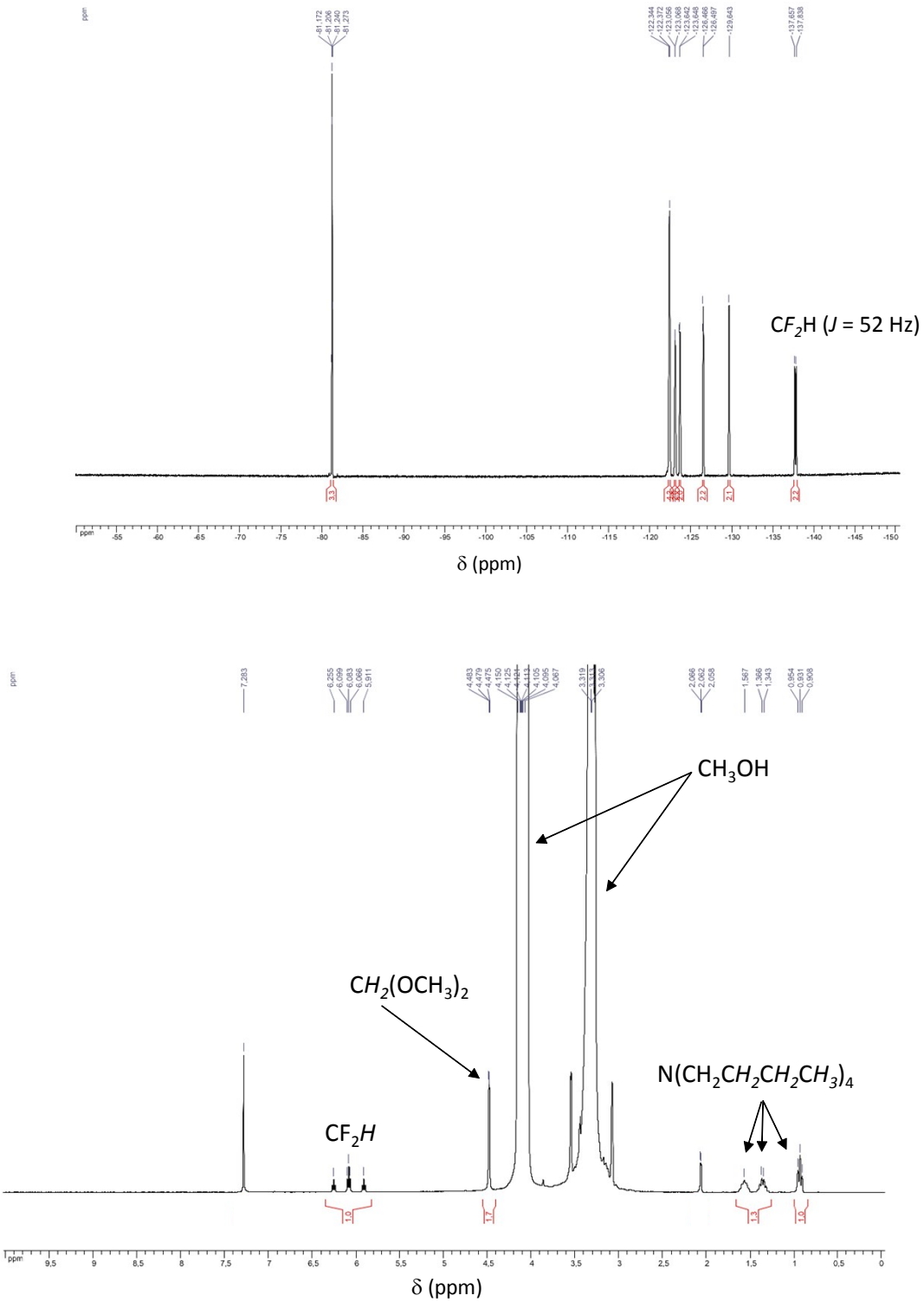


Figure S3 : ^{19}F (282 MHz) and ^{1}H (300 MHz) NMR spectra in $CDCl_3$ of an aliquot of the reaction mixture obtained after irradiation for 2 h of a deaerated MeOH solution (freeze-pump-thaw cycles, flame-sealed glassware) containing $C_8F_{17}I$ (0.15 M) and Bu_4NCl (10 mol%). Addition of an aliquot of an authentic sample of $CH_2(OCH_3)_2$ confirmed the proposed assignment.

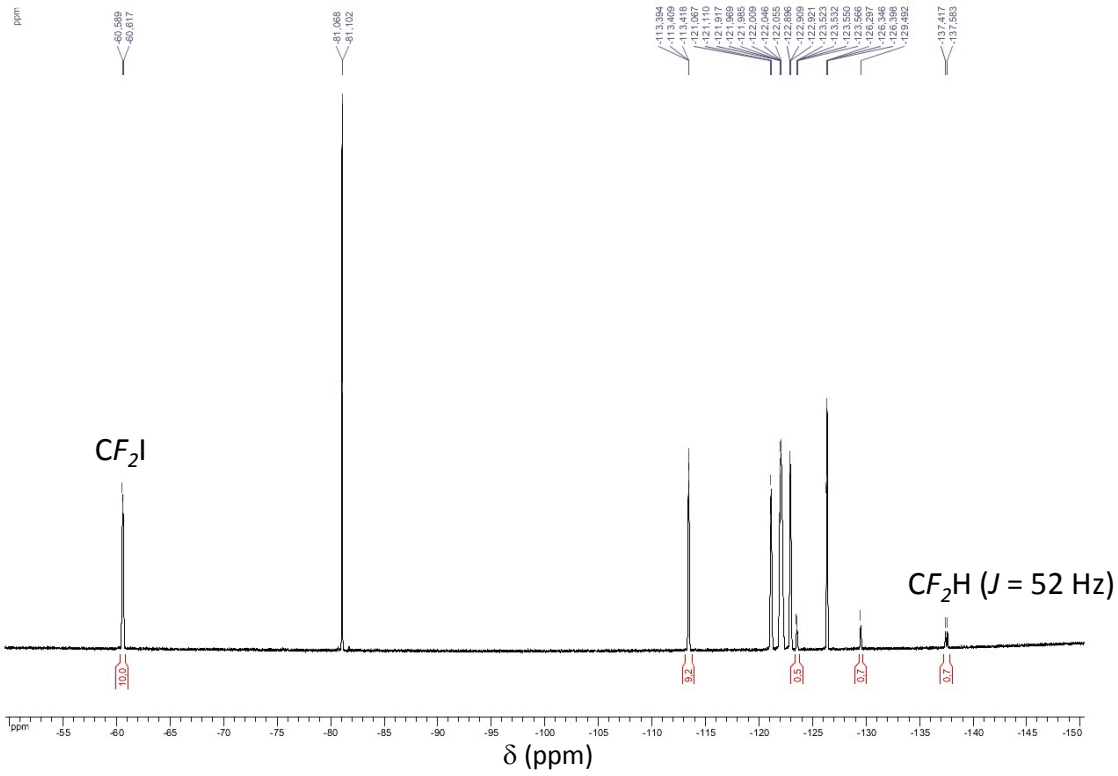
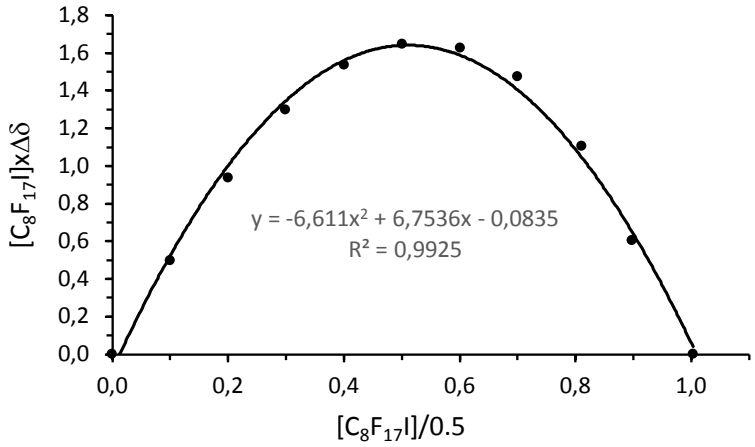


Figure S4. ^{19}F (282 MHz) NMR spectrum in $CDCl_3$ of an aliquot of the reaction mixture obtained after irradiation for 2 h of a deaerated MeOH solution (freeze-pump-thaw cycles, flame-sealed glassware) containing $C_8F_{17}I$ (0.15 M).

III. Determination of the binding stoichiometry of $C_8F_{17}I$ with Cl^- ($Bu_4N^+Cl^-$) in $CDCl_3$

The binding stoichiometry of $C_8F_{17}I$ with Cl^- ($Bu_4N^+Cl^-$) was determined by Job's plot analysis using ^{19}F NMR and the conditions employed by Chen and coworkers i.e. : $CDCl_3$ (0.5 mL); total amount of $C_8F_{17}I$ and $Bu_4N^+Cl^-$ kept constant at 0.25 mmol (0.5 M); molar ratios $[C_8F_{17}I]/[C_8F_{17}I + Cl^-]$ were 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0. Analysis of the NMR spectra afforded the results presented below.

$[C_8F_{17}I]$ (M)	δ CF_2I (ppm)	$\Delta\delta$ (ppm)	$[C_8F_{17}I]/[C_8F_{17}I + Cl^-]$	$[C_8F_{17}I]x\Delta\delta$ (M.ppm)
0	0	0	0	0
0.05	69.226	9.975	0.1	0.496
0.10	68.609	9.358	0.2	0.937
0.15	67.900	8.649	0.3	1.296
0.20	66.906	7.655	0.4	1.534
0.25	65.832	6.581	0.5	1.647
0.30	64.659	5.408	0.6	1.625
0.35	63.456	4.205	0.7	1.473
0.40	61.974	2.723	0.8	1.104
0.45	60.595	1.344	0.9	0.604
0.50	59.251	0	1.0	0

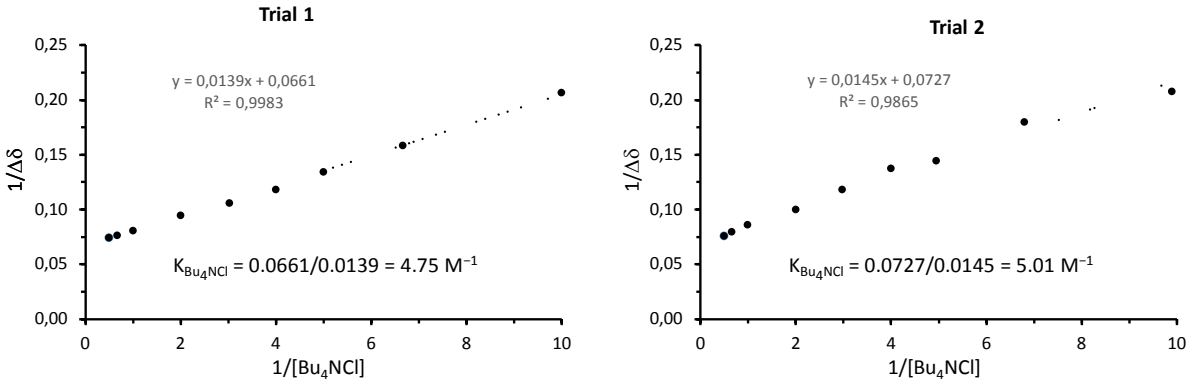


IV. Determination of the association constant (K_a) between $C_8F_{17}I$ and Cl^- ($Bu_4N^+Cl^-$) in $CDCl_3$

The association constant between $C_8F_{17}I$ and Cl^- ($Bu_4N^+Cl^-$) was determined with Hanna and Ashbaugh's graphical method using ^{19}F NMR and the conditions employed by Chen and coworkers i.e. : $CDCl_3$ (0.6mL); amount of $C_8F_{17}I$ kept constant at 0.03 mmol; amount of

$Bu_4N^+Cl^-$ varied from 0.06 to 1.2 mmol. Analysis of the NMR spectra afforded the results presented below.

Trial 1				Trial 2			
Cl^- (M)	1/ Cl^- (M^{-1})	Δδ (ppm)	1/Δδ	Cl^- (M)	1/ Cl^- (M^{-1})	Δδ (ppm)	1/Δδ
2	0.5	13.4727	0.0742	2	0.5	13.1543	0.0760
1.5	0.67	13.0661	0.0765	1.5	0.67	12.5283	0.0798
1	1.0	12.3411	0.0810	1	1.0	11.6243	0.0860
0.5	2.0	10.5643	0.0947	0.5	2.0	9.9859	0.1001
0.33	3.03	9.4127	0.1062	0.34	2.98	8.4493	0.1184
0.25	4.0	8.4684	0.1181	0.25	4.0	7.2583	0.1378
0.2	5.0	7.4312	0.1346	0.202	4.95	6.9250	0.1444
0.15	6.67	6.3073	0.1585	0.147	6.80	5.5603	0.1798
0.1	10	4.8308	0.2070	0.101	9.90	4.8156	0.2077

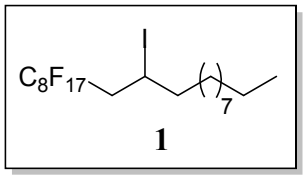


V. General procedure for the ATRAs of R_fI to alkenes and alkynes conducted on 1 mmol scale (scheme 1)

In a test tube (borosilicate glass, wall thickness 0.7 mm, diameter 1.6 cm, height 10 cm), or a Schlenk tube (wall thickness 1.8 mm, diameter 2 cm), was introduced a magnetic stir bar and a solution of anhydrous CH_3OH (7 mL) containing Bu_4NCl **A** or NaCl **B** (10 or 20 mol%), R_fI and the alkene or alkyne. Degassing was rapidly initiated (to avoid I_2 formation due to possible oxidation of adventitious HI) by gentle argon bubbling for 30 minutes (test tube) or, even better, by freeze-pump-thaw cycles and filling the tube with argon after the last vacuum pumping (the reaction mixture must remain colorless). It should be noted that a special attention should be taken in the deoxygenation procedure. The reaction was initiated by irradiating at 320-390 nm using a TLC lamp placed at ~ 1 cm from the test tube (irradiation times given in schemes 1-3).

Once the reaction was completed, the CH_3OH solvent was evaporated and the residue was purified by flash chromatography over silica gel (pentane/EtOAc).

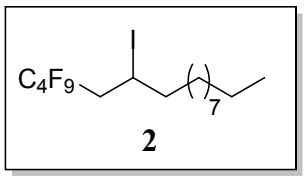
Compound 1: Synthesized from **A** (28 mg, 0.1 mmol) or **B** (5.8 mg, 0.1 mmol), dodec-1-ene (221 µL, 1 mmol) and $C_8F_{17}I$ (573.2 mg, 1.05 mmol) in CH_3OH (7 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to afford **1** as yellow oil in 87% yield (622 mg) with **A** and 85% yield (608 mg) with **B**.



1

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 4.40-4.26 (m, 1H), 3.06-2.63 (m, 2H), 1.94-1.67 (m, 2H), 1.62-1.17 (m, 16H), 0.88 (t, *J* = 6.3 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 41.7 (t, *J* = 20.7 Hz), 40.3, 31.9, 29.7, 29.54, 29.51, 29.4, 29.3, 28.5, 22.7, 20.9, 14.1; **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm) = -80.8, -111.1 to -115.3 (m), -121.60, -121.62, -121.9, -122.8, -123.6, -126.1; **EI-MS** (*m/z*, relative intensity): 714 (M–H, 2), 587 (M–I, 4), 531 (M–$C_4H_8I^+$, 5), 517 (M–CF_3HI^+, 5), 489 (M–$C_3H_5F_3I^+$, 5), 85 ($C_6H_{13}^+$, 40), 71 ($C_5H_{11}^+$, 66), 57 ($C_4H_9^+$, 100), 43 ($C_3H_7^+$, 70).

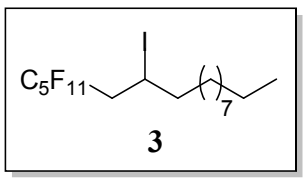
Compound 2: Synthesized from **A** (28 mg, 0.1 mmol) or **B** (5.8 mg, 0.1 mmol), dodec-1-ene (221 µL, 1 mmol) and C_4F_9I (180 µL, 1.05 mmol) in CH_3OH (7 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to affod **2** as yellow oil in 80% yield (412 mg) with **A** and 78% yield (401 mg) with **B**.



2

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 4.40-4.27 (m, 1H), 3.08-2.63 (m, 2H), 1.95-1.72 (m, 2H), 1.59-1.17 (m, 16H), 0.88 (t, *J* = 6.3 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 41.8 (t, *J* = 20.6 Hz), 40.5, 32.1, 29.8, 29.72, 29.69, 29.4, 28.7, 22.8, 21.0, 14.2; **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm) = -81.1, -111.3 to -115.6 (m), -124.6, -125.9; **HRMS** (FI+): Calcd. for $C_{16}H_{24}F_9I$: 514.0779, Found: 514.0801.

Compound 3: Synthesized from **A** (28 mg, 0.1 mmol) or **B** (5.8 mg, 0.1 mmol), dodec-1-ene (221 µL, 1 mmol) and $C_5F_{11}I$ (204 µL, 1.05 mmol) in CH_3OH (7 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to afford **3** as yellow oil in 85% yield (479.4 mg) with **A** and 82% yield (462.5 mg) with **B**.

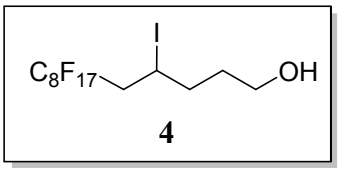


3

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 4.41-4.25 (m, 1H), 3.07-2.64 (m, 2H), 1.92-1.67 (m, 2H), 1.59-1.12 (m, 16H), 0.88 (t, *J* = 6.6 Hz,

3H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 41.9 (t, *J* = 20.9 Hz), 40.5, 32.1, 29.8, 29.73, 29.71, 29.55, 29.49, 28.7, 22.9, 21.1, 14.2; **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm) = -72.1, -111.0 to -116.5 (m), -116.6, -185.9; **EI-MS** (*m/z*, relative intensity): 563 (M-H, 5), 437 (M-I, 5), 395 (M-$C_3H_6I^+$, 5), 367 (M-$C_5H_{10}I^+$, 4), 339 (M-$C_7H_{14}I^+$, 4), 85 ($C_6H_{13}^+$, 40), 71 ($C_5H_{11}^+$, 66), 57 ($C_4H_9^+$, 100), 43 ($C_3H_7^+$, 80).

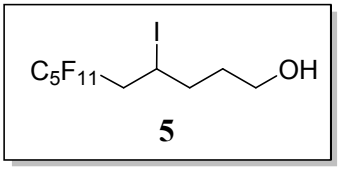
Compound 4: Synthesized from **A** (28 mg, 0.1 mmol) or **B** (5.8 mg, 0.1 mmol), pent-4-en-1-ol (102 µL, 1 mmol) and $C_8F_{17}I$ (573.2 mg, 1.05 mmol) in CH_3OH (7 mL). The residue was purified by flash chromatography over silica gel (pentane/EtOAc : 80/20) to afford **4** as yellow oil in 65% yield (411 mg) with **A** and 81% yield (510 mg) with **B**.



4

M.p. = 61-63 °C; **^{1}H-NMR** ($CDCl_3$, 300 MHz) δ (ppm) = 4.45-4.29 (m, 1H), 3.78-3.64 (m, 2H), 3.07-2.66 (m, 2H), 2.03-1.55 (m, 4H), 1.39 (s, 1H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 61.8, 41.9 (t, *J* = 21 Hz), 37.0, 32.8, 20.4; **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm) = -80.8, -111.1 to -115.3 (m), -121.58, -121.62, -121.9, -122.8, -123.6, -126.2; **CI-MS** (*m/z*, relative intensity): 631 (M-H, 5), 615 ($C_{13}H_9F_{17}I^+$, 100), 505 (M–I, 60), 487 ($C_{13}H_8F_{17}^+$, 50).

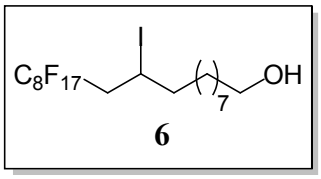
Compound 5: Synthesized from **A** (28 mg, 0.1 mmol) or **B** (5.8 mg, 0.1 mmol), pent-4-en-1-ol (102 µL, 1 mmol) and $C_5F_{11}I$ (204 µL, 1.05 mmol) in CH_3OH (7 mL). The residue was purified by flash chromatography over silica gel (pentane/EtOAc: 85/15) to afford **5** as colorless oil in 54 % yield (260 mg) with **A** and 77% yield (370 mg) with **B**.



5

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 4.44-4.29 (m, 1H), 3.69 (t, *J* = 6.3 Hz, 2H), 3.07-2.66 (m, 2H), 1.98-1.67 (m, 4H), 1.66 (s, 1H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 61.8, 41.9 (t, *J* = 21 Hz), 37.0, 32.8, 20.5; **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm) = -72.0, -111.0 to -115.2 (m), -116.6, -185.9; **EI-MS** (*m/z*, relative intensity): 465 (M–H_2O, 100), 355 (M–I, 40), 37 ($C_{10}H_9F_{11}$, 35).

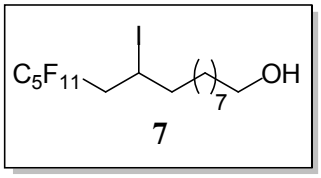
Compound 6: Synthesized from **A** (28 mg, 0.1 mmol) or **B** (5.8 mg, 0.1 mmol), undec-10-en-1-ol (200 µL, 1 mmol) and $C_8F_{17}I$ (573.2 mg, 1.05 mmol) in CH_3OH (7 mL). The residue was purified by flash chromatography over silica gel (pentane/EtOAc, 85/15) to afford **6** as yellow oil in 85% yield (605 mg) with **A** and 82% (584 mg) yield with **B**.



6

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 4.38-4.26 (m, 1H), 3.64 (t, *J* = 6.3 Hz, 2H), 3.04-2.65 (m, 2H), 1.92-1.69 (m, 2H), 1.65-1.49 (m, 2H), 1.45-1.18 (m, 12H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 63.2, 41.8 (t, *J* = 20.8 Hz), 40.5, 32.9, 29.7, 29.6, 29.5, 29.4, 28.6, 25.9, 21.0; **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm) = -80.8, -111.8 to -115.5 (m), -121.57, -121.60, -121.9, -122.7, -123.6, -126.2; **HRMS** (ESI): Calcd. for $C_{19}H_{22}F_{17}ONaI$: 739.0336; Found: 739.0336.

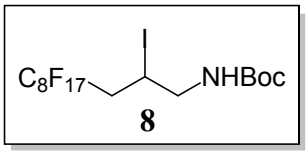
Compound 7: Synthesized from **B** (5.8 mg, 0.1 mmol), undec-10-en-1-ol (200 µL, 1 mmol) and $C_5F_{11}I$ (204 µL, 1.05 mmol) in CH_3OH (7 mL). The residue was purified by flash chromatography over silica gel (pentane/EtOAc, 85/15) to afford **7** as yellow oil in 80% yield (450 mg).



7

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 4.40-4.27 (m, 1H), 3.66 (t, *J* = 6.9 Hz, 2H), 3.06-2.71 (m, 2H), 1.92-1.71 (m, 2H), 1.65-1.54 (m, 3H), 1.44-1.26 (m, 11H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 63.1, 41.8 (t, *J* = 20.8 Hz), 40.4, 32.9, 29.7, 29.6, 29.5, 29.4, 28.6, 25.8, 21.1; **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm) = -72.0, -111.1 to -115.9 (m), -116.5, -185.8; **CI-MS** (*m/z*, relative intensity): 565 (M, 2), 549 ($C_{16}H_{21}F_{11}I^+$, 100), 439 ($C_{16}H_{22}F_{11}O^+$, 20), 421 ($C_7H_2F_{11}I^+$, 100), 365 ($C_{12}H_{12}F_{11}^+$, 30); **HRMS** (CI+): Calcd. for $C_{16}H_{21}F_{11}I$ (M-H_2O): 549.0512; Found: 549.0533.

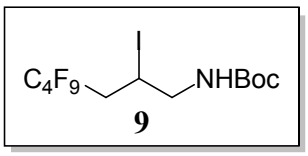
Compound 8: Synthesized from **A** (28 mg, 0.1 mmol) or **B** (5.8 mg, 0.1 mmol), tert-butyl allylcarbamate (157 mg, 1 mmol) and $C_8F_{17}I$ (573.2 mg, 1.05 mmol) in CH_3OH (7 mL). The residue was purified by flash chromatography over silica gel (pentane/EtOAc, 95/5), to afford **8** as a yellow solid in 71% yield (500 mg) with **A** and 67% yield (473 mg) with **B**.



8

Mp = 84-86 °C; **^{1}H-NMR** ($CDCl_3$, 300 MHz) δ (ppm) = 5.01 (brs, 1H), 4.43-4.31 (m, 1H), 3.67-3.33 (m, 2H), 2.98-2.62 (m, 2H), 1.45 (s, 9H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 155.8, 80.4, 49.1, 38.8 (t, *J* = 21.2 Hz), 28.4, 18.8; **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm) = -80.9, -111.5 to -115.0 (m), -121.7, -121.97, -121.98, -122.8, -123.7, -126.2; **HRMS** (ESI): Calcd. for $C_{16}H_{15}NO_2F_{17}NaI$: 725.9768, Found: 725.9765.

Compound 9: Synthesized from **A** (28 mg, 0.1 mmol), tert-butyl allylcarbamate (157 mg, 1 mmol) and C_4F_9I (180 µL, 1.05 mmol) in CH_3OH (7 mL). The residue was purified by flash

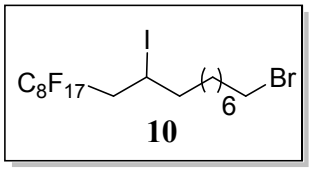


9

chromatography over silica gel (pentane/EtOAc, 95/5), to afford **9** as a yellow solid in 61% yield (307 mg,).

Mp = 68-70 °C; **^{1}H-NMR** ($CDCl_3$, 300 MHz) δ (ppm) = 5.04 (brs, 1H), 4.93-4.30 (m, 1H), 3.65-3.33 (m, 2H), 2.98-2.64 (m, 2H), 1.44 (s, 9H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 155.7, 80.4, 49.1, 38.6 (t, *J* = 21.1 Hz), 28.4, 18.7; **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm) = -81.1, -111.5 to -115.2 (m), -124.7, -126.0; **HRMS** (FI+): Calcd. for $C_{12}H_{15}NO_2F_9I$: 503.0003, Found: 503.0010.

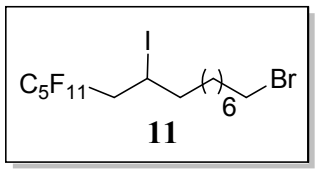
Compound 10: Synthesized from **A** (28 mg, 0.1 mmol) or **B** (5.8 mg, 0.1 mmol), 10-bromodec-1-ene (201 µL, 1 mmol) and $C_8F_{17}I$ (573.2 mg, 1.05 mmol) in CH_3OH (7 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to **10** as yellow oil in 89% yield (681 mg) with **A** and 80% yield (610 mg) with **B**.



10

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 4.40-4.25 (m, 1H), 3.40 (t, *J* = 6.9 Hz, 2H), 3.06-2.62 (m, 2H), 1.94-1.66 (m, 4H), 1.59-1.19 (m, 10H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 41.7 (t, *J* = 20.8 Hz), 40.4, 34.0, 32.9, 29.7, 29.3, 28.8, 28.5, 28.2, 21.0; **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm) = -80.9, -111.0 to -115.5 (m), -121.64, -121.67, -122.0, -122.8, -123.7, -126.2; **CI-MS** (*m/z*, relative intensity): 765 (M–H, 5), 685 (M–Br, 100), 637 (M–I, 90), 557 ($C_{18}H_{18}F_{17}^{+}$, 80), 503 ($C_{14}H_{10}F_{17}^{+}$, 30).

Compound 11: Synthesized from **B** (5.8 mg, 0.1 mmol), 10-bromodec-1-ene (201 µL, 1 mmol) and $C_5F_{11}I$ (204 µL, 1.05 mmol) in CH_3OH (7 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to afford **11** as colorless oil in 83% yield (513 mg).

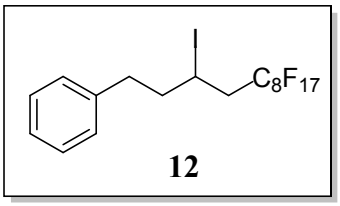


11

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 4.39-4.25 (m, 1H), 3.40 (t, *J* = 6.9 Hz, 2H), 3.04-2.68 (m, 2H), 1.92-1.69 (m, 4H), 1.56-1.19 (m, 10H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 41.9 (t, *J* = 20.8 Hz), 40.4, 34.0, 32.9, 29.7, 29.3, 28.8, 28.5, 28.2, 21.0; **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm) = -72.0, -110.8 to -115.4 (m), -116.5, -185.8; **HRMS** (CI+): Calcd. for $C_{15}H_{19}BrF_{11}$ (M-I) : 487.0494; Found: 487.0507.

Compound 12: Synthesized from **B** (5.8 mg, 0.1 mmol), but-3-en-1-ylbenzene (150 µL, 1 mmol) and $C_8F_{17}I$ (573 mg, 1.05 mmol) in CH_3OH (7 mL). The residue was purified by flash

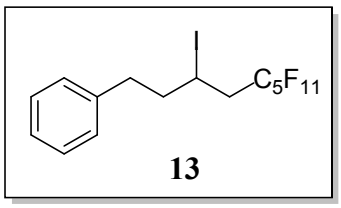
chromatography over silica gel (100% pentane) to afford **12** as pink solid in 88% yield (600 mg).



12

M.p. = 44-46 °C; **^{1}H-NMR** ($CDCl_3$, 300 MHz) δ (ppm) = 7.44-7.33 (m, 2H), 7.29-7.18 (m, 3H), 4.41-4.25 (m, 1H), 3.10-2.67 (m, 4H), 2.29-2.06 (m, 2H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 140.1, 128.8, 128.7, 126.6, 42.0 (t, *J* = 16.5 Hz), 41.9, 35.9, 20.2; **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm) = -81.1, -110.0 to -115.1 (m), -121.70, -121.73, -122.1, -122.9, -123.7, -126.4; **HRMS** (FI+): Calcd. for $C_{18}H_{12}F_{17}I$: 677.9712; Found: 677.9731.

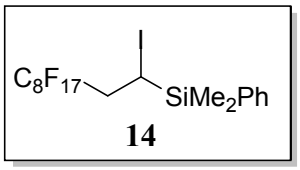
Compound 13: Synthesized from **A** (28 mg, 0.1 mmol), but-3-en-1-ylbenzene (150 µL, 1 mmol) and $C_5F_{11}I$ (204 µL, 1.05 mmol) in CH_3OH (7 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to afford **13** as yellow oil in 68% yield (460 mg).



13

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 7.40-7.31 (m, 2H), 7.27-7.19 (m, 3H), 4.30 (ddd, *J* = 5.1 Hz, *J* = 8.4 Hz and *J* = 13.3 Hz, 1H), 3.12-2.66 (m, 4H), 2.27-2.03 (m, 2H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 140.0, 128.8, 128.6, 126.5, 42.0 (t, *J* = 16.5 Hz), 41.9, 35.9, 20.3; **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm) = -72.0, -110.4 to -115.1 (m), -116.5, -185.9; **EI-MS** (*m/z*, relative intensity): 528 (M, 5), 401 (M-I, 5), 91 ($C_7H_7^+$, 100).

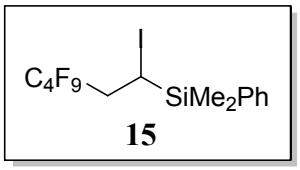
Compound 14: Synthesized from **A** (28 mg, 0.1 mmol) or **B** (5.8 mg, 0.1 mmol), dimethyl(phenyl)(vinyl)silane (192 µL, 1 mmol) and $C_8F_{17}I$ (573.2 mg, 1.05 mmol) in CH_3OH (7 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to afford **14** as colorless oil in 76% yield (535 mg) with **A** and 76% yield (535 mg) with **B**.



14

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 7.59-7.52 (m, 2H), 7.46-7.37 (m, 3H), 3.38 (dd, *J* = 2.7 Hz and *J* = 10.5 Hz, 1H), 2.79-2.37 (m, 2H), 0.53 (s, 3H), 0.52 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 134.5, 134.1, 130.3, 128.3, 38.4 (t, *J* = 21.5 Hz), -0.6, -3.0, -4.4; **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm) = -80.9, -112.9 to -116.7 (m), -121.7, -122.60, -122.4, -122.8, -123.7, -126.2; ; **HRMS** (FI+): Calcd. for $C_{18}H_{14}F_{17}ISi$: 707.9638, Found: 707.9628.

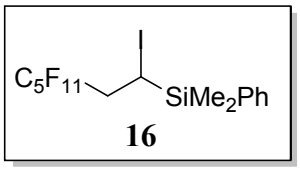
Compound 15: Synthesized from **A** (28 mg, 0.1 mmol) or **B** (5.8 mg, 0.1 mmol), dimethyl(phenyl)(vinyl)silane (192 µL, 1 mmol) and C_4F_9I (180 µL, 1.05 mmol) in CH_3OH (7 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to afford **15** as colorless oil in 80% yield (408 mg) with **A** and 79% yield (400 mg) with **B**.



15

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 7.57-7.51 (m, 2H), 7.47-7.35 (m, 3H), 3.37 (dd, *J* = 2.7 Hz and *J* = 10.2 Hz, 1H), 2.78-2.37 (m, 2H), 0.53 (s, 3H), 0.51 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 134.5, 134.1, 130.3, 128.3, 35.1 (t, *J* = 21.8 Hz), -0.6, -3.0, -4.4; **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm) = -81.1, -113.0 to -116.8 (m), -124.7, -126.0; **HRMS** (FI+): Calcd. for $C_{14}H_{14}F_9ISi$: 507.9765; Found: 507.9772.

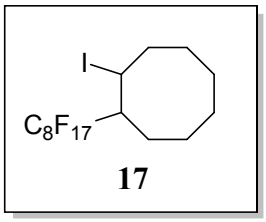
Compound 16: Synthesized from **A** (28 mg, 0.1 mmol) or **B** (5.8 mg, 0.1 mmol), dimethyl(phenyl)(vinyl)silane (192 µL, 1 mmol) and $C_5F_{11}I$ (204 µL, 1.05 mmol) in CH_3OH (7 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to afford **16** as colorless oil in 82 % yield (458 mg) with **A** and 85% yield (474 mg) with **B**.



16

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 7.58-7.51 (m, 2H), 7.47-7.37 (m, 3H), 3.37 (dd, *J* = 2.7 Hz and *J* = 10.5 Hz, 1H), 2.80-2.38 (m, 2H), 0.53 (s, 3H), 0.52 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 134.5, 134.1, 130.3, 128.3, 35.3 (t, *J* = 21.8 Hz), -0.4, -3.1, -4.4; **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm) = -72.0, -112.7 to -116.9 (m), -185.8; **HRMS** (FI+): Calcd. for $C_{15}H_{14}F_{11}ISi$: 557.9734; Found: 557.9746.

Compound 17: Synthesized from **A** (28 mg, 0.1 mmol) or **B** (5.8 mg, 0.1 mmol), (*Z*)-cyclooctene (130 µL, 1 mmol) and $C_8F_{17}I$ (573.2 mg, 1.05 mmol) in CH_3OH (7 mL). The residue was purified by flash chromatography over silica gel (pentane 100%) to afford **17** (d.r = 1:1) as yellow oil in 89% yield (584 mg) with **A** and 77% yield (505 mg) with **B**.

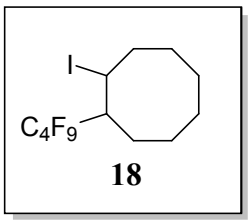


17

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 4.67-4.56 (m, 0.5H, d1 or d2), 4.55-4.48 (m, 0.5H, d1 or d2), 2.52-2.23 (m, 3H, d1 and d2), 2.18-1.96 (m, 3H, d1 and d2), 1.93-1.34 (m, 7H, d1 and d2); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 41.1 (t, *J* = 20.0 Hz, d1 or d2), 40.7 (t, *J* = 20.2 Hz, d1 or d2), 36.1 (d1 or d2), 35.0 (d1 or d2), 34.7 (d1 or d2), 34.0 (d1 or d2), 27.3 (d1 or d2), 27.2 (d1 or d2), 26.6 (d1 and d2), 25.5 (d1 or d2), 25.1 (d1 or d2), 25.0 (d1 or d2), 23.8 (d1 or d2), 23.6 (d1 or d2); **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm) = -81.0 (d1

or d2), -115.3 to -117.9 (m, d1 or d2), -119.9 (d1 or d2), -121.6 (d1 or d2), -121.9 (d1 or d2), -122.4 (d1 or d2), -126.2 (d1 or d2); **EI-MS** (*m/z*, relative intensity): 529 (M-I, 5), 109 ($C_8H_{13}^+$, 40), 81 ($C_6H_9^+$, 26), 69 ($C_5H_9^+$, 65), 55 ($C_4H_9^+$, 70), 43 ($C_3H_7^+$, 100).

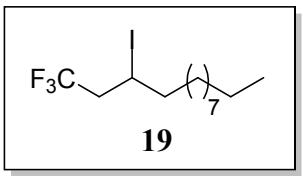
Compound 18: Synthesized from **A** (28 mg, 0.1 mmol) or **B** (5.8 mg, 0.1 mmol), (*Z*)-cyclooctene (130 µL, 1 mmol) and C_4F_9I (180 µL, 1.05 mmol) in CH_3OH (7 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to afford **18** (d.r = 1:1) as yellow oil in 63% yield (289 mg) with **A** and 79% yield (360 mg) with **B**.



18

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 4.64-4.56 (m, 0.5H, d1 or d2), 4.55-4.47 (m, 0.5H, d1 or d2), 2.53-2.22 (m, 3H, d1 and d2), 2.18-1.95 (m, 3H, d1 and d2), 1.92-1.33 (m, 7H, d1 and d2); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 40.9 (q, *J* = 20.0 Hz, d1 or d2), 40.6 (q, *J* = 20.2 Hz, d1 or d2), 39.7 (d1 or d2), 38.3 (d1 or d2), 36.1 (d1 or d2), 34.0 (d1 or d2), 35.0 (d1 or d2), 34.7 (d1 or d2), 33.9 (d1 and d2), 27.3 (d1 or d2), 27.2 (d1 or d2), 26.5 (d1 or d2), 25.0 (d1 or d2), 24.9 (d1 or d2), 23.7 (d1 or d2), 23.6 (d1 or d2); **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm) = -81.1 (d1 or d2), -115.4 to -118.3 (m, d1 or d2), -120.9 (d1 or d2), -126.3 (d1 or d2).

Compound 19: Synthesized from **A** (56 mg, 0.2 mmol) or **B** (11.6 mg, 0.2 mmol), dodec-1-ene (221 µL, 1 mmol), CF_3I (3 mmol, i.e. 6 mL of a 2 M stock solution in CH_3OH), and CH_3OH (1 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to afford **19** as yellow oil in 76% yield (277 mg) with **A** and 69% yield (250 mg) with **B**.

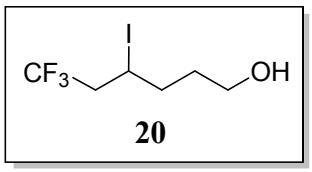


19

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 4.26-4.14 (m, 1H), 3.00-2.67 (m, 2H), 1.87-1.66 (m, 2H), 1.60-1.15 (m, 16H), 0.88 (t, *J* = 6.6 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 125.8 (q, *J* = 276.9 Hz), 45.1 (q, *J* = 28.1 Hz), 39.9, 32.1, 29.71, 29.69, 29.53, 29.47, 28.7, 22.8, 20.0, 14.3; **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm) = -64.0 (t, *J* = 10.4 Hz); **EI-MS** (*m/z*, relative intensity): 363 (M, 97), 237 (M-I, 75), 84 ($C_2H_3F_3^+$, 100), 70 (CF_3H or C_5H_{10}, 97), 56 (C_4H_8, 94); **HRMS** (ESI): Calcd. for $C_{13}H_{23}F_3I$: 363.0796; Found: 363.0806.

Compound 20: Synthesized from **A** (56 mg, 0.2 mmol) or **B** (11.6 mg, 0.2 mmol), pent-4-en-1-ol (102 µL, 1 mmol), CF_3I (3 mmol, i.e. 6 mL of a 2 M stock solution in CH_3OH), and CH_3OH (1 mL). The residue was purified by flash chromatography over silica gel (pentane/EtOAc:

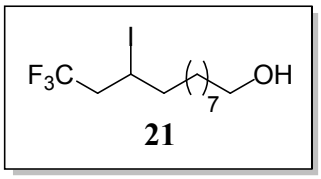
85/15) to afford **20** as yellow oil in 79% yield (223 mg) with **A** and 71% yield (200 mg) with **B**.



20

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 4.29-4.15 (m, 1H), 3.69 (t, *J* = 6.0 Hz, 2H), 2.98 (s, 1H), 2.97-2.70 (m, 2H), 1.93-1.57 (m, 4H),; **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 125.7 (q, *J* = 276.9 Hz), 61.7, 45.0 (q, *J* = 28.1 Hz), 36.2, 32.5, 21.3; **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm) = -63.9 (t, *J* = 10.2 Hz); **CI-MS** (*m/z*, relative intensity): 265 (M-H_2O, 100), 155 (M-I, 50), 137 ($C_6H_8F1_3^+$, 55).

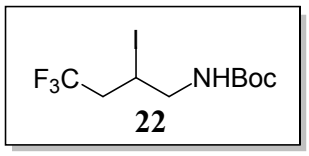
Compound 21: Synthesized from **A** (56 mg, 0.2 mmol) or **B** (11.6 mg, 0.2 mmol), undec-10-en-1-ol (200 µL, 1 mmol), CF_3I (3 mmol, i.e. 6 mL of a 2 M stock solution in CH_3OH), and CH_3OH (1 mL). The residue was purified by flash chromatography over silica gel (pentane/EtOAc, 85/15) to afford **21** as yellow oil in 81% yield (296 mg) with **A** and 88% yield (321 mg) with **B**.



21

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 4.24-4.10 (m, 1H), 3.63 (t, *J* = 6.6 Hz, 2H), 2.99-2.63 (m, 2H), 1.82-1.64 (m, 3H), 1.56-1.44 (m, 3H), 1.35-1.23 (m, 10H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 125.7 (q, *J* = 277.0 Hz), 63.0, 45.0 (q, *J* = 28.0 Hz), 39.8, 32.8, 29.6, 29.5, 29.4, 29.3, 28.6, 25.8, 22.0; **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm) = -63.9 (t, *J* = 10.4 Hz); **HRMS** (ESI): Calcd. for $C_{12}H_{22}F_3NaI$: 389.0559; Found: 389.0551.

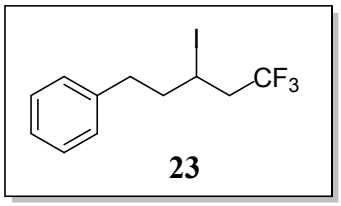
Compound 22: Synthesized from **A** (56 mg, 0.2 mmol) or **B** (11.6 mg, 0.2 mmol), tert-butyl allylcarbamate (157 mg, 1 mmol), CF_3I (3 mmol, i.e. 6 mL of a 2 M stock solution in CH_3OH), and CH_3OH (1 mL). The residue was purified by flash chromatography over silica gel (pentane/EtOAc: 95/5) to afford **22** as white solid in 65% yield (229 mg) with **A** and 59% yield (207 mg) with **B**.



22

M.p.= 67-69 °C; **^{1}H-NMR** ($CDCl_3$, 300 MHz) δ (ppm) = 5.05 (brs, 1H), 4.32-4.16 (m, 1H), 3.62-3.31 (m, 2H), 2.89-2.62 (m, 2H), 1.44 (s, 9H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 155.7, 125.5 (q, *J* = 276 Hz), 80.3, 48.7, 41.9 (q, *J* = 28.0 Hz), 28.4, 20.1; **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm) = -63.9 (t, *J* = 9.9 Hz); **HRMS** (FI+): Calcd. for $C_9H_{15}O_2F_3NI$: 353.0099; Found: 353.0104.

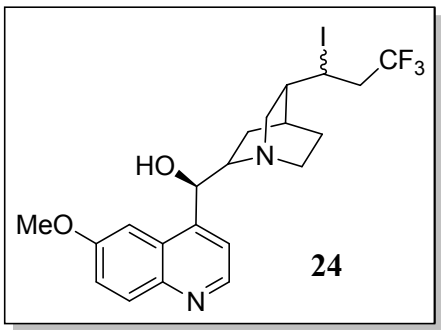
Compound 23: Synthesized from **A** (56 mg, 0.2 mmol) or **B** (11.6 mg, 0.2 mmol), but-3-en-1-ylbenzene (150 µL, 1 mmol), CF_3I (3 mmol, i.e. 6 mL of a 2 M stock solution in CH_3OH), and CH_3OH (1 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to afford **23** as yellow oil in 84% yield (283 mg) with **B**.



23

^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.30-7.19 (m, 2H), 7.14-7.07 (m, 3H), 4.14-3.95 (m, 1H), 2.98-2.76 (m, 2H), 2.75-2.52 (m, 2H), 2.14-1.87 (m, 2H); **^{13}C-NMR** ($CDCl_3$, 101 MHz) δ (ppm) = 140.1, 128.7, 128.6, 126.5, 125.7 (q, J = 278 Hz), 45.1 (q, J = 29.2 Hz), 41.3, 35.6, 21.1; **^{19}F-NMR** ($CDCl_3$, 376 MHz) δ (ppm) = -63.7 (t, J = 11.3 Hz); **CI-MS** (*m/z*, relative intensity): 327 (M, 25), 201 (M-I, 30), 91 ($C_7H_7^+$, 100); **HRMS** (CI+): Calcd. for $C_{11}H_{12}F_3I$: 327.9935; Found: 327.9947.

Compound 24: Synthesized from **B** (11.6 mg, 0.2 mmol), (-)-Quinine (324 mg, 1 mmol), CF_3I (3 mmol, i.e. 6 mL of a 2 M stock solution in CH_3OH), and CH_3OH (1 mL). The residue was purified by flash chromatography over silica gel (EtOAc 100%) to afford **24** (d.r = 2:1) as yellow solid in 73% yield (380 mg).

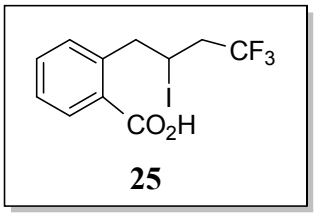


24

M.p. = 203-205 °C; **^{1}H-NMR** ($CDCl_3$, 300 MHz) δ (ppm) = 8.69-8.57 (m, 1H, d1 and d2), 7.81-7.60 (m, 2H, d1 and d2), 7.13-7.00 (m, 2H, d1 and d2), 6.58-6.52 (m, 0.66H, d1), 6.49-6.44 (m, 0.33H, d2), 5.92 (brs, 1H, d1 and d2), 4.44-4.26 (m, 1H, d1 and d2), 3.82-3.52 (m, 5H, d1 and d2), 3.48-3.34 (m, 1H, d1 and d2), 3.28-3.05 (m, 1H, d1 and d2), 2.90-2.47 (m, 4H, d1 and d2), 2.41-2.05 (m, 3H, d1 and d2), 1.99-1.80 (m, 1H, d1 and d2), 1.45-1.27 (m, 1H, d1 and d2); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) (**d1**) = 158.71, 146.85, 144.2, 143.2, 130.8, 126,88, 125.58, 123.20, 119.3, 100.5, 65.7, 60.2, 59.3, 58.7, 44.3, 42.2-41.8 (m), 41.7, 25.4, 24.2, 21.1, 17.8; (**d2**) = 158.74, 146.81, 144.0, 143.3, 130.9, 126,91, 125.55, 123.22, 122.9, 100.4, 65.9, 60.0, 58.5, 54.5, 44.1, 42.2-41.8 (m), 39.6, 28.3, 24.4, 20.1, 17.6; **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm) = -62.8 (t, J = 9.6 Hz, d1), -63.1 (t, J = 9.6 Hz, d2); **HRMS** (ESI): [M+H] $C_{21}H_{25}N_2O_2F_3I$: 521.0907; Found: 521.0914.

Compound 25: Synthesized from **A** (56 mg, 0.2 mmol) or **B** (11.6 mg, 0.2 mmol), 2-allylbenzoic acid (162 mg, 1 mmol), CF_3I (3 mmol, i.e. 6 mL of a 2 M stock solution in CH_3OH), and CH_3OH (1 mL). The residue was purified by flash chromatography over silica

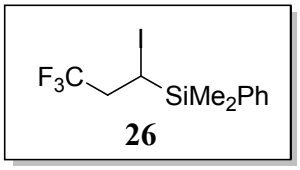
gel (pentane/EtOAc, 90/10) to afford **25** as yellow oil in 73% yield (263 mg) with **A** and 56% yield (100 mg) with **B**.



25

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 8.18 (dd, *J* = 1.2 Hz and *J* = 7.8 Hz, 1H), 7.58 (td, *J* = 1.2 Hz and *J* = 7.5 Hz, 1H), 7.44 (td, *J* = 1.5 Hz and *J* = 7.5 Hz, 1H), 7.33 (dd, *J* = 0.9 Hz and *J* = 7.8 Hz, 1H), 4.61-4.43 (m, 1H), 3.85 (dd, *J* = 4.8 Hz and *J* = 13.8 Hz, 1H), 3.38 (dd, *J* = 9.6 Hz and *J* = 13.8 Hz, 1H), 3.13-2.78 (m, 2H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 172.4, 141.7, 133.4, 133.1, 132.6, 130.0, 127.9, 125.8 (q, *J* = 276.8 Hz), 45.5, 44.9 (q, *J* = 29.2 Hz), 21.5 (q, *J* = 3.0 Hz); **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm) = -63.5 (t, *J* = 10.2 Hz); **HRMS** (ESI): Calcd. for [M-I] $C_{11}H_{10}O_2F_3$: 231.0638; Found: 231.0642.

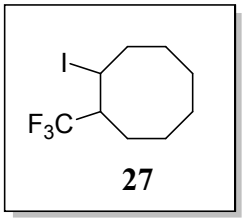
Compound 26: Synthesized from **A** (56 mg, 0.2 mmol) or **B** (11.6 mg, 0.2 mmol), dimethyl(phenyl)(vinyl)silane (192 µL, 1 mmol), CF_3I (3 mmol, i.e. 6 mL of a 2 M stock solution in CH_3OH), and CH_3OH (1 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to afford **26** as colorless oil in 77% yield (270 mg) with **A** and 81% yield (290 mg) with **B**.



26

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 7.58-7.52 (m, 2H), 7.47-7.36 (m, 3H), 3.28 (dd, *J* = 2.7 Hz and *J* = 11.1 Hz, 1H), 2.71-2.40 (m, 2H), 0.53 (s, 3H), 0.51 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 134.6, 134.1, 130.2, 128.3, 126.2 (q, *J* = 277.0 Hz), 38.4 (q, *J* = 28.9 Hz), 2.1 (q, *J* = 2.3 Hz), -2.9, -4.5; **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm) = -65.0 (t, *J* = 11.3 Hz); **HRMS** (FI+): Calcd. for $C_{11}H_{14}F_3ISi$: 357.9861; Found: 357.9850.

Compound 27: Synthesized from **A** (56 mg, 0.2 mmol) or **B** (11.6 mg, 0.2 mmol), (*Z*)-cyclooctene (130 µL, 1 mmol), CF_3I (3 mmol, i.e. 6 mL of a 2 M stock solution in CH_3OH), and CH_3OH (1 mL). The residue was purified by flash chromatography over silica gel (pentane 100%) to afford **27** (d.r = 1:1) as yellow oil in 71% yield (218 mg) with **A** and 64% yield (196 mg) with **B**.

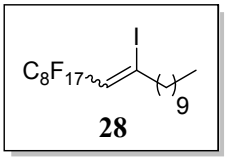


27

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 4.64-4.44 (m, 1H, d1 and d2), 2.53-2.20 (m, 3H, d1 and d2), 2.17-2.02 (m, 3H, d1 and d2), 1.99-1.75 (m, 3H, d1 and d2), 2.53-2.20 (m, 5H, d1 and d2); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 128.5 (q, *J* = 277.8 Hz, d1 or d2), 128.4 (q, *J* = 277.7

Hz, d1 or d2), 42.5 (q, J = 24.5 Hz, d1 or d2), 42.3 (q, J = 24.6 Hz, d1 or d2), 38.7 (d1 or d2), 38.1 (d1 or d2), 36.1 (d1 or d2), 35.4 (d1 or d2), 35.2 (d1 or d2), 68.5 (d1 or d2), 34.1 (d1 and d2), 26.92 (d1 or d2), 26.89 (d1 or d2), 26.1 (d1 or d2), 25.8 (d1 or d2), 25.5-25.2 (m, d1 or d2), 24.5-24.1 (m, d1 or d2); **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm) = -73.3 (d, J = 9.3 Hz, d1 or d2), -73.4 (d, J = 9.3 Hz, d1 or d2); **HRMS** (EI): Calcd. for [M-I] $C_9H_{14}F_3$: 179.1047; Found: 179.1049.

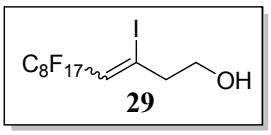
Compound 28: Synthesized from **A** (28 mg, 0.1 mmol) or **B** (5.8 mg, 0.1 mmol), dodec-1-yne (130 µL, 1 mmol) and $C_8F_{17}I$ (573.2 mg, 1.05 mmol) in CH_3OH (7 mL). The residue was purified by flash chromatography over silica gel (pentane 100%) to afford **28** (d.r = 3:1) as yellow oil in 81% yield (577 mg) with **A** and 69% yield (489 mg) with **B**.



28

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 6.34 (t, J = 14.4 Hz, 1H, d1), 6.39 (t, J = 13.2 Hz, 0.25H, d2), 2.77-2.57 (m, 2.5H, d1+d2), 1.67-1,52 (m, 2.5H, d1+d2), 1.31-1,19 (m, 17.5H, d1+d2), 0.88 (t, J = 6.4 Hz, 3.75H, d1+d2); **^{13}C-NMR** ($CDCl_3$, 75 MHz)): **d1**: δ (ppm) = 126.7 (t, J = 24.03 Hz), 123.3, 41.3, 32.1, 29.7, 29.5, 29.4, 28.6, 22.9, 14.2; **d2** : δ (ppm) = 123.2, 121.8 (t, J = 23.93 Hz), 48.6, 32.1, 29.7, 29.5, 29.2, 28.2, 22.9, 14.2; **EI-MS** (*m/z*, relative intensity): 712 (M, 2), 585 (M-I, 2), 529 (M-$C_4H_8I^+$, 10), 97 ($C_7H_{13}^+$, 50), 83 ($C_6H_{11}^+$, 60), 57 ($C_4H_9^+$, 90), 43 ($C_3H_7^+$, 100); **HRMS** (CI+): Calcd. for [M-H] $C_{20}H_{21}F_{17}I$: 711.0416; Found: 711.0426.

Compound 29: Synthesized from **A** (56 mg, 0.1 mmol), but-3-yn-1-ol (77 µL, 1 mmol) and $C_8F_{17}I$ (573 mg, 1.05 mmol) in CH_3OH (7 mL). The residue was purified by flash chromatography over silica gel (pentane/EtOAc, 90/10) to afford **29** (d.r = 2.3:1) as yellow solid in 71% yield (438 mg).

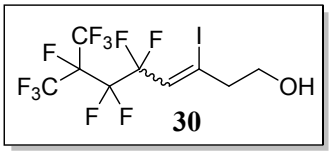


29

Mp = 65-67 °C; **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ (ppm) = 6.48 (t, J = 14.0 Hz, 0.65H, d1), 6.40 (t, J = 13.2 Hz, 0.31H, d2), 3.90-3.80 (m, 2H, d1+d2), 3.02-2.87 (m, 2H, d1+d2), 1.69 (brs, 1H, d1), 1.25 (brs, 0.4H, d2); **^{13}C-NMR** ($CDCl_3$, 101 MHz)): **d1**: δ (ppm) = 129.2 (t, J = 23.8 Hz), 117.2, 62.0, 43,8; **d2** : δ (ppm) = 124.5 (t, J = 23.8 Hz), 118.7, 60.7, 51.1; **HRMS** (ESI): Calcd. for $C_{12}H_5F_{17}IO$: 614.9108; Found: 614.9105.

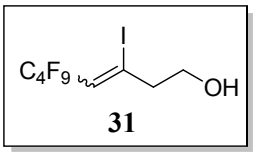
Compound 30: Synthesized from **B** (5.8 mg, 0.1 mmol), but-3-yn-1-ol (77 µL, 1 mmol) and $C_5F_{11}I$ (204 µL, 1.05 mmol) in CH_3OH (7 mL). The residue was purified by flash

chromatography over silica gel (pentane/EtOAc, 90/10) to afford **30** (d.r = 3:1) as yellow oil in 91% yield (422 mg).



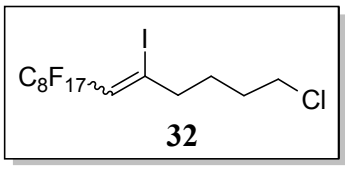
^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 6.48 (t, *J* = 14.4 Hz, 1H, d1), 6.39 (t, *J* = 13.2 Hz, 0.4H, d2), 3.89-3.78 (m, 2.8H, d1+d2), 3.04-2.84 (m, 2.8H, d1+d2), 1.89 (brs, 1.4H, d1+d2); **^{13}C-NMR** ($CDCl_3$, 101 MHz)): **d1**: δ (ppm) = 129.3 (t, *J* = 24.03 Hz), 117.2, 62.0, 43,7; **d2** : δ (ppm) = 124.6 (t, *J* = 23.9 Hz), 120.3, 60.7, 51.0; **CI-MS** (*m/z*, relative intensity): 466 (M, 5), 449 ($C_9H_5F_{11}I^+$, 45), 437 ($C_8H_5F_{11}I^+$, 75), 417 ($C_8H_4F_{10}I^+$, 100), 338 ($C_9H_5F_{11}O^+$, 82); **HRMS** (CI+): Calcd. for $C_9H_5F_{11}I$ ($M-H_2O$): 448.9260; Found: 448.9273.

Compound 31: Synthesized from **B** (5.8 mg, 0.1 mmol), but-3-yn-1-ol (77 µL, 1 mmol) and C_4F_9I (180 µL, 1.05 mmol) in CH_3OH (7 mL). The residue was purified by flash chromatography over silica gel (pentane/EtOAc, 90/10) to afford **31** (d.r = 4:1) as yellow oil in 53% yield (219 mg).



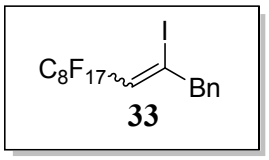
^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 6.47 (t, *J* = 14.4 Hz, 0.8H, d1), 6.39 (t, *J* = 13.2 Hz, 0.2H, d2), 3.84 (t, *J* = 6.3 Hz, 2H, d1+d2), 3.00-2.85 (m, 2H, d1+d2), 1.89 (s, 1H, d1+d2); **^{13}C-NMR** ($CDCl_3$, 75 MHz): **d1**: δ (ppm) = 129.0 (t, *J* = 23.5 Hz), 117.2, 62.0, 43,8; **d2**: δ (ppm) = 124.3 (t, *J* = 23.5 Hz), 114.3, 60.7, 51.0; **HRMS** (CI+): Calcd. for $C_8H_6F_9IO$: 415.99319; Found: 415.9323.

Compound 32: Synthesized from **A** (56 mg, 0.1 mmol), 6-chlorohex-1-yne (122 µL, 1 mmol) and $C_8F_{17}I$ (573 mg, 1.05 mmol) in CH_3OH (7 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to afford **32** (d.r = 3:1) as yellow oil in 57% yield (188 mg).



^{1}H-NMR ($CDCl_3$, 300 MHz) (**d1**) δ (ppm) = 6.36 (t, *J* = 14.4 Hz, 1H), 3.55 (t *J* = 6.3 Hz, 2H), 2.75-2.61 (m, 2H), 1.89-1.68 (m, 4H); (**d2**) δ (ppm) = 6.27 (t, *J* = 13.2 Hz, 1H), 3.56 (t *J* = 6.0 Hz, 2H), 2.79-2.63 (m, 2H), 1.85-1.68 (m, 4H); **^{13}C-NMR** ($CDCl_3$, 101 MHz) δ (ppm) = 127.3 (t, *J* = 23.7 Hz), 121.8, 44.5, 40.3, 31.2, 27.4.

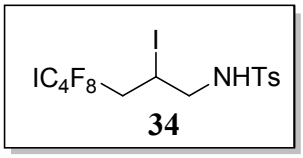
Compound 33: Synthesized from **A** (56 mg, 0.1 mmol), prop-2-ynylbenzene (124 µL, 1 mmol) and $C_8F_{17}I$ (573 mg, 1.05 mmol) in CH_3OH (7 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to afford **33** (d.r = 2.1:1) as yellow solid in 82% yield (543 mg).



33

Mp = 49-51 °C; **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ (ppm) =7.46-7.29 (m, 4.5H, d1+d2), 7.24-7,15 (m, 3H, d1+d2), 6.51 (t, *J* = 14.0 Hz, 1H, d1), 6.39 (t, *J* = 13.2 Hz, 0.5H, d2), 4.06 (s, 2H, d1), 4.03 (s, 1H, d2); **^{13}C-NMR** ($CDCl_3$, 101 MHz)): **d1**: δ (ppm) = 136.9, 129.1, 128.9, 127.7 (t, *J* = 23.8 Hz), 127.6, 46.8; **d2** : δ (ppm) = 136.4, 129.3, 129.0, 127.8,123.4 (t, *J* = 24.0 Hz), 51.8; **EI-MS** (*m/z*, relative intensity): 662 (M, 10), 535 (M-I, 15), 243 ($C_9H_8I^+$, 20), 166 ($C_{10}H_8F_2^+$, 70), 146 ($C_{10}H_7F^+$, 100), 115 ($C_9H_8^+$, 70), 69 (CF_3^+, 10).

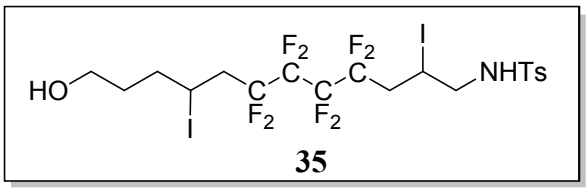
Compound 34: Synthesized from **B** (5.8 mg, 0.1 mmol), *N*-allyl-4-methylbenzenesulfonamide (106 mg, 0.5 mmol) and IC_4F_8I (309 mg, 0.68 mmol) in CH_3OH (1.5 mL). The residue was purified by flash chromatography over silica gel (pentane/EtOAc, 90/10) to afford **34** as a solid in 79% yield (260 mg).



34

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 7.80-7.73 (m, 2H), 7.37-7.28 (m, 2H), 5.09 (t, *J* = 6.6 Hz, 1H), 4.30-4.18 (m, 2H), 4.30-4.18 (m, 2H), 3.42-3.23 (m, 2H), 2.93-2.61 (m, 2H), 2.43 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 144.2, 136.7, 130.1, 127.2, 51,0, 38.5 (t, *J* = 21.0 Hz), 21.7, 17.0; **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm) = -58.7, -111.7 to -114.7 (m), -112.7, -122.6; **HRMS** (ESI): Calcd. for $C_{14}H_{13}NO_2F_8NaSI_2$: 687.8521; Found: 687.8522.

Compound 35: Synthesized from **B** (3.4 mg, 0.06 mmol), pent-4-en-1-ol (25.8 mg, 0.3 mmol) and **34** (190 mg, 0.29 mmol) in CH_3OH (3 mL). The residue was purified by flash chromatography over silica gel (pentane/EtOAc, 80/20) to afford **35** as yellow oil in 64% yield (139 mg).

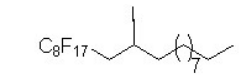


35

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 7.78-7.69 (m, 2H), 7.36-7.30 (m, 2H), 5.35-5.20 (m, 1H), 4.44-4.29 (m, 1H), 4.27-4.15 (m, 1H), 3.69 (t, *J* = 6.3 Hz, 2H), 3.38-3.23 (m, 2H), 3.03-2.57 (m, 4H), 2.42 (s, 3H), 1.97-1.63 (m, 5H); **^{13}C-NMR** ($CDCl_3$, 75 MHz) δ (ppm) = 144.2, 136.7, 130.1, 127.1, 61.7, 51,0, 41.8 (t, *J* = 20.5 Hz), 38.5 (t, *J* = 21.1 Hz), 37.0, 32.7, 21.6, 20.8, 17.0; **^{19}F-NMR** ($CDCl_3$, 282 MHz) δ (ppm) = -110.3, -115.6, -122.7, -123.9; **HRMS** (ESI): Calcd. for $C_{19}H_{23}O_3F_8NaSI_2$: 773.9252; Found: 773.9273.

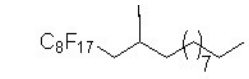
VI. ^{1}H-, ^{13}C- and ^{19}F-NMR spectra

^{1}H-NMR



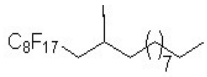
Compound **1**, $CDCl_3$, 300 MHz

^{13}C-NMR



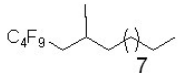
Compound **1**, $CDCl_3$, 75 MHz

^{19}F-NMR



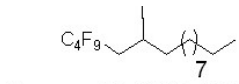
Compound **1**, $CDCl_3$, 282 MHz

^{1}H-NMR



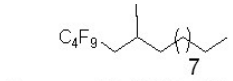
Compound **2**, $CDCl_3$, 300 MHz

^{13}C-NMR



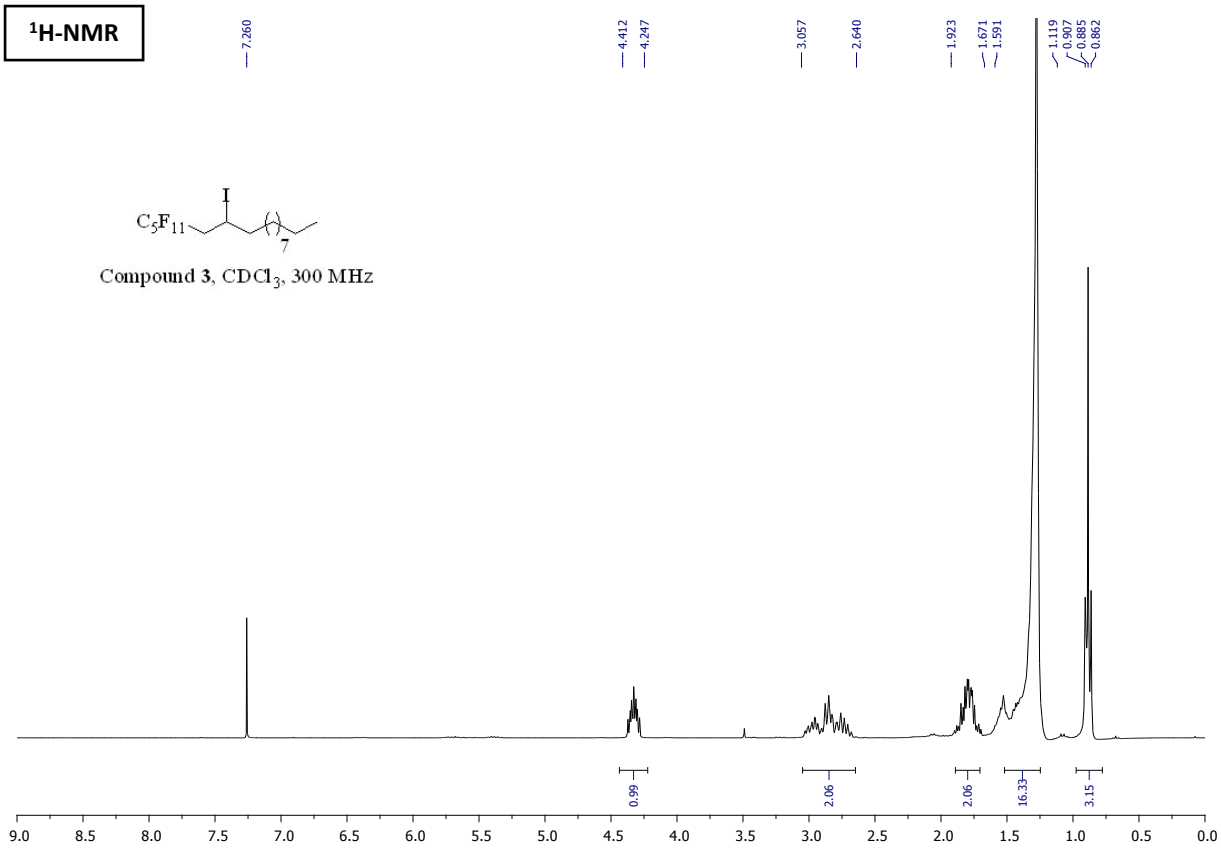
Compound **2**, $CDCl_3$, 75 MHz

^{19}F-NMR



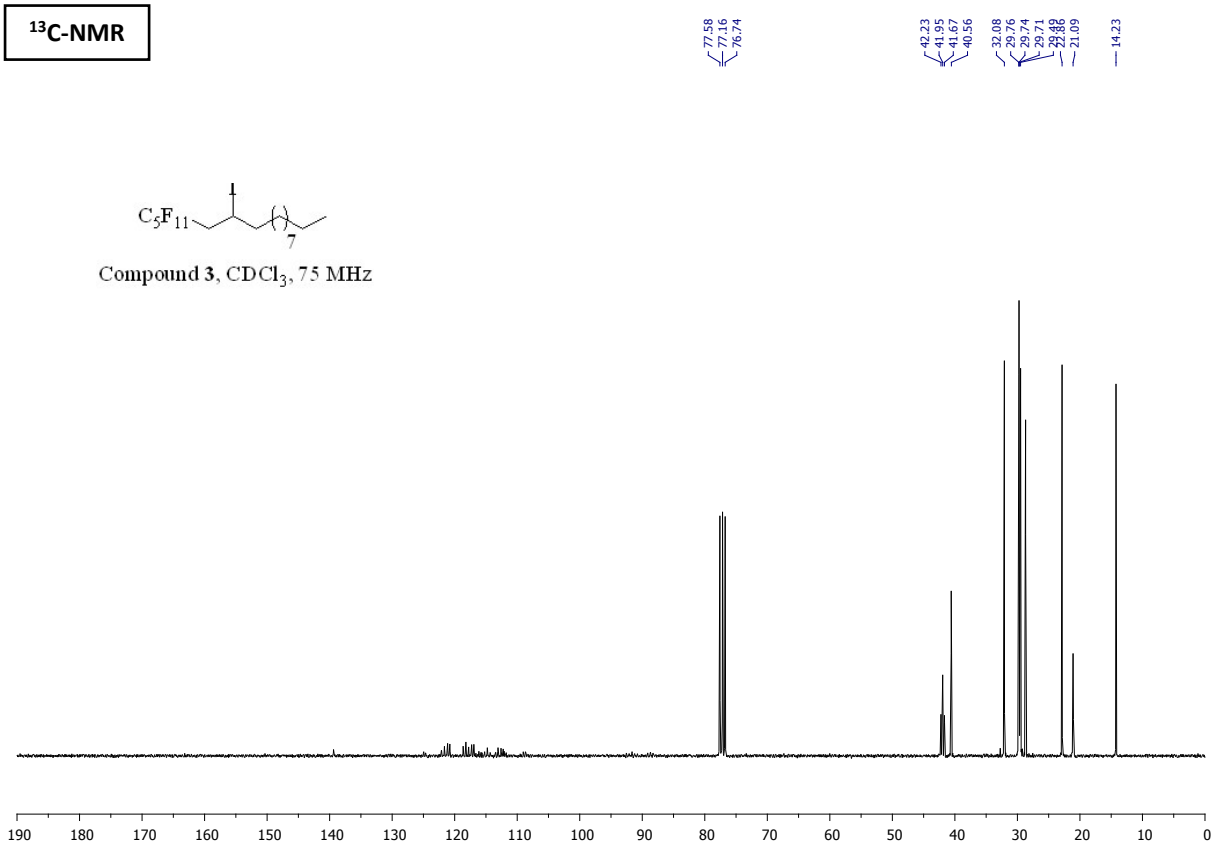
Compound **2**, $CDCl_3$, 282 MHz

^{1}H-NMR



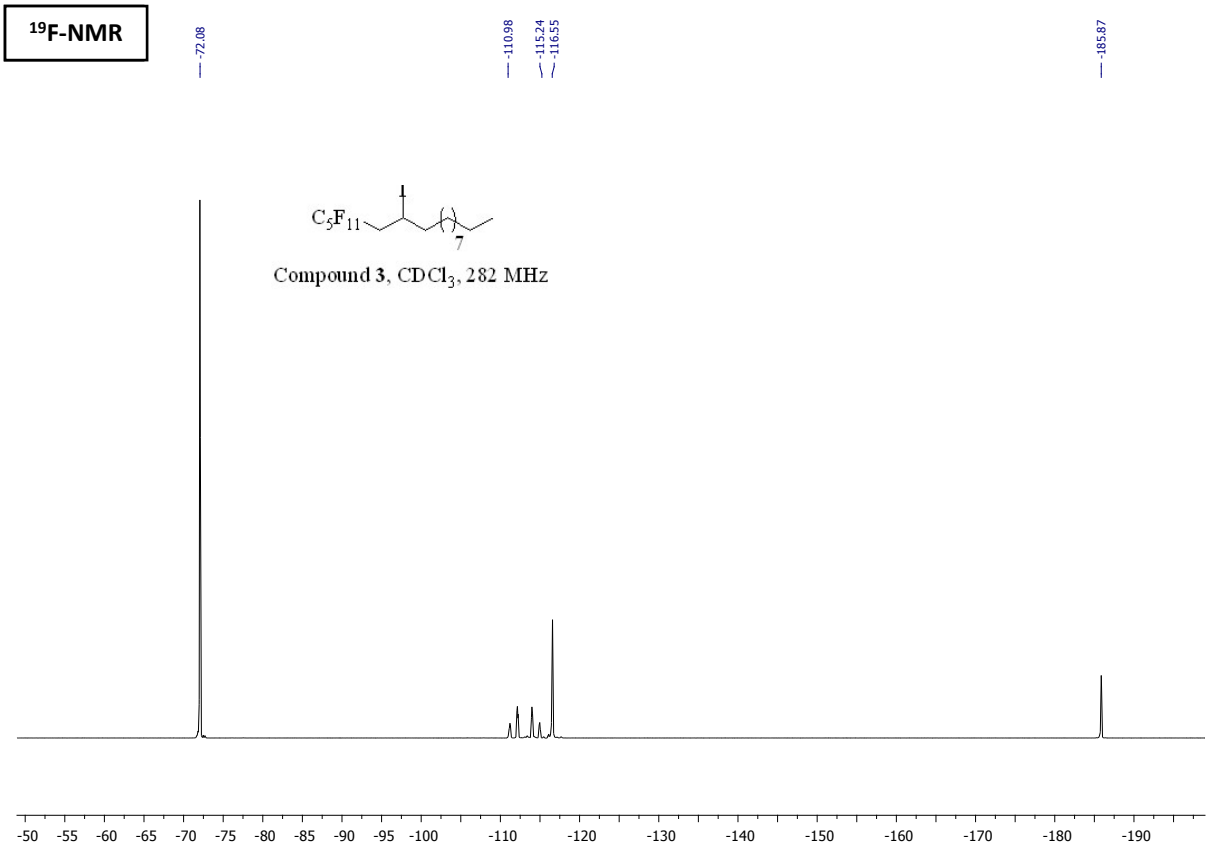
Compound **3**, $CDCl_3$, 300 MHz

^{13}C-NMR



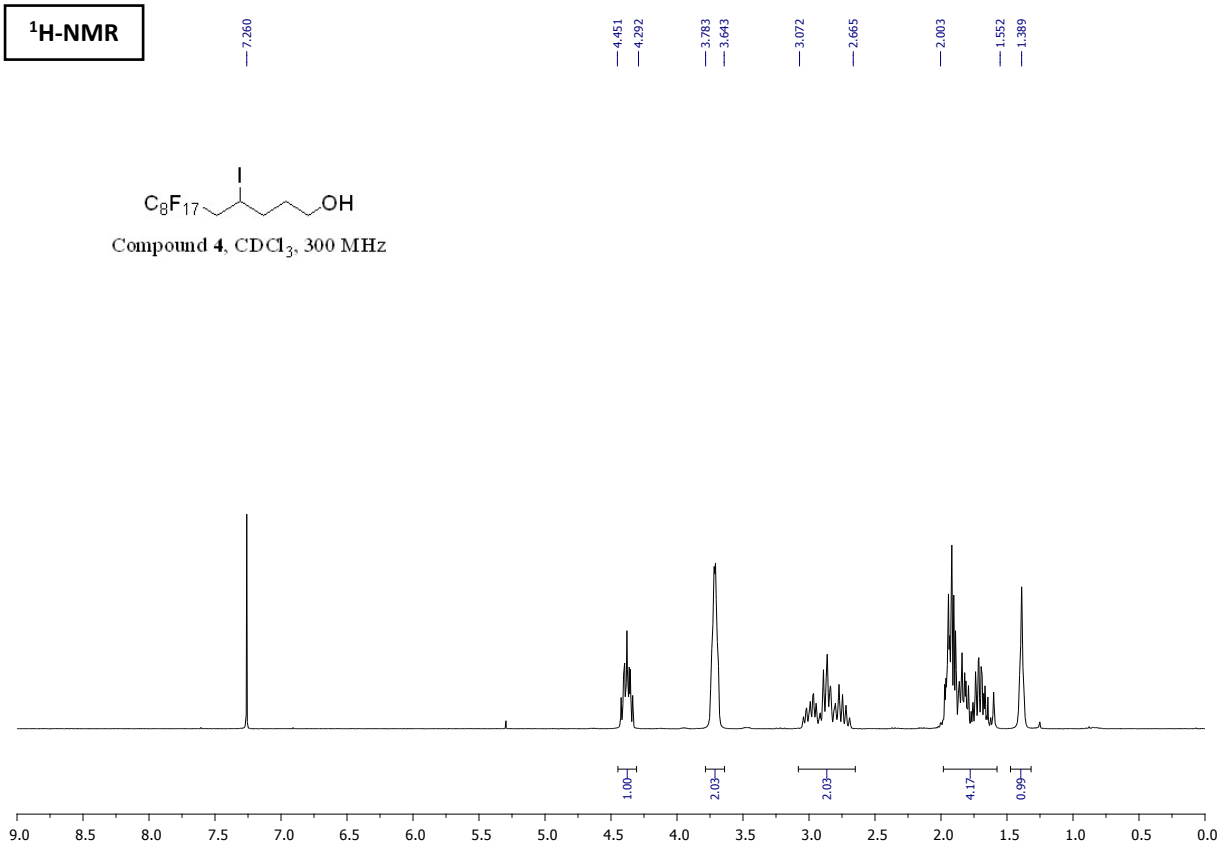
Compound **3**, $CDCl_3$, 75 MHz

^{19}F-NMR



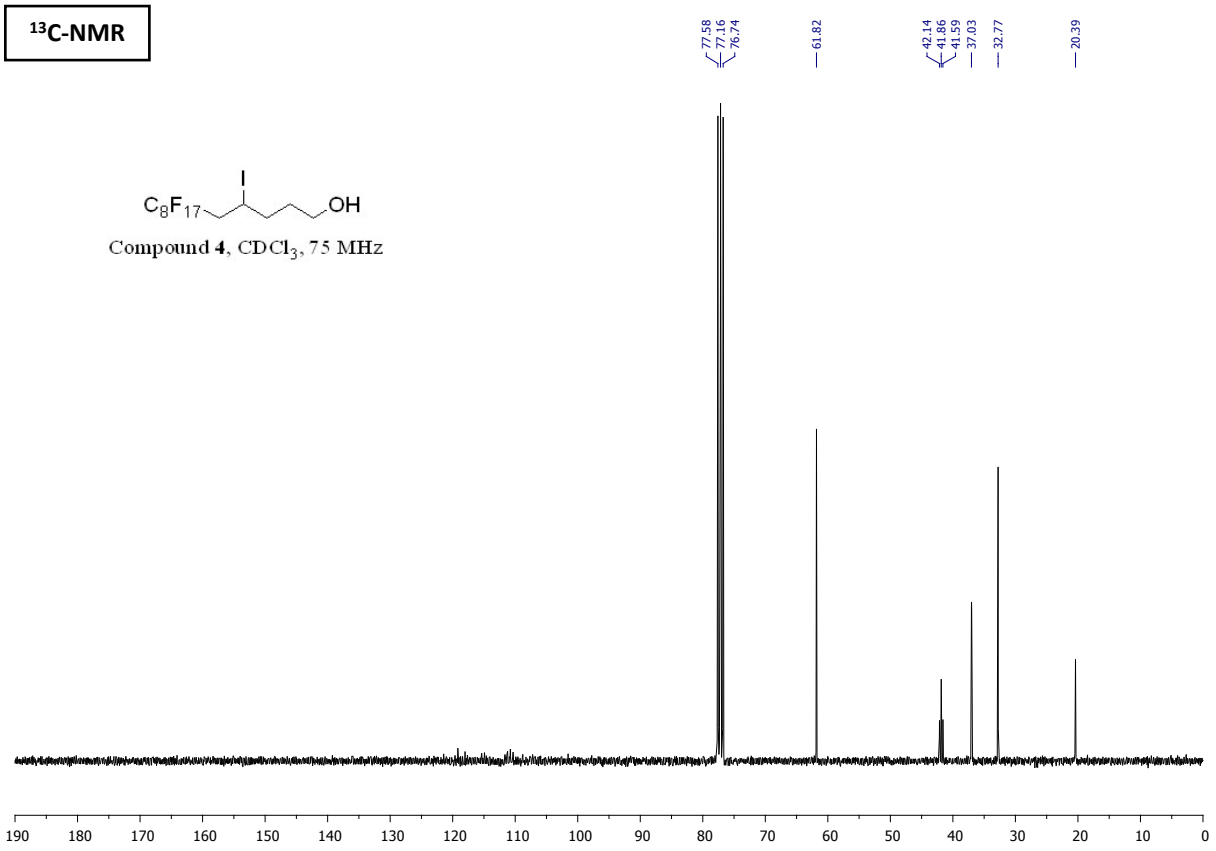
Compound **3**, $CDCl_3$, 282 MHz

^{1}H-NMR



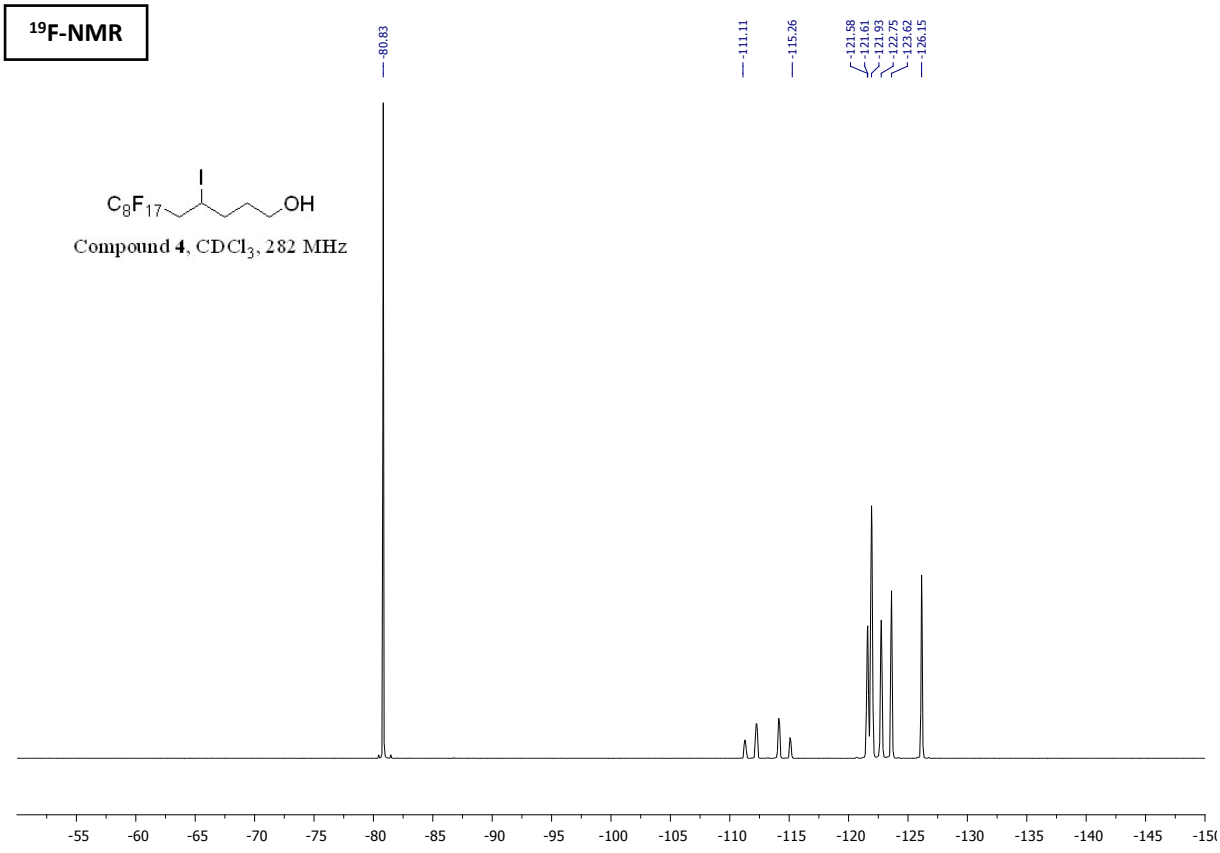
Compound **4**, $CDCl_3$, 300 MHz

^{13}C-NMR



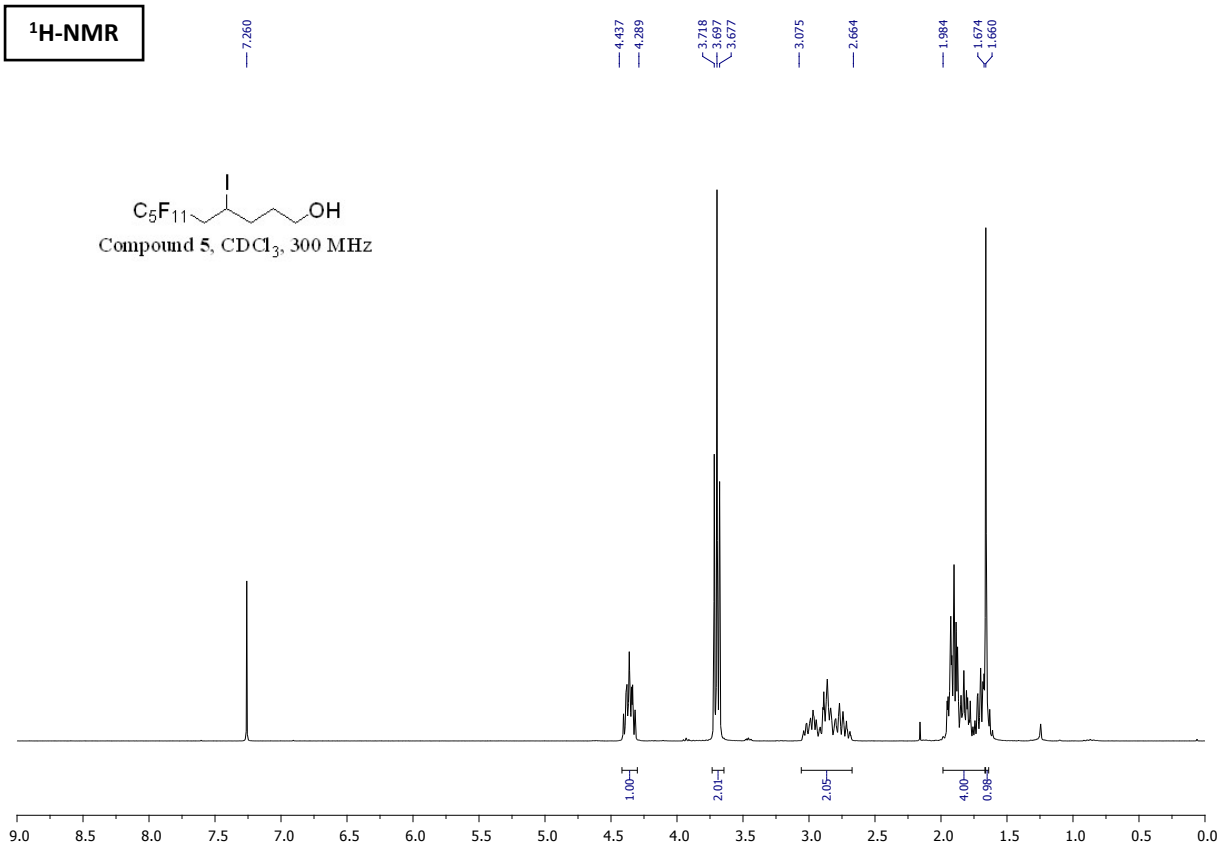
Compound **4**, $CDCl_3$, 75 MHz

^{19}F-NMR

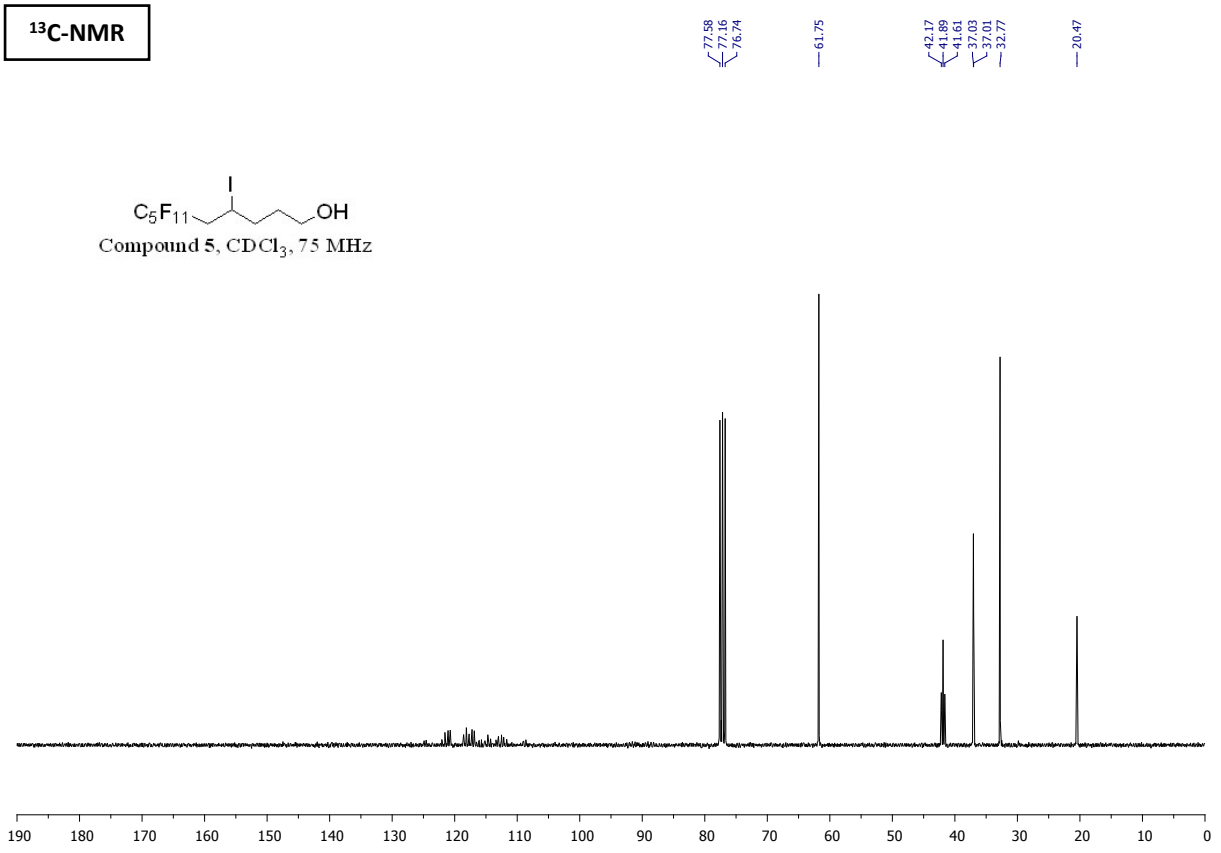


Compound **4**, $CDCl_3$, 282 MHz

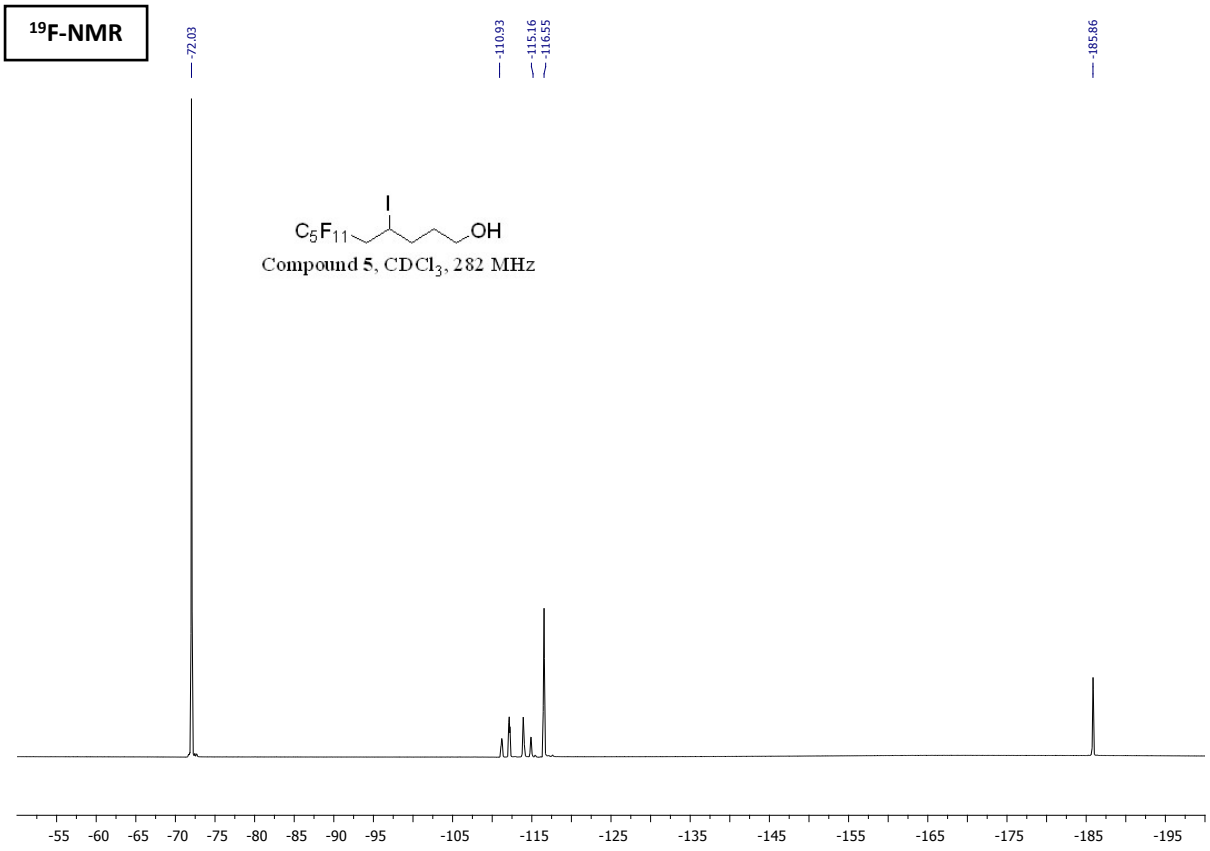
^{1}H-NMR



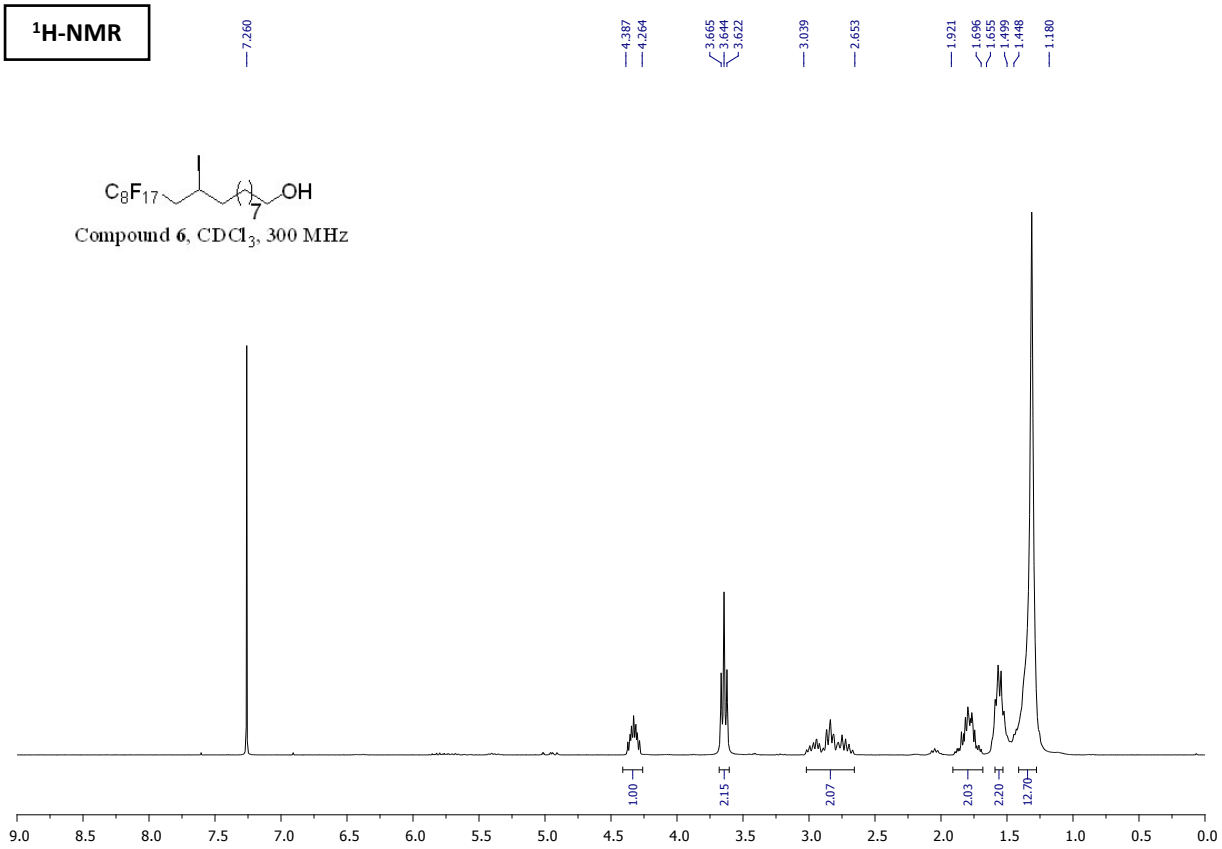
^{13}C-NMR



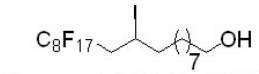
^{19}F-NMR



^{1}H-NMR

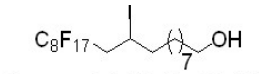


^{13}C-NMR



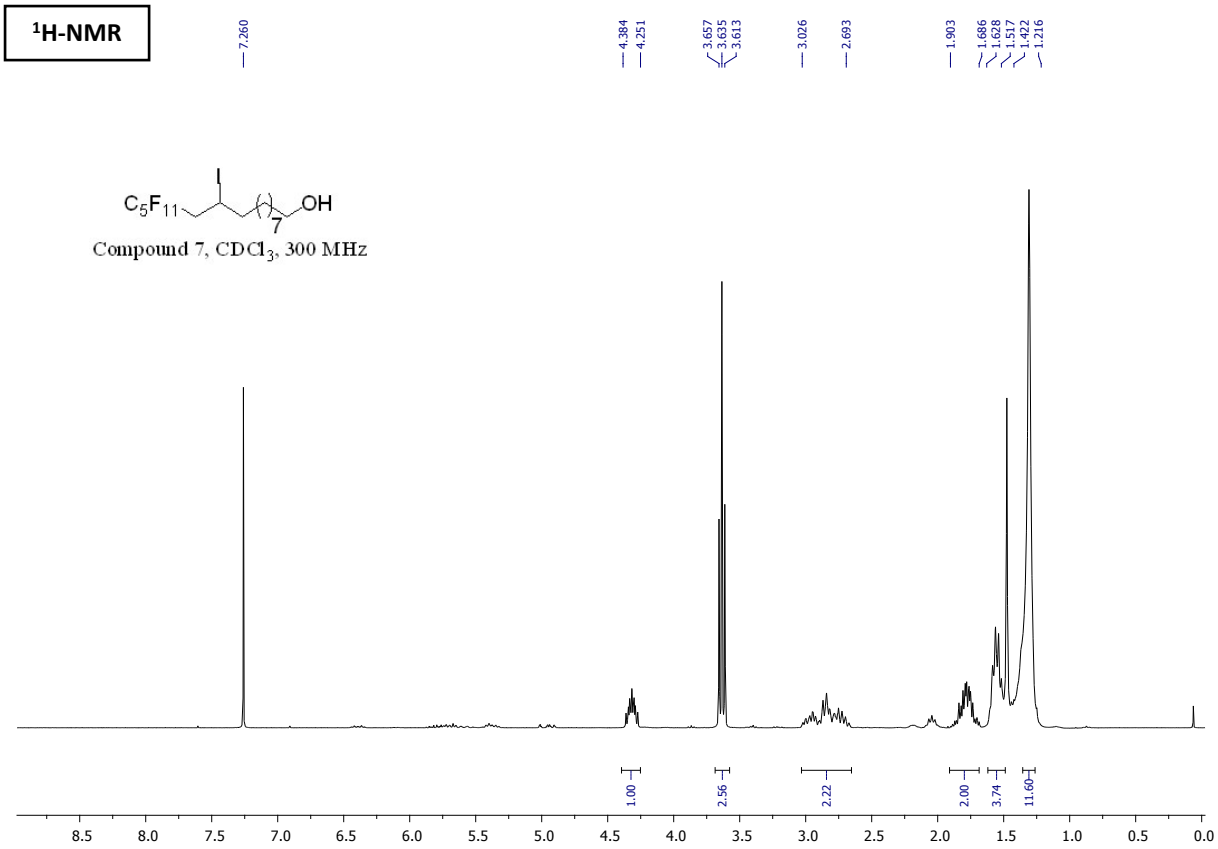
Compound **6**, $CDCl_3$, 75 MHz

^{19}F-NMR



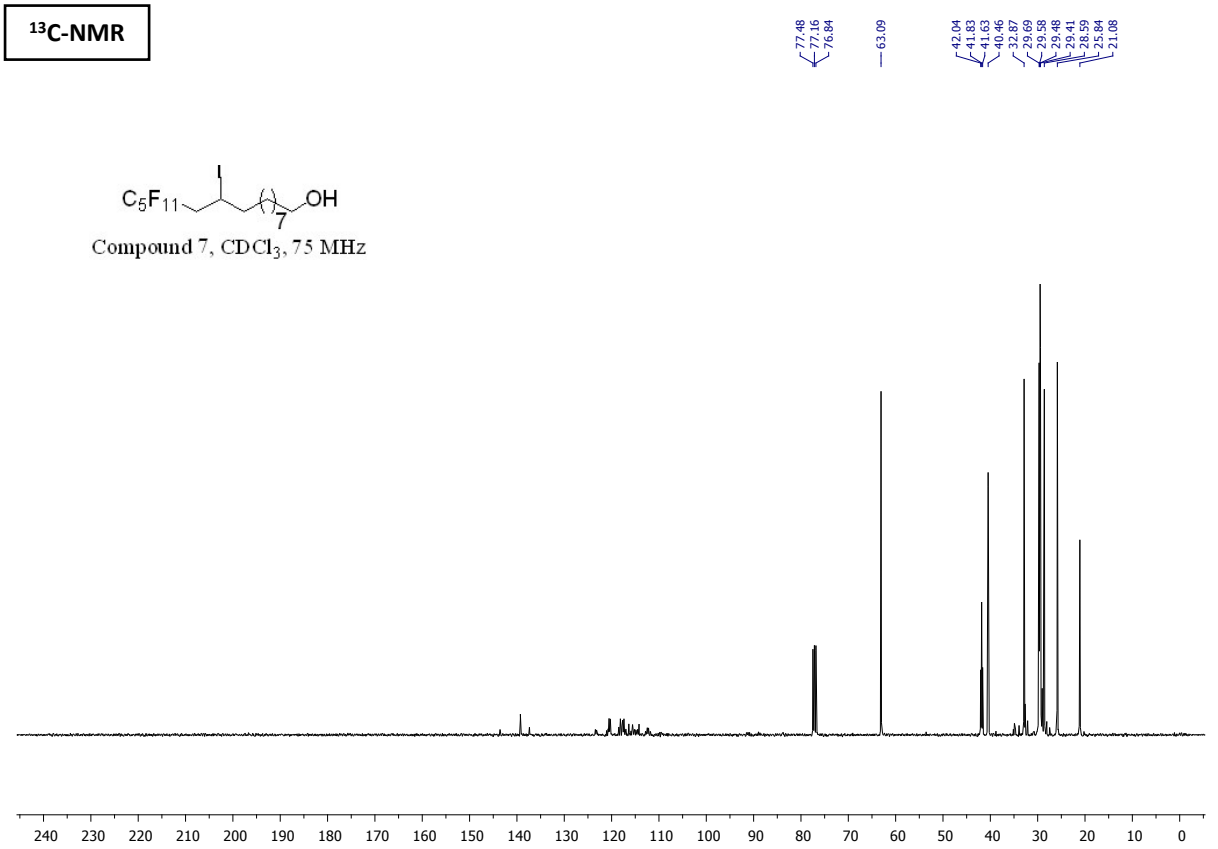
Compound **6**, $CDCl_3$, 282 MHz

^{1}H-NMR



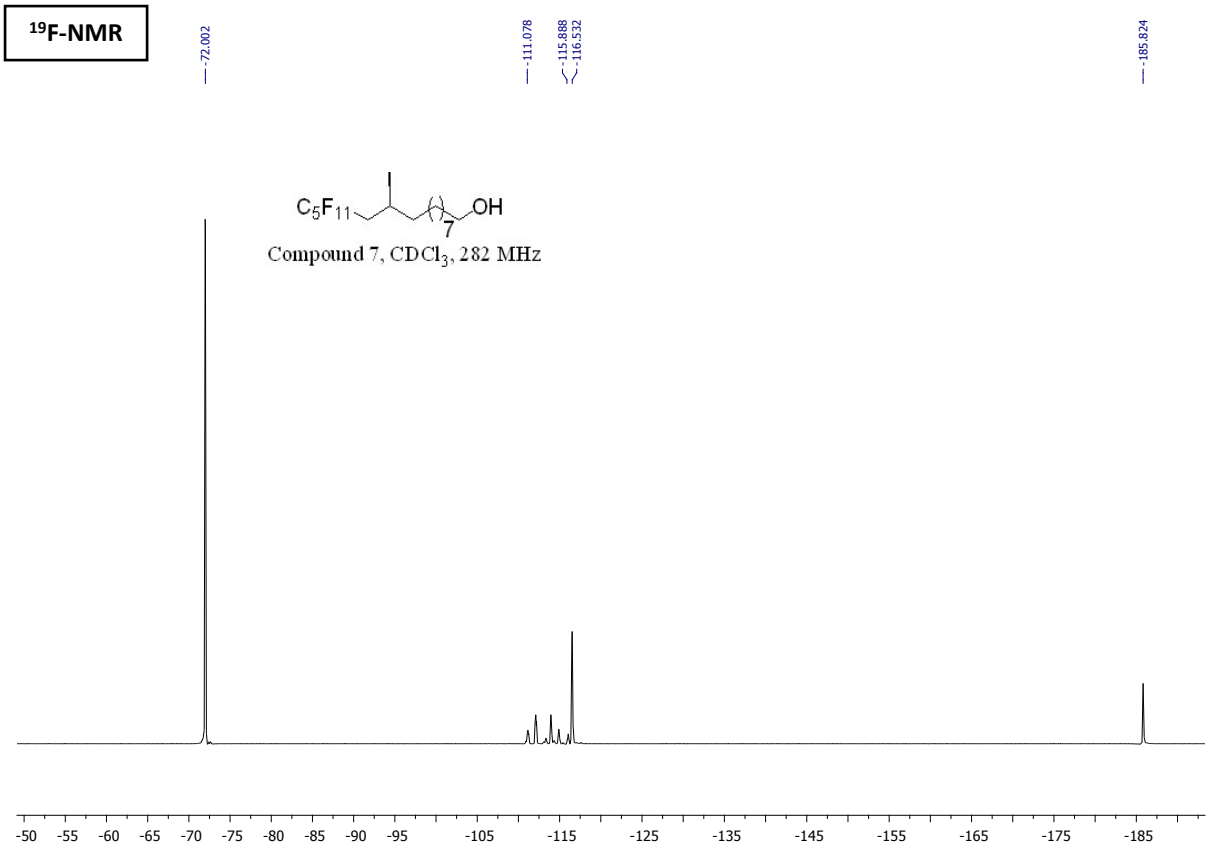
Compound 7, $CDCl_3$, 300 MHz

^{13}C-NMR



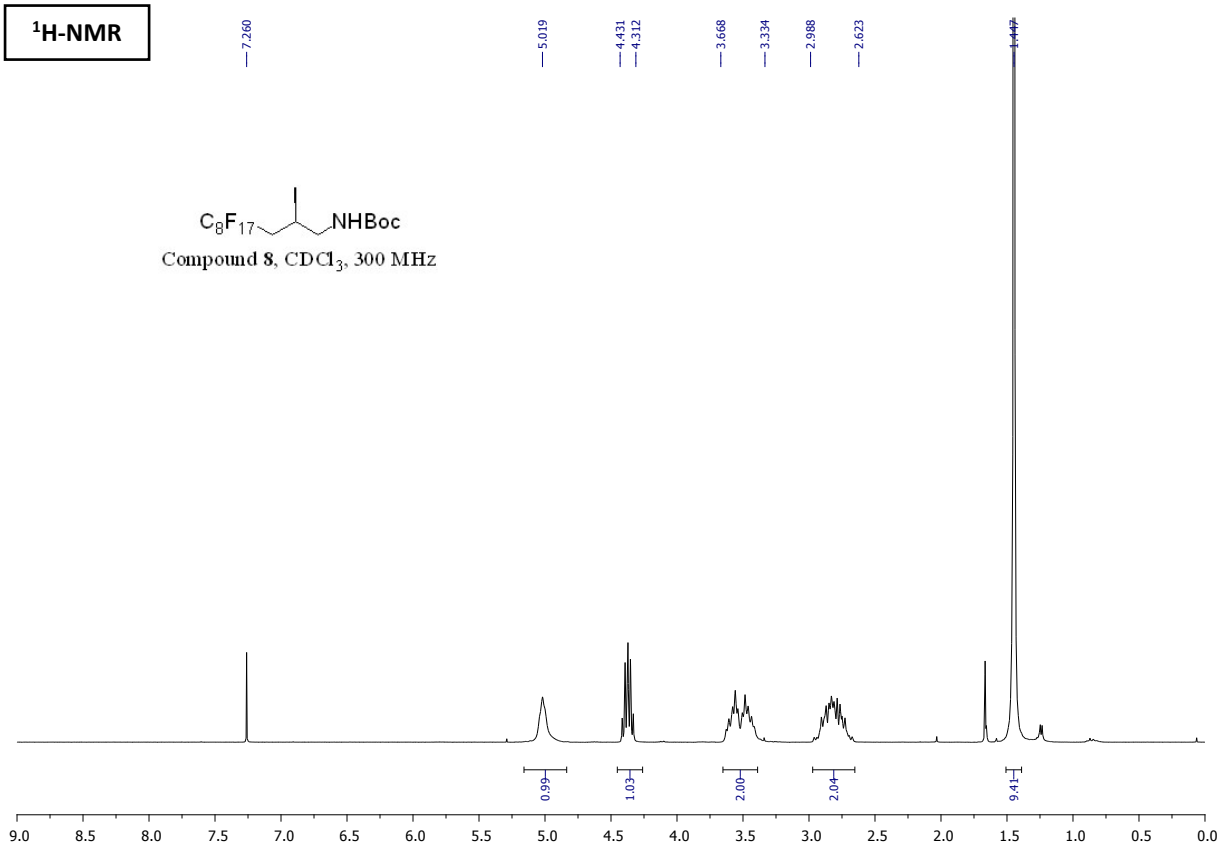
Compound 7, $CDCl_3$, 75 MHz

^{19}F-NMR



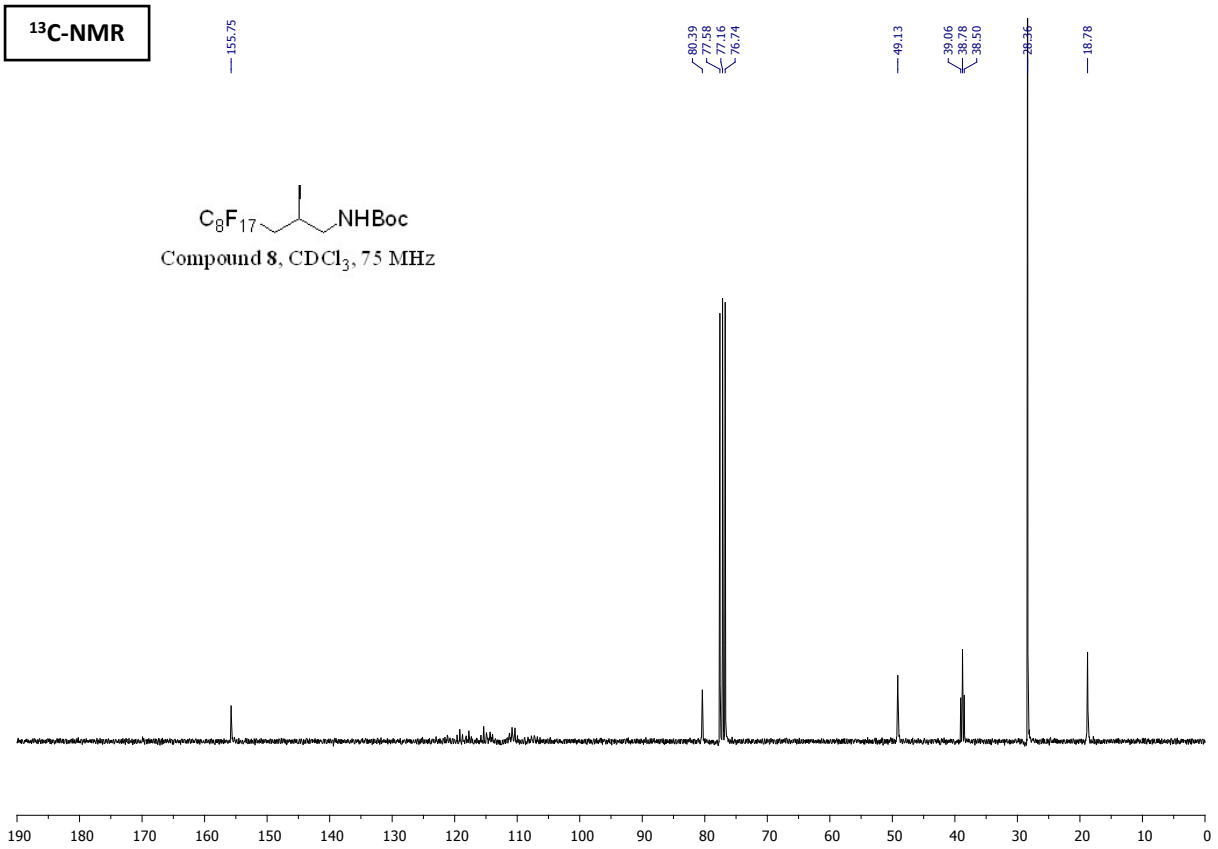
Compound 7, $CDCl_3$, 282 MHz

^{1}H-NMR

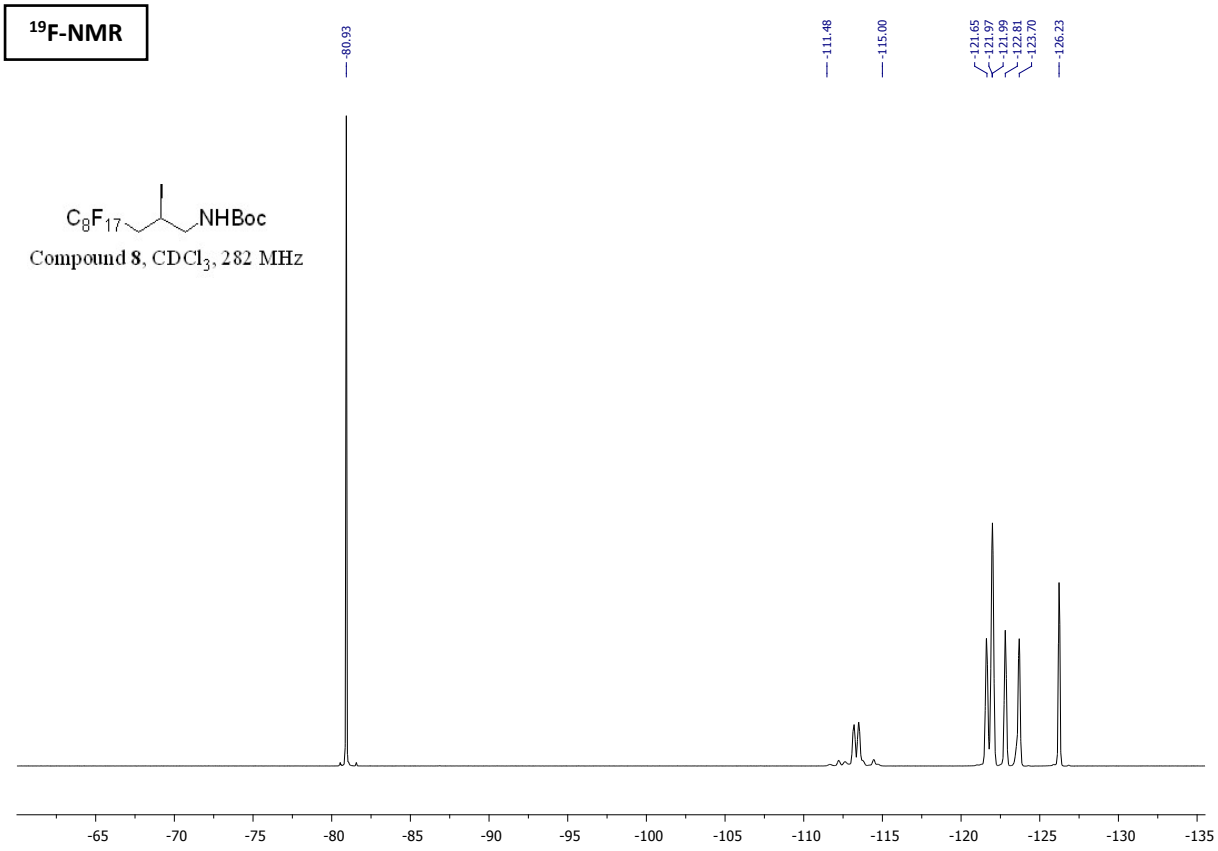


Compound **8**, $CDCl_3$, 300 MHz

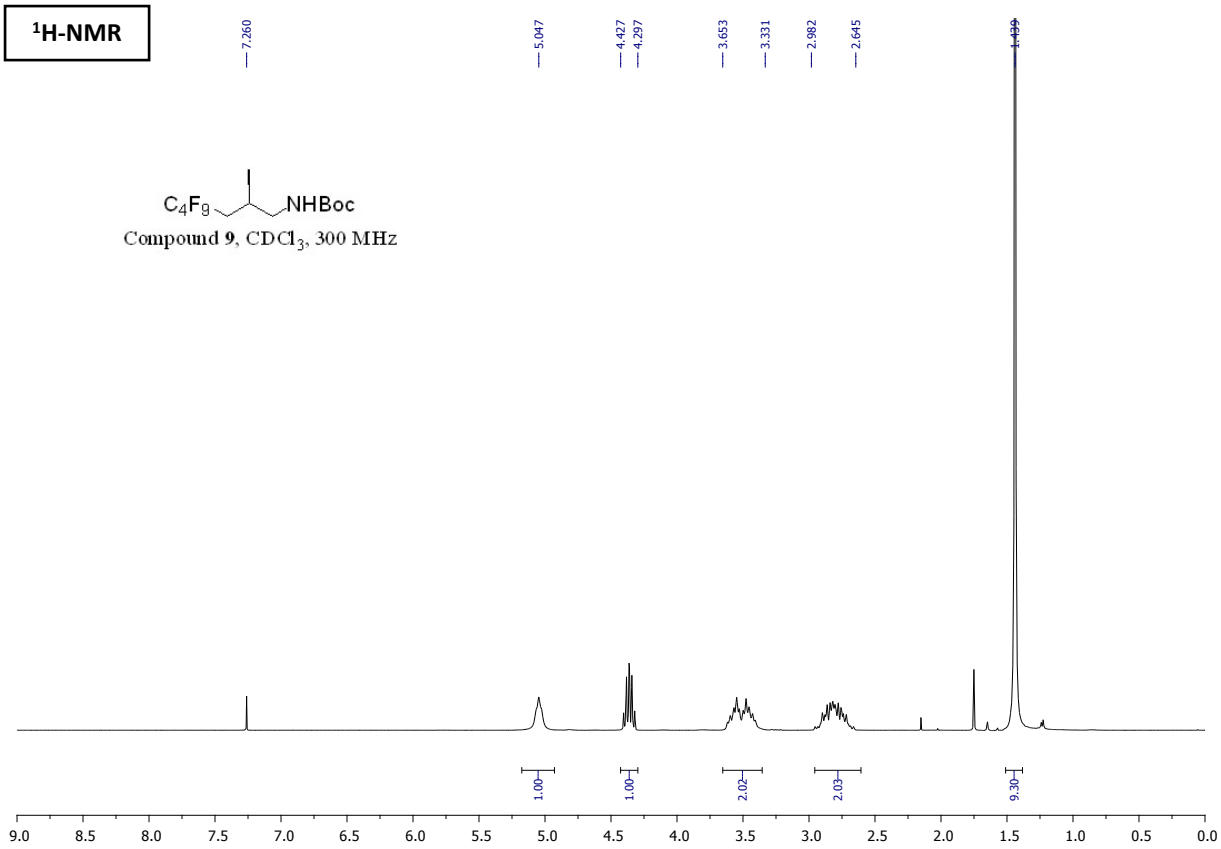
^{13}C-NMR



^{19}F-NMR



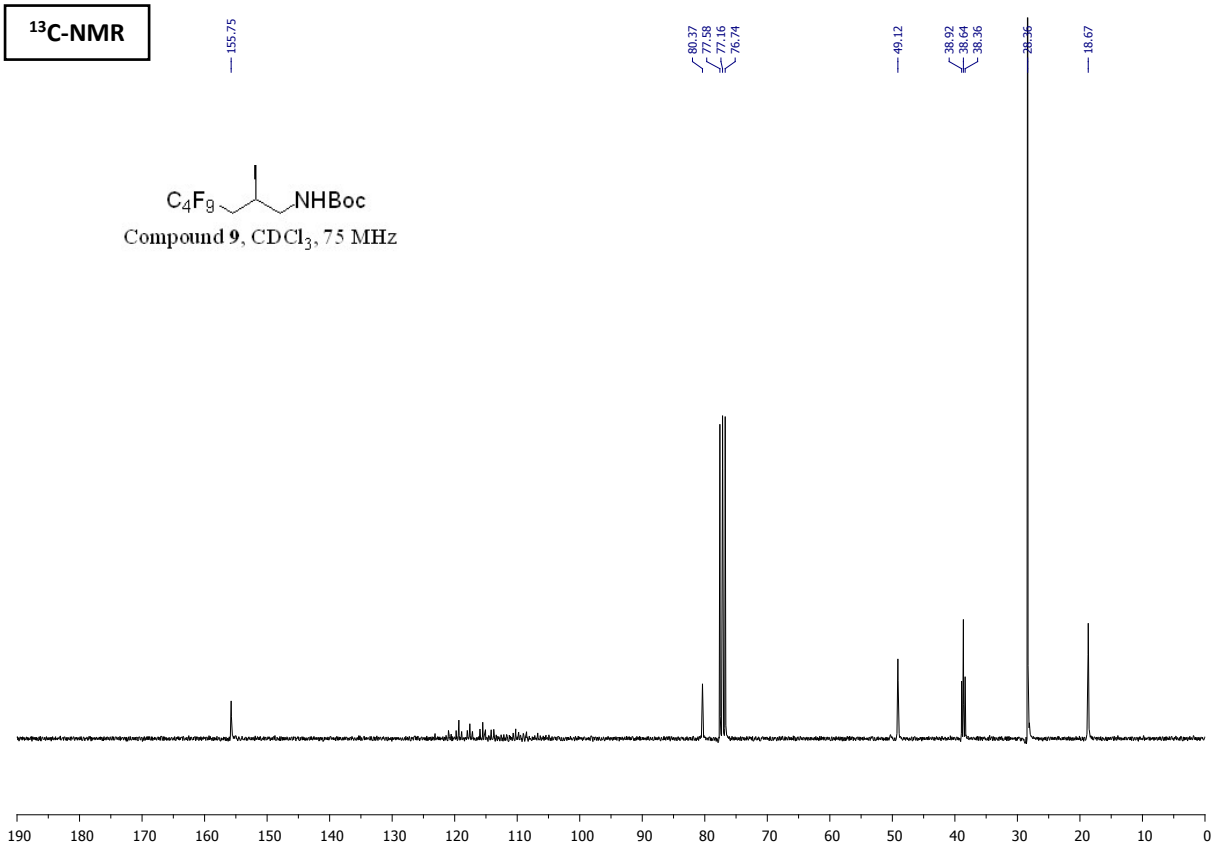
^{1}H-NMR



C_4F_9 NHBoc

Compound **9**, $CDCl_3$, 300 MHz

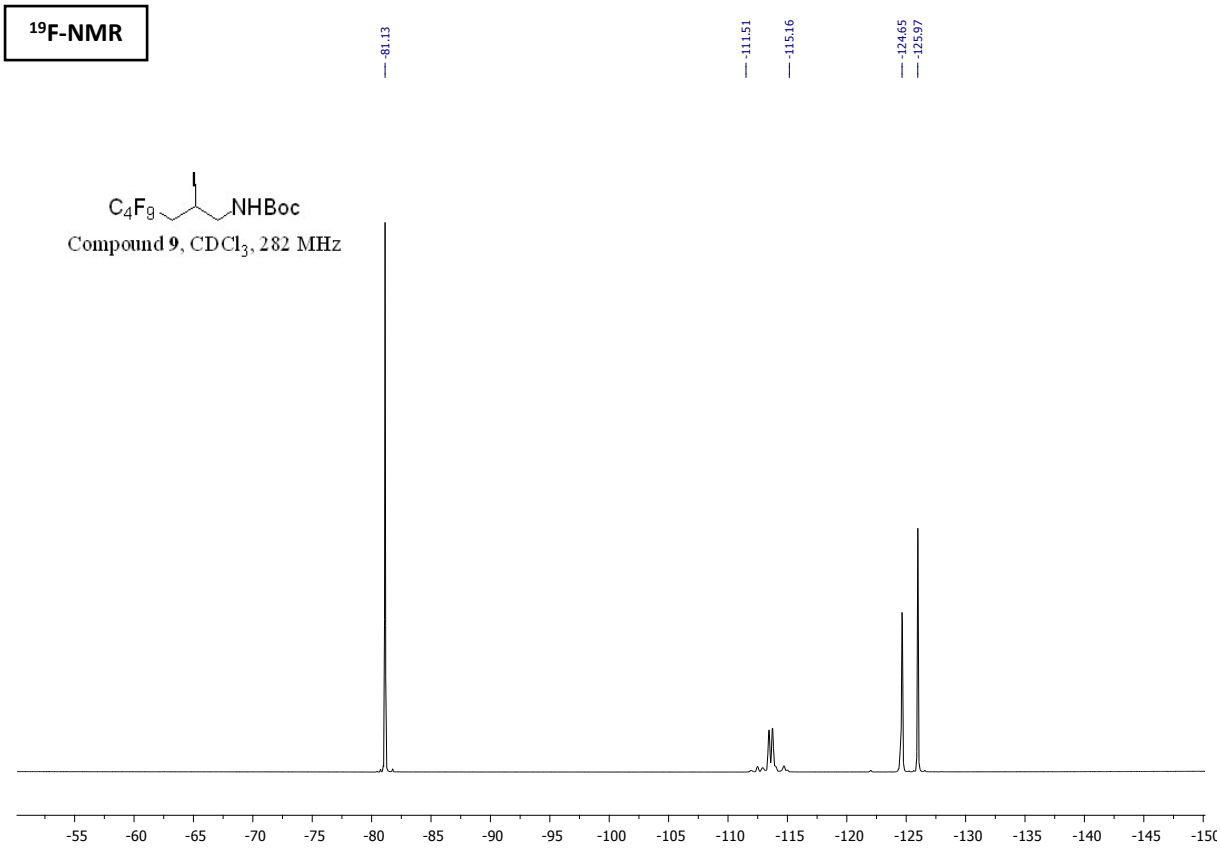
^{13}C-NMR



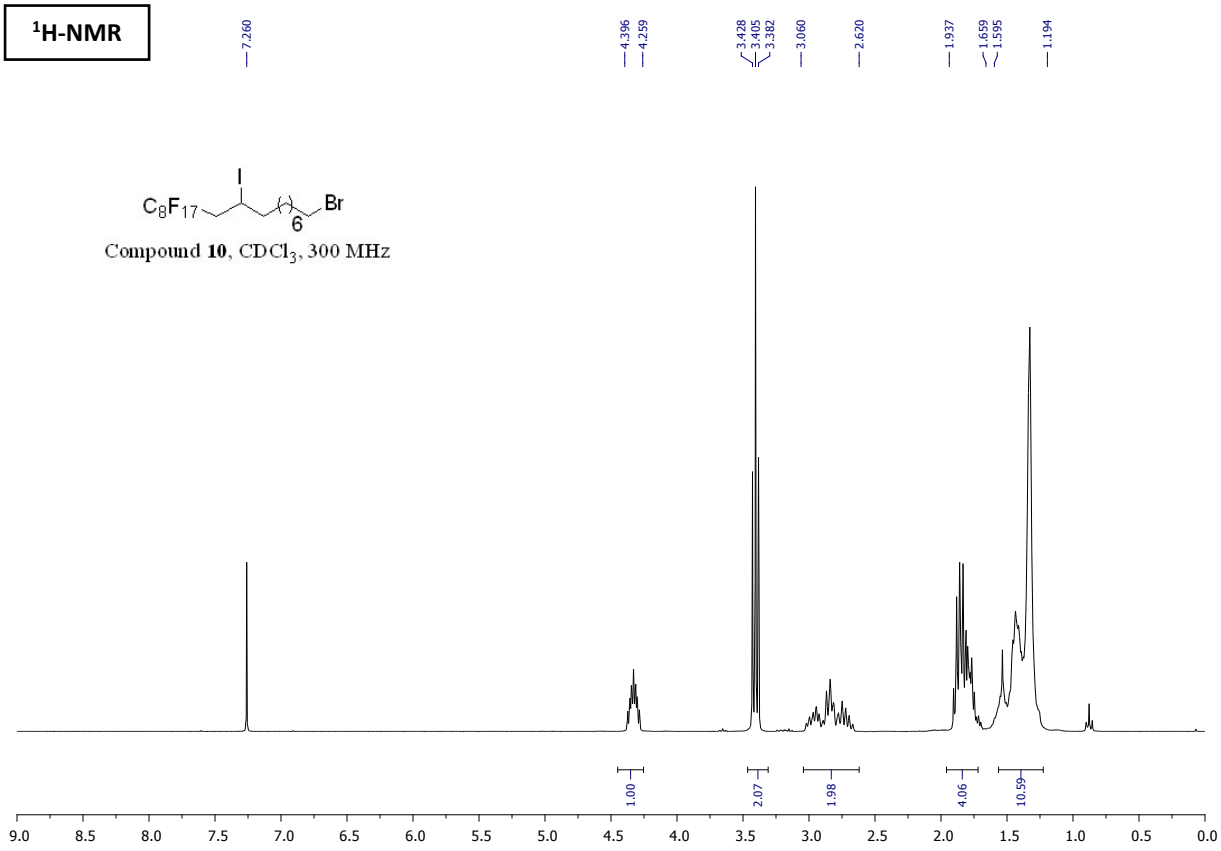
C_4F_9 NHBoc

Compound **9**, $CDCl_3$, 75 MHz

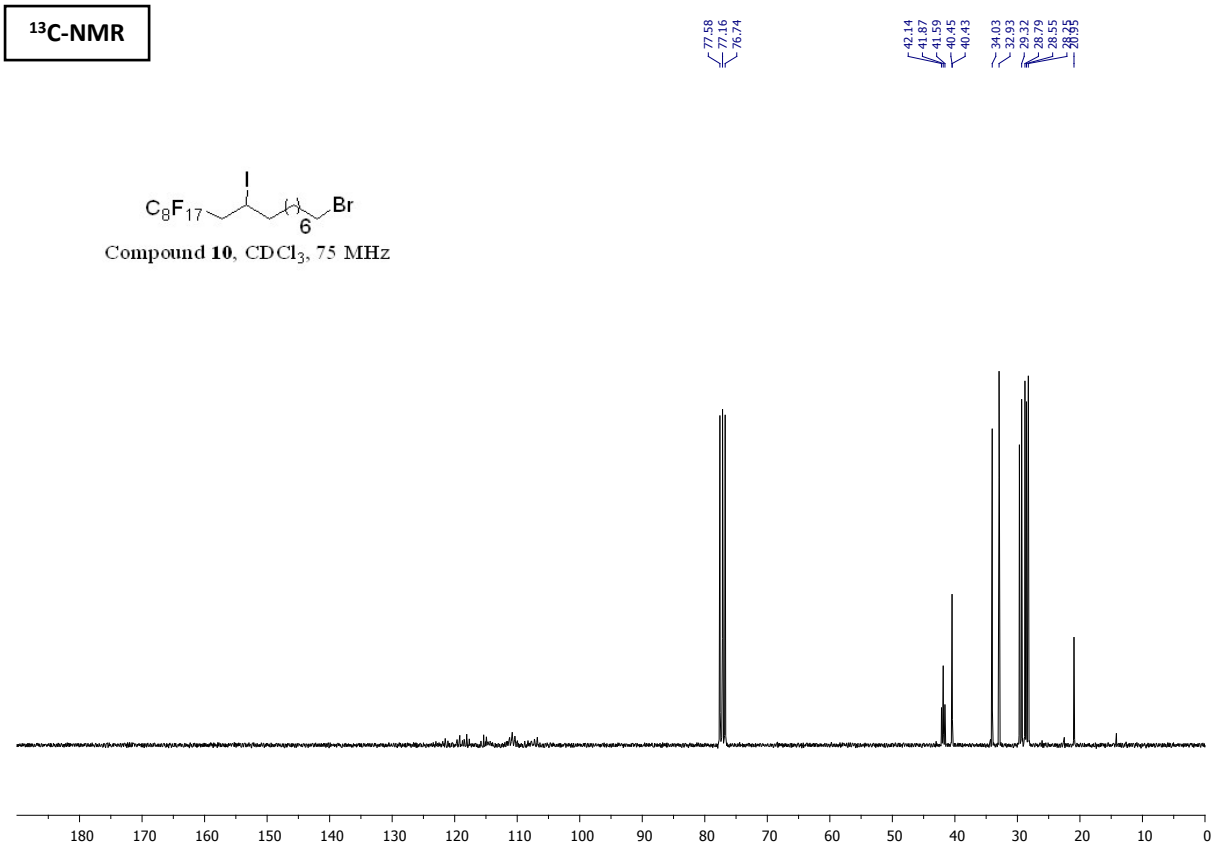
^{19}F-NMR



^{1}H-NMR

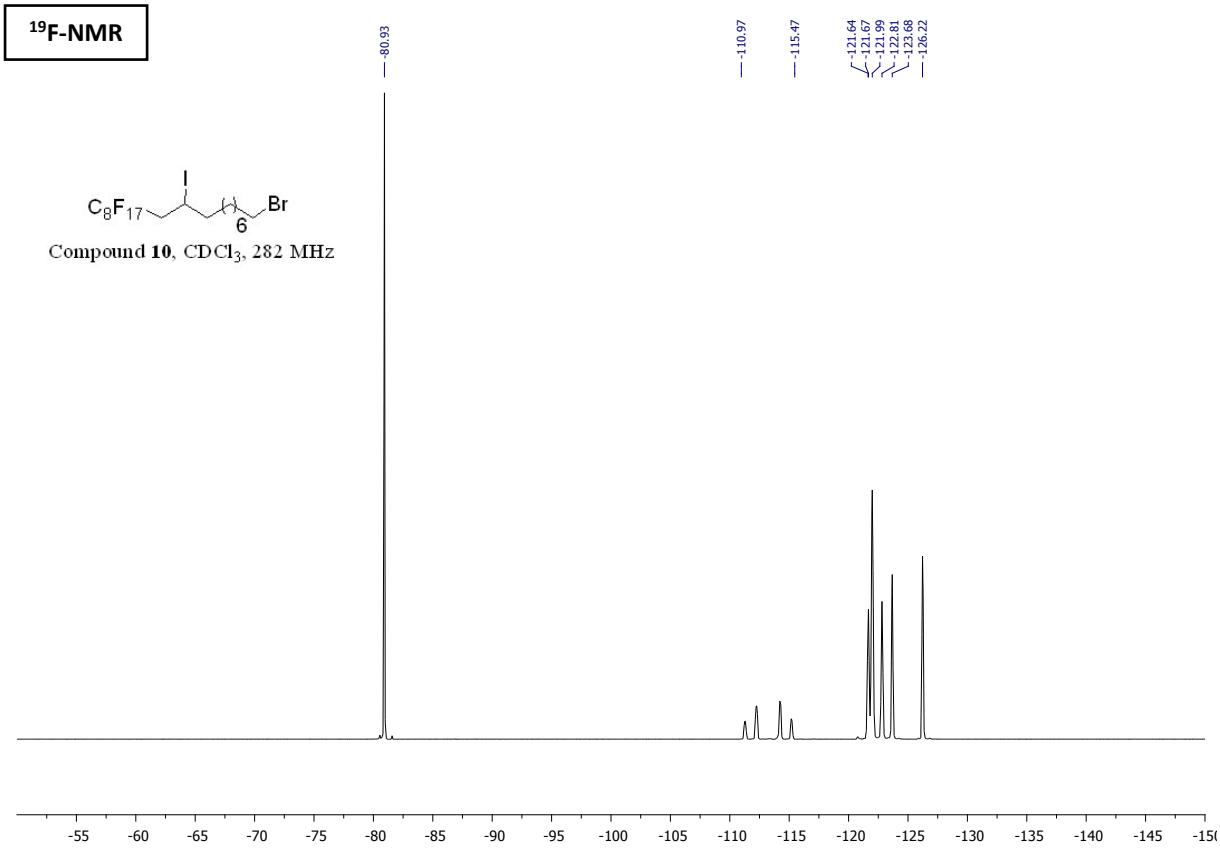


^{13}C-NMR



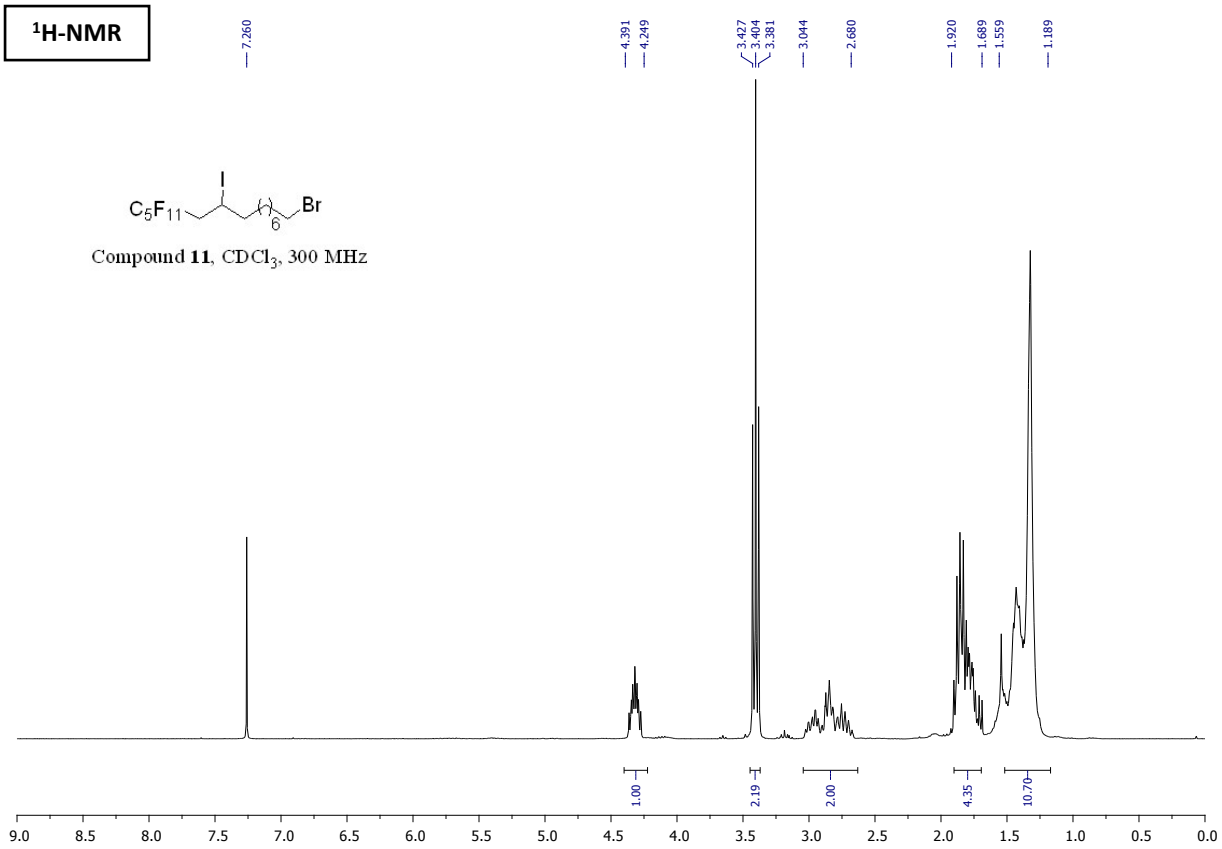
Compound **10**, $CDCl_3$, 75 MHz

^{19}F-NMR



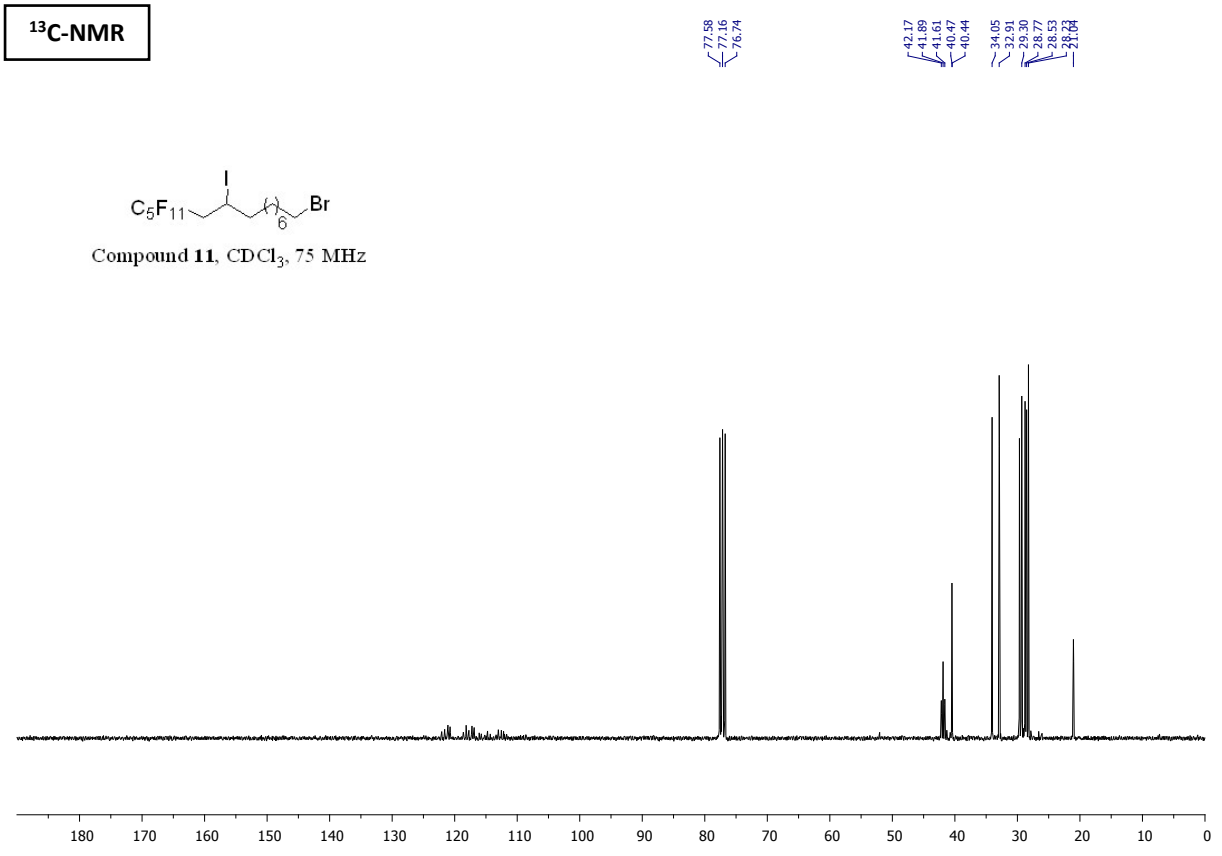
Compound **10**, $CDCl_3$, 282 MHz

^{1}H-NMR



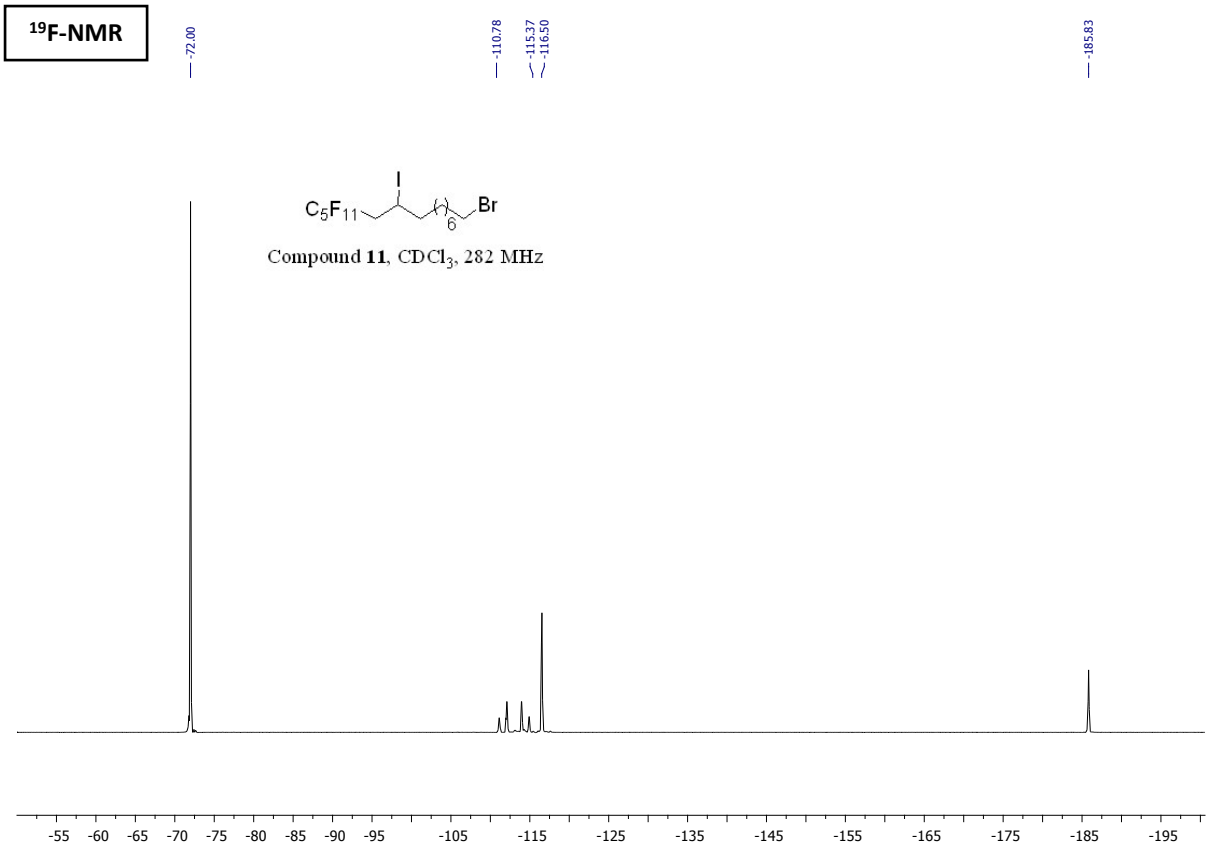
Compound **11**, $CDCl_3$, 300 MHz

^{13}C-NMR



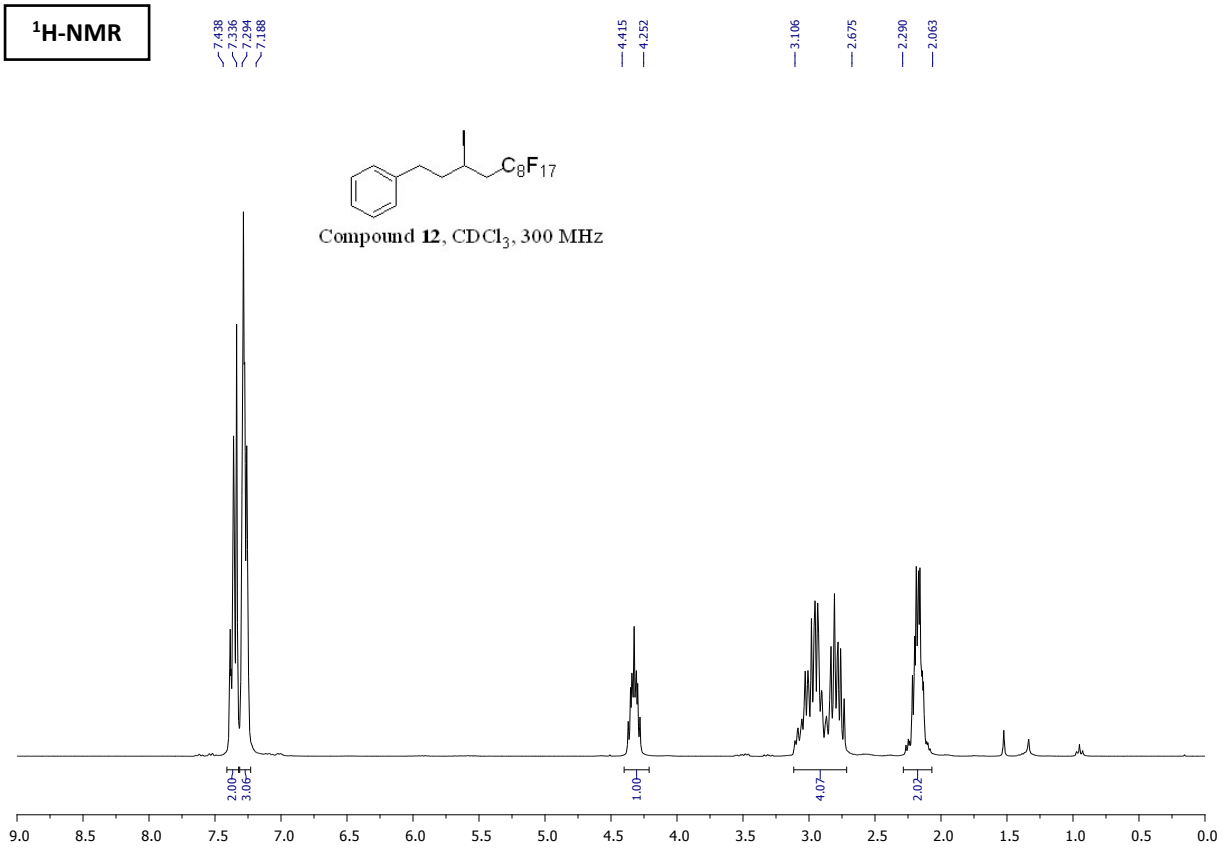
Compound **11**, $CDCl_3$, 75 MHz

^{19}F-NMR



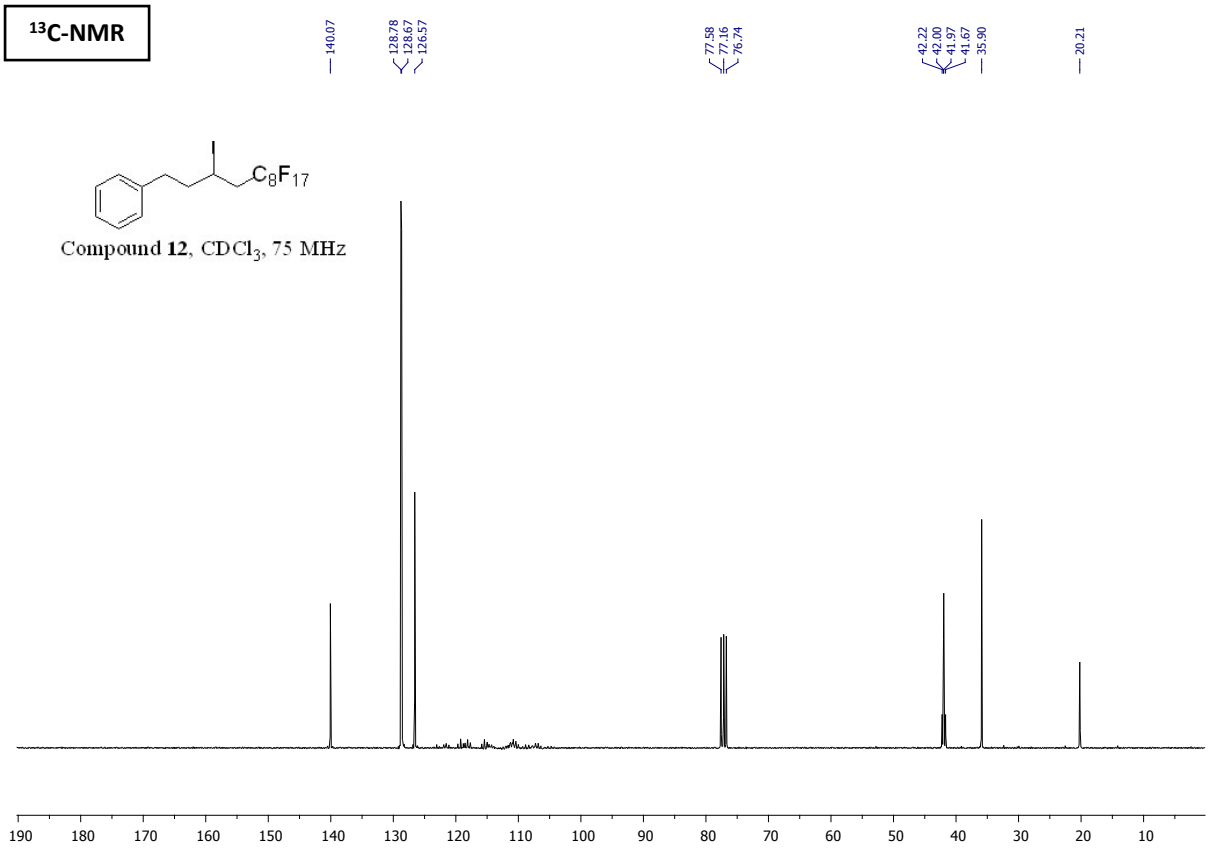
Compound **11**, $CDCl_3$, 282 MHz

^{1}H-NMR



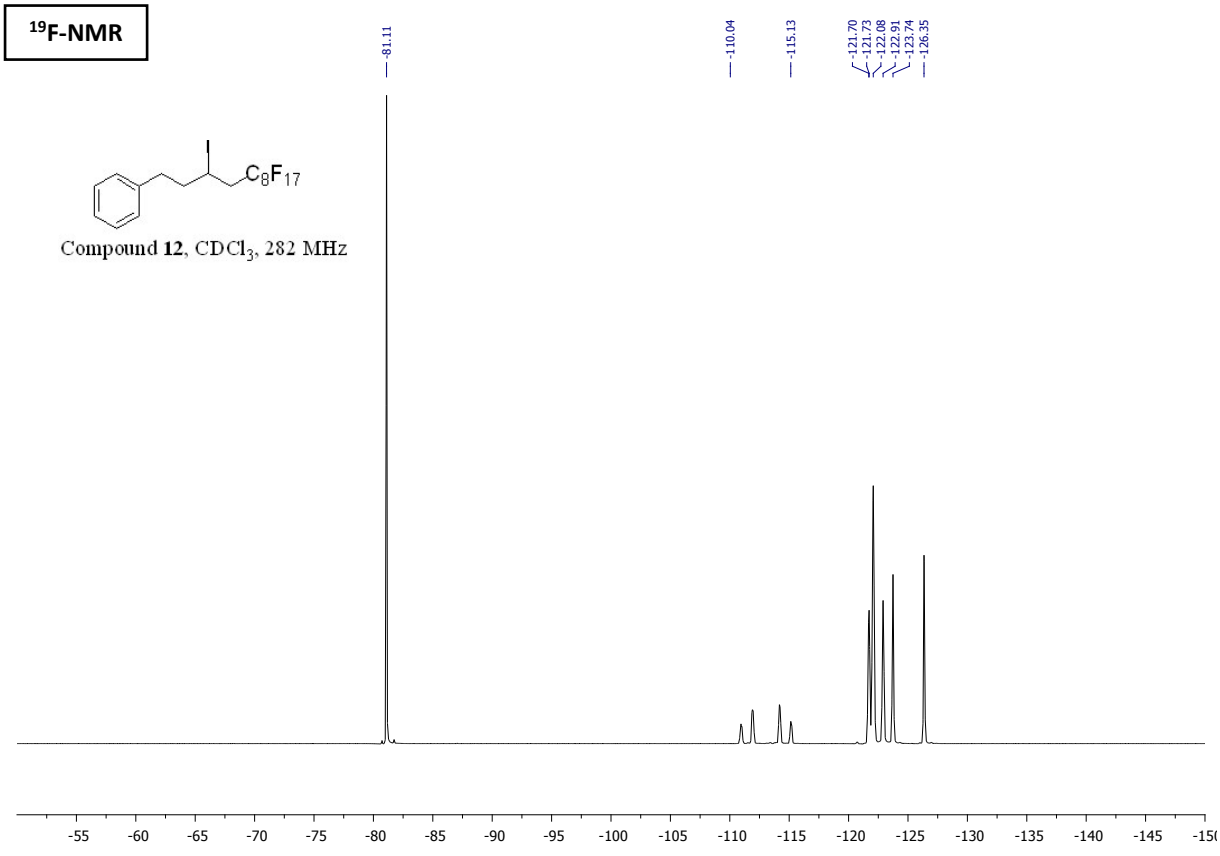
Compound **12**, $CDCl_3$, 300 MHz

^{13}C-NMR



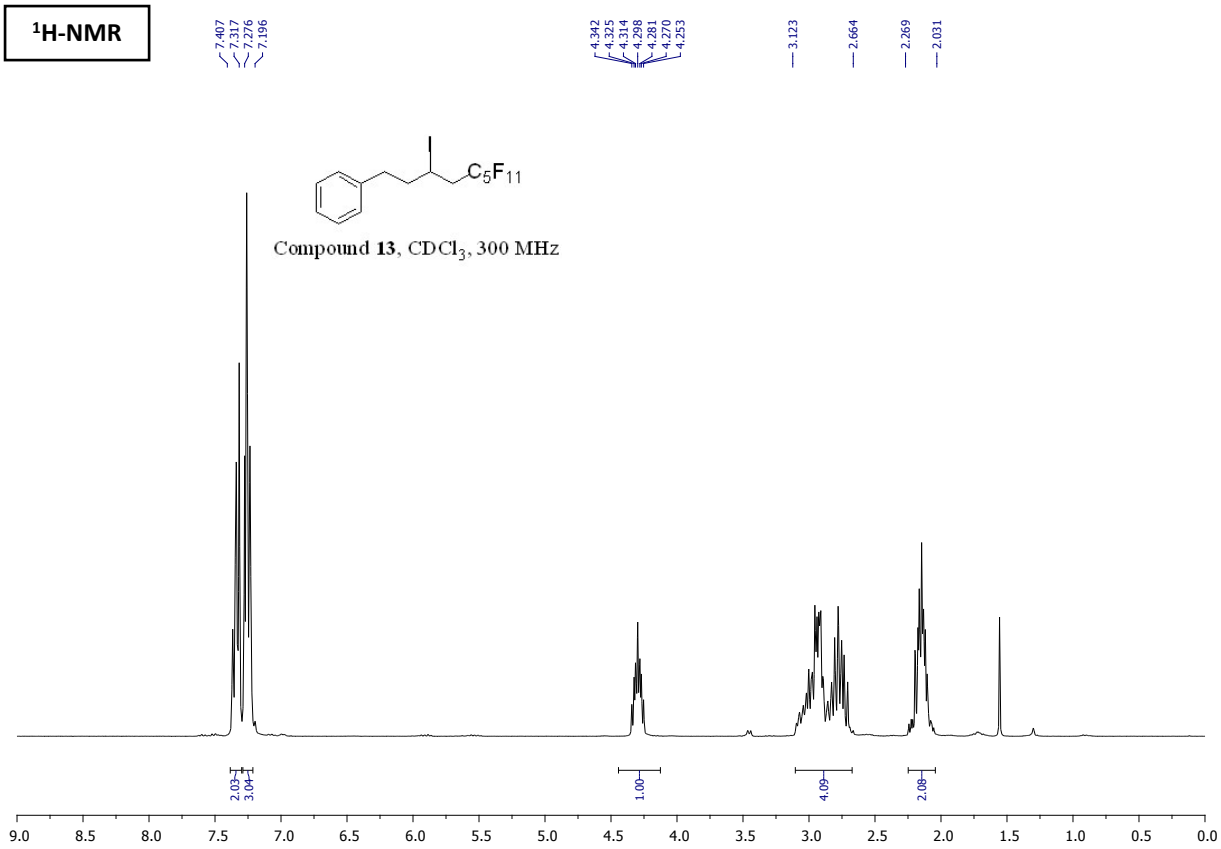
Compound **12**, $CDCl_3$, 75 MHz

^{19}F-NMR



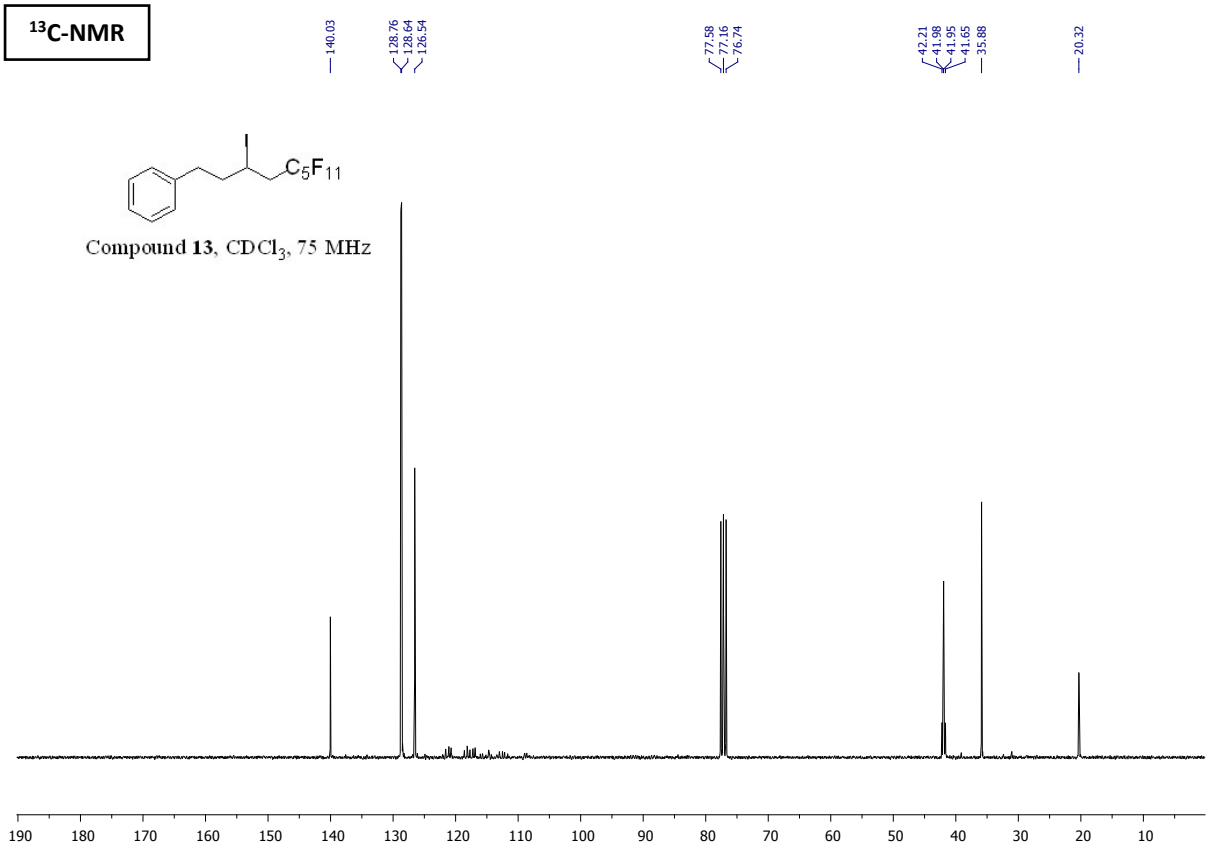
Compound **12**, $CDCl_3$, 282 MHz

^{1}H-NMR



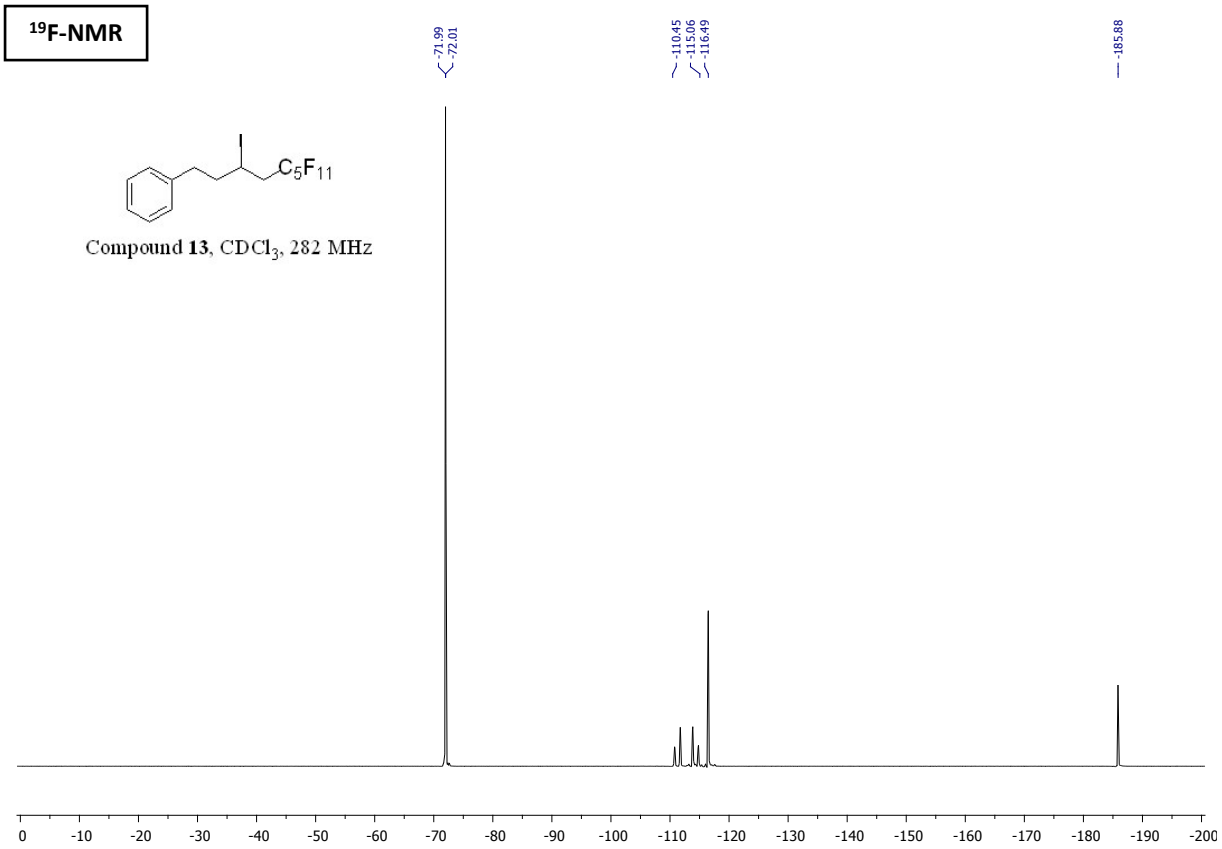
Compound **13**, $CDCl_3$, 300 MHz

^{13}C-NMR



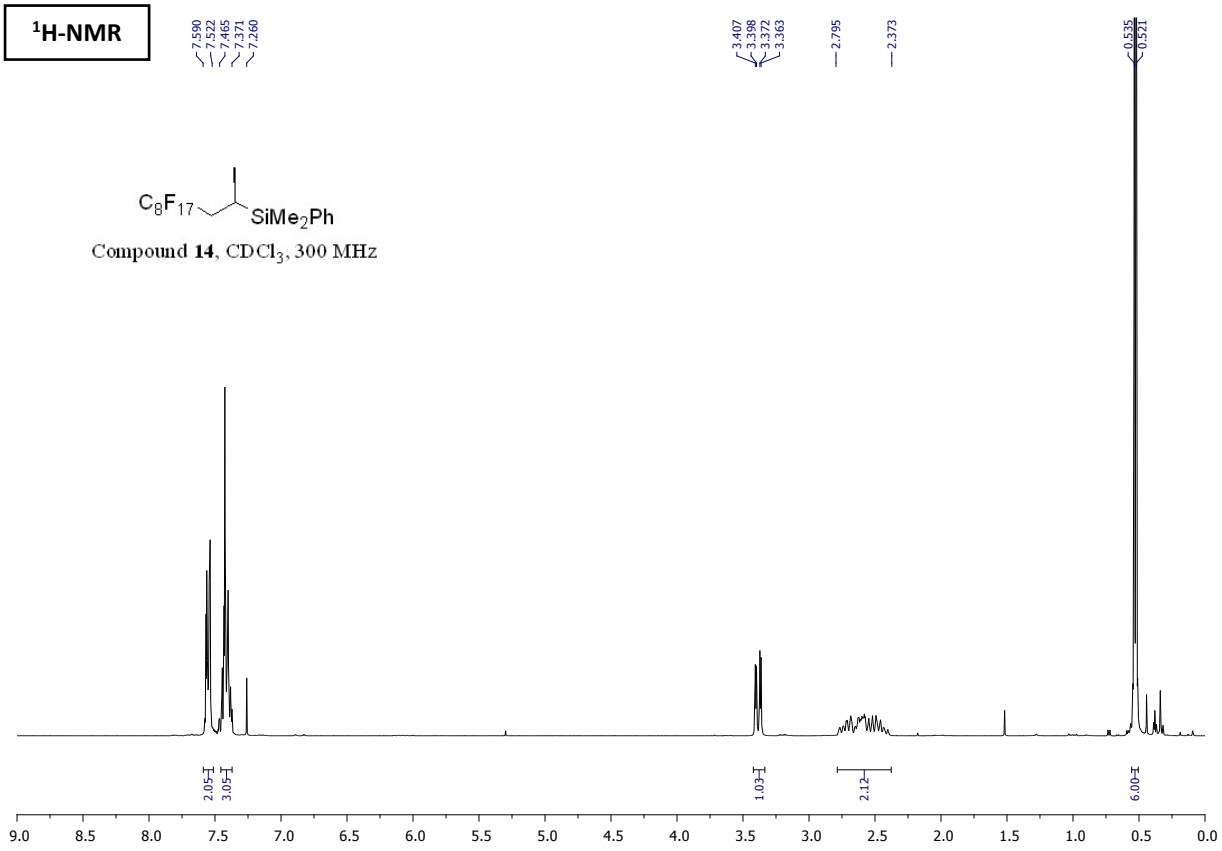
Compound **13**, $CDCl_3$, 75 MHz

^{19}F-NMR



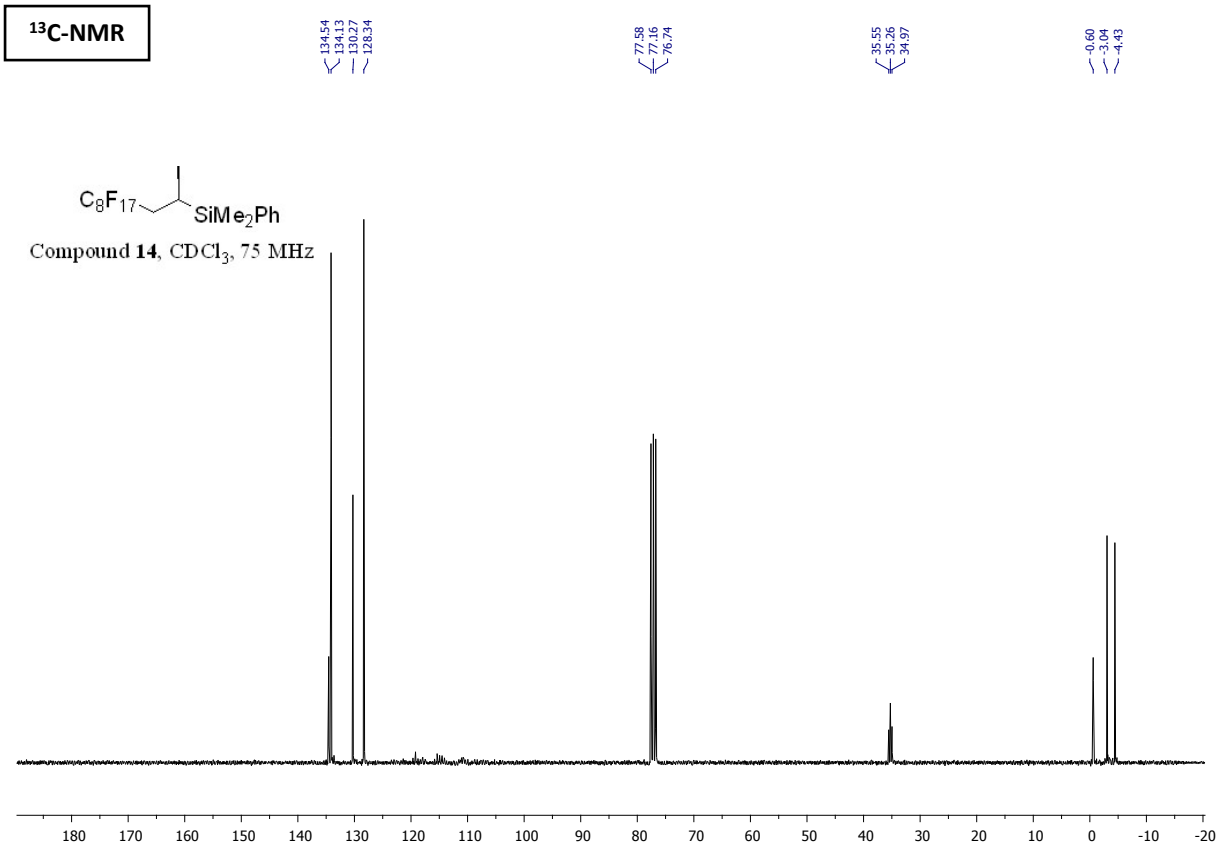
Compound **13**, $CDCl_3$, 282 MHz

^{1}H-NMR

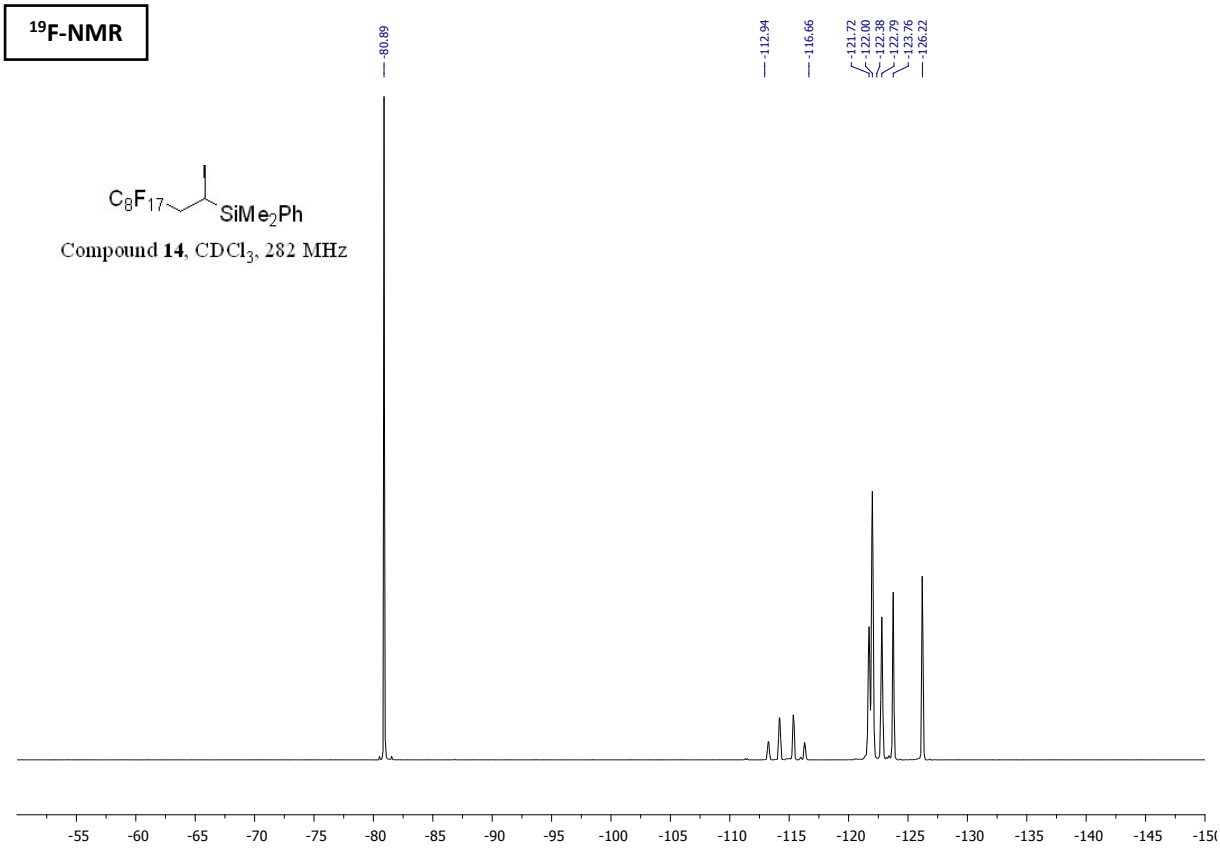


Compound **14**, $CDCl_3$, 300 MHz

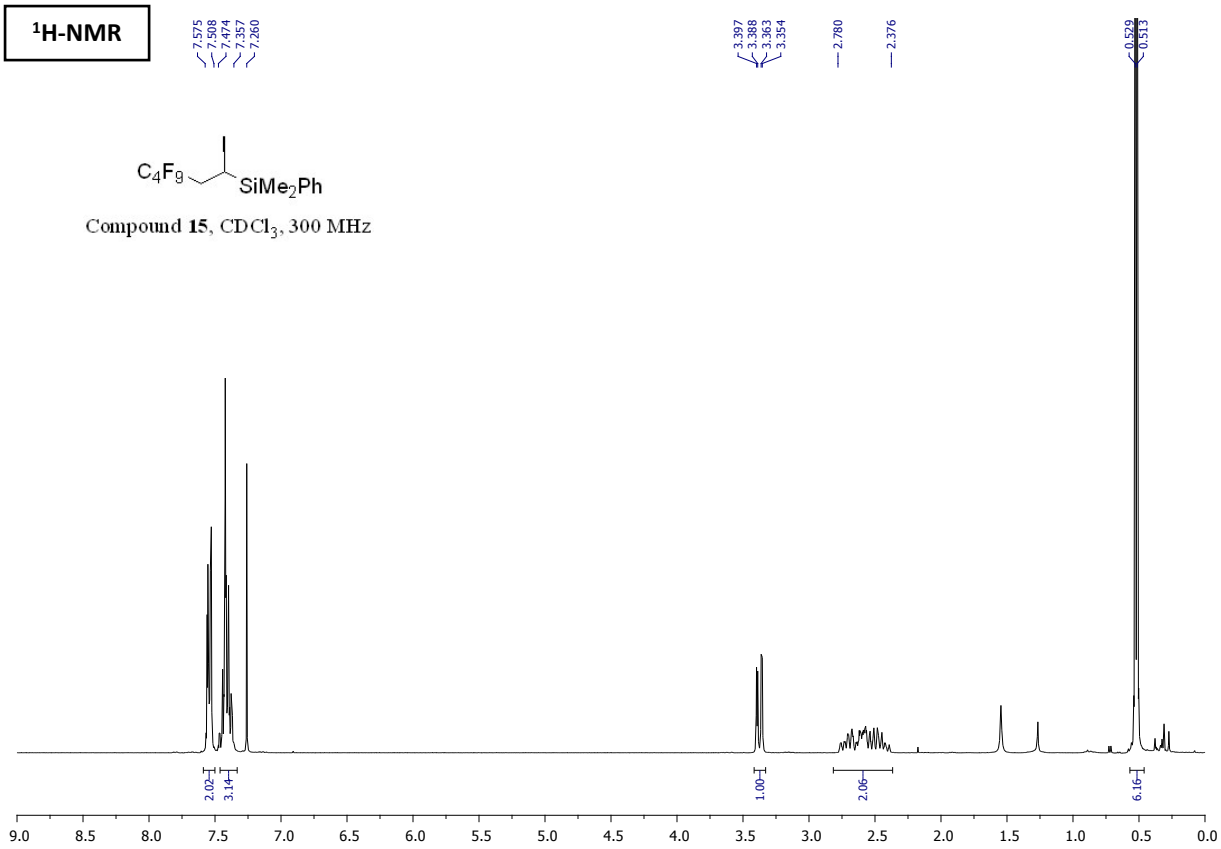
^{13}C-NMR



^{19}F-NMR



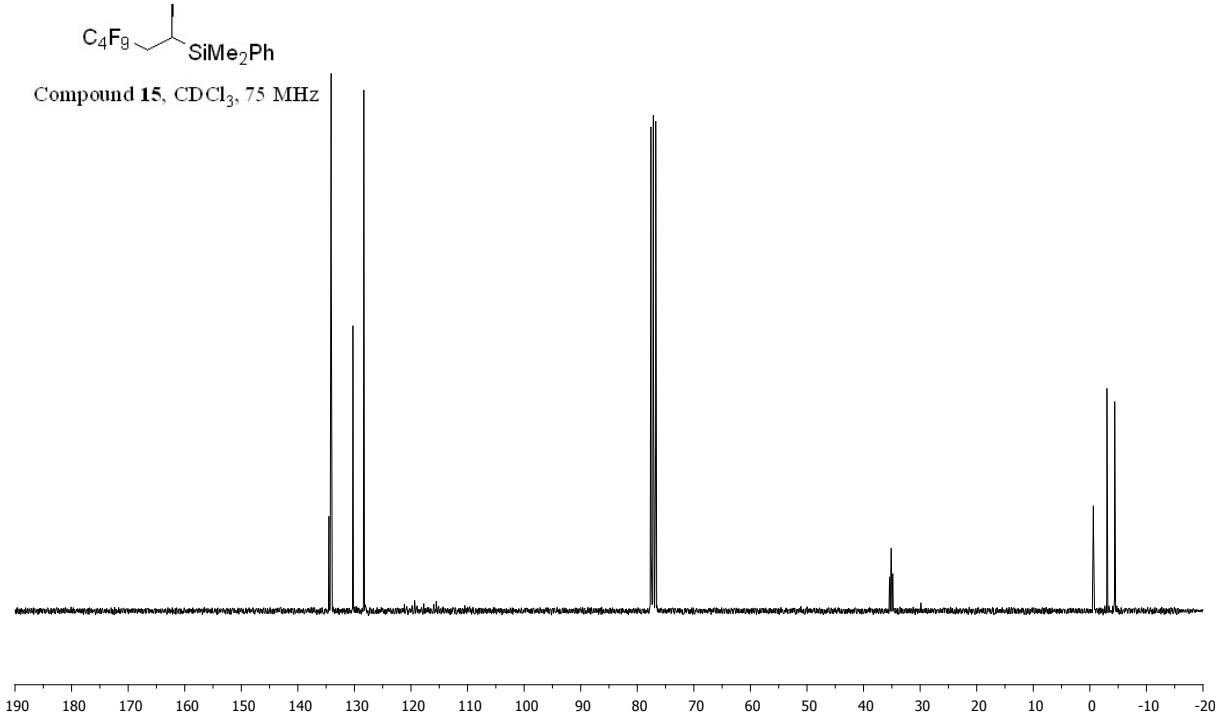
^{1}H-NMR



C_4F_9 SiMe$_2$Ph

Compound **15**, $CDCl_3$, 300 MHz

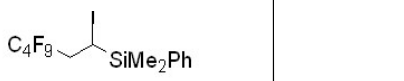
^{13}C-NMR



C_4F_9 SiMe$_2$Ph

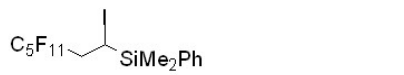
Compound **15**, $CDCl_3$, 75 MHz

^{19}F-NMR



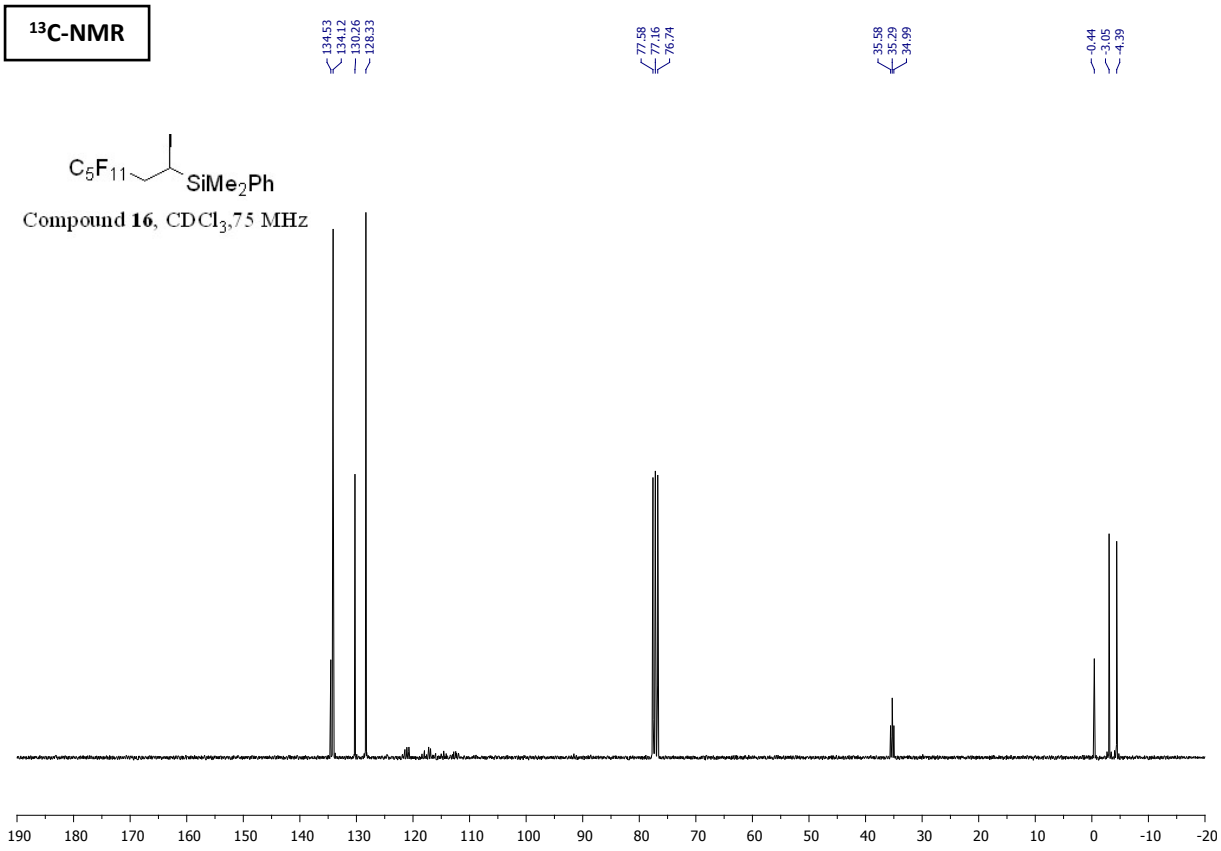
Compound **15**, $CDCl_3$, 282 MHz

^{1}H-NMR

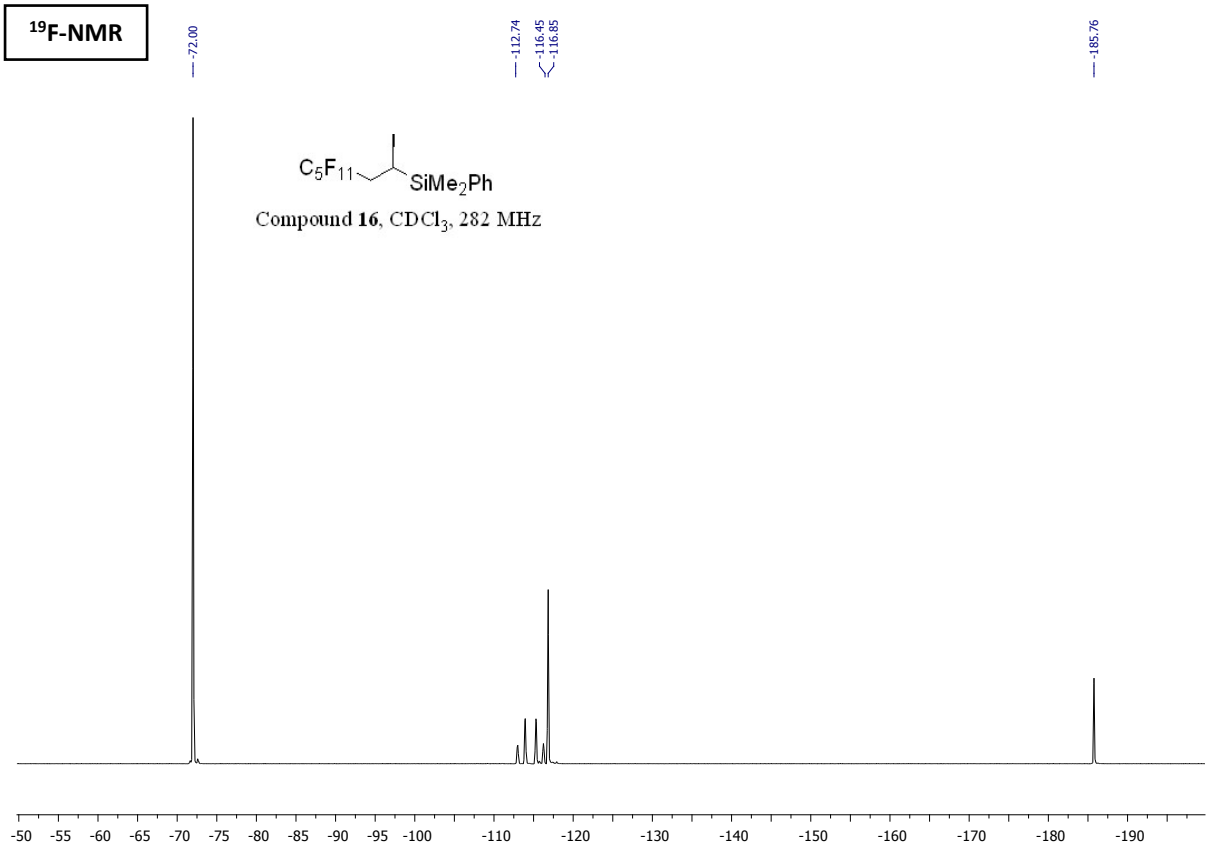


Compound **16**, $CDCl_3$, 300 MHz

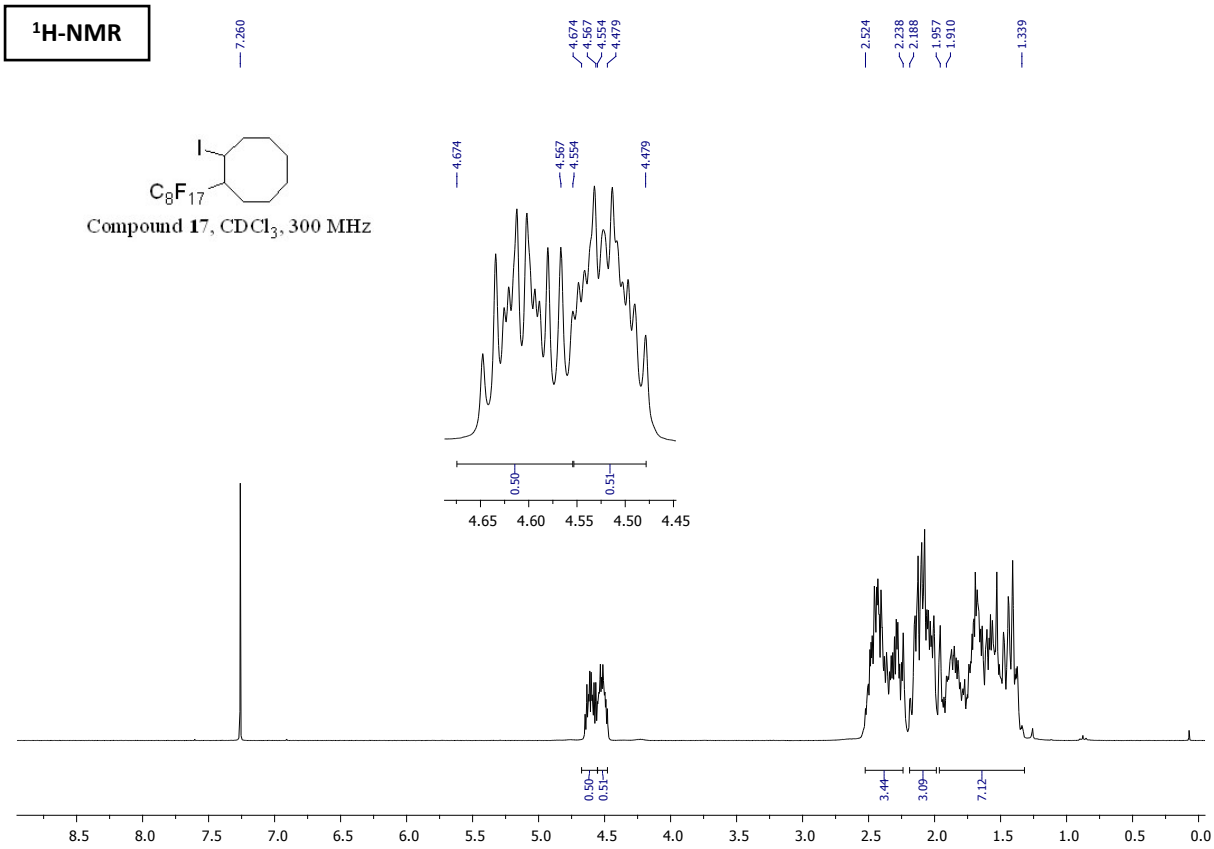
^{13}C-NMR



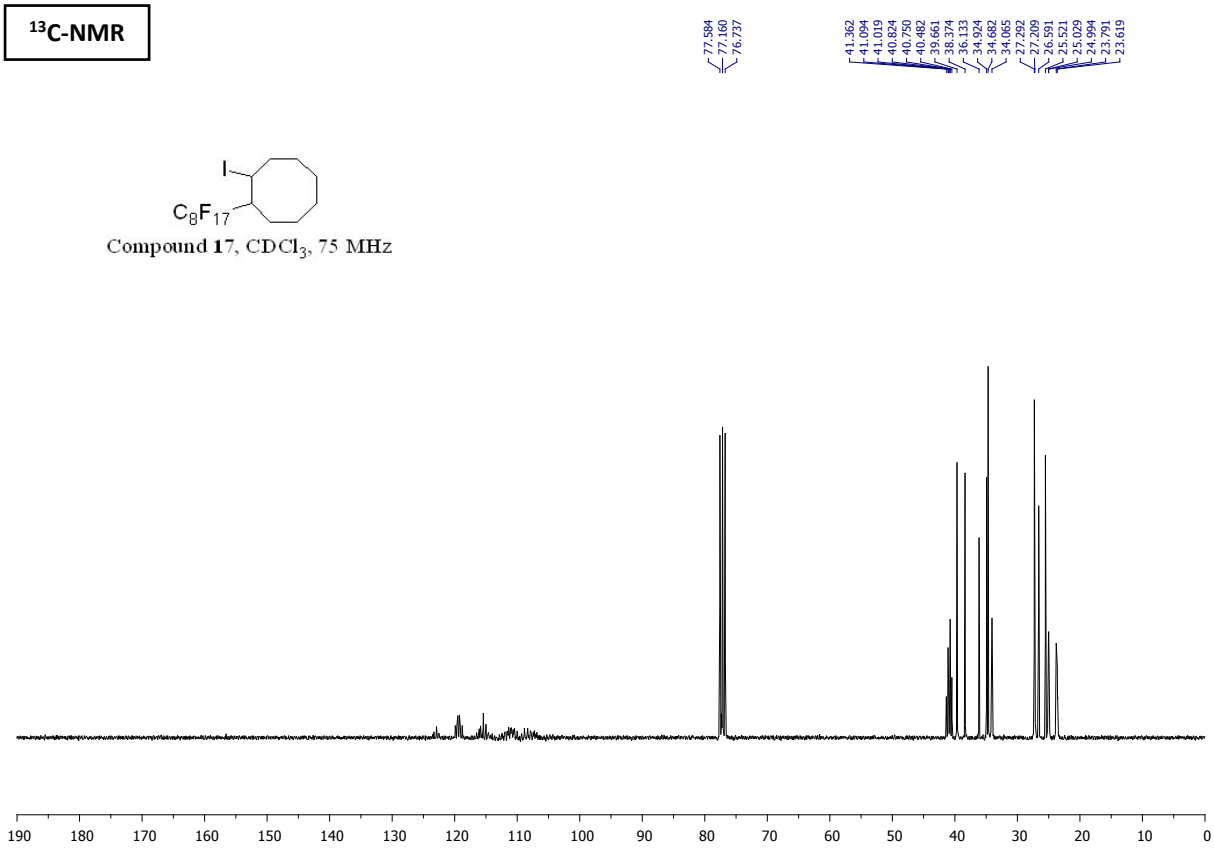
^{19}F-NMR



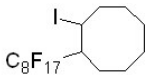
^{1}H-NMR



^{13}C-NMR

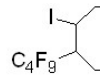


^{19}F-NMR



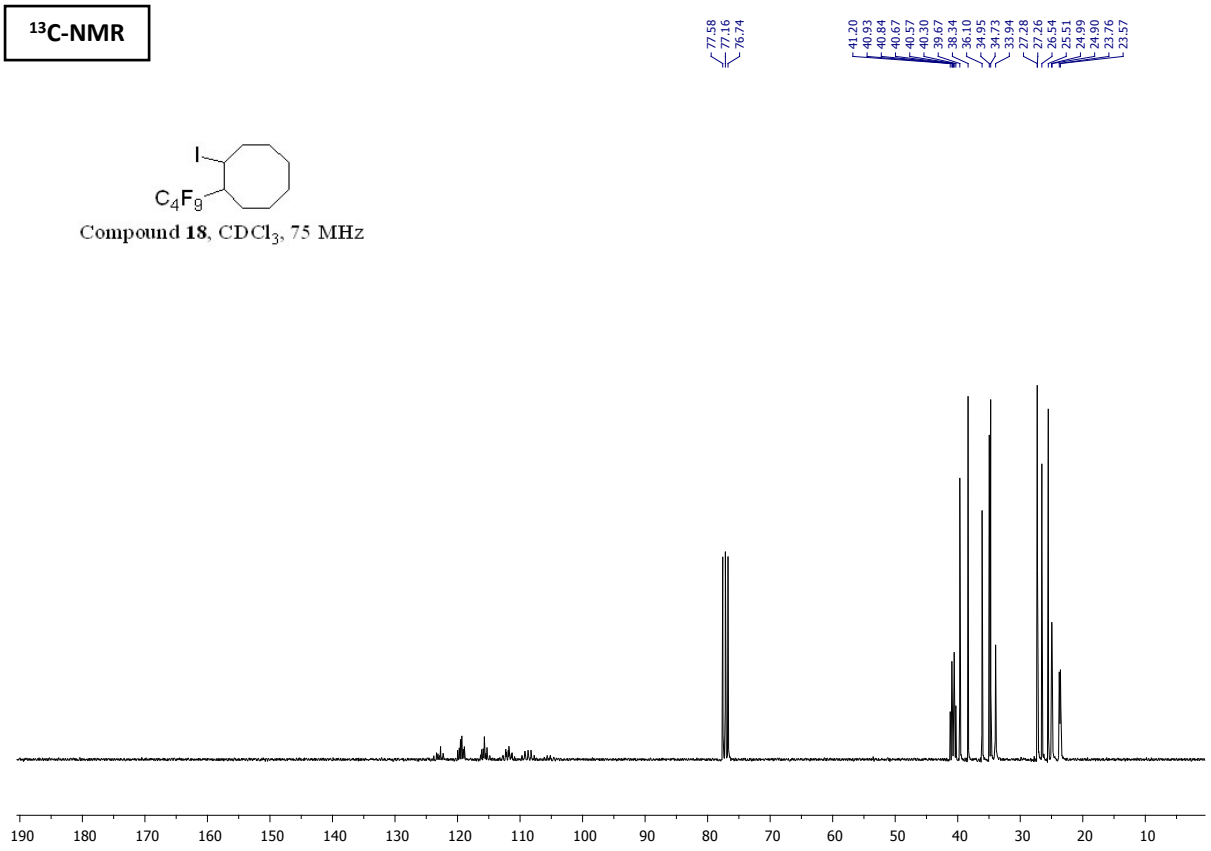
Compound **17**, $CDCl_3$, 282 MHz

^{1}H-NMR



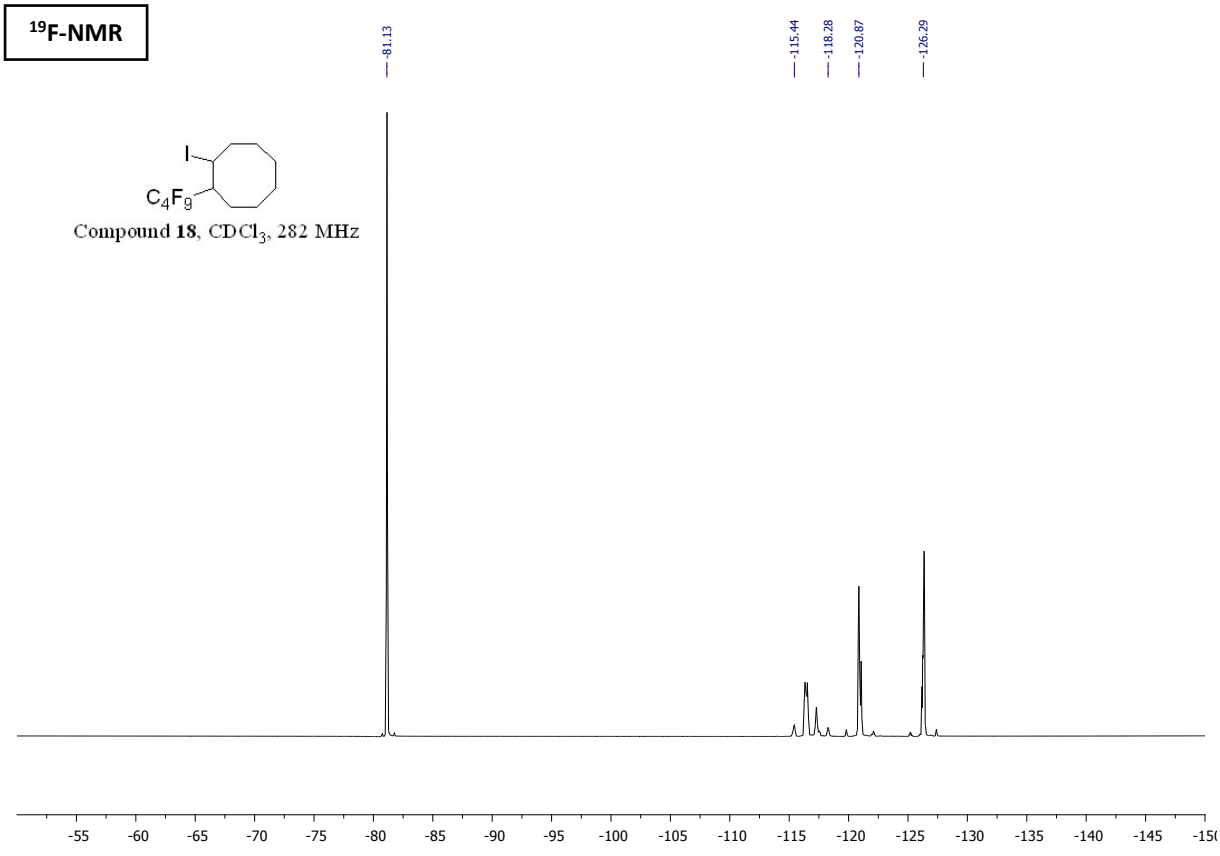
Compound **18**, $CDCl_3$, 300 MHz

^{13}C-NMR



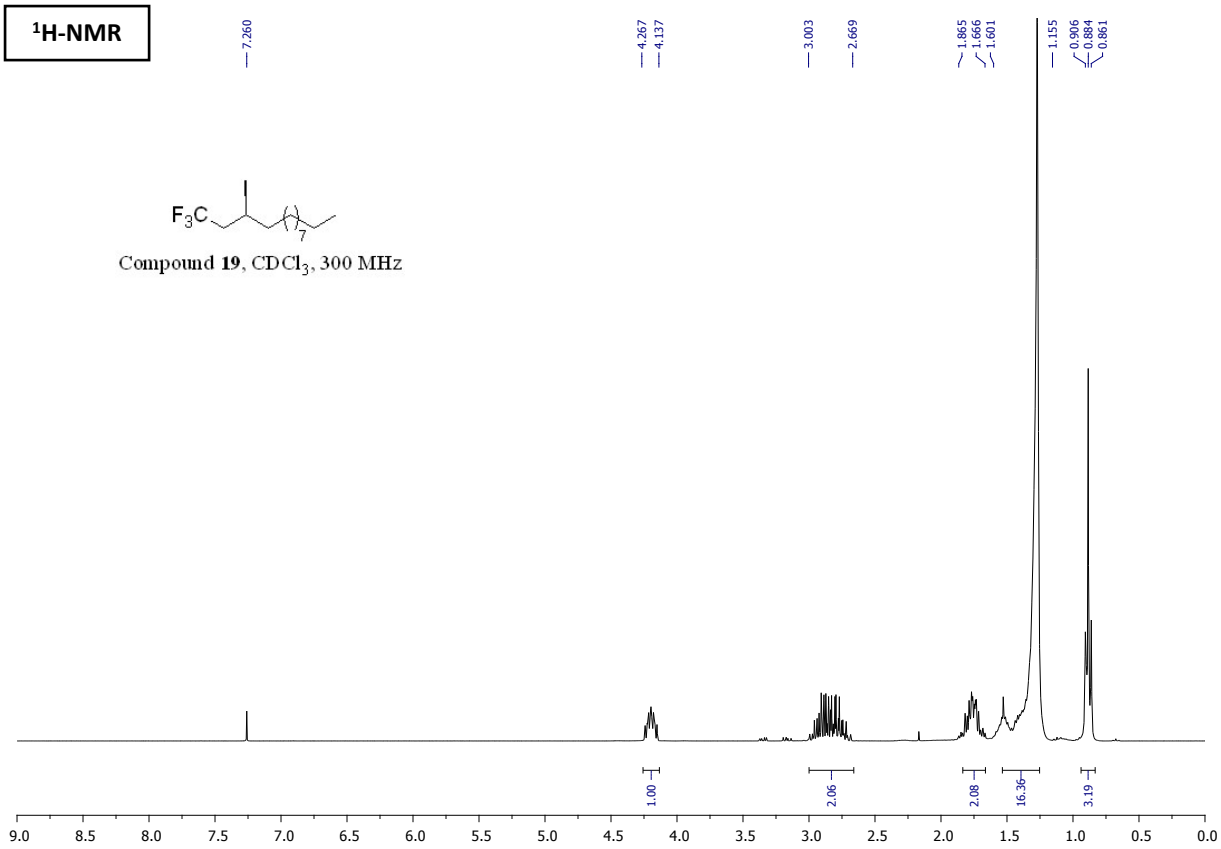
Compound **18**, $CDCl_3$, 75 MHz

^{19}F-NMR



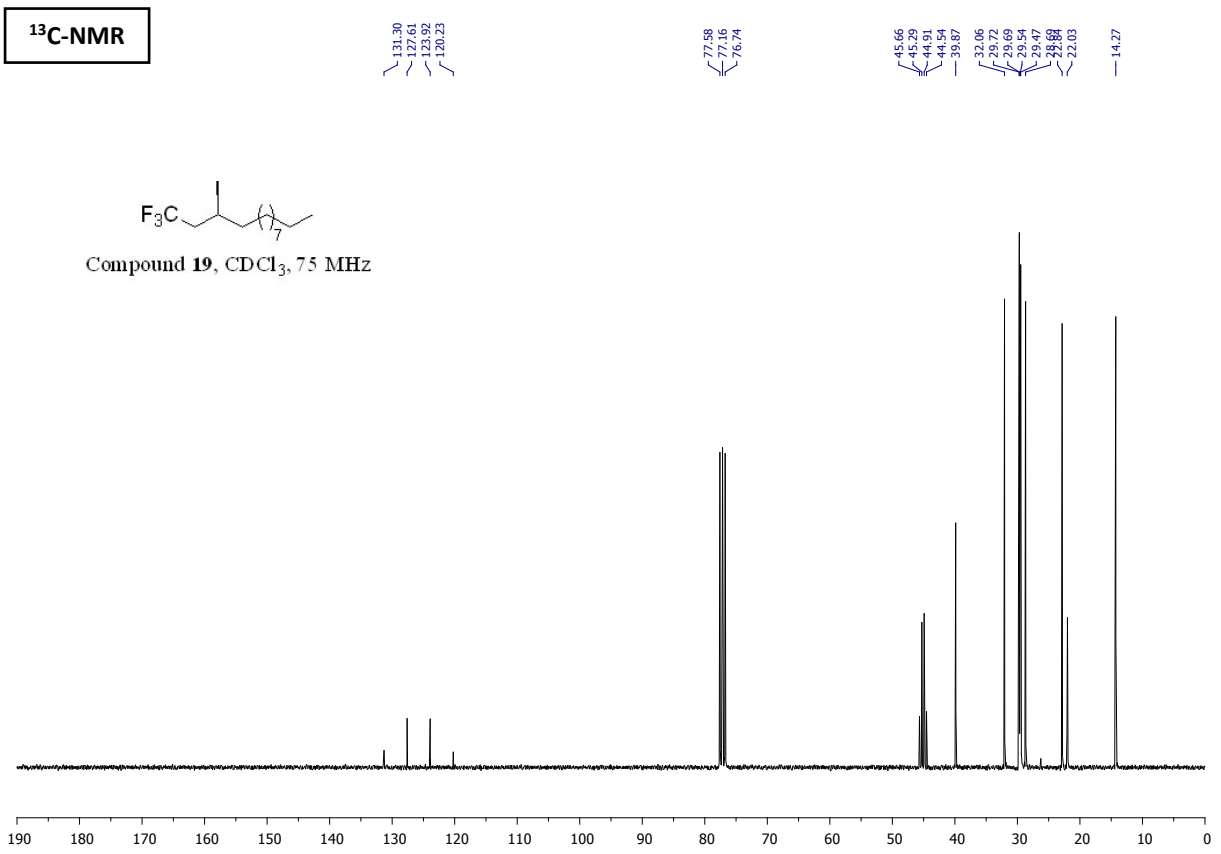
Compound **18**, $CDCl_3$, 282 MHz

^{1}H-NMR



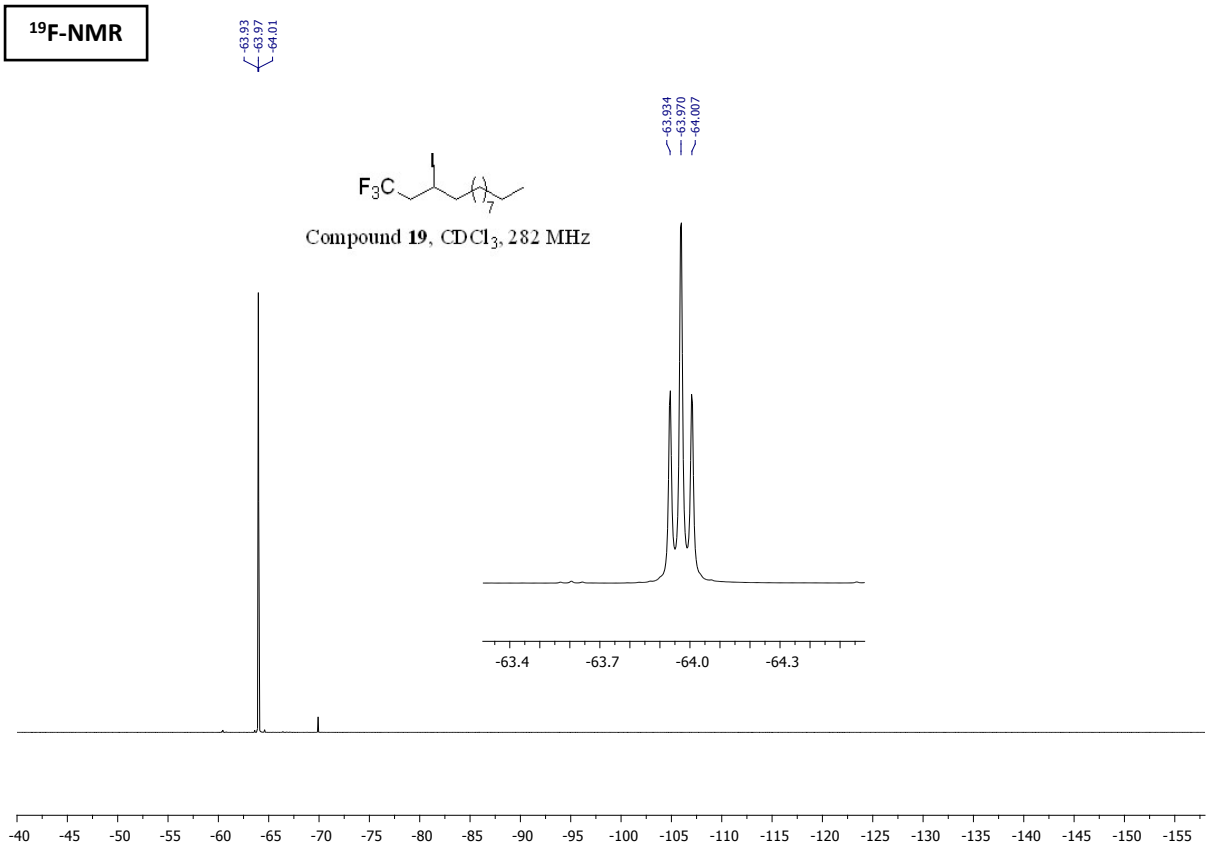
Compound **19**, $CDCl_3$, 300 MHz

^{13}C-NMR



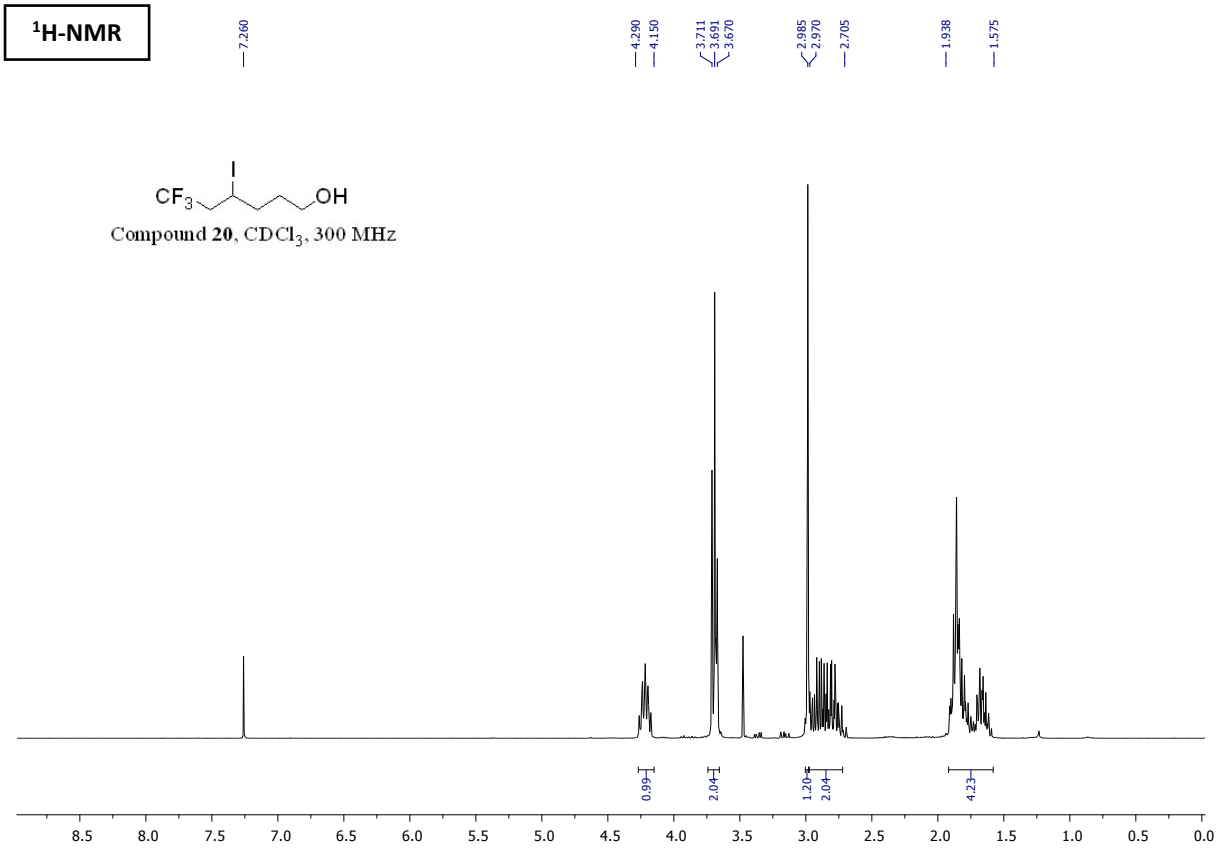
Compound **19**, $CDCl_3$, 75 MHz

^{19}F-NMR



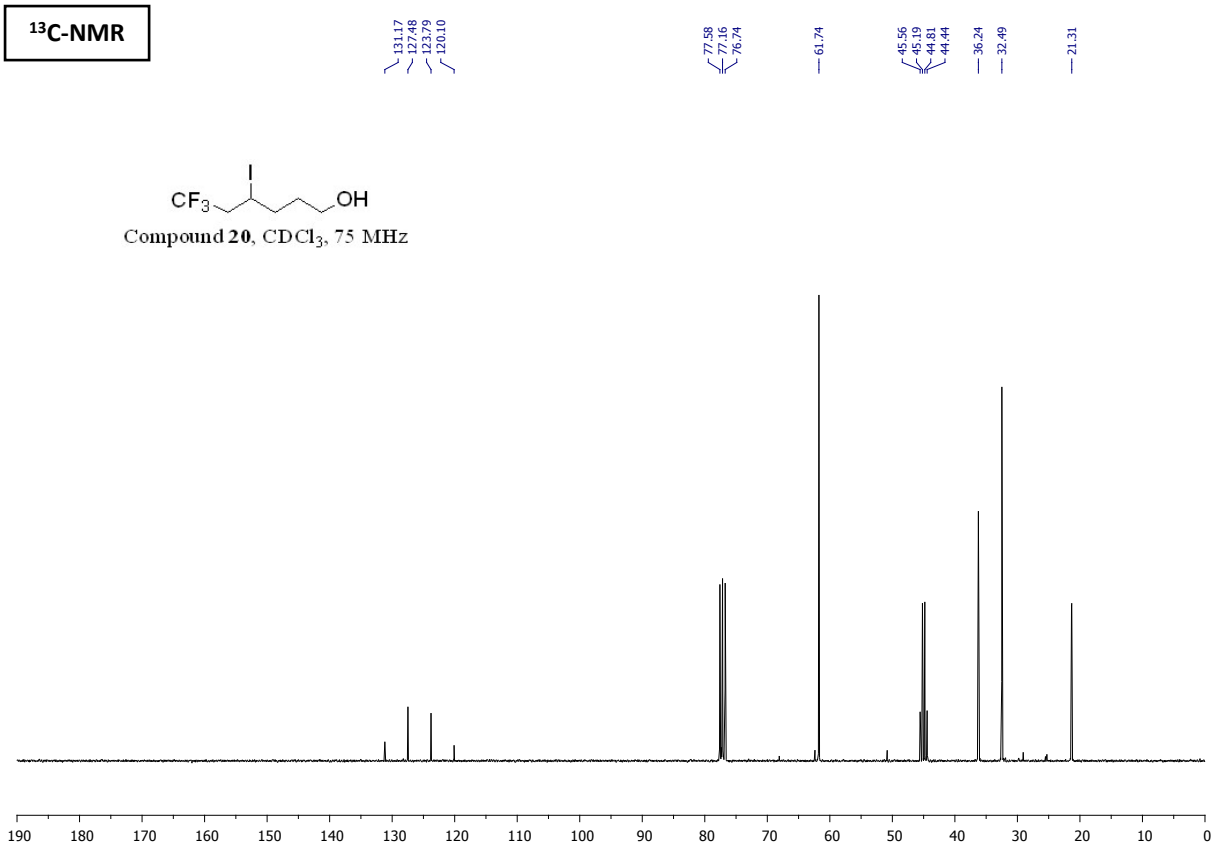
Compound **19**, $CDCl_3$, 282 MHz

^{1}H-NMR



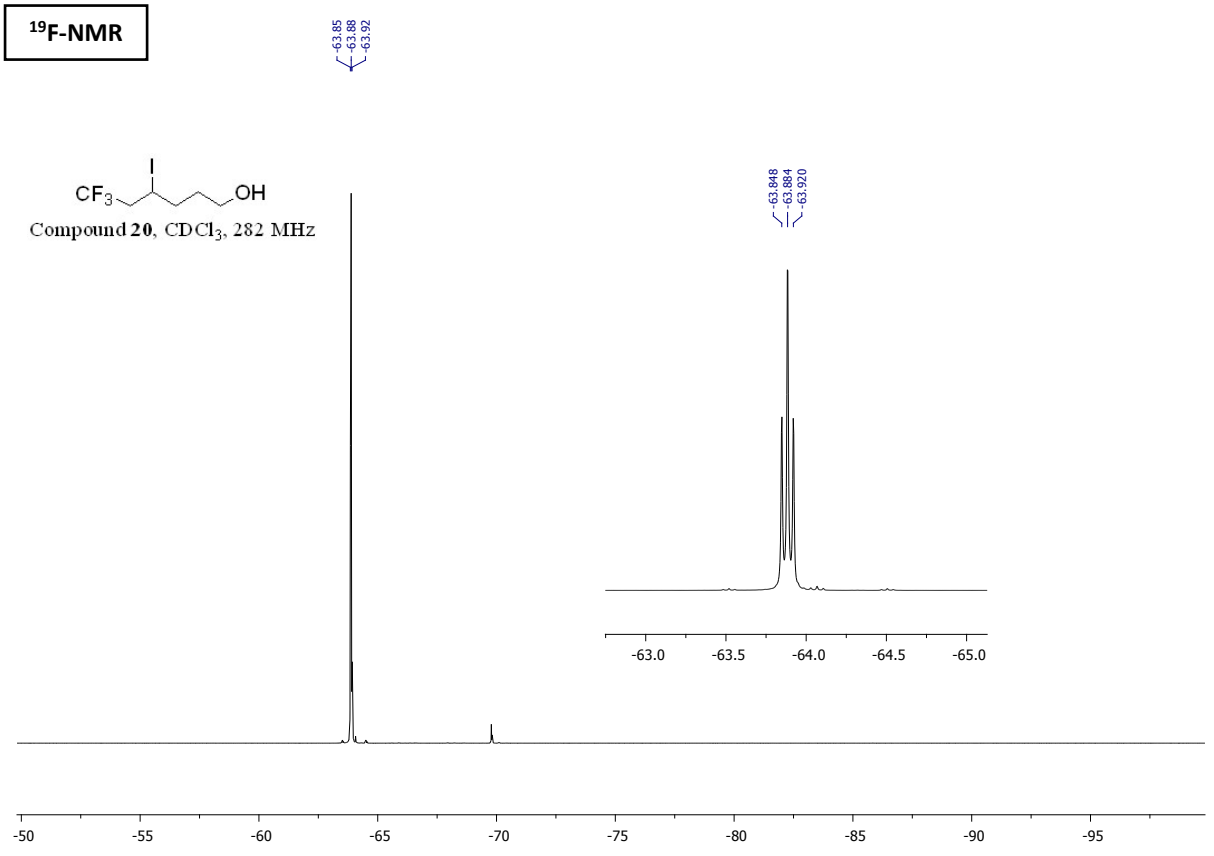
Compound **20**, $CDCl_3$, 300 MHz

^{13}C-NMR



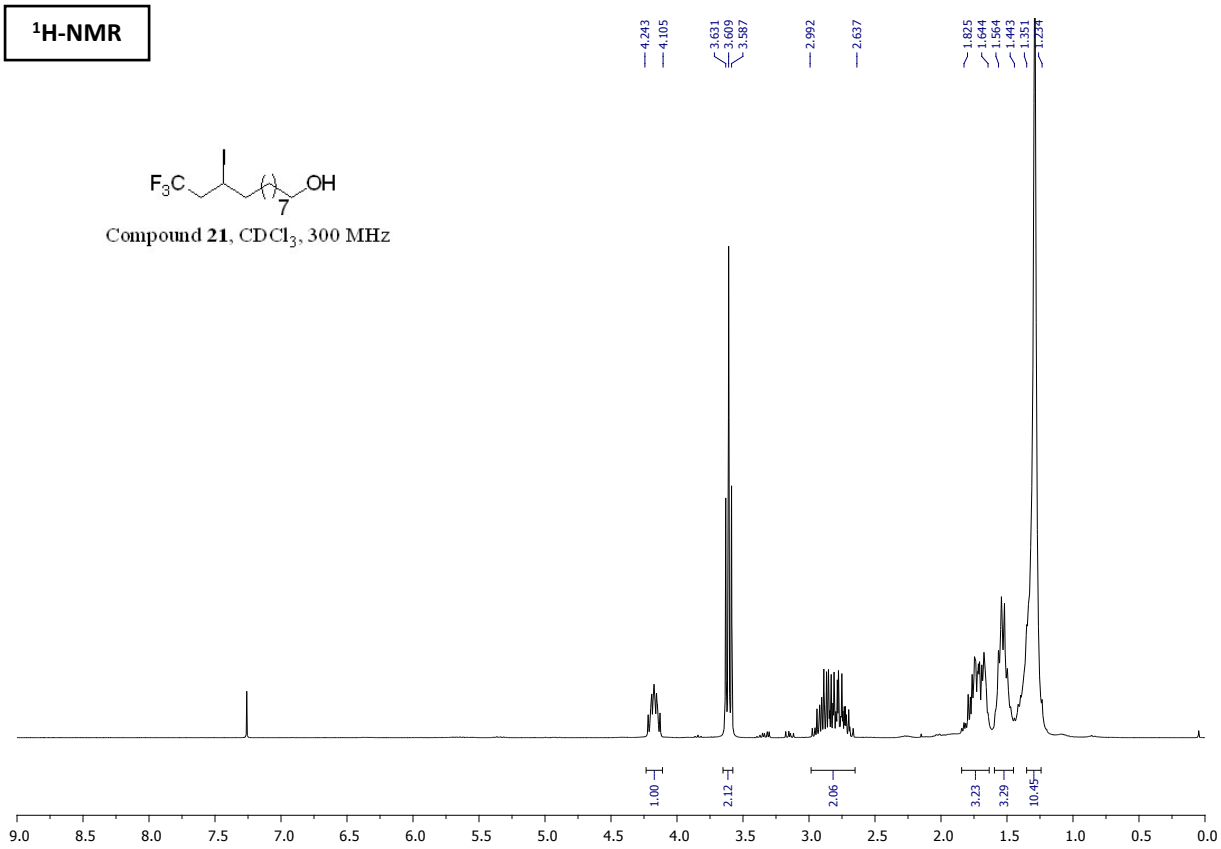
Compound **20**, $CDCl_3$, 75 MHz

^{19}F-NMR



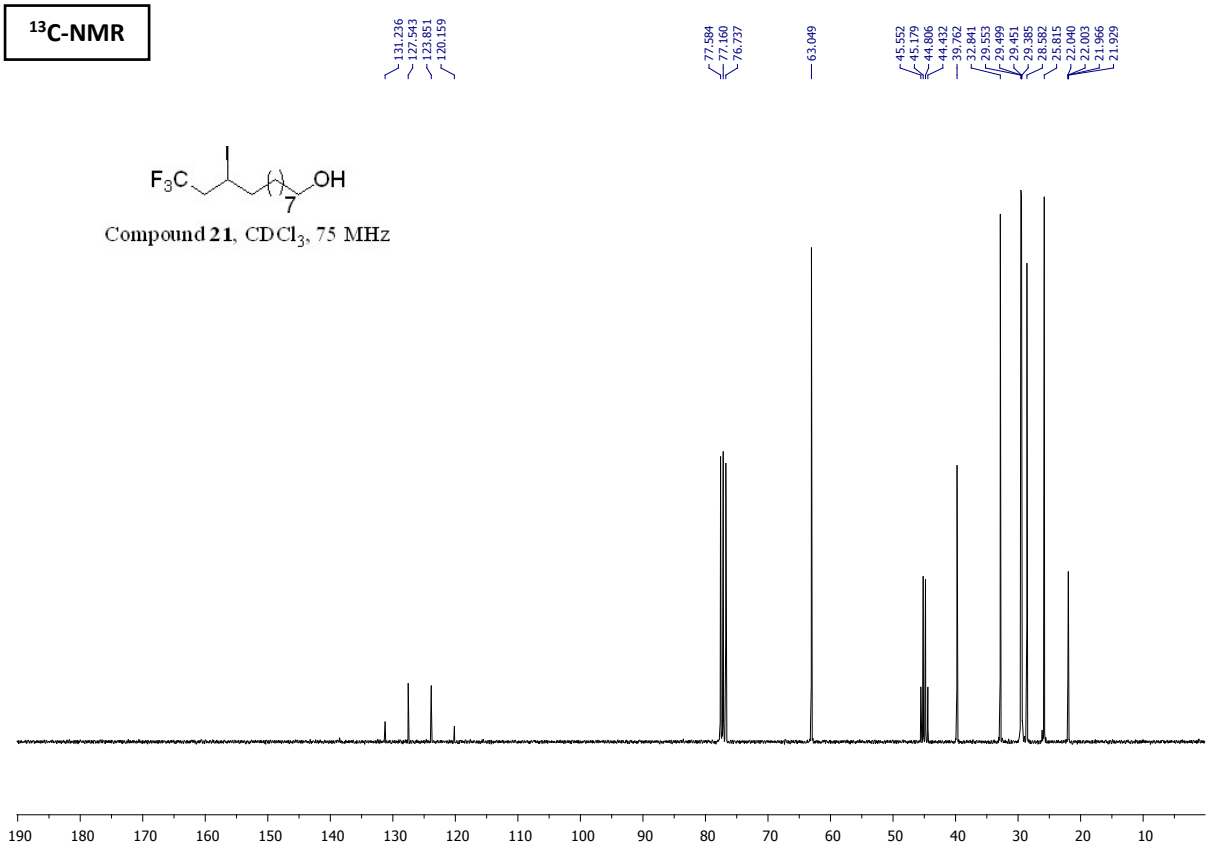
Compound **20**, $CDCl_3$, 282 MHz

^{1}H-NMR



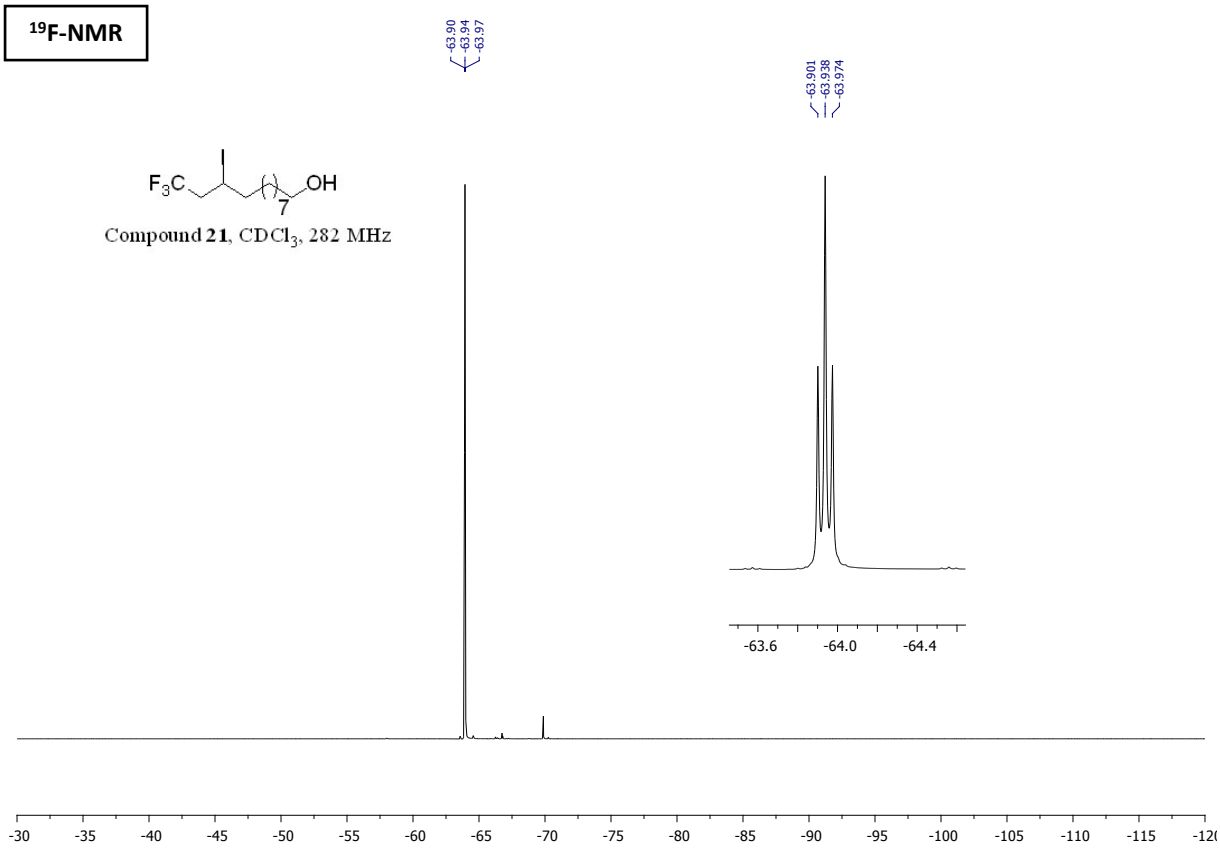
Compound **21**, $CDCl_3$, 300 MHz

^{13}C-NMR



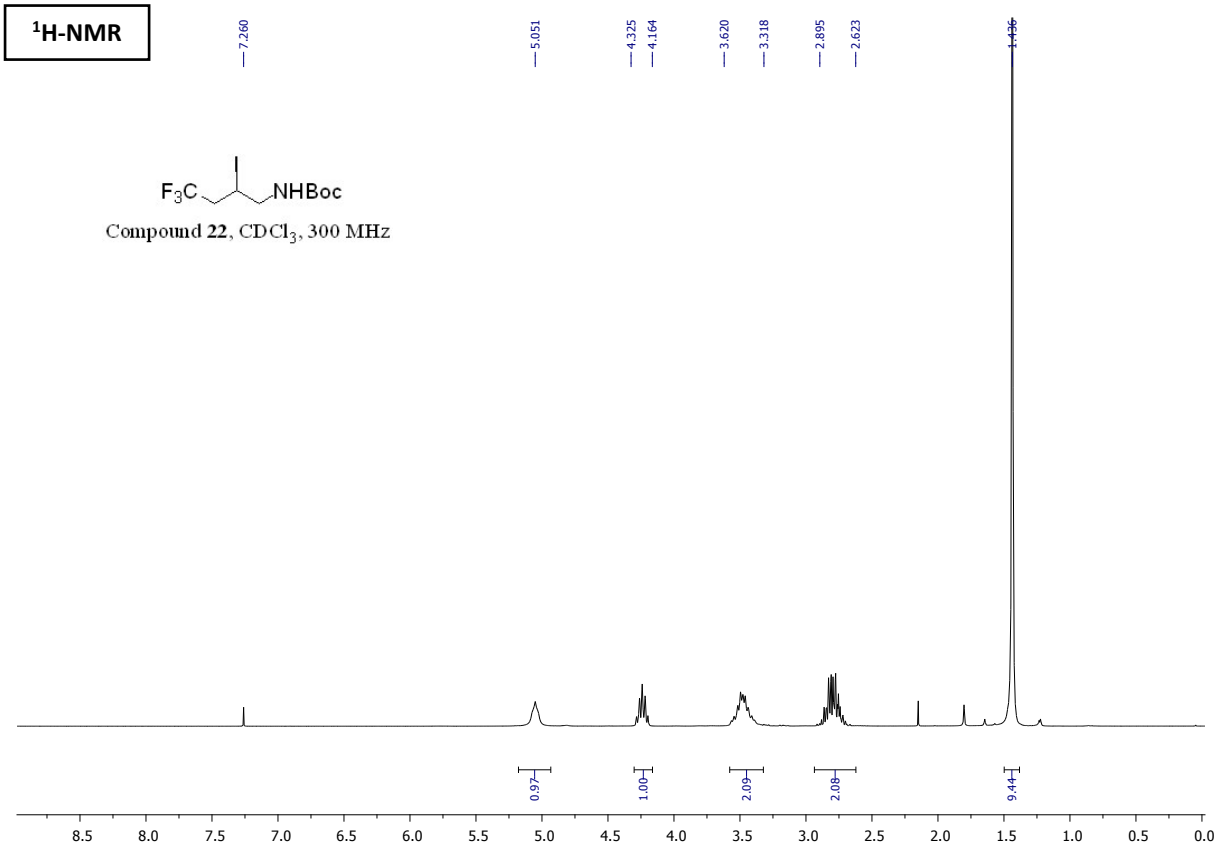
Compound **21**, $CDCl_3$, 75 MHz

^{19}F-NMR



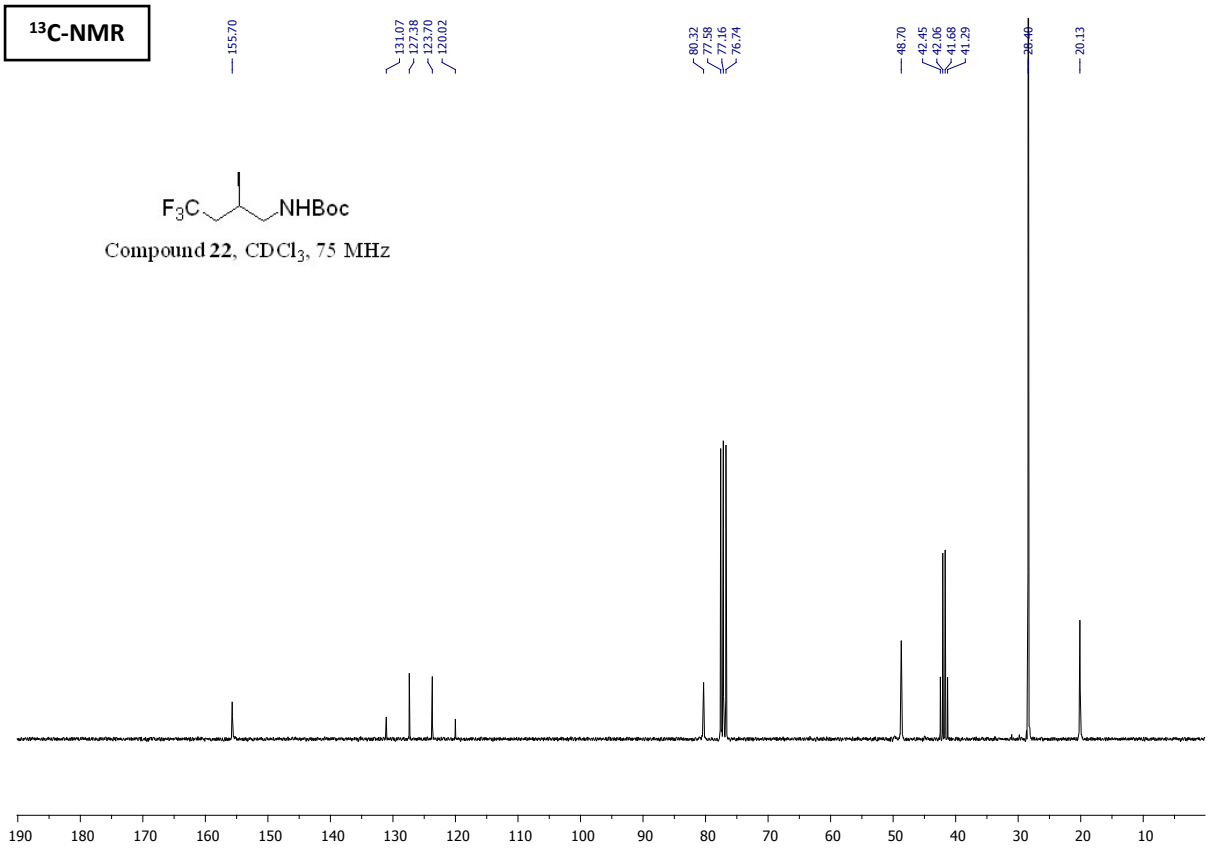
Compound **21**, $CDCl_3$, 282 MHz

^{1}H-NMR



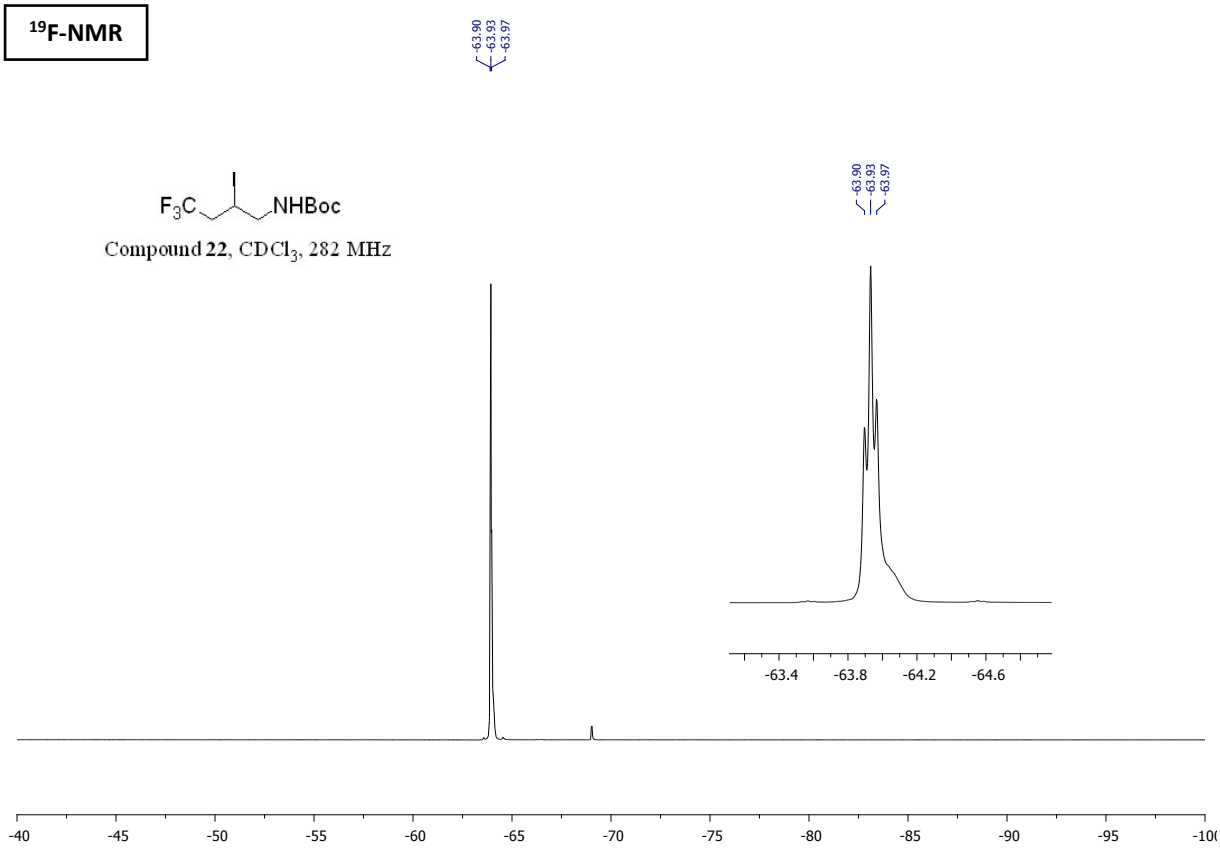
Compound **22**, $CDCl_3$, 300 MHz

^{13}C-NMR



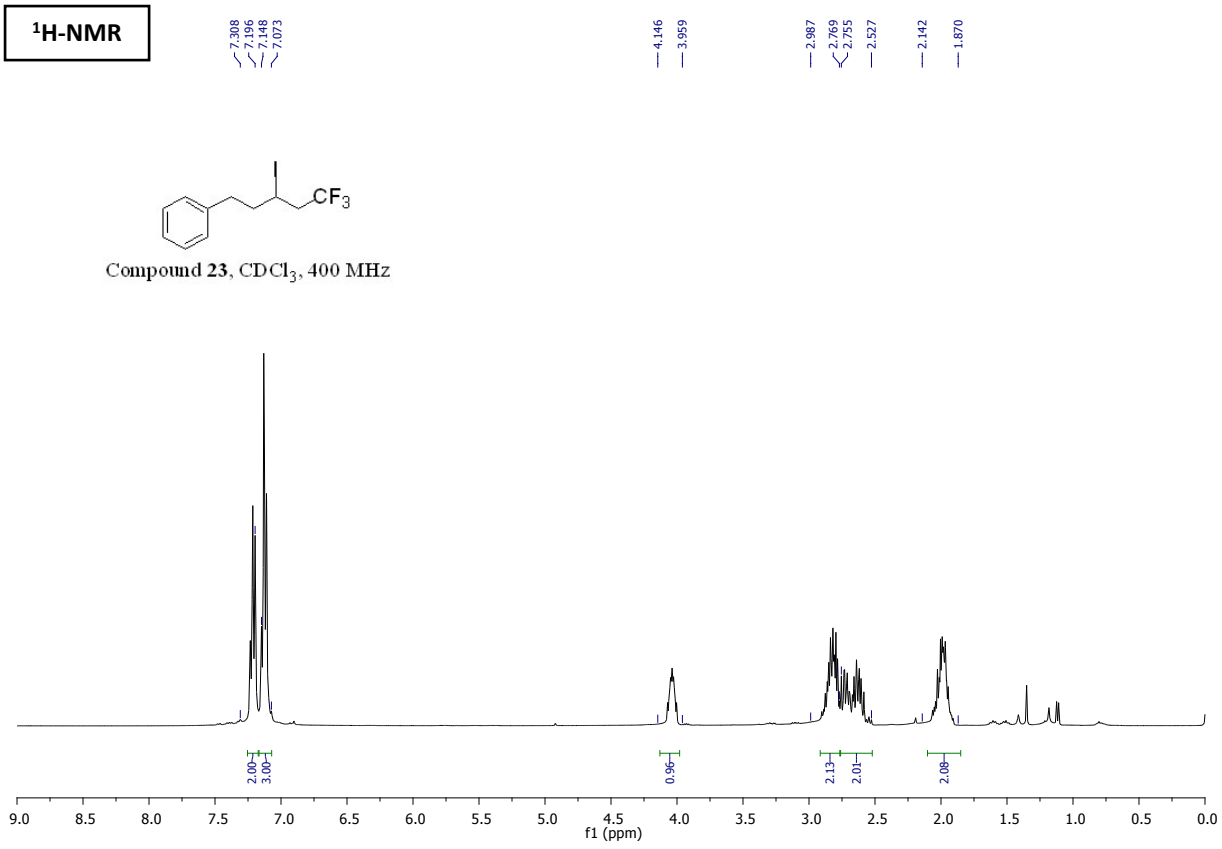
Compound **22**, $CDCl_3$, 75 MHz

^{19}F-NMR



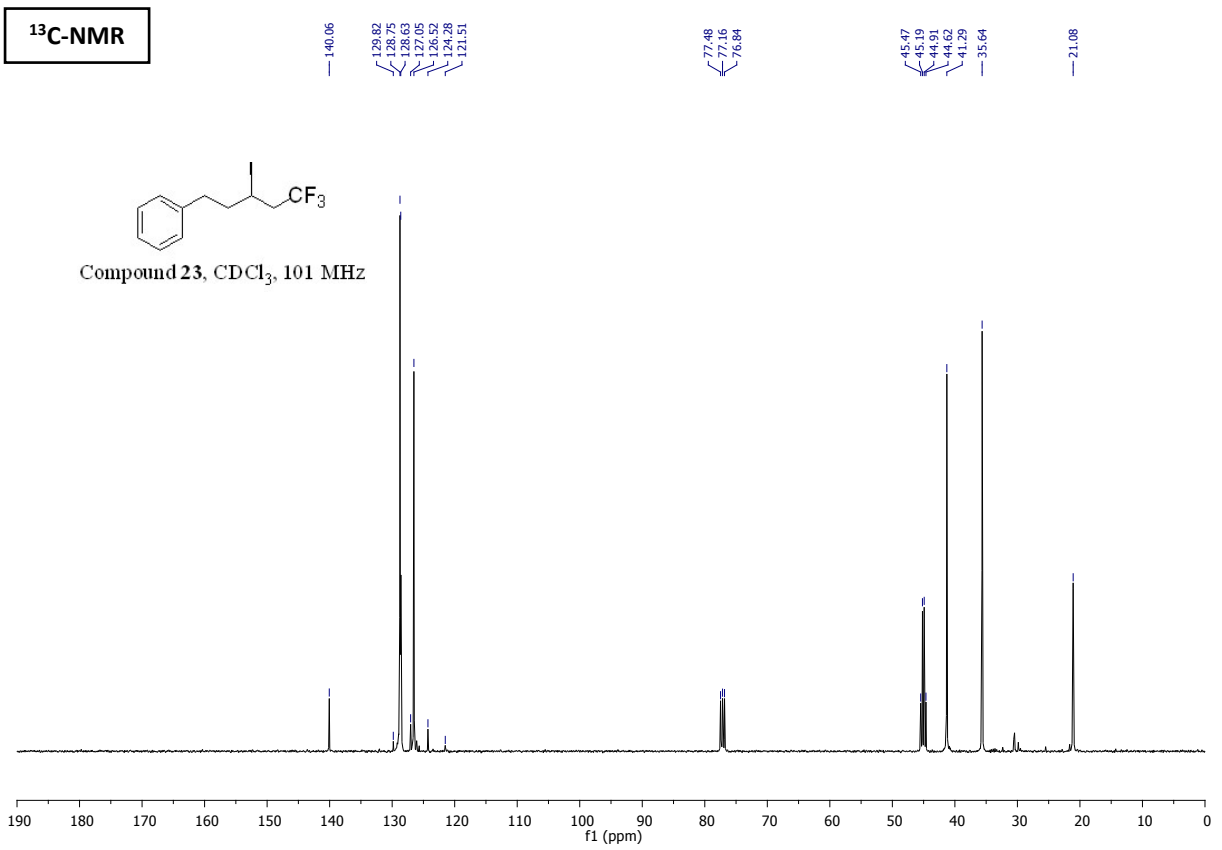
Compound **22**, $CDCl_3$, 282 MHz

^{1}H-NMR



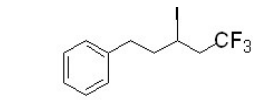
Compound **23**, $CDCl_3$, 400 MHz

^{13}C-NMR



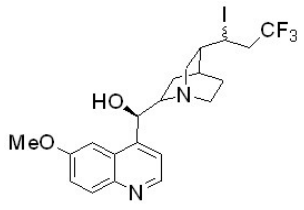
Compound **23**, $CDCl_3$, 101 MHz

^{19}F-NMR



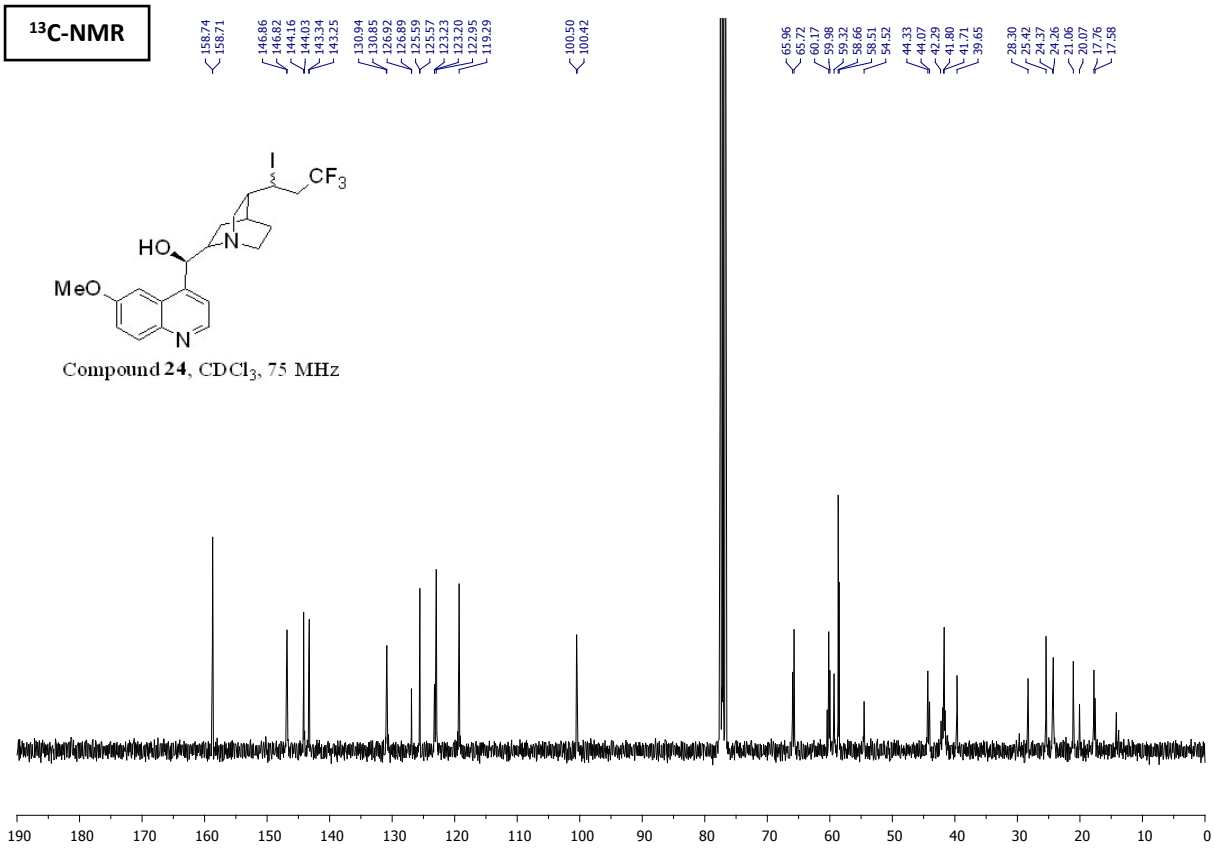
Compound **23**, $CDCl_3$, 376 MHz

^{1}H-NMR



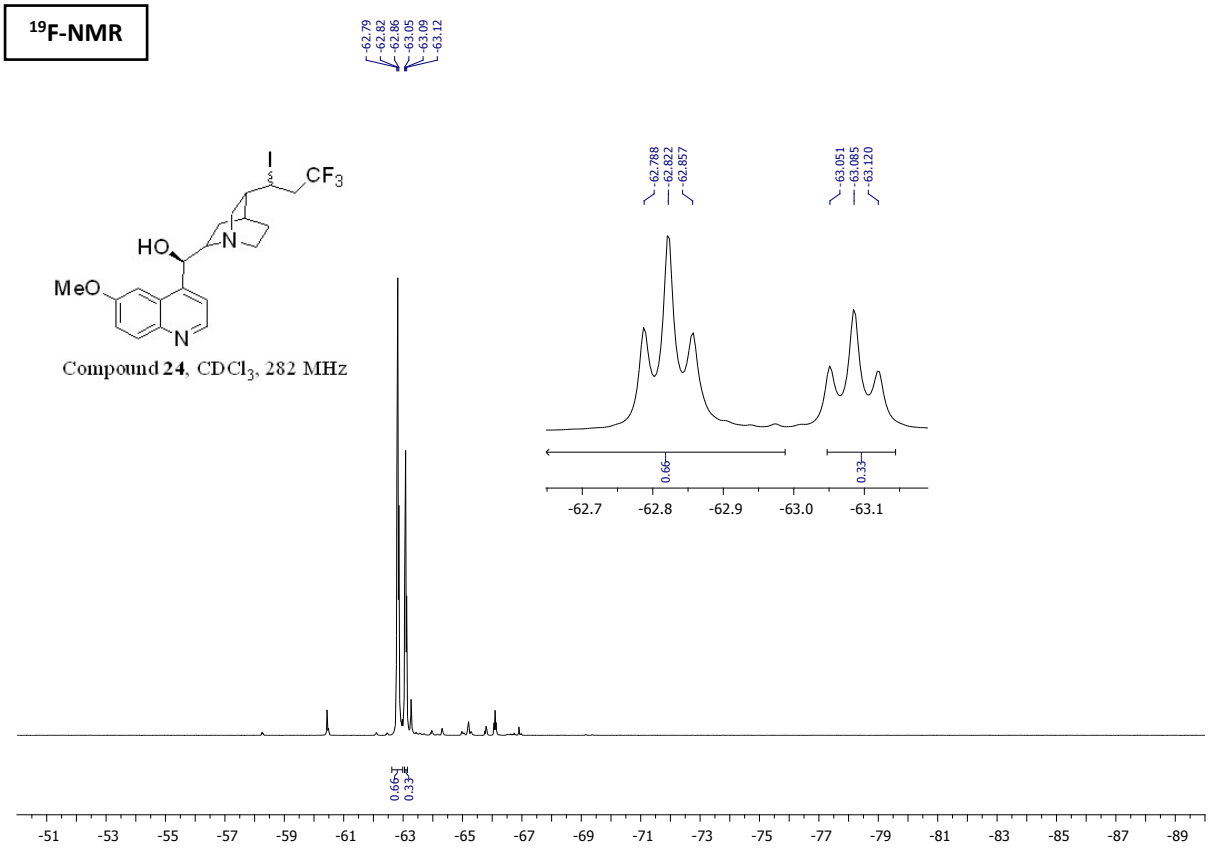
Compound **24**, $CDCl_3$, 300 MHz

^{13}C-NMR



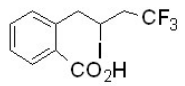
Compound **24**, $CDCl_3$, 75 MHz

^{19}F-NMR



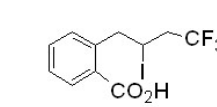
Compound **24**, $CDCl_3$, 282 MHz

^{1}H-NMR



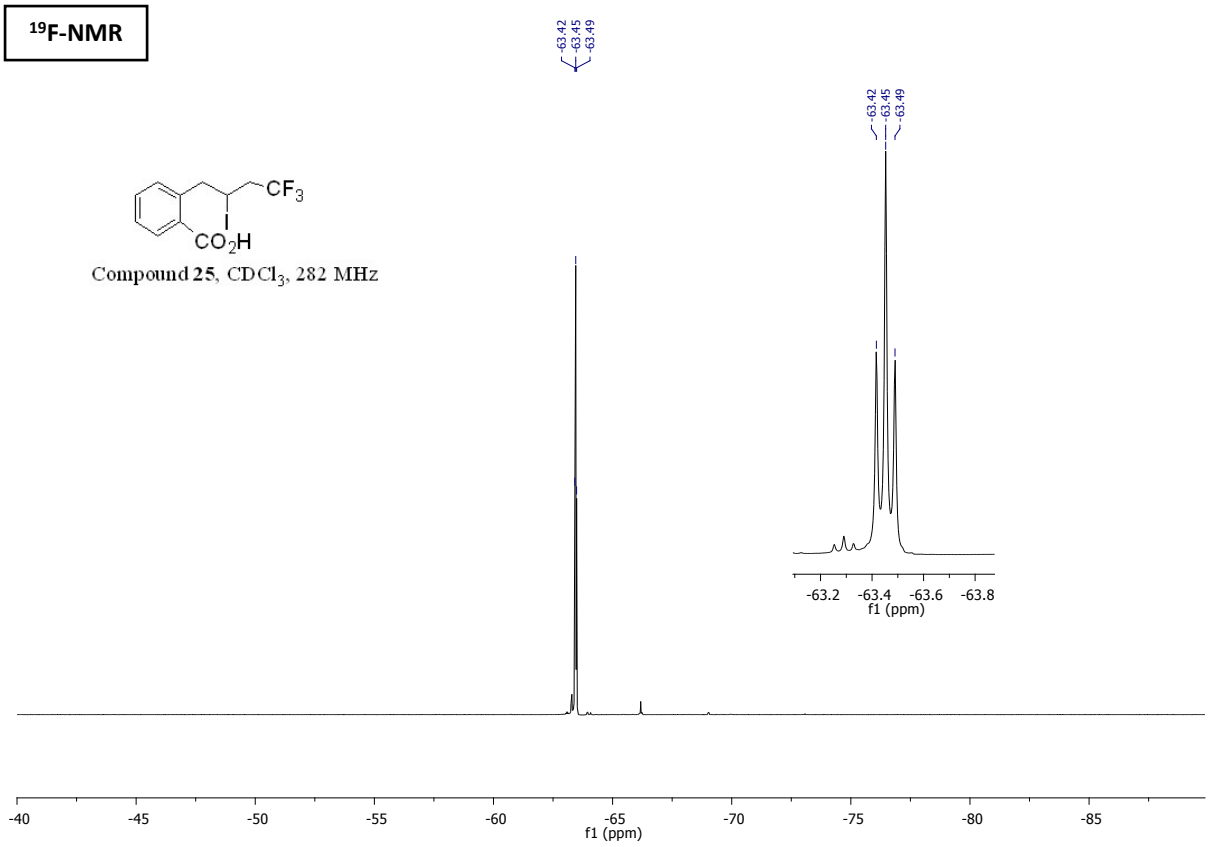
Compound **25**, $CDCl_3$, 300 MHz

^{13}C-NMR



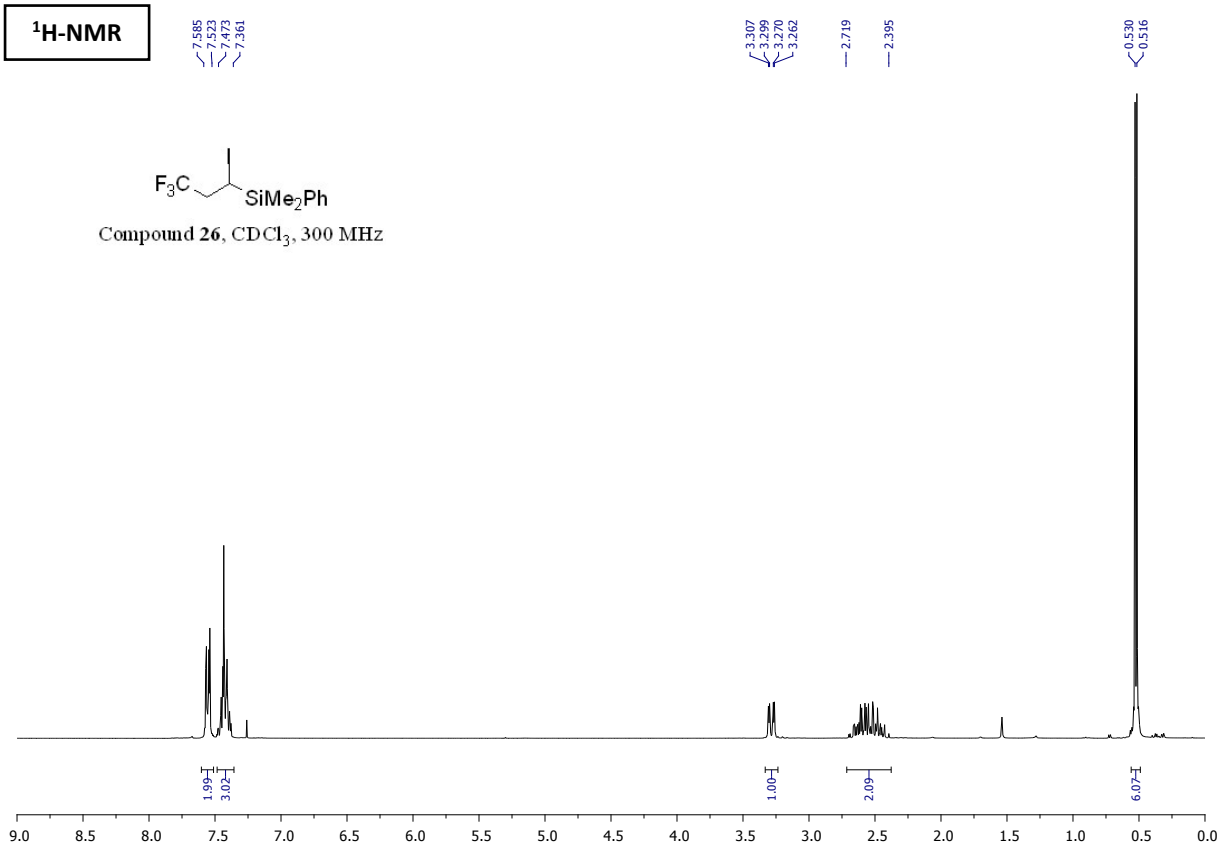
Compound **25**, $CDCl_3$, 75 MHz

^{19}F-NMR



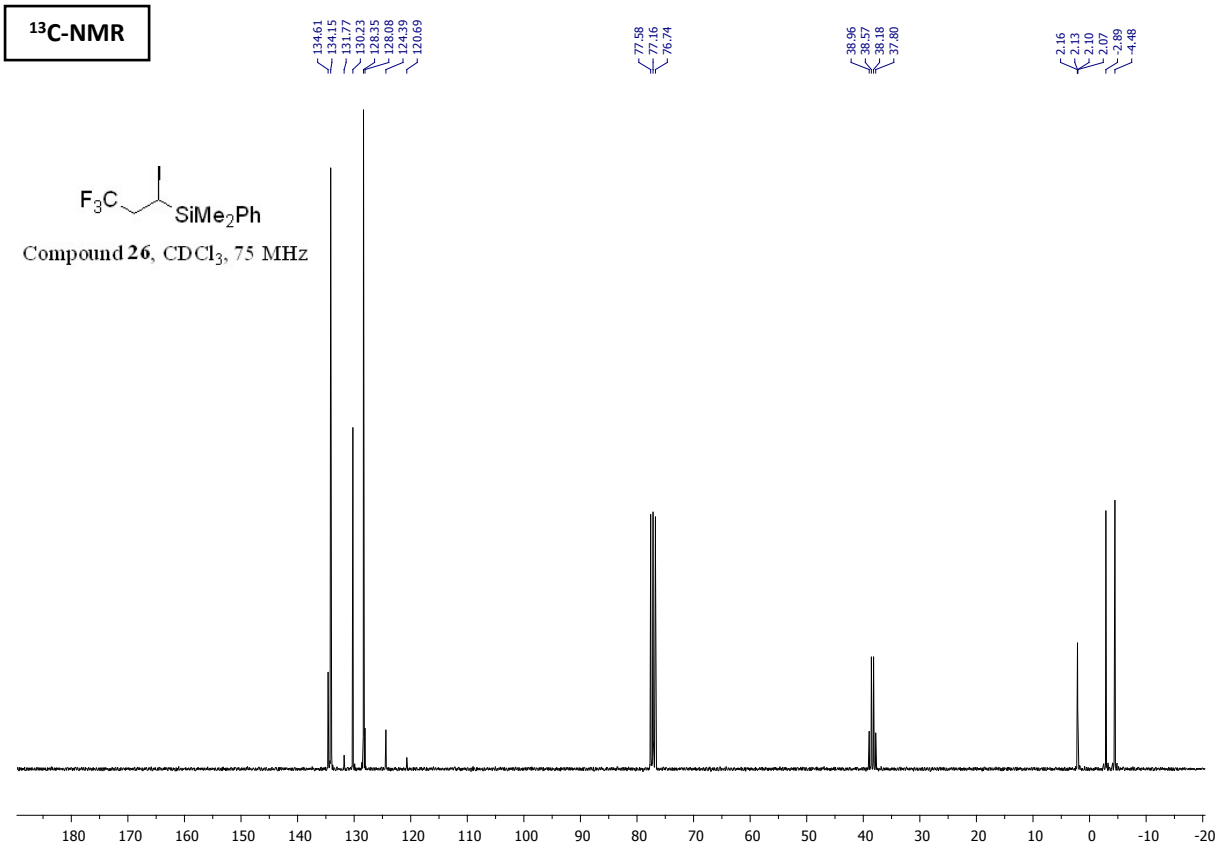
Compound **25**, $CDCl_3$, 282 MHz

^{1}H-NMR

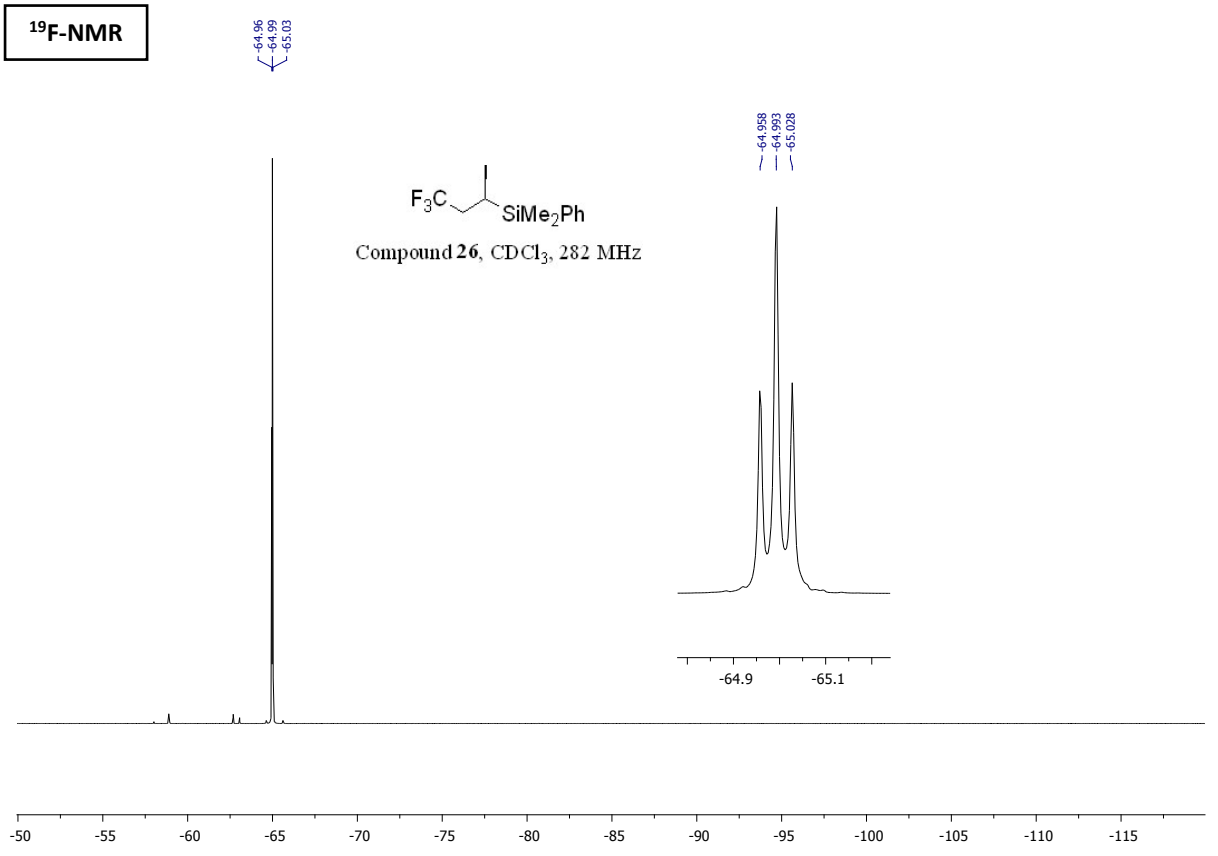


Compound **26**, $CDCl_3$, 300 MHz

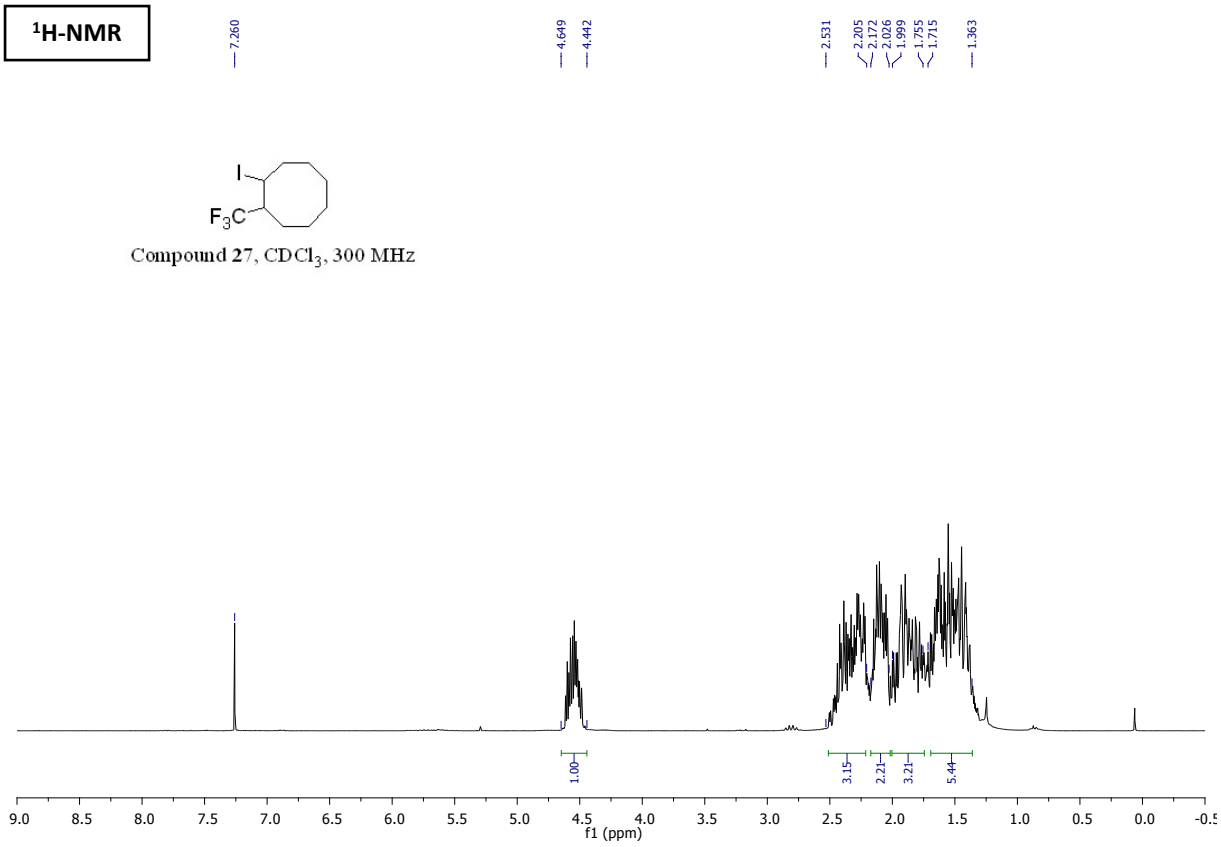
^{13}C-NMR



^{19}F-NMR

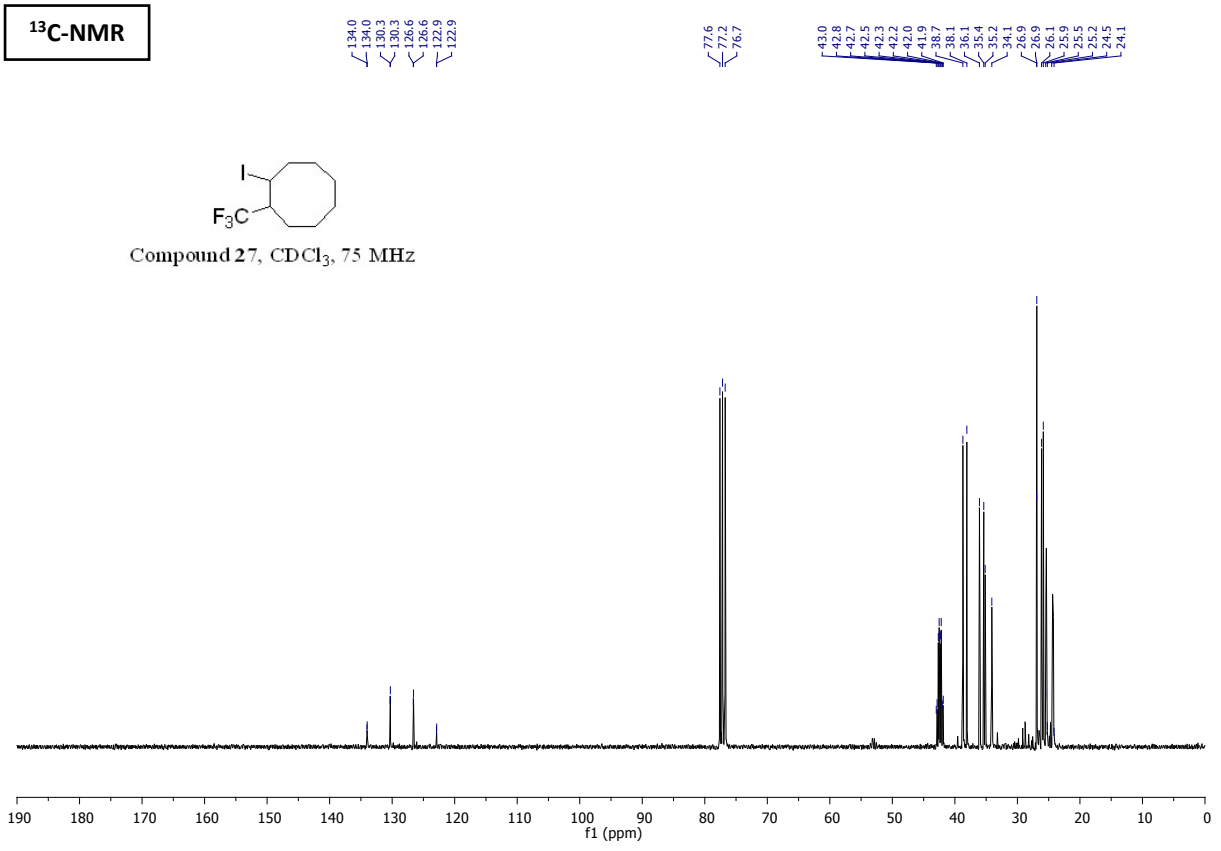


^{1}H-NMR



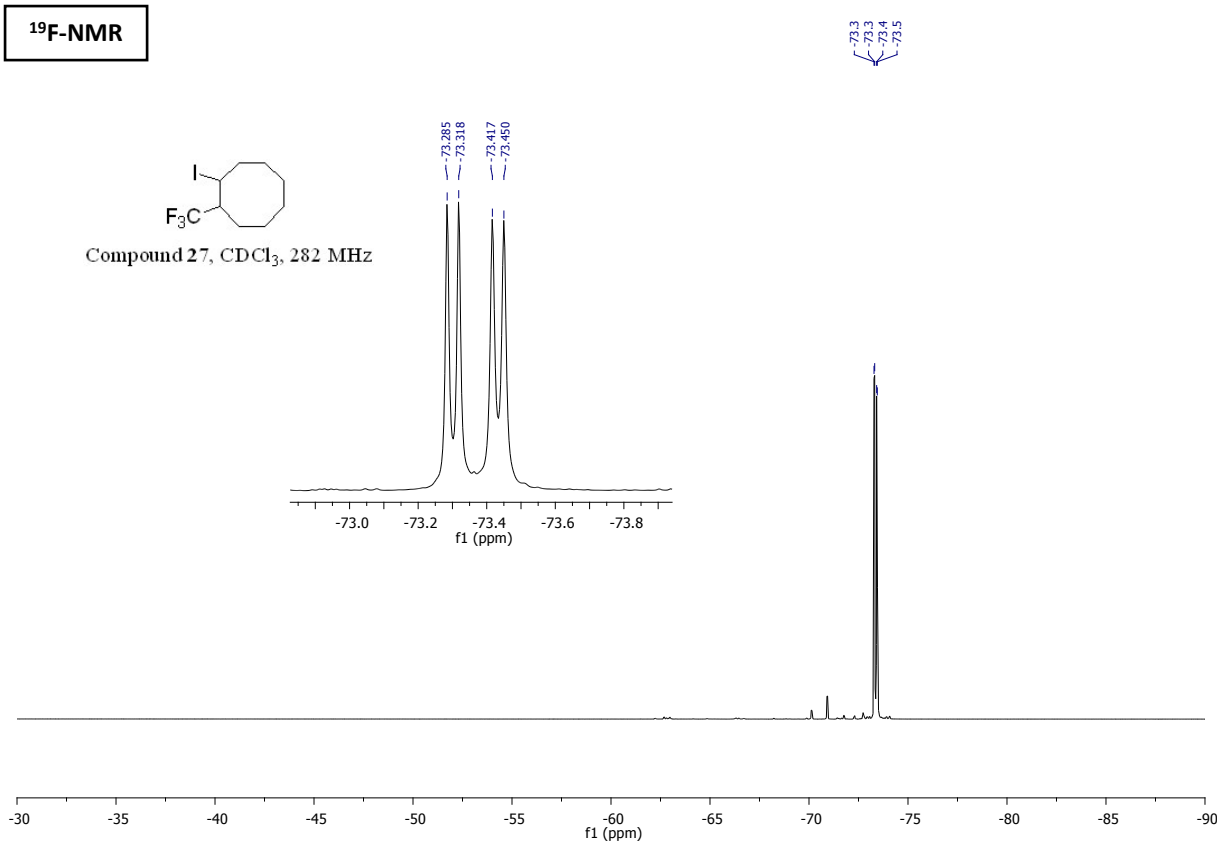
Compound **27**, $CDCl_3$, 300 MHz

^{13}C-NMR



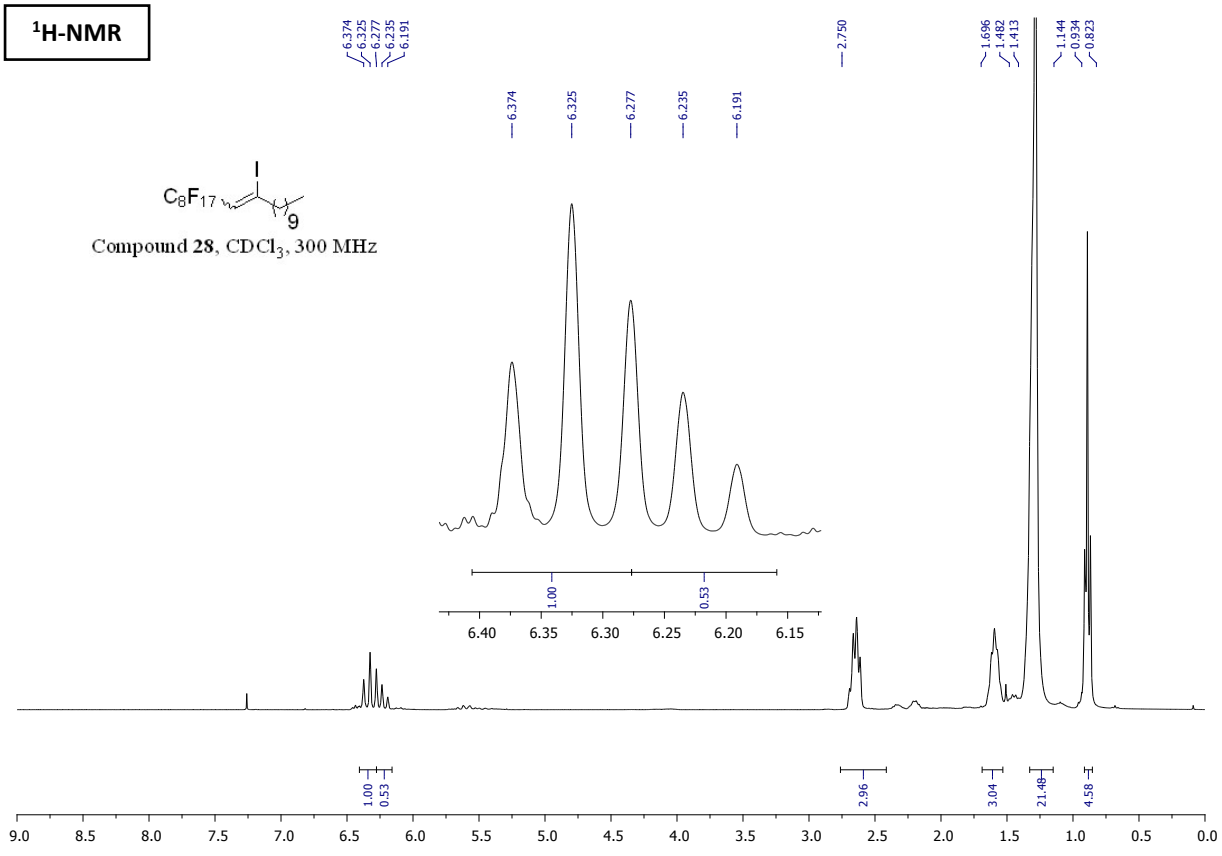
Compound **27**, $CDCl_3$, 75 MHz

^{19}F-NMR



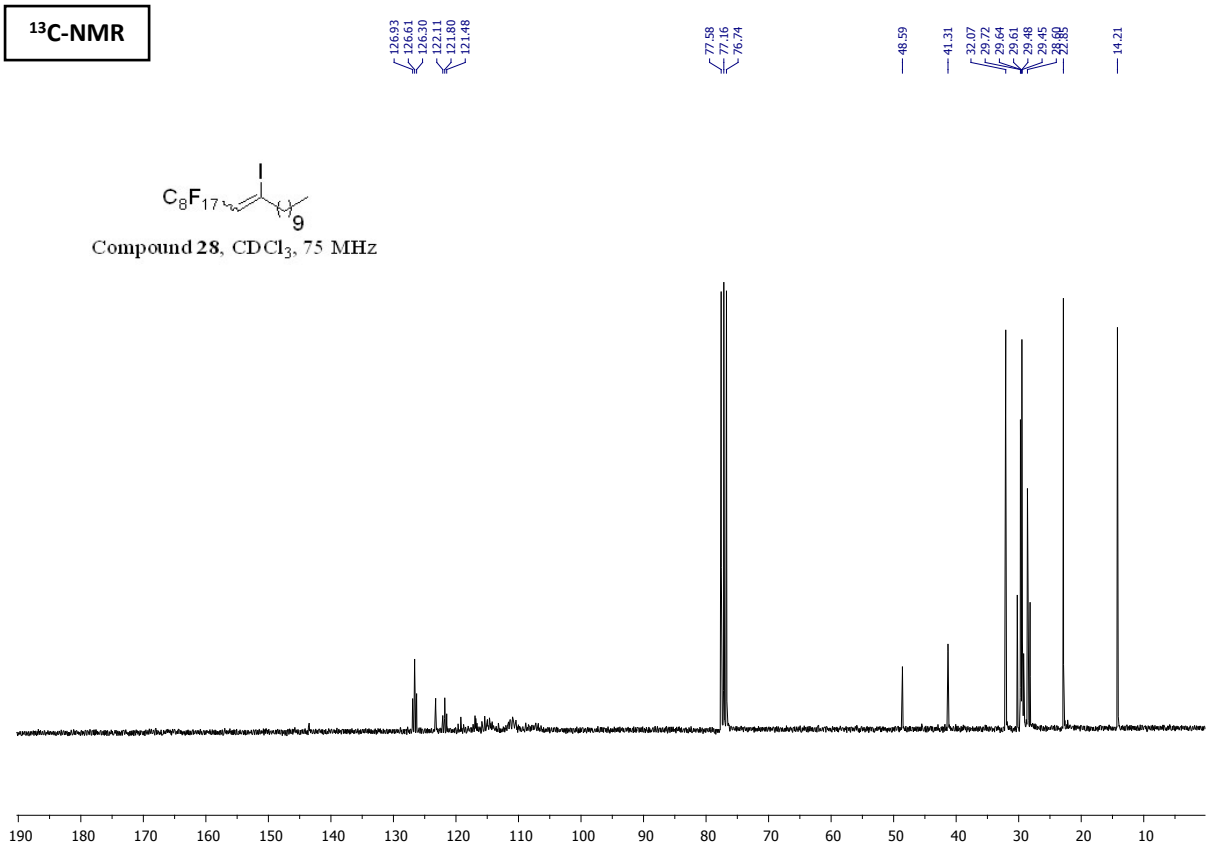
Compound **27**, $CDCl_3$, 282 MHz

^{1}H-NMR



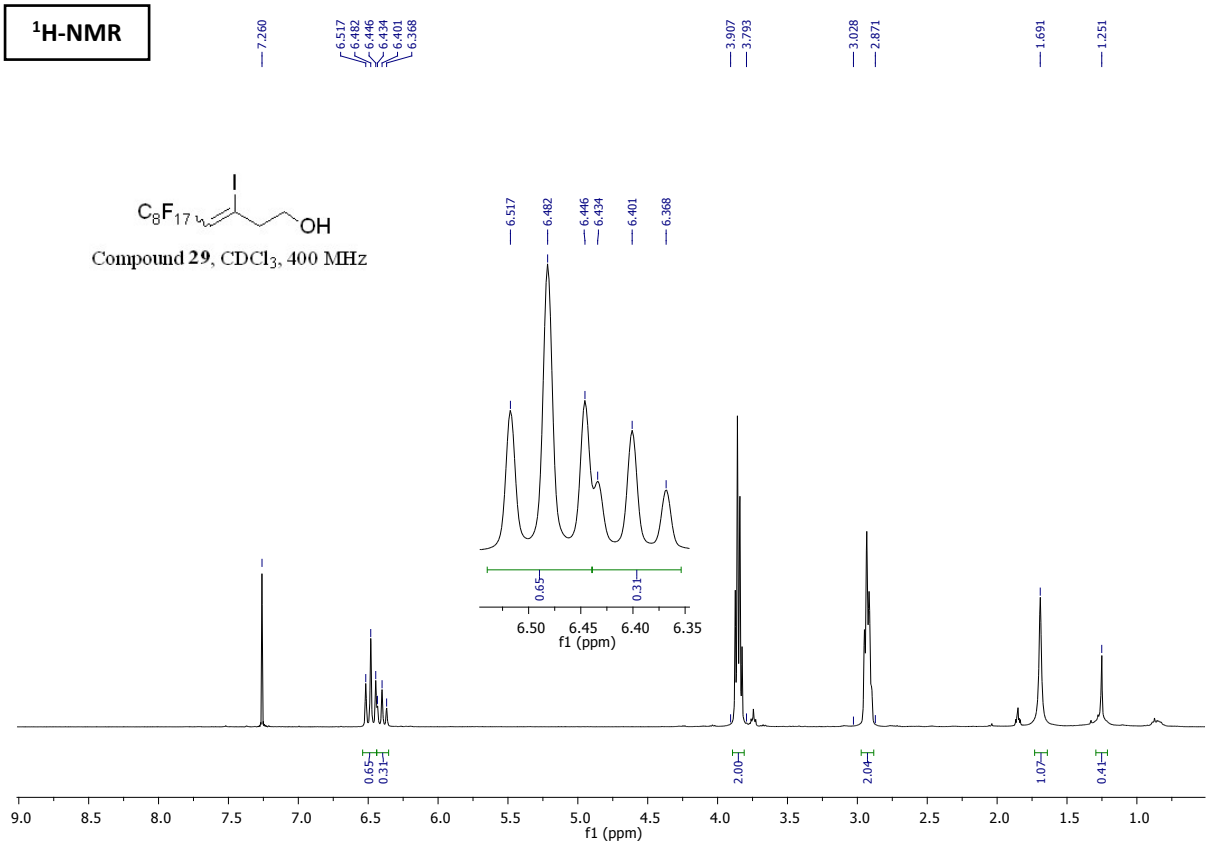
Compound **28**, $CDCl_3$, 300 MHz

^{13}C-NMR



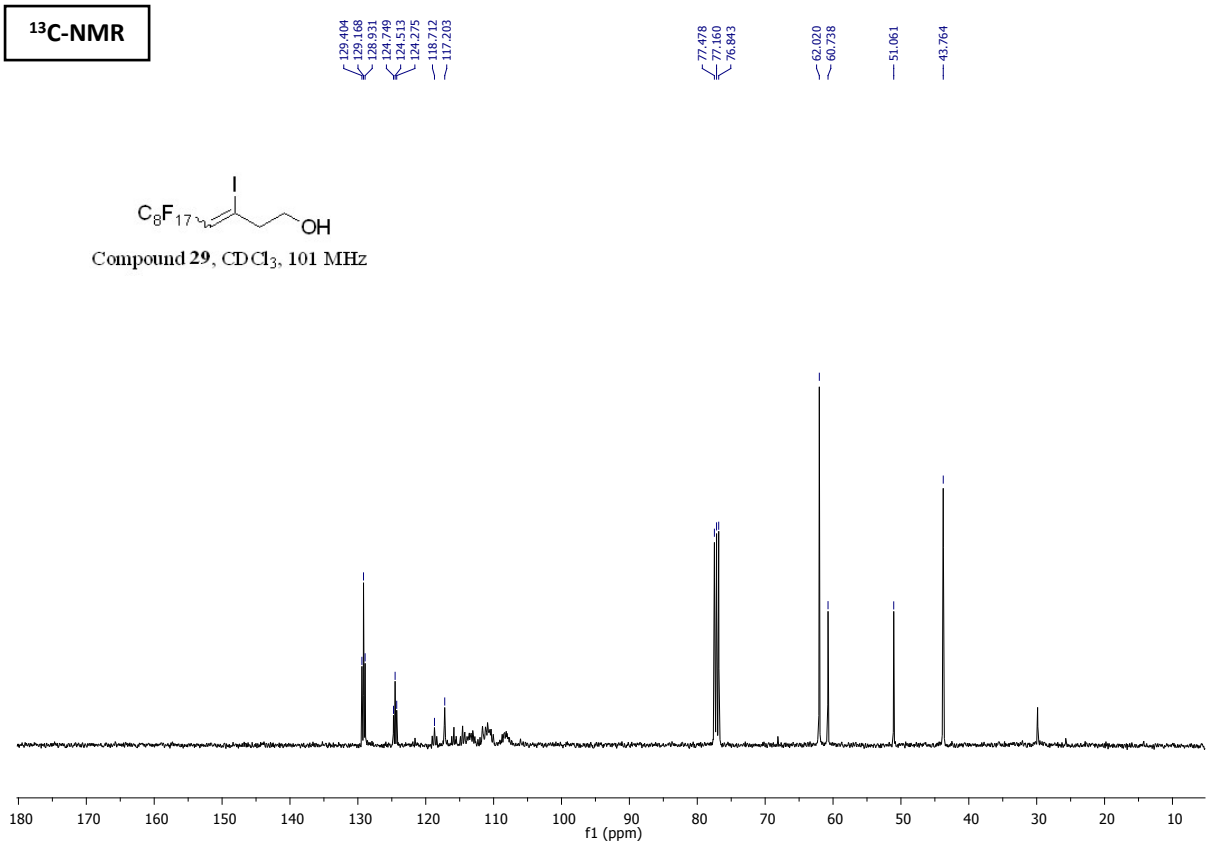
Compound **28**, $CDCl_3$, 75 MHz

^{1}H-NMR



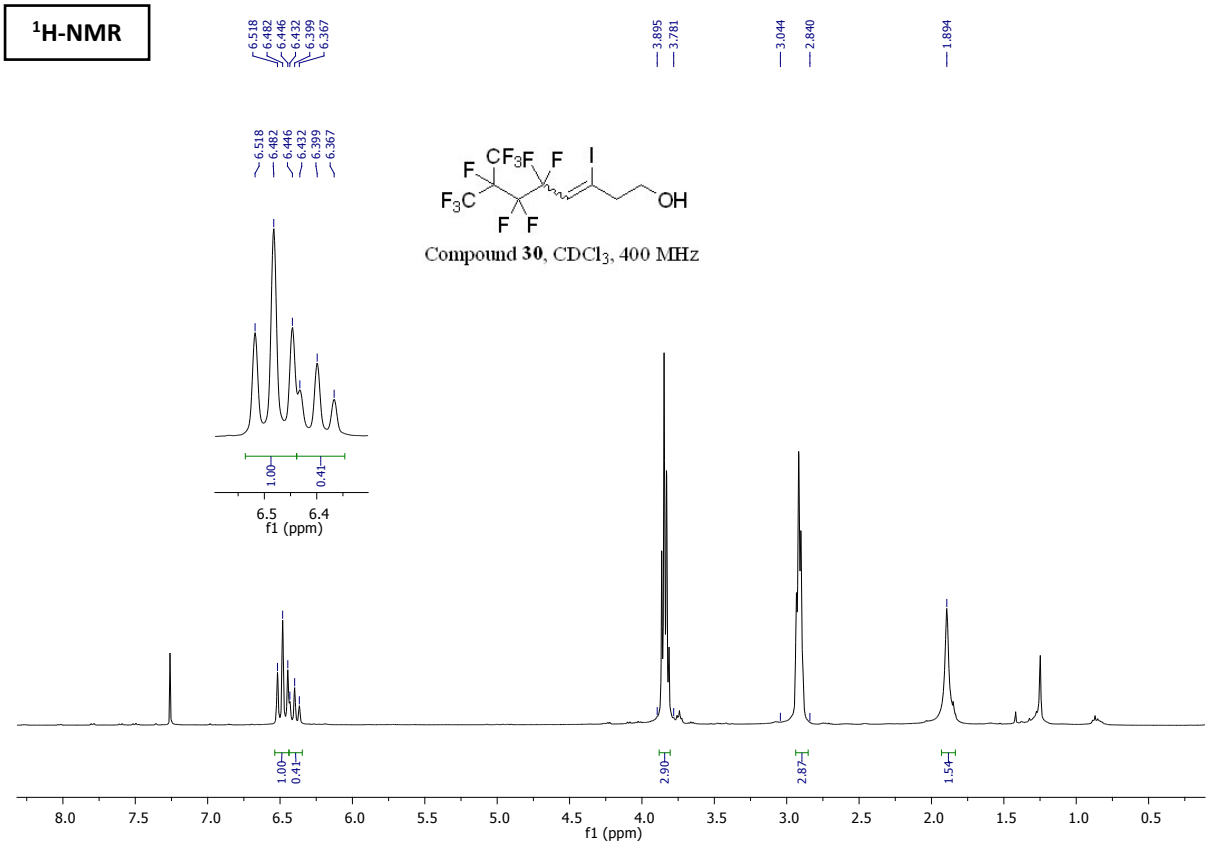
Compound **29**, $CDCl_3$, 400 MHz

^{13}C-NMR



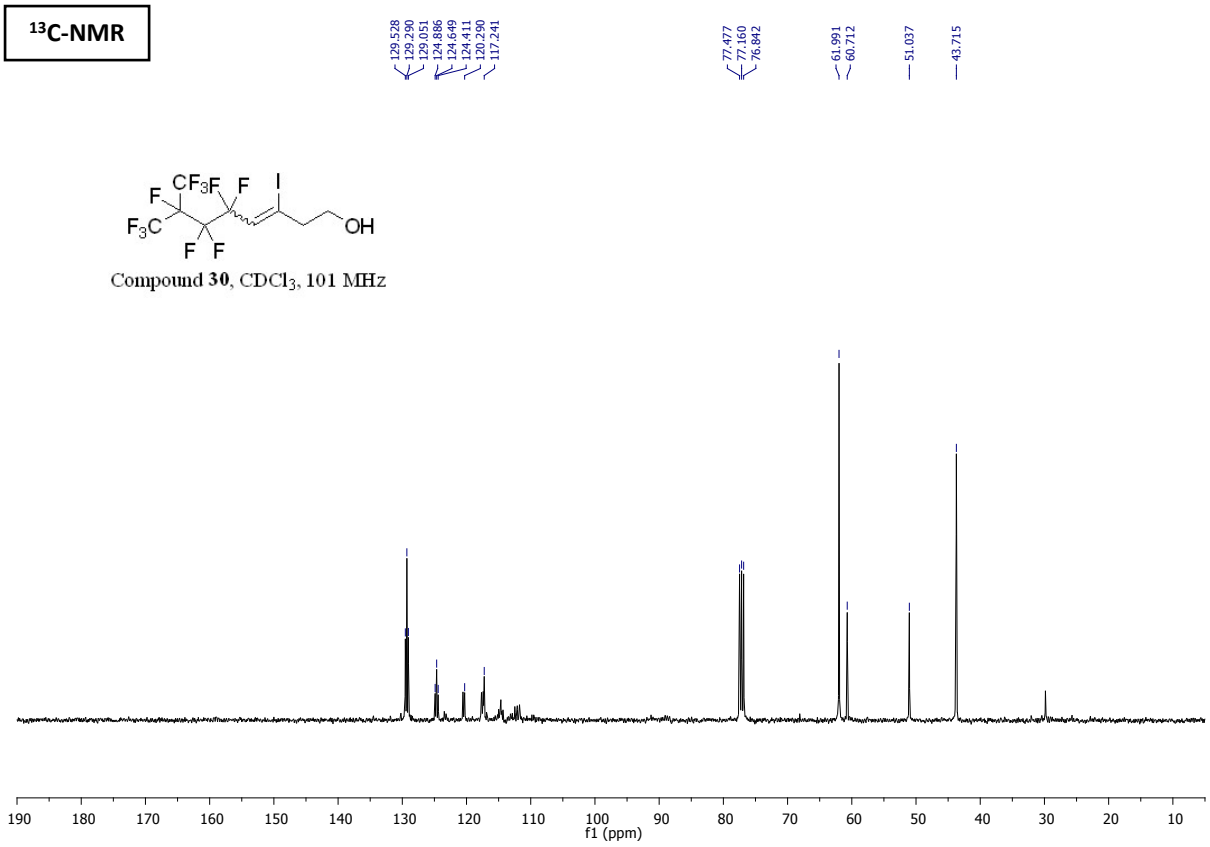
Compound **29**, $CDCl_3$, 101 MHz

^{1}H-NMR



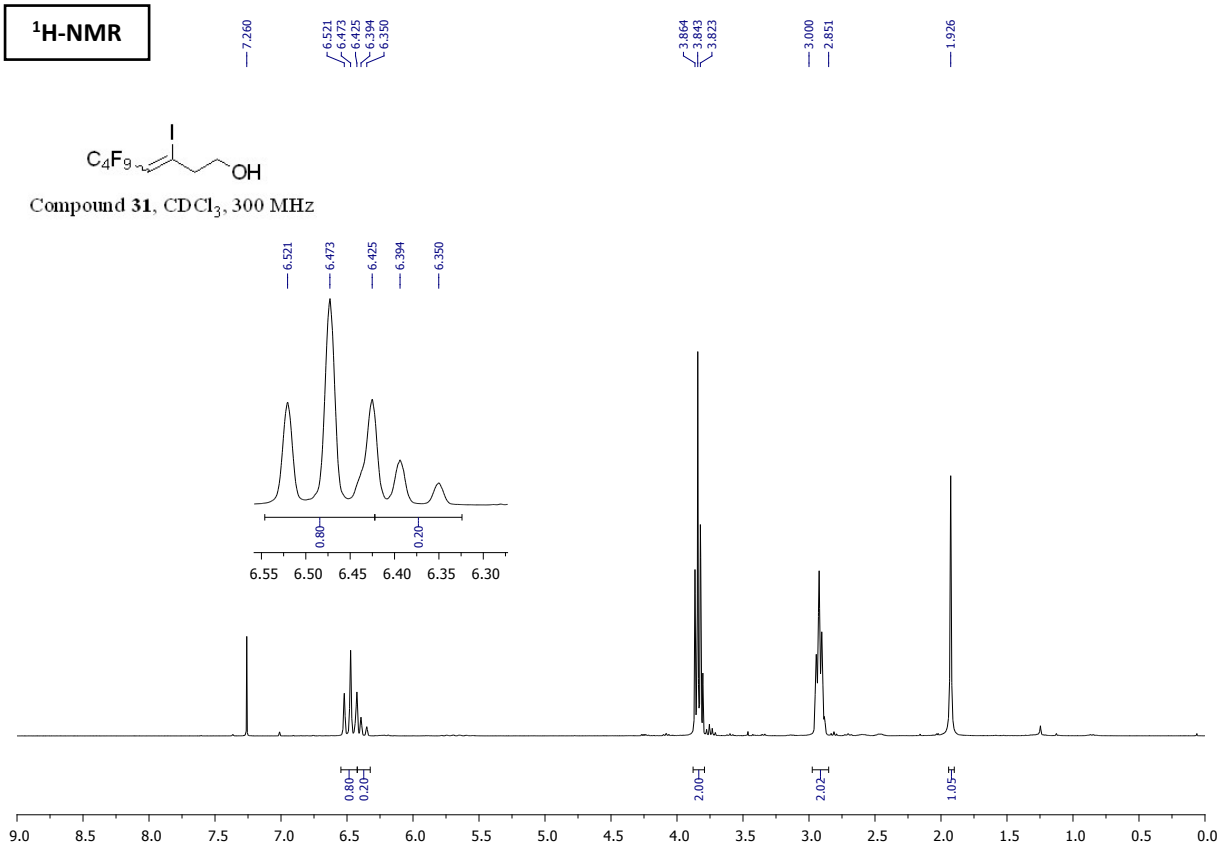
Compound **30**, $CDCl_3$, 400 MHz

^{13}C-NMR



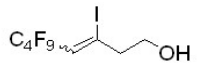
Compound **30**, $CDCl_3$, 101 MHz

^{1}H-NMR

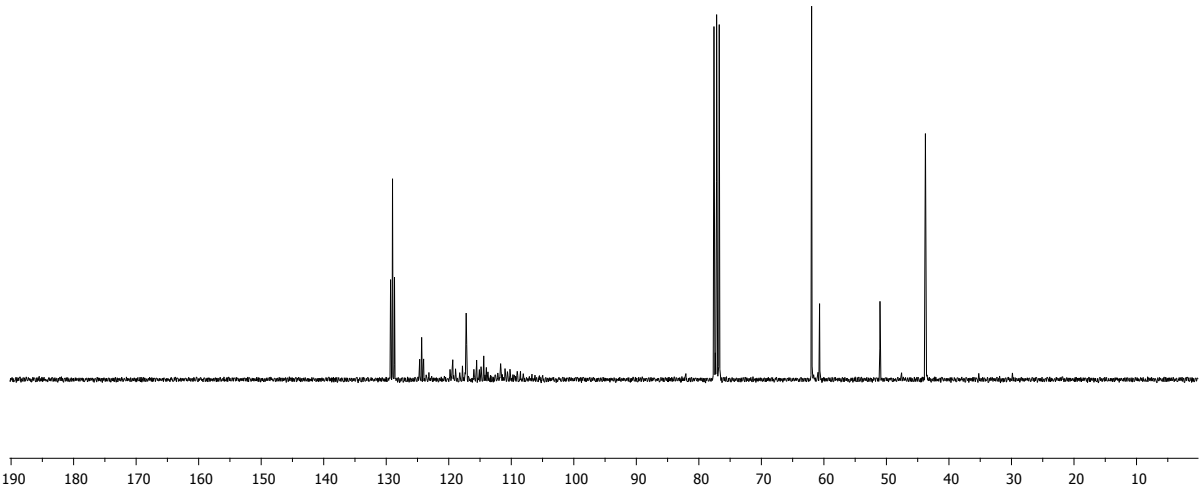


Compound **31**, $CDCl_3$, 300 MHz

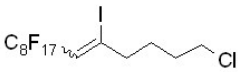
^{13}C-NMR



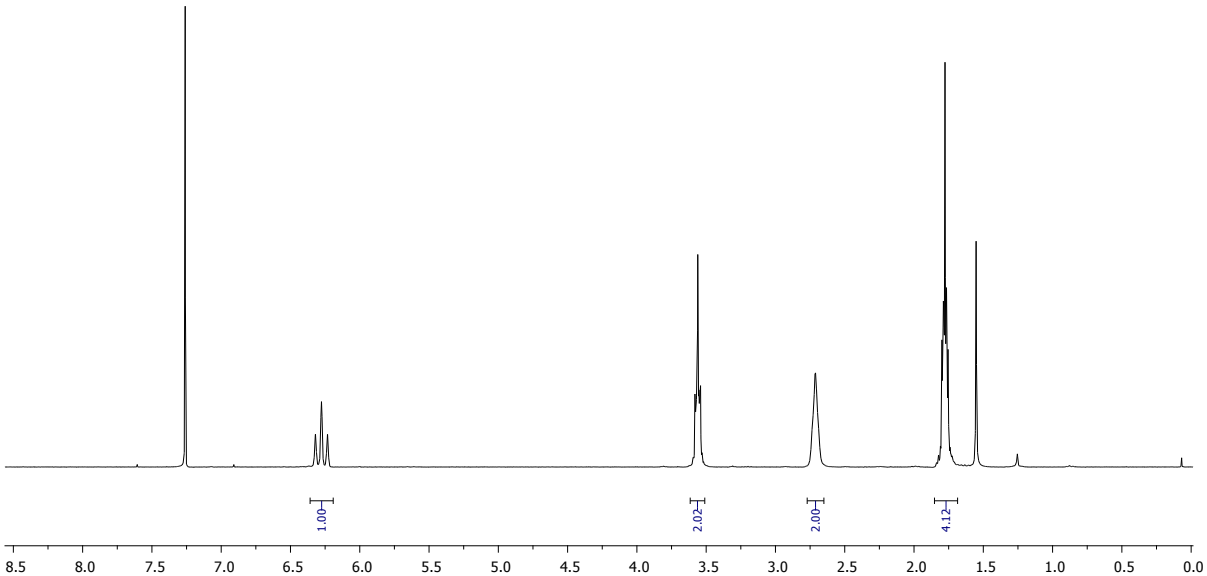
Compound **31**, $CDCl_3$, 75 MHz



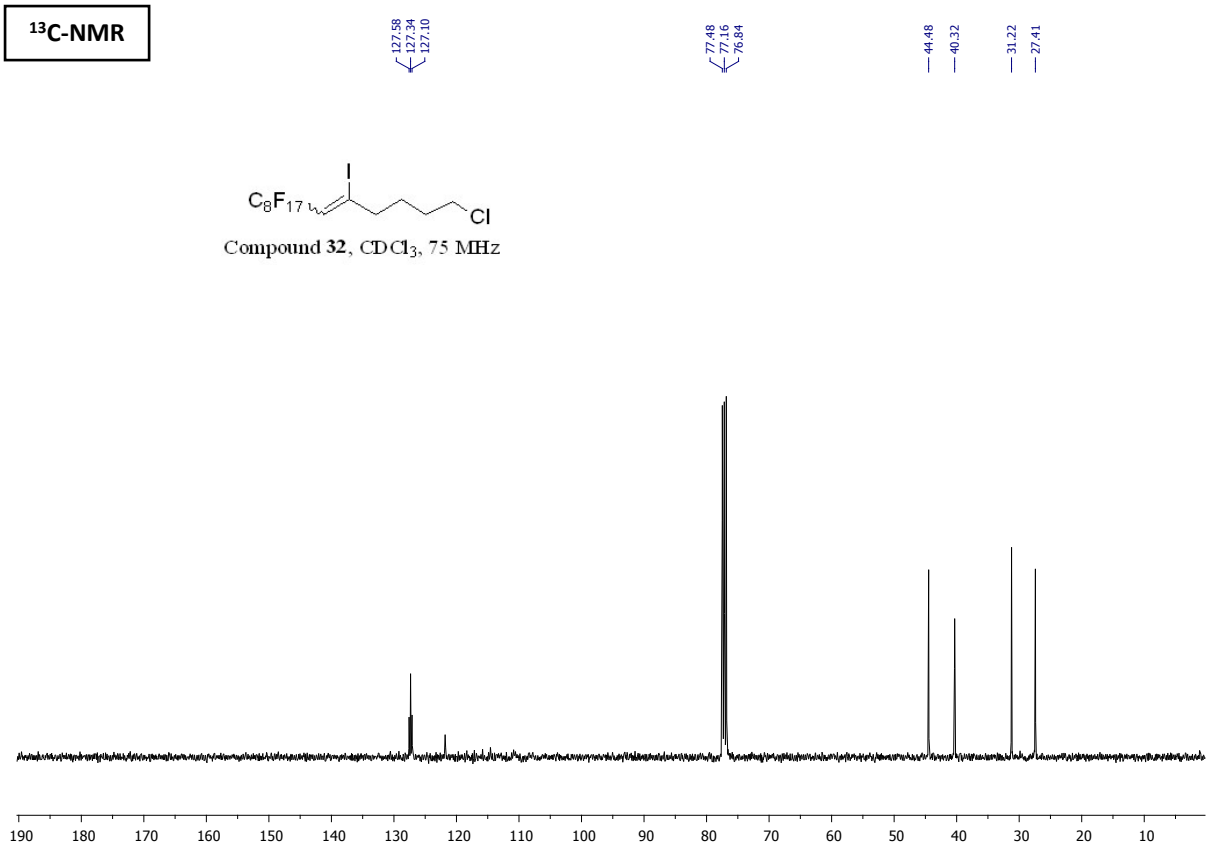
^{1}H-NMR



Compound **32**, $CDCl_3$, 300 MHz

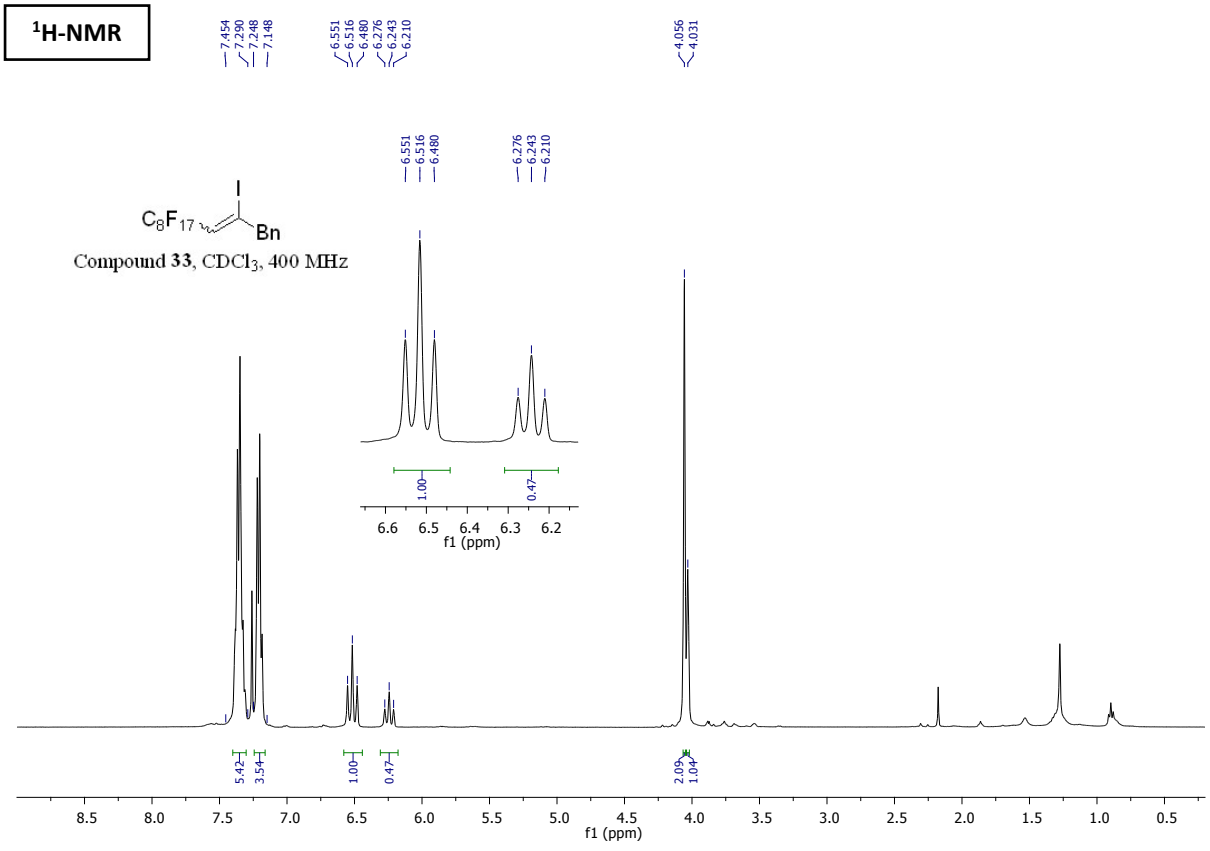


^{13}C-NMR



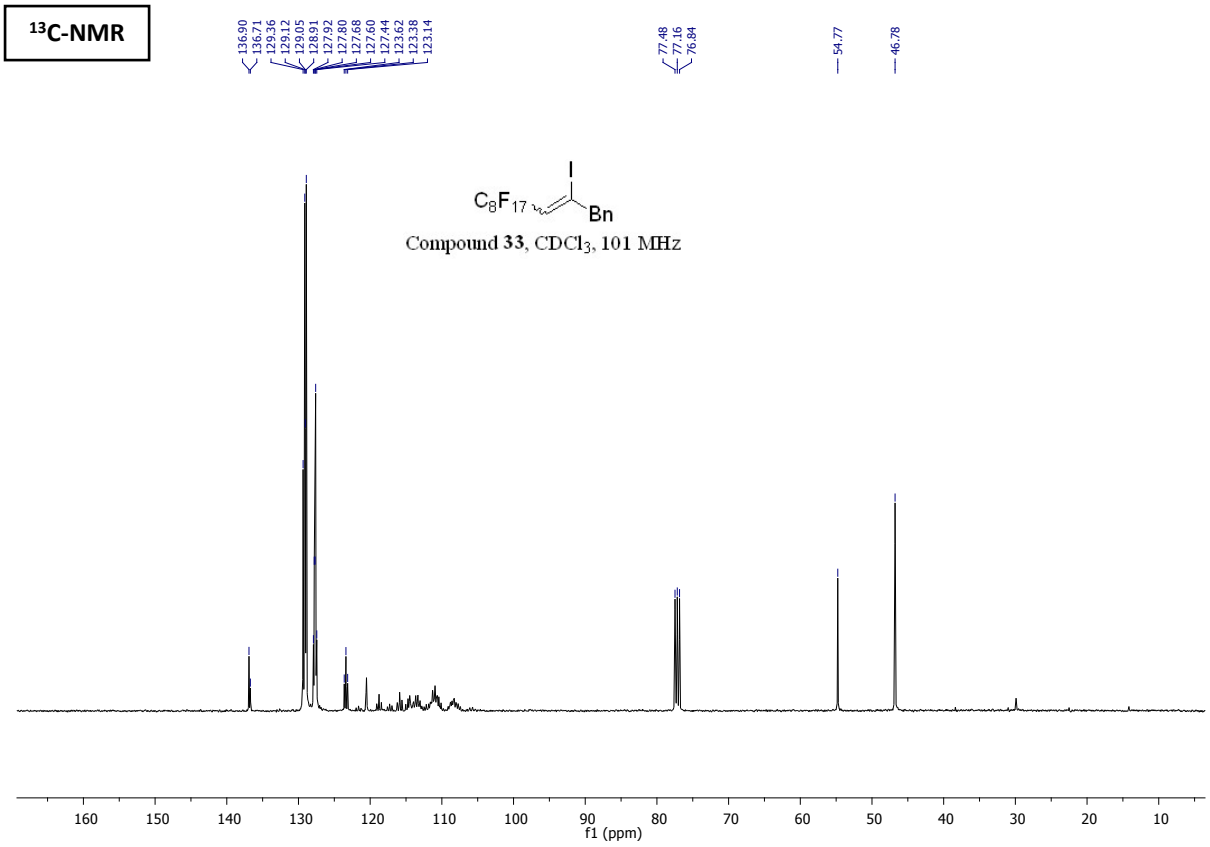
Compound **32**, $CDCl_3$, 75 MHz

^{1}H-NMR



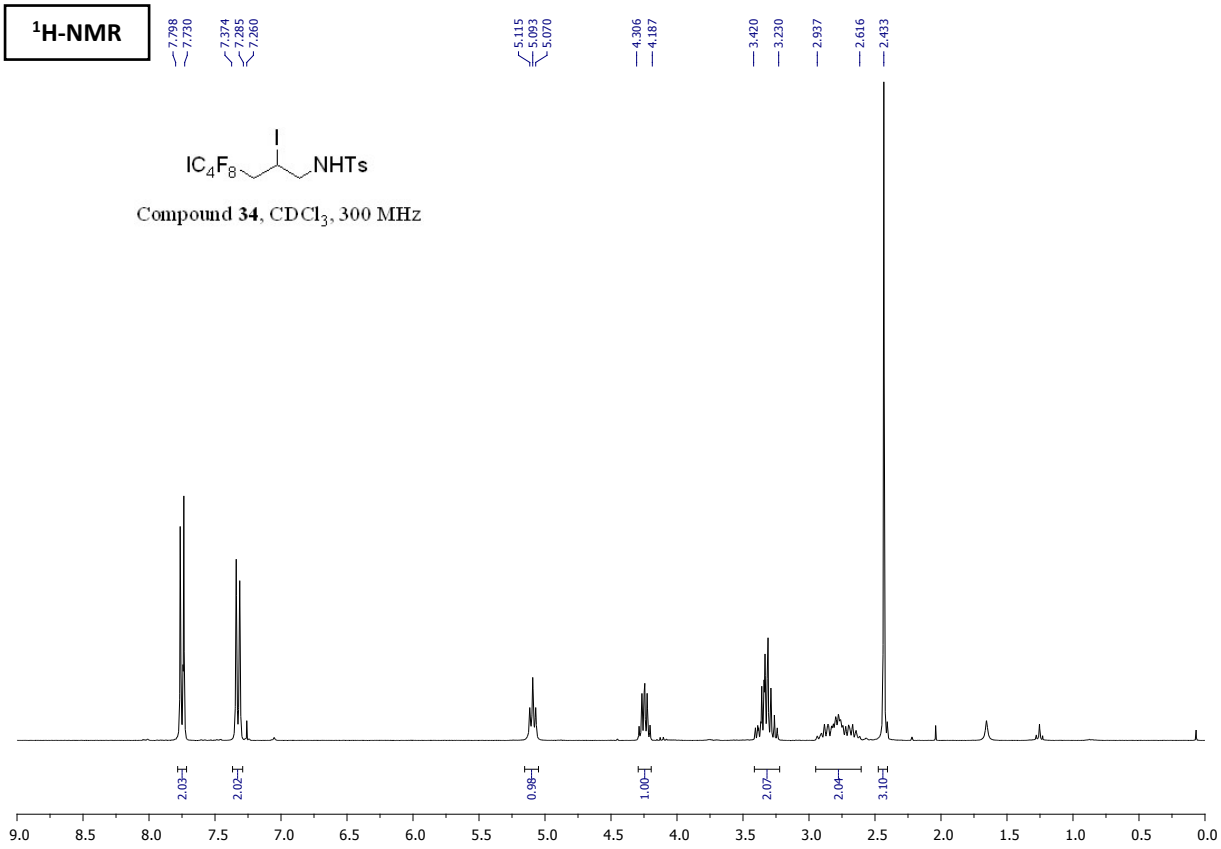
Compound **33**, $CDCl_3$, 400 MHz

^{13}C-NMR



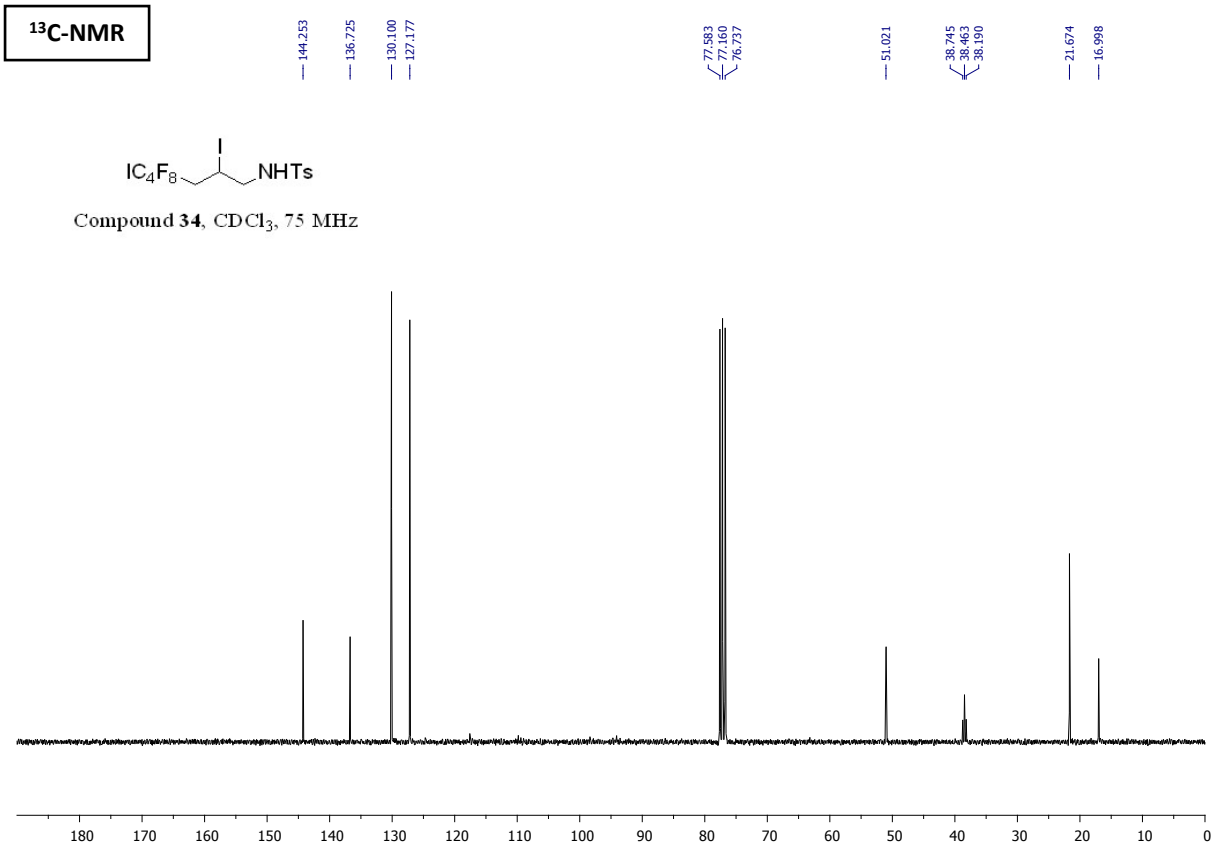
Compound **33**, $CDCl_3$, 101 MHz

^{1}H-NMR



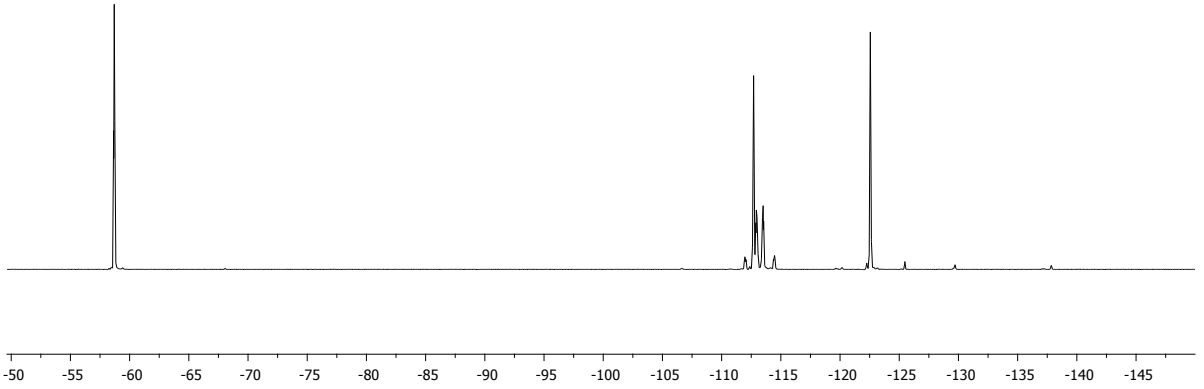
Compound **34**, $CDCl_3$, 300 MHz

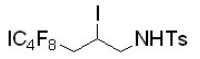
^{13}C-NMR



Compound **34**, $CDCl_3$, 75 MHz

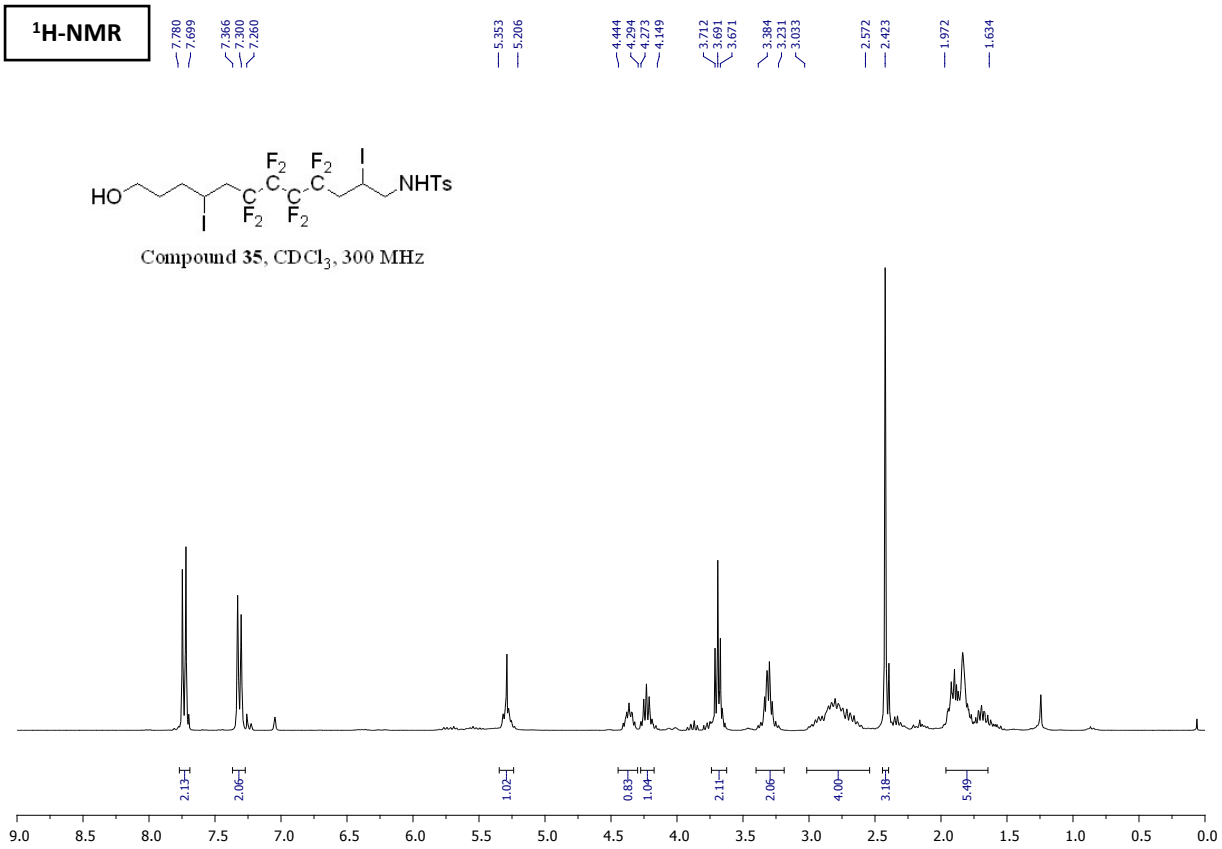
^{19}F-NMR



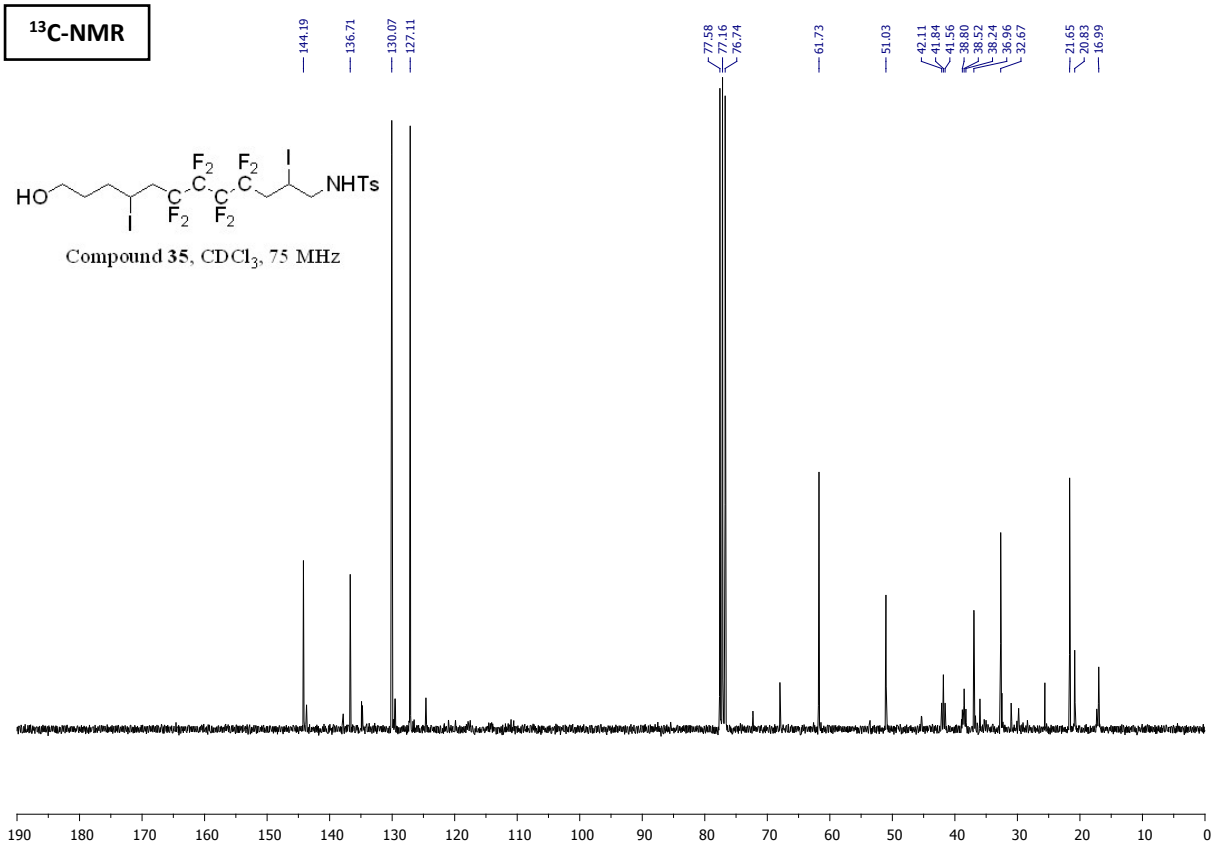


Compound **34**, $CDCl_3$, 282 MHz

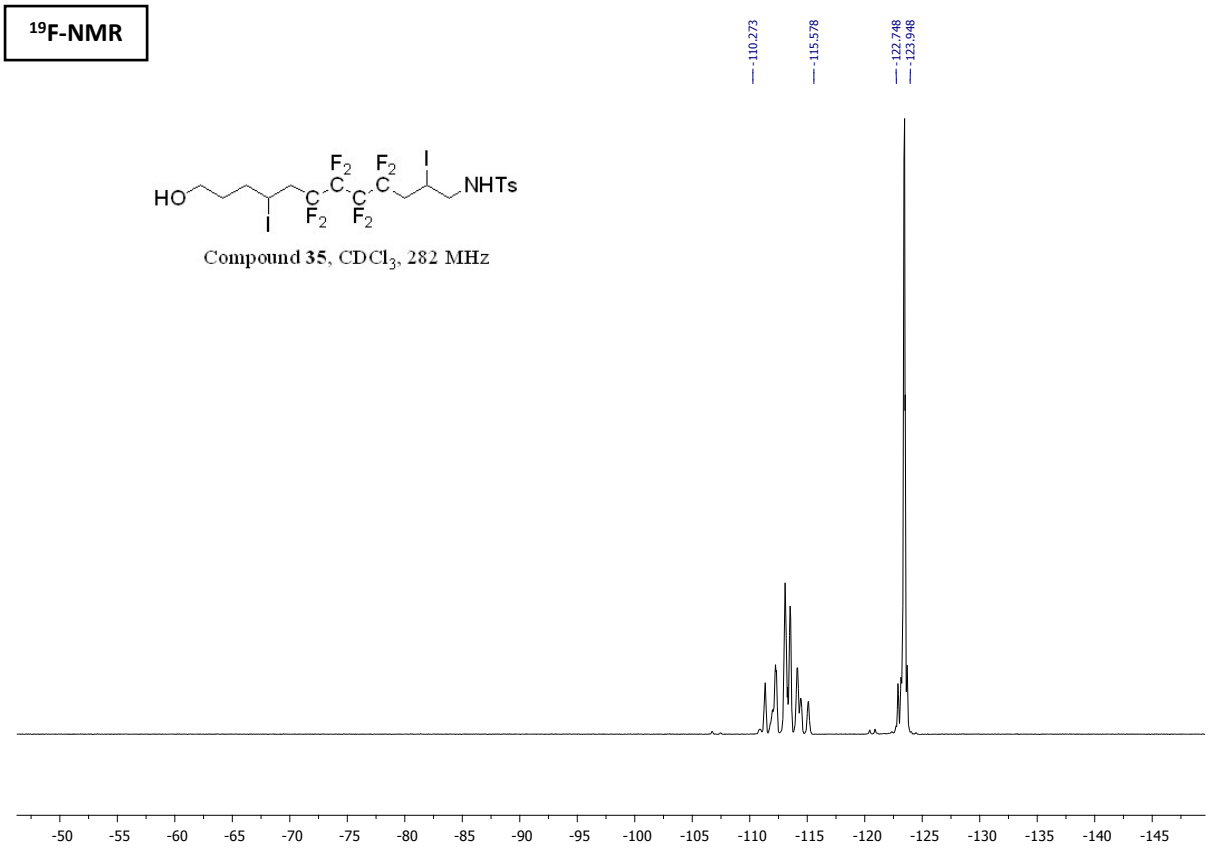
^{1}H-NMR



^{13}C-NMR



^{19}F-NMR



Compound **35**, $CDCl_3$, 282 MHz