Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

for

Straightforward Synthesis of Bench-Stable Heteroatom-Centered Difluoromethylated Entities via the Controlled Nucleophilic Transfer from Activated $TMSCHF_2$

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1. Materials and methods

Melting Points were determined on a Reichert-Kofler hot-stage microscope and are uncorrected. Mass spectra were obtained on a Shimadzu QP 1000 instrument (EI, 70 eV) and on a Bruker maXis 4G instrument (ESI-TOF, HRMS). ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker Avance III 400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C, 40 MHz for ^{15}N, 376 MHz for ^{19}F) at 297 K using a, directly detecting broadband observe (BBFO) probe. The centre of the solvent signal was used as an internal standard which was related to TMS with δ 7.26 ppm (^{1}H in $CDCl_3$), δ 77.00 ppm (^{13}C in $CDCl_3$). ^{15}N spectra (gsHMBC) were referenced against neat, external nitromethane, ^{19}F NMR spectra by absolute referencing via *Ξ* ratio. Spin-spin coupling constants (*J*) are given in Hz.

In nearly all cases, full and unambiguous assignment of all resonances was performed by combined application of standard NMR techniques, such as APT, HSQC, HMBC, COSY and NOESY experiments.

All the reactions were carried out under inert atmosphere of argon. THF was distilled over Na/benzophenone. Chemicals were purchased from Sigma-Aldrich, Acros, Alfa Aesar and TCI Europe. Solutions were evaporated under reduced pressure with a rotary evaporator.

TLC was carried out on aluminium sheets precoated with silica gel 60F254 (Merchery-Nagel, Merk); the spots were visualised under UV light (λ = 254 nm).

All the synthesized compounds were kept at -20 °C without any noticeable alteration detectable after four months.

CAUTION! Compounds embodying heteroatoms such as Sn, Te and Se – *inter alia* – must be manipulated and stored with particular care because of their inherent toxicity.

2. General Procedures

General Procedure 1 (Halostannanes, halogermanes, halosilanes, NHC-Au-Cl)

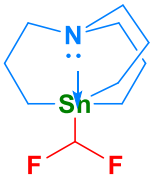
The electrophile (halostannane, halogermane, 1.0 equiv) was dissolved in dry THF under Argon and cooled down to 0 °C. Then, $TMSCHF_2$ (1.5 equiv) was added and, after 5 min, the solution of potassium *tert*-pentoxide (in toluene 0.9 M, 1.4 equiv) was added dropwise and, then the mixture was stirred at this temperature for 1 h. The reaction mixture was quenched with aqueous saturated NH_4Cl solution and then was allowed to warm to rt. The resulting organic phase was extracted 3 times with Et_2O, washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude compounds were purified as reported below through column chromatography.

General Procedure 2 (diselenides, disulfides, ditellurides)

The electrophile (1.0 equiv) was dissolved in dry THF under Argon and cooled down to -20°C. Then, $TMSCHF_2$ (1.5 equiv) was added and, after 5 min, the solution of potassium *tert*-pentoxide (in toluene 0.9 M, 1.4 equiv) was added dropwise and, then the mixture was stirred at this temperature for 1 h. The reaction mixture was quenched with aqueous saturated NH_4Cl solution and then was allowed to warm to rt. The resulting organic phase was extracted 3 times with Et_2O, washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude compounds were purified as reported below through column chromatography.

3. Spectral and Characterization Data

5-(difluoromethyl)-1-aza-5-stannabicyclo[3.3.3]undecane (2)



By following the General Procedure 1, starting from 5-Chloro-1-aza-5-stanna-bicyclo[3.3.3]undecane (200 mg, 0.68 mmol, 1.0 equiv), (difluoromethyl)trimethylsilane (0.1 mL, 1.02 mmol, 1.5 equiv), potassium *tert*-pentoxide 0.9 M (1.1 mL, 0.95 mmol, 1.4 equiv) and dry THF (5 mL), the desired compound **2** was obtained in 91 % yield (192 mg) as colourless solid after column chromatography on silica gel (hexane/diethyl ether 98:2).

^{1}H NMR (400 MHz, C_6D_6) δ: 6.26 (t, $^{2}J_{H,F}$ = 45.2 Hz, 1H, CHF_2), 1.82 (m, 6H, H-2,8,9), 1.33 (m, 6H, H-3,7,10), 0.77 (m, 6H, H-4,6,11).

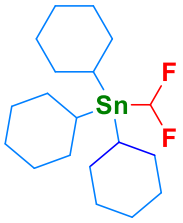
^{13}C NMR (100 MHz, C_6D_6) δ: 134.9 (t, $^{1}J_{C,F}$ = 284.5 Hz, 1C, CHF_2), 54.5 (3C, C-2,8,9), 22.9 (3C, C-3,7,10), 4.9 (t, $^{3}J_{C,F}$ = 3.0 Hz, 3C, C-4,6,11).

^{19}F NMR (376 MHz, C_6D_6) δ: -127.2 (d, $^{2}J_{H,F}$ = 45.2 Hz, F-1, CHF_2).

HRMS (ESI), *m/z*: calcd. for $C_{10}H_{19}F_2NSnNa^+$: 334.0400 $[M+Na]^+$; found: 334.0403.

Reaction run at *15 mmol* scale. Starting from 5-Chloro-1-aza-5-stanna-bicyclo[3.3.3]undecane (4416 mg, 15.0 mmol, 1 equiv), (difluoromethyl)trimethylsilane (3.0 mL, 22.5 mmol, 1.5 equiv), potassium *tert*-pentoxide 0.9 M (23.0 mL, 21.0 mmol, 1.4 equiv) and dry THF (5 mL), the desired compound **2** was obtained in 90% yield (4184 mg) as colourless solid after column chromatography on silica gel (hexane/diethyl ether 98:2). Spectroscopic and spectrometric data match with the above reported ones for the reaction at 0.68 mmol scale.

Tricyclohexyl (difluoromethyl) stannane (3)



By following the General Procedure 1, starting from chlorotricyclohexylstannane (200 mg, 0.49 mmol, 1 equiv), (difluoromethyl)trimethylsilane (0.1 mL, 0.74 mmol, 1.5 equiv), potassium *tert*-pentoxide 0.9 M (0.8 mL, 0.69 mmol, 1.4 equiv) and dry THF (5 mL), the desired compound **3**[1] was obtained in 83 % yield (173 mg) as transparent oil without any purification step.

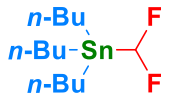
^{1}H NMR (400 MHz, C_6D_6) δ: 6.47 (t, $^{2}J_{H,F}$ = 44.7 Hz, 1H, CHF_2), 1.92 (m, 3H, Cy H-5), 1.68 (m, 3H, Cy H-1), 1.66 (m, 3H, Cy H-5), 1.64 (m, 3H, Cy H-6), 1.62 (m, 3H, Cy H-4), 1.29 (m, 3H, Cy H-6), 1.28 (m, 3H, Cy H-4).

^{13}C NMR (100 MHz, C_6D_6) δ: 132.1 (t, $^{1}J_{C,F}$ = 280.9 Hz, 1C, CHF_2), 32.5 (3C, Cy C-5), 29.4 (m, 3C, Cy C-6), 28.1 (t, $^{1}J_{C,F}$ = 2.3 Hz, 3C, SnCH), 27.3 (3C, Cy C-4).

^{19}F NMR (376 MHz, C_6D_6) δ: -121.7 (d, $^{2}J_{H,F}$ = 44.7 Hz, F-1, CHF_2).

HRMS (ESI), *m/z*: calcd. $C_{17}H_{37}FNOSn$: 410.1876 $[M+]^+$; found: 410.1876.

Tri-*n*-butyl (difluoromethyl) stannane (4)



By following the General Procedure 1, starting from tri-*n*-butylchlorostannane (200 mg, 0.61 mmol, 1 equiv), (difluoromethyl)trimethylsilane (0.1 mL, 0.92 mmol, 1.5 equiv), potassium *tert*-pentoxide 0.9 M (0.9 mL, 0.86 mmol, 1.4 equiv) and dry THF (5 mL), the desired compound **4**[1] was obtained in 88% yield (184 mg) as transparent oil without any further purification step.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.43 (t, $^{2}J_{H,F}$ = 44.9 Hz, 1H, CHF_2), 1.56 (m, 6H, CH_2), 1.06 (m, 6H, $SnCH_2$), 0.91 (m, 9H, CH_3) .

^{13}C NMR (100 MHz, $CDCl_3$) δ: 129.9 (t, $^{1}J_{C,F}$ = 280.3 Hz, 1C, CHF_2), 28.7 (3C, CH_2), 27.2 (3C, CH_2), 13.6 (3C, CH_3), 9.1 (m, 3C, $SnCH_2$).

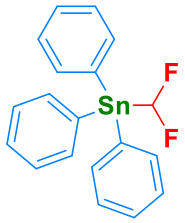
^{19}F NMR (376 MHz, $CDCl_3$) δ: -124.6 (d, $^{2}J_{H,F}$ = 44.9 Hz, F-1, CHF_2).

^{119}Sn NMR (MHz, $CDCl_3$) δ: -47.8 (t, $^2J_{H,Sn}$ = 216.8 Hz, Sn-1).

HRMS (ESI), *m/z*: calcd. for $C_{13}H_{28}F_2SnNa^+$: 364.0575 $[M+Na]^+$; found: 364.0579.

IR (KBr / cm^{-1}): 2957, 2925, 2872, 2854, 1465, 1418, 1376, 1357, 1340, 1292, 1249, 1182, 1150, 1072, 1044, 1021, 1002, 960, 874, 768, 745, 690, 667, 593, 505.

(difluoromethyl)(triphenyl)stannane (5)



By following the General Procedure 1, starting from chlorotriphenylstannane (200 mg, 0.52 mmol, 1 equiv), (difluoromethyl)trimethylsilane (0.1 mL, 0.78 mmol, 1.5 equiv), potassium *tert*-pentoxide 0.9 M (0.8 mL, 0.72 mmol, 1.4 equiv) and dry THF (5 mL), the desired compound **5**[1] was obtained in 85% yield (177 mg) as colourless solid without any further purification step.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (m, 6H, Ph H-2,6), 7.44 (m, 9H, Ph H-3,4,5), 6.86 (t, $^2J_{H,F}$ = 44.7 Hz, 1H, CHF_2).

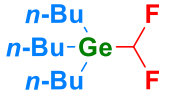
^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.2 (6C, Ph C-2,6), 135.1 (t, $^3J_{C,F}$ = 2.7 Hz, 3C, Ph C-1), 129.8 (3C, Ph C-4), 129.0 (6C, Ph C-3,5), 129.6 (t, $^1J_{C,F}$ = 281.4 Hz, CHF_2).

^{19}F NMR (376 MHz, $CDCl_3$) δ: -122.1 (d, $^2J_{H,F}$ = 44.7 Hz, F-1, CHF_2).

^{119}Sn NMR (MHz, $CDCl_3$) δ: -176.3 (t, $^2J_{H,Sn}$ = 278.7 Hz, Sn-1).

EI-MS m/z (%): 351.0 (M^+, 100), 196.9 (M^+, 48), 119.9 (M^+, 42), 77.1 (M^+, 18), 51.2 (M^+, 32).

Tri-*n*-butyl (difluoromethyl) germane (6)



By following the General Procedure 1, starting from tri-*n*-butylchlorogermane (200 mg, 0.72 mmol, 1 equiv), (difluoromethyl)trimethylsilane (0.2 mL, 1.07 mmol, 1.5 equiv), potassium *tert*-pentoxide 0.9 M (1.1 mL, 1.29 mmol, 1.4 equiv) and dry THF (5 mL), the desired compound was obtained in 91% yield (194 mg) as transparent oil after column chromatography on neutral alumina grade IV (n-hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.15 (t, $^{2}J_{H,F}$ = 46.6 Hz, 1H, CHF_2), 1.38 (m, 6H, CH_2), 1.34 (m, 6H, CH_2), 0.92 (m, 6H, $SnCH_2$), 0.90 (t, $^{3}J_{H,H}$ = 7.2 Hz, 9H, CH_3).

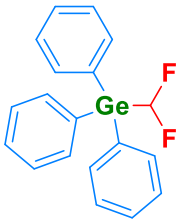
^{13}C NMR (100 MHz, $CDCl_3$) δ: 126.5 (t, $^{1}J_{C,F}$ = 269.5 Hz, 1C, CHF_2), 26.9 (3C, CH_2), 26.4 (3C, CH_2), 13.6 (3C, CH_3), 10.6 (m, 3C, $SnCH_2$).

^{19}F NMR (376 MHz, $CDCl_3$) δ: -130.6 (d, $^{2}J_{H,F}$ = 46.6 Hz, F-1, CHF_2).

HRMS (ESI), *m/z*: calcd. for $C_{13}H_{28}F_2GeNa^+$: 317.9875 $[M+Na]^+$; found: 317.9878.

IR (KBr / cm^{-1}): 2957, 2924, 2872, 2856, 1465, 1421, 1377, 1341, 1294, 1269, 1173, 1083, 1028, 1002, 964, 884, 717, 696, 644, 556.

(difluoromethyl)(triphenyl)germane (7)



By following the General Procedure 1, starting from chlorotriphenylgermane (200 mg, 0.59 mmol, 1 equiv), (difluoromethyl)trimethylsilane (0.1 mL, 0.88 mmol, 1.5 equiv), potassium *tert*-pentoxide 0.9 M (0.9 mL, 0.82 mmol, 1.4 equiv) and dry THF (5 mL), the desired compound was obtained in 88% yield (184 mg) as transparent oil without any further purification step.

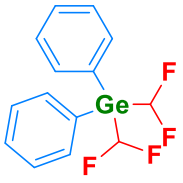
^{1}H NMR (400 MHz, C_6D_6) δ: 7.54 (m, 6H, Ph H-2,6), 7.14 (m, 3H, Ph H-4), 7.13 (m, 6H, Ph H-3,5), 6.39 (t, $^{2}J_{H,F}$ = 46.3 Hz, 1H, CHF_2).

^{13}C NMR (100 MHz, C_6D_6) δ: 135.6 (6C, Ph C-2,6), 132.5 (t, $^{3}J_{C,F}$ = 2.6 Hz, 3C, Ph C-1), 130.1 (3C, Ph C-4), 128.9 (6C, Ph C-3,5), 125.4 (t, $^{1}J_{C,F}$ = 270.4 Hz, CHF_2).

^{19}F NMR (376 MHz, C_6D_6) δ: -127.9 (d, $^{2}J_{H,F}$ = 46.3 Hz, F-1, CHF_2).

EI-MS m/z (%): 305.0 (M^+, 100), 222.9 (M^+, 8), 151.0 (M^+, 37), 77.1 (M^+, 8), 51.0 (M^+, 15).

bis(difluoromethyl)(diphenyl)germane (8)



By following the General Procedure 1, starting from dichlorodiphenylgermane (200 mg, 0.67 mmol, 1 equiv), (difluoromethyl)trimethylsilane (0.3 mL, 2.02 mmol, 3.0 equiv), potassium *tert*-pentoxide 0.9 M (2.1 mL, 1.88 mmol, 2.8 equiv) and dry THF (5 mL), the desired compound was obtained in 83% yield (183 mg) as transparent oil after column chromatography on silica gel (*n*-hexane/ethyl acetate 8:2).

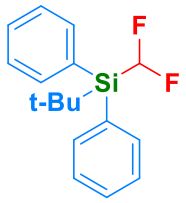
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (m, 4H, Ph H-2,6), 7.52 (m, 2H, Ph H-4), 7.46 (m, 4H, Ph H-3,5), 6.64 (tt, $^{2}J_{H,F}$ = 46.6 Hz, $^{4}J_{H,F}$ = 3.0 Hz, 2H, CHF_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.0 (4C, Ph C-2,6), 130.8 (2C, Ph C-4), 129.0 (m, 4C, Ph C-3,5), 128.0(m, 2C, Ph C-1), 123.1 (tt, $^{1}J_{C,F}$ = 269.8 Hz, $^{3}J_{C,F}$ = 4.3 Hz, 2C, CHF_2).

^{19}F NMR (376 MHz, $CDCl_3$) δ: -128.0 (d, $^{2}J_{H,F}$ = 46.6 Hz, 4F, CHF_2).

HRMS (ESI), *m/z*: calcd. for $C_{16}H_{26}N_7O^+$: 332.2197 [M+]$^+$; found: 332.2193.

(difluoromethyl)(2-methyl-2-propanyl) diphenylsilane (9)



By following the General Procedure 1, starting from *tert*-butylchlorodiphenylsilane (0.2 mL, 0.73 mmol, 1 equiv), (difluoromethyl)trimethylsilane (0.2 mL, 1.09 mmol, 1.5 equiv), potassium *tert*-pentoxide 0.9 M (1.1 mL, 1.02 mmol, 1.4 equiv) and dry THF (5 mL), the desired compound was obtained in 78% yield (165 mg) as transparent oil after column chromatography on neutral alumina grade IV (*n*-hexane).

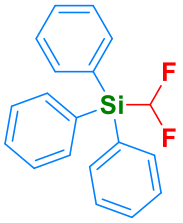
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (m, 4H, Ph H-2,6), 7.46 (m, 2H, Ph H-4), 7.40 (m, 4H, Ph H-3,5), 6.42 (t, $^{2}J_{H,F}$ = 45.6 Hz, 1H, CHF_2), 1.19 (s, 9H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.1 (4C, Ph C-2,6), 130.0 (t, $^{3}J_{C,F}$ = 2.2 Hz, 2C, Ph C-1), 130.2 (2C, Ph C-4), 128.0 (4C, Ph C-3,5), 123.7 (t, $^{1}J_{C,F}$ = 256.4 Hz, CHF_2), 27.7 (3C, CH_3), 18.2 (1C, $C(CH_3)_3$).

^{19}F NMR (376 MHz, $CDCl_3$) δ: -133.1 (d, $^{2}J_{H,F}$ = 45.6 Hz, CHF_2).

HRMS (ESI), *m/z*: calcd. for $C_{17}H_{20}F_2SiNa^+$: 313.1201 [M+Na]$^+$; found: 313.1195.

(difluoromethyl)triphenylsilane (10)



By following the General Procedure 1, starting from chlorotriphenylsilane (200 mg, 0.68 mmol, 1 equiv), (difluoromethyl)trimethylsilane (0.2 mL, 1.02 mmol, 1.5 equiv), potassium *tert*-pentoxide 0.9 M (1.1 mL, 0.95 mmol, 1.4 equiv) and dry THF (5 mL), the desired compound **10** was obtained in 81% yield (171 mg) as a colourless solid without any further purification step.

^{1}H NMR (400 MHz, C_6D_6) δ: 7.62 (m, 6H, Ph H-2,6), 7.17 (m, 6H, Ph H-3,5), 7.12 (m, 4H, Ph H-4), 6.30 (t, $^{2}J_{H,F}$ = 45.8 Hz, 1H, CHF_2).

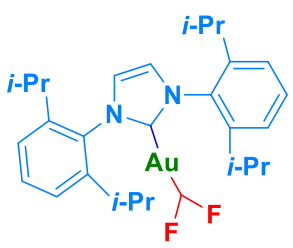
^{13}C NMR (100 MHz, C_6D_6) δ: 136.6 (6C, Ph C-2,6), 130.9 (3C, Ph C-4), 130.0 (3C, Ph C-1), 128.6 (6C, Ph C-3,5), 123.3 (t, $^{1}J_{C,F}$ = 255.9 Hz, CHF_2).

^{19}F NMR (376 MHz, C_6D_6) δ: -134.3 (d, $^{2}J_{H,F}$ = 45.8 Hz, F-1, CHF_2).

HRMS (ESI), *m/z*: calcd. for $C_{19}H_{16}F_2SiNa^+$: 333.4019 $[M+Na]^+$; found: 333.4021.

Reaction run at *15 mmol* scale. Starting from chlorotriphenylsilane (4123 mg, 15.0 mmol, 1 equiv), (difluoromethyl)trimethylsilane (3.0 mL, 22.5 mmol, 1.5 equiv), potassium *tert*-pentoxide 0.9 M (23.3 mL, 21.0 mmol, 1.4 equiv) and dry THF (5 mL), the desired compound **10** was obtained in 85% yield (3703 mg) as a colourless solid after column chromatography on silica gel (hexane). Spectroscopic and spectrometric data match with the above reported ones for the reaction at 0.7 mmol scale.

Difluoromethyl[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]gold(I) (11)



By following the General Procedure 1, starting from 1,3-Bis(2,6-di-isopropylphenyl)imidazol-2-ylidene gold(I) chloride (50 mg, 0.08 mmol, 1 equiv), (difluoromethyl)trimethylsilane (0.02 mL, 0.12 mmol, 1.5 equiv), potassium *tert*-pentoxide 0.9 M (0.1 mL, 0.11 mmol, 1.4 equiv) and dry THF (5mL), the desired compound **11**[2] was obtained in 93% yield (47 mg) as transparent oil after column chromatography on silica gel (hexane/diethyl ether 6:4).

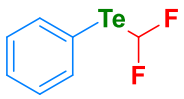
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (m, 2H, Ph H-4), 7.30 (m, 4H, Ph H-3,5), 7.09 (s, 2H, CHimid), 6.40 (t, $^{2}J_{H,F}$ = 46.2 Hz, 1H, CHF_2), 2.51 (m, 4H, CH), 1.40 (d, $^{3}J_{H,H}$ = 6.9 Hz, 6H, $CH(CH_3)_2$), 1.32(d, $^{3}J_{H,H}$ = 6.9 Hz, 6H, $CH(CH_3)_2$), 1.28 (d, $^{3}J_{H,H}$ = 6.9 Hz, 6H, $CH(CH_3)_2$), 1.20 (d, $^{3}J_{H,H}$ = 6.9 Hz, 6H, $CH(CH_3)_2$).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.1 (1C, CAu), 162.0 (CHF_2), 145.6 (2C, Ph C-1), 135.3 (4C, Ph C-2,6), 130.3 (2C, Ph C-4), 124.2 (2C, CHimid), 123.9 (4C, Ph C-3,5), 28.7 (2C, CH), 28.6 (2C, CH), 24.3 (2C, $CH(CH_3)_2$), 24.0 (2C, $CH(CH_3)_2$), 22.9 (2C, $CH(CH_3)_2$), 22.6 (2C, $CH(CH_3)_2$).

^{19}F NMR (376 MHz, $CDCl_3$) δ: -107.9 (d, $^{2}J_{H,F}$ = 46.2 Hz, F-1, CHF_2).

HRMS (ESI), *m/z*: calcd. for $C_{28}H_{37}AuF_2N_2Na^+$: 659.5605 $[M+Na]^+$; found: 659.5609.

[(difluoromethyl)tellanyl] benzene (12)



By following the General Procedure 2, starting from 1,2-diphenylditellane (200 mg, 0.49 mmol, 1 equiv), (difluoromethyl)trimethylsilane (0.1 mL, 0.74 mmol, 1.5 equiv), potassium *tert*-pentoxide 0.9 M (0.8 mL, 0.69 mmol, 1.4 equiv) and dry THF (5 mL), the desired compound **12**[3] was obtained in 90% yield (112 mg) as transparent oil after column chromatography on silica gel (*n*-hexane).

^{1}H NMR (400 MHz, C_6D_6) δ: 7.65 (m, 2H, Ph H-2,6), 6.94 (m, 1H, Ph H-4), 6.86 (m, 2H, Ph H-3,5), 6.91 (t, $^{2}J_{H,F}$ = 51.8 Hz, 1H, CHF_2).

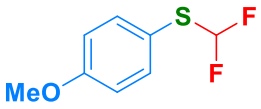
^{13}C NMR (100 MHz, C_6D_6) δ: 141.1 (2C, Ph C-2,6), 129.7 (2C, Ph C-3,5), 129.3 (1C, Ph C-4), 110.1 (t, $^{3}J_{C,F}$ = 2.4 Hz, 1C, Ph C-1), 103.3 (t, $^{1}J_{C,F}$ = 296.3 Hz, CHF_2).

^{19}F NMR (376 MHz, C_6D_6) δ: -89.5 (d, $^{2}J_{H,F}$ = 51.8 Hz, F-1, CHF_2).

EI-MS m/z (%): 254.0 (M^+, 7), 205.0 (M^+, 15), 77.1 (M^+, 100), 51.0 (M^+, 62).

IR(KBr / cm^{-1}): 1470,1425, 1250, 1040, 730, 690.

1-[(difluoromethyl)sulfanyl]-4-methoxybenzene (13)



By following the General Procedure 2, starting from 1,2-bis(4-methoxyphenyl)disulfane (200 mg, 0.72 mmol, 1 equiv), (difluoromethyl)trimethylsilane (0.2 mL, 1.08 mmol, 1.5 equiv), potassium *tert*-pentoxide 0.9 M (1.1 mL, 1.01 mmol, 1.4 equiv) and dry THF (5 mL), the desired compound **13**[4] was obtained in 96 % yield (131 mg) as transparent oil after column chromatography on silica gel (hexane/diethyl ether 9:1).

^{1}H NMR (400 MHz, C_6D_6) δ: 7.32 (m, 2H, Ph H-2,6), 6.53 (m, 2H, Ph H-3,5), 6.22 (t, $^{2}J_{H,F}$ = 57.1 Hz, 1H, CHF_2), 3.14 (s, 3H, OCH_3).

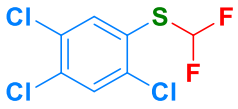
^{13}C NMR (100 MHz, C_6D_6) δ: 161.6 (1C, Ph C-4), 137.9 (2C, Ph C-2,6), 116.4 (t, $^{3}J_{C,F}$ = 3.2 Hz, 1C, Ph C-1), 115.2 (2C, Ph C-3,5), 121.4 (t, $^{1}J_{C,F}$ = 274.9 Hz, CHF_2).

^{19}F NMR (376 MHz, C_6D_6) δ: -92.0 (d, $^{2}J_{H,F}$ = 57.1 Hz, F-1, CHF_2).

HRMS (ESI), *m/z*: calcd. for $C_8H_8F_2OSNa^+$: 213.1996 $[M+Na]^+$; found: 213.1998.

IR (KBr / cm^{-1}): 2965, 2840, 1592, 1572, 1495, 1463, 1319, 1291, 1251, 1175, 1098, 1066, 1030, 831, 790.

1-[(difluoromethyl)sulfanyl]-2,4,5 trichlorobenzene (14)



By following the General Procedure 2, starting from 1,2-bis(2,4,5-trichlorophenyl)disulfane (200 mg, 0.47 mmol, 1 equiv), (difluoromethyl)trimethylsilane (0.1 mL, 0.71 mmol, 1.5 equiv), potassium *tert*-pentoxide 0.9 M (0.7 mL, 0.66 mmol, 1.4 equiv) and dry THF (5 mL), the desired compound **14** was obtained in 88 % yield (109 mg) as transparent oil after column chromatography on silica gel (hexane/diethyl ether 9:1).

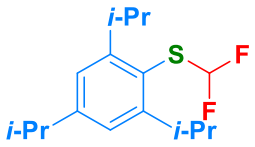
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 (s, Ph H-6), 7.63 (s, Ph H-3), 6.89 (t, $^{2}J_{H,F}$ = 56.4 Hz, 1H, CHF_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.2 (1C, Ph C-3), 135.3 (1C, Ph C-2), 134.3 (1C, PH C-4), 133.1 (1C, PH C-5), 131.5 (1C, PH C-6), 119.4 (t, $^{1}J_{C,F}$ = 277.7 Hz, CHF_2).

^{19}F NMR (376 MHz, $CDCl_3$) δ: -92.0 (d, $^{2}J_{H,F}$ = 56.4 Hz, F-1, CHF_2).

HRMS (ESI), *m/z*: calcd. for $C_7H_3Cl_3F_2SNa^+$: 286.5088 $[M+Na]^+$; found: 286.5091.

1-[(difluoromethyl)sulfanyl]-2,4,6 triisopropyl-benzene (15)



By following the General Procedure 2, starting from 1,2-bis(2,4,6 triisopropyl-phenyl)disulfane (200 mg, 0.43 mmol, 1 equiv), (difluoromethyl)trimethylsilane (0.1 mL, 0.64 mmol, 1.5 equiv), potassium *tert*-pentoxide 0.9 M (0.7 mL, 0.59 mmol, 1.4 equiv) and dry THF (5 mL), the desired compound **15** was obtained in 91 % yield (111 mg) as transparent oil after column chromatography on silica gel (*n*-hexane).

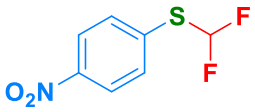
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.07 (m, 2H, Ph H-3,5), 6.62 (t, $^{2}J_{H,F}$ = 57.2 Hz, 1H, CHF_2), 3.88 (dt, $^{4}J_{H,H}$ = 13.7 Hz, $^{3}J_{H,H}$ = 6.9 Hz, 2H, C2,6H$(CH_3)_2$), 2.88 (dt, $^{4}J_{H,H}$ = 13.8 Hz, $^{3}J_{H,H}$ = 8.1 Hz, 1H, C4H$(CH_3)_2$), 1.26 (d, $^{3}J_{H,H}$ = 6.9 Hz, 6H, C4H$(CH_3)_2$), 1.22 (d, $^{3}J_{H,H}$ = 6.9 Hz, 12H, C2,6H$(CH_3)_2$).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.5 (2C, Ph C-2,6), 151.6 (Ph C-4), 122.4 (Ph C-3), 121.8 (t, $^{1}J_{C,F}$ = 245.1 Hz, CHF_2), 34.3 (C4H$(CH_3)_2$), 31.6 (2C, C2,6H$(CH_3)_2$), 24.1 (2C, C4H$(CH_3)_2$), 23.8 (4C, C2,6H$(CH_3)_2$).

^{19}F NMR (376 MHz, $CDCl_3$) δ: -91.3 (d, $^{2}J_{H,F}$ = 57.2 Hz, F-1, CHF_2).

HRMS (ESI), *m/z*: calcd. for $C_{16}H_{24}F_2SNa^+$: 309.4128 $[M+Na]^+$; found: 309.4130.

1-[(difluoromethyl)sulfanyl]-4-nitrobenzene (16)



By following the General Procedure 2, starting from 1,2-bis(4-nitrophenyl) disulfane (200 mg, 0.65 mmol, 1 equiv), (difluoromethyl)trimethylsilane (0.1 mL, 0.97 mmol, 1.5 equiv), potassium *tert*-pentoxide 0.9 M (1.0 mL, 0.91 mmol, 1.4 equiv) and dry THF (5 mL), the desired compound **16** was obtained in 83 % yield (110 mg) as transparent oil after column chromatography on silica gel (hexane/diethyl ether 9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.23 (m, 2H, Ph H-2,6), 7.72 (m, 2H, Ph H-3,5), 6.94 (t, $^{2}J_{H,F}$ = 55.9 Hz, 1H, CHF_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.9 (1C, Ph C-4), 134.3 (2C, Ph C-2,6), 126.4 (1C, Ph C-1), 124.16 (2C, Ph C-3,5), 119.6 (t, $^{1}J_{C,F}$ = 276.8 Hz, CHF_2).

^{19}F NMR (376 MHz, $CDCl_3$) δ: -91.2 (d, $^{2}J_{H,F}$ = 55.9 Hz, F-1, CHF_2).

HRMS (ESI), *m/z*: calcd. for $C_7H_5F_2NO_2SNa^+$: 228.1711 $[M+Na]^+$; found: 228.1714.

[(difluoromethyl)selanyl] benzene (17)

By following the General Procedure 2, starting from 1,2-diphenyldiselane (200 mg, 0.64 mmol, 1 equiv), (difluoromethyl)trimethylsilane (0.1 mL, 0.96 mmol, 1.5 equiv), potassium *tert*-pentoxide 0.9 M (0.9 mL, 0.89 mmol, 1.4 equiv) and dry THF (5 mL), the desired compound **17**[5] was obtained in 85% yield (113 mg) as transparent oil after column chromatography on silica gel (*n*-hexane).

^{1}H NMR (400 MHz, C_6D_6) δ: 7.42 (m, 2H, Ph H-2,6), 6.94 (m, 1H, Ph H-4), 6.88 (m, 2H, Ph H-3,5), 6.50 (t, $^{2}J_{H,F}$ = 55.2 Hz, 1H, CHF_2).

^{13}C NMR (100 MHz, C_6D_6) δ: 136.6 (2C, Ph C-2,6), 129.6 (2C, Ph C-3,5), 129.3 (1C, Ph C-4), 123.9 (m, 1C, Ph C-1), 117.5 (t, $^{1}J_{C,F}$ = 288.8 Hz, CHF_2).

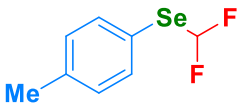
^{19}F NMR (376 MHz, C_6D_6) δ: -90.1 (d, $^{2}J_{H,F}$ = 55.2 Hz, F-1, CHF_2).

^{77}Se NMR (76 MHz, C_6D_6) δ: 502.5 (dt, $^{2}J_{Se,F}$ = 53.3 Hz, $^{2}J_{Se,H}$ = 23.0 Hz, Se-1).

HRMS (ESI), *m/z*: calcd. for $C_7H_6F_2SeNa^+$: 230.0686 $[M+Na]^+$; found: 230.0687.

IR (KBr / cm^{-1}): 1470, 1435, 1265, 1060, 740.

1-[(difluoromethyl)selanyl]-4-methylbenzene (18)



By following the General Procedure 2, starting from 1,2-di-*p*-tolyldiselane (200 mg, 0.59 mmol, 1 equiv), (difluoromethyl)trimethylsilane (0.1 mL, 0.89 mmol, 1.5 equiv), potassium *tert*-pentoxide 0.9 M (0.9 mL, 0.82 mmol, 1.4 equiv) and dry THF (5 mL), the desired compound **18**[5] was obtained in 85% yield (110 mg) as transparent oil after column chromatography on silica gel (*n*-hexane).

^{1}H NMR (400 MHz, C_6D_6) δ: 7.39 (m, 2H, Ph H-2,6), 6.74 (m, 2H, Ph H-3,5), 6.56 (t, $^{2}J_{H,F}$ = 55.3 Hz, 1H, CHF_2), 1.94 (s, 3H, CH_3).

^{13}C NMR (100 MHz, C_6D_6) δ: 139.6 (1C, Ph C-4), 136.8 (2C, Ph C-2,6), 130.5 (2C, Ph C-3,5), 120.3 (t, $^{3}J_{C,F}$ = 2.8 Hz, 1C, Ph C-1), 117.5 (t, $^{1}J_{C,F}$ = 288.8 Hz, CHF_2), 21.0 (1C, CH_3).

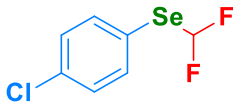
^{19}F NMR (376 MHz, C_6D_6) δ: -90.3 (d, $^{2}J_{H,F}$ = 55.3 Hz, F-1, CHF_2).

^{77}Se NMR (76 MHz, C_6D_6) δ: 492.8 (dt, $^{2}J_{Se,F}$ = 51.5 Hz, $^{2}J_{Se,H}$ = 23.3 Hz, Se-1).

HRMS (ESI), *m/z*: calcd. for $C_8H_8F_2SeNa^+$: 244.0952 $[M+Na]^+$; found: 244.0955.

IR (KBr / cm^{-1}): 3025, 2965, 2924, 2868, 1491, 1448, 1397, 1292, 1271, 1211, 1183, 1078, 1063, 1016, 805, 706, 690, 669.

1-chloro-4-[(difluoromethyl)selanyl] benzene (19)



By following the General Procedure 2, starting from 1,2-bis(4-chlorophenyl) diselane (200 mg, 0.52 mmol, 1 equiv), (difluoromethyl)trimethylsilane (0.1 mL, 0.79 mmol, 1.5 equiv), potassium *tert*-pentoxide 0.9 M (0.8 mL, 0.73 mmol, 1.4 equiv) and dry THF (5 mL), the desired compound **19**[6] was obtained in 75% yield (95 mg) as transparent oil after column chromatography on silica gel (*n*-hexane).

^{1}H NMR (400 MHz, C_6D_6) δ: 7.08 (m, 2H, Ph H-3,5), 6.82 (m, 2H, Ph H-2,6), 6.37 (t, $^2J_{H,F}$ = 55.0 Hz, 1H, CHF_2).

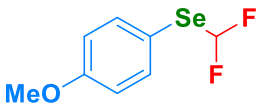
^{13}C NMR (100 MHz, C_6D_6) δ: 137.9 (2C, Ph C-3,5), 136.2 (1C, Ph C-1), 129.8 (2C, Ph C-2,6), 121.6 (t, $^3J_{C,F}$ = 2.8 Hz, 1C, Ph C-4), 117.0 (t, $^1J_{C,F}$ = 289.4 Hz, CHF_2).

^{19}F NMR (376 MHz, C_6D_6) δ: -90.3 (d, $^2J_{H,F}$ = 55.0 Hz, F-1, CHF_2).

^{77}Se NMR (76 MHz, C_6D_6) δ: 474.5 (dt, $^2J_{Se,F}$ = 50.7 Hz, $^2J_{Se,H}$ = 25.0 Hz, Se-1).

HRMS (ESI), *m/z*: calcd. for $C_7H_5ClF_2SeNa^+$: 264.5136 $[M+Na]^+$; found: 264.5139.

1-[(difluoromethyl)selanyl]-4-methoxybenzene (20)



By following the General Procedure 2, starting from 1,2-bis(4-methoxyphenyl)diselane (200 mg, 0.53 mmol, 1 equiv), (difluoromethyl)trimethylsilane (0.1 mL, 0.80 mmol, 1.5 equiv), potassium *tert*-pentoxide 0.9 M (0.8 mL, 0.75 mmol, 1.4 equiv) and dry THF (5 mL), the desired compound **20**[4] was obtained in 82% yield (104 mg) as transparent oil without any further purification step.

^{1}H NMR (400 MHz, C_6D_6) δ: 7.40 (m, 2H, Ph H-2,5), 6.53 (m, 2H, Ph H-3,6), 6.55 (t, $^{2}J_{H,F}$ = 55.4 Hz, 1H, CHF_2), 3.16 (s, 3H, OCH_3).

^{13}C NMR (100 MHz, C_6D_6) δ: 161.3 (1C, Ph C-4), 138.7 (2C, Ph C-2,6), 117.4 (t, $^{1}J_{C,F}$ = 289.0 Hz, CHF_2), 115.4 (2C, Ph C-3,5), 113.8 (t, $^{3}J_{C,F}$ = 2.9 Hz, 1C, Ph C-1), 54.8 (1C, OCH_3).

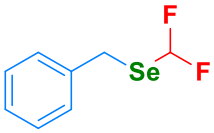
^{19}F NMR (376 MHz, C_6D_6) δ: -90.8 (d, $^{2}J_{H,F}$ = 55.4 Hz, F-1, CHF_2).

^{77}Se NMR (76 MHz, C_6D_6) δ: 285.9 (dt, $^{2}J_{Se,F}$ = 49.6 Hz, $^{2}J_{Se,H}$ = 23.9 Hz, Se-1).

HRMS (ESI), *m/z*: calcd. for $C_8H_8F_2OSeNa^+$: 260.0946 [M+Na]$^+$; found: 260.0949.

IR (KBr / cm-1): 3069, 3007, 2964, 2942, 2908, 2840, 1592, 1572, 1493, 1462, 1441, 1404, 1290, 1271, 1251, 1176, 1104, 1079, 1062, 1039, 1005, 827, 811, 793, 712, 691, 670, 631, 602.

benzyl(difluoromethyl)selane (21)



By following the General Procedure 2, starting from dibenzyl diselane (200 mg, 0.59 mmol, 1 equiv), (difluoromethyl)trimethylsilane (0.1 mL, 0.88 mmol, 1.5 equiv), potassium *tert*-pentoxide 0.9 M (0.9 mL, 0.82 mmol, 1.4 equiv) and dry THF (5 mL), the desired compound **21** was obtained in 80% yield (109 mg) as transparent oil after column chromatography on silica gel (*n*-hexane).

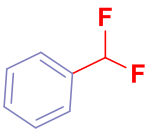
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24 (m, 3H, Ph H-3,4,5), 7.19 (m, 2H, Ph H-2,6), 6.69 (t, $^{2}J_{H,F}$ = 55.2 Hz, 1H, CHF_2), 4.03 (s, 2H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.3 (1C, Ph C-1), 128.9 (2C, Ph C-2,6), 128.8 (2C, Ph C-3,5), 127.4 (1C, Ph C-4), 115.6 (t, $^{1}J_{C,F}$ = 289.8 Hz, CHF_2), 26.3 (t, $^{3}J_{C,F}$ = 2.9 Hz, 1C, CH_2).

^{19}F NMR (376 MHz, $CDCl_3$) δ: -93.0 (d, $^{2}J_{H,F}$ = 55.2 Hz, F-1, CHF_2).

HRMS (ESI), *m/z*: calcd. for $C_8H_8F_2SeNa^+$: 244.0952 [M+Na]$^+$; found: 244.0955.

difluoromethyl) benzene (22)



To a mixture of $Pd(dba)_2$ (73mg, 0.13 mmol, 0.1 equiv), JackiePhos (102 mg, 0.13 mmol, 0.1 equiv), CuI (485mg, 2.55 mmol, 2.0 equiv), and KF (148 mg, 2.55 mmol, 2.0 equiv) under Argon atmosphere, 5-(difluoromethyl)-1-aza-5-stannabicyclo[3.3.3]undecane (592 mg, 1.91 mmol, 1.5 equiv) and bromobenzene (200 mg, 1.27 mmol, 1 equiv) were added, diluted in dry MeCN (3 mL), and stirred at 70 °C for 36 h. The reaction mixture was cooled to room temperature and diluted with diethyl ether. The organic layer was washed sequentially with saturated aqueous KF and brine, extracted 3 times with Et_2O, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The desired compound **22** was obtained in 76% yield (124 mg) as colourless oil after column chromatography on silica gel (*n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (m, 2H, Ph H-2,6), 7.49 (m, 3H, Ph H-3,4,5), 6.67 (t, $^2J_{H,F}$ = 56.5 Hz, 1H, CHF_2).

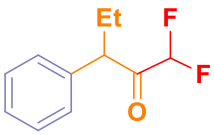
^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.3 (t, 1C, $^2J_{C,F}$ = 22.3 Hz, Ph C-1), 130.7 (t, 1C, $^5J_{C,F}$ = 1.9 Hz, Ph C-4), 128.7 (2C, Ph C-3,5), 125.5 (t, 1C, $^3J_{C,F}$ = 6.1 Hz, 2C, Ph C-2,6), 114.8 (t, $^1J_{C,F}$ = 238.5 Hz, CHF_2).

^{19}F NMR (376 MHz, $CDCl_3$) δ: -110.4 (d, $^2J_{H,F}$ = 56.8 Hz, F-1, CHF_2).

MS (EI, 70 eV), *m/z*: 128.

IR (KBr / cm^{-1}): 1607,1375, 1218, 1093, 1016, 824.

1,1-difluoro-3-phenylpentan-2-one (24)



To a mixture of $Pd(PPh_3)_4$ (63 mg, 0.055 mmol, 0.05 equiv), and CuI (419mg, 2.19 mmol, 2.0 equiv) under Argon atmosphere, 5-(difluoromethyl)-1-aza-5-stannabicyclo[3.3.3]undecane (512 mg, 1.64 mmol, 1.5 equiv) and 2-phenylbutanoyl chloride (200 mg, 1.09 mmol, 1 equiv) were added, diluted in dry MeCN (3 mL), and stirred at 70°C for 12 h. The reaction mixture was cooled to room temperature and diluted with diethyl ether. The organic layer was washed sequentially with brine, extracted 3 times with Et_2O, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The desired compound **24** was obtained in 83% yield (180 mg) as a transparent oil after column chromatography on silica gel (*n*-hexane).

^{1}H NMR (400 MHz, C_6D_6) δ: 7.35 (m, 2H, Ph H-3,5), 7.29 (m, H, Ph H-4), 7.22 (m, 2H, Ph H2,6), 5.66 (t, $^2J_{H,F}$ = 53.8 Hz, 1H, CHF_2), 3.97 (m, 1H,H-3), 2.11 (m, 1H, H-4), 1.80 (m, 1H, H-5), 0.86 (t, $^3J_{H,F}$= 7.4 Hz, 3H, CH_3).

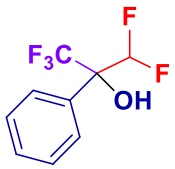
^{13}C NMR (100 MHz, C_6D_6) δ: 199.0 (C=O), 136.1 (Ph C-1), 129.1 (2C, Ph C-3,5), 128.6 (2C, Ph C-2,6), 127.8 (Ph C-4), 109.3 (t, $^1J_{C,F}$= 252.7 Hz, CHF_2), 54.6 (C-3), 25.3 (C-4), 11.7 (C-5).

^{19}F NMR (376 MHz, C_6D_6) δ: -129.1 (d, AB system, $^2J_{F,F}$ = 318.0 Hz, $^2J_{H,F}$ = 53.8 Hz, CHF_2), -126.4 (dd, AB system, $^2J_{F,F}$ = 318.0 Hz, $^2J_{H,F}$ = 53.6 Hz, $^2J_{H,F}$ = 2.2 Hz, CHF_2).

HRMS (ESI), *m/z*: calcd. for $C_{11}H_{12}F_2ONa^+$: 221.0748 $[M+Na]^+$; found: 221.0749.

IR (KBr / cm^{-1}): 3080, 1714.

1,1,1,3,3-pentafluoro-2-phenyl-2-propanol (26)



To a solution of 2,2,2-trifluoro-1-phenylethan-1-one (200 mg, 1.15 mmol, 1 equiv) in dry THF under Argon and cooled down to 0°C, (difluoromethyl)triphenylsilane (535 mg, 1.72 mmol, 1.5 equiv) was added, after 5 min the solution of potassium *tert*-pentoxide in toluene 0.9 M (1.8 mL, 1.61 mmol, 1.4 equiv) was added dropwise and, then the mixture was stirred at this temperature for 4 h. The reaction mixture was quenched with aqueous saturated NH_4Cl solution and then was allowed to warm to rt. The resulting organic phase was extracted 3 times with Et_2O, washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The desired compound **26** was obtained in 76% yield (226 mg) as brown oil after column chromatography on silica gel (n-hexane/diethyl ether 9:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (m, 2H, Ph H-2,6), 7.46 (m, 3H, Ph H-3,4,5), 6.20 (qt, $^2J_{H,F}$ = 54.1 Hz, $^4J_{H,F}$ = 0.7 Hz, 1H, CHF_2), 3.20 (brs, OH).

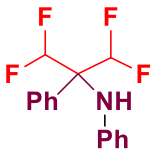
^{13}C NMR (100 MHz, $CDCl_3$) δ: 131.0 (m, 1C, Ph C-1), 129.8 (Ph C-4), 128.7 (2C, Ph C-3,5), 126.2 (m, 2C, Ph C-2,6), 123.4 (q, $^1J_{C,F}$ = 286.7 Hz, 1C, CF_3), 113.3 (t, $^1J_{C,F}$ = 250.7 Hz, CHF_2), 76.5 (m, COH).

^{19}F NMR (376 MHz, $CDCl_3$) δ: -131.34 (dq, $^2J_{H,F}$ = 54.1 Hz, $^2J_{F,F}$ = 8.9 Hz, F-1, CHF_2), -131.26 (dq, $^2J_{H,F}$ = 54.1 Hz, $^2J_{F,F}$ = 8.9 Hz, F-2, CHF_2), -75.8 (t, $^2J_{H,F}$ = 8.9 Hz, F-3, CF_3).

HRMS (ESI), *m/z*: calcd. for $C_9H_7F_5ONa^+$: 249.0309 $[M+Na]^+$; found: 249.0311.

IR (KBr / cm^{-1}) : 3402, 1506, 1463, 1272, 1186, 1130.

_N_-(1,1,3,3-tetrafluoro-2-phenylpropan-2-yl)aniline (28)



To a solution of (*E*)-*N*-phenylbenzimidoyl chloride (200 mg, 0.93 mmol, 1 equiv) in dry THF under Argon and cooled down to 0°C, (difluoromethyl)triphenylsilane (432 mg, 1.39 mmol, 1.5 equiv) was added, after 5 min the solution of potassium *tert*-pentoxide in toluene 0.9 M (1.4 mL, 1.29 mmol, 1.4 equiv) was added dropwise and, then the mixture was stirred at this temperature for 6 h. The reaction mixture was quenched with aqueous saturated NH_4Cl solution and then was allowed to warm to rt. The resulting organic phase was extracted 3 times with Et_2O, washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The desired compound **28** was obtained in 81% yield (213 mg) as transparent oil after column chromatography on silica gel (n-hexane).

^{1}H NMR (400 MHz, C_6D_6) δ: 7.44 (m, 2H, Ph1 H-2,6), 7.03 (m, 3H, Ph1 H-3,4,5), 6.83 (m, 2H, Ph H-3,5), 6.62 (m, 1H, Ph H-4), 6.23 (m, 2H, Ph H-2,6), 5.80 (mt, $^2J_{H,F}$ = 54.3 Hz, 2H, CHF_2), 4.29 (s, NH).

^{13}C NMR (100 MHz, C_6D_6) δ: 143. 8 (Ph C-1), 132. 4 (Ph1 C-1), 129.13 (Ph1 C-3,5), 129.2 (Ph1 C-4), 129.09 (Ph C-3,5), 128.4 (Ph1 C-2,6), 120.0 (Ph C-4), 117,1 (Ph C-2,6), 116.0 (t, $^1J_{C,F}$=253.3 Hz, CHF_2), 66.1 (q, $^2J_{C,F}$=18.8 Hz C-2).

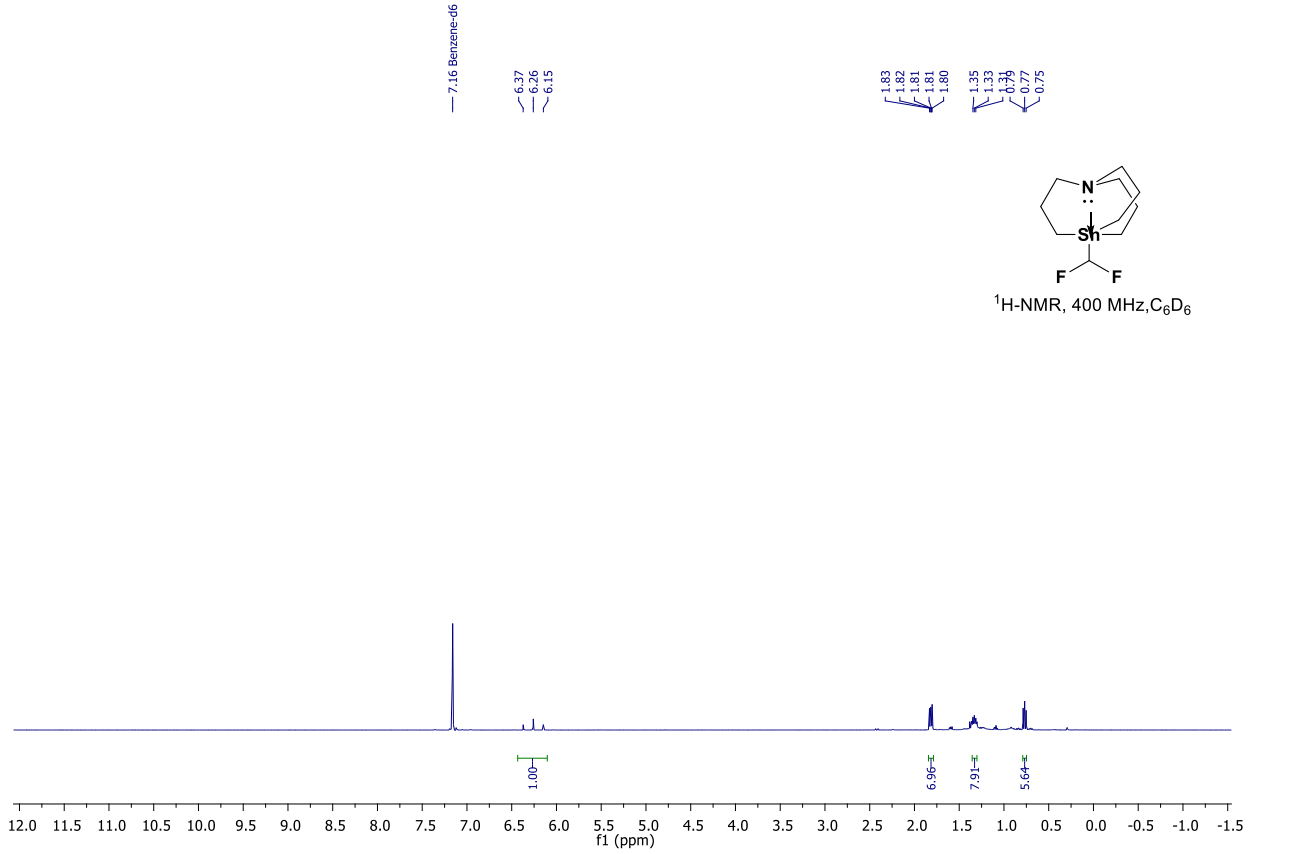
^{19}F NMR (376 MHz, C_6D_6) δ: -125.8 (m, CHF_2), -128.1 (m, CHF_2).

HRMS (ESI), *m/z*: calcd. for $C_{15}H_{13}F_4N_3\ Na^+$: 306.0876 $[M+Na]^+$; found: 306.0872.

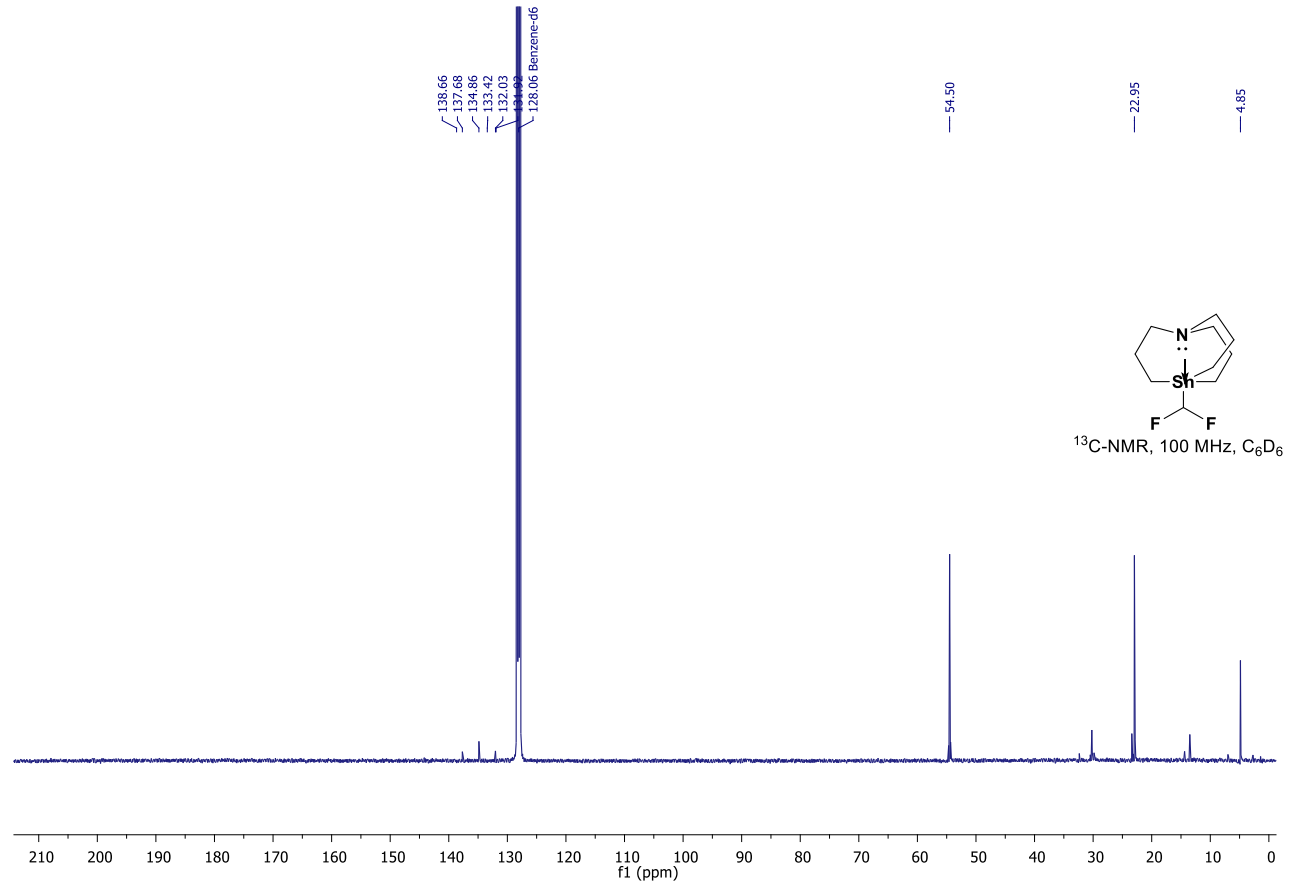
IR (KBr / cm-1): 3414, 1602, 1505.

4. ^{1}H-, ^{13}C- and ^{19}F-NMR Spectra

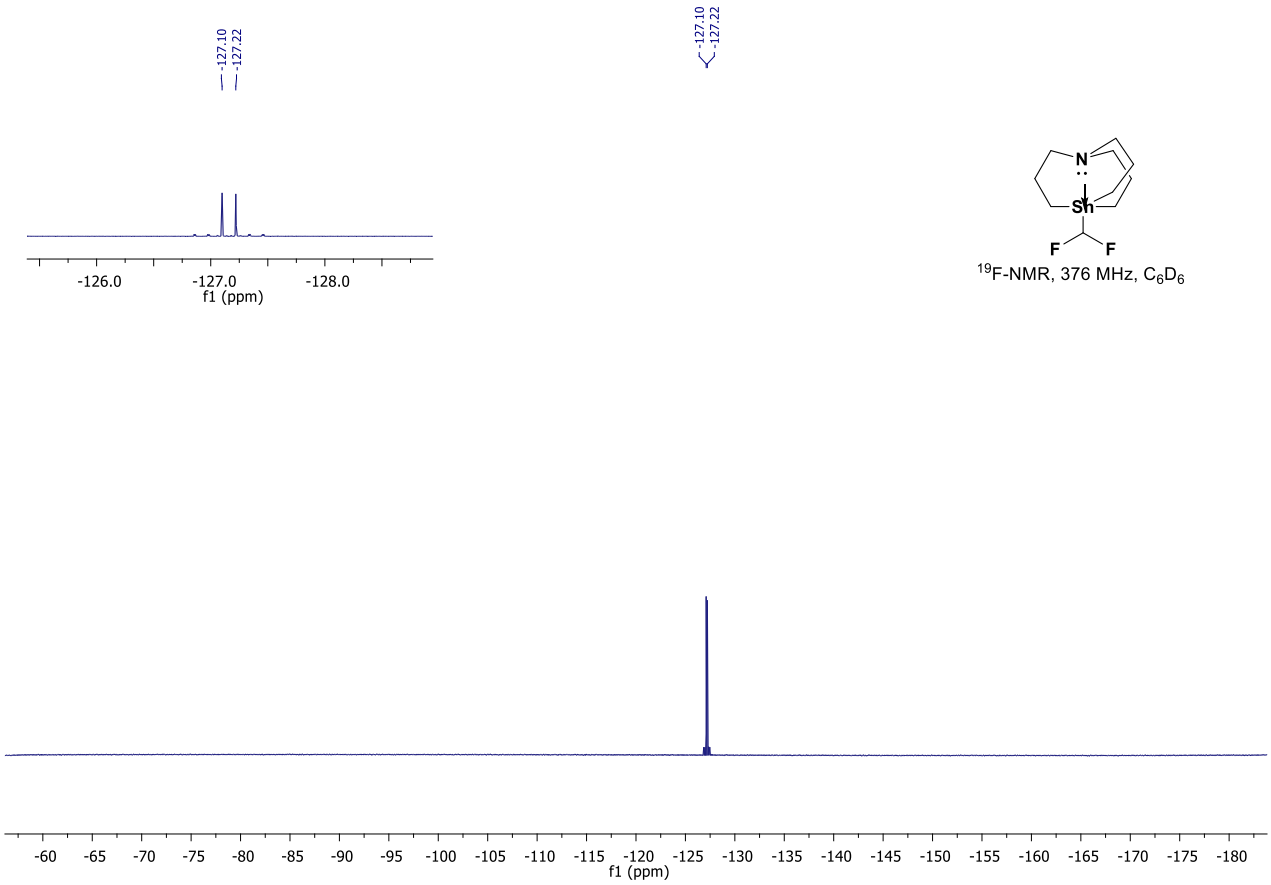
Compound 2



^{1}H-NMR, 400 MHz,C_6D_6

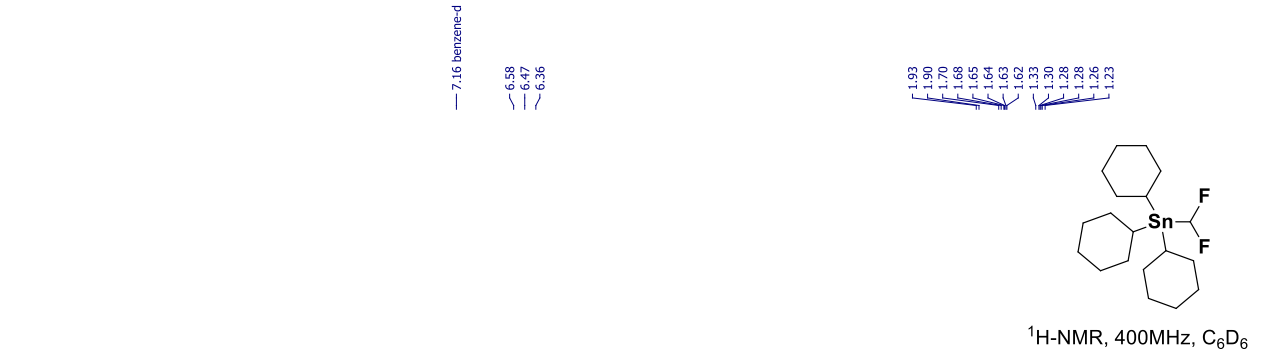


^{13}C-NMR, 100 MHz, C_6D_6

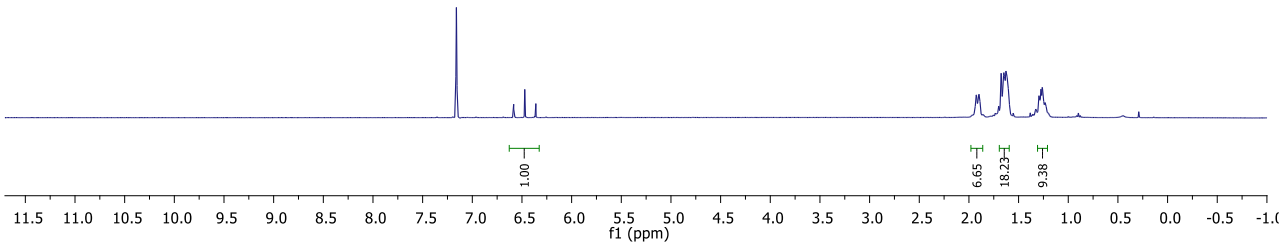


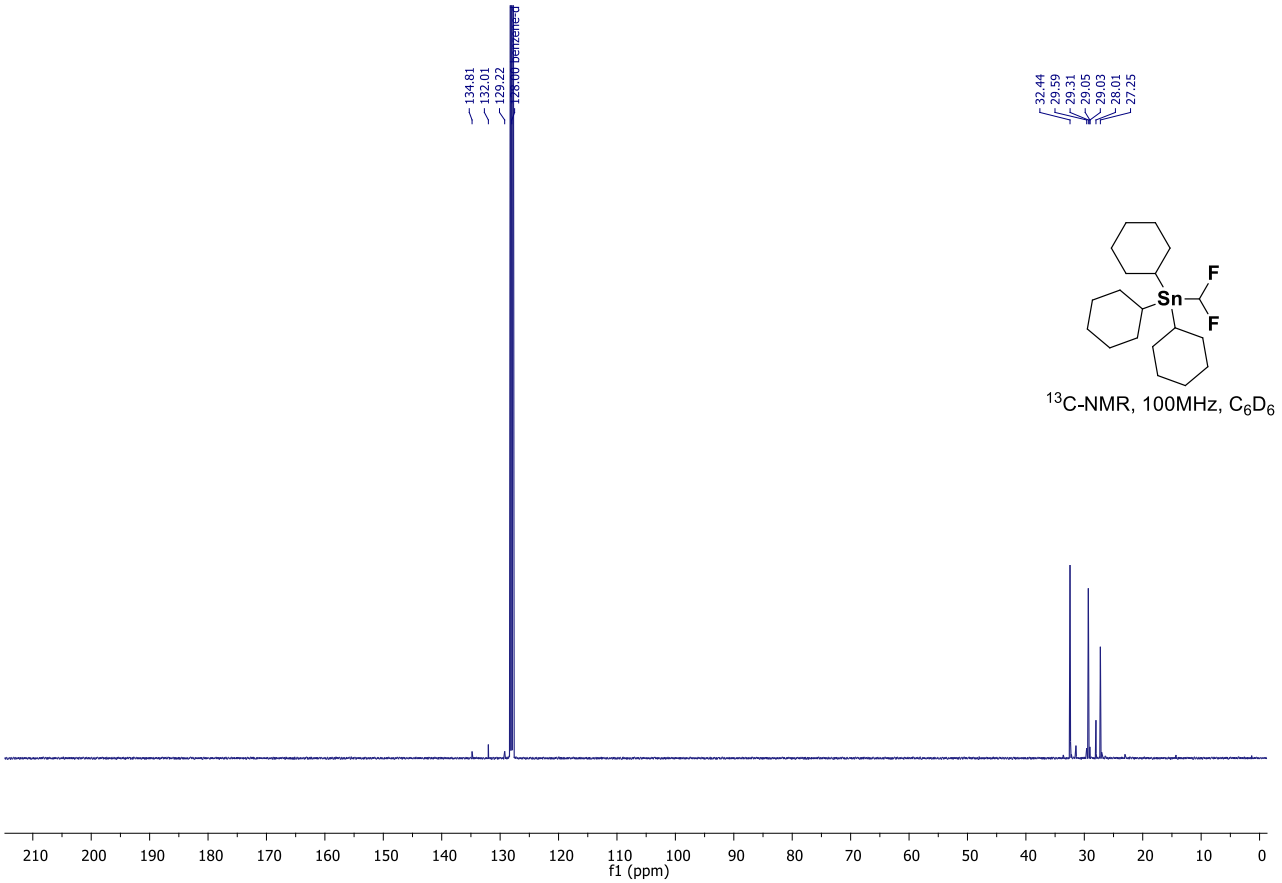
^{19}F-NMR, 376 MHz, C_6D_6

Compound 3

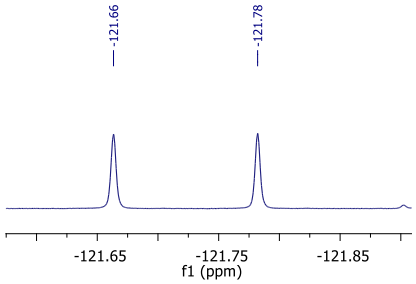


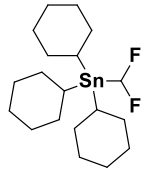
^{1}H-NMR, 400MHz, C_6D_6



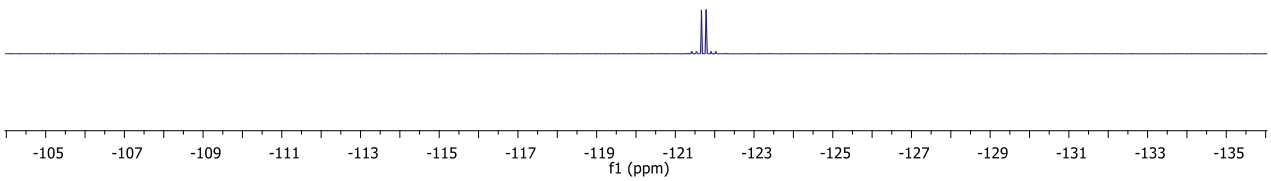


^{13}C-NMR, 100MHz, C_6D_6

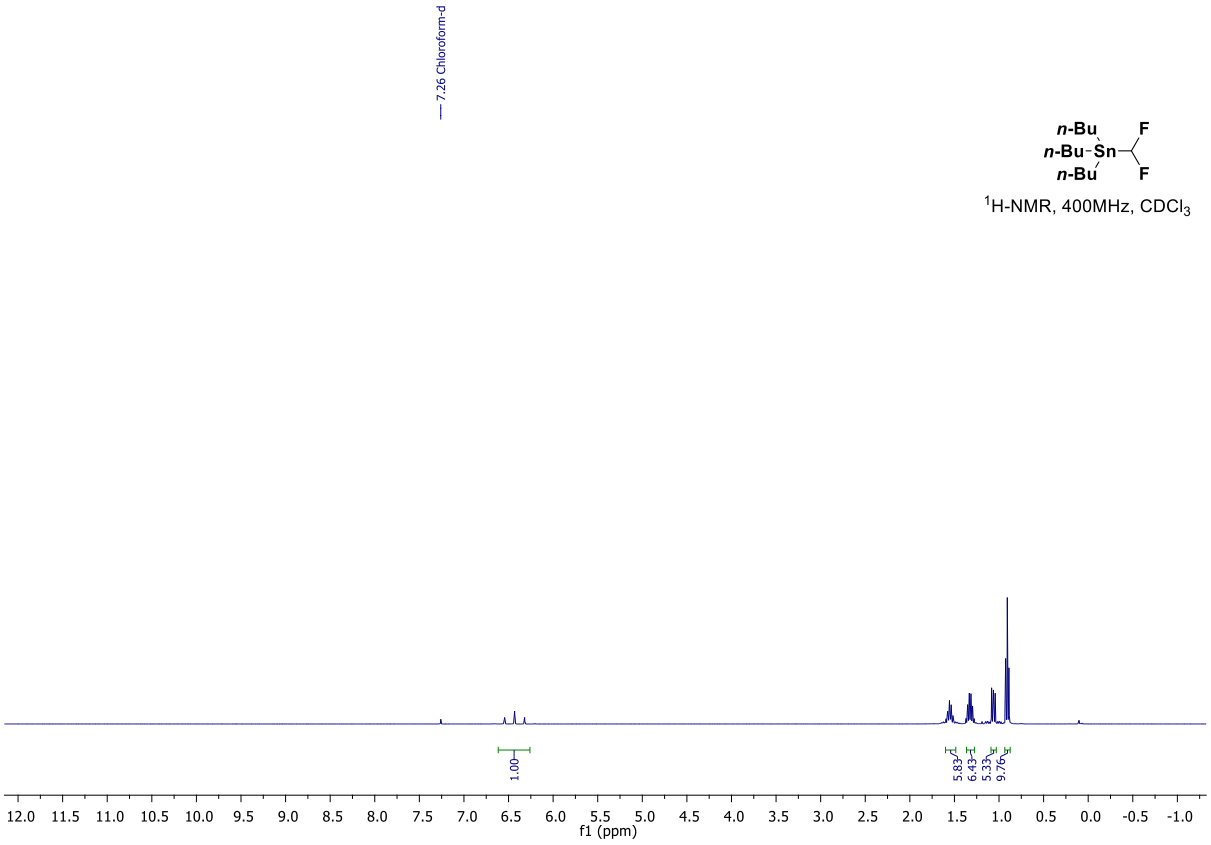




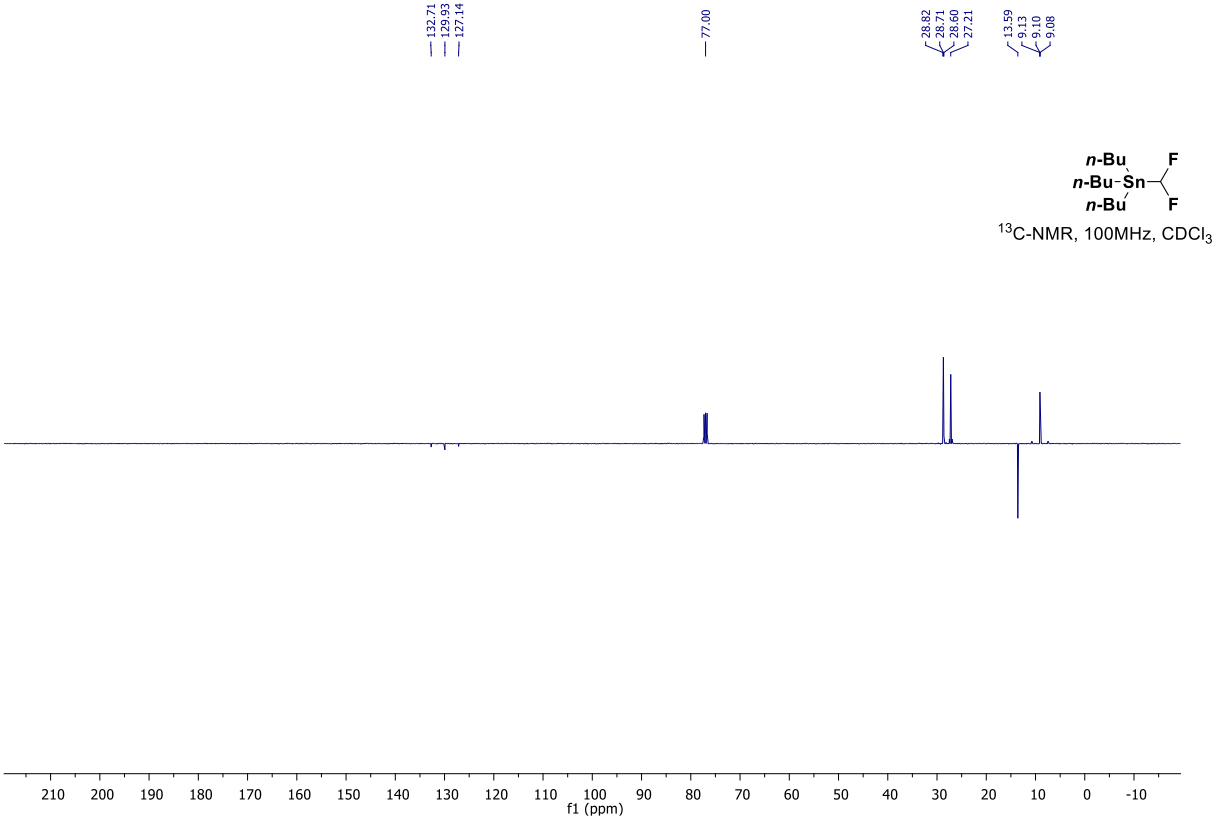
^{19}F-NMR, 376MHz, C_6D_6



Compound 4

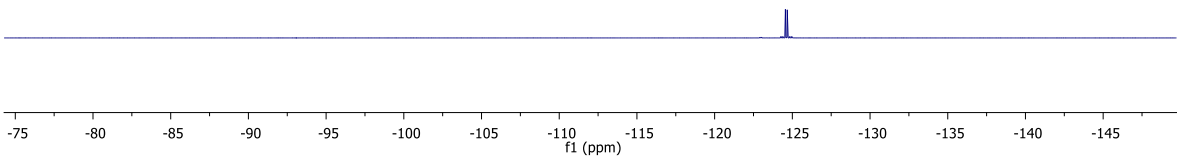


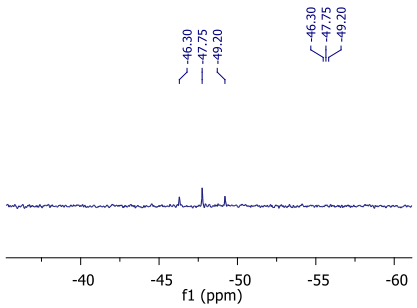
^{1}H-NMR, 400MHz, $CDCl_3$

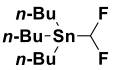


^{13}C-NMR, 100MHz, $CDCl_3$

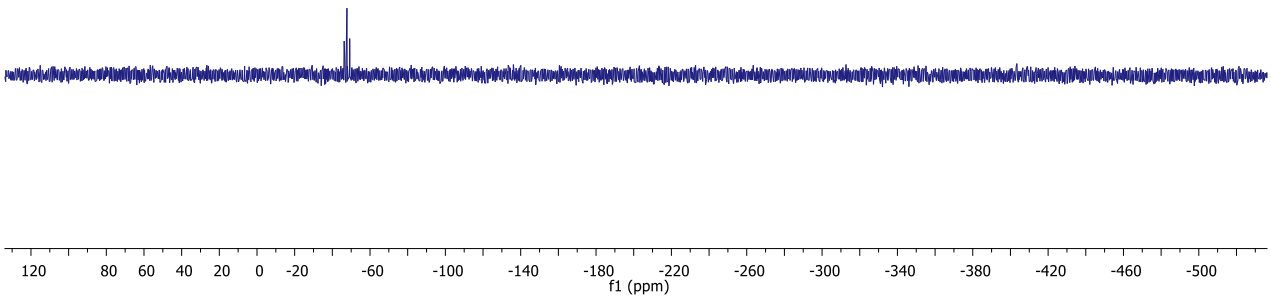
^{19}F-NMR, 376MHz, $CDCl_3$



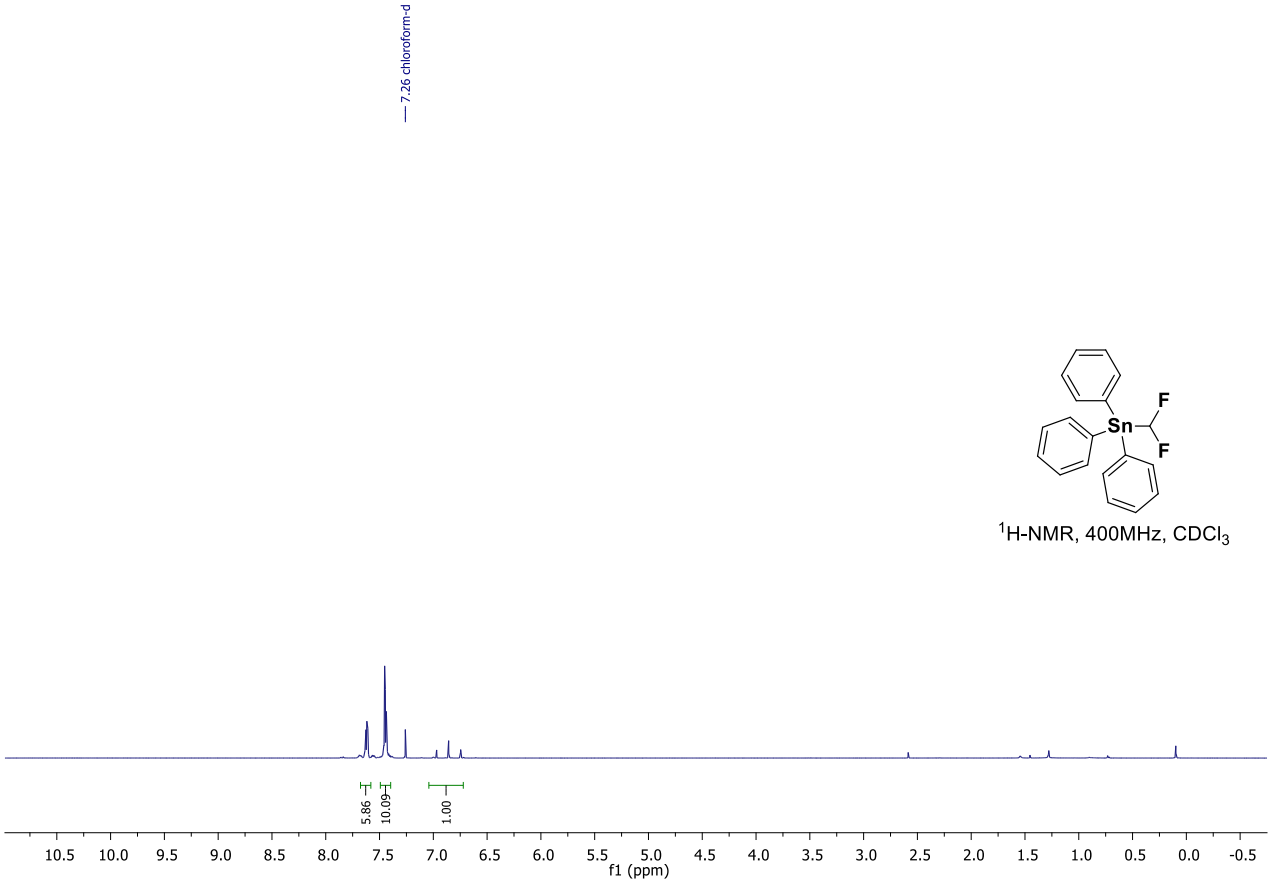




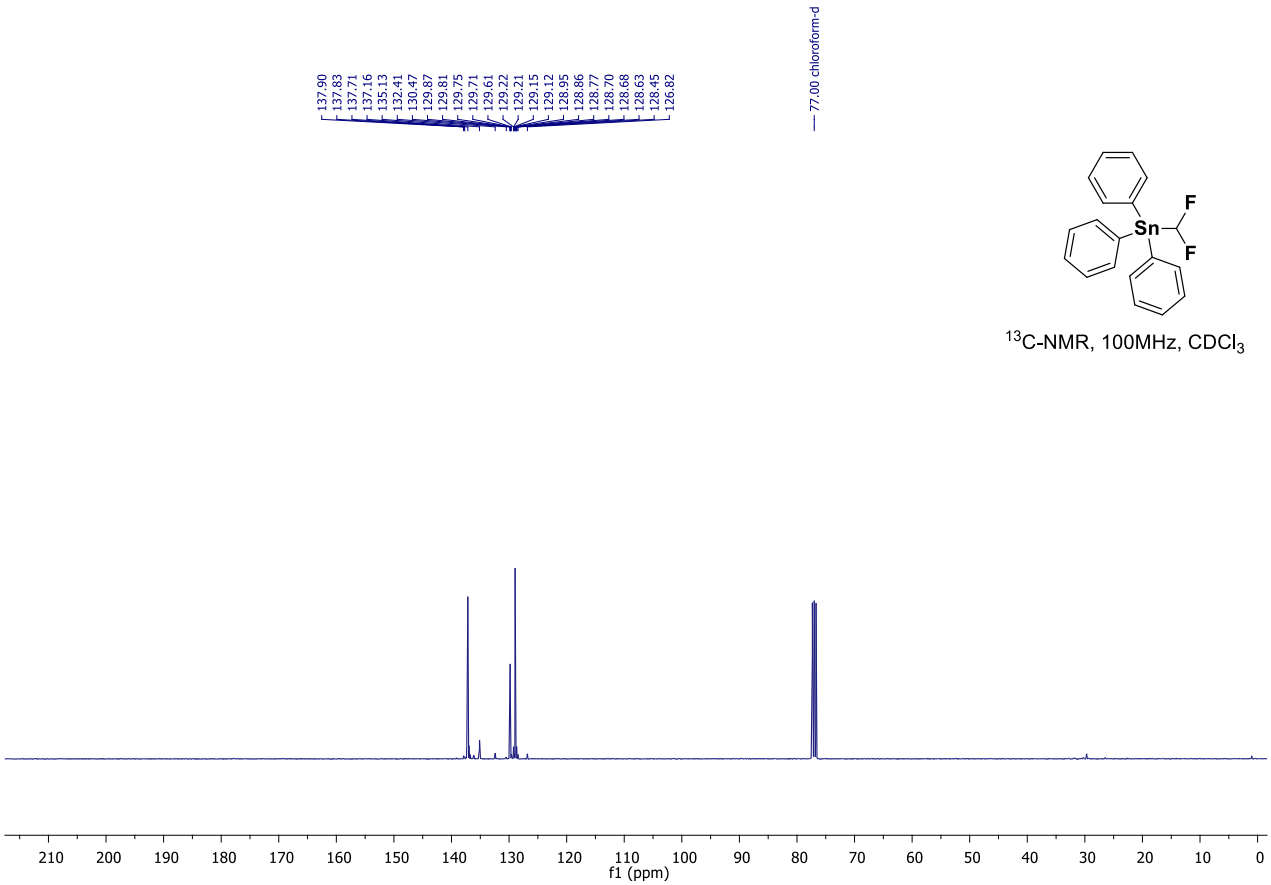
^{119}Sn-NMR, 400MHz, $CDCl_3$



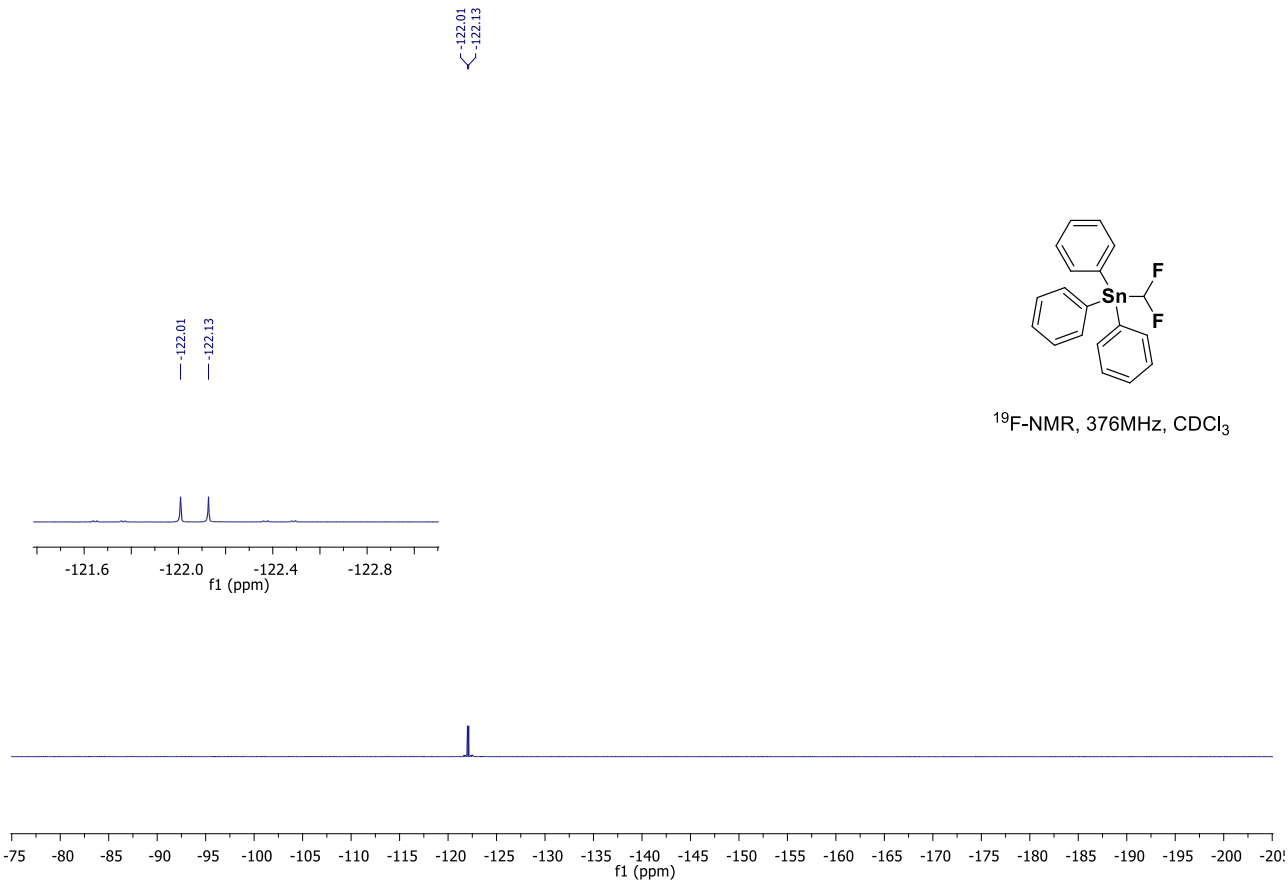
Compound 5



^{1}H-NMR, 400MHz, $CDCl_3$



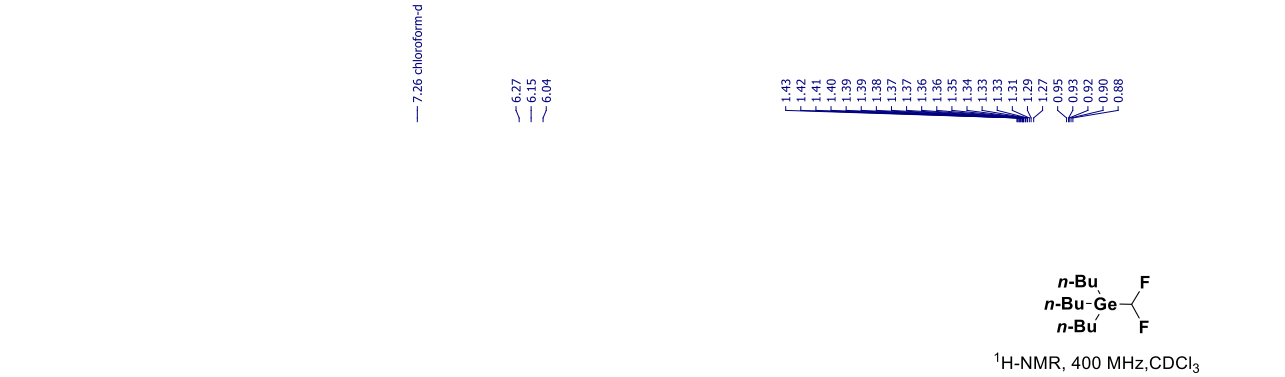
^{13}C-NMR, 100MHz, $CDCl_3$



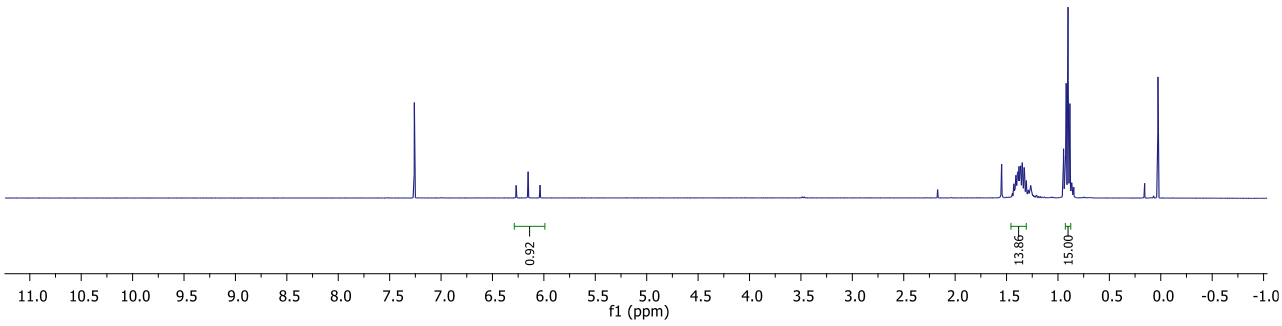
^{19}F-NMR, 376MHz, $CDCl_3$

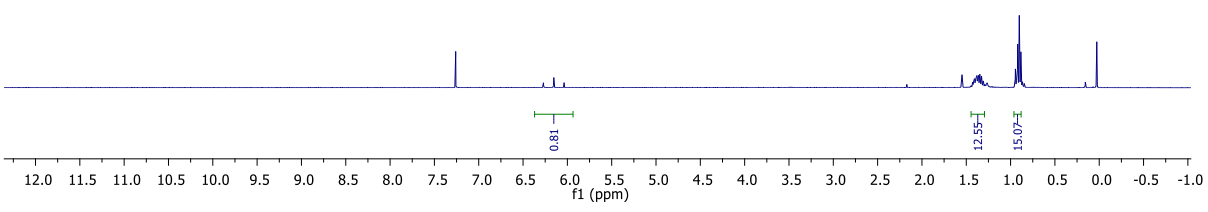
^{119}Sn-NMR, 400MHz, $CDCl_3$

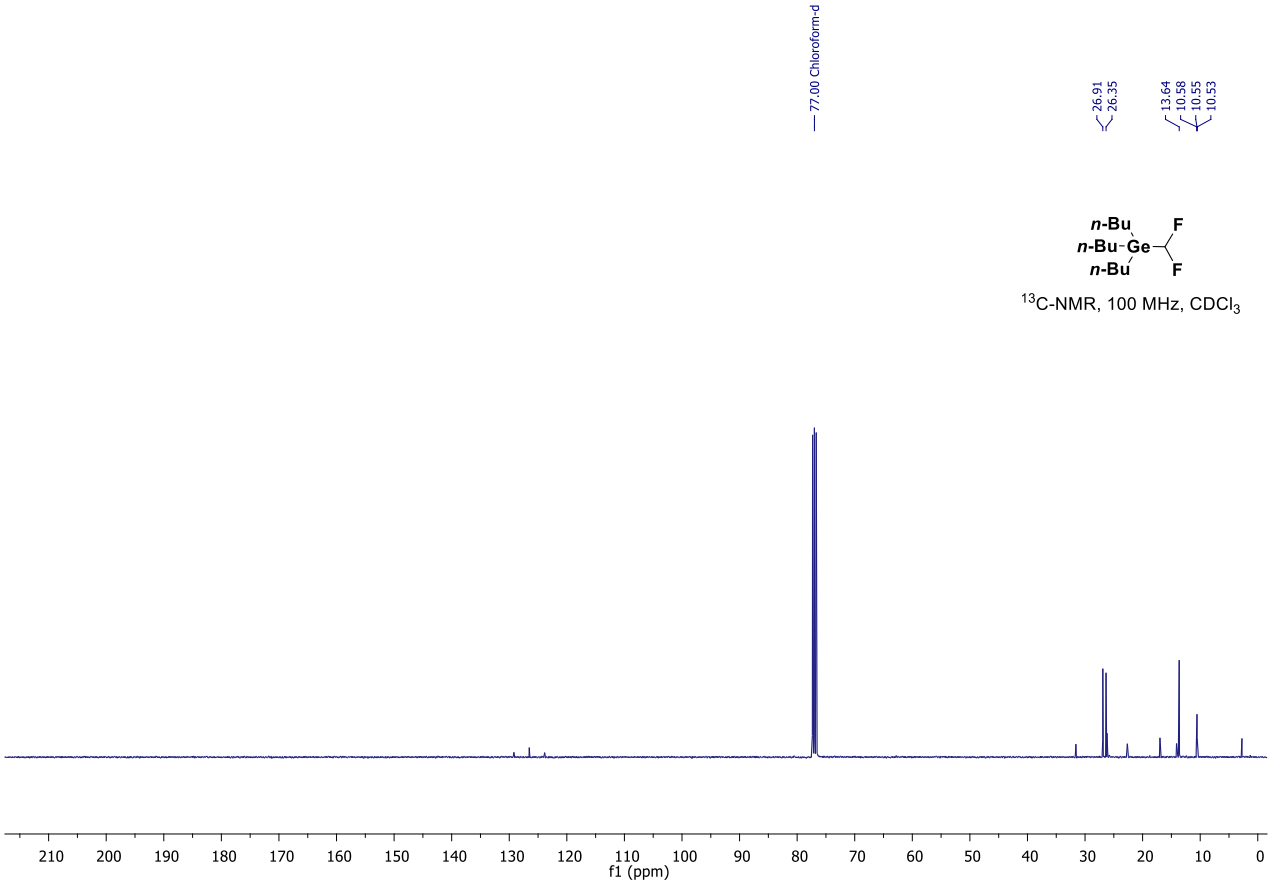
Compound 6



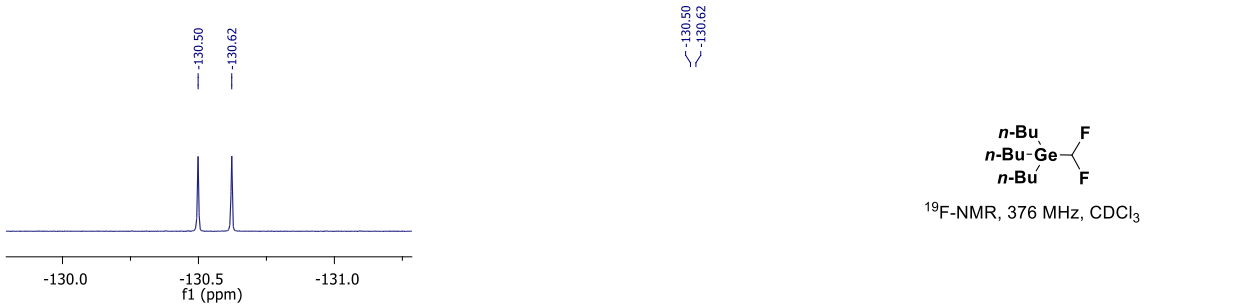
^{1}H-NMR, 400 MHz,$CDCl_3$



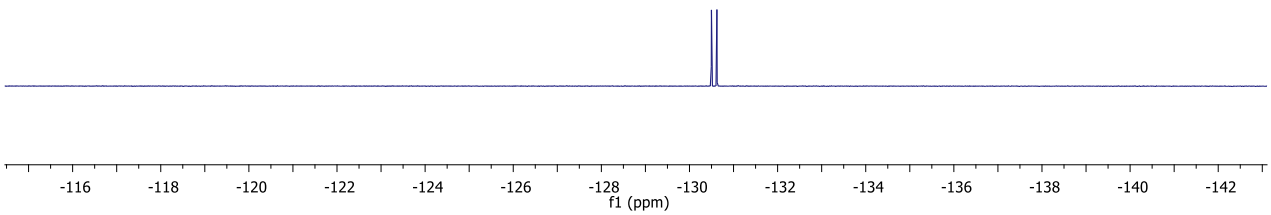




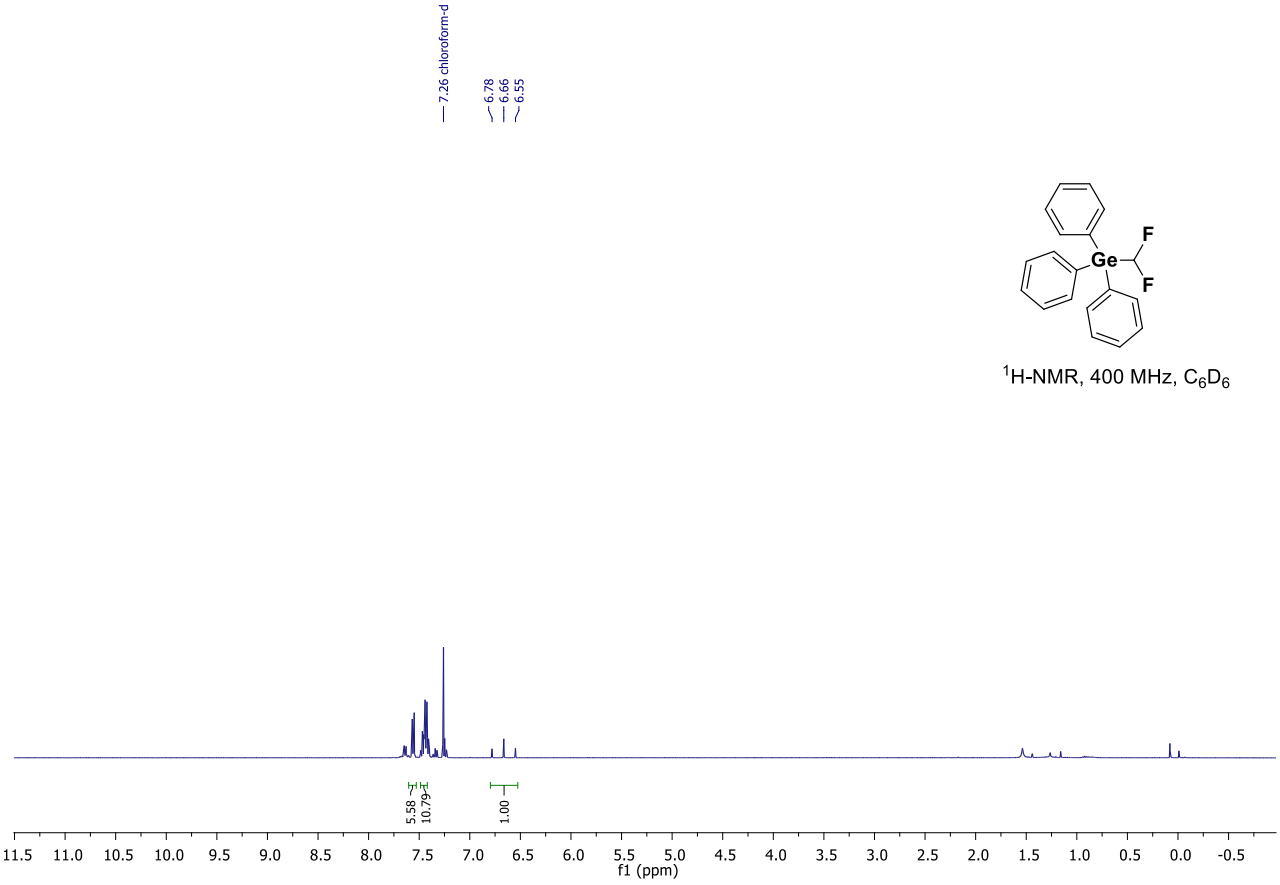
^{13}C-NMR, 100 MHz, $CDCl_3$



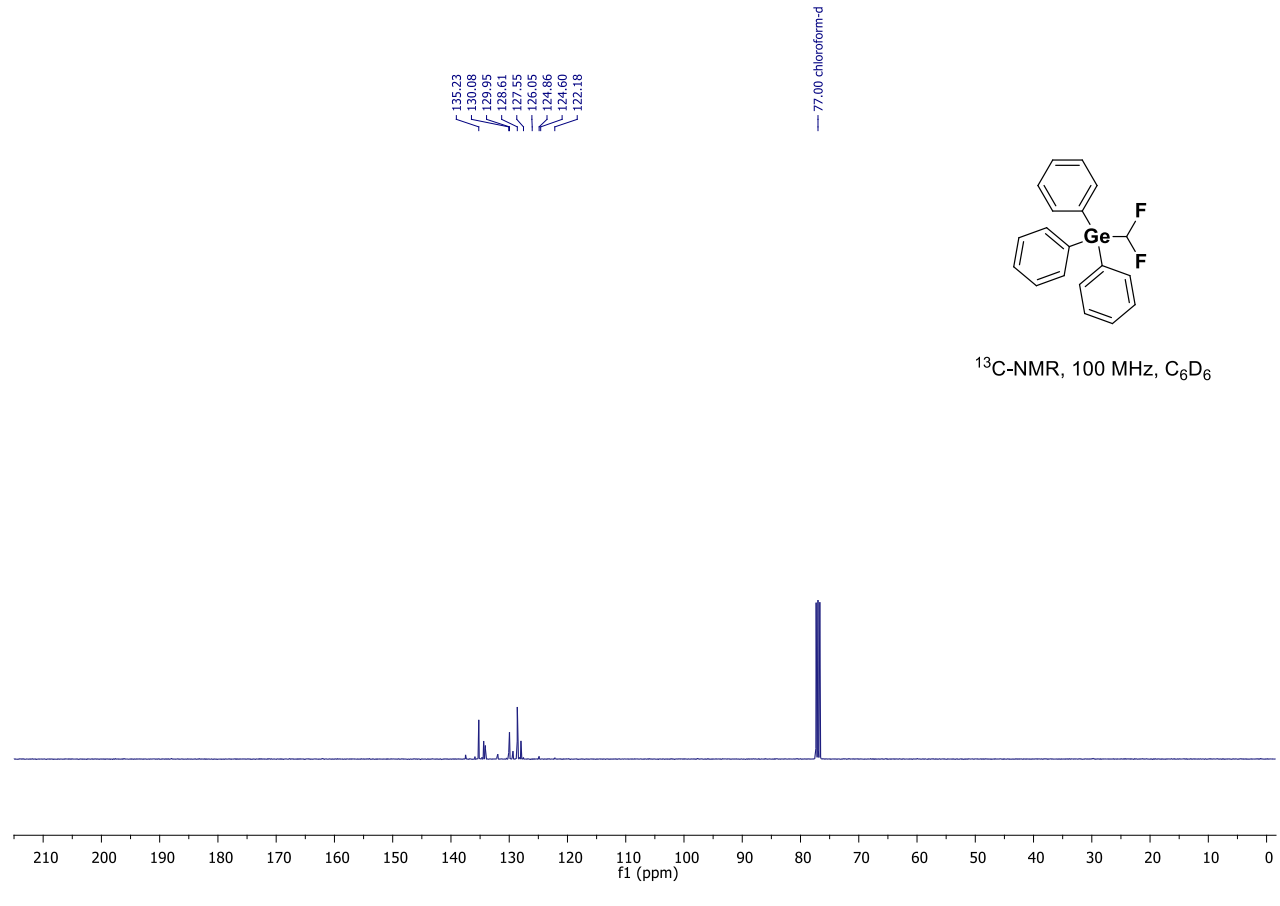
^{19}F-NMR, 376 MHz, $CDCl_3$



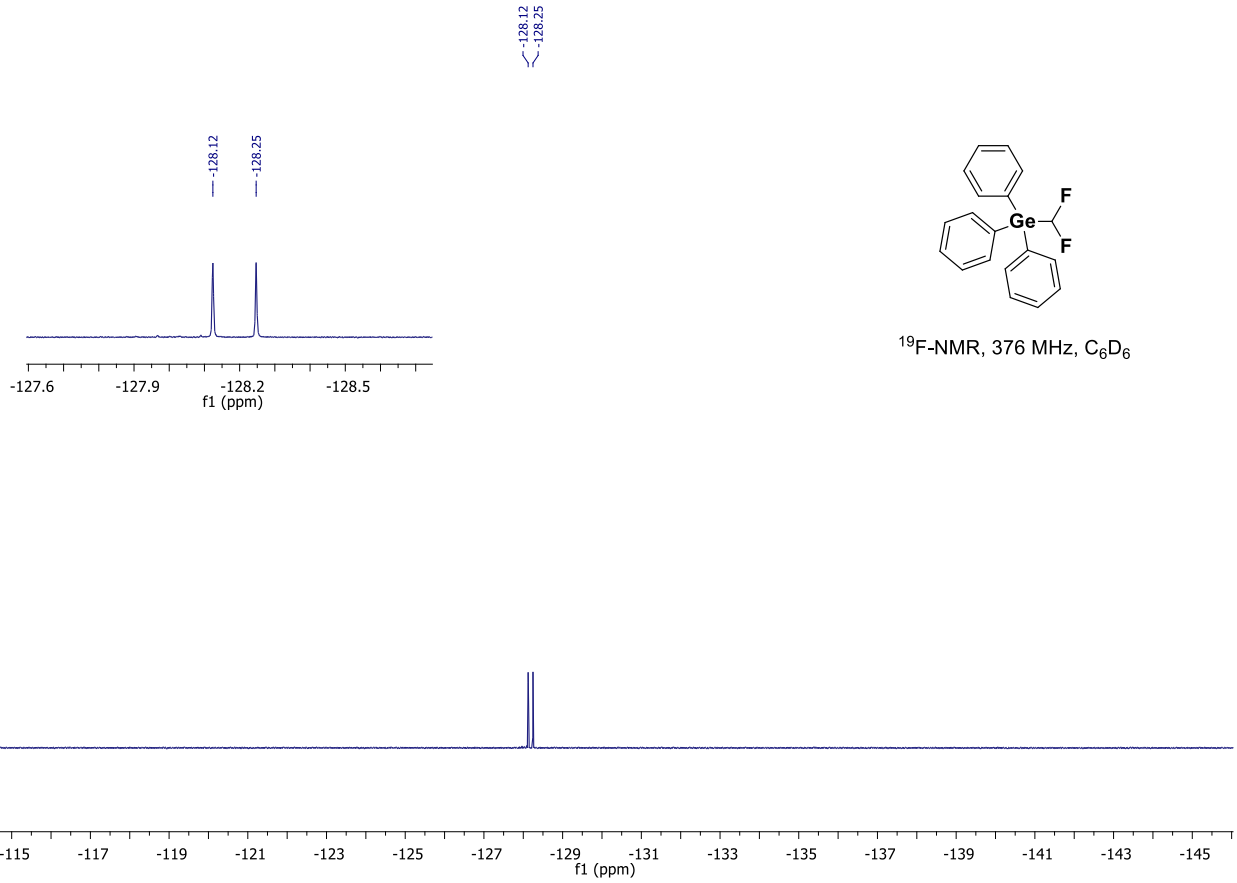
Compound 7



^{1}H-NMR, 400 MHz, C_6D_6

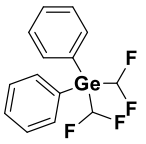


^{13}C-NMR, 100 MHz, C_6D_6

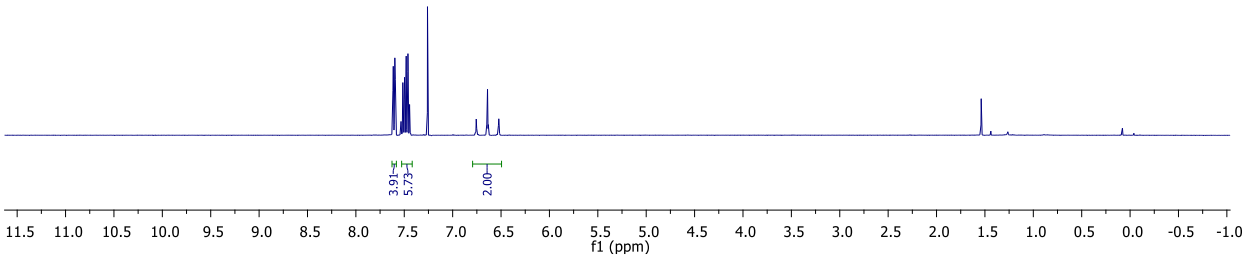


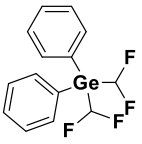
^{19}F-NMR, 376 MHz, C_6D_6

Compound 8

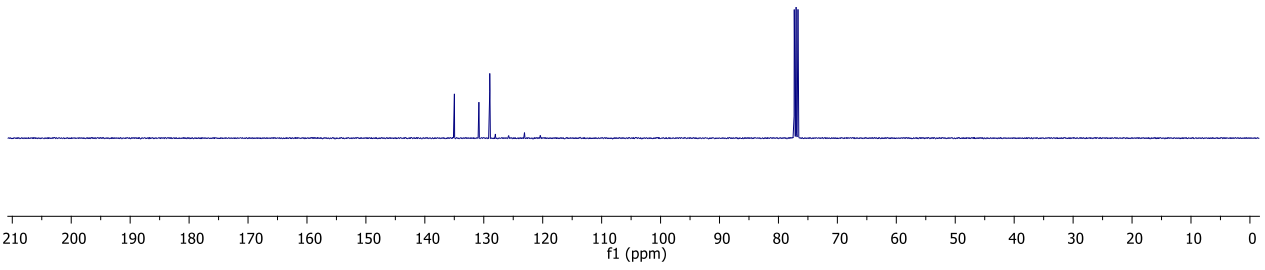


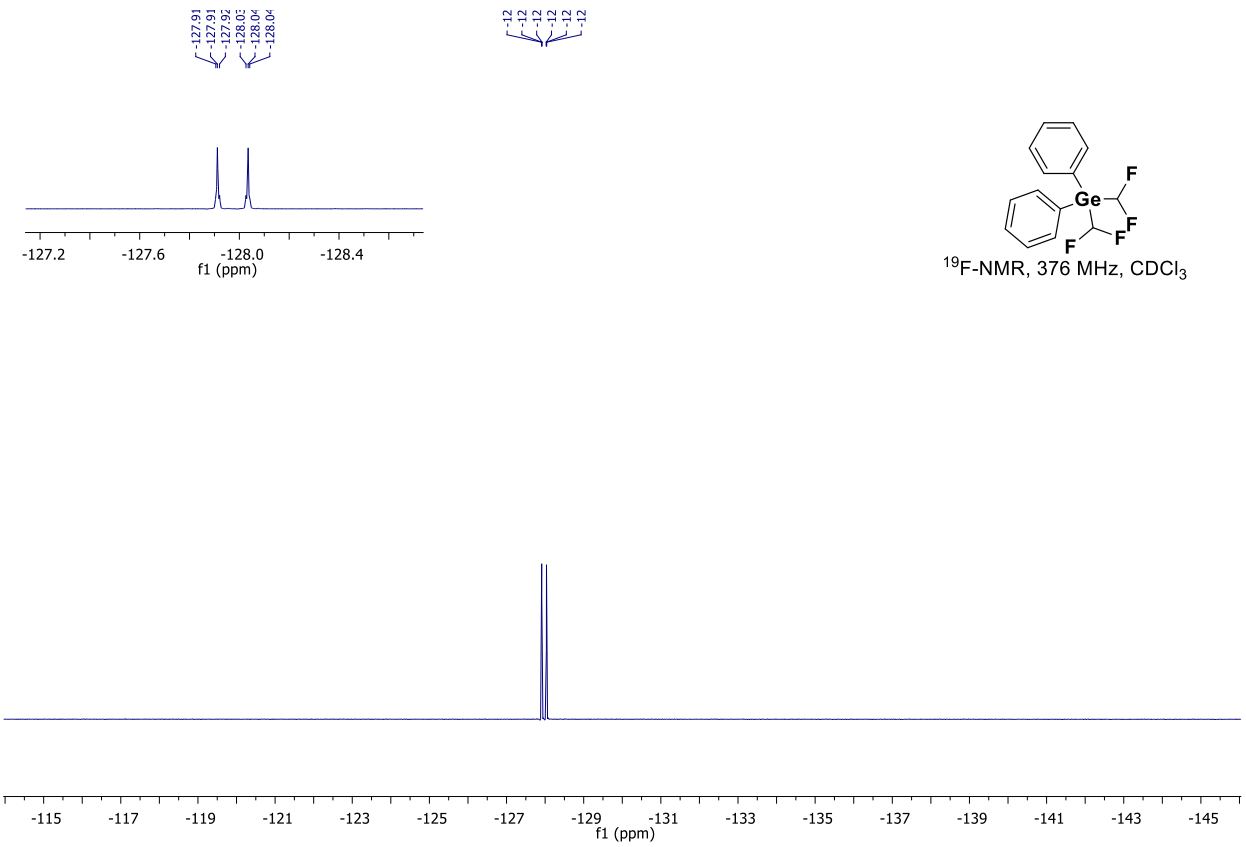
^{1}H-NMR, 400 MHz, $CDCl_3$





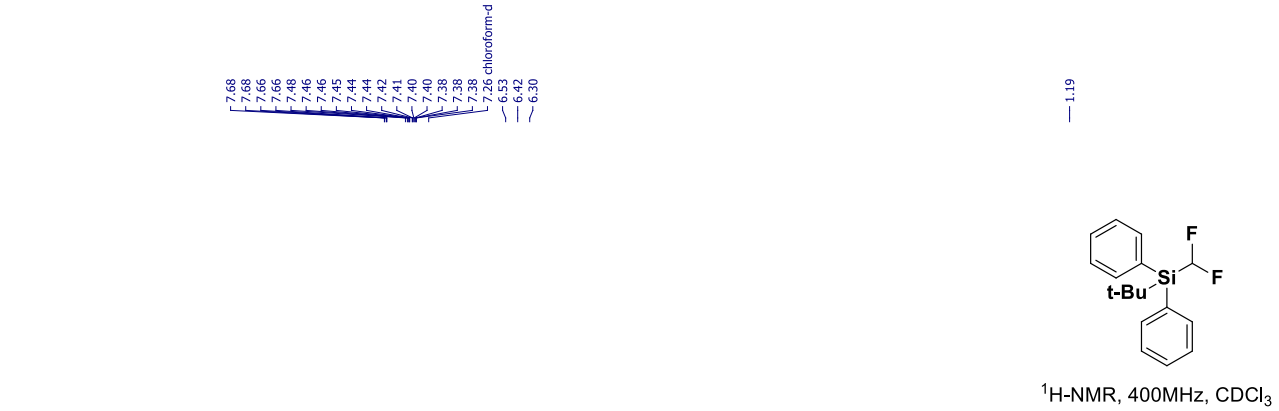
^{13}C-NMR, 100 MHz, $CDCl_3$



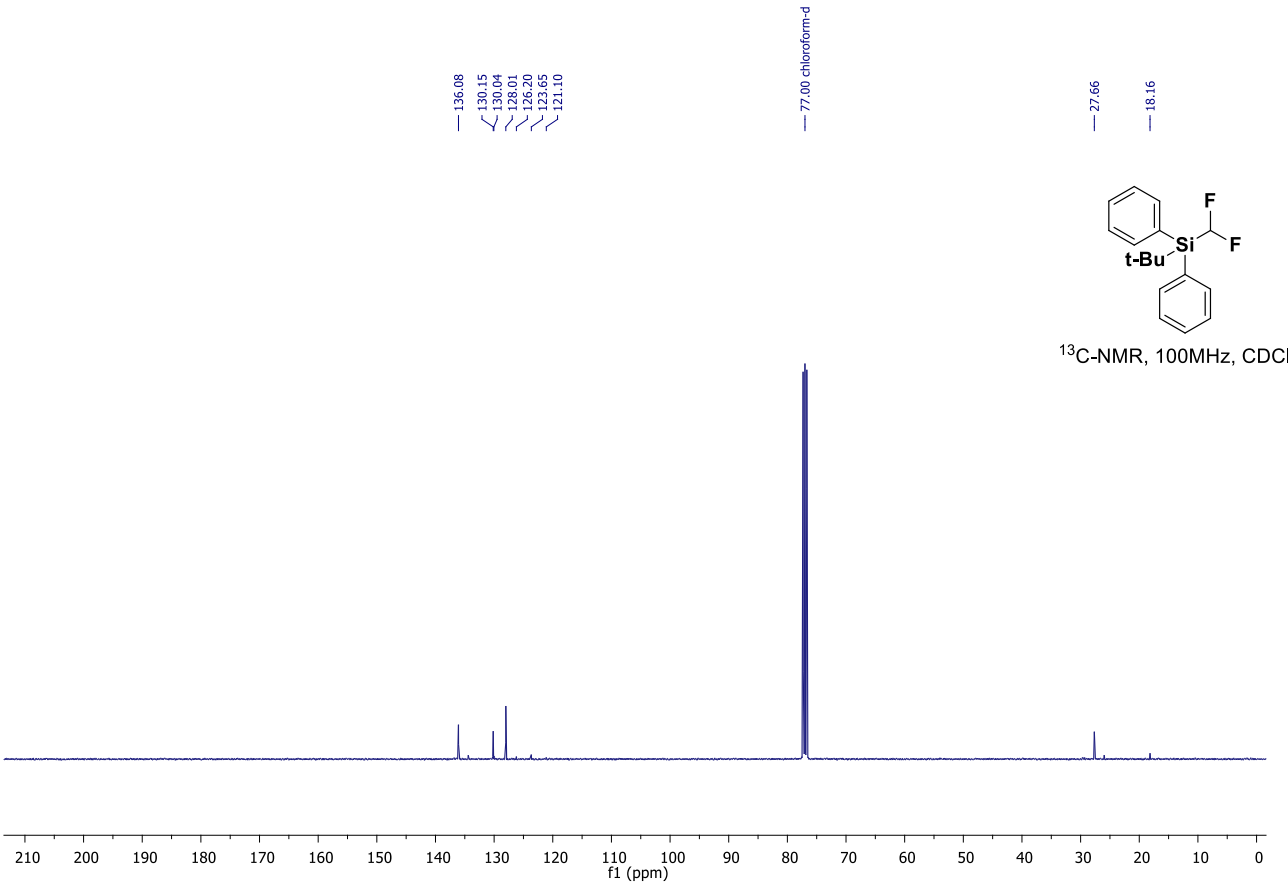


^{19}F-NMR, 376 MHz, $CDCl_3$

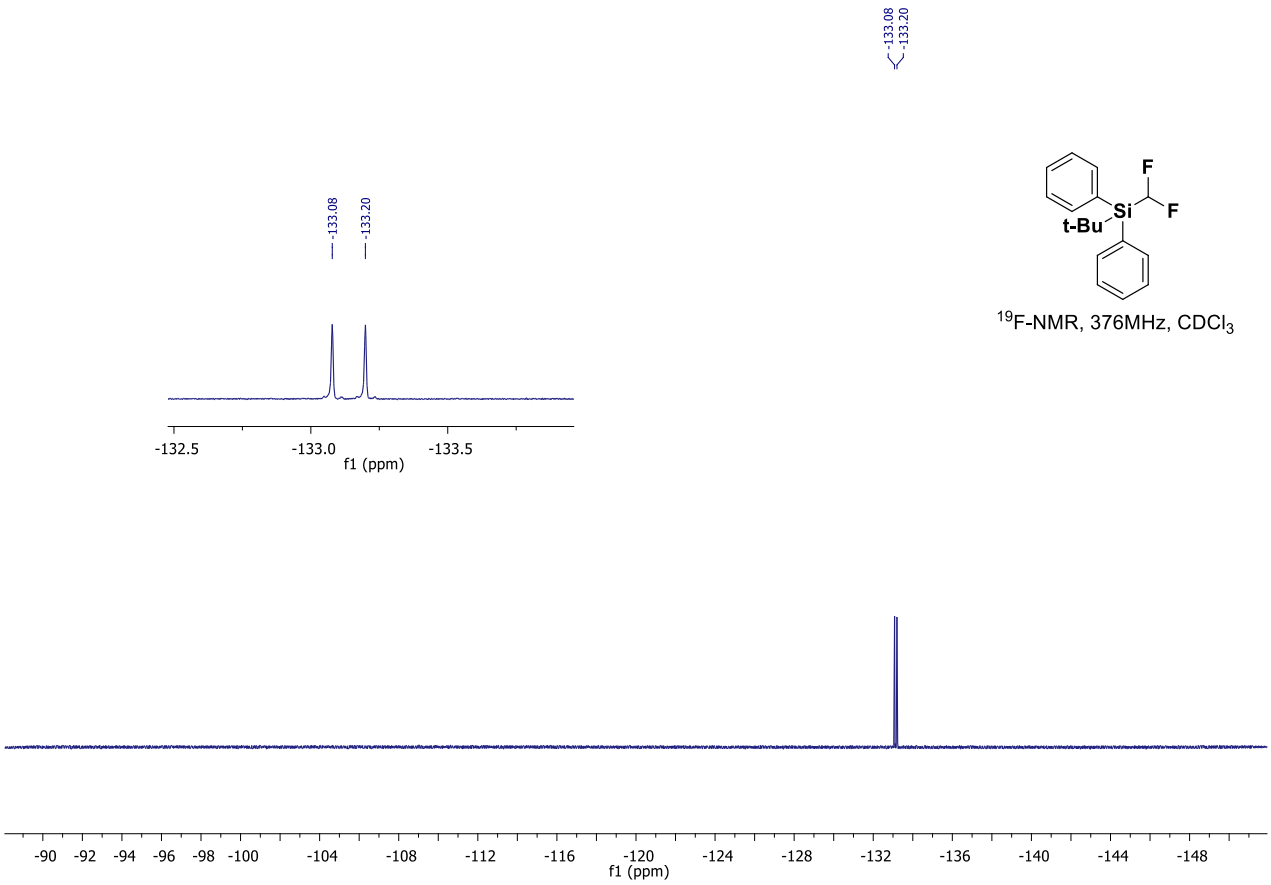
Compound 9



^{1}H-NMR, 400MHz, $CDCl_3$

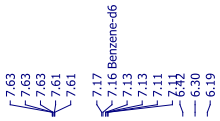


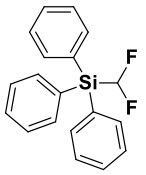
^{13}C-NMR, 100MHz, $CDCl_3$



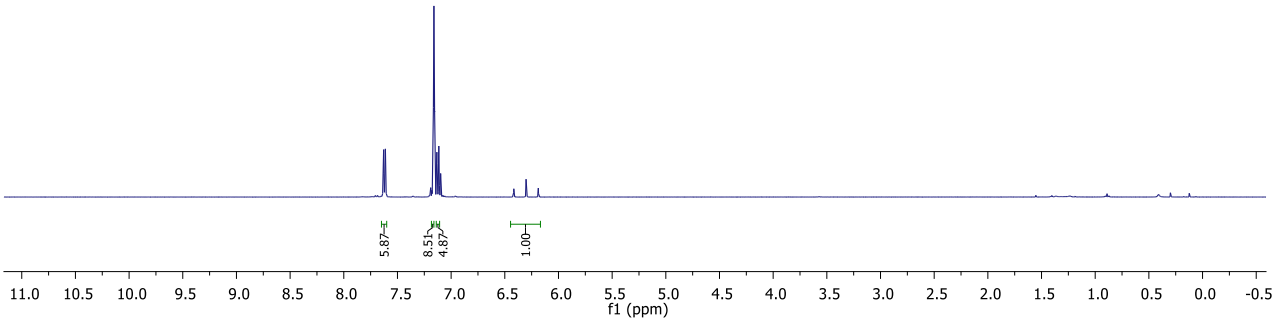
^{19}F-NMR, 376MHz, $CDCl_3$

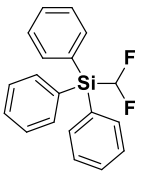
Compound 10



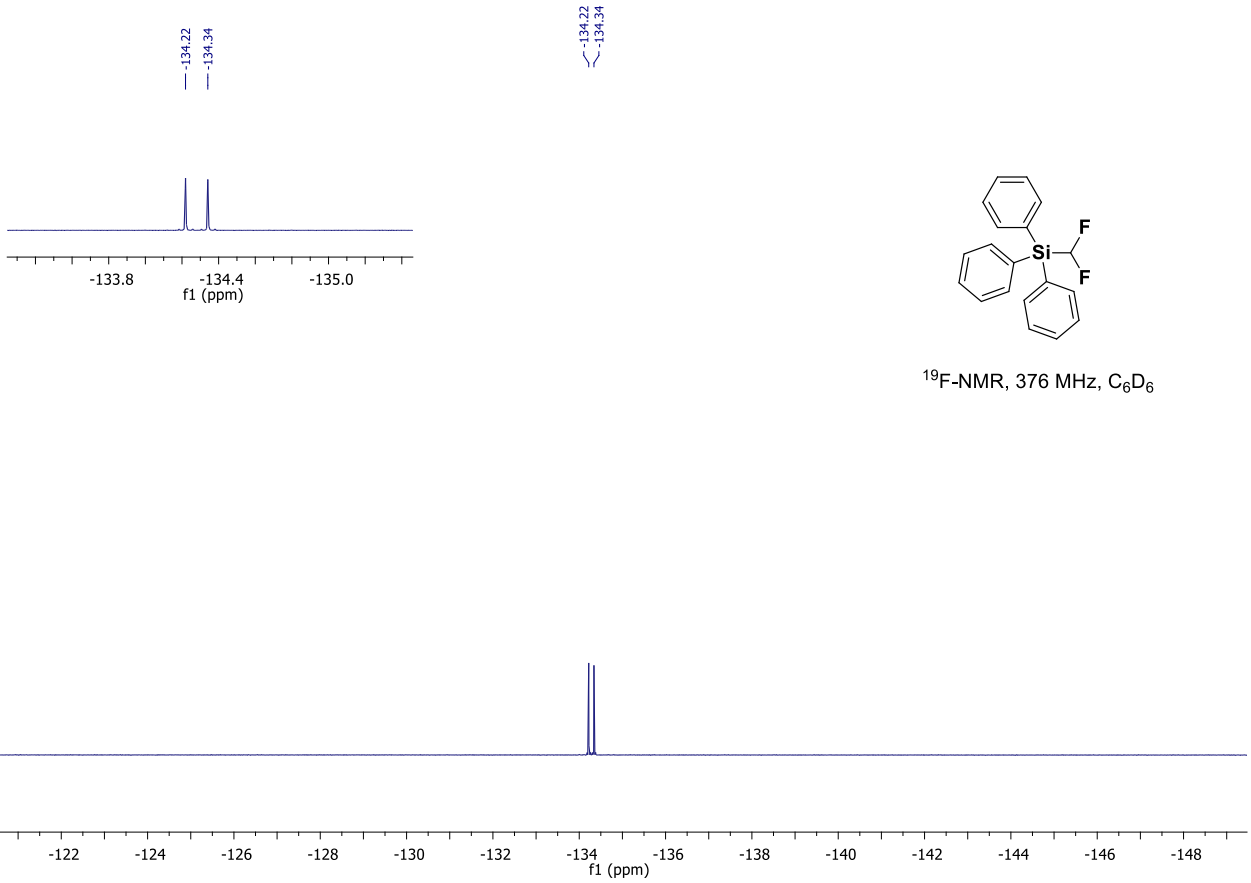


^{1}H-NMR, 400 MHz, C_6D_6



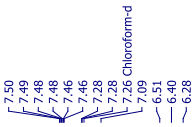


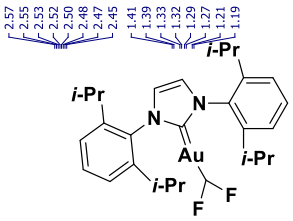
^{13}C-NMR, 100 MHz, C_6D_6



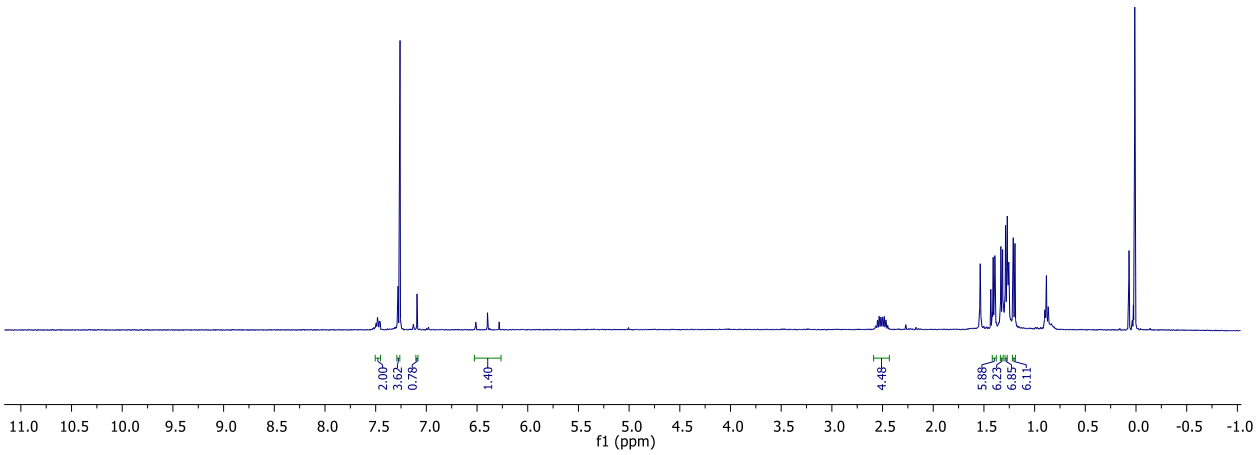
^{19}F-NMR, 376 MHz, C_6D_6

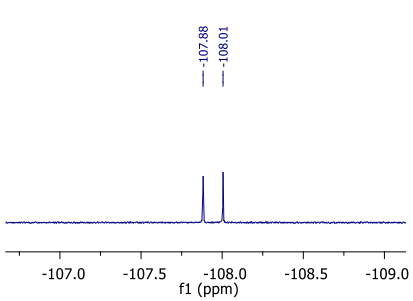
Compound 11

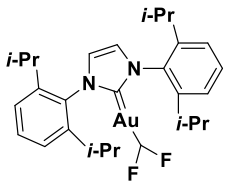




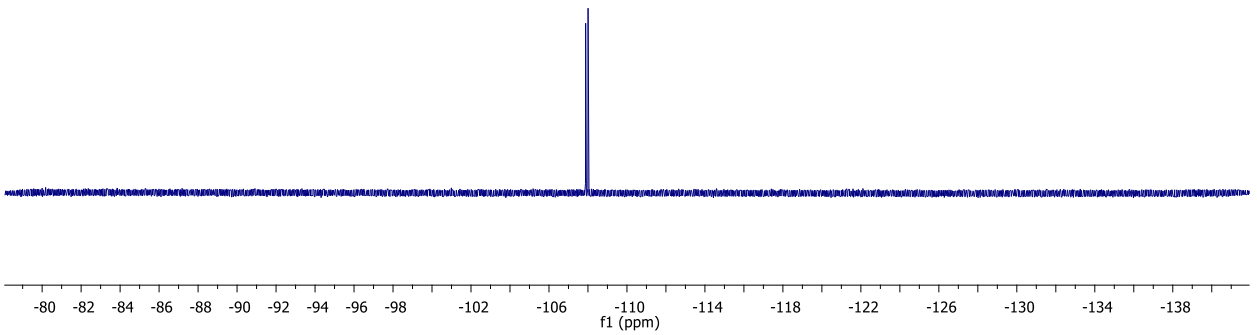
^{1}H-NMR, 400 MHz, $CDCl_3$



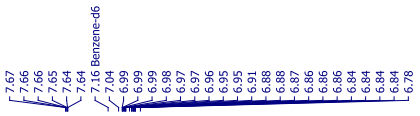


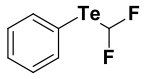


^{19}F-NMR, 376 MHz, $CDCl_3$

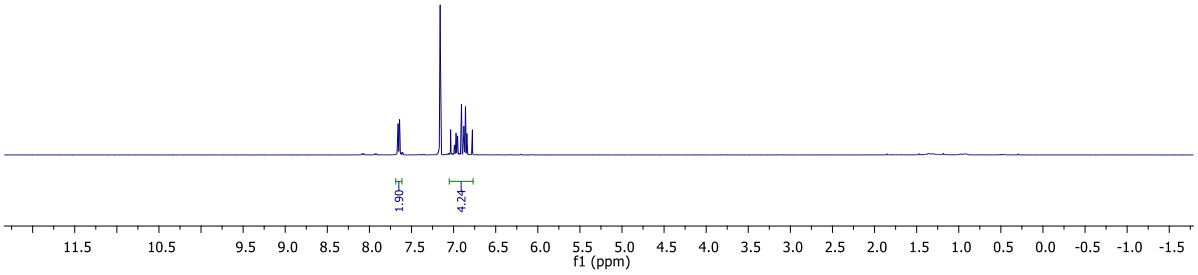


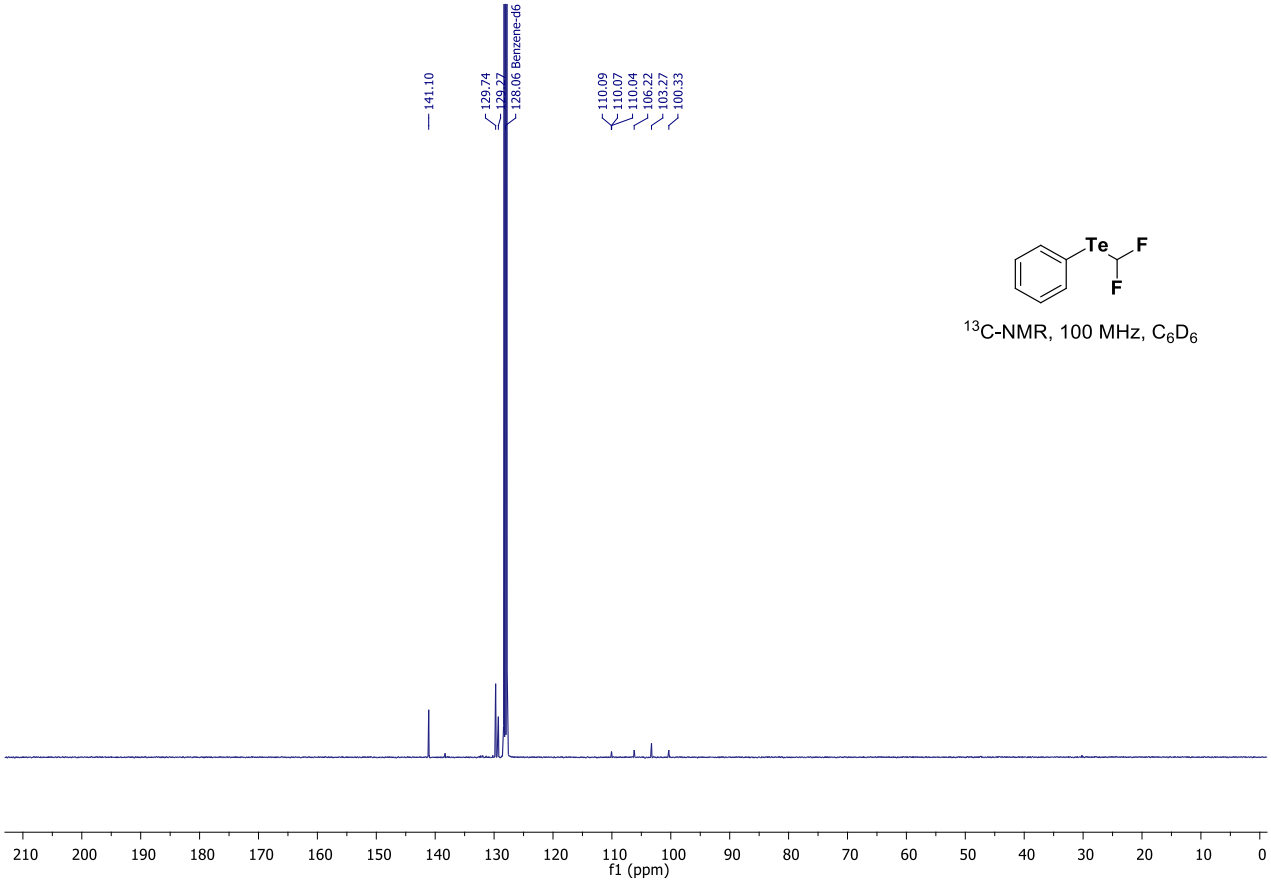
Compound 12



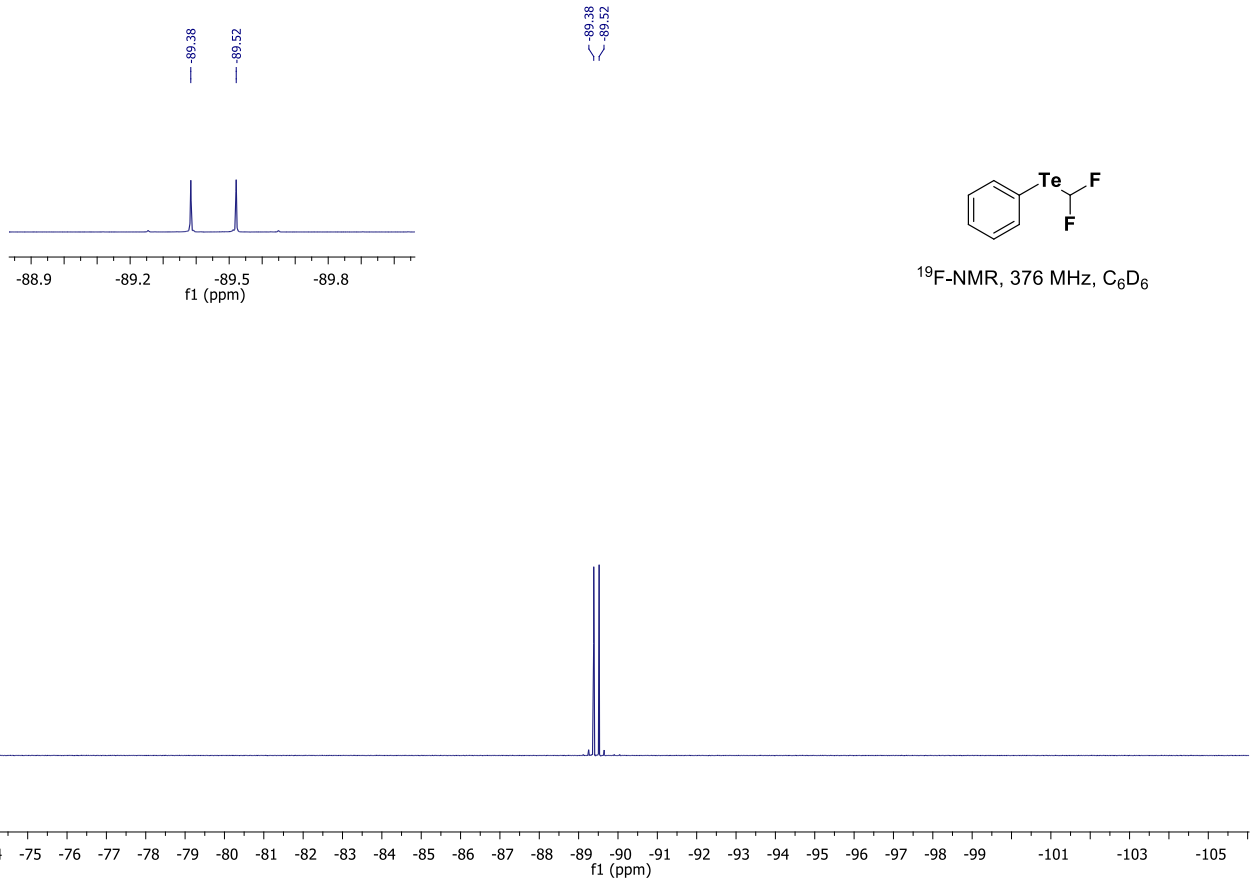


^{1}H-NMR, 400 MHz,C_6D_6



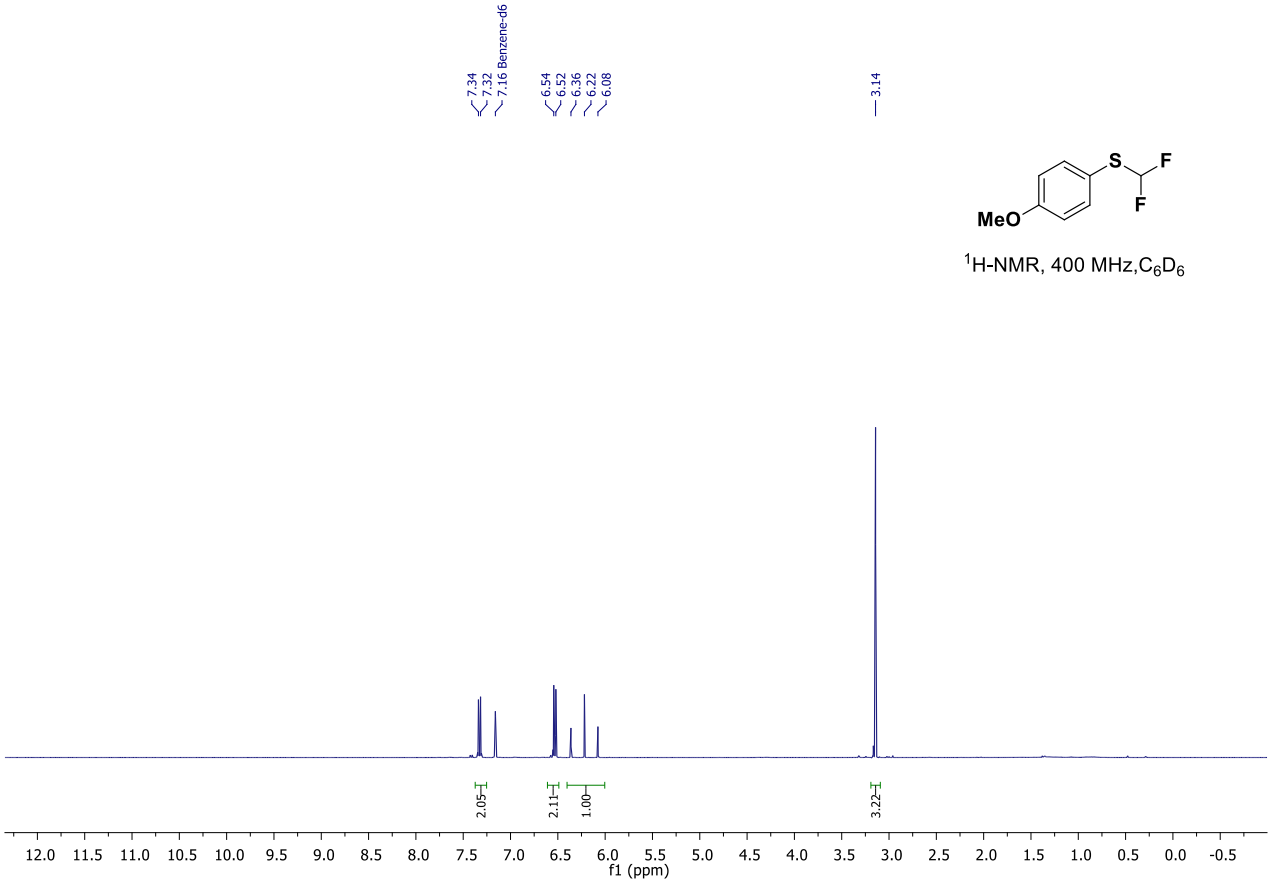


^{13}C-NMR, 100 MHz, C_6D_6

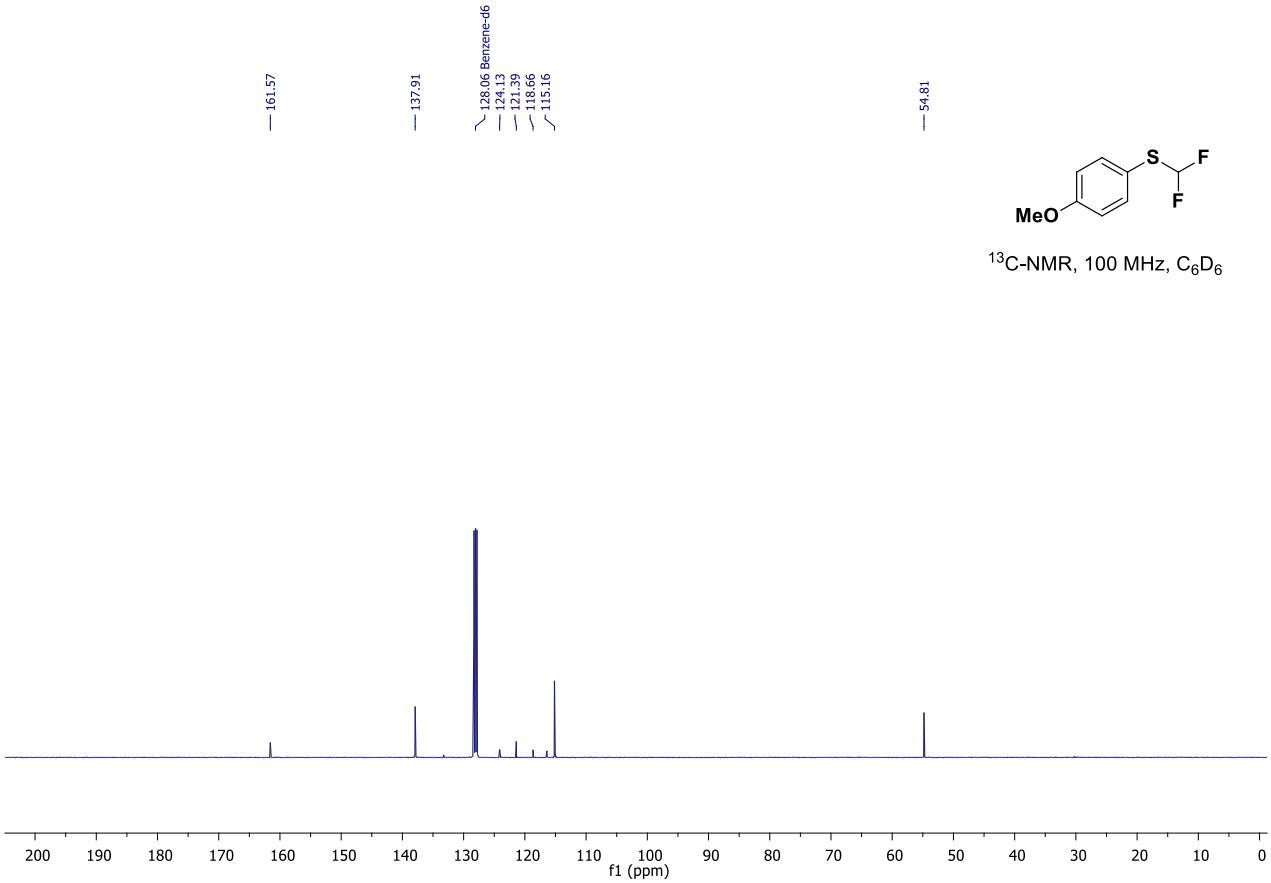


^{19}F-NMR, 376 MHz, C_6D_6

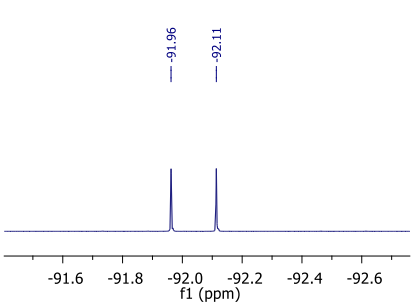
Compound 13

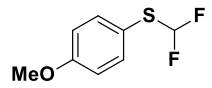


^{1}H-NMR, 400 MHz,C_6D_6



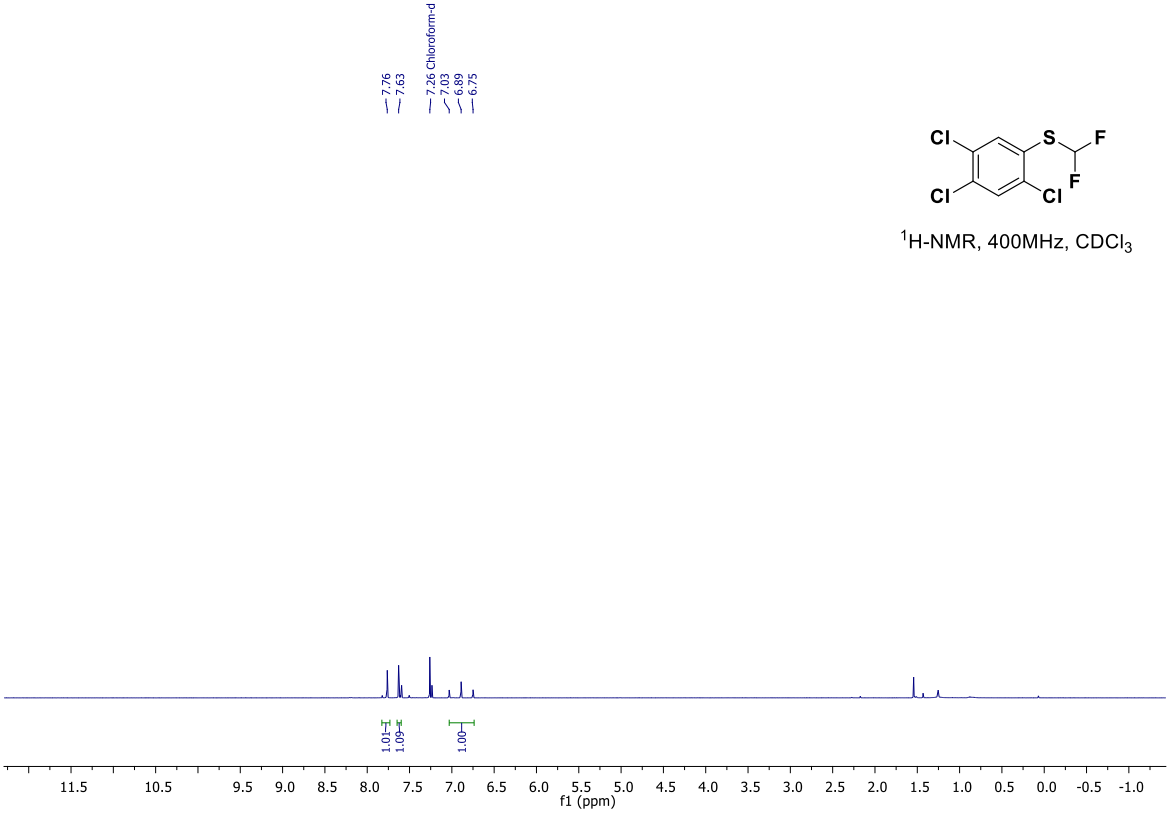
^{13}C-NMR, 100 MHz, C_6D_6



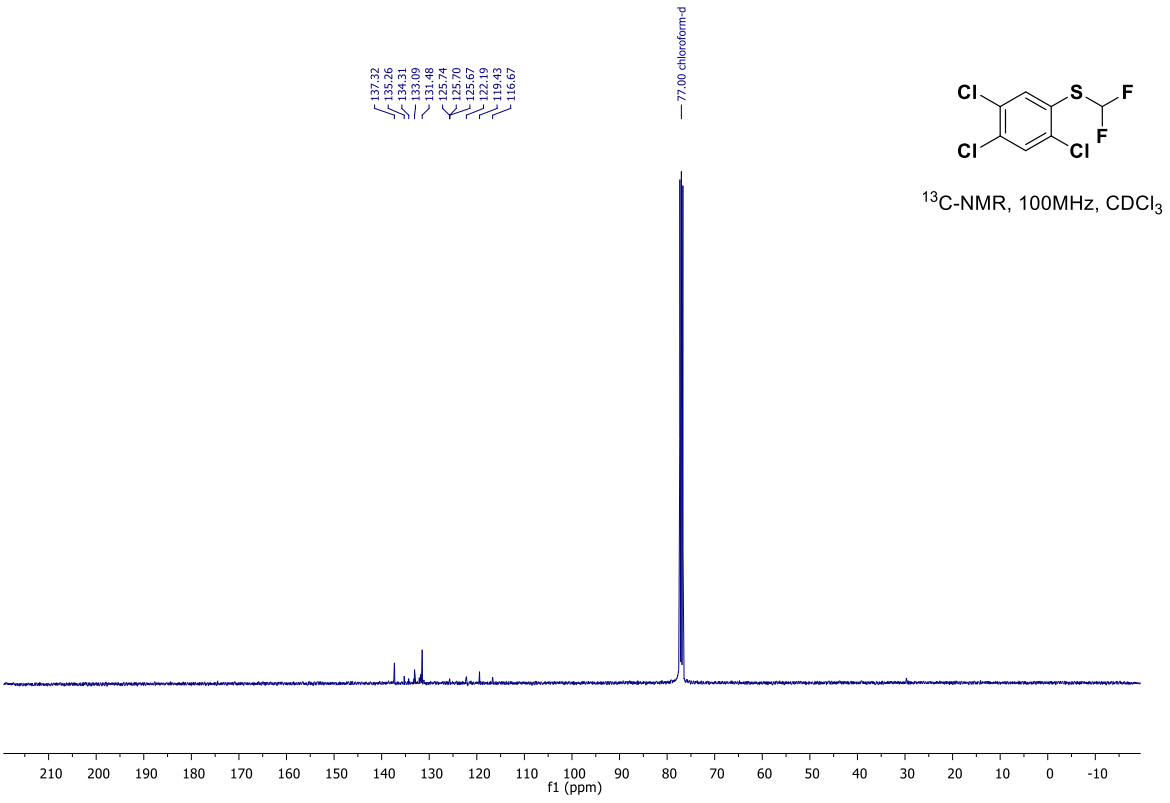


^{19}F-NMR, 376 MHz, C_6D_6

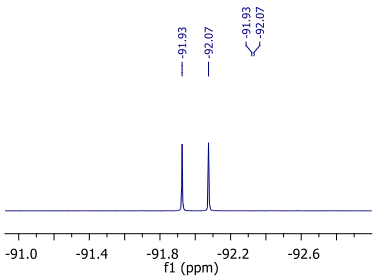
Compound 14

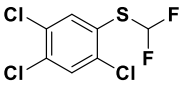


^{1}H-NMR, 400MHz, $CDCl_3$

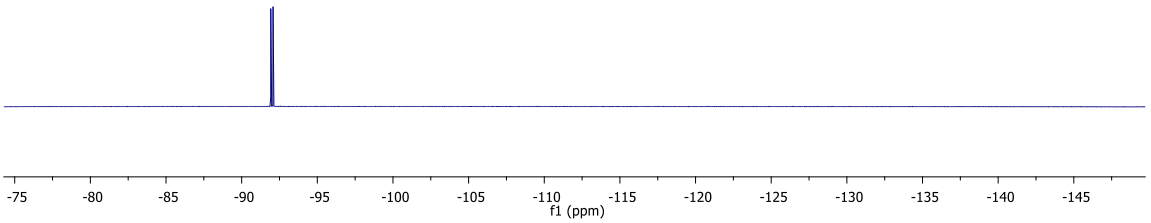


^{13}C-NMR, 100MHz, $CDCl_3$

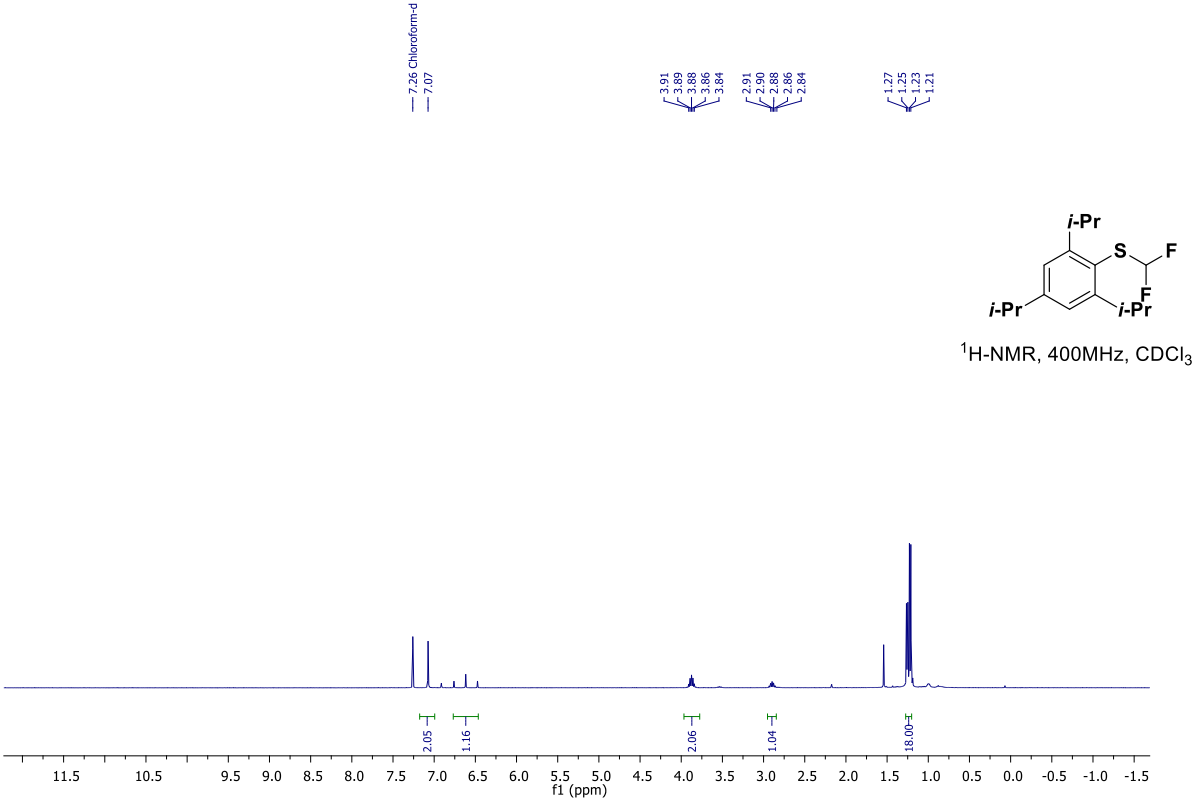




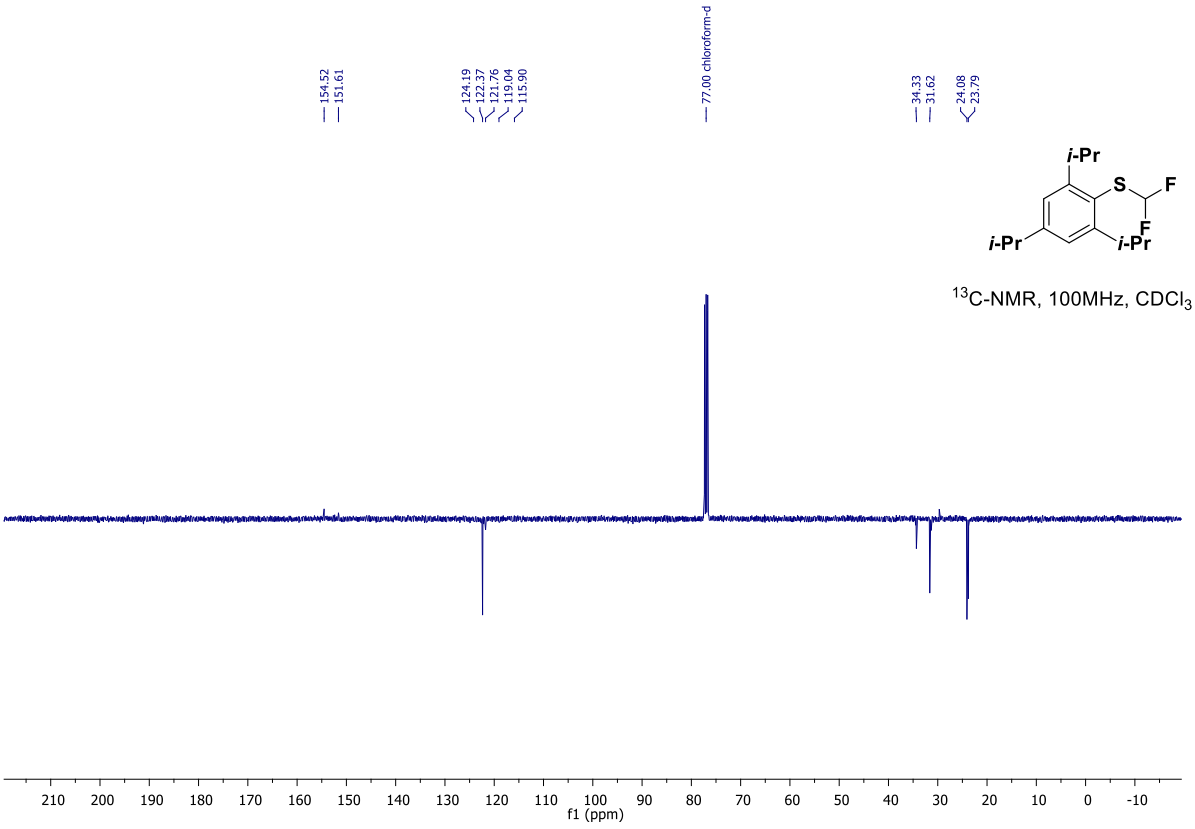
^{19}F-NMR, 376MHz, $CDCl_3$



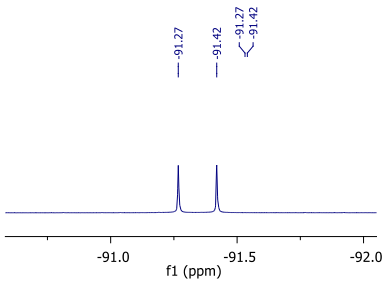
Compound 15

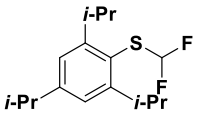


^{1}H-NMR, 400MHz, $CDCl_3$

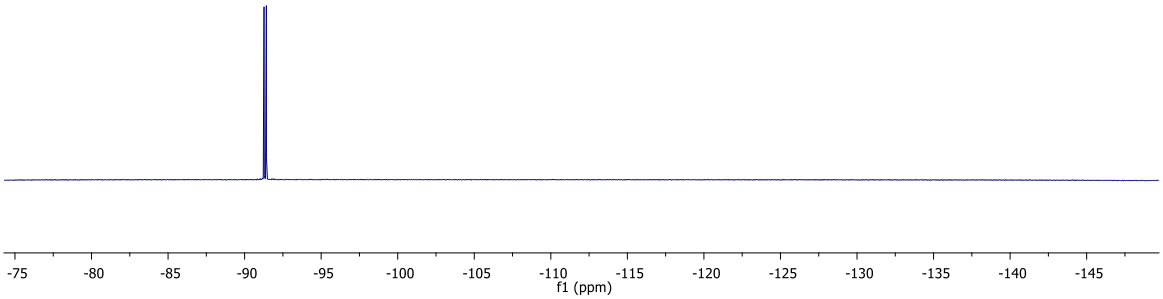


^{13}C-NMR, 100MHz, $CDCl_3$

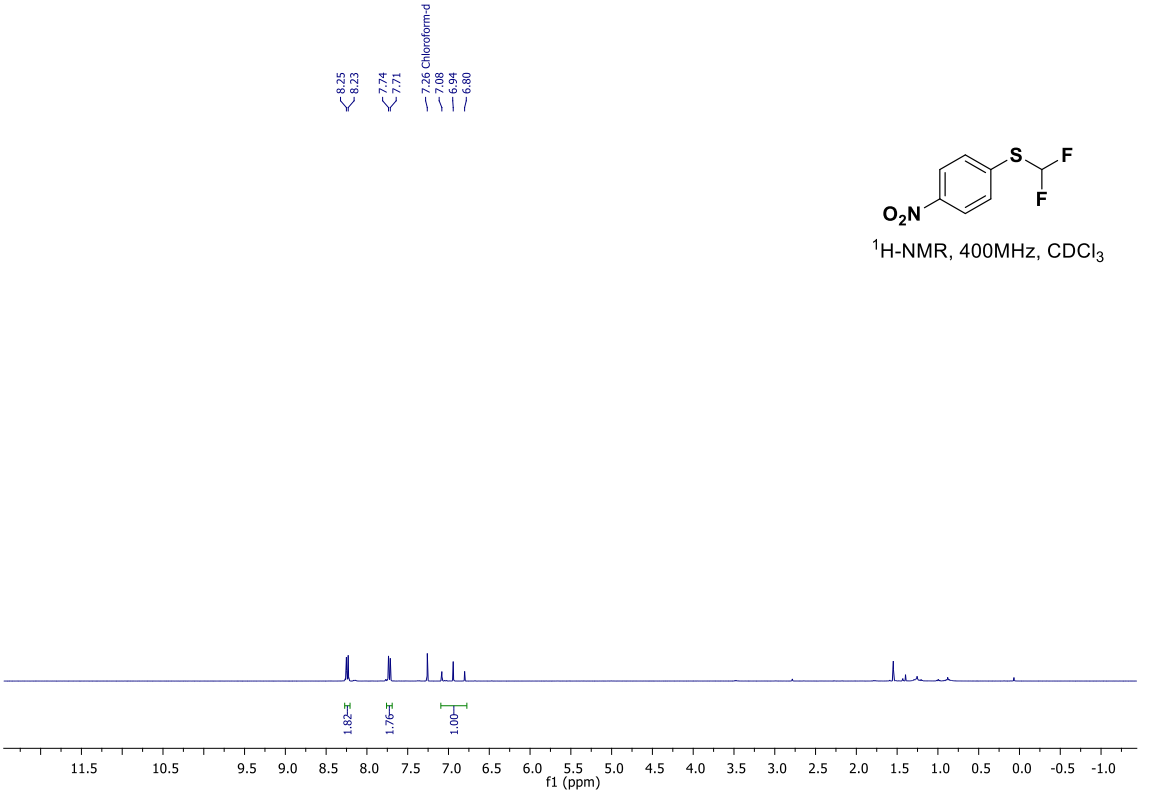




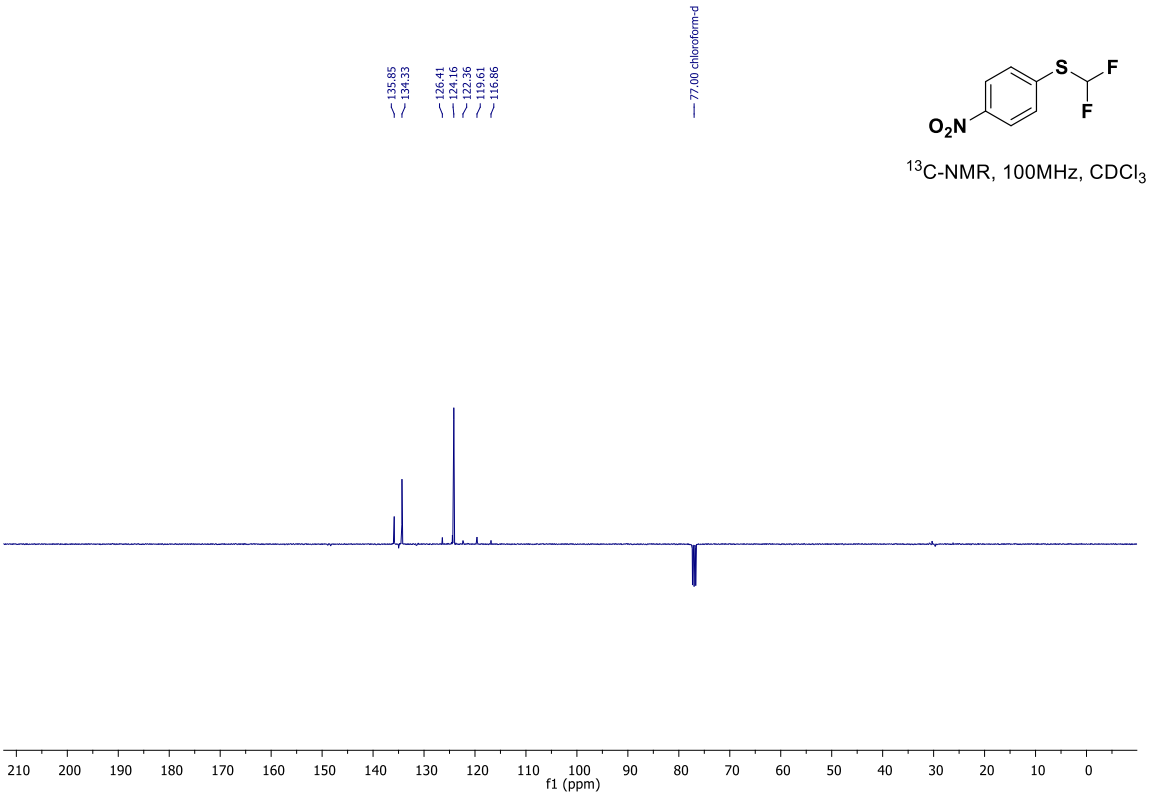
^{19}F-NMR, 376MHz, $CDCl_3$



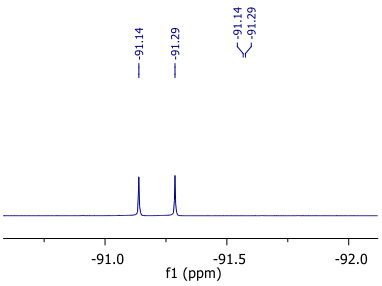
Compound 16

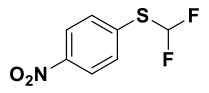


^{1}H-NMR, 400MHz, $CDCl_3$

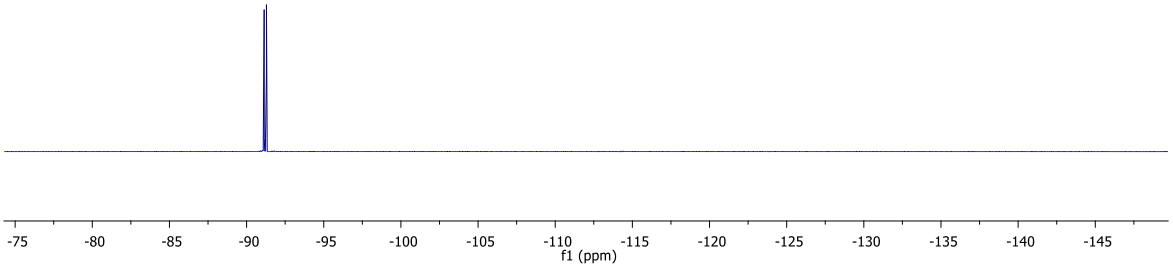


^{13}C-NMR, 100MHz, $CDCl_3$

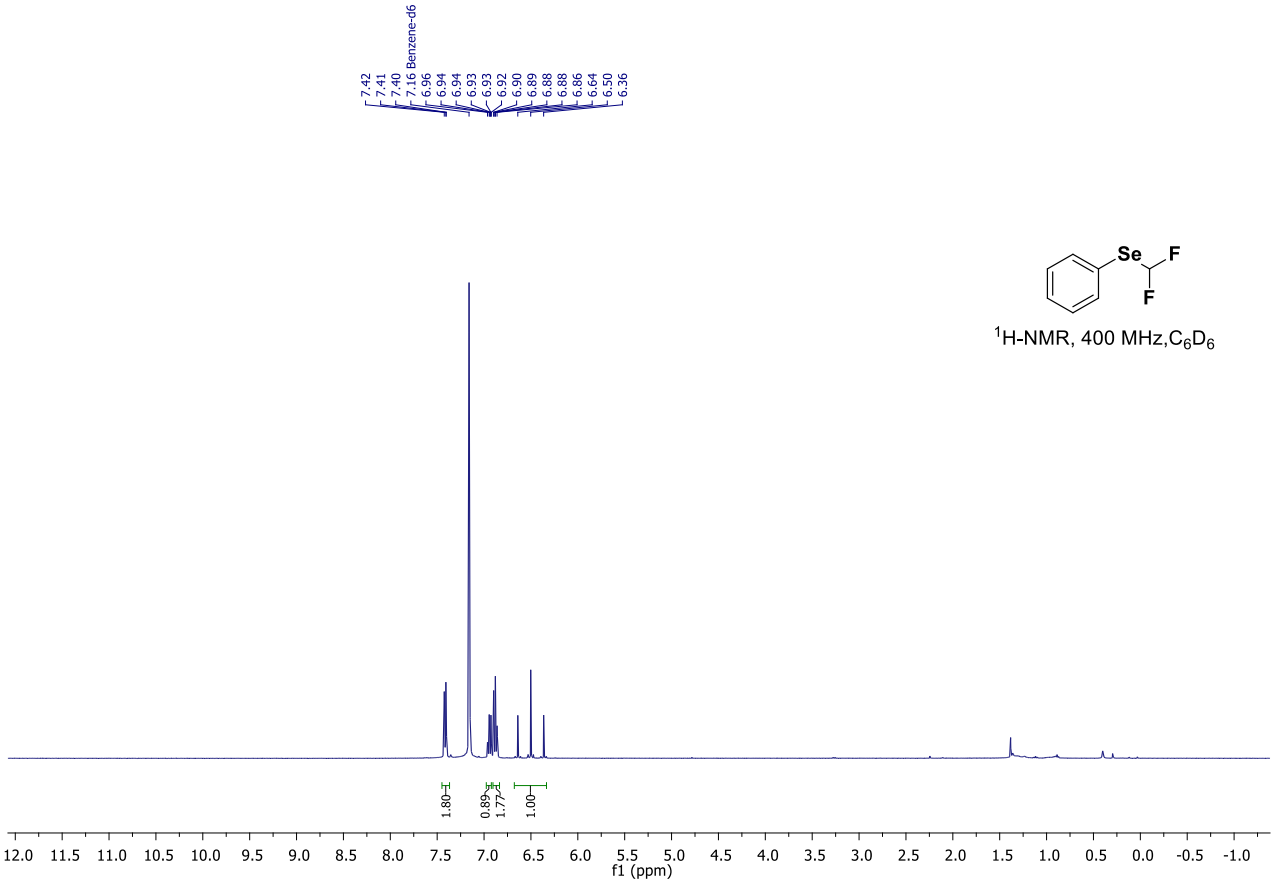


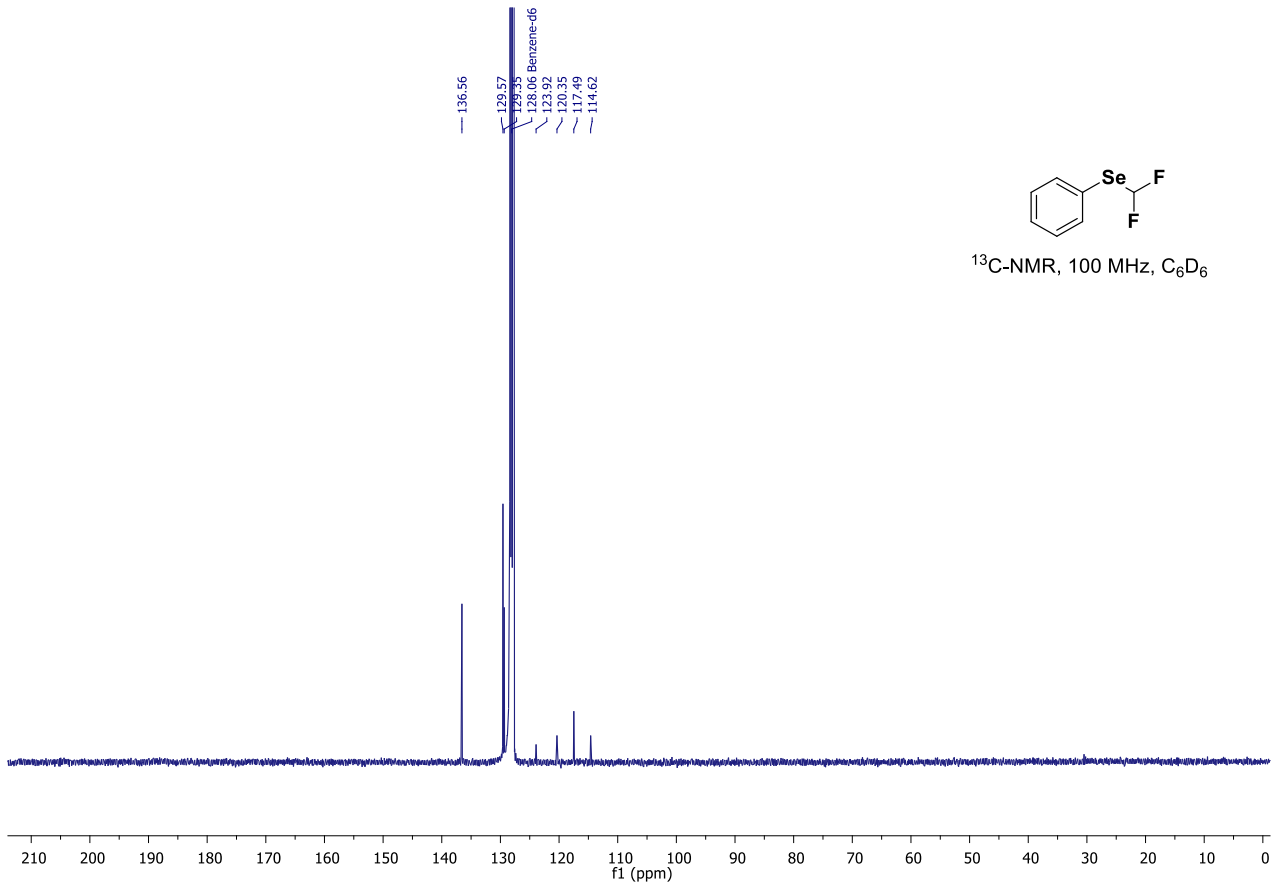


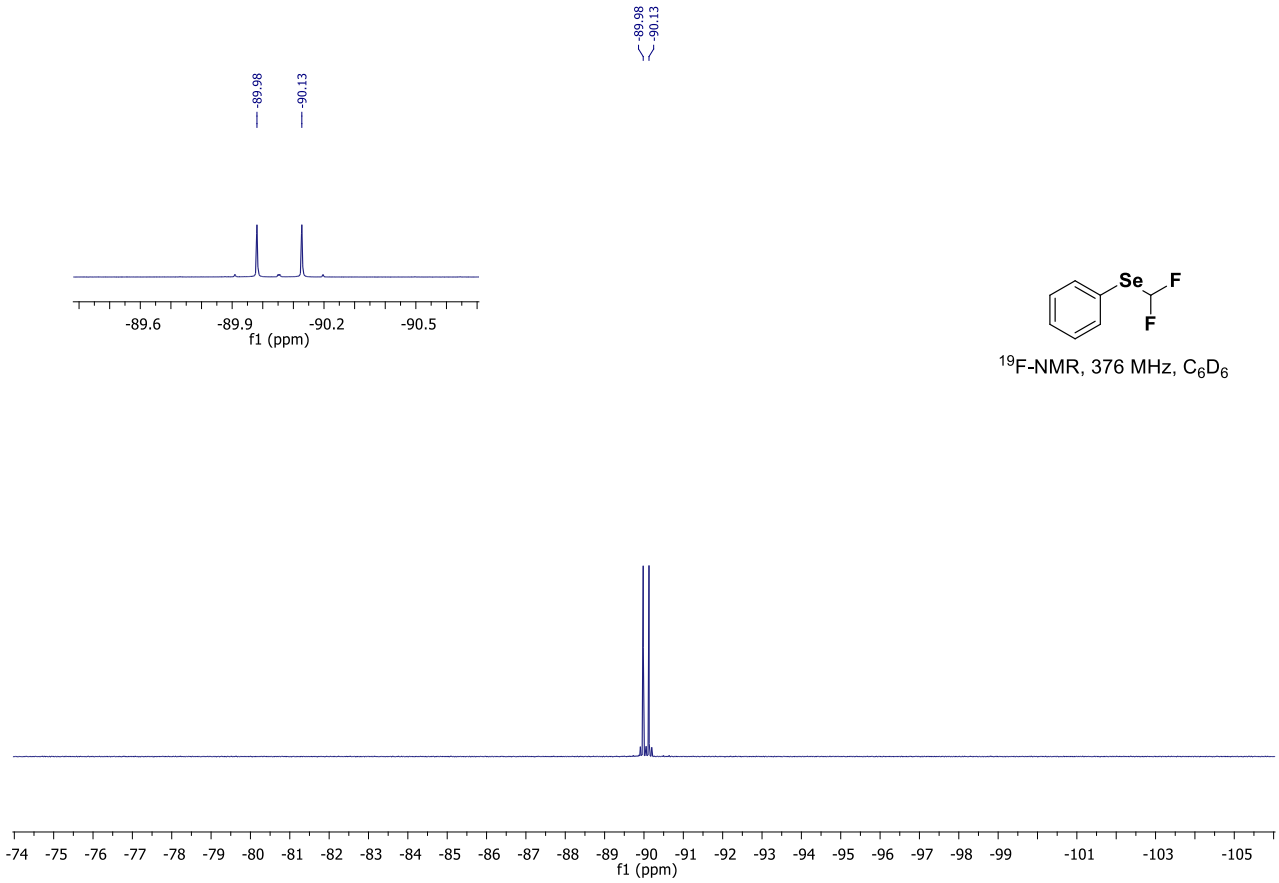
^{19}F-NMR, 376MHz, $CDCl_3$



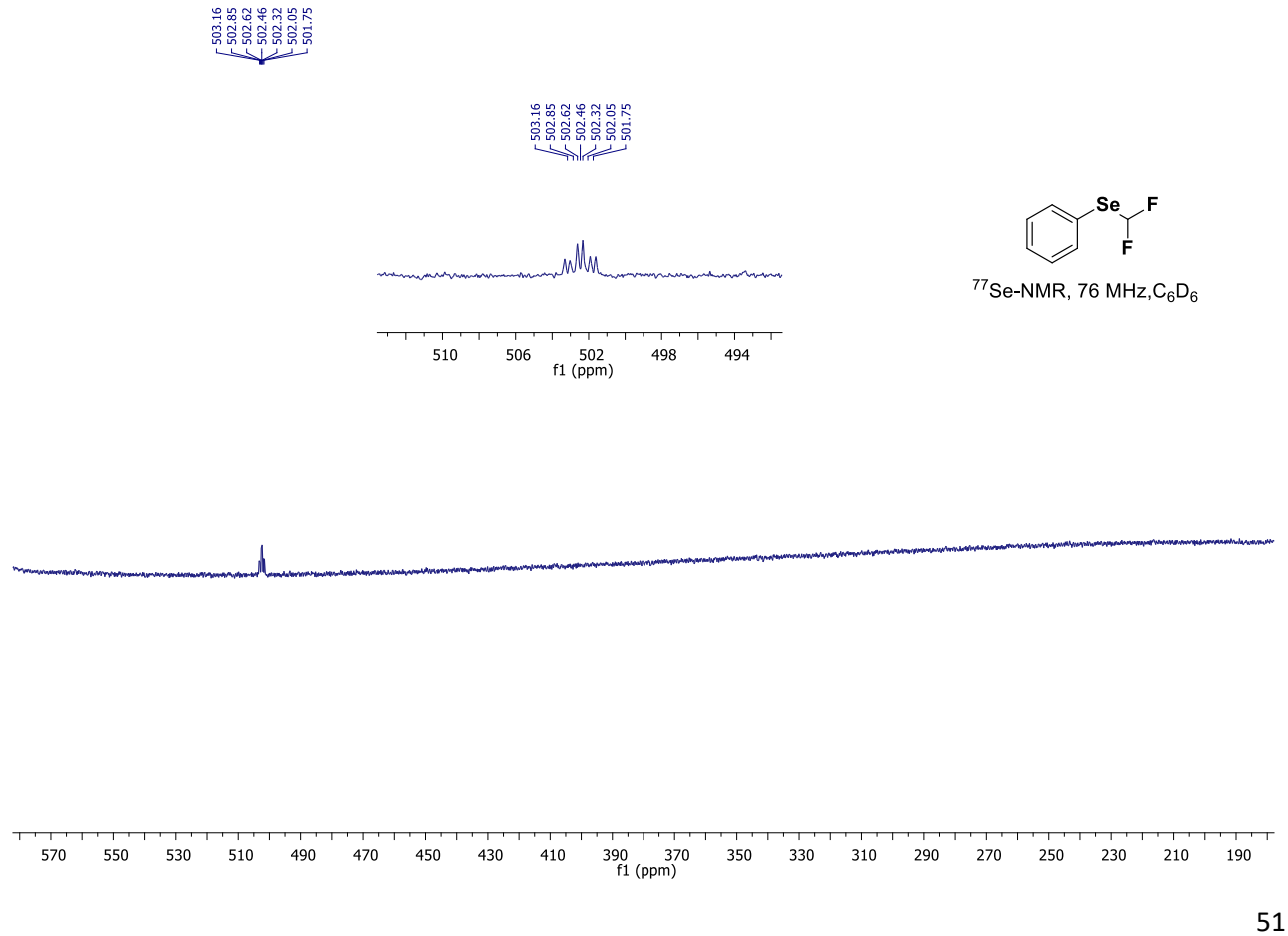
Compound 17


7.42
7.41
7.40
7.16 Benzene-d6
6.96
6.94
6.94
6.93
6.93
6.92
6.90
6.89
6.88
6.88
6.86
6.64
6.50
6.36
Se
F
F
1H-NMR, 400 MHz,C6D6
1.80
0.89
1.77
1.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


136.56
129.57
129.35
128.06 Benzene-d6
123.92
120.35
117.49
114.62
Se
F
F
13C-NMR, 100 MHz, C6D6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

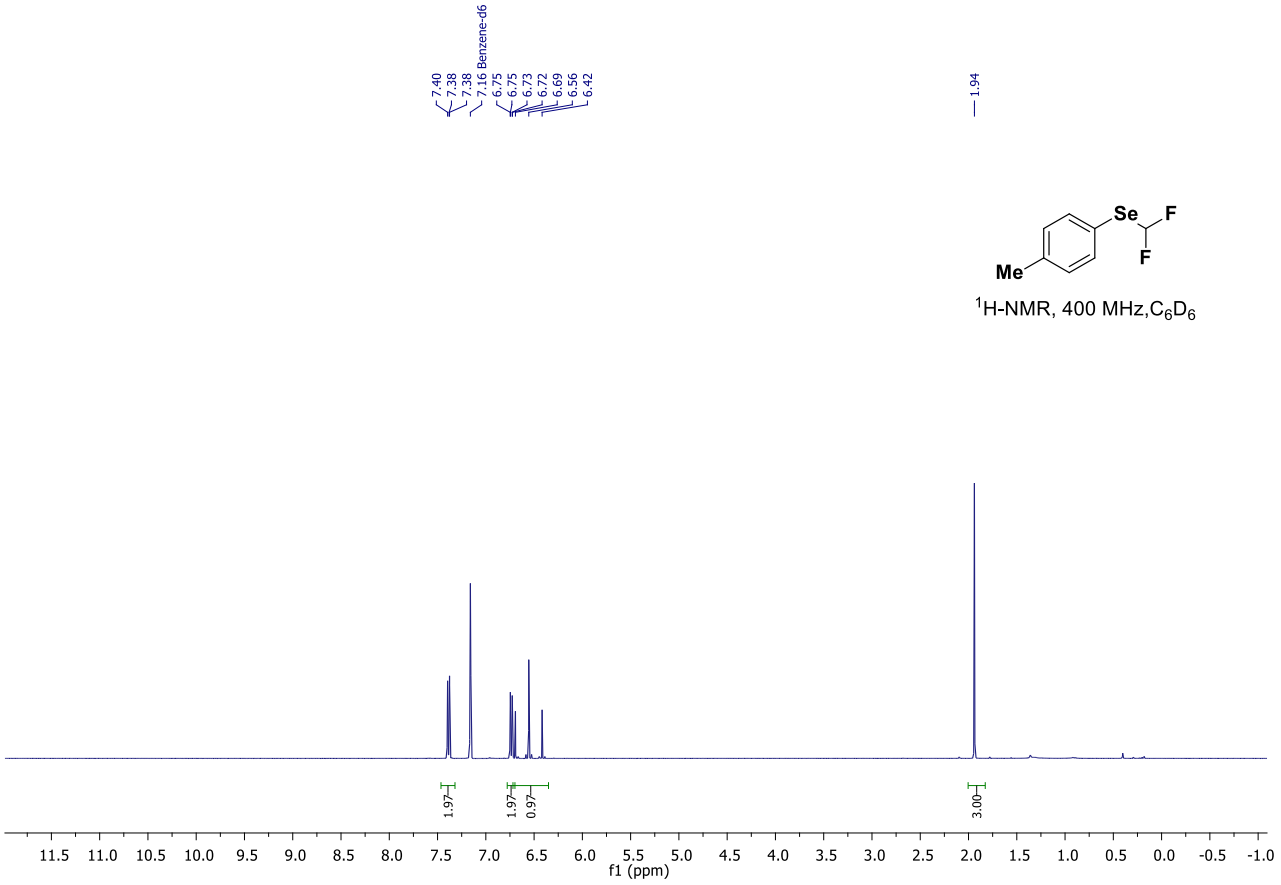


^{19}F-NMR, 376 MHz, C_6D_6

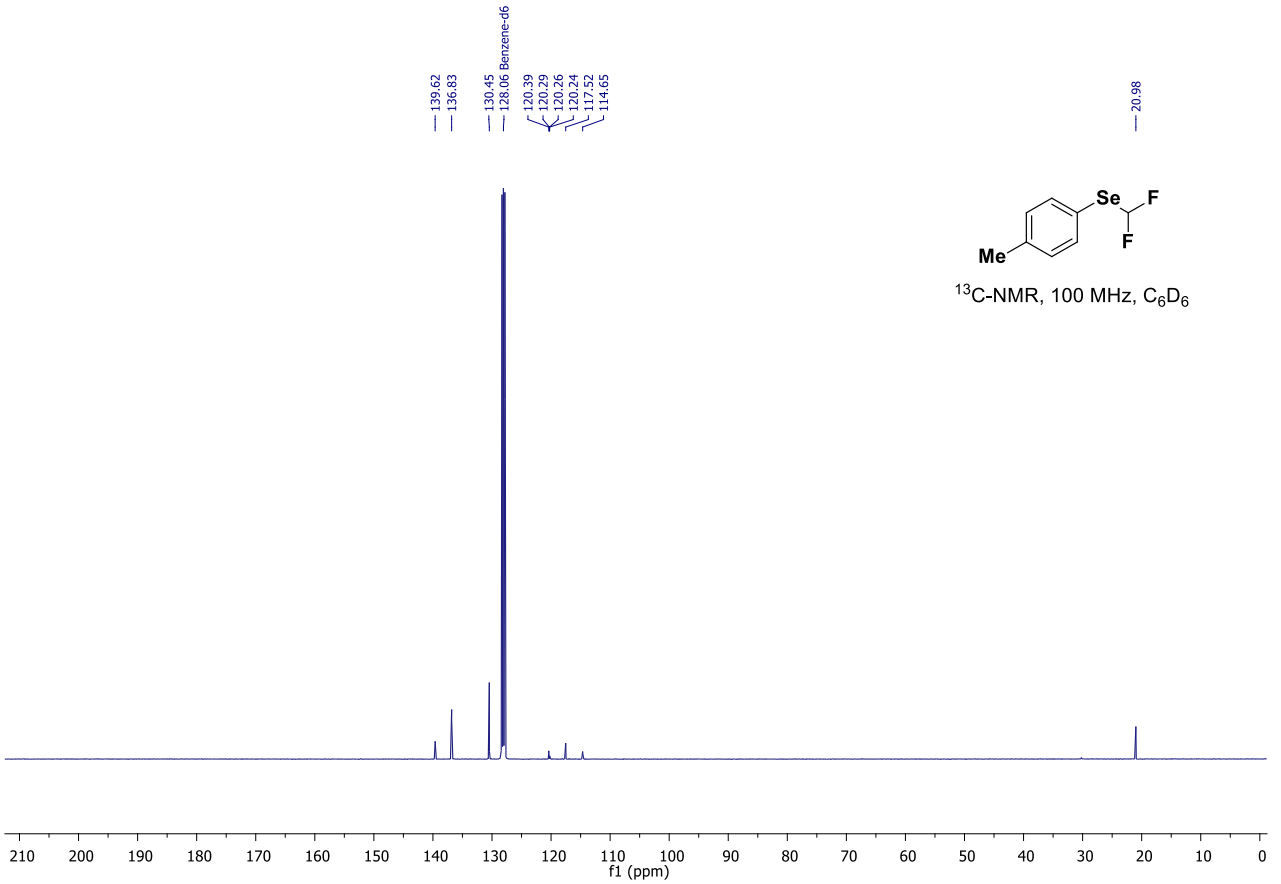


^{77}Se-NMR, 76 MHz,C_6D_6

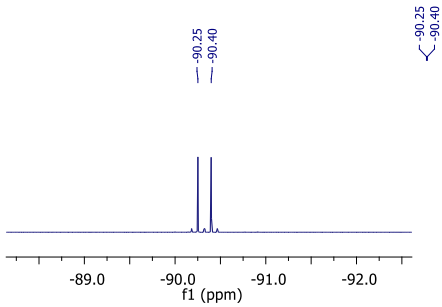
Compound 18

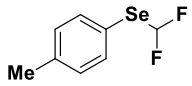


^{1}H-NMR, 400 MHz,C_6D_6

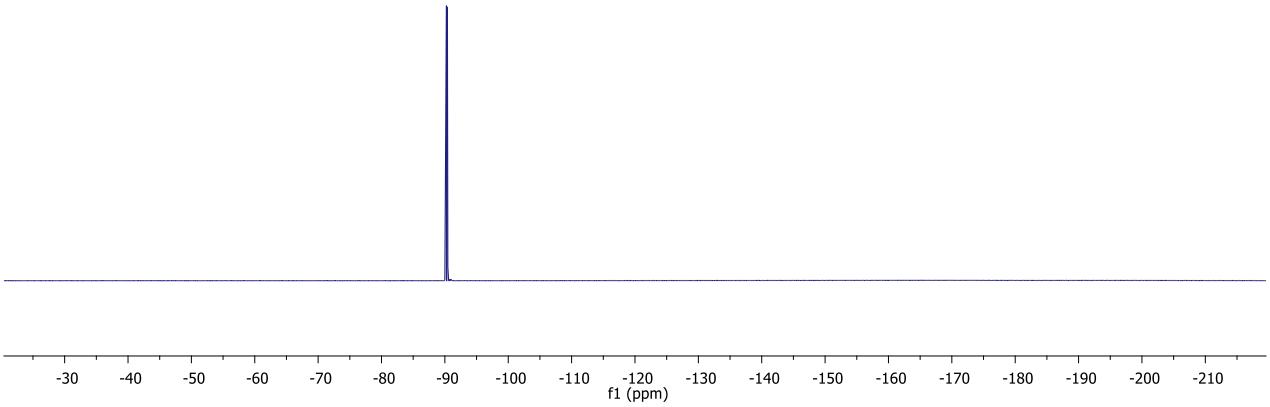


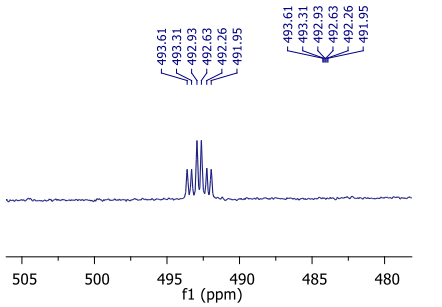
^{13}C-NMR, 100 MHz, C_6D_6

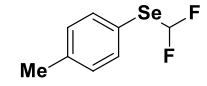




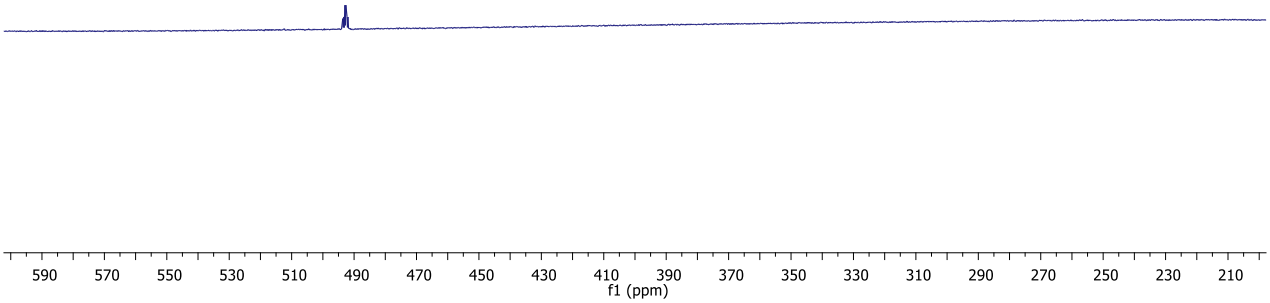
^{19}F-NMR, 376 MHz, C_6D_6



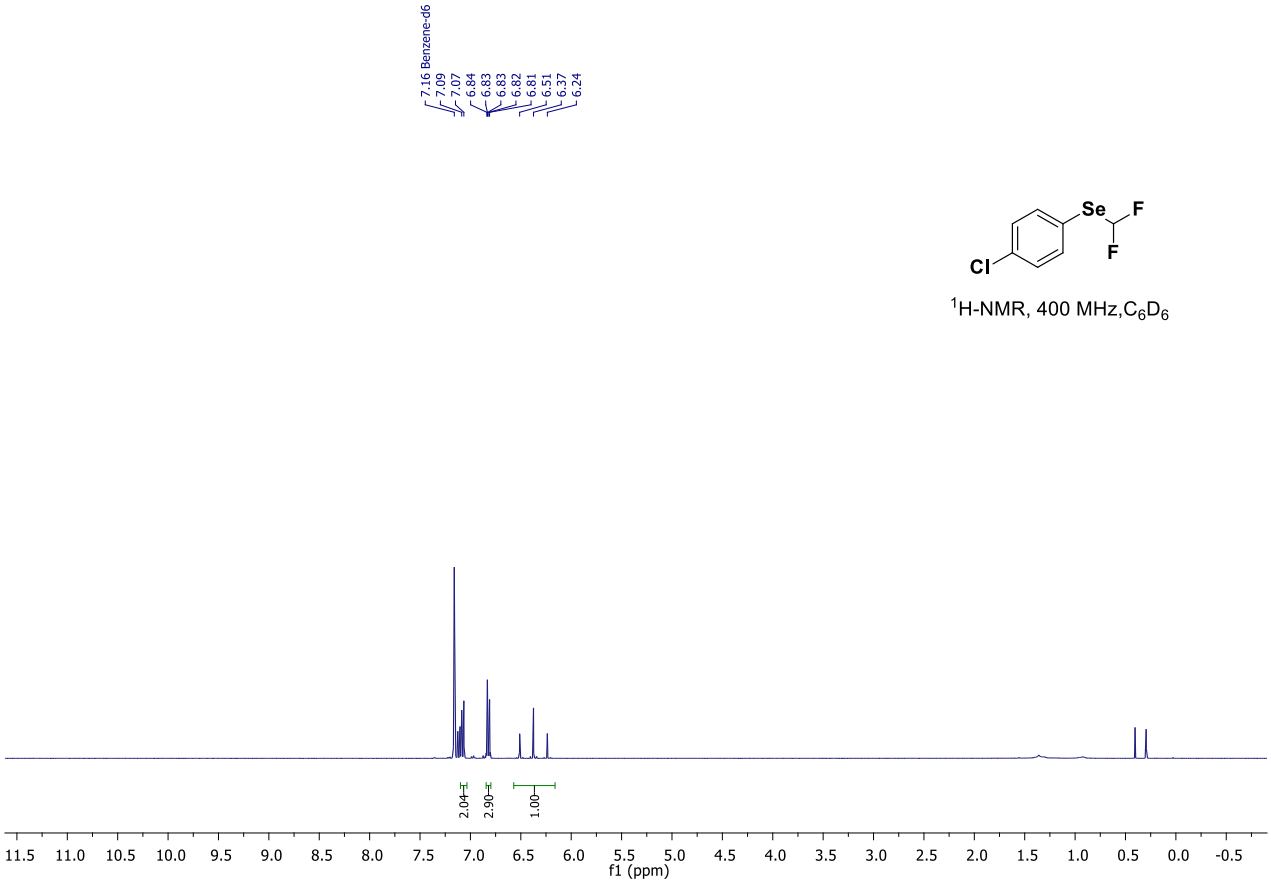




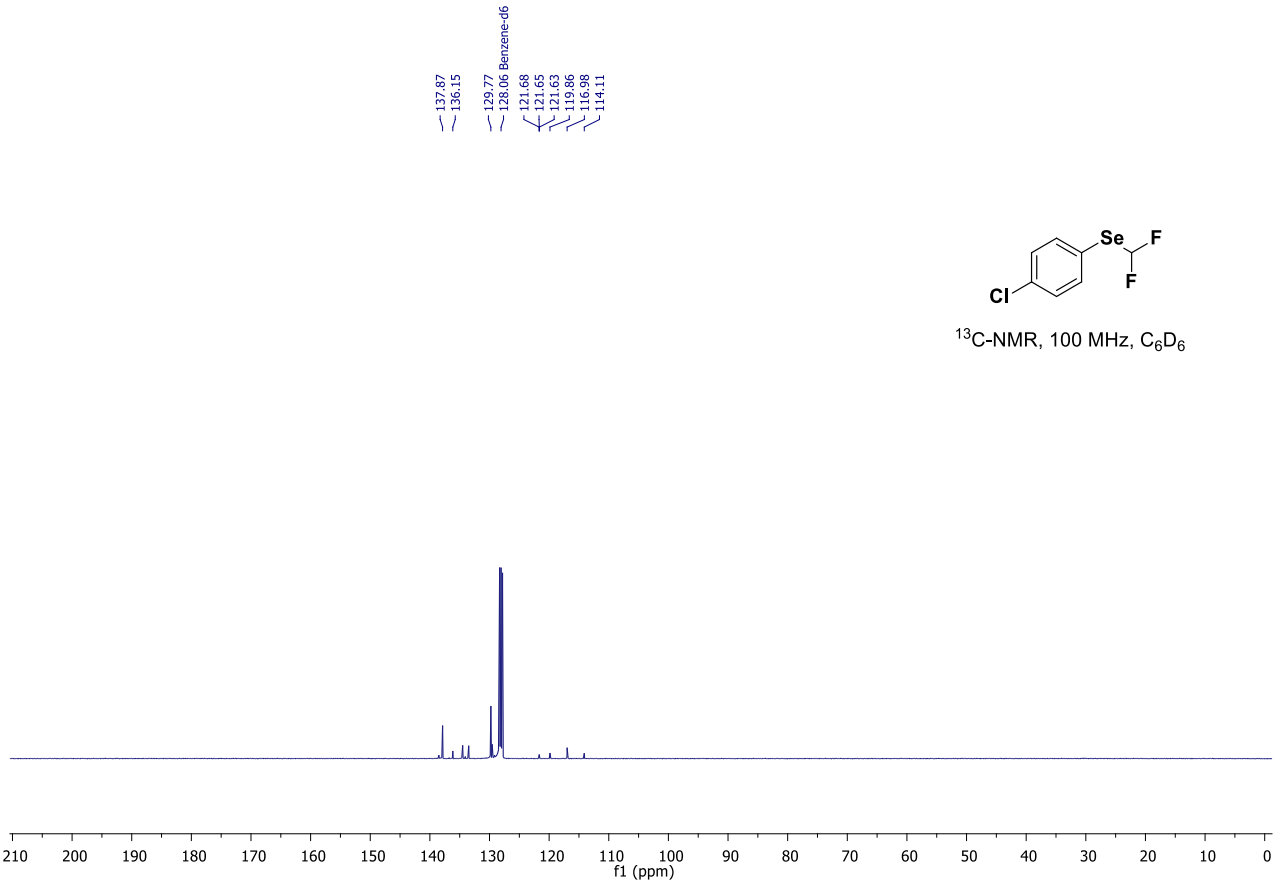
^{77}Se-NMR, 76 MHz,C_6D_6



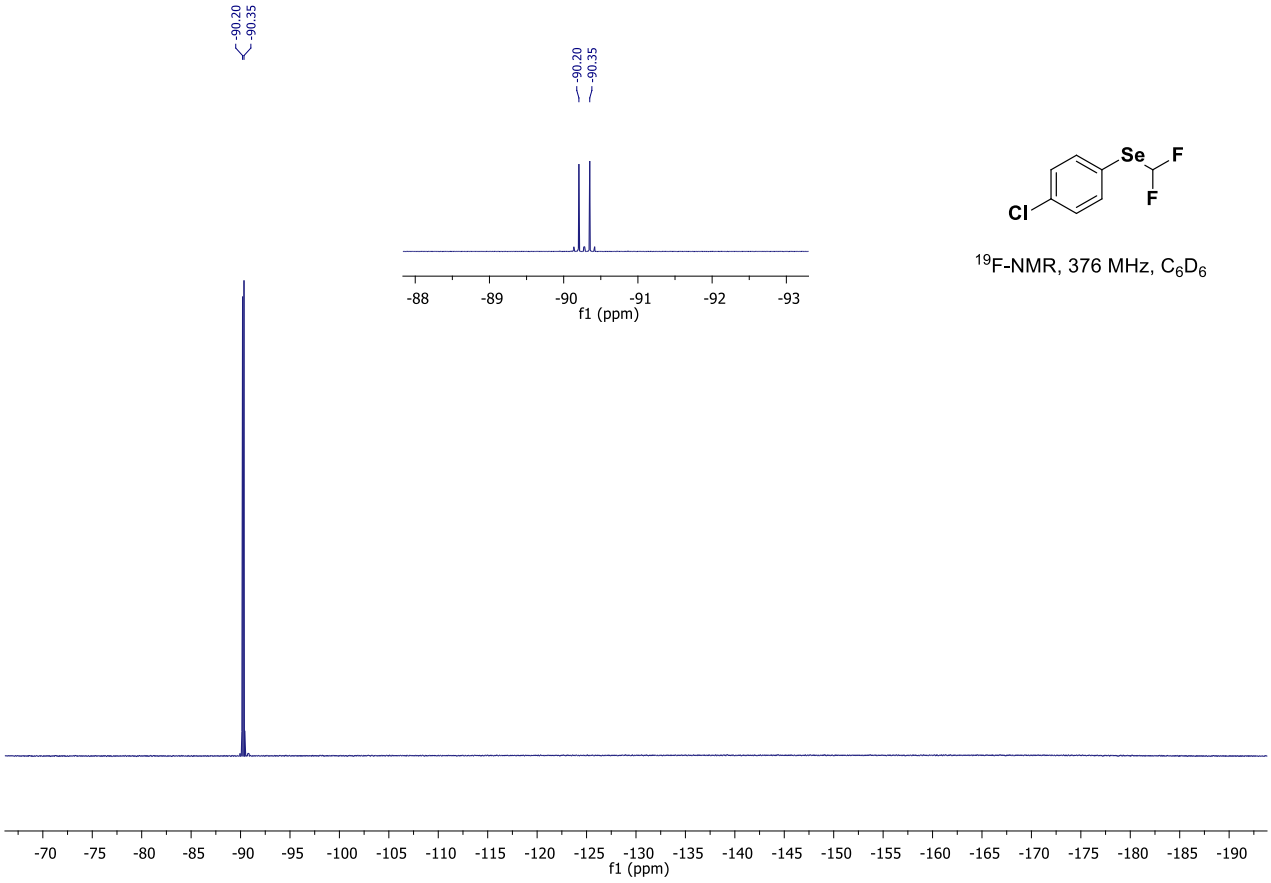
Compound 19



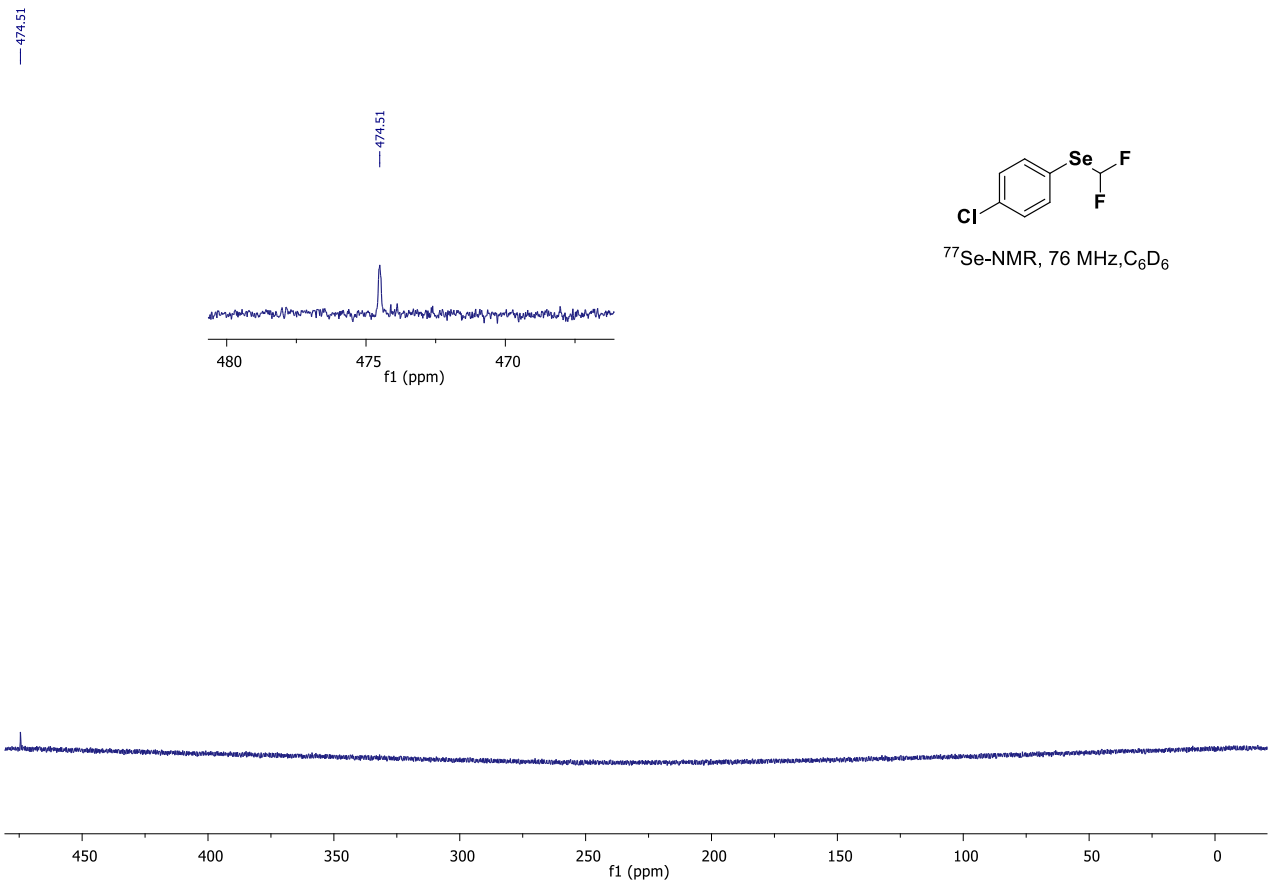
^{1}H-NMR, 400 MHz,C_6D_6



^{13}C-NMR, 100 MHz, C_6D_6

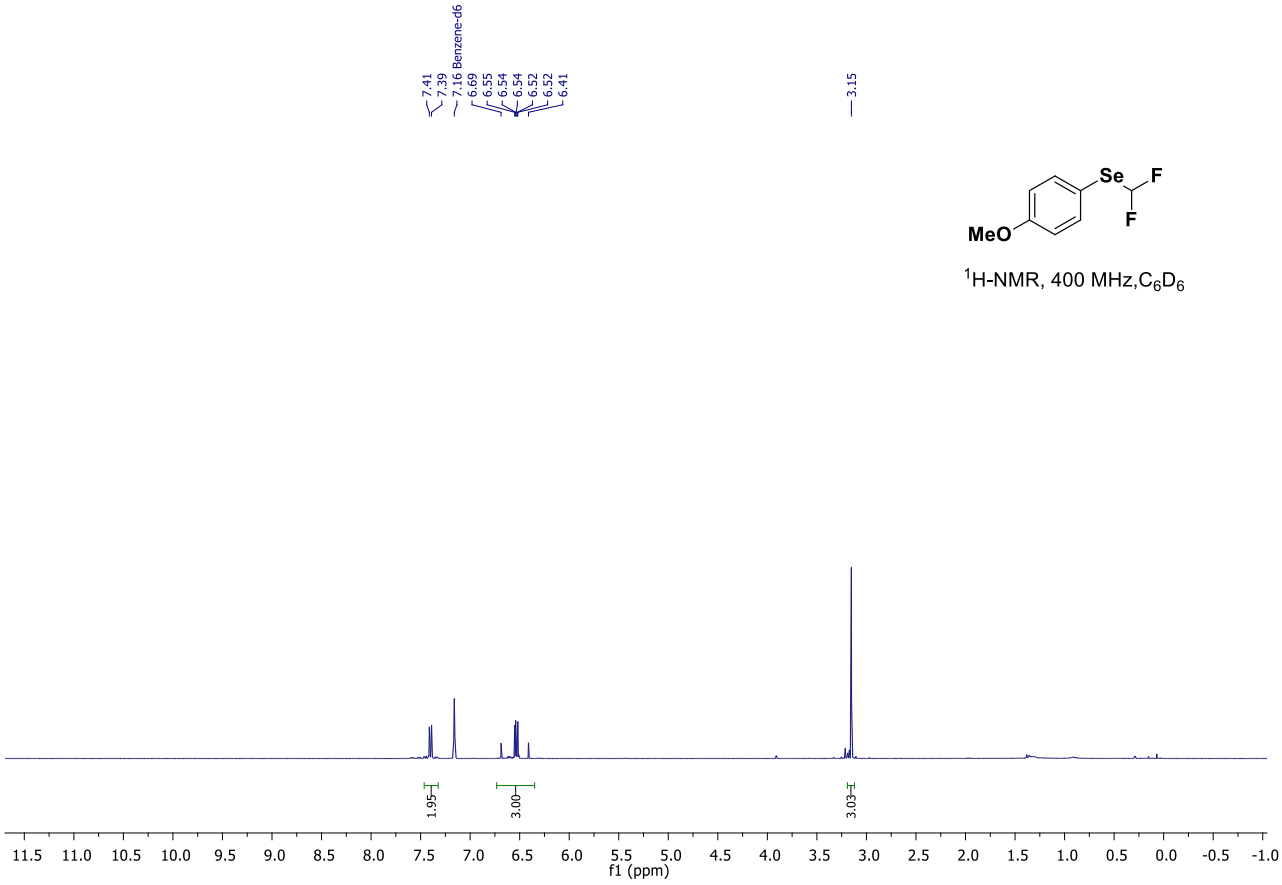


^{19}F-NMR, 376 MHz, C_6D_6

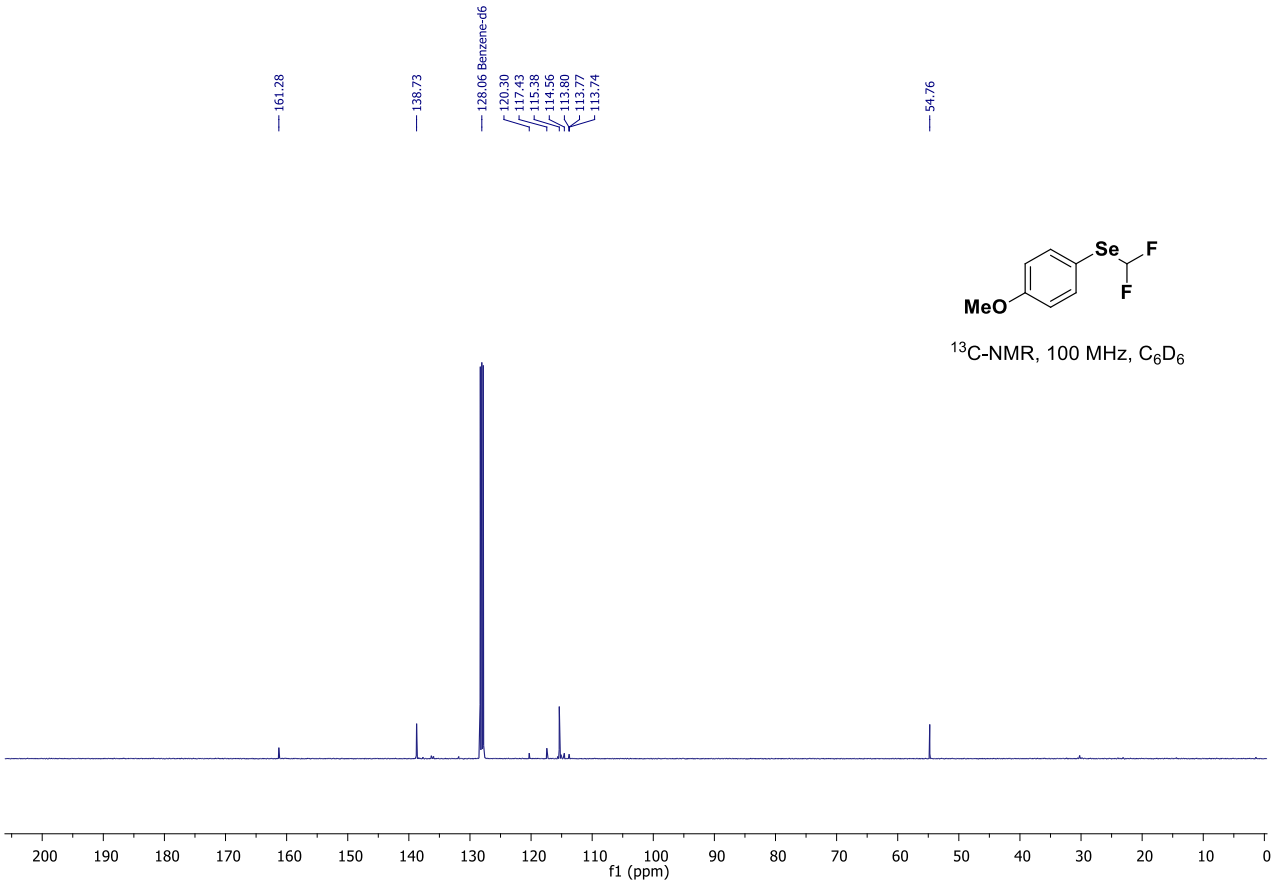


^{77}Se-NMR, 76 MHz,C_6D_6

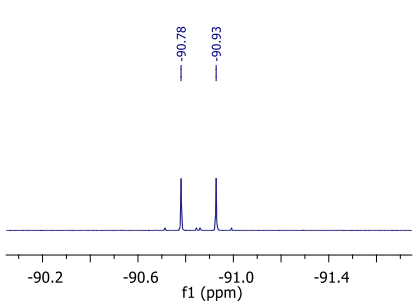
Compound 20

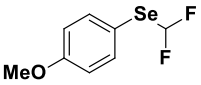


^{1}H-NMR, 400 MHz,C_6D_6

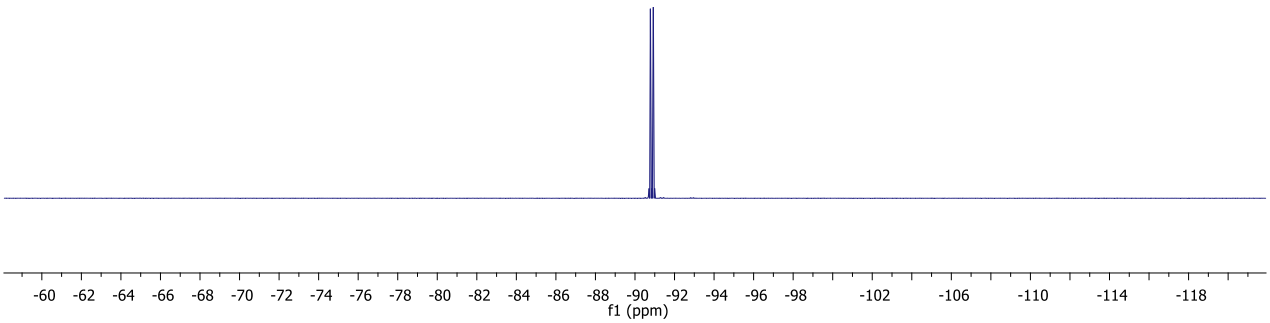


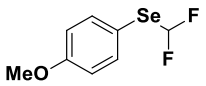
^{13}C-NMR, 100 MHz, C_6D_6



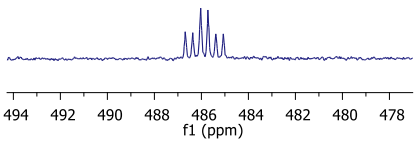


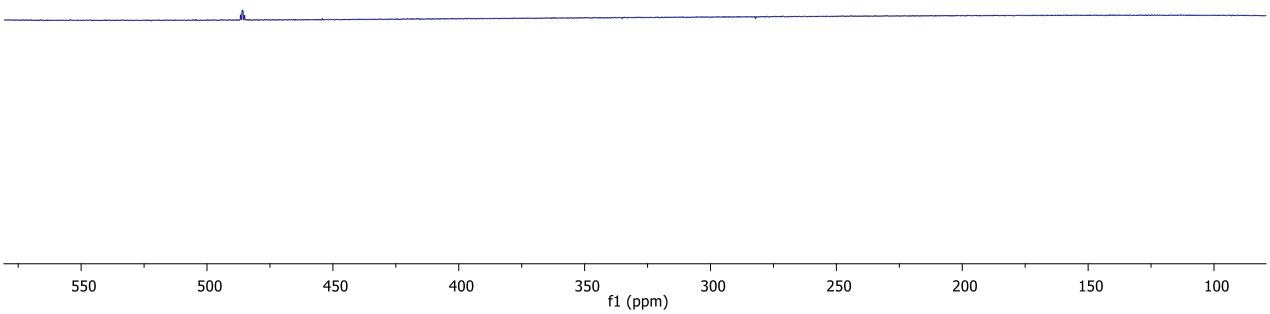
^{19}F-NMR, 376 MHz, C_6D_6



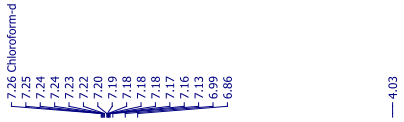


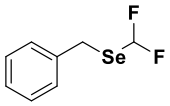
^{77}Se-NMR, 76 MHz,C_6D_6



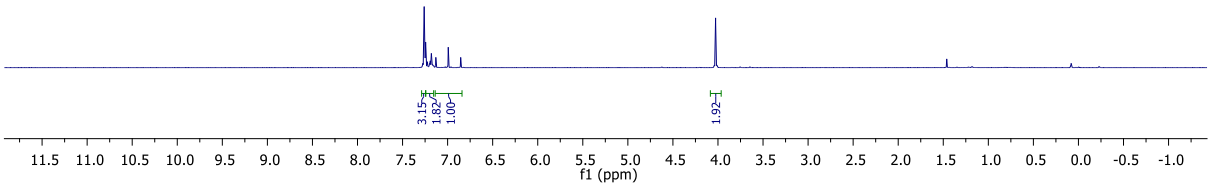


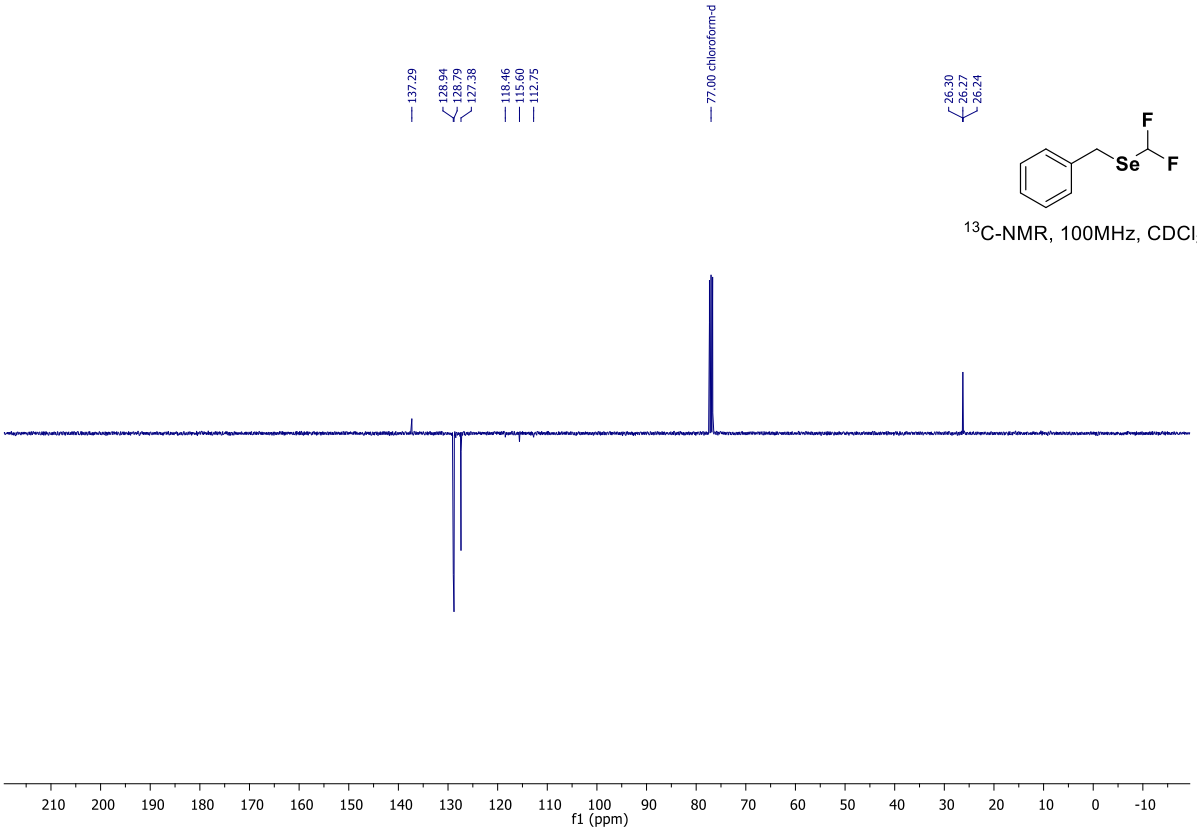
Compound 21



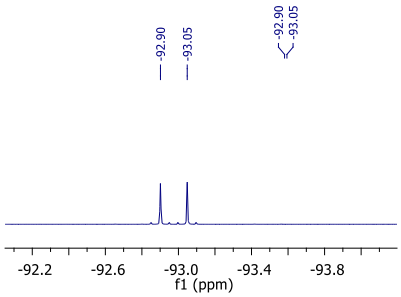


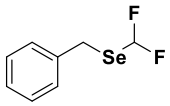
^{1}H-NMR, 400MHz, $CDCl_3$



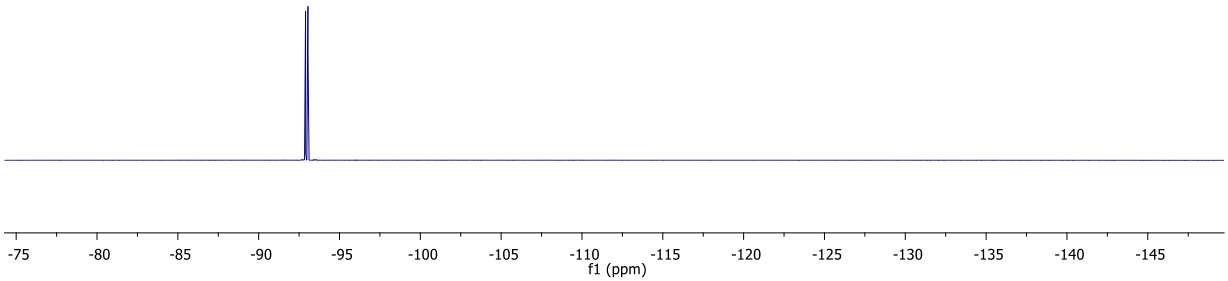


^{13}C-NMR, 100MHz, $CDCl_3$

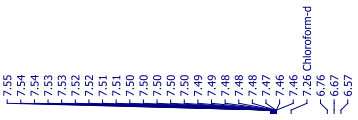


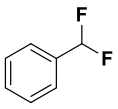


^{19}F-NMR, 376MHz, $CDCl_3$

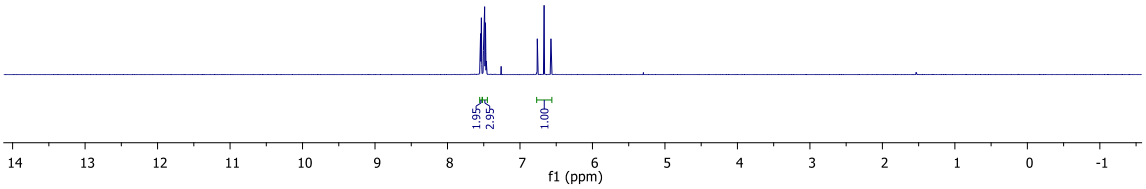


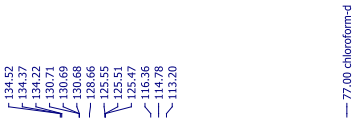
Compound 22

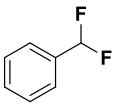




^{1}H-NMR, 400MHz, $CDCl_3$







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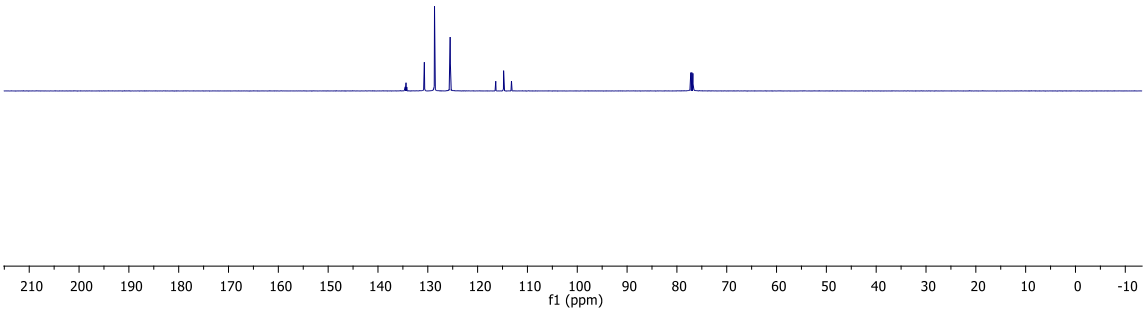
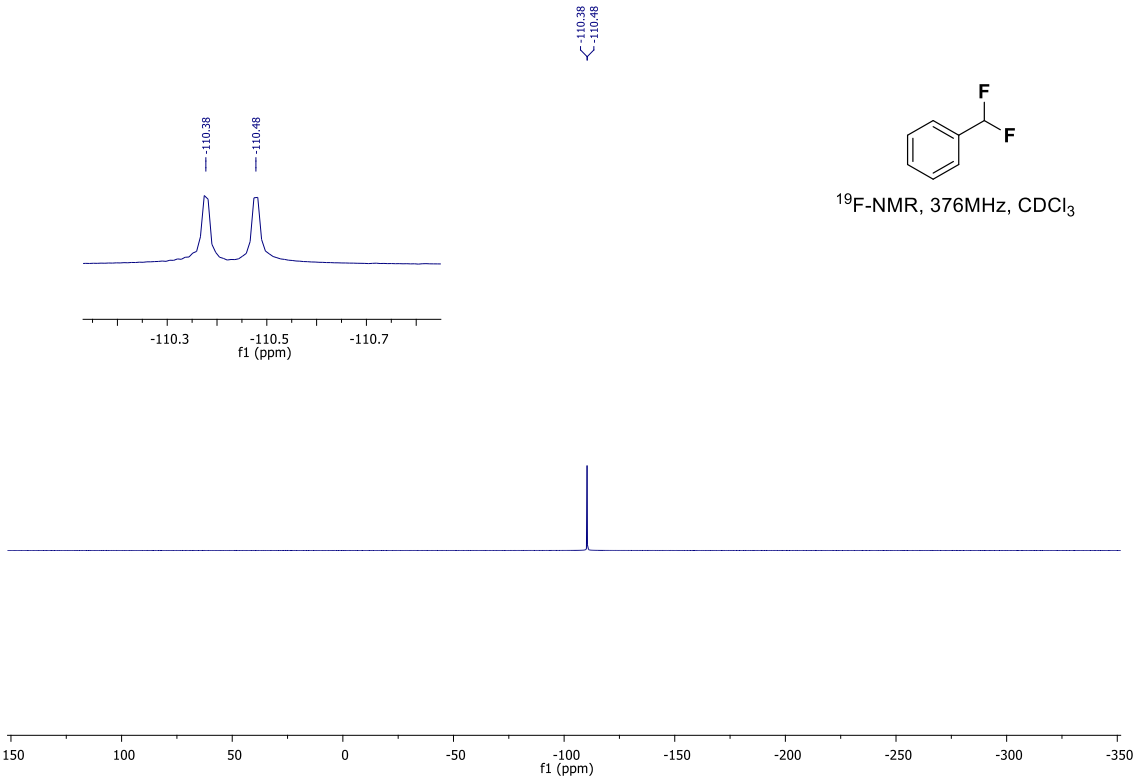
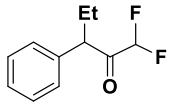


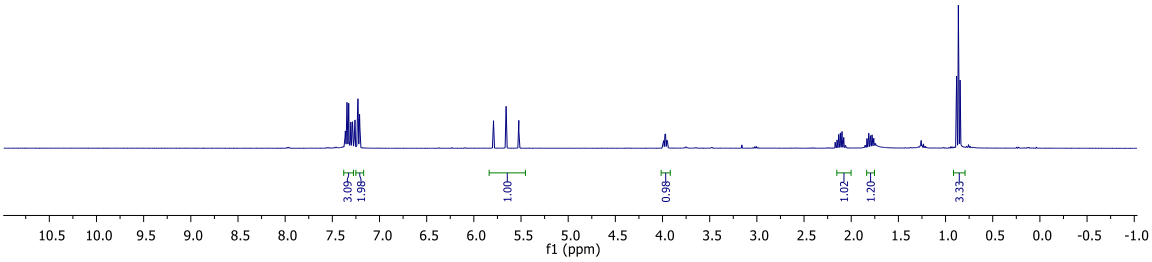


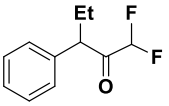
^{19}F-NMR, 376MHz, $CDCl_3$

Compound 24

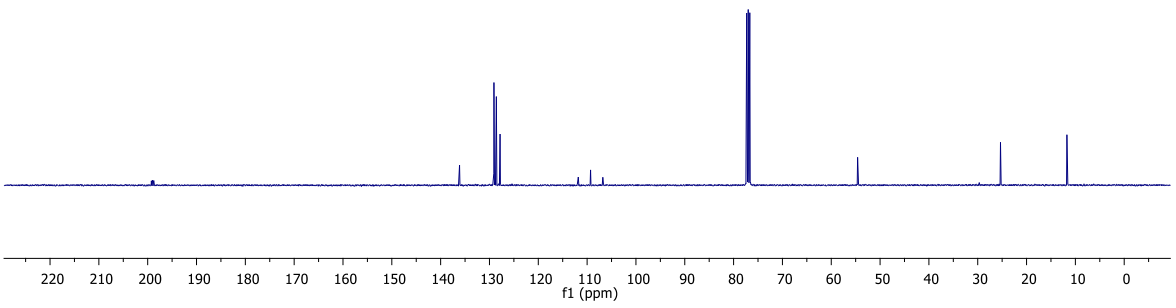


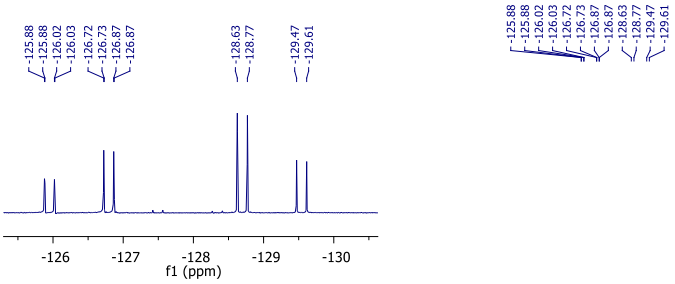
^{1}H-NMR, 400MHz, $CDCl_3$

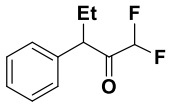




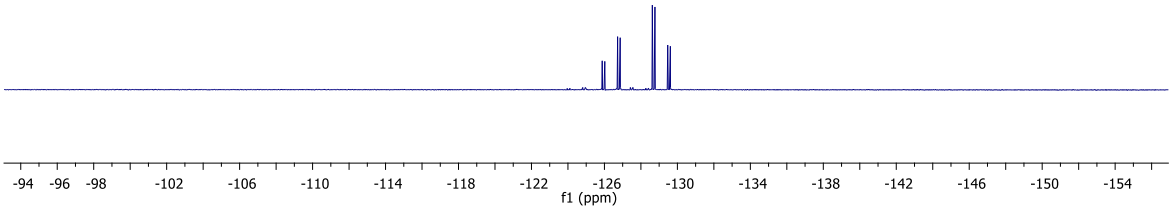
^{13}C-NMR, 100MHz, $CDCl_3$



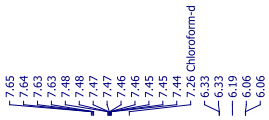


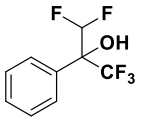


^{19}F-NMR, 376MHz, $CDCl_3$

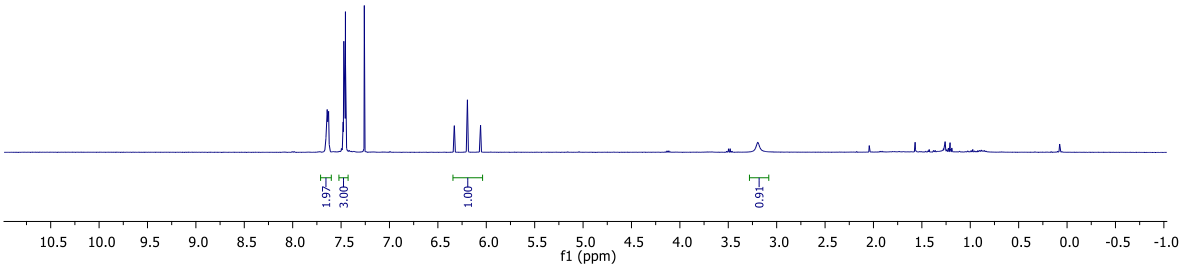


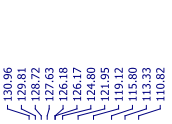
Compound 26

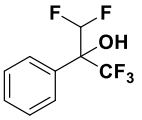




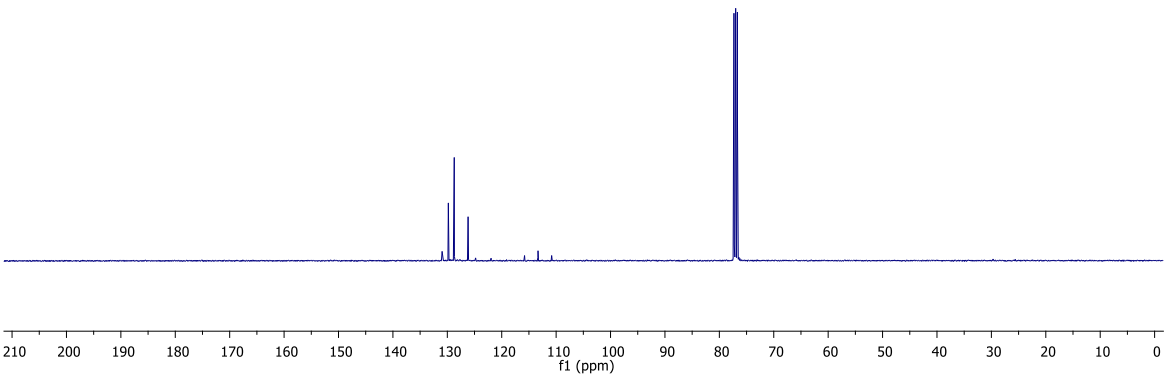
^{1}H-NMR, 400MHz, $CDCl_3$

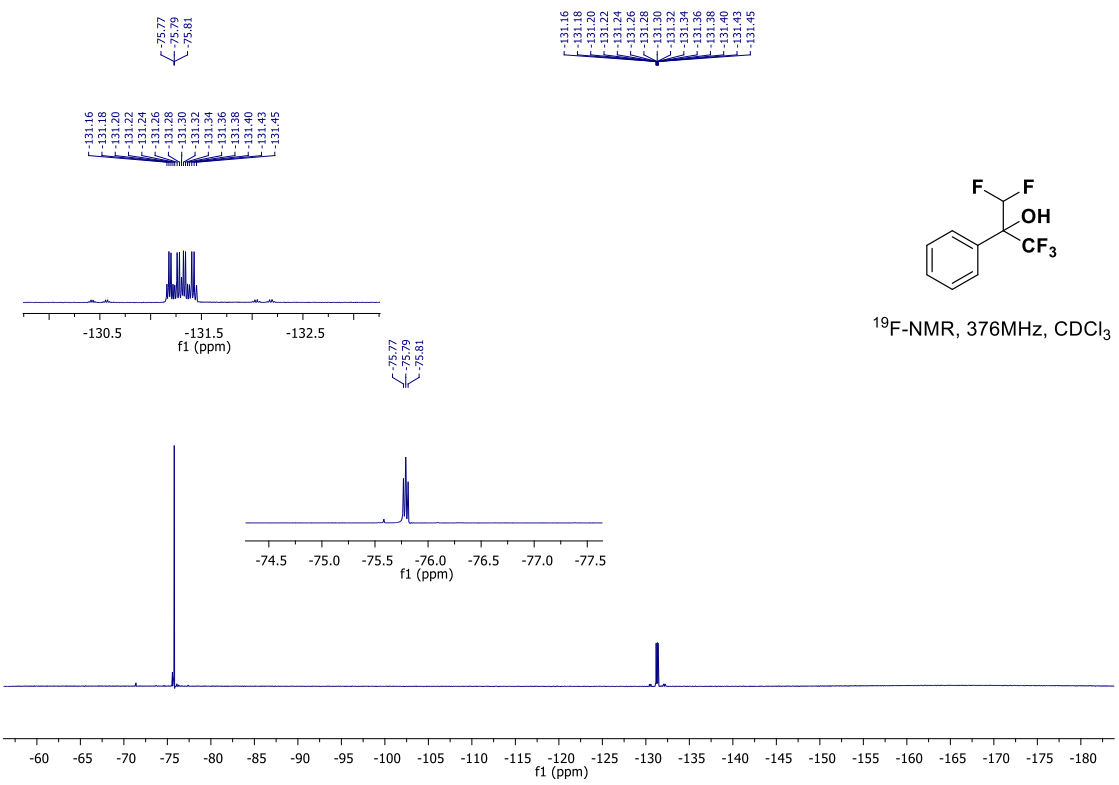






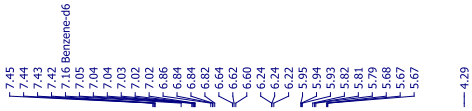
^{13}C-NMR, 100MHz, $CDCl_3$

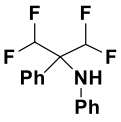




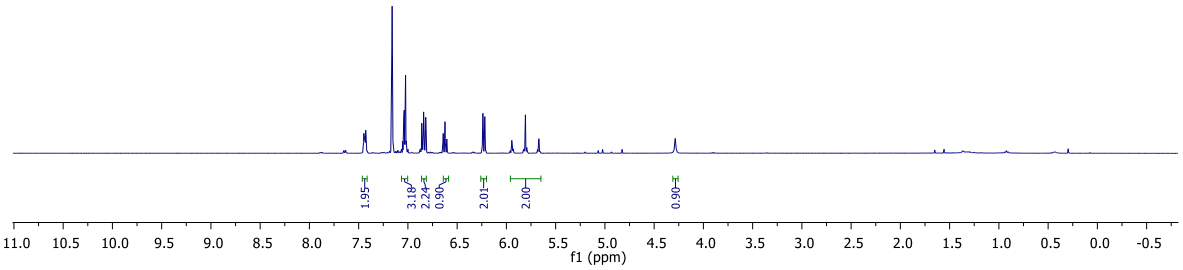
^{19}F-NMR, 376MHz, $CDCl_3$

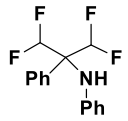
Compound 28



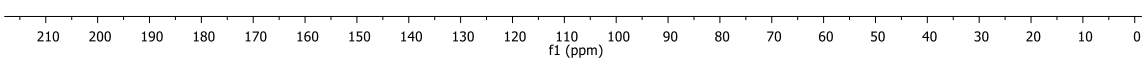


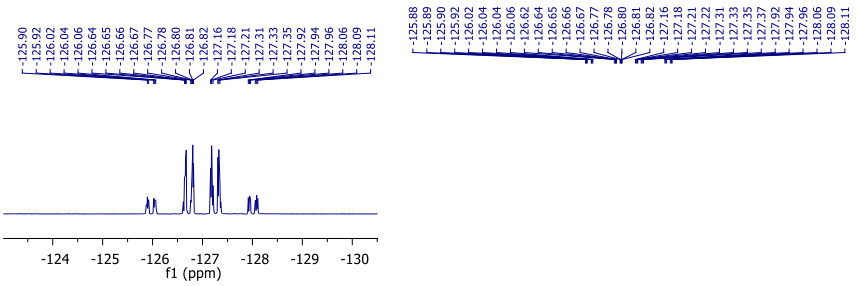
^{1}H-NMR, 400MHz, C_6D_6

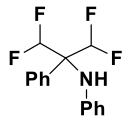




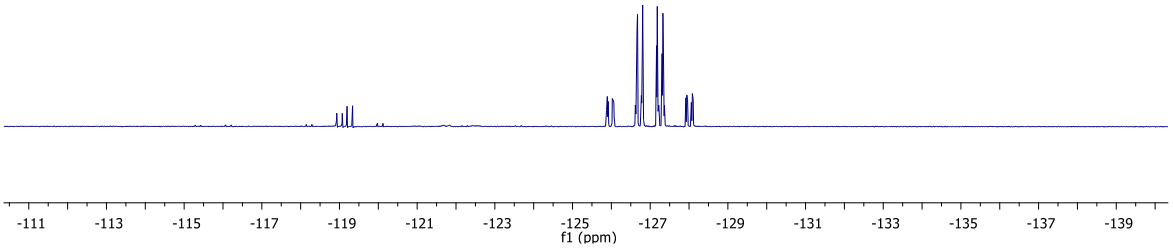
^{13}C-NMR, 100MHz, C_6D_6







^{19}F-NMR, 376MHz, C_6D_6



5.X-Ray Analysis

The X-ray intensity data were measured on Bruker D8 Venture and Stoe Stadivari equipped with multilayer monochromator, Mo and Cu K/α micro focus sealed tube, Oxford cooling system. The structures were solved by *Direct Methods*. Non-hydrogen atoms were refined with *anisotropic displacement parameters*. Hydrogen atoms were inserted at calculated positions and refined with riding model. Additionally to the software from Bruker and Stoe listed in the cif files following programs were used: *OLEX2*[7] for structure solution, refinement, molecular diagrams and graphical user-interface *Shelxle*[8] for refinement and graphical user-interface *SHELXS-2015*[9] for structure solution, *SHELXL-2015*[9] for refinement, *Platon*[10] for symmetry check. Experimental data and CCDC-Codes Experimental data (Available online: http://www.ccdc.cam.ac.uk/conts/retrieving.html) can be found in Table 1. Crystal data, data collection parameters, and structure refinement details are given in Table 2. Structures visualized in Figures 1 and 2

Table 1 Experimental parameter and CCDC-Code.

Sample	Machine	Source	Temp.	Detector Distance	Time/ Frame	#Frames	Frame width	CCDC
	Bruker		[K]	[mm]	[s]		[°]	
Compound 5	Bruker D8 Venture	Mo	140	36	1	2388	0.36	2150363
Compound 2	Stoe Stadivari	Cu	100	40	10	3380	0.36	2150362

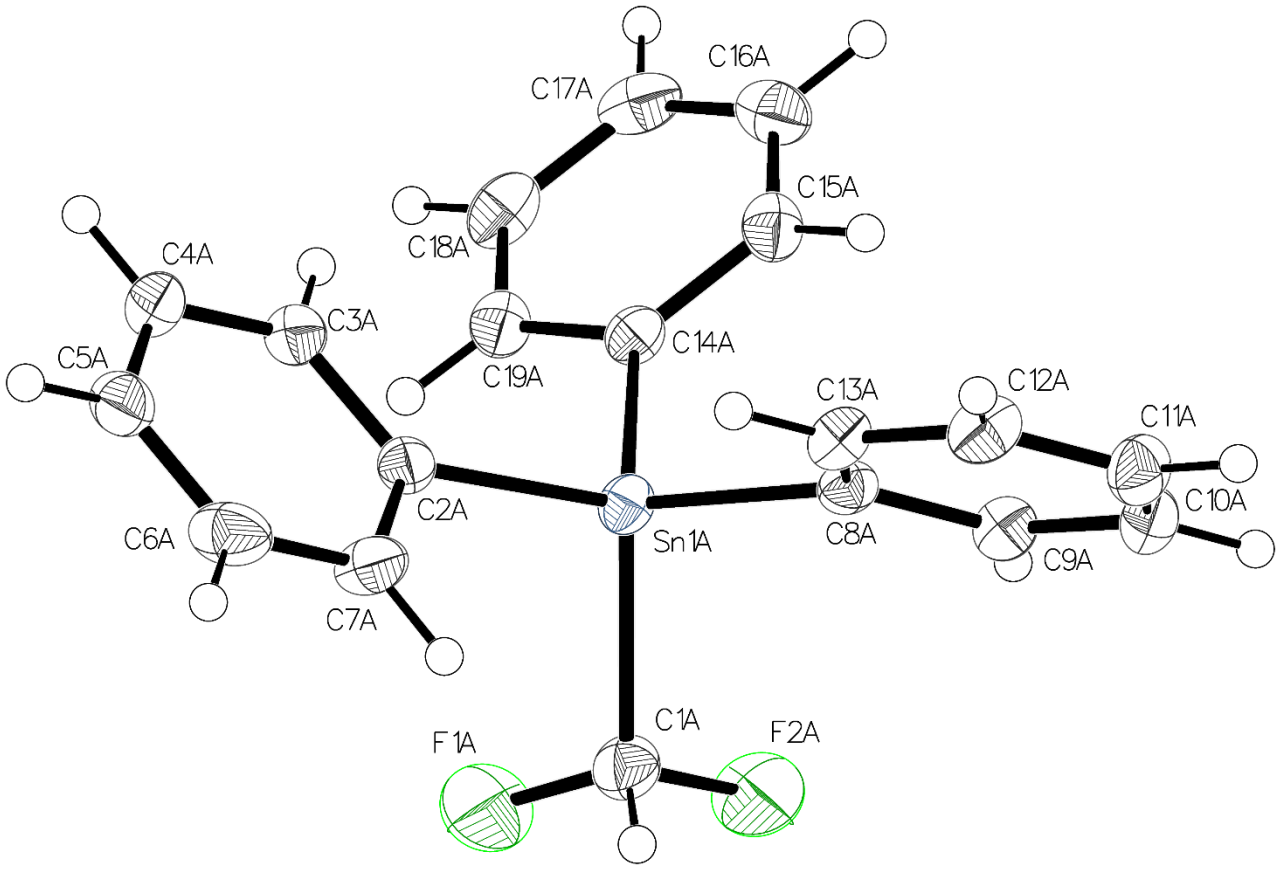


Figure 1 Structure of **5** drawn with 50% displacement ellipsoid. Second independent molecule omitted for clarity. The bond precision for single carbon carbon bonds is 0.0041 Å.

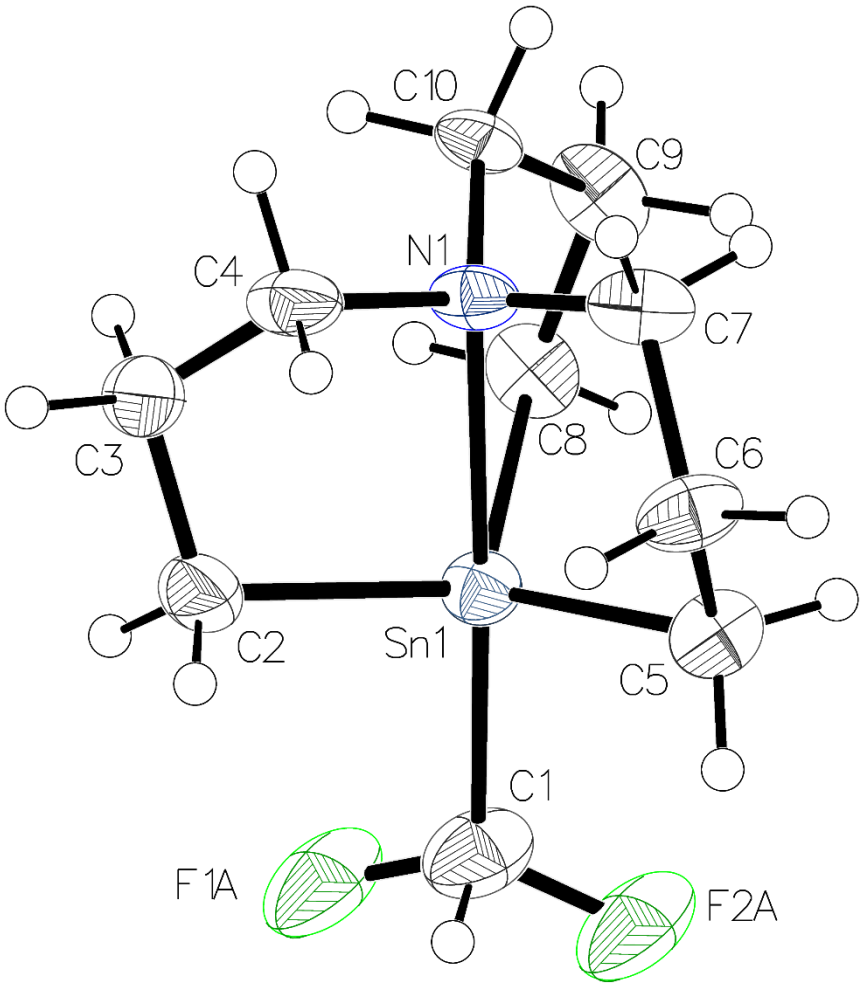


Figure 2 Structure of **2** drawn with 50% displacement ellipsoid. Disorder omitted for clarity. The bond precision for single carbon carbon bonds is 0.0123 Å. The degree of main residue disorder is 14%. Additionally the the crystal is twinned with BASF factor of 0.35 with the twin law (-1,0,0,0,-1,0,0,0,-1).

Table 2

Identification code	MaMi803_P-1	MaMi1213a_3
Empirical formula	$C_{19}H_{16}F_2Sn$	$C_{10}H_{19}F_2NSn$
Formula weight	401.01	309.95
Temperature/K	140.0	100
Crystal system	triclinic	tetragonal
Space group	P-1	$P4_32_12$
a/Å	9.4404(2)	8.987(4)
b/Å	9.7492(2)	8.987(4)
c/Å	18.7631(4)	28.74(4)
α/°	78.2253(17)	90
β/°	84.6029(10)	90
γ/°	79.0665(9)	90
Volume/Å^3	1657.11(6)	2321(4)
Z	4	8

ρ_{calc}g/cm^3	1.607	1.774
μ/mm^{-1}	1.555	17.467
F(000)	792.0	1232.0
Crystal size/mm^3	0.15 × 0.15 × 0.13	0.1 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)	Cu Kα (λ = 1.54186)
2Θ range for data collection/°	4.334 to 60.26	10.314 to 148.75
Index ranges	-13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -25 ≤ l ≤ 26	-7 ≤ h ≤ 10, -6 ≤ k ≤ 10, -35 ≤ l ≤ 29
Reflections collected	62306	8620
Independent reflections	9756 [R_{int} = 0.0467, R_{sigma} = 0.0339]	2195 [R_{int} = 0.0266, R_{sigma} = 0.0204]
Data/restraints/parameters	9756/0/397	2195/0/135
Goodness-of-fit on F^2	1.080	1.086
Final R indexes [I>=2σ (I)]	R_1 = 0.0317, wR_2 = 0.0722	R_1 = 0.0344, wR_2 = 0.0852
Final R indexes [all data]	R_1 = 0.0482, wR_2 = 0.0764	R_1 = 0.0383, wR_2 = 0.0874
Largest diff. peak/hole / e Å^{-3}	1.38/-2.10	0.99/-0.54
Flack parameter		0.35(3)

6. References

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