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Supporting Information

Fe-Catalyzed Insertion of Fluoromethylcarbenes Generated from Sulfonium Salts Into X-H Bonds (X = Si, C, P)

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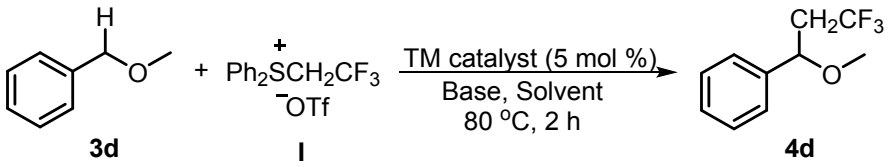
1. General Information.

^{1}H, ^{13}C and ^{19}F NMR spectra were detected on a 500 MHz, 400 MHz or 300 MHz NMR spectrometer. Data for ^{1}H NMR, ^{13}C NMR and ^{19}F NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, coupling constant (s) in Hz). Mass spectra were obtained on GC-MS or LC-MS (ESI). High resolution mass data were recorded on a high resolution mass spectrometer in the EI, ESI or MALDI mode. Unless otherwise noted, all reagents were obtained commercially and used without further purification. Substrates **1c, 1f** and **1g** were prepared according to literature.[1]

2. Screening Reaction Conditions for C-H Insertion

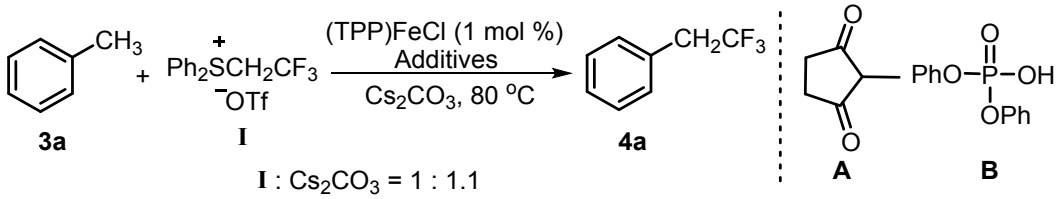


3d **I** **4d**

entry	TM catalyst [a]	base	solvent	yield (%) [b]
1	FeCl(TPP)	CsF	DMA	trace
2	Co(TPP)	CsF	DMA	N.D.
3	Ni(TPP)	CsF	DMA	N.D.
4	Cu(TPP)	CsF	DMA	N.D.
5	MnCl(TPP)	CsF	DMA	N.D.
6	Co(Schiff base)	CsF	DMA	N.D.
7	CuBr	CsF	DMA	N.D.
8	CuTc	CsF	DMA	N.D.
9	CuOAc	CsF	DMA	N.D.
10	$Cu(acac)_2$	CsF	DMA	N.D.
11	FeCl(TPP) + $Rh_2(OAc)_4$	CsF	DMA	N.D.
12	FeCl(TPP) + $Rh_2(esp)_2$	CsF	DMA	N.D.
13	FeCl(TPP) + $AgPF_6$	CsF	DMA	N.D.
14	FeCl(TPP) + $NiCl_2(PPh_3)_3$	CsF	DMA	N.D.
15	FeCl(TPP) + $Cu(acac)_2$	CsF	DMA	N.D.
16	FeCl(TPP) + $PdCl_2(PPh_3)_2$	CsF	DMA	N.D.
17	FeCl(TPP)	CsOAc	DMA	trace
18	FeCl(TPP)	$CsHCO_3$	DMA	trace
19	FeCl(TPP)	Cs_2CO_3	DMA	trace

20	FeCl(TPP)	$KHCO_3$	DMA	trace
21	FeCl(TPP)	K_2CO_3	DMA	trace
22	FeCl(TPP)	$NaHCO_3$	DMA	trace
23	FeCl(TPP)	Na_2CO_3	DMA	trace
24	FeCl(TPP)	$Na_2C_2O_4$	DMA	trace
25	FeCl(TPP)	^{t}BuOK	DMA	N.D.
26	FeCl(TPP)	KH_2PO_4	DMA	trace
27	FeCl(TPP)	K_2HPO_4	DMA	trace
28	FeCl(TPP)	K_3PO_4	DMA	trace
29	FeCl(TPP)	KOH	DMA	trace
30	FeCl(TPP)	KOH+H_2O	DMA	trace
31	FeCl(TPP)	NaOH	DMA	trace
32	FeCl(TPP)	LiOH	DMA	trace
33	FeCl(TPP)	$Ca(OH)_2$	DMA	trace
34	FeCl(TPP)	KF	DMA	trace
35	FeCl(TPP)	DBU	DMA	N.D.
36	FeCl(TPP)	Et_3N	DMA	N.D.
37	FeCl(TPP)	DMAP	DMA	N.D.
38	FeCl(TPP)	Cs_2CO_3	DMF	trace
39	FeCl(TPP)	Cs_2CO_3	CH_3CN	N.D.
40	FeCl(TPP)	Cs_2CO_3	^{n}Hexane	N.D.
41	FeCl(TPP)	Cs_2CO_3	Cyclohexane	N.D.[c]
42	FeCl(TPP)	Cs_2CO_3	Dioxane	N.D.[c]
43	FeCl(TPP)	Cs_2CO_3	THF	N.D.[c]
44	FeCl(TPP)	Cs_2CO_3	Toluene	N.D.[c]

[a]Reaction conditions: **3d** (0.1 mmol), sulfonium salt **I** (0.11 mmol), FeCl(TPP) (0.005 mmol) and CsF (0.12 mmol) in DMA (1.5 mL) at 80 °C for 2 h; [b]The yields were determined by ^{19}FNMR; [c]Trifluoromethyl carbene was found to insert into the C-H bond of the solvents.



entry[a]	additives	yield (%) [b]
1[c]	-	25%
2	-	20-43
3	10 % $Na_2S_2O_4$	33
4	15 % $Na_2S_2O_4$	43
5	20 % $Na_2S_2O_4$	46
6	25 % $Na_2S_2O_4$	40
7	25 % $Na_2S_2O_4$	36
8	$Na_2S_2O_4$	29
9	20 % $Na_2S_2O_4$	25-60
10 [d]	**20 % $Na_2S_2O_4$**	**44**
11	H_2O	37
12	Hantzsch ester	11
13	Ph_2MeSiH	38
14	Ph_2SiH_2	3
15	Et_3SiH	3
16	**A**	N.D.
17	**B**	12

[a] FeCl(TPP) (0.002 mmol), sulfonium salt **I** (0.2 mmol), Cs_2CO_3 (0.22 mmol), additives (0.2 mmol), and **3a (**1.2 mL) at 80 °C for 10 h; [b]The yields were determined by ^{19}FNMR; [c]The loading of the catalyst is 0.004 mmol; [d]The mixture of $Na_2S_2O_4$(0.04 mmol, 20 mol%) and Fe(TPP)Cl(0.002 mmol) in 0.5 mL **3a** was stirred at 60 °C for 10 min under a N_2 atmosphere, and then a mixture of **I** (0.2 mmol), Cs_2CO_3 (0.22 mmol) and **3a** (1 mL) was added. The resulting mixture was stirred at 80 °C for a further 2 h.

3. Procedure for the Preparation of 1c, 1f and 1g.

The preparation for the Grignard reagent: Into a three-necked flask (250 mL) was added a grain of iodine and magnesium powder (110 mmol, 2.64 g, 1.1 equiv.) under a N_2 atmosphere. Dry pentyl bromide (0.7 mL) and dry THF (100 mL) was added and the mixture was warmed until the brown solution turned colorless. The remained pentyl bromide (100 mmol in total, 1.0 equiv.) was

added dropwise. The solution was stirred at 80 °C for an hour and cooled slowly to room temperature as a grey solution.

For the Preparation of 1c: Into a round-bottom flask (100 mL) was added dry THF (10 mL) and trichlorosilane (5 mmol, 0.6776 g, 1.0 equiv.) under a N_2 atmosphere. After the dropwise addition of pentylmagnesium bromide (30 mmol, 50 mL, 6.0 equiv.) at -78 °C, the solution was warmed up slowly and stirred overnight at room temperature. The reaction was quenched with water at 0 °C and extracted with dichloromethane (20 mL). The organic layer was washed with water (20 mL X 3) and dried over anhydrous Na_2SO_4. After filtration, the solvent was removed by concentration. The residue was subjected to flash column chromatography with the use of hexane as eluent to give the final product **1c** (colorless oil, 0.95 g, 78% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.69 - 3.63 (m, 1H), 1.37 - 1.25 (m, 18H), 0.87 (t, J = 6.6 Hz, 9H), 0.60 - 0.53 (m, 6H).

For the Preparation of 1f: Into a round-bottom flask (100 mL) was added dry THF (10 mL) and dichloromethylsilane (10 mmol, 1.15 g, 1.0 equiv.) under a N_2 atmosphere. After the dropwise addition of pentylmagnesium bromide (30 mmol, 50 mL, 6.0 equiv.) at -78 °C, the solution was warmed up slowly and stirred overnight at room temperature. The reaction was quenched with water at 0 °C and extracted with dichloromethane (20 mL). The organic layer was washed with water (20 mL X 3) and dried over anhydrous Na_2SO_4. After filtration, the solvent was removed by concentration. The residue was subjected to flash column chromatography with the use of hexane as eluent to give the final product **1f** (colorless oil, 1.637 g, 88% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 - 3.73 (m, 1H), 1.41 - 1.24 (m, 12H), 0.88 (t, J = 6.7 Hz, 6H), 0.62 - 0.51 (m, 4H), 0.03 (d, J = 3.7 Hz, 3H).

For the Preparation of 1g: Into a round-bottom flask (100 mL) was added benzylmagnesium chloride (1 M in THF, 30 mL, 1.5 equiv.) under a N_2 atmosphere. The solution of

chlorodimethylsilane (20 mmol, 1.892 g, 1.0 equiv.) in dry THF (10 mL) was added dropwise at 0 ^{o}C, and then the solution was warmed up slowly and stirred overnight at room temperature. The reaction was quenched with water at 0 ^{o}C and extracted with dichloromethane (20 mL). The organic layer was washed with water (20 mL X 3) and dried over anhydrous Na_2SO_4. After filtration, the solvent was removed by concentration. The residue was subjected to flash column chromatography with the use of hexane as eluent to give the final product **1g** (colorless oil, 1.503 g, 50% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.6 Hz, 2H), 7.18 - 7.07 (m, 3H), 4.07 - 4.01 (m, 1H), 2.25 - 2.19 (m, 2H), 0.18 - 0.08 (m, 6H).

4. General Procedure for X-H Insertion.

For the insertion into 1a-1g: Into a mixture of **1a-g** (0.4 mmol, 1.0 equiv.), sulfonium salt **I** (0. 8 mmol, 334.7 mg, 2.0 equiv.), cesium fluoride (1.0 mmol, 151.9 mg, 2.5 equiv.), Fe(TPP)Cl (0.008 mmol, 5.6 mg, 2 mol %) and $Na_2S_2O_4$ (0.08 mmol, 14.0 mg, 20 mol %) was added DMA (4 mL) under N_2 atmosphere. The mixture was stirred at room temperature for 2 hours and then was diluted with CH_2Cl_2 (15 mL) and water (15 mL). The organic phase was separated and washed with water (15 mL, three times), and then dried over Na_2SO_4. After filtration, the solvent was removed by concentration. The residue was subjected to flash column chromatography with the use of hexane as eluent to give the final product **2a-2g**.

Triethyl(2,2,2-trifluoroethyl)silane **(2a)**. Colorless oil, 42 mg, 53%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.54 (q, *J* = 14.3 Hz, 2H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.62 (q, *J* = 7.9 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.29 (t, *J* = 14.3 Hz, 3F).

Tributyl(2,2,2-trifluoroethyl)silane **(2b)**: Colorless oil, 98.3 mg, 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 (q, *J* = 14.2 Hz, 2H), 1.38 - 1.21 (m, 12H), 0.88 (t, *J* = 7.1 Hz, 9H), 0.66 - 0.58 (m,

6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.26 (t, *J* = 14.2 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 128.71 (q, *J* = 274.2 Hz), 26.59 (s), 25.60 (s), 19.99 (q, *J* = 29.4 Hz), 13.60 (s), 11.97 (s). IR (neat) ν = 2959, 2926, 2874, 1465, 1413, 1378, 1342, 1279, 1253, 1220, 1198, 1093, 1036, 909, 888, 795, 737 cm^{-1}. HRMS (EI): calcd. for $C_{12}H_{27}Si$ [M-CH_2CF_3]$^+$: 199.1882, Found: 199.1881.

Tripentyl(2,2,2-trifluoroethyl)silane **(2c)**: Colorless oil, 107.7 mg, 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 (q, *J* = 14.2 Hz, 2H), 1.34 - 1.23 (m, 18H), 0.87 (t, *J* = 6.6 Hz, 9H), 0.65 - 0.56 (m, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.26 (t, *J* = 14.2 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 128.70 (q, *J* = 274.3 Hz), 35.85 (s), 23.02 (s), 22.16 (s), 20.01 (q, *J* = 29.3 Hz), 13.88 (s), 12.21 (s). IR (neat) ν = 2958, 2924, 2859, 1466, 1413, 1379, 1279, 1252, 1220, 1092, 1031, 908, 804, 737 cm^{-1}. HRMS (EI): calcd. for $C_{15}H_{33}Si$ [M-CH_2CF_3]$^+$: 241.2352, Found: 241.2359.

Trihexyl(2,2,2-trifluoroethyl)silane **(2d)**: Colorless oil, 130.4 mg, 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.52 (q, *J* = 14.3 Hz, 2H), 1.35 - 1.20 (m, 24H), 0.87 (t, *J* = 6.9 Hz, 9H), 0.65 - 0.55 (m, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.22 (t, *J* = 14.3 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 128.73 (q, *J* = 274.2 Hz), 33.37 (s), 31.45 (s), 23.38 (s), 22.59 (s), 20.04 (q, *J* = 29.3 Hz), 14.03 (s), 12.32 (s). IR (neat) ν = 2958, 2924, 2857, 1467, 1413, 1378, 1278, 1252, 1219, 1090, 1031, 908, 796, 737 cm^{-1}. HRMS (EI): calcd. for $C_{18}H_{39}Si$ [M-CH_2CF_3]$^+$: 283.2821, Found: 283.2818.

Trioctyl(2,2,2-trifluoroethyl)silane **(2e)**: Colorless oil, 146.1 mg, 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.52 (q, *J* = 14.2 Hz, 2H), 1.34 - 1.19 (m, 36H), 0.87 (t, *J* = 6.8 Hz, 9H), 0.64 - 0.55 (m, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.21 (t, *J* = 14.2 Hz, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 128.72 (q, *J* = 274.3 Hz), 33.67 (s), 31.91 (s), 29.22 (s), 29.17 (s), 23.39 (s), 22.67 (s), 20.07 (q, *J* = 29.3 Hz), 14.07 (s), 12.31 (s). IR (neat) ν = 2957, 2924, 2854, 1467, 1413, 1379, 1278, 1252, 1220, 1091, 1034, 908, 737 cm^{-1}. HRMS (EI): calcd. for $C_{24}H_{51}Si$ [M-CH_2CF_3]$^+$: 367.3760, Found: 367.3754.

Methyldipentyl(2,2,2-trifluoroethyl)silane **(2f)**: Colorless oil, 55.2 mg, 74%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 (q, *J* = 14.2 Hz, 2H), 1.34 - 1.24 (m, 12H), 0.87 (t, *J* = 6.6 Hz, 6H), 0.63 - 0.55 (m, 4H), 0.08 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.45 (t, *J* = 14.2 Hz, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 128.65 (q, *J* = 274.2 Hz), 35.73 (s), 23.02 (s), 22.20 (s), 21.37 (d, *J* = 29.1 Hz), 13.89 (s), 13.65 (s), -4.92 (d, *J* = 0.8 Hz). IR (neat) ν = 2959, 2924, 2874, 1467, 1413, 1280, 1250, 1219, 1093, 1032, 819, 766 cm^{-1}. HRMS (EI): calcd. for $C_{11}H_{25}Si$ $[M\text{-}CH_2CF_3]^+$: 185.1726, Found: 185.1732.

Benzyldimethyl(2,2,2-trifluoroethyl)silane **(2g)**: Colorless oil, 37.2 mg, 40%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, *J* = 6.9 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 2H), 2.18 (s, 2H), 1.54 (q, *J* = 14.0 Hz, 2H), 0.11 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.32 (t, *J* = 14.0 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.60 (s), 128.46 (q, *J* = 274.2 Hz), 128.45 (s), 128.15 (s), 124.54 (s), 25.26 (s), 22.23 (q, *J* = 29.1 Hz), -3.24 (s). IR (neat) ν = 3026, 2959, 2925, 2853, 1601, 1494, 1453, 1417, 1281, 1250, 1221, 1163, 1058, 1093, 1032, 908, 847, 829, 767, 737,700 cm^{-1}. HRMS (EI): calcd. for $C_{11}H_{15}F_3Si$ $[M]^+$: 232.0895, Found: 232.0894.

For the insertion into 1i: Into a mixture of **1i** (0.4 mmol, 71.7 mg, 1.0 equiv.), sulfonium salt **I** (0. 8 mmol, 334.7 mg, 2.0 equiv.), cesium carbonate (1.0 mmol, 325.8 mg, 2.5 equiv.), Fe(TPP)Cl (0.008 mmol, 5.6 mg, 2 mol %) and $Na_2S_2O_4$ (0.08 mmol, 14.0 mg, 20 mol %) was added toluene (3 mL) under N_2 atmosphere. The mixture was stirred at 80 ^{o}C for 2 hours and then was subjected to flash column chromatography with the use of hexane/dichloromethane (100:1-10:1) as eluent to give the final product.

Tert-butoxy(butyl)(methyl)(2,2,2-trifluoroethyl)silane **(2i)**: Colorless oil, 45.2 mg, 44%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.60 (q, *J* = 14.1 Hz, 2H), 1.35 - 1.28 (m, 4H), 1.24 (s, 9H), 0.88 (t, *J* = 7.0 Hz, 3H), 0.68 - 0.61 (m, 2H), 0.24 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.47 (t, *J* = 14.1 Hz,

3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 128.13 (q, *J* = 274.1 Hz), 72.96 (s), 31.89 (s), 26.30 (s), 25.11 (s), 24.50 (q, *J* = 28.6 Hz), 17.47 (s), 13.69 (s), -0.08 (s). IR (neat) ν = 2976, 2930, 2875, 1466, 1412, 1390, 1366, 1282, 1253, 1221, 1196, 1093, 1061, 1033, 878, 830, 817, 782 cm^{-1}. HRMS (EI): calcd. for $C_{10}H_{20}F_3OSi$ $[M\text{-}CH_3]^+$: 241.1236, Found: 241.1237.

For the insertion into 1k-1m: Into a mixture of **1l-m** (0.4 mmol, 1.0 equiv.), sulfonium salt **II** (0. 8 mmol, 320.3 mg, 2.0 equiv.), cesium fluoride (1.0 mmol, 151.9 mg, 2.5 equiv.), Fe(TPP)Cl (0.008 mmol, 5.6 mg, 2 mol %) and Zinc powder (0.08 mmol, 5.2 mg, 20 mol %) was added DMF (4 mL) under N_2 atmosphere. The mixture was stirred at room temperature for 2 hours and then was diluted with CH_2Cl_2 (15 mL) and water (15 mL). The organic phase was separated and washed with water (15 mL, three times), and then dried over Na_2SO_4. After filtration, the solvent was removed by concentration. The residue was subjected to flash column chromatography with the use of hexane as eluent to give the final product **2l-m**.

Tributyl(2,2-difluoroethyl)silane **(2l)**: Colorless oil, 95.6 mg, 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 (tt, *J* = 58.3, 5.3 Hz, 1H), 1.36 - 1.19 (m, 14H), 0.87 (t, *J* = 7.1 Hz, 9H), 0.62 - 0.54 (m, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.14 (dt, *J* = 58.3, 21.7 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 117.95 (t, *J* = 238.1 Hz), 26.69 (s), 25.83 (s), 20.39 (t, *J* = 20.2 Hz), 13.72 (s), 12.27 (s). IR (neat) ν = 2958, 2924, 2873, 1465, 1415, 1379, 1352, 1297, 1238, 1200, 1111, 1082, 1013, 981, 953, 887, 794, 735 cm^{-1}. HRMS (EI): calcd. for $C_{12}H_{27}Si$ $[M\text{-}CH_2CF_2H]^+$: 199.1882, Found: 199.1888.

Tripentyl(2,2-difluoroethyl)silane **(2m)**: Colorless oil, 110.2 mg, 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 (tt, *J* = 58.3, 5.3 Hz, 1H), 1.40 - 1.14 (m, 20H), 0.87 (t, *J* = 6.7 Hz, 9H), 0.63 - 0.49 (m, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.15 (dt, *J* = 58.3, 21.7 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 117.91 (t, *J* = 238.2 Hz), 35.93 (s), 23.23 (s), 22.23 (s), 20.42 (t, *J* = 20.3 Hz), 13.95 (s), 12.50 (s). IR (neat) ν = 2958, 2922, 2858, 1466, 1414, 1379, 1198, 1111, 1096, 1018, 983, 958, 804,

737 cm^{-1}. HRMS (EI): calcd. for $C_{15}H_{33}Si$ $[M- CH_2CF_2H]^+$: 241.2352, Found: 241.2355.

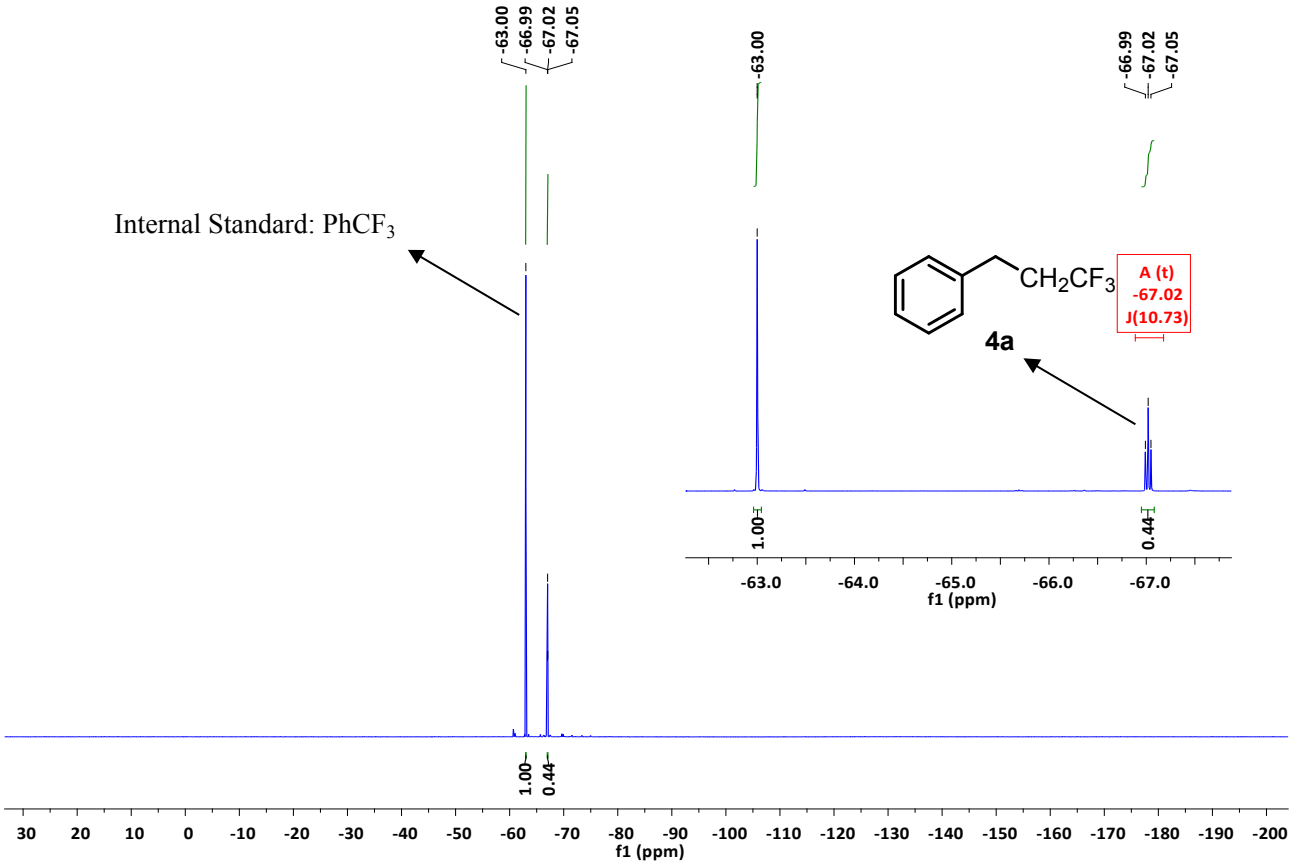
For the insertion into C-H bond: Into a mixture of Fe(TPP)Cl (0.005 mmol, 3.5 mg, 1 mol %) and $Na_2S_2O_4$ (0.1 mmol, 17.4 mg, 20 mol %) was added substrate (1 mL) under N_2 atmosphere. The mixture was stirred at 60°C for 10 min. Sulfonium salt **1** (0.5 mmol, 209.2 mg, 1.0 equiv), cesium carbonate (0.55 mmol, 179.2 mg, 1.1 equiv.) and substrate (2 mL) were then added. The resulting mixture was stirred at 80 °C for another 2 h and then was subjected to flash column chromatography with the use of hexane/dichloromethane (10:1) as eluent to give the crude product.

For the insertion into 5: Into a mixture of **5** (0.5 mmol, 95.0 mg, 1.0 equiv.), sulfonium salt **I** (1.0 mmol, 418.4 mg, 2.0 equiv.), cesium carbonate (1.0 mmol, 407.3 mg, 2.5 equiv.), Fe(TPP)Cl (0.01 mmol, 7.0 mg, 2 mol %) and $Na_2S_2O_4$ (0.1 mmol, 17.4 mg, 20 mol %) was added toluene (3 mL) under N_2 atmosphere. The mixture was stirred at 80 °C for 2 hours and then was subjected to flash column chromatography with the use of hexane/ethyl acetate (2:1-1:1) as eluent to give the final product.

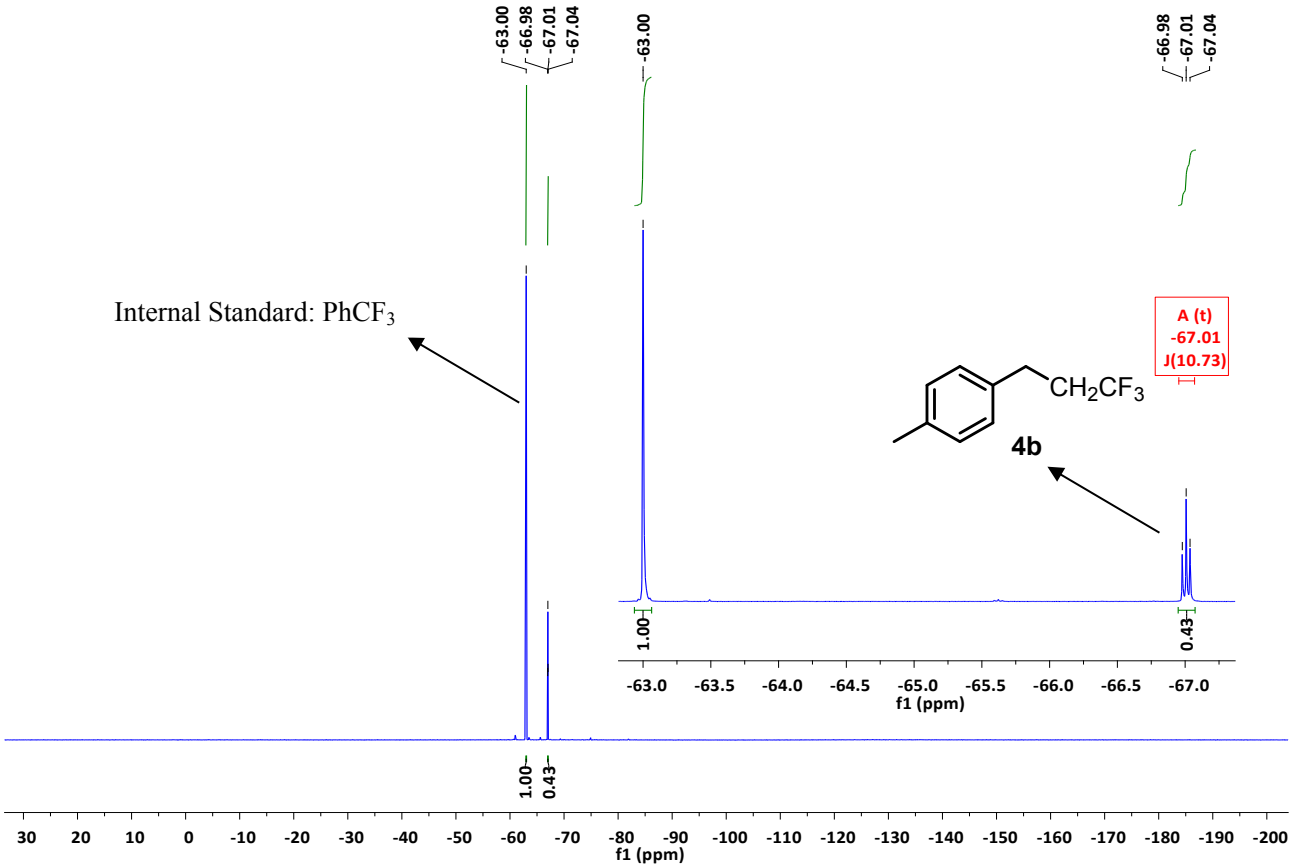
Diphenyl(2,2,2-trifluoroethyl)phosphane **(6)**: Colorless oil, 57.7 mg, 43%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 - 7.30 (m, 9H), 2.89 (q, J = 11.6 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.89 (dt, J = 14.5, 11.6 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.36 (d, J = 11.1 Hz), 132.66 (d, J = 20.5 Hz), 129.01 (d, J = 63.0 Hz), 128.77 (s), 126.53 (qd, J = 275.7, 16.2 Hz), 35.07 (qd, J = 27.6, 23.0 Hz). IR (neat) ν = 3056, 2924, 2850, 1482, 1435, 1413, 1292, 1259, 1229, 1111, 1071, 1047, 1027, 738, 695 cm^{-1}. HRMS (EI): calcd. for $C_{14}H_{12}F_3P$ $[M]^+$: 268.0629, Found: 268.0631.

5. ^{19}F NMR Spectra for C-H Insertion.

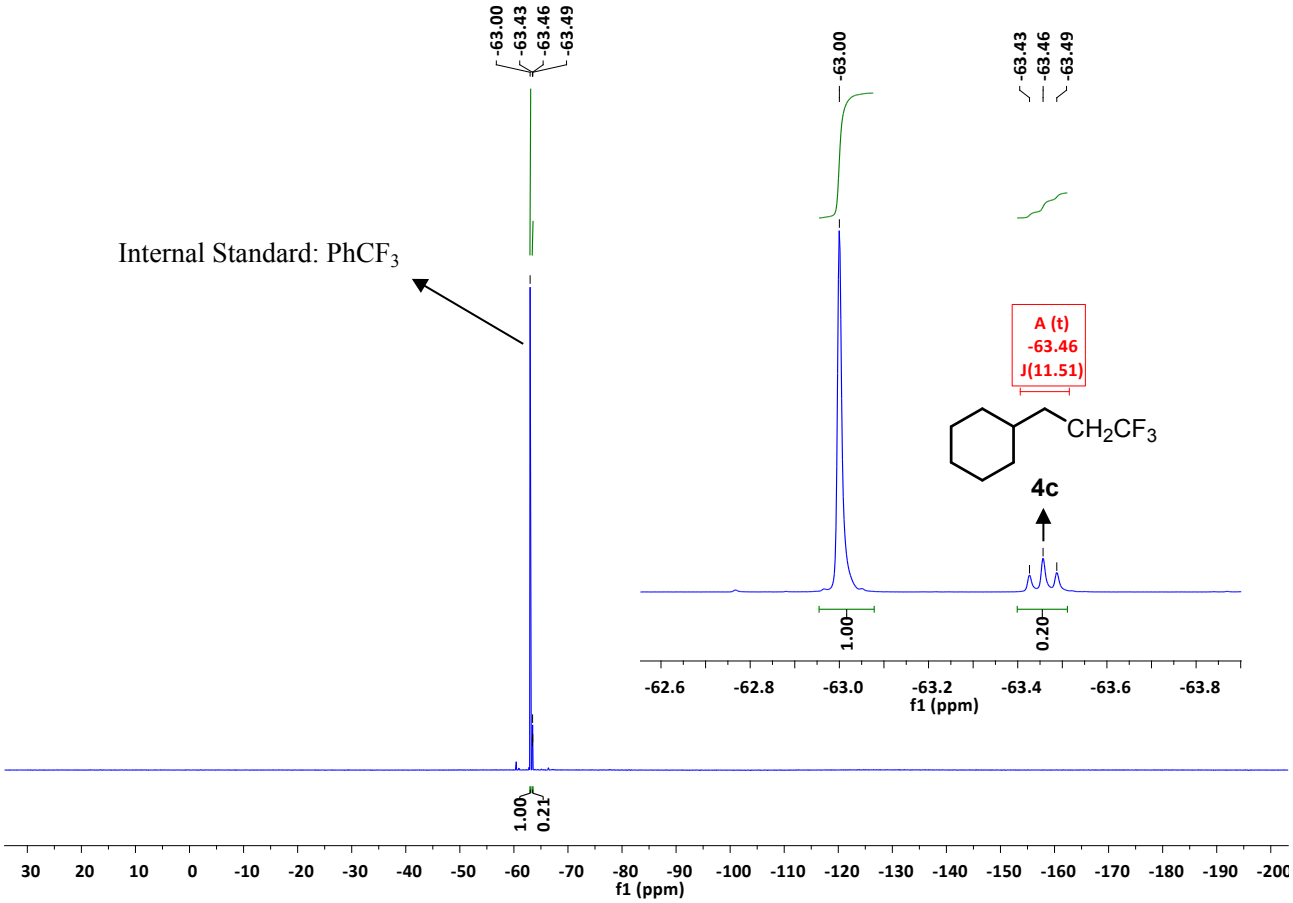
^{19}F NMR:



^{19}F NMR:



^{19}F NMR：



6. Reference

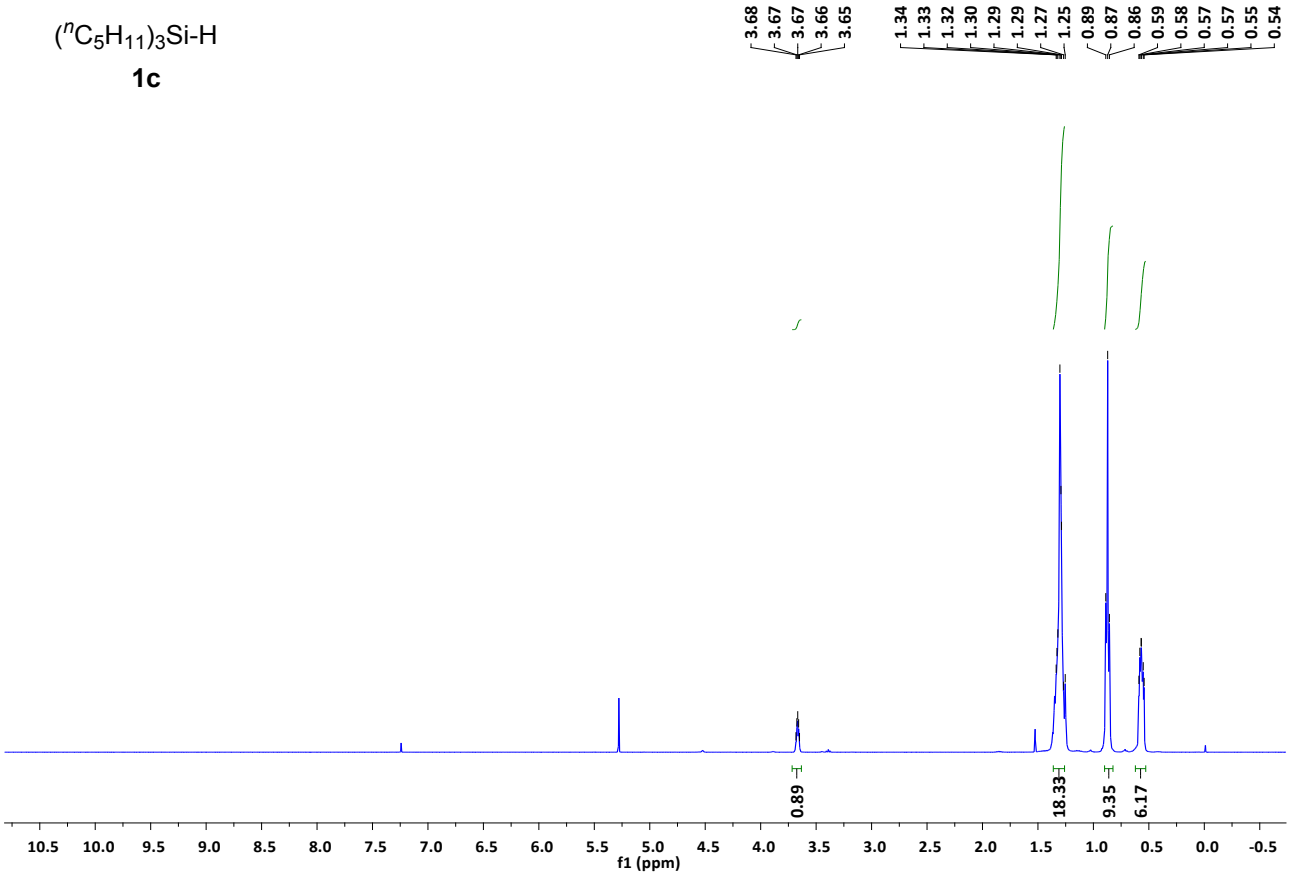
1. J. W. Jenkins and H. W. Post, *J. Org. Chem.*, 1950, **15**, 552-555.

7. Copies of ^{1}H NMR, ^{19}F NMR and ^{13}C NMR Spectra of 1c, 1f, 1g, 2, 6

^{1}H NMR:

$(^{n}C_5H_{11})_3Si\text{-}H$

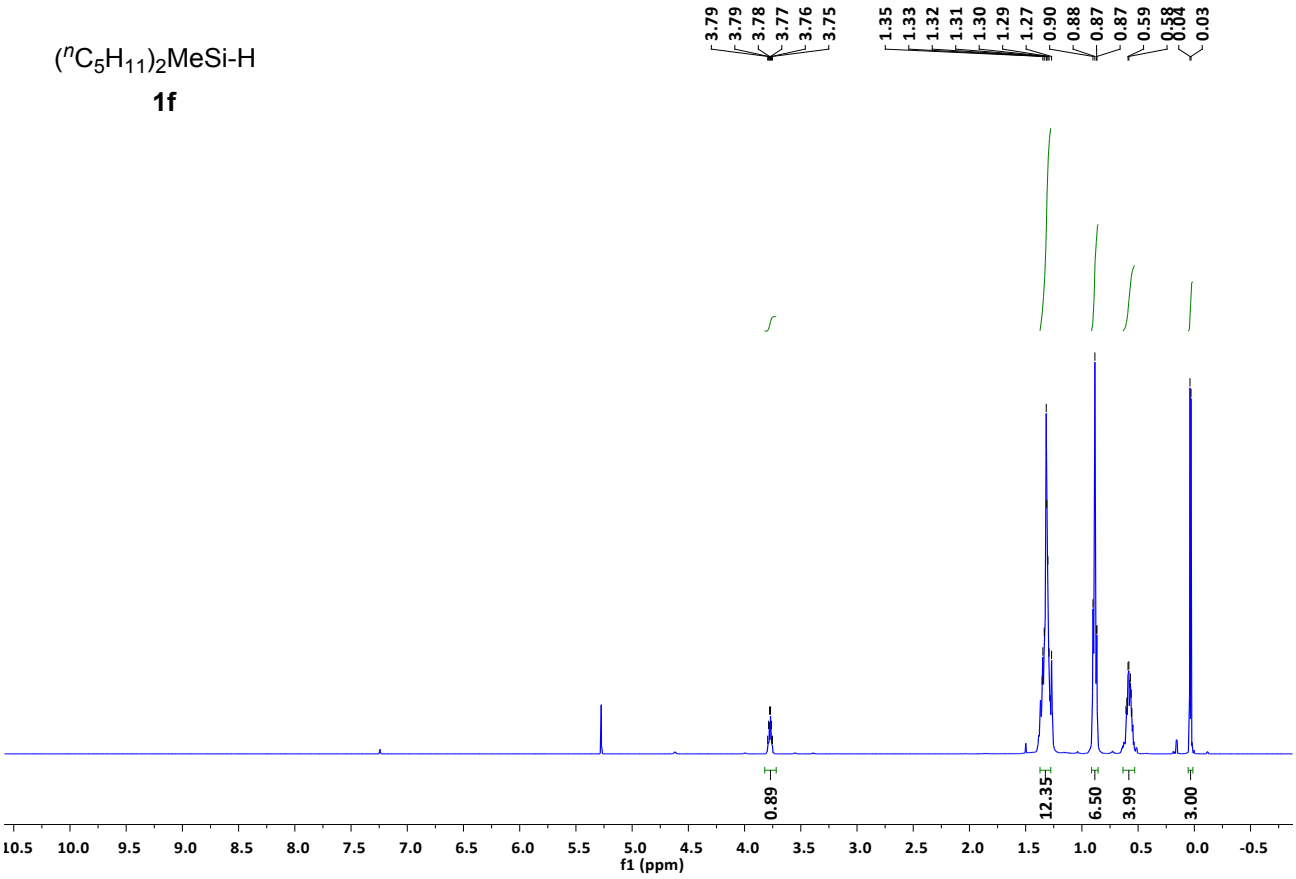
1c



^{1}H NMR:

$(^{n}C_5H_{11})_2MeSi\text{-}H$

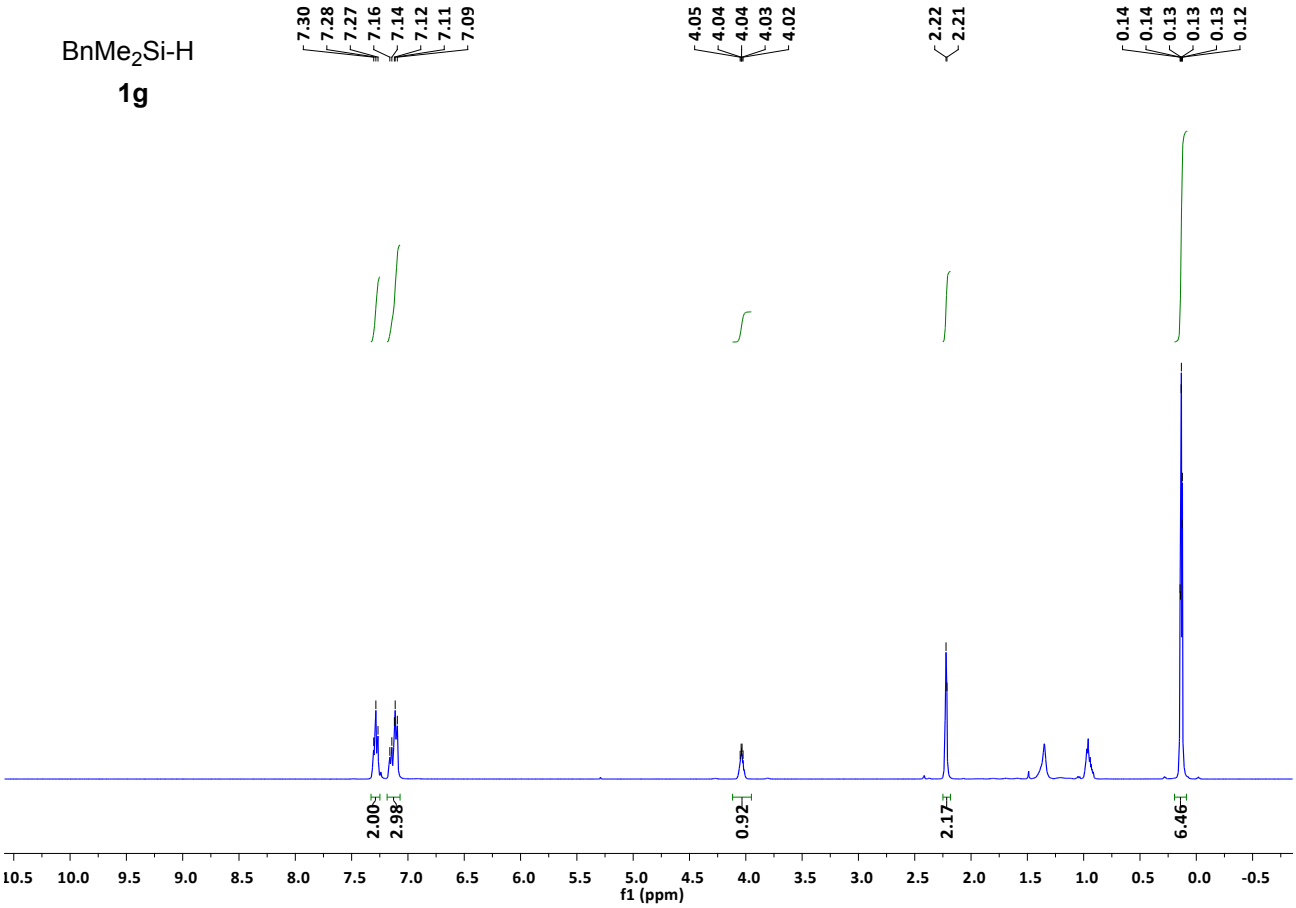
1f



^{1}H NMR：

$BnMe_2Si$-H

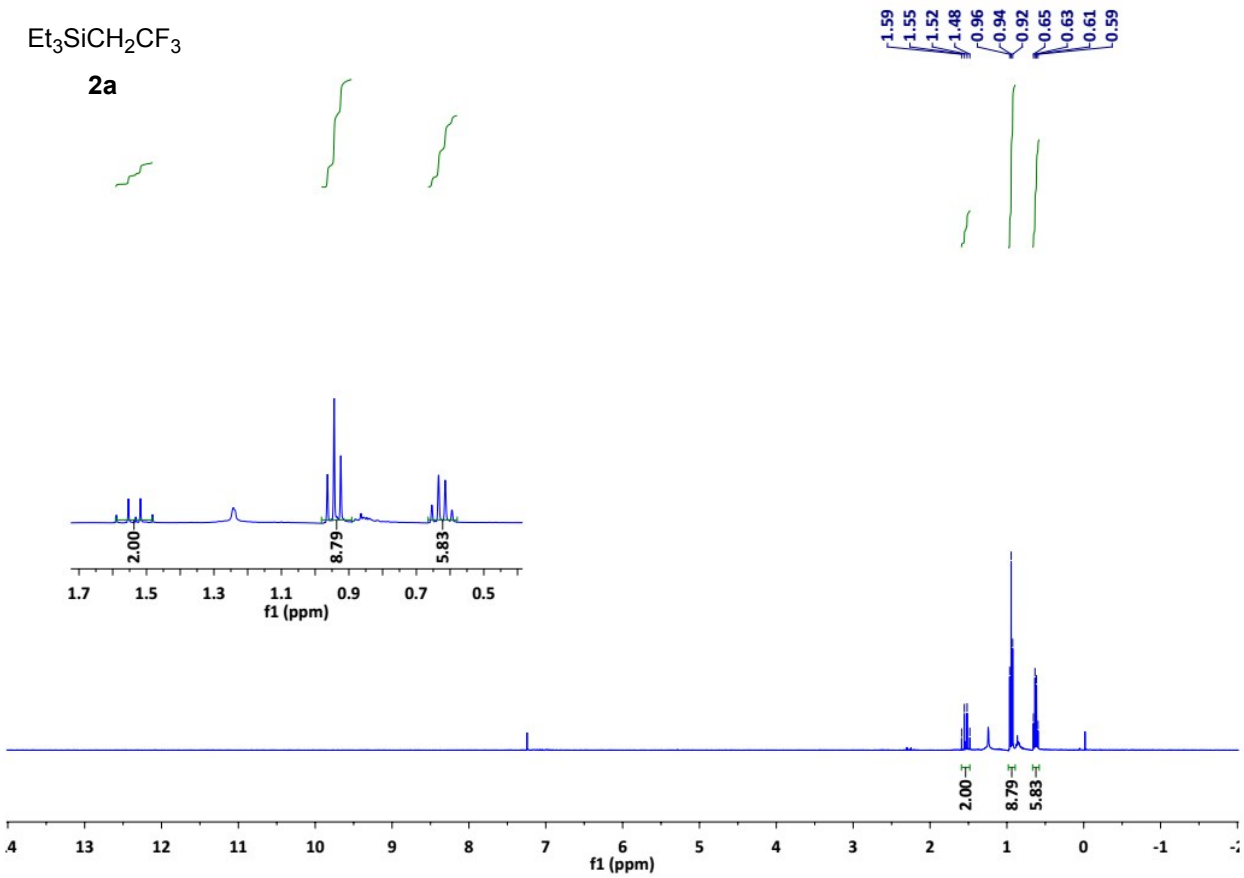
1g



^{1}H NMR：

$Et_3SiCH_2CF_3$

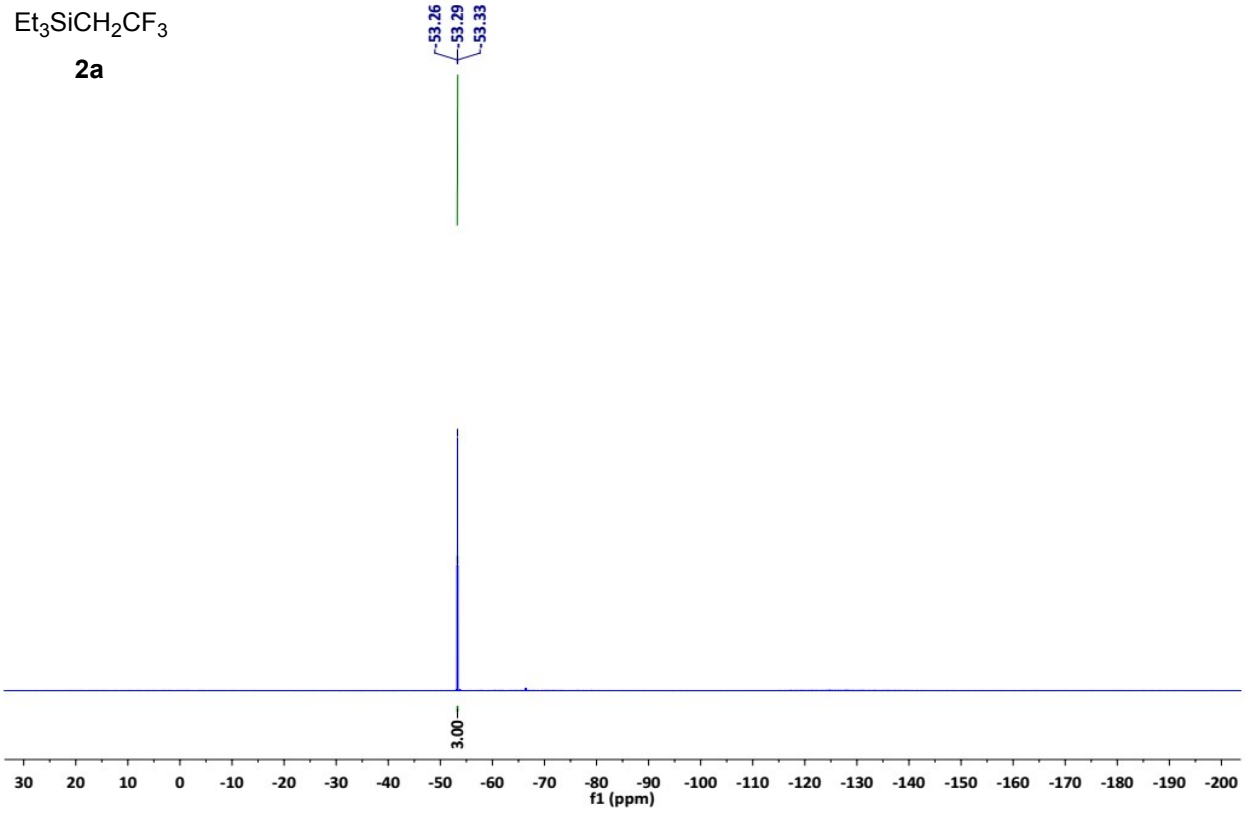
2a



^{19}F NMR：

$Et_3SiCH_2CF_3$

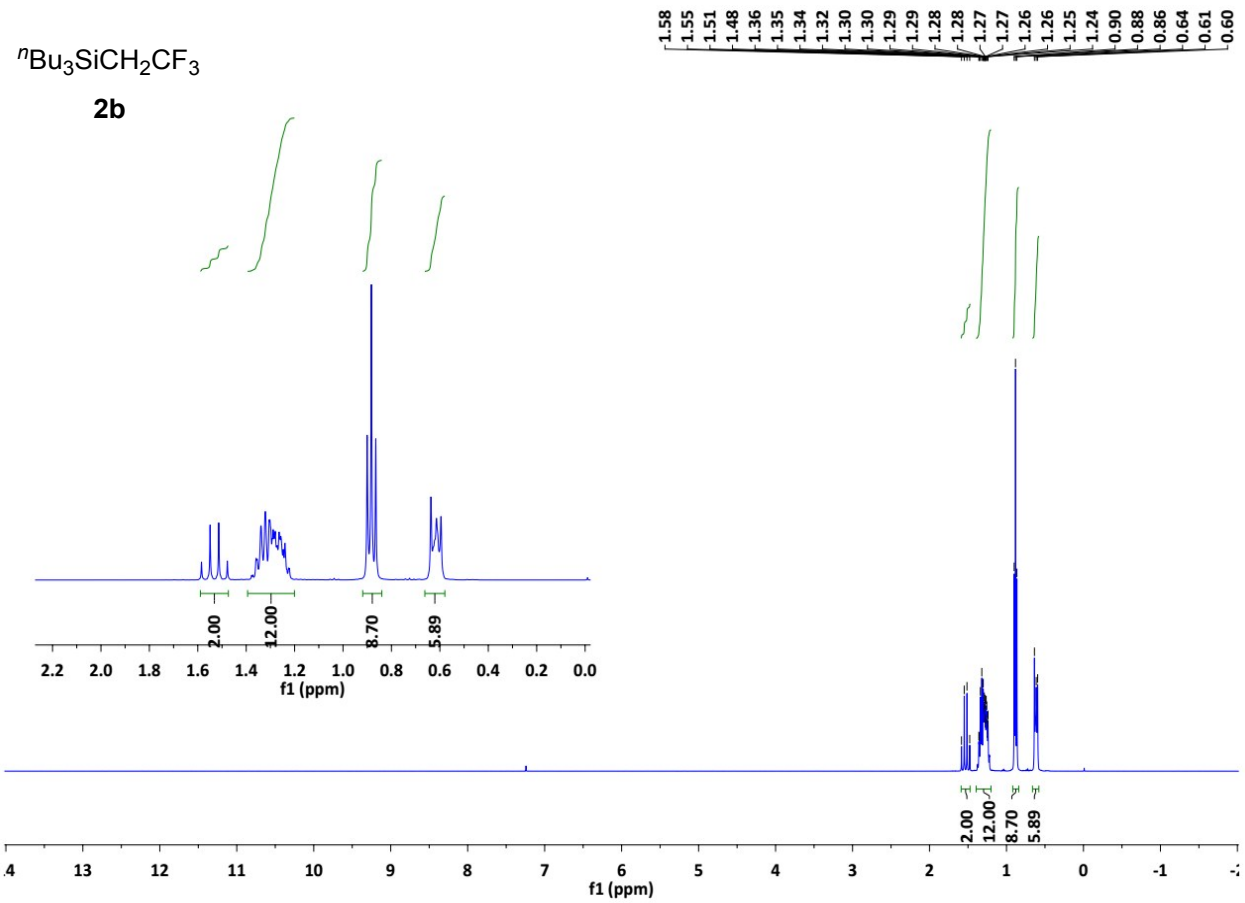
2a



^{1}H NMR：

$^{n}Bu_3SiCH_2CF_3$

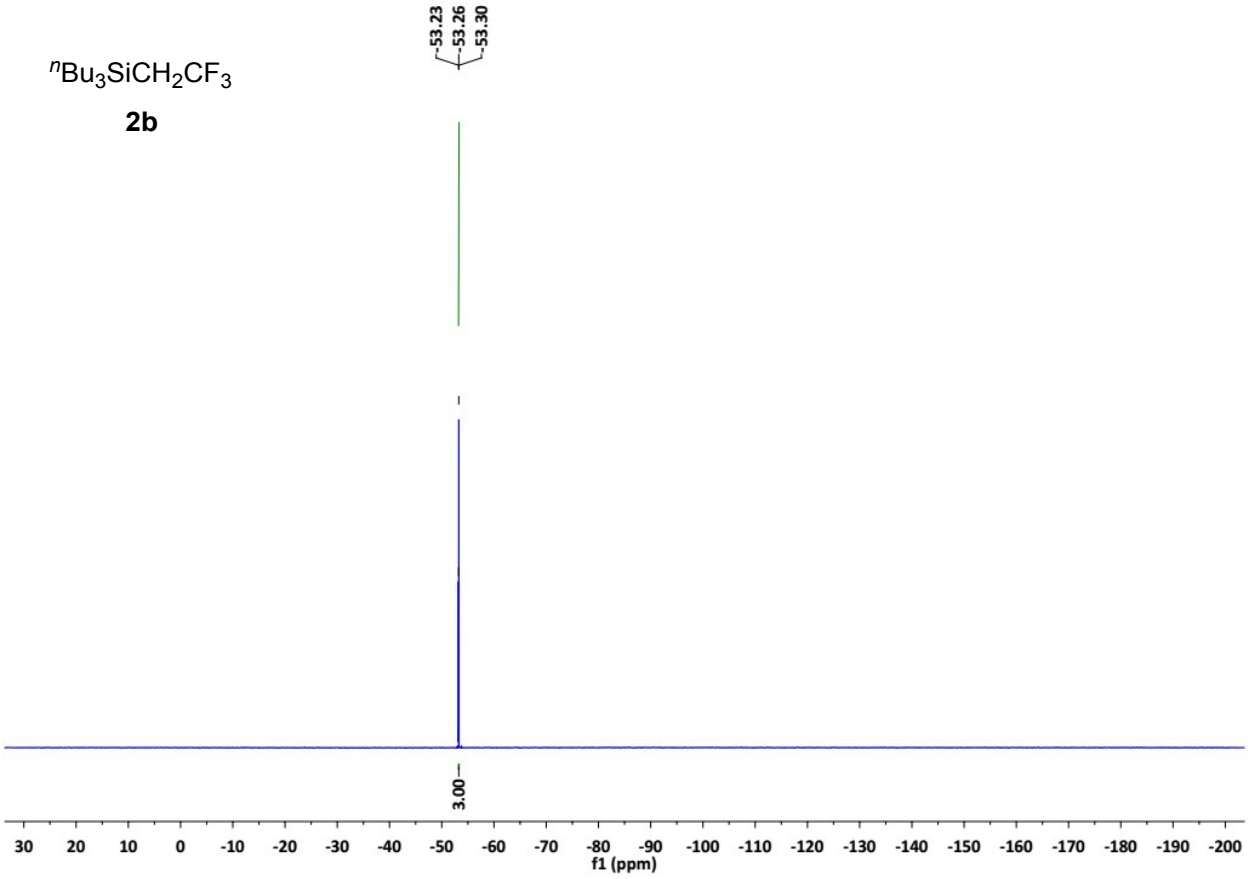
2b



^{19}F NMR：

$^{n}Bu_3SiCH_2CF_3$

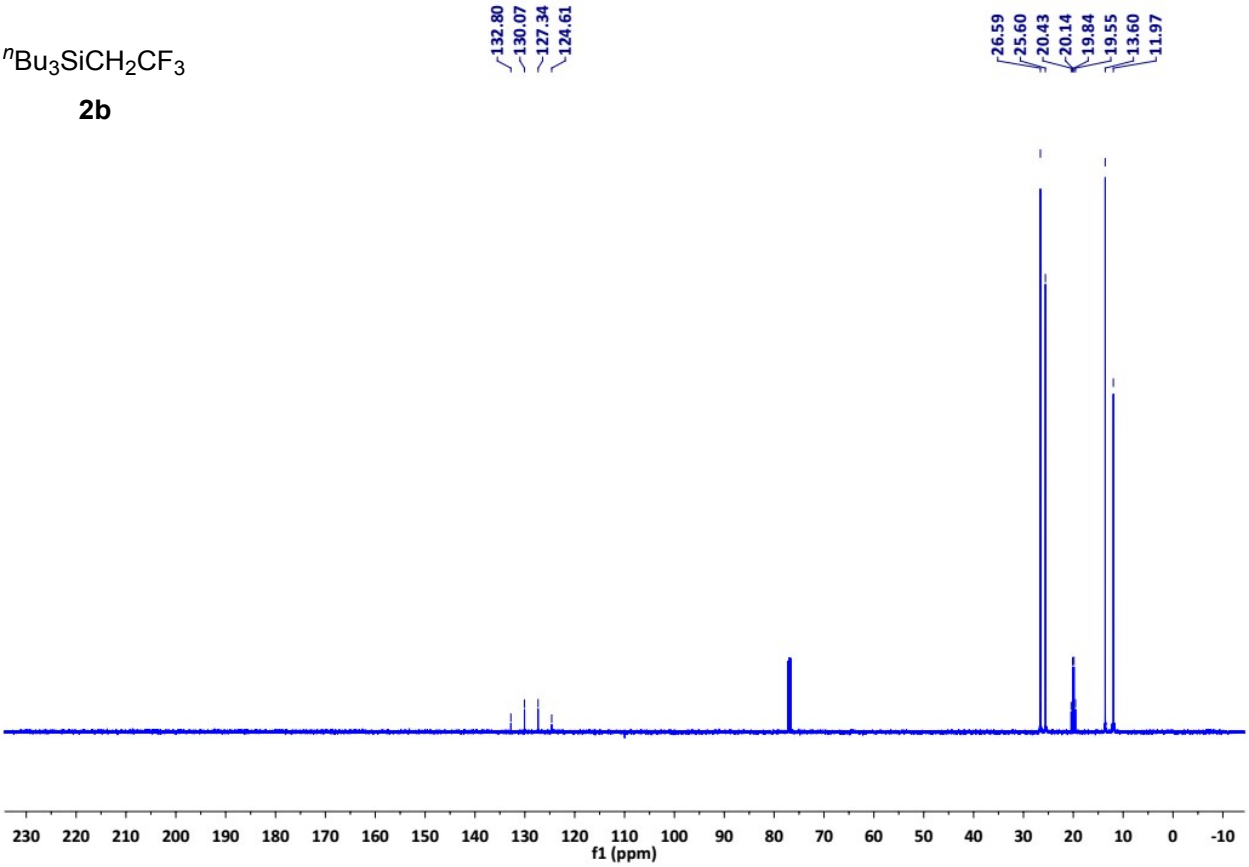
2b



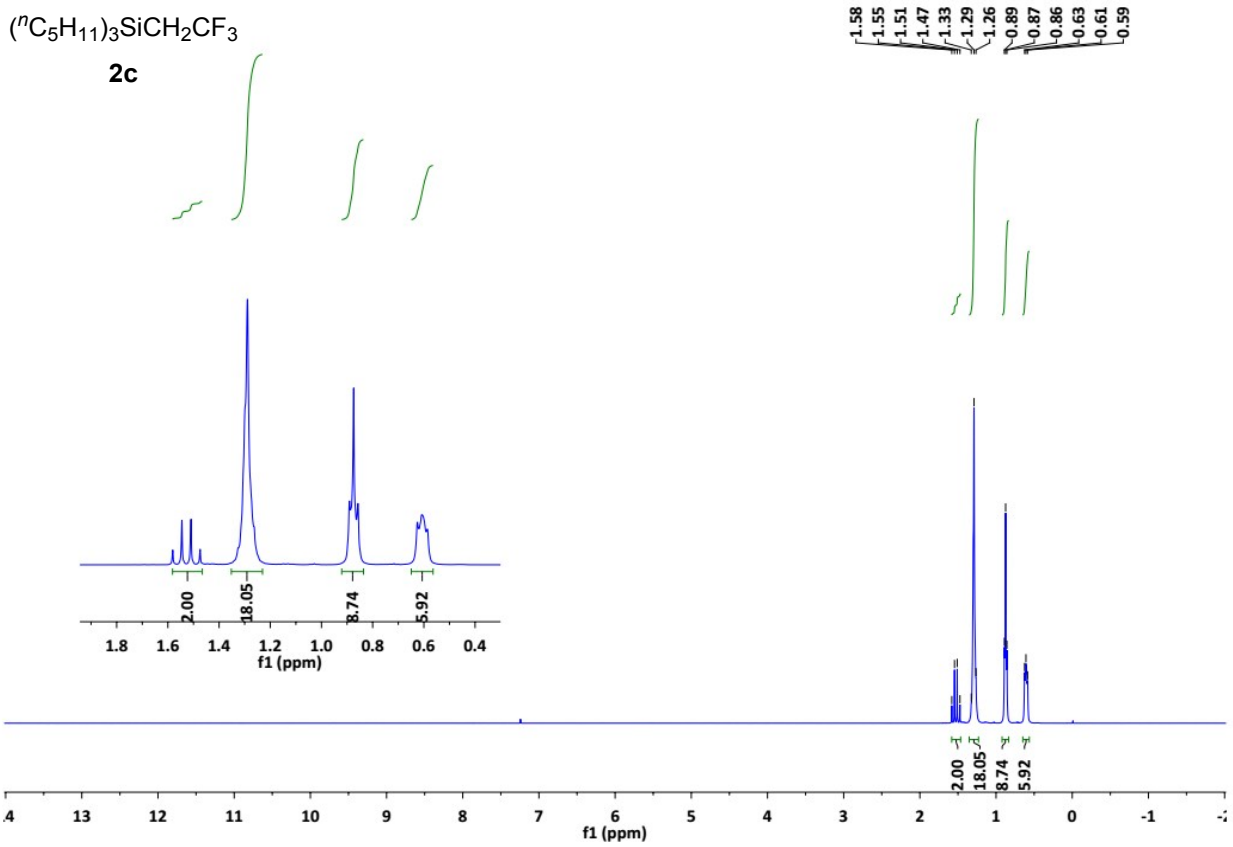
^{13}C NMR：

$^{n}Bu_3SiCH_2CF_3$

2b



^{1}H NMR：



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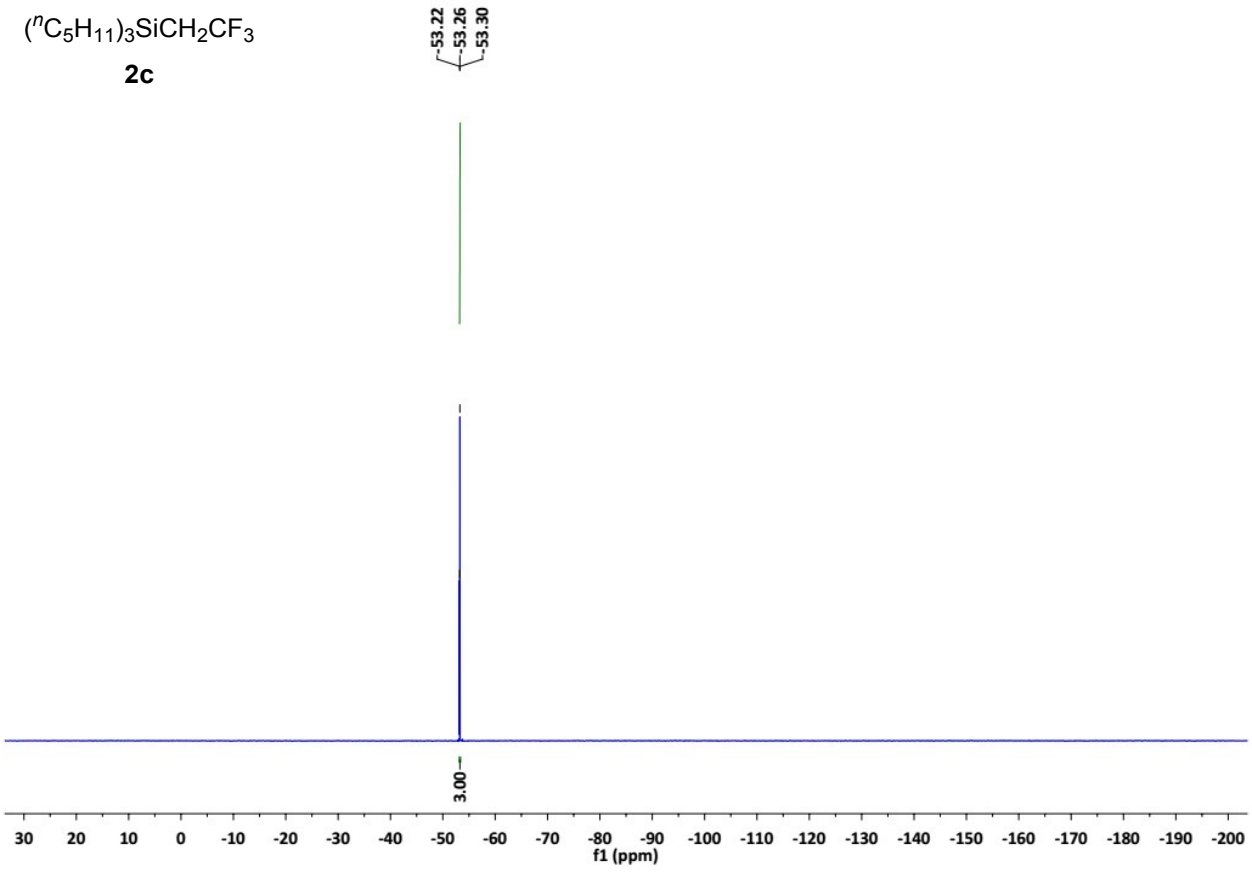
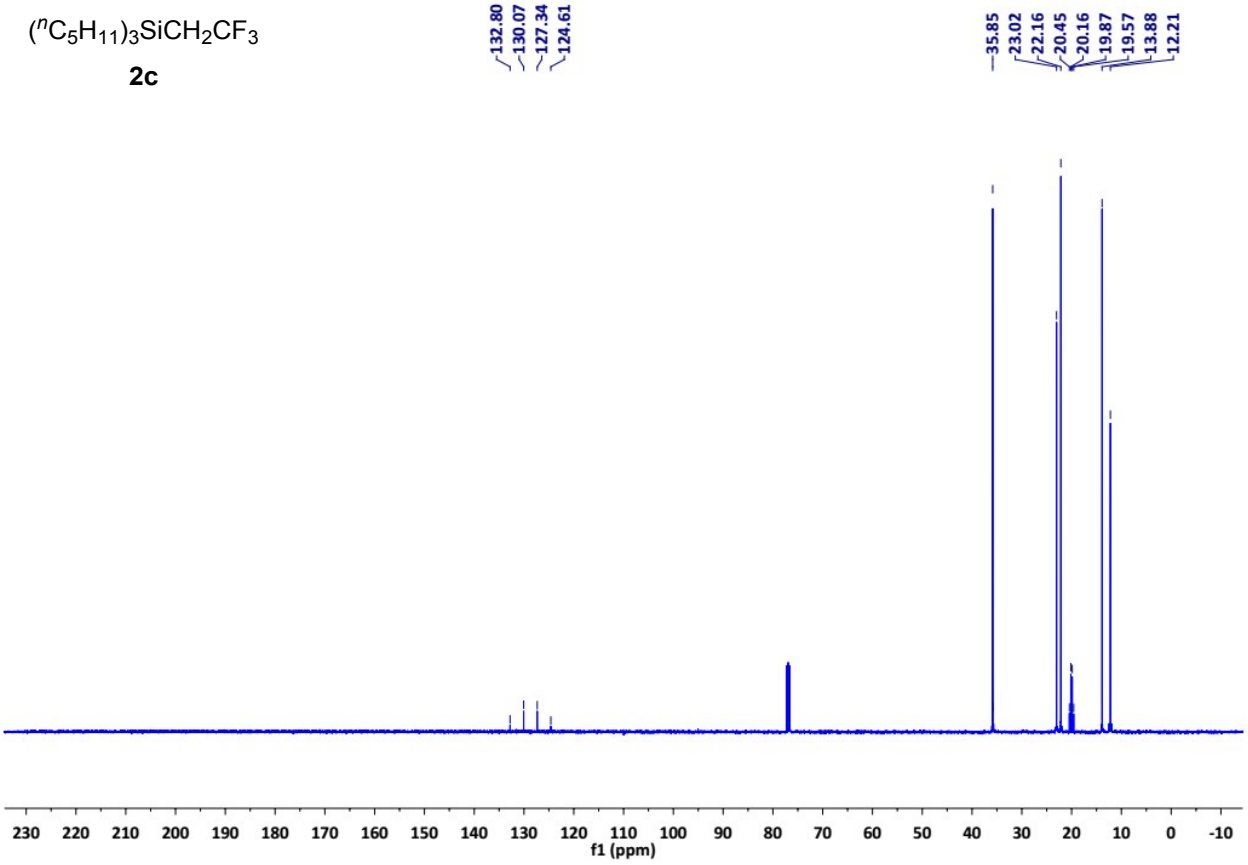


^{13}C NMR：

$(^{n}C_5H_{11})_3SiCH_2CF_3$

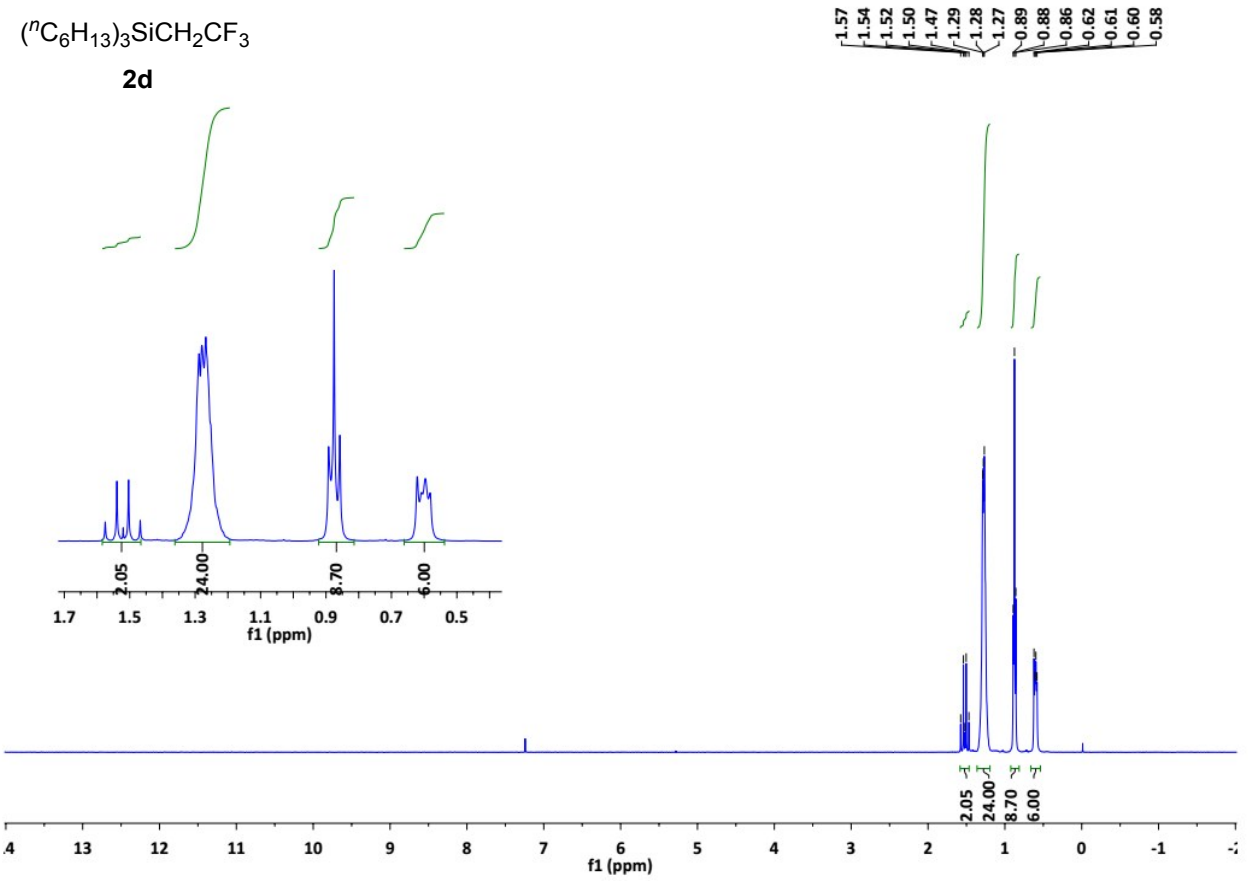
2c



^{1}H NMR：

$(^{n}C_6H_{13})_3SiCH_2CF_3$

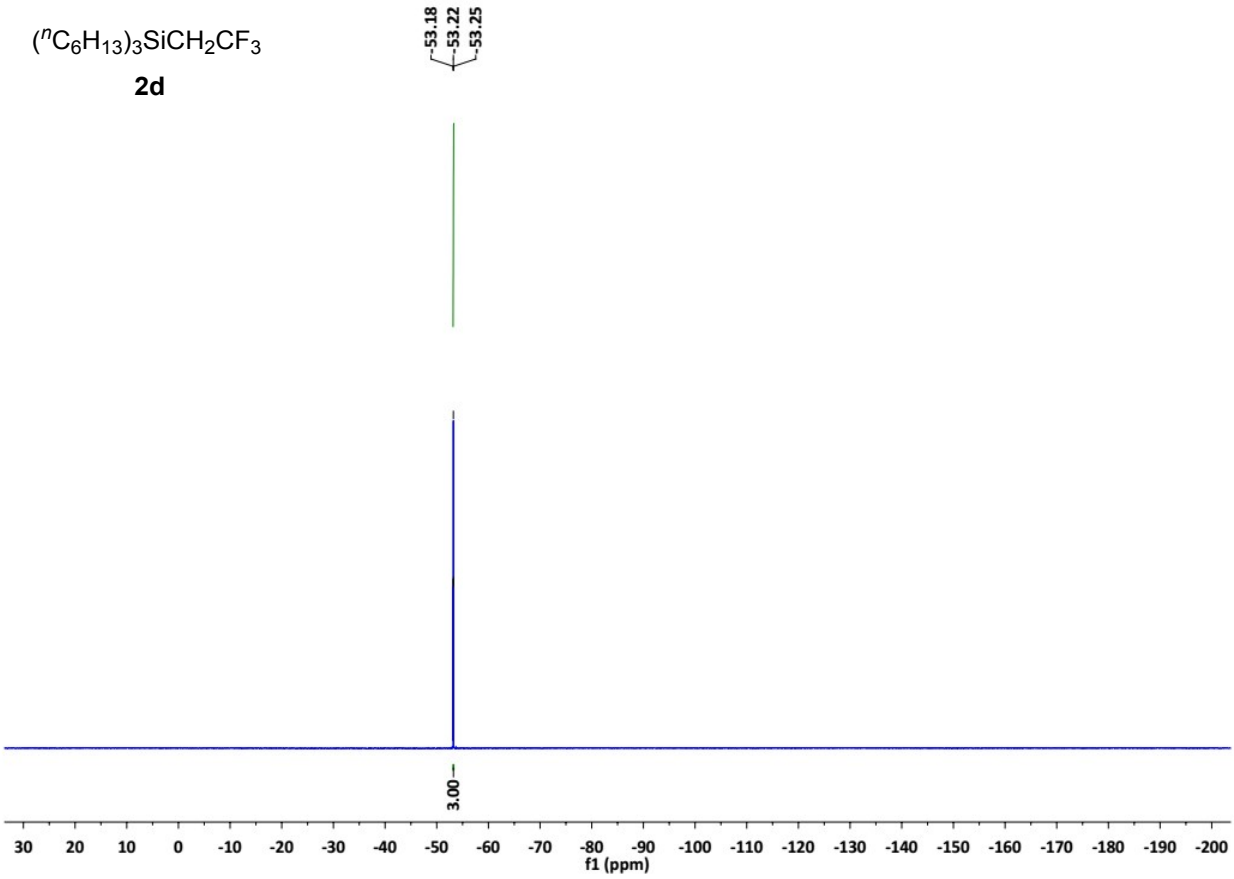
2d



^{19}F NMR：

$(^{n}C_6H_{13})_3SiCH_2CF_3$

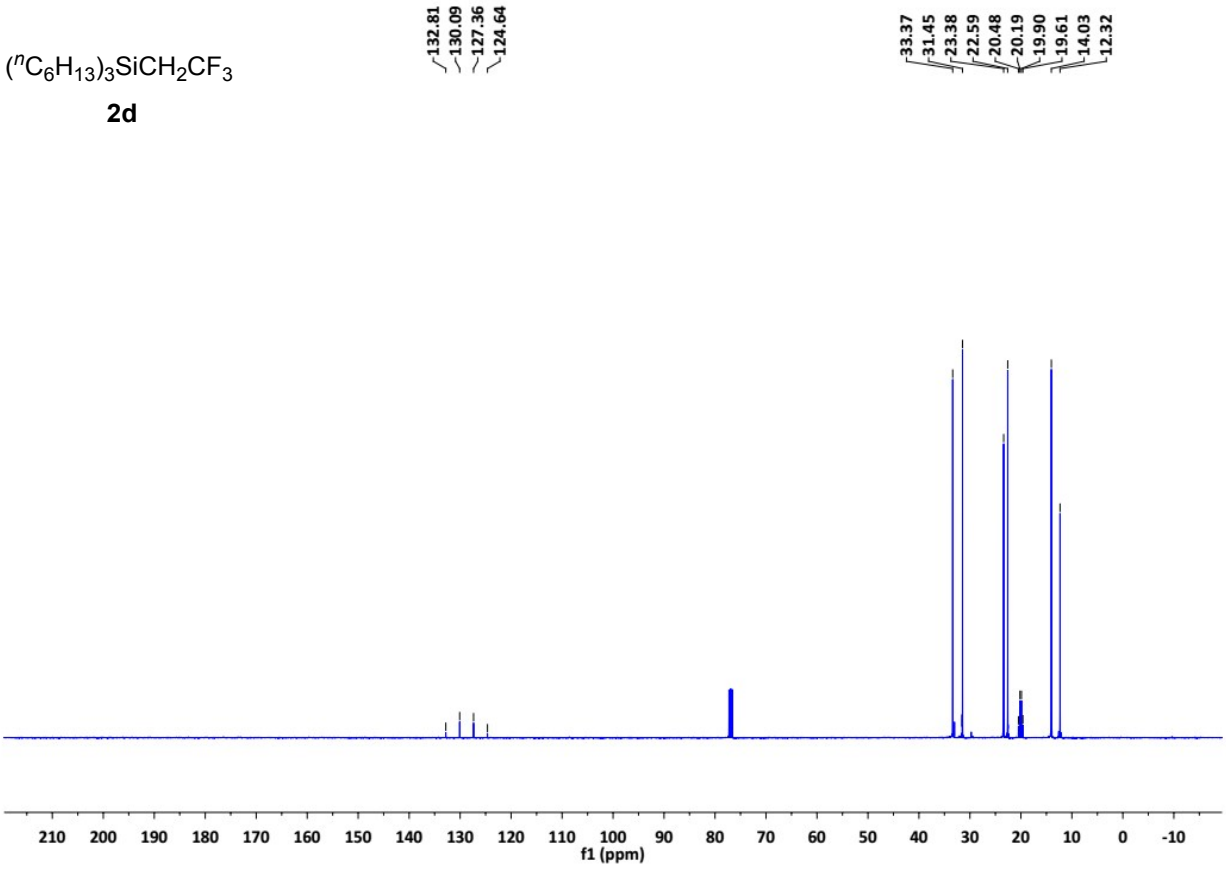
2d



^{13}C NMR：

$(^{n}C_6H_{13})_3SiCH_2CF_3$

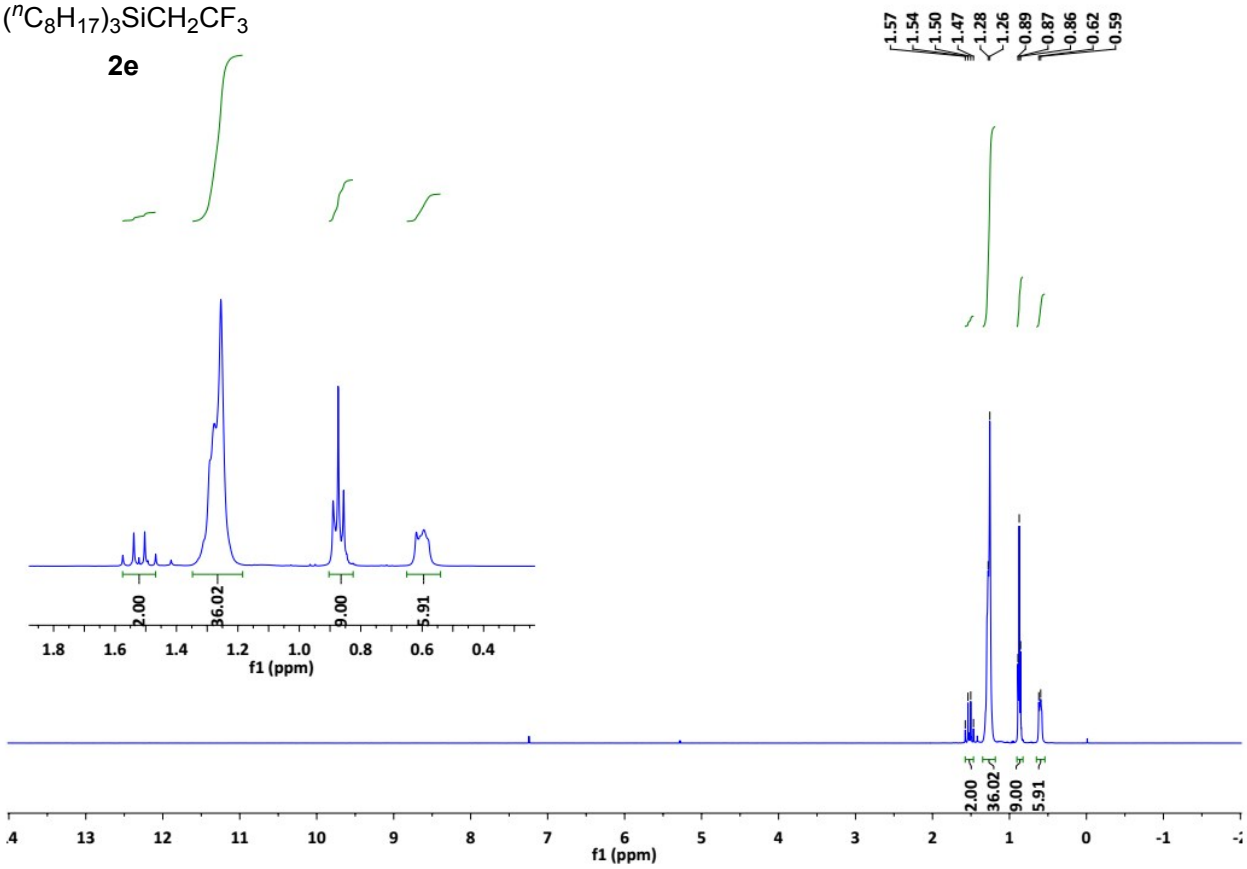
2d



^{1}H NMR：

$(^{n}C_8H_{17})_3SiCH_2CF_3$

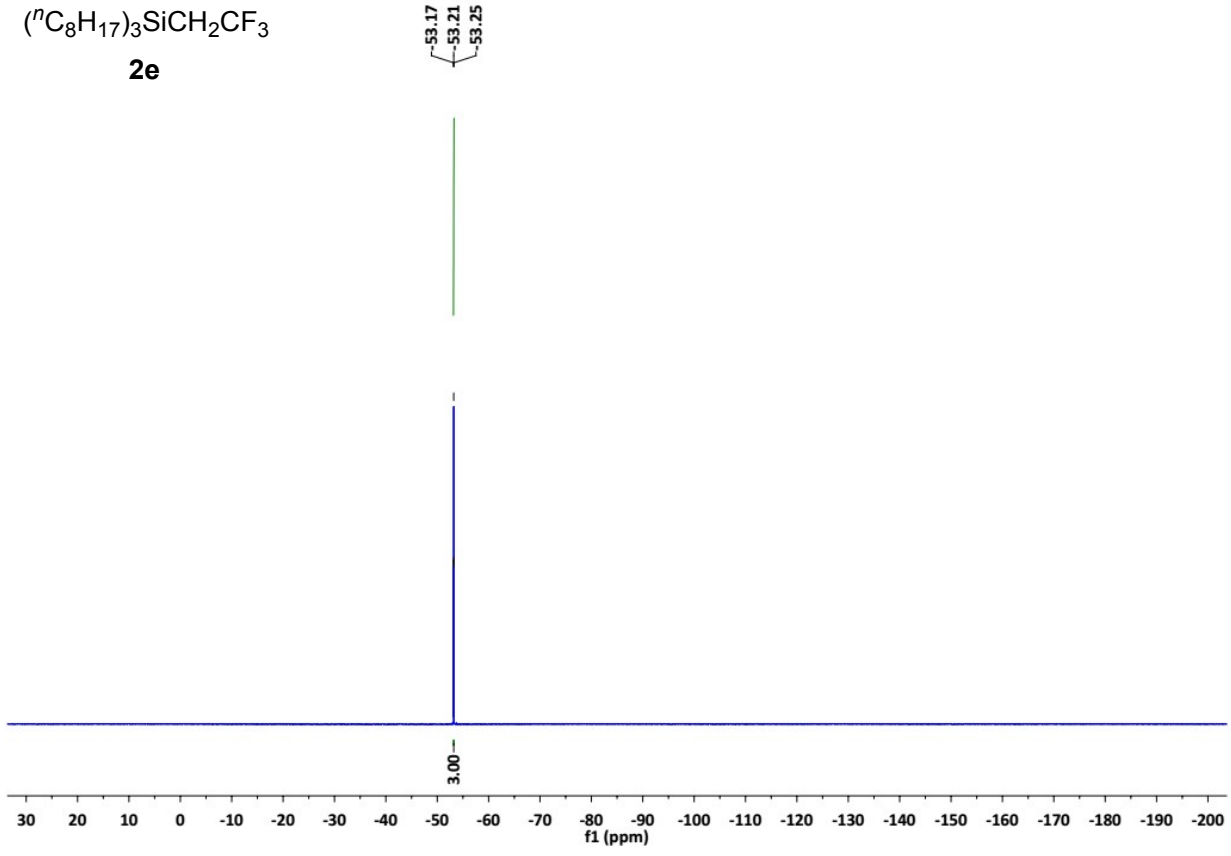
2e



^{19}F NMR：

$(^{n}C_8H_{17})_3SiCH_2CF_3$

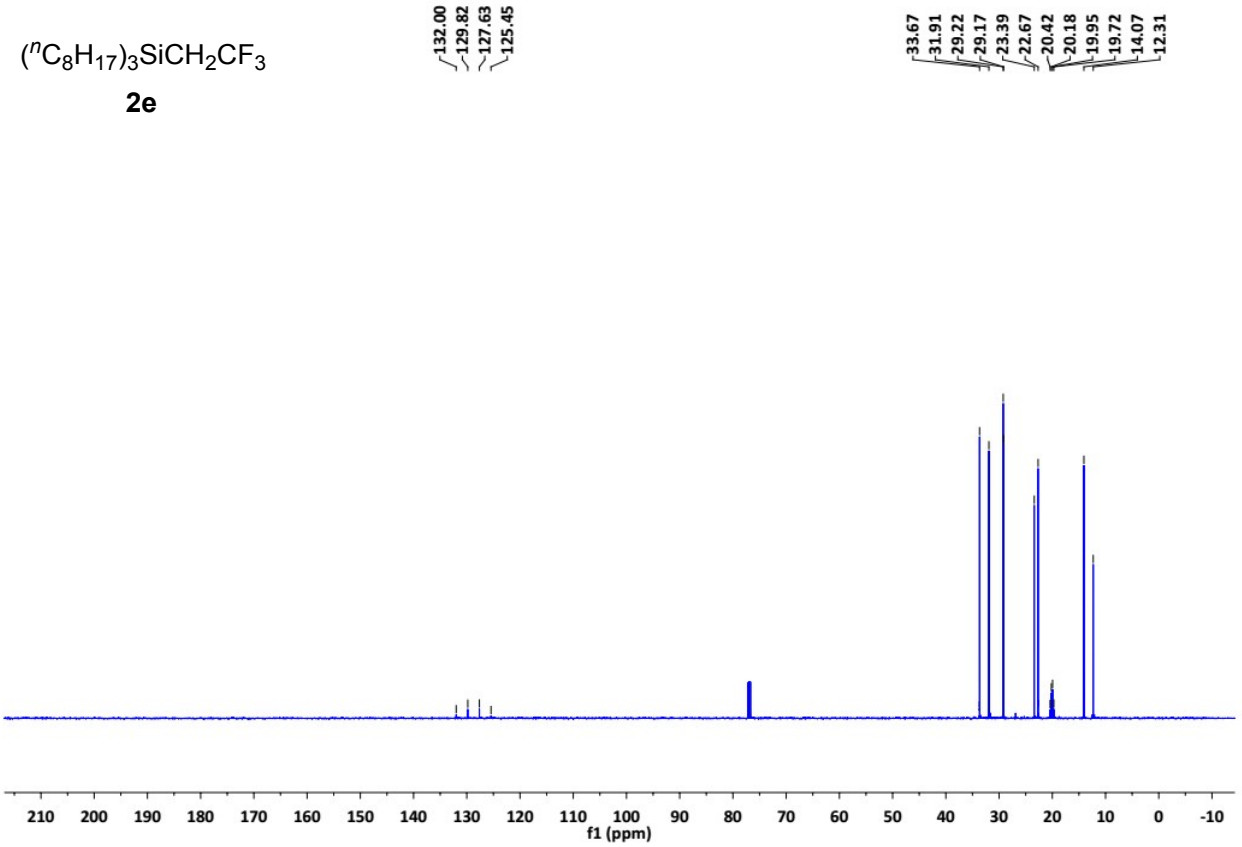
2e



^{13}C NMR：

$(^{n}C_8H_{17})_3SiCH_2CF_3$

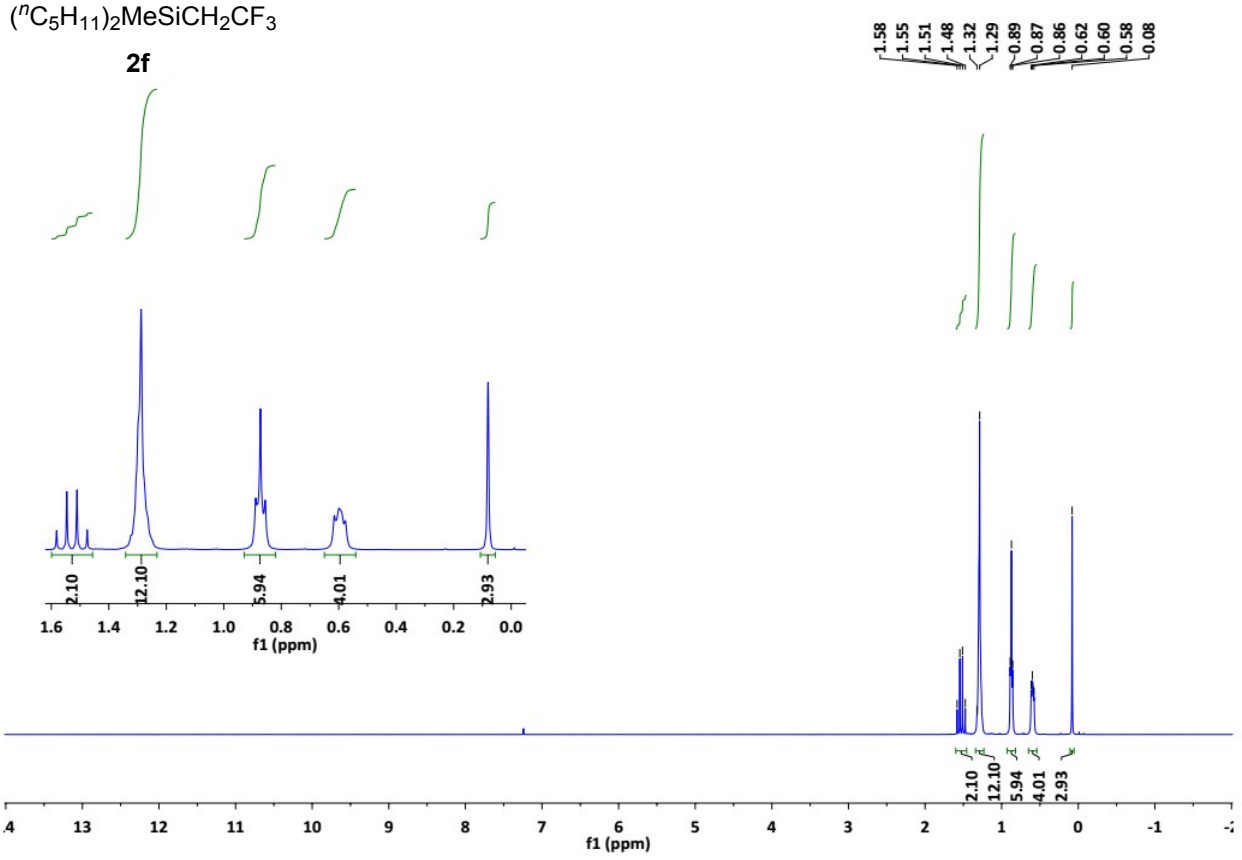
2e



^{1}H NMR：

$(^{n}C_5H_{11})_2MeSiCH_2CF_3$

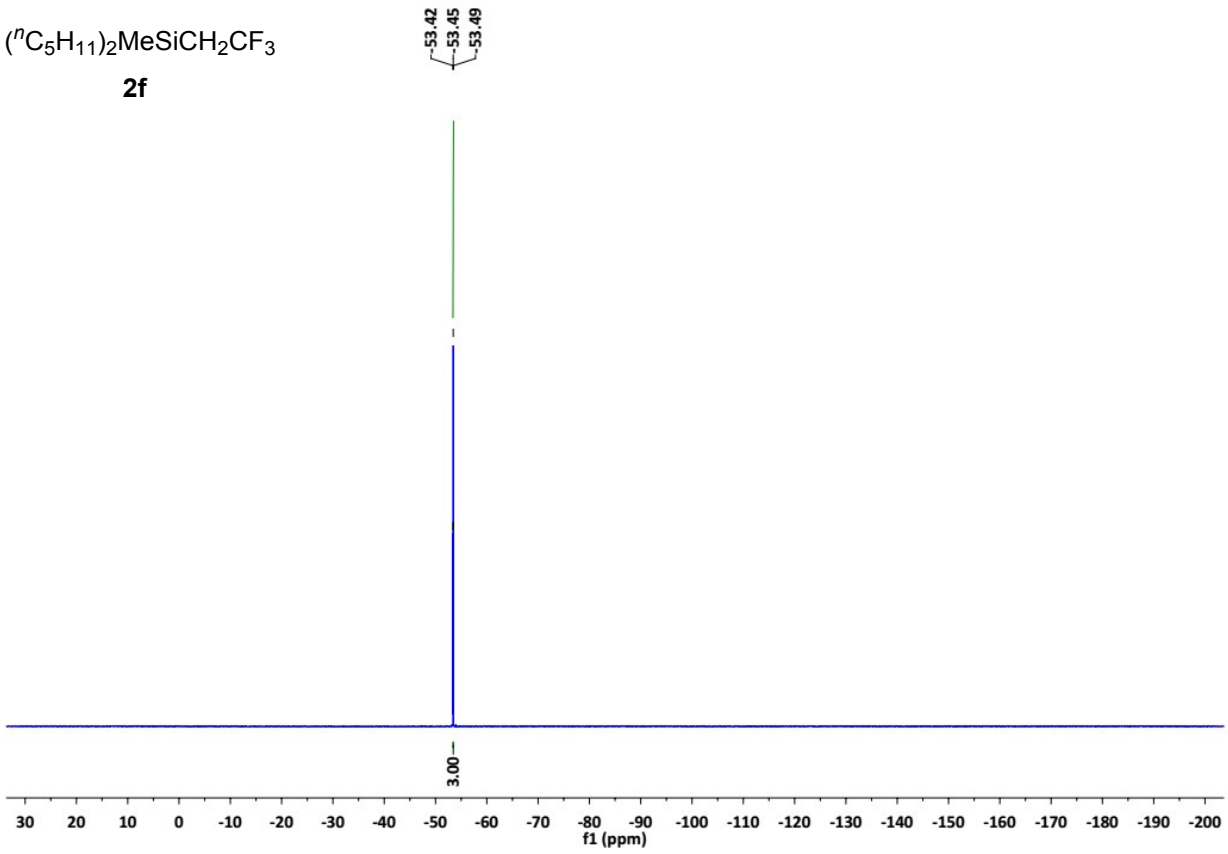
2f



^{19}F NMR：

$(^{n}C_5H_{11})_2MeSiCH_2CF_3$

2f



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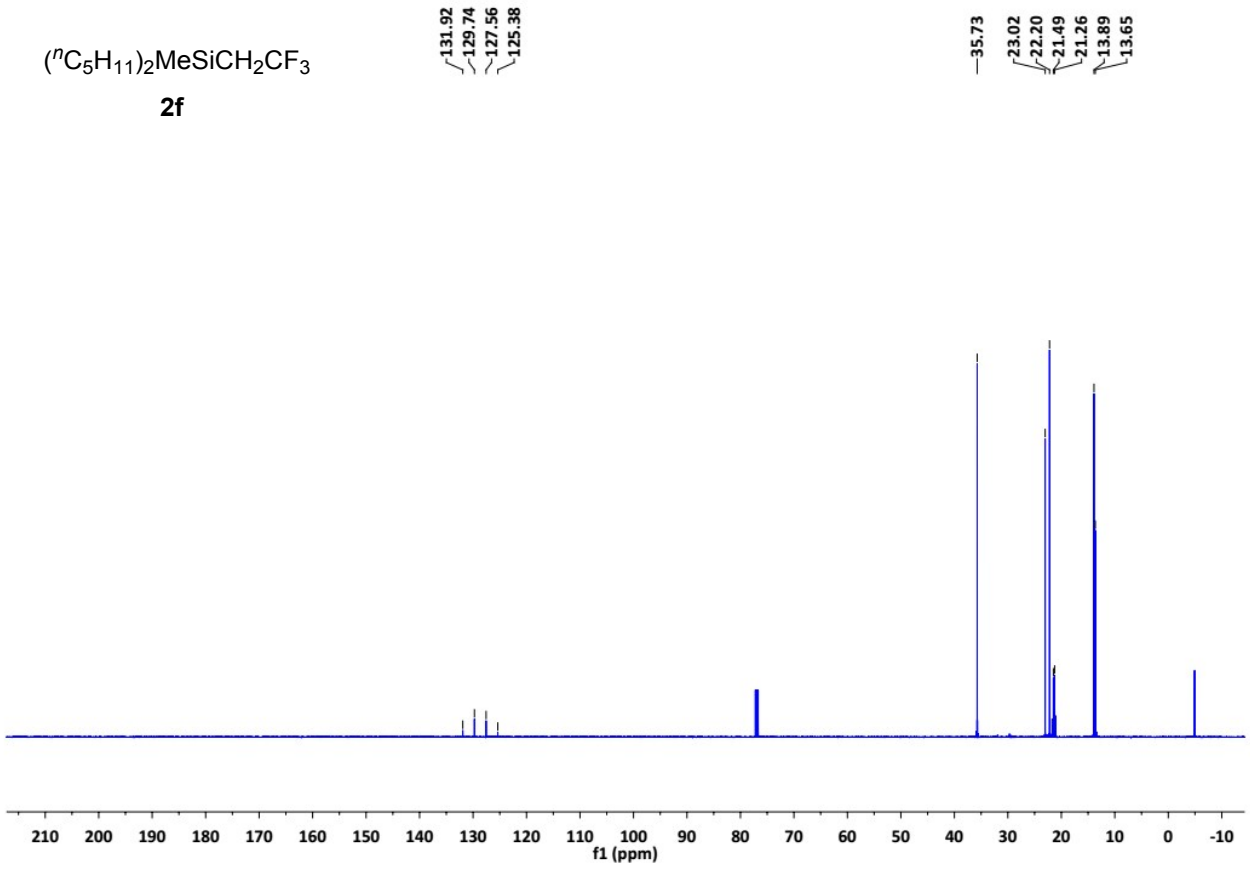
$(^{n}C_5H_{11})_2MeSiCH_2CF_3$

2f



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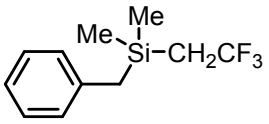

2g

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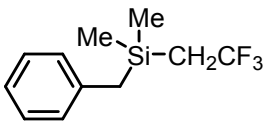

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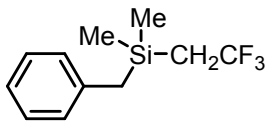

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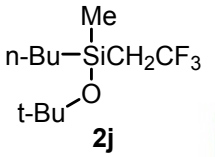

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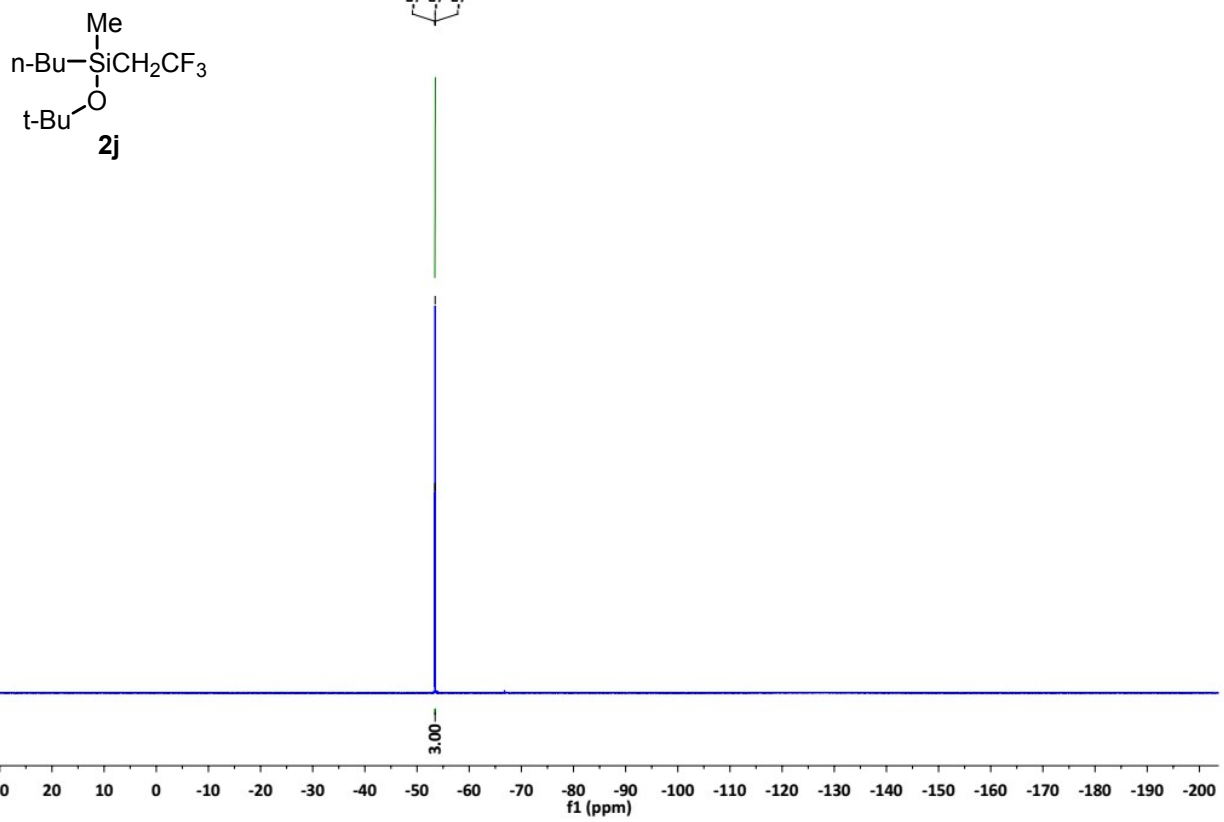

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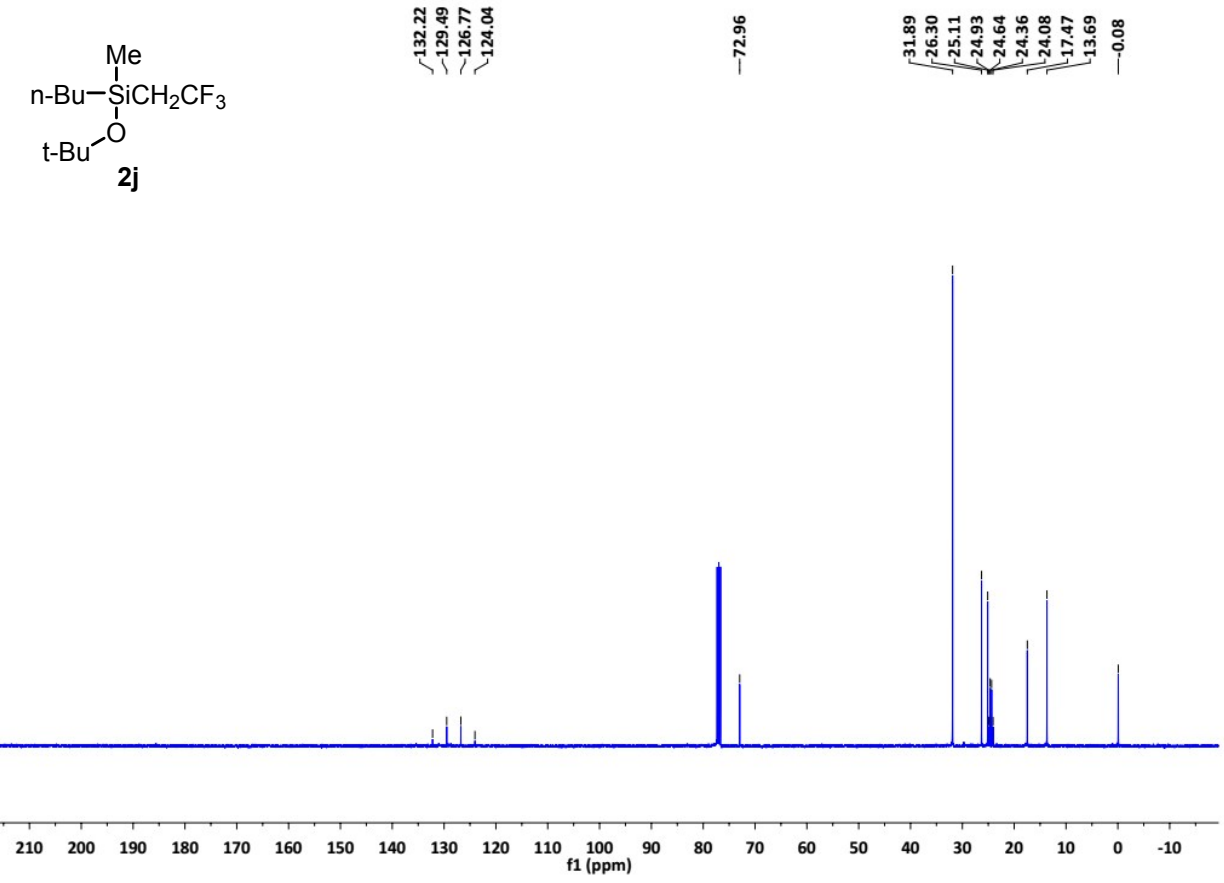
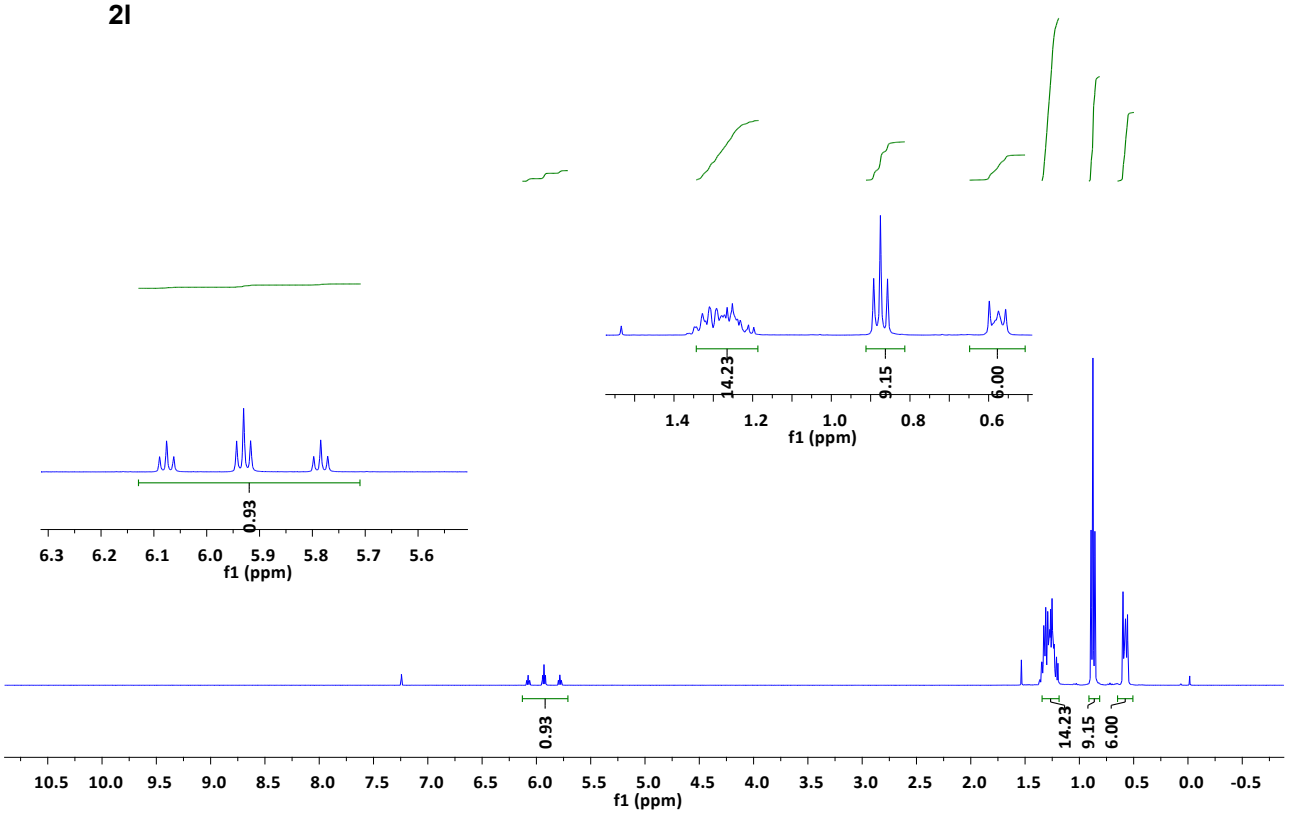


^{1}H NMR:

$^{n}Bu_3SiCH_2CF_2H$

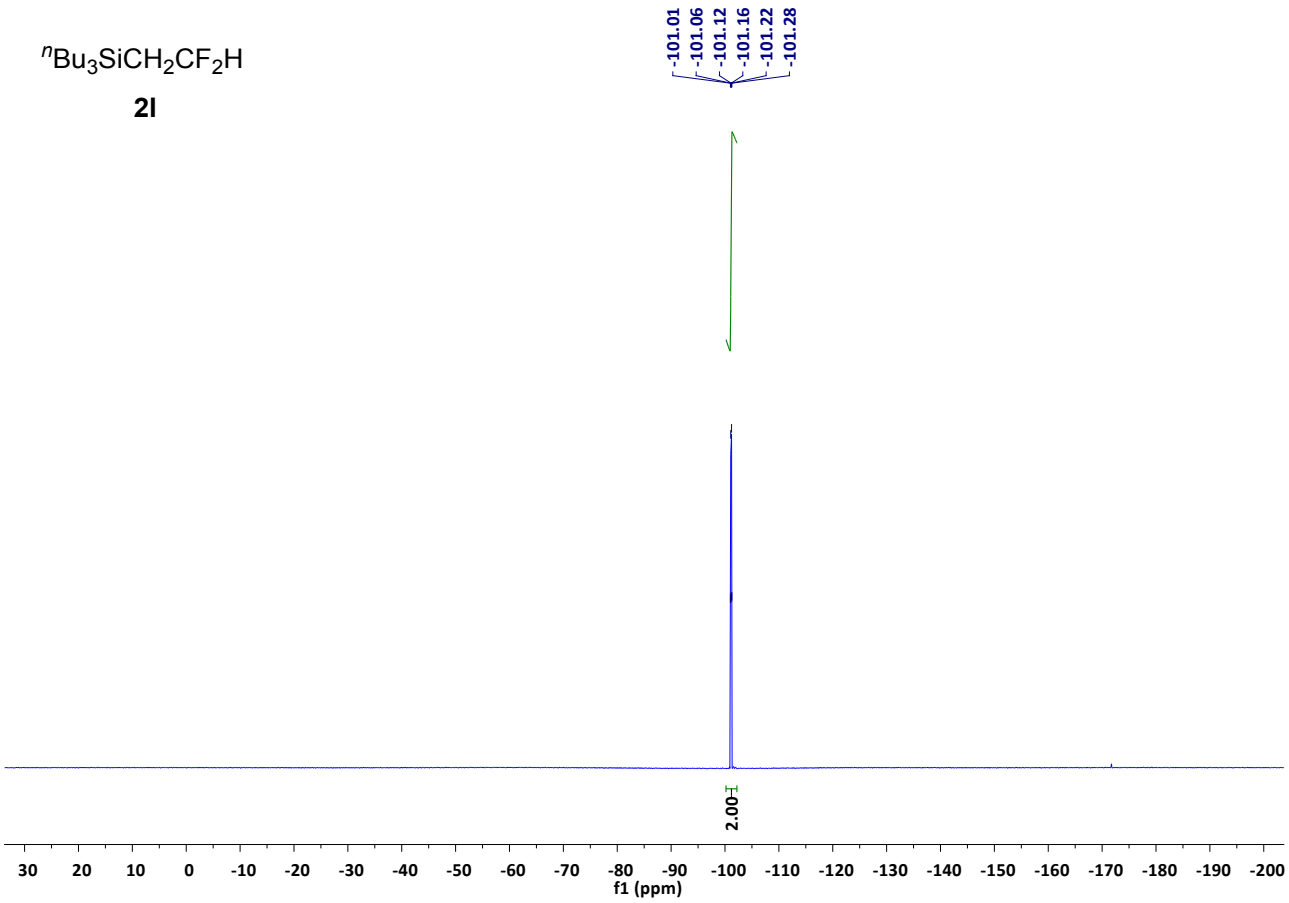
2l



^{19}F NMR:

$^{n}Bu_3SiCH_2CF_2H$

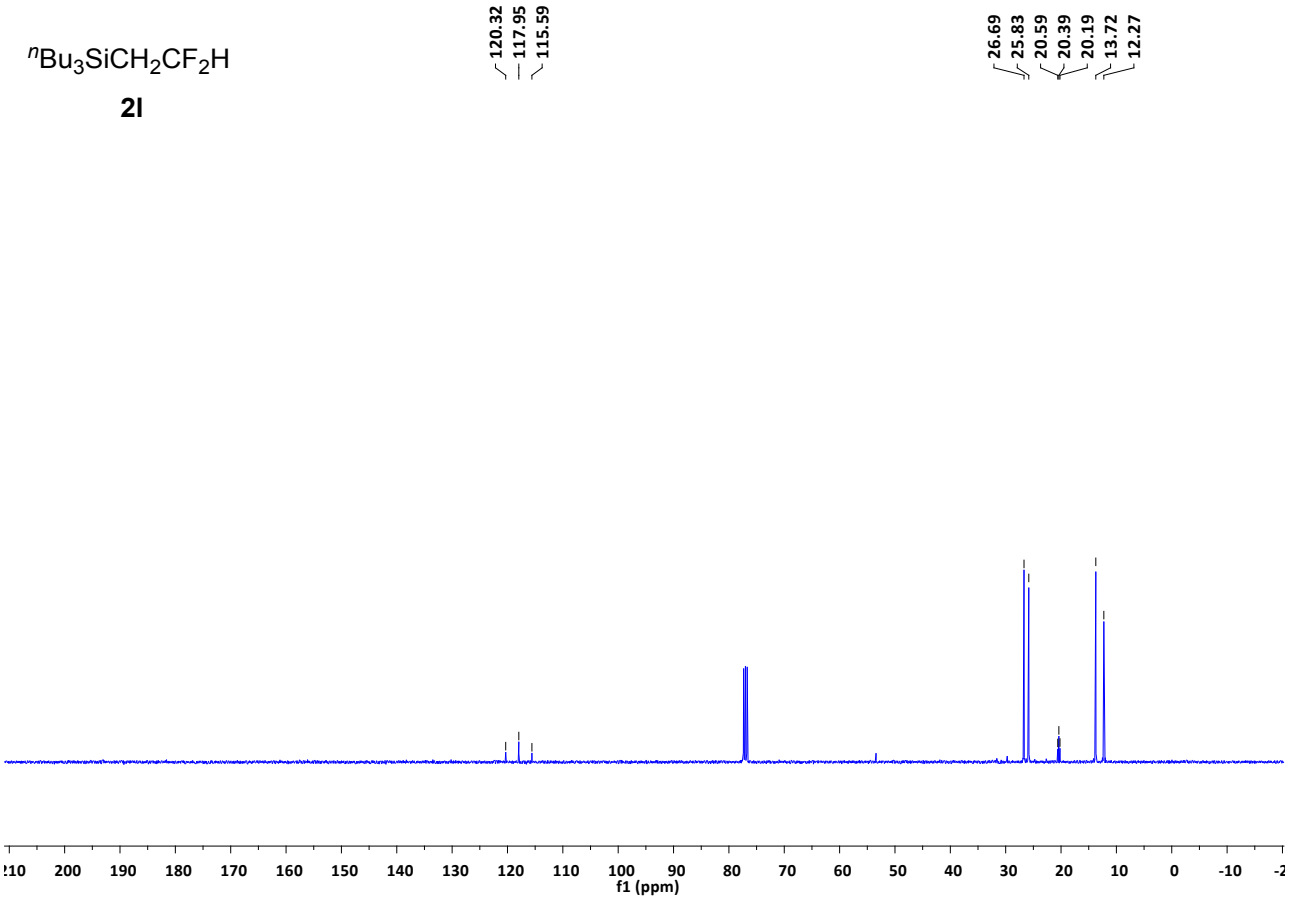
2l



^{13}C NMR：

$^{n}Bu_3SiCH_2CF_2H$

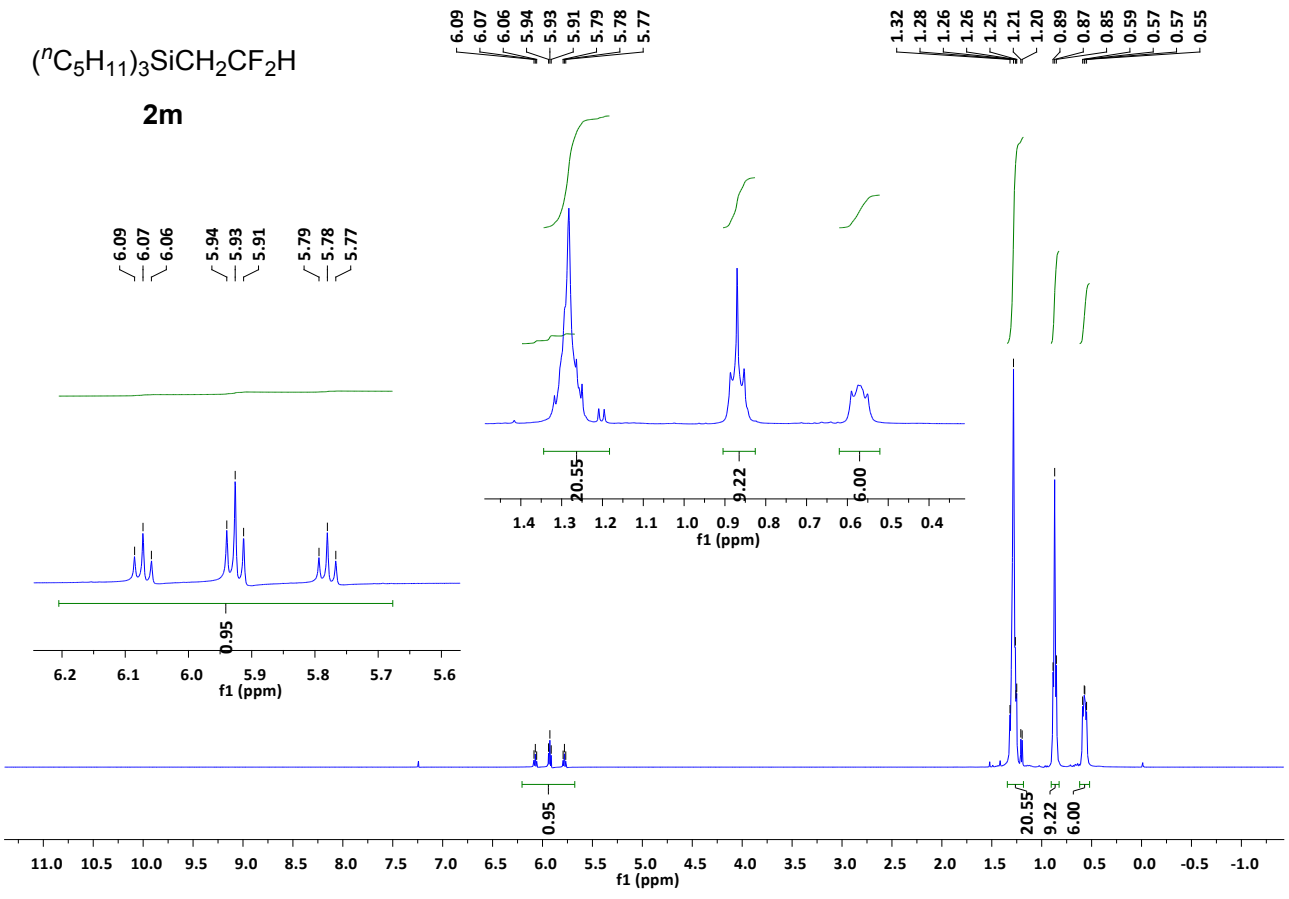
2l



^{1}H NMR：

$(^{n}C_5H_{11})_3SiCH_2CF_2H$

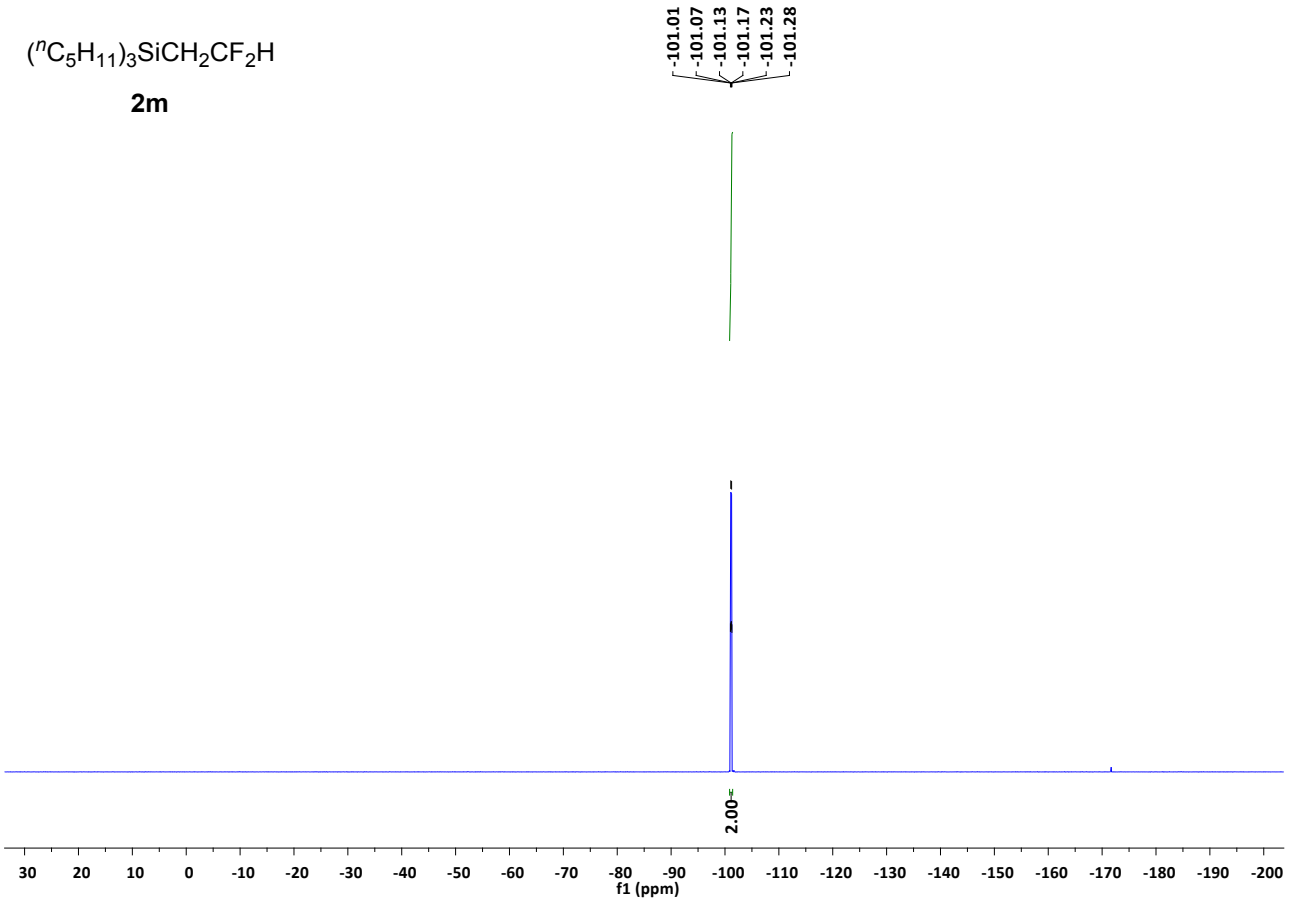
2m



^{19}F NMR：

$(^{n}C_5H_{11})_3SiCH_2CF_2H$

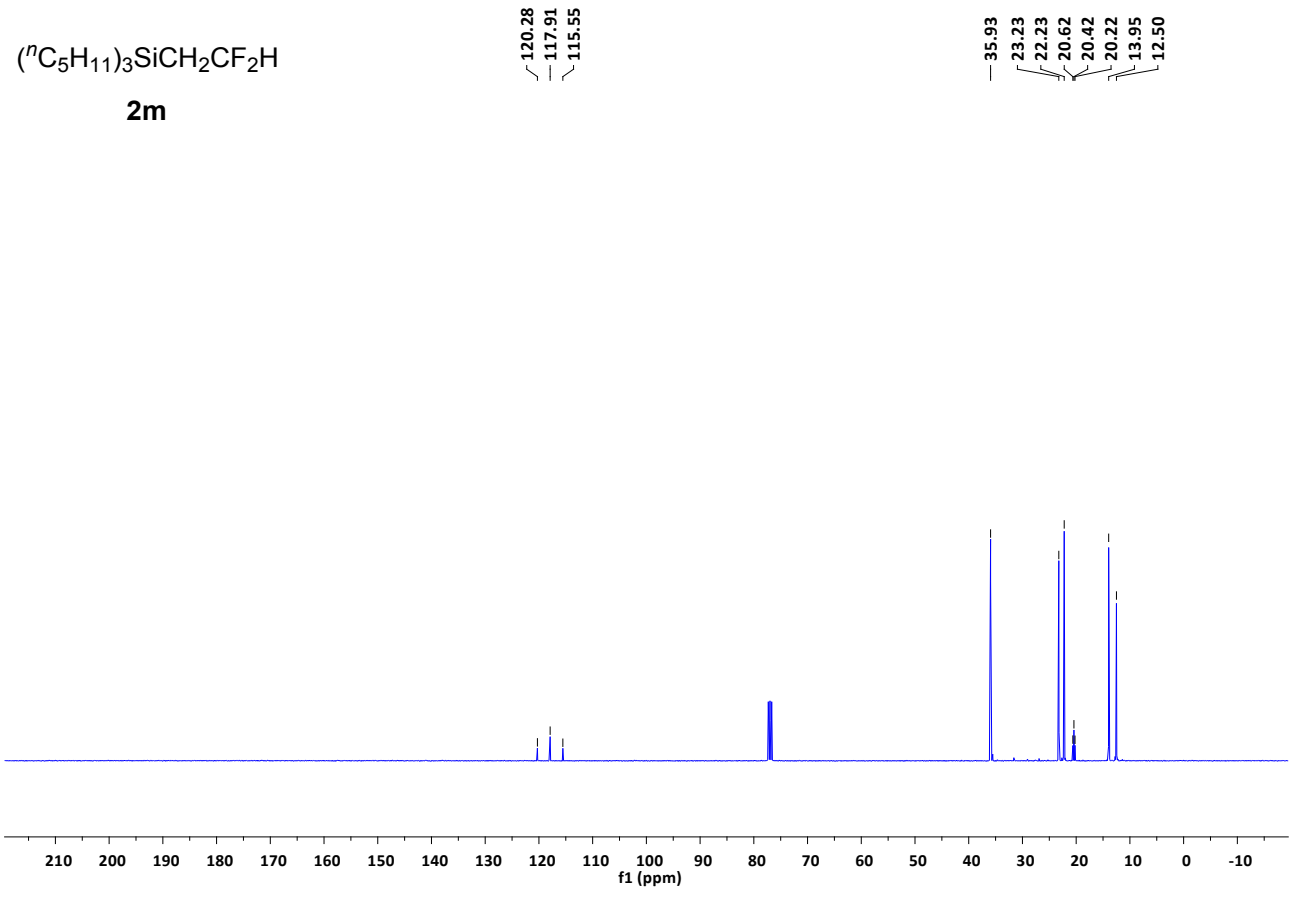
2m



^{13}C NMR：

$(^{n}C_5H_{11})_3SiCH_2CF_2H$

2m



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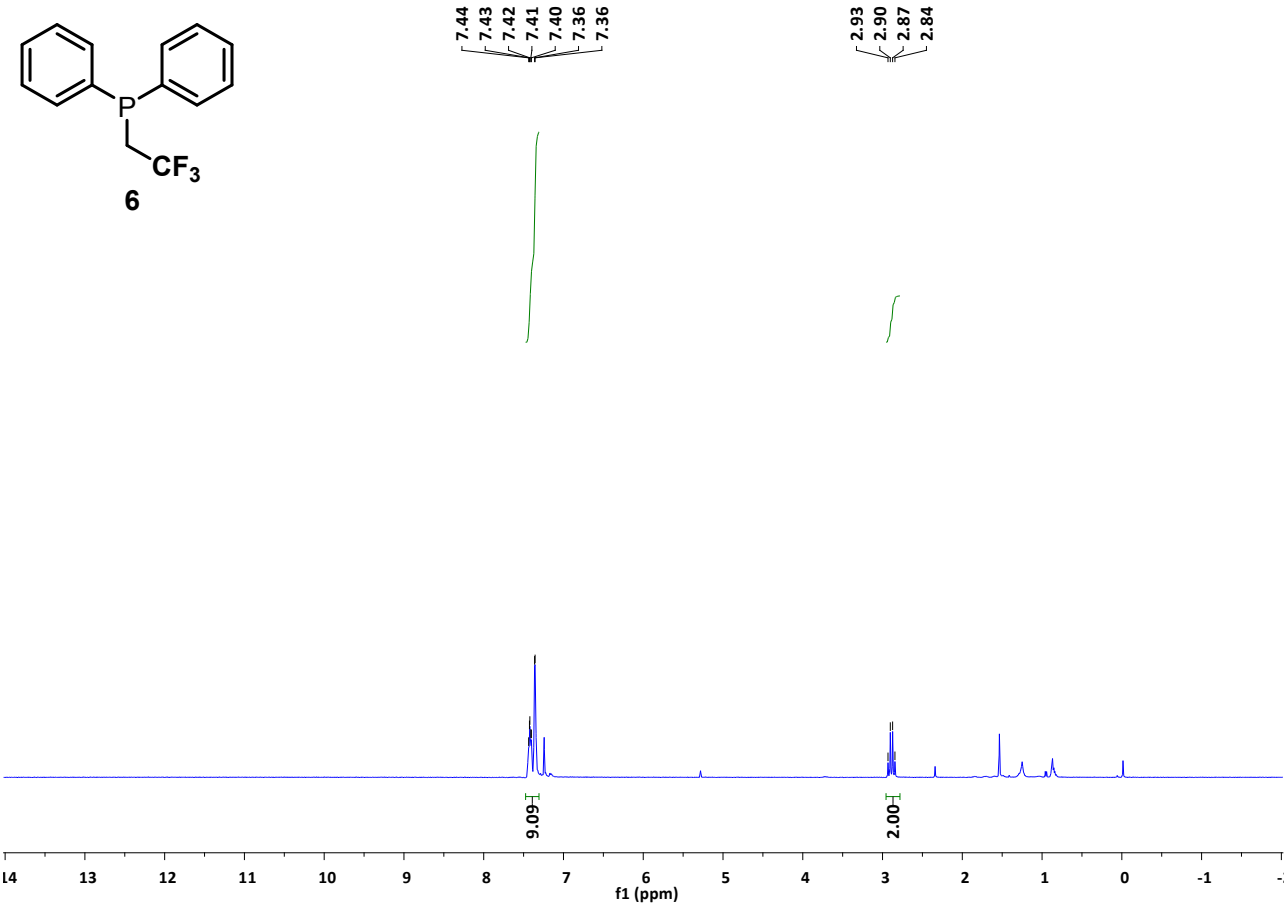

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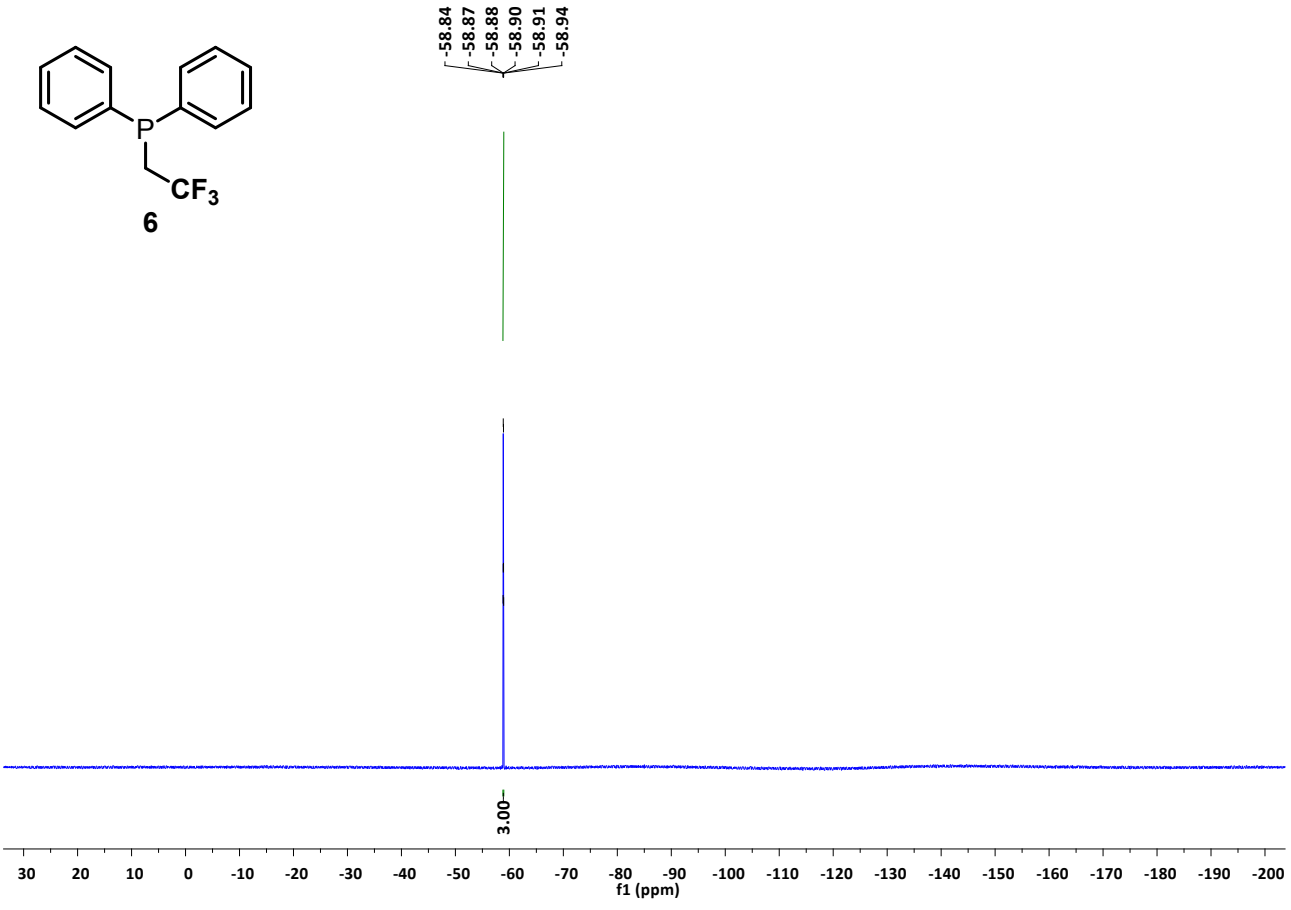

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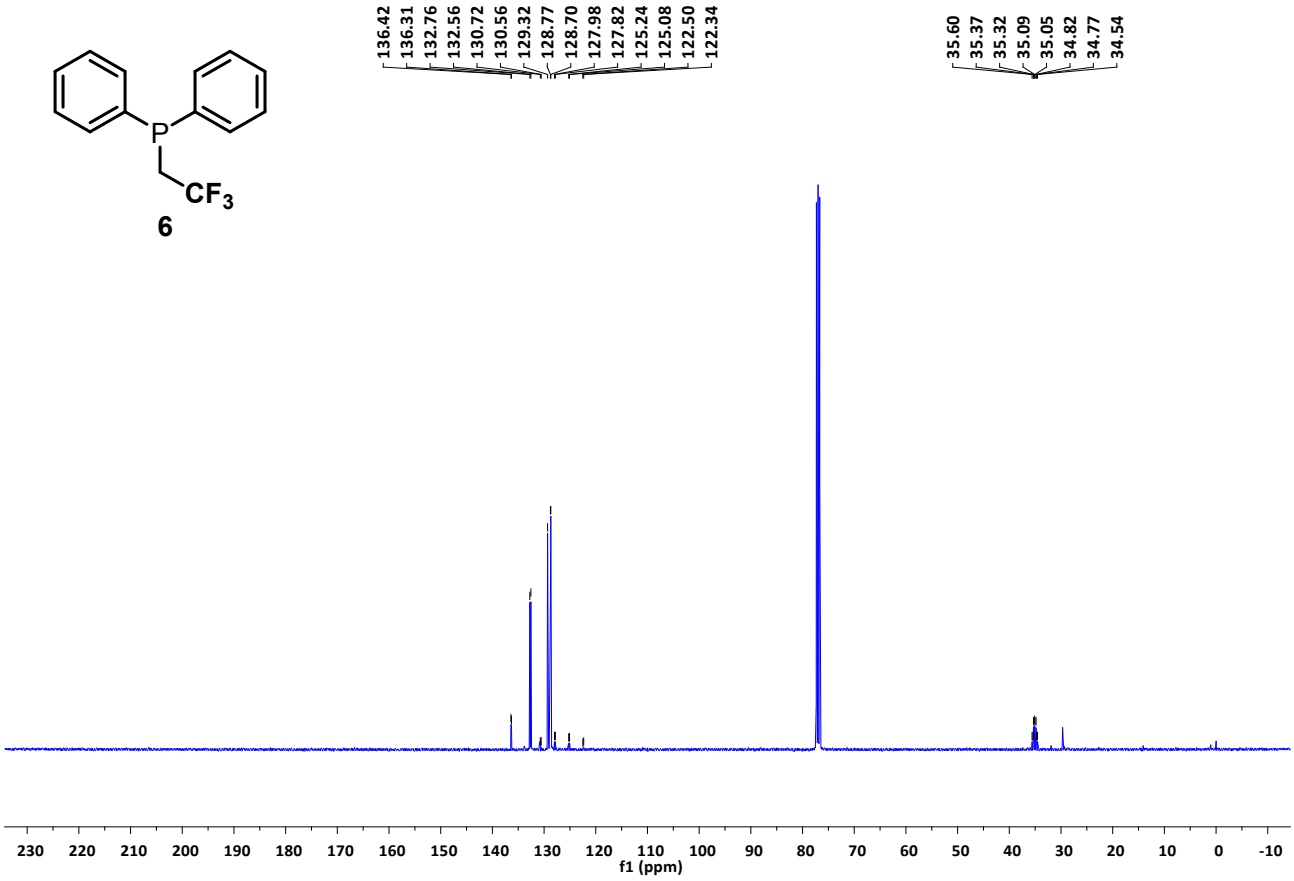
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122.50
122.34
35.60
35.37
35.32
35.09
35.05
34.82
34.77
34.54
P
CF3
6
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)