Electronic Supplementary Information to

Ga^+-Catalyzed Hydrosilylation? About the Surprising System $Ga^+/HSiR_3$/Olefin, Proof of Oxidation with Subvalent Ga^+ and Silylium Catalysis with the Perfluoroalkoxyaluminate Anion

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Table of Contents

1 General Procedures

All manipulations were carried out under exclusion of moisture and air through usage of a *MBraun* glovebox filled with nitrogen (O_2/H_2O < 1ppm) and standard Schlenk techniques. All glassware used in reactions have been stored overnight in an oven at 180 °C and were additionally dried with a heat gun prior to usage.
All solvents were stored under an atmosphere of argon or nitrogen in sealed vessels. Fluorobenzene and *ortho*-difluorobenzene (*o*DFB) were dried over CaH_2 for two days, distilled and degassed prior to use. The water content of the solvents was below 10 ppm, as determined by Carl Fischer titration.

$HSiMe_3$, $HSiMe_2Et$, $HSiEt_3$, H_2SiPh_2, H_3SiPh, 1-hexene, 1-octene, allylbenzene, 1,1-diphenylethylene, 1-methylcyclohexene, 2-methyl-but-2-ene, 1,5-cyclooctadiene, trifluorotoluene, 1-fluorobutane and *n*-perfluorohexane were dried over CaH_2 or molecular sieves, distilled and degassed prior to use. 1-Fluoroadamantane was sublimed prior to use. Hex-5-en-2-one, 1,5-hexadiene, HSi^iPr_3, 5-bromopent-1-ene and dimethylchlorosilane were dried over molecular sieves, degassed and used without further purification. $HSiMe_3$ is contaminated by traces of $ClSiMe_3$ (ca. 2 %) but we could not observe an influence on the reactions by this impurity.

Li[*pf*] ([*pf*]$^-$ = $[Al(OR^F)_4]^-$, R^F = $C(CF_3)_3$),[1] Ag[*pf*],[1,2] $[Ga(PhF)_2][pf]$ (**1**)[3] and $[Ph_3C][pf]$[4] were prepared according to literature protocols. Note that the number of fluorobenzene molecules coordinated to Ga^+ in **1** can vary, depending on the vacuum applied when drying the product. Thus, the formula $[Ga(PhF)_2][pf]$ is used for the sake of simplicity instead of $[Ga(PhF)_x][pf]$ ($1 < x < 3$). The exact ratio x was determined *via* ^{19}F NMR spectroscopy. Dimethyl(pent-4-en-1-yl)silane was also prepared according to literature procedure.[5]

For the hydrosilylation and hydrodefluorination reactions, the components were mixed in Young valve NMR tubes or flame sealed NMR tubes. Note that **1** should be added as the last component in both hydrosilylation and hydrodefluorination reactions, since silanes react wit Ga^+ under anion decomposition and ligand redistribution. Olefins oligomerize in the presence of **1**, yet this reaction is considerably slower. This is also the case for the reaction of fluoroalkanes with Ga^+, which yield crude mixtures of products.

One exemplary protocol is given in the following: *o*DFB (60 µl), a stock solution of 1-hexene in *o*DFB (0.35 M, 0.2 ml, 70 µmol, 1.0 eq.), a stock solution of $HSiMe_3$ (0.35 M, 0.2 ml, 70 µmol, 1.0 eq.) and a solution of **1** in *o*DFB (0.035 M, 0.2 ml, 7.0 µmol, 0.1 eq.) were mixed in an NMR tube. For reaction monitoring, the reaction mixture was frozen as quickly as possible at –78 °C after mixing the components and was thawed inside the NMR spectrometer. Note that, due to the volatility of the silane and the olefin, the molar ratio of the components as determined by NMR spectroscopy may differ from the intended ratio. Therefore, only the ratios determined by NMR spectroscopy are given.

1.1 NMR Spectroscopy

^{1}H-, ^{13}C-, ^{19}F-, ^{27}Al-, ^{71}Ga and 2D NMR spectra were detected on an *Avance DPX 200* (200 MHz), *Avance III HD* (300 MHz) and *Avance II+ 400* (400 MHz) NMR spectrometers from *Bruker*. NMR spectra were analyzed using *Bruker TopSpin 3.2.* ^{1}H NMR chemical shifts are given with respect to tetramethylsilane (TMS). All ^{1}H NMR spectra were calibrated using the solvent signal. The chemical shifts of standard solvents were taken from literature[6] and the shift of *o*DFB (δ = 6.96 ppm) was determined experimentally by adding TMS to the aromatic solvent. The most intensive signal of the downfield multiplet of *o*DFB appears at 6.96 ppm, when the signal of TMS is at 0.00 ppm (**Figure S 1**).

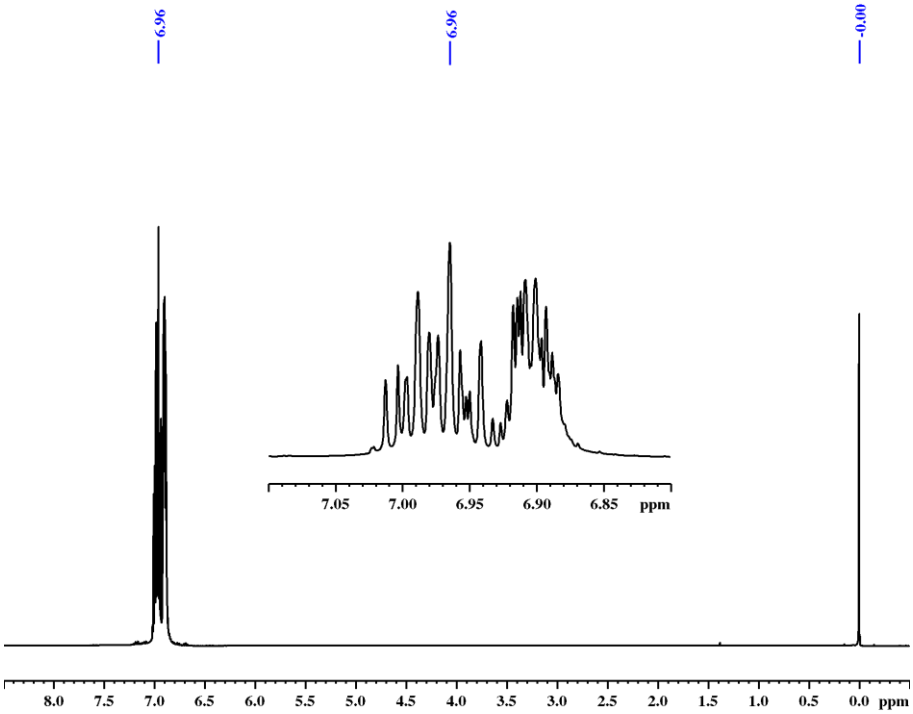


Figure S 1 ^{1}H NMR spectrum (400.17 MHz, *o*DFB, 298 K) of TMS in *o*DFB.

Heteroatomic spectra were calibrated according to the IUPAC χ-table.[7] The signal in the ^{71}Ga NMR spectra at –760 - –750 ppm can be assigned to complexes of the type $[Ga(fluoroarene)_x]^+$ (fluoroarene = PhF or *o*DFB; x = 2 or 3).[3] Deviating ^{71}Ga shifts indicate that the Ga^+ is coordinated either by the silane or the olefin, respectively the fluoroalkane substrate. Unless otherwise stated, the ^{19}F and ^{27}Al NMR spectra show signals at ca. –75 ppm and 35 ppm, respectively, indicating the presence of non-decomposed $[Al(OR^F)_4]^-$ anion. The broad resonance at ca. 60 ppm in the ^{27}Al NMR spectra is caused by the probe head.

For all reaction mixtures presented herein, ^{1}H, ^{19}F, ^{27}Al, ^{71}Ga and 2D correlated spectra, e.g. ^{1}H,^{13}C-HMBC, ^{1}H,^{13}C-HSQC or ^{1}H,^{29}Si-HMBC spectra were recorded. The reaction product of the hydrosilylation of the $HSiMe_3$/1-hexene/**1** is exemplarily characterized. For all other reaction mixtures, only the most relevant spectra are shown and discussed. If a reaction with a specific silane/substrate/initiator combination was repeated with different molar ratios of the components, usually the spectra of only one combination are

shown. The molecular structures of the main products are shown and the NMR signals different from these species represent either unreacted starting material or side products that are only present in traces.

1.2 Gas Chromatography

Gas chromatographic measurements were performed with a *Perkin Elmer Clarus 480* gas chromatograph. We employed a *Restek* 5 Å molecular sieve separating column (366 cm * 0.32 cm), and argon (pressure: 290 kPa) as the carrier gas. Gases were detected with a thermal conductivity detector. The temperature of the thermal conductivity detector was adjusted to 200 °C and the temperature of the analytical column was adjusted to 70 °C. Calibration was performed with hydrogen 5.0 gas.

1.3 Cyclic Voltammetry

Cyclic voltammograms were recorded in an argon-filled glovebox using a *Biologic SP-300* potentiostat. For measurements and data processing, the software *EC-LAB* (*V11.21*) was employed. To increase conductivity, a 0.1 M solution of $[NBu_4][pf]$ was used as supporting electrolyte. A three-electrode setup was employed with a Pt wire quasi-reference electrode, a Pt net as counter electrode and a 1 mm Pt disc working electrode. Prior to measurements, the working electrodes were thoroughly polished with ^{i}PrOH and diamond grinding paste (*MetaDi II, Diamond Polishing Compound* with grain size 15, 9, 6, 3, 1 and 0.25 µm).

1.4 STEM and EDX Spectroscopy

Scanning Transmission Electron Microscopy (STEM) and Energy-Dispersive X-Ray Spectroscopy (EDX) measurements were performed on a *FEI Talos F200X* (scanning) transmission electron microscope with a *Super-X EDX* system. A *Gatan 914.5* cryo holder was used. The sample was cooled to –170 °C before insertion into the microscope and kept at this temperature during measurements. A voltage of 200 kV was applied. For measurements and data processing, the *Velox* software was used.

1.5 Single Crystal X-Ray Diffraction

Crystals were obtained from *ortho*-difluorobenzene at –25 °C. Single crystal X-ray diffraction data for $(H_5C_2)_3Si–F–Al[OC(CF_3)_3]_3$ were collected from a shock-cooled single crystal at 100(2) K on a *Bruker APEX2 QUAZAR* three-circle diffractometer with a microfocus sealed X-ray tube using mirror optics as monochromator and a Bruker *APEXII* detector. Crystals were selected under perfluoropolyether oil, mounted on 0.1 to 0.2 mm diameter CryoLoops and quench-cooled using an *Oxford Cryostream 800* open flow N_2 cooling device.[8] Data were collected at 100 K using monochromated Mo K_α radiation (λ = 0.71073 Å).

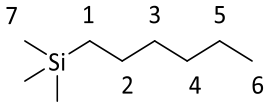
All data were integrated with SAINT and a multi-scan absorption correction using SADABS was applied.[9] The structure was solved by direct methods using SHELXT and refined by full-matrix least-squares methods against F^2 by SHELXL-2018/3[10] employing shelXle.[11] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond lengths restraints and displacement parameter restraints. Some parts of the disorder model were introduced by the program DSR.[12] Graphical representations were prepared using Olex2-1.3.[13]

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre.[14] CCDC 2024333 contains the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/structures. This report and the CIF file were generated using FinalCif.[15]

2 NMR Data and Spectra

2.1 Hydrosilylation Reactions

2.1.1 $HSiMe_3$ + 1-Hexene + 1 (1.2 : 1.0 : 0.1, 1.2 : 1.0 : 0.01 and 1.0 : 1.0 : 0.005)



^{1}H NMR [400.17 MHz, *o*DFB, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K]: δ = 4.00 (dec, 1 H, **H**Si$(CH_3)_3$, $^{3}J_{SiH,CH}$ = 3.6 Hz), 3.94 (non, 1 H, **H**Si$(CH_3)_2(C_6H_{13})$, $^{3}J_{SiH,CH}$ = 3.6 Hz), 1.28 (m, 4 H, **H**^{2} and **H**^{3}), 1.26 (m, 2 H, **H**^{5}), 1.23 (m, 2 H, **H**^{4}), 0.87 (m, 3 H, **H**^{6}), 0.46 (m, 2 H, **H**^{1}), 0.35 (s, 9 H, ClSi(C**H**$_3)_3$), 0.11 (s, 18 H, O[Si(C**H**$_3)_3]_2$), 0.04 (d, 9 H, HSi(C**H**$_3)_3$, $^{3}J_{CH,SiH}$ = 3.6 Hz), 0.04 (d, 6 H, HSi(C**H**$_3)_2(C_6H_{13})$, $^{3}J_{CH,SiH}$ = 3.6 Hz), 0.00 (s, 12 H, Si(C**H**$_3)_4$) –0.01 (s, 9 H, **H**^{7}) ppm.

^{13}C NMR [100.62 MHz, *o*DFB, 298 K]: δ = 150.5 (2 C, **C**^{1}F in *o*DFB), 124.3 (2 C, **C**^{3} in *o*DFB), 116.8 (2 C, **C**^{2} in *o*DFB), 33.3 (1 C, **C**^{3}), 31.5 (1 C, **C**^{4}), 23.7 (1 C, **C**^{2}), 22.5 (1 C, **C**^{5}), 16.3 (1 C, **C**^{1}), 13.3 (1 C, **C**^{6}), –1.2 (4 C, Si(**C**$H_3)_4$), –2.7 (3 C, **C**^{7}) ppm.

^{19}F NMR [376.54 MHz, *o*DFB, 298 K]: δ = –75.3 (s, 36 F, $[Al(OC(C\mathbf{F}_3)_3)_4]^-$), –113.8 ($m_c$, 1 F, $C_6H_5\mathbf{F}$), –139.4 (m_c, 2 F, $oC_6\mathbf{F}_2H_4$) ppm.

^{27}Al NMR [104.27 MHz, *o*DFB, 298 K]: δ = 35.0 (s, 1 Al, $[\mathbf{Al}(OC(CF_3)_3)_4]^-$) ppm.

^{29}Si NMR [79.50 MHz, *o*DFB, 298 K]: δ = 31.8 (1 Si, Cl**Si**$(CH_3)_3$), 7.5 (1 Si, O[**Si**$(CH_3)_3]_2$), 1.0 (1 Si, $(H_3C)_3$**Si**(C_6H_{13})), –12.7 (1 Si, H**Si**$(CH_3)_2(C_6H_{13})$), –16.1 (1 Si, H**Si**$(CH_3)_3$) ppm.

^{71}Ga NMR [122.04 MHz, *o*DFB, 298 K]: δ = –755.4 ($\Delta\nu_{1/2}$ = 510 Hz, br, 1 Ga, [**Ga**(fluoroarene)$_x]^+$) ppm.

It should be noted that $SiMe_4$ and $HSi(Me)_2$(Hex) are formed after the consumption of the olefin, as evident from the new ^{1}H NMR signal of **H**Si$(Me)_2$(Hex) at 3.94 ppm (see **Figure S 16**). With an initial $HSiMe_3$/1-hexene ratio of approximately 1.2, 10 % of the hydrosilylation product $(Me)_3$Si(Hex) is converted to $SiMe_4$ and $HSi(Me)_2$(Hex), respectively, under consumption of excess $HSiMe_3$.

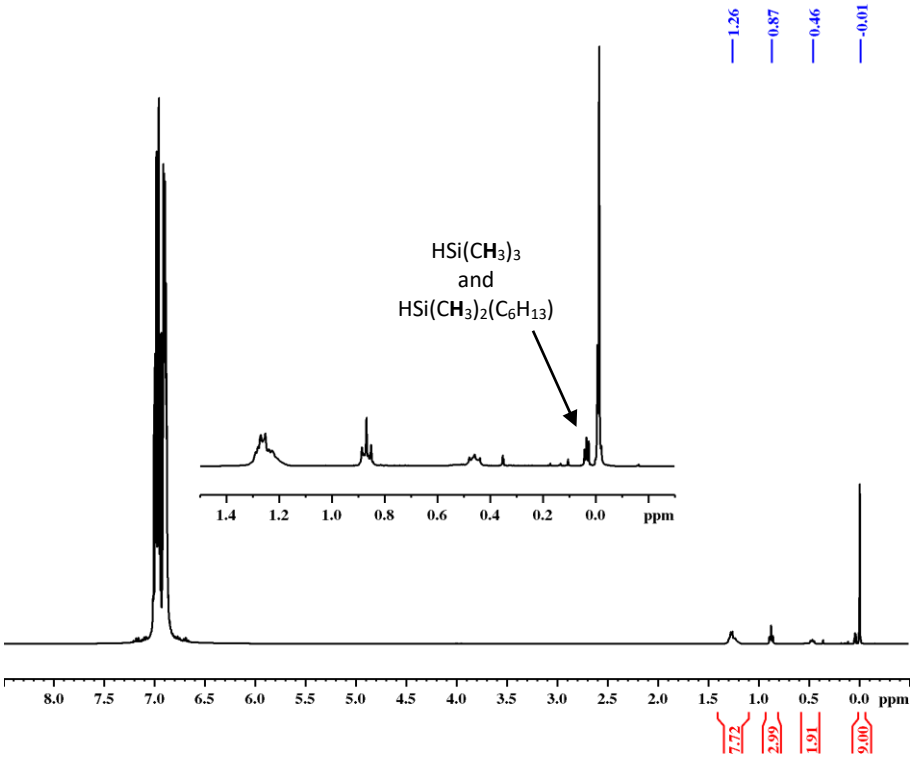


Figure S 2 ^{1}H NMR spectrum (400.17 MHz, *o*DFB, 298 K) of a $HSiMe_3$/1-hexene/**1** (1.2 : 1.0 : 0.1) mixture, 12 h after mixing the components (spectrum calibrated to δ ($oC_6F_2\mathbf{H}_4$) = 6.96 ppm).

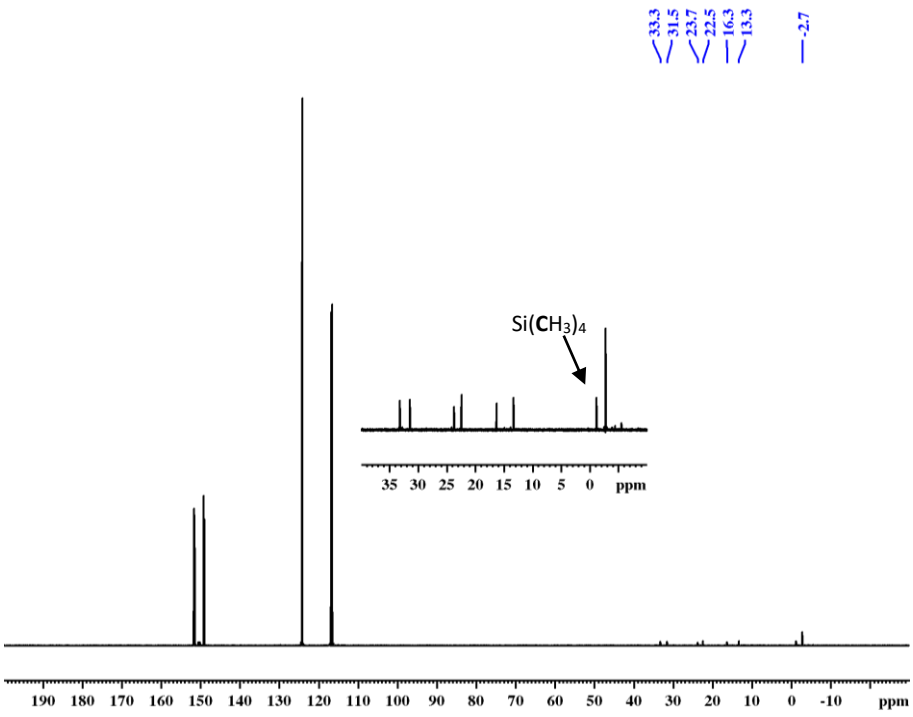


Figure S 3 ^{13}C NMR spectrum (100.62 MHz, *o*DFB, 298 K) of a $HSiMe_3$/1-hexene/**1** (1.2 : 1.0 : 0.1) mixture, 3 d after mixing the components.

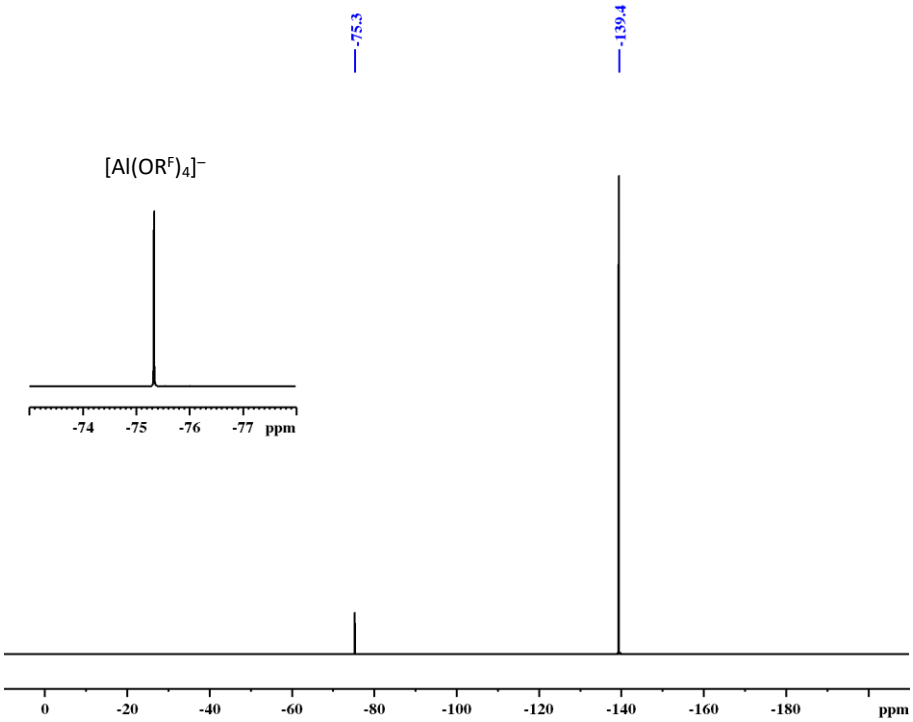


Figure S 4 ^{19}F NMR spectrum (282.45 MHz, *o*DFB, 298 K) of a HSiMe$_3$/1-hexene/**1** (1.2 : 1.0 : 0.1) mixture, 12.5 h after mixing the components.

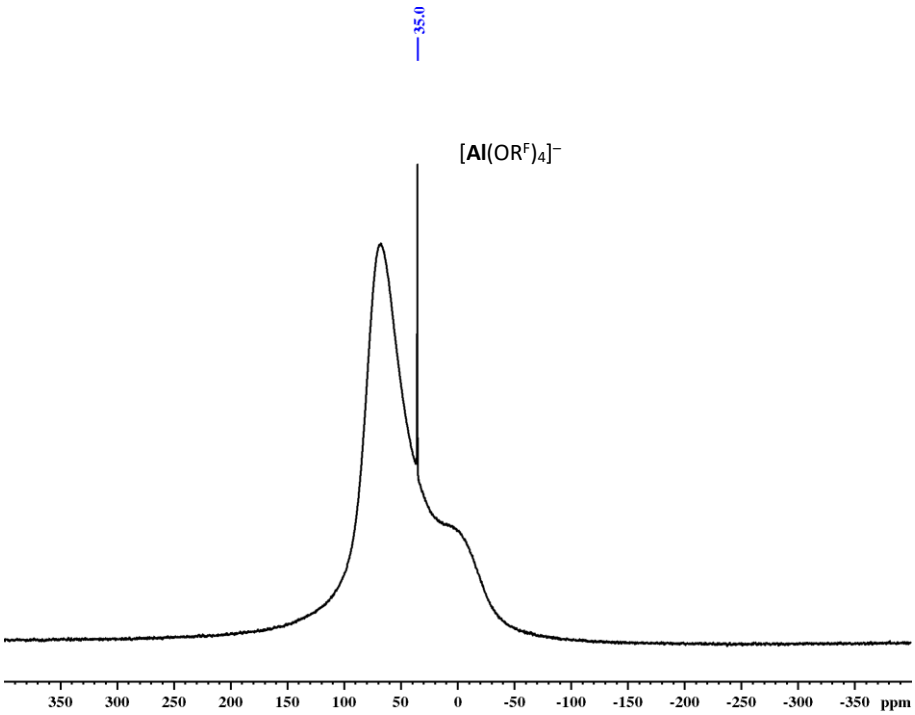


Figure S 5 ^{27}Al NMR spectrum (104.27 MHz, *o*DFB, 298 K) of a HSiMe$_3$/1-hexene/**1** (1.2 : 1.0 : 0.1) mixture, 9 h after mixing the components.

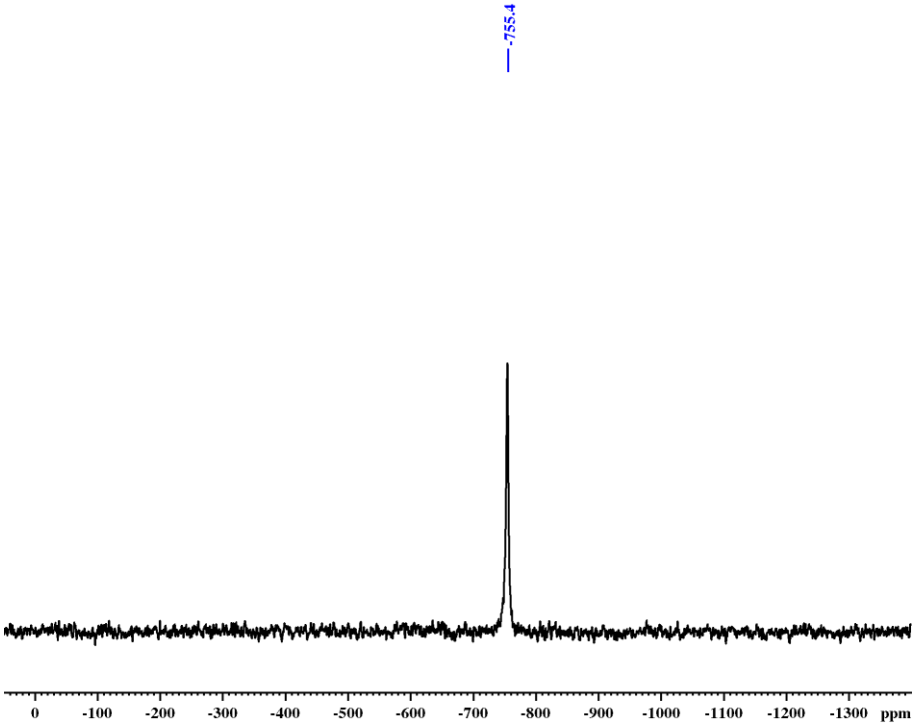


Figure S 6 ^{71}Ga NMR spectrum (122.04 MHz, *o*DFB, 298 K) of a $HSiMe_3$/1-hexene/**1** (1.2 : 1.0 : 0.1) mixture, 9 h after mixing the components.

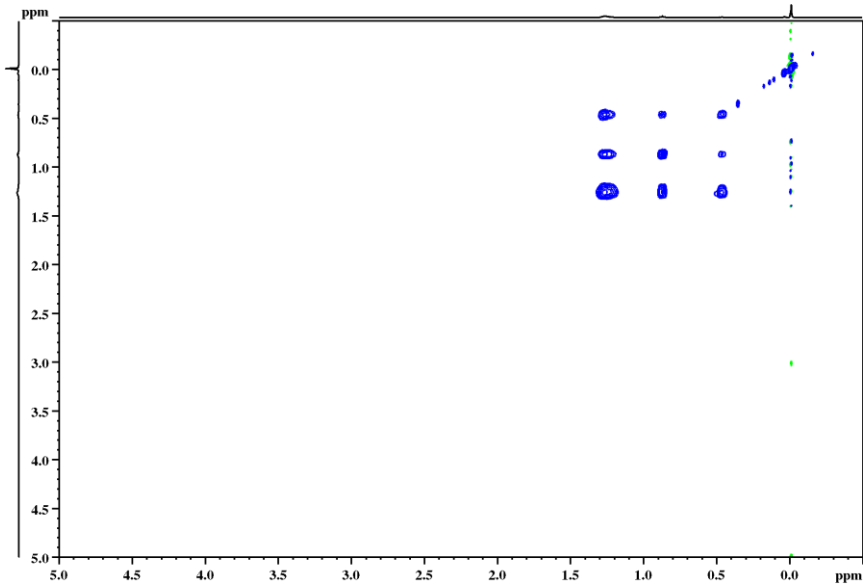


Figure S 7 ^{1}H TOCSY NMR spectrum (400.17 MHz, *o*DFB, 298 K, mixing time = 0.2 s) of a $HSiMe_3$/1-hexene/**1** (1.2 : 1.0 : 0.1) mixture, 18 h after mixing the components (^{1}H NMR spectrum calibrated to δ (*o*$C_6F_2\mathbf{H}_4$) = 6.96 ppm).

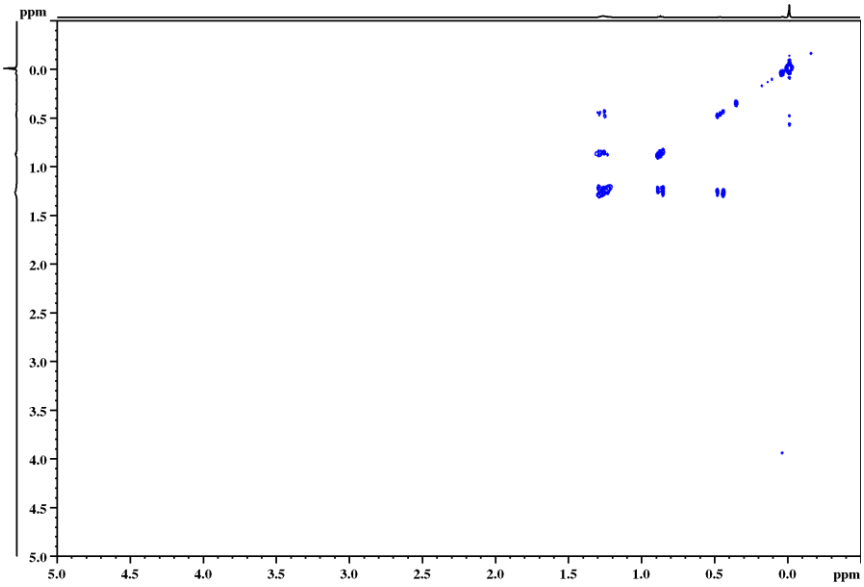


Figure S 8 ^{1}H,^{1}H-COSY NMR spectrum (400.17 MHz, *o*DFB, 298 K) of a $HSiMe_3$/1-hexene/**1** (1.2 : 1.0 : 0.1) mixture, 1 d after mixing the components (^{1}H NMR spectrum calibrated to δ (*o*C_6F_2**H**$_4$) = 6.96 ppm).

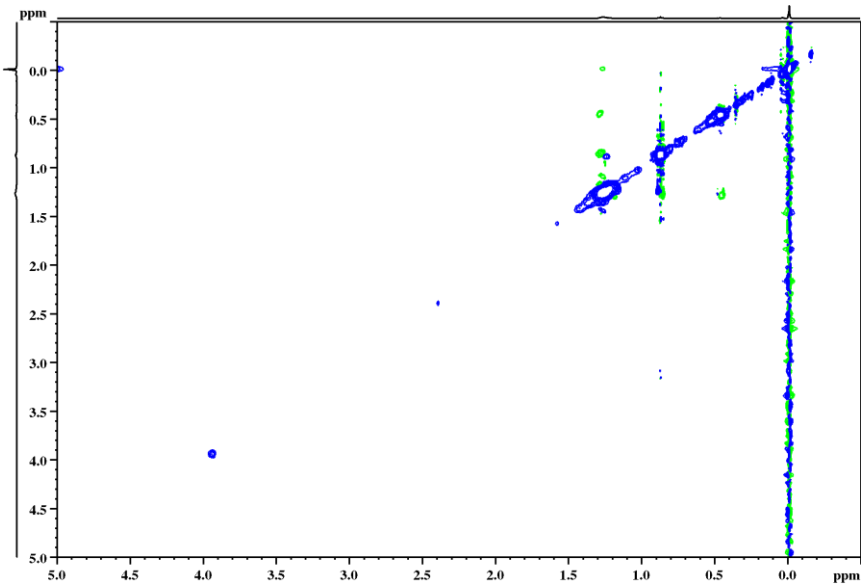


Figure S 9 ^{1}H NOESY spectrum (400.17 MHz, *o*DFB, 298 K, mixing time = 0.8 s) of a $HSiMe_3$/1-hexene/**1** (1.2 : 1.0 : 0.1) mixture, 1 d after mixing the components (^{1}H NMR spectrum calibrated to δ (*o*C_6F_2**H**$_4$) = 6.96 ppm).

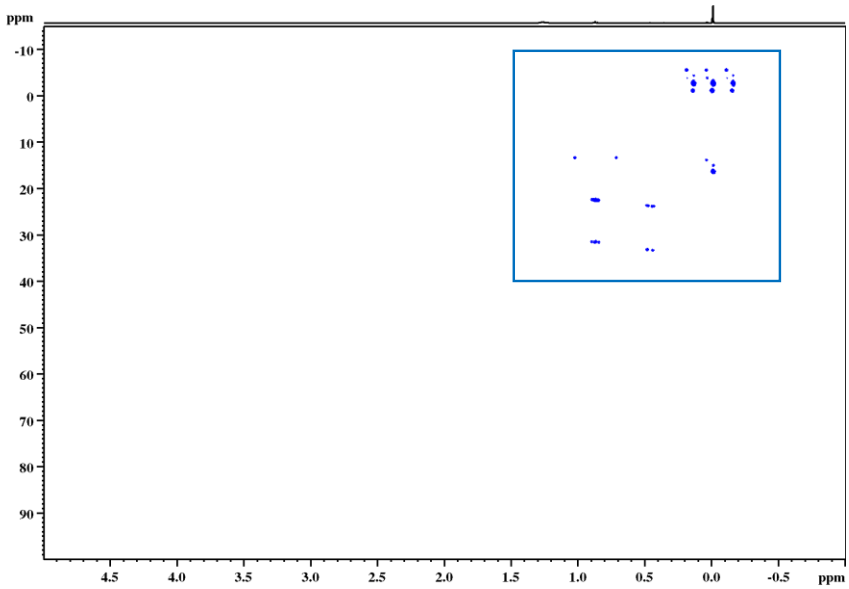


Figure S 10 $^{1}H,^{13}C$-HMBC NMR spectrum (400.17 MHz, *o*DFB, 298 K, optimized for *J* = 8 Hz) of a $HSiMe_3$/1-hexene/**1** (1.2 : 1.0 : 0.1) mixture, 7 h after mixing the components (^{1}H NMR spectrum calibrated to δ (*o*$C_6F_2\mathbf{H}_4$) = 6.96 ppm).

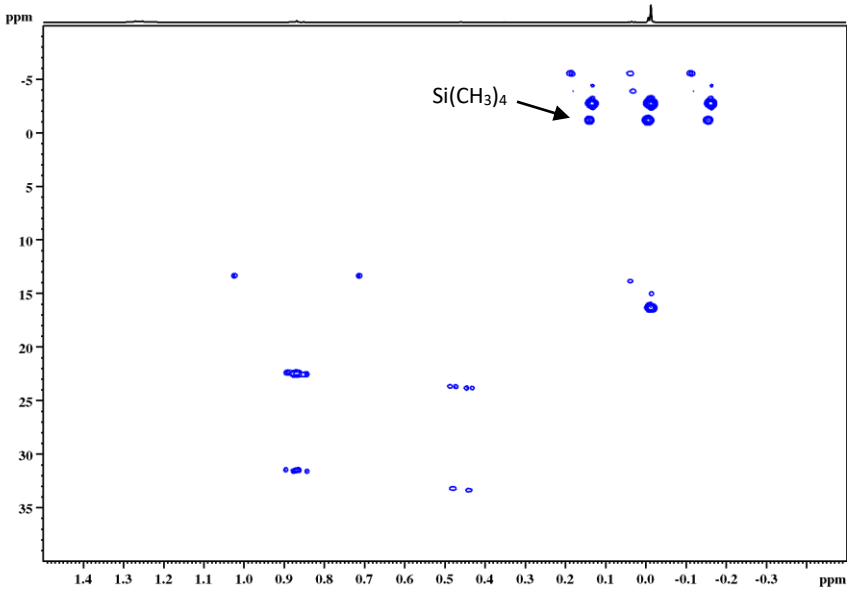


Figure S 11 $^{1}H,^{13}C$-HMBC NMR spectrum (400.17 MHz, *o*DFB, 298 K, optimized for *J* = 8 Hz) of a $HSiMe_3$/1-hexene/**1** (1.2 : 1.0 : 0.1) mixture, 7 h after mixing the components (^{1}H NMR spectrum calibrated to δ (*o*$C_6F_2\mathbf{H}_4$) = 6.96 ppm; selected area from the spectrum in **Figure S 10**).

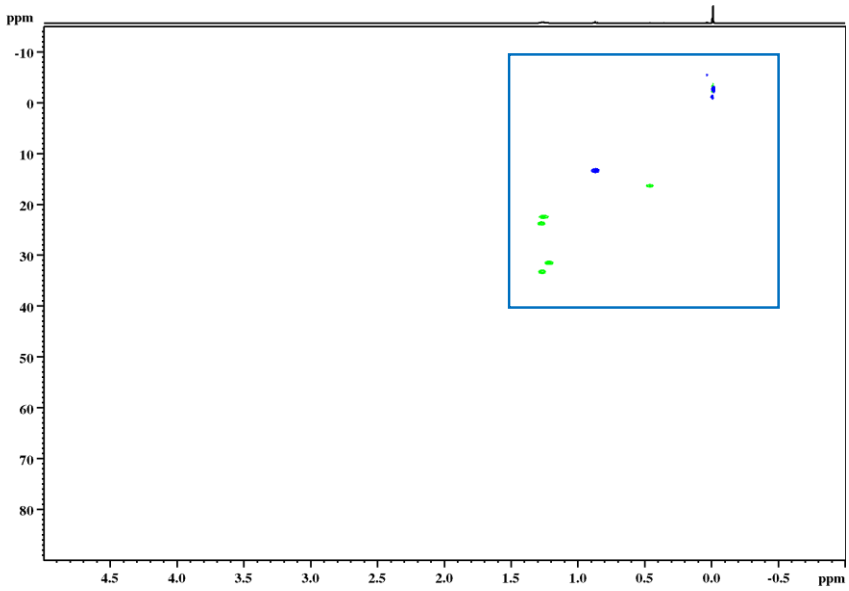


Figure S 12 Edited $^{1}H,^{13}C$-HSQC NMR spectrum (400.17 MHz, *o*DFB, 298 K, optimized for *J* = 130 Hz; CH_2: green, CH_3 and CH: blue) of a $HSiMe_3$/1-hexene/**1** (1.2 : 1.0 : 0.1) mixture, 7 h after mixing the components (^{1}H NMR spectrum calibrated to δ ($oC_6F_2\mathbf{H}_4$) = 6.96 ppm).

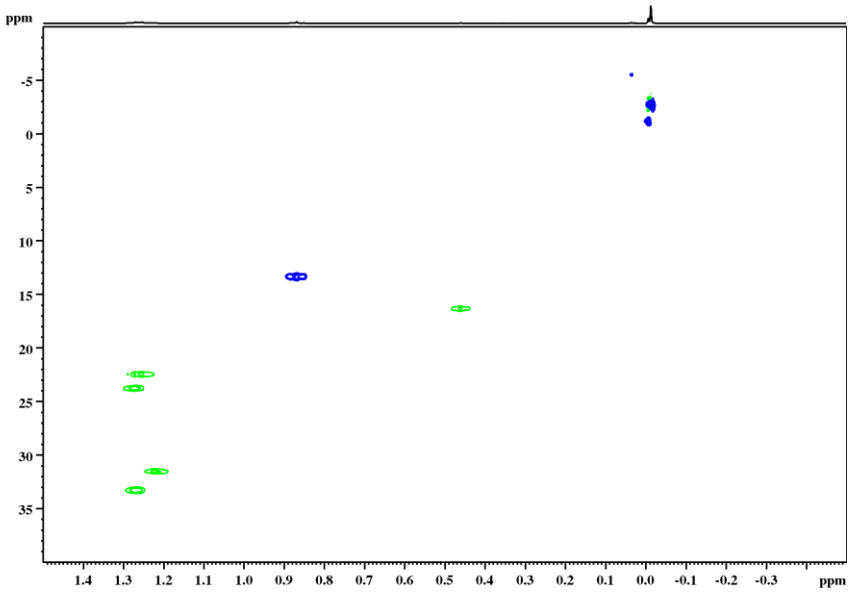


Figure S 13 Edited $^{1}H,^{13}C$-HSQC NMR spectrum (400.17 MHz, *o*DFB, 298 K, optimized for *J* = 130 Hz; CH_2: green, CH_3 and CH: blue) of a $HSiMe_3$/1-hexene/**1** (1.2 : 1.0 : 0.1) mixture, 7 h after mixing the components (^{1}H NMR spectrum calibrated to δ ($oC_6F_2\mathbf{H}_4$) = 6.96 ppm; selected area from the spectrum in **Figure S 12**).

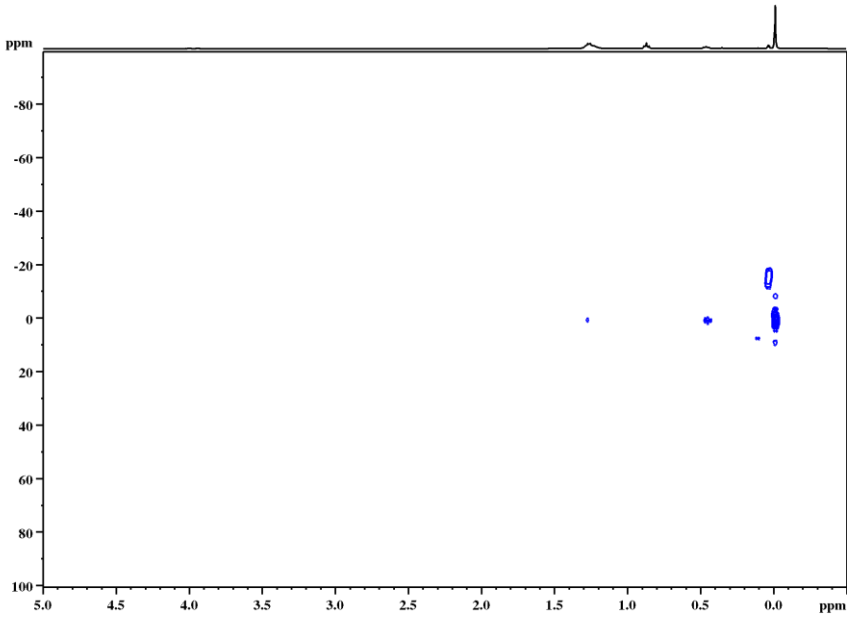


Figure S 14 $^{1}H,^{29}Si$-HMBC NMR spectrum (400.17 MHz, *o*DFB, 298 K, optimized for J = 8 Hz) of a $HSiMe_3$/1-hexene/**1** (1.2 : 1.0 : 0.1) mixture, 1 d after mixing the components (^{1}H NMR spectrum calibrated to δ (*o*$C_6F_2\mathbf{H}_4$) = 6.96 ppm).

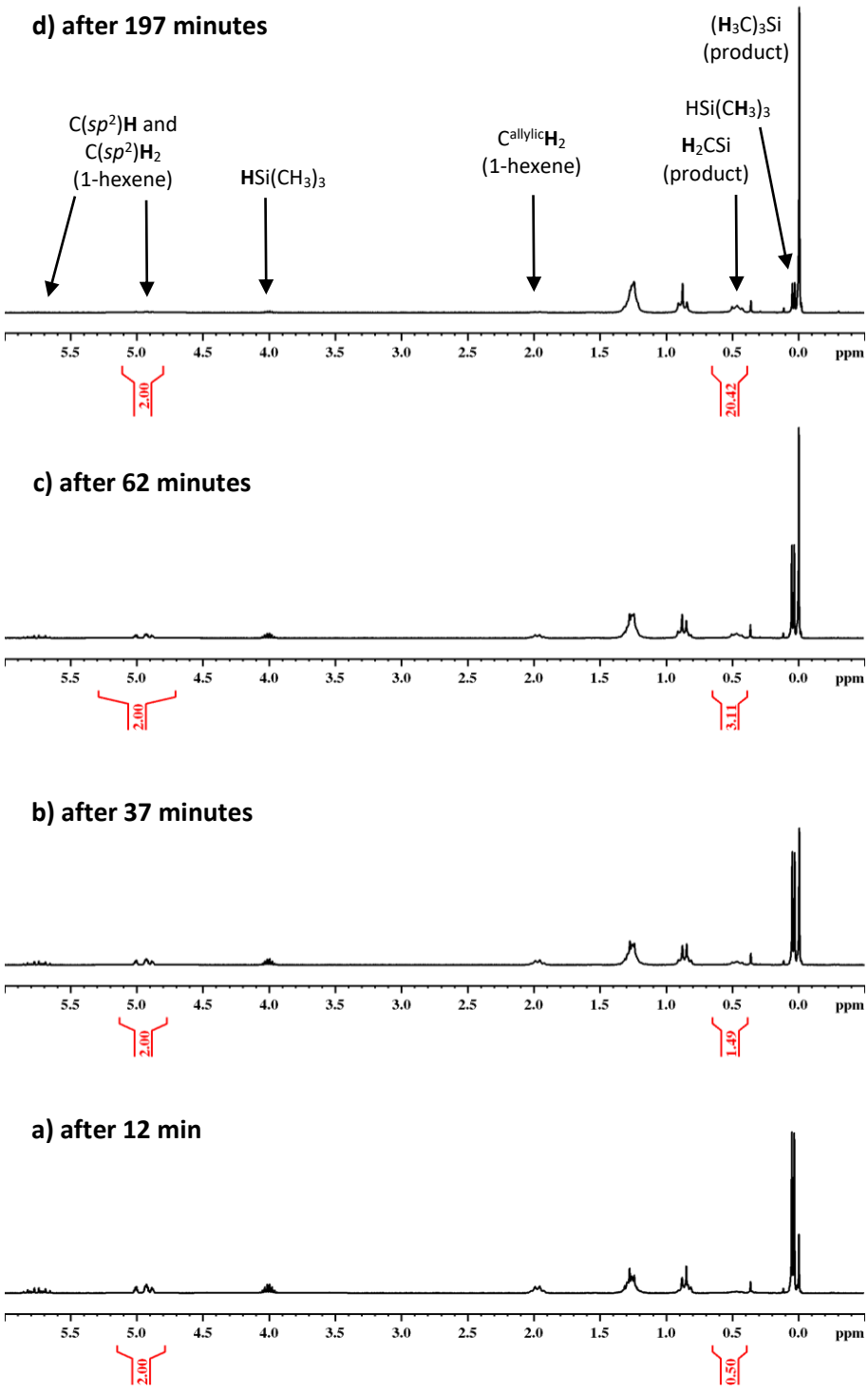


Figure S 15 ^{1}H NMR (200.13 MHz, *o*DFB, 298 K) spectra of a $HSiMe_3$/1-hexene/**1** mixture (1.2 : 1.0 : 0.1) at different times after mixing the components at rt. Signal intensities were normalized with respect to the solvent signal (spectra calibrated to δ (*o*C_6F_2**H**$_4$) = 6.96 ppm).

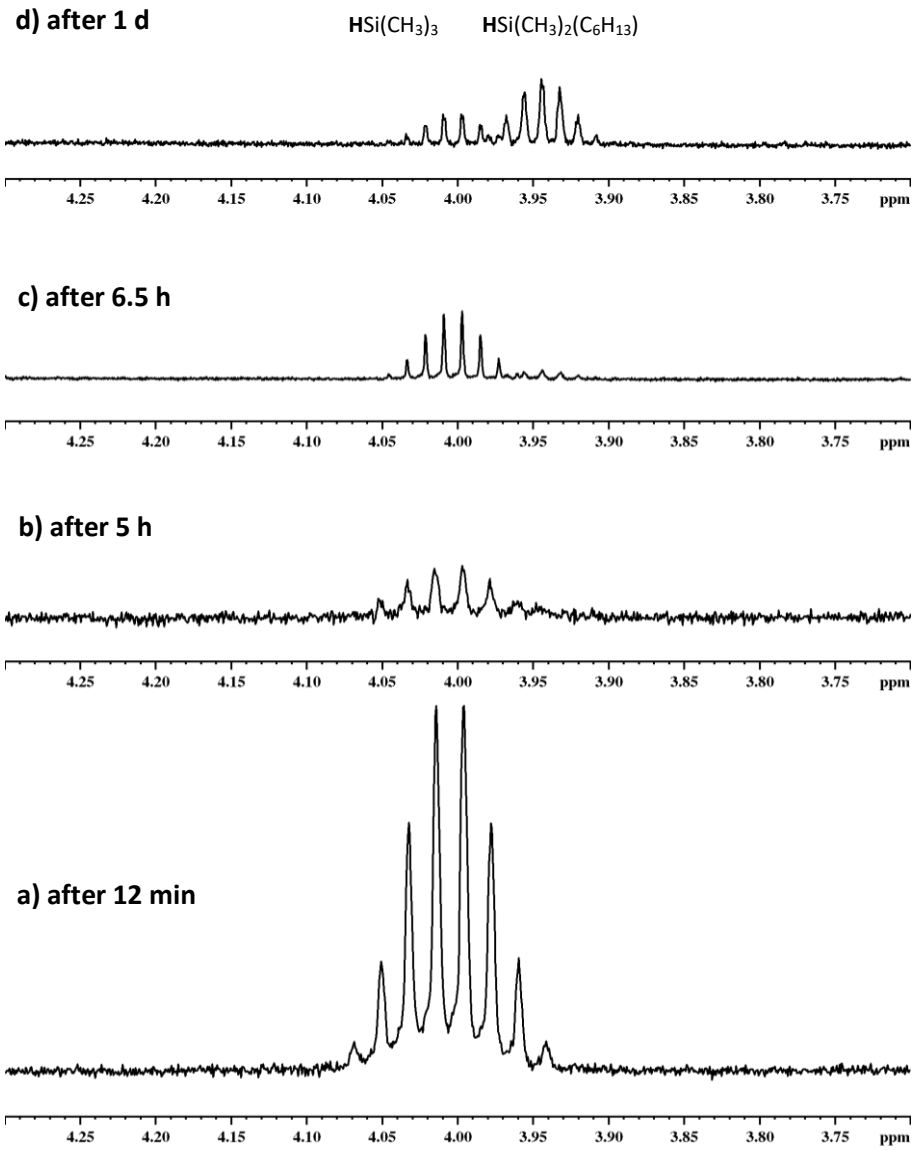
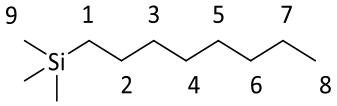


Figure S 16 ^{1}H NMR (*o*DFB, 298 K) spectra of a $HSiMe_3$/1-hexene/**1** mixture (1.2 : 1.0 : 0.1) at different times after mixing the components at rt (a and b: 200.13 MHz, c and d: 300.18 MHz; spectra calibrated to δ (*o*C_6F_2**H**$_4$) = 6.96 ppm).

2.1.2 $HSiMe_3$ + 1-Octene + 1 (1.0 : 1.0 : 0.14)



^{1}H NMR [400.17 MHz, *o*DFB, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K]: δ = 1.29 (m, 2 H, **H**^{2}), 1.28 (m, 2 H, **H**^{3}), 1,25 (m, 2 H, **H**^{7}), 1.24 (m, 4 H, **H**^{4} und **H**^{5}), 1.24 (m, 2 H, **H**^{6}), 0.87 (t, 3 H, **H**^{8}, $^{3}J_{H8,H7}$ = 6.7 Hz), 0.48 (m, 2 H, **H**^{1}), 0.36 (s, 6 H, $(\mathbf{H}_3C)_2(C_8H_{17})SiCl$), 0.11 (s, 18 H, $O[Si(C\mathbf{H}_3)_3]_2$), 0.00 (s, 9 H, **H**^{9}) ppm.

^{13}C NMR [100.62 MHz, *o*DFB, 298 K]: δ = 150.5 (2 C, **C**^{1}F in *o*DFB), 124.3 (2 C, **C**^{3} in *o*DFB), 116.8 (2 C, **C**^{2} in *o*DFB), 33.6 (1 C, **C**^{3}), 31.9 (1 C, **C**^{6}), 29.30 (1 C, **C**^{4} oder **C**^{5}), 29.28 (1 C, **C**^{4} or **C**^{5}), 23.8 (1 C, **C**^{2}), 22.5 (1 C, **C**^{7}), 16.4 (1 C, **C**^{1}), 13.4 (1 C, **C**^{8}), –2.7 (3 C, **C**^{9}) ppm.

^{29}Si NMR [79.50 MHz, *o*DFB, 298 K]: δ = 31.6 (1 Si, $(H_3C)_2(C_8H_{17})\mathbf{Si}Cl$), 7.7 (1 Si, $O[\mathbf{Si}(CH_3)_3]_2$), 0.1 (1 Si, $(H_3C)_3\mathbf{Si}(C_8H_{17})$) ppm.

^{71}Ga NMR [91.54 MHz, *o*DFB, 298 K]: δ = –756.4 ($\Delta\nu_{1/2}$ = 189 Hz; br, 1 Ga, $[\mathbf{Ga}(\text{fluoroarene})_x]^+$) ppm.

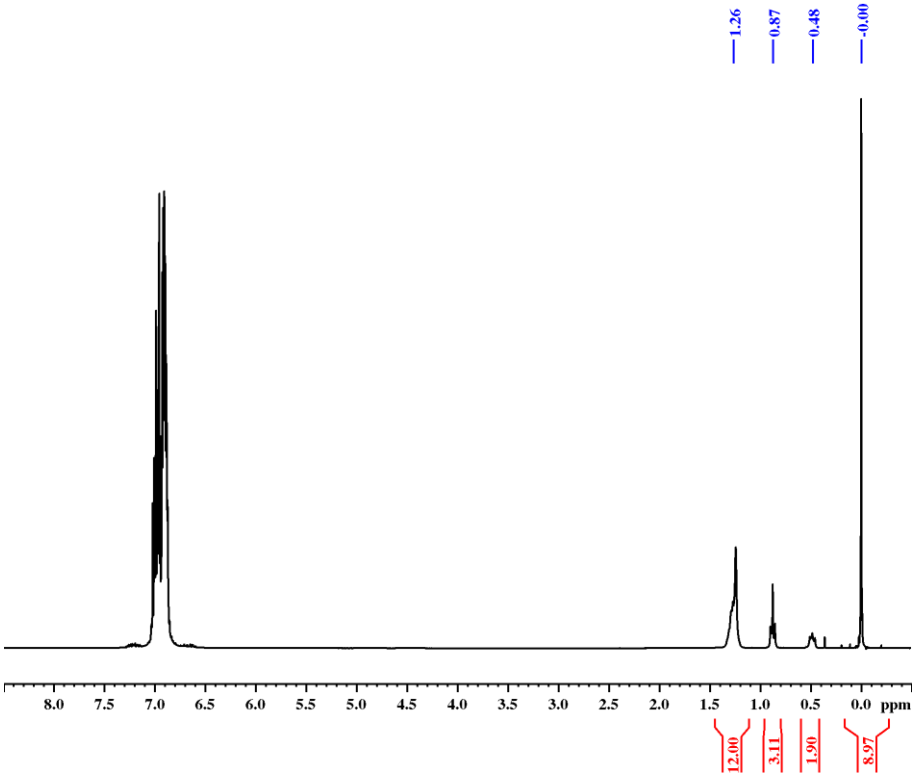
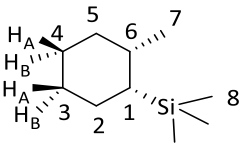


Figure S 17 ^{1}H NMR spectrum (300.18 MHz, *o*DFB, 298 K) of a $HSiMe_3$/1-octene/**1** (1.0 : 1.0 : 0.14) mixture, 3 h after mixing the components (spectrum calibrated to δ ($oC_6F_2\mathbf{H}_4$) = 6.96 ppm).

2.1.3 $HSiMe_3$ + 1-Methylcyclohexene + 1 (1.0 : 1.0 : 0.1)



^{1}H NMR [400.17 MHz, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K]: δ = 1.94 (m, 1 H, **H**^{6}), 1.64 (m, 1 H, **H**$^{3}_{B}$), 1.46 (m, 1 H, **H**$^{4}_{B}$), 1.43 (m, 2 H, **H**^{5}), 1.39 (m, 1 H, **H**$^{4}_{A}$), 1.38 (m, 2 H, **H**^{2}), 1.18 (m, 1 H, **H**$^{3}_{A}$), 0.91 (d, 3 H, **H**^{7}, $^{3}J_{H7,H6}$ = 7.2 Hz), 0.74 (m, 1 H, **H**^{1}), 0.32 (s, 6 H, (C_7H_{13})SiCl(C**H**$_3$)$_2$), 0.00 (s, 12 H, Si(C**H**$_3$)$_4$) –0.04 (s, 9 H, **H**^{8}) ppm.

^{13}C NMR [100.62 MHz, *o*DFB, 298 K]: δ = 150.5 (2 C, **C**^{1}F in *o*DFB), 124.3 (2 C, **C**^{3} in *o*DFB), 116.8 (2 C, **C**^{2} in *o*DFB), 34.8 (1C, **C**^{5}), 30.5 (1C, **C**^{1}), 29.5 (1C, **C**^{6}), 28.1 (1C, **C**^{3}), 21.9 (1C, **C**^{2}), 21.1 (1C, **C**^{4}), 15.6 (1C, **C**^{7}), –1.1 (4 C, Si(**C**H$_3$)$_4$), –3.0 (3C, **C**^{8}) ppm.

^{29}Si NMR [79.50 MHz, *o*DFB, 298 K]: δ = 1.2 (1 Si, (H_3C)$_3$**Si**(C_7H_{13})) ppm.

^{71}Ga NMR [122.04 MHz, *o*DFB, 298 K]: δ = –754.9 ppm ($\Delta\nu_{1/2}$ = 420 Hz, br, 1 Ga, [**Ga**(fluoroarene)$_x$]$^{+}$; signal disapperas after 5 days).

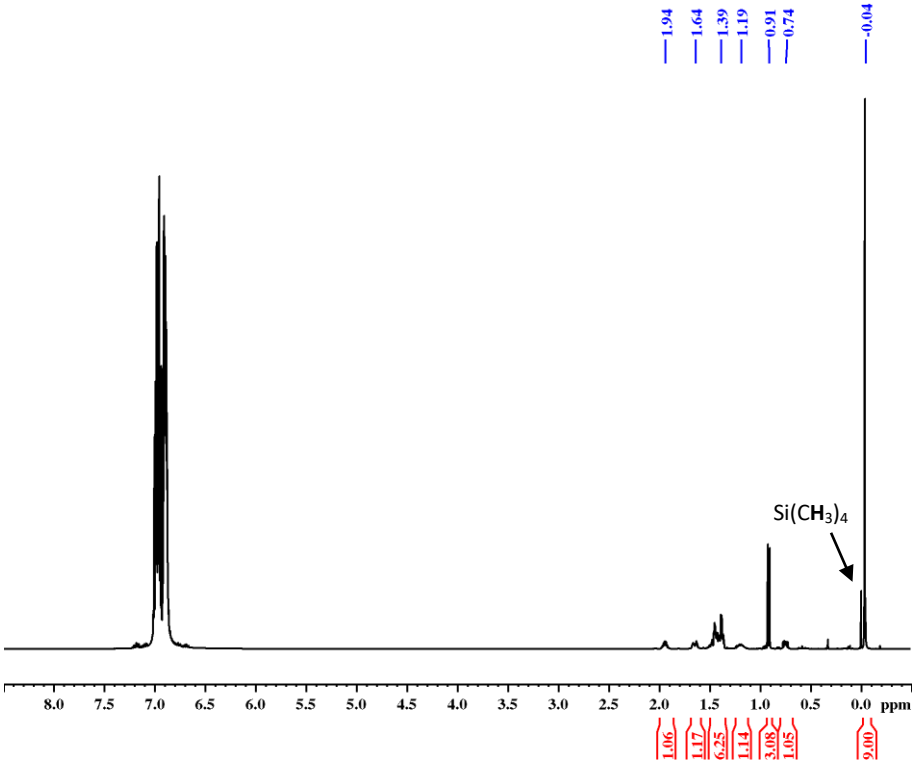


Figure S 18 ^{1}H NMR spectrum (400.17 MHz, *o*DFB, 298 K) of a $HSiMe_3$/1-methylcyclohexene/**1** (1.0 : 1.0 : 0.1) mixture, 5 d after mixing the components (spectrum calibrated to δ ($oC_6F_2H_4$) = 6.96 ppm).

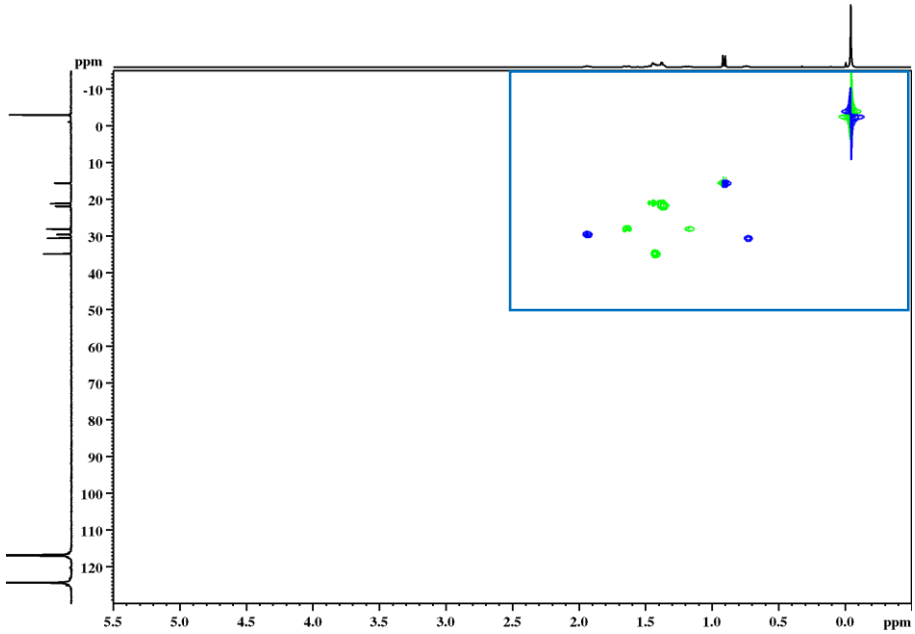


Figure S 19 Edited $^{1}H,^{13}C$-HSQC NMR spectrum (400.17 MHz, *o*DFB, 298 K, optimized for *J* = 145 Hz; CH_2: green, CH_3 and CH: blue) of a $HSiMe_3$/1-methylcyclohexene/**1** (1.0 : 1.0 : 0.1) mixture, 1 d after mixing the components (^{1}H NMR spectrum calibrated to δ ($oC_6F_2\mathbf{H}_4$) = 6.96 ppm).

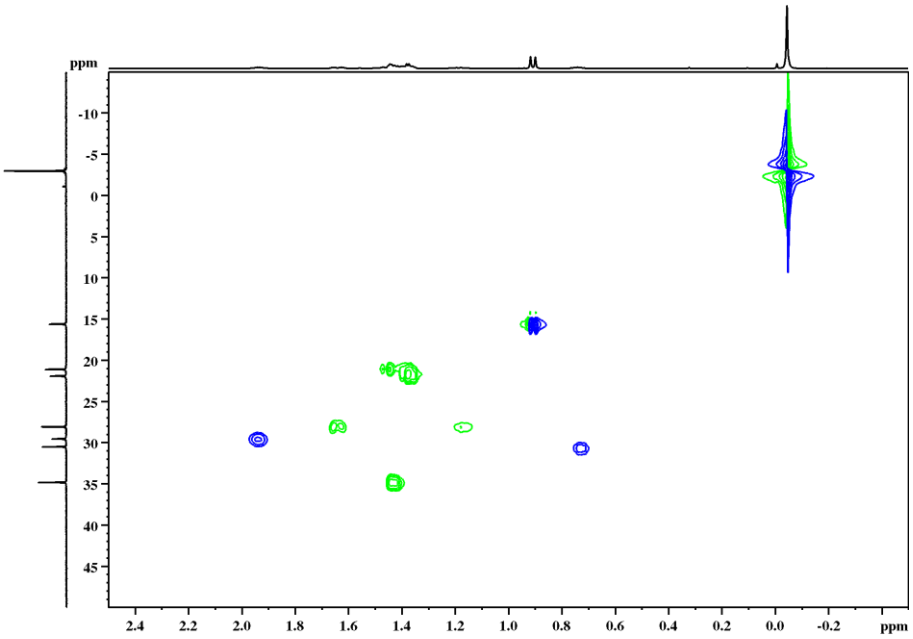


Figure S 20 Edited $^{1}H,^{13}C$-HSQC NMR spectrum (400.17 MHz, *o*DFB, 298 K, optimized for *J* = 145 Hz; CH_2: green, CH_3 and CH: blue) of a $HSiMe_3$/1-methylcyclohexene/**1** (1.0 : 1.0 : 0.1) mixture, 1 d after mixing the components (^{1}H NMR spectrum calibrated to δ ($oC_6F_2\mathbf{H}_4$) = 6.96 ppm; selected area from the spectrum in **Figure S 19**).

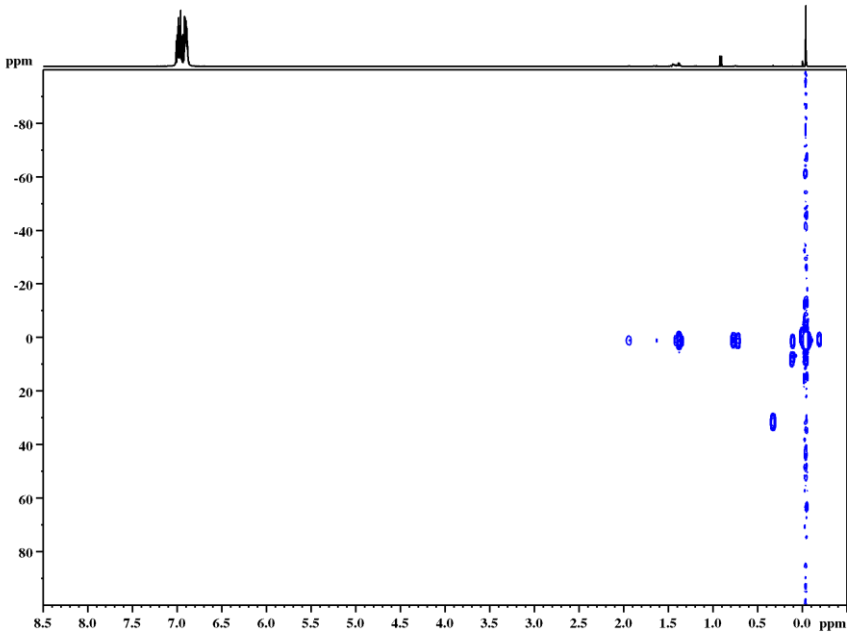


Figure S 21 $^{1}H,^{29}Si$-HMBC NMR spectrum (400.17 MHz, *o*DFB, 298 K, optimized for J = 8 Hz) of a $HSiMe_3$/1-methylcyclohexene/**1** (1.0 : 1.0 : 0.1) mixture, 1 d after mixing the components (^{1}H NMR spectrum calibrated to δ (*o*$C_6F_2\mathbf{H}_4$) = 6.96 ppm).

The ^{1}H-DPFGSENOE NMR spectrum in **Figure S 22** shows that if **7** is irradiated, a NOE is observed for **8** and not for **1**. This indicates that the methyl group is disposed *trans* to the **H**–$CSiMe_3$ hydrogen atom. The respective conformer is depicted in **Figure S 22**.

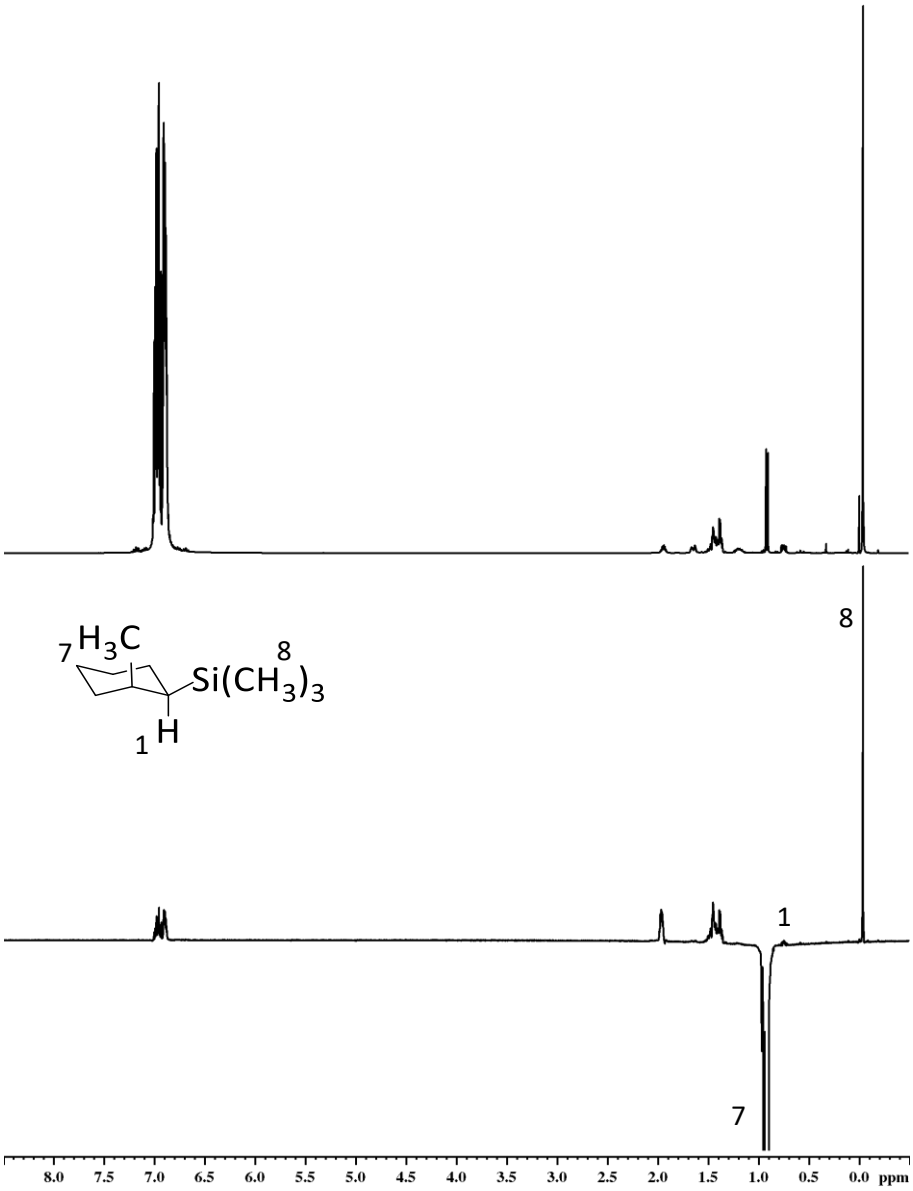
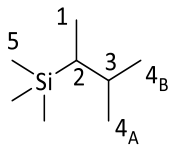


Figure S 22 ^{1}H NMR spectrum (400.17 MHz, *o*DFB, 298 K; top) ^{1}H DPFGSENOE NMR spectrum (*o*DFB, 400.17 MHz, 298 K, mixing time = 1 s; bottom) of (2-methylcyclohexyl)trimethylsilane, obtained by mixing $HSiMe_3$, 1-methylcyclohexene and **1** (1.0 : 1.0 : 0.1) at rt, irradiated on frequency of C–C**H**$_3$ hydrogen atoms (0.91 ppm; spectra calibrated to δ (*o*C_6F_2**H**$_4$) = 6.96 ppm).

2.1.4 $HSiMe_3$ + 2-Methylbut-2-ene + 1 (1.1 : 1.0 : 0.05)



^{1}H NMR [400.17 MHz, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K]: δ = 4.00 (dec, 1 H, **H**Si(CH$_3$)$_3$, $^{3}J_{SiH,CH}$ = 3.5 Hz), 1.80 (septd, 1 H, **H**^{3}, $^{3}J_{H3,H4A}$ = $^{3}J_{H3,H4B}$ = 6.8 Hz, $^{3}J_{H3,H2}$ = 4.3 Hz), 0.91 (d, 3 H, **H**$^{4}_{A}$, $^{3}J_{H4A,H3}$ = 6.9 Hz), 0.86 (d, 3 H, **H**^{1}, $^{3}J_{H1,H2}$ = 7.6 Hz), 0.83 (d, 3 H, **H**$^{4}_{B}$, $^{3}J_{H4B,H3}$ = 6.9 Hz), 0.55 (qd, 1 H, **H**^{2}, $^{3}J_{H2,H1}$ = 7.6 Hz, $^{3}J_{H2,H3}$ = 4.3 Hz), 0.35 (s, 9 H, ClSi(C**H**$_3$)$_3$), 0.03 (d, 9 H, HSi(C**H**$_3$)$_3$, $^{3}J_{CH,SiH}$ = 3.5 Hz), –0.03 (m, 9 H, **H**^{5}) ppm.

^{13}C NMR [100.62 MHz, *o*DFB, 298 K]: δ = 150.5 (2 C, **C**^{1}F in *o*DFB), 124.3 (2 C, **C**^{3} in *o*DFB), 116.8 (2 C, **C**^{2} in *o*DFB), 28.8 (1 C, **C**^{3}), 27.2 (1 C, **C**^{2}), 22.1 (1 C, **C**$^{4}_{A}$), 19.3 (1 C, **C**$^{4}_{B}$), 8.9 (1 C, **C**^{1}), –2.50 (3 C, **C**^{5}) ppm.

^{29}Si NMR [79.50 MHz, *o*DFB, 298 K]: δ = 3.3 (1 Si, (H$_3$C)$_3$**Si**[CH(CH$_3$)CH(CH$_3$)$_2$]) ppm.

^{71}Ga NMR [122.04 MHz, *o*DFB, 298 K]: δ = –755.3 ppm (Δν$_{1/2}$ = 540 Hz, br, 1 Ga, [**Ga**(fluoroarene)$_x$]$^{+}$).

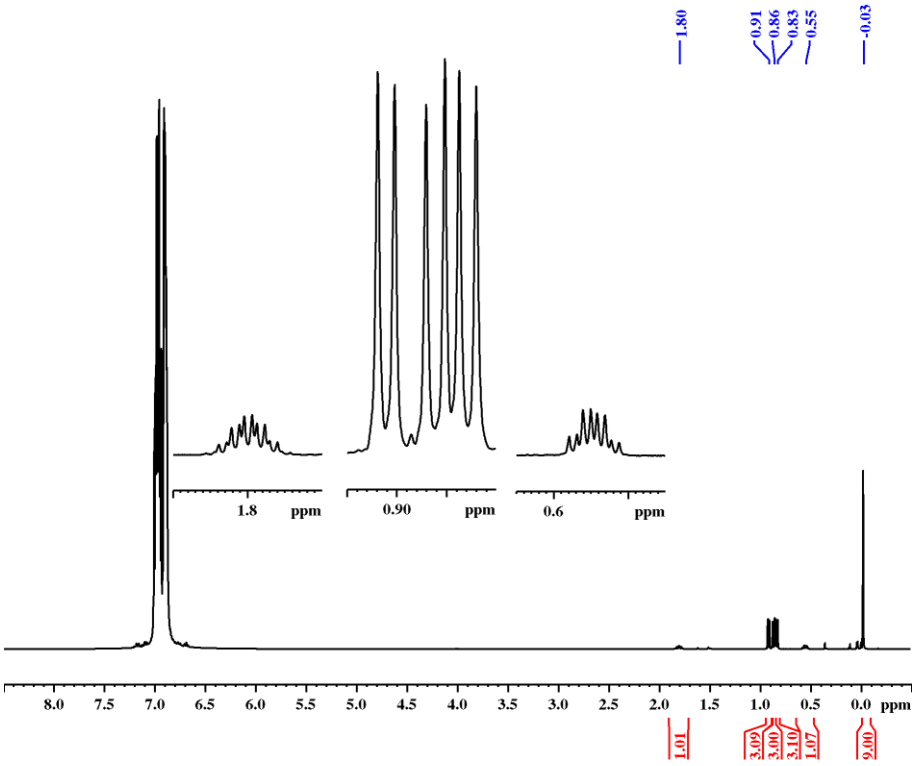


Figure S 23 ^{1}H NMR spectrum (400.17 MHz, *o*DFB, 298 K) of a $HSiMe_3$/2-Methylbut-2-ene/**1** (1.1 : 1.0 : 0.05) mixture, 1 d after mixing the components (spectrum calibrated to δ (*o*C$_6$F$_2$**H**$_4$) = 6.96 ppm).

2.1.5 $HSiMe_3$ + 1,5-Hexadiene + 1 (2.2 : 1.0 : 0.1)

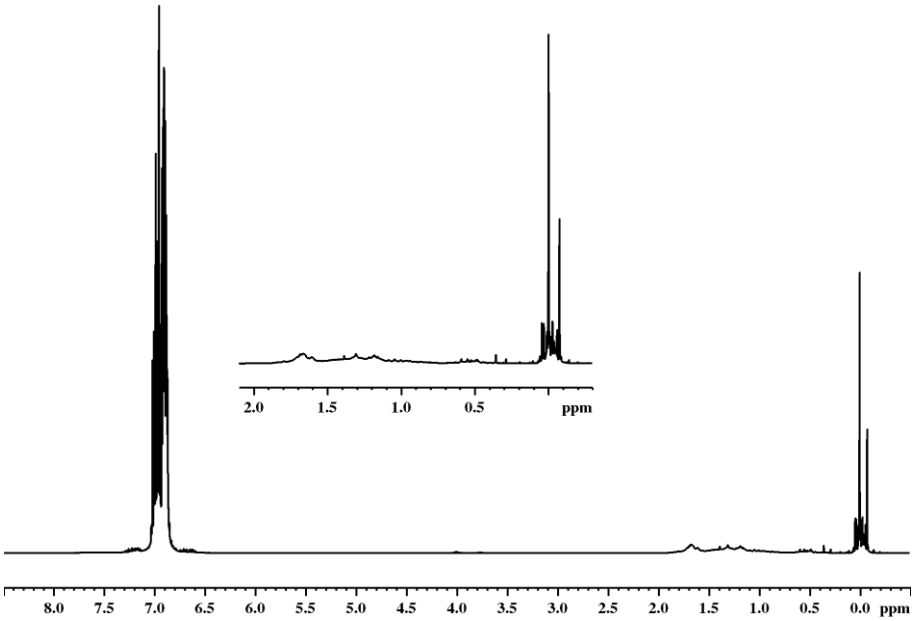
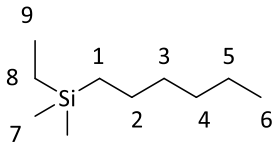


Figure S 24 ^{1}H NMR spectrum (300.18 MHz, *o*DFB, 298 K) of a $HSiMe_3$/1,5-hexene/**1** (2.2 : 1.0 : 0.1) mixture, 5.5 d after mixing the components (spectrum calibrated to δ ($oC_6F_2\mathbf{H}_4$) = 6.96 ppm).

2.1.6 $HSiMe_2Et$ + 1-Hexene + 1 (0.4 : 1.0 : 0.1 and 1.0 : 1.0 : 0.01)



^{1}H NMR [300.18 MHz, *o*DFB, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K]: δ = 1.38 (br, oligomers (ca. 60 %)), 1.27 (m, 2 H, **H**^{2}), 1.26 (m, 2 H, **H**^{3}), 1.25 (m, 2 H, **H**^{5}), 1.24 (m, 2 H, **H**^{4}), 0.93 (t, 3 H, **H**^{9}, $^3J_{H9,H8}$ = 7.9 Hz), 0.88 (t, 3 H, **H**^{6}, $^3J_{H6,H5}$ = 7.0 Hz), 0.48 (q, 2 H, **H**^{8}, $^3J_{H8,H9}$ = 7.9 Hz), 0.47 (m, 2 H, **H**^{1}), 0.07 (s, 12 H, $O[Si(C\mathbf{H}_3)_2(C_2H_5)]_2$, –0.01 (s, 9 H, $(H_{13}C_6)Si(C\mathbf{H}_3)_3$), –0.04 (s, 6 H, **H**^{7}), –0.07 (s, 3 H, $(H_{13}C_6)Si(C_2H_5)_2C\mathbf{H}_3$) ppm.

With a 1.0 : 1.0 ratio of $HSiMe_2Et$ to 1-hexene, no broad signals in the aliphatic region of the ^{1}H NMR spectrum are observed.

^{13}C NMR [75.48 MHz, *o*DFB, 298 K]: δ = 150.5 (2 C, **C**^{1}F in *o*DFB), 124.3 (2 C, **C**^{3} in *o*DFB), 116.8 (2 C, **C**^{2} in *o*DFB), 33.4 (1 C, **C**^{3}), 31.5 (1 C, **C**^{4}), 23.7 (1 C, **C**^{2}), 22.5 (1 C, **C**^{5}), 14.5 (1 C, **C**^{1}), 13.4 (1 C, **C**^{6}), 6.6 (1 C, **C**^{8}), 6.6 (1 C, **C**^{9}), –2.7 (3 C, $H_{13}C_6$–$Si(\mathbf{C}H_3)_3$), –4.9 (2 C, **C**^{7}), –7.2 (1 C, $(H_{13}C_6)Si(C_2H_5)_2\mathbf{C}H_3$) ppm.

^{29}Si NMR [59.64 MHz, *o*DFB, 298 K]: δ = 8.7 (1 Si, $O[\mathbf{Si}(CH_3)_2(C_2H_5)]_2$), 5.2 (1 Si, $H_3C(H_5C_2)_2\mathbf{Si}(C_6H_{13})$), 3.2 (1 Si, $(H_3C)_2(H_5C_2)\mathbf{Si}(C_6H_{13})$), 0.6 (1 Si, $(H_3C)_3\mathbf{Si}(C_6H_{13})$) ppm.

^{71}Ga NMR [91.54 MHz, *o*DFB, 298 K]: δ = –757.4 ($\Delta\nu_{1/2}$ = 220 Hz; br, 1 Ga, $[\mathbf{Ga}(\text{fluoroarene})_x]^+$) ppm.

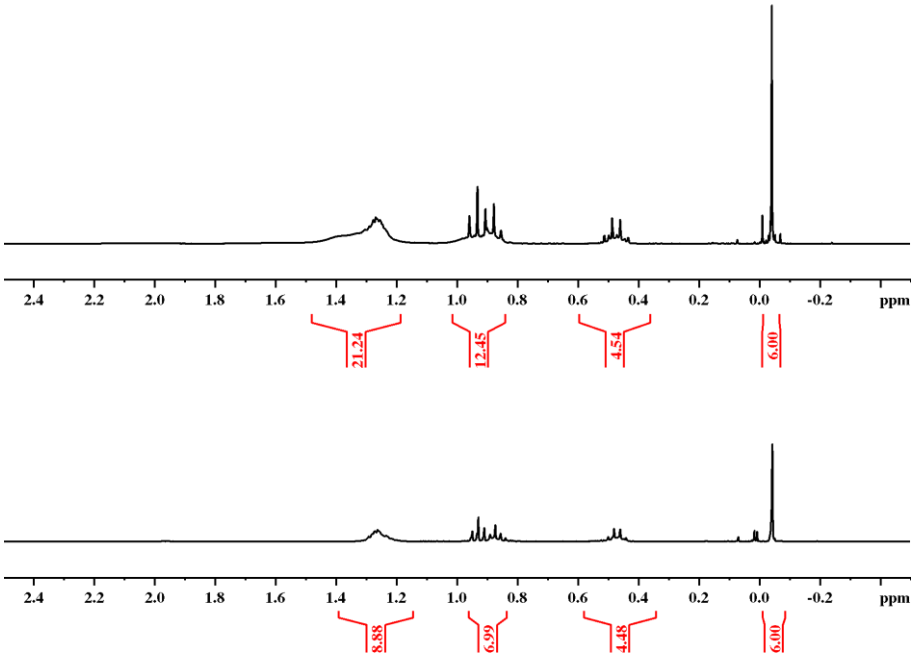
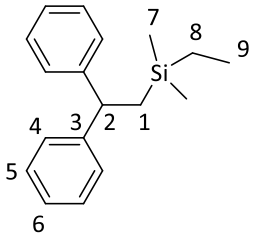


Figure S 25 From bottom to top: ^{1}H NMR spectrum of a HSiMe$_2$Et/1-hexene/**1** (1.0 : 1.0 : 0.01) mixture (400.17 MHz, *o*DFB, 298 K), 4 d after mixing the components (mixture heated to 60 °C for 9 h) and of a HSiMe$_2$Et/1-hexene/**1** (2.5 : 1.0 : 0.1) mixture, 10 h after mixing the components (300.18 MHz, *o*DFB, 298 K; spectra calibrated to δ (*o*C$_6$F$_2$**H**$_4$) = 6.96 ppm).

2.1.7 HSiMe$_2$Et + 1,1-Diphenylethylene + 1 (4.7 : 1.0 : 0.02 and 0.9 : 1.0 : 0.01)



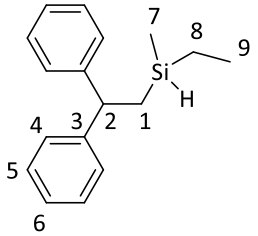
^{1}H NMR [400.17 MHz, *o*DFB, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K]: δ = 7.28 (m, 4 H, **H**^{4}), 7.19 (m, 4 H, **H**^{5}), 7.08 (m, 2 H, **H**^{6}), 4.09 (t, 1 H, **H**^{2}, $^3J_{H2,H1}$ = 8.1 Hz), 1.38 (d, 2 H, **H**^{1}, $^3J_{H1,H2}$ = 8.1 Hz), 0.86 (t, 3 H, **H**^{9}, $^3J_{H9,H8}$ = 7.9 Hz), 0.35 (q, 2 H, **H**^{8}, $^3J_{H8,H9}$ = 7.9 Hz), –0.18 (s, 6 H, **H**^{7}) ppm.

^{13}C NMR [100.62 MHz, *o*DFB, 298 K]: δ = 150.5 (2 C, **C**^{1}F in *o*DFB), 147.4 (2 C, **C**^{3}), 128.2 (4 C, **C**^{5}), 127.4 (4 C, **C**^{4}), 125.8 (2 C, **C**^{6}), 124.3 (2 C, **C**^{3} in *o*DFB), 116.8 (2 C, **C**^{2} in *o*DFB), 47.4 (1 C, **C**^{2}), 22.1 (1 C, **C**^{1}), 6.9 (1 C, **C**^{8}), 6.5 (1 C, **C**^{9}), –4.4 (2 C, **C**^{7}) ppm.

^{19}F NMR [376.54 MHz, *o*DFB, 298 K]: δ = –70.1 (m$_c$, 6 F, OC(C**F**$_3$)$_2$CF$_2$), –75.3 (s, 36 F, [Al(OC(C**F**$_3$)$_3$)$_4$]$^-$), –109.2 (m$_c$, 2 F, OC(CF$_3$)$_2$C**F**$_2$), –113.8 (m$_c$, 1 F, C$_6$H$_5$**F**), –120.2 (unknown species), –139.4 (m$_c$, 2 H, *o*C$_6$**F**$_2$H$_4$) ppm.

^{29}Si NMR [79.50 MHz, *o*DFB, 298 K]: δ = 3.3 (1 Si, **Si**) ppm.

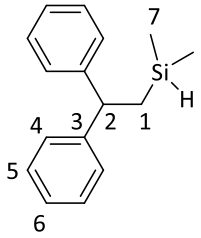
^{71}Ga NMR [91.54 MHz, *o*DFB, 298 K]: δ = –703.3 (Δν$_{1/2}$ = 930 Hz, br, 1 Ga, [**Ga**(ligand)$_x$]$^+$) ppm.



^{1}H NMR [400.17 MHz, *o*DFB, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K]: 7.26 (m, 4 H, **H**^{4}), 7.19 (m, 4 H, **H**^{5}), 7.08 (m, 2 H, **H**^{6}), 4.10 (dd, 1 H, **H**^{2}, $^{3}J_{H2,H1A} = {}^{3}J_{H2,H1B}$ = 8.1 Hz), 3.77 (m, 1 H, Si**H**), 1.46 (m, 1 H, **H**$^{1}{}_{A}$), 1.39 (m, 1 H, **H**$^{1}{}_{B}$), 0.89 (t, 3 H, **H**^{9}, $^{3}J_{H9,H8}$ = 7.8 Hz), 0.45 (m, 1 H, **H**$^{8}{}_{A}$), 0.39 (m, 1 H, **H**$^{8}{}_{B}$), –0.13 (d, 3 H, **H**^{7}, $^{3}J_{H7,SiH}$ = 3.7 Hz) ppm.

^{13}C NMR [100.62 MHz, *o*DFB, 298 K]: δ = 146.95 (1 C, **C**$^{3}{}_{A}$), 146.91 (1 C, **C**$^{3}{}_{B}$), 128.2 (4 C, **C**^{5}), 127.4 (4 C, **C**^{4}), 125.85 (2 C, **C**^{6}), 47.8 (1 C, **C**^{2}), 19.8 (1 C, **C**^{1}), 6.9 or 6.1 (1 C, **C**^{9}), 4.4 (1 C, **C**^{8}), –7.5 (1 C, **C**^{7}) ppm.

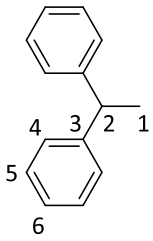
^{29}Si NMR [79.50 MHz, *o*DFB, 298 K]: δ = –8.3 (1 Si, **Si**) ppm.



^{1}H NMR [400.17 MHz, *o*DFB, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K]: δ = 7.26 (m, 4 H, **H**^{4}), 7.19 (m, 4 H, **H**^{5}), 7.08 (m, 2 H, **H**^{6}), 4.09 (t, 1 H, **H**^{2}), 3.87 (m, 1 H, Si**H**), 1.40 (d, 2 H, **H**^{1}), –0.10 (d, 6 H, **H**^{7}) ppm.

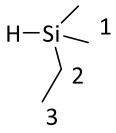
^{13}C NMR [100.62 MHz, *o*DFB, 298 K]: δ = 147.4 (2 C, **C**^{3}), 128.2 (4 C, **C**^{5}), 127.4 (4 C, **C**^{4}), 125.8 (2 C, **C**^{6}), 47.8 (1 C, **C**^{2}), 21.5 (1 C, **C**^{1}), –8.0 (2 C, **C**^{7}) ppm.

^{29}Si NMR [79.50 MHz, *o*DFB, 298 K]: δ = –13.7 (1 Si, **Si**) ppm.



^{1}H NMR [400.17 MHz, *o*DFB, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K]: δ = 4.04 (q, 1 H, **H**^{2}, $^{3}J_{H2,H1}$ = 7.2 Hz), 1.55 (d, 2 H, **H**^{1}, $^{3}J_{H1,H2}$ = 7.2 Hz) ppm. The shifts of the hydrogen atoms H^{4}-H^{6} are too similar to the other product signals signals and thus cannot be assigned.

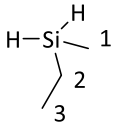
^{13}C NMR [100.62 MHz, *o*DFB, 298 K]: δ = 146.4 (2 C, **C**^{3}), 128.2 (4 C, **C**^{5}), 127.5 (4 C, **C**^{4}), 125.8 (2 C, **C**^{6}), 44.8 (1 C, **C**^{2}), 21.3 (1 C, **C**^{1}) ppm.



^{1}H NMR [400.17 MHz, *o*DFB, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K]: δ = 3.91 (m, 1 H, Si**H**), 0.95 (t, 3 H, **H**^{3}, $^{3}J_{H3,H2}$ = 7.7 Hz), 0.52 (d, 2 H, **H**^{2}), 0.02 (d, 6 H, **H**^{1}, $^{3}J_{H1,SiH}$ = 3.6 Hz) ppm.

^{13}C NMR [100.62 MHz, *o*DFB, 298 K]: δ = 7.0 (1 C, **C**^{3}), 5.6 (1 C, **C**^{2}), –6.0 (1 C, **C**^{1}) ppm.

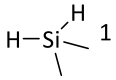
^{29}Si NMR [79.50 MHz, *o*DFB, 298 K]: δ = –10.9 (1 Si, **Si**) ppm.



^{1}H NMR [400.17 MHz, *o*DFB, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K]: δ = 3.74 (m, 2 H, Si**H**), 0.97 (t, 3 H, **H**^{3}), 0.57 (m, 2 H, **H**^{2}), 0.05 (t, 3 H, **H**^{1}) ppm.

^{13}C NMR [100.62 MHz, *o*DFB, 298 K]: δ = 6.9 or 6.1 (1 C, **C**^{3}), 2.2 (1 C, **C**^{2}), –10.1 (1 C, **C**^{1}) ppm.

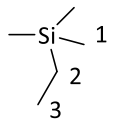
^{29}Si NMR [79.50 MHz, *o*DFB, 298 K]: δ = –30.8 (1 Si, **Si**) ppm.



^{1}H NMR [400.17 MHz, *o*DFB, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K]: δ = 3.79 (m, 2 H, Si**H**), 0.06 (t, 6 H, **H**^{1}) ppm.

^{13}C NMR [100.62 MHz, *o*DFB, 298 K]: δ = –8.1 (2 C, **C**^{1}) ppm.

^{29}Si NMR [79.50 MHz, *o*DFB, 298 K]: δ = –38.0 (1 Si, **Si**) ppm.



^{1}H NMR [400.17 MHz, *o*DFB, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K]: δ = 0.94 (t, 3 H, **H**^{3}, $^{3}J_{H3,H2}$ = 8.2 Hz), 0.46 (q, 2 H, **H**^{2}, $^{3}J_{H2,H3}$ = 8.2 Hz), –0.03 (s, 9 H, **H**^{1}) ppm.

^{13}C NMR [100.62 MHz, *o*DFB, 298 K]: δ = 7.9 (1 C, **C**^{2}), 6.5 (1 C, **C**^{3}), –3.3 (3 C, **C**^{1}) ppm.

^{29}Si NMR [79.50 MHz, *o*DFB, 298 K]: δ = 2.3 (1 Si, **Si**) ppm.

The spectra in **Figure S 26** illustrate well the reaction delay with 1,1-diphenylethylene and $HSiMe_2Et$.

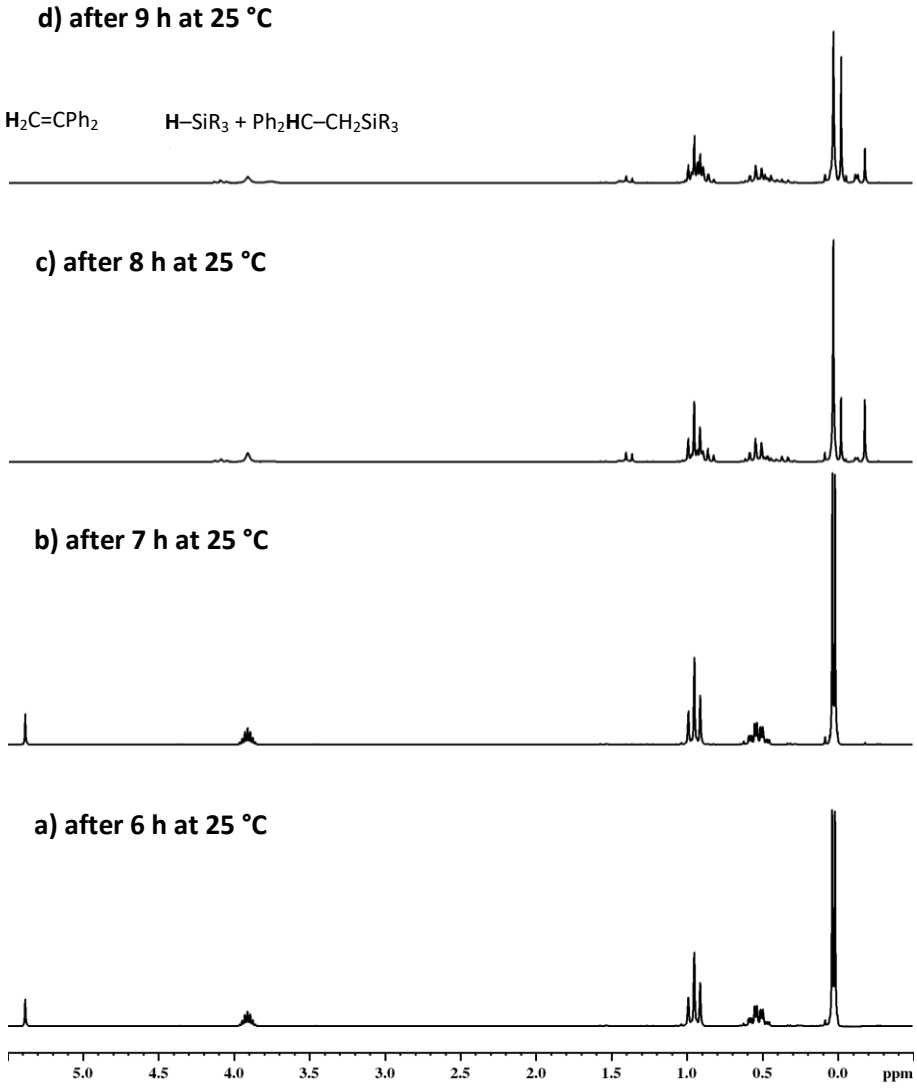


Figure S 26 ^{1}H NMR (200.13 MHz, *o*DFB, 298 K) spectra of a $HSiMe_2Et$/1,1-diphenylethylene/**1** (4.7 : 1.0 : 0.02) mixture. From bottom to top: 6 h, 7 h, 8 h and 9 h after mixing the components at rt. Signal intensities were normalized with respect to the solvent signal (spectra calibrated to δ (*o*$C_6F_2\mathbf{H}_4$) = 6.96 ppm).

In a $HSiMe_2Et$/1,1-diphenylethylene/**1** (0.9 : 1.0 : 0.01) mixture, the signals of the addition product $Ph_2HC–CSiMe_2Et$ (57 %), the olefin $Ph_2C=CH_2$ (23 %), the silane $HSiMe_2Et$ (12 %), the silane Me_3SiEt (6 %) and of Ph_2CHCH_3 (3 %) can be observed.

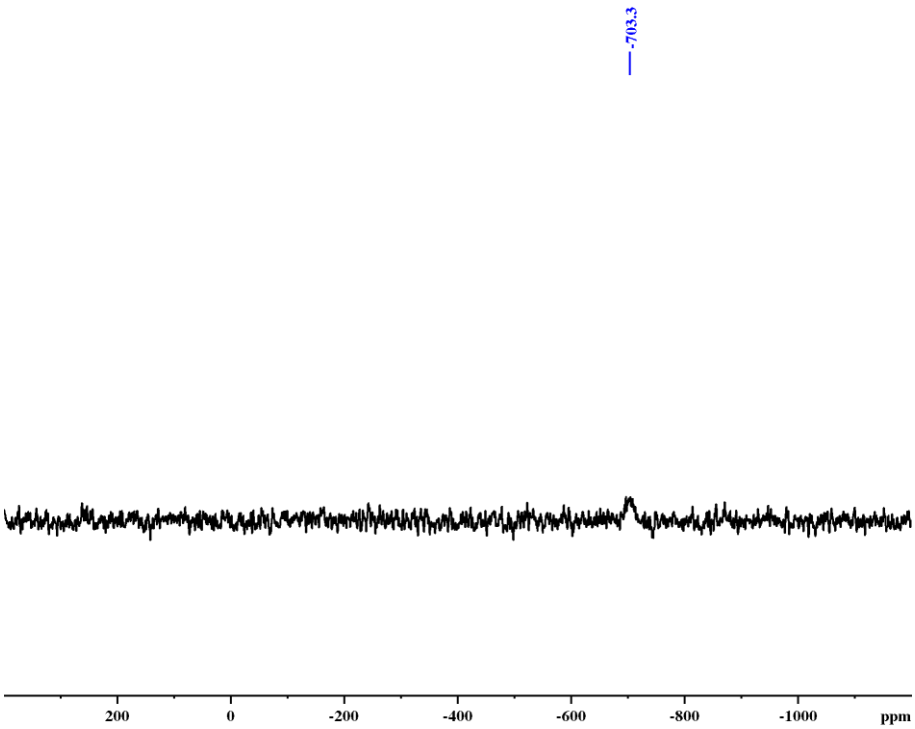


Figure S 27 ^{71}Ga NMR spectrum (91.55 MHz, *o*DFB, 298 K) of a $HSiMe_2Et$/1,1-diphenylethylene/**1** (4.7 : 1.0 : 0.02) mixture, 1 h after mixing the components.

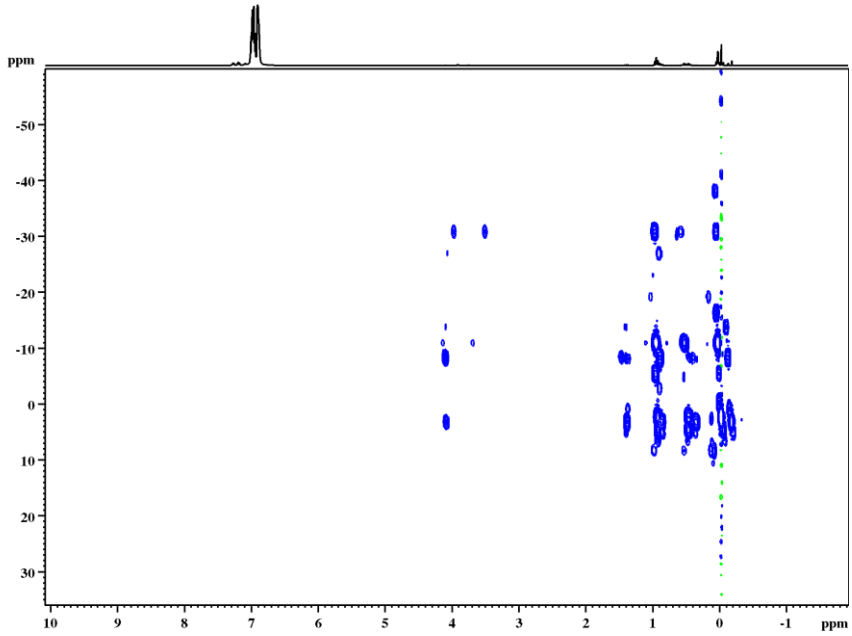


Figure S 28 ^{1}H,^{29}Si-HMBC NMR spectrum (400.17 MHz, *o*DFB, 298 K, optimized for J = 8 Hz) of a $HSiMe_2Et$/1,1-diphenylethylene/**1** (4.7 : 1.0 : 0.02) mixture, 1 d after mixing the components (^{1}H NMR spectrum calibrated to δ (*o*C_6F_2**H**$_4$) = 6.96 ppm).

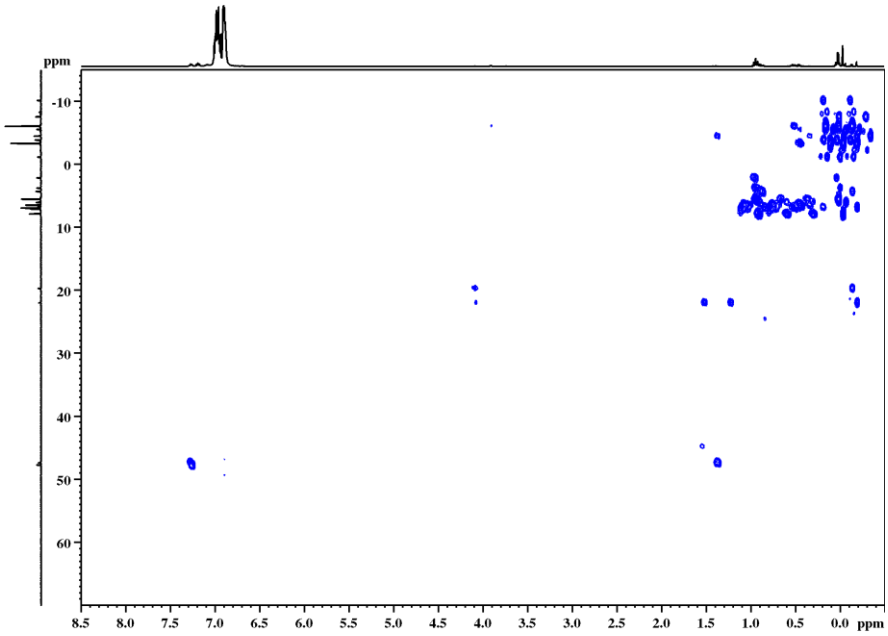


Figure S 29 $^{1}H,^{13}C$-HMBC NMR spectrum (400.17 MHz, *o*DFB, 298 K, optimized for J = 8 Hz) of a $HSiMe_2Et$/1,1-diphenylethylene/**1** (4.7 : 1.0 : 0.02) mixture, 1 d after mixing the components (^{1}H NMR spectrum calibrated to δ ($oC_6F_2\mathbf{H}_4$) = 6.96 ppm).

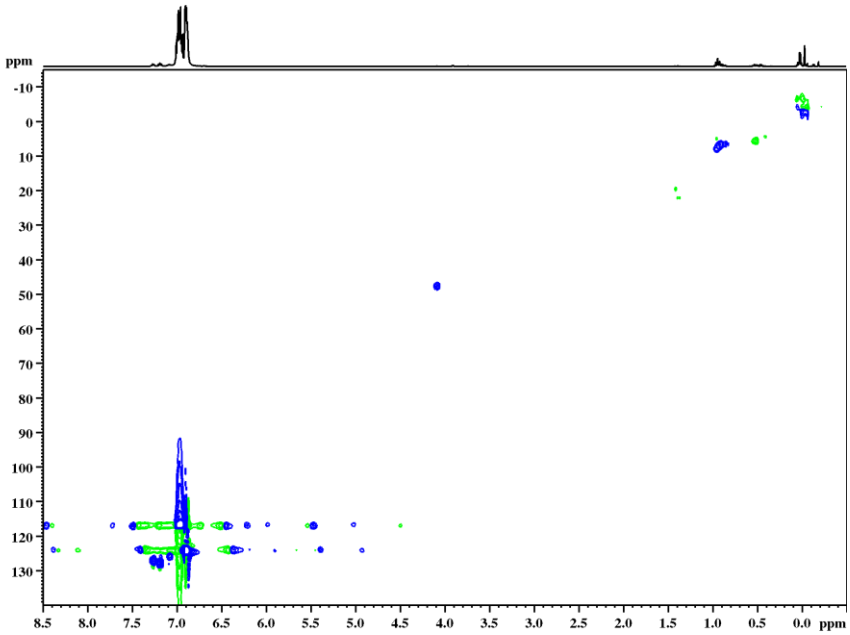
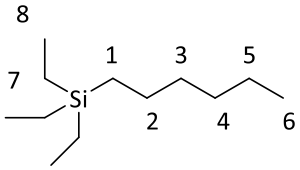


Figure S 30 Edited $^{1}H,^{13}C$-HSQC NMR spectrum (400.17 MHz, *o*DFB, 298 K, optimized for J = 145 Hz; CH_2: green, CH_3 and CH: blue) of a $HSiMe_2Et$/1,1-diphenylethylene/**1** (4.7 : 1.0 : 0.02) mixture, 1 d after mixing the components (^{1}H NMR spectrum calibrated to δ ($oC_6F_2\mathbf{H}_4$) = 6.96 ppm).

2.1.8 $HSiEt_3$ + 1-Hexene + 1 (1.1 : 1.0 : 0.1)



^{1}H NMR [300.18 MHz, *o*DFB, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K]: δ = 1.28 (m, 2 H, **H**^{2}), 1.28 (m, 2 H, **H**^{3}), 1.26 (m, 2 H, **H**^{5}), 1.25 (m, 2 H, **H**^{4}), 0.94 (t, 9 H, **H**^{8}, $^{3}J_{H8,H7}$ = 8.0 Hz), 0.88 (m, 3 H, **H**^{6}), 0.49 (m, 2 H, **H**^{1}), 0.49 (q, 6 H, **H**^{7}, $^{3}J_{H7,H8}$ = 8.0 Hz) ppm.

^{13}C NMR [100.62 MHz, *o*DFB, 298 K]: δ = 150.5 (2 C, **C**^{1}F in *o*DFB), 124.3 (2 C, **C**^{3} in *o*DFB), 116.8 (2 C, **C**^{2} in *o*DFB), 33.6 (2 C, **C**^{3}), 31.5 (2 C, **C**^{4}), 23.7 (2 C, **C**^{2}), 22.5 (2 C, **C**^{5}), 13.4 (1 C, **C**^{6}), 11.0 (1 C, **C**^{1}), 6.7 (3 C, **C**^{8}), 3.0 (3 C, **C**^{7}) ppm.

^{29}Si NMR [59.64 MHz, *o*DFB, 298 K]: δ = 6.4 (1 Si, $(H_5C_2)_3$**Si**(C_6H_{13})), 0.2 (1 Si, H**Si**$(C_2H_5)_3$) ppm.

^{71}Ga NMR [122.04 MHz, *o*DFB, 298 K]: δ = –754.2 ($\Delta\nu_{1/2}$ = 638 Hz; br, 1 Ga, [**Ga**(fluoroarene)$_x$]$^{+}$) ppm.

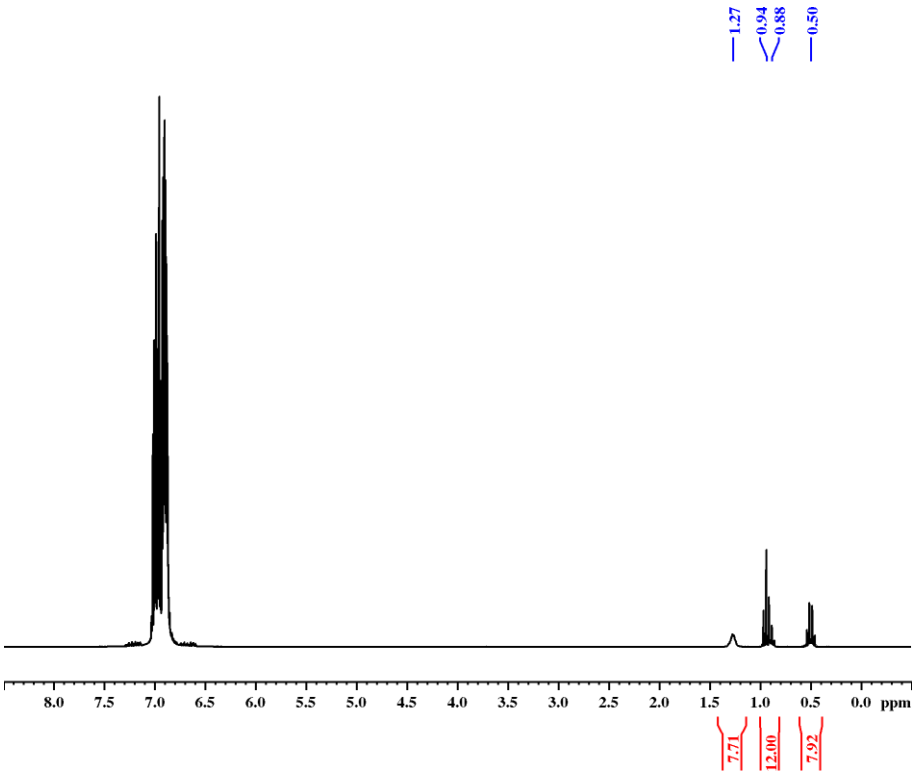
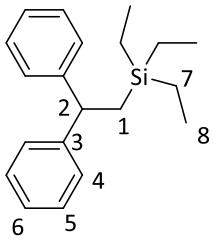


Figure S 31 ^{1}H NMR spectrum (300.18 MHz, *o*DFB, 298 K) of a $HSiEt_3$/1-hexene/**1** (1.1 : 1.0 : 0.1) mixture, 5 d (mixture heated to 60 °C for 1 d) after mixing the components (^{1}H NMR spectrum calibrated to δ ($oC_6F_2H_4$) = 6.96 ppm).

2.1.9 $HSiEt_3$ + 1,1-Diphenylethylene + 1 (4.2 : 1.0 : 0.02 and 1.0 : 1.0 : 0.42)



^{1}H NMR [400.17 MHz, *o*DFB, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K]: δ = 7.30 (m, 4 H, **H**^{4}), 7.20 (m, 4 H, **H**^{5}), 7.09 (m, 2 H, **H**^{6}), 4.09 (t, 1 H, **H**^{2}, $^{3}J_{H2,H1}$ = 7.9 Hz), 3.71 (sept, 1 H, **H**Si(C$^{1'}$H$_2$C$^{2'}$H$_3$)$_3$, $^{3}J_{SiH,H1'}$ = 3.2 Hz), 1.41 (d, 2 H, **H**^{1}, $^{3}J_{H1,H2}$ = 7.9 Hz), 0.97 (t, 9 H, HSi(C$^{1'}$H$_2$C$^{2'}$**H**$_3$)$_3$, $^{3}J_{H2',H1'}$ = 8.0 Hz), 0.85 (t, 9 H, **H**^{8}, $^{3}J_{H8,H7}$ = 7.9 Hz), 0.56 (qd, 6 H, HSi(C$^{1'}$**H**$_2$C$^{2'}$H$_3$)$_3$, $^{3}J_{H1',H2'}$ = 8.0 Hz, $^{3}J_{H1',SiH}$ = 3.2 Hz), 0.37 (q, 6 H, **H**^{7}, $^{3}J_{H7,H8}$ = 7.9 Hz) ppm.

^{13}C NMR [100.62 MHz, *o*DFB, 298 K]: δ = 150.5 (2 C, **C**^{1}F in *o*DFB), 147.9 (2 C, **C**^{3}), 128.4 (4 C, **C**^{5}), 127.4 (4 C, **C**^{4}), 126.7 (2 C, **C**^{6}), 124.3 (2 C, **C**^{3} in *o*DFB), 116.8 (2 C, **C**^{2} in *o*DFB), 47.5 (1 C, **C**^{2}), 16.2 (1 C, **C**^{1}), 6.3 (3 C, **C**^{8}), 3.0 (3 C, **C**^{7}) ppm.

^{29}Si NMR [79.50 MHz, *o*DFB, 298 K]: δ = 6.4 (1 Si, Ph_2CHCH_2**Si**$(C_2H_5)_3$), 0.1 (1 Si, $(H_5C_2)_3$**Si**H) ppm.

^{71}Ga NMR [91.54 MHz, *o*DFB, 298 K]: δ = –739.0 ($\Delta\nu_{1/2}$ = 1030 Hz, br, 1 Ga, [**Ga**(ligand)$_x$]$^{+}$) ppm.

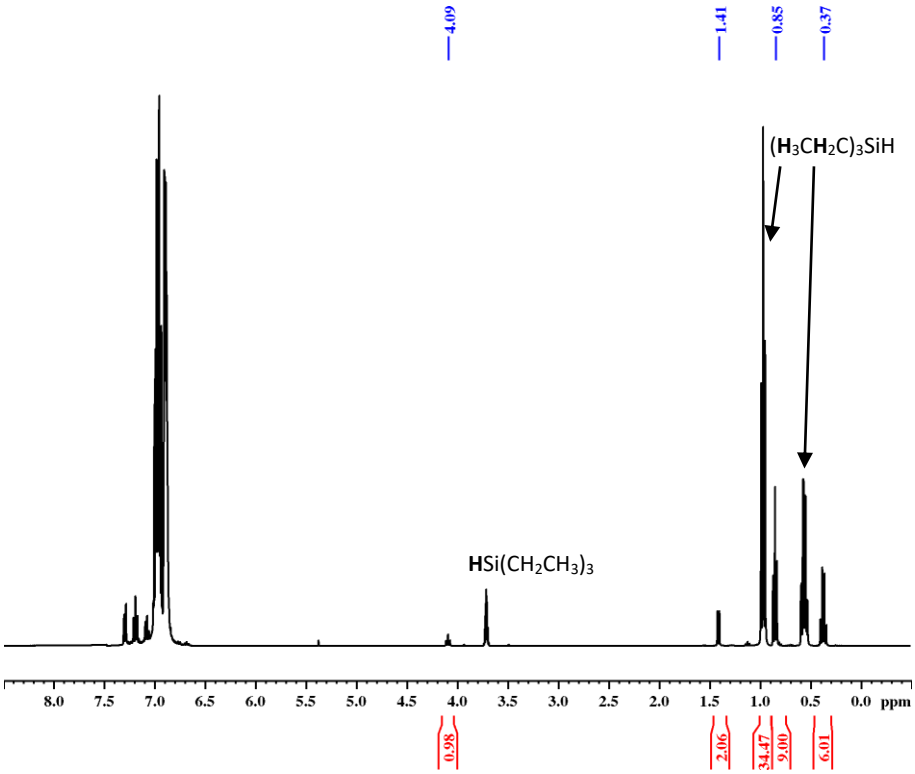


Figure S 32 ^{1}H NMR (400.17 MHz, *o*DFB) spectra of a $HSiEt_3$/1,1-diphenylethylene/**1** (4.2 : 1.0 : 0.02) mixture, 6 d (mixture heated to 60 °C for 4 h) after mixing the components (spectrum calibrated to δ (oC_6F_2**H**$_4$) = 6.96 ppm).

The ^{1}H NMR spectrum in **Figure S 32** illustrates well that a surplus of $HSiEt_3$ does not lead to side reactions with 1,1-diphenylethylene, unlike with $HSiMe_2Et$ (cf. section 2.1.7).

In a separate experiment, it was envisaged to observe the postulated intermediate, the β-silylcarbocation *via* NMR spectroscopy. To this end, a mixture of $HSiEt_3$ and 1,1-diphenylethylene (3.0 M, 70 µl, 0.21 mmol, respectively), was added to a solution of **1** in *o*DFB (0.15 M, 0.6 ml, 88 µmol, 0.42 eq.). The reaction mixture was quickly frozen at –78 °C after mixing the components and was thawed inside the NMR spectrometer.

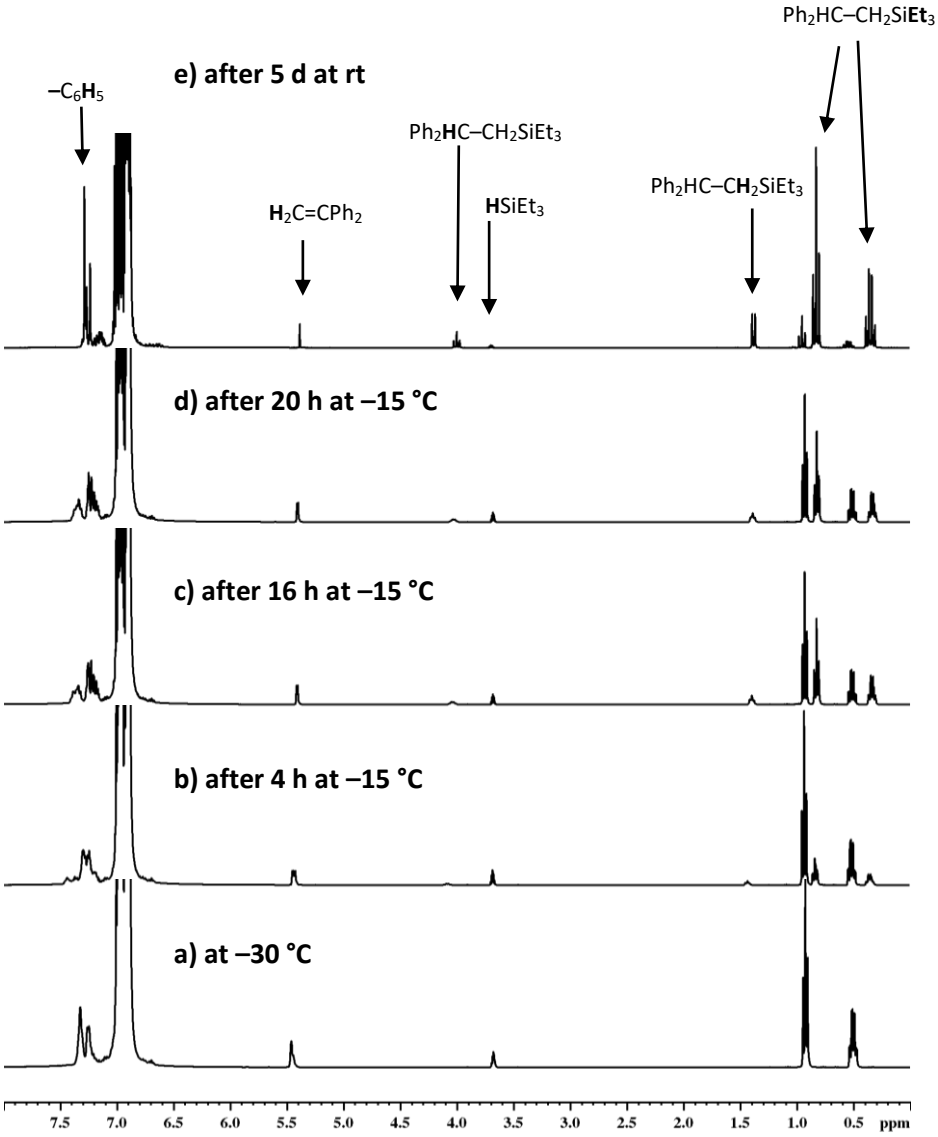
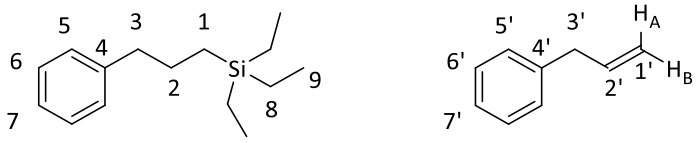


Figure S 33 ^{1}H NMR (400.17 MHz, *o*DFB) spectra of a $HSiEt_3$/1,1-diphenylethylene/**1** (1.0 : 1.0 : 0.42) mixture. From bottom to top: at –30 °C directly after mixing the components; after 4 h at –15 °C; after 16 h at –15 °C; after 20 h at –15 °C; after 5 d at rt (300.18 MHz). Signal intensities were normalized with respect to the solvent signal (spectra calibrated to δ (*o*$C_6F_2\mathbf{H}_4$) = 6.96 ppm).

2.1.10 $HSiEt_3$ + Allylbenzene + 1 (0.9 : 1.0 : 0.1)



^{1}H NMR [400.17 MHz, *o*DFB, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K]: δ = 7.24 (m, 2 H, **H**^{6}), 7.20 (m, 2 H, **H**^{5}), 7.16 (m, 1 H, **H**^{7}), 7.10-7.27 (m, 5 H, **H**^{5}, **H**^{6}, **H**^{7}), 5.90 (m_c, 1 H, **H**$^{2'}$), 5.05 (m_c, 1 H, **H**$^{2'}{}_{A}$), 5.02 (m_c, 1 H, **H**$^{2'}{}_{B}$), 4.55 (s, 2 H, **H**$_2$), 3.29 (m, 2 H, **H**$^{3'}$), 2.62 (m, 2 H, **H**^{3}), 1.64 (m_c, 2 H, **H**^{2}), 0.94 (t, 9 H, **H**^{9}, $^{3}J_{H9,H8}$ = 7.9 Hz), 0.58 (m_c, 2 H, **H**^{1}), 0.50 (q, 6 H, **H**^{8}, $^{3}J_{H8,H9}$ = 7.9 Hz) ppm.

^{13}C NMR [100.62 MHz, *o*DFB, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K]: δ = 150.5 (2 C, **C**^{1}F in *o*DFB), 142.9 (1 C, **C**^{4}), 140.0 (1 C, **C**$^{4'}$), 137.3 (1 C, **C**$^{2'}$), 128.4 (2 C, **C**^{5}), 125.6 (1 C, **C**^{7}), 124.3 (2 C, **C**^{3} in *o*DFB), 116.8 (2 C, **C**^{2} in *o*DFB), 116.8 (2 C, **C**^{6}), 115.1 (1 C, **C**$^{1'}$), 40.0 (1 C, **C**^{3}), 39.9 (1 C, **C**$^{3'}$), 26.0 (1 C, **C**^{2}), 11.0 (1 C, **C**^{1}), 6.7 (3 C, **C**^{9}), 3.0 (3 C, **C**^{8}) ppm.

^{19}F NMR [282.45 MHz, *o*DFB, 298 K]: δ = –70.1 (m_c, 6 F, OC(C**F**$_3$)$_2$CF$_2$), –75.3 (s, 36 F, [Al(OC(C**F**$_3$)$_3$)$_4$]$^-$), –75.5 (s, 27 F, (H$_5$C$_2$)$_3$Si–F–Al[OC(C**F**$_3$)$_3$]$_3$), –75.8 (unknown species), –109.3 (m_c, 2 F, OC(CF$_3$)$_2$C**F**$_2$), –113.7 (m_c, 1 F, C$_6$H$_5$**F**), –139.3 (m_c, 2 F, *o*C$_6$**F**$_2$H$_4$), –167.7 (unknown species), –168.6 (br, 1 F, (H$_5$C$_2$)$_3$Si–**F**–Al[OC(CF$_3$)$_3$]$_3$, $^{1}J_{F,Si}$ = 337 Hz), –174.0 (unknown species), –175.6 (br, 1 F, (H$_5$C$_2$)$_3$Si**F**), –184.5 (unknown species) ppm.

^{29}Si NMR [59.64 MHz, *o*DFB, 298 K]: δ = 83.6 (br, 1 Si, (H$_5$C$_2$)$_3$**Si**–F–Al[OC(CF$_3$)$_3$]$_3$, $^{1}J_{Si,F}$ = 288 Hz), 6.6 (1 Si, H$_5$C$_6$(CH$_2$)$_3$**Si**(C$_2$H$_5$)$_3$) ppm.

^{71}Ga NMR [91.54 MHz, *o*DFB, 298 K]: δ = –748.6 ($\Delta\nu_{1/2}$ = 215 Hz, br, 1 Ga, [**Ga**(ligand)$_x$]$^+$) ppm.

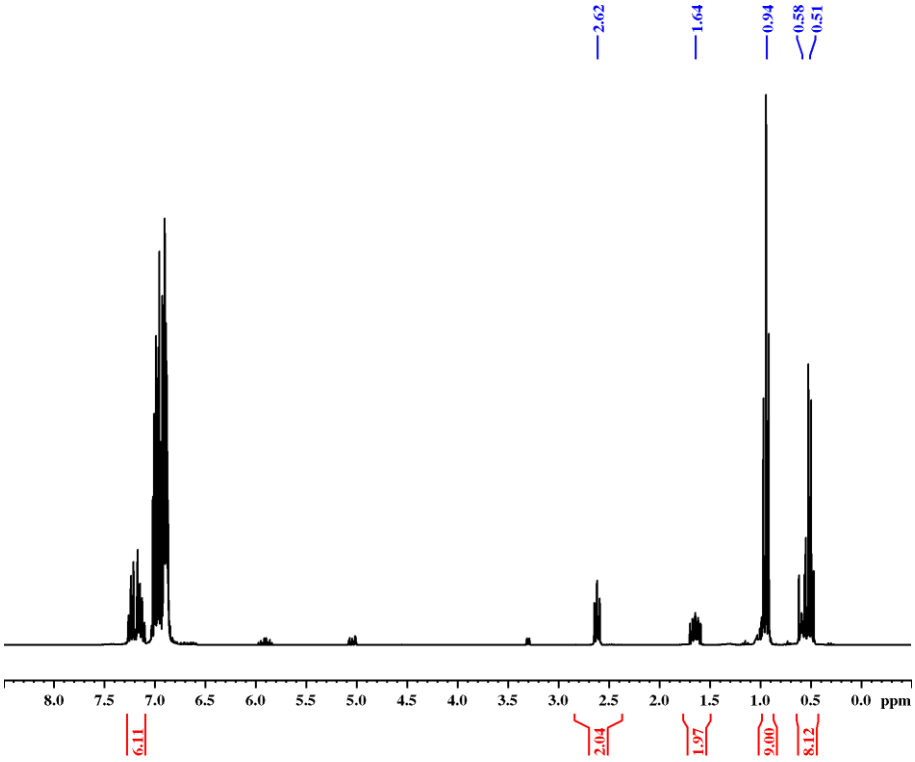
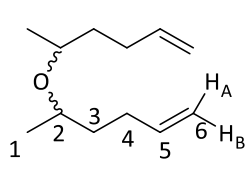
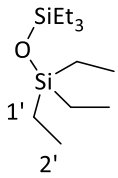


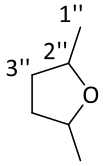
Figure S 34 ^{1}H NMR (300.18 MHz, *o*DFB, 298 K) of a HSiEt$_3$/allylbenzene/**1** (0.9 : 1.0 : 0.1) mixture, 9.5 d after mixing the components (mixture heated to 60 °C for 2.5 d; spectrum calibrated to δ (*o*C$_6$F$_2$**H**$_4$) = 6.96 ppm).

2.1.11 $HSiEt_3$ + 5-Hexen-2-one + 1 (0.9 : 1.0 : 0.1)

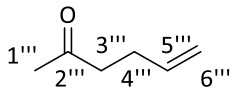


ca. 1:1 mixture of two diastereoisomers





diastereoisomer unknown



^{1}H NMR (400.17 MHz, *o*DFB, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K): δ = 5.77 (m_c, 4 H, **H**^{5}), 5.73 (m, 1 H, **H**$^{5'''}$), 4.97 (m_c, 4 H, **H**$^{6}{}_{A}$), 4.90 (m_c, 4 H, **H**$^{6}{}_{B}$), 4.08 (m_c, 2 H, **H**$^{2''}$), 3.39/3.37 (m, 4 H, **H**^{2}), 2.39 (m_c, 2 H, **H**$^{3'''}$), 2.24 (m_c, 2 H, **H**$^{4'''}$), 2.09 (m, 8 H, **H**^{4}), 1.95 (m_c, 2 H, **H**$^{3''}$), 1.54/1.39 (m, 8 H, **H**^{3}), 1.37 (m_c, 2 H, **H**$^{3''}$), 1.14 (d, 6 H, **H**$^{1''}$, $^{3}J_{H1'',H2''}$ = 6.1 Hz), 1.07/1.03 (d, 12 H, **H**^{1}, $^{3}J_{H1,H2}$ = 6.1 Hz), 0.95 (t, 18 H, **H**$^{2'}$, $^{3}J_{C2'H,C1'H}$ = 8.1 Hz), 0.52 (q, 12 H, **H**$^{1'}$, $^{3}J_{H1',H2'}$ = 8.1 Hz), 0.20 (unknown species) ppm.

^{13}C NMR [100.62 MHz, *o*DFB, 298 K]: δ = 207.2 (1 C, **C**$^{2'''}$), 150.5 (2 C, **C**^{1}F in *o*DFB), 138.6 (4 C, **C**^{5}), 136.8 (1 C, **C**$^{5'''}$), 124.3 (2 C, **C**^{3} in *o*DFB), 116.8 (2 C, **C**^{2} in *o*DFB), 113.7 (4 C, **C**^{6}), 74.2 (2 C, **C**$^{2''}$), 72.4/71.3 (4 C, **C**^{2}), 42.1 (1 C, **C**$^{3'''}$), 36.7/36.3 (4 C, **C**^{3}), 33.7 (2 C, **C**$^{3''}$), 30.0/29.7 (4 C, **C**^{4}), 27.4 (1 C, **C**$^{4'''}$), 21.0 (2 C, **C**$^{1''}$), 20.3/19.5 (4 C, **C**^{1}), 6.1 (12 C, **C**$^{1'}$ and **C**$^{2'}$) ppm.

^{29}Si NMR [79.5 MHz, *o*DFB, 298 K]: δ = 8.8 (1 Si, O[**Si**(C_2H_5)$_3$]$_2$) ppm.

^{71}Ga NMR [122.04 MHz, oDFB, 298 K]: no signal.

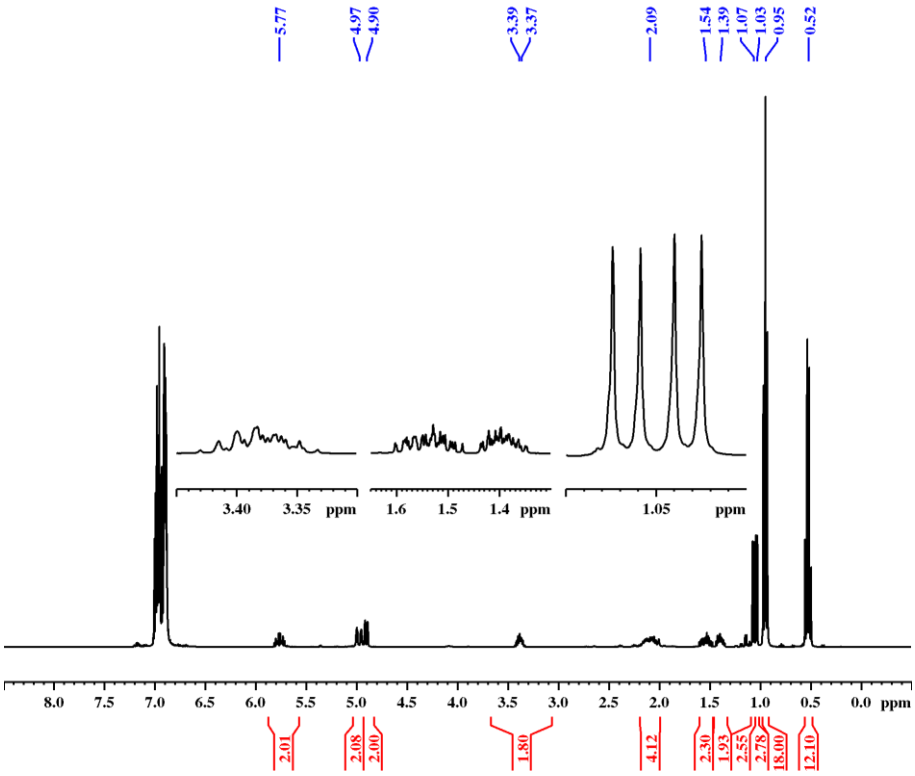


Figure S 35 ^{1}H NMR spectrum (300.18 MHz, *o*DFB, 298 K) of a $HSiEt_3$/5-hexen-2-one/**1** (0.9 : 1.0 : 0.1) mixture, 7 h after mixing the components (spectrum calibrated to δ ($oC_6F_2H_4$) = 6.96 ppm).

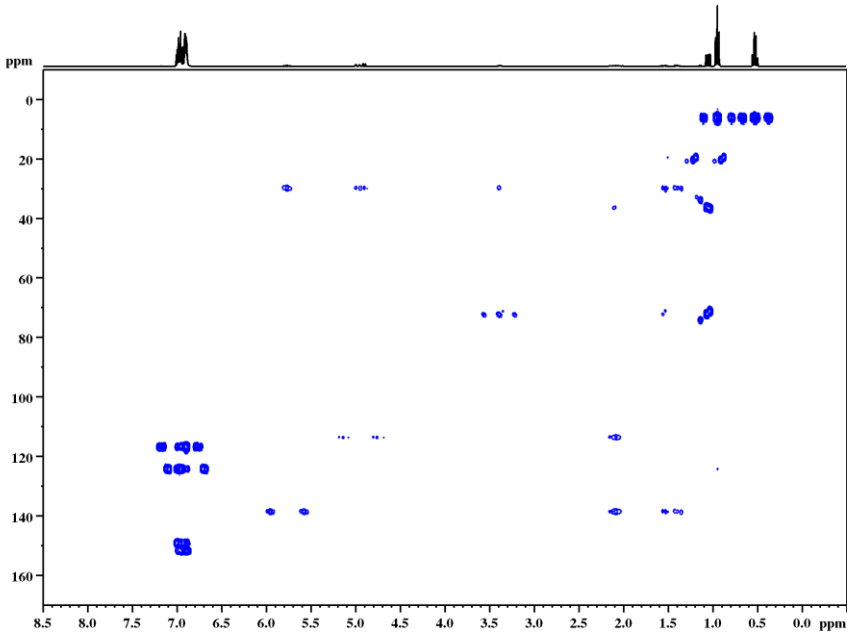


Figure S 36 $^{1}H,^{13}C$-HMBC NMR spectrum (400.17 MHz, *o*DFB, 298 K, optimized for J = 8 Hz) of a $HSiEt_3$/5-hexen-2-one/**1** (0.9 : 1.0 : 0.1) mixture, 12 h after mixing the components (^{1}H NMR spectrum calibrated to δ ($oC_6F_2\mathbf{H}_4$) = 6.96 ppm).

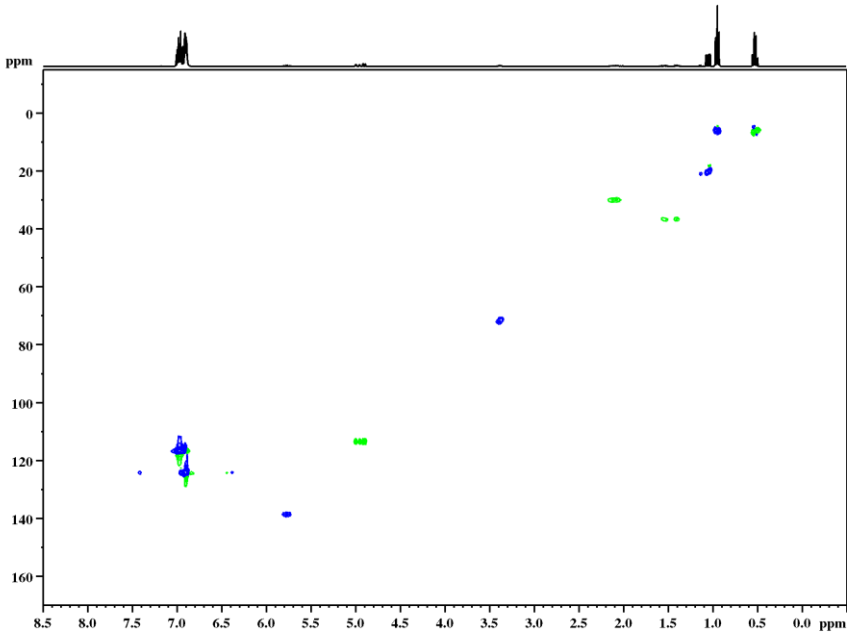


Figure S 37 Edited $^{1}H,^{13}C$-HSQC NMR spectrum (400.17 MHz, *o*DFB, 298 K, optimized for J = 145 Hz; CH_2: green, CH_3 and CH: blue) of a $HSiEt_3$/5-hexen-2-one/**1** (0.9 : 1.0 : 0.1) mixture, 17 h after mixing the components (^{1}H NMR spectrum calibrated to δ ($oC_6F_2\mathbf{H}_4$) = 6.96 ppm).

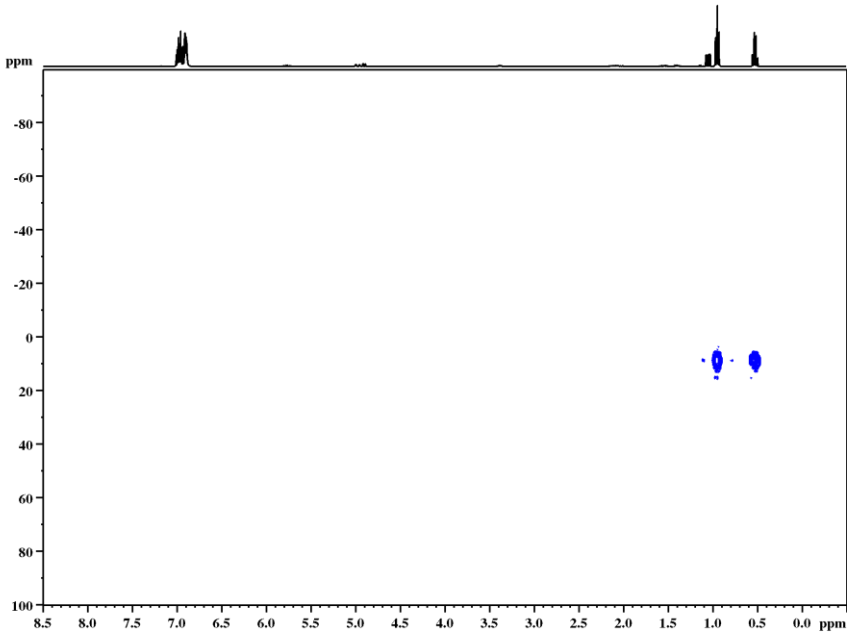
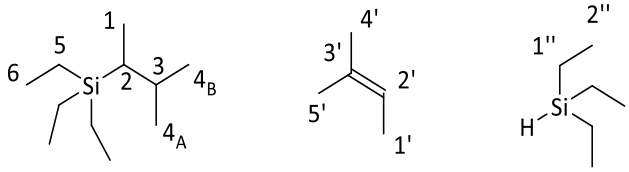


Figure S 38 ^{1}H,^{29}Si-HMBC NMR spectrum (400.17 MHz, *o*DFB, 298 K, optimized for J = 8 Hz) of a $HSiEt_3$/5-hexen-2-one/**1** (0.9 : 1.0 : 0.1) mixture, 7 h after mixing the components (^{1}H NMR spectrum calibrated to δ (*o*C_6F_2**H**$_4$) = 6.96 ppm).

2.1.12 $HSiEt_3$ + 2-Methylbut-2-ene + 1 (0.8 : 1.0 : 0.05)



^{1}H NMR [400.17 MHz, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K]: δ = 5.13 (m, 1 H, **H**$^{2'}$), 3.69 (sept, 1 H, **H**Si(CH_2CH_3)$_3$, $^{3}J_{SiH,CH}$ = 3.2 Hz), 1.82 (septd, 1 H, **H**^{3}, $^{3}J_{H3,H4A}$ = $^{3}J_{H3,H4B}$ = 6.8 Hz, $^{3}J_{H3,H2}$ = 3.8 Hz), 1.61 (m, 3 H, **H**$^{4'}$), 1.51 (m, 3 H, **H**$^{5'}$), 1.49 (m, 3 H, **H**$^{1'}$), 0.93 (t, 18 H, **H**$^{2''}$ and **H**^{6}, $^{3}J_{H6,H5}$ = $^{3}J_{H2'',H1''}$ = 7.9 Hz), 0.92 (d, 3 H, **H**$^{4}_{A}$, $^{3}J_{H4A,H3}$ = 6.8 Hz), 0.87 (d, 1 H, **H**^{1}, $^{3}J_{H1,H2}$ = 7.6 Hz), 0.84 (d, 3 H, **H**$^{4}_{B}$, $^{3}J_{H4B,H3}$ = 6.8 Hz), 0.73 (qd, 1 H, **H**^{2}, $^{3}J_{H2,H1}$ = 7.6 Hz, $^{3}J_{H2,H3}$ = 3.8 Hz), 0.54 (m, 6 H, **H**$^{1''}$), 0.52 (m, 6 H, **H**^{5}) ppm.

^{13}C NMR [100.62 MHz, *o*DFB, 298 K]: δ = 150.5 (2 C, **C**^{1}F in *o*DFB), 131.4 (1 C, **C**$^{3'}$), 124.3 (2 C, **C**^{3} in *o*DFB), 118.3 (1 C, **C**$^{2'}$), 116.8 (2 C, **C**^{2} in *o*DFB), 28.4 (1 C, **C**^{3}), 24.6 (1 C, **C**$^{4'}$), 23.9 (1 C, **C**^{2}), 22.5 (1 C, **C**$^{4}_{A}$), 19.2 (1 C, **C**$^{4}_{B}$), 16.1 (1 C, **C**$^{5'}$), 12.3 (1 C, **C**$^{1'}$), 8.6 (1 C, **C**^{1}), 7.2 (6 C, **C**$^{2''}$ and **C**^{6}), 2.9 (3 C, **C**^{5}), 1.9 (3 C, **C**$^{1''}$) ppm.

^{29}Si NMR [79.50 MHz, *o*DFB, 298 K]: δ = 7.3 (1 Si, $(H_3CH_2C)_3$**Si**[$CH(CH_3)CH(CH_3)_2$]) ppm.

^{71}Ga NMR [122.04 MHz, *o*DFB, 298 K]: δ = –744.6 ($\Delta\nu_{1/2}$ = 1670 Hz, br, 1 Ga, [**Ga**(fluoroarene)$_x$]$^{+}$) ppm (signal disappears after 5 d at 60 °C).

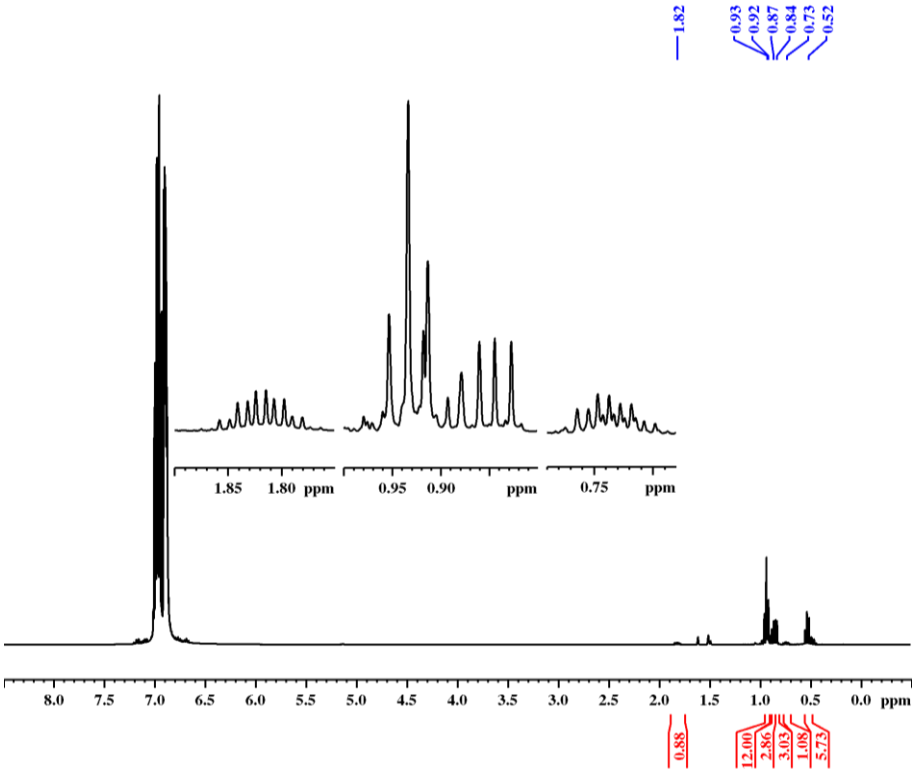


Figure S 39 ^{1}H NMR spectrum (400.17 MHz, *o*DFB, 298 K) of a $HSiEt_3$/2-Methylbut-2-ene/**1** (0.8 : 1.0 : 0.05) mixture, 13 d after mixing the components (mixture heated to 60 °C for 7 d and to 80 °C for 2.5 d; spectrum calibrated to δ (*o*C_6F_2**H**$_4$) = 6.96 ppm).

2.1.13 H_3SiPh + Allylbenzene + 1 (0.5 : 1.0 : 0.1) and H_2SiPh_2 + 1-Hexene + 1 (0.3 : 1.0 : 0.1)

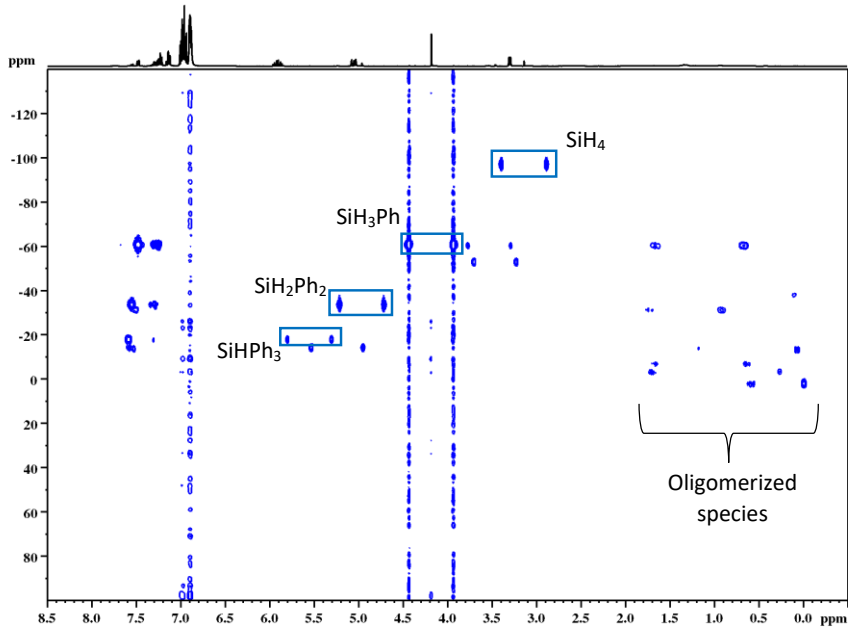


Figure S 40 ^{1}H,^{29}Si-HMBC NMR spectrum (400.17 MHz, *o*DFB, 298 K, optimized for *J* = 8 Hz) of a H_3SiPh/allylbenzene/**1** (0.5 : 1.0 : 0.1) mixture, 2.5 d (mixture was heated to 60 °C for 1 d) after mixing the components (^{1}H NMR spectrum calibrated to δ (*o*C_6F_2**H**$_4$) = 6.96 ppm).

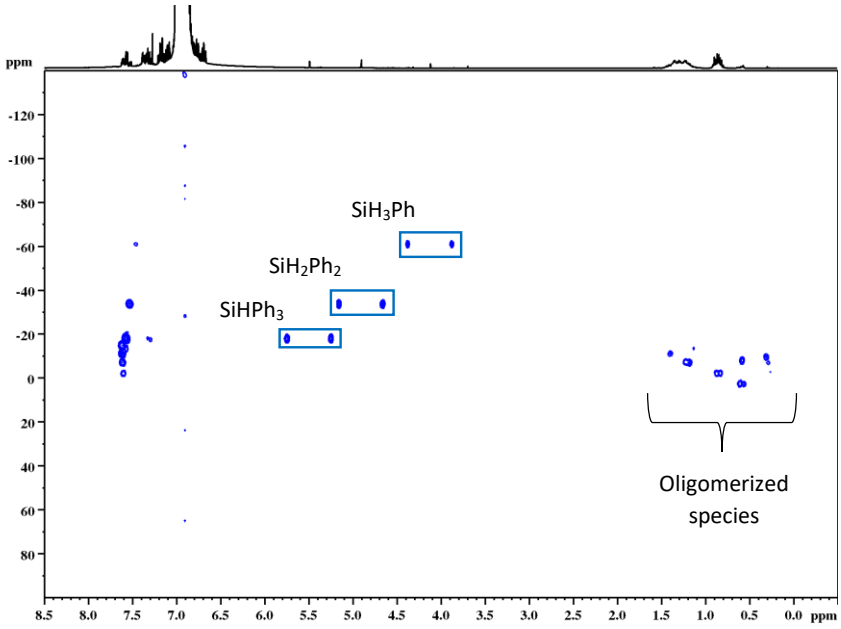
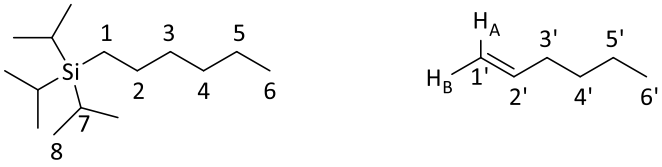


Figure S 41 $^{1}H,^{29}Si$-HMBC NMR spectrum (400.17 MHz, *o*DFB, 298 K, optimized for J = 8 Hz) of a H_2SiPh_2/1-hexene/**1** (0.3 : 1.0 : 0.1) mixture, 7 h after mixing the components (^{1}H NMR spectrum calibrated to δ (*o*$C_6F_2\mathbf{H}_4$) = 6.96 ppm).

2.1.14 HSi^{i}Pr$_3$ + 1-Hexene + 1 (1.8 : 1.0 : 0.1)



^{1}H NMR [400.17 MHz, *o*DFB, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K]: δ = 5.75 (m_c, 1 H, **H**$^{2'}$), 4.96 (m_c, 1 H, **H**$^{1'}{}_{A}$), 4.90 (m_c, 1 H, **H**$^{1'}{}_{B}$), 3.39 (m, 1 H, **H**Si[CH(CH$_3$)$_2$]$_3$), 1.97 (m_c, 2 H, **H**$^{3'}$), 1.49 (m, 3 H, [(H$_3$C)$_2$**H**C]$_3$Si–F–Al[OC(CF$_3$)$_3$]$_3$), 1.33 (m, 2 H, **H**^{2}), 1.30 (m, 2 H, **H**^{3}), 1.29 (m, 2 H, **H**$^{4'}$), 1.27 (m, 4 H, **H**^{5}), 1.26 (m, 4 H, **H**^{4}), 1.25 (m, 2 H, **H**$^{5'}$), 1.15 (m, 3 H, [(**H**$_3$C)$_2$HC]$_3$Si–F–Al[OC(CF$_3$)$_3$]$_3$), 1.04 (m, 21 H, HSi[C**H**(C**H**$_3$)$_2$]$_3$), 1.02 (m, 18 H, **H**^{8}), 0.98 (m, 3 H, **H**^{7}), 0.89 (s, 3 H, **H**^{6}), 0.85 (m, 3 H, **H**$^{6'}$), 0.58 (m, 2 H, **H**^{1}) ppm.

^{13}C NMR [100.62 MHz, *o*DFB, 298 K]: δ = 150.5 (2 C, **C**^{1}F in *o*DFB), 138.8 (1 C, **C**$^{2'}$), 124.3 (2 C, **C**^{3} in *o*DFB), 116.8 (2 C, **C**^{2} in *o*DFB), 113.5 (1 C, **C**$^{1'}$), 34.1 (1 C, **C**^{3}), 33.4 (1 C, **C**$^{3'}$), 31.4 (1 C, **C**^{4}), 30.9 (1 C, **C**$^{4'}$), 24.3 (1 C, **C**^{2}), 22.6 (1 C, **C**^{5}), 21.9 (1 C, **C**$^{5'}$), 18.8 (3 C, HSi[**C**H(CH$_3$)$_2$]$_3$), 13.4 (1 C, **C**^{6}), 13.2 (1 C, **C**$^{6'}$), 10.9 (3 C, **C**^{7}), 10.2 (6 C, HSi[CH(**C**H$_3$)$_2$]$_3$), ca. 10 (6 C, **C**^{8}), 9.2 (1 C, **C**^{1}) ppm.

^{19}F NMR [376.54 MHz, *o*DFB, 298 K]: δ = –70.0 (m_c, 6 F, OC(C**F**$_3$)$_2$CF$_2$), –74.9 (s, 9 F, HOC(C**F**$_3$)$_3$), –75.4 (s, 36 F, [Al(OC(C**F**$_3$)$_3$)$_4$]$^-$), –75.8 (s, 27 F, [(H$_3$C)$_2$HC]$_3$Si–F–Al[OC(C**F**$_3$)$_3$]$_3$), –109.2 (m_c, 2 F, OC(CF$_3$)$_2$C**F**$_2$), –113.7 (tt, 1 F, Ph**F**, $^{3}J_{F,C^{ortho}H}$ = 9.2 Hz, $^{4}J_{F,C^{meta}H}$ = 5.7 Hz), –139.3 (m_c, 2 F, *o*C$_6$**F**$_2$H$_4$), –175.2 (br, 1 F, [(H$_3$C)$_2$HC]$_3$Si–**F**–Al[OC(CF$_3$)$_3$]$_3$, $^{1}J_{F,Si}$ = 354 Hz), –185.4 (unknown species) ppm.

^{27}Al NMR [104.27 MHz, *o*DFB, 298 K]: δ = 34.9(1 Al, [**Al**(OC(CF$_3$)$_3$)$_4$]$^-$) ppm.

^{29}Si NMR [79.50 MHz, *o*DFB, 298 K]: δ = 76.5 (1 Si, [(H$_3$C)$_2$HC]$_3$**Si**–F–Al[OC(CF$_3$)$_3$]$_3$), 12.0 (1 Si, H**Si**[CH(CH$_3$)$_2$]$_3$), 5.9 (1 Si, (H$_{13}$C$_6$)**Si**[CH(CH$_3$)$_2$]$_3$) ppm.

^{71}Ga NMR [122.04 MHz, *o*DFB, 298 K]: δ = –727.3 ($\Delta\nu_{1/2}$ = 1960 Hz; br, 1 Ga, [**Ga**(ligand)$_x$]$^+$) ppm (signal disappears after 2 d at 60 °C).

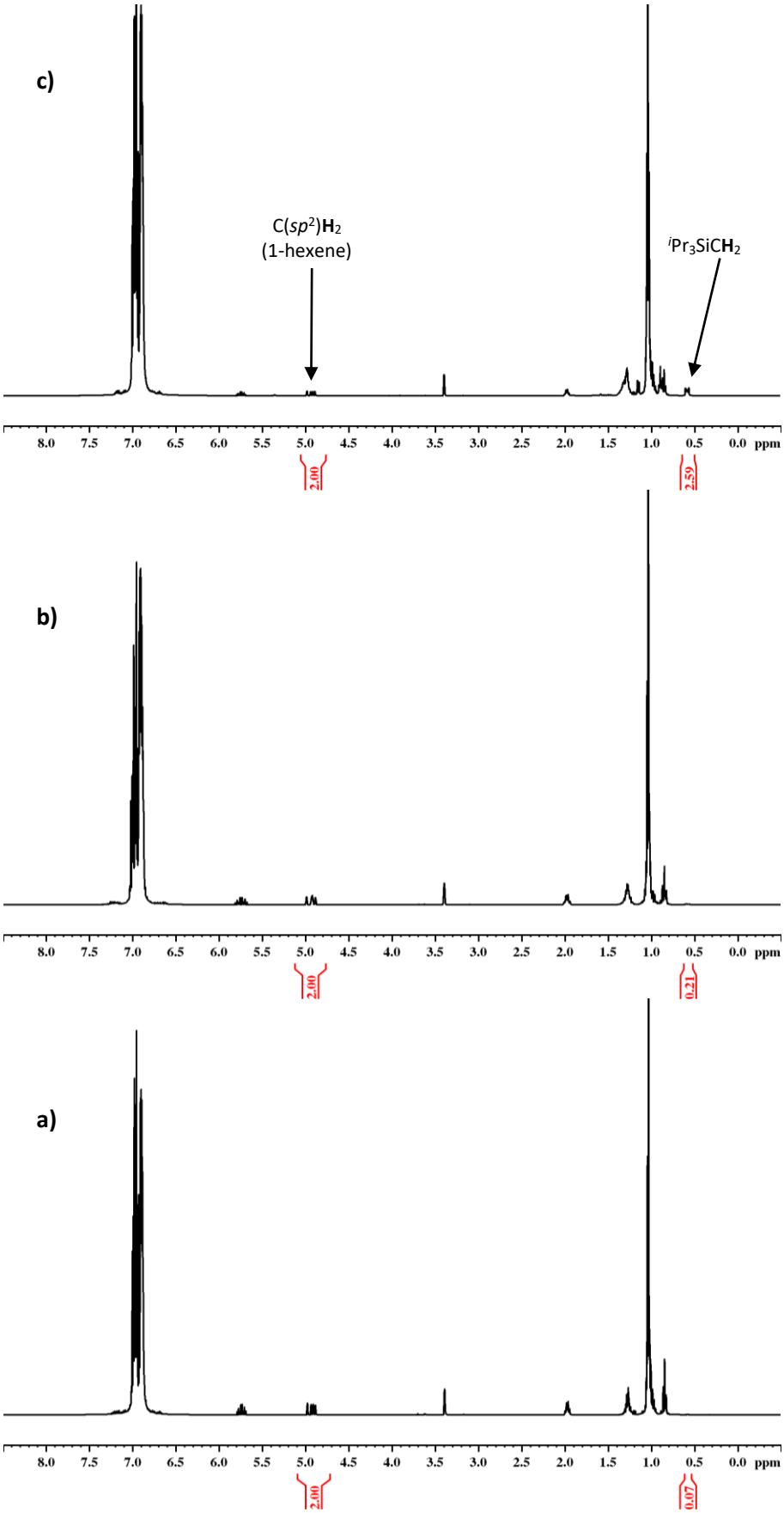


Figure S 42 From bottom to top: ^{1}H NMR spectra (*o*DFB, 298 K) of a HSi^{i}Pr$_3$/1-hexene/**1** (1.8 : 1.0 : 0.1) mixture, 2 h (400.17 MHz), 3 d (300.18 MHz) and 13 d (400.17 MHz; mixture heated to 60 °C for 2 d) after mixing the components (spectra calibrated to δ (*o*C$_6$F$_2$**H**$_4$) = 6.96 ppm).

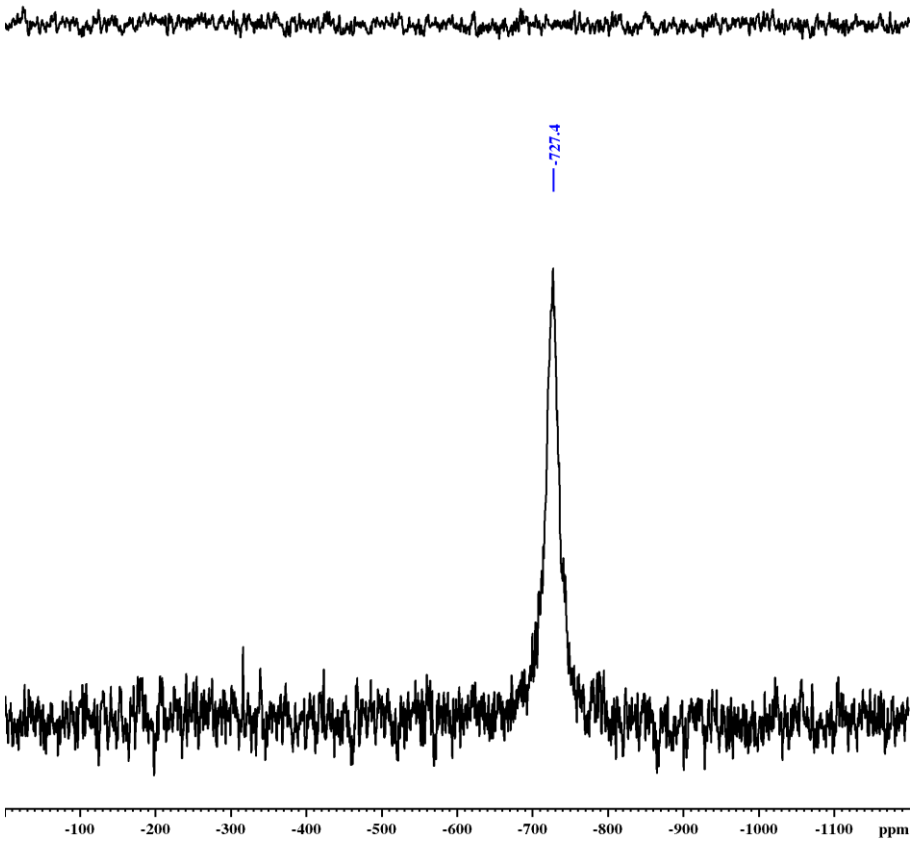


Figure S 43 ^{71}Ga NMR spectra (298 K, *o*DFB) of a HSi^{i}Pr$_3$/1-hexene/**1** (1.8 : 1.0 : 0.1) mixture, 30 min (bottom; 122.04 MHz) and 13 d (top; 91.54 MHz; mixture heated to 60 °C for 2 d) after mixing the components.

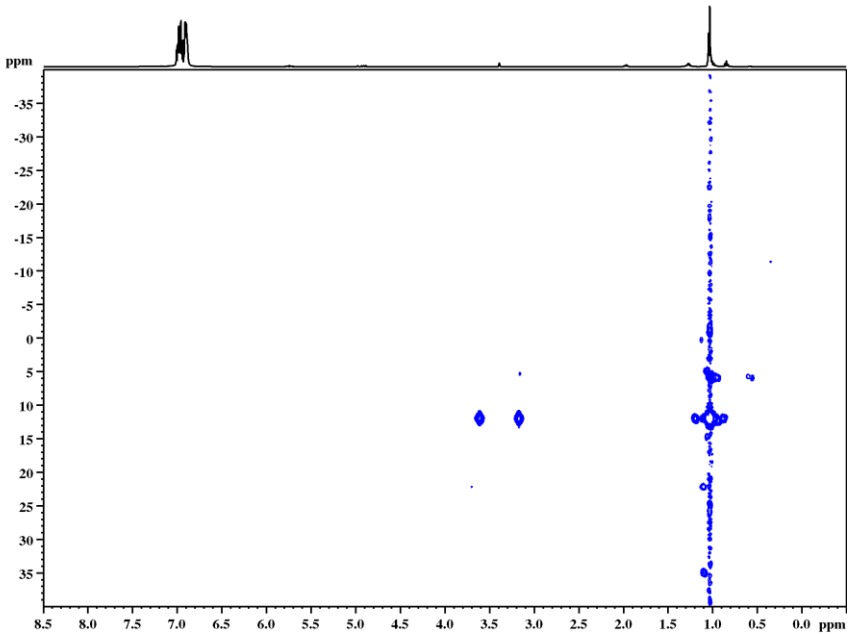


Figure S 44 $^{1}H,^{29}Si$-HMBC NMR (400.17 MHz, *o*DFB, 298 K, optimized for J = 20 Hz) of a HSi^{i}Pr$_3$/1-hexene/**1** (1.8 : 1.0 : 0.1) mixture, 28 h after mixing the components (^{1}H NMR spectrum calibrated to δ (*o*C_6F_2**H**$_4$) = 6.96 ppm).

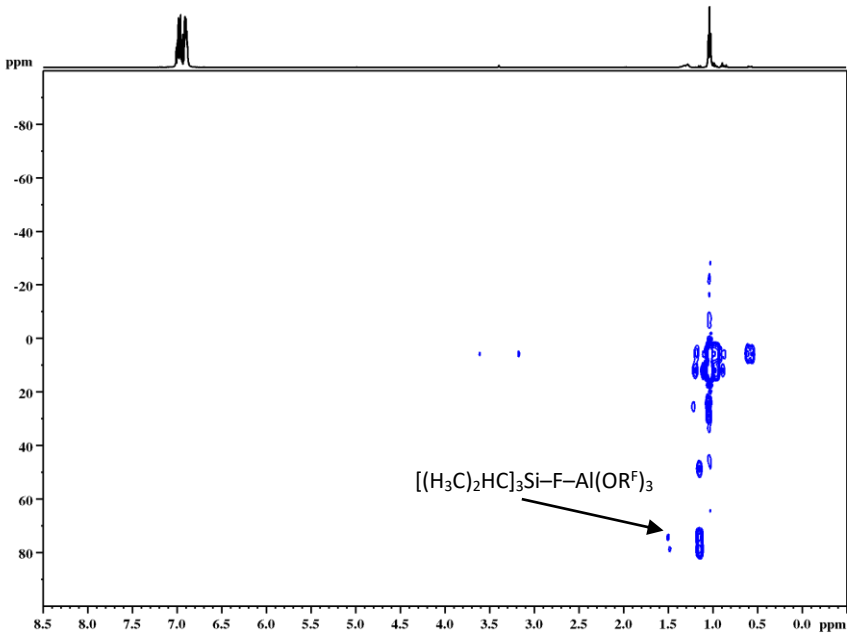
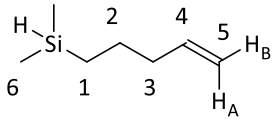


Figure S 45 $^{1}H,^{29}Si$-HMBC NMR (400.17 MHz, *o*DFB, 298 K, optimized for J = 8 Hz) of a HSi^{i}Pr$_3$/1-hexene/**1** (1.8 : 1.0 : 0.1) mixture, 35 d (mixture heated to 60 °C for 2 d) after mixing the components (^{1}H NMR spectrum calibrated to δ (*o*C_6F_2**H**$_4$) = 6.96 ppm).

2.1.15 Dimethyl(pent-4-en-1-yl)silane



^{1}H NMR [400.17 MHz, $CDCl_3$, calibrated to δ ($CDCl_3$) = 7.26 ppm, 298 K]: δ = 5.80 (m_c, 1 H, **H**^{4}), 5.00 (m_c, 1 H, **H**$^{5}_{A}$), 4.95 (m_c, 1 H, **H**$^{5}_{B}$), 3.85 (sept, $^{3}J_{SiH,H6}$ = 3.6 Hz, 1 H, Si**H**), 3.75 (m, 2 H, O(C**H**$_2$CH$_2$)$_2$), 2.08 (m_c, 2 H, **H**^{3}), 1.85 (m, 2 H, O(CH$_2$C**H**$_2$)$_2$), 1.55 (s, 2 H, **H**$_2$O), 1.45 (m_c, 2 H, **H**^{2}), 1.26 (m, 6 H, H$_3$C(C**H**$_2$)$_3$CH$_3$), 0.88 (m, 6 H, **H**$_3$C(CH$_2$)$_3$C**H**$_3$), 0.60 (m_c, 2 H, **H**^{1}), 0.07 (d, $^{3}J_{H6,SiH}$ = 3.6 Hz, 6 H, **H**^{6}) ppm.

^{13}C NMR [100.62 MHz, $CDCl_3$, 298 K]: δ = 139.0 (1 C, **C**^{4}), 114.6 (1 C, **C**^{5}), 37.4 (1 C, **C**^{3}), 23.8 (1 C, **C**^{2}), 14.1 (1 C, **C**^{1}), –4.5 (1 C, **C**^{6}) ppm.

^{29}Si NMR [79.50 MHz, $CDCl_3$, 298 K]: δ = –13.1 (1 Si, **Si**) ppm.

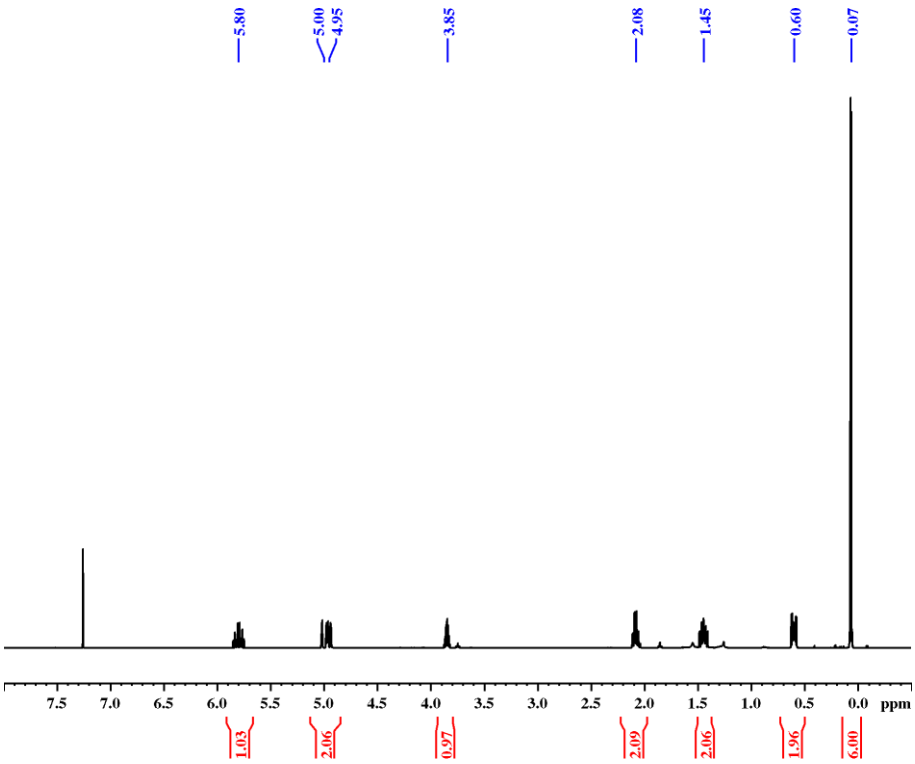


Figure S 46 ^{1}H NMR spectrum (400.17 MHz, $CDCl_3$, 298 K) of dimethyl(pent-4-en-1-yl)silane (spectrum calibrated to C**H**Cl$_3$ = 7.26 ppm).

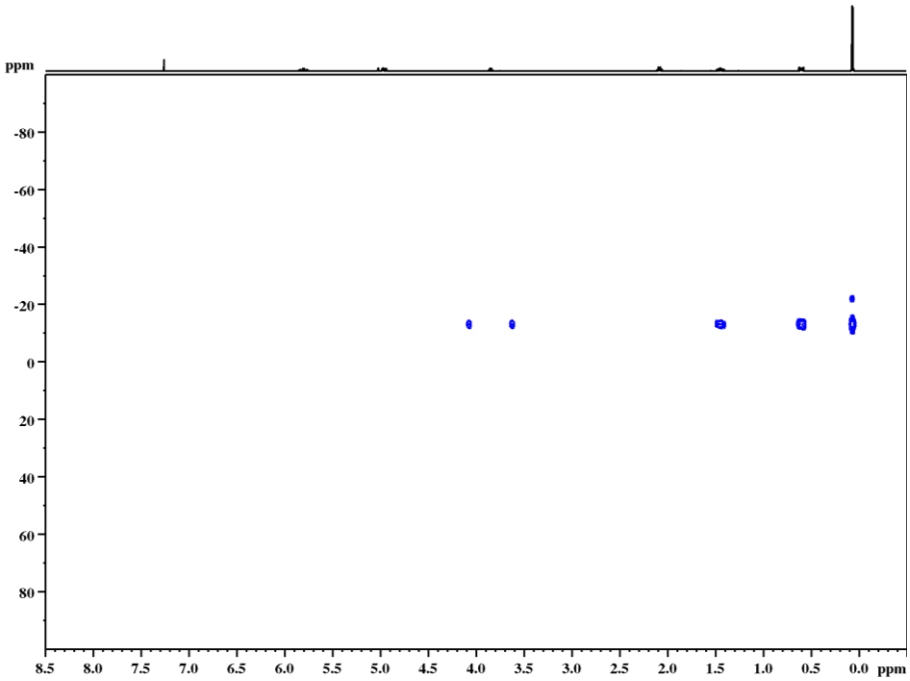
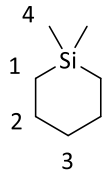


Figure S 47 ^{1}H,^{29}Si-HMBC NMR spectrum (400.17 MHz, $CDCl_3$, 298 K, optimized for J = 8 Hz) of dimethyl(pent-4-en-1-yl)silane (spectrum calibrated to C**H**Cl_3 = 7.26 ppm).

2.1.16 Dimethyl(pent-4-en-1-yl)silane + 1 (1.0 : 0.1)



^{1}H NMR [400.17 MHz, *o*DFB, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K]: δ = 4.34 (m, 2 H, $(H_2CHC)_2O$–Al$[OC(CF_3)_3]_3$), 2.04 (m, 2 H, $(H_2CH_2C)_2O$–Al$[OC(CF_3)_3]_3$), 1.64 (m, 4 H, **H**^{2}), 1.36 (m, 2 H, **H**^{3}), 1.27 (m, 6 H, $H_3C(CH_2)_3CH_3$), 0.85 (m, 6 H, $H_3C(CH_2)_3CH_3$), 0.56 (m, 4 H, **H**^{1}), –0.01 (s, 6 H, **H**^{4}) ppm.

^{13}C NMR [100.62 MHz, *o*DFB, 298 K]: δ = 150.5 (2 C, **C**^{1}F in *o*DFB), 124.3 (2 C, **C**^{3} in *o*DFB), 116.8 (2 C, **C**^{2} in *o*DFB), 30.1 (1 C, **C**^{3}), 24.3 (2 C, **C**^{2}), 14.0 (2 C, **C**^{1}), –3.9 (2 C, **C**^{4}) ppm.

^{19}F NMR [376.54 MHz, *o*DFB, 298 K]: δ = –69.9 (m_c, 6 F, $OC(CF_3)_2CF_2$), –75.4 (s, 9 F, $HOC(CF_3)_3$), –75.6 (unknown species), –75.9 (s, 36 F, $[Al(OC(CF_3)_3)_4]^-$), –109.2 (m_c, 2 F, $OC(CF_3)_2CF_2$), –113.6 (m_c, 1 F, C_6H_5F), –139.2 (m_c, 2 F, $oC_6F_2H_4$), –161.9/–166.8 (unknown species/ br, 1 F, $FSi(CH_3)_2(C_5H_9)$) ppm.

^{27}Al NMR [104.27 MHz, *o*DFB, 298 K]: δ = 38.3 (br, 1 Al, $(H_2CH_2C)_2O$–**Al**$[OC(CF_3)_3]_3$), 34.8 (s, 1 Al, $[Al(OC(CF_3)_3)_4]^-$) ppm.

^{29}Si NMR [79.50 MHz, *o*DFB, 298 K]: δ = 32.7 (1 Si, F**Si**$(CH_3)_2(C_5H_9)$), –4.0 (1 Si, $(H_3C)_2$**Si**$[(CH_2CH_2)_2CH_2]$) ppm.

^{71}Ga NMR [122.04 MHz, *o*DFB, 298 K]: no signal.

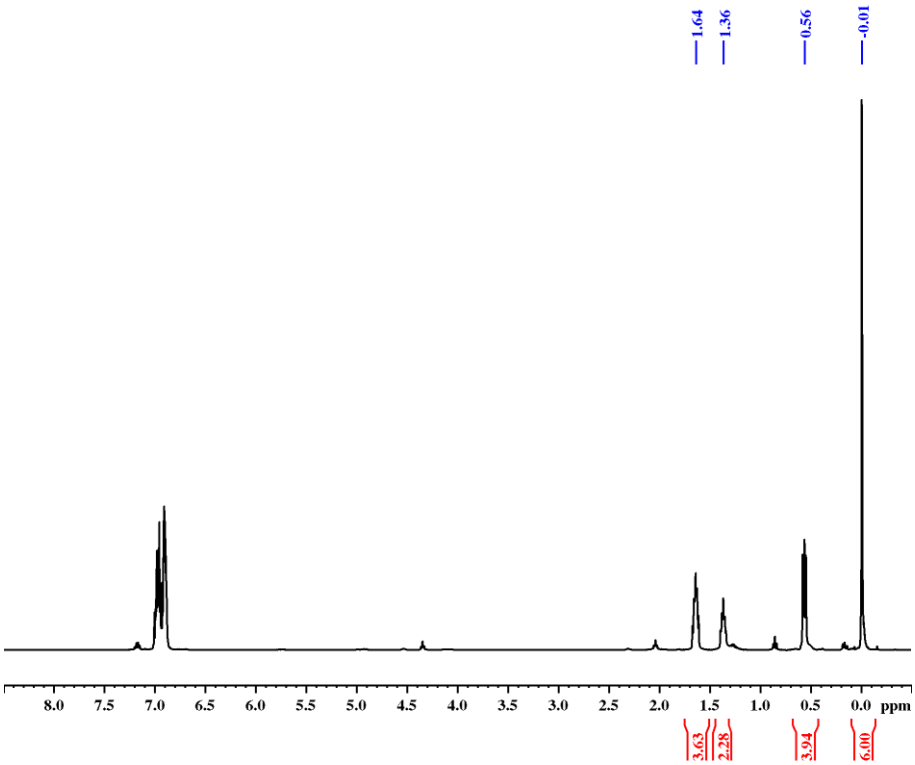


Figure S 48 ^{1}H NMR spectrum (400.17 MHz, *o*DFB, 298 K) of a dimethyl(pent-4-en-1-yl)silane/**1** (1.0 : 0.1) mixture, 10 h after mixing the components (spectrum calibrated to δ (*o*C_6F_2**H**$_4$) = 6.96 ppm).

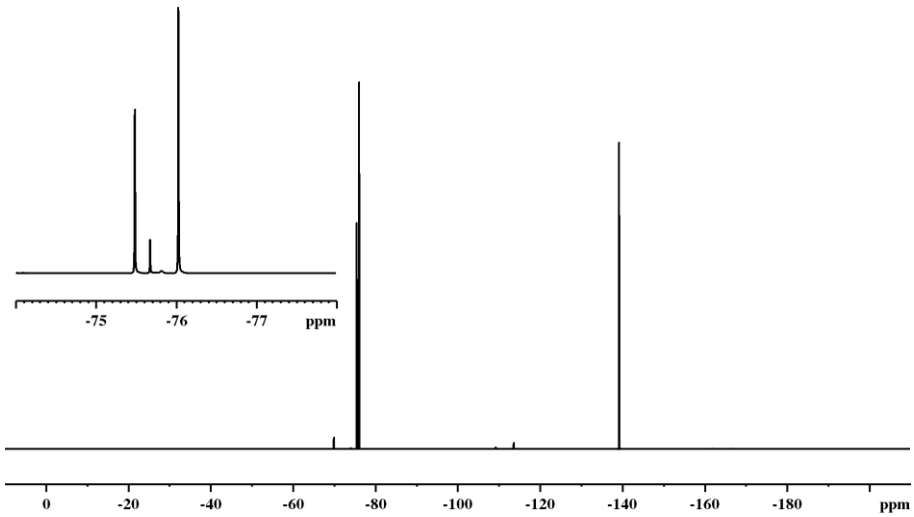


Figure S 49 ^{19}F NMR spectrum (376.54 MHz, *o*DFB, 298 K) of a dimethyl(pent-4-en-1-yl)silane/**1** (1.0 : 0.1) mixture, 8 h after mixing the components.

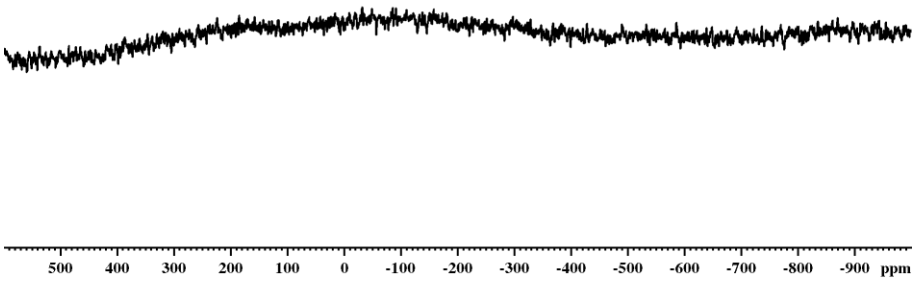


Figure S 50 ^{71}Ga NMR spectrum (122.04 MHz, *o*DFB, 298 K) of a dimethyl(pent-4-en-1-yl)silane/**1** (1.0 : 0.1) mixture, 8 h after mixing the components. No ^{71}Ga signal is detected.

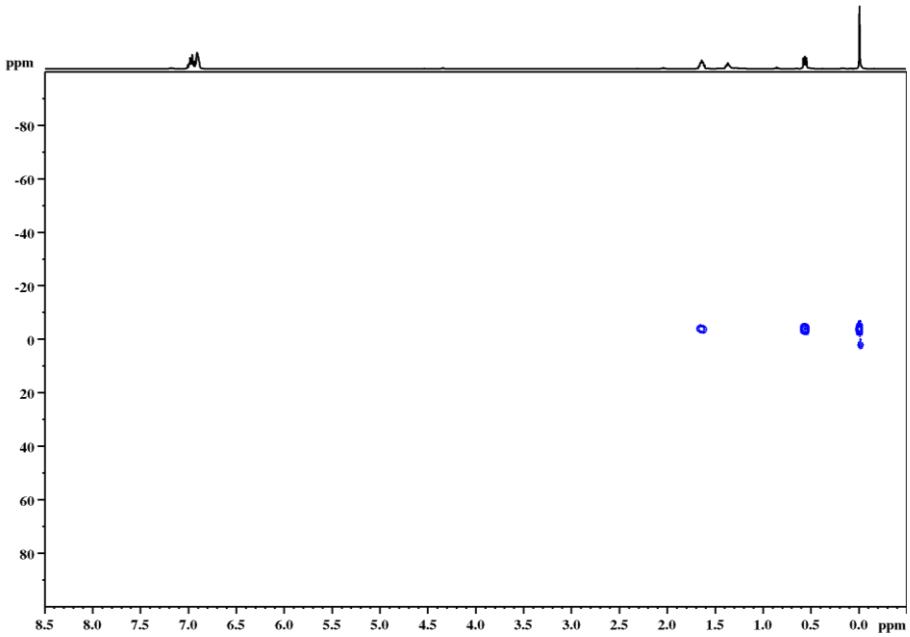


Figure S 51 ^{1}H,^{29}Si-HMBC NMR spectrum (400.17 MHz, *o*DFB, 298 K, optimized for J = 8 Hz) of a dimethyl(pent-4-en-1-yl)silane/**1** (1.0 : 0.1) mixture, 8 h after mixing the components (^{1}H NMR spectrum calibrated to δ (*o*$C_6F_2\mathbf{H}_4$) = 6.96 ppm).

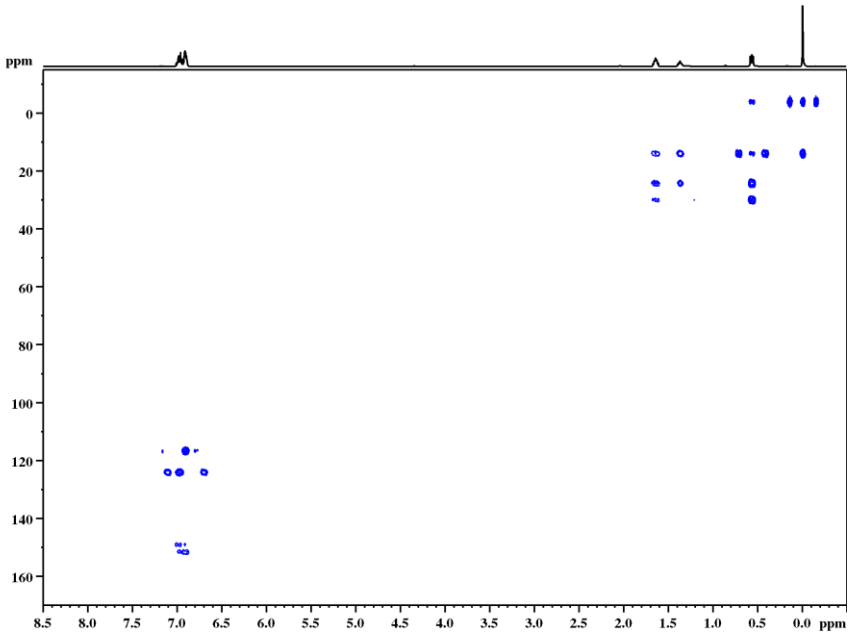


Figure S 52 $^{1}H,^{13}C$-HMBC NMR spectrum (400.17 MHz, *o*DFB, 298 K, optimized for J = 8 Hz) of a dimethyl(pent-4-en-1-yl)silane/**1** (1.0 : 0.1) mixture, 18 h after mixing the components (^{1}H NMR spectrum calibrated to δ (*o*$C_6F_2\mathbf{H}_4$) = 6.96 ppm).

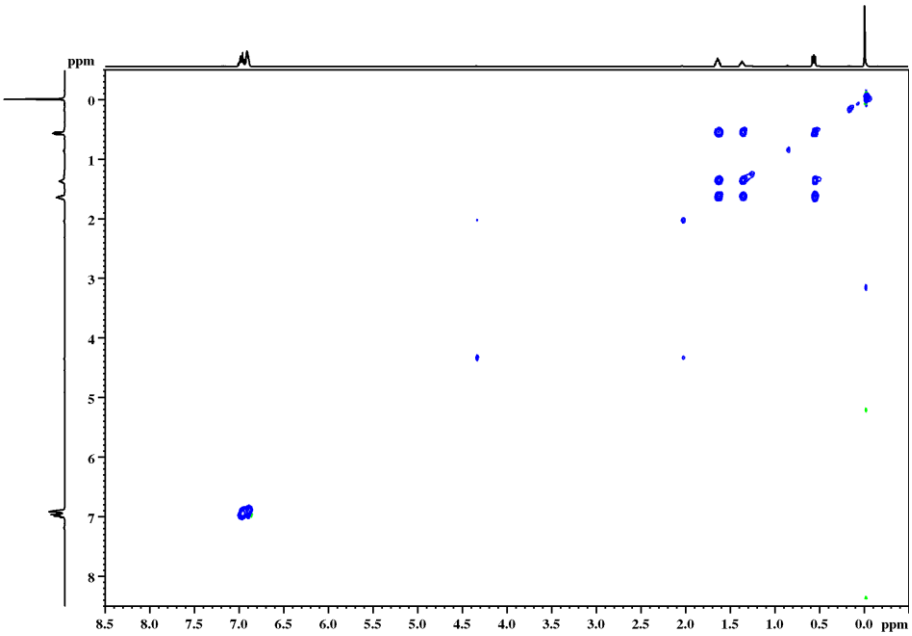


Figure S 53 ^{1}H TOCSY NMR spectrum (400.17 MHz, *o*DFB, 298 K, mixing time = 0.2 s) of a dimethyl(pent-4-en-1-yl)silane/**1** (1.0 : 0.1) mixture, 18 h after mixing the components (^{1}H NMR spectrum calibrated to δ (*o*$C_6F_2\mathbf{H}_4$) = 6.96 ppm).

2.1.17 $HSiMe_3$ + 1-Hexene + $[Ph_3C][pf]$ (1.1 : 1.0 : 0.01, 1.1 : 1.0 : 0.005, 1.1 : 1.0 : 0.003, 2.0 : 1.0 : 0.002, 1.0 : 1.0 : 0.002)

^{1}H NMR [200.13 MHz, *o*DFB, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K]: δ = 5.75 (m_c, 1 H, **H**$^{2'}$), 4.96 (m_c, 1 H, **H**$^{1'}{}_A$), 4.90 (m_c, 1 H, **H**$^{1'}{}_B$), 4.00 (dec, 1 H, **H**Si(CH_3)$_3$, $^3J_{SiH,CH}$ = 3.6 Hz), 1.28 (m, 4 H, **H**^{2} and **H**^{3}), 1.26 (m, 2 H, **H**^{5}), 1.23 (m, 2 H, **H**^{4}), 0.87 (m, 3 H, **H**^{6}), 0.46 (m, 2 H, **H**^{1}), 0.35 (s, 9 H, ClSi(C**H**$_3$)$_3$), 0.11 (s, 18 H, O[Si(C**H**$_3$)$_3$]$_2$), 0.04 (d, 9 H, HSi(C**H**$_3$)$_3$, $^3J_{CH,SiH}$ = 3.6 Hz), –0.01 (s, 9 H, **H**^{7}) ppm.

^{19}F NMR [376.54 MHz, *o*DFB, 298 K]: δ = –70.0 (m_c, 6 F, OC(C**F**$_3$)$_2$C**F**$_2$), –75.3 (s, 36 F, [Al(OC(C**F**$_3$)$_3$)$_4$]$^-$), –75.9 (s, 27 F, (H_3C)$_3$Si–F–Al[OC(C**F**$_3$)$_3$]$_3$), –76.0 (unknown species), –109.2 (m_c, 2 F, OC(CF_3)$_2$C**F**$_2$), –139.4 (m_c, 2 F, *o*C_6**F**$_2$H$_4$) ppm.

Reducing the initiator loading from 1 mol-% to 0.5, 0.3 and 0.2 mol-% does not significantly affect the degree of anion decomposition (cf. **Figure S 55** and **Figure S 57**).

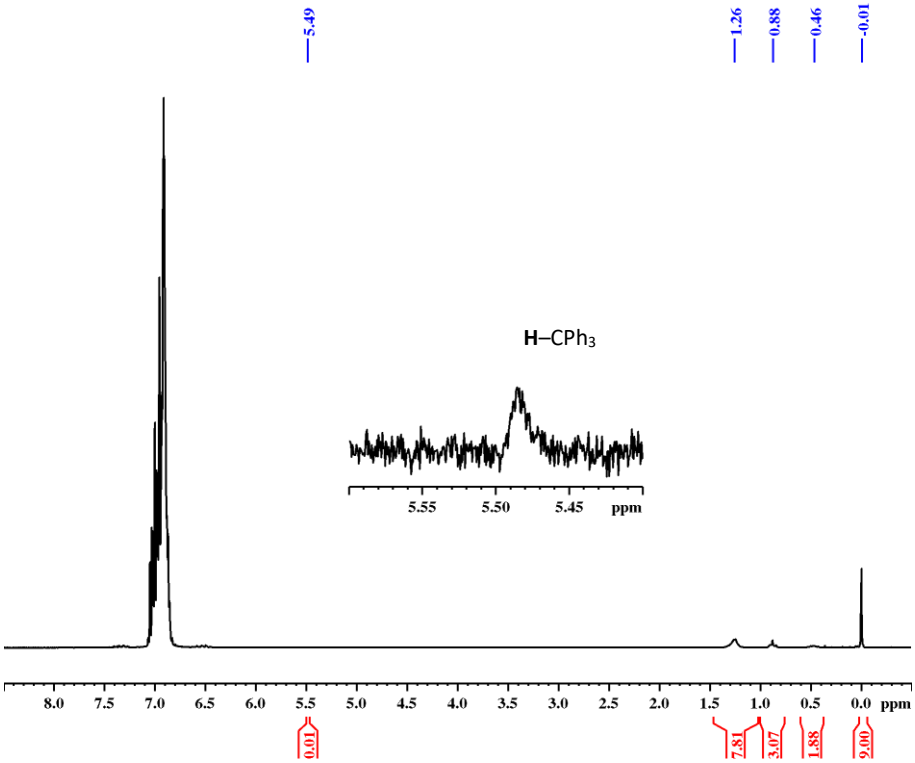


Figure S 54 ^{1}H NMR spectrum (200.13 MHz, *o*DFB, 298 K) of a $HSiMe_3$/1-hexene/$[Ph_3C][pf]$ (1.1 : 1.0 : 0.01) mixture, 15 min after mixing the components (spectrum calibrated to δ (*o*C_6F_2**H**$_4$) = 6.96 ppm).

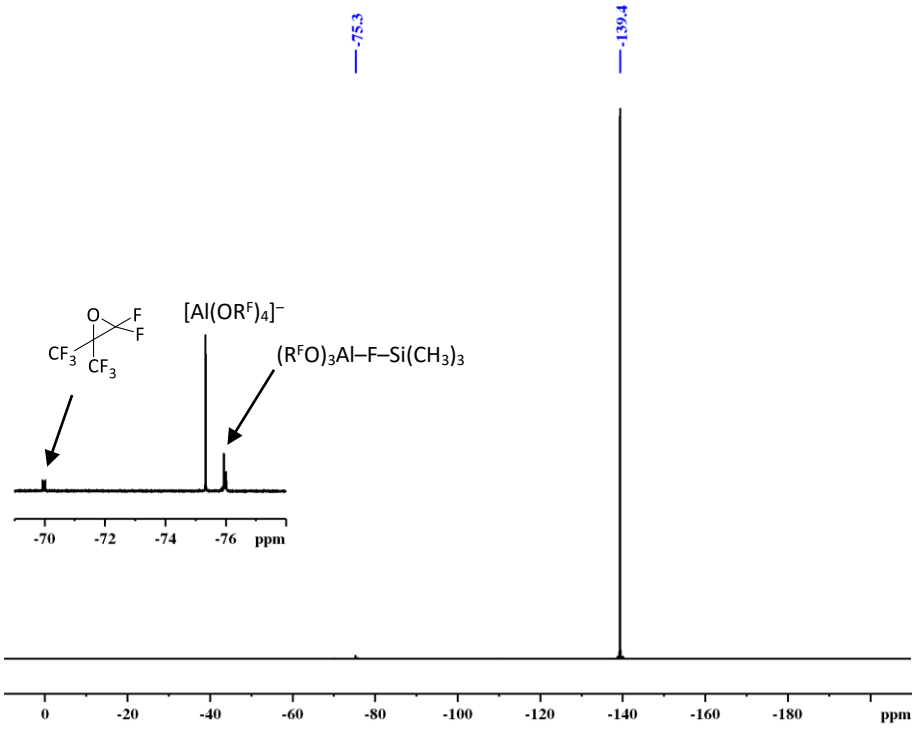


Figure S 55 ^{19}F NMR spectrum (188.31 MHz, *o*DFB, 298 K) of a $HSiMe_3$/1-hexene/$[Ph_3C][pf]$ (1.1 : 1.0 : 0.01) mixture, 1 h after mixing the components.

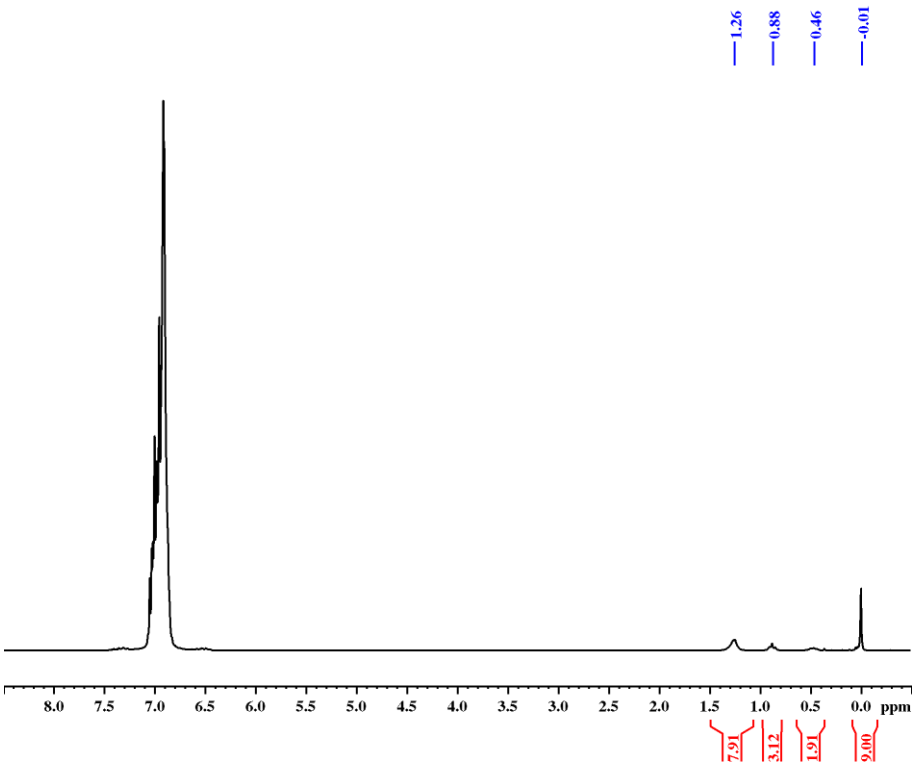


Figure S 56 ^{1}H NMR spectrum (200.13 MHz, *o*DFB, 298 K) of a $HSiMe_3$/1-hexene/$[Ph_3C][pf]$ (1.0 : 1.0 : 0.002) mixture, 40 min after mixing the components (spectrum calibrated to δ ($oC_6F_2\mathbf{H}_4$) = 6.96 ppm).

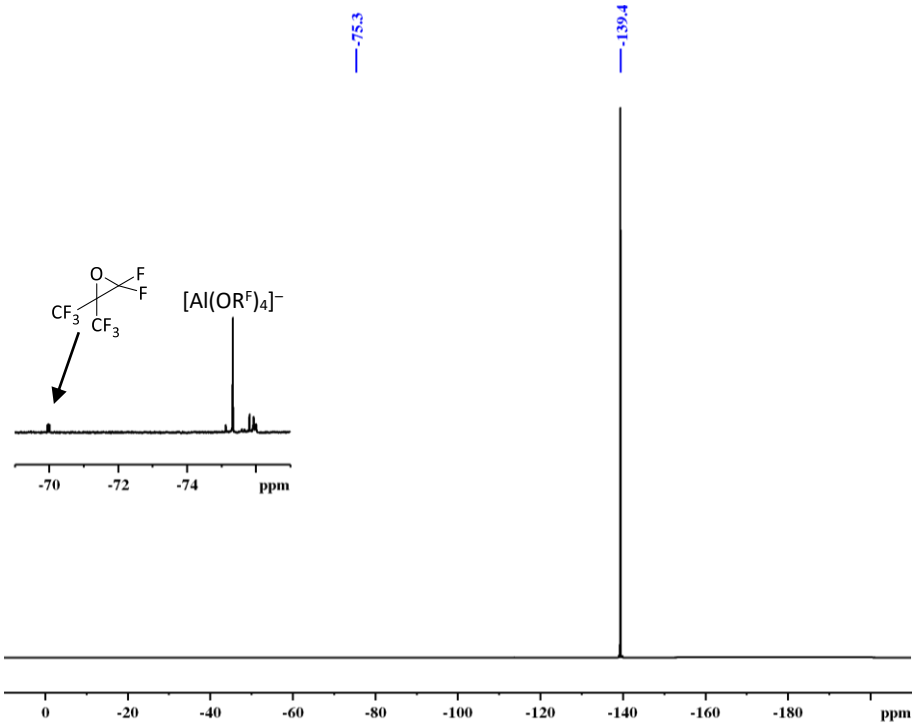
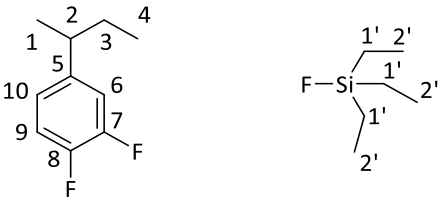


Figure S 57 ^{19}F NMR spectrum (282.45 MHz, *o*DFB, 298 K) of a $HSiMe_3$/1-hexene/$[Ph_3C][pf]$ (1.0 : 1.0 : 0.002) mixture, 9 h after mixing the components.

2.2 Hydrodefluorination Reactions

2.2.1 $HSiEt_3$ + 1-Fluorobutane + 1 (1.1 : 1.0 : 0.04)



^{1}H NMR [400.17 MHz, *o*DFB, calibrated to δ (*o*DFB) = 6.96 ppm, 278 K]: δ = 6.85 (m, 1H, **H**^{6}), 6.75 (m, 1 H, **H**^{10}), 4.50 (s, 2 H, $\mathbf{H}_2$), 4.47 (unknown species), 3.68 (s, 1 H, **H**Si$(C_2H_5)_3$), 2.42 (m, 1 H, **H**^{2}), 1.45 (m, 2 H, **H**^{3}), 1.22 (m, 4 H, $H_3CC\mathbf{H}_2C\mathbf{H}_2CH_3$), 1.10 (d, 3 H, **H**^{1}, $^{3}J_{H1,H2}$ = 7.0 Hz), 0.84 (m, 6 H, $\mathbf{H}_3CCH_2CH_2C\mathbf{H}_3$), 0.95 (t, 9 H, $FSi(C^{1'}H_2C^{2'}\mathbf{H}_3)_3$, $^{3}J_{H2',H1'}$ = 7.9 Hz), 0.74 (t, 3 H, **H**^{4}, $^{3}J_{H4,H3}$ = 7.4 Hz), 0.62 (q, 6 H, $FSi(C^{1'}\mathbf{H}_2C^{2'}H_3)_3$, $^{3}J_{H1',H2'}$ = 7.9 Hz) ppm.

^{13}C NMR [100.62 MHz, *o*DFB, 278 K]: δ = 150.5 (2 C, **C**^{1}F in *o*DFB), 144.8 (1 C, **C**^{5}), 124.3 (2 C, **C**^{3} in *o*DFB), 122.6 (1 C, **C**^{10}), 116.8 (2 C, **C**^{2} in *o*DFB), 115.1 (1 C, **C**^{6}), 41.0 (1 C, **C**^{2}), 30.7 (1 C, **C**^{3}), 20.8 (1 C, **C**^{1}), 11.1 (1 C, **C**^{4}) ppm.

The shifts of the carbon atoms C^7-C^9 are too similar to the *o*DFB signals and thus cannot be assigned.

^{19}F NMR [376.54 MHz, *o*DFB, 278 K]: δ = –70.1 (m_c, 6 F, $OC(C\mathbf{F}_3)_2CF_2$), –75.2 (s, 9 F, $HOC(C\mathbf{F}_3)_3$), –75.5 (s, 27 F, $(H_3CH_2C)_3Si–F–Al[OC(C\mathbf{F}_3)_3]_3$), –76.0 (s, 36 F, $[Al(OC(C\mathbf{F}_3)_3)_4]^-$), –109.3 ($m_c$, 2 F, $OC(CF_3)_2C\mathbf{F}_2$), –113.8 (m_c, 1 F, Ph**F**), –139.4/–143.4 (1 F, **F**^{7} or **F**^{8}), –139.4/–143.4 (dddd, 1 F, **F**^{7} or **F**^{8}, $^{3}J_{F,F}$ = 21.0 Hz, $^{3}J_{F,H}$ = 10.4 Hz, $^{4}J_{F,H}$ = 7.7 Hz, $^{4\text{ or }5}J_{F,H}$ = 4.3 Hz), –139.4 (m_c, 2 F, $oC_6\mathbf{F}_2H_4$), –144.1 (unknown species), –145.6 (unknown aromatic species), –168.6 (br, 1 F, $(H_5C_2)_3Si–\mathbf{F}–Al[OC(CF_3)_3]_3$) –175.9 (br, 1 F, **F**Si$(C^{1'}H_2C^{2'}H_3)_3$) ppm.

^{29}Si NMR [79.50 MHz, *o*DFB, 278 K]: δ = 32.6 (1 Si, $(H_5C_2)_3\mathbf{Si}F$), 0.1 (1 Si, $(H_5C_2)_3\mathbf{Si}H$) ppm.

^{71}Ga NMR [122.04 MHz, *o*DFB, 278 K]: δ = –727.4 ($\Delta\nu_{1/2}$ = 960 Hz; br, 1 Ga, $[\mathbf{Ga}(ligand)_x]^+$) ppm (signal disappears after 3 days).

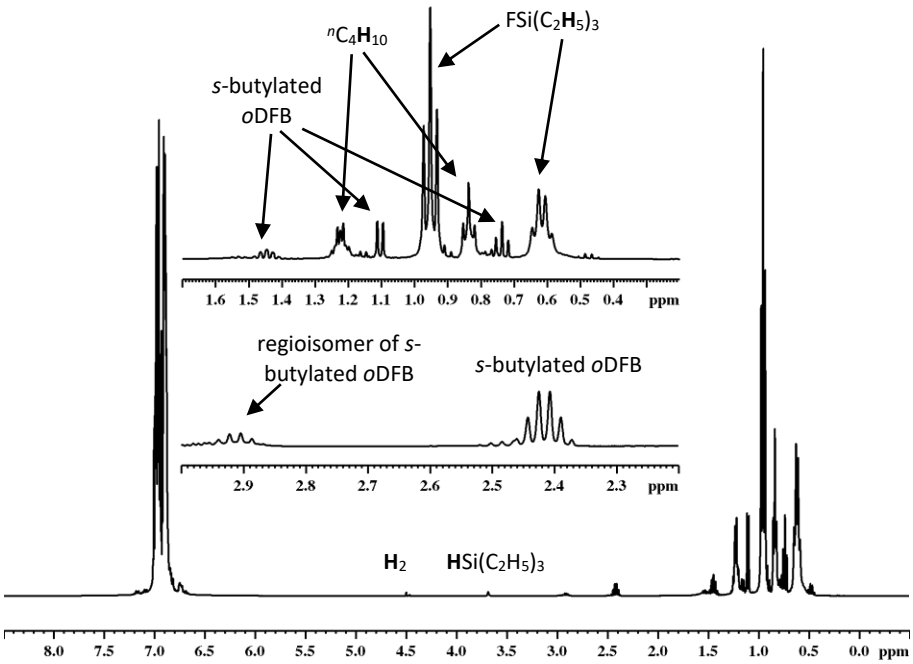


Figure S 58 ^{1}H NMR spectrum (400.17 MHz, *o*DFB, 298 K) of a $HSiEt_3$/F–^{n}Bu/**1** (1.1 : 1.0 : 0.04) mixture, 3 d after mixing the components (spectrum calibrated to δ ($oC_6F_2\mathbf{H}_4$) = 6.96 ppm).

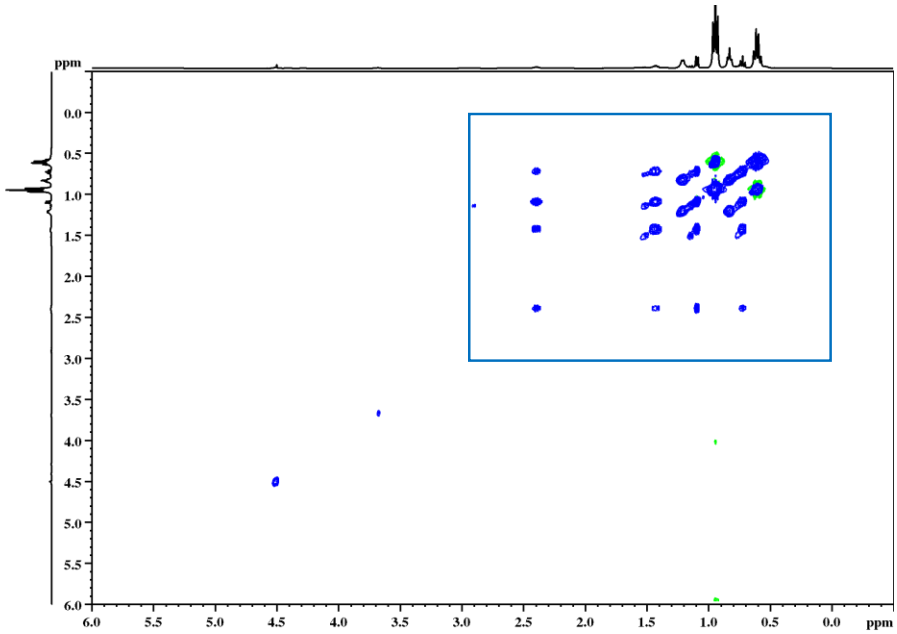


Figure S 59 ^{1}H TOCSY NMR (400.17 MHz, *o*DFB, 298 K, mixing time: 0.2 s) of a $HSiEt_3$/F–^{n}Bu/**1** (1.1 : 1.0 : 0.04) mixture, 8 h after mixing the components (^{1}H NMR spectrum calibrated to δ (*o*$C_6F_2\mathbf{H}_4$) = 6.96 ppm).

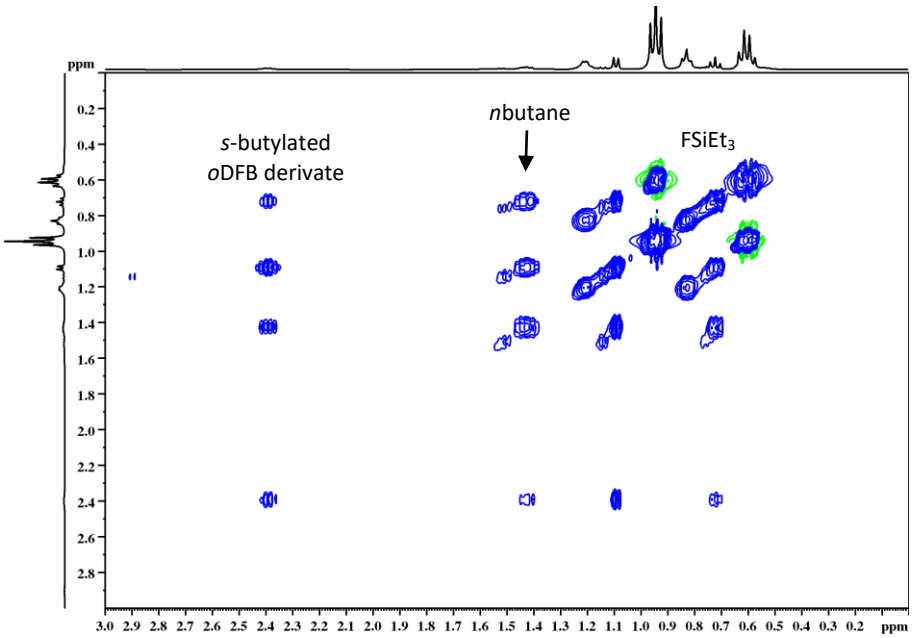


Figure S 60 ^{1}H TOCSY NMR (400.17 MHz, *o*DFB, 298 K, mixing time: 0.2 s) of a $HSiEt_3$/F–^{n}Bu/**1** (1.1 : 1.0 : 0.04) mixture, 8 h after mixing the components (^{1}H NMR spectrum calibrated to δ (*o*$C_6F_2\mathbf{H}_4$) = 6.96 ppm; selected area from the spectrum in **Figure S 59**).

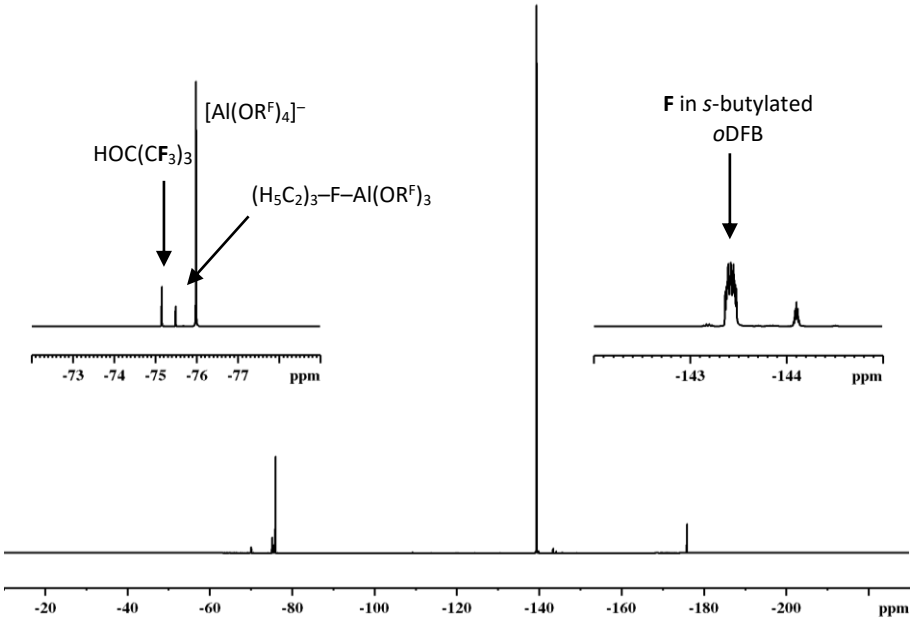


Figure S 61 ^{19}F NMR spectrum (376.54 MHz, *o*DFB, 298 K) of a HSiEt$_3$/F–^{n}Bu/**1** (1.1 : 1.0 : 0.04) mixture, 3 d after mixing the components.

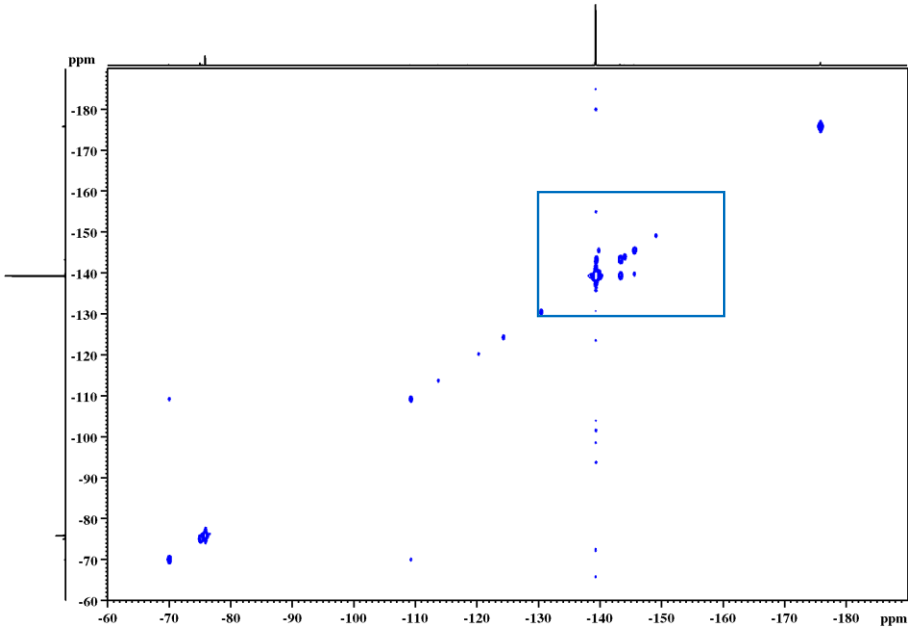


Figure S 62 ^{19}F,^{19}F-COSY NMR spectrum (282.45 MHz, *o*DFB, 298 K) of a HSiEt$_3$/F–^{n}Bu/**1** (1.1 : 1.0 : 0.04) mixture, 3 d after mixing the components.

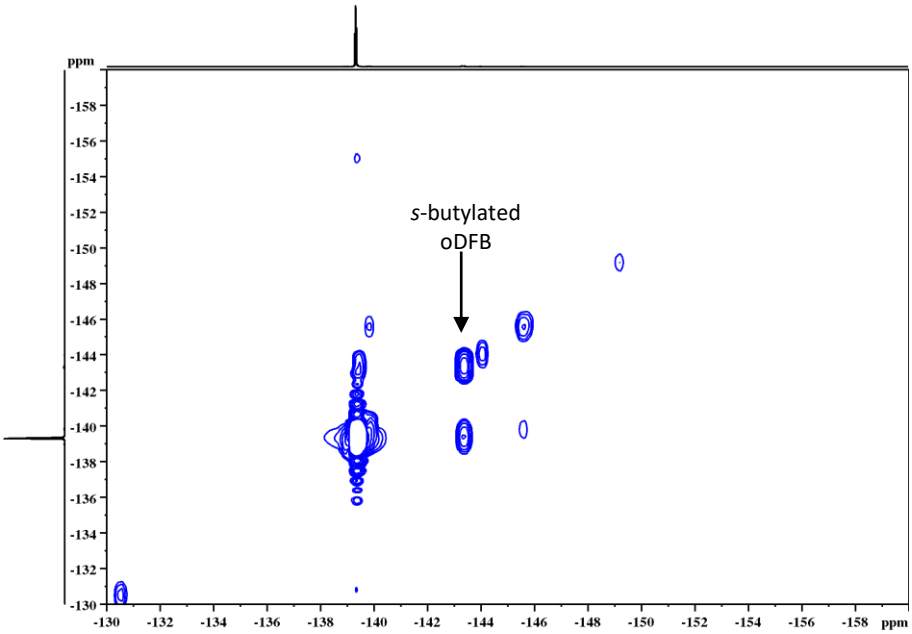


Figure S 63 ^{19}F,^{19}F-COSY NMR spectrum (282.45 MHz, *o*DFB, 298 K) of a HSiEt$_3$/F–^{n}Bu/**1** (1.1 : 1.0 : 0.04) mixture, 3 d after mixing the components (selected area from the spectrum in **Figure S 62**).

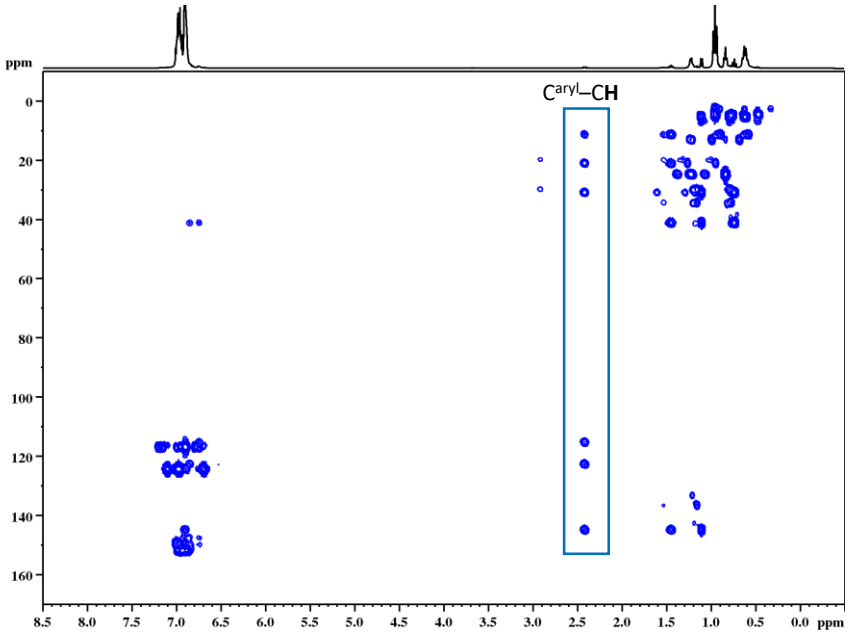


Figure S 64 ^{1}H,^{13}C-HMBC NMR (400.17 MHz, *o*DFB, 298 K, optimized for J = 8 Hz) of a HSiEt$_3$/F–^{n}Bu/**1** (1.1 : 1.0 : 0.04) mixture, 3 d after mixing the components (^{1}H NMR spectrum calibrated to δ (*o*C$_6$F$_2$**H**$_4$) = 6.96 ppm).

2.2.2 $HSiEt_3$ + Trifluorotoluene + 1 (4.0 : 1.0 : 0.05)

^{1}H NMR [400.17 MHz, *o*DFB, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K]: δ = 7.26 (m, $C^{aromatic}$–**H**), 4.51 (s, 2 H, $\mathbf{H}_2$), 3.81 (m, $C^{aromatic}$–C$\mathbf{H}_2$–$C^{aromatic}$), 3.68 (sept, 1 H, **H**Si($C^{1'}H_2C^{2'}H_3$)$_3$, $^{3}J_{SiH,H1'}$ = 3.2 Hz), 2.17 (m, $C^{aromatic}$–C$\mathbf{H}_3$), 0.96 (t, 18 H, FSi($C^{1}H_2C^{2}\mathbf{H}_3$)$_3$ and HSi($C^{1'}H_2C^{2'}\mathbf{H}_3$)$_3$, $^{3}J_{H2(')H1(')}$ = 7.9 Hz), 0.62 (qd, 6 H, FSi($C^{1}\mathbf{H}_2C^{2}H_3$)$_3$, $^{3}J_{H1,H2}$ = 7.9 Hz, $^{3}J_{H1,H2}$ = 6.3 Hz), 0.55 (qd, 6 H, HSi($C^{1'}\mathbf{H}_2C^{2'}H_3$)$_3$, $^{3}J_{H1',H2'}$ = 7.9 Hz, $^{3}J_{H1',SiH}$ = 3.2 Hz) ppm.

^{19}F NMR [376.54 MHz, *o*DFB, 298 K]: δ = –63.5 (s, 3 F, PhC$\mathbf{F}_3$), –75.1 (s, 9 F, HOC($C\mathbf{F}_3$)$_3$), –75.4 (s, 36 F, [Al(OC($C\mathbf{F}_3$)$_3$)$_4$]$^-$), –113.8 (tt, 1 F, Ph**F**, $^{3}J_{F,C}{}^{ortho}{}_{H}$ = 9.2 Hz, $^{4}J_{\mathbf{F},C}{}^{meta}{}_{H}$ = 5.8 Hz), –139.4 (m_c, 2 F, *o*$C_6\mathbf{F}_2H_4$), –175.8 (sept, 1 F, **F**Si($C^{1}H_2C^{2}H_3$)$_3$, $^{3}J_{F,C}{}^{1}{}_{H}$ = 6.3 Hz) ppm.

^{29}Si NMR [79.50 MHz, *o*DFB, 298 K]: δ = 32.1 (d, 1 Si, $(H_5C_2)_3$**Si**F, $^{1}J_{\mathbf{Si},F}$ = 289.5 Hz) ppm.

^{71}Ga NMR [122.04 MHz, *o*DFB, 298 K]: δ = –741.9 ($\Delta\nu_{1/2}$ = 275 Hz; br, 1 Ga, [**Ga**(ligand)$_x$]$^+$) ppm.

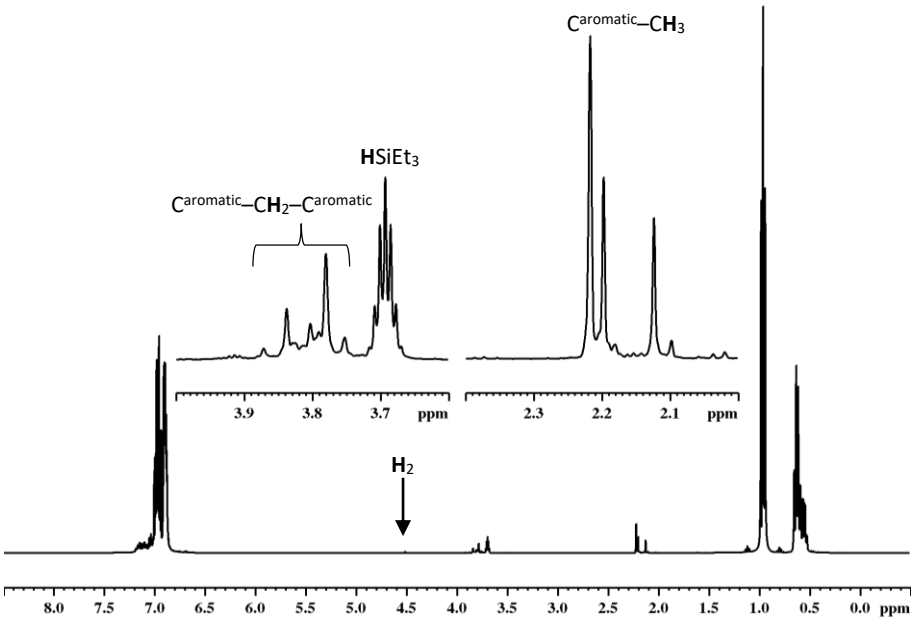


Figure S 65 ^{1}H NMR spectrum (400.17 MHz, *o*DFB, 298 K) of a $HSiEt_3$/Ph–CF_3/**1** (4.0 : 1.0 : 0.05) mixture, 3.5 d after mixing the components (spectrum calibrated to δ (*o*$C_6F_2\mathbf{H}_4$) = 6.96 ppm).

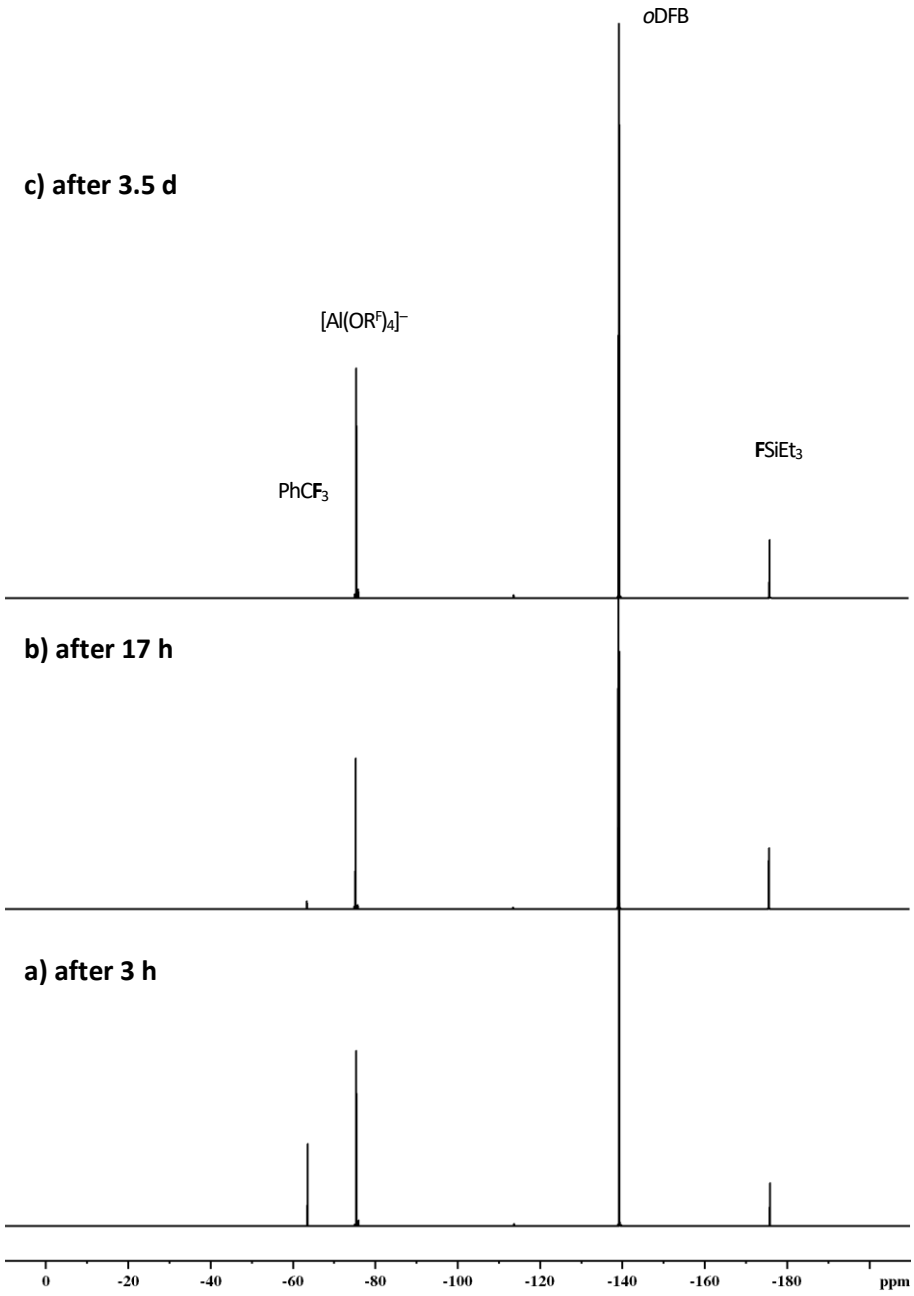


Figure S 66 ^{19}F NMR spectra (376.54 MHz, *o*DFB, 298 K) of a mixture of a $HSiEt_3$/$PhCF_3$/**1** (4.0 : 1.0 : 0.05) mixture, 3 h (bottom), 17 h (middle) and 3.5 d (top) after mixing the components. Spectra were normalized to signal intensity of solvent signal.

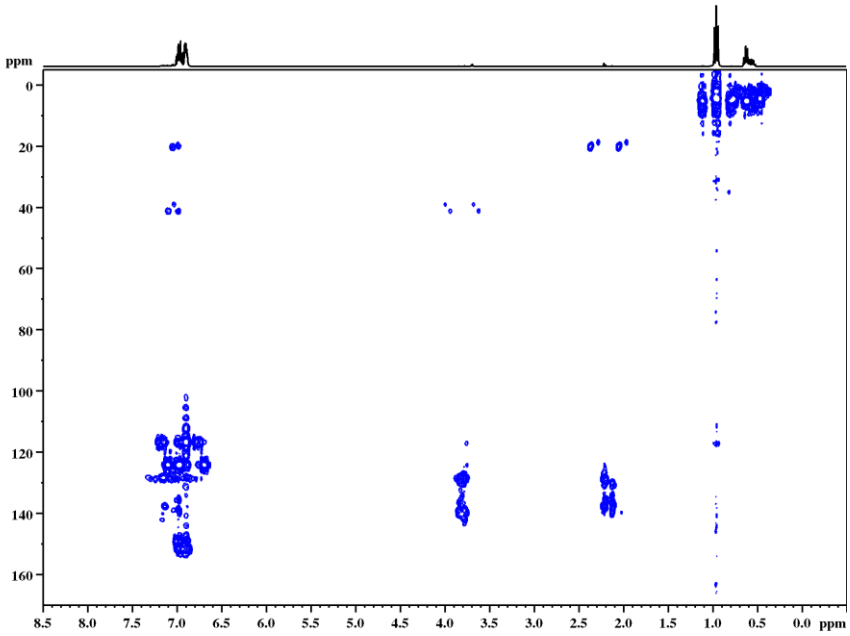


Figure S 67 $^{1}H,^{13}C$-HMBC NMR spectrum (400.17 MHz, *o*DFB, 298 K, optimized for J = 8 Hz) of a $HSiEt_3/PhCF_3$/**1** (4.0 : 1.0 : 0.05) mixture, 1 d after mixing the components (^{1}H NMR spectrum calibrated to δ ($oC_6F_2\mathbf{H}_4$) = 6.96 ppm).

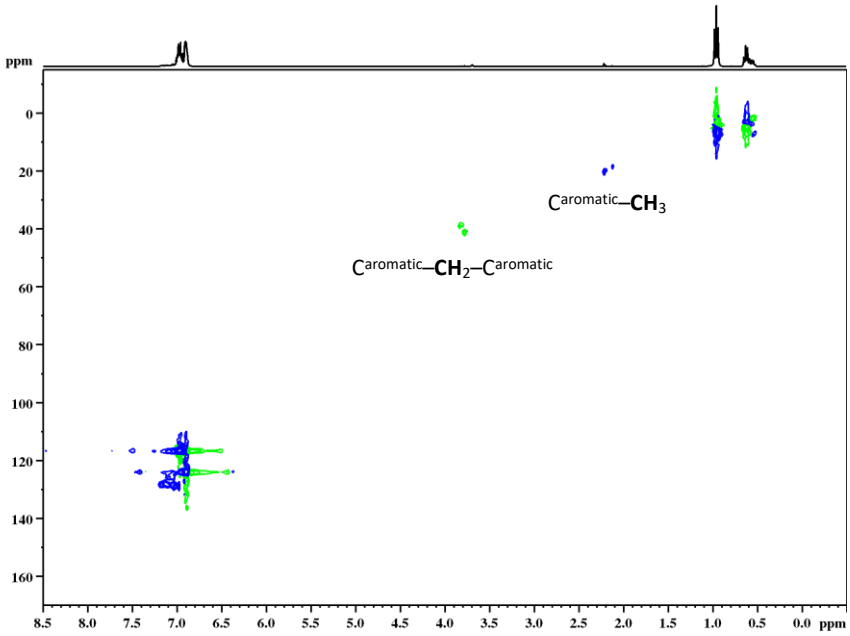
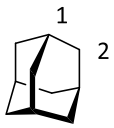


Figure S 68 Edited $^{1}H,^{13}C$-HSQC NMR spectrum (400.17 MHz, *o*DFB, 298 K, optimized for J = 145 Hz; CH_2: green, CH_3 and CH: blue) of a $HSiEt_3/PhCF_3$/**1** (4.0 : 1.0 : 0.05) mixture, 1 d after mixing the components (^{1}H NMR spectrum calibrated to δ ($oC_6F_2\mathbf{H}_4$) = 6.96 ppm).

2.2.3 $HSiEt_3$ + 1-Fluoroadamantane + 1 (2.8 : 1.0 : 0.05, 2.0 : 1.0 : 0.05 and 2.0 : 1.0 : 0.001)



^{1}H NMR [400.17 MHz, *o*DFB, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K]: δ = 4.50 (s, 2 H, $\mathbf{H}_2$), 3.69 (sept, 1 H, $\mathbf{H}Si(C^{1'}H_2C^{2'}H_3)_3$, $^{3}J_{SiH,C1'H}$ = 3.1 Hz), 1.79 (m, 4 H, $\mathbf{H}^1$), 1.72 (m, 12 H, $\mathbf{H}^2$) 0.95 (t, 18 H, $HSi(C^{1'}H_2C^{2'}\mathbf{H}_3)_3$ and $FSi(C^{1''}H_2C^{2''}\mathbf{H}_3)_3$, $^{3}J_{H2'(')H1(')}$ = 7.9 Hz), 0.62 (q, 6 H, $FSi(C^{1''}\mathbf{H}_2C^{2''}H_3)_3$, $^{3}J_{H1'',H2''}$ = 7.9 Hz), 0.54 (qd, 6 H, $HSi(C^{1'}\mathbf{H}_2C^{2'}H_3)_3$, $^{3}J_{H1',H2'}$ = 7.9 Hz, $^{3}J_{H1',SiH}$ = 3.1 Hz) ppm.

^{13}C NMR [100.62 MHz, *o*DFB, 298 K]: δ = 150.5 (2 C, $\mathbf{C}^1$F in *o*DFB), 124.3 (2 C, $\mathbf{C}^3$ in *o*DFB), 116.8 (2 C, $\mathbf{C}^2$ in *o*DFB), 38.4 (6 C, $\mathbf{C}^2$), 29.2 (4 C, $\mathbf{C}^1$), 8.3 (3 C, $HSi(C^{1'}H_2\mathbf{C}^{2'}H_3)_3$), 6.1 (3 C, $FSi(C^{1''}H_2\mathbf{C}^{2''}H_3)_3$), 5.3 (3 C, $FSi(\mathbf{C}^{1''}H_2C^{2''}H_3)_3$), 3.0 (3 C, $HSi(\mathbf{C}^{1'}H_2C^{2'}H_3)_3$) ppm.

^{19}F NMR [376.54 MHz, *o*DFB, 298 K]: δ = –75.1 (s, 9 F, $HOC(C\mathbf{F}_3)_3$), –75.4 (s, 36 F, $[Al(OC(C\mathbf{F}_3)_3)_4]^-$), –75.9 (br, 27 F, $(H_5C_2)_3Si–F–Al[OC(C\mathbf{F}_3)_3]_3$), –113.8 ($m_c$, 1 F, $C_6H_5\mathbf{F}$), –128.4 (s, 1 F, Ad–**F**) –139.4 (m_c, 2 F, $oC_6\mathbf{F}_2H_4$), –168.7 (br, 1 F, $(H_5C_2)_3Si–\mathbf{F}–Al[OC(CF_3)_3]_3$), –175.8 (br, 1 F, $(H_5C_2)_3Si\mathbf{F}$) ppm.

^{29}Si NMR [79.50 MHz, *o*DFB, 298 K]: δ = 32.7 (d, 1 Si, $(H_5C_2)_3\mathbf{Si}F$, $^{1}J_{Si,F}$ = 289.5 Hz), 0.1 (1 Si, $(H_5C_2)_3\mathbf{Si}H$) ppm.

^{71}Ga NMR [122.04 MHz, *o*DFB, 298 K]: δ = –742.5 ($\Delta\nu_{1/2}$ = 375 Hz; br, 1 Ga, $[\mathbf{Ga}(ligand)_x]^+$) ppm.

With 0.1 % of initiator **1**, no ^{71}Ga signal is observed.

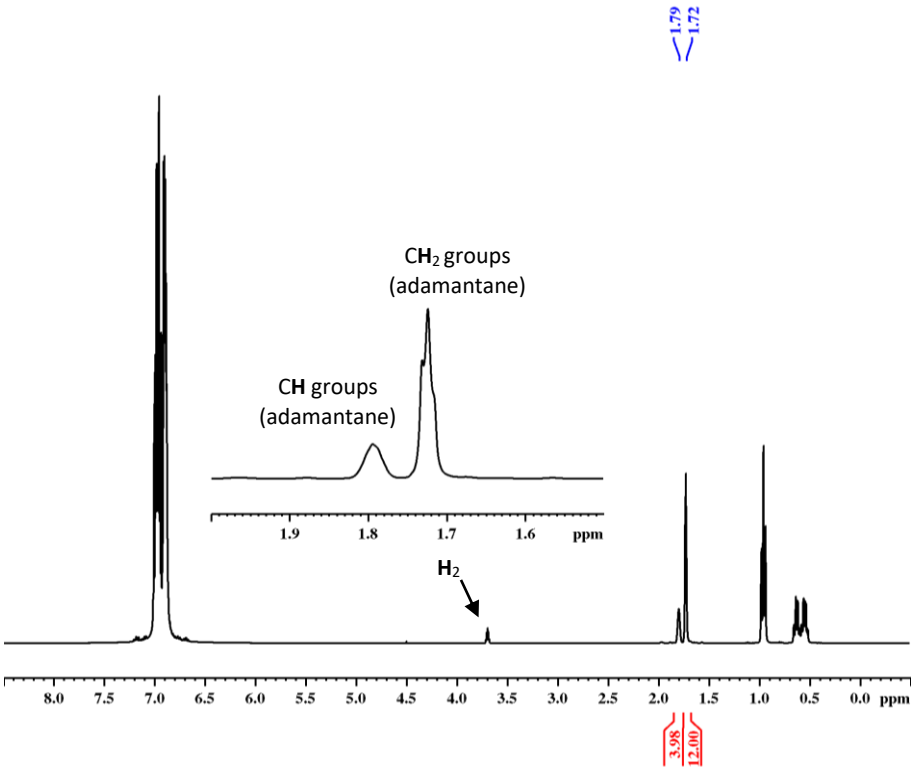


Figure S 69 ^{1}H NMR spectrum (400.17 MHz, *o*DFB, 298 K) of a $HSiEt_3$/1-fluoroadamantane/**1** (2.0 : 1.0 : 0.05) mixture, 2 h after mixing the components (spectrum calibrated to δ ($oC_6F_2\mathbf{H}_4$) = 6.96 ppm).

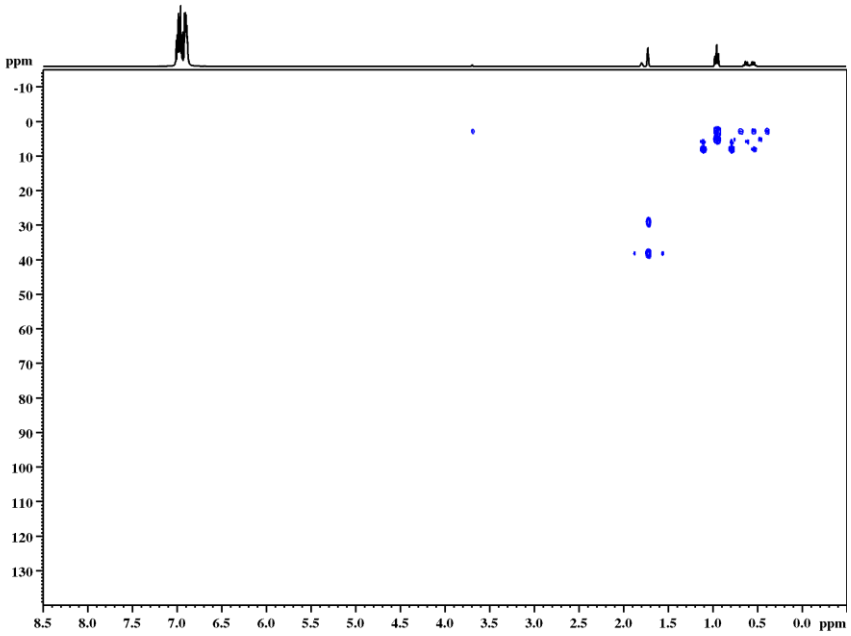


Figure S 70 $^{1}H,^{13}C$-HMBC NMR spectrum (400.17 MHz, *o*DFB, 298 K, optimized for J = 8 Hz) of a $HSiEt_3$/1-fluoroadamantane/**1** (2.0 : 1.0 : 0.05) mixture, after 4 h at rt (^{1}H NMR spectrum calibrated to δ (*o*$C_6F_2\mathbf{H}_4$) = 6.96 ppm).

With 5 mol-% of **1**, immediate hydrodefluorination was observed by ^{19}F NMR spectroscopy. In order to monitor the reaction progress in a separate experiment, only 0.1 % of **1** in *o*DFB were employed. The reaction progress monitored by ^{19}F NMR spectroscopy (**Figure S 71**). With the lower initiator loading, reaction progress was considerably slower and formation of $Et_3Si–F–Al[OC(CF_3)_3]_3$ was not observed.

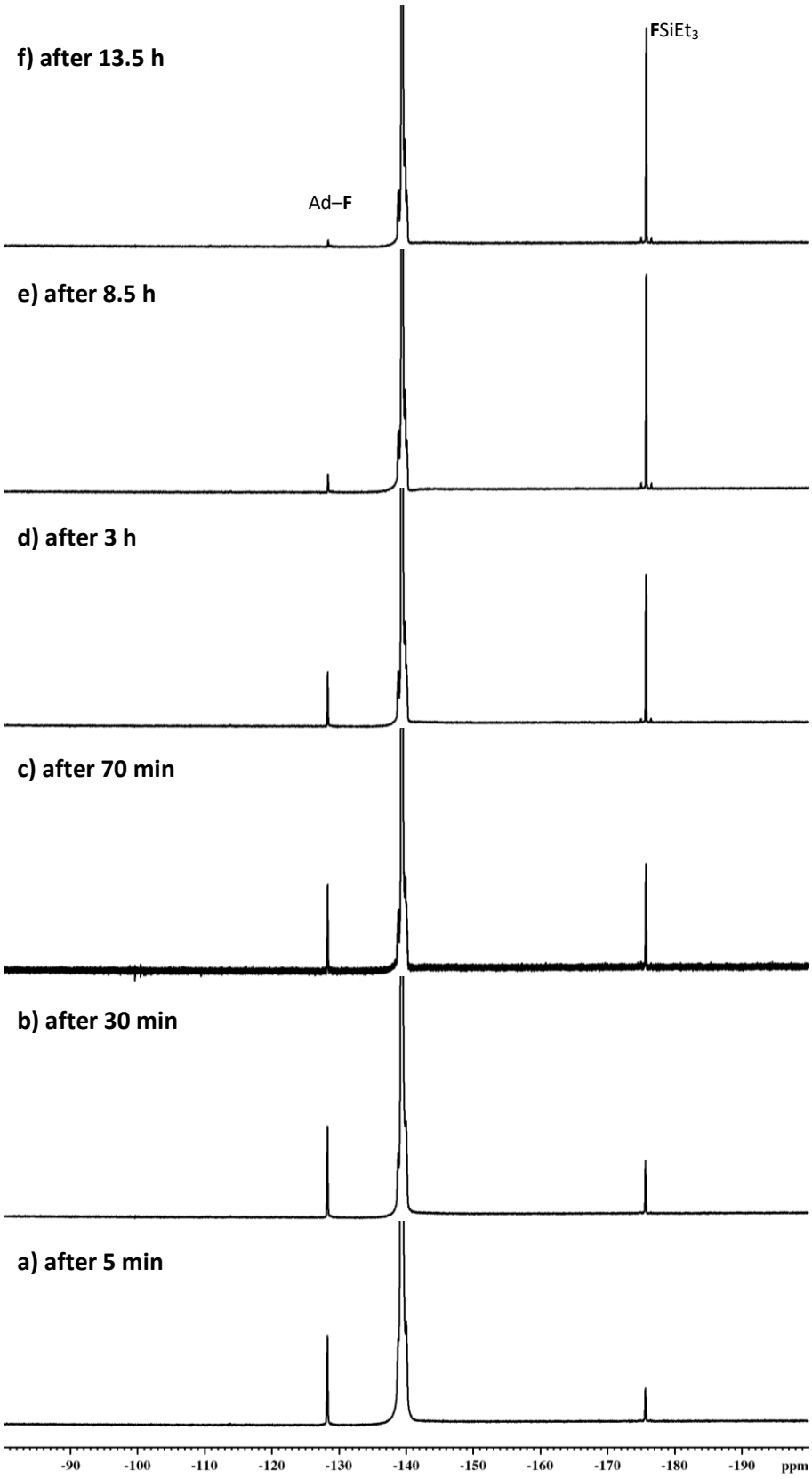


Figure S 71 ^{19}F NMR spectra (188.31 MHz, *o*DFB, 298 K) of a $HSiEt_3$/1-fluoroadamantane/**1** (2.0 : 1.0 : 0.001) mixture, at different times after mixing the components at rt. Spectra were normalized to signal intensity of solvent signal.

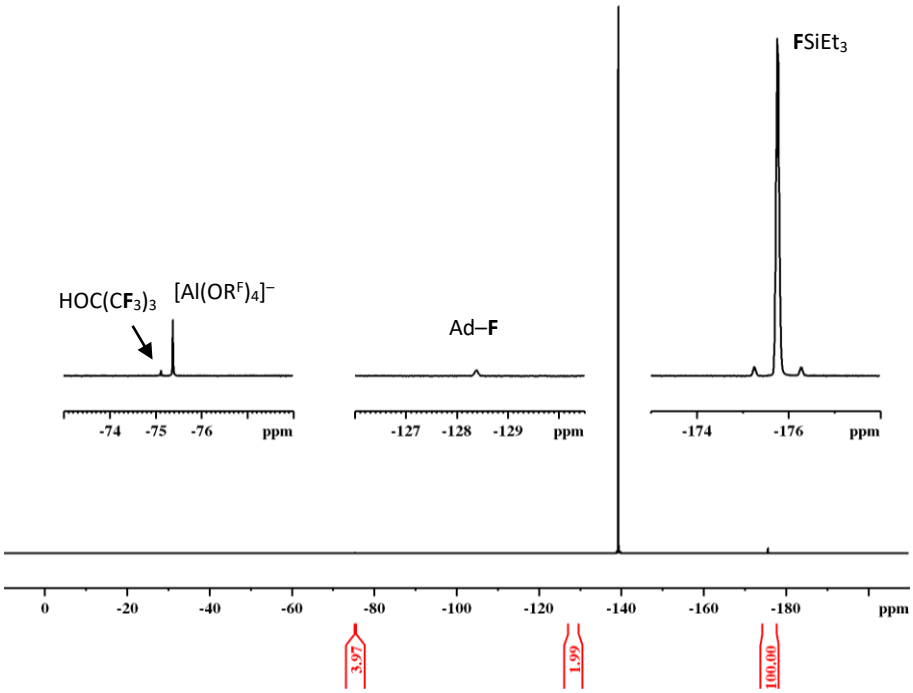
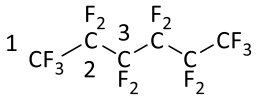


Figure S 72 ^{19}F NMR spectrum (282.45 MHz, *o*DFB, 298 K) of a $HSiEt_3$/1-fluoroadamantane/**1** (2.0 : 1.0 : 0.001) mixture, 18 h after mixing the components at rt.

2.2.4 $HSiEt_3$ + *n*-Perfluorohexane + 1 (15 : 1.0 : 0.56)



^{1}H NMR [400.17 MHz, *o*DFB, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K]: δ = 7.25 (unknown species), 4.72 (unknown species), 4.51 (s, 2 H, $\mathbf{H}_2$), 3.68 (sept, 1 H, $\mathbf{H}Si(C^{1'}H_2C^{2'}H_3)_3$, $^{3}J_{SiH,H1'}$ = 3.2 Hz), 1.03 (br, 15 H, $(\mathbf{H}_5C_2)_3Si–F–Al[OC(CF_3)_3]_3$), 0.96 (t, 9 H, $HSi(C^{1'}H_2C^{2'}\mathbf{H}_3)_3$, $^{3}J_{H2',H1'}$ = 7.9 Hz), 0.56 (qd, 6 H, $HSi(C^{1'}\mathbf{H}_2C^{2'}H_3)_3$, $^{3}J_{H1',H2'}$ = 7.9 Hz, $^{3}J_{H1',SiH}$ = 3.2 Hz) ppm.

^{19}F NMR [376.54 MHz, *o*DFB, 298 K]: δ = –70.3 (m_c, 6 F, $OC(C\mathbf{F}_3)_2CF_2$), –75.3 (s, 9 F, $HOC(C\mathbf{F}_3)_3$), –75.9 (unknown species), –76.2 (s, 27 F, $(H_5C_2)_3Si–F–Al[OC(C\mathbf{F}_3)_3]_3$), –82.2 (m, 6 F, $\mathbf{F}^1$), –109.7 (m_c, 2 F, $OC(CF_3)_2C\mathbf{F}_2$), –113.9 (tt, 1 F, Ph**F**, $^{3}J_{F,CH}$ = 9.2 Hz, $^{4}J_{F,CH}$ = 5.8 Hz), –123.8 (m, 4 F, $\mathbf{F}^3$), –127.2 (m, 4 F, $\mathbf{F}^2$), –139.4 (m_c, 2 F, $oC_6\mathbf{F}_2H_4$), –168.4 (br, 1 F, $(H_5C_2)_3Si–\mathbf{F}–Al[OC(CF_3)_3]_3$, $^{1}J_{F,Si}$ = 337.0 Hz), –176.5 (br, 1 F, $(H_5C_2)_3Si\mathbf{F}$) ppm.

^{27}Al NMR [104.27 MHz, *o*DFB, 298 K]: δ = 37.5 (br, 1 Al, $(H_5C_2)_3Si–F–\mathbf{Al}[OC(CF_3)_3]_3$) ppm.

^{29}Si NMR [59.64 MHz, *o*DFB, 298 K]: δ = 81.9 (br, 1 Si, $(H_5C_2)_3\mathbf{Si}–F–Al[OC(CF_3)_3]_3$, $^{1}J_{Si,F}$ = 278.0 Hz), 31.5 (br, 1 Si, $(H_5C_2)_3\mathbf{Si}F$, $^{1}J_{Si,F}$ = 289.5 Hz), 0.1 (1 Si, $(H_5C_2)_3\mathbf{Si}H$) ppm.

^{71}Ga NMR [122.04 MHz, *o*DFB, 298 K]: δ = –755.1 ($\Delta\nu_{1/2}$ = 195 Hz; br, 1 Ga, $[\mathbf{Ga}(\text{fluoroarene})_x]^+$) ppm (signal disappears after 5 days).

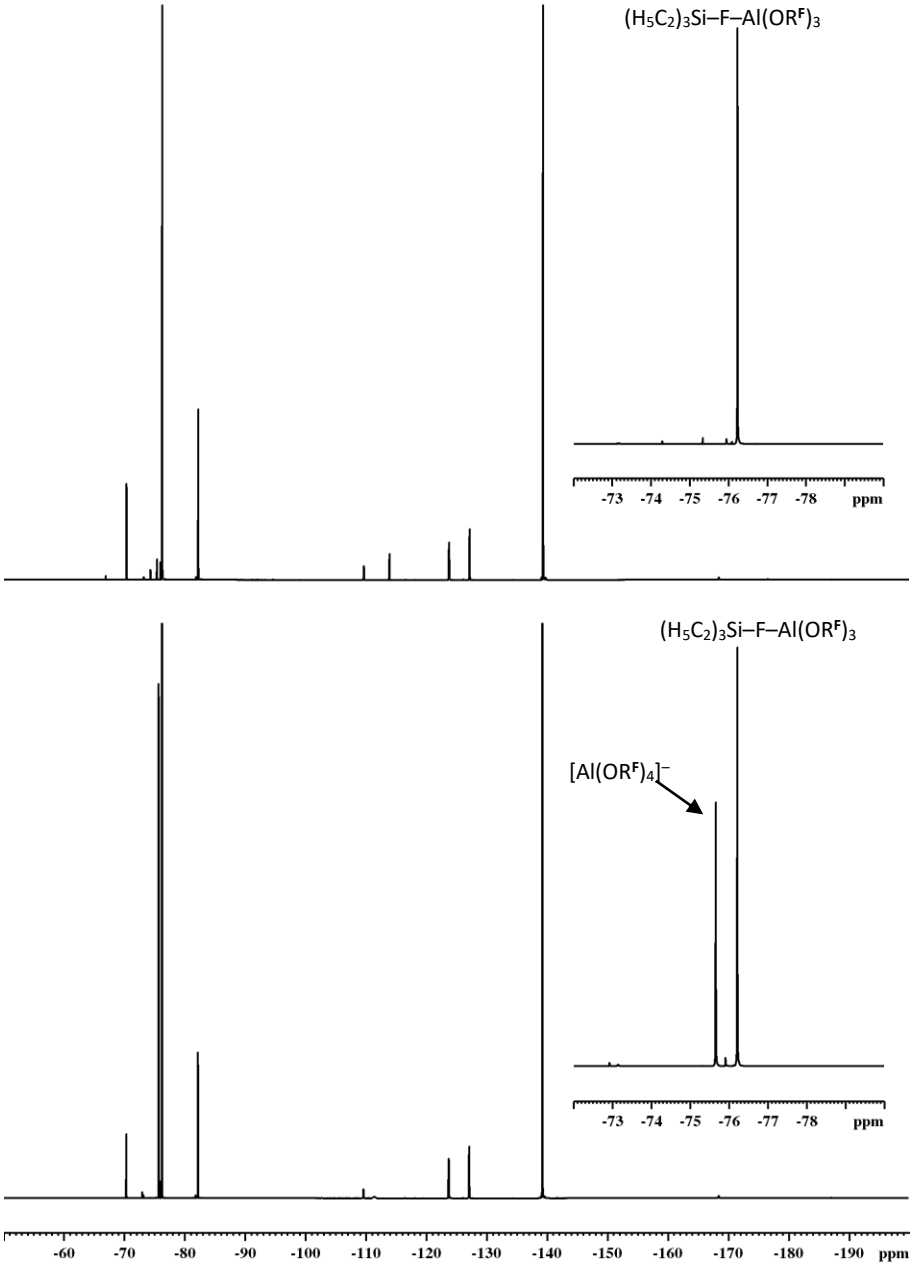


Figure S 73 ^{19}F NMR spectra (376.54 MHz, *o*DFB, 298 K) of a $HSiEt_3$/*n*-perfluorohexane/**1** (15 : 1.0 : 0.56) mixture, 5 h (bottom) and 15 d (top) after mixing the components.

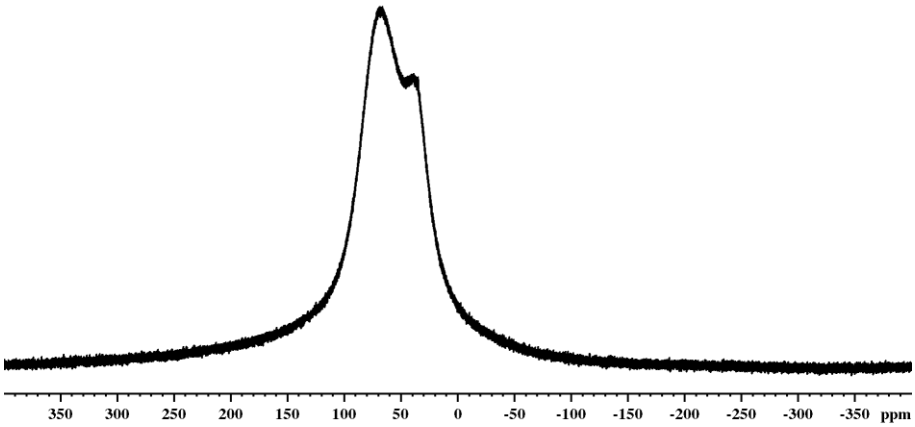


Figure S 74 ^{27}Al NMR spectrum (78.22 MHz, *o*DFB, 298 K) of a $HSiEt_3$/*n*-perfluorohexane/**1** (15 : 1.0 : 0.56) mixture, 14 d after mixing the components.

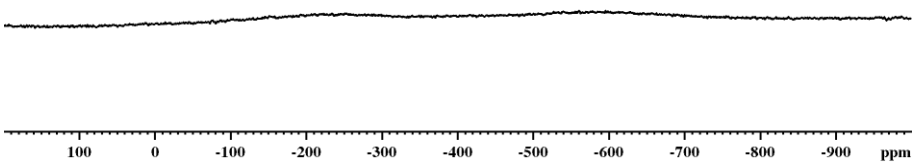
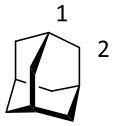


Figure S 75 ^{71}Ga NMR spectrum (122.04 MHz, *oD*FB, 298 K) of a $HSiEt_3$/*n*-perfluorohexane/**1** (15 : 1.0 : 0.56) mixture, 5 d after mixing the components. No ^{71}Ga signal is detected.

2.2.5 $HSiEt_3$ + 1-Fluoroadamantane + $[Ph_3C][pf]$ (2.0 : 1.0 : 0.002)



^{1}H NMR [200.13 MHz, *o*DFB, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K]: δ = 4.50 (s, 2 H, $\mathbf{H}_2$), 3.69 (sept, 1 H, $\mathbf{H}Si(C^{1'}H_2C^{2'}H_3)_3$, $^3J_{SiH,C1'H}$ = 3.1 Hz), 1.79 (m, 4 H, $\mathbf{H}^1$), 1.72 (m, 12 H, $\mathbf{H}^2$) 0.95 (t, 18 H, $HSi(C^{1'}H_2C^{2'}\mathbf{H}_3)_3$ and $FSi(C^{1''}H_2C^{2''}\mathbf{H}_3)_3$, $^3J_{H2'('),H1(')}$ = 7.9 Hz), 0.62 (q, 6 H, $FSi(C^{1''}\mathbf{H}_2C^{2''}H_3)_3$, $^3J_{H1'',H2''}$ = 7.9 Hz), 0.54 (qd, 6 H, $HSi(C^{1'}\mathbf{H}_2C^{2'}H_3)_3$, $^3J_{H1',H2'}$ = 7.9 Hz, $^3J_{H1',SiH}$ = 3.1 Hz) ppm.

^{19}F NMR [188.31 MHz, *o*DFB, 298 K]: δ = –75.1 (s, 9 F, $HOC(C\mathbf{F}_3)_3$), –75.4 (s, 36 F, $[Al(OC(C\mathbf{F}_3)_3)_4]^-$), –139.4 ($m_c$, 2 F, $oC_6\mathbf{F}_2H_4$), –175.7 (br, 1 F, $(H_5C_2)_3Si\mathbf{F}$) ppm.

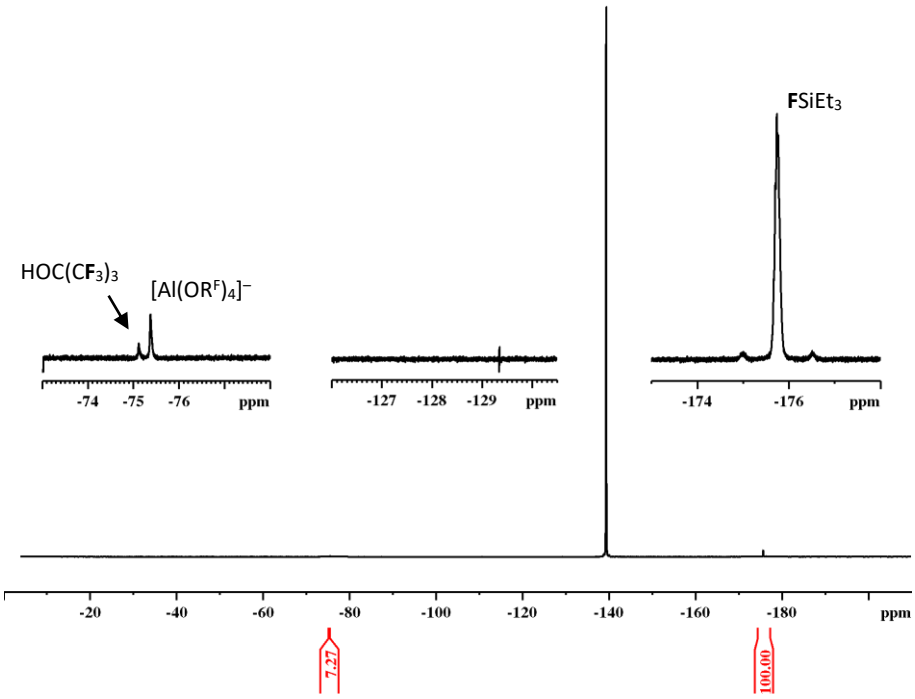


Figure S 76 ^{19}F NMR spectrum (188.31 MHz, *o*DFB, 298 K) of a $HSiEt_3$/1-fluoroadamantane/$[Ph_3C][pf]$ (2.0 : 1.0 : 0.002) mixture, 40 min after mixing the components at rt.

2.3 Reactions of Silanes with K[*pf*] (K = $[Ga(PhF)_2]^+$; $[NO]^+$; Ag^+)

2.3.1 $HSiMe_3$ + 1 (4.8 : 1.0)

A solution of $HSiMe_3$ in *o*DFB (0.7 M, 0.58 ml, 0.41 mmol, 4.8 eq.) was added to **1** (0.10 g, 85 µmol, 1.0 eq.). The reaction mixture was frozen as quickly as possible at –78 °C after mixing the components and was thawed inside the NMR spectrometer.

^{1}H NMR [400.17 MHz, *o*DFB, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K]: δ = 4.51 (s, 2 H, **H**$_2$), 4.00 (br, 1 H, $(H_3C)_3Si$–**H**), 3.78 (sept, 2 H, $(H_3C)_2Si\mathbf{H}_2$, $^3J_{SiH,CH}$ = 4.1 Hz), 0.57 (br, 9 H, $(\mathbf{H}_3C)_3Si$–F–Al$[OC(CF_3)_3]_3$, $^3J_{H,F}$ = 13 Hz), 0.35 (br. s, 9 H, $(\mathbf{H}_3C)_3SiCl$), 0.05 (t, 6 H, $(\mathbf{H}_3C)_2SiH_2$, $^3J_{CH,SiH}$ = 4.1 Hz), 0.03 (br. s, 9 H, $(\mathbf{H}_3C)_3Si$–H), 0.00 (s, 12 H, $(\mathbf{H}_3C)_4Si$) ppm.

^{19}F NMR [376.54 MHz, oDFB, 298 K]: δ = –70.1 (m_c, 6 F, $OC(C\mathbf{F}_3)_2CF_2$), –75.4 (s, 36 F, $[Al(OC(C\mathbf{F}_3)_3)_4]^-$), –76.1 (s, 27 F, $(H_3C)_3Si$–F–Al$[OC(C\mathbf{F}_3)_3]_3$), –109.4 (m_c, 2 F, $OC(CF_3)_2C\mathbf{F}_2$), –113.9 (tt, 1 F, Ph**F**, $^3J_{F,C^{ortho}H}$ = 9.2 Hz, $^4J_{F,C^{meta}H}$ = 5.7 Hz), –139.5 (m_c, 2 F, $oC_6\mathbf{F}_2H_4$), –156.5 (br, 1 F, $(H_3C)_3Si$–**F**–Al$[OC(CF_3)_3]_3$, $^1J_{F,Si}$ = 284 Hz, $^3J_{F,H}$ = 13 Hz) ppm.

^{27}Al NMR [104.27 MHz, *o*DFB, 298 K]: δ = 34.9 (s, 1 Al, $[\mathbf{Al}(OC(CF_3)_3)_4]^-$) ppm (signal intensity decreases over time).

^{29}Si NMR [79.5 MHz, *o*DFB, 298 K]: δ = 81.9 (br, 1 Si, $(H_3C)_3\mathbf{Si}$–F–Al$[OC(CF_3)_3]_3$, $^1J_{Si,F}$ = 265 Hz), 30.7 (1 Si, $(H_3C)_3\mathbf{Si}Cl$), 0.0 ppm (1 Si, $(H_3C)_4\mathbf{Si}$), –16.7 (1 Si, $(H_3C)_3\mathbf{Si}H$), –38.2 (1 Si, $(H_3C)_2\mathbf{Si}H_2$) ppm.

^{71}Ga NMR [122.04 MHz, *o*DFB, 298 K]: δ = –756.0 (br, $\Delta\nu_{1/2}$ = 195 Hz, 1 Ga, $[Ga(fluoroarene)_x]^+$).

It is obvious from the stack plot in **Figure S 77** that the concentration of the **H**–Si hydrogen atoms decreased, compared to the **H**–C–Si protons. This is in line with the formation of H_2 from these hydrogen atoms.

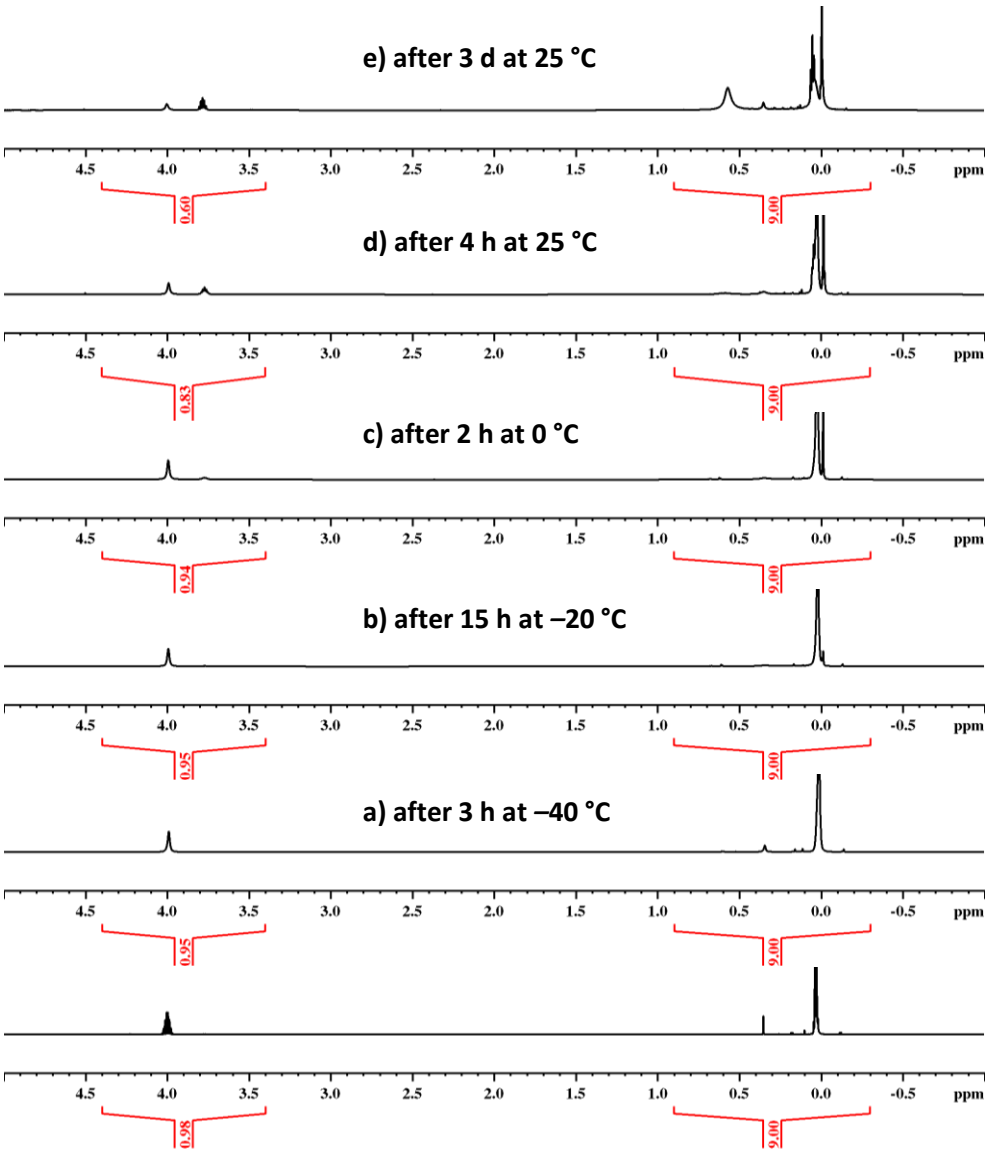


Figure S 77 From bottom to top: ^{1}H NMR spectra of $HSiMe_3$ in *o*DFB at rt (300.18 MHz), $HSiMe_3$/**1** (4.8 : 1.0) after 3 h at 233 K, after 15 h at 253 K, after 2 h at 273 K, after 4 h at 298 K and after 3 days at 298 K (400.17 MHz). The integral sum of all **H**–C–Si hydrogen atoms was set to 9.00. Since the $HSiMe_3$ stock solution contained ca. 2 % $ClSiMe_3$, the ration of **H**–Si to **H**–C–Si protons is smaller than 1.00 in the bottom spectrum.

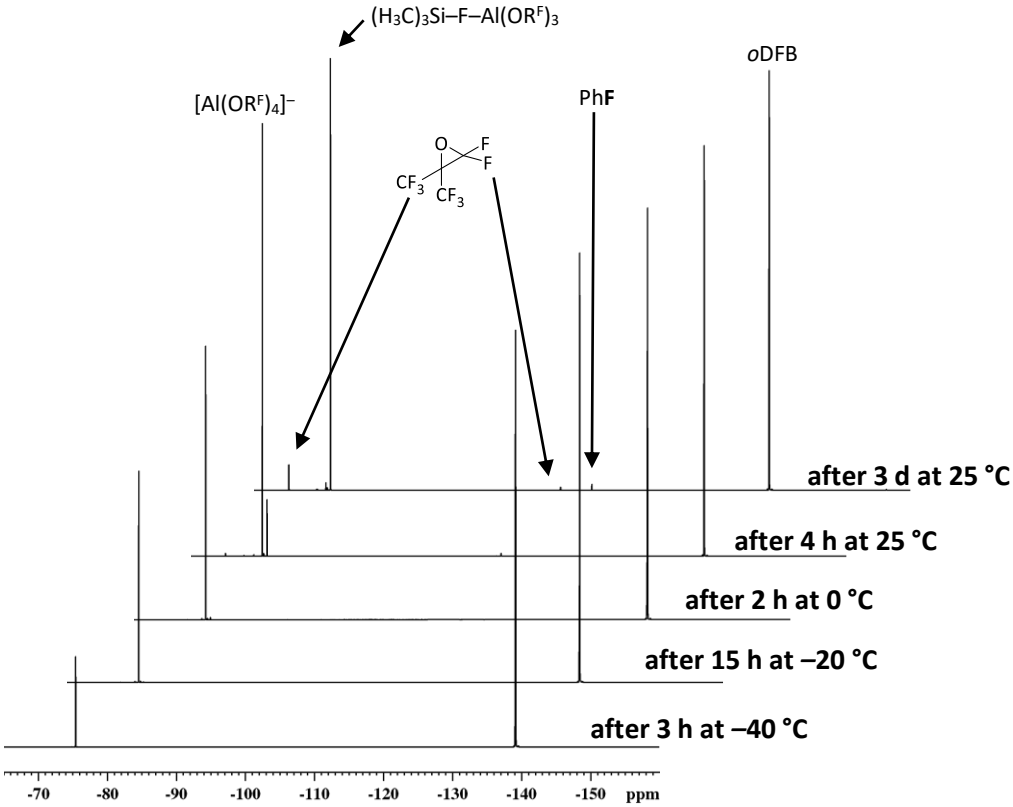


Figure S 78 From bottom to top: ^{19}F NMR spectra (376.54 MHz, *o*DFB) of $HSiMe_3$/**1** (4.8 : 1.0) after 3 h at 233 K, after 15 h at 253 K, after 2 h at 273 K, after 4 h at 298 K and after 3 d at 298 K. Signal intensities are normalized to the *o*DFB signal.

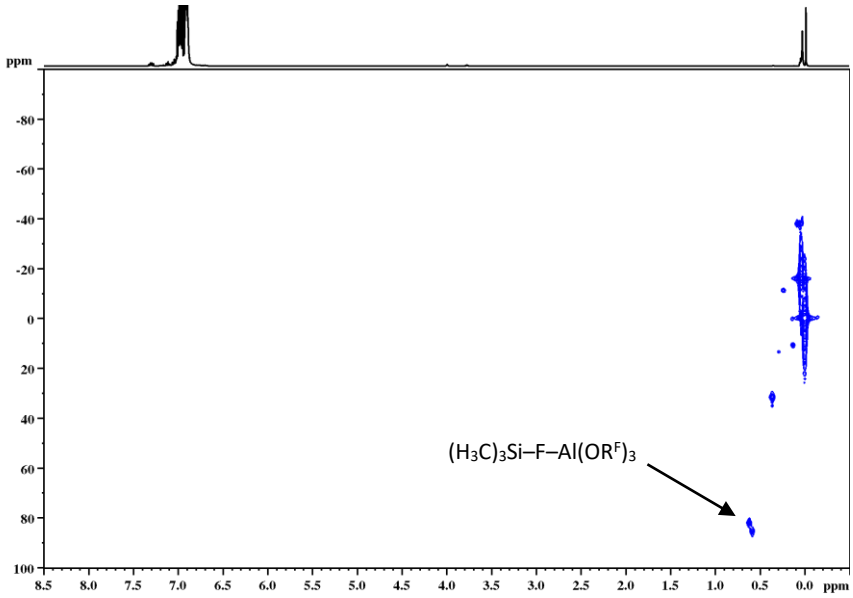


Figure S 79 ^{1}H,^{29}Si-HMBC NMR spectrum (400.17 MHz, *o*DFB, 298 K, optimized for J = 8 Hz) of a $HSiMe_3$/**1** (4.8 : 1.0) mixture, after 10 h at rt (^{1}H NMR spectrum calibrated to δ (*o*C_6F_2**H**$_4$) = 6.96 ppm).

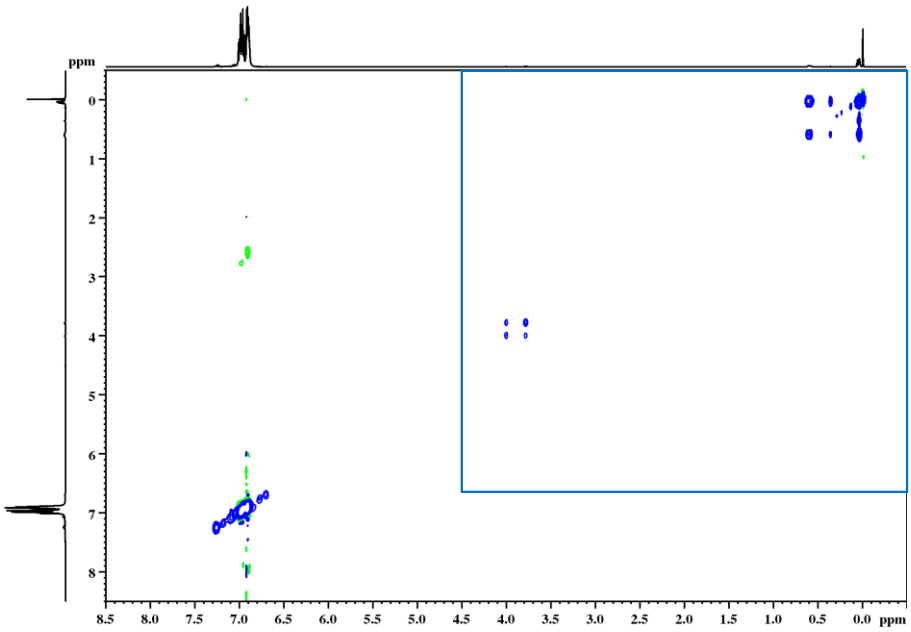


Figure S 80 ^{1}H EXSY NMR spectrum (400.17 MHz, *o*DFB, 298 K, mixing time = 1.0 s) of a $HSiMe_3$/**1** (4.8 : 1.0) mixture, 2 d after mixing the components (^{1}H NMR spectrum calibrated to δ (*o*C_6F_2**H**$_4$) = 6.96 ppm).

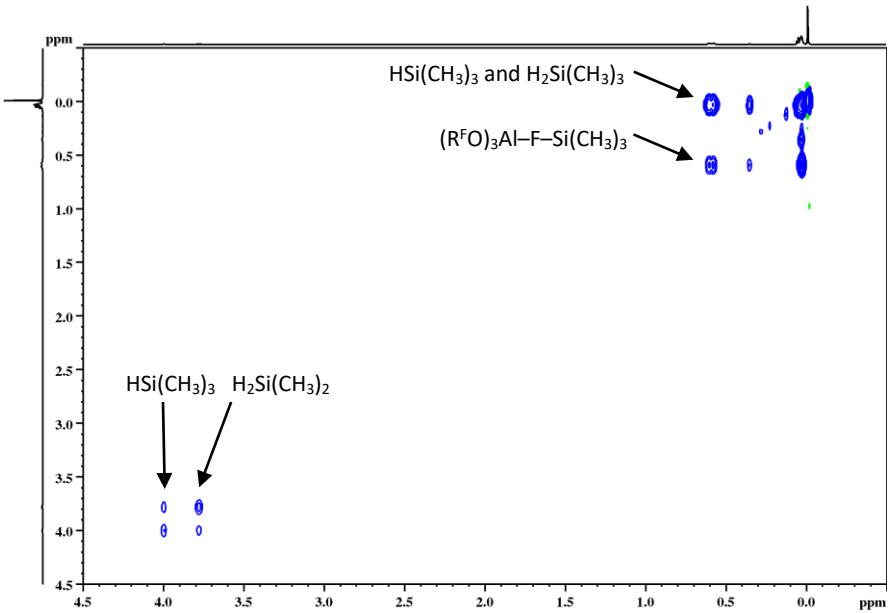
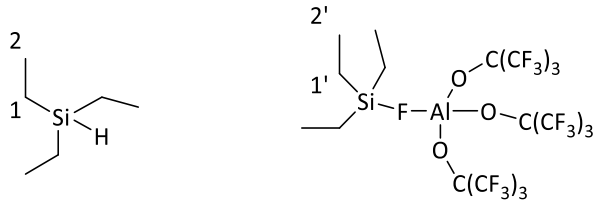


Figure S 81 ^{1}H EXSY NMR spectrum (400.17 MHz, *o*DFB, 298 K, mixing time = 1.0 s) of a $HSiMe_3$/**1** (4.8 : 1.0) mixture, 2 d after mixing the components (^{1}H NMR spectrum calibrated to δ (*o*C_6F_2**H**$_4$) = 6.96 ppm; selected area from the spectrum in **Figure S 80**).

2.3.2 $HSiEt_3$ + 1 (1.0 : 1.0 and 4.0 : 1.0)

$HSiEt_3$ in *o*DFB (0.35 M, 0.24 ml, 84 µmol, 1.0 eq.) was added to a solution of **1** in *o*DFB (0.24 M, 0.36 ml, 86 µmol, 1.0 eq.). The mixture was kept at rt for 3 d and heated to 60 °C for 2 d.

In a separate experiment, $HSiEt_3$ (60 µl, 0.044 g, 0.38 mmol, 4.0 eq.) was added to a solution of **1** in *o*DFB (0.18 M, 0.54 ml, 95 µmol, 1.0 eq.).



^{1}H NMR [300.18 MHz, *o*DFB, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K]: δ = 4.51 (s, 1 H, **H**$_2$), 3.69 (s, 1 H, $(H_5C_2)_3$Si**H**), 1.04 (br, 15 H, $(\mathbf{H}_5C_2)_3$Si–F–Al[OC$(CF_3)_3]_3$), 0.95 (t, 9 H, **H**^{2}, $^3J_{H2,H1}$ = 8.0 Hz), 0.92 (unknown compound), 0.48 (unknown species), 0.55 (q, 6 H, **H**^{1}, $^3J_{H1,H2}$ = 8.0 Hz), 0.48 (unknown species) ppm.

^{19}F NMR [282.45 MHz, *o*DFB, 298 K]: δ = –70.1 (m_c, 6 F, OC(C**F**$_3$)$_2$CF$_2$), –75.5 (s, 36 F, $[Al(OC(C\mathbf{F}_3)_3)_4]^-$), –76.0 (s, 27 F, $(H_5C_2)_3$Si–F–Al$[OC(C\mathbf{F}_3)_3]_3$), –109.4 (m_c, 2 F, OC$(CF_3)_2$C**F**$_2$), –112.4 (br, 1 F, C_6H_5**F**), –139.4 (m_c, 2 F, *o*C_6**F**$_2H_4$), –168.7 (br, 1 F, $(H_5C_2)_3$Si–**F**–Al$[OC(CF_3)_3]_3$, $^1J_{F,Si}$ = 337 Hz) ppm.

^{27}Al NMR [78.22 MHz, *o*DFB, 298 K]: δ = 34.9 (s, 1 Al, [**Al**$(OC(CF_3)_3)_4]^-$) ppm.

^{29}Si NMR [59.64 MHz, *o*DFB, 298 K]: δ = 83.5 (br, 1 Si, $(H_5C_2)_3$**Si**–F–Al$[OC(CF_3)_3]_3$, $^1J_{Si,F}$ = 288 Hz), 32.9 (br, 1 Si, $(H_5C_2)_3$**Si**–F, $^1J_{Si,F}$ = 288 Hz), 2.1 (1 Si, $(H_5C_2)_3$**Si**H) ppm.

^{71}Ga NMR [91.5 MHz, *o*DFB, 298 K]: δ = –755.1 ($\Delta\nu_{1/2}$ = 220 Hz; br, 1 Ga, $[Ga(fluoroarene)_x]^+$) ppm.

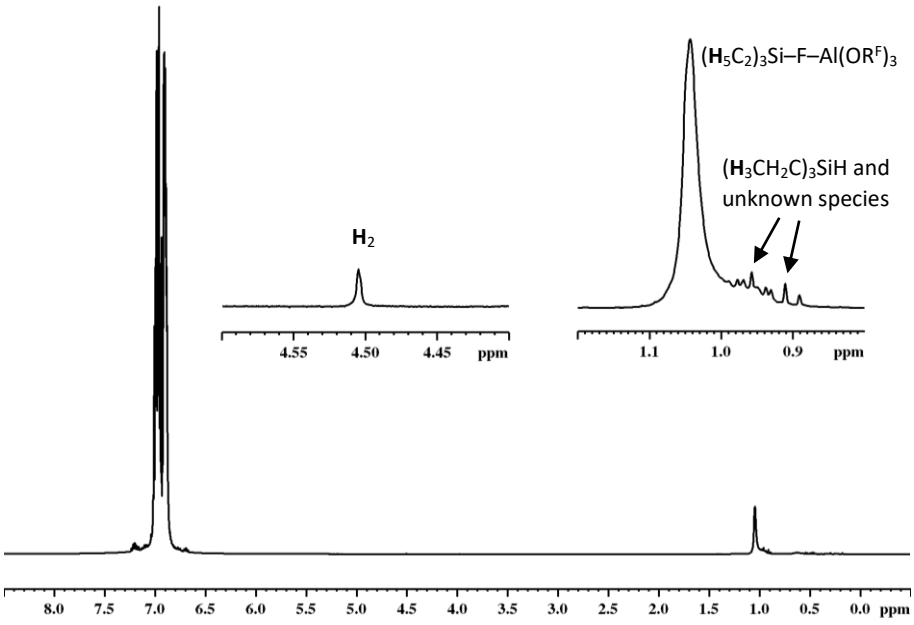


Figure S 82 ^{1}H NMR spectrum (400.17 MHz, *o*DFB, 298 K) of a $HSiEt_3$/**1** (1.0 : 1.0) mixture, 5 d (mixture heated to 60 °C for 2 d) after mixing the components (spectrum calibrated to δ (*o*C_6F_2**H**$_4$) = 6.96 ppm).

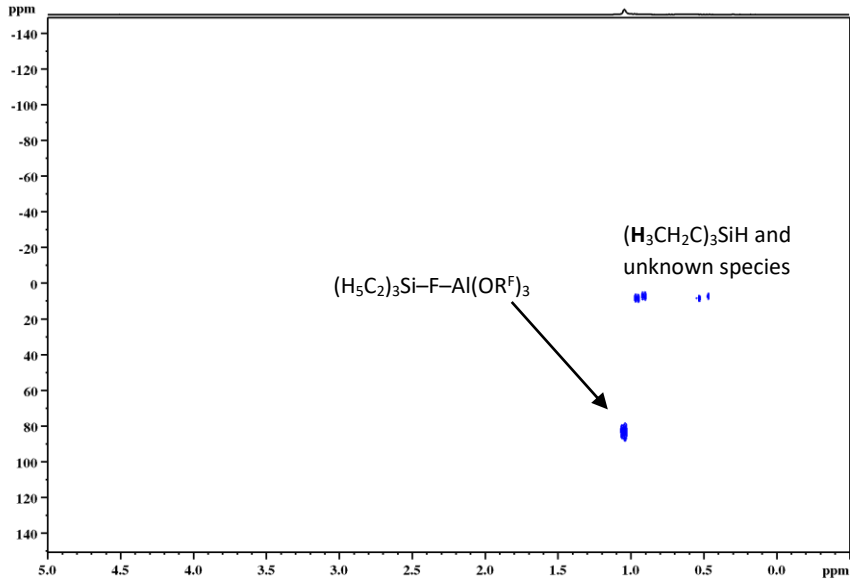


Figure S 83 $^{1}H,^{29}Si$-HMBC NMR spectrum (400.17 MHz, *o*DFB, 298 K, optimized for *J* = 12 Hz) of a $HSiEt_3$/**1** (1.0 : 1.0) mixture, 5 d (mixture heated to 60 °C for 2 d) after mixing the components (^{1}H NMR spectrum calibrated to δ ($oC_6F_2\mathbf{H}_4$) = 6.96 ppm).

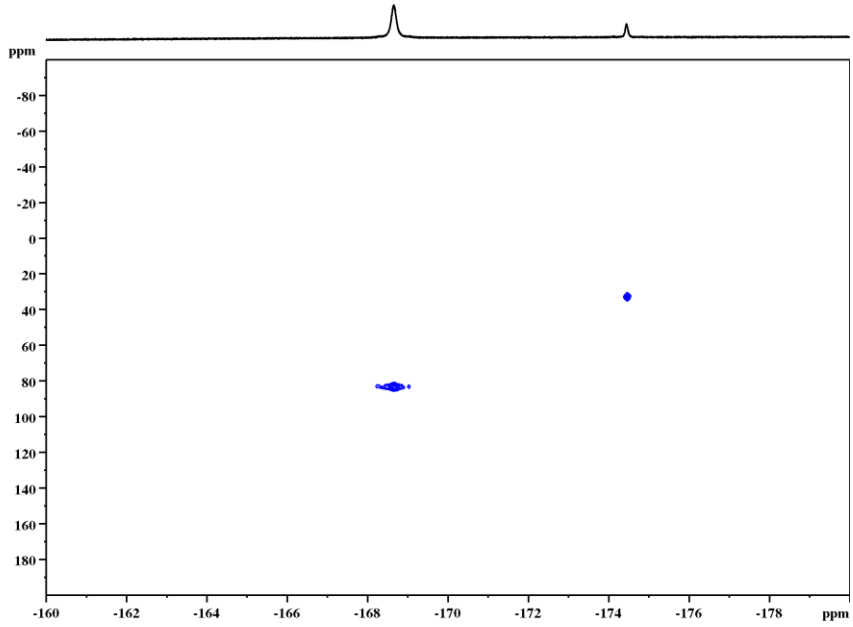


Figure S 84 $^{19}F,^{29}Si\{^{1}H\}$-HSQC NMR spectrum (376.54 MHz, *o*DFB, 298 K, optimized for *J* = 280 Hz) of a $HSiEt_3$/**1** (1.0 : 1.0) mixture, 5 d (mixture heated to 60 °C for 2 d) after mixing the components (^{1}H NMR spectrum calibrated to δ ($oC_6F_2\mathbf{H}_4$) = 6.96 ppm).

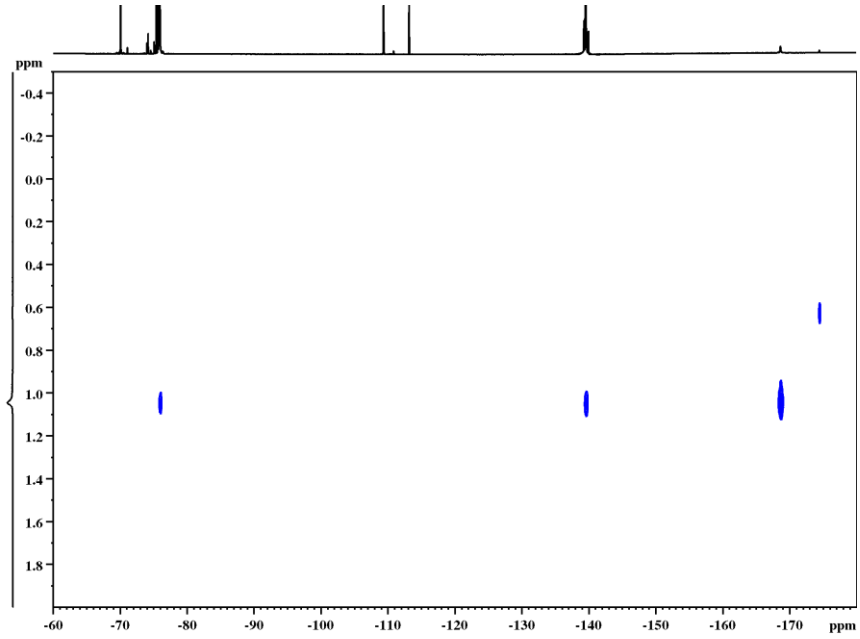


Figure S 85 $^{19}F,^{1}H$-COSY NMR spectrum (376.54 MHz, *o*DFB, 298 K) of a $HSiEt_3$/**1** (1.0 : 1.0) mixture, 5 d after mixing the components (^{1}H NMR spectrum calibrated to δ (*o*$C_6F_2\mathbf{H}_4$) = 6.96 ppm).

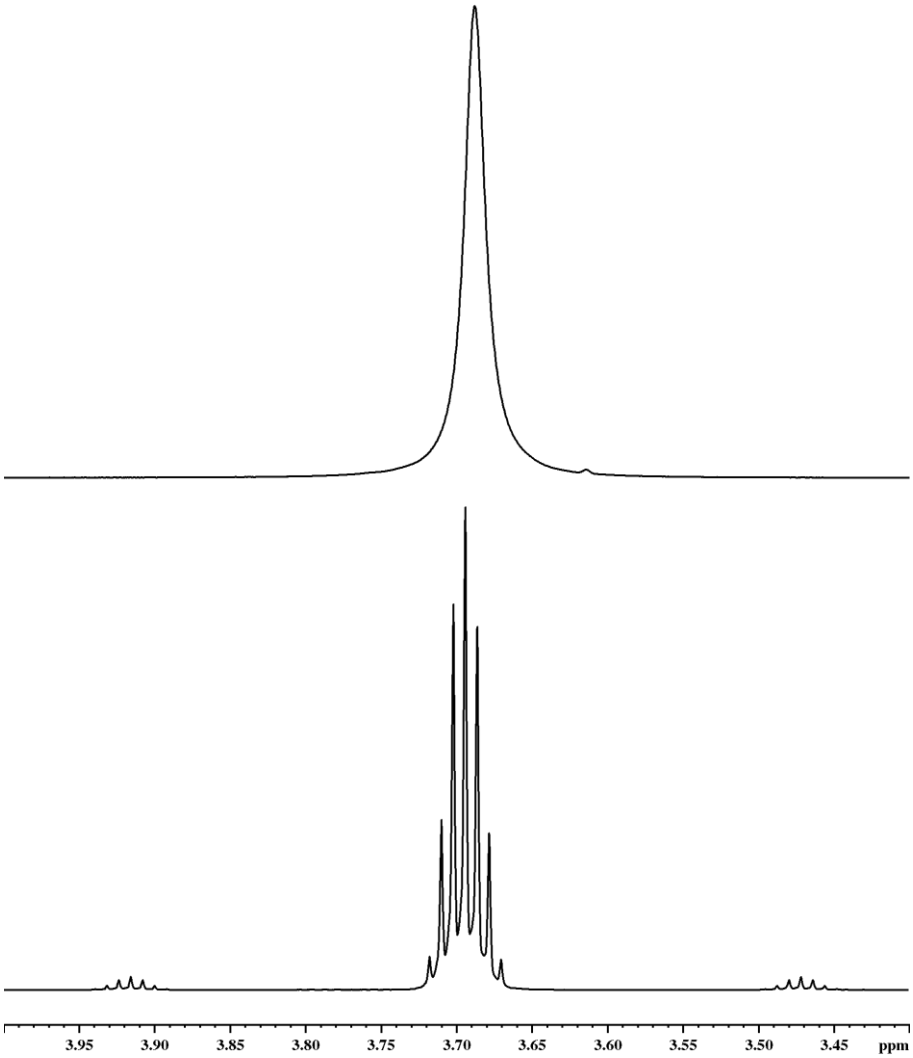


Figure S 86 ^{1}H NMR (*o*DFB, 298 K) signal of the H–Si hydrogen atom in $HSiEt_3$ (bottom; 400.17 MHz) and in a $HSiEt_3$/**1** (4.0 : 1.0) mixture in *o*DFB (top; 300.18 MHz).

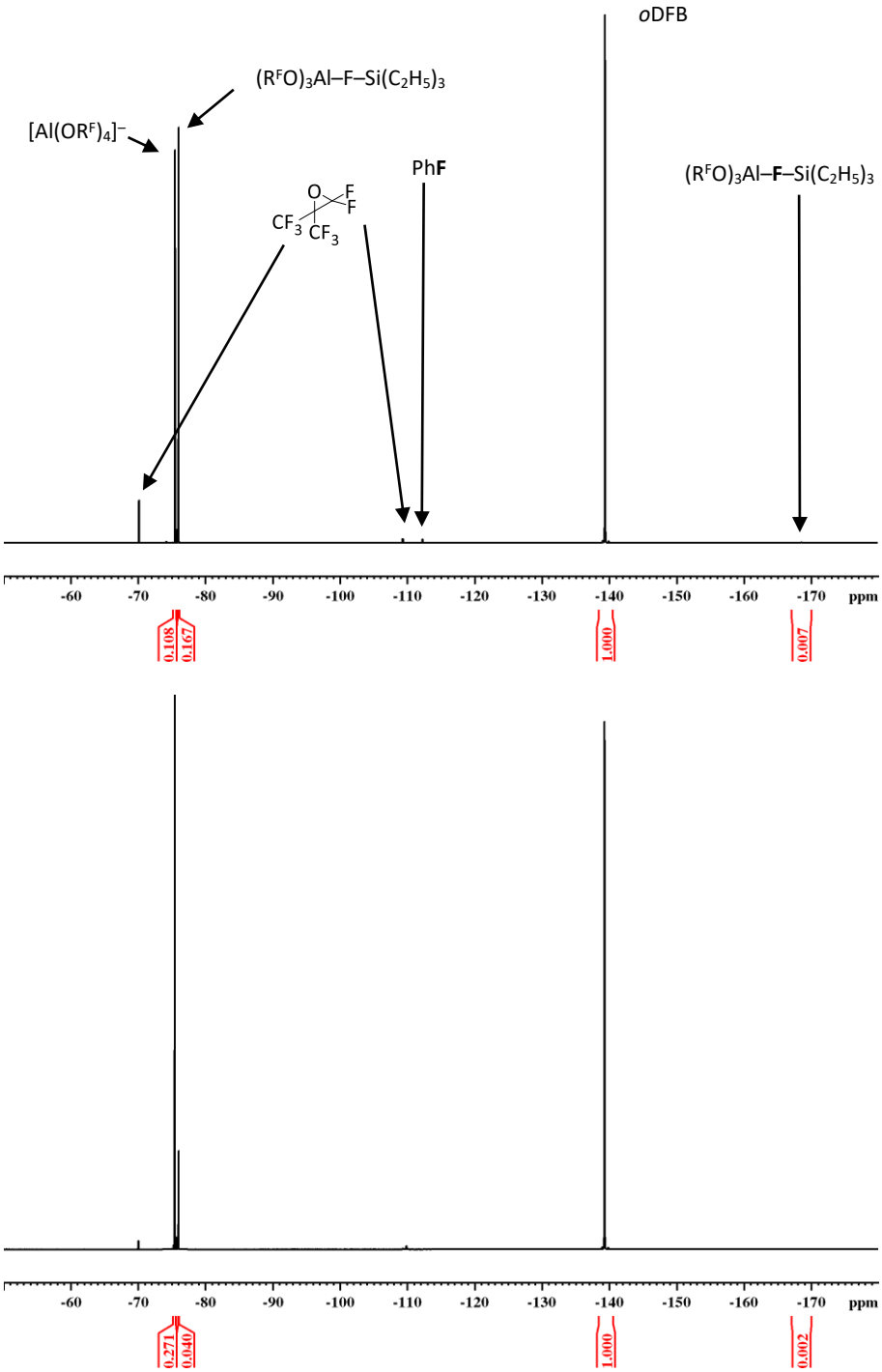


Figure S 87 ^{19}F NMR spectra (282.45 MHz, *o*DFB, 298 K) of a $HSiEt_3$/**1** (4.0 : 1.0) mixture, 2 h at and 12 h after mixing the components. Signal intensities are normalized to the *o*DFB signal.

2.3.3 $HSiMe_3$ + NO[*pf*] (4.9 : 1.0)

NO[*pf*] (85.2 mg, 85 µmol, 1.0 eq.) was added to a solution of $HSiMe_3$ in *o*DFB (0.6 M, 0.70 ml, 0.42 mmol, 4.9 eq.) at rt in a Young-valve NMR tube. The reaction solution immediately became green and foaming of the reaction mixture was observed.

^{1}H NMR [300.18 MHz, *o*DFB, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K]: δ = 8.47 (unknown species), 4.77 (N**H**$_x$ groups), 4.51 (s, 2 H, **H**$_2$), 4.00 (dec, 1 H, $(H_3C)_3Si$–**H,** $^3J_{SiH,CH}$ = 3.6 Hz), 3.78 (sept, 2 H, $(H_3C)_2Si$**H**$_2$, $^3J_{SiH,CH}$ = 4.2 Hz), 3.70 (s, 1 H, **H**OC$(CF_3)_3$), 3.24 (unknown species), 0.71 (unknown species), 0.56 (d, 9 H, $(\mathbf{H}_3C)_3Si$–F–Al$[OC(CF_3)_3]_3$, $^3J_{H,F}$ = 13 Hz), 0.36 (s, 9 H, $(\mathbf{H}_3C)_3SiCl$), 0.18 (unknown species), 0.06 (t, 6 H, $(\mathbf{H}_3C)_2SiH_2$, $^3J_{CH,SiH}$ = 4.2 Hz), 0.04 (d, 9 H, $(\mathbf{H}_3C)_3Si$–H, $^3J_{CH,SiH}$ = 3.6 Hz), 0.00 (s, 12 H, $(\mathbf{H}_3C)_4Si$) ppm.

^{19}F NMR [282.45 MHz, *o*DFB, 298 K]: δ = –70.1 (m_c, 6 F, OC(C**F**$_3)_2CF_2$), –75.2 (s, 9 F, HOC(C**F**$_3)_3$), –75.4 (s, 36 F, $[Al(OC(C\mathbf{F}_3)_3)_4]^-$), –76.1 (s, 27 F, $(H_3C)_3Si$–F–Al$[OC(C\mathbf{F}_3)_3]_3$, –109.3 (m_c, 2 F, $OC(CF_3)_2C\mathbf{F}_2$), –139.5 (m_c, 2F, *o*$C_6\mathbf{F}_2H_4$), –156.5 (dec, 1 F, $(H_3C)_3Si$–**F**–Al$[OC(CF_3)_3]_3$, $^3J_{\mathbf{F},H}$ = 13 Hz, $^1J_{F,Si}$ = 284 Hz) ppm.

^{27}Al NMR [78.22 MHz, *o*DFB, 298 K]: δ = 35.0 (s, 1 Al, $[\mathbf{Al}(OC(CF_3)_3)_4]^-$) ppm.

^{29}Si NMR [59.64 MHz, *o*DFB, 298 K]: δ = 78.8 (d, 1 Si, $(H_3C)_3\mathbf{Si}$–F–Al$[OC(CF_3)_3]_3$, $^1J_{Si,F}$ = 288 Hz), 46.1 (unknown species), 37.6 (unknown species), 31.2 (unknown species), 0.0 (1 Si, $(H_3C)_4\mathbf{Si}$), –16.2 (1 Si, $(H_3C)_3\mathbf{Si}$H), –18.8 (unknown species), –38.1 (1 Si, $(H_3C)_2\mathbf{Si}H_2$) ppm.

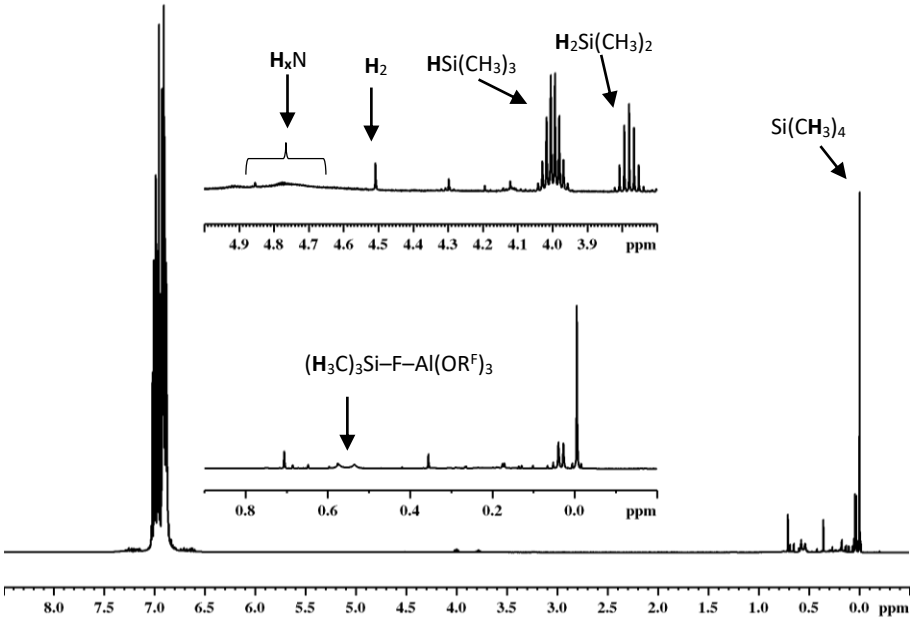


Figure S 88 ^{1}H NMR spectrum (300.18 MHz, *o*DFB, 298 K) of a $HSiMe_3$/NO[*pf*] (4.9 : 1.0) mixture, 7 d after mixing the components (spectrum calibrated to δ (*o*$C_6F_2\mathbf{H}_4$) = 6.96 ppm).

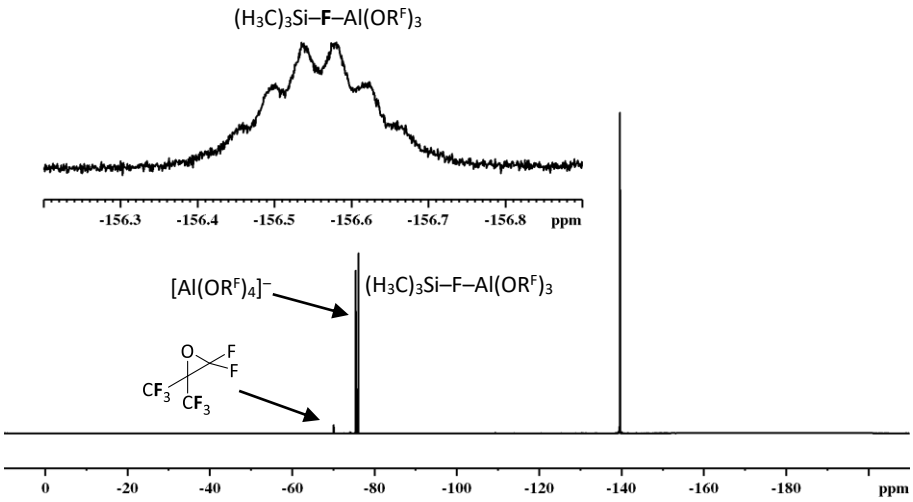


Figure S 89 ^{19}F NMR spectrum (282.45 MHz, *o*DFB, 298 K) of a $HSiMe_3$/NO[*pf*] (4.9 : 1.0) mixture, 7 d after mixing the components.

2.3.4 $HSiMe_3$ + Ag[*pf*] (4.6 : 1.0)

Ag[*pf*] (98.3 mg, 91 µmol, 1.0 eq.) was added to a solution of $HSiMe_3$ in *o*DFB (0.6 M, 0.70 ml, 0.420 mmol, 4.6 eq.) at rt in a Young-valve NMR tube. Gas evolution was observed, but less pronounced than with NO[*pf*].

^{1}H NMR [400.17 MHz, *o*DFB, calibrated to δ (*o*DFB) = 6.96 ppm, 298 K]: δ = 4.52 (s, 2 H, **H**$_2$), 3.98 (br, 1 H, $(H_3C)_3Si$–**H**), 3.79 (br, 2 H, $(H_3C)_2Si$**H**$_2$), 0.61 (br, 9 H, (**H**$_3$C)$_3$Si–F–Al[OC(CF$_3$)$_3$]$_3$, 0.36 (br, 9 H, (**H**$_3$C)$_3$SiCl), 0.06 (br, (**H**$_3$C)$_3$Si–H and (**H**$_3$C)$_2$SiH$_2$), 0.00 (br, 12 H, (**H**$_3$C)$_4$Si) ppm.

^{19}F NMR [376.54 MHz, *o*DFB, 298 K]: δ = –70.1 (m$_c$, 6 F, OC(C**F**$_3$)$_2$CF$_2$), –75.4 (s, 36 F, [Al(OC(C**F**$_3$)$_3$)$_4$]$^-$), –76.1 (s, 27 F, $(H_3C)_3Si$–F–Al[OC(C**F**$_3$)$_3$]$_3$), –109.4 (m$_c$, 2 F, OC(CF$_3$)$_2$C**F**$_2$), –139.5 (m$_c$, 2F, *o*C$_6$**F**$_2$H$_4$), –156.5 (br, 1 F, $(H_3C)_3Si$–**F**–Al[OC(CF$_3$)$_3$]$_3$ ppm.

^{27}Al NMR [104.27 MHz, *o*DFB, 298 K]: δ = 34.9 (s, 1 Al, [**Al**(OC(CF$_3$)$_3$)$_4$]$^-$) ppm.

Due to immediate formation of a metallic mirror and of a metallic precipitate, most likely due to formation of elemental silver, the signal splittings are less resolved than in the spectra of the $HSiMe_3$/NO[*pf*] mixture. Thus, no 2D spectra were recorded.

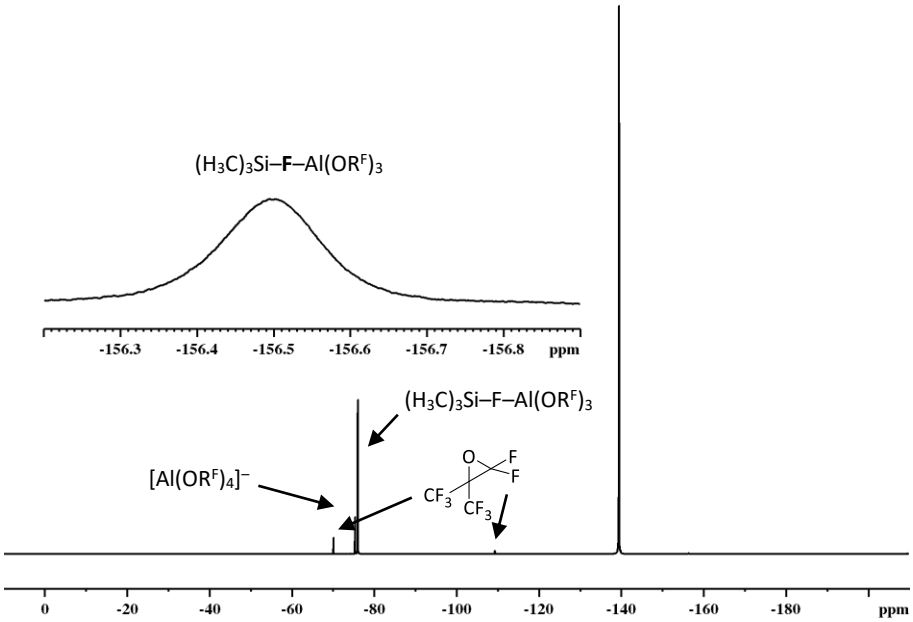


Figure S 90 ^{19}F NMR spectrum (376.54 MHz, *o*DFB, 298 K) of a $HSiMe_3$/Ag[*pf*] (4.6 : 1.0) mixture, 1 h after mixing the components.

3 Detection of H_2 and Formation of Elemental Gallium

3.1 Gas Chromatography

The components (**1**: ca. 34 µmol; $HSiMe_3$: 5.8 eq.; $HSiEt_3$: 22.1 eq.; total volume of the mixtures in *o*DFB: ca. 0.6 ml) were mixed inside a nitrogen filled glovebox (accounting for the intense N_2 signal in every gas chromatogram) in an injection vial equipped with a teflon septum (see **Figure S 91**). The last component was added outside the glovebox *via* the teflon septum, immediately before beginning with the gas chromatographic analysis. For every measurement, 150 µL of the gas space above the reaction solution was collected.

Figure S 91 Solutions of **1** and $HSiEt_3$ (left) and of **1**, hexene and $HSiEt_3$ (right) in *o*DFB. For gas chromatography measurements, the gas space above the reaction solution was analyzed.

Exemplary gas chromatograms (solutions of **1**/$HSiEt_3$ and **1**/1-hexene/$HSiEt_3$) are shown in **Figure S 92** and **Figure S 93**. Calibration with hydrogen gas reveals that, under the chosen conditions, H_2 is detected 1.5–2 min after the gas injection (**Figure S 94**).

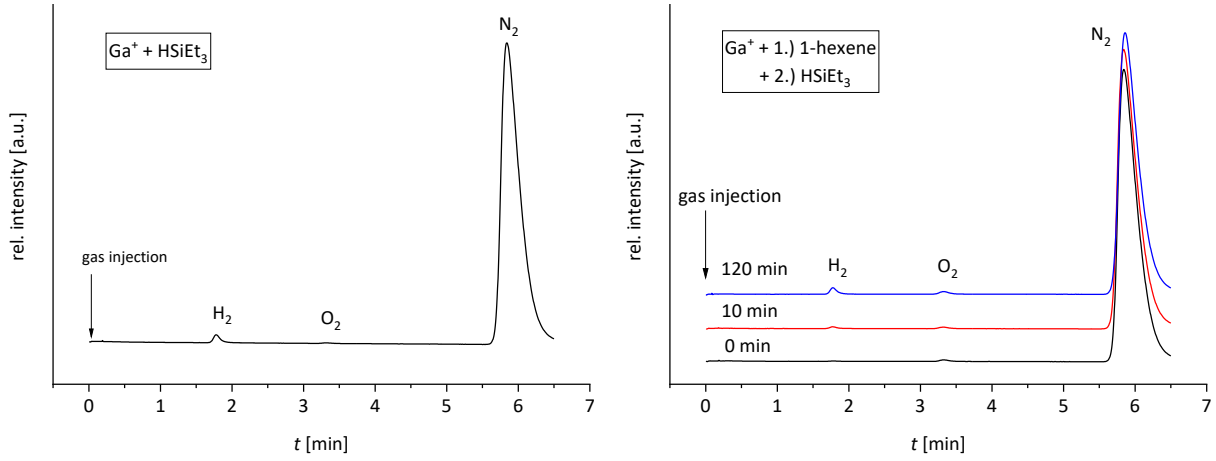


Figure S 92 Gas chromatograms of the gas space above the reaction solutions of **1** and $HSiEt_3$ (0.05 : 1.0; left) and of **1**, hexene and $HSiEt_3$ (0.05 : 0.2 : 1.0; right) in *o*DFB.

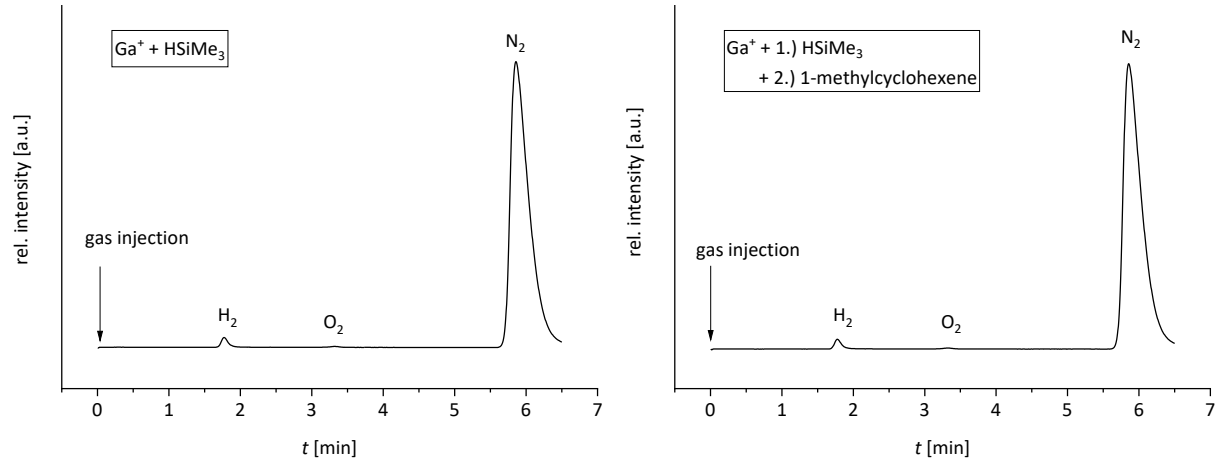


Figure S 93 Gas chromatograms of the gas space above the reaction solutions of **1** and $HSiMe_3$ (0.17 : 1.0; left) and of **1**, 1-methylcyclohexene and $HSiMe_3$ (0.17 : 0.9 : 1.0; right) in *o*DFB.

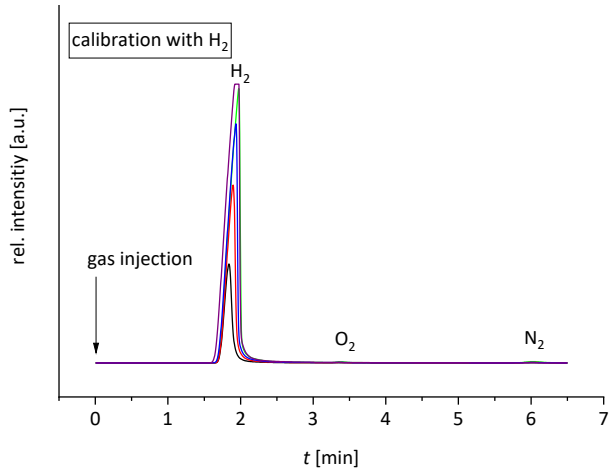


Figure S 94 Gas chromatograms of H_2. Different volumes of H_2 were collected (black: 50 µL; red: 100 µL; blue: 150 µL, green: 200 µL, purple: 250 µL).

3.2 Cyclic Voltammetry Measurements

The measurements were performed with a solution of **1** (5 mM) in *o*DFB, [NBu_4][*pf*] (0.1 M) as supporting electrolyte and [Fc][*pf*] (5 mM) as internal reference. The cyclic voltammograms of **1**, collected with different scan rates and both with and without addition of [Fc][*pf*], are shown in **Figure S 95**.

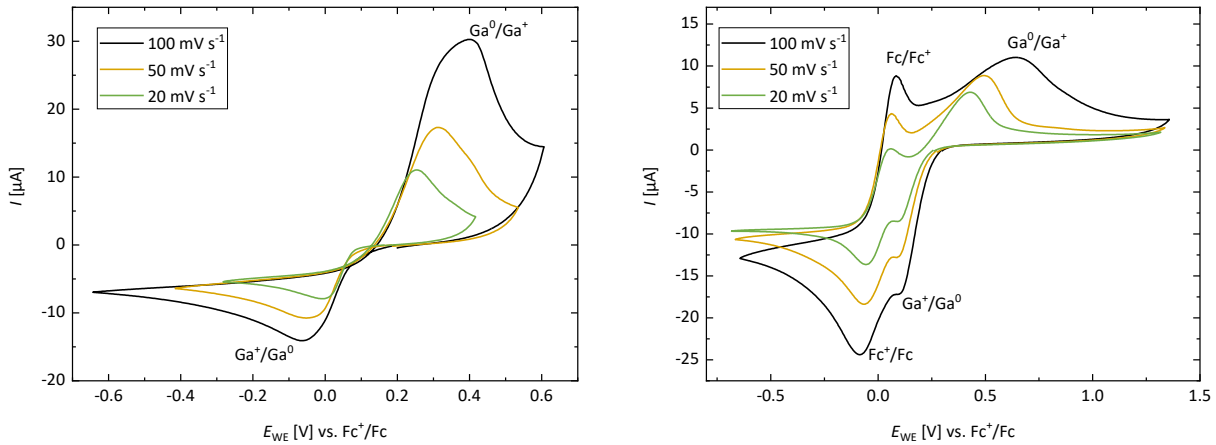


Figure S 95 Cyclic voltammograms of a solution of **1** (5 mM) in *o*DFB (left) and of **1** and [Fc][*pf*] (5 mM, respectively) in *o*DFB (right) with different scan rates at rt (conducting salt: [NBu_4][*pf*] (0.1 M); reference electrode: quasi-platinum electrode (q-Pt)).

The results are summarized in **Table S 1**.

Table S 1 Half wave potential $E_{1/2}$ vs. Fc^+/Fc and the anodic peak current I_{ac} obtained by cyclic voltammetry of **1** in *o*DFB at different scan rates υ.

υ [mV s^{-1}]	**$E_{1/2}$ [V]**	**I_{ac} [µA]**
20	0.26	6.87
50	0.29	8.87
100	0.37	11.03

As the peak potentials vary with the scan rate, the reaction is most likely not electrochemically reversible.

The potential window of *o*DFB is shown in **Figure S 96**. Additionally, the cyclic voltammogram in **Figure S 96** shows that, in *o*DFB, Ga^+ cannot be oxidized to Ga^{3+} electrochemically. The rapidly increasing current indicates solvent decomposition.

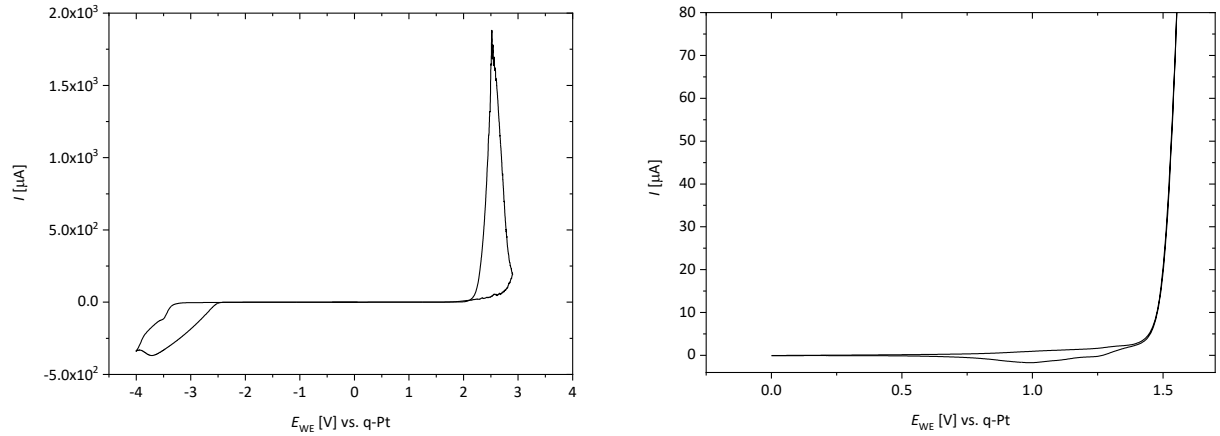


Figure S 96 Potential window of *o*DFB (left) and cyclic voltammogram of a solution of **1** (0.005 M) in *o*DFB (right) at rt (conducting salt: [NBu_4][*pf*] (0.1 M); reference electrode: quasi-platinum electrode (q-Pt); scan rate: 20 mV s^{-1} and 100 mV s^{-1}, respectively).

3.3 STEM and EDX

3.3.1 Residue of Hydrosilylation Reaction

$HSiMe_2Et$ (0.21 ml, 0.14 g, 1.6 mmol, 2.2 eq.), 1-hexene (90 µl, 60 mg, 0.72 mmol, 1.0 eq.) and **1** (80 mg, 71 µmol, 0.1 eq.) were mixed in *o*DFB (0.6 ml). NMR spectra revealed that, after 3 d, the olefin was completely consumed. The solid residue was dried at 60 °C and subsequently analyzed by high-angle annular dark-field imaging (HAADF) and scanning transmission electron microscopy (STEM) in high vacuum at –170 °C.

STEM analysis of the residue reveals the presence of Ga-rich particles (**Figure S 97**).

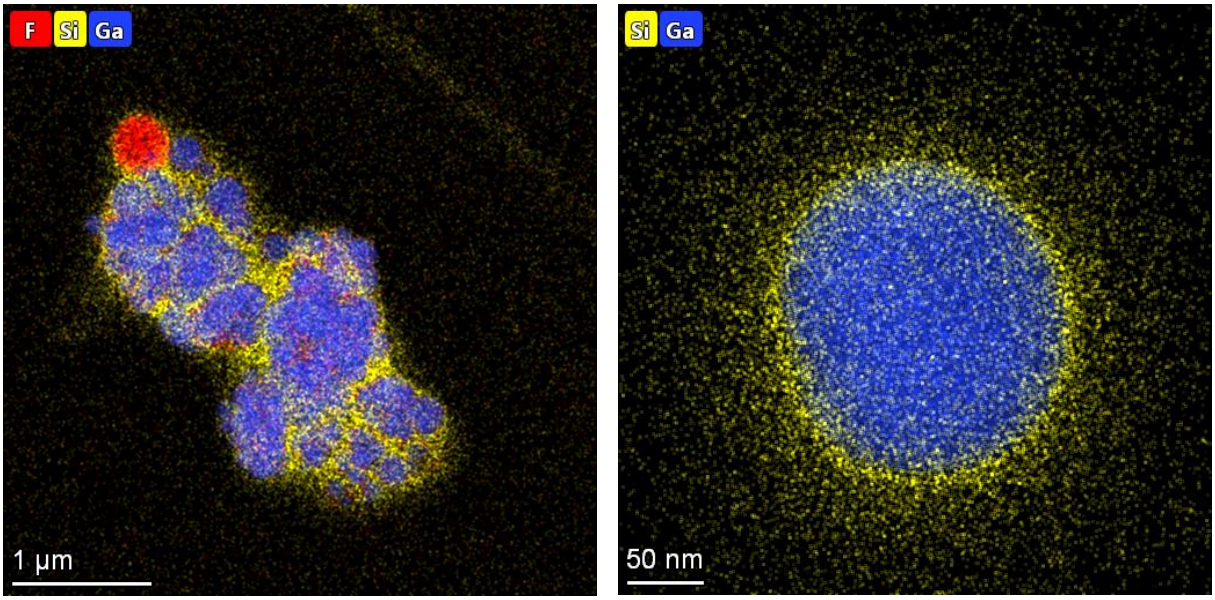


Figure S 97 STEM element mapping (left: fluorine + silicon + gallium; right: silicon + Ga) of the residue of the $HSiMe_2Et$/1-hexene/**1** (2.2 : 1.0 : 0.1) reaction mixture for the bulk sample (left) and for a Ga particle (right). The sample was not kept under inert conditions after completion of the reaction.

The Ga-rich particles are embedded in a Ga-poor matrix rich of oxygen and silicon. This is confirmed by a weight percent line scan for the elements oxygen, silicon and gallium (**Figure S 98**), an EDX spectrum (**Figure S 99**) and STEM element maps (**Figure S 100**). Besides this, **Figure S 100** shows the presence of a F-rich area, probably due to traces of non-vaporized *o*DFB. A transmission electron microscopy (TEM) image of Ga particles is shown in **Figure S 101**. In the TEM picture, the Si/O shell is visible as a bright halo around the Ga particle).

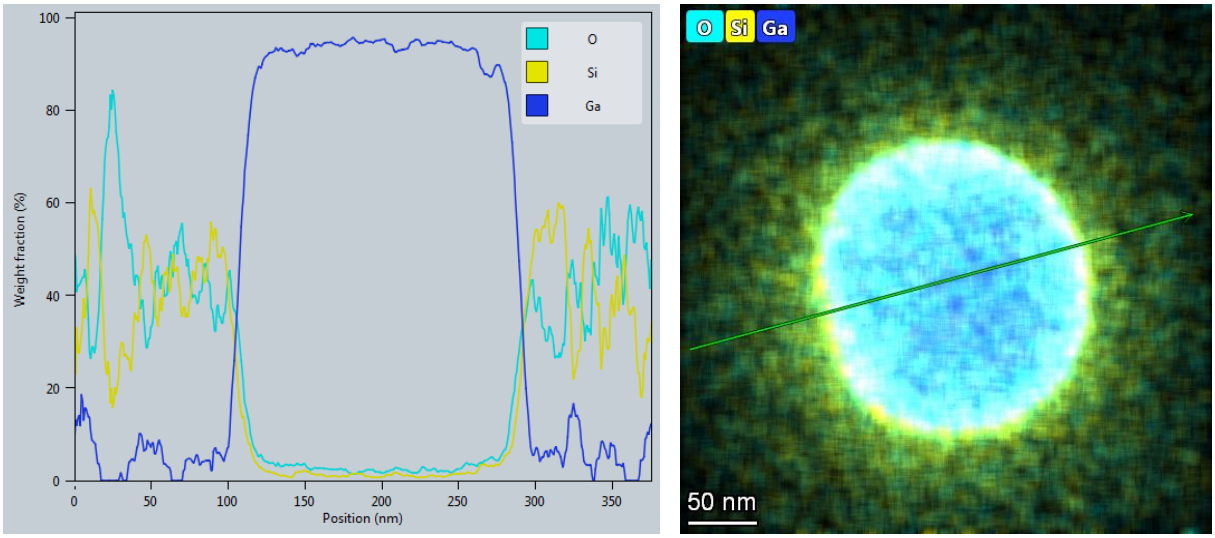


Figure S 98 Weight percent line scan for the elements oxygen, silicon gallium (left) along a defined path (right) of the residue of the $HSiMe_2Et$/1-hexene/**1** (2.2 : 1.0 : 0.1) reaction mixture. The same path was scanned for the EDX line scan depicted in **Figure 4**.

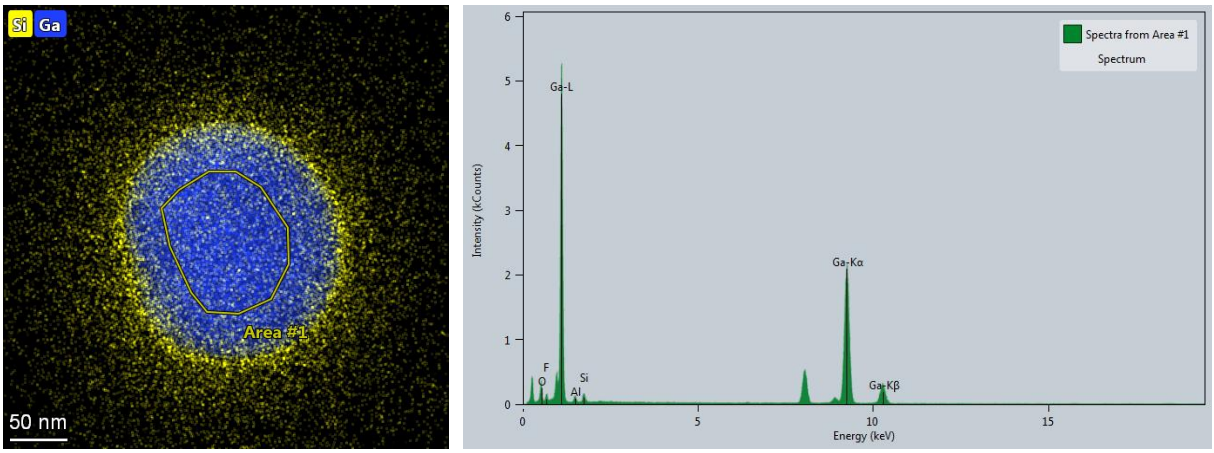


Figure S 99 EDX spectrum (right) of a defined sample area (left) of the residue of the $HSiMe_2Et$/1-hexene/**1** (2.2 : 1.0 : 0.1) reaction mixture.

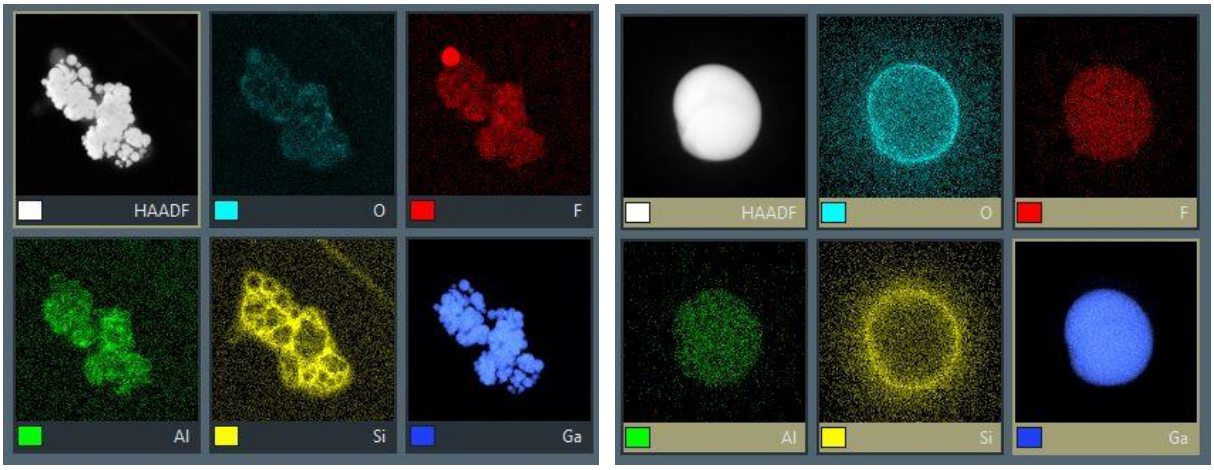


Figure S 100 HAADF images and STEM element maps (oxygen, fluorine, aluminium, silicon and gallium) of the area associated with the dark-field image of the residue of the $HSiMe_2Et$/1-hexene/**1** (2.2 : 1.0 : 0.1) reaction mixture for the bulk sample (left) and for a gallium particle (right).

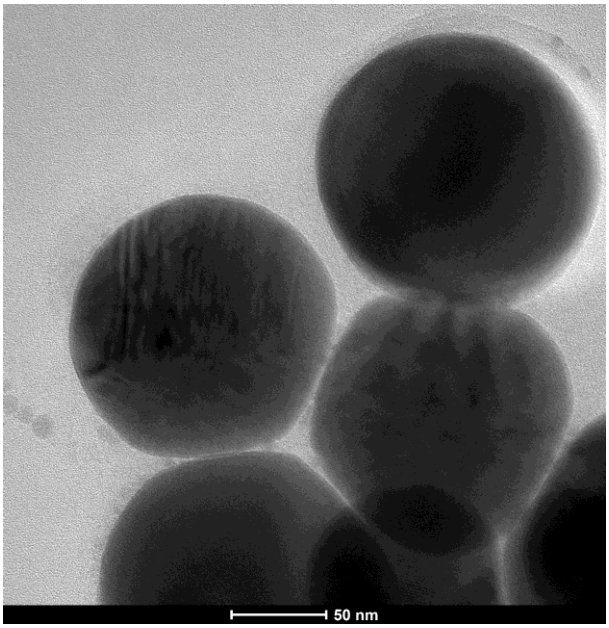


Figure S 101 TEM image of Ga-rich particles in the residue of the $HSiMe_2Et$/1-hexene/**1** (2.2 : 1.0 : 0.1) reaction mixture.

3.3.2 Residue of Hydrodefluorination Reaction

$HSiEt_3$ (100 µl, 73 mg, 0.63 mmol, 1.5 eq.), 1-fluorobutane (40 µl, 31 mg, 0.41 mmol, 1.0 eq.) and **1** (87 mM in *o*DFB, 0.2 ml, 17.4 µmol, 0.04 eq.) were mixed in *o*DFB (0.32 ml). NMR studies revealed complete reaction after 3 d at rt. The solid residue was dried at 60 °C and subsequently analyzed by HAADF and STEM in high vacuum at -170 °C. A HAADF image and STEM element maps are shown in **Figure S 102**. The higher fluorine content compared to the sample analyzed in section 3.3.1 is due to the formation of $FSiEt_3$ and *s*-butylated *o*DFB derivates. The Ga-rich particles are somewhat smaller than in the residue of the hydrosilylation

reaction discussed in the previous section, probably due to the lower catalyst loading and the lower substrate concentrations.

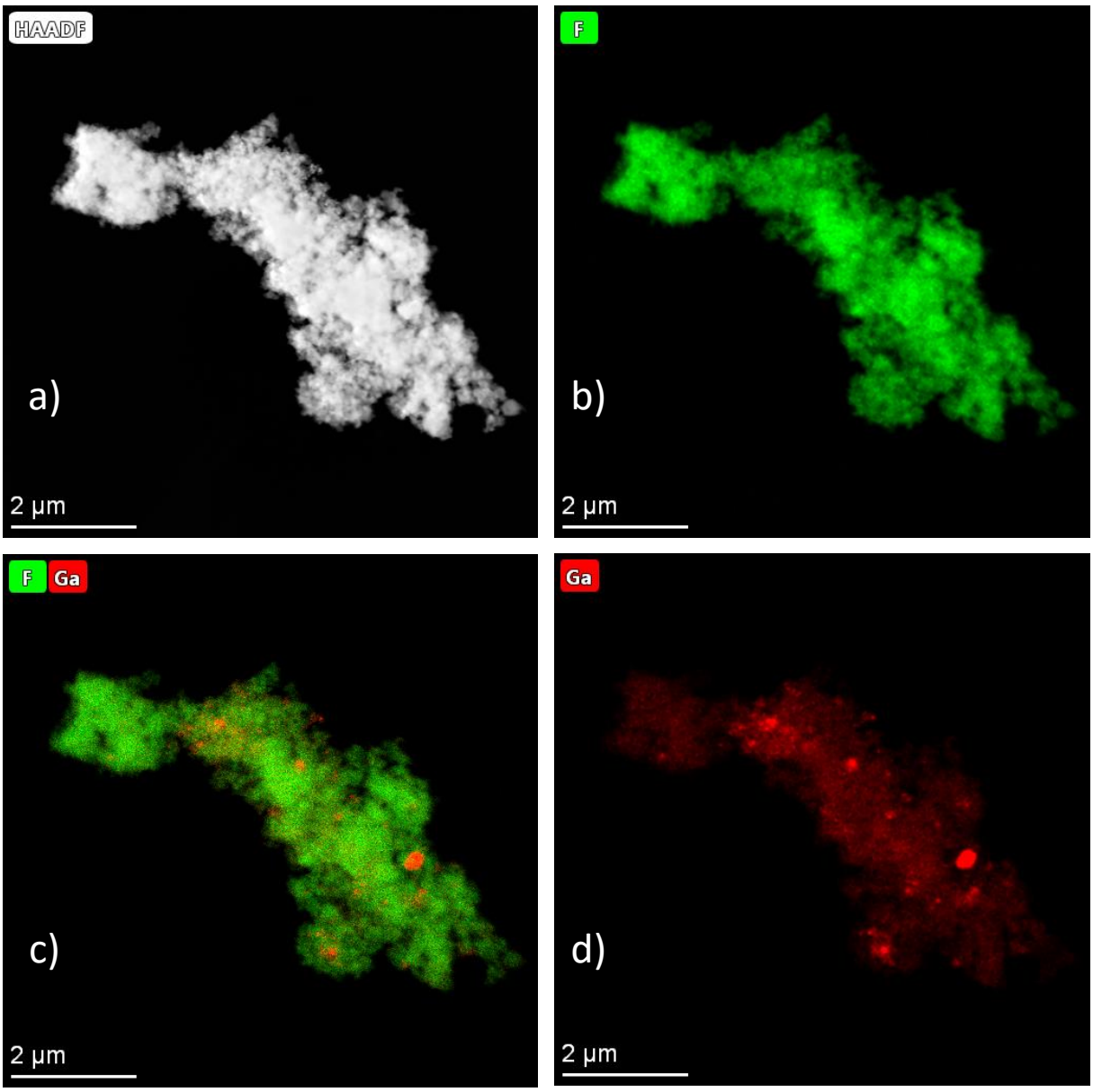


Figure S 102 HAADF image (a) and STEM element maps (b: fluorine, c: fluorine + gallium, d: gallium) associated with the dark-field image of the residue of the $HSiEt_3$/F–^{n}Bu/**1** (1.5 : 1.0 : 0.04) reaction mixture. The sample was not kept under inert conditions after completion of the reaction.

Again, gallium is not evenly distributed over the sample. Instead, the gallium content is especially high where the fluorine content is comparatively low. This is well-illustrated by the line scan in **Figure S 103**. This strongly implies that gallium is not present as Ga^+ or Ga^{3+} ions, since this would require close proximity of $[pf]^-$ anions, but rather as small Ga^0 nanoparticles. These nanoparticles are especially well recognizable in the Ga element map (**Figure S 102**, d).

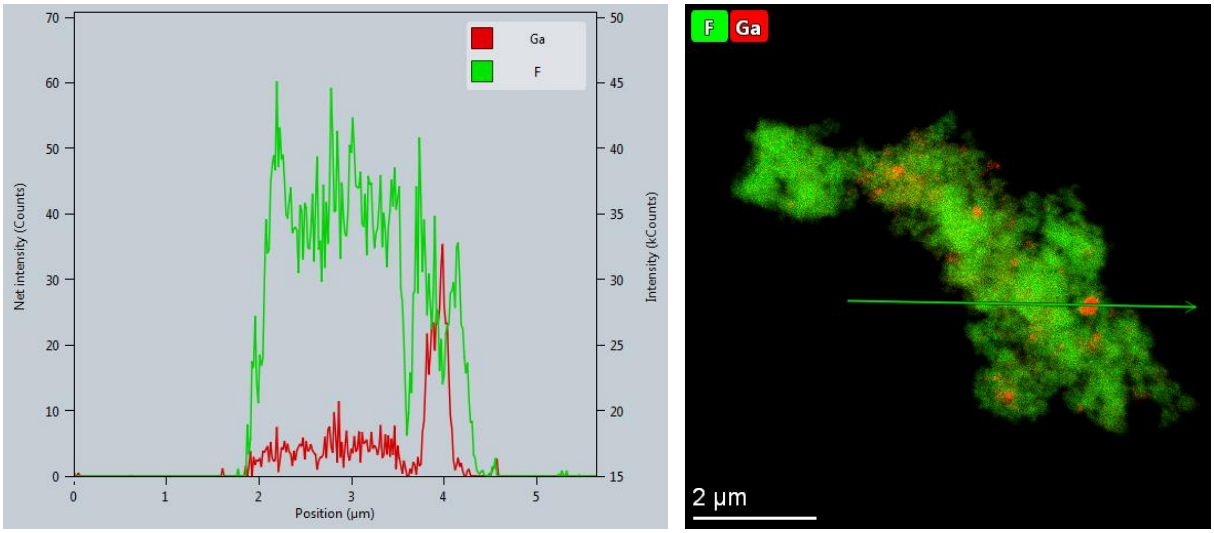


Figure S 103 EDX line scan for the elements fluorine and gallium (left) along a defined path (right) of the residue of the $HSiEt_3$/F–^{n}Bu/**1** (1.5 : 1.0 : 0.04) reaction mixture.

4 Single Crystal X-Ray Diffraction Data

Crystals of $Et_3Si–F–[Al(OR^F)_3]$ were obtained from a concentrated solution of $HSiEt_3$ (60 µl, 44 mg, 0.38 mmol, 4.3 eq.) and **1** in *o*DFB (1.47 M, 60 µl, 88 µmol, 4.3 eq.) at –25 °C. The molecular structure of $Et_3Si–F–[Al(OR^F)_3]$ is shown in **Figure S 104**, including a minor disorder.

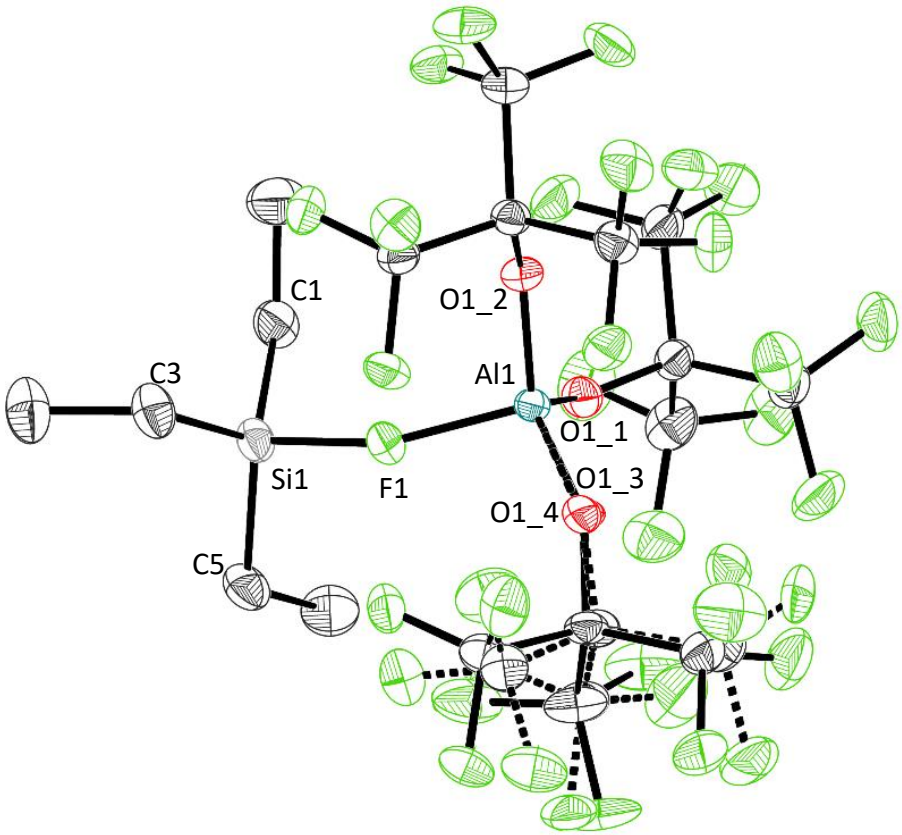


Figure S 104 Molecular structure of $Et_3Si–F–Al(OR^F)_3$. Thermal ellipsoids are shown at the 50% probability level. Disorder is shown. Hydrogen atoms are omitted.

Table S 2 Crystal data and summary of the data collection and refinement for $(H_5C_2)_3Si–F–Al[OC(CF_3)_3]_3$.

CCDC number	2024333
Empirical formula	$C_{18}H_{15}AlF_{28}O_3Si$
Formula weight	866.37
Temperature [K]	100(2)
Crystal system	monoclinic
Space group (number)	$P2_1/n$ (14)
a [Å]	9.757(5)
b [Å]	17.585(10)
c [Å]	17.518(9)
α [°]	90
β [°]	90.187(8)
γ [°]	90
Volume [Å^3]	3006(3)
Z	4
ρ_{calc} [gcm^{-3}]	1.914
μ [mm^{-1}]	0.305
F(000)	1704
Crystal size [mm^3]	0.20×0.19×0.19
Crystal colour	colourless
Crystal shape	block
Radiation	MoK_α (λ = 0.71073 Å)
2Θ range [°]	3.28 to 49.60 (0.85 Å)
Index ranges	-11 ≤ h ≤ 11 -20 ≤ k ≤ 20 -20 ≤ l ≤ 20
Reflections collected	67382
Independent reflections	5180 R_{int} = 0.1070 R_{sigma} = 0.0420
Completeness to Θ = 24.800°	99.8 %
Data / Restraints / Parameters	5180/3138/590
Goodness-of-fit on F^2	1.034
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0366 wR_2 = 0.0919
Final R indexes [all data]	R_1 = 0.0524 wR_2 = 0.1017
Largest peak/hole [eÅ^{-3}]	0.64/-0.40

Table S 3 Selected bond lengths in $(H_5C_2)_3Si–F–Al[OC(CF_3)_3]_3$.

Atom–Atom	Bond Length [pm]
Al1–O1_1	170.80(19)
Al1–O1_2	169.92(18)
Al1–O1_3	169.2(5)
Al1–O1_4	171(3)
Al1–F1	178.82(16)
F1–Si1	173.18(17)
Si1–C1	183.5(3)
Si1–C3	184.5(3)
Si1–C5	184.3(3)

Table S 4 Selected bond angles in $(H_5C_2)_3Si–F–Al[OC(CF_3)_3]_3$.

Atom–Atom–Atom	Angle [°]
O1_3–Al1–O1_2	115.3(3)
O1_3–Al1–O1_1	117.3(3)
O1_2–Al1–O1_1	113.52(9)
O1_2–Al1–O1_4	114.3(15)
O1_1–Al1–O1_4	118.9(15)
Si1–F1–Al1	157.67(9)
C1–Si1–C5	114.44(14)
C1–Si1–C3	116.80(14)
C5–Si1–C3	115.20(14)

5 Photographs

5.1 Mixture of Fc and 1 in *o*DFB

Figure S 105 Solution of Fc in *o*DFB before (left) and after addition of 1.0 eq. of **1** (right).

5.2 Ga^0 Formation and H_2 Evolution in Hydrosilylation Reactions

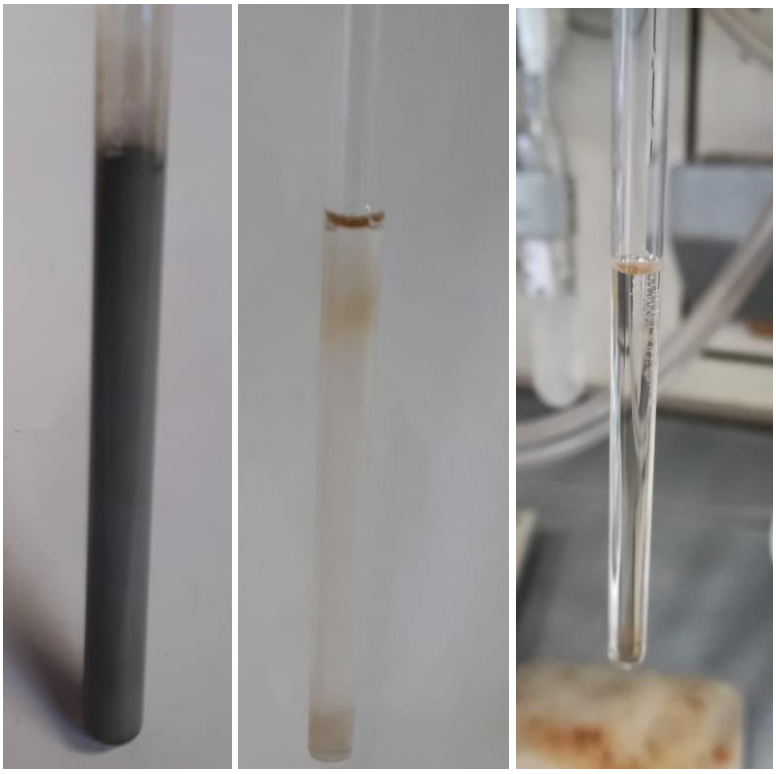


Figure S 106 Metallic mirror formed inside an NMR tube upon mixing **1** and $HSiMe_3$ (1.0 : 4.8) in *o*DFB (left), metallic clouding in a $HSiMe_3$/1-methylcyclohexene/**1** (1.0 : 1.0 : 0.1) mixture in *o*DFB (middle) and gas evolution in the same mixture (right).

6 Quantum Chemical Calculations

6.1 General Remarks

Unless stated otherwise, quantum chemical calculations were performed with *Turbomole* (version 7.2 or 7.5).[16,17–21] Structures were optimized using density functional theory (DFT),[17] internal coordinates, resolution of identity-approximation (RI),[22,23] D3(BJ)-dispersion correction[24] and a fine integration gridsize (gridsize = m5). Calculations were performed on RI-B3LYP[25](D3BJ)/def2-TZVPP[26] or RI-BP86[18–20](D3BJ)/def2-TZVPP level of theory. Thermal and entropic contributions to the Gibbs energy were calculated without scaling factor at standard conditions (298.15 K, 0.1 MPa) with the FREEH module. Every species presented herein was checked in terms of reasonable geometry and electronic occupation with the EIGER module. Vibrational analyses were performed with the AOFORCE module, in order to detect imaginary frequencies.[21] To counteract imaginary frequencies, the convergence criteria for geometry optimization were modified from the default 10^{-7} H (energy) and 10^{-4} a.u. (gradient) to 10^{-8} H und 10^{-5} a.u., respectively.

For each molecular species, the standard enthalpy $H°$ at 298.15 K and 0.1 MPa was calculated from the electronic SCF energy E_{SCF} and the sum of translational, rotational, and vibrational energy including zero-point energy E_{vrt} (FREEH energy) using the following equation:

$$H° = E_{SCF} + E_{vrt} + R \cdot T \qquad \text{equation 1}$$

E_{SCF}: electronic SCF energy
E_{vrt}: sum of translational, rotational, and vibrational energy including zero-point energy
R: universal gas constant (ca. 8.314 J K^{-1} mol^{-1})
T: temperature in Kelvin (298.15 K)

The Gibbs free energy $G°$ follows from the standard enthalpy $H°$ and the standard entropy $S°$:

$$G° = H° - S° \cdot T \qquad \text{equation 2}$$

Coupled Cluster (CC) calculations were performed as single point calculations on the optimized RI-B3LYP(D3BJ)/def2-TZVPP structures with a double zeta (DZ) basis set and extrapolation of the correlation energy with MP2 calculations from DZ to quadruple zeta (QZ) basis set [CCSD(T)/DZ→QZ].[27] The basis sets aug-cc-pVXZ- (H, C and F), aug-cc-pV(X+d)Z- (Si) and aug-cc-pVXZ-PP (Ga) (X = D/Q) were

employed.[28] For Ga, a relativistic effective core potential (ecp) was used (defpp-ecp).[29] The values on CCSD(T)/DZ→QZ level were calculated according to the following equation:

$$E[\text{CCSD(T)/DZ}\rightarrow\text{QZ}] = E[\text{CCSD(T)/DZ}] + E[\text{MP2/QZ}] - E[\text{MP2/DZ}] \qquad \text{equation 3}$$

The results of the vibrational analysis were taken from the RI-B3LYP(D3BJ)/def2-TZVPP gas phase calculations.

Solvation effects were incorporated using the conductor like screening modell (COSMO)[30] for *o*DFB as the solvent. A dielectric constant of 13.38 at 298 K was assumed for this solvent.[31] Single point calculations were performed on the optimized gas phase structures and the results from the vibrational analysis were taken from the respective gas phase calculations.

In order to find transition state structures, relaxed potential energy surface scans along selected bond lengths or bond angles were performed with *Orca* (version 4.2.1)[32] on the RI-BP86(D3BJ)/def2-SVP[23,26] level of theory. The geometry of the most energy-rich species was chosen as the start geometry for the transition state structure search in *Turbomole* on the RI-BP86(D3BJ)/def2-TZVPP and RI-B3LYP(D3BJ)/def2-TZVPP level of theory. The transition states thus obtained display one imaginary frequency and were distorted along the reaction coordinate to make sure that the transition state describes the desired transformation.

6.2 Calculated Thermodynamics and Kinetics

6.2.1 Activation Barriers in a Hypothetical Ga^+-Centered Chalk-Harrod Mechanism

Table S 5 Activation barriers for the key steps in the hypothetical Ga^+-centered Chalk-Harrod mechanism.

Level of Theory	$\Delta G^{\neq}$ ($\Delta H^{\neq}$) oxidative addition [kJ mol^{-1}]	$\Delta G^{\neq}$ ($\Delta H^{\neq}$) hydrometalation [kJ mol^{-1}]	$\Delta G^{\neq}$ ($\Delta H^{\neq}$) reductive elimination [kJ mol^{-1}]
RI-BP86(D3BJ)/def2-TZVPP	211.13 (208.69)	58.09 (55.44)	155.75 (148.85)
RI-BP86(D3BJ)/def2-TZVPP (COSMO)[b]	211.82 (209.38)	60.75 (58.10)	166.10 (159.20)
RI-B3LYP(D3BJ)/def2-TZVPP	228.95 (229.32)	- (-)[a]	179.44 (172.30)
CCSD(T)/DZ → QZ	215.12 (215.49)	- (-)[a]	169.55 (162.41)

a) No transition state was found. b) Reactions in *o*DFB (ε_r = 13.38).

6.2.2 Thermodynamics of the Redoxreaction between $[Ga(oDFB)_2]^+$ and $HSiMe_3$ in *o*DFB

Table S 6 Calculated reaction enthalpies and free Gibbs energies for the postulated redox reaction between $[Ga(oDFB)_2]^+$ and $HSiMe_3$ in *o*DFB (ε_r = 13.38).

Reaction	RI-BP86(D3BJ)/def2-TZVPP		RI-B3LYP(D3BJ)/def2-TZVPP	
	$\Delta_r H°$ [kJ mol^{-1}]	$\Delta_r G°$ [kJ mol^{-1}]	$\Delta_r H°$ [kJ mol^{-1}]	$\Delta_r G°$ [kJ mol^{-1}]
$[Ga(oDFB)_2]^+_{(solv)} \rightarrow [Ga(oDFB)]^+_{(solv)} + oDFB_{(solv)}$	44.60	4.34	33.41	–4.62
$[Ga(oDFB)]^+_{(solv)} + 2\ HSiMe_{3(solv)} \rightarrow [Ga(oDFB)(HSiMe_3)_2]^+_{(solv)}$	–70.22	5.55	–52.00	22.74
$[Ga(oDFB)(HSiMe_3)_2]^+_{(solv)} \rightarrow [Ga(oDFB)]^0_{(solv)} + [Me_3Si–H–SiMe_3]^+_{(solv)} + 0.5\ H_{2(g)}$	220.27	155.75	226.94	163.74
$[Ga(oDFB)]^0_{(solv)} \rightarrow Ga^0_{(solv)}$[a] + $oDFB_{(solv)}$	40.54	17.48	20.16	–2.53
$Ga^0_{(solv)} \rightarrow Ga^0_{(g)}$[a]	16.30	16.30	16.61	16.61
$[Ga]^0_{(g)} \rightarrow [Ga]^0_{(solid)}$[31]	–271.96	–233.74	–271.96	–233.74
Sum:	–21.47	–34.31	–26.85	–37.80

a) The entropy of a single atom was calculated with the Sackur-Tetrode equation.

6.2.3 Thermodynamics of the $[SiMe_3]^+$-Transfer between $[Me_3Si(oDFB)]^+$ and $HSiMe_3$

The reaction enthalpies $\Delta_r H°$ and Gibbs free reaction energies $\Delta_r G°$ for the exchange reactions: $[Me_3Si(oDFB)]^+ + HSiMe_3 \rightarrow [H(SiMe_3)_2]^+ + oDFB$

were calculated and are listed in **Table S 7**. Since different coordination modes of *o*DFB and the trimethylsilylium ion are conceivable in the $[Me_3Si(oDFB)]^+$ adduct, four different $[Me_3Si(oDFB)]^+$ complexes were calculated: with coordination of the electrophilic silicon to one of the fluorine atoms ($[Me_3Si(oDFB)]^+$ (F-coordination)), to the adjacent *ipso* carbon atom ($[Me_3Si(oDFB)]^+$ (C1-coordination)), the carbon atom in *meta* and *ortho* position relative to the fluorine atoms ($[Me_3Si(oDFB)]^+$ (C2-coordination)) and to the carbon atom in *meta* and *para* position relative to the fluorine atoms ($[Me_3Si(oDFB)]^+$ (C3-coordination)).

Table S 7 Calculated reaction enthalpies and free Gibbs energies for the conversion of a $[Me_3Si]^+$/*o*DFB adduct into a $[Me_3Si]^+$/$HSiMe_3$ adduct in the gas phase and in *o*DFB (ε_r = 13.38).

Reaction	RI-BP86(D3BJ)/def2-TZVPP		RI-B3LYP(D3BJ)/def2-TZVPP		RI-BP86(D3BJ)/def2-TZVPP (COSMO)		RI-B3LYP(D3BJ)/def2-TZVPP (COSMO)	
	$\Delta_r H°$ [kJ mol^{-1}]	$\Delta_r G°$ [kJ mol^{-1}]	$\Delta_r H°$ [kJ mol^{-1}]	$\Delta_r G°$ [kJ mol^{-1}]	$\Delta_r H°$ [kJ mol^{-1}]	$\Delta_r G°$ [kJ mol^{-1}]	$\Delta_r H°$ [kJ mol^{-1}]	$\Delta_r G°$ [kJ mol^{-1}]
$[Me_3Si(o\text{DFB})]^+$ (F-coordination) + Me_3SiH → $[(Me_3Si)_2H]^+$ + *o*DFB	–54.53	–57.22	–41.41	–45.32	–59.33	–62.02	–47.73	–51.63
$[Me_3Si(o\text{DFB})]^+$ (C1-coordination) + Me_3SiH → $[(Me_3Si)_2H]^+$ + *o*DFB	–60.82	–64.70	–63.59	–69.01	–57.48	–61.36	–59.96	–65.39
$[Me_3Si(o\text{DFB})]^+$ (C2-coordination) + Me_3SiH → $[(Me_3Si)_2H]^+$ + *o*DFB	–44.96	–52.95	–51.08	–58.98	–40.12	–48.12	–45.45	–53.35
$[Me_3Si(o\text{DFB})]^+$ (C3-coordination) + Me_3SiH → $[(Me_3Si)_2H]^+$ + *o*DFB	–40.64	–48.45	–47.54	–55.48	–33.21	–41.02	–39.41	–47.35

6.2.4 Thermodynamics of the Reaction between Ga^+ and $HSiMe_3$ according to the Piers-Oestreich Mechanism

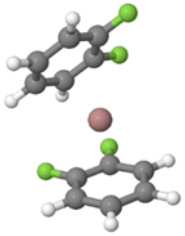
Table S 8 Calculated reaction enthalpies and free Gibbs energies for the reaction between Ga^+ and $HSiMe_3$ according to the Piers-Oestreich mechanism in the gas phase and in *o*DFB (ε_r = 13.38).

Reaction	RI-BP86(D3BJ)/def2-TZVPP		RI-B3LYP(D3BJ)/def2-TZVPP		RI-BP86(D3BJ)/def2-TZVPP (COSMO)		RI-B3LYP(D3BJ)/def2-TZVPP (COSMO)	
	$\Delta_r H°$ [kJ mol^{-1}]	$\Delta_r G°$ [kJ mol^{-1}]	$\Delta_r H°$ [kJ mol^{-1}]	$\Delta_r G°$ [kJ mol^{-1}]	$\Delta_r H°$ [kJ mol^{-1}]	$\Delta_r G°$ [kJ mol^{-1}]	$\Delta_r H°$ [kJ mol^{-1}]	$\Delta_r G°$ [kJ mol^{-1}]
$Ga^+ + Me_3SiH$ → $GaH + [SiMe_3]^+$	+112.28	+93.03	+126.57	+106.70	+161.75	+142.50	+172.18	+152.30
$[Ga(o\text{DFB})_2]^+$ + *o*DFB + Me_3SiH → $GaH(o\text{DFB})_2$ + $[Me_3Si(o\text{DFB})]^+$ (C3-coordination)	+155.42	+193.03	+168.80	+207.15	+137.71	+175.31	+153.39	+191.73
$[Ga(o\text{DFB})_2]^+$ + Me_3SiH + propylene → $GaH(o\text{DFB})_2$ + $[Me_3SiCH_2CHCH_3]^+$	+132.79	+170.39	+140.22	+178.76	+107.44	+145.04	+117.99	+156.52

6.3 Calculated Coordinates, Energies and Vibrational Spectra

In the following sections, the SCF energy, the zero-point energy (ZPE), the sum of translational, rotational, and vibrational energy including zero-point energy (FREEH energy) and the entropy (FREEH entropy) of all geometry-optimized species are listed along with the COSMO single point energy and correlation energy on the MP2/DZ, MP2/QZ, CCSD(T)/DZ and CCSD(T)/DZ→QZ level for selected species. Besides this, the method used, the symmetry of the species as well as the cartesian coordinates and the vibrational spectrum are given.

6.3.1 $[Ga(oDFB)_2]^+$



```
Method: (RI-)BP86(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:
C          -0.87793         0.60280         1.84154
C           0.11589         1.15038         2.67609
C           1.16092         0.35134         3.14309
H           1.91101         0.79733         3.79482
C           1.21270        -1.00164         2.77780
H           2.01934        -1.62793         3.15474
C           0.22299        -1.54847         1.94783
H           0.25224        -2.60196         1.67568
C          -0.82744        -0.74495         1.47709
H          -1.61751        -1.14824         0.84573
F          -1.87023         1.38455         1.41175
F           0.04051         2.43761         3.01617
C           1.64622        -1.62180        -2.16256
H           2.16916        -2.56806        -2.02982
C           2.29111        -0.48811        -2.67953
H           3.34320        -0.54887        -2.95178
C           1.58530         0.70877        -2.85155
H           2.08489         1.58668        -3.25695
C           0.22722         0.78485        -2.51093
H          -0.34747         1.70054        -2.64403
C          -0.41896        -0.34861        -2.01369
C           0.29022        -1.54936        -1.83746
F          -1.71859        -0.30841        -1.69810
F          -0.35196        -2.61974        -1.35124
Ga          1.56828         0.25929         0.14760

SCF energy GEOOPT = -2786.811309270 H
ZPE = 435.3 kJ/mol
FREEH energy = 478.39 kJ/mol
FREEH entropy = 0.57311 kJ/mol/K

$vibrational spectrum
#  mode     symmetry     wave number    IR intensity    selection rules
#                         cm**(-1)        km/mol          IR     RAMAN
     1                       -0.00         0.00000        -       -
     2                       -0.00         0.00000        -       -
     3                        0.00         0.00000        -       -
     4                        0.00         0.00000        -       -
     5                        0.00         0.00000        -       -
```

6		0.00	0.00000	-	-
7	a	12.71	0.60398	YES	YES
8	a	20.74	0.89519	YES	YES
9	a	51.63	0.34407	YES	YES
10	a	71.54	1.95161	YES	YES
11	a	73.69	2.08642	YES	YES
12	a	85.14	0.29545	YES	YES
13	a	91.65	0.08514	YES	YES
14	a	120.40	31.90291	YES	YES
15	a	131.33	24.91613	YES	YES
16	a	189.35	0.08435	YES	YES
17	a	192.58	0.08456	YES	YES
18	a	279.95	0.47428	YES	YES
19	a	280.90	0.37022	YES	YES
20	a	295.77	3.23893	YES	YES
21	a	300.94	0.46580	YES	YES
22	a	430.00	0.06117	YES	YES
23	a	430.68	0.07247	YES	YES
24	a	441.76	2.08944	YES	YES
25	a	445.00	13.33779	YES	YES
26	a	534.51	1.79149	YES	YES
27	a	535.85	2.86574	YES	YES
28	a	540.00	1.60671	YES	YES
29	a	541.25	1.34510	YES	YES
30	a	561.70	3.40266	YES	YES
31	a	562.05	4.14103	YES	YES
32	a	683.56	0.03834	YES	YES
33	a	685.13	0.17881	YES	YES
34	a	755.71	26.35341	YES	YES
35	a	757.65	17.67808	YES	YES
36	a	771.66	106.39712	YES	YES
37	a	779.89	86.36722	YES	YES
38	a	842.61	11.82024	YES	YES
39	a	847.00	12.91404	YES	YES
40	a	853.57	0.60916	YES	YES
41	a	857.21	2.52886	YES	YES
42	a	929.31	4.15383	YES	YES
43	a	931.46	8.74136	YES	YES
44	a	960.57	0.21999	YES	YES
45	a	962.81	0.00852	YES	YES
46	a	1018.65	4.65484	YES	YES
47	a	1019.82	2.72468	YES	YES
48	a	1094.42	12.95362	YES	YES
49	a	1096.21	8.54886	YES	YES
50	a	1149.07	2.42772	YES	YES
51	a	1151.48	1.20421	YES	YES
52	a	1199.03	17.68218	YES	YES
53	a	1208.29	21.89934	YES	YES
54	a	1255.44	9.48672	YES	YES
55	a	1258.83	13.15340	YES	YES
56	a	1269.13	82.57684	YES	YES
57	a	1276.77	128.93590	YES	YES
58	a	1340.98	0.63782	YES	YES
59	a	1342.19	0.70894	YES	YES
60	a	1441.66	25.49543	YES	YES
61	a	1442.48	21.46704	YES	YES
62	a	1490.58	179.21631	YES	YES
63	a	1493.72	233.15448	YES	YES
64	a	1570.21	20.07654	YES	YES
65	a	1573.12	15.55608	YES	YES
66	a	1576.45	5.78169	YES	YES
67	a	1577.25	19.76677	YES	YES
68	a	3127.16	0.96583	YES	YES
69	a	3127.29	2.40944	YES	YES
70	a	3132.40	0.40935	YES	YES
71	a	3134.36	0.19134	YES	YES
72	a	3138.31	6.43709	YES	YES
73	a	3139.68	8.64352	YES	YES
74	a	3145.43	1.98025	YES	YES

75	a	3146.23	1.85017	YES	YES

Total COSMO energy + OC correction = -2786.8784492627 H

Method: (RI-)B3LYP(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:

C	-0.86778	0.59876	1.85544
C	0.09398	1.13381	2.71842
C	1.11931	0.33569	3.20675
H	1.84227	0.77111	3.88229
C	1.18254	-1.00679	2.83038
H	1.97065	-1.63316	3.22268
C	0.22306	-1.54173	1.96972
H	0.26064	-2.58427	1.68877
C	-0.80844	-0.73726	1.48001
H	-1.57259	-1.13008	0.82494
F	-1.83954	1.38286	1.40351
F	0.00995	2.41216	3.06527
C	1.64675	-1.61588	-2.20297
H	2.16567	-2.55545	-2.07386
C	2.27597	-0.49890	-2.75530
H	3.31021	-0.56770	-3.05984
C	1.57247	0.69166	-2.92415
H	2.05808	1.55326	-3.35889
C	0.23226	0.77742	-2.54557
H	-0.34021	1.68505	-2.67747
C	-0.39511	-0.33877	-2.00931
C	0.31075	-1.53011	-1.83573
F	-1.67576	-0.28758	-1.64798
F	-0.31442	-2.58143	-1.30478
Ga	1.65041	0.30530	0.16996

SCF energy GEOOPT = -2785.996856804 H
ZPE = 447.7 kJ/mol
FREEH energy = 490.05 kJ/mol
FREEH entropy = 0.57413 kJ/mol/K

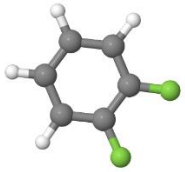
$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		-0.00	0.00000	-	-
2		-0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	7.53	0.74156	YES	YES
8	a	23.44	0.99680	YES	YES
9	a	55.03	0.17196	YES	YES
10	a	67.72	1.98378	YES	YES
11	a	70.62	2.72303	YES	YES
12	a	79.16	0.57108	YES	YES
13	a	86.38	0.14694	YES	YES
14	a	109.22	32.12364	YES	YES
15	a	119.36	21.78928	YES	YES
16	a	197.15	0.03691	YES	YES
17	a	200.25	0.08305	YES	YES
18	a	290.23	0.52135	YES	YES
19	a	291.86	0.46759	YES	YES
20	a	306.34	2.74586	YES	YES
21	a	310.80	0.38447	YES	YES
22	a	444.93	0.07972	YES	YES
23	a	445.52	0.10023	YES	YES
24	a	463.63	2.74354	YES	YES
25	a	467.10	11.81181	YES	YES
26	a	553.88	3.82175	YES	YES

27	a	554.27	4.29757	YES	YES
28	a	560.66	0.37976	YES	YES
29	a	562.62	0.38954	YES	YES
30	a	582.12	4.05563	YES	YES
31	a	582.53	4.82586	YES	YES
32	a	717.11	0.08848	YES	YES
33	a	717.78	0.13685	YES	YES
34	a	778.66	28.56503	YES	YES
35	a	780.63	20.28180	YES	YES
36	a	800.29	106.15260	YES	YES
37	a	809.51	92.65815	YES	YES
38	a	869.18	12.95376	YES	YES
39	a	873.36	14.16791	YES	YES
40	a	891.42	0.03526	YES	YES
41	a	897.21	2.70051	YES	YES
42	a	973.67	5.42201	YES	YES
43	a	977.23	9.43869	YES	YES
44	a	1006.83	0.38013	YES	YES
45	a	1008.82	0.01471	YES	YES
46	a	1045.73	5.02080	YES	YES
47	a	1046.80	3.23952	YES	YES
48	a	1126.70	12.15537	YES	YES
49	a	1128.40	8.14449	YES	YES
50	a	1184.46	1.68138	YES	YES
51	a	1186.39	0.84680	YES	YES
52	a	1236.10	19.83399	YES	YES
53	a	1246.09	25.58295	YES	YES
54	a	1298.51	10.97242	YES	YES
55	a	1301.97	13.36493	YES	YES
56	a	1305.81	82.15926	YES	YES
57	a	1313.29	138.30661	YES	YES
58	a	1339.08	0.13881	YES	YES
59	a	1341.12	0.24648	YES	YES
60	a	1488.93	25.96092	YES	YES
61	a	1490.13	21.61009	YES	YES
62	a	1539.98	175.12999	YES	YES
63	a	1542.82	231.47154	YES	YES
64	a	1620.22	23.88572	YES	YES
65	a	1624.05	13.35283	YES	YES
66	a	1627.11	10.41422	YES	YES
67	a	1628.02	16.84349	YES	YES
68	a	3197.35	1.87236	YES	YES
69	a	3197.75	0.96638	YES	YES
70	a	3202.76	0.36515	YES	YES
71	a	3205.58	0.76643	YES	YES
72	a	3208.47	6.07498	YES	YES
73	a	3211.95	6.80306	YES	YES
74	a	3216.09	1.41846	YES	YES
75	a	3217.50	3.43679	YES	YES

Total COSMO energy + OC correction = -2786.0664059537 H

6.3.2 *o*DFB



Method: (RI-)BP86(D3BJ)/def2-TZVPP
Symmetry: c2v

Cartesian coordinates in Ångström:

F	-1.3581562	0.0000000	2.3356685
C	-0.6988885	0.0000000	1.1567638
C	-1.4024593	0.0000000	-0.0417837
H	-2.4910061	0.0000000	-0.0118671
C	-0.6981958	0.0000000	-1.2491161
H	-1.2467930	0.0000000	-2.1897330
C	0.6981958	0.0000000	-1.2491161
H	1.2467930	0.0000000	-2.1897330
C	1.4024593	0.0000000	-0.0417837
H	2.4910061	0.0000000	-0.0118671
C	0.6988885	0.0000000	1.1567638
F	1.3581562	0.0000000	2.3356685

SCF energy GEOOPT = -430.9297580145 H
ZPE = 214.5 kJ/mol
FREEH energy = 230.62 kJ/mol
FREEH entropy = 0.32340 kJ/mol/K

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		-0.00	0.00000	-	-
2		-0.00	0.00000	-	-
3		-0.00	0.00000	-	-
4		-0.00	0.00000	-	-
5		-0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a2	180.38	0.00000	NO	YES
8	a1	278.24	0.17441	YES	YES
9	b2	282.29	0.08526	YES	YES
10	b1	430.24	0.04953	YES	YES
11	b2	445.51	3.96068	YES	YES
12	b1	535.78	3.09601	YES	YES
13	a2	546.25	0.00000	NO	YES
14	a1	565.28	4.19042	YES	YES
15	a2	672.37	0.00000	NO	YES
16	b2	736.50	77.91245	YES	YES
17	a1	755.72	31.52172	YES	YES
18	a2	816.67	0.00000	NO	YES
19	b1	839.34	18.72874	YES	YES
20	b2	905.01	4.28699	YES	YES
21	a2	929.65	0.00000	NO	YES
22	a1	1022.83	6.13253	YES	YES
23	b1	1092.97	22.88888	YES	YES
24	a1	1143.47	1.81654	YES	YES
25	b1	1184.41	37.78156	YES	YES
26	b1	1248.22	3.40804	YES	YES
27	a1	1259.05	137.34276	YES	YES
28	a1	1342.73	0.59297	YES	YES
29	b1	1447.87	10.14845	YES	YES
30	a1	1495.19	181.45883	YES	YES
31	b1	1593.72	8.39314	YES	YES
32	a1	1599.66	19.53633	YES	YES
33	b1	3113.66	0.95811	YES	YES
34	a1	3124.65	8.27822	YES	YES
35	b1	3132.72	3.34927	YES	YES

```
    36        a1           3138.63         2.00024       YES     YES

Total COSMO energy + OC correction = -430.9340627238 H


Method: (RI-)B3LYP(D3BJ)/def2-TZVPP
Symmetry: c2v

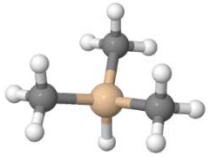
Cartesian coordinates in Ångström:
F    -1.3493548    0.0000000    2.3225385
C    -0.6943851    0.0000000    1.1502786
C    -1.3954266    0.0000000   -0.0412482
H    -2.4758746    0.0000000   -0.0114693
C    -0.6948486    0.0000000   -1.2431612
H    -1.2390044    0.0000000   -2.1769927
C     0.6948486    0.0000000   -1.2431612
H     1.2390044    0.0000000   -2.1769927
C     1.3954266    0.0000000   -0.0412482
H     2.4758746    0.0000000   -0.0114693
C     0.6943851    0.0000000    1.1502786
F     1.3493548    0.0000000    2.3225385

SCF energy GEOOPT = -430.6996733127 H
ZPE = 220.7 kJ/mol
FREEH energy = 236.38 kJ/mol
FREEH entropy = 0.32053 kJ/mol/K

$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection rules
#                         cm**(-1)        km/mol          IR     RAMAN
     1                      -0.00         0.00000        -       -
     2                      -0.00         0.00000        -       -
     3                      -0.00         0.00000        -       -
     4                      -0.00         0.00000        -       -
     5                       0.00         0.00000        -       -
     6                       0.00         0.00000        -       -
     7        a2           188.67         0.00000       NO      YES
     8        a1           288.64         0.22913       YES     YES
     9        b2           293.25         0.01869       YES     YES
    10        b1           444.97         0.07557       YES     YES
    11        b2           463.91         3.69474       YES     YES
    12        b1           553.02         3.67954       YES     YES
    13        a2           565.61         0.00000       NO      YES
    14        a1           585.07         4.84286       YES     YES
    15        a2           704.69         0.00000       NO      YES
    16        b2           767.16        80.35864       YES     YES
    17        a1           778.60        33.73728       YES     YES
    18        a2           857.91         0.00000       NO      YES
    19        b1           865.31        19.60949       YES     YES
    20        b2           948.95         4.76860       YES     YES
    21        a2           972.96         0.00000       NO      YES
    22        a1          1050.20         6.55823       YES     YES
    23        b1          1125.99        20.93874       YES     YES
    24        a1          1178.68         1.18714       YES     YES
    25        b1          1223.24        40.66542       YES     YES
    26        b1          1292.54         3.76076       YES     YES
    27        a1          1297.27       142.31569       YES     YES
    28        a1          1336.04         0.05082       YES     YES
    29        b1          1494.80        11.18032       YES     YES
    30        a1          1545.01       182.33393       YES     YES
    31        b1          1643.78         8.42516       YES     YES
    32        a1          1648.30        21.88516       YES     YES
    33        b1          3183.83         1.01523       YES     YES
    34        a1          3194.98         7.94506       YES     YES
    35        b1          3203.17         3.02123       YES     YES
    36        a1          3208.78         1.93168       YES     YES

Total COSMO energy + OC correction = -430.7042973736 H
```

6.3.3 $HSiMe_3$



```
Method: (RI-)BP86(D3BJ)/def2-TZVPP
Symmetry: c3v

Cartesian coordinates in Ångström:
Si   -0.0000000    0.0000000   -0.4911428
C    -0.8928468    1.5464560    0.1105343
H     0.0000000    0.0000000   -1.9913985
C    -0.8928468   -1.5464560    0.1105343
C     1.7856935    0.0000000    0.1105343
H    -1.9317968   -1.5707361   -0.2462046
H    -0.9146097   -1.5841505    1.2092057
H    -0.3943989   -2.4583531   -0.2462046
H    -1.9317968    1.5707361   -0.2462046
H    -0.3943989    2.4583531   -0.2462046
H    -0.9146097    1.5841505    1.2092057
H     2.3261957    0.8876171   -0.2462046
H     2.3261957   -0.8876171   -0.2462046
H     1.8292195    0.0000000    1.2092057

SCF energy GEOOPT = -409.9720059361 H
ZPE = 303.3 kJ/mol
FREEH energy = 323.28 kJ/mol
FREEH entropy = 0.33347 kJ/mol/K

$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection rules
#                         cm**(-1)       km/mol          IR     RAMAN
     1                       -0.00         0.00000         -       -
     2                       -0.00         0.00000         -       -
     3                       -0.00         0.00000         -       -
     4                       -0.00         0.00000         -       -
     5                        0.00         0.00000         -       -
     6                        0.00         0.00000         -       -
     7        a2            146.44         0.00000        NO      NO
     8        e             162.23         0.00008        YES     YES
     9        e             162.23         0.00008        YES     YES
    10        e             198.83         0.70205        YES     YES
    11        e             198.83         0.70205        YES     YES
    12        a1            234.14         1.18689        YES     YES
    13        e             601.97         8.11243        YES     YES
    14        e             601.97         8.11243        YES     YES
    15        a1            604.04         1.66939        YES     YES
    16        a2            662.92         0.00000        NO      NO
    17        e             692.66        13.07001        YES     YES
    18        e             692.66        13.07001        YES     YES
    19        e             827.34        16.44682        YES     YES
    20        e             827.34        16.44682        YES     YES
    21        a1            846.95        56.09559        YES     YES
    22        e             887.74       151.05653        YES     YES
    23        e             887.74       151.05653        YES     YES
    24        e            1238.35        28.67308        YES     YES
    25        e            1238.35        28.67308        YES     YES
    26        a1           1248.26         5.16025        YES     YES
    27        a2           1406.54         0.00000        NO      NO
    28        e            1410.58         0.10739        YES     YES
    29        e            1410.58         0.10739        YES     YES
    30        e            1420.31         2.53200        YES     YES
    31        e            1420.31         2.53200        YES     YES
    32        a1           1428.33         8.81640        YES     YES
    33        a1           2120.10       151.29735        YES     YES
    34        e            2963.18         8.60878        YES     YES
```

35	e	2963.18	8.60878	YES	YES
36	a1	2963.74	3.46417	YES	YES
37	e	3037.43	1.35369	YES	YES
38	e	3037.43	1.35369	YES	YES
39	a1	3039.15	29.59897	YES	YES
40	a2	3043.07	0.00000	NO	NO
41	e	3043.67	17.94357	YES	YES
42	e	3043.67	17.94357	YES	YES

Total COSMO energy + OC correction = -409.9740032233 H

Method: (RI-)B3LYP(D3BJ)/def2-TZVPP
Symmetry: c3v

Cartesian coordinates in Ångström:

Si	-0.0000000	0.0000000	-0.4924224
C	-0.8897936	1.5411678	0.1097604
H	0.0000000	0.0000000	-1.9815521
C	-0.8897936	-1.5411678	0.1097604
C	1.7795873	0.0000000	0.1097604
H	-1.9222678	-1.5657179	-0.2436108
H	-0.9102875	-1.5766643	1.2013153
H	-0.3948175	-2.4475917	-0.2436108
H	-1.9222678	1.5657179	-0.2436108
H	-0.3948175	2.4475917	-0.2436108
H	-0.9102875	1.5766643	1.2013153
H	2.3170854	0.8818738	-0.2436108
H	2.3170854	-0.8818738	-0.2436108
H	1.8205751	0.0000000	1.2013153

SCF energy GEOOPT = -409.8147496552 H
ZPE = 310.9 kJ/mol
FREEH energy = 330.50 kJ/mol
FREEH entropy = 0.33093 kJ/mol/K

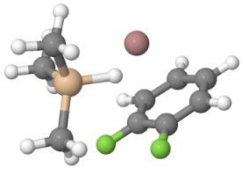
$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		-0.00	0.00000	-	-
2		-0.00	0.00000	-	-
3		-0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a2	149.49	0.00000	NO	NO
8	e	166.65	0.00004	YES	YES
9	e	166.65	0.00004	YES	YES
10	e	204.35	0.94086	YES	YES
11	e	204.35	0.94086	YES	YES
12	a1	242.03	1.87441	YES	YES
13	a1	616.67	2.11680	YES	YES
14	e	623.76	9.65714	YES	YES
15	e	623.76	9.65714	YES	YES
16	a2	686.88	0.00000	NO	NO
17	e	707.09	15.39024	YES	YES
18	e	707.09	15.39024	YES	YES
19	e	853.29	16.83122	YES	YES
20	e	853.29	16.83122	YES	YES
21	a1	874.70	58.05770	YES	YES
22	e	919.92	160.63749	YES	YES
23	e	919.92	160.63749	YES	YES
24	e	1289.51	31.69987	YES	YES
25	e	1289.51	31.69987	YES	YES
26	a1	1298.30	5.82574	YES	YES
27	a2	1454.52	0.00000	NO	NO
28	e	1458.19	0.10100	YES	YES
29	e	1458.19	0.10100	YES	YES

30	e	1467.47	2.59533	YES	YES
31	e	1467.47	2.59533	YES	YES
32	a1	1474.98	8.94438	YES	YES
33	a1	2175.62	162.63763	YES	YES
34	e	3022.85	8.07862	YES	YES
35	e	3022.85	8.07862	YES	YES
36	a1	3023.74	3.52263	YES	YES
37	e	3089.89	1.49440	YES	YES
38	e	3089.89	1.49440	YES	YES
39	a1	3092.17	34.29529	YES	YES
40	a2	3095.61	0.00000	NO	NO
41	e	3096.60	21.01637	YES	YES
42	e	3096.60	21.01637	YES	YES

Total COSMO energy + OC correction = -409.8166919085 H

6.3.4 [Ga(*o*DFB)HSiMe$_3$]$^+$



Method: (RI-)BP86(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:

Ga	0.42935	-0.49020	1.53591
Si	2.52920	0.30415	-0.85346
C	4.23556	0.59028	-0.15195
H	4.42233	1.65809	0.02056
H	4.99553	0.22740	-0.85884
H	4.38459	0.05732	0.79668
C	2.12280	-1.52758	-1.01648
H	2.30791	-2.10362	-0.09638
H	2.77739	-1.97011	-1.78255
H	1.09014	-1.70650	-1.34848
C	2.14051	1.27054	-2.39983
H	2.28552	2.34680	-2.24176
H	1.10913	1.10581	-2.73456
H	2.81428	0.95542	-3.20972
H	-2.28162	-2.06536	-0.30980
C	-2.13723	-1.09451	0.16290
C	-2.56071	-0.84311	1.47597
H	-3.03745	-1.63818	2.04603
C	-2.36432	0.41821	2.04937
H	-2.68874	0.61456	3.06959
C	-1.75141	1.44461	1.31226
H	-1.60047	2.43881	1.73107
C	-1.36512	1.20719	-0.01036
F	-0.81973	2.17933	-0.74439
C	-1.54950	-0.06581	-0.58050
F	-1.17178	-0.27453	-1.84690
H	1.54589	0.80610	0.23734

SCF energy GEOOPT = -2765.847057574 H
ZPE = 521.8 kJ/mol
FREEH energy = 568.93 kJ/mol
FREEH entropy = 0.59373 kJ/mol/K

$vibrational spectrum

#	mode	symmetry	wave number	IR intensity	selection rules

#		cm**(-1)	km/mol	IR	RAMAN
1		-0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	24.44	0.40732	YES	YES
8	a	32.93	0.16813	YES	YES
9	a	47.78	0.72393	YES	YES
10	a	52.09	1.72028	YES	YES
11	a	63.10	2.18755	YES	YES
12	a	82.28	2.29909	YES	YES
13	a	89.92	0.07055	YES	YES
14	a	115.94	23.75345	YES	YES
15	a	129.05	12.33748	YES	YES
16	a	141.90	0.02637	YES	YES
17	a	157.77	0.05014	YES	YES
18	a	167.69	0.28225	YES	YES
19	a	187.71	0.02281	YES	YES
20	a	201.21	0.78896	YES	YES
21	a	203.40	1.94095	YES	YES
22	a	245.91	0.23855	YES	YES
23	a	279.65	0.40867	YES	YES
24	a	292.79	1.88492	YES	YES
25	a	430.47	0.07459	YES	YES
26	a	443.66	8.01997	YES	YES
27	a	535.64	2.63189	YES	YES
28	a	539.61	1.47748	YES	YES
29	a	561.72	2.89194	YES	YES
30	a	591.59	11.68644	YES	YES
31	a	607.17	3.30868	YES	YES
32	a	632.50	21.56564	YES	YES
33	a	669.64	0.30160	YES	YES
34	a	683.50	0.11123	YES	YES
35	a	704.32	4.73260	YES	YES
36	a	718.92	6.17959	YES	YES
37	a	755.74	21.40456	YES	YES
38	a	772.89	94.57368	YES	YES
39	a	820.05	145.49766	YES	YES
40	a	825.34	8.79589	YES	YES
41	a	843.40	11.93410	YES	YES
42	a	845.45	73.40108	YES	YES
43	a	858.41	0.76946	YES	YES
44	a	872.08	114.96004	YES	YES
45	a	925.66	146.79106	YES	YES
46	a	932.34	31.97965	YES	YES
47	a	964.26	0.15900	YES	YES
48	a	1020.59	3.15378	YES	YES
49	a	1095.35	10.64091	YES	YES
50	a	1152.20	0.95191	YES	YES
51	a	1202.91	20.30874	YES	YES
52	a	1247.31	36.48884	YES	YES
53	a	1248.79	38.37248	YES	YES
54	a	1256.14	9.53570	YES	YES
55	a	1259.06	3.99475	YES	YES
56	a	1272.05	73.48273	YES	YES
57	a	1336.84	0.98827	YES	YES
58	a	1398.04	2.71997	YES	YES
59	a	1399.25	0.31704	YES	YES
60	a	1403.34	0.50600	YES	YES
61	a	1412.31	2.89494	YES	YES
62	a	1417.70	9.99643	YES	YES
63	a	1420.55	7.87622	YES	YES
64	a	1440.42	27.69227	YES	YES
65	a	1491.58	181.62743	YES	YES
66	a	1572.28	6.43839	YES	YES
67	a	1574.82	13.46939	YES	YES
68	a	1846.91	911.65158	YES	YES

69	a	2952.32	9.51228	YES	YES
70	a	2971.39	0.31012	YES	YES
71	a	2975.35	0.04306	YES	YES
72	a	3019.70	2.77810	YES	YES
73	a	3035.40	2.41402	YES	YES
74	a	3045.88	1.38471	YES	YES
75	a	3050.90	0.46384	YES	YES
76	a	3057.81	1.66820	YES	YES
77	a	3068.57	0.93961	YES	YES
78	a	3127.65	3.37158	YES	YES
79	a	3131.91	0.43498	YES	YES
80	a	3138.53	6.85036	YES	YES
81	a	3147.10	2.68911	YES	YES

Total COSMO energy + OC correction = -2765.9115708152 H

Method: (RI-)B3LYP(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:

Ga	0.45475	0.57183	1.74348
Si	2.56117	-0.03530	-0.85569
C	4.25204	-0.49515	-0.22422
H	4.47169	-0.02556	0.73585
H	5.01492	-0.16568	-0.93313
H	4.35339	-1.57470	-0.10745
C	2.06821	-0.89090	-2.43129
H	2.11875	-1.97493	-2.32588
H	2.75062	-0.60175	-3.23383
H	1.05736	-0.62314	-2.73696
C	2.29566	1.81940	-0.91219
H	2.52716	2.30951	0.03719
H	1.27708	2.08076	-1.20510
H	2.96174	2.26232	-1.65618
H	-1.79117	-2.25662	1.45991
C	-1.87568	-1.21981	1.16512
C	-2.48086	-0.26817	1.99009
H	-2.86721	-0.56960	2.95290
C	-2.59378	1.05488	1.57110
H	-3.06698	1.78922	2.20646
C	-2.09681	1.44190	0.32578
H	-2.17932	2.46018	-0.02811
C	-1.51202	0.49037	-0.50185
F	-1.05290	0.83228	-1.70406
C	-1.40753	-0.83945	-0.08717
F	-0.85513	-1.73187	-0.90183
H	1.57477	-0.51212	0.22743

SCF energy GEOOPT = -2765.106383133 H
ZPE = 535.8 kJ/mol
FREEH energy = 582.18 kJ/mol
FREEH entropy = 0.59074 kJ/mol/K

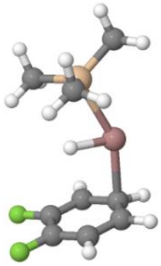
$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		-0.00	0.00000	-	-
2		-0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	26.02	0.24898	YES	YES
8	a	34.01	0.36319	YES	YES
9	a	43.07	1.68908	YES	YES
10	a	54.62	0.92409	YES	YES
11	a	58.60	0.36539	YES	YES
12	a	77.38	2.52063	YES	YES

13	a	85.04	0.15691	YES	YES
14	a	108.67	31.73313	YES	YES
15	a	123.19	8.03486	YES	YES
16	a	147.28	0.05095	YES	YES
17	a	164.25	0.02025	YES	YES
18	a	169.83	0.05090	YES	YES
19	a	195.43	0.08594	YES	YES
20	a	208.05	1.14620	YES	YES
21	a	208.64	1.61754	YES	YES
22	a	255.74	0.29875	YES	YES
23	a	290.66	0.42585	YES	YES
24	a	304.23	1.97482	YES	YES
25	a	445.44	0.09576	YES	YES
26	a	464.59	7.76124	YES	YES
27	a	554.04	4.38282	YES	YES
28	a	560.82	0.29055	YES	YES
29	a	582.25	3.49523	YES	YES
30	a	609.41	13.31458	YES	YES
31	a	628.92	6.58979	YES	YES
32	a	652.97	31.44855	YES	YES
33	a	696.76	0.16321	YES	YES
34	a	716.35	0.10999	YES	YES
35	a	722.28	6.69010	YES	YES
36	a	733.19	8.08938	YES	YES
37	a	778.85	25.10456	YES	YES
38	a	801.42	93.84048	YES	YES
39	a	853.17	69.62278	YES	YES
40	a	853.46	75.18085	YES	YES
41	a	870.08	13.12074	YES	YES
42	a	872.98	76.79809	YES	YES
43	a	895.46	0.32903	YES	YES
44	a	905.31	129.09597	YES	YES
45	a	950.80	179.90807	YES	YES
46	a	974.93	6.94834	YES	YES
47	a	1009.82	0.14696	YES	YES
48	a	1047.40	3.54103	YES	YES
49	a	1127.31	9.88877	YES	YES
50	a	1187.08	0.59702	YES	YES
51	a	1240.14	22.42878	YES	YES
52	a	1298.14	38.41934	YES	YES
53	a	1300.38	44.28723	YES	YES
54	a	1301.51	19.15328	YES	YES
55	a	1306.74	45.64763	YES	YES
56	a	1311.67	23.24187	YES	YES
57	a	1336.16	0.41612	YES	YES
58	a	1448.44	0.28891	YES	YES
59	a	1451.53	2.10043	YES	YES
60	a	1451.93	0.64519	YES	YES
61	a	1460.83	3.04028	YES	YES
62	a	1467.15	7.77140	YES	YES
63	a	1469.51	7.63786	YES	YES
64	a	1488.18	27.30824	YES	YES
65	a	1540.78	179.71995	YES	YES
66	a	1623.88	6.39133	YES	YES
67	a	1625.24	13.29199	YES	YES
68	a	1888.95	1251.89036	YES	YES
69	a	3018.86	6.39484	YES	YES
70	a	3030.55	0.36188	YES	YES
71	a	3035.10	0.10101	YES	YES
72	a	3082.29	3.81175	YES	YES
73	a	3096.53	3.11933	YES	YES
74	a	3098.43	2.42715	YES	YES
75	a	3103.82	1.17322	YES	YES
76	a	3109.84	2.94808	YES	YES
77	a	3123.41	1.57788	YES	YES
78	a	3197.99	2.67797	YES	YES
79	a	3202.72	0.36677	YES	YES
80	a	3208.75	6.50724	YES	YES
81	a	3217.05	2.01702	YES	YES

```
CCS(T)-DZ energy = -1097.0593475942 H (T1 = 0.010398; D1 = 0.0384)
MP2-DZ energy = -1096.8816553243 H
MP2-QZ energy = -1097.8648768420 H
CCSDT)-QZ energy (approximated) = -1098.0425691119 H
```

6.3.5 Transition State Oxidative Addition



```
Method: (RI-)BP86(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:
Ga          2.14697       -1.81618        1.51433
Si          3.66856        0.10979        0.70097
C           4.90733        0.21039        2.09189
H           4.43774        0.48314        3.04433
H           5.62956        1.00343        1.82783
H           5.46078       -0.72685        2.22187
C           4.36884       -0.59690       -0.86933
H           4.74295       -1.62030       -0.73806
H           5.23657        0.02723       -1.14097
H           3.64521       -0.57675       -1.69062
C           2.56346        1.59862        0.59527
H           1.94451        1.71810        1.49387
H           1.91564        1.56837       -0.28686
H           3.21555        2.48559        0.53461
H           1.71634       -4.64109       -0.07000
C           0.94395       -3.87635        0.00723
C           0.48449       -3.41365        1.26951
H           0.76040       -3.96203        2.17063
C          -0.55667       -2.44841        1.31870
H          -0.93483       -2.11064        2.28302
C          -1.14872       -1.98752        0.14193
H          -1.95785       -1.25901        0.16080
C          -0.71855       -2.48330       -1.08512
F          -1.27150       -2.05692       -2.21684
C           0.34655       -3.39979       -1.15292
F           0.76226       -3.82069       -2.34591
H           1.74018       -0.99221        0.04959

SCF energy GEOOPT = -2765.763998762 H
ZPE = 513.6 kJ/mol
FREEH energy = 559.55 kJ/mol
FREEH entropy = 0.58556 kJ/mol/K

$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection rules
#                         cm**(-1)        km/mol          IR     RAMAN
     1        a            -404.85         0.00000       YES      YES
     2                       -0.00         0.00000         -        -
     3                        0.00         0.00000         -        -
     4                        0.00         0.00000         -        -
     5                        0.00         0.00000         -        -
     6                        0.00         0.00000         -        -
```

7		0.00	0.00000	-	-
8	a	16.30	0.56510	YES	YES
9	a	21.09	0.46582	YES	YES
10	a	46.37	2.42444	YES	YES
11	a	67.05	0.54505	YES	YES
12	a	91.59	0.48870	YES	YES
13	a	96.69	0.06077	YES	YES
14	a	105.09	29.27214	YES	YES
15	a	125.00	0.67365	YES	YES
16	a	135.06	0.39097	YES	YES
17	a	176.55	0.30807	YES	YES
18	a	178.79	1.81512	YES	YES
19	a	182.96	4.05964	YES	YES
20	a	202.23	50.35531	YES	YES
21	a	213.28	2.37374	YES	YES
22	a	251.01	36.27090	YES	YES
23	a	281.12	0.18351	YES	YES
24	a	319.43	3.49642	YES	YES
25	a	378.59	3.49099	YES	YES
26	a	417.91	6.38946	YES	YES
27	a	428.76	1.99480	YES	YES
28	a	445.64	4.33920	YES	YES
29	a	535.53	5.18108	YES	YES
30	a	554.51	2.21491	YES	YES
31	a	556.05	21.59798	YES	YES
32	a	591.44	44.67803	YES	YES
33	a	663.41	22.84261	YES	YES
34	a	676.62	1.59604	YES	YES
35	a	683.53	1.38481	YES	YES
36	a	696.68	0.18125	YES	YES
37	a	735.31	12.12936	YES	YES
38	a	759.67	14.16690	YES	YES
39	a	764.71	10.90327	YES	YES
40	a	797.38	280.96566	YES	YES
41	a	814.52	186.37868	YES	YES
42	a	837.78	22.47974	YES	YES
43	a	846.21	3.60754	YES	YES
44	a	853.83	52.33757	YES	YES
45	a	862.24	60.34185	YES	YES
46	a	913.03	4.91520	YES	YES
47	a	949.71	1.56538	YES	YES
48	a	998.15	11.35453	YES	YES
49	a	1086.42	8.76216	YES	YES
50	a	1141.78	3.44134	YES	YES
51	a	1211.40	24.10362	YES	YES
52	a	1233.23	26.70255	YES	YES
53	a	1238.57	32.66150	YES	YES
54	a	1249.52	2.04418	YES	YES
55	a	1254.08	26.75253	YES	YES
56	a	1280.37	146.58633	YES	YES
57	a	1356.40	2.73919	YES	YES
58	a	1373.28	0.08109	YES	YES
59	a	1377.27	149.23728	YES	YES
60	a	1390.07	14.82168	YES	YES
61	a	1395.71	23.36834	YES	YES
62	a	1399.03	0.30022	YES	YES
63	a	1409.46	115.86392	YES	YES
64	a	1417.72	16.97384	YES	YES
65	a	1431.83	30.83283	YES	YES
66	a	1492.56	255.96524	YES	YES
67	a	1551.11	64.78903	YES	YES
68	a	1572.68	35.57725	YES	YES
69	a	2943.01	4.07644	YES	YES
70	a	2960.65	5.04368	YES	YES
71	a	2962.05	5.11340	YES	YES
72	a	3038.52	0.07493	YES	YES
73	a	3039.76	0.18515	YES	YES
74	a	3040.72	0.15759	YES	YES
75	a	3079.32	0.00053	YES	YES

76	a	3084.46	0.10983	YES	YES
77	a	3085.53	0.25776	YES	YES
78	a	3109.94	12.75854	YES	YES
79	a	3124.73	1.74727	YES	YES
80	a	3129.61	8.66003	YES	YES
81	a	3141.15	4.27523	YES	YES

Total COSMO energy + OC correction = -2765.8282477452 H

Method: (RI-)B3LYP(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:

Ga	2.11836	-1.77904	1.56065
Si	3.80394	0.24777	0.67875
C	4.99368	0.27785	2.09437
H	4.51007	0.54276	3.03310
H	5.74097	1.05001	1.86850
H	5.51527	-0.67012	2.21462
C	4.43589	-0.51566	-0.87638
H	4.80389	-1.52917	-0.71612
H	5.29203	0.08664	-1.20277
H	3.68697	-0.52069	-1.66434
C	2.63326	1.66967	0.59567
H	2.04302	1.76643	1.50709
H	1.96830	1.60234	-0.26176
H	3.23793	2.57993	0.50859
H	1.57919	-4.75639	-0.06150
C	0.82687	-3.98321	0.01143
C	0.35138	-3.53542	1.25759
H	0.65109	-4.05203	2.15923
C	-0.65647	-2.55444	1.30803
H	-1.04667	-2.23219	2.26344
C	-1.20011	-2.04785	0.13276
H	-1.98363	-1.30369	0.14635
C	-0.74441	-2.51856	-1.08577
F	-1.24469	-2.04373	-2.21769
C	0.27786	-3.46657	-1.14672
F	0.71356	-3.86998	-2.33395
H	1.74217	-1.02859	0.05661

SCF energy GEOOPT = -2765.015200859 H
ZPE = 526.2 kJ/mol
FREEH energy = 572.10 kJ/mol
FREEH entropy = 0.59199 kJ/mol/K

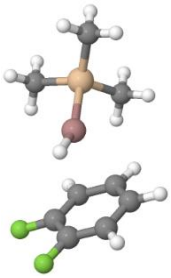
$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1	a	-519.25	0.00000	YES	YES
2		-0.00	0.00000	-	-
3		-0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7		0.00	0.00000	-	-
8	a	14.04	0.50658	YES	YES
9	a	20.54	0.93033	YES	YES
10	a	39.51	1.69971	YES	YES
11	a	50.38	0.33397	YES	YES
12	a	83.72	0.17419	YES	YES
13	a	95.74	0.22715	YES	YES
14	a	112.63	34.05203	YES	YES
15	a	121.41	1.83050	YES	YES
16	a	130.30	6.58294	YES	YES
17	a	168.45	1.00588	YES	YES
18	a	169.60	0.18477	YES	YES

19	a	182.45	12.61865	YES	YES
20	a	209.40	93.19232	YES	YES
21	a	215.86	7.35348	YES	YES
22	a	218.35	1.87960	YES	YES
23	a	290.80	0.82217	YES	YES
24	a	318.63	2.28128	YES	YES
25	a	325.66	9.45851	YES	YES
26	a	390.03	3.45775	YES	YES
27	a	444.37	1.30062	YES	YES
28	a	460.30	7.68674	YES	YES
29	a	552.68	5.77104	YES	YES
30	a	574.17	16.30611	YES	YES
31	a	578.88	3.47374	YES	YES
32	a	601.38	48.59712	YES	YES
33	a	678.64	21.55077	YES	YES
34	a	685.27	3.44281	YES	YES
35	a	711.86	0.26818	YES	YES
36	a	725.88	0.86960	YES	YES
37	a	760.36	7.02018	YES	YES
38	a	783.05	14.87275	YES	YES
39	a	784.54	11.59590	YES	YES
40	a	819.66	406.46729	YES	YES
41	a	838.09	165.65190	YES	YES
42	a	869.11	16.23023	YES	YES
43	a	882.14	5.55566	YES	YES
44	a	891.01	51.42468	YES	YES
45	a	897.46	68.69941	YES	YES
46	a	960.37	5.17004	YES	YES
47	a	993.38	5.74551	YES	YES
48	a	1032.33	21.58070	YES	YES
49	a	1122.42	9.99127	YES	YES
50	a	1178.98	4.00946	YES	YES
51	a	1246.25	30.03667	YES	YES
52	a	1290.29	35.34772	YES	YES
53	a	1292.16	37.10866	YES	YES
54	a	1297.79	30.59975	YES	YES
55	a	1302.54	1.29008	YES	YES
56	a	1315.12	159.02418	YES	YES
57	a	1357.56	3.43174	YES	YES
58	a	1417.74	0.36171	YES	YES
59	a	1423.03	141.23508	YES	YES
60	a	1433.60	14.14575	YES	YES
61	a	1440.94	11.35083	YES	YES
62	a	1443.93	0.20267	YES	YES
63	a	1459.15	151.59702	YES	YES
64	a	1462.65	60.42924	YES	YES
65	a	1484.03	26.56189	YES	YES
66	a	1543.58	238.25629	YES	YES
67	a	1610.88	68.88488	YES	YES
68	a	1624.25	38.56666	YES	YES
69	a	2998.08	7.14112	YES	YES
70	a	3014.22	7.57063	YES	YES
71	a	3016.33	8.16486	YES	YES
72	a	3094.82	0.11487	YES	YES
73	a	3095.27	0.03068	YES	YES
74	a	3097.86	0.27472	YES	YES
75	a	3140.28	0.21590	YES	YES
76	a	3146.87	0.38875	YES	YES
77	a	3147.60	1.05297	YES	YES
78	a	3183.30	5.32683	YES	YES
79	a	3196.92	0.64795	YES	YES
80	a	3203.57	5.76026	YES	YES
81	a	3212.22	2.59053	YES	YES

CCSD(T)-DZ energy = -1096.9700840883 H (T1 = 0.011209; D1 = 0.0418)
MP2-DZ energy = -1096.7921281823 H
MP2-QZ energy = -1097.7786969341 H
CCSD(T)-QZ energy (approximated) = -1097.9566528401 H

6.3.6 Oxidative Addition Product



Method: (RI-)BP86(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:

Ga	0.20616	0.92611	-0.85215
Si	2.54515	0.23008	-0.96550
C	3.04967	-0.30487	0.76106
H	2.96547	0.50880	1.49316
H	4.10612	-0.61236	0.73497
H	2.47184	-1.16690	1.11975
C	2.55328	-1.19772	-2.18496
H	1.94315	-2.04544	-1.84735
H	3.58887	-1.55718	-2.28715
H	2.20884	-0.89621	-3.18247
C	3.50975	1.71673	-1.57492
H	3.45415	2.56350	-0.87887
H	3.16997	2.05466	-2.56236
H	4.56890	1.43188	-1.66775
H	-0.40534	-1.85370	0.27388
C	-1.03506	-0.98680	0.47537
C	-0.63274	0.03380	1.37361
H	0.32398	-0.05342	1.88784
C	-1.51009	1.08678	1.67668
H	-1.20684	1.86319	2.37703
C	-2.79385	1.12191	1.11783
H	-3.49397	1.92291	1.35024
C	-3.19097	0.11779	0.24320
F	-4.40284	0.13132	-0.30316
C	-2.31012	-0.93094	-0.09028
F	-2.71795	-1.88178	-0.92803
H	-1.12699	1.62774	-1.27950

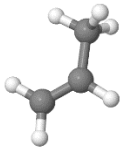
SCF energy GEOOPT = -2765.823186980 H
ZPE = 519.9 kJ/mol
FREEH energy = 566.84 kJ/mol
FREEH entropy = 0.60107 kJ/mol/K

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		-0.00	0.00000	-	-
2		-0.00	0.00000	-	-
3		-0.00	0.00000	-	-
4		-0.00	0.00000	-	-
5		-0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	9.00	0.08291	YES	YES
8	a	12.89	0.37895	YES	YES
9	a	49.40	2.89175	YES	YES
10	a	54.57	4.14744	YES	YES
11	a	71.91	19.14467	YES	YES
12	a	83.54	10.73572	YES	YES
13	a	129.08	0.32257	YES	YES
14	a	140.02	6.64400	YES	YES
15	a	156.14	0.06210	YES	YES
16	a	168.07	0.14963	YES	YES

17	a	176.68	9.12973	YES	YES
18	a	188.04	1.94034	YES	YES
19	a	190.97	4.24400	YES	YES
20	a	202.11	1.36605	YES	YES
21	a	205.81	0.64576	YES	YES
22	a	281.11	0.46470	YES	YES
23	a	294.66	1.15238	YES	YES
24	a	307.55	5.25748	YES	YES
25	a	415.16	4.41351	YES	YES
26	a	431.50	0.19878	YES	YES
27	a	443.63	1.71681	YES	YES
28	a	534.84	8.62562	YES	YES
29	a	548.85	7.67618	YES	YES
30	a	557.23	38.41150	YES	YES
31	a	560.31	2.51201	YES	YES
32	a	597.16	8.36535	YES	YES
33	a	677.24	0.00765	YES	YES
34	a	685.43	5.14845	YES	YES
35	a	687.24	4.92976	YES	YES
36	a	698.26	0.18879	YES	YES
37	a	733.24	5.53671	YES	YES
38	a	738.69	4.14519	YES	YES
39	a	758.53	17.52688	YES	YES
40	a	786.78	142.45690	YES	YES
41	a	831.69	248.69266	YES	YES
42	a	843.23	25.56971	YES	YES
43	a	847.42	45.70755	YES	YES
44	a	847.63	46.44385	YES	YES
45	a	855.97	10.04942	YES	YES
46	a	917.62	2.40585	YES	YES
47	a	963.42	5.28514	YES	YES
48	a	1011.65	14.14237	YES	YES
49	a	1089.05	16.01157	YES	YES
50	a	1147.31	2.15194	YES	YES
51	a	1210.57	22.96116	YES	YES
52	a	1245.74	20.23143	YES	YES
53	a	1247.15	19.53019	YES	YES
54	a	1255.74	31.28791	YES	YES
55	a	1257.99	0.78017	YES	YES
56	a	1280.29	150.92012	YES	YES
57	a	1353.73	2.23834	YES	YES
58	a	1397.19	0.06804	YES	YES
59	a	1402.51	0.02089	YES	YES
60	a	1403.34	1.25122	YES	YES
61	a	1410.75	9.25530	YES	YES
62	a	1414.00	14.10766	YES	YES
63	a	1422.33	4.77148	YES	YES
64	a	1438.36	16.08304	YES	YES
65	a	1494.32	286.54387	YES	YES
66	a	1563.33	31.89119	YES	YES
67	a	1573.46	24.14920	YES	YES
68	a	1913.10	152.36608	YES	YES
69	a	2965.18	0.88811	YES	YES
70	a	2965.92	0.88991	YES	YES
71	a	2967.00	0.16966	YES	YES
72	a	3037.50	2.10310	YES	YES
73	a	3039.15	1.09897	YES	YES
74	a	3041.50	0.47439	YES	YES
75	a	3056.11	2.55853	YES	YES
76	a	3059.67	1.48292	YES	YES
77	a	3061.10	0.81272	YES	YES
78	a	3112.13	0.49479	YES	YES
79	a	3121.10	3.55855	YES	YES
80	a	3133.71	2.08676	YES	YES
81	a	3143.85	4.67455	YES	YES

6.3.7 Propylene



Method: (RI-)BP86(D3BJ)/def2-TZVPP
Symmetry: cs

Cartesian coordinates in Ångström:

C	-1.2831402	0.5488629	0.0000000
C	0.0524548	0.5445213	0.0000000
H	-1.8522606	1.4781376	0.0000000
H	-1.8548911	-0.3815232	0.0000000
H	0.5818811	1.5028675	0.0000000
C	0.9107875	-0.6829742	0.0000000
H	0.3048634	-1.5985028	0.0000000
H	1.5701524	-0.7056945	0.8815405
H	1.5701524	-0.7056945	-0.8815405

SCF energy GEOOPT = -117.9613790223 H
ZPE = 203.0 kJ/mol
FREEH energy = 213.90 kJ/mol
FREEH entropy = 0.26572 kJ/mol/K

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		-0.00	0.00000	-	-
2		-0.00	0.00000	-	-
3		-0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a"	203.39	0.58854	YES	YES
8	a'	412.25	1.07167	YES	YES
9	a"	572.65	12.96592	YES	YES
10	a"	902.55	44.21762	YES	YES
11	a'	909.85	3.64539	YES	YES
12	a'	917.71	3.73156	YES	YES
13	a"	995.12	12.08393	YES	YES
14	a"	1031.94	2.29287	YES	YES
15	a'	1157.18	0.36429	YES	YES
16	a'	1289.53	0.07192	YES	YES
17	a'	1358.94	2.48063	YES	YES
18	a'	1403.56	1.11072	YES	YES
19	a"	1430.47	7.06690	YES	YES
20	a'	1445.92	15.54274	YES	YES
21	a'	1661.48	16.09282	YES	YES
22	a'	2950.73	23.89806	YES	YES
23	a"	2997.99	16.18280	YES	YES
24	a'	3032.99	6.01242	YES	YES
25	a'	3056.35	33.93681	YES	YES
26	a'	3062.35	3.99585	YES	YES
27	a'	3147.33	17.36253	YES	YES

Total COSMO energy + OC correction = -117.9636476727 H

Method: (RI-)B3LYP(D3BJ)/def2-TZVPP
Symmetry: cs

Cartesian coordinates in Ångström:

C	-1.2770426	0.5471180	0.0000000
C	0.0500130	0.5434705	0.0000000
H	-1.8422261	1.4696168	0.0000000
H	-1.8454874	-0.3758320	0.0000000
H	0.5759076	1.4942771	0.0000000

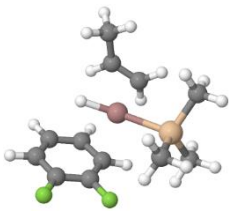
```
C      0.9086231   -0.6818384    0.0000000
H      0.3068598   -1.5910271    0.0000000
H      1.5616764   -0.7028924    0.8766231
H      1.5616764   -0.7028924   -0.8766231

SCF energy GEOOPT = -117.8809716550 H
ZPE = 208.6 kJ/mol
FREEH energy = 219.27 kJ/mol
FREEH entropy = 0.26470 kJ/mol/K

$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection rules
#                         cm**(-1)        km/mol          IR     RAMAN
     1                      -0.00         0.00000         -       -
     2                      -0.00         0.00000         -       -
     3                      -0.00         0.00000         -       -
     4                       0.00         0.00000         -       -
     5                       0.00         0.00000         -       -
     6                       0.00         0.00000         -       -
     7        a"           206.39         0.48105       YES     YES
     8        a'           428.18         1.05636       YES     YES
     9        a"           592.43        12.64295       YES     YES
    10        a'           926.67         3.33967       YES     YES
    11        a"           947.97        47.33450       YES     YES
    12        a'           951.81         3.18348       YES     YES
    13        a"          1028.10        10.57105       YES     YES
    14        a"          1074.34         2.61962       YES     YES
    15        a'          1194.06         0.31883       YES     YES
    16        a'          1331.54         0.04522       YES     YES
    17        a'          1410.85         1.90850       YES     YES
    18        a'          1452.94         0.84478       YES     YES
    19        a"          1479.66         6.85067       YES     YES
    20        a'          1494.79        14.87714       YES     YES
    21        a'          1711.26        15.45890       YES     YES
    22        a'          3015.92        24.27925       YES     YES
    23        a"          3058.18        18.87475       YES     YES
    24        a'          3093.43        10.42870       YES     YES
    25        a'          3125.26        29.34219       YES     YES
    26        a'          3131.44         3.75746       YES     YES
    27        a'          3213.15        17.38193       YES     YES

Total COSMO energy + OC correction = -117.8831638547 H
```

6.3.8 [HGaSiMe$_3$(*o*DFB)(propylene)]$^+$



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Method: (RI-)BP86(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:
C          1.09567        0.59339       -1.29952
H          1.88919        0.00824       -0.83454
C          1.03654        1.99700       -1.17628
H          1.74889        2.50552       -0.52841
C          0.11152        2.72999       -1.92221
H          0.07552        3.81420       -1.83573
C         -0.76225        2.08082       -2.79691
```

H	-1.49105	2.63279	-3.38876
C	-0.70836	0.69502	-2.93066
C	0.22915	-0.04519	-2.20174
F	-1.53114	0.05703	-3.76778
F	0.30659	-1.37258	-2.37776
Ga	-0.61351	0.26216	0.61372
C	0.72668	1.29150	2.30528
C	-0.14302	2.33459	2.19924
H	0.62515	0.56176	3.10997
H	1.66672	1.28075	1.75163
C	-1.34000	2.53743	3.05920
H	0.05496	3.10381	1.44751
H	-1.51939	1.69314	3.73536
H	-2.23945	2.72745	2.45695
H	-1.18882	3.44160	3.67072
Si	-0.17873	-2.05526	1.23520
C	-0.58057	-2.19779	3.06736
C	1.62607	-2.43919	0.88957
C	-1.34911	-3.08777	0.19368
H	2.30862	-1.76203	1.42009
H	1.85356	-2.40346	-0.18339
H	1.84547	-3.46030	1.23576
H	-2.39970	-2.83393	0.38602
H	-1.21086	-4.14913	0.45022
H	-1.15568	-2.97420	-0.87977
H	0.12227	-1.64125	3.70071
H	-0.51002	-3.25707	3.35777
H	-1.60029	-1.86333	3.29878
H	-1.68343	1.28352	0.10102

SCF energy GEOOPT = -2883.817778650 H
ZPE = 729.1 kJ/mol
FREEH energy = 789.63 kJ/mol
FREEH entropy = 0.68942 kJ/mol/K

$vibrational spectrum

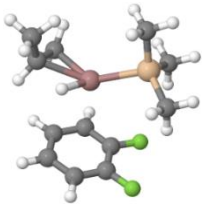
# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		-0.00	0.00000	-	-
2		-0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	19.31	0.14213	YES	YES
8	a	30.45	0.29589	YES	YES
9	a	36.96	0.04814	YES	YES
10	a	51.23	0.79894	YES	YES
11	a	56.93	0.87147	YES	YES
12	a	63.46	0.11448	YES	YES
13	a	82.88	0.39255	YES	YES
14	a	94.21	0.94536	YES	YES
15	a	109.32	2.16593	YES	YES
16	a	116.69	8.52433	YES	YES
17	a	143.69	1.16051	YES	YES
18	a	147.86	6.43471	YES	YES
19	a	152.92	0.42881	YES	YES
20	a	164.63	2.40255	YES	YES
21	a	171.45	3.89060	YES	YES
22	a	177.32	1.69803	YES	YES
23	a	183.09	5.25880	YES	YES
24	a	190.68	5.39994	YES	YES
25	a	199.50	7.87373	YES	YES
26	a	209.27	0.84538	YES	YES
27	a	210.57	0.62132	YES	YES
28	a	274.93	3.49704	YES	YES
29	a	280.21	0.40132	YES	YES
30	a	293.91	6.68323	YES	YES
31	a	315.59	10.26770	YES	YES

32	a	413.18	1.40573	YES	YES
33	a	430.34	0.15879	YES	YES
34	a	450.04	0.49031	YES	YES
35	a	528.44	47.04924	YES	YES
36	a	538.39	5.76597	YES	YES
37	a	550.50	12.92577	YES	YES
38	a	556.53	21.09079	YES	YES
39	a	564.99	18.81106	YES	YES
40	a	600.29	8.80449	YES	YES
41	a	663.95	24.38765	YES	YES
42	a	676.30	0.46146	YES	YES
43	a	682.91	6.21594	YES	YES
44	a	686.09	4.97977	YES	YES
45	a	693.56	1.28968	YES	YES
46	a	731.47	3.08255	YES	YES
47	a	737.04	6.73223	YES	YES
48	a	756.97	21.52039	YES	YES
49	a	762.73	93.85912	YES	YES
50	a	828.91	248.95593	YES	YES
51	a	838.81	32.33677	YES	YES
52	a	844.67	49.34207	YES	YES
53	a	845.69	48.32583	YES	YES
54	a	854.77	13.05599	YES	YES
55	a	896.75	32.38940	YES	YES
56	a	916.20	7.45545	YES	YES
57	a	923.52	27.86528	YES	YES
58	a	928.89	21.92532	YES	YES
59	a	966.52	0.30218	YES	YES
60	a	989.02	8.03027	YES	YES
61	a	1021.14	6.01731	YES	YES
62	a	1027.72	4.16039	YES	YES
63	a	1093.23	15.45413	YES	YES
64	a	1150.11	2.23766	YES	YES
65	a	1170.31	2.67244	YES	YES
66	a	1200.17	35.65520	YES	YES
67	a	1243.09	30.68291	YES	YES
68	a	1243.52	21.96685	YES	YES
69	a	1248.85	19.71517	YES	YES
70	a	1255.78	0.90277	YES	YES
71	a	1272.11	99.58308	YES	YES
72	a	1280.65	1.03273	YES	YES
73	a	1345.40	4.41858	YES	YES
74	a	1355.68	20.28243	YES	YES
75	a	1388.54	17.77984	YES	YES
76	a	1399.70	0.95666	YES	YES
77	a	1404.18	0.23751	YES	YES
78	a	1406.35	1.94745	YES	YES
79	a	1412.82	8.69413	YES	YES
80	a	1416.93	13.82170	YES	YES
81	a	1420.87	10.38554	YES	YES
82	a	1424.55	2.37690	YES	YES
83	a	1439.57	24.05629	YES	YES
84	a	1443.48	19.49014	YES	YES
85	a	1491.31	163.54220	YES	YES
86	a	1573.93	15.87094	YES	YES
87	a	1582.88	31.12912	YES	YES
88	a	1585.87	32.75685	YES	YES
89	a	1921.44	111.41797	YES	YES
90	a	2962.82	2.32081	YES	YES
91	a	2965.63	0.95496	YES	YES
92	a	2967.17	0.82762	YES	YES
93	a	2967.62	0.23631	YES	YES
94	a	3018.21	0.84548	YES	YES
95	a	3037.31	1.87412	YES	YES
96	a	3038.55	2.49091	YES	YES
97	a	3042.08	0.64454	YES	YES
98	a	3055.87	3.02534	YES	YES
99	a	3057.37	1.12953	YES	YES
100	a	3057.97	1.88597	YES	YES

101	a	3058.50	2.50214	YES	YES
102	a	3067.04	0.67833	YES	YES
103	a	3080.46	5.60124	YES	YES
104	a	3111.02	2.22879	YES	YES
105	a	3124.79	0.14899	YES	YES
106	a	3133.73	2.21566	YES	YES
107	a	3144.31	1.52996	YES	YES
108	a	3147.90	0.82355	YES	YES

Total COSMO energy + OC correction = -2883.8785054308 H

6.3.9 Transition State Hydrometalation



Method: (RI-)BP86(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:

C	2.72357	-0.71997	-1.79078
H	3.76794	-0.98110	-1.61486
C	2.35410	0.51418	-2.36973
H	3.12080	1.26475	-2.55416
C	1.02912	0.74537	-2.74758
H	0.74687	1.69494	-3.19782
C	0.06327	-0.24600	-2.56839
H	-0.97504	-0.08892	-2.85735
C	0.42264	-1.47449	-2.01625
C	1.74636	-1.71881	-1.64493
F	-0.49013	-2.43760	-1.84609
F	2.08520	-2.91455	-1.14399
Ga	2.47459	0.34356	0.50031
C	3.98232	1.76994	0.44644
C	2.83677	2.62826	0.29124
H	4.49776	1.79777	1.40786
H	4.63511	1.62618	-0.41478
C	2.35328	3.48885	1.41896
H	2.59652	2.97415	-0.71579
H	2.44266	2.98346	2.38902
H	1.32238	3.83058	1.27952
H	3.00684	4.37617	1.45592
Si	1.91943	-1.33992	2.17512
C	1.89646	-0.30258	3.74098
C	3.29759	-2.60448	2.16149
C	0.24083	-2.04868	1.75547
H	4.27526	-2.14667	2.35857
H	3.34770	-3.14558	1.20901
H	3.10686	-3.34270	2.95564
H	-0.52327	-1.26640	1.66716
H	-0.06398	-2.72556	2.56863
H	0.25437	-2.63567	0.82957
H	2.86742	0.16760	3.94284
H	1.66738	-0.96406	4.59113
H	1.12375	0.47612	3.71042
H	1.44786	1.63400	0.21454

SCF energy GEOOPT = -2883.795134491 H
ZPE = 727.5 kJ/mol

FREEH energy = 785.62 kJ/mol
FREEH entropy = 0.68054 kJ/mol/K

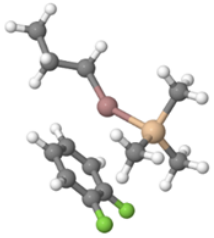
$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1	a	-725.79	0.00000	YES	YES
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7		0.00	0.00000	-	-
8	a	7.14	0.48189	YES	YES
9	a	29.01	1.58927	YES	YES
10	a	40.92	0.27917	YES	YES
11	a	48.30	0.15743	YES	YES
12	a	51.13	0.06726	YES	YES
13	a	64.59	1.03367	YES	YES
14	a	74.50	1.38686	YES	YES
15	a	105.95	0.75060	YES	YES
16	a	117.97	10.66098	YES	YES
17	a	125.84	3.66127	YES	YES
18	a	150.97	0.49088	YES	YES
19	a	156.06	0.92699	YES	YES
20	a	165.26	3.37910	YES	YES
21	a	168.89	0.66585	YES	YES
22	a	175.75	0.77156	YES	YES
23	a	185.34	3.81793	YES	YES
24	a	196.83	8.67495	YES	YES
25	a	210.35	1.48486	YES	YES
26	a	215.18	0.91095	YES	YES
27	a	237.40	1.21394	YES	YES
28	a	280.73	0.04817	YES	YES
29	a	286.29	14.86897	YES	YES
30	a	294.57	19.55816	YES	YES
31	a	399.83	4.66966	YES	YES
32	a	407.08	5.97961	YES	YES
33	a	429.59	0.21603	YES	YES
34	a	454.29	1.02271	YES	YES
35	a	496.05	30.92470	YES	YES
36	a	537.28	3.15486	YES	YES
37	a	551.30	2.34838	YES	YES
38	a	562.60	2.53326	YES	YES
39	a	597.73	18.65792	YES	YES
40	a	678.41	0.10161	YES	YES
41	a	681.86	4.06884	YES	YES
42	a	686.73	3.80659	YES	YES
43	a	694.69	19.89440	YES	YES
44	a	699.09	2.47553	YES	YES
45	a	719.80	44.19346	YES	YES
46	a	732.21	2.87252	YES	YES
47	a	743.74	5.05960	YES	YES
48	a	757.99	15.70409	YES	YES
49	a	768.07	95.31982	YES	YES
50	a	824.39	300.98654	YES	YES
51	a	837.88	12.35322	YES	YES
52	a	850.05	47.77906	YES	YES
53	a	851.85	42.21730	YES	YES
54	a	857.52	39.36262	YES	YES
55	a	877.93	42.60216	YES	YES
56	a	903.73	30.17112	YES	YES
57	a	923.84	13.31158	YES	YES
58	a	929.99	1.97042	YES	YES
59	a	968.53	0.30010	YES	YES
60	a	987.73	18.66160	YES	YES
61	a	1018.76	7.79661	YES	YES
62	a	1089.17	7.41014	YES	YES
63	a	1092.58	20.91906	YES	YES

64	a	1149.16	1.52998	YES	YES
65	a	1169.07	1.58753	YES	YES
66	a	1196.65	5.13836	YES	YES
67	a	1199.38	23.16332	YES	YES
68	a	1240.34	28.62393	YES	YES
69	a	1244.41	22.05031	YES	YES
70	a	1246.36	23.21775	YES	YES
71	a	1256.49	2.19874	YES	YES
72	a	1270.09	91.49374	YES	YES
73	a	1343.44	1.25167	YES	YES
74	a	1347.54	9.01692	YES	YES
75	a	1367.17	17.03659	YES	YES
76	a	1394.79	0.02198	YES	YES
77	a	1402.58	2.70957	YES	YES
78	a	1404.42	0.34009	YES	YES
79	a	1409.19	9.59241	YES	YES
80	a	1412.28	7.19924	YES	YES
81	a	1419.00	22.13974	YES	YES
82	a	1424.24	7.15031	YES	YES
83	a	1437.30	15.05033	YES	YES
84	a	1440.10	3.90229	YES	YES
85	a	1443.35	6.05139	YES	YES
86	a	1490.16	156.94587	YES	YES
87	a	1572.38	14.51763	YES	YES
88	a	1588.95	34.38947	YES	YES
89	a	1659.12	54.66504	YES	YES
90	a	2960.10	0.78440	YES	YES
91	a	2963.02	0.47732	YES	YES
92	a	2967.78	0.10113	YES	YES
93	a	2968.79	0.10129	YES	YES
94	a	3028.92	3.02167	YES	YES
95	a	3037.06	1.36337	YES	YES
96	a	3043.12	0.88569	YES	YES
97	a	3043.89	0.16260	YES	YES
98	a	3058.34	2.25064	YES	YES
99	a	3061.11	1.66084	YES	YES
100	a	3069.47	0.54906	YES	YES
101	a	3071.87	4.71505	YES	YES
102	a	3072.68	0.71376	YES	YES
103	a	3092.31	2.29558	YES	YES
104	a	3107.14	4.26322	YES	YES
105	a	3126.65	0.47385	YES	YES
106	a	3134.10	2.20364	YES	YES
107	a	3143.23	0.29410	YES	YES
108	a	3145.15	1.18897	YES	YES

Total COSMO energy + OC correction = -2883.8548496527 H

6.3.10 [(*n*Pr)GaSiMe$_3$(*o*DFB)]$^+$



Method: (RI-)BP86(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:

C	-2.03447	1.07742	-0.65455
H	-2.43619	1.23783	-1.65416
C	-1.01405	1.88704	-0.12954
H	-0.62865	2.71687	-0.72012
C	-0.53507	1.66567	1.17626
H	0.23072	2.31708	1.59543
C	-1.09167	0.65116	1.96686
H	-0.75428	0.47349	2.98647
C	-2.11839	-0.13049	1.44897
C	-2.58661	0.07835	0.14347
F	-2.66282	-1.10755	2.18340
F	-3.57199	-0.69245	-0.32518
Ga	0.97710	0.09871	-0.67189
C	2.05043	1.52381	-1.54095
C	2.54022	2.66252	-0.62797
H	2.90709	0.99602	-1.99410
H	1.45219	1.91922	-2.37847
C	3.42009	3.65924	-1.38839
H	1.67960	3.19583	-0.19559
H	4.30972	3.16528	-1.80128
H	3.75934	4.46722	-0.72763
H	2.86961	4.11313	-2.22369
Si	0.62802	-2.26761	-0.05341
C	2.14580	-2.99722	-0.89621
C	-0.95609	-2.93930	-0.79125
C	0.72349	-2.45832	1.80894
H	-1.06252	-2.69195	-1.85498
H	-1.85240	-2.59755	-0.26215
H	-0.92423	-4.03678	-0.70961
H	1.58624	-1.93637	2.24198
H	0.83976	-3.52964	2.03390
H	-0.18693	-2.11307	2.31144
H	2.13120	-2.85769	-1.98522
H	2.15753	-4.08129	-0.70399
H	3.08573	-2.58549	-0.50535
H	3.10489	2.25145	0.22316

SCF energy GEOOPT = -2883.841086341 H
ZPE = 741.9 kJ/mol
FREEH energy = 801.17 kJ/mol
FREEH entropy = 0.68803 kJ/mol/K

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		-0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	17.87	0.64641	YES	YES
8	a	24.79	0.05424	YES	YES
9	a	33.34	0.42460	YES	YES

10	a	52.14	2.24516	YES	YES
11	a	58.87	0.06320	YES	YES
12	a	63.20	0.00651	YES	YES
13	a	66.00	0.11351	YES	YES
14	a	74.69	0.92707	YES	YES
15	a	106.05	1.33226	YES	YES
16	a	122.70	0.52984	YES	YES
17	a	143.66	2.27136	YES	YES
18	a	150.99	3.23404	YES	YES
19	a	154.22	4.53456	YES	YES
20	a	162.05	6.82669	YES	YES
21	a	166.58	0.35645	YES	YES
22	a	176.74	0.99948	YES	YES
23	a	193.35	1.06388	YES	YES
24	a	202.68	2.93817	YES	YES
25	a	212.67	0.22305	YES	YES
26	a	218.61	2.67767	YES	YES
27	a	243.37	0.06337	YES	YES
28	a	263.05	14.61040	YES	YES
29	a	281.37	0.32892	YES	YES
30	a	302.57	4.26169	YES	YES
31	a	318.04	0.17706	YES	YES
32	a	430.75	0.14530	YES	YES
33	a	446.92	3.91284	YES	YES
34	a	537.26	3.07672	YES	YES
35	a	555.54	0.10500	YES	YES
36	a	562.19	3.29919	YES	YES
37	a	577.20	12.37420	YES	YES
38	a	598.28	10.19408	YES	YES
39	a	631.48	18.66216	YES	YES
40	a	675.92	0.10943	YES	YES
41	a	681.30	6.19766	YES	YES
42	a	686.81	3.29122	YES	YES
43	a	703.94	0.12908	YES	YES
44	a	729.49	2.60037	YES	YES
45	a	740.29	5.79348	YES	YES
46	a	760.21	19.27821	YES	YES
47	a	769.49	7.50542	YES	YES
48	a	787.37	135.17033	YES	YES
49	a	829.57	211.52652	YES	YES
50	a	843.55	28.37968	YES	YES
51	a	846.84	17.50144	YES	YES
52	a	847.89	34.62836	YES	YES
53	a	850.11	23.33942	YES	YES
54	a	874.93	1.13479	YES	YES
55	a	928.39	2.73747	YES	YES
56	a	957.40	0.96588	YES	YES
57	a	966.35	4.61837	YES	YES
58	a	1008.69	1.39868	YES	YES
59	a	1014.54	12.28513	YES	YES
60	a	1031.74	17.49881	YES	YES
61	a	1094.66	10.67421	YES	YES
62	a	1142.62	2.04462	YES	YES
63	a	1145.49	23.20746	YES	YES
64	a	1195.22	1.94702	YES	YES
65	a	1203.85	25.31668	YES	YES
66	a	1245.01	18.24988	YES	YES
67	a	1247.50	20.22621	YES	YES
68	a	1255.70	5.67929	YES	YES
69	a	1258.68	7.20920	YES	YES
70	a	1273.63	120.50302	YES	YES
71	a	1287.00	0.97436	YES	YES
72	a	1309.05	1.74554	YES	YES
73	a	1349.66	1.29122	YES	YES
74	a	1369.30	0.65544	YES	YES
75	a	1389.04	5.16674	YES	YES
76	a	1397.04	0.01096	YES	YES
77	a	1401.63	1.93557	YES	YES
78	a	1402.40	0.35385	YES	YES

79	a	1411.30	8.71008	YES	YES
80	a	1412.03	7.44251	YES	YES
81	a	1421.63	2.97176	YES	YES
82	a	1439.52	13.93105	YES	YES
83	a	1443.26	11.83730	YES	YES
84	a	1449.30	11.79582	YES	YES
85	a	1456.70	4.63229	YES	YES
86	a	1495.26	188.28314	YES	YES
87	a	1576.35	33.67418	YES	YES
88	a	1580.68	12.52496	YES	YES
89	a	2941.89	2.10052	YES	YES
90	a	2956.19	19.38770	YES	YES
91	a	2962.29	0.19124	YES	YES
92	a	2969.90	0.06015	YES	YES
93	a	2970.68	0.06375	YES	YES
94	a	2971.23	21.81030	YES	YES
95	a	2976.95	3.74121	YES	YES
96	a	2997.83	11.17236	YES	YES
97	a	3035.70	0.93345	YES	YES
98	a	3042.52	21.91332	YES	YES
99	a	3042.90	0.69056	YES	YES
100	a	3044.02	0.50200	YES	YES
101	a	3048.25	13.81184	YES	YES
102	a	3054.31	1.56082	YES	YES
103	a	3075.26	1.07882	YES	YES
104	a	3078.27	0.79017	YES	YES
105	a	3118.55	0.15049	YES	YES
106	a	3127.64	0.23336	YES	YES
107	a	3136.89	4.29658	YES	YES
108	a	3141.86	2.17773	YES	YES

Total COSMO energy + OC correction = -2883.9046861716 H

Method: (RI-)B3LYP(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:

C	-1.61404	0.41644	-2.00917
H	-1.46249	0.50311	-3.07596
C	-1.27611	1.44965	-1.13248
H	-0.87951	2.37479	-1.52579
C	-1.50896	1.31202	0.24200
H	-1.28635	2.12831	0.91470
C	-2.09183	0.14667	0.73985
H	-2.29740	0.02127	1.79335
C	-2.43733	-0.86466	-0.13802
C	-2.19977	-0.73196	-1.50410
F	-2.98240	-1.99138	0.31426
F	-2.53605	-1.72810	-2.31744
Ga	1.15437	0.38234	-0.28698
C	2.04159	2.14122	-0.50790
C	1.53070	3.30506	0.35519
H	3.09817	1.94523	-0.29368
H	1.98822	2.39530	-1.57154
C	2.37819	4.56367	0.17192
H	0.49371	3.53192	0.09796
H	3.41413	4.38352	0.46172
H	1.99651	5.38209	0.78242
H	2.37377	4.88953	-0.86930
Si	1.22028	-2.06340	0.13670
C	0.56460	-3.00249	-1.33704
C	0.31850	-2.44778	1.72694
C	3.07344	-2.28352	0.32618
H	-0.76266	-2.38470	1.62114
H	0.62899	-1.80104	2.54797
H	0.56081	-3.47543	2.01156

```
H          3.62015       -2.01853       -0.57973
H          3.27566       -3.33818        0.53259
H          3.48112       -1.70550        1.15656
H         -0.51798       -2.94830       -1.42979
H          0.82960       -4.05552       -1.20727
H          1.00961       -2.66812       -2.27447
H          1.53018        3.02120        1.41088

SCF energy GEOOPT = -2883.011185549 H
ZPE = 762.3 kJ/mol
FREEH energy = 820.27 kJ/mol
FREEH entropy = 0.67719 kJ/mol/K

$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection rules
#                         cm**(-1)        km/mol          IR     RAMAN
     1                       -0.00         0.00000        -       -
     2                       -0.00         0.00000        -       -
     3                       -0.00         0.00000        -       -
     4                       -0.00         0.00000        -       -
     5                        0.00         0.00000        -       -
     6                        0.00         0.00000        -       -
     7        a              18.00         0.45392      YES     YES
     8        a              27.25         0.28658      YES     YES
     9        a              36.27         0.49398      YES     YES
    10        a              52.91         2.63191      YES     YES
    11        a              62.17         0.03643      YES     YES
    12        a              63.11         0.07412      YES     YES
    13        a              70.14         0.15245      YES     YES
    14        a              77.85         1.18884      YES     YES
    15        a             109.54         1.09759      YES     YES
    16        a             129.43         0.14691      YES     YES
    17        a             148.52         2.00347      YES     YES
    18        a             157.46         0.57674      YES     YES
    19        a             158.21         7.15564      YES     YES
    20        a             167.49         6.76122      YES     YES
    21        a             172.15         0.82881      YES     YES
    22        a             182.35         1.12538      YES     YES
    23        a             199.53         0.39879      YES     YES
    24        a             210.40         3.65286      YES     YES
    25        a             220.97         0.20801      YES     YES
    26        a             226.23         4.22646      YES     YES
    27        a             250.79         0.24458      YES     YES
    28        a             270.52        18.67125      YES     YES
    29        a             291.74         0.44552      YES     YES
    30        a             314.77         5.76594      YES     YES
    31        a             326.24         0.04102      YES     YES
    32        a             445.78         0.17216      YES     YES
    33        a             467.36         3.89675      YES     YES
    34        a             554.80         3.55338      YES     YES
    35        a             576.66         0.14304      YES     YES
    36        a             582.86         3.51848      YES     YES
    37        a             592.54        11.23330      YES     YES
    38        a             610.07        13.78421      YES     YES
    39        a             649.28        18.43452      YES     YES
    40        a             700.85         6.87125      YES     YES
    41        a             702.40         1.69260      YES     YES
    42        a             707.31         4.33904      YES     YES
    43        a             735.85         0.05668      YES     YES
    44        a             754.40         2.28682      YES     YES
    45        a             764.05         5.89064      YES     YES
    46        a             783.57        20.30481      YES     YES
    47        a             798.01         7.14733      YES     YES
    48        a             817.95       147.11794      YES     YES
    49        a             858.38       221.03664      YES     YES
    50        a             871.75        14.79760      YES     YES
    51        a             874.70        40.99009      YES     YES
    52        a             876.68        50.34284      YES     YES
    53        a             888.33         0.54867      YES     YES
```

54	a	896.20	1.20309	YES	YES
55	a	973.52	3.28968	YES	YES
56	a	999.20	4.02458	YES	YES
57	a	1005.72	0.62335	YES	YES
58	a	1029.76	1.37551	YES	YES
59	a	1042.16	15.36027	YES	YES
60	a	1067.50	15.61230	YES	YES
61	a	1128.14	10.07152	YES	YES
62	a	1180.46	3.12530	YES	YES
63	a	1194.40	19.04661	YES	YES
64	a	1239.16	1.77317	YES	YES
65	a	1242.26	27.90726	YES	YES
66	a	1298.87	21.60123	YES	YES
67	a	1300.65	14.35188	YES	YES
68	a	1301.78	15.14849	YES	YES
69	a	1309.84	67.82953	YES	YES
70	a	1313.17	63.86884	YES	YES
71	a	1331.47	1.10088	YES	YES
72	a	1348.20	0.26758	YES	YES
73	a	1361.31	1.53990	YES	YES
74	a	1421.50	0.73712	YES	YES
75	a	1439.16	5.17326	YES	YES
76	a	1447.07	0.01042	YES	YES
77	a	1451.47	1.18771	YES	YES
78	a	1451.72	1.48470	YES	YES
79	a	1460.73	8.26973	YES	YES
80	a	1461.12	7.23532	YES	YES
81	a	1470.04	3.40768	YES	YES
82	a	1488.71	15.86802	YES	YES
83	a	1492.76	11.25191	YES	YES
84	a	1498.17	11.28547	YES	YES
85	a	1506.79	4.18428	YES	YES
86	a	1545.42	185.91288	YES	YES
87	a	1627.12	37.47152	YES	YES
88	a	1631.58	12.38082	YES	YES
89	a	3004.20	1.25184	YES	YES
90	a	3022.45	17.47423	YES	YES
91	a	3023.43	0.17086	YES	YES
92	a	3030.77	0.13161	YES	YES
93	a	3031.38	0.18842	YES	YES
94	a	3034.71	22.04466	YES	YES
95	a	3039.70	3.30314	YES	YES
96	a	3059.39	14.15734	YES	YES
97	a	3090.79	1.11319	YES	YES
98	a	3096.90	0.87541	YES	YES
99	a	3097.86	0.75062	YES	YES
100	a	3100.78	26.56943	YES	YES
101	a	3105.97	17.31381	YES	YES
102	a	3108.00	2.35118	YES	YES
103	a	3134.32	0.92042	YES	YES
104	a	3138.00	0.86859	YES	YES
105	a	3191.59	0.25652	YES	YES
106	a	3199.99	0.24827	YES	YES
107	a	3208.41	4.74631	YES	YES
108	a	3211.98	1.32302	YES	YES

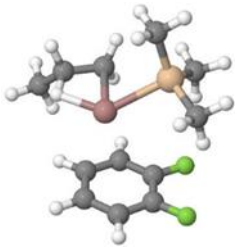
CCSD(T)-DZ energy = -1214.6805948872 H (T1 = 0.010912; D1 = 0.0394)

MP2-DZ energy = -1214.4528620812 H

MP2-QZ energy = -1215.5856772072 H

CCSD(T)-QZ energy (approximated) = -1215.8134100132 H

6.3.11 Transition State Reductive Elimination



```
Method: (RI-)BP86(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:
C         -1.01000        1.36665       -1.13364
H         -0.40809        1.44342       -2.03691
C         -0.91136        2.30940       -0.08791
H         -0.22112        3.14601       -0.18379
C         -1.78694        2.24263        1.01247
H         -1.72347        2.98963        1.80109
C         -2.73093        1.22376        1.09710
H         -3.41718        1.14532        1.93869
C         -2.80094        0.26943        0.08157
C         -1.95483        0.34401       -1.03116
F         -3.68977       -0.72712        0.15049
F         -2.07063       -0.57085       -2.00630
Ga         0.73442        0.38783        0.73213
C          2.30555        0.45751       -0.86537
C          2.67731        1.60993       -0.01891
H          3.00881       -0.37280       -0.88451
H          1.88905        0.68926       -1.84665
C          2.64069        2.99707       -0.65507
H          1.92852        1.74466        0.95907
H          3.51179        3.10160       -1.31463
H          2.67486        3.79879        0.09242
H          1.74629        3.13004       -1.27717
Si         0.90787       -2.05581        0.11982
C          0.92235       -2.36676       -1.71408
C         -0.65317       -2.70188        0.92021
C          2.45314       -2.53961        1.04945
H         -1.55880       -2.36739        0.40075
H         -0.72508       -2.42639        1.97871
H         -0.62268       -3.80230        0.85250
H          3.36915       -2.13391        0.60581
H          2.51911       -3.63917        1.00746
H          2.40888       -2.25433        2.10771
H          0.09249       -1.86037       -2.22096
H          0.78144       -3.44992       -1.86137
H          1.86450       -2.07549       -2.18988
H          3.59127        1.42962        0.56362

SCF energy GEOOPT = -2883.780076202 H
ZPE = 732.7 kJ/mol
FREEH energy = 789.84 kJ/mol
FREEH entropy = 0.66488 kJ/mol/K

$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection rules
```

#		cm**(-1)	km/mol	IR	RAMAN
1	a	-132.84	0.00000	YES	YES
2		-0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7		0.00	0.00000	-	-
8	a	8.39	0.61071	YES	YES
9	a	28.59	0.29252	YES	YES
10	a	45.11	0.12577	YES	YES
11	a	55.18	0.91816	YES	YES
12	a	65.78	0.08501	YES	YES
13	a	81.96	0.45625	YES	YES
14	a	105.92	1.56069	YES	YES
15	a	116.90	0.98356	YES	YES
16	a	130.13	7.59656	YES	YES
17	a	139.05	10.76307	YES	YES
18	a	144.28	5.09134	YES	YES
19	a	150.83	2.41001	YES	YES
20	a	176.30	7.64954	YES	YES
21	a	179.78	1.32832	YES	YES
22	a	189.15	2.60559	YES	YES
23	a	199.69	12.46493	YES	YES
24	a	205.91	0.53367	YES	YES
25	a	213.94	3.24410	YES	YES
26	a	218.31	0.35450	YES	YES
27	a	260.85	19.92497	YES	YES
28	a	263.93	26.15901	YES	YES
29	a	281.40	1.22614	YES	YES
30	a	289.71	1.19794	YES	YES
31	a	354.27	15.12690	YES	YES
32	a	414.93	4.66543	YES	YES
33	a	430.44	0.16585	YES	YES
34	a	450.47	1.83037	YES	YES
35	a	534.53	1.94705	YES	YES
36	a	539.30	2.84002	YES	YES
37	a	561.45	2.72732	YES	YES
38	a	590.40	6.42485	YES	YES
39	a	596.93	23.49027	YES	YES
40	a	666.93	3.56090	YES	YES
41	a	673.81	4.45231	YES	YES
42	a	682.13	0.26608	YES	YES
43	a	694.92	0.08217	YES	YES
44	a	705.67	0.90574	YES	YES
45	a	740.82	8.54214	YES	YES
46	a	752.90	4.83796	YES	YES
47	a	758.16	19.80913	YES	YES
48	a	773.36	140.15145	YES	YES
49	a	786.44	3.51948	YES	YES
50	a	818.05	274.49605	YES	YES
51	a	837.75	6.34226	YES	YES
52	a	847.51	6.42472	YES	YES
53	a	855.91	62.63493	YES	YES
54	a	857.34	49.45846	YES	YES
55	a	900.27	0.61504	YES	YES
56	a	918.22	2.46516	YES	YES
57	a	933.41	8.15175	YES	YES
58	a	960.43	2.87112	YES	YES
59	a	1013.01	11.12962	YES	YES
60	a	1021.81	24.53065	YES	YES
61	a	1072.93	18.21786	YES	YES
62	a	1093.78	13.87440	YES	YES
63	a	1139.22	1.58708	YES	YES
64	a	1147.33	1.85442	YES	YES
65	a	1198.62	25.39438	YES	YES
66	a	1206.20	11.36865	YES	YES
67	a	1238.94	28.88315	YES	YES
68	a	1243.64	37.18841	YES	YES

69	a	1250.21	16.55415	YES	YES
70	a	1255.76	1.39456	YES	YES
71	a	1271.73	104.76491	YES	YES
72	a	1298.63	8.23621	YES	YES
73	a	1345.60	7.17402	YES	YES
74	a	1364.04	3.65671	YES	YES
75	a	1383.75	0.31874	YES	YES
76	a	1396.57	5.11986	YES	YES
77	a	1399.83	4.47331	YES	YES
78	a	1403.04	0.74466	YES	YES
79	a	1403.85	4.43580	YES	YES
80	a	1419.03	8.22449	YES	YES
81	a	1421.36	2.07991	YES	YES
82	a	1437.98	18.05061	YES	YES
83	a	1444.63	13.92042	YES	YES
84	a	1445.69	2.68594	YES	YES
85	a	1489.28	167.56189	YES	YES
86	a	1530.38	15.17878	YES	YES
87	a	1571.16	10.46811	YES	YES
88	a	1582.27	41.97427	YES	YES
89	a	1705.09	35.93274	YES	YES
90	a	2957.02	0.89266	YES	YES
91	a	2963.16	2.67351	YES	YES
92	a	2966.20	0.58763	YES	YES
93	a	2978.46	8.68185	YES	YES
94	a	3005.99	2.23655	YES	YES
95	a	3041.63	0.70670	YES	YES
96	a	3042.87	0.26669	YES	YES
97	a	3048.54	0.57291	YES	YES
98	a	3049.96	6.48744	YES	YES
99	a	3058.93	9.55001	YES	YES
100	a	3064.78	3.30998	YES	YES
101	a	3077.13	0.88499	YES	YES
102	a	3079.16	0.24224	YES	YES
103	a	3086.09	0.17602	YES	YES
104	a	3122.86	0.22229	YES	YES
105	a	3135.64	1.24250	YES	YES
106	a	3139.48	2.60918	YES	YES
107	a	3147.07	2.23843	YES	YES
108	a	3147.68	3.04150	YES	YES

Total COSMO energy + OC correction = -2883.8397345555 H

Method: (RI-)B3LYP(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:

C	-0.99057	1.50573	-1.04676
H	-0.36528	1.60626	-1.92176
C	-0.99962	2.46563	-0.02628
H	-0.34612	3.32288	-0.09570
C	-1.89561	2.35238	1.03780
H	-1.91058	3.10431	1.81292
C	-2.77034	1.27789	1.10417
H	-3.47193	1.16537	1.91856
C	-2.74562	0.31622	0.10580
C	-1.87047	0.43304	-0.96655
F	-3.56230	-0.73557	0.15865
F	-1.87946	-0.50126	-1.92384
Ga	0.77040	0.32859	0.74139
C	2.30180	0.41996	-0.81756
C	2.65332	1.63640	-0.03044
H	3.05670	-0.35443	-0.82292
H	1.90441	0.60663	-1.80856
C	2.59513	2.97424	-0.76185
H	1.92520	1.80397	0.90400
H	3.42196	3.02462	-1.46977

```
H          2.67589        3.81622       -0.07549
H          1.67177        3.07665       -1.33121
Si         0.92900       -2.18604        0.11631
C          0.98070       -2.42110       -1.71765
C         -0.65795       -2.77816        0.87908
C          2.45375       -2.64832        1.06822
H         -1.53721       -2.39458        0.36431
H         -0.72661       -2.53237        1.93720
H         -0.67054       -3.86981        0.77979
H          3.36230       -2.22247        0.64746
H          2.54067       -3.73906        1.01457
H          2.38258       -2.37799        2.12105
H          0.17292       -1.88742       -2.21572
H          0.83152       -3.48944       -1.90796
H          1.93097       -2.12506       -2.15525
H          3.58171        1.50855        0.52675

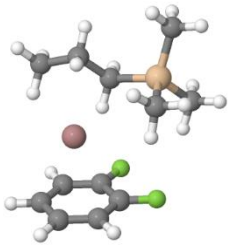
SCF energy GEOOPT = -2882.941657363 H
ZPE = 753.8 kJ/mol
FREEH energy = 810.02 kJ/mol
FREEH entropy = 0.65324 kJ/mol/K

$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection rules
#                         cm**(-1)       km/mol          IR     RAMAN
     1        a            -154.63        0.00000       YES     YES
     2                       -0.00        0.00000         -       -
     3                       -0.00        0.00000         -       -
     4                        0.00        0.00000         -       -
     5                        0.00        0.00000         -       -
     6                        0.00        0.00000         -       -
     7                        0.00        0.00000         -       -
     8        a              21.08        0.93927       YES     YES
     9        a              31.15        0.52601       YES     YES
    10        a              46.30        0.01183       YES     YES
    11        a              58.05        1.20660       YES     YES
    12        a              66.78        0.41778       YES     YES
    13        a              76.07        0.69450       YES     YES
    14        a             100.24        8.86698       YES     YES
    15        a             112.51        9.84164       YES     YES
    16        a             119.49       20.56505       YES     YES
    17        a             137.36       12.75182       YES     YES
    18        a             140.36        2.69002       YES     YES
    19        a             158.19        0.38389       YES     YES
    20        a             172.95        6.89648       YES     YES
    21        a             180.31        3.56613       YES     YES
    22        a             192.59        2.30200       YES     YES
    23        a             203.05       11.81686       YES     YES
    24        a             206.37        7.96233       YES     YES
    25        a             213.60        8.39276       YES     YES
    26        a             224.18        1.03535       YES     YES
    27        a             247.09       46.74052       YES     YES
    28        a             289.38        5.98077       YES     YES
    29        a             291.29        0.64360       YES     YES
    30        a             301.78        0.86776       YES     YES
    31        a             337.75       14.53412       YES     YES
    32        a             428.59        5.01813       YES     YES
    33        a             445.01        0.17078       YES     YES
    34        a             467.38        1.30497       YES     YES
    35        a             553.76        3.71011       YES     YES
    36        a             561.04        2.21933       YES     YES
    37        a             580.74        4.35194       YES     YES
    38        a             589.21        1.39960       YES     YES
    39        a             606.16       31.92786       YES     YES
    40        a             687.33        4.16089       YES     YES
    41        a             693.61        5.46078       YES     YES
    42        a             712.19        0.19939       YES     YES
    43        a             724.97        0.13435       YES     YES
    44        a             748.68        3.49252       YES     YES
```

45	a	768.89	6.97176	YES	YES
46	a	777.07	5.33394	YES	YES
47	a	780.94	23.06360	YES	YES
48	a	796.93	135.75633	YES	YES
49	a	836.24	80.70460	YES	YES
50	a	846.20	228.26543	YES	YES
51	a	867.52	10.34117	YES	YES
52	a	884.46	4.85968	YES	YES
53	a	889.28	63.14743	YES	YES
54	a	890.93	57.57414	YES	YES
55	a	932.10	6.41593	YES	YES
56	a	966.37	8.16156	YES	YES
57	a	970.30	6.54881	YES	YES
58	a	1009.17	0.94325	YES	YES
59	a	1045.08	8.71559	YES	YES
60	a	1065.54	3.97302	YES	YES
61	a	1092.25	27.39568	YES	YES
62	a	1127.62	17.66319	YES	YES
63	a	1184.80	1.39417	YES	YES
64	a	1187.62	1.95299	YES	YES
65	a	1233.63	27.79671	YES	YES
66	a	1276.23	9.39917	YES	YES
67	a	1292.34	51.69126	YES	YES
68	a	1294.29	27.67332	YES	YES
69	a	1296.71	23.28381	YES	YES
70	a	1306.27	49.81894	YES	YES
71	a	1308.38	37.19388	YES	YES
72	a	1340.16	14.05238	YES	YES
73	a	1343.05	1.38639	YES	YES
74	a	1416.12	2.81296	YES	YES
75	a	1430.67	0.28083	YES	YES
76	a	1443.21	6.93540	YES	YES
77	a	1446.87	6.09736	YES	YES
78	a	1450.61	2.01327	YES	YES
79	a	1451.57	0.97893	YES	YES
80	a	1467.64	7.68956	YES	YES
81	a	1468.85	1.90472	YES	YES
82	a	1487.65	16.30082	YES	YES
83	a	1493.91	7.78399	YES	YES
84	a	1496.03	4.12185	YES	YES
85	a	1540.35	164.00870	YES	YES
86	a	1555.97	9.75682	YES	YES
87	a	1626.80	9.58420	YES	YES
88	a	1636.17	30.54743	YES	YES
89	a	1977.41	111.56445	YES	YES
90	a	3013.04	2.18816	YES	YES
91	a	3020.41	4.03125	YES	YES
92	a	3023.48	1.02525	YES	YES
93	a	3045.32	11.08413	YES	YES
94	a	3073.36	1.27084	YES	YES
95	a	3098.72	0.23336	YES	YES
96	a	3101.30	0.21992	YES	YES
97	a	3107.68	0.63301	YES	YES
98	a	3114.08	9.63019	YES	YES
99	a	3117.77	7.95546	YES	YES
100	a	3121.44	6.23765	YES	YES
101	a	3138.06	0.52537	YES	YES
102	a	3141.18	0.30650	YES	YES
103	a	3148.37	0.29189	YES	YES
104	a	3196.51	5.55476	YES	YES
105	a	3199.10	1.05536	YES	YES
106	a	3205.96	0.53399	YES	YES
107	a	3211.24	2.46987	YES	YES
108	a	3218.01	0.65998	YES	YES

CCSD(T)-DZ energy = -1214.6120358830 H (T1 = 0.012759; D1 = 0.0774)
MP2-DZ energy = -1214.3856063253 H
MP2-QZ energy = -1215.5212173206 H
CCSD(T)-QZ energy (approximated) = -1215.7476468783 H

6.3.12 [Ga(SiMe$_3$^{n}Pr)(*o*DFB)]$^+$



Method: (RI-)BP86(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:

C	-1.92087	2.21926	-0.47101
H	-1.80358	2.63762	-1.46975
C	-1.93717	3.03133	0.67297
H	-1.82595	4.10883	0.56611
C	-2.10712	2.46078	1.94192
H	-2.12815	3.09178	2.82859
C	-2.25898	1.07342	2.07890
H	-2.40170	0.60571	3.05227
C	-2.25535	0.26552	0.93857
C	-2.08981	0.83854	-0.33593
F	-2.41822	-1.05598	1.04173
F	-2.10136	0.04800	-1.41221
Ga	0.50944	1.41014	1.00339
C	1.54515	-0.16558	-1.33784
C	2.67073	0.81577	-0.97971
H	1.55578	-0.34185	-2.42605
H	0.54679	0.30624	-1.18747
C	2.47292	2.21380	-1.56562
H	2.80059	0.88933	0.12320
H	2.39265	2.17071	-2.65964
H	3.29359	2.89381	-1.30545
H	1.53331	2.67647	-1.20638
Si	1.57605	-1.85125	-0.44560
C	3.27035	-2.62262	-0.65284
C	0.21014	-2.92896	-1.13815
C	1.25089	-1.55272	1.40357
H	0.36642	-3.12401	-2.20801
H	-0.77710	-2.46088	-1.02466
H	0.17828	-3.90066	-0.62647
H	1.96934	-0.85892	1.86968
H	1.35270	-2.49959	1.95524
H	0.22143	-1.21202	1.60752
H	3.51452	-2.76008	-1.71535
H	3.30881	-3.61139	-0.17531
H	4.06193	-2.00798	-0.20267
H	3.63132	0.40019	-1.31535

SCF energy GEOOPT = -2883.857999889 H
ZPE = 739.6 kJ/mol
FREEH energy = 798.29 kJ/mol
FREEH entropy = 0.67896 kJ/mol/K

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	15.44	0.38916	YES	YES

8	a	29.69	0.09411	YES	YES
9	a	38.63	0.06132	YES	YES
10	a	50.42	5.44716	YES	YES
11	a	54.04	1.49881	YES	YES
12	a	77.59	8.00991	YES	YES
13	a	82.10	1.60178	YES	YES
14	a	90.81	1.24833	YES	YES
15	a	101.50	1.09370	YES	YES
16	a	113.13	2.22389	YES	YES
17	a	121.25	30.86879	YES	YES
18	a	150.29	0.00501	YES	YES
19	a	165.22	1.10151	YES	YES
20	a	166.75	4.18969	YES	YES
21	a	190.31	0.05931	YES	YES
22	a	194.00	0.11786	YES	YES
23	a	196.64	1.84320	YES	YES
24	a	216.21	4.56594	YES	YES
25	a	226.61	8.67989	YES	YES
26	a	235.07	11.59935	YES	YES
27	a	259.31	1.47542	YES	YES
28	a	280.08	0.47831	YES	YES
29	a	288.12	4.06063	YES	YES
30	a	297.45	1.34719	YES	YES
31	a	333.91	3.92261	YES	YES
32	a	430.44	0.06329	YES	YES
33	a	443.92	6.01168	YES	YES
34	a	536.08	2.84343	YES	YES
35	a	541.33	0.95380	YES	YES
36	a	561.86	3.79777	YES	YES
37	a	575.89	2.47681	YES	YES
38	a	591.37	0.31779	YES	YES
39	a	659.72	0.51748	YES	YES
40	a	661.40	4.78622	YES	YES
41	a	666.58	3.05518	YES	YES
42	a	689.18	0.09663	YES	YES
43	a	690.85	2.76265	YES	YES
44	a	704.73	14.51765	YES	YES
45	a	746.66	7.20372	YES	YES
46	a	756.62	22.26848	YES	YES
47	a	773.20	15.66040	YES	YES
48	a	776.33	88.80498	YES	YES
49	a	832.75	47.54710	YES	YES
50	a	835.35	61.10807	YES	YES
51	a	841.70	116.36076	YES	YES
52	a	845.29	22.53873	YES	YES
53	a	858.96	0.61902	YES	YES
54	a	881.11	11.20461	YES	YES
55	a	934.68	4.91892	YES	YES
56	a	953.57	20.05211	YES	YES
57	a	967.61	0.05131	YES	YES
58	a	1017.13	0.92653	YES	YES
59	a	1019.19	3.22425	YES	YES
60	a	1047.93	16.24685	YES	YES
61	a	1095.90	10.80827	YES	YES
62	a	1151.14	1.30009	YES	YES
63	a	1166.85	7.40547	YES	YES
64	a	1176.37	5.97317	YES	YES
65	a	1204.26	19.06856	YES	YES
66	a	1228.67	24.36774	YES	YES
67	a	1251.15	36.44629	YES	YES
68	a	1257.33	13.83906	YES	YES
69	a	1258.22	26.79588	YES	YES
70	a	1260.43	2.75444	YES	YES
71	a	1273.32	78.62912	YES	YES
72	a	1308.59	3.52911	YES	YES
73	a	1339.63	0.60284	YES	YES
74	a	1370.71	5.50797	YES	YES
75	a	1393.60	5.74357	YES	YES
76	a	1400.26	1.25825	YES	YES

77	a	1406.14	0.12955	YES	YES
78	a	1408.59	0.34441	YES	YES
79	a	1419.08	2.78748	YES	YES
80	a	1421.48	6.21678	YES	YES
81	a	1424.89	9.29501	YES	YES
82	a	1427.21	4.42382	YES	YES
83	a	1441.81	28.76558	YES	YES
84	a	1444.89	3.51447	YES	YES
85	a	1453.18	13.23522	YES	YES
86	a	1491.74	195.73660	YES	YES
87	a	1573.10	16.52612	YES	YES
88	a	1573.69	9.90167	YES	YES
89	a	2826.11	20.31910	YES	YES
90	a	2832.31	181.30089	YES	YES
91	a	2896.89	76.60488	YES	YES
92	a	2930.27	59.33003	YES	YES
93	a	2969.00	1.17350	YES	YES
94	a	2970.69	0.91849	YES	YES
95	a	2974.17	3.67256	YES	YES
96	a	2996.91	10.74651	YES	YES
97	a	2999.73	6.09929	YES	YES
98	a	3013.24	32.40538	YES	YES
99	a	3015.88	6.46512	YES	YES
100	a	3045.75	5.29686	YES	YES
101	a	3046.12	0.92258	YES	YES
102	a	3047.85	5.05430	YES	YES
103	a	3048.91	6.12326	YES	YES
104	a	3054.36	8.60673	YES	YES
105	a	3127.34	1.99798	YES	YES
106	a	3132.62	0.50309	YES	YES
107	a	3138.31	7.40955	YES	YES
108	a	3145.81	2.54892	YES	YES

Method: (RI-)B3LYP(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:

C	-2.13723	1.90170	-1.22633
H	-1.72843	2.55701	-1.98275
C	-2.88148	2.39303	-0.15191
H	-3.05511	3.45602	-0.06692
C	-3.40990	1.51675	0.79589
H	-3.99546	1.89627	1.62072
C	-3.19663	0.14231	0.67926
H	-3.60461	-0.55939	1.39343
C	-2.46441	-0.34563	-0.39626
C	-1.93845	0.53169	-1.34829
F	-2.25840	-1.65040	-0.53641
F	-1.24797	0.03877	-2.37041
Ga	-0.41670	1.27553	1.16127
C	1.94873	0.40522	-0.72827
C	2.56215	1.42431	0.23869
H	2.43943	0.50119	-1.70168
H	0.90086	0.66621	-0.95621
C	2.32952	2.87610	-0.17144
H	2.19005	1.26726	1.26463
H	2.74379	3.06921	-1.16125
H	2.78218	3.57675	0.52993
H	1.25940	3.11463	-0.23326
Si	2.02400	-1.41640	-0.19253
C	1.36952	-2.48419	-1.57872
C	0.91134	-1.62601	1.32694
C	3.78137	-1.85497	0.26666
H	-0.14891	-1.49160	1.08705

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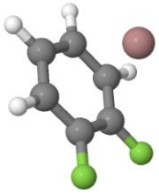
H          1.18807       -0.96438        2.15337
H          0.99339       -2.64345        1.71591
H          4.45949       -1.68871       -0.57253
H          3.85728       -2.90744        0.54560
H          4.14384       -1.26478        1.11012
H          0.34843       -2.21286       -1.85175
H          1.36707       -3.53748       -1.29264
H          1.98870       -2.38830       -2.47245
H          3.63341        1.23640        0.32438

SCF energy GEOOPT = -2883.032126768 H
ZPE = 760.3 kJ/mol
FREEH energy = 817.95 kJ/mol
FREEH entropy = 0.67323 kJ/mol/K

$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection rules
#                         cm**(-1)        km/mol          IR     RAMAN
     1                      -0.00         0.00000        -       -
     2                      -0.00         0.00000        -       -
     3                       0.00         0.00000        -       -
     4                       0.00         0.00000        -       -
     5                       0.00         0.00000        -       -
     6                       0.00         0.00000        -       -
     7        a             15.29         0.40431       YES     YES
     8        a             31.10         0.31919       YES     YES
     9        a             40.15         0.11794       YES     YES
    10        a             54.76         2.93568       YES     YES
    11        a             56.59         3.71634       YES     YES
    12        a             72.63        10.62572       YES     YES
    13        a             80.98         2.41468       YES     YES
    14        a             88.00         2.14879       YES     YES
    15        a             99.21         0.48535       YES     YES
    16        a            114.15         3.76977       YES     YES
    17        a            121.17        24.96204       YES     YES
    18        a            150.56         1.92852       YES     YES
    19        a            153.30         0.90196       YES     YES
    20        a            169.63         0.03094       YES     YES
    21        a            197.29         0.06105       YES     YES
    22        a            200.58         2.51600       YES     YES
    23        a            201.14         0.17094       YES     YES
    24        a            217.77         0.31409       YES     YES
    25        a            225.47         9.20674       YES     YES
    26        a            243.26        12.52196       YES     YES
    27        a            261.96         1.91710       YES     YES
    28        a            290.86         0.49933       YES     YES
    29        a            293.95         3.44403       YES     YES
    30        a            308.44         1.02781       YES     YES
    31        a            344.77         4.94380       YES     YES
    32        a            445.43         0.09268       YES     YES
    33        a            465.33         5.63214       YES     YES
    34        a            554.43         4.15583       YES     YES
    35        a            562.63         0.24280       YES     YES
    36        a            582.23         4.42282       YES     YES
    37        a            594.60         1.78106       YES     YES
    38        a            623.99         0.92132       YES     YES
    39        a            680.16         8.04956       YES     YES
    40        a            686.60         2.54489       YES     YES
    41        a            689.88         5.68557       YES     YES
    42        a            708.10         4.96737       YES     YES
    43        a            722.50         0.07553       YES     YES
    44        a            733.60        12.77959       YES     YES
    45        a            772.73         8.44771       YES     YES
    46        a            780.01        25.03982       YES     YES
    47        a            805.93       101.00749       YES     YES
    48        a            807.63         3.04345       YES     YES
    49        a            861.32        49.46176       YES     YES
    50        a            863.01        62.86033       YES     YES
    51        a            871.01        89.26451       YES     YES
```

52	a	872.46	53.07083	YES	YES
53	a	897.23	0.08392	YES	YES
54	a	902.97	15.24257	YES	YES
55	a	977.64	5.52006	YES	YES
56	a	995.04	20.76377	YES	YES
57	a	1011.60	0.04220	YES	YES
58	a	1039.17	0.47415	YES	YES
59	a	1046.04	3.43568	YES	YES
60	a	1079.63	16.05338	YES	YES
61	a	1127.96	9.76784	YES	YES
62	a	1186.14	0.93548	YES	YES
63	a	1219.22	7.90881	YES	YES
64	a	1227.57	5.84054	YES	YES
65	a	1242.76	20.32578	YES	YES
66	a	1278.28	24.78876	YES	YES
67	a	1301.31	9.88807	YES	YES
68	a	1302.37	41.18080	YES	YES
69	a	1307.69	79.06097	YES	YES
70	a	1311.15	9.14535	YES	YES
71	a	1312.20	32.68203	YES	YES
72	a	1338.72	0.09346	YES	YES
73	a	1362.81	4.10388	YES	YES
74	a	1422.95	4.52638	YES	YES
75	a	1450.24	3.65196	YES	YES
76	a	1453.50	0.98726	YES	YES
77	a	1455.20	0.06525	YES	YES
78	a	1458.35	0.56550	YES	YES
79	a	1467.48	2.73689	YES	YES
80	a	1470.45	6.79904	YES	YES
81	a	1475.51	8.55439	YES	YES
82	a	1480.06	3.09118	YES	YES
83	a	1489.10	28.79474	YES	YES
84	a	1497.41	2.77842	YES	YES
85	a	1508.17	12.77541	YES	YES
86	a	1541.36	201.10311	YES	YES
87	a	1622.74	22.28230	YES	YES
88	a	1624.25	7.67397	YES	YES
89	a	2910.70	24.54097	YES	YES
90	a	2918.81	179.27612	YES	YES
91	a	2971.99	85.08357	YES	YES
92	a	2997.28	66.05600	YES	YES
93	a	3028.90	1.35486	YES	YES
94	a	3030.82	0.92210	YES	YES
95	a	3037.72	6.56434	YES	YES
96	a	3056.78	15.31914	YES	YES
97	a	3062.75	8.42598	YES	YES
98	a	3076.52	40.90403	YES	YES
99	a	3079.66	8.62018	YES	YES
100	a	3098.59	2.37294	YES	YES
101	a	3099.38	5.28260	YES	YES
102	a	3100.77	8.66386	YES	YES
103	a	3103.06	8.37811	YES	YES
104	a	3110.31	11.02999	YES	YES
105	a	3197.51	1.68850	YES	YES
106	a	3203.17	0.35846	YES	YES
107	a	3208.61	7.60484	YES	YES
108	a	3215.73	2.18383	YES	YES

6.3.13 [Ga(*o*DFB)]$^+$



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Method: (RI-)BP86(D3BJ)/def2-TZVPP
Symmetry: cs

Cartesian coordinates in Ångström:
Ga   -0.7429500   -2.1449242    0.0000000
C     0.0926330    0.1505535    1.4102153
C     1.2085925   -0.3308467    0.7026370
C     1.2085925   -0.3308467   -0.7026370
C     0.0926330    0.1505535   -1.4102153
C    -1.0116069    0.6475681   -0.7065575
C    -1.0116069    0.6475681    0.7065575
F    -2.0646529    1.1302566   -1.3535416
F    -2.0646529    1.1302566    1.3535416
H     0.0711583    0.1697149    2.4995842
H     2.0755839   -0.6944722    1.2518877
H     2.0755839   -0.6944722   -1.2518877
H     0.0711583    0.1697149   -2.4995842

SCF energy GEOOPT = -2355.847550274 H
ZPE = 217.8 kJ/mol
FREEH energy = 239.26 kJ/mol
FREEH entropy = 0.38139 kJ/mol/K

$vibrational spectrum
#  mode     symmetry     wave number    IR intensity    selection rules
#                         cm**(-1)        km/mol          IR     RAMAN
     1                       -0.00         0.00000         -       -
     2                       -0.00         0.00000         -       -
     3                       -0.00         0.00000         -       -
     4                       -0.00         0.00000         -       -
     5                       -0.00         0.00000         -       -
     6                       -0.00         0.00000         -       -
     7        a'             88.05         2.78736       YES     YES
     8        a"             98.48         0.03716       YES     YES
     9        a'            172.71        23.13988       YES     YES
    10        a"            194.30         0.18545       YES     YES
    11        a'            280.06         0.71309       YES     YES
    12        a'            302.94         1.33765       YES     YES
    13        a"            430.51         0.16200       YES     YES
    14        a'            443.24         5.67129       YES     YES
    15        a"            533.16         1.29456       YES     YES
    16        a"            539.37         2.93512       YES     YES
    17        a'            560.26         3.29810       YES     YES
    18        a"            680.02         0.32012       YES     YES
    19        a'            756.98        18.11613       YES     YES
    20        a'            791.43        87.88387       YES     YES
    21        a"            848.88        11.98297       YES     YES
    22        a"            860.79         1.48753       YES     YES
    23        a'            930.34         3.13321       YES     YES
    24        a"            958.56         0.05110       YES     YES
    25        a'           1016.53         3.93637       YES     YES
    26        a"           1094.76         8.40521       YES     YES
    27        a'           1151.58         1.25464       YES     YES
    28        a"           1212.37        16.32096       YES     YES
    29        a"           1264.63        23.04236       YES     YES
    30        a'           1284.06       116.23664       YES     YES
    31        a'           1338.24         1.11234       YES     YES
    32        a"           1437.96        38.84850       YES     YES
    33        a'           1493.45       271.83102       YES     YES
```

34	a'	1558.52	33.82505	YES	YES
35	a"	1565.48	14.23280	YES	YES
36	a"	3125.54	3.87092	YES	YES
37	a'	3130.04	0.01660	YES	YES
38	a"	3135.43	17.34408	YES	YES
39	a'	3142.82	6.44413	YES	YES

Total COSMO energy + OC correction = -2355.9254826099 H

Method: (RI-)B3LYP(D3BJ)/def2-TZVPP
Symmetry: cs

Cartesian coordinates in Ångström:

Ga	-0.7755043	-2.2021792	0.0000000
C	0.0954325	0.1563922	1.4025573
C	1.2048239	-0.3246352	0.6988592
C	1.2048239	-0.3246352	-0.6988592
C	0.0954325	0.1563922	-1.4025573
C	-1.0020297	0.6477000	-0.7011691
C	-1.0020297	0.6477000	0.7011691
F	-2.0522963	1.1253253	-1.3447300
F	-2.0522963	1.1253253	1.3447300
H	0.0753107	0.1795712	2.4836150
H	2.0666052	-0.6831615	1.2434702
H	2.0666052	-0.6831615	-1.2434702
H	0.0753107	0.1795712	-2.4836150

SCF energy GEOOPT = -2355.266974613 H
ZPE = 223.9 kJ/mol
FREEH energy = 245.02 kJ/mol
FREEH entropy = 0.38116 kJ/mol/K

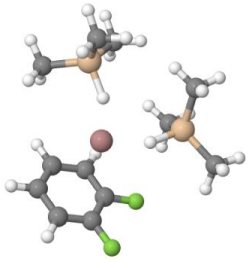
$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		-0.00	0.00000	-	-
2		-0.00	0.00000	-	-
3		-0.00	0.00000	-	-
4		-0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a'	81.60	3.64508	YES	YES
8	a"	93.56	0.10582	YES	YES
9	a'	151.31	25.46430	YES	YES
10	a"	199.31	0.15126	YES	YES
11	a'	290.44	0.69022	YES	YES
12	a'	312.43	1.21033	YES	YES
13	a"	445.35	0.18911	YES	YES
14	a'	463.55	5.46962	YES	YES
15	a"	553.26	3.52103	YES	YES
16	a"	558.37	1.32874	YES	YES
17	a'	580.82	3.91733	YES	YES
18	a"	710.49	0.30312	YES	YES
19	a'	780.13	20.39903	YES	YES
20	a'	819.07	92.00235	YES	YES
21	a"	875.46	14.13081	YES	YES
22	a"	896.75	0.46435	YES	YES
23	a'	973.38	3.60174	YES	YES
24	a"	1002.59	0.04894	YES	YES
25	a'	1043.57	4.81361	YES	YES
26	a"	1126.62	7.81309	YES	YES
27	a'	1186.81	0.92714	YES	YES
28	a"	1250.20	20.47802	YES	YES
29	a"	1306.08	22.46182	YES	YES
30	a'	1319.58	128.66401	YES	YES
31	a'	1341.27	0.55797	YES	YES
32	a"	1485.63	38.34730	YES	YES
33	a'	1542.09	268.84700	YES	YES

34	a'	1609.66	35.65192	YES	YES
35	a"	1616.59	13.71945	YES	YES
36	a"	3196.77	3.07741	YES	YES
37	a'	3201.55	0.01117	YES	YES
38	a"	3206.77	15.78726	YES	YES
39	a'	3213.99	5.15442	YES	YES

Total COSMO energy + OC correction = -2355.3470376193 H

6.3.14 $[Ga(HSiMe_3)_2(oDFB)]^+$



Method: (RI-)BP86(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:

H	-1.7812785	-0.3755286	-2.5739298
Ga	-1.8898056	0.9300408	1.1527266
H	-2.9503283	0.6593447	4.8199694
H	-2.9820220	-1.4369098	3.4648418
H	-0.8309622	-2.6782252	-0.6602189
C	-2.0703233	0.3606371	4.2537608
C	-0.7452971	-0.0257650	-2.6701434
C	-2.0908346	-0.8132566	3.4903216
H	-0.7606547	1.0637690	-2.8068331
H	-0.3336446	-0.4669520	-3.5891490
C	0.2050612	-2.3507218	-0.8159517
C	-0.9207127	1.1562894	4.2960583
H	-0.3542244	0.1958559	0.0095972
H	-0.8806575	2.0740654	4.8805969
Si	0.2999553	-0.5209006	-1.1969680
C	-0.9513280	-1.2089639	2.7695452
H	0.6122929	-2.9302234	-1.6569574
H	-0.9287745	-2.1311259	2.1911890
H	0.7939157	-2.6041756	0.0747912
C	0.2091712	0.7694354	3.5773328
C	0.1980231	-0.4174773	2.8252448
F	1.3211304	1.5101524	3.6015229
C	2.0434192	0.1414761	-1.2749524
F	1.3069713	-0.7842609	2.1671664
H	2.0543602	1.2292691	-1.4228273
H	2.5798643	-0.3158813	-2.1189534
H	2.6005286	-0.0880899	-0.3579299
H	-2.5878208	-0.8301698	0.2124597
H	-4.5998742	-2.5003168	1.7036948
Si	-3.9766883	-1.2147547	-0.3426428
H	-5.0787831	-0.7886335	1.8579773
C	-5.0073651	-1.6360580	1.1623885
H	-3.2692083	-3.5302899	-0.9360623
C	-3.6932304	-2.6738459	-1.4764456
H	-4.7224357	1.1670100	-0.5469246
H	-3.0234583	-2.4252493	-2.3094262
C	-4.5996406	0.3133105	-1.2287219
H	-3.9317711	0.6193632	-2.0448464
H	-6.0313736	-1.8934603	0.8564440
H	-4.6532987	-2.9949267	-1.9062415

```
H    -5.5863968    0.1116239   -1.6696739

SCF energy GEOOPT = -3175.846166012 H
ZPE = 827.6 kJ/mol
FREEH energy = 899.79 kJ/mol
FREEH entropy = 0.79421 kJ/mol/K

$vibrational spectrum
```

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		-0.00	0.00000	-	-
2		-0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	15.11	0.55782	YES	YES
8	a	26.28	0.09952	YES	YES
9	a	34.00	0.79061	YES	YES
10	a	43.00	0.19720	YES	YES
11	a	48.33	0.33983	YES	YES
12	a	51.82	0.50569	YES	YES
13	a	52.19	0.00883	YES	YES
14	a	59.82	0.04920	YES	YES
15	a	68.42	0.07739	YES	YES
16	a	70.76	2.14592	YES	YES
17	a	74.44	0.45661	YES	YES
18	a	84.80	0.20705	YES	YES
19	a	112.93	9.15442	YES	YES
20	a	121.17	22.24358	YES	YES
21	a	137.59	0.04992	YES	YES
22	a	143.20	0.09396	YES	YES
23	a	149.12	2.13183	YES	YES
24	a	154.85	0.16666	YES	YES
25	a	159.72	0.12759	YES	YES
26	a	165.08	0.09012	YES	YES
27	a	175.44	0.15439	YES	YES
28	a	193.32	1.65405	YES	YES
29	a	200.94	1.07204	YES	YES
30	a	205.13	0.19647	YES	YES
31	a	206.36	0.25266	YES	YES
32	a	209.58	1.26902	YES	YES
33	a	246.67	0.96992	YES	YES
34	a	257.18	0.23231	YES	YES
35	a	280.98	0.43437	YES	YES
36	a	294.42	2.68056	YES	YES
37	a	431.06	0.07337	YES	YES
38	a	442.59	4.47971	YES	YES
39	a	536.18	2.64805	YES	YES
40	a	542.20	1.13454	YES	YES
41	a	562.69	2.83352	YES	YES
42	a	593.95	13.16242	YES	YES
43	a	599.51	6.93444	YES	YES
44	a	601.11	8.77411	YES	YES
45	a	604.15	0.80705	YES	YES
46	a	630.75	10.97887	YES	YES
47	a	644.04	29.14747	YES	YES
48	a	667.96	0.16661	YES	YES
49	a	670.49	0.15499	YES	YES
50	a	685.95	0.34012	YES	YES
51	a	707.76	9.21525	YES	YES
52	a	708.42	1.86243	YES	YES
53	a	715.99	2.36601	YES	YES
54	a	718.07	9.95870	YES	YES
55	a	757.08	19.45766	YES	YES
56	a	766.17	116.09818	YES	YES
57	a	816.73	83.35957	YES	YES
58	a	821.70	104.44819	YES	YES
59	a	827.12	14.87307	YES	YES

60	a	832.72	72.68208	YES	YES
61	a	839.78	35.11057	YES	YES
62	a	841.43	6.55972	YES	YES
63	a	845.98	95.15811	YES	YES
64	a	848.37	19.62412	YES	YES
65	a	862.74	77.10331	YES	YES
66	a	867.80	108.95834	YES	YES
67	a	887.79	121.56262	YES	YES
68	a	918.61	127.65857	YES	YES
69	a	924.06	5.22791	YES	YES
70	a	960.15	0.60125	YES	YES
71	a	1020.11	4.42921	YES	YES
72	a	1095.37	13.14233	YES	YES
73	a	1149.31	2.02346	YES	YES
74	a	1200.86	32.45479	YES	YES
75	a	1242.09	24.33445	YES	YES
76	a	1244.21	29.65160	YES	YES
77	a	1247.40	24.30659	YES	YES
78	a	1249.38	32.37334	YES	YES
79	a	1252.88	21.28413	YES	YES
80	a	1256.04	2.46938	YES	YES
81	a	1258.55	10.07277	YES	YES
82	a	1272.26	106.16670	YES	YES
83	a	1339.94	0.07887	YES	YES
84	a	1397.43	0.67409	YES	YES
85	a	1398.40	0.46741	YES	YES
86	a	1402.11	0.78727	YES	YES
87	a	1402.76	1.34970	YES	YES
88	a	1405.90	1.25438	YES	YES
89	a	1408.82	2.99034	YES	YES
90	a	1412.58	5.66780	YES	YES
91	a	1414.09	11.41944	YES	YES
92	a	1415.46	2.86459	YES	YES
93	a	1418.14	4.38764	YES	YES
94	a	1422.70	7.02300	YES	YES
95	a	1426.34	6.05499	YES	YES
96	a	1443.43	18.91618	YES	YES
97	a	1491.79	187.63929	YES	YES
98	a	1577.24	5.44908	YES	YES
99	a	1580.78	23.24428	YES	YES
100	a	1893.40	1012.14935	YES	YES
101	a	1928.47	1082.62027	YES	YES
102	a	2965.97	1.25527	YES	YES
103	a	2967.94	2.19485	YES	YES
104	a	2971.28	0.15282	YES	YES
105	a	2971.55	1.16751	YES	YES
106	a	2972.47	0.69779	YES	YES
107	a	2972.77	0.42712	YES	YES
108	a	3037.48	2.53601	YES	YES
109	a	3042.94	4.31728	YES	YES
110	a	3045.21	1.03147	YES	YES
111	a	3045.45	1.81170	YES	YES
112	a	3046.16	2.95647	YES	YES
113	a	3047.48	1.89822	YES	YES
114	a	3049.61	3.12178	YES	YES
115	a	3050.12	3.61584	YES	YES
116	a	3055.70	5.97225	YES	YES
117	a	3059.69	2.64463	YES	YES
118	a	3061.58	2.32853	YES	YES
119	a	3062.64	2.00872	YES	YES
120	a	3127.98	0.73871	YES	YES
121	a	3133.86	0.28645	YES	YES
122	a	3140.07	3.21828	YES	YES
123	a	3147.46	0.94597	YES	YES

Total COSMO energy + OC correction = -3175.9036668908 H

Method: (RI-)B3LYP(D3BJ)/def2-TZVPP

Symmetry: c1

Cartesian coordinates in Ångström:

H	-1.7212312	-0.3833538	-2.6390595
Ga	-1.8813527	1.0185988	1.1521969
H	-2.8689705	0.6178596	4.8966568
H	-2.9634221	-1.4147487	3.4784498
H	-0.7994824	-2.6523271	-0.6702114
C	-2.0105477	0.3249351	4.3099472
C	-0.6898206	-0.0389862	-2.7181809
C	-2.0656949	-0.8152249	3.5111610
H	-0.7013144	1.0400007	-2.8795122
H	-0.2596651	-0.4979726	-3.6108900
C	0.2286331	-2.3187478	-0.8120482
C	-0.8491931	1.0910909	4.3626441
H	-0.3706807	0.2222929	-0.0463790
H	-0.7813393	1.9786459	4.9757246
Si	0.3167374	-0.4978206	-1.2127821
C	-0.9511683	-1.2038905	2.7626117
H	0.6514073	-2.9007980	-1.6338581
H	-0.9559324	-2.0975222	2.1553053
H	0.8010879	-2.5542561	0.0851606
C	0.2547329	0.7084891	3.6168765
C	0.2065873	-0.4399951	2.8265889
F	1.3758949	1.4228568	3.6478543
C	2.0539473	0.1689748	-1.2568455
F	1.2886141	-0.7966651	2.1317741
H	2.0661930	1.2456179	-1.4311872
H	2.6154973	-0.3039071	-2.0656745
H	2.5789261	-0.0330483	-0.3229231
H	-2.6911214	-0.7339715	0.2017969
H	-4.6528272	-2.4190307	1.7189101
Si	-4.0409584	-1.1912996	-0.3532261
H	-5.1807726	-0.7312288	1.8106327
C	-5.0772542	-1.5920266	1.1476224
H	-3.2507503	-3.4935504	-0.8461656
C	-3.6939734	-2.6794940	-1.4209617
H	-4.8536976	1.1422583	-0.6701299
H	-3.0257742	-2.4419476	-2.2488101
C	-4.6994725	0.2708319	-1.3098189
H	-4.0312354	0.5589777	-2.1225839
H	-6.0825788	-1.8890831	0.8421198
H	-4.6292701	-3.0491485	-1.8474837
H	-5.6662566	0.0240948	-1.7534726

SCF energy GEOOPT = -3174.944543716 H
ZPE = 848.8 kJ/mol
FREEH energy = 920.06 kJ/mol
FREEH entropy = 0.79234 kJ/mol/K

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		-0.00	0.00000	-	-
2		-0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	16.96	0.48891	YES	YES
8	a	23.35	0.25449	YES	YES
9	a	32.87	0.90849	YES	YES
10	a	42.90	0.26434	YES	YES
11	a	47.27	0.50016	YES	YES
12	a	48.67	0.34440	YES	YES
13	a	53.72	0.83511	YES	YES
14	a	59.59	0.02112	YES	YES
15	a	65.07	0.19777	YES	YES
16	a	65.42	2.17680	YES	YES

17	a	71.56	0.76874	YES	YES
18	a	81.92	0.05834	YES	YES
19	a	104.80	14.25544	YES	YES
20	a	112.27	21.88157	YES	YES
21	a	122.32	4.89399	YES	YES
22	a	143.58	0.03080	YES	YES
23	a	150.10	0.02015	YES	YES
24	a	159.55	0.10416	YES	YES
25	a	166.40	0.07932	YES	YES
26	a	169.80	0.04792	YES	YES
27	a	176.07	0.06177	YES	YES
28	a	197.48	0.89552	YES	YES
29	a	206.71	1.45224	YES	YES
30	a	209.97	1.17599	YES	YES
31	a	211.13	0.04122	YES	YES
32	a	214.14	1.14976	YES	YES
33	a	254.85	0.90823	YES	YES
34	a	260.47	0.26663	YES	YES
35	a	291.62	0.45645	YES	YES
36	a	303.97	1.81664	YES	YES
37	a	445.87	0.08639	YES	YES
38	a	463.44	4.52690	YES	YES
39	a	554.36	3.81843	YES	YES
40	a	563.39	0.47377	YES	YES
41	a	583.16	3.57266	YES	YES
42	a	613.63	9.91557	YES	YES
43	a	615.12	9.15778	YES	YES
44	a	620.82	11.95621	YES	YES
45	a	626.74	1.85390	YES	YES
46	a	640.81	11.21840	YES	YES
47	a	655.70	40.41330	YES	YES
48	a	693.91	0.08087	YES	YES
49	a	696.44	0.08550	YES	YES
50	a	718.42	0.44509	YES	YES
51	a	723.05	12.70837	YES	YES
52	a	723.35	1.99788	YES	YES
53	a	728.92	11.00995	YES	YES
54	a	730.61	2.43796	YES	YES
55	a	780.17	21.27547	YES	YES
56	a	795.93	117.10770	YES	YES
57	a	848.80	91.09010	YES	YES
58	a	851.78	88.10259	YES	YES
59	a	855.53	8.09286	YES	YES
60	a	860.20	35.66432	YES	YES
61	a	865.98	48.61388	YES	YES
62	a	870.47	9.21259	YES	YES
63	a	873.07	122.86686	YES	YES
64	a	884.94	14.64373	YES	YES
65	a	895.76	119.08841	YES	YES
66	a	901.01	66.49193	YES	YES
67	a	917.60	144.44025	YES	YES
68	a	933.91	168.24264	YES	YES
69	a	968.89	5.20769	YES	YES
70	a	1006.43	0.37833	YES	YES
71	a	1047.79	4.97535	YES	YES
72	a	1128.06	13.01102	YES	YES
73	a	1185.05	1.48981	YES	YES
74	a	1238.52	36.06140	YES	YES
75	a	1295.12	29.02026	YES	YES
76	a	1296.46	46.91817	YES	YES
77	a	1298.21	3.47374	YES	YES
78	a	1300.03	28.33065	YES	YES
79	a	1301.63	38.89861	YES	YES
80	a	1305.96	26.71557	YES	YES
81	a	1309.72	5.35071	YES	YES
82	a	1310.19	83.17761	YES	YES
83	a	1337.76	0.42879	YES	YES
84	a	1448.38	0.41824	YES	YES
85	a	1448.57	0.60514	YES	YES

86	a	1451.74	0.54287	YES	YES
87	a	1452.26	1.49651	YES	YES
88	a	1454.92	1.09895	YES	YES
89	a	1458.15	2.93042	YES	YES
90	a	1461.70	6.91645	YES	YES
91	a	1463.37	9.85380	YES	YES
92	a	1464.04	2.81106	YES	YES
93	a	1466.84	4.35093	YES	YES
94	a	1470.60	7.29636	YES	YES
95	a	1475.21	5.80673	YES	YES
96	a	1491.22	18.72581	YES	YES
97	a	1541.96	184.97543	YES	YES
98	a	1628.61	5.91915	YES	YES
99	a	1631.53	24.31240	YES	YES
100	a	1933.88	1400.04633	YES	YES
101	a	1960.79	1134.03717	YES	YES
102	a	3027.59	0.88949	YES	YES
103	a	3028.44	2.74295	YES	YES
104	a	3032.06	0.74745	YES	YES
105	a	3032.36	0.58642	YES	YES
106	a	3033.05	0.40100	YES	YES
107	a	3035.38	0.79048	YES	YES
108	a	3093.73	2.47946	YES	YES
109	a	3097.54	5.93208	YES	YES
110	a	3098.97	1.61310	YES	YES
111	a	3099.61	2.91410	YES	YES
112	a	3100.62	1.95349	YES	YES
113	a	3102.35	5.91498	YES	YES
114	a	3102.65	5.04763	YES	YES
115	a	3103.45	4.95368	YES	YES
116	a	3110.82	9.01971	YES	YES
117	a	3114.80	4.21843	YES	YES
118	a	3114.82	0.18647	YES	YES
119	a	3119.32	4.00801	YES	YES
120	a	3198.54	0.75637	YES	YES
121	a	3205.24	0.38822	YES	YES
122	a	3210.75	2.90583	YES	YES
123	a	3217.71	0.55457	YES	YES

```
Total COSMO energy + OC correction = -3175.0036867883 H
```

6.3.15 H_2

```
Method: (RI-)BP86(D3BJ)/def2-TZVPP
Symmetry: d6h

Cartesian coordinates in Ångström:
H     0.0000000    0.0000000   -0.3748385
H     0.0000000    0.0000000    0.3748385

SCF energy GEOOPT = -1.1779528498 H
ZPE = 25.86 kJ/mol
FREEH energy = 32.05 kJ/mol
FREEH entropy = 0.13068 kJ/mol/K

$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection rules
#                         cm**(-1)        km/mol         IR     RAMAN
     1                       -0.00         0.00000        -       -
     2                        0.00         0.00000        -       -
     3                        0.00         0.00000        -       -
     4                        0.00         0.00000        -       -
```

```
     5                        0.00         0.00000        -       -
     6        a1g          4322.77         0.00000       NO      YES

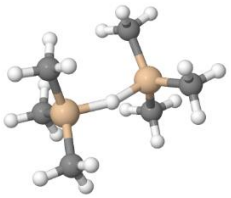

Method: (RI-)B3LYP(D3BJ)/def2-TZVPP
Symmetry: d6h

Cartesian coordinates in Ångström:
H     0.0000000    0.0000000   -0.3714262
H     0.0000000    0.0000000    0.3714262

SCF energy GEOOPT = -1.1735255118 H
ZPE = 26.41 kJ/mol
FREEH energy = 32.61 kJ/mol
FREEH entropy = 0.13053 kJ/mol/K

$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection rules
#                         cm**(-1)        km/mol          IR     RAMAN
     1                        0.00         0.00000        -       -
     2                        0.00         0.00000        -       -
     3                        0.00         0.00000        -       -
     4                        0.00         0.00000        -       -
     5                        0.00         0.00000        -       -
     6        a1g          4415.27         0.00000       NO      YES
```

6.3.16 $[H(SiMe_3)_2]^+$



```
Method: (RI-)BP86(D3BJ)/def2-TZVPP
Symmetry: c2

Cartesian coordinates in Ångström:
H     1.0796845   -2.7829932   -1.7316325
H     0.6077833   -3.3774893    1.5746527
H    -2.0594129   -2.8983926   -0.4403395
Si   -0.0638610   -1.5842761    0.0589370
C    -1.8753724   -1.8274669   -0.2634791
C     0.5924256   -2.2791546    1.6503933
C     1.0541490   -1.7284188   -1.4164249
H    -2.4884136   -1.5253698    0.5950469
H     1.6185660   -1.9457207    1.8499281
H     0.6950570   -1.1423764   -2.2717778
H     2.0838960   -1.4306677   -1.1826360
H    -0.0424798   -2.0133474    2.5048428
H    -2.2127371   -1.2837776   -1.1545681
H     0.0000000    0.0000000    0.4294539
Si    0.0638610    1.5842761    0.0589370
H     2.2127371    1.2837776   -1.1545681
H    -1.6185660    1.9457207    1.8499281
H    -2.0838960    1.4306677   -1.1826360
H    -0.6950570    1.1423764   -2.2717778
H     0.0424798    2.0133474    2.5048428
H     2.4884136    1.5253698    0.5950469
C    -1.0541490    1.7284188   -1.4164249
C     1.8753724    1.8274669   -0.2634791
C    -0.5924256    2.2791546    1.6503933
```

```
H    -1.0796845    2.7829932   -1.7316325
H    -0.6077833    3.3774893    1.5746527
H     2.0594129    2.8983926   -0.4403395

SCF energy GEOOPT = -819.1210648444 H
ZPE = 589.6 kJ/mol
FREEH energy = 633.25 kJ/mol
FREEH entropy = 0.53738 kJ/mol/K

$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection rules
#                         cm**(-1)        km/mol          IR     RAMAN
     1                       -0.00         0.00000        -       -
     2                       -0.00         0.00000        -       -
     3                       -0.00         0.00000        -       -
     4                       -0.00         0.00000        -       -
     5                        0.00         0.00000        -       -
     6                        0.00         0.00000        -       -
     7        a              21.33         0.00009      YES     YES
     8        b              42.29         0.02251      YES     YES
     9        a              55.14         0.04845      YES     YES
    10        b             128.84         0.01437      YES     YES
    11        a             131.86         0.03195      YES     YES
    12        a             138.87         0.00004      YES     YES
    13        b             139.67         0.11851      YES     YES
    14        a             140.45         0.00583      YES     YES
    15        a             145.75         0.00937      YES     YES
    16        b             147.73         0.03677      YES     YES
    17        a             156.50         0.00074      YES     YES
    18        b             159.80         0.06206      YES     YES
    19        a             204.93         2.56931      YES     YES
    20        b             205.78         2.12156      YES     YES
    21        b             216.45        17.56004      YES     YES
    22        a             219.22         0.03275      YES     YES
    23        b             219.43         6.75569      YES     YES
    24        a             291.27         0.89751      YES     YES
    25        b             590.19        10.60323      YES     YES
    26        b             597.12        31.24441      YES     YES
    27        a             603.68         0.30387      YES     YES
    28        a             646.33         2.89961      YES     YES
    29        b             678.49         0.00460      YES     YES
    30        a             679.80         0.00513      YES     YES
    31        b             684.69         0.89038      YES     YES
    32        a             685.62         0.00088      YES     YES
    33        b             730.61         5.06189      YES     YES
    34        a             738.43         9.63684      YES     YES
    35        a             752.92         0.32990      YES     YES
    36        b             752.97         0.50182      YES     YES
    37        b             794.33       444.89282      YES     YES
    38        b             807.90         7.82000      YES     YES
    39        a             840.75         5.12549      YES     YES
    40        b             857.92        10.49350      YES     YES
    41        a             858.25         1.10118      YES     YES
    42        a             862.02        92.19857      YES     YES
    43        b             870.83       194.84408      YES     YES
    44        a             922.79        97.14123      YES     YES
    45        b            1249.53         1.56810      YES     YES
    46        a            1250.30         9.30316      YES     YES
    47        a            1252.11        50.33843      YES     YES
    48        b            1252.28        65.37553      YES     YES
    49        b            1257.00         2.74835      YES     YES
    50        a            1264.19         3.40984      YES     YES
    51        b            1387.63         0.23841      YES     YES
    52        a            1390.95         0.02083      YES     YES
    53        a            1396.04         0.01124      YES     YES
    54        b            1396.51         0.51358      YES     YES
    55        a            1397.93         0.03238      YES     YES
    56        b            1398.52         0.31241      YES     YES
    57        b            1404.04        14.10090      YES     YES
```

58	a	1404.32	8.93251	YES	YES
59	b	1409.32	0.04511	YES	YES
60	a	1410.47	7.12280	YES	YES
61	b	1419.50	12.77544	YES	YES
62	a	1419.68	1.50070	YES	YES
63	b	1989.38	1684.14202	YES	YES
64	b	2970.12	1.47753	YES	YES
65	a	2970.13	3.78989	YES	YES
66	b	2970.94	4.16046	YES	YES
67	a	2971.26	0.68073	YES	YES
68	b	2972.05	5.65315	YES	YES
69	a	2972.18	0.09575	YES	YES
70	b	3043.21	0.30319	YES	YES
71	a	3043.40	0.58849	YES	YES
72	a	3044.40	0.81800	YES	YES
73	b	3044.45	0.87106	YES	YES
74	b	3045.28	0.76964	YES	YES
75	a	3045.66	0.03312	YES	YES
76	b	3068.51	0.33317	YES	YES
77	a	3069.15	0.53448	YES	YES
78	b	3069.63	0.33212	YES	YES
79	a	3069.63	0.08078	YES	YES
80	a	3069.88	0.30030	YES	YES
81	b	3069.92	0.10057	YES	YES

Total COSMO energy + OC correction = -819.1841268281 H

Method: (RI-)B3LYP(D3BJ)/def2-TZVPP
Symmetry: c2

Cartesian coordinates in Ångström:

H	1.0704254	-2.7993718	-1.7200666
H	0.6225404	-3.3381726	1.5966875
H	-2.0599859	-2.8948144	-0.4095770
Si	-0.0634214	-1.5827463	0.0554899
C	-1.8725309	-1.8303193	-0.2444439
C	0.6069215	-2.2459317	1.6477203
C	1.0370346	-1.7473386	-1.4239688
H	-2.4720222	-1.5213386	0.6121212
H	1.6279874	-1.9098808	1.8290306
H	0.6661484	-1.1816332	-2.2787447
H	2.0589944	-1.4361159	-1.2078106
H	-0.0144638	-1.9639128	2.4977663
H	-2.2165212	-1.2956646	-1.1296407
H	0.0000000	-0.0000000	0.3786935
Si	0.0634214	1.5827463	0.0554899
H	2.2165212	1.2956646	-1.1296407
H	-1.6279874	1.9098808	1.8290306
H	-2.0589944	1.4361159	-1.2078106
H	-0.6661484	1.1816332	-2.2787447
H	0.0144638	1.9639128	2.4977663
H	2.4720222	1.5213386	0.6121212
C	-1.0370346	1.7473386	-1.4239688
C	1.8725309	1.8303193	-0.2444439
C	-0.6069215	2.2459317	1.6477203
H	-1.0704254	2.7993718	-1.7200666
H	-0.6225404	3.3381726	1.5966875
H	2.0599859	2.8948144	-0.4095770

SCF energy GEOOPT = -818.8066468517 H
ZPE = 604.7 kJ/mol
FREEH energy = 647.47 kJ/mol
FREEH entropy = 0.53280 kJ/mol/K

$vibrational spectrum

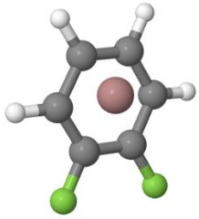
# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		-0.00	0.00000	-	-

2		-0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	18.54	0.00014	YES	YES
8	b	42.91	0.03295	YES	YES
9	a	54.76	0.05988	YES	YES
10	b	132.67	0.00910	YES	YES
11	a	135.66	0.03273	YES	YES
12	a	142.55	0.00235	YES	YES
13	b	143.81	0.10060	YES	YES
14	a	145.01	0.00213	YES	YES
15	a	149.64	0.00257	YES	YES
16	b	150.67	0.01151	YES	YES
17	a	161.36	0.00051	YES	YES
18	b	164.38	0.05667	YES	YES
19	a	210.66	3.29542	YES	YES
20	b	211.12	2.89452	YES	YES
21	b	222.87	31.27139	YES	YES
22	a	225.37	0.03041	YES	YES
23	b	225.38	1.54646	YES	YES
24	a	306.89	0.70003	YES	YES
25	b	607.81	35.51332	YES	YES
26	a	616.31	0.26249	YES	YES
27	b	619.81	10.95435	YES	YES
28	a	662.68	4.63483	YES	YES
29	b	704.92	0.00495	YES	YES
30	a	706.00	0.00377	YES	YES
31	b	707.15	1.03824	YES	YES
32	a	707.91	0.00075	YES	YES
33	b	748.36	8.54097	YES	YES
34	a	754.45	11.97388	YES	YES
35	b	774.14	0.54819	YES	YES
36	a	774.27	0.19312	YES	YES
37	b	820.30	469.37636	YES	YES
38	b	849.53	2.07391	YES	YES
39	a	871.29	10.93364	YES	YES
40	b	885.35	9.03134	YES	YES
41	a	885.40	0.14695	YES	YES
42	a	888.41	70.68829	YES	YES
43	b	901.61	213.70924	YES	YES
44	a	944.80	128.66696	YES	YES
45	b	1302.94	1.58027	YES	YES
46	a	1303.51	6.65496	YES	YES
47	a	1305.19	57.44838	YES	YES
48	b	1305.29	68.91042	YES	YES
49	b	1309.27	2.45443	YES	YES
50	a	1315.96	2.91297	YES	YES
51	b	1437.01	0.18034	YES	YES
52	a	1440.35	0.01574	YES	YES
53	a	1445.04	0.01587	YES	YES
54	b	1445.15	0.36398	YES	YES
55	a	1446.38	0.02254	YES	YES
56	b	1447.05	0.43340	YES	YES
57	b	1452.35	14.44379	YES	YES
58	a	1452.47	9.78430	YES	YES
59	b	1457.29	0.04778	YES	YES
60	a	1458.11	6.17256	YES	YES
61	a	1466.54	1.36255	YES	YES
62	b	1466.72	12.55323	YES	YES
63	b	2038.85	2002.24873	YES	YES
64	b	3030.32	1.08946	YES	YES
65	a	3030.37	2.79190	YES	YES
66	a	3031.62	0.58179	YES	YES
67	b	3031.66	3.29095	YES	YES
68	b	3032.41	4.19544	YES	YES
69	a	3033.22	0.35819	YES	YES
70	b	3098.33	0.46360	YES	YES

71	a	3098.63	0.04340	YES	YES
72	a	3098.93	0.90573	YES	YES
73	b	3099.05	0.79962	YES	YES
74	b	3100.10	0.05756	YES	YES
75	a	3100.82	0.09795	YES	YES
76	b	3121.67	0.12816	YES	YES
77	a	3122.35	0.04544	YES	YES
78	b	3122.62	0.92597	YES	YES
79	a	3123.25	1.48277	YES	YES
80	b	3123.66	0.35691	YES	YES
81	a	3123.80	0.06131	YES	YES

Total COSMO energy + OC correction = -818.8702709872

6.3.17 [Ga(*o*DFB)]^0



Method: (RI-)BP86(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:

H	-0.3883611	-2.5161142	-0.5687550
H	1.1967028	-1.8551267	1.2633053
C	-0.1562566	-1.4743547	-0.3607970
C	0.7144027	-1.0933334	0.6523651
F	-1.6597969	-0.8160246	-2.0951716
Ga	-1.1835705	1.1316426	2.0785325
C	-0.7887360	-0.4639416	-1.1237913
C	0.9843450	0.2636252	0.9077081
C	-0.4908279	0.8737393	-0.9278700
H	1.7268770	0.5374325	1.6563719
C	0.3866342	1.2860197	0.1035149
F	-1.0724422	1.8093406	-1.7076699
H	0.7310293	2.3170953	0.1222570

SCF energy GEOOPT = -2356.036035592 H
ZPE = 210.3 kJ/mol
FREEH energy = 233.50 kJ/mol
FREEH entropy = 0.40801 kJ/mol/K

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		-0.00	0.00000	-	-
2		-0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	15.17	0.91186	YES	YES
8	a	77.30	0.59055	YES	YES
9	a	111.45	1.31114	YES	YES
10	a	191.68	0.55590	YES	YES
11	a	254.55	1.89681	YES	YES
12	a	276.18	0.95702	YES	YES
13	a	390.37	14.49005	YES	YES

14	a	422.22	0.47061	YES	YES
15	a	496.73	1.50783	YES	YES
16	a	533.49	3.70647	YES	YES
17	a	544.19	1.38463	YES	YES
18	a	632.02	2.46666	YES	YES
19	a	668.90	10.98546	YES	YES
20	a	703.88	61.84128	YES	YES
21	a	741.04	29.94725	YES	YES
22	a	788.26	1.70166	YES	YES
23	a	834.83	13.35046	YES	YES
24	a	906.75	3.43347	YES	YES
25	a	982.15	17.44353	YES	YES
26	a	1073.12	16.09121	YES	YES
27	a	1133.05	5.34661	YES	YES
28	a	1156.13	55.18167	YES	YES
29	a	1220.64	46.18177	YES	YES
30	a	1237.17	86.00869	YES	YES
31	a	1339.57	5.54612	YES	YES
32	a	1415.68	16.03690	YES	YES
33	a	1449.56	99.65895	YES	YES
34	a	1497.11	37.30522	YES	YES
35	a	1557.23	299.88873	YES	YES
36	a	3106.36	3.96951	YES	YES
37	a	3123.02	5.32132	YES	YES
38	a	3140.44	0.93459	YES	YES
39	a	3147.39	0.88854	YES	YES

Total COSMO energy + OC correction = -2356.0416045204 H

Method: (RI-)B3LYP(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:

H	-0.4095291	-2.4976127	-0.5539338
H	1.1645290	-1.8366624	1.2631309
C	-0.1671947	-1.4620020	-0.3655259
C	0.7049636	-1.0833341	0.6396552
F	-1.6140094	-0.8281051	-2.1321726
Ga	-1.2047108	1.1701616	2.3609252
C	-0.7597009	-0.4746284	-1.1584512
C	0.9946367	0.2668214	0.8594160
C	-0.4660978	0.8580562	-0.9640302
H	1.7185103	0.5482277	1.6109360
C	0.4039985	1.2562267	0.0543390
F	-1.0379983	1.7842162	-1.7467389
H	0.6726029	2.2986350	0.1324503

SCF energy GEOOPT = -2355.448736450 H
ZPE = 218.8 kJ/mol
FREEH energy = 241.28 kJ/mol
FREEH entropy = 0.40623 kJ/mol/K

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	21.09	0.90171	YES	YES
8	a	57.35	0.25030	YES	YES
9	a	86.56	4.33534	YES	YES
10	a	197.54	1.14713	YES	YES
11	a	281.57	0.54323	YES	YES
12	a	286.79	0.92806	YES	YES
13	a	405.61	12.70248	YES	YES

14	a	442.21	1.05754	YES	YES
15	a	549.46	2.11689	YES	YES
16	a	557.25	4.88339	YES	YES
17	a	567.66	1.66549	YES	YES
18	a	686.66	0.78427	YES	YES
19	a	723.54	19.47561	YES	YES
20	a	757.99	92.28392	YES	YES
21	a	801.52	12.21601	YES	YES
22	a	864.69	15.36052	YES	YES
23	a	884.83	1.75510	YES	YES
24	a	961.11	2.14197	YES	YES
25	a	1030.26	17.04594	YES	YES
26	a	1116.18	16.43370	YES	YES
27	a	1174.33	4.94382	YES	YES
28	a	1207.93	62.17562	YES	YES
29	a	1278.46	79.29482	YES	YES
30	a	1284.52	46.03351	YES	YES
31	a	1342.68	30.03774	YES	YES
32	a	1474.73	24.55224	YES	YES
33	a	1524.26	124.44334	YES	YES
34	a	1585.09	28.18201	YES	YES
35	a	1616.41	293.26138	YES	YES
36	a	3181.97	4.34764	YES	YES
37	a	3196.43	3.78623	YES	YES
38	a	3211.56	0.33781	YES	YES
39	a	3216.22	4.55243	YES	YES

```
Total COSMO energy + OC correction = -2355.4559182091 H
```

6.3.18 Ga^0

```
Method: (RI-)BP86(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:
Ga   -4.8494400    2.1451200    0.0000000

SCF energy GEOOPT = -1925.087155276 H

Total COSMO energy + OC correction = -1925.0933651453 H


Method: (RI-)B3LYP(D3BJ)/def2-TZVPP
Symmetry: c1

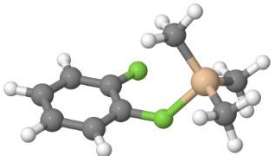
Cartesian coordinates in Ångström:
Ga   -4.8494400    2.1451200    0.0000000

SCF energy GEOOPT = -1924.738114091 H

Total COSMO energy + OC correction = -1924.7444404291 H
```

E_{vrt} of a single atom equals 3/2 RT ≈ 3.718 kJ mol^{-1}. The standard entropy of Ga^0 was calculated with the Sackur-Tetrode equation ($S°$ ≈ 0.162 kJ K^{-1} mol^{-1}).[33]

6.3.19 [$Me_3Si(oDFB)]^+$ (F-coordination)



Method: (RI-)BP86(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:

F	-2.3859141	-0.1066631	-0.1597243
C	-1.5869966	0.3711298	-1.1310125
C	-1.9545333	0.3362964	-2.4712712
H	-2.9235674	-0.0807447	-2.7415152
C	-1.0716645	0.8417579	-3.4298093
H	-1.3602717	0.8176635	-4.4790436
C	0.1661208	1.3777151	-3.0635439
H	0.8415785	1.7736246	-3.8190856
C	0.5479464	1.4181619	-1.7171833
H	1.4971200	1.8412861	-1.3939790
C	-0.3494953	0.9081198	-0.8070892
F	-0.0056669	0.9574334	0.5966870
H	-1.7555020	-0.6331022	2.5692895
C	-0.7579799	-0.4529806	2.9882297
H	-0.7498113	0.5168367	3.5020224
H	-0.5650770	-1.2301267	3.7447885
H	-0.5624226	-2.1604147	0.1709531
Si	0.5527327	-0.5546421	1.6984777
C	0.4655405	-1.9385914	0.4813240
H	0.8631929	-2.8399201	0.9755619
C	2.2333793	0.0645301	2.1400665
H	1.0857555	-1.7553673	-0.4053427
H	2.1908026	1.0422835	2.6369879
H	2.6911294	-0.6443898	2.8481495
H	2.8936039	0.1301039	1.2660621

SCF energy GEOOPT = -840.0577620914 H
ZPE = 500.2 kJ/mol
FREEH energy = 539.84 kJ/mol
FREEH entropy = 0.51827 kJ/mol/K

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		-0.00	0.00000	-	-
2		-0.00	0.00000	-	-
3		-0.00	0.00000	-	-
4		-0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	22.52	0.32896	YES	YES
8	a	37.00	1.13912	YES	YES
9	a	66.77	0.76308	YES	YES
10	a	115.60	0.00287	YES	YES
11	a	135.95	0.09323	YES	YES
12	a	138.40	1.44869	YES	YES
13	a	149.59	0.61669	YES	YES
14	a	152.14	0.77195	YES	YES
15	a	162.83	6.44630	YES	YES
16	a	214.08	0.88247	YES	YES
17	a	219.75	2.90212	YES	YES
18	a	233.47	8.31584	YES	YES
19	a	259.13	41.26517	YES	YES
20	a	277.62	3.47877	YES	YES
21	a	332.71	48.49759	YES	YES
22	a	428.03	24.29565	YES	YES
23	a	440.73	5.01016	YES	YES

24	a	523.09	13.66000	YES	YES
25	a	535.24	1.47702	YES	YES
26	a	551.33	54.36816	YES	YES
27	a	608.03	12.87532	YES	YES
28	a	665.81	0.32697	YES	YES
29	a	666.46	1.62598	YES	YES
30	a	671.89	0.13051	YES	YES
31	a	683.14	0.00512	YES	YES
32	a	698.89	161.67503	YES	YES
33	a	742.33	72.90009	YES	YES
34	a	759.32	8.34671	YES	YES
35	a	763.43	12.73518	YES	YES
36	a	810.79	54.65098	YES	YES
37	a	828.22	62.09093	YES	YES
38	a	830.45	5.85346	YES	YES
39	a	873.02	109.25977	YES	YES
40	a	874.34	103.74097	YES	YES
41	a	929.97	3.05724	YES	YES
42	a	978.59	0.00751	YES	YES
43	a	1017.95	3.00426	YES	YES
44	a	1028.11	66.73931	YES	YES
45	a	1116.67	11.44252	YES	YES
46	a	1152.84	1.60553	YES	YES
47	a	1232.61	29.13345	YES	YES
48	a	1256.00	42.57756	YES	YES
49	a	1256.04	59.71629	YES	YES
50	a	1261.11	44.48632	YES	YES
51	a	1265.22	9.72613	YES	YES
52	a	1343.10	7.62868	YES	YES
53	a	1383.71	0.03403	YES	YES
54	a	1392.26	1.81072	YES	YES
55	a	1393.01	1.19009	YES	YES
56	a	1399.54	6.12177	YES	YES
57	a	1402.65	5.42342	YES	YES
58	a	1416.06	16.88620	YES	YES
59	a	1447.48	18.69119	YES	YES
60	a	1479.12	133.42098	YES	YES
61	a	1565.17	4.35819	YES	YES
62	a	1627.98	15.45085	YES	YES
63	a	2967.56	6.97288	YES	YES
64	a	2968.87	7.10309	YES	YES
65	a	2971.32	4.34365	YES	YES
66	a	3040.69	0.07828	YES	YES
67	a	3042.18	0.30423	YES	YES
68	a	3044.75	0.97308	YES	YES
69	a	3070.08	0.12224	YES	YES
70	a	3074.95	0.41258	YES	YES
71	a	3076.45	0.16957	YES	YES
72	a	3130.26	2.40814	YES	YES
73	a	3137.61	1.21980	YES	YES
74	a	3142.66	5.43709	YES	YES
75	a	3150.30	2.07168	YES	YES

Total COSMO energy + OC correction = -840.1213044373 H

Method: (RI-)B3LYP(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:

F	-2.2980269	-0.1740087	-0.1594825
C	-1.5455865	0.3437410	-1.1377754
C	-1.9572043	0.3440755	-2.4574589
H	-2.9208158	-0.0768272	-2.7074793
C	-1.1182191	0.8911358	-3.4236699
H	-1.4382603	0.8955395	-4.4555576
C	0.1176392	1.4318347	-3.0826793
H	0.7562022	1.8574756	-3.8424855

```
C     0.5411697    1.4354106   -1.7556133
H     1.4881091    1.8577202   -1.4522366
C    -0.3136887    0.8857479   -0.8368752
F     0.0735870    0.8959796    0.5440199
H    -1.7585787   -0.5957478    2.4995683
C    -0.7794642   -0.4191340    2.9434993
H    -0.7745629    0.5595804    3.4240768
H    -0.6242199   -1.1700488    3.7238779
H    -0.5164828   -2.1996288    0.1937210
Si    0.5652105   -0.5722126    1.7023648
C     0.4984193   -1.9846389    0.5252265
H     0.8698768   -2.8727069    1.0458904
C     2.2336000    0.0399133    2.1764950
H     1.1389062   -1.8290205   -0.3432622
H     2.1850512    1.0239145    2.6437588
H     2.6654548   -0.6493619    2.9080640
H     2.9118840    0.0812676    1.3240132

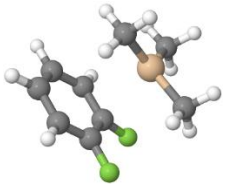
SCF energy GEOOPT = -839.6754847237 H
ZPE = 513.9 kJ/mol
FREEH energy = 552.53 kJ/mol
FREEH entropy = 0.50930 kJ/mol/K

$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection rules
#                         cm**(-1)       km/mol          IR     RAMAN
     1                        0.00         0.00000        -       -
     2                        0.00         0.00000        -       -
     3                        0.00         0.00000        -       -
     4                        0.00         0.00000        -       -
     5                        0.00         0.00000        -       -
     6                        0.00         0.00000        -       -
     7        a              30.52         0.31768       YES     YES
     8        a              38.00         1.32793       YES     YES
     9        a              70.64         0.86236       YES     YES
    10        a             119.71         0.00315       YES     YES
    11        a             139.18         0.01096       YES     YES
    12        a             142.68         1.49057       YES     YES
    13        a             153.23         0.67945       YES     YES
    14        a             158.54         0.94644       YES     YES
    15        a             169.33         6.81087       YES     YES
    16        a             219.12         1.53299       YES     YES
    17        a             226.34         3.51743       YES     YES
    18        a             240.81        11.65812       YES     YES
    19        a             264.87        50.21211       YES     YES
    20        a             288.16         2.79940       YES     YES
    21        a             339.21        43.66865       YES     YES
    22        a             445.68        24.95097       YES     YES
    23        a             457.53         6.94905       YES     YES
    24        a             541.72        14.68029       YES     YES
    25        a             553.27         1.05922       YES     YES
    26        a             573.06        65.70433       YES     YES
    27        a             619.01        11.40920       YES     YES
    28        a             692.72         4.36634       YES     YES
    29        a             696.71         0.16108       YES     YES
    30        a             697.61         0.45384       YES     YES
    31        a             710.26         0.11403       YES     YES
    32        a             722.96       173.52519       YES     YES
    33        a             773.99        70.19233       YES     YES
    34        a             780.15        11.62432       YES     YES
    35        a             784.70        22.16851       YES     YES
    36        a             836.53        43.12427       YES     YES
    37        a             857.49        74.39573       YES     YES
    38        a             872.01         2.40638       YES     YES
    39        a             900.11       115.87173       YES     YES
    40        a             900.82       100.73518       YES     YES
    41        a             973.73         3.31130       YES     YES
    42        a            1023.93         0.02394       YES     YES
    43        a            1044.65         4.22365       YES     YES
```

44	a	1066.99	69.46565	YES	YES
45	a	1149.89	13.49212	YES	YES
46	a	1187.46	2.22233	YES	YES
47	a	1272.38	38.05335	YES	YES
48	a	1302.06	68.21262	YES	YES
49	a	1309.16	44.46131	YES	YES
50	a	1309.90	37.74023	YES	YES
51	a	1316.30	8.32816	YES	YES
52	a	1338.79	5.05219	YES	YES
53	a	1433.25	0.02499	YES	YES
54	a	1441.68	0.93282	YES	YES
55	a	1442.55	2.16602	YES	YES
56	a	1447.86	5.92612	YES	YES
57	a	1451.24	5.81878	YES	YES
58	a	1463.93	17.12015	YES	YES
59	a	1494.47	17.54362	YES	YES
60	a	1529.00	143.07298	YES	YES
61	a	1616.24	4.10339	YES	YES
62	a	1674.62	17.53859	YES	YES
63	a	3028.97	6.44053	YES	YES
64	a	3029.62	5.56712	YES	YES
65	a	3032.20	2.54857	YES	YES
66	a	3096.61	0.07272	YES	YES
67	a	3097.75	0.14657	YES	YES
68	a	3100.24	0.29332	YES	YES
69	a	3123.35	0.08422	YES	YES
70	a	3130.30	0.21529	YES	YES
71	a	3132.13	0.11946	YES	YES
72	a	3200.77	2.00037	YES	YES
73	a	3208.17	0.99102	YES	YES
74	a	3213.02	5.56909	YES	YES
75	a	3220.45	1.70132	YES	YES

Total COSMO energy + OC correction = -839.7393862849 H

6.3.20 [Me$_3$Si(*o*DFB)]$^+$ (C1-coordination)



Method: (RI-)BP86(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:

F	0.6100143	2.3857583	3.2058681
C	0.1437623	1.9777883	2.0122947
C	-1.2444563	1.8503667	1.7979260
H	-1.9183893	2.0208041	2.6359647
C	-1.7176189	1.6058099	0.5045904
H	-2.7892897	1.5240742	0.3347552
C	-0.8213480	1.4997606	-0.5600950
H	-1.1943970	1.3298200	-1.5687695
C	0.5590307	1.6183362	-0.3551081
H	1.2680150	1.5492901	-1.1790390
C	1.0407587	1.8686733	0.9222516
F	2.3441172	2.0345882	1.1487496
H	-2.1980391	-0.3781013	3.7989175
C	-1.1373432	-0.4493912	4.0653276
H	-0.8654776	0.3810124	4.7294115

```
H    -0.9930293   -1.3816668    4.6375083
H    -1.6997389   -1.4057984    0.9559568
Si   -0.0297101   -0.5431556    2.5845432
C    -0.6174890   -1.4801581    1.1059099
H    -0.3668505   -2.5394901    1.2892705
C     1.7837866   -0.6145343    2.9479351
H    -0.0982538   -1.1822188    0.1870569
H     2.1124846    0.1915335    3.6148594
H     1.9607284   -1.5684716    3.4744719
H     2.3995527   -0.6117396    2.0412428

SCF energy GEOOPT = -840.0557592750 H
ZPE = 501.5 kJ/mol
FREEH energy = 540.87 kJ/mol
FREEH entropy = 0.51429 kJ/mol/K

$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection rules
#                         cm**(-1)        km/mol          IR     RAMAN
     1                      -0.00         0.00000        -       -
     2                      -0.00         0.00000        -       -
     3                       0.00         0.00000        -       -
     4                       0.00         0.00000        -       -
     5                       0.00         0.00000        -       -
     6                       0.00         0.00000        -       -
     7        a             17.23         1.92910       YES     YES
     8        a             41.13         0.53438       YES     YES
     9        a            101.76         0.51209       YES     YES
    10        a            126.72         0.24151       YES     YES
    11        a            139.38         0.56943       YES     YES
    12        a            146.93         2.31141       YES     YES
    13        a            152.02         7.94957       YES     YES
    14        a            165.04        14.93444       YES     YES
    15        a            175.28         0.23139       YES     YES
    16        a            192.60         3.16178       YES     YES
    17        a            214.27         4.70696       YES     YES
    18        a            217.06         2.25297       YES     YES
    19        a            226.99        26.29926       YES     YES
    20        a            278.65         1.10166       YES     YES
    21        a            302.82        10.98382       YES     YES
    22        a            430.14         0.10538       YES     YES
    23        a            442.97        20.50950       YES     YES
    24        a            535.26         4.13566       YES     YES
    25        a            541.96         2.36845       YES     YES
    26        a            563.34         6.50900       YES     YES
    27        a            596.06        14.23668       YES     YES
    28        a            656.41         5.50128       YES     YES
    29        a            668.78         3.43066       YES     YES
    30        a            675.07         8.14841       YES     YES
    31        a            690.37         0.21415       YES     YES
    32        a            741.10        11.06809       YES     YES
    33        a            752.32        18.54572       YES     YES
    34        a            759.54        24.49146       YES     YES
    35        a            764.62        48.73192       YES     YES
    36        a            817.23       209.70948       YES     YES
    37        a            841.86         9.01644       YES     YES
    38        a            857.99        26.54310       YES     YES
    39        a            871.28        42.73092       YES     YES
    40        a            872.65        68.09123       YES     YES
    41        a            943.63         6.12928       YES     YES
    42        a            982.82         0.69420       YES     YES
    43        a           1023.63         2.33282       YES     YES
    44        a           1097.15        13.41028       YES     YES
    45        a           1156.20         2.98176       YES     YES
    46        a           1198.12        31.39394       YES     YES
    47        a           1245.72        74.96192       YES     YES
    48        a           1247.91        37.24180       YES     YES
    49        a           1249.53         6.19140       YES     YES
    50        a           1258.45         4.92284       YES     YES
```

51	a	1275.91	60.83132	YES	YES
52	a	1342.88	1.63250	YES	YES
53	a	1376.46	0.37084	YES	YES
54	a	1388.46	7.17616	YES	YES
55	a	1391.92	6.03304	YES	YES
56	a	1396.84	1.19432	YES	YES
57	a	1397.71	7.58323	YES	YES
58	a	1416.01	7.67860	YES	YES
59	a	1442.59	21.73734	YES	YES
60	a	1481.71	167.67249	YES	YES
61	a	1567.06	9.73467	YES	YES
62	a	1580.65	18.31467	YES	YES
63	a	2956.79	8.81967	YES	YES
64	a	2958.60	7.24177	YES	YES
65	a	2961.64	6.86000	YES	YES
66	a	3038.82	0.57634	YES	YES
67	a	3042.59	0.66021	YES	YES
68	a	3043.25	2.97627	YES	YES
69	a	3079.84	0.40422	YES	YES
70	a	3083.71	0.75328	YES	YES
71	a	3088.00	0.20637	YES	YES
72	a	3127.88	1.44789	YES	YES
73	a	3134.24	0.38365	YES	YES
74	a	3139.38	7.02690	YES	YES
75	a	3147.34	1.97596	YES	YES

Total COSMO energy + OC correction = -840.1223997040 H

Method: (RI-)B3LYP(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:

F	0.5398397	2.3506834	3.2170904
C	0.0939650	1.9727067	2.0117489
C	-1.2815498	1.8822195	1.7649237
H	-1.9677789	2.0519697	2.5822677
C	-1.7248308	1.6489998	0.4681150
H	-2.7851581	1.5890081	0.2714134
C	-0.8087161	1.5249644	-0.5704595
H	-1.1582954	1.3622463	-1.5800399
C	0.5608425	1.6167774	-0.3324818
H	1.2839510	1.5359101	-1.1319609
C	1.0097882	1.8526237	0.9521723
F	2.3039794	1.9879902	1.2117231
H	-2.1477844	-0.3583175	3.8169431
C	-1.0939654	-0.4381541	4.0778923
H	-0.8061778	0.4040745	4.7071542
H	-0.9620389	-1.3476011	4.6751686
H	-1.7055490	-1.3883335	0.9891898
Si	-0.0045978	-0.5901420	2.5981866
C	-0.6324989	-1.5002290	1.1279423
H	-0.4205710	-2.5618749	1.3032156
C	1.8081294	-0.6432323	2.9238345
H	-0.1151988	-1.2173726	0.2124367
H	2.1372491	0.1752233	3.5630281
H	2.0064395	-1.5782797	3.4611540
H	2.4013473	-0.6489703	2.0111418

SCF energy GEOOPT = -839.6674205237 H
ZPE = 515.0 kJ/mol
FREEH energy = 553.53 kJ/mol
FREEH entropy = 0.50420 kJ/mol/K

$vibrational spectrum

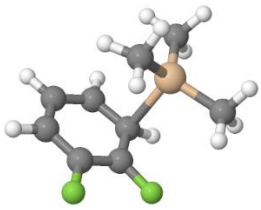
# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		-0.00	0.00000	-	-
2		-0.00	0.00000	-	-

3		-0.00	0.00000	-	-
4		-0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	35.52	1.09311	YES	YES
8	a	42.56	1.37682	YES	YES
9	a	99.56	0.61239	YES	YES
10	a	124.85	0.15056	YES	YES
11	a	139.59	0.71279	YES	YES
12	a	148.49	0.44618	YES	YES
13	a	155.72	9.45379	YES	YES
14	a	162.98	20.17346	YES	YES
15	a	172.88	1.77407	YES	YES
16	a	199.71	3.78155	YES	YES
17	a	219.96	4.51809	YES	YES
18	a	222.44	3.47898	YES	YES
19	a	230.33	33.95337	YES	YES
20	a	289.47	1.37824	YES	YES
21	a	310.78	11.55836	YES	YES
22	a	444.95	0.07286	YES	YES
23	a	462.30	27.49215	YES	YES
24	a	552.68	5.02928	YES	YES
25	a	558.35	3.58699	YES	YES
26	a	583.36	7.71783	YES	YES
27	a	606.55	12.43130	YES	YES
28	a	678.04	4.82828	YES	YES
29	a	691.49	3.08831	YES	YES
30	a	703.89	15.31185	YES	YES
31	a	719.00	0.19802	YES	YES
32	a	765.13	10.12404	YES	YES
33	a	774.43	20.35140	YES	YES
34	a	780.84	15.29357	YES	YES
35	a	791.55	60.91709	YES	YES
36	a	846.47	212.70843	YES	YES
37	a	867.23	9.54452	YES	YES
38	a	892.52	39.72471	YES	YES
39	a	902.35	70.38765	YES	YES
40	a	903.56	35.46716	YES	YES
41	a	986.96	5.17410	YES	YES
42	a	1028.31	0.51871	YES	YES
43	a	1050.69	2.44618	YES	YES
44	a	1130.80	13.19413	YES	YES
45	a	1190.88	3.16216	YES	YES
46	a	1234.66	33.37697	YES	YES
47	a	1290.96	58.01192	YES	YES
48	a	1300.16	35.52400	YES	YES
49	a	1301.89	47.73258	YES	YES
50	a	1310.36	14.65373	YES	YES
51	a	1315.38	35.80649	YES	YES
52	a	1341.86	1.07255	YES	YES
53	a	1424.69	0.33203	YES	YES
54	a	1436.10	8.21067	YES	YES
55	a	1440.39	7.81081	YES	YES
56	a	1444.44	2.84627	YES	YES
57	a	1444.97	3.49289	YES	YES
58	a	1463.09	8.89134	YES	YES
59	a	1491.47	21.59595	YES	YES
60	a	1531.57	163.73576	YES	YES
61	a	1617.54	9.34421	YES	YES
62	a	1631.53	21.60349	YES	YES
63	a	3015.67	9.16950	YES	YES
64	a	3017.45	7.12200	YES	YES
65	a	3021.28	6.22484	YES	YES
66	a	3095.98	0.45706	YES	YES
67	a	3099.81	1.61642	YES	YES
68	a	3102.20	1.34146	YES	YES
69	a	3137.45	0.41730	YES	YES
70	a	3141.07	0.84579	YES	YES
71	a	3146.87	0.21320	YES	YES

```
    72        a            3198.04          1.13489       YES      YES
    73        a            3205.30          0.27616       YES      YES
    74        a            3210.16          6.54258       YES      YES
    75        a            3217.41          1.61765       YES      YES

Total COSMO energy + OC correction = -839.7351078452 H
```

6.3.21 $[Me_3Si(oDFB)]^+$ (C2-coordination)



```
Method: (RI-)BP86(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:
F    -0.1722710    1.9051896    2.0888612
C     0.2140558    1.7079095    0.8347915
C    -0.7017704    1.1809489   -0.1131930
H    -1.7648229    1.2222938    0.1413233
C    -0.2981296    1.1187059   -1.4814811
H    -1.0237123    0.8058329   -2.2292678
C     1.0016955    1.4372092   -1.8420205
H     1.3162403    1.3689987   -2.8815280
C     1.9157857    1.8727840   -0.8711012
H     2.9413643    2.1291872   -1.1370816
C     1.5276106    2.0048322    0.4600226
F     2.3845082    2.4418423    1.3809405
H    -2.2789426   -0.6529623    2.0876894
C    -1.2585676   -1.0529948    2.0386647
H    -0.6367955   -0.5364315    2.7784586
H    -1.3059045   -2.1157448    2.3270817
H    -2.6396469   -1.2468016   -1.0260122
Si   -0.5521287   -1.0008342    0.3216746
C    -1.6636711   -1.7460098   -0.9688895
H    -1.8521195   -2.7910456   -0.6763424
C     1.2376526   -1.4708532    0.1978668
H    -1.2059444   -1.7562743   -1.9651774
H     1.8512420   -1.0215175    0.9873690
H     1.2873267   -2.5640858    0.3267064
H     1.6769451   -1.2401788   -0.7793557

SCF energy GEOOPT = -840.0621454583 H
ZPE = 503.3 kJ/mol
FREEH energy = 541.78 kJ/mol
FREEH entropy = 0.50050 kJ/mol/K

$vibrational spectrum
#  mode     symmetry     wave number    IR intensity    selection rules
#                         cm**(-1)        km/mol          IR     RAMAN
     1                        0.00         0.00000        -       -
     2                        0.00         0.00000        -       -
     3                        0.00         0.00000        -       -
     4                        0.00         0.00000        -       -
     5                        0.00         0.00000        -       -
     6                        0.00         0.00000        -       -
     7        a              26.47         0.52092       YES     YES
     8        a              73.99         0.02037       YES     YES
     9        a              97.49         2.59383       YES     YES
```

10	a	131.56	0.27440	YES	YES
11	a	153.20	0.51343	YES	YES
12	a	157.18	0.44506	YES	YES
13	a	165.30	1.61684	YES	YES
14	a	171.24	1.04593	YES	YES
15	a	187.26	0.60641	YES	YES
16	a	214.08	1.90303	YES	YES
17	a	218.17	2.65340	YES	YES
18	a	237.47	5.36643	YES	YES
19	a	251.85	61.51414	YES	YES
20	a	281.88	0.34031	YES	YES
21	a	306.46	27.02279	YES	YES
22	a	426.88	0.58740	YES	YES
23	a	455.26	7.16059	YES	YES
24	a	537.47	2.44395	YES	YES
25	a	557.59	16.17324	YES	YES
26	a	561.10	6.61585	YES	YES
27	a	602.94	21.99766	YES	YES
28	a	671.57	2.79246	YES	YES
29	a	678.07	1.40818	YES	YES
30	a	683.67	0.11348	YES	YES
31	a	706.20	21.25000	YES	YES
32	a	751.35	16.06092	YES	YES
33	a	752.49	11.33582	YES	YES
34	a	760.03	17.38306	YES	YES
35	a	782.49	67.60398	YES	YES
36	a	808.83	204.35984	YES	YES
37	a	837.66	37.41682	YES	YES
38	a	856.25	46.81212	YES	YES
39	a	860.35	44.81469	YES	YES
40	a	901.45	47.40561	YES	YES
41	a	939.69	29.81492	YES	YES
42	a	985.14	0.81874	YES	YES
43	a	1015.79	7.41916	YES	YES
44	a	1087.47	13.49295	YES	YES
45	a	1156.95	0.58746	YES	YES
46	a	1203.01	33.26128	YES	YES
47	a	1247.20	59.87365	YES	YES
48	a	1251.78	27.65027	YES	YES
49	a	1252.97	17.26950	YES	YES
50	a	1262.90	5.91903	YES	YES
51	a	1277.12	86.52856	YES	YES
52	a	1361.33	6.79599	YES	YES
53	a	1387.97	0.18638	YES	YES
54	a	1397.94	1.22104	YES	YES
55	a	1399.20	4.29872	YES	YES
56	a	1403.04	8.66560	YES	YES
57	a	1405.95	4.49508	YES	YES
58	a	1418.01	6.00459	YES	YES
59	a	1431.50	22.72223	YES	YES
60	a	1483.40	215.56990	YES	YES
61	a	1562.12	37.03862	YES	YES
62	a	1585.73	45.70445	YES	YES
63	a	2966.22	4.38647	YES	YES
64	a	2968.39	3.67870	YES	YES
65	a	2971.21	3.30577	YES	YES
66	a	3041.20	0.18993	YES	YES
67	a	3044.18	0.93921	YES	YES
68	a	3045.57	0.39651	YES	YES
69	a	3070.93	0.17054	YES	YES
70	a	3079.42	1.63440	YES	YES
71	a	3080.58	0.21875	YES	YES
72	a	3080.97	8.22379	YES	YES
73	a	3127.79	3.85057	YES	YES
74	a	3138.63	3.64294	YES	YES
75	a	3149.67	2.71129	YES	YES

Total COSMO energy + OC correction = -840.1293578694 H

Method: (RI-)B3LYP(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:

F	-1.0421936	1.9476132	3.3918777
C	-0.6583370	1.7688554	2.1419696
C	-1.5664861	1.2458794	1.1969839
H	-2.6212891	1.2719791	1.4511887
C	-1.1637689	1.1909284	-0.1637892
H	-1.8801889	0.8781320	-0.9085973
C	0.1269091	1.5193590	-0.5216367
H	0.4403963	1.4575840	-1.5533661
C	1.0321488	1.9566033	0.4480076
H	2.0485233	2.2196381	0.1862411
C	0.6431750	2.0777202	1.7719758
F	1.4929527	2.5110304	2.6919342
H	-3.1390586	-0.5808818	3.4025491
C	-2.1293698	-0.9889420	3.3607752
H	-1.5086038	-0.4699171	4.0886207
H	-2.1868784	-2.0398332	3.6621660
H	-3.4986649	-1.1826350	0.3053157
Si	-1.4231304	-0.9596055	1.6509394
C	-2.5335475	-1.6872844	0.3592093
H	-2.7292149	-2.7263734	0.6403177
C	0.3619803	-1.4219778	1.5264086
H	-2.0780077	-1.6919094	-0.6299690
H	0.9707197	-0.9628221	2.3037685
H	0.4187000	-2.5062145	1.6657097
H	0.7934245	-1.1986161	0.5524297

SCF energy GEOOPT = -839.6725493117 H
ZPE = 516.8 kJ/mol
FREEH energy = 554.49 kJ/mol
FREEH entropy = 0.49592 kJ/mol/K

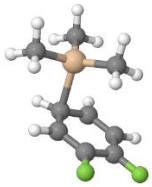
$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		-0.00	0.00000	-	-
2		-0.00	0.00000	-	-
3		-0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	26.06	0.59300	YES	YES
8	a	74.81	0.01104	YES	YES
9	a	100.66	3.43920	YES	YES
10	a	135.36	0.43143	YES	YES
11	a	156.15	2.46639	YES	YES
12	a	160.25	0.41834	YES	YES
13	a	167.62	3.98823	YES	YES
14	a	176.35	2.40449	YES	YES
15	a	191.70	2.92952	YES	YES
16	a	220.45	2.37476	YES	YES
17	a	224.22	4.66118	YES	YES
18	a	237.63	96.73890	YES	YES
19	a	243.98	0.50121	YES	YES
20	a	292.27	0.25874	YES	YES
21	a	310.86	14.21118	YES	YES
22	a	441.80	0.53064	YES	YES
23	a	472.39	7.82192	YES	YES
24	a	554.63	3.04919	YES	YES
25	a	574.88	21.05632	YES	YES
26	a	581.07	6.69273	YES	YES
27	a	613.47	22.13299	YES	YES
28	a	694.21	3.61995	YES	YES
29	a	700.32	2.12006	YES	YES
30	a	711.61	0.05836	YES	YES

31	a	737.18	27.30418	YES	YES
32	a	773.48	18.03766	YES	YES
33	a	776.04	9.61494	YES	YES
34	a	783.95	19.02782	YES	YES
35	a	813.53	87.07433	YES	YES
36	a	835.05	199.66275	YES	YES
37	a	865.94	41.48725	YES	YES
38	a	886.04	49.60152	YES	YES
39	a	889.82	51.32199	YES	YES
40	a	935.20	56.94040	YES	YES
41	a	982.32	27.77415	YES	YES
42	a	1029.15	1.75472	YES	YES
43	a	1045.16	6.61032	YES	YES
44	a	1119.34	13.00027	YES	YES
45	a	1194.08	0.21377	YES	YES
46	a	1241.67	40.41573	YES	YES
47	a	1289.65	50.91165	YES	YES
48	a	1304.88	47.56426	YES	YES
49	a	1305.82	31.27478	YES	YES
50	a	1313.39	34.94507	YES	YES
51	a	1317.62	49.17579	YES	YES
52	a	1364.93	10.00395	YES	YES
53	a	1436.98	0.14317	YES	YES
54	a	1446.66	1.22568	YES	YES
55	a	1447.73	5.20253	YES	YES
56	a	1451.03	8.66733	YES	YES
57	a	1454.13	4.03960	YES	YES
58	a	1465.63	6.68147	YES	YES
59	a	1479.35	23.17154	YES	YES
60	a	1532.78	215.72048	YES	YES
61	a	1613.28	34.62413	YES	YES
62	a	1634.65	57.67859	YES	YES
63	a	3026.45	4.03325	YES	YES
64	a	3028.70	3.06865	YES	YES
65	a	3031.14	3.07369	YES	YES
66	a	3096.47	0.15701	YES	YES
67	a	3100.08	0.55020	YES	YES
68	a	3102.27	0.10325	YES	YES
69	a	3127.05	0.25160	YES	YES
70	a	3136.50	0.33545	YES	YES
71	a	3138.13	0.20891	YES	YES
72	a	3153.58	9.49517	YES	YES
73	a	3198.41	3.68758	YES	YES
74	a	3209.63	3.56842	YES	YES
75	a	3220.81	2.36940	YES	YES

Total COSMO energy + OC correction = -839.7409995150 H

6.3.22 [$Me_3Si(oDFB)]^+$ (C3-coordination)



Method: (RI-)BP86(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:

F	-0.7648283	1.8918483	3.4555509
C	-0.5750214	1.7026278	2.1606988
C	-1.6612752	1.4277262	1.3263245
H	-2.6607920	1.3953847	1.7570668
C	-1.4357455	1.2240101	-0.0263813
H	-2.2736555	1.0361501	-0.6950775
C	-0.1111115	1.2392915	-0.5482336
H	0.0235261	1.3678738	-1.6265566
C	0.9736925	1.5943369	0.3069624
H	1.9859869	1.6984260	-0.0802581
C	0.7400536	1.7894422	1.6532292
F	1.7345243	2.0754622	2.4903972
H	-0.8609933	-1.4874227	1.4778323
C	0.1187819	-1.6376706	1.0100381
H	0.9015375	-1.2592245	1.6777147
H	0.2706205	-2.7248962	0.9157009
H	-2.1222982	-1.4585431	-1.3796719
Si	0.2223451	-0.9320848	-0.7031235
C	-1.1353455	-1.4661623	-1.8576852
H	-0.9225092	-2.5021753	-2.1645544
C	1.9170348	-0.9944206	-1.4690910
H	-1.1752481	-0.8600219	-2.7720284
H	2.7071426	-0.6949942	-0.7699348
H	2.1101964	-2.0390625	-1.7595053
H	1.9933816	-0.3859009	-2.3794141

SCF energy GEOOPT = -840.0638184796 H
ZPE = 503.4 kJ/mol
FREEH energy = 541.85 kJ/mol
FREEH entropy = 0.50111 kJ/mol/K

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		-0.00	0.00000	-	-
2		-0.00	0.00000	-	-
3		-0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	31.40	0.37809	YES	YES
8	a	64.51	0.36960	YES	YES
9	a	84.82	0.60207	YES	YES
10	a	130.32	0.02239	YES	YES
11	a	152.28	0.12979	YES	YES
12	a	157.46	0.08380	YES	YES
13	a	164.26	0.08451	YES	YES
14	a	182.52	0.14985	YES	YES
15	a	187.54	0.58499	YES	YES
16	a	214.76	2.00443	YES	YES
17	a	217.28	2.33552	YES	YES
18	a	233.81	0.68402	YES	YES
19	a	260.68	65.49664	YES	YES
20	a	283.16	0.73837	YES	YES
21	a	325.16	29.73443	YES	YES
22	a	432.98	1.72051	YES	YES

23	a	443.62	5.43009	YES	YES
24	a	539.12	5.19070	YES	YES
25	a	556.36	24.26229	YES	YES
26	a	566.54	20.24986	YES	YES
27	a	603.41	24.76940	YES	YES
28	a	672.65	2.47525	YES	YES
29	a	679.06	1.30825	YES	YES
30	a	681.81	0.29700	YES	YES
31	a	714.17	13.57851	YES	YES
32	a	750.41	20.42722	YES	YES
33	a	752.26	9.57546	YES	YES
34	a	761.36	11.38873	YES	YES
35	a	801.84	298.36131	YES	YES
36	a	820.28	23.28224	YES	YES
37	a	841.62	11.53126	YES	YES
38	a	854.87	75.41102	YES	YES
39	a	857.66	55.02590	YES	YES
40	a	875.11	21.13552	YES	YES
41	a	930.62	32.94884	YES	YES
42	a	966.15	16.59508	YES	YES
43	a	1001.25	6.25791	YES	YES
44	a	1087.34	11.25048	YES	YES
45	a	1142.32	6.02027	YES	YES
46	a	1215.87	29.90747	YES	YES
47	a	1250.72	29.35440	YES	YES
48	a	1252.24	26.77534	YES	YES
49	a	1254.69	28.77015	YES	YES
50	a	1262.51	4.79574	YES	YES
51	a	1292.41	131.78464	YES	YES
52	a	1371.72	1.82302	YES	YES
53	a	1390.90	0.20539	YES	YES
54	a	1399.92	0.69187	YES	YES
55	a	1400.49	3.61645	YES	YES
56	a	1404.63	8.49880	YES	YES
57	a	1408.50	6.44727	YES	YES
58	a	1420.53	8.24019	YES	YES
59	a	1434.33	37.43830	YES	YES
60	a	1495.19	240.85647	YES	YES
61	a	1551.12	66.85345	YES	YES
62	a	1586.73	54.33271	YES	YES
63	a	2968.11	2.20495	YES	YES
64	a	2969.11	3.65384	YES	YES
65	a	2971.82	3.58486	YES	YES
66	a	3040.94	0.39678	YES	YES
67	a	3042.44	0.56589	YES	YES
68	a	3045.25	0.30209	YES	YES
69	a	3069.00	0.91680	YES	YES
70	a	3069.24	0.28265	YES	YES
71	a	3072.60	5.19154	YES	YES
72	a	3079.68	0.29036	YES	YES
73	a	3134.74	2.07843	YES	YES
74	a	3139.60	6.69782	YES	YES
75	a	3145.69	5.74532	YES	YES

Total COSMO energy + OC correction = -840.1320163853 H

Method: (RI-)B3LYP(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:

F	-0.7652219	1.9113227	3.4385535
C	-0.5757558	1.7156446	2.1529168
C	-1.6565710	1.4389805	1.3243617
H	-2.6489745	1.4110908	1.7513551
C	-1.4304502	1.2275761	-0.0203493
H	-2.2620624	1.0390036	-0.6834482

```
C    -0.1120894    1.2367521   -0.5384981
H     0.0233286    1.3559226   -1.6090676
C     0.9662118    1.5931230    0.3135090
H     1.9723163    1.6912710   -0.0686399
C     0.7315988    1.7957516    1.6498989
F     1.7204759    2.0808368    2.4836128
H    -0.8509535   -1.5058434    1.4663931
C     0.1230592   -1.6544427    1.0034684
H     0.8977250   -1.2727432    1.6666503
H     0.2777722   -2.7341167    0.9130910
H    -2.1114898   -1.4566081   -1.3781838
Si    0.2255023   -0.9504987   -0.7038341
C    -1.1324243   -1.4670605   -1.8555169
H    -0.9296040   -2.4945617   -2.1710692
C     1.9136277   -0.9964659   -1.4693245
H    -1.1707207   -0.8551747   -2.7573130
H     2.6965788   -0.6974776   -0.7734564
H     2.1149494   -2.0295855   -1.7672420
H     1.9831714   -0.3826968   -2.3678676

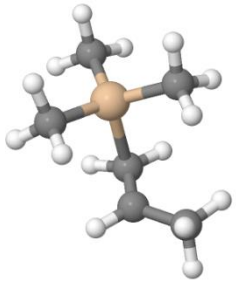
SCF energy GEOOPT = -839.6739429941 H
ZPE = 517.0 kJ/mol
FREEH energy = 554.61 kJ/mol
FREEH entropy = 0.49578 kJ/mol/K

$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection rules
#                         cm**(-1)       km/mol          IR     RAMAN
     1                      -0.00         0.00000        -       -
     2                      -0.00         0.00000        -       -
     3                       0.00         0.00000        -       -
     4                       0.00         0.00000        -       -
     5                       0.00         0.00000        -       -
     6                       0.00         0.00000        -       -
     7        a             31.47         0.43509       YES     YES
     8        a             65.52         0.36355       YES     YES
     9        a             88.69         0.68523       YES     YES
    10        a            134.90         0.02369       YES     YES
    11        a            156.25         0.19078       YES     YES
    12        a            160.63         0.08959       YES     YES
    13        a            168.86         0.07881       YES     YES
    14        a            186.26         0.29443       YES     YES
    15        a            192.87         2.09535       YES     YES
    16        a            220.80         2.56361       YES     YES
    17        a            224.09         3.10577       YES     YES
    18        a            239.55         1.83098       YES     YES
    19        a            252.60        98.15676       YES     YES
    20        a            293.48         0.51126       YES     YES
    21        a            332.33        23.53515       YES     YES
    22        a            448.28         1.41829       YES     YES
    23        a            463.06         5.66227       YES     YES
    24        a            556.22         6.55446       YES     YES
    25        a            574.78        41.77283       YES     YES
    26        a            584.45        15.78585       YES     YES
    27        a            614.17        22.48158       YES     YES
    28        a            695.80         3.34808       YES     YES
    29        a            701.61         2.52663       YES     YES
    30        a            709.38         0.05326       YES     YES
    31        a            743.12        20.15208       YES     YES
    32        a            772.20        21.87633       YES     YES
    33        a            775.79        10.77374       YES     YES
    34        a            784.44        11.96307       YES     YES
    35        a            828.74       321.41078       YES     YES
    36        a            852.99        15.68010       YES     YES
    37        a            871.42        18.34406       YES     YES
    38        a            884.49        78.03215       YES     YES
    39        a            886.76        58.99374       YES     YES
    40        a            913.80        20.96475       YES     YES
    41        a            968.83        39.15736       YES     YES
```

42	a	1005.35	18.60906	YES	YES
43	a	1034.88	1.71945	YES	YES
44	a	1119.82	10.77890	YES	YES
45	a	1180.38	5.55984	YES	YES
46	a	1254.34	37.01000	YES	YES
47	a	1297.36	20.68819	YES	YES
48	a	1304.69	39.80774	YES	YES
49	a	1305.64	29.92975	YES	YES
50	a	1314.85	3.97426	YES	YES
51	a	1332.60	142.29822	YES	YES
52	a	1382.44	2.97279	YES	YES
53	a	1440.08	0.23357	YES	YES
54	a	1448.60	0.42944	YES	YES
55	a	1449.33	4.11337	YES	YES
56	a	1452.62	7.91011	YES	YES
57	a	1456.87	5.91251	YES	YES
58	a	1468.03	8.94690	YES	YES
59	a	1478.83	38.11079	YES	YES
60	a	1542.69	247.59438	YES	YES
61	a	1600.68	77.09826	YES	YES
62	a	1633.83	58.41301	YES	YES
63	a	3028.76	2.04113	YES	YES
64	a	3029.78	2.79665	YES	YES
65	a	3032.21	3.34610	YES	YES
66	a	3096.07	0.32950	YES	YES
67	a	3097.82	0.39854	YES	YES
68	a	3101.97	0.11625	YES	YES
69	a	3124.55	0.33755	YES	YES
70	a	3124.76	0.51767	YES	YES
71	a	3136.51	0.35083	YES	YES
72	a	3145.16	5.54175	YES	YES
73	a	3206.01	2.35926	YES	YES
74	a	3211.10	6.83317	YES	YES
75	a	3216.89	5.34411	YES	YES

Total COSMO energy + OC correction = -839.7433456559 H

6.3.23 $[Me_3SiCH_2CHCH_3]^+$



Method: (RI-)BP86(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:

C	-1.3408342	-0.0572886	-1.2618714
C	-1.5600853	-0.2811809	0.0746508
H	-1.1570004	-0.9287632	-1.8990794
C	-1.3178630	1.2558721	-1.9265390
Si	0.5552897	-0.2876455	0.6016061
C	0.3077038	-0.8863772	2.3488702
C	1.4311956	-1.4988871	-0.5032426

```
C     1.1320193    1.4728228    0.4749589
H    -1.7868084   -1.2942332    0.4148201
H    -1.8998908    0.5393379    0.7129386
H     1.3030251   -0.9067813    2.8214145
H    -0.3290816   -0.2154335    2.9379032
H    -0.1034530   -1.9023160    2.3885766
H     2.4367842   -1.6718678   -0.0901307
H     1.5593002   -1.1284750   -1.5280897
H     0.9239063   -2.4720931   -0.5372523
H     0.4812260    2.1669705    1.0220487
H     2.1288400    1.5279357    0.9401639
H     1.2391993    1.8219129   -0.5588617
H    -0.4152539    1.3777967   -2.5445514
H    -1.4346779    2.0982828   -1.2377242
H    -2.1535410    1.2704111   -2.6506093

SCF energy GEOOPT = -527.1038637156 H
ZPE =   492.6 kJ/mol
FREEH energy =   524.61 kJ/mol
FREEH entropy =   0.44344 kJ/mol/K

$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection rules
#                         cm**(-1)        km/mol          IR     RAMAN
     1                      -0.00         0.00000        -       -
     2                      -0.00         0.00000        -       -
     3                       0.00         0.00000        -       -
     4                       0.00         0.00000        -       -
     5                       0.00         0.00000        -       -
     6                       0.00         0.00000        -       -
     7        a             28.32         0.22862       YES     YES
     8        a            113.10         4.33442       YES     YES
     9        a            150.20         1.00602       YES     YES
    10        a            155.70         1.05524       YES     YES
    11        a            165.20         0.82231       YES     YES
    12        a            168.58         0.30432       YES     YES
    13        a            180.93         0.12025       YES     YES
    14        a            192.72         2.27407       YES     YES
    15        a            214.62         1.05312       YES     YES
    16        a            219.32         2.35600       YES     YES
    17        a            230.53         5.20632       YES     YES
    18        a            265.06         3.62161       YES     YES
    19        a            330.21        71.21563       YES     YES
    20        a            415.84         1.28511       YES     YES
    21        a            602.16        16.98594       YES     YES
    22        a            673.21         1.25397       YES     YES
    23        a            678.77         2.63098       YES     YES
    24        a            682.07         0.30772       YES     YES
    25        a            703.14         8.71003       YES     YES
    26        a            748.37         7.66518       YES     YES
    27        a            765.65        18.12385       YES     YES
    28        a            820.50       197.88537       YES     YES
    29        a            851.20        40.32167       YES     YES
    30        a            861.10        77.47315       YES     YES
    31        a            898.56        51.35413       YES     YES
    32        a            929.81         2.16002       YES     YES
    33        a            966.78        54.10294       YES     YES
    34        a            986.16        18.21231       YES     YES
    35        a           1051.65         8.52594       YES     YES
    36        a           1188.56         0.88726       YES     YES
    37        a           1245.49        15.44802       YES     YES
    38        a           1257.53        36.01951       YES     YES
    39        a           1265.34         9.30993       YES     YES
    40        a           1281.08        19.91425       YES     YES
    41        a           1334.74        46.62976       YES     YES
    42        a           1377.90        17.48884       YES     YES
    43        a           1388.81         1.62551       YES     YES
    44        a           1396.88         5.68476       YES     YES
    45        a           1398.78         1.39946       YES     YES
```

46	a	1405.37	8.11790	YES	YES
47	a	1407.96	10.18875	YES	YES
48	a	1411.78	19.57430	YES	YES
49	a	1420.52	4.97758	YES	YES
50	a	1440.78	25.80944	YES	YES
51	a	1568.93	63.72808	YES	YES
52	a	2943.59	26.69964	YES	YES
53	a	2965.38	4.92116	YES	YES
54	a	2969.93	2.48631	YES	YES
55	a	2971.04	3.15004	YES	YES
56	a	2998.46	0.99767	YES	YES
57	a	3037.76	5.51138	YES	YES
58	a	3041.37	0.41388	YES	YES
59	a	3041.86	0.45987	YES	YES
60	a	3045.31	2.01672	YES	YES
61	a	3063.14	0.31634	YES	YES
62	a	3066.05	0.14574	YES	YES
63	a	3071.34	0.44333	YES	YES
64	a	3075.96	0.04969	YES	YES
65	a	3087.41	4.46487	YES	YES
66	a	3134.73	1.86256	YES	YES

Total COSMO energy + OC correction = -527.1729324187 H

Method: (RI-)B3LYP(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:

C	-1.3393133	-0.0532190	-1.2655917
C	-1.5558857	-0.2916878	0.0588829
H	-1.1468359	-0.9079772	-1.9081919
C	-1.3297253	1.2670711	-1.9168826
Si	0.5684608	-0.2914235	0.6061770
C	0.3098772	-0.8756501	2.3484559
C	1.4340586	-1.5062690	-0.4927441
C	1.1385352	1.4641507	0.4655486
H	-1.7674528	-1.3031554	0.3874016
H	-1.8999867	0.5122137	0.7017535
H	1.2911751	-0.8990124	2.8322019
H	-0.3267666	-0.2034825	2.9228619
H	-0.1051632	-1.8821570	2.3905596
H	2.4337855	-1.6833624	-0.0868781
H	1.5574108	-1.1407548	-1.5121987
H	0.9233864	-2.4696045	-0.5229268
H	0.4819613	2.1559574	0.9938133
H	2.1239009	1.5311772	0.9359044
H	1.2500823	1.7985190	-0.5647824
H	-0.4296743	1.4029641	-2.5212130
H	-1.4506192	2.0919519	-1.2195626
H	-2.1612111	1.2837504	-2.6325887

SCF energy GEOOPT = -526.8659659023 H
ZPE = 505.6 kJ/mol
FREEH energy = 537.07 kJ/mol
FREEH entropy = 0.43930 kJ/mol/K

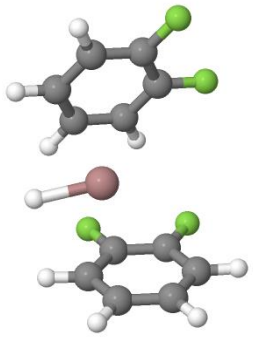
$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		-0.00	0.00000	-	-
2		-0.00	0.00000	-	-
3		-0.00	0.00000	-	-
4		-0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	29.32	0.21423	YES	YES
8	a	118.33	4.68185	YES	YES

9	a	154.69	1.53989	YES	YES
10	a	158.96	1.23036	YES	YES
11	a	168.72	0.81985	YES	YES
12	a	173.53	0.76604	YES	YES
13	a	184.82	0.10537	YES	YES
14	a	197.87	2.99053	YES	YES
15	a	221.04	2.20772	YES	YES
16	a	224.34	2.80995	YES	YES
17	a	237.30	6.35054	YES	YES
18	a	273.51	4.09436	YES	YES
19	a	317.04	88.68038	YES	YES
20	a	431.18	1.41549	YES	YES
21	a	613.53	19.86992	YES	YES
22	a	697.32	1.30356	YES	YES
23	a	701.77	3.69716	YES	YES
24	a	708.48	0.26960	YES	YES
25	a	725.59	8.64959	YES	YES
26	a	771.58	8.07540	YES	YES
27	a	788.90	19.10893	YES	YES
28	a	847.70	213.95651	YES	YES
29	a	880.22	41.80195	YES	YES
30	a	889.39	78.74435	YES	YES
31	a	917.74	41.73131	YES	YES
32	a	964.66	4.92781	YES	YES
33	a	1004.58	83.26515	YES	YES
34	a	1022.74	21.36785	YES	YES
35	a	1098.54	8.67042	YES	YES
36	a	1224.69	1.04968	YES	YES
37	a	1301.61	18.90796	YES	YES
38	a	1309.64	37.11323	YES	YES
39	a	1316.65	9.33943	YES	YES
40	a	1322.01	20.77756	YES	YES
41	a	1390.95	37.52531	YES	YES
42	a	1428.19	18.08869	YES	YES
43	a	1439.33	1.04639	YES	YES
44	a	1445.99	3.33262	YES	YES
45	a	1447.23	1.06651	YES	YES
46	a	1454.44	6.71050	YES	YES
47	a	1456.47	9.14121	YES	YES
48	a	1462.30	27.91670	YES	YES
49	a	1468.06	2.63030	YES	YES
50	a	1490.49	23.77038	YES	YES
51	a	1617.86	74.15955	YES	YES
52	a	3012.15	20.53879	YES	YES
53	a	3027.00	3.45121	YES	YES
54	a	3030.23	2.22690	YES	YES
55	a	3031.97	2.52159	YES	YES
56	a	3065.00	0.49911	YES	YES
57	a	3096.45	0.23337	YES	YES
58	a	3097.45	0.47806	YES	YES
59	a	3100.36	1.02104	YES	YES
60	a	3107.85	5.42955	YES	YES
61	a	3117.71	0.41038	YES	YES
62	a	3127.89	0.62861	YES	YES
63	a	3128.94	0.19154	YES	YES
64	a	3135.90	0.69076	YES	YES
65	a	3153.58	3.20025	YES	YES
66	a	3203.35	1.82769	YES	YES

Total COSMO energy + OC correction = -526.9355330880 H

6.3.24 GaH(*o*DFB)$_2$



Method: (RI-)BP86(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:

C	-0.9012345	0.7311495	2.2034721
C	0.0420640	1.1949167	3.1220534
C	1.1493456	0.4173661	3.4498717
H	1.8714931	0.8075081	4.1652185
C	1.3007179	-0.8451208	2.8655030
H	2.1632665	-1.4589297	3.1166541
C	0.3593573	-1.3052669	1.9376501
H	0.4840979	-2.2785316	1.4677574
C	-0.7424686	-0.5116796	1.5995125
H	-1.4847278	-0.8454953	0.8770274
F	-1.9538868	1.5117232	1.8884620
F	-0.1198293	2.4126312	3.6764750
C	1.5868347	-1.4650604	-2.0322135
H	2.1813906	-2.3279312	-1.7408929
C	2.1503019	-0.3735774	-2.7068691
H	3.2104041	-0.3918574	-2.9543529
C	1.3598889	0.7226723	-3.0646030
H	1.8041713	1.5674693	-3.5876704
C	0.0005382	0.7491966	-2.7447108
H	-0.6339932	1.5966733	-2.9969527
C	-0.5503904	-0.3221351	-2.0544560
C	0.2359856	-1.4251546	-1.7054203
F	-1.8577838	-0.3204116	-1.7174926
F	-0.3421362	-2.4645972	-1.0614470
Ga	2.3018648	0.3715024	0.3076928
H	3.2249081	-1.0799799	0.4311110

SCF energy GEOOPT = -2787.589516181 H
ZPE = 445.4 kJ/mol
FREEH energy = 491.50 kJ/mol
FREEH entropy = 0.60398 kJ/mol/K

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		-0.00	0.00000	-	-
2		-0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	17.47	0.45738	YES	YES
8	a	22.10	0.34999	YES	YES
9	a	28.41	0.34625	YES	YES
10	a	40.89	0.34790	YES	YES
11	a	48.14	0.77410	YES	YES
12	a	63.00	0.81861	YES	YES
13	a	70.33	0.46965	YES	YES
14	a	94.00	3.11046	YES	YES

15	a	113.14	1.54431	YES	YES
16	a	188.91	0.32283	YES	YES
17	a	190.68	0.32263	YES	YES
18	a	277.12	0.73904	YES	YES
19	a	280.04	0.31412	YES	YES
20	a	287.37	0.42177	YES	YES
21	a	289.03	2.37322	YES	YES
22	a	305.80	45.52627	YES	YES
23	a	407.89	89.41587	YES	YES
24	a	430.06	0.38404	YES	YES
25	a	430.41	1.92958	YES	YES
26	a	441.20	2.85810	YES	YES
27	a	442.96	3.66970	YES	YES
28	a	534.52	3.90267	YES	YES
29	a	534.70	3.96180	YES	YES
30	a	539.08	1.21236	YES	YES
31	a	542.01	0.05415	YES	YES
32	a	562.46	4.65754	YES	YES
33	a	563.30	3.76179	YES	YES
34	a	679.38	0.50225	YES	YES
35	a	680.07	0.40634	YES	YES
36	a	742.22	124.06395	YES	YES
37	a	752.48	97.38534	YES	YES
38	a	753.91	12.41351	YES	YES
39	a	759.03	37.26865	YES	YES
40	a	815.10	3.76922	YES	YES
41	a	832.62	3.72388	YES	YES
42	a	839.13	12.41152	YES	YES
43	a	841.46	17.45690	YES	YES
44	a	901.76	8.13280	YES	YES
45	a	912.92	2.17532	YES	YES
46	a	942.77	0.71120	YES	YES
47	a	945.57	0.08624	YES	YES
48	a	1021.42	2.53442	YES	YES
49	a	1022.06	6.68711	YES	YES
50	a	1091.41	22.23290	YES	YES
51	a	1094.33	9.48577	YES	YES
52	a	1143.46	1.55958	YES	YES
53	a	1145.00	1.83867	YES	YES
54	a	1181.22	18.90507	YES	YES
55	a	1190.35	35.75088	YES	YES
56	a	1249.14	3.97294	YES	YES
57	a	1250.29	7.22053	YES	YES
58	a	1257.40	92.89945	YES	YES
59	a	1261.08	149.77767	YES	YES
60	a	1345.82	1.69661	YES	YES
61	a	1348.25	0.27914	YES	YES
62	a	1396.08	512.69001	YES	YES
63	a	1443.32	16.31264	YES	YES
64	a	1446.56	7.16045	YES	YES
65	a	1490.82	159.52377	YES	YES
66	a	1495.19	175.94628	YES	YES
67	a	1585.73	4.93565	YES	YES
68	a	1588.03	9.39249	YES	YES
69	a	1592.98	35.61699	YES	YES
70	a	1595.25	14.65662	YES	YES
71	a	3119.58	1.06429	YES	YES
72	a	3125.50	0.28183	YES	YES
73	a	3131.60	4.36538	YES	YES
74	a	3133.62	1.78074	YES	YES
75	a	3140.17	0.33227	YES	YES
76	a	3141.94	0.59738	YES	YES
77	a	3147.29	1.18698	YES	YES
78	a	3148.52	0.52171	YES	YES

Total COSMO energy + OC correction = -2787.6015077557 H

Method: (RI-)B3LYP(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:

C	-1.5491847	0.9508441	2.1338901
C	-0.6335372	1.3820048	3.0830911
C	0.4544224	0.5949115	3.4180609
H	1.1538600	0.9581410	4.1575047
C	0.6175418	-0.6421179	2.8004123
H	1.4654675	-1.2614950	3.0531119
C	-0.2986621	-1.0716045	1.8440741
H	-0.1665913	-2.0242980	1.3535076
C	-1.3860296	-0.2705765	1.5057970
H	-2.1071538	-0.5787409	0.7630715
F	-2.5856376	1.7405565	1.8191255
F	-0.8063573	2.5773211	3.6648818
C	0.9463990	-1.2612880	-2.1911052
H	1.5428118	-2.1136583	-1.9025586
C	1.4879389	-0.1939408	-2.9048654
H	2.5307384	-0.2208680	-3.1869738
C	0.6943606	0.8942143	-3.2522439
H	1.1194534	1.7210210	-3.8026430
C	-0.6456265	0.9329460	-2.8839983
H	-1.2809002	1.7720402	-3.1282168
C	-1.1748098	-0.1206661	-2.1643202
C	-0.3857039	-1.2123774	-1.8247279
F	-2.4619046	-0.1062317	-1.7825070
F	-0.9384778	-2.2272329	-1.1367537
Ga	1.7704300	0.6236515	0.2233273
H	2.6371528	-0.8425560	0.3410582

SCF energy GEOOPT = -2786.772650777 H
ZPE = 458.5 kJ/mol
FREEH energy = 503.77 kJ/mol
FREEH entropy = 0.60120 kJ/mol/K

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		-0.00	0.00000	-	-
2		-0.00	0.00000	-	-
3		-0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	19.52	0.33312	YES	YES
8	a	22.45	0.44083	YES	YES
9	a	27.54	0.48006	YES	YES
10	a	38.80	0.41415	YES	YES
11	a	46.44	0.59089	YES	YES
12	a	62.03	0.21937	YES	YES
13	a	67.58	1.34366	YES	YES
14	a	84.37	2.54399	YES	YES
15	a	99.90	1.19049	YES	YES
16	a	197.02	0.18122	YES	YES
17	a	197.99	0.34269	YES	YES
18	a	288.14	0.97982	YES	YES
19	a	290.76	0.40986	YES	YES
20	a	297.68	7.08567	YES	YES
21	a	298.60	0.69747	YES	YES
22	a	307.12	32.01646	YES	YES
23	a	388.63	65.31514	YES	YES
24	a	445.12	0.10341	YES	YES
25	a	445.22	0.10889	YES	YES
26	a	461.81	2.18438	YES	YES
27	a	464.68	5.29519	YES	YES
28	a	552.96	4.42077	YES	YES
29	a	553.60	4.30649	YES	YES
30	a	562.02	0.06274	YES	YES

31	a	565.03	0.07751	YES	YES
32	a	583.47	4.86591	YES	YES
33	a	583.90	4.19214	YES	YES
34	a	714.94	0.29872	YES	YES
35	a	715.83	0.31455	YES	YES
36	a	773.29	116.42909	YES	YES
37	a	777.20	43.94219	YES	YES
38	a	780.61	23.16487	YES	YES
39	a	787.07	96.86591	YES	YES
40	a	862.24	0.40061	YES	YES
41	a	866.03	15.48208	YES	YES
42	a	867.56	19.21538	YES	YES
43	a	875.14	3.10466	YES	YES
44	a	951.65	8.31106	YES	YES
45	a	961.25	3.51396	YES	YES
46	a	989.87	0.32333	YES	YES
47	a	995.97	0.18846	YES	YES
48	a	1049.65	2.92152	YES	YES
49	a	1050.16	8.06560	YES	YES
50	a	1125.52	22.42938	YES	YES
51	a	1128.07	8.94472	YES	YES
52	a	1180.37	1.21122	YES	YES
53	a	1180.87	1.09676	YES	YES
54	a	1220.39	19.57841	YES	YES
55	a	1228.52	39.53956	YES	YES
56	a	1294.01	14.81162	YES	YES
57	a	1294.97	35.50527	YES	YES
58	a	1296.41	67.85938	YES	YES
59	a	1299.91	150.91817	YES	YES
60	a	1339.30	0.44811	YES	YES
61	a	1341.73	0.04877	YES	YES
62	a	1460.14	557.82902	YES	YES
63	a	1492.51	17.77774	YES	YES
64	a	1494.71	7.71930	YES	YES
65	a	1542.63	162.60786	YES	YES
66	a	1545.56	177.71039	YES	YES
67	a	1638.18	5.41899	YES	YES
68	a	1640.77	6.49519	YES	YES
69	a	1643.75	34.47316	YES	YES
70	a	1646.00	14.92561	YES	YES
71	a	3189.50	1.17368	YES	YES
72	a	3195.61	0.52410	YES	YES
73	a	3201.32	4.36487	YES	YES
74	a	3205.69	1.40197	YES	YES
75	a	3211.21	0.76485	YES	YES
76	a	3211.69	0.66356	YES	YES
77	a	3218.84	0.51576	YES	YES
78	a	3219.86	1.11847	YES	YES

Total COSMO energy + OC correction = -2786.7852348499 H

6.3.25 Ga^{+}

Method: (RI-)BP86(D3BJ)/def2-TZVPP
Symmetry: c1

Cartesian coordinates in Ångström:
Ga -1.8990300 -1.6211200 0.0000000

```
SCF energy GEOOPT = -1924.862486930 H

Total COSMO energy + OC correction = -1924.9684617896


Method: (RI-)B3LYP(D3BJ)/def2-TZVPP
Symmetry: c1

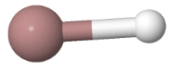
Cartesian coordinates in Ångström:
Ga   -1.8990300   -1.6211200    0.0000000

SCF energy GEOOPT = -1924.520500140 H

Total COSMO energy + OC correction = -1924.6264767041
```

E_{vrt} of a single atom equals 3/2 RT ≈ 3.718 kJ mol^{-1}. The standard entropy of Ga^+ was calculated with the Sackur-Tetrode equation ($S°$ ≈ 0.162 kJ K^{-1} mol^{-1}).[33]

6.3.26 GaH



```
Method: (RI-)BP86(D3BJ)/def2-TZVPP
Symmetry: c6v

Cartesian coordinates in Ångström:
Ga     0.0000000    0.0000000    0.8485780
H      0.0000000    0.0000000   -0.8485780

SCF energy GEOOPT = -1925.698665128 H
ZPE =   9.063 kJ/mol
FREEH energy =    15.27 kJ/mol
FREEH entropy =   0.20009 kJ/mol/K

$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection rules
#                         cm**(-1)        km/mol          IR     RAMAN
     1                        0.00         0.00000        -       -
     2                        0.00         0.00000        -       -
     3                        0.00         0.00000        -       -
     4                        0.00         0.00000        -       -
     5                        0.00         0.00000        -       -
     6        a1           1515.24       735.52932       YES     YES


Total COSMO energy + OC correction = -1925.7067707148 H


Method: (RI-)B3LYP(D3BJ)/def2-TZVPP
Symmetry: c6v

Cartesian coordinates in Ångström:
Ga     0.0000000    0.0000000    0.8444464
```

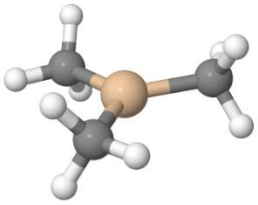
```
H     0.0000000    0.0000000   -0.8444464

SCF energy GEOOPT = -1925.347427293 H
ZPE =   9.289 kJ/mol
FREEH energy =    15.50 kJ/mol
FREEH entropy =   0.20000 kJ/mol/K

$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection rules
#                         cm**(-1)        km/mol         IR     RAMAN
     1                      -0.00         0.00000        -       -
     2                      -0.00         0.00000        -       -
     3                       0.00         0.00000        -       -
     4                       0.00         0.00000        -       -
     5                       0.00         0.00000        -       -
     6        a1          1553.02       776.30237       YES     YES


Total COSMO energy + OC correction = -1925.3558229767 H
```

6.3.27 $[SiMe_3]^+$



```
Method: (RI-)BP86(D3BJ)/def2-TZVPP
Symmetry: c3h

Cartesian coordinates in Ångström:
Si    0.0000000   -0.0000000    0.0000000
C     1.7251422    0.6168571    0.0000000
C    -1.3967850    1.1855885    0.0000000
C    -0.3283572   -1.8024455    0.0000000
H    -1.3160152    1.8462208    0.8798044
H    -2.3774263    0.6967029    0.0000000
H    -1.3160152    1.8462208   -0.8798044
H     0.5853507   -2.4072630    0.0000000
H    -0.9408665   -2.0628130   -0.8798044
H    -0.9408665   -2.0628130    0.8798044
H     1.7920755    1.7105601    0.0000000
H     2.2568818    0.2165922   -0.8798044
H     2.2568818    0.2165922    0.8798044

SCF energy GEOOPT = -409.0882082807 H
ZPE =   277.9 kJ/mol
FREEH energy =   298.98 kJ/mol
FREEH entropy =   0.36095 kJ/mol/K

$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection rules
#                         cm**(-1)        km/mol         IR     RAMAN
     1                      -0.00         0.00000        -       -
     2                      -0.00         0.00000        -       -
     3                       0.00         0.00000        -       -
     4                       0.00         0.00000        -       -
```

5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	e"	35.25	0.00000	NO	YES
8	e"	35.25	0.00000	NO	YES
9	a"	74.80	1.22921	YES	NO
10	e'	212.66	2.36275	YES	YES
11	e'	212.66	2.36275	YES	YES
12	a"	213.78	1.06511	YES	NO
13	a'	601.36	0.00000	NO	YES
14	e"	613.68	0.00000	NO	YES
15	e"	613.68	0.00000	NO	YES
16	a'	692.91	0.00000	NO	YES
17	e'	746.60	7.36842	YES	YES
18	e'	746.60	7.36842	YES	YES
19	a"	803.37	58.58409	YES	NO
20	e'	880.68	123.19084	YES	YES
21	e'	880.68	123.19084	YES	YES
22	e'	1241.16	54.31796	YES	YES
23	e'	1241.16	54.31796	YES	YES
24	a'	1247.62	0.00000	NO	YES
25	e'	1373.06	5.90561	YES	YES
26	e'	1373.06	5.90561	YES	YES
27	e"	1373.62	0.00000	NO	YES
28	e"	1373.62	0.00000	NO	YES
29	a'	1379.71	0.00000	NO	YES
30	a"	1382.50	24.35868	YES	NO
31	e'	2949.47	44.40745	YES	YES
32	e'	2949.47	44.40745	YES	YES
33	a'	2954.32	0.00000	NO	YES
34	a"	3008.42	23.63015	YES	NO
35	e"	3008.97	0.00000	NO	YES
36	e"	3008.97	0.00000	NO	YES
37	e'	3078.08	6.57712	YES	YES
38	e'	3078.08	6.57712	YES	YES
39	a'	3078.57	0.00000	NO	YES

Total COSMO energy + OC correction = -409.1692322225 H

Method: (RI-)B3LYP(D3BJ)/def2-TZVPP
Symmetry: c3h

Cartesian coordinates in Ångström:

Si	-0.0000000	0.0000000	0.0000000
C	1.7213862	0.6136367	0.0000000
C	-1.3921181	1.1839458	0.0000000
C	-0.3292681	-1.7975825	0.0000000
H	-1.3139172	1.8386259	0.8749448
H	-2.3656474	0.6970452	0.0000000
H	-1.3139172	1.8386259	-0.8749448
H	0.5791648	-2.3972333	0.0000000
H	-0.9353381	-2.0571986	-0.8749448
H	-0.9353381	-2.0571986	0.8749448
H	1.7864825	1.7001881	0.0000000
H	2.2492553	0.2185727	-0.8749448
H	2.2492553	0.2185727	0.8749448

SCF energy GEOOPT = -408.9346887937 H
ZPE = 285.0 kJ/mol
FREEH energy = 305.79 kJ/mol
FREEH entropy = 0.35938 kJ/mol/K

$vibrational spectrum

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1		-0.00	0.00000	-	-
2		-0.00	0.00000	-	-

3		-0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	e"	34.96	0.00000	NO	YES
8	e"	34.96	0.00000	NO	YES
9	a"	75.11	0.73241	YES	NO
10	e'	217.14	3.10758	YES	YES
11	e'	217.14	3.10758	YES	YES
12	a"	219.78	2.11806	YES	NO
13	a'	610.02	0.00000	NO	YES
14	e"	640.32	0.00000	NO	YES
15	e"	640.32	0.00000	NO	YES
16	a'	719.76	0.00000	NO	YES
17	e'	763.22	9.87823	YES	YES
18	e'	763.22	9.87823	YES	YES
19	a"	833.75	61.36790	YES	NO
20	e'	905.94	124.10936	YES	YES
21	e'	905.94	124.10936	YES	YES
22	e'	1294.36	51.22209	YES	YES
23	e'	1294.36	51.22209	YES	YES
24	a'	1300.51	0.00000	NO	YES
25	e'	1421.05	5.82102	YES	YES
26	e'	1421.05	5.82102	YES	YES
27	e"	1423.83	0.00000	NO	YES
28	e"	1423.83	0.00000	NO	YES
29	a'	1426.90	0.00000	NO	YES
30	a"	1431.58	24.43036	YES	NO
31	e'	3010.24	37.58700	YES	YES
32	e'	3010.24	37.58700	YES	YES
33	a'	3014.97	0.00000	NO	YES
34	a"	3064.92	18.23169	YES	NO
35	e"	3065.48	0.00000	NO	YES
36	e"	3065.48	0.00000	NO	YES
37	e'	3133.39	5.19946	YES	YES
38	e'	3133.39	5.19946	YES	YES
39	a'	3133.84	0.00000	NO	YES

Total COSMO energy + OC correction = -409.0168434402 H

7 References

1 I. Krossing and A. Reisinger, *Coord. Chem. Rev.*, 2006, **250**, 2721–2744.
2 I. Krossing, *Chem.–Eur. J.*, 2001, **7**, 490–502.
3 J. M. Slattery, A. Higelin, T. Bayer and I. Krossing, *Angew. Chem., Int. Ed.*, 2010, **49**, 3228–3231.
4 I. Krossing, H. Brands, R. Feuerhake and S. Koenig, *J. Fluor. Chem.*, 2001, **112**, 83–90.
5 W. B. Reid, J. R. McAtee and D. A. Watson, *Organometallics*, 2019, **38**, 3796–3803.
6 G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176–2179.
7 R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, R. Goodfellow and P. Granger, *Magn. Reson. Chem.*, 2002, **40**, 489–505.
8 J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105–107.
9 (a) Bruker, *SAINT, V8.40A*, Bruker AXS Inc., Madison, Wisconsin, USA; (b) Bruker, *SADABS, 2016/2:*, Bruker AXS Inc., Madison, Wisconsin, USA; (c) L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *J. Appl. Crystallogr.*, 2015, **48**, 3–10.
10 (a) G. M. Sheldrick, *Acta Crystallogr. C*, 2015, **71**, 3–8; (b) G. M. Sheldrick, *Acta Crystallogr. A*, 2015, **71**, 3–8.
11 C. B. Hübschle, G. M. Sheldrick and B. Dittrich, *J. Appl. Crystallogr.*, 2011, **44**, 1281–1284.
12 (a) D. Kratzert, J. J. Holstein and I. Krossing, *J. Appl. Crystallogr.*, 2015, **48**, 933–938; (b) D. Kratzert and I. Krossing, *J. Appl. Crystallogr.*, 2018, **51**, 928–934.
13 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.
14 C. R. Groom, I. J. Bruno, M. P. Lightfoot and S. C. Ward, *Acta Crystallogr. B*, 2016, **72**, 171–179.
15 D. Kratzert, *FinalCif, V66*, https://www.xs3.uni-freiburg.de/research/finalcif.
16 (a) R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, *Chem. Phys. Lett.*, 1989, **162**, 165–169; (b) M. von Arnim and R. Ahlrichs, *J. Comput. Chem.*, 1998, **19**, 1746–1757; (c) K. Eichkorn, O. Treutler, H. Öhm, M. Häser and R. Ahlrichs, *Chem. Phys. Lett.*, 1995, **240**, 283–290; (d) A. Schäfer, H. Horn and R. Ahlrichs, *J. Chem. Phys.*, 1992, **97**, 2571–2577; (e) P. Deglmann and F. Furche, *J. Chem. Phys.*, 2002, **117**, 9535–9538.
17 O. Treutler and R. Ahlrichs, *J. Chem. Phys.*, 1995, **102**, 346–354.
18 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098–3100.
19 J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822–8824.
20 J. P. Perdew, *Phys. Rev. B*, 1986, **34**, 7406.
21 P. Deglmann, F. Furche and R. Ahlrichs, *Chem. Phys. Lett.*, 2002, **362**, 511–518.
22 (a) R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2004, **6**, 5119; (b) M. Sierka, A. Hogekamp and R. Ahlrichs, *J. Chem. Phys.*, 2003, **118**, 9136–9148.
23 F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057–1065.
24 (a) S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104; (b) S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456–1465.
25 (a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372–1377; (b) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652; (c) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789.
26 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.
27 (a) A. D. Boese, J. M. L. Martin and W. Klopper, *J. Phys. Chem. A*, 2007, **111**, 11122–11133; (b) W. Klopper and H. P. Luthi, *Mol. Phys.*, 1999, **96**, 559–570.
28 (a) T. H. Dunning, *J. Chem. Phys.*, 1989, **90**, 1007–1023; (b) R. A. Kendall, T. H. Dunning and R. J. Harrison, *J. Chem. Phys.*, 1992, **96**, 6796–6806; (c) D. E. Woon and T. H. Dunning, *J. Chem. Phys.*, 1993, **98**, 1358–1371; (d) F. Weigend, A. Köhn and C. Hättig, *J. Chem. Phys.*, 2002, **116**, 3175–3183.
29 K. A. Peterson, D. Figgen, M. Dolg and H. Stoll, *J. Chem. Phys.*, 2007, **126**, 124101.

30 A. Klamt and G. Schüürmann, *J. Chem. Soc., Perkin Trans. 2*, 1993, 799–805.
31 W. M. Haynes, *CRC Handbook of Chemistry and Physics, 93rd Edition*, CRC Press, London, 93rd edn., 2016.
32 (a) F. Neese, *WIREs Comput. Mol. Sci.*, 2012, **2**, 73–78; (b) F. Neese, *WIREs Comput. Mol. Sci.*, 2018, **8**. DOI: 10.1002/wcms.1327.
33 M. Ligare, *Am. J. Phys.*, 2010, **78**, 815–819.