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Intramolecular Donor-stabilized Tetra-Coordinated Germanium(IV) Di-Cations and their Lewis Acidic Properties

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Experimental Procedures

General Procedure

All manipulations were carried out under a protective atmosphere of argon applying standard Schlenk techniques or in a dry box. Tetrahydrofuran (THF) was refluxed over sodium/benzophenone. Dichloromethane (DCM) and acetonitrile (MeCN) were stirred and refluxed over calcium hydride and kept over 3 Å molecular sieves. All solvents were distilled and stored under argon and degassed prior to use. $CDCl_3$ was dried, distilled and stored under argon and degassed prior to use. CD_2Cl_2, CD_3CN ampoules were purchased from Sigma Aldrich and used as it is. All chemicals were used as purchased. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to external $SiMe_4$ using the residual signals of the deuterated solvent (^1H) or the solvent itself (^{13}C). $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR were referenced to external $C_6H_5CF_3$ (TFT) and 85% H_3PO_4 respectively. NMR spectra were recorded on Bruker AVANCE III HD ASCEND 9.4 Tesla/400 MHz, Jeol 9.4 Tesla/400 MHz and Bruker AVANCE III HD ASCEND 14.1 Tesla/600 MHz. Melting points were determined under argon in closed NMR tubes and are uncorrected. Elemental analyses were performed on Elementar vario EL analyzer and FLASH 2000 Elemental CHNS/O Analyser. Single crystal data were collected on both Bruker SMART APEX four-circle diffractometer equipped with a CMOS photon 100 detector (Bruker Systems Inc.) with a Cu Kα radiation (1.5418 Å), and Bruker SMART APEX Duo, Bruker APEX-II CCD diffractometers using Mo Kα radiation (0.71073 Å). Mass spectra were measured in AB Sciex 4800 plus HRMS on the Waters Synapt, USA.

Synthesis of L^{iPr}-Br [S1] 5,6-Dibromoacenaphthene (6.00 g, 19.2 mmol) was dissolved in tetrahydrofuran (THF) (100 mL) and cooled to -78°C. *n*-BuLi (12.0 mL of 1.6 M solution in hexane, 19 mmol) was added dropwise to it, maintaining -78°C and stirred for 2 hours at the same temperature. Chlorodiisopropylphosphine (3.0 mL, 19.2 mmol) taken in THF (25 mL) was added dropwise to the resultant mixture maintaining -78°C. The solution mixture was then allowed to warm to room temperature and stirred overnight. The solvent was removed completely by evaporation and toluene was added to the solid residue. The toluene solution was separated from the suspended solid through filtration. The toluene extract was completely evaporated to give 5-Bromo,6-(diisopropylphosphino)acenaphthene **L^{iPr}** as yellow solid in 76% (5.1 g) yield.

^1H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.4 Hz, 1H, Acn-C*H*), 7.69 (dd, *J* = 7.3, 2.5 Hz, 1H, Acn-C*H*), 7.30 (td, *J* = 7.2, 1.4 Hz, 1H, Acn-C*H*), 7.09 (dd, *J* = 7.4, 1.4 Hz, 1H, Acn-C*H*), 3.39 – 3.27 (m, 4H, Acn-CH_2), 2.24 (doublet of septet, *J* = 7.1, 1.9 Hz, 2H, ^{i}Pr-C*H*), 1.19 (dd, $^3J_{PH}$ = 12.7, $^3J_{HH}$ = 6.9 Hz, 6H, ^{i}Pr-CH_3), 1.07 (dd, $^3J_{PH}$ = 13.5, $^3J_{HH}$ = 7.0 Hz, 6H, ^{i}Pr-CH_3) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 148.01 (s, Acn-*C*), 147.05 (d, *J* = 1.7 Hz, Acn-*C*), 141.67 (d, *J* = 4.4 Hz, Acn-*C*), 135.38 (s, Acn-*C*), 134.93 (d, *J* = 2.2 Hz, Acn-*C*), 134.12 (d, *J* = 18.6 Hz, Acn-*C*), 130.29 (d, *J* = 34.3 Hz, Acn-*C*H), 120.34 (s, Acn-*C*H), 119.70 (s, Acn-*C*H), 115.65 (s, Acn-*C*H), 30.20 (s, Acn-*C*H_2), 29.80 (s, Acn-*C*H_2), 25.61 (d, $^1J_{PC}$ = 17.8 Hz, ^{i}Pr-*C*H), 20.69 (d, $^2J_{PC}$ = 15.4 Hz, ^{i}Pr-*C*H_3), 19.35 (d, $^2J_{PC}$ = 16.4 Hz, ^{i}Pr-*C*H_3) ppm.

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ -1.58 (s) ppm.

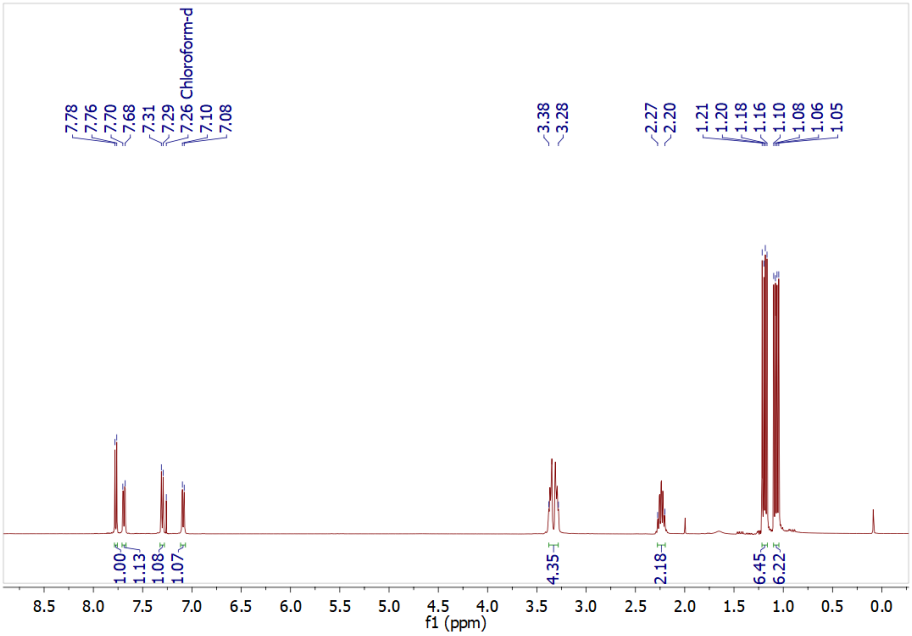


Fig. S1 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **L^{iPr}-Br**.

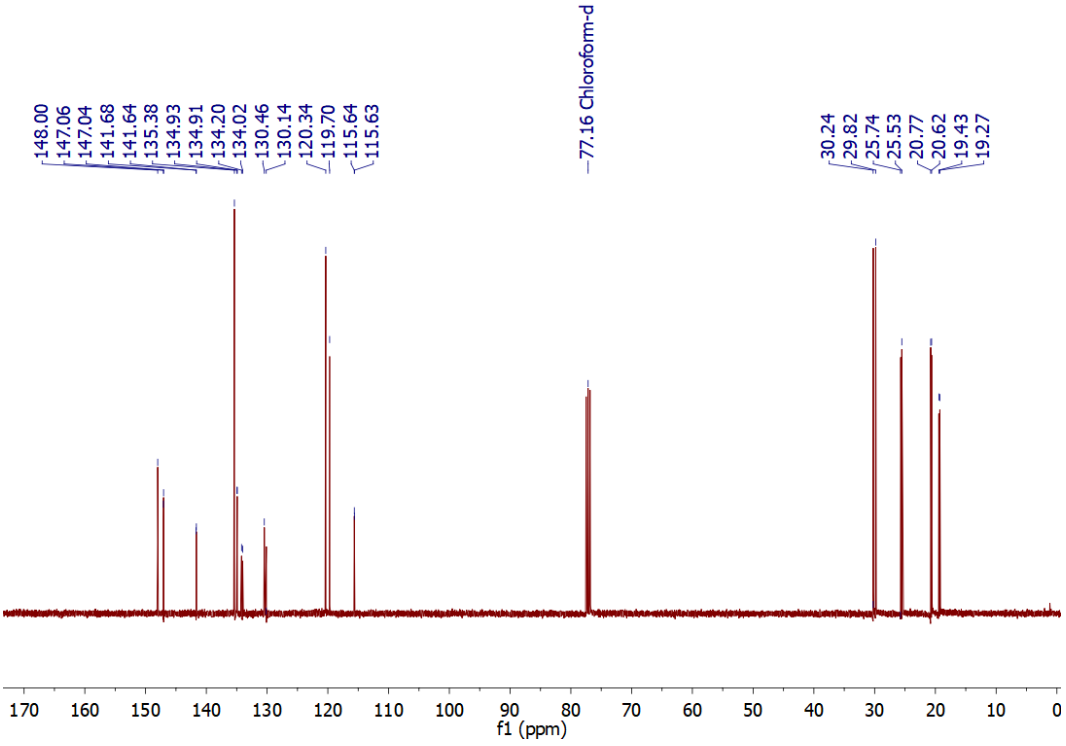


Fig. S2 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$, 298 K) of **L^{iPr}-Br**.

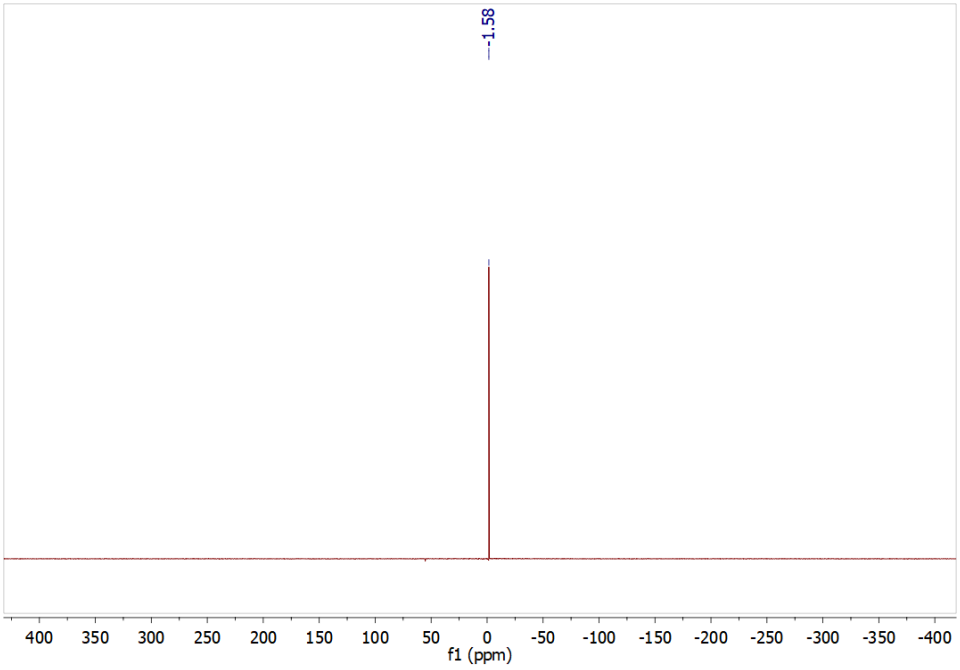


Fig. S3. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 298 K) of **L^{iPr}-Br**.

Synthesis of L^{Ph}-Br: [S2] 5,6-Dibromo acenaphthene (4.50 g, 14.4 mmol) was dissolved in THF (100 mL) and cooled to -78 °C. *n*-BuLi (9.0 mL of 1.6 M solution in hexane, 14.4 mmol) was added dropwise to it maintaining -78 °C and stirred for 2 hours at the same temperature. Chlorodiphenylphosphine (2.6 mL, 14.4 mmol) taken in THF (25 mL) was added dropwise to the resultant mixture maintaining -78 °C. The solution mixture was then allowed to warm to room temperature and stirred overnight. The solvent was removed completely by evaporation and dichloromethane (DCM) was added to the solid residue. The DCM solution was separated from the suspended solid through filtration. The DCM extract was completely evaporated to give 5-Bromo,6-(diphenylphosphino) acenaphthene **L^{Ph}** as yellow solid. Yellow crystals of **L^{Ph}** have been obtained in 52% yield (3.1 g) from concentrated DCM solution.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.4 Hz, 1H), 7.32 (m, 6H), 7.29 (m, 4H), 7.12 (m, 2H), 7.08 (d, *J* = 4.4 Hz, 1H), 3.34 (s, 4H, Acn-C*H*$_2$) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.67 (s, Acn-*C*), 146.93 (d, *J* = 2.0 Hz, Acn-*C*), 141.71 (d, *J* = 4.1 Hz, Acn-*C*), 139.35 (d, *J* = 14.2 Hz, Acn-*C*H), 138.01 (s, Acn-*C*), 134.84 (s, Acn-*C*H), 134.32 (d, *J* = 20.1 Hz, Acn-*C*), 133.49 (d, *J* = 18.6 Hz, Ph-*C*H), 130.11 (d, *J* = 33.3 Hz, Ph-*C*), 128.64 (d, *J* = 6.8 Hz, Ph-*C*H), 128.55 (s, Ph-*C*H), 120.85 (s, Acn-*C*H), 120.40 (s, Acn-*C*H), 115.97 (s, Acn-*C*Br), 30.28 (s, Acn-*C*H$_2$), 30.04 (s, Acn-*C*H$_2$) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ -9.40 ppm.

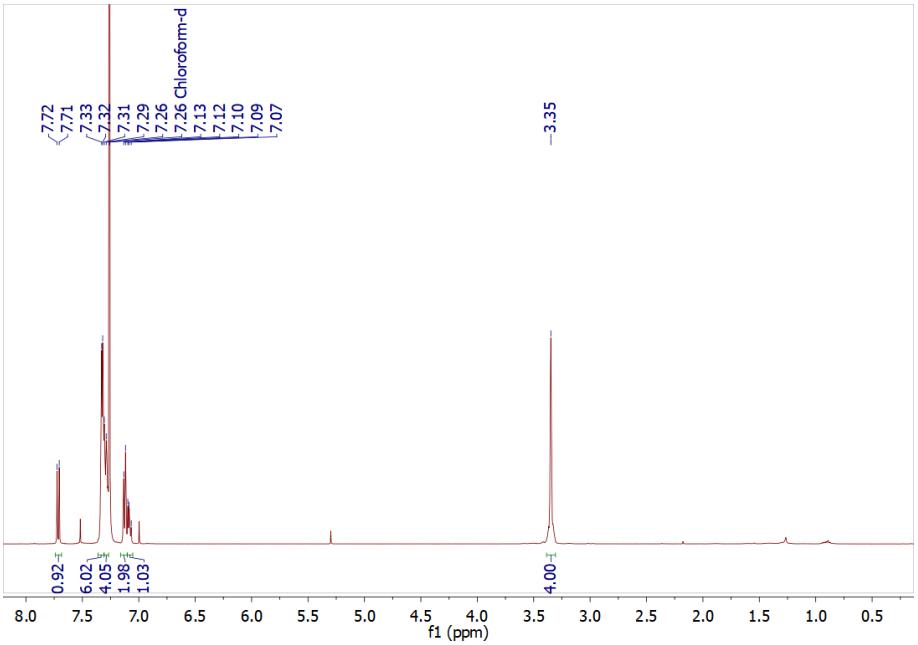


Fig. S4 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **L^{Ph}-Br**.

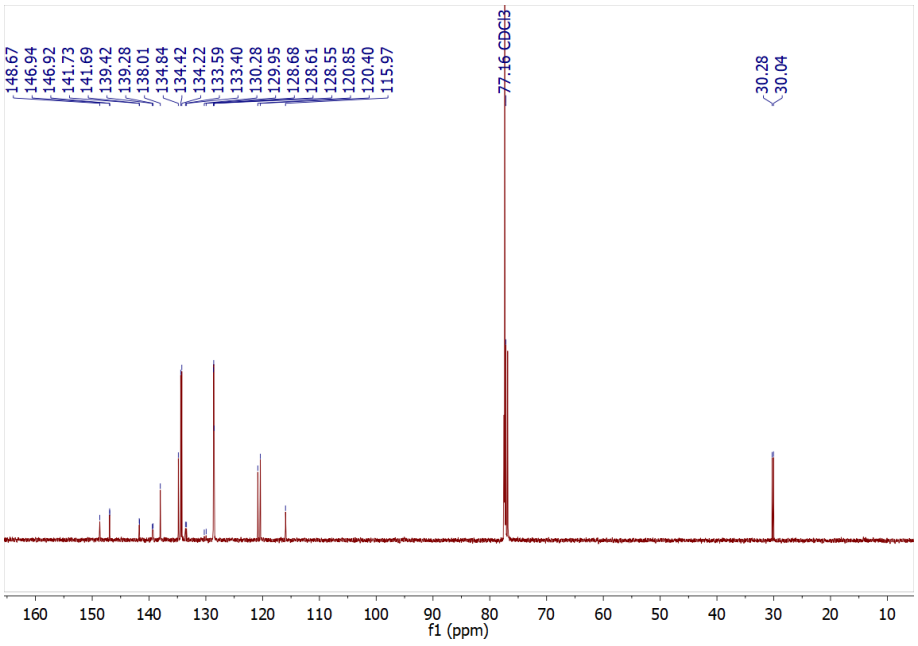


Fig. S5 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$, 298 K) of **L^{Ph}-Br**.

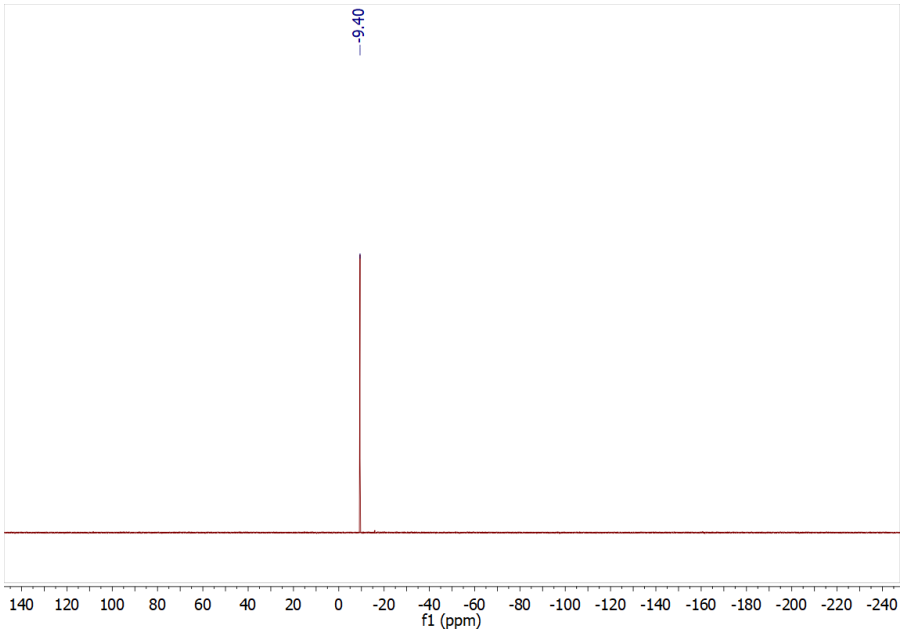


Fig. S6 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 298 K) of **L^{Ph}-Br**.

Synthesis of 1^{iPr}: 5-Bromo,6-(diisopropylphosphino)acenaphthene **L^{iPr}** (4.50 g, 12.9 mmol) was dissolved in THF (50 mL) and cooled to -78 °C. *n*-BuLi (8.1 mL of 1.6 M solution in hexane, 13 mmol) was added dropwise to it maintaining -78 °C and stirred for 2 hours at the same temperature. Germanium tetrachloride (1.0 mL, 8.6 mmol) taken in THF (20 mL) was added dropwise to the resultant mixture maintained at -78 °C. The solution mixture was then allowed to warm to room temperature and stirred overnight. The solvent was removed completely by evaporation and dichloromethane (DCM) was added to the solid residue. The dichloromethane solution was separated from the suspended solid through filtration. The dichloromethane extract was evaporated completely to give crude yellow solid. The crude yellow solid was dissolved in minimum volume of THF. Colorless single crystals of **1^{iPr}** were obtained from concentrated THF solution maintained at room temperature in 75% (2.7 g) yield. Single crystals were also obtained from concentrated MeCN solution in similar yield. Melting point: > 200°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (td, *J* = 7.2, 1.8 Hz, 2H, Acn-C*H*), 7.93 (m, *J* = 6.8, 3.3 Hz, 2H, Acn-C*H*), 7.68 (m, *J* = 7.2, 5.8 Hz, 4H, Acn-C*H*), 3.57 (s, 8H, Acn-CH_2), 3.09 – 2.99 (m, 4H, ^{i}Pr-C*H*), 1.26 (q, *J* = 7.0 Hz, 12H, ^{i}Pr-CH_3), 1.16 (q, *J* = 8.0 Hz, 12H, ^{i}Pr-CH_3) ppm.

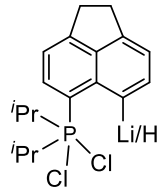
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.14 (t, *J* = 1.4 Hz, Acn-*C*), 152.23 (s, Acn-*C*), 139.76 (t, *J* = 4.7 Hz, Acn-*C*), 139.16 (t, *J* = 10.0 Hz, Acn-*C*), 135.99 (t, *J* = 5.8 Hz, Acn-*C*), 135.03 (s, Acn-*C*), 133.04 – 131.60 (m, Acn-*CH*), 121.29 (t, *J* = 2.9 Hz, Acn-*CH*), 120.99 (t, *J* = 1.6 Hz, Acn-*CH*), 114.39 – 114.10 (m, Acn-*CH*), 31.24 (s, Acn-*C*H_2), 30.74 (s, Acn-*C*H_2), 25.18 (br., ^{i}Pr-*C*H) 19.13 (t, *J* = 2.9 Hz, ^{i}Pr-*C*H_3), 18.01 (s, ^{i}Pr-*C*H_3) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ -11.06 ppm.

Elemental Analysis: Calcd. for $C_{36}H_{44}Cl_4Ge_2P_2$: C, 52.36; H, 5.37. Found: C, 52.40; H, 5.31.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) of the crude yellow solid: δ -11.06, -19.52 ppm.

Proposed structure of the oxidized product showing peak at -19.5 ppm in $^{31}P\{^{1}H\}$ NMR spectrum:



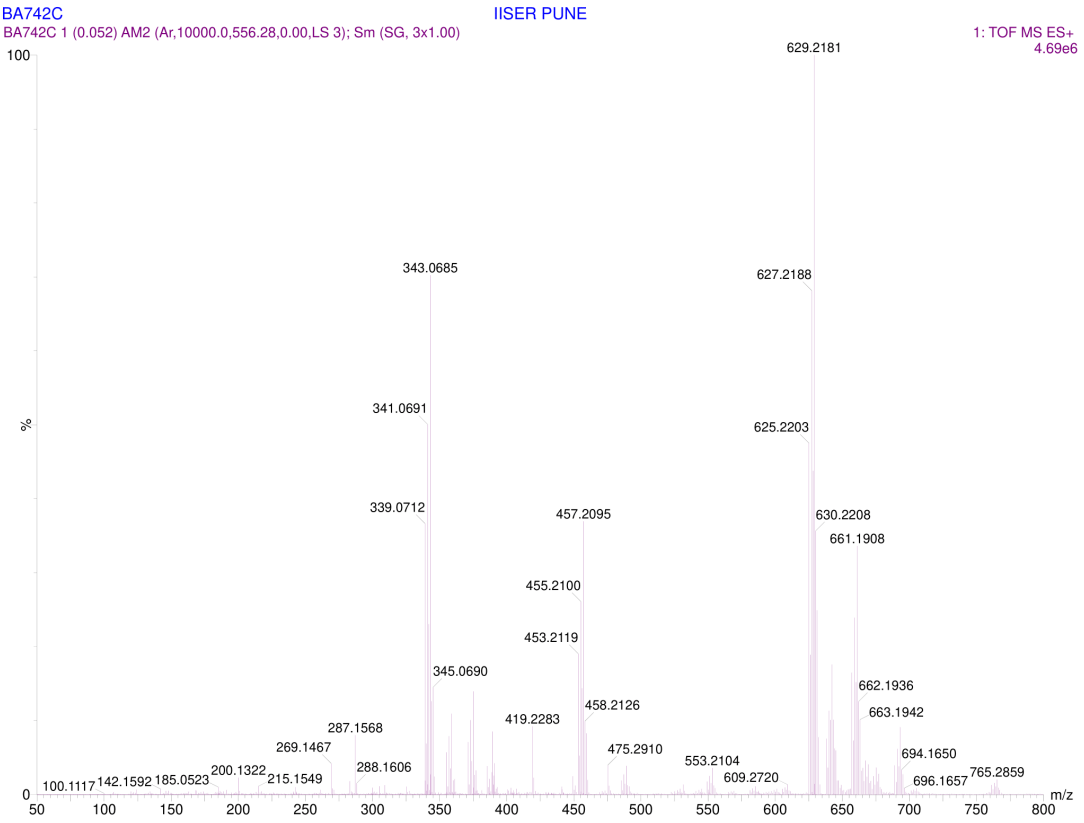


Fig. S7 ESI-MS (dichloromethane) found m/z 341.0691, calculated for $[C_{18}H_{24}Cl_2P]^+$ m/z 341.0988.

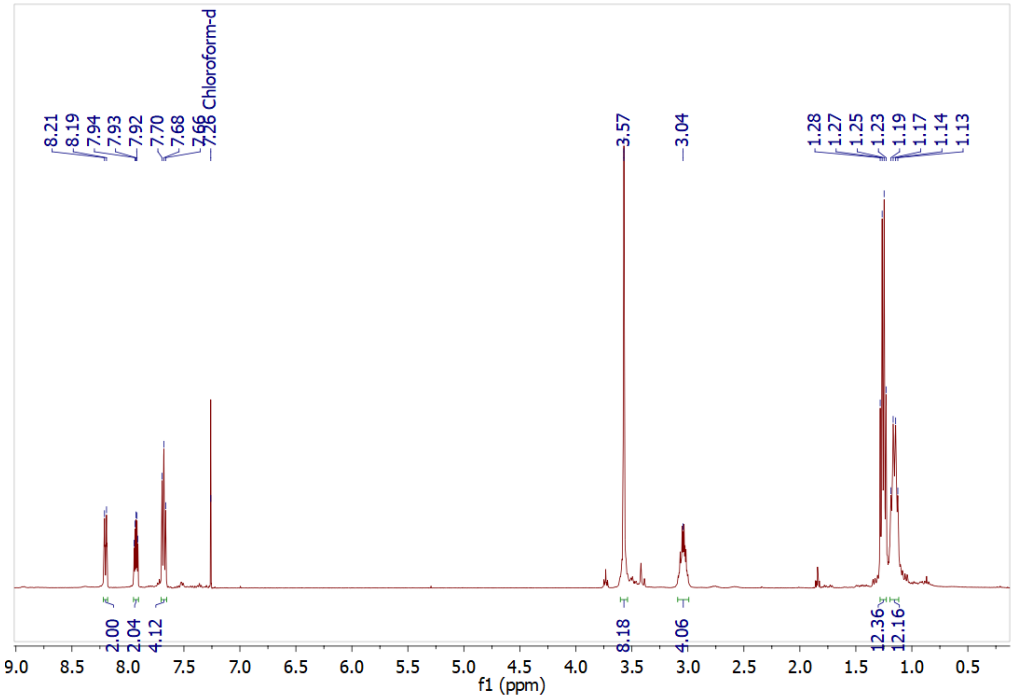


Fig. S8 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **1**^{iPr}.

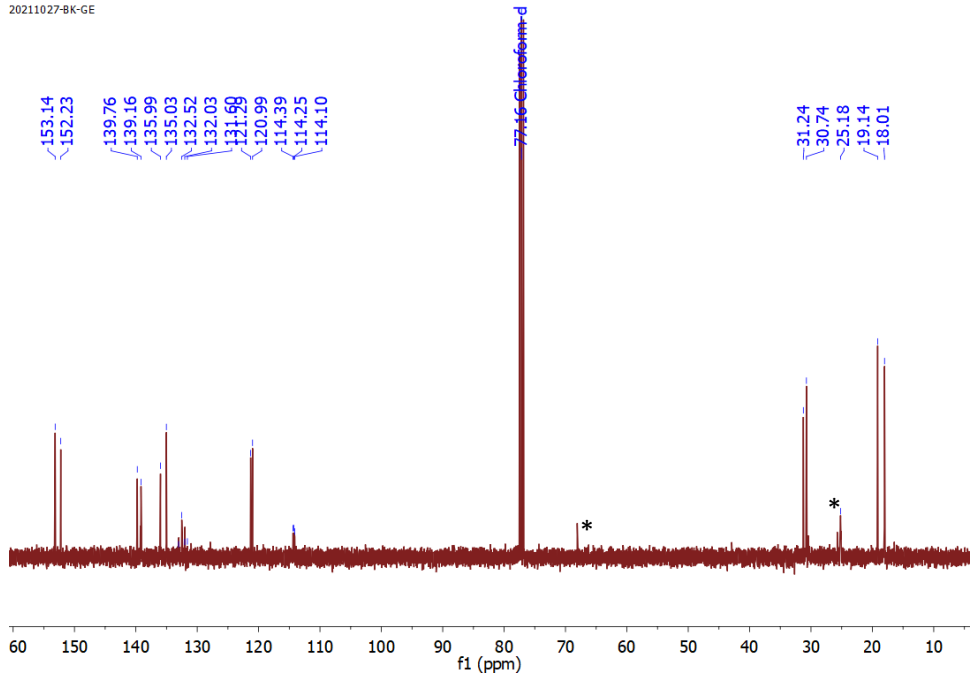


Fig. S9 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$, 298 K) of **1**^{iPr}. (* = peak for THF)

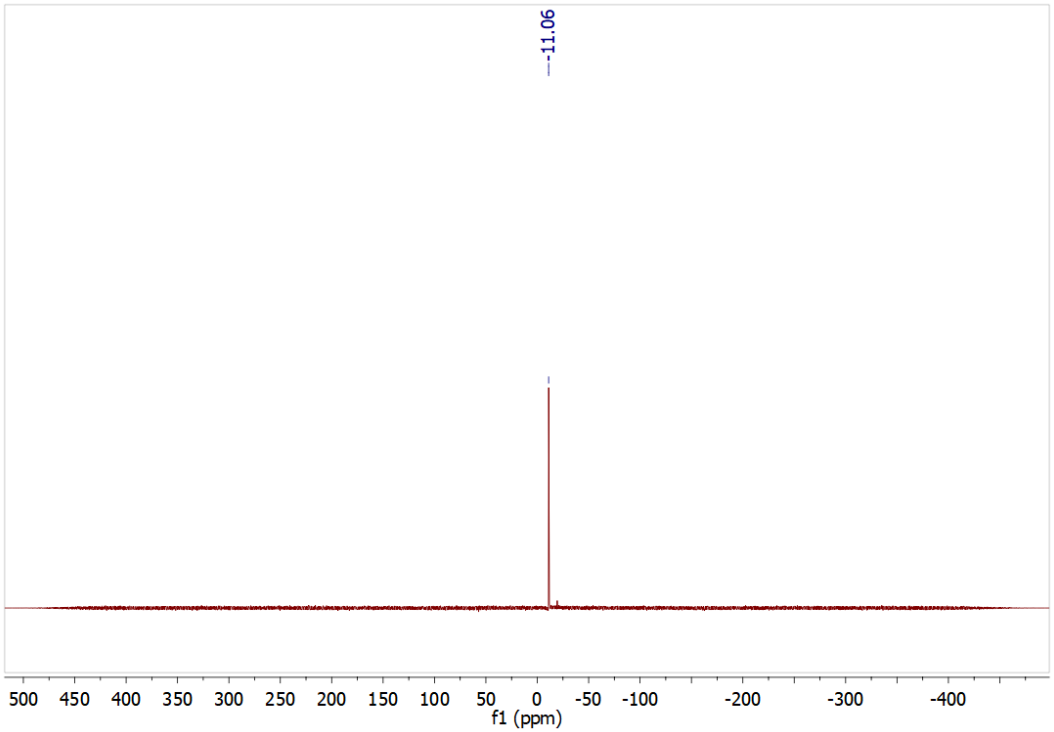


Fig. S10 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 298 K) of **1**^{iPr}.

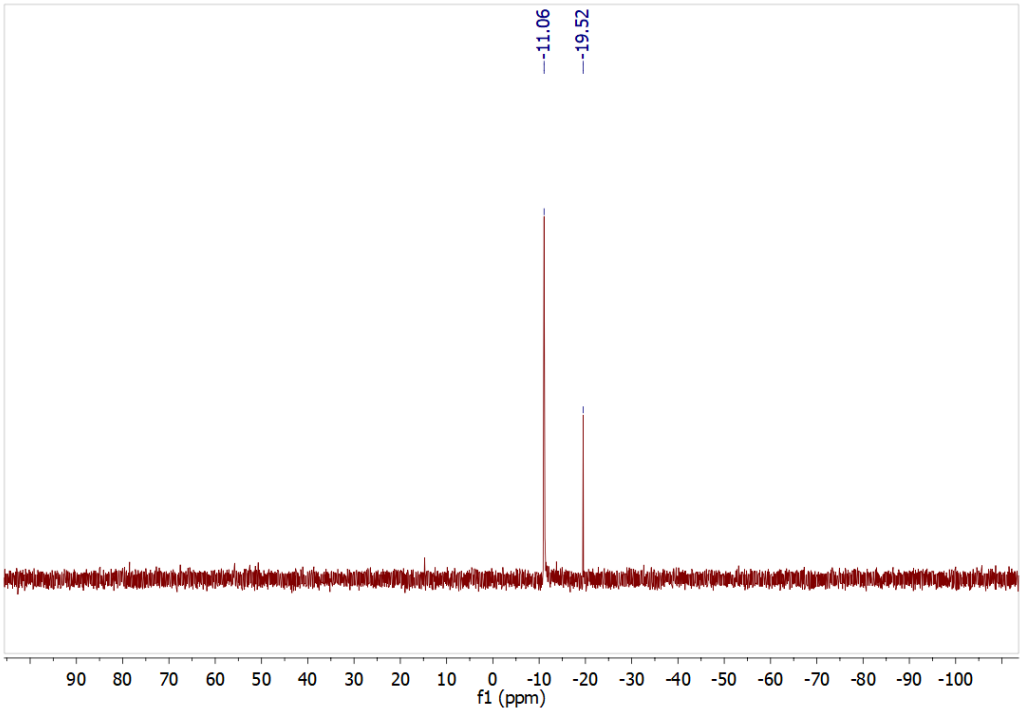


Fig. S11 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 298 K) of the crude yellow solid from the reaction mixture of **1**^{iPr}.

Synthesis of 1^{Ph}: 5-Bromo,6-(diphenylphosphino) acenaphthene **L**^{Ph} (4 g, 9.6 mmol) was dissolved in THF (30 mL) and cooled to -78 °C. *n*-BuLi (6 mL of 1.6 M solution in hexane, 9.6 mmol) was added dropwise to it maintaining -78 °C and stirred for 2 hours at the same temperature. Germanium tetrachloride (0.56 mL, 4.8 mmol) taken in THF (10 mL) was added drop wise to the resultant mixture maintaining -78 °C. The solution mixture was then allowed to warm to room temperature and stirred overnight. The solvent was removed completely by evaporation and dichloromethane

was added to the solid residue. The dichloromethane solution was separated from the suspended solid through filtration. The dichloromethane extract was evaporated completely to give crude solid. The crude solid was dissolved in minimum volume of THF. Colorless single crystals of **1^{Ph}** were obtained from concentrated THF solution maintained at room temperature in 60% (2.4 g) yield. Melting point: >200 °C.

^{1}H NMR ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.96 (d, *J* = 7.4 Hz, 2H), 7.48 (d, *J* = 7.4 Hz, 2H), 7.37 – 7.31 (m, 2H), 7.27 (s, 2H), 7.25 (br, 2H), 7.14 (br, 10H), 6.66 (br, 4H), 6.11 (br, 4H), 3.44 (s, 8H) ppm.

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 150.42 (s, Acn-*C*), 148.66 (m, Acn-*C*), 139.93 (s, Acn-*C*), 139.84 (s, Acn-*C*), 137.95 (m, Acn-*C*H), 135.55 (s, Acn-*C*), 132.88 (s, Ph-*C*), 132.72 (s, Ph-*C*H), 129.19 (s, Acn-*C*H), 128.38 (s, Ph-*C*H), 128.19 (m, Ph-*C*H), 127.94 (m, Ph-*C*H), 125.45 (s, Acn-*C*H), 120.95 (s, Acn-*C*H), 120.04 (s, Acn-*C*), 30.77 (s, Acn-*C*H$_2$), 30.19 (s, Acn-*C*H$_2$) ppm.

^{31}P{^{1}H} NMR (162 MHz, Chloroform-*d*) δ -34.79 ppm.

Elemental Analysis: Calcd. for $C_{48}H_{36}Cl_2GeP_2$: C, 70.45; H, 4.43. Found: C, 70.29; H, 5.15.

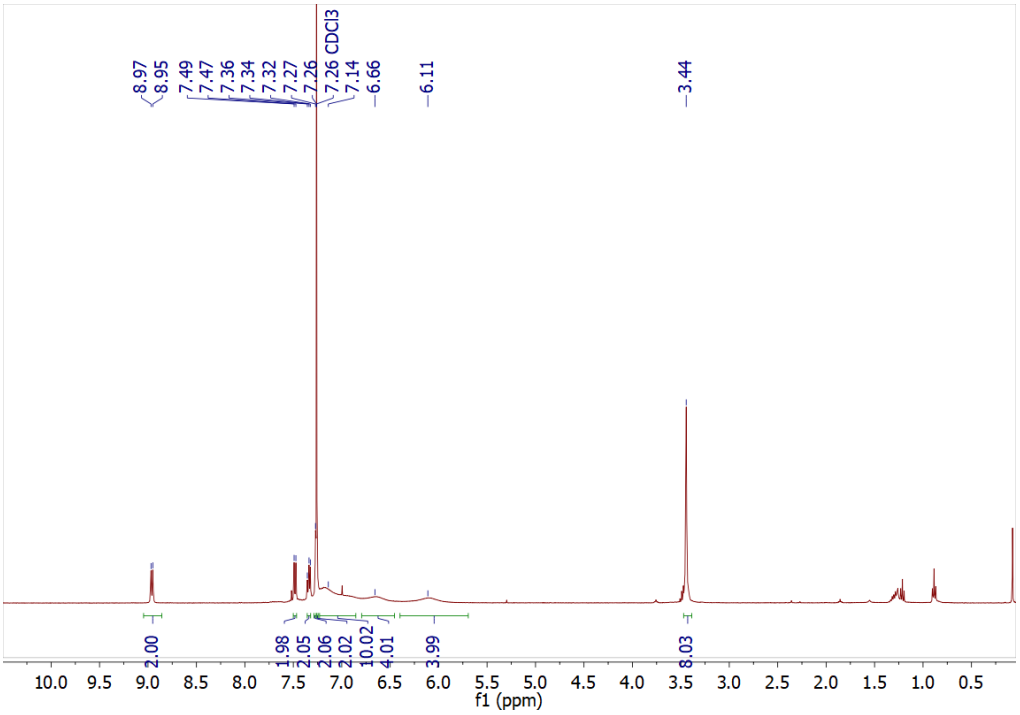


Fig. S12 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **1^{Ph}**.

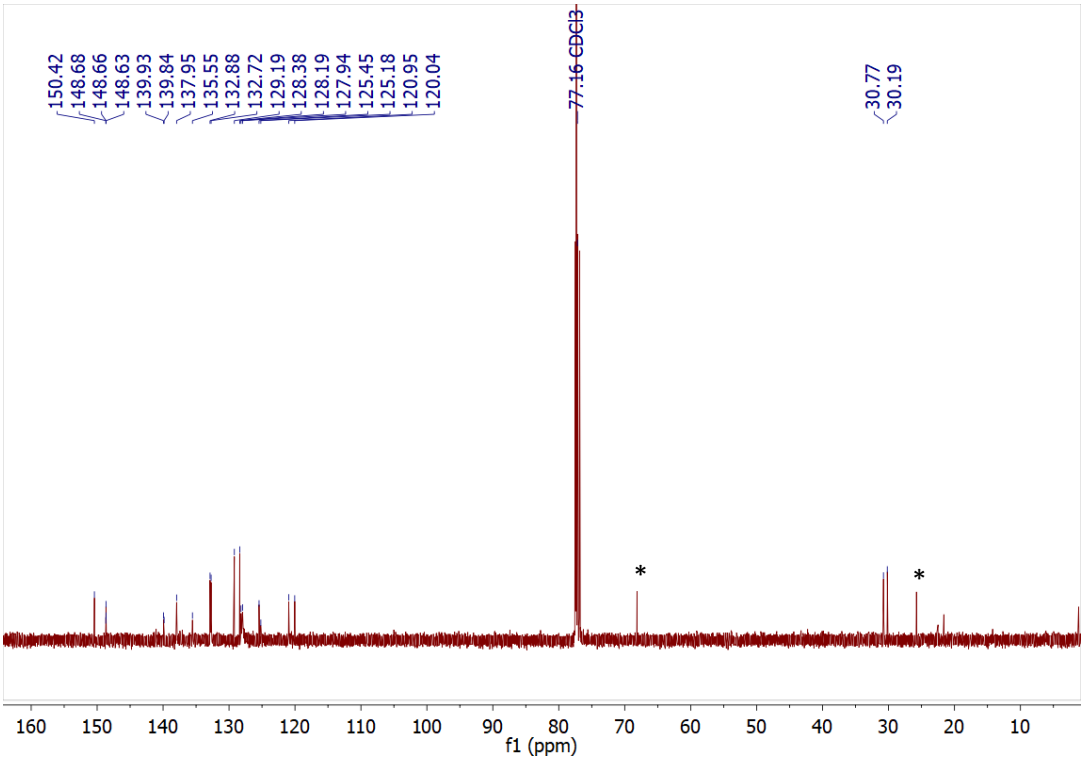


Fig. S13 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$, 298 K) of **1**^{Ph} (* = peak for THF)

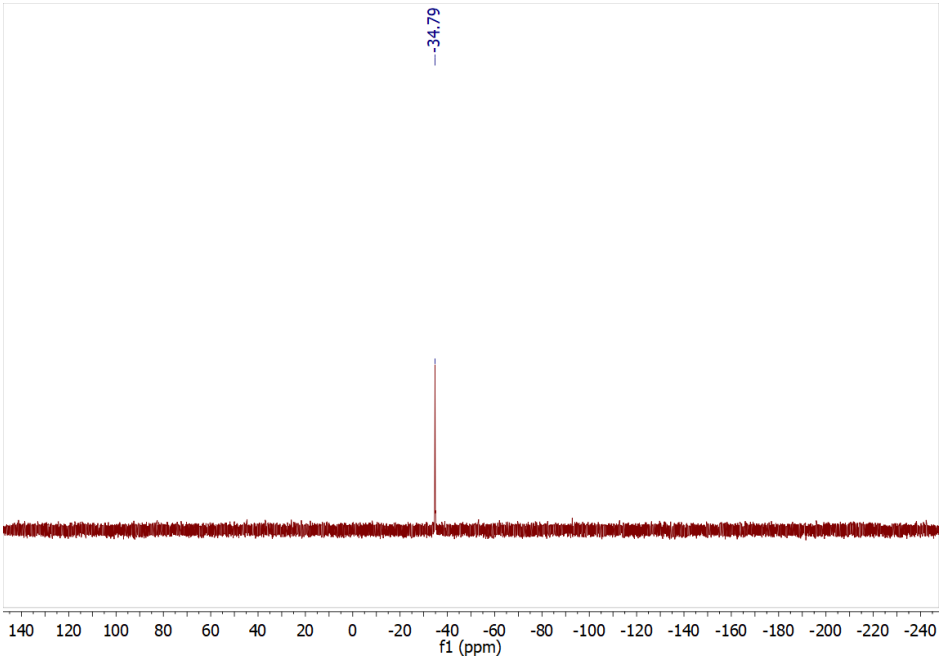


Fig. S14 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, CDCl3, 298 K) of **1**^{Ph}

Synthesis of 2^{iPr}: One equivalent of **1**^{iPr} (0.1 g, 0.12 mmol) was dissolved in 10 mL of THF and was mixed with one equivalent of trimethylsilyl trifluoromethanesulfonate (TMSOTf) (22 μL, 0.12 mmol) dissolved in 5 mL of THF. The reaction mixture was stirred for 4 hours. The solution was concentrated and kept for crystallization under room temperature conditions. Colorless single crystals of **2**^{iPr} appeared after five days in 86% (0.08 g) yield. Single crystals

were also obtained from DCM solution in similar yield. Melting point: >200° C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.2 Hz, 2H, Acn-C*H*), 8.05 (br., 2H, Acn-C*H*), 7.71 (d, *J* = 7.1 Hz, 2H, Acn-C*H*), 7.65 (d, *J* = 7.2 Hz, 2H, Acn-C*H*), 3.58 (m, 8H, Acn-CH_2), 3.17 (br., 4H, ^{i}Pr-C*H*), 1.31 (q, *J* = 7.4 Hz, 12H, ^{i}Pr-CH_3), 1.19 (q, *J* = 8.2 Hz, 12H, ^{i}Pr-CH_3) ppm.

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 153.29 (s, Acn-*C*), 153.01 (br, Acn-*C*), 139.69 (t, *J* = 4.6 Hz, Acn-*C*), 136.43 (br, Acn-*C*), 135.45 (br, Acn-*C*), 121.60 (br, Acn-*C*), 121.40 (br, Acn-*CH*), 121.09 (q, *J* = 320.9 Hz, OTf), 113.33 (br, Acn-*CH*), 31.25 (s, Acn-*C*H_2), 30.81 (s, Acn-*C*H_2), 25.16 (br., ^{i}Pr-*C*H), 18.99 (s, ^{i}Pr-*C*H_3), 17.83 (s, ^{i}Pr-*C*H_3).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = -10.77 ppm.

^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ = -78.08 ppm.

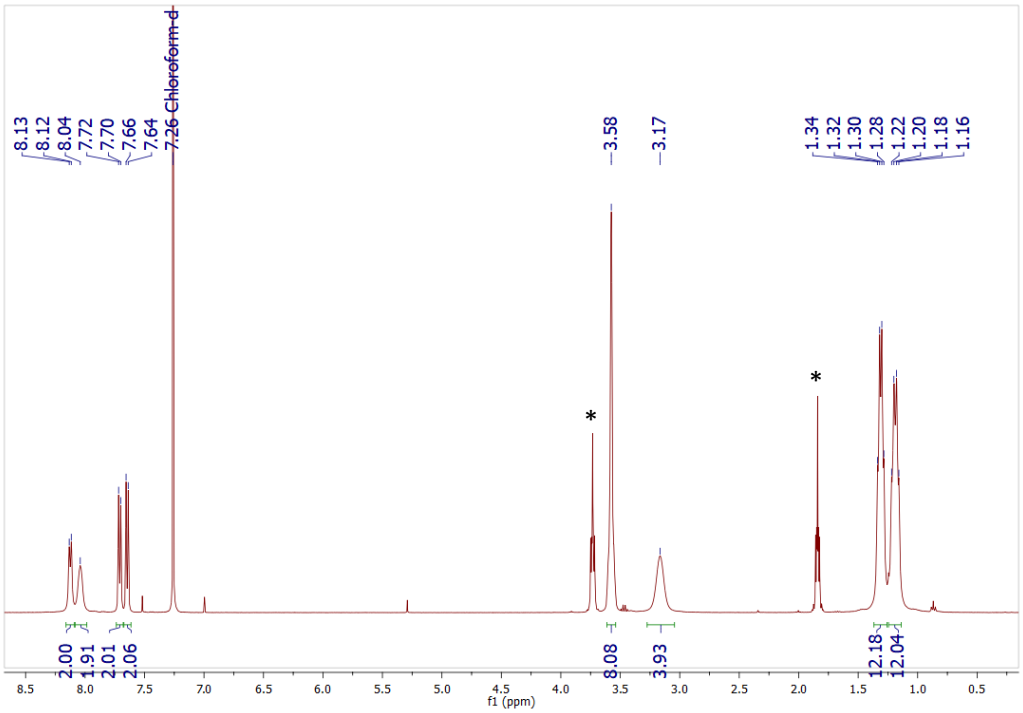


Fig. S15 ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of **2^{iPr}**. (* = peak for THF)

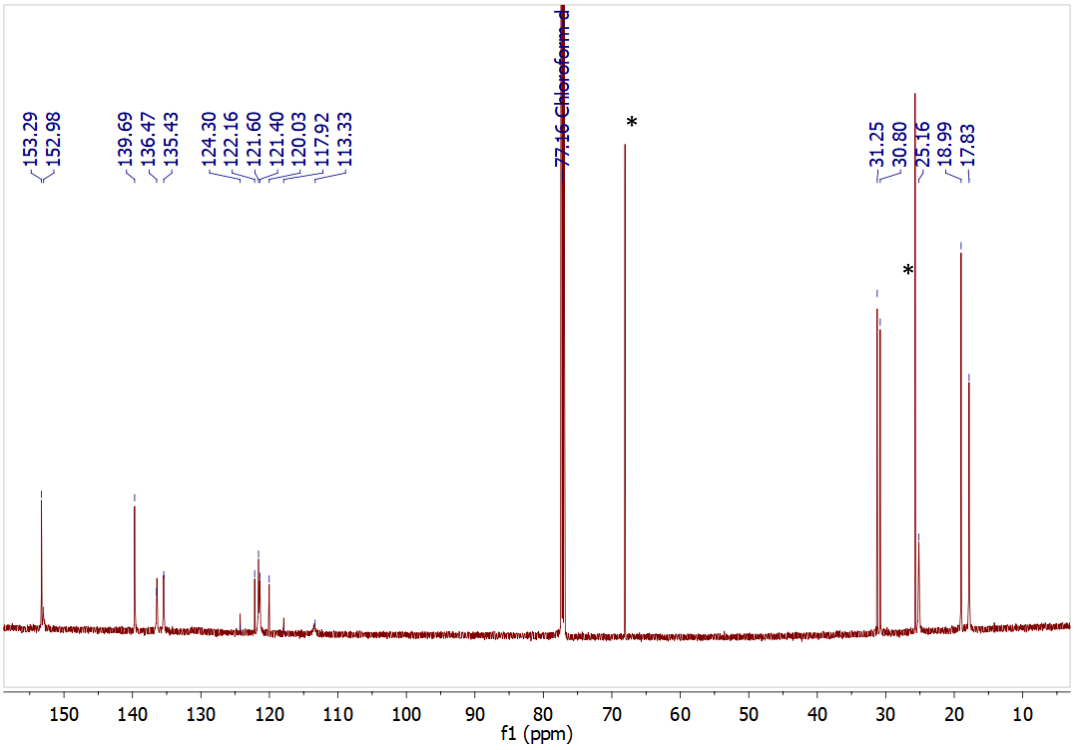


Fig. S16 $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$, 298 K) of **2**$^{i\mathrm{Pr}}$. (* = peak for THF)

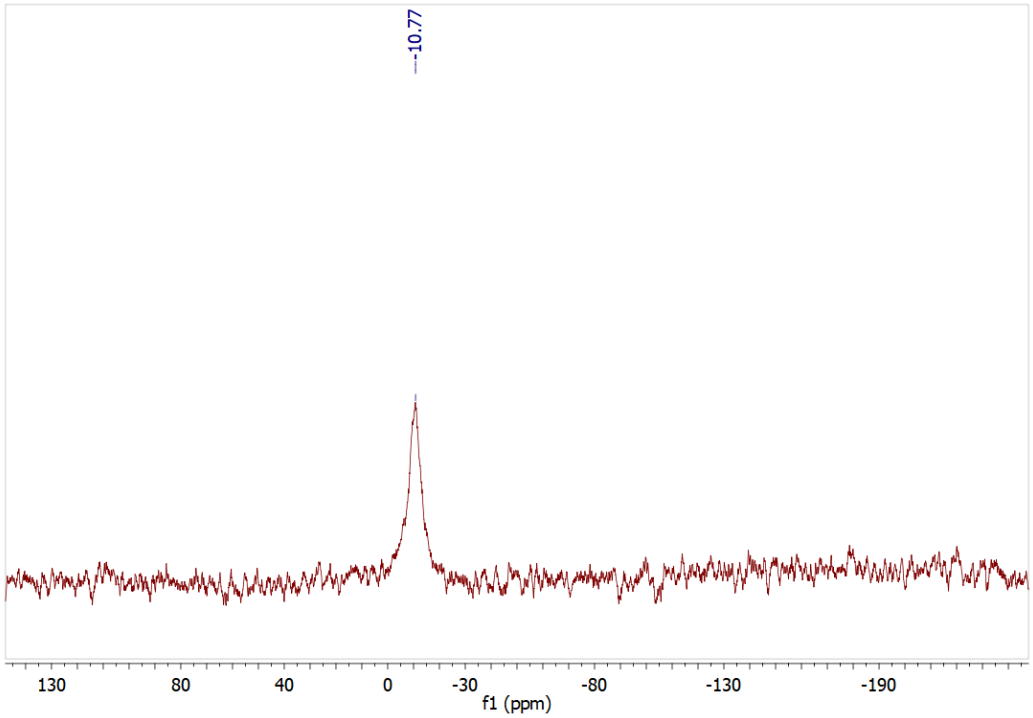


Fig. S17 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 298 K) of **2**$^{i\mathrm{Pr}}$.

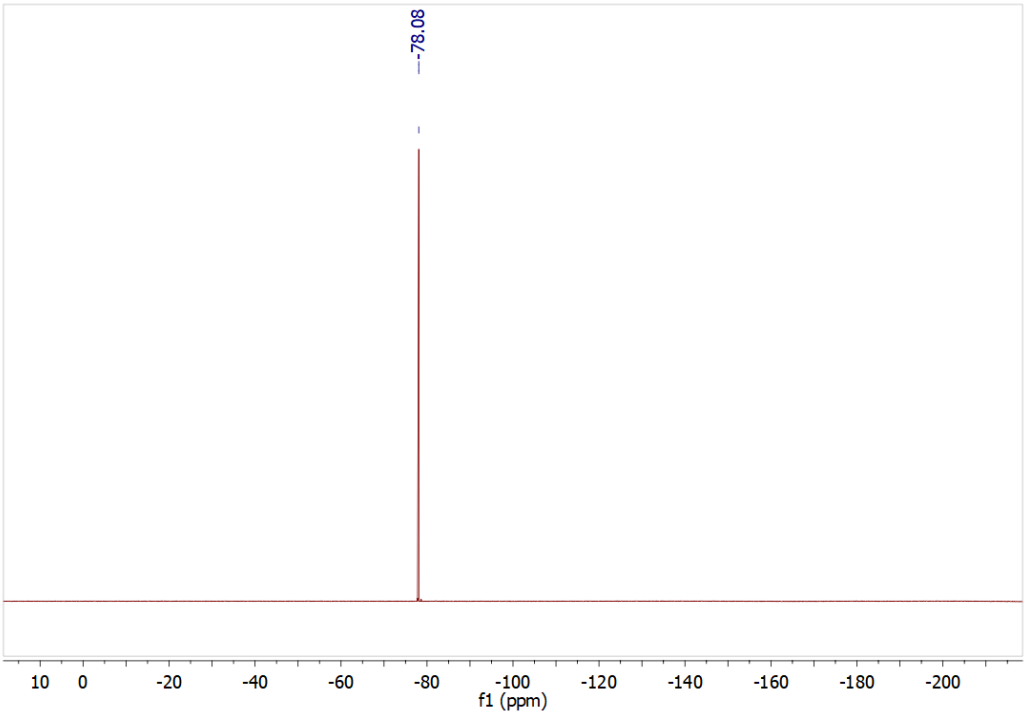


Fig. S18 $^{19}F\{^{1}H\}$ NMR spectrum (377 MHz, $CDCl_3$, 298 K) of **2^{iPr}**.

Synthesis of 2^{Ph}: One equivalent of **1^{Ph}** (0.1 g, 0.12 mmol) was dissolved in 10 mL of dichloromethane and one equivalent of trimethylsilyl trifluoromethanesulfonate (TMSOTf) (22 μL, 0.12 mmol) was added to it. The reaction mixture was stirred overnight. The solution was evaporated completely to get a white solid. The white solid was dissolved in THF. Colorless single crystals of **2^{Ph}** were obtained in 84% (0.1 g) yield from the THF solution layered with pentane and kept at room temperature. Melting point: >200 °C.

^{1}H NMR (600 MHz, Methylene Chloride-d_2, 298 K) δ 8.15 (d, *J* = 7.0 Hz, 1H, Acn-C*H*), 7.89-7.82 (m, 1H, Acn-C*H*), 7.63 (d, *J* = 7.2 Hz, 1H, Acn-C*H*), 7.43 (d, *J* = 7.1 Hz, 1H, Acn-C*H*), 7.31 (t, *J* = 7.2 Hz, 2H, Ph-C*H*), 7.11 (t, *J* = 7.4 Hz, 4H, Ph-C*H*), 6.89 (s, 4H, Ph-C*H*), 3.60-3.49 (m, 4H, Acn-CH_2) ppm.

^{13}C{^{1}H} NMR (151 MHz, Methylene Chloride-d_2) δ 154.73 (s, Acn-*C*), 153.50 (s, Acn-*C*), 140.45 – 140.21 (m, Acn-*C*), 139.57 (s, Acn-*C*), 139.40 – 139.09 (m, Acn-*C*H), 138.58 (s, Acn-*C*), 132.85 (s, Ph-*C*H), 131.61 (s, Ph-*C*), 129.50 (s, Acn-*C*H), 128.07 – 127.61 (m, Ph-*C*H), 125.39 (m, Ph-*C*H), 122.44 (s, Acn-*C*H), 121.90 (s, Acn-*C*H), 121.63 (q, *J* = 322.1 Hz, OTf), 119.79 – 118.87 (m, Acn-*C*), 31.53 (s, Acn-*C*H_2), 31.19 (s, Acn-*C*H_2) ppm.

^{31}P{^{1}H} NMR (162 MHz, Methylene Chloride-d_2, 298 K) δ -13.20 ppm.

^{31}P{^{1}H} NMR (162 MHz, Methylene Chloride-d_2, 203 K) δ -3.0 (d, $^{2}J_{P\text{-}P}$ = 110 Hz), -20.5 (d, $^{2}J_{P\text{-}P}$ = 110 Hz) ppm.

^{19}F{^{1}H} NMR (377 MHz, Methylene Chloride-d_2) δ -78.84 ppm.

Elemental Analysis: Calcd. for $C_{49}H_{36}ClF_3GeO_3P_2S$: C, 63.15; H, 3.89; S, 3.44. Found: C, 63.94; H, 3.83; S, 2.98.

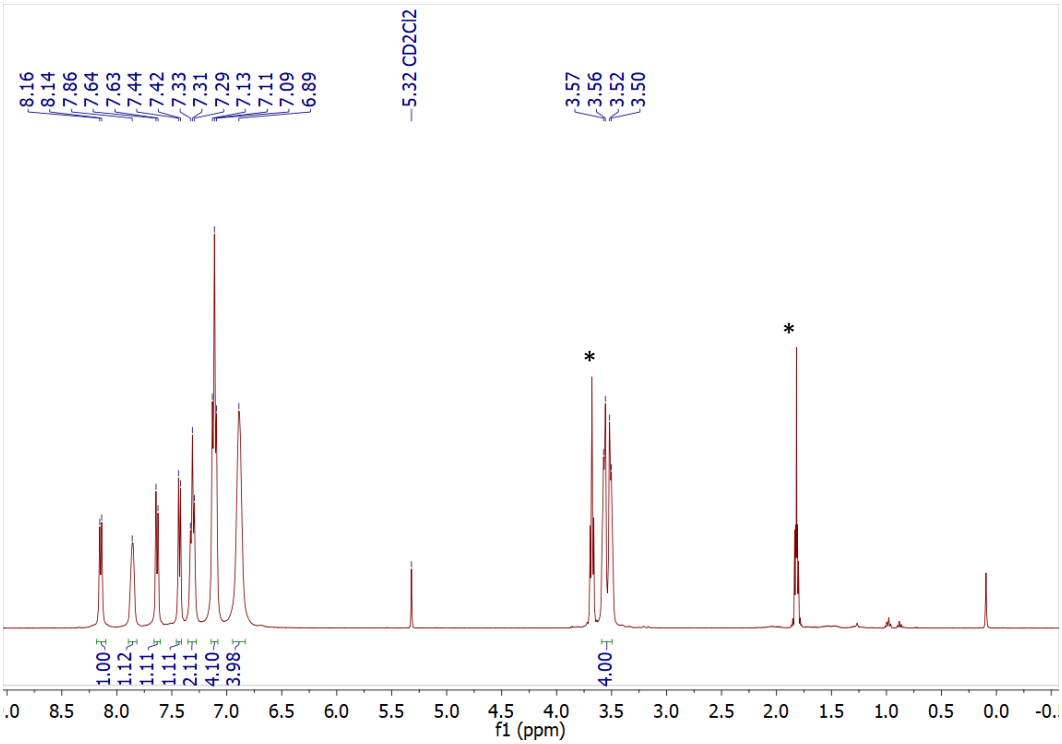


Fig. S19 ^{1}H NMR spectrum (600 MHz, CD_2Cl_2, 298 K) of **2^{Ph}**. (* = peak for THF)

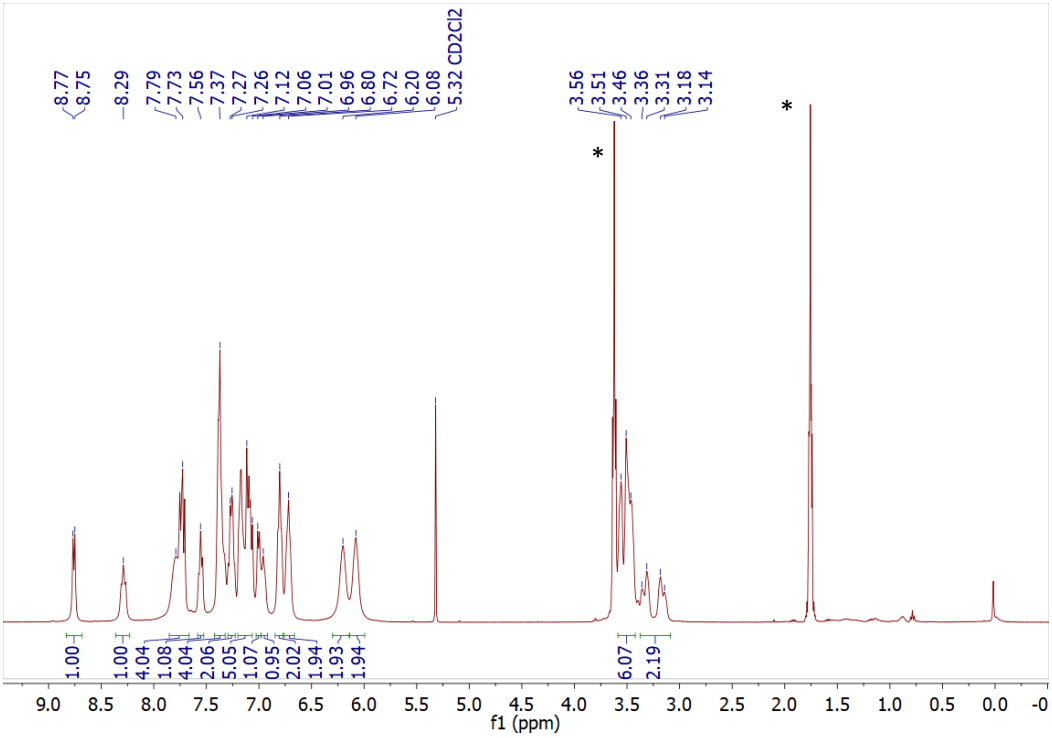


Fig. S20 ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 203 K) of **2^{Ph}**. (* = peak for THF)

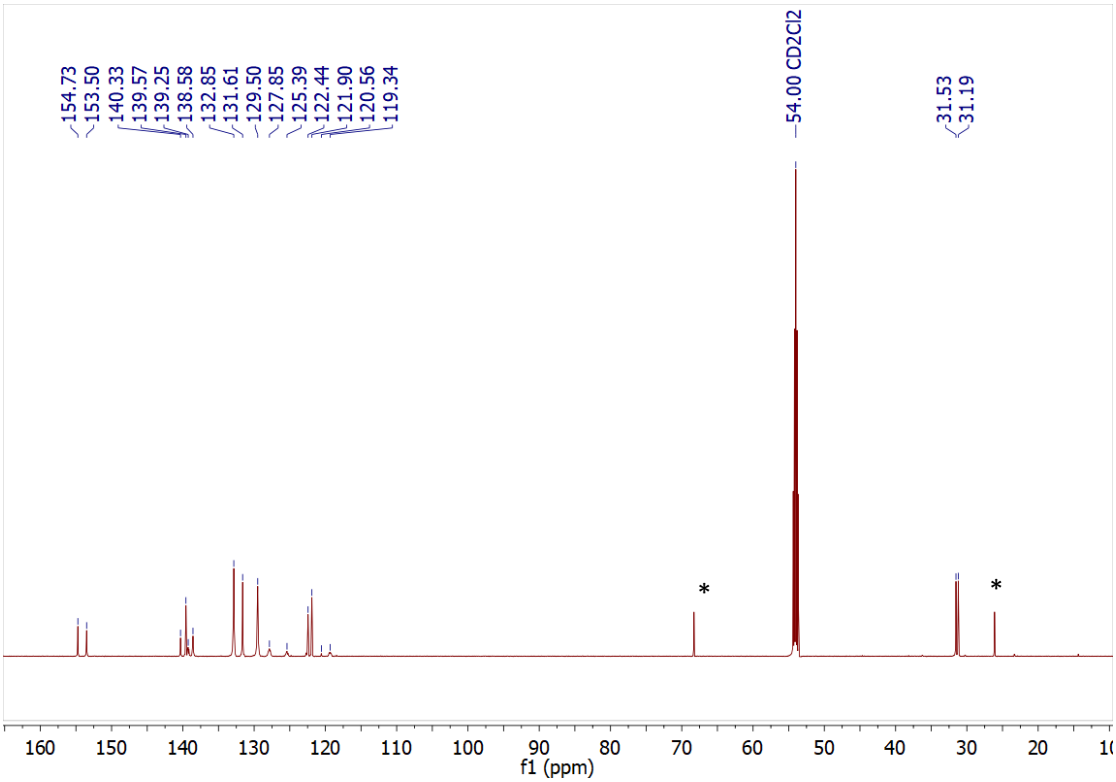


Fig. S21 $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, CD_2Cl_2, 298 K) of **2^{Ph}**. (* = peak for THF)

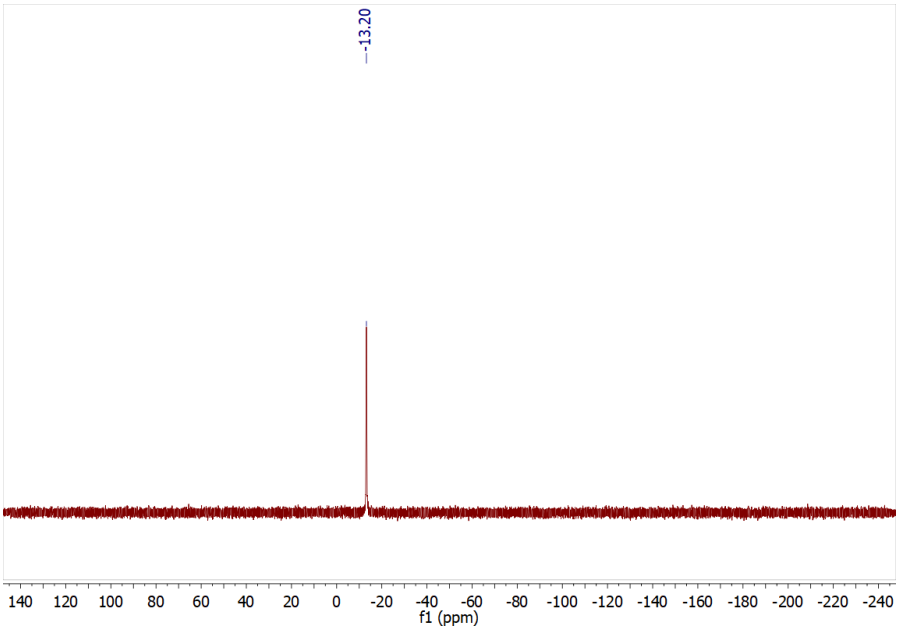


Fig. S22 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, CD_2Cl_2, 298 K) of **2^{Ph}**.

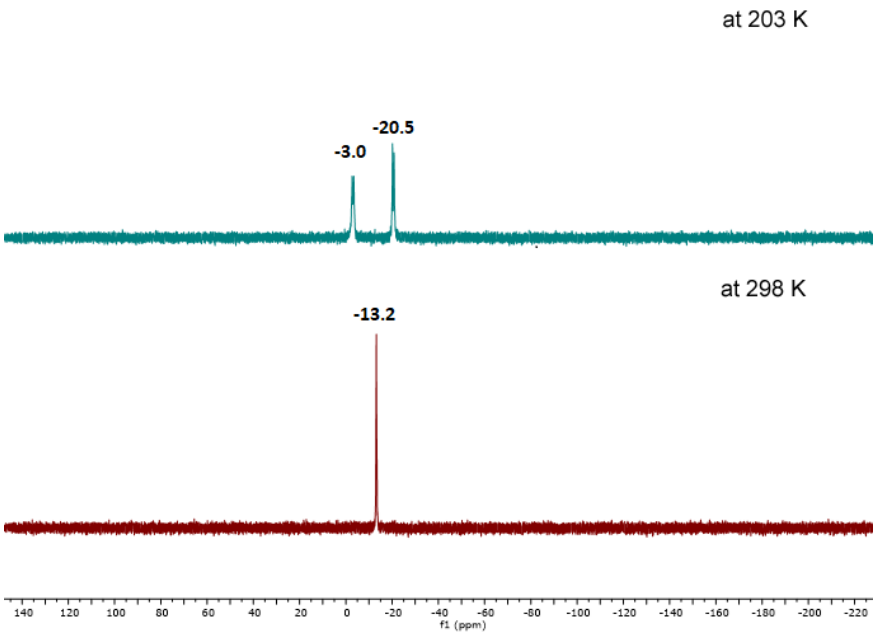


Fig. S23 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, CD_2Cl_2) of **2^{Ph}** at 298 K and 203 K.

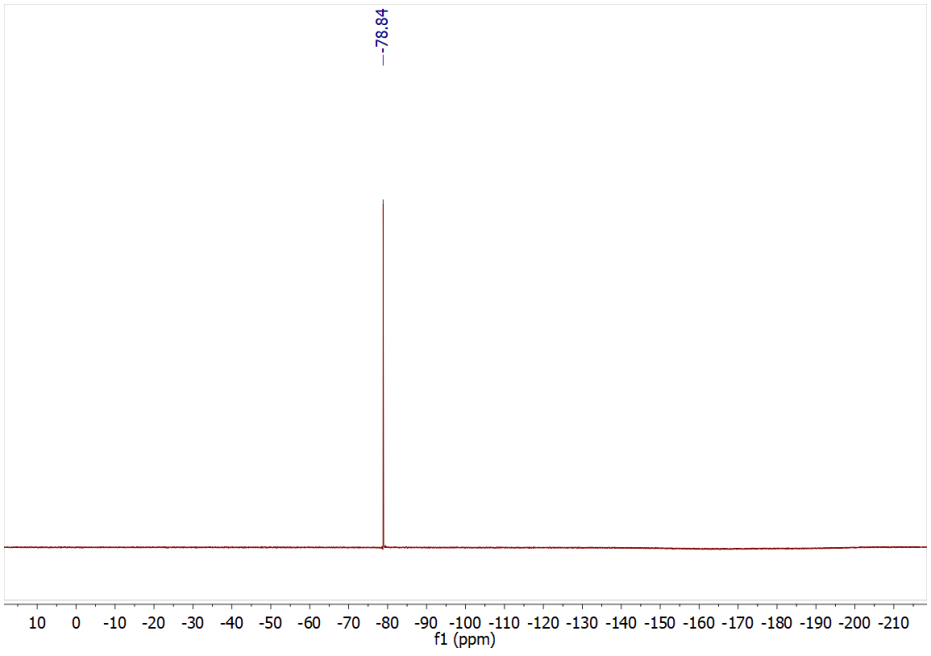


Fig. S24 $^{19}F\{^{1}H\}$ NMR spectrum (377 MHz, CD_2Cl_2, 298 K) of **2^{Ph}**

Synthesis of 3^{iPr}: One equivalent of **1^{iPr}** (0.1 g, 0.12 mmol) was dissolved in 10 mL of DCM and was mixed with two equivalents of TMSOTf (43 μL, 0.24 mmol) dissolved in 5 mL of DCM. The reaction mixture was stirred for 4 hours at room temperature. The solution was then evaporated completely to get a white solid. Colorless single crystals of **3^{iPr}** (yield = 82 % (0.09 g)) were obtained by dissolving the white solid in DCM solvent and layering with pentane; maintaining room temperature conditions. Single crystals were also obtained from concentrated THF solution in

similar yield. Melting point: 138-140° C.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.42 – 8.35 (m, 2H, Acn-C*H*), 7.86 (d, *J* = 7.1 Hz, 2H, Acn-C*H*), 7.80 (d, *J* = 7.2 Hz, 2H, Acn-C*H*), 7.65 (d, *J* = 7.2 Hz, 2H, Acn-C*H*), 3.80 – 3.70 (m, 2H, ^{i}Pr-C*H*), 3.70 – 3.59 (m, 8H, Acn-CH_2), 3.52 – 3.41 (m, 2H, ^{i}Pr-C*H*), 1.78 (dd, *J* = 18.2, 6.7 Hz, 6H, ^{i}Pr-CH_3), 1.48 (dd, *J* = 20.9, 6.8 Hz, 6H, ^{i}Pr-CH_3), 1.36 (dd, *J* = 21.2, 7.0 Hz, 6H, ^{i}Pr-CH_3), 1.25 (dd, *J* = 20.9, 6.9 Hz, 6H, ^{i}Pr-CH_3) ppm.

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 157.03 (s, Acn-*C*), 154.81 (s, Acn-*C*), 141.84 (s, Acn-*C*), 140.08 (t, *J* = 4.5 Hz, Acn-*C*), 138.46 (s, Acn-*C*), 136.98 (s, Acn-*C*), 123.64 (s, Acn-*CH*), 123.07 (s, Acn-*CH*), 119.88 (s, Acn-*CH*), 110.65 (s, Acn-*CH*), 31.95 (s, Acn-*C*H_2), 31.67 (s, Acn-*C*H_2), 26.99 – 25.84 (m, ^{i}Pr-*C*H), 25.79 – 24.82 (m, ^{i}Pr-*C*H), 19.83 (s, ^{i}Pr-*C*H_3), 18.56 (d, *J* = 12.1 Hz, ^{i}Pr-*C*H_3), 17.16 (s, ^{i}Pr-*C*H_3) ppm.

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ = + 28.37 ppm.

^{19}F{^{1}H} NMR (377 MHz, CD_2Cl_2) δ = -78.84 ppm.

^{1}H NMR (600 MHz, CD_3CN, 273 K) δ 8.36 (t, *J* = 6 Hz, 2H, Acn-C*H*), 7.95 (d, *J* = 12 Hz, 2H, Acn-C*H*), 7.85 (d, *J* = 6 Hz, 2H, Acn-C*H*), 7.65 (d, *J* = 12 Hz, 2H, Acn-C*H*), 3.65 (br., 2H, ^{i}Pr-C*H*), 3.61 (m, 8H, Acn-CH_2), 3.19 (br., 2H, ^{i}Pr-C*H*), 1.68 (d, *J* = 18, 6H, ^{i}Pr-CH_3), 1.40 (d, *J* = 18 Hz, 6H, ^{i}Pr-CH_3), 1.28 (d, *J* = 18 Hz, 6H, ^{i}Pr-CH_3), 1.14 (d, *J* = 18 Hz, 6H, ^{i}Pr-CH_3) ppm.

^{31}P{^{1}H} NMR (162 MHz, CD_3CN) δ = + 26.95 ppm.

ESI-MS (acetonitrile) found m/z 306.1060, calculated for $[C_{36}H_{44}GeP_2]^{2+}$ m/z 306.1060.

Elemental Analysis: Calcd. for $C_{38}H_{44}F_6GeO_6P_2S_2$: C, 50.19; H, 4.88. Found: C, 51.99; H, 4.46.

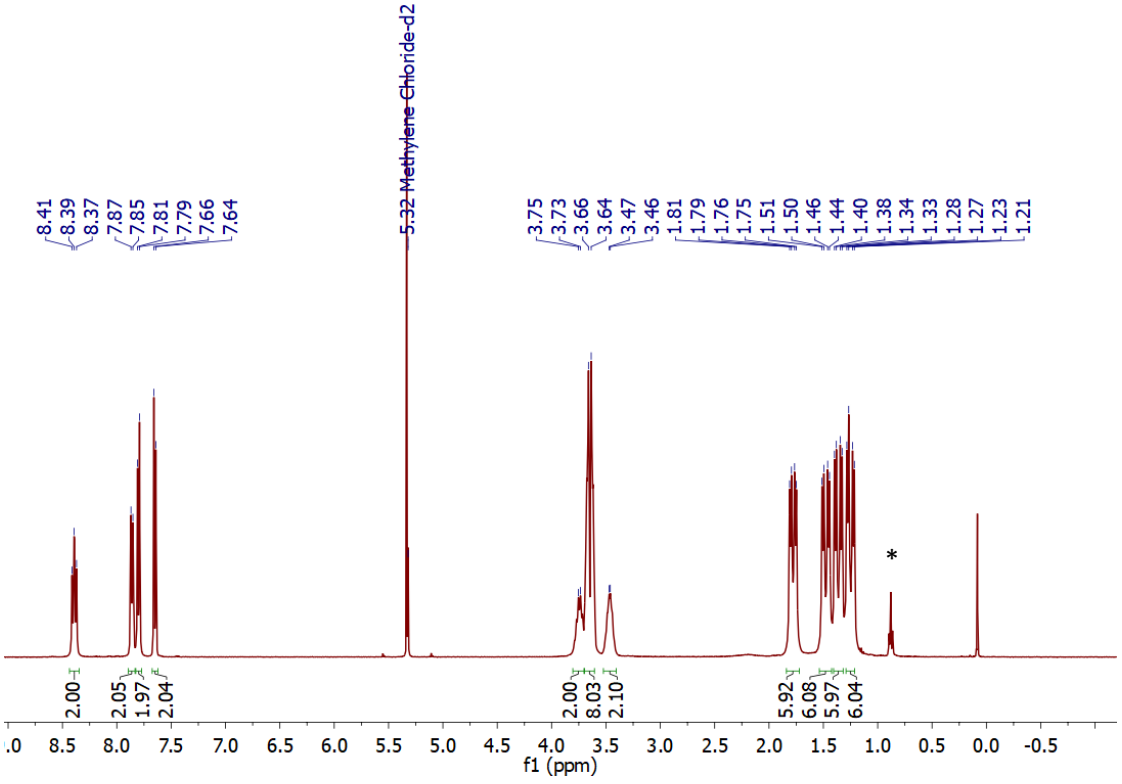


Fig. S25 ^{1}H NMR spectrum (600 MHz, CD_2Cl_2, 298 K) of **3^{iPr}**. (* = peak for hexane)

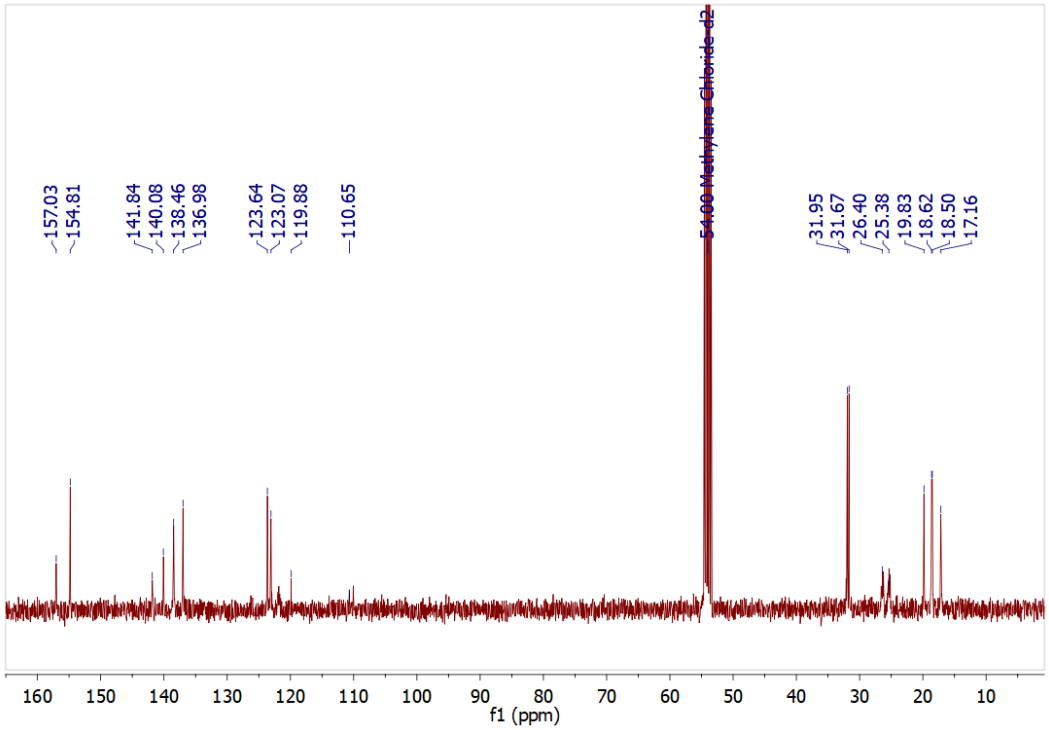


Fig. S26 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, CD_2Cl_2, 298 K) of **3**$^{i\mathrm{Pr}}$.

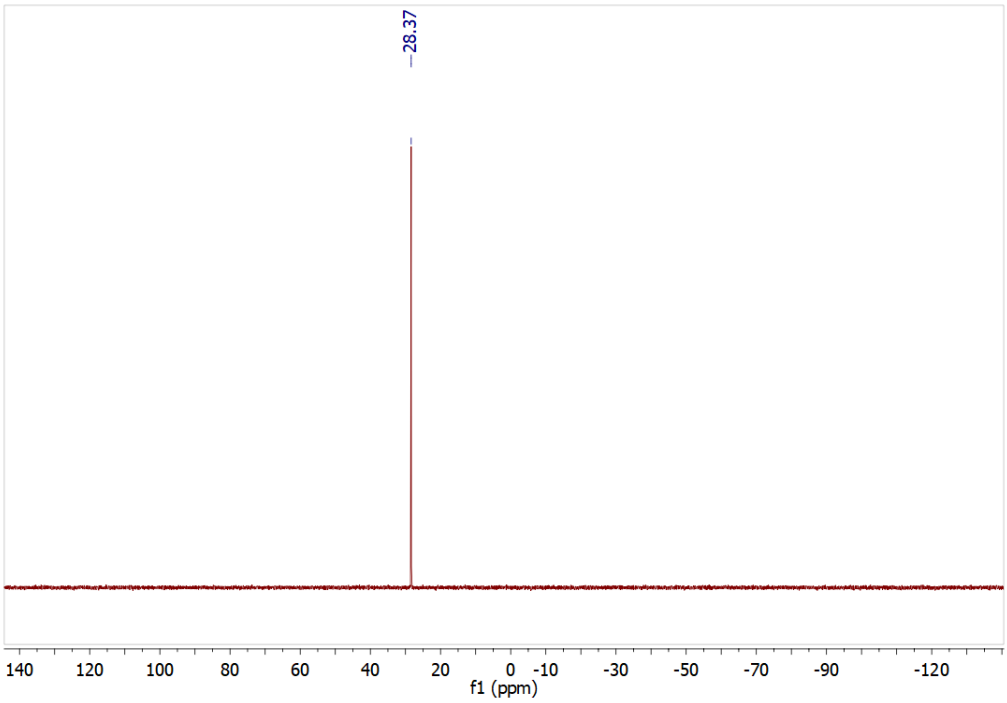


Fig. S27 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, CD_2Cl_2, 298 K) of **3**$^{i\mathrm{Pr}}$.

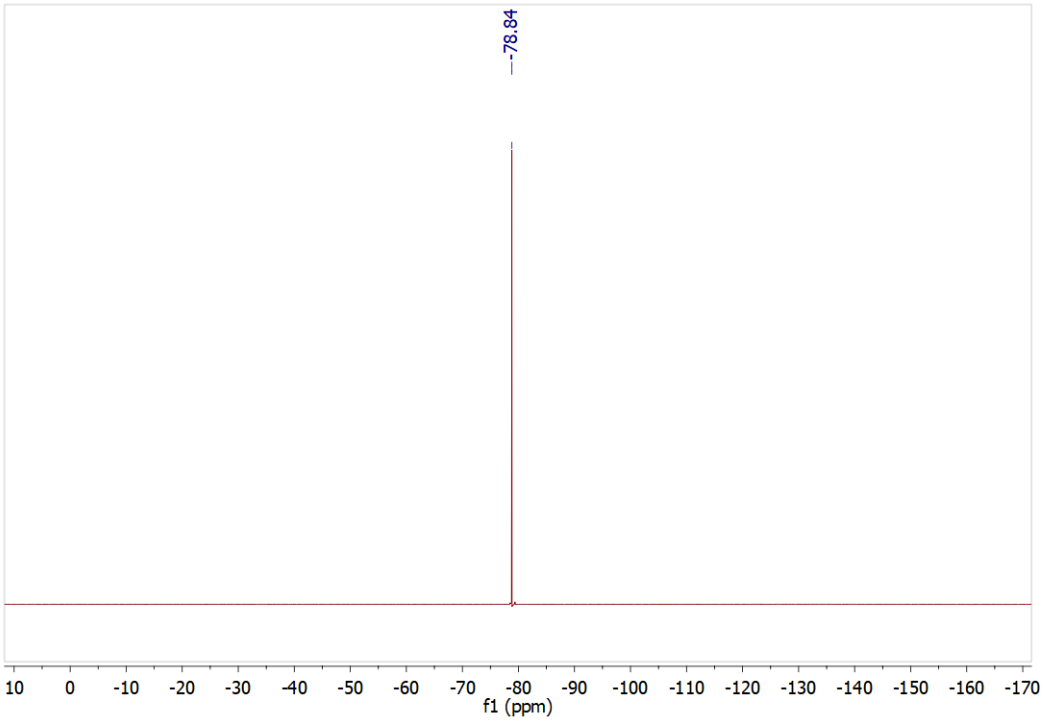


Fig. S28 $^{19}F\{^{1}H\}$ NMR spectrum (377 MHz, CD_2Cl_2, 298 K) of **3^{iPr}**.

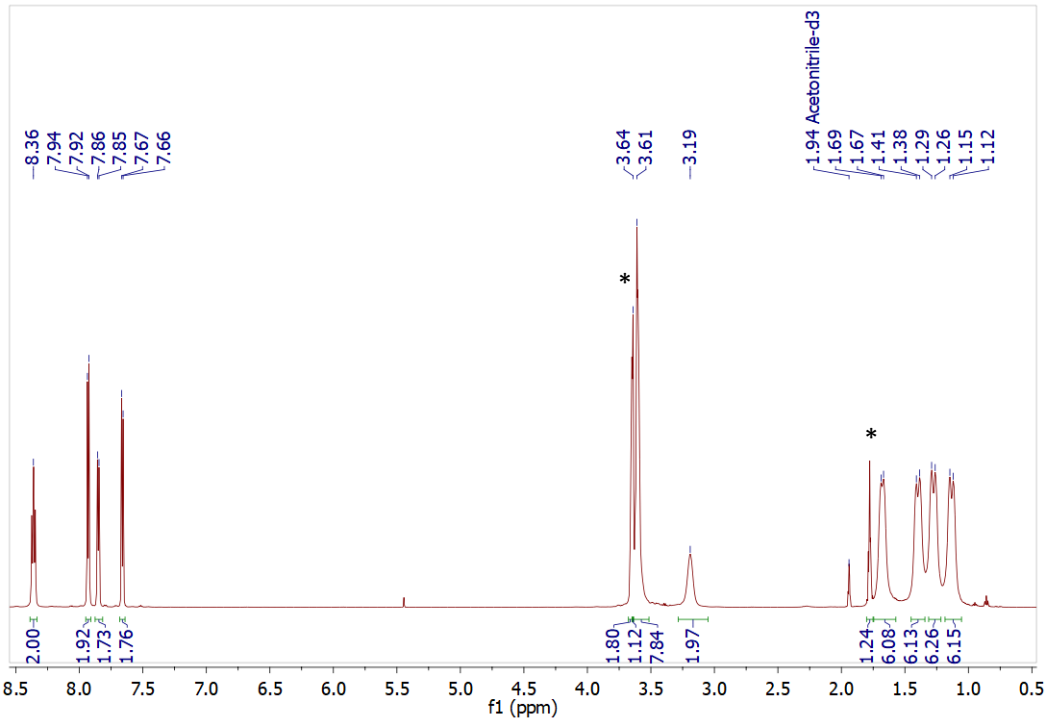


Fig. S29 ^{1}H NMR spectrum (400 MHz, CD_3CN, 273 K) of **3^{iPr}**. (* = peak for THF)

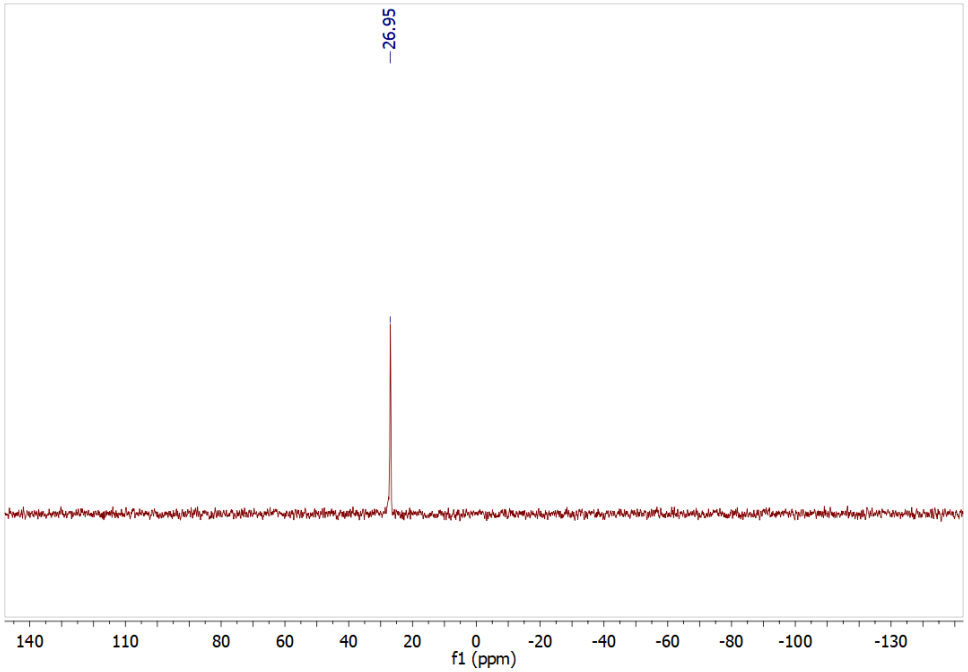


Fig. S30 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, CD_3CN, 298 K) of **3**^{iPr}.

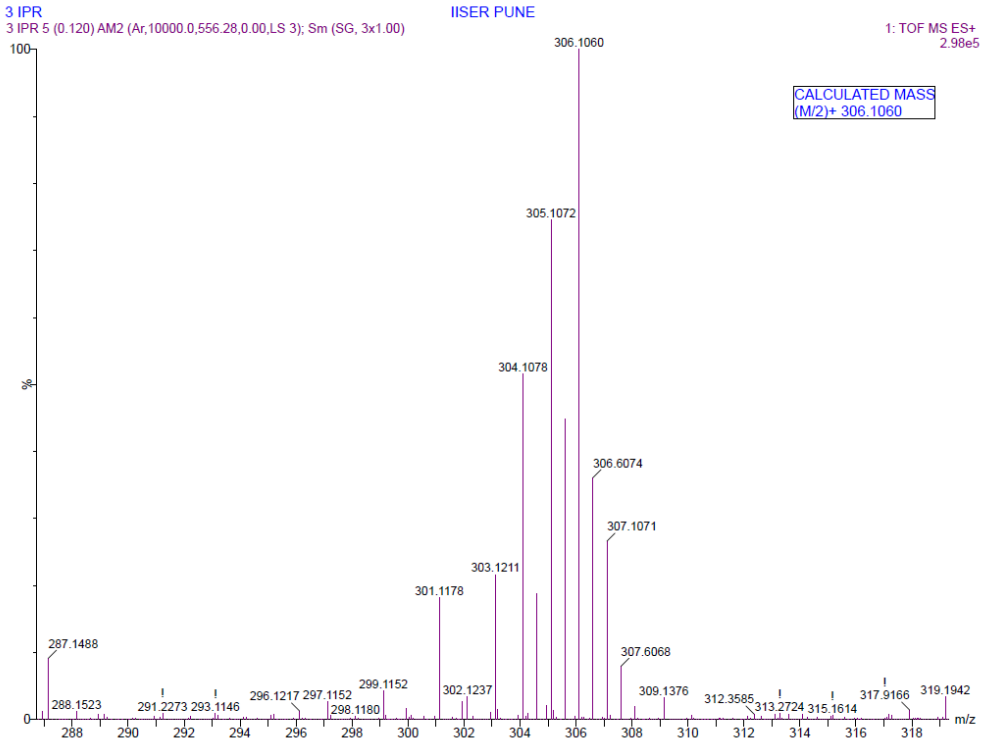


Fig. S31 ESI-MS for **3**^{iPr}

Synthesis of 3^{Ph}: One equivalent of **1**^{Ph} (0.1 g, 0.12 mmol) was dissolved in 10 mL of DCM and two equivalents of TMSOTf (44 μL, 0.24 mmol) was added to it. The reaction mixture was stirred overnight at room temperature. The solution was then evaporated completely to get a white solid. Colorless single crystals of **3**^{Ph} (yield = 81 % (0.1 g)) were obtained by dissolving the white solid in DCM solvent and layering with pentane; maintaining room temperature

conditions. Melting point: 155-157 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.94 (dd, *J* = 10.8, 7.3 Hz, 1H, Acn-C*H*), 7.77 (d, *J* = 7.1 Hz, 1H, Acn-C*H*), 7.71-7.63 (m, 5H, Acn-C*H,* Ph-C*H*), 7.54 (br., 2H, Ph-C*H*), 7.43 (br., 1H, Ph-C*H*), 7.40 (d, *J* = 7.1 Hz, 1H, Ph-C*H*), 7.21 (br., 2H, Ph-C*H*), 6.99 (d, *J* = 7.1 Hz, 1H, Ph-C*H*), 3.85 – 3.47 (m, 4H) ppm.

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 156.83 (s, Acn-*C*), 153.73 (s, Acn-*C*), 141.89 – 141.39 (m, Acn-*C*), 139.77 – 139.56 (m, Acn-*C*), 137.50 (s, Acn-*C*H), 137.30 (m, Acn-*C*), 134.75 (br., Ph-*C*), 134.49 (s, Ph-*C*H), 130.46 (m, Acn-*C*H), 122.56 (s, Ph-*C*H), 120.47 (q, *J* = 321.2 Hz, OTf), 117.15 – 116.28 (m, Acn-*C*H), 116.09 – 115.08 (m, Acn-*C*H), 113.95 – 112.82 (m, Acn-*C*), 31.61 (s, Acn-*C*H$_2$), 31.38 (s, Acn-*C*H$_2$) ppm.

^{31}P{^{1}H} NMR (162 MHz, Chloroform-*d*) δ -6.32 ppm.

^{19}F{^{1}H} NMR (565 MHz, Chloroform-*d*) δ -79.74 ppm.

ESI-MS (acetonitrile) found m/z 374.0751, calculated for $[C_{48}H_{36}GeP_2]^{2+}$ m/z 374.0747.

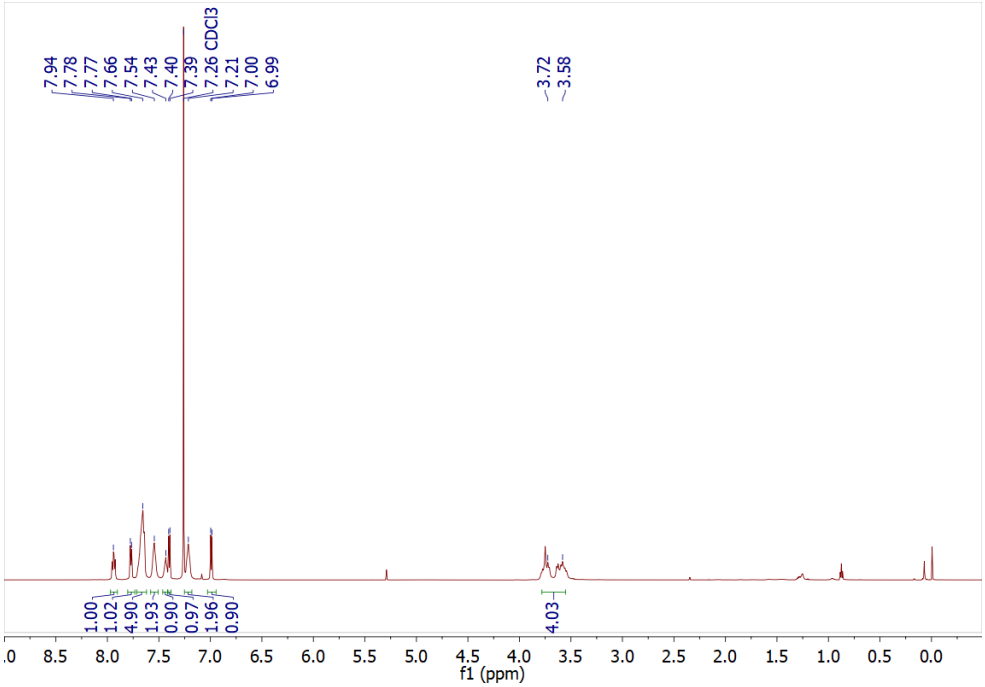


Fig. S32 ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of **3^{Ph}**.

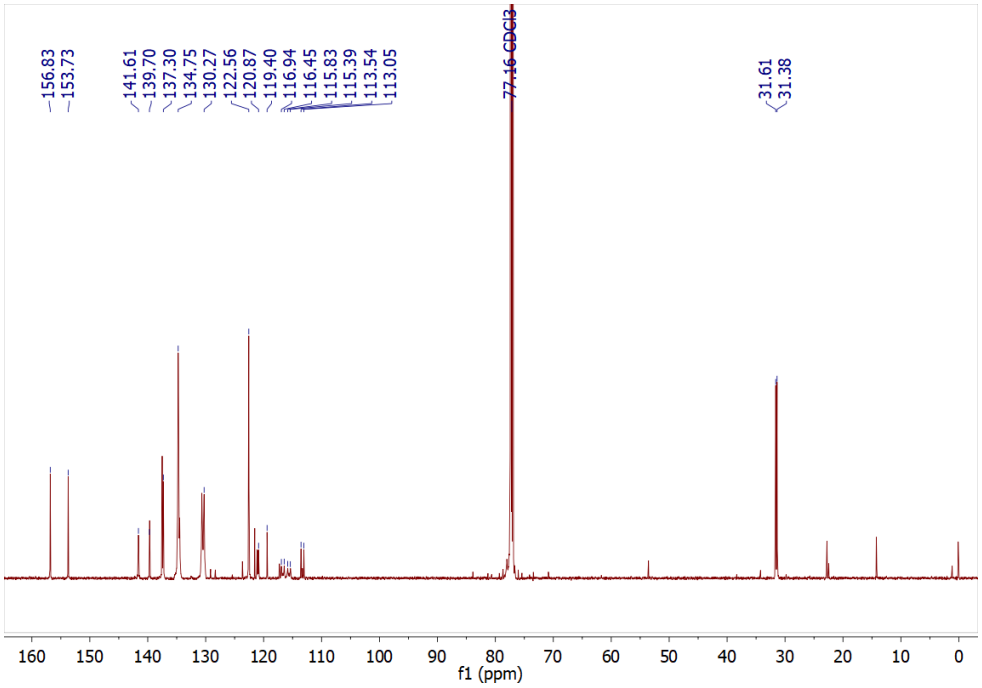


Fig. S33 $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$, 298 K) of **3^{Ph}**.

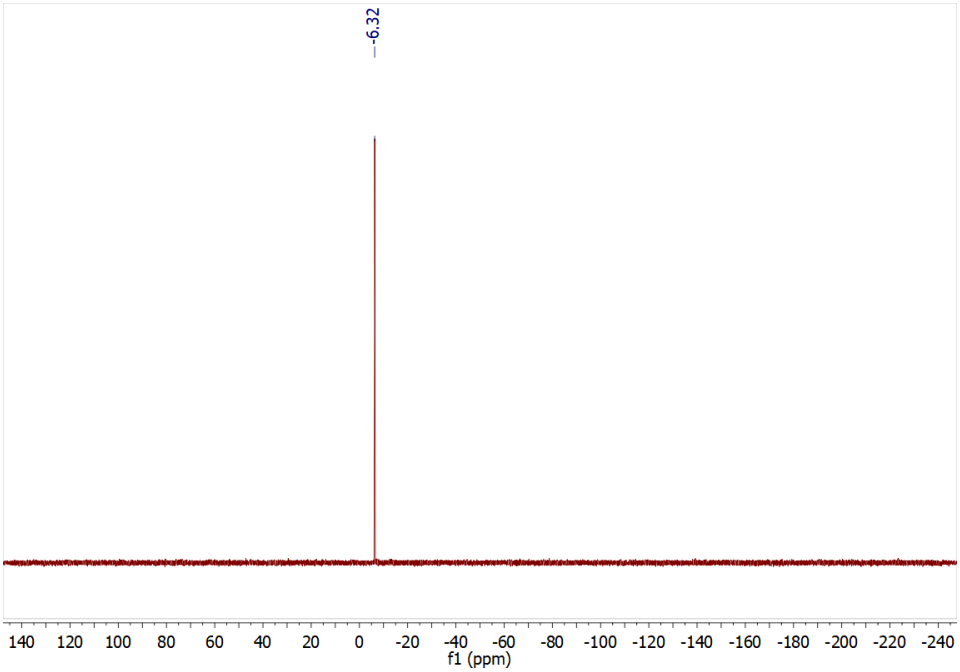


Fig. S34 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 298 K) of **3^{Ph}**.

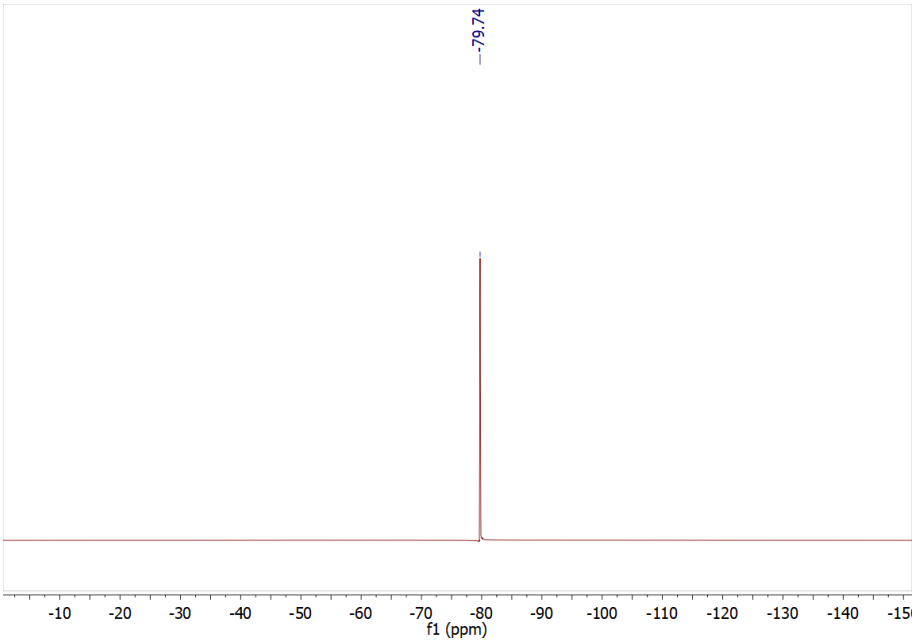


Fig. S35 $^{19}F\{^{1}H\}$ NMR spectrum (565 MHz, CD_2Cl_2, 298 K) of **3^{Ph}**.

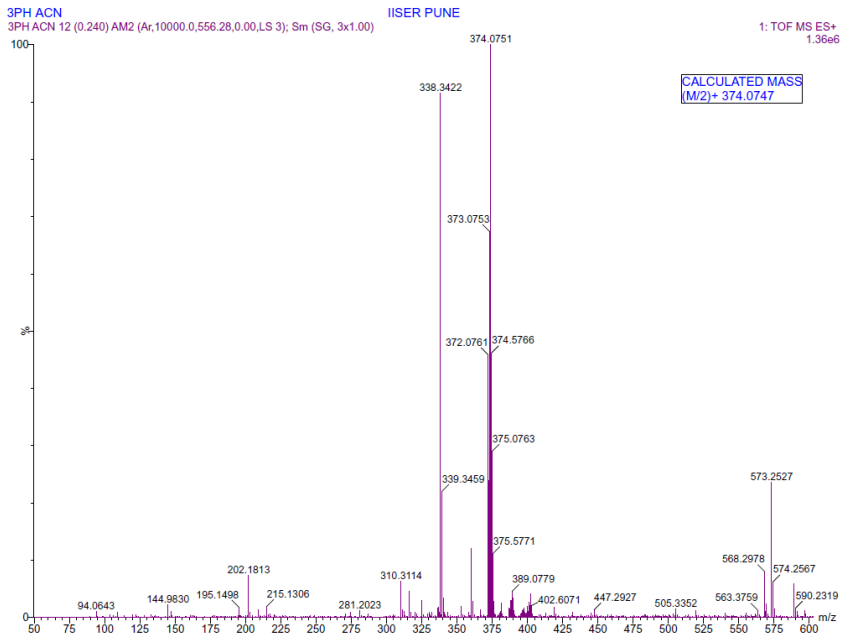


Fig. S36 ESI-MS for **3^{Ph}**

<u>Reaction of 3^{iPr} with Et_3PO (Effective Lewis acidity determination by Guttmann Beckett method):</u>

To a solution of **3^{iPr}** (0.03 g, 0.03 mmol, 1 equiv.) in CD_2Cl_2, triethylphosphine oxide ($OPEt_3$) was successively added (0.2 equiv. to 3 equiv.) and the reaction was monitored by $^{31}P\{^{1}H\}$ NMR spectroscopy.

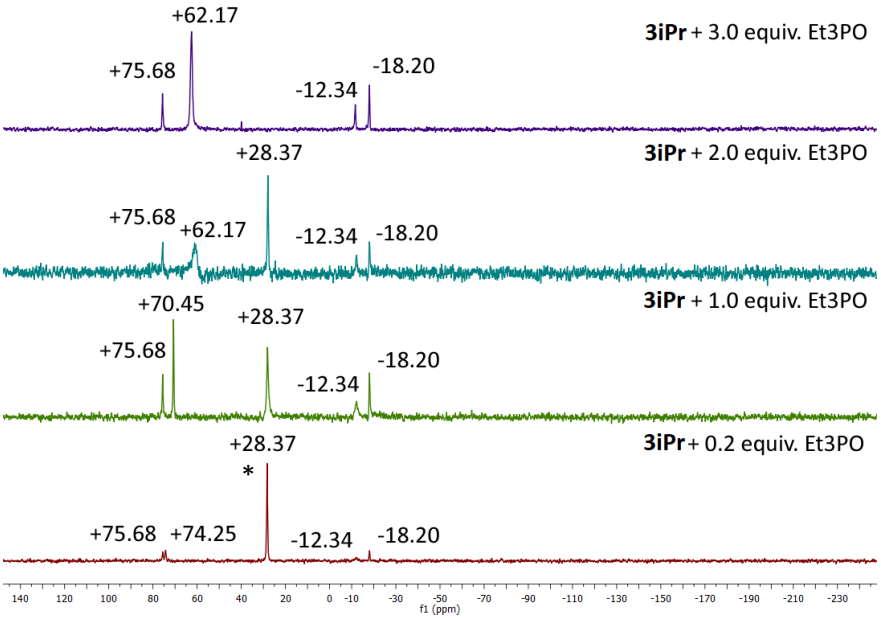


Fig. S37 $^{31}P\{^{1}H\}$ NMR spectra (162 MHz, CD_2Cl_2, 298 K) from the addition of varying equivalents of Et_3PO to **3**^{iPr}. (* = peak for compound **3**^{iPr})

Low temperature *in-situ* NMR scale reaction between 3^{iPr} and Et_3PO:

An NMR tube was charged with **3^{iPr}** (0.03 g, 0.03 mmol) and Et_3PO (0.004 g, 0.03 mmol) in 0.6 mL CD_2Cl_2 at -78 ºC. The reaction mixture was analyzed by $^{31}P\{^1H\}$ NMR measurements at -78 ºC and subsequently raised to room temperature and recorded.

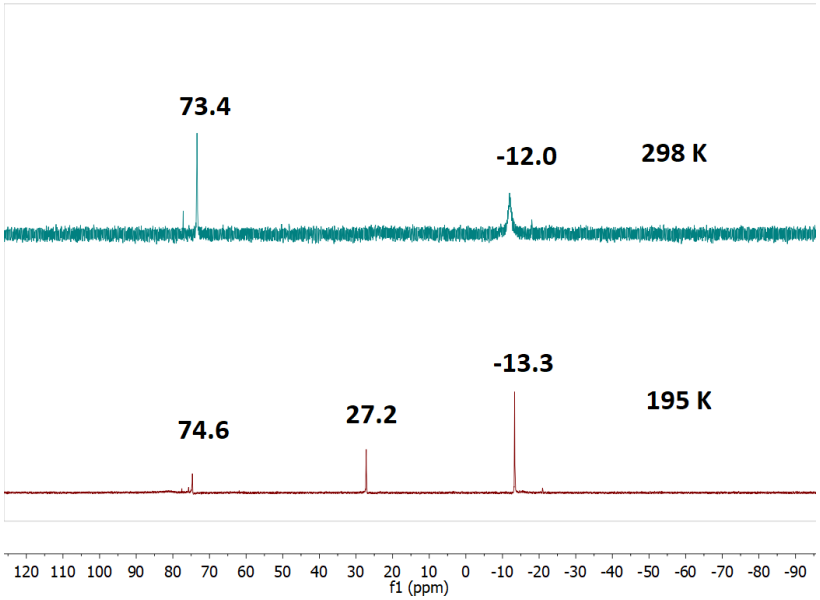


Fig. S38 $^{31}P\{^1H\}$ Variable Temperature NMR spectra (162 MHz, CD_2Cl_2) from the addition of one equivalent of Et_3PO to **3^{iPr}**. (peak at +27.2 obtained at 195 K is for compound **3^{iPr}**)

***In-situ* NMR reaction of 3^{Ph} with Et_3PO (Effective Lewis acidity determination by Guttmann Beckett method):**

An NMR tube was charged with **3^{Ph}** (0.03 g, 0.03 mmol, 1 equiv.) in $CDCl_3$ and triethylphosphine oxide ($OPEt_3$) in 0.2 equiv. was added to it. The $^{31}P\{^1H\}$ NMR spectra was measured after one hour of the addition.

Similar reaction was performed using 2 equiv. of $OPEt_3$ and was monitored by $^{31}P\{^1H\}$ NMR study.

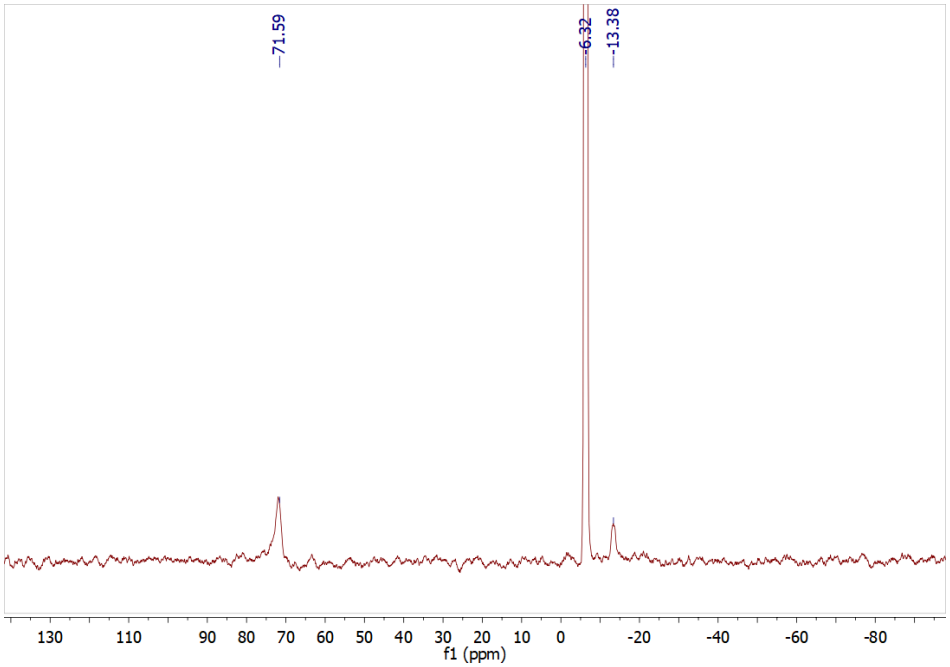


Fig. S39 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 298 K) of $\mathbf{3^{Ph}}$+ 0.2 equivalent of Et_3PO added and measured after 1 hour of addition.

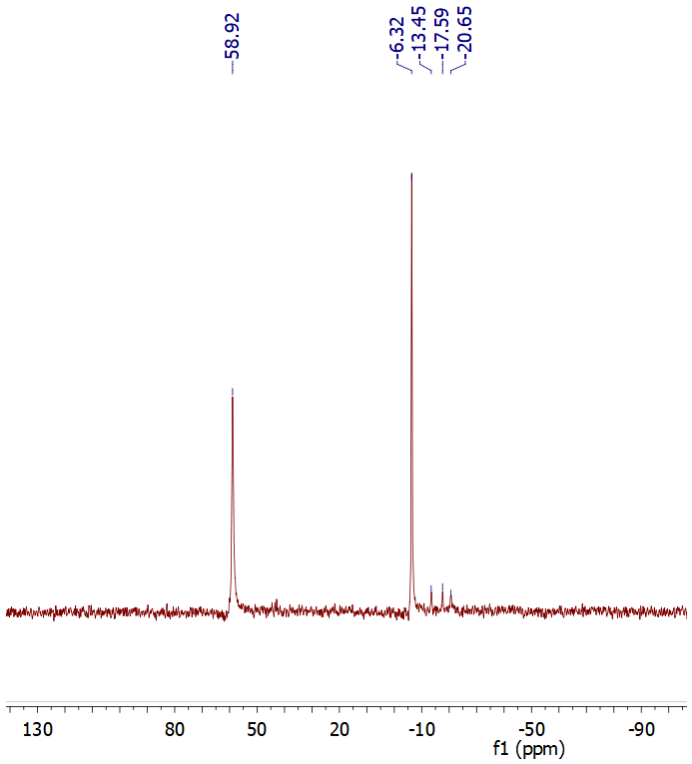


Fig. S40 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 298 K) of $\mathbf{3^{Ph}}$+ 2 equivalent of Et_3PO added and measured after 1 hour of addition.

Synthesis of $3^{Ph}OPEt_3$: Et_3PO (0.004 g, 0.03 mmol) was added to **3^{Ph}** (0.03 g, 0.03 mmol) dissolved in 10 mL of DCM, maintaining temperature of the reaction mixture at -35 ºC. The resultant solution was shaken well and then layered with pentane. Colorless single crystals of **$3^{Ph}OPEt_3$** were obtained after 4 days from the DCM/pentane layering kept at -35 ºC in 79% (0.03 g) yield.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 (t, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 6.9 Hz, 2H), 7.69 – 7.61 (m, 10H), 7.53 (s, 4H), 7.40 (d, *J* = 6.7 Hz, 4H), 7.20 (s, 4H), 7.03 (d, *J* = 6.8 Hz, 2H), 3.83 – 3.48 (m, 8H, Acn-CH_2), 1.74 (dq, *J* = 15.4, 7.7 Hz, 6H, Et-CH_2), 1.15 (dt, *J* = 15.9, 7.7 Hz, 9H, Et-CH_3) ppm.

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 156.60 (s, Acn-*C*), 153.57 (s, Acn-*C*), 141.41 (t, *J* = 9.9 Hz, Acn-*C*), 140.22 – 139.14 (m, Acn-*C*), 137.44 (s, Acn-*C*H), 137.14 (br., Acn-*C*), 134.59 (s, Ph-*C*), 134.19 (s, Ph-*C*H), 130.46 (s, Ph-*C*H), 130.08 (s, Ph-*C*H), 122.36 (s, Ph-*C*H), 121.34 – 120.90 (m, Acn-*C*H), 120.43 (q, *J* = 321.0 Hz, *OTf*), 117.41 – 116.58 (m, Acn-*C*H), 116.27 – 115.53 (m, Acn-*C*H), 113.80 – 113.02 (m, Acn-*C*), 31.48 (s, Acn-CH_2), 31.26 (s, Acn-CH_2), 19.23 (d, *J* = 65.6 Hz, Et-CH_2), 5.62 (d, *J* = 4.7 Hz, Et-CH_3) ppm.

^{31}P{^{1}H} NMR (162 MHz, Methylene Chloride-d_2) δ +68.53, -6.30 (**3^{Ph}**), -20.52 ppm.

^{19}F{^{1}H} NMR (565 MHz, Chloroform-*d*) δ -79.70 ppm.

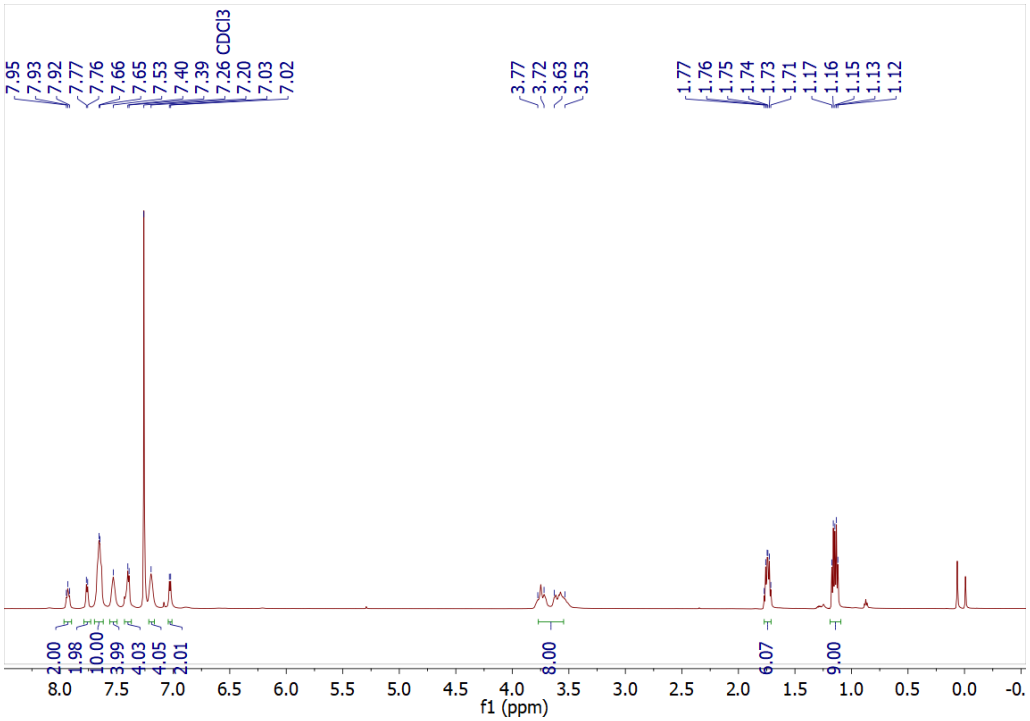


Fig. S41 ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of **$3^{Ph}Et_3PO$** depicting the equilibrium in mono-adduct formation.

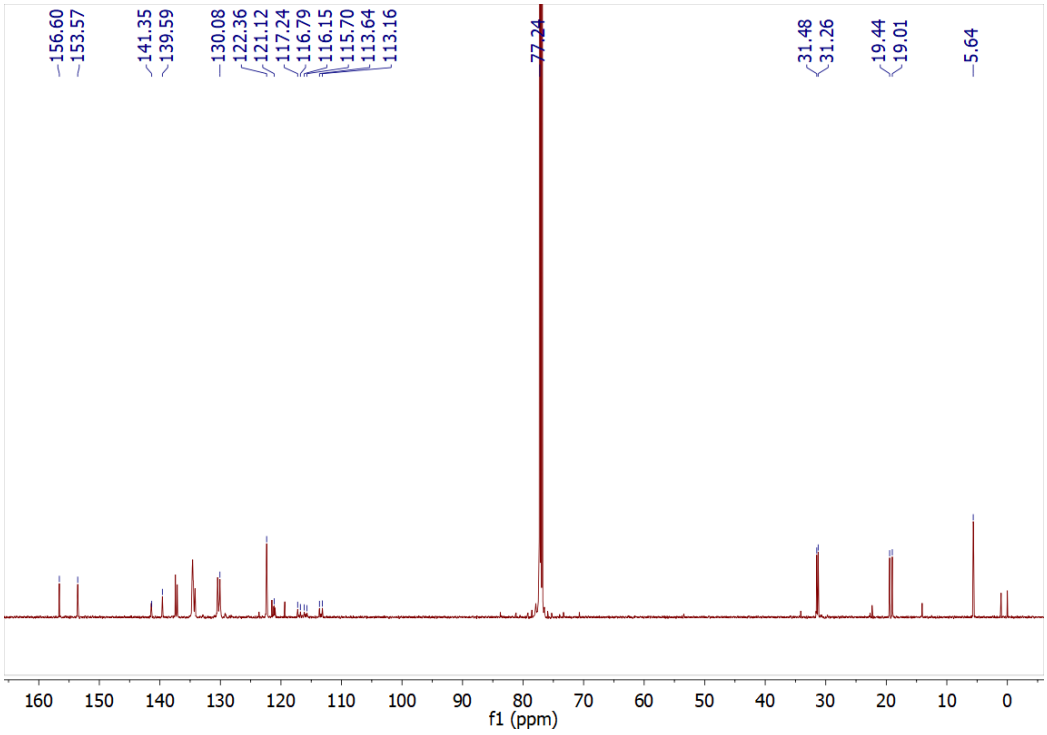


Fig. S42 $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$, 298 K) of **3^{Ph}Et$_3$PO**.

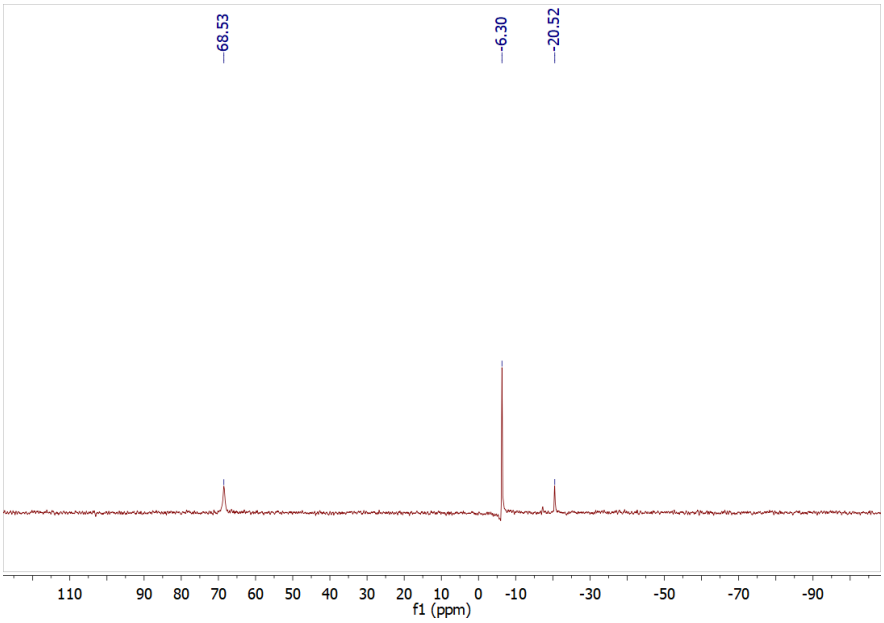


Fig. S43 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 298 K) of **3^{Ph}Et$_3$PO** depicting the equilibrium in mono-adduct formation.

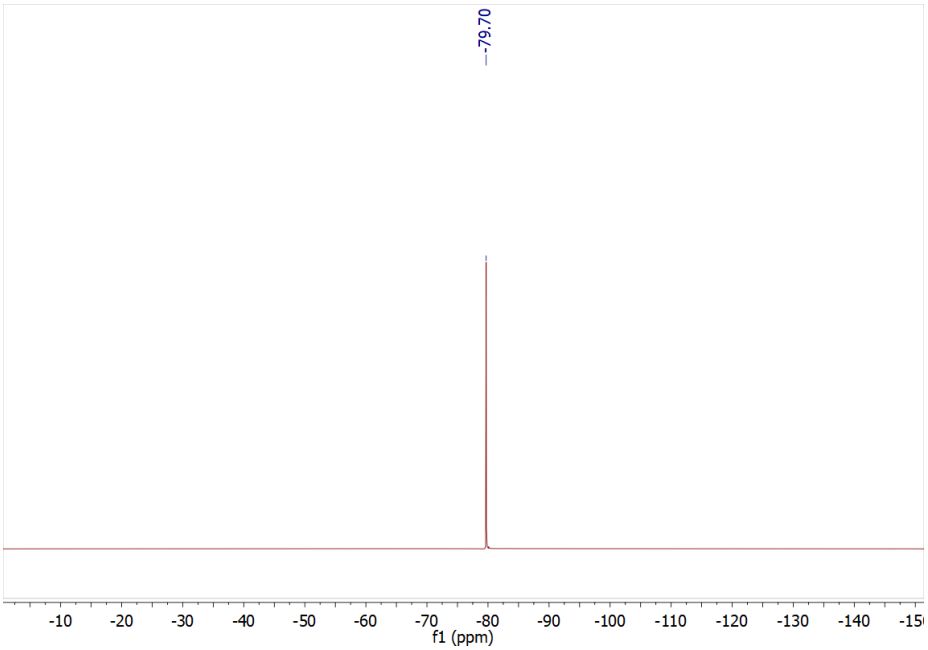


Fig. S44 $^{19}F\{^{1}H\}$ NMR spectrum (565 MHz, $CDCl_3$, 298 K) of **$3^{Ph}Et_3PO$**.

<u>Synthesis of 3^{iPr}DMAP:</u> Compound **3^{iPr}** (0.06 g, 0.07 mmol) and 4-dimethylamino pyridine (DMAP) (0.008 g, 0.07 mmol) were taken in 1:1 ratio in 10 mL DCM as solvent and stirred overnight at room temperature. Few colorless single crystals of **3^{iPr}DMAP** were obtained from dichloromethane/hexane layering maintained at room temperature, along with the formation of 4-(dimethylamino) pyridinium triflate crystals. The crystals of **3^{iPr}DMAP** were however unstable when dissolved in ($CDCl_3$:DCM taken in 1:1 ratio) solvent mixture for solution-state NMR studies.

Room temperature NMR of **3^{iPr}DMAP** showing the instability and formation of 4-(dimethylamino) pyridinium triflate:

^{1}H NMR (400 MHz, $CDCl_3$:DCM (1:1)) δ 12.83 (br, 1H,), 8.25 (br, 1H), 8.04 (d, *J* = 7.2 Hz, 2H), 7.86 (d, *J* = 6.1 Hz, 1H), 7.83 – 7.78 (m, 2H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.51 (dd, *J* = 13.8, 6.9 Hz, 2H), 7.30 (d, *J* = 7.1 Hz, 1H), 6.79 – 6.66 (m, 2H), 3.55 – 3.41 (m, 8H), 3.21 (s, 6H), 2.97 – 2.58 (br, 3H), 1.45 (br, 6H), 1.05 (br, 18H).

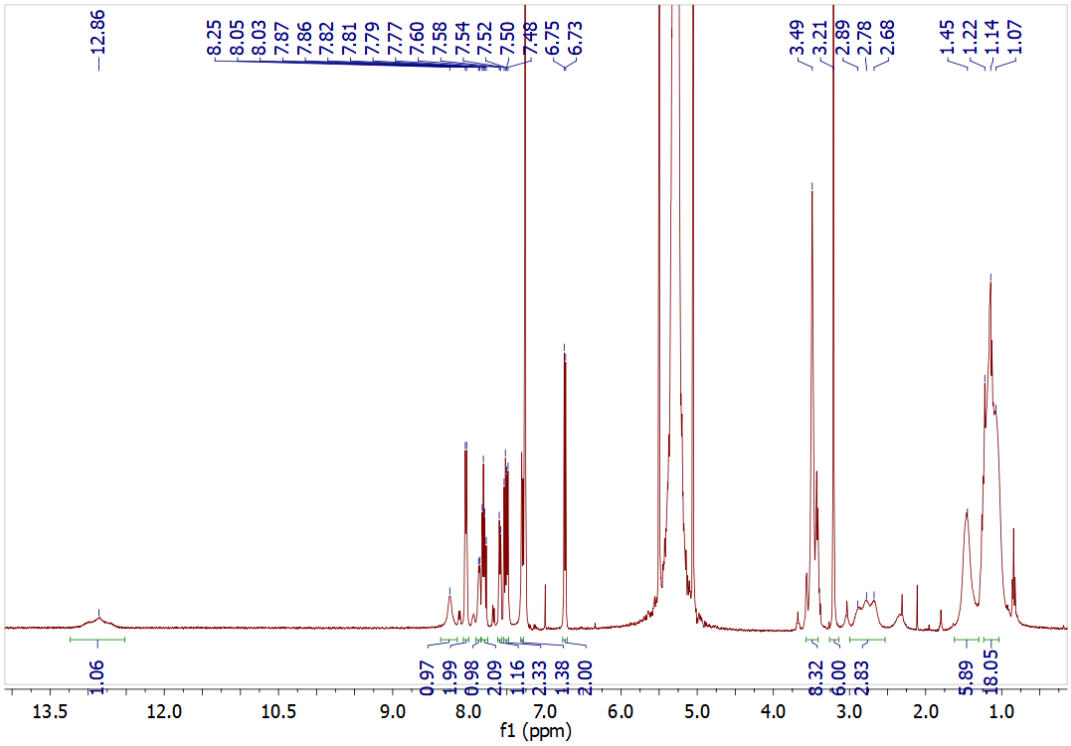


Fig. S45 ^{1}H NMR spectrum of the crystals of **3^{iPr}DMAP** (400 MHz, $CDCl_3$:DCM (1:1), 298 K) showing complex mixture and formation of **[DMAPH][OTf]**.

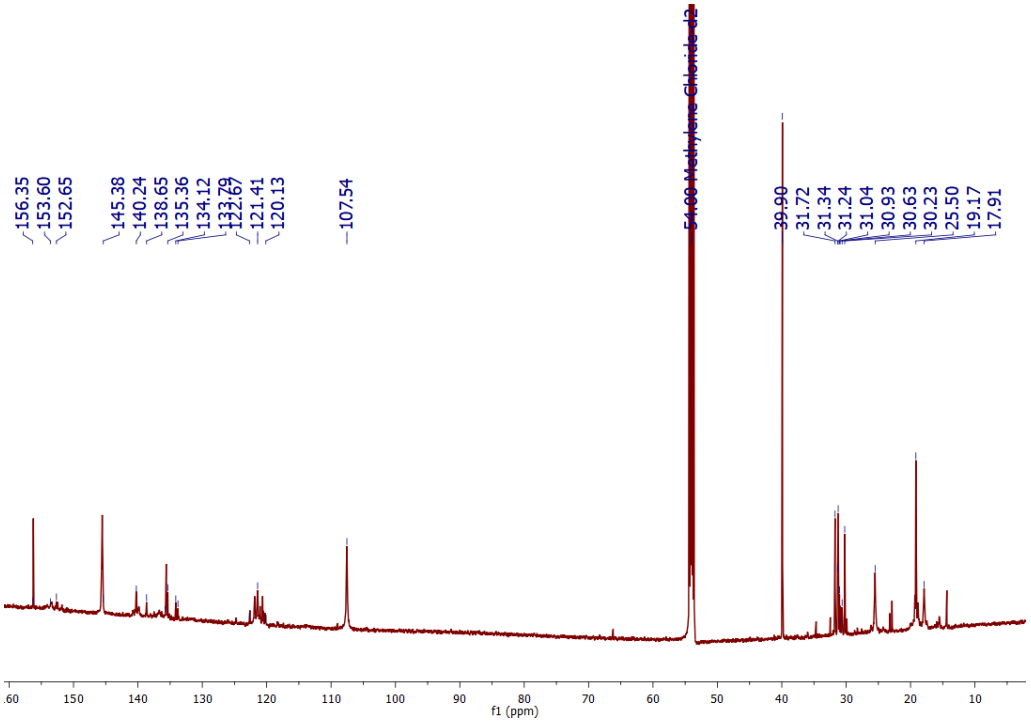


Fig. S46 $^{13}C\{^{1}H\}$ NMR spectrum of the crystals of **3^{iPr}DMAP** (151 MHz, CD_2Cl_2, 298 K) showing complex mixture and formation of **[DMAPH][OTf]**.

Low temperature *in-situ* NMR for the preparation of 3^{iPr}DMAP and its subsequent transformation upon raising until room temperature:

An NMR tube was charged with **3^{iPr}** (0.020 g, 0.02 mmol) and DMAP (0.0025 g, 0.02 mmol) in 0.5 mL CD_2Cl_2 at -40 ºC. The reaction mixture was analysed through $^{31}P\{^1H\}$ NMR measurements.

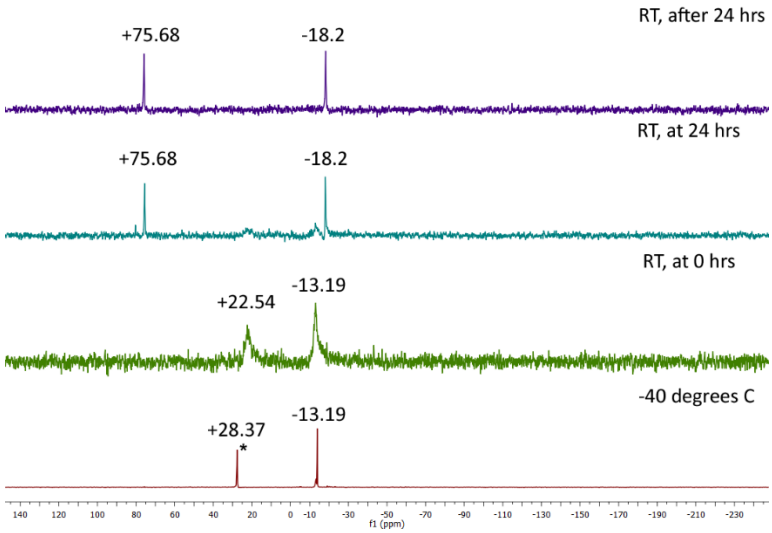


Fig. S47 $^{31}P\{^1H\}$ NMR spectra (162 MHz, CD_2Cl_2) showing the instability of *in-situ* generated **3^{iPr}DMAP** (* = peak for compound **3^{iPr}**)

Variable Temperature NMR study for the *in-situ* reaction of 3^{Ph} with DMAP:

An NMR tube was charged with **3^{Ph}** (0.04 g, 0.04 mmol) and DMAP (0.005 g, 0.04 mmol) in 0.5 mL $CDCl_3$ at room temperature. The reaction was monitored by $^{31}P\{^1H\}$ NMR measurement at varied temperatures from room temperature to – 70 °C.

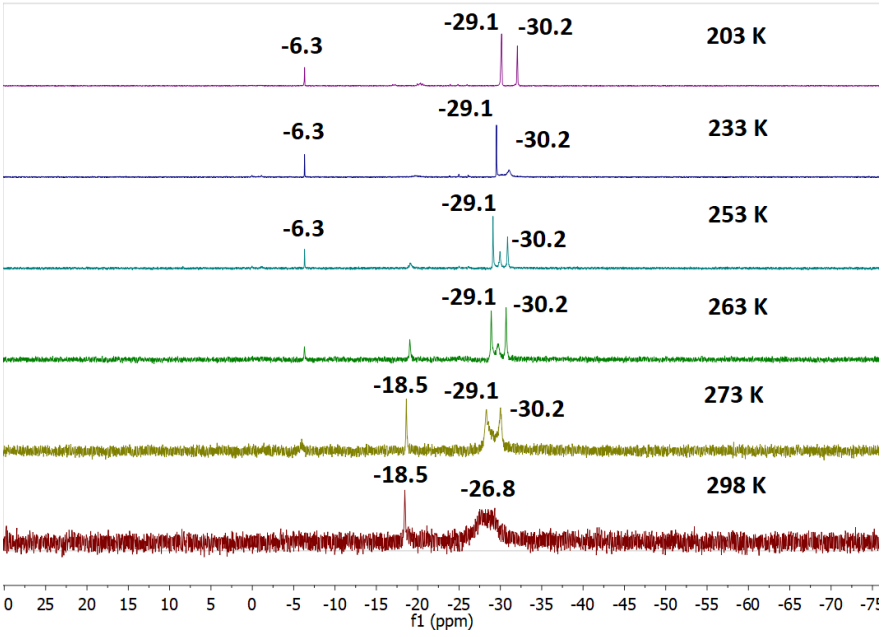


Fig. S48 Variable temperature $^{31}P\{^1H\}$ NMR spectra (162 MHz, CD_2Cl_2) showing the adduct formation between **3^{Ph}** and DMAP taken in 1:1 ratio (peak at -6.3 ppm is assigned to **3^{Ph}** generated)

Synthesis of $3^{Ph}(DMAP)_2$: Compound $\mathbf{3^{Ph}}$ (0.03 g, 0.03 mmol) and DMAP (0.008 g, 0.06 mmol) were dissolved in 5 - 7 mL DCM, maintaining temperature of the reaction mixture at -35 ºC. The resultant solution was shaken well and then layered with pentane. Colorless single crystals of $\mathbf{3^{Ph}(DMAP)_2}$ were obtained after 3 days in 74% (0.03 g) yield from the DCM/pentane layering kept at -35 ºC.

^{1}H NMR (600 MHz, Chloroform-*d*, 298K) δ 7.81 (br, 4H, DMAP-*H*), 7.70 (s, 1H), 7.62 (d, *J* = 7.0 Hz, 2H), 7.46 – 7.40 (m, 3H), 7.35 (s, 4H), 7.27 (br, 4H), 7.08 (br, 6H), 6.88 (br, 4H), 6.60-6.55 (m, 2H), 6.47 (d, *J* = 5.2 Hz, 4H, DMAP-*H*), 6.22 (s, 2H), 3.60 (s, 4H, Acn-CH_2), 3.51 – 3.30 (m, 4H, Acn-CH_2), 3.08 (s, 12H, DMAP-CH_3).

^{31}P{^{1}H} NMR (162 MHz, Methylene Chloride-d_2, 298K) δ -18.32, -26.73 (br).

^{31}P{^{1}H} NMR (162 MHz, Methylene Chloride-d_2, 238K) δ -29.16.

^{19}F{^{1}H} NMR (565 MHz, Chloroform-*d*) δ -79.21.

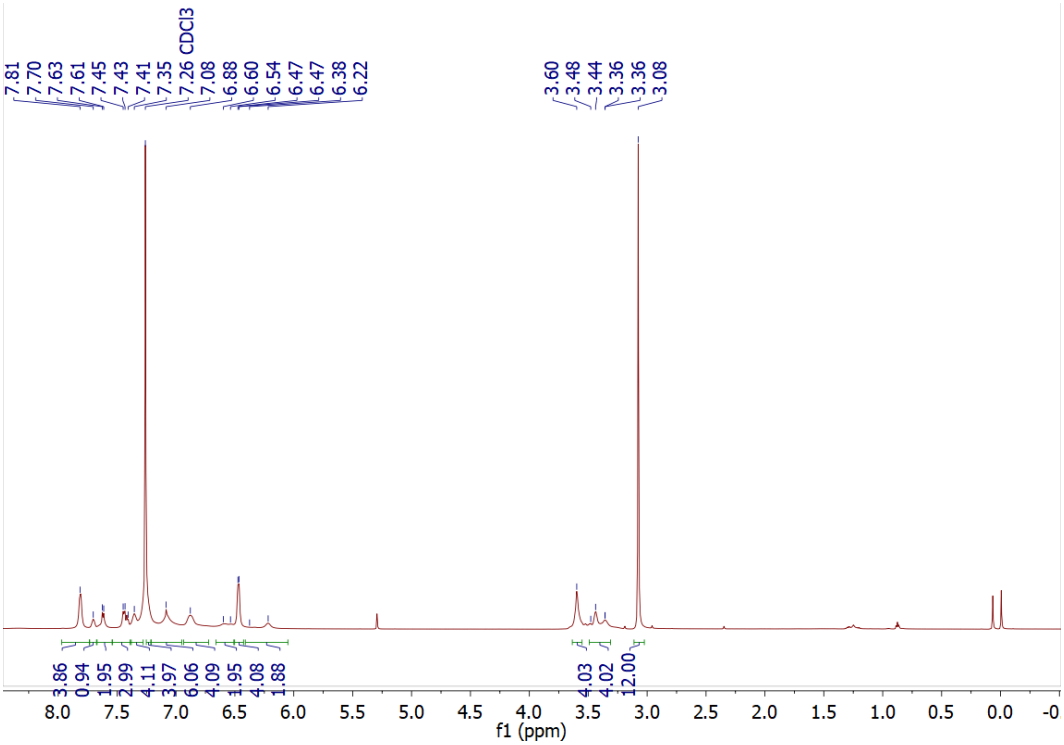


Fig. S49 ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 298 K) of $\mathbf{3^{Ph}(DMAP)_2}$.

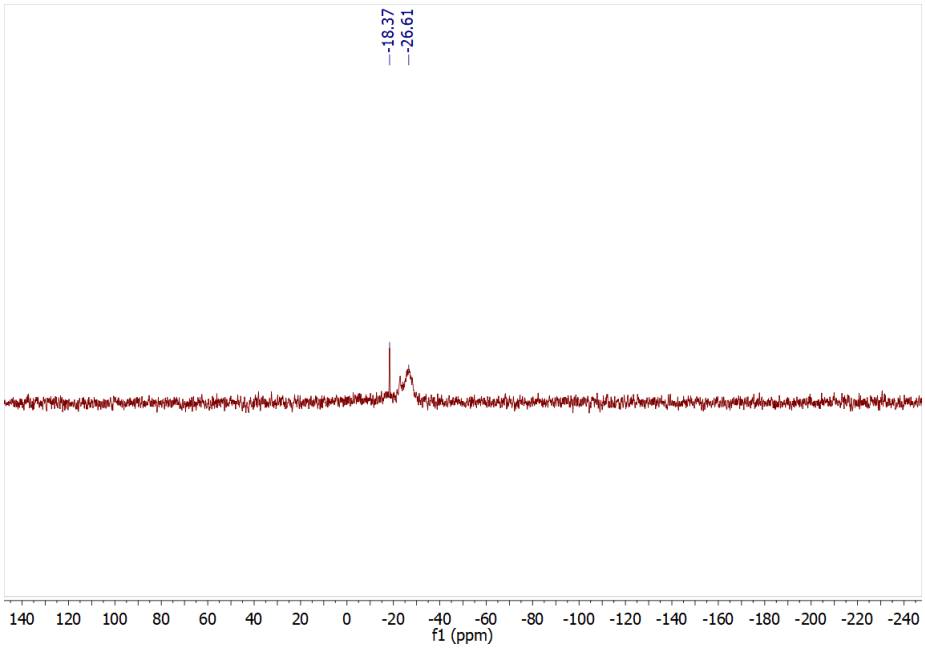


Fig. S50 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 298 K) of **3^{Ph}(DMAP)$_2$**.

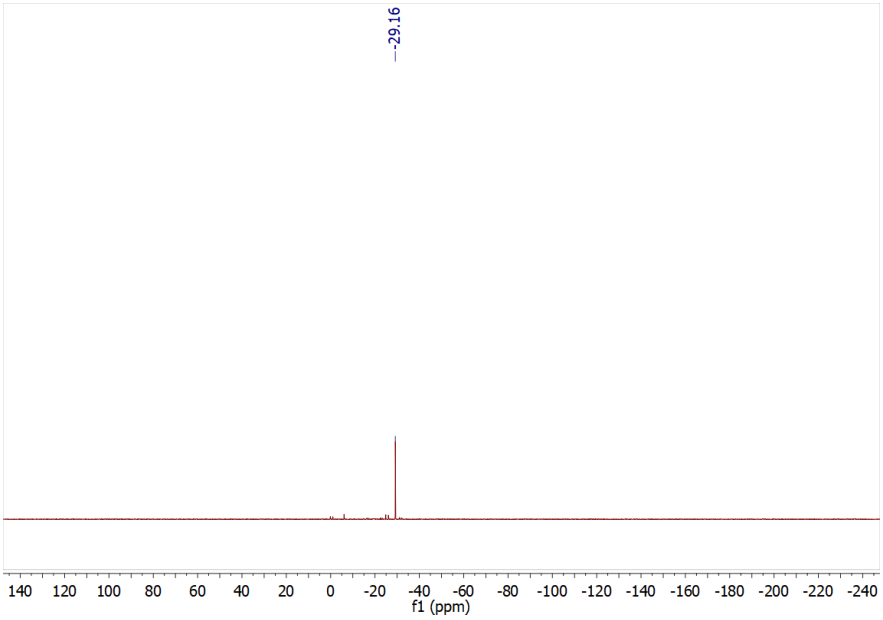


Fig. S51 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 238 K) of **3^{Ph}(DMAP)$_2$**.

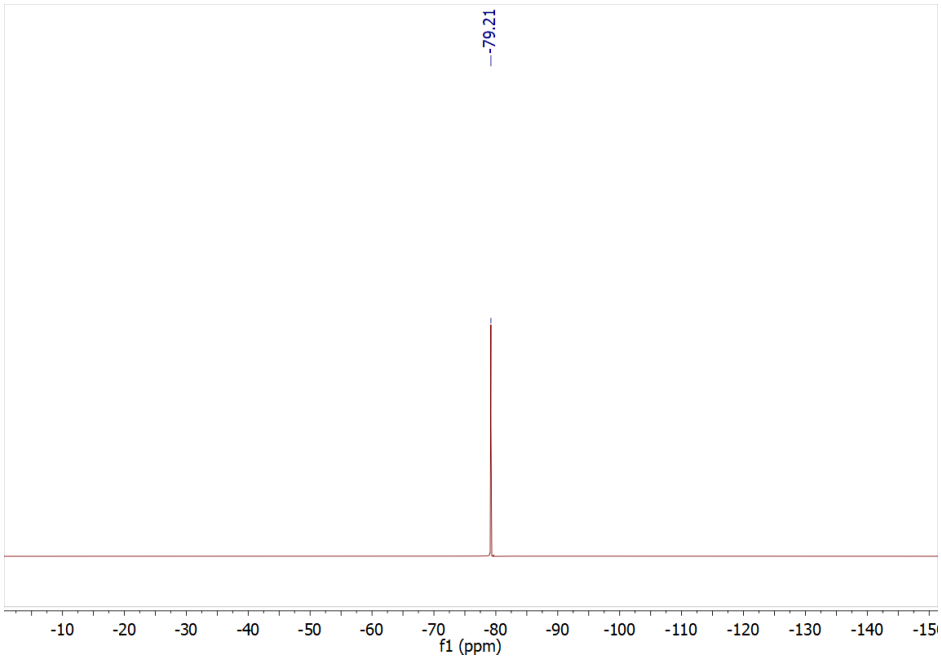


Fig. S52 $^{19}F\{^{1}H\}$ NMR spectrum (565 MHz, $CDCl_3$, 298 K) of **3^{Ph}(DMAP)$_2$**.

Synthesis of $3^{iPr}F$:

Compound **3^{iPr}** (0.1 g, 0.11 mmol) and KF (0.007 g, 0.11 mmol) were taken in 25 mL THF solvent and stirred overnight at room temperature. The solution was then filtered. The filtrate was layered with hexane and kept at -35°C. Colorless single crystals of **$3^{iPr}F$** were obtained in 62% (0.05 g) yield. Melting point: >200 °C.

^{1}H NMR (600 MHz, CD_3CN) δ 8.11 (d, *J* = 7.1 Hz, 2H, Acn-C*H*), 7.99 (dt, *J* = 6.8, 3.3 Hz, 2H, Acn-C*H*), 7.69 (d, *J* = 7.1 Hz, 2H, Acn-C*H*), 7.66 (d, *J* = 7.0 Hz, 2H, Acn-C*H*), 3.56 (q, *J* = 7.8 Hz, 8H, Acn-CH_2), 3.07 – 2.98 (m, 4H, , ^{i}Pr-C*H*), 1.13 (q, *J* = 6.8 Hz, 12H, ^{i}Pr-CH_3), 0.96 (q, *J* = 7.6 Hz, 12H, ^{i}Pr-CH_3) ppm.

$^{13}C\{^{1}H\}$ NMR) (151 MHz, CD_3CN) δ 153.59 (s, Acn-*C*), 153.15 (s, Acn-*C*), 140.67 (t, *J* = 9.0 Hz, Acn-*C*), 139.66 (t, *J* = 4.5 Hz, Acn-*C*), 136.69 (t, *J* = 4.5 Hz, Acn-*C*), 135.53 (s, Acn-*C*), 121.69 (t, *J* = 2.8 Hz, Acn-*CH*), 121.58 (q, *J* = 320.9 Hz, OTf), 121.49 (s, Acn-*CH*), 115.44 – 115.12 (m, Acn-*CH*), 31.34 (s, Acn-CH_2), 31.03 (s, Acn-CH_2), 23.91 (m, ^{i}Pr-*C*H), 18.61 (s, ^{i}Pr-*C*H_3), 17.21 (s, ^{i}Pr-*C*H_3) ppm.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ -10.23 (d, *J* = 184.9 Hz) ppm.

$^{19}F\{^{1}H\}$ NMR (377 MHz, $CDCl_3$) δ -78.12, -141.03 (t, *J* = 184.9 Hz) ppm.

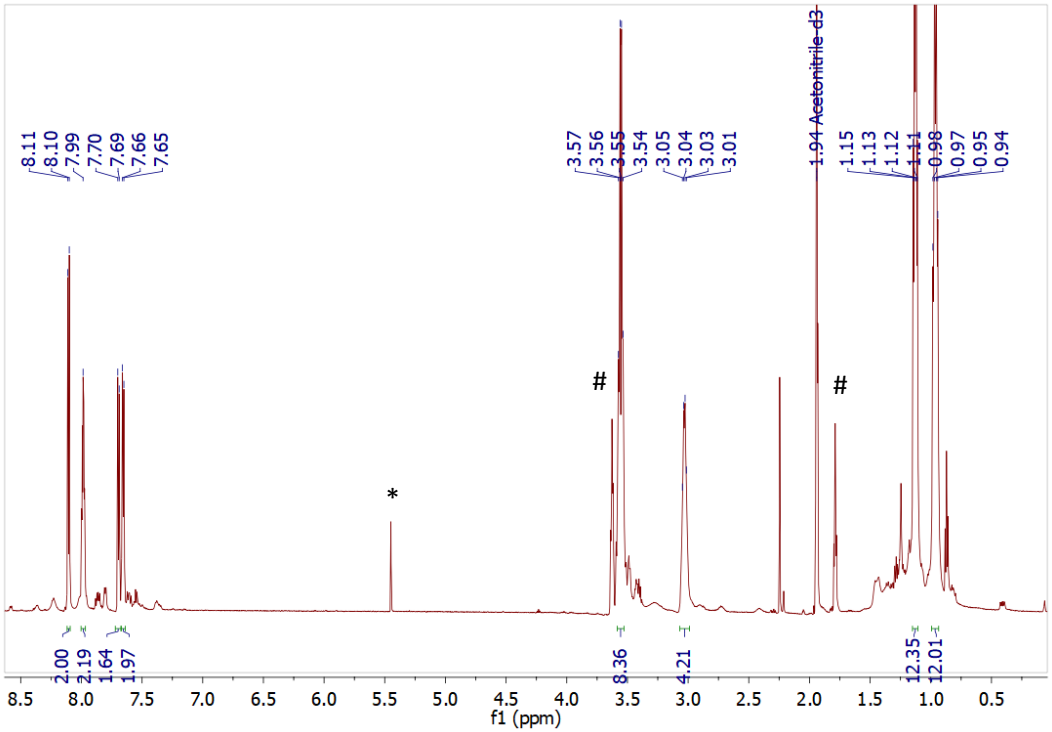


Fig. S53 ^{1}H NMR spectrum (600 MHz, CD_3CN, 298 K) of **3^{iPr}F**. (* = peak for DCM, # = peak for THF)

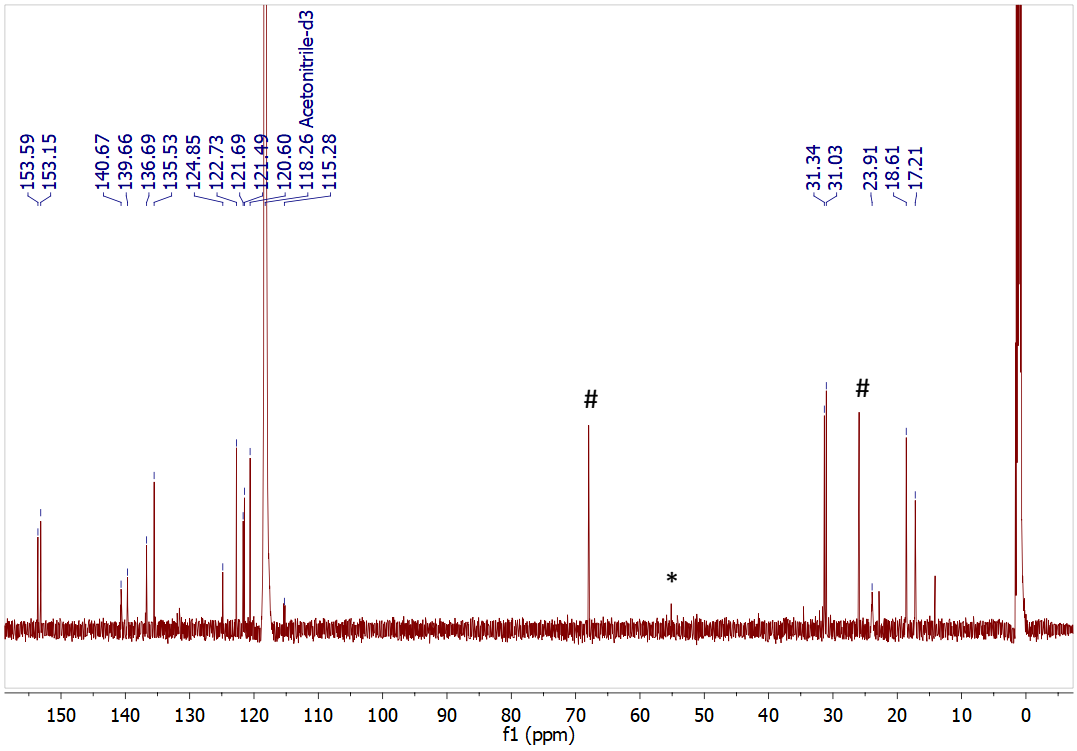


Fig. S54 $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, CD_3CN, 298 K) of **3^{iPr}F**. (* = peak for DCM, # = peak for THF)

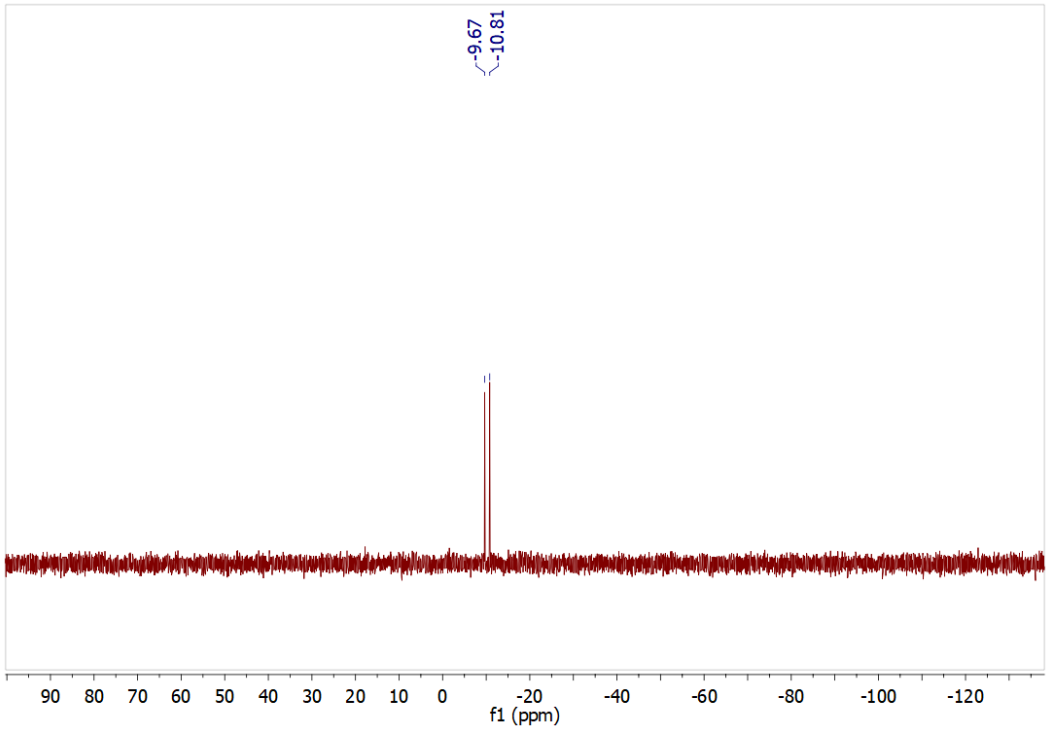


Fig. S55 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 298 K) of **3^{iPr}F**.

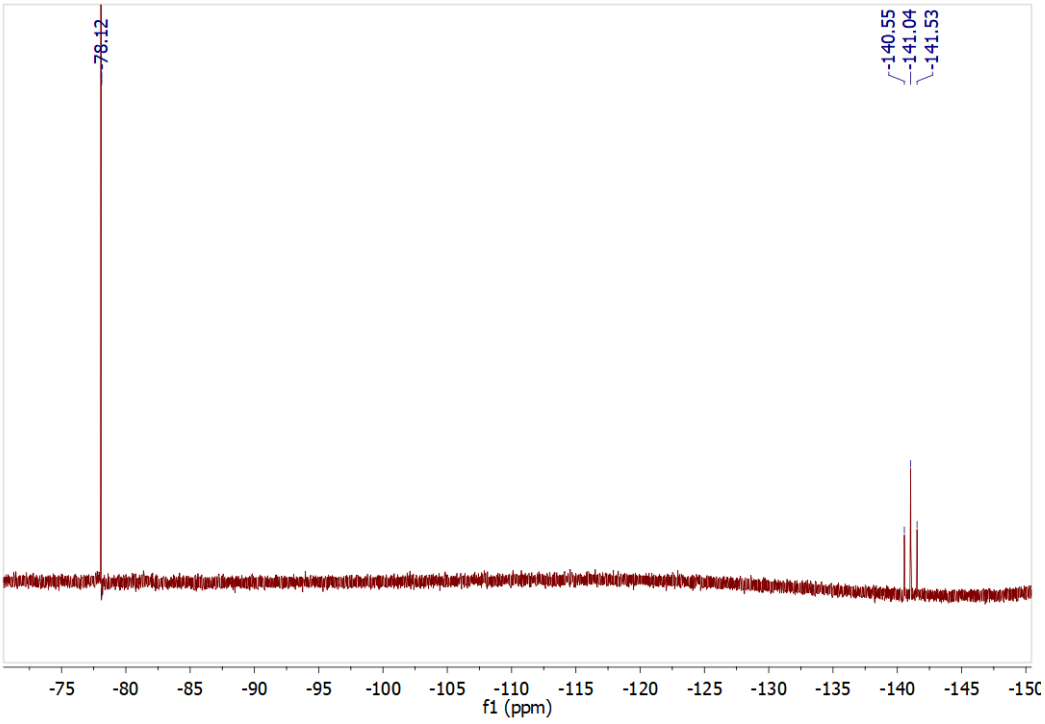


Fig. S56 $^{19}F\{^{1}H\}$ NMR spectrum (377 MHz, $CDCl_3$, 298 K) of **3^{iPr}F**.

Synthesis of 3^{Ph}F:

Compound **3^{Ph}** (0.1 g, 0.1 mmol) and KF (0.006 g, 0.1 mmol) were dissolved in 10 mL DCM and stirred overnight at

room temperature. The solution was then filtered. The filtrate was evaporated to get a white solid. Colorless single crystals of **3^{Ph}F** were obtained (yield = 64% (0.06 g)) by dissolving the white solid in THF and layering with pentane, kept at room temperature. Melting point: >200 °C

In-situ preparation of **3^{Ph}F**: An NMR tube was charged with compound **3^{Ph}** (0.03 g, 0.03 mmol), 18-*crown*-6 (0.008 g, 0.03 mmol) and KF (0.0018 g, 0.03 mmol) in 0.5 mL $CDCl_3$ under room temperature conditions. The product formation has been analyzed by NMR spectroscopy.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (br, 2H), 7.72 (br, 2H), 7.58 (s, 2H), 7.33 (d, *J* = 6.6 H, 2H), 7.29 (br, 2H), 7.21 (br, 4H), 7.08 (s, 8H), 6.87 (br, 6H), 3.61 (18-crown-6), 3.55-3.41 (m, 8H, Acn-C*H*$_2$) ppm.

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 153.23-151.74 (s, Acn-*C*), 139.42 (br.), 138.46 (br.), 137.14 (br), 132.21 (s), 130.80 (br.), 128.88 (s), 128.29, 122.40, 121.58, 121.03, 120.98 (q, *J* = 320.6 Hz, OTf), 69.86 (s, 18-crown-6), 30.79 (s, Acn-*C*H$_2$), 30.53 (s, Acn-*C*H$_2$) ppm.

^{31}P{^{1}H} NMR (162 MHz, Chloroform-*d,* 298 K) δ -17.54 (br) ppm.

^{31}P{^{1}H} NMR (162 MHz, Chloroform-*d,* 195 K) δ -10.27 (m, $J_{P\text{-}P}$ = 119.8 Hz, $J_{P\text{-}F}$ = 98.9 Hz), -23.66 (m, $J_{P\text{-}P}$ = 119.8 Hz, $J_{P\text{-}F}$ = 98.9 Hz) ppm.

^{19}F{^{1}H} NMR (377 MHz, Chloroform-*d*) δ -150.32 (t, *J* = 100.6 Hz) ppm.

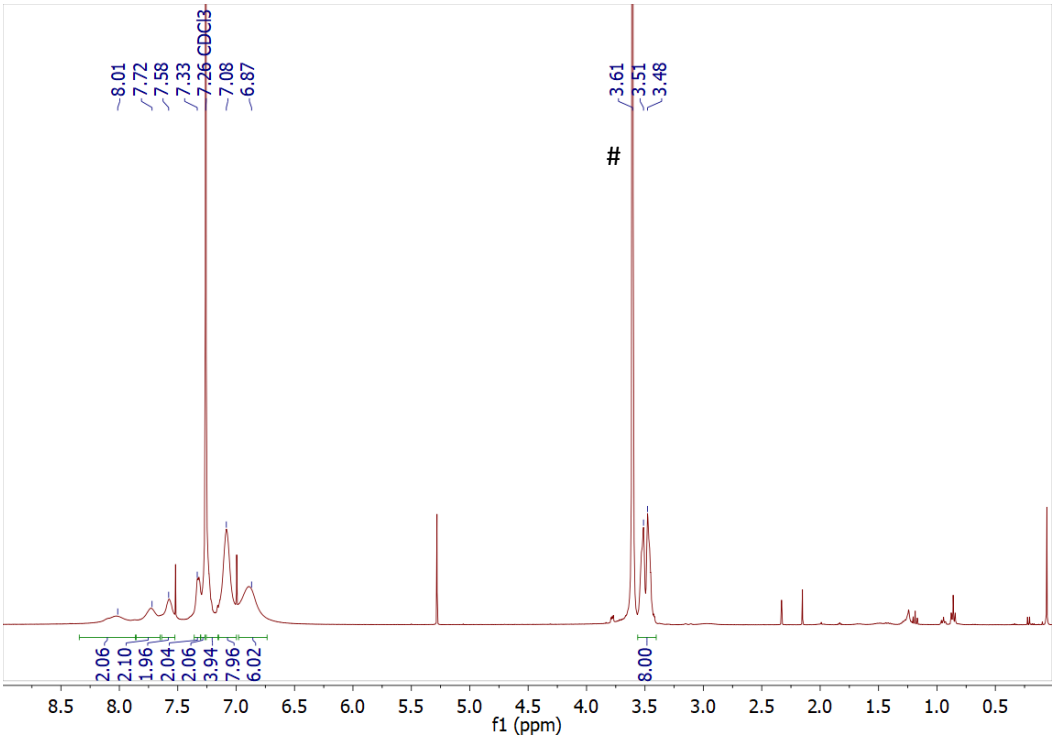


Fig. S57 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of *in-situ* generated **3^{Ph}F**. (# = peak for 18-crown-6).

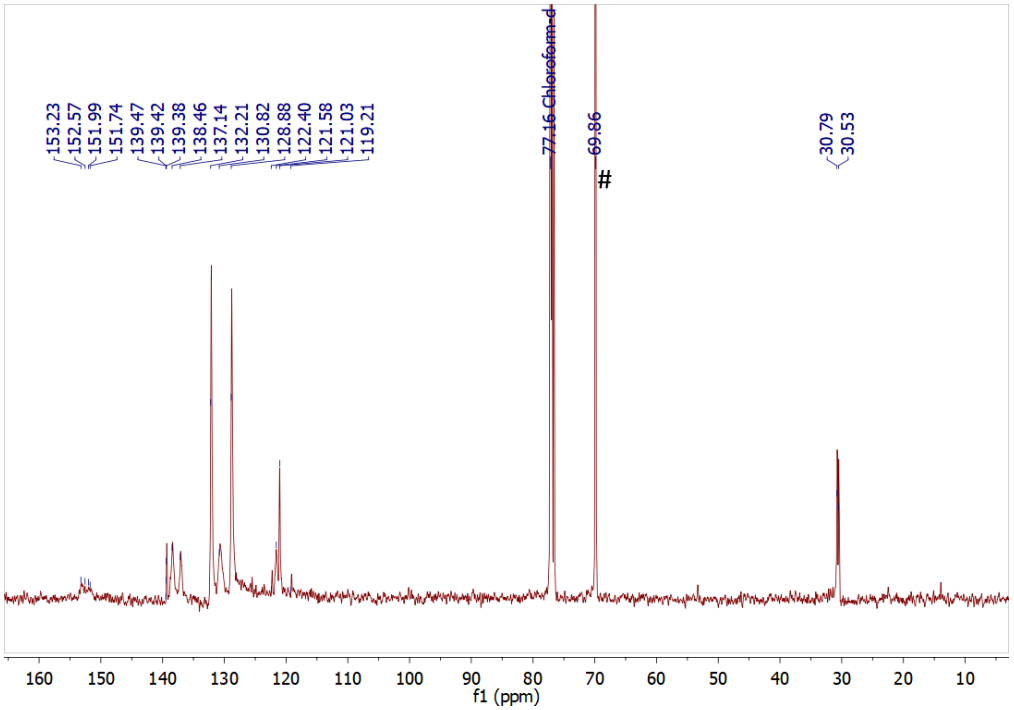


Fig. S58 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$, 298 K) of *in-situ* generated **3^{Ph}F** (# = peak for 18-crown-6).

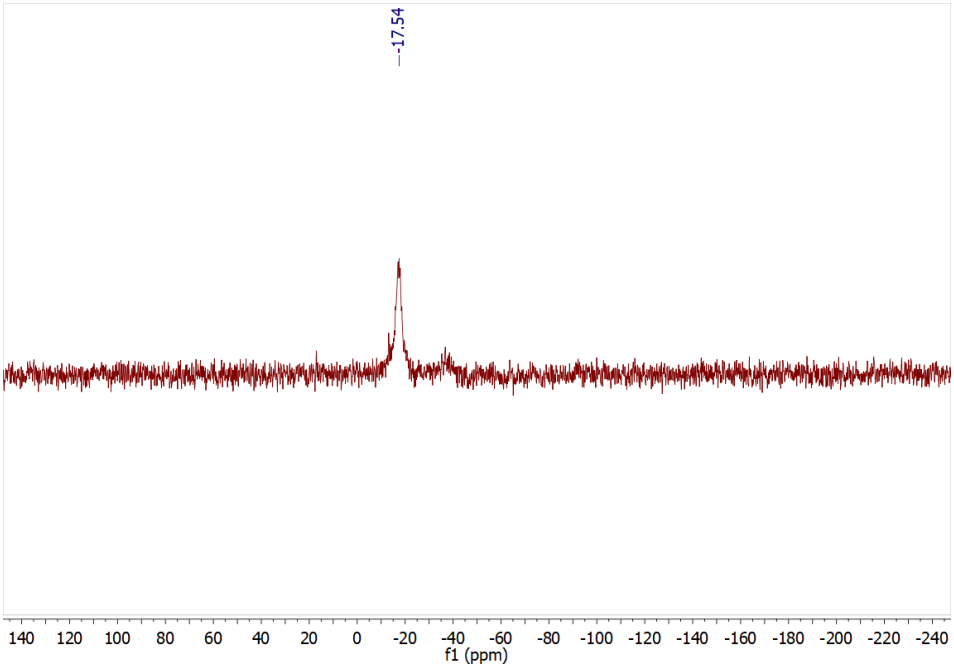


Fig. S59 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 298 K) of *in-situ* generated **3^{Ph}F**

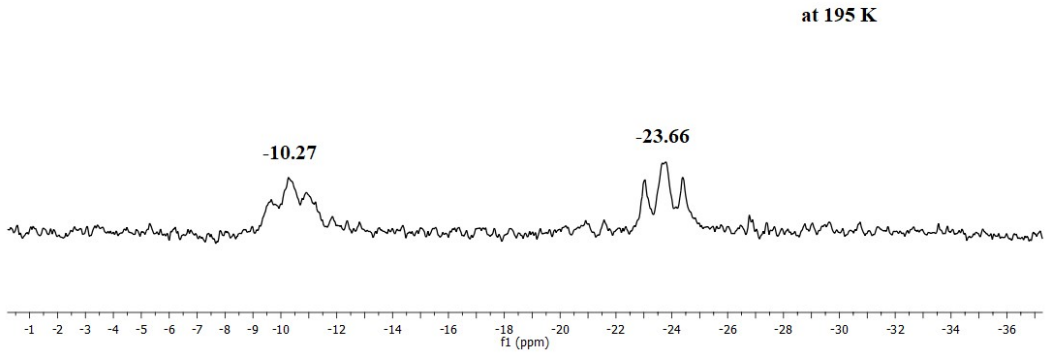


Fig. S60 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 195 K) of *in-situ* generated **3^{Ph}F**

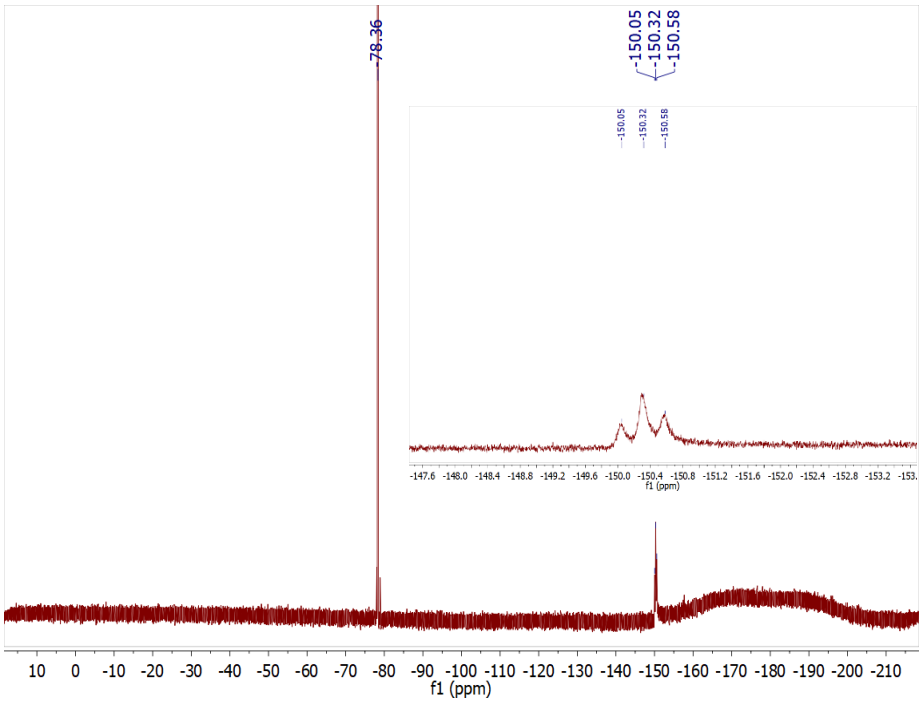


Fig. S61 $^{19}F\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 298 K) of *in-situ* generated **3^{Ph}F**

Reaction of 3^{Ph} and Trityl Chloride:

An NMR tube was charged with **3^{Ph}** (0.03 g, 0.03 mmol) and trityl chloride (0.008 g, 0.03 mmol) taken in 0.5 mL of $CDCl_3$ at room temperature. The reaction was analyzed by $^{31}P\{^1H\}$ NMR spectroscopy.

$^{31}P\{^1H\}$ NMR (162 MHz, Chloroform-*d*) δ – 6.31 (**3^{Ph}**), -13.46 (**2^{Ph}**) ppm.

Single crystals of **2^{Ph}** appeared in the NMR tube upon standing.

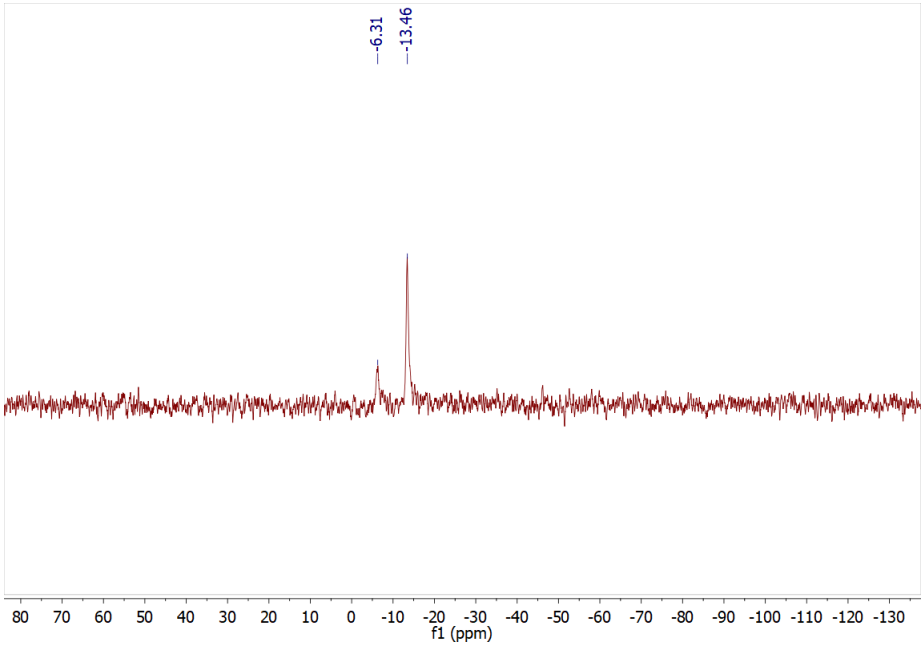


Fig. S62 $^{31}P\{^1H\}$ NMR spectrum (162 MHz, $CDCl_3$, 298 K) showing the Cl^- ion abstraction from Ph_3CCl by the Ge center of **3^{Ph}**.

Synthesis of $3^{iPr}H$:

To one equivalent of **3^{iPr}** (0.06 g, 0.07 mmol) dissolved in 10 mL of THF, was added one equivalent of $LiEt_3BH$ (66 μL of 1M solution in THF, 0.07 mmol). The reaction mixture was stirred overnight at room temperature. Solvent was evaporated to get a white solid. Colorless single crystals of **$3^{iPr}H$** (yield = 80 % (0.04 g)) were obtained from THF/pentane layering kept at -35 °C. Melting point: 158-160°C (decomposes).

^1H NMR (400 MHz, CD_2Cl_2) δ 7.95 – 7.88 (m, 3H, Acn-C*H*), 7.83 (d, *J* = 7.1 Hz, 1H, Acn-C*H*), 7.66 – 7.58 (m, 2H, Acn-C*H*), 7.49 (d, *J* = 7.0 Hz, 1H, Acn-C*H*), 7.45 (d, *J* = 7.0 Hz, 1H, Acn-C*H*), 7.22 (t, *J* = 35.7 Hz, 1H, Ge-*H*), 3.54 (s, 8H, Acn-CH_2), 2.79 (br, 4H, ^{i}Pr-C*H*), 1.41 – 1.30 (m, 9H, ^{i}Pr-CH_3), 1.28 – 1.16 (m, 9H, ^{i}Pr-CH_3), 1.06 – 1.01 (m, 6H, ^{i}Pr-CH_3) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2) δ 152.96 (s, Acn-*C*), 151.99 (s, Acn-*C*), 138.35 (t, *J* = 3.9 Hz, Acn-*C*), 135.24 (s, Acn-*C*), 135.09 (s, Acn-*C*), 121.48 (t, *J* = 2.7 Hz, Acn-*C*), 121.34 (s, Acn-*C*H), 121.04 (s, Acn-*C*H), 31.32 (s, Acn-*C*H_2), 31.10 (s, Acn-*C*H_2), 25.62 (br., ^{i}Pr-*C*H), 24.56 (br., ^{i}Pr-*C*H), 19.87 (br, ^{i}Pr-*C*H_3), 18.51 (br, ^{i}Pr-*C*H_3) ppm.

$^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2) δ = -5.15 ppm.

$^{19}F\{^1H\}$ NMR (377 MHz, CD_2Cl_2) δ = -77.01 ppm.

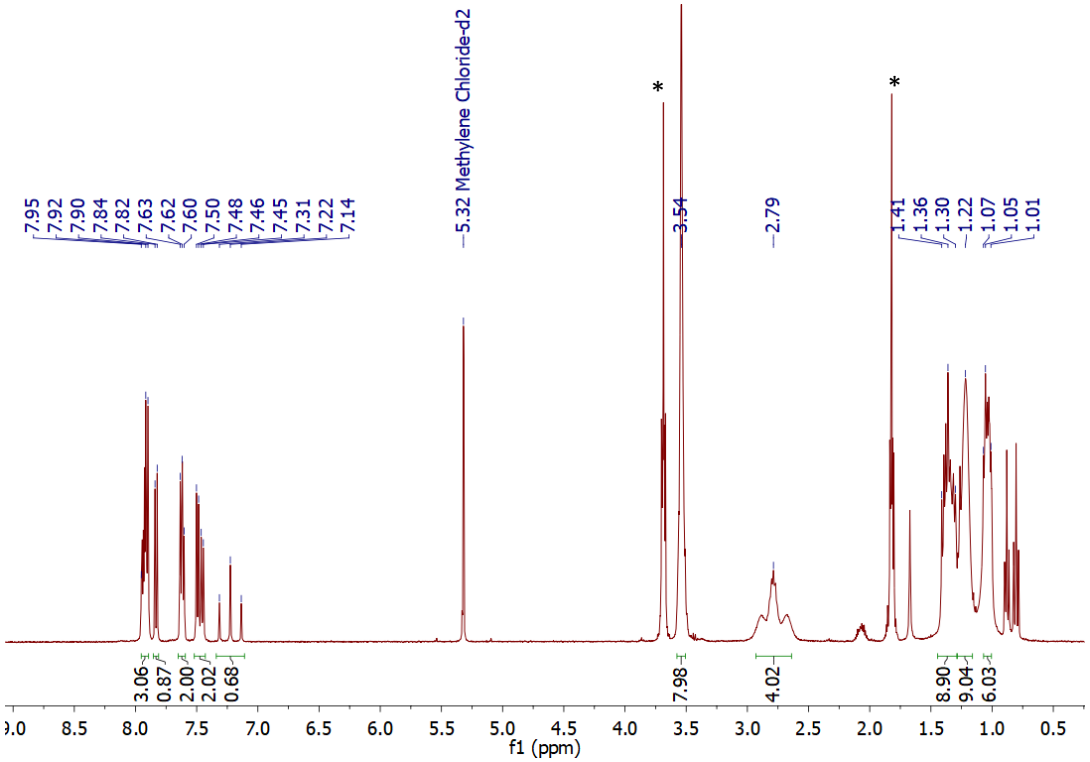


Fig. S63 ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of **3^{iPr}H**. (* = peak for THF)

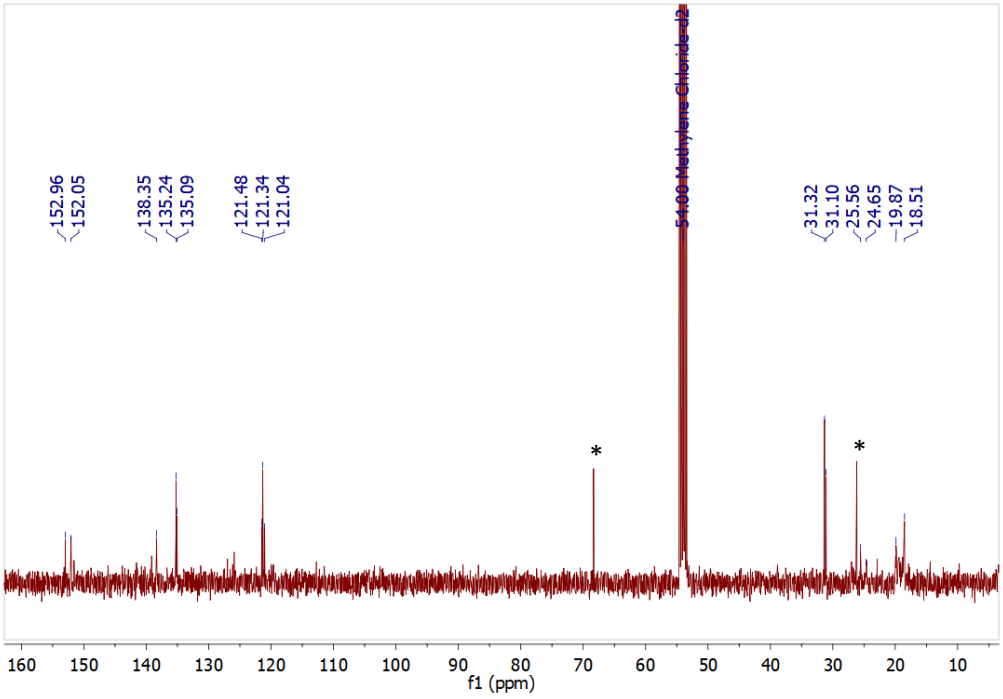


Fig. S64 ^{13}C{^{1}H} NMR spectrum (101 MHz, CD_2Cl_2, 298 K) of **3^{iPr}H**. (* = peak for THF)

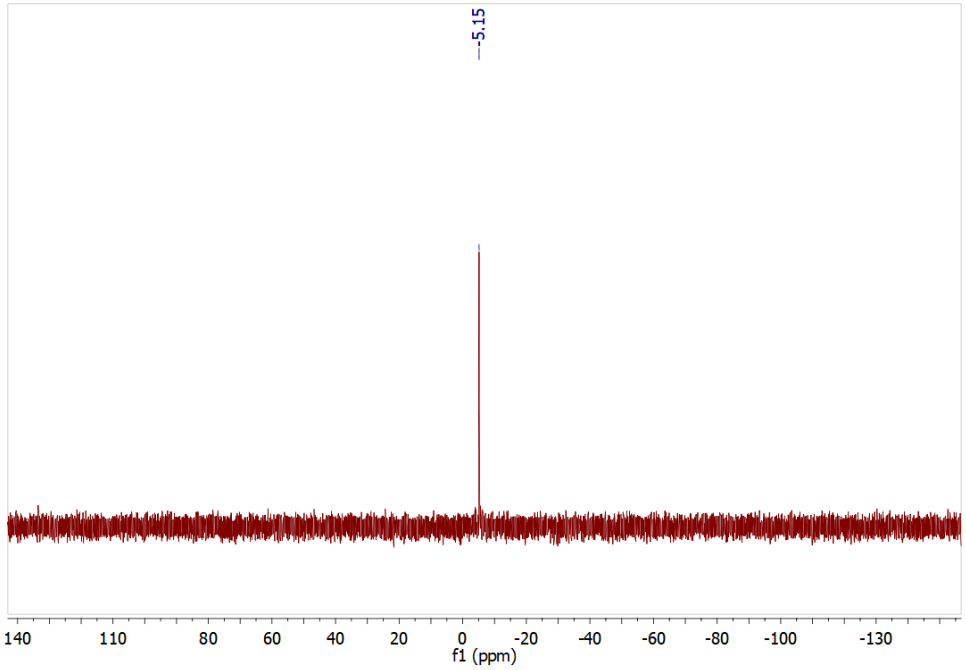


Fig. S65 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, CD_2Cl_2, 298 K) of **3^{iPr}H**.

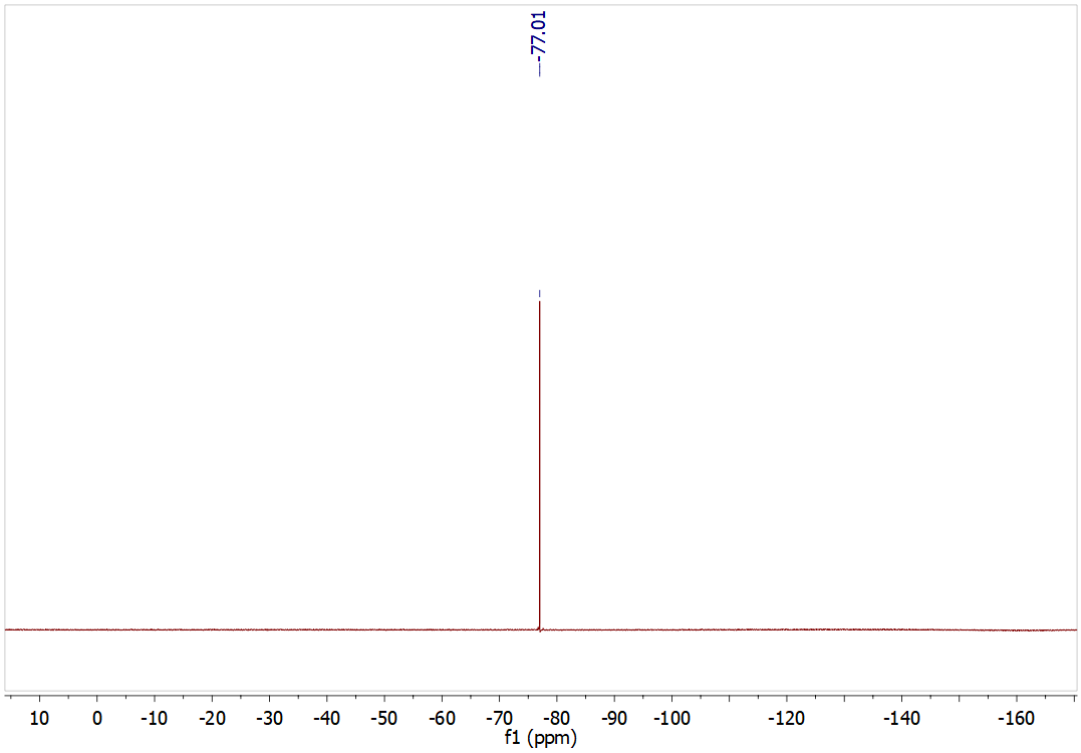


Fig. S66 $^{19}F\{^{1}H\}$ NMR spectrum (377 MHz, CD_2Cl_2, 298 K) of **3^{iPr}H**.

Synthesis of 3^{Ph}H$_2$:

To the solution of **3^{Ph}** (0.1 g, 0.1 mmol) in 15 mL of THF was added $LiEt_3BH$ (0.2 mL of 1 M solution in THF, 0.2 mmol) and the reaction mixture was stirred overnight at room temperature. Solvent was evaporated to get a white

solid. Toluene was added to this and the solid residue was filtered off. Colorless single crystals of **3^{Ph}H$_2$** were obtained from concentrated toluene solution at room temperature in 73% (0.05 g).

In-situ NMR: An NMR tube was charged with compound **3^{Ph}** (0.03 g, 0.03 mmol) and $LiEt_3BH$ (60 μL of 1 M solution in THF, 0.06 mmol) in 0.5 mL $CDCl_3$ under room temperature conditions. The product formation has been analysed by NMR spectroscopy. The NMR data revealed a mixture of products.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.40 (t, *J* = 20.2 Hz, Ge-*H*$_2$).

^{31}P{^{1}H} NMR (162 MHz, Chloroform-*d*) δ -19.07, -19.82, -20.06.

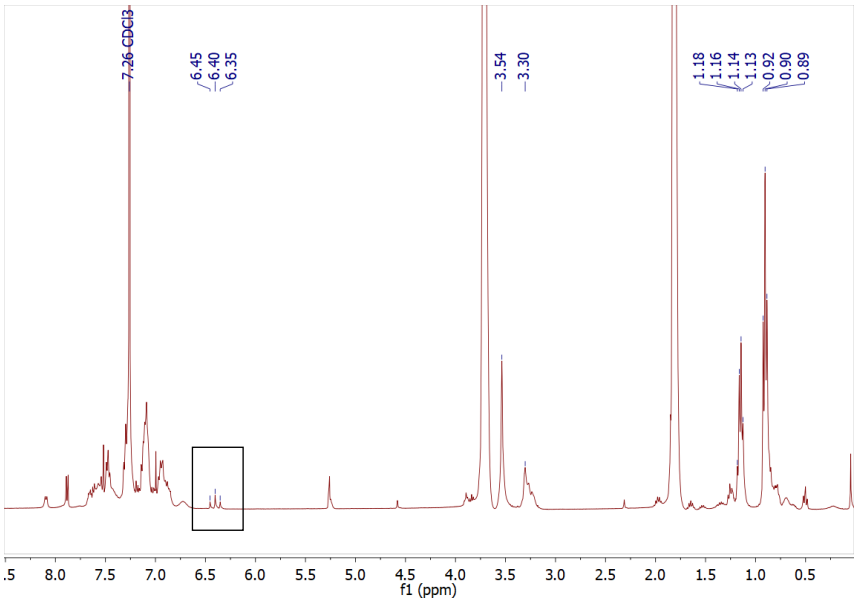


Fig. S67 ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of the reaction mixture showing the formation of **3^{Ph}H$_2$**.

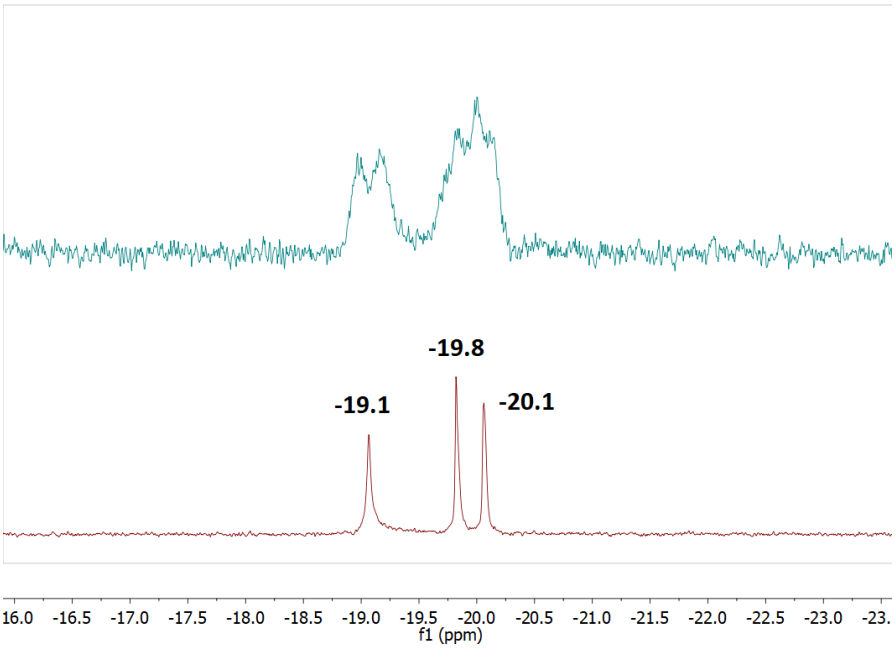


Fig. S68 Bottom: ^{31}P{^{1}H}; Top: ^{31}P NMR spectra (162 MHz, CD_2Cl_2, 298 K) of the reaction mixture showing the formation of **3^{Ph}H$_2$**.

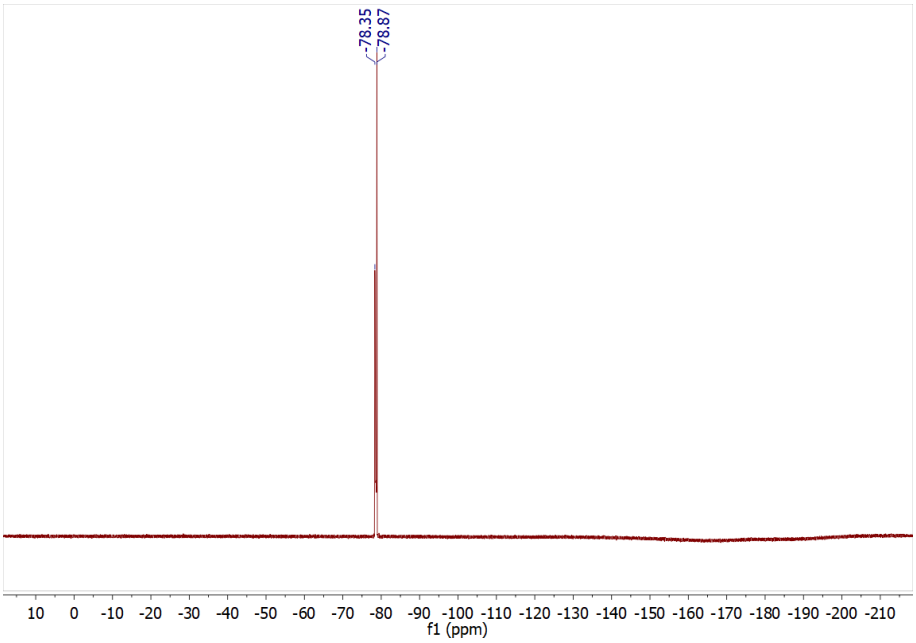


Fig. S69 $^{19}F\{^{1}H\}$ NMR spectrum (377 MHz, CD_2Cl_2, 298 K) of the reaction mixture

Synthesis of $3^{Ph}Et$, $3^{Ph}H(Et)$:

To the solution of **3^{Ph}** (0.1 g, 0.1 mmol) in 15 mL of THF was added $LiEt_3BH$ (0.1 mL of 1 M solution in THF, 0.1 mmol) and the reaction mixture was stirred overnight at room temperature. Solvent was evaporated to get a white solid. Colorless single crystals of **$3^{Ph}Et$** crystals were obtained from THF solution layered with pentane at room temperature.

Colorless single crystals of **$3^{Ph}H(Et)$** were obtained from acetonitrile solution kept at room temperature.

Si-H bond activation reaction by 3^{iPr} from Et_3SiH:

An NMR tube was charged with **3^{iPr}** (0.03 g, 0.03 mmol) and four equivalents of Et_3SiH (20 µL, 0.12 mmol) taken in 0.5 mL of CD_2Cl_2 at room temperature. The reaction was analyzed by ^{1}H, $^{31}P\{^{1}H\}$, 1D HSQC and 2D HSQC NMR spectroscopy.[S3]

$^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, 298 K): δ +28.51 (**3^{iPr}**), +20.28 (*P*-H), +12.16 (*P*$^{i}Pr_2$)

The P-H bond formed showed signals at δ(^{1}H) = 8.48 ppm and at δ(^{31}P) = 20.11 ppm having $^{1}J_{P\text{-}H}$ = 476 Hz.

ESI-MS (acetonitrile) found for the reaction mixture containing **3^{iPr}-PH** m/z 613.2220, calculated for $[C_{36}H_{45}GeP_2]^{+}$ m/z 613.2203.

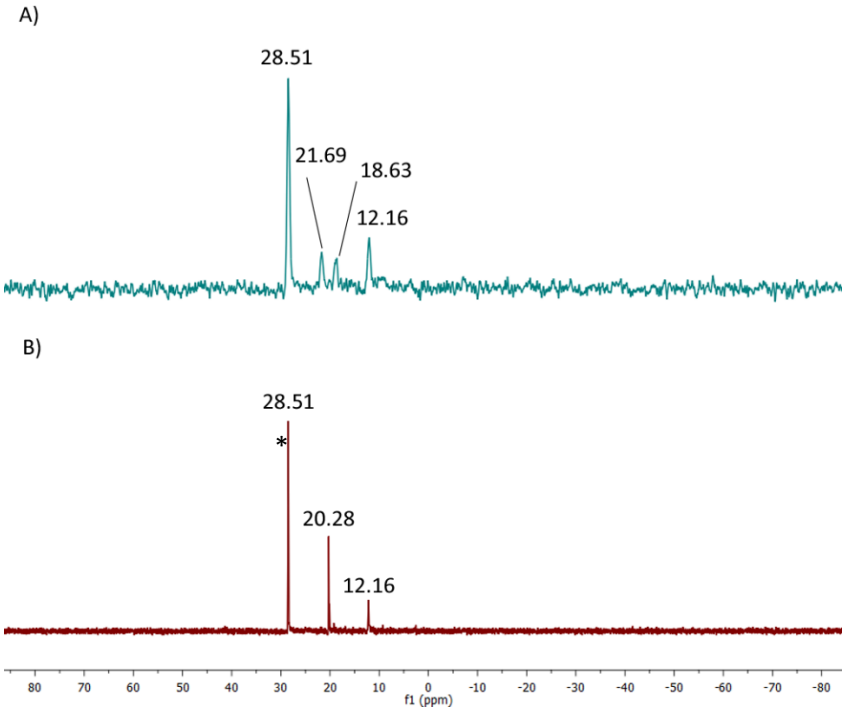


Fig. S70 ^{31}P (162 MHz, CD_2Cl_2, 298 K) of the **3^{iPr}** + Et_3SiH reaction mixture: A) ^{31}P ($J_{P\text{-}H} \approx 476$ Hz); B) ^{31}P{^{1}H} (* = peak for compound **3^{iPr}**)

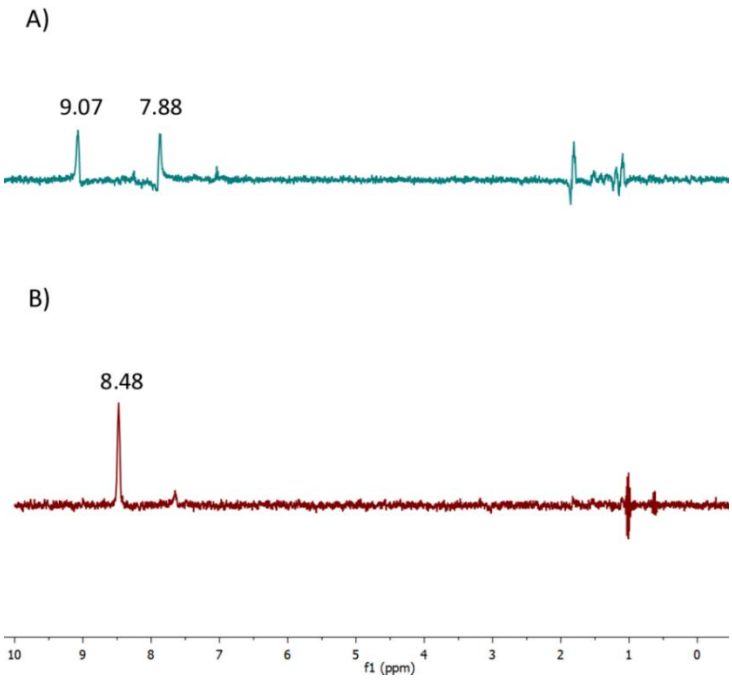


Fig. S71 1D ^{1}H-^{31}P HSQC with CNST2 optimized at 480 Hz (400 MHz, CD_2Cl_2, 298 K) of the **3^{iPr}** + Et_3SiH reaction mixture: A) ^{1}H-^{31}P ($^{1}J_{P\text{-}H} = 476$ Hz); B) ^{1}H-{^{31}P}

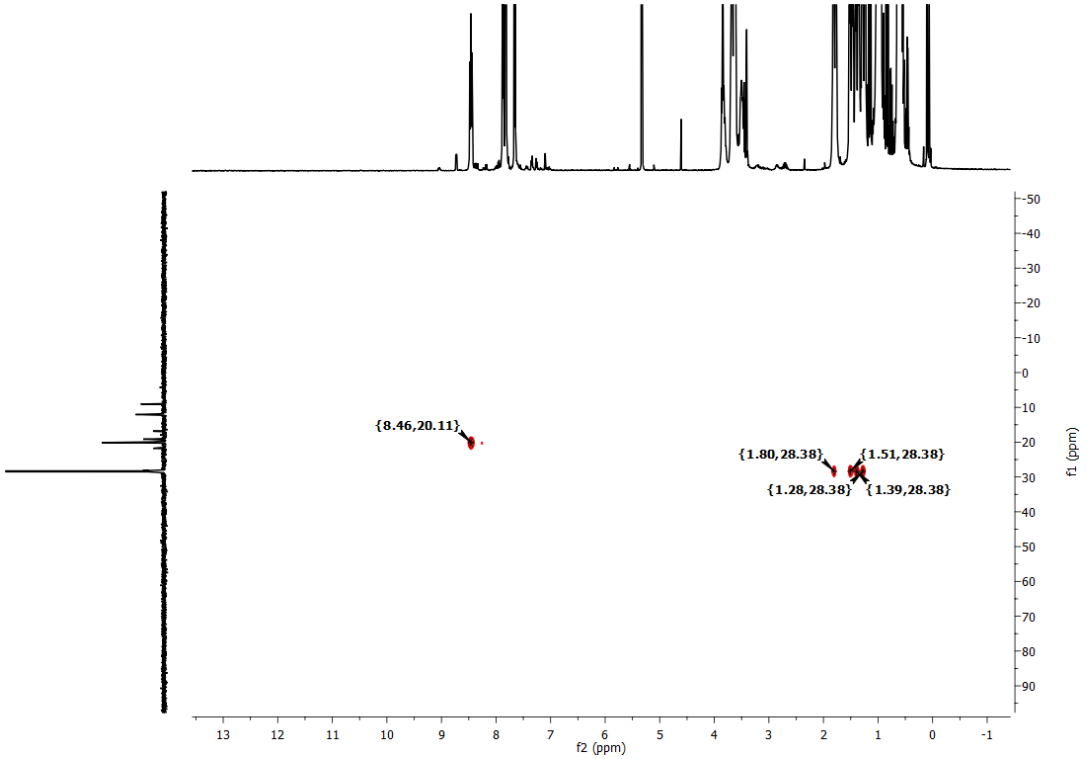


Fig. S72 2D ^{1}H-^{31}P HSQC with CNST2 optimized at 480 Hz (400 MHz/162 MHz, CD_2Cl_2, 298 K) of the **3^{iPr}** + Et_3SiH reaction mixture. (Note: additional cross peaks arising from $^{3}J_{P\text{-}H}$ = 20 Hz couplings in *P*{CH(C*H*$_3$)$_2$} of **3^{iPr}** have been observed)

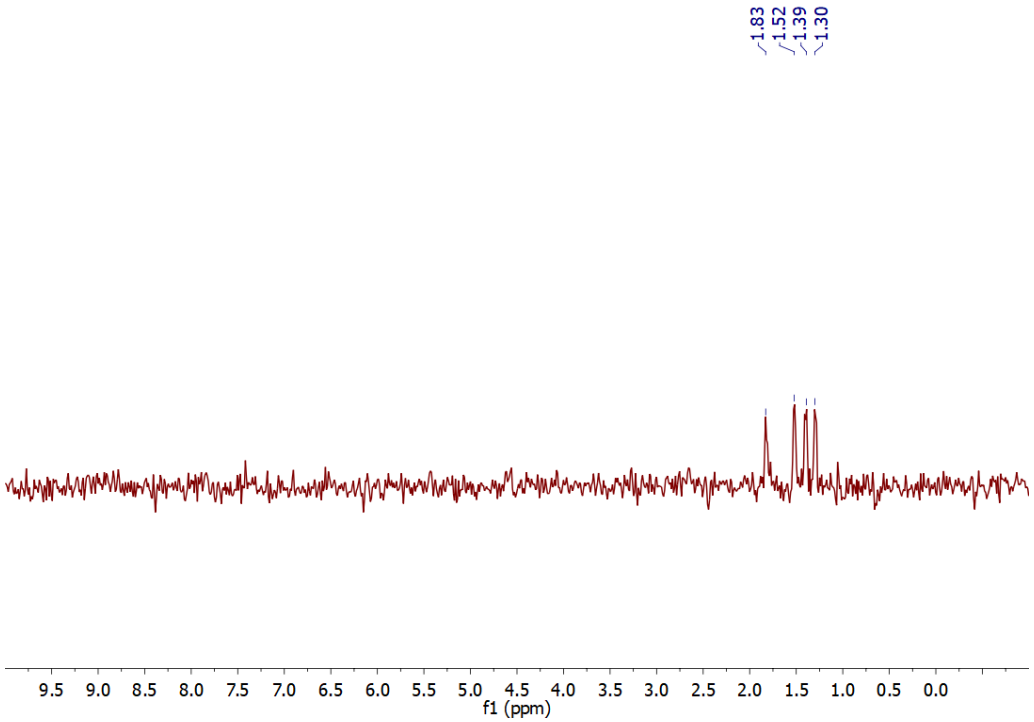


Fig. S73 1D 1H-^{31}P HSQC with CNST2 optimized at 480 Hz (400 MHz, CD_2Cl_2, 298 K) of **3^{iPr}**. (Note: control experiment shows the same peaks arising from **3^{iPr}** as represented in Fig. S69-S70)

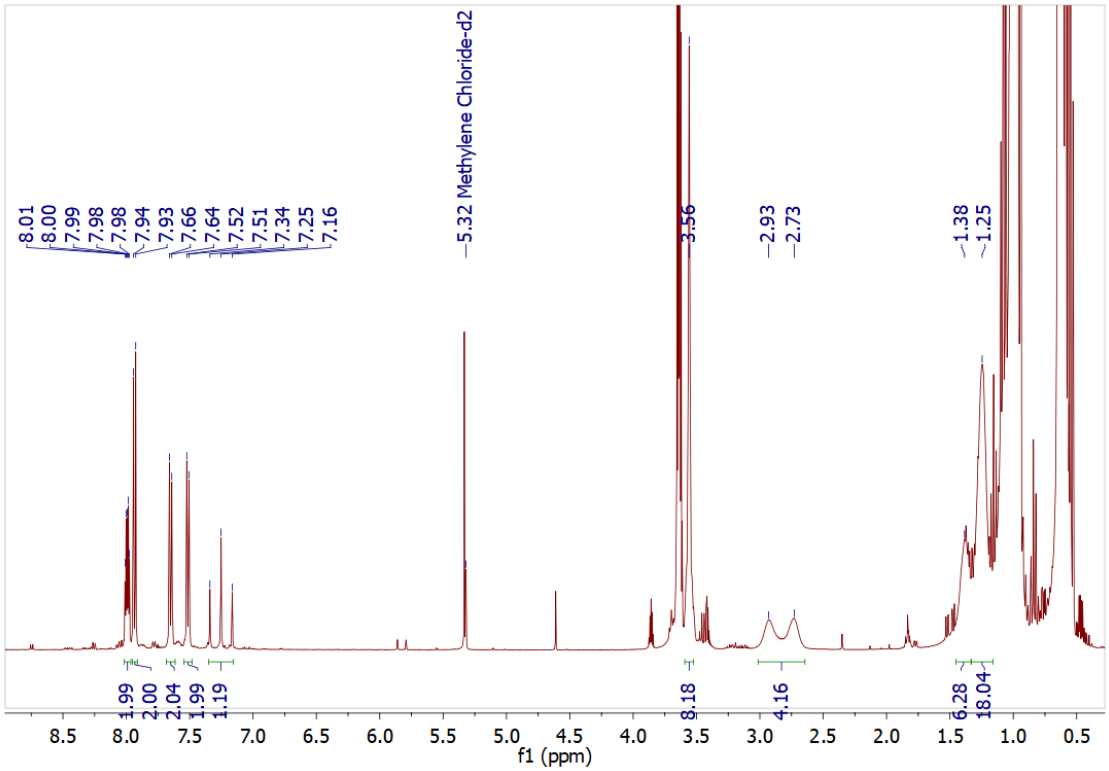


Fig. S74 ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of the **3**^{iPr} + Et_3SiH reaction mixture after 14 days.

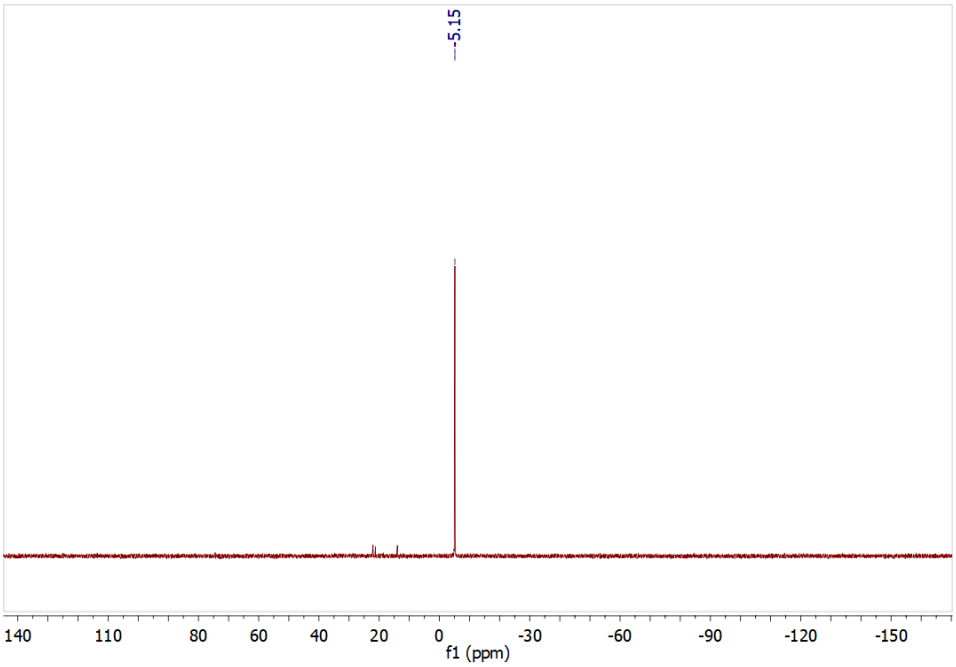


Fig. S75 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, CD_2Cl_2, 298 K) of the **3**^{iPr} + Et_3SiH reaction mixture after 14 days.

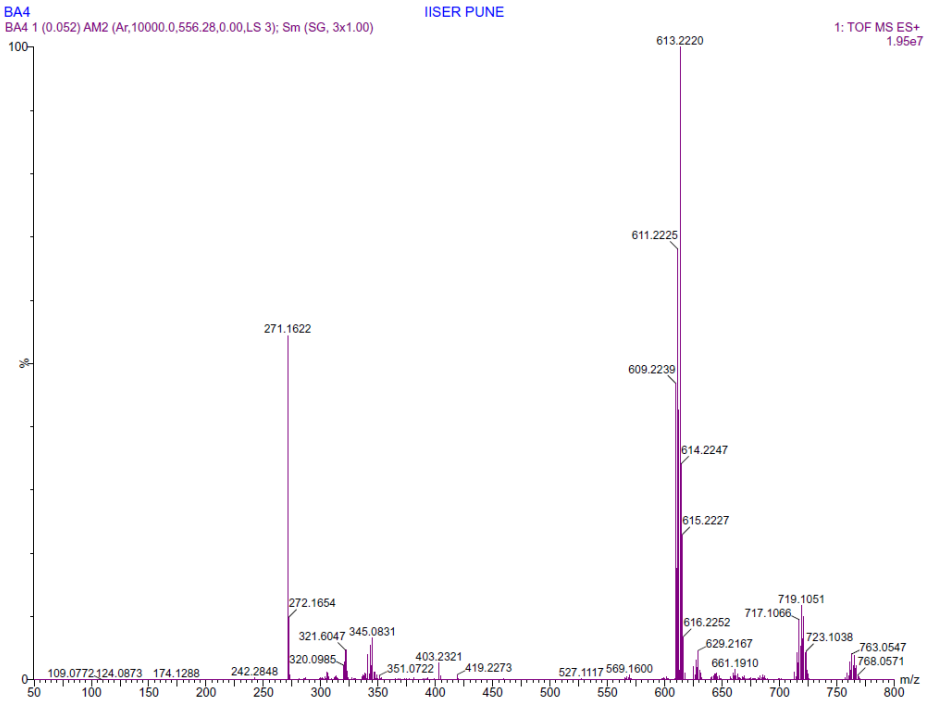


Fig. S76 ESI-MS (acetonitrile) found for the reaction mixture containing **3^{iPr}-PH**.

Si-H bond activation reaction by 3^{Ph} from Et_3SiH:

An NMR tube was charged with **3^{Ph}** (0.03 g, 0.03 mmol) and Et_3SiH (10 µL, 0.06 mmol) taken in 0.5 mL of $CDCl_3$ at room temperature. The reaction was analyzed by ^{1}H, ^{31}P, $^{31}P\{^{1}H\}$ and ^{1}H-^{31}P 1D HSQC NMR measurements after one hour of addition and at 24 hours.

The P-H bond formed showed signals at $\delta(^{1}H)$ = 10.0 ppm having $^{1}J_{P\text{-}H}$ = 534 Hz. (Initially formed in small amounts and then converted into Ge-H within 24 hours)

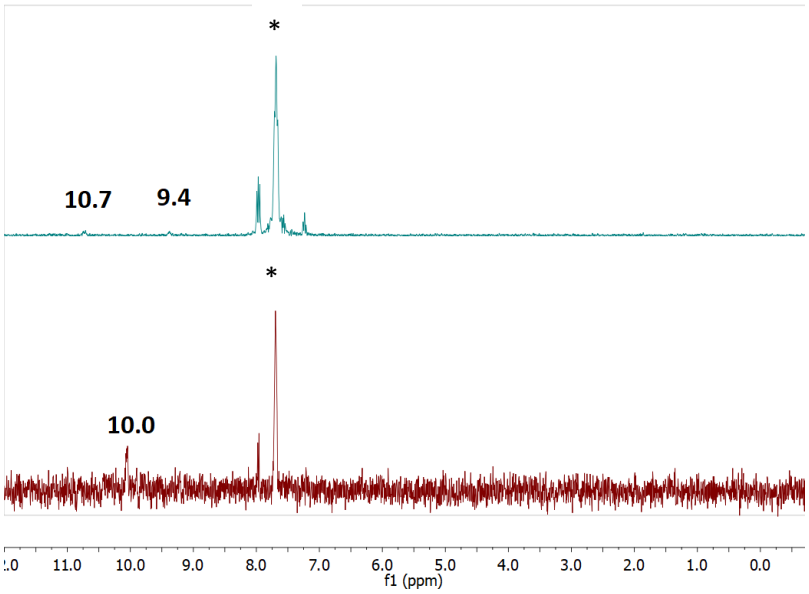


Fig. S77 1D ^{1}H-^{31}P HSQC with CNST2 optimized at 480 Hz (400 MHz, $CDCl_3$, 298 K) of the **3^{Ph}** + Et_3SiH reaction mixture after 1 hour of addition: A) ^{1}H-^{31}P ($^{1}J_{P\text{-}H}$ = 534 Hz) (top); B) ^{1}H-$\{^{31}P\}$ (bottom). (*) Peaks are related to **3^{Ph}** (see below spectra).

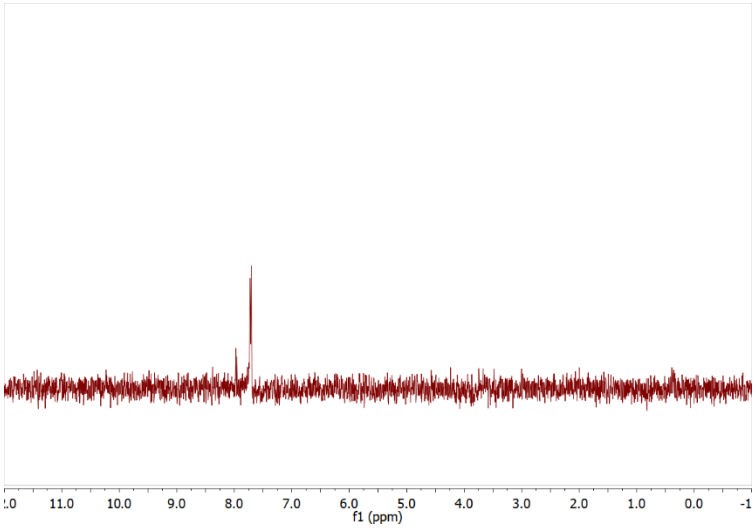


Fig. S78 1D 1H-^{31}P HSQC with CNST2 optimized at 480 Hz (400 MHz, $CDCl_3$, 298 K) of **3^{Ph}**. (Note: control experiment shows the same peaks arising from **3^{Ph}** as represented in Fig. S75).

NMR study after 24 hours showing the formation of $3^{Ph}H$:

^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.94 (d, *J* = 7.1 Hz, 2H, Acn-C*H*), 7.68 (dt, *J* = 7.4, 4.2 Hz, 2H, Ph-C*H*), 7.55 (d, *J* = 7.3 Hz, 2H, Acn-C*H*), 7.51 (t, *J* = 6.4 Hz, 6H, Acn-C*H*), 7.34 (t, *J* = 7.8 Hz, 8H, Ph-C*H*), 7.19 – 7.12 (m,

8H, Ph-C*H*), 7.01 (t, *J* = 30.4 Hz, 1H, Ge-*H*), 3.57 (s, 8H, Acn-CH_2), 1.08 - 0.93, 0.62 – 0.58 (*Et*$_3$SiOTf, *Et*$_3$SiH) ppm.

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 153.45, 151.87, 140.38 (t, *J* = 12.5 Hz), 139.90 (t, *J* = 4.7 Hz), 138.70 (t, *J* = 4.2 Hz), 137.92, 133.25 (t, *J* = 6.9 Hz), 131.83, 129.80 (t, *J* = 4.8 Hz), 128.57, 128.22 (d, *J* = 25.3 Hz), 123.54 (t, *J* = 21.8 Hz), 122.02 (t, *J* = 3.3 Hz), 121.62, 121.45 (d, *J* = 9.0 Hz), 118.23, 30.99 (s, Acn-*C*H_2), 30.81 (s, Acn-*C*H_2), 8.26 – 2.59 (*Et*$_3$SiOTf, *Et*$_3$SiH) ppm.

^{31}P{^{1}H} NMR (162 MHz, Chloroform-*d*) δ -19.0 ppm.

^{31}P NMR (162 MHz, Chloroform-*d*) δ -19.0 (d, $^2J_{P\text{-}H}$ = 30.4 Hz) ppm.

^{19}F{^{1}H} NMR (377 MHz, Chloroform-*d*) δ -77.43 ppm.

^{29}Si{^{1}H} NMR (80 MHz, Chloroform-*d*) δ +44.99 (Et$_3$*Si*OTf), +0.26 (Et$_3$*Si*H) ppm.

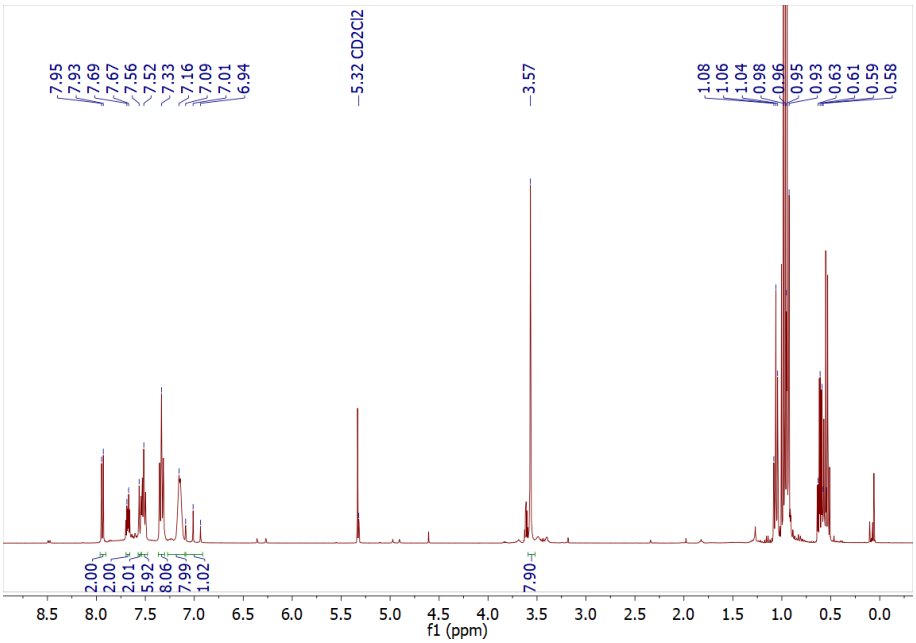


Fig. S79 ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of **3^{Ph}** + Et$_3$SiH resulting in the formation of **3^{Ph}H**.

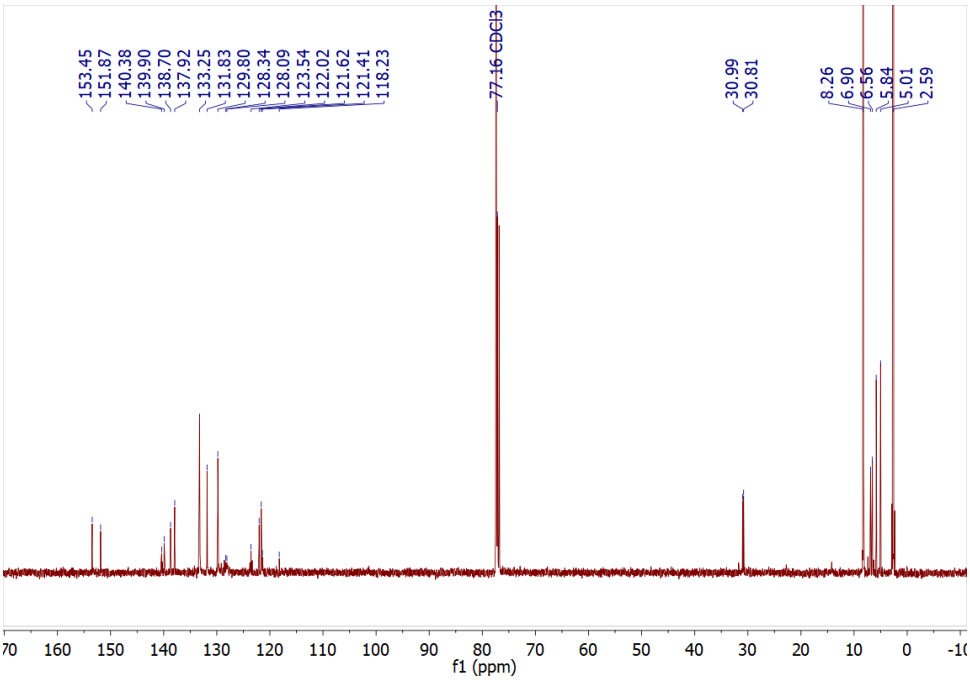


Fig. S80 ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$, 298 K) of **3^{Ph}** + Et$_3$SiH resulting in the formation of **3^{Ph}H**.

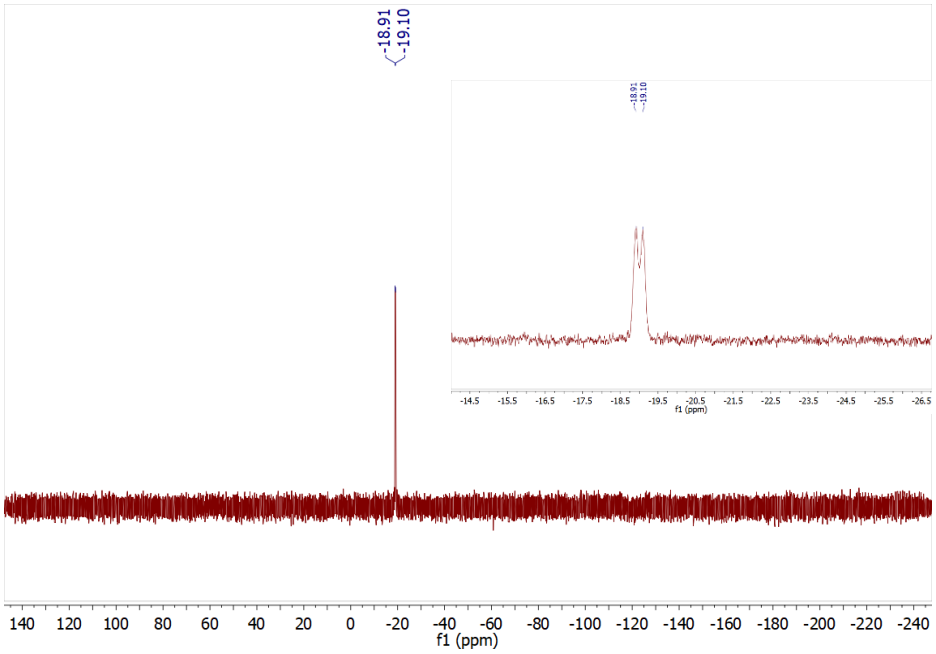


Fig. S81 ^{31}P NMR spectrum (162 MHz, $CDCl_3$, 298 K) of $\mathbf{3^{Ph}}$ + Et_3SiH resulting in the formation of $\mathbf{3^{Ph}H}$.

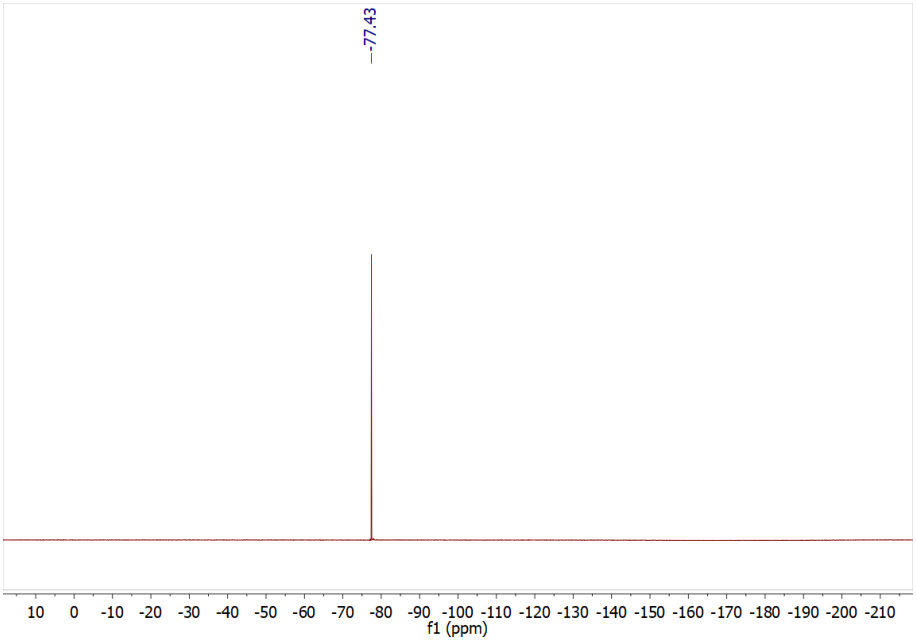


Fig. S82 $^{19}F\{^1H\}$ NMR spectrum (377 MHz, $CDCl_3$, 298 K) of $\mathbf{3^{Ph}}$ + Et_3SiH resulting in the formation of $\mathbf{3^{Ph}H}$.

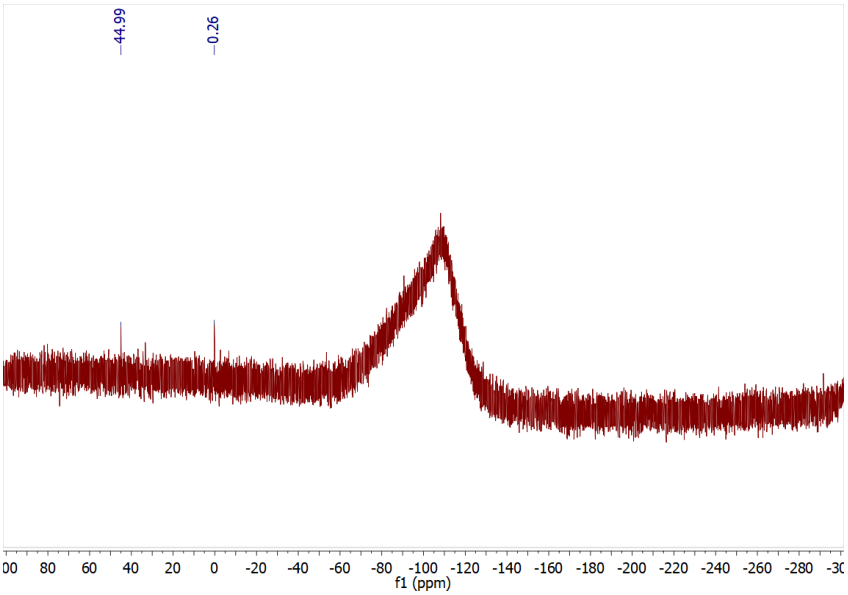


Fig. S83 $^{29}Si\{^{1}H\}$ NMR spectrum (80 MHz, CD_2Cl_2, 298 K) of **3^{Ph}** + Et_3SiH resulting in the formation of **3^{Ph}H** and Et_3SiOTf.

Reaction of 3^{Ph} and aldehyde:

An NMR tube was charged with **3^{Ph}** (0.03 g, 0.03 mmol) and excess (20 µL) of methyl benzaldehyde taken in 0.5 mL of $CDCl_3$ (0.5 mL) at room temperature. The reaction is analyzed by $^{31}P\{^{1}H\}$ NMR measurement.

$^{31}P\{^{1}H\}$ NMR (162 MHz, Chloroform-*d*) δ 36.02-32.08, -19.26 ppm.

Single crystals of the product after aldehyde insertion into Ge-P bond **3^{Ph}Oald** were obtained from THF solution.

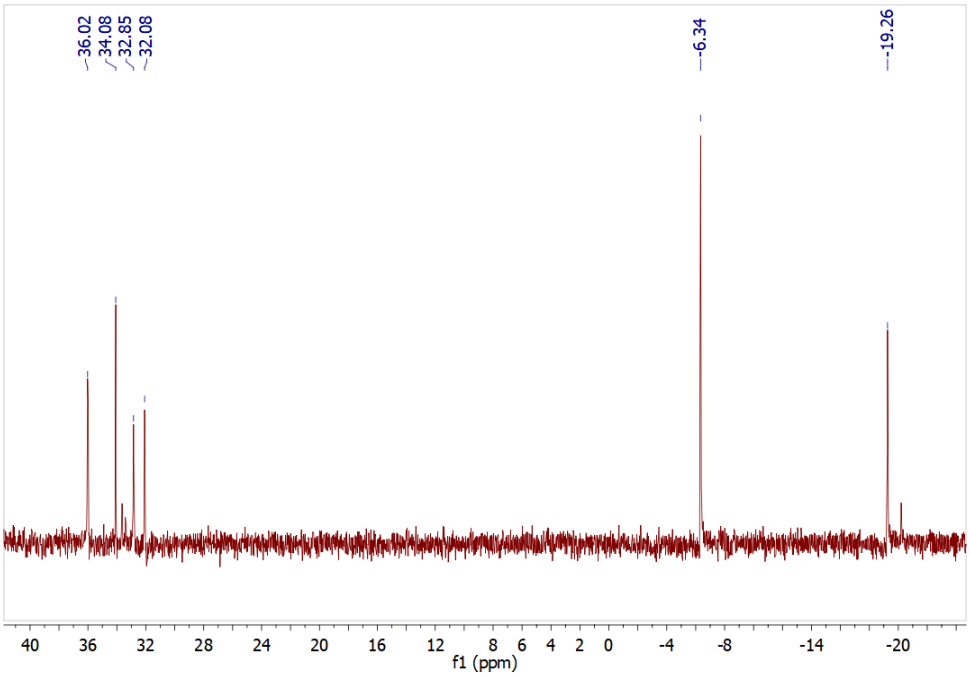


Fig. S84 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$, 298 K) of **3^{Ph}** + *p*-methyl benzaldehyde.

Hydrosilylation of aldehydes by 3^{iPr}:

An NMR tube was charged with methyl benzaldehyde (12 µL, 0.10 mmol), Et_3SiH (32 µL, 0.20 mmol), catalyst **3^{iPr}** (0.005 mmol) in CD_2Cl_2 (0.5 mL). The reaction was analyzed by ^1H NMR measurement and conversion was calculated by integration against internal standard $C_6(Me)_6$.

Triethyl((4-methylbenzyl)oxy)silane: **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 7.27 (d, *J* = 8.0 Hz, 2H, aryl-*H*), 7.18 (d, *J* = 8.0 Hz, 2H, aryl-*H*), 4.51 (s, 2H, C*H*$_2$), 2.37 (s, 3H, methyl-*H*), 1.02 (m, 9H, (C*H*$_3$CH$_2$)$_3$Si), 0.64 (m, 6H, (CH$_3$C*H*$_2$)$_3$Si) ppm.

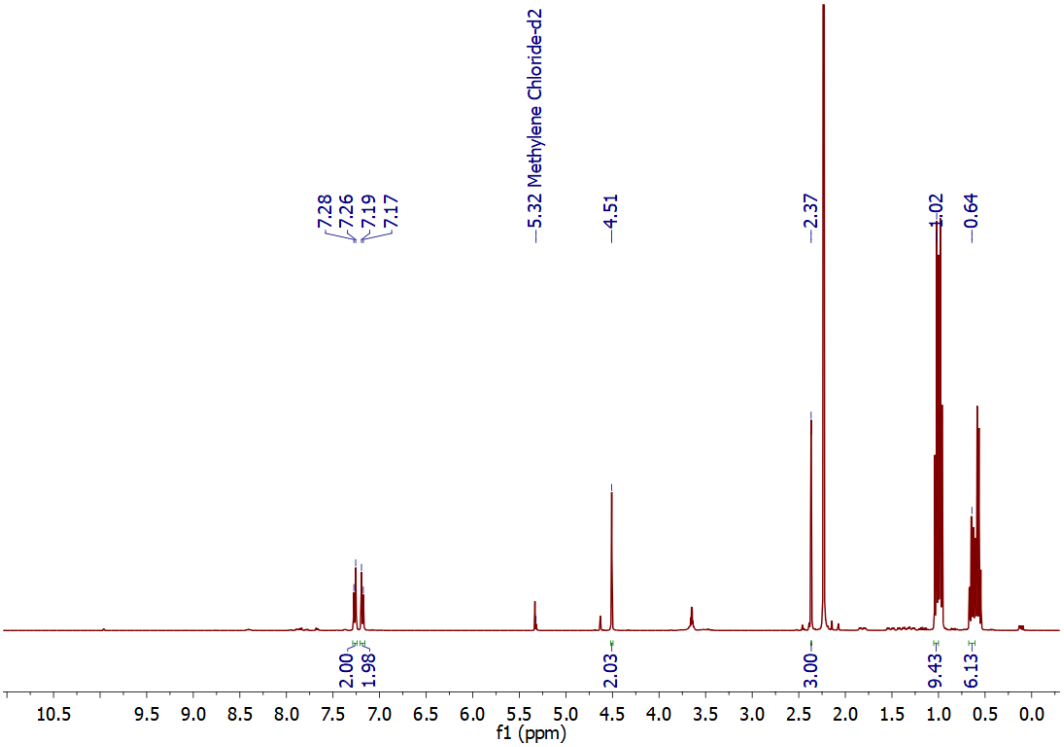


Fig. S85 ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) for the hydrosilylation of *p*-Methyl benzaldehyde using Et_3SiH and 5 mol% of **3^{iPr}** as catalyst (hexamethylbenzene as internal standard) recorded after 24 hours

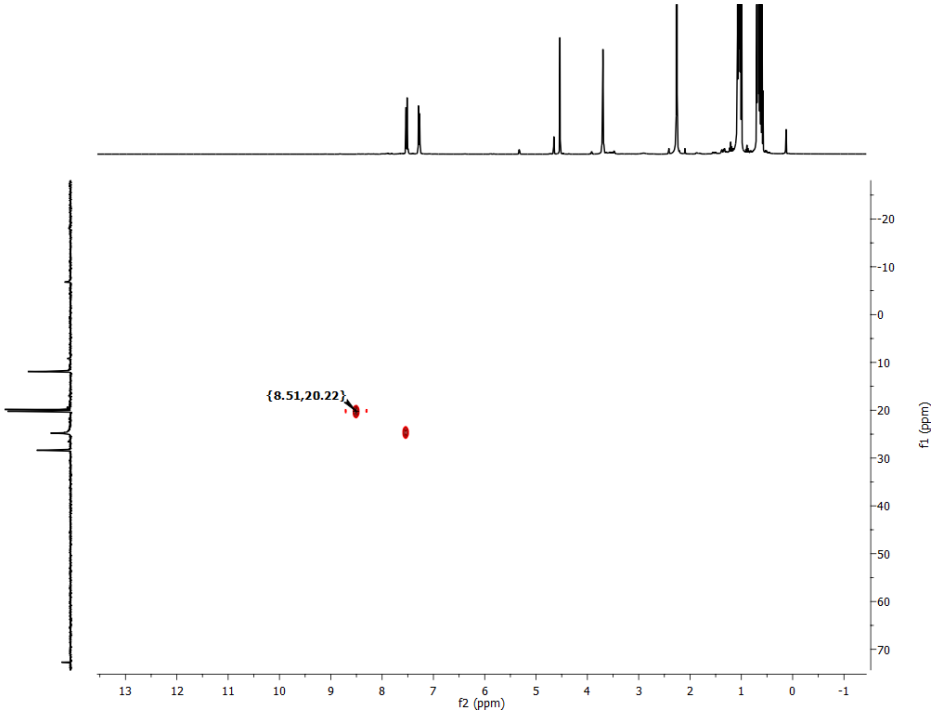


Fig. S86 2D ^{1}H-^{31}P HSQC with CNST2 optimized at 480 Hz (400 MHz/162 MHz, CD_2Cl_2, 298 K) of the catalytic reaction mixture (*p*-Methyl benzaldehyde+Et_3SiH and 5 mol% of **3**$^{i\mathbf{Pr}}$ as catalyst)

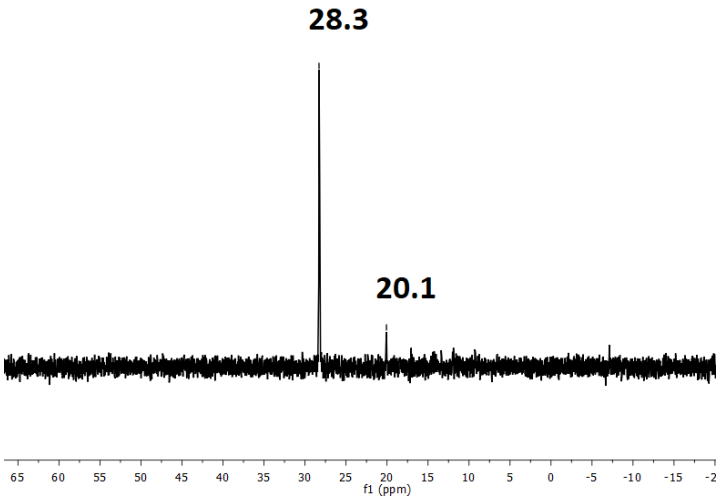


Fig. S87 $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, 298 K) of the initial catalytic reaction mixture (*p*-Methyl benzaldehyde+Et_3SiH and 5 mol% of **3**$^{i\mathbf{Pr}}$ as catalyst)

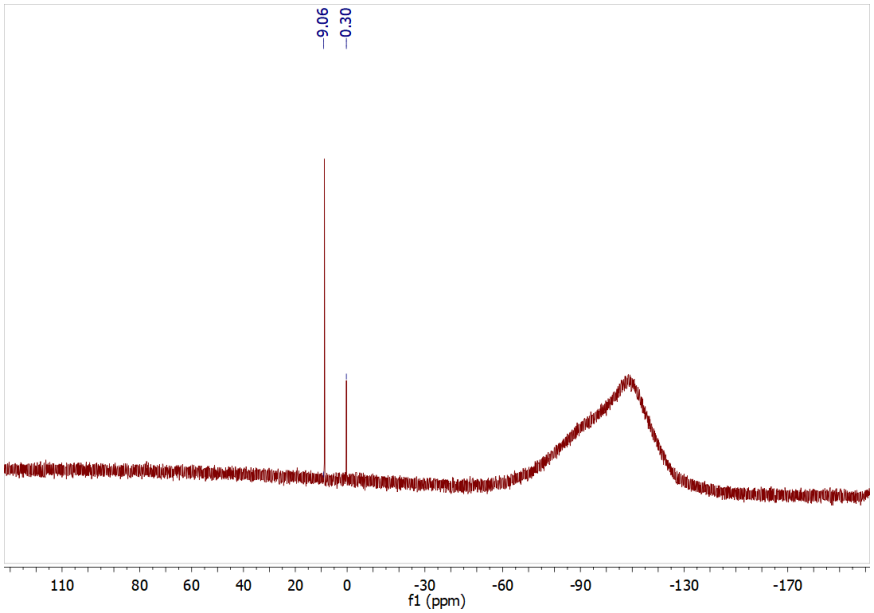


Fig. S88 $^{29}Si\{^{1}H\}$ NMR (80 MHz, CD_2Cl_2, 298 K, no. of scans = 2000, T1 = 15 secs) of the catalytic reaction mixture (*p*-Methyl benzaldehyde+Et_3SiH and 5 mol% of **3**$^{i\mathbf{Pr}}$ as catalyst); no Et_3SiOTf peak observed.

Hydrosilylation of aldehydes by 3^{Ph}:

An NMR tube was charged with methyl benzaldehyde (12 µL, 0.10 mmol), Et_3SiH (19 µL, 0.12 mmol), catalyst **3**^{Ph} (0.0001 mmol) in $CDCl_3$ (0.5 mL). The reaction was analyzed by ^{1}H NMR measurement and conversion was calculated by integration against internal standard $C_6(Me)_6$.

Triethyl((4-methylbenzyl)oxy)silane: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.0 Hz, 2H, aryl-H), 7.18 (d, *J* = 8.0 Hz, 2H, aryl-H), 4.52 (s, 2H, CH_2), 2.36 (s, 3H, *p*-methyl-H), 0.95 (m, 9H, $(CH_3CH_2)_3Si$), 0.55 (m, 6H, $(CH_3CH_2)_3Si$) ppm.

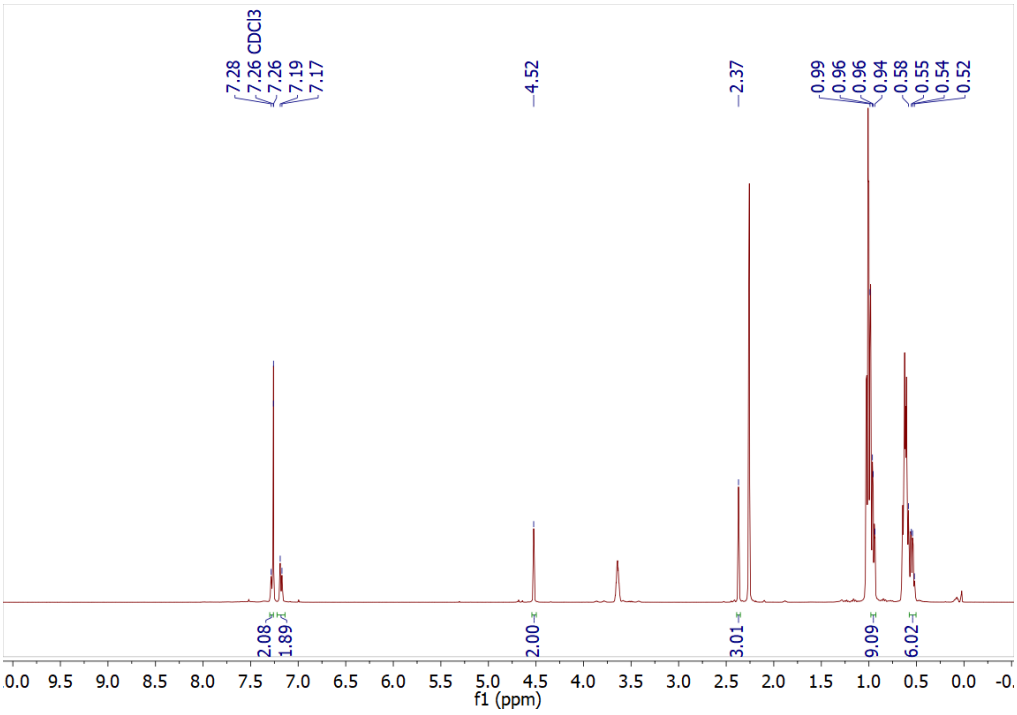


Fig. S89 ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) for the hydrosilylation of *p*-Methyl benzaldehyde using Et_3SiH and 1 mol% of **3**^{Ph} as catalyst (hexamethylbenzene as internal standard) recorded after 24 hours

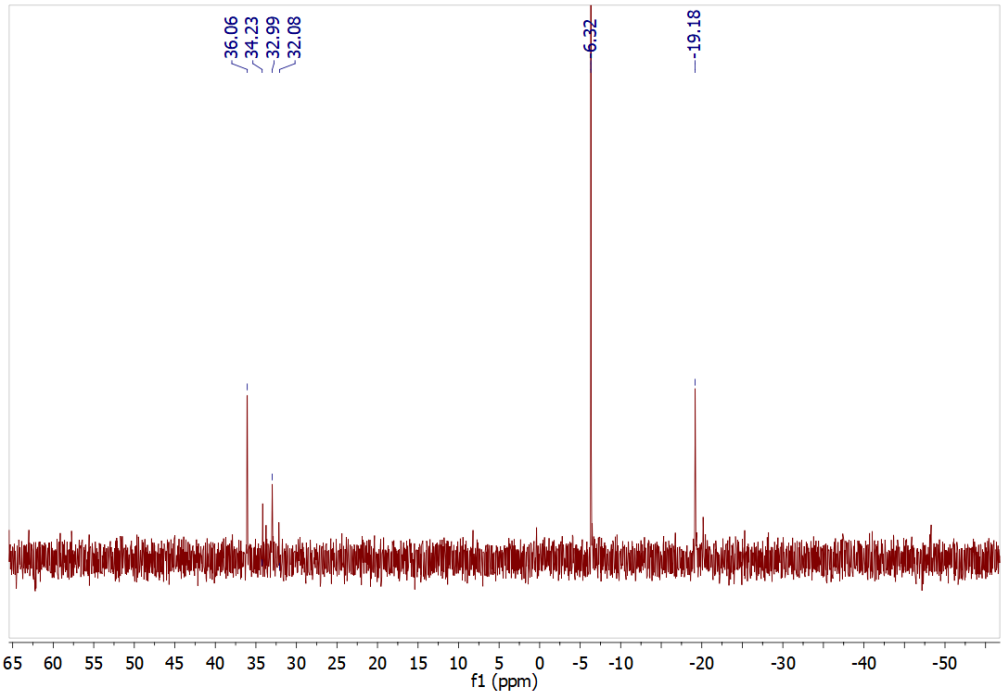


Fig. S90 $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) of the initial catalytic reaction mixture (*p*-Methyl benzaldehyde+Et_3SiH and 1 mol% of **3^{Ph}** as catalyst)

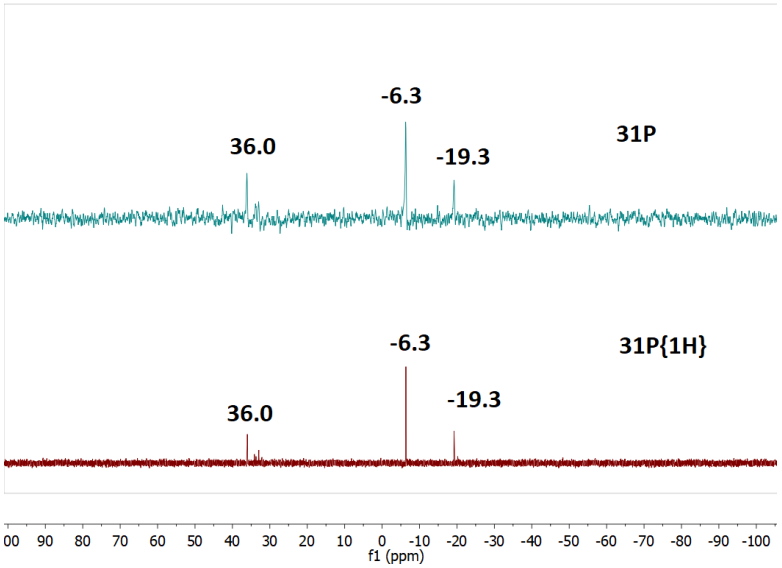


Fig. S91 ^{31}P and $^{31}P\{^{1}H\}$ NMR spectra of the initial catalytic reaction mixture in the case of **3^{Ph}** as catalyst, depicting the aldehyde insertion into the Ge-P bond predominantly. (peak at -6.3 ppm is for compound **3^{Ph}**).

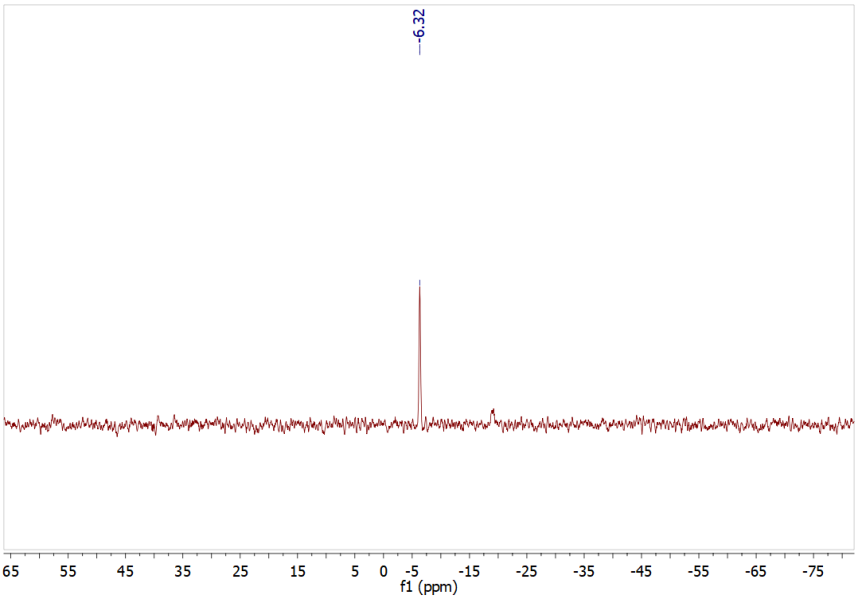


Fig. S92 $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) at the end of the catalytic reaction (*p*-Methyl benzaldehyde + Et_3SiH and 1 mol% of **3^{Ph}** as catalyst)

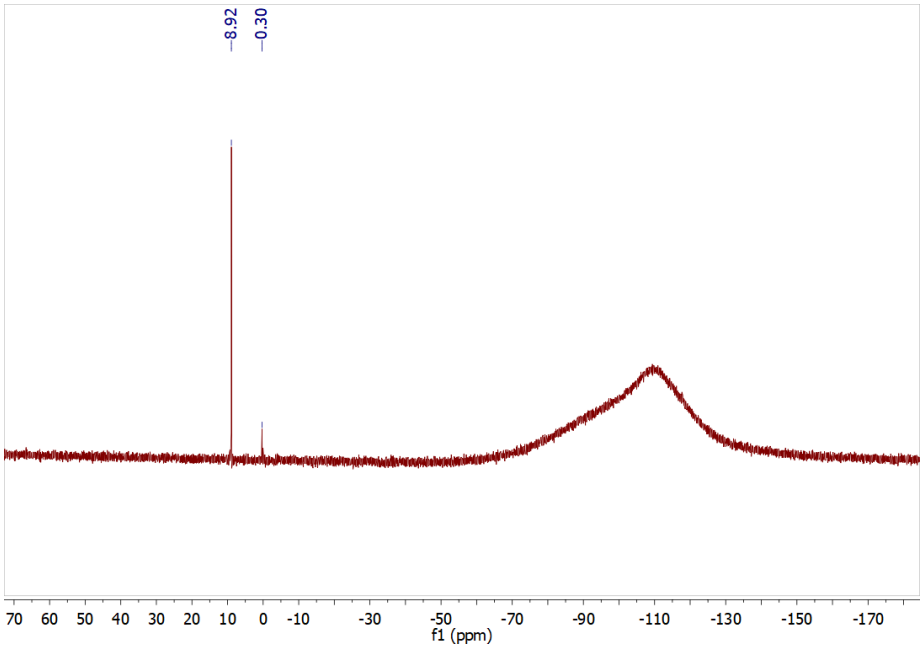


Fig. S93 $^{29}Si\{^{1}H\}$ NMR (80 MHz, $CDCl_3$, 298 K, no. of scans = 2000, T1 = 15 secs) of the catalytic reaction mixture (*p*-Methyl benzaldehyde+Et_3SiH and 1 mol% of **3^{Ph}** as catalyst); no Et_3SiOTf peak observed.

Control Experiment:

An NMR tube was charged with methyl benzaldehyde (12 µL, 0.10 mmol), Et_3SiH (32 µL, 0.20 mmol) in CD_2Cl_2 (0.5 mL). The reaction was analyzed by ^1H NMR measurement after 24 hours. No hydrosilylated product was formed.

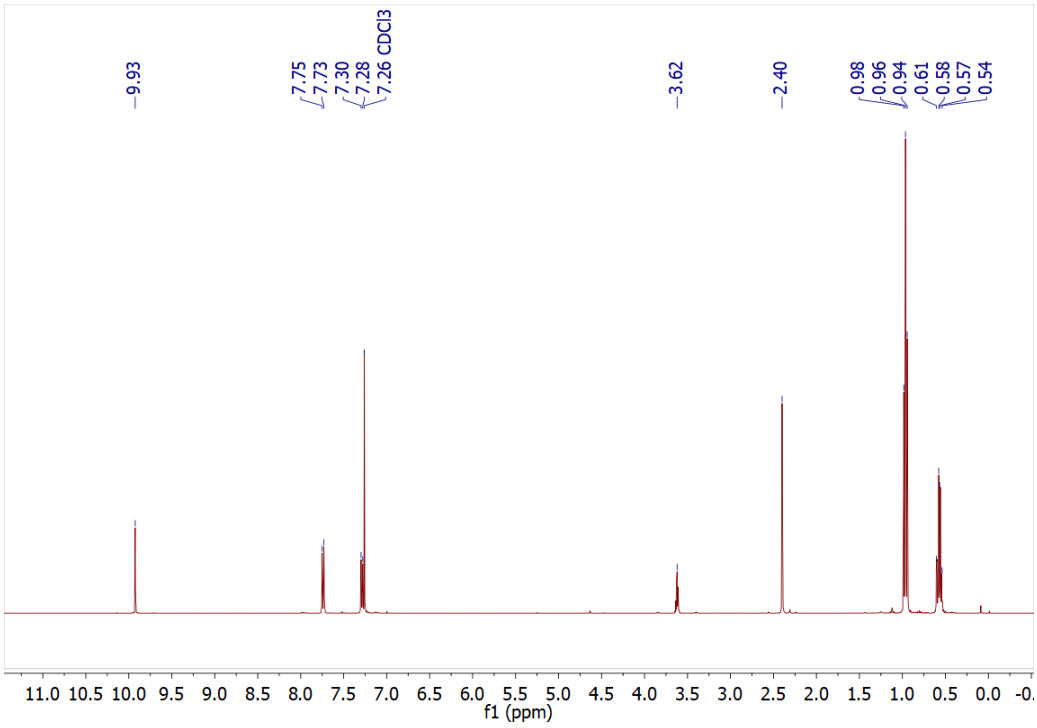


Fig. S94 ^1H NMR (400 MHz, $CDCl_3$, 298 K) for Control Experiment

Single Crystal X-ray Diffraction Analyses

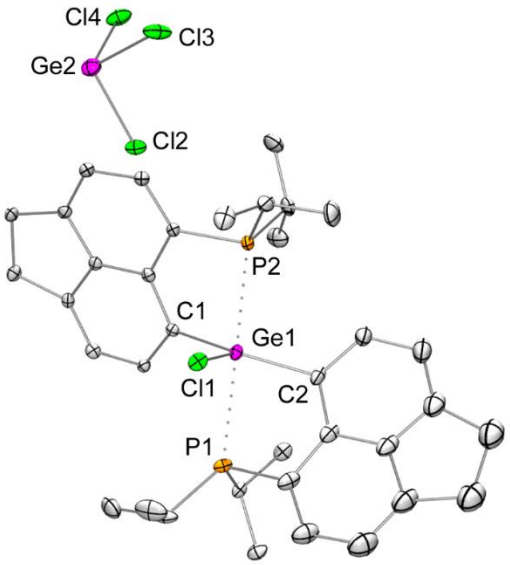


Fig. S95 Molecular structure of **1**^{iPr} in the solid state (thermal ellipsoids at 30%, H atoms and solvent molecule are omitted for clarity). Selected bond lengths [Å]: Ge1-C1 = 1.959(5), Ge1-C2 = 1.955(5), Ge1-Cl1 = 2.194(1), Ge1-P1 = 2.544(1), Ge1-P2 = 2.654(1); selected bond angles [°]: C1-Ge1-C2 = 147.3(2), Cl1-Ge1-C1 = 107.1(2), Cl1-Ge1-C2 = 105.4(1), P1-Ge1-P2 = 177.9(1), P1-Ge1-Cl1 = 90.4(1), P1-Ge1-C1 = 99.5(2), P1-Ge1-C2 = 84.0(1).

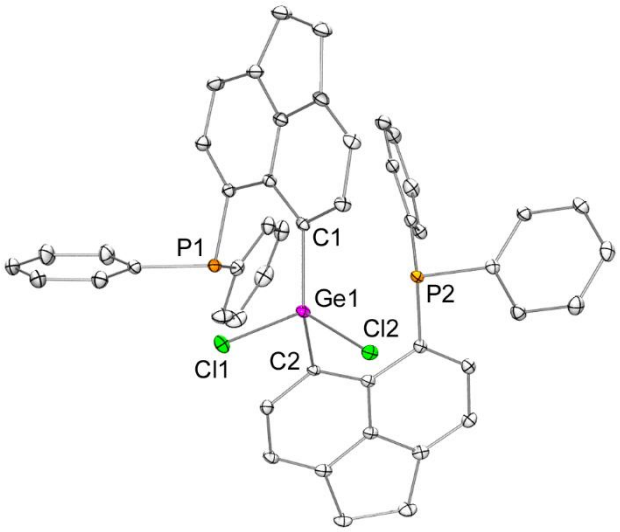


Fig. S96 Molecular structure of **1**^{Ph} in the solid state (thermal ellipsoids at 30%, H atoms and solvent molecules are omitted for clarity). Selected bond lengths [Å]: Ge1-C1 = 1.973(2), Ge1-C2 = 1.973(2), Ge1-Cl1 = 2.233(1), Ge1-Cl2 = 2.245(1), Ge1···P1 = 2.982(1), Ge1···P2 = 2.964(1); selected bond angles [°]: C1-Ge1-C2 = 143.7(1), Cl1-Ge1-C1 = 102.3(1), Cl1-Ge1-C2 = 104.7(1), C2-Ge1-Cl2 = 97.3(1), C1-Ge1-Cl2 = 105.2(1), Cl1-Ge1-Cl2 = 92.8(1).

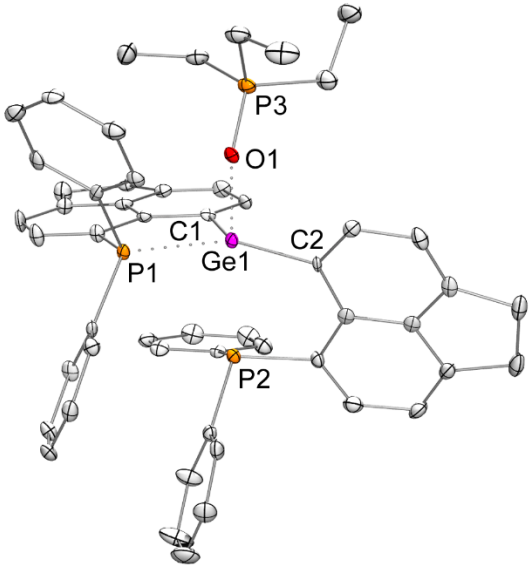


Fig. S97 Molecular structure of **3^{Ph}OPEt$_3$** (H atoms, solvent molecule and triflate anion have been removed for clarity; thermal ellipsoid 30%). Selected bond lengths [Å] and angles [°]: a) Ge1-C1 = 1.918(7), Ge1-C2 = 1.934(7), Ge1-O1 = 1.944(5), Ge1-P1 = 2.362(2), Ge1-P2 = 2.744(2); C1-Ge1-C2 = 126.2(3), C1-Ge1-O1=96.5(3), C2-Ge1-O1 = 96.6(3), C1-Ge1-P1 = 92.1(2), C2-Ge1-P1 = 140.1(2), O1-Ge1-P1 = 88.6(2), C1-Ge1-P2 = 83.8(2), C2-Ge1-P2 = 82.6(2), O1-Ge1-P2 = 179.2(2), P1-Ge1-P2 = 92.1(1), Ge1-O1-P3 = 141.5(3).

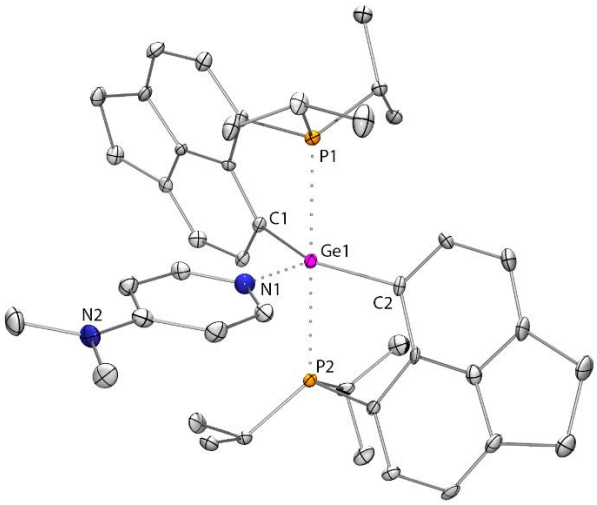


Fig. S98 Molecular structure **3^{iPr}DMAP** (H atoms, solvent molecule and triflate anion have been removed for clarity; thermal ellipsoid 30%). Selected bond lengths [Å] and angles [°]: Ge1-N1 = 1.964(6), Ge1-C1 = 1.951(7), Ge1-C2 = 1.954(7), Ge1-P1 = 2.610(3), Ge1-P2 = 2.596(3), and C1-Ge1-C2 = 147.9(3), N1-Ge1-C1 = 104.6(3), N1-Ge1-C2 = 107.5(3), P1-Ge1-P2 = 179.6(1).

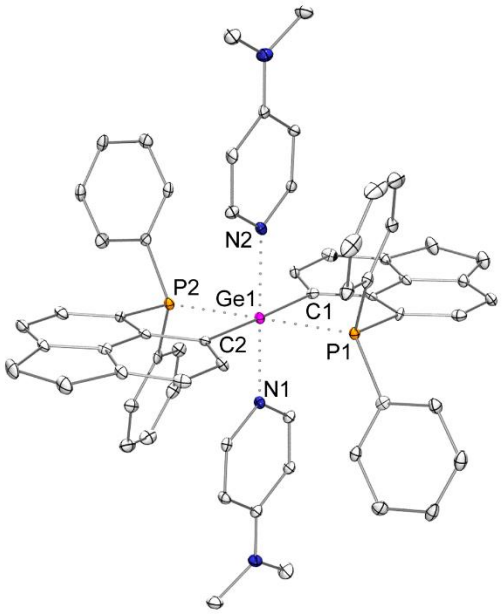


Fig. S99 Molecular structure of **3^{Ph}(DMAP)$_2$** (H atoms, solvent molecule and triflate anion have been removed for clarity; thermal ellipsoid 30%). Selected bond lengths [Å] and angles [°]: Ge1-C1 = 1.975(5), Ge1-C2 1.980(5), Ge1-N1 = 2.157(4), Ge1-N2 = 2.234(4), Ge1-P2 = 2.597(2), Ge1-P1 = 2.624(1); C1-Ge1-C2 = 177.8(2), P2-Ge1-P1 = 179.5(1), N1-Ge1-N2 = 179.0(2), C1-Ge1-N1 = 91.7(2), C1-Ge1-N2 = 88.1(2), C1-Ge1-P2 = 97.1(2), C1-Ge1-P1 = 83.5(2), N1-Ge1-P1 = 93.7(1), N2-Ge1-P1 = 85.3(1), P1-Ge1-C2 = 95.8(2).

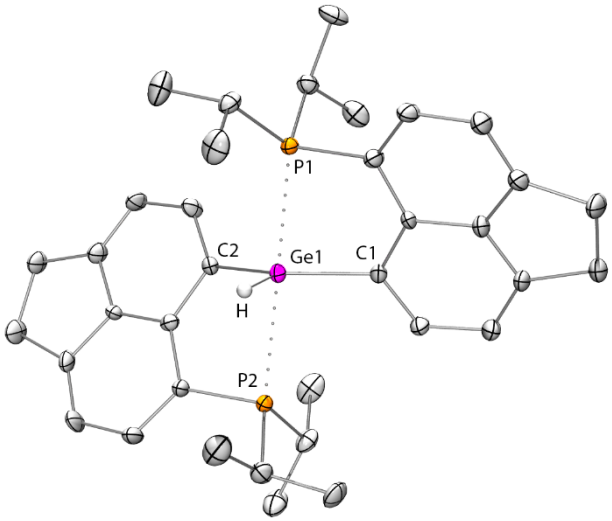


Fig. S100 Molecular structure of **3^{iPr}H** (H atoms except Ge-H, solvent molecules and triflate anions have been removed for clarity; thermal ellipsoid 30%). Selected bond lengths [Å] and angles [°]: a) Ge1-H1 = 1.54(3), Ge1-C1 = 1.965(6), Ge1-C2 = 1.953(6), Ge1-P1 = 2.551(2), Ge1-P2 = 2.654(2); C1-Ge1-C2 = 138.7(2), H1-Ge1-C1 = 110(4), H1-Ge1-C2 = 112(4), P1-Ge1-P2 = 176.9(1).

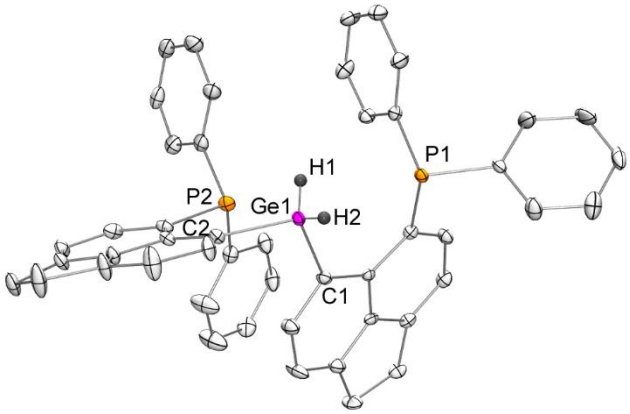


Fig. S101 Molecular structure of **3^{Ph}H$_2$** (H atoms except Ge-H, solvent molecules and triflate anions have been removed for clarity; thermal ellipsoid 30%). Selected bond lengths [Å] and angles [°]: Ge1-C1 = 1.979(4), Ge1-C2 = 1.977(4), Ge1-H1 = 1.56(3), Ge1-H2 = 1.77(3); C1-Ge1-C2 = 108.0(1), H1-Ge1-H2 = 108.5(15), C2-Ge1-H1 = 118.6(12), C1-Ge1-H1 = 106.7(12), C2-Ge1-H2 = 110.1(10), C1-Ge1-H2 = 104.1(10).

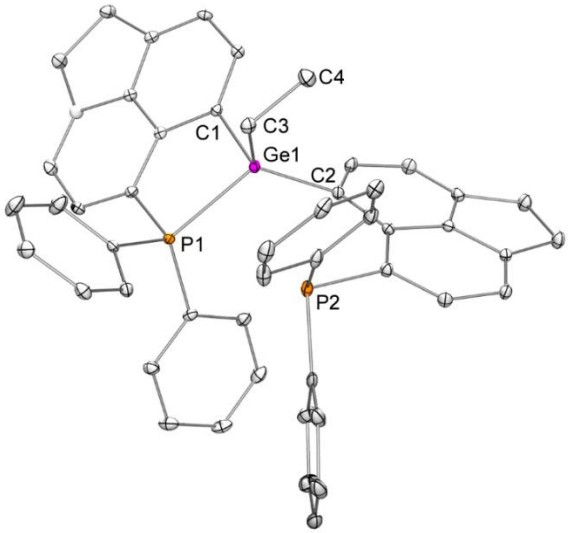


Fig. S102 Molecular structure of **3^{Ph}Et** in the solid state (thermal ellipsoids at 30%, H atoms, triflate counter anion and solvent molecule are omitted for clarity). Selected bond lengths [Å]: Ge1-C2 = 1.950(3), Ge1-C3 = 1.952(3), Ge1-C1 = 1.970(3), Ge1-P1 = 2.370(1), Ge1···P2 = 3.326(1); selected bond angles [°]: C2-Ge1-C3 = 118.4(1), C2-Ge1-C1 = 108.5(1), C3-Ge1-C1 = 109.3(1), C2-Ge1-P1 = 116.8(1), C3-Ge1-P1 = 110.8(1), C1-Ge1-P1 = 88.6(1).

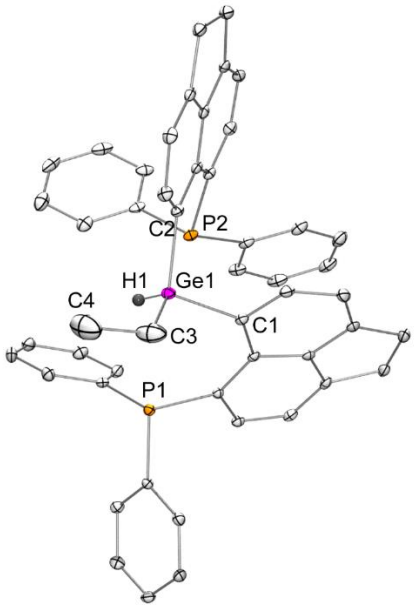


Fig. S103 Molecular structure of **3^{Ph}H(Et)** in the solid state (thermal ellipsoids at 30%, H atoms except the Ge-H and solvent molecule are omitted for clarity). Selected bond lengths [Å]: Ge1-C3 = 1.963(4), Ge1-C1 = 1.962(2), Ge1-C2 = 1.988(2), Ge1-H1 = 1.61(3), Ge1···P1 = 3.364(1), Ge1···P2 = 3.251(1); selected bond angles [°]: C3-Ge1-C1 = 108.0(2), C3-Ge1-C2 = 107.5(1), C1-Ge1-C2 = 106.4(1), C3-Ge1-H1 = 98.7(1), C1-Ge1-H1 = 126.6(9), C2-Ge1-H1 = 108.2(9).

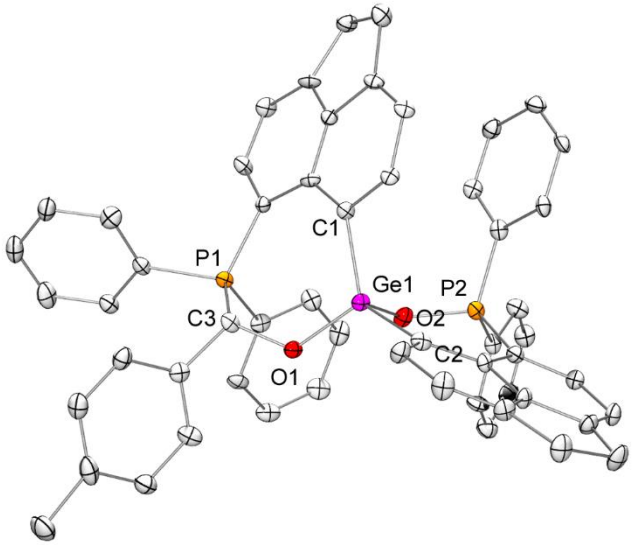


Fig. S104 Molecular structure of **3^{Ph}Oald** in the solid state (thermal ellipsoids at 30%, H atoms and triflate counter anions are omitted for clarity). Selected bond lengths [Å]: Ge1-C1 = 1.916(9), Ge1-C2 = 1.923(9), Ge1-O1 = 1.746(6), Ge1-O2 = 1.868(7), O1-C3 = 1.416(11), C3-P1 = 1.879(9), P2-O2 = 1.559(7); selected bond angles [°]: Ge1-O1-C3 = 121.2(6), O1-C3-P1 = 107.7(6), C1-Ge1-C2 = 122.1(4), C1-Ge1-O1 = 114.8(3), C2-Ge1-O1 = 113.7(3), O1-Ge1-O2 = 97.5(3), Ge1-O2-P2 = 122.0(4).

Note: The inadvertent presence of oxygen as phosphine oxide occurred probably during crystallization period from THF solution.

Table S1 X-ray refinement parameters

	1^{iPr}	**1^{Ph}**	**2^{iPr}**	**2^{Ph}**
CCDC Numbers	2223776	2256454	2223777	2256455
Empirical formula	$C_{36}H_{44}ClGeP_2$, (Cl_3Ge), (C_2H_3N)	$C_{48}H_{36}Cl_2GeP_2$, $2(C_4H_8O)$	$C_{36}H_{44}ClGeP_2$, (CF_3SO_3), (CH_2Cl_2)	$C_{48}H_{36}ClGeP_2$, (CF_3SO_3), (C_4H_8O)
Formula weight	866.68	962.40	880.69	1003.92
Temperature	100(2) K	150(2) K	150(2) K	150(2) K
Wavelength	1.54178 Å	1.54178 Å	0.71073 Å	0.71073 Å
Crystal System	monoclinic	Monoclinic	monoclinic	Monoclinic
Space Group	P 21/c	P 2_1/c	P 2/c	P 2_1/c
Unit cell dimensions	a = 8.4966(3) Å, b = 24.3150(8) Å, c = 19.5124(6) Å; α/° = 90°, β/° = 98.653(2)°, γ/° = 90°	a = 22.1656(19) Å, b = 10.1752(9) Å, c = 20.7492(17) Å; α/° = 90°, β/° = 102.393(3)°, γ/° = 90°	a = 17.954(4) Å, b = 9.494(2) Å, c = 26.010(5) Å; α/° = 90.00(3)°, β/° = 102.93(3)°, γ/° = 90.00(3)°	a = 15.128(4) Å, b = 10.410(3) Å, c = 29.642(8) Å; α/° = 90°, β/° = 102.314(8)°, γ/° = 90°
Volume (Å^3)	3985.3(2)	4570.7(7)	4321.4(16)	4561(2)
Z	4	4	4	4
Density(calculated) (Mg/m^3)	1.444	1.399	1.354	1.462
Absorption coefficient (mm^{-1})	5.291	2.985	1.063	0.906
F(000)	1776.0	2000	1816	2064.0
Crystal size (mm^3)	0.258 × 0.192 × 0.118	0.12 × 0.11 × 0.08	0.424 × 0.314 × 0.253	0.21 x 0.08 x 0.07
Theta range for data collection (°)	2.92 to 66.93	2.041 to 66.830	1.164 to 25.058	2.079 to 25.197
Index ranges	-10 ≤ h ≤ 10, -27 ≤ k ≤ 28, -23 ≤ l ≤ 23	-26 ≤ h ≤ 26, -12 ≤ k ≤ 12, -24 ≤ l ≤ 24	-20 ≤ h ≤ 20, -10 ≤ k ≤ 11, -30 ≤ l ≤ 30	-18 ≤ h ≤ 18, -10 ≤ k ≤ 12, -35 ≤ l ≤ 35
Reflections collected	52044	68036	45776	71394
Independent reflections	7065 [R_{int} = 0.0546]	8073 [R_{int} = 0.0514]	7545 [R_{int} = 0.0920]	8139 [R_{int} = 0.0497]
Completeness to theta	θ = 67.001° 99.5 %	θ = 66.830° 99.5 %	θ = 25.058° 98.4 %	θ = 25.197° 99.2 %
Absorption Correction	multi-scan	multi-scan	multi-scan	multi-scan
Max. and min. transmission	0.753 and 0.613	0.7528 and 0.3001	0.808 and 0.689	0.7452 and 0.5304
Refinement Method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	7065/89/474	8073/18/568	7545/18/470	8139/0/586
Goodness-of-fit on F^2	1.174	1.043	1.025	1.090
Final R indices [I>2sigma(I)]	R_1 = 0.0659, wR_2 = 0.1407	R_1 = 0.0379, wR_2 = 0.0978	R_1 = 0.0484, wR_2 = 0.1052	R_1 = 0.0492, wR_2 = 0.1183
R indices (all data)	R_1 = 0.0721, wR_2 = 0.1435	R_1 = 0.0413, wR_2 = 0.1007	R_1 = 0.0911, wR_2 = 0.1234	R_1 = 0.0522, wR_2 = 0.1202

Largest diff. peak and hole (e.Å^{-3})	1.85 and -0.71	0.631 and -0.632	0.861 and -0.980	2.360 and -0.819

	3^{iPr}	**3^{Ph}**	**3^{iPr}(DMAP)**	**3^{Ph}(DMAP)$_2$**	**3^{Ph}OPEt$_3$**
CCDC Numbers	2223780	2256456	2223784	2256457	2256458
Empirical formula	$C_{36}H_{44}GeP_2$, 2(CF_3SO_3), C_4H_8O	$C_{48}H_{36}GeP_2$, 2(CF_3O_3S), 2(CH_2Cl_2)	$C_{43}H_{54}GeN_2P_2$, 2(CF_3SO_3), 2(CH_2Cl_2)	$C_{62}H_{56}GeN_4P_2$,2(CF_3O_3S), 2(CH_2Cl_2)	$C_{54}H_{51}GeOP_3$, 2(CF_3O_3S), CCl_2, CH_2Cl_2
Formula weight	981.48	1215.29	1201.40	1459.63	1347.42
Temperature	100 (2) K	150(2) K	100 (2) K	150 (2) K	150 (2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal System	triclinic	Monoclinic	monoclinic	Triclinic	Monoclinic
Space Group	P -1	P $2_1/c$	P$2_1/c$	P -1	C 2/c
Unit cell dimensions	a = 11.7903(11)Å, b = 13.0614(11)Å, c = 15.7650(14)Å; α/° = 70.049(2)°, β/° = 85.111(3)°, γ/° = 75.622(3)°	a = 21.183(6) Å, b = 14.414(4) Å, c = 16.645(4) Å; α/° = 90°, β/° = 96.823(9)°, γ/° = 90°	a = 11.282(11) Å, b = 30.08(3) Å, c = 15.527(16) Å; α/° = 90°, β/° = 102.04(3)°, γ/° = 90°	a = 13.652(3) Å, b = 15.573(3) Å, c = 16.333(3) Å; α/° = 79.755(6)°, β/° = 79.751(6)°, γ/° = 71.778(6)°	a = 47.155(9) Å, b = 13.050(3) Å, c = 19.811(4) Å; α/° = 90°, β/° = 100.229(5)°, γ/° = 90°
Volume (Å^3)	2210.6(3)	5046(2)	5153(9)	3217.7(11)	11998(4)
Z	2	4	4	2	8
Density(calculated) (Mg/m^3)	1.475	1.600	1.549	1.507	1.492
Absorption coefficient (mm^{-1})	0.933	1.039	1.017	0.830	0.908
F(000)	1016.0	2464	2472.0	1496.0	5504.0
Crystal size (mm^3)	0.41 × 0.36 × 0.20	0.23 x 0.18 x 0.13	0.32 × 0.21 × 0.11	0.16 x 0.12 x 0.11	0.18 x 0.09 x 0.08
Theta range for data collection (°)	2.25 to 27.45	1.936 to 26.267	2.43 to 17.38	1.901 to 25.027	2.398 to 25.027
Index ranges	-14 ≤ h ≤ 13, -16 ≤ k ≤ 14, -19 ≤ l ≤ 19	-26<=h<=26, -17<=k<=17, -18<=l<=20	-12 ≤ h ≤ 13, -36 ≤ k ≤ 36, -18 ≤ l ≤ 18	-16<=h<=16, -18<=k<=18, -19<=l<=19	-56 ≤ h ≤ 56, -15 ≤ k ≤ 15, -21 ≤ l ≤ 23
Reflections collected	34618	110112	114081	66971	108030
Independent reflections	8674 [R_{int} = 0.0944]	10060 [R_{int} = 0.0661]	9588 [R_{int} = 0.1208]	11368 [R_{int} = 0.1564]	10600 [R_{int} = 0.2547]
Completeness to theta	θ = 25.998° 99.7 %	θ = 25.242° 99.9 %	θ = 25.5° 99.9 %	θ = 25.027° 99.9 %	θ = 25.027° 99.9 %
Absorption Correction	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
Max. and min. transmission	0.746 and 0.526	0.7453 and 0.6733	0.095 and 0.069	0.745 and 0.634	0.745 and 0.392
Refinement Method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	8674/24/549	10060/0/658	9588/12/611	11368 / 6 / 812	10600/31/728
Goodness-of-fit on F^2	1.030	1.029	1.029	1.053	1.083
Final R indices [I>2sigma(I)]	R_1 = 0.0763, wR_2 = 0.1602	R_1 = 0.0472, wR_2 = 0.1241	R_1 = 0.0933, wR_2 = 0.2238	R_1 = 0.0722, wR_2 = 0.1826	R_1 = 0.0992, wR_2 = 0.1888

R indices (all data)	R_1 = 0.1232, wR_2 = 0.1883	R_1 = 0.0597, wR_2 = 0.1322	R_1 = 0.1293, wR_2 = 0.2506	R_1 = 0.1290, wR_2 = 0.2102	R_1 = 0.1761, wR_2 = 0.2198
Largest diff. peak and hole (e.Å^{-3})	1.86 and -0.85	2.12 and -1.14	3.11 and -2.11	2.40 and -1.37	1.21 and -0.96

	3^{iPr}F	**3^{Ph}F**
CCDC Numbers	2223782	2256463
Empirical formula	$C_{36}H_{44}FGeP_2$, CF_3SO_3, C_4H_8O	$C_{48}H_{36}FGeP_2$, CF_3O_3S
Formula weight	851.41	915.37
Temperature	100(2) K	150(2) K
Wavelength	1.54178 Å	0.71073 Å
Crystal System	monoclinic	Monoclinic
Space Group	P2/c	$P2_1/c$
Unit cell dimensions	a= 17.3764(16) Å b = 9.2749(9) Å c = 25.485(2) Å; α/° = 90° β/° = 103.688(3) ° γ/° = 90°	a = 10.046(3) Å, b = 18.494(6) Å, c = 23.535(8) Å; α/° = 90°, β/° = 97.484(12)°, γ/° = 90°
Volume (Å^3)	3990.6(6)	4335(3)
Z	4	4
Density(calculated) (Mg/m^3)	1.417	1.402
Absorption coefficient (mm^{-1})	2.791	0.888
F(000)	1776.0	1872.0
Crystal size (mm^3)	0.428× 0.314 × 0.254	0.11 x 0.09 x 0.08
Theta range for data collection (°)	3.90 to 65.26	1.75 to 25.26
Index ranges	-20 ≤ h ≤ 20, -10 ≤ k ≤ 10, -29 ≤ l ≤ 29	-11<=h<=11, -21<=k<=22, -28<=l<=27
Reflections collected	64684	40939
Independent reflections	6821 [R_{int} = 0.0939]	7709 [R_{int} = 0. 0.0933]
Completeness to theta	θ = 65.545° 99.2 %	θ = 25.242° 98.4 %
Absorption Correction	multi-scan	multi-scan
Max. and min. transmission	0.753 and 0.613	0.745 and 0.326
Refinement Method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	6821/3/488	7709 / 2 / 541
Goodness-of-fit on F^2	1.050	1.050
Final R indices [I>2sigma(I)]	R_1 = 0.0307, wR_2 = 0.0767	R_1 = 0.0441, wR_2 = 0.0998
R indices (all data)	R_1 = 0.0437, wR_2 = 0.0789	R_1 = 0.0776, wR_2 = 0.1135

Largest diff. peak and hole (e.Å^{-3})	0.62 and -0.56	0.61 and -0.39

	$3^{iPr}H$	**$3^{Ph}H_2$**	**$3^{Ph}Et$**	**$3^{Ph}HEt$**	**$3^{Ph}Oald$**
CCDC Numbers	2223781	2256466	2256467	2256468	2256567
Empirical formula	$C_{36}H_{45}GeP_2$, CF_3SO_3, $4(C_4H_8O)$	$C4_8H_{38}GeP_2$, $0.5(C_{14})$	$C_{50}H_{41}GeP_2$, C F_3O_3S, C_4H_8O	$C_{50}H4_2GeP_2$	C56 H44 Ge O2 P2, 2(C F3 O3 S)
Formula weight	1049.73	833.38	997.53	777.36	1183.29
Temperature	100(2) K	150(2) K	150 (2) K	150(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal System	monoclinic	Triclinic	Monoclinic	Monoclinic	triclinic
Space Group	Pn	P-1	P 21/n	P 21/n	P -1
Unit cell dimensions	a = 13.481(3) Å, b = 9.414(2) Å, c = 21.087(4) Å; α/° = 90°, β/° = 96.178(7)°, γ/° = 90°	a = 11.025 (6) Å, b = 13.376(8) Å, c = 14.809(8) Å; α/° = 99.098(16) ° β/° = 91.984(15)° γ/° = 102.355(19)°	a = 12.192(2) Å, b = 21.924(4) Å, c = 18.159(4) Å; α/° = 90°, β/° = 103.59(3)°, γ/° = 90°	a = 12.221(3) Å b = 18.490(4) Å c = 16.895(4) Å α/° = 90°, β/° = 93.001(8)°, γ/° = 90°	a = 9.896(5) Å b = 15.315(8) Å c = 17.580(8) Å α/° = 105.270(13) °, β/° = 93.870(14) °, γ/° = 100.521(14) °
Volume (Å^3)	2660.7(10)	2101(2)	4718.0(17)	3812.3(15)	2508(2)
Z	2	2	4	4	2
Density(calculated) (Mg/m^3)	1.310	1.317	1.404	1.354	1.567
Absorption coefficient (mm^{-1})	0.735	0.843	0.821	0.923	0.840
F(000)	1112.0	860	2064	1616	1210
Crystal size (mm^3)	0.2 × 0.16 × 0.15	0.14 x 0.12 x 0.09	0.19 x 0.08 x 0.06	0.14 x 0.11 x 0.08	0.13 x 0.11 x 0.08
Theta range for data collection (°)	2.37 to 28.34	2.19 to 24.45	1.953 to 25.073	1.999 to 25.082	1.409 to 25.243
Index ranges	-18 ≤ h ≤ 17, -12 ≤ k ≤ 12, -28 ≤ l ≤ 27	-13<=h<=13, -15<=k<=15, -16<=l<=17	-13<=h<=14, -26<=k<=26, -21<=l<=21	-14<=h<=14, -21<=k<=22, -20<=l<=19	-11<=h<=11, -18<=k<=18, -20<=l<=20
Reflections collected	74267	33447	84884	72290	28610
Independent reflections	12086 [R_{int} = 0.1814]	7377 [R_{int} = 0.0865]	8338 [R_{int} = 0.0637]	6754 [R_{int} = 0.0547]	8911 [R_{int} = 0.1357]
Completeness to theta	θ = 28.577° 99.6 %	θ = 25. 028° 99.5 %	θ = 25.073° 99.6 %	θ = 25.082° 99.7 %	θ = 25.242° 98.1 %
Absorption Correction	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
Max. and min. transmission	0.746 and 0.659	0.745 and 0.685	0.7452 and 0.6772	0.7452 and 0.6326	0.7452 and 0.4970
Refinement Method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	12086/137/574	7377 / 0 / 594	8338 / 0 / 596	6754 / 8 / 483	8911/654/768
Goodness-of-fit on F^2	1.052	1.018	1.054	1.007	1.041

Final R indices [I>2sigma(I)]	R_1 = 0.0561, wR_2 = 0.1493	R_1 = 0.0525, wR_2 = 0.1040	R1 = 0.0383, wR2 = 0.0938	R1 = 0.0356, wR2 = 0.0901	R1 = 0.1035, wR2 = 0.2554
R indices (all data)	R_1 = 0.1244, wR_2 = 0.1805	R_1 = 0.0907, wR_2 = 0.1168	R1 = 0.0480, wR2 = 0.1006	R1 = 0.0440, wR2 = 0.0951	R1 = 0.1962, wR2 = 0.3296
Largest diff. peak and hole (e.Å^{-3})	1.01 and -0.65	0.452 and -0.352	0.88 and -0.46	0.599 and -0.612	2.090 and -1.189

Computational Study

The gas-phase optimizations of the initial geometries originated from corresponding X-ray files were performed using ORCA 5.0.0 package program at the TPSS-D3(BJ)/def2-TZVPP level of theory.[S4] The RIJCOSX (RI approximation for the Coulomb integrals) was applied in all cases with combinations of corresponding auxiliary basis set.[S5] We have corrected that the optimized geometries are minima on their potential energy surface (PES) with the help of frequency calculations. Then the NBO (natural bond orbital) output files were prepared from the optimized geometries using Gaussian 16 Rev.B.01 at the B3LYP-D3(BJ)/def2-TZVPP level of theory.[S6] From NBO analyses, we have produced selected NBO partial charges, donor-acceptor interactions, and Wiberg bond indexes.[S7,S8] Additionally, we also examine the maps of the molecular ESP to find out the positively and negatively charged sides of the studied compounds. For a meaningful comparison, we chose the same range of the ESP bars in all figures with 0.05 (red) – 0.45 (blue). In order to get deeper insights on bonding situations of the corresponding structures, we have also employed atoms in molecule (AIM) analysis using Multiwfn 3.8 package program.[S9] To gain more insights on the H migration mechanisms from P to Ge atoms for **3^{iPr}** and **3^{Ph}** cases, we have performed calculations to find out related transition states at the B3LYP-D3(BJ)/def2-SVP//B3LYPD3(BJ)/6-31G(d,p) level of theory with Gaussian 16 Rev.B.01 package program. The optimized structures were identified by characterization of their Hessian matrix as a minimum or transition state (with an imaginary frequency). All the figures were prepared by Gaussview 5.0 package program.[S10]

The fluoride ion affinities (FIA) and hydride ion affinities (HIA) of **3o^{iPr}**, **3o^{Ph}**, **SbF_5**, and **$B(PhF_5)_3$** with respect to the scheme proposed by Krossing (TMS system).[S11] Additionally, the solvation correction was performed with CPCM(CH_2Cl_2) to get solvated models of FIA and HIA as implemented in ORCA.

$$LA + Me_3SiF \xrightarrow[\text{level of choice}]{\Delta H} [LA\text{-}F]^- + Me_3Si^+ \quad \text{eq. 1}$$

$$Me_3SiF \xrightarrow[\text{CCSD(T)/CBS (952.5 kj mol}^{-1}\text{)}]{\Delta H} Me_3Si^+ + F^- \quad \text{eq. 2}$$

$$LA + F^- \longrightarrow [LA\text{-}F]^- \quad = \text{eq. 1- eq. 2}$$

Deformation and preparation energies were calculated for the first FIA of **3o^{iPr}**, and **3o^{Ph}**. The interaction energies were derived from the equation below depending on the single point energies.[S12]

$E_{int} = E_{[3o^{iPr}\text{-}F]^+} - (E_{F^-(frag1)} + E_{3o^{iPr+2}(frag2)})$ which is 901.0 kj mol^{-1} for **3o^{iPr}**
$E_{int} = E_{[3o^{Ph}\text{-}F]^+} - (E_{F^-(frag1)} + E_{3o^{Ph+2}(frag2)})$ which is 884.9 kj mol^{-1} for **3o^{Ph}**
$E_{def(frag1)} = E_{SP(frag1)} - E_{opt(frag1)}$ which is 0.0 kj mol^{-1} for **3o^{iPr}** and **3o^{Ph}**
$E_{def(frag2)} = E_{SP(frag2)} - E_{opt(frag2)}$ which is 126.2 kj mol^{-1} for **3o^{iPr}**
$E_{def(frag2)} = E_{SP(frag2)} - E_{opt(frag2)}$ which is 148.1 kj mol^{-1} for **3o^{Ph}**

Frag1 = F^-
Frag2 = **3o^{iPr}** or **3o^{Ph}**

Table S2 Selected theoretical, and experimental (in parentheses) Bond lengths along with corresponding WBI values in square brackets for **2o^{iPr}**, **2o^{Ph}**, **3o^{iPr}**, and **3o^{Ph}**.

Bond	Ge-C1	Ge-C2	Ge-P1	Ge-P2	Ge-Cl
2o^{iPr}	1.975 (1.951) [0.750]	1.975 (1.960) [0.750]	2.618 (2.653) [0.487]	2.610 (2.544) [0.495]	2.206 (2.194) [0.744]
2o^{Ph}	1.944 (1.922) [0.750]	1.944 (1.926) [0.803]	2.383 (2.357) [0.712]	2.994 (3.012) [0.183]	2.217 (2.215) [0.738]
3o^{iPr}	1.937 (1.925) [0.830]	1.935 (1.924) [0.832]	2.387 (2.362) [0.804]	2.380 (2.350) [0.801]	-
3o^{Ph}	1.931 (2.349) [0.835]	1.930 (2.340) [0.835]	2.365 (1.920) [0.770]	2.366 (1.926) [0.770]	-

Table S3 Selected donor-acceptor interactions in **2o^{iPr}** and **2o^{Ph}.**

2o^{iPr}	$LP_{Cl} \rightarrow Lp^*_{Ge}$ 303.56 kcal mol^{-1}
	$LP_{P1} \rightarrow Lp^*_{Ge}$ 127.68 kcal mol^{-1}
	$LP_{P2} \rightarrow Lp^*_{Ge}$ 123.41 kcal mol^{-1}
2o^{Ph}	$LP_{Cl} \rightarrow Lp^*_{Ge}$ 267.97 kcal mol^{-1}
	$LP_{P2} \rightarrow Lp^*_{Ge}$ 31.92 kcal mol^{-1}

Table S4 Selected bonding orbitals and hybridizations for **2o^{iPr}**, **2o^{Ph}**, **3o^{iPr}**, and **3o^{Ph}**.

	BD_{Ge-P1}	**BD_{Ge-P2}**	**BD_{Ge-C1}**	**BD_{Ge-C2}**	**LP^*_{Ge}**	**LP_{P1}**	**LP_{P2}**
2o^{iPr}	- No BD	- No BD	Ge $sp^{1.18}$ C1 $sp^{2.64}$	Ge $sp^{1.18}$ C2 $sp^{2.64}$	Ge sp^{1}(LP*1) Ge $sp^{11.36}$(LP*2)	P $sp^{1.13}$	P $sp^{1.13}$
2o^{Ph}	Ge $sp^{3.30}$ P1 $sp^{3.42}$	- No BD	Ge $sp^{2.11}$ C1 $sp^{2.48}$	Ge $sp^{1.45}$ C2 $sp^{2.69}$	Ge $sp^{25.05}$(LP*)	No LP	P $sp^{1.25}$
	BD_{Ge-P1}	**BD_{Ge-P2}**	**BD_{Ge-C1}**	**BD_{Ge-C2}**	**LP^*_{Ge}**	**LP_{P1}**	**LP_{P2}**
3o^{iPr}	Ge $sp^{4.00}$ P1 $sp^{3.66}$	Ge $sp^{4.11}$ P1 $sp^{3.61}$	Ge $sp^{2.34}$ C1 $sp^{2.60}$	Ge $sp^{2.26}$ C2 $sp^{2.61}$	- No LP*	- No LP	- No LP
3o^{Ph}	Ge $sp^{4.25}$ P1 $sp^{3.80}$	Ge $sp^{4.26}$ P1 $sp^{3.80}$	Ge $sp^{2.21}$ C1 $sp^{2.62}$	Ge $sp^{2.23}$ C2 $sp^{2.61}$	- No LP*	- No LP	- No LP

Table S5 Selected NBO partial charges for **2o^{iPr}**, **2o^{Ph}**, **3o^{iPr}**, and **3o^{Ph}**.

	Ge	P1	P2	Cl
2o^{iPr}	1.290	1.033	1.030	-0.410
2o^{Ph}	1.343	1.165	0.942	-0.416
3o^{iPr}	1.136	1.161	1.145	-
3o^{Ph}	1.157	1.174	1.174	-

Table S6 Selected AIM parameters for the corresponding BCPs in **2o^{iPr}**, **2o^{Ph}**, **3o^{iPr}**, and **3o^{Ph}**.

	2o^{iPr}			**2o^{Ph}**		**3o^{iPr}**		**3o^{Ph}**	
	Ge-P1	**Ge-P2**	**Ge-Cl**	**Ge-P1**	**Ge-P2**	**Ge-P1**	**Ge-P2**	**Ge-P1**	**Ge-P2**
ρ**(r)**	0.059	0.058	0.095	0.089	0.026	0.089	0.090	0.092	0.092
$\nabla^2\rho$**(r)**	-0.006	-0.005	0.128	-0.044	0.031	-0.052	-0.052	-0.052	-0.052
H_b	-0.021	-0.020	-0.040	-0.041	-0.003	-0.041	-0.042	-0.044	-0.044
G(r)	0.019	0.019	0.072	0.030	0.011	0.028	0.029	0.031	0.031
K(r)	0.021	0.020	0.040	0.041	0.003	0.041	0.042	0.044	0.044
V(r)	-0.040	-0.040	-0.112	-0.072	-0.014	-0070	-0.072	-0.075	-0.075
Ɛ(r)	0.031	0.033	0.009	0.037	0.026	0.013	0.010	0.011	0.011

Negative Laplacian values at the BCPs are associated with shared interactions, indicating covalent bonds, and positive Laplacian values are reflecting closed shell interactions such as ionic or dative bonds. In the case of **2o^{Ph}**, the higher positive $\nabla^2\rho$**(r)** value on Ge-P2 show dative bonding character. In addition to that, the total electron density at the corresponding BCPs in 3o is determined to be higher compared to that for 2o.

Table S7 FIA and HIA calculations at the Ge site for **2o^{iPr}**, **2o^{Ph}**, **3o^{iPr}**, and **3o^{Ph}, SbF_5**, and **$B(PhF_5)_3$** at the TPSS-D3(BJ)/def2-TZVPP level of theory.

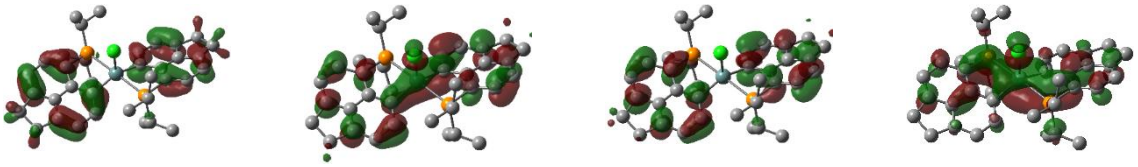
	electr. energy sp LA [kJ mol-1]	total thermal correction LA [kJ mol-1]	electr. energy sp TMSF [kJ mol-1]	total thermal correction TMSF [kJ mol-1]	→	electr. energy sp LAF [kJ mol-1]	total thermal correction LAF [kJ mol-1]	electr. energy sp TMS [kJ mol-1]	total thermal correction TMS [kJ mol-1]	deltaH	FIA(gas)
FIA											
3o^{iPr}_FIA	-10916518,548726	108,5	-1336970,229967	22,2	→	-11179631,270812	113,1	-1073775,135490	14,4	79,2	873,3
3o^{Ph}_FIA	-12105192,398375	112,8	-1336970,229967	22,2	→	-12368289,040454	115,8	-1073775,135490	14,4	93,7	858,8
SbF_5	**-1942108,495774**	**19,5**	**-1336970,229967**	**22,2**	→	**-2204843,000589**	**22,3**	**-1073775,135490**	**14,4**	**455,7**	**496,8**
HIA											
3o^{iPr}_HIA	-10916518,548726	108,5	-1076072,823952	19,9	→	-10918802,900000	110,4	-1073775,135490	14,4	9,8	949,2
3o^{Ph}_HIA	-12105192,398375	112,8	-1076072,823952	19,9	→	-12107453,913536	113,0	-1073775,135490	14,4	30,8	928,2
3o^{Ph}_HIA2	-12107453,913536	113,0	-1076072,823952	19,9		-12109416,247961	115,7	-1073775,135490	14,4	332,5	626,5
$B(PhF_5)_3$	**-5800599,954353**	**77,1**	**-1076072,823952**	**19,9**	→	**-5802448,926715**	**76,1**	**-1073775,135490**	**14,4**	**442,1**	**516,9**

Table S8 Solvated models of FIA and HIA at the Ge site for **2o^{iPr}**, **2o^{Ph}**, **3o^{iPr}**, and **3o^{Ph}, SbF$_5$**, and **B(PhF$_5$)$_3$** at the TPSS-D3(BJ)/def2-TZVPP level of theory.

Gas	LA	F$^-$	→	LAF	deltaH
3o^{iPr}_FIA	-10916518,548726	-262213,286341	→	-11179631,270812	-899,4
3o^{Ph}_FIA	-12105192,398375	-262213,286341	→	-12368289,040454	-883,4
SbF$_5$	**-1942108,495774**	**-262213,286341**	→	**-2204843,000589**	**-521,2**
Gas	**LA**	**H$^-$**	→	**LAH**	**deltaH**
3o^{iPr}_HIA	-10916518,548726	-1322,132272	→	-10918802,900000	-962,2
3o^{Ph}_HIA	-12105192,398375	-1322,132272	→	-12107453,913536	-939,4
3o^{Ph}_HIA2	-12107453,913536	-1322,132272	→	-12109416,247961	-640,2
B(PhF$_5$)$_3$	**-5800599,954353**	**-1322,132272**	→	**-5802448,926715**	**-526,8**

Solv	LA	F$^-$	→	LAF	deltaH	FIAsolv
3o^{iPr}_FIA	-10916992,736221	-262558,003831	→	-11179770,736910	-220,0	193,9
3o^{Ph}_FIA	-12105632,267642	-262558,003831	→	-12368404,924309	-214,7	190,1
SbF$_5$	**-1942122,235673**	**-262558,003831**	→	**-2205035,132147**	**-354,9**	**330,5**
Solv	**LA**	**H$^-$**	→	**LAH**	**deltaH**	**HIAsolv**
3o^{iPr}_HIA	-10916992,736221	-1679,274785	→	-10918938,893443	-266,9	253,9
3o^{Ph}_HIA	-12105632,267642	-1679,274785	→	-12107592,207506	-280,7	269,4
3o^{Ph}_HIA2	-12107592,207506	-1679,274785	→	-12109464,022351	-192,5	178,8
B(PhF$_5$)$_3$	**-5800617,955360**	**-1679,274785**	→	**-5802577,253341**	**-280,0**	**270,1**

Fig. S105 Selected FMOs for **2**^{iPr} at the B3LYPD3(BJ)/def2-TZVPP//TPSS-B3(DJ)/def2-TZVPP level of theory (Isovalue: 0.03). H atoms are omitted for clarity



HOMO **LUMO** **LUMO+1** **LUMO+2**

Fig. S106 Electrostatic Potential map for **2**^{iPr} at the B3LYPD3(BJ)/def2-TZVPP//TPSS-B3(DJ)/def2-TZVPP level of theory. H atoms are omitted for clarity

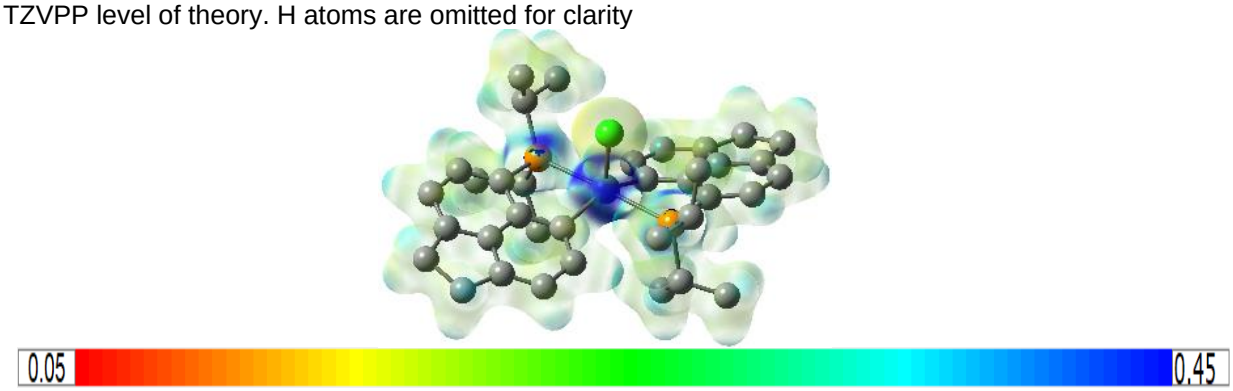
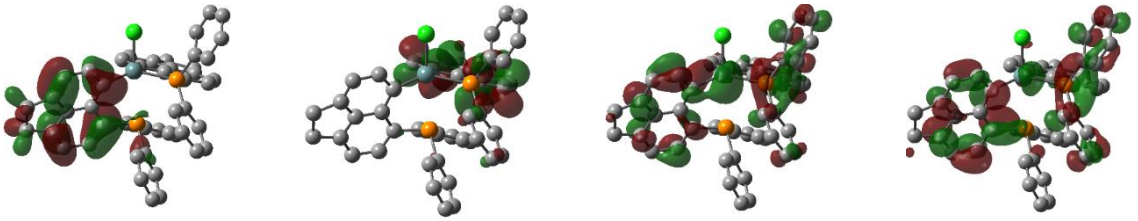


Fig. S107 Selected FMOs for **2**^{Ph} at the B3LYPD3(BJ)/def2-TZVPP//TPSS-B3(DJ)/def2-TZVPP level of theory (Isovalue: 0.03). H atoms are omitted for clarity



HOMO **LUMO** **LUMO+1** **LUMO+2**

Fig. S108 Electrostatic Potential map for **2**^{Ph} at the B3LYPD3(BJ)/def2-TZVPP//TPSS-B3(DJ)/def2-TZVPP level of theory. H atoms are omitted for clarity

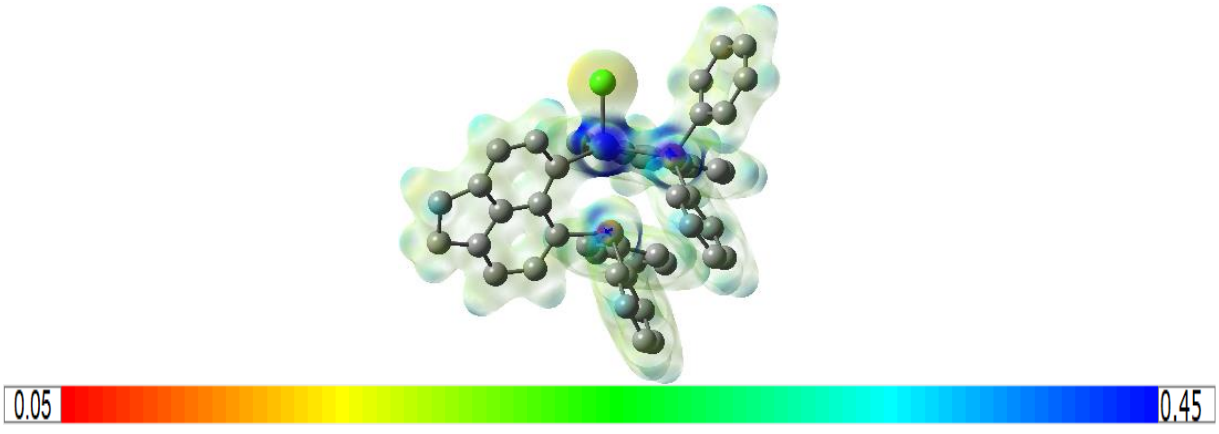
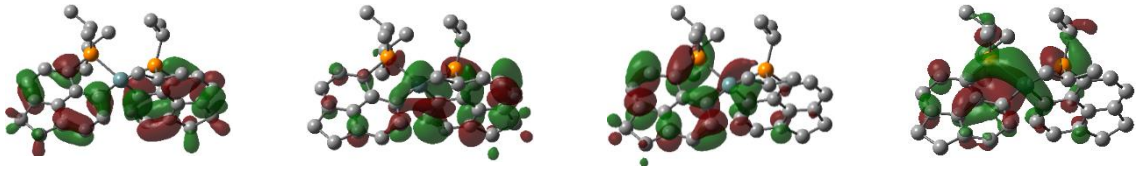
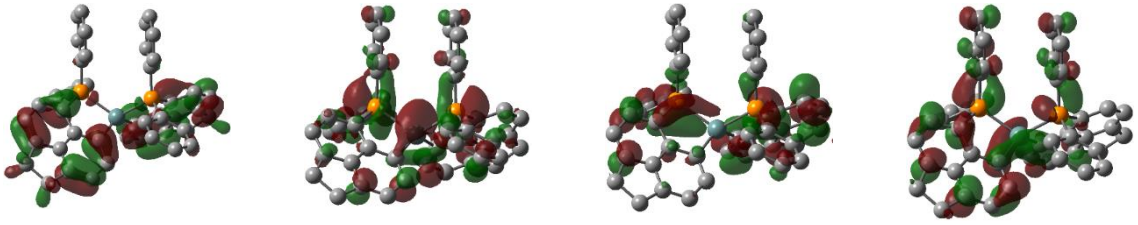


Fig. S109 Selected FMOs for **3^{iPr}** at the B3LYPD3(BJ)/def2-TZVPP//TPSS-B3(DJ)/def2-TZVPP level of theory (Isovalue: 0.03). H atoms are omitted for clarity

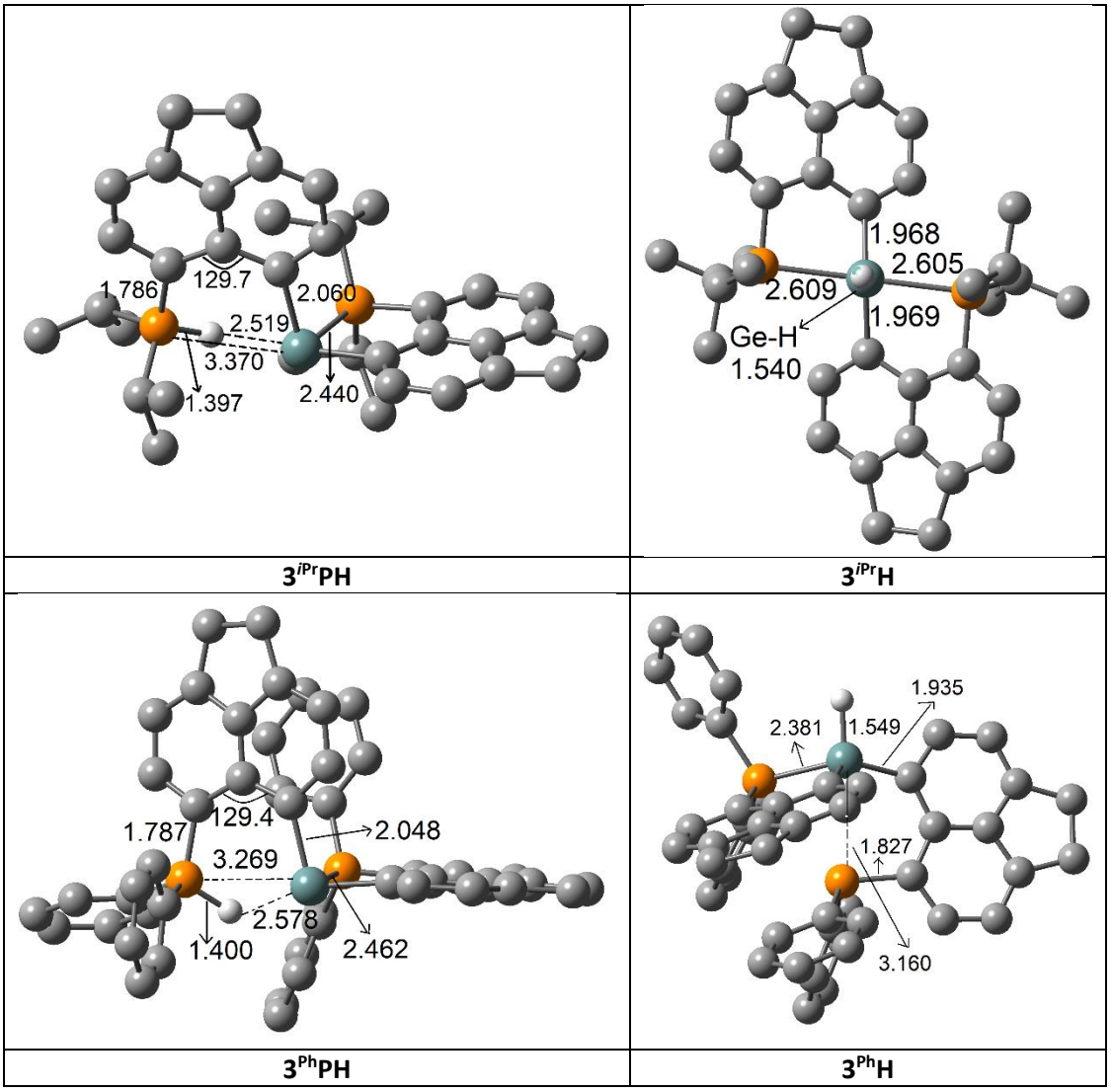


HOMO **LUMO** **LUMO+1** **LUMO+2**

Fig. S110 Selected FMOs for **3^{Ph}** at the B3LYPD3(BJ)/def2-TZVPP//TPSS-B3(DJ)/def2-TZVPP level of theory (Isovalue: 0.03). H atoms are omitted for clarity



HOMO **LUMO** **LUMO+1** **LUMO+2**



$3^{iPr}PH$	$3^{iPr}H$
$3^{Ph}PH$	$3^{Ph}H$

Fig. S111 Optimized geometry of $3^{iPr}PH$, $3^{Ph}PH$, $3^{iPr}H$, and $3^{Ph}H$ at the B3LYP-D3(BJ)/6-31G(d,p) level of theory.

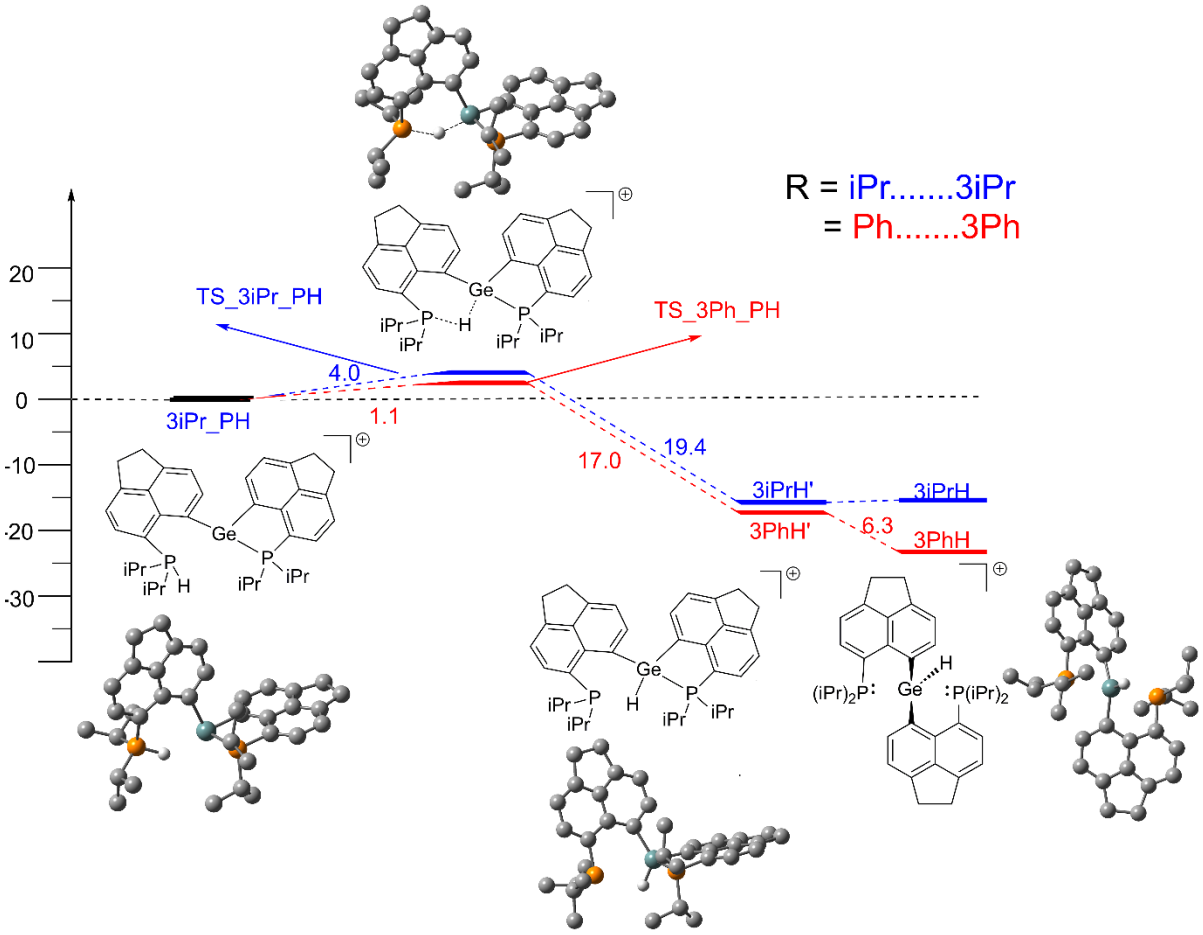


Fig. S112 Proposed reaction mechanism for the H migration from P to Ge atom for **3**^{iPr} and **3**^{Ph} systems at the B3LYP-D3(BJ)/def2-SVP//B3LYPD3(BJ)/6-31G(d,p) level of theory.

Table S9 Cartesian coordinates of **2o**^{iPr} at the TPSS-D3(BJ)/def2-TZVPP level of theory.

Ge	0.00368451	-0.00332225	0.19666867
Cl	-0.00393750	-0.00213356	2.40288655
P	-1.57738842	2.08234474	0.13261779
P	1.58229281	-2.08107802	0.13435835
C	4.06243499	1.06073011	-0.30009140
C	2.89161499	0.28105332	-0.16282732
C	4.06103043	2.41516376	-0.69253913
C	1.65887952	2.27423873	-0.75002699
H	0.71950383	2.79446557	-0.88735715
C	5.36162124	0.57169537	-0.05330445
C	2.84822724	3.02321364	-0.93992735
H	2.77790516	4.06249718	-1.24649409
C	3.08023108	-1.08720139	0.19371786
C	1.64272994	0.93914647	-0.37497876
C	5.51443689	-0.74292574	0.34389327
H	6.49068514	-1.16582144	0.55941787
C	-1.71046257	2.92592655	-1.53455438
H	-0.88816333	3.65163998	-1.55651423
C	6.35737661	1.68829438	-0.29132642
H	7.09175043	1.40977677	-1.05354483
H	6.92040258	1.91162600	0.62045189

C	4.36471320	-1.56101067	0.44789698
H	4.49940169	-2.60138444	0.72862021
C	5.49069805	2.91184676	-0.74305480
H	5.63512433	3.77430974	-0.08508744
H	5.75609155	3.23934409	-1.75338622
C	-1.63876311	-0.93922199	-0.37607220
C	-1.48462544	1.88231420	-2.63940858
H	-2.26532319	1.11652819	-2.61119384
H	-0.51333998	1.38703854	-2.54038228
H	-1.51893819	2.36612216	-3.62039655
C	-3.02619219	3.68388580	-1.74555705
H	-2.99256465	4.19354312	-2.71410163
H	-3.20044946	4.44333469	-0.97866122
H	-3.87659764	2.99740872	-1.75637769
C	-2.88670800	-0.28124659	-0.15869873
C	-1.65646136	-2.27267389	-0.75709211
H	-0.71780201	-2.79186016	-0.90214301
C	-3.07396383	1.08624299	0.20142627
C	1.70419367	-2.94759286	-1.52099705
H	0.89823057	-3.69194194	-1.51034307
C	1.70740739	-3.42253676	1.40873196
H	2.52349771	-4.06798011	1.05865890
C	1.43728891	-1.93200294	-2.64229968
H	2.19686538	-1.14451744	-2.63911960
H	0.45349022	-1.46315950	-2.54237238
H	1.47510189	-2.43338529	-3.61434749
C	-1.71542900	3.43400852	1.39433739
H	-2.55513781	4.05287651	1.05245081
C	-0.43770904	4.28812872	1.39580327
H	-0.55278448	5.11067820	2.10816575
H	-0.22616055	4.72582868	0.41551039
H	0.42585928	3.69085447	1.70224801
C	2.06738157	-2.88535666	2.80071001
H	1.25327191	-2.28605372	3.21092284
H	2.96813757	-2.26780194	2.78069329
H	2.24523642	-3.73241005	3.47090804
C	3.03382493	-3.67888304	-1.73895525
H	2.99113563	-4.22444234	-2.68734291
H	3.24896049	-4.40496131	-0.95001151
H	3.86376855	-2.97001661	-1.79471750
C	-4.05797736	-1.06027868	-0.29543347
C	-2.84656213	-3.02055098	-0.94691399
H	-2.77751879	-4.05837692	-1.25889785
C	-4.35780415	1.55918094	0.46037634
H	-4.49204039	2.59898012	0.74303351
C	-2.03501960	2.90109949	2.79781488
H	-1.19260020	2.33822824	3.20246665
H	-2.91245332	2.25035138	2.80009094
H	-2.23367138	3.74965482	3.46013685
C	0.40558797	-4.23950602	1.44054843
H	0.51177128	-5.06262981	2.15365596
H	0.16077899	-4.67452840	0.46698849

H	-0.43318174	-3.61564895	1.76203726
C	-4.05819034	-2.41332365	-0.69288983
C	-5.35652870	-0.57211139	-0.04347004
C	-5.48809476	-2.90869965	-0.74379801
H	-5.63207585	-3.77844882	-0.09540546
H	-5.75641049	-3.22437906	-1.75733665
C	-5.50804776	0.74126342	0.35812322
H	-6.48359877	1.16388940	0.57755104
C	-6.35271186	-1.68878951	-0.27815769
H	-7.09648594	-1.40911435	-1.03071657
H	-6.90476989	-1.91765715	0.63910061

Table S10 Cartesian coordinates of **3o^{iPr}** at the TPSS-D3(BJ)/def2-TZVPP level of theory.

Ge	-0.01779106	-0.03589719	-0.04710725
P	1.49265676	0.71126685	1.63382353
P	-1.60867867	1.47639540	-0.98534239
C	-2.71724255	-0.83295838	-0.00550319
C	1.47007359	-0.67899600	-1.10920209
C	-3.66673050	-2.98263876	0.79393025
C	2.69120033	-0.68780664	-0.37652169
C	1.43076521	-1.25861809	-2.37461369
H	0.49541237	-1.28731348	-2.92657827
C	-3.01679705	0.41906404	-0.62394541
C	-2.39769017	-3.43097919	1.11748643
H	-2.23000765	-4.42040666	1.53071218
C	5.06626925	-1.41933064	-0.37184937
C	-1.42653169	-1.29594003	0.37157572
C	-3.80508251	-1.69554653	0.23488375
C	2.89057862	-0.17325983	0.94256203
C	-4.34387421	0.74421883	-0.91222532
H	-4.57912169	1.70252583	-1.36538332
C	3.80520272	-1.29338509	-0.99026402
C	-1.28803550	-2.57660818	0.90075233
H	-0.30039823	-2.95198762	1.15188286
C	3.76854893	-1.85949914	-2.28130814
C	-5.41514016	-0.13692620	-0.63563942
H	-6.42632698	0.16899109	-0.88258667
C	5.22964023	-0.93418773	0.91530639
H	6.17385011	-1.01917657	1.44285009
C	-5.14307181	-1.37002459	-0.06658519
C	2.57384311	-1.83795216	-2.98005976
H	2.48524983	-2.26926992	-3.97191419
C	-1.98870137	3.11387222	-0.21374274
H	-2.96339773	3.34441552	-0.66694041
C	0.06818885	2.12158209	-3.16758845
H	0.16589891	3.18060409	-2.92311660
H	0.21727226	2.01540407	-4.24582749
H	0.86451236	1.56569899	-2.66538311
C	1.14174969	0.21083547	3.36896908
H	2.03226076	0.54634935	3.91699293
C	5.14015368	-2.41155777	-2.60384193

C	-1.32671973	1.58167548	-2.81249208
H	-1.38598412	0.52636268	-3.11163233
C	1.85336888	2.52466045	1.53691353
H	0.89061955	3.02700808	1.68465363
C	-5.03829981	-3.61430174	0.89314804
C	2.82747705	2.95862553	2.64367332
H	2.42799829	2.78565141	3.64534572
H	3.01700204	4.03090812	2.53978517
H	3.78720001	2.44318807	2.54810830
C	4.13533321	-0.31032698	1.55919603
H	4.28031717	0.06574857	2.56762902
C	6.00293739	-2.12346589	-1.32853654
C	-2.45559947	2.35367999	-3.51509079
H	-2.47398516	3.40439980	-3.21328603
H	-3.43562671	1.91055102	-3.32680370
H	-2.27842765	2.32226946	-4.59392534
C	-6.02393991	-2.53193859	0.33550737
C	-2.18916414	2.92664785	1.29719231
H	-1.24225150	2.68520979	1.78855200
H	-2.90797305	2.13497836	1.52109122
H	-2.56071135	3.86043108	1.72738225
C	2.40371049	2.84815522	0.13939427
H	3.38138033	2.38246224	-0.00517328
H	2.52228789	3.93065224	0.03989312
H	1.74408919	2.50164566	-0.66253601
C	-1.00993513	4.24583891	-0.54339877
H	-1.34546879	5.15450452	-0.03566000
H	-0.96670388	4.46032211	-1.61204183
H	-0.00057249	4.02012347	-0.19384719
C	1.01699071	-1.31389555	3.49319926
H	0.09601355	-1.66405891	3.02144882
H	0.97332249	-1.57988804	4.55281944
H	1.86775154	-1.83369890	3.04579072
C	-0.09519605	0.94483860	3.90838787
H	0.00177799	2.03213080	3.84550954
H	-0.23310981	0.68514712	4.96149914
H	-0.99535925	0.63685293	3.36750573
H	-6.59886469	-2.90550484	-0.51735422
H	-5.27661373	-3.88548362	1.92611089
H	-6.75318653	-2.22345492	1.09150547
H	-5.08484790	-4.53866670	0.30886119
H	5.09210640	-3.48213570	-2.82535910
H	5.55895440	-1.92791988	-3.49194765
H	6.87056906	-1.49725239	-1.55920931
H	6.39305363	-3.04584779	-0.88722476

Table S11 Cartesian coordinates of **2o^{Ph}** at the TPSS-D3(BJ)/def2-TZVPP level of theory.

Ge	7.18590000	6.19240000	16.61840000
Cl	8.20520000	5.02600000	15.03190000
P	6.01550000	7.73260000	18.90480000
P	8.13760000	5.08480000	18.50240000
C	5.49250000	5.28780000	16.92710000

C	7.24560000	8.01720000	15.95060000
C	5.49860000	4.46430000	18.08480000
C	3.17680000	4.60400000	16.45010000
C	6.36730000	9.02600000	16.46210000
C	4.32430000	3.74500000	18.37420000
C	9.30240000	3.75240000	18.12380000
C	3.16290000	3.80570000	17.57660000
C	6.47120000	3.40520000	20.05780000
C	6.68010000	8.81240000	20.23120000
C	6.59660000	4.28440000	18.98260000
C	6.25560000	10.20210000	15.67660000
C	4.35020000	5.34210000	16.13980000
C	5.61100000	9.00970000	17.67150000
C	4.46240000	6.29270000	20.70550000
C	4.63950000	11.21440000	17.14200000
C	4.78060000	10.08680000	17.97910000
C	7.00140000	10.44300000	14.50170000
C	8.45550000	6.10270000	21.09630000
C	5.26950000	2.70780000	20.32530000
C	8.89100000	6.11800000	19.76680000
C	4.18870000	2.88190000	19.47780000
C	6.63190000	11.80400000	13.95200000
H	6.25720000	11.72940000	12.92630000
H	7.50620000	12.46230000	13.91860000
C	5.40270000	11.27970000	15.99230000
C	2.79410000	2.29320000	19.46090000
C	7.98120000	8.26900000	14.79600000
C	6.10650000	8.96380000	21.49920000
C	8.83110000	2.66500000	17.36980000
C	2.10640000	2.91510000	18.19780000
C	10.20850000	7.65780000	21.68270000
C	7.82370000	9.55820000	19.90570000
H	8.26970000	9.45900000	18.92000000
C	7.81040000	10.57570000	22.09700000
C	4.44220000	7.08800000	19.54680000
C	10.63740000	3.78370000	18.54750000
C	8.37900000	10.43820000	20.82920000
C	9.69200000	1.62320000	17.04400000
C	9.97920000	6.92290000	19.39310000
C	6.67480000	9.83760000	22.42720000
C	3.23220000	7.25060000	18.85970000
C	11.49260000	2.73370000	18.21620000
C	7.89110000	9.48250000	14.07150000
C	9.11380000	6.87650000	22.04970000
C	11.02380000	1.65730000	17.46410000
C	3.29610000	5.70000000	21.17990000
C	2.06710000	6.64700000	19.33210000
C	10.63900000	7.68210000	20.35500000
C	5.54070000	12.34950000	14.93030000
C	2.09320000	5.87630000	20.49380000
H	4.34340000	5.96550000	15.25010000
H	9.25830000	11.01580000	20.56070000
H	11.69330000	0.84240000	17.20810000
H	4.24250000	10.07210000	18.92290000
H	5.83060000	13.30970000	15.36820000
H	1.13650000	6.78390000	18.79000000
H	8.63030000	7.48960000	14.41080000
H	10.30780000	6.95300000	18.35780000
H	7.60380000	5.49540000	21.38160000
H	2.31280000	4.68500000	15.79750000

H	2.25190000	2.54320000	20.37840000
H	8.24450000	11.26110000	22.81790000
H	5.20570000	8.42020000	21.76150000
H	11.48120000	8.30210000	20.06580000
H	4.58810000	12.51380000	14.41590000
H	6.21670000	9.95050000	23.40510000
H	3.20340000	7.84170000	17.95090000
H	1.77560000	2.14090000	17.49860000
H	1.21970000	3.49460000	18.47290000
H	5.39660000	6.13250000	21.23320000
H	3.97070000	12.01850000	17.43310000
H	8.49950000	9.61710000	13.18260000
H	3.32860000	5.09590000	22.08120000
H	11.00540000	4.61050000	19.14440000
H	7.79760000	2.63760000	17.04080000
H	2.82840000	1.20050000	19.40370000
H	12.52430000	2.75730000	18.55180000
H	10.71750000	8.25960000	22.42790000
H	8.76630000	6.87300000	23.07710000
H	9.32490000	0.78570000	16.46010000
H	5.22410000	2.04060000	21.18030000
H	7.32650000	3.22740000	20.70320000
H	1.18200000	5.41710000	20.86440000

Table S12 Cartesian coordinates of **3o^{Ph}** at the TPSS-D3(BJ)/def2-TZVPP level of theory.

Ge	3.37660000	7.68790000	8.35720000
P	5.26400000	6.82410000	7.22110000
P	3.09870000	7.01530000	10.60750000
C	1.64090000	6.97950000	7.89470000
C	5.25440000	9.54430000	7.41660000
C	7.83380000	9.91690000	6.23880000
H	8.81980000	10.01910000	5.79770000
C	0.81740000	5.48960000	11.28340000
H	1.23530000	5.37670000	12.27970000
C	-0.27530000	6.43050000	6.45380000
H	-0.73420000	6.49670000	5.47250000
C	7.29820000	8.62300000	6.43600000
H	7.89350000	7.76270000	6.14360000
C	3.34460000	10.68490000	8.39950000
H	2.37440000	10.65360000	8.88620000
C	1.00890000	6.33020000	8.99350000
C	4.67510000	6.11360000	5.67940000
C	1.53020000	6.20230000	10.31830000
C	2.93850000	8.51070000	11.58990000
C	0.99830000	7.01850000	6.66050000
H	1.47900000	7.50860000	5.81910000
C	-0.89950000	5.78290000	7.50580000
C	4.27280000	5.87060000	11.34250000
C	7.08310000	11.02080000	6.61200000
C	5.81590000	10.81640000	7.19530000
C	3.76430000	5.04370000	5.72920000
H	3.41790000	4.65910000	6.68430000
C	6.03490000	8.42370000	6.99480000
C	-0.97860000	5.03780000	9.73530000
C	3.97970000	9.49660000	8.04930000
C	-0.24730000	5.74020000	8.75580000
C	-0.43890000	4.90340000	11.00500000
H	-0.95520000	4.36190000	11.79080000
C	6.38720000	5.70470000	8.06710000

C	5.09590000	6.63010000	4.44570000
H	5.78380000	7.46810000	4.40990000
C	8.20380000	4.05150000	9.37390000
H	8.92060000	3.41020000	9.87620000
C	4.36630000	4.57830000	10.79870000
H	3.74870000	4.29430000	9.95150000
C	8.01570000	5.36380000	9.81730000
H	8.58160000	5.74040000	10.66250000
C	4.01510000	9.41420000	11.62530000
H	4.92390000	9.21050000	11.06620000
C	7.10850000	6.19360000	9.16950000
H	6.97680000	7.22000000	9.49910000
C	5.16990000	12.02010000	7.54580000
C	3.90960000	10.58050000	12.37650000
H	4.74080000	11.27680000	12.41130000
C	1.75310000	8.79220000	12.28370000
H	0.91640000	8.10340000	12.23750000
C	6.00790000	4.01530000	12.47710000
H	6.67640000	3.28860000	12.92690000
C	-2.22120000	5.05520000	7.63030000
H	-2.28590000	4.22520000	6.91990000
H	-3.05820000	5.72350000	7.40520000
C	6.57050000	4.38820000	7.62370000
H	6.02600000	4.01830000	6.76170000
C	5.05150000	6.23560000	12.44860000
H	4.96590000	7.22790000	12.87810000
C	2.73260000	10.85560000	13.07750000
H	2.65230000	11.76740000	13.66010000
C	3.29980000	4.48070000	4.54460000
H	2.60160000	3.65120000	4.57930000
C	3.92440000	11.95390000	8.14560000
H	3.38100000	12.84880000	8.43140000
C	6.06350000	13.17630000	7.15020000
H	6.30630000	13.80470000	8.01260000
H	5.56370000	13.82440000	6.42340000
C	1.65750000	9.96700000	13.02760000
H	0.74320000	10.18670000	13.56840000
C	5.91780000	5.30000000	13.01270000
H	6.51060000	5.57270000	13.87930000
C	3.72760000	4.98830000	3.31510000
H	3.36130000	4.54890000	2.39320000
C	-2.26930000	4.55210000	9.11320000
H	-3.13680000	4.95110000	9.64820000
H	-2.34520000	3.46150000	9.16870000
C	5.23350000	3.65520000	11.37050000
H	5.30180000	2.65370000	10.95980000
C	4.61890000	6.06140000	3.26630000
H	4.94460000	6.45640000	2.30990000
C	7.48360000	3.56600000	8.28260000
H	7.64100000	2.55130000	7.93260000
C	7.34350000	12.50940000	6.54070000
H	7.51460000	12.82920000	5.50800000
H	8.24500000	12.77650000	7.10140000

Table S13 Cartesian coordinates of **3o^{iPr}**_FIA at the TPSS-D3(BJ)/def2-TZVPP level of theory.

Ge	9.42140000	1.50840000	6.18890000
P	9.69730000	2.59090000	8.50390000

P	9.69450000	0.42570000	3.87380000
F	11.21520000	1.50780000	6.18830000
C	8.17310000	3.57390000	4.44870000
H	7.91950000	2.76060000	3.77980000
C	9.67070000	4.26770000	7.84490000
C	9.23710000	6.84530000	6.75040000
C	9.10000000	-1.35210000	5.84120000
C	8.76080000	3.28520000	5.67350000
C	11.22930000	2.33520000	9.50970000
H	11.10870000	2.96760000	10.39800000
C	9.83930000	6.72150000	7.98780000
H	10.14770000	7.58890000	8.56300000
C	7.89770000	4.89340000	4.00690000
H	7.42090000	5.04270000	3.04290000
C	9.10510000	4.36950000	6.53630000
C	8.87310000	-2.65810000	6.32930000
C	10.03500000	5.42610000	8.52590000
H	10.48250000	5.34330000	9.51180000
C	8.75830000	-0.26730000	6.70450000
C	11.22680000	0.68020000	2.86820000
H	11.10460000	0.05020000	1.97830000
C	8.85590000	8.05070000	5.91570000
C	8.26960000	-2.93530000	7.57310000
C	9.82870000	-3.70530000	4.38890000
H	10.13510000	-4.57320000	3.81330000
C	9.22730000	-3.82820000	5.62670000
C	10.02650000	-2.41020000	3.85090000
H	10.47360000	-2.32820000	2.86470000
C	8.27680000	5.95380000	4.80460000
C	8.17080000	-0.55520000	7.92970000
H	7.91920000	0.25850000	8.59890000
C	7.89310000	-1.87430000	8.37130000
H	7.41660000	-2.02280000	9.33560000
C	8.39840000	3.53110000	10.87110000
H	8.41810000	4.56750000	10.52330000
H	9.29630000	3.34160000	11.46470000
H	7.53360000	3.41820000	11.53320000
C	8.25870000	2.55880000	9.69350000
H	8.24430000	1.53580000	10.08930000
C	9.66500000	-1.25120000	4.53230000
C	8.88040000	5.67580000	6.04820000
C	12.49690000	2.77130000	8.76170000
H	13.35740000	2.65920000	9.42890000
H	12.44080000	3.81650000	8.44770000
H	12.65720000	2.15520000	7.87590000
C	8.84510000	-5.03300000	6.46190000
C	8.25600000	0.46110000	2.68430000
H	8.24320000	1.48450000	2.28950000
C	12.49370000	0.23980000	3.61460000
H	12.65490000	0.85280000	4.50250000
H	13.35450000	0.35310000	2.94790000
H	12.43630000	-0.80630000	3.92510000

C	8.18760000	7.45580000	4.63010000
C	8.17680000	-4.43710000	7.74700000
C	6.96160000	2.82150000	8.91160000
H	6.09930000	2.71210000	9.57620000
H	6.83370000	2.13040000	8.07240000
H	6.95620000	3.83920000	8.51130000
C	11.30020000	2.15440000	2.43490000
H	10.41030000	2.47060000	1.88210000
H	12.16770000	2.30200000	1.78460000
H	11.41300000	2.80440000	3.30750000
C	8.39450000	-0.51020000	1.50570000
H	9.29350000	-0.32230000	0.91330000
H	7.53070000	-0.39440000	0.84290000
H	8.41130000	-1.54710000	1.85240000
C	11.29990000	0.86200000	9.94650000
H	11.40830000	0.20920000	9.07550000
H	10.41090000	0.55000000	10.50300000
H	12.16910000	0.71370000	10.59450000
C	6.95830000	0.19960000	3.46570000
H	6.95160000	-0.81820000	3.86560000
H	6.09640000	0.31010000	2.80070000
H	6.83080000	0.89070000	4.30500000
H	8.68780000	-4.76490000	8.65760000
H	8.16090000	-5.69260000	5.91900000
H	9.73860000	8.64880000	5.66720000
H	7.13370000	-4.75650000	7.83960000
H	8.17210000	8.71070000	6.45860000
H	8.70010000	7.78230000	3.71990000
H	7.14530000	7.77750000	4.53640000
H	9.72720000	-5.63170000	6.71080000

Table S14 Cartesian coordinates of **3o^{Ph}**_FIA at the TPSS-D3(BJ)/def2-TZVPP level of theory.

Ge	7.15600000	6.26670000	16.68040000
P	6.00230000	7.79000000	18.88770000
P	8.16750000	5.11970000	18.51310000
C	5.50800000	5.27580000	16.95450000
C	7.16940000	8.05100000	15.93380000
C	5.53270000	4.45860000	18.11700000
C	3.20550000	4.54010000	16.48590000
C	6.31670000	9.07690000	16.44300000
C	4.37120000	3.72340000	18.41780000
C	9.33350000	3.80650000	18.06910000
C	3.20830000	3.75350000	17.62050000
C	6.52220000	3.45060000	20.10780000
C	6.69690000	8.83360000	20.22290000
C	6.63520000	4.30900000	19.01510000
C	6.18130000	10.23100000	15.63290000
C	4.36110000	5.30440000	16.17180000
C	5.59530000	9.08310000	17.67310000
C	4.43740000	6.35480000	20.69170000

C	4.62660000	11.28500000	17.13310000
C	4.78210000	10.17070000	17.98720000
C	6.87290000	10.42540000	14.41730000
C	8.39490000	6.15750000	21.11110000
C	5.33050000	2.74150000	20.39010000
C	8.93330000	6.08760000	19.82190000
C	4.24880000	2.87890000	19.53730000
C	6.48950000	11.77430000	13.84550000
H	6.06310000	11.67300000	12.84260000
H	7.36700000	12.42200000	13.74900000
C	5.34850000	11.32140000	15.95490000
C	2.86320000	2.26890000	19.53180000
C	7.84820000	8.24860000	14.73390000
C	6.09170000	9.03560000	21.46860000
C	9.02910000	2.99410000	16.96500000
C	2.16860000	2.85150000	18.25370000
C	10.24510000	7.54470000	21.80610000
C	7.89330000	9.50390000	19.92460000
H	8.36510000	9.36160000	18.95620000
C	7.87250000	10.54690000	22.10360000
C	4.43140000	7.13600000	19.52370000
C	10.47120000	3.54050000	18.84450000
C	8.47250000	10.35900000	20.85640000
C	9.86300000	1.92920000	16.64120000
C	10.12840000	6.76250000	19.52320000
C	6.68330000	9.88500000	22.40500000
C	3.23340000	7.27840000	18.81120000
C	11.30000000	2.47030000	18.50970000
C	7.72640000	9.43800000	13.97220000
C	9.05260000	6.88590000	22.10010000
C	10.99890000	1.66680000	17.41050000
C	3.26850000	5.75390000	21.14900000
C	2.06610000	6.66630000	19.26650000
C	10.78090000	7.48470000	20.51750000
C	5.45240000	12.36150000	14.85930000
C	2.07810000	5.90760000	20.43630000
H	4.33550000	5.93070000	15.28430000
H	9.39500000	10.87600000	20.61150000
H	11.64890000	0.83710000	17.15220000
H	4.26440000	10.17380000	18.94250000
H	5.77750000	13.32750000	15.25840000
H	1.14510000	6.78720000	18.70470000
H	8.47390000	7.44870000	14.35240000
H	10.54880000	6.71290000	18.52270000
H	7.46640000	5.64640000	21.33760000
H	2.33930000	4.59820000	15.83380000
H	2.31520000	2.53260000	20.44200000
H	8.32600000	11.21170000	22.83180000
H	5.15290000	8.54790000	21.70680000
H	11.70500000	8.00420000	20.28600000
H	4.47960000	12.52910000	14.38540000
H	6.20310000	10.03790000	23.36670000

H	3.21630000	7.86300000	17.89780000
H	1.86020000	2.05660000	17.56740000
H	1.26640000	3.41450000	18.51200000
H	5.36050000	6.21380000	21.24330000
H	3.97240000	12.09910000	17.42970000
H	8.28680000	9.53630000	13.04770000
H	3.28960000	5.16160000	22.05830000
H	10.70720000	4.15790000	19.70410000
H	8.15730000	3.20320000	16.35590000
H	2.91340000	1.17580000	19.50070000
H	12.17990000	2.26650000	19.11140000
H	10.75330000	8.11350000	22.57750000
H	8.62730000	6.94530000	23.09600000
H	9.62940000	1.30670000	15.78380000
H	5.29440000	2.09260000	21.25950000
H	7.37900000	3.30200000	20.75860000
H	1.16510000	5.44170000	20.79370000
F	8.06140000	5.39660000	15.40160000

Table S15 Cartesian coordinates of **3o^{iPr}**_HIA at the TPSS-D3(BJ)/def2-TZVPP level of theory.

Ge	-1.12800000	4.64370000	8.82510000
H	-1.20070000	6.18240000	8.79100000
P	1.02340000	4.79030000	7.36330000
P	-3.28680000	4.67830000	10.29030000
C	2.10090000	4.88170000	8.80830000
C	3.43740000	5.27360000	8.81340000
H	3.87590000	5.67950000	7.90660000
C	4.26330000	5.15570000	9.95770000
H	5.29680000	5.48380000	9.90450000
C	3.73500000	4.59740000	11.10630000
C	2.37830000	4.21430000	11.11390000
C	1.51380000	4.37180000	10.00780000
C	0.14190000	4.02610000	10.19730000
C	-0.23790000	3.48570000	11.41790000
H	-1.27770000	3.22590000	11.57590000
C	0.66330000	3.27110000	12.49410000
H	0.29470000	2.83050000	13.41570000
C	1.97750000	3.66300000	12.34870000
C	3.17210000	3.63310000	13.28030000
H	3.42110000	2.60500000	13.56300000
H	2.96980000	4.17440000	14.20950000
C	4.33420000	4.29540000	12.46470000
H	4.68760000	5.21250000	12.94710000
H	5.19990000	3.63130000	12.38020000
C	1.67260000	3.32940000	6.40020000
H	1.01200000	3.25650000	5.52760000
C	1.51770000	2.06250000	7.25570000
H	1.82190000	1.18520000	6.67690000
H	0.48470000	1.91310000	7.58480000
H	2.15120000	2.11990000	8.14540000

C	3.11310000	3.50150000	5.90570000
H	3.23550000	4.39160000	5.28270000
H	3.39280000	2.63170000	5.30220000
H	3.81060000	3.56190000	6.74550000
C	1.31490000	6.28860000	6.31950000
H	2.38310000	6.29720000	6.06920000
C	0.98070000	7.56490000	7.10520000
H	-0.08730000	7.61400000	7.33530000
H	1.23800000	8.44190000	6.50340000
H	1.53780000	7.61760000	8.04450000
C	0.49450000	6.17940000	5.02450000
H	0.78940000	5.31520000	4.42250000
H	0.64400000	7.07690000	4.41650000
H	-0.57410000	6.09270000	5.24660000
C	-2.34650000	3.86430000	7.48920000
C	-1.93050000	3.29000000	6.29610000
H	-0.87640000	3.08970000	6.14780000
C	-2.81430000	2.96330000	5.23340000
H	-2.41620000	2.50180000	4.33470000
C	-4.15130000	3.27570000	5.36110000
C	-4.58940000	3.85890000	6.56840000
C	-3.73920000	4.12520000	7.66460000
C	-4.36190000	4.64640000	8.84120000
C	-5.72120000	4.94850000	8.81940000
H	-6.18740000	5.36120000	9.70910000
C	-6.53490000	4.72610000	7.68180000
H	-7.58780000	4.98740000	7.72100000
C	-5.96850000	4.15190000	6.55960000
C	-6.54340000	3.74890000	5.21700000
H	-6.95040000	4.61890000	4.69120000
H	-7.36760000	3.03820000	5.33170000
C	-5.34000000	3.12200000	4.43420000
H	-5.52200000	2.06690000	4.20470000
H	-5.17130000	3.62700000	3.47830000
C	-3.68980000	6.18160000	11.29030000
H	-4.76000000	6.13080000	11.52620000
C	-3.42170000	7.45590000	10.47680000
H	-2.35410000	7.56870000	10.26790000
H	-3.74820000	8.32970000	11.04930000
H	-3.95910000	7.44980000	9.52460000
C	-2.88630000	6.15880000	12.60040000
H	-3.13590000	5.29300000	13.22030000
H	-3.10390000	7.05980000	13.18210000
H	-1.81040000	6.13670000	12.39840000
C	-3.83620000	3.20370000	11.29410000
H	-3.18560000	3.20980000	12.17750000
C	-5.29220000	3.28310000	11.76650000
H	-5.98170000	3.26520000	10.91830000
H	-5.48710000	4.18110000	12.35920000
H	-5.51470000	2.41470000	12.39530000
C	-3.57160000	1.92470000	10.48550000
H	-3.80760000	1.04650000	11.09410000

H	-2.52710000	1.84890000	10.16750000
H	-4.20050000	1.89720000	9.59090000

Table S16 Cartesian coordinates of **3o^{Ph}**_HIA at the TPSS-D3(BJ)/def2-TZVPP level of theory.

Ge	7.25120000	6.12340000	16.53020000
P	6.01480000	7.72400000	18.95930000
P	8.16560000	5.14080000	18.49680000
C	5.55840000	5.22520000	16.90160000
C	7.21290000	7.96670000	15.94080000
C	5.55390000	4.45410000	18.09640000
C	3.23340000	4.53400000	16.46040000
C	6.36170000	8.98960000	16.46890000
C	4.37970000	3.74650000	18.41350000
C	9.32010000	3.81130000	18.05690000
C	3.21900000	3.77600000	17.61440000
C	6.51560000	3.50160000	20.12800000
C	6.62990000	8.82880000	20.29030000
C	6.64230000	4.32710000	19.01270000
C	6.23410000	10.15700000	15.67050000
C	4.40960000	5.25450000	16.11990000
C	5.63920000	8.99350000	17.69960000
C	4.37290000	6.33330000	20.72050000
C	4.67400000	11.20400000	17.16960000
C	4.82630000	10.08280000	18.01280000
C	6.93360000	10.37250000	14.46150000
C	8.43700000	6.20120000	21.07480000
C	5.31800000	2.80270000	20.41470000
C	8.95090000	6.13330000	19.77490000
C	4.24250000	2.93130000	19.55380000
C	6.55950000	11.73010000	13.90650000
H	6.14430000	11.64560000	12.89730000
H	7.44000000	12.37640000	13.82960000
C	5.40290000	11.24830000	15.99760000
C	2.84830000	2.34040000	19.55780000
C	7.89780000	8.19570000	14.74760000
C	6.02410000	9.00300000	21.53960000
C	8.92040000	2.92370000	17.04360000
C	2.16150000	2.91200000	18.27040000
C	10.28300000	7.61430000	21.72750000
C	7.80400000	9.54140000	19.99730000
H	8.27980000	9.41920000	19.02780000
C	7.75650000	10.56720000	22.18390000
C	4.40600000	7.10990000	19.54940000
C	10.55300000	3.62940000	18.69610000
C	8.35800000	10.40820000	20.93310000
C	9.75090000	1.87150000	16.67280000
C	10.12720000	6.82680000	19.44850000
C	6.59010000	9.86460000	22.48160000
C	3.22440000	7.26850000	18.81360000
C	11.37930000	2.57090000	18.31810000
C	7.79050000	9.39560000	14.00340000

C	9.10570000	6.93970000	22.04790000
C	10.98290000	1.69580000	17.30780000
C	3.18390000	5.75940000	21.16060000
C	2.03670000	6.68150000	19.24920000
C	10.78980000	7.56210000	20.42750000
C	5.51450000	12.30310000	14.91790000
C	2.01000000	5.93230000	20.42500000
H	4.39790000	5.84760000	15.20930000
H	9.26260000	10.95710000	20.68950000
H	11.63010000	0.87480000	17.01660000
H	4.30950000	10.08160000	18.96860000
H	5.83500000	13.26410000	15.33250000
H	1.12940000	6.81560000	18.66820000
H	8.53020000	7.40560000	14.34940000
H	10.52420000	6.78660000	18.43820000
H	7.51340000	5.68860000	21.31820000
H	2.36770000	4.59670000	15.80800000
H	2.30440000	2.62700000	20.46320000
H	8.19000000	11.24070000	22.91640000
H	5.10210000	8.48410000	21.77820000
H	11.69850000	8.09800000	20.17380000
H	4.54550000	12.47570000	14.43820000
H	6.10690000	9.99450000	23.44530000
H	3.23550000	7.84520000	17.89500000
H	1.82860000	2.11110000	17.60280000
H	1.27650000	3.50420000	18.52250000
H	5.28450000	6.17300000	21.28730000
H	4.02120000	12.01760000	17.47090000
H	8.35910000	9.51020000	13.08580000
H	3.17570000	5.17270000	22.07390000
H	10.86410000	4.30230000	19.48750000
H	7.95770000	3.04730000	16.55550000
H	2.88340000	1.24640000	19.54330000
H	12.33240000	2.43110000	18.81800000
H	10.79860000	8.19290000	22.48660000
H	8.69810000	6.99920000	23.05110000
H	9.43810000	1.18790000	15.89030000
H	5.27080000	2.17560000	21.29940000
H	7.36300000	3.37190000	20.79490000
H	1.08090000	5.48790000	20.76830000
H	8.07230000	5.37690000	15.44830000

Table S17 Cartesian coordinates of **3o^{Ph}**_HIA2 at the TPSS-D3(BJ)/def2-TZVPP level of theory.

Ge	2.93010000	7.41470000	10.23570000
P	0.77630000	5.31050000	11.24270000
P	5.02410000	5.14790000	9.22520000
C	4.82870000	4.44250000	10.91160000
C	0.54860000	4.77300000	9.51660000
C	4.39830000	4.71180000	13.27140000
C	2.19110000	6.54870000	8.60930000
C	3.38120000	2.90200000	8.59210000
H	3.14860000	2.83710000	9.64830000
C	1.23350000	5.49080000	8.47920000

C	0.92510000	5.07470000	7.15270000
C	0.05870000	4.00530000	6.83810000
C	3.99280000	5.38420000	14.44480000
C	4.27430000	3.88070000	8.13590000
C	4.29640000	5.25830000	11.96140000
C	2.34930000	6.70800000	6.13400000
H	2.80100000	7.20240000	5.27810000
C	-0.74610000	6.26150000	11.59460000
C	2.70470000	7.11300000	7.44180000
H	3.44980000	7.89880000	7.53880000
C	-0.29110000	3.71260000	9.18990000
H	-0.78070000	3.17790000	9.99910000
C	-0.54440000	3.30580000	7.86020000
H	-1.20760000	2.46620000	7.67000000
C	3.65270000	6.53160000	11.85370000
C	0.53140000	3.76070000	12.18880000
C	1.46190000	5.66660000	5.99060000
C	3.29560000	7.18990000	13.02730000
H	2.79420000	8.15200000	12.94770000
C	5.33910000	3.18150000	11.21110000
H	5.75750000	2.58970000	10.40170000
C	3.47210000	6.65200000	14.32680000
H	3.16120000	7.22970000	15.19330000
C	4.89860000	3.42390000	13.55430000
C	1.53070000	1.68950000	12.97630000
H	2.38400000	1.01850000	13.01350000
C	6.82650000	4.85040000	8.98760000
C	4.53280000	3.96140000	6.75720000
H	5.20150000	4.73070000	6.38090000
C	-1.75710000	6.49190000	10.65360000
H	-1.68470000	6.04230000	9.66860000
C	1.62150000	2.87690000	12.25580000
H	2.54880000	3.12870000	11.75010000
C	-0.64420000	3.43590000	12.87970000
H	-1.49280000	4.11160000	12.84320000
C	5.36060000	2.64140000	12.51640000
H	5.75680000	1.64300000	12.68030000
C	3.94960000	3.06100000	5.86960000
H	4.17440000	3.12920000	4.80890000
C	-0.00380000	3.83510000	5.33470000
H	-1.03020000	3.92980000	4.96430000
H	0.35020000	2.84110000	5.04190000
C	3.07530000	2.07900000	6.33940000
H	2.62010000	1.37690000	5.64700000
C	-2.85300000	7.29410000	10.97620000
H	-3.62870000	7.46700000	10.23550000
C	0.35460000	1.37320000	13.66110000
H	0.28540000	0.45160000	14.23150000
C	-2.95710000	7.86820000	12.24270000
H	-3.81190000	8.48970000	12.49200000
C	7.68880000	5.84430000	9.47600000
H	7.26690000	6.73520000	9.93470000
C	9.61280000	4.56060000	8.77670000
H	10.68970000	4.44790000	8.69320000
C	9.07100000	5.69650000	9.38110000
H	9.72510000	6.47210000	9.76890000
C	4.78940000	3.15970000	15.04150000
H	5.75230000	2.87230000	15.47610000
H	4.09490000	2.33350000	15.23190000
C	4.24960000	4.49670000	15.64580000

H	3.33860000	4.33670000	16.23160000
H	4.98440000	4.95130000	16.31970000
C	7.37970000	3.71510000	8.38020000
H	6.72750000	2.94170000	7.98620000
C	-0.84840000	6.86270000	12.86140000
H	-0.05670000	6.70920000	13.59060000
C	0.92290000	4.95770000	4.76670000
H	1.73650000	4.53860000	4.16540000
H	0.36970000	5.64580000	4.11810000
C	2.78560000	2.01000000	7.70140000
H	2.09150000	1.26410000	8.07590000
C	8.76360000	3.57440000	8.27330000
H	9.17860000	2.68930000	7.79910000
C	-1.95110000	7.64770000	13.18710000
H	-2.02140000	8.09780000	14.17320000
C	-0.72870000	2.25090000	13.61300000
H	-1.64650000	2.01200000	14.14290000
H	3.99620000	8.36790000	9.63990000
H	1.81680000	8.30900000	10.84220000

Table S18 Cartesian coordinates of **SbF_5** at the TPSS-D3(BJ)/def2-TZVPP level of theory.

Sb	-0.31810000	2.24030000	0.66130000
F	-1.25800000	3.86080000	0.66130000
F	-0.31610000	2.24030000	2.54350000
F	1.55540000	2.24030000	0.66130000
F	-1.25810000	0.61980000	0.66130000
F	-0.31610000	2.24030000	-1.22090000

Table S19 Cartesian coordinates of **SbF_6** at the TPSS-D3(BJ)/def2-TZVPP level of theory.

Sb	-0.31850000	2.24030000	0.66130000
F	-1.84110000	3.40860000	0.66130000
F	-0.31850000	2.24030000	2.58030000
F	1.20410000	1.07200000	0.66130000
F	-1.48680000	0.71770000	0.66130000
F	-0.31850000	2.24030000	-1.25770000
F	0.84980000	3.76290000	0.66130000

Table S20 Cartesian coordinates of **$B(PhF_5)_3$** at the TPSS-D3(BJ)/def2-TZVPP level of theory.

F	-4.40370000	20.18610000	15.67490000
F	-4.15970000	15.60150000	16.66450000
F	-1.90620000	17.24280000	12.88480000
F	-5.58530000	19.52750000	12.79590000
F	-0.27620000	19.29850000	14.65930000
F	-5.05480000	18.11180000	17.25570000
C	-3.94360000	18.96430000	15.33550000
C	-4.28850000	17.91150000	16.17370000
F	-2.58800000	15.18320000	14.47350000
F	-2.12020000	20.94070000	10.58650000
F	2.18880000	19.49140000	13.60360000
C	-3.81160000	21.11280000	12.96520000
F	-7.40580000	21.43260000	12.26360000
C	-0.16540000	19.73970000	13.38980000

C	-3.12590000	18.80940000	14.20540000
F	-2.20750000	22.87320000	13.08370000
C	-6.12610000	21.77260000	12.47530000
C	-1.31240000	20.11130000	12.67130000
C	-3.02050000	16.41960000	14.76060000
C	-3.82790000	16.62880000	15.87820000
B	-2.74820000	20.01130000	13.27970000
C	-5.16640000	20.80900000	12.75930000
C	-2.67720000	17.50250000	13.96060000
C	-1.08200000	20.58220000	11.36910000
F	0.35510000	21.10660000	9.55010000
F	-6.65710000	24.05460000	12.15420000
F	2.52090000	20.39040000	11.04860000
F	-4.05310000	24.75920000	12.56820000
C	-3.47890000	22.47340000	12.87640000
C	1.11990000	19.83620000	12.87130000
C	1.29370000	20.29980000	11.56750000
C	0.18520000	20.67010000	10.80650000
C	-4.41350000	23.46870000	12.61920000
C	-5.74600000	23.11280000	12.41180000

Table S21 Cartesian coordinates of **$B(PhF_5)_3$-H** at the TPSS-D3(BJ)/def2-TZVPP level of theory.

F	-4.10930000	20.05000000	16.33350000
F	-4.41920000	15.34890000	16.18780000
F	-2.14540000	17.60990000	12.73950000
F	-5.19620000	19.48090000	12.72530000
F	0.18150000	20.04320000	14.90730000
F	-4.96670000	17.74010000	17.41560000
C	-3.79200000	18.90140000	15.68340000
C	-4.25470000	17.72350000	16.26320000
F	-2.99470000	15.32240000	13.84570000
F	-2.36690000	20.43250000	10.89830000
F	2.43900000	19.93660000	13.44630000
C	-3.71950000	21.28970000	13.24520000
F	-7.07260000	21.10740000	11.71860000
C	0.05600000	20.13730000	13.55910000
C	-3.05490000	18.95270000	14.49760000
F	-2.42340000	23.25890000	13.59890000
C	-5.91860000	21.63080000	12.19720000
C	-1.20810000	20.27990000	12.98300000
C	-3.25540000	16.50110000	14.46000000
C	-3.98100000	16.50780000	15.64540000
B	-2.53110000	20.40150000	13.94210000
C	-4.92730000	20.81280000	12.73700000
C	-2.81800000	17.70760000	13.91610000
C	-1.20130000	20.33850000	11.58960000
F	-0.10140000	20.34550000	9.46420000
F	-6.66340000	23.81670000	11.61600000
F	2.32670000	20.09320000	10.71050000
F	-4.31500000	24.87050000	12.56500000
C	-3.56640000	22.67540000	13.15580000

C	1.24040000	20.07270000	12.82930000
C	1.19040000	20.15040000	11.44170000
C	-0.04390000	20.28370000	10.81610000
C	-4.52340000	23.53310000	12.62100000
C	-5.71600000	23.00460000	12.13820000
H	-2.18340000	21.02630000	14.91610000

Table S22 Cartesian coordinates of **Me_3SiF** at the TPSS-D3(BJ)/def2-TZVPP level of theory.

Si	-0.87460000	1.46140000	0.00000000
C	-0.21810000	2.28520000	1.54690000
H	-0.55490000	3.32710000	1.60670000
H	-0.56540000	1.77130000	2.45010000
H	0.87740000	2.28870000	1.56240000
C	-2.74490000	1.39400000	-0.00010000
H	-3.17230000	2.40400000	-0.00010000
H	-3.12450000	0.87250000	-0.88570000
H	-3.12460000	0.87250000	0.88540000
C	-0.21790000	2.28500000	-1.54690000
H	0.87760000	2.28850000	-1.56220000
H	-0.56510000	1.77110000	-2.45000000
H	-0.55480000	3.32690000	-1.60680000
F	-0.33480000	-0.07330000	0.00010000

Table S23 Cartesian coordinates of **Me_3SiH** at the TPSS-D3(BJ)/def2-TZVPP level of theory.

Si	-0.86370000	1.43030000	0.00000000
C	-0.22280000	2.29620000	1.54590000
H	-0.56900000	3.33570000	1.58400000
H	-0.57060000	1.79640000	2.45660000
H	0.87230000	2.30940000	1.57080000
C	-2.74760000	1.40460000	-0.00010000
H	-3.15290000	2.42330000	-0.00010000
H	-3.13980000	0.89090000	-0.88470000
H	-3.13990000	0.89090000	0.88450000
C	-0.22260000	2.29600000	-1.54580000
H	0.87250000	2.30930000	-1.57060000
H	-0.57020000	1.79610000	-2.45660000
H	-0.56880000	3.33560000	-1.58410000
H	-0.36700000	0.02420000	0.00010000

Table S24 Cartesian coordinates of **Me_3Si** at the TPSS-D3(BJ)/def2-TZVPP level of theory.

Si	-1.05180000	1.96440000	0.00000000
C	-0.20390000	2.31580000	1.58820000
H	-0.42250000	3.36320000	1.85630000
H	-0.57850000	1.69000000	2.40350000
H	0.88290000	2.22400000	1.50500000
C	-2.79870000	1.40460000	-0.00010000
H	-3.43550000	2.30520000	0.00130000
H	-3.04930000	0.83390000	-0.89900000
H	-3.04870000	0.83170000	0.89760000

C	-0.20370000	2.31570000	-1.58810000
H	0.88330000	2.22670000	-1.50420000
H	-0.57630000	1.68770000	-2.40260000
H	-0.42500000	3.36200000	-1.85800000

Table S25 Cartesian coordinates and energies of **3^{iPr}_PH** at the B3LYP-D3(BJ)/def2-SVP//B3LYPD3(BJ)/6-311G(d,p) level of theory.

Ge	0.28485900	-0.56368800	-0.93582400
H	-1.71695100	-1.60734000	-0.97756800
P	-3.09403600	-1.21149600	-0.87822100
P	1.34294100	-1.21655300	1.19433300
C	-3.13232600	0.32383900	0.06891000
C	-4.38583100	0.64675700	0.59951600
H	-5.18860500	-0.08289400	0.54750600
C	-4.68215800	1.88893600	1.19244200
H	-5.67121900	2.07528000	1.59829800
C	-3.69304700	2.84659800	1.19580000
C	-2.41984700	2.54019400	0.65913100
C	-2.03561900	1.27469400	0.11683300
C	-0.66083200	1.13924700	-0.30624100
C	0.12427000	2.29316400	-0.25912000
H	1.15115400	2.21732400	-0.59837400
C	-0.29536000	3.55484800	0.22410000
H	0.39706100	4.39193300	0.21909800
C	-1.57006300	3.67027800	0.71996400
C	-2.30509200	4.84092200	1.33710400
H	-2.37736200	5.67598800	0.63171600
H	-1.78208700	5.22532100	2.21906200
C	-3.71271000	4.27399200	1.69686800
H	-3.89832700	4.30303400	2.77647500
H	-4.52089800	4.84693700	1.23008300
C	-3.63749900	-0.92339600	-2.63466600
H	-3.47134300	-1.89204300	-3.12357900
C	-2.73256800	0.12521500	-3.30792800
H	-3.05393500	0.25191700	-4.34618800
H	-1.68346700	-0.18153900	-3.31297400
H	-2.80501300	1.09666500	-2.81164700
C	-5.12526100	-0.55436200	-2.73413900
H	-5.78152600	-1.32916800	-2.32668200
H	-5.39152200	-0.42200300	-3.78709900
H	-5.33736900	0.38685500	-2.21841300
C	-4.11886100	-2.55044900	-0.10218300
H	-5.16078700	-2.21213600	-0.14835100
C	-3.73119100	-2.76623900	1.37005600
H	-2.70029100	-3.12024100	1.46049100
H	-4.38251400	-3.53111700	1.80343600
H	-3.83687500	-1.85588100	1.96400400
C	-3.99018600	-3.84702700	-0.92421700
H	-4.34338700	-3.73242700	-1.95219200
H	-4.59629900	-4.62803500	-0.45597300
H	-2.95583600	-4.20442900	-0.95221000
C	2.08806800	0.15511500	-1.38784300

C	2.40758800	0.73348800	-2.61113400
H	1.62797500	0.84405100	-3.36230100
C	3.70807700	1.20763800	-2.94508000
H	3.87765000	1.64996200	-3.92277200
C	4.72206000	1.09064400	-2.01963700
C	4.42069000	0.50180900	-0.77308900
C	3.13776600	0.03104200	-0.42764200
C	3.00652000	-0.55005200	0.87354600
C	4.11094600	-0.61690600	1.71803100
H	4.01501400	-1.07067200	2.69997700
C	5.38465600	-0.11821400	1.33892500
H	6.21364600	-0.19225700	2.03638800
C	5.53741000	0.44142900	0.08580200
C	6.73236500	1.04810200	-0.62596700
H	7.55295700	0.32726500	-0.70892600
H	7.12966300	1.90535200	-0.07144300
C	6.19098500	1.47333700	-2.03590000
H	6.32484800	2.54648700	-2.20987200
H	6.72804800	0.96012000	-2.84093100
C	1.53580700	-3.08028500	1.21257400
H	2.12852300	-3.32309200	2.10267500
C	2.30354100	-3.55685300	-0.03167800
H	1.76234900	-3.31690000	-0.95314500
H	2.42222500	-4.64441600	0.01216100
H	3.29874800	-3.11224900	-0.09299400
C	0.16492700	-3.76460200	1.31189100
H	0.28722100	-4.85215300	1.33763300
H	-0.44193100	-3.51525300	0.43416100
H	-0.38585900	-3.47325200	2.21223200
C	0.69102500	-0.68565800	2.87563000
H	-0.39012200	-0.85932000	2.79166300
C	1.22658100	-1.50421200	4.06133300
H	2.30554700	-1.37519700	4.18798600
H	1.01814300	-2.57312900	3.97266300
H	0.74973800	-1.15310000	4.98268200
C	0.91940700	0.82011300	3.08591000
H	0.41824600	1.13872300	4.00567300
H	0.52543000	1.41155200	2.25775500
H	1.98481500	1.04535200	3.18709300

Zero-point correction= 0.711609 (Hartree/Particle)
Thermal correction to Energy= 0.746294
Thermal correction to Enthalpy= 0.747238
Thermal correction to Gibbs Free Energy= 0.646678
Sum of electronic and zero-point Energies= -4156.608995
Sum of electronic and thermal Energies= -4156.574310
Sum of electronic and thermal Enthalpies= -4156.573366
Sum of electronic and thermal Free Energies= -4156.673926

Table S26 Cartesian coordinates and energies of ^{3Ph}**_PH** at the B3LYP-D3(BJ)/def2-SVP//B3LYPD3(BJ)/6-311G(d,p) level of theory.

Ge	0.50638300	0.60682000	0.94527900

H	-1.67773000	1.47900200	-0.50848100
P	-2.63265900	0.82374500	0.28050100
P	1.48837100	0.23370700	-1.29162300
C	-2.48748800	-0.98080500	0.20817900
C	-3.64386000	-1.63266100	-0.23518500
H	-4.46941000	-1.04450700	-0.61799500
C	-3.80622600	-3.03208300	-0.19882300
H	-4.72464100	-3.47581700	-0.56955000
C	-2.79276400	-3.78781800	0.34656600
C	-1.61637100	-3.14732700	0.79901800
C	-1.36720500	-1.74682700	0.72847700
C	-0.07565000	-1.29971300	1.15823200
C	0.79100100	-2.24952800	1.69825300
H	1.76482700	-1.90979100	2.03783900
C	0.50109000	-3.62885700	1.81520200
H	1.23597200	-4.30132500	2.24884300
C	-0.70430500	-4.08502100	1.33662500
C	-1.29800400	-5.47673200	1.26691100
H	-1.41123400	-5.90962300	2.26696000
H	-0.65381100	-6.16088800	0.70460400
C	-2.68098200	-5.27990200	0.57016000
H	-2.73684300	-5.81987700	-0.38168100
H	-3.50900300	-5.65128500	1.18344100
C	2.38152700	0.56477900	1.59473900
C	2.77070300	0.65325700	2.92642300
H	2.00784000	0.65074300	3.70249100
C	4.12668500	0.76599700	3.34926200
H	4.34761700	0.82814900	4.41126800
C	5.12417200	0.81143700	2.40063600
C	4.75271100	0.72157400	1.04209500
C	3.41828300	0.57790500	0.61239800
C	3.22352800	0.47961600	-0.80053200
C	4.31043800	0.55240000	-1.66612100
H	4.14725000	0.48689200	-2.73841200
C	5.63842100	0.70885800	-1.19382300
H	6.45504000	0.76294800	-1.90753600
C	5.85735800	0.78458100	0.16855500
C	7.12140000	0.93936700	0.99377700
H	7.64889400	1.86474500	0.73756100
H	7.82388400	0.12086500	0.80216500
C	6.63388700	0.94730900	2.48525300
H	7.07892700	0.12421100	3.05504900
H	6.92594500	1.87093500	2.99651000
C	-2.50187000	1.46678200	1.96457900
C	-2.31386200	2.84614600	2.14696000
C	-2.61527900	0.61269900	3.06826000
C	-2.24894000	3.36573900	3.43485900
H	-2.20383700	3.50532400	1.29091400
C	-2.54764100	1.14560000	4.35697800
H	-2.74085800	-0.45498200	2.92627200
C	-2.36387600	2.51567500	4.54039200
H	-2.09998700	4.43087200	3.57970000
H	-2.63317400	0.48686800	5.21521400
H	-2.30832200	2.92507100	5.54412100
C	-4.21848800	1.37773900	-0.41475600
C	-5.37203200	1.47303900	0.37972100
C	-4.26734000	1.73988300	-1.77028100
C	-6.56698200	1.91213200	-0.18715800
H	-5.33447300	1.21404500	1.43309300
C	-5.46702300	2.17835300	-2.32900800

H	-3.37378500	1.68775400	-2.38671000
C	-6.61503200	2.26228400	-1.53882000
H	-7.45850000	1.98742100	0.42703700
H	-5.50306800	2.46080400	-3.37618400
H	-7.54701000	2.60829200	-1.97458100
C	1.05403200	1.54963400	-2.49566300
C	1.14507100	1.36208600	-3.88362300
C	0.66824100	2.80601400	-1.99611700
C	0.85299600	2.41220700	-4.75484400
H	1.43817300	0.39812100	-4.28600000
C	0.38330300	3.85286900	-2.87262500
H	0.60507300	2.96637000	-0.92215800
C	0.47243200	3.65750600	-4.25226200
H	0.92770200	2.25695600	-5.82682600
H	0.09494500	4.82232100	-2.47752200
H	0.24976300	4.47350200	-4.93291800
C	1.32595000	-1.35709700	-2.17441600
C	2.34845800	-2.31642000	-2.14277300
C	0.11473000	-1.66834600	-2.81618100
C	2.16997400	-3.55362400	-2.76331800
H	3.28546500	-2.09450800	-1.64408000
C	-0.05671600	-2.90340700	-3.43725000
H	-0.68992700	-0.93953900	-2.84839100
C	0.97149200	-3.84870400	-3.41289200
H	2.97260500	-4.28434800	-2.74155500
H	-0.99197200	-3.12740200	-3.94121800
H	0.83806400	-4.80993000	-3.89962600

Zero-point correction= 0.702677 (Hartree/Particle)
Thermal correction to Energy= 0.737790
Thermal correction to Enthalpy= 0.738735
Thermal correction to Gibbs Free Energy= 0.635871
Sum of electronic and zero-point Energies= -4608.777021
Sum of electronic and thermal Energies= -4608.741908
Sum of electronic and thermal Enthalpies= -4608.740964
Sum of electronic and thermal Free Energies= -4608.843828

Table S27 Cartesian coordinates and energies of **TS_3$^{i\mathrm{Pr}}$_PH** at the B3LYP-D3(BJ)/def2-SVP//B3LYPD3(BJ)/6-311G(d,p) level of theory.

Ge	-0.29188600	0.38259100	-0.72287800
H	1.21427900	1.45867700	-0.93985700
P	2.85569800	1.39191900	-0.92394100
P	-1.41951300	1.11175400	1.31488300
C	3.16693600	-0.17731100	-0.03231700
C	4.48048700	-0.40840800	0.38285600
H	5.21990300	0.37484500	0.25334100
C	4.92749500	-1.62083000	0.94833300
H	5.96370800	-1.72471700	1.25473700
C	4.02523100	-2.65333500	1.05396700
C	2.68910500	-2.44720500	0.63735400
C	2.17063900	-1.21992100	0.12624500
C	0.75822700	-1.21258900	-0.17609300
C	0.05698400	-2.41197100	-0.05532000
H	-0.99677200	-2.41057600	-0.31680300
C	0.61169800	-3.62959100	0.40252000
H	-0.00877900	-4.51885100	0.46543900
C	1.93238700	-3.63572700	0.78036100
C	2.80691100	-4.74129600	1.33289900
H	2.87301200	-5.57783000	0.62860500

H	2.39610700	-5.15115600	2.26168300
C	4.19737200	-4.07023600	1.55695300
H	4.48391100	-4.07665900	2.61457700
H	4.99654300	-4.58968300	1.01780100
C	3.27535600	1.09368400	-2.72896500
H	3.24230600	2.09617400	-3.17394400
C	2.17687800	0.24402600	-3.39754300
H	2.47357600	0.01037000	-4.42495800
H	1.22329400	0.77837600	-3.43804900
H	2.01184300	-0.70322300	-2.87347600
C	4.67506900	0.50409700	-2.94935600
H	5.46524700	1.12350100	-2.51419000
H	4.87269000	0.43099600	-4.02388300
H	4.75582800	-0.50033000	-2.52490400
C	4.02611400	2.71723400	-0.29463100
H	5.04729700	2.38341100	-0.51721400
C	3.88516200	2.91414400	1.22261800
H	2.88755200	3.28145800	1.48196000
H	4.60923200	3.66198400	1.56103000
H	4.06533400	1.99366300	1.78213300
C	3.77353500	4.03300500	-1.05234800
H	3.95176200	3.94333500	-2.12692400
H	4.45141100	4.80413300	-0.67343100
H	2.74948800	4.39092000	-0.90346200
C	-2.04203700	-0.30891600	-1.30438500
C	-2.28848500	-0.94674700	-2.51433400
H	-1.46065000	-1.12691600	-3.19623300
C	-3.57925300	-1.39031200	-2.91614000
H	-3.69593100	-1.88378300	-3.87667200
C	-4.65163500	-1.17912700	-2.07667100
C	-4.41820500	-0.53352600	-0.84342200
C	-3.14628400	-0.09426200	-0.42504100
C	-3.08544600	0.54143800	0.85699000
C	-4.24709100	0.69575600	1.60899000
H	-4.20373300	1.19004100	2.57495500
C	-5.51016100	0.23662200	1.15439400
H	-6.38524600	0.38191900	1.78045300
C	-5.59252500	-0.38265800	-0.07725500
C	-6.75640400	-0.97761900	-0.84695500
H	-7.53245200	-0.22743400	-1.03334600
H	-7.23539500	-1.78284500	-0.27940700
C	-6.12963400	-1.50629200	-2.18405700
H	-6.29341500	-2.58237200	-2.30601100
H	-6.58240300	-1.02342100	-3.05669600
C	-1.48228500	2.97895200	1.36278300
H	-2.14305200	3.24024800	2.19836900
C	-2.09110400	3.53394900	0.06469100
H	-1.46236700	3.30311700	-0.80214800
H	-2.16782500	4.62338300	0.13898900
H	-3.09154700	3.13807000	-0.12181500
C	-0.08434100	3.56009800	1.61980100
H	-0.13610700	4.65241500	1.66722300
H	0.59441500	3.29204000	0.80324300
H	0.35263200	3.20852700	2.55951300
C	-0.89742400	0.49413200	3.00782000
H	0.18830500	0.65810200	3.00817900
C	-1.51512200	1.26719100	4.18373500
H	-2.60025800	1.13499200	4.22705600
H	-1.29894800	2.33789300	4.15399600
H	-1.10504100	0.87679100	5.12096400

C	-1.15665600	-1.01634200	3.12670800
H	-0.73635900	-1.38318200	4.06837900
H	-0.69594500	-1.57207400	2.30826900
H	-2.22883800	-1.23297000	3.12941200

Zero-point correction= 0.708221 (Hartree/Particle)
Thermal correction to Energy= 0.742492
Thermal correction to Enthalpy= 0.743437
Thermal correction to Gibbs Free Energy= 0.644310
Sum of electronic and zero-point Energies= -4156.603720
Sum of electronic and thermal Energies= -4156.569449
Sum of electronic and thermal Enthalpies= -4156.568505
Sum of electronic and thermal Free Energies= -4156.667631

Table S28 Cartesian coordinates and energies of **TS_3^{Ph}_PH** at the B3LYP-D3(BJ)/def2-SVP//B3LYPD3(BJ)/6-311G(d,p) level of theory.

Ge	-0.56548700	-0.19707200	-0.95453800
H	1.02269300	0.77068900	-1.00024100
P	2.59727500	0.53720100	-0.76460500
P	-1.70102200	0.90563600	0.88471700
C	2.65654000	-0.92080900	0.32882100
C	3.87443500	-1.18603700	0.95870800
H	4.67507400	-0.45837600	0.87305000
C	4.12903200	-2.36024300	1.69871300
H	5.09768400	-2.50293700	2.16768600
C	3.13169500	-3.30536000	1.77683600
C	1.88690000	-3.05093700	1.15456400
C	1.56095600	-1.86379900	0.43740300
C	0.21041500	-1.77742900	-0.05923800
C	-0.63547900	-2.86764500	0.14170200
H	-1.64770100	-2.80463400	-0.24693000
C	-0.27254100	-4.04966000	0.82633300
H	-0.99426300	-4.85329600	0.93991600
C	0.99513400	-4.13234300	1.35055000
C	1.67844000	-5.22440900	2.14647300
H	1.73149800	-6.15577300	1.57210500
H	1.12520900	-5.45752700	3.06253400
C	3.10012200	-4.65870400	2.45437100
H	3.27410500	-4.56268600	3.53188600
H	3.89239200	-5.31111000	2.07178800
C	-2.34550500	-0.67625000	-1.63402000
C	-2.61889000	-1.47086900	-2.74083200
H	-1.79996900	-1.97412600	-3.24953900
C	-3.92907900	-1.65628800	-3.26547500
H	-4.06687200	-2.29669500	-4.13191200
C	-4.98873600	-1.00221900	-2.67489200
C	-4.72874800	-0.19069800	-1.54998200
C	-3.44482800	-0.02606800	-0.99550100
C	-3.36339200	0.81332700	0.16053700
C	-4.50154900	1.45213700	0.64346700
H	-4.42208400	2.11148900	1.50352500
C	-5.77476400	1.27489800	0.04419800
H	-6.63386800	1.79599200	0.45556200
C	-5.88754900	0.43761900	-1.04928300
C	-7.07082100	0.02570000	-1.90478400
H	-7.54475800	0.89803400	-2.36783600
H	-7.84470200	-0.46292300	-1.30294600
C	-6.47404000	-0.94646500	-2.98194100
H	-6.93140500	-1.93996200	-2.92064400

H	-6.65987700	-0.58218900	-3.99791800
C	3.00244300	-0.02116400	-2.45157800
C	2.27883000	0.54054200	-3.51683500
C	3.99492500	-0.97775000	-2.71260600
C	2.56165400	0.16082800	-4.82924400
H	1.48730700	1.25822900	-3.32000200
C	4.27430000	-1.35029000	-4.02630100
H	4.54238000	-1.43216700	-1.89276800
C	3.56000700	-0.78049600	-5.08348100
H	2.00159600	0.59739700	-5.65015900
H	5.04611300	-2.08713500	-4.22541100
H	3.77846900	-1.07562500	-6.10513900
C	3.83656700	1.75803800	-0.22716200
C	4.78832200	2.27839600	-1.11847200
C	3.76252100	2.26806400	1.08186500
C	5.65970500	3.28394900	-0.69880400
H	4.85371900	1.89650800	-2.13145900
C	4.64160800	3.26573300	1.49427100
H	3.02496800	1.88016500	1.77854800
C	5.59075600	3.77657500	0.60465800
H	6.39719300	3.67687000	-1.39168600
H	4.58409900	3.64796900	2.50866700
H	6.27272900	4.55681400	0.92767000
C	-1.23548600	2.65757700	1.12023200
C	-1.33274300	3.28445000	2.37118800
C	-0.79988900	3.39364300	0.00552200
C	-1.00435000	4.63438100	2.50147700
H	-1.65756200	2.72225500	3.24057600
C	-0.47680400	4.74202000	0.14366100
H	-0.71744000	2.91366700	-0.96624200
C	-0.57833600	5.36346000	1.39052900
H	-1.08279000	5.11492900	3.47174300
H	-0.14384600	5.30722900	-0.72121000
H	-0.32399800	6.41359600	1.49541900
C	-1.65900900	0.10396300	2.52039400
C	-2.82068500	-0.26913000	3.21002200
C	-0.40047000	-0.16800400	3.08293900
C	-2.72265100	-0.88164500	4.46030800
H	-3.79687400	-0.08694800	2.77410300
C	-0.31010500	-0.77179600	4.33451500
H	0.50587900	0.08814400	2.54267000
C	-1.47109200	-1.12892000	5.02481100
H	-3.62605400	-1.16514300	4.99115600
H	0.66522100	-0.97243300	4.76676500
H	-1.39908600	-1.60378800	5.99838200

Zero-point correction= 0.699178 (Hartree/Particle)
Thermal correction to Energy= 0.734765
Thermal correction to Enthalpy= 0.735709
Thermal correction to Gibbs Free Energy= 0.629846
Sum of electronic and zero-point Energies= -4608.772712
Sum of electronic and thermal Energies= -4608.737126
Sum of electronic and thermal Enthalpies= -4608.736181
Sum of electronic and thermal Free Energies= -4608.842045

Table S29 Cartesian coordinates and energies of **3$^{i\text{Pr}}$H'** at the B3LYP-D3(BJ)/def2-SVP//B3LYPD3(BJ)/6-311G(d,p) level of theory.

Ge	0.37793200	-0.13628700	-0.89961100
H	0.00002900	-1.09652600	-2.03644100
P	-2.65281000	-1.31129000	-0.69659800
P	1.27513400	-1.47912600	0.85287800
C	-3.11560700	0.30972700	0.04827300
C	-4.40509200	0.55819900	0.51624300
H	-5.14006900	-0.23821700	0.47255100
C	-4.82910300	1.79737500	1.04658400
H	-5.85101800	1.91485200	1.39475300
C	-3.92393200	2.83099700	1.08315600
C	-2.60810700	2.60539900	0.61486500
C	-2.13478300	1.36197700	0.10510300
C	-0.74451400	1.34235600	-0.29259900
C	-0.00537100	2.52169700	-0.17670500
H	1.03839700	2.51670100	-0.46720600
C	-0.51985700	3.74641600	0.30576400
H	0.12473400	4.61890600	0.35159700
C	-1.82949600	3.78284900	0.71587300
C	-2.66741700	4.90646100	1.28689400
H	-2.73507700	5.74134000	0.58085300
H	-2.21990400	5.31100100	2.20108100
C	-4.06397500	4.26318900	1.55561700
H	-4.33015300	4.30452100	2.61753500
H	-4.86232300	4.78397200	1.01639400
C	-3.29278400	-1.11203400	-2.48541000
H	-2.85034700	-1.96813800	-3.01193800
C	-2.75946300	0.17912900	-3.13629000
H	-2.98223400	0.16483600	-4.20828900
H	-1.68156600	0.32165200	-3.02583800
H	-3.25042100	1.05840100	-2.70900900
C	-4.81856300	-1.16746100	-2.64848800
H	-5.25142200	-2.11352700	-2.31532000
H	-5.08091900	-1.04660000	-3.70566000
H	-5.30474900	-0.35489200	-2.09888300
C	-3.84005100	-2.55581400	0.07341300
H	-4.87025800	-2.21447800	-0.07653800
C	-3.58741500	-2.68457400	1.58313100
H	-2.57837600	-3.06298100	1.78368600
H	-4.29289400	-3.39684200	2.02461500
H	-3.70400300	-1.73138000	2.10584700
C	-3.68783400	-3.91915800	-0.62359000
H	-3.91659500	-3.87256900	-1.69174300
H	-4.37121900	-4.64727900	-0.17360800
H	-2.67160000	-4.31181000	-0.51712000
C	2.17799600	0.53775200	-1.23349600
C	2.60748600	1.30381800	-2.31046400
H	1.89783500	1.57128700	-3.08982700
C	3.94027300	1.78293900	-2.44217000
H	4.20629200	2.37812200	-3.31057400
C	4.85992200	1.48717600	-1.45780300
C	4.44469500	0.68946000	-0.37071900
C	3.13599900	0.18778300	-0.23775300
C	2.90001800	-0.66952900	0.88737400
C	3.92748100	-0.92776400	1.79042800
H	3.75597900	-1.59470300	2.62977100
C	5.22128800	-0.36393200	1.64468100
H	5.98521600	-0.59176700	2.38149700

C	5.48229800	0.43820400	0.55079400
C	6.73466600	1.15059900	0.07731500
H	7.56428000	0.44871100	-0.05809600
H	7.07032600	1.88674100	0.81584000
C	6.32541300	1.83463100	-1.27366100
H	6.47834500	2.91841000	-1.23904100
H	6.92840600	1.46328500	-2.10911700
C	1.54804100	-3.24274900	0.29787100
H	2.07566400	-3.72724700	1.12930500
C	2.44985200	-3.28435700	-0.94804100
H	1.97750400	-2.79297100	-1.80480200
H	2.62307700	-4.32923400	-1.22258300
H	3.42082900	-2.81719300	-0.77344500
C	0.20732100	-3.94402400	0.04480200
H	0.38653100	-4.96428200	-0.30784400
H	-0.36109600	-3.40430900	-0.71744000
H	-0.40928800	-4.00688000	0.94577700
C	0.36495900	-1.41715500	2.47699500
H	-0.65772000	-1.69928300	2.19829300
C	0.88999200	-2.41606600	3.52035700
H	1.90529400	-2.16945000	3.84418500
H	0.88141600	-3.44874900	3.16194800
H	0.24884600	-2.37187100	4.40628800
C	0.34466000	0.02557300	3.00976900
H	-0.28180100	0.06946900	3.90563600
H	-0.06544300	0.72146600	2.27483100
H	1.34880800	0.36239100	3.28275400

Zero-point correction= 0.711994 (Hartree/Particle)
Thermal correction to Energy= 0.748085
Thermal correction to Enthalpy= 0.749029
Thermal correction to Gibbs Free Energy= 0.642587
Sum of electronic and zero-point Energies= -4156.629202
Sum of electronic and thermal Energies= -4156.593111
Sum of electronic and thermal Enthalpies= -4156.592167
Sum of electronic and thermal Free Energies= -4156.698609

Table S30 Cartesian coordinates and energies of **3^{Ph}H'** at the B3LYP-D3(BJ)/def2-SVP//B3LYPD3(BJ)/6-311G(d,p) level of theory.

Ge	0.73069300	-0.49471400	0.82047100
H	0.18985800	0.32364400	1.98709300
P	-2.26108500	0.56073900	0.57440500
P	1.49957200	1.00615300	-0.86120600
C	-2.69185300	-1.17173600	0.07656400
C	-4.00865000	-1.52757700	-0.20608900
H	-4.78539200	-0.78113600	-0.08400900
C	-4.39747400	-2.80744500	-0.66167800
H	-5.44565800	-3.01228500	-0.85831200
C	-3.42222300	-3.75894100	-0.84893000
C	-2.07755300	-3.41969700	-0.57465000
C	-1.64931300	-2.14782200	-0.10224600
C	-0.23321900	-2.02141300	0.13181200
C	0.59795900	-3.10596100	-0.15105300
H	1.66585700	-3.00191400	0.01068200
C	0.13706800	-4.35075500	-0.63640100
H	0.84625200	-5.15009600	-0.82844200
C	-1.21336100	-4.50841200	-0.83847500
C	-2.02030500	-5.69319100	-1.32616700
H	-1.88395000	-6.56015200	-0.67074700

H	-1.69599000	-6.00719300	-2.32433800
C	-3.50021500	-5.19398200	-1.32732400
H	-3.94968100	-5.25774800	-2.32418500
H	-4.13076300	-5.79719500	-0.66519000
C	2.58173100	-0.92678500	1.23830500
C	3.05018800	-1.84644000	2.16845100
H	2.34111400	-2.48128500	2.69391700
C	4.42782900	-2.00074200	2.48701600
H	4.72119500	-2.74155500	3.22476700
C	5.35534000	-1.19156800	1.86570200
C	4.89576600	-0.24898900	0.92234300
C	3.53918800	-0.10595700	0.57407700
C	3.24761500	0.90605500	-0.39707200
C	4.26723600	1.70310400	-0.90794000
H	4.02767100	2.49260800	-1.61506300
C	5.62126500	1.53005700	-0.52384700
H	6.38161100	2.17842300	-0.94800100
C	5.93525600	0.54009800	0.38742600
C	7.24767200	0.09648000	1.00460400
H	7.73505700	0.92394800	1.53129600
H	7.95271900	-0.23870400	0.23629500
C	6.86262900	-1.06592100	1.98475600
H	7.36226800	-2.00183700	1.71265000
H	7.16404700	-0.84124000	3.01324200
C	-2.47490800	0.54265700	2.41044400
C	-2.74861600	1.73694600	3.09837800
C	-2.20722200	-0.61647200	3.15854600
C	-2.79074000	1.76124600	4.49250500
H	-2.94631500	2.64987000	2.54451500
C	-2.24659400	-0.58721100	4.55342200
H	-1.96796500	-1.54688000	2.65238300
C	-2.54343600	0.59898500	5.22500300
H	-3.01953600	2.69031000	5.00631100
H	-2.05023000	-1.49610500	5.11456500
H	-2.57977700	0.61873500	6.30977000
C	-3.66121100	1.58732100	-0.04097500
C	-4.90664400	1.69182800	0.60255500
C	-3.45401100	2.30376800	-1.23044000
C	-5.91887200	2.48337800	0.05988600
H	-5.08166700	1.16320500	1.53406500
C	-4.47061300	3.08811500	-1.77654100
H	-2.48834000	2.25416200	-1.72604400
C	-5.70472300	3.17887700	-1.13212600
H	-6.87575000	2.55642400	0.56805900
H	-4.29582800	3.63470700	-2.69841000
H	-6.49465200	3.79405700	-1.55209900
C	0.92198300	2.72730100	-0.77868700
C	0.77587000	3.49818400	-1.94075800
C	0.66617100	3.29509200	0.48041100
C	0.38714100	4.83477100	-1.83898100
H	0.95934000	3.06065000	-2.91677800
C	0.28148600	4.63040900	0.57074600
H	0.75744400	2.69637100	1.38183600
C	0.14278700	5.40038400	-0.58713700
H	0.27559700	5.43153500	-2.73870600
H	0.08462500	5.06838600	1.54397900
H	-0.16018300	6.43999700	-0.51234700
C	1.23080200	0.33900900	-2.53088000
C	2.25681200	0.31288300	-3.48725800
C	-0.04216900	-0.15854200	-2.85659200

C	2.00222100	-0.18345600	-4.76549100
H	3.25094400	0.66590800	-3.23547200
C	-0.28811300	-0.64765200	-4.13786000
H	-0.83432200	-0.16554700	-2.11573100
C	0.73152100	-0.66009100	-5.09188500
H	2.79824800	-0.20164700	-5.50300500
H	-1.27374700	-1.02757900	-4.38684000
H	0.53743300	-1.04648600	-6.08758500

Zero-point correction= 0.702474 (Hartree/Particle)
Thermal correction to Energy= 0.738225
Thermal correction to Enthalpy= 0.739170
Thermal correction to Gibbs Free Energy= 0.634858
Sum of electronic and zero-point Energies= -4608.801510
Sum of electronic and thermal Energies= -4608.765758
Sum of electronic and thermal Enthalpies= -4608.764814
Sum of electronic and thermal Free Energies= -4608.869125

Table S31 Cartesian coordinates and energies of **3^{iPr}H** at the B3LYP-D3(BJ)/def2-SVP//B3LYPD3(BJ)/6-311G(d,p) level of theory.

Ge	-1.12800000	4.64370000	8.82510000
H	-1.20070000	6.18240000	8.79100000
P	1.02340000	4.79030000	7.36330000
P	-3.28680000	4.67830000	10.29030000
C	2.10090000	4.88170000	8.80830000
C	3.43740000	5.27360000	8.81340000
H	3.87590000	5.67950000	7.90660000
C	4.26330000	5.15570000	9.95770000
H	5.29680000	5.48380000	9.90450000
C	3.73500000	4.59740000	11.10630000
C	2.37830000	4.21430000	11.11390000
C	1.51380000	4.37180000	10.00780000
C	0.14190000	4.02610000	10.19730000
C	-0.23790000	3.48570000	11.41790000
H	-1.27770000	3.22590000	11.57590000
C	0.66330000	3.27110000	12.49410000
H	0.29470000	2.83050000	13.41570000
C	1.97750000	3.66300000	12.34870000
C	3.17210000	3.63310000	13.28030000
H	3.42110000	2.60500000	13.56300000
H	2.96980000	4.17440000	14.20950000
C	4.33420000	4.29540000	12.46470000
H	4.68760000	5.21250000	12.94710000
H	5.19990000	3.63130000	12.38020000
C	1.67260000	3.32940000	6.40020000
H	1.01200000	3.25650000	5.52760000
C	1.51770000	2.06250000	7.25570000
H	1.82190000	1.18520000	6.67690000
H	0.48470000	1.91310000	7.58480000
H	2.15120000	2.11990000	8.14540000
C	3.11310000	3.50150000	5.90570000
H	3.23550000	4.39160000	5.28270000
H	3.39280000	2.63170000	5.30220000
H	3.81060000	3.56190000	6.74550000
C	1.31490000	6.28860000	6.31950000
H	2.38310000	6.29720000	6.06920000
C	0.98070000	7.56490000	7.10520000
H	-0.08730000	7.61400000	7.33530000
H	1.23800000	8.44190000	6.50340000

H	1.53780000	7.61760000	8.04450000
C	0.49450000	6.17940000	5.02450000
H	0.78940000	5.31520000	4.42250000
H	0.64400000	7.07690000	4.41650000
H	-0.57410000	6.09270000	5.24660000
C	-2.34650000	3.86430000	7.48920000
C	-1.93050000	3.29000000	6.29610000
H	-0.87640000	3.08970000	6.14780000
C	-2.81430000	2.96330000	5.23340000
H	-2.41620000	2.50180000	4.33470000
C	-4.15130000	3.27570000	5.36110000
C	-4.58940000	3.85890000	6.56840000
C	-3.73920000	4.12520000	7.66460000
C	-4.36190000	4.64640000	8.84120000
C	-5.72120000	4.94850000	8.81940000
H	-6.18740000	5.36120000	9.70910000
C	-6.53490000	4.72610000	7.68180000
H	-7.58780000	4.98740000	7.72100000
C	-5.96850000	4.15190000	6.55960000
C	-6.54340000	3.74890000	5.21700000
H	-6.95040000	4.61890000	4.69120000
H	-7.36760000	3.03820000	5.33170000
C	-5.34000000	3.12200000	4.43420000
H	-5.52200000	2.06690000	4.20470000
H	-5.17130000	3.62700000	3.47830000
C	-3.68980000	6.18160000	11.29030000
H	-4.76000000	6.13080000	11.52620000
C	-3.42170000	7.45590000	10.47680000
H	-2.35410000	7.56870000	10.26790000
H	-3.74820000	8.32970000	11.04930000
H	-3.95910000	7.44980000	9.52460000
C	-2.88630000	6.15880000	12.60040000
H	-3.13590000	5.29300000	13.22030000
H	-3.10390000	7.05980000	13.18210000
H	-1.81040000	6.13670000	12.39840000
C	-3.83620000	3.20370000	11.29410000
H	-3.18560000	3.20980000	12.17750000
C	-5.29220000	3.28310000	11.76650000
H	-5.98170000	3.26520000	10.91830000
H	-5.48710000	4.18110000	12.35920000
H	-5.51470000	2.41470000	12.39530000
C	-3.57160000	1.92470000	10.48550000
H	-3.80760000	1.04650000	11.09410000
H	-2.52710000	1.84890000	10.16750000
H	-4.20050000	1.89720000	9.59090000

Zero-point correction= 0.712918 (Hartree/Particle)
Thermal correction to Energy= 0.747827
Thermal correction to Enthalpy= 0.748771
Thermal correction to Gibbs Free Energy= 0.648678
Sum of electronic and zero-point Energies= -4156.634173
Sum of electronic and thermal Energies= -4156.599265
Sum of electronic and thermal Enthalpies= -4156.598320
Sum of electronic and thermal Free Energies= -4156.698414

Table S32 Cartesian coordinates and energies of **3^{Ph}H** at the B3LYP-D3(BJ)/def2-SVP//B3LYPD3(BJ)/6-311G(d,p) level of theory.

Ge	0.73069300	-0.49471400	0.82047100
H	0.18985800	0.32364400	1.98709300

P	-2.26108500	0.56073900	0.57440500
P	1.49957200	1.00615300	-0.86120600
C	-2.69185300	-1.17173600	0.07656400
C	-4.00865000	-1.52757700	-0.20608900
H	-4.78539200	-0.78113600	-0.08400900
C	-4.39747400	-2.80744500	-0.66167800
H	-5.44565800	-3.01228500	-0.85831200
C	-3.42222300	-3.75894100	-0.84893000
C	-2.07755300	-3.41969700	-0.57465000
C	-1.64931300	-2.14782200	-0.10224600
C	-0.23321900	-2.02141300	0.13181200
C	0.59795900	-3.10596100	-0.15105300
H	1.66585700	-3.00191400	0.01068200
C	0.13706800	-4.35075500	-0.63640100
H	0.84625200	-5.15009600	-0.82844200
C	-1.21336100	-4.50841200	-0.83847500
C	-2.02030500	-5.69319100	-1.32616700
H	-1.88395000	-6.56015200	-0.67074700
H	-1.69599000	-6.00719300	-2.32433800
C	-3.50021500	-5.19398200	-1.32732400
H	-3.94968100	-5.25774800	-2.32418500
H	-4.13076300	-5.79719500	-0.66519000
C	2.58173100	-0.92678500	1.23830500
C	3.05018800	-1.84644000	2.16845100
H	2.34111400	-2.48128500	2.69391700
C	4.42782900	-2.00074200	2.48701600
H	4.72119500	-2.74155500	3.22476700
C	5.35534000	-1.19156800	1.86570200
C	4.89576600	-0.24898900	0.92234300
C	3.53918800	-0.10595700	0.57407700
C	3.24761500	0.90605500	-0.39707200
C	4.26723600	1.70310400	-0.90794000
H	4.02767100	2.49260800	-1.61506300
C	5.62126500	1.53005700	-0.52384700
H	6.38161100	2.17842300	-0.94800100
C	5.93525600	0.54009800	0.38742600
C	7.24767200	0.09648000	1.00460400
H	7.73505700	0.92394800	1.53129600
H	7.95271900	-0.23870400	0.23629500
C	6.86262900	-1.06592100	1.98475600
H	7.36226800	-2.00183700	1.71265000
H	7.16404700	-0.84124000	3.01324200
C	-2.47490800	0.54265700	2.41044400
C	-2.74861600	1.73694600	3.09837800
C	-2.20722200	-0.61647200	3.15854600
C	-2.79074000	1.76124600	4.49250500
H	-2.94631500	2.64987000	2.54451500
C	-2.24659400	-0.58721100	4.55342200
H	-1.96796500	-1.54688000	2.65238300
C	-2.54343600	0.59898500	5.22500300
H	-3.01953600	2.69031000	5.00631100
H	-2.05023000	-1.49610500	5.11456500
H	-2.57977700	0.61873500	6.30977000
C	-3.66121100	1.58732100	-0.04097500
C	-4.90664400	1.69182800	0.60255500
C	-3.45401100	2.30376800	-1.23044000
C	-5.91887200	2.48337800	0.05988600
H	-5.08166700	1.16320500	1.53406500
C	-4.47061300	3.08811500	-1.77654100
H	-2.48834000	2.25416200	-1.72604400

C	-5.70472300	3.17887700	-1.13212600
H	-6.87575000	2.55642400	0.56805900
H	-4.29582800	3.63470700	-2.69841000
H	-6.49465200	3.79405700	-1.55209900
C	0.92198300	2.72730100	-0.77868700
C	0.77587000	3.49818400	-1.94075800
C	0.66617100	3.29509200	0.48041100
C	0.38714100	4.83477100	-1.83898100
H	0.95934000	3.06065000	-2.91677800
C	0.28148600	4.63040900	0.57074600
H	0.75744400	2.69637100	1.38183600
C	0.14278700	5.40038400	-0.58713700
H	0.27559700	5.43153500	-2.73870600
H	0.08462500	5.06838600	1.54397900
H	-0.16018300	6.43999700	-0.51234700
C	1.23080200	0.33900900	-2.53088000
C	2.25681200	0.31288300	-3.48725800
C	-0.04216900	-0.15854200	-2.85659200
C	2.00222100	-0.18345600	-4.76549100
H	3.25094400	0.66590800	-3.23547200
C	-0.28811300	-0.64765200	-4.13786000
H	-0.83432200	-0.16554700	-2.11573100
C	0.73152100	-0.66009100	-5.09188500
H	2.79824800	-0.20164700	-5.50300500
H	-1.27374700	-1.02757900	-4.38684000
H	0.53743300	-1.04648600	-6.08758500

Zero-point correction= 0.702474 (Hartree/Particle)
Thermal correction to Energy= 0.738225
Thermal correction to Enthalpy= 0.739170
Thermal correction to Gibbs Free Energy= 0.634858
Sum of electronic and zero-point Energies= -4608.801510
Sum of electronic and thermal Energies= -4608.765758
Sum of electronic and thermal Enthalpies= -4608.764814
Sum of electronic and thermal Free Energies= -4608.869125

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1 *i*Pr

Graphic report

	Weight [mg]	Name	N [%]	C [%]	H [%]	S [%]	Date Time
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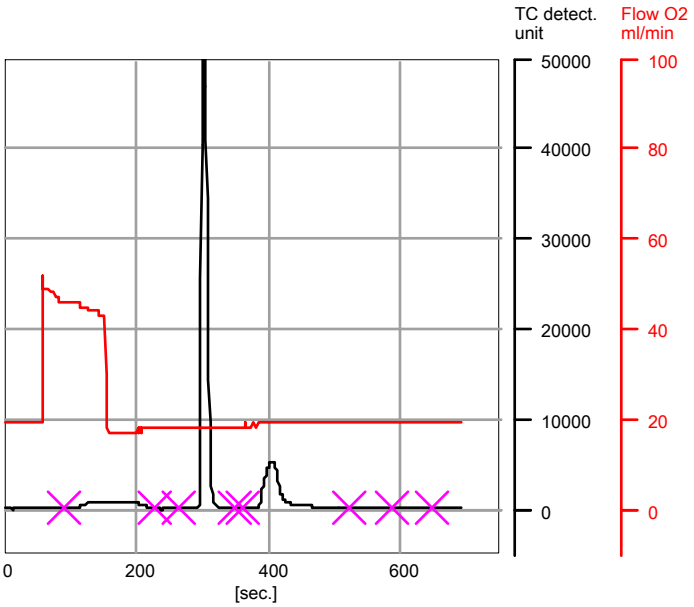

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Parameter report

Temperatures		
	Comb. tube	1150
	Reduct. Tube	850
	CO2 col.standby	0
	H2O col.standby	0
	SO2 col.standby	140
	Cool temp.	170
Time values		
	Flush time	10
	O2 delay	30
	Integrator reset delay peak N	20
	Integrator reset delay peak C	10
	Integrator reset delay peak H	3
	Integrator reset delay peak S	25
	H2O col.delay	1
Ball valve		
	Min. permitted ball valve current	20
	Max. permitted ball valve current	100
	Critical ball valve current	250
	Acoustic signal	no

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Methods report

Name	O2 dosing time	Autozero delay N	Autozero delay C	Autozero delay S	Peak anticipation N	Peak anticipation C	Peak anticipation H	Peak anticipation S	Desorpt.CO2	Desorpt.H2O	Desorpt.SO2	H2O col.delay
10mg120s	120	2	2	15	85	90	60	60	240	150	220	
10mg120sIRMS	120	2	2	15	150	210	240	120	260	170	230	
10mg120sIRMS_cal	120	2	2	15	85	90	60	60	130	150	220	
20mg150s	150	2	2	15	90	120	60	60	240	150	220	
20mg150sIRMS	150	2	2	15	150	210	240	120	260	170	230	
20mg150sIRMS_cal	150	2	2	15	90	120	60	60	130	150	220	
2mg70s	70	2	2	15	85	70	60	60	240	150	220	
2mg70sIRMS	70	2	2	15	150	210	240	120	260	170	230	
2mg70sIRMS_cal	70	2	2	15	85	70	60	60	130	150	220	
2mg80s	80	2	2	15	85	70	60	60	240	150	220	
30mg180s	180	2	2	15	120	120	60	60	240	150	220	
30mg180sIRMS	180	2	2	15	150	210	300	120	260	170	230	
30mg180sIRMS_cal	180	2	2	15	120	120	60	60	130	150	220	
40mg210s	210	2	2	15	150	120	60	60	240	150	220	
5mg90s	90	2	2	15	85	80	60	60	240	150	220	
5mg90s_2	90	2	2	15	85	80	60	60	240	150	230	
5mg90sIRMS	90	2	2	15	150	210	240	120	260	170	230	
5mg90sIRMS_cal	90	2	2	15	85	80	60	60	130	150	220	
Blank with O	60	2	2	15	85	70	60	60	240	150	220	
Blank without O	2	2	2	15	85	90	60	60	240	150	230	
Blnk Without 0	0	2	2	15	85	90	60	60	240	150	230	

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Coefficients report

Mode	CHNS			
	N	C	H	S
Coeff. a	-1.734218e-003	-1.190440e-004	1.392304e-003	1.249275e-003
Coeff. b	4.313727e-005	5.272650e-005	2.266024e-005	1.127746e-004
Coeff. c	-3.084791e-009	-8.078815e-011	-2.737666e-009	-1.211686e-010
Coeff. d	4.742319e-013	7.513235e-015	4.195303e-013	0.000000e+000
Coeff. e	0.000000e+000	0.000000e+000	0.000000e+000	0.000000e+000
Min.:	279.00	1241.00	165.00	230.00
Max.:	2781.00	10207.00	2800.00	2011.00
Modification time:				
Coeff. a	3.030178e-003	-1.487859e-002	1.248219e-002	-5.615332e-003
Coeff. b	3.709786e-005	5.342338e-005	1.522943e-005	1.166004e-004
Coeff. c	3.080614e-013	5.327586e-013	-8.301562e-012	-6.857837e-010
Coeff. d	2.886365e-017	6.288573e-019	3.025840e-017	3.598743e-014
Coeff. e	0.000000e+000	0.000000e+000	0.000000e+000	0.000000e+000
Min.:	2781.00	10207.00	2800.00	2011.00
Max.:	83332.00	397880.00	206642.00	17742.00
Modification time:				

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1 Ph

Graphic report

	Weight [mg]	Name	N [%]	C [%]	H [%]	S [%]	Date Time
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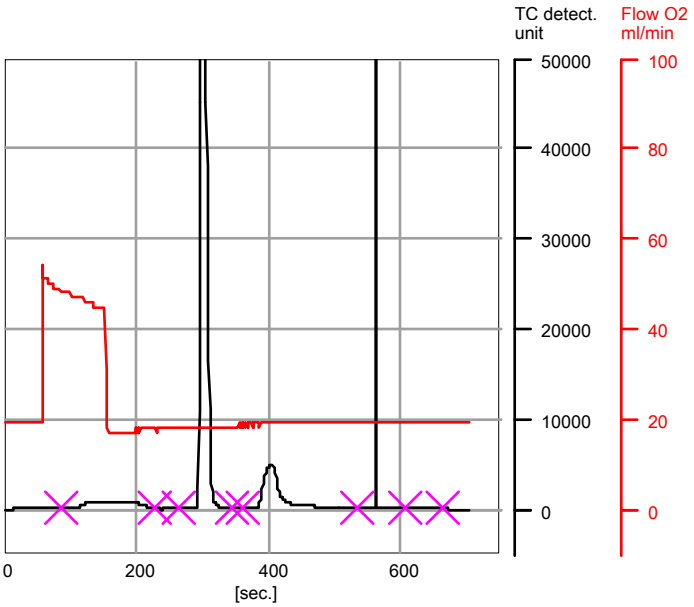

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Parameter report

Temperatures		
	Comb. tube	1150
	Reduct. Tube	850
	CO2 col.standby	0
	H2O col.standby	0
	SO2 col.standby	140
	Cool temp.	170
Time values		
	Flush time	10
	O2 delay	30
	Integrator reset delay peak N	20
	Integrator reset delay peak C	10
	Integrator reset delay peak H	3
	Integrator reset delay peak S	25
	H2O col.delay	1
Ball valve		
	Min. permitted ball valve current	20
	Max. permitted ball valve current	100
	Critical ball valve current	250
	Acoustic signal	no

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CHNS Elemental Analysis Report

Methods report

Name	O2 dosing time	Autozero delay N	Autozero delay C	Autozero delay S	Peak anticipation N	Peak anticipation C	Peak anticipation H	Peak anticipation S	Desorpt.CO2	Desorpt.H2O	Desorpt.SO2	H2O col.delay
10mg120s	120	2	2	15	85	90	60	60	240	150	220	
10mg120sIRMS	120	2	2	15	150	210	240	120	260	170	230	
10mg120sIRMS_cal	120	2	2	15	85	90	60	60	130	150	220	
20mg150s	150	2	2	15	90	120	60	60	240	150	220	
20mg150sIRMS	150	2	2	15	150	210	240	120	260	170	230	
20mg150sIRMS_cal	150	2	2	15	90	120	60	60	130	150	220	
2mg70s	70	2	2	15	85	70	60	60	240	150	220	
2mg70sIRMS	70	2	2	15	150	210	240	120	260	170	230	
2mg70sIRMS_cal	70	2	2	15	85	70	60	60	130	150	220	
2mg80s	80	2	2	15	85	70	60	60	240	150	220	
30mg180s	180	2	2	15	120	120	60	60	240	150	220	
30mg180sIRMS	180	2	2	15	150	210	300	120	260	170	230	
30mg180sIRMS_cal	180	2	2	15	120	120	60	60	130	150	220	
40mg210s	210	2	2	15	150	120	60	60	240	150	220	
5mg90s	90	2	2	15	85	80	60	60	240	150	220	
5mg90s_2	90	2	2	15	85	80	60	60	240	150	230	
5mg90sIRMS	90	2	2	15	150	210	240	120	260	170	230	
5mg90sIRMS_cal	90	2	2	15	85	80	60	60	130	150	220	
Blank with O	60	2	2	15	85	70	60	60	240	150	220	
Blank without O	2	2	2	15	85	90	60	60	240	150	230	
Blnk Without 0	0	2	2	15	85	90	60	60	240	150	230	

IISER, Pune
Chemistry Department
CHNS Elemental Analysis Report

Coefficients report

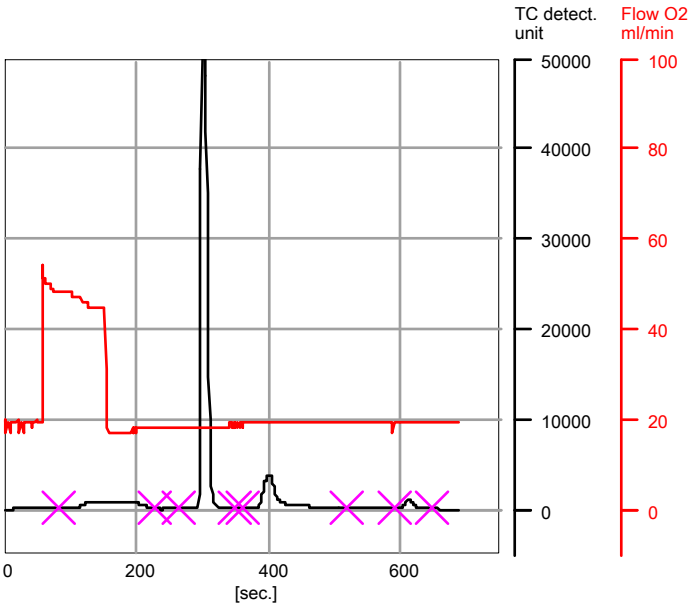
Mode	CHNS			
	N	C	H	S
Coeff. a	-1.734218e-003	-1.190440e-004	1.392304e-003	1.249275e-003
Coeff. b	4.313727e-005	5.272650e-005	2.266024e-005	1.127746e-004
Coeff. c	-3.084791e-009	-8.078815e-011	-2.737666e-009	-1.211686e-010
Coeff. d	4.742319e-013	7.513235e-015	4.195303e-013	0.000000e+000
Coeff. e	0.000000e+000	0.000000e+000	0.000000e+000	0.000000e+000
Min.:	279.00	1241.00	165.00	230.00
Max.:	2781.00	10207.00	2800.00	2011.00
Modification time:				
Coeff. a	3.030178e-003	-1.487859e-002	1.248219e-002	-5.615332e-003
Coeff. b	3.709786e-005	5.342338e-005	1.522943e-005	1.166004e-004
Coeff. c	3.080614e-013	5.327586e-013	-8.301562e-012	-6.857837e-010
Coeff. d	2.886365e-017	6.288573e-019	3.025840e-017	3.598743e-014
Coeff. e	0.000000e+000	0.000000e+000	0.000000e+000	0.000000e+000
Min.:	2781.00	10207.00	2800.00	2011.00
Max.:	83332.00	397880.00	206642.00	17742.00
Modification time:				

IISER, Pune
Chemistry Department
CHNS Elemental Analysis Report

2^{Ph}

Graphic report

	Weight [mg]	Name	N [%]	C [%]	H [%]	S [%]	Date Time
47	5.0430	2 PH 3	0.77	63.94	3.834	2.980	07.09.2023 21:05



IISER, Pune
Chemistry Department
CHNS Elemental Analysis Report

Parameter report

Temperatures		
	Comb. tube	1150
	Reduct. Tube	850
	CO2 col.standby	0
	H2O col.standby	0
	SO2 col.standby	140
	Cool temp.	170
Time values		
	Flush time	10
	O2 delay	30
	Integrator reset delay peak N	20
	Integrator reset delay peak C	10
	Integrator reset delay peak H	3
	Integrator reset delay peak S	25
	H2O col.delay	1
Ball valve		
	Min. permitted ball valve current	20
	Max. permitted ball valve current	100
	Critical ball valve current	250
	Acoustic signal	no

IISER, Pune
Chemistry Department
CHNS Elemental Analysis Report

Methods report

Name	O2 dosing time	Autozero delay N	Autozero delay C	Autozero delay S	Peak anticipation N	Peak anticipation C	Peak anticipation H	Peak anticipation S	Desorpt.CO2	Desorpt.H2O	Desorpt.SO2	H2O col.delay
10mg120s	120	2	2	15	85	90	60	60	240	150	220	
10mg120sIRMS	120	2	2	15	150	210	240	120	260	170	230	
10mg120sIRMS_cal	120	2	2	15	85	90	60	60	130	150	220	
20mg150s	150	2	2	15	90	120	60	60	240	150	220	
20mg150sIRMS	150	2	2	15	150	210	240	120	260	170	230	
20mg150sIRMS_cal	150	2	2	15	90	120	60	60	130	150	220	
2mg70s	70	2	2	15	85	70	60	60	240	150	220	
2mg70sIRMS	70	2	2	15	150	210	240	120	260	170	230	
2mg70sIRMS_cal	70	2	2	15	85	70	60	60	130	150	220	
2mg80s	80	2	2	15	85	70	60	60	240	150	220	
30mg180s	180	2	2	15	120	120	60	60	240	150	220	
30mg180sIRMS	180	2	2	15	150	210	300	120	260	170	230	
30mg180sIRMS_cal	180	2	2	15	120	120	60	60	130	150	220	
40mg210s	210	2	2	15	150	120	60	60	240	150	220	
5mg90s	90	2	2	15	85	80	60	60	240	150	220	
5mg90s_2	90	2	2	15	85	80	60	60	240	150	230	
5mg90sIRMS	90	2	2	15	150	210	240	120	260	170	230	
5mg90sIRMS_cal	90	2	2	15	85	80	60	60	130	150	220	
Blank with O	60	2	2	15	85	70	60	60	240	150	220	
Blank without O	2	2	2	15	85	90	60	60	240	150	230	
Blnk Without 0	0	2	2	15	85	90	60	60	240	150	230	

IISER, Pune
Chemistry Department
CHNS Elemental Analysis Report

Coefficients report

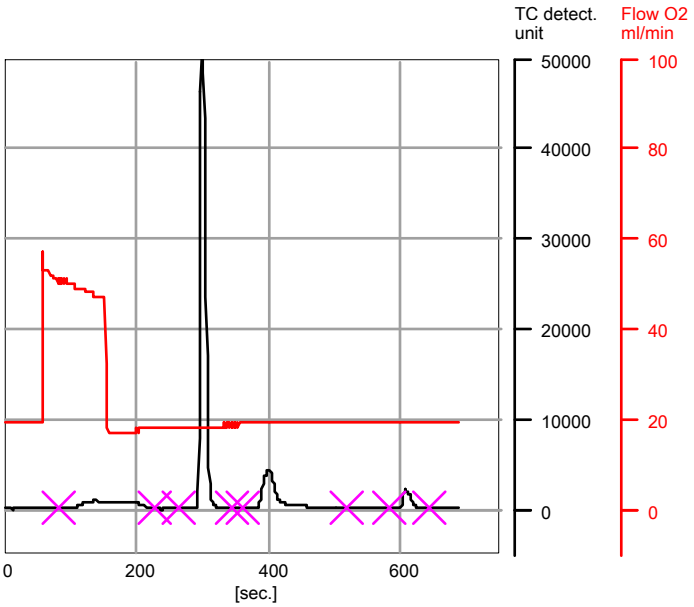
Mode	CHNS			
	N	C	H	S
Coeff. a	-1.734218e-003	-1.190440e-004	1.392304e-003	1.249275e-003
Coeff. b	4.313727e-005	5.272650e-005	2.266024e-005	1.127746e-004
Coeff. c	-3.084791e-009	-8.078815e-011	-2.737666e-009	-1.211686e-010
Coeff. d	4.742319e-013	7.513235e-015	4.195303e-013	0.000000e+000
Coeff. e	0.000000e+000	0.000000e+000	0.000000e+000	0.000000e+000
Min.:	279.00	1241.00	165.00	230.00
Max.:	2781.00	10207.00	2800.00	2011.00
Modification time:				
Coeff. a	3.030178e-003	-1.487859e-002	1.248219e-002	-5.615332e-003
Coeff. b	3.709786e-005	5.342338e-005	1.522943e-005	1.166004e-004
Coeff. c	3.080614e-013	5.327586e-013	-8.301562e-012	-6.857837e-010
Coeff. d	2.886365e-017	6.288573e-019	3.025840e-017	3.598743e-014
Coeff. e	0.000000e+000	0.000000e+000	0.000000e+000	0.000000e+000
Min.:	2781.00	10207.00	2800.00	2011.00
Max.:	83332.00	397880.00	206642.00	17742.00
Modification time:				

IISER, Pune
Chemistry Department
CHNS Elemental Analysis Report

3 *i*Pr

Graphic report

	Weight [mg]	Name	N [%]	C [%]	H [%]	S [%]	Date Time
22	5.1720	BA 3IPR 1	1.72	51.99	4.463	6.609	13.09.2023 17:00



IISER, Pune
Chemistry Department
CHNS Elemental Analysis Report

Parameter report

Temperatures		
	Comb. tube	1150
	Reduct. Tube	850
	CO2 col.standby	0
	H2O col.standby	0
	SO2 col.standby	140
	Cool temp.	170
Time values		
	Flush time	10
	O2 delay	30
	Integrator reset delay peak N	20
	Integrator reset delay peak C	10
	Integrator reset delay peak H	3
	Integrator reset delay peak S	25
	H2O col.delay	1
Ball valve		
	Min. permitted ball valve current	20
	Max. permitted ball valve current	100
	Critical ball valve current	250
	Acoustic signal	no

IISER, Pune
Chemistry Department
CHNS Elemental Analysis Report

Methods report

Name	O2 dosing time	Autozero delay N	Autozero delay C	Autozero delay S	Peak anticipation N	Peak anticipation C	Peak anticipation H	Peak anticipation S	Desorpt.CO2	Desorpt.H2O	Desorpt.SO2	H2O col.delay
10mg120s	120	2	2	15	85	90	60	60	240	150	220	
10mg120sIRMS	120	2	2	15	150	210	240	120	260	170	230	
10mg120sIRMS_cal	120	2	2	15	85	90	60	60	130	150	220	
20mg150s	150	2	2	15	90	120	60	60	240	150	220	
20mg150sIRMS	150	2	2	15	150	210	240	120	260	170	230	
20mg150sIRMS_cal	150	2	2	15	90	120	60	60	130	150	220	
2mg70s	70	2	2	15	85	70	60	60	240	150	220	
2mg70sIRMS	70	2	2	15	150	210	240	120	260	170	230	
2mg70sIRMS_cal	70	2	2	15	85	70	60	60	130	150	220	
2mg80s	80	2	2	15	85	70	60	60	240	150	220	
30mg180s	180	2	2	15	120	120	60	60	240	150	220	
30mg180sIRMS	180	2	2	15	150	210	300	120	260	170	230	
30mg180sIRMS_cal	180	2	2	15	120	120	60	60	130	150	220	
40mg210s	210	2	2	15	150	120	60	60	240	150	220	
5mg90s	90	2	2	15	85	80	60	60	240	150	220	
5mg90s_2	90	2	2	15	85	80	60	60	240	150	230	
5mg90sIRMS	90	2	2	15	150	210	240	120	260	170	230	
5mg90sIRMS_cal	90	2	2	15	85	80	60	60	130	150	220	
Blank with O	60	2	2	15	85	70	60	60	240	150	220	
Blank without O	2	2	2	15	85	90	60	60	240	150	230	
Blnk Without 0	0	2	2	15	85	90	60	60	240	150	230	

IISER, Pune
Chemistry Department
CHNS Elemental Analysis Report

Coefficients report

Mode	CHNS			
	N	C	H	S
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Coeff. b	4.313727e-005	5.272650e-005	2.266024e-005	1.127746e-004
Coeff. c	-3.084791e-009	-8.078815e-011	-2.737666e-009	-1.211686e-010
Coeff. d	4.742319e-013	7.513235e-015	4.195303e-013	0.000000e+000
Coeff. e	0.000000e+000	0.000000e+000	0.000000e+000	0.000000e+000
Min.:	279.00	1241.00	165.00	230.00
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Coeff. b	3.709786e-005	5.342338e-005	1.522943e-005	1.166004e-004
Coeff. c	3.080614e-013	5.327586e-013	-8.301562e-012	-6.857837e-010
Coeff. d	2.886365e-017	6.288573e-019	3.025840e-017	3.598743e-014
Coeff. e	0.000000e+000	0.000000e+000	0.000000e+000	0.000000e+000
Min.:	2781.00	10207.00	2800.00	2011.00
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Modification time:				