Supplementary Information for

Substitution of Hyp (Hyp = $Si(SiMe_3)_3$) at metalloid $[Ge_9(Hyp)_3]^-$ clusters using phosphine stabilized Au(I)Cl.

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Experimental data

General

All reactions were carried out under a nitrogen atmosphere using standard Schlenk technique. Solids were weighed in in a Glovebox Systems glovebox under an argon atmosphere. THF was dried over sodium and benzophenone and distilled twice prior to use, n-pentane was dried with CaH_2 and distilled prior to use. Deuterated solvents were stored under nitrogen atmosphere and 3 Å molecular sieve. $KGe_9(Hyp_3)$ (Hyp = $Si(SiMe_3)_3$)[1] and $(Bu_3P)AuCl$[2] were obtained according to literature, Bu_3P was acquired from Sigma Aldrich and distilled prior to use. *i*Pr_2PCl was acquired from Acros Organics and used after confirming NMR puritiy. *m*-*i*$Pr_2POC_6H_4OP$*i*Pr_2 was synthesized according to literature procedure and used with 97 % purity according to ^1H-NMR spectroscopy.[3]

NMR spectra were recorded on a Bruker AVIII-300WB or a Bruker AVII+500 spectrometer. ^1H-, ^{13}C-, and ^{29}Si-NMR spectra are referenced to Me_4Si and ^{31}P-NMR spectra are referenced to 85 % H_3PO_4 as external standards. ^1H-NMR spectra were calibrated to the residue proton signal of the solvent (C_6D_6 7.16 ppm, THF-d_8, 1.72), ^{13}C-NMR signals were calibrated to the solvent signal (C_6D_6 128.06 ppm).[4]

Synthesis of $[(n\mathrm{Bu}_3\mathrm{P})\mathrm{AuGe}_9(\mathrm{Hyp})_2\mathrm{Au}(\mathrm{P}n\mathrm{Bu}_3)]_2$ (1)

$(n\mathrm{Bu}_3\mathrm{P})\mathrm{AuCl}$ (311 µmol) and $n\mathrm{Bu}_3\mathrm{P}$ (0.08 ml, 311µmol) were dissolved in THF and cooled to -78 °C. $\mathrm{KGe}_9(\mathrm{Hyp}_3)$ was dissolved in THF separately and cooled to -78 °C. Via a steel cannula, the light red $\mathrm{KGe}_9(\mathrm{Hyp}_3)$ solution was added to the colourless solution over the course of 2 minutes while stirring. The solution turned into a dark maroon almost instantly. While stirring the reaction was allowed to warm to room temperature slowly and after 12 h the solvent was removed in vacuo. 460 mg of substance were then extracted with *n*-pentane and stored at -30 °C. After removing about half of the solvent in vacuo and filtration into a new flask black blocklike crystals can be obtained with 42 % yield.

Alternative synthesis: $(n\mathrm{Bu}_3\mathrm{P})\mathrm{AuCl}$ (244 µmol) and was dissolved in THF and cooled to -78 °C. $\mathrm{K}_2\mathrm{Ge}_9(\mathrm{Hyp})_2$ (122 µmol) was dissolved in THF separately and cooled to -78 °C. The $\mathrm{K}_2\mathrm{Ge}_9(\mathrm{Hyp})_2$ was added to the $(n\mathrm{Bu}_3\mathrm{P})\mathrm{AuCl}$ solution while stirring over 2 min and warmed to room temperature overnight. After removal of the solvent in vacuo the product was extracted with *n*-pentane and stored at -30 °C to crystallize with a 33 % yield.

^{1}H-NMR (300 MHz, $\mathrm{C}_6\mathrm{D}_6$): δ = 0.57 (s, 108 H, $\mathrm{Si}(\mathrm{Si}Me_3)_3$), 1.00 (t b, 18 H, $^3J_{\mathrm{HH}}$ = 6.80 Hz, terminal$(\mathrm{P\text{-}CH_2CH_2CH_2}CH_3)_2$), 1.25 (t b, 18 H, $^3J_{\mathrm{HH}}$ = 7.08 Hz, bridging$(\mathrm{P\text{-}CH_2CH_2CH_2}CH_3)_2$), 1.40 (m b, 12 H, terminal $(\mathrm{P\text{-}CH_2CH_2}CH_2\mathrm{CH_3})_2$), 1.63 (s b, 24 H, bridging$(\mathrm{P\text{-}CH_2CH_2}CH_2\mathrm{CH_3})_2$ and terminal$(\mathrm{P\text{-}CH_2}CH_2\mathrm{CH_2CH_3})_2$), 1.77 (m b, 12 H, bridging $(\mathrm{P\text{-}CH_2}CH_2\mathrm{CH_2CH_3})_2$), 1.77 (m b, 12 H, bridging $(\mathrm{P\text{-}CH_2}CH_2\mathrm{CH_2CH_3})_2$), 2.09 (s b, 12 H, terminal$(\mathrm{P\text{-}}CH_2\mathrm{CH_2CH_2CH_3})_2$), 2.26 (s b, 12 H, bridging$(\mathrm{P\text{-}}CH_2\mathrm{CH_2CH_2CH_3})_2$) ppm.

^{31}P{^{1}H}-NMR (121.49 MHz, $\mathrm{C}_6\mathrm{D}_6$): δ = 50.10 (m, terminal-P), 66.42 (m, bridging-P) ppm.

^{29}Si-ineptnd-NMR (59.63 MHz, $\mathrm{C}_6\mathrm{D}_6$): δ = -104.82 (s, $Si(\mathrm{SiMe}_3)_3$), -8.42 (decet, $^3J_{\mathrm{SiH}}$ = 6.39 Hz, $\mathrm{Si}(Si\mathrm{Me}_3)_3$) ppm.

Elemental analysis: (exp.) C 26.06 %, H 5.64 %, (calc.) C 25.901 %, H 5.589 %.

Synthesis of *p*-*i*$Pr_2POC_6H_4OP$*i*Pr_2

This compound was synthesized after a modified literature procedure.[5] Hydroquinone (550 mg; 5 mmol) was dissolved in THF (40 ml), Et_3N (4.2 ml; 30 mmol) was added and then *i*Pr_2PCl (1.6 ml, 10 mmol) was dissolved in 10 ml of THF and added slowly over 15 minutes while stirring. A colourless solid precipitates. After stirring over night the solvent was removed in vacuo and the crude product extracted with toluene (40 ml). After removing the toluene in vacuo a colourless oil remains, which is then dried in vacuo by adding pentane (10 ml) twice. *p*-*i*$Pr_2POC_6H_4OP$*i*Pr_2 is then received as a colourless solid with 90 % yield. 100 mg of the product were stored in 25 ml of THF at -30 °C to receive crystals suitable for x-ray diffraction.

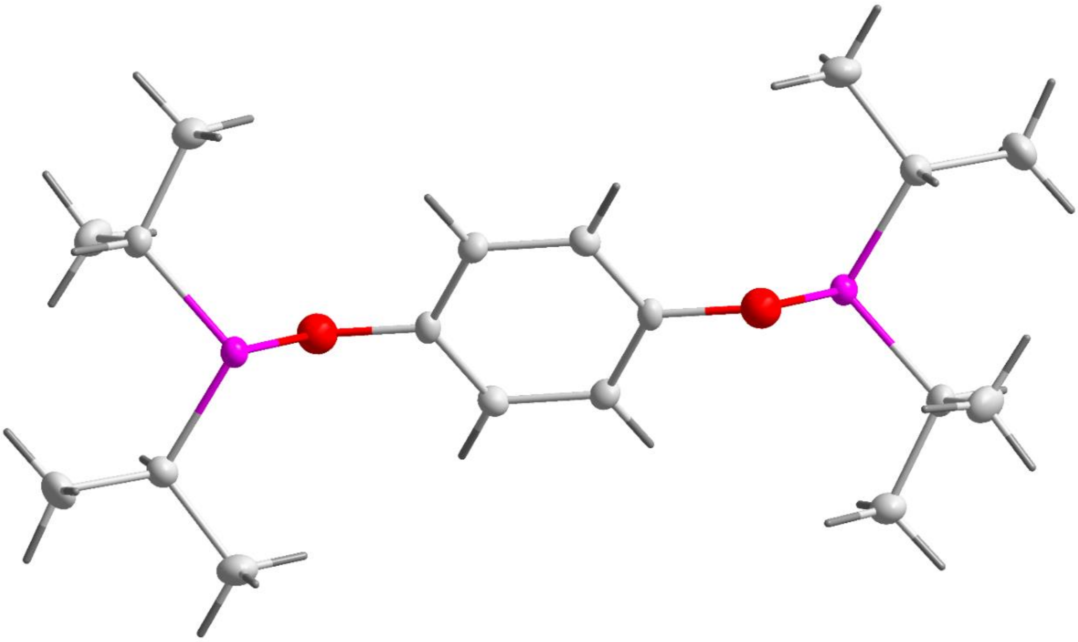

Figure S1: Molecular structure of *p*-*i*$Pr_2POC_6H_4OP$*i*Pr_2. Ellipsoids with 50 % probability. H-atoms as wires. Selected bond lengths [pm] and angles [°]: P1-O1 167.64(10), P-C111 185.39(14), P1-C121 184.72(14), O1-C1 138.79(14), C1-C2 138.95(18), C1-C3 138.88(18), C2-C3 139.35(17), C1-O1-P1 119.95(8), O1-C1-C2 118.08(11), O1-C1-C3^1 121.43(11), C1-C2-C3 119.61(12), C111-P1-C121 102.42(6).

^{1}H-NMR (300 MHz, C_6D_6): δ = 0.98 (dd, 12 H, -PCH(C*H*$_3$)$_2$), 1.14 (dd, 12 H, -PCH(C*H*$_3$)$_2$), 1.76 (d sept, 4 H, $^3J_{HH}$ = 7.10 Hz, $^2J_{HP}$ = 2.64 Hz,7.17 (br, 4 H, C_6H_4) PC*H*(CH_3)$_2$) ppm.

^{31}P{^{1}H}-NMR (121.49 MHz, C_6D_6): δ = 148.65 (s, P) ppm.

Elemental analysis: (exp.) C 63.30 %, H 9.18 %, (calc.) C 63.142 %, H 9.42 %.

Synthesis of $[\mathrm{Au}(i\mathrm{Pr_2POC_6H_4OP}i\mathrm{Pr_2})\mathrm{AuGe_9Hyp_2}]_2$ **(2)**

m-$i\mathrm{Pr_2POC_6H_4OP}i\mathrm{Pr_2}$ (65 mg, 213 µmol) was added to (tht)AuCl (112 mg, 350 µmol) in THF and stirred for 1 h. The solvent and free THT was removed in vacuo and the resulting colourless solid was redissolved in THF. $\mathrm{KGe_9(Hyp_3)}$ (500 mg, 350 µmol) was dissolved in THF and both solutions were cooled to -78 °C. While stirring the $\mathrm{KGe_9(Hyp_3)}$ solution was added to the other solution via a steel cannula. The reaction mixture turns to a black and brown solution almost instantly. The solution was then stirred overnight and brought to ambient temperature. The solvent was then removed in vacuo and 460 mg of substance extracted in *n*-pentane. The product crystallized at -30 °C in the form of black rhombohedral crystals with a yield of 37 %.

^{1}H-NMR (300 MHz, $\mathrm{C_6D_6}$): $\delta = 0.50$ (s, 108 H, $\mathrm{Si(Si}Me_3)_3$), 1,18-1,41 (m, $\mathrm{PCH(}CH_3)_2$), 2.23 (m, $\mathrm{P}CH\mathrm{(CH_3)_2}$) , 6.85 (s, $\mathrm{H_a}$), 7.65-7.80 (m, $\mathrm{H_b}$, $\mathrm{H_c}$ $\mathrm{H_d}$) ppm (see figure S1 for H assignments).

^{31}P{^{1}H}-NMR (121.49 MHz, $\mathrm{C_6D_6}$): $\delta = 148.23$ (s, free phosphine), 192.08 (s, unknown precursor), 193.50 (s) ppm.

^{29}Si-ineptnd-NMR (59.63 MHz, thf-d8): $\delta = -104.42$ (s, $Si\mathrm{(SiMe_3)_3}$), -9.08 (decet, $^3J_{\mathrm{SiH}} = 6.39$ Hz, $\mathrm{Si(}Si\mathrm{Me_3)_3}$) ppm.

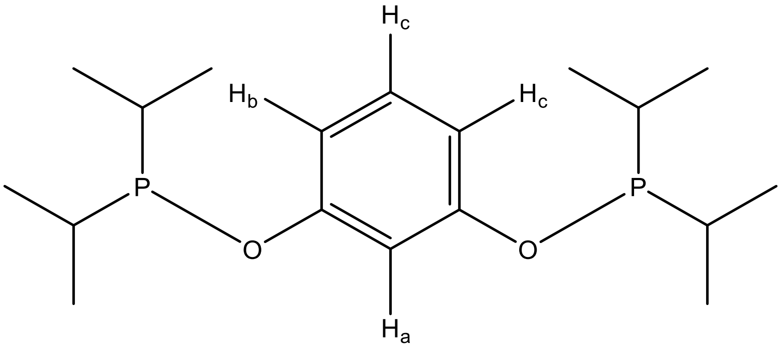

Fig S2: Molecular structure of the phoshine backbone with named H atoms for NMR peak assignment.

Elemental analysis: (exp.) C 21.23 %, H 4.49 %, (calc.) C 21.939 %, H 4.657 %.

Crystallographic data

Crystals were mounted on the diffractometer at 100 K. The data were collected on a XtaLAB Synergy-S X-ray diffractometer equipped with a PhotonJet-S microfocus X-ray source for monochromated MoKα radiation (λ = 0.71073 Å) and equipped with an Oxford Cryosystems cryostat. A numerical absorption correction was applied. The structure was solved by direct methods and refined against F^2 for all observed reflections. We used the programs SHELXS and SHELXL[6] within the Olex2 program package.[7]

The H atom positions in all compounds were refined using a riding model. The supplementary crystallographic data can be obtained online free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ; Fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk.

Table S1: crystallographic data.

	[(*n*Bu$_3$P)AuGe$_9$(Hyp)$_2$ Au(P*n*Bu$_3$)]$_2$ (**1**)	[Au(*i*Pr$_2$PC$_6$H$_4$P*i*Pr$_2$)Au Ge$_9$Hyp$_2$]$_2$ (**2**)	1,4-*i*Pr$_2$POC$_6$H$_4$OP*i*Pr$_2$
Empirical formula	$C_{84}H_{216}Au_4Ge_{18}P_4Si_{16}$	$C_{72}H_{172}Au_4Ge_{18}O_4P_4Si_{16}$	$C_{18}H_{32}O_2P_2$
Formula weight	3894.36	3769.89	342.37
Temperature/K	100.00(11)	100	100
Crystal system	monoclinic	monoclinic	Triclinic
Space group	$P2_1/n$	C2/c	$P\bar{1}$
a/Å	18.2022(2)	15.7399(19)	5.6229(12)
b/Å	15.1707(2)	24.623(3)	7.5296(16)
c/Å	27.4875(3)	35.814(4)	11.956(3)
α/°	90	90	85.464(3)
β/°	101.1190(10)	96.305(2)	80.159(3)
γ/°	90	90	79.593(18)
Volume/Å^3	7447.92(15)	13796(3)	489.92(18)
Z	2	4	1

ρ_{calc}g/cm^3	1.737	1.815	1.160
μ/mm^{-1}	7.695	8.307	0.227
F(000)	3792.0	7248.0	186.0
Crystal size/mm^3	0.154 × 0.123 × 0.053	0.215 × 0.15 × 0.14	0.389 × 0.183 × 0.106
Radiation	Mo Kα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.002 to 51.998	4.008 to 61.188	5.508 to 56.732
Index ranges	-22 ≤ h ≤ 22, -18 ≤ k ≤ 18, -33 ≤ l ≤ 33	-22 ≤ h ≤ 22, -35 ≤ k ≤ 35, -51 ≤ l ≤ 38	-7 ≤ h ≤ 7, -10 ≤ k ≤ 10, -15 ≤ l ≤ 15
Reflections collected	174242	97050	7786
Independent reflections	14643 [R_{int} = 0.0508, R_{sigma} = 0.0208]	21106 [R_{int} = 0.0685, R_{sigma} = 0.0588]	2457 [Rint = 0.0320, Rsigma = 0.0326]
Data/restraints/parameters	14643/48/642	21106/12/598	245/0/104
Goodness-of-fit on F^2	1.040	1.013	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0278, wR_2 = 0.0633	R_1 = 0.0350, wR_2 = 0.0707	R1 = 0.0326, wR2 = 0.0818
Final R indexes [all data]	R_1 = 0.0375, wR_2 = 0.0692	R_1 = 0.0555, wR_2 = 0.0774	R1 = 0.0372, wR2 = 0.0858
Largest diff. peak/hole / e Å^{-3}	3.31/-2.38	1.23/-1.08	0.41/-0.22
CDCC number	2170156	2170157	2170158

NMR spectroscopy

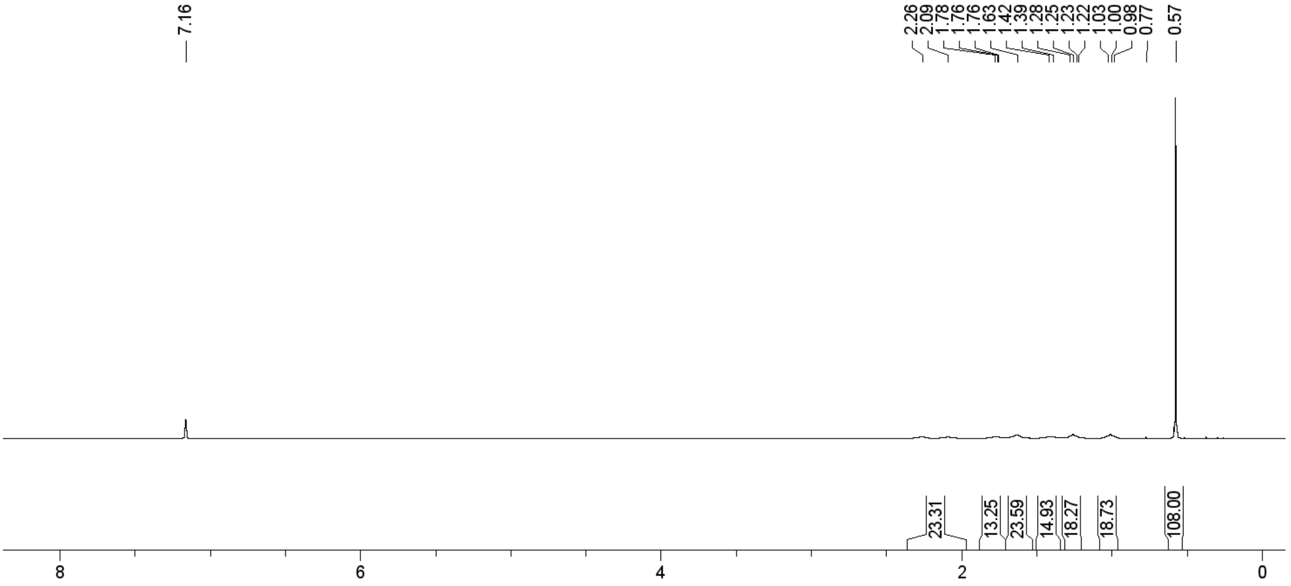

Figure S3: ^{1}H-NMR spectrum of **1** in C_6D_6.

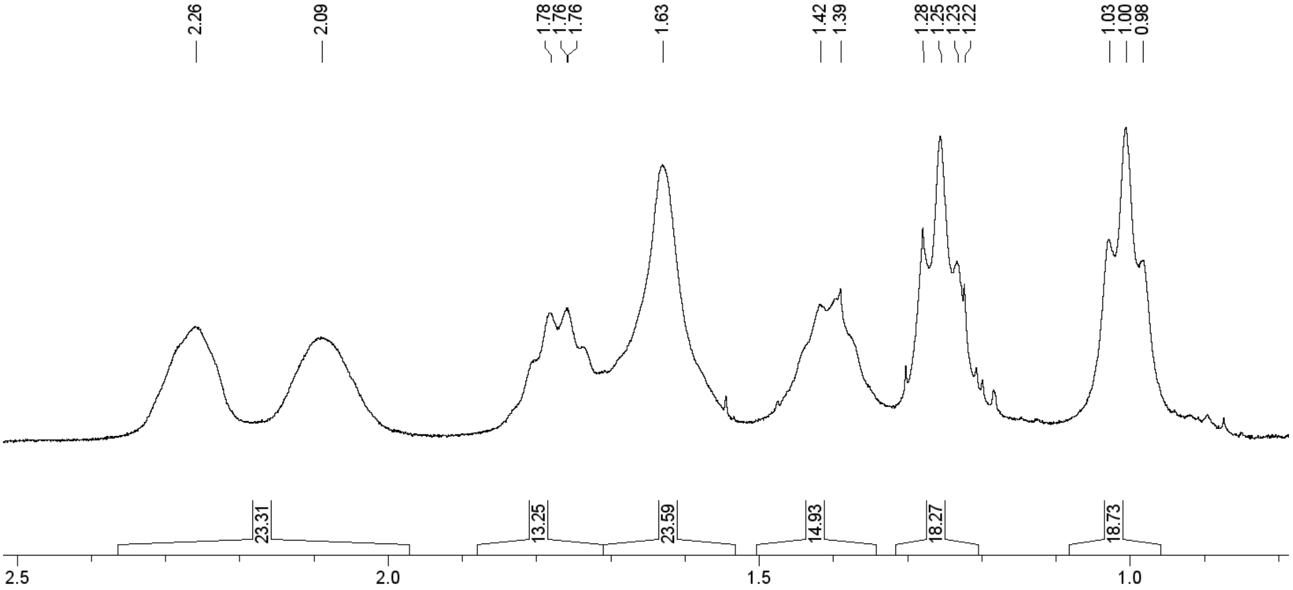

Figure S4: Detailled cutout of the ^{1}H-NMR spectrum of **1** in C_6D_6.

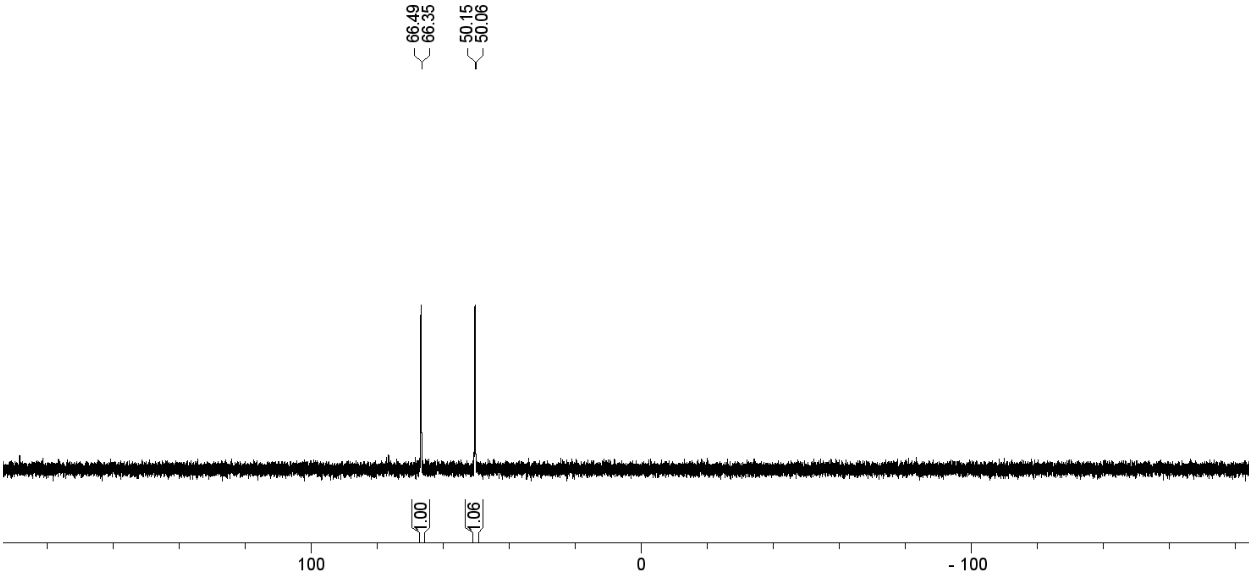

Figure S5: ^{31}P-{^{1}H}-NMR spectrum of **1** in C_6D_6.

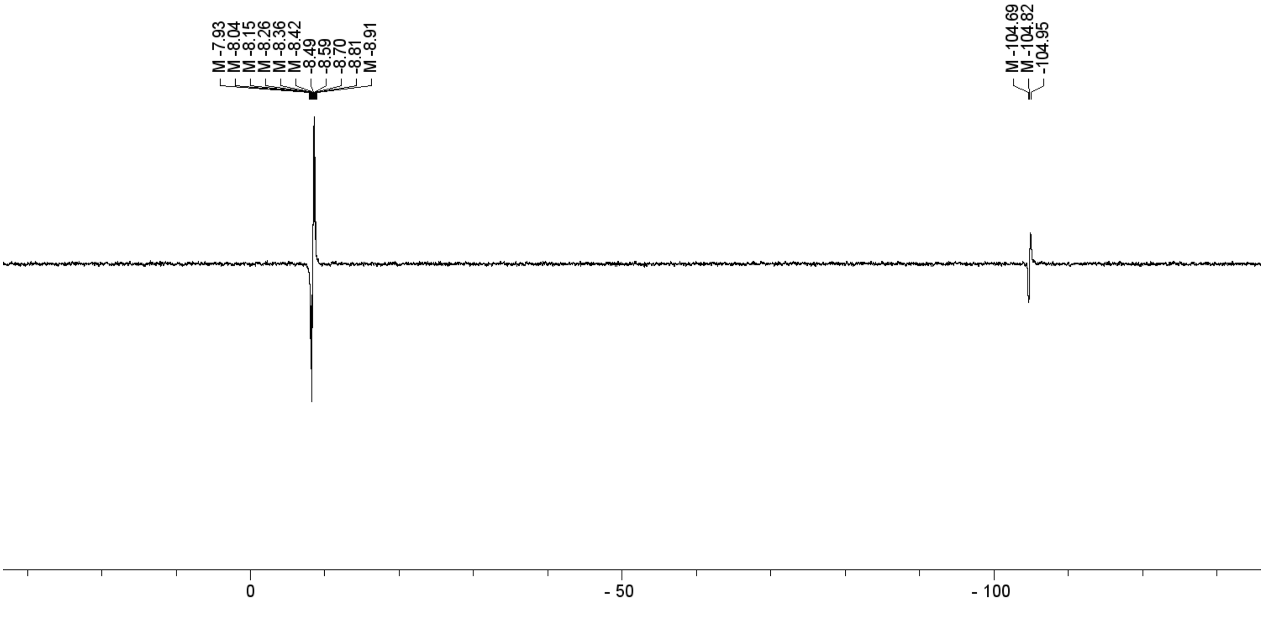

Figure S6: ^{29}Si-inept-nd-NMR spectrum of **1** in C_6D_6.

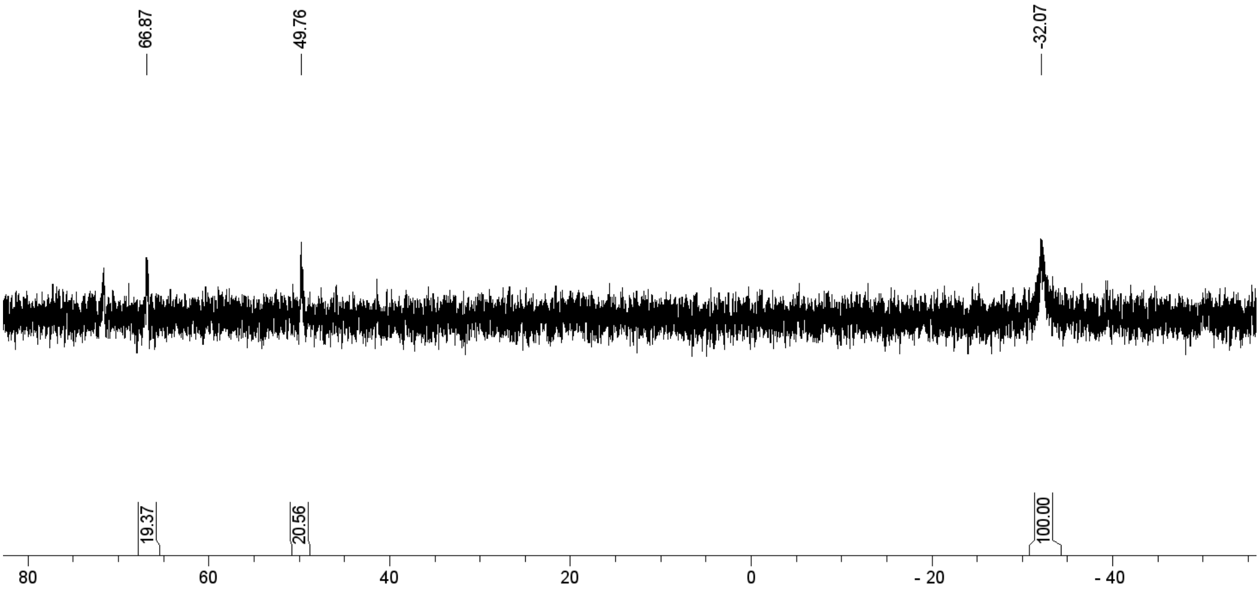

Figure S7: ^{31}P-{^{1}H}-NMR spectrum of *n*Bu$_3$PAuCl, *n*Bu$_3$P and KGe$_9$Hyp$_3$ in THF and C_6D_6 5 min after reaction start at -78 °C (flask temperature) measured at 25 °C.

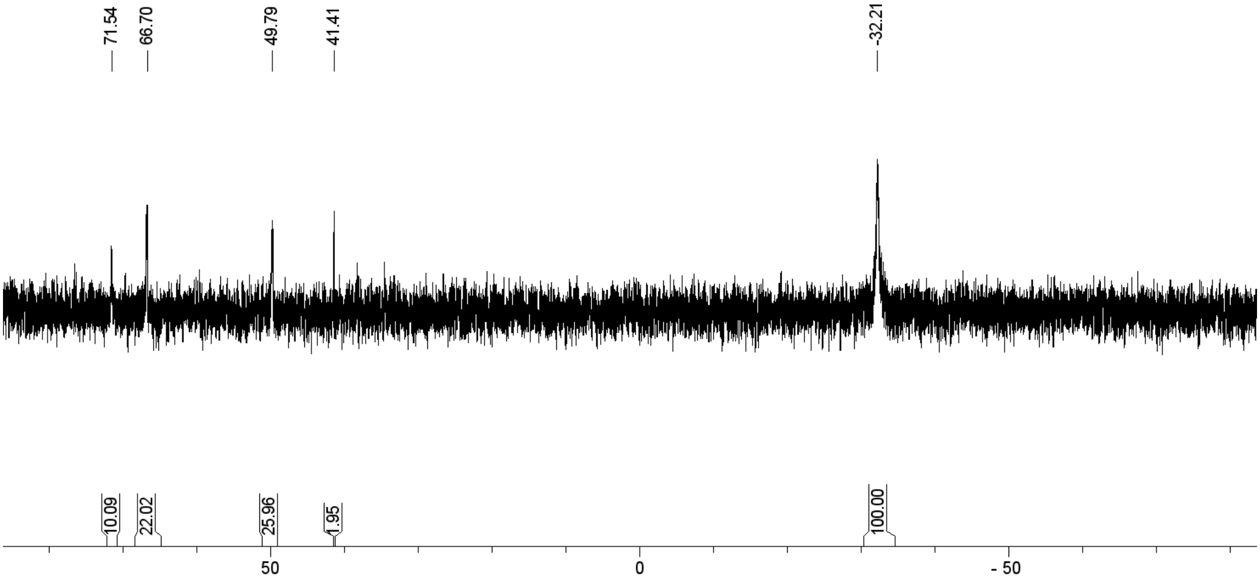

Figure S8: ^{31}P-{^{1}H}-NMR spectrum of (*n*Bu$_3$P)AuCl, *n*Bu$_3$P and KGe$_9$(Hyp$_3$) in THF and C_6D_6 3 h after reaction start at -50 °C (flask temperature) measured at 25 °C.

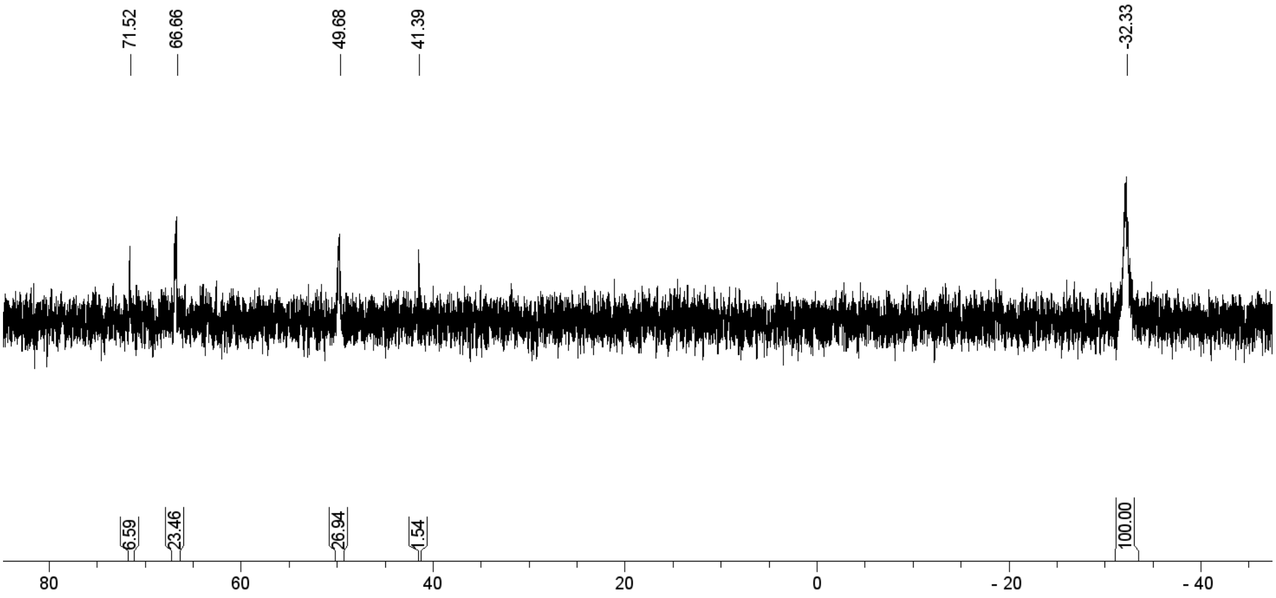

Figure S9: ^{31}P-{^{1}H}-NMR spectrum of (nBu$_3$P)AuCl, nBu$_3$P and KGe$_9$(Hyp$_3$) in THF and C_6D_6 5.5 h after reaction start at +5 °C (flask temperature) measured at 25 °C.

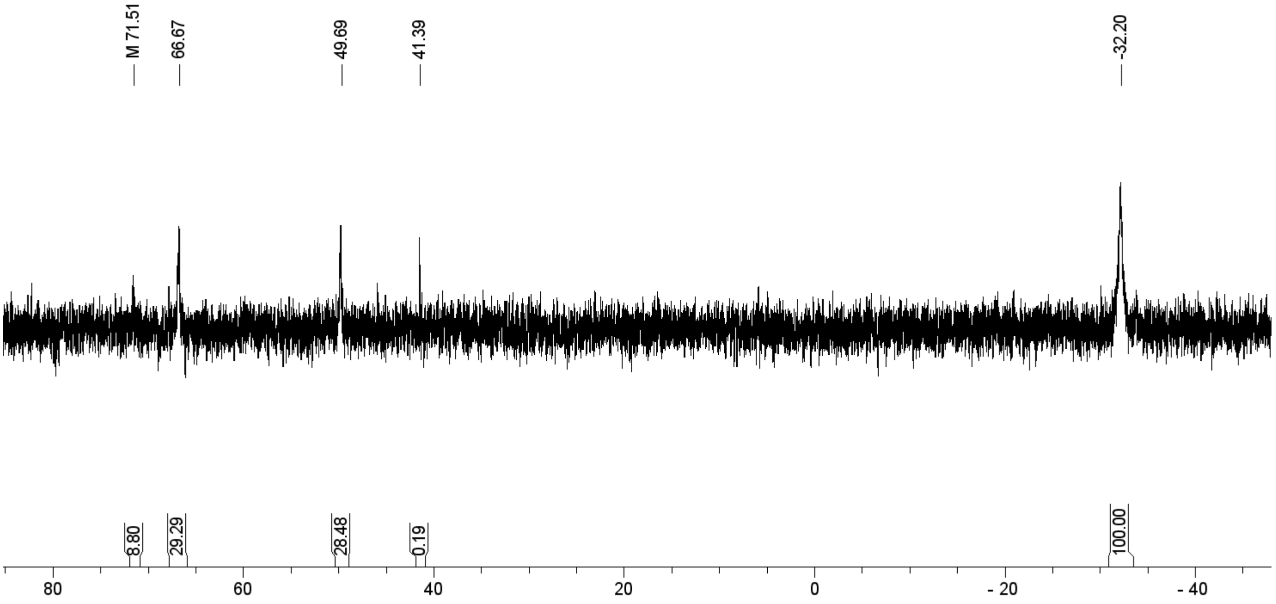

Figure S10: ^{31}P-{^{1}H}-NMR spectrum of (nBu$_3$P)AuCl, nBu$_3$P and KGe$_9$(Hyp$_3$) in THF and C_6D_6 7.5 h after reaction start at 25 °C.

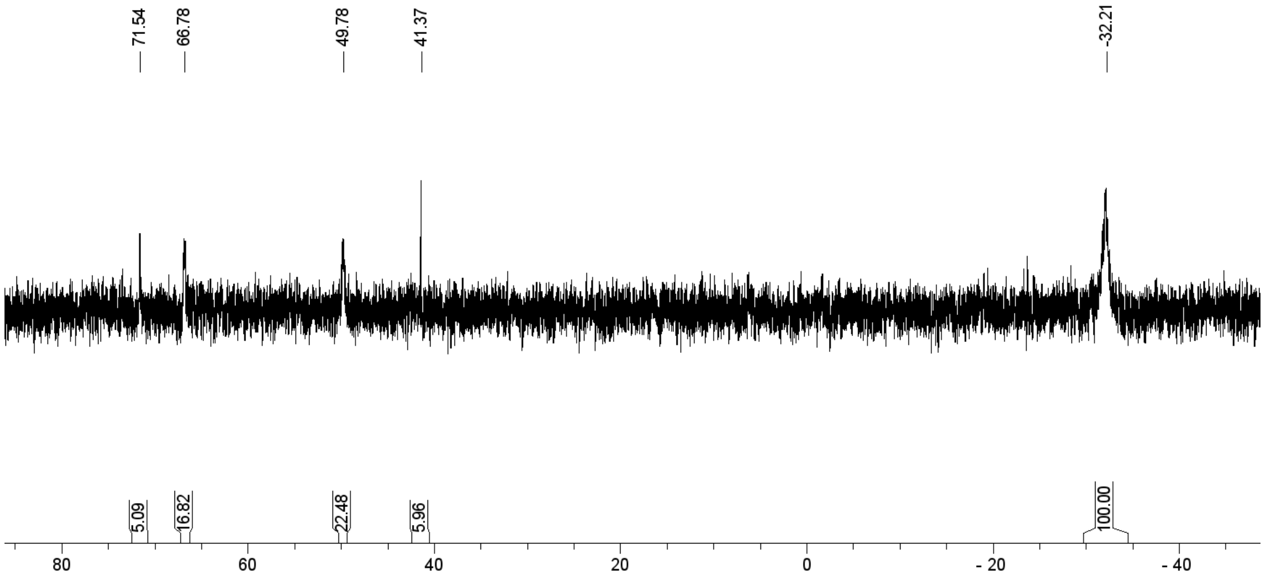

Figure S11: ^{31}P-{^{1}H}-NMR spectrum of (*n*Bu$_3$P)AuCl, *n*Bu$_3$P and KGe$_9$(Hyp$_3$) in THF and C_6D_6 25 h after reaction start at 25 °C.

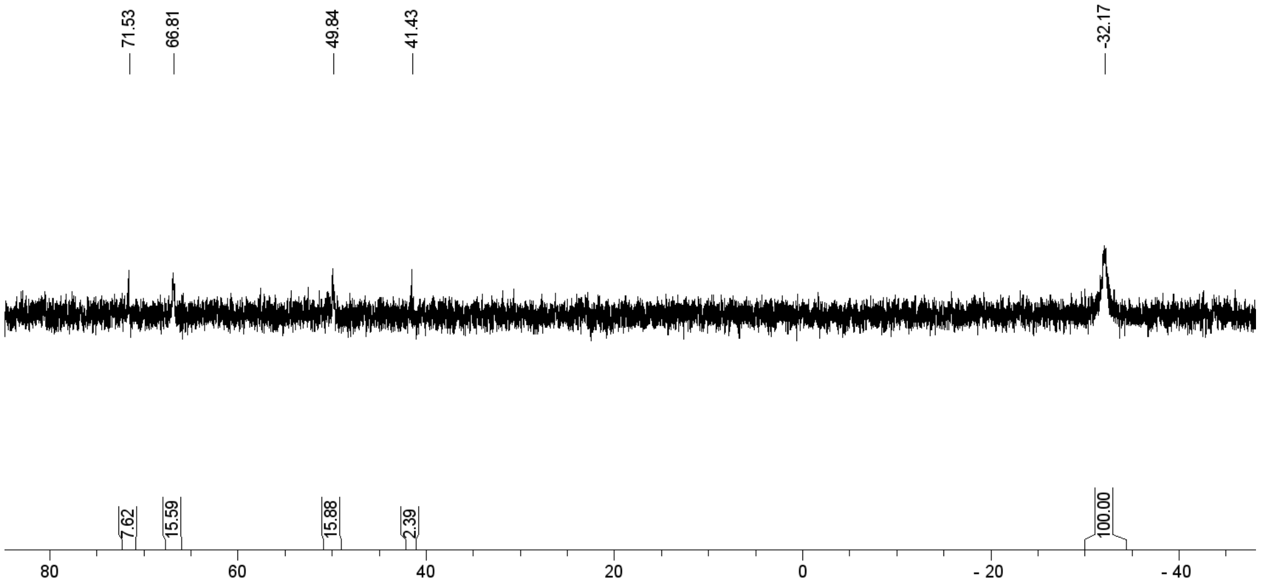

Figure S12: ^{31}P-{^{1}H}-NMR spectrum of (*n*Bu$_3$P)AuCl, *n*Bu$_3$P and KGe$_9$(Hyp$_3$) in THF and C_6D_6 32 h after reaction start at 25 °C.

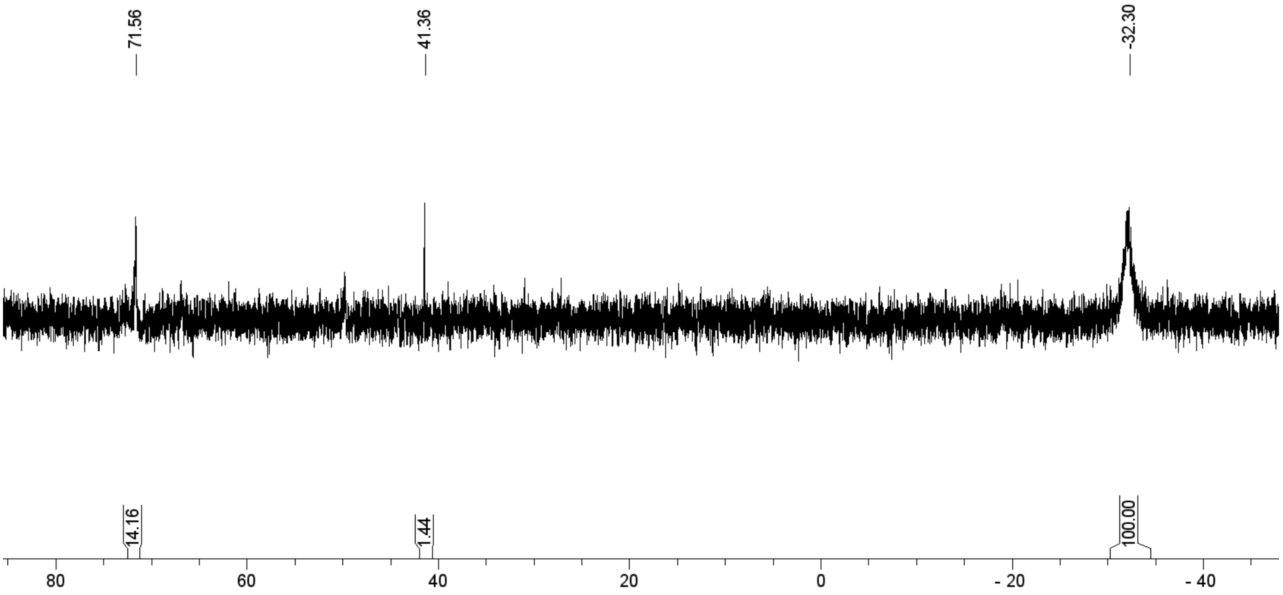

Figure S13: ^{31}P-{^{1}H}-NMR spectrum of (*n*Bu$_3$P)AuCl, *n*Bu$_3$P and KGe$_9$(Hyp$_3$) in THF and C$_6$D$_6$ 4 d after reaction start at 25 °C.

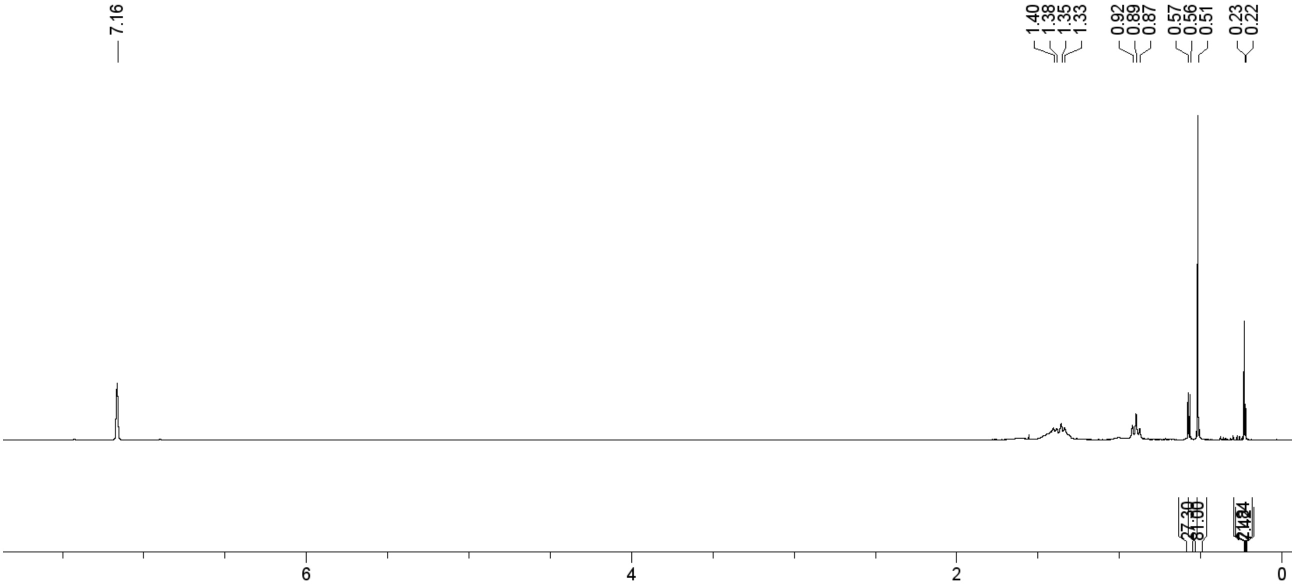

Figure S14: ^{1}H-NMR spectrum of (*n*Bu$_3$P)AuCl, *n*Bu$_3$P and KGe$_9$(Hyp$_3$) in C$_6$D$_6$ 4 d during the reaction at 25 °C.

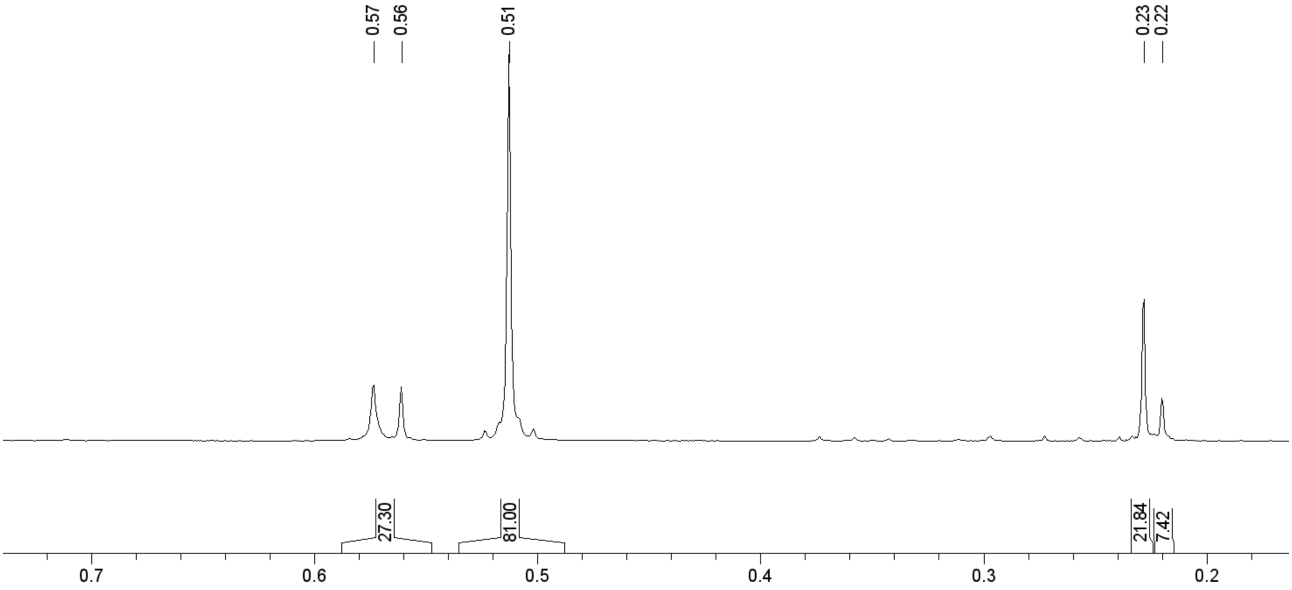

Figure S15: Detailled cutout ^{1}H-NMR spectrum of (nBu$_3$P)AuCl, nBu$_3$P and KGe$_9$(Hyp$_3$) in C$_6$D$_6$ 4 d during the reaction at 25 °C.

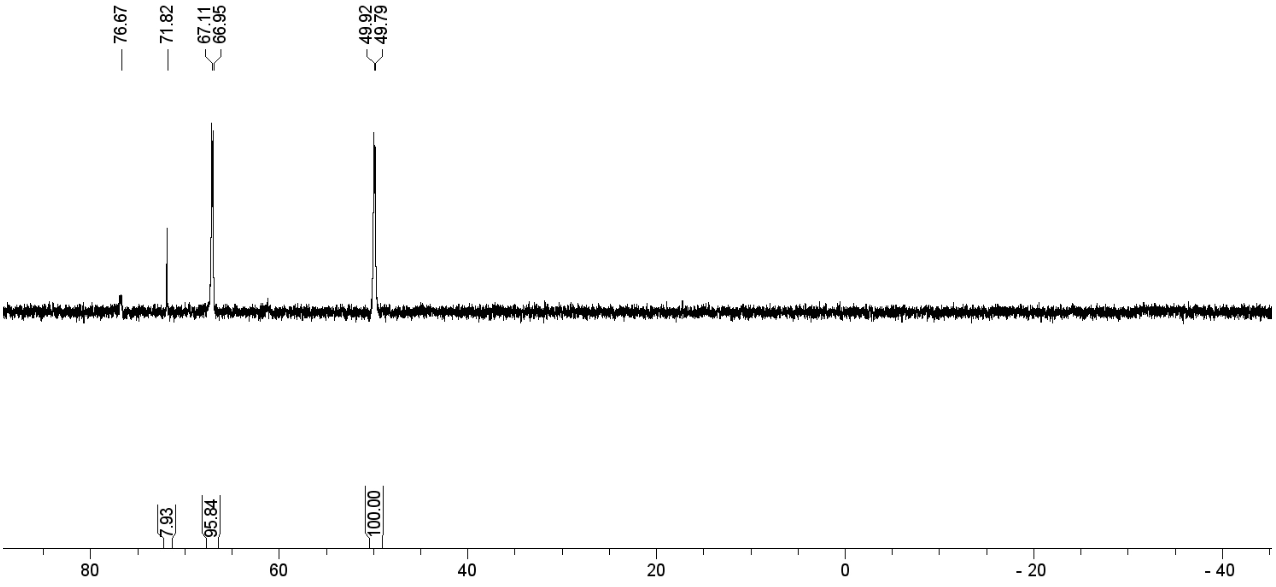

Figure S16: ^{31}P-{^{1}H}-NMR spectrum of **1** and Hyp-Cl in THF-d$_8$ directly after start of the reaction at 25 °C.

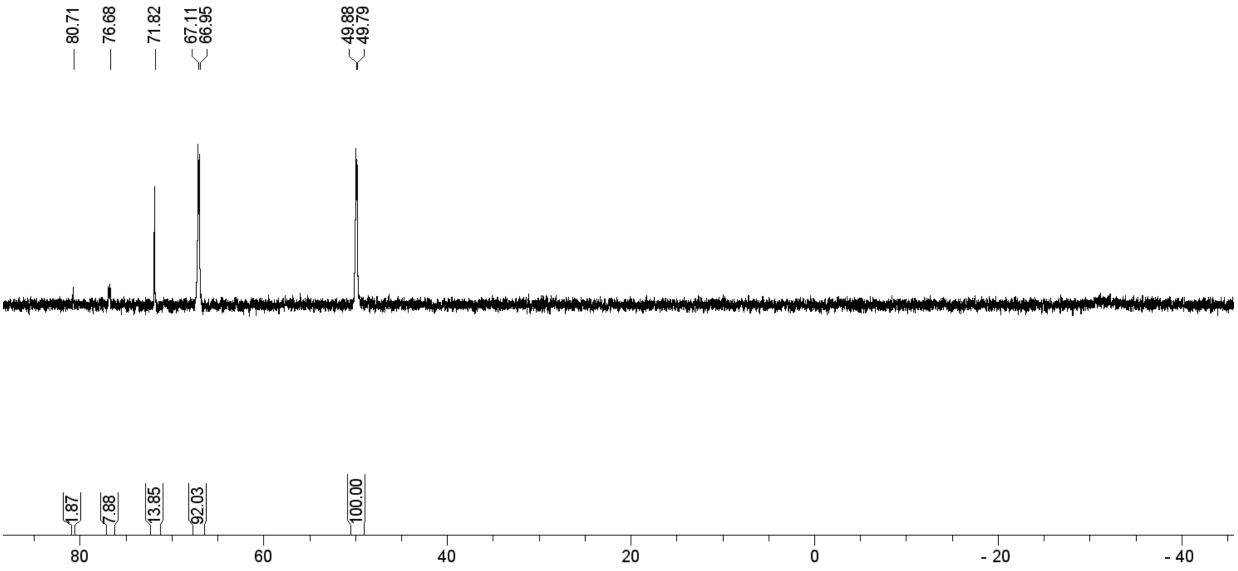

Figure S17: ^{31}P-{^{1}H}-NMR spectrum of **1** and Hyp-Cl in THF-d$_8$ 1 h after start of the reaction at 25 °C.

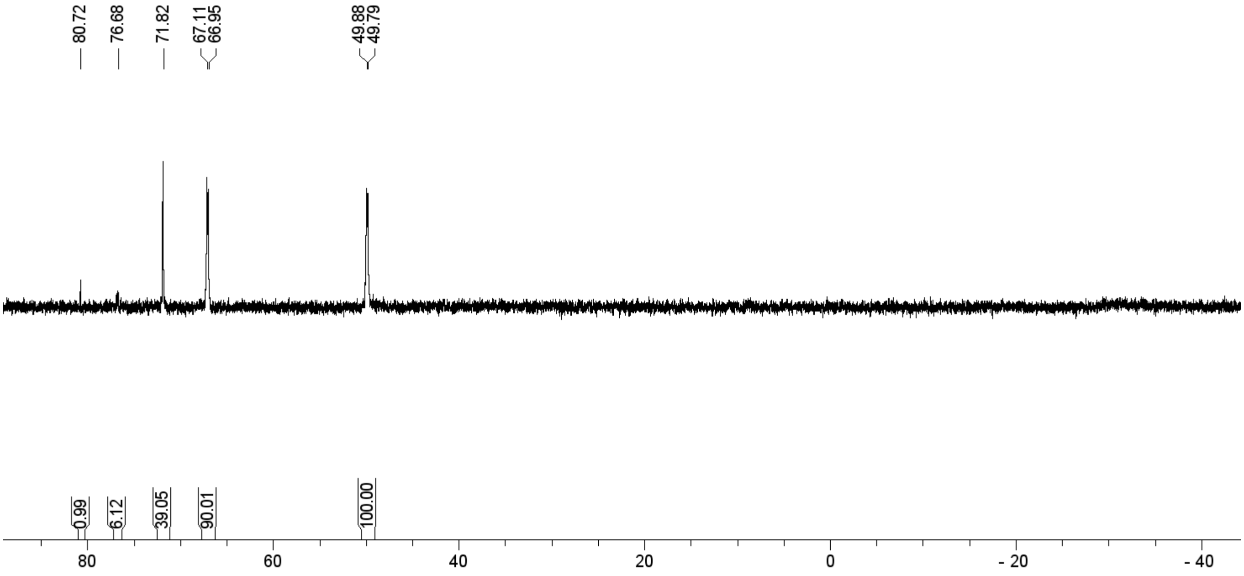

Figure S18: ^{31}P-{^{1}H}-NMR spectrum of **1** and Hyp-Cl in THF-d$_8$ 4 h after start of the reaction at 25 °C.

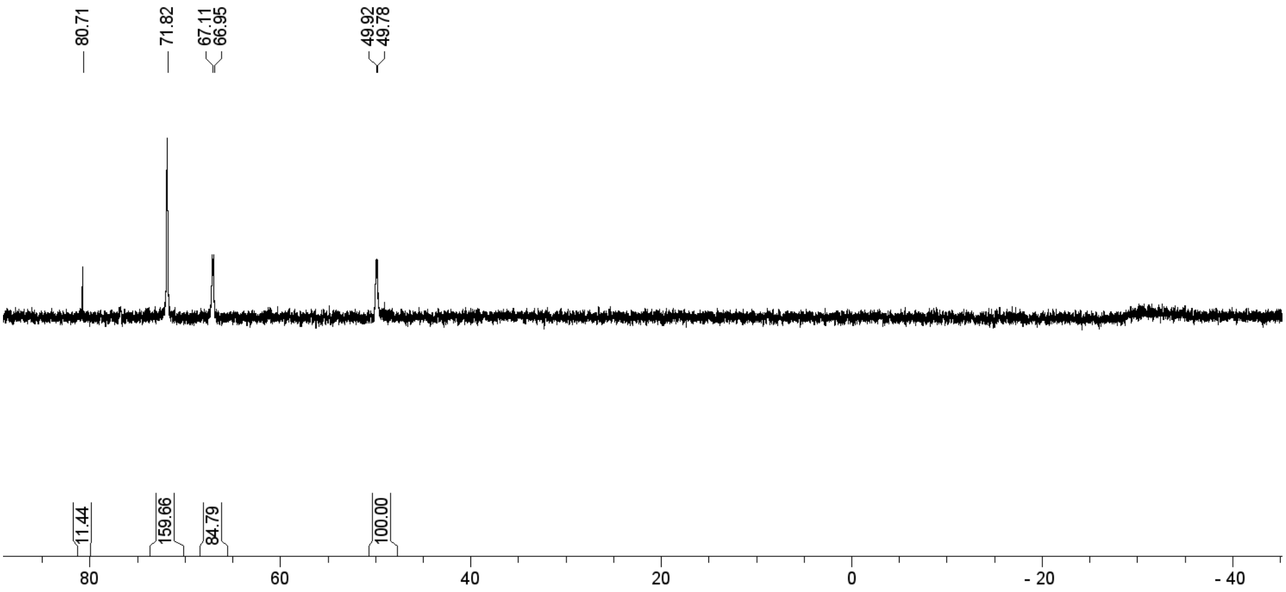

Figure S19: ^{31}P-{^{1}H}-NMR spectrum of **1** and Hyp-Cl in THF-d_8 19 h after start of the reaction at 25 °C.

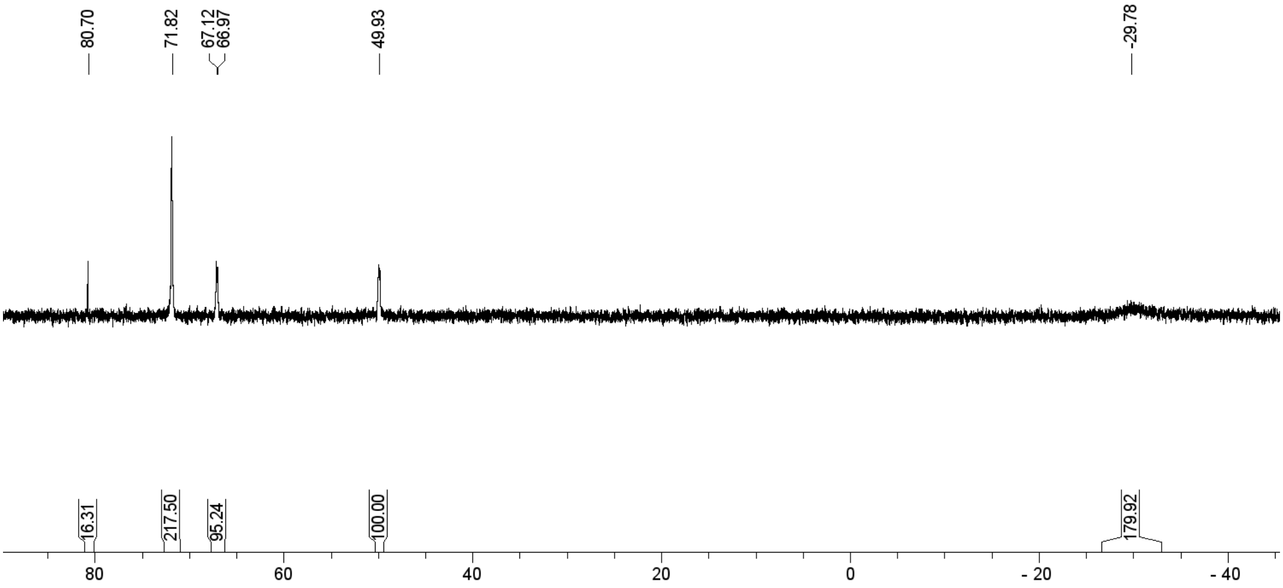

Figure S20: ^{31}P-{^{1}H}-NMR spectrum of **1** and Hyp-Cl in THF-d_8 22.5 h after start of the reaction at 25 °C.

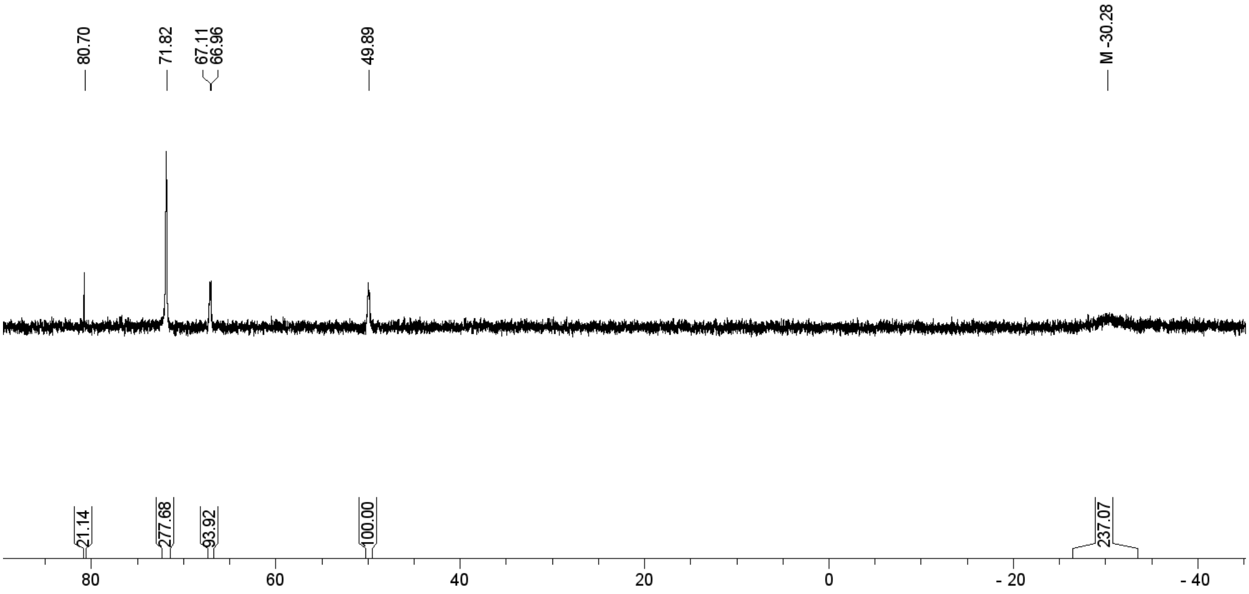

Figure S21: ^{31}P-{^{1}H}-NMR spectrum of **1** and Hyp-Cl in THF-d$_8$ 25.5 h after start of the reaction at 25 °C.

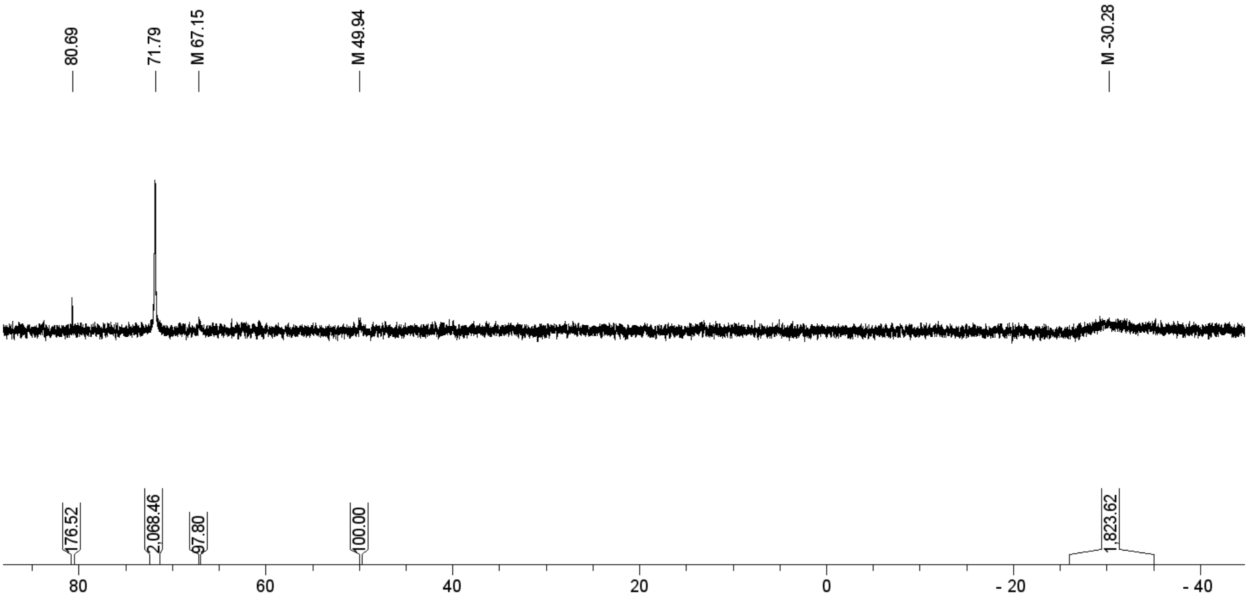

Figure S22: ^{31}P-{^{1}H}-NMR spectrum of **1** and Hyp-Cl in THF-d$_8$ 49.5 h after start of the reaction at 25 °C.

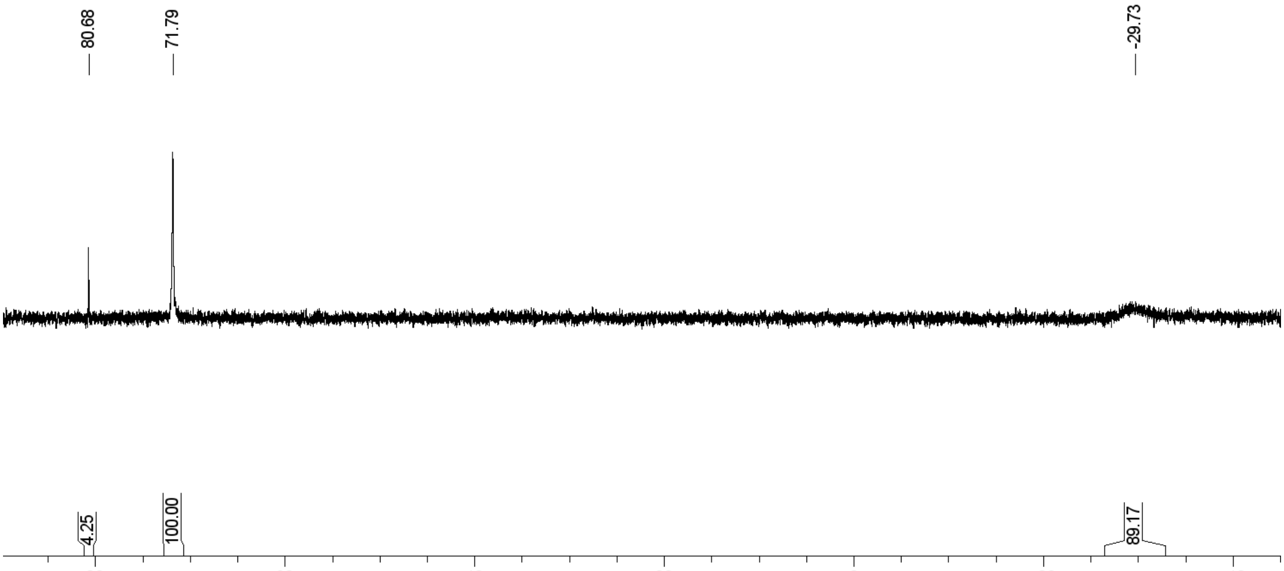

Figure S23: ^{31}P-{^{1}H}-NMR spectrum of **1** and Hyp-Cl in THF-d_8 73.5 h after start of the reaction at 25 °C.

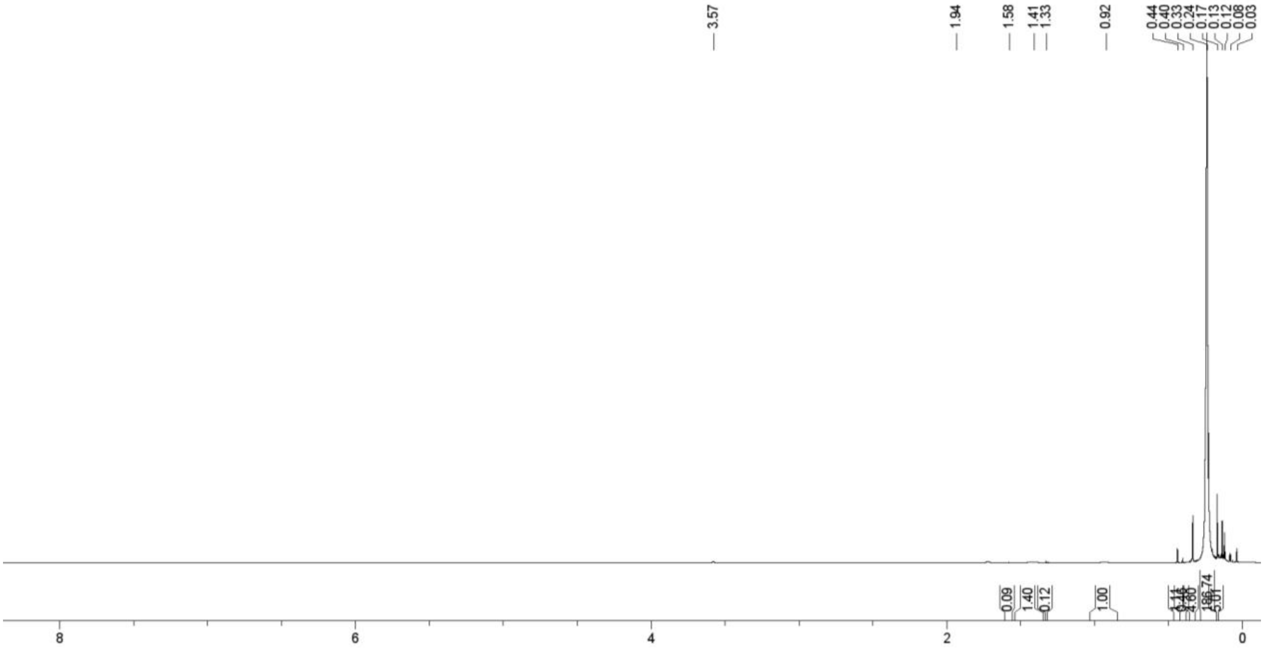

Figure S24: ^{1}H-NMR spectrum of **1** and Hyp-Cl in THF-d_8 73.5 h after start of the reaction at 25 °C.

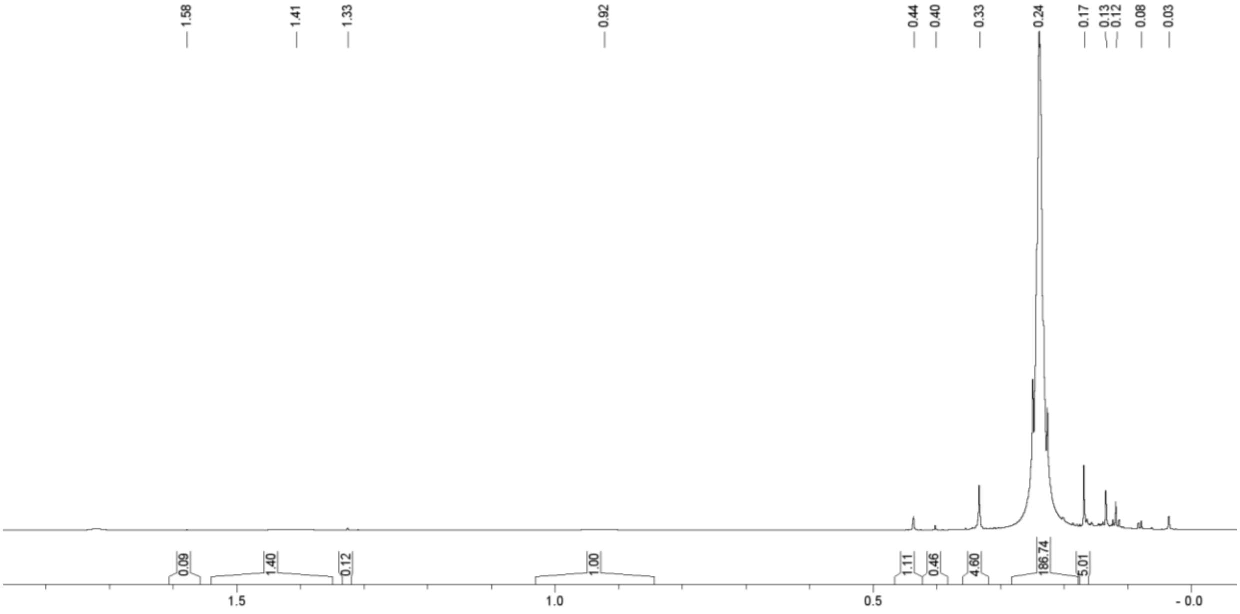

Figure S25: Cutout of the ^{1}H-NMR spectrum of **1** and Hyp-Cl in THF-d_8 73.5 h after start of the reaction at 25 °C.

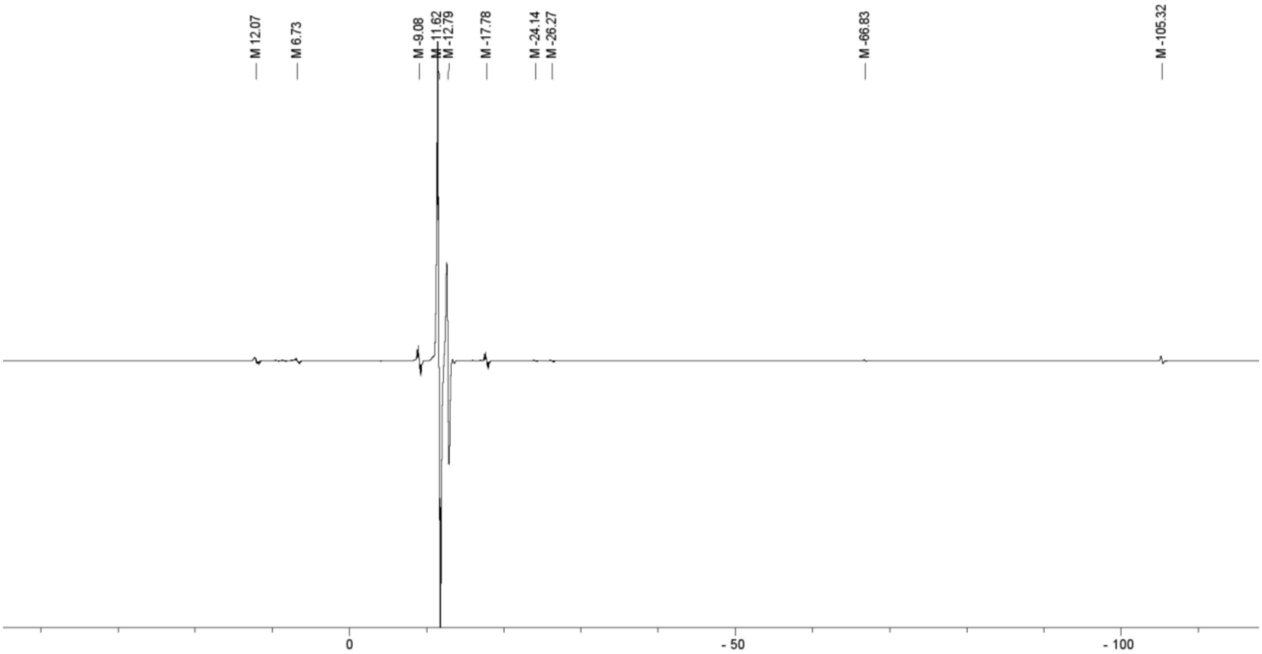

Figure S26: ^{29}Si-inept-nd-NMR spectrum of **1** and Hyp-Cl in THF-d_8 73.5 h after start of the reaction at 25 °C.

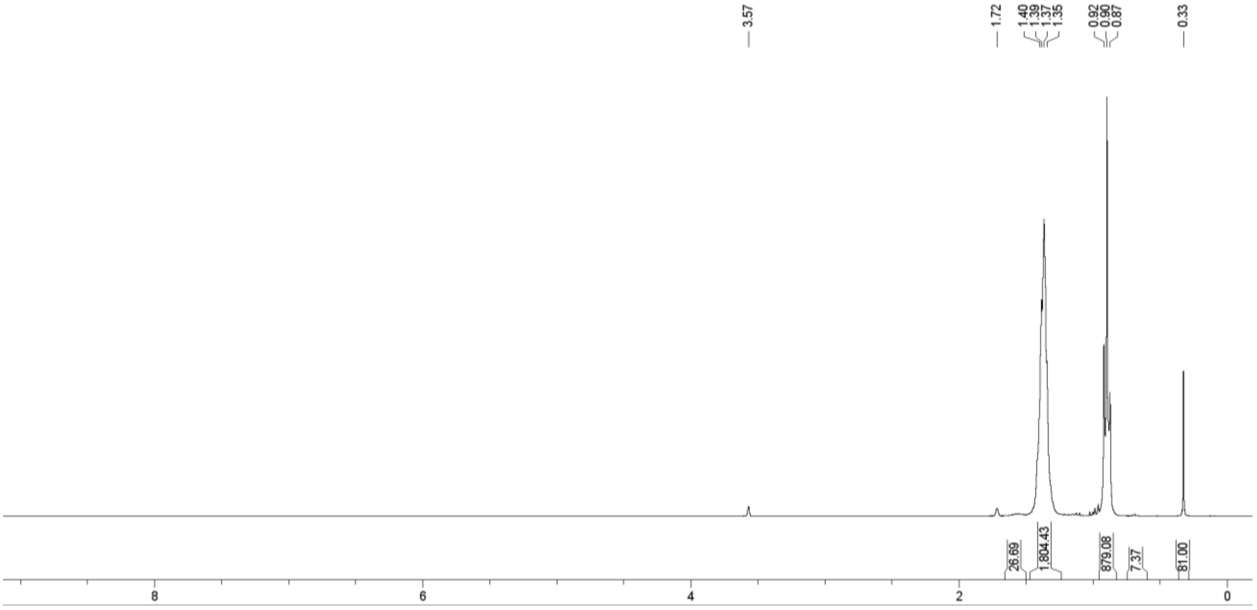

Figure S27: ^{1}H-NMR spectrum of *n*Bu$_3$PAuGe$_9$Hyp$_3$ and exc. *n*Bu$_3$P in THF-d$_8$ 24 h after mixing.

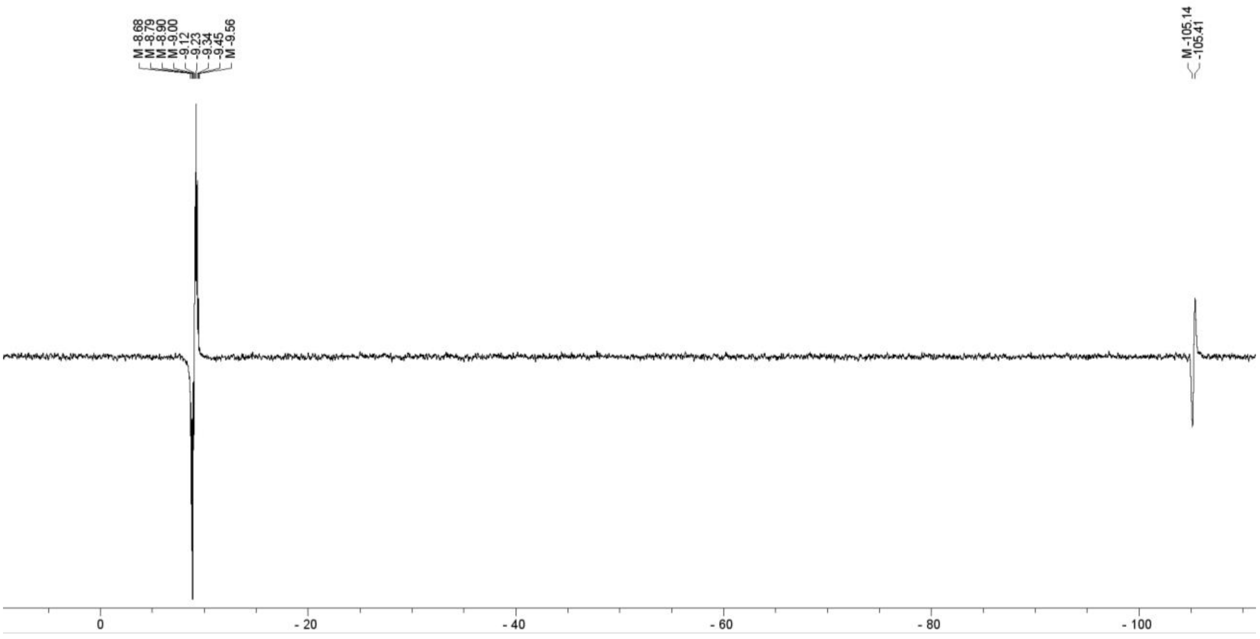

Figure S28: ^{29}Si-inept-nd-NMR spectrum of *n*Bu$_3$PAuGe$_9$Hyp$_3$ and exc. *n*Bu$_3$P in THF-d$_8$ 24 h after mixing.

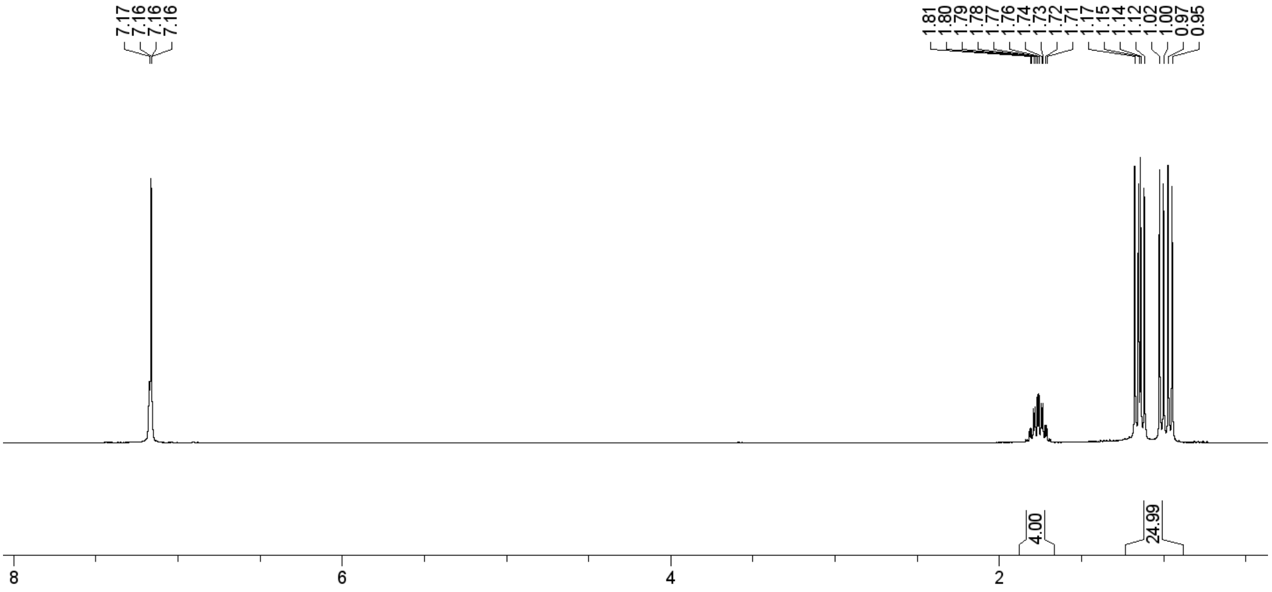

Figure S29: ^{1}H-NMR spectrum of *p*-iPr$_2$POC$_6$H$_4$OPiPr$_2$ in C$_6$D$_6$ at 25 °C.

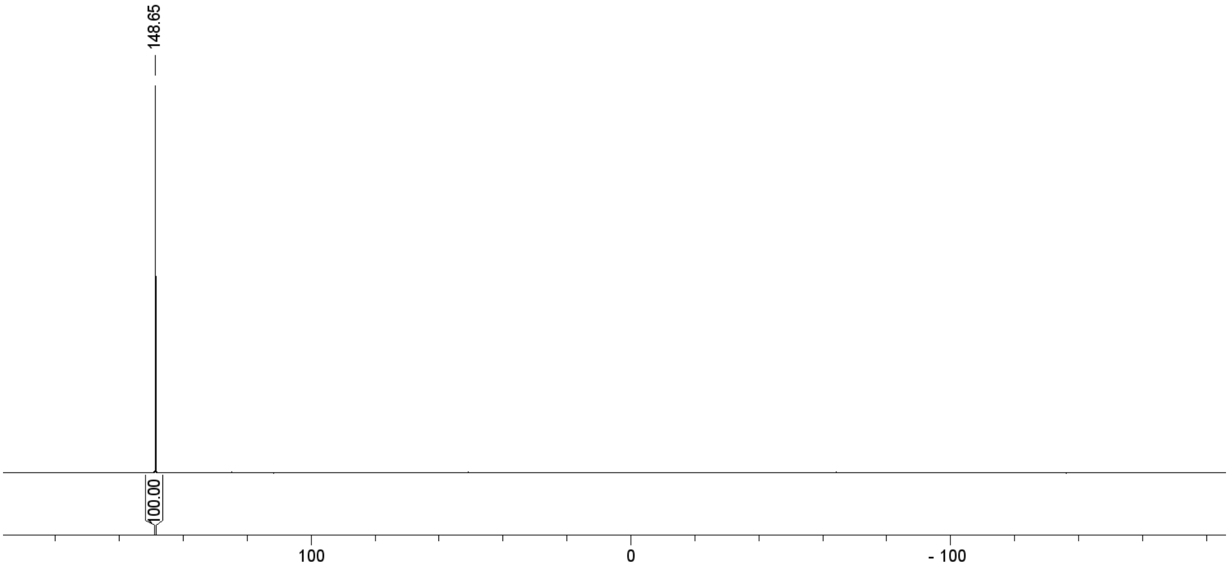

Figure S30: ^{31}P-{^{1}H}-NMR spectrum of *p*-iPr$_2$POC$_6$H$_4$OPiPr$_2$ in C$_6$D$_6$ at 25 °C.

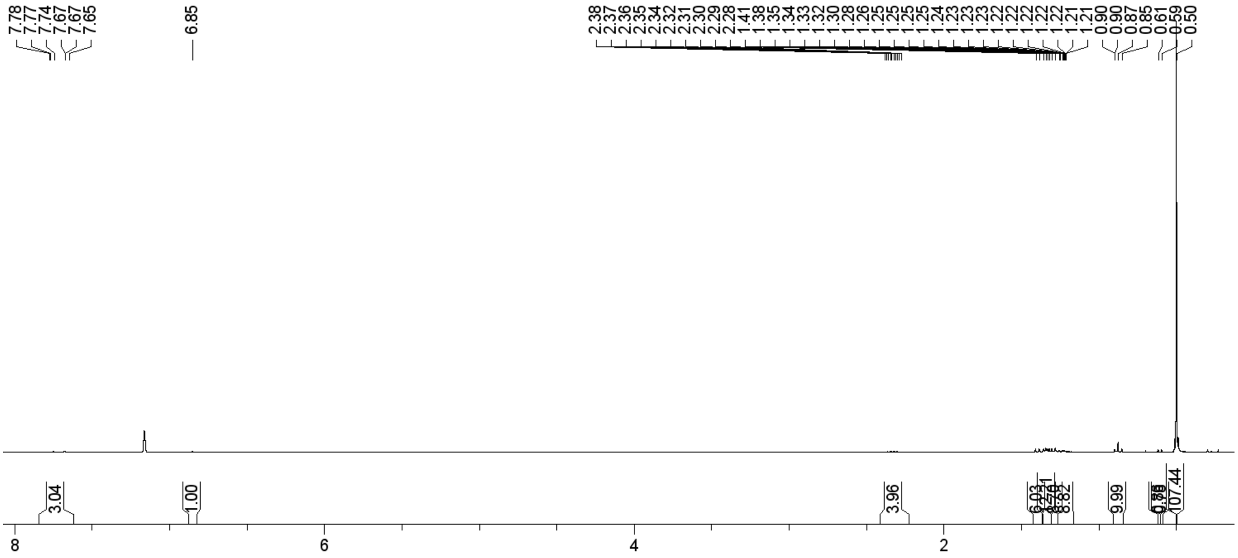

Figure S31: ^{1}H-NMR spectrum of **2** in C_6D_6.

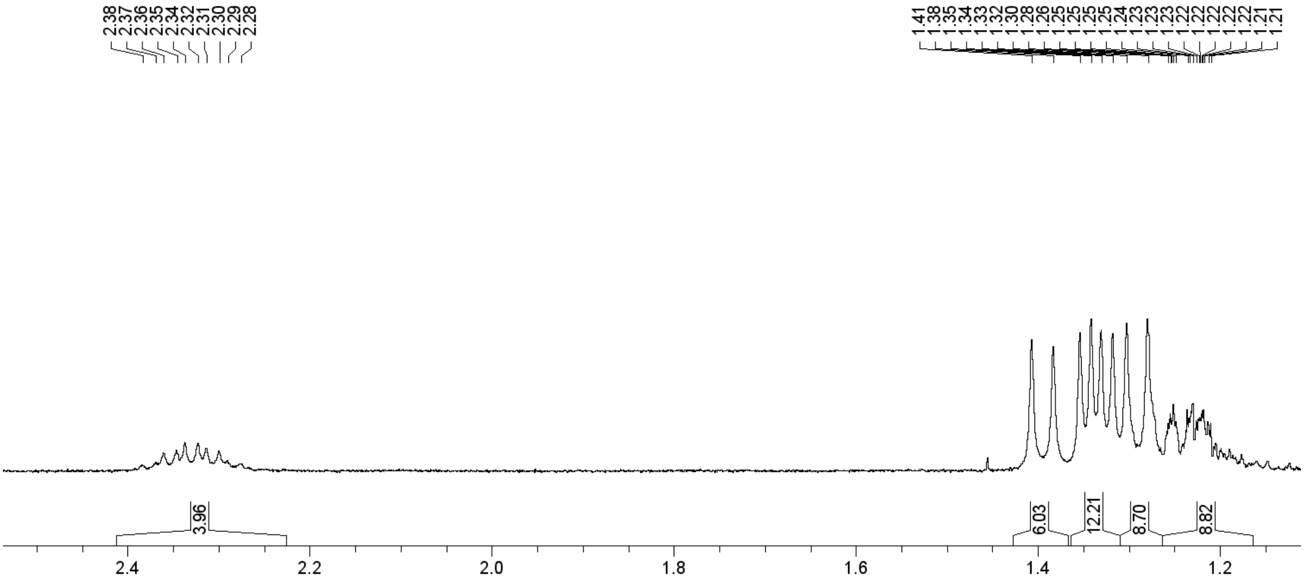

Figure S32: Cutout of the ^{1}H-NMR specturm of **2** in C_6D_6.

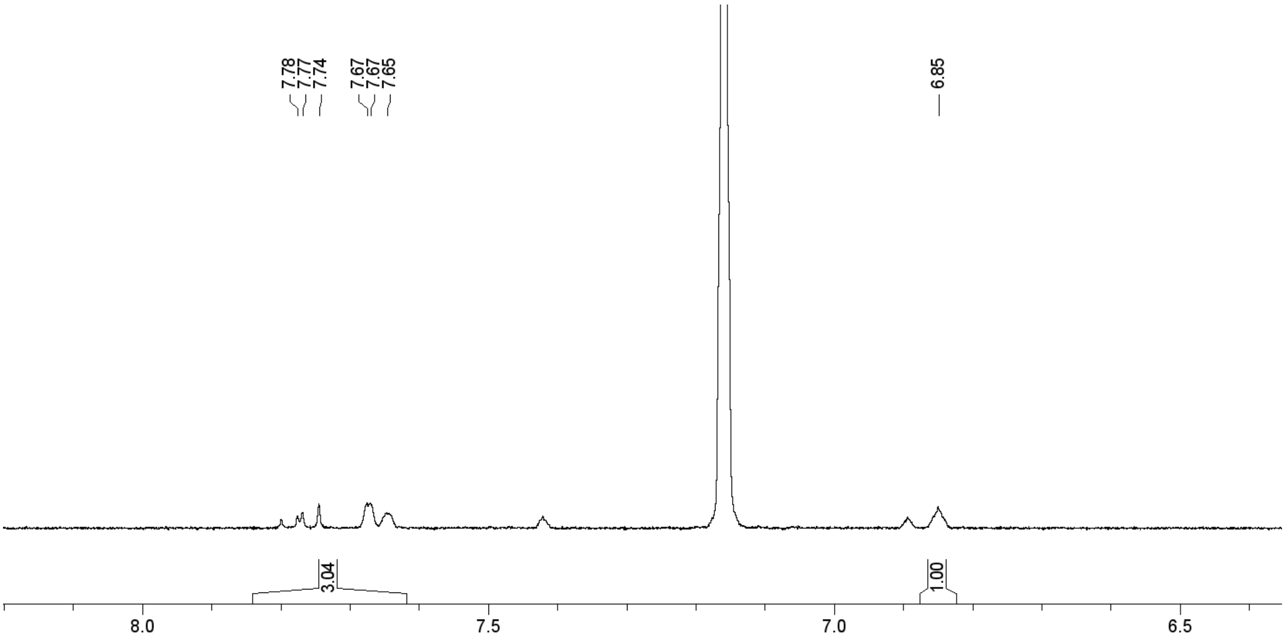

Figure S33: Cutout of the ^{1}H-NMR specturm of **2** in C_6D_6.

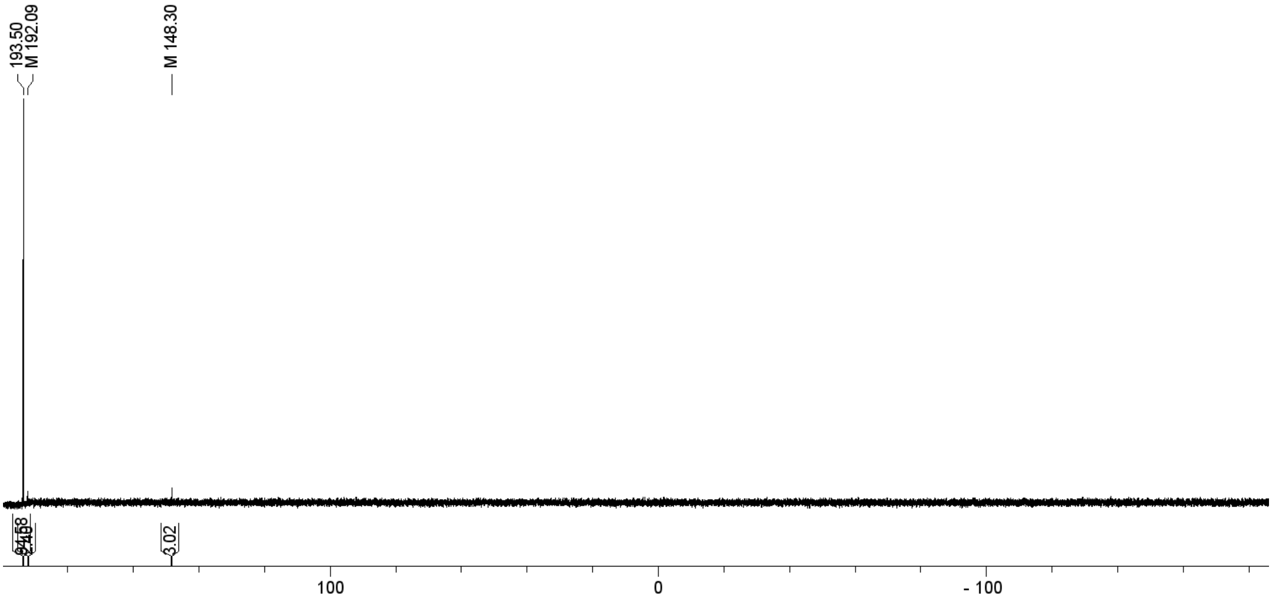

Figure S34: ^{31}P{^{1}H}-NMR specturm of **2** in C_6D_6 after 5 minutes.

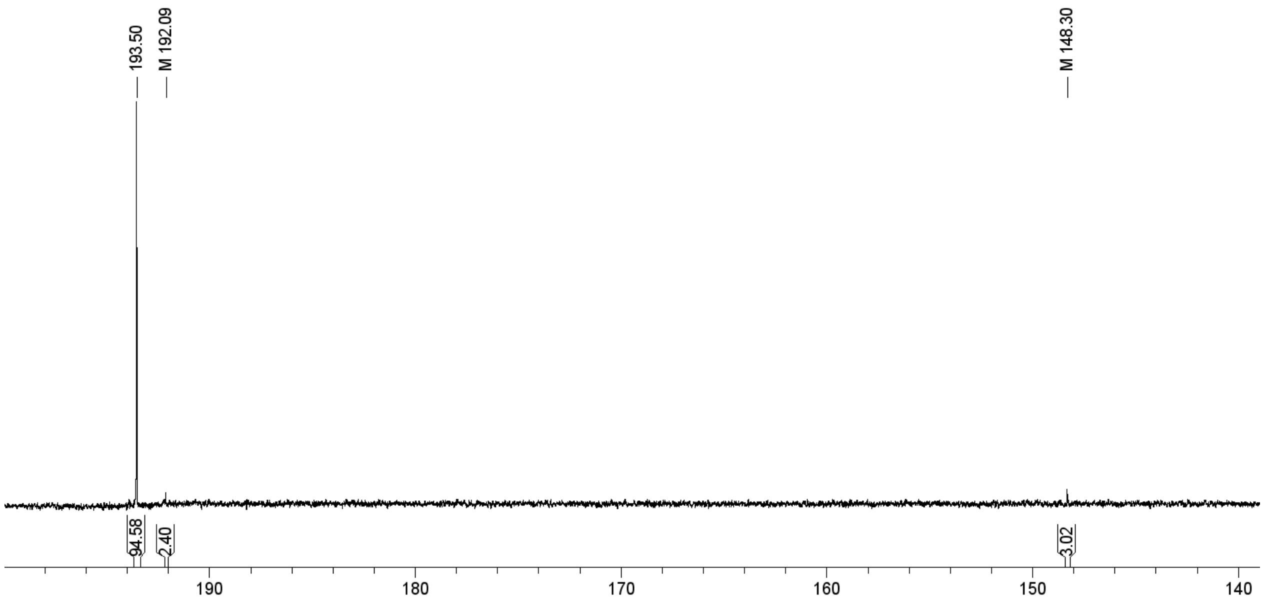

Figure S35: Cutout of the $^{31}P\{^{1}H\}$-NMR specturm of **2** in C_6D_6 after 5 minutes.

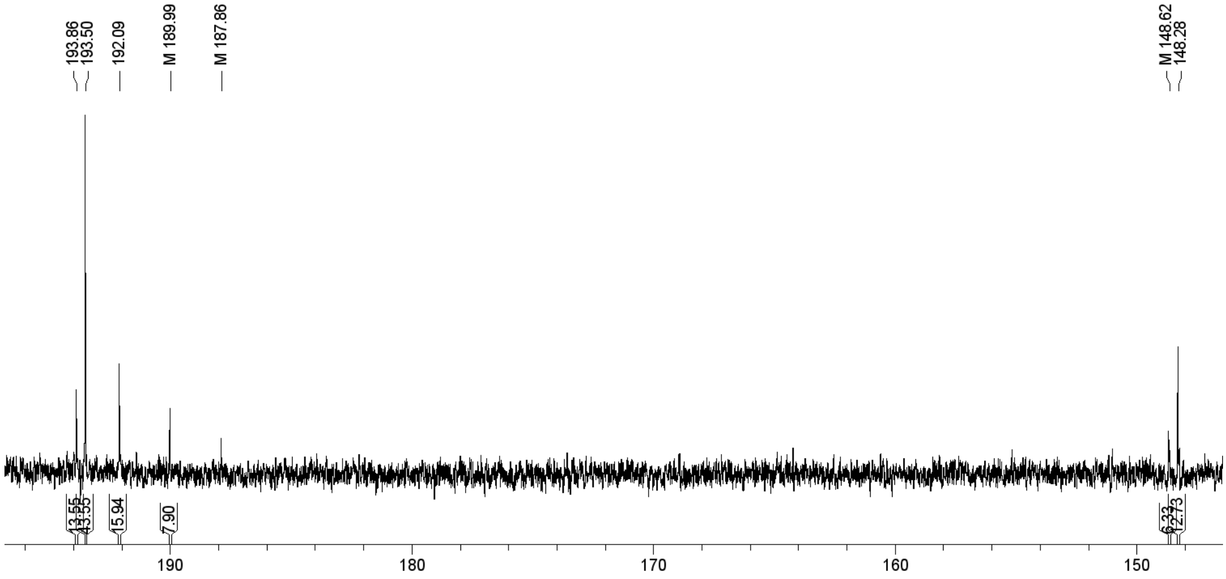

Figure S36: cutout of the $^{31}P\{^{1}H\}$-NMR specturm of **2** in C_6D_6 after 12 hours.

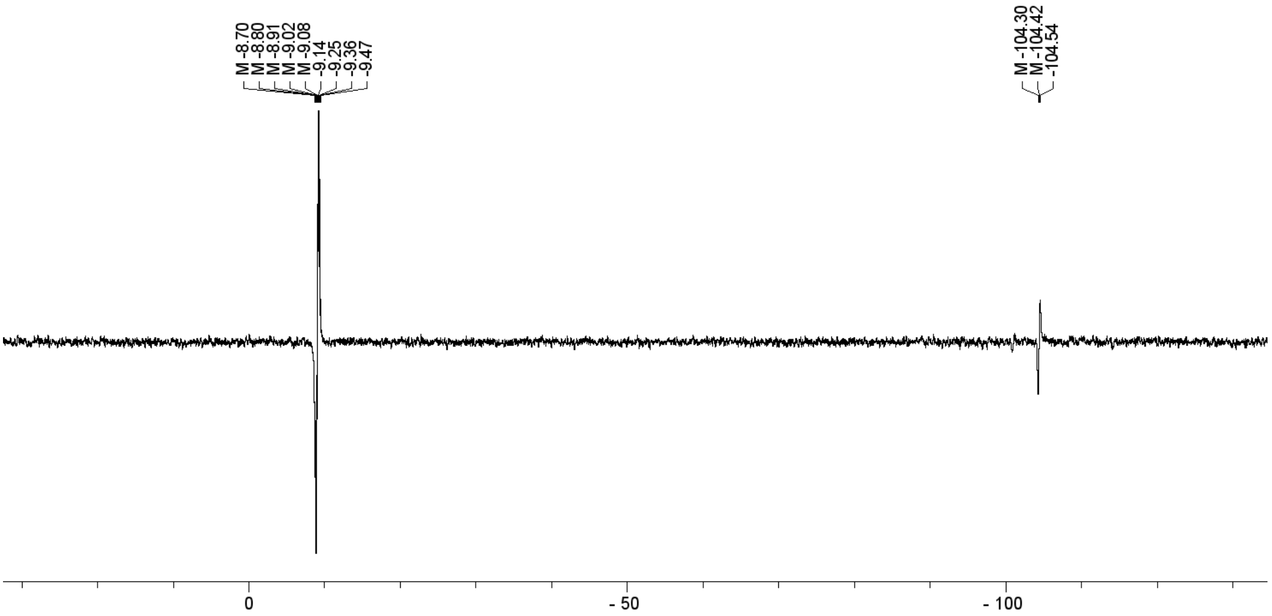

Figure S37: ^{29}Si-inept-nd-NMR spectrum of **2** in THF-d_8.

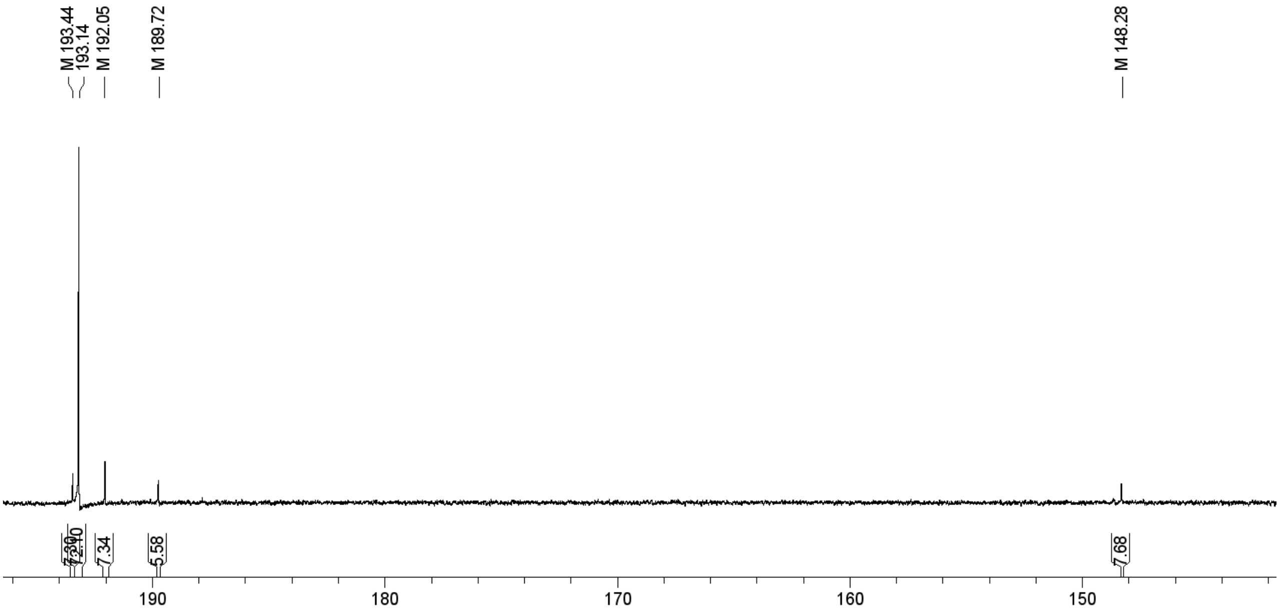

Figure S38: ^{31}P{^{1}H}-NMR spectrum of **2** in THF-d_8 at 25 °C.

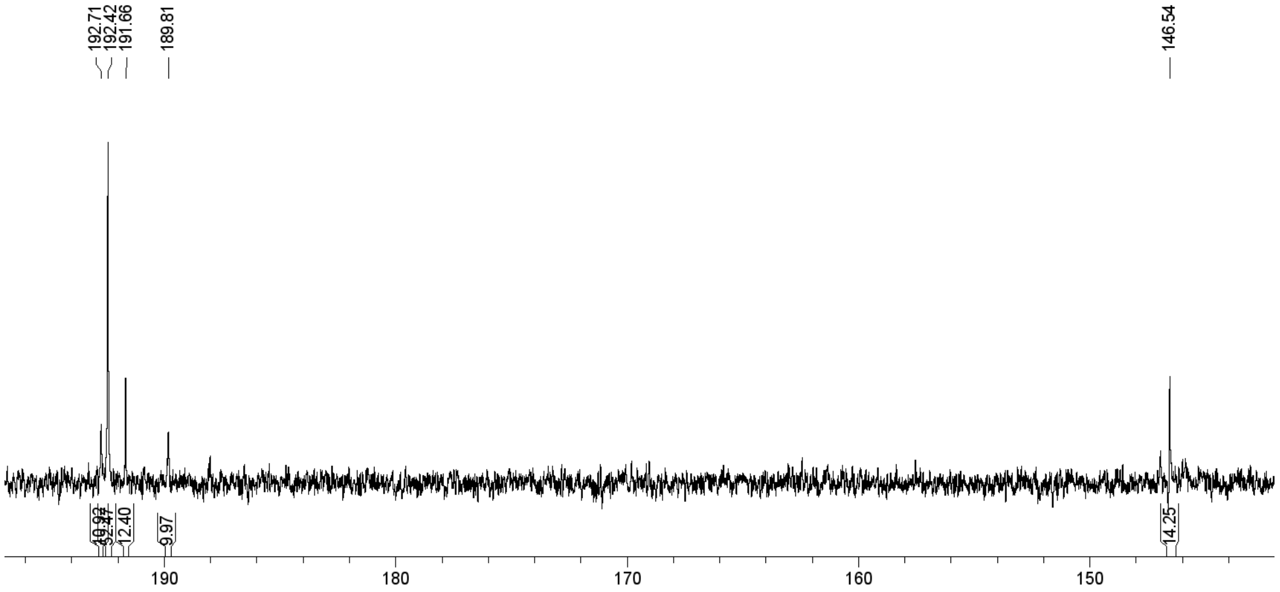

Figure S39: ^{31}P{^{1}H}-NMR spectrum of **2** in THF-d$_8$ at -60 °C.

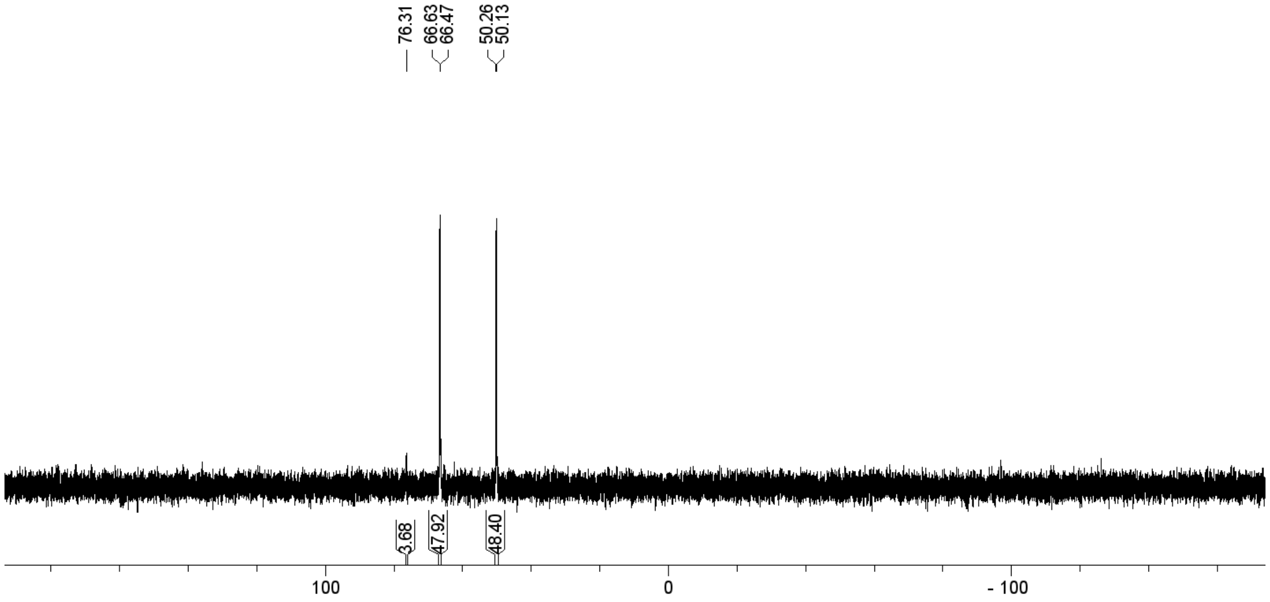

Figure S40: ^{31}P{^{1}H}-NMR spectrum of **1** with HSi^{t}Bu$_2$Cl in toluene-d$_8$ directly after adding the silyl chloride.

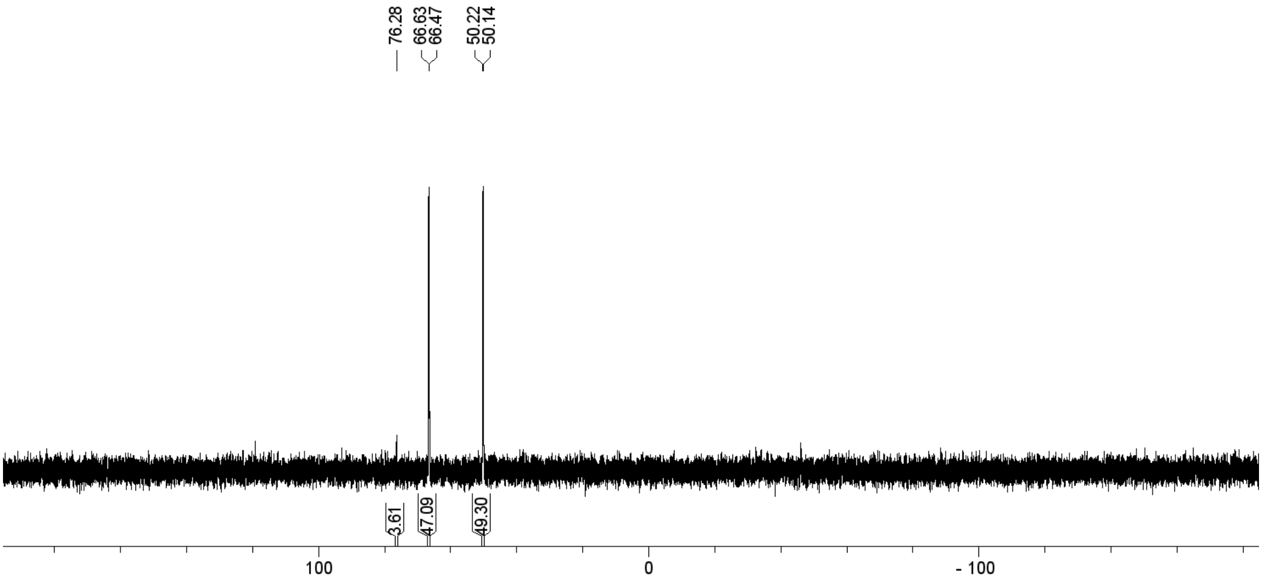

Figure S41: $^{31}P\{^{1}H\}$-NMR spectrum of **1** with HSi^{t}Bu$_2$Cl in toluene-d$_8$ 15 h after adding the silyl chloride at room temperature.

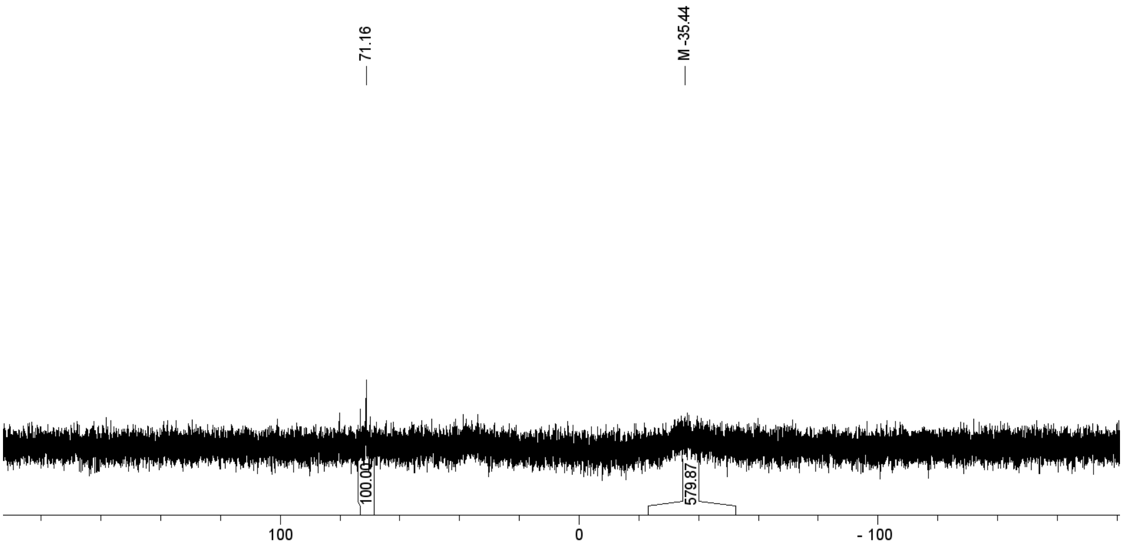

Figure S42: $^{31}P\{^{1}H\}$-NMR spectrum of **1** with HSi^{t}Bu$_2$Cl in toluene-d$_8$ after heating the mixture for 4 h at 85 °C.

Dynamic Light Scattering

DLS spectra were recorded on a Malvern Systems Zetasizer in THF at 25 °C in cuvettes with a glass stopper under Ar atmosphere.

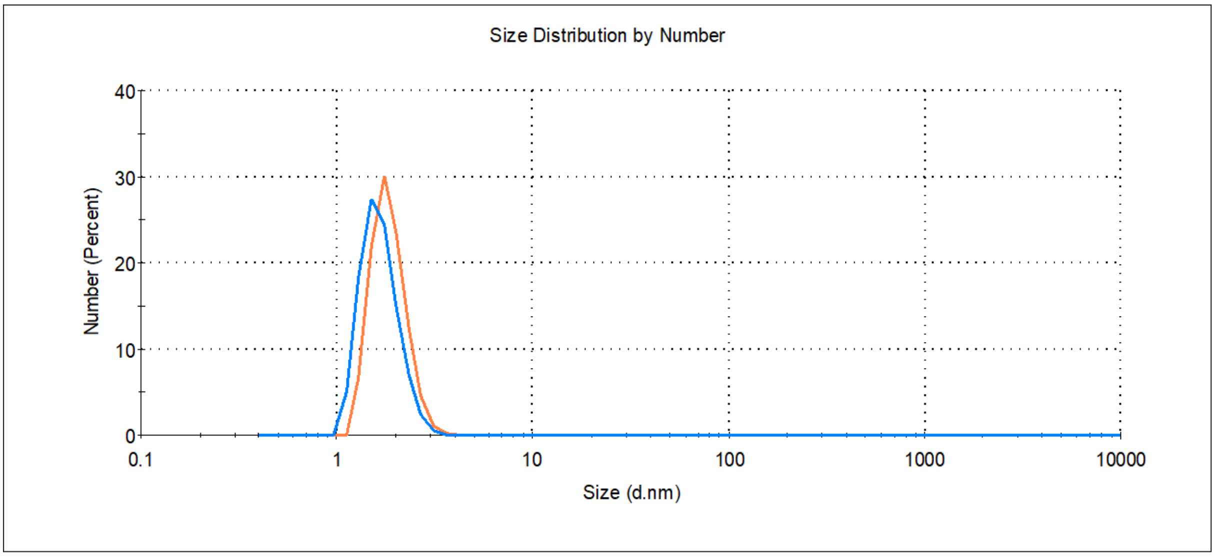

Figure S43: DLS spectra of **1** (blue) and **2** (orange) in THF at 25 °C.

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