Supporting Information

Ge^{II}-H/Si^{IV}-H dehydrocoupling and cycloaddition chemistry of a Ni^0 bis(hydridogermylene) complex

Emeric Schubert,[a] and Terrance J. Hadlington[a,*]

Table of Contents

1. General synthetic considerations

Unless described otherwise, all experiments and manipulations were carried out under dry, oxygen free argon atmosphere using standard Schlenk techniques, or in an MBraun inert atmosphere glovebox containing an atmosphere of high purity argon. Diethylether and THF are distilled over a Na/benzophenone mixture and stored over activated 3Å molecular sieves. Benzene-d_6 was degassed and stored over a potassium mirror. All other solvents were dried over activated 4Å molecular sieves and vigorously degassed prior to use. Known compounds (*i.e.* ^{Ph}L(H)Ge: (**1**),[1] Ni(cod)$_2$)[2] were synthesised following reported literature procedures. Phenylsilane was dried and stored over activated 3Å molecular sieves. For ethylene reactivity studies, 2.5 grade ethylene was used without further purification. NMR spectra were recorded on a Bruker AV 400 MHz Spectrometer. ^{1}H and ^{13}C spectra were referenced to residual solvent signals internally. ^{29}Si{^{1}H} NMR spectra were externally calibrated with $SiMe_4$. ^{31}P{^{1}H} NMR spectra were externally calibrated with H_3PO_4. Liquid Injection Field Desorption Ionization Mass Spectrometry (LIFDI-MS) was measured directly from an inert atmosphere glovebox with a Thermo Fisher Scientific Exactive Plus Orbitrap equipped with an ion source from Linden CMS.[3] Infrared spectra were measured with the Alpha FT-IR from Bruker containing a platinum diamond ATR device. The compounds were measured as solids in an MBraun Labmaster dp inert atmosphere glovebox containing a dry oxygen free atmosphere of high purity argon. Elemental analyses (C, H, N) were performed with a combustion analyzer (elementar vario EL, Bruker).

2. Experimental Procedures and data

[(^{Ph}L(H)Ge)$_2$·Ni], 2. A solution of hydrido-germylene ^{Ph}L(H)Ge: (**1**) (3.00 g, 5.33 mmol, 2.0 eq.) in toluene (80 mL) was added dropwise to a cooled (-78°C), rapidly stirred suspension of Ni(cod)$_2$ (734 mg, 2.67 mmol, 1.0 eq.) in toluene (20 mL). The mixture was allowed to warm to room temperature overnight with stirring, resulting in a dark red solution. After this time, all volatiles were removed *in vacuo* at 50°C, to ensure removal of free COD. Pentane (50 mL) is subsequently added to the residue, forming a dark red-brown solution which is quickly filtered with a canula filter. After 24h dark red crystals had formed, which were isolated by filtration and washed with pentane (2 x 5 mL), and dried *in vacuo* yielding **2** (1.40 g, 1.92 mmol, 72%). The same crystals were suitable for single-crystal X-ray diffraction analysis.

N.B. The removal of residual cyclooctadiene is performed by gently heating the flask (50 – 60°C) for an extended period (ca. 1h) under dynamic vacuum. This step considerably improves the yield.

^{1}H NMR (400 MHz, C_6D_6, 298K): δ = 0.56 (d, $^3J_{HH}$ = 6.8 Hz, 6H, ^{i}Pr-C*H*$_3$), 1.07 – 0.81 (br m, 26H, Si-^{i}Pr-C*H*, ^{i}Pr-C*H*$_3$), 1.41 – 1.21 (br m, 18H, ^{i}Pr-C*H*$_3$), 1.54 – 1.45 (br m, 2H Si-^{i}Pr-C*H*), 2.42 – 2.13 (br m, 4H, Ph$_2$P-C*H*$_2$), 3.05 – 2.80 (br m, 2H Dipp-^{i}Pr-C*H*), 3.94 – 3.65 (br m, 2H, Dipp-^{i}Pr-C*H*), 7.14 – 6.82 (br m, 18H, Ar-*H*), 7.74 – 7.37 (br m, 8H, Ar-*H*), 9.45 (br, 2H, Ge-*H*).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298K): δ = 14.3, 14.4, 14.9, 16.6, 16.7 (Ph$_2$P-*C*H$_2$), 16.9, 18.1, 18.7, 19.6, 19.9, 22.7, 23.0, 23.3, 26.6, 27.3, 27.8 (Dipp-^{i}Pr-*C*H), 28.3 (Dipp-^{i}Pr-*C*H), 123.8 (Ar-*C*), 124.0, 124.9, 127.9, 128.2, 129.1, 131.7, 134.1, 140.5, 144.2, 145.2, 148.4.

^{29}Si{^{1}H} NMR (79 MHz, C_6D_6, 298K) δ = 4.1.

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298K) δ = 20.5.

MS/LIFDI-HRMS: found (calcd.) m/z: 1182.35 (1182.36) for $[M-2H]^+$

Elemental analysis: calc. for $C_{62}H_{88}Ge_2N_2NiP_2Si_2$: C, 62.92%; H, 7.50%; N, 2.37%; found: C, 62.06%; H, 7.52%; N, 2.39%. *Element analyses gave low values for C, possibly due to Si-carbide/Ni-carbide formation.*

IR ν/cm^{-1} (ATR): 1872, 1849 (*Ge-H*).

[{^{Ph}L(H)Ge-Ge(^{Ph}L)Si(Ph)(H)$_2$}·Ni], 3. PhSiH$_3$ (1.11 g, 1.26 mL, 10.22 mmol) is added to a solution of **1** (2.41 g, 2.04 mmol, 1.0 eq.) in toluene (50 mL) at room temperature. After a few minutes, the solution changes from a dark red-brown colour to red. The mixture is left stirring for three days. Finally, the volatiles are removed *in vacuo* and the residue is extracted with diethyl ether (30 mL). The solvent is removed, and pentane (30 mL) is added. The solution is left undisturbed for a week, resulting red crystals suitable for XRD measurements (1.95 g, 1.51 mmol, 74%).

NMR reaction: A J. Young's NMR tube was loaded with 50 mg of **2** and 0.5 mL of C_6D_6 were added. $PhSiH_3$ (1.5 eq.) were added via an *Eppendorf* pipet. The sample was monitored at room temperature using ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Over 18h, the sample turned from deep purple-red to bright red, and the ^1H NMR spectra indicates incomplete conversion to product (*i.e.* **3**), as well as dihydrogen (Figure S24.)

Two diastereoisomers of compound **3** are distinguishable in ^1H, ^{29}Si, and ^{31}P NMR spectra for this compound, aided by the use of 2D NMR, see Figs. S13-S16. These are denoted as ***A*** and ***B*** below.

^1H NMR (400 MHz, C_6D_6, 298K): δ = -4.33 – -4.57 (m, $^1J_{SiH}$ = 72 Hz, 1H, Ni-*H*-Si ***B***), -3.93 – -4.17 (m, $^1J_{SiH}$ = 80 Hz, 1H, Ni-*H*-Si ***A***), 0.06 (d, *J* = 7.4 Hz, 3H, Si-iPr-C*H*$_3$), 0.33 – 0.15 (m, 18 H, Si-iPr-C*H*$_3$, Ali-*H*), 0.49 (d, *J* = 7.1 Hz, 3H, Si-iPr-C*H*$_3$), 0.66 – 0.54 (m, 13H, Si-iPr-C*H*, Ali-*H*), 0.79 – 0.75 (m, 4H, Dipp-iPr-C*H*$_3$ ***B***, Ali-*H*), 0.89 – 0.81 (m, 11H, Si-iPr-C*H*, Dipp-iPr-C*H*$_3$, Ali-*H*), 0.97 – 0.92 (m, 5H, Dipp-iPr-C*H*$_3$, Ali-*H*), 1.14 – 0.99 (m, 11H, P-C*H*, Si-iPr-C*H*, Dipp-iPr-C*H*$_3$ ***B***, Dipp-iPr-C*H*$_3$), 1.16 (d, *J* = 6.5 Hz, 3H, Dipp-iPr-C*H*$_3$ ***B***), 1.21 (d, *J* = 6.6 Hz, 3H, Dipp-iPr-C*H*$_3$ ***A***), 1.31 (d, *J* = 6.7 Hz, 3H, Dipp-iPr-C*H*$_3$ ***B***), 1.37 – 1.33 (m, 7H, Si-iPr-C*H*, Dipp-iPr-C*H*$_3$ ***B***, Si-iPr-C*H*$_3$), 1.39 (d, *J* = 6.5 Hz, 3H, Dipp-iPr-C*H*$_3$ ***B***), 1.49 – 1.42 (m, 9H, Dipp-iPr-C*H*$_3$ ***A***), 1.58 (d, *J* = 6.6 Hz, 3H, Dipp-iPr-C*H*$_3$ ***A***), 1.68 – 1.62 (m, 1H, P-C*H*), 1.85 – 1.76 (m, 2H, P-C*H*) , 2.09 – 1.91 (m, 9H, P-C*H*, Dipp-iPr-C*H*$_3$ ***A***, Dipp-iPr-C*H*$_3$ ***B***), 2.23 – 2.16 (m, 1H, P-C*H*), 2.72 (hept, *J* = 6.5 Hz, 1H, Dipp-iPr-C*H* ***B***), Dipp-iPr-C*H* ***B***, 3.09 – 2.96 (m, 1H, Dipp-iPr-C*H* ***A***), 3.57 – 3.46 (m, 1H, Dipp-iPr-C*H* ***A***), 3.73 – 3.61 (m, 1H, Dipp-iPr-C*H* ***B***), 3.96 – 3.84 (m, 2H, Dipp-iPr-C*H* ***A***, Dipp-iPr-C*H* ***B***), 4.40 – 4.28 (m, 1H, Dipp-iPr-C*H* ***B***), 4.68 – 4.56 (m, 1H, Dipp-iPr-C*H* ***A***), 6.56 – 6.45 (m, 1H, Si-*H* ***B***), 6.68 (t, *J* = 7.2 Hz, H, Ar-*H*), 6.79 (t, *J* = 7.3 Hz, 2H, Ar-*H*), 6.88 – 6.83 (m, 2H, Ar-*H*), 7.08 – 6.99 (m, 14H, Ar-*H*), 7.14 – 7.09 (m, 12H, Ar-*H*), 7.20 – 7.18 (m, 3H, Ar-*H*), 7.29 – 7.20 (m, 9H, Ar-*H*), 7.43 – 7.34 (m, 4H, Ar-*H*, Si-*H* ***A***), 7.49 (t, *J* = 7.8 Hz, 2H, Ar-*H*), 7.71 – 7.63 (m, 3H, Ar-*H*), 7.76 (d, *J* = 6.7 Hz, 2H, Ar-*H*, Si-Ph-*H* ***A***), 7.90 – 7.82 (m, 4H, Ar-*H*), 8.07 – 8.00 (m, 4H, Ar-*H*, Si-Ph-*H* ***B***), 9.55 (dt, *J* = 6.4, 3.7 Hz, 1H, Ge-*H* ***B***), 10.16 – 10.09 (m, 1H, Ge-*H* ***A***).

$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298K): δ = 7.9 (d, Ph_2P-*C*H_2), 10.8 (d, Ph_2P-*C*H_2), 13.9, 14.0, 14.2, 14.3, 14.7, and 16.4 (^{i}Pr-*C*H_3), 16.3 (d, Ph_2P-*C*H_2), 17.0 (d, Ph_2P-*C*H_2), 17.5, 17.7, 18.0, 19.0, 19.2, 20.0, 20.4, 21.2, 22.7, 24.0, 24.7, 24.7, 24.9, 25.3, 25.5, 27.7, 27.8, 28.1, 28.2, 28.3, 28.6, 28.6, 28.7, 28.9, 29.0, and 34.4 (^{i}Pr-*C*H/*C*H_3), 124.5, 124.6, 124.8, 124.9, 125.1, 125.3, 125.4, 125.4, 125.5, 127.6, 127.8, 128.1, 128.3, 128.8, 128.8, 128.9, 129.1, 129.1, 129.2, 129.7, 129.8, 129.9, 130.0, 130.4, 131.1, 131.2, 131.4, 131.5, 131.6, 133.7, 133.9, 135.4, 135.6, 135.7, 135.8, 136.0, 136.1, 136.5, 136.5, 136.9, 137.8, 137.9, 139.0, 139.1, 139.2, 139.4, 139.5, 139.5, 145.2, 145.9, 146.0, 146.5, 146.6, 146.9, 147.0, 147.1, 147.2, 147.6, 147.8, 147.9, 148.2, 148.4, 148.4, 148.5, 148.7, 148.8, 149.7, 150.0 (Ar-*C*).

^{29}Si NMR (79 MHz, C_6D_6, 298K): -3.21 (iPr-*Si* ***B***), -2.64 (iPr-*Si* ***A***), 6.47 (iPr-*Si* ***B***), 7.14 (iPr-*Si* ***A***), 46.2 (dd, $^2J_{SiP}$ = 41.1 Hz, $^2J_{SiP}$ = 18.2, Ni-H-*Si* ***B***), 60.4 (dd, $^2J_{SiP}$ = 34.8 Hz, $^2J_{SiP}$ = 24.5, Ni-H-*Si* ***A***).

^{31}P{^{1}H} NMR (162 MHz, Tol-d8, 298K): δ = 8.6 (d, $^2J_{PP}$ = 16.6 Hz, ***B***), 11.1 (d, $^2J_{PP}$ = 23.5 Hz, ***A***), 21.8 (d, $^2J_{PP}$ = 16.6 Hz, ***B***), 23.2 (d, $^2J_{PP}$ = 23.5 Hz, ***A***).

MS/LIFDI-HRMS: found (calcd.) m/z: 1286.37 (1286.40) for $[M-2H]^+$

Elemental analysis: calc. for $C_{68}H_{94}Ge_2N_2NiP_2Si_2$: C, 63.33%; H, 7.35%; N, 2.17%; found: C, 62.63%; H, 7.35%; N, 2.13%.

IR v/cm^{-1} (ATR): *no peaks are observed attributable to Ge/Si-H stretching frequencies* (*viz.* Fig. S14).

[{(^{PhiP}DippGeH)$_2$C$_2$H$_4$}Ni], 4. A solution of **1** (200 mg, 232,3 µmol) in toluene (15 mL) was subjected to an atmosphere of ethylene (1 bar). After 1 hour, the colour changed to clear orange. The solvent was removed, and the oily residue was dissolved in diethyl ether (8 mL). After 7 days, needle shaped orange crystals suitable for XRD measurements were collected (74 mg, 36%).

^{1}H NMR (400 MHz, C_6D_6, 298K): δ = 0.51 (s, 2H, Ge-C*H*$_2$), 0.72 (d, *J* = 7.2 Hz, 6H, Si-^{i}Pr-C*H*$_3$), 0.80 (d, *J* = 7.5 Hz, 6H, Si-^{i}Pr-C*H*$_3$), 0.88 (d, *J* = 7.3 Hz, 6H, Si-^{i}Pr-C*H*$_3$), 0.99 (dq, *J* = 14.9, 7.2 Hz, 2H, Si-^{i}Pr-C*H*), 1.14 (t, *J* = 5.9 Hz, 12H, Dipp-^{i}Pr-C*H*$_3$, Si-^{i}Pr-C*H*$_3$), 1.23 (d, *J* = 6.7 Hz, 6H, Dipp-^{i}Pr-C*H*$_3$), 1.29 (t, *J* = 7.0 Hz, 2H), 1.35 (d, *J* = 6.7 Hz, 6H, Dipp-^{i}Pr-C*H*$_3$), 1.41 (d, *J* = 6.7 Hz, 6H, Dipp-^{i}Pr-C*H*$_3$), 1.55 (s, 2H, Ge-C*H*$_2$), 1.70 (t, *J* = 13.6 Hz, 2H, Ph$_2$PC*H*$_2$), 1.98 – 1.88 (m, 2H, Ph$_2$PC*H*$_2$), 3.52 (p, *J* = 6.9 Hz, 2H, Dipp-^{i}Pr-C*H*$_3$), 3.74 (p, *J* = 6.7 Hz, 2H, Dipp-^{i}Pr-C*H*$_3$), 6.07 (d, *J* = 8.2 Hz, 2H, Ge*H*), 7.09 - 6.81 (m, 14H, Ar-C*H*), 7.30 (t, *J* = 8.3 Hz, 4H, Ar-C*H*), 7.61 (t, *J* = 8.3 Hz, 4H, Ar-C*H*).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298K): δ = 10.0, 14.6 (Si-^{i}Pr-*C*), 15.1 (Si-^{i}Pr-*C*), 15.7, 18.7 (Si-^{i}Pr-*C*), 19.3 (Si-^{i}Pr-*C*), 19.8 (Si-^{i}Pr-*C*), 20.0 (Si-^{i}Pr-*C*), 25.3 (Dipp-^{i}Pr-*C*), 25.5 (Dipp-^{i}Pr-*C*), 26.4 (Dipp-^{i}Pr-*C*), 27.4 (Dipp-^{i}Pr-*C*), 27.6, 27.7, 124.3 (Ar-*C*), 124.3, 124.6, 128.9, 129.5, 133.1, 133.9, 134.0, 134.1, 137.8, 138.2, 139.5, 139.9, 145.7, 147.5, 147.6.

^{29}Si NMR (79 MHz, C_6D_6, 298K): δ = 0.0.

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298K): δ = 12.4.

MS/LIFDI-HRMS: found (calcd.) m/z: 1208.39 (1208.39) for $[M-2H]^+$

Elemental analysis: calc. for $C_{64}H_{92}Ge_2N_2NiP_2Si_2$: C, 63.45%; H, 7.65%; N, 2.31%; found: C, 63.67%; H, 7.77%; N, 2.39%.

IR v/cm^{-1} (ATR): 1959, 1868 (Ge-H).

Printed spectra

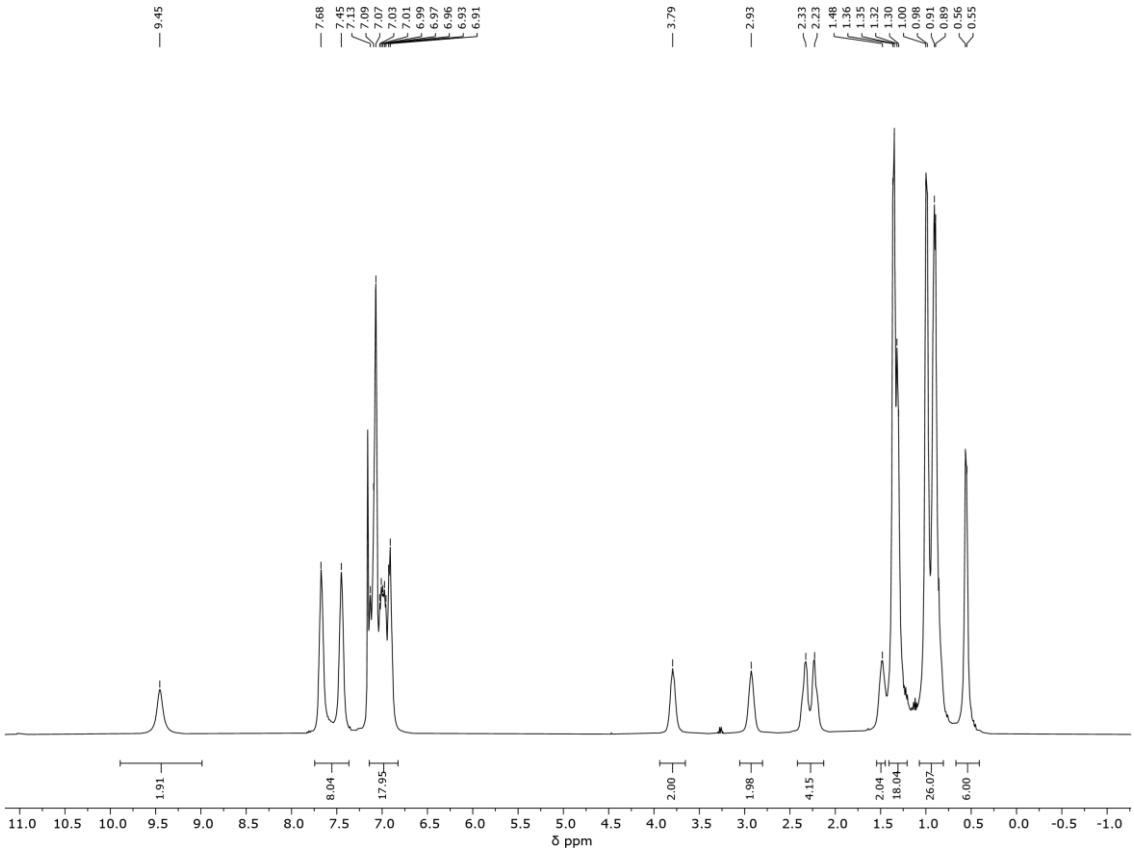

Figure S1. ^{1}H NMR spectrum of **2** in C_6D_6 at ambient temperature.

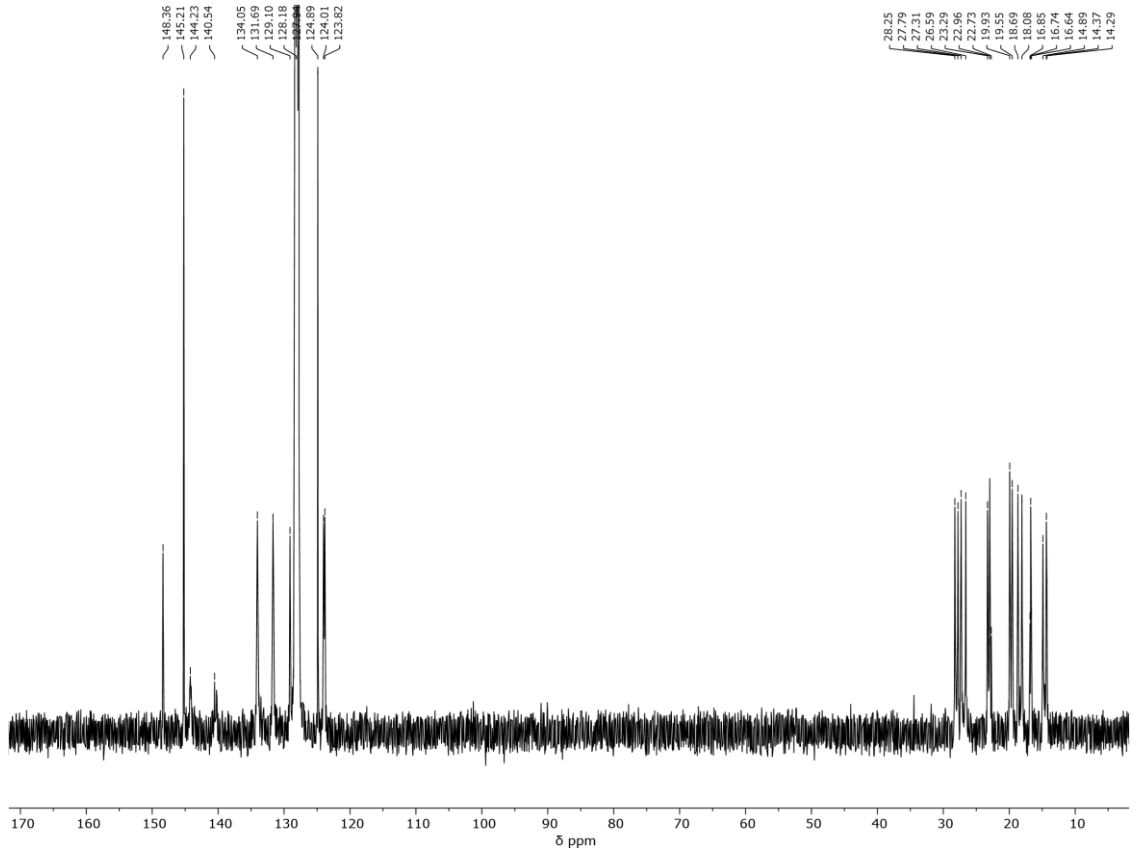

Figure S2. ^{13}C NMR spectrum of **2** in C_6D_6 at ambient temperature.

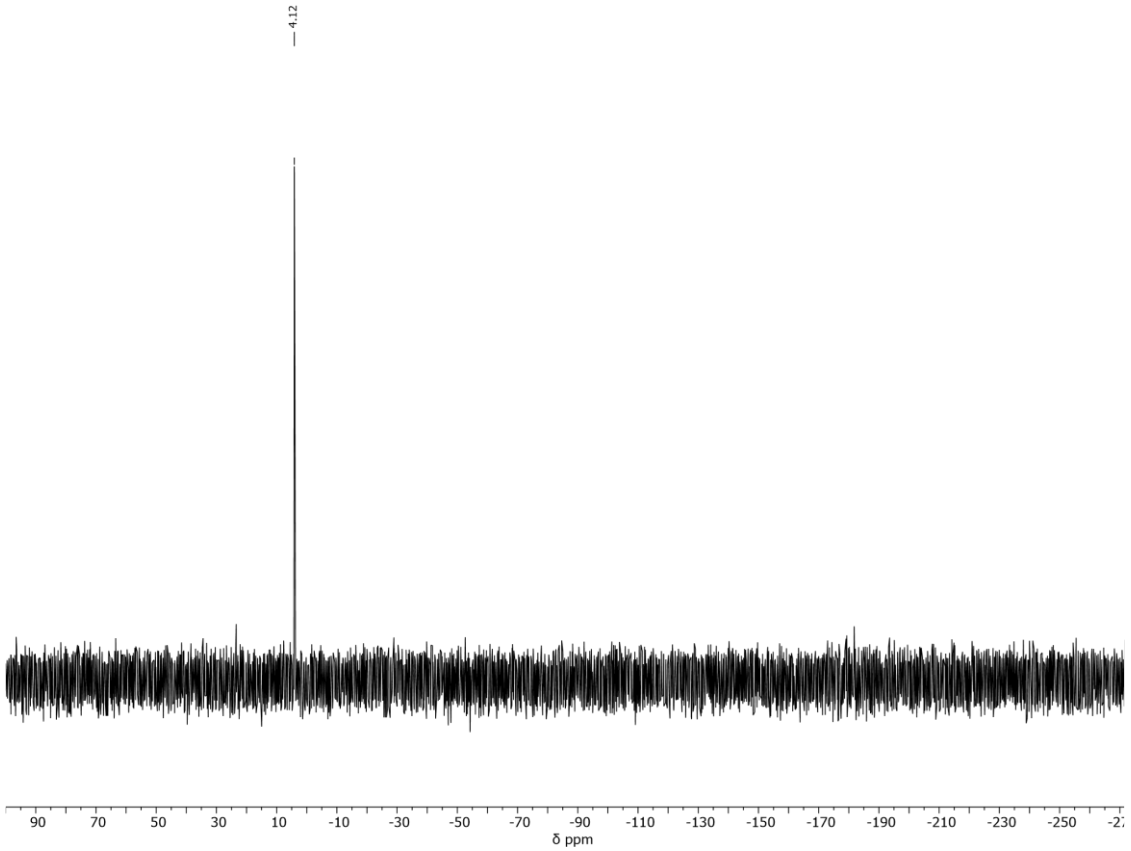

Figure S3. ^{29}Si NMR spectrum of **2** in C_6D_6 at ambient temperature.

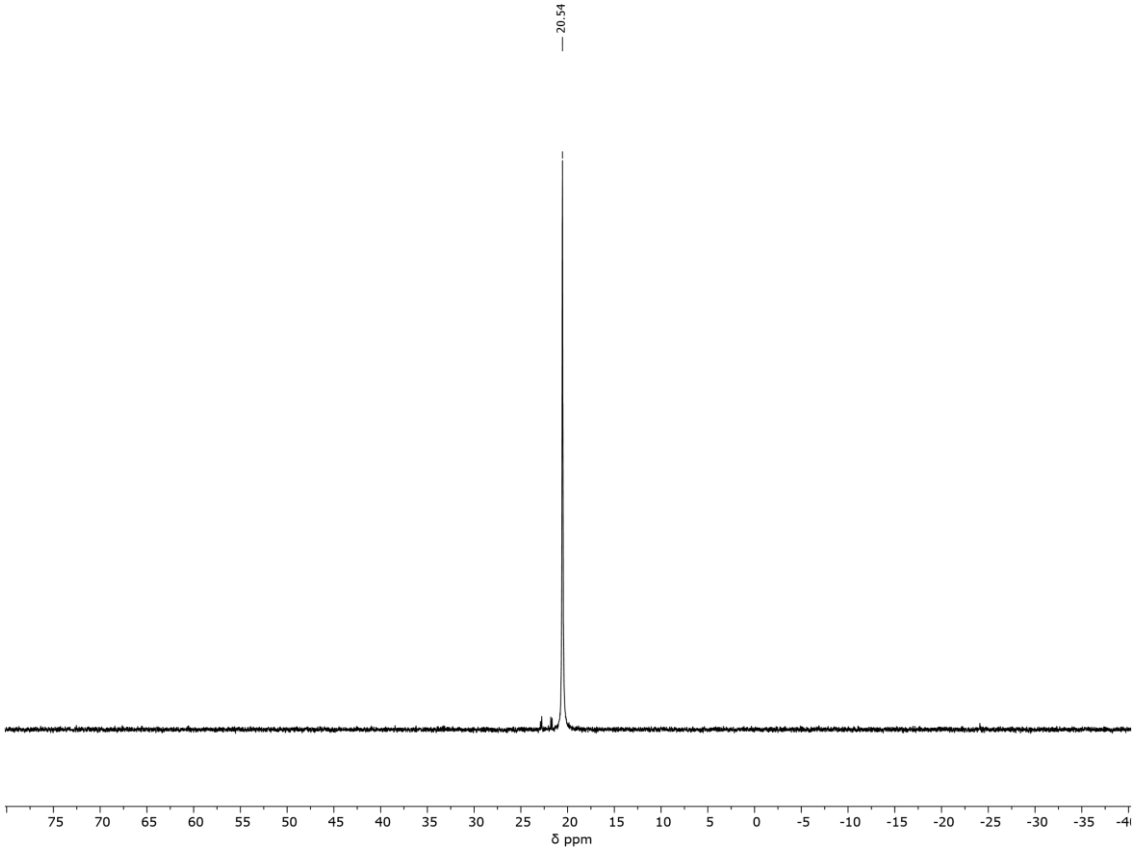

Figure S4. ^{31}P NMR spectrum of **2** in C_6D_6 at ambient temperature.

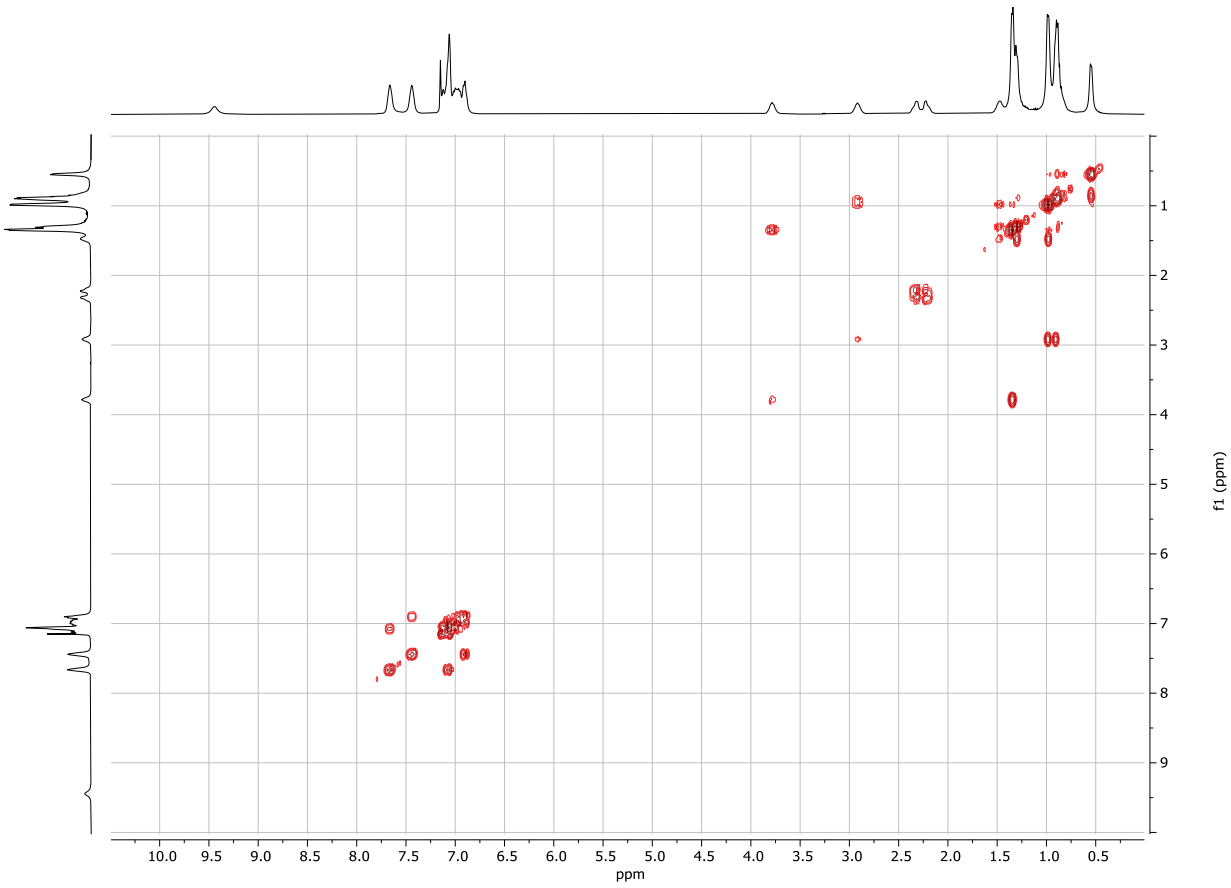

Figure S5. COSY NMR of **2** in C_6D_6 at ambient temperature.

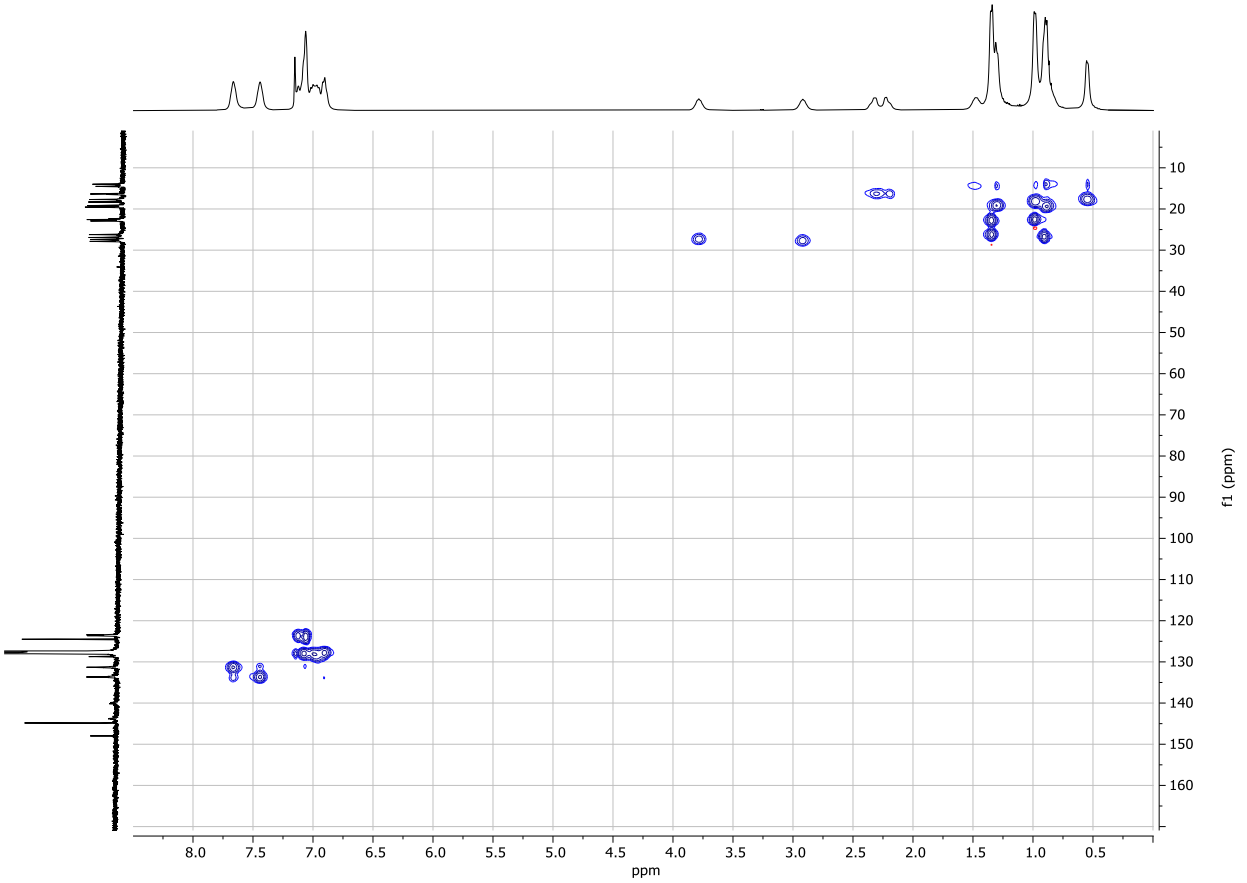

Figure S6. HSQC NMR of **2** in C_6D_6 at ambient temperature.

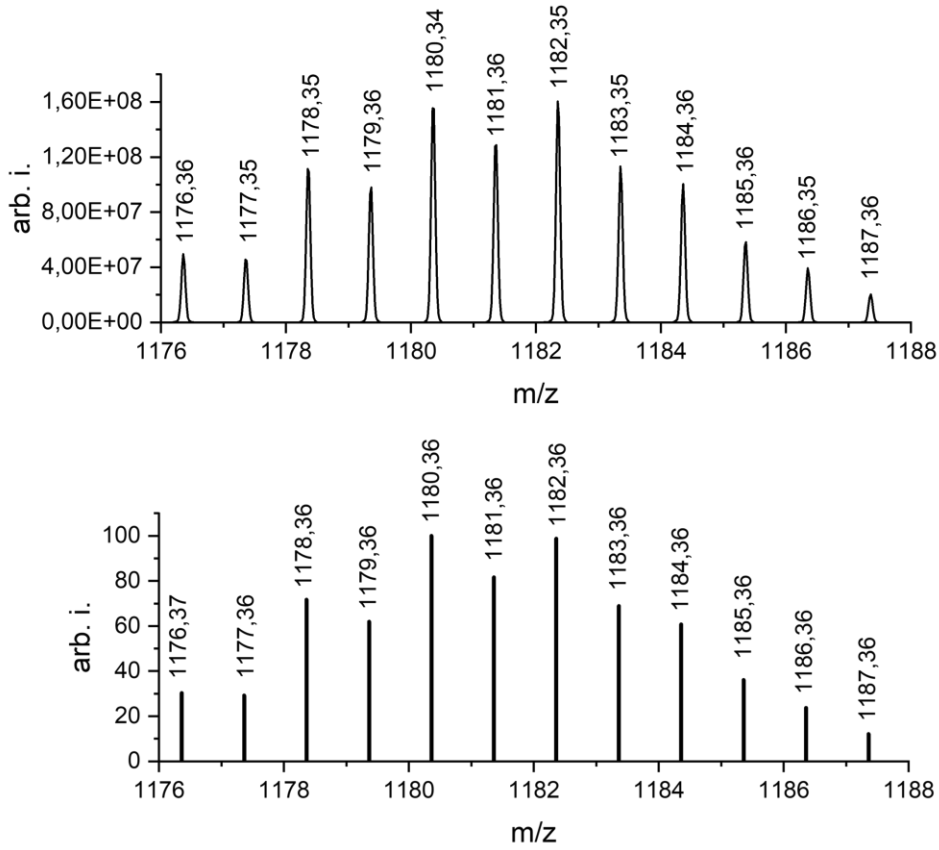

Figure S7. *Top*: Cutout from LIFDI/MS of **2**; *bottom*: calculated MS spectrum of **2**.

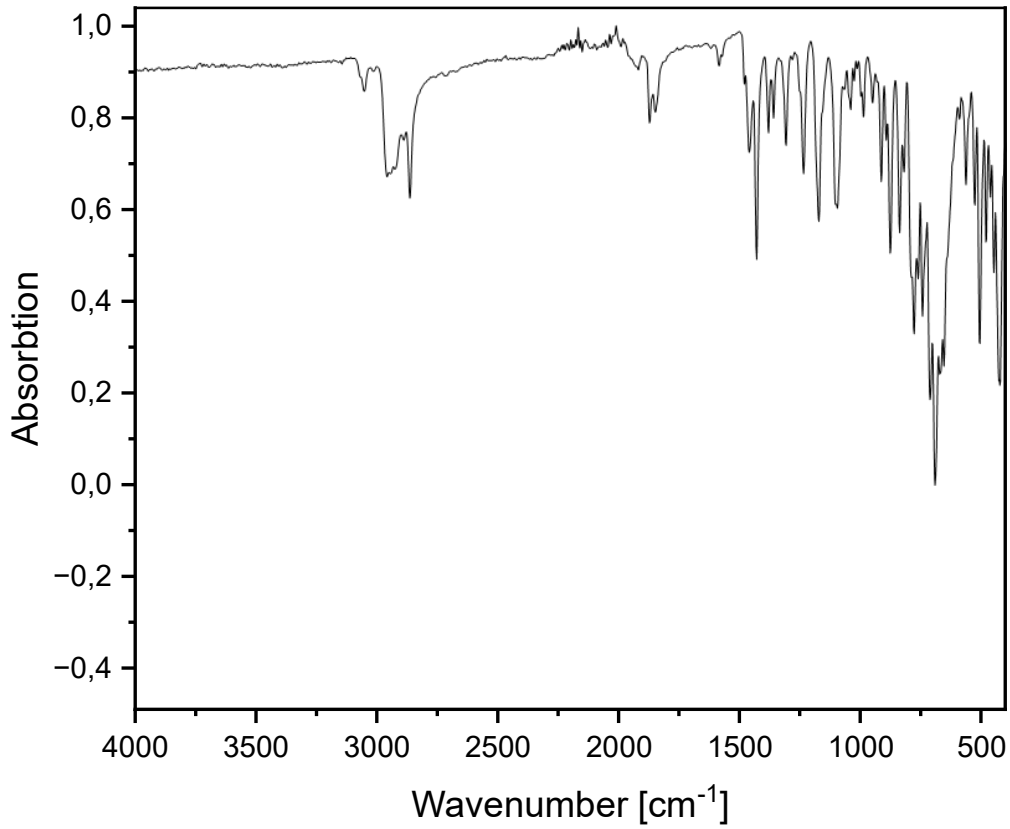

Figure S8. ATR-IR spectrum of **2** at ambient temperature.

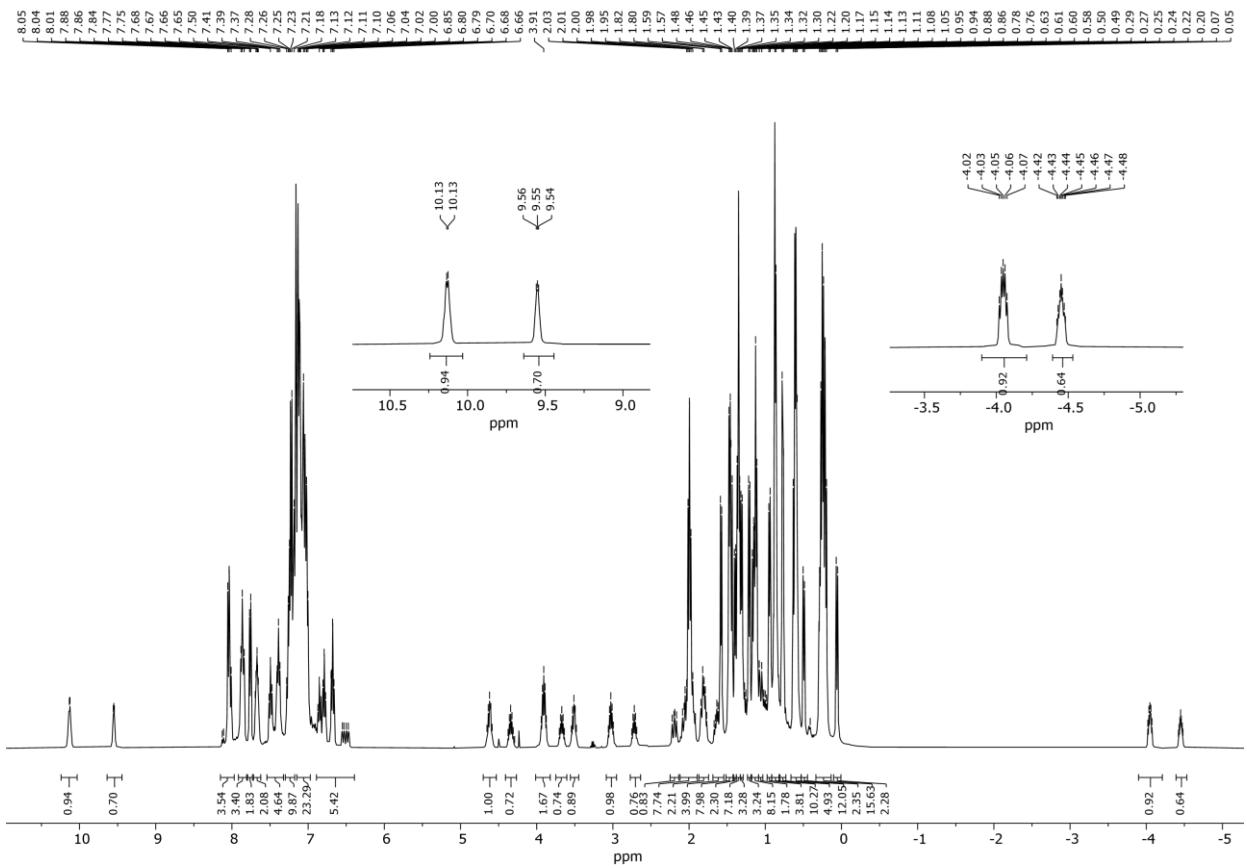

Figure S9. ^{1}H NMR spectrum of **3** in C_6D_6 at ambient temperature.

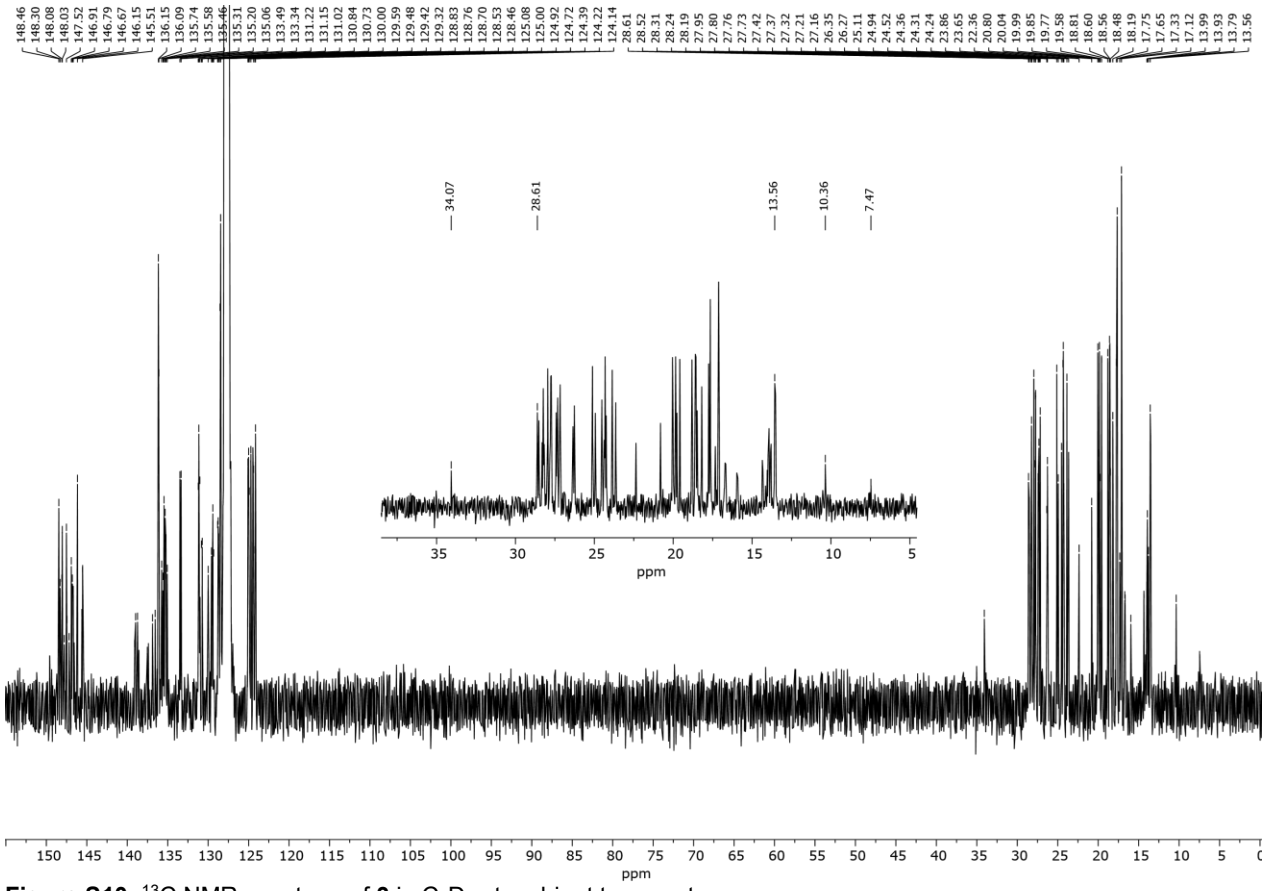

Figure S10. ^{13}C NMR spectrum of **3** in C_6D_6 at ambient temperature.

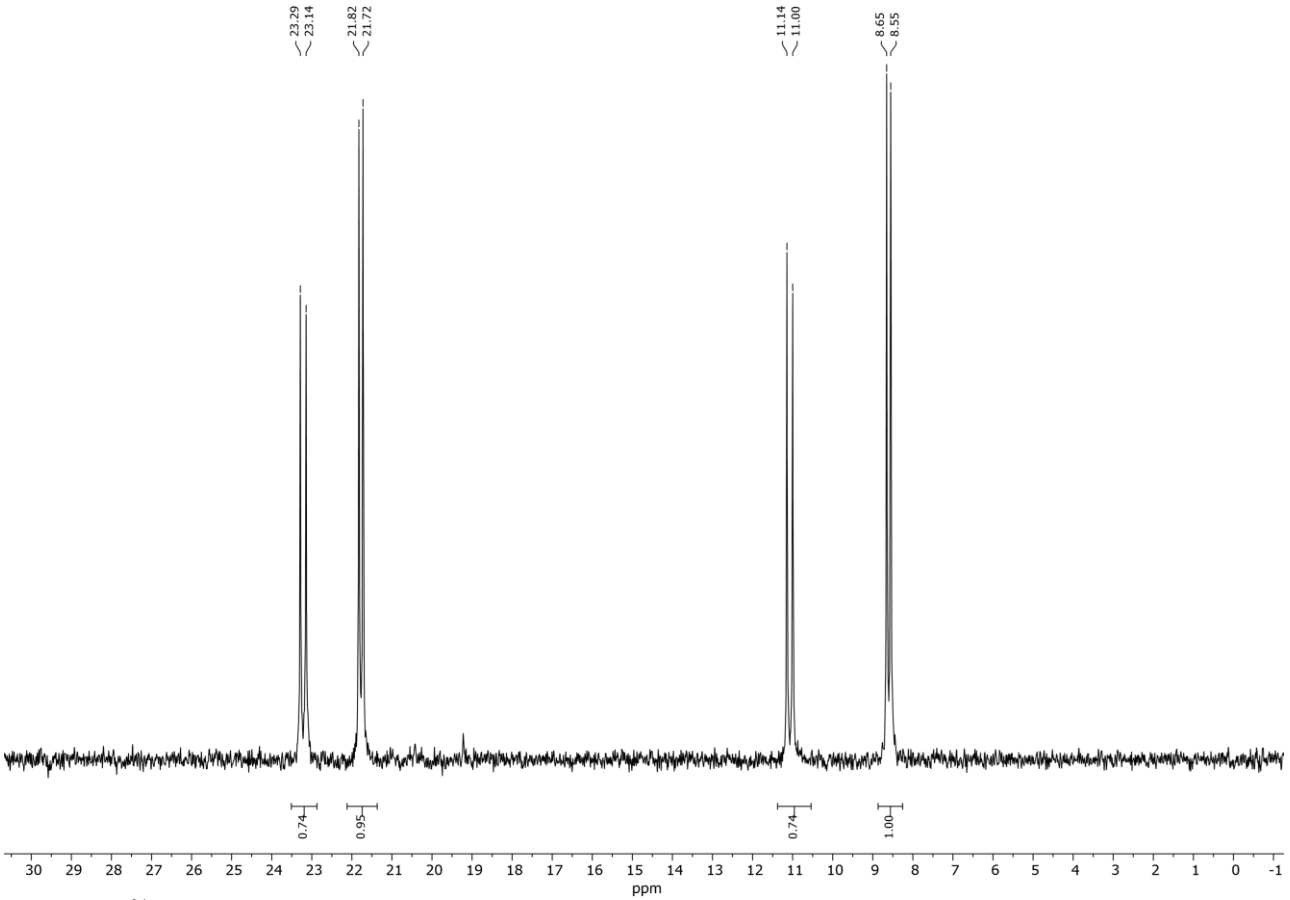

Figure S11. ^{31}P NMR spectrum of **3** in toluene-d_8 at ambient temperature.

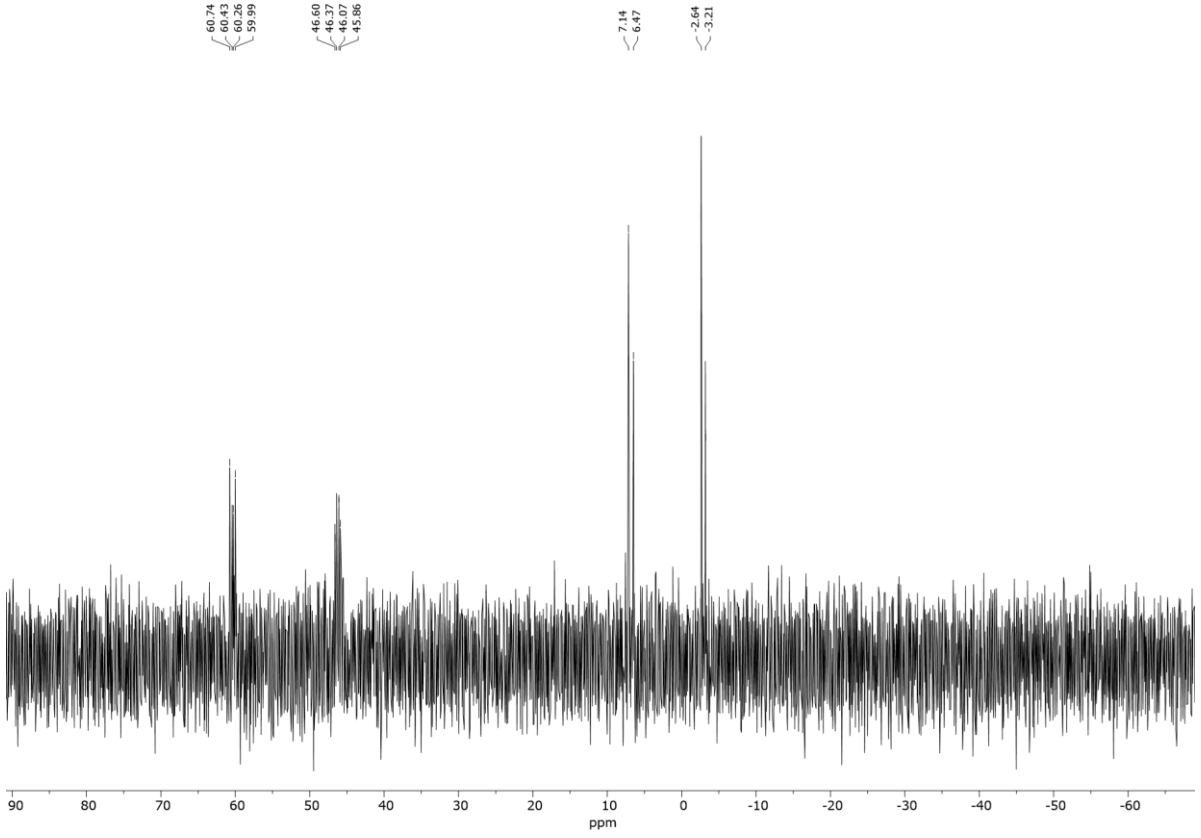

Figure S12. ^{29}Si NMR spectrum of **3** in C_6D_6 at ambient temperature.

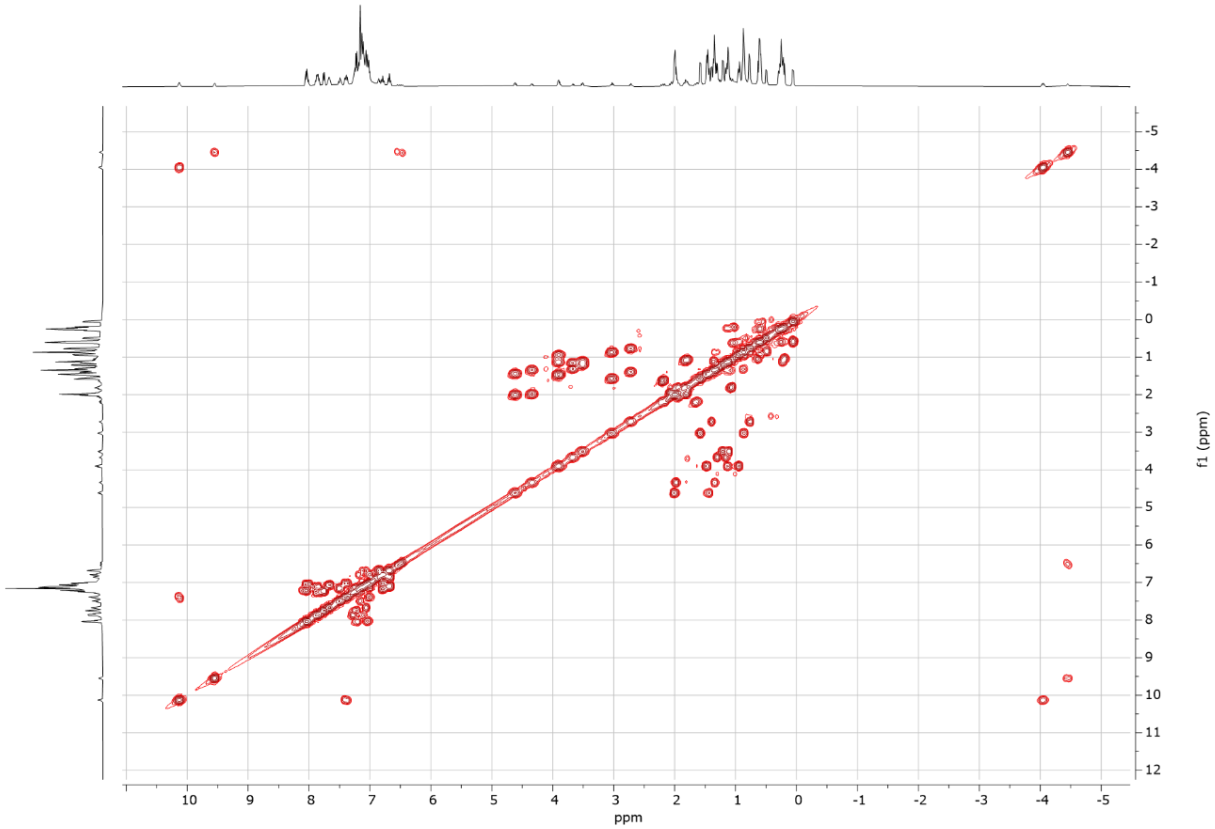

Figure S13. COSY spectrum of **3** in C_6D_6 at ambient temperature.

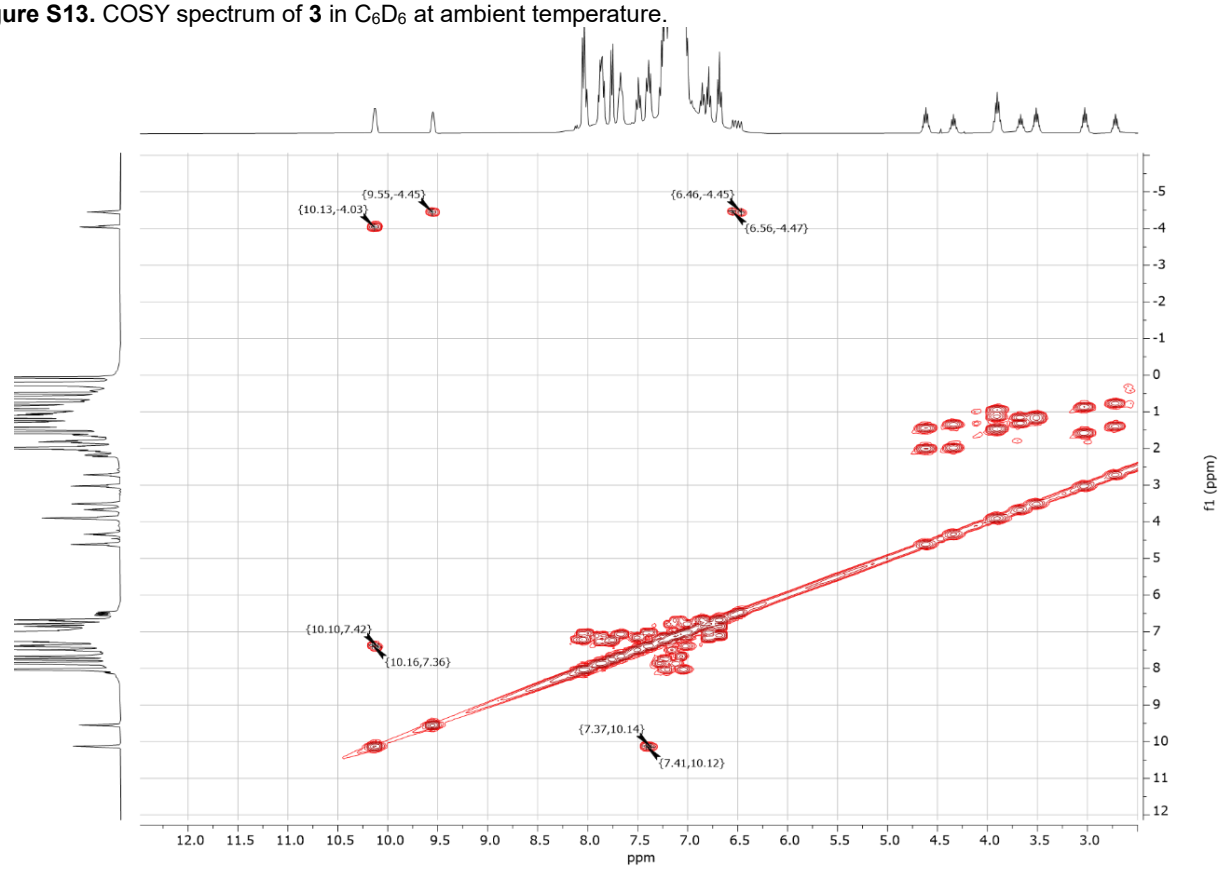

Figure S14. Zoomed in COSY NMR spectrum of **3** in C_6D_6 at ambient temperature.

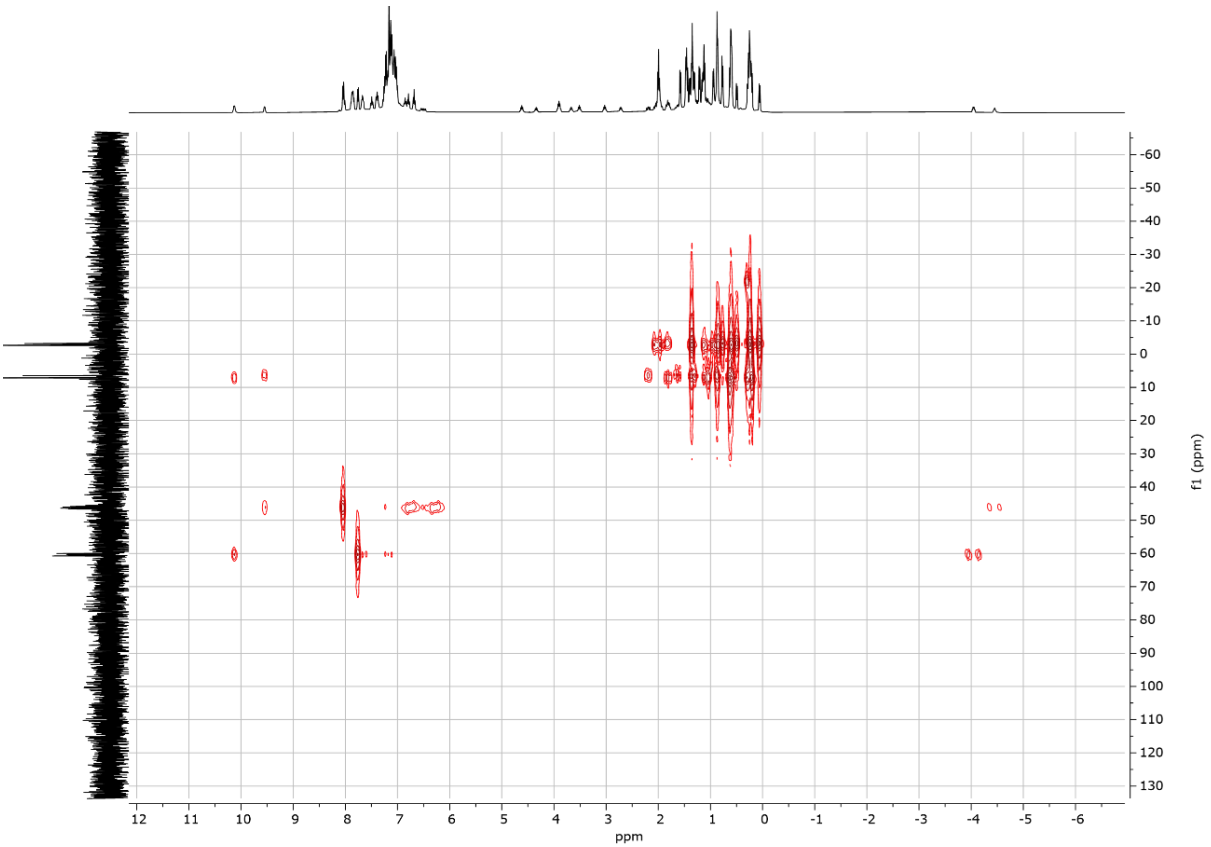

Figure S15. HMBC (^{1}H,^{29}Si) NMR spectrum of **3** in C_6D_6 at ambient temperature.

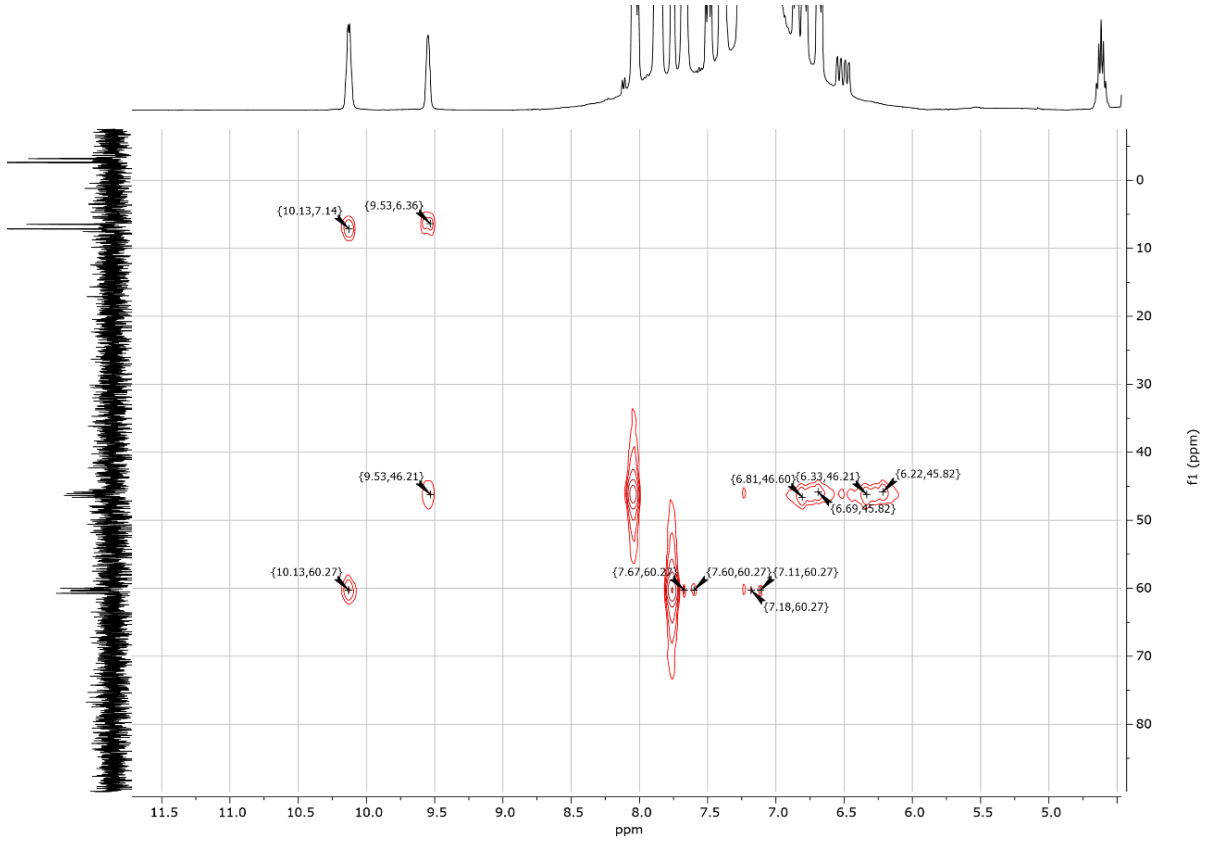

Figure S16. Zoomed in HMBC (^{1}H, ^{29}Si) NMR spectrum of **3** in C_6D_6 at ambient temperature.

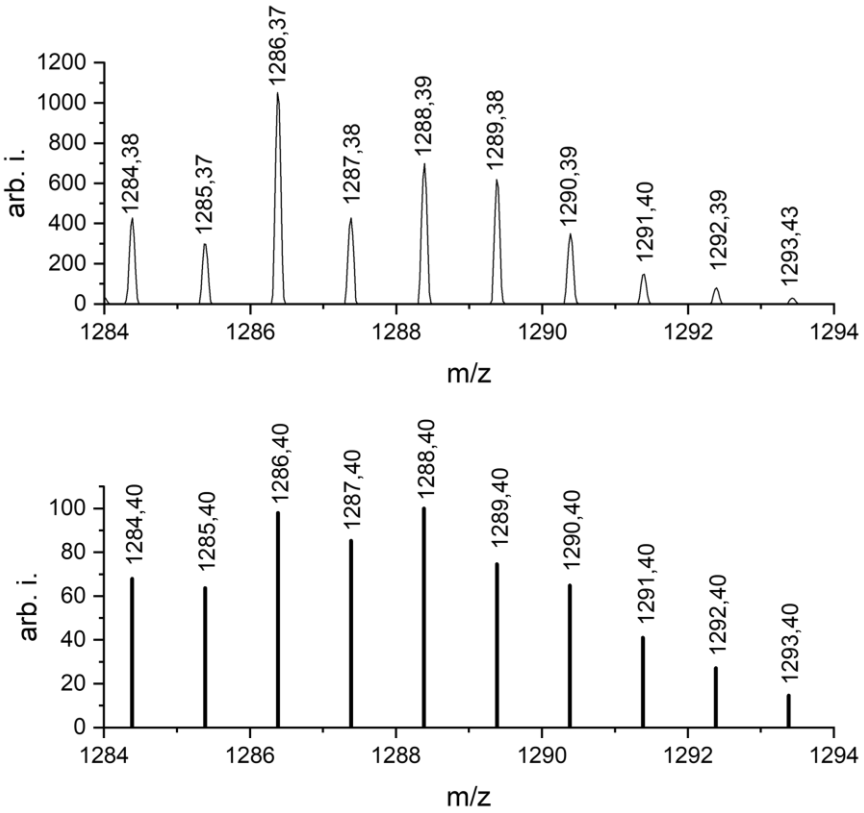

Figure S17. *Top*: Cutout from LIFDI/MS of **3**; *bottom*: calculated MS spectrum of **3**.

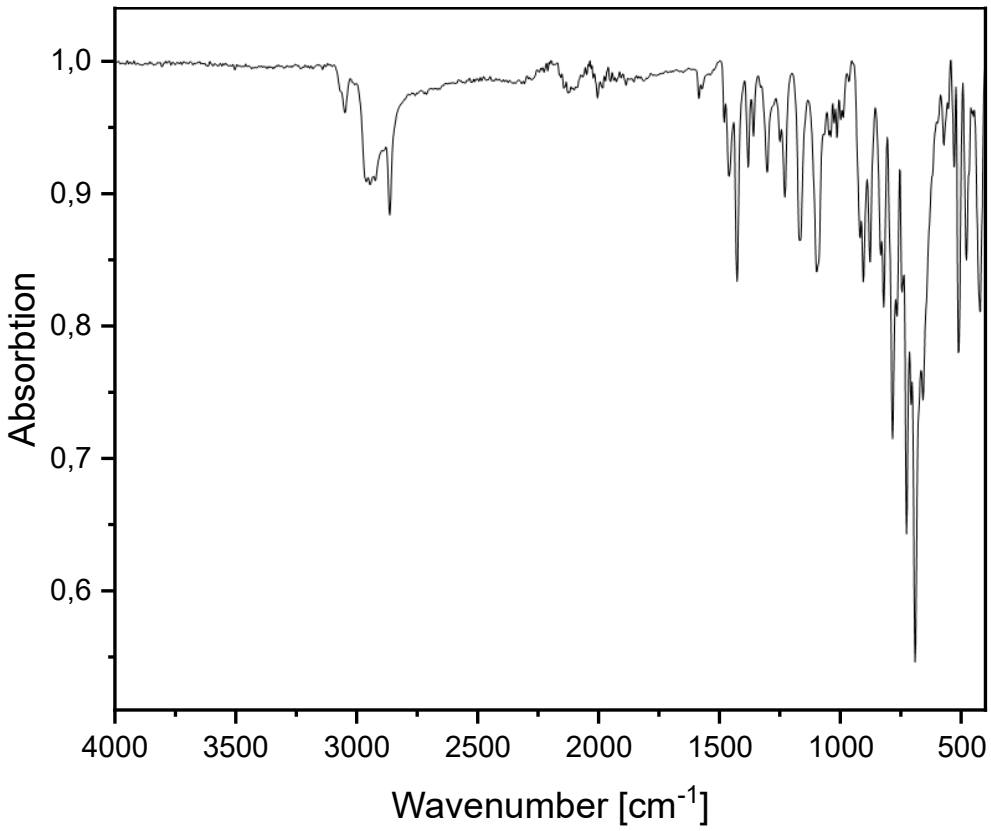

Figure S18. ATR-IR spectrum of **3** at ambient temperature.

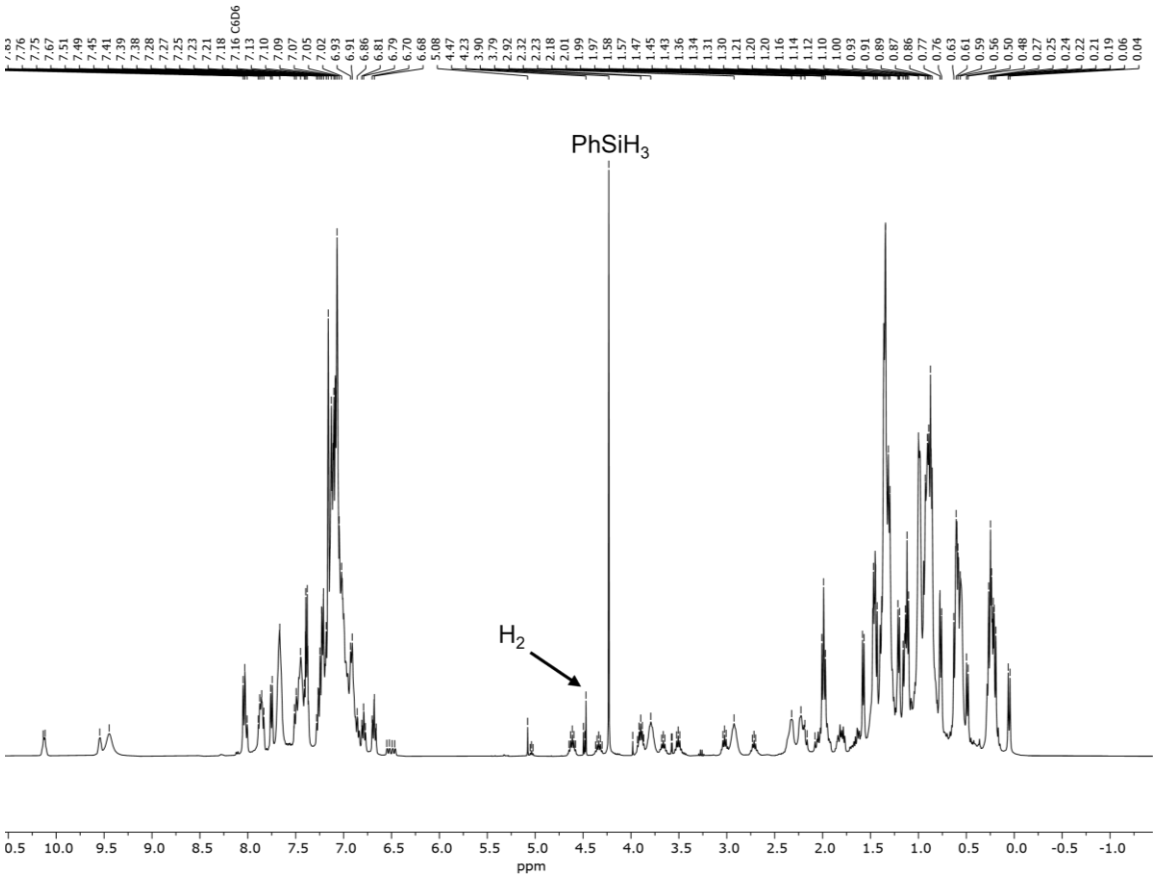

Figure S19. Reaction of **2** with $PhSiH_3$ (1.5 eq.) after 18h at ambient temperature, forming **3** and H_2.

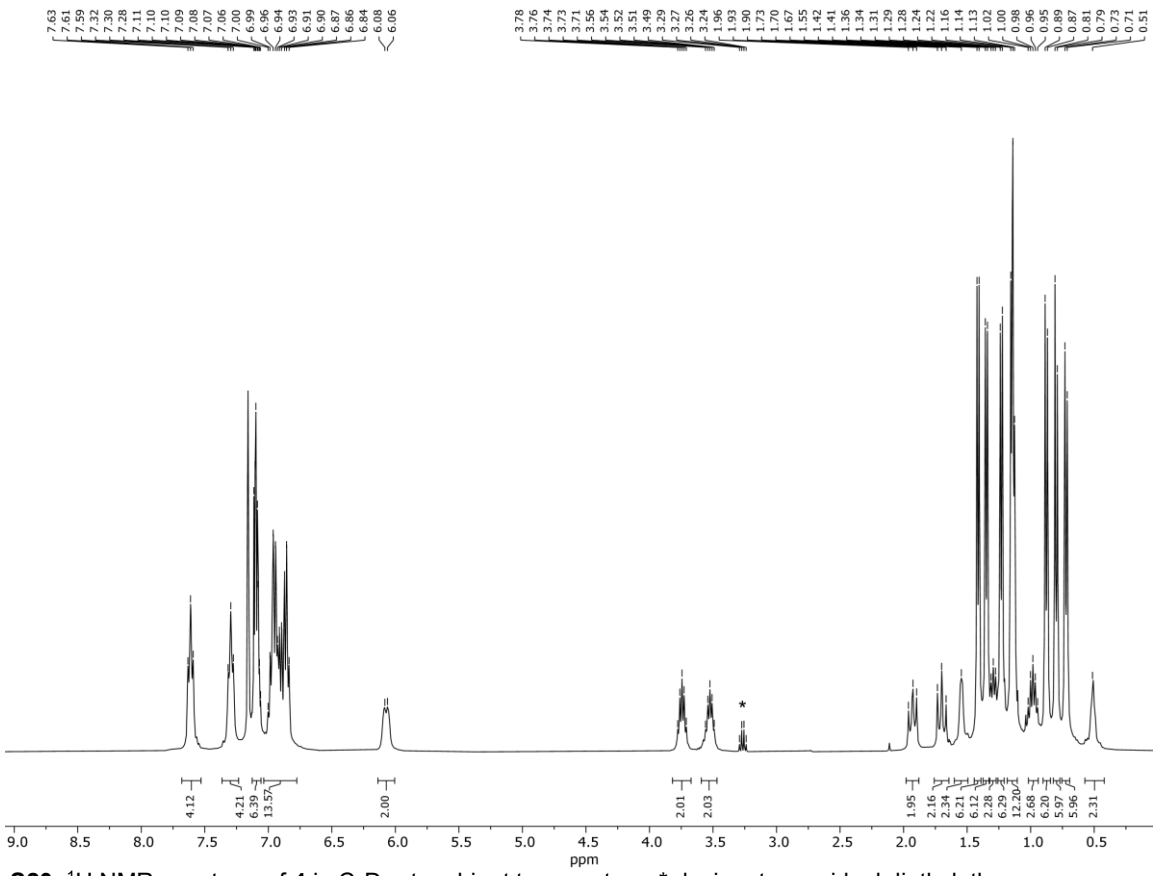

Figure S20. ^1H NMR spectrum of **4** in C_6D_6 at ambient temperature. * designates residual diethylether.

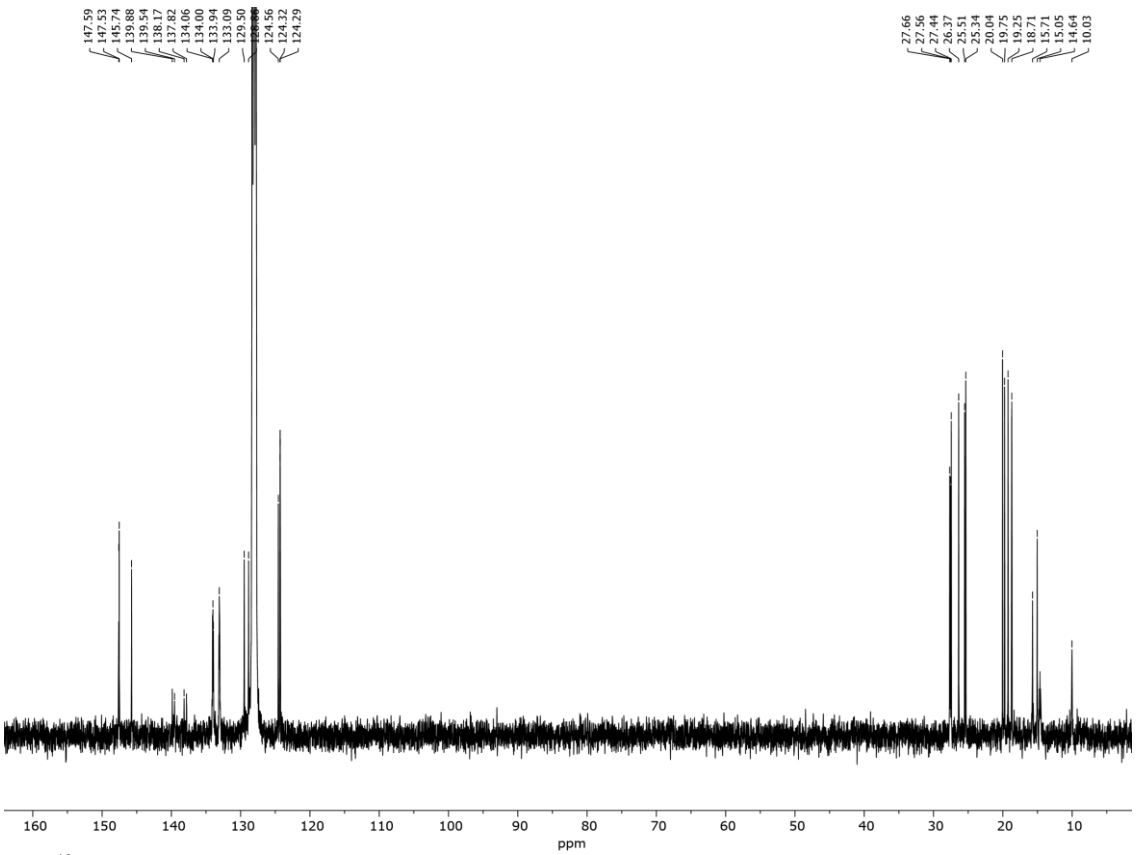

Figure S21. ^{13}C NMR spectrum of **4** in C_6D_6 at ambient temperature.

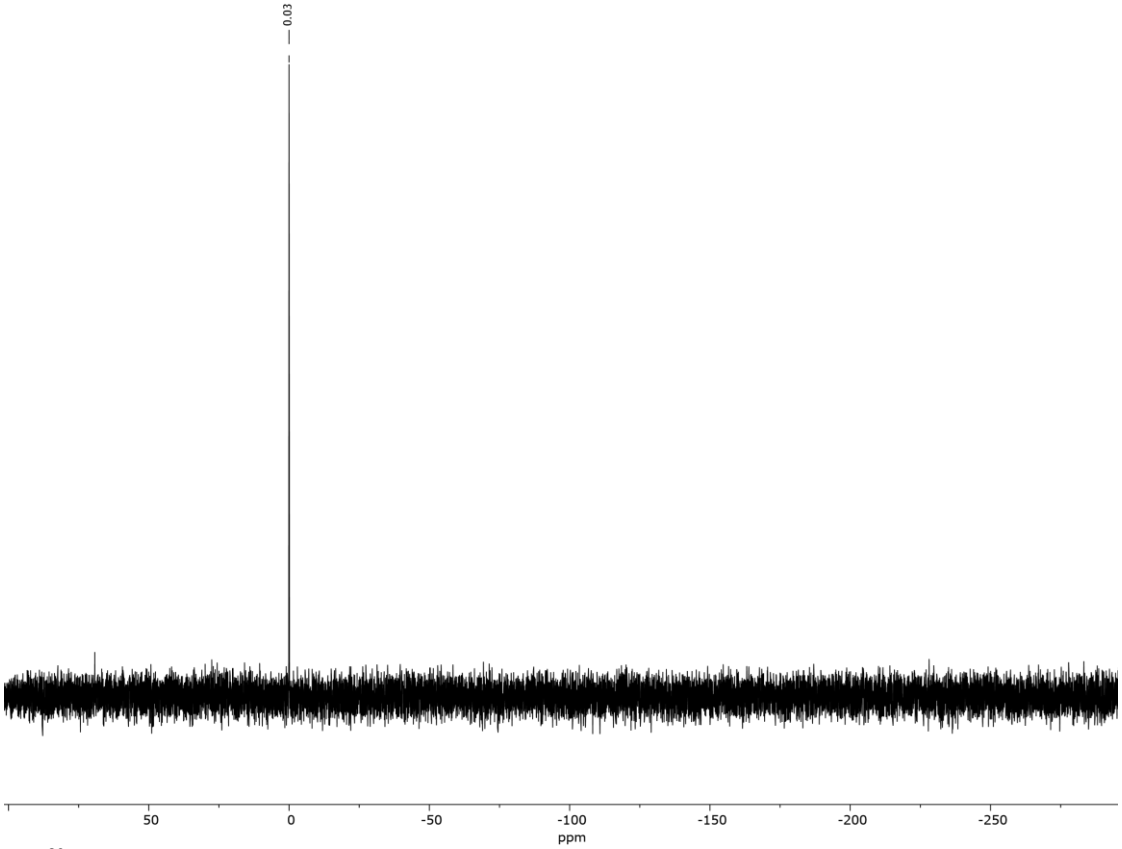

Figure S22. ^{29}Si NMR spectrum of **4** in C_6D_6 at ambient temperature.

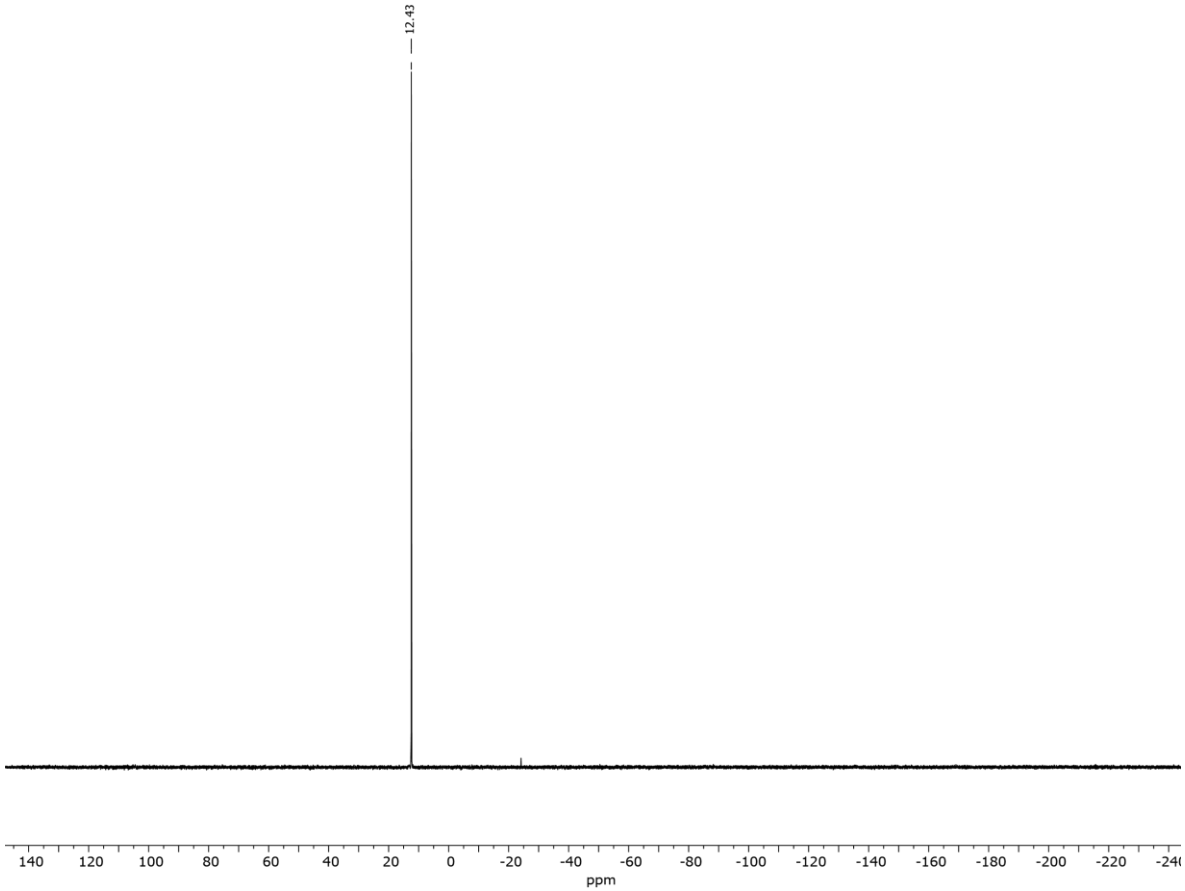

Figure S23. ^{31}P NMR spectrum of **4** in C_6D_6 at ambient temperature.

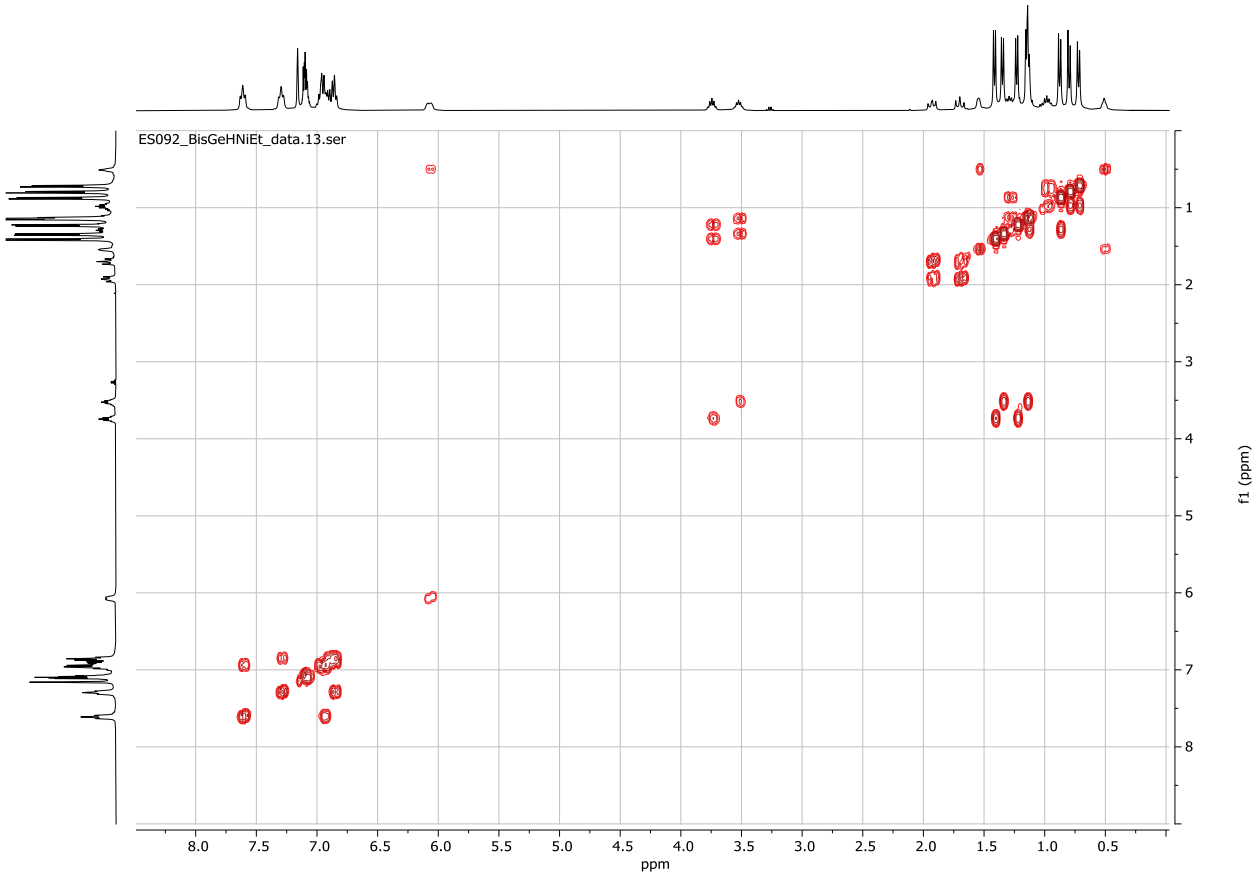

Figure S24. COSY spectrum of **4** in C_6D_6 at ambient temperature.

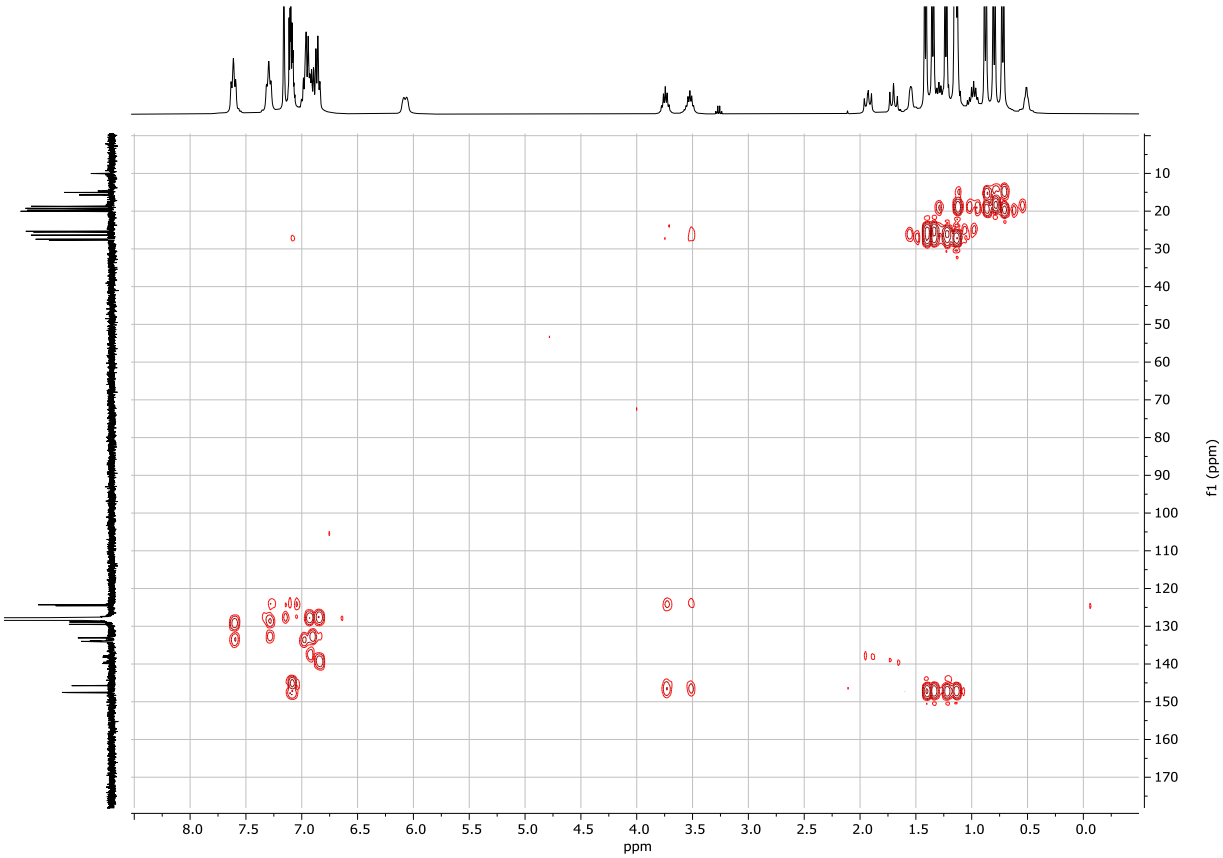

Figure S25. HMBC spectrum of **4** in C_6D_6 at ambient temperature.

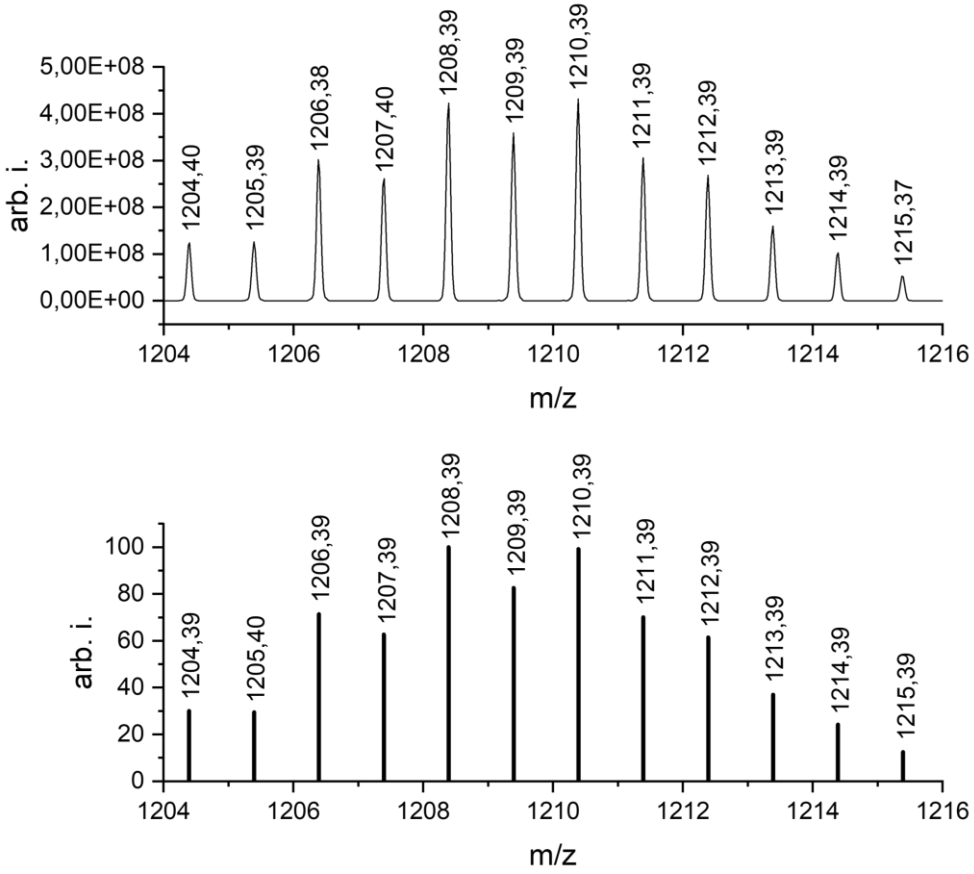

Figure S26. *Top*: Cutout from LIFDI/MS of **4**; *bottom*: calculated MS spectrum of **4**.

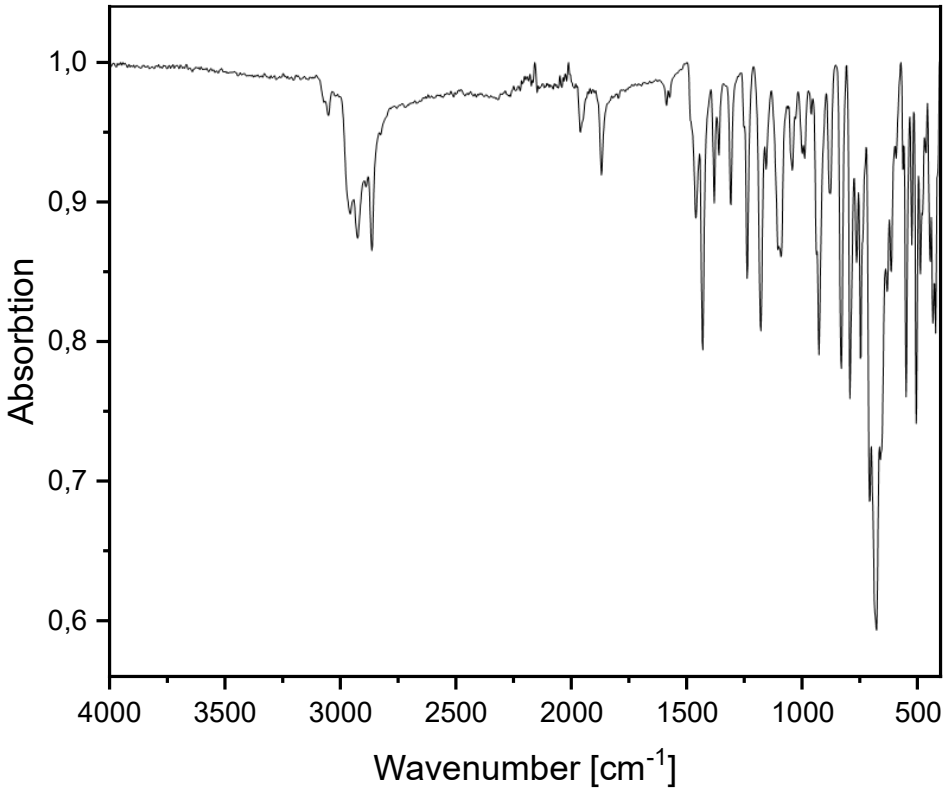

Figure S27. ATR-IR spectrum of **4** at ambient temperature.

3. X-ray crystallographic details

Single crystals of **2**-**4** suitable for X-ray structural analysis were mounted in perfluoroalkyl ether oil on a nylon loop and positioned in a 150 K cold N_2 gas stream. Data collection was performed with a STOE StadiVari diffractometer (MoKα radiation) equipped with a DECTRIS PILATUS 300K detector. Structures were solved by Direct Methods (SHELXS-97),[4] or using SHELXT-16,[5] and refined by full-matrix least-squares calculations against F^2 (SHELXL-2018).[6] The positions of the hydrogen atoms were calculated and refined using a riding model, aside from Ge-*H*, Ni-*H*, and Si-*H* ligands, which were located and freely refined. All non-hydrogen atoms were treated with anisotropic displacement parameters. Crystal data, details of data collections, and refinements for all structures can be found in their CIF files, which are available free of charge via www.ccdc.cam.ac.uk/data_request/cif, and are summarized in Table S1.

Table S1. Selected crystallographic information for **2**-**4**.

	2	**3**	**4**
empirical form.	$C_{62}H_{88}Ge_2N_2NiP_2Si_2$	$C_{70.50}H_{100}Ge_2N_2NiP_2Si_3$	$C_{64}H_{92}Ge_2N_2NiP_2Si_2$
formula wt	1183.35	1325.62	1211.40
crystal syst.	monoclinic	triclinic	triclinic
space group	*P2₁/c*	*P-1*	*P-1*
a (Å)	19.381(4)	13.978(3)	11.277(2)
b (Å)	41.341(8)	22.012(4)	14.795(3)
c (Å)	17.115(3)	23.376(5)	20.380(4)
α (deg.)	90	82.38(3)	101.97(3)
β (δεγ)	116.12(3)	78.37(3)	94.78(3)
γ (deg.)	90	84.61(3)	107.40(3)
vol (Å^3)	12313(5)	6966(3)	3135.3(13)
Z	8	4	2
ρ(calc) (g.cm^{-3})	1.277	1.264	1.283
μ (mm^{-1})	1.402	1.263	1.378
F(000)	4992	2804	1280
T (K)	150(2)	150(2)	150(2)
reflns collect.	92213	93409	42753
unique reflns	24049	27377	12306
R_{int}	0.0715	0.0625	0.0732
R1 [$I>2\sigma(I)$]	0.0434	0.0429	0.0400
*w*R2 (all data)	0.0862	0.0828	0.0778
CCDC No.	2453067	2453069	2453068

Response to B-Level CheckCIF alert for 3:

B-Alert: *Hirshfeld Test Diff (M-X) Ge4 --Ni2 . 11.7 s.u.*

Response: This is due to minor disorder in the core of one isomer of 3. This has been modelled, but leads to the given alert.

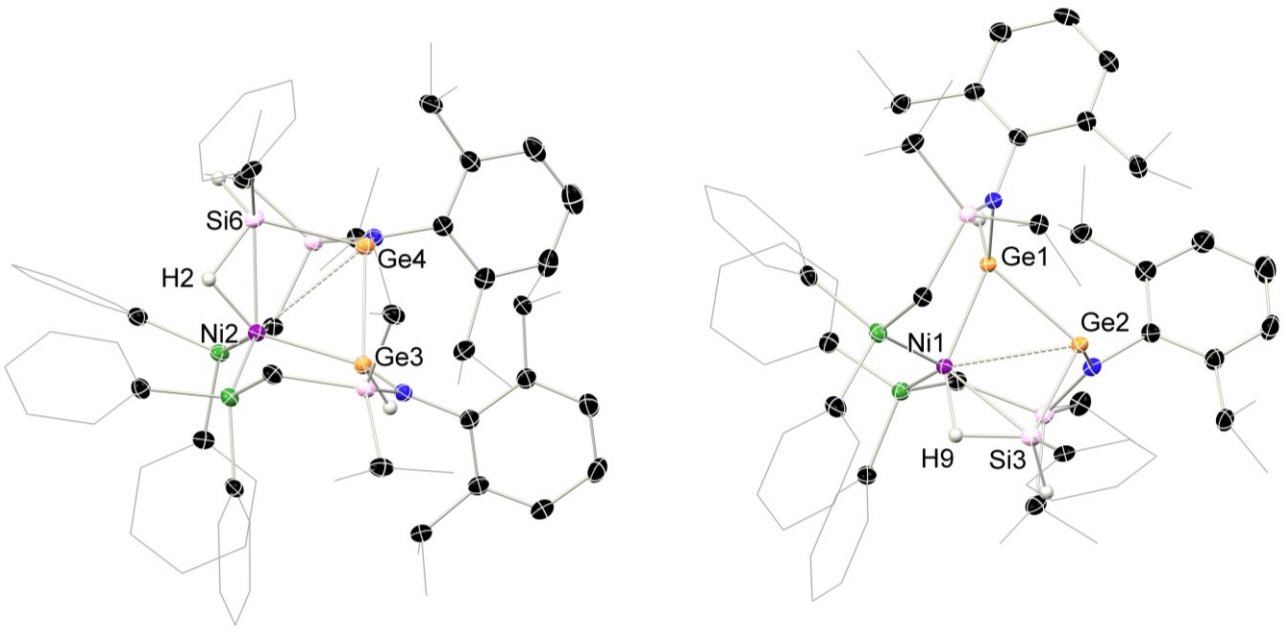

Figure S28. The full asymmetric unit for compound **3**, showing the second diasteroisomer.

4. Computational methods and details

Computational experiments were performed using the ORCA 5.0.4 program.[7] This utilised truncated models in which ^{i}Pr and P-*Ph* groups are replaced with methyl substituents (see Fig. S26 below). The ωB97XD functional was used, with the def2-TZVP basis set for Ni, Ge, and P, and the def2-SVP basis set for all atoms.[8,9,10,11] The RIJCOSX approximation was also used throughout.[12] Stationary points were confirmed as true minima by vibrational frequency analysis (no negative eigenvalues). NBO analysis was carried out using the NBO 6.0 program implemented in ORCA,[13] using optimized geometries from above.

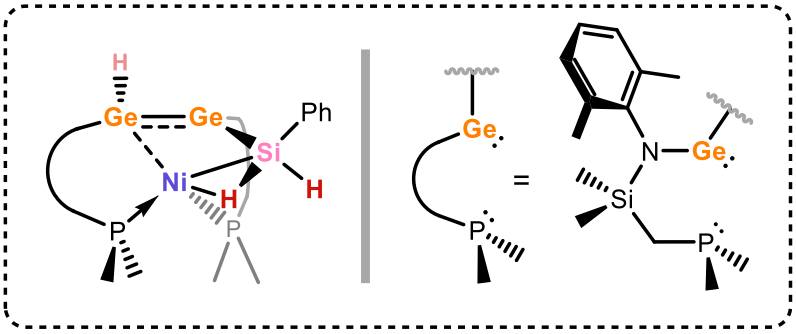

Figure S29. The truncated model (**3'**) used for calculations.

Table S2. Comparison of experimental and calculated bond lengths in **3**/**3'**.

Metrical parameter	**3** (X-ray)	**3'** (calc)
Ge1-Ge2	2.460(1) Å	2.463 Å
Ge2-Si3	2.374(1) Å	2.387 Å
Ge1-Ni1	2.262(1) Å	2.262 Å
Ge2-Ni1	2.798(1) Å	2.796 Å
Si3-Ni1	2.328(1) Å	2.280 Å
Ge1-Ge2-Si3	99.17(3)°	97.8°
Ge1-Ni1-Si3	106.63(3)°	107.5°
Ni1-Ge1-Ge2	72.53(2)°	72.6°
Ni1-Si3-Ge2	73.03(3)°	73.6°

Table S3. NBO derived bonding parameters withing the allyl unit.

Alpha orbitals	**Occupation**	**Atom**	**Polarization**	**s-character**	**p-character**	**d-character**
Bond	1.85	Ge1	62.67%	51.50%	47.82%	0.65%
		Ge2	37.33%	6.69%	92.39%	0.90%

Bond	1.85	Ge2	42.79%	9.04%	89.92%	1.02%
		Si3	57.21%	32.59%	66.95%	0.01%
Lone pair	1.72	Ge2	-	73.55%	26.26%	0.18%
Empty orbital	0.72	Ge1	-	1.33%	97.82%	0.81%

Table S4. NBO derived Natural Charges in **3'**.

Ge	Si	Ni	P
0.73393 (Ge1)	1.96239 (Si1)	0.07438	0.95126 (P1)
0.26595 (Ge2)	1.95327 (Si2)		0.86238 (P2)
	0.59228 (Si3)		

Table S5. Calculated Cartesian geometry of **3'**.

Atom	x-coordinate	y-coordinate	z-coordinate
Ge	4.02592	17.86587	4.08861
Ge	2.58188	18.3123	2.14357
Ni	4.64521	16.44998	2.44962
P	6.75715	16.83492	2.83946
P	3.75193	14.59436	3.3211
Si	6.70099	19.7149	4.24334
Si	0.85256	15.46991	2.31582
Si	3.99356	17.36781	0.46702
N	5.10511	19.20706	4.79263
N	1.01918	17.21238	2.32901
C	4.71019	19.40192	7.22288
C	4.52613	19.895	5.9073
C	6.70866	21.46339	3.5536
H	6.40407	22.19644	4.31705
H	3.5415	13.22378	1.32136
H	7.72947	21.72193	3.2272
C	3.73693	21.05314	5.70121
C	5.46743	18.1297	7.50987
H	5.9019	17.69983	6.60156
C	5.23653	18.57491	-0.29981
C	7.3039	18.56659	2.86466
H	6.97194	18.99488	1.90518
H	8.4072	18.6083	2.87044
C	7.49735	16.12024	4.34409
C	0.15771	18.16954	4.94279
H	0.67814	18.00031	-0.23253
C	4.39687	14.02512	4.93274
C	3.95876	13.07887	2.32567
C	-0.14252	18.03483	2.42166
H	-0.42008	18.46773	5.82864
H	-0.91057	18.46639	-0.9037
H	3.28351	17.41006	5.3805

H	3.24317	16.75203	-0.67658
H	5.03435	12.87504	2.22155
H	8.89086	20.10189	5.33295
H	6.0365	21.56448	2.68858
H	-1.05694	13.95079	2.78395
C	1.95837	14.66875	3.63922
H	1.83223	15.27093	4.55472
H	1.5827	13.65629	3.86916
C	-0.5828	18.51504	3.67814
H	-3.30209	20.32594	2.66158
C	7.14931	18.99619	-1.7542
C	-0.85015	18.40245	1.25293
H	7.40384	15.02633	4.2997
H	8.56199	16.38605	4.42549
C	-0.92508	15.0446	2.76273
H	-1.19938	15.4433	3.75213
C	3.18664	21.71145	6.80785
H	2.57921	22.60628	6.64011
H	7.87826	18.62798	-2.48128
H	4.79719	17.37669	7.95367
H	1.13387	13.56986	0.74117
H	7.62672	15.03179	1.47469
H	4.29146	14.82843	5.67592
H	6.28202	18.30736	8.22859
C	3.44554	21.60818	4.32846
H	3.80456	20.94858	3.53118
H	2.9559	21.77359	8.95425
C	3.39238	21.24653	8.10168
H	6.96707	16.47137	5.23911
H	3.47124	12.2142	2.8014
C	1.23742	14.66422	0.65534
H	2.25941	14.88387	0.31252
C	7.82386	16.11052	1.5495
C	-1.97882	19.22278	1.35782
H	-2.51943	19.50086	0.44782
H	0.54194	15.00998	-0.12372
H	7.56791	20.30852	6.50613
C	-2.41764	19.68667	2.59441
H	3.85368	13.13528	5.28549
C	-1.71739	19.3313	3.74395
H	-2.05468	19.69272	4.72032
C	-0.41007	17.90842	-0.10002
H	-0.65624	16.84315	-0.234
H	3.91378	22.5959	4.19537
H	1.12939	18.68703	4.98827
H	0.37113	17.09319	5.01147
H	2.36102	21.74147	4.19384
H	5.4642	13.78098	4.83699
H	4.82873	16.00472	0.91456
C	6.18104	18.13233	-1.24078
H	6.16829	17.09005	-1.57825
C	4.14547	20.09352	8.29932

H	4.29694	19.70826	9.31248
C	7.92747	19.68662	5.67047
H	8.10866	18.67118	6.05271
C	7.18661	20.32869	-1.34011
H	7.94418	21.00781	-1.74049
C	5.28614	19.92107	0.09595
H	4.56199	20.29773	0.82653
C	6.24944	20.79156	-0.41623
H	6.26869	21.83484	-0.08944
H	8.88771	16.27474	1.77771
H	-1.63156	15.45776	2.02535
H	7.58507	16.57753	0.58427

5. References

1 P. M. Keil and T. J. Hadlington, *Zeitschrift anorg allge chemie*, 2022, **648**, e202200141.

2 A. J. Sicard and R. T. Baker, *Org. Process Res. Dev.*, 2020, **24**, 2950–2952.

3 M. Muhr, P. Heiß, M. Schütz, R. Bühler, C. Gemel, M. H. Linden, H. B. Linden and R. A. Fischer, *Dalton Trans.*, 2021, **50**, 9031–9036.

4 G. M. Sheldrick, SHELXL-97, Program for Crystal Strucutre Refinement, Göttingen, 1997.

5 G. M. Sheldrick, *Acta Crystallogr A Found Adv*, 2015, **71**, 3–8.

6 G. M. Sheldrick, *Acta Crystallogr C Struct Chem*, 2015, **71**, 3–8.

7 F. Neese, *WIREs Comput Mol Sci*, 2012, **2**, 73–78.

8 A. D. Becke, *The Journal of Chemical Physics*, 1997, **107**, 8554–8560.

9 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297.

10 J.-D. Chai and M. Head-Gordon, *The Journal of Chemical Physics*, 2008, **128**, 084106.

11 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *The Journal of Chemical Physics*, 2010, **132**, 154104.

12 F. Neese, F. Wennmohs, A. Hansen and U. Becker, *Chemical Physics*, 2009, **356**, 98–109.

13 E. D. Glendening, C. R. Landis and F. Weinhold, *J Comput Chem*, 2013, **34**, 1429–1437.