Electronic Supplementary Information for the paper

Entitled

Interconversion between a Silaimine and an Aminosilylene Supported by an Iminophosphonamide Ligand

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1-General procedure

Unless otherwise noted, all experiments were carried out under an argon atmosphere by using standard Schlenk techniques or in a UNICO glovebox. All solvents were dried by 4A molecular sieves or potassium mirror before use. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AVANCE-400 (400, 100, and 162 MHz, respectively) spectrometer, ^{1}H, ^{13}C, ^{31}P, ^{29}Si, and ^{77}Se, NMR spectra were recorded on a Bruker AVANCE-500 (500, 125, 202, 99, and 95 MHz, respectively) spectrometer. All melting points were determined on a Mel-Temp capillary tube apparatus and were uncorrected. Elemental analyses were carried out at the Molecular Analysis and Life Science Center of Saitama University. All materials were obtained from commercial supplier and used without further purification.

2-Experimental procedures and characterization data

2-1 Synthesis of silaimine 3.

In a Schlenk tube, chlorosilylene **1**[S1] (366 mg, 0.94 mmol) and $KN(SiMe_3)_2$ (190 mg, 0.94 mmol) were dissolved into toluene (20 mL) at room temperature. Then the reaction mixture was kept stirring at this temperature for 3 hours. The reaction mixture was filtered and all volatiles of the filtrate were removed under reduced pressure. Recrystallization from toluene at –10 °C gave silaimine **3** (350 mg, 72%) as colorless crystals. Mp: 92–95 °C (decomp.). ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ = 0.53 (s, 9H, Si-CH_3), 0.66 (s, 9H, Si-CH_3), 1.08 (s, 18H, CH_{3tBu}), 7.04–7.09 (m, 6H, CH_{Ar}), 7.84–7.89 (m, 2H, CH_{Ar}), 8.20 (br s, 2H, CH_{Ar}). $^{13}C\{^{1}H\}$ NMR (100 MHz, 25 °C, C_6D_6): δ = 0.9 ($SiCH_3$), 6.6 ($SiCH_3$), 32.7 (d, J_{CP} = 6.4 Hz, CH_{3tBu}), 52.9 (C_{tBu}), 128.8 (d, J_{CP} = 12.6 Hz, CH_{Ar}), 128.9 (d, J_{CP} = 91.4 Hz, C_{Ar}), 130.0 (d, J_{CP} = 90.4 Hz, C_{Ar}), 133.1 (d, J_{CP} = 2.9 Hz, CH_{Ar}), 133.2 (d, J_{CP} = 3.0 Hz, CH_{Ar}), 133.6 (d, J_{CP} = 11.3 Hz, CH_{Ar}), 135.0 (br, CH_{Ar}). $^{31}P\{^{1}H\}$ NMR (202 MHz, 25 °C, C_6D_6,): δ = 38.5. $^{29}Si\{^{1}H\}$ NMR (C_6D_6, 99 MHz): δ = –43.2 (d, J_{SiP} = 5.8 Hz, N-Si-N), –28.6 (d, J_{SPi} = 6.5 Hz, Si-$\underline{Si}Me_3$), –26.4

(N-SiMe$_3$). Anal. Calcd for $C_{26}H_{46}N_3Si_3P$: C, 60.53; H, 8.99; N, 8.15. Found: C, 60.49; H, 9.12; N, 8.07.

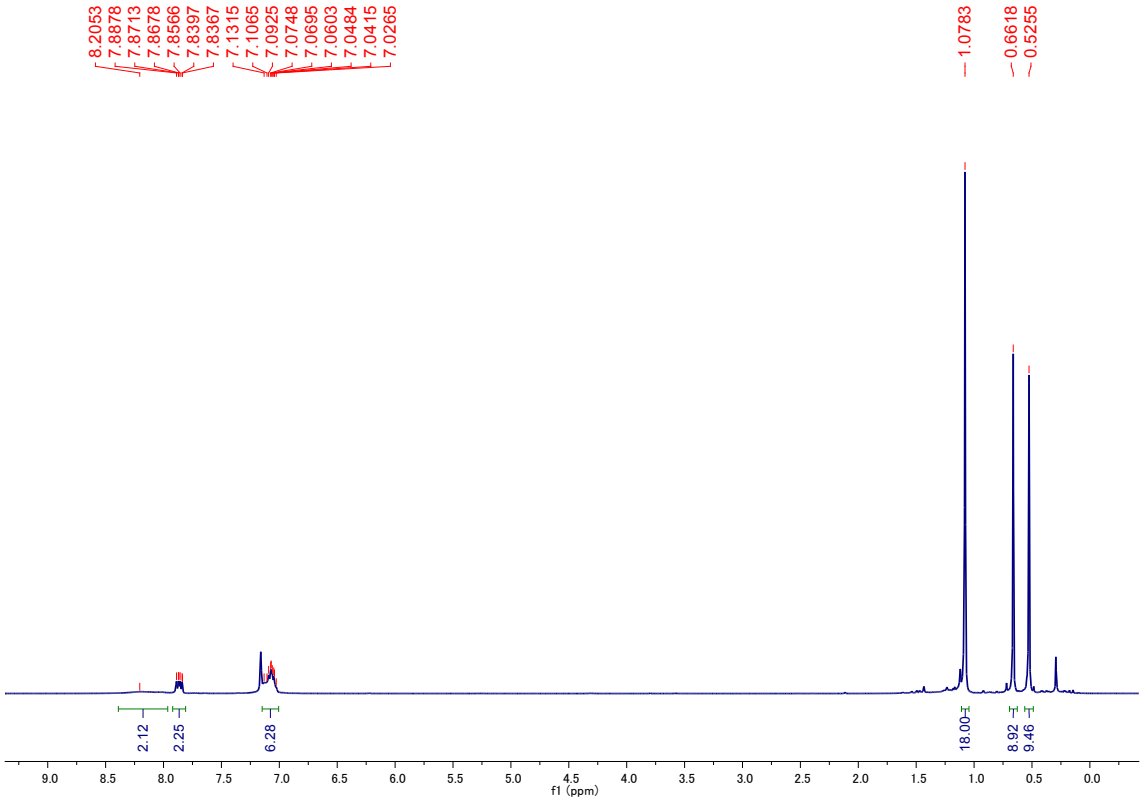

Figure S1. ^{1}H NMR specrum (400 MHz, 25 °C, C_6D_6) of **3**.

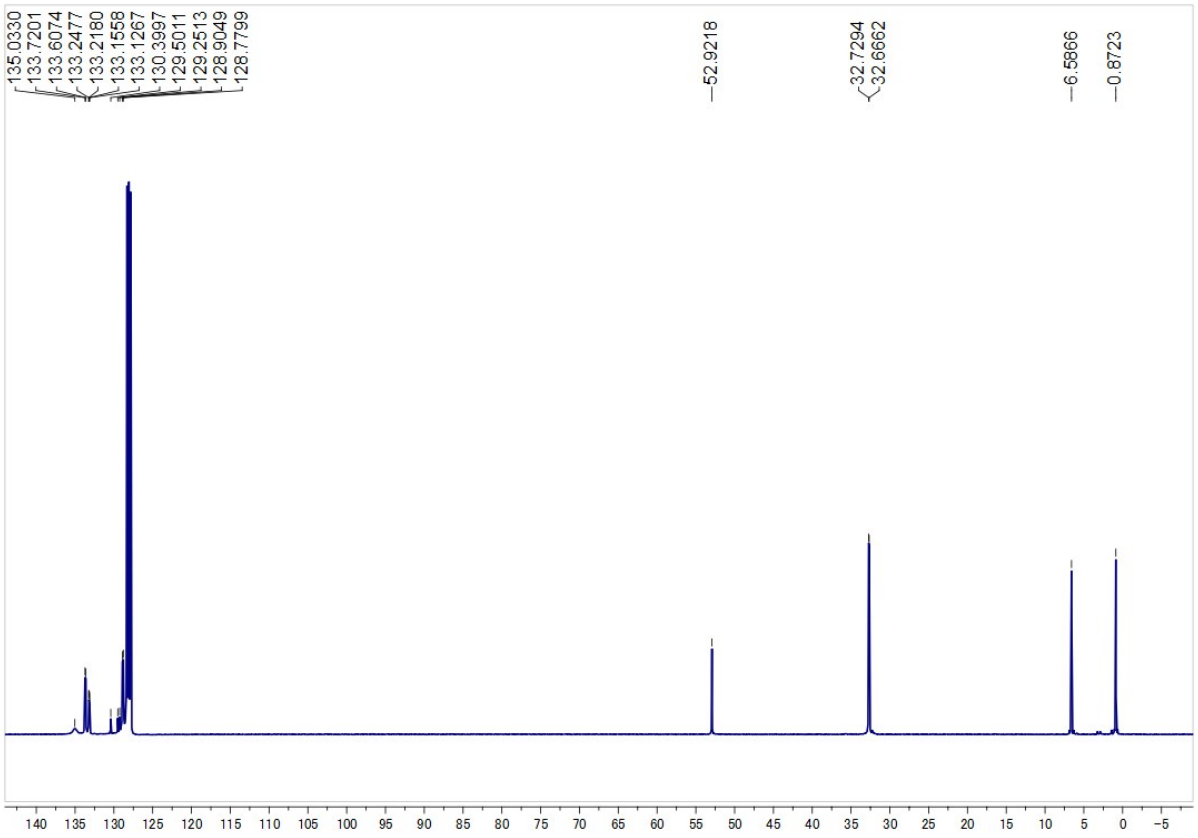

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, C_6D_6) of **3**.

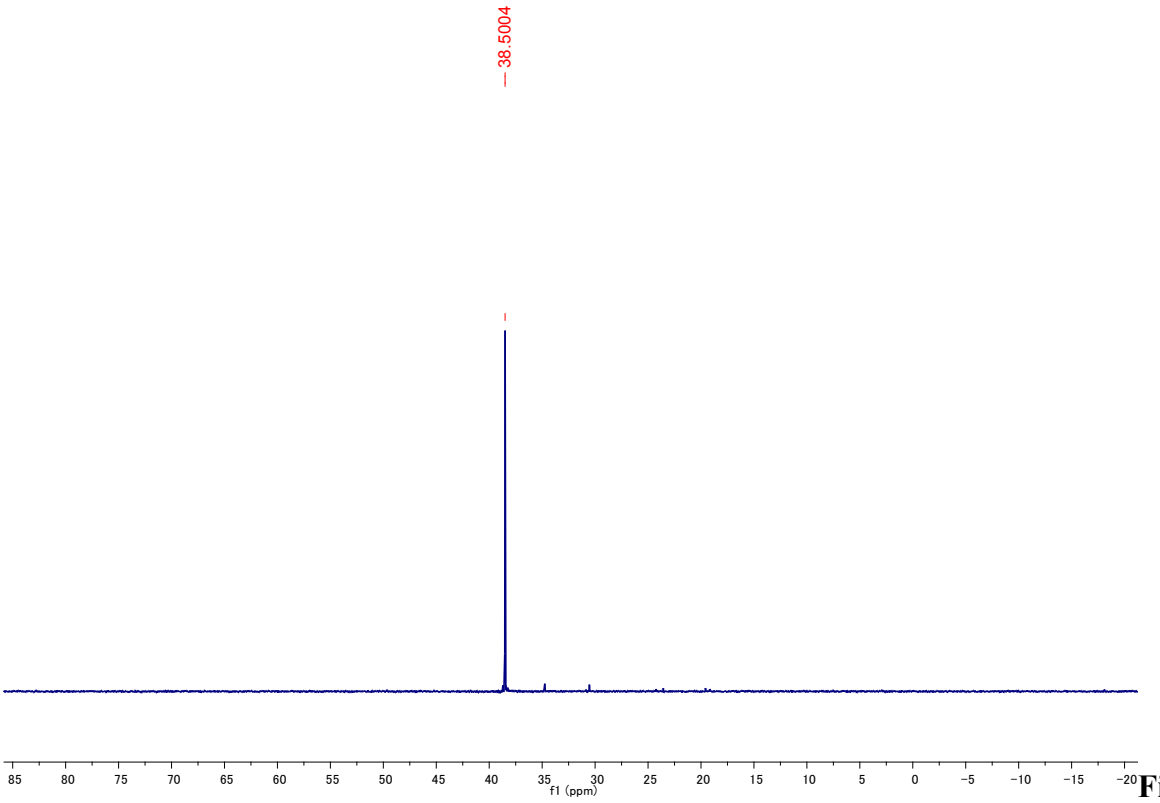

Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 25 °C, C_6D_6) of **3**.

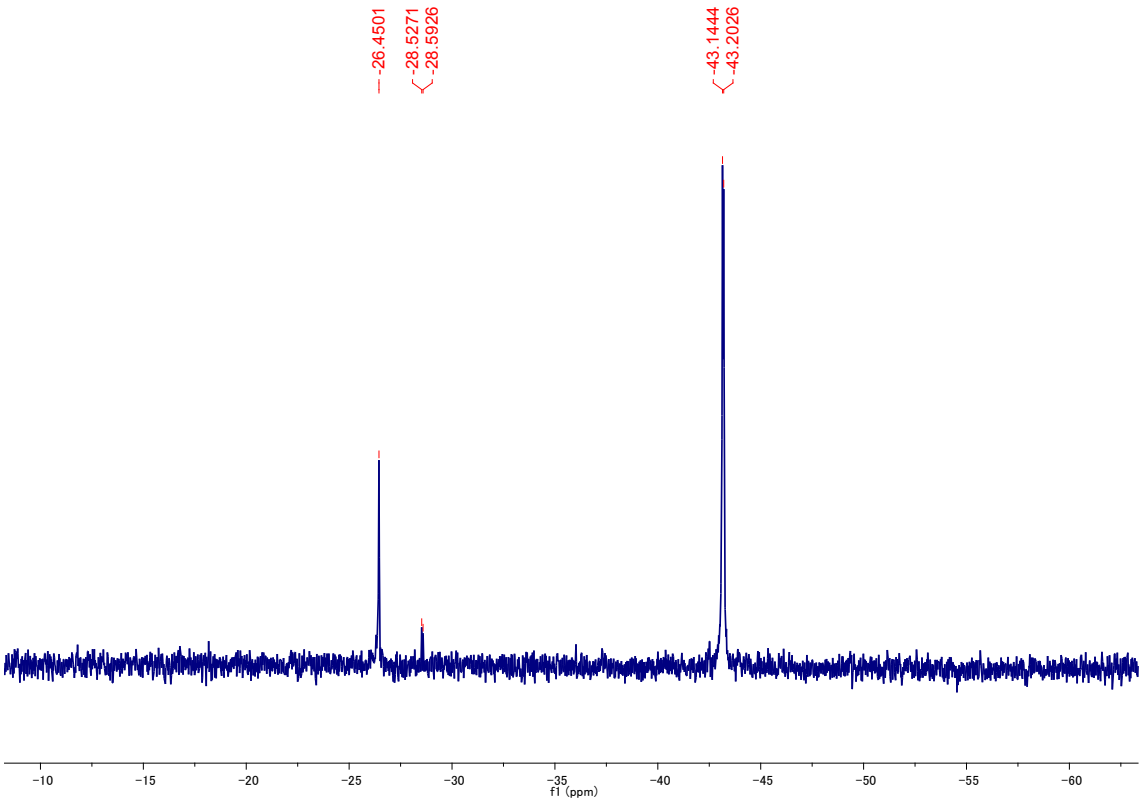

Figure S4. $^{29}Si\{^{1}H\}$ NMR specrum (99 MHz, 25 °C, C_6D_6) of **3**.

2-2 Direct observation of aminosilylene 2 using low-temperature NMR spectroscopy.

In a J. Young NMR tube, to a mixture of **1** and $KN(SiMe_3)_2$, THF-d_8 (0.6 mL) was added by vacuum transfer using liquid nitrogen. This mixture was warm up to –80 ºC and the color of the solution changed to dark red. As results of NMR measurements at –50 ºC, the formation of aminosilylene **3** as a main product was confirmed by all NMR spectra. ^{1}H NMR (500 MHz, –50 °C, THF-d_8): δ 0.22 (s, 9H, Si-CH_3), 0.33 (s, 9H, Si-CH_3), 1.15 (s, 18H, CH_{3tBu}). $^{13}C\{^{1}H\}$ NMR (125 MHz, –50 °C, THF-d_8): δ 5.6 (Si-CH_3), 5.9 (Si-CH_3), 32.1 (d, J_{CP} = 6.0 Hz, CH_{3tBu}), 52.4 (C_{tBu}), 127.9 (d, J_{CP} = 11.8 Hz, CH_{Ar}), 131.7 (CH_{Ar}), 132.4 (CH_{Ar}), 134.1 (d, J_{CP} = 11.7 Hz, CH_{Ar}). $^{31}P\{^{1}H\}$ NMR (202 MHz, –50 °C, THF-d_8): δ = 20.6. $^{29}Si\{^{1}H\}$ NMR (99 MHz, –50 °C, THF-d_8): δ = –1.0 (Si-CH_3), –5.2 (Si-CH_3), 47.4 (d, J_{SiP} = 4.9 Hz, N–Si–N).

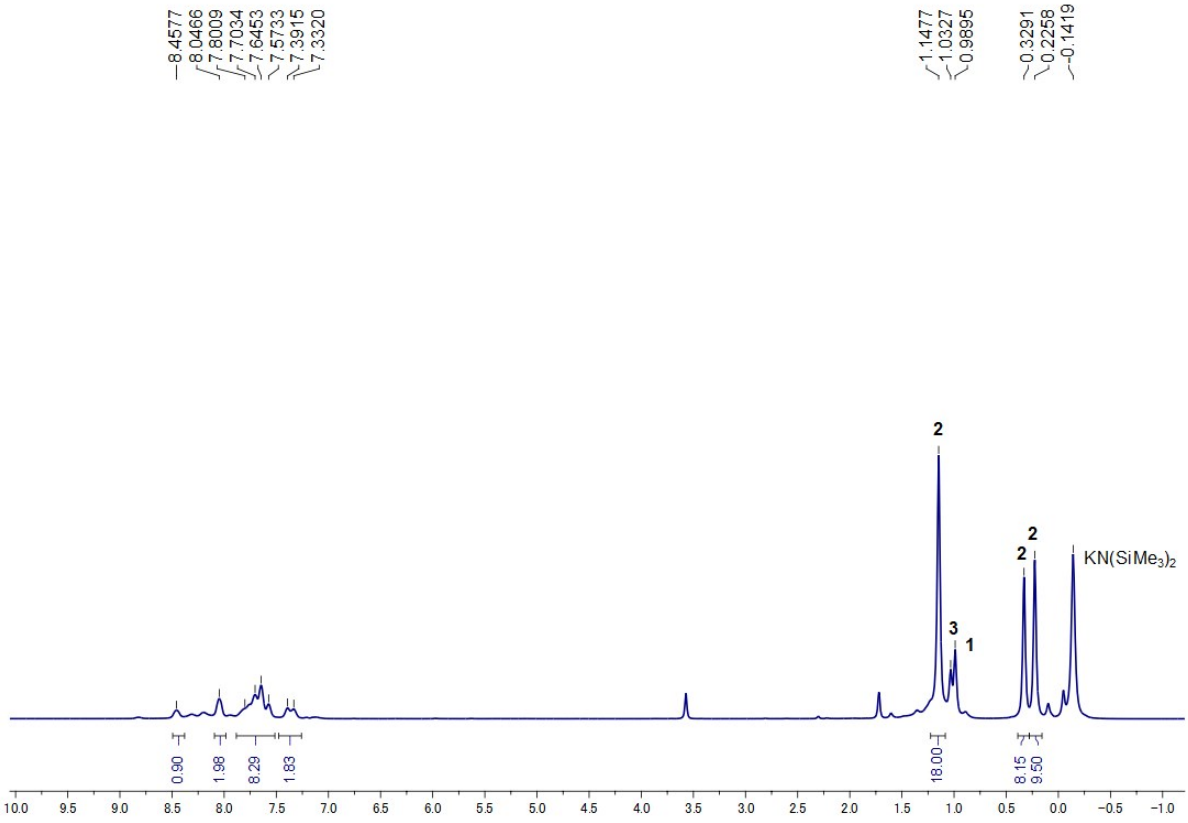

Figure S5. ^{1}H NMR spectrum (500 MHz, –50 °C, THF-d_8) of **2**.

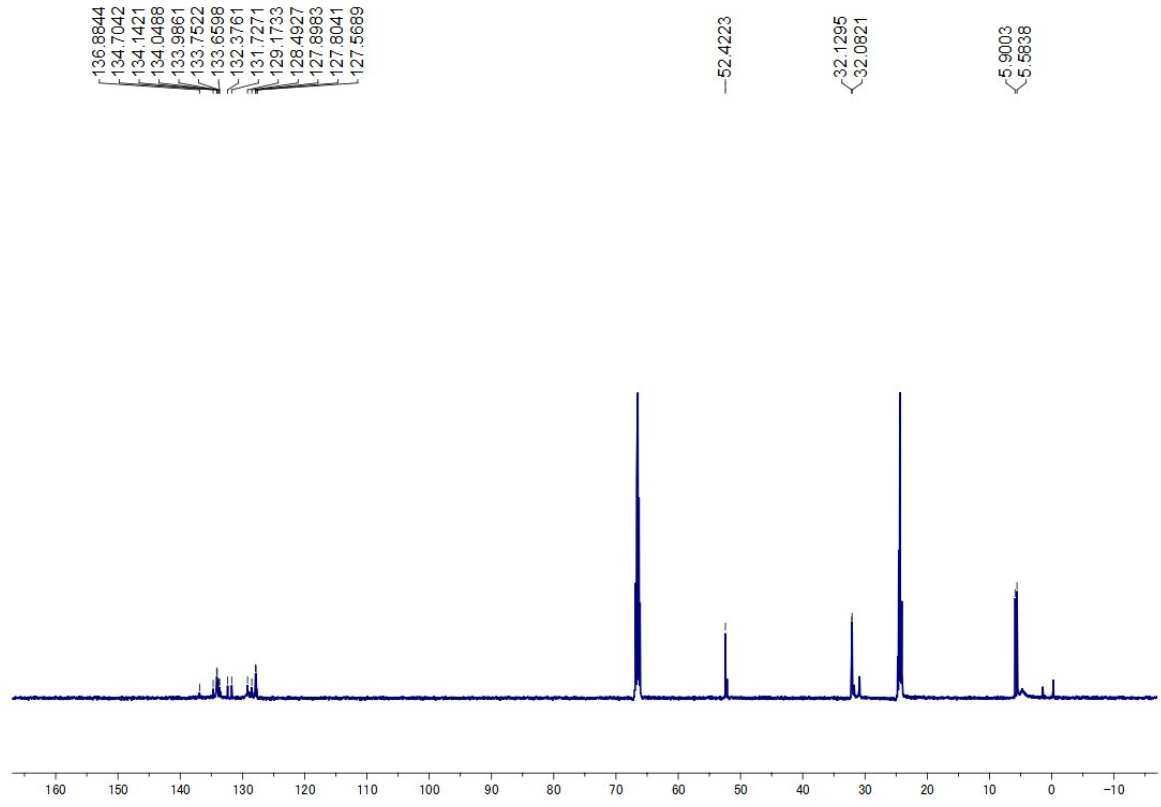

Figure S6. ^{13}C{^{1}H} NMR spectrum (125 MHz, –50 °C, THF-d_8) of **2**.

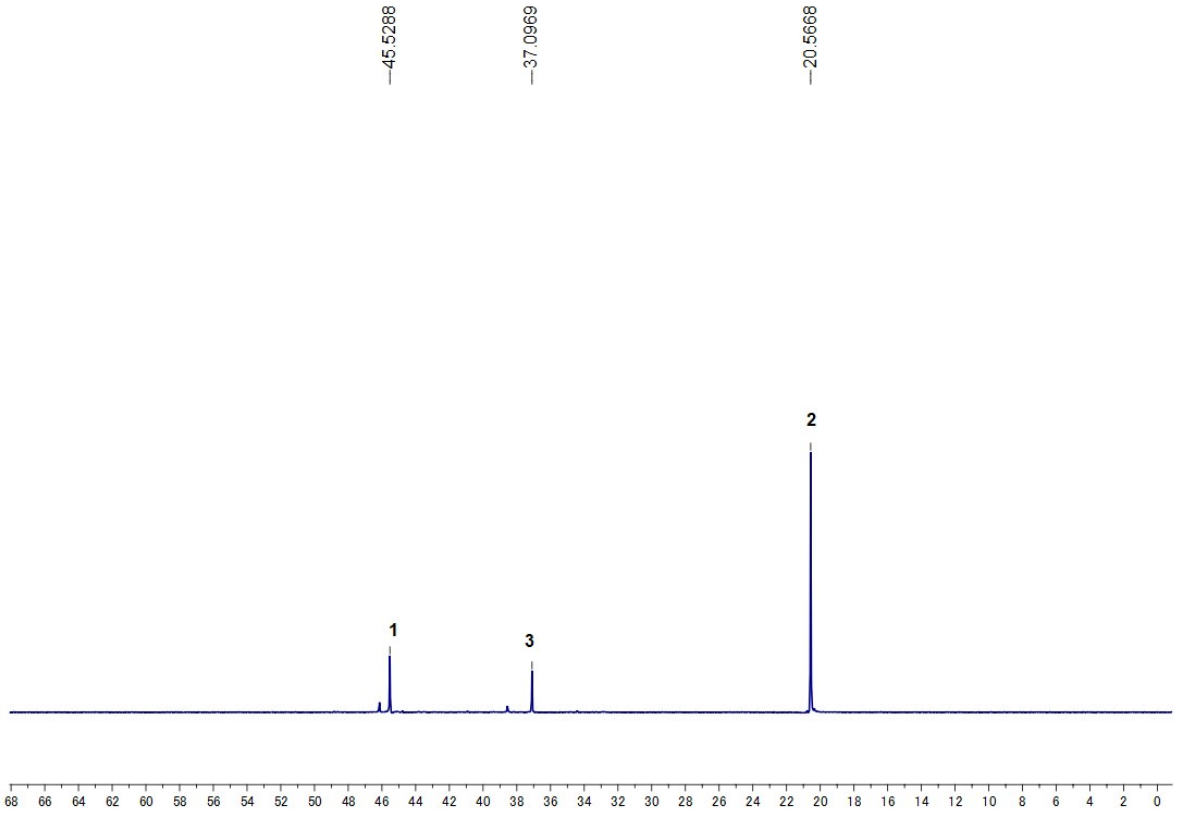

Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, –50 °C, THF-d_8) of **2**.

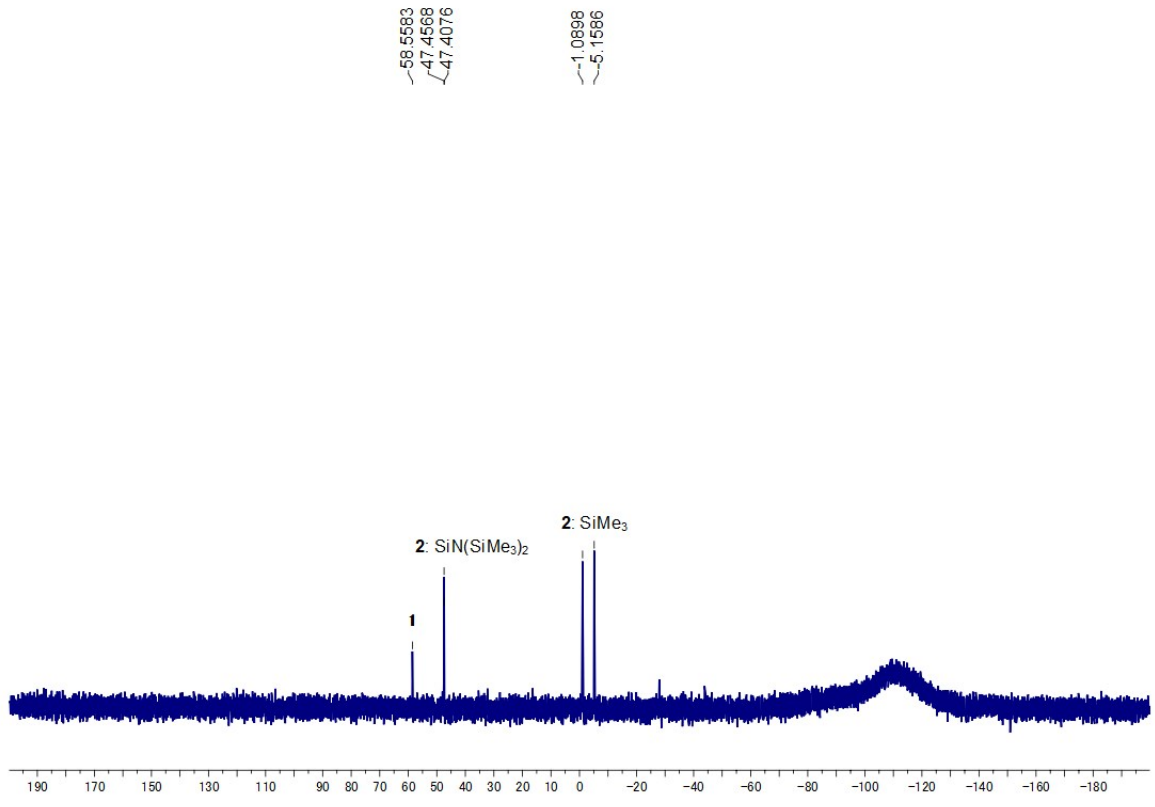

Figure S8. $^{29}Si\{^{1}H\}$ NMR spectrum (99 MHz, –50 °C, THF-d_8) of **2**.

2-3 Trapping reaction of silaimine 3 with elemental selenium.

In an NMR tube, C_6D_6 (0.4 mL) was added to a mixture of silaimine **3** (49 mg, 0.095 mmol) and elemental selenium (6.6 mg, 0.084 mmol) at ambient temperature. The mixture was heated at 80 °C for 26 hours. The reaction mixture was concentrated under reduced pressure, then silaselonourea **6** (27 mg, 55%) was obtained as yellow crystals. Mp. 235–236 °C (decomp.). ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ 0.44 (s, 9H, Si-CH_3), 1.04 (s, 9H, Si-CH_3), 1.42 (s, 18H, CH_{3tBu}), 7.01–7.05 (m, 4H, CH_{Ar}), 7.13–7.15 (m, 2H, CH_{Ar}), 7.83 (dd, J_{HH} = 13.0 and 7.4 Hz, 2H, CH_{Ar}), 8.71 (br s, 2H, CH_{Ar}). ^{13}C{^{1}H} NMR (100 MHz, 25 °C, C_6D_6): δ 7.6 (Si-CH_3), 9.3 (Si-CH_3), 32.6 (d, J_{CP} = 5.8 Hz, CH_{3tBu}), 55.6 (C_{tBu}), 127.9 (overlapped, C_{Ar}), 127.6 (d, J_{CP} = 13.0 Hz, CH_{Ar}), 128.2 (overlapped, CH_{Ar}), 129.9 (d, J_{CP} = 94.2 Hz, C_{Ar}), 133.2 (d, J_{CP} = 2.6 Hz, CH_{Ar}), 133.5 (d, J_{CP} = 3.1 Hz, CH_{Ar}), 135.6 (d, J_{CP} = 11.8 Hz, CH_{Ar}), 137.8 (br, CH_{Ar}). ^{31}P{^{1}H} NMR (162 MHz, 25 °C, C_6D_6): δ = 35.4. ^{29}Si{^{1}H} NMR (99 MHz, 25 °C, C_6D_6): δ = 2.5 (Si-CH_3), –1.1 (Si-CH_3), –20.3 (Si=Se). ^{77}Se{^{1}H} NMR (95 MHz, 25 °C, C_6D_6): δ –244.0 (d, J_{SeP} = 3.4 Hz). Anal. Calcd for $C_{26}H_{46}N_3Si_3PSe$: C, 52.25; H, 7.74; N, 7.06. Found: C, 52.06; H, 8.10; N, 7.18.

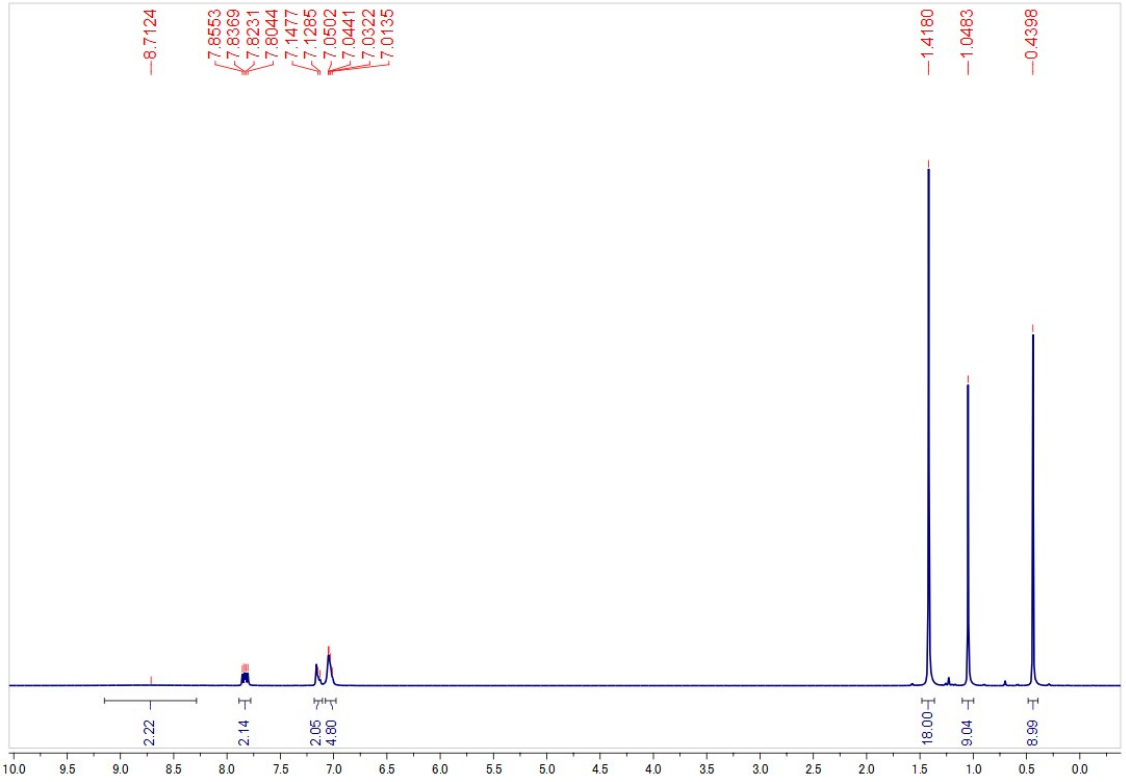

Figure S9. ^{1}H NMR spectrum (500 MHz, 25 °C, C_6D_6) of **6**.

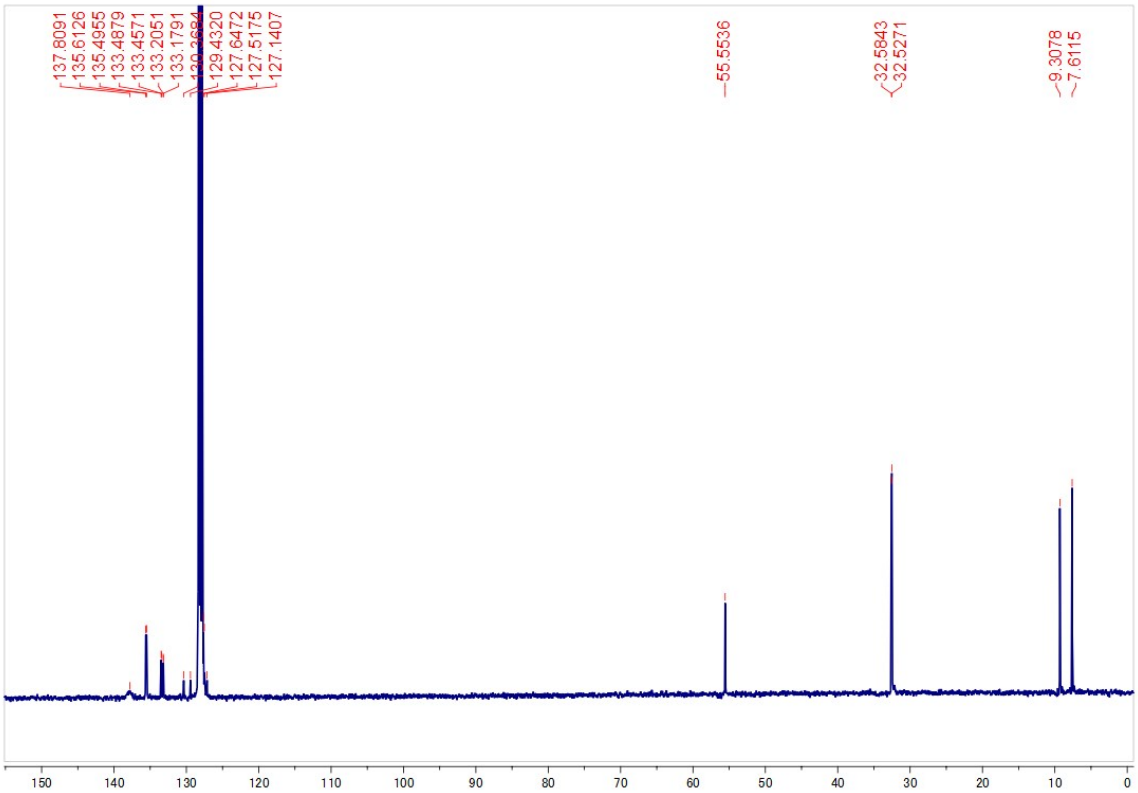

Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, 25 °C, C_6D_6) of **6**.

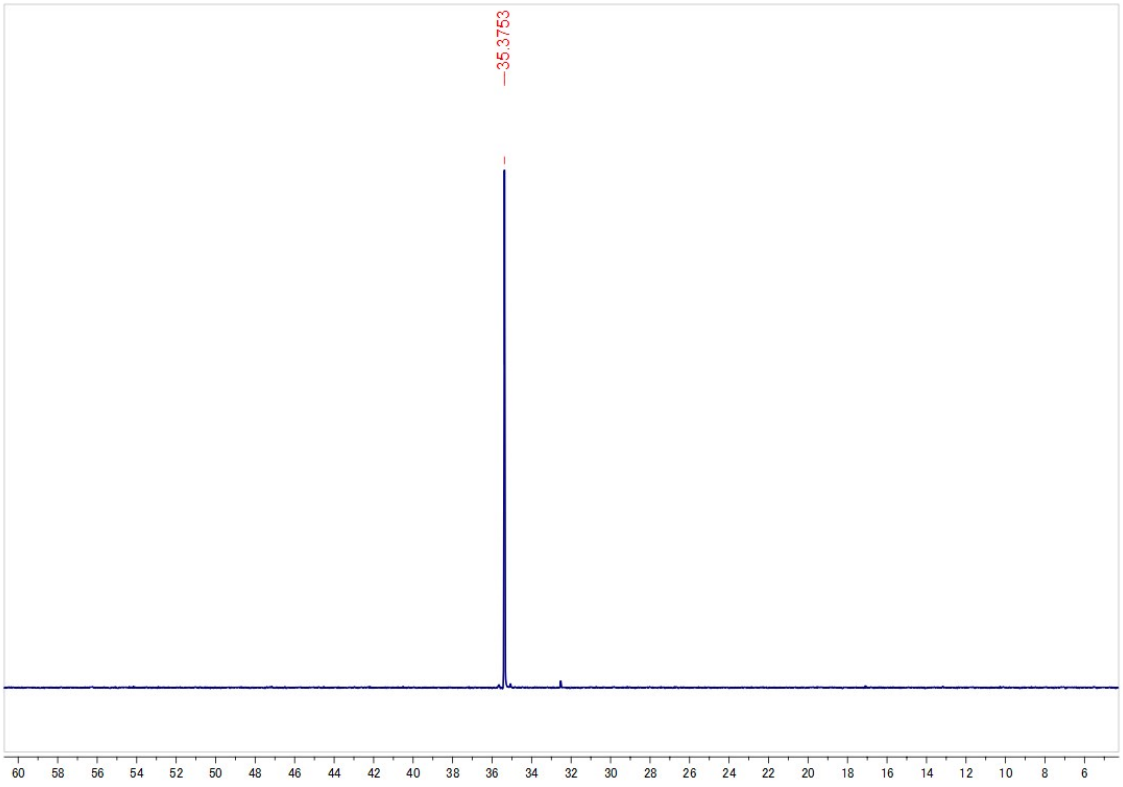

Figure S11. $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 25 °C, C_6D_6) of **6**.

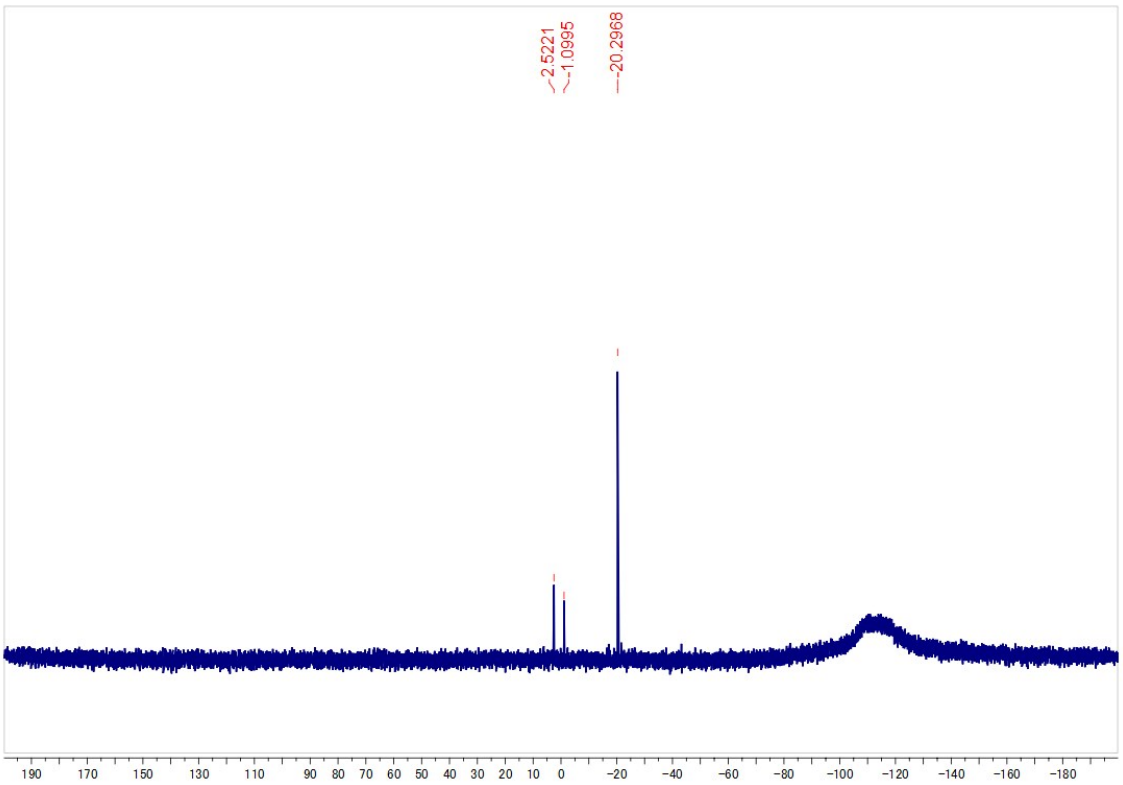

Figure S12. $^{29}Si\{^{1}H\}$ NMR spectrum (99 MHz, 25 °C, C_6D_6) of **6**.

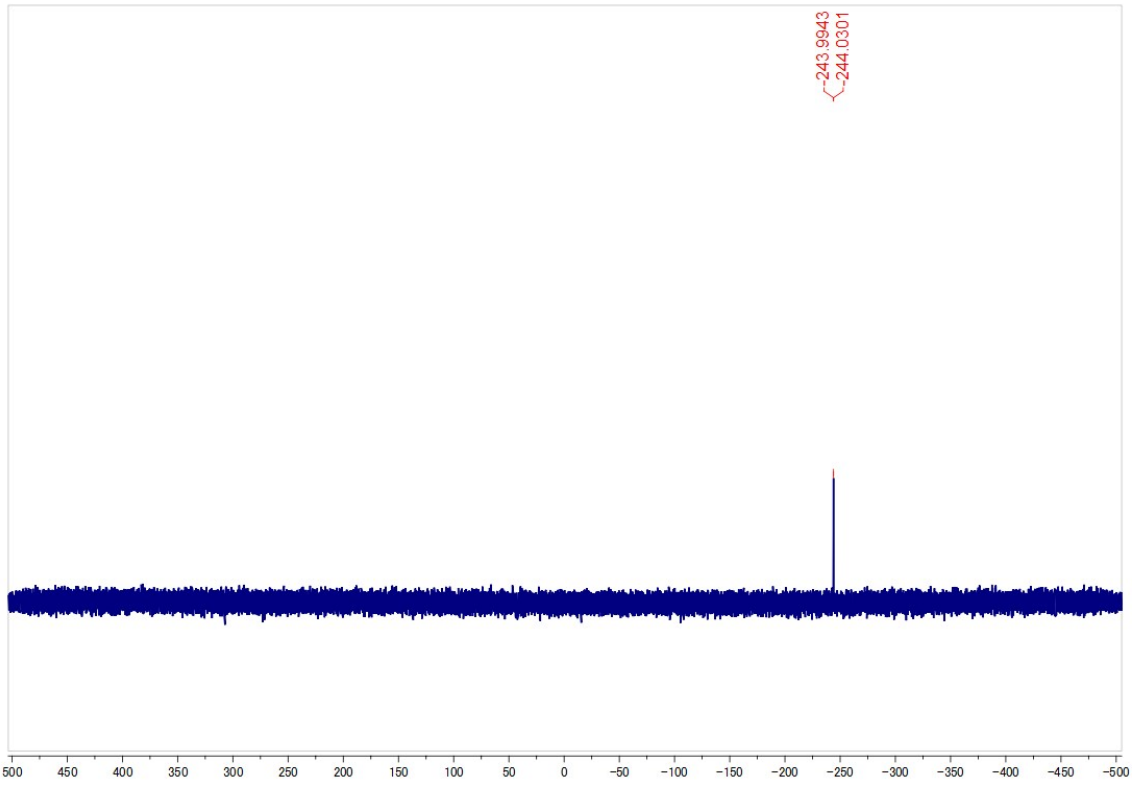

Figure S13. $^{77}Se\{^{1}H\}$ NMR spectrum (95 MHz, 25 °C, C_6D_6) of **6**.

2-4 Reaction of chlorosilylene 1 with elemental selenium.

In a Schlenck tube, chlorosilylene **1** (190 mg, 0.486 mmol) and elemental selenium (38 mg, 0.481 mmol) were dissolved into THF (3 mL) at ambient temperature. The resulting solution was stirred for 2 h at room temperature. The reaction mixture was filtered and all volatiles of the filtrate were removed under reduced pressure. Recrystallization from THF at –10°C gave a silaselenocarbonyl **7** (98 mg, 43%) as colorless crystals. Mp. 240–241 °C (decomp.). ^{1}H NMR (500 MHz, 25 °C, C_6D_6): δ 1.20 (s, 18H, CH_3), 6.98–7.04 (m, 4H, Ar), 7.06–7.12 (m, 2H, Ar), 7.90 (dd, J_{HH} = 12.4 and 7.7 Hz, 2H, Ar), 8.05 (dd, J_{HH} = 12.8 and 7.7 Hz, 2H, Ar). ^{13}C{^{1}H} NMR (125 MHz, 25 °C, C_6D_6): δ 31.9 (d, J_{CP} = 5.7 Hz, CH_{3tBu}), 55.4 (C_{tBu}), 126.3 (d, J_{CP} = 99.1 Hz, C_{Ar}), 126.9 (d, J_{CP} = 98.4 Hz, C_{Ar}), 128.4 (CH_{Ar}), 129.4 (d, J_{CP} = 13.2 Hz, CH_{Ar}), 133.9 (d, J_{CP} = 12.0 Hz, CH_{Ar}), 134.1 (d, J_{CP} = 3.1 Hz, CH_{Ar}), 134.2 (d, J_{CP} = 3.1 Hz, CH_{Ar}), 154.5 (d, J_{CP} = 12.0 Hz, CH_{Ar}). ^{31}P{^{1}H} NMR (202 MHz, 25 °C, C_6D_6): δ = 39.9. ^{29}Si{^{1}H} NMR (99 MHz, 25 °C, C_6D_6): δ = –25.5 (d, J_{SiP}= 4.7 Hz, Si=Se). ^{77}Se{^{1}H} NMR (95 MHz, 25 °C, C_6D_6): δ –267.9.

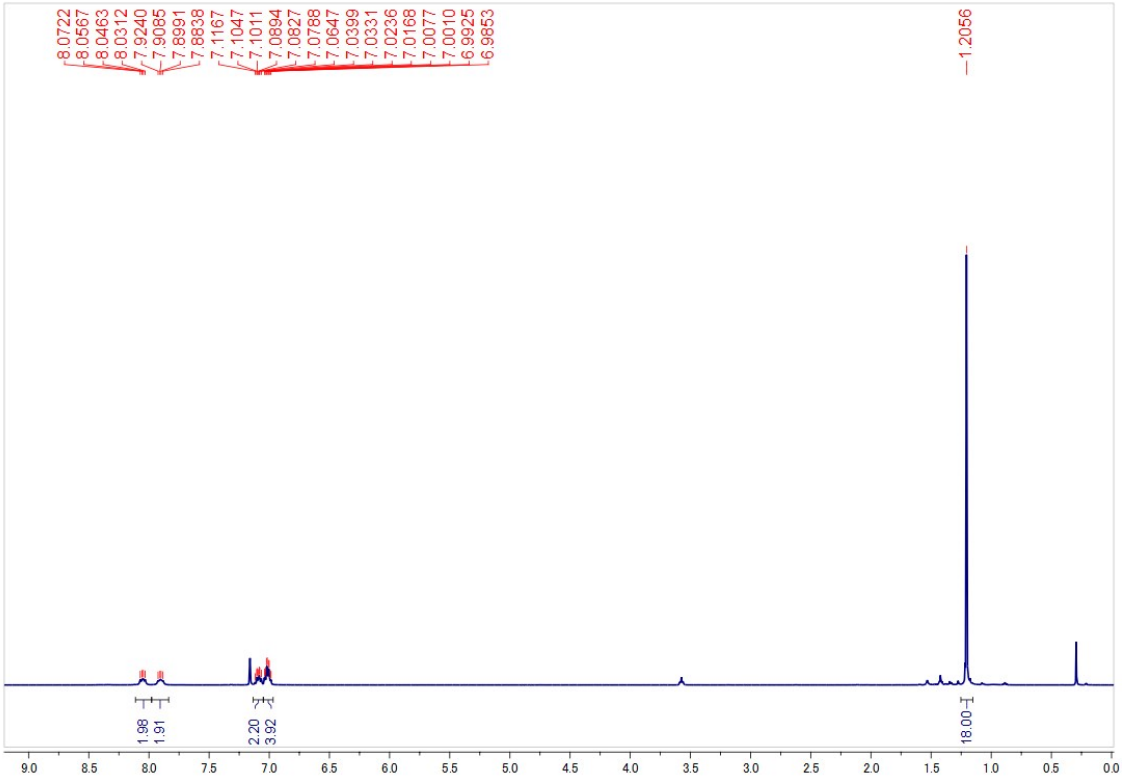

Figure S14. ^{1}H NMR specrum (500 MHz, 25 °C, C_6D_6) of 7.

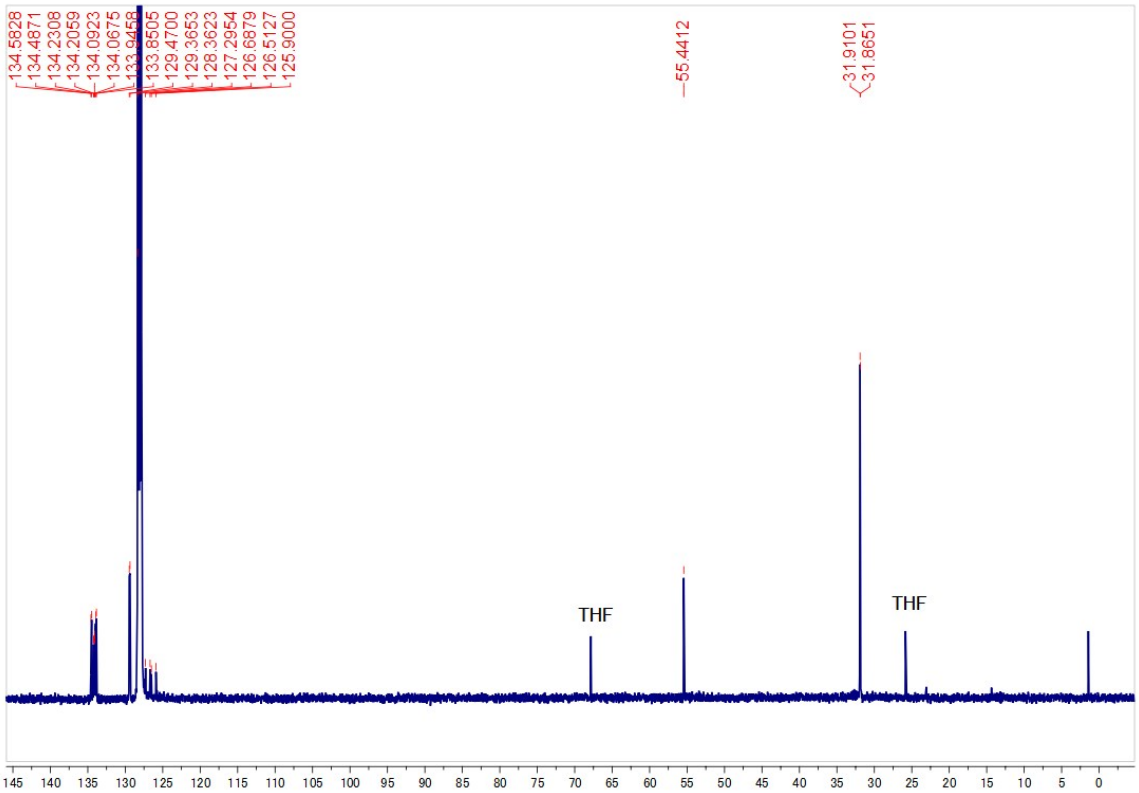

Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, 25 °C, C_6D_6) of 7.

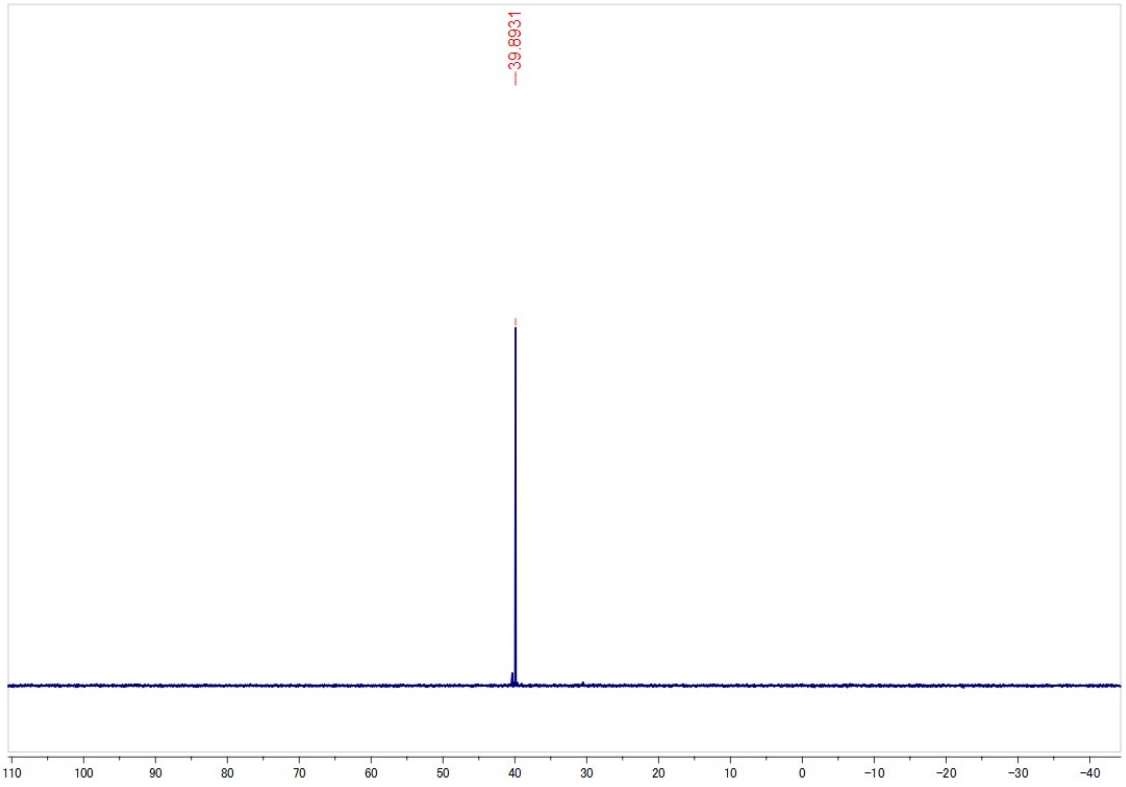

Figure S16. $^{31}P\{^{1}H\}$ NMR specrum (202 MHz, 25 °C, C_6D_6) of 7.

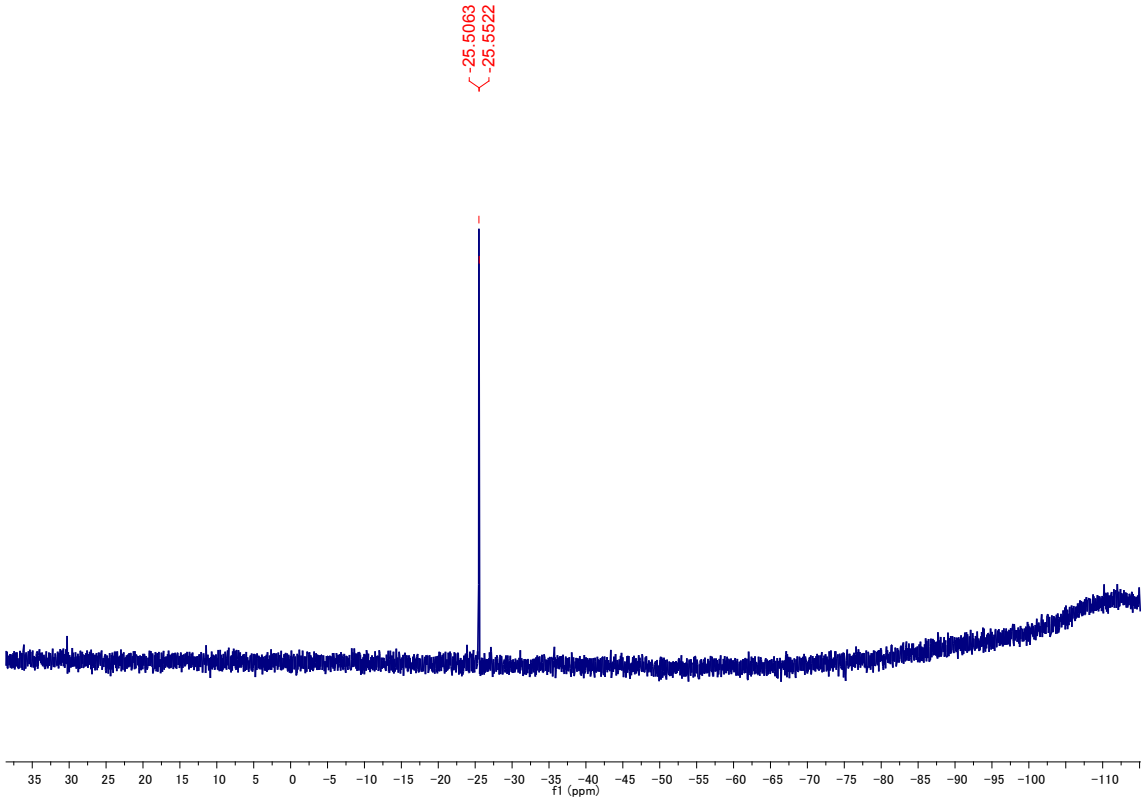

Figure S17. $^{29}Si\{^{1}H\}$ NMR specrrum (99 MHz, 25 °C, C_6D_6) of 7.

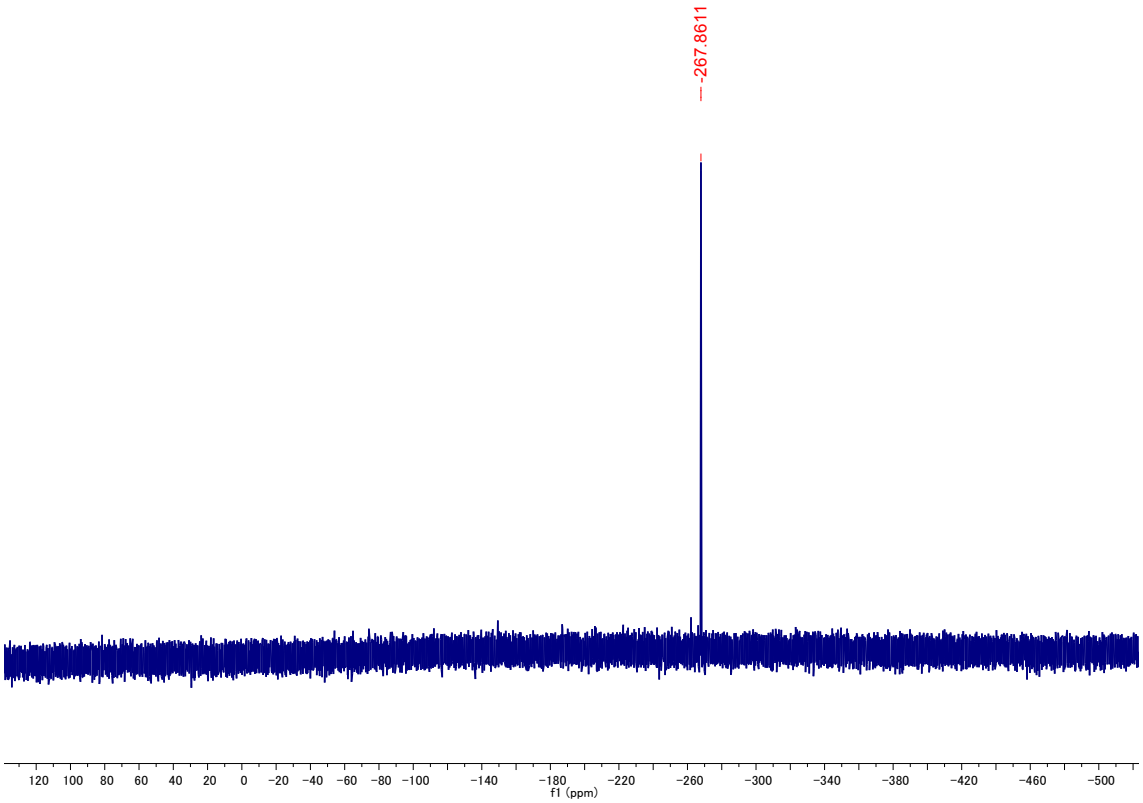

Figure S18. $^{77}Se\{^{1}H\}$ NMR specrum (95 MHz, 25 °C, C_6D_6) of 7.

3-Crystallographic data collection and structure determination

Colorless single crystals of **3** and **7** were grown of saturated toluene solution at −10 °C. Yellow single crystals of **6** were obtained from a C_6D_6 solution at room temperature. The intensity data were collected at 100 K on a Bruker SMART APEX II diffractometer employing graphite-monochromated MoKα radiation (λ = 0.71073 Å). The intensity data were collected at 100 K on a Bruker SMART APEX II diffractometer employing graphite-monochromated MoKα radiation (λ = 0.71073 Å). Structures were solved by direct methods (SHELXT)[S2] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL).[S3] Hydrogen atoms were located by assuming ideal geometry and were included in the structure calculations without further refinement of the parameters. Hydrogen atoms were located by assuming ideal geometry and were included in the structure calculations without further refinement of the parameters. The crystallographic data for the structures reported in this paper have been deposited with The Cambridge Crystallographic Data Centre as supplementary publication nos. 2052725 (**3**), 2052726 (**6**), and 2052727 (**7**).

Table S1. Crystallographic data and details of refinement for **3**, **6**, and **7**.

	3	**6**	**7**
Formula	$C_{26}H_{46}N_3PSi_3$	$C_{26}H_{46}N_3PSeSi_3$, C_6H_6	$C_{20}H_{28}N_2SiPClSe$
Formula weight	515.90	672.96	470.82
Color	colorless	yellow	colorless
Crystal size / mm	0.08 × 0.06 × 0.06	0.17 × 0.15 × 0.10	0.06 × 0.05 × 0.03
Temperature / K	100	100	100
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$C2/c$
a /Å	11.204(5)	10.9693(8)	15.6803(19)
b /Å	17.824(5)	19.9448(15)	10.0386(12)
c /Å	15.275(5)	15.9939(12)	42.425(5)
a / deg.	90	90	90
b / deg.	97.916(5)	91.8748(10)	92.403(2)
g / deg.	90	90	90
V /Å^3	3021.4(19)	3497.3(5)	6672.2(2)
Z	4	4	12
D_{calcd} / g cm^{-3}	1.134	1.278	1.403
No. of unique data	5626	6415	6563
No. of parameters	310	428	390
No. of restraints	0	198	14
R_1 ($I > 2s(I)$)	0.0362	0.0334	0.0525
wR_2 (all data)	0.1062	0.0861	0.1404
GOF	1.013	1.029	1.011

4-Computational details

Geometries of all systems have been optimized with the Gaussian-09 program using[S4] B3LYP-D3[S5]/6-31+G(d,p) level of theory on **2** and **4** for comparison of the HOMO energy levels, ωB97XD[S6]/6-31+G(d,p) on **2**, **3**, TS**2**, **4**, **5**, and TS**4** for exploration of energy profiles, and B3LYP-D3[S5]/6-311+G(2df,3pd) level of theory on **2** and **3** for GIAO calculations, respectively. Harmonic vibrational frequencies were calculated in order to verify that these structures correspond to energy minima (all frequencies are real) or to transition states (only one imaginary frequency corresponding to the transition vector). Transition state were verified by intrinsic reaction coordinate (IRC) calculations.

Atomic Coordinates for **2** at B3LYP-D3/6-31+G(d,p) level of theory.

P	1.39808400	-0.01491300	-0.00632200	H	4.97454500	3.17345000	-1.29060800
Si	-1.02474600	-1.04701700	-0.17269200	C	0.35420200	1.97068000	-2.68623000
Si	-2.80294000	1.61930200	0.40037900	H	-0.49877400	2.41486600	-2.16741400
Si	-3.95075300	-1.13058700	-0.25087700	H	0.32929000	2.29541400	-3.73280400
N	0.29437200	-0.40950700	1.14759800	H	1.26856500	2.36078500	-2.23175200
N	0.25239400	0.01312500	-1.17657000	C	1.48202900	-0.18605000	-3.35289000
C	2.66195500	-1.32423500	-0.25030200	H	2.44019000	0.10836700	-2.91469500
N	-2.53652400	-0.06549500	-0.04708000	H	1.47925800	0.14605500	-4.39674900
C	-3.97169100	1.75414000	1.89149900	H	1.42954800	-1.27779200	-3.33878800
H	-4.97428100	1.35480400	1.71419400	C	3.95089200	-1.24887200	0.29975900
H	-4.07985500	2.80699700	2.18123500	H	4.27373400	-0.35180900	0.81803800
H	-3.54581000	1.21471800	2.74586400	C	4.42966400	-3.49524700	-0.46586500
C	2.39971000	1.50986900	0.21351200	H	5.11378300	-4.33460700	-0.55087600
C	3.44822600	1.78518700	-0.68326300	C	-4.37246700	-1.98106600	1.38625500
H	3.70967300	1.06871000	-1.45503000	H	-4.51749000	-1.24681000	2.18631500
C	-3.71774300	-2.45919400	-1.58138400	H	-3.55875200	-2.65099000	1.68671700
H	-4.69363000	-2.92054000	-1.78468900	H	-5.28806100	-2.57895700	1.29976600
H	-3.01689100	-3.24098000	-1.28107000	C	1.59811200	-0.30975100	3.27271500
H	-3.35316000	-2.02159800	-2.51732700	H	2.55852200	-0.33694600	2.74695300
C	0.29011000	0.43179500	-2.59604500	H	1.74067500	-0.79565600	4.24382700
C	4.17099600	2.97384600	-0.58779400	H	1.33210400	0.73498100	3.45355500

C	4.83068700	-2.32904400	0.19053800
H	5.82563200	-2.25833800	0.62036200
C	-1.01226200	-0.05062000	-3.26100500
H	-1.09158600	-1.14138700	-3.21950300
H	-1.02543200	0.25724100	-4.31170300
H	-1.88746200	0.37301000	-2.76246500
C	2.26314600	-2.50526500	-0.89864300
H	1.25350000	-2.58698500	-1.29073300
C	0.49752100	-1.03783800	2.48137300
C	-5.48792000	-0.18353200	-0.83782800
H	-5.33343900	0.23463900	-1.83847600
H	-5.81834800	0.62225800	-0.17815400
H	-6.30828200	-0.90885800	-0.90804700
C	3.86431500	3.90051500	0.41410000
H	4.42778400	4.82583400	0.49070800
C	2.83377500	3.62962300	1.31681800
H	2.59142800	4.34210500	2.09974000
C	-1.22882200	2.49275300	0.94335200
H	-0.82017300	2.01903900	1.83789100
H	-1.46561300	3.53833900	1.17525600
H	-0.45931300	2.47953400	0.17048400
C	3.14297800	-3.58098500	-1.00860800
H	2.82167600	-4.48861400	-1.51103600
C	0.85891200	-2.53628600	2.37917600
H	0.12930000	-3.06229300	1.75750100
H	0.86211900	-2.99038300	3.37677800
H	1.84915300	-2.68089500	1.93974900
C	2.10305600	2.44377500	1.21464100
H	1.29835300	2.25091800	1.90955100
C	-0.83966100	-0.89039000	3.23193800
H	-1.12345100	0.16330000	3.31123400
H	-0.75804500	-1.30851700	4.24100200
H	-1.64328200	-1.41618800	2.70837600
C	-3.49891400	2.64139300	-1.03818000
H	-2.88182900	2.51880200	-1.93549000
H	-3.49045900	3.70598900	-0.77222800
H	-4.52509100	2.37085600	-1.29943500

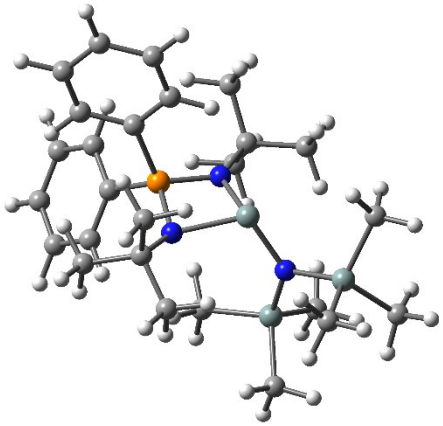

Figure S19. Optimized geometry of **2** [B3LYP-D3/6-31+G(d,p) level of theory].

Atomic Coordinates for **4** at B3LYP-D3/6-31+G(d,p) level of theory.

Si	0.67233000	0.05528100	-1.18967700
Si	2.02249300	-0.09646600	1.72180900
Si	3.61531700	0.07857100	-0.88554300
N	-0.72247400	1.08023800	-0.33256600
N	-0.69790600	-1.06465800	-0.44295700
C	-2.97002200	-0.02792900	0.00301500
N	2.05103300	-0.04409500	-0.04605700
C	3.10941800	1.28046200	2.44730600
H	4.15767400	1.22948400	2.14014700
H	3.08141000	1.23387500	3.54294100
H	2.72369200	2.26150900	2.14588200
C	3.59714800	-0.77999000	-2.57187000
H	4.62752500	-0.83177200	-2.94785900
H	2.98570400	-0.25720300	-3.31125000
H	3.21855800	-1.80515500	-2.48834900
C	-1.00242000	-2.50569800	-0.53780400
C	-1.49291800	-3.04267000	0.82063800
H	-0.75082200	-2.84754500	1.60070800
H	-1.65016600	-4.12488500	0.75941000
H	-2.43837600	-2.58107200	1.11371200
C	-2.04165500	-2.80335000	-1.63763200
H	-3.02737200	-2.41206100	-1.37684000
H	-2.13620100	-3.88530200	-1.78186300
H	-1.72508600	-2.35392200	-2.58444600
C	-3.47537800	-0.14363700	1.30446800
H	-2.78672200	-0.22461900	2.13954000
C	-5.73695200	-0.00958100	0.45003600
H	-6.80900700	-0.00113100	0.62307900
C	4.07728500	1.89637000	-1.13119600
H	4.11499000	2.42789900	-0.17413300
H	3.33455300	2.39709000	-1.76310300
H	5.05550300	1.99697900	-1.61689900
C	-2.06919400	2.91856300	0.72172300
H	-3.06733700	2.52107500	0.53099200
H	-2.14421900	4.01050600	0.75440800
H	-1.74121400	2.56992900	1.70525900
C	-4.85381300	-0.13582500	1.52636200
H	-5.23641900	-0.22356000	2.53890800
C	0.32288600	-3.20158500	-0.90136200
H	0.68063000	-2.87251500	-1.88245700
H	0.17859500	-4.28587500	-0.93511100
H	1.09795900	-2.97434200	-0.16446100
C	-3.85793900	0.09550400	-1.07356700
H	-3.46779800	0.17308200	-2.08360400
C	-1.06420200	2.51658100	-0.37500200
C	5.02210300	-0.77291600	0.06016100
H	4.87180200	-1.85750900	0.09532300
H	5.17616700	-0.41743400	1.08199200
H	5.95005300	-0.58863900	-0.49560300
C	0.32496200	0.16354300	2.51026600
H	-0.10681000	1.13684700	2.27322400
H	0.46210700	0.10423300	3.59722100
H	-0.38619200	-0.61081800	2.21691000
C	-5.23613500	0.10498400	-0.85043300
H	-5.91716000	0.19990300	-1.69106800
C	-1.62725700	2.89734100	-1.76064300
H	-0.92313000	2.61404700	-2.54840100
H	-1.80176800	3.97791200	-1.81743200
H	-2.57899300	2.39165500	-1.94589400
C	0.25912800	3.26946500	-0.13899400
H	0.67086200	3.03117100	0.84586000
H	0.09506500	4.35001900	-0.19579800

H	1.00538300	2.99784200	-0.89191600	H	2.55192300	-1.78327200	3.47397800
C	2.60016400	-1.77871700	2.37777700	H	3.62201700	-2.03294000	2.08616900
H	1.93981800	-2.57538900	2.01575700	C	-1.49582900	-0.00789700	-0.2242660

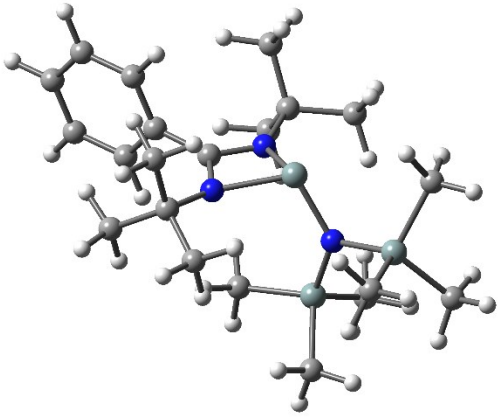

Figure S20. Optimized geometry of **4**.

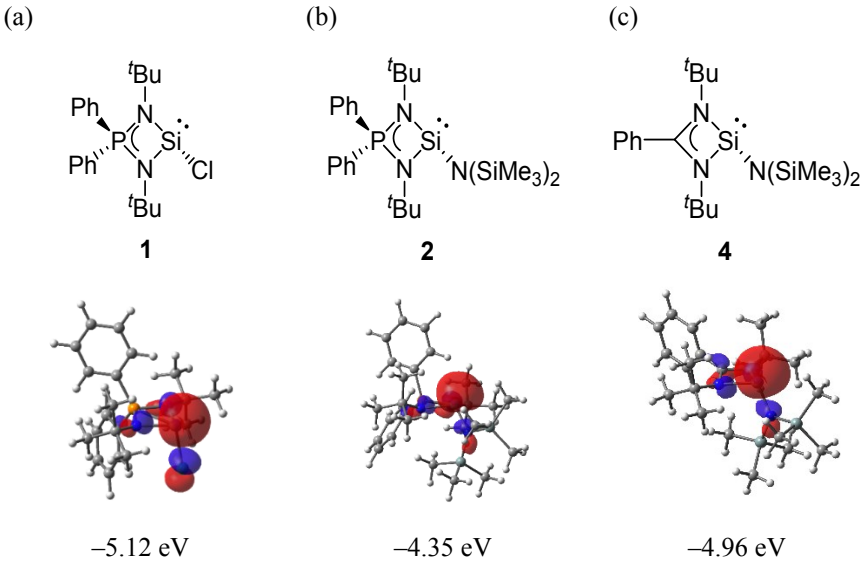

Figure S21. HOMO diagrams for **1**[S1], **2**, and **4**.

Atomic Coordinates for **2** at ωB97XD/6-31+G(d,p) level of theory

P	1.38624000	-0.01466900	-0.01314500	H	-3.52787300	-2.73906000	1.57104400
Si	-1.00819200	-1.04361100	-0.17962700	H	-5.26325000	-2.58814000	1.24058000
Si	-2.77609100	1.59869200	0.44064600	C	1.57198700	-0.33986400	3.25551600
Si	-3.92415900	-1.11335000	-0.27129100	H	2.53618900	-0.34960600	2.73533200
N	0.29428700	-0.42529700	1.13084900	H	1.71447400	-0.83835700	4.21964400
N	0.24877200	0.01915600	-1.17476500	H	1.29282800	0.69903600	3.45149900
C	2.65488200	-1.30642400	-0.25704900	C	4.81749300	-2.29108800	0.20679500
N	-2.50992500	-0.06686700	-0.04316100	H	5.80571600	-2.21439000	0.64892600
C	-3.91082300	1.68854300	1.95129400	C	-1.02993300	-0.05383200	-3.23432400
H	-4.88850800	1.22136600	1.80512700	H	-1.10139800	-1.14481600	-3.17939000
H	-4.07974700	2.73572800	2.22936100	H	-1.05383300	0.24324700	-4.28749800
H	-3.43084300	1.18968300	2.80139500	H	-1.90452100	0.36831100	-2.73182300
C	2.37770400	1.50533500	0.20914200	C	2.27027700	-2.48442500	-0.90800000
C	3.41064000	1.78681500	-0.69576800	H	1.26350400	-2.57255800	-1.30845300
H	3.66456900	1.07560300	-1.47543200	C	0.48791600	-1.06487200	2.44985200
C	-3.71462400	-2.37373200	-1.65893800	C	-5.45916900	-0.13711400	-0.79271200
H	-4.67873000	-2.86926800	-1.83003200	H	-5.31389300	0.32614900	-1.77442200
H	-2.96514400	-3.13319100	-1.42759300	H	-5.78101000	0.63840600	-0.09346700
H	-3.42252400	-1.88171100	-2.59311100	H	-6.28227700	-0.85570600	-0.88751200
C	0.26795900	0.44201400	-2.58356900	C	3.83836200	3.88671900	0.40813800
C	4.13133000	2.97159200	-0.60205800	H	4.39933100	4.81293200	0.48314000
H	4.92256500	3.17834600	-1.31543100	C	2.82663700	3.60783600	1.32204500
C	0.30899400	1.97631000	-2.66654400	H	2.59494500	4.31342800	2.11326300
H	-0.55001700	2.40348000	-2.14183500	C	-1.20373000	2.46838500	0.97343700
H	0.27284600	2.30525200	-3.71095200	H	-0.77933300	1.97387200	1.84993300
H	1.21944600	2.38057100	-2.21481700	H	-1.44021600	3.50683700	1.23375300
C	1.45584400	-0.15868900	-3.34880300	H	-0.44733500	2.47724400	0.18619800
H	2.41446900	0.14042200	-2.91470800	C	3.15685600	-3.55035800	-1.00978200
H	1.44420500	0.17989800	-4.38999700	H	2.84875800	-4.45977700	-1.51550800
H	1.41028900	-1.25100000	-3.34137400	C	0.85893300	-2.55420600	2.33305900
C	3.93208700	-1.22024700	0.30460300	H	0.14682100	-3.07485900	1.68672500
H	4.24215500	-0.31913500	0.82482000	H	0.84149700	-3.02296200	3.32291000
C	4.43189900	-3.45508200	-0.45310600	H	1.86074000	-2.68746700	1.91517400
H	5.12286600	-4.28886000	-0.52983500	C	2.09806000	2.42537500	1.22019100
C	-4.32514800	-2.02790100	1.32782400	H	1.30339000	2.22493200	1.92551200
H	-4.42125600	-1.32852700	2.16559400	C	-0.85325200	-0.93495000	3.18545300

H	-1.13661900	0.11735500	3.28401100	H	-2.97402100	2.44684300	-1.90184200
H	-0.78328200	-1.37498900	4.18552300	H	-3.38660000	3.70550200	-0.72879900
H	-1.65080500	-1.44925800	2.64036800	H	-4.56413400	2.44897300	-1.13035700
C	-3.50148000	2.64004100	-0.96088300				

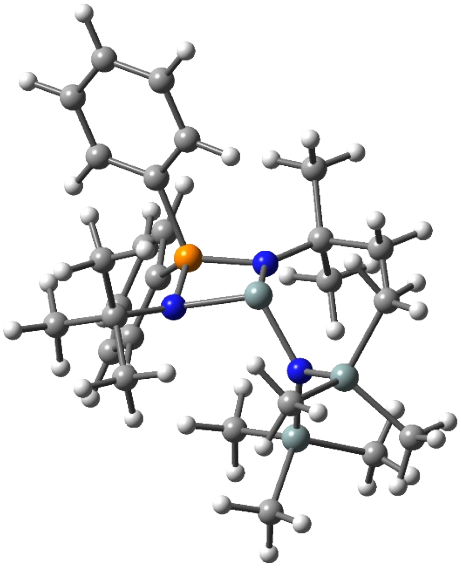

Figure S22. Optimized geometry of **2**.

Atomic Coordinates for **3** at ωB97XD/6-31+G(d,p) level of theory

P	-1.23163440	0.33399965	0.00149858	H	1.27524199	-3.83306365	-2.13848670
Si	1.09695005	-0.74372284	-0.00173016	H	2.30974528	-4.88223818	-1.16122183
Si	3.80622257	1.06848875	-0.23479915	C	-1.35373575	0.48678014	-3.23194625
Si	1.40352921	-3.05006258	0.26101187	H	-2.33826056	0.60669293	-2.76730356
N	-0.29406502	-0.33482636	-1.15429021	H	-1.51789178	0.25657545	-4.28905174
N	-0.19973980	-0.12091634	1.18444002	H	-0.82285989	1.44003427	-3.16493998
C	-2.88284692	-0.39497390	0.14334078	C	-5.20946752	-0.57314611	-0.48926499
N	2.44731225	0.10390665	-0.13074307	H	-6.07010475	-0.17841331	-1.01936204
C	5.00662929	0.46514472	-1.56865312	C	0.89527990	-0.56131444	3.28837454
H	5.32496228	-0.56240596	-1.35842172	H	0.45199665	-1.56275573	3.29079833
H	5.90322251	1.09330683	-1.63423517	H	1.03452443	-0.23993581	4.32509342
H	4.51887011	0.46516733	-2.55061089	H	1.88001322	-0.61304196	2.81290351
C	-1.39740491	2.12833409	-0.16715722	C	-2.99664059	-1.58474659	0.86895952
C	-2.45440556	2.86811294	0.37010023	H	-2.12573568	-1.97671029	1.38367659
H	-3.29922169	2.36822035	0.83453979	C	-0.55113833	-0.64035213	-2.56976263
C	-0.17052570	-3.96054423	0.79995658	C	2.73913525	-3.32550759	1.57019196
H	0.01412931	-5.03749184	0.88734220	H	2.40113726	-3.03009904	2.56842356
H	-0.98799639	-3.81554255	0.08483020	H	3.62776145	-2.73287276	1.32908330
H	-0.50828493	-3.60196140	1.77930542	H	3.02806192	-4.38216646	1.61099691
C	-0.01080448	0.42580224	2.54390576	C	-1.32652269	4.91301886	-0.23918018
C	-2.41884993	4.25991395	0.32827924	H	-1.29894611	5.99792354	-0.26502073
H	-3.24059357	4.83243767	0.74619592	C	-0.26290441	4.17740734	-0.76134834
C	0.66743894	1.80535566	2.50984740	H	0.60216876	4.67994714	-1.18173839
H	1.57076650	1.75880255	1.89642871	C	3.37754042	2.87353973	-0.66236490
H	0.94209033	2.11231914	3.52477147	H	2.89063861	2.93549508	-1.64434931
H	0.00357256	2.56947147	2.09580828	H	4.26956100	3.51111382	-0.69171414
C	-1.36207054	0.52165539	3.26096604	H	2.68865746	3.29141723	0.08246768
H	-2.04742961	1.19544732	2.73423904	C	-4.20936655	-2.26300449	0.91598187
H	-1.22220916	0.92204256	4.26989294	H	-4.28770597	-3.18838931	1.47726864
H	-1.83844215	-0.46001328	3.34074971	C	-1.32305506	-1.96380279	-2.68576936
C	-3.99523256	0.10584492	-0.54101349	H	-0.77274197	-2.76946778	-2.19165704
H	-3.92076952	1.02266014	-1.11796852	H	-1.46829905	-2.23762004	-3.73626328
C	-5.31707399	-1.75676663	0.23818386	H	-2.30748539	-1.88574165	-2.21280059
H	-6.26463047	-2.28481663	0.27531478	C	-0.29585538	2.78909622	-0.72493160
C	2.02875830	-3.83848156	-1.34423154	H	0.54883599	2.21000351	-1.09056531
H	2.91436867	-3.31055912	-1.71405505	C	0.80945889	-0.75648747	-3.26731331

H	1.37475696	0.17357807	-3.16248215	H	4.10608964	1.51489744	2.20903833
H	0.66626244	-0.97185142	-4.33085960	H	5.64424550	1.74398176	1.35619256
H	1.41252550	-1.55954283	-2.83530874	H	5.05153655	0.10752107	1.70504170
C	4.74532720	1.11823096	1.41100445				

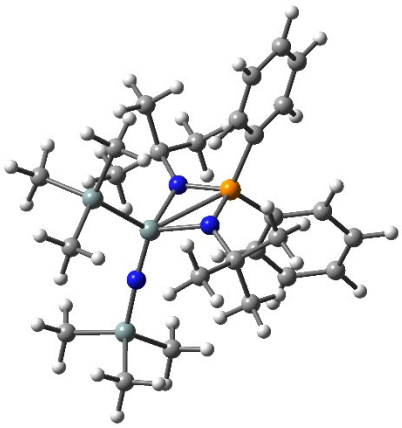

Figure S23. Optimized geometry of **3**.

Atomic Coordinates for TS**2** at ωB97XD/6-31+G(d,p) level of theory

P	-1.43494855	0.02561040	0.01229929	H	3.04479663	-2.80872296	-2.04971075
Si	1.04127123	-0.68798281	0.04619040	H	4.65828193	-2.88467754	-1.33563884
Si	3.24324415	1.67704958	-0.30403824	C	-1.70272275	-0.17033538	-3.21590288
Si	3.08598230	-1.81694175	0.25935501	H	-2.64717703	-0.36733100	-2.69797178
N	-0.34554083	-0.32665304	-1.15508560	H	-1.80531024	-0.55445000	-4.23540218
N	-0.29529429	-0.05257936	1.17460644	H	-1.55558434	0.91186909	-3.27170420
C	-2.73566889	-1.22365905	0.21154691	C	-4.90517906	-2.16182879	-0.29909879
N	2.47276474	0.15924369	-0.06743004	H	-5.87987961	-2.06932834	-0.76699088
C	4.66708101	1.50273100	-1.52995025	C	0.93910698	-0.19005297	3.25354110
H	5.40166742	0.76891585	-1.18058011	H	0.83295707	-1.27952617	3.24755543
H	5.18636863	2.45629394	-1.68007861	H	0.99326372	0.15018492	4.29220168
H	4.29539962	1.16055657	-2.50269472	H	1.87967465	0.06745208	2.75800498
C	-2.24685812	1.63309246	-0.17838329	C	-2.39432276	-2.39865263	0.89119040
C	-3.41175249	1.97162688	0.51870864	H	-1.40828070	-2.49225264	1.33803986
H	-3.92356275	1.23209467	1.12761474	C	-0.52081728	-0.85637751	-2.52132824
C	2.70312036	-3.54555605	1.02255012	C	4.50928427	-1.27219378	1.40316682
H	3.60179315	-4.17215582	1.11140119	H	4.12297286	-0.84470633	2.33617054
H	1.96623923	-4.07329697	0.40464557	H	5.13519366	-0.50877081	0.92917095
H	2.27163304	-3.43527301	2.02611140	H	5.14389435	-2.12683019	1.66580329
C	-0.24761817	0.47682314	2.54724897	C	-3.26937255	4.22220626	-0.33904399
C	-3.92127123	3.26378072	0.43570302	H	-3.66919245	5.22936305	-0.40196020
H	-4.82574423	3.52251493	0.97664281	C	-2.10667673	3.88953699	-1.03149040
C	-0.03494947	1.99816657	2.51704538	H	-1.59192449	4.63455759	-1.62929025
H	0.86138904	2.23625079	1.93851496	C	2.03434957	2.95685037	-1.00292988
H	0.09380196	2.38973059	3.53184872	H	1.59761480	2.59646215	-1.94183903
H	-0.88658957	2.51170778	2.06011646	H	2.53862521	3.90872988	-1.20713188
C	-1.54101444	0.13932345	3.29856223	H	1.21850745	3.15508461	-0.29863276
H	-2.41449071	0.59353067	2.81839260	C	-3.30646472	-3.44438175	0.97834733
H	-1.49193003	0.52614800	4.32115728	H	-3.03504089	-4.35355758	1.50470550
H	-1.69800068	-0.94212078	3.34490497	C	-0.74311029	-2.37636383	-2.48867227
C	-3.99377824	-1.11301725	-0.38831245	H	0.07898714	-2.86783161	-1.95916736
H	-4.26714279	-0.21311632	-0.93123430	H	-0.79076007	-2.77901185	-3.50603163
C	-4.56253728	-3.32602528	0.38485719	H	-1.67889954	-2.62741446	-1.97929344
H	-5.27429148	-4.14269751	0.45238145	C	-1.59530482	2.59863265	-0.95045458
C	3.77338410	-2.24699442	-1.45374559	H	-0.68054787	2.33617144	-1.47149337
H	4.06335548	-1.35248378	-2.01260038	C	0.76766787	-0.53312556	-3.28839461

H	0.94157082	0.54723055	-3.30346003	H	3.14660461	2.50108498	2.06002769
H	0.69281176	-0.89388869	-4.31918190	H	4.40217099	3.35770392	1.14874243
H	1.63613432	-1.00415305	-2.82041890	H	4.69136642	1.70982414	1.73378005
C	3.93559628	2.37848544	1.30929703				

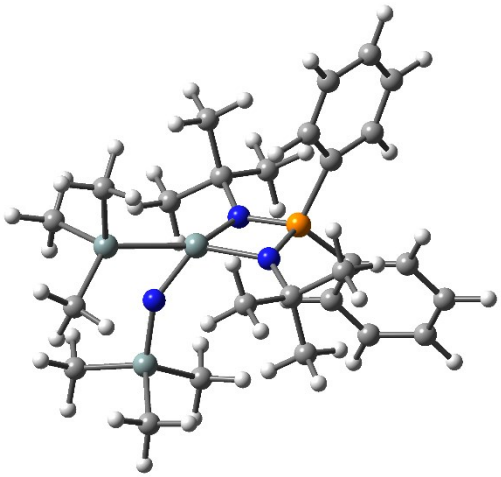

Figure S24. Optimized geometry of TS**2** [ωB97XD/6-31+G(d,p)].

Atomic Coordinates for **4** at ωB97XD/6-31+G(d,p) level of theory

Si	0.65685083	0.06557053	-1.18510940
Si	2.00041586	-0.13064933	1.70288943
Si	3.59525810	0.10031835	-0.87656120
N	-0.71285166	1.07876594	-0.32062834
N	-0.69032134	-1.05590490	-0.44309758
C	-2.95427331	-0.02182849	0.00396116
N	2.03327275	-0.03572432	-0.05466162
C	3.12743111	1.18678090	2.45725947
H	4.17725901	1.09978576	2.16439551
H	3.08214899	1.12429854	3.55088714
H	2.78348074	2.18602669	2.16632492
C	3.56355810	-0.65700741	-2.60190332
H	4.59239978	-0.71418041	-2.97911364
H	2.96741059	-0.07588884	-3.30913001
H	3.15615923	-1.67378201	-2.58003467
C	-0.99528956	-2.48788845	-0.55022124
C	-1.48727031	-3.03115725	0.79886554
H	-0.74748716	-2.83769866	1.58184419
H	-1.64093651	-4.11289109	0.73080306
H	-2.43602459	-2.57472834	1.09173980
C	-2.02853739	-2.77301119	-1.65099770
H	-3.01629837	-2.38825212	-1.38677245
H	-2.12049149	-3.85272868	-1.80833509
H	-1.71127902	-2.31151425	-2.59142667
C	-3.46682356	-0.14483371	1.29605074
H	-2.78428555	-0.23214387	2.13611438
C	-5.71253608	-0.00111583	0.42384998
H	-6.78542020	0.00859971	0.58754686
C	4.09545946	1.91083203	-1.03041969
H	4.14143005	2.40185983	-0.05299090
H	3.36773095	2.45350635	-1.64436278
H	5.07656881	2.01125272	-1.50876249
C	-2.04704684	2.89764954	0.75340528
H	-3.05112193	2.52207550	0.54600523
H	-2.10492008	3.98889502	0.81473078
H	-1.73178525	2.51811348	1.72986619
C	-4.84288266	-0.13523228	1.50449391
H	-5.23647587	-0.22970380	2.51148829
C	0.32680408	-3.17640144	-0.91553691
H	0.68594686	-2.83436469	-1.89182921
H	0.18456654	-4.26003978	-0.96234534
H	1.09919555	-2.95466446	-0.17372097
C	-3.82689876	0.10943753	-1.07754695
H	-3.42415087	0.19414834	-2.08248555
C	-1.04396664	2.50936869	-0.34198721
C	4.96649054	-0.83650057	0.02576287
H	4.78897053	-1.91642973	-0.02201106
H	5.11018572	-0.56204659	1.07373621
H	5.90912162	-0.63724006	-0.49791522
C	0.32186754	0.16414948	2.50624167
H	-0.07628361	1.16124600	2.30974969
H	0.46430351	0.05987736	3.58879683
H	-0.41785311	-0.57526302	2.19200318
C	-5.20246622	0.12049224	-0.86755787
H	-5.87660670	0.22149359	-1.71211898
C	-1.59479037	2.91239170	-1.71948435
H	-0.89247743	2.62565527	-2.50725319
H	-1.75246129	3.99536521	-1.76512259
H	-2.55420051	2.42367012	-1.91204553
C	0.28172989	3.24153706	-0.08983622
H	0.68587287	2.98541929	0.89400207
H	0.13185682	4.32429158	-0.13545971
H	1.02761329	2.96763481	-0.84258068
C	2.52287931	-1.83998565	2.31123631
H	1.78127481	-2.59056372	2.01498792
H	2.57887738	-1.84695490	3.40631278
H	3.49312147	-2.15809384	1.92251147
C	-1.48193514	-0.00390238	-0.21836557

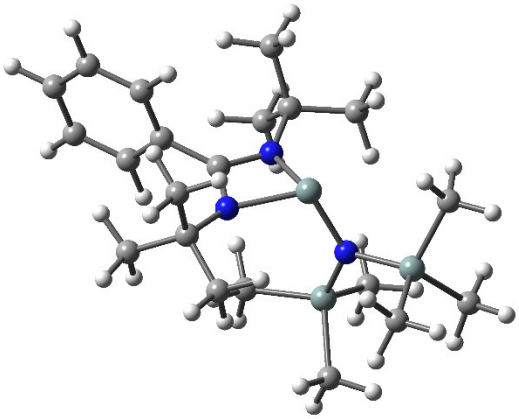

Figure S25. Optimized geometry of **4**.

Atomic Coordinates for **5** at ωB97XD/6-31+G(d,p) level of theory

Si	1.01954700	0.42741600	-0.10743200
Si	3.41370800	-1.68514700	0.35174500
Si	1.11212800	2.71736800	-0.57659100
N	-0.42076300	0.16118300	1.06421500
N	-0.46591700	-0.20277900	-1.05176700
C	-2.65877200	-0.52875200	0.12472000
N	2.36039400	-0.42574800	-0.01145100
C	5.20631700	-1.19982900	0.00038300
H	5.34208200	-0.97141500	-1.06288700
H	5.90692000	-1.99971700	0.26833700
H	5.47845300	-0.30328800	0.56884200
C	-0.61275500	3.34785600	-1.04448100
H	-0.59632200	4.42116800	-1.26506100
H	-1.32900100	3.18629600	-0.23070200
H	-0.98956400	2.82558300	-1.93076400
C	-0.68921700	-0.76616700	-2.38959700
C	-0.51148900	-2.28992000	-2.32076900
H	0.47238600	-2.53644400	-1.91243900
H	-0.60004400	-2.73115000	-3.31887900
H	-1.27872000	-2.74034200	-1.68349300
C	-2.06735300	-0.40576700	-2.95969700
H	-2.87972500	-0.92333100	-2.44504400
H	-2.10417600	-0.69216300	-4.01530900
H	-2.24405200	0.67239700	-2.89131600
C	-3.07216000	-1.84067400	0.35734600
H	-2.33138400	-2.61758500	0.51941700
C	-5.37518900	-1.13863400	0.19447200
H	-6.43385600	-1.37574900	0.22125000
C	1.74532300	3.69494700	0.91435100
H	2.68951600	3.27780500	1.28004500
H	1.03126900	3.69171200	1.74440700
H	1.92356000	4.73953900	0.63453200
C	-1.44451200	-0.69914600	3.15104600
H	-2.46151900	-0.82278000	2.77257900
H	-1.50872200	-0.51204100	4.22727700
H	-0.89511500	-1.63266800	2.99623600
C	-4.43003500	-2.14374500	0.39030200
H	-4.74891700	-3.16511700	0.57056300
C	0.39735400	-0.16307200	-3.28916700
H	0.25666400	0.91808800	-3.39002900
H	0.34498700	-0.60850100	-4.28656600
H	1.39427800	-0.35112600	-2.87771000
C	-3.60409000	0.47808100	-0.07253700
H	-3.27397700	1.49361900	-0.26987500
C	-0.71637400	0.46841600	2.47079000
C	2.30525800	2.99916200	-2.01155500
H	1.93599600	2.55364600	-2.94051500
H	3.27515400	2.54307600	-1.78883000
H	2.45819400	4.07021800	-2.18621000
C	3.30536700	-2.18574800	2.17789700
H	3.55376000	-1.33823900	2.82757500
H	3.99365200	-3.00505400	2.41768400
H	2.28935100	-2.51555800	2.42775600
C	-4.96093300	0.17231200	-0.03507200
H	-5.69482000	0.95648900	-0.19004300
C	-1.54857300	1.75349500	2.58395100
H	-1.03627500	2.58818200	2.09647800
H	-1.70014800	2.01194100	3.63681600
H	-2.53235900	1.62944000	2.12277600
C	0.64466800	0.66871900	3.14933700
H	1.25539500	-0.23415200	3.06595800
H	0.50128800	0.90216000	4.20827800
H	1.19760300	1.49434700	2.69102600
C	3.04496100	-3.24291400	-0.66608400
H	2.05673400	-3.64805900	-0.41668000
H	3.78530800	-4.03086500	-0.48211600
H	3.05528700	-3.01760300	-1.73925000
C	-1.20954600	-0.20633000	0.05283200

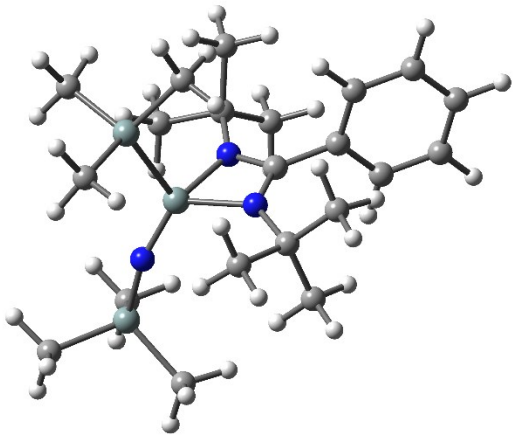

Figure S26. Optimized geometry of **5**.

Atomic Coordinates for TS**4** at ωB97XD/6-31+G(d,p) level of theory

Si	-0.82324600	0.22128000	-0.67507400	H	1.21909400	-4.09552300	0.45574000
Si	-2.29828800	-0.49521600	2.03908200	H	0.36109300	-2.76491500	1.26000000
Si	-3.01389300	0.39868400	-1.50274600	C	4.82962700	-0.41895000	1.36439600
N	0.65944400	-0.92414800	-0.65786400	H	5.22810900	-0.66308900	2.34365400
N	0.70463600	1.14712200	-0.10267000	C	-0.29877700	3.26352100	0.39424600
C	2.93755200	-0.02016600	-0.07786300	H	-0.94180100	3.19220000	-0.48874200
N	-2.04271800	-0.04640300	0.40584400	H	-0.12664200	4.32252200	0.60601200
C	-2.75479500	-2.32295900	2.19511500	H	-0.83294700	2.81600600	1.23736900
H	-3.65880900	-2.54352200	1.61671700	C	3.80133800	0.21678700	-1.14758300
H	-2.94471800	-2.60155100	3.23837100	H	3.39357700	0.45179700	-2.12598100
H	-1.95608500	-2.97005100	1.81483400	C	0.87735700	-2.36839100	-0.81343100
C	-2.94477700	0.70205500	-3.39724400	C	-3.90680200	1.93374000	-0.85559000
H	-3.94944900	0.81355200	-3.82824900	H	-3.28672600	2.83112900	-0.95739000
H	-2.45100700	-0.13530900	-3.90590600	H	-4.17022500	1.82250100	0.19896700
H	-2.37263200	1.60989000	-3.62375200	H	-4.81980900	2.09960100	-1.44027900
C	1.03998800	2.55364600	0.15557100	C	-0.71545100	-0.19543900	3.04120700
C	1.91553100	2.69672700	1.40777100	H	0.13492400	-0.70984200	2.57665000
H	1.45260600	2.18722900	2.25829500	H	-0.80578700	-0.55341400	4.07328200
H	2.02375200	3.75691100	1.65644200	H	-0.47940100	0.87451100	3.07311700
H	2.91585800	2.28591500	1.25581400	C	5.17776200	0.13651200	-0.95861800
C	1.73931100	3.17110700	-1.06403600	H	5.84777500	0.32057900	-1.79211400
H	2.71664900	2.71036300	-1.23347700	C	2.02011200	-2.66565800	-1.79336200
H	1.89560300	4.24311400	-0.90664300	H	1.85054100	-2.15407200	-2.74584800
H	1.12754600	3.03847000	-1.96170400	H	2.06811500	-3.74217100	-1.98470600
C	3.45293300	-0.33620900	1.17987600	H	2.98847500	-2.35385900	-1.39523100
H	2.77475900	-0.50293900	2.01158300	C	-0.43515300	-2.93440500	-1.37165600
C	5.69305400	-0.18253800	0.29632100	H	-1.26470600	-2.74071600	-0.68473200
H	6.76640000	-0.24779300	0.44211200	H	-0.34410700	-4.01528800	-1.51039300
C	-4.07646400	-1.16382500	-1.38566200	H	-0.67486200	-2.48050000	-2.33874400
H	-4.52303600	-1.25548100	-0.39106100	C	-3.69625000	0.51708400	2.79827800
H	-3.47496200	-2.06260900	-1.56124000	H	-3.48312300	1.58944800	2.72471400
H	-4.87441900	-1.14490600	-2.13720900	H	-3.84839200	0.27105900	3.85546200
C	1.16077700	-3.00686500	0.55417600	H	-4.63905700	0.33029400	2.27152100
H	2.11059400	-2.65609200	0.96708000	C	1.46540400	0.06490800	-0.27177400

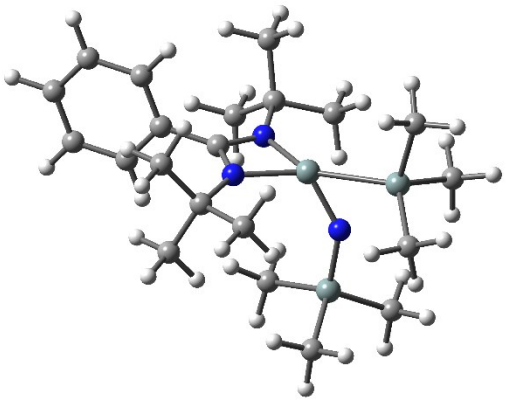

Figure S27. Optimized geometry of TS**4** [ωB97XD/6-31+G(d,p)].

Table S2. Total energies and Gibbs energies (in a.u.) of calculated structures at ωB97XD/6-31+G(d,p).

Compounds	E (a.u.)	E+ZPE (a.u.)	G (a.u.)
2	-2392.41228433	-2391.731671	-2391.800693
3	-2392.41756610	-2391.739485	-2391.812908
TS**2**	-2392.37499531	-2391.697518	-2391.768219
4	-1857.58027029	-1856.988588	-1857.052776
5	-1857.56309722	-1856.973210	-1857.041113
TS**4**	-1857.52184308	-1856.933030	-1857.000666

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