Electronic Supplementary Information for the paper

Entitled

Formation of Silaimines from a Sterically Demanding Iminophosphonamido Chlorosilylene via intramolecular N–P bond Cleavage

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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, ^{29}Si NMR spectra were recorded on a Bruker AVANCE-500 (99 MHz) 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 except **6**[S1] and 1,3-diisopropyl-4,5-dimethyl-imidazole-2-ylidene[S2] that were prepared by the respective literature procedures.

2- Experimental procedures and characterization data

2-1 Synthesis of dichlorosilane 7.

To a mixture of iminophosphonamide **6** (6.30 g, 11.7 mmol) and NEt_3 (2.0 mL, 14.3 mmol) in THF (80 mL), $HSiCl_3$ (1.2 mL, 11.9 mmol) was added at –80 ˚C and then the reaction mixture was stirred at –80 ˚C for 30 min. The mixture was gradually warmed up to room temperature, and it was kept stirring at this temperature for 9 hours. The reaction mixture was filtered and all volatiles of the filtrate were removed under reduced pressure. The residue was washed with hexane and dried under reduced pressure to give the corresponding dichlorosilane **7** (6.35 g, 84%) as colorless crystals. Mp: 171–173 °C (decomp.). ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ 0.57 (br d, J_{HH} = 6.7 Hz, 12H, CH_{3iPr}), 1.42 (br d, J_{HH} = 6.7 Hz, 12H, CH_{3iPr}), 3.80 (sept, J_{HH} = 6.7 Hz, 4H, CH_{iPr}), 6.69 (td, J_{HH} = 7.8 Hz, J_{HP} = 3.5 Hz, 4H, CH_{Ar}), 6.89 (t, J_{HH} = 7.2 Hz, 2H, CH_{Ar}), 6.94 (d, J_{HP} =2.7 Hz, 1H, Si-H), 7.08–7.11 (m, 3H, CH_{Ar}), 7.15–7.19 (m, 3H, CH_{Ar}), 7.36 (dd, J_{HP} = 11.6 Hz, J_{HH} = 8.1 Hz, CH_{Ar}). $^{13}C\{^{1}H\}$ NMR (100 MHz, 25 °C, C_6D_6): δ 24.1

(br s, $CH_{3i\mathrm{Pr}}$), 25.9 (br s, $CH_{3i\mathrm{Pr}}$), 29.5 ($CH_{i\mathrm{Pr}}$), 125.1 (d, J_{CP} = 1.2 Hz, CH_{Ar}), 127.5 (d, J_{CP} = 2.1 Hz, CH_{Ar}), 128.4 (d, J_{CP} = 13.1 Hz, CH_{Ar}), 128.9 (C_{Ar}), 133.4 (d, J_{CP} = 2.7 Hz, CH_{Ar}), 133.8 (d, J_{CP} = 10.0 Hz, CH_{Ar}), 134.2 (C_{Ar}), 148.9 (d, J_{CP} = 3.9 Hz, C_{Ar}). $^{31}P\{^{1}H\}$ NMR (162 MHz, 25 °C, C_6D_6): δ 25.5. ^{29}Si NMR (99 MHz, 25 °C, C_6D_6): δ –89.4 (dd, J_{SiH} = 369.8 Hz, J_{SiP} = 2.3 Hz).

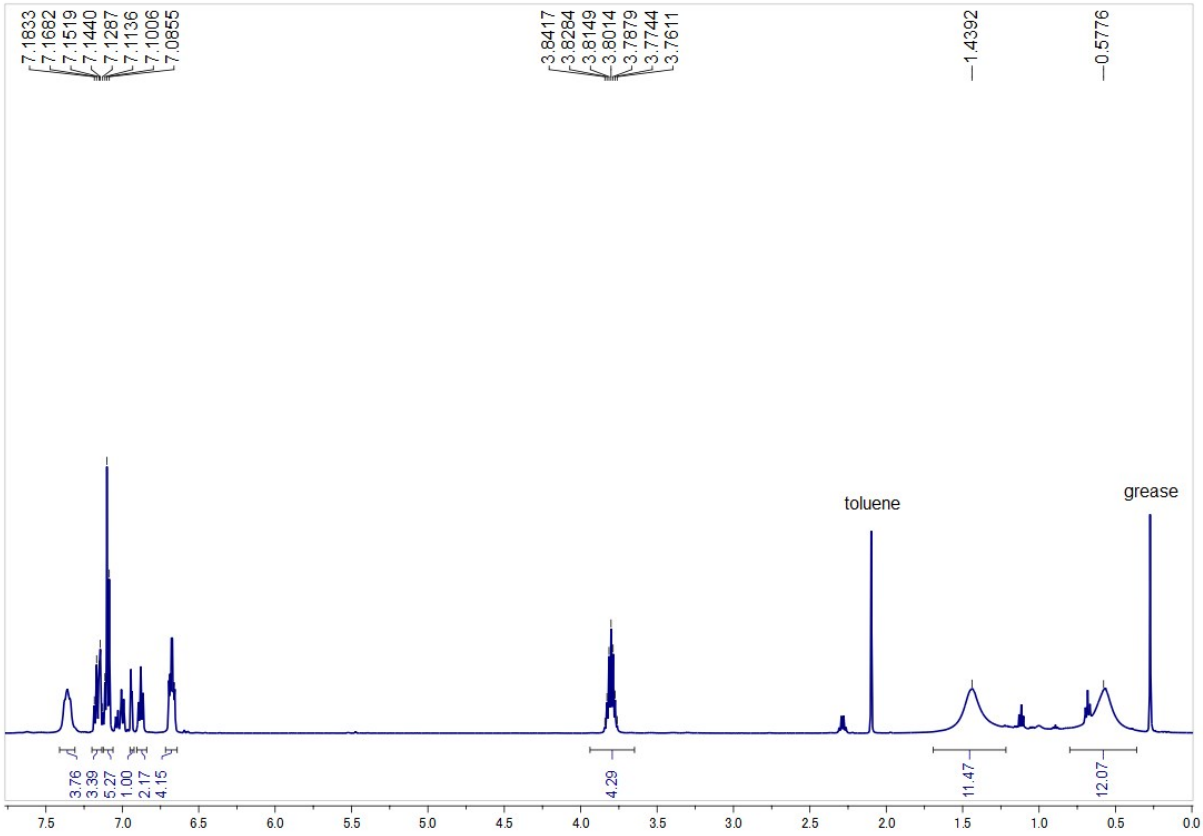

Figure S1. ^{1}H NMR spectrum (400 MHz, 25 °C, C_6D_6) of **7**.

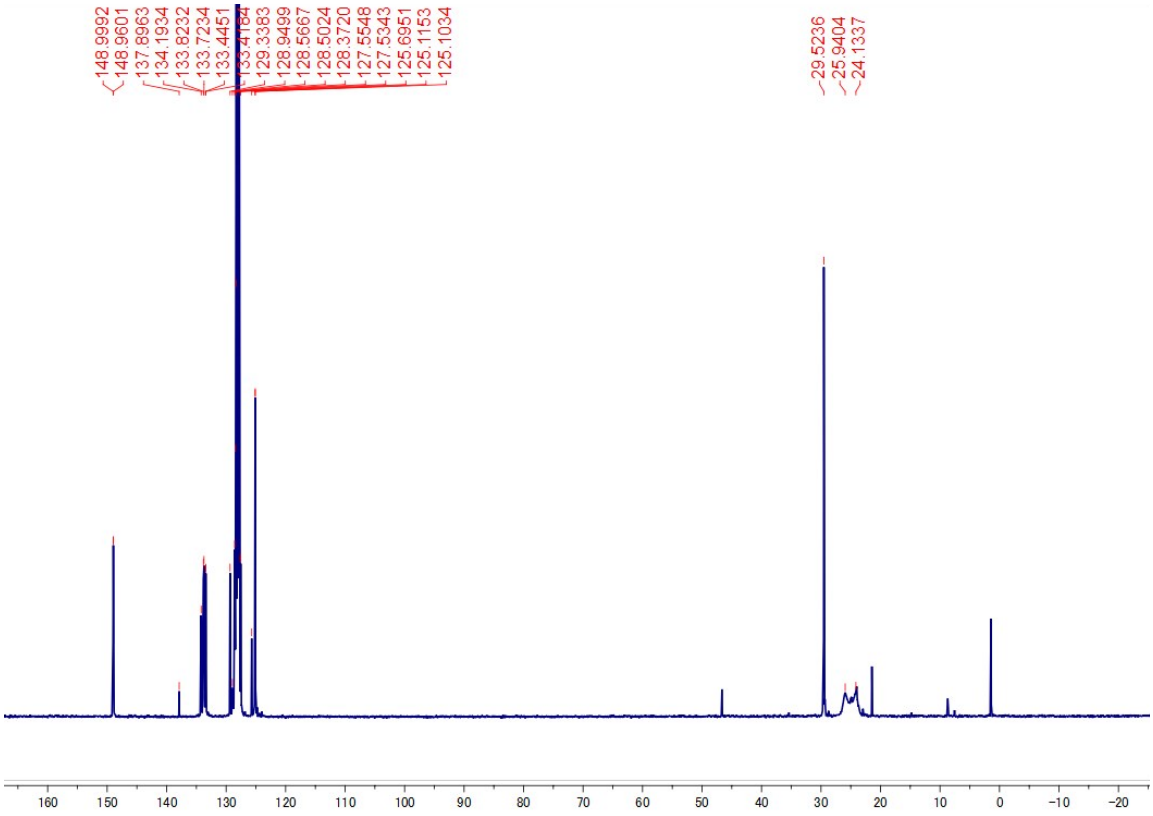

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, C_6D_6) of **7**.

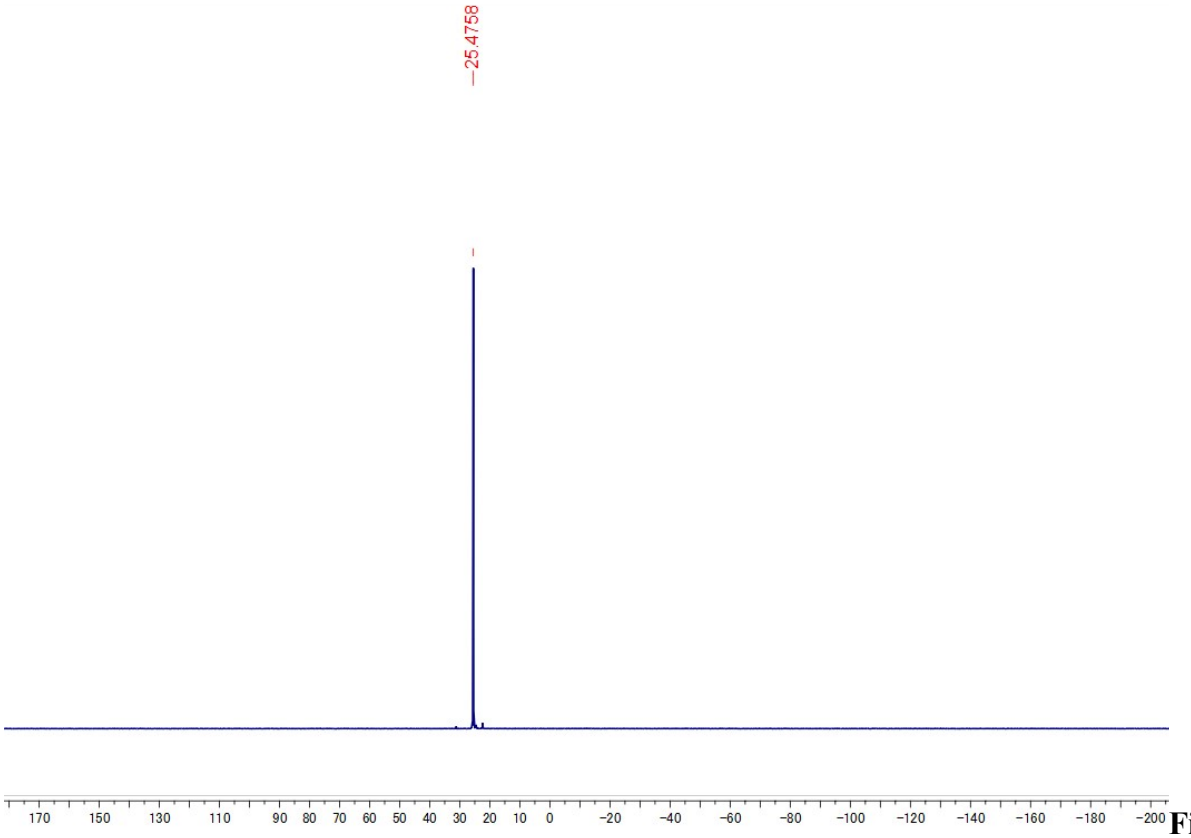

Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 25 °C, C_6D_6) of **7**.

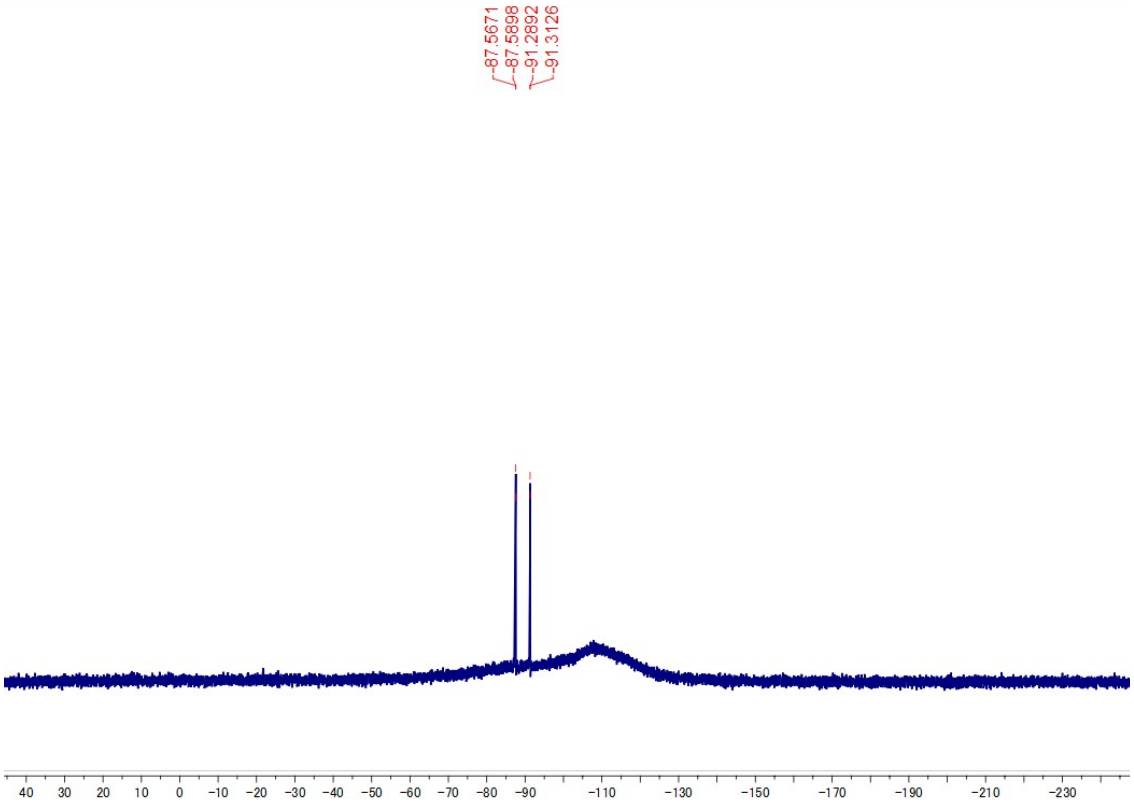

Figure S4. $^{29}Si\{^{1}H\}$ NMR spectrum (99 MHz, 25 °C, C_6D_6) of **7**.

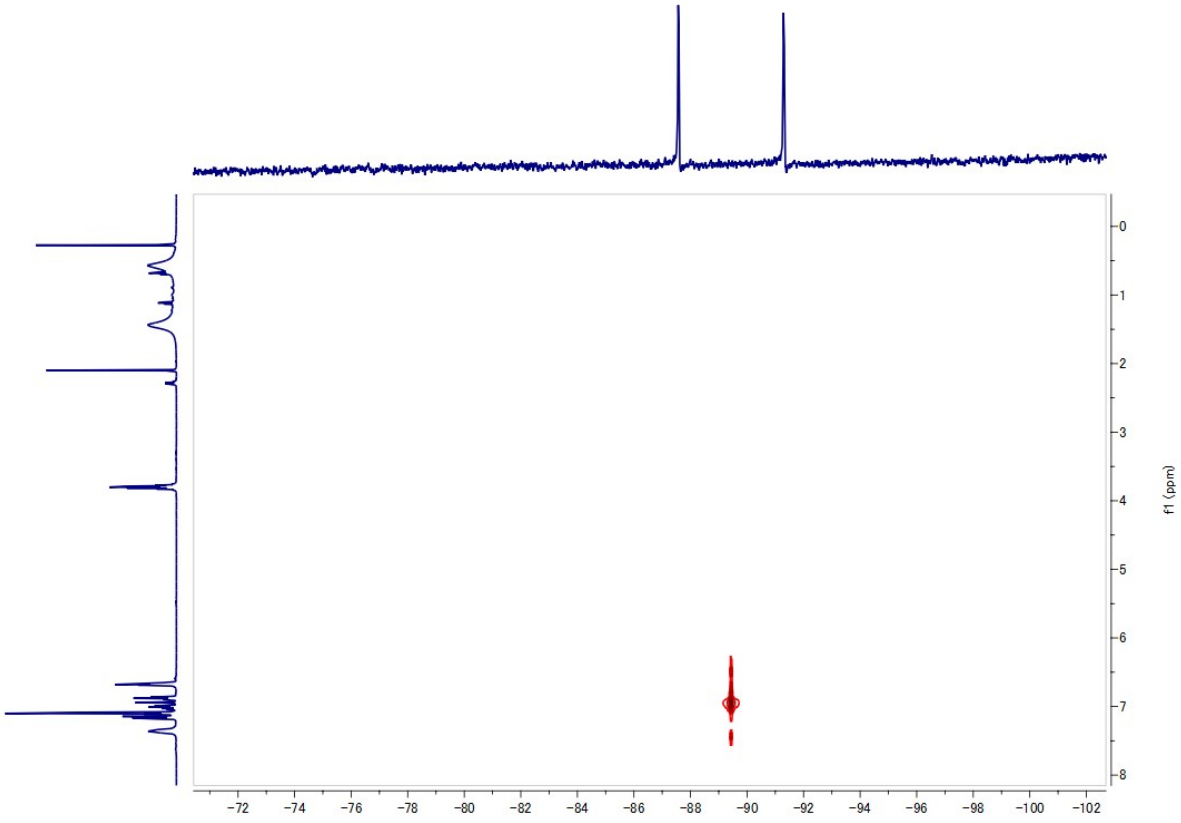

Figure S5. ^{29}Si-^{1}H HETCOR NMR spectrum (25 °C, C_6D_6) of **7**.

2-2 Synthesis of chlorosilylene 5.

A toluene (30 mL) solution of 1,3-diisopropyl-4,5-dimethylimidazole-2-ylidene (2.25 g, 12.5 mmol) and dichlorosilane **7** (6.35 g, 10 mmol) was heated at 60 ˚C for 25 hours. The resulting precipitates were filtered off and the filtrate was concentrated under reduced pressure. Recrystallization from a saturated toluene solution at ambient temperature give the corresponding chlorosilylene **5** (4.20 g, 70%) as yellow crystals. Single crystals suitable for X-ray diffraction analysis were obtained from a C_6D_6 solution at 10 °C. Mp: 205–206 °C (decomp.). ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ 0.43 (d, J_{HH} = 6.7 Hz, 6H, $CH_{3i\mathrm{Pr}}$), 0.97 (d, J_{HH} = 6.7 Hz, 6H, $CH_{3i\mathrm{Pr}}$), 1.41 (d, J_{HH} = 6.5 Hz, 6H, $CH_{3i\mathrm{Pr}}$), 1.46 (d, J_{HH} = 6.5 Hz, 6H, $CH_{3i\mathrm{Pr}}$), 4.11 (sept, J_{HH} = 6.7 Hz, 2H, $CH_{i\mathrm{Pr}}$), 4.25 (sept, J_{HH} = 6.5 Hz, 2H, $CH_{i\mathrm{Pr}}$), 6.63 (td, J_{HH} = 7.7 Hz, J_{HP} = 3.3 Hz, 2H, CH_{Ar}), 6.85–6.90 (m, 3H, CH_{Ar}), 6.93–6.97 (m, 1H, CH_{Ar}), 7.00–7.11 (m, 5H, CH_{Ar}), 7.13–7.16 (m, 5H, CH_{Ar}), 8.17 (dd, J_{HP} = 11.8 Hz, J_{HH} =7.9 Hz, CH_{Ar}). ^{13}C{^{1}H} NMR (100 MHz, 25 °C, C_6D_6): δ 23.1 ($CH_{3i\mathrm{Pr}}$), 23.9 ($CH_{3i\mathrm{Pr}}$), 25.6 ($CH_{3i\mathrm{Pr}}$), 29.0 ($CH_{i\mathrm{Pr}}$), 29.4 ($CH_{3i\mathrm{Pr}}$), 30.0 ($CH_{i\mathrm{Pr}}$), 125.0 (CH_{Ar}), 127.0 (d, J_{CP} = 2.8 Hz, CH_{Ar}), 128.4 (d, J_{CP} = 2.2 Hz, CH_{Ar}), 128.5 (d, J_{CP} = 3.2 Hz, CH_{Ar}), 129.0 (d, J_{Cp} = 89.8 Hz, C_{Ar}), 131.1 (d, J_{CP} = 8.3 Hz, CH_{Ar}), 131.4 (d, J_{Cp} = 92.9 Hz, C_{Ar}), 132.8 (d, J_{CP} = 2.7 Hz, CH_{Ar}), 133.4 (d, J_{Cp} = 2.9 Hz, CH_{Ar}), 134.7 (J_{CP} = 1.6 Hz, C_{Ar}), 148.7 (d, J_{CP} = 6.3 Hz, C_{Ar}), 148.8 (d, J_{CP} = 7.8 Hz, C_{Ar}). ^{31}P{^{1}H} NMR (162 MHz, 25 °C, C_6D_6): δ 44.1. ^{29}Si{^{1}H} NMR (99 MHz, 25 °C, C_6D_6): δ 62.6 (d, J_{SiP} = 11.6 Hz). Anal. Calcd for $C_{36}H_{44}ClN_2PSi$: C, 72.15; H, 7.40; N, 7.68. Found: C, 71.77; H, 7.40; N, 4.28.

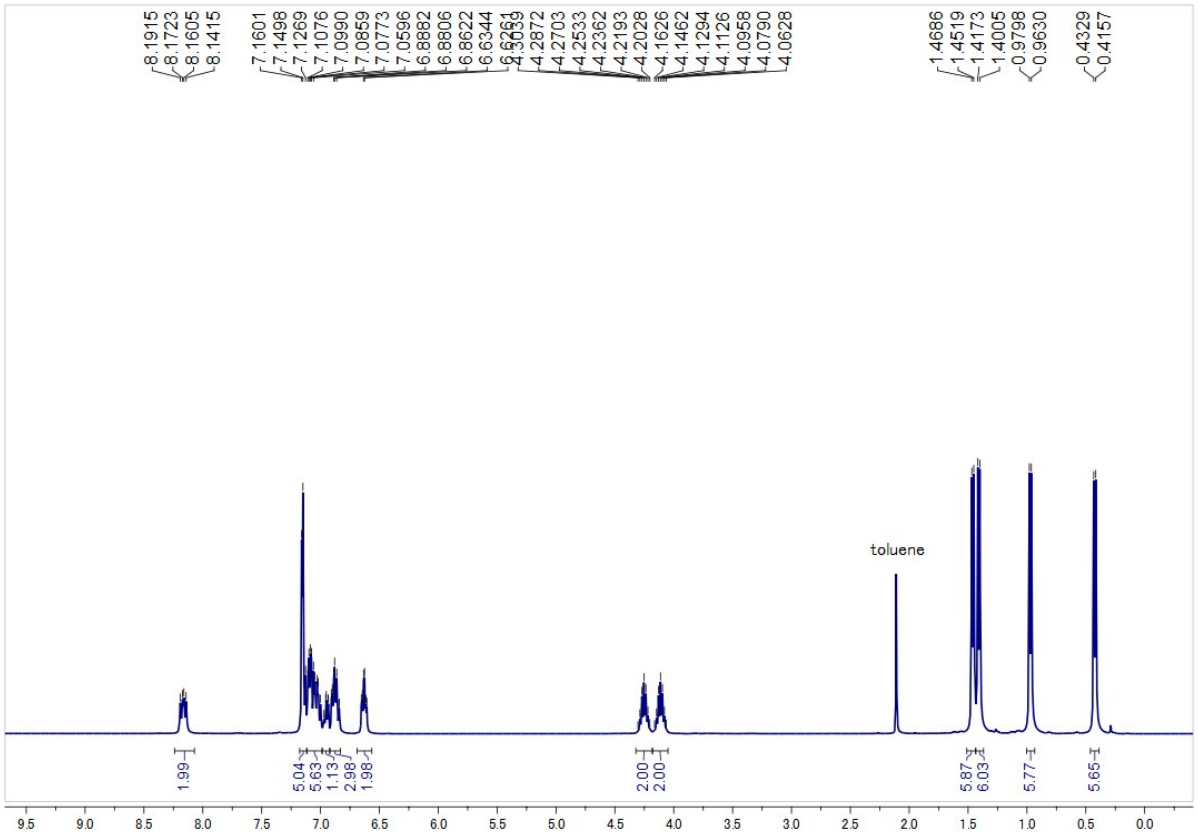

Figure S6. ^{1}H NMR spectrum (400 MHz, 25 °C, C_6D_6) of **5**.

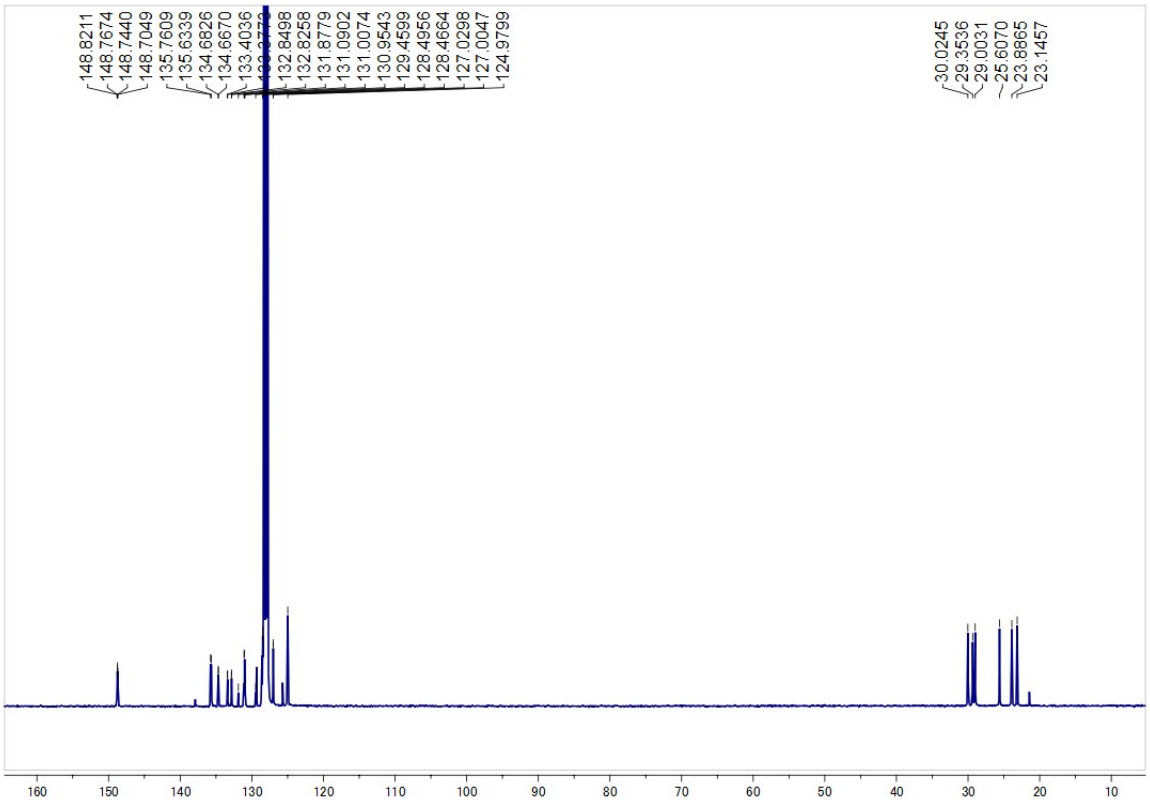

Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, C_6D_6) of **5**.

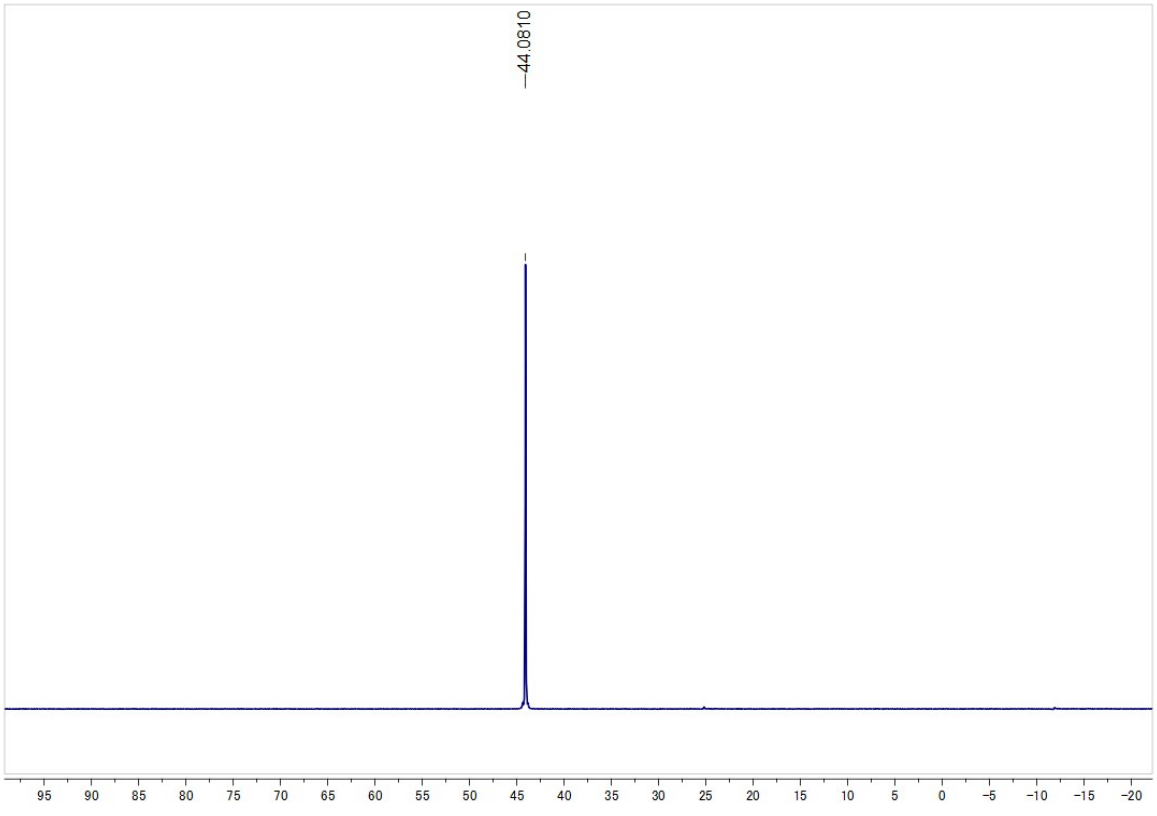

Figure S8. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 25 °C, C_6D_6) of **5**.

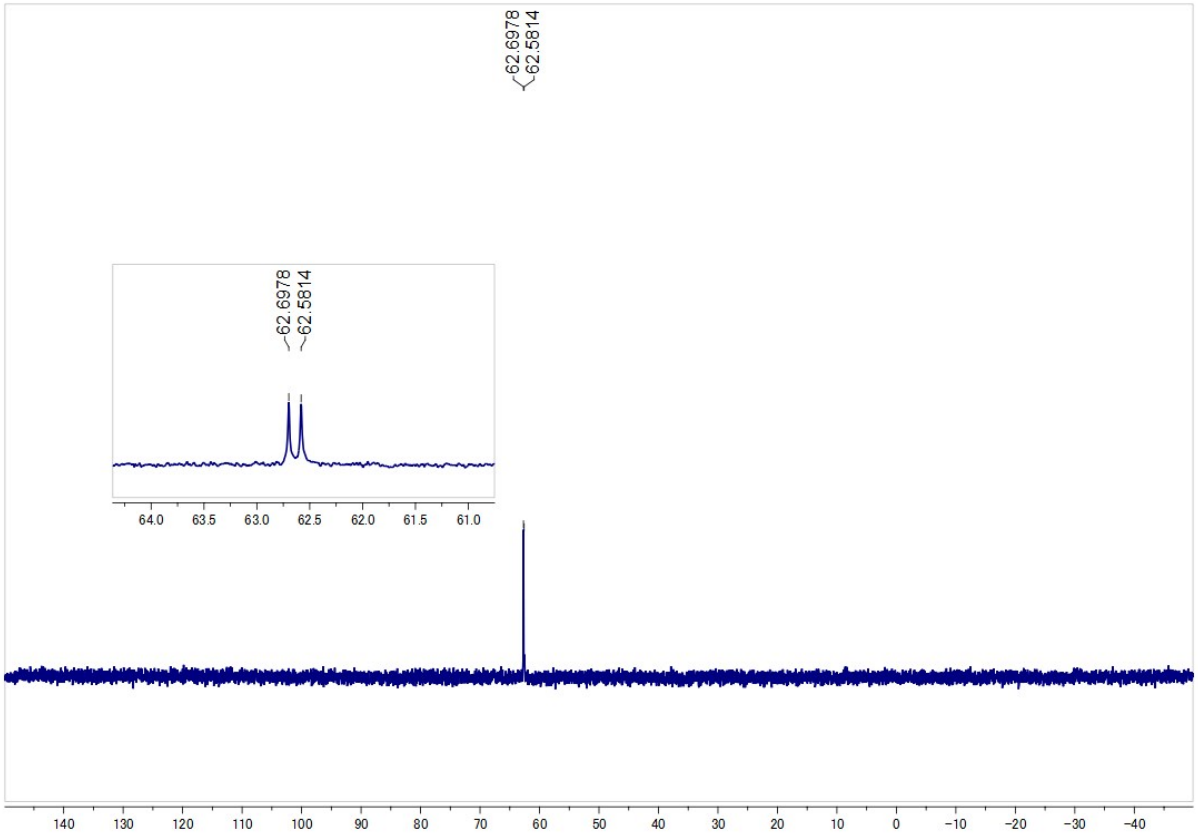

Figure S9. $^{29}Si\{^{1}H\}$ NMR spectrum (99 MHz, 25 °C, C_6D_6) of **5**.

2-3 Reaction of 5 with $KN(SiMe_3)_2$

To a mixture of chlorosilylene **5** (590 mg, 0.983 mmol) and $KN(SiMe_3)_2$ (200 mg, 0.983 mmol), toluene (15 mL) was added at ambient temperature and stirred for 12 hours. The insoluble precipitates were filtered off and all volatiles of the filtrate were removed under reduced pressure. Recrystallization from a saturated toluene solution gave the corresponding silaimine **9** (610 mg, 86%) as yellow crystals. Mp: 85–86 °C (decomp.). ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ 0.24 (d, J_{HH} = 6.6 Hz, 6H, $CH_{3i\mathrm{Pr}}$), 0.57 (s, 18H, Si-CH_3), 1.16 (d, J_{HH} = 6.8 Hz, 12H, $CH_{3i\mathrm{Pr}}$), 1.21 (d, J_{HH} = 6.7 Hz, 6H, $CH_{3i\mathrm{Pr}}$), 3.26 (sept, J_{HH} = 6.7 Hz, 2H, $CH_{i\mathrm{Pr}}$), 3.42 (sept, J_{HH} = 6.8 Hz, 2H, $CH_{i\mathrm{Pr}}$), 6.89–7.03 (m, 10H, CH_{Ar}), 7.10–7.14 (m, 2H, CH_{Ar}), 7.28–7.32 (m, 4H, CH_{Ar}). $^{13}C\{^{1}H\}$ NMR (100 MHz, 25 °C, C_6D_6): δ 4.3 ($SiCH_3$), 4.4 ($SiCH_3$), 23.6 ($CH_{3i\mathrm{Pr}}$), 24.6 ($CH_{3i\mathrm{Pr}}$), 26.3 ($CH_{3i\mathrm{Pr}}$), 27.8 ($CH_{i\mathrm{Pr}}$), 29.9 ($CH_{i\mathrm{Pr}}$), 119.0 (CH_{Ar}), 122.9 (CH_{Ar}), 125.1 (CH_{Ar}), 127.2 (CH_{Ar}), 128.4 (d, J_{CP} = 7.3 Hz, CH_{Ar}), 130.2 (CH_{Ar}), 135.2 (d, J_{CP} = 24.2 Hz, CH_{Ar}), 137.1 (d, J_{CP} = 21.5 Hz, C_{Ar}), 139.4 (d, J_{CP} = 6.8 Hz, C_{Ar}), 139.6 (C_{Ar}), 143.0 (C_{Ar}), 146.9 (C_{Ar}). $^{31}P\{^{1}H\}$ NMR (162 MHz, 25 °C, C_6D_6): δ 58.8. $^{29}Si\{^{1}H\}$ NMR (99 MHz, 25 °C, C_6D_6): δ –33.5 (d, J_{SiP} = 51.4 Hz, *Si*=N), 6.2 (d, J_{SiP} = 3.3 Hz, *Si*Me_3). Anal. Calcd for $C_{42}H_{62}N_3PSi_3$: C, 69.66; H, 8.63; N, 5.80. Found: C, 70.04; H, 8.71; N, 5.62.

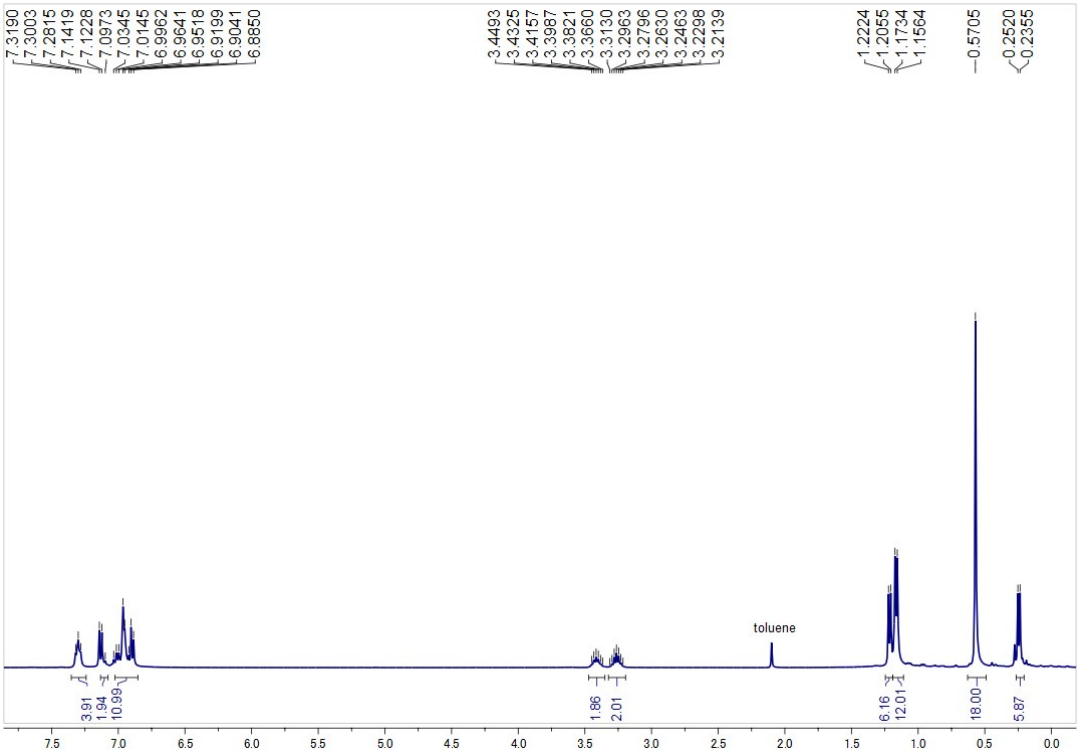

Figure S10. ^{1}H NMR spectrum (400 MHz, 25 °C, C_6D_6) of **9**.

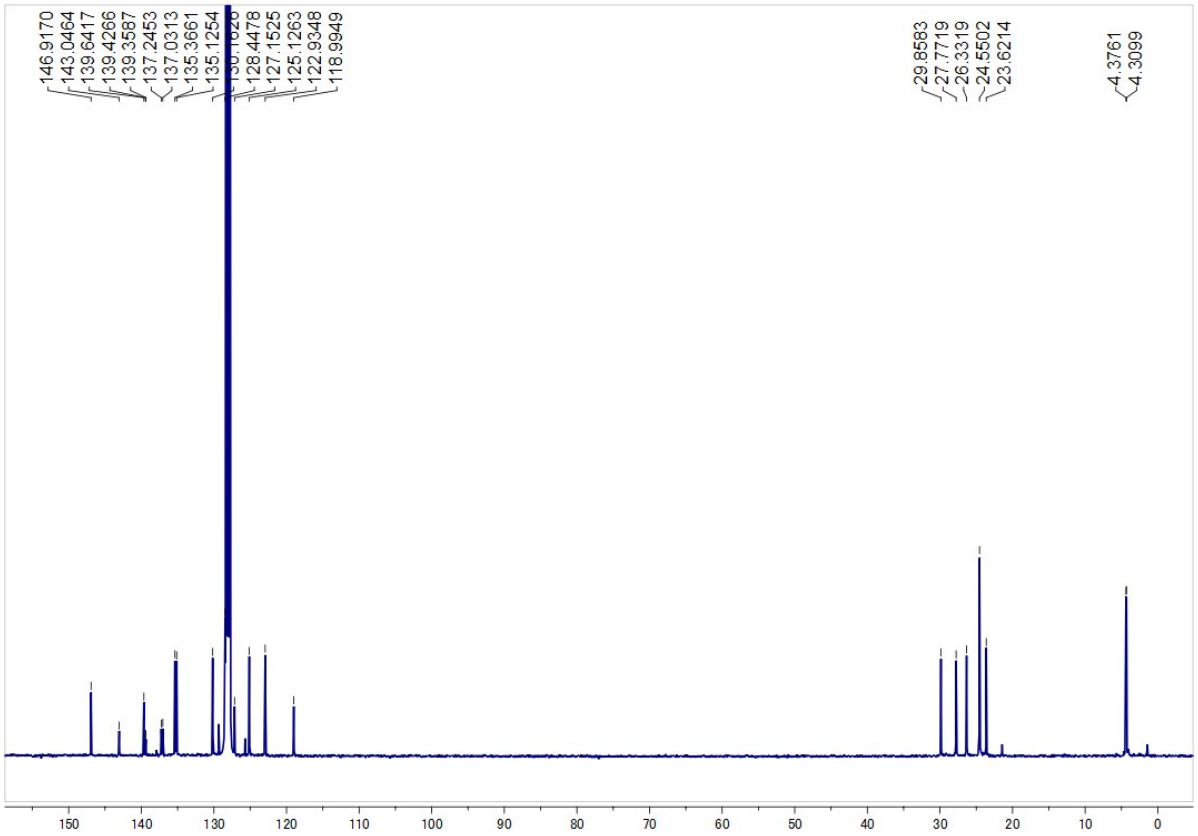

Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, C_6D_6) of **9**.

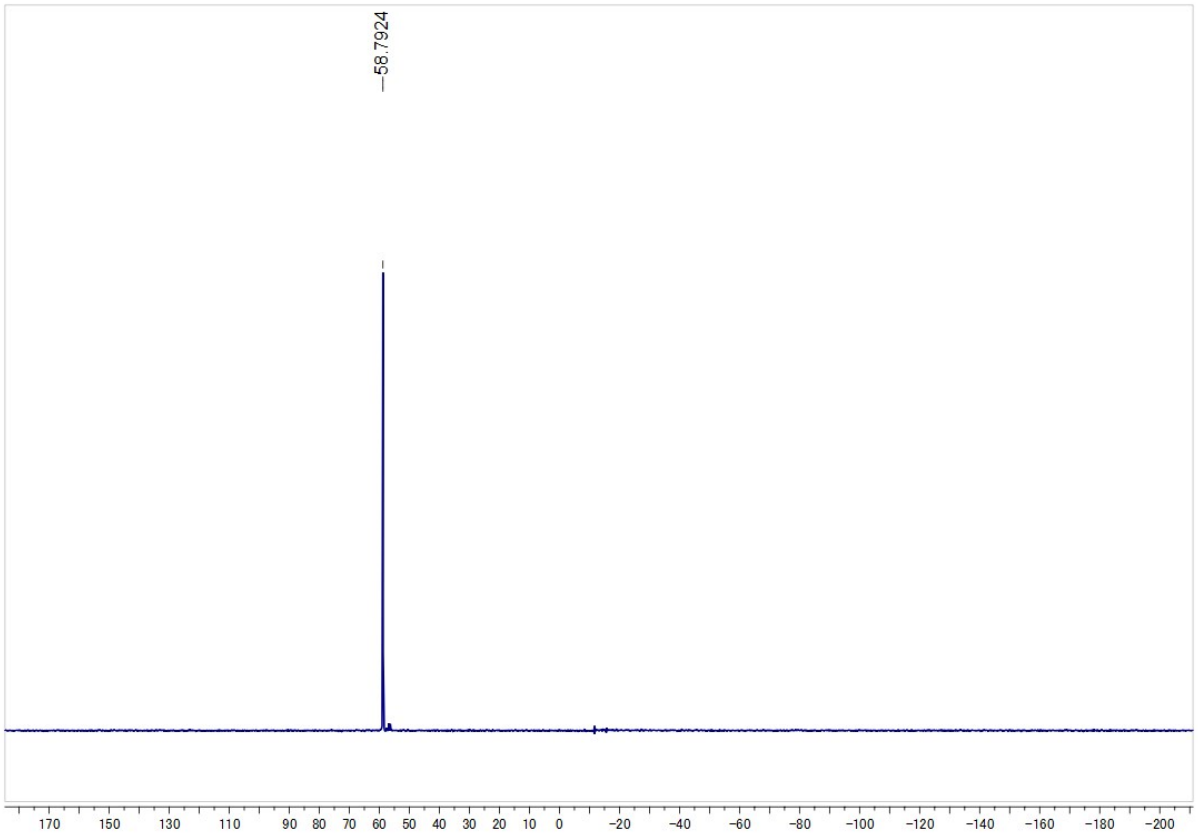

Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 25 °C, C_6D_6) of **9**.

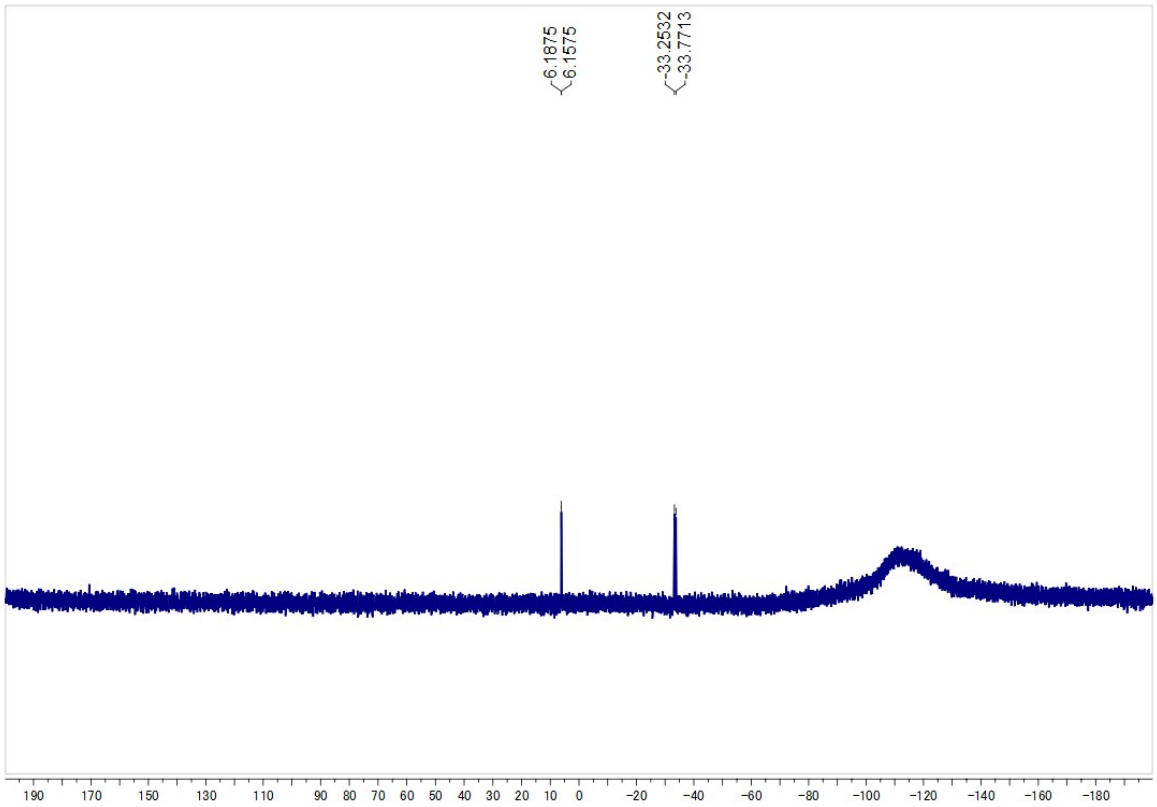

Figure S13. $^{29}Si\{^{1}H\}$ NMR spectrum (99 MHz, 25 °C, C_6D_6) of **9**.

2-4 Reaction of 5 with K[CpFe(CO)$_2$]

In a Schlenk tube, to a mixture of chlorosilylene **5** (320 mg, 0.534 mmol) and K[CpFe(CO)$_2$] (125 mg, 0.579 mmol), 5 mL of toluene was added at ambient temperature and kept stirring for 18 hours at this temperature. The insoluble salts were removed by filtrate and all volatiles were removed under reduced pressure. Recrystallization from saturated toluene solution gave **11** (178 mg, 48%) as dark red crystals. Mp: 155–156 °C (decomp.). ^{1}H NMR (400 MHz, 25 °C, C_6D_6): δ 0.50 (br s, 6H, $CH_{3i\mathrm{Pr}}$), 1.18 (br s, 6H, $CH_{3i\mathrm{Pr}}$), 1.28 (d, J_{HH} = 6.7 Hz, 6H, $CH_{3i\mathrm{Pr}}$), 1.40 (br d, J_{HH} = 5.5 Hz, 6H, $CH_{3i\mathrm{Pr}}$), 3.48 (br s, 2H, $CH_{i\mathrm{Pr}}$), 3.53 (br s, 2H, $CH_{i\mathrm{Pr}}$), 4.37 (s, 5H, CH_{Cp}), 6.89 (t, J_{HH} = 7.5 Hz, 1H, CH_{Ar}), 7.00–7.09 (m, 9H, CH_{Ar}), 7.20 (d, J_{HH} = 7.5 Hz, 2H, CH_{Ar}), 7.53 (br s, 4H, CH_{Ar}). $^{13}C\{^{1}H\}$ NMR (100 MHz, 25 °C, C_6D_6): δ 23.1 ($CH_{3i\mathrm{Pr}}$), 23.6 ($CH_{3i\mathrm{Pr}}$), 23.7 ($CH_{3i\mathrm{Pr}}$), 26.4 ($CH_{3i\mathrm{Pr}}$), 28.5 ($CH_{i\mathrm{Pr}}$), 30.0 ($CH_{i\mathrm{Pr}}$), 83.8 (C_{Cp}), 117.2 (CH_{Ar}), 122.7 (CH_{Ar}), 124.6 (CH_{Ar}), 126.8 (CH_{Ar}), 128.3 (d, I_{CP} = 6.9 Hz, CH_{Ar}), 134.4 (C_{Ar}), 134.9 (br d, J_{CP} = 15.2 Hz, CH_{Ar}), 141.6 (C_{Ar}), 141.7 (C_{Ar}), 147.5 (C_{Ar}), 213.8 (CO). $^{31}P\{^{1}H\}$ NMR (162 MHz, 25 °C, C_6D_6): δ 44.6. $^{29}Si\{^{1}H\}$ NMR (99 MHz, 25 °C, C_6D_6): δ 63.0 (d, J_{SiP} = 68.5 Hz). Anal. Calcd for $C_{39}H_{47}FeN_2O_2PSi$: C, 67.82; H, 6.86; N, 4.06. Found: C, 67.90; H, 6.92; N, 4.16.

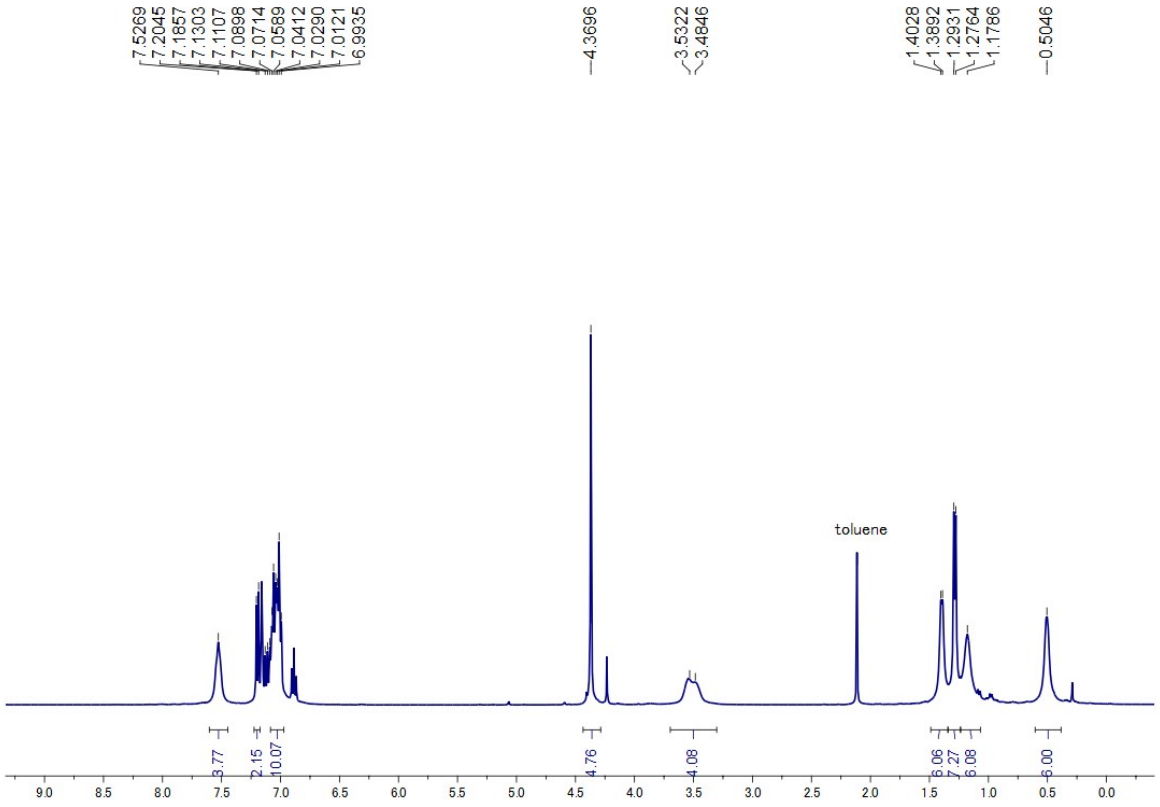

Figure S14. ^{1}H NMR spectrum (400 MHz, 25 °C, C_6D_6) of **11**.

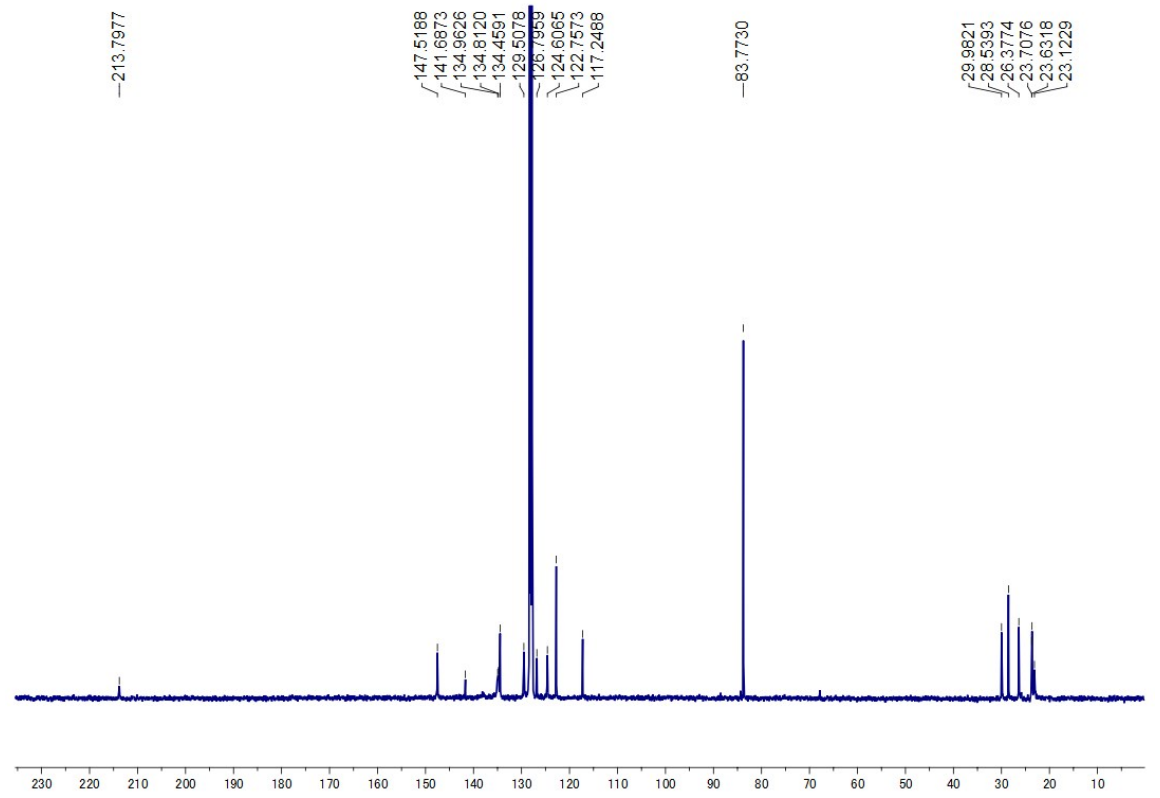

Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 25 °C, C_6D_6) of **11**.

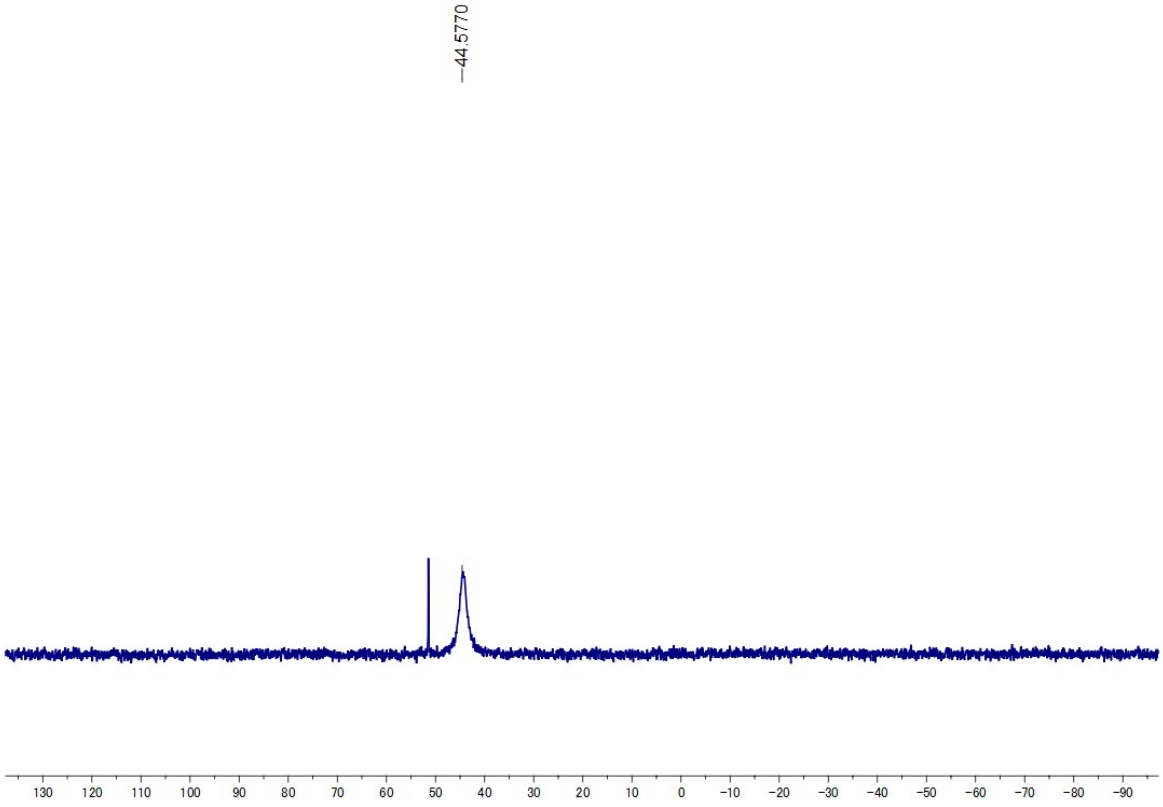

Figure S16. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 25 °C, C_6D_6) of **11**.

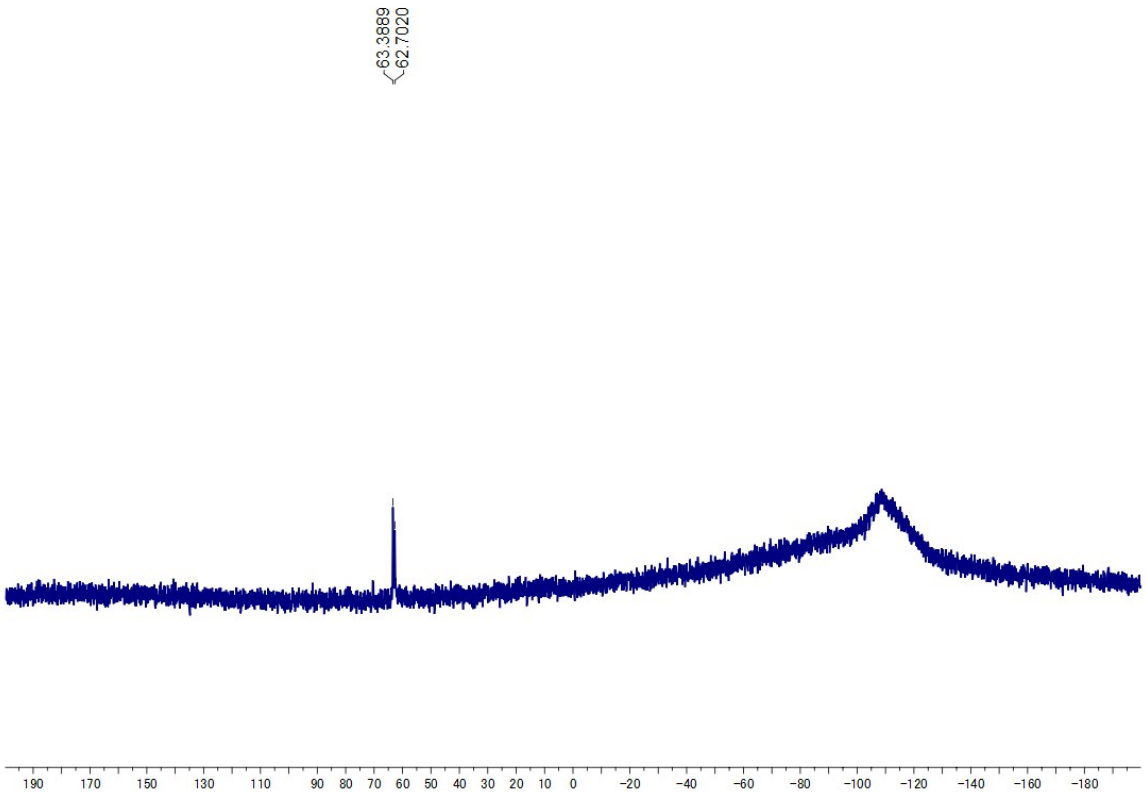

Figure S17. $^{29}Si\{^{1}H\}$ NMR spectrum (99 MHz, 25 °C, C_6D_6) of **11**.

3- Crystallographic data collection and structure determination

Colorless single crystals of **7** and yellow single crystals of **5** were grown of saturated C_6D_6 toluene solution at room temperature. Yellow single crystals of **9** were obtained from toluene solution at −10 °C. Red single crystals of **10** were obtained from a C_6D_6 solution at 10 °C. The intensity data were collected at 100, 150, or 173 K on a Bruker SMART APEX or APEX II diffractometer employing graphite-monochromated MoKα radiation (λ = 0.71073 Å). Structures were solved by direct methods (SHELXT)[S3] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL).[S4] 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. 2082216 (**5**), 2082217 (**7**), 2082218 (**9**), and 2082219 (**11**).

Table S1. Crystallographic data and details of refinement for **5** and **7**.

	5	**7**
Formula	$C_{36}H_{44}ClN_2PSi$, 2 (C_6H_6)	$C_{36}H_{45}Cl_2N_2PSi$
Formula weight	755.45	635.70
Color	colorless	colorless
Crystal size / mm	0.10 × 0.08 × 0.07	0.14 × 0.08 × 0.06
Temperature / K	100	150
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_1/n$
a /Å	11.8829(11)	10.5282(8)
b /Å	15.5031(14)	37.197(3)
c /Å	23.241(2)	17.9830(17)
a / deg.	90	90
b / deg.	90	103.1270(10)
g / deg.	90	90
V /Å^3	4281.4(7)	6858.4(10)
Z	4	8
D_{calcd} / g cm^{-3}	1.172	1.231
No. of unique data	7888	12557
No. of parameters	486	781
No. of restraints	0	6
R_1 ($I > 2s(I)$)	0.0446	0.0663
wR_2 (all data)	0.0906	0.1668
GOF	1.010	1.047
Flack parameter	0.04(6)	–

Table S2. Crystallographic data and details of refinement for **9** and **11**.

	9	**11**
Formula	$C_{42}H_{62}N_3PSi_3$	$C_{43}H_{49}FeN_2O_2PSi$
Formula weight	724.18	740.75
Color	yellow	red
Crystal size / mm	0.54 × 0.30 × 0.20	0.22 × 0.20 × 0.19
Temperature / K	100	173
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a /Å	19.7520(8)	10.6138(9)
b /Å	18.9120(8)	18.8185(16)
c /Å	22.5192(9)	19.6086(17)
a / deg.	90	90
b / deg.	92.0010(10)	92.1190(10)
g / deg.	90	90
V /Å^3	8406.9(6)	3913.9(6)
Z	8	4
D_{calcd} / g cm^{-3}	1.144	1.257
No. of unique data	15636	7208
No. of parameters	911	459
No. of restraints	0	0
R_1 ($I > 2s(I)$)	0.0695	0.0354
wR_2 (all data)	0.1993	0.0854
GOF	1.053	1.010

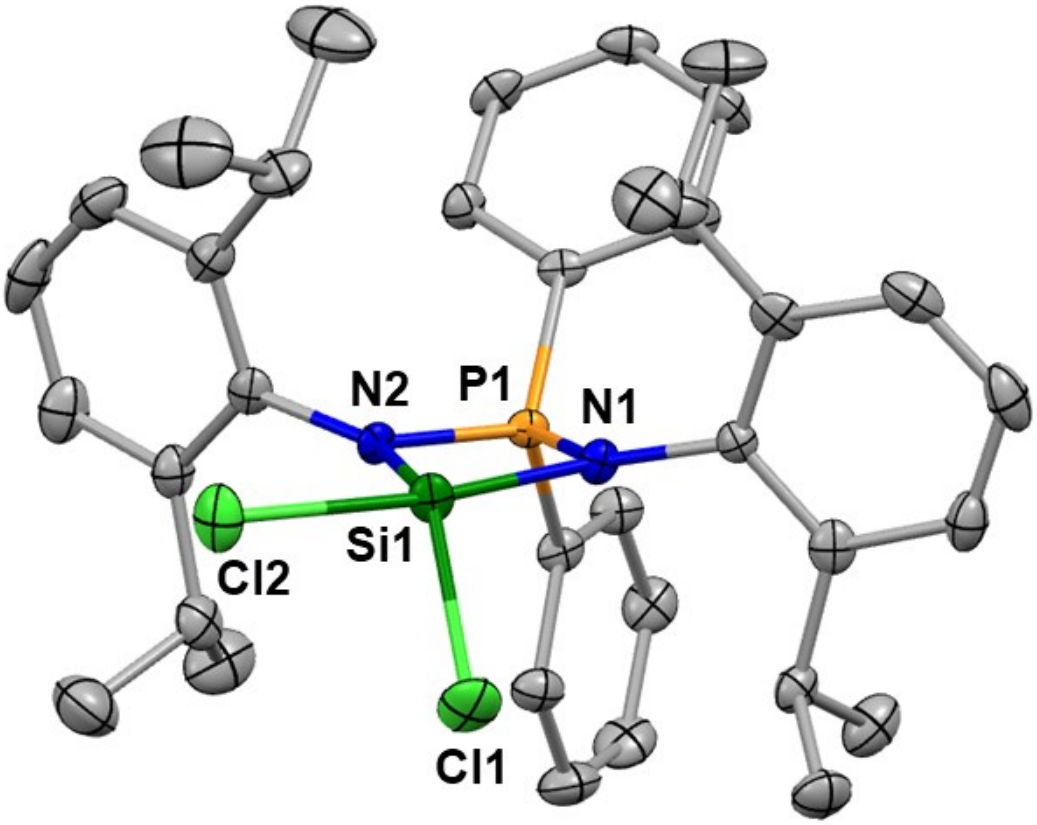

Figure S18. ORTEP of **7** with 50% thermal ellipsoids. All hydrogen atoms and one of the two independent molecules of **7** in the unit cell are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Si1–N1 = 1.947(3), Si1–N2 = 1.803(3), Si1–Cl1 = 2.0852(13), Si1–Cl2 = 2.1743(13), N1–Si1–N2 = 76.15(11), N1–Si1–Cl2 = 168.52(9), N2–Si1–Cl1 = 117.88(9), N2–Si1–H1 = 126.9(14), Cl1–Si1–H1 = 115.2(14).

4- Computational details

Geometries of all systems have been optimized with the Gaussian-09 program using[S5] B3LYP-D3[S6]/def2-svp for Fe and 6-31+G(d,p) for the others level of theory on **5**, **8**, **9, 10**, **13**, **14**, and **15**. Harmonic vibrational frequencies were calculated in order to verify that these structures correspond to energy minima (all frequencies are real).

Atomic Coordinates for **5** at B3LYP-D3/6-31+G(d,p) level of theory.

P	0.01931191	0.23930272	0.38341173	H	-1.69493783	-1.62151378	1.90735097
Cl	-0.36628446	1.90438888	-2.96984405	C	1.90551737	-2.74238455	-0.90513673
Si	-0.12569128	-0.20125149	-2.24209258	H	0.89939254	-2.32480449	-0.84575491
N	1.12956855	0.12088091	-0.83112057	C	4.26145911	-1.90511487	-0.60872190
N	-1.21020778	-0.14008435	-0.64385582	H	4.57265379	-2.94557152	-0.60323874
C	0.33303245	-0.88820138	1.77395688	C	4.83558651	0.43087546	-0.53507774
C	2.51363473	-0.23177059	-0.74240580	H	5.58909422	1.20995355	-0.46671336
C	3.11043598	2.26271042	-0.74400817	C	5.22495211	-0.90543531	-0.49442827
H	2.05072533	2.30737062	-0.99457872	H	6.27422810	-1.16716200	-0.39013024
C	3.48903082	0.79111392	-0.67511438	C	-3.55605885	0.59112806	-0.36360298
C	-2.99790317	-1.80710467	-0.36125447	C	-2.01987739	-2.96064018	-0.56445108
C	-0.08734132	1.87719178	1.18856031	H	-1.01556665	-2.58333459	-0.36541542
C	2.90033930	-1.59910793	-0.73296221	C	-5.30087106	-1.07786189	-0.04049009
C	-0.06436495	3.04073623	0.40003537	H	-6.34706972	-1.32274444	0.12000698
H	0.01316735	2.96576008	-0.67898169	C	3.31942413	2.95380978	0.61662590
C	-0.15029718	4.29477474	0.99895154	H	4.37711267	2.94220675	0.90448701
H	-0.12835257	5.18505836	0.37758150	H	2.74684686	2.45743947	1.40654892
C	1.61518381	-0.91412745	2.35061098	H	2.98872102	3.99701877	0.57373469
H	2.41817138	-0.31211943	1.93808564	C	3.86235722	3.00453946	-1.86391449
C	-0.26586855	4.40699005	2.38824095	H	3.70081091	2.51945912	-2.83139759
H	-0.33252321	5.38700794	2.85169795	H	4.94155339	3.04380509	-1.67734732
C	-2.59350278	-0.44391778	-0.43338998	H	3.50061301	4.03622410	-1.93713611
C	-0.21059923	1.99548857	2.58321629	C	-0.30048896	3.25628977	3.17807795
H	-0.23329274	1.11178434	3.21075818	H	-0.39544604	3.33511289	4.25690458
C	-3.19659150	2.05573815	-0.55988156	C	1.86413742	-1.72955207	3.45455463
H	-2.12801330	2.10800367	-0.75347474	H	2.85918538	-1.75570529	3.88803262
C	-0.69652433	-1.66081068	2.32719972	C	-3.50157276	2.89678886	0.69226431

H	-2.96992299	2.51251337	1.56831911	H	1.29473192	-4.16189038	-2.44248275
H	-4.57353882	2.90080009	0.92020312	C	-4.89874526	0.24877338	-0.14974151
H	-3.18679136	3.93405692	0.53797683	H	-5.64085633	1.03915982	-0.08559477
C	2.00822951	-3.81667623	0.19239734	C	-3.88917584	2.63801000	-1.80647767
H	1.89164152	-3.38552791	1.18912377	H	-4.97987738	2.64575589	-1.69839849
H	2.96942330	-4.34088823	0.15861853	H	-3.63306549	2.05926080	-2.69839396
H	1.22109838	-4.56598286	0.05185736	H	-3.55777586	3.66935142	-1.97054673
C	0.83916043	-2.51394453	3.99370424	C	-2.25380984	-4.15128762	0.38333461
H	1.03693492	-3.15033159	4.85118270	H	-3.17282523	-4.69416594	0.13797060
C	-4.35378010	-2.09312796	-0.16206604	H	-2.31844360	-3.83920770	1.42949724
H	-4.67713328	-3.12773747	-0.10823776	H	-1.42416833	-4.86099873	0.29501884
C	-0.43941794	-2.47629619	3.43181254	C	-2.05365032	-3.44380418	-2.02938803
H	-1.23954560	-3.07817319	3.85194889	H	-1.81202924	-2.63340989	-2.72177243
C	2.04816126	-3.37852020	-2.30229563	H	-3.04896329	-3.82776371	-2.28114775
H	3.03882414	-3.83114028	-2.42481277	H	-1.32539441	-4.24853757	-2.18379401
H	1.91070770	-2.63223293	-3.08966103				

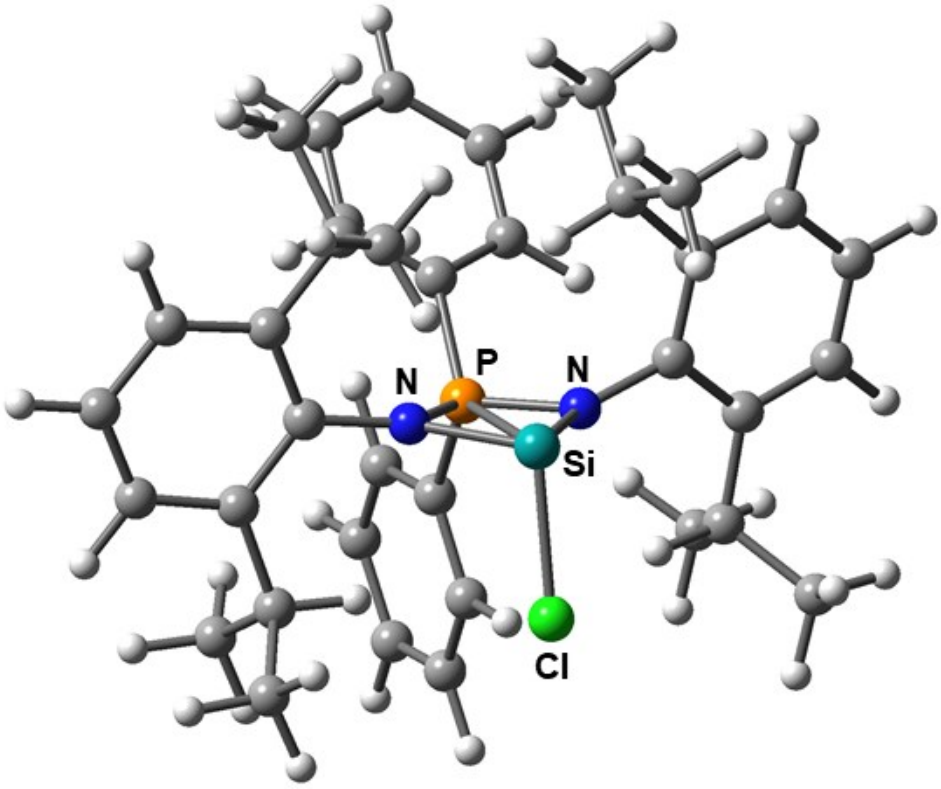

Figure S19. Optimized geometry of **5**.

Atomic Coordinates for **8** at B3LYP-D3/6-31+G(d,p) level of theory.

Si	0.16563215	0.72768955	-1.58399487	H	-1.24391121	4.92916621	1.34978215
P	-0.20505564	-0.72200017	0.68659261	H	0.41271623	4.34123108	1.55167320
Si	2.31302190	2.84813332	-1.51345205	C	-0.13139687	-0.76546052	3.54455113
Si	-0.49709207	3.68862201	-0.66840189	H	-0.56369920	-1.75946813	3.51136024
N	0.66011677	2.40420383	-1.04670708	C	0.96482703	1.80394964	3.66089767
N	-1.23798912	0.17451106	-0.22804919	H	1.38415742	2.80482067	3.69960719
C	-2.48476961	-1.03478952	-2.67174720	C	3.57222723	-0.10819751	1.31109348
H	-1.42611396	-1.00871365	-2.41688469	H	2.75162073	0.59326810	1.15732977
N	1.09769698	-0.48810560	-0.28540790	C	0.71380174	1.09580554	4.84176968
C	-2.67003578	0.09375420	-0.33031488	H	0.94381607	1.54420982	5.80392785
C	-3.51202930	0.58908649	0.70345489	C	3.18580671	3.60830267	-0.01521026
C	2.18760553	-1.40970114	-0.44114975	H	2.71131866	4.55349640	0.27279292
C	-5.49084125	-0.04796944	-0.57031753	H	4.23926559	3.81811723	-0.23551578
H	-6.57170954	-0.10263030	-0.66274195	H	3.14875876	2.93840836	0.84934571
C	-2.98353626	1.22804305	1.97842991	C	4.42604629	-2.16139808	0.15154687
H	-1.90751175	1.34962177	1.86932632	H	5.33118297	-2.04170280	0.73904970
C	-0.64501845	-2.46877604	0.95291580	C	0.34190289	-3.33040713	1.46636667
C	0.12284973	-0.06182111	2.36004551	H	1.33702802	-2.95624411	1.68334550
C	0.67790309	1.22652010	2.42731757	C	-4.66788423	-0.50860215	-1.59125530
H	0.87620922	1.77017046	1.50881331	H	-5.11914764	-0.92299099	-2.48757186
C	3.38031644	-1.24407233	0.31512854	C	0.16828082	-0.18812861	4.78148274
C	4.89029772	0.66034406	1.09561809	H	-0.03020241	-0.74131318	5.69468212
H	5.76286804	0.03567677	1.31405917	C	2.08938276	-2.48943440	-1.36252273
H	4.93251975	1.52521767	1.76656111	C	-3.27059876	-0.46528293	-1.49676326
H	4.98300337	1.02330061	0.06969719	C	3.50596589	-0.62986911	2.75956655
C	-2.20862788	3.31867631	-1.37555408	H	4.33762190	-1.31563499	2.95850639
H	-2.14021100	3.16727553	-2.45943114	H	2.57367885	-1.16452533	2.95481368
H	-2.85587692	4.18795196	-1.20547459	H	3.56784502	0.19909914	3.47212899
H	-2.70651471	2.44863050	-0.94882590	C	-3.24647628	0.32185539	3.19700062
C	-0.58438582	4.06842706	1.18550780	H	-4.32202238	0.23767130	3.38977812
H	-0.95106431	3.24676387	1.79876833	H	-2.76738645	0.72949901	4.09317811

H	-2.85990006	-0.68857059	3.03678974	H	-2.02314092	-0.54950596	-4.74235307
C	4.33751367	-3.21267756	-0.75506006	H	-2.33887347	0.86806515	-3.73164193
H	5.16496022	-3.90602750	-0.87689234	C	-1.92329482	-2.97121316	0.66930347
C	-1.22525902	-5.17305358	1.40142847	H	-2.69478767	-2.31907430	0.27986182
H	-1.45001397	-6.22191030	1.57144317	C	0.85913955	-2.74179583	-2.22482769
C	3.28860494	1.36356748	-2.16634495	H	0.05392919	-2.10946232	-1.85258061
H	3.33321710	0.48970783	-1.51950519	C	1.11945217	-2.33950540	-3.68935304
H	4.31873763	1.70411771	-2.33437442	H	1.40972232	-1.28830181	-3.76056520
H	2.89315754	1.04258284	-3.13650581	H	0.21397215	-2.48208001	-4.29026096
C	0.05063778	-4.67630630	1.68684473	H	1.91739927	-2.95246517	-4.12463536
H	0.82196851	-5.33557260	2.07309414	C	3.17755088	-3.36006913	-1.50773492
C	-0.05908141	5.37738342	-1.41552131	H	3.10984922	-4.17448087	-2.22220816
H	0.88296820	5.79462042	-1.04678524	C	-2.85362404	-2.50025838	-2.96989178
H	-0.85924888	6.06363000	-1.11001753	H	-2.70192363	-3.13646847	-2.09291677
H	-0.02967816	5.36737684	-2.50844525	H	-2.22358883	-2.88484374	-3.77895531
C	0.36283586	-4.19772451	-2.14215790	H	-3.89631548	-2.60491785	-3.28845647
H	1.08497172	-4.89916399	-2.57335352	C	-3.57723114	2.62986720	2.21961371
H	-0.57038961	-4.30505046	-2.70231698	H	-4.65068346	2.58320349	2.43063575
H	0.17617237	-4.49770032	-1.10844889	H	-3.43072797	3.27721096	1.35148739
C	-4.90290395	0.48909776	0.56797242	H	-3.09107505	3.10004932	3.08138549
H	-5.53693571	0.85473499	1.36975890	C	2.44016514	4.06542301	-2.96552488
C	-2.20830693	-4.32043281	0.89410460	H	1.69227777	3.83606625	-3.73310755
H	-3.20026388	-4.70093363	0.66986592	H	3.42970698	3.94578676	-3.42403286
C	-2.64785687	-0.16219426	-3.92980521	H	2.33045536	5.11498854	-2.68593010
H	-3.68869479	-0.14824969	-4.27339541				

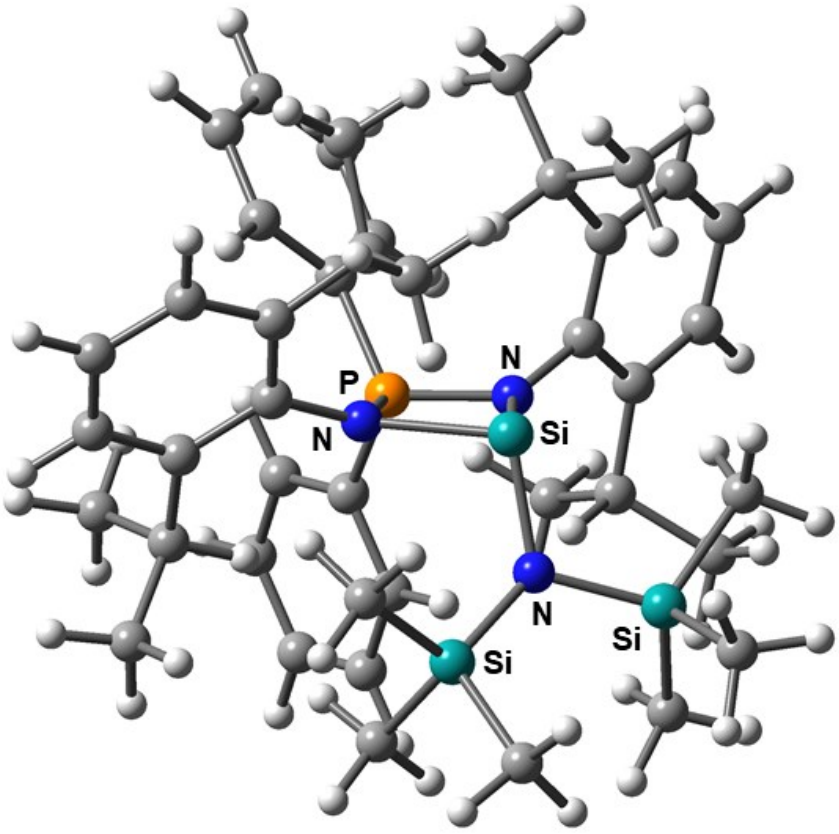

Figure S20. Optimized geometry of **8**.

Atomic Coordinates for **9** at B3LYP-D3/6-31+G(d,p) level of theory.

P	-2.18389727	0.85486926	-0.76402567	H	-6.00277351	-2.49263908	-3.42980683
Si	0.74085415	0.45549592	-0.12890346	C	-3.72179376	-0.02899501	-2.87022091
Si	1.66734770	2.82028741	1.33048114	H	-3.24452455	0.80415343	-3.37931166
Si	0.61268648	3.17088072	-1.58829356	C	-3.02027559	-0.86835019	3.23516378
N	-0.87639955	-0.16699510	-0.11970971	H	-3.76139708	-0.71455039	2.44811308
N	1.93502409	-0.55914029	0.00131723	H	-3.12250583	-0.04711198	3.95215154
N	0.83484468	2.17096977	-0.12091757	H	-3.26231614	-1.80230604	3.75461218
C	3.22036440	-1.03081673	0.11121984	C	-0.57291763	-1.15646116	3.79307928
C	-1.07295577	-1.56898768	0.22231952	H	-0.74309409	-2.12610446	4.27350553
C	4.29910547	-0.47675375	-0.64841848	H	-0.65854386	-0.38081694	4.56237129
C	-0.91684397	-2.56460262	-0.77360051	H	0.44961959	-1.14749241	3.41519101
C	3.48262297	-2.13173256	0.97924178	C	-1.69483871	-3.26798796	1.83170044
C	-1.44723077	-1.91952368	1.54162363	H	-1.98446225	-3.54793208	2.84014275
C	-3.37907948	-0.31244363	-1.53768202	C	2.36422756	-2.79833327	1.76729197
C	-3.12861305	1.49131457	0.69504254	H	1.44888133	-2.23441138	1.57626939
C	5.58151714	-1.01530737	-0.50406364	C	-4.93905370	-2.17814180	-1.57786116
H	6.40260306	-0.59985806	-1.07941926	H	-5.40405522	-3.01912097	-1.07181929
C	-0.45077739	-2.26999622	-2.19560230	C	-1.42044811	-2.81890989	-3.25997535
H	-0.40706975	-1.18505934	-2.32555351	H	-1.41974254	-3.91436851	-3.27136090
C	-1.17206982	-3.89708896	-0.42711881	H	-1.11052998	-2.48145039	-4.25539801
H	-1.05080549	-4.67166612	-1.17783053	H	-2.44459382	-2.48503218	-3.08835043
C	-4.00530451	-1.39728903	-0.89676978	C	-4.66667460	-0.80379666	-3.54959717
H	-3.76349737	-1.63806376	0.13156951	H	-4.91891401	-0.56926561	-4.57952334
C	-1.58965359	-0.90241879	2.66630778	C	1.02766866	4.56100684	1.68897720
H	-1.37969016	0.08163368	2.24989377	H	1.30618925	5.28831058	0.92073715
C	4.78648920	-2.62477972	1.09114407	H	1.46102585	4.90352308	2.63629038
H	4.97921237	-3.46297037	1.75596292	H	-0.06245111	4.57874636	1.79162271
C	5.83951730	-2.07672776	0.36340934	C	0.96628822	-2.83362090	-2.42462928
H	6.84602491	-2.47299224	0.46304850	H	1.66978480	-2.44589022	-1.68621597
C	4.04597092	0.62509446	-1.66932595	H	1.32472949	-2.56865725	-3.42584226
H	3.22424153	1.24018275	-1.29058782	H	0.96163901	-3.92721259	-2.35203915
C	-4.51822093	1.37047040	0.85188191	C	-1.56954571	-4.25307131	0.85763066
H	-5.09508855	0.76162882	0.16443915	H	-1.76343926	-5.29369843	1.10190862
C	-2.42630819	2.31809092	1.59153241	C	-0.84298385	4.35006960	-1.39192786
H	-1.36100385	2.46333561	1.45404880	H	-1.75553494	3.81651899	-1.11527956
C	-5.27407560	-1.88245368	-2.90395318	H	-1.02596211	4.87364743	-2.33834709

H	-0.64273330	5.10687721	-0.62728331	H	2.69747449	-0.60228364	-2.87752582
C	-5.17706390	2.02502014	1.89808699	C	5.24426143	1.56038738	-1.89772993
H	-6.25213627	1.91185582	2.00665617	H	5.62160015	1.96880079	-0.95537142
C	1.26619733	1.72887848	2.81713600	H	4.95150155	2.39701956	-2.54214697
H	0.19409347	1.62993202	3.00938684	H	6.07166392	1.04820557	-2.40069232
H	1.72051792	2.18134127	3.70726603	C	0.38149143	2.04884787	-3.08862877
H	1.69059473	0.72545004	2.71343412	H	1.17288291	1.29697699	-3.16376986
C	2.16347311	4.20080640	-1.91436791	H	0.43322028	2.66318357	-3.99602404
H	2.40274156	4.89615546	-1.10424038	H	-0.58534105	1.54033489	-3.08326008
H	2.00116303	4.79816147	-2.81996945	C	-4.46113980	2.80974441	2.80369781
H	3.03735324	3.56545520	-2.08494313	H	-4.97424727	3.31055539	3.61945465
C	3.53673967	2.82861191	1.12730563	C	2.63562569	-2.78049752	3.28302910
H	3.91036730	1.80512339	1.01697200	H	3.52620044	-3.36593038	3.53787992
H	4.00562933	3.26474571	2.01781402	H	1.78843198	-3.20844574	3.83068669
H	3.86352874	3.40380555	0.25723573	H	2.79759906	-1.75931957	3.64586173
C	-3.07849517	2.95616794	2.64465357	C	2.11834784	-4.23837229	1.27729360
H	-2.51080120	3.57603353	3.33331706	H	1.88855219	-4.25076327	0.20810880
C	3.59307500	0.00988663	-3.00941964	H	1.27040135	-4.68376056	1.80882616
H	4.38168676	-0.63457195	-3.41420638	H	2.99933881	-4.86933867	1.44447893
H	3.37877950	0.78958730	-3.75081809				

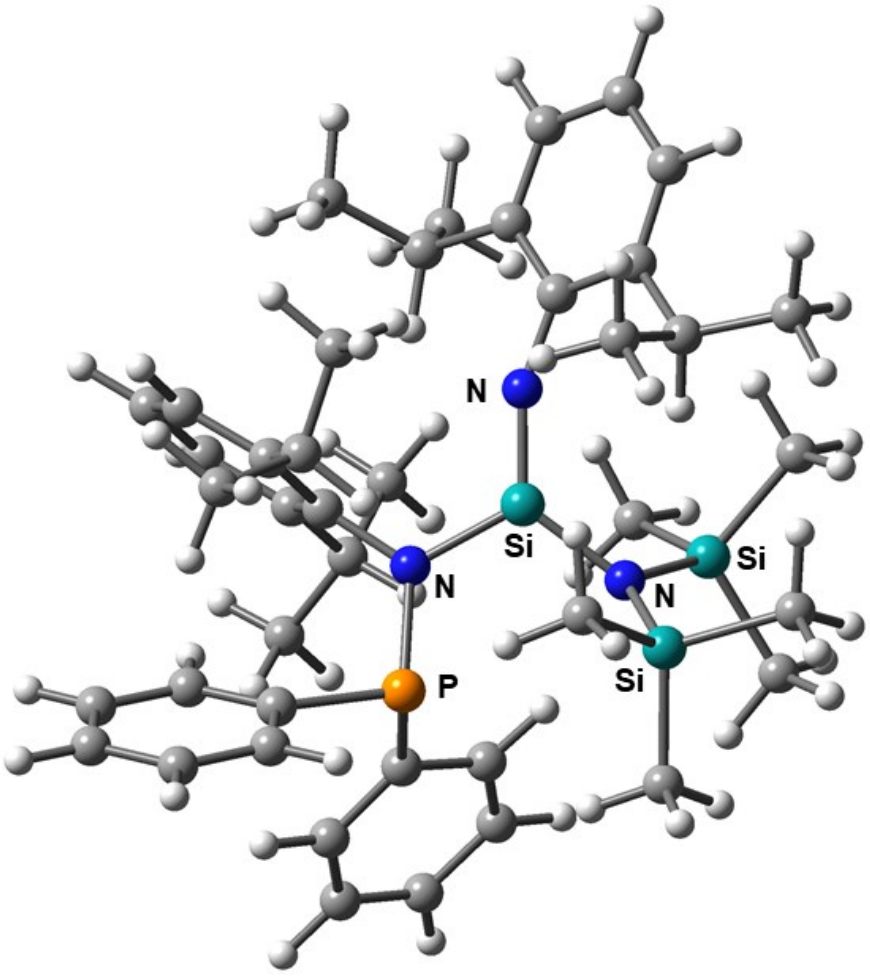

Figure S21. Optimized geometry of **9**.

Atomic Coordinates for **10** at B3LYP-D3/Def2-svp for Fe, 6-31+G(d,p) for the others level of theory.

P	-0.86906700	-0.64714100	0.52264300	C	-2.46624300	2.63569500	0.44302200
Si	0.79377400	0.62726900	-1.16359600	C	-2.13158400	0.54512500	-2.81863600
N	0.58752900	-1.02680800	-0.13589800	H	-1.33591000	-0.07118600	-2.39569000
N	-0.83656800	0.87765200	-0.11718800	C	-4.24290300	3.21829300	-1.11470600
C	-2.32137000	-1.60859800	-0.01151000	H	-5.11974100	3.81091100	-1.36041000
C	1.32416100	-2.24927100	-0.21087200	C	1.99742100	-2.43617200	3.39183100
C	2.40596800	-1.75437500	2.07516700	H	2.60064400	-3.33109400	3.58177200
H	1.80232100	-0.85664000	1.95872100	H	0.94536000	-2.73319100	3.37654100
C	2.16642400	-2.63893700	0.86044100	H	2.14053500	-1.74968100	4.23230800
C	-2.61969500	1.50602900	-1.73717300	C	3.87613900	-1.29627900	2.13090100
C	-0.99239600	-0.79792300	2.34599600	H	4.16882100	-0.82805900	1.18772500
C	1.26534300	-3.04297400	-1.39390300	H	4.55274900	-2.13828600	2.31460900
C	-0.29278900	0.08921700	3.17663500	H	4.01272700	-0.56392200	2.93358700
H	0.30501500	0.87930000	2.74969800	C	-1.80195700	-1.95760300	4.32455000
C	-0.35390700	-0.03764700	4.56224900	H	-2.38759300	-2.75893700	4.76516400
H	0.19408100	0.66283400	5.18510800	C	-3.32368300	-3.65110000	-0.84576700
C	-2.18763300	-2.90559500	-0.52014300	H	-3.21119600	-4.65490000	-1.24437400
H	-1.20379000	-3.34044300	-0.64248600	C	-2.71076400	2.30896400	2.92789200
C	-1.11105800	-1.05948200	5.14126400	H	-2.94426200	1.25065600	2.77769500
H	-1.15886900	-1.15829500	6.22180500	H	-3.65635400	2.86145800	2.97182900
C	-1.98005300	1.67285800	-0.47646900	H	-2.21415800	2.40426500	3.89942900
C	-1.74570400	-1.82952700	2.93518200	C	-0.28604700	-3.74331200	-3.32481900
H	-2.29238200	-2.53442000	2.31968600	H	-0.92737800	-4.28014500	-2.62108700
C	-1.81594200	2.86007700	1.79975300	H	0.37388700	-4.47759200	-3.79926200
H	-0.87752100	2.30508900	1.79737800	H	-0.92514200	-3.32555000	-4.11004800
C	-3.60388500	-1.07096600	0.19892500	C	-4.59638400	-3.10912500	-0.65175500
H	-3.72303400	-0.07331800	0.60851100	H	-5.47873000	-3.68924600	-0.90549800
C	0.51234800	-2.60974400	-2.65032600	C	-3.74249500	2.29316400	-2.02586200
H	-0.19539600	-1.82734800	-2.36801800	H	-4.23508200	2.17694700	-2.98665700
C	1.98881500	-4.24179100	-1.43276600	C	-4.73451400	-1.82001000	-0.12582400
H	1.94820500	-4.85503700	-2.32731400	H	-5.72156500	-1.39444000	0.02720800
C	2.85918600	-3.85388700	0.77186900	C	1.49110200	-2.00027000	-3.67622800
H	3.49455500	-4.16126600	1.59732700	H	2.22469800	-2.74901200	-3.99780800
C	2.76634800	-4.66187900	-0.35627200	H	2.02618200	-1.14686300	-3.25338300
H	3.31150800	-5.60018100	-0.40703300	H	0.94630300	-1.64697200	-4.55944900

C	-3.60125700	3.38449800	0.10873200	C	4.01362700	0.77917100	-1.42697600
H	-3.98369700	4.11333200	0.81713100	H	3.91670600	-0.29694600	-1.46883300
C	-1.47084100	4.33817900	2.05960800	C	3.53856800	1.70920800	-2.38953300
H	-2.37211000	4.95375000	2.15916300	C	4.65266000	1.52565600	-0.38521400
H	-0.86428600	4.74915100	1.24974500	H	2.97173500	1.47147600	-3.27812300
H	-0.90699300	4.42857400	2.99521600	C	3.86822700	3.02109000	-1.93467700
C	-3.22207200	-0.41114600	-3.33474100	H	5.11055100	1.11064800	0.50126800
H	-4.01993100	0.12456100	-3.86042700	C	4.58489100	2.90945200	-0.70989600
H	-3.67534400	-0.98160500	-2.52221400	H	3.61264200	3.94399200	-2.43734200
H	-2.78206000	-1.12138300	-4.04417400	H	4.95755500	3.72569200	-0.10800100
C	-1.50230100	1.32444700	-3.99010100	C	1.33316100	3.31348300	-0.58268200
H	-0.68391500	1.96039800	-3.64121500	C	2.33051700	1.84076200	1.22166300
H	-2.24764300	1.95843500	-4.48396100	O	0.54058300	4.15917900	-0.68491400
H	-1.09507400	0.62907600	-4.73336500	O	2.25648300	1.74286100	2.38353800
Fe	2.58491200	2.10200000	-0.46661900				

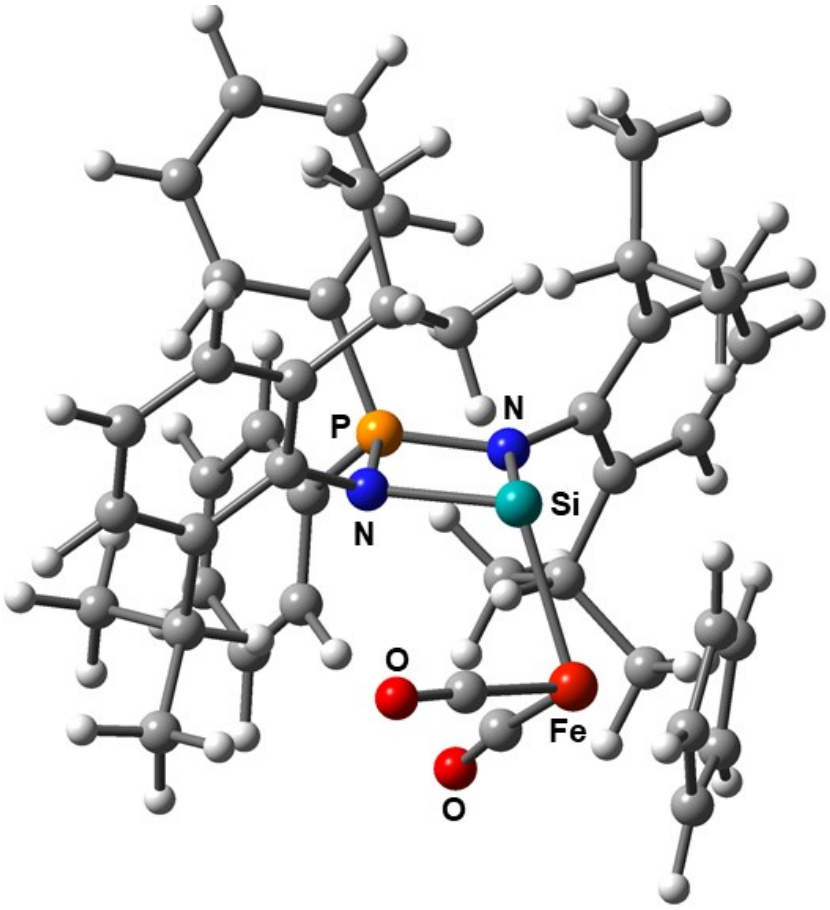

Figure S22. Optimized geometry of **10**.

Atomic Coordinates for **12** at B3LYP-D3/6-31+G(d,p) level of theory.

P	1.39808400	-0.01491300	-0.00632200	H	-3.55875200	-2.65099000	1.68671700
Si	-1.02474600	-1.04701700	-0.17269200	H	-5.28806100	-2.57895700	1.29976600
Si	-2.80294000	1.61930200	0.40037900	C	1.59811200	-0.30975100	3.27271500
Si	-3.95075300	-1.13058700	-0.25087700	H	2.55852200	-0.33694600	2.74695300
N	0.29437200	-0.40950700	1.14759800	H	1.74067500	-0.79565600	4.24382700
N	0.25239400	0.01312500	-1.17657000	H	1.33210400	0.73498100	3.45355500
C	2.66195500	-1.32423500	-0.25030200	C	4.83068700	-2.32904400	0.19053800
N	-2.53652400	-0.06549500	-0.04708000	H	5.82563200	-2.25833800	0.62036200
C	-3.97169100	1.75414000	1.89149900	C	-1.01226200	-0.05062000	-3.26100500
H	-4.97428100	1.35480400	1.71419400	H	-1.09158600	-1.14138700	-3.21950300
H	-4.07985500	2.80699700	2.18123500	H	-1.02543200	0.25724100	-4.31170300
H	-3.54581000	1.21471800	2.74586400	H	-1.88746200	0.37301000	-2.76246500
C	2.39971000	1.50986900	0.21351200	C	2.26314600	-2.50526500	-0.89864300
C	3.44822600	1.78518700	-0.68326300	H	1.25350000	-2.58698500	-1.29073300
H	3.70967300	1.06871000	-1.45503000	C	0.49752100	-1.03783800	2.48137300
C	-3.71774300	-2.45919400	-1.58138400	C	-5.48792000	-0.18353200	-0.83782800
H	-4.69363000	-2.92054000	-1.78468900	H	-5.33343900	0.23463900	-1.83847600
H	-3.01689100	-3.24098000	-1.28107000	H	-5.81834800	0.62225800	-0.17815400
H	-3.35316000	-2.02159800	-2.51732700	H	-6.30828200	-0.90885800	-0.90804700
C	0.29011000	0.43179500	-2.59604500	C	3.86431500	3.90051500	0.41410000
C	4.17099600	2.97384600	-0.58779400	H	4.42778400	4.82583400	0.49070800
H	4.97454500	3.17345000	-1.29060800	C	2.83377500	3.62962300	1.31681800
C	0.35420200	1.97068000	-2.68623000	H	2.59142800	4.34210500	2.09974000
H	-0.49877400	2.41486600	-2.16741400	C	-1.22882200	2.49275300	0.94335200
H	0.32929000	2.29541400	-3.73280400	H	-0.82017300	2.01903900	1.83789100
H	1.26856500	2.36078500	-2.23175200	H	-1.46561300	3.53833900	1.17525600
C	1.48202900	-0.18605000	-3.35289000	H	-0.45931300	2.47953400	0.17048400
H	2.44019000	0.10836700	-2.91469500	C	3.14297800	-3.58098500	-1.00860800
H	1.47925800	0.14605500	-4.39674900	H	2.82167600	-4.48861400	-1.51103600
H	1.42954800	-1.27779200	-3.33878800	C	0.85891200	-2.53628600	2.37917600
C	3.95089200	-1.24887200	0.29975900	H	0.12930000	-3.06229300	1.75750100
H	4.27373400	-0.35180900	0.81803800	H	0.86211900	-2.99038300	3.37677800
C	4.42966400	-3.49524700	-0.46586500	H	1.84915300	-2.68089500	1.93974900
H	5.11378300	-4.33460700	-0.55087600	C	2.10305600	2.44377500	1.21464100
C	-4.37246700	-1.98106600	1.38625500	H	1.29835300	2.25091800	1.90955100
H	-4.51749000	-1.24681000	2.18631500	C	-0.83966100	-0.89039000	3.23193800

H	-1.12345100	0.16330000	3.31123400	H	-2.88182900	2.51880200	-1.93549000
H	-0.75804500	-1.30851700	4.24100200	H	-3.49045900	3.70598900	-0.77222800
H	-1.64328200	-1.41618800	2.70837600	H	-4.52509100	2.37085600	-1.29943500
C	-3.49891400	2.64139300	-1.03818000				

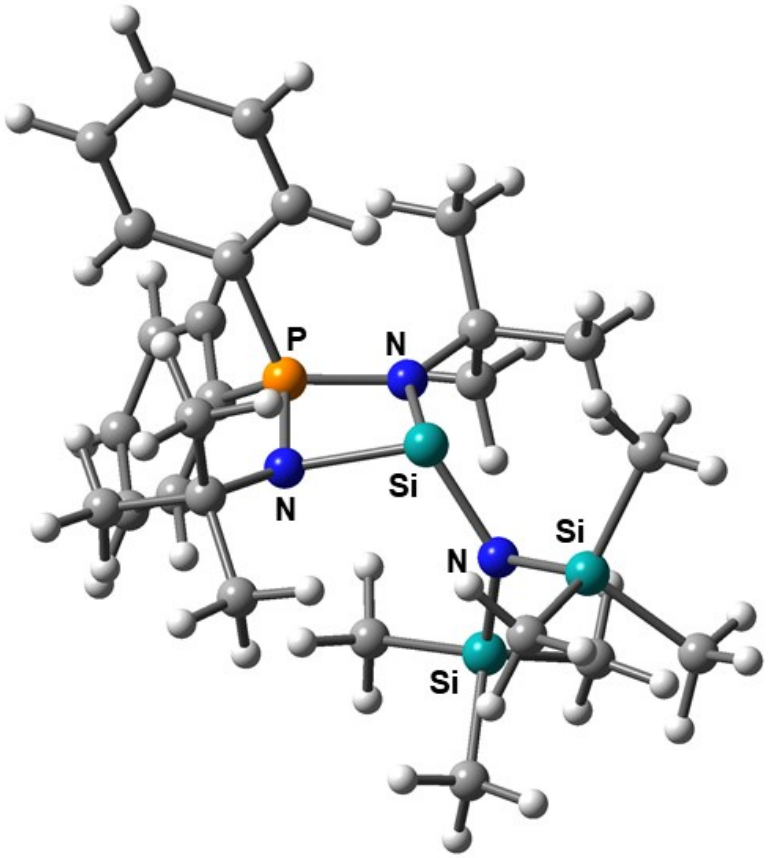

Figure S23. Optimized geometry of **12**.

Atomic Coordinates for **13** at B3LYP-D3/6-31+G(d,p) level of theory.

P	-1.24557700	0.29612300	0.00899900	H	1.70230700	-3.65216500	-2.15644600
Si	1.14470000	-0.69179400	0.10534000	H	2.73403800	-4.66876200	-1.13937900
Si	3.78286000	1.20166800	-0.22730100	C	-1.21449300	0.56137600	-3.23504700
Si	1.54210000	-2.99982500	0.29000500	H	-2.23143400	0.58518100	-2.83060800
N	-0.19794700	-0.27077900	-1.12279300	H	-1.29494200	0.36744800	-4.30948100
N	-0.24549600	-0.15431500	1.23644900	H	-0.76480700	1.54749700	-3.09489200
C	-2.86214300	-0.53729200	0.03716600	C	-5.14616900	-0.82176500	-0.73212400
N	2.47603900	0.20565300	0.10185600	H	-5.99770800	-0.45563900	-1.29788300
C	5.00800200	0.39857000	-1.44148200	C	0.73769000	-0.62979300	3.40275300
H	5.40579300	-0.53570800	-1.02673000	H	0.32655000	-1.64344100	3.35506600
H	5.85602500	1.05616800	-1.67184400	H	0.80588000	-0.33137800	4.45390700
H	4.50387200	0.15325300	-2.38474500	H	1.74880400	-0.64085200	2.98567700
C	-1.52445700	2.08946100	-0.10956400	C	-2.94919500	-1.76111200	0.71920400
C	-2.65222700	2.73753800	0.41646300	H	-2.08909400	-2.12307000	1.27093800
H	-3.46855600	2.16365800	0.84350500	C	-0.36475400	-0.53613400	-2.56941600
C	-0.01725000	-4.04464900	0.61965700	C	2.76601200	-3.29005900	1.71210000
H	0.23202200	-5.11304300	0.62937300	H	2.32330000	-3.06228600	2.68704100
H	-0.78912900	-3.88621700	-0.14136600	H	3.64541900	-2.64968900	1.58540600
H	-0.44979600	-3.79716100	1.59633500	H	3.09763000	-4.33574400	1.72536300
C	-0.15587300	0.35568300	2.63080000	C	-1.66829100	4.88439400	-0.11882900
C	-2.72326500	4.13263000	0.40700700	H	-1.72479800	5.96903400	-0.12138200
H	-3.59783900	4.63023300	0.81546400	C	-0.53639200	4.24137800	-0.63163700
C	0.48250400	1.75932900	2.67260400	H	0.29440700	4.81905400	-1.02519200
H	1.43268500	1.74801700	2.13254000	C	3.24841100	2.85946700	-1.01558600
H	0.66405500	2.06055800	3.71055500	H	2.70299300	2.68826300	-1.95327700
H	-0.16966600	2.50697500	2.21347500	H	4.10741000	3.50335400	-1.24410500
C	-1.55312400	0.38604700	3.27281300	H	2.58707800	3.41104200	-0.33557400
H	-2.22249000	1.07435400	2.74547100	C	-4.12617200	-2.50768200	0.67532200
H	-1.48027200	0.73135900	4.30930800	H	-4.18236300	-3.45442800	1.20407000
H	-2.01072200	-0.60781900	3.27041900	C	-1.03715200	-1.90749400	-2.77666200
C	-3.96848300	-0.07260900	-0.69215700	H	-0.44561800	-2.69623800	-2.30501200
H	-3.91637000	0.86790600	-1.23105700	H	-1.13068100	-2.13805000	-3.84387700
C	-5.22661900	-2.03917800	-0.04964700	H	-2.03697700	-1.92028600	-2.33179100
H	-6.14309600	-2.62084500	-0.08393600	C	-0.46162600	2.84994000	-0.62559400
C	2.37805100	-3.64270100	-1.29480100	H	0.42905600	2.34879500	-0.99058900
H	3.24275200	-3.02016200	-1.55021200	C	1.03756300	-0.52996200	-3.20374100

H	1.52784800	0.43479500	-3.04717200	H	4.07682800	2.14599300	2.07657100
H	0.96058700	-0.72014700	-4.27936400	H	5.58356500	2.30819300	1.15250100
H	1.67785400	-1.30080500	-2.76797100	H	5.12224200	0.73742300	1.84075300
C	4.73538600	1.64277100	1.35772100				

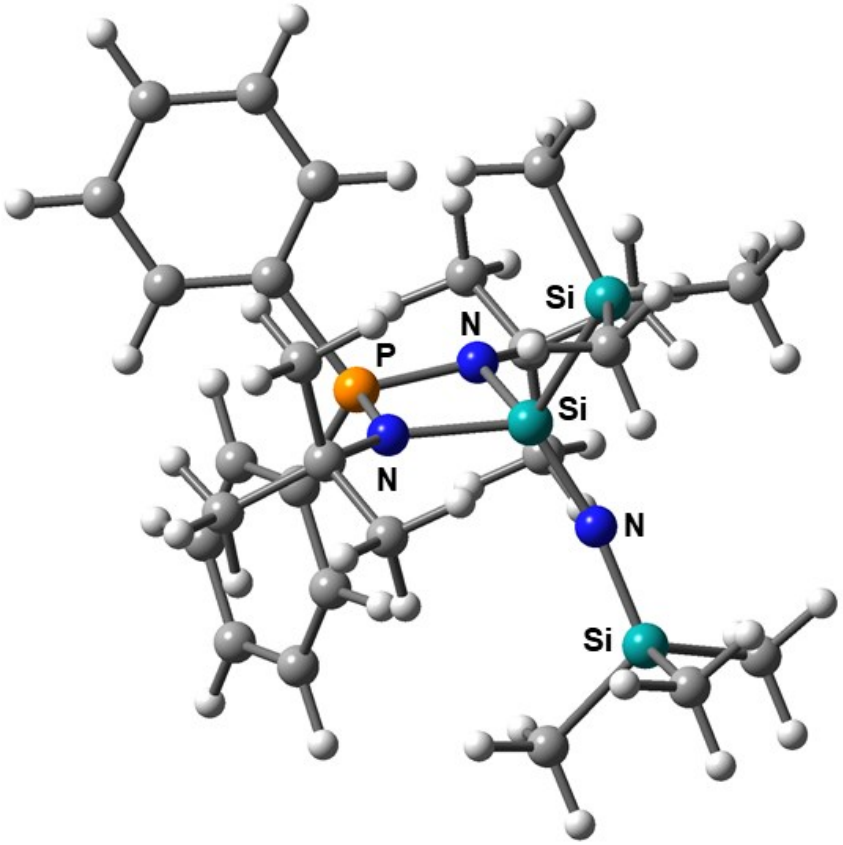

Figure S24. Optimized geometry of **13**.

Atomic Coordinates for **14** at B3LYP-D3/6-31+G(d,p) level of theory.

P	1.45410088	0.06359643	0.42737668	H	-2.32743305	0.81485803	-2.81100541
Si	-1.12851360	-0.63798058	-0.31459141	C	-3.50939678	1.47483057	2.75006663
Si	-2.36864979	2.10743739	-0.64572899	H	-3.74023326	2.51443181	2.49529698
Si	-1.78184837	0.95866719	2.18237378	H	-3.55942559	1.38939407	3.84248408
N	0.50970782	-0.50674104	-0.92115387	H	-4.28858031	0.83492855	2.32371713
N	-1.85906416	-2.03222837	-0.53996028	C	-4.25423422	2.19951973	-0.58617755
N	-1.72082290	0.82379938	0.40077040	H	-4.70562664	1.24692793	-0.88189125
C	2.76835457	-1.18791468	0.78568841	H	-4.59407297	2.96434859	-1.29587748
C	2.35239720	1.56555586	-0.13788441	H	-4.64447658	2.46302885	0.39968423
C	4.11818573	-1.09538894	0.41223109	C	2.40734786	3.57555256	-1.51211849
H	4.46756579	-0.24546374	-0.16501773	H	2.01161260	4.14630002	-2.34774617
C	3.39272420	2.10268864	0.64282049	C	-1.39039831	-0.70569028	2.98363185
H	3.77489134	1.54906474	1.49634450	H	-2.05378188	-1.50748762	2.64829270
C	1.85652796	2.33002881	-1.20465242	H	-1.51625168	-0.59496460	4.06800225
H	1.03273058	1.94198963	-1.79150821	H	-0.35662337	-1.01414186	2.80334416
C	4.60091002	-3.20386092	1.50628406	C	3.45801830	4.08804088	-0.74634304
H	5.30787943	-3.98157306	1.78022356	H	3.88718142	5.05706031	-0.98352113
C	2.35809992	-2.29832133	1.54564618	C	-3.13215388	-2.69557652	-0.38264312
H	1.31834325	-2.38799664	1.84851901	C	-3.60267058	-3.15793957	-1.78050343
C	5.02703598	-2.09402879	0.77181082	H	-2.83797263	-3.78923353	-2.24407818
H	6.06713167	-2.00660104	0.47014070	H	-4.53816894	-3.72682517	-1.71722558
C	3.26058097	-3.30403779	1.89192981	H	-3.76800580	-2.29058005	-2.42954941
H	2.91901249	-4.16033733	2.46623653	C	-4.23122459	-1.81075142	0.24513326
C	-1.65713428	3.78470246	-0.15561020	H	-4.40752087	-0.92452749	-0.37182616
H	-2.06512415	4.14173635	0.79558020	H	-5.17724198	-2.35771698	0.33672198
H	-1.91348744	4.52762484	-0.92067413	H	-3.93749163	-1.47280483	1.24367728
H	-0.56647602	3.74563824	-0.06837142	C	-2.91508577	-3.93861751	0.50957677
C	-0.55606714	2.23611955	2.83605769	H	-2.14706094	-4.58403616	0.07197784
H	0.45952106	2.02116953	2.49339368	H	-2.57570759	-3.63622689	1.50610380
H	-0.55966483	2.20905561	3.93303954	H	-3.84126179	-4.51595668	0.61864795
H	-0.81057009	3.25435433	2.52873118	C	0.99960721	-1.29746598	-2.13075089
C	3.94556982	3.34738970	0.33512222	C	-0.04991884	-1.18880628	-3.25191705
H	4.75548327	3.74001458	0.94359951	H	-1.00982172	-1.60726454	-2.94128308
C	-1.93131278	1.77012218	-2.45085666	H	-0.18923341	-0.14999998	-3.56012120
H	-0.85632297	1.78784722	-2.64196739	H	0.29707467	-1.75388835	-4.12334737
H	-2.39029600	2.56062674	-3.05709235	C	1.19849805	-2.78307976	-1.77050899

H	0.27884447	-3.18752521	-1.34107411	H	2.64271594	-1.30595354	-3.51993898
H	1.44601799	-3.34976858	-2.67559283	H	2.19129744	0.32421852	-2.99680433
H	2.01519283	-2.91660875	-1.05974109	H	3.11353195	-0.73871524	-1.92266112
C	2.31537471	-0.70805661	-2.66317199				

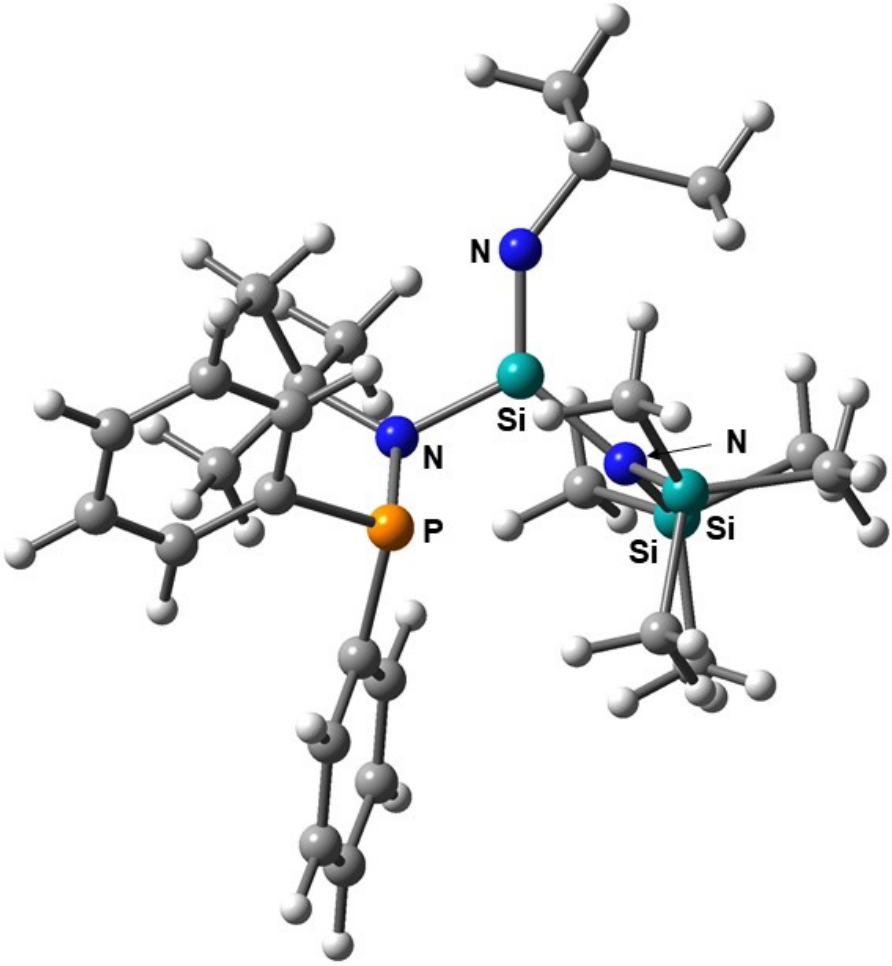

Figure S25. Optimized geometry of **14**.

Atomic Coordinates for **15** at B3LYP/6-31+G(d,p) level of theory.

Si	-0.87750056	-0.14564594	-1.12855739	H	-3.32911767	0.15350760	3.71888040
P	0.71063721	0.23525632	0.89506672	C	-1.79231026	3.14838150	0.96687426
Si	-0.70902097	-0.86803271	-3.36074972	H	-1.89428470	2.06819512	0.87087508
Si	-4.10193197	-0.33175188	-0.72811478	C	-1.57637810	0.58154022	4.91084970
N	-2.42886071	-0.14010365	-0.67913552	H	-2.12473225	0.65459348	5.84566787
N	0.28954971	-1.10065657	0.01675928	C	-2.11398844	-0.04300044	-4.33053542
C	2.69592472	-2.05761841	-1.47352057	H	-3.07839494	-0.18437566	-3.83696085
H	2.11729920	-1.14859035	-1.65605471	H	-2.17426783	-0.47305870	-5.33837406
N	0.13256222	1.22550835	-0.30162058	H	-1.94404644	1.03469694	-4.43524878
C	0.75327752	-2.44268459	0.21162617	C	-0.19063639	4.92616586	0.19669515
C	0.01905108	-3.33763095	1.02778514	H	-0.80688805	5.63645839	0.73966342
C	0.30796052	2.64358333	-0.44392445	C	3.17727248	1.54545858	1.23016066
C	1.82144988	-4.96339658	0.83320537	H	2.72568847	2.40609506	0.75120080
H	2.24814128	-5.92767638	1.09471626	C	2.49355317	-4.11208415	-0.04007325
C	-1.37975998	-3.01505339	1.53016759	H	3.43729842	-4.43245133	-0.47133616
H	-1.62595566	-2.00725388	1.19876651	C	-0.19361374	0.77559903	4.89463206
C	2.45505662	0.35371116	1.37442690	H	0.33816625	1.00443017	5.81334403
C	-0.16015957	0.38214892	2.49709612	C	1.35310008	3.11518234	-1.28441555
C	-1.55503108	0.20355278	2.52088840	C	1.97291875	-2.85911687	-0.39080190
H	-2.08656992	0.00334063	1.59391670	C	-1.77123498	3.52442940	2.45859064
C	-0.51983598	3.56335499	0.24389987	H	-1.72779752	4.61104616	2.59340002
C	-3.02322972	3.76204873	0.27112713	H	-0.91261938	3.08448824	2.97292002
H	-3.02559053	4.85556897	0.34543541	H	-2.67847940	3.16237785	2.95212346
H	-3.94086858	3.39037365	0.73990236	C	-1.47868030	-3.06899553	3.06448739
H	-3.04942833	3.48989230	-0.78738615	H	-1.29986839	-4.08242267	3.44122605
C	-4.80627960	-0.40106379	1.04315010	H	-2.47836714	-2.76284738	3.38983616
H	-4.35391307	-1.22177508	1.61409899	H	-0.75447422	-2.39739881	3.53497618
H	-5.89293012	-0.55048114	1.04365280	C	0.89343959	5.38864616	-0.54150583
H	-4.59678633	0.53473187	1.57640045	H	1.13663728	6.44736564	-0.55599838
C	-4.99873939	1.09041339	-1.61536305	C	5.06792343	0.53547389	2.35965722
H	-4.88957070	2.03470964	-1.07338276	H	6.08424950	0.60503685	2.73598608
H	-6.07145659	0.87787663	-1.70883955	C	0.86318512	-0.65705947	-4.41577010
H	-4.59592335	1.23901607	-2.62403331	H	0.71953008	0.16725778	-5.11969116
C	0.51453720	0.67838374	3.69398857	H	1.03639642	-1.56853737	-4.99827043
H	1.58623106	0.83829956	3.70097846	H	1.76769422	-0.45278775	-3.84104054
C	-2.25338977	0.29997939	3.72050123	C	4.48522471	1.62931492	1.71552850

H	5.04271603	2.55298895	1.59302787
C	-4.66335705	-1.92668751	-1.60286884
H	-4.38492323	-1.91508177	-2.66348241
H	-5.75375402	-2.03975426	-1.54966635
H	-4.21093344	-2.81415883	-1.14850395
C	3.63274378	2.30784650	-2.18664290
H	3.98688482	3.31452745	-2.43410511
H	4.08130452	1.61644334	-2.90859850
H	4.01478024	2.04621020	-1.19780640
C	0.57862414	-4.58537753	1.33312191
H	0.02683982	-5.27106138	1.96928378
C	4.33977586	-0.64701022	2.52746957
H	4.78658050	-1.49922624	3.03010942
C	2.73885267	-2.87748456	-2.78266334
H	3.34625845	-3.77940462	-2.65595481
H	3.18586301	-2.28818077	-3.58889400
H	1.74183993	-3.18745813	-3.10128106
C	3.03593340	-0.74025471	2.04281055
H	2.48073010	-1.66258488	2.17678858
C	2.09812041	2.20763227	-2.25902621
H	1.82480725	1.17423502	-2.03306847
C	1.61967337	2.53328223	-3.69055904
H	0.54228705	2.37096638	-3.79445316
H	2.13454163	1.90743367	-4.42456430
H	1.82526093	3.58074455	-3.93599688
C	1.63603206	4.48640020	-1.29991922
H	2.44098669	4.85601307	-1.92822411
C	4.13166620	-1.63563996	-1.10708957
H	4.16217269	-0.97241841	-0.24420846
H	4.58846524	-1.10841990	-1.95216187
H	4.75524741	-2.50897044	-0.88494631
C	-2.41180705	-3.95573826	0.87820106
H	-2.25573664	-4.99698552	1.18299431
H	-2.34688811	-3.90769332	-0.21257004
H	-3.42629115	-3.66419689	1.17092437
C	-1.10453906	-2.72056339	-3.16982037
H	-0.41009922	-3.22371419	-2.48930653
H	-1.05919387	-3.22714027	-4.14210525
H	-2.11267291	-2.84528439	-2.76334784

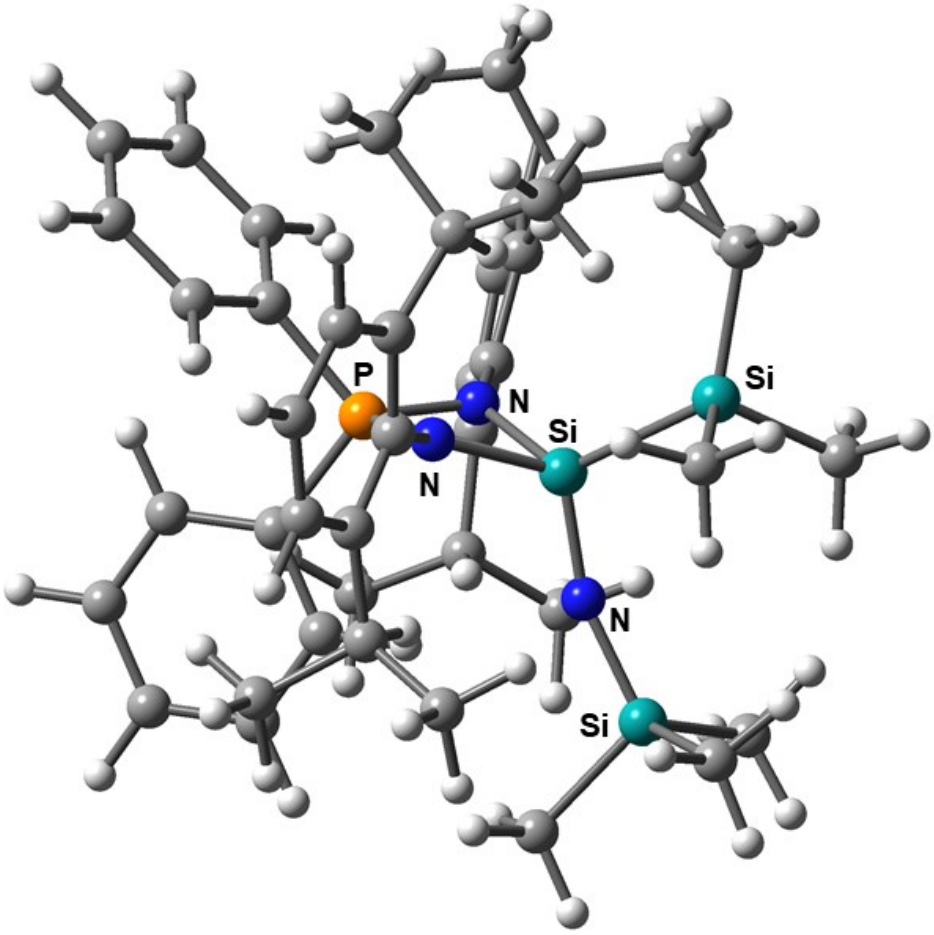

Figure S26. Optimized geometry of **15**.

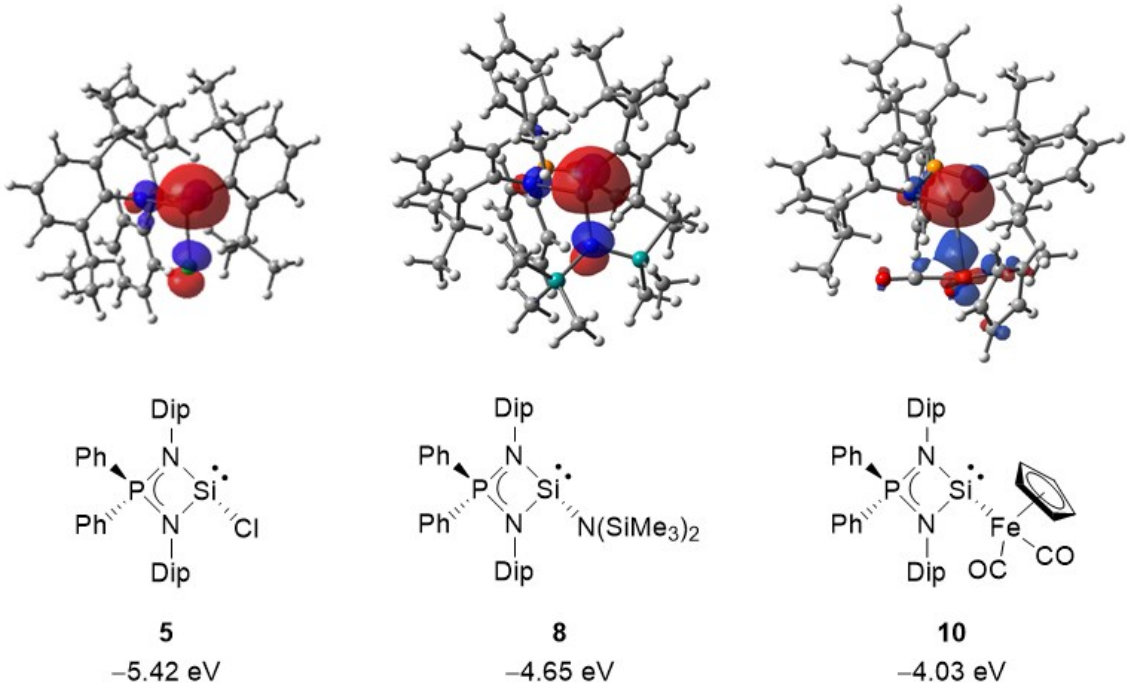

Figure S27. HOMO diagrams for **5**, **8**, and **10** (isosurface level = ±0.05 e/(a.u.)^3).

Table S3. Total energies and Gibbs energies (in a.u.) of calculated structures at B3LYP-D3/6-31+G(d,p).

Compounds	E (a.u.)	E+ZPE (a.u.)	G (a.u.)
8	-3012.37956887	-3011.429328	-3011.547668
10	-3012.40765927	-3011.459169	-2391.812908
12	-2392.93008860	-2392.257265	-2392.328080
13	-2392.93699916	-2392.265303	-2392.339126
14	-2392.93408149	-2392.262759	-2392.336928
15	-3012.37136819	-3011.421919	-3011.510635

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