Supplementary Information

ortho-Phenylene-bridged phosphorus/silicon Lewis pairs

Lucas Wickemeyer, Jan Schwabedissen, Pia C. Trapp, Beate Neumann, Hans-Georg Stammler and Norbert W. Mitzel*

* Lehrstuhl für Anorganische Chemie und Strukturchemie; Centrum für Molekulare Materialien CM$_2$, Fakultät für Chemie, Universität Bielefeld, Universitätsstraße 25, 33615 Bielefeld, Germany. E-mail: mitzel@uni-bielefeld.de

Table of contents

1) General information

All operations with air- and moisture-sensitive compounds were performed under conventional Schlenk techniques or in a glove box. Diethyl ether and *n*-pentane were dried over $LiAlH_4$. C_6D_6 was dried over Na/K alloy, distilled, degassed and stored over Na/K alloy. 2-(Lithiophenyl)di-*iso*-propylphosphine was prepared according to literature procedures.[1] Antimony trifluoride (Alfa Aesar, 98 %) was used as received. Tetrachlorosilane, trichloromethylsilane, dichlorodimethylsilane and chlorotrimethylsilane (abcr) were distilled and stored over Mg turnings. NMR spectra were recorded using *Bruker Avance III 300* and *Avance III 500 HD* spectrometer at ambient temperature. Chemical shifts were referenced to the residual proton or carbon signal of the solvent (C_6D_6: ^1H: 7.16 ppm, ^{13}C: 128.1 ppm) or externally (^{19}F: Cl_3CF, ^{29}Si: $SiMe_4$, ^{31}P: 85 % H_3PO_4 in H_2O). Elemental analyses were carried out by co-workers of the University of Bielefeld using an EURO EA Element Analyser.

2) Crystallographic data

Crystals suitable for X-ray diffraction of **2**, **3** and **4** were grown by slowly evaporating a saturated solution of the respective compound in *n*-hexane. The crystals were selected, coated with Paratone-N oil, mounted on a glass fibre and transferred onto the goniometer of the diffractometer into a nitrogen gas cold stream solidifying the oil. Data collection was performed on a Rigaku SuperNova diffractometer. Crystals of **5** and **6** were grown by *in situ* methods. At room temperature, a thin capillary was filled with **5**. At 222 K the supercooled melt was treated with ultrasound, at 267 K polycrystalline material was growing in the capillary. At 287.4 K all material except a small seed crystal was melted manually. After slow cooling to 284 K with 1 K/h the entire capillary was filled with a single crystal, which was cooled to 157 K with 12 K/h for data collection. For **6**, a capillary was filled with the liquid. At 160 K the supercooled melt was treated with ultrasonic, while raising the temperature to 220 K polycrystalline material was growing in the capillary. At 253.5 K all material except a small seed crystal was melted manually. After slow cooling to 237 K with 1 K/h a single crystal had grown, which was cooled to 100 K with 30 K/h for data collection. Using Olex2[2] the structures were solved with the ShelXS[3] (**2**) or ShelXT[4] (**3–6**) structure solution programs using Direct Methods (**2**) or Intrinsic Phasing (**3–6**) and refined with the ShelXL[5] refinement package using Least Squares minimization. Hydrogen atoms were refined isotropically (**2, 6**) or were taken into account using a riding model (**3**, **4**, **5**).

Details of the X-ray investigation are given in Table S1 and S2. CCDC 2218772-2218776 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/conts/retrieving.html.
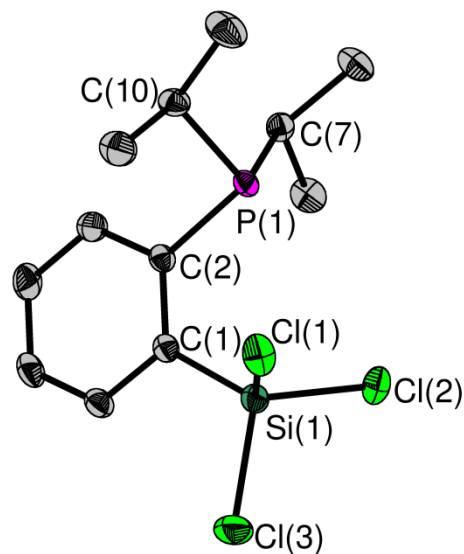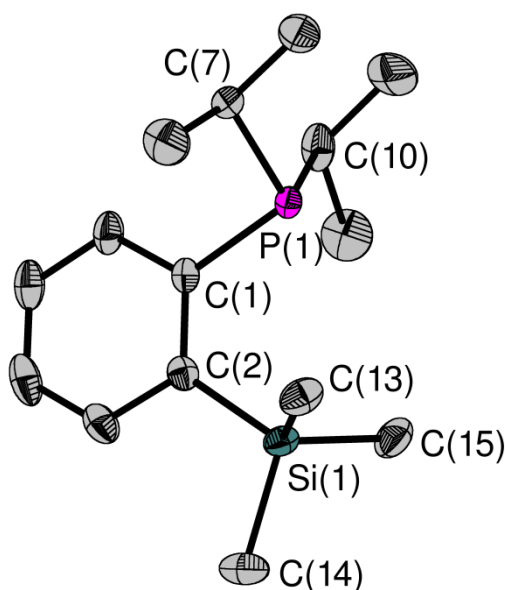
Figure S1. Molecular structure of **2** in the solid state. Ellipsoids are set at 50 % probability. Hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: Si(1)···P(1) 3.348(1), P(1)–C(2) 1.845(1), P(1)–C(7) 1.863(1), P(1)–C(10) 1.861(2), Si(1)–C(1) 1.854(2), Si(1)–Cl(1) 2.030(1), Si(1)–Cl(2) 2.030(1), Si(1)–Cl(3) 2.036(1); C(2)–P(1)–C(7) 100.6(1), C(2)–P(1)–C(10) 99.3(1), C(10)–P(1)–C(7) 104.0(1), P(1)–C(2)–C(1) 120.5(1), Cl(1)–Si(1)–Cl(3) 105.6(1), Cl(2)–Si(1)–Cl(1) 107.9(1), Cl(2)–Si(1)–Cl(3) 105.6(1), C(1)–Si(1)–Cl(1) 113.1(1), C(1)–Si(1)–Cl(2) 115.1(1), C(1)–Si(1)–Cl(3) 108.9(1), C(2)–C(1)–Si(1) 123.0(1).
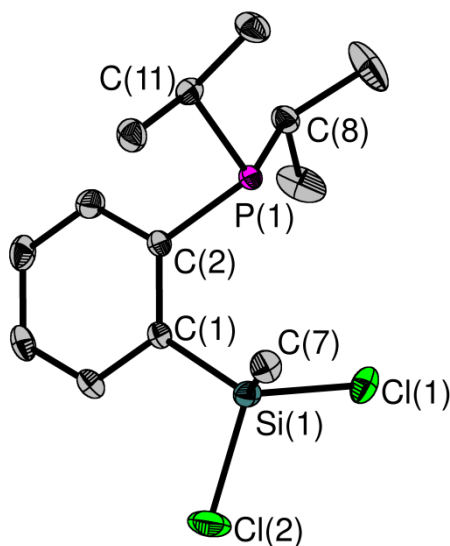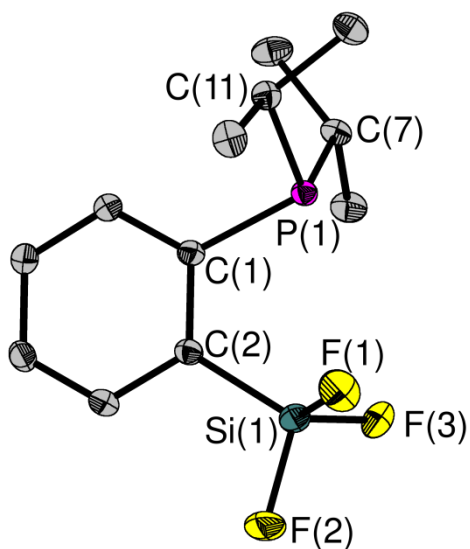

Figure S2: Molecular structure of **3** in the solid state. Ellipsoids are set at 50 % probability. Hydrogen atoms were omitted for clarity. The structure shows a disorder of Cl(2) over two sites (61:39). Only one position in shown here. Selected bond lengths [Å] and angles [°]: Si(1)···P(1) 3.338(1), P(1)–C(2) 1.844(1), P(1)–C(8) 1.868(1), P(1)–C(11) 1.866(1), Si(1)–C(1) 1.867(1), Si(1)–Cl(1) 2.061(1), Si(1)–Cl(2) 2.062(1), Si(1)–C(7) 1.853(1); C(2)–P(1)–C(8) 100.3(1), C(2)–P(1)–C(11) 100.7(1), C(11)–P(1)–C(8) 103.3(1), P(1)–C(2)–C(1) 119.9(1), Cl(1)–Si(1)–Cl(2) 102.3(1),Cl(2)–Si(1)–C(7) 107.4(1), C(7)–Si(1)–Cl(1) 109.0(1), C(1)–Si(1)–Cl(1) 110.2(1), C(1)–Si(1)–Cl(2) 107.9(1), C(1)–Si(1)–C(7) 118.9(1), C(2)–C(1)–Si(1) 122.7(1).
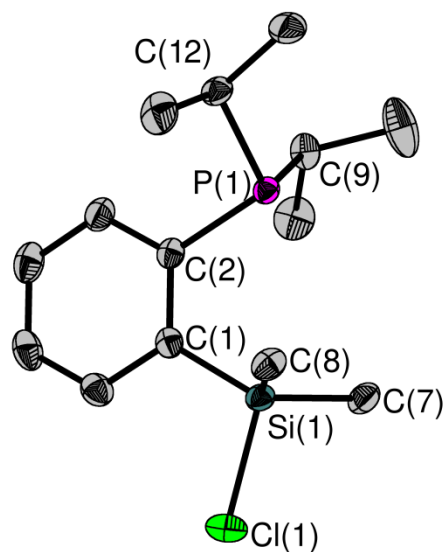
Figure S3: Molecular structure of **4** in the solid state. Ellipsoids are set at 50 % probability. Hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: Si(1)···P(1) 3.295(1), P(1)–C(2) 1.841(2), P(1)–C(9) 1.874(2), P(1)–C(12) 1.860(2), Si(1)–C(1) 1.884(2), Si(1)–Cl(1) 2.096(1), Si(1)–C(7) 1.852(2), Si(1)–C(8) 1.852(2); C(2)–P(1)–C(9) 102.2(1), C(2)–P(1)–C(12) 101.6(1), C(12)–P(1)–C(9) 101.9(1), P(1)–C(2)–C(1) 119.5(1), Cl(1)–Si(1)–C(7) 103.9(1), C(8)–Si(1)–C(7) 114.3(1), C(8)–Si(1)–Cl(1) 103.4(1), C(1)–Si(1)–Cl(1) 105.9(1), C(1)–Si(1)–C(7) 114.9(1), C(1)–Si(1)–C(8) 112.8(1), C(2)–C(1)–Si(1) 121.2(2).

Figure S4: Molecular structure of **5** in the solid state. Ellipsoids are set at 30 % probability. Hydrogen atoms were omitted for clarity. The structure shows a disorder of C(11) and C(12) at two positions with a ratio of 60:40. Only one position is shown here. Selected bond lengths [Å] and angles [°]:Si(1)···P(1) 3.431(1), P(1)–C(1) 1.843(1), P(1)–C(7) 1.866(2), P(1)–C(10) 1.869(2), Si(1)–C(2) 1.896(2), Si(1)–C(13) 1.862(2), Si(1)–C(14) 1.878(2), Si(1)–C(15) 1.859(2); C(1)–P(1)–C(7) 100.2(1), C(1)–P(1)–C(10) 100.5(1), C(10)–P(1)–C(7) 102.0(1), P(1)–C(1)–C(2) 120.9(1), C(13)–Si(1)–C(14) 106.9(1),C(14)–Si(1)–C(15) 107.5(1), C(13)–Si(1)–C(15) 110.4(1), C(2)–Si(1)–C(13) 111.7(1), C(2)–Si(1)–C(14) 108.1(1), C(2)–Si(1)–C(15) 112.0(1), C(1)–C(2)–Si(1) 124.5(1).

Figure S5: Molecular structure of **6** in the solid state. Ellipsoids are set at 50 % probability. Hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]:Si(1)···P(1) 3.197(1), P(1)–C(1) 1.836(1), P(1)–C(7) 1.865(1), P(1)–C(11) 1.855(1), Si(1)–C(2) 1.835(1), Si(1)–F(1) 1.570(1), Si(1)–F(2) 1.579(1), Si(1)–F(3) 1.574(1); C(1)–P(1)–C(7) 105.0(1), C(1)–P(1)–C(11) 101.7(1), C(11)–P(1)–C(7) 104.6(1), P(1)–C(1)–C(2) 116.1(1), P(1)-C(1)-C(6) 124.8(1), F(1)–Si(1)–F(2) 104.1(1),F(2)–Si(1)–F(3) 104.8(1), F(3)–Si(1)–F(1) 107.5(1), C(2)–Si(1)–F(1) 116.9(1), C(2)–Si(1)–F(2) 107.7(1), C(2)–Si(1)–F(3) 114.7(1), C(1)–C(2)–Si(1) 122.0(1), Si(1)-C(2)-C(3) 118.4(1).

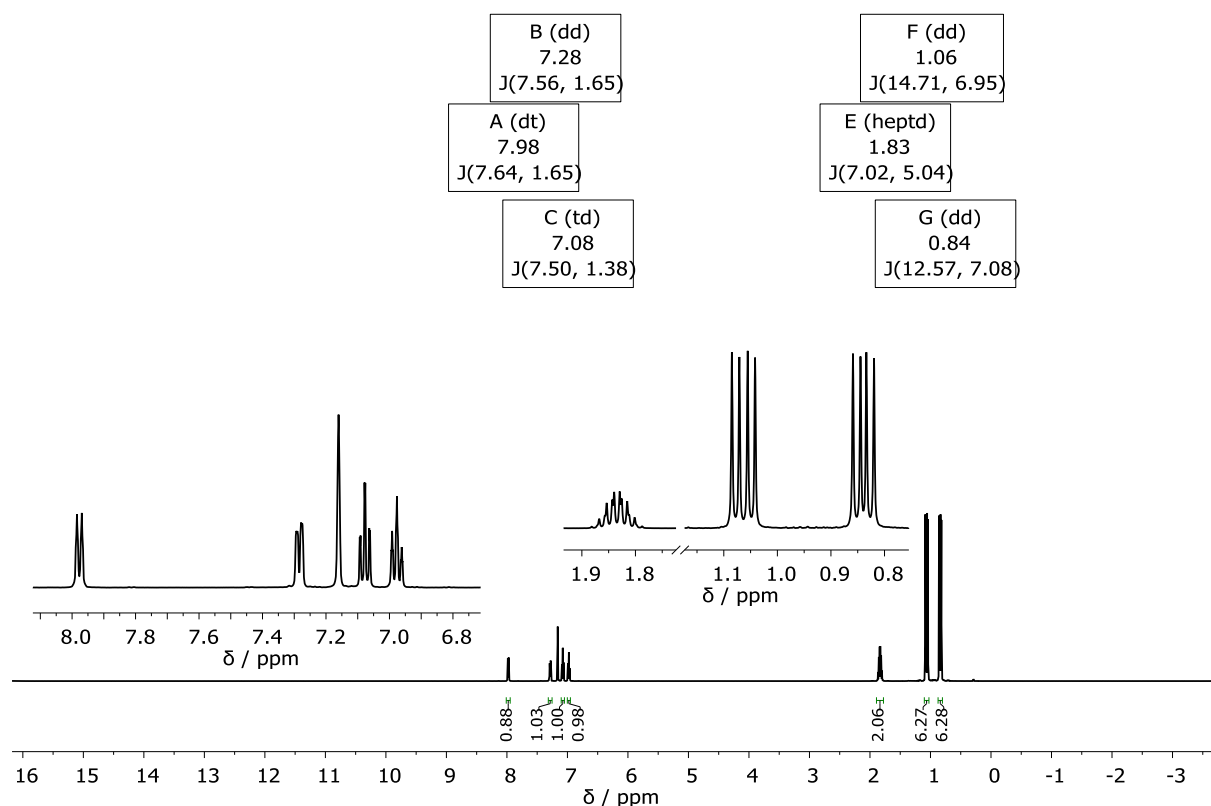**Table S1:** Crystallographic data for compounds **2–4**.

Compound	2	3	4
Empirical formula	$C_{12}H_{18}Cl_3PSi$	$C_{13}H_{21}Cl_2PSi$	$C_{14}H_{24}ClPSi$
M_r	327.67	307.26	286.84
T [K]	100.0(1)	100.0(1)	100.0(1)
Radiation	Mo Kα	Mo Kα	Mo Kα
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_1/n$	$P2_12_12_1$
a [Å]	8.2705(2)	8.2622(1)	8.7929(3)
b [Å]	13.2991(2)	13.2613(2)	9.6522(4)
c [Å]	14.4551(3)	14.6945(2)	19.1617(6)
β [°]	93.316(2)	93.677(1)	90
Volume [Å³]	1587.27(6)	1606.73(4)	1626.3(1)
Z	4	4	4
ρ_{calc} [g/cm³]	1.371	1.270	1.172
μ [mm⁻¹]	0.732	0.557	0.387
$F(000)$	680	648	616
2Θ range [°]	4.2 – 64.3	4.1 – 64.5	6.3 – 59.3
Index ranges	$-12 \leq h \leq 12$ $-18 \leq k \leq 19$ $-21 \leq l \leq 20$	$-12 \leq h \leq 12$ $-19 \leq k \leq 19$ $-21 \leq l \leq 21$	$-11 \leq h \leq 11$ $-12 \leq k \leq 12$ $-24 \leq l \leq 26$
Refl. collected	26209	57203	19157
Independent refl.	5245	5437	4044
R_{int}	0.0458	0.0324	0.0431
Refl. with $I>2\sigma(I)$	4134	4925	3783
Data / restraints / parameters	5245 / 0 / 226	5437 / 0 / 169	4044 / 0 / 160
Goodness-of-Fit on F^2	1.065	1.065	1.058
R_1/wR_2 [$I > 2\sigma(I)$]	0.0375 /0.0808	0.0275 / 0.0686	0.0316 / 0.0718
R_1/wR_2 (all data)	0.0522 / 0.0895	0.0319 / 0.0710	0.0360 / 0.0749
ρ_{fin} (max/min) [e Å⁻³]	0.43 / −0.51	0.45 / −0.25	0.27 / −0.32
Flack parameter	-	-	-0.01(3)
CCDC	2218772	2218773	2218774

Table S2: Crystallographic data for compounds **5** and **6**.

Compound	5	6
Empirical formula	$C_{15}H_{27}PSi$	$C_{12}H_{18}F_3PSi$
M_r	266.42	278.32
T [K]	157.0(1)	100.0(1)
Radiation	Mo Kα	Mo Kα
Crystal system	orthorhombic	triclinic
Space group	$P2_12_12_1$	$P\bar{1}$
a [Å]	8.6606(2)	8.4767(1)
b [Å]	10.2287(2)	12.7939(3)
c [Å]	19.1829(3)	13.9557(3)
α [°]	90	109.201(2)
β [°]	90	95.359(1)
γ [°]	90	99.483(1)
Volume [Å^3]	1699.3(1)	1392.0(1)
Z	4	4
ρ_{calc} [g/cm^3]	1.041	1.328
μ [mm^{-1}]	0.214	0.294
$F(000)$	584	584
2Θ range [°]	5.8 – 66.3	4.9 – 73.7
Index ranges	$-13 \le h \le 13$ $-15 \le k \le 15$ $-29 \le l \le 29$	$-14 \le h \le 14$ $-20 \le k \le 21$ $-23 \le l \le 23$
Refl. collected	50646	45533
Independent refl.	6480	13318
R_{int}	0.0332	0.0238
Refl. with $I > 2\sigma(I)$	5894	11340
Data / restraints / parameters	6480 / 0 / 182	13318 / 0 / 451
Goodness-of-Fit on F^2	1.065	1.021
R_1/wR_2 [$I > 2\sigma(I)$]	0.0315 / 0.0803	0.0315 / 0.0796
R_1/wR_2 (all data)	0.0363 / 0.0834	0.0397 / 0.0844
ρ_{fin} (max/min) [e Å^{-3}]	0.24 / −0.18	0.56 / −0.31
Flack parameter	0.012(18)	-
CCDC	2218775	2218776

3) NMR spectra

B (dd)
7.28
J(7.56, 1.65)

A (dt)
7.98
J(7.64, 1.65)

C (td)
7.08
J(7.50, 1.38)

F (dd)
1.06
J(14.71, 6.95)

E (heptd)
1.83
J(7.02, 5.04)

G (dd)
0.84
J(12.57, 7.08)

Figure S6: ^{1}H NMR spectrum of a solution of ^{i}Pr$_2$P(o-C$_6$H$_4$)SiCl$_3$ (**2**) in C$_6$D$_6$ (500 MHz, 293K).

D (d)
133.24
J(2.12)

B (d)
140.64
J(45.01)

A (d)
145.77
J(18.20)

F (m)
129.13

C (d)
135.93
J(14.97)

E (s)
132.15

H (m)
20.53

G (d)
26.61
J(13.17)
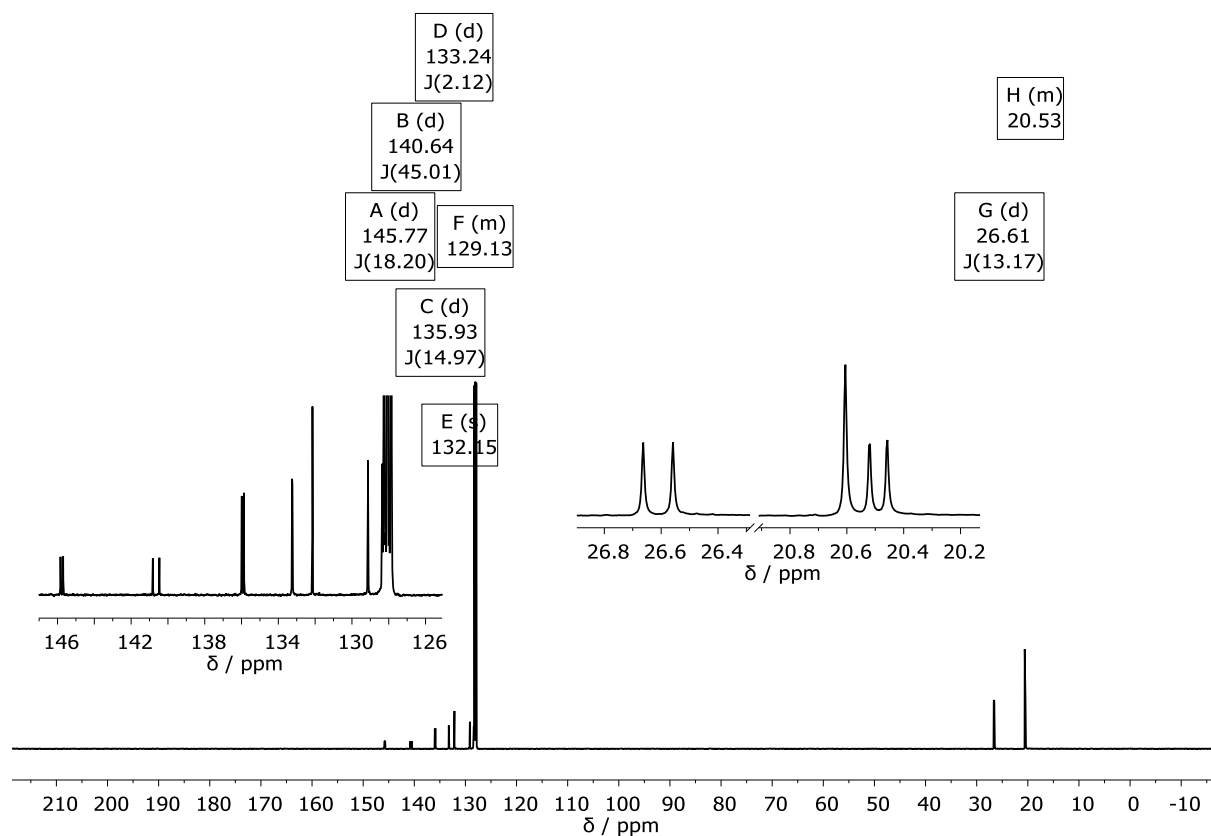
Figure S7: ^{13}C{^{1}H} NMR spectrum of a solution of ^{i}Pr$_2$P(o-C$_6$H$_4$)SiCl$_3$ (**2**) in C$_6$D$_6$ (126 MHz, 293K).
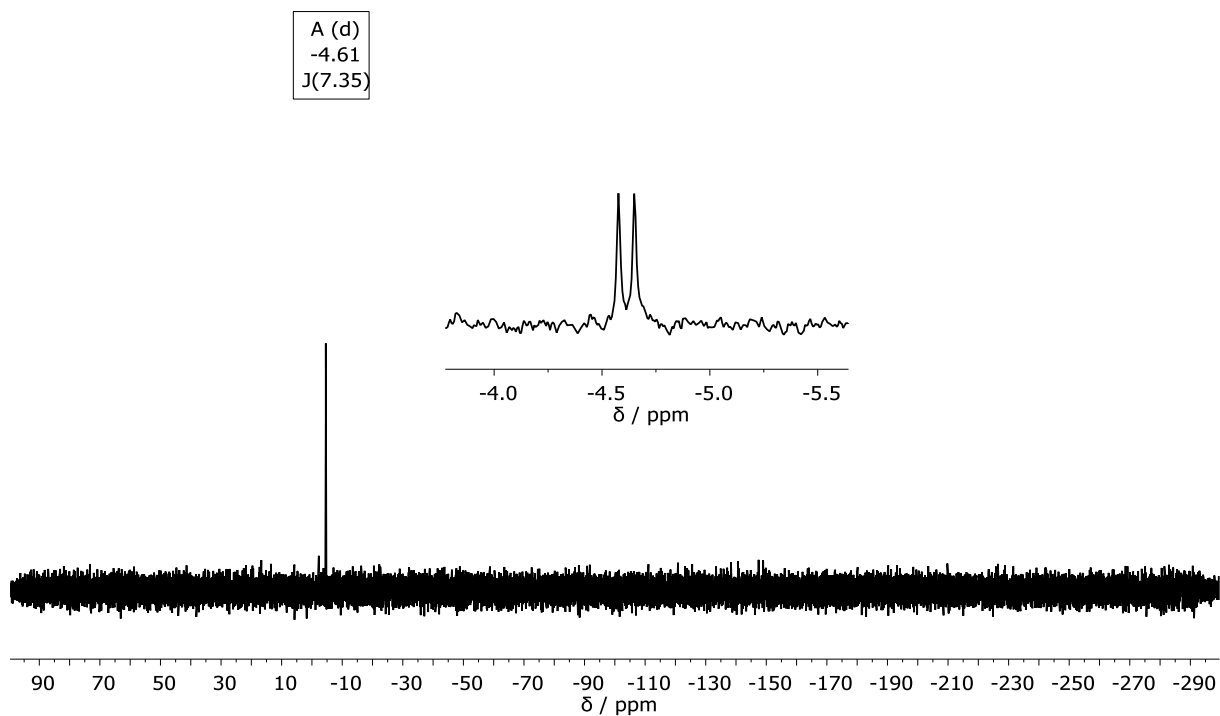
Figure S8: $^{29}Si\{^1H\}$ NMR spectrum of a solution of $^iPr_2P(o\text{-}C_6H_4)SiCl_3$ (**2**) in C_6D_6 (99 MHz, 293K).
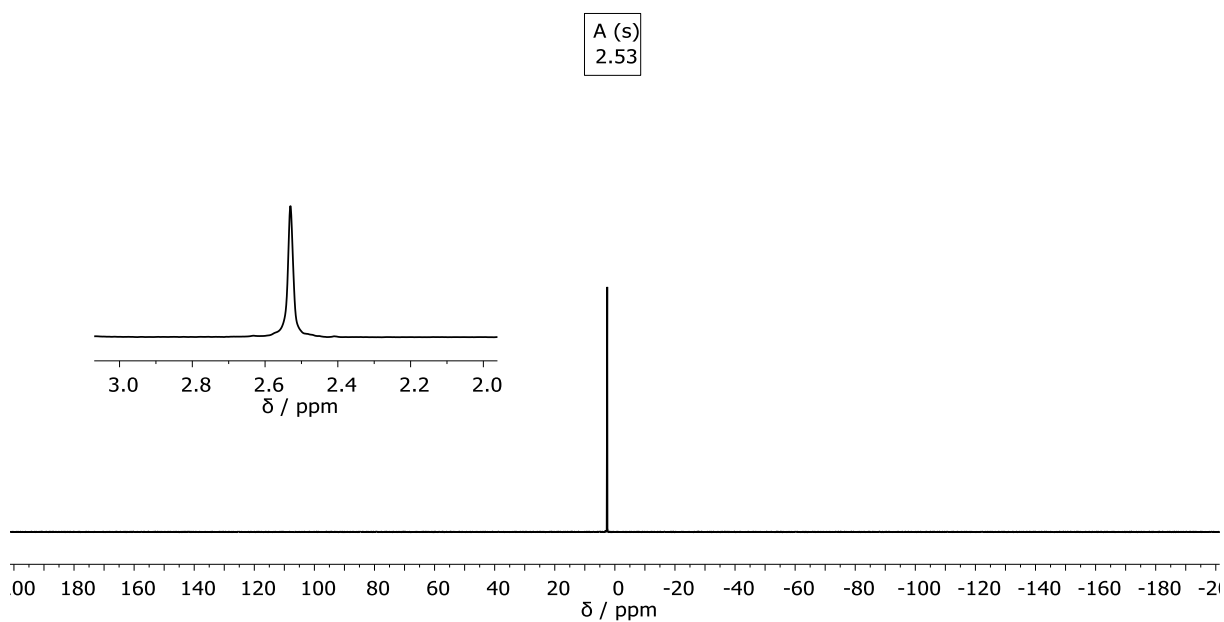
Figure S9: $^{31}P\{^1H\}$ NMR spectrum of a solution of $^iPr_2P(o\text{-}C_6H_4)SiCl_3$ (**2**) in C_6D_6 (202 MHz, 293K).
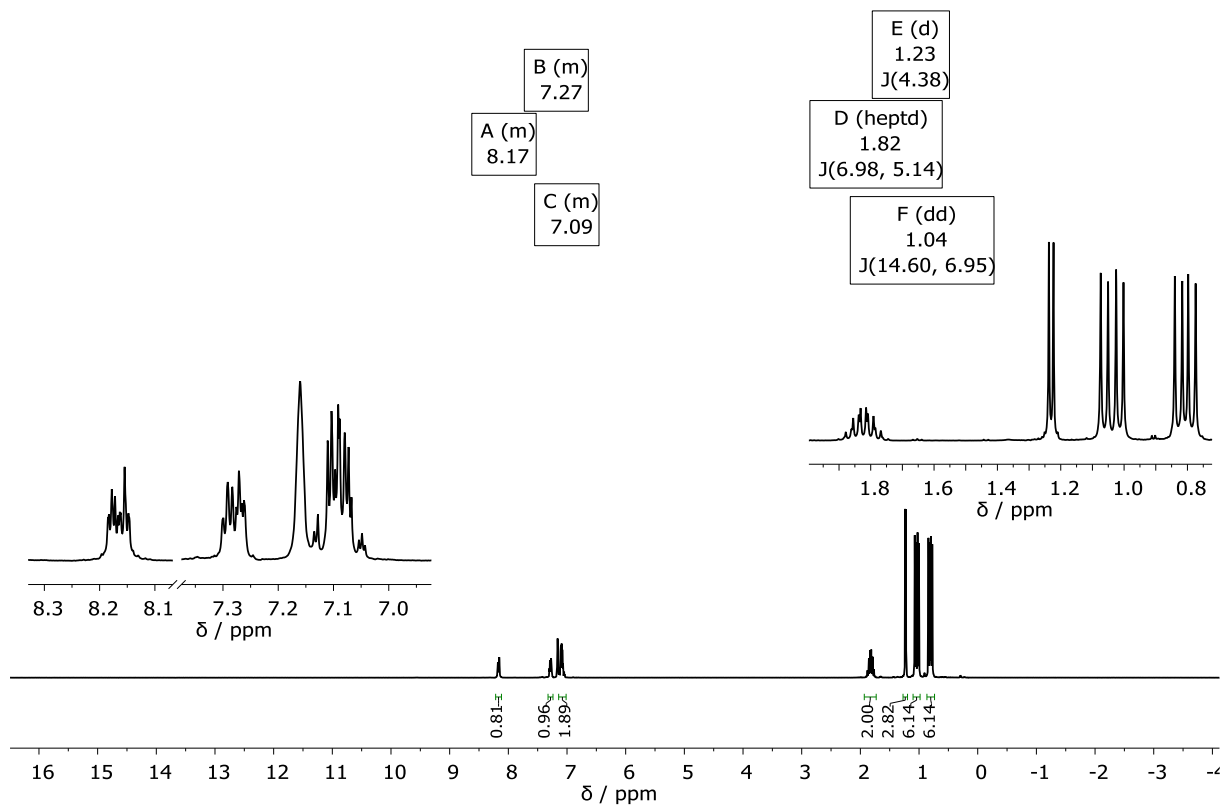
Figure S10: ^{1}H NMR spectrum of a solution of $^iPr_2P(o\text{-}C_6H_4)SiCl_2Me$ (**3**) in C_6D_6 (300 MHz, 293K).
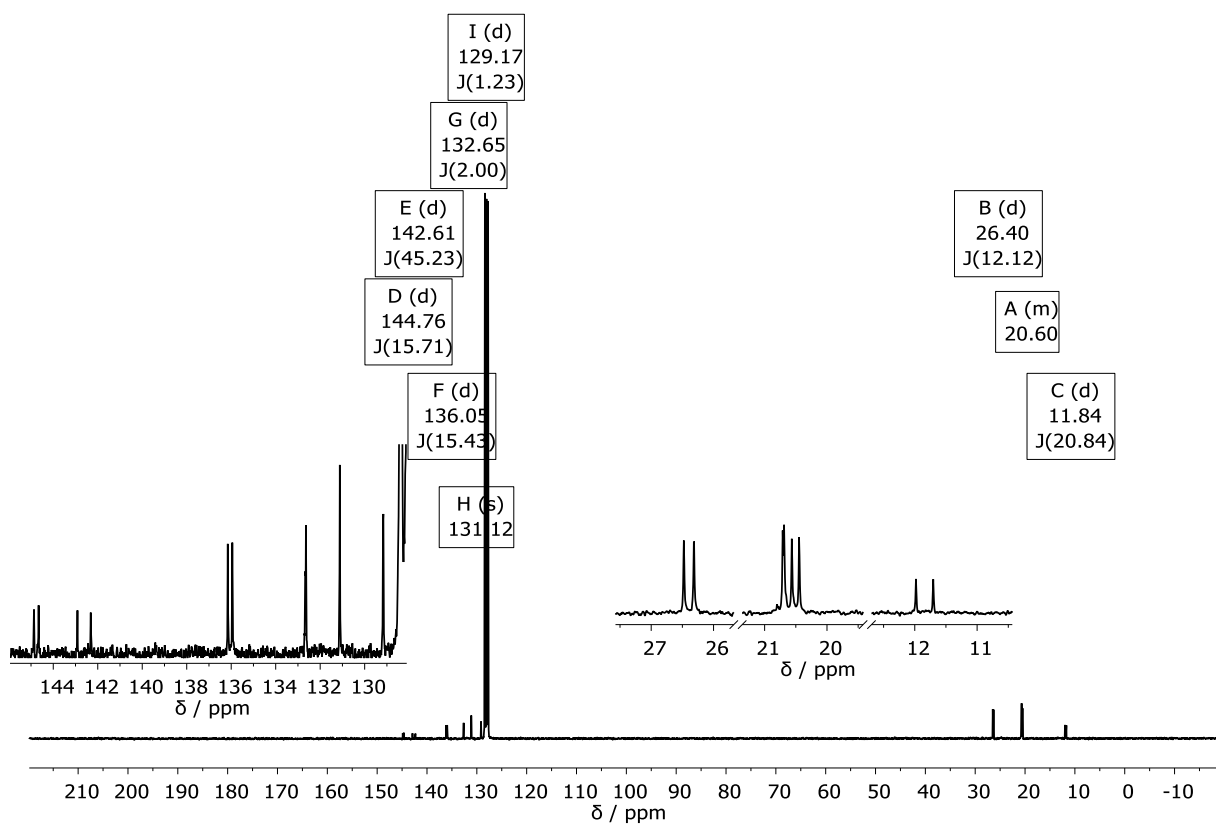
Figure S11: $^{13}C\{^1H\}$ NMR spectrum of a solution of $^iPr_2P(o\text{-}C_6H_4)SiCl_2Me$ (**3**) in C_6D_6 (75 MHz, 293K).

Figure S12: $^{29}Si\{^{1}H\}$ NMR spectrum of a solution of $^{i}Pr_2P(o\text{-}C_6H_4)SiCl_2Me$ (**3**) in C_6D_6 (99 MHz, 293K).

Figure S13: $^{31}P\{^{1}H\}$ NMR spectrum of a solution of $^{i}Pr_2P(o\text{-}C_6H_4)SiCl_2Me$ (**3**) in C_6D_6 (121 MHz, 293K).
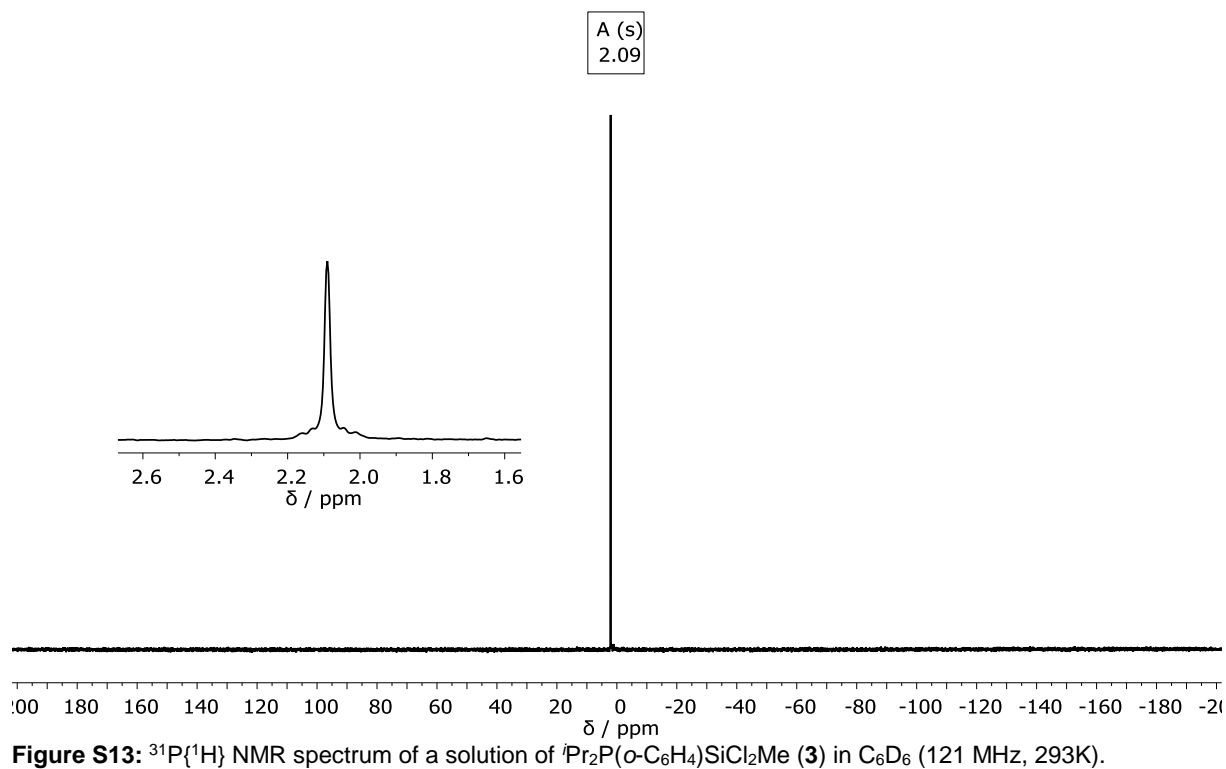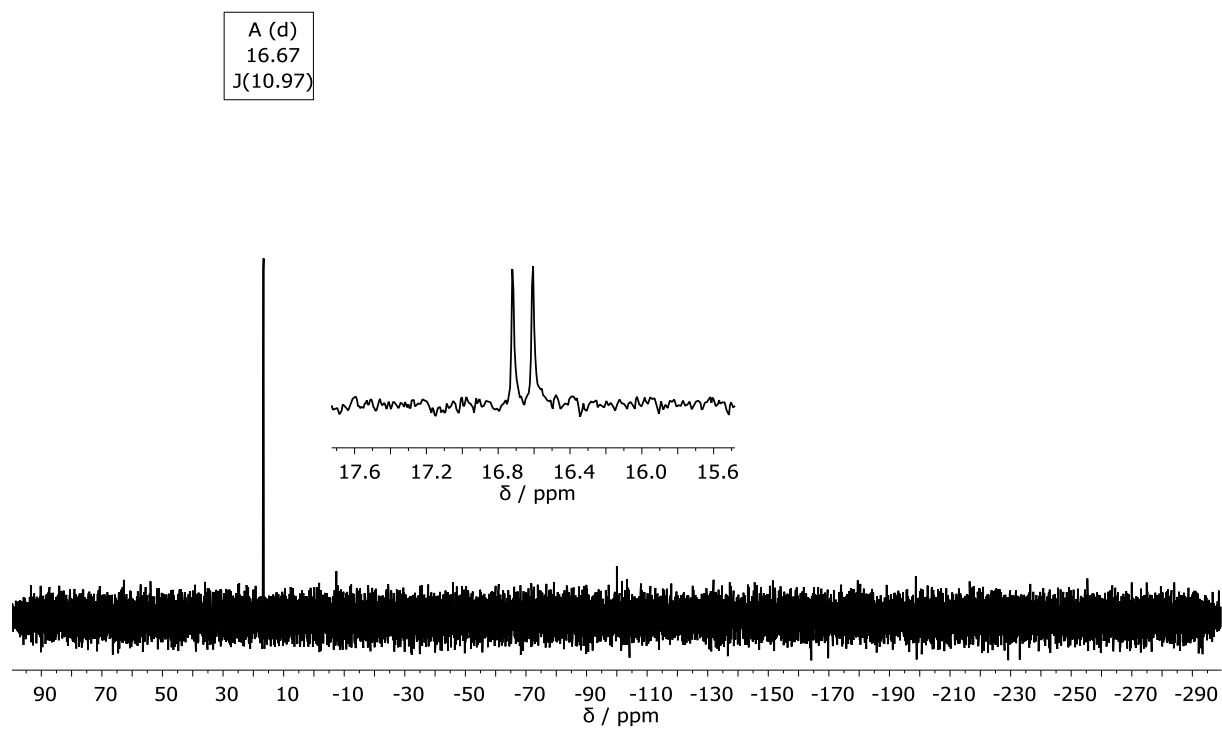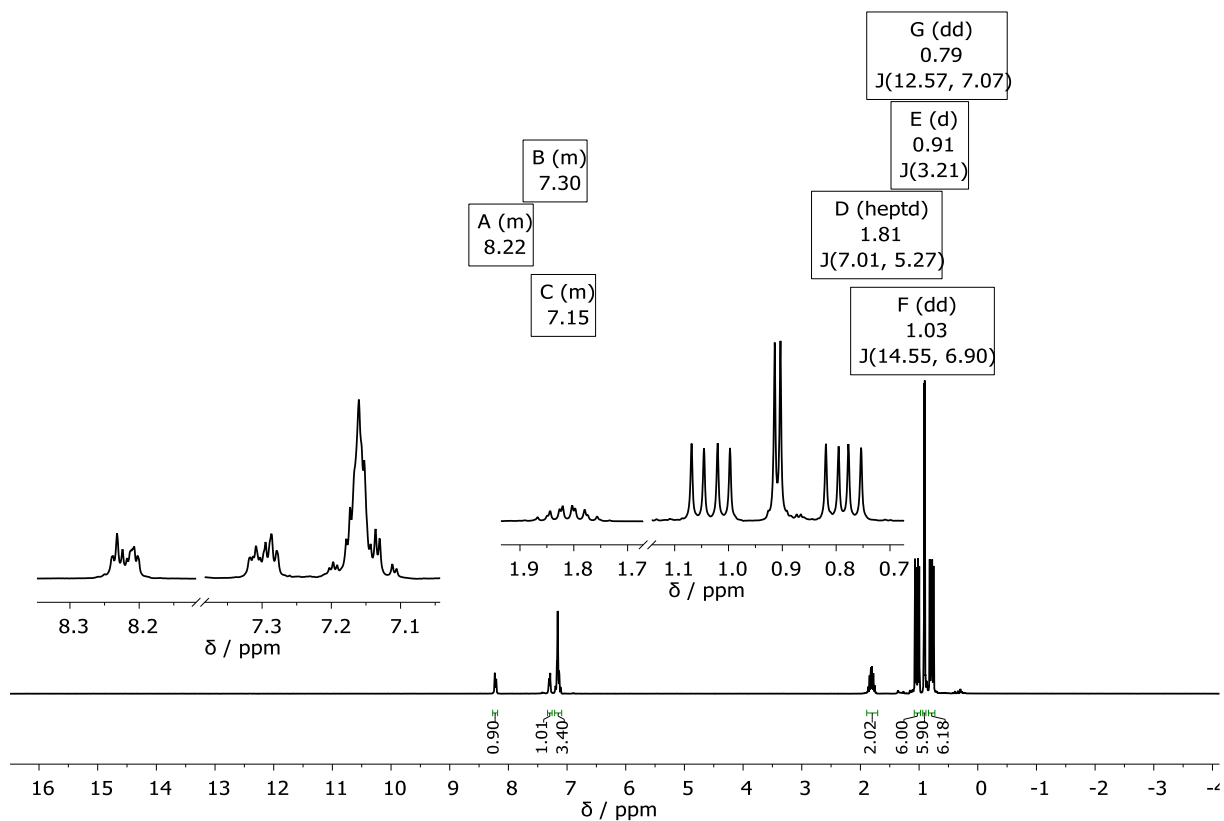
Figure S14: ^{1}H NMR spectrum of a solution of ^{i}Pr$_2$P(o-C$_6$H$_4$)SiClMe$_2$ (**4**) in C$_6$D$_6$ (300 MHz, 293K).
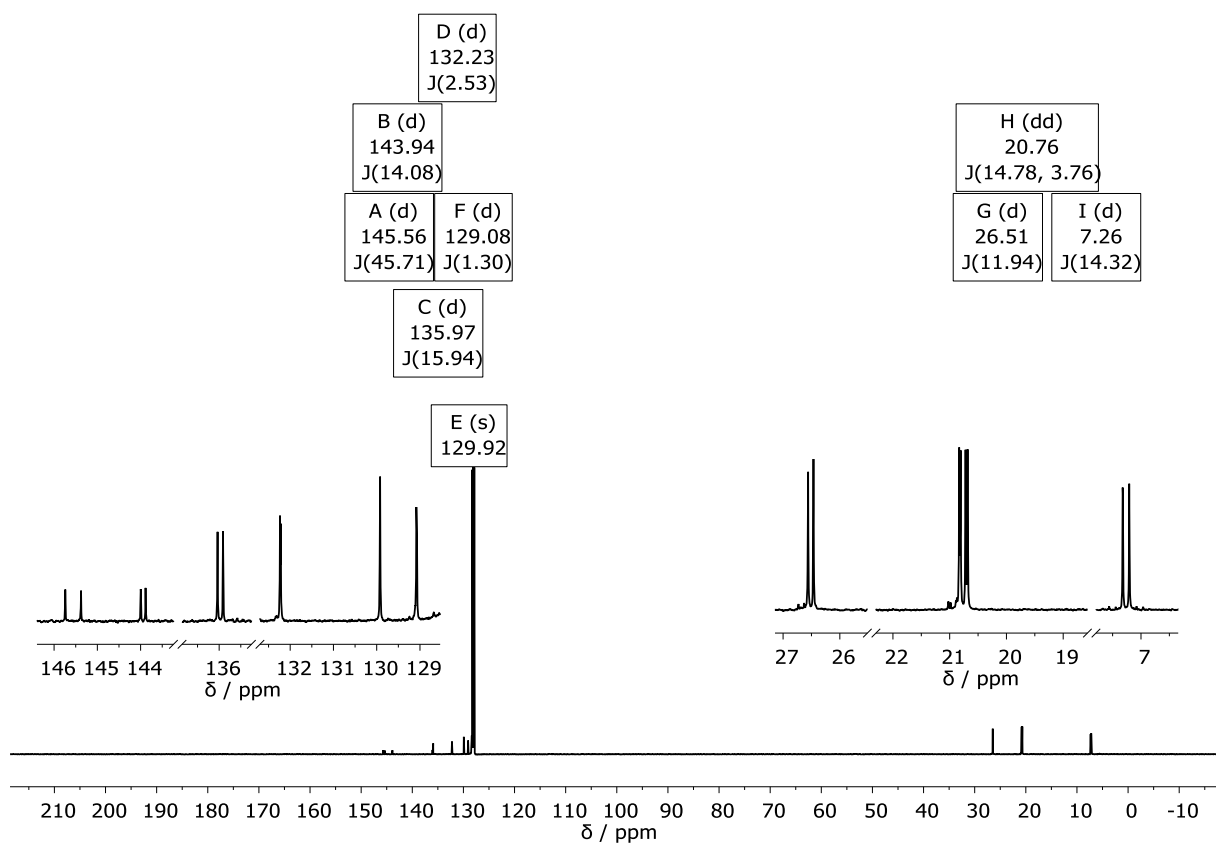
Figure S15: ^{13}C{^{1}H} NMR spectrum of a solution of ^{i}Pr$_2$P(o-C$_6$H$_4$)SiClMe$_2$ (**4**) in C$_6$D$_6$ (126 MHz, 293K).
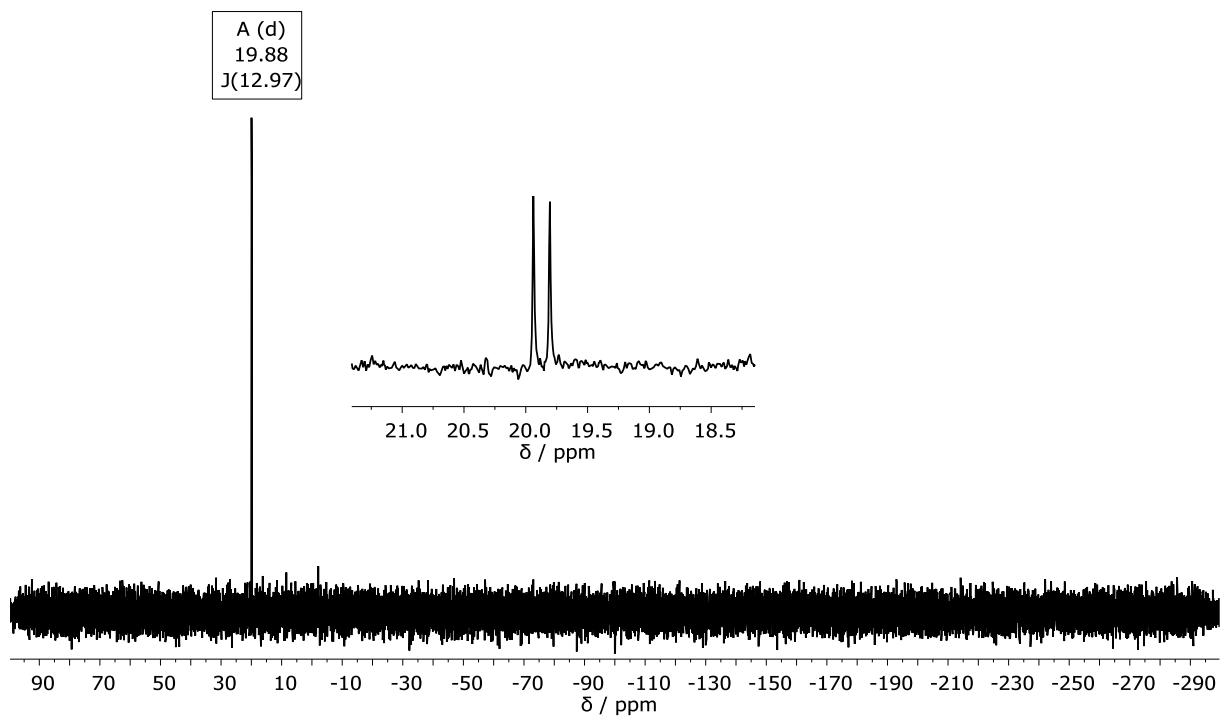
Figure S16: $^{29}Si\{^{1}H\}$ NMR spectrum of a solution of $^{i}Pr_2P(o\text{-}C_6H_4)SiClMe_2$ (**4**) in C_6D_6 (99 MHz, 293K).
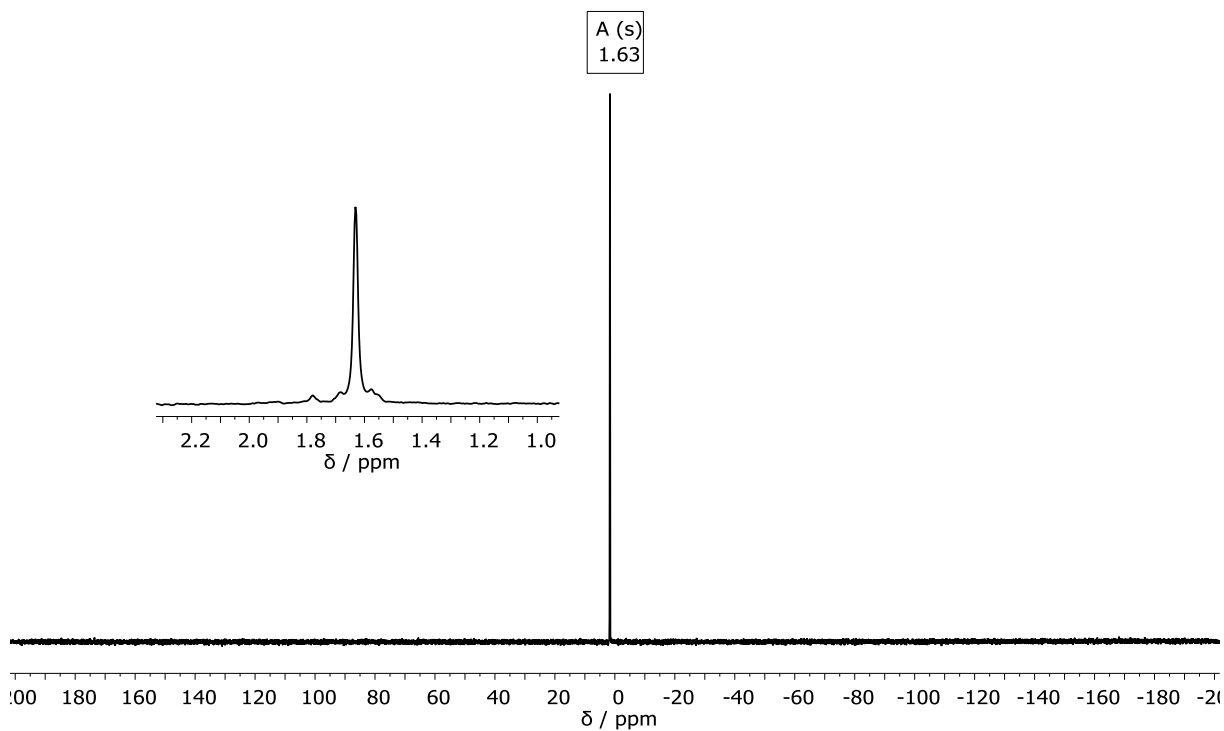
Figure S17: $^{31}P\{^{1}H\}$ NMR spectrum of a solution of $^{i}Pr_2P(o\text{-}C_6H_4)SiClMe_2$ (**4**) in C_6D_6 (121 MHz, 293K).
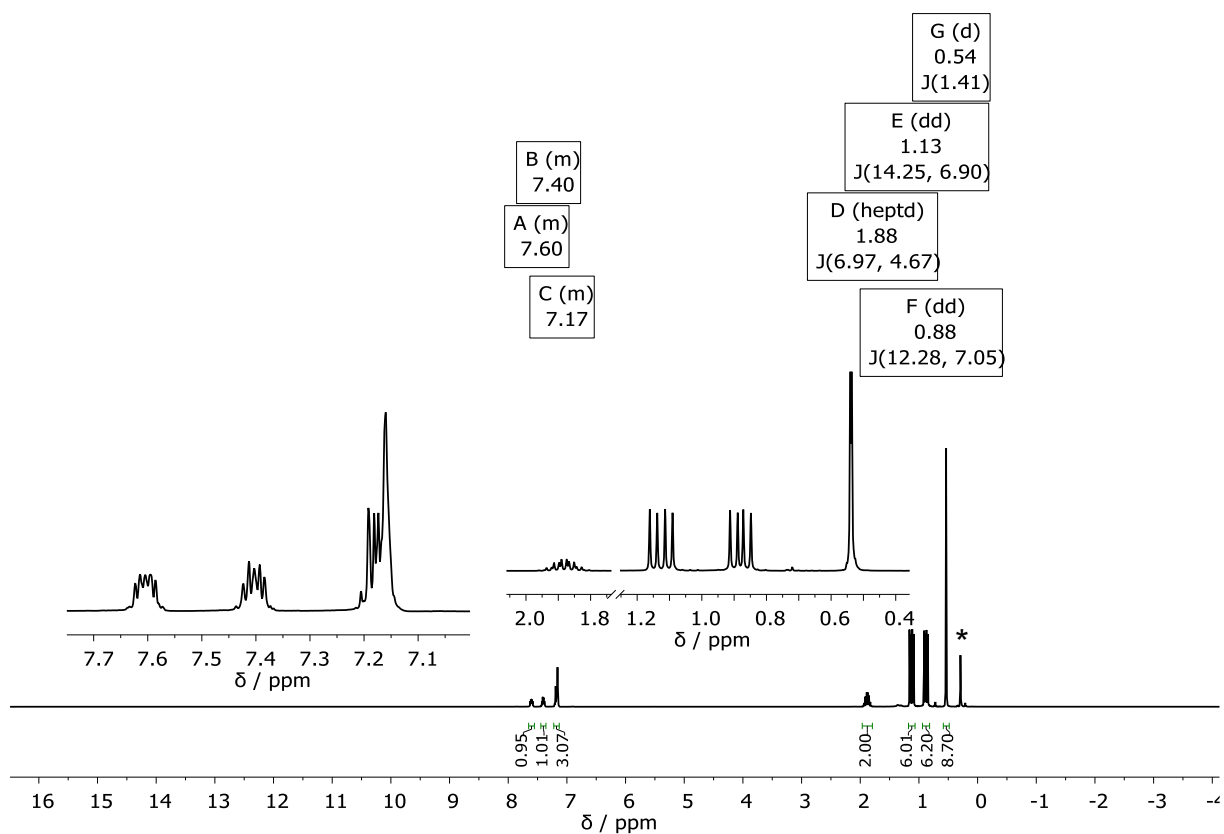
Figure S18: ¹H NMR spectrum of a solution of $^{i}Pr_2P(o-C_6H_4)SiMe_3$ (**5**) in C_6D_6 (300 MHz, 293K). * denotes an impurity from silicon grease.
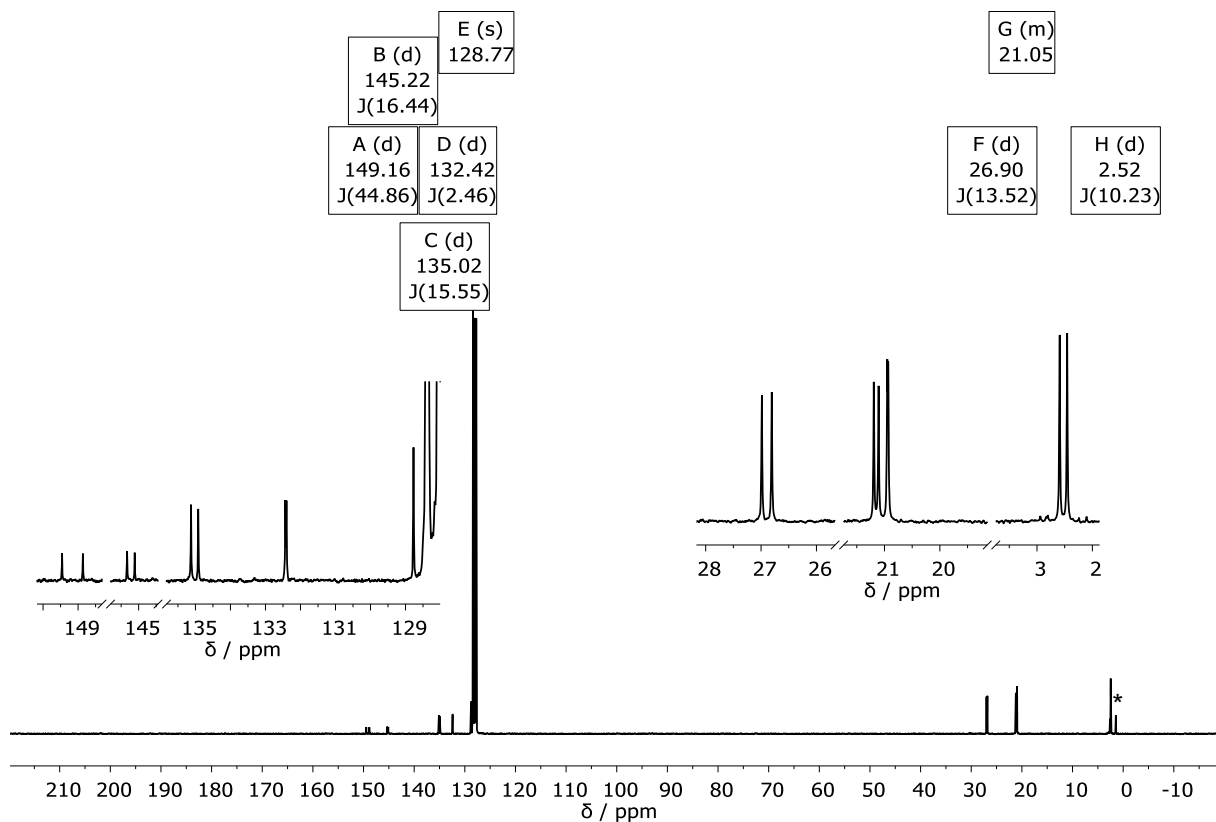
Figure S19: $^{13}C\{^{1}H\}$ NMR spectrum of a solution of $^{i}Pr_2P(o-C_6H_4)SiMe_3$ (**5**) in C_6D_6 (75 MHz, 293K). * denotes an impurity from silicon grease.

A (d)
-4.33
J(9.09)
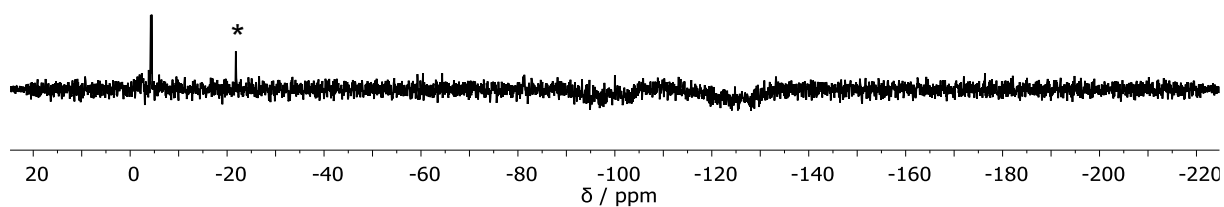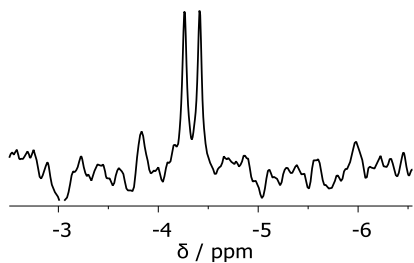
Figure S20: $^{29}Si\{^1H\}$ NMR spectrum of a solution of $^iPr_2P(o\text{-}C_6H_4)SiMe_3$ (**5**) in C_6D_6 (60 MHz, 293K). * denotes an impurity from silicon grease.

A (s)
1.72
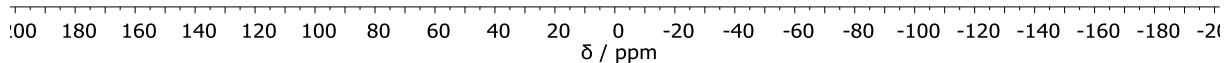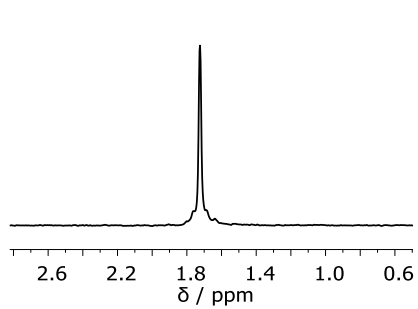
Figure S21: $^{31}P\{^1H\}$ NMR spectrum of a solution of $^iPr_2P(o\text{-}C_6H_4)SiMe_3$ (**4**) in C_6D_6 (121 MHz, 293K).
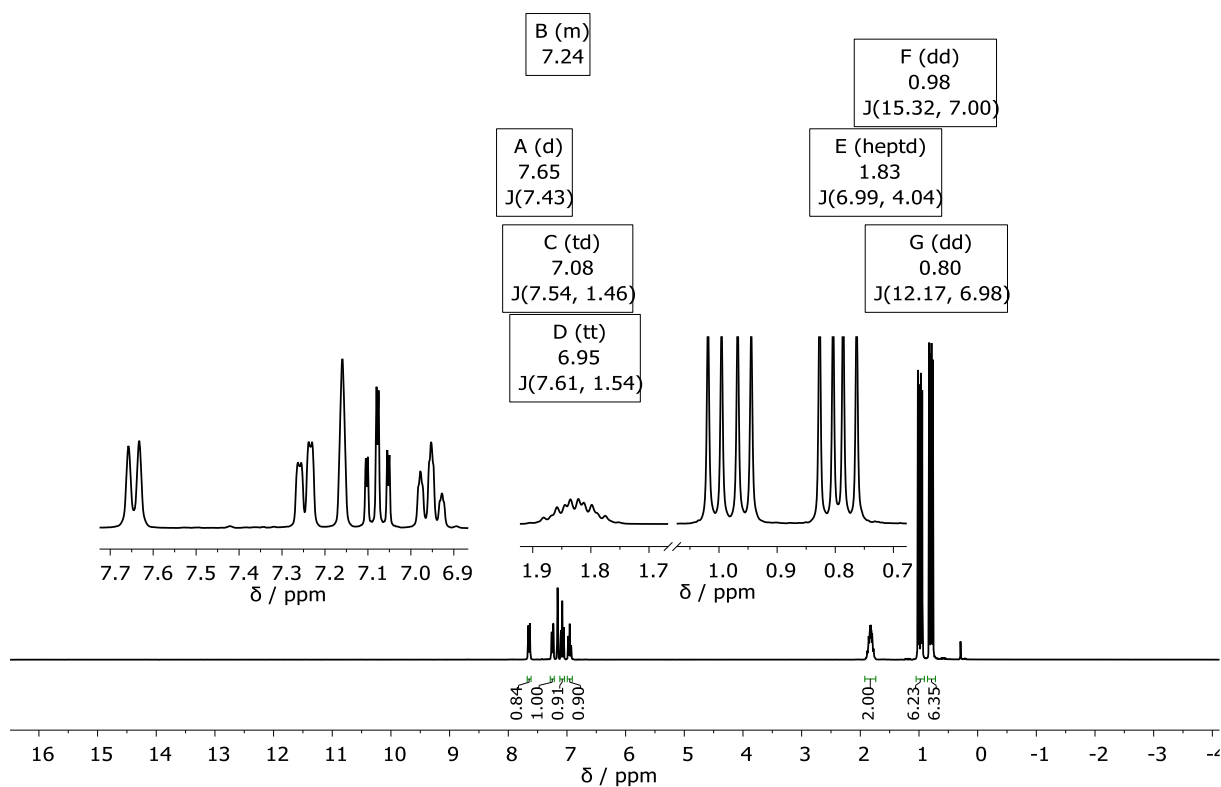
Figure S22: ^{1}H NMR spectrum of a solution of ^{i}Pr$_2$P(o-C$_6$H$_4$)SiF$_3$ (**6**) in C$_6$D$_6$ (300 MHz, 293K).
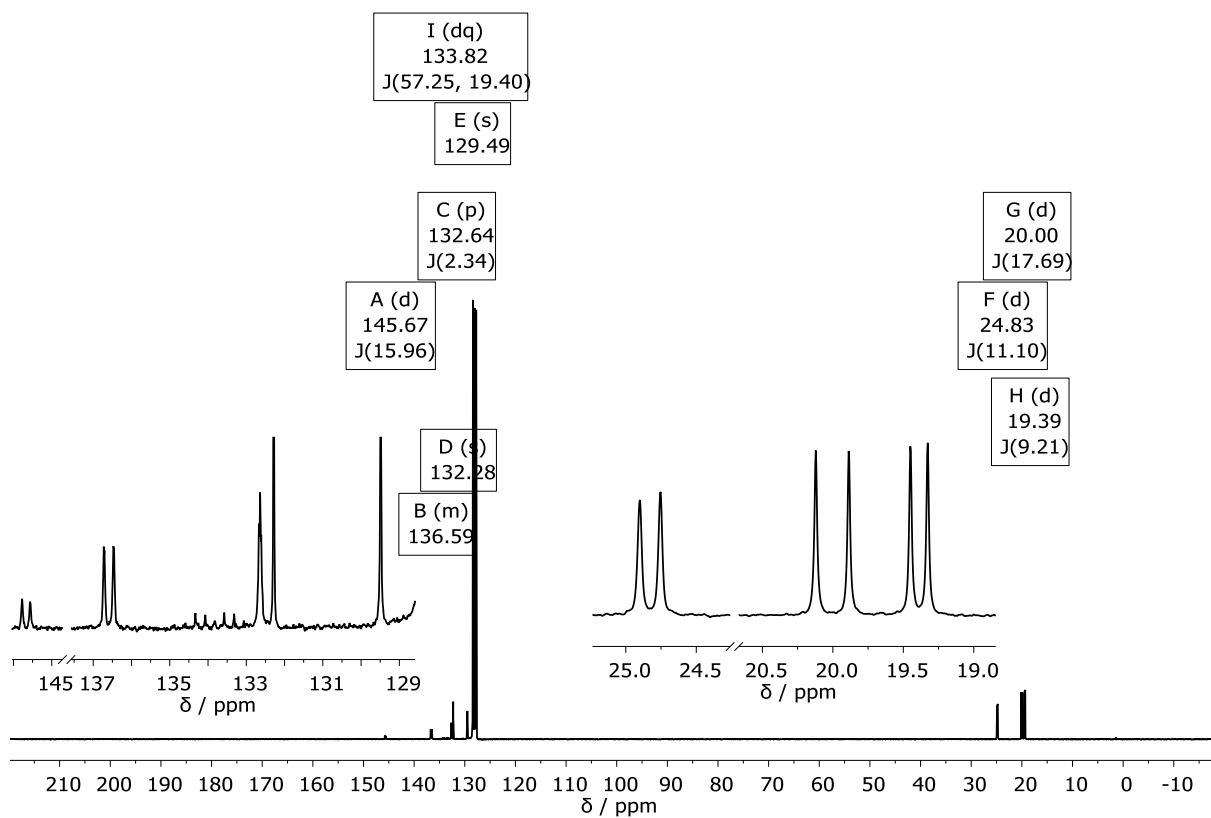
Figure S23: ^{13}C{^{1}H} NMR spectrum of a solution of ^{i}Pr$_2$P(o-C$_6$H$_4$)SiF$_3$ (**6**) in C$_6$D$_6$ (75 MHz, 293K).
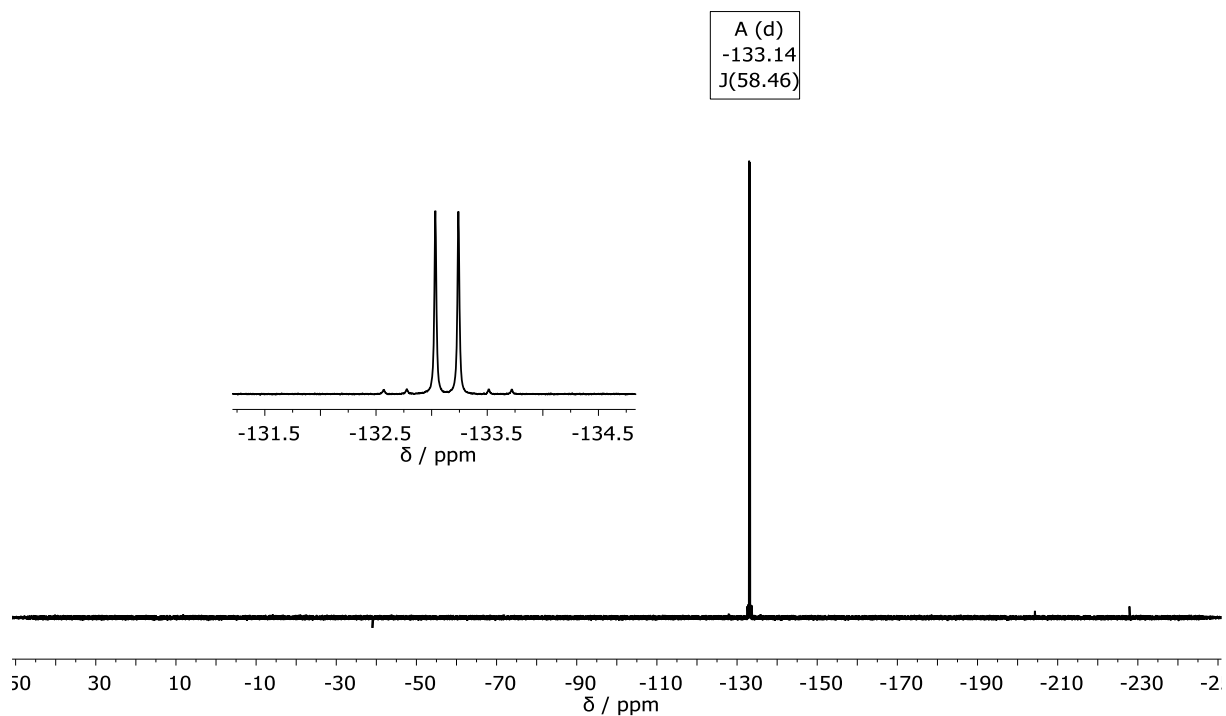
Figure S24: ^{19}F NMR spectrum of a solution of ^{i}Pr$_2$P(o-C$_6$H$_4$)SiF$_3$ (**6**) in C$_6$D$_6$ (282 MHz, 293K).
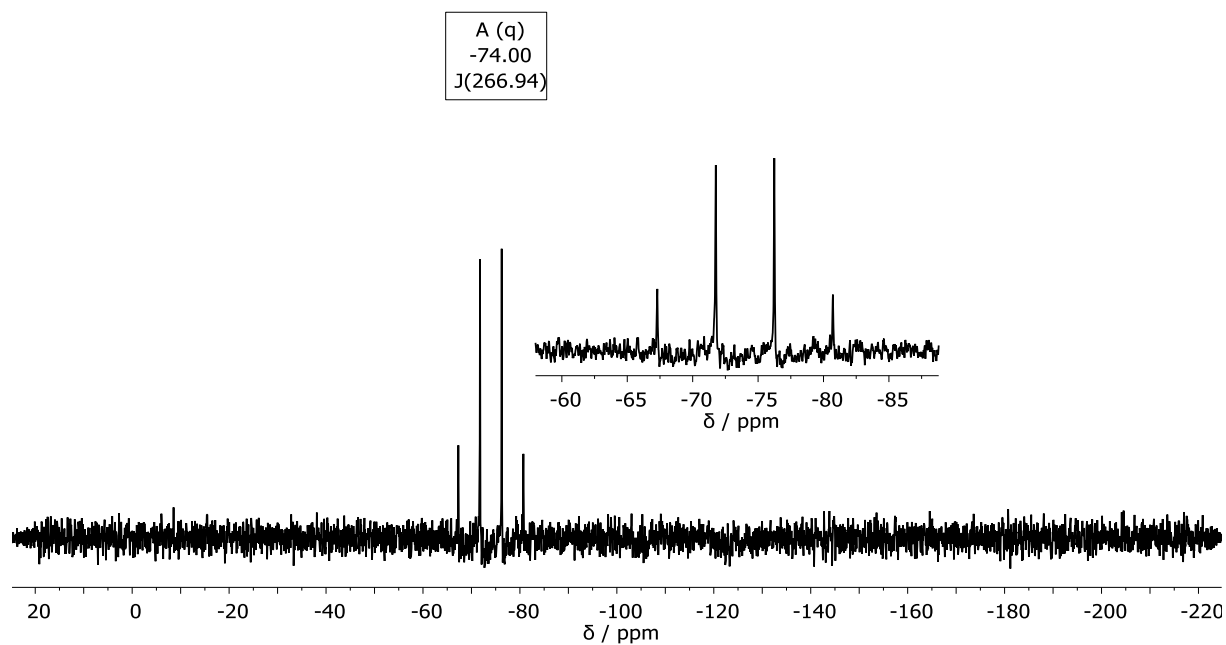
Figure S25: ^{29}Si{^{1}H} NMR spectrum of a solution of ^{i}Pr$_2$P(o-C$_6$H$_4$)SiF$_3$ (**6**) in C$_6$D$_6$ (60 MHz, 293K).
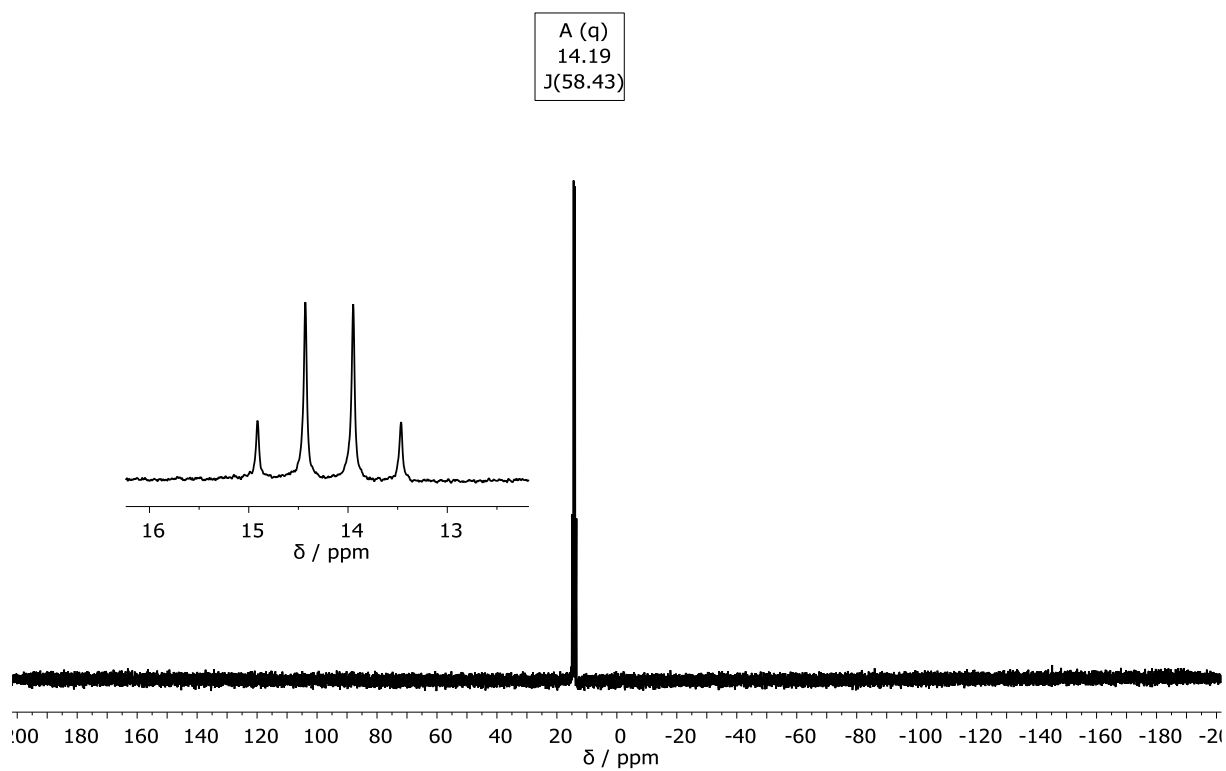
Figure S26: $^{31}P\{^{1}H\}$ NMR spectrum of a solution of $^{i}Pr_2P(o\text{-}C_6H_4)SiF_3$ (**6**) in C_6D_6 (121 MHz, 293K).

4) Optimized geometries

In the following, the Cartesian coordinates of the optimized geometries for the different phenylene-bridged phosphino silyl compounds are listed. The optimization was carried out using the APFD[6] functional with the def2TZVPP[7] basis set as implemented in the Gausian16/B01 suite of program.[8]

2:
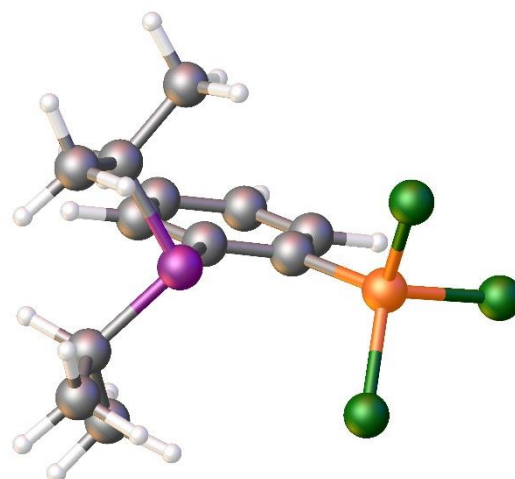
Atom	X	Y	Z
H	1.693650	4.370680	-0.102544
C	1.087807	3.472253	-0.078999
C	-0.297043	3.560287	-0.091186
H	-0.782251	4.529370	-0.128488
C	-1.059752	2.403670	-0.058420
H	-2.141013	2.483793	-0.079144
C	-0.462656	1.145270	-0.012883
P	-1.462945	-0.398752	0.040125
C	0.938776	1.055076	-0.009163
Si	1.821299	-0.587610	0.028473
C	1.699159	2.228830	-0.041021
H	2.780436	2.174256	-0.037066
C	-2.571282	-0.203588	-1.453941
C	-2.589299	0.019188	1.466820
C	-1.800844	0.320349	-2.662330
H	-3.370733	0.503217	-1.198881
C	-3.181260	-1.564266	-1.791156
C	-1.759675	0.087112	2.745193
C	-3.715385	-0.998613	1.607973
H	-3.030873	1.003724	1.275246
H	-3.322476	-2.015944	1.683781
H	-4.411891	-0.965431	0.769600
H	-4.288315	-0.798179	2.517505
H	-1.314280	-0.884039	2.970853
H	-2.391004	0.370885	3.591562
H	-0.949535	0.814560	2.671772
H	-2.397405	-2.264442	-2.089277
H	-3.881567	-1.470301	-2.625830
H	-3.717238	-2.012551	-0.954951
H	-1.428210	1.333389	-2.514428
H	-2.447651	0.322706	-3.543947
H	-0.943851	-0.319558	-2.885294
Cl	1.492370	-1.648449	1.740231
Cl	3.847539	-0.250454	-0.023830
Cl	1.428262	-1.755317	-1.601477

3:
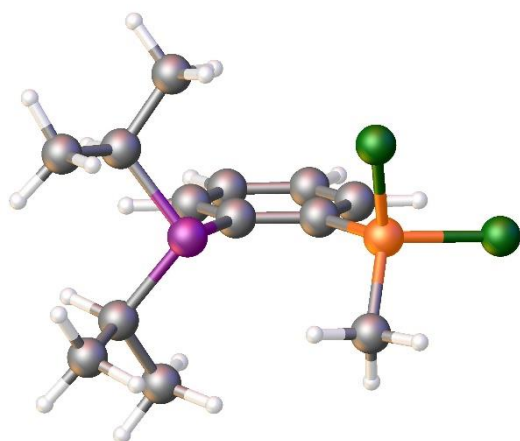
Atom	X	Y	Z
H	-1.928693	4.109295	-0.865971
C	-1.286197	3.257720	-0.673069
C	0.093341	3.391774	-0.742285
H	0.539009	4.350044	-0.985410
C	0.900310	2.292458	-0.498464
H	1.977502	2.407548	-0.547970
C	0.352579	1.049636	-0.182648
P	1.430055	-0.410631	0.118986
C	-1.043453	0.911386	-0.099963
Si	-1.853807	-0.721998	0.349710
C	-1.844911	2.030336	-0.352373
H	-2.922929	1.942977	-0.298577
C	2.600775	0.235744	1.427999
C	2.449450	-0.365852	-1.442401
C	1.837071	0.976985	2.521562
H	3.312624	0.922426	0.953092
C	3.359151	-0.937387	2.047853
C	1.541230	-0.668751	-2.630498
C	3.613743	-1.348501	-1.393233
H	2.851081	0.647902	-1.551888
H	3.271375	-2.357519	-1.149005
H	4.370968	-1.060060	-0.663735
H	4.103042	-1.394823	-2.370002
H	1.130318	-1.677729	-2.558629
H	2.107594	-0.602081	-3.563418
H	0.702218	0.025558	-2.695901
H	2.667039	-1.600329	2.573289
H	4.089502	-0.575541	2.777028
H	3.891789	-1.540089	1.313465
H	1.353569	1.881564	2.154762
H	2.516717	1.258079	3.330587
H	1.062661	0.337822	2.954625
Cl	-1.616851	-2.089004	-1.172847
Cl	-3.896569	-0.378290	0.458820
C	-1.394229	-1.484959	1.974995
H	-0.378421	-1.873924	1.942277
H	-2.088047	-2.297088	2.198282
H	-1.471464	-0.736133	2.765959

4:
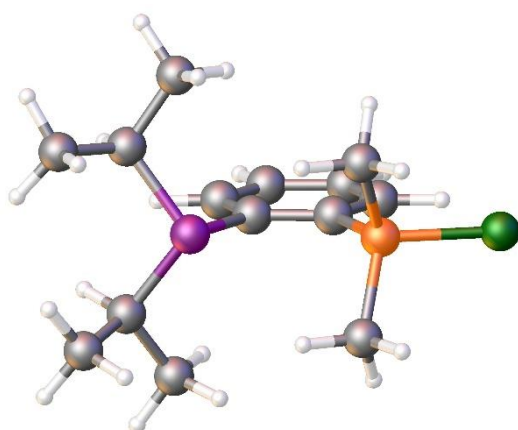
Atom	X	Y	Z
H	2.210387	3.999004	0.027297
C	1.524813	3.158928	0.023108
C	0.153997	3.376159	0.008967
H	-0.241688	4.385812	-0.001873
C	-0.706883	2.291336	0.006224
H	-1.777099	2.467521	-0.015425
C	-0.219807	0.983868	0.015581
P	-1.376110	-0.445650	0.017841
C	1.167240	0.754244	0.020135
Si	1.884872	-0.995487	-0.002835
C	2.020256	1.863851	0.026711
H	3.092892	1.712961	0.032096
C	-2.476482	-0.067792	-1.444519
C	-2.421601	0.010625	1.494580
C	-1.645482	0.354819	-2.653018
H	-3.155074	0.748898	-1.168939
C	-3.293198	-1.309624	-1.801620
C	-1.555461	-0.076837	2.747949
C	-3.650016	-0.881016	1.628576
H	-2.752146	1.047217	1.365546
H	-3.374256	-1.939052	1.630851
H	-4.369329	-0.720018	0.825321
H	-4.162993	-0.673307	2.571866
H	-1.237253	-1.106020	2.930432
H	-2.120607	0.254327	3.623289
H	-0.659809	0.542050	2.672512
H	-2.630434	-2.121867	-2.110200
H	-3.965343	-1.094014	-2.636869
H	-3.898662	-1.679585	-0.974879
H	-1.108277	1.287546	-2.485493
H	-2.292213	0.485063	-3.524983
H	-0.908256	-0.411947	-2.905077
C	1.518407	-1.982211	1.534665
Cl	3.967186	-0.762348	-0.008906
C	1.503728	-1.925453	-1.573044
H	1.704456	-1.387844	2.430350
H	2.164463	-2.861895	1.566541
H	0.478317	-2.306843	1.536822
H	0.456433	-2.226821	-1.593741
H	2.128182	-2.819314	-1.631262
H	1.712515	-1.305753	-2.446462

5:
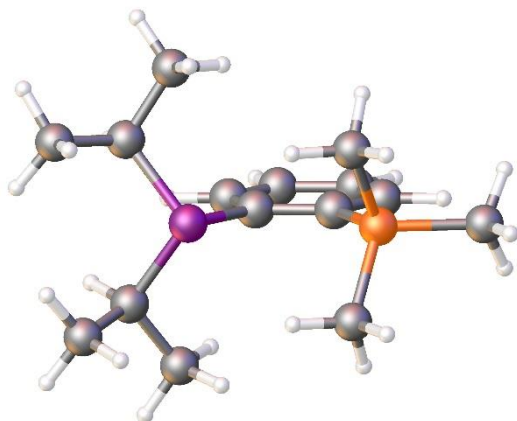
Atom	X	Y	Z
H	2.679806	3.770972	-0.153827
C	1.940612	2.978223	-0.117521
C	0.586889	3.282274	-0.143410
H	0.256012	4.313351	-0.203685
C	-0.341100	2.254914	-0.093919
H	-1.397639	2.500491	-0.124316
C	0.058049	0.919361	-0.019044
P	-1.205220	-0.419367	0.048615
C	1.426845	0.596973	-0.000407
Si	2.113987	-1.172707	0.069377
C	2.345541	1.653598	-0.049172
H	3.408144	1.440289	-0.034851
C	-2.241851	-0.046252	-1.464599
C	-2.250618	0.224671	1.454648
C	-1.358267	0.250794	-2.672776
H	-2.867328	0.829431	-1.251293
C	-3.136198	-1.246239	-1.775193
C	-1.426259	0.164384	2.737236
C	-3.546989	-0.560789	1.610443
H	-2.496640	1.270968	1.242133
H	-3.352334	-1.633345	1.695538
H	-4.228516	-0.406013	0.773458
H	-4.069586	-0.247982	2.518922
H	-1.169781	-0.868030	2.987115
H	-1.994879	0.576978	3.575186
H	-0.495952	0.728412	2.651791
H	-2.525642	-2.116950	-2.027095
H	-3.777836	-1.030243	-2.634266
H	-3.779087	-1.530486	-0.942723
H	-0.762005	1.152899	-2.540680
H	-1.975079	0.376359	-3.567070
H	-0.669791	-0.576637	-2.863756
C	1.621309	-2.042314	1.656211
C	3.991855	-1.068544	0.037744
C	1.583448	-2.167423	-1.430793
H	1.848720	-1.425376	2.528096
H	2.173742	-2.980616	1.753297
H	0.555366	-2.267614	1.662518
H	0.517509	-2.392369	-1.398361
H	2.132919	-3.111924	-1.465316
H	1.795072	-1.621882	-2.352942
H	4.365628	-0.594972	-0.872527
H	4.398828	-2.082266	0.070668
H	4.393237	-0.526833	0.896795

6:
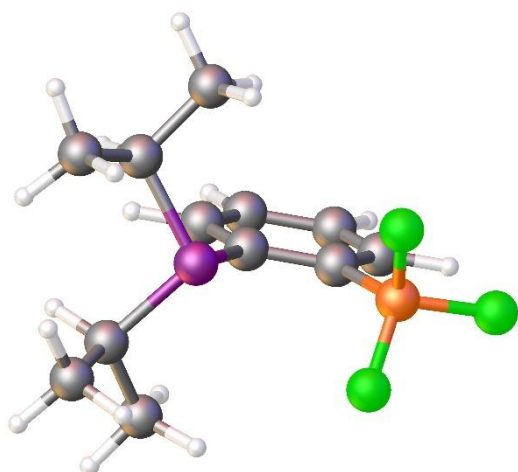
Atom	X	Y	Z
H	3.168651	3.424012	-0.109974
C	2.332794	2.734306	-0.086563
C	1.029671	3.217418	-0.109350
H	0.848879	4.285855	-0.152781
C	-0.039975	2.335506	-0.077763
H	-1.052489	2.723457	-0.102254
C	0.177562	0.960981	-0.023617
P	-1.159669	-0.293001	0.033883
C	1.489610	0.471378	-0.004079
Si	1.814233	-1.341023	0.057723
C	2.562462	1.367955	-0.035658
H	3.579636	0.993825	-0.020145
C	-2.174645	0.129683	-1.474242
C	-2.146490	0.364762	1.469593
C	-1.264499	0.364688	-2.677147
H	-2.749218	1.040633	-1.266548
C	-3.131439	-1.022779	-1.778422
C	-1.295094	0.233129	2.729850
C	-3.472019	-0.369592	1.633550
H	-2.350567	1.425554	1.283942
H	-3.320654	-1.450443	1.695589
H	-4.161171	-0.169741	0.812601
H	-3.963198	-0.052277	2.557414
H	-1.040640	-0.812315	2.919953
H	-1.842414	0.609358	3.598182
H	-0.361598	0.793111	2.654243
H	-2.567803	-1.927409	-2.018343
H	-3.754722	-0.778194	-2.642912
H	-3.794271	-1.261758	-0.947558
H	-0.631251	1.243331	-2.556236
H	-1.865510	0.500942	-3.580180
H	-0.611634	-0.496675	-2.843255
F	1.326611	-2.060308	1.375883
F	3.390151	-1.530027	0.041672
F	1.289695	-2.148170	-1.194780

5) SAPT calculations

For the energy decomposition analysis, the optimized geometries of the different conformers were used in the PSI4[9] program. The different contributions in kJ mol^{-1} of the interactions between the phosphanyl and the silyl moieties are given in Table S3. The SAPT calculation was performed using the density-fitted self-consistent field method at the Hartree-Fock level of theory with the jun-cc-pVDZ basis set. The separator for the F-SAPT calculation, based on the SAPT0 approximation, was set as the linking phenylene group in order to determine only the energetic contributions occurring between the potential Lewis acidic centres and the basic centre.

Table S3. Calculated interaction energies between the phosphanyl and the silyl moieties in the vicinal donor acceptor systems **2**–**6** [kJ mol^{-1}].

	2	3	4	5	6
total SAPT	61	53	46	45	64
electrostatic	36	23	7	12	44
exchange	65	68	76	67	50
induction	−18	−46	−14	−11	−21
dispersion	−22	−22	−23	−22	−9
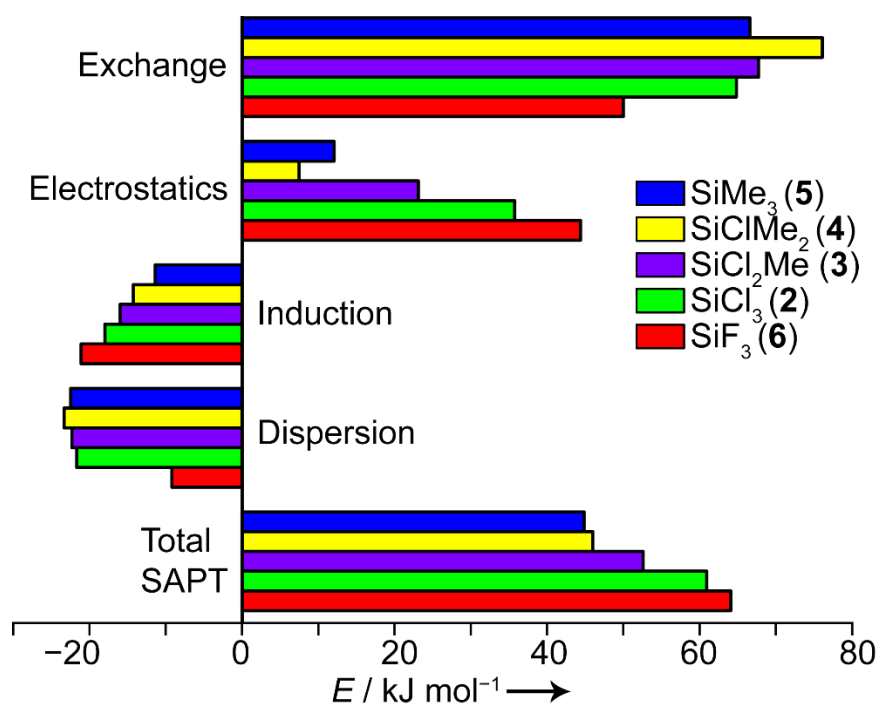
Figure S27. SAPT decomposition of energy in kJ mol^{-1} of the interactions between the phosphanyl and the silyl groups in **2**–**6**.

6) *ortho*-, *meta*- and *para*-interaction energies

Interaction energies were calculated according to previously reported *peri*-interaction energies[10] at the APFD/def2-TZVPP[6,7] level of theory according to Scheme 3 in the manuscript.

Table S4. Calculated enthalpies for the isodesmic reactions forming the *ortho*- meta- or *para*-substituted phenylphosphanes in kJ mol^{-1}.

compound	*ortho*-IE	*meta*-IE	*para*-IE
iPr$_2$P–(C$_6$H$_4$)–SiCl$_3$	−10	−21	−23
iPr$_2$P–(C$_6$H$_4$)–SiCl$_2$Me	−5	−11	−12
iPr$_2$P–(o-C$_6$H$_4$)–SiClMe$_2$	−7	−12	−9
iPr$_2$P–(o-C$_6$H$_4$)–SiMe$_3$	−5	−13	−11
iPr$_2$P–(o-C$_6$H$_4$)–SiF$_3$	−12	−10	−12

7) References

1   a) M. Tamm, B. Dreßel, K. Baum, T. Lügger and T. Pape, *J. Organomet. Chem.*, 2003, **677**, 1–9; b) M. Sircoglou, M. Mercy, N. Saffon, Y. Coppel, G. Bouhadir, L. Maron and D. Bourissou, *Angew. Chem. Int. Ed.*, 2009, **48**, 3454–3457; c) J. C. DeMott, W. Gu, B. J. McCulloch, D. E. Herbert, M. D. Goshert, J. R. Walensky, J. Zhou and O. V. Ozerov, *Organometallics*, 2015, **34**, 3930–3933.

2   O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.

3   G. M. Sheldrick, *Acta Crystallogr. A*, 2008, **64**, 112–122.

4   G. M. Sheldrick, *Acta Crystallogr. A*, 2015, **71**, 3–8.

5   G. M. Sheldrick, *Acta Crystallogr. C*, 2015, **71**, 3–8.

6   A. Austin, G. A. Petersson, M. J. Frisch, F. J. Dobek, G. Scalmani and K. Throssell, *J. Chem. Theory Comput.*, 2012, **8**, 4989–5007.

7   F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.

8   M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, *Gaussian, Inc., Wallingford CT*, Gaussian 16, Revision B.01, 2016.

9   R. M. Parrish, L. A. Burns, D. G. A. Smith, A. C. Simmonett, A. E. DePrince, E. G. Hohenstein, U. Bozkaya, A. Y. Sokolov, R. Di Remigio, R. M. Richard, J. F. Gonthier, A. M. James, H. R. McAlexander, A. Kumar, M. Saitow, X. Wang, B. P. Pritchard, P. Verma, H. F. Schaefer, K. Patkowski, R. A. King, E. F. Valeev, F. A. Evangelista, J. M. Turney, T. D. Crawford and C. D. Sherrill, *J. Chem. Theory Comput.*, 2017, **13**, 3185–3197.

10 a) S. Furan, E. Hupf, E. Lork, S. Mebs and J. Beckmann, *Eur. J. Inorg. Chem.*, 2017, **2017**, 3302–3311; b) E. Hupf, E. Lork, S. Mebs and J. Beckmann, *Organometallics*, 2015, **34**, 3873–3887.