Electronic Supplementary Information

Phosphanyl-Substituted Siloles: Synthesis, Structural Characterization and an Unexpected Secondary Isotope Effect in the ^{31}P NMR Spectrum at Room Temperature

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Stereoisomers of 3

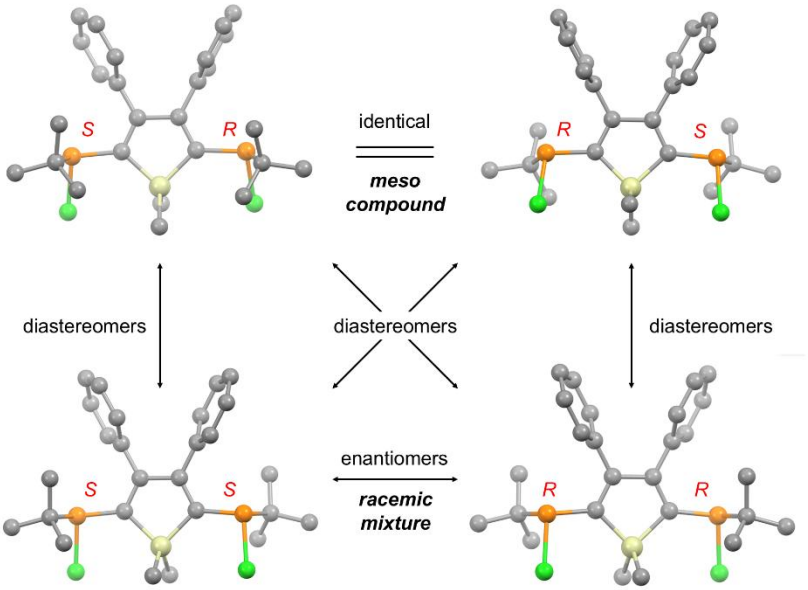

Fig. S1. Stereoisomers of **3** showing the racemic and meso forms.

UV-Vis absorption spectrum of 2

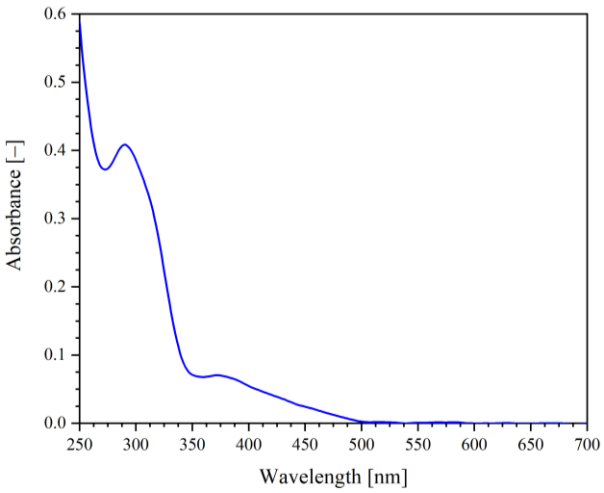

Fig. S2. UV-Vis absorption spectrum of **2** in dichloromethane (~10^{-5} M).

NMR spectra

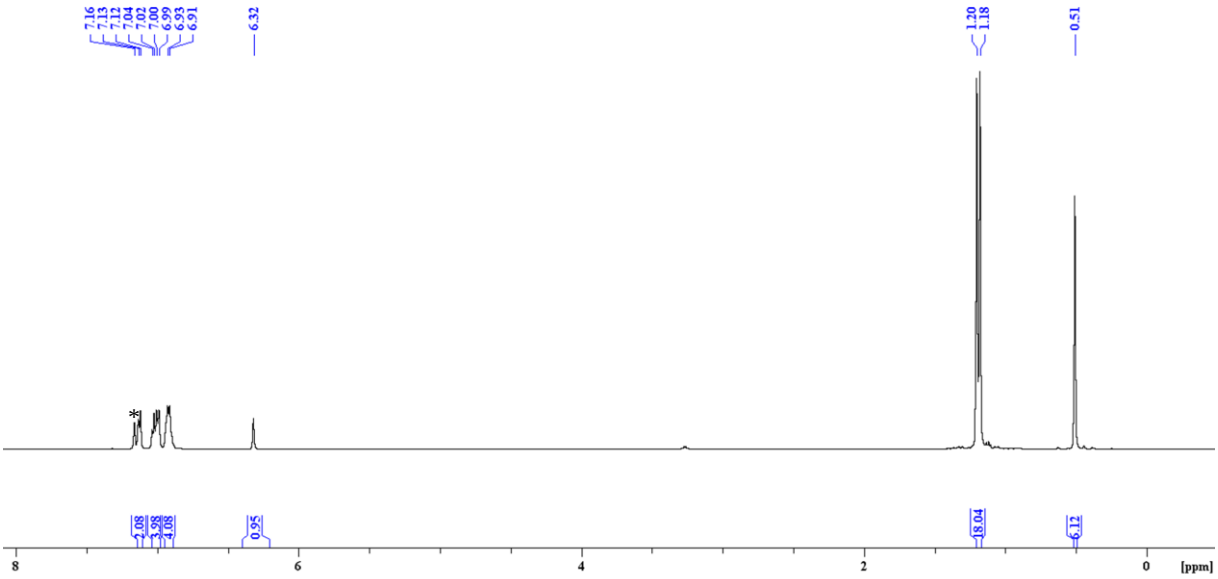

Fig. S3. ^{1}H NMR spectrum of **1** in C_6D_6 (*: C_6D_6 residual).

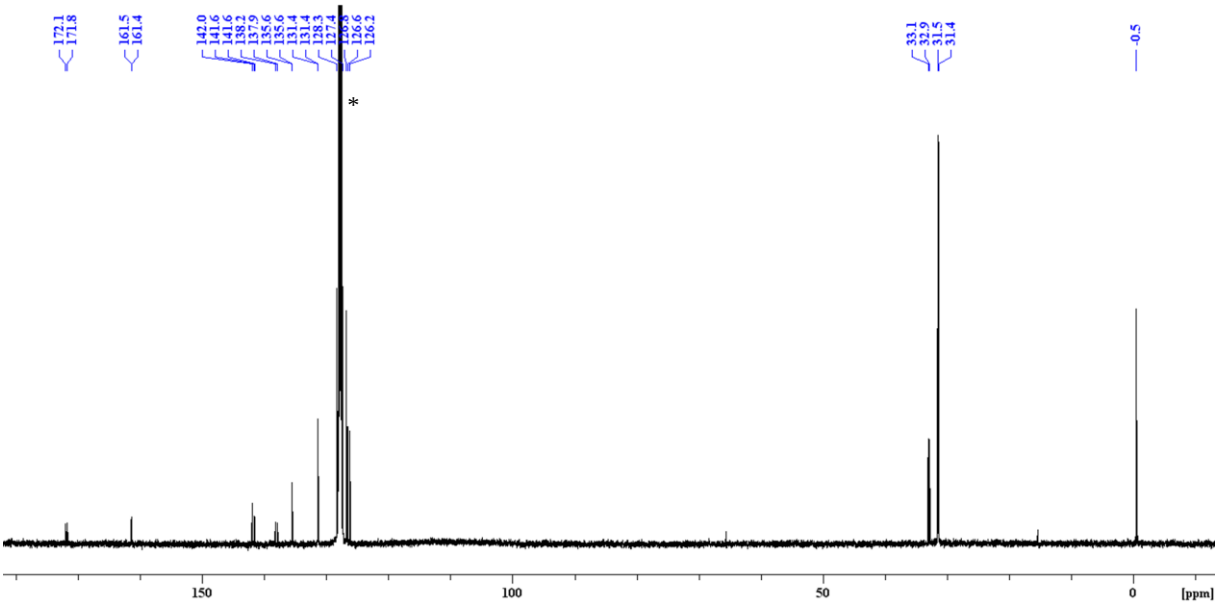

Fig. S4. $^{13}C\{^{1}H\}$ NMR spectrum of **1** in C_6D_6 (*: C_6D_6).

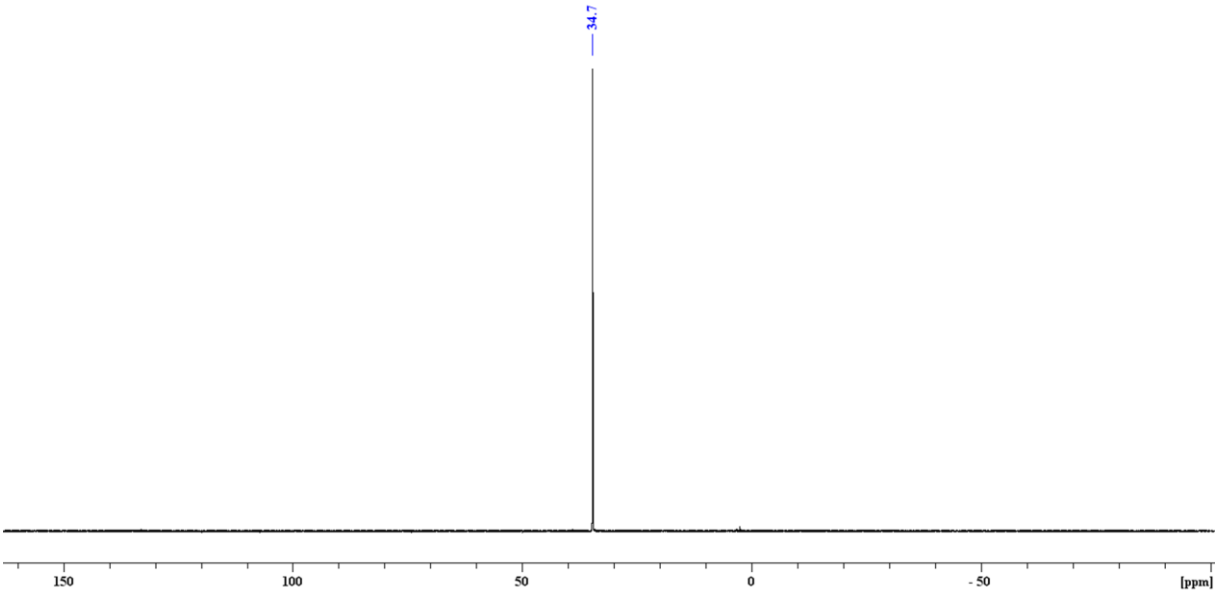

Fig. S5. $^{31}P\{^{1}H\}$ NMR spectrum of **1** in C_6D_6.

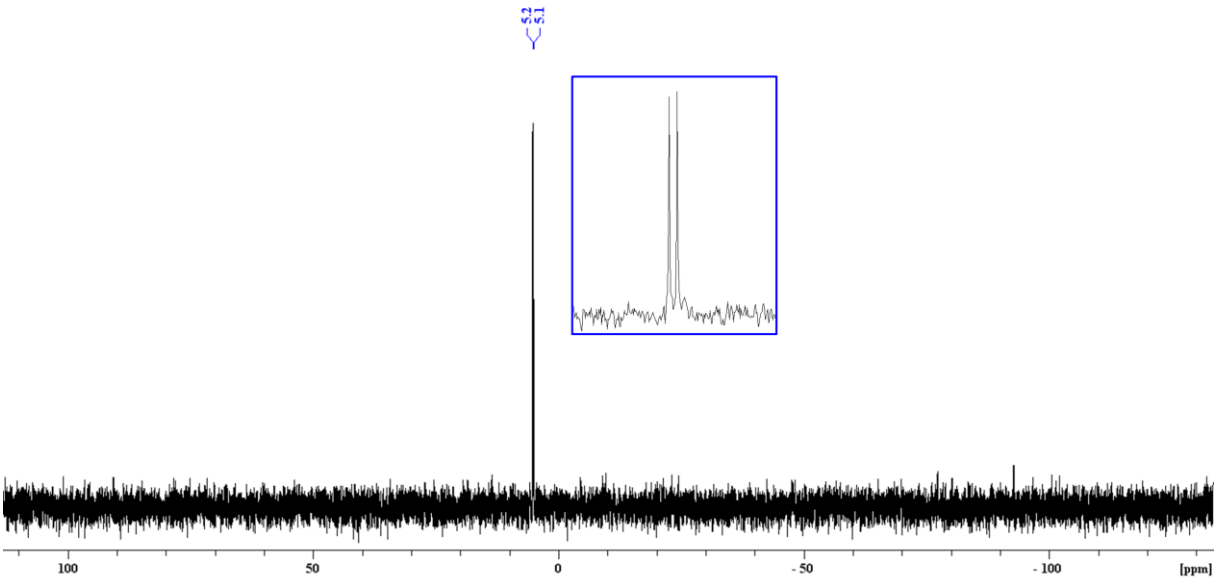

Fig. S6. $^{29}Si\{^{1}H\}$ NMR spectrum of **1** in C_6D_6.

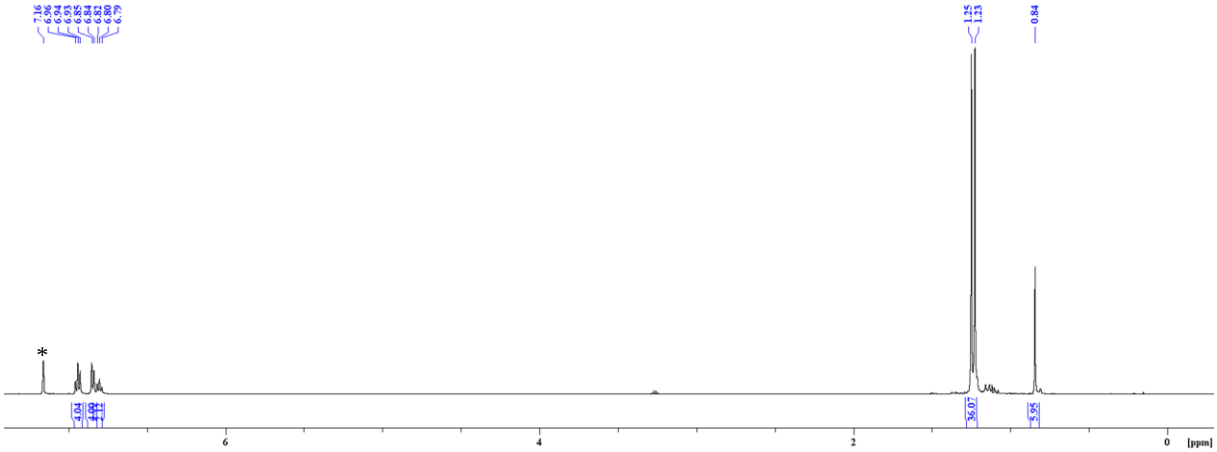

Fig. S7. ^{1}H NMR spectrum of **2** in C_6D_6 (*: C_6D_6 residual).

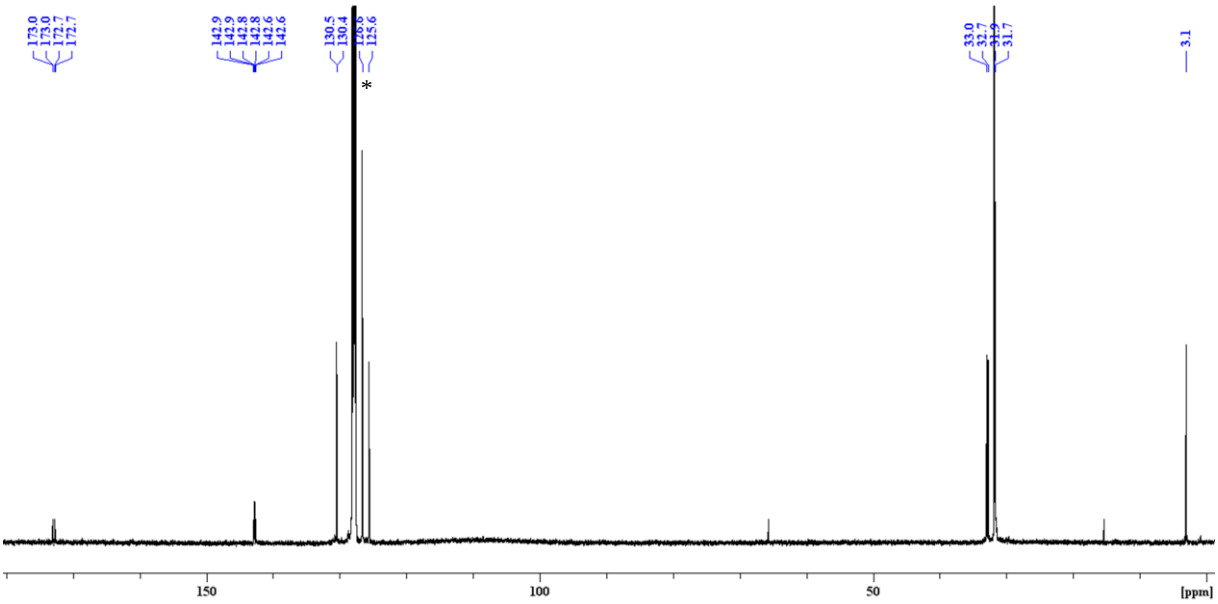

Fig. S8. ^{13}C{^{1}H} NMR spectrum of **2** in C_6D_6 (*: C_6D_6).

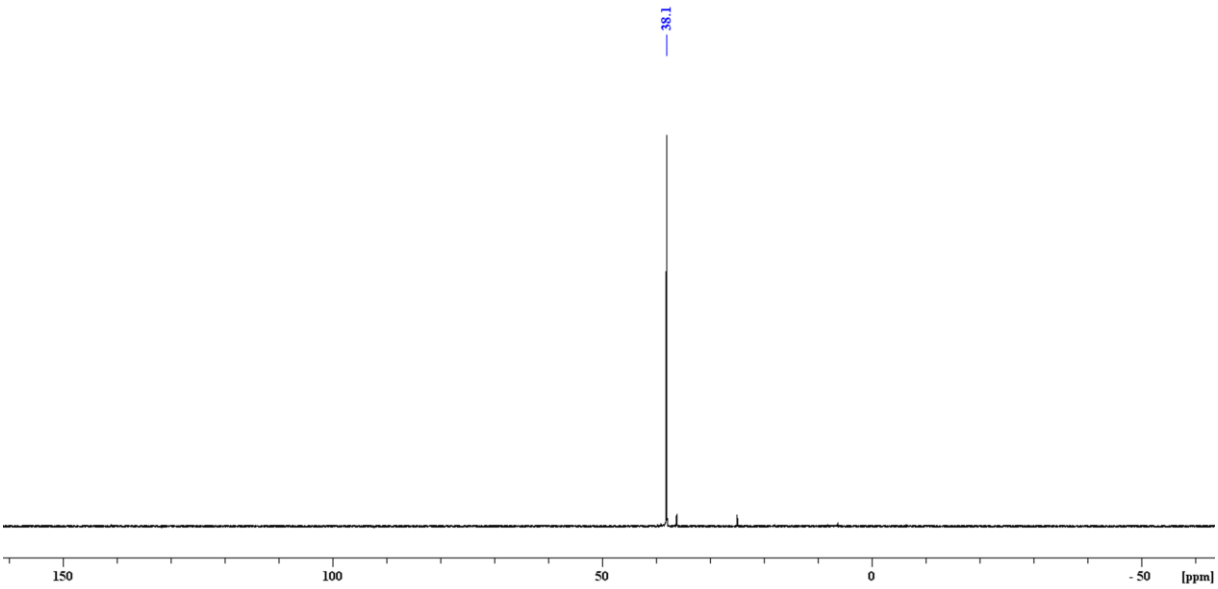

Fig. S9. $^{31}P\{^{1}H\}$ NMR spectrum of **2** in C_6D_6.

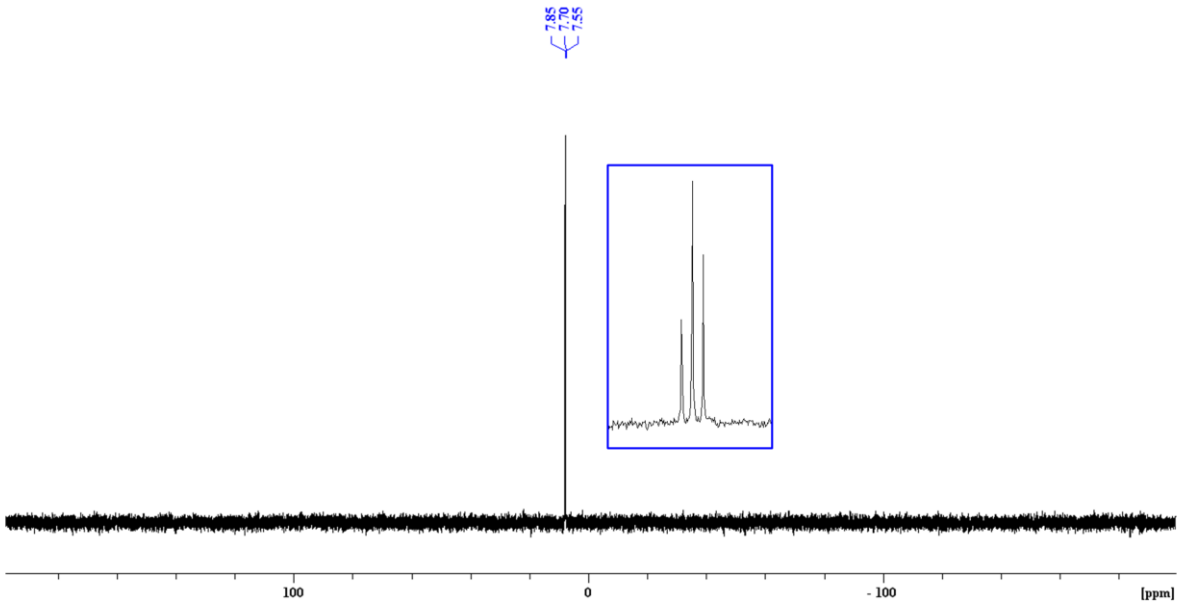

Fig. S10. $^{29}Si\{^{1}H\}$ NMR spectrum of **2** in C_6D_6.

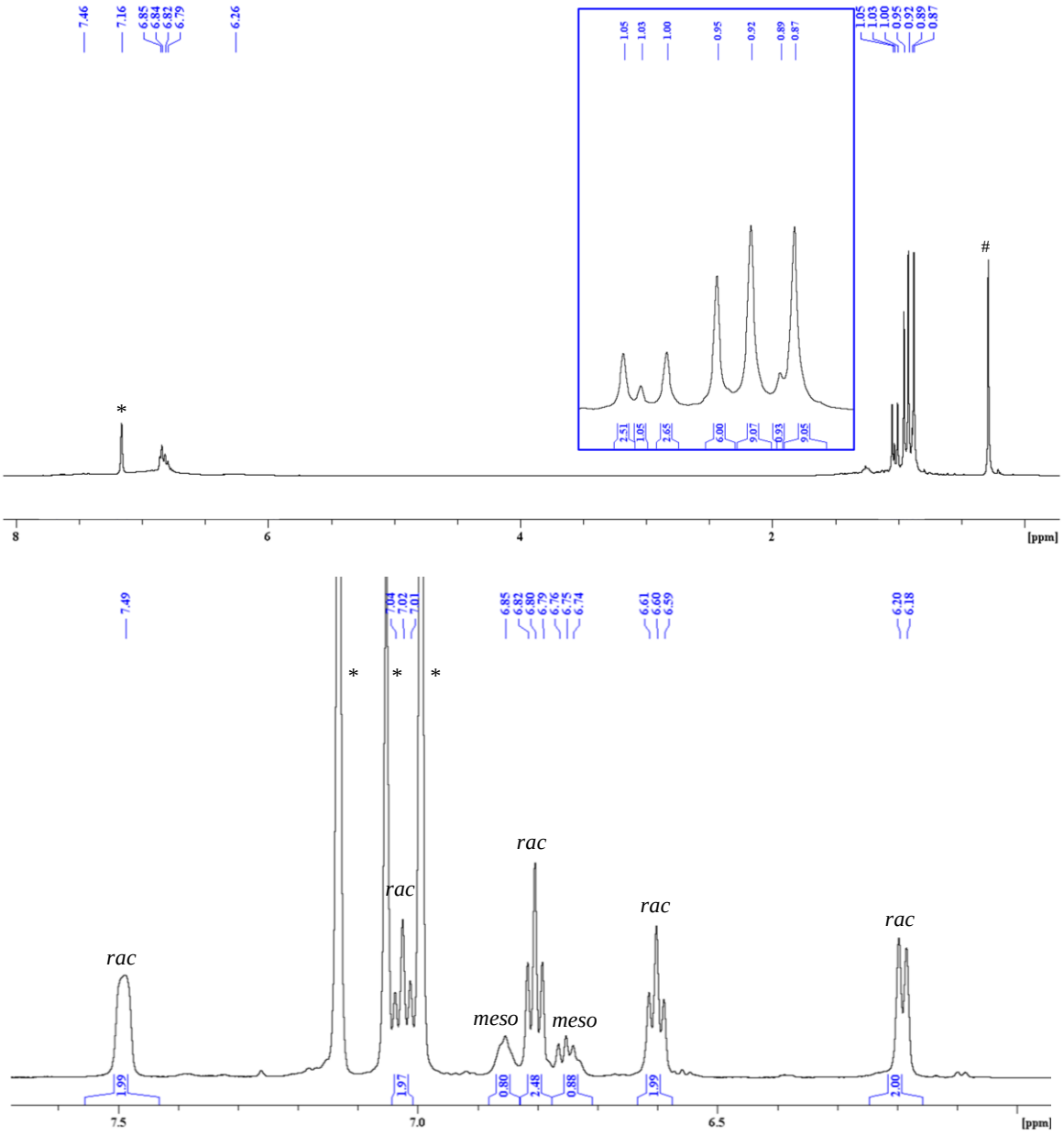

Fig. S11. Top: ^{1}H NMR spectrum of **3** in C_6D_6 (*: C_6D_6 residual, #: silicon grease). Bottom: ^{1}H NMR spectrum of **3** at −20 °C in toluene-d_8 (*: toluene-d_8 residual, *rac*: racemic mixture, *meso*: *meso*-compound).

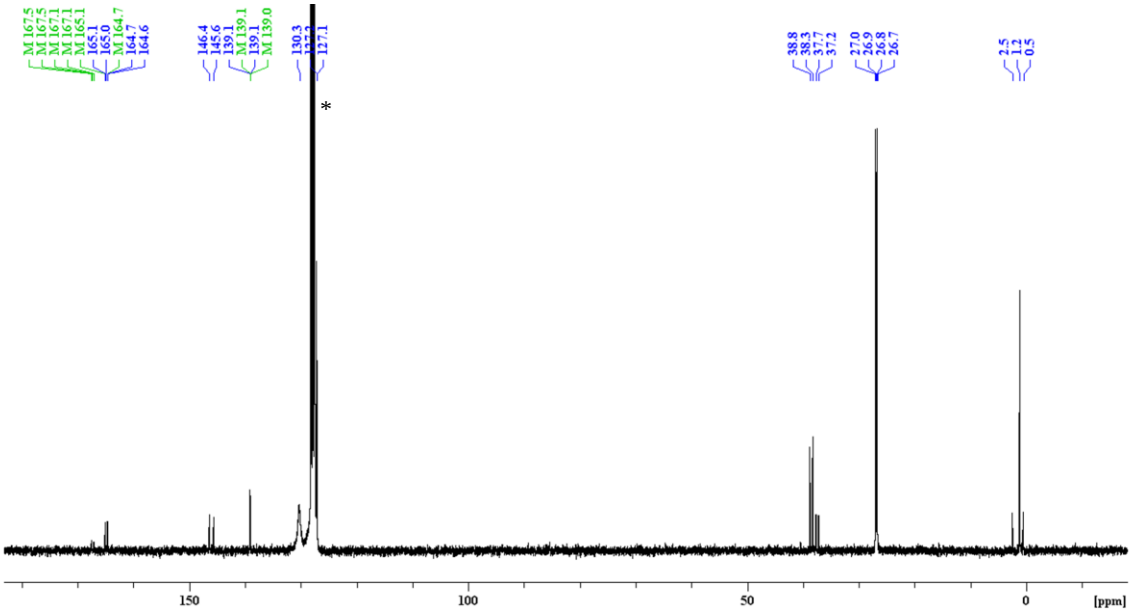

Fig. S12. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6 (*: C_6D_6).

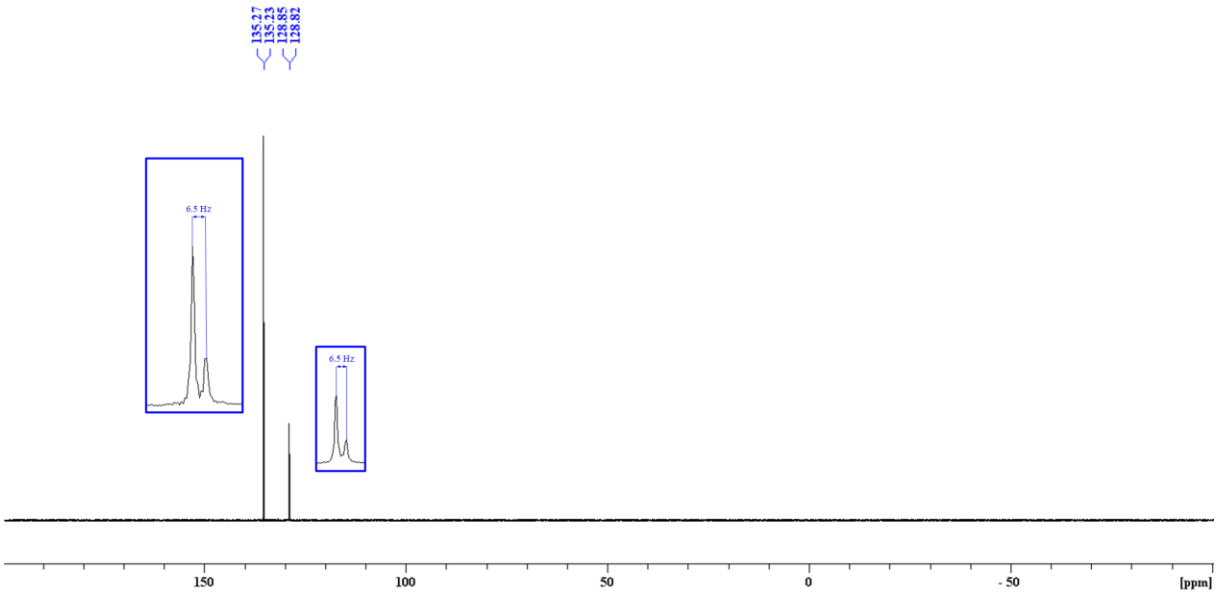

Fig. S13. $^{31}P\{^{1}H\}$ NMR spectrum of **3** in C_6D_6. The inset shows an enlarged section of the spectrum where the peaks corresponding to the different chlorine isotopes are visible.

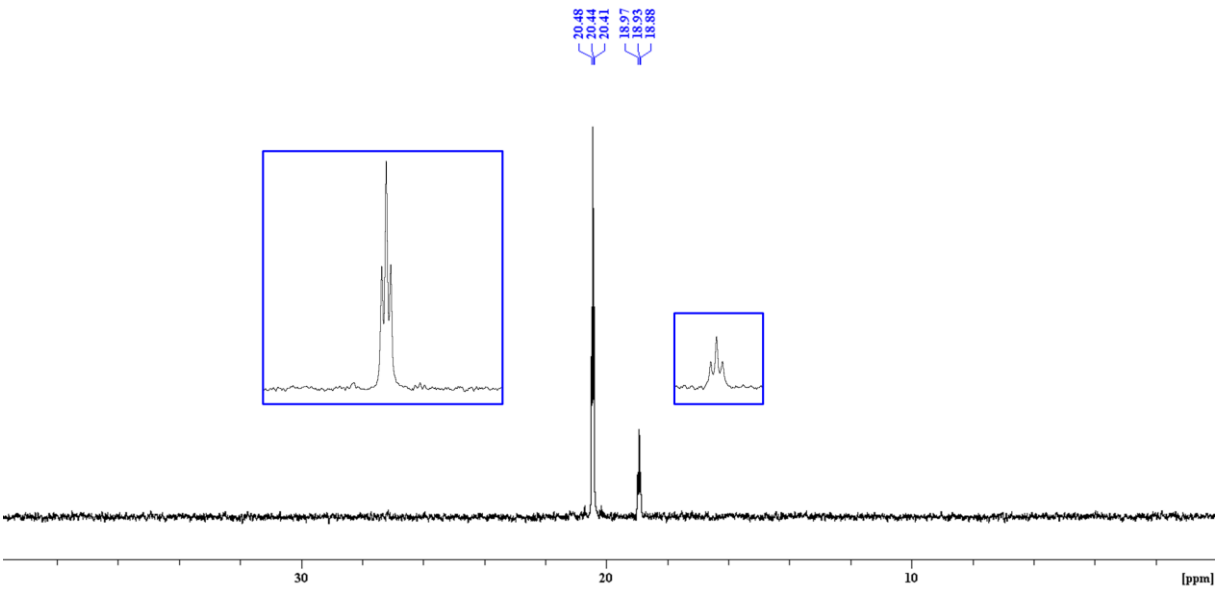

Fig. S14. $^{29}Si\{^{1}H\}$ NMR spectrum of **3** in C_6D_6.

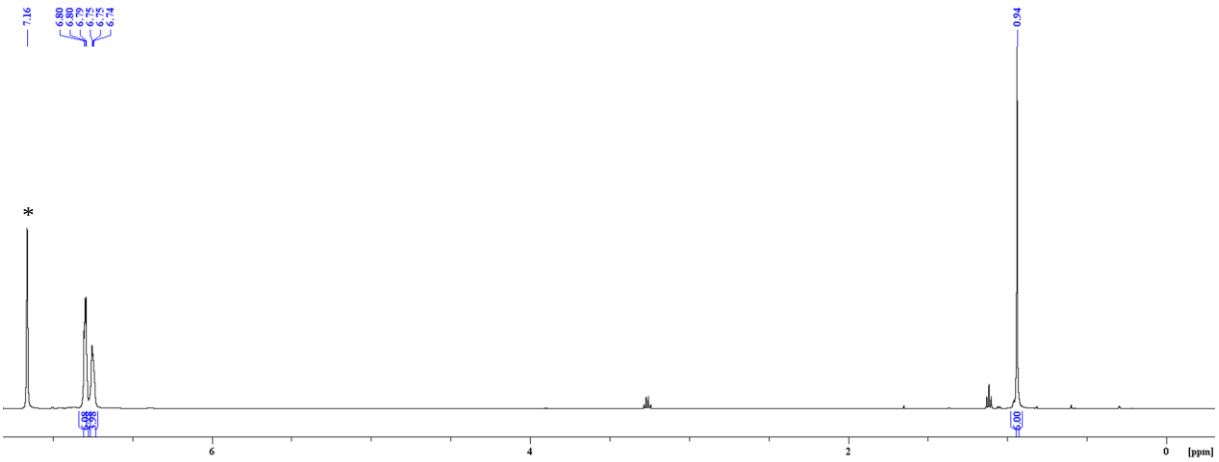

Fig. S15. ^{1}H NMR spectrum of **4** in C_6D_6 (*: C_6D_6 residual).

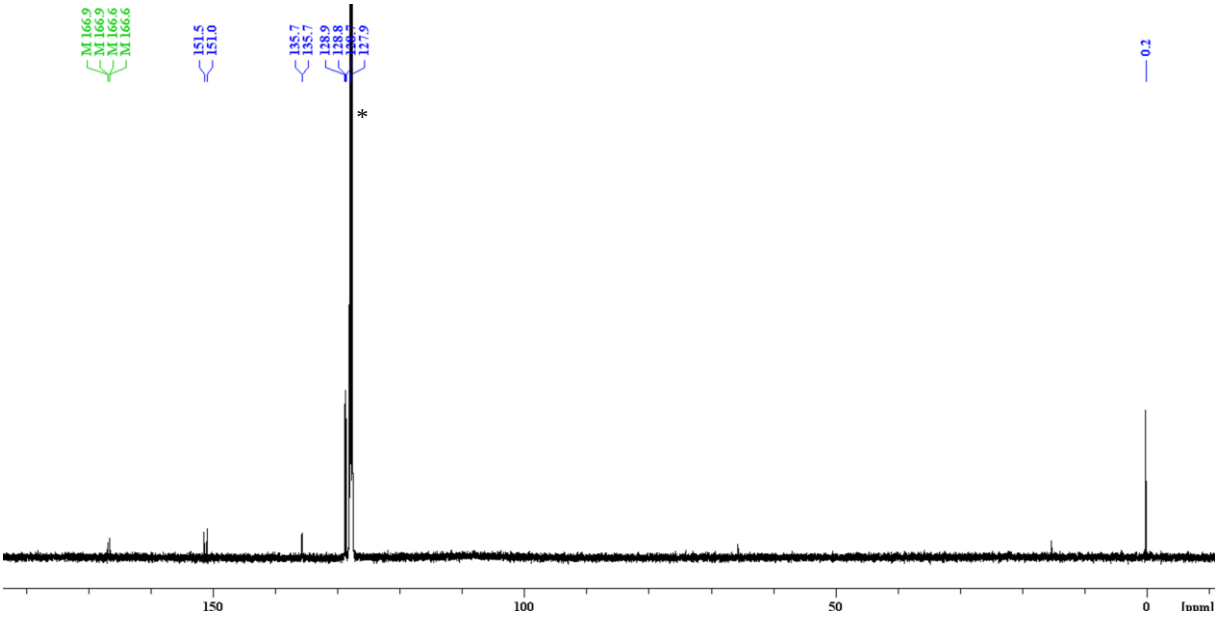

Fig. S16. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in C_6D_6 (*: C_6D_6).

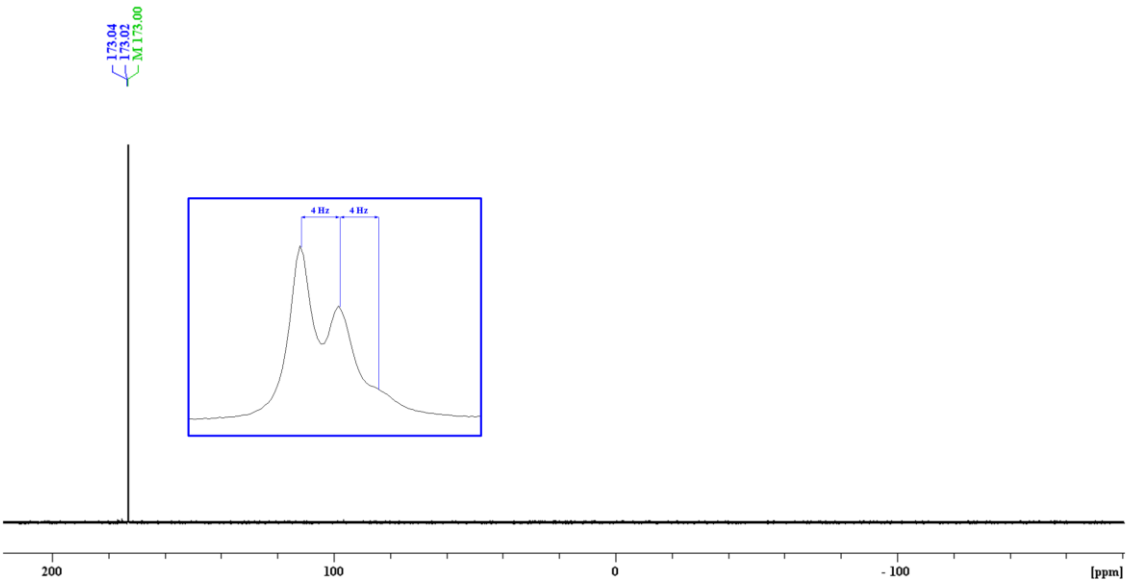

Fig. S17. $^{31}P\{^{1}H\}$ NMR spectrum of **4** in C_6D_6. The inset shows an enlarged section of the spectrum where the peaks corresponding to the different chlorine isotopes are visible. It is noteworthy that the third peak appears only as a shoulder and does not show a well-resolved separation.

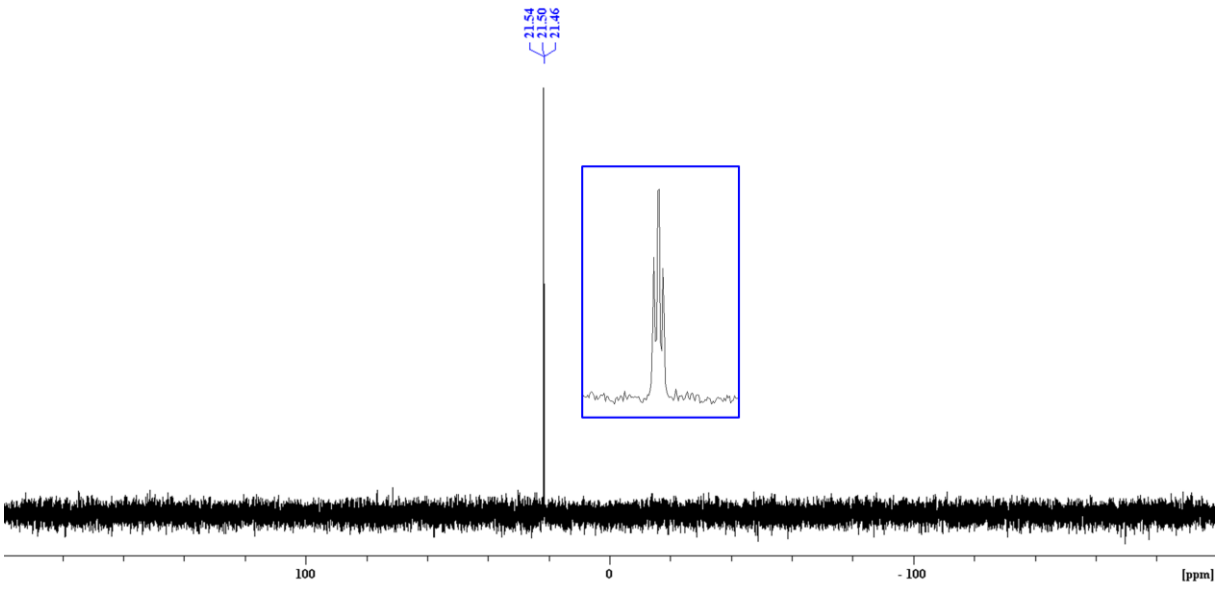

Fig. S18. $^{29}Si\{^{1}H\}$ NMR spectrum of **4** in C_6D_6.

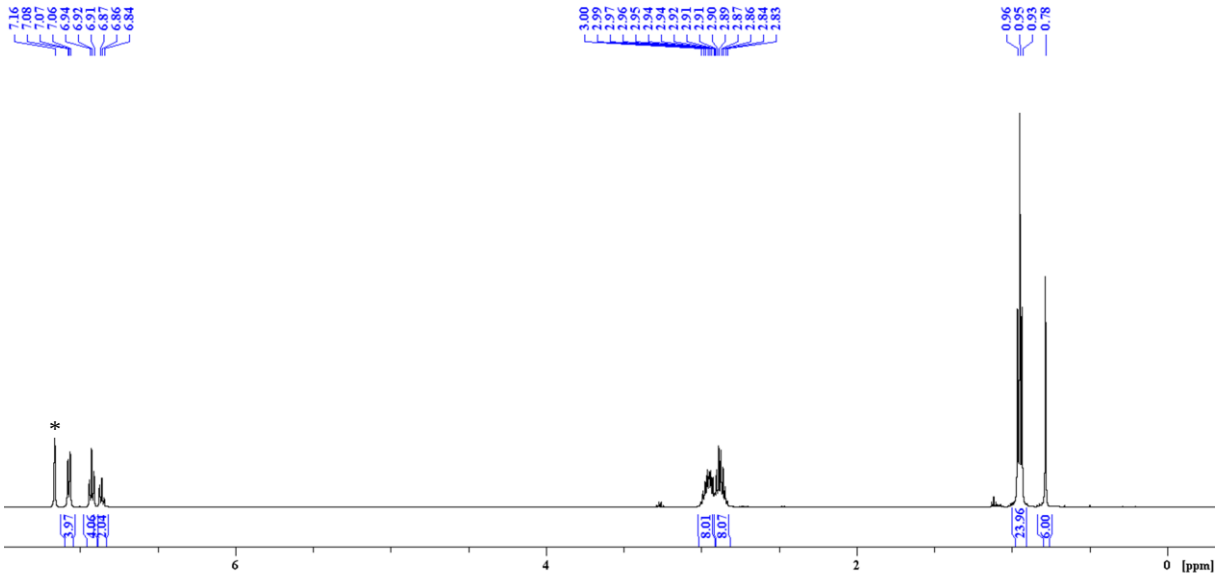

Fig. S19. ^{1}H NMR spectrum of **5** in C_6D_6 (*: C_6D_6 residual).

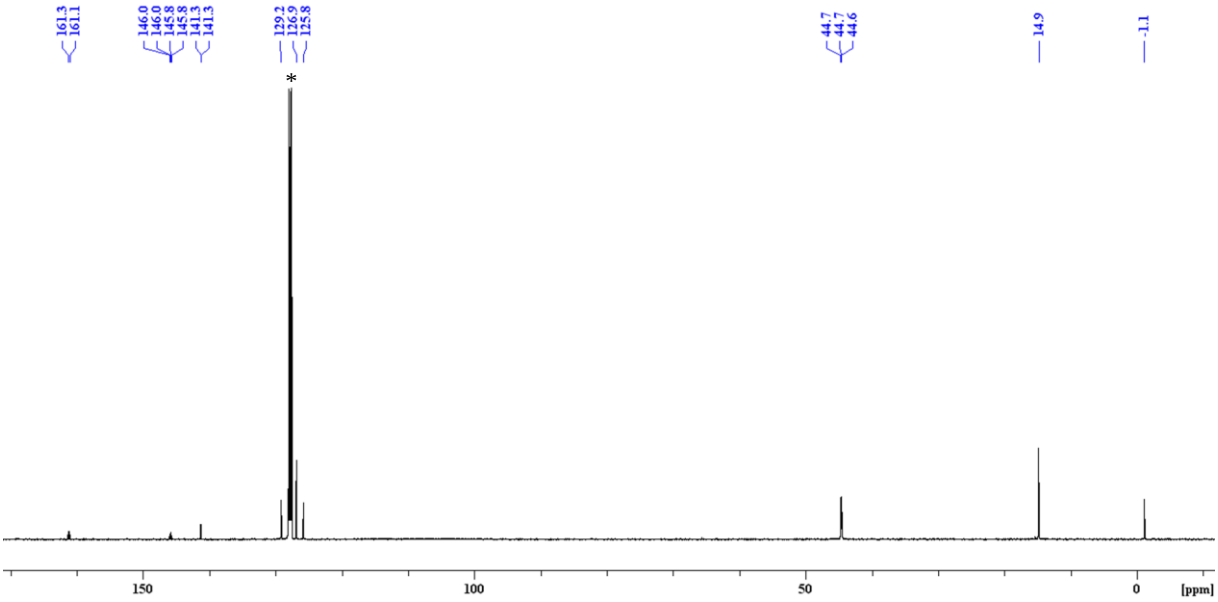

Fig. S20. $^{13}C\{^{1}H\}$ NMR spectrum of **5** in C_6D_6 (*: C_6D_6).

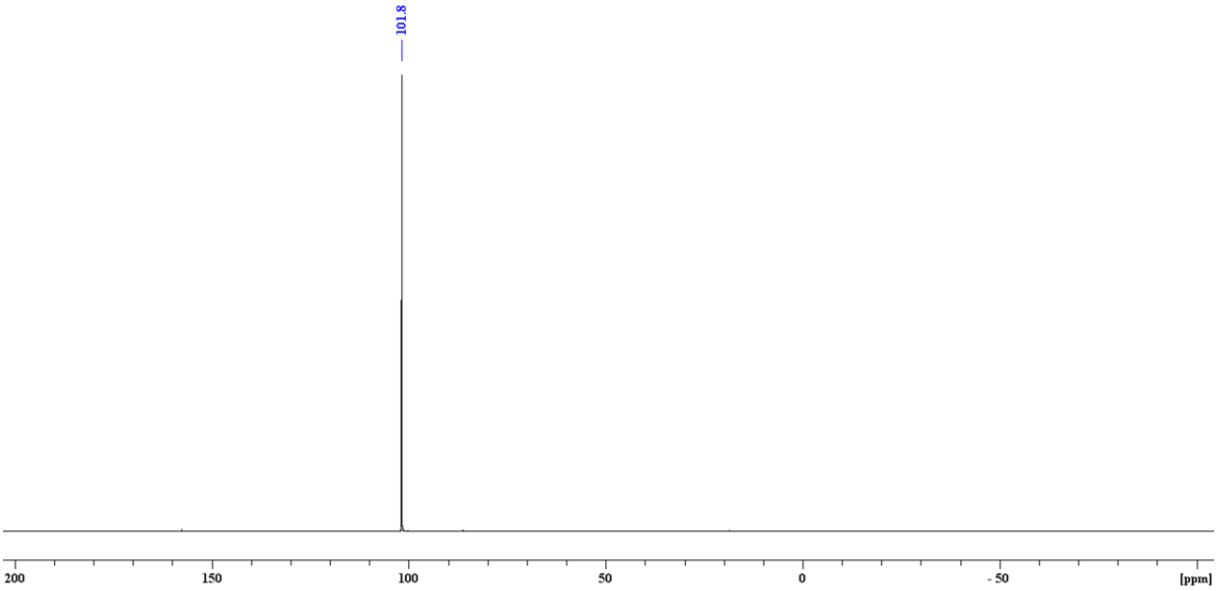

Fig. S21. $^{31}P\{^{1}H\}$ NMR spectrum of **5** in C_6D_6.

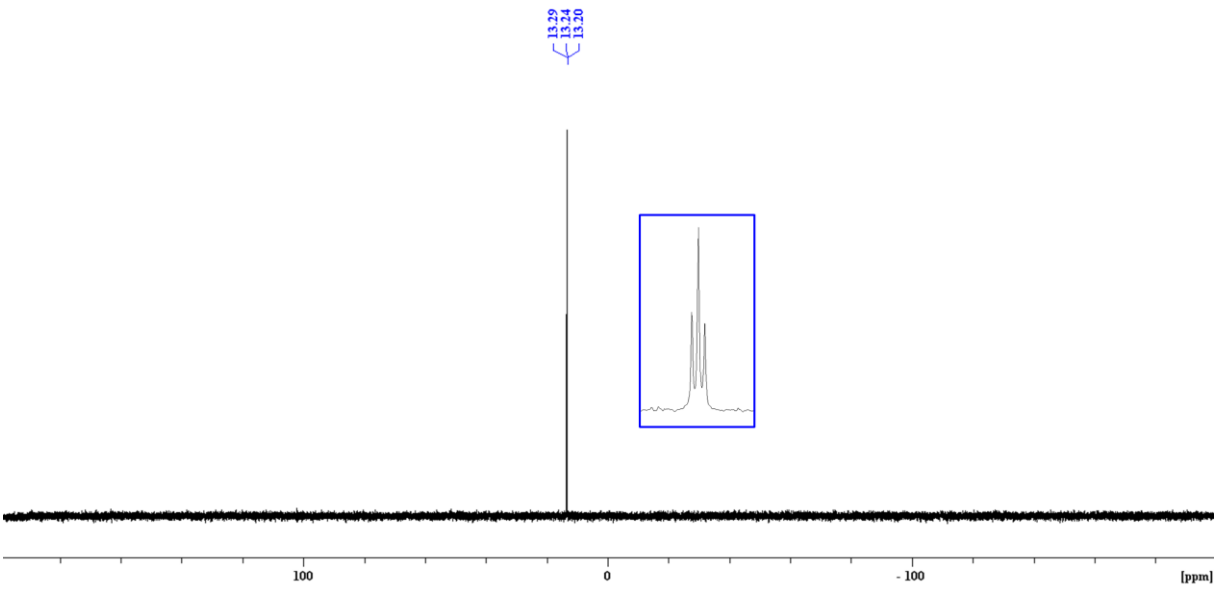

Fig. S22. $^{29}Si\{^{1}H\}$ NMR spectrum of **5** in C_6D_6.

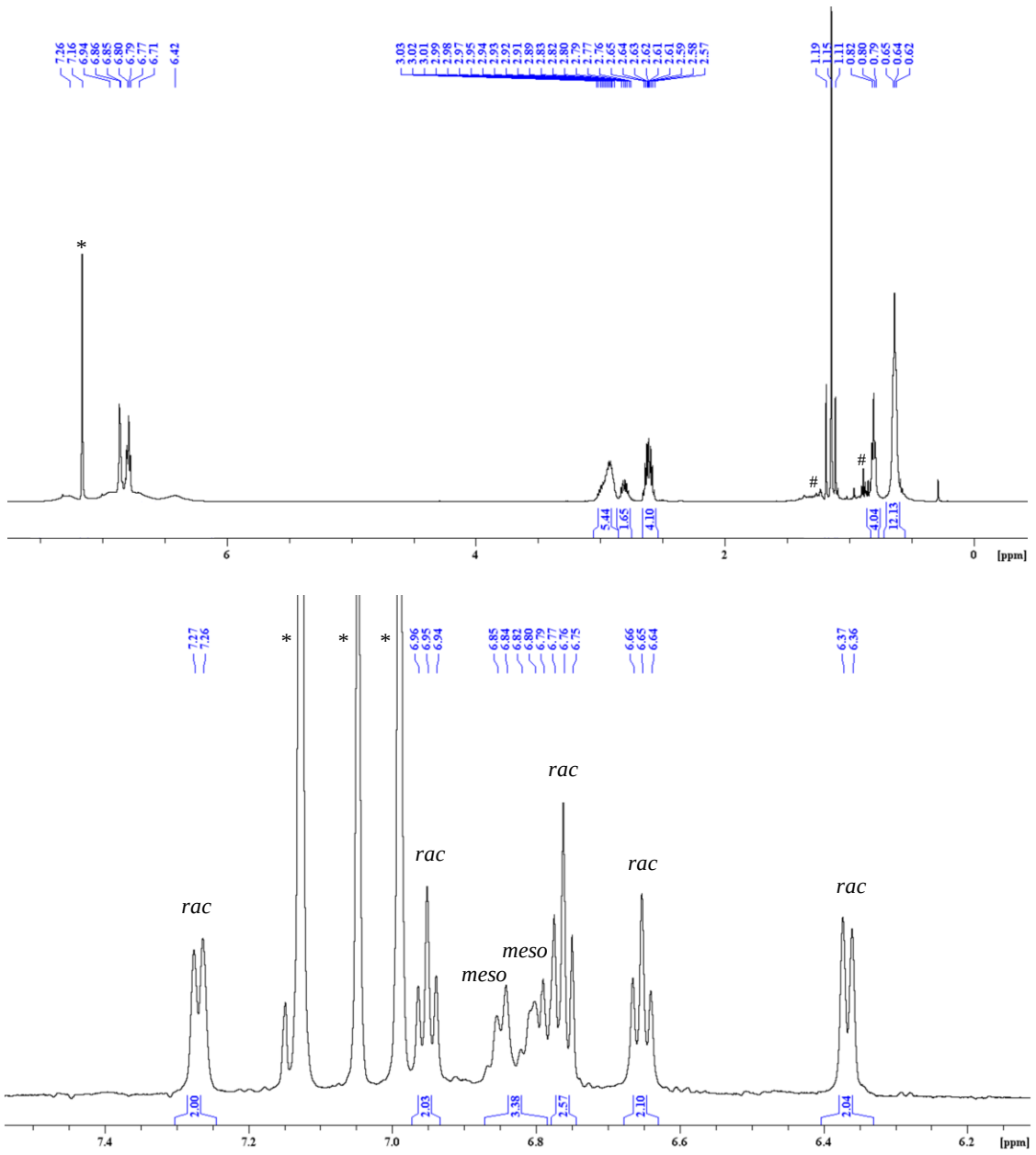

Fig. S23. Top: ^{1}H NMR spectrum of **6** in C_6D_6 (*: C_6D_6. residual, #: *n*-hexane). Bottom: ^{1}H NMR spectrum of **6** at –20 °C in toluene-d_8 (*: toluene-d_8 residual, *rac*: racemic mixture, *meso*: *meso*-compound).

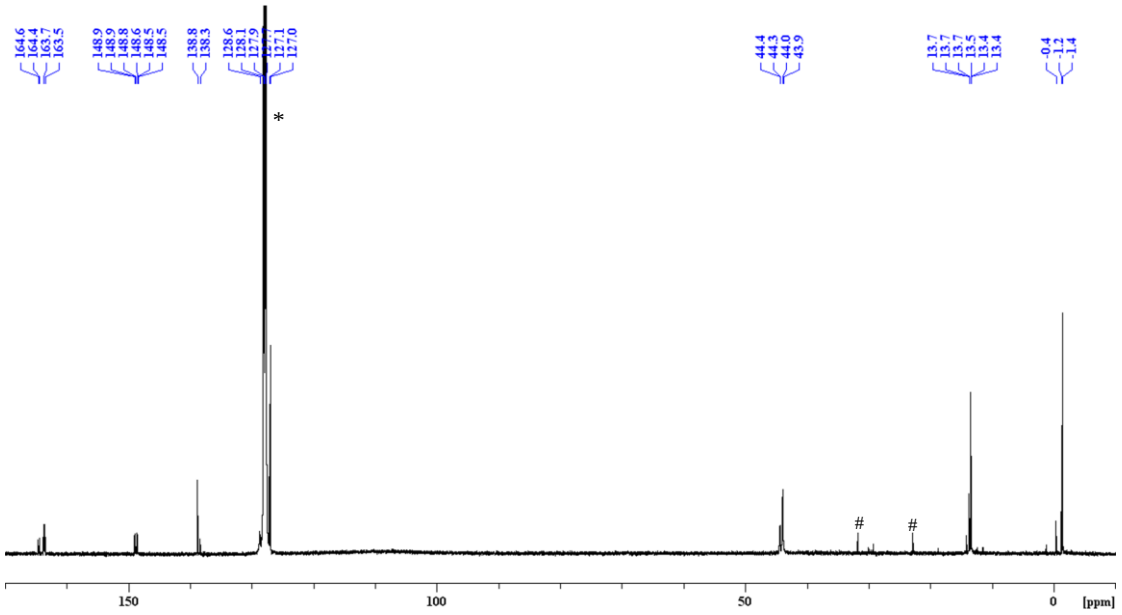

Fig. S24. $^{13}C\{^{1}H\}$ NMR spectrum of **6** in C_6D_6 (*: C_6D_6, #: *n*-hexane).

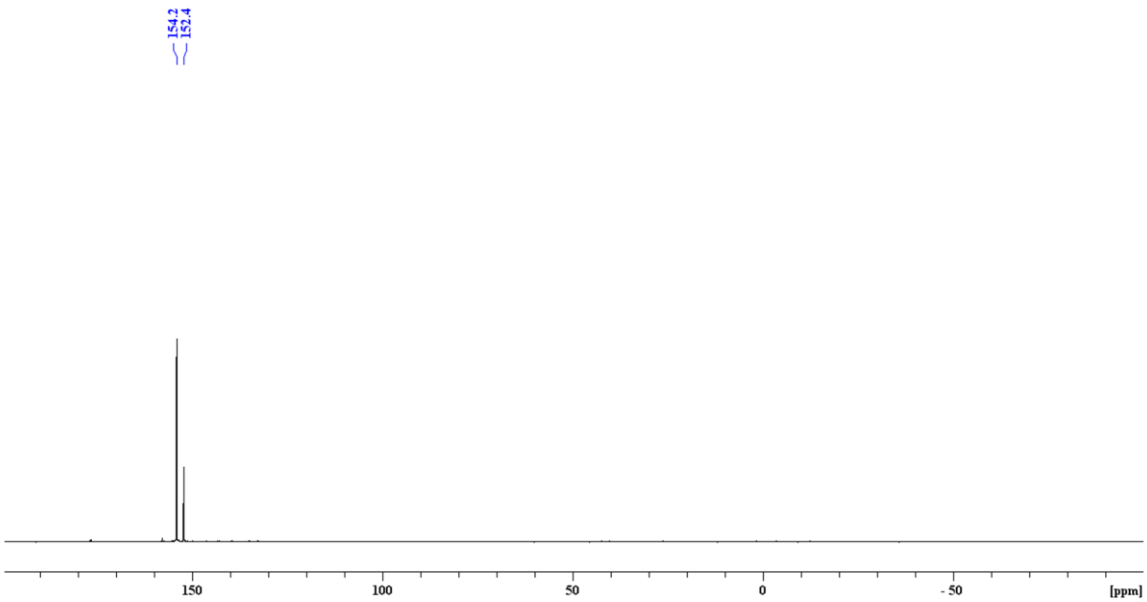

Fig. S25. $^{31}P\{^{1}H\}$ NMR spectrum of **6** in C_6D_6.

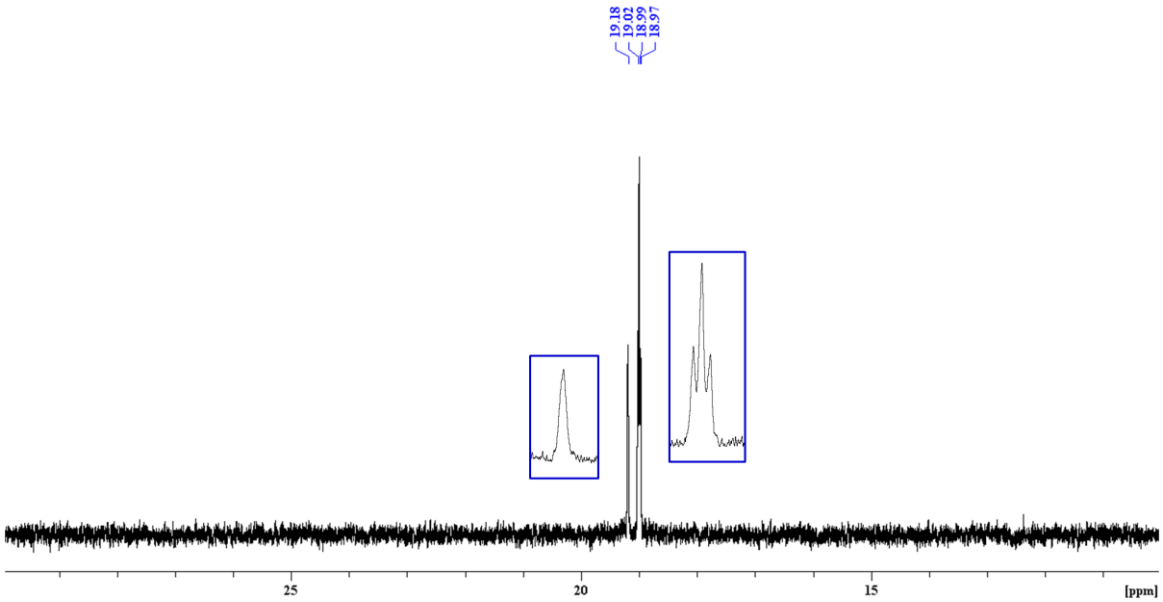

Fig. S26. $^{29}Si\{^{1}H\}$ NMR spectrum of **6** in C_6D_6.

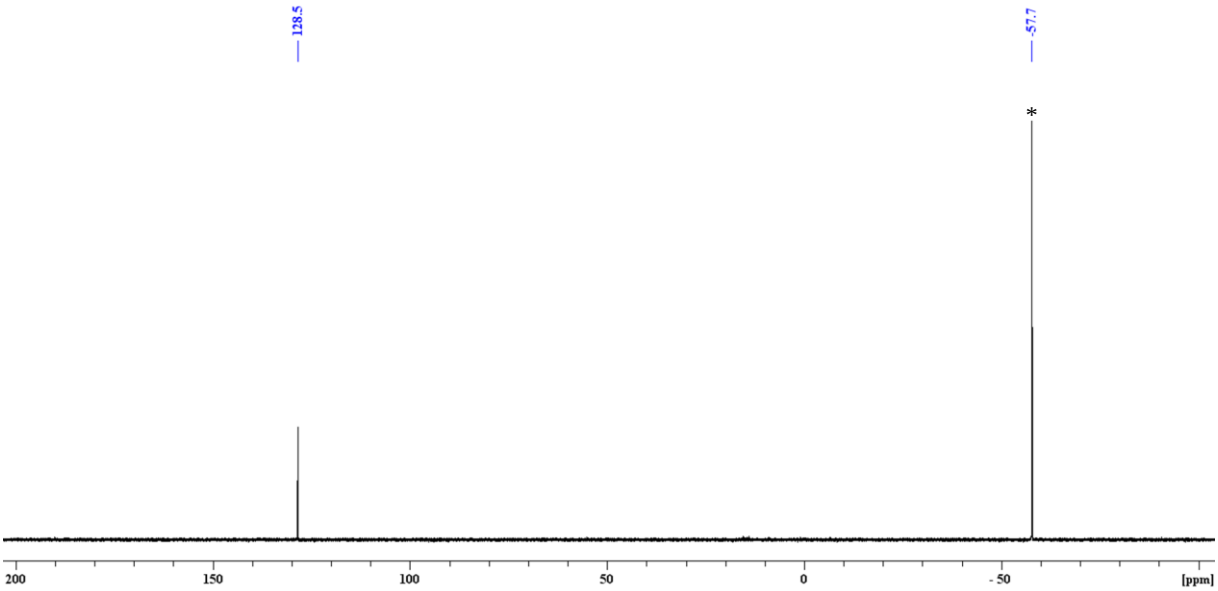

Fig. S27. $^{31}P\{^{1}H\}$ NMR spectrum of ^{t}BuPBr-substituted silole in C_6D_6 (*: $^{t}Bu_5P_5$).

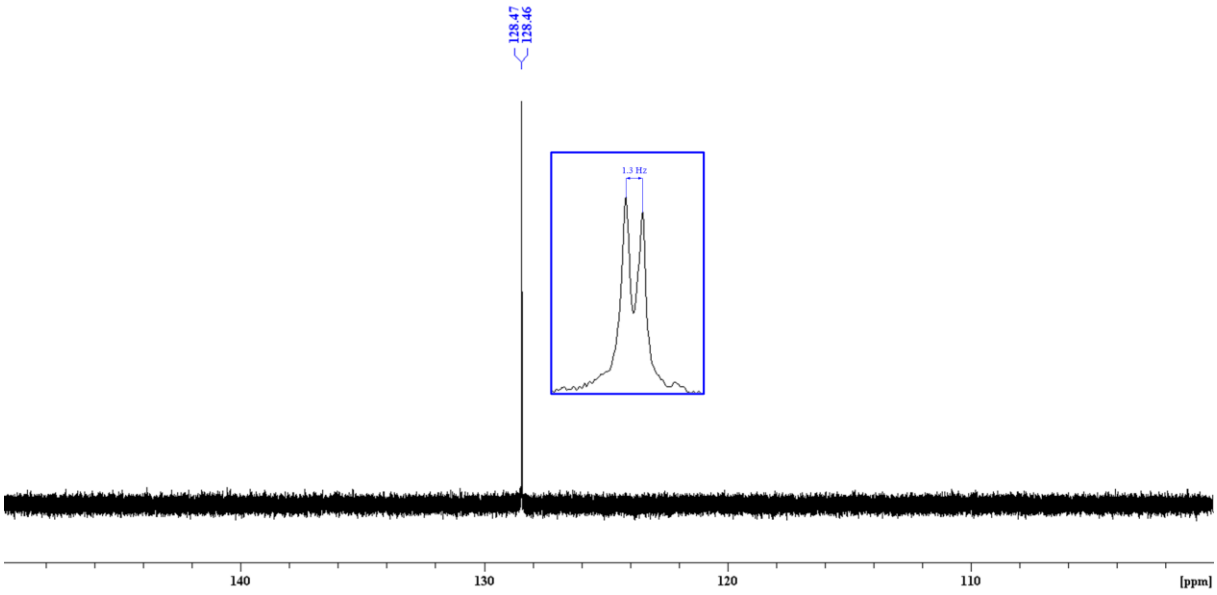

Fig. S28. $^{31}P\{^{1}H\}$ NMR spectrum recorded over a narrow spectral window of ^{t}BuPBr-substituted silole in C_6D_6. The inset shows an enlarged section of the spectrum where the peaks corresponding to the different bromine isotopes are visible.

Crystal structure and refinement details

X-ray crystallographic intensity data were collected using a Rigaku R-Axis RAPID II diffractometer. The diffraction data were solved with the ShelXT (Sheldrick 2015) program and refined with ShelXL managed in Olex2 1.5 (Dolomanov et al. 2009). The model was refined with ShelXL 2018/3 (Sheldrick 2015) using full-matrix least-squares minimization on F^2. The PLATON program (Spek 2020) was used to validate the compounds, and the publication materials were prepared with Mercury (Macrae et al. 2020) and Olex2 1.5 (Dolomanov et al. 2009). The crystallographic data for compounds **1**–**6** were deposited (including fcf files) in the Cambridge Crystallographic Data Centre (CCDC) with the No. 2506206 (**1**), 2506203 (**2**), 2506202 (**3-R,R**), 2506205 (**4**), 2506204 (**5**) and 2506207 (**6-R,R**).

The crystals were found to be stable at low temperatures under a nitrogen atmosphere. A small amount of crystalline material was removed from the sample vial using a spatula under a continuous nitrogen flow and subsequently mixed with perfluorinated oil. The crystals were examined under a microscope to assess their quality and suitability in terms of size and morphology. During an examination period of approximately 30 seconds, partial degradation was observed in several cases, as indicated by the gradual disappearance of crystal edges. The stability varied among samples: compounds 2–4 remained stable for approximately one minute, compound 5 for about 30 seconds, and compound 6 for roughly 10 seconds. Under polarized light, a rapid loss of crystal brightness was also noted, consistent with structural deterioration. Similarly, crystals remaining on the tip of the spatula showed visible disintegration over comparable timescales. To mitigate these effects, the procedure was repeated using a fresh portion of crystalline material. A selected crystal was rapidly isolated from the oil and immediately transferred into a cold nitrogen stream to minimize degradation. The crystal was then mounted on a glass fiber and immobilized in perfluorinated oil under cryogenic conditions. After several attempts, a crystal of suitable quality for further analysis was successfully selected.

Crystal data of **1***:* $C_{26}H_{35}PSi$, *Fwt.*: 406.60, orange, chunk, size: 0.550 x 0.370 x 0.370 mm, monoclinic, space group $P\ 2_1/c$, a = 11.0209(3) Å, b = 9.2749(2) Å, c = 24.0095(6) Å, $\alpha = 90°$, $\beta = 102.914(7)°$, $\gamma = 90°$, V = 2392.12(12) Å^3, T = 136(2) K, $Z = 4$, Z' = 1, $F(000) = 880$, D_x = 1.129 Mg/m^3, μ = 1.540 mm^{-1}.

A crystal of **1** was mounted on a glass fiber. Cell parameters were determined by least-squares using 52582 ($3.775° \leq \theta \leq 68.31°$) reflections.

Intensity data were collected on a Rigaku RAXIS-RAPID II (SPIDER) diffractometer (graphite monochromator; Cu-$K\alpha$ radiation, λ = 1.54187 Å) at 136(2) K in the range $3.778° \leq \theta \leq 68.282°$. A total of 55890 reflections were collected of which 4333 were unique [R(int) = 0.0335, $R(\sigma)$ = 0.0161]; intensities of 4248 reflections were greater than $2\sigma(I)$. Completeness to θ = 0.989.

A numerical absorption correction was applied to the data (the minimum and maximum transmission factors were 0.911381 and 0.950997).

The structure was solved by direct methods (and subsequent difference syntheses).

Anisotropic full-matrix least-squares refinement on F^2 for all non-hydrogen atoms yielded R_1 = 0.0498 and wR^2 = 0.1144 for 1332 [$I>2\sigma(I)$] and R_1 = 0.0511 and wR^2 = 0.1149 for all (4333) intensity data, (number of parameters = 299, goodness-of-fit = 1.309, the maximum and mean shift/esd is 0.001 and 0.000).

The maximum and minimum residual electron density in the final difference map was 0.343 and -0.263e.Å^{-3}.

The weighting scheme applied was $w = 1/[\sigma^2(F_o^2)+(0.0103P)^2+3.2410P]$ where $P = (F_o^2+2F_c^2)/3$.

Hydrogen atomic positions were calculated from assumed geometries except H4. Hydrogen atoms were included in structure factor calculations but they were not refined. The isotropic displacement parameters of the hydrogen atoms were approximated from the U(eq) value of the atom they were bonded to.

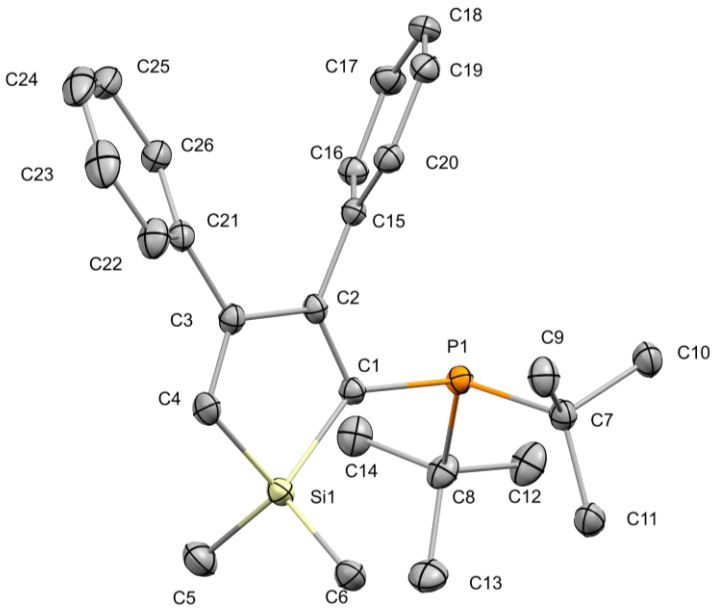

Fig. S29. ORTEP view of an asymmetric unit of **1** (ellipsoids are set to 30% probability, hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and bond angles [°]: P1–C1 1.839(3), Si1–C1 1.893(3), Si1–C4 1.849(3), C1–C2 1.369(3), C3–C4 1.339(4), C2–C3 1.512(4), C1–P1–C7 106.0(1), C1–P1–C8 104.4(1), C7–P1–C8 109.9(1).

Crystal data of **2***:* $C_{34}H_{52}P_2Si$, *Fwt.*: 550.78, orange, platelet, size: 0.5 x 0.45 x 0.08 mm, triclinic, space group *P* -1, *a* = 12.1017(2) Å, *b* = 15.4320(3) Å, *c* = 19.2932(4) Å, α = 76.834(5)°, β = 80.872(6)°, γ = 73.527(5)°, *V* = 3347.25(16) Å^3, *T* = 130(2) K, *Z* = 4, Z' = 2, *F*(000) = 1200, D_x = 1.093 Mg/m^3, μ = 1.652 mm^{-1}.

A crystal of **2** was mounted on a glass fiber. Cell parameters were determined by least-squares using 57436 (3.045° ≤ θ ≤ 68.305°) reflections.

Intensity data were collected on a Rigaku RAXIS-RAPID II (SPIDER) diffractometer (graphite monochromator; Cu-*K*α radiation, λ = 1.54187 Å) at 130(2) K in the range 3.043° ≤ θ ≤ 68.242°. A total of 72337 reflections were collected of which 12003 were unique [*R*(int) = 0.0483, *R*(σ) = 0.0407]; intensities of 10520 reflections were greater than 2σ(*I*). Completeness to θ = 0.978. A numerical absorption correction was applied to the data (the minimum and maximum transmission factors were 0.855576 and 0.966434).

The structure was solved by direct methods (and subsequent difference syntheses).

Anisotropic full-matrix least-squares refinement on F^2 for all non-hydrogen atoms yielded R_1 = 0.0616 and wR^2 = 0.1267 for 1332 [I>2σ(I)] and R_1 = 0.0734 and wR^2 = 0.1318 for all (12003) intensity data, (number of parameters = 695, goodness-of-fit = 1.116, the maximum and mean shift/esd is 0.002 and 0.000).

The maximum and minimum residual electron density in the final difference map was 0.508 and -0.259e.Å^{-3}.

The weighting scheme applied was $w = 1/[\sigma^2(F_o^2)+(0.0388P)^2+3.8687P]$ where $P = (F_o^2+2F_c^2)/3$.

Hydrogen atomic positions were calculated from assumed geometries. Hydrogen atoms were included in structure factor calculations but they were not refined. The isotropic displacement parameters of the hydrogen atoms were approximated from the *U*(eq) value of the atom they were bonded to.

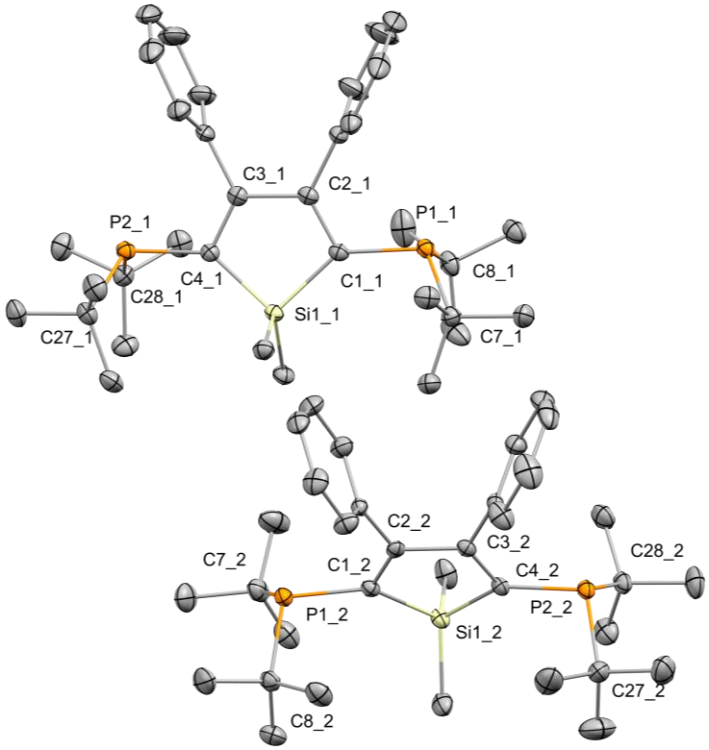

Fig. S30. ORTEP view of an asymmetric unit of **2** (ellipsoids are set to 30% probability, hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and bond angles [°]: P1_1–C1_1 1.842(3), P2_1–C4_1 1.842(3), P1_2–C1_2 1.846(3), P2_2–C4_2 1.841(3), Si1_1–C1_1 1.883(2), Si1_1–C4_1 1.887(3), Si1_2–C1_2 1.881(3), Si1_2–C4_2 1.886(3), C1_1–C2_1 1.365(4), C3_1–C4_1 1.355(3), C1_2–C2_2 1.368(3), C3_2–C4_2 1.362(4), C2_1–C3_1 1.521(4), C2_2–C3_2 1.504(4), C1_1–P1_1–C7_1 105.8(1), C1_1–P1_1–C8_1 103.0(1), C7_1–P1_1–C8_1 110.3(1), C4_1–P2_1–C27_1 105.1(1), C4_1–P2_1–C28_1 105.1(1), C27_1–P2_1–C28_1 109.3(1), C1_2–P1_2–C7_2 105.8(1), C1_2–P1_2–C8_2 104.1(1), C7_2–P1_2–C8_2 109.5(1), C4_2–P2_2–C27_2 103.7(1), C4_2–P2_2–C28_2 104.7(1), C27_2–P2_2–C28_2 111.0(1).

Crystal data of **3(R,R)***:* $C_{26}H_{34}Cl_2P_2Si$, *Fwt.*: 507.46, yellow, needle, size: 0.5 x 0.1 x 0.1 mm, monoclinic, space group *P* 1 2_1/*c* 1, *a* = 11.8923(8) Å, *b* = 19.4430(12) Å, *c* = 12.2900(9) Å, α = 90°, β = 108.735(8)°, γ = 90°, *V* = 2691.1(3) $Å^3$, *T* = 103(2) K, *Z* = 4, *Z'* = 1, *F*(000) = 1072, D_x = 1.252 Mg/m^3, μ = 0.417 mm^{-1}.

A crystal of **3(R,R)** was mounted on a glass fiber. Cell parameters were determined by least-squares using 19850 (3.075° ≤ θ ≤ 25.325°) reflections.

Intensity data were collected on a Rigaku RAXIS-RAPID II (SPIDER) diffractometer (graphite monochromator; Mo-*K*α radiation, λ = 0.71075 Å) at 103(2) K in the range 3.077° ≤ θ ≤ 25.345°. A total of 24402 reflections were collected of which 4797 were unique [*R*(int) = 0.0798, *R*(σ) = 0.0576]; intensities of 3775 reflections were greater than 2σ(*I*). Completeness to θ = 0.974.

A numerical absorption correction was applied to the data (the minimum and maximum transmission factors were 0.961087 and 0.989508).

The structure was solved by dual methods (and subsequent difference syntheses).

Anisotropic full-matrix least-squares refinement on F^2 for all non-hydrogen atoms yielded R_1 = 0.0552 and wR^2 = 0.0890 for 1332 [I>2σ(I)] and R_1 = 0.0800 and wR^2 = 0.0958 for all (4797) intensity data, (number of parameters = 288, goodness-of-fit = 1.094, the maximum and mean shift/esd is 0.001 and 0.000).

The maximum and minimum residual electron density in the final difference map was 0.363 and -0.264e.$Å^{-3}$.

The weighting scheme applied was $w = 1/[\sigma^2(F_o^2)+(0.0264P)^2+2.4260P]$ where $P = (F_o^2+2F_c^2)/3$.

Hydrogen atomic positions were calculated from assumed geometries. Hydrogen atoms were included in structure factor calculations but they were not refined. The isotropic displacement parameters of the hydrogen atoms were approximated from the *U*(eq) value of the atom they were bonded to.

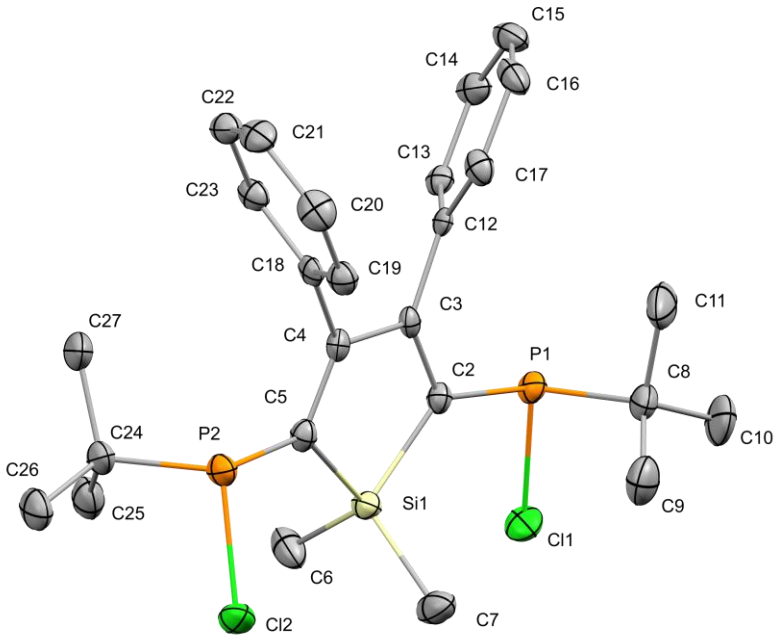

Fig. S31. ORTEP view of an asymmetric unit of **3** (ellipsoids are set to 30% probability, hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and bond angles [°]: P1–C2 1.772(3), P2–C5 1.783(3), Si1–C2 1.887(3), Si1–C5 1.835(3), C2–C3 1.336(3), C4–C5 1.363(4), C3–C4 1.476(4), C2–P1–C8 102.6(1), C2–P1–Cl1 97.90(9), C8–P1–Cl1 99.3(1), C5–P2–C24 104.4(1), C5–P2–Cl2 101.11(9), C24–P2–Cl2 99.8(1).

Crystal data of **4***:* $C_{18}H_{16}Cl_4P_2Si$, *Fwt.*: 464.14, colourless, platelet, size: 0.5 x 0.25 x 0.15 mm, triclinic, space group *P* -1, a = 7.7008(4) Å, b = 9.6319(4) Å, c = 14.6801(7) Å, α = 76.479(5)°, β = 83.334(6)°, γ = 89.034(6)°, V = 1051.48(9) Å^3, T = 143.15 K, Z = 2, Z' = 2, F(000) = 472, D_x = 1.466 Mg/m^3, μ = 0.772 mm^{-1}.

A crystal of **4** was mounted on a glass fiber. Cell parameters were determined by least-squares using 46581 (3.17° ≤ θ ≤ 27.47°) reflections.

Intensity data were collected on a Rigaku RAXIS-RAPID II (SPIDER) diffractometer (graphite monochromator; Mo-*K*α radiation, λ = 0.71075Å) at 143(2) K in the range 3.169° ≤ θ ≤ 26.022°. A total of 51535 reflections were collected of which 4113 were unique [R(int) = 0.0598, R(σ) = 0.0241]; intensities of 3684 reflections were greater than 2σ(I). Completeness to θ = 0.993.

A numerical absorption correction was applied to the data (the minimum and maximum transmission factors were 0.829797 and 0.949980).

The structure was solved by dual methods (and subsequent difference syntheses).

Anisotropic full-matrix least-squares refinement on F^2 for all non-hydrogen atoms yielded R_1 = 0.0452 and wR^2 = 0.0864 for 1332 [I>2σ(I)] and R_1 = 0.0553 and wR^2 = 0.0900 for all (4113) intensity data, (number of parameters = 228, goodness-of-fit = 1.129, the maximum and mean shift/esd is 0.001 and 0.000).

The maximum and minimum residual electron density in the final difference map was 0.338 and -0.343e.Å^{-3}.

The weighting scheme applied was $w = 1/[\sigma^2(F_o^2)+(0.0222P)^2+1.5015P]$ where $P = (F_o^2+2F_c^2)/3$.

Hydrogen atomic positions were calculated from assumed geometries. Hydrogen atoms were included in structure factor calculations but they were not refined. The isotropic displacement parameters of the hydrogen atoms were approximated from the U(eq) value of the atom they were bonded to.

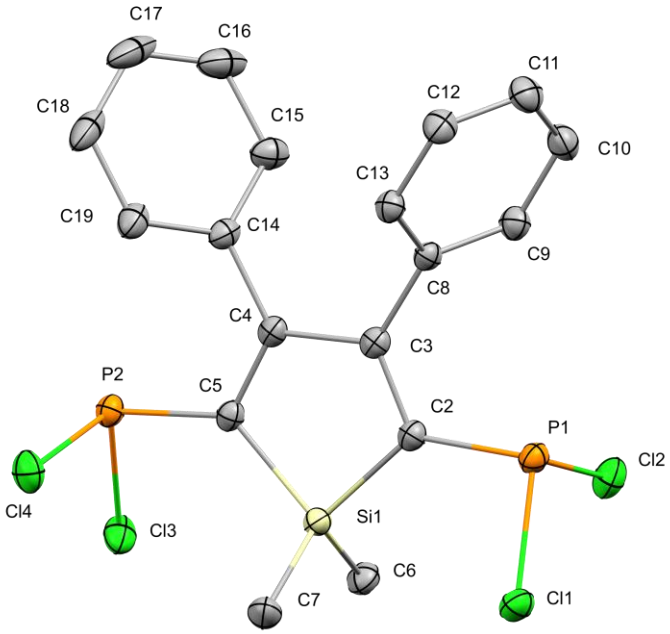

Fig. S32. ORTEP view of an asymmetric unit of **4** (ellipsoids are set to 30% probability, hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and bond angles [°]: P1–C2 1.808(3), P2–C5 1.802(3), Si1–C2 1.883(3), Si1–C5 1.885(3), C2–C3 1.362(3), C4–C5 1.364(4), C3–C4 1.509(4), C2–P1–Cl1 98.3(1), C2–P1–Cl2 99.7(1), Cl1–P1–Cl2 97.63(4), C5–P2–Cl3 98.6(1), C5–P2–Cl4 99.5(1), Cl3–P2–Cl4 98.17(5).

Crystal data of **5***:* $C_{34}H_{56}N_4P_2Si$, *Fwt.*: 610.85, yellow, chunk, size: 0.5 x 0.35 x 0.35 mm, triclinic, space group *P* -1, *a* = 12.2422(9) Å, *b* = 12.6991(10) Å, *c* = 13.8765(10) Å, α = 111.787(8)°, β = 94.422(7)°, γ = 114.409(8)°, *V* = 1755.1(3) $Å^3$, *T* = 138.15 K, *Z* = 2, Z' = 1, *F*(000) = 664, D_x = 1.156 Mg/m^3, μ = 0.186 mm^{-1}.

A crystal of **5** was mounted on a glass fiber. Cell parameters were determined by least-squares using 56089 ($3.030° \leq \theta \leq 26.170°$) reflections.

Intensity data were collected on a Rigaku RAXIS-RAPID II (SPIDER) diffractometer (Graphite Monochromator; Mo-*K* α radiation, λ = 0.7107 Å) at 139(2) K in the range $3.027° \leq \theta \leq 25.349°$. A total of 56478 reflections were collected of which 6396 were unique [*R*(int) = 0.1949, *R(*σ) = 0.1033]; intensities of 4552 reflections were greater than 2*(*σ(*I*). Completeness to θ = 0.995.

An empirical absorption correction was applied to the data (the minimum and maximum transmission factors were 0.6540 and 1.0000).

The structure was solved by direct methods (and subsequent difference syntheses).

Anisotropic full-matrix least-squares refinement on F^2 for all non-hydrogen atoms yielded R_1 = 0.0744 and wR^2 = 0.1691 for 1332 [$I>2\sigma(I)$] and R_1 = 0.1136 and wR^2 = 0.1845 for all (6396) intensity data, (number of parameters = 380, goodness-of-fit = 1.035, the maximum and mean shift/esd is 0.000 and 0.000).

The maximum and minimum residual electron density in the final difference map was 0.839 and -0.372e.$Å^{-3}$.

The weighting scheme applied was $w = 1/[\sigma^2(F_o^2)+(0.1010P)^2]$ where $P = (F_o^2+2F_c^2)/3$.

Hydrogen atomic positions were calculated from assumed geometries. Hydrogen atoms were included in structure factor calculations but they were not refined. The isotropic displacement parameters of the hydrogen atoms were approximated from the *U*(eq) value of the atom they were bonded to. Structure 5 is refined as a twin crystal structure in which, the ratio is 0.774(3) and 0.226(3) (based on estimates from the Olex program).

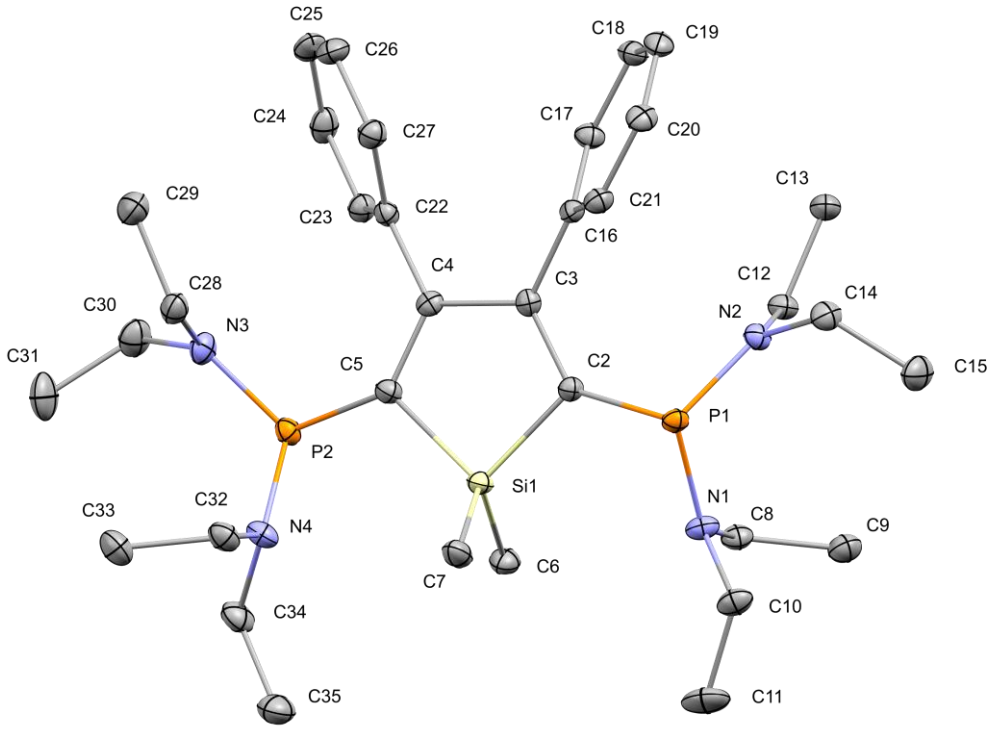

Fig. S33. ORTEP view of an asymmetric unit of **5** (ellipsoids are set to 30% probability, hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and bond angles [°]: P1–C2 1.813(4), P2–C5 1.810(4), Si1–C2 1.883(5), Si1–C5 1.888(4), C2–C3 1.367(6), C4–C5 1.373(7), C3–C4 1.518(5), C2–P1–N1 99.8(2), C2–P1–N2 105.7(2), N1–P1–N2 111.7(2), C5–P2–N3 105.6(2), C5–P2–N4 99.6(2), N3–P2–N4 111.8(2).

Crystal data of **6(R,R)***:* $C_{26}H_{36}Cl_2N_2P_2Si$, *Fwt.*: 537.50, yellow, chunk, size: 0.4 x 0.34 x 0.3 mm, monoclinic, space group *P* 1 $2_1/c$ 1, a = 6.4771(6) Å, b = 20.348(2) Å, c = 22.374(2) Å, α = 90°, β = 97.944(7)°, γ = 90°, V = 2920.5(5) Å^3, T = 103.15 K, Z = 4, Z' = 1, F(000) = 1136, D_x = 1.222 Mg/m^3, μ = 0.390 mm^{-1}.

A crystal of **6(R,R)** was mounted on a glass fiber. Cell parameters were determined by least-squares using 51246 (3.14° ≤ θ ≤ 26.095°) reflections.

Intensity data were collected on a Rigaku RAXIS-RAPID II (SPIDER) diffractometer (graphite monochromator; Mo-*K*α radiation, λ = 0.71075 Å) at 103(2) K in the range 3.141° ≤ θ ≤ 26.112°. A total of 78739 reflections were collected of which 78739 were unique [R(int) = 0.0754, R(σ) = 0.2060]; intensities of 34224 reflections were greater than 2σ(I). Completeness to θ = 0.997.

An empirical absorption correction was applied to the data (the minimum and maximum transmission factors were 0.395 and 1.000).

The structure was solved by direct methods (and subsequent difference syntheses).

Anisotropic full-matrix least-squares refinement on F^2 for all non-hydrogen atoms yielded R_1 = 0.1207 and wR^2 = 0.3021 for 1332 [I>2σ(I)] and R_1 = 0.2261 and wR^2 = 0.3646 for all (78739) intensity data, (number of parameters = 282, goodness-of-fit = 1.064, the maximum and mean shift/esd is 0.000 and 0.000).

The maximum and minimum residual electron density in the final difference map was 0.680 and -0.771e.Å^{-3}.

The weighting scheme applied was $w = 1/[\sigma^2(F_o^2)+(0.1483P)^2+3.0156P]$ where $P = (F_o^2+2F_c^2)/3$.

Hydrogen atomic positions were calculated from assumed geometries. Hydrogen atoms were included in structure factor calculations but they were not refined. The isotropic displacement parameters of the hydrogen atoms were approximated from the U(eq) value of the atom they were bonded to.

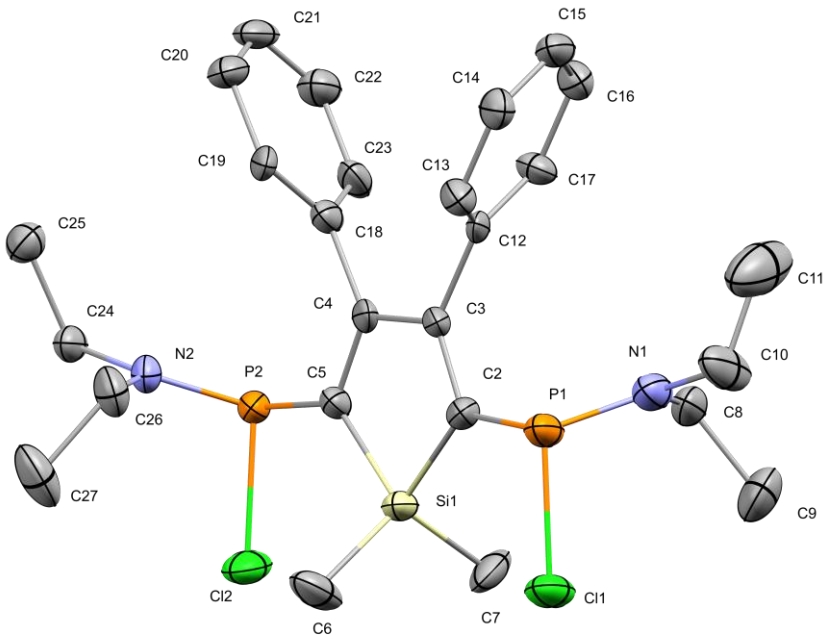

Fig. S34. ORTEP view of an asymmetric unit of **6** (ellipsoids are set to 30% probability, hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and bond angles [°]: P1–C2 1.82(1), P2–C5 1.83(1), Si1–C2 1.90(1), Si1–C5 1.89(1), C2–C3 1.34(1), C4–C5 1.34(1), C3–C4 1.52(2), C2–P1–N1 103.0(6), C2–P1–Cl1 97.0(4), N1–P1–Cl1 105.7(4), C5–P2–N2 102.8(5), C5–P2–Cl2 96.7(4), N2–P2–Cl2 105.0(4).

Table S1. Crystal data and structure refinement details of **1**–**3**.

SXRD number	**1**	**2**	**3(R,R)**
CCDC number	2506206	2506203	2506202
Empirical formula	$C_{26}H_{35}PSi$	$C_{34}H_{52}P_2Si$	$C_{26}H_{34}Cl_2P_2Si$
Formula weight (g/mol)	406.60	550.78	507.46
Temperature (K)	136(2)	130.15	103.15
Radiation and wavelength	Cu-K_α, λ =1.54187 Å	Cu-K_α, λ =1.54187 Å	Mo-K_α, λ =0.71075 Å
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P\ 2_1/c$	$P\ -1$	$P\ 2_1/c$
Unit cell dimensions	a = 11.0209(3) Å b = 9.2749(2) Å c = 24.0095(6) Å α = 90° β = 102.914(7)° γ = 90°	a = 12.1017(2) Å b = 15.4320(3) Å c = 19.2932(4) Å α = 76.834(5)° β = 80.872(6)° γ = 73.527(5)°	a = 11.8923(8) Å b = 19.4430(12) Å c = 12.2900(9) Å α = 90° β = 108.735(8)° γ = 90°
Volume	2392.12(12) Å^3	3347.25(16) Å^3	2691.1(3) Å^3
Z, Z'	4, 1	4, 2	4, 1
Density (calculated)	1.129 Mg/m^3	1.093 Mg/m^3	1.252 Mg/m^3
Absorption coefficient, μ	1.540 mm^{-1}	1.652 mm^{-1}	0.417 mm^{-1}
F(000)	880	1200	1072
Crystal colour	orange	orange	yellow
Crystal description	block	platelet	needle
Crystal size	0.550 × 0.370 × 0.370 mm	0.5 × 0.45 × 0.08 mm	0.5 × 0.1 × 0.1 mm
Absorption correction	numerical	numerical	numerical
Max. and min. transmission	0.911381 and 0.950997	0.855576 and 0.966434	0.961087 and 0.989508
θ-range for data collection	3.778° ≤ θ ≤ 68.282°	3.043° ≤ θ ≤ 68.242°	3.077° ≤ θ ≤ 25.345°
Index ranges	−13 ≤ h ≤ 13; −10 ≤ k ≤ 10; −28 ≤ l ≤ 28	−14 ≤ h ≤ 14; −18 ≤ k ≤ 18; −23 ≤ l ≤ 23	−14 ≤ h ≤ 14; −23 ≤ k ≤ 23; −14 ≤ l ≤ 14
Reflections collected	55890	72337	24402
Completeness to 2θ	0.990	0.980	0.980
Independent reflections	4333 [R(int) =0.0335]	12003 [R(int) =0.0483]	4797 [R(int) =0.0798]
Reflections I>2σ(I)	4248	10520	3775
Data / restraints / parameters	4333 / 0 / 299	12003 /0 / 695	4797 /0 / 288
Goodness-of-fit on F^2	1.309	1.116	1.094
Final R indices [I>2σ(I)]	R_1 = 0.0498, wR^2 = 0.1144	R_1 = 0.0616, wR^2 = 0.1267	R_1 = 0.0552, wR^2 = 0.0890
R indices (all data)	R_1 = 0.0511, wR^2 = 0.1149	R_1 = 0.0734, wR^2 = 0.1318	R_1 = 0.0800, wR^2 = 0.0958
Max. and mean shift/esd	0.001; 0.000	0.002; 0.000	0.001; 0.000
Largest diff. peak and hole	0.343; -0.263 e.Å^{-3}	0.508; -0.259 e.Å^{-3}	0.363; -0.264 e.Å^{-3}

Table S1. (contd.). Crystal data and structure refinement details of **4**–**6**.

SXRD structure	**4**	**5**	**6(R,R)**
CCDC number	2506205	2506204	2506207
Empirical formula	$C_{18}H_{16}Cl_4P_2Si$	$C_{34}H_{56}N_4P_2Si$	$C_{26}H_{36}Cl_2N_2P_2Si$
Formula weight (g/mol)	464.14	610.85	537.50
Temperature (K)	143.15	138.15	103.15
Radiation and wavelength	Mo-K_α, λ =0.71075 Å	Mo-K_α, λ =0.7107 Å	Mo-K_α, λ =0.71075 Å
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\,\bar{1}$	$P\,\bar{1}$	$P\,2_1/c$
Unit cell dimensions	a = 7.7008(4) Å b = 9.6319(4) Å c = 14.6801(7) Å α = 76.479(5)° β = 83.334(6)° γ = 89.034(6)°	a = 12.2422(9) Å b = 12.6991(10) Å c = 13.8765(10) Å α = 111.787(8)° β = 94.422(7)° γ = 114.409(8)°	a = 6.4771(6) Å b = 20.348(2) Å c = 22.374(2) Å α = 90° β = 97.944(7)° γ = 90°
Volume	1051.48(9) Å^3	1755.1(3) Å^3	2920.5(5) Å^3
Z, Z'	2, 1	2, 1	4, 1
Density (calculated)	1.466 Mg/m^3	1.156 Mg/m^3	1.222 Mg/m^3
Absorption coefficient, μ	0.772 mm^{-1}	0.186 mm^{-1}	0.390 mm^{-1}
F(000)	472	664	1136
Crystal colour	colourless	yellow	yellow
Crystal description	platelet	block	block
Crystal size	0.5 × 0.25 × 0.15 mm	0.5 × 0.35 × 0.35 mm	0.4 × 0.34 × 0.3 mm
Absorption correction	numerical	empirical	empirical
Max. and min. transmission	0.829797 and 0.949980	0.317 and 2.244	0.395 and 1.000
θ-range for data collection	3.169° ≤ θ ≤ 26.022°	3.027° ≤ θ ≤ 25.349°	3.141° ≤ θ ≤ 26.112°
Index ranges	$-9 \le h \le 9$; $-11 \le k \le 11$; $-18 \le l \le 18$	$-14 \le h \le 14$; $-15 \le k \le 15$; $-16 \le l \le 16$	$-7 \le h \le 7$; $-25 \le k \le 25$; $-27 \le l \le 27$
Reflections collected	51535	56478	78739
Completeness to 2θ	0.992	0.995	0.998
Independent reflections	4113 [R(int) = 0.0598]	6396 [R(int) = 0.1949]	78739 [R(int) = 0.0754]
Reflections I>2σ(I)	3684	4552	34224
Data / restraints / parameters	4113 / 0 / 228	6396 / 0 / 380	78739 / 0 / 282
Goodness-of-fit on F^2	1.129	1.035	1.064
Final R indices [I>2σ(I)]	R_1 = 0.0452, wR^2 = 0.0864	R_1 = 0.0744, wR^2 = 0.1691	R_1 = 0.1207, wR^2 = 0.3021
R indices (all data)	R_1 = 0.0553, wR^2 = 0.0900	R_1 = 0.1136, wR^2 = 0.1845	R_1 = 0.2261, wR^2 = 0.3646
Max. and mean shift/esd	0.001; 0.000	0.000; 0.000	0.000; 0.000
Largest diff. peak and hole	0.338; -0.343 e.Å^{-3}	0.839; -0.372 e.Å^{-3}	0.680; -0.771 e.Å^{-3}

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Calculated structures

Atomic coordinates of **(iPr2P)2-silole** at ωB97X-D/cc-pVDZ

Energy: –2141.607930

C	1.883269	-2.497297	-1.409143
C	1.442512	-1.989612	-0.183184
C	1.639433	-2.748847	0.974604
C	2.268103	-3.990600	0.909639
C	2.701939	-4.490218	-0.316860
C	2.507418	-3.740079	-1.475989
C	0.744748	-0.671116	-0.103516
C	1.367816	0.535869	-0.177083
P	3.180744	0.568186	-0.496766
C	3.525743	2.322452	-1.090725
C	4.864151	2.337288	-1.842998
Si	0.000075	1.836645	-0.000052
C	0.054794	2.899234	1.560669
C	-1.367748	0.535970	0.177097
P	-3.180660	0.568337	0.496851
C	-3.525663	2.322708	1.090578
C	-4.863991	2.337643	1.842978
C	-0.744750	-0.671058	0.103571
C	-1.442607	-1.989507	0.183258
C	-1.883297	-2.497239	1.409219
C	-2.507536	-3.739977	1.476034
C	-2.702215	-4.490025	0.316872
C	-2.268446	-3.990361	-0.909632
C	-1.639688	-2.748651	-0.974566
C	-3.869087	0.379295	-1.249901
C	-5.379323	0.630127	-1.267663
H	-3.713782	-0.703357	-1.407936
C	-3.152559	1.112814	-2.383674
C	-0.054715	2.899051	-1.560878
C	3.869071	0.379403	1.250037

C	5.379354	0.629956	1.267791
H	3.713528	-0.703198	1.408220
C	3.152801	1.113266	2.383745
H	2.731785	2.453361	-1.847865
C	3.450621	3.493759	-0.112806
H	-2.731625	2.453721	1.847617
C	-3.450628	3.493922	0.112544
H	-0.768936	3.630549	1.535784
H	0.993258	3.457617	1.679115
H	-0.078475	2.264224	2.449974
H	5.007631	3.304188	-2.352812
H	4.912128	1.539004	-2.597773
H	5.713942	2.198651	-1.156139
H	5.890682	0.091396	0.455026
H	5.812581	0.291287	2.222900
H	5.613814	1.701603	1.165484
H	1.739237	-1.904768	-2.314287
H	2.846817	-4.124242	-2.439735
H	3.191059	-5.464614	-0.369867
H	2.414734	-4.572304	1.821603
H	1.290188	-2.362467	1.934673
H	0.769901	3.629385	-1.536856
H	-0.992606	3.458583	-1.678457
H	0.076921	2.263773	-2.450230
H	-5.007354	3.304565	2.352785
H	-4.911955	1.539381	2.597780
H	-5.713859	2.199055	1.156206
H	-5.890708	0.091799	-0.454777
H	-5.812633	0.291320	-2.222686
H	-5.613630	1.701822	-1.165554
H	-1.739141	-1.904781	2.314391
H	-2.846883	-4.124183	2.439782
H	-3.191408	-5.464386	0.369863
H	-2.415198	-4.571995	-1.821622

H	-1.290499	-2.362231	-1.934640
H	-3.571304	4.449573	0.650598
H	-2.493431	3.533048	-0.420972
H	-4.252139	3.441208	-0.640073
H	-3.576702	0.811357	-3.356499
H	-3.256738	2.204708	-2.303063
H	-2.079479	0.873189	-2.399257
H	3.576546	0.811369	3.356608
H	3.257885	2.205095	2.303298
H	2.079548	0.874446	2.399121
H	3.571234	4.449374	-0.650935
H	2.493442	3.532864	0.420750
H	4.252166	3.441132	0.639789

Atomic coordinates of **1** at ωB97X-D/cc-pVDZ

Energy: –1642.433484

C	-1.612407	1.538461	1.466551
C	-1.157255	1.221093	0.183258
C	-1.257385	2.183454	-0.823839
C	-1.786628	3.443014	-0.552363
C	-2.227682	3.755212	0.732144
C	-2.139293	2.797885	1.741348
C	-0.629396	-0.155204	-0.070917
C	0.688889	-0.507318	-0.049124
P	1.922173	0.861936	0.125454
C	3.087112	0.251023	1.503679
Si	0.714497	-2.408972	-0.168146
C	1.021611	-3.289896	1.478955
C	-1.134632	-2.492666	-0.445898
H	-1.792126	-3.352868	-0.592491
C	-1.643646	-1.254572	-0.282433
C	-3.105936	-0.972792	-0.263983
C	-3.918797	-1.603321	0.685064
C	-5.292986	-1.371653	0.713520

C	-5.874725	-0.507591	-0.211552
C	-5.074498	0.120782	-1.165590
C	-3.701767	-0.106960	-1.189405
C	1.759074	-3.199817	-1.521008
C	2.848874	0.869384	-1.554462
H	0.380346	-2.853760	2.260581
H	2.064498	-3.252072	1.822227
H	0.738986	-4.349407	1.365593
H	1.426640	-4.240578	-1.664476
H	2.825654	-3.226717	-1.249551
H	1.656674	-2.672585	-2.481061
H	-0.923150	1.940904	-1.833830
H	-1.853968	4.185142	-1.350150
H	-2.641763	4.742161	0.945969
H	-2.484817	3.031896	2.750055
H	-1.547808	0.787770	2.257051
H	-3.084352	0.387510	-1.940224
H	-5.522733	0.795425	-1.897299
H	-6.950294	-0.322829	-0.189925
H	-5.910747	-1.867327	1.464858
H	-3.460206	-2.274527	1.414250
C	4.095051	1.375995	1.786884
C	2.161330	0.110739	2.726464
C	3.856918	-1.061677	1.298299
C	3.469962	2.271969	-1.682012
C	3.942579	-0.178967	-1.772486
C	1.792143	0.718644	-2.658476
H	4.299238	-0.127617	-2.816354
H	4.812569	-0.000089	-1.125666
H	3.582780	-1.200375	-1.595026
H	3.964064	2.376284	-2.663608
H	2.703734	3.057165	-1.596029
H	4.228862	2.460123	-0.907934
H	2.264052	0.879004	-3.642805

H	1.331101	-0.279766	-2.658815
H	0.988607	1.461899	-2.550433
H	4.682056	1.134058	2.689590
H	4.808575	1.502416	0.957974
H	3.590450	2.339812	1.955269
H	2.763299	-0.076245	3.631944
H	1.570568	1.026041	2.889859
H	1.458202	-0.726875	2.609233
H	4.171650	-1.467428	2.275525
H	3.258941	-1.834727	0.800641
H	4.765798	-0.916591	0.701597

Atomic coordinates of **2** at ωB97X-D/cc-pVDZ

Energy: –2298.813927

C	-1.450828	2.990856	0.849737
C	-1.425072	2.089420	-0.219005
C	-1.982832	2.479354	-1.440923
C	-2.555499	3.739196	-1.590714
C	-2.584484	4.627503	-0.516451
C	-2.032794	4.247841	0.705660
C	-0.749400	0.760345	-0.097245
C	-1.378407	-0.448767	-0.155741
P	-3.230791	-0.425668	-0.243378
C	-3.696493	-1.929433	-1.313159
C	-3.269741	-3.333681	-0.864431
Si	0.000080	-1.746601	0.000035
C	-0.262081	-2.820669	1.533346
C	1.378498	-0.448710	0.155766
P	3.230870	-0.425587	0.243350
C	3.696539	-1.929294	1.313230
C	3.269821	-3.333571	0.864566
C	0.749454	0.760380	0.097208
C	1.425069	2.089485	0.218958
C	1.450896	2.990868	-0.849829

C	2.032805	4.247881	-0.705762
C	2.584363	4.627627	0.516383
C	2.555308	3.739373	1.590689
C	1.982700	2.479504	1.440908
C	3.826118	-0.699016	-1.563510
C	3.911483	-2.139709	-2.073185
C	5.228172	-0.064960	-1.625999
C	2.905496	0.105086	-2.491734
C	5.224899	-1.913325	1.480323
C	3.062666	-1.613710	2.681093
C	0.262360	-2.820739	-1.533203
C	-3.826174	-0.698938	1.563458
C	-3.911496	-2.139584	2.073272
C	-5.228285	-0.064986	1.625731
C	-2.905711	0.105344	2.491683
C	-5.224867	-1.913497	-1.480123
C	-3.062751	-1.613905	-2.681097
H	0.619835	-3.427055	1.778908
H	-1.103812	-3.511665	1.374613
H	-0.498999	-2.192027	2.405392
H	-3.385725	-0.627910	-3.050646
H	-3.369313	-2.372402	-3.421332
H	-1.963879	-1.611766	-2.635485
H	-5.524703	-2.656176	-2.239262
H	-5.587734	-0.926429	-1.805801
H	-5.741175	-2.176645	-0.544203
H	-3.323668	0.098399	3.512789
H	-2.825157	1.153655	2.169930
H	-1.890813	-0.315775	2.536417
H	-5.198034	0.996168	1.336780
H	-5.624088	-0.133307	2.653916
H	-5.942919	-0.572899	0.960986
H	-1.962939	1.781863	-2.280209
H	-2.984460	4.027881	-2.552136

H	-3.033567	5.615574	-0.632811
H	-2.044435	4.937936	1.551164
H	-0.996636	2.711283	1.802063
H	-0.619487	-3.427243	-1.778718
H	1.104172	-3.511627	-1.374418
H	0.499211	-2.192134	-2.405295
H	3.385593	-0.627694	3.050628
H	3.369160	-2.372171	3.421394
H	1.963796	-1.611585	2.635368
H	5.524670	-2.655905	2.239584
H	5.587732	-0.926215	1.805910
H	5.741294	-2.176590	0.544485
H	3.323362	0.098078	-3.512877
H	2.824873	1.153421	-2.170076
H	1.890634	-0.316135	-2.536334
H	5.197868	0.996218	-1.337144
H	5.623864	-0.133345	-2.654223
H	5.942923	-0.572753	-0.961289
H	1.962752	1.782056	2.280228
H	2.984167	4.028123	2.552136
H	3.033399	5.615719	0.632735
H	2.044502	4.937933	-1.551300
H	0.996812	2.711229	-1.802186
H	3.341257	-4.034208	1.714916
H	2.238098	-3.368522	0.498237
H	3.914051	-3.725731	0.068533
H	4.186254	-2.133467	-3.142724
H	4.685547	-2.715076	-1.545962
H	2.956776	-2.672184	-1.979008
H	-4.186423	-2.133251	3.142771
H	-4.685437	-2.715064	1.545992
H	-2.956736	-2.671995	1.979291
H	-3.341100	-4.034354	-1.714757
H	-2.238047	-3.368590	-0.498023

H	-3.914012	-3.725831	-0.068422

Atomic coordinates of **3(R,R)** at ωB97X-D/cc-pVDZ

Energy: –2903.669274

C	1.507368	2.830805	0.570964
C	1.414110	1.857654	-0.431847
C	1.953887	2.136791	-1.692510
C	2.588152	3.353274	-1.939517
C	2.689992	4.307179	-0.929188
C	2.145895	4.042168	0.327659
C	0.733273	0.551163	-0.183427
C	-0.733352	0.551452	0.183183
C	-1.413714	1.858197	0.431626
C	-1.953283	2.137358	1.692410
C	-2.587090	3.354005	1.939675
C	-2.688758	4.308091	0.929479
C	-2.144892	4.043068	-0.327446
C	-1.506756	2.831529	-0.570992
C	1.331819	-0.667791	-0.275888
P	3.095885	-0.842415	-0.753387
C	4.066917	-0.762964	0.883078
C	4.029697	0.703835	1.335022
Si	-0.000367	-1.996598	0.000432
C	-0.327045	-3.060058	-1.512995
C	-1.332231	-0.667313	0.275812
P	-3.096376	-0.841439	0.753084
C	-4.066744	-0.762527	-0.883821
C	-3.521595	-1.656450	-1.995579
C	0.326123	-3.058686	1.514858
Cl	3.160984	-2.939631	-1.089537
C	3.522107	-1.656536	1.995275
C	5.512793	-1.151365	0.539637
Cl	-3.162143	-2.938494	1.090104
C	-4.029386	0.704100	-1.336257

C	-5.512719	-1.150915	-0.540811
H	-0.368176	-2.454444	-2.430452
H	-1.285493	-3.586480	-1.393041
H	0.473694	-3.804556	-1.626291
H	1.284569	-3.585220	1.395451
H	-0.474657	-3.803077	1.628611
H	0.367098	-2.452338	2.431841
H	-1.873129	1.393273	2.486723
H	-3.002009	3.555479	2.928836
H	-3.186148	5.260369	1.122157
H	-2.213017	4.787409	-1.122579
H	-1.072773	2.636720	-1.553417
H	1.073303	2.635898	1.553345
H	2.214190	4.786403	1.122877
H	3.187707	5.259328	-1.121669
H	3.003297	3.554730	-2.928586
H	1.873567	1.392858	-2.486951
H	-4.750101	0.844416	-2.158888
H	-4.298191	1.403847	-0.528583
H	-3.035678	0.982462	-1.712020
H	-6.142475	-1.041348	-1.439116
H	-5.585799	-2.194641	-0.201854
H	-5.929991	-0.502331	0.245603
H	-4.146377	-1.543414	-2.897830
H	-2.492063	-1.377661	-2.262510
H	-3.534576	-2.717647	-1.708562
H	6.142833	-1.041526	1.437712
H	5.585835	-2.195151	0.200897
H	5.929720	-0.502891	-0.247049
H	4.751117	0.844659	2.156951
H	4.297496	1.403443	0.526892
H	3.036263	0.982037	1.711626
H	4.147077	-1.543229	2.897361
H	2.492640	-1.377633	2.262355

H	3.535016	-2.717841	1.708610

Atomic coordinates of **3(S,S)** at ωB97X-D/cc-pVDZ

Energy: –2903.669274

C	1.953477	2.136978	1.692606
C	1.413896	1.858032	0.431800
C	1.507269	2.831358	-0.570810
C	2.145772	4.042678	-0.327196
C	2.689678	4.307496	0.929771
C	2.587668	3.353433	1.939934
C	0.733344	0.551406	0.183239
C	1.332084	-0.667423	0.275821
P	3.096211	-0.841755	0.753106
Cl	3.161731	-2.938920	1.089555
Si	0.000142	-1.996558	0.000106
C	-0.326604	-3.058919	1.514316
C	-1.331907	-0.667572	-0.275992
P	-3.095990	-0.842270	-0.753338
Cl	-3.161299	-2.939564	-1.089117
C	-0.733291	0.551314	-0.183403
C	-1.414042	1.857850	-0.431895
C	-1.507572	2.831107	0.570768
C	-2.146363	4.042293	0.327255
C	-2.690422	4.307043	-0.929663
C	-2.588258	3.353050	-1.939876
C	-1.953771	2.136724	-1.692648
C	0.326919	-3.059819	-1.513439
C	4.066784	-0.762417	-0.883638
C	4.028990	0.704249	-1.335982
C	5.512862	-1.150268	-0.540478
C	3.521988	-1.656453	-1.995476
C	-4.066685	-0.762581	0.883310
C	-4.029742	0.704363	1.334857
C	-5.512533	-1.151470	0.540324

C	-3.521398	-1.655719	1.995624
H	-0.367528	-2.452691	2.431382
H	0.474119	-3.803390	1.628012
H	-1.285121	-3.585297	1.394831
H	-0.473896	-3.804262	-1.626682
H	1.285361	-3.586233	-1.393553
H	0.367926	-2.454210	-2.430910
H	1.073330	2.636653	-1.553281
H	2.214195	4.787028	-1.122295
H	3.187360	5.259617	1.122471
H	3.002622	3.554729	2.929116
H	1.873093	1.392906	2.486908
H	-1.873273	1.392709	-2.486991
H	-3.003329	3.554297	-2.929020
H	-3.188346	5.259055	-1.122274
H	-2.214909	4.786598	1.122385
H	-1.073538	2.636430	1.553200
H	4.146627	-1.543055	-2.897779
H	3.535472	-2.717682	-1.708583
H	2.492297	-1.378089	-2.262267
H	6.142629	-1.040460	-1.438749
H	5.929804	-0.501486	0.245946
H	5.586338	-2.193955	-0.201506
H	4.750197	0.845026	-2.158108
H	3.035405	0.982087	-1.712444
H	4.296823	1.404097	-0.528069
H	-6.142315	-1.041794	1.438597
H	-5.929941	-0.503182	-0.246265
H	-5.585341	-2.195297	0.201646
H	-4.146028	-1.542096	2.897906
H	-3.534421	-2.717118	1.709326
H	-2.491819	-1.376736	2.262189
H	-4.750863	0.845139	2.157055
H	-3.036245	0.983040	1.710933

H	-4.298193	1.403633	0.526644

Atomic coordinates of **3(R,S/S,R)** at ωB97X-D/cc-pVDZ

Energy: –2903.666632

C	1.615407	2.719951	0.945864
C	1.473742	1.952673	-0.214238
C	2.000836	2.443454	-1.414328
C	2.662458	3.668295	-1.450937
C	2.805911	4.420861	-0.286835
C	2.280896	3.942751	0.912498
C	0.755246	0.641139	-0.223281
C	-0.754031	0.642151	-0.222767
C	-1.470480	1.954826	-0.213431
C	-1.616033	2.719300	0.948007
C	-2.279142	3.943427	0.914784
C	-2.797856	4.425542	-0.285667
C	-2.650525	3.675684	-1.451046
C	-1.991271	2.449577	-1.414628
C	1.357233	-0.572522	-0.344342
P	3.183509	-0.696975	-0.429331
C	3.663803	-1.145983	1.357529
C	3.484660	0.144137	2.170067
Si	-0.001321	-1.846638	-0.717753
C	-0.001373	-2.167674	-2.573593
C	-1.357909	-0.570576	-0.343612
P	-3.184429	-0.691271	-0.428907
C	-3.666252	-1.143989	1.356621
C	-3.483248	0.143231	2.172894
C	-0.002613	-3.456692	0.242558
Cl	3.358807	-2.614927	-1.330238
C	2.830577	-2.264415	1.981137
C	5.149607	-1.531103	1.328966
Cl	-3.363444	-2.606594	-1.334684
C	-2.836777	-2.266818	1.977235

C	-5.153250	-1.524382	1.326669
H	-0.000149	-1.212721	-3.121062
H	-0.897813	-2.734835	-2.862995
H	0.894006	-2.736825	-2.862411
H	0.889803	-4.038621	-0.034280
H	-0.897424	-4.035821	-0.032447
H	-0.001262	-3.311724	1.331333
H	-1.213557	2.349721	1.892372
H	-2.388609	4.524559	1.832148
H	-3.315689	5.385901	-0.312729
H	-3.052785	4.045411	-2.395765
H	-1.879510	1.859983	-2.326562
H	1.208089	2.353556	1.889389
H	2.387262	4.526038	1.828858
H	3.325590	5.380221	-0.313998
H	3.069565	4.034871	-2.394807
H	1.892121	1.851743	-2.325259
H	-3.205671	-2.479427	2.994996
H	-2.903698	-3.195609	1.392851
H	-1.777912	-1.980061	2.057832
H	-5.509226	-1.695991	2.356003
H	-5.767085	-0.723021	0.885878
H	-5.325540	-2.445738	0.751233
H	-3.897490	-0.006246	3.183729
H	-2.418920	0.396778	2.281485
H	-3.997722	1.005213	1.719253
H	5.504853	-1.700812	2.358866
H	5.319179	-2.454640	0.756235
H	5.766014	-0.732917	0.885995
H	3.898151	-0.003842	3.181433
H	4.001970	1.003197	1.714120
H	2.421151	0.401465	2.277659
H	3.198751	-2.475548	2.999463
H	1.772676	-1.973845	2.060952

H	2.894317	-3.194995	1.399245

Atomic coordinates of **4** at ωB97X-D/cc-pVDZ

Energy: –3508.482162

C	-0.020579	0.155736	-0.007421
C	-0.018524	0.004206	1.383752
C	1.205006	-0.100968	2.058129
C	2.401365	-0.069762	1.350658
C	2.392797	0.081401	-0.036916
C	1.181551	0.195120	-0.713576
C	-1.301321	-0.031137	2.139262
C	-2.260410	-0.985251	2.000066
Si	-3.739216	-0.568521	3.117703
C	-4.043964	-1.748213	4.540676
C	-2.826638	0.980396	3.732275
C	-1.607143	1.057309	3.135211
C	-0.590125	2.110554	3.407223
C	-0.017087	2.229481	4.678367
C	0.940075	3.212122	4.930503
C	1.329861	4.083421	3.917178
C	0.762046	3.969681	2.647165
C	-0.186122	2.985850	2.390608
C	-5.268192	-0.257545	2.080975
P	-3.303980	2.258353	4.933805
Cl	-3.000935	1.162187	6.715425
Cl	-5.395128	2.087849	4.789048
P	-1.980544	-2.356474	0.839841
Cl	-3.214961	-1.700715	-0.745659
Cl	-3.266199	-3.784451	1.694783
H	-5.095510	0.552962	1.357941
H	-6.125421	0.008073	2.716133
H	-5.510869	-1.173500	1.519557
H	-4.551349	-2.659519	4.192983
H	-4.680533	-1.248899	5.288029

H	-3.098985	-2.030022	5.027633
H	-0.312501	1.539514	5.471436
H	1.380403	3.293634	5.925539
H	2.078017	4.853037	4.114538
H	1.063169	4.651094	1.849878
H	-0.620443	2.893880	1.393641
H	1.216344	-0.209397	3.144011
H	3.348077	-0.160723	1.885569
H	3.333494	0.111133	-0.589366
H	1.166511	0.315087	-1.798016
H	-0.968974	0.257199	-0.538957

Atomic coordinates of **5** at ωB97X-D/cc-pVDZ

Energy: –2520.182394

C	-0.903478	3.056881	2.012011
C	-1.138555	2.388283	0.803722
C	-1.924504	3.015187	-0.167509
C	-2.472234	4.275938	0.064865
C	-2.242567	4.926471	1.274524
C	-1.455486	4.311438	2.248618
C	-0.547111	1.037412	0.584487
C	-1.272169	-0.098652	0.397854
Si	-0.061742	-1.551440	0.510478
C	-0.001872	-2.739172	-0.949756
C	1.432107	-0.389078	0.586268
C	0.950662	0.881406	0.631957
C	1.797003	2.109699	0.612899
C	1.647373	3.052182	-0.411796
C	2.432443	4.201077	-0.442138
C	3.379039	4.428634	0.556214
C	3.530522	3.500734	1.585140
C	2.743986	2.351147	1.614070
C	-0.387924	-2.486726	2.114456
P	3.242081	-0.690079	0.429250

N	3.513674	-0.237200	-1.197390
N	3.195280	-2.481290	0.351048
P	-3.104064	-0.070154	0.493895
N	-3.441133	-1.769785	0.717502
N	-3.524358	0.296902	-1.143356
H	-0.190602	-1.840066	2.983321
H	0.222659	-3.396692	2.202591
H	-1.451175	-2.768666	2.128710
H	-0.801176	-3.492058	-0.893077
H	0.971993	-3.251526	-0.908422
H	-0.079620	-2.213779	-1.913993
H	0.906300	2.882384	-1.194386
H	2.302812	4.923476	-1.250118
H	3.993367	5.330685	0.535048
H	4.263713	3.673699	2.375172
H	2.862879	1.627993	2.422321
H	-2.094522	2.516089	-1.121090
H	-3.080348	4.751007	-0.707439
H	-2.671478	5.913267	1.458114
H	-1.267243	4.815173	3.198484
H	-0.280460	2.583497	2.773543
C	4.265265	-3.080983	-0.449767
C	3.099185	-3.026290	1.707616
C	4.814769	0.335480	-1.521641
C	2.700856	-0.707572	-2.315810
C	2.719193	-4.502298	1.732396
H	4.031299	-2.876428	2.291353
H	2.325192	-2.451582	2.241784
H	4.019271	-4.145902	-0.599040
H	4.228388	-2.627845	-1.450347
C	5.690771	-2.962122	0.097396
H	2.504572	-4.821970	2.763508
H	1.825044	-4.686538	1.116569
H	3.529207	-5.142886	1.352027

H	6.405619	-3.396069	-0.618630
H	5.970580	-1.909517	0.260901
H	5.815030	-3.494678	1.052713
C	1.615636	0.256542	-2.796910
H	3.382202	-0.938723	-3.155985
H	2.231706	-1.663356	-2.036265
C	4.745610	1.666348	-2.262495
H	5.351269	0.482777	-0.571617
H	5.411596	-0.388293	-2.115587
H	5.759739	2.069319	-2.411239
H	4.285929	1.554958	-3.256982
H	4.156999	2.394917	-1.685682
H	1.123938	-0.150815	-3.695611
H	0.845638	0.403866	-2.026260
H	2.032928	1.241465	-3.050199
C	-4.660071	1.190847	-1.345809
C	-2.659226	0.083786	-2.294936
C	-3.320957	-0.604641	-3.486079
H	-2.241115	1.053736	-2.641125
H	-1.792721	-0.507556	-1.969672
C	-5.980395	0.479826	-1.639736
H	-4.780277	1.816750	-0.445663
H	-4.416540	1.885591	-2.172108
H	-2.574143	-0.784170	-4.275498
H	-3.758323	-1.571048	-3.193766
H	-4.119473	0.013768	-3.923161
H	-6.795413	1.210804	-1.764145
H	-5.921864	-0.128111	-2.554078
H	-6.247684	-0.191472	-0.810301
C	-3.545341	-2.647287	-0.441594
C	-4.340885	-2.061502	1.833039
C	-3.431317	-4.129563	-0.101728
H	-4.483538	-2.470998	-1.006758
H	-2.731921	-2.382538	-1.131984

H	-4.099912	-3.063630	2.228038
H	-4.095542	-1.356123	2.641857
C	-5.835149	-1.975232	1.527071
H	-3.373146	-4.720704	-1.028443
H	-2.527311	-4.331842	0.494099
H	-4.299851	-4.495404	0.466314
H	-6.426093	-2.251078	2.414171
H	-6.112490	-0.948785	1.240844
H	-6.127055	-2.650326	0.707294

Atomic coordinates of **6(R,R)** at ωB97X-D/cc-pVDZ

Energy: –3014.357797

C	-1.889110	1.893200	-1.805392
C	-1.467812	1.578890	-0.508682
C	-1.694506	2.503230	0.517352
C	-2.346033	3.704917	0.257797
C	-2.767254	4.008344	-1.036799
C	-2.533467	3.101254	-2.068219
C	-0.760489	0.293432	-0.237009
C	-1.316325	-0.938787	-0.370743
P	-3.040255	-1.105174	-0.965328
Cl	-3.169696	-3.277335	-0.893877
Si	0.008117	-2.238946	0.021320
C	0.480640	-3.201759	-1.520185
C	1.264602	-0.877394	0.429703
P	2.968248	-0.988476	1.083071
Cl	3.247652	-3.135505	0.796503
C	0.672348	0.328182	0.226318
C	1.343998	1.649075	0.398207
C	1.547376	2.487492	-0.703774
C	2.153476	3.730159	-0.545145
C	2.558068	4.156176	0.720019
C	2.358437	3.328176	1.823278
C	1.755010	2.081908	1.663236

C	-0.397346	-3.314464	1.504850
N	-3.914904	-0.599150	0.385576
C	-5.286395	-0.139196	0.133228
C	-3.604502	-1.014897	1.751822
N	3.870385	-0.261220	-0.138676
C	3.588713	-0.378167	-1.568140
H	0.717519	-2.509962	-2.343540
H	-0.361866	-3.836427	-1.833108
H	1.359324	-3.833018	-1.326497
H	0.457985	-3.968580	1.730858
H	-1.281861	-3.934228	1.298126
H	-0.598083	-2.692893	2.391228
H	-1.345439	2.281270	1.527532
H	-2.519446	4.412700	1.070260
H	-3.273114	4.953524	-1.241403
H	-2.852937	3.333246	-3.085802
H	-1.703714	1.185481	-2.615831
H	1.592257	1.437785	2.529988
H	2.670140	3.654594	2.817114
H	3.027433	5.133519	0.845375
H	2.305908	4.372805	-1.413994
H	1.218999	2.164074	-1.693351
C	-3.711031	0.112778	2.770496
H	-4.269190	-1.851026	2.041035
H	-2.580834	-1.411983	1.757329
C	-5.384353	1.377739	0.014593
H	-5.663179	-0.606734	-0.791301
H	-5.932131	-0.512317	0.945965
C	5.190811	0.245994	0.239364
C	4.522804	-1.325990	-2.315509
H	2.551320	-0.722131	-1.674968
H	3.624600	0.629781	-2.017149
H	5.251269	0.203990	1.337602
H	5.986611	-0.418820	-0.142420

C	5.429051	1.677520	-0.226324
H	6.387888	2.044314	0.170125
H	5.476974	1.751995	-1.323556
H	4.623272	2.336363	0.129659
H	4.199256	-1.416435	-3.363577
H	5.562024	-0.963135	-2.321162
H	4.506454	-2.325678	-1.857455
H	-6.423782	1.684820	-0.181437
H	-5.040895	1.874774	0.933442
H	-4.752210	1.737715	-0.811285
H	-3.405254	-0.249804	3.763711
H	-3.061713	0.953379	2.486252
H	-4.741011	0.491025	2.858624

Atomic coordinates of **6(S,S)** at ωB97X-D/cc-pVDZ

Energy: –3014.347892

C	0.384661	3.234505	1.061354
C	0.642467	2.331448	0.023145
C	1.036983	2.824202	-1.224743
C	1.174582	4.196363	-1.429545
C	0.921270	5.088008	-0.390173
C	0.529444	4.602828	0.857974
C	0.451169	0.866400	0.233077
C	1.437905	-0.072959	0.201550
P	3.143892	0.550376	-0.022658
Cl	3.316436	0.029608	-2.128109
C	-0.949195	0.367568	0.477088
C	-1.092429	-0.975332	0.608372
Si	0.616467	-1.769431	0.448731
C	0.740824	-2.826509	-1.102388
C	-2.074386	1.346146	0.523446
C	-2.439833	2.065243	-0.620226
C	-3.471903	2.996794	-0.568597
C	-4.148337	3.228350	0.629106

C	-3.791313	2.516289	1.772428
C	-2.761199	1.578350	1.719505
P	-2.739437	-1.702593	0.928565
Cl	-2.150678	-3.812318	0.844958
N	-3.536569	-1.399641	-0.522752
C	-5.001484	-1.429303	-0.487900
C	-2.932081	-1.327415	-1.850853
C	1.114682	-2.645068	2.035303
N	4.158700	-0.578882	0.726549
C	4.185370	-2.015583	0.473757
C	5.344844	-0.007470	1.382090
H	1.179947	-1.920041	2.860768
H	2.082531	-3.156038	1.942524
H	0.349648	-3.395326	2.284556
H	0.157791	-3.750440	-0.977322
H	1.782320	-3.092495	-1.337042
H	0.341311	-2.266603	-1.961888
H	1.238402	2.126066	-2.039595
H	1.484649	4.567301	-2.408039
H	1.029087	6.162283	-0.550591
H	0.330748	5.295957	1.677303
H	0.066034	2.858856	2.035548
H	-1.901205	1.899529	-1.555064
H	-3.745491	3.551351	-1.467880
H	-4.952647	3.964911	0.670679
H	-4.314294	2.692783	2.714079
H	-2.476686	1.026191	2.617602
C	6.400711	0.576862	0.445248
H	5.013887	0.773986	2.084571
H	5.782194	-0.807258	2.002095
H	4.215457	-2.542606	1.444702
H	3.237566	-2.287569	-0.005416
C	5.329503	-2.510823	-0.409210
H	-5.316336	-1.891284	0.460504

C	-5.616461	-0.040032	-0.611344
H	-5.369957	-2.092501	-1.289201
C	-2.859757	-2.667198	-2.579279
H	-3.514969	-0.601611	-2.442499
H	-1.923997	-0.900796	-1.753015
H	-6.715524	-0.103864	-0.594930
H	-5.285824	0.600605	0.219487
H	-5.321028	0.452062	-1.550634
H	-2.432144	-2.526109	-3.583996
H	-2.229713	-3.378321	-2.027485
H	-3.856762	-3.118630	-2.697698
H	7.243560	0.977266	1.030064
H	6.790758	-0.173791	-0.255641
H	5.977093	1.402818	-0.146727
H	5.205434	-3.588513	-0.597818
H	5.333332	-1.985049	-1.374491
H	6.308430	-2.372078	0.073504

Atomic coordinates of **6(R,S/S,R)** at ωB97X-D/cc-pVDZ

Energy: –3014.353605

C	-2.278009	2.204388	-1.558189
C	-1.510620	1.767781	-0.473596
C	-1.477468	2.545318	0.688800
C	-2.216245	3.721762	0.774959
C	-2.989531	4.143969	-0.306327
C	-3.014573	3.384676	-1.474318
C	-0.740127	0.493840	-0.555037
C	-1.294445	-0.741187	-0.671076
P	-3.099792	-0.947587	-0.878705
Cl	-3.166719	-3.119170	-0.683707
C	0.762763	0.543029	-0.499092
C	1.406075	-0.649766	-0.583282
Si	0.105039	-2.019972	-0.761279
C	0.145961	-3.186293	0.711502

C	1.437290	1.869813	-0.388489
C	2.029398	2.277569	0.810698
C	2.637285	3.527373	0.910079
C	2.668563	4.379342	-0.192480
C	2.081041	3.979319	-1.392197
C	1.462556	2.735752	-1.487140
P	3.228926	-0.684622	-0.700740
Cl	3.467552	-2.824876	-1.071367
N	3.692303	-0.486991	0.916567
C	5.097550	-0.161770	1.193973
C	2.965694	-1.045023	2.056103
C	0.134988	-2.891434	-2.421487
N	-3.702249	-0.376519	0.592536
C	-5.129266	-0.041429	0.601952
C	-3.090959	-0.708202	1.880480
H	0.187703	-2.155191	-3.237871
H	-0.783468	-3.485421	-2.541802
H	1.007699	-3.555901	-2.492740
H	1.122058	-3.693248	0.751925
H	-0.648354	-3.941222	0.625430
H	-0.003255	-2.634774	1.652967
H	-0.869774	2.221223	1.535781
H	-2.184878	4.314811	1.690825
H	-3.566206	5.068238	-0.240258
H	-3.608988	3.712822	-2.328928
H	-2.296789	1.612747	-2.475782
H	2.008465	1.609198	1.672296
H	3.091724	3.835305	1.853745
H	3.148044	5.356903	-0.116539
H	2.100605	4.641821	-2.259175
H	0.993703	2.427808	-2.423744
C	-3.360741	0.333584	2.959375
H	-3.427636	-1.705275	2.221465
H	-2.007092	-0.783529	1.714608

H	-5.267268	0.874465	1.199671
H	-5.404858	0.224526	-0.429921
C	-6.042272	-1.153201	1.112435
H	5.133067	0.165241	2.247100
H	5.734310	-1.063861	1.126364
C	5.667681	0.945077	0.316418
H	3.014864	-0.303933	2.876326
H	1.907488	-1.128707	1.773912
C	3.480108	-2.393633	2.554921
H	2.858259	-2.742214	3.393666
H	3.444186	-3.146020	1.754985
H	4.518118	-2.324115	2.914267
H	6.673946	1.210458	0.674012
H	5.755433	0.635441	-0.734431
H	5.029710	1.841052	0.354893
H	-7.094267	-0.835949	1.049560
H	-5.917694	-2.068550	0.514460
H	-5.832442	-1.404051	2.163739
H	-2.749763	0.110060	3.846743
H	-3.101558	1.340684	2.600512
H	-4.413398	0.341351	3.280136