Supporting Information

Formation of an NHC-Stabilized Heterocyclic Housane and its Isomerization into a Cyclopentenyl Anion Analogue

Benedikt J. Guddorf,[a] Christian Mück-Lichtenfeld,[b] Alexander Hepp,[a] Felicitas Lips[a]*

Westfälische Wilhelms-Universität Münster
[a] Institut für Anorganische und Analytische Chemie, Corrensstraße 28-30, 48149 Münster, (Deutschland)
[b] Institut für Organische Chemie and Center for Multiscale Theory and Computation, Corrensstraße 40, 48149 Münster, (Deutschland)

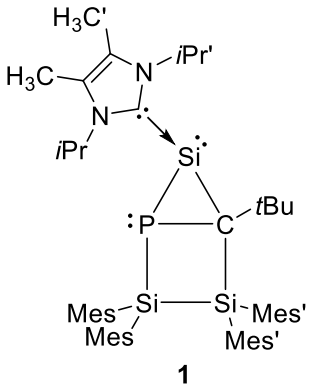
Table of content

1. General experimental procedures

All reactions were performed with the use of modified Schlenk techniques with additional manipulations using a MBraun Glovebox. All solvents were dried over sodium benzophenone or CaH_2, distilled and stored over 4 Å molecular sieves prior to use. Silicon tetrachloride was purchased from Aldrich and used without further purification. The starting material **E**[S1] and 1,3-diisopropyl-4,5-dimethyl-imidazol-2-ylidene ($NHC^{iPr2Me2}$)[S2] were prepared according to literature procedures. All NMR data were obtained on Bruker Avance I and III spectrometer and were referenced to the deuterated solvent (C_6D_6, THF-d_8, PhMe-d_8) according to an IUPAC recommendation. Additionally, the ^1H and ^{13}C NMR spectra were referenced internally to residual solvent resonances at 300 K. ^1H, ^{13}C, and ^{29}Si NMR spectra were referenced to tetramethylsilane (TMS; δ = 0 ppm). ^{31}P NMR spectra were referenced to H_3PO_4. Further explanation of the ^{29}Si NMR experiments: ^{29}Si DEPT-19.5 = ^{29}Si NMR measurement with Distortionless Enhancement Polarization Transfer method, pulse angle 19.5°, coupling to 9 protons as polarization source with coupling $^2J_{Si–H}$ = 7 Hz; $^{29}Si\{^1H\}IG$ = Inverse gated decoupled ^{29}Si proton decoupled NMR measurement; $^{29}Si\{/\}$ = ^{29}Si proton coupled NMR measurement. ^{13}C DEPT-135 = Distortionless Enhancement of Polarization Transfer using a 135 degree decoupler pulse. All ^{13}C NMR spectra were recorded proton decoupled.

IR spectra were recorded as KBr pellets on a Shimadzu IR PRESTIGE 21. UV-visible spectra were recorded as dilute THF solutions in 1 mL quartz cuvettes using an Agilent Cary 100 spectrometer. Mass spectrometry was performed with a Varian MAT 212 Micromass Quattro LC-Z device. CHN elemental analysis was performed with a Vario EL III CHN Instrument. Melting points were measured in glass capillaries sealed under argon gas by using a Stuart Melting Point Apparatus SMP3 and are uncorrected.

2. Details for the synthesis and spectroscopic data for 1



1

Synthesis of 1: The NHC-coordinated trisilacyclopropylidene **E** (280 mg, 0.38 mmol, 1.0 eq.) was dissolved in 50 mL THF and *t*BuCP (0.15 ml, 1.5 mmol, 4.0 eq.) was added at room temperature. The reaction was stirred for 16 h under the exclusion of light. The resulting yellow solution was concentrated to a volume of 1 mL and 5 mL *n*-hexane was slowly added. Pale yellow crystals of **1** suitable for X-ray diffraction analysis were obtained at room temperature after 16 h.

Yield: 260 mg (0.31 mmol, 82%), pale yellow crystals.

^{1}H-NMR (300 K, 400 MHz, C_6D_6) δ/ppm: 7.01 (s, 1H, Mes'), 6.99 (s, 1H, Mes), 6.69 (overlapping, 2H, Mes'), 6.66 (overlapping, 2H, Mes & Mes'), 6.62 (overlapping, sept., $^{3}J_{HH}$ = 6.8 Hz, 1H, C*H*$(CH_3)_2$'), 6.60 (s, 1H, Mes), 6.57 (s, 1H, Mes), 5.51 (sept., $^{3}J_{HH}$ = 6.8 Hz, 1H, C*H*$(CH_3)_2$, 3.82 (s, 3H *ortho*-CH_3), 3.80 (s, 3H *ortho*-CH_3'), 3.20 (s, 3H *ortho*-CH_3'), 2.79 (s, 3H *ortho*-CH_3), 2.27 (s, 3H *ortho*-CH_3'), 2.27 (s, 3H *para*-CH_3'), 2.20 (s, 3H *ortho*-CH_3), 2.19 (s, 3H *ortho*-CH_3), 2.16 (s, 3H *para*-CH_3), 2.08 (s, 3H *para*-CH_3'), 2.05 (s, 3H *para*-CH_3), 1.89 (s, 3H *ortho*-CH_3'), 1.47 (s, 6H, [C(CH_3)]$_2$'), 1.44 (s, 6H, [C(CH_3)]$_2$), 1.37 (s, 9H, C(CH_3)$_3$), 1.23 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.20 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$'), 0.90 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$).

^{13}C{^{1}H}-NMR (300 K, 100 MHz, C_6D_6) δ/ppm: 174.2 (d, $^{2}J_{CP}$ = 9.2 Hz, NCN), 146.2 (d, $^{2}J_{CP}$ = 1.6 Hz, *ipso*-C_{Mes}), 146.1 (*ortho*-C_{Mes}), 145.1 (*ortho*-$C_{Mes'}$), 144.8 (*ipso*-$C_{Mes'}$), 144.7 (*ortho*-C_{Mes}), 144.5 (*ipso*-$C_{Mes'}$), 143.6 (d, $^{3}J_{CP}$ = 1.2 Hz, *ortho*-C_{Mes}), 143.3 (*ortho*-$C_{Mes'}$), 142.7 (*ortho*-$C_{Mes'}$), 141.9 (*ortho*-C_{Mes}), 141.3 (*ortho*-$C_{Mes'}$), 140.8 (d, $^{2}J_{CP}$ = 4.3 Hz, *ipso*-C_{Mes}), 137.2 (*para*-$C_{Mes'}$), 137.0 (*para*-C_{Mes}), 136.7 (*para*-$C_{Mes'}$), 135.2 (*para*-C_{Mes}), 130.9 (*meta*-$C_{Mes'}$), 130.3 (*meta*-$C_{Mes'}$), 129.7 (*meta*-C_{Mes}), 129.1 (*meta*-C_{Mes}), 129.0 (*meta*-C_{Mes}), 128.9 (*meta*-$C_{Mes'}$), 128.1 (*meta*-$C_{Mes'}$), 128.0 (*meta*-C_{Mes}), 127.0 ([*C*(CH_3)]$_2$),

125.7 ([*C*(CH_3)]$_2$'), 53.7 (d, $^1J_{CP}$ = 45.4 Hz, PC*t*Bu), 53.3 (*C*H(CH_3)$_2$'), 51.9 (d, $^4J_{CP}$ = 20.6 Hz, *C*H(CH_3)$_2$), 39.3 (d, $^2J_{CP}$ = 12.5 Hz, *C*(CH_3)$_3$), 33.8 (d, $^3J_{CP}$ = 7.8 Hz, C(*C*H_3)$_3$), 32.0 (d, $^5J_{CP}$ = 2.4 Hz, *ortho*-CH_3'), 28.6 (*ortho*-CH_3'), 27.8 (*ortho*-CH_3), 27.4 (*ortho*-CH_3'), 26.9 (*ortho*-CH_3), 26.2 (d, $^4J_{CP}$ = 23.6 Hz, *ortho*-CH_3), 25.2 (*ortho*-CH_3'), 24.6 (d, $^4J_{CP}$ = 13.5 Hz, *ortho*-CH_3), 21.5 (CH(C*H*$_3$)$_2$'), 21.4 (d, $^4J_{CP}$ = 2.5 Hz, CH(C*H*$_3$)$_2$), 21.2 (*para*-CH_3'), 21.0 (*para*-CH_3), 20.9 (CH(C*H*$_3$)$_2$'), 20.9 (*para*-CH_3), 20.8 (*para*-CH_3'), 20.5 (CH(*C*H_3)$_2$), 10.1 ([C(CH_3)]$_2$), 9.9 ([C(*C*H_3)]$_2$').

^{31}P{^{1}H}-NMR (300 K, 162 MHz, C_6D_6) δ/ppm: −158.6 (P-C*t*Bu).

^{31}P{/}-NMR (300 K, 162 MHz, C_6D_6) δ/ppm: −158.6 (d, $^5J_{PH}$ = 9.9 Hz, P-C*t*Bu).

^{29}Si DEPT-19.5-NMR (300 K, 80 MHz, C_6D_6) δ/ppm: 23.6 (Mes_2SiC), −13.0 (Mes_2SiP).

^{29}Si{^{1}H}IG-NMR (300 K, 80 MHz, C_6D_6) δ/ppm: 23.6 (s, Mes_2*Si*C*t*Bu), −13.0 (d, $^1J_{SiP}$ = 40.8 Hz, Mes_2*Si*P), −112.9 (d, $^1J_{SiP}$ = 46.8 Hz, *Si*-NHC).

Melting point: 182 °C (decomposition).

CHN-analysis: $C_{52}H_{73}N_2Si_3$ + 1 THF calc. C, 73.63; H, 8.94; N 3.07;
found C, 73.48; H, 8.95 , N, 2.97.

MS (ESI, positve mode): calc.: *m*/z = 841.48919 $[M-H]^+$, found: *m*/z = 841.49116 $[M-H].^+$

FT-IR (KBr-pellet) $\tilde{\upsilon}$/cm^{-1}: 2970 (vs), 2951 (vs), 2916 (vs), 2858 (vs), 2725 (m), 2467 (w), 2405 (w), 1749 (w), 1716 (w), 1634 (m), 1603 (vs), 1547 (m), 1460 (vs), 1404 (s), 1379 (vs), 1368 (vs), 1356 (vs), 1339 (s), 1315 (m), 1290 (s), 1233 (s), 1213 (s), 1194 (s), 1167 (m), 1134 (w), 1109 (w), 1067 (s), 1026 (s), 951 (w), 926 (w), 907 (w), 881 (w), 847 (vs), 790 (w), 743 (s), 600 (vs), 571 (s), 552 (s), 507 (w), 478 (w), 451 (m), 424 (m).

UV/vis (c = 1.7·10^{-4} mol/L in THF): λ_{max} = 375 nm (ε = 5705 L mol^{-1} cm^{-1}).

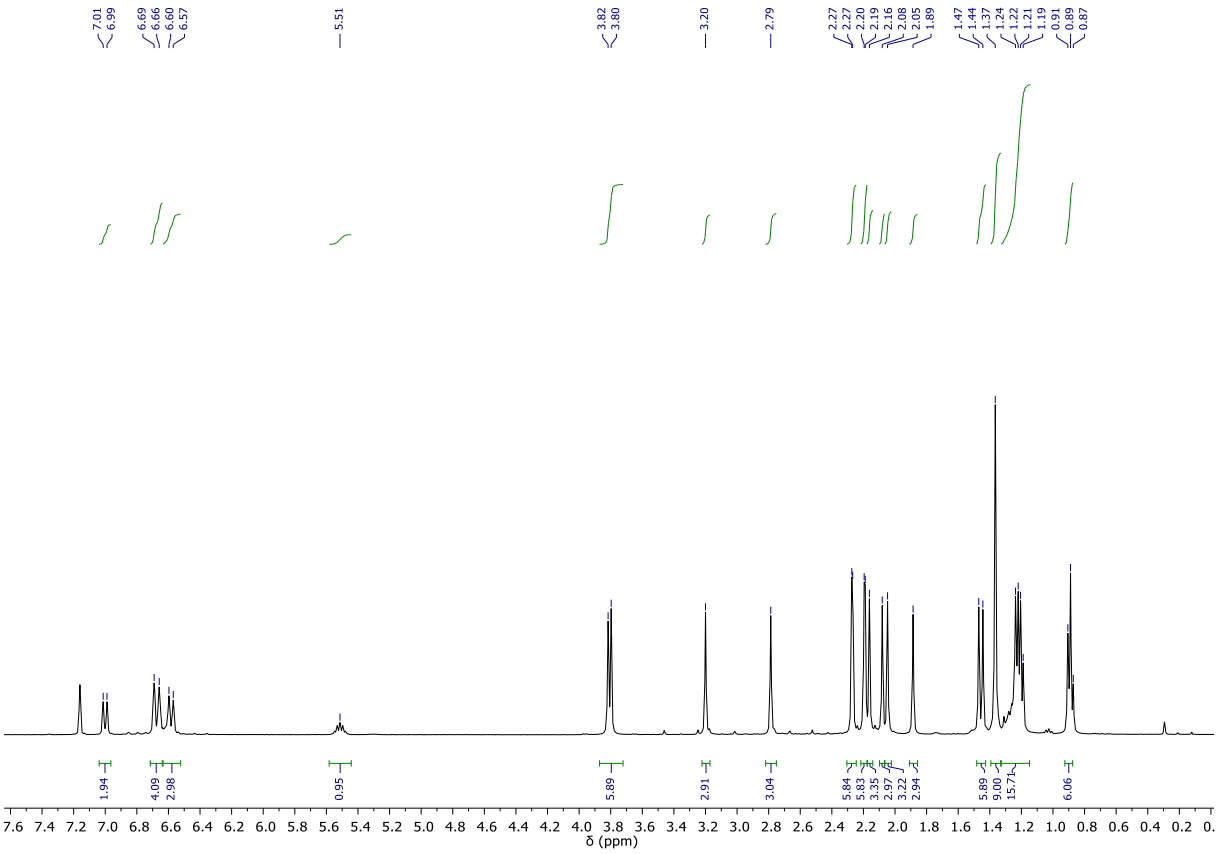


Figure S1. ^{1}H-NMR-spectrum (300 K, 400 MHz, C_6D_6) of compound **1**.

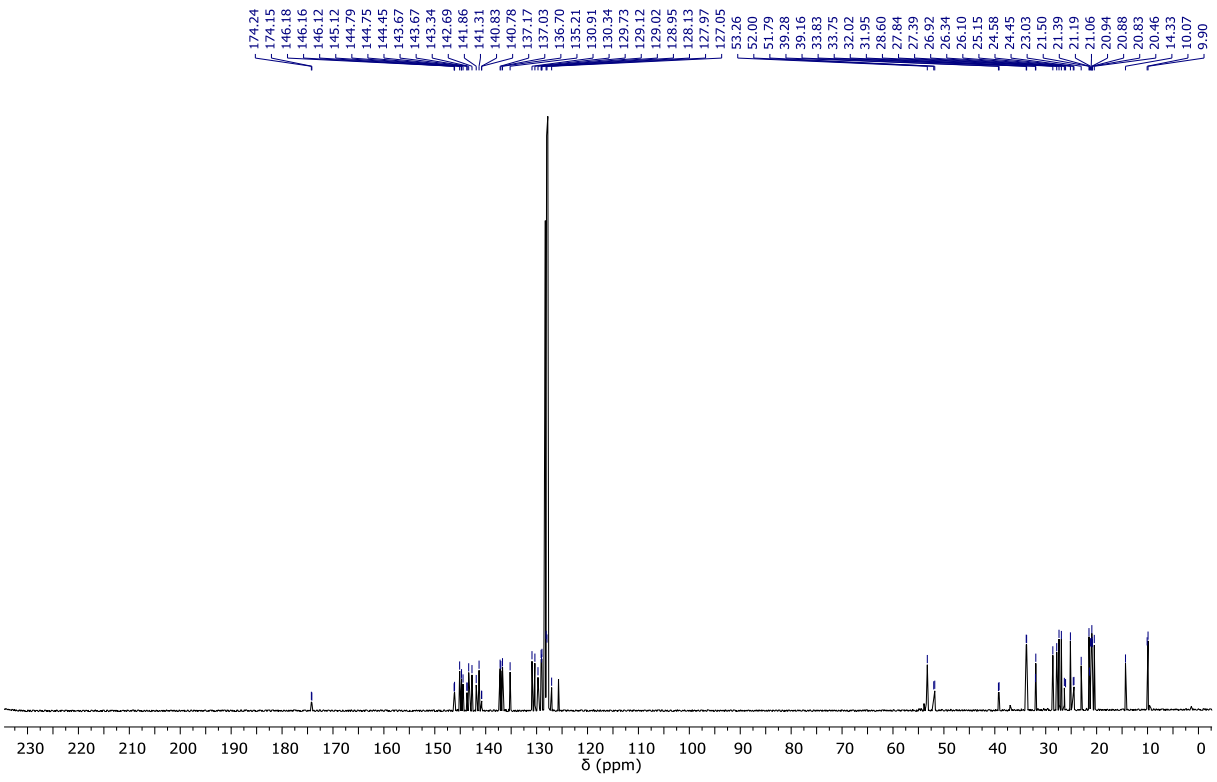


Figure S2. ^{13}C{^{1}H}-NMR-spectrum (300 K, 100 MHz, C_6D_6) of compound **1**.

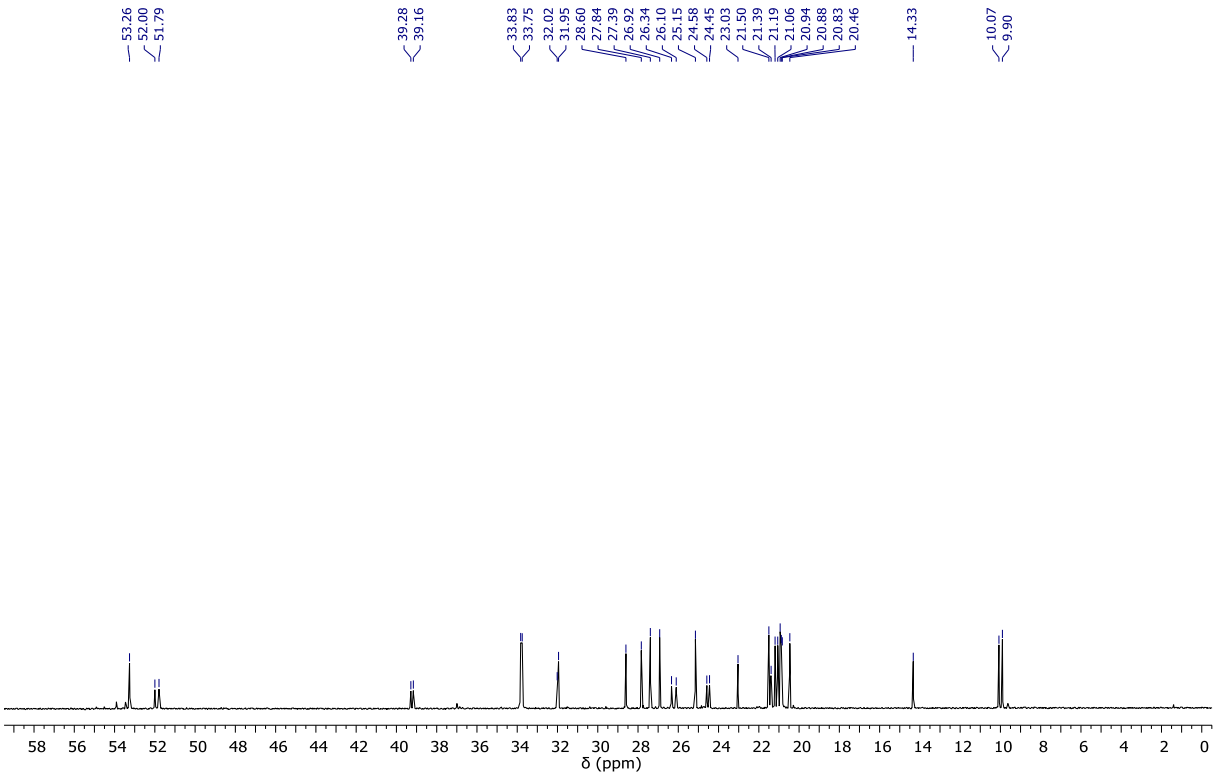


Figure S3. $^{13}C\{^{1}H\}$-NMR-spectrum (300 K, 100 MHz, C_6D_6) zoom 60-0 ppm of compound **1**.

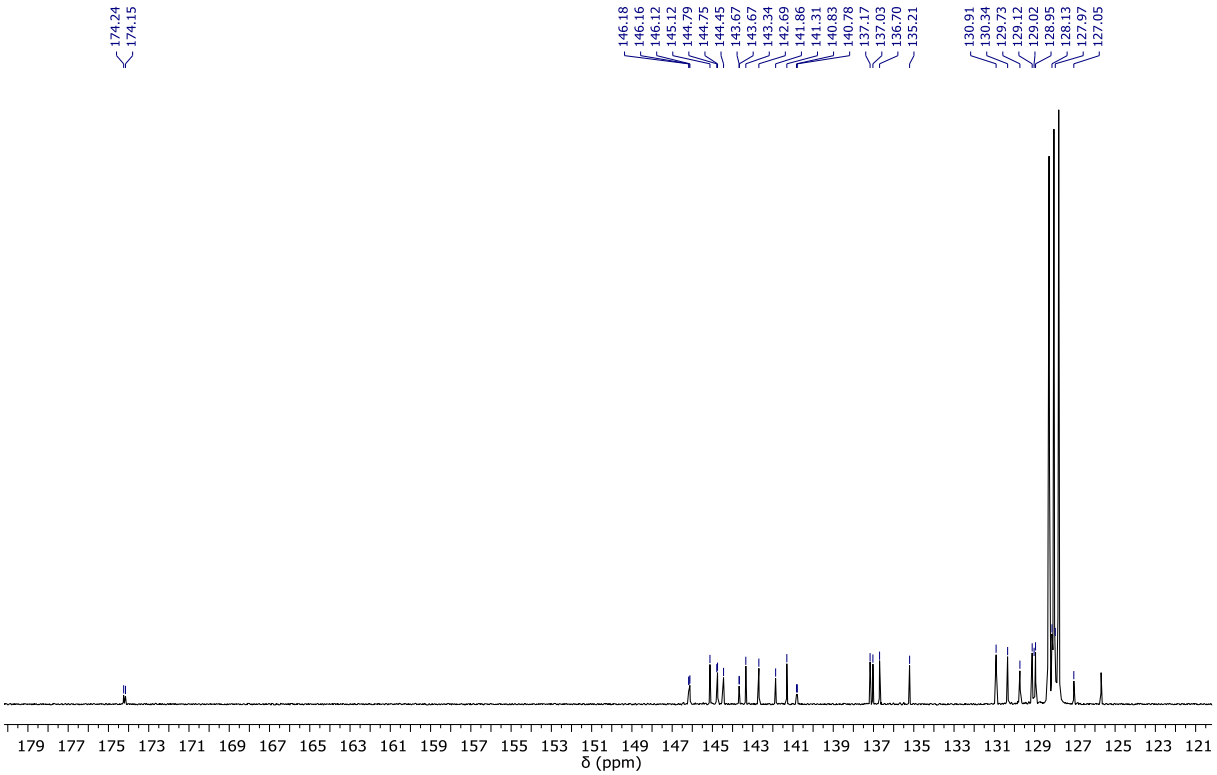


Figure S4. $^{13}C\{^{1}H\}$-NMR-spectrum (300 K, 100 MHz, C_6D_6) of compound **1** zoom into the region 180-120 ppm.

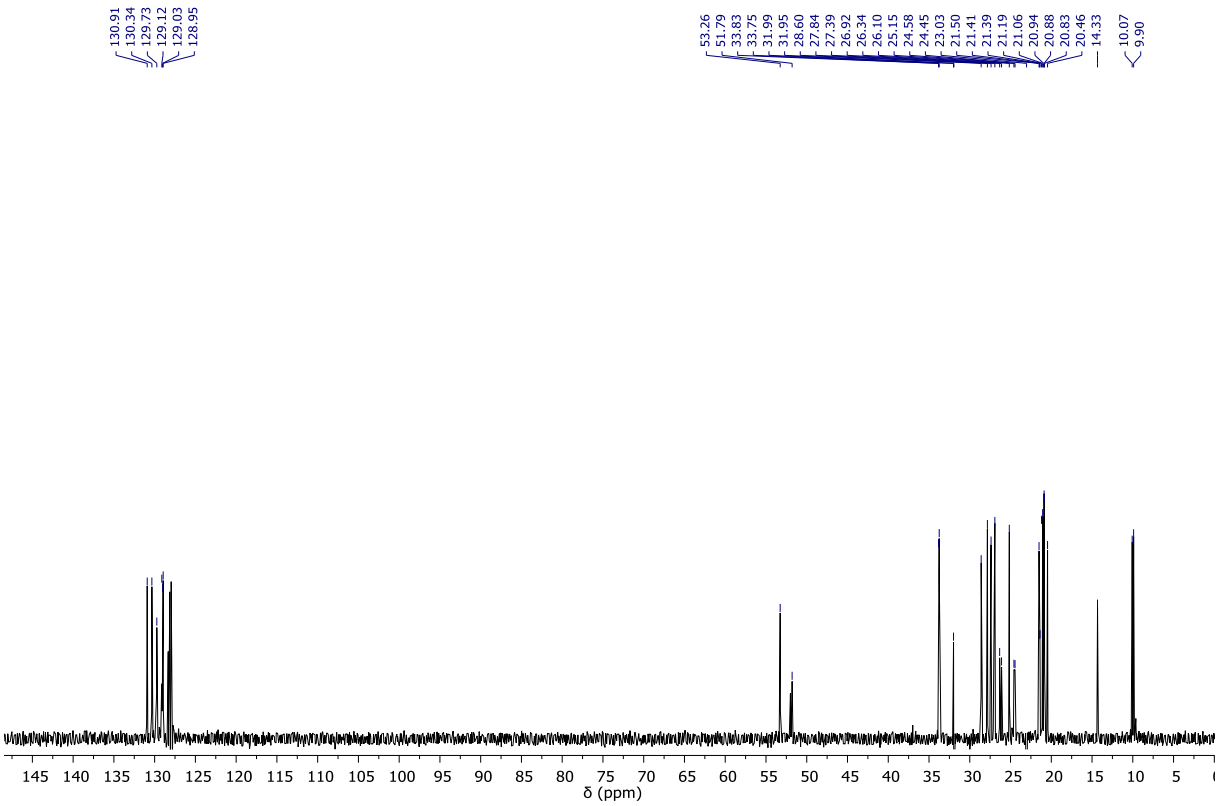


Figure S5. ^{13}C DEPT-135-NMR-spectrum (300 K, 100 MHz, C_6D_6) of compound **1**.

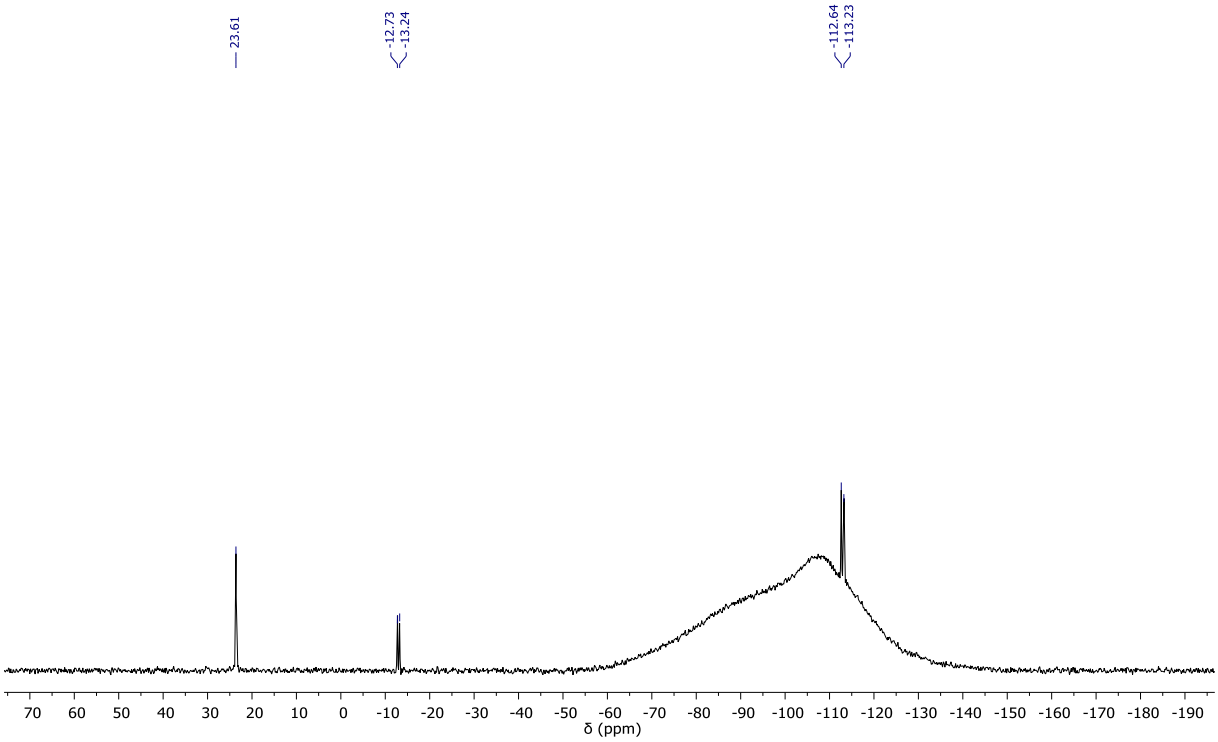


Figure S6. $^{29}Si\{^1H\}IG$-NMR-spectrum (300 K, 80 MHz, C_6D_6) of compound **1**.

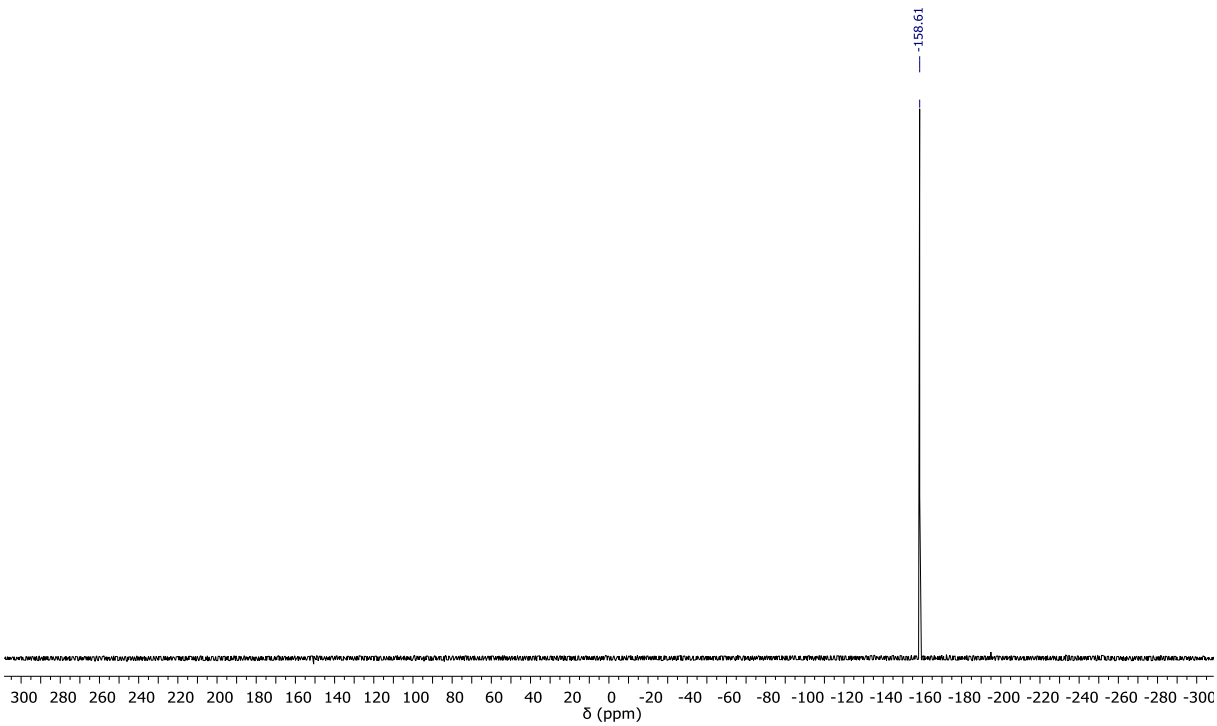


Figure S7. $^{31}P\{^{1}H\}$-NMR-spectrum (300 K, 162 MHz, C_6D_6) of compound **1**.

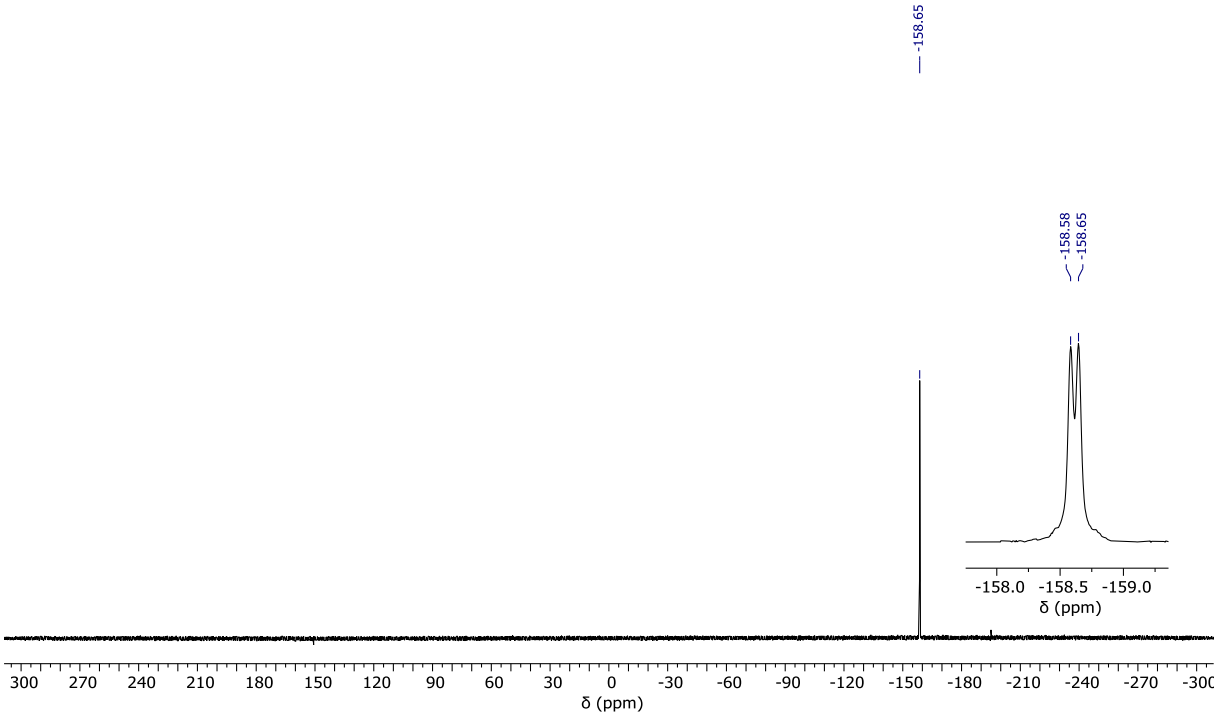


Figure S8. $^{31}P\{/\}$-NMR-spectrum (300 K, 162 MHz, C_6D_6) of compound **1**.

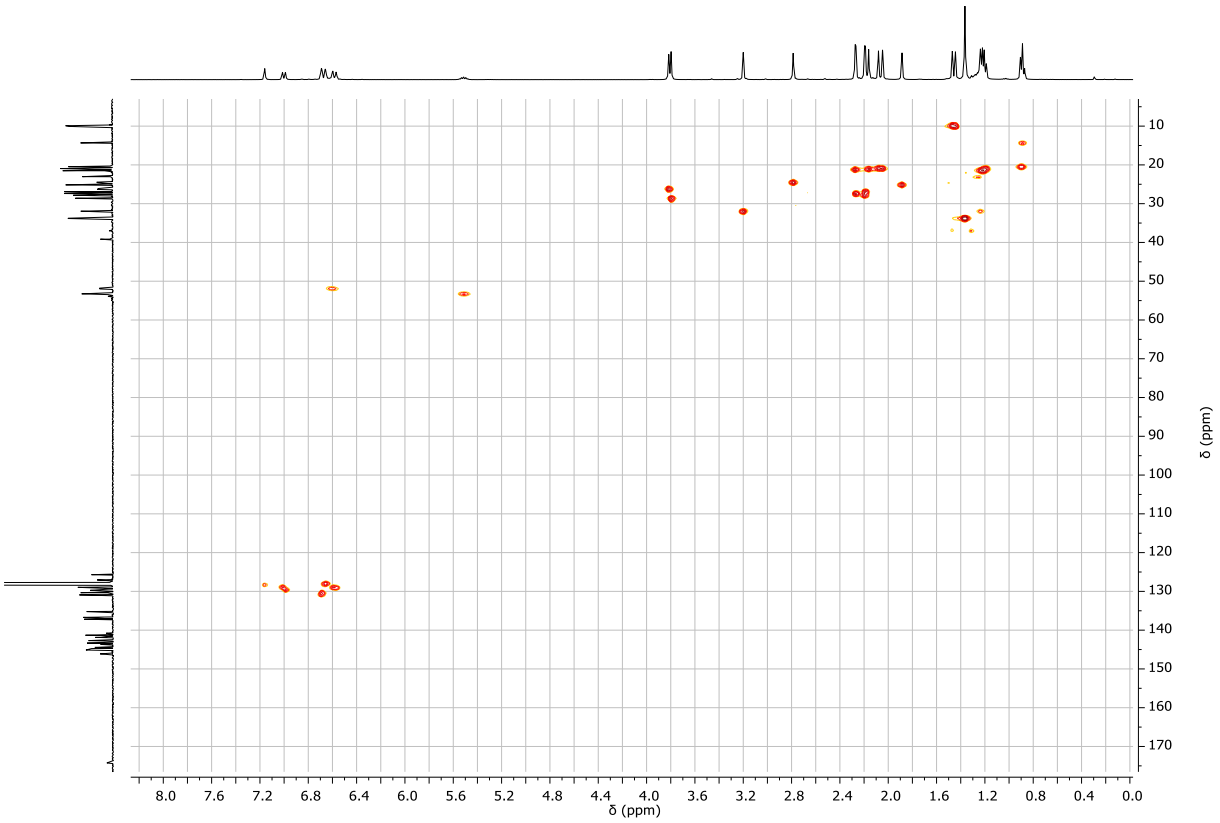


Figure S9. H,C-HSQC-NMR-spectrum (300 K, C_6D_6) of compound **1**.

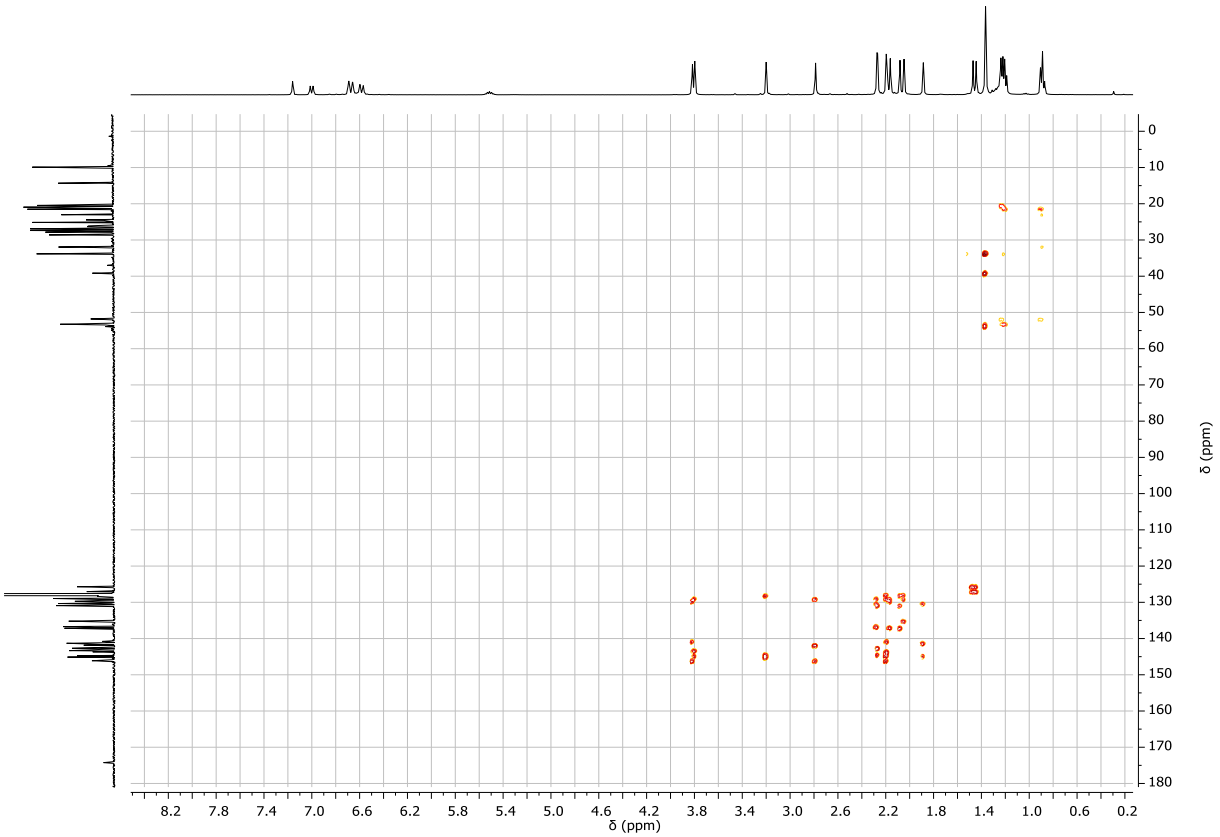


Figure S10. H,C-HMBC-NMR-spectrum (300 K, C_6D_6) of compound **1**.

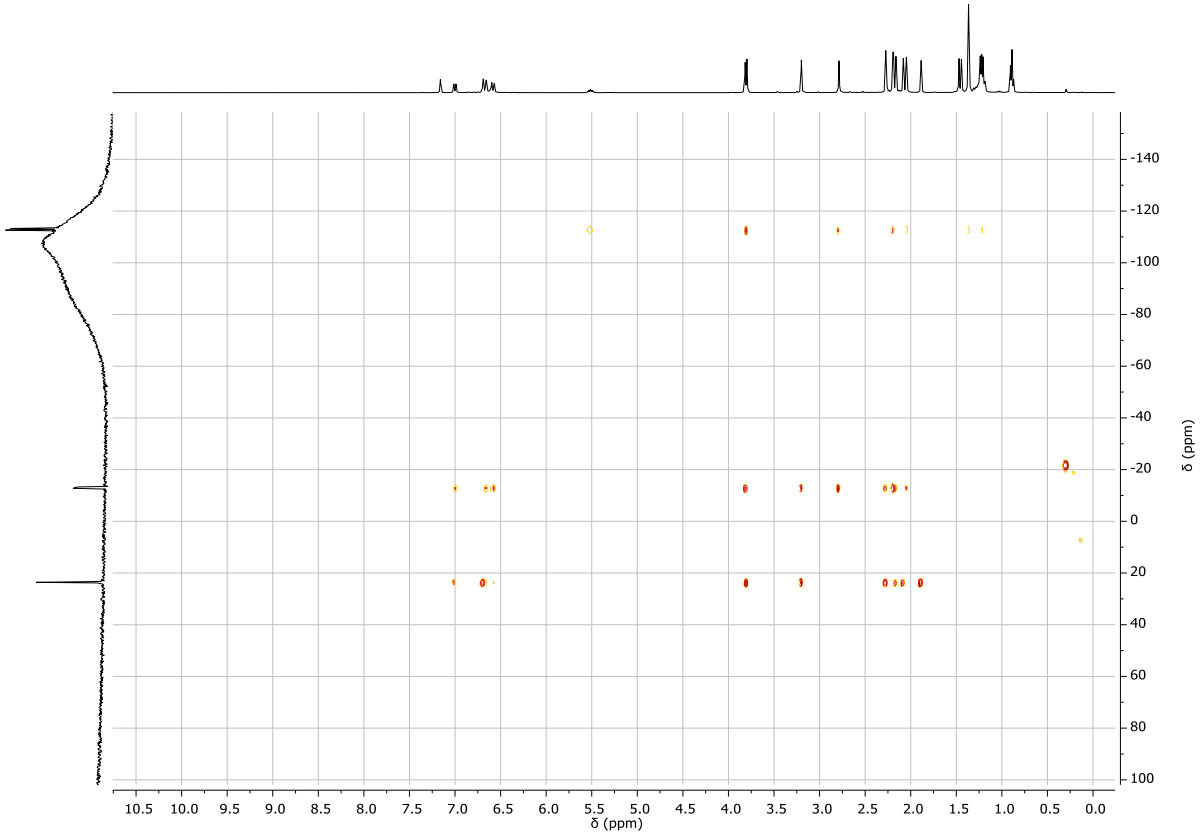


Figure S11. H,Si-HMBC-NMR-spectrum (300 K, C_6D_6) of compound **1**.

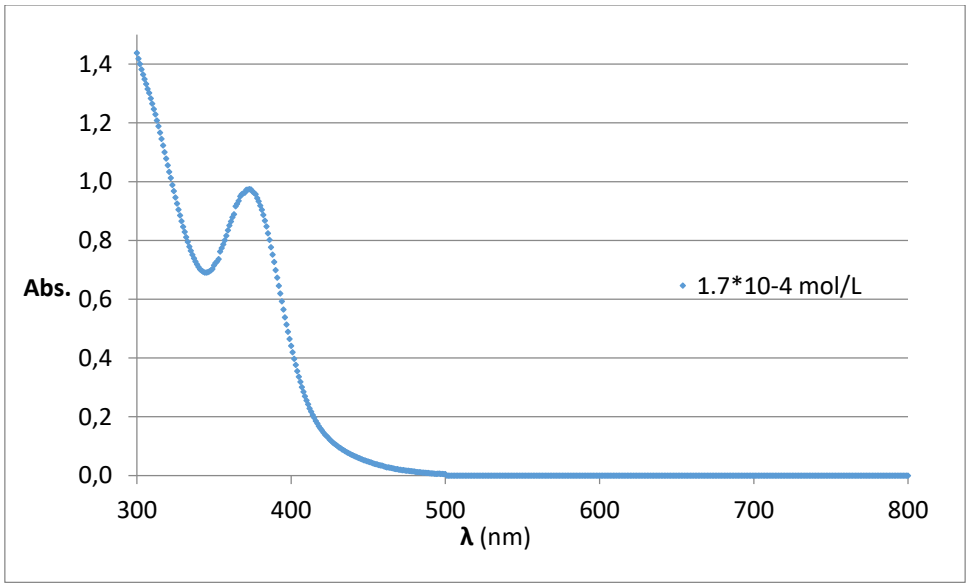


Figure S12. UV-Vis-spectrum (293 K, THF, λ = 300–800 nm) of compound **1**.

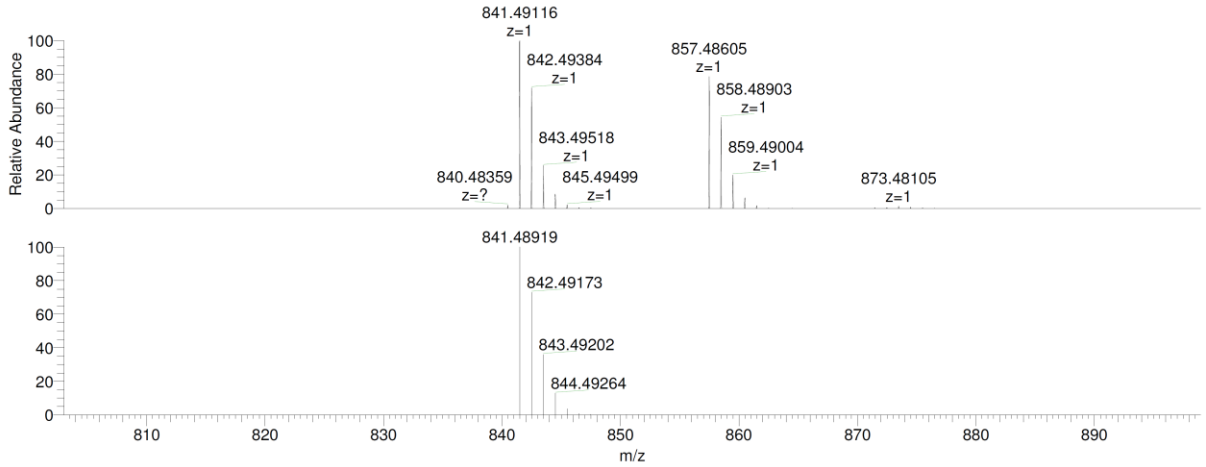


Figure S13. ESI-MS-spectrum (positive mode) of compound **1**.

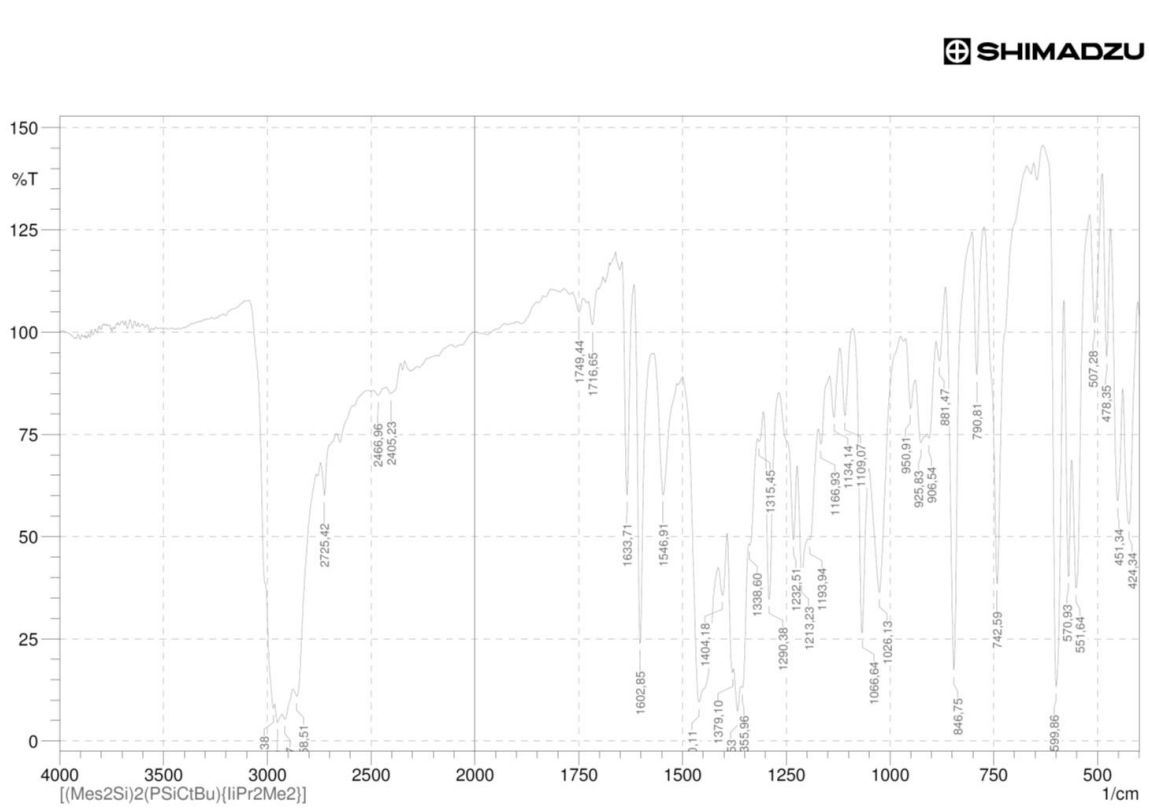
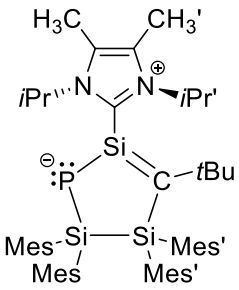


Fig. S14. FT-IR-spectrum (KBr pellet) of compound **1**.

3. Details for the synthesis and spectroscopic data for 2



2

Synthesis of 2: A yellow solution of **1** (170 mg, 0.2 mmol) in THF (5 mL) was irradiated with UV-light (high-pressure mercury lamp) for 2 h. The solution darkens to red during irradiation. During this reaction an ice bath was used to keep the reaction at ca. 0 °C. It was concentrated to a volume of 2 mL and was layered with 2 mL of *n*-hexane. Gold yellow crystals of **2** suitable for X-ray diffraction analysis formed at room temperature after 16 h. This reaction also takes place when **1** is heated to 60 °C for 16 hours.

Yield: 130 mg (0.15 mmol, 77%), gold yellow crystals.

^{1}H-NMR (300 K, 400 MHz, C_6D_6) δ/ppm: 7.13 (s, 1H, Mes'), 6.85 (s, 2H, Mes and Mes'), 6.80 (s, 1H, Mes'), 6.75 (s, 1H, Mes), 6.54 (s, 1H, Mes), 6.44 (s, 1H, Mes), 6.36 (s, 1H, Mes'), 5.37-5.22 (m, 2H, C*H*$(CH_3)_2$), 3.46 (s, 3H, *ortho*-CH_3'), 3.25 (s, 3H, *ortho*-CH_3'), 3.18 (s, 3H, *ortho*-CH_3), 3.02 (s, 3H, *ortho*-CH_3), 2.77 (s, 3H, *ortho*-CH_3), 2.67 (s, 3H, *ortho*-CH_3'), 2.53 (s, 3H, *ortho*-CH_3'), 2.24 (s, 3H, *para*-CH_3'), 2.16 (s, 3H, *para*-CH_3'), 2.15 (s, 3H, *para*-CH_3), 2.13 (s, 3H, *ortho*-CH_3), 2.05 (s, 3H, *para*-CH_3), 1.36 (d, $^{3}J_{HH}$ = 7.0 Hz, CH(C*H*$_3$)$_2$'), 1.34 (s, 3H, [C(CH_3)]$_2$), 1.31 (s, 9H, C(CH_3), 1.29 (s, 3H, [C(CH_3)]$_2$'), 1.17 (d, $^{3}J_{HH}$ = 7.0 Hz, CH(C*H*$_3$)$_2$'), 1.04 (d, $^{3}J_{HH}$ = 7.0 Hz, CH(C*H*$_3$)$_2$), 1.02 (d, $^{3}J_{HH}$ = 7.0 Hz, CH(C*H*$_3$)$_2$).

^{13}C{^{1}H}-NMR (300 K, 100 MHz, C_6D_6) δ/ppm: 158.1 (d, $^{2}J_{CP}$ = 24.1 Hz, NCN), 148.2 (*ortho*-$C_{Mes'}$), 147.6 (d, $^{2}J_{CP}$ = 14.8 Hz, *ipso*-C_{Mes}), 146.4 (*ortho*-$C_{Mes'}$), 145.9 (*ortho*-C_{Mes}), 145.4 (*ortho*-$C_{Mes'}$), 144.8 (*ortho*-C_{Mes}), 143.2 (*ortho*-$C_{Mes'}$), 141.7 (*ortho*-C_{Mes}), 140.7 (*ipso*-$C_{Mes'}$), 137.9 (*ipso*-$C_{Mes'}$), 136.6 (*para*-$C_{Mes'}$), 136.2 (d, $^{2}J_{CP}$ = 3.3 Hz, *ipso*-C_{Mes}) 135.7 (*para*-C_{Mes}), 135.5 (*para*-C_{Mes}), 130.5 (*meta*-$C_{Mes'}$), 130.3 (*meta*-C_{Mes}), 130.1 (*meta*-C_{Mes}), 129.8 (*meta*-$C_{Mes'}$), 129.2 (*meta*-$C_{Mes'}$), 129.1 (*meta*-C_{Mes}), 128.8 (*meta*-$C_{Mes'}$), 127.9 (*meta*-C_{Mes}), 127.1 ([*C*(CH_3)]$_2$), 126.9 ([*C*(CH_3)]$_2$'), 101.3 (d, $^{2}J_{CP}$ = 14.5 Hz, *C*-*t*Bu), 54.9 (*C*H(CH_3)$_2$), 54.5 (*C*H(CH_3)$_2$'), 38.6 (d, $^{3}J_{CP}$ = 3.8 Hz, *C*(CH_3)$_3$), 37.0 (C(*C*H_3)$_3$), 31.6 (*ortho*-CH_3), 30.4 (*ortho*-CH_3), 29.6 (*ortho*-CH_3'), 27.7 (*ortho*-CH_3), 27.1 (*ortho*-CH_3'), 26.9 (*ortho*-CH_3), 25.2 (*ortho*-

CH_3'), 24.8 (*ortho*-CH_3'), 22.1 (d, $^4J_{CP}$ = 4.6 Hz, *C*H(CH_3)$_2$), 22.0 (d, $^4J_{CP}$ = 2.9 Hz, *C*H(CH_3)$_2$'), 21.2 (*para*-$C_{Mes'}$), 21.0 (overlapping, *para*-C_{Mes} *and para*-$C_{Mes'}$), 20.9 (*para*-C_{Mes}), 20.7 (CH(*C*H_3)$_2$), 20.3 (CH(*C*H_3)$_2$'), 9.7 (overlapping, [C(CH_3)]$_2$ and [C(CH_3)]$_2$').

^{31}P{^{1}H}-NMR (300 K, 162 MHz, C_6D_6) *δ*/ppm: −195.0 (s).

^{31}P{/}-NMR (300 K, 162 MHz, C_6D_6) *δ*/ppm: −195.0 (s).

^{29}Si{^{1}H}IG-NMR (300 K, 80 MHz, C_6D_6) *δ*/ppm: 96.3 (d, $^1J_{SiP}$ = 139.8 Hz, *Si*-NHC), −6.7 (d, $^1J_{SiP}$ = 67.7 Hz, (Mes$_2$*Si*P), −19.9 (d, $^2J_{SiP}$ = 11.9 Hz, (Mes$_2$*Si*C*t*Bu).

Melting point: 194 °C (decomposition).

CHN-analysis: calc.: C, 74.23; H, 8.75; N, 3.33; found: C, 74.25; H, 8.72; N, 3.26.

MS (ESI, positve mode): calc.: *m*/z = 841.48919 $[M-H]^+$, found: *m*/z = 841.49085 $[M-H]^+$.

FT-IR (KBr-pellet) $\tilde{\upsilon}$/cm^{-1}: 3063 (m), 3019 (s), 2968 (s), 2924 (s), 2857 (m), 2731 (m), 1956 (w), 1892 (w), 1811 (w), 1771 (w), 1601 (s), 1549 (m), 1530 (m), 1454 (s), 1439 (s), 1406 (m), 1375 (m), 1323 (vs), 1242(m), 1157 (vs), 1126 (s), 1069 (vs), 1024 (s), 988 (w), 922(m), 876 (w), 851 (s), 800 (w), 770 (w), 745 (s), 694 (s), 654 (m), 623 (m), 602 (w), 557 (w), 517 (w), 498 (w), 478 (w), 434 (w), 413 (w).

UV/vis (c = 2.1·10^{-4} mol/L in THF): λ_{max} = 418 nm (ε = 1715 L mol^{-1} cm^{-1}).

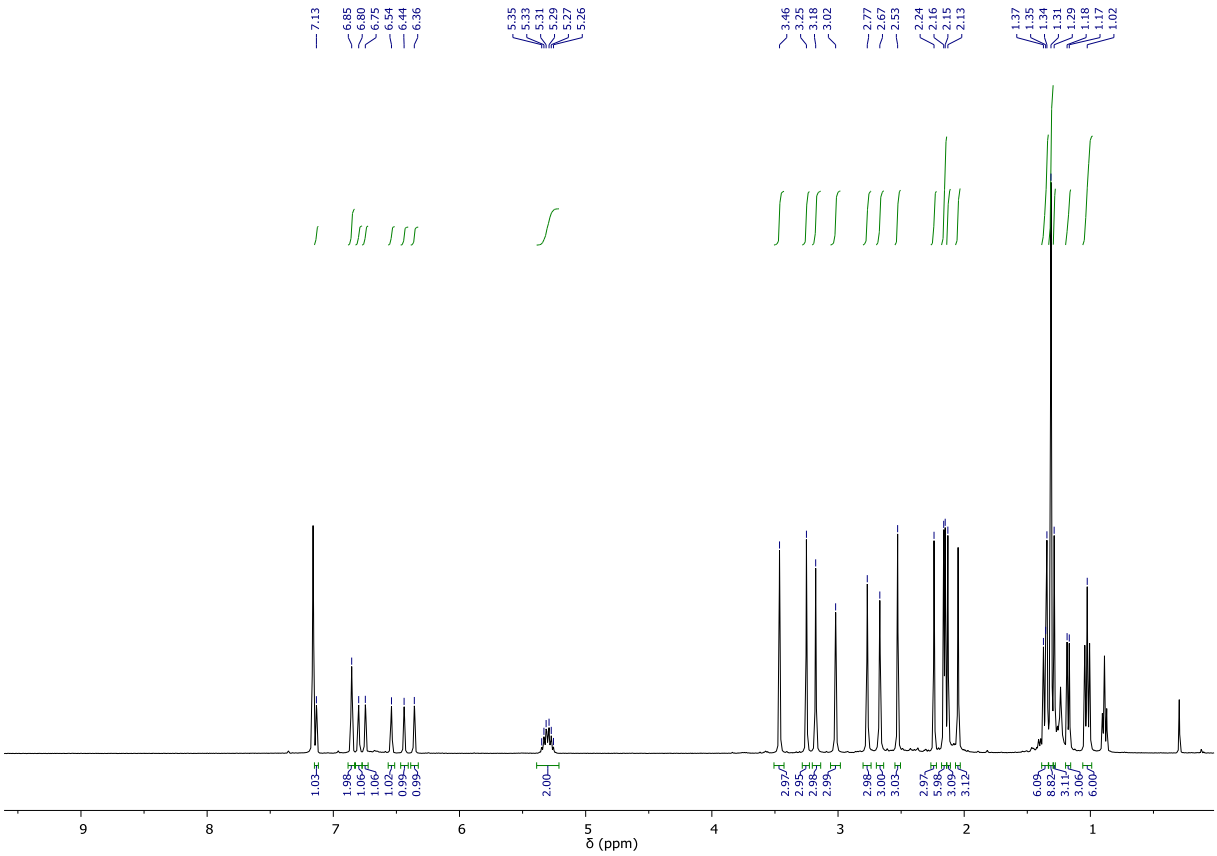


Figure S15. ^{1}H-NMR-spectrum (300 K, 400 MHz, C_6D_6) of compound **2**.

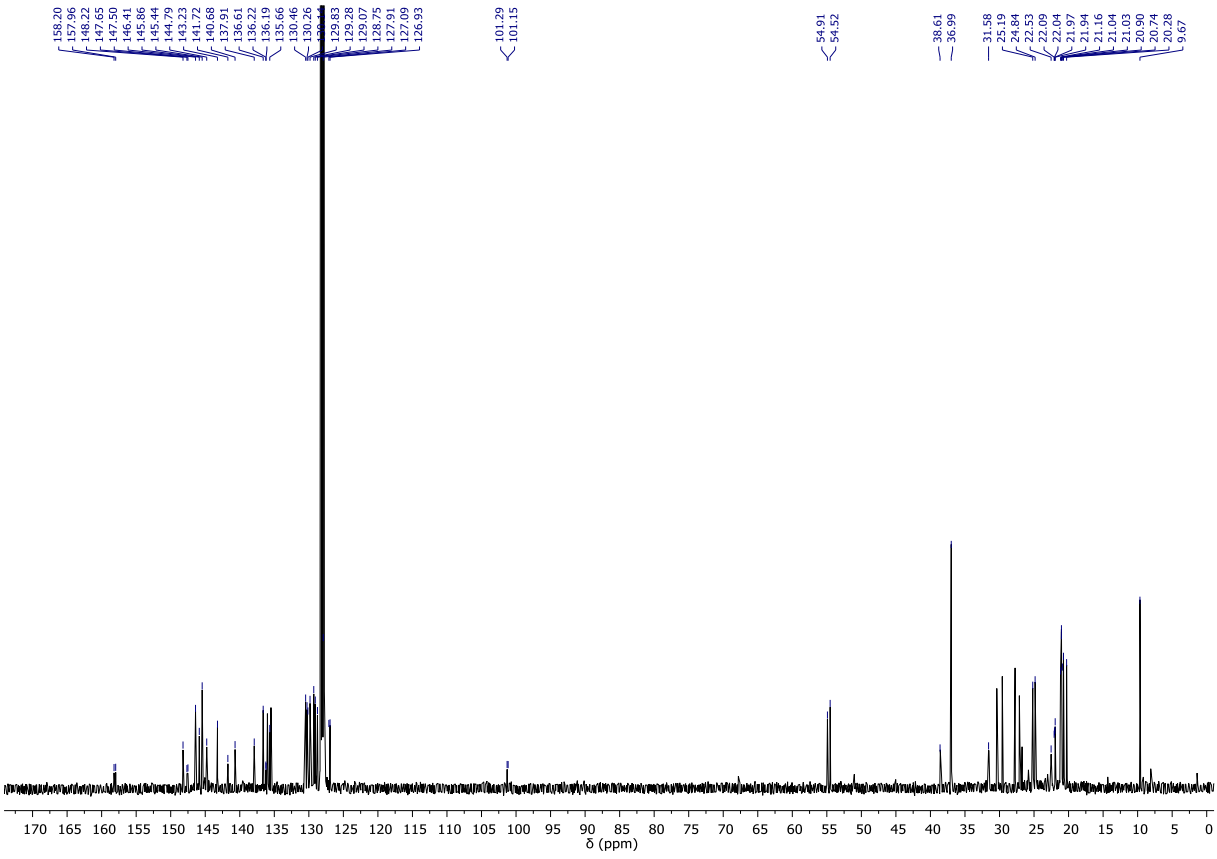


Figure S16. ^{13}C{^{1}H}-NMR-spectrum (300 K, 100 MHz, C_6D_6) of compound **2**.

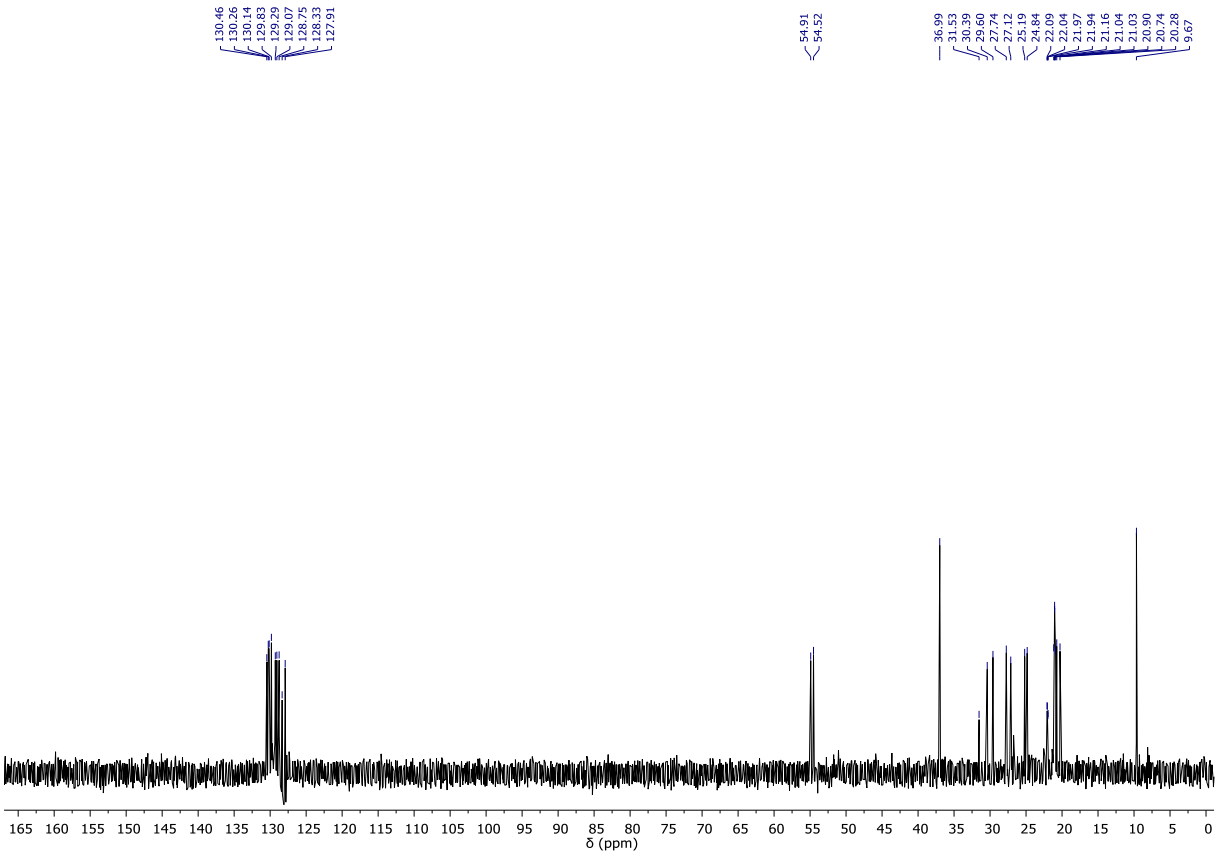


Figure S17. ^{13}C DEPT-135-NMR-spectrum (300 K, 100 MHz, C_6D_6) of compound **2**.

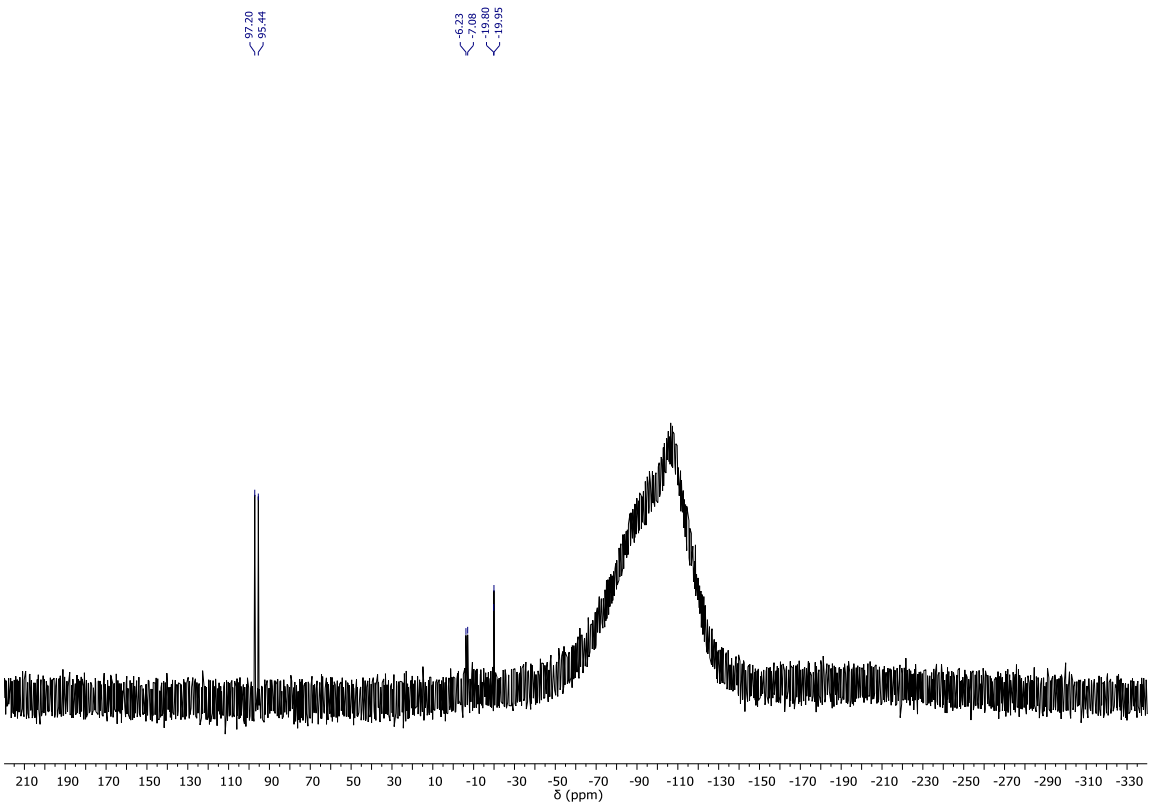


Figure S18. $^{29}Si\{^1H\}IG$-NMR-spectrum (300 K, 80 MHz, C_6D_6) of compound **2**.

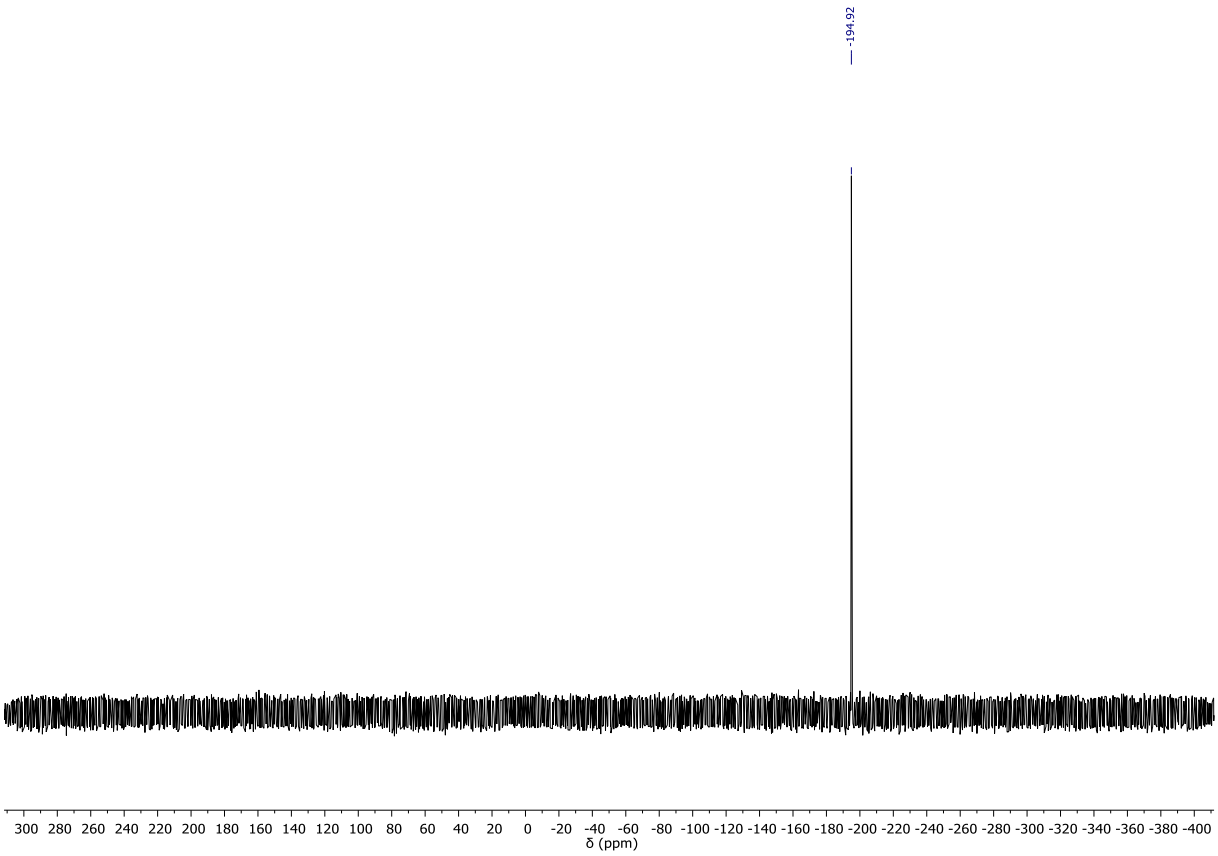


Figure S19. $^{31}P\{^{1}H\}$-NMR-spectrum (300 K, 162 MHz, C_6D_6) of compound **2**.

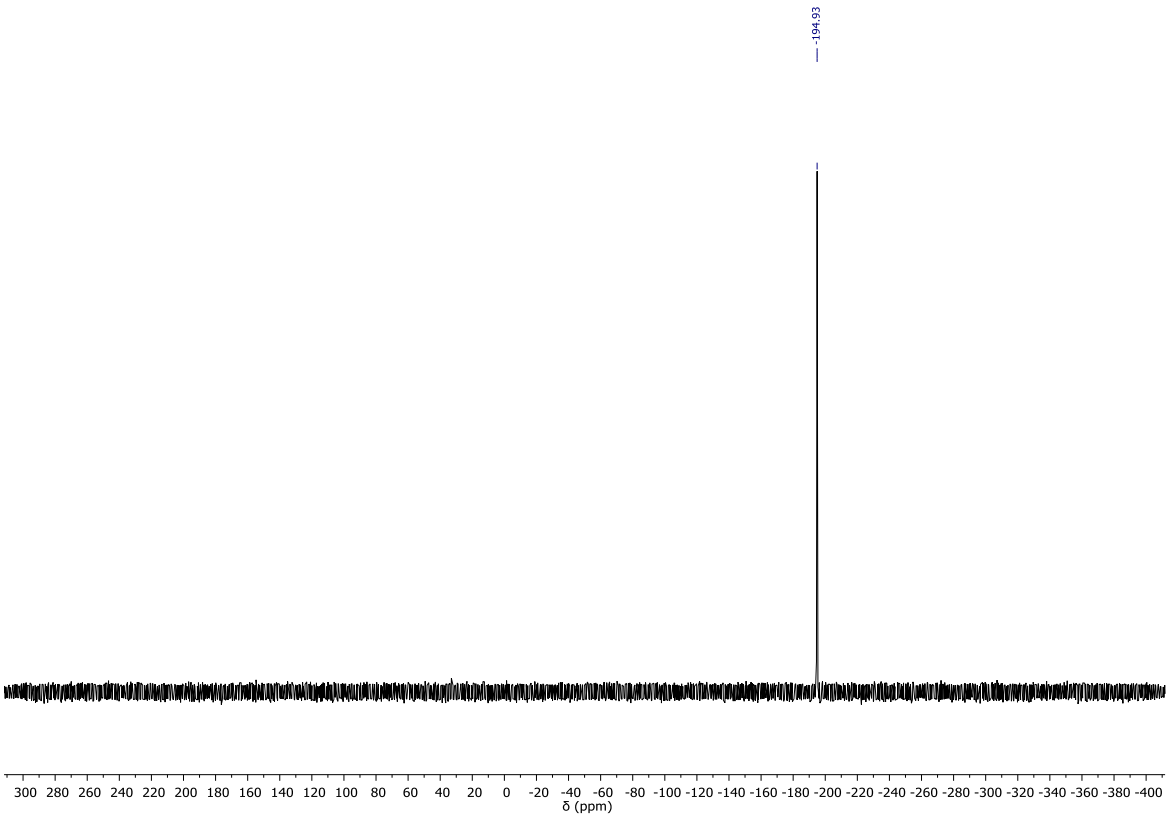


Figure S20. $^{31}P\{/\}$-NMR-spectrum (300 K, 162 MHz, C_6D_6) of compound **2**.

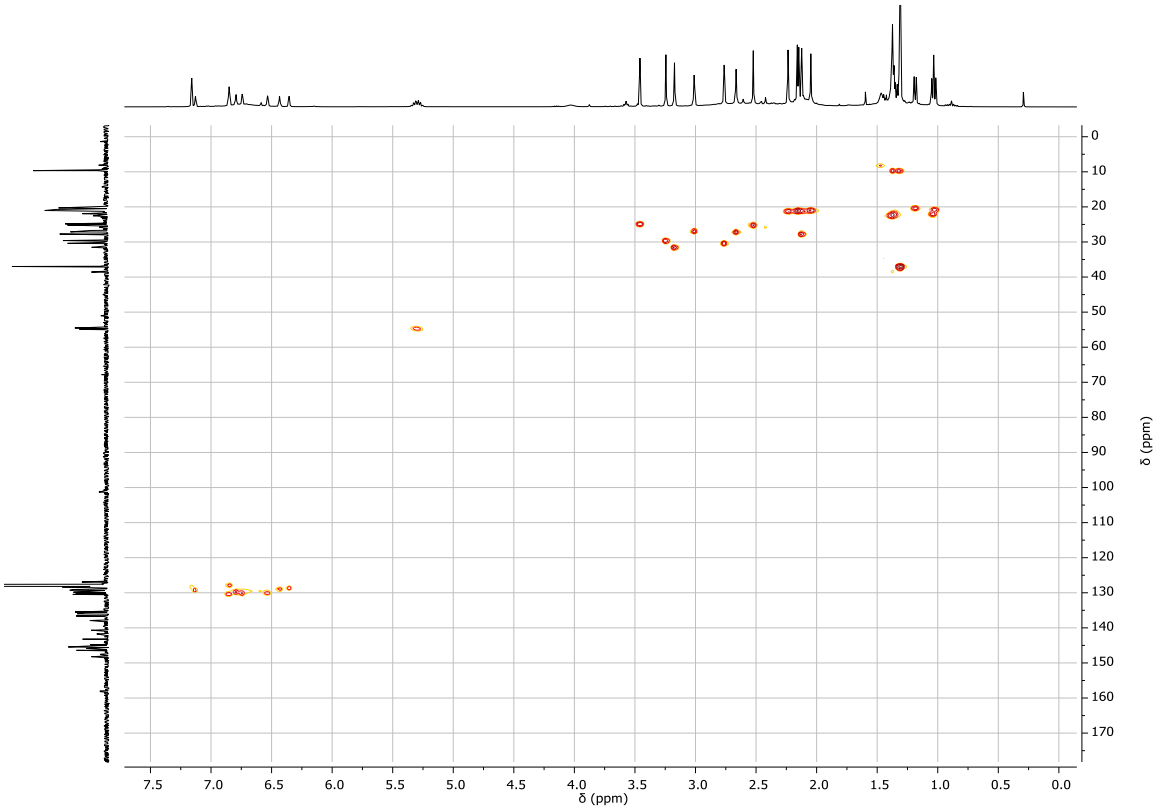


Figure S21. H,C-HSQC-NMR-spectrum (300 K, C_6D_6) of compound **2**.

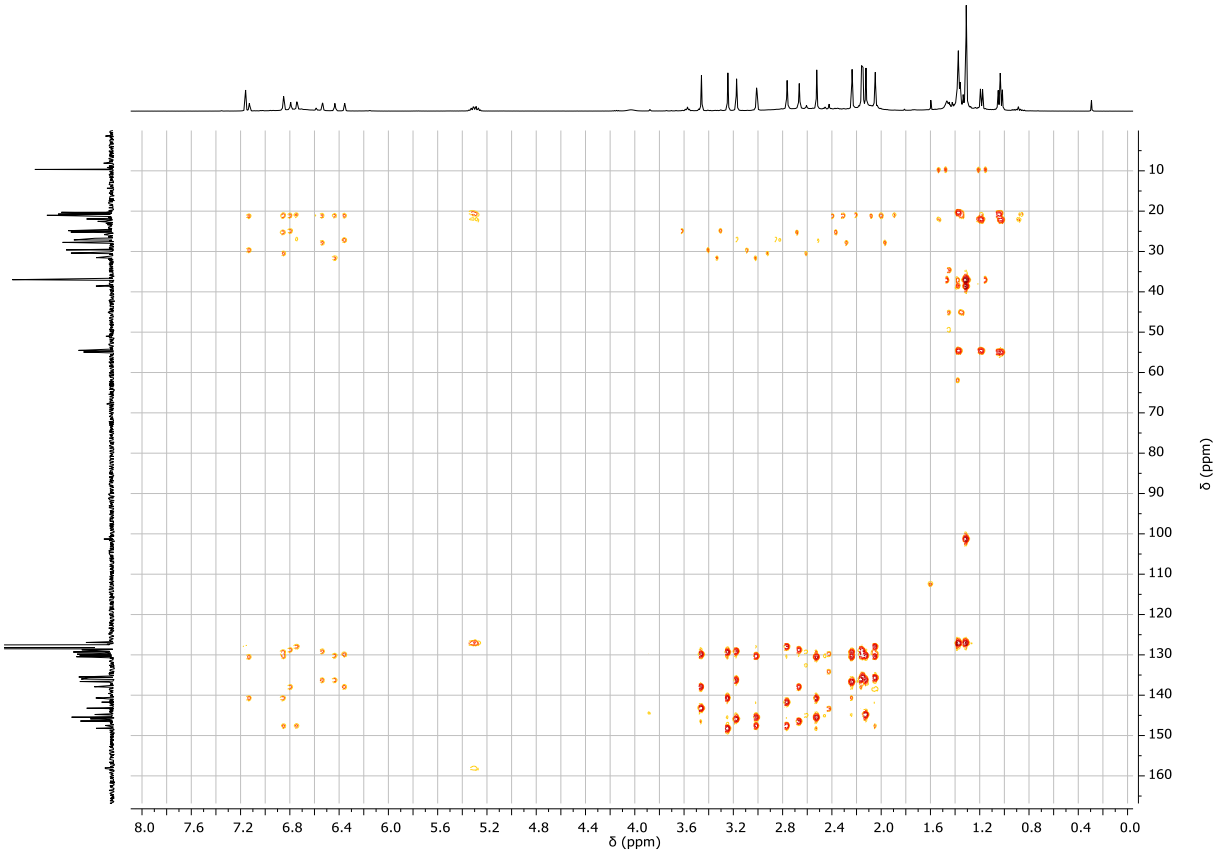


Figure S22. H,C-HMBC-NMR-spectrum (300 K, C_6D_6) of compound **2**.

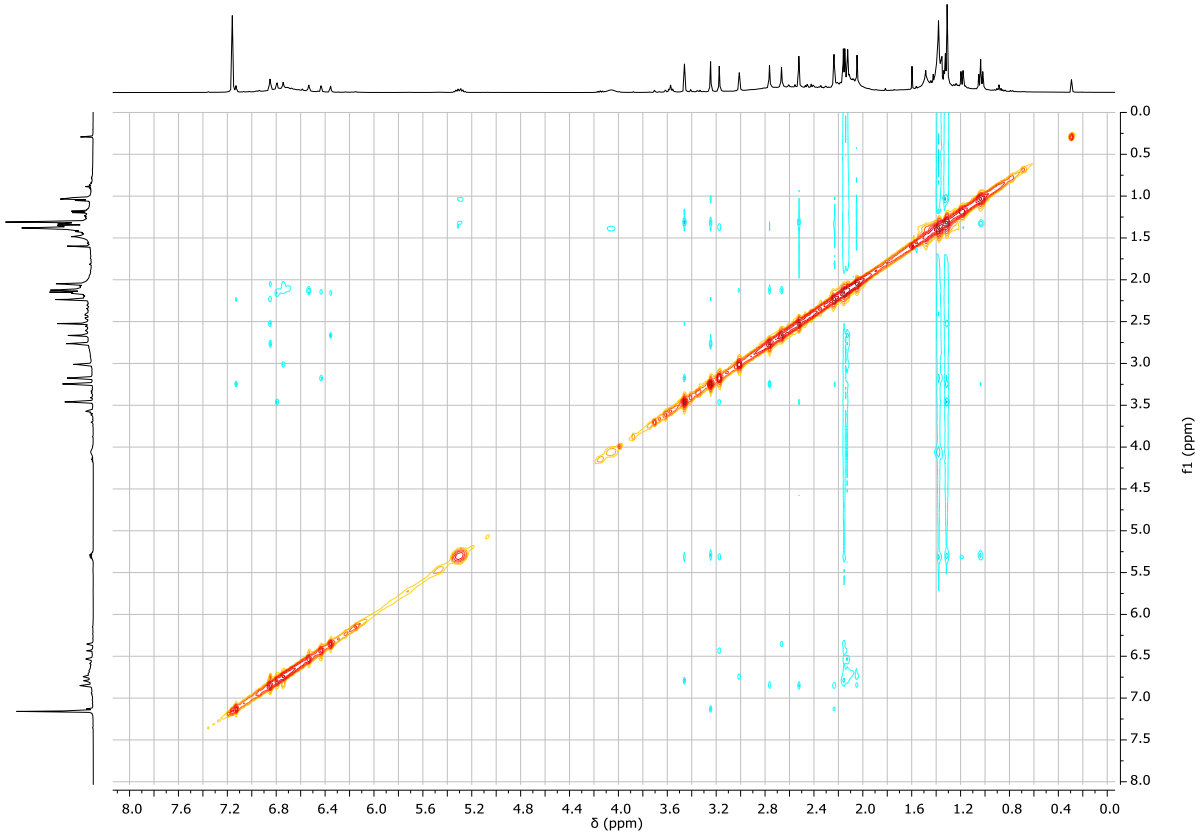


Figure S23. H,H-ROESY-NMR-spectrum (300 K, 400 MHz, C_6D_6) of compound **2**.

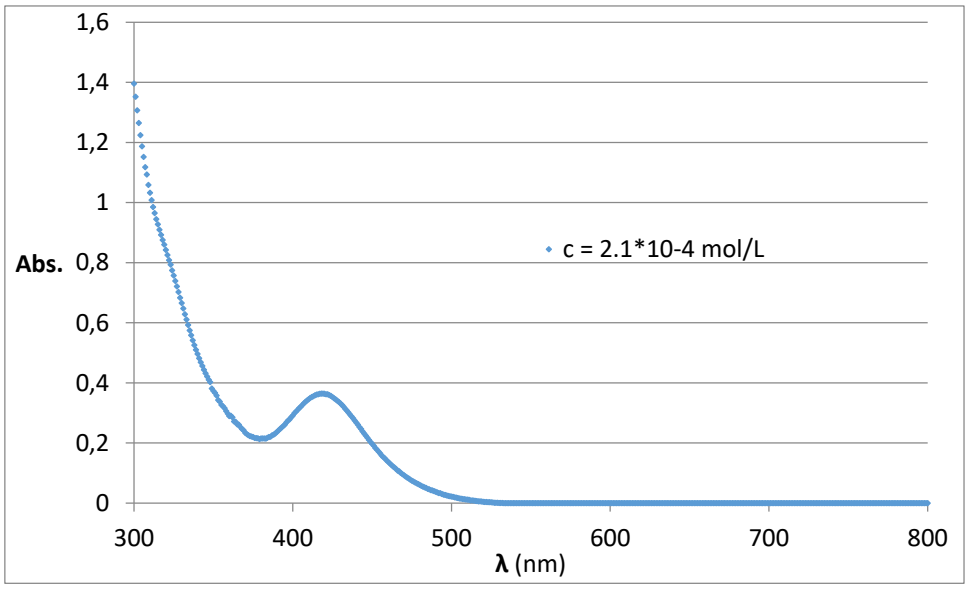


Figure S24. UV-Vis-spectrum (293 K, THF, λ = 300–800 nm) of compound **2**.

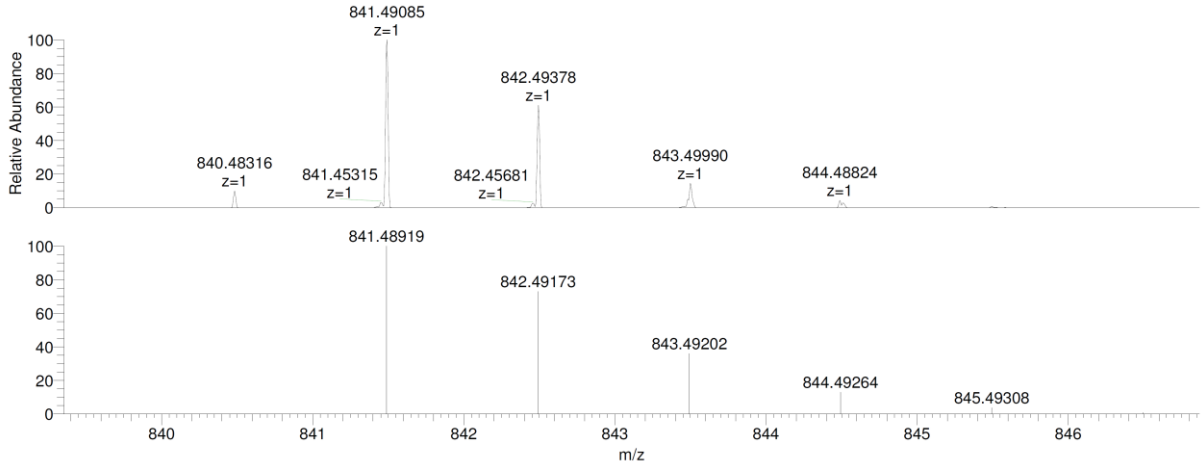


Figure S25. ESI-MS-spectrum (positive mode) of compound **2**.

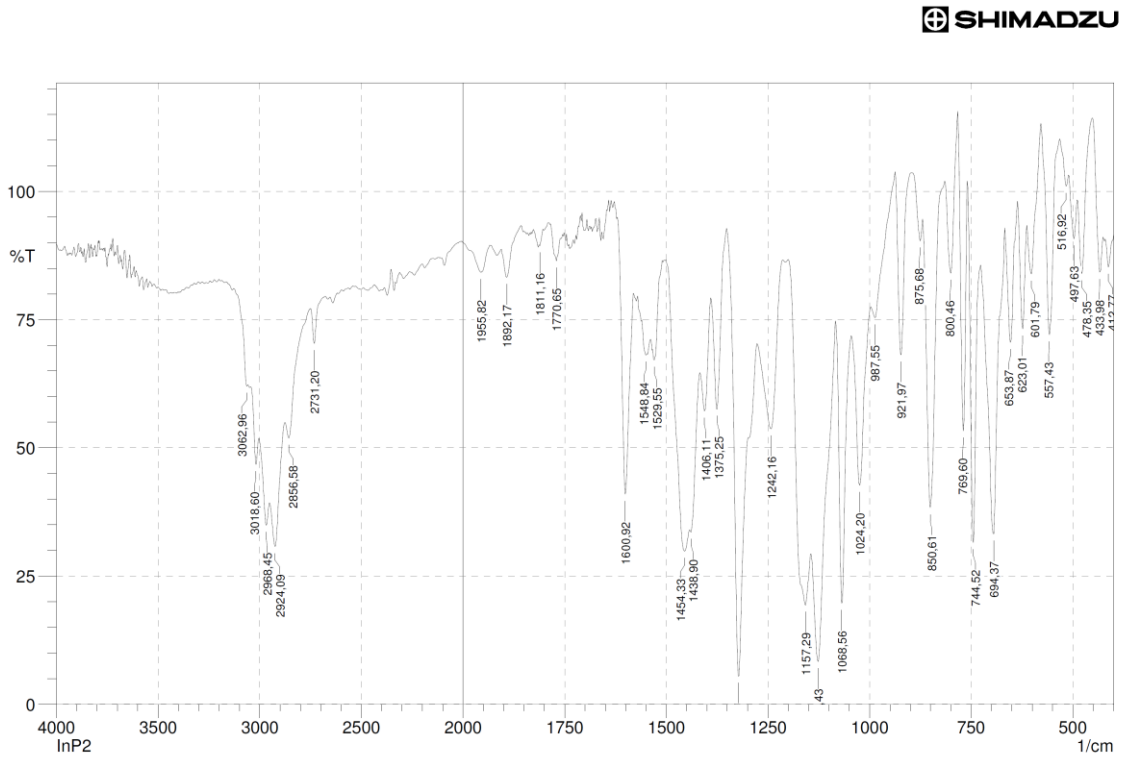
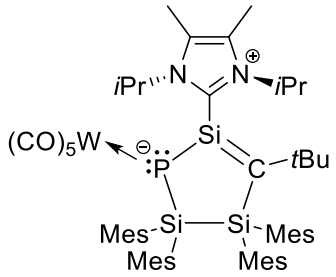


Figure S26. FT-IR-spectrum (KBr pellet) of compound **2**.

4. Details for the synthesis and spectroscopic data for 3



3

Synthesis of 3: A solution of $W(CO)_5THF$ (110 mg, 3.1 mmol, 1.1 eq. $W(CO)_6$ in 10 mL of THF was freshly prepared within 4 h of irradiation with a high pressure mercury lamp at ambient conditions. The solution of $W(CO)_5THF$ was added dropwise to the solution of **2** (250 mg, 0.3 mmol, 1 eq., dissolved in 20 mL of THF) at room temperature. During this process, the colour changed gradually to dark red within 30 min. and the reaction was stirred for additional 16 h. The solution was concentrated to a volume of 5 mL and was layered with the same amount of *n*-hexane. Red orange crystals of **3** suitable for X-ray diffraction analysis were obtained after 16 h at ambient conditions.

Yield: 304 mg (0.26 mmol, 87%), red orange crystals.

^{1}H-NMR (300 K, 400 MHz, THF-d_8) δ/ppm 6.87 (s, 1H, *meta*-H_{Mes}), 6.76 (s, 1H, *meta*-H_{Mes}), 6.68 (s, 1H, *meta*-H_{Mes}), 6.57 (s, 1H, *meta*-H_{Mes}), 6.34 (overlapping, 2H, 2x *meta*-H_{Mes}), 6.19 (s, 1H, *meta*-H_{Mes}), 6.02 (s, 1H, *meta*-H_{Mes}), 5.73 (br, 1H, C*H*$(CH_3)_2$), 5.10 (sept., $^3J_{HH}$ = 6.9 Hz, 1H, C*H*$(CH_3)_2$'), 3.15 (s, 3H, *ortho*-CH_3), 3.01 (s, 3H, *ortho*-CH_3'), 2.72 (s, 3H, *ortho*-CH_3'), 2.43 (s, 3H, [C$(CH_3)]_2$), 2.41 (s, 3H, [C$(CH_3)]_2$'), 2.35 (s, 3H, *ortho*-CH_3), 2.32 (s, 3H, *ortho*-CH_3'), 2.27 (s, 3H, *ortho*-CH_3'), 2.23 (s, 3H, *para*-CH_3'), 2.11 (overlapping, 6H, *para*-CH_3 and *ortho*-CH_3), 2.03 (s, 3H, *para*-CH_3), 2.01 (s, 3H, *para*-CH_3'), 1.84 (d, $^3J_{HH}$ = 6.9 Hz, 3H, C*H*$(CH_3)_2$'), 1.77 (d, $^3J_{HH}$ = 6.9 Hz, 3H, C*H*$(CH_3)_2$), 1.70, (d, $^3J_{HH}$ = 6.9 Hz, 3H, C*H*$(CH_3)_2$) 1.67 (d, $^3J_{HH}$ = 6.9 Hz, 3H, C*H*$(CH_3)_2$'), 1.28 (s, 3H, *ortho*-CH_3), 0.98 (s, 9H, C$(CH_3)_3$).

^{13}C{^{1}H}-NMR (300 K, 100 MHz, THF-d_8) δ/ppm: 200.9 (br, $CO_{ax.}$), 200.0 (t, $^1J_{CW}$ = 126 Hz, 4x $CO_{ep.}$), 151.2 (d, $^2J_{CP}$ = 18.6 Hz, NCN), 147.3 (*ortho*-$C_{Mes'}$), 146.5 (*ortho*-$C_{Mes'}$), 145.7 (*ortho*-C_{Mes}), 144.9 (*ortho*-C_{Mes}), 144.4 (br, *ortho*-$C_{Mes'}$), 142.9 (*ortho*-$C_{Mes'}$), 141.7 (*ortho*-C_{Mes}), 141.3 (br, *ipso*-C_{Mes}), 140.1 (*ipso*-$C_{Mes'}$), 138.1 (*ipso*-$C_{Mes'}$), 137.9 (*para*-C_{Mes}), 137.5 (*para*-$C_{Mes'}$), 136.6 (*para*-C_{Mes}), 136.4 (*para*-$C_{Mes'}$), 135.3 (br, *ipso*-C_{Mes}), 131.6 ([*C*$(CH_3)]_2$'), 131.5 ([*C*$(CH_3)]_2$), 131.2 (*meta*-C_{Mes}), 130.7 (*meta*-$C_{Mes'}$), 130.1 (*meta*-$C_{Mes'}$), 129.9 (*meta*-

C_{Mes}), 129.7 (*meta*-$C_{Mes'}$), 129.5 (*meta*-$C_{Mes'}$), 129.1 (*meta*-C_{Mes}), 129.0 (*meta*-C_{Mes}), 126.4 (br, C=Si), 56.1 (*C*H(CH_3)$_2$'), 55.7 (d, $^4J_{CP}$ = 4.6 Hz *C*H(CH_3)$_2$), 40.3 (d, $^3J_{CP}$ = 2.4 Hz, *C*(CH_3)$_3$), 37.2 (C(*C*H_3)$_3$), 33.4 (*ortho*-CH_3'), 31.0 (d, $^2J_{CP}$ = 17.0 Hz, *ortho*-CH_3), 29.7 (*ortho*-CH_3), 28.6 (*ortho*-CH_3), 27.8 (*ortho*-CH_3'), 27.0 (d, $^2J_{CP}$ = 16.8 Hz, *ortho*-CH_3), 26.4 (*ortho*-CH_3'), 25.1 (*ortho*-CH_3'), 23.4 (CH(*C*H_3)$_2$'), 22.6 (CH(*C*H_3)$_2$'), 21.6 (CH(*C*H_3)$_2$) 21.0 (overlapping, CH(*C*H_3)$_2$ and *para*-CH_3), 20.9 (*para*-CH_3), 20.8 (overlapping, *para*-CH_3 and *para*-CH_3') 10.8 ([C(*C*H_3)]$_2$'), 10.4 ([C(*C*H_3)]$_2$).

^{31}P{^{1}H}-NMR (300 K, 162 MHz, THF-d$_8$) δ/ppm: −257.6 (s, $^1J_{PW}$ = 135 Hz, P-W(CO)$_5$).

^{31}P{/}-NMR (300 K, 162 MHz, THF-d$_8$) δ/ppm: −257.6 (s, $^1J_{PW}$ = 135 Hz, P-W(CO)$_5$).

^{29}Si{^{1}H}IG-NMR (300 K, 80 MHz, THF-d$_8$) δ/ppm: 93.7 (d, $^1J_{SiP}$ = 80.5 Hz, Si{NHC}), −7.5 (d, $^1J_{SiP}$ = 43.6 Hz, (Mes$_2$*Si*P)), −16.4 (s, (Mes$_2$*Si*C-*t*Bu).

Melting point: 203 °C (decomposition).

CHN-analysis: calc.: C, 58.75; H, 6.31; N, 2.40; found: C, 58.79; H, 6.68; N, 2.24.

MS (ESI, positive mode): calc.: m/z = 1165.41520 $[M-H]^+$, found: m/z = 1165.41708 $[M-H]^+$.

FT-IR (KBr-pellet): $\tilde{\upsilon}$/cm^{-1}: 2953 (m), 2916 (m), 2868(m), 2052(s), 1965 (vs), 1906 (vs), 1873 (vs), 1620 (vw), 1603 (w), 1543 (vw), 1458 (w), 1447 (w), 1383 (w), 1373 (w), 1308 (vw), 1287 (vw), 1244 (m), 1200 (w), 1155 (w), 1047 (vw), 1024 (vw), 984 (vw), 907 (vw), 874 (w), 847 (w), 787 (w), 598 (w), 584 (w), 565 (vw), 552 (vw), 511 (vw), 465 (w).

UV/vis (c = 9.2·10^{-5} mol/L in THF): λ_{max} = 464 nm (ε = 4520 L·mol^{-1}·cm^{-1}), 336 nm (ε = 9520 L·mol^{-1}·cm^{-1}).

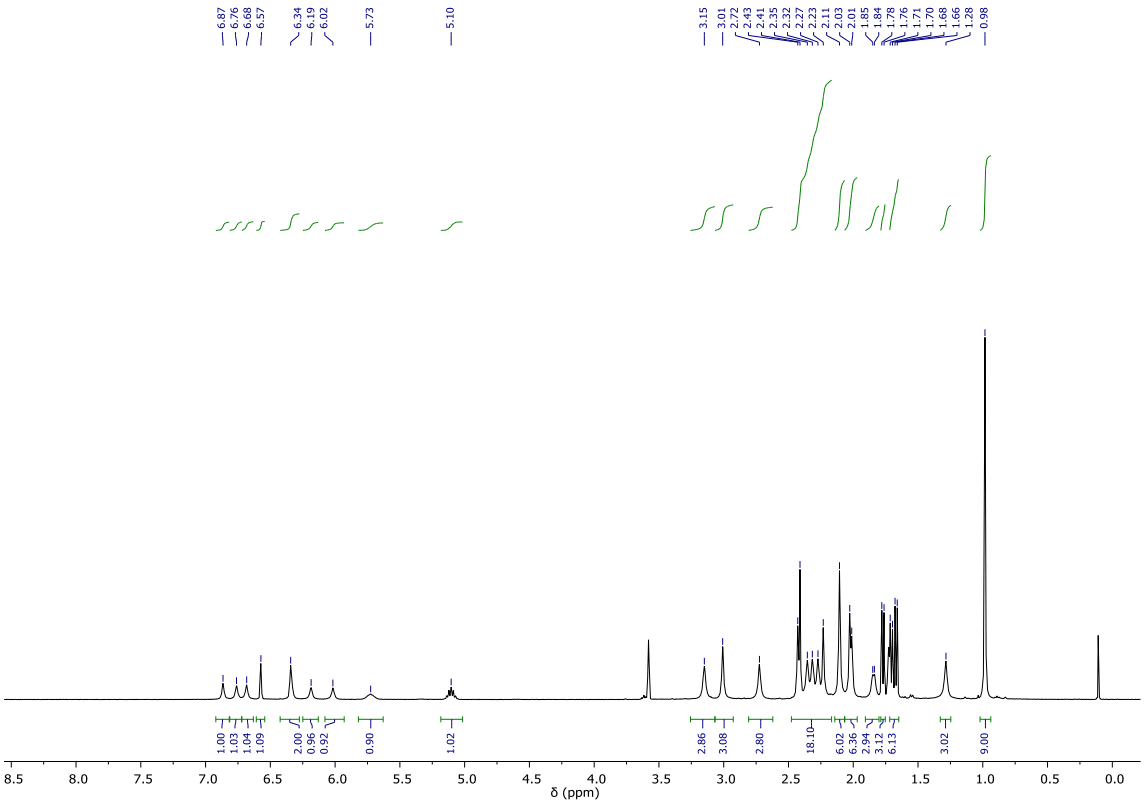


Figure S27. ^{1}H-NMR-spectrum (300 K, 400 MHz, C_6D_6) of compound **3**.

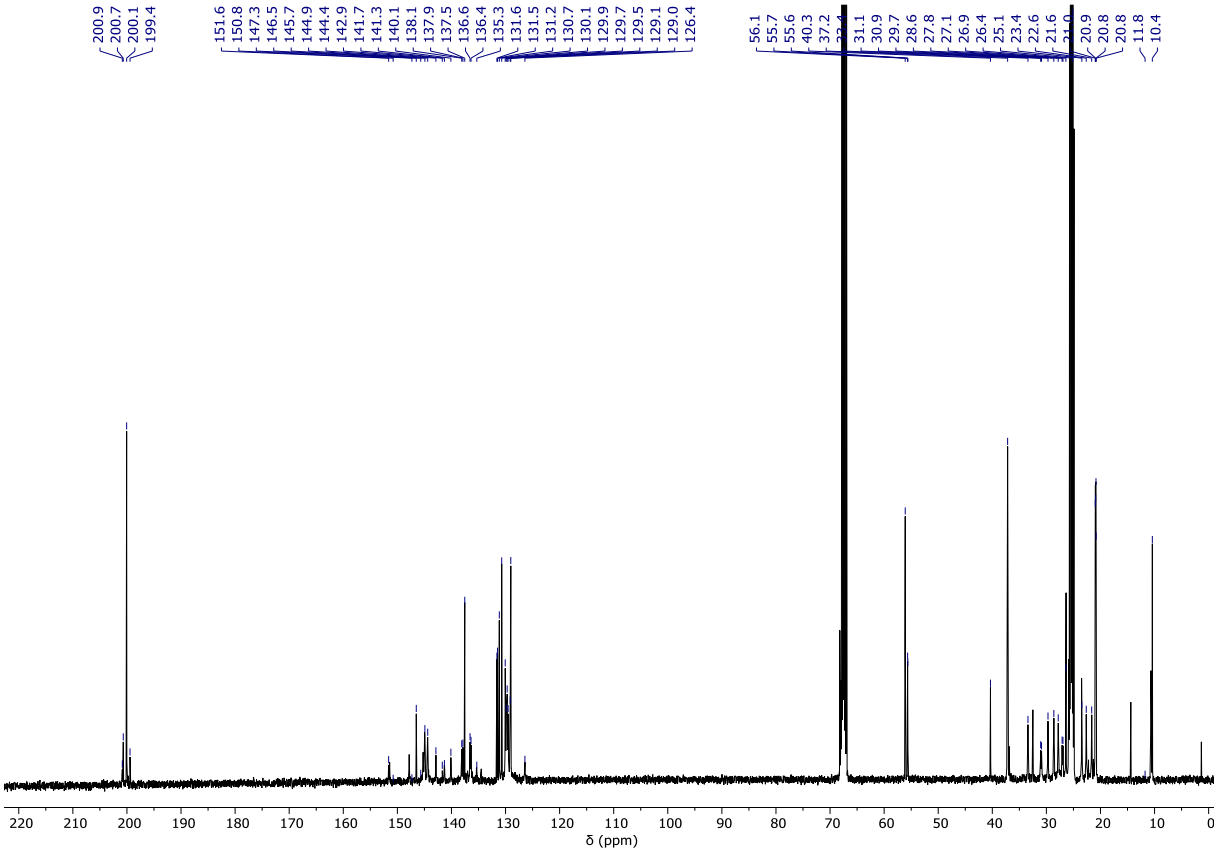


Figure S28. ^{13}C{^{1}H}-NMR-spectrum (300 K, 100 MHz, C_6D_6) of compound **3**.

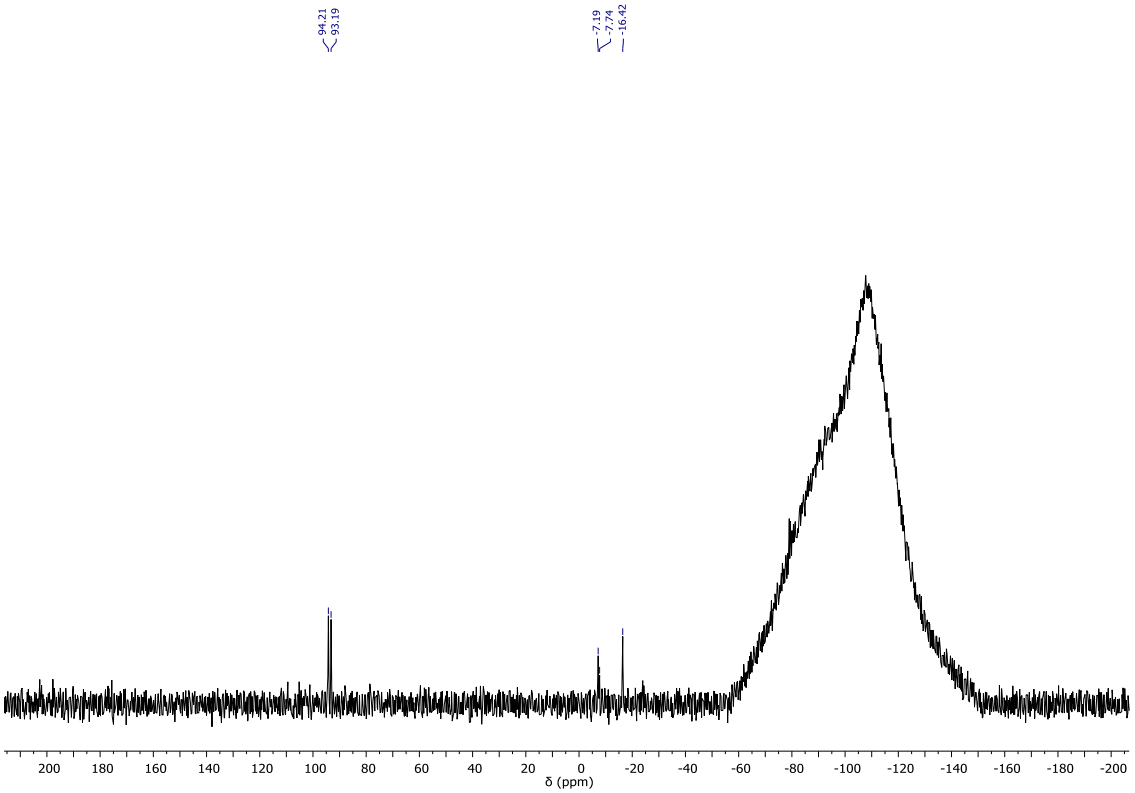


Figure S29. $^{29}Si\{^{1}H\}$IG-NMR-spectrum (300 K, 80 MHz, C_6D_6) of compound **3**.

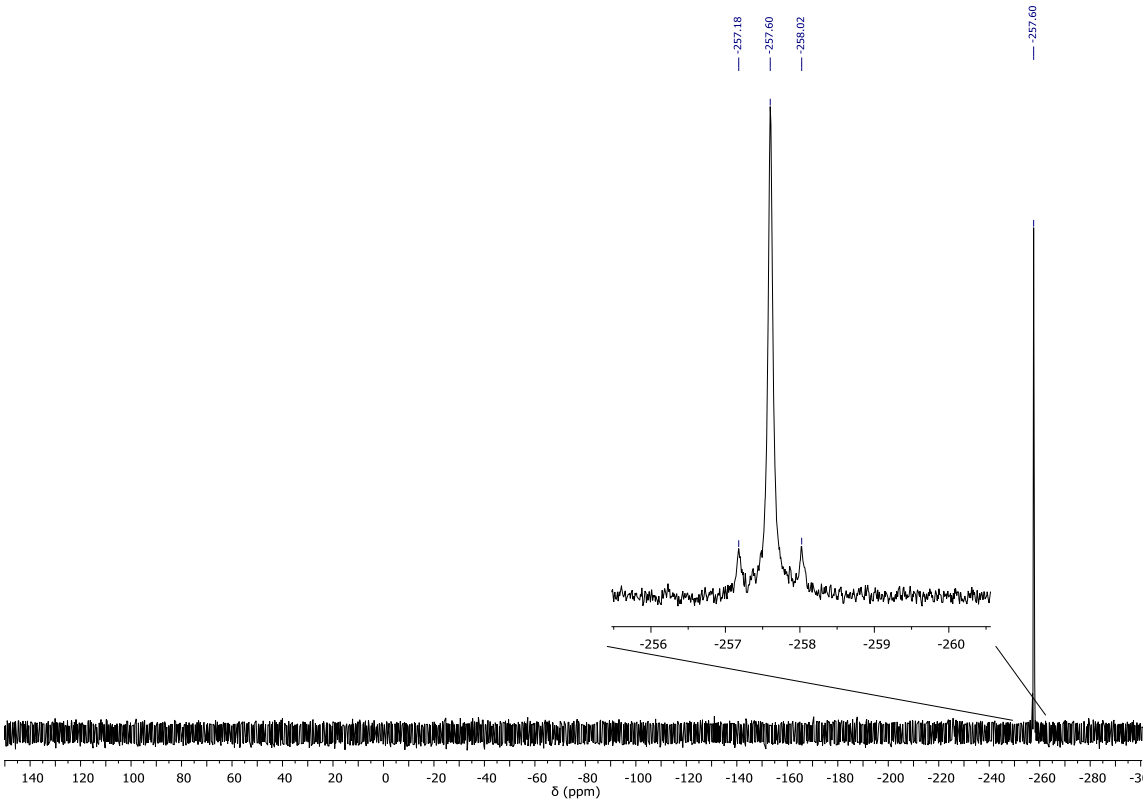


Figure S30. $^{31}P\{^{1}H\}$-NMR-spectrum (300 K, 162 MHz, C_6D_6) of compound **3**.

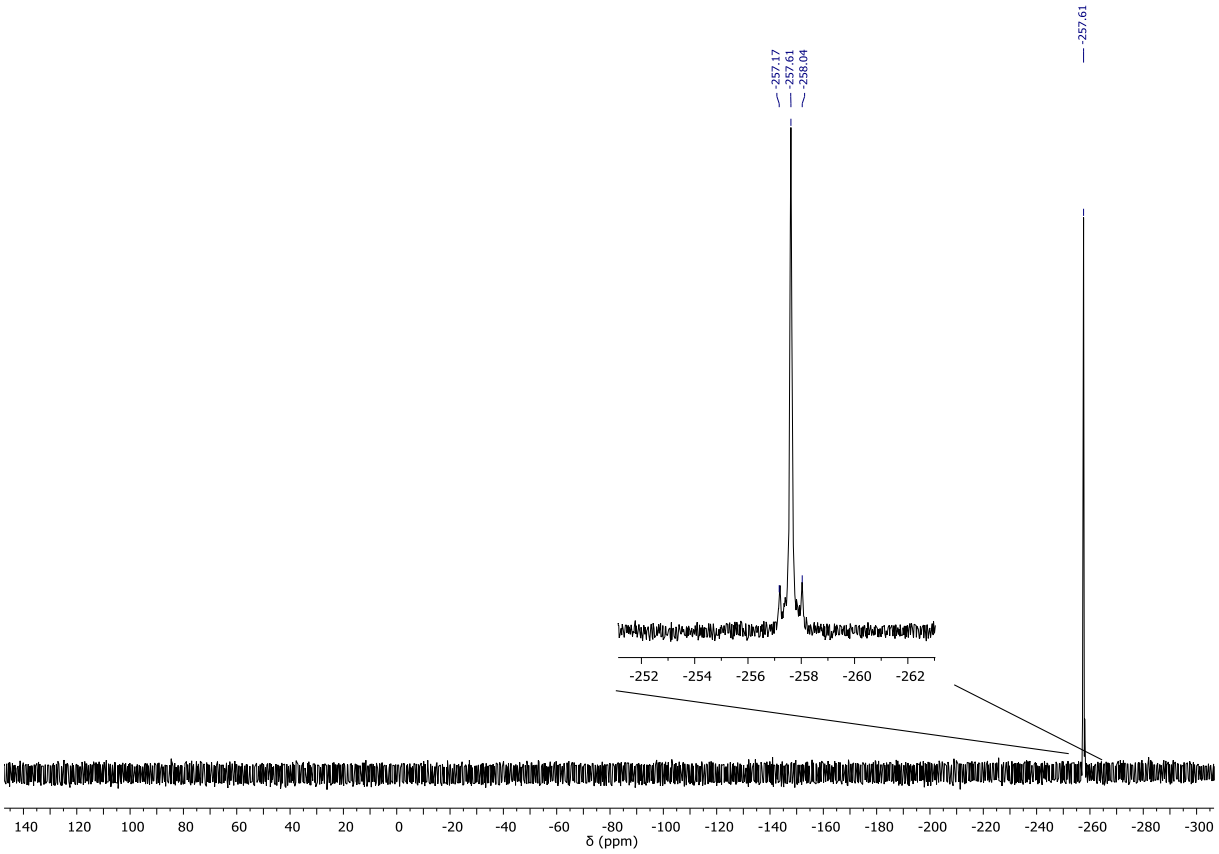


Figure S31. $^{31}P\{/\}$-NMR-spectrum (300 K, 162 MHz, C_6D_6) of compound **3**.

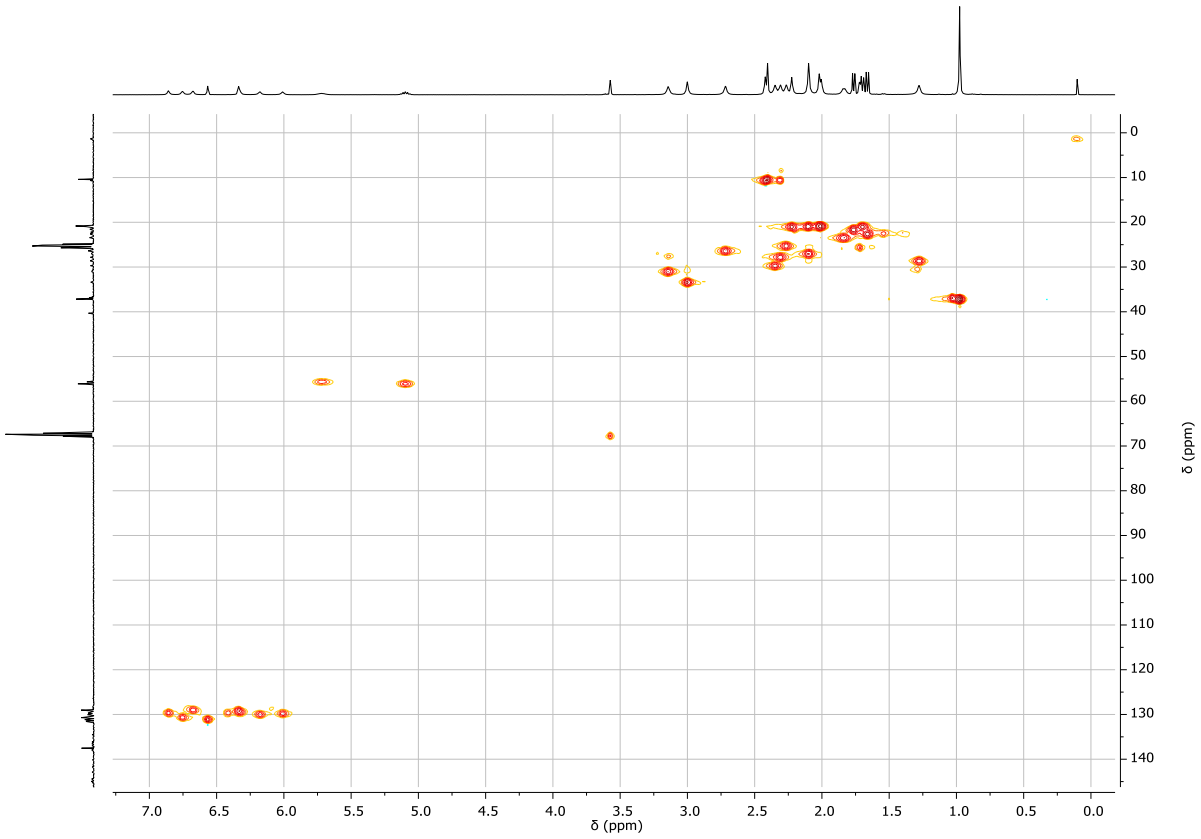


Figure S32. H,C-HSQC-NMR-spectrum (300 K, C_6D_6) of compound **3**.

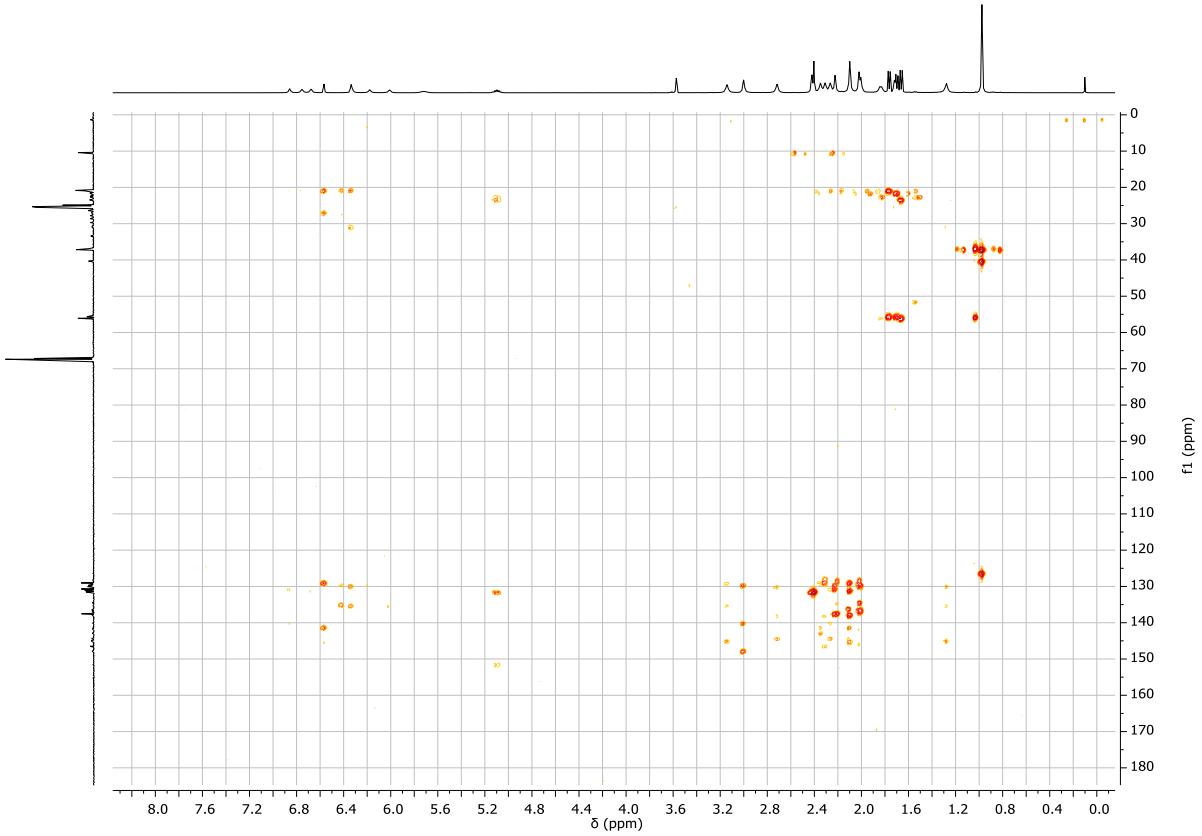


Figure S33. H,C-HMBC-NMR-spectrum (300 K, C_6D_6) of compound **3**.

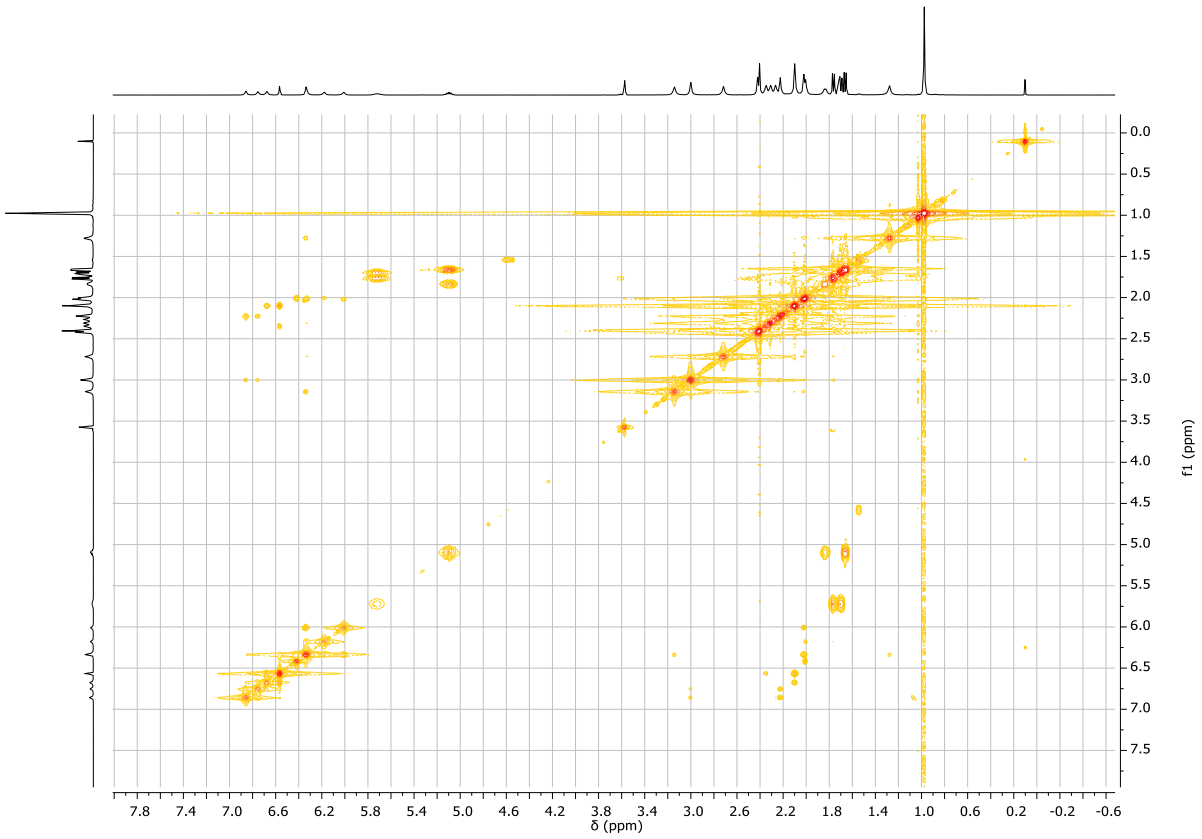


Figure S34. H,H-COSY-NMR-spectrum (300 K, C_6D_6) of compound **3**.

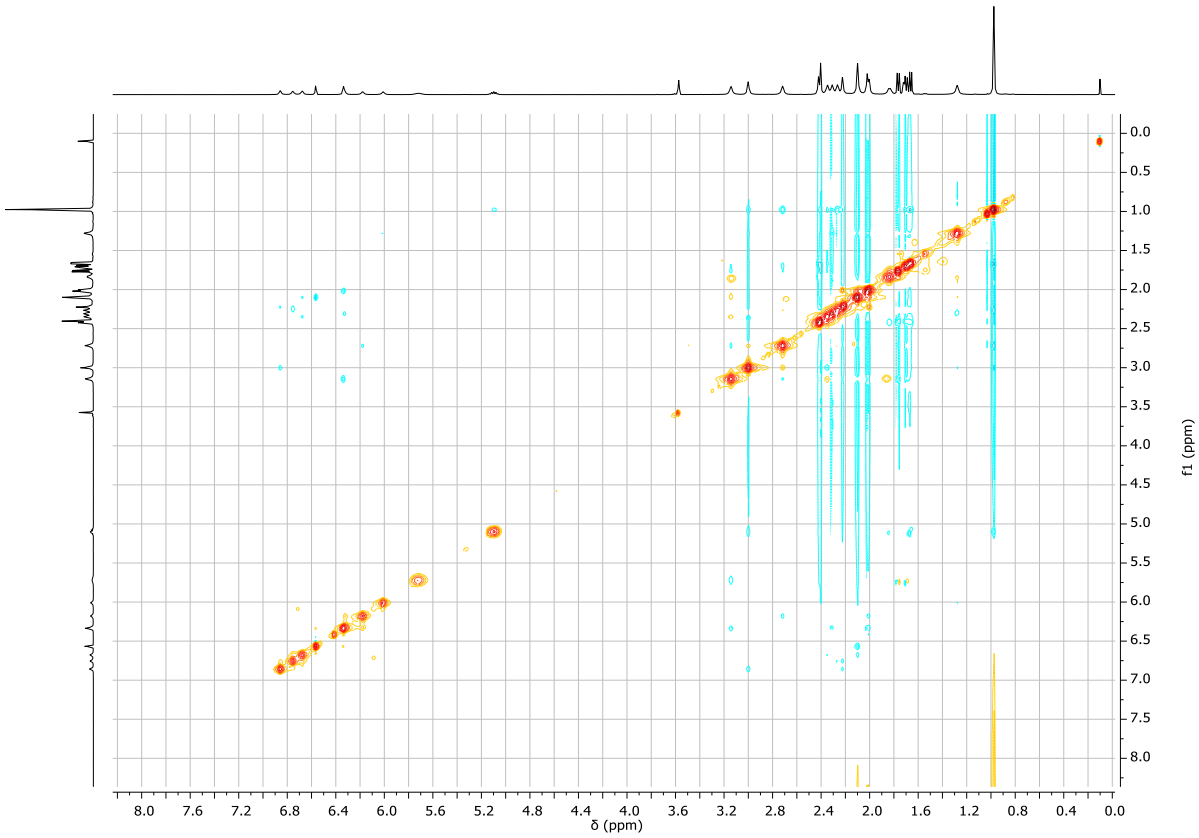


Figure S35. H,H-ROESY-NMR-spectrum (300 K, C_6D_6) of compound **3**.

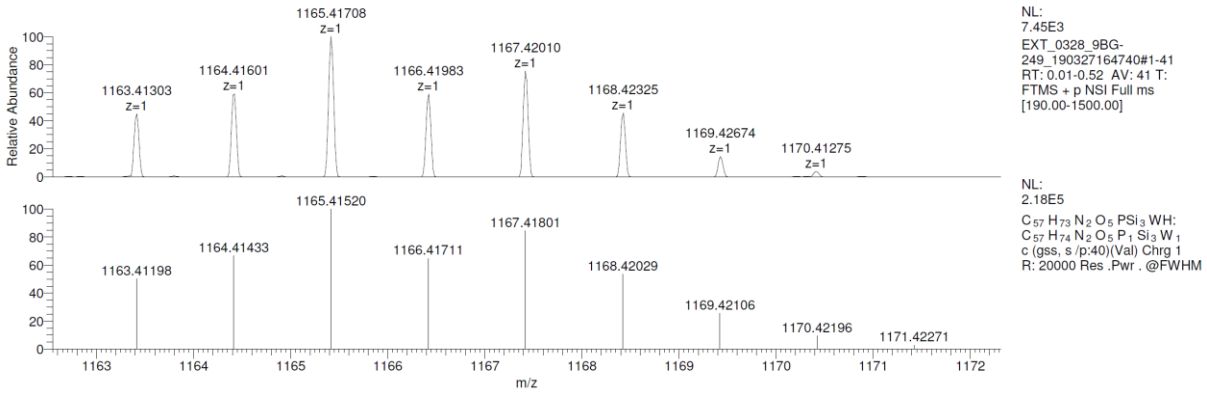


Figure S36. ESI-MS-spectrum (positive mode) (300 K, C_6D_6) of compound **3**.

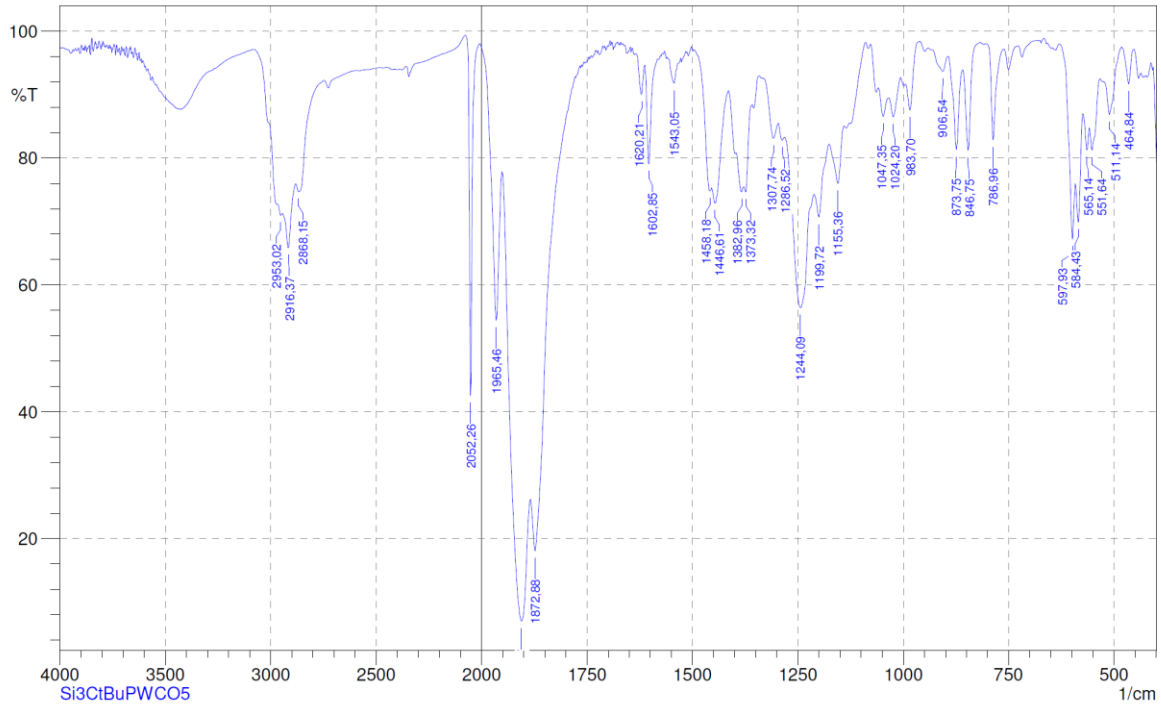


Figure S37. FT-IR spectrum (KBr-pellet) of compound **6**.

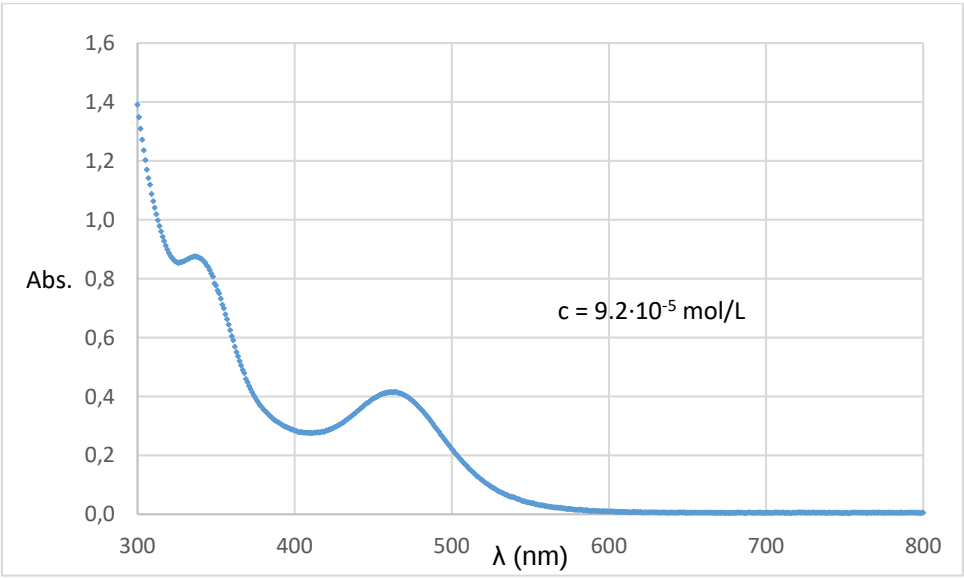


Figure S38. UV-VIS-spectrum (THF, λ = 300–800 nm) of compound **3**.

5. Details of the single crystal x-ray diffraction analysis

Crystals of **1**(·THF) and **2**(·solvent) and **3**(·0.5C_6H_{14}·THF·solvent) were removed from a Schlenk tube under an argon atmosphere and covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber and quickly placed in a low temperature Argon stream. The data were collected at 100 K on a Bruker Venture with Mo K_α radiation (λ = 0.71073 Å). The crystal structure was solved by direct methods using SHELX version 6.1 program package.[S3] Non-hydrogen atoms were refined anisotropically. Absorption corrections were applied using SADABS program (*SADABS*, an empirical absorption correction program, part of the SAINTPlus NT version 5.0 package; Bruker AXS: Madison, WI 1998). Data collected were corrected for Lorentz and polarization effects with Saint[S3] and absorption using Blessing's method and merged as incorporated with the program.[S4,S5] The SHELXTL[S6] program package was now implemented to determine the space group based upon intensity statistics. The structure was determined by direct methods with a majority of the non-hydrogen atoms from the molecule of interest being located directly using the program XT.[S7] Refinement of the structure was achieved using the program XL.[S8] Difference-Fourier least-squares refinement cycles were required to locate the remaining non-hydrogen atoms.

5.1. Refinement details

For compound **1**(·THF) the molecular structure and the co-crystallized THF solvent molecule were refined without any restraints.

For compound **2**(·solvent) two positions for THF molecules were found in the asymmetric unit. However, refining these molecules results in large anisotropic parameters and short H···H from one THF molecule to the molecular structure of **2**. Therefore, the Platon squeeze[S9] routine was applied which results in 1.88 THF molecules in the asymmetric unit. Additionally, one reflex was omitted because it was affected by the beamstop.

During the refinement of compound **3**(·0.5C_6H_{14}·THF·solvent) half a molecule of hexane and one molecule of THF and a disordered THF molecule was found in the asymmetric unit besides a highly disordered molecule which could not be clearly identified as THF or hexane. Therefore, the Platon squeeze[S9] routine was employed to account for the latter two highly disordered solvent molecules. Additionally, five reflexes were omitted.

Table S1. Crystal data and structure refinement for **1**(·THF), **2**(·solvent) and **3**(·0.5C_6H_{14}·THF·solvent).

Compound	**1**(·THF)	**2**(·solvent)	**3**(·0.5C_6H_{14}·THF ·solvent)
Empirical formula	$C_{56}H_{81}N_2OPSi_3$	$C_{52}H_{73}N_2PSi_3$	$C_{64}H_{88}N_2O_6PSi_3W$
Formula weight /g·mol^{-1}	913.46	841.36	1280.45
Crystal color, shape	pale yellow, plate	yellow, block	orange, plate
Crystal size /mm^3	0.190×0.528×0.622	0.164×0.261×0.278	0.478×0.678×0.889
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	P-1	P-1
a /Å b /Å c /Å	13.9104(9) 21.1124(7) 17.7837(7)	12.4344(6) 14.9016(7) 16.3149(7)	14.1641(8) 14.7127(9) 19.0224(12)
α /° β /° γ /°	90 90.887(4) 90	89.3050(10) 68.4160(10) 88.9410(10)	69.805(2) 71.090(2) 70.621(2)
V /Å^3	5222.1(4)	2810.5(2)	3409.9(4)
Z	4	2	2
T /K	100(2)	100(2)	100(2)
Completeness to θ 25.24° /%	99.7	96.7	98.2
ρ_{calc} /g·cm^{-3}	1.162	0.994	1.247
μ(Mo) /mm^{-1}	0.161	0.144	1.816
2Θ range /°	2.99-54.29	4.41-54.29	4.67-54.29
Reflections measured	68237	11948	39092
Independent reflections	11547	30315	14787
R(int)	0.0260	0.0487	0.0404
Ind. reflections ($I > 2\sigma(I)$)	10371	10254	13915
Parameters	581	537	715
Restraints	0	0	0
R_1 ($I > 2\sigma(I)$)	0.0492	0.0469	0.0324
wR_2 (all data)	0.1359	0.1254	0.0847
GooF (all data)	1.040	1.077	1.043
Max. peak/hole /e$^-$·Å^{-3}	1.401/-0.765	0.478 /-0.383	1.828 /-1.784
Absorption correction type	multi-scan	multi-scan	multi-scan
Min. /Max. transmission	0.6359 /0.7455	0.6191 /0.7455	0.4274 /0.7455

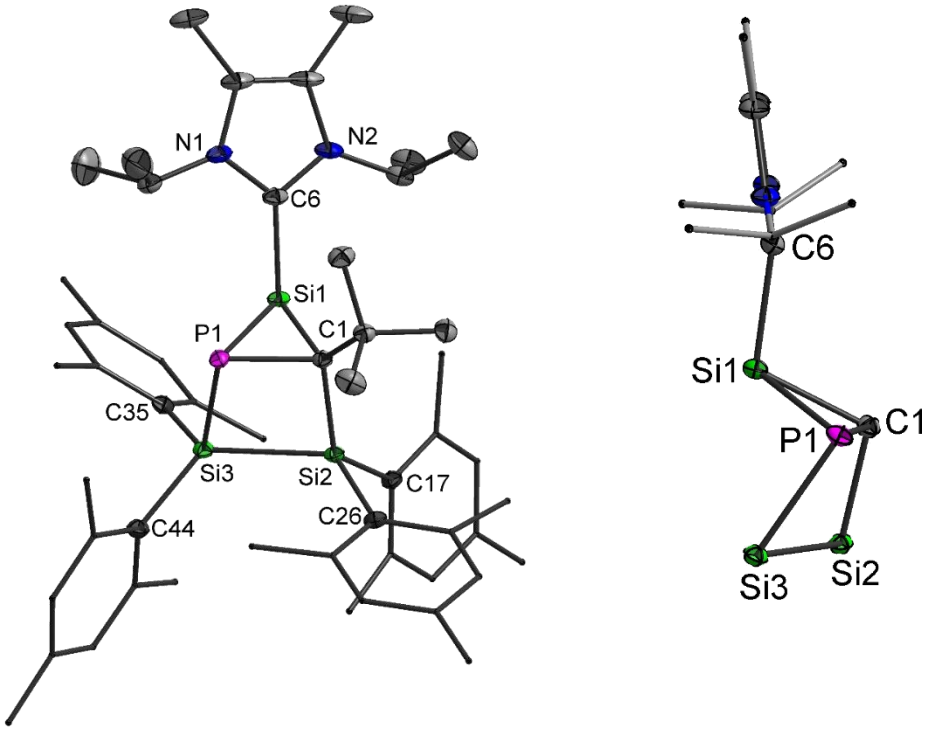


Figure S39. Molecular structure of compound **1**.

Selected distances /Å

P1–C1 1.9249(17), P1–Si1 2.2728(6), Si1–C1 1.9744(17), Si1–C6 1.9774(17), N1–C6 1.357(2), N2–C6 1.361(2), P1–Si3 2.2798(6), Si2–Si3 2.4764(6), Si2–C1 1.9378(17), C1–C2 1.570(2), C2–C3 1.534(2), C2–C4 1.534(2), C2–C5 1.526(2), Si2–C26 1.9481(17), Si2–C17 1.9235(17), Si2–C35 1.9269(17), Si3–C44 1.9346(18).

Selected angle /°

C1-P1-Si1 55.37(5), C1-Si1-P1 53.34(5), P1-C1-Si1 71.29(6), Si1-P1-Si3 86.45(2), Si2-C1-Si1 105.67(8), P1-C1-Si2 99.74(7), C1-Si2-Si3 86.27(5), P1-Si3-Si2 76.65(2), C1-P1-Si3 92.36(5), C6-Si1-P1 103.83(6), C1-Si1-C6 110.29(7), C17-Si2-C26 100.09(7), C35-Si3-P1 106.08(5), C44-Si3-P1 120.63(6), C17-Si2-Si3 113.20(5), C26-Si2-Si3 122.47(5), C17-Si2-C1 127.53(7), C35-Si3-C44 103.95(7), C1-Si2-C26 109.31(7), C35-Si3-Si2 123.72(5), C44-Si3-Si2 123.09(6), C2-C1-P1 112.64(11), C2-C1-Si2 123.70(11), C2-C1-Si1 127.45(11), C5-C2-C3 108.22(15), C5-C2-C4 107.05(15), C3-C2-C4 105.41(15), C5-C2-C1 111.02(14), C5-C2-C4 107.05(14), C4-C2-C1 112.47(13).

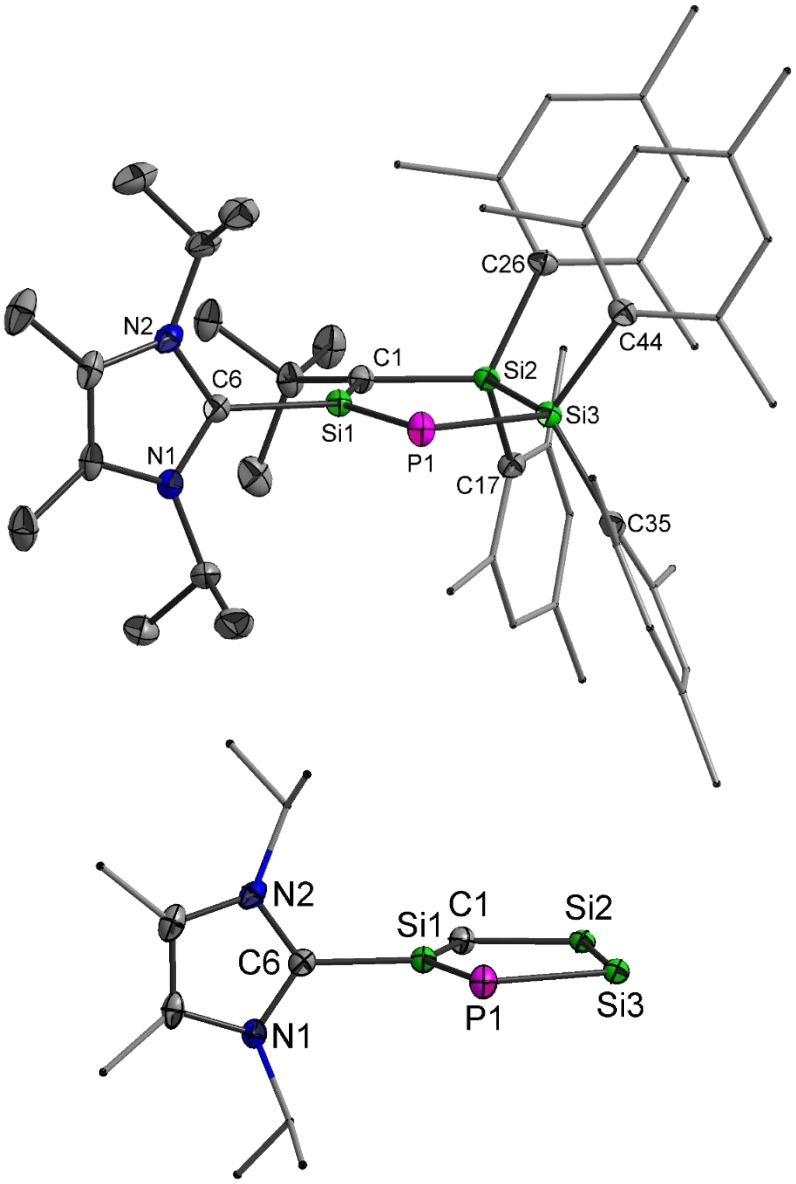


Figure S40. Molecular structure of compound **2**.

Selected distances /Å

Si1–C6 1.9141(18), P1–Si1 2.0960(6), P1–Si3 2.2603(7), Si1–C1 1.7351(18), Si2–C1 1.8677(18), Si2–Si3 2.5385(7), Si2–C17 1.9289(18), Si2–C26 1.9348(18), Si3–C44 1.9393(17), Si3–C35 1.9482(18), N1–C6 1.346(2), N2–C6 1.345(2), C1–C2 1.554(2), C2–C3 1.538(3), C2–C4 1.540(3), C2–C5 1.536(3).

Selected angles /°

Si1-P1-Si3 92.17(2), C1-Si1-P1 133.37(6), Si1-C1-Si2 107.33(9), C1-Si2-Si3 104.91(6), P1-Si3-Si2 102.23(2), C6-Si1-P1 106.21(6), C1-Si1-C6 120.42(8), C2-C1-Si1 125.44(13), C2-C1-Si2 125.95(13), C1-Si2-C17 105.74(8), C1-Si2-C26 116.63(8), C17-Si2-C26 112.86(8), C17-Si2-Si3 116.81(6), C26-Si2-Si3 100.04(5), C44-Si3-C35 107.66(7), C44-Si3-P1 113.45(6), C35-Si3-P1 100.37(6),

C44-Si3-Si2 106.85(6), C35-Si3-Si2 126.14(6), C5-C2-C3 107.38(15), C5-C2-C4 107.29(16), C3-C2-C4 106.39(16), C5-C2-C1 111.94(15), C3-C2-C1 112.95(15), C4-C2-C1 110.58(15).

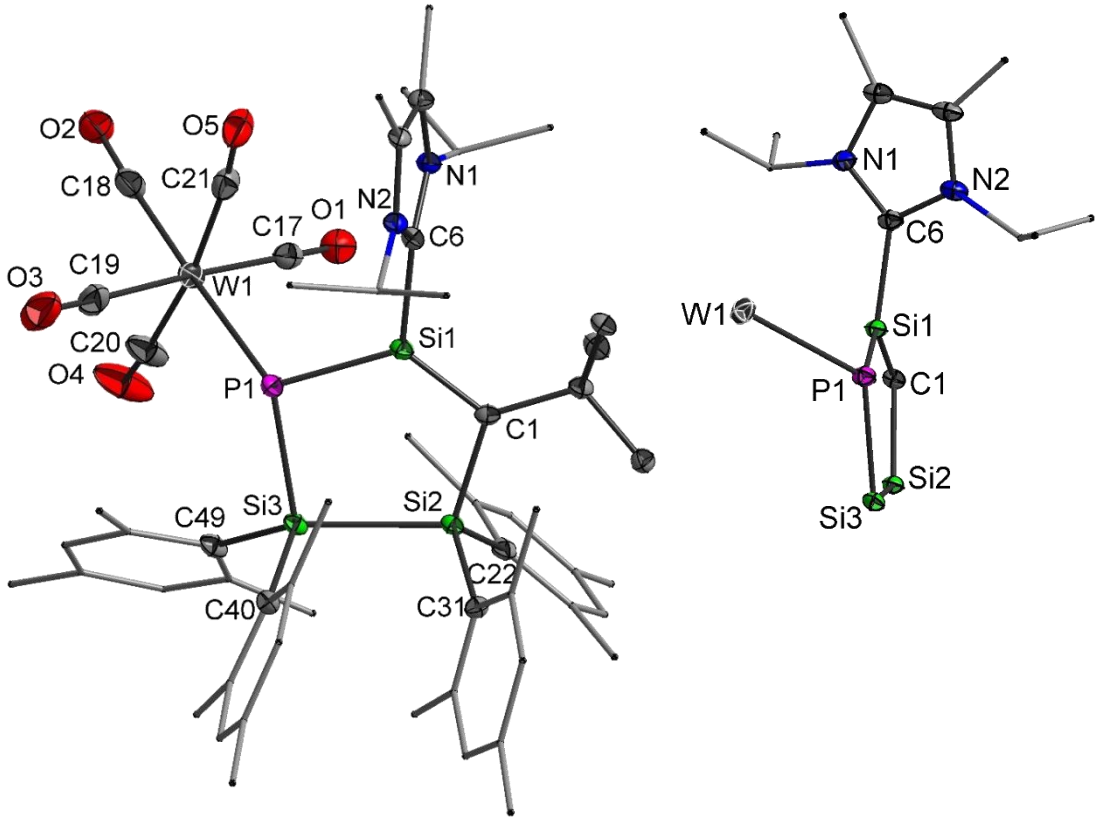


Figure S41. Molecular structure of compound **3**.

Selected distances /Å

P1–Si1 2.1512(10), Si1–C1 1.737(3), Si1–C6 1.931(3), Si2–C1 1.886(3), P1–Si3 2.3025(9), Si2–Si3 2.5101(10), Si2–C31 1.926(3), Si2–C22 1.928(3), Si3–C49 1.927(3), Si3–C40 1.941(3), W1–C18 1.961(3), W1–C17 2.025(3), W1–C21 2.036(3), W1–C19 2.047(4), W1–C20 2.053(4), W1–P1 2.6502(7), O1–C17 1.149(4), O2–C18 1.161(4), O3–C19 1.146(4), O4–C20 1.135(4), O5–C21 1.137(4), C1–C2 1.557(4), C2–C4 1.537(4), C2–C5 1.537(4), C2–C3 1.540(3)

Selected angles /°

Si1-P1-Si3 95.90(4), Si1-P1-W1 106.81(3), Si3-P1-W1 126.21(3), C1-Si1-C6 122.06(12), C1-Si1-P1 126.63(9), Si1-C1-Si2 110.73(14),

C6-Si1-P1 109.58(8), C1-Si2-C31 114.95(11), C1-Si2-C22 104.84(11),
C31-Si2-C22 113.39(11), C1-Si2-Si3 106.49(8), C31-Si2-Si3 99.79(8),
C22-Si2-Si3 117.62(8), C49-Si3-C40 104.45(12), C49-Si3-P1 102.88(9),
C40-Si3-P1 114.27(8), C49-Si3-Si2 130.48(9), C40-Si3-Si2 105.00(8),
P1-Si3-Si2 100.07(3), C18-W1-C17 89.44(13), C18-W1-C21 83.68(13),
C17-W1-C21 95.59(12), C18-W1-C19 92.07(13), C17-W1-C19 177.25(13),
C21-W1-C19 86.86(14), C18-W1-C20 86.72(14), C17-W1-C20 83.79(14),
C21-W1-C20 170.40(13), C19-W1-C20 94.00(16), C18-W1-P1 171.75(10),
C17-W1-P1 94.84(8), C21-W1-P1 88.87(9), C19-W1-P1 83.96(9), C20-W1-P1 100.73(10).

6. Computational details

6.1. Methods

All structures were optimized without geometry constraints with density functional theory (DFT), using the resolution of the identity approximation[S10] and an atom-pairwise dispersion correction (D3).[S11] A flexible triple zeta basis set (def2-TZVP)[S12] was used in all calculations. Optimizations were performed with the TPSS[S13] functional. For the calculation of zero point vibrational energies and free enthalpy contributions (G_{298}), a rotor approximation was applied for vibrational modes with wave numbers below 100 cm^{-1}.[S14] All geometry optimizations and vibrational frequency calculations were performed with the TURBOMOLE 7.3 program.[S15]

6.2. DFT-optimized structure of 1 (opt-1)

Comparison of the structural parameters of the DFT-optimized structure with those obtained from single crystal X-ray diffraction.

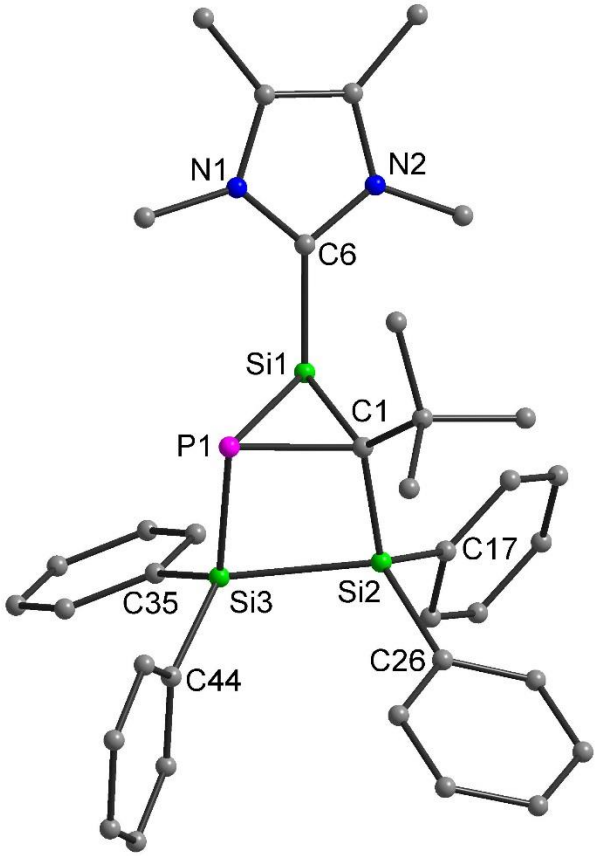


Figure S42. DFT-optimized structure of **1 (opt-1)**.

Table S2. Bond lengths /Å and angles /° of **opt-1**.

Parameter	TPSS-D3/def2-TZVP	From crystal structure
P1–Si1	2.2869	2.2728
Si1–C1	1.9784	1.9744
C1–P1	1.9427	1.9249
C1–Si2	1.9137	1.9378
Si2–Si3	2.3458	2.4764
Si3–P1	2.2711	2.2798
Si1–C6	1.9497	1.9773
Si2–C17	1.8888	1.9235
Si2–C26	1.8943	1.9481
Si3–C35	1.8777	1.9346
Si3–C44	1.8867	1.9269
P1-Si1-C1	53.596	53.338
Si1-C1-P1	71.351	71.291
C1-P1-Si1	55.052	55.370
P1-C1-Si2	101.964	99.742
C1-Si2-Si3	87.543	86.273
Si2-Si3-P1	80.910	76.649
Si3-P1-C1	89.015	92.358
angle between the three-membered ring and the four-membered ring		

6.3. Natural Population Analysis of opt-1

Table S3. Partial atomic charges calculated from NPA[S16] analysis of **opt-1**.

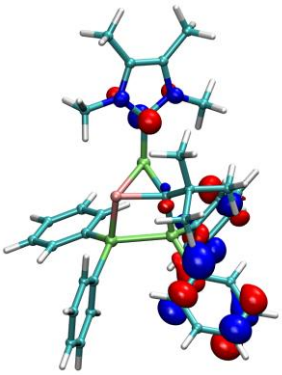
Atom	Charge	Atom	Charge
P1	-0.19	*N1*	-0.31
Si1	0.51	*N2*	-0.32
C1	-1.08	*C17*	-0.48
Si2	1.35	*C26*	-0.49
Si3	0.96	*C35*	-0.48
C6	0.08	*C44*	-0.47

6.4. Calculated Wiberg Bond Indices of opt-1

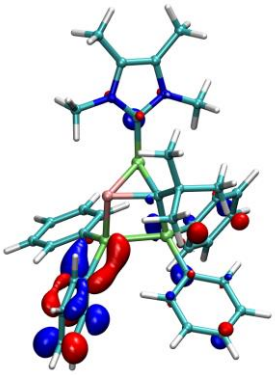
Table S4. Wiberg Bond Orders[S17] of **opt-1** calculated with the NBO[S18] program of Gaussian.[S19]

	opt-1
P1–Si1	0.83
Si1–C6	0.80
Si1–C1	0.73
C1–Si2	0.74
Si2–Si3	0.88
Si3–P1	0.91
P1–C1	0.91
Si2–C17	0.74
Si2–C26	0.75
Si3–C35	0.80
Si3–C44	0.78

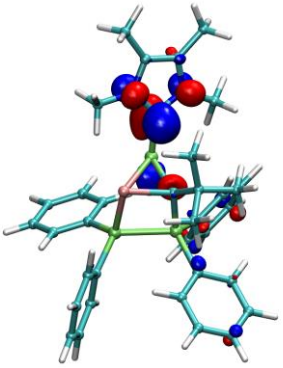
6.5. Calculated Molecular orbitals for opt-1 (Isovalue set at +/– 0.05 a.u.)



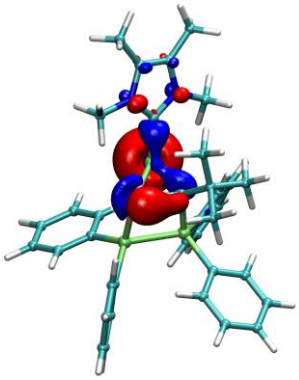
LUMO+2 (-0.946 eV)



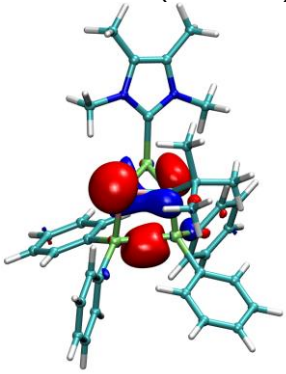
LUMO+1 (-1.220 eV)



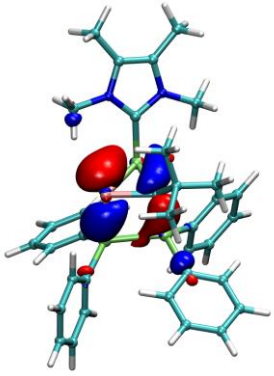
LUMO (-1.369 eV)



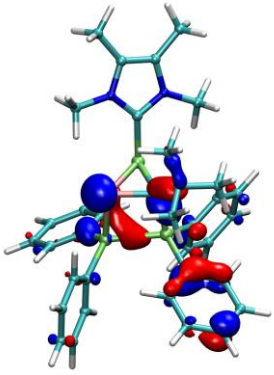
HOMO (-4.070 eV)



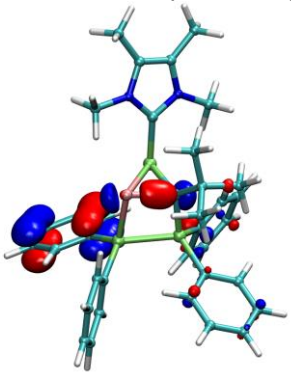
HOMO–1 (-4.523 eV)



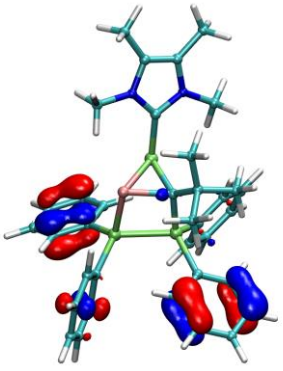
HOMO–2 (-4.738 eV)



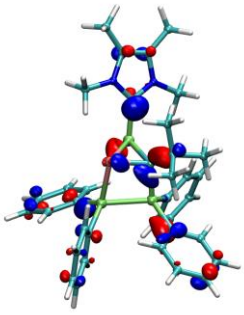
HOMO–3 (-5.477 eV)



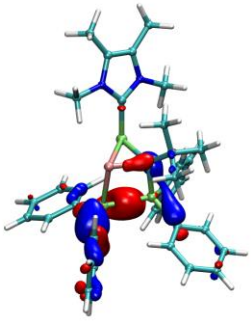
HOMO–4 (-5.707 eV)



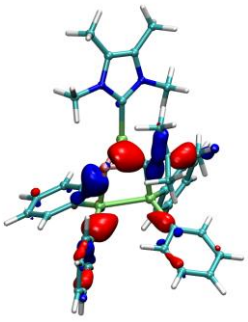
HOMO–5 (-5.751 eV)



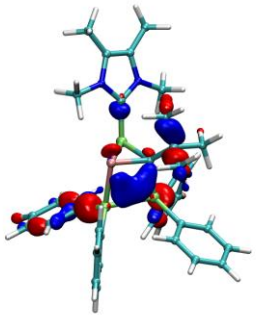
HOMO–12 (-6.299 eV)



HOMO–13 (-6.517 eV)



HOMO–15 (-6.921 eV)



HOMO–16 (-7.141 eV)

Figure S43. Molecular orbitals of **opt-1** isosurface set at +/– 0.05 a.u..

6.6. DFT-optimized structure of opt-1 in the triplet state

Table S5. Total energies and ZPE corrected energies for **opt-1** in the singlet and in the triplet state.

Parameter	TPSS-D3/def2-TZVP
opt-1 in the singlet state	
Total energy /Hartree	-2716.996979854
Total energy – ZPE /Hartree	-2716.3268037
opt-1 in the triplet state	
Total energy /Hartree	-2716.957911944
Total energy – ZPE /Hartree	-2716.2886932
ΔE (Singlet→Triplet) /kcal·mol^{-1}	**23.91**

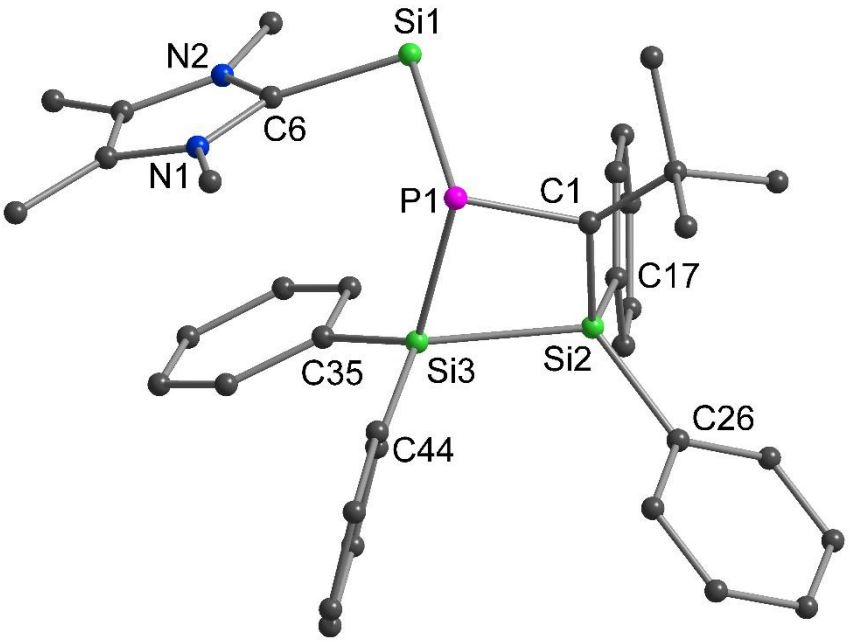


Figure S44. Calculated molecular structure of **opt-1** in the triplet state.

Table S6. Bond lengths /Å and angles /° of **opt-1** in the triplet state.

Parameter	TPSS-D3/def2-TZVP	From crystal structure
P1–Si1	2.3311	2.2728
Si1–C1	3.3240	1.9744
C1–P1	1.8046	1.9249
C1–Si2	1.8496	1.9378
Si2–Si3	2.3329	2.4764
Si3–P1	2.2731	2.2798
Si1–C6	1.9226	1.9773
Si2–C17	1.8843	1.9235
Si2–C26	1.8822	1.9481
Si3–C35	1.8817	1.9346
Si3–C44	1.8854	1.9269
P1-Si1-C1	31.409	53.338
Si1-C1-P1	42.314	71.291
C1-P1-Si1	106.277	55.370
P1-C1-Si2	106.182	99.742
C1-Si2-Si3	85.326	86.273
Si2-Si3-P1	78.736	76.649
Si3-P1-C1	88.162	92.358

7. DFT-optimized structure of 2 (opt-2)

Comparison of the structural parameters of the DFT-optimized structure with those obtained from single crystal X-ray diffraction.

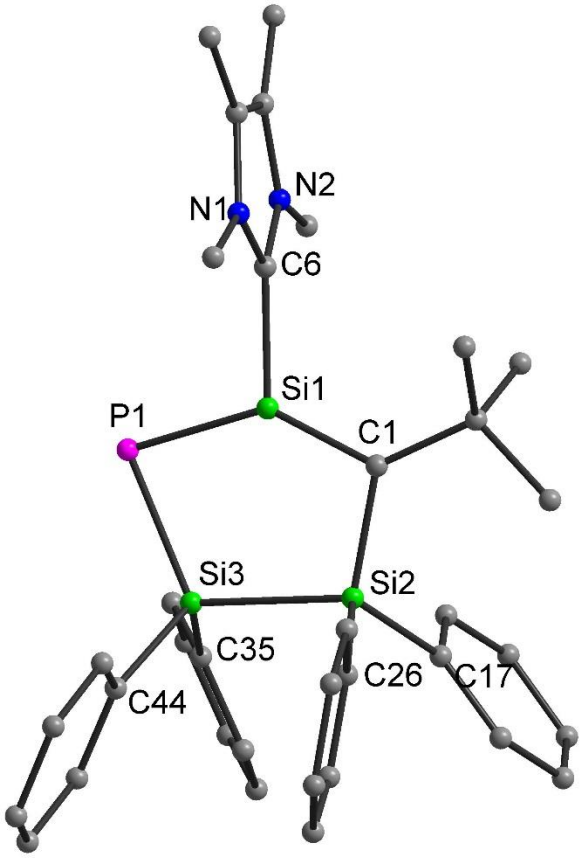


Figure S45. DFT-optimized structure of **2 (opt-2)**.

Table S7. Bond lengths /Å and angles /° of **opt-2**.

Parameter	TPSS-D3/def2-TZVP	From crystal structure
P1–Si1	2.1125	2.0960
Si1–C1	1.7479	1.7351
C1–Si2	1.8452	1.8677
Si2–Si3	2.3877	2.5385
Si3–P1	2.2477	2.2603
Si1–C6	1.9256	1.9141
Si2–C17	1.8899	1.9289
Si2–C26	1.8873	1.9348
Si3–C35	1.8884	1.9482
Si3–C44	1.8876	1.9393
P1-Si1-C1	138.069	133.368
Si1-C1-Si2	103.835	107.325
C1-Si2-Si3	104.437	104.906
Si2-Si3-P1	109.231	102.232
Si3-P1-Si1	84.201	92.168
P1-Si1-C6	106.262	106.205
C6-Si1-C1	115.654	120.423

7.1. Natural Population Analysis of opt-2

Table S8. Partial atomic charges calculated from NPA[S16] analysis of **opt-2**.

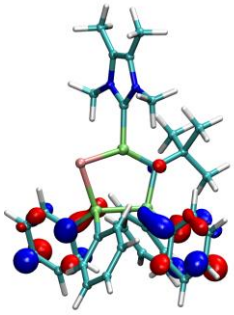
Atom	Charge	Atom	Charge
P1	-0.62	*N1*	-0.29
Si1	1.04	*N2*	-0.29
C1	-1.27	*C17*	-0.47
Si2	1.33	*C26*	-0.47
Si3	0.96	*C35*	-0.46
C6	0.08	*C44*	-0.46

7.2. Calculated Wiberg Bond Indices of opt-2

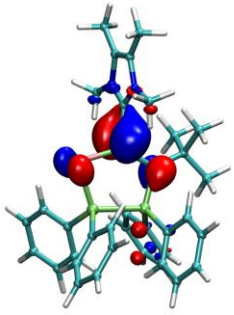
Table S9. Wiberg Bond Orders[S17] of **opt-2** calculated with the NBO[S18] program of Gaussian.[S19]

	opt-2
P1–Si1	1.43
Si1–C6	0.67
Si1–C1	1.22
C1–Si2	0.82
Si2–Si3	0.81
Si3–P1	0.98
P1–C1	0.98
Si2–C17	0.74
Si2–C26	0.74
Si3–C35	0.77
Si3–C44	0.77

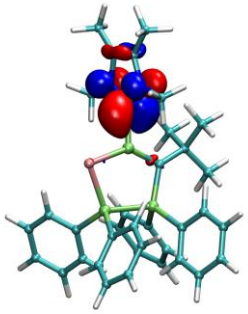
7.3. Calculated Molecular orbitals for opt-2 (Isovalue set at +/– 0.05 a.u.)



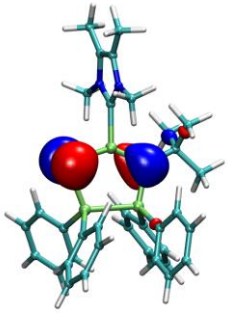
LUMO+2 (-0.923 eV)



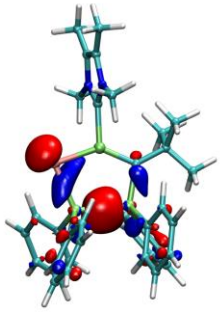
LUMO+1 (-1.063 eV)



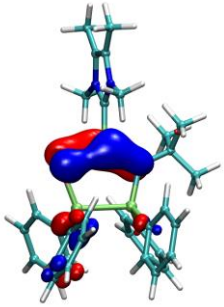
LUMO (-1.761 eV)



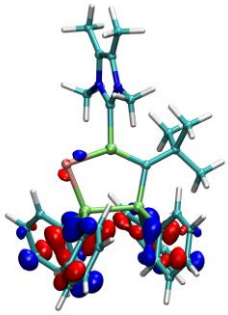
HOMO (-3.732 eV)



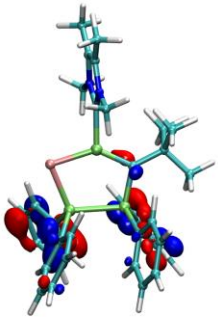
HOMO–1 (-4.667 eV)



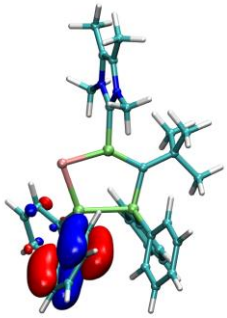
HOMO–2 (-5.244 eV)



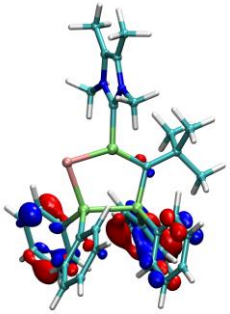
HOMO–3 (-5.365 eV)



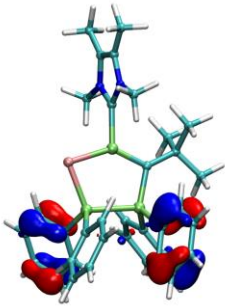
HOMO–4 (-5.475 eV)



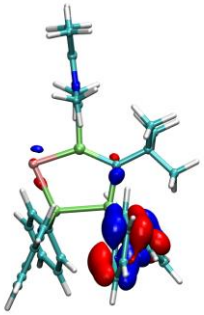
HOMO–5 (-5.521 eV)



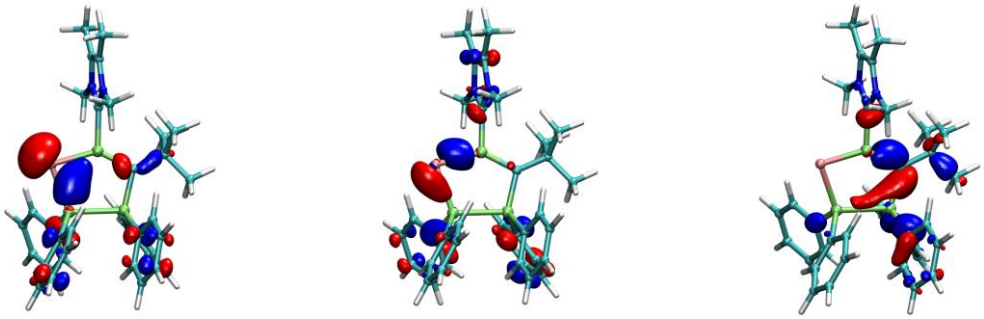
HOMO–6 (-5.621 eV)



HOMO–7 (-5.685 eV)



HOMO–8 (-5.712 eV)



HOMO–10 (-6.003 eV) **HOMO–11** (-6.063 eV) **HOMO–12** (-6.136 eV)

Figure S46. Molecular orbitals of **opt-2** isosurface set at +/– 0.05 a.u..

7.4. DFT-optimized structure of opt-2 in the triplet state

Table S10. Total energies and ZPE corrected energies for **opt-2** in the singlet and in the triplet state.

Parameter	TPSS-D3/def2-TZVP
opt-2 in the singlet state	
Total energy /Hartree	-2717.0097832
Total energy – ZPE /Hartree	-2716.3395232
opt-2 in the triplet state	
Total energy /Hartree	-2716.969982781
Total energy – ZPE /Hartree	-2716.3001551
ΔE (Singlet→Triplet) /kcal·mol^{-1}	**24.70**

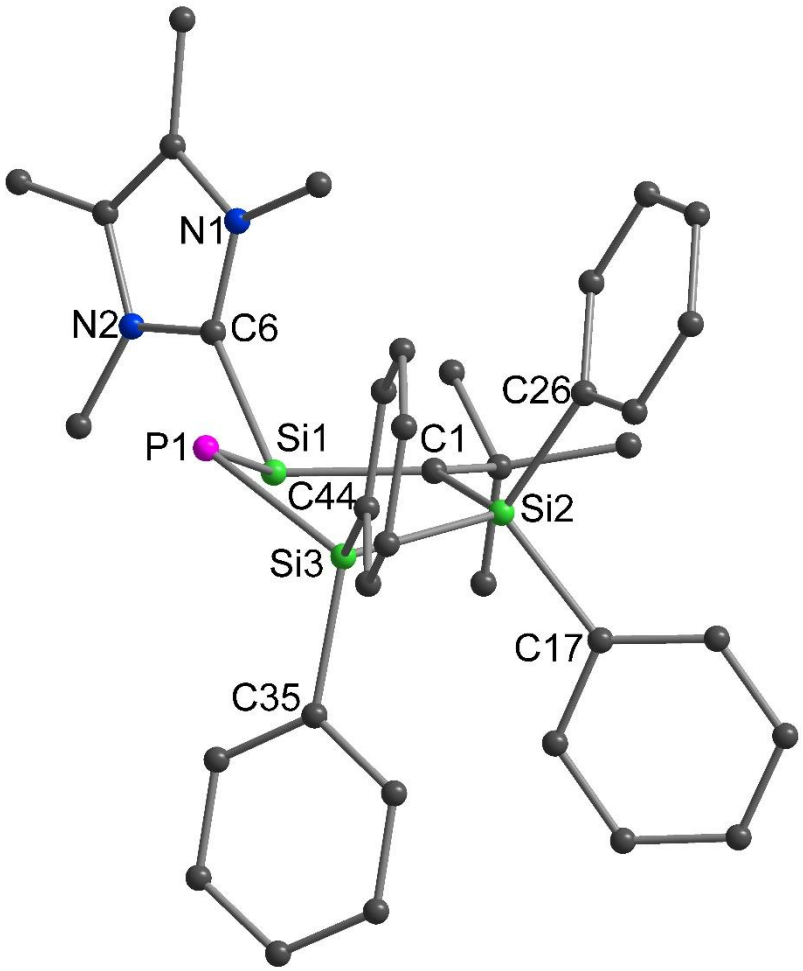


Figure S47. Calculated molecular structure of **opt-2** in the triplet state.

Table S11. Bond lengths /Å and angles /° of **opt-2** in the triplet state.

Parameter	TPSS-D3/def2-TZVP	From crystal structure
P1–Si1	2.2086	2.0960
Si1–C1	1.8710	1.7351
C1–Si2	1.8623	1.8677
Si2–Si3	2.3605	2.5385
Si3–P1	2.2291	2.2603
Si1–C6	1.9581	1.9141
Si2–C17	1.8911	1.9289
Si2–C26	1.8906	1.9348
Si3–C35	1.8860	1.9482
Si3–C44	1.8872	1.9393
P1-Si1-C1	112.538	133.368
Si1-C1-Si2	113.290	107.325
C1-Si2-Si3	103.428	104.906
Si2-Si3-P1	101.821	102.232
Si3-P1-Si1	92.421	92.168
P1-Si1-C6	98.261	106.205
C6-Si1-C1	109.948	120.423

8. Postulated Mechanism for the formation of model compound opt-1

8.1. Method

All structures and transitions states were optimized and thermodynamical corrections calculated as described in section 4.1 (TPSS-D3/def2-TZVP). In addition, single point calculations were performed with the hybrid functional PW6B95(-D3)[S20] and the def2-TZVP triple zeta basis set. Free energies of solvation were obtained with the COSMO-RS[S21] model for 298 K using THF as solvent.

8.2. Energies

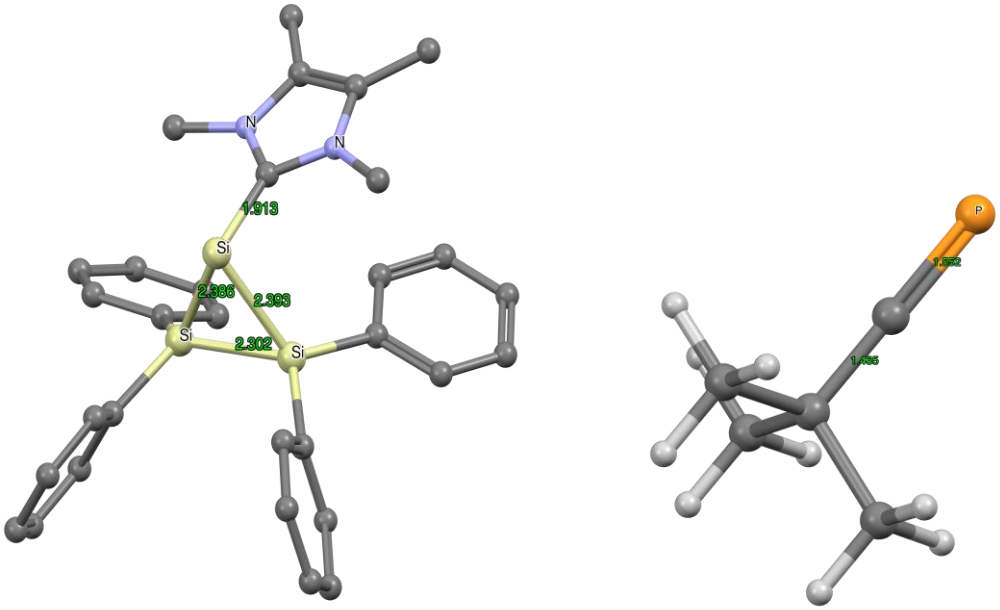
Table S12: DFT-calculated energies (PW6B95-D3//TPSS-D3/def2-TZVP), thermostatistical free energy contributions (G(298)) and solvation free energies (COSMO-RS(THF)) for all reported intermediates and transition structures.

	TPSS-D3/ def2-TZVP [E_h]	*G(298)* [kcal/mol]	*PW6B95-D3/ def2-TZVP* [E_h]	*COSMO-RS THF* [kcal/mol]	$\Delta E^{a)}$ *(PW6B95-D3)* [kcal/mol]	$\Delta G_{298,solv}{}^{a)}$ *(PW6B95-D3)* [kcal/mol]
opt-E	-2179.4998466	301.134	-2181.6246249	-20.143	0.0	0.0
tBuCP	-537.4181496	58.862	-537.8915124	-1.764	0.0	0.0
NHC	-383.6660079	90.683	-384.0682716	-5.609		
			Intermediates and Transition Structures			
Int-1	-2716.9366954	374.981	-2719.5321832	-24.991	-10.1	1.8
Int-2	-2716.9492949	374.681	-2719.5449013	-25.330	-18.0	-6.8
Int-3	-2716.9655093	375.459	-2719.5603764	-24.575	-27.8	-15.0
Int-4	-2716.9835629	376.509	-2719.5817497	-27.172	-41.2	-29.9
Int-5	-2333.1807567	265.398	-2335.3750041	-15.975	+45.7	
opt-1	-2716.9971106	376.905	-2719.5952621	-24.983	-49.7	-35.8
opt-2	-2717.0098165	375.477	-2719.6091807	-27.947	-58.4	-48.9
TS1	-2716.9370956	375.374	-2719.5284893	-26.535	-7.8	3.0
TS2	-2716.9571692	376.056	-2719.5528923	-25.317	-23.1	-10.4
TS3	-2716.9467102	375.306	-2719.5422081	-24.766	-16.4	-3.9
TS4	-2716.9685027	376.625	-2719.5661567	-26.184	-31.4	-19.0

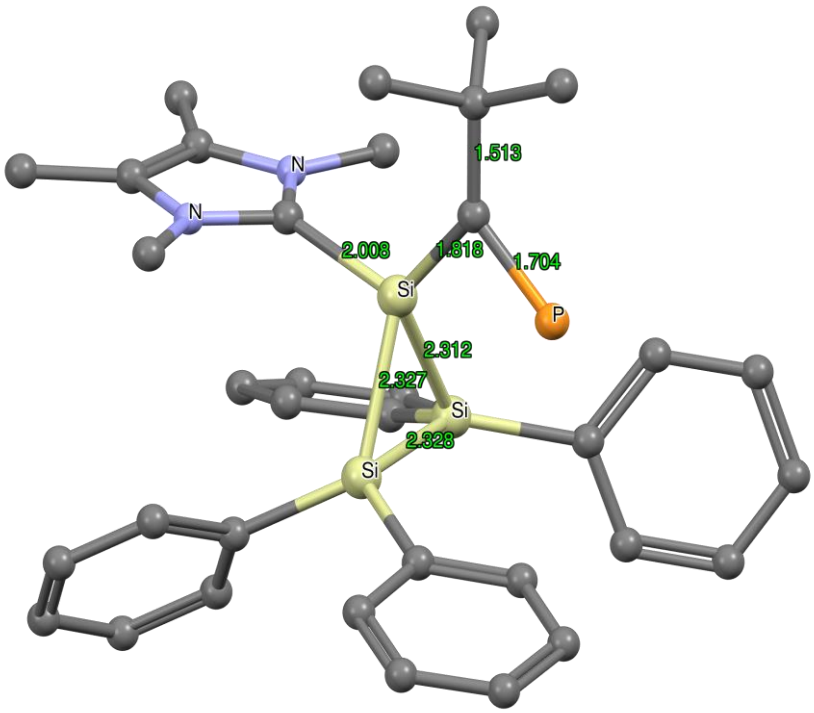
a) Energy and Free energy relative to separated Silylene and tBu-C≡P

8.3. Optimized Structures

Figure S48 Optimized molecular structures (TPSS-D3/def2-TZVP) of intermediates and transition structures of the formation of **opt-1** from the NHC-coordinated silylene and *t*Bu-C≡P. Interatomic distances are given in Å.

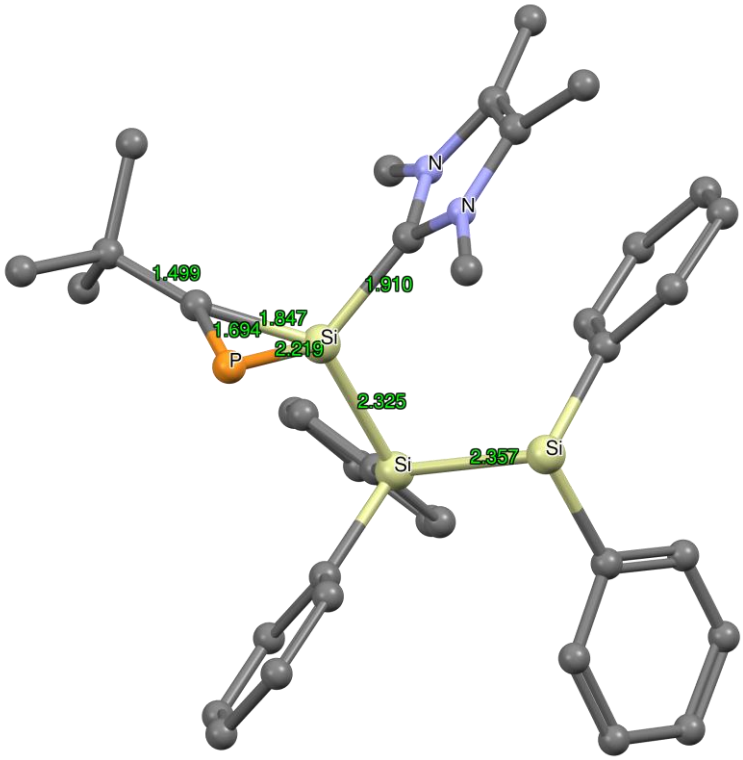


opt-E **tBu-C≡P**

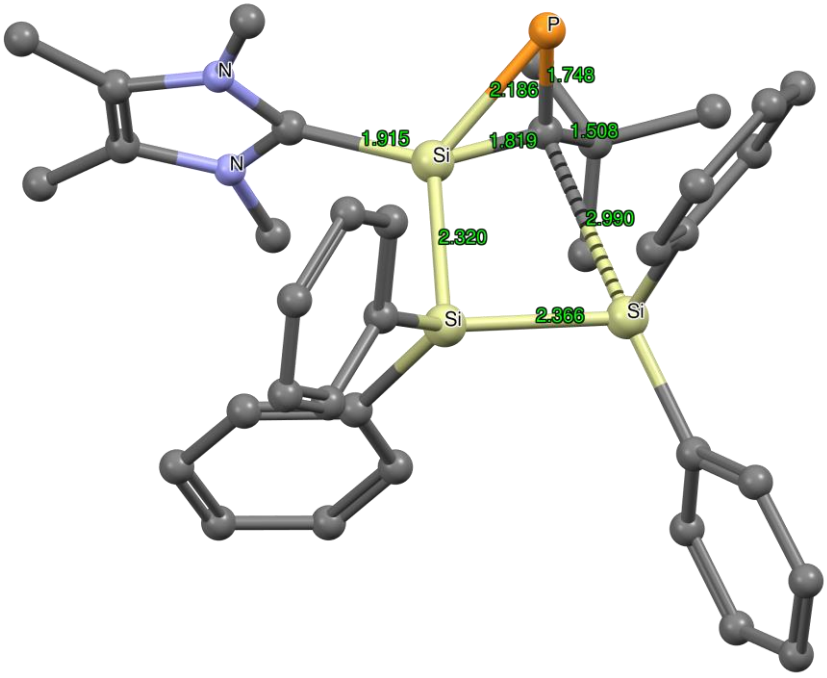


Int-1

Figure S48 (continued) Optimized molecular structures (TPSS-D3/def2-TZVP) of intermediates and transition structures of the formation of **opt-1** from the NHC-coordinated silylene and tBu-C≡P. Interatomic distances are given in Å.

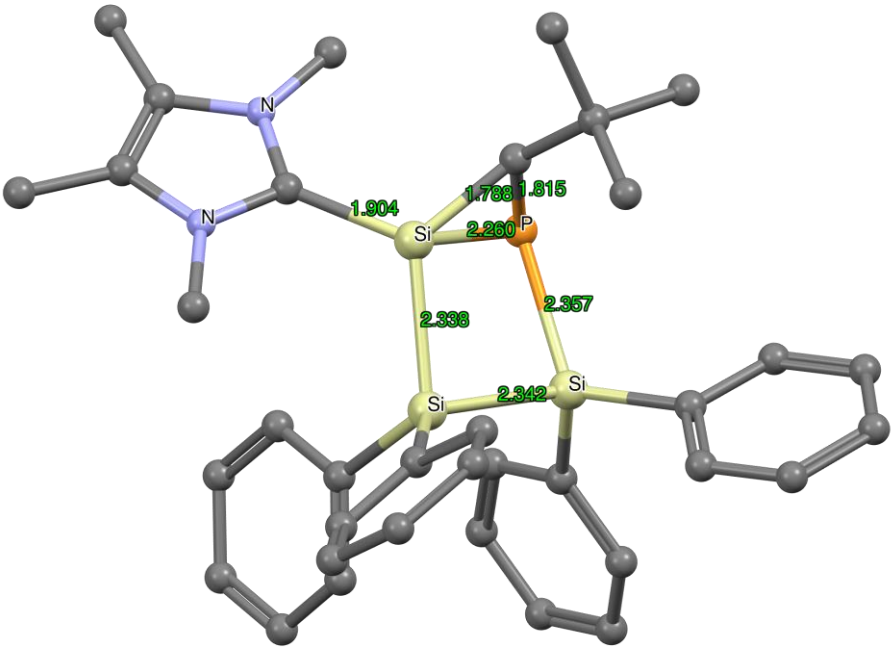


Int-2

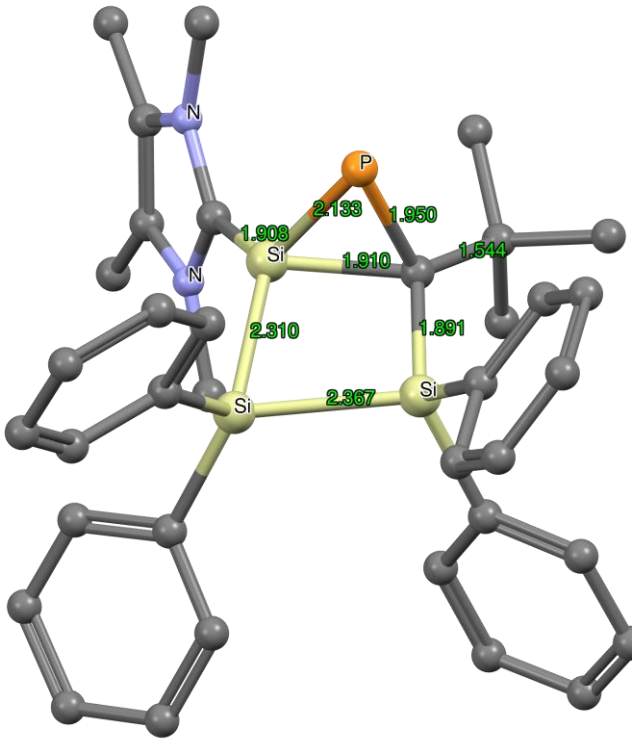


TS1

Figure S48 (continued) Optimized molecular structures (TPSS-D3/def2-TZVP) of intermediates and transition structures of the formation of **opt-1** from the NHC-coordinated silylene and *t*Bu-C≡P. Interatomic distances are given in Å.

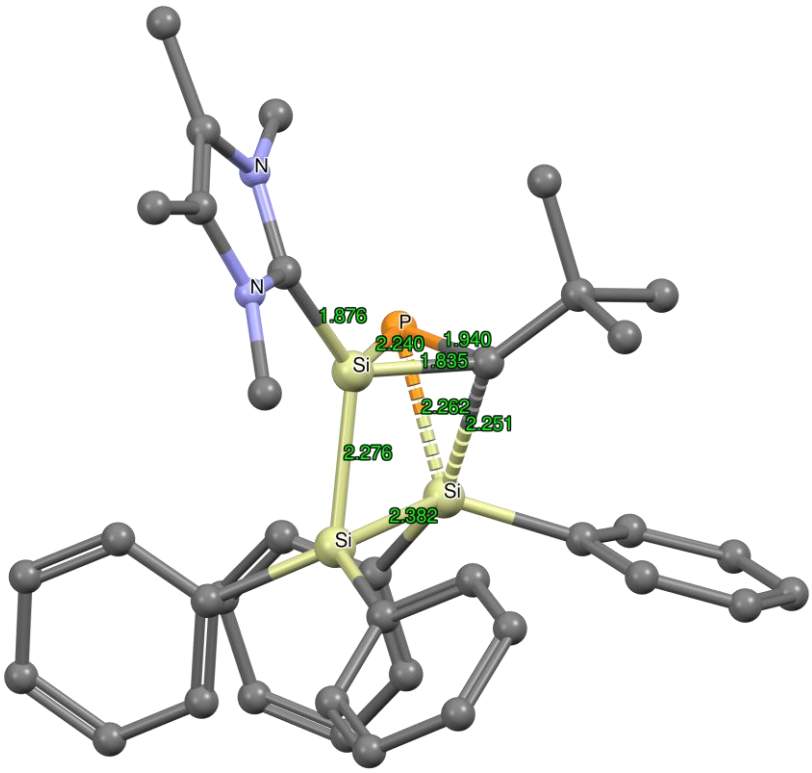


Int-3

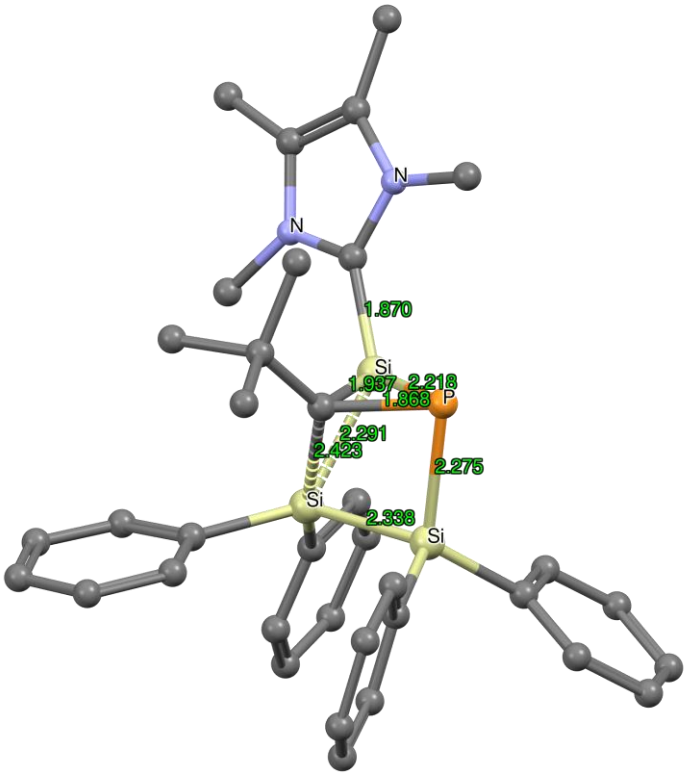


Int-4

Figure S48 (continued) Optimized molecular structures (TPSS-D3/def2-TZVP) of intermediates and transition structures of the formation of **opt-1** from the NHC-coordinated silylene and tBu-C≡P. Interatomic distances are given in Å.

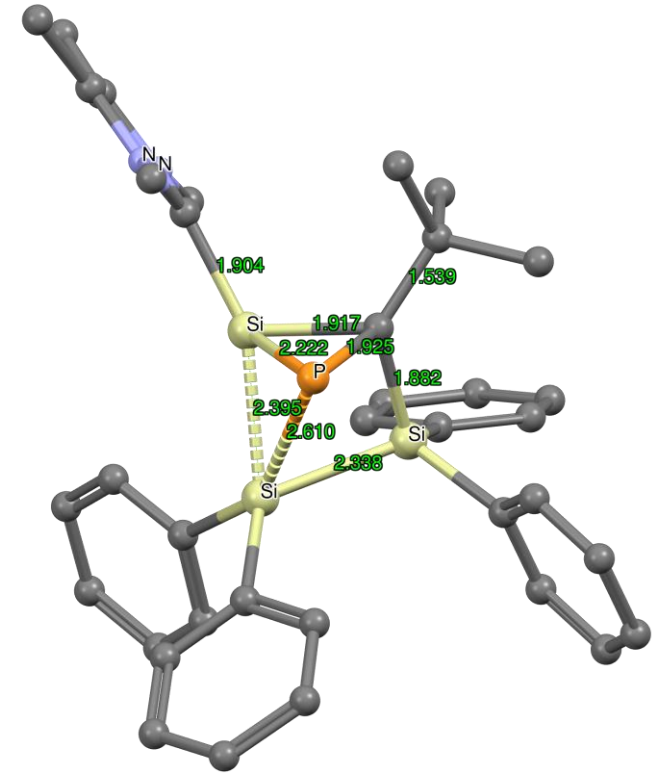


TS2

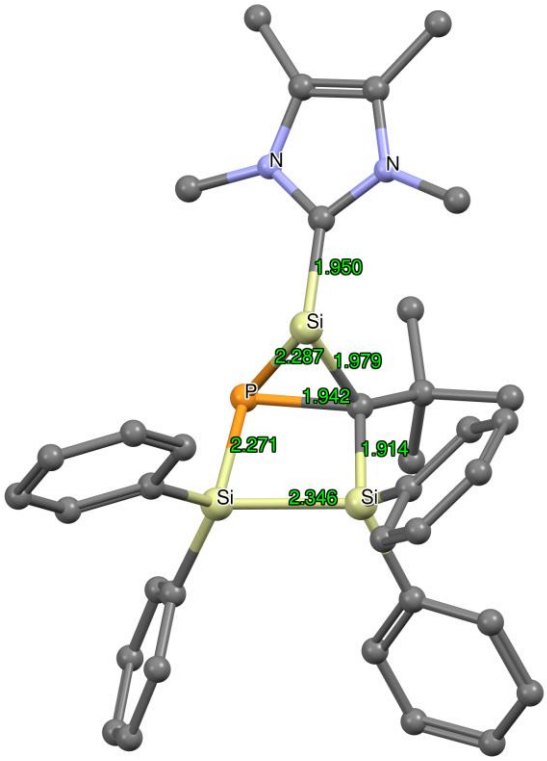


TS3

Figure S48 (continued) Optimized molecular structures (TPSS-D3/def2-TZVP) of intermediates and transition structures of the formation of **opt-1** from the NHC-coordinated silylene and *t*Bu-C≡P. Interatomic distances are given in Å.

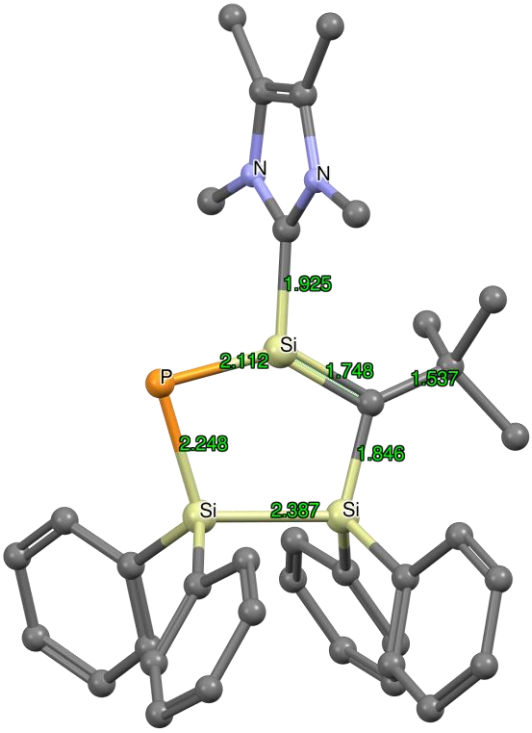


TS4

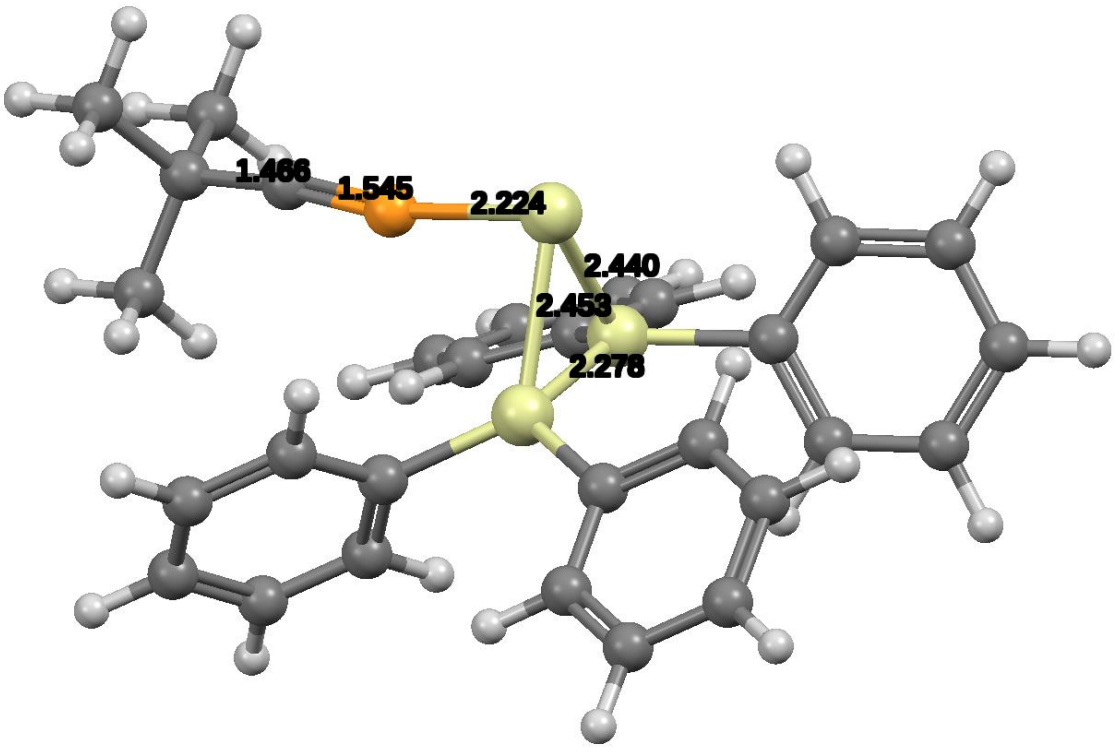


opt-1

Figure S48 (continued) Optimized molecular structures (TPSS-D3/def2-TZVP) of intermediates and transition structures of the formation of **opt-1** from the NHC-coordinated silylene and tBu-C≡P. Interatomic distances are given in Å.



opt-2



Int-5

Calculated free energy for the replacement of NHC from **opt-E** by *t*-BuCP:

opt-E + *t*-BuCP → **Int-5** + NHC

$\Delta G_{298,solv(THF)}$ = +46.0 kcal/mol

9. References

1. B. J. Guddorf, A. Hepp, F. Lips, *Chem. Eur. J.* **2018**, *24*, 10334−10338.
2. N. Kuhn, T. Kratz, *Synthesis*, **1993**, *6*, 561−562.
3. Bruker (2010) SMART APEX (2012-10.6) and (2012) SAINT (Version 8.27a). Bruker AXS Inc., Madison, Wisconsin, USA.
4. An Empirical Correction for Absorption Anisotropy, Blessing, R. H. (1995). Acta Cryst., A*51*, 33–38.
5. Sheldrick, G.M., SADABS (2012/1) 'Siemens Area Detector Absorption Correction' Universität Göttingen, Göttingen, Germany.
6. Sheldrick, G.M., (2002). SHELXTL. Version 6.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
7. Sheldrick, G. M., (1997). SHELXS97. Universität Göttingen: Göttingen, Germany.
8. Sheldrick, G. M., SHELXL2014 structure refinement program.
9. a) P. v. d. Sluis, A. L. Spek, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1990**, *46*, 194–201; b) A. L. Spek, *Acta Cryst.* **2015**, C*71*, 9–18.
10. R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2004**, *6*, 5119–5121.
11. a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104, 1–19; b) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456–1465.
12. F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
13. J. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria, *Phys. Rev. Lett.* **2003**, *91*, 146401, 1–4.
14. S. Grimme, *Chem. Eur. J.* **2012**, *18*, 9955–9964.
15. TURBOMOLE V7.0 2015, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH.
16. A. E. Reed, R. B. Weinstock, F. Weinhold. *J. Chem. Phys.* **1985**, *83*, 735–746.
17. K. Wiberg, *Tetrahedron* **1968**, *24*, 1083–1096.
18. NBO Version 6.0, E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold.
19. Gaussian 16, Revision B.01, 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, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
20. Y. Zhao, D. G. Truhlar, *J. Phys. Chem. A* **2005**, *109*, 5656–5667.
21. a) A. Klamt, *J. Phys. Chem.* **1995**, *99*, 2224–2235. b) F. Eckert and A. Klamt, COSMO*therm*, Version C3.0; COSMO*logic* GmbH & Co. KG, Leverkusen, Germany, **2013**.

10. Cartesian Coordinates of all Compounds

10.1. Cartesian coordinates of opt-1 in the triplet state

Housane in the triplet state
Energy(tpss-d3/def2-TZVP)= -2716.9579119 + 0.6692187 Hartree
Lowest Freq. = 8.76 cm^-1

P	0.4973806	-0.1442606	2.0022333
Si	2.4824073	-1.1963330	1.3801693
Si	-0.4667995	0.8434876	0.1961799
Si	-1.6634134	-1.1556626	0.3151981
N	4.0131599	0.1452667	-0.6839028
N	3.2346318	1.6574312	0.6482118
C	-0.7896995	-1.4068655	1.9259612
C	-1.1009673	-2.3291648	3.0879858
C	-1.9460948	-1.5401881	4.1181053
H	-1.3906214	-0.6647362	4.4708998
H	-2.8813491	-1.1963059	3.6645030
H	-2.1870984	-2.1752984	4.9803619
C	0.1919042	-2.8189983	3.7658289
H	0.7858162	-1.9729618	4.1311756
H	-0.0446595	-3.4652784	4.6199577
H	0.8123847	-3.3843726	3.0623764
C	-1.9137398	-3.5405050	2.5930515
H	-1.3431706	-4.1190990	1.8588425
H	-2.1667870	-4.2019256	3.4304248
H	-2.8486143	-3.2158116	2.1229134
C	3.2365663	0.3011090	0.4391625
C	4.4598240	1.3679245	-1.1719639
C	3.9617195	2.3253827	-0.3341619
C	4.2813685	-1.1400551	-1.3153930
H	3.5338125	-1.8513581	-0.9511988
C	5.2902787	1.4873199	-2.4007243
H	5.5430319	2.5347422	-2.5787513
H	4.7507582	1.1190036	-3.2811783
H	6.2256732	0.9218590	-2.3150030
C	4.0783243	3.8084354	-0.3744647
H	4.6410768	4.1131122	-1.2593950
H	4.5961127	4.2048178	0.5076015
H	3.0904247	4.2802584	-0.4240190
C	2.6006140	2.3315886	1.7738130
H	2.3952403	1.5908315	2.5475501
C	-1.3971928	2.3893588	0.7431968
C	-2.1906283	3.1083144	-0.1710251
C	-2.9538366	4.2002273	0.2385520
H	-3.5635437	4.7369192	-0.4837579
C	-2.9426513	4.5985018	1.5772904
C	-2.1652445	3.8981022	2.5001800
H	-2.1557930	4.2001856	3.5443844
C	-1.4027590	2.8052286	2.0854506
C	0.5330337	1.2478371	-1.3457643
C	0.7521144	2.5716625	-1.7669694
C	1.4301887	2.8518829	-2.9539945
H	1.5804286	3.8837951	-3.2617918
C	1.8984199	1.8084062	-3.7532282
C	1.7043271	0.4867633	-3.3453063
H	2.0581661	-0.3333146	-3.9656741
C	1.0376453	0.2104823	-2.1530080
C	-3.5445163	-1.0937107	0.3351883
C	-4.1911196	-0.0231276	0.9797094
C	-5.5815944	0.0405103	1.0520149
H	-6.0604830	0.8781038	1.5526356
C	-6.3572306	-0.9699418	0.4797661
C	-5.7354465	-2.0411179	-0.1632801
H	-6.3354162	-2.8311643	-0.6078994
C	-4.3431392	-2.1000946	-0.2341359
C	-1.0713239	-2.3471232	-1.0191945
C	-1.5884955	-2.2935078	-2.3262497
C	-1.0429836	-3.0672428	-3.3496259
H	-1.4567999	-3.0102448	-4.3532267
C	0.0405962	-3.9092285	-3.0867848
C	0.5688701	-3.9759121	-1.7967764
H	1.4127221	-4.6278863	-1.5852352
C	0.0168849	-3.2023038	-0.7746963
H	1.6598799	2.7997757	1.4679095
H	3.2775700	3.0964352	2.1632442
H	5.2813003	-1.4998045	-1.0533855
H	4.1973060	-1.0355296	-2.3990562
H	-0.8104839	2.2508045	2.8114754
H	-2.2196437	2.8028411	-1.2148330
H	-3.5413896	5.4464886	1.8987942
H	0.8934243	-0.8223968	-1.8501182
H	0.3723169	3.3939718	-1.1648724
H	2.4061919	2.0235396	-4.6899956
H	-3.8692952	-2.9417228	-0.7339089
H	-3.5978664	0.7710120	1.4269036
H	-7.4416279	-0.9224365	0.5348492
H	-2.4200450	-1.6280967	-2.5493233
H	0.4518427	-3.2375156	0.2210204
H	0.4688666	-4.5106140	-3.8845304

10.2. Cartesian coordinates of opt-2 in the triplet state

5-membered Ring in the triplet state
Energy(tpss-d3/def2-TZVP)= -2716.9699828 + 0.6698277 Hartree
Lowest Freq. = 6.36 cm^-1

P	14.4604718	4.4861126	10.2063629
Si	12.8665484	6.0148906	10.2245047
Si	11.3871076	3.8292803	11.8854538
Si	13.7226898	3.5584342	12.0941758
N	13.1568490	7.5517127	7.6988971
N	12.4713829	5.5554333	7.2775457
C	11.2214988	5.3290513	10.7938906
C	9.9295283	6.1491927	10.6738336
C	8.6692631	5.3139788	10.9722984
H	8.5554149	4.4955458	10.2548571
H	8.7095672	4.8843968	11.9770685
H	7.7752543	5.9471694	10.9110059
C	9.9922169	7.3203894	11.6860783
H	10.0195163	6.9410735	12.7105857
H	10.8926418	7.9219416	11.5166525
H	9.1087880	7.9633840	11.5750593
C	9.7738241	6.7526928	9.2623847
H	9.7723322	5.9693627	8.4959403
H	8.8278351	7.3034118	9.1901807
H	10.5885191	7.4512996	9.0415593
C	12.8076428	6.3827389	8.3022072
C	13.0387260	7.4628872	6.3135364
C	12.5998276	6.1939512	6.0471861
C	13.6036288	8.7459848	8.4137966
H	13.5323759	8.5259855	9.4833549
C	13.3642001	8.5979735	5.4056272
H	13.2085097	8.3008971	4.3664067
H	14.4086968	8.9130041	5.5137692
H	12.7311505	9.4705580	5.6052694
C	12.2944741	5.5142264	4.7576654
H	11.2520099	5.1775394	4.7182965
H	12.9330128	4.6362859	4.6057080
H	12.4594350	6.1998881	3.9239130
C	12.0530404	4.1647920	7.4419901
H	12.1017236	3.9264502	8.5038145
C	10.5753024	4.0669492	13.5768591
C	9.5640356	3.2325844	14.0828569
C	9.0118015	3.4496172	15.3457255
H	8.2293338	2.7913803	15.7153526
C	9.4597496	4.5122433	16.1323086
C	10.4626313	5.3545185	15.6490740
H	10.8234534	6.1797744	16.2574916
C	11.0125897	5.1302983	14.3884610
C	10.7024097	2.2412343	11.1214165
C	10.1398634	2.2036535	9.8362762
C	9.7117258	1.0062351	9.2619356
H	9.2761624	1.0050210	8.2653137

C	9.8369778	-0.1895591	9.9703573
C	10.3925398	-0.1775402	11.2508688
H	10.5053406	-1.1056834	11.8048245
C	10.8239065	1.0222698	11.8134187
C	14.3254504	4.3936750	13.6740697
C	15.1077615	5.5588170	13.6301613
C	15.4962255	6.2110192	14.8010622
H	16.1013005	7.1125663	14.7444689
C	15.1089589	5.7071238	16.0436053
C	14.3280765	4.5517154	16.1091053
H	14.0115190	4.1608712	17.0727102
C	13.9377886	3.9073983	14.9363139
C	14.2239265	1.7390226	12.0991498
C	14.8823739	1.1218804	13.1751282
C	15.2213864	-0.2316375	13.1324399
H	15.7322665	-0.6881030	13.9766765
C	14.9113688	-0.9962108	12.0071875
C	14.2671207	-0.3983956	10.9222490
H	14.0218740	-0.9865955	10.0415958
C	13.9289652	0.9519319	10.9712284
H	12.7310281	3.5094319	6.8900644
H	11.0318069	4.0389292	7.0720524
H	12.9623148	9.5934035	8.1574020
H	14.6400187	8.9736318	8.1510501
H	15.4069038	5.9569332	12.6628751
H	13.3023154	3.0274593	15.0042395
H	15.4096316	6.2144391	16.9566601
H	15.1423074	1.7069783	14.0533709
H	13.4233317	1.4068685	10.1223727
H	10.0331381	3.1320406	9.2812793
H	9.5062479	-1.1250582	9.5270215
H	11.2814587	1.0078573	12.7997796
H	15.1739064	-2.0504568	11.9738134
H	11.8031791	5.7854283	14.0303615
H	9.0308978	4.6818496	17.1165089
H	9.1984812	2.4068124	13.4774234

10.3. Cartesian coordinates of NHC-coordinated trisilacyclopropylidene E

NHC-coordinated trisilacyclopropylidene
E(TPSS-D3/def2-TZVP) = -2179.499846642
(conv)
Lowest Freq. = 13.79 cm^-1

Si	-2.2392002	-0.6021097	0.2808929
Si	-1.2107360	1.2161319	1.4331843
Si	-0.2489497	0.2287984	-0.5233551
C	-1.9018210	2.6931577	0.4325901
N	-1.1337845	3.7084689	-0.0719786
C	-1.9172944	4.6845573	-0.6843815
C	0.3206690	3.7379807	0.0256985
C	-3.2160350	4.2892925	-0.5341553
N	-3.1873162	3.0782469	0.1599454
C	-4.3789779	2.3787008	0.6266652
H	0.7685458	3.1718408	-0.7953493
H	0.6103219	3.2804884	0.9752660
H	0.6557052	4.7758684	-0.0072770
H	-4.9646035	3.0414007	1.2709010
H	-4.0481288	1.5084607	1.1931328
H	-4.9861307	2.0473534	-0.2183446
C	-1.3311472	5.8602799	-1.3844541
C	-4.4898636	4.9128321	-0.9885229
H	-4.2794732	5.8286577	-1.5451129
H	-5.1399820	5.1738385	-0.1445685
H	-5.0542006	4.2386198	-1.6439978
H	-0.7751854	6.5114270	-0.6990495
H	-2.1261173	6.4559802	-1.8385668
H	-0.6464364	5.5424341	-2.1794695
H	3.5642728	-1.5809140	2.1764012
C	3.0399111	-1.6414281	1.2260061
C	1.9614977	-0.7935831	0.9705214
C	1.2606855	-0.8542320	-0.2452892
C	1.6786954	-1.8002643	-1.1998710
H	1.1429059	-1.8850118	-2.1430879
C	2.7609949	-2.6425321	-0.9531501
H	3.0665746	-3.3671575	-1.7037242
C	3.4440226	-2.5660660	0.2631736
H	4.2830264	-3.2283267	0.4594804
H	1.6471115	-0.0745992	1.7249154
H	-1.4506295	-5.5590809	3.1544041
C	-1.6143060	-4.6236368	2.6259965
C	-1.0252865	-3.4448344	3.0861207
H	-0.4007249	-3.4595530	3.9757527
C	-1.2410926	-2.2450811	2.4103533
H	-0.7901838	-1.3290900	2.7870998
C	-2.0374630	-2.1956562	1.2527454
C	-2.6200715	-3.3947214	0.8025483
H	-3.2386946	-3.3880991	-0.0922017
C	-2.4170417	-4.5939545	1.4839425
H	-2.8808980	-5.5077944	1.1208947
H	-5.0280786	-1.2583552	1.0130012
C	-5.0543977	-0.9499375	-0.0302301
C	-6.2792767	-0.8804430	-0.6910433
H	-7.1948063	-1.1386141	-0.1646917
C	-6.3318375	-0.4767579	-2.0280891
H	-7.2866908	-0.4176331	-2.5434549
C	-5.1488783	-0.1696713	-2.7022425
H	-5.1787352	0.1204575	-3.7496417
C	-3.9231406	-0.2510336	-2.0394617
H	-3.0074281	-0.0343596	-2.5817042
C	-3.8509646	-0.6231915	-0.6858955
H	1.9322190	0.6308477	-2.5066976
C	1.0859931	1.2135544	-2.8616190
C	-0.1258684	1.1813881	-2.1425676
C	-1.1900919	1.9621564	-2.6353834
H	-2.1394319	1.9683177	-2.1073719
C	-1.0532503	2.7371464	-3.7846991
H	-1.8950067	3.3276130	-4.1390239
C	0.1573531	2.7542129	-4.4817420
H	0.2654877	3.3562918	-5.3797935
C	1.2253960	1.9862757	-4.0146574
H	2.1720217	1.9892839	-4.5493195

10.4. Cartesian coordinates of *t*Bu-C≡P

tBuCP
E(TPSS-D3/def2-TZVP) = -537.4181496253
(conv)
Lowest Freq. = 142.92 cm^-1

P	0.2134127	0.0159388	0.0067967
C	1.7645359	0.0225578	0.0608395
C	3.2289315	0.0284933	0.1115802
C	3.6889385	-0.0057781	1.5895806
H	3.3128189	0.8667656	2.1310120
H	4.7840804	-0.0010600	1.6305754
H	3.3221255	-0.9080330	2.0869292
C	3.7705899	-1.2168112	-0.6320677
H	4.8658737	-1.2152111	-0.5956556
H	3.4533193	-1.2094255	-1.6785670
H	3.4042592	-2.1349148	-0.1643077
C	3.7584118	1.3140334	-0.5697471
H	3.3838565	2.2045066	-0.0572022
H	3.4404992	1.3553848	-1.6152799
H	4.8536880	1.3208930	-0.5337130

10.5. Cartesian coordinates of opt-1

opt-1
E(TPSS-D3/def2-TZVP) = -2716.997110593
(conv)
Lowest Freq. = 14.68 cm^-1

Si	-2.5378845	0.2347239	0.6343386
Si	-1.0718861	2.8962556	1.7103978
Si	-0.3331543	0.6124042	-0.0722501
C	-1.1566297	4.8413951	1.8207963
N	-2.1884125	5.7184795	1.9986058
C	-1.7247419	6.9797805	2.3778009
C	-3.6059695	5.3913985	1.8724256
C	-0.3631244	6.8924025	2.4456375
N	-0.0403791	5.5777460	2.1184532
C	1.3110963	5.0339931	2.0831292
H	-3.6826958	4.4252831	1.3703065

H	-4.1056458	6.1608678	1.2791199
H	-4.0664452	5.3352083	2.8637498
H	1.7833140	5.2271101	1.1154827
H	1.2393318	3.9523307	2.2429431
H	1.9056027	5.4854115	2.8797956
C	-2.6415743	8.1259326	2.6317224
C	0.6665369	7.9136813	2.7859052
H	0.1883018	8.8794291	2.9626443
H	1.3921756	8.0398175	1.9736869
H	1.2235098	7.6447480	3.6915579
H	-3.2132396	8.3937083	1.7350541
H	-2.0664331	9.0026907	2.9373768
H	-3.3605875	7.8990338	3.4276291
H	3.8978305	1.5296393	2.5441773
C	3.1145598	0.8075576	2.3253006
C	2.0839644	1.1397241	1.4465980
C	1.0634868	0.2266233	1.1394328
C	1.1103181	-1.0367687	1.7519207
H	0.3287115	-1.7640003	1.5398062
C	2.1319520	-1.3744730	2.6395290
H	2.1416749	-2.3551508	3.1082437
C	3.1383144	-0.4515426	2.9283041
H	3.9348802	-0.7108569	3.6206597
H	2.0680494	2.1242044	0.9870380
H	-3.7095052	-1.5896262	5.9964539
C	-3.4872118	-1.2473831	4.9889054
C	-2.2552360	-0.6552663	4.7052431
H	-1.5141417	-0.5353662	5.4914826
C	-1.9682632	-0.2202844	3.4119634
H	-1.0087113	0.2437393	3.2032741
C	-2.9072147	-0.3672393	2.3742306
C	-4.1416110	-0.9686336	2.6791380
H	-4.8813219	-1.1023693	1.8931889
C	-4.4313947	-1.4031892	3.9725041
H	-5.3919029	-1.8651284	4.1869797
H	-4.3911475	0.9330241	-1.6095962
C	-4.3612123	-0.1538413	-1.5617985
C	-5.0728059	-0.9077238	-2.4964560
H	-5.6625187	-0.4079001	-3.2608171
C	-5.0262188	-2.3013693	-2.4500249
H	-5.5756372	-2.8909456	-3.1791890
C	-4.2710682	-2.9366557	-1.4613720
H	-4.2306814	-4.0221824	-1.4213797
C	-3.5631632	-2.1790864	-0.5302970
H	-2.9756473	-2.6866626	0.2319349
C	-3.5903812	-0.7730316	-0.5641837
H	2.2553157	-0.3163572	-1.1707622
C	1.5019744	-0.6136066	-1.8965079
C	0.1496010	-0.3132196	-1.6528720
C	-0.7957763	-0.7424042	-2.6020082
H	-1.8495661	-0.5364629	-2.4454414
C	-0.4071421	-1.4344281	-3.7475785
H	-1.1598798	-1.7600854	-4.4609133
C	0.9420258	-1.7118031	-3.9753175
H	1.2461173	-2.2523841	-4.8678808
C	1.8969913	-1.2985319	-3.0460752
H	2.9492807	-1.5153133	-3.2123006
P	-2.6887757	2.4496944	0.1556852
C	-0.7793641	2.4690444	-0.1994284
C	-0.3155129	3.3536341	-1.3832767
C	-0.7655639	4.8171384	-1.2448752
H	-1.8403404	4.8694017	-1.0335950
H	-0.5750507	5.3568917	-2.1805883
H	-0.2299216	5.3327175	-0.4436934
C	1.2187666	3.3038226	-1.4842132
H	1.5714509	3.9110264	-2.3270697
H	1.5677981	2.2769066	-1.6403593
H	1.6820862	3.6880175	-0.5689381
C	-0.9112044	2.8200506	-2.7032218
H	-2.0054357	2.8339614	-2.6539118
H	-0.5885425	1.7956992	-2.8988695
H	-0.5911805	3.4469306	-3.5452520

10.6. Cartesian coordinates of opt-2

opt-2
E(TPSS-D3/def2-TZVP) = -2717.009817681
(conv)
Lowest Freq. = 4.19 cm^-1

Si	-2.4963328	-0.7671178	0.8290076
Si	-1.6599515	1.9879593	1.3502648
Si	-0.4524500	-0.0603715	-0.1827478
C	-1.8098340	3.7620856	2.0828702
N	-1.2545038	4.2241555	3.2287438
C	-1.6896787	5.5182281	3.5079520
C	-0.3439915	3.4393227	4.0617381
C	-2.5479532	5.8625779	2.4966748
N	-2.6058710	4.7644309	1.6400286
C	-3.4333791	4.6738675	0.4368897
H	-0.1793794	2.4814915	3.5635618
H	-0.7932525	3.2691563	5.0429807
H	0.6081175	3.9641883	4.1686050
H	-4.4668488	4.9241920	0.6855789
H	-3.3900260	3.6427577	0.0792690
H	-3.0573464	5.3534944	-0.3320110
C	-1.2367478	6.2721646	4.7097571
C	-3.3221221	7.1108594	2.2507881
H	-3.1079873	7.8431358	3.0318859
H	-4.4018607	6.9212942	2.2530013
H	-3.0635908	7.5604334	1.2852095
H	-1.5127008	5.7544108	5.6356846
H	-1.6988329	7.2612328	4.7268221
H	-0.1488990	6.4067434	4.7135155
H	3.3934862	-1.2231508	2.8321133
C	2.6944295	-1.6052044	2.0916788
C	1.8010274	-0.7384483	1.4612050
C	0.8867495	-1.2004445	0.5018256
C	0.8914109	-2.5755888	0.2072050
H	0.1701363	-2.9765089	-0.5016327
C	1.7784140	-3.4487281	0.8329041
H	1.7508548	-4.5096774	0.5988217
C	2.6853577	-2.9644840	1.7773747
H	3.3723893	-3.6451833	2.2732352
H	1.7908923	0.3166087	1.7287126
H	-0.9405013	-5.4230476	3.9003072
C	-1.2650051	-4.5531034	3.3351390
C	-0.7695839	-3.2856803	3.6512356
H	-0.0531498	-3.1668869	4.4600335
C	-1.1827449	-2.1757393	2.9203327
H	-0.7878691	-1.1932105	3.1692889
C	-2.0908817	-2.2995621	1.8539005
C	-2.5870773	-3.5785263	1.5591901
H	-3.2992249	-3.7050876	0.7476108
C	-2.1795323	-4.6955957	2.2921640
H	-2.5765780	-5.6777533	2.0467880
H	-5.2175976	0.1952922	0.0198052
C	-4.9373118	-0.5716352	-0.7001521
C	-5.7886543	-0.8743495	-1.7643522
H	-6.7370005	-0.3519443	-1.8666624
C	-5.4234970	-1.8456137	-2.6973490
H	-6.0820141	-2.0787934	-3.5301484
C	-4.2040073	-2.5117748	-2.5607811
H	-3.9053959	-3.2588431	-3.2915738
C	-3.3585172	-2.2030939	-1.4973600
H	-2.3989399	-2.7098955	-1.4225325
C	-3.7087457	-1.2306852	-0.5428661
H	1.0902554	-1.5969526	-2.3387271
C	0.2600074	-1.0867793	-2.8210721
C	-0.6046880	-0.2917545	-2.0523545
C	-1.6561023	0.3641376	-2.7175804
H	-2.3477757	0.9761498	-2.1419727
C	-1.8420931	0.2299058	-4.0910092
H	-2.6704868	0.7370855	-4.5790777
C	-0.9742543	-0.5712038	-4.8366295
H	-1.1190372	-0.6837353	-5.9079710
C	0.0786949	-1.2274034	-4.1984431
H	0.7608639	-1.8485876	-4.7739196
P	-3.2911136	0.8901977	2.1228109
C	-0.2803135	1.7087797	0.3141011
C	0.7441593	2.7085394	-0.2448437
C	0.0415206	3.7089666	-1.1882642

H	-0.4715285	3.1736156	-1.9927385
H	0.7618391	4.4085801	-1.6342937
H	-0.7043412	4.2916818	-0.6341434
C	1.4358193	3.4987361	0.8843272
H	2.2027548	4.1708135	0.4772915
H	1.9163785	2.8150875	1.5923491
H	0.7109729	4.1116047	1.4310539
C	1.8374706	1.9792519	-1.0506946
H	1.4036496	1.4446089	-1.9007519
H	2.3678640	1.2531566	-0.4266252
H	2.5693142	2.6999092	-1.4369860

10.7. Cartesian coordinates of Int-1

Int-1
E(TPSS-D3/def2-TZVP) = -2716.936695402
(conv)
Lowest Freq. = 14.21 cm^-1

Si	-2.1645749	0.7834807	0.4835277
Si	-0.7635569	2.6076607	0.2518741
Si	0.0987865	0.4559601	0.0472731
C	-0.5845098	3.3155177	2.1226544
N	-1.6051838	3.5823907	2.9815542
C	-1.1462513	3.7435372	4.2851115
C	-3.0110486	3.6856279	2.5944009
C	0.2131318	3.5850699	4.2372654
N	0.5277098	3.3332713	2.9037859
C	1.8864363	3.1963103	2.3877764
H	-3.6128245	3.0294674	3.2258130
H	-3.0926287	3.3611739	1.5562966
H	-3.3464020	4.7218990	2.6917534
H	2.4060057	4.1572068	2.4477478
H	1.8105301	2.8773821	1.3471099
H	2.4260974	2.4404479	2.9598422
C	-2.0650122	4.0010275	5.4276616
C	1.2443577	3.6245842	5.3112541
H	0.7756582	3.8520737	6.2710511
H	2.0039750	4.3906055	5.1159602
H	1.7589778	2.6609712	5.4057054
H	-2.6383350	4.9242084	5.2837593
H	-1.4943481	4.0981528	6.3537843
H	-2.7775580	3.1770189	5.5491469
H	4.2062670	-0.3633539	2.8915123
C	3.1670752	-0.6363386	2.7227366
C	2.4444500	-0.0296805	1.6950132
C	1.1020091	-0.3659895	1.4371859
C	0.5186797	-1.3522526	2.2528651
H	-0.5134255	-1.6438932	2.0751397
C	1.2308782	-1.9586084	3.2884316
H	0.7505905	-2.7142670	3.9049643
C	2.5575585	-1.5996096	3.5294175
H	3.1160449	-2.0727365	4.3327103
H	2.9389491	0.7166929	1.0762740
H	-4.3317032	0.0108607	5.8103487
C	-3.9195873	0.1162059	4.8102075
C	-2.5516859	0.3410667	4.6312850
H	-1.8924963	0.4072813	5.4939869
C	-2.0271537	0.4749916	3.3472411
H	-0.9613113	0.6533199	3.2289553
C	-2.8458536	0.3828615	2.2044588
C	-4.2180385	0.1414333	2.4081223
H	-4.8769271	0.0615357	1.5466859
C	-4.7499016	0.0129927	3.6922036
H	-5.8135372	-0.1722659	3.8211091
H	-4.0596083	2.5697456	-0.9426067
C	-4.2605360	1.5627120	-1.3004524
C	-5.2452393	1.3602976	-2.2667912
H	-5.8123684	2.2052904	-2.6484095
C	-5.4940011	0.0750169	-2.7511641
H	-6.2571213	-0.0842515	-3.5082451
C	-4.7530990	-1.0039737	-2.2657880
H	-4.9385069	-2.0057551	-2.6448599
C	-3.7685466	-0.7971351	-1.2993150
H	-3.1890577	-1.6441136	-0.9383490
C	-3.5052475	0.4884018	-0.7953305
H	2.7634499	-0.5468157	-0.9055205
C	2.0733947	-0.6314949	-1.7407731
C	0.7312455	-0.2436173	-1.5839144
C	-0.1346228	-0.4104387	-2.6793315
H	-1.1793588	-0.1320495	-2.5783418
C	0.3259621	-0.9307227	-3.8880237
H	-0.3639764	-1.0528167	-4.7189101
C	1.6668565	-1.2901154	-4.0311255
H	2.0284379	-1.6894057	-4.9751137
C	2.5397130	-1.1417773	-2.9524294
H	3.5838300	-1.4279102	-3.0525763
P	-1.1846250	2.6605837	-2.1817889
C	-0.8157108	3.8776509	-1.0474117
C	-0.6457311	5.3770848	-1.1620443
C	0.7428123	5.7587590	-0.6068782
H	0.8319296	5.4500192	0.4416839
H	0.8976720	6.8436623	-0.6601552
H	1.5345596	5.2648585	-1.1793892
C	-0.7719795	5.8399703	-2.6201732
H	-0.6606531	6.9286772	-2.6912024
H	-1.7475465	5.5577096	-3.0298133
H	-0.0055390	5.3659727	-3.2420328
C	-1.7313562	6.0602749	-0.3021034
H	-1.6414913	5.7495153	0.7452628
H	-2.7304087	5.7880326	-0.6583910
H	-1.6306678	7.1519662	-0.3467082

10.8. Cartesian coordinates of Int-2

Int-2
E(TPSS-D3/def2-TZVP) = -2716.949294854
(conv)
Lowest Freq. = 9.91 cm^-1

Si	-3.0270538	0.3911712	0.7876280
Si	-0.6493500	2.8445383	0.2330791
Si	-0.8467103	0.5507113	-0.0943110
C	-1.4246285	3.3649111	1.8997026
N	-2.6387687	3.9178557	2.1379395
C	-2.8099103	4.1576551	3.4967269
C	-3.6577348	4.1152742	1.1018542
C	-1.6573798	3.7463443	4.1158018
N	-0.8264768	3.2659193	3.1132363
C	0.4886909	2.6726119	3.3400825
H	-3.8114226	3.1540592	0.5914812
H	-3.3235119	4.8780101	0.3941586
H	-4.5810507	4.4353742	1.5831276
H	1.1728100	3.4198421	3.7508310
H	0.8698262	2.3071089	2.3848456
H	0.3885484	1.8290453	4.0251694
C	-4.0652849	4.7093744	4.0756282
C	-1.2660104	3.7306403	5.5507263
H	-2.0633072	4.1611890	6.1594295
H	-0.3523937	4.3103939	5.7269157
H	-1.0979983	2.7041998	5.8938580
H	-4.3162536	5.6879804	3.6517011
H	-3.9493434	4.8279153	5.1548123
H	-4.9106572	4.0337927	3.9023249
H	3.9176636	-0.2215062	1.4677101
C	2.9484264	-0.6736983	1.2705276
C	1.9024377	0.1045991	0.7727079
C	0.6397989	-0.4503278	0.5065516
C	0.4617837	-1.8265177	0.7507074
H	-0.5091219	-2.2811202	0.5665404
C	1.5064158	-2.6102909	1.2397843
H	1.3470498	-3.6706178	1.4181275
C	2.7512548	-2.0353552	1.5060910
H	3.5633090	-2.6455289	1.8924707
H	2.0719673	1.1605109	0.5719826
H	-2.4289802	0.3270207	6.6250590
C	-2.5032118	0.3583660	5.5406684
C	-1.4697629	-0.1455238	4.7465556
H	-0.5852936	-0.5747855	5.2139087
C	-1.5808443	-0.1306740	3.3541459
H	-0.7774653	-0.5586338	2.7606046
C	-2.7149646	0.3949451	2.7026205
C	-3.7330086	0.9044849	3.5323075
H	-4.6311316	1.3077247	3.0645059
C	-3.6403274	0.8840609	4.9260825
H	-4.4581681	1.2676691	5.5328011

H	-3.2898209	-1.2216780	-1.7049178
C	-3.3416489	-1.9435359	-0.8923088
C	-3.4725592	-3.2957243	-1.1988713
H	-3.5194494	-3.6106971	-2.2389374
C	-3.5450597	-4.2461446	-0.1761864
H	-3.6509965	-5.3017040	-0.4124888
C	-3.4874311	-3.8209067	1.1513769
H	-3.5501924	-4.5482899	1.9582051
C	-3.3410478	-2.4652815	1.4532984
H	-3.2799227	-2.1621133	2.4955411
C	-3.2541241	-1.4897540	0.4412242
H	0.9026505	-0.7212883	-2.1874311
C	0.1037328	-0.2048491	-2.7139688
C	-0.8763087	0.4821656	-1.9798926
C	-1.9002069	1.1363293	-2.6914063
H	-2.6808153	1.6537185	-2.1370959
C	-1.9409504	1.1054730	-4.0845770
H	-2.7421800	1.6142426	-4.6146470
C	-0.9577365	0.4161532	-4.7974237
H	-0.9889799	0.3886837	-5.8834636
C	0.0627929	-0.2410291	-4.1085962
H	0.8283352	-0.7829866	-4.6584261
P	-1.0433868	4.3168847	-1.3795592
C	0.3717746	4.2221691	-0.4524623
C	1.6827392	4.9463682	-0.3810579
C	1.7034144	5.7440521	0.9437326
H	0.8995894	6.4866323	0.9610839
H	2.6629349	6.2627047	1.0519661
H	1.5730477	5.0738384	1.7995929
C	2.8317496	3.9181274	-0.3686331
H	3.7981305	4.4335775	-0.3269315
H	2.8076077	3.2936468	-1.2667945
H	2.7507325	3.2645234	0.5061752
C	1.8431425	5.9075702	-1.5703957
H	1.0197927	6.6294230	-1.5956061
H	1.8372649	5.3536206	-2.5147147
H	2.7869425	6.4595346	-1.4968386

10.9. Cartesian coordinates of Int-3

Int-3
E(TPSS-D3/def2-TZVP) = -2716.965509309
(conv)
Lowest Freq. = 9.24 cm^-1

Si	-2.4003358	0.1534012	1.4198290
Si	-0.6196854	2.7296453	1.1927409
Si	-0.3119389	0.5398514	0.4337698
C	0.8939969	3.6120215	1.9369546
N	0.9361525	4.4614353	2.9963111
C	2.2445421	4.8462761	3.2706677
C	-0.2450422	4.8724149	3.7611278
C	3.0393375	4.2251810	2.3428142
N	2.1873867	3.4815624	1.5307121
C	2.6293888	2.6537965	0.4063142
H	-0.3246617	4.2725376	4.6713401
H	-1.1221508	4.6983380	3.1205598
H	-0.1510212	5.9302582	4.0150957
H	3.3775192	3.2014249	-0.1702954
H	1.7695215	2.4344257	-0.2273599
H	3.0494807	1.7134970	0.7720639
C	2.5888733	5.7686049	4.3881247
C	4.5140765	4.2599060	2.1369349
H	4.9843037	4.8645479	2.9151494
H	4.7782782	4.6974410	1.1666782
H	4.9483315	3.2545300	2.1791542
H	2.1463800	6.7610278	4.2422311
H	3.6722844	5.8893791	4.4524417
H	2.2307252	5.3832160	5.3493355
H	2.7070263	-0.1596227	4.4141673
C	2.2825823	-0.6174101	3.5237869
C	1.4755270	0.1364325	2.6705840
C	0.9007612	-0.4249848	1.5178485
C	1.1580767	-1.7843271	1.2601958
H	0.7030807	-2.2617721	0.3955317
C	1.9605691	-2.5438225	2.1091892
H	2.1296419	-3.5959541	1.8957723
C	2.5288302	-1.9610796	3.2436328
H	3.1481975	-2.5549037	3.9103840
H	1.2573131	1.1714625	2.9238137
H	-1.7063883	-4.5104814	4.7786793
C	-1.8579248	-3.6331909	4.1551105
C	-2.6297498	-3.7224249	2.9948672
H	-3.0832443	-4.6703042	2.7150648
C	-2.8174340	-2.5980397	2.1910579
H	-3.4182646	-2.6796550	1.2881029
C	-2.2394413	-1.3614395	2.5277342
C	-1.4820584	-1.2881341	3.7108934
H	-1.0359043	-0.3401868	4.0004246
C	-1.2870686	-2.4105874	4.5132017
H	-0.6885379	-2.3326688	5.4173675
H	-2.7225693	-0.8455537	-1.3904675
C	-3.7181776	-0.6034564	-1.0266278
C	-4.8174079	-0.7876202	-1.8664404
H	-4.6719866	-1.1702584	-2.8735684
C	-6.1003832	-0.4780386	-1.4139547
H	-6.9575637	-0.6142231	-2.0679838
C	-6.2790881	0.0086639	-0.1172776
H	-7.2767607	0.2496445	0.2406804
C	-5.1772618	0.1922823	0.7165172
H	-5.3278193	0.5790367	1.7221517
C	-3.8750420	-0.1041879	0.2776656
H	2.0759682	-0.6295029	-1.0143125
C	1.4070288	-0.2211960	-1.7681554
C	0.1866315	0.3575658	-1.3726346
C	-0.6485644	0.8753909	-2.3820266
H	-1.5963383	1.3317660	-2.1087111
C	-0.2828364	0.8162572	-3.7250901
H	-0.9472120	1.2216613	-4.4839986
C	0.9319982	0.2348815	-4.0961919
H	1.2169682	0.1843689	-5.1435834
C	1.7760969	-0.2826152	-3.1126533
H	2.7232112	-0.7373110	-3.3929935
P	-2.2728451	2.1716027	2.6297505
C	-2.2124223	3.5126673	1.4087730
C	-3.2514444	4.0954043	0.4661446
C	-4.6272721	4.0614684	1.1558039
H	-4.9297731	3.0268249	1.3472483
H	-5.3907283	4.5326928	0.5244402
H	-4.5884841	4.5886470	2.1151113
C	-2.8611378	5.5605312	0.1824337
H	-3.5718554	6.0335501	-0.5083931
H	-1.8624568	5.6027459	-0.2687593
H	-2.8387822	6.1377270	1.1131635
C	-3.3399223	3.3458416	-0.8770469
H	-3.5814054	2.2914910	-0.7166295
H	-2.3772491	3.4068426	-1.3977479
H	-4.1123461	3.7793743	-1.5274823

10.10. Cartesian coordinates of Int-4

Int-4
E(TPSS-D3/def2-TZVP) = -2716.983562871
(conv)
Lowest Freq. = 15.28 cm^-1

Si	-2.2937462	0.3520107	1.1118906
Si	-0.3694690	2.4199858	0.9158198
Si	-0.0191179	0.1787944	0.4799219
C	0.6351848	3.6328370	1.9935556
N	1.3103280	3.3300883	3.1368186
C	1.9871454	4.4412285	3.6274465
C	1.2557226	2.0313854	3.8067616
C	1.7253080	5.4683187	2.7586959
N	0.9011988	4.9480963	1.7656521
C	0.3592816	5.7271253	0.6493102
H	0.6367095	1.3682356	3.2015320
H	0.8109801	2.1474050	4.7982661
H	2.2571729	1.6057251	3.8906573
H	-0.2243169	6.5633391	1.0416158
H	-0.2969976	5.0643106	0.0738426
H	1.1796005	6.1026412	0.0316311
C	2.7982289	4.3943278	4.8755939
C	2.1653558	6.8910427	2.7668191
H	2.7998133	7.0814507	3.6348680
H	1.3092494	7.5737868	2.8157912

H	2.7381438	7.1405253	1.8663734
H	2.1863165	4.1169704	5.7418219
H	3.2379947	5.3738422	5.0733881
H	3.6135079	3.6657365	4.7975418
H	4.3981354	-0.7971745	2.6812716
C	3.3844046	-1.1582964	2.5238644
C	2.4824359	-0.4054841	1.7716108
C	1.1671756	-0.8490015	1.5405653
C	0.7941326	-2.0890754	2.0867449
H	-0.2134252	-2.4635781	1.9270866
C	1.6883858	-2.8452593	2.8453554
H	1.3722421	-3.7979097	3.2623355
C	2.9853557	-2.3807339	3.0683514
H	3.6829487	-2.9696159	3.6578822
H	2.8052261	0.5448865	1.3478649
H	-3.5398510	-2.9139916	5.7637815
C	-3.3053287	-2.3085686	4.8921530
C	-4.2230984	-2.1961556	3.8473557
H	-5.1771598	-2.7144783	3.9040091
C	-3.9170449	-1.4232316	2.7256210
H	-4.6369764	-1.3533677	1.9138548
C	-2.6938976	-0.7384446	2.6203883
C	-1.7881593	-0.8677572	3.6883292
H	-0.8291364	-0.3575383	3.6378216
C	-2.0811234	-1.6412538	4.8092005
H	-1.3562581	-1.7292110	5.6150311
H	-2.5080094	-2.1484958	-0.3744097
C	-3.3063912	-1.5151654	-0.7586650
C	-4.1303251	-2.0028422	-1.7724506
H	-3.9746254	-3.0044318	-2.1651130
C	-5.1473249	-1.1980549	-2.2879283
H	-5.7897428	-1.5714942	-3.0812017
C	-5.3307774	0.0915152	-1.7852737
H	-6.1171672	0.7251622	-2.1878145
C	-4.5004869	0.5729876	-0.7731285
H	-4.6405895	1.5842863	-0.4032309
C	-3.4750520	-0.2210452	-0.2366928
H	2.2137647	-1.2982868	-0.8691503
C	1.5282597	-0.9785479	-1.6501276
C	0.3806517	-0.2401333	-1.3115107
C	-0.4987656	0.1339894	-2.3447086
H	-1.3907397	0.7034449	-2.0964922
C	-0.2289470	-0.2072893	-3.6687507
H	-0.9231473	0.0872651	-4.4517488
C	0.9206539	-0.9323646	-3.9889914
H	1.1273420	-1.2012728	-5.0218759
C	1.7990517	-1.3189706	-2.9759933
H	2.6927651	-1.8894985	-3.2169059
P	-1.9829068	2.9130521	-0.3901202
C	-2.2004147	2.2156260	1.4182105
C	-2.9838561	3.0054677	2.4886200
C	-4.4895703	2.7580215	2.2743988
H	-4.7958115	3.1279390	1.2901842
H	-5.0837326	3.2747507	3.0387786
H	-4.7189423	1.6876411	2.3288115
C	-2.5982450	2.5375245	3.9034776
H	-3.1566892	3.1022289	4.6610461
H	-1.5281813	2.7018816	4.0768626
H	-2.8084646	1.4754387	4.0453173
C	-2.7195837	4.5162872	2.3953604
H	-2.9109426	4.8810995	1.3815150
H	-1.6769731	4.7415028	2.6501831
H	-3.3614386	5.0562065	3.1024279

10.11. Cartesian coordinates of TS1

TS1
E(TPSS-D3/def2-TZVP) = -2716.937095600
(conv)
Lowest Freq. = -37.91 cm^-1

Si	-2.8629024	0.4604923	1.0640360
Si	-0.6440178	2.6319018	0.4333396
Si	-0.8974433	0.4302696	-0.2522771
C	0.5521415	3.5975086	-0.7092355
N	1.9001498	3.6716283	-0.5495693
C	2.5123178	4.1630208	-1.6993181
C	2.6046893	3.2451772	0.6604204
C	1.5068324	4.4070749	-2.5981054
N	0.3196693	4.0527986	-1.9660236
C	-1.0011479	4.1092274	-2.5877634
H	3.0801453	2.2748378	0.4969523
H	1.8663971	3.1617481	1.4605530
H	3.3551024	3.9928887	0.9251805
H	-1.2531606	5.1437462	-2.8348869
H	-1.7195456	3.7176198	-1.8685858
H	-1.0130199	3.4868931	-3.4850414
C	3.9868988	4.3408210	-1.8090942
C	1.5395327	4.9188283	-3.9958334
H	2.5699536	5.1117255	-4.3011372
H	0.9753557	5.8531618	-4.0969623
H	1.1073140	4.1900515	-4.6912845
H	4.3625846	5.0672403	-1.0788597
H	4.2450269	4.7036292	-2.8061276
H	4.5170797	3.3959863	-1.6437854
H	3.2546839	-0.6667306	2.3407330
C	2.6719863	-0.9120015	1.4559136
C	1.5017266	-0.2079637	1.1779015
C	0.7181914	-0.5049545	0.0465870
C	1.1482302	-1.5532999	-0.7870237
H	0.5589486	-1.8203822	-1.6615331
C	2.3205671	-2.2595170	-0.5150862
H	2.6326565	-3.0645937	-1.1757992
C	3.0891907	-1.9391445	0.6056044
H	3.9999526	-2.4917144	0.8202419
H	1.1720300	0.5746118	1.8590701
H	-0.7848453	-0.5840748	6.4112306
C	-1.1597075	-0.3972919	5.4080430
C	-0.6899977	-1.1505661	4.3311219
H	0.0517847	-1.9296199	4.4916179
C	-1.1728958	-0.9066363	3.0445034
H	-0.7987342	-1.5064037	2.2190547
C	-2.1363629	0.0880683	2.7945890
C	-2.5875618	0.8362684	3.8987153
H	-3.3263937	1.6182538	3.7379963
C	-2.1135039	0.5971445	5.1886354
H	-2.4824492	1.1915420	6.0209013
H	-4.9182672	-0.0590899	-1.0429958
C	-4.8851072	-0.9625133	-0.4360697
C	-5.7473837	-2.0118736	-0.7487072
H	-6.4164952	-1.9283604	-1.6021118
C	-5.7625282	-3.1623505	0.0421579
H	-6.4376786	-3.9810012	-0.1927328
C	-4.9107822	-3.2442220	1.1449953
H	-4.9211585	-4.1314010	1.7742743
C	-4.0411729	-2.1953841	1.4447987
H	-3.3843612	-2.2809759	2.3062460
C	-3.9952931	-1.0298961	0.6542681
H	1.0212003	0.6550952	-2.5437529
C	0.0250109	0.7663106	-2.9664822
C	-1.0990660	0.6467577	-2.1255319
C	-2.3667784	0.7977258	-2.7148689
H	-3.2515246	0.7119834	-2.0913070
C	-2.5109503	1.0549645	-4.0783615
H	-3.5043645	1.1601048	-4.5069185
C	-1.3825997	1.1672582	-4.8937672
H	-1.4922261	1.3577768	-5.9581301
C	-0.1113200	1.0197197	-4.3316380
H	0.7734792	1.0964105	-4.9598237
P	-1.0226649	3.4398328	2.4291820
C	-2.1645088	3.3678828	1.1082139
C	-3.4580061	4.0968603	0.8418602
C	-3.0923350	5.5746908	0.5522053
H	-2.5681687	6.0104074	1.4082367
H	-4.0003622	6.1560629	0.3532672
H	-2.4357076	5.6493939	-0.3220153
C	-4.2277118	3.5245096	-0.3575167
H	-5.1324117	4.1157585	-0.5446604
H	-4.5042435	2.4857268	-0.1517788
H	-3.6192544	3.5358633	-1.2680080
C	-4.3560391	4.0313783	2.0897038
H	-3.8246765	4.4095663	2.9699928
H	-4.6425549	2.9905987	2.2740702
H	-5.2632538	4.6299619	1.9446504

10.12. Cartesian coordinates of TS2

TS2
E(TPSS-D3/def2-TZVP) = -2716.957169181
(conv)
Lowest Freq. = -70.84 cm^-1

Si	-2.5235331	0.7419087	0.7080324
Si	-0.4445265	2.4635920	1.2707135
Si	-0.1868799	0.2791203	0.6877082
C	0.8034513	3.7145869	1.9008196
N	0.7095195	4.7596847	2.7780629
C	1.9457563	5.3818251	2.9379219
C	-0.5199195	5.1797271	3.4403329
C	2.8371326	4.7047936	2.1495671
N	2.1203197	3.6916812	1.5190531
C	2.6679129	2.7127623	0.5806552
H	-0.2958346	5.4571515	4.4726088
H	-1.2251694	4.3408224	3.4158614
H	-0.9633975	6.0298620	2.9156641
H	3.6620377	3.0372309	0.2739888
H	2.0199530	2.6423390	-0.2968089
H	2.7274609	1.7254264	1.0474342
C	2.1344274	6.5614480	3.8277124
C	4.2943170	4.9235241	1.9298720
H	4.6353391	5.7679181	2.5324492
H	4.5178273	5.1490457	0.8802842
H	4.8836773	4.0452224	2.2177102
H	1.4687098	7.3857389	3.5467728
H	3.1637376	6.9194609	3.7592005
H	1.9337806	6.3147727	4.8771338
H	1.5700720	-1.0150534	5.2113811
C	1.1493687	-1.3799299	4.2776195
C	0.8818733	-0.4893625	3.2377272
C	0.3308001	-0.9317853	2.0230552
C	0.0525522	-2.3044648	1.8889822
H	-0.4100033	-2.6748769	0.9773976
C	0.3179953	-3.1978178	2.9239697
H	0.0767616	-4.2504672	2.8046571
C	0.8678001	-2.7372733	4.1216287
H	1.0661115	-3.4323464	4.9331104
H	1.0851810	0.5710928	3.3757210
H	-3.6772645	-4.0095318	3.8830320
C	-3.5135927	-3.1104976	3.2941741
C	-3.7054768	-3.1314207	1.9114946
H	-4.0239833	-4.0487663	1.4209574
C	-3.4892708	-1.9761486	1.1582986
H	-3.6375415	-2.0103824	0.0803473
C	-3.0807587	-0.7730592	1.7607591
C	-2.9046220	-0.7768796	3.1538861
H	-2.5845339	0.1398643	3.6472559
C	-3.1126358	-1.9266643	3.9153424
H	-2.9578799	-1.9028059	4.9915064
H	-2.1114437	0.6949153	-2.2596010
C	-3.1839609	0.6363448	-2.0939831
C	-4.0464775	0.5835017	-3.1882492
H	-3.6446263	0.5862874	-4.1986111
C	-5.4278073	0.5378525	-2.9850181
H	-6.1041179	0.5142060	-3.8355566
C	-5.9355097	0.5147150	-1.6853199
H	-7.0096681	0.4745090	-1.5219554
C	-5.0641685	0.5364812	-0.5950003
H	-5.4683098	0.4930974	0.4139813
C	-3.6747237	0.6204202	-0.7789456
H	1.8614418	-1.7530559	-0.2163459
C	1.7190449	-1.0502883	-1.0338173
C	0.8021057	0.0042853	-0.8894034
C	0.6527936	0.9020796	-1.9634376
H	-0.0502836	1.7262266	-1.8663541
C	1.3868962	0.7511731	-3.1380686
H	1.2526254	1.4553317	-3.9554991
C	2.2911569	-0.3065468	-3.2649636
H	2.8634970	-0.4290181	-4.1805720
C	2.4549621	-1.2056354	-2.2102776
H	3.1580198	-2.0296158	-2.3031924
P	-2.5459905	2.5725394	2.0371655
C	-1.9033495	2.8521009	0.2279778
C	-2.2984586	4.0692332	-0.5944901
C	-3.8097298	4.0329466	-0.9013738
H	-4.0707745	3.1513736	-1.4900631
H	-4.1037553	4.9294955	-1.4615666
H	-4.3820783	4.0029918	0.0324542
C	-1.9945801	5.3824886	0.1544172
H	-2.3298837	6.2556820	-0.4210456
H	-0.9161384	5.4785619	0.3320671
H	-2.5142226	5.3870307	1.1194901
C	-1.5125608	4.0558797	-1.9176680
H	-1.7451600	3.1520006	-2.4890295
H	-0.4329300	4.0779544	-1.7211211
H	-1.7673612	4.9275120	-2.5335668

10.13. Cartesian coordinates of TS3

TS3
E(TPSS-D3/def2-TZVP) = -2716.946710219
(conv)
Lowest Freq. = -129.94 cm^-1

Si	-2.2144135	0.3959606	1.8737466
Si	-1.3657024	3.1991353	1.7232847
Si	-1.5323738	1.6631585	0.0316277
C	-1.0019130	5.0245487	1.9053401
N	-1.1282594	5.8654307	2.9765738
C	-0.6905137	7.1497451	2.6525462
C	-1.6688979	5.4765360	4.2744704
C	-0.2567998	7.1045656	1.3567621
N	-0.4409527	5.7936653	0.9193954
C	-0.1617260	5.3141744	-0.4328598
H	-1.0394587	5.8875434	5.0672071
H	-1.6784167	4.3840003	4.3239109
H	-2.6933361	5.8421349	4.3859464
H	-1.0139101	5.5034771	-1.0924665
H	0.0234901	4.2384801	-0.3917465
H	0.7260999	5.8189102	-0.8168143
C	-0.7363007	8.2744903	3.6276003
C	0.3148724	8.1665311	0.4828796
H	0.3204664	9.1206132	1.0139674
H	-0.2720882	8.2929534	-0.4341654
H	1.3472218	7.9396752	0.1902030
H	-1.7527763	8.4361393	4.0046819
H	-0.4023500	9.1972054	3.1483920
H	-0.0863956	8.0903455	4.4914913
H	3.5409539	1.7459043	-0.0706761
C	2.6466529	1.3234623	-0.5232294
C	1.3831931	1.7339731	-0.0951532
C	0.2046467	1.2149221	-0.6541194
C	0.3480284	0.2604574	-1.6789740
H	-0.5413400	-0.1582171	-2.1459948
C	1.6044123	-0.1642472	-2.1100934
H	1.6850662	-0.9103059	-2.8970871
C	2.7598175	0.3684429	-1.5339239
H	3.7398743	0.0424166	-1.8721752
H	1.3025701	2.4690810	0.7073934
H	1.7324725	-3.0762569	4.3083477
C	0.9865404	-2.4303453	3.8523619
C	-0.3539566	-2.8185370	3.8265354
H	-0.6536902	-3.7676161	4.2642515
C	-1.3094120	-1.9915839	3.2348282
H	-2.3498851	-2.3074649	3.2138231
C	-0.9477728	-0.7618725	2.6583894
C	0.4072618	-0.3893568	2.6975290
H	0.7132370	0.5526297	2.2499245
C	1.3663273	-1.2120234	3.2858738
H	2.4101338	-0.9080799	3.2962367
H	-2.6597732	-1.9559285	0.1745477
C	-3.6344160	-1.7041480	0.5887183
C	-4.7471814	-2.4575724	0.2181876
H	-4.6348101	-3.2882152	-0.4738264
C	-6.0064139	-2.1392232	0.7313121
H	-6.8768552	-2.7211326	0.4400112
C	-6.1419959	-1.0724234	1.6204949
H	-7.1194365	-0.8213571	2.0245588
C	-5.0231769	-0.3247049	1.9897252
H	-5.1388110	0.5069584	2.6800233
C	-3.7518178	-0.6201247	1.4777653
H	-0.9978540	2.7898465	-2.6841769
C	-2.0138594	2.4003675	-2.7034606

C	-2.5334355	1.7659034	-1.5629953
C	-3.8293342	1.2293076	-1.6386550
H	-4.2476162	0.7382467	-0.7654305
C	-4.5818085	1.3283908	-2.8072047
C	-4.0623672	1.9962756	-3.9195539
H	-4.6552540	2.0910779	-4.8255588
C	-2.7761306	2.5344844	-3.8654311
H	-2.3647825	3.0493165	-4.7303995
P	-2.8562151	2.2333626	0.0512278
C	-3.2230200	2.8282469	1.3186872
C	-4.3405393	3.8328688	1.0249218
C	-5.6743337	3.0612370	0.9254421
H	-5.6119626	2.2745708	0.1708276
H	-6.4932699	3.7422312	0.6594843
H	-5.9127048	2.5960790	1.8875336
C	-4.5034619	4.9105961	2.1167687
H	-5.3817066	5.5389004	1.9156524
H	-3.6229759	5.5614396	2.1421141
H	-4.6283701	4.4481233	3.1022924
C	-4.0764431	4.5516564	-0.3110193
H	-4.0027474	3.8446756	-1.1385477
H	-3.1366238	5.1140351	-0.2524622
H	-4.8848172	5.2616338	-0.5274269
H	-5.5773590	0.8937303	-2.8486586

10.14. Cartesian coordinates of TS4

TS4
E(TPSS-D3/def2-TZVP) = -2716.968502674
(conv)
Lowest Freq. = -77.75 cm^-1

Si	-2.3691357	0.1616579	1.2335008
Si	-0.5032018	2.1196122	2.0922740
Si	-0.1346538	0.3134030	0.5634487
C	-0.0449704	3.5626971	3.2474829
N	0.2006995	3.3643451	4.5793035
C	0.7367324	4.5037585	5.1673811
C	-0.0888468	2.1171375	5.2860498
C	0.8386548	5.4412523	4.1736267
N	0.3605312	4.8443456	3.0103857
C	0.2689023	5.5204845	1.7169887
H	-0.3019107	1.3500286	4.5346718
H	-0.9603195	2.2404829	5.9341668
H	0.7792039	1.8217002	5.8794743
H	-0.4601753	6.3330293	1.7757787
H	-0.0662666	4.7788759	0.9836598
H	1.2486357	5.9211491	1.4442535
C	1.0870154	4.5689515	6.6136758
C	1.3361406	6.8447023	4.2036528
H	1.6242865	7.1181672	5.2208232
H	0.5669391	7.5492037	3.8669696
H	2.2117982	6.9759832	3.5573586
H	0.2194660	4.3491616	7.2465143
H	1.4456294	5.5686423	6.8670321
H	1.8763481	3.8526803	6.8707787
H	3.2552032	-0.8673315	4.1921892
C	2.6408218	-1.2391663	3.3748643
C	1.8787496	-0.3522501	2.6117104
C	1.0889926	-0.7928417	1.5419108
C	1.0988128	-2.1709341	1.2547083
H	0.5074079	-2.5480298	0.4223605
C	1.8378606	-3.0688707	2.0243237
H	1.8085891	-4.1314141	1.7955273
C	2.6134400	-2.6047587	3.0888744
H	3.1937381	-3.3020877	3.6874326
H	1.8805422	0.7102048	2.8554718
H	-3.6358182	-2.9038137	5.9866428
C	-3.4023150	-2.3486107	5.0817549
C	-4.4105924	-2.0527105	4.1622609
H	-5.4311341	-2.3762841	4.3517927
C	-4.1074615	-1.3460520	2.9979513
H	-4.9009443	-1.1282070	2.2858595
C	-2.7976033	-0.9128373	2.7284620
C	-1.7965468	-1.2289844	3.6640053
H	-0.7708335	-0.9258393	3.4653973
C	-2.0918673	-1.9392558	4.8277582
H	-1.2986813	-2.1837100	5.5304939
H	-3.3421431	-2.4709440	0.3481241
C	-3.7139101	-1.7571303	-0.3842830
C	-4.4265883	-2.2246079	-1.4880869
H	-4.6054914	-3.2902956	-1.6068421
C	-4.9060276	-1.3246197	-2.4412401
H	-5.4603515	-1.6859714	-3.3034805
C	-4.6680976	0.0412315	-2.2815609
H	-5.0350773	0.7477748	-3.0219049
C	-3.9571009	0.5025923	-1.1738384
H	-3.7635123	1.5661483	-1.0691537
C	-3.4669069	-0.3844587	-0.1996337
H	2.4237640	-0.5876657	-0.7120182
C	1.7075822	-0.4532864	-1.5186224
C	0.4019928	-0.0261952	-1.2220193
C	-0.4964853	0.1252423	-2.2925628
H	-1.5045923	0.4751929	-2.0919626
C	-0.1175894	-0.1652077	-3.6003428
H	-0.8386364	-0.0618619	-4.4075122
C	1.1883577	-0.5804840	-3.8760415
H	1.4899827	-0.7938050	-4.8984289
C	2.1026765	-0.7158569	-2.8322405
H	3.1224957	-1.0319702	-3.0382301
P	-1.2974659	2.5979947	0.0734925
C	-2.3462450	2.0117855	1.5771259
C	-3.4694810	2.8552919	2.2057854
C	-4.7984527	2.5779949	1.4770701
H	-4.7373044	2.8926838	0.4311124
H	-5.6180719	3.1285794	1.9554812
H	-5.0440167	1.5110198	1.4963823
C	-3.6315278	2.4648717	3.6881909
H	-4.4766582	3.0000945	4.1394564
H	-2.7237884	2.7229374	4.2452527
H	-3.8020250	1.3903733	3.7984746
C	-3.1830088	4.3632793	2.1209835
H	-2.9987734	4.6648005	1.0845889
H	-2.3052913	4.6255003	2.7208084
H	-4.0363481	4.9338383	2.5079880

10.15 Cartesian coordinates of Int-5

Int-5
E(TPSS-D3/def2-TZVP) = -2333.180756727
(conv)
Lowest Freq. = 5.82 cm^-1
Int 5 (014/c1/tpss-d3.def2-TZVP)

Si	-0.9033896	1.3443983	0.2110211
Si	-0.8954523	-0.7676400	1.0648923
Si	0.2500140	0.9665135	2.3425764
C	-4.8191855	3.8767048	0.6720560
C	-4.3513698	3.1098537	1.7419323
H	-4.9020779	3.0872309	2.6785201
C	-3.1757394	2.3750781	1.6121406
C	-2.4469767	2.3826568	0.4089864
C	-2.4275048	-1.1646954	2.0799775
C	-3.6981464	-1.1484993	1.4776833
C	-4.8472820	-1.4145983	2.2203488
H	-5.8212331	-1.3904799	1.7390310
C	-4.7469107	-1.7012438	3.5829964
C	1.4267899	2.2505048	-3.7606333
C	1.5909766	3.0811227	-2.6498918
H	2.2661735	3.9311641	-2.7009850
C	0.8967044	2.8145590	-1.4714867
C	0.0186586	1.7196886	-1.3804337
C	-0.1397949	0.9000170	-2.5111200
C	0.5600107	1.1596820	-3.6901816
H	0.4290132	0.5109055	-4.5521219
C	-0.1241378	-2.2816531	0.2866855
C	0.7792352	-2.1905868	-0.7878861
C	1.3468868	-3.3355078	-1.3429276
H	2.0378384	-3.2459295	-2.1774789
C	1.0255284	-4.5956982	-0.8347083
C	0.1281229	-4.7042392	0.2287716
H	-0.1297013	-5.6824489	0.6260074
C	-0.4423907	-3.5589186	0.7829589
C	-2.3475885	-1.4482792	3.4542483
C	-3.4952174	-1.7186705	4.1999609
H	-3.4141437	-1.9352100	5.2618642

C	-4.1043690	3.9034441	-0.5259335
H	-4.4615619	4.5019883	-1.3599469
C	-2.9301676	3.1615823	-0.6571792
P	2.0012681	0.5685872	1.0316385
C	3.3341919	0.1475742	0.3723499
C	4.5265704	-0.1955007	-0.4093981
H	-5.6427251	-1.9034289	4.1639255
H	-1.3765622	-1.4463822	3.9446102
H	-3.7864509	-0.9079655	0.4210067
H	-1.1455819	-3.6556105	1.6067485
H	1.4682726	-5.4882062	-1.2683109
H	1.0350694	-1.2169220	-1.1944617
H	-2.3812974	3.1878231	-1.5956196
H	-5.7343841	4.4534574	0.7741376
H	-2.8234014	1.7850565	2.4554524
H	1.0443264	3.4564934	-0.6061736
H	-0.8124274	0.0471488	-2.4628855
H	1.9741879	2.4528927	-4.6772087
C	4.9593252	-1.6403606	-0.0605255
H	4.1517713	-2.3451969	-0.2763037
H	5.2150675	-1.7204560	0.9998440
H	5.8383511	-1.9125374	-0.6563326
C	4.1853599	-0.1017627	-1.9171643
H	3.8499417	0.9057859	-2.1750393
H	3.3882939	-0.8041877	-2.1744881
H	5.0750430	-0.3459362	-2.5094345
C	5.6692427	0.7919271	-0.0732639
H	5.3763246	1.8163019	-0.3205791
H	6.5617502	0.5304849	-0.6533901
H	5.9168610	0.7481244	0.9911211