Supporting Information

Facile Rotation around a Silicon-Phosphorus Double Bond Enabled through Coordination to Tungsten

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1 Experimental Details

1.1 General Considerations

All experiments and manipulations were carried out under dry oxygen-free atmosphere using standard Schlenk techniques or in an MBraun inert atmosphere dry box containing an atmosphere of purified nitrogen. Solvents were dried using an M Braun purification system and stored over 3 Å molecular sieves. Hexacarbonyltungsten (Merck, 98%) was sublimed prior to use. The starting materials, phosphasilene **1**[1] and phosphinosilylene **4**[2], were prepared according to the literature. The deuterated solvents were degassed by freeze-pump-thaw technique and stored over 3 Å molecular sieves. The ^{1}H, $^{13}C\{^{1}H\}$, $^{29}Si\{^{1}H\}$, and $^{31}P\{^{1}H\}$ spectra were recorded on Bruker Avance II 200 MHz, 400 MHz, Bruker Avance III 500 MHz and Bruker Avance 400 MHz Solid State Spectrometers. ^{1}H chemical shifts were referenced to the residual protons of C_6D_6 at 7.15 ppm and the residual methyl-protons of toluene-d_8 at 2.14 ppm. ^{13}C chemical shifts were referenced to the carbon atoms of C_6D_6 at 128.00 ppm and the methyl-carbons of toluene-d_8 at 20.4 ppm. The $^{29}Si\{^{1}H\}$ NMR spectra were referenced to tetramethylsilane as an external standard and $^{31}P\{^{1}H\}$ NMR spectra were externally calibrated with H_3PO_4 in sealed capillaries. Melting points were determined from vacuum sealed capillaries on an electronic "Melting point tester" device from BSGT company and are uncorrected. For this purpose samples were sealed off in capillaries under vacuum and heated slowly to observed decomposition or melting. High resolution mass spectra were recorded on an Orbitrap LTQ XL of Thermo Scientific mass spectrometer. Elemental analysis was conducted on a Thermo Finnigan Flash EA 1112 series. IR spectra were recorded on a PerkinElmer Spectrum 100 FTIR. The UV/Vis spectrum was recorded with an Analytik Jena Specord S600 Spectrometer in 10 mm quartz cuvettes.

Single-Crystal X-ray Structure Determinations. Crystals were mounted on a glass capillary in perfluorinated oil and measured in a cold N_2 flow. The data of compounds **2** and **3** was collected on an Oxford Diffraction SuperNova at 150 K (Cu-Kα radiation, λ = 1.5418 Å). The structures were solved by direct methods or Patterson and refined on F2 with the SHELX-97[3] software package. The positions of the hydrogen atoms were calculated and considered isotropically according to a riding model.

1.2 Synthesis of **2**

Preparation of LSi(TMS)P(TMS)(W{CO}$_5$), 2. Three times a solution of $W(CO)_6$ (242 mg, 0.69 mmol) in thf (10 mL) was treated for two hours with UV-light to give $W(CO)_5$·thf in situ. These solutions were subsequently added to a solution of **2** (300 mg, 0.69 mmol) in thf (10 mL) at -50 °C. The reaction mixture was stirred at r.t. for 16 h. Volatiles were removed under vacuum. The residue was washed with hexane (6 mL) and cooled to -30 °C, when the hexane solution was removed. The unreacted $W(CO)_6$ was removed by sublimation at 60 °C under vacuum. The resulting yellow solid is product **2** (482 mg, 92%). Single crystals of **2** were obtained from hexane at -28 °C.

Mp 147 °C (decomposition, presumably **3** formed before decomposition of **2**).

NMR data of **2** at 298 K: ^{1}H NMR (200.13 MHz, C_6D_6, 298 K): δ = 0.37 (s, 9 H, SiTMS), 0.60 (d, $^3J_{P-H}$ = 5.3 Hz, 9 H, PTMS), 1.07 (s, 18 H, *t*Bu), 6.7-7.1 (m, 4 H, Ph), 7.50 (m, 1 H, Ph) ppm. ^{13}C{^{1}H} NMR (125.76 MHz, C_6D_6, 298 K): δ = 0.9 (SiTMS), 6.4 (d, $^2J_{C-P}$ = 12.5 Hz, PTMS), 31.8 (C*Me*$_3$), 55.6 (*C*Me$_3$), 128.5, 128.6, 130.7, 130.9 (Ph), 201.0 (CO) ppm. ^{29}Si{^{1}H} NMR (DEPT, J = 5 Hz, 79.49 MHz, C_6D_6, 298 K): δ = -13.1 (d, $^2J_{Si-P}$ = 9.0 Hz, SiTMS), 8.8 (d, $^1J_{Si-P}$ = 15.8 Hz, PTMS) ppm.

NMR data of (*E*)-**2**: ^{1}H NMR (500.25 MHz, toluene-d_8, 213 K): δ = 0.40 (s, 9 H, SiTMS), 0.67 (d, $^3J_{P-H}$ = 5.2 Hz, 9 H, PTMS), 1.13 (s, 18 H, *t*Bu), 6.8-7.2 (m, 4 H, Ph, overlapping with toluene-d$_8$), 7.62 (m, 1 H, Ph) ppm. ^{13}C{^{1}H} NMR (125.79 MHz, toluene-d_8, 213 K): δ = 0.5 (SiTMS), 6.5 (d, $^2J_{C-P}$ = 12.3 Hz, PTMS), 31.3 (C*Me*$_3$), 55.2 (*C*Me$_3$), 172.3 (NCN), 201.0 (CO) ppm. ^{29}Si{^{1}H} NMR (99.39 MHz, toluene-d_8, 213 K): δ = -12.8 (s, SiTMS), 8.9 (d, $^1J_{P-Si}$ = 15.7 Hz, PTMS), 49.8 (d, $^1J_{Si-P}$ = 106 Hz, Si=P) ppm. ^{31}P{^{1}H} NMR (202.50 MHz, toluene-d_8, 213 K): δ = -282.0 (s with satellite: $^1J_{P-W}$ = 123 Hz) ppm.

NMR data of (*Z*)-**2**: ^{1}H NMR (500.25 MHz, toluene-d_8, 213 K): δ = 0.55 (s, 9 H, SiTMS), 0.75 (d, $^3J_{P-H}$ = 5.2 Hz, 9H, PTMS), 1.01 (s, 18 H, *t*Bu), 6.8-7.2 (m, 4 H, Ph, overlapping with toluene-d_8), 7.21 (m, 1 H, Ph) ppm. ^{13}C{^{1}H} NMR (125.79 MHz, toluene-d_8, 213 K): 0.3 (SiTMS), 5.5 (d, $^2J_{C-P}$ = 11.0 Hz, PTMS), 31.4 (C*Me*$_3$), 55.2 (*C*Me$_3$), 172.3 (NCN), 200.3 (CO) ppm. ^{29}Si{^{1}H} NMR (99.39 MHz, toluene-d_8, 213 K): δ = -13.3 (SiTMS), 8.4 (d, $^1J_{Si-P}$ = 18.8 Hz, PTMS), 45.9 (d, $^1J_{Si-P}$ = 106 Hz, Si=P) ppm. ^{31}P{^{1}H} NMR (202.50 MHz, toluene-d_8, 213 K): δ = -304.3 (s with satellite: $^1J_{P-W}$ = 128 Hz) ppm.

Solid state NMR data of **2**: ^{29}Si{^{1}H} NMR (79.44 MHz, 298 K): δ = -14.1 (SiTMS), 5.9 (PTMS), 47.7 (d, $^1J_{Si-P}$ = 97.6 Hz, Si=P) ppm. ^{31}P{^{1}H} NMR (161.87 MHz, 298 K): δ = -279.3 ppm.

UV/Vis(hexane): λ_{max} (ε) = 354 nm (5800 L mol^{-1} cm^{-1}). IR (KBr): ν = 2054 (CO), 1916 (s, CO), 1904 (CO), 1872 (CO) cm^{-1}. HRMS (APCI, toluene, *m*/*z*): calculated for $C_{25}H_{41}N_2O_4PSi_3W$ [MH$^+$-CO]: 733.1694, found: 733.1682. Elemental analysis calcd. for $C_{26}H_{41}N_2O_5PSi_3W$: C 41.05, H 5.43, N 3.68; found: C 40.16, H 5.26, N 3.42.

Note: The $^{13}C\{^1H\}$ NMR signals of the phenyl-carbon atoms could not be assigned based on the strong overlap with the toluene-d_8 carbon signals. Presumably the excess tungsten carbonyl was only needed, because with the set up of our UV lamp did not achieve a quantitative formation of $W(CO)_5$·thf from $W(CO)_6$.

1.3 Synthesis of **3**

Preparation of LSi(W{CO}$_5$)P(TMS)$_2$, 3. Hexane (20 mL) was added to LSiCl (302 mg, 1.02 mmol) and LiP(TMS)$_2$·dimethoxyethane (289 mg, 1.04 mmol) at 0 °C. The reaction mixture was stirred for 1.5 h at r.t. and the solution was filtered. A solution of $W(CO)_6$ (352 mg, 1.00 mmol) in thf (15 mL) was treated for 2 h with UV light. The resulting $W(CO)_5$·thf solution was added to the first solution at -40 °C. After 30 min, the cold bath was removed and the reaction mixture was stirred at r.t. for 30 min. Volatiles were removed under vacuum. The product was extracted with hexane (20 mL) and the amount of solvent was reduced under vacuum. At -28 °C a light yellow colored solid of **3** (219 mg, 29%) was obtained. Single crystals of **3** were grown from hexane at -28 °C.

Mp 147-148 °C (decomposition). ^{1}H NMR (200.13 MHz, C_6D_6, 298 K): δ = 0.51 (d, $^3J_{P-H}$ = 4.2 Hz, 18 H, TMS) 1.23 (s, 18 H, *t*Bu), 6.8-7.0 (m, 3 H, Ph), 7.2-7.5 (m, 2 H, Ph) ppm. ^{13}C NMR (100.61 MHz, C_6D_6, 298 K): δ = 5.3 (d, $^2J_{C-P}$ = 11.5 Hz, TMS), 31.5 (C*Me*$_3$), 55.5 (*C*Me$_3$), 130.4, 130.5, 131.9 (Ar), 167.1 (NCN), 202.0 (CO) ppm. ^{29}Si$\{^1H\}$ NMR (79.49 MHz, C_6D_6, 298 K): δ = 4.1 (d, $^1J_{Si-P}$ = 21.5 Hz, TMS), 70.7 (d, $^1J_{P-Si}$ = 134 Hz, satellite $^1J_{Si-W}$ = 137 Hz, LSi) ppm. ^{31}P NMR (161.97 MHz, C_6D_6, 298 K): δ = -199.4 (s with satellites: $^2J_{P-W}$ = 23 Hz, $^1J_{P-Si}$ = 134 Hz) ppm. IR (KBr): ν = 2054 (s, CO), 1918 (s, CO), 1905 (shoulder, CO) cm^{-1}. HRMS (APCI, toluene, m/z): calcd for $C_{26}H_{42}N_2O_5PSi_3W^+$ (MH$^+$), 761.1643; found, 761.1664. Elemental analysis calcd. for $C_{26}H_{41}N_2O_5PSi_3W$: C 41.05, H 5.43, N 3.68; found: C 41.06, H 5.37, N 3.53.

2. Spectral Data of Compounds 1, 2 and 3

2.1 NMR Spectra of **1** at Variable Temperatures

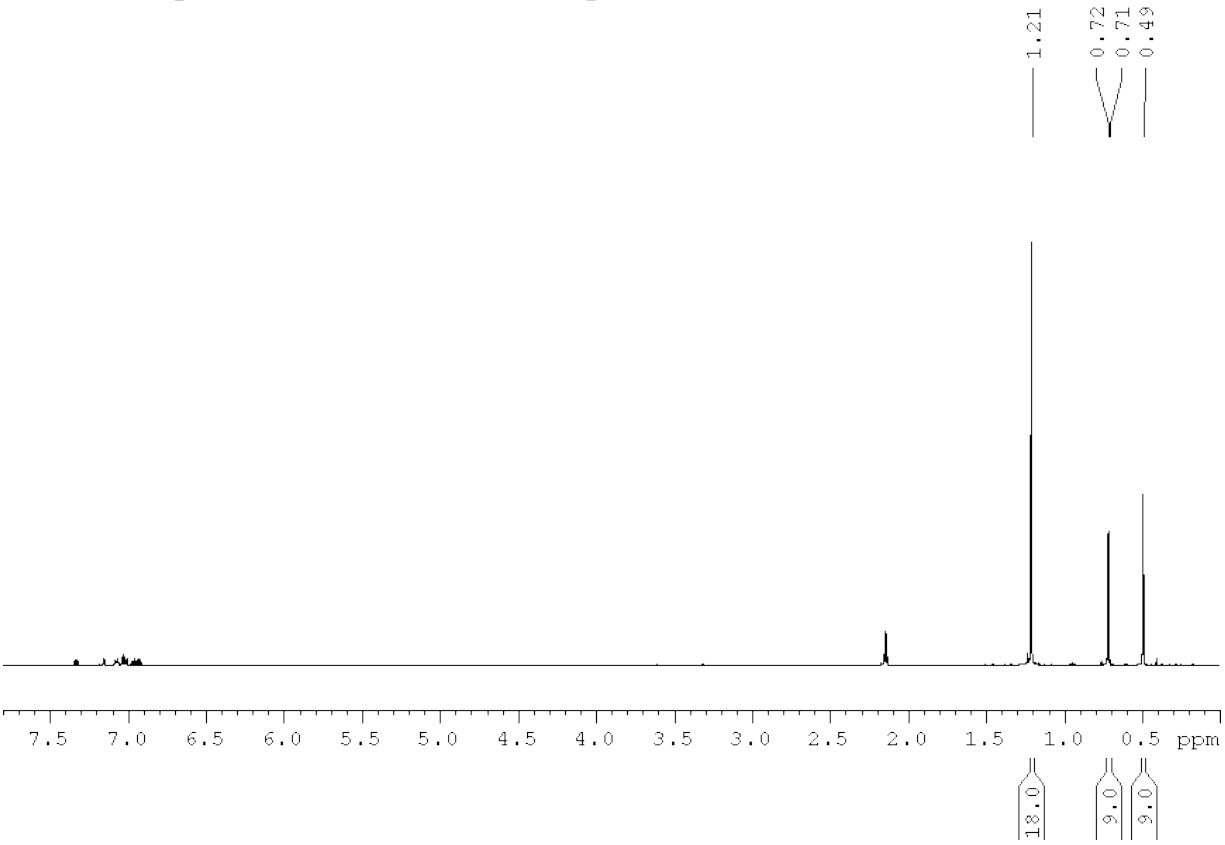

Figure S1. ^{1}H NMR spectrum of compound **1** in toluene-d_8 at r.t.

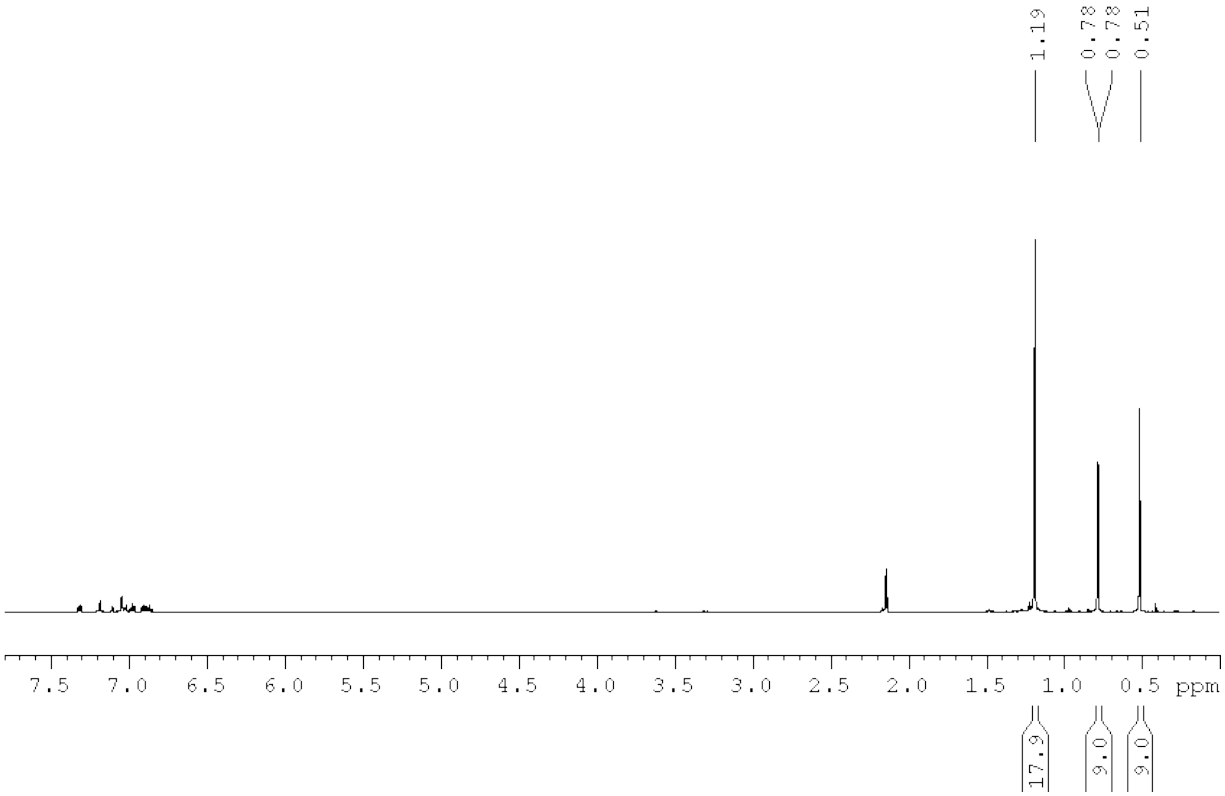

Figure S2. ^{1}H NMR spectrum of compound **1** in toluene-d_8 at -20 °C.

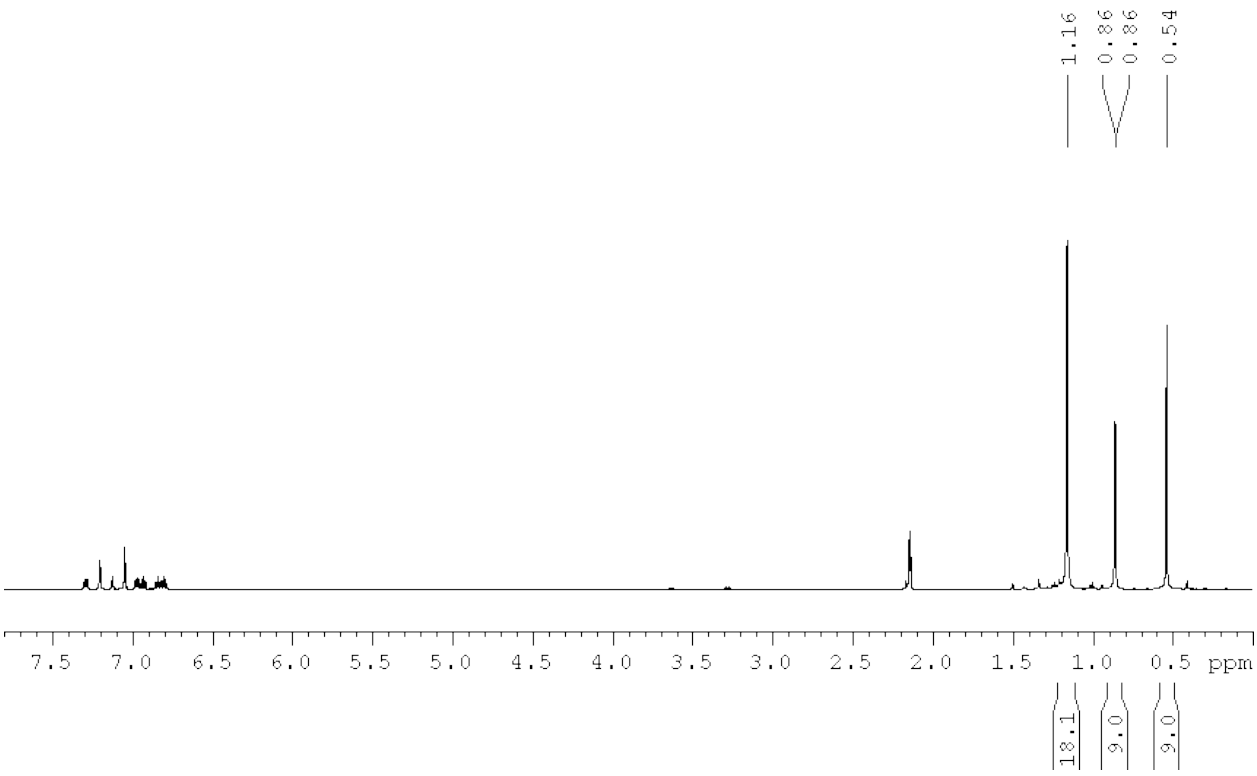

Figure S3. ^{1}H NMR spectrum of compound **1** in toluene-d_8 at -60 °C.

2.2 NMR Spectra of **2** at Room Temperature in C_6D_6

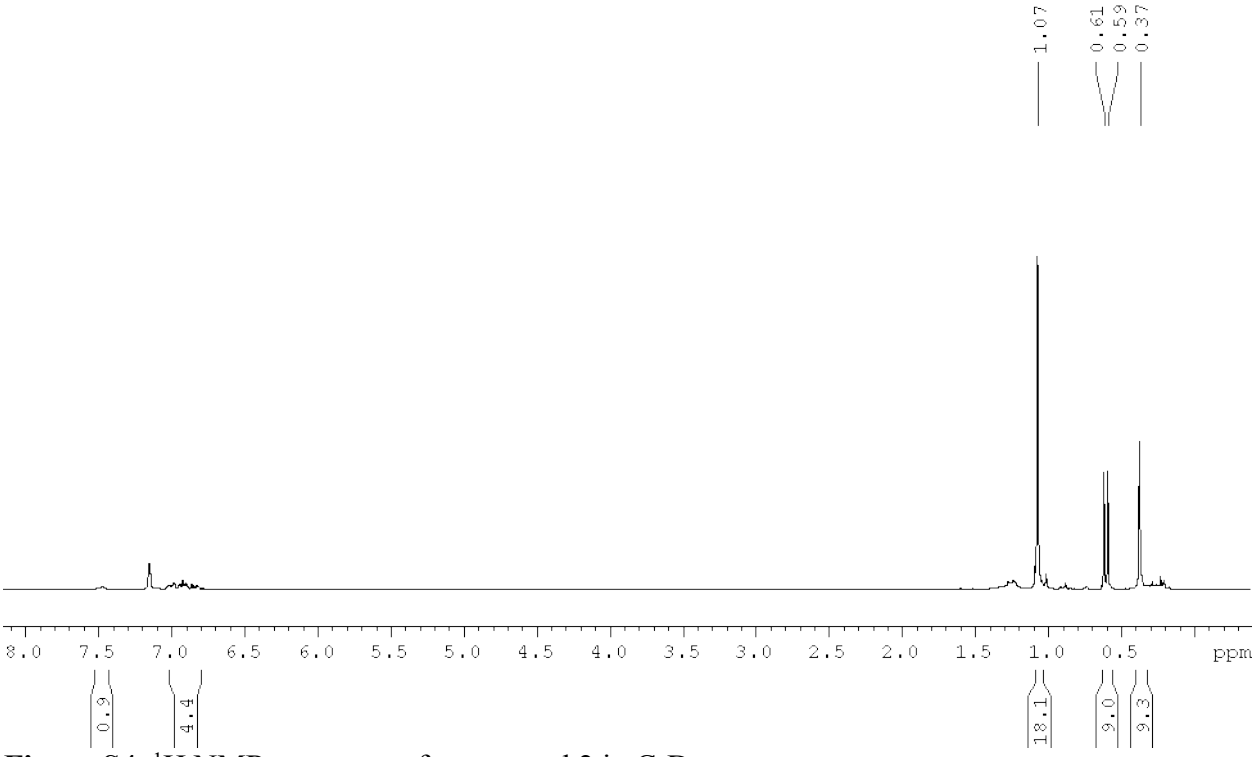

Figure S4. ^{1}H NMR spectrum of compound **2** in C_6D_6 at r.t.

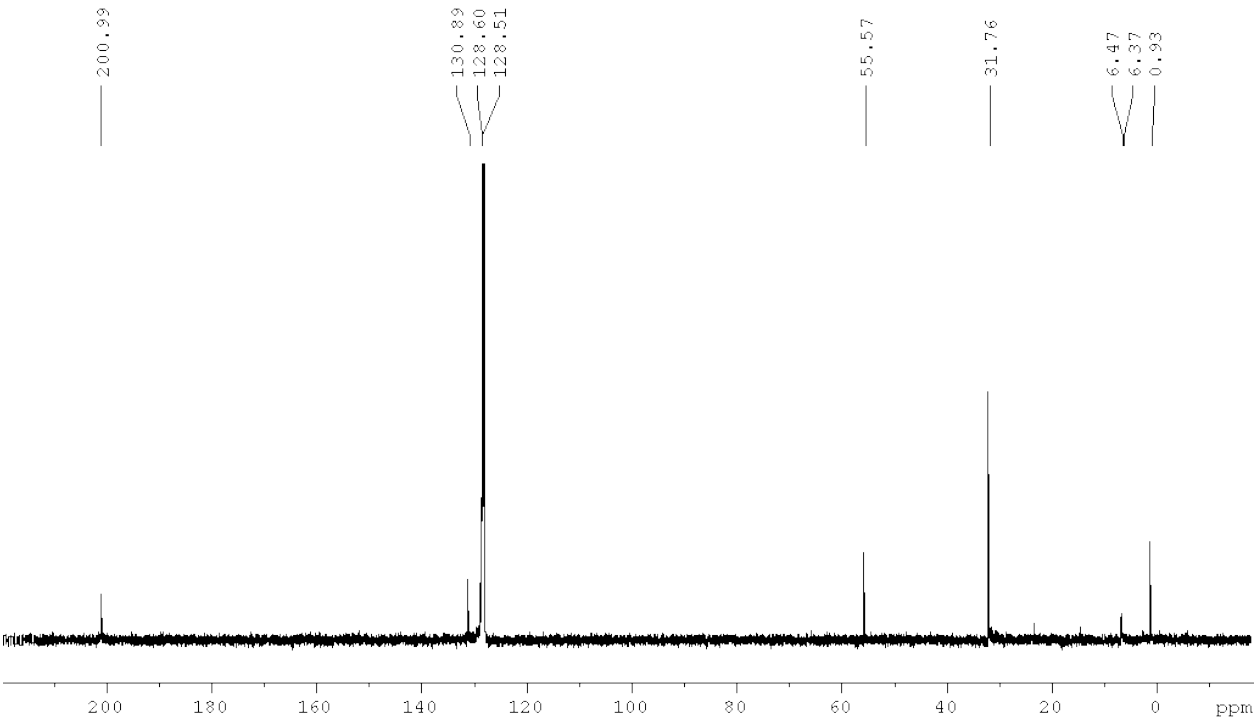

Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2** in C_6D_6 at r.t.

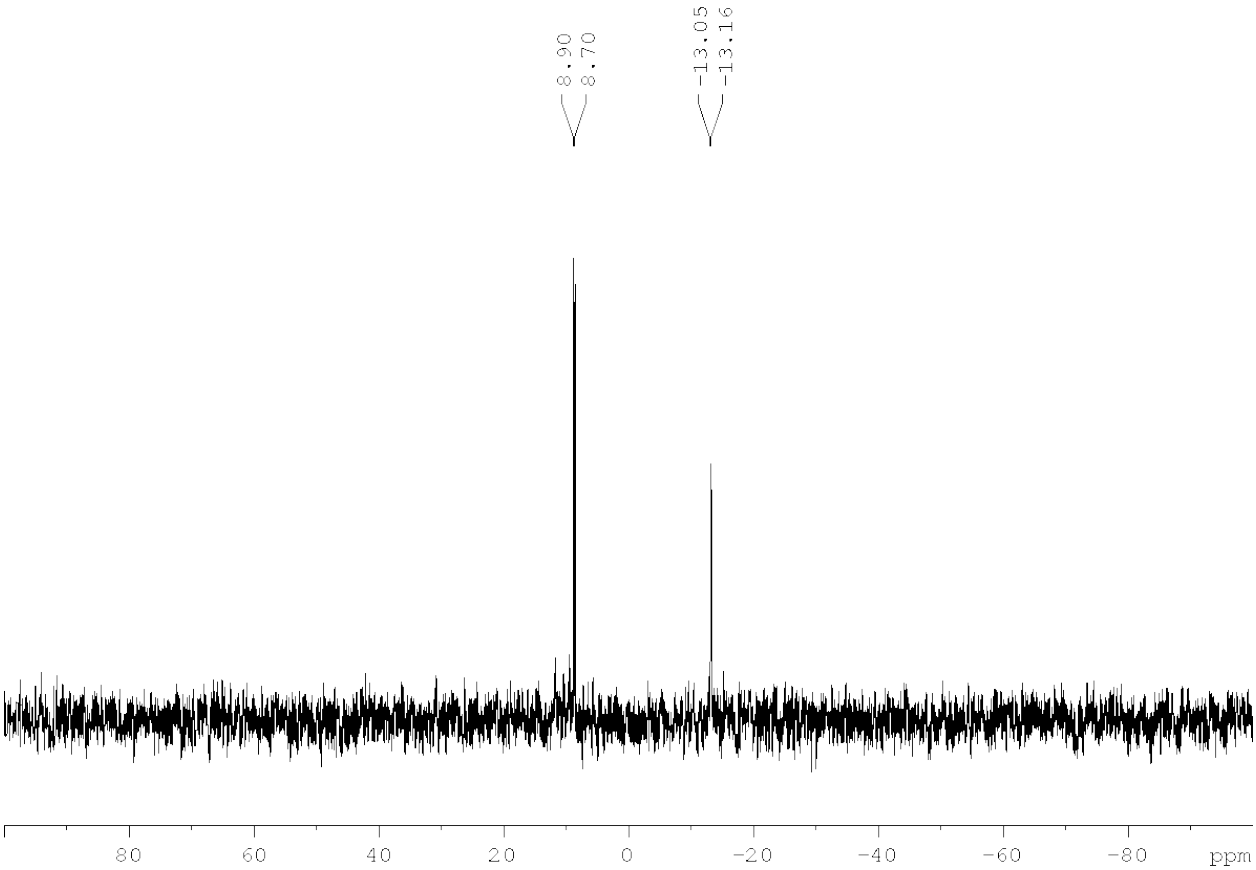

Figure S6. $^{29}Si\{^{1}H\}$ DEPT spectrum of **2** in C_6D_6 at r.t.

2.3 NMR Spectra of **2** at Variable Temperatures in Toluene-d_8

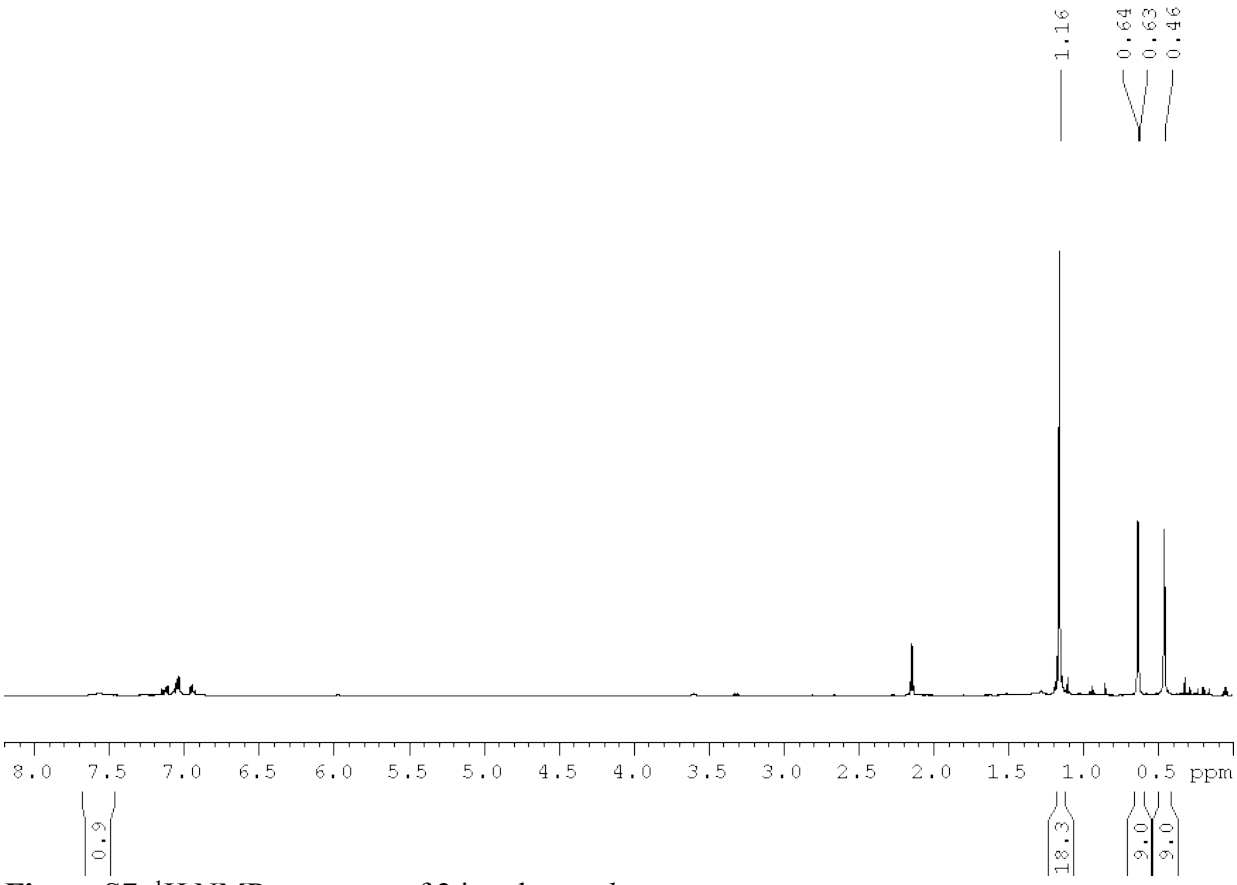

Figure S7. ^{1}H NMR spectrum of **2** in toluene-d_8 at r.t..

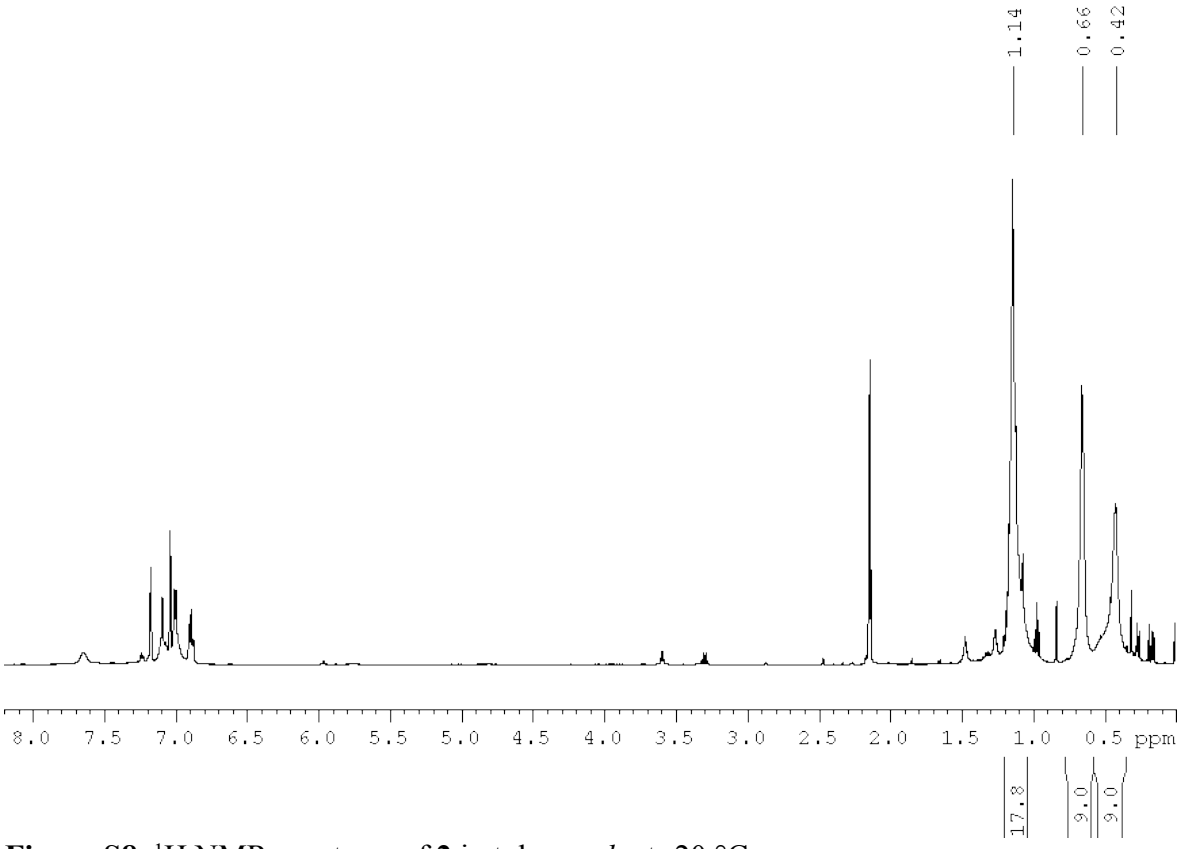

Figure S8. ^{1}H NMR spectrum of **2** in toluene-d_8 at -20 °C

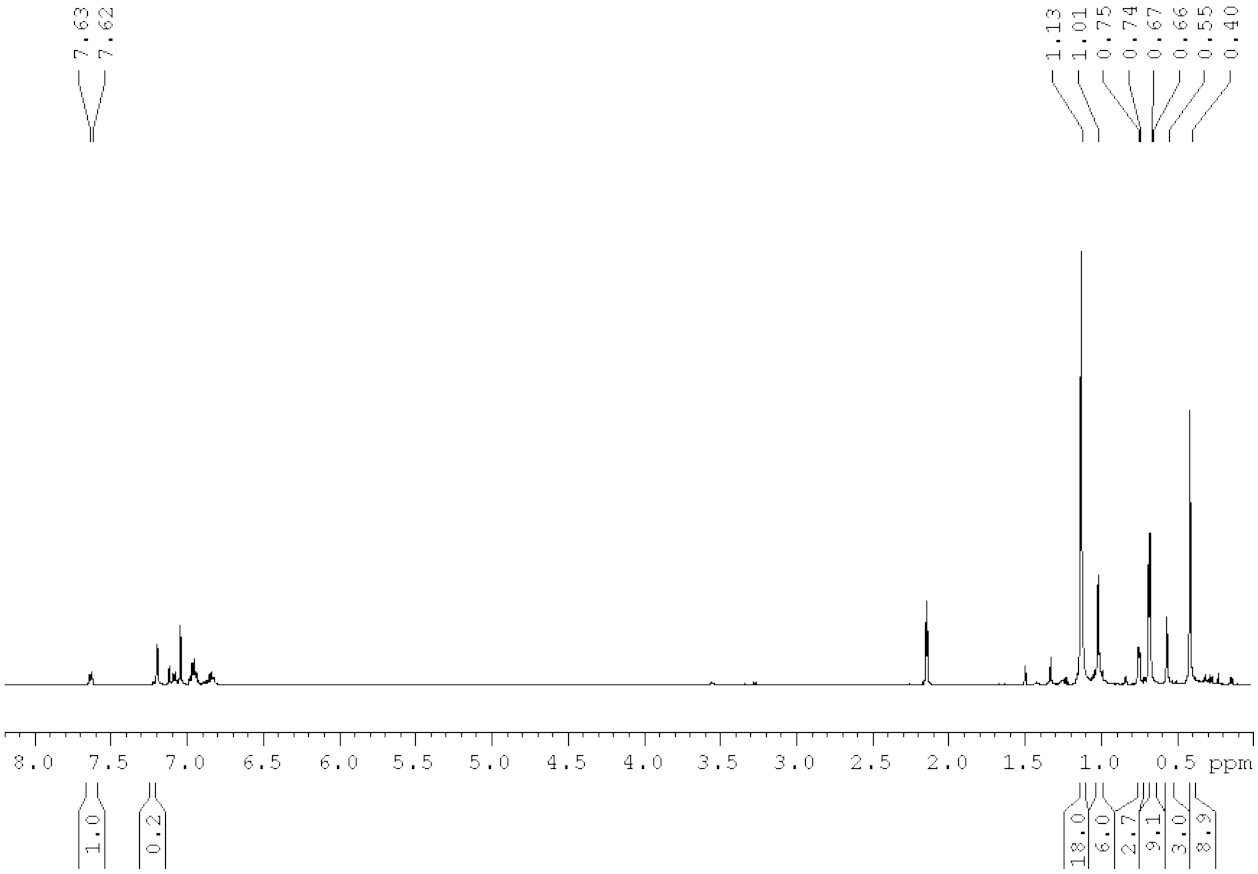

Figure S9. ^{1}H NMR spectrum of **2** in toluene-d_8 at -60 °C.

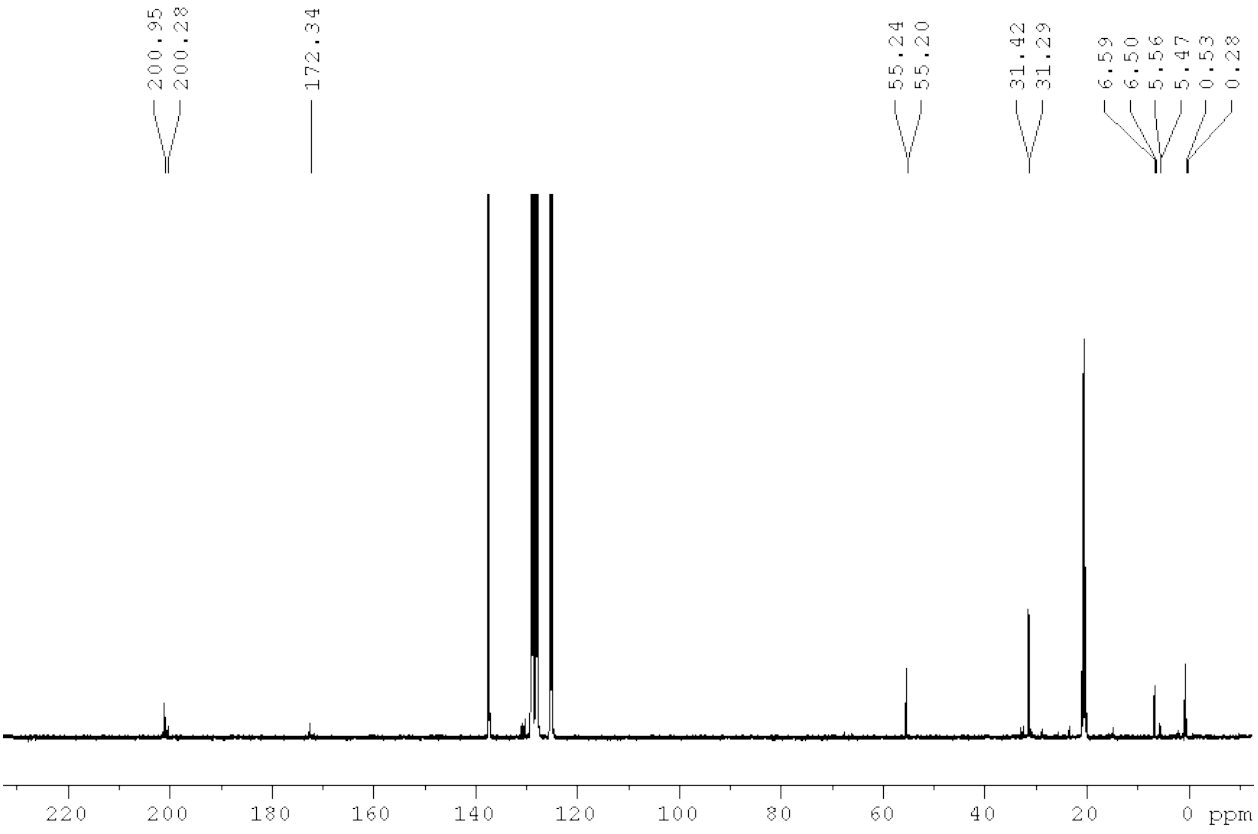

Figure S10. ^{13}C{^{1}H} NMR spectrum of **2** in toluene-d_8 at -60 °C.

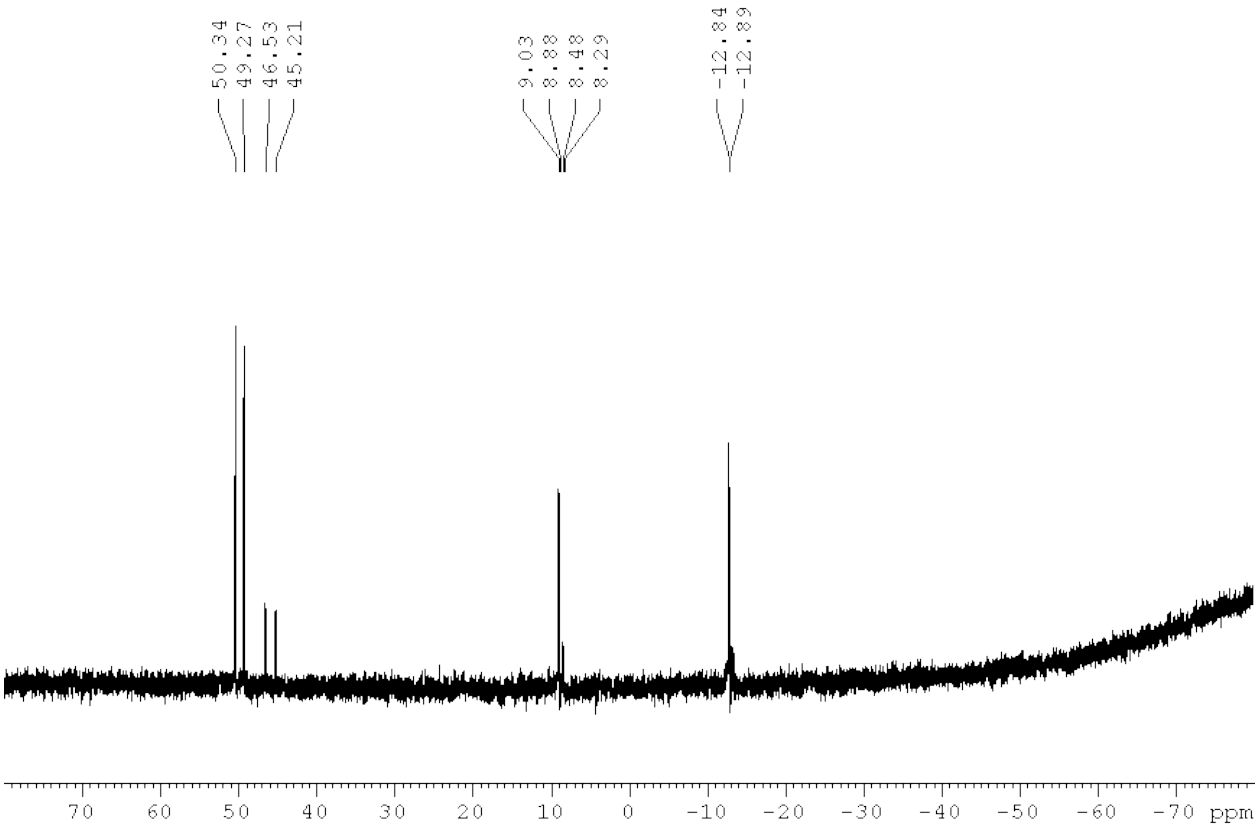

Figure S11. $^{29}Si\{^{1}H\}$ NMR spectrum of **2** in toluene-d_8 at -60 °C

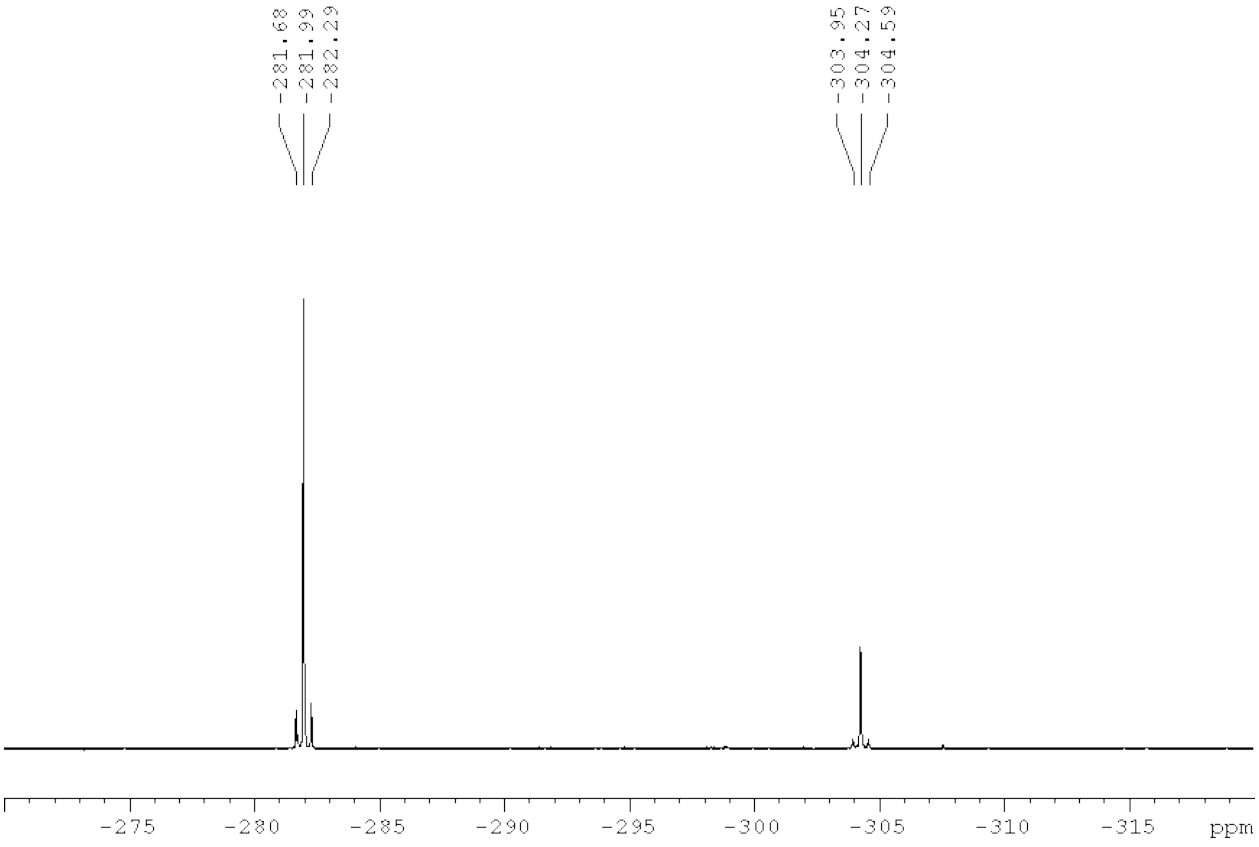

Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum of **2** in toluene-d_8 at -60 °C.

2.4 Solid State NMR Spectra of **2**

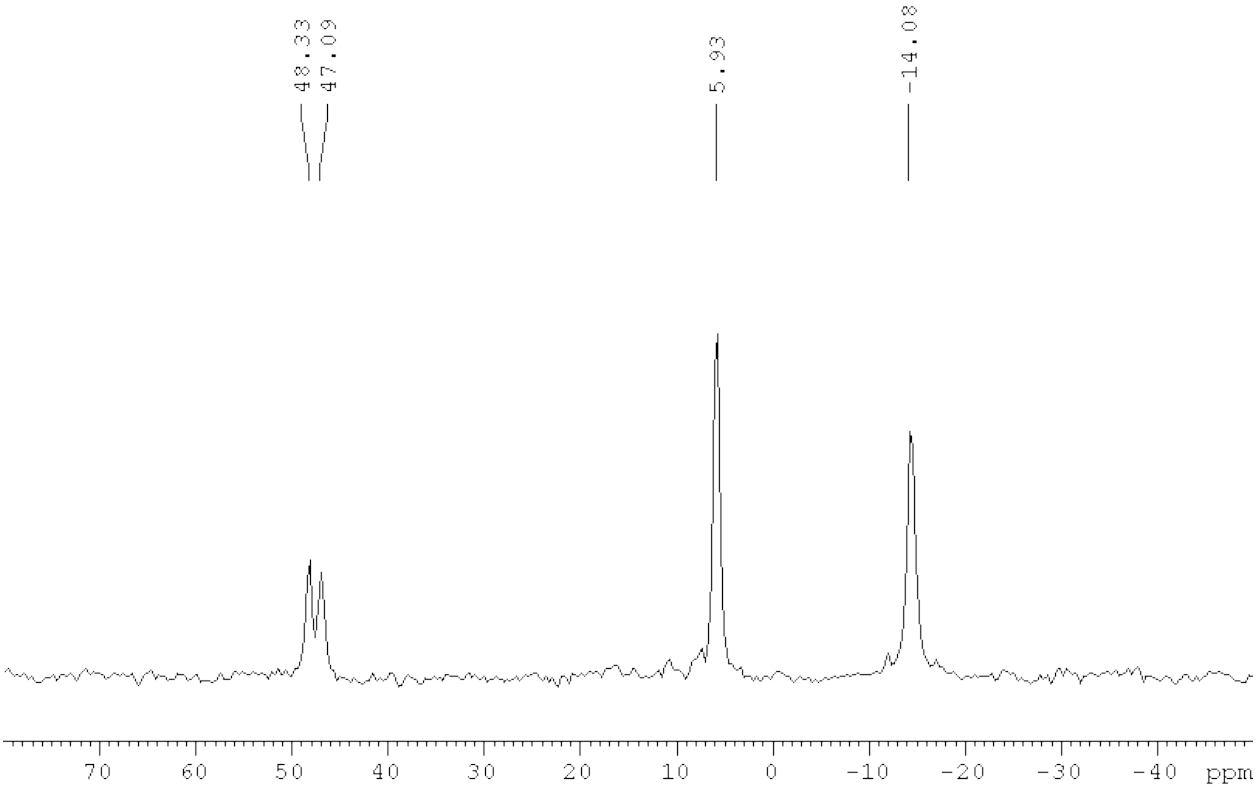

Figure S13. Solid state $^{29}Si\{^{1}H\}$ NMR spectrum of compound **2**.

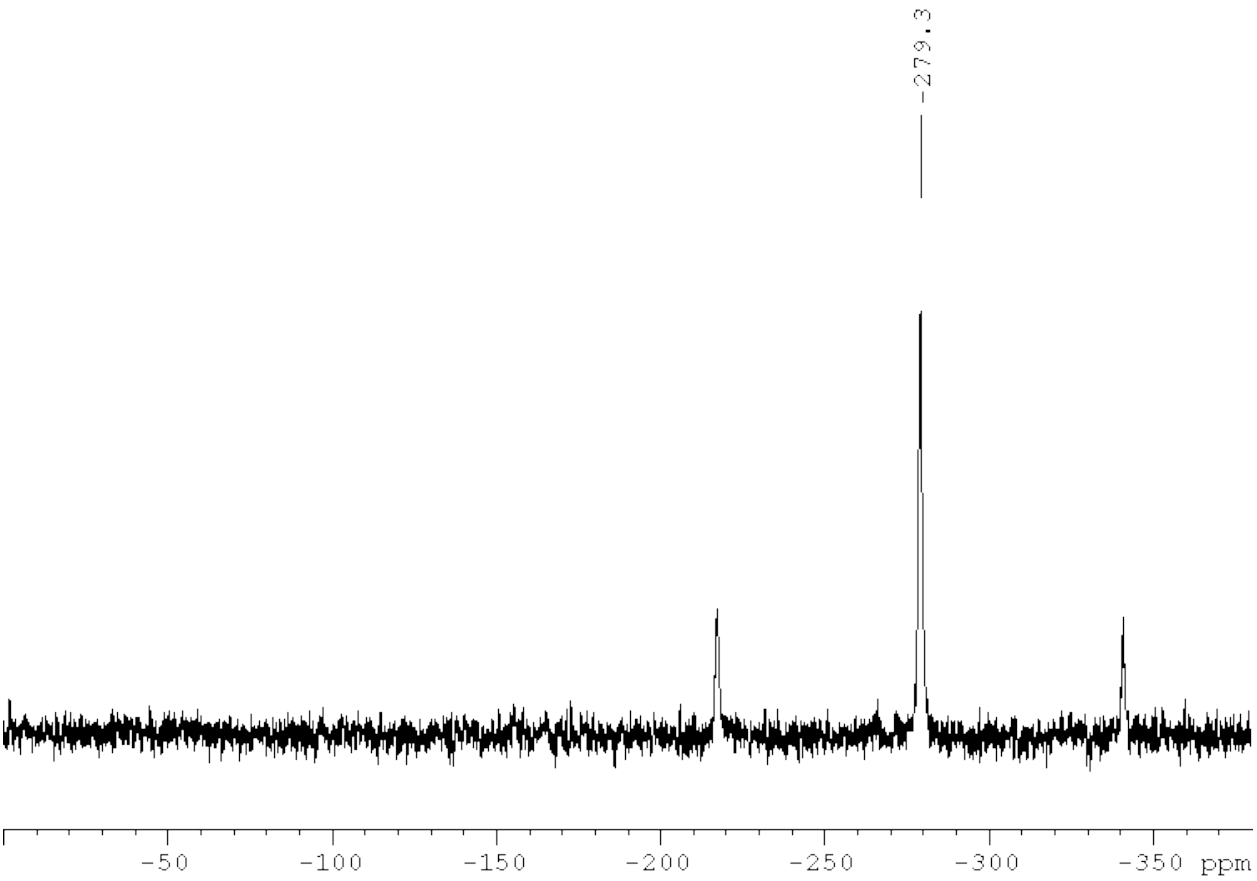

Figure S14. Solid state $^{31}P\{^{1}H\}$ NMR spectrum of compound **2**.

2.5 NMR Spectra of **3**

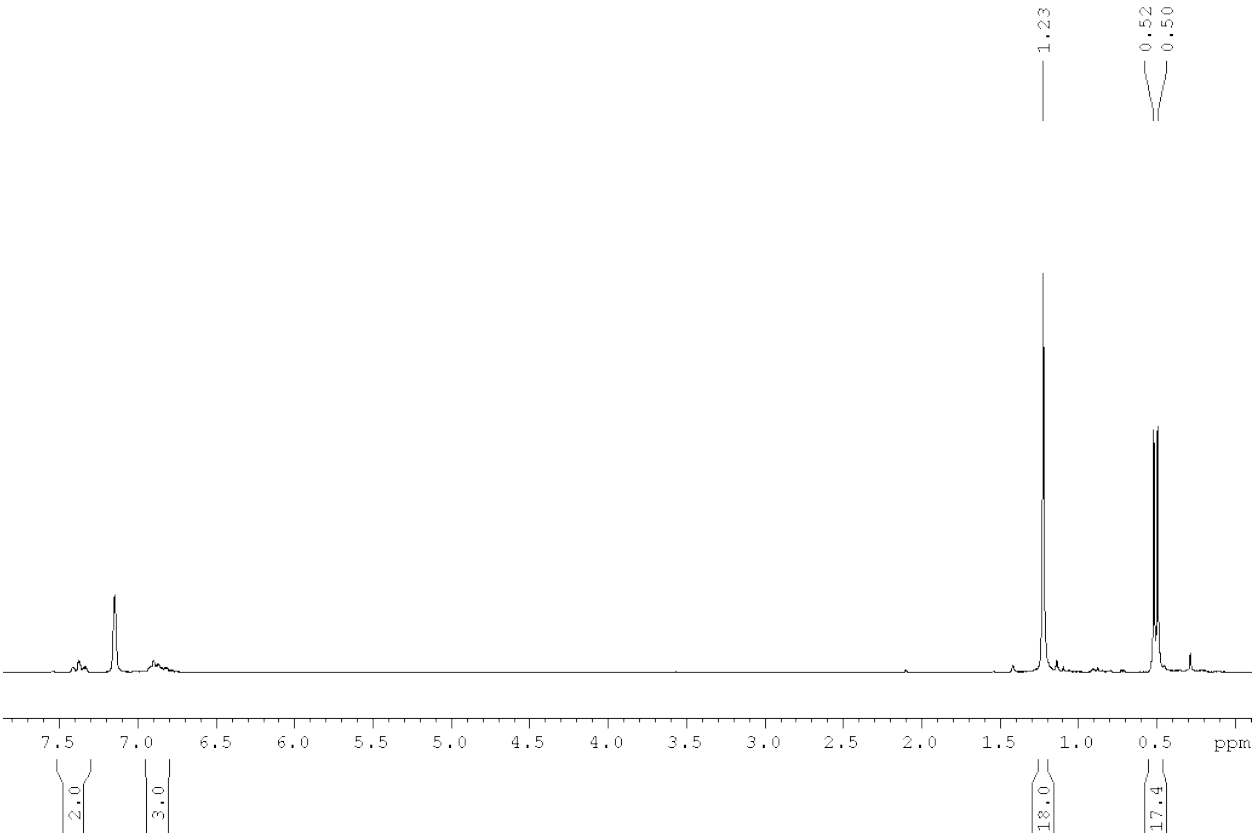

Figure S15. ^{1}H NMR spectrum of compound **3** in C_6D_6.

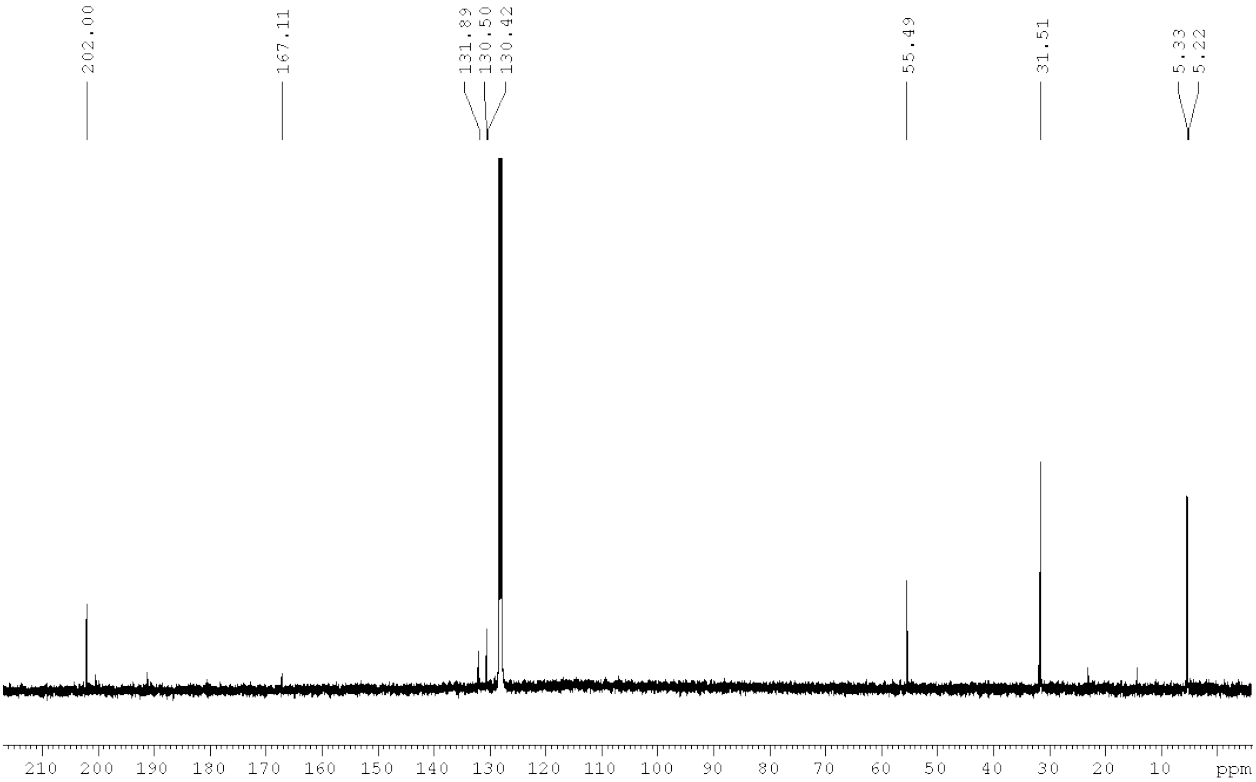

Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum for compound **3** in C_6D_6.

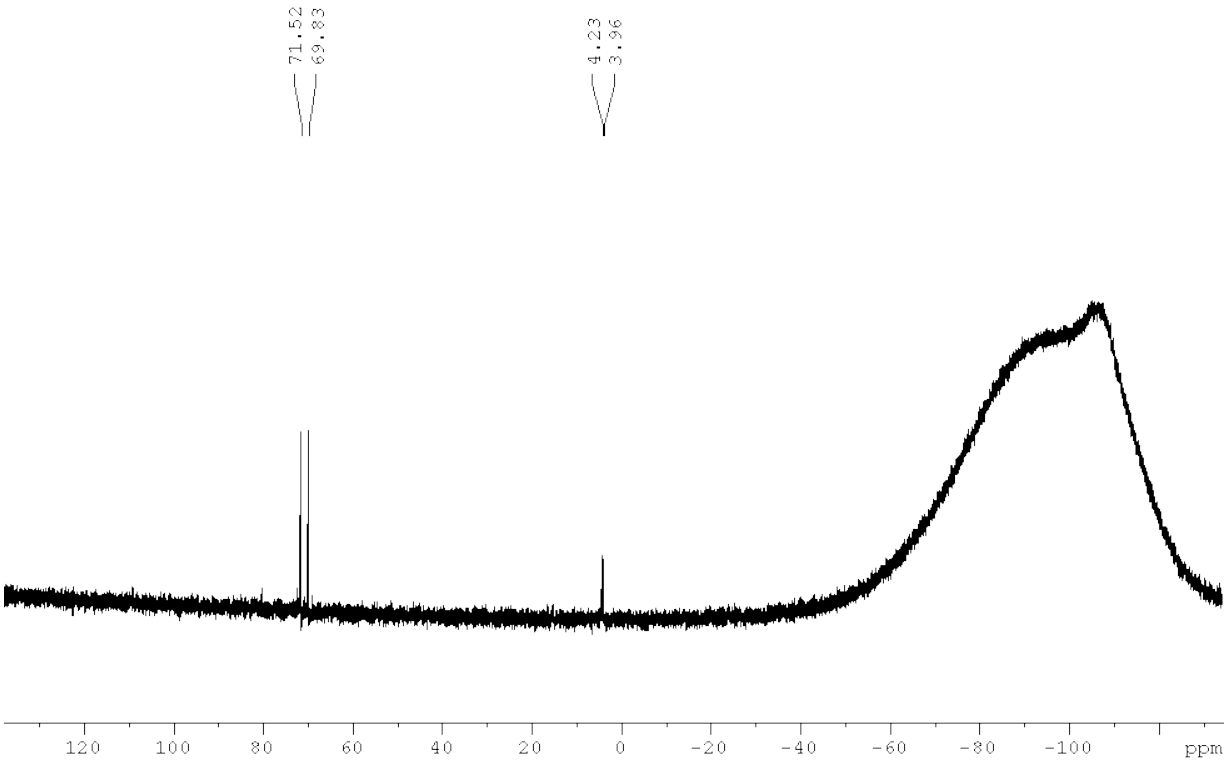

Figure S17. $^{29}Si\{^{1}H\}$ NMR spectrum for compound **3** in C_6D_6.

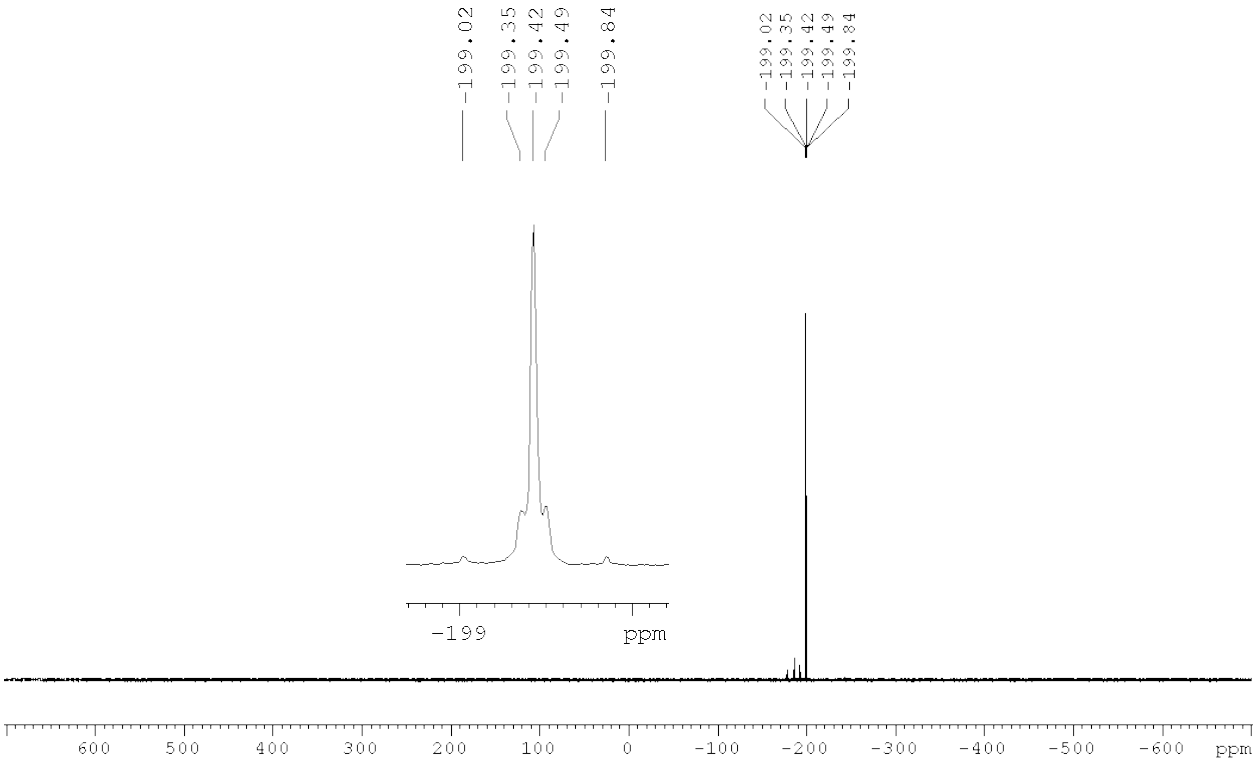

Figure S18. $^{31}P\{^{1}H\}$ NMR spectrum for compound **3** in C_6D_6 with a detail of the tungsten satellites.

2.6 IR spectra of compounds **2** and **3**

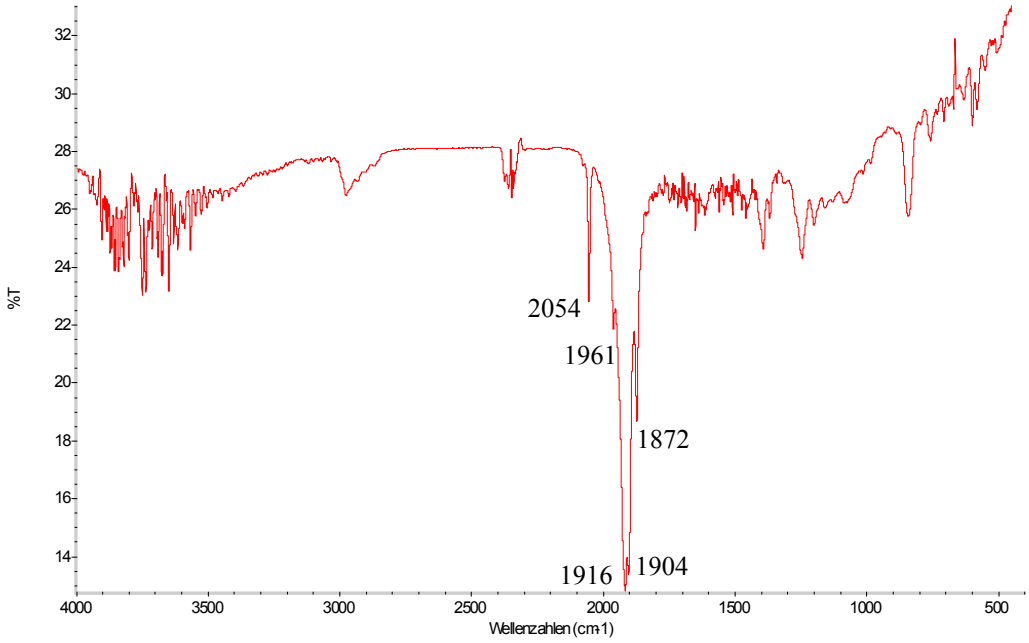

Figure S19. IR spectrum (KBr) of compound **2**.

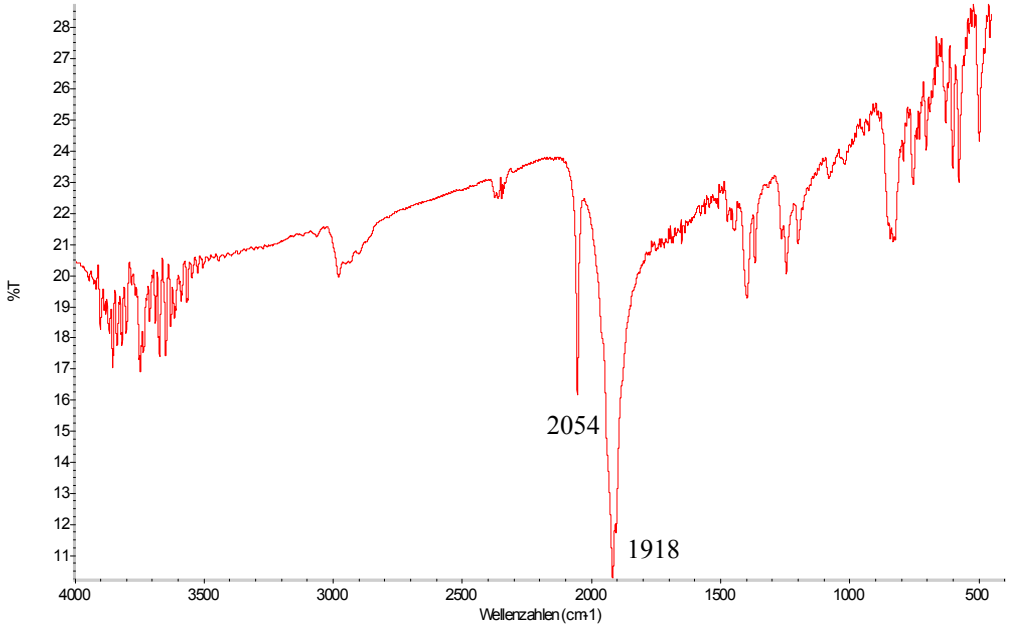

Figure S20. IR spectrum (KBr) of compound **3**.

2.7 UV/Vis Spectrum of **2**

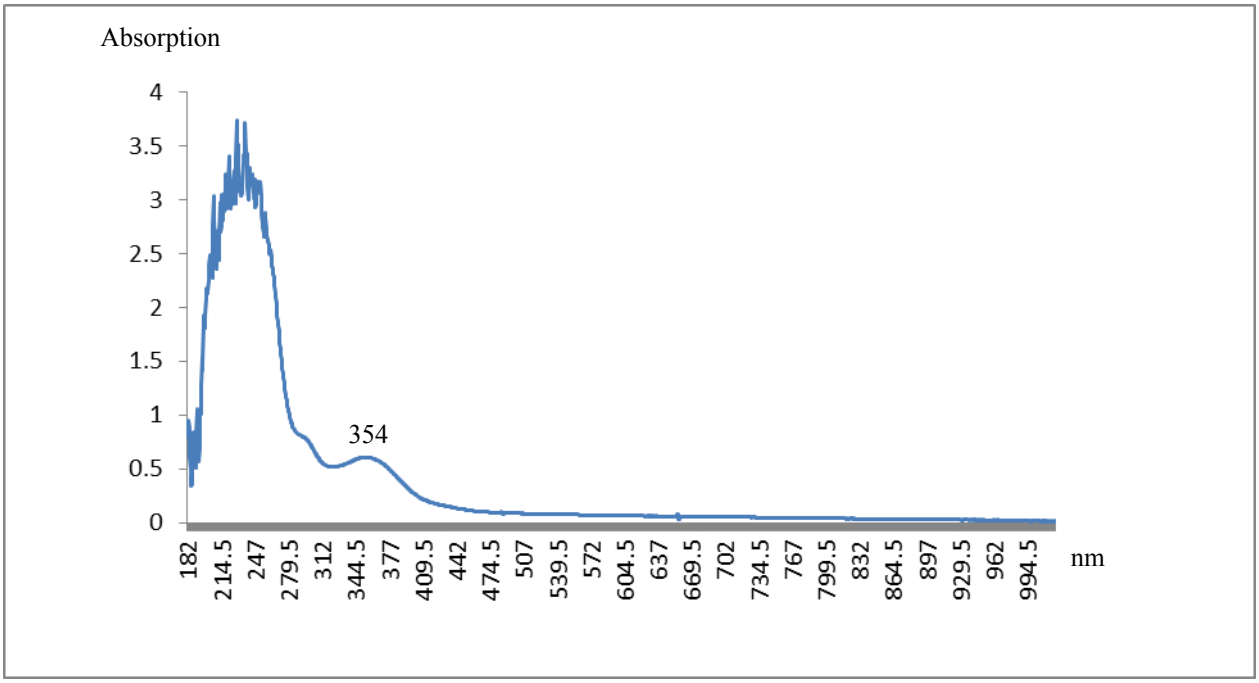

Figure S21. UV/Vis spectrum of compound **2** in hexane.

3. Single-Crystal X-ray Structure Determinations of 2 and 3

Table S1. Crystallographic data and structure refinement for compounds **2** and **3**.

Empirical formula	$C_{26}H_{41}N_2O_5PSi_3W$, **2**	$C_{52}H_{82}N_4O_{10}P_2Si_6W_2$, **3**
Formula weight	760.70	1521.40
Temperature	150(2) K	150(2) K
Wavelength	1.541840 Å	1.541840 Å
Crystal system	Orthorhombic	Monoclinic
Space group	Pna21	I2/a
a/Å	20.7398(2)	18.8405(3)
b/Å	9.20180(10)	10.1491(2)
c/Å	17.6394(2)	34.9207(5)
α/°	90.00	90.00
β/°	90.00	92.3180(10)
γ/°	90.00	90.00
Volume	3366.37(6) $Å^3$	6671.87(19) $Å^3$
Z	4	4
Density (calculated)	1.501 Mg/m^3	1.515 Mg/m^3
Absorption coefficient	8.118 mm^{-1}	8.192 mm^{-1}
F(000)	1528	3056
Crystal size [mm^3]	0.21 x 0.15 x 0.03	0.27 x 0.23 x 0.09
Theta range for data collection	4.25 to 73.07°	2.61 to 73.52º
Index range	-24≤h≤18, -11≤k≤10, -21≤l≤19	–22≤h≤21, –12≤k≤8, –41≤l≤38
Reflections collected	5353	5992
Independent reflections	5172	5488
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5353/ 20/ 355	5992 / 118 / 542
Goodness-of-fit on F^2	1.067	1.065
Final R indices [I>2sigma(I)]	R1 = 0.0468 wR2 = 0.1188	R1 = 0.0361, wR2 = 0.0854
R indices (all data)	R1 = 0.0485 wR2 = 0.1210	R1 = 0.0397, wR2 = 0.0881

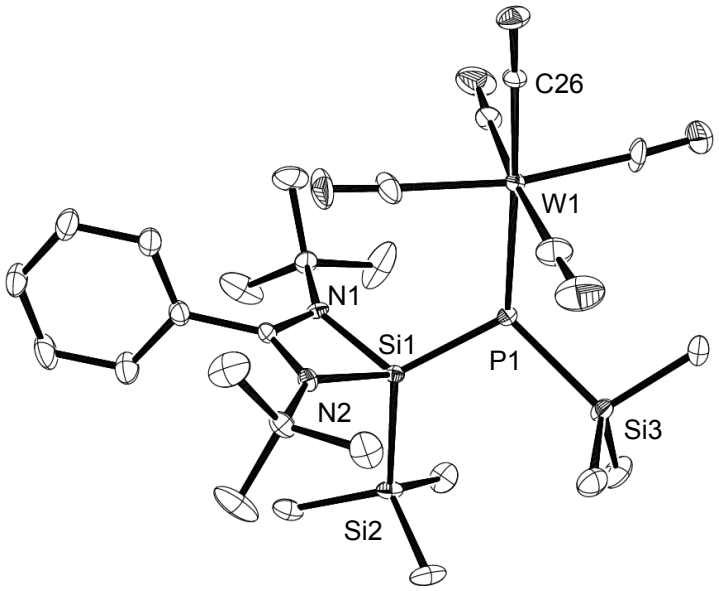

Figure S22. Molecular structure of of compound **2**. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond length (Å) and angles (°) in **2**: Si1–P1 2.158(2), Si1–Si2 2.369(2), P1–Si3 2.253(2), P1–W1 2.6265(18), W1–C26 2.002(9), N1–Si1 1.826(5), N2–Si1 1.848(5); Si1–P1–W1 118.82(8), Si3–P1–W1 115.55(8), P1–W1–C26 174.6(2).

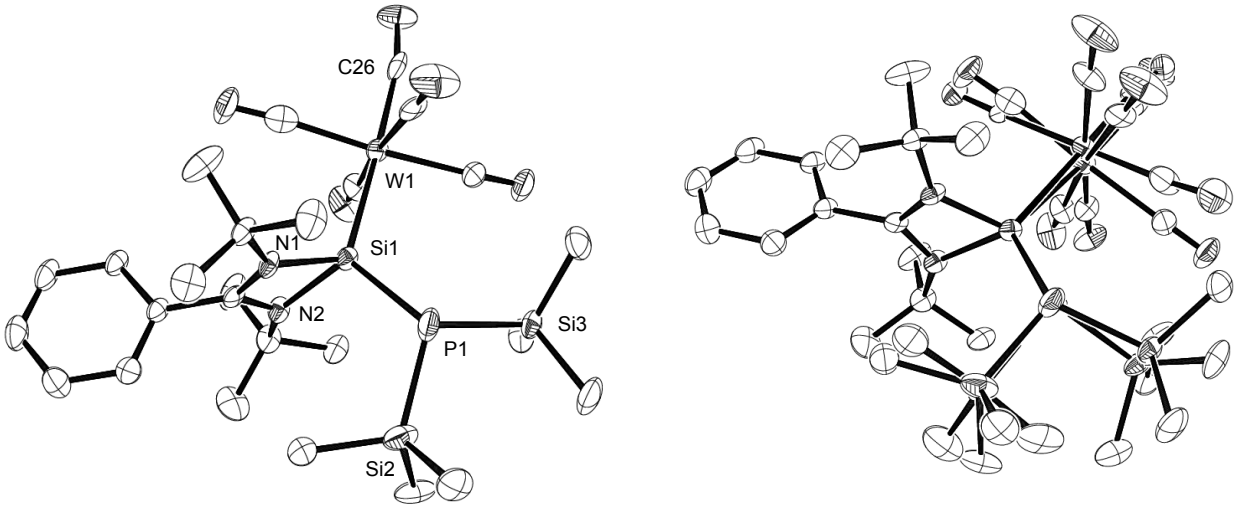

Figure S23. Molecular structure of compound **3**. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity. One of the disordered fractions is depicted on the left and the disorder is shown on the right. Selected bond length (Å) and angles (°) in **3**: Si1–P1 2.249(9), Si1–W1 2.562(3), P1–Si2 2.228(13), P1–Si3 2.177(10), Si1–N7 1.872(3), Si1–N8 1.871(3), W–C26 2.002(9); W1–Si1–P1 122.0(3), Si1–W1–C26 176.1(9).

Table S2. Selected interatomic distances and angles for **2**.

Interatomic distances (Å)		Angles (º)	
P1-Si1	2.158(2)	W1-P1-Si1	118.82(8)
P1-W1	2.6265(18)	W1-P1-Si3	115.55(8)
P1-Si3	2.253(2)	Si1-P1-Si3	108.85(10)
Si1-N1	1.826(5)	P1-Si1-Si2	120.28(9)
Si1-N2	1.848(5)	P1-Si1-N1	115.10(18)
Si1-Si2	2.369(2)	P1-Si1-N2	126.54(16)
N1-C1	1.326(8)	N1-Si1-Si2	107.85(17)
N2-C1	1.340(8)	N2-Si1-Si2	104.97(18)
W1-C26	2.002(9)	N1-Si1-N2	71.3(2)
C26-O5	1.128(12)	N1-C1-N2	106.9(5)
W1-C25	2.065(9)	P1-W1-C26	174.6(2)
C25-O4	1.079(12)	P1-W1-C25	90.6(2)
W1-C24	2.045(8)	P1-W1-C24	90.6(3)
C24-O3	1.125(13)	P1-W1-C23	96.3(4)
W1-C23	2.093(6)	P1-W1-C22	88.5(3)
C23-O2	1.086(9)		
W1-C22	2.032(10)		
C22-O1	1.152(16)		

Table S3. Selected interatomic distances and angles for **3**.

Interatomic distances (Å)		Angles (º)	
Si1-P1A	2.249(9)	W1A-Si1-P1A	122.0(3)
Si1-P1B	2.237(6)	W1B-Si1-P1B	120.69(19)
Si1-W1A	2.562(3)	Si1-P1A-Si2A	117.6(5)
Si1-W1B	2.619(2)	Si1-P1A-Si3A	118.2(5)
P1A-Si2A	2.228(13)	Si2A-P1A-Si3A	107.8(4)
P1A-Si3A	2.177(10)	Si1-P1B-Si2B	116.8(3)
P1B-Si2B	2.260(10)	Si1-P1B-Si3B	107.5(3)
P1B-Si3B	2.375(9)	Si2B-P1B-Si3B	101.8(3)
Si1-N1	1.872(3)	P1A-Si1-N1	103.0(3)
Si1-N2	1.871(3)	P1A-Si1-N2	112.7(3)
N1-C1	1.338(5)	P1B-Si1-N1	104.3(2)
N2-C1	1.329(5)	P1B-Si1-N2	113.4(2)
W1A-C26A	2.002(9)	N1-Si1-N2	69.69(14)
C26A-O5A	1.151(11)	N1-C1-N2	106.6(3)
W1B-C26B	2.006(7)	N1-Si1-W1A	121.93(12)
C26B-O5B	1.152(9)	N2-Si1-W1A	116.05(12)
W1A-C25A	2.099(13)	N1-Si1-W1B	115.62(12)
C25A-O4A	1.131(15)	N2-Si2-W1B	120.50(12)
W1B-C25B	1.969(9)	Si1-W1A-C26A	176.1(9)
C25B-O4B	1.148(12)	Si1-W1A-C25A	99.0(3)
W1A-C24A	2.053(14)	Si1-W1A-C24A	87.2(4)
C24A-O3A	1.147(17)	Si1-W1A-C23A	87.0(7)
W1B-C24B	2.023(9)	Si1-W1A-C22A	96.2(4)
C24B-O3B	1.137(11)	Si1-W1B-C26B	172.8(9)
W1A-C23A	2.036(9)	Si1-W1B-C25B	91.6(3)
C23A-O2A	1.130(10)	Si1-W1B-C24B	96.2(2)
W1B-C23B	2.057(7)	Si1-W1B-C23B	84.3(4)

C23B-O2B	1.132(8)	Si1-W1B-C22B	89.5(3)
W1A-C22A	2.045(17)		
C22A-O1A	1.13(2)		
W1B-C22B	2.015(10)		
C22B-O1B	1.157(13)		

4. Additional Results of Computational Investigations

4.1 The Transition State with a 0° Torsion Angle

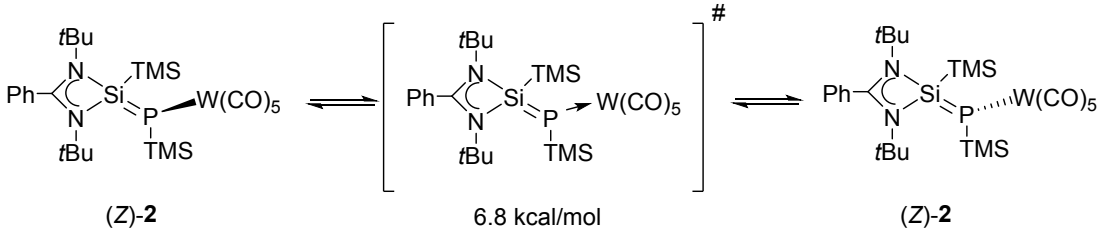

Figure S24. Interconversion of the two (*Z*)-**2** orientations through a transition state with a Si2-Si1-P1-W1 torsion angle of 0°.

4.2 Description and Depiction of the MOs of (*E*)-**2**

More detailed description of the molecular orbitals of (*E*)-2. TD-DFT calculation on the B3LYP/cc-pVTZ//B97-D/6-31G(d) level of theory predicted the UV/Vis-transition of (*E*)-**2** to be at 383 nm (3.24 eV, oscillator strength 0.050), which is red shifted from **1** (333 nm). The UV/Vis transition of (*E*)-**2** occurs mainly from the HOMO to the LUMO (weight 0.55, Figure S25). The HOMO of (*E*)-**2** (-4.13 eV) is determined by the antibonding combination of the π orbital of the phosphasilene and a filled d-orbital of tungsten, while the LUMO of (*E*)-**2** (-1.92 eV) is marked by the π* orbitals of the phenyl ring. The electron transitions to the LUMO+1 (-1.70 eV, weight 0.11), which is best described as the Si-P antibonding orbital and the LUMO+2 (-1.51 eV, weight 0.15) show a significantly lower contribution. In the case of **1**, UV/Vis transitions were calculated to occur from the HOMO (-5.94 eV, determined by the π orbital of the phosphasilene) to the LUMO and LUMO+2 (-0.16 eV and +0.45 eV, marked by the benzene moiety and the N-C-N-Si four membered ring, weight 0.12 and 0.68, respectively) as well as the LUMO+3 (+1.32 eV, the π* orbital of silicon-phosphorus double bond, weight 0.32).[2] Thus, the influence of the coordination to tungsten is determined by the interaction between the silicon-phosphorus bond and tungsten leading to a higher lying HOMO orbital and lower lying LUMO orbitals of (*E*)-**2**.

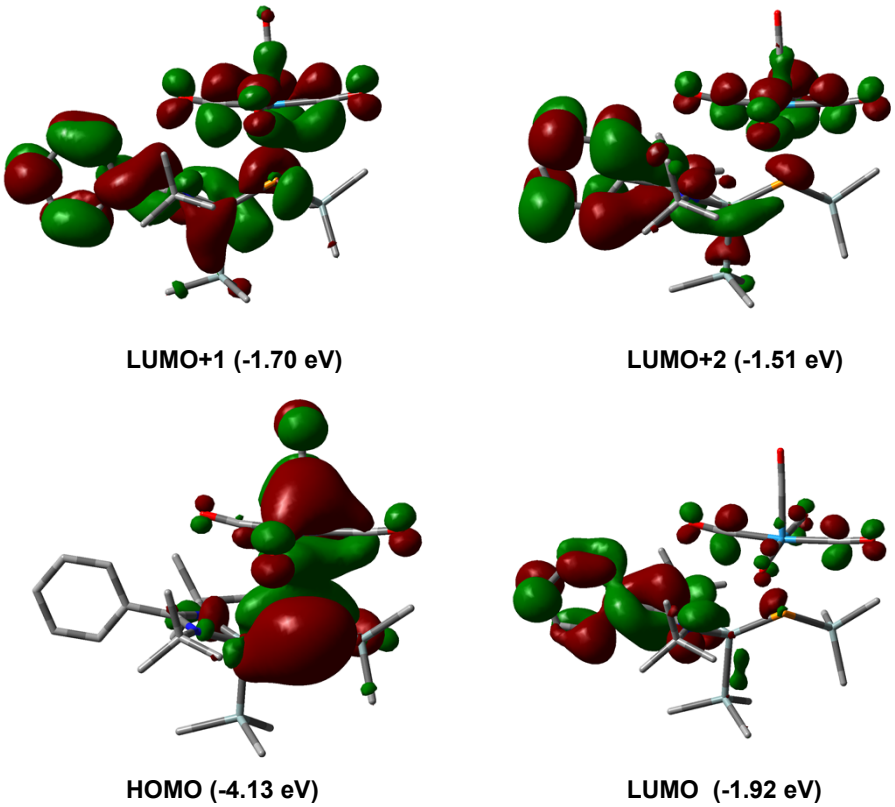

Figure S25. Molecular orbitals of (*E*)-**2** that are involved in the UV/Vis transition calculated at the B97-D/6-31G(d) level of theory.

4.3 Mechanism for the Formation of **3** from **2**

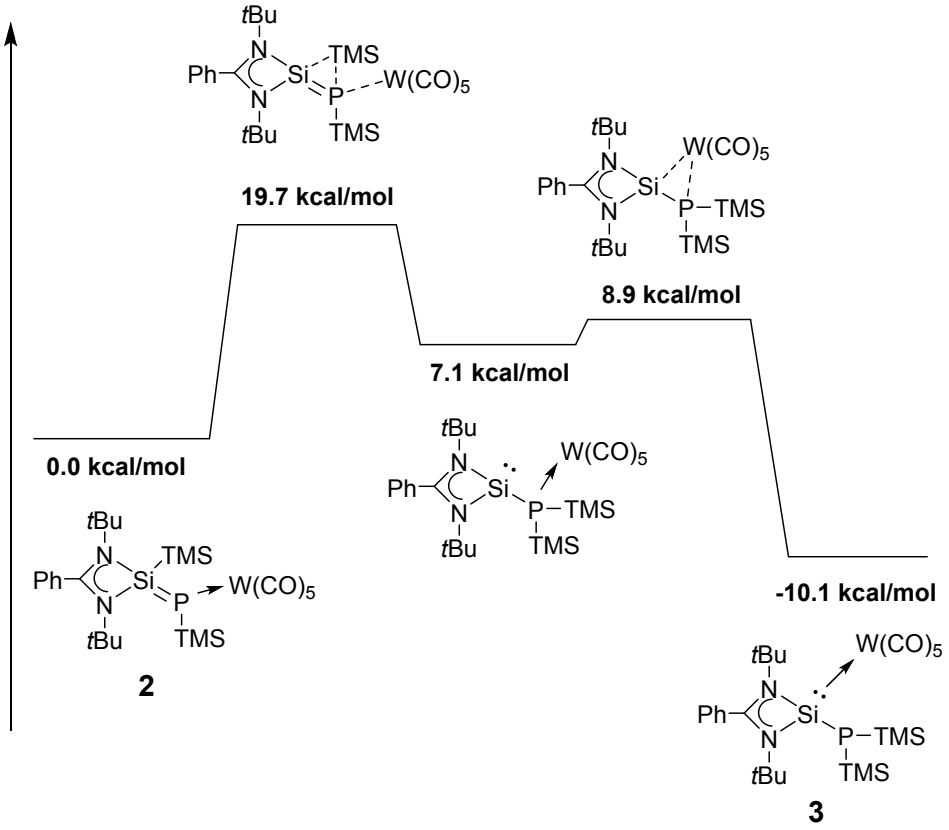

Figure S26. Mechanism for the formation of **3** from **2** based on DFT calculations on the B97-D/6-31G(d) level of theory.

5. Computational Details

DFT calculations were performed at the RI-B97-D/6-31G* level of theory.[4-8] TD-DFT calculations were carried out at the CAM-B3LYP/cc-pVTZ//RI-B97-D/6-31G* level of theory.[9-10] Stationary points on the potential energy surface (PES) were characterized by harmonic vibrational frequency calculations. Transition states, with one imaginary frequency, were confirmed by intrinsic reaction coordinate (IRC) calculations. Calculations were carried out using GAUSSIAN 09 program.[11]

Table S4. Cartesian geometry of (*E*)-**2** at B97-D/6-31G* level in Angstrom [Å].

C	4.623714	-3.586753	-0.606770
C	3.480271	-2.794501	-0.423289
C	3.613407	-1.401484	-0.269504
C	4.893960	-0.811673	-0.302261
C	6.032304	-1.610318	-0.481385
C	5.899273	-2.999921	-0.635439
C	2.437357	-0.507645	-0.078663
N	1.869551	0.277176	-1.011229
C	2.123627	0.411113	-2.465900
C	0.931332	1.210512	-3.027104
N	1.828464	-0.218463	1.094118
Si	0.872464	1.177794	0.315088
Si	2.116231	3.143512	0.710101
C	1.793903	4.450455	-0.650804
C	2.018291	-0.792063	2.455801
C	1.639645	-2.290913	2.443536
C	1.058212	-0.034441	3.393282
C	3.465132	-0.612660	2.967789
P	-1.249880	1.099582	0.663361
Si	-2.191244	2.968006	-0.208188
C	-1.797590	3.367048	-2.036077
C	3.431447	1.200363	-2.705282
C	2.192876	-0.962019	-3.167825
W	-2.422767	-1.170897	-0.032079
C	-3.318754	-2.886191	-0.541607
O	-3.816098	-3.900884	-0.862817
C	-2.677365	-0.388312	-1.910928
O	-2.813937	0.065255	-2.981828
C	-0.698769	-2.086730	-0.587916
O	0.209846	-2.756526	-0.914964
C	-2.129583	-1.815221	1.897725
O	-1.988078	-2.172560	3.003272
C	-4.270486	-0.491298	0.579031

O	-5.337736	-0.221240	0.966932
C	-4.072374	2.682876	-0.101942
C	-1.779156	4.500535	0.864226
C	1.682811	3.840733	2.434912
C	3.985740	2.717682	0.671190
H	4.303031	0.635246	-2.342984
H	3.558608	1.384417	-3.784279
H	1.276276	-1.537944	-2.981877
H	2.292464	-0.792273	-4.252332
H	3.058031	-1.548697	-2.831359
H	2.491051	-3.245462	-0.418896
H	0.865227	2.195203	-2.539435
H	1.069513	1.369914	-4.107384
H	-0.014735	0.675356	-2.862835
H	4.513556	-4.665878	-0.730064
H	-4.595254	3.609174	-0.401370
H	-4.398196	1.876693	-0.777668
H	-2.397777	4.240366	-2.353046
H	-0.739272	3.614579	-2.213205
H	-2.060575	2.522247	-2.692950
H	4.992609	0.265496	-0.166942
H	0.016082	-0.135316	3.057914
H	1.147242	-0.451756	4.408761
H	1.311278	1.038081	3.431772
H	3.722459	0.455653	3.037778
H	3.540868	-1.048662	3.977152
H	4.194206	-1.117370	2.320633
H	0.594215	3.896263	2.597856
H	2.111480	3.210906	3.234170
H	2.099638	4.857380	2.551931
H	4.583402	3.604031	0.951838
H	4.234019	1.909413	1.378950
H	4.309387	2.402839	-0.336069
H	3.393078	2.171610	-2.188652
H	2.306630	4.178723	-1.592472
H	0.722460	4.572852	-0.875971
H	2.183752	5.433714	-0.330286
H	2.370083	-2.879411	1.872026
H	1.624213	-2.667559	3.478252
H	0.642847	-2.430638	2.005757
H	-4.399627	2.421420	0.917605
H	-1.832082	4.256183	1.939470
H	-0.779284	4.919476	0.661754
H	-2.521562	5.295614	0.664062
H	6.785346	-3.621818	-0.777132

H	7.020512	-1.146172	-0.498834

Table S5. Cartesian geometry of transtion state on Scheme 1 at B97-D/6-31G* level in Angstrom [Å].

C	5.718936	-3.279404	-1.748733
C	4.457713	-3.177236	-2.358622
C	3.488060	-2.314078	-1.828156
C	3.782746	-1.543942	-0.686830
C	5.043616	-1.654250	-0.070286
C	6.008822	-2.521818	-0.601788
C	2.761944	-0.596785	-0.163446
N	1.749051	-0.879409	0.674542
C	1.420466	-2.159618	1.366673
C	2.625599	-2.726606	2.149631
N	2.713882	0.730805	-0.416440
Si	1.160653	0.888989	0.657574
P	-0.841693	1.027038	-0.151186
W	-2.966466	-0.662562	-0.070454
C	-4.168651	0.848081	-0.777726
O	-4.965633	1.646941	-1.081233
C	3.599460	1.581465	-1.257723
C	3.825748	1.007730	-2.672577
C	2.987395	2.995154	-1.367900
C	4.964242	1.741507	-0.535832
Si	1.896297	1.965284	2.621983
C	3.541181	1.154811	3.175970
C	2.182589	3.829797	2.305155
C	0.574055	1.788820	3.986309
C	0.941051	-3.186465	0.318914
C	0.307974	-1.813812	2.374461
Si	-0.908799	2.781249	-1.548770
C	-0.208353	4.336649	-0.680400
C	0.056323	2.150049	-3.082302
C	-2.711140	3.129424	-2.026363
C	-4.682804	-1.662499	-0.111369
O	-5.702396	-2.246002	-0.146095
C	-2.362280	-1.213993	-1.954556
O	-1.958995	-1.501931	-3.013227
C	-2.324009	-2.440041	0.697768
O	-2.144145	-3.510269	1.142598
C	-3.202254	0.065590	1.836230
O	-3.270098	0.499020	2.918393
H	5.467279	0.774004	-0.417008
H	5.620073	2.395488	-1.132303
H	2.863614	0.837227	-3.179196

H	4.402717	1.740146	-3.258835
H	4.388938	0.066892	-2.647976
H	2.508206	-2.222991	-2.298895
H	2.728111	3.385241	-0.373183
H	3.767209	3.654088	-1.782911
H	2.136469	3.062106	-2.050329
H	4.227434	-3.768470	-3.246681
H	-2.812164	4.107626	-2.526996
H	-3.041287	2.359432	-2.741081
H	0.400174	2.896450	-3.820836
H	0.892042	1.515531	-2.747325
H	-0.639711	1.473168	-3.610216
H	5.251941	-1.077952	0.832474
H	-0.569642	-1.400556	1.864485
H	0.001200	-2.712784	2.929029
H	0.680529	-1.068031	3.092920
H	2.926915	-2.041834	2.957918
H	2.321143	-3.682800	2.603169
H	3.488572	-2.918825	1.500815
H	-0.432567	2.009920	3.593927
H	0.545890	0.778967	4.425559
H	0.786139	2.501749	4.802862
H	3.891126	1.593734	4.126857
H	3.417752	0.070712	3.334425
H	4.336853	1.293970	2.426104
H	4.823915	2.199515	0.454604
H	3.094272	4.014676	1.712846
H	1.334443	4.296621	1.780238
H	2.303647	4.348710	3.272332
H	1.782042	-3.509967	-0.310327
H	0.520236	-4.066858	0.824737
H	0.164619	-2.740513	-0.316827
H	-3.399763	3.054962	-1.179217
H	-0.701432	4.424758	0.302069
H	0.874312	4.290614	-0.504705
H	-0.418520	5.259440	-1.250304
H	6.472604	-3.951731	-2.162894
H	6.983539	-2.608744	-0.118228

Table S6. Cartesian geometry of (Z)-**2** at B97-D/6-31G* level in Angstrom [Å].

C	7.353885	-0.839065	-0.291528
C	6.460729	-1.888302	-0.019534
C	5.084230	-1.635918	0.073500
C	4.596105	-0.327692	-0.107501
C	5.491818	0.723594	-0.382946

C	6.867271	0.466029	-0.473539
C	3.136745	-0.053756	-0.004914
Si	0.871077	0.542734	0.110860
P	-0.810996	-0.569143	0.881439
W	-3.228730	0.068881	-0.035877
C	-3.714096	-1.863762	-0.525186
O	-4.091345	-2.936928	-0.800588
N	2.238289	-0.123439	-1.007077
C	2.394838	-0.550047	-2.420389
C	2.711107	-2.061525	-2.479524
N	2.465219	0.332692	1.094451
C	2.949774	0.635622	2.465850
C	3.785282	1.935388	2.467977
C	1.043232	-0.264187	-3.100295
C	3.504540	0.242660	-3.145579
Si	0.785447	2.864758	-0.317987
C	2.547624	3.393115	-0.854131
C	-0.431576	3.300688	-1.714874
C	0.348359	3.812947	1.279345
C	3.789401	-0.531066	3.031575
C	1.700086	0.827012	3.349016
Si	-0.323470	-2.750642	0.574330
C	-0.626055	-3.411405	-1.194022
C	1.499008	-3.108495	1.043536
C	-1.469713	-3.704433	1.763083
C	-5.075336	0.563157	-0.620247
O	-6.155962	0.860636	-0.971162
C	-3.872017	-0.323032	1.883025
O	-4.234701	-0.553847	2.967992
C	-2.980164	2.026625	0.509099
O	-2.939858	3.150135	0.838992
C	-2.499211	0.377185	-1.922754
O	-2.103223	0.534828	-3.013593
H	4.497369	0.028336	-2.729122
H	3.505964	-0.045517	-4.208660
H	1.961543	-2.637363	-1.920797
H	2.703526	-2.395446	-3.529141
H	3.706567	-2.265551	-2.059741
H	4.387790	-2.443006	0.302384
H	0.826816	0.814484	-3.098191
H	1.070880	-0.610195	-4.143923
H	0.222783	-0.777978	-2.582303
H	6.834017	-2.903872	0.124509
H	-1.320109	-4.793612	1.655661
H	-1.275202	-3.431530	2.813632

H	1.720435	-4.184762	0.929283
H	2.191479	-2.548695	0.397267
H	1.703375	-2.826573	2.088775
H	5.105633	1.731046	-0.540863
H	1.087225	-0.084898	3.368341
H	2.021041	1.072320	4.373149
H	1.072477	1.649072	2.974265
H	3.194201	2.774691	2.073501
H	4.085292	2.174956	3.500537
H	4.694782	1.818822	1.861324
H	-0.588112	3.457128	1.732906
H	1.150590	3.733728	2.031492
H	0.215655	4.883892	1.043751
H	2.608252	4.495094	-0.890989
H	3.314888	3.041849	-0.146489
H	2.802505	3.010613	-1.854694
H	3.314663	1.324257	-3.080772
H	-0.189964	2.778484	-2.654250
H	-1.466611	3.045462	-1.448705
H	-0.389938	4.387138	-1.910270
H	4.745332	-0.640231	2.503287
H	4.003131	-0.328459	4.092746
H	3.230162	-1.475309	2.960422
H	-2.528485	-3.489370	1.547798
H	-1.702409	-3.506826	-1.397380
H	-0.195429	-2.770613	-1.977606
H	-0.174896	-4.415597	-1.296537
H	8.425000	-1.037473	-0.361986
H	7.556965	1.284208	-0.689176

Table S7. Cartesian geometry of transtion state on Figure S24 at B97-D/6-31G* level in Angstrom [Å].

C	6.949431	-0.718252	0.056092
C	7.500620	0.557809	-0.147830
C	6.655197	1.667532	-0.320523
C	5.262755	1.504163	-0.290408
C	4.709169	0.224808	-0.083364
C	5.556898	-0.886663	0.091957
C	3.234228	0.047766	-0.038692
N	2.427488	-0.116362	-1.106662
C	2.723007	-0.206064	-2.564732
C	1.361881	-0.396221	-3.268550
N	2.452908	-0.012564	1.058956
C	2.782338	0.093081	2.503946
C	3.560073	-1.160447	2.971029

Si	0.942545	-0.450500	0.016055
Si	0.787327	-2.783620	0.220445
C	-0.295136	-3.498502	-1.179159
P	-0.788421	0.768466	-0.196153
Si	-0.231619	2.937571	0.039434
C	-1.615123	3.983145	-0.741391
W	-3.315603	-0.095088	-0.192316
C	-3.249770	0.196882	1.841200
O	-3.165054	0.378400	2.992712
C	-4.239785	1.717073	-0.456696
O	-4.942390	2.641622	-0.605785
C	-5.196555	-0.749784	-0.199898
O	-6.296129	-1.164782	-0.193772
C	-3.075605	-0.268979	-2.227830
O	-2.903691	-0.348743	-3.380412
C	-2.989593	-2.094468	0.074804
O	-3.064681	-3.254150	0.234716
C	3.608362	1.361717	2.810086
C	1.443932	0.158057	3.269062
C	3.631621	-1.416261	-2.880243
C	3.393413	1.083770	-3.093072
C	2.526769	-3.573004	0.052065
C	0.154106	-3.178795	1.980090
C	-0.064327	3.521617	1.856854
C	1.417128	3.365448	-0.824348
H	4.555426	-1.206692	2.500796
H	3.695112	-1.126333	4.065681
H	3.067771	2.265813	2.484751
H	3.766447	1.426052	3.900372
H	4.593964	1.337380	2.324135
H	4.599625	2.363226	-0.416887
H	0.817050	-0.720828	3.043939
H	1.646956	0.166669	4.352811
H	0.879704	1.062190	3.003460
H	7.079710	2.662859	-0.477790
H	-1.364639	5.055536	-0.628734
H	-1.750741	3.772165	-1.816378
H	1.602628	4.453083	-0.735013
H	2.269032	2.842581	-0.354406
H	1.403479	3.108942	-1.897859
H	5.119980	-1.877588	0.239202
H	0.651334	0.394800	-2.979648
H	1.509890	-0.363402	-4.360491
H	0.916476	-1.370361	-3.008171
H	3.119610	-2.362306	-2.644583

H	3.862020	-1.416149	-3.959886
H	4.581764	-1.367703	-2.327927
H	-1.208062	-2.910698	-1.357065
H	0.278664	-3.527974	-2.123474
H	-0.600027	-4.533533	-0.938860
H	2.421022	-4.672680	0.114676
H	3.002020	-3.342131	-0.914875
H	3.220505	-3.263021	0.853566
H	2.996546	-2.074040	2.720999
H	0.971950	-3.063544	2.715813
H	-0.672202	-2.518613	2.286619
H	-0.213797	-4.218849	2.041905
H	4.416130	1.194952	-2.703706
H	3.453591	1.024185	-4.193079
H	2.802594	1.971114	-2.826091
H	-2.580321	3.813657	-0.239965
H	-0.868461	3.109150	2.491405
H	0.905006	3.235537	2.302993
H	-0.138599	4.625153	1.900833
H	8.586055	0.687469	-0.173539
H	7.602991	-1.585130	0.187159

Table S8. Cartesian geometry of transtion state (19.7 kcal/mol) on Figure S26 at B97-D/6-31G* level in Angstrom [Å].

C	6.867271	0.466029	-0.473539
C	7.353885	-0.839065	-0.291528
C	6.460729	-1.888302	-0.019534
C	5.084230	-1.635918	0.073500
C	4.596105	-0.327692	-0.107501
C	5.491818	0.723594	-0.382946
C	3.136745	-0.053756	-0.004914
N	2.465219	0.332692	1.094451
C	2.949774	0.635622	2.465850
C	1.700086	0.827012	3.349016
N	2.238289	-0.123439	-1.007077
C	2.394838	-0.550047	-2.420389
C	3.504540	0.242660	-3.145579
Si	0.871077	0.542734	0.110860
Si	-0.720494	1.934153	1.277502
C	-1.765224	0.877000	2.474392
P	-0.810996	-0.569143	0.881439
Si	-0.323470	-2.750642	0.574330
C	-1.469713	-3.704433	1.763083
W	-3.515329	-0.829556	-1.074343
C	-2.359589	-1.021169	-2.752170

O	-1.713691	-1.156161	-3.719734
C	-3.625083	-2.871121	-0.900903
O	-3.788275	-4.027904	-0.829699
C	-5.189916	-0.942932	-2.160004
O	-6.168507	-1.004652	-2.806484
C	-4.586987	-0.686861	0.680873
O	-5.190835	-0.614468	1.676913
C	-3.649944	1.205389	-1.254405
O	-3.829724	2.358058	-1.362857
C	2.711107	-2.061525	-2.479524
C	1.043232	-0.264187	-3.100295
C	3.785282	1.935388	2.467977
C	3.789401	-0.531066	3.031575
C	0.294771	3.200148	2.296508
C	-1.880810	2.863389	0.088949
C	-0.626055	-3.411405	-1.194022
C	1.499008	-3.108495	1.043536
H	4.497369	0.028336	-2.729122
H	3.505964	-0.045517	-4.208660
H	1.961543	-2.637363	-1.920797
H	2.703526	-2.395446	-3.529141
H	3.706567	-2.265551	-2.059741
H	4.387790	-2.443006	0.302384
H	0.826816	0.814484	-3.098191
H	1.070880	-0.610195	-4.143923
H	0.222783	-0.777978	-2.582303
H	6.834017	-2.903872	0.124509
H	-1.320109	-4.793612	1.655661
H	-1.275202	-3.431530	2.813632
H	1.720435	-4.184762	0.929283
H	2.191479	-2.548695	0.397267
H	1.703375	-2.826573	2.088775
H	5.105633	1.731046	-0.540863
H	1.087225	-0.084898	3.368341
H	2.021041	1.072320	4.373149
H	1.072477	1.649072	2.974265
H	3.194201	2.774691	2.073501
H	4.085292	2.174956	3.500537
H	4.694782	1.818822	1.861324
H	-2.265846	0.041109	1.964524
H	-1.153106	0.466997	3.294627
H	-2.551600	1.506997	2.926891
H	-0.375379	3.741331	2.987458
H	1.071947	2.709949	2.903584
H	0.783220	3.946730	1.651192

H	3.314663	1.324257	-3.080772
H	-1.326278	3.489166	-0.628266
H	-2.510886	2.173214	-0.488931
H	-2.547616	3.524261	0.671105
H	4.745332	-0.640231	2.503287
H	4.003130	-0.328459	4.092746
H	3.230162	-1.475309	2.960422
H	-2.528485	-3.489370	1.547797
H	-1.702409	-3.506826	-1.397380
H	-0.195429	-2.770613	-1.977606
H	-0.174896	-4.415597	-1.296537
H	8.425000	-1.037473	-0.361986
H	7.556965	1.284208	-0.689176

Table S9. Cartesian geometry of intermediate (7.1 kcal/mol) on Figure S26 at B97-D/6-31G* level in Angstrom [Å].

C	6.867271	0.466029	-0.473539
C	7.353885	-0.839065	-0.291528
C	6.460729	-1.888302	-0.019534
C	5.084230	-1.635918	0.073500
C	4.596105	-0.327692	-0.107501
C	5.491818	0.723594	-0.382946
C	3.136745	-0.053756	-0.004914
N	2.465219	0.332692	1.094451
C	2.949774	0.635622	2.465850
C	1.700086	0.827012	3.349016
N	2.238289	-0.123439	-1.007077
C	2.394838	-0.550047	-2.420389
C	3.504540	0.242660	-3.145579
Si	0.871077	0.542734	0.110860
Si	-1.239472	1.701860	1.807999
C	-2.467865	1.010882	3.094535
P	-0.810996	-0.569143	0.881439
Si	-0.323470	-2.750642	0.574330
C	-1.469713	-3.704433	1.763083
W	-3.515329	-0.829556	-1.074343
C	-2.359589	-1.021169	-2.752170
O	-1.713691	-1.156161	-3.719734
C	-3.625083	-2.871121	-0.900903
O	-3.788275	-4.027904	-0.829699
C	-5.189916	-0.942932	-2.160004
O	-6.168507	-1.004652	-2.806484
C	-4.586987	-0.686861	0.680873
O	-5.190835	-0.614468	1.676913
C	-3.649944	1.205389	-1.254405

O	-3.829724	2.358058	-1.362857
C	2.711107	-2.061525	-2.479524
C	1.043232	-0.264187	-3.100295
C	3.785282	1.935388	2.467977
C	3.789401	-0.531066	3.031575
C	-0.371927	2.893866	3.032077
C	-2.303069	2.552162	0.478254
C	-0.626055	-3.411405	-1.194022
C	1.499008	-3.108495	1.043536
H	4.497369	0.028336	-2.729122
H	3.505964	-0.045517	-4.208660
H	1.961543	-2.637363	-1.920797
H	2.703526	-2.395446	-3.529141
H	3.706567	-2.265551	-2.059741
H	4.387790	-2.443006	0.302384
H	0.826816	0.814484	-3.098191
H	1.070880	-0.610195	-4.143923
H	0.222783	-0.777978	-2.582303
H	6.834017	-2.903872	0.124509
H	-1.320109	-4.793612	1.655661
H	-1.275202	-3.431530	2.813632
H	1.720435	-4.184762	0.929283
H	2.191479	-2.548695	0.397267
H	1.703375	-2.826573	2.088775
H	5.105633	1.731046	-0.540863
H	1.087225	-0.084898	3.368341
H	2.021041	1.072320	4.373149
H	1.072477	1.649072	2.974265
H	3.194201	2.774691	2.073501
H	4.085292	2.174956	3.500537
H	4.694782	1.818822	1.861324
H	-3.084671	0.196615	2.687321
H	-1.948669	0.637501	3.992642
H	-3.152761	1.816061	3.414914
H	-1.090096	3.215769	3.806676
H	0.475103	2.411420	3.544548
H	0.002241	3.797766	2.526744
H	3.314663	1.324257	-3.080772
H	-1.724322	3.277645	-0.115233
H	-2.741672	1.825558	-0.219570
H	-3.131484	3.096612	0.965685
H	4.745332	-0.640231	2.503287
H	4.003130	-0.328459	4.092746
H	3.230162	-1.475309	2.960422
H	-2.528485	-3.489370	1.547797

H	-1.702409	-3.506826	-1.397380
H	-0.195429	-2.770613	-1.977606
H	-0.174896	-4.415597	-1.296537
H	8.425000	-1.037473	-0.361986
H	7.556965	1.284208	-0.689176

Table S10. Cartesian geometry of transtion state (8.9 kcal/mol) on Figure S26 at B97-D/6-31G* level in Angstrom [Å].

C	3.588250	-0.904198	0.200294
C	4.745750	-0.141251	-0.037847
C	6.012612	-0.731039	0.093721
C	6.127348	-2.082179	0.456489
C	4.971175	-2.844676	0.695567
C	3.704660	-2.259093	0.570691
C	2.225168	-0.328451	0.036673
N	1.517230	-0.253867	-1.103887
C	1.895979	-0.595192	-2.500483
C	0.607406	-0.545912	-3.348299
N	1.418686	0.105292	1.026649
Si	-0.049748	0.196304	-0.153762
W	-2.253394	0.481887	-1.954314
C	-1.179004	-1.276139	-1.911395
O	-0.636611	-2.307739	-1.853819
C	1.696530	0.339913	2.466469
C	0.367000	0.822580	3.077848
C	2.170422	-0.933374	3.201237
C	2.772256	1.438211	2.626633
P	-0.530344	2.277483	-0.897234
Si	-1.032444	3.674325	0.836000
C	-1.217078	5.404020	0.040049
Si	1.305108	3.586456	-1.208439
C	1.886663	4.495256	0.370572
C	0.831694	4.912492	-2.498055
C	2.769519	2.596689	-1.926841
C	2.538756	-1.995813	-2.608876
C	2.875848	0.470269	-3.041579
C	-1.027786	1.322855	-3.368321
O	-0.417887	1.881822	-4.195504
C	-3.427925	-0.271343	-3.426091
O	-4.092076	-0.718382	-4.279166
C	-3.317685	2.223387	-1.996829
O	-3.998675	3.176820	-1.999611
C	-3.662867	-0.103180	-0.588924
O	-4.535214	-0.367414	0.145148
C	-2.714260	3.213347	1.592582

C	0.278402	3.805355	2.213617
H	-0.257483	5.801924	-0.325926
H	-1.607661	6.111110	0.793381
H	2.798035	5.080173	0.150898
H	2.116169	3.811381	1.202105
H	1.116237	5.198770	0.723522
H	1.703094	5.556481	-2.714803
H	0.010891	5.558872	-2.149850
H	1.240509	4.179171	1.831228
H	3.680172	3.220689	-1.886930
H	2.949933	1.616095	3.699266
H	2.448526	2.379310	2.164076
H	7.113451	-2.540369	0.553520
H	5.054742	-3.895690	0.978237
H	2.803307	-2.845180	0.754802
H	-1.922986	5.387695	-0.806353
H	0.006163	1.719641	2.554053
H	0.517401	1.071894	4.138895
H	-0.402218	0.039143	3.008109
H	4.654388	0.906832	-0.322784
H	-2.999470	3.992789	2.321914
H	-2.692227	2.251173	2.122192
H	-3.499614	3.157396	0.822916
H	0.512244	4.442797	-3.443362
H	-0.079979	4.517905	2.978682
H	0.455233	2.845800	2.718219
H	2.592148	2.323624	-2.977546
H	2.963282	1.678175	-1.360253
H	6.907849	-0.133867	-0.089815
H	1.477769	-1.766727	3.036027
H	2.208643	-0.719251	4.281499
H	3.176748	-1.231066	2.878632
H	3.720337	1.121332	2.167312
H	-0.097050	-1.330616	-3.049740
H	0.872022	-0.701353	-4.405336
H	0.113367	0.431957	-3.248651
H	3.535533	-2.020735	-2.149504
H	2.645187	-2.249187	-3.675595
H	1.903104	-2.755508	-2.135836
H	2.399832	1.461234	-3.038691
H	3.793621	0.505914	-2.438207
H	3.150196	0.215523	-4.077704

Table S11. Cartesian geometry of **3** at B97-D/6-31G* level in Angstrom [Å].

C	4.745750	-0.141250	-0.037847

C	6.012612	-0.731037	0.093721
C	6.127349	-2.082177	0.456489
C	4.971176	-2.844674	0.695567
C	3.704661	-2.259092	0.570691
C	3.588250	-0.904197	0.200294
C	2.225168	-0.328450	0.036673
N	1.418686	0.105292	1.026649
C	1.696530	0.339914	2.466469
C	2.170422	-0.933373	3.201237
N	1.517230	-0.253867	-1.103887
Si	-0.049748	0.196304	-0.153762
P	-0.530345	2.277483	-0.897234
Si	1.066174	3.820664	-0.398376
C	0.910692	5.220154	-1.687893
C	1.895979	-0.595191	-2.500483
C	2.538757	-1.995812	-2.608876
C	2.875848	0.470270	-3.041579
C	0.607406	-0.545913	-3.348299
W	-1.859562	-1.648614	0.017351
C	-2.854217	-0.581027	1.459460
O	-3.437082	-0.077316	2.339913
C	2.772255	1.438212	2.626633
C	0.367000	0.822580	3.077848
C	-3.373201	-2.995162	0.110681
O	-4.258693	-3.757786	0.165310
C	-0.827707	-2.618590	1.487645
O	-0.231866	-3.244217	2.279071
C	-0.896456	-2.945908	-1.240687
O	-0.384402	-3.767046	-1.898869
Si	-2.393052	3.106953	0.127301
C	-3.944971	2.190074	-0.476275
C	-2.360773	3.131379	2.032997
C	-2.525679	4.917081	-0.477115
C	2.825272	3.099033	-0.556688
C	0.872009	4.605403	1.334796
H	-1.720984	5.553233	-0.076038
H	-3.488136	5.342803	-0.141737
H	1.698920	5.314936	1.518550
H	0.876813	3.862913	2.147502
H	-0.072025	5.168227	1.406141
H	1.690910	5.982911	-1.513240
H	-0.068980	5.721221	-1.643764
H	-1.536888	3.748914	2.422194
H	3.548908	3.817391	-0.131752
H	2.949932	1.616096	3.699266

H	2.448525	2.379311	2.164076
H	7.113452	-2.540367	0.553520
H	5.054743	-3.895688	0.978237
H	2.803387	-2.844407	0.757625
H	-2.492754	4.980805	-1.577035
H	0.006162	1.719641	2.554053
H	0.517402	1.071894	4.138895
H	-0.402218	0.039143	3.008109
H	4.654388	0.906833	-0.322784
H	-4.837636	2.709127	-0.083169
H	-3.984032	1.148152	-0.130407
H	-4.006080	2.183602	-1.575603
H	1.041870	4.827108	-2.709937
H	-3.309111	3.565148	2.399040
H	-2.273625	2.125126	2.464850
H	3.095771	2.928738	-1.609226
H	2.931795	2.151126	-0.015986
H	6.907849	-0.133865	-0.089815
H	1.477769	-1.766727	3.036027
H	2.208644	-0.719250	4.281499
H	3.176748	-1.231065	2.878632
H	3.720337	1.121333	2.167312
H	-0.097050	-1.330617	-3.049740
H	0.872022	-0.701354	-4.405336
H	0.113367	0.431956	-3.248651
H	3.535534	-2.020734	-2.149504
H	2.645188	-2.249186	-3.675595
H	1.903105	-2.755507	-2.135836
H	2.399831	1.461235	-3.038691
H	3.793621	0.505915	-2.438207
H	3.150196	0.215524	-4.077704
C	-2.731221	-0.746643	-1.617724
O	-3.203089	-0.301748	-2.587834

6. References

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