Supporting information

Electron Induced Conversion of Silylones to Six-membered Cyclic Silylenes

Sudipta Roy, Kartik Chandra Mondal, Lennard Krause, Peter Stollberg, Regine Herbst-Irmer, Dietmar Stalke, Jann Meyer, A. Claudia Stückl, Bholanath Maity, Debasis Koley,* Suresh Kumar Vasa, Sheng Qi Xiang, Rasmus Linser and Herbert W. Roesky**

Content:

S1. Syntheses of compounds 2a and 2b

General Remarks

All manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk techniques and in a dinitrogen filled glove box where the O_2 and H_2O levels were usually kept below 1 ppm. $(Cy\text{-}cAAC)_2Si$ (**1a**) [cAAC = Cy-cAAC: = $:C(CH_2)(CMe_2)(C_6H_{10})N\text{-}2,6\text{-}iPr_2C_6H_3$] and $(Me_2\text{-}cAAC)_2Si$ (**1b**) [cAAC = Me_2-cAAC: = $:C(CH_2)(CMe_2)_2N\text{-}2,6\text{-}iPr_2C_6H_3$] were prepared according to the literature procedure. [S1] The crystals of silylones (**1a-b**) are stable in air for forty five minutes and after that they slowly loose their blue color. After twenty four hours they completely turn to colorless solid (mixture of cAAC=O, SiO_2 and $(cAACH)_2Si(OH)_2$) which is concluded from NMR resonances and MASS spectrometry.

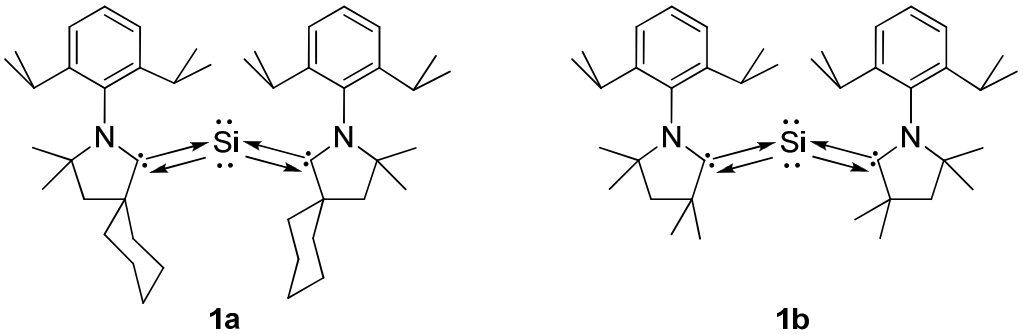


Figure S1: Structures of precursors $(Cy\text{-}cAAC)_2Si$ (**1a**) and $(Me_2\text{-}cAAC)_2Si$ (**1b**).[S1]

All solvents were dried initially with the M-Braun solvent drying system and then deoxygenated by stirring for 4-5 hours over Na/K alloy followed by distillation in vacuum and degassed. ^1H, ^{13}C and ^{29}Si NMR spectra were recorded on Bruker Avance 500 MHz NMR spectrometer. Deuterated NMR solvent C_6D_6 was dried prior to use by stirring for 2 days over Na/K alloy followed by distillation in vacuum and degassed. EI-MS spectra were obtained with a Finnigan MAT 8230 or a Varian MAT CH5 instrument (70 eV) by EI-MS methods. Melting points were measured in sealed glass tubes on a Büchi B-540 melting point apparatus.

Important points about the reactivity of silylones (**1a-b**): Silylones were reacted with metal carbonyls, R_3B and other organic molecules like $R\text{-}N_3$ etc. The reactions did not produce exclusively one product rather a mixture of compounds and hence isolations and characterizations were restricted. To get control over these reactions is challenging due to the following reasons: 1) The HOMO is the π-bonded (three center-two-electron π–bond between two carbene carbon atoms and the central silicon atom) electron pair. 2) The π–back bonding (donation of electron from silicon to carbene carbon atoms) is higher than that of the σ–donation

from carbene carbon atoms to the central silicon atom. We realized that the conventional methods towards the activation of small organic molecules at silicon center of silylone are futile. Combined with previously reported theoretical calculations [S1] on silylones and several attempts for the activation of small organic molecules at central silicon atom led to the above mentioned conclusion. The unprecedented synthetic route (Figure S2) is thus very important.

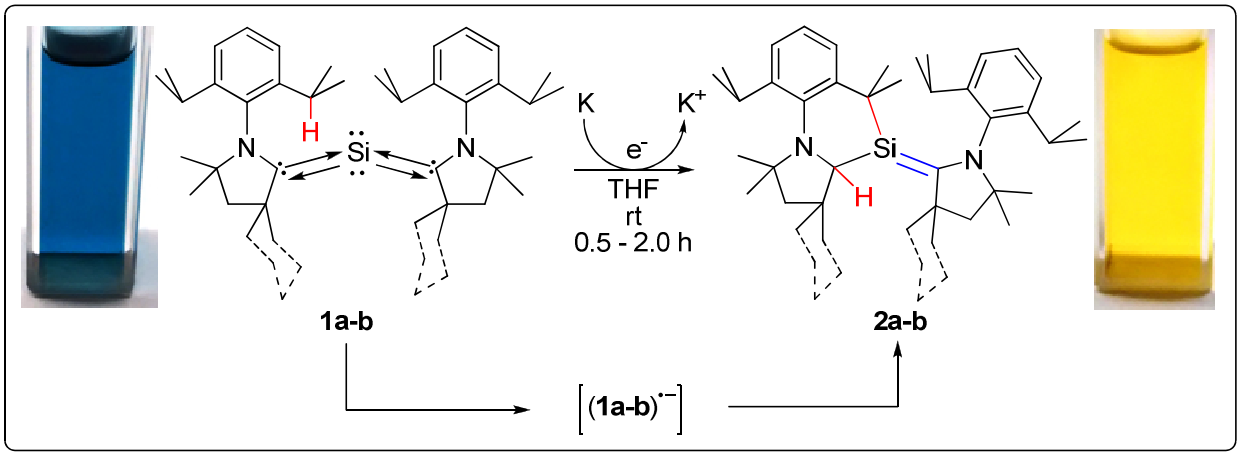


Figure S2. Conversion of compounds **1a-b** to **2a-b**.

Synthesis of compound 2a: To a 1:1 molar mixture of compound **1a** (272 mg, 0.4 mmol) and metallic potassium (15 mg, 0.4 mmol), tetrahydrofuran (THF) (15 mL) was added at room temperature. The resulting dark purple solution was stirred along with the piece of metallic potassium for thirty five minutes to obtain a greenish-yellow solution. The solution was then filtered to separate the unreacted potassium (11 mg, 67 mol%) indicating that 33 mol% of K was consumed during the reaction. The THF solution was concentrated under vacuo to 0.5 mL to which 1 mL and stored at -32 °C in a freezer to form bright orange-yellow blocks of **2a** in 80% yield. The volume of the solvent plays a crucial role on the rate of conversion. On decreasing the volume of the solvent the reaction proceeds faster.

Compound 2a: Melting range 223-224 °C, UV-vis absorption band at λ_{ab} = 423 nm.

^{1}H NMR (500 MHz, 298 K, C_6D_6, ppm) δ: 7.19 (d, J = 7.5 Hz, $1H_{Ar}$), 7.11-7.09 (m, 2.7, $3H_{Ar}$), 6.89 (t, J = 7.6 Hz, $1H_{Ar}$), 6.82 (d, J = 6.4 Hz, $1H_{Ar}$), 4.57 (s, 1H, $C_{carbene}$-H), 3.77 – 3.69 (m, 1H, $CHMe_2$), 3.32 (dt, J = 13.3, 6.6 Hz, 1H, $CHMe_2$), 2.94 (dt, J = 13.7, 6.8 Hz, 1H, $CHMe_2$), 2.43 (d, J = 13.0 Hz, 1H, $H_{cyclohexyl}$), 2.33 – 2.19 (m, 4H, $H_{cyclohexyl}$), 2.16 – 2.02 (m, 3H; $H_{cyclohexyl}$), 1.96 – 1.79 (m, 4H), 1.77 – 1.64 (m, 7H), 1.51 – 1.40 (m, 12H, $2xNCMe_2$), 1.28 (dd, J = 6.8, 2.4 Hz, 4H), 1.19 – 1.06 (m, 12H), 0.97 – 0.75 (m, 9H), 0.63 (d, J = 6.8 Hz, 2H, $CH_{2cyclohexyl}$), 0.46 (s, 2H, $CH_{2cyclohexyl}$).

^{13}C NMR (126 MHz, 298 K, C_6D_6, ppm) δ: 173.50 (C_{cAAC}), 151.13, 148.72, 147.01, 146.05, 142.20, 139.61, 125.84, 125.17, 123.34, 122.29, 121.36, 69.47 (C_{cAAC} –H), 67.62, 63.76, 54.11, 52.95, 51.05, 46.07, 44.68, 41.37, 40.55, 39.78, 32.49, 31.91, 30.65, 28.76, 28.66, 28.29, 27.02, 26.90, 26.88, 26.78, 26.33, 26.22, 26.09, 25.30, 24.67, 24.44, 24.43, 23.75, 23.58, 23.42.

^{29}Si NMR (99 MHz, 298 K, C_6D_6, ppm) δ: 55.98.

EI-MS: m/z (%) 678.4 (100%)[M^+], 679.5 (63%)[M^+], 680.5 (23%)[M^+]. Mass spectrometry was performed on solid sample of **2a**.

Synthesis of compound 2b: To a 1:1 molar mixture of compound **1a** (240 mg, 0.4 mmol) and metallic potassium (15 mg, 0.4 mmol), tetrahydrofuran (THF) (15 mL) was added at room temperature. The resulting dark purple solution was stirred along with the piece of metallic potassium for two hours to obtain a greenish-yellow solution. The solution was then filtered to separate the unreacted potassium (11 mg, 67 mol%) indicating that 33 mol% of K was consumed during the reaction. The THF solution was concentrated under vacuo to 0.5 mL to which 1 mL of *n*-hexane was added and the resulting solution was stored at -32 °C in a freezer to form bright orange-yellow blocks of **2b** in 40% yield.

Point to be noted that in both the cases reaction solutions should not be stirred for longer than the time mentioned above since the products (**2a-b**) can undergo further rearrangements to produce a mixture of different products.

Compound 2b: Melting range 211-212 °C, UV-vis absorption band at λ_{ab} = 420 nm.

^{1}H NMR (500 MHz, 298 K, C_6D_6, ppm) δ: 7.11 – 7.07 (m, 4H), 6.88 (t, J = 7.6 Hz, 1H), 6.82 (dd, J = 7.7 Hz, 1.7, 1H), 4.29 (s, 1H, C_{cAAC}-H), 3.79 – 3.72 (m, 1H), 3.30 (dq, J = 13.5, 6.7 Hz, 1H), 2.92 (dt, J = 13.8, 6.9 Hz, 1H), 2.14 (d, J = 12.9 Hz, 1H), 1.84 (t, J = 8.8 Hz, 1H), 1.76 (s, 3H), 1.59 (d, J = 6.7 Hz, 3H), 1.46 (s, 3H), 1.45 – 1.38 (m, 19H), 1.37 (s, 3H), 1.16 (d, J = 6.8 Hz, 4H), 1.09 (d, J = 7.0 Hz, 6H), 0.76 (s, 3H), 0.63 (d, J = 6.9 Hz, 3H), 0.45 (s, 3H).

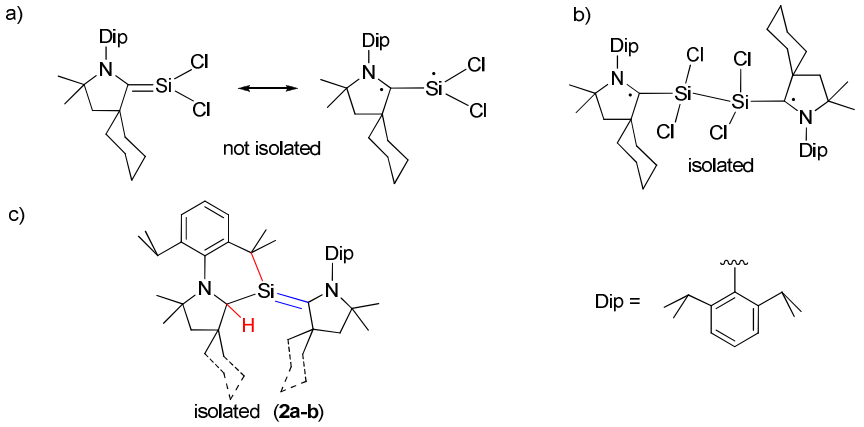
^{13}C NMR (126 MHz, 298 K, C_6D_6, ppm) δ: 172.10 (C_{cAAC}), 151.17, 148.88, 148.43, 147.04, 142.60, 139.86, 125.97, 125.37, 123.53, 122.40, 121.57, 67.14, 66.25 (C_{cAAC} –H), 63.63, 60.79, 59.38, 47.86, 40.98, 35.93, 35.57, 34.42, 33.47, 32.26, 31.65, 30.76, 28.87, 28.84, 28.73, 27.75, 27.28, 27.13, 27.01, 26.90, 26.64, 26.08, 24.61, 23.95, 23.68.

^{29}Si NMR (99 MHz, 298 K, C_6D_6, ppm) δ: 54.55.

EI-MS: m/z (%): 598.4 (100%)[M^+], 599.4 (63%)[M^+], 600.4 (24%)[M^+]. Mass spectrometry was performed on solid sample of **2b**.

Additional experiment: A similar reaction was performed following the synthesis of compound **2a** in THF-d_8 and the NMR spectra confirmed the presence of C_{cAAC} –H resonance and no incorporation of the deuterium from THF-d_8 (confirmed by ^{13}C NMR spectrum) was observed.

Scheme S1. Electronic structures of a) 1,2-singlet diradical (Cy-cAAC·)Si(·)Cl_2, b) 1,4-singlet diradical (Cy-cAAC·)$_2Si_2Cl_4$ c) silylene with three coordinate silicon 2a-b.



S2. Solid-state NMR characterization of compounds 1a and 2a

Solid-state NMR spectra of compound **1a** show a slight polymorphism with a chemical difference of the ^{29}Si resonance of 1.8 ppm in a stoichiometry of approximately 1.7:1. The chemical shift anisotropy of **1a** was obtained to be 125.8 and 129.3 ppm for the two peaks at 66.6 and 68.4, respectively, with an asymmetry of 0.52 in both cases (see Figure S4A). $^{1}H/^{29}Si$ cross polarization (CP) buildup curves show half-maximum intensity after approximately 1.2 ms (see Figure S3A).

Compound **2a** shows a single ^{29}Si resonance at 55.0 ppm. Fitting of spinning side bands resulted in a CSA of 58.0 ppm with an asymmetry of 0.7 (see Figure S4B). CP buildup (half-maximum intensity after 1.2 ms) occurs with similar time behaviour as for **1a** (see Figure S3B).

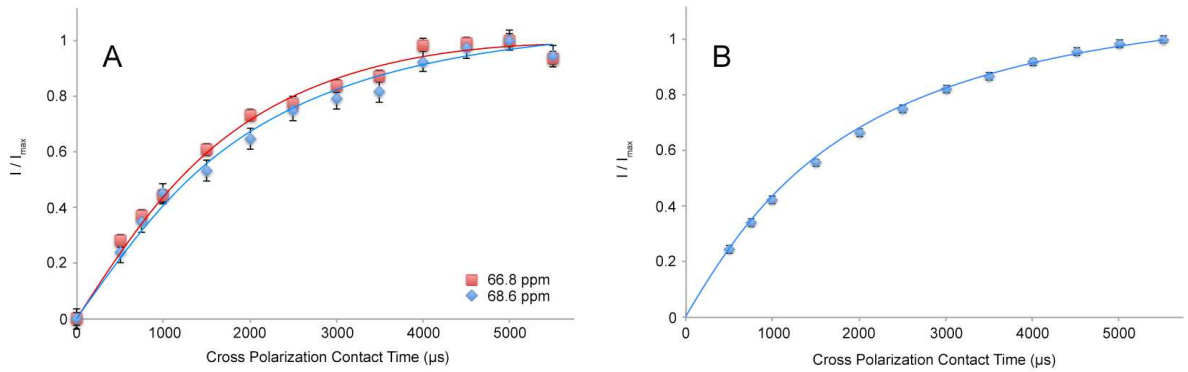


***Figure S3*:** CP buildup curves for **1a** (A) and **2a** (B). Intensities are scaled to reflect relative values with respect to the maximal values obtained within the time course from 0 to 5.5 ms. In (A) the two resonances resulting from crystal polymorphism are displayed in red (66.8 ppm) and blue (68.6 ppm).

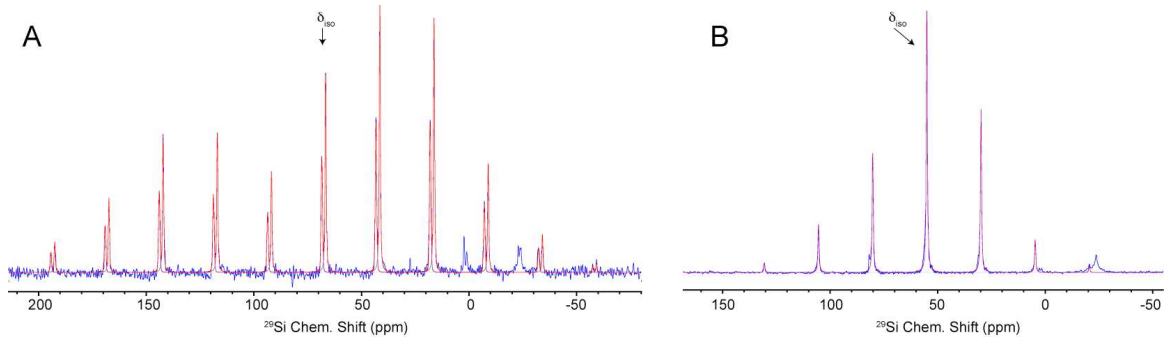


***Figure S4*:** Chemical Shift Anisotropy determination as observed at 3 kHz MAS. (**A**) ^{29}Si spectrum of **1a**. The data was fit to yield a CSA of 125.8 and 129.3 ppm for the two peaks at 66.6 and 68.4 ppm. (**B**) Spectrum of **2a** at 3 kHz MAS, fit to yield a CSA of 58.0.

Experimental Details: Isotropic chemical shift spectra and cross polarization (CP) buildup was determined using 11 kHz MAS. For the buildup curves, 1024 scans were acquired over 1.5 h for each data point. Determination of chemical shift anisotropies (CSAs) from spinning side band patterns was pursued using a 5.5 ms CP contact time at 3 kHz MAS, using 10240 scans, recorded in 14 h for each of **1a** and **2a**. Spectral deconvolution and CSA fitting was done using Bruker Topspin software. All experiments were pursued at 600 MHz Larmor frequency in a 4 mm rotor at approximately 15 C. Direct acquisition times were set to 15 ms in the presence of 83 kHz Waltz-64 decoupling. Recycle delays were set to 5s. ^{1}H hard pulses were applied at 83 kHz and CP B_1 fields were set to approximately 50 kHz on ^{29}Si and 60 kHz on protons.

S3. UV-visible spectra of compounds 1a, 1b, 2a and 2b

UV-vis spectra were recorded on Varian Cary 5000 (Varian) spectrophotometer.

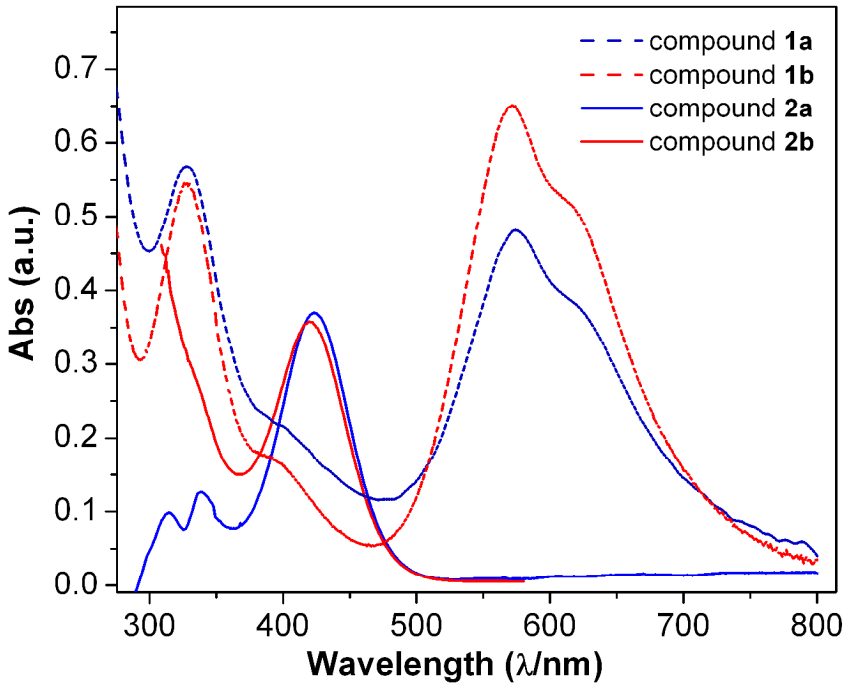


Figure S5. UV-vis spectra of compounds **1a-b** (dotted line) and **2a-b** (solid line) in *n*-hexane.

S4. Cyclic voltammogram of compounds 1a-b

Cyclic voltammograms of 1a

The cyclic voltammetry experiments have been performed at a Metrohm-Autolab potentiostat PGSTAT 101 in combination with Autolab NOVA 10.1.3. All experiments have been performed under argon atmosphere in deoxygenated and anhydrous 0.1 M [*n*-Bu_4N]PF_6 THF solution.
The setup consisted of a glassy carbon (GC) working electrode (WE), a Pt wire as the counter electrode (CE) and a Ag wire as reference electrode (RE). The recorded voltammograms have been referenced to the internal standard $Cp^*_2Fe/Cp^*_2Fe^+$, which was added after the measurement.

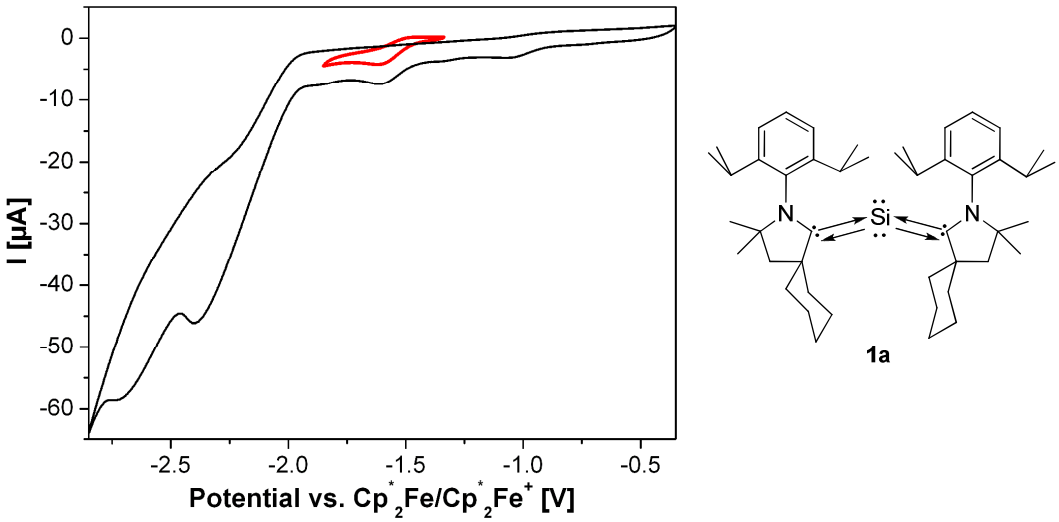


Figure S6: Cyclic voltammogram of $(Cy\text{-}CAAC)_2Si$ (**1a**) in THF solution (0.1 M [*n*-Bu_4N]PF_6); a scan rate of 50 mVs^1 (CE: Pt, WE: GC, RE: Ag) scanned from -0.35 V to -2.85 V. The voltammogram shows three irreversible reductions and one quasi-reversible reduction (red curve).

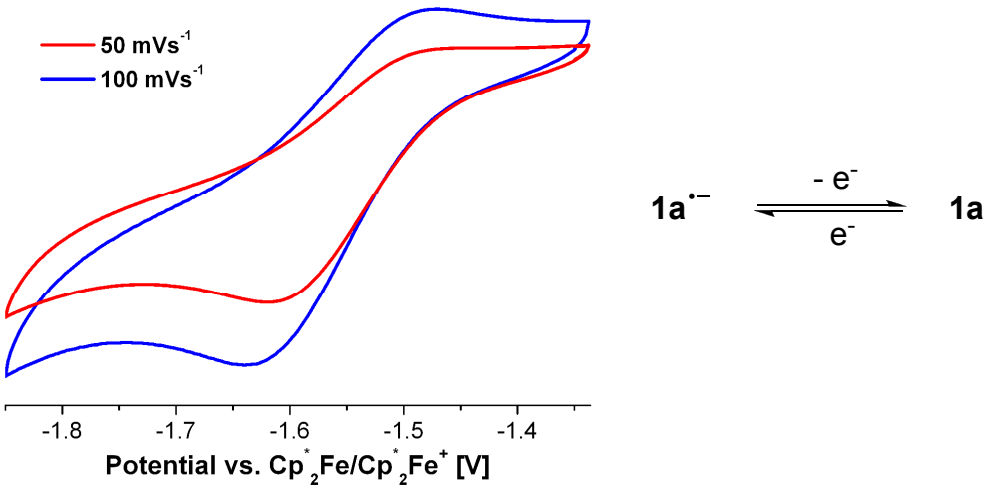


Figure S7: Section cyclic voltammogram of $(Cy\text{-}CAAC)_2Si$ (**1a**) in THF solution (0.1 M [*n*-Bu_4N]PF_6) at indicated scan rates (CE: Pt, WE: GC, RE: Ag).

Compounds **1a-b** were investigated by cyclic voltammetry in 0.1 M [*n*-Bu_4N]PF_6 THF solution (CE: Pt, WE: GC, RE: Ag). The voltammograms are referred against Cp^*_2Fe/ $Cp^*_2Fe^+$ and show a quasi-reversible reduction at $E_{1/2}$ = 1.55 V (**1a**) and 1.50 V (**1b**) which indicate the formation of radical anion (**1a-b**)$^{\bullet-}$. In addition the measurements show three irreversible reductions (E = -1.07, -2.39 and -2.72 V for **1a**, see *Figure S6*).

Cyclic voltammogram of 1b

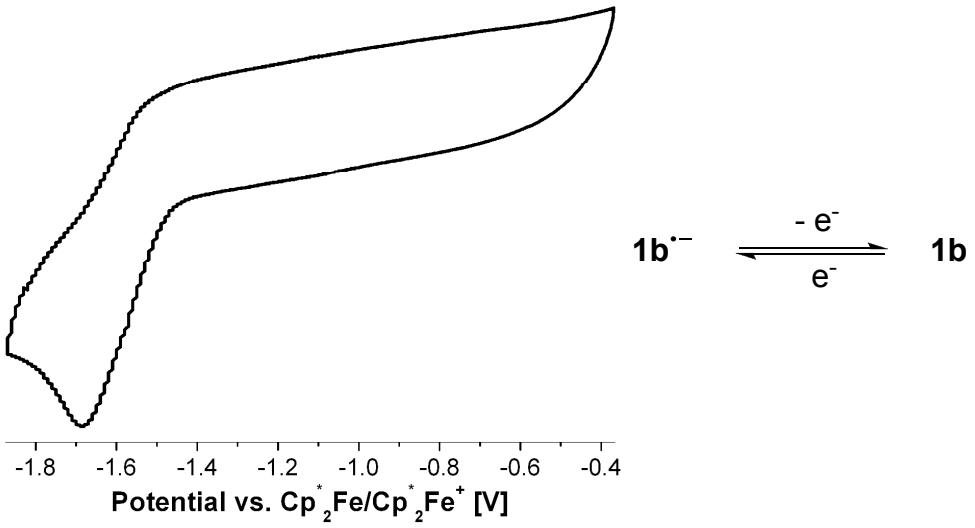


Figure S8: Section cyclic voltammogram of $(Me_2\text{-}CAAC)_2Si$ (**1b**) in THF solution (0.1 M [*n*-Bu_4N]PF_6) at 50 mVs^- scan rates (CE: Pt, WE: GC, RE: Ag); $E_{1/2}$ = 1.50 V.

S6. EPR spectroscopy

Continuous-wave (CW) EPR spectra were recorded at X-band microwave frequencies (9 GHz) using a Bruker ElexSys E500 spectrometer with a Bruker SuperX CW bridge. The spectrometer was equipped with the Bruker SHQ rectangular microwave cavity (Bruker 4122SHQ) and a helium flow cryostat (Oxford Instruments) for low temperature experiments. $(cAAC)_2Si$ (**1a-b**) has diamagnetic singlet spin ground state (S = 0). $(Me_2\text{-}CAAC)_2Si$ (**1b**) was reacted with potassium for thirty minutes to *in situ* generated radical anion $(Me_2\text{-}CAAC)_2Si^{\cdot -}$ (**1b**$^{\cdot -}$). The EPR spectrum of the resultant solution was recorded.

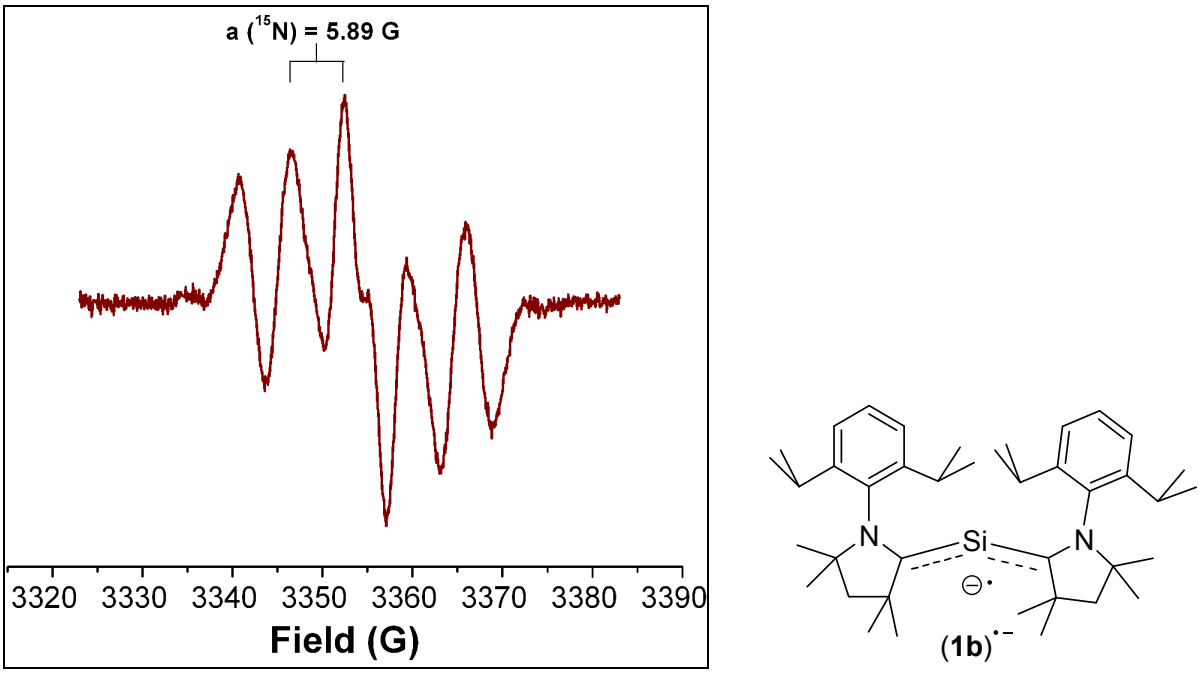


Figure S9. X-band EPR spectrum (left) of THF solution of $(Me_2\text{-CAAC})_2Si^{\cdot-}$ (**1b**$^{\cdot-}$) at 298 K ($\nu_{\mu W}$ = 9.418 GHz, B_{mod} = 0.5 G at 100 kHz). The g = 2.0058, α (^{15}N; I = 1) = 5.89 G and α (^{13}C; I = 1/2) = 40 G (left). The structure of radical anion $(Me_2\text{-CAAC})_2Si$ (**1b**$^{\cdot-}$) (right).

EPR spectrum of $(Me_2\text{-CAAC})_2Si$ (**1b**$^{\cdot-}$) suggests that the radical electron is delocalized between two carbene carbon atoms and one silicon atom. The hyperfine lines originate due to the coupling of a radical electron with two nitrogen nuclei (^{15}N; I = 1).

S6. Crystal data of 2a and 2b

All experiments were performed on Bruker SMART APEX II systems based on D8 three-circle goniometers with Incoatec microfocus X-ray sources (IμS) and Incoatec QUAZAR mirror optics.[S2] Suitable single crystals of **2a** and **2b** were mounted at low temperature in inert oil under argon atmosphere by applying the X–Temp2 device. [S3-4] The data were collected at 100 K crystal temperature (Mo source: Bruker CRYOFLEX; Ag source Oxford Cryosystems CRYOSTREAM 700), 50 kV and 600 μA for both machines and an appropriate 0.5° omega scan strategy for the wavelength in question. Data reduction was performed with SAINT v7.68A[S5] out of the APEX II v2.2012.2 0 program package. [S6] SADABS (version 2014/4) was employed for the incident beam scaling, determination of the spherical harmonic coefficients, outlier rejection and determination of the error model parameters. All the structures were solved by direct methods with SHELXS.[S7] They were refined by full-matrix least-squares against F^2 using SHELXL-2014/3 with the help of the SHELXle graphical user interface.[S8] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms, except H(1), were set to idealized positions and refined using a riding model with their isotropic displacement parameters constrained to be 1.5 times the equivalent isotropic displacements of the atoms to which they

were attached for methyl hydrogens and 1.2 times for all other hydrogens. The coordinates of H(1) were freely refined.

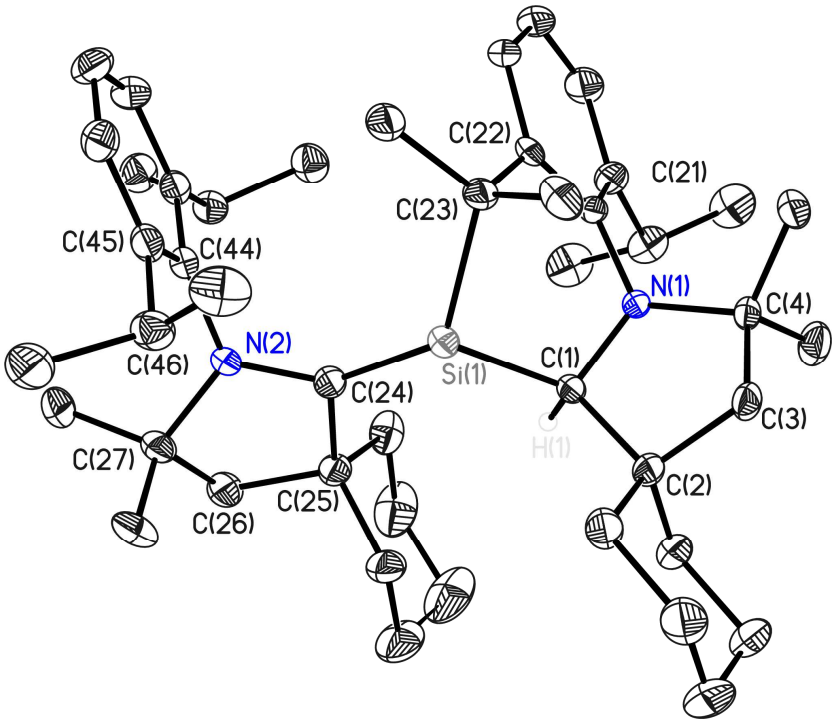


Figure S10: Ortep picture of compound **2a**.

Table S1: Refinement parameters of compound **2a**.

2a		
Empirical formula	$C_{46}H_{70}N_2Si$	
CCDC number	1023881	
Formula weight	679.13	
Temperature	100(2) K	
Wavelength	0.56086 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 9.533(2) Å	α = 90°
	b = 18.139(2) Å	β = 93.00(2)°
	c = 22.863(3) Å	γ = 90°
Volume	3948.0(11) Å^3	

Z	4
Density (calculated)	1.143 Mg/m^3
Absorption coefficient	0.057 mm^{-1}
F(000)	1496
Crystal size	0.100 x 0.090 x 0.070 mm^3
Theta range for data collection	1.663 to 19.809°.
Index ranges	-11<=h<=11, -21<=k<=21, -27<=l<=27
Reflections collected	61908
Independent reflections	7289 [*R*(int) = 0.0870]
Completeness to theta = 19.665°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4249 and 0.4004
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7289 / 0 / 457
Goodness-of-fit on F^2	1.040
Final R indices [*I*>2sigma(I)]	*R*1 = 0.0540, *wR*2 = 0.1400
R indices (all data)	*R*1 = 0.0831, *wR*2 = 0.1562
Extinction coefficient	n/a
Largest diff. peak and hole	0.445 and -0.436 e.$Å^{-3}$

checkCIF/PLATON (standard)

Structure factors have been supplied for datablock(s) P21n_a

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No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report

Structure factor report

Datablock: P21n_a

Bond precision: C-C = 0.0036 A Wavelength=0.56086
Cell: a=9.533(2) b=18.139(2) c=22.863(3)

alpha=90 beta=93.00(2) gamma=90

Temperature: 100 K

	Calculated	Reported
Volume	3948.0(11)	3948.0(11)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C46 H70 N2 Si	C46 H70 N2 Si
Sum formula	C46 H70 N2 Si	C46 H70 N2 Si
Mr	679.13	679.13
Dx,g cm-3	1.143	1.143
Z	4	4
Mu (mm-1)	0.057	0.057
F000	1496.0	1496.0
F000'	1496.29	
h,k,lmax	11,21,27	11,21,27
Nref	7300	7289
Tmin,Tmax	0.994,0.996	0.400,0.425
Tmin'	0.994	

Correction method= MULTI-SCAN

Data completeness= 0.998 Theta(max)= 19.809

R(reflections)= 0.0540(5196) wR2(reflections)= 0.1562(7289)

S = 1.040 Npar= 457

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

Crystal system given = monoclinic

PLAT410_ALERT_2_B Short Intra H...H Contact H1 .. H30B .. 1.89 Ang.

Alert level C

RADNW01_ALERT_1_C The radiation wavelength lies outside the expected range for the supplied radiation type. Expected range 0.56080-0.56085 Wavelength given = 0.56086

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Alert level G

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PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 5 Note

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully

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   3 ALERT level C = Check. Ensure it is not caused by an omission or
oversight
   3 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   2 ALERT type 2 Indicator that the structure model may be wrong or
deficient
   2 ALERT type 3 Indicator that the structure quality may be low
   2 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
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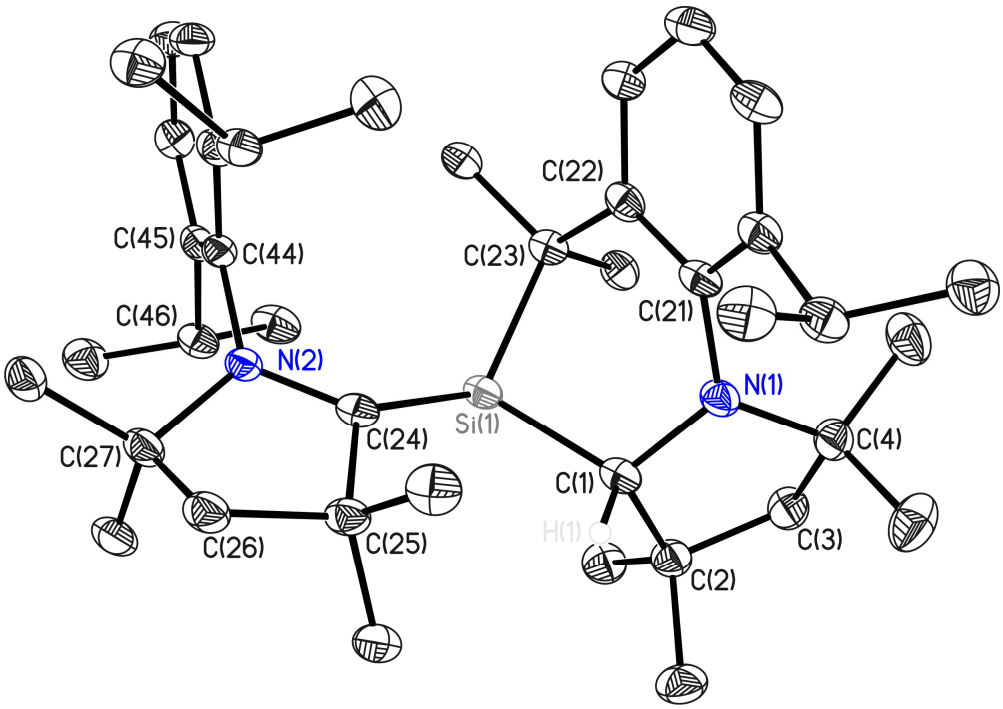

Figure S11: Ortep picture of compound **2b**.

Table S2: Refinement parameters of compound **2b**.

2b	
Empirical formula	C_{40} H_{62} N_2 Si
CCDC number	1023882
Formula weight	599.00
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic

Space group	$P2_1/n$	
Unit cell dimensions	a = 9.273(2) Å	α = 90°
	b = 16.959(2) Å	β = 90.75(2)°
	c = 22.383(3) Å	γ = 90°
Volume	3519.7(10) Å^3	
Z	4	
Density (calculated)	1.130 Mg/m^3	
Absorption coefficient	0.096 mm^{-1}	
F(000)	1320	
Crystal size	0.120 x 0.100 x 0.040 mm^3	
Theta range for data collection	1.507 to 26.505°.	
Index ranges	-11<=h<=11, -21<=k<=21, -28<=l<=27	
Reflections collected	59445	
Independent reflections	7255 [R(int) = 0.0857]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7454 and 0.6614	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7255 / 0 / 408	
Goodness-of-fit on F^2	1.036	
Final R indices [I>2sigma(I)]	R1 = 0.0489, wR2 = 0.1063	
R indices (all data)	R1 = 0.0908, wR2 = 0.1235	
Extinction coefficient	0.0045(5)	
Largest diff. peak and hole	0.294 and -0.328 e.Å^{-3}	

checkCIF/PLATON (standard)

Structure factors have been supplied for datablock(s) P21n_b

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report

Structure factor report

Datablock: P21n_b

Bond precision: C-C = 0.0030 A Wavelength=0.71073

Cell: a=9.273(2) b=16.959(2) c=22.383(3)
alpha=90 beta=90.75(2) gamma=90

Temperature: 100 K

	Calculated	Reported
Volume	3519.7(10)	3519.7(10)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C40 H62 N2 Si	C40 H62 N2 Si
Sum formula	C40 H62 N2 Si	C40 H62 N2 Si
Mr	599.01	599.00
Dx,g cm-3	1.130	1.130
Z	4	4
Mu (mm-1)	0.096	0.096
F000	1320.0	1320.0
F000'	1320.71	
h,k,lmax	11,21,28	11,21,28
Nref	7295	7255
Tmin,Tmax	0.989,0.996	0.661,0.745
Tmin'	0.989	

Correction method= MULTI-SCAN

Data completeness= 0.995 Theta(max)= 26.505

R(reflections)= 0.0489(4878) wR2(reflections)= 0.1235(7255)

S = 1.036 Npar= 408

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level G

PLAT793_ALERT_4_G The Model has Chirality at C1 ..... S Verify
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 41 Note

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
0 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
2 **ALERT level G** = General information/check it is not something unexpected

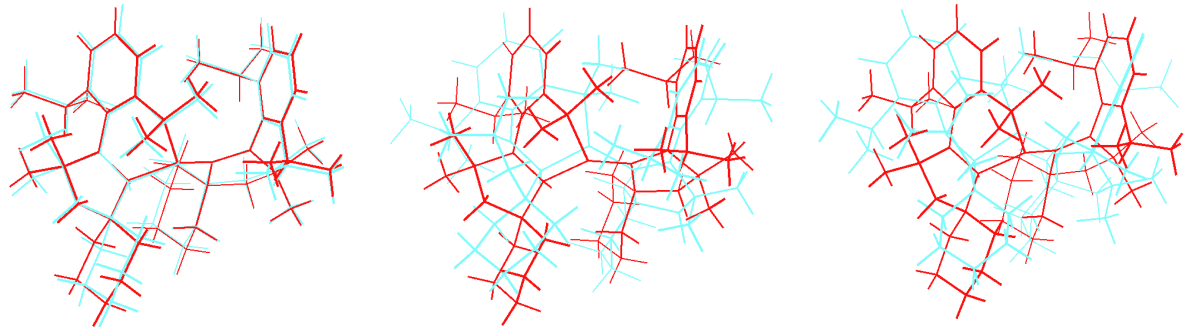
0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
0 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low

```
2 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check
```

S7. Theoretical calculation on 2a

Computational Details:

All calculations were performed in Gaussian09 quantum package.[S9] All intermediates are optimized with the global-hybrid meta-GGA to DFT functional, U/R-M06-2X[S10] with SVP[S11] basis sets for all atoms. Geometry optimization of **2a** also carried out using CASSCF(2,2) [S12] level with SVP basis sets. Geometry was fully optimized without symmetry constraints. Harmonic force constants were computed at the optimized geometry to confirm if the optimized geometry is located at minima or saddle point on the potential energy surface. For further validation of the energy change, we have also performed single point calculation of optimized geometry incorporating higher basis set TZVP[S13] for all atoms. Solvation energies in THF (ε = 7.426) were evaluated by a self-consistent reaction field (SCRF) approach using the SMD continuum solvation model.[S14] NBO analysis and Mulliken spin density calculations were performed at U/R-M06-2X/TZVP//U/R-M06-2X/SVP level. All the energy values reported in the manuscript are at U/R-M06-2X/TZVP//U/R-M06-2X/SVP level. The wavefunction file generated from the quantum code was used to perform QTAIM[S15] analysis in the AIMALL program suite. We have applied Bader's AIM (Atoms-in-molecule)[S16] concept to characterize the electron distribution in **2a**. Any bonded pair of atoms has a bond path, *i.e;* a connecting line with maximum electron density. The bond critical point (BCP) is a point on this line where the gradient $\nabla\rho(r)$ of the density is equal to zero. The magnitude of the electron density, $\rho(r)$ and its Laplacian, $\nabla^2\rho(r)$ at the BCP provide information about the strength and type of bond. The Laplacian indicates whether the density is locally concentrated ($\nabla^2\rho<0$) or depleted ($\nabla^2\rho>0$). Optimized geometries and orbital diagrams are rendered in the Chemcraft visualization software.[S17]



Closed-shell singlet **Diradical singlet** **triplet**

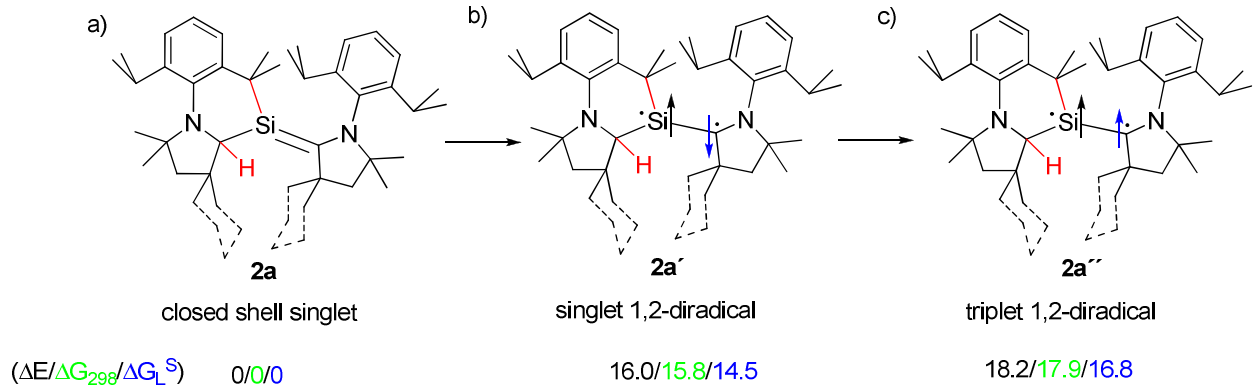
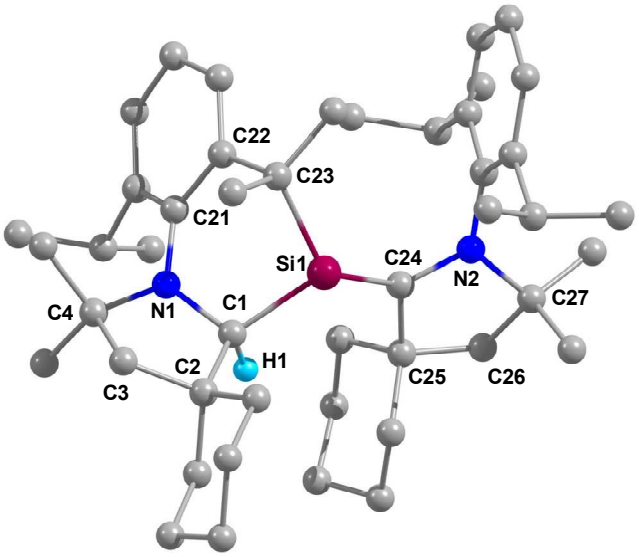


Figure S12: Superposition of crystal structure of **2a** with optimized geometries of different spin states at U/R-M06-2X/SVP level (top). Calculated energy values (bottom) of the a) singlet (**2a**), b) singlet 1,2-diradical (**2a´**) and c) triplet 1,2 diradical (**2a´´**) species implying the preference for singlet ground state (**2a**) (bottom).

Table S3. Calculated geometrical parameters in closed-shell singlet, triplet and diradical singlet electronic states of compound **2a**.



	Crystal Structure	R/U-M06-2X/SVP		
		Singlet	Triplet	Singlet

				diradical
d (Si1-C1)	1.95	1.95	1.94	1.93
d (Si1-C24)	1.82	1.81	1.88	1.84
d (C1-N1)	1.46	1.46	1.47	1.47
d (C24-N2)	1.38	1.37	1.40	1.39
A (C23-Si1-C1)	101.8	100.7	103.8	106.4
A (C2-C1-N1)	104.6	106.0	101.3	101.0
A (C2-C1-Si1)	120.8	118.6	118.5	117.1
A (N1-C1-Si1)	111.7	111.2	109.3	108.7
A (C23-Si1-C24)	126.4	127.1	116.3	112.5
A (C24-Si1-C1)	112.7	114.3	120.7	118.1
A (C25-C24-Si1)	122.4	122.0	131.0	126.3
A (N2-C24-Si1)	129.7	129.9	119.8	126.0
A (C25-C24-N2)	106.2	106.9	108.2	107.6
A (C4-N1-C1)	114.6	112.9	110.5	111.9
A (C21-N1-C1)	121.0	122.5	121.7	121.4
A (C24-N2-C27)	113.5	113.5	111.0	110.3

Table S4. BCP parameters for **2a**

Atoms	ρ(r), a.u.	$\nabla^2\rho$(r), a.u.	ε	DI
Si1-C24	+0.12	+0.42	+0.51	0.99
Si1-C23	+0.10	+0.16	+0.13	0.58
Si1-C1	+0.10	+0.19	+0.15	0.56
C24-N2	+0.30	-0.77	+0.06	1.16

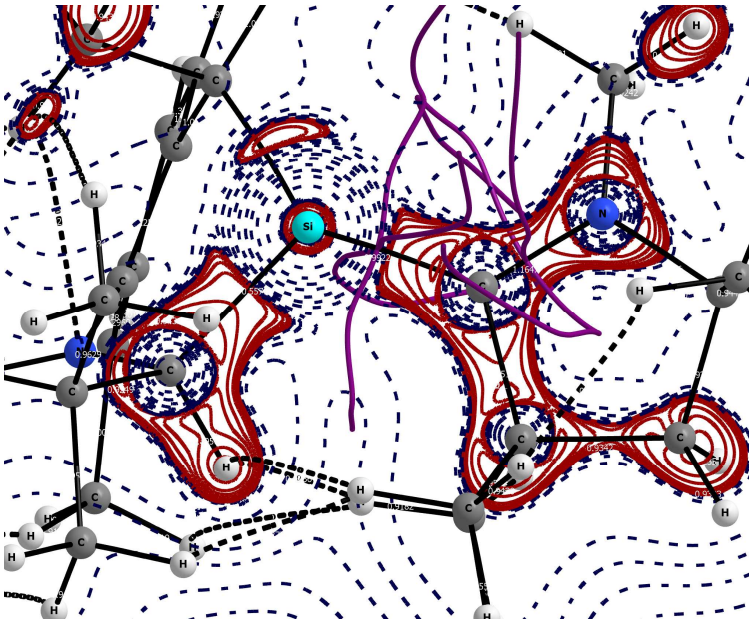
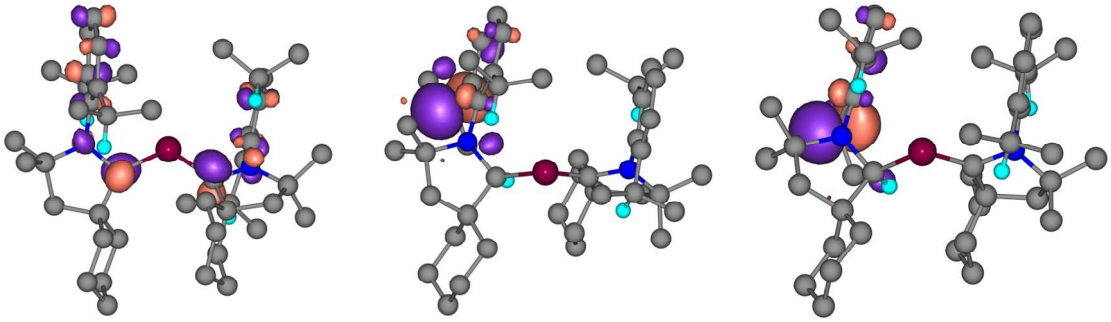


Figure S13. Contour plot of Laplacian distribution [$\nabla^2\rho$(r)] in the Si1-C24-N2 plane of **2a**. For other conventions refer Figure 1. Solid lines indicate the areas of charge concentration ($\nabla^2\rho$(r) < 0) while dotted lines mean the charge depletion ($\nabla^2\rho$(r) > 0). The range of contours of the Laplacian is -8×10^2 to $+8\times10^2$. Solid lines connecting atomic nuclei (black) are the bond paths and those lines (purple) separating the atomic basins indicates the zero-flux surface crossing the molecular plane.



LUMO [**(1a)**$^{-}$] SOMO (**IM$_1$**) LUMO (**IM$_1$**)

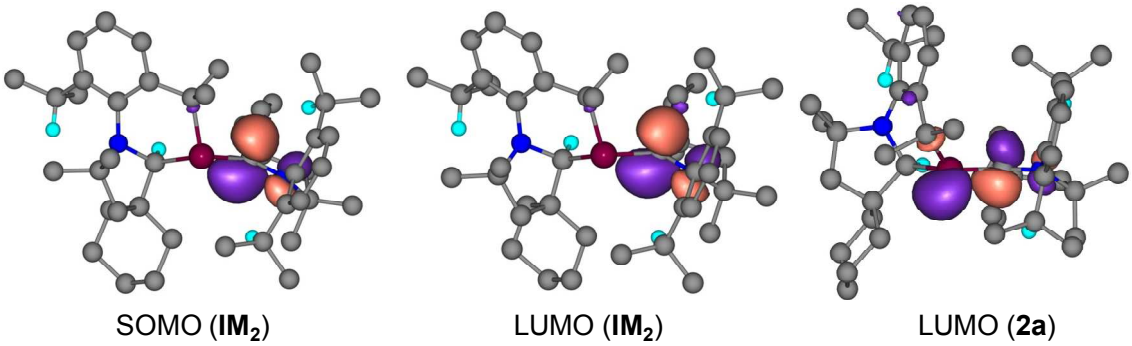


Figure S14. KS-MO of some intermediates (isosurface = 0.006 au). Hydrogen atoms are omitted for clarity.

Table S5. The energy changes (in kcal/mol) for all steps involved in the transformation **1a→2a**. The term ΔE_e and ΔG_{298} are electronic energy and Gibbs free energy change at M06-2X/SVP level, ΔG_L^S is the Gibbs free energy change in solvent at M06-2X/TZVP//M06-2X/SVP level.

Steps	ΔE_e	ΔG_{298}	ΔG_L^S
1a → (1a)$^{\cdot-}$	-8.7	-12.0	-13.2
(1a)$^{\cdot-}$ → IM$_1$	17.4	16.4	17.9
IM$_1$ → IM$_2$	-24.7	-22.6	-23.3
IM$_2$ → 2a	-7.6	-4.8	-2.6

Scheme S2. Energy change (ΔG_L^S at U/R-M06-2X/TZVP//U/R-M06-2X/SVP level) of hydrogen transfer step for model systems.

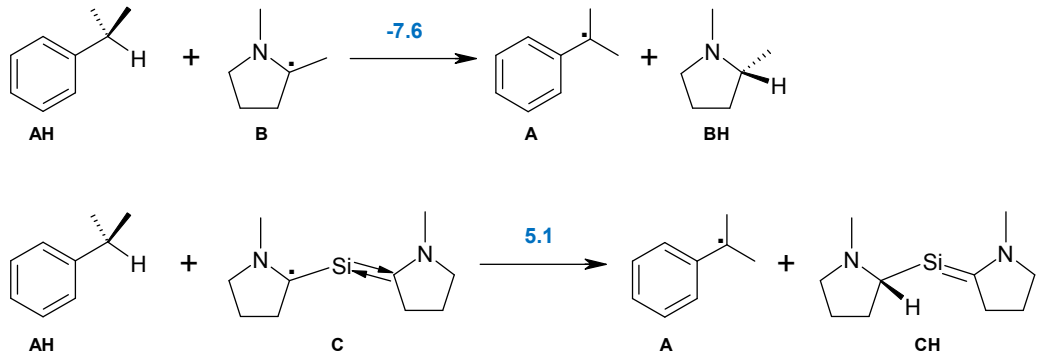


Table S6. NPA charge of selected atoms for all species shown in Scheme 3 (see text).

	Si1	C1	N1	C23	C24	N2	H1
1a	0.536	-0.157	-0.478	-0.254	-0.158	-0.478	0.220
(1a)$^{\cdot-}$	0.480	-0.375	-0.537	-0.256	-0.358	-0.534	0.234
IM$_1$	0.498	-0.415	-0.551	0.150	-0.492	-0.567	0.166
IM$_2$	0.728	-0.441	-0.530	-0.464	-0.228	-0.537	0.178
2a(closed shell singlet)	1.280	-0.454	-0.527	-0.458	-0.288	-0.498	0.201
2a′(diradical singlet)	1.426	-0.519	-0.520	-0.529	-0.317	-0.488	0.208
2a″(triplet)	1.539	-0.531	-0.511	-0.574	-0.370	-0.467	0.212

Table S7. Cartesian coordinates (in Å) of the optimized structures of reactant, intermediates and product at R/U-M06-2X/SVP level of theory.

1a

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XYZ

Si	3.85581	1.78191	2.00468
N	3.01280	0.26578	4.11753
C	3.08947	0.27243	2.75138
N	4.66667	2.87707	-0.36562
C	2.17099	-0.84298	2.23969
C	2.09846	-0.74343	4.71274
C	3.80906	1.12537	4.94738
C	5.12251	0.73486	5.29399

C	5.84894	1.53633	6.18056
H	6.85973	1.23540	6.46401
C	5.31738	2.71584	6.68607
H	5.89699	3.32728	7.37949
C	4.05606	3.12985	6.27460
H	3.66021	4.08253	6.63252
C	3.28518	2.36353	5.39479
C	3.02168	-2.05185	1.78278
H	3.62882	-2.42304	2.62281
H	3.73527	-1.69877	1.02794
C	1.27118	-0.37905	1.08158
H	1.89707	0.07371	0.29669
H	0.62212	0.43020	1.44921
C	2.88799	-1.87668	5.37858
H	2.19007	-2.62230	5.78632
H	3.48399	-1.47690	6.21163
H	3.56505	-2.38418	4.67980
C	1.16796	-0.14660	5.76597
H	0.51416	-0.94039	6.15628
H	0.53290	0.63968	5.34029
H	1.73879	0.27116	6.60843
C	5.82780	-0.45574	4.66168
H	5.10801	-0.96858	4.00912
C	6.36449	-1.45648	5.68948

H	5.57691	-1.83850	6.35230
H	7.13881	-0.99486	6.32078
H	6.82734	-2.31375	5.17795
C	6.97413	0.04869	3.77449
H	7.41329	-0.78193	3.20005
H	7.77184	0.49582	4.38823
H	6.60951	0.81103	3.07093
C	1.95806	2.94628	4.92307
H	1.50336	2.22468	4.22740
C	0.99705	3.21344	6.09017
H	0.01167	3.51993	5.70814
H	1.37364	4.03587	6.71728
H	0.86023	2.33901	6.73852
C	2.17073	4.25742	4.14983
H	2.84466	4.11444	3.29436
H	2.59072	5.03585	4.80659
H	1.20644	4.62680	3.76779
C	4.49034	1.67811	0.26939
C	6.12498	1.45014	-1.49711
H	7.12830	1.54544	-1.05296
H	6.24936	0.99408	-2.48943
C	5.49161	2.84337	-1.60129
C	4.04581	4.09293	0.07909
C	4.75012	4.97678	0.93382

C	4.14638	6.19166	1.27325
H	4.68214	6.88482	1.92508
C	2.87684	6.52538	0.81678
H	2.42937	7.48258	1.08916
C	2.16800	5.61690	0.04122
H	1.15103	5.85705	-0.27618
C	2.72311	4.38602	-0.32347
C	6.56053	3.93336	-1.62655
H	7.13880	3.84489	-2.55804
H	7.25474	3.83292	-0.78352
H	6.10685	4.93514	-1.59972
C	4.61884	3.01832	-2.84963
H	4.13499	4.00549	-2.83109
H	3.83848	2.25070	-2.92752
H	5.24765	2.96412	-3.75016
C	6.10131	4.65659	1.56221
H	6.41106	3.66337	1.20307
C	5.99787	4.57943	3.09375
H	5.72646	5.55935	3.51772
H	6.97053	4.28867	3.51991
H	5.25129	3.83826	3.40953
C	7.17045	5.69480	1.19302
H	7.24349	5.86564	0.11173
H	8.15610	5.37216	1.56084

H	6.94623	6.66236	1.66739
C	1.83164	3.38197	-1.03907
H	2.43232	2.48767	-1.25433
C	1.25254	3.91677	-2.35227
H	0.58981	4.77605	-2.16887
H	0.65100	3.13881	-2.84594
H	2.03357	4.24075	-3.05275
C	0.69439	2.95622	-0.10044
H	0.00611	3.79655	0.08143
H	1.09804	2.62321	0.86669
H	0.11406	2.13231	-0.54447
C	1.31415	-1.19896	3.47573
H	0.36603	-0.64062	3.42723
H	1.06124	-2.26695	3.53561
C	2.19095	-3.18496	1.17756
C	0.43346	-1.51796	0.50055
H	-0.17971	-1.14011	-0.33184
H	-0.27360	-1.88514	1.26547
C	1.31249	-2.67800	0.03480
H	0.69439	-3.49560	-0.36604
H	1.95758	-2.33593	-0.79377
C	5.23219	0.61604	-0.55031
C	6.09805	-0.30157	0.32978
C	4.21772	-0.23715	-1.34792

C	6.75623	-1.42670	-0.46827
H	5.47617	-0.71952	1.13694
H	6.86013	0.31542	0.82959
C	4.86867	-1.38012	-2.12955
H	3.49870	-0.66327	-0.63727
H	3.63197	0.40810	-2.02077
C	5.71854	-2.26246	-1.21629
H	7.34950	-2.06221	0.20689
H	7.46784	-0.99815	-1.19622
H	4.08625	-1.97712	-2.62364
H	5.50330	-0.97755	-2.93714
H	6.20823	-3.05771	-1.79852
H	5.06169	-2.76666	-0.48551
H	2.86325	-3.98169	0.82270
H	1.55153	-3.64484	1.94996

(1a)$^{\cdot-}$ 119

XYZ

Si	3.83594	1.81460	2.01440
N	2.96559	0.29220	4.17187
C	3.10023	0.27597	2.74655
N	4.73543	2.93257	-0.36216
C	2.21053	-0.86869	2.24799
C	2.11629	-0.76798	4.72710
C	3.75900	1.10838	5.02503

C	5.09169	0.74179	5.34229
C	5.80285	1.49394	6.28159
H	6.82686	1.20327	6.53005
C	5.24036	2.61109	6.88991
H	5.80804	3.18306	7.62676
C	3.96224	3.01297	6.52072
H	3.53885	3.92391	6.95153
C	3.21526	2.29493	5.58081
C	3.02718	-2.09437	1.77210
H	3.64719	-2.47518	2.59862
H	3.72964	-1.74294	1.00585
C	1.29693	-0.40440	1.09627
H	1.91976	0.06028	0.31543
H	0.65564	0.40515	1.47724
C	2.94063	-1.90455	5.35685
H	2.27563	-2.70034	5.72787
H	3.51701	-1.51428	6.20939
H	3.64500	-2.34730	4.64105
C	1.15039	-0.26450	5.80298
H	0.52838	-1.09952	6.16233
H	0.48616	0.51249	5.40358
H	1.70018	0.14884	6.66247
C	5.81761	-0.38578	4.62432
H	5.09539	-0.86665	3.95100

C	6.39842	-1.43461	5.57781
H	5.63256	-1.86896	6.23469
H	7.18149	-0.99762	6.21759
H	6.86265	-2.25253	5.00473
C	6.93269	0.20003	3.74879
H	7.40354	-0.59056	3.14259
H	7.71430	0.66410	4.37273
H	6.52181	0.96345	3.07102
C	1.88828	2.88186	5.11903
H	1.45911	2.17592	4.39255
C	0.90489	3.10081	6.27573
H	-0.07265	3.42883	5.88876
H	1.26995	3.89191	6.95008
H	0.75214	2.19491	6.87735
C	2.11277	4.21217	4.38532
H	2.79034	4.07033	3.53116
H	2.53848	4.96788	5.06618
H	1.15454	4.60067	4.00442
C	4.49504	1.68268	0.29798
C	6.11448	1.43550	-1.48580
H	7.10736	1.51282	-1.01343
H	6.26075	0.98273	-2.47909
C	5.51793	2.84541	-1.59948
C	4.10811	4.15001	0.01928

C	4.81400	5.10286	0.79755
C	4.22612	6.34688	1.05124
H	4.77456	7.08203	1.64588
C	2.95012	6.65172	0.59283
H	2.50810	7.62875	0.79890
C	2.22749	5.68466	-0.09833
H	1.20420	5.90097	-0.41617
C	2.77659	4.43074	-0.38028
C	6.63101	3.89409	-1.68351
H	7.19853	3.75930	-2.61796
H	7.32716	3.79729	-0.84054
H	6.21196	4.91212	-1.68032
C	4.64533	3.01478	-2.85582
H	4.19155	4.01757	-2.85785
H	3.83757	2.27311	-2.89969
H	5.25877	2.91427	-3.76513
C	6.14887	4.78992	1.46003
H	6.43850	3.77858	1.13808
C	6.00041	4.75729	2.98837
H	5.71500	5.74952	3.37570
H	6.95741	4.47398	3.45544
H	5.24098	4.01999	3.28610
C	7.24620	5.79194	1.07958
H	7.35908	5.90190	-0.00718

H	8.21438	5.47493	1.49804
H	7.02260	6.78777	1.49467
C	1.88336	3.37957	-1.02140
H	2.49582	2.48231	-1.18256
C	1.28271	3.83057	-2.35641
H	0.60566	4.68809	-2.21571
H	0.69060	3.01537	-2.80125
H	2.05399	4.12759	-3.08001
C	0.76258	2.99511	-0.04688
H	0.08220	3.84663	0.11947
H	1.18918	2.68950	0.92021
H	0.17018	2.15768	-0.44968
C	1.34547	-1.22472	3.48119
H	0.40191	-0.65751	3.42665
H	1.08091	-2.29193	3.54452
C	2.18172	-3.21974	1.16978
C	0.44618	-1.52935	0.50416
H	-0.16563	-1.14126	-0.32645
H	-0.26298	-1.89797	1.26809
C	1.30912	-2.69798	0.02905
H	0.68089	-3.50609	-0.37998
H	1.96123	-2.35590	-0.79424
C	5.18710	0.61504	-0.55690
C	6.03838	-0.33175	0.31074

C	4.18377	-0.22696	-1.38176
C	6.68157	-1.47043	-0.48321
H	5.40980	-0.73143	1.12235
H	6.81091	0.27163	0.81072
C	4.82360	-1.37137	-2.17273
H	3.45750	-0.65491	-0.67887
H	3.60553	0.42988	-2.05009
C	5.64130	-2.28069	-1.25627
H	7.25225	-2.12623	0.19441
H	7.41193	-1.05339	-1.20096
H	4.04094	-1.95129	-2.68964
H	5.48244	-0.96975	-2.96267
H	6.12552	-3.08246	-1.83747
H	4.96097	-2.77569	-0.54082
H	2.83923	-4.02886	0.81052
H	1.53375	-3.66917	1.94274

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XYZ

Si	0.99811	8.85253	16.77839
N	1.54184	10.47627	14.37098
N	2.38105	7.71024	18.91368
C	2.41598	11.45745	14.92528
C	3.70460	11.71144	14.33179
C	0.67532	10.79668	13.23196

C	4.24652	11.04549	13.14402
C	2.93468	9.74084	20.17272
C	1.45847	9.05172	14.83249
H	2.42889	8.55895	14.67468
C	2.01073	8.71610	19.83861
C	0.72649	8.72934	20.43190
C	0.45828	8.39325	13.81440
C	4.52434	12.73140	14.86389
H	5.50801	12.90028	14.42343
C	-0.29314	9.60514	13.23935
H	-0.72800	9.43047	12.24293
H	-1.12376	9.84382	13.92452
C	2.33865	7.88968	17.48499
C	4.31035	9.80201	19.53546
H	4.47001	8.83212	19.04765
C	2.00796	12.29670	16.00369
C	2.97674	6.42629	19.27548
C	0.40033	9.73324	21.35105
H	-0.59428	9.73738	21.80451
C	4.04951	6.28215	18.17241
H	4.28591	5.22509	17.97076
H	4.98073	6.75904	18.52296
C	3.50014	7.03277	16.92758
C	2.56481	10.73378	21.08289

H	3.27673	11.52588	21.32805
C	1.30728	10.73349	21.67891
H	1.03340	11.51620	22.38948
C	-0.32134	7.68831	20.08154
H	0.08715	7.09937	19.24823
C	0.63745	12.26222	16.67295
H	0.07399	11.42581	16.23865
C	5.11508	11.83313	12.20735
H	6.19274	11.73304	12.44809
H	4.87295	12.90491	12.21433
H	4.99412	11.45609	11.17837
C	2.87499	13.28382	16.49433
H	2.54531	13.90040	17.33292
C	4.12900	13.49941	15.94494
H	4.79223	14.26518	16.35256
C	4.35961	10.88103	18.44931
H	5.35445	10.92019	17.97578
H	4.14689	11.87487	18.87731
H	3.61408	10.67577	17.66667
C	-0.11238	12.09567	13.43127
H	0.56860	12.95508	13.53093
H	-0.74158	12.03827	14.32782
H	-0.76275	12.27479	12.56060
C	5.42768	10.00661	20.56239

H	6.41128	9.91408	20.07626
H	5.37219	9.26704	21.37579
H	5.38161	11.00877	21.01668
C	1.21521	7.60826	12.71404
H	1.92687	8.26052	12.19291
H	1.82394	6.83309	13.21152
C	-0.53168	7.41080	14.46923
H	-1.10666	7.93682	15.24539
H	0.04294	6.63300	15.00250
C	1.41191	10.95087	11.88191
H	0.68156	11.06193	11.06382
H	2.05959	10.09729	11.65471
H	2.04228	11.85318	11.89719
C	3.59450	6.44319	20.67062
H	4.08947	5.48069	20.87214
H	2.82422	6.60619	21.43992
H	4.33928	7.24729	20.76234
C	4.61230	7.90699	16.30028
H	4.15919	8.58251	15.56010
H	5.03362	8.56058	17.07840
C	1.95815	5.27398	19.17932
H	1.37067	5.37843	18.25503
H	1.26188	5.29385	20.02938
H	2.46404	4.29499	19.17372

C	2.99755	6.02443	15.86998
H	2.27700	5.33883	16.34112
H	2.42625	6.58677	15.11914
C	-1.47279	6.74638	13.46271
H	-2.16024	6.06451	13.98820
H	-2.10404	7.51381	12.98007
C	-0.59775	6.76469	21.27382
H	-1.27258	5.94294	20.98543
H	-1.07835	7.32362	22.09350
H	0.32851	6.32661	21.67434
C	0.30361	6.91686	11.69727
H	-0.24916	7.67182	11.11182
H	0.91426	6.35356	10.97310
C	-1.62082	8.33114	19.58857
H	-1.40878	8.97892	18.72579
H	-2.10597	8.92314	20.38199
H	-2.33181	7.55161	19.27136
C	0.73718	12.01804	18.18436
H	-0.26929	11.86965	18.60666
H	1.19579	12.87863	18.69997
H	1.31684	11.11500	18.41312
C	-0.12766	13.57691	16.44863
H	-1.15674	13.48034	16.82922
H	-0.17627	13.86810	15.39197

H	0.34906	14.40346	16.99932
C	-0.69264	5.98940	12.39003
H	-1.37423	5.52980	11.65566
H	-0.13713	5.16459	12.87074
C	4.10442	5.23597	15.16711
H	4.60706	4.56331	15.88484
H	3.66455	4.58813	14.39086
C	5.72067	7.09602	15.62562
H	6.25168	6.48639	16.37985
H	6.47235	7.77406	15.18762
C	5.14454	6.17096	14.55499
H	4.65860	6.78491	13.77531
H	5.94414	5.59652	14.05912
C	4.30508	9.56963	12.94828
H	4.28992	9.30609	11.87701
H	5.25311	9.16734	13.35979
H	3.48758	9.04731	13.44803

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XYZ

Si	1.83571	9.63661	16.74853
N	1.44376	10.78753	14.14538
N	2.56121	7.62336	18.67098
C	2.38806	11.83287	14.28460
C	2.97099	12.18953	15.52196

C	0.00654	11.15872	14.26025
C	2.99594	11.30064	16.77438
C	3.07336	9.07045	20.59786
C	1.68685	9.46402	14.77178
H	2.57561	9.04163	14.26522
C	2.12352	8.40103	19.78137
C	0.74941	8.47477	20.12041
C	0.41245	8.71099	14.29395
C	3.69064	13.39859	15.57073
H	4.11052	13.71831	16.52643
C	-0.66319	9.79176	14.52740
H	-1.55932	9.65859	13.90210
H	-0.97505	9.73622	15.58169
C	2.90873	8.13046	17.39196
C	4.56486	9.10719	20.28861
H	4.69727	8.67331	19.28796
C	2.73030	12.55500	13.10547
C	2.77626	6.16757	18.75173
C	0.36039	9.16322	21.27335
H	-0.70122	9.21352	21.52733
C	4.06735	6.05554	17.92722
H	4.24045	5.03176	17.56010
H	4.91581	6.32372	18.58124
C	3.92385	7.10960	16.79996

C	2.63580	9.74998	21.74044
H	3.37097	10.25550	22.37125
C	1.29189	9.79379	22.08899
H	0.97122	10.32666	22.98639
C	-0.33328	7.83068	19.27314
H	0.16166	7.43337	18.37799
C	2.46387	11.93276	11.74054
H	1.49133	11.43698	11.77421
C	4.48369	10.96395	16.97815
H	5.06994	11.85069	17.29089
H	4.93035	10.59185	16.04550
H	4.60687	10.18779	17.74264
C	3.45255	13.74313	13.20787
H	3.69184	14.31786	12.31151
C	3.89560	14.19132	14.45131
H	4.44087	15.13406	14.53629
C	5.09835	10.54776	20.27459
H	6.10348	10.57722	19.82592
H	5.18076	10.94232	21.29997
H	4.45029	11.21958	19.70054
C	-0.27925	12.13850	15.40884
H	0.20694	13.11058	15.23127
H	0.08413	11.72353	16.36041
H	-1.36570	12.30231	15.49309

C	5.40636	8.30299	21.28873
H	6.47652	8.41181	21.05283
H	5.17174	7.23196	21.28568
H	5.24888	8.67788	22.31269
C	0.54767	8.34033	12.80095
H	0.79488	9.24255	12.22076
H	1.41618	7.66188	12.70783
C	0.06572	7.43609	15.07186
H	-0.03876	7.68538	16.14047
H	0.90468	6.72952	14.98535
C	-0.54616	11.78847	12.97333
H	-1.60458	12.05112	13.12527
H	-0.49029	11.09172	12.12400
H	-0.00343	12.71153	12.71716
C	2.94177	5.65634	20.17691
H	3.15247	4.57613	20.15574
H	2.02492	5.81986	20.76259
H	3.76304	6.16407	20.69314
C	5.28183	7.78006	16.50365
H	5.10484	8.58769	15.77685
H	5.66240	8.26043	17.41847
C	1.62883	5.37694	18.08687
H	1.27173	5.89440	17.18747
H	0.77824	5.26765	18.77224

H	1.96841	4.36720	17.80592
C	3.45980	6.43533	15.48491
H	2.54861	5.85352	15.66679
H	3.18939	7.22744	14.77077
C	-1.19611	6.75422	14.53878
H	-1.40965	5.84654	15.12628
H	-2.06510	7.42226	14.67058
C	-1.02532	6.68988	20.02962
H	-1.71247	6.14339	19.36424
H	-1.61735	7.08549	20.87066
H	-0.30451	5.97137	20.44708
C	-0.68261	7.63329	12.22925
H	-1.54115	8.32658	12.21615
H	-0.50254	7.34765	11.17995
C	-1.36700	8.85543	18.79708
H	-0.85179	9.66194	18.25460
H	-1.93839	9.27493	19.64139
H	-2.08535	8.37510	18.11250
C	2.44656	12.93068	10.58520
H	2.14049	12.42716	9.65563
H	3.44214	13.36664	10.40639
H	1.74472	13.75694	10.77593
C	3.50076	10.82907	11.49571
H	3.32480	10.33016	10.52882

H	3.43979	10.07355	12.29246
H	4.51961	11.24817	11.49279
C	-1.04544	6.40017	13.05834
H	-1.96355	5.92801	12.67177
H	-0.23723	5.65381	12.95576
C	4.50230	5.51542	14.83988
H	4.67238	4.63362	15.48239
H	4.10642	5.12862	13.88698
C	6.32950	6.82712	15.92770
H	6.53983	6.01683	16.64921
H	7.27941	7.36358	15.77251
C	5.83583	6.22186	14.61702
H	5.69885	7.03214	13.87956
H	6.57982	5.52686	14.19489
C	2.51103	12.09111	18.00594
H	2.45221	11.42934	18.88586
H	3.17816	12.93699	18.26250
H	1.49795	12.49074	17.84961

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XYZ

Si	2.14624	10.13245	16.72089
N	2.36954	11.55729	14.28747
N	3.77864	9.39328	18.98898
C	2.72016	12.66529	15.09692

C	2.08535	12.88487	16.35592
C	1.63525	11.69623	13.01097
C	1.20054	11.82058	17.01046
C	3.95614	11.48132	20.22630
C	2.38666	10.18074	14.78858
H	3.37353	9.73399	14.58550
C	3.23483	10.29516	19.94657
C	2.02077	10.00978	20.60322
C	1.37434	9.37438	13.88091
C	2.31849	14.09401	17.01870
H	1.82276	14.29441	17.96639
C	0.69040	10.47602	13.04471
H	0.45071	10.14080	12.02655
H	-0.26889	10.75917	13.50323
C	3.58005	9.51410	17.63422
C	5.27630	11.80099	19.53950
H	5.63219	10.87248	19.07332
C	3.72189	13.57023	14.67241
C	4.66112	8.25539	19.35871
C	1.54044	10.92962	21.54339
H	0.60185	10.72180	22.06258
C	5.57042	8.20340	18.12581
H	5.96059	7.19067	17.95132
H	6.43675	8.86392	18.29089

C	4.72336	8.73097	16.93866
C	3.42922	12.37427	21.16192
H	3.96866	13.29608	21.38767
C	2.22958	12.10367	21.81726
H	1.83525	12.81173	22.54795
C	1.23921	8.72817	20.35809
H	1.76405	8.17061	19.57337
C	4.70469	13.23162	13.56460
H	4.40351	12.26524	13.14566
C	0.88281	12.16673	18.46439
H	0.24760	13.06700	18.50631
H	1.78049	12.35437	19.06517
H	0.31717	11.35750	18.93770
C	3.91028	14.77395	15.36413
H	4.66126	15.48298	15.00752
C	3.18275	15.05877	16.50745
H	3.32217	16.00387	17.03491
C	5.09713	12.82521	18.41554
H	6.06498	13.04414	17.93725
H	4.68992	13.77089	18.80592
H	4.40710	12.45780	17.64181
C	0.84367	13.00367	12.95104
H	1.51678	13.87289	12.93434
H	0.18005	13.10935	13.82023

H	0.23416	13.02242	12.03545
C	6.34484	12.26763	20.53249
H	7.31952	12.34553	20.02881
H	6.44612	11.57389	21.38029
H	6.10953	13.26255	20.93921
C	2.15518	8.39406	12.96958
H	2.90237	8.94182	12.37768
H	2.72339	7.70136	13.61247
C	-0.15418	11.72702	16.28647
H	-0.04931	11.45099	15.23506
H	-0.65531	12.70855	16.32989
H	-0.80853	10.98888	16.77707
C	0.33736	8.54208	14.65814
H	-0.25438	9.19894	15.31409
H	0.87165	7.84362	15.32617
C	2.52533	11.61735	11.75156
H	1.90361	11.41146	10.86743
H	3.27813	10.82209	11.83531
H	3.05117	12.56153	11.56909
C	5.42938	8.52167	20.64928
H	6.09795	7.67235	20.85097
H	4.74252	8.62649	21.50223
H	6.03954	9.43197	20.58308
C	5.58039	9.72674	16.11606

H	4.94635	10.28917	15.41532
H	5.99437	10.47719	16.80936
C	3.88405	6.93713	19.51102
H	3.18717	6.78635	18.67502
H	3.31042	6.91601	20.44585
H	4.59055	6.09430	19.53202
C	4.24013	7.55763	16.05916
H	3.77061	6.79643	16.69922
H	3.44508	7.91439	15.39533
C	-0.58733	7.74324	13.73791
H	-1.31842	7.18329	14.34055
H	-1.16967	8.43530	13.10488
C	1.20302	7.88223	21.63816
H	0.79536	6.88109	21.43183
H	0.56126	8.35530	22.39758
H	2.20300	7.76692	22.08109
C	1.26599	7.55410	12.05110
H	0.76530	8.19945	11.31036
H	1.89102	6.85563	11.47395
C	-0.18708	8.96368	19.84835
H	-0.18085	9.37186	18.82805
H	-0.74769	9.65120	20.50086
H	-0.73315	8.00907	19.81941
C	4.73791	14.27823	12.44706

H	5.36121	13.93341	11.60781
H	5.16699	15.22506	12.80939
H	3.73269	14.50091	12.06139
C	6.10789	13.04717	14.15890
H	6.81910	12.72582	13.38217
H	6.09907	12.29261	14.95870
H	6.48101	13.98841	14.59129
C	0.21171	6.79143	12.85031
H	-0.45574	6.23263	12.17687
H	0.71493	6.04559	13.49031
C	5.34802	6.92398	15.21550
H	6.05957	6.38703	15.86632
H	4.90745	6.16472	14.55065
C	6.69415	9.03671	15.33036
H	7.41306	8.56608	16.02436
H	7.25831	9.78674	14.75510
C	6.11366	7.96878	14.40607
H	5.42684	8.44861	13.68552
H	6.90893	7.48932	13.81563

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XYZ

Si	2.25191	9.52330	16.52655
N	1.42116	10.76313	14.16857
N	2.55425	7.60663	18.61472

C	2.35466	11.83087	14.25312
C	3.03659	12.15502	15.44779
C	-0.01159	11.08485	14.42258
C	3.19654	11.21527	16.65505
C	3.02926	9.06444	20.55047
C	1.74010	9.41850	14.66135
H	2.59203	9.03055	14.07234
C	2.09444	8.46505	19.66742
C	0.71398	8.72175	19.83217
C	0.45005	8.64565	14.29028
C	3.73541	13.37147	15.49884
H	4.23764	13.65705	16.42480
C	-0.62879	9.68604	14.64708
H	-1.55287	9.56061	14.06555
H	-0.89708	9.56300	15.70642
C	3.05495	8.05287	17.38777
C	4.52904	8.81701	20.48819
H	4.71637	8.12560	19.65437
C	2.55543	12.62113	13.08987
C	2.74245	6.14256	18.76391
C	0.29469	9.59220	20.84339
H	-0.77151	9.79417	20.96367
C	4.05920	5.94402	17.99624
H	4.15068	4.91878	17.61039

H	4.90179	6.10760	18.68799
C	4.08217	7.01680	16.87898
C	2.56175	9.92783	21.54648
H	3.28012	10.39531	22.22333
C	1.20770	10.20100	21.69417
H	0.86503	10.88117	22.47541
C	-0.34275	8.05841	18.97016
H	0.18391	7.55158	18.15115
C	2.15587	12.09915	11.71737
H	1.34861	11.37589	11.86019
C	4.70732	10.91064	16.74169
H	5.27308	11.80786	17.04300
H	5.09875	10.58683	15.76551
H	4.91319	10.11951	17.47193
C	3.26350	13.81904	13.18994
H	3.40136	14.44112	12.30394
C	3.81692	14.21861	14.40291
H	4.34972	15.16768	14.48117
C	5.30931	10.11253	20.22957
H	6.36777	9.88981	20.02523
H	5.27335	10.76777	21.11360
H	4.90553	10.67712	19.38283
C	-0.21257	11.97261	15.65882
H	0.22326	12.97157	15.50703

H	0.25331	11.52541	16.54881
H	-1.28771	12.08877	15.86341
C	5.05709	8.18680	21.78566
H	6.11575	7.90957	21.67105
H	4.49526	7.29390	22.08770
H	4.99324	8.90704	22.61522
C	0.47067	8.32699	12.77988
H	0.62758	9.25565	12.21092
H	1.35139	7.68813	12.58681
C	0.22350	7.33980	15.05591
H	0.18913	7.54945	16.13686
H	1.08263	6.67330	14.88270
C	-0.66932	11.79018	13.23217
H	-1.71563	12.02141	13.48146
H	-0.66645	11.15756	12.33328
H	-0.16049	12.73793	13.00349
C	2.84699	5.70201	20.21607
H	2.97739	4.61092	20.25468
H	1.93764	5.96097	20.77836
H	3.70630	6.16772	20.71080
C	5.49390	7.62948	16.74973
H	5.44801	8.45956	16.02761
H	5.79222	8.06710	17.71634
C	1.59531	5.37352	18.08708

H	1.36949	5.79677	17.09956
H	0.68058	5.41467	18.69228
H	1.87118	4.31569	17.96327
C	3.71373	6.40604	15.50696
H	2.75516	5.87711	15.58608
H	3.56322	7.23031	14.78859
C	-1.05229	6.62182	14.61297
H	-1.17600	5.69207	15.18979
H	-1.93001	7.25076	14.84206
C	-1.11629	7.00806	19.77709
H	-1.80219	6.44435	19.12620
H	-1.71607	7.49242	20.56318
H	-0.44275	6.29433	20.27250
C	-0.77878	7.58892	12.29946
H	-1.66071	8.24630	12.38138
H	-0.67890	7.34411	11.23102
C	-1.31609	9.06951	18.35834
H	-0.77672	9.88820	17.86224
H	-1.97232	9.50891	19.12491
H	-1.96286	8.57603	17.61636
C	1.67330	13.17977	10.75090
H	1.29194	12.71886	9.82781
H	2.48771	13.86000	10.45872
H	0.86733	13.78711	11.18856

C	3.34073	11.32572	11.12353
H	3.07876	10.90205	10.14179
H	3.63746	10.50151	11.78868
H	4.21182	11.98672	10.99364
C	-1.01757	6.31781	13.11502
H	-1.94792	5.82267	12.79779
H	-0.19658	5.60652	12.91685
C	4.76756	5.44524	14.94857
H	4.81483	4.54087	15.57889
H	4.45591	5.10481	13.94931
C	6.54060	6.62846	16.26215
H	6.62980	5.79542	16.98131
H	7.52785	7.11318	16.22107
C	6.15387	6.07980	14.89160
H	6.14640	6.90907	14.16293
H	6.89758	5.35101	14.53546
C	2.75133	11.89297	17.96753
H	2.80819	11.19055	18.81456
H	3.39122	12.75741	18.21128
H	1.71305	12.24965	17.90858

2a (Diradical singlet)

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XYZ

Si	1.94015	9.39756	16.57480
N	1.42555	10.69873	14.17386

N	2.89295	7.70164	18.71177
C	2.35424	11.74316	14.42779
C	2.78472	12.07841	15.73058
C	-0.01786	11.06205	14.20644
C	2.70203	11.15369	16.96181
C	3.22063	9.24230	20.62052
C	1.65884	9.33183	14.66263
H	2.53707	8.92440	14.12872
C	2.34559	8.54344	19.74354
C	0.94062	8.70883	19.88813
C	0.36815	8.60871	14.15767
C	3.46790	13.29393	15.89912
H	3.77343	13.60030	16.90083
C	-0.69621	9.69448	14.40057
H	-1.57488	9.58962	13.74966
H	-1.05585	9.59916	15.43868
C	2.89228	8.02623	17.36028
C	4.73816	9.09590	20.63215
H	5.02209	8.48087	19.76384
C	2.79102	12.50884	13.31413
C	3.19975	6.25042	18.89567
C	0.45629	9.59196	20.85955
H	-0.62247	9.72171	20.96428
C	4.21943	6.04911	17.77444

H	4.28176	4.99481	17.46977
H	5.21389	6.34839	18.14354
C	3.78200	6.99585	16.63140
C	2.67762	10.10215	21.58215
H	3.35116	10.63967	22.25210
C	1.30898	10.29289	21.69975
H	0.90832	10.97792	22.44846
C	-0.10432	7.92713	19.10388
H	0.41215	7.37141	18.31222
C	2.64331	11.95327	11.90493
H	1.70866	11.38768	11.86296
C	4.17199	10.89479	17.36318
H	4.64491	11.81982	17.73284
H	4.75925	10.54141	16.50451
H	4.23326	10.13481	18.15203
C	3.47791	13.70239	13.53255
H	3.79140	14.31286	12.68469
C	3.77751	14.11842	14.82734
H	4.28972	15.06699	14.99701
C	5.47329	10.44216	20.54020
H	6.55104	10.26994	20.40161
H	5.35469	11.01415	21.47219
H	5.11533	11.06639	19.71613
C	-0.38327	11.99849	15.36406

H	0.10375	12.97993	15.26433
H	-0.08401	11.55790	16.32493
H	-1.47289	12.15011	15.38609
C	5.20826	8.41045	21.92757
H	6.27630	8.15263	21.86035
H	4.64391	7.50178	22.16341
H	5.08892	9.09955	22.77731
C	0.55094	8.29284	12.65729
H	0.87449	9.20085	12.12608
H	1.38240	7.56900	12.57181
C	-0.05902	7.31385	14.86586
H	-0.18193	7.50041	15.94588
H	0.72526	6.55327	14.75831
C	-0.47541	11.72714	12.90254
H	-1.54101	11.99019	12.98020
H	-0.35419	11.05448	12.04158
H	0.08736	12.65347	12.71193
C	3.77494	5.91693	20.26152
H	3.90580	4.82780	20.33663
H	3.09647	6.23223	21.06905
H	4.75432	6.38442	20.41227
C	5.00843	7.74244	16.05439
H	4.64697	8.50142	15.33749
H	5.50735	8.29012	16.86962

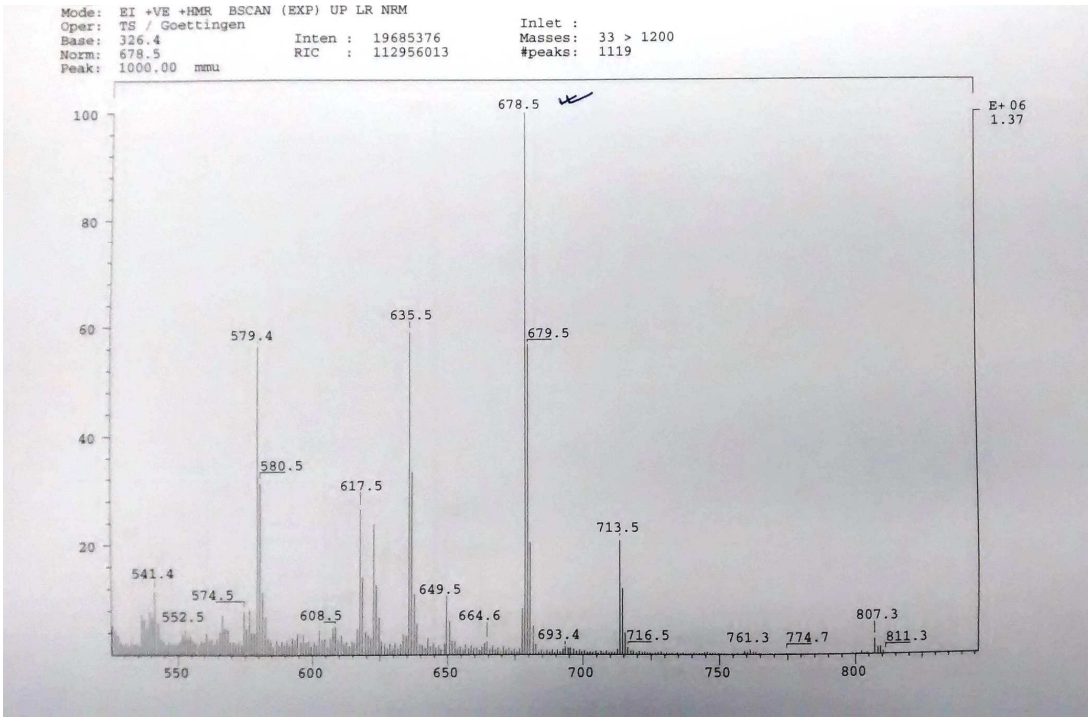
C	1.96003	5.37670	18.66105
H	1.45645	5.63675	17.72051
H	1.24010	5.48682	19.48033
H	2.25915	4.31922	18.61430
C	3.12080	6.22534	15.47240
H	2.26748	5.64076	15.84300
H	2.71786	6.95841	14.75879
C	-1.34412	6.74043	14.26164
H	-1.62436	5.81994	14.79652
H	-2.17888	7.44727	14.40398
C	-0.82743	6.93692	20.03073
H	-1.45094	6.24423	19.44511
H	-1.48877	7.47663	20.72595
H	-0.13009	6.34811	20.64205
C	-0.69078	7.68415	12.00763
H	-1.50384	8.42853	11.97600
H	-0.47459	7.42562	10.95961
C	-1.14751	8.82978	18.43458
H	-0.67008	9.59897	17.81165
H	-1.78366	9.33078	19.17950
H	-1.80898	8.22830	17.79140
C	2.60733	13.01776	10.81147
H	2.37823	12.55335	9.84120
H	3.57718	13.52743	10.70408

H	1.84280	13.78267	11.01455
C	3.77447	10.94718	11.65489
H	3.68737	10.50092	10.65218
H	3.73902	10.13710	12.39857
H	4.75637	11.43949	11.73274
C	-1.16271	6.44588	12.77140
H	-2.09544	6.05458	12.33691
H	-0.40454	5.65048	12.66006
C	4.08781	5.31102	14.71644
H	4.43643	4.49865	15.37645
H	3.55189	4.82380	13.88731
C	5.98992	6.81685	15.33785
H	6.40114	6.08130	16.05161
H	6.84489	7.40056	14.96447
C	5.29721	6.08158	14.19388
H	4.96070	6.81963	13.44406
H	5.99684	5.40385	13.68188
C	2.00426	11.83175	18.15599
H	2.04659	11.18537	19.04544
H	2.50287	12.77945	18.41757
H	0.94787	12.05713	17.95699

……

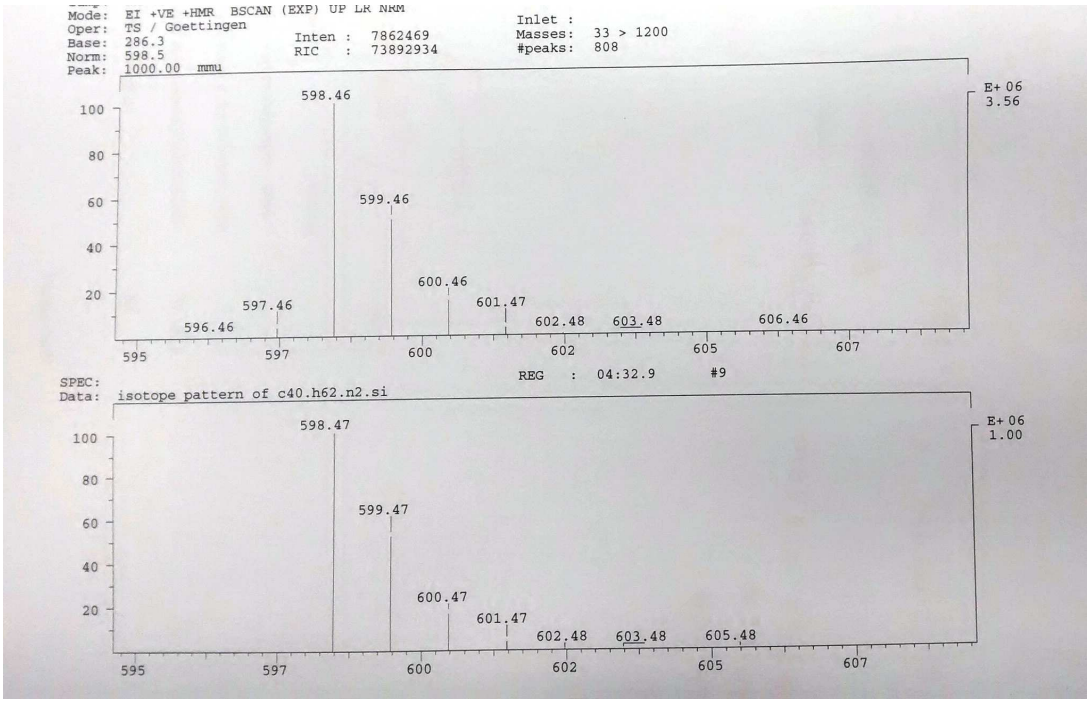
S8. Mass spectra of compounds 1a, 1b, 2a and 2b:

Mass spectra of compound 1a



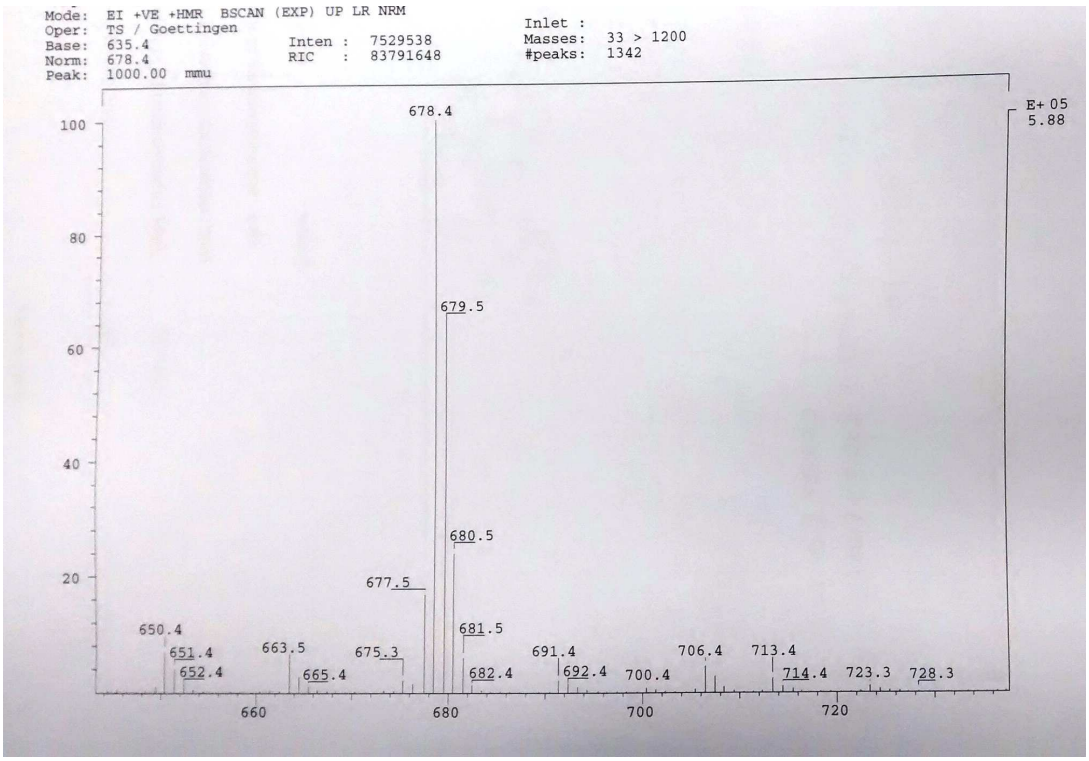
EI-MS: m/z (%) 678.5 (100%)[M^+], 679.5 (58%)[M^+], 680.5 (20%)[M^+]. Mass spectrometry was performed on solid sample of **1a**.

Mass spectra of compound 1b

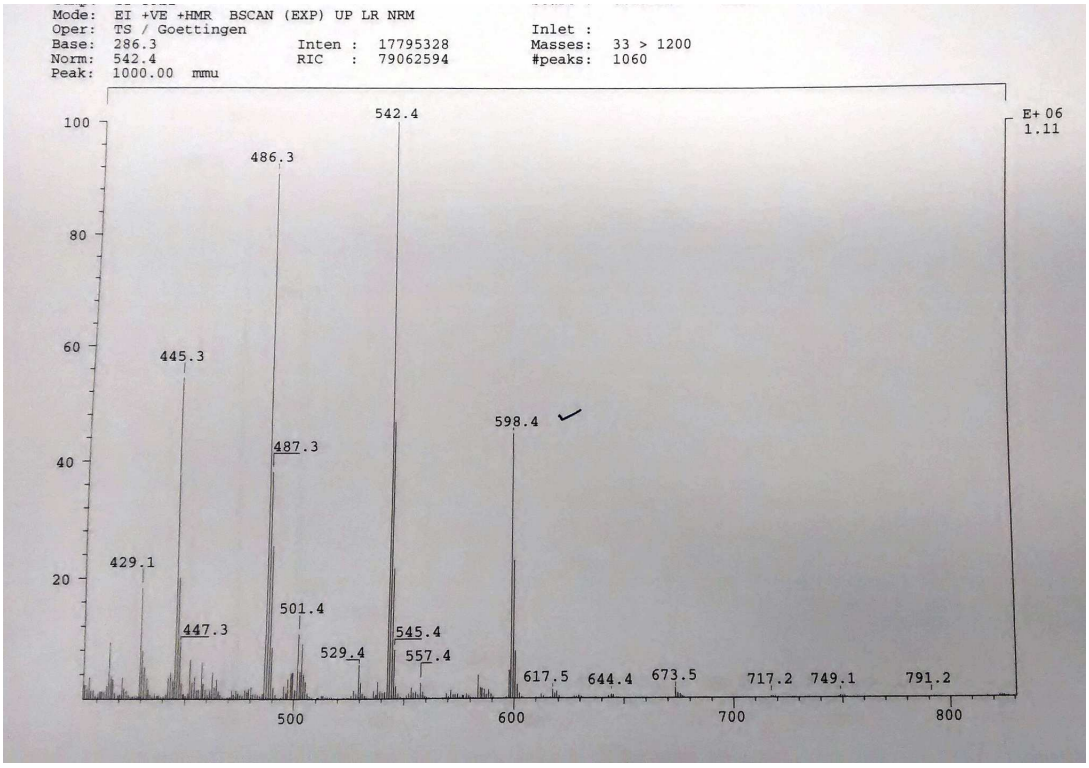


EI-MS: m/z (%) 598.47 (100%)[M^+], 599.47 (58%)[M^+], 600.47 (20%)[M^+]. Mass spectrometry was performed on solid sample of **1b**.

Mass spectra of compound 2a



Mass spectra of compound 2b



S9. Geometry of the atoms in 2a

One carbene carbon atom (C24) adopts a nearly ideal trigonal planar geometry with a sum of angles of 358.4° which is close to those of mono radical (357.33°)[S22] and diradical (Cy-cAAC·)$_2$SiCl$_2$ (354.8°, 355.7°),[S23] while the corresponding sum of angles of proton containing carbene carbon atom (C1) is 336.5°. The latter value is wider by 6° when compared with that of (Me$_2$-cAAC-H)$_2$O (330.26°).[S24]

S10. References

S1 (a) Mondal, K. C.; Roesky, H. W.; Schwarzer, M. C.; Frenking, G.; Tkach, I.; Wolf, H.; Kratzert, D.; Herbst-Irmer, R.; Niepötter, B.; Stalke, D. *Angew. Chem. Int. Ed.* **2013**, *52*, 1801–1805; *Angew.Chem.* **2013**, *125,* 1845–1850. (b) Mondal, K. C.; Samuel, P. P.; Tretiakov, M.; Singh, A. P.; Roesky, H. W.; Stückl, A. C.; Niepötter, B.; Carl, E.; Wolf, H.; Herbst-Irmer, R.; Stalke, D. *Inorg. Chem.* **2013**, *52*, 4736–4743. (c) Niepötter, B.; Herbst-Irmer, R.; Kratzert, D.; Samuel, P. P.; Mondal, K. C.; Roesky, H. W.; Jerabek, P.; Frenking, G.; Stalke, D. *Angew. Chem. Int. Ed.* **2014**, *53*, 2766–2770; *Angew. Chem.* **2014**, *126*, 2806–2811.

S2 Schulz, T.; Meindl, K.; Leusser, D.; Stern, D.; Graf, J.; Michaelsen, C.; Ruf, M.; Sheldrick, G. M.; Stalke, D. *J. Appl. Cryst.* **2009**, *42*, 885–891.

S3 Stalke, D. *Chem. Soc. Rev*. **1998**, *27*, 171–178.

S4 Kottke, T.; Stalke, D. *J. Appl. Crystallogr*. **1993**, *26*, 615–619.

S5 Bruker **2009**. SAINT. Version 7.68A. Bruker AXS Inc., Madison, Wisconsin (USA).

S6 Bruker **2009**. APEX2. Version 2.2012.2 0. Bruker AXS Inc., Madison, Wisconsin (USA).

S7 Sheldrick, G. **2008**, *Acta Cryst. A 64*, 112-122.

S8 Hübschle, C. B.; Sheldrick, G. M.; Dittrich, B. **2011** *J. Appl. Cryst. 44*, 1281-1284.

S9 for Gaussian09: Gaussian09, Revision **C.01**, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, Jr. J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2010**.

S10 Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Theory and Comput*. **2006**, *2*, 364–382.

S11 Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys*. **1992**, *97*, 2571–2577.

S12 Eade, R. H. A.; Robb, M. A. *Chem. Phys. Lett*. **1981**, *83*, 362–368.

S13 Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys*. **1994**, *100*, 5829–5835.

S14 Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378–6396.

S15 AIMAll (Version 13.11.04, Standard), Copyright © 1997-2013, T. A. Keith http://aim.tkgristmill.com

S16 Bader, R. F. W. *Chem. Rev*. **1991**, *94*, 893–928

S17 http://www.chemcraftprog.com

S18 Goldfogel, M. J.; Roberts, C. C.; Meek, S. J. *J. Am. Chem. Soc*. **2014**, *136*, 6227−6230.

S19 Chen, W.-C.; Lee, C.-Y.; Lin, B.-C.; Hsu, Y.-C.; Shen, J.-S.; Hsu, C.-P.; Yap, G. P. A.; Ong, T.-G. *J. Am. Chem. Soc*. **2014**, *136*, 914−917.

S20 Ruiz, D. A.; Melaimi, M.; Bertrand, G. *Chem. Asian J.* **2013**, *8*, 2940 – 2942.

S21 Kaufhold, O.; Hahn, F. E. *Angew. Chem. Int. Ed*. **2008**, *47*, 4057–4061; *Angew. Chem*. **2008**, *120*, 4122 – 4126.

S22 Mondal, K. C.; Roesky, H. W.; Stückl, A. C.; Ehret, F.; Kaim, W.; Dittrich, B.; Maity, B.; Koley. D. *Angew. Chem. Int. Ed.* **2013***, 52,* 11804-11807; *Angew. Chem.* **2013***, 125,* 12020-12023.

S23 Mondal, K. C.; Samuel, P. P.; Tretiakov, M.; Singh, A. P.; Roesky, H. W.; Stückl, A. C.; Niepötter, B.; Carl, E.; Wolf, H.; Herbst-Irmer, R.; Stalke, D. *Inorg. Chem*. **2013**, *52*, 4736-4743.

S24 See Supporting Information of Li, Y.; Mondal, K. C.; Roesky, H. W.; Zhu, H.; Stollberg, P.; Herbst-Irmer, R.; Stalke, D.; Andrada, D. M. *J. Am. Chem. Soc*. **2013**, *135*, 12422−12428.