Supporting Information

A Facile Access to a Novel NHC-Stabilized Silyliumylidene Ion and Its C-H Activation of Phenylacetylene

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1. Experimental Data

General Considerations

All experiments and manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk techniques or in an MBraun drybox containing an atmosphere of purified nitrogen. Glass junctions were coated with the PTFE-based grease Merkel Triboflon III. Solvents were dried by standard methods and freshly distilled prior to use. NMR spectra for $TippSiHCl_2$, **1a** and **1b** were recorded on Bruker AvanceIII 400 spectrometer while the ^{1}H- and ^{13}C- NMR spectra for **2** were recorded on Bruker AvanceIII 700 spectrometer for higher resolution. Whereas the ^{29}Si NMR spectra for **2** was recorded on Bruker AvanceIII 500 spectrometer in the DEPT mode. Chemical shift values are referenced to (residual) solvent signals (^{1}H- and $^{13}C\{^{1}H\}$ NMR). Abbreviations: s = singlet, br = broadened, d = doublet, t = triplet, m= multiplet. High resolution mass spectra were recorded on Thermo Fisher Scientific LTQ Orbitrap XL. Melting points were determined on an electronic "Melting point tester" device from BSGT company and are uncorrected. Reagents purchased from commercial sources were used as received if not stated otherwise. *m*-Terphenyl dichlorosilane[1] and tetramethylcarbene[2] were synthesized according to literature procedures.

$TippSiHCl_2$

A solution of $TippLi{\cdot}OEt_2$ (10 mmol) in 40 ml diethylether is added drop wise to two equivalents (stoichiometric excess) of $SiHCl_3$ in 10 ml diethylether at -78 °C. The reaction was stirred for overnight at room temperature and afterwards the volatiles are removed under reduced pressure and the product extracted with hexane. Overnight standing of the saturated hexane solution in refrigerator (-30 °C) yielded colourless crystalline product in 33 % yield.

^{1}H NMR δ (400 MHz, 298 K, C_6D_6) = 1.10 (d, ^{3}JH-H = 7.0 Hz, 6 H, C^{4}-CHMe_2, *i*Pr), 1.17 (d, ^{3}JH-H = 7.0 Hz, 12 H, $C^{2,6}$-CHMe_2, *i*Pr) 2.66 (sept, ^{3}JH-H = 7.0 Hz, 1 H, C^{4}-C*H*Me$_2$, *i*Pr), 3.54 (sept, ^{3}JH-H = 7.0 Hz, 2 H, $C^{2,6}$-C*H*Me$_2$, *i*Pr), 6.43 (Si-*H*), 7.05 (s, 2 H, $C^{3,5}$-*H*, C_6H_2).

^{13}C NMR δ (400 MHz, 298 K, C_6D_6) = 23.8 (s, C^{4}-CHMe_2, *i*Pr), 24.6 (s, $C^{2,6}$-CHMe_2, *i*Pr), 33.6 ($C^{2,6}$-*C*HMe$_2$, *i*Pr), 34.9 (C^{4}-*C*HMe$_2$, *i*Pr), 122.1 (s, $C^{3,5}$-H, C_6H_2), 125.1 (Si-*C*,C_6H_2), 154.0 (C^{4}-C_6H_2), 156.4 ($C^{2,6}$-C_6H_2).

^{29}Si NMR δ (400 MHz, 298 K, C_6D_6) = -8.29

Compound 1a

Synthesis procedure

200 mg of m-TerSiHCl$_2$ dissolved in 2 mL freshly distilled benzene is treated with three equivalents of ^{Me4}NHC dissolved in 2 mL benzene. Immediate precipitation is observed and the reaction mixture is allowed to stand for overnight. Yellow-orange crystals of donor-stabilized silyliumylidene cation are produced in the reaction mixture. These crystals are separated from the imidazolium hydrogenchloride salt by by washing with hexane. The suspended imidazolium salt in hexane is removed via syringe while heavier crystals of **1a** settle down. Several washings are done to separate the imidazolium salt from the crystals of **1a**. The compound is insoluble in less polar solvents and decomposes slowly in dichloromethane. It shows good solubility in acetonitrile. Yield = 54 %

Alternate procedure

Two equivalents of ^{Me4}NHC dissolved in 2 mL benzene are added dropwise to a stirring solution of 200 mg of m-TerSiHCl$_2$ dissolved in 2 mL freshly distilled benzene. Immediate precipitation is observed and the reaction mixture is allowed to stir for half an hour. The solution is separated from the residue by filtration and a third equivalent of ^{Me4}NHC in 1mL benzene is added to the solution with occasional stirring. The solution is allowed to stand for overnight. Crystals of **1a** are produced by overnight standing at room temperature. Yield = 32 %

M.P = 212-214 ^{o}C

^{1}H NMR δ (400 MHz, 298 K, CD_3CN) = 2.02 (s, 12H, 4xC-*Me*, NHC^{Me4}), 2.06 (s, 12H, 2xC^{2,6}-*Me*, Mes), 2.15 (s, 6H, 2xC^{4}-*Me*, Mes), 3.28 (br, s, 12H, 4xN-*Me*, NHC^{Me4}), 6.68 (s, 4H, 2xC^{3,5}-*H*, Mes), 6.93 (d, ^{3}JH-H= 7.5 Hz, 2H, C^{3,5}-*H*, C_6H_3), 7.35 (t, ^{3}JH-H= 7.5 Hz, 1H, C^{4}-*H*, C_6H_3).

^{1}H NMR δ (400 MHz, 253 K, CD_3CN) = 1.96, 2.01, 2.04 , 2.08, 2.12(2s, 2x6H, 2xC-*Me*, NHC^{Me4} + s, 6H, 2xC^{2}-*Me*, Mes + s, 6H, 2xC^{4}-*Me*, Mes + s, 6H, 2xC^{6}-*Me*, Mes), 2.94, 3.50 (s, 2x6H, 2xN-*Me*, NHC^{Me4}), 6.59, 6.74 (s, 4H, 2xC^{3,5}-*H*, Mes), 6.90 (d, ^{3}JH-H= 7.6 Hz, 2H, C^{3,5}-*H*, C_6H_3), 7.35 (t, ^{3}JH-H= 7.6 Hz, 1H, C^{4}-*H*, C_6H_3)

^{13}C NMR δ (400 MHz, 298 K, CD_3CN) = 9.1 (s, 2xC^{4,5}-*Me*, NHC^{Me4}), 20.9 (s, C^{4}-*Me*, Mes), 21.8 (s, br, C^{2,6}-*Me*, Mes), 35.5 (s, br, 4xN-*Me*, NHC^{Me4}), 128.1 (s, *C*^{4}-H, C_6H_3), 128.2(s, 2x*C*^{4,5}-Me, NHC^{Me4}), 128.3 (s, 2x*C*^{3,5}-H, Mes), 129.3 (2x*C*^{4}-Mes), 130.2 (s, *C*^{3,5}-H, C_6H_3), 137.0 (2x*C*^{2,6}-Mes), 141.0 (s, 2x*C*^{l}-Mes), 144.7 (s, Si-*C*^{l}, C_6H_3), 148.70 (*C*^{2,6}-C_6H_3),160.3 (s, 2xSi-*C*, NHC^{Me4}).

^{29}Si NMR δ (400 MHz, 298 K, CD_3CN) = -68.85

Compound 1b

Synthesis procedure

200 mg of $TippSiHCl_2$ dissolved in 5 mL freshly distilled benzene is heated to 50 °C and three equivalents of ^{Me4}NHC dissolved in 5 mL benzene are added dropwise. Immediate precipitation is observed and heating is stopped once the addition is complete and the reaction mixture is allowed to stir for another half hour. The solution is afterwards separated from the solid residue. Evaporation of the solution yields the bright yellow product which shows good solubility in benzene. The recrystallization in benzene produces crystalline product which is not soluble in less polar solvents anymore and soluble in acetonitrile.
Yield = 45 %

M.P = 180-182 °C

^{1}H NMR δ (400 MHz, 298 K, C_6D_6) = 1.15-1.21 (br, 6H, 2xC^4-CH*Me*$_2$, *i*Pr + 12H, 2x$C^{2,6}$-CH*Me*$_2$, *i*Pr), 1.96 (s, 12H, 4xC-*Me*, NHC^{Me4}), 3.55 (s, 12H, 4xN-*Me*, NHC^{Me4}), 2.78 (sept, ^{3}JH-H= 7.0 Hz, 1H, C^4-C*H*Me$_2$, *i*Pr), 4.05 (sept, ^{3}JH-H= 7.0 Hz, 2H, $C^{2,6}$-C*H*Me$_2$, *i*Pr), 6.43 (Si-*H*), 7.05 (s, 2H, $C^{3,5}$-*H*, C_6H_2).

^{1}H NMR δ (400 MHz, 298 K, CD_3CN) = 0.95 (d, ^{3}JH-H= 7.0 Hz, 12H, $C^{2,6}$- CH*Me*$_2$, *i*Pr), 1.18 (d, ^{3}JH-H= 7.0 Hz, 6H, C^4-CH*Me*$_2$, *i*Pr), 2.16 (s, 12H, 4xC-*Me*, NHC^{Me4}), 2.83 (sept, ^{3}JH-H= 7.0 Hz, 1 H, C^4-C*H*Me$_2$, *i*Pr), 3.35 (s, 12H, 4xN-*Me*, NHC^{Me4}), 3.59 (sept, ^{3}JH-H= 7.0 Hz, 2H, $C^{2,6}$-C*H*Me$_2$, *i*Pr), 7.02(s, 2 H, $C^{3,5}$-*H*, C_6H_2).

^{13}C NMR δ (400 MHz, 298 K, C_6D_6) = 9.1 (s, 2x$C^{4,5}$-*Me*, NHC^{Me4}), 24.0 (s, C^4-CH*Me*$_2$, *i*Pr), 24.6 (s, $C^{2,6}$-CH*Me*$_2$, *i*Pr), 34.2 (s, br, 4xN-*Me*, NHC^{Me4}), 34.4 (C^4-*C*HMe$_2$, *i*Pr), 35.7 ($C^{2,6}$- *C*HMe$_2$, *i*Pr), 121.5 (s, *C*^{3,5}-H, C_6H_2), 135.6 (Si-*C,* C_6H_2), 149.7 (*C*^{4}-C_6H_2), 157.0 (*C*^{2,6}-C_6H_2), 159.7 (s, 2xSi-*C*, NHC^{Me4}).

^{29}Si NMR δ (400 MHz, 298 K, C_6D_6) = -69.50

COMPOUND 2

200 mg of **1a** are dissolved in 2 mL acetonitrile. A solution of 3 equivalents of phenyl acetylene in 2 mL acetonitrile is added dropwise to the soltuion of **1a** at -20 °C. The color of the solution changes from pale yellow to deep red upon reaching room temperature. The stirring is stopped and the reaction solution is placed in -30 °C freezer where XRD quality crystals are produced after overnight placement. Compound 2 shows good solubility in benzene and is less soluble in polar solvents.

Yield = 68 %

M.P = 182-184 °C

^{1}H NMR δ (700 MHz, 298 K, C_6D_6) =2.13 (s, 6H, 2xC^4-*Me*, Mes), 2.38(s, 12H, $C^{2,6}$-*Me*, Mes), 5.16 (d, ^{3}JH-H= 15.0 Hz, 1H, C-*H*-Si), 6.82(s, 4H, 2x$C^{3,5}$-*H*, Mes), 6.87 (m, 4H, 2x$C^{3,5}$*H*, Ph-C≡ + 2H, 2xC^4-*H*, Ph-C≡), 6.97 (d, ^{3}JH-H= 15.0 Hz, 1H, C-*H*-Ph), 7.03 (m, 4H, 2x$C^{2,6}$-*H*, Ph-C≡ + 1H, C^4*H*, Ph-CH=), 7.05(d, ^{3}JH-H= 7.6 Hz, 2H, $C^{3,5}$-*H*, C_6H_3), 7.12(t, ^{3}JH-H= 7.6 Hz, 2H, $C^{3,5}$-*H*, Ph-CH=), 7.31(t, ^{3}JH-H= 7.6 Hz, 1H, C^4-*H*, C_6H_3), 7.37(d, ^{3}JH-H= 7.4 Hz, 2H,$C^{2,6}$*H*-Ph, Ph-CH=).

^{13}C NMR δ (700 MHz, 298 K, C_6D_6) =21.2 (s, C^4-*Me*, Mes), 21.9 (s, $C^{2,6}$-*Me*, Mes), 90.9 (Si-*C*≡),106.7 (Ph-*C*≡), 123.9 (s, 2x *C*^{1}-Ph, Ph-C≡), 126.5 (Si-*C*H=), 127.7, 128.0, 128.3, 128.4 (s, *C*^{3,5}H, Ph-CH= + s, *C*^{3,5}H, Ph-C≡ + s, *C*^{4}H, Ph-CH= + s, *C*^{4}H, Ph-

C≡), 128.6 (s, 2x$C^{3,5}$-H, Mes), 129.8 (s, $C^{3,5}$-H, C_6H_3), 130.0 (s, $C^{2,6}$H, Ph-CH=), 131.1 (s, C^4-H, C_6H_3), 131.5 (s, Si-*C*, C_6H_3), 132.3 (s, 2x $C^{2,6}$H-Ph, Ph-C≡), 137.0 (2xC^4-Mes), 137.4 (s, 2x$C^{2,6}$-Mes), 138.8 (s, C^1-Ph, Ph-C=), 140.5 (s, 2xC^1-Mes), 145.3(Ph-*C*H=), 150.4 (s, 2x$C^{2,6}$-C_6H_3).

^{29}Si NMR δ (500 MHz, 298 K, C_6D_6) = -62.28

NMR Spectra

TippSiHCl$_2$

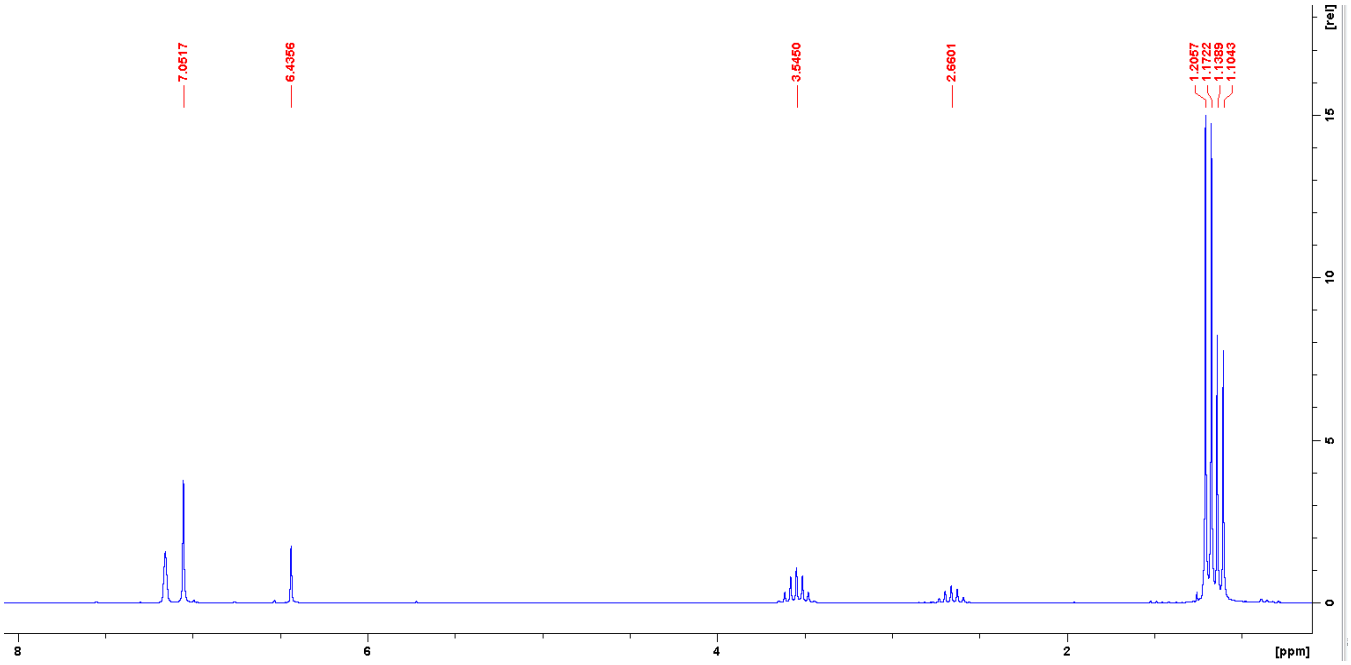


Figure S1. ^{1}H NMR of **TippSiHCl$_2$**. δ (400 MHz, 298 K, C_6D_6)

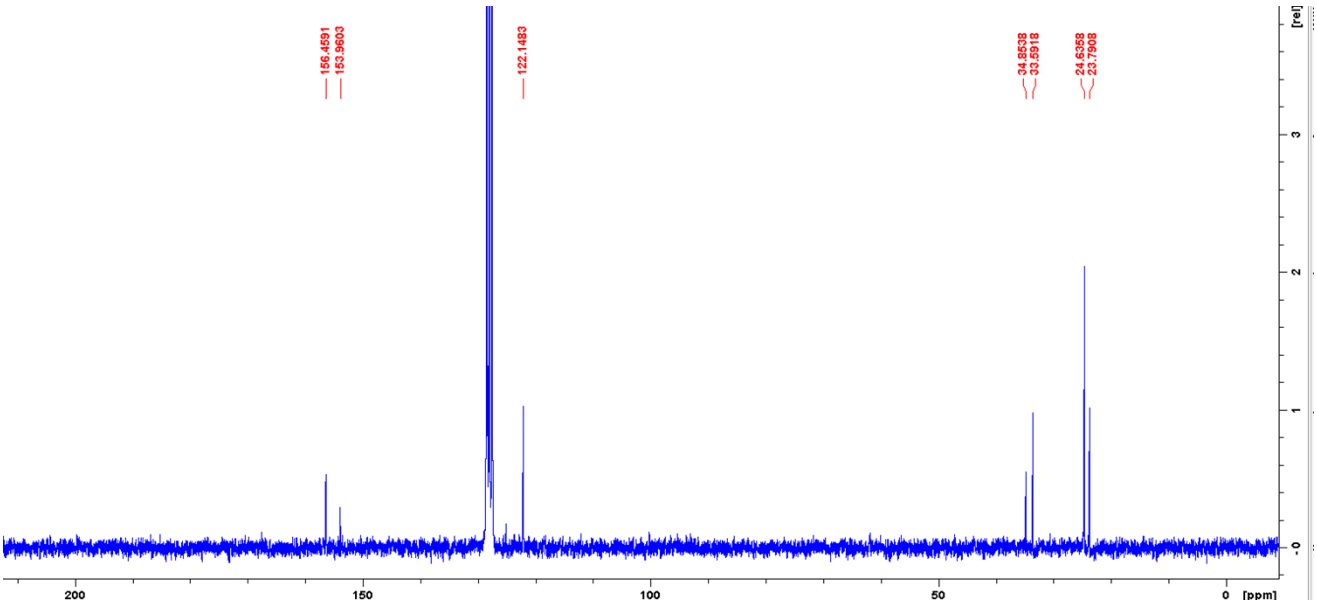


Figure S2. ^{13}C NMR of **TippSiHCl$_2$**. δ (400 MHz, 298 K, C_6D_6)

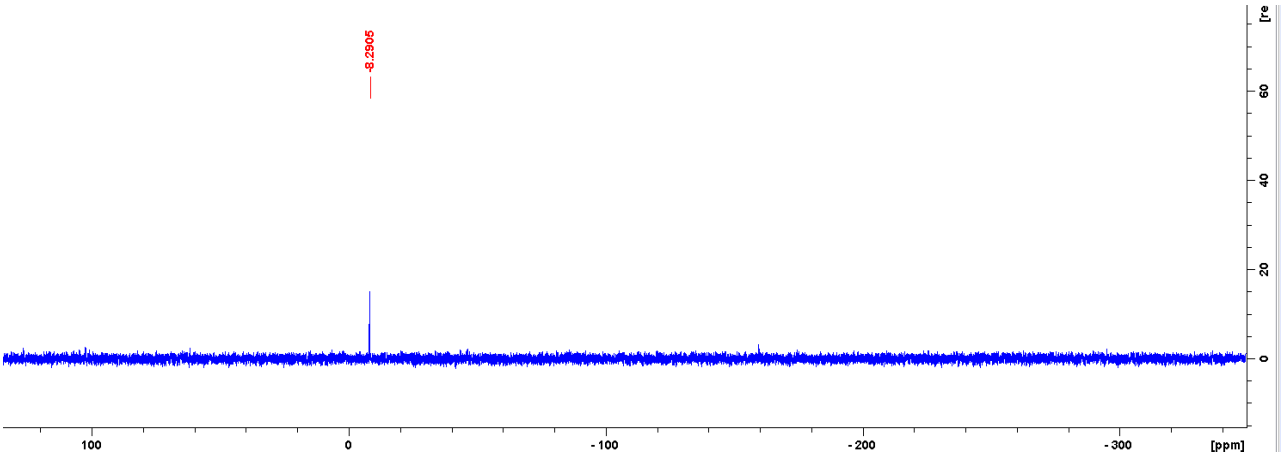


Figure S3. ^{29}Si NMR of **TippSiHCl$_2$**. δ (400 MHz, 298 K, C_6D_6)

Compound 1a

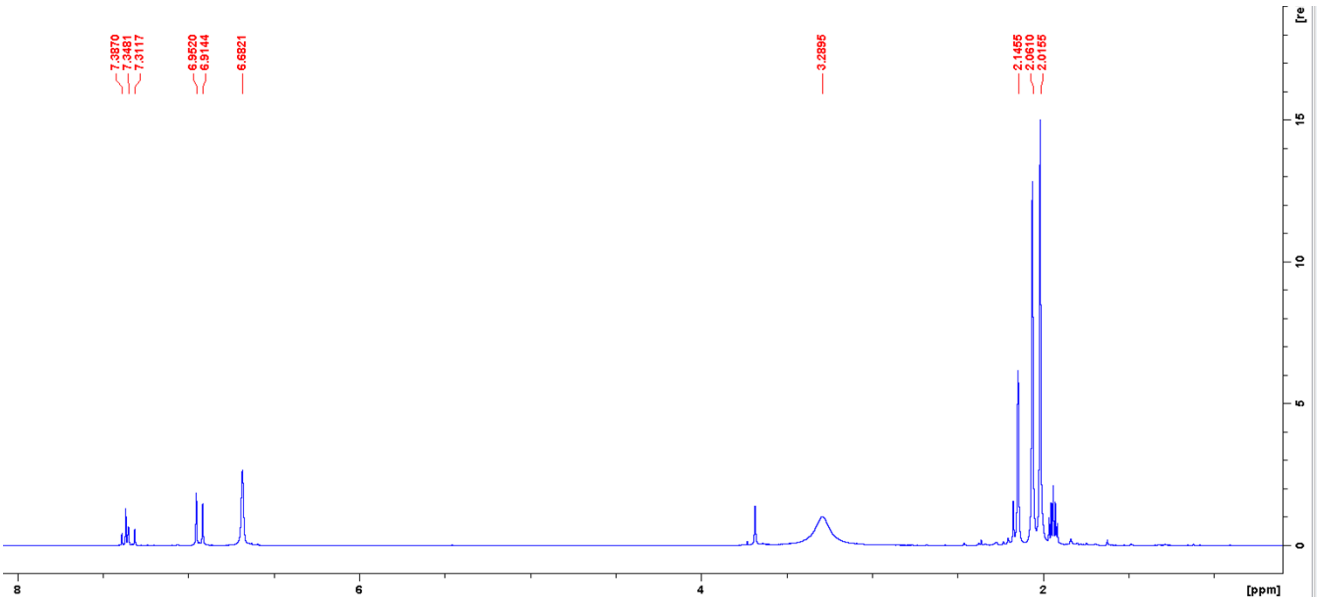


Figure S4. ^{1}H NMR of **1a**. δ (400 MHz, 298 K, CD_3CN)

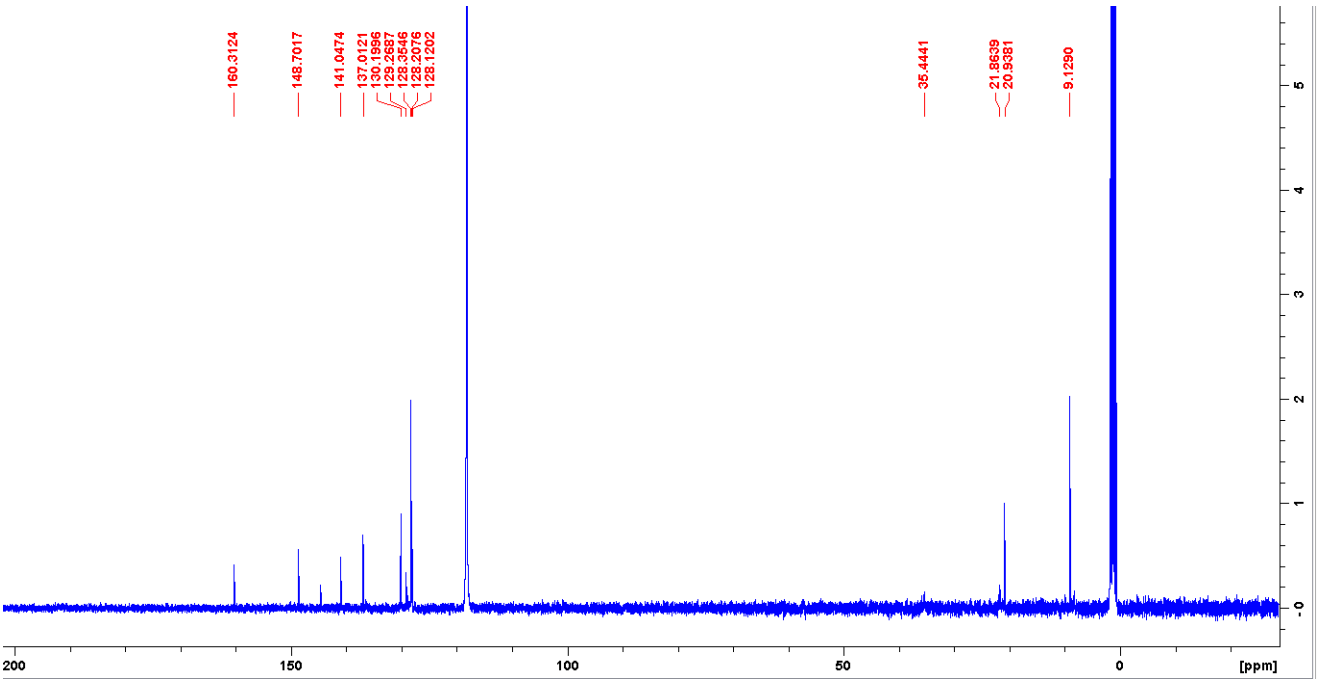


Figure S5. ^{13}C NMR of **1a**. δ (400 MHz, 298 K, CD_3CN)

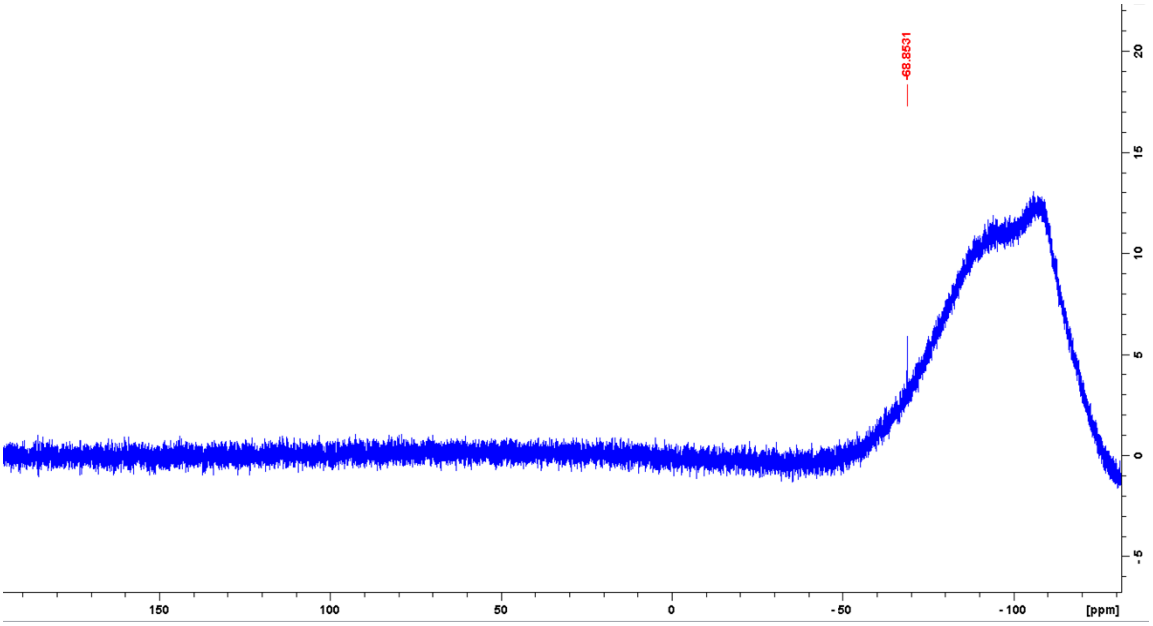


Figure S6. ^{29}Si NMR of **1a**. δ (400 MHz, 298 K, CD_3CN)

COMPOUND 1b

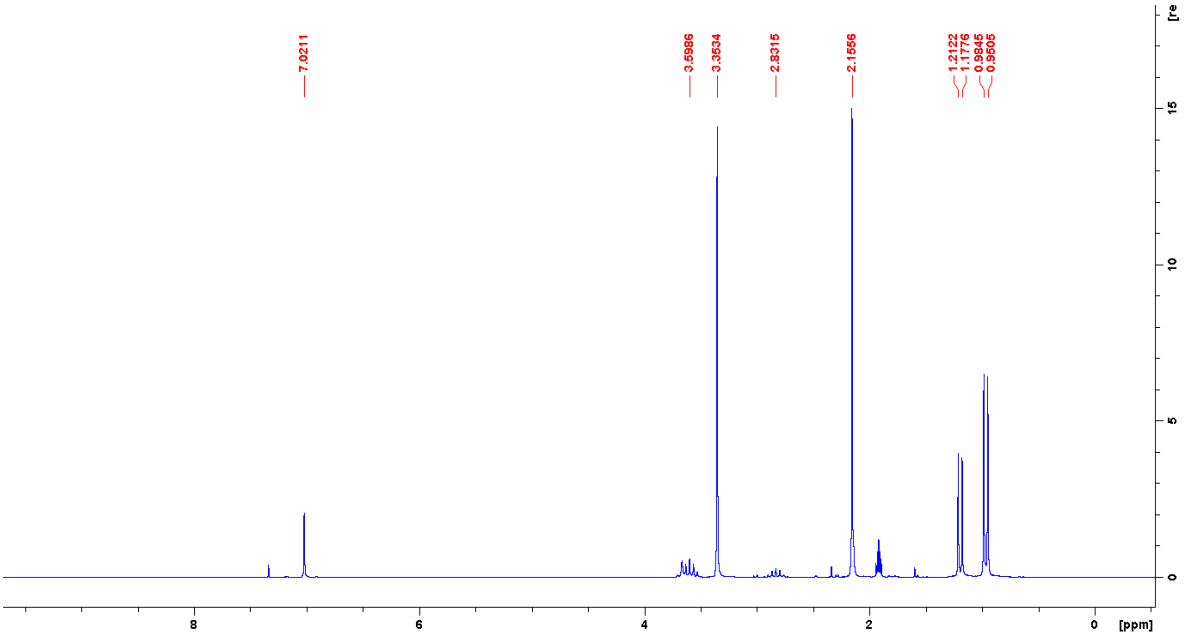


Figure S7 .^{1}H NMR of **1b**. δ (400 MHz, 298 K, CD_3CN)

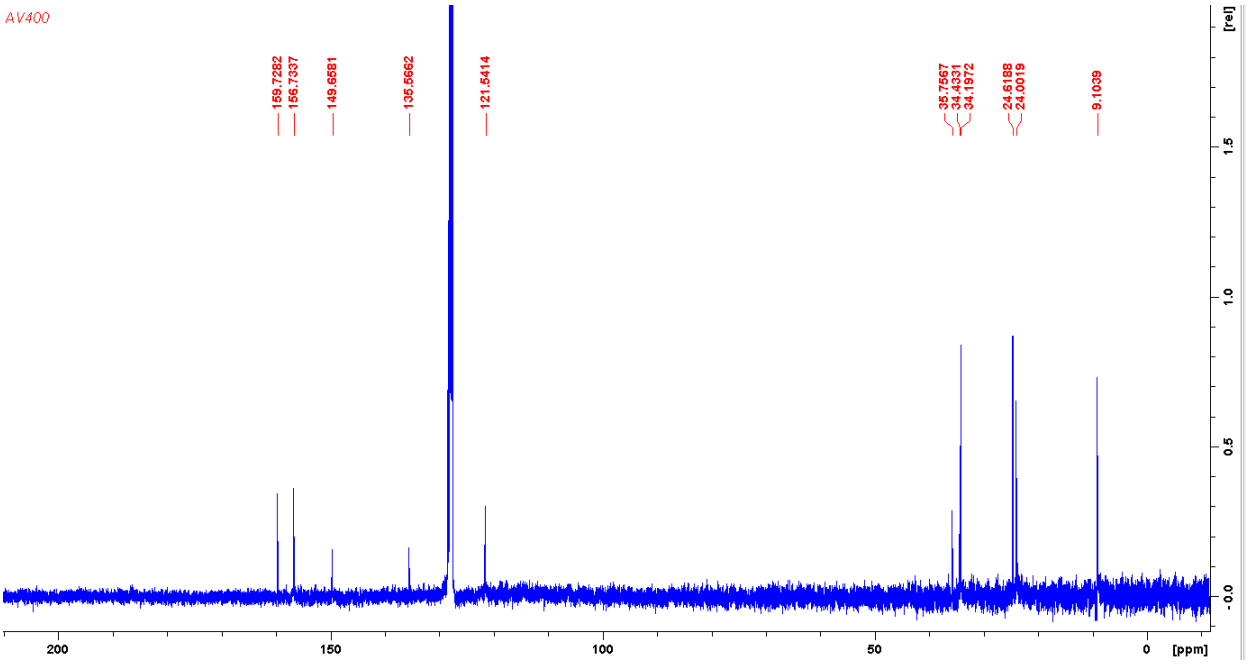


Figure S8. ^{13}C NMR of **1b**. δ (400 MHz, 298 K, CD_3CN)

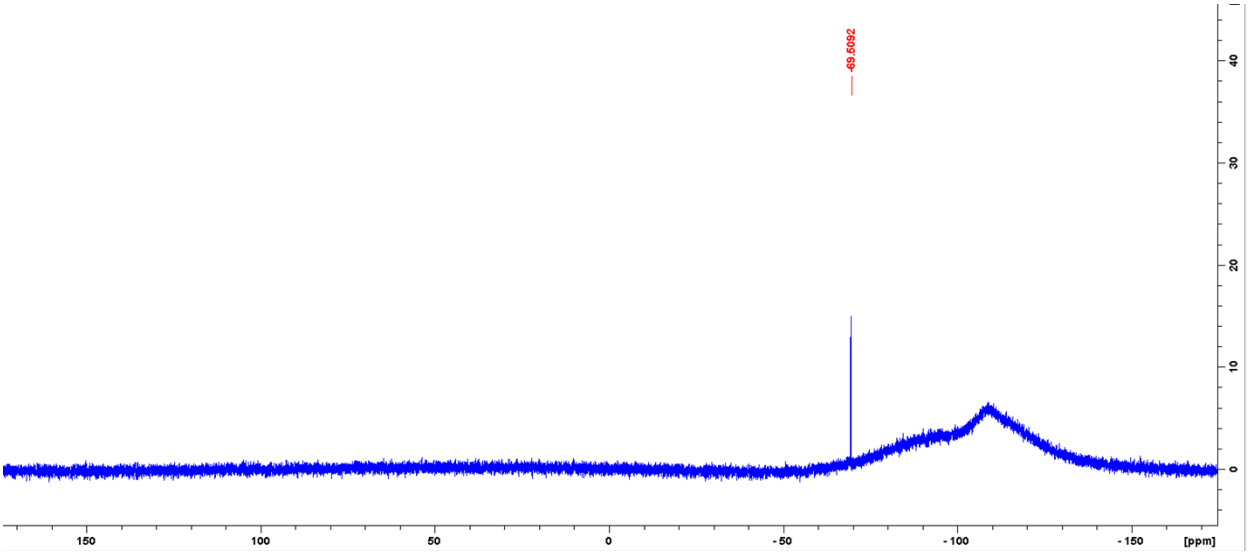


Figure S9. ^{29}Si NMR of **1b**. δ (400 MHz, 298 K, CD_3CN)

Compound 2

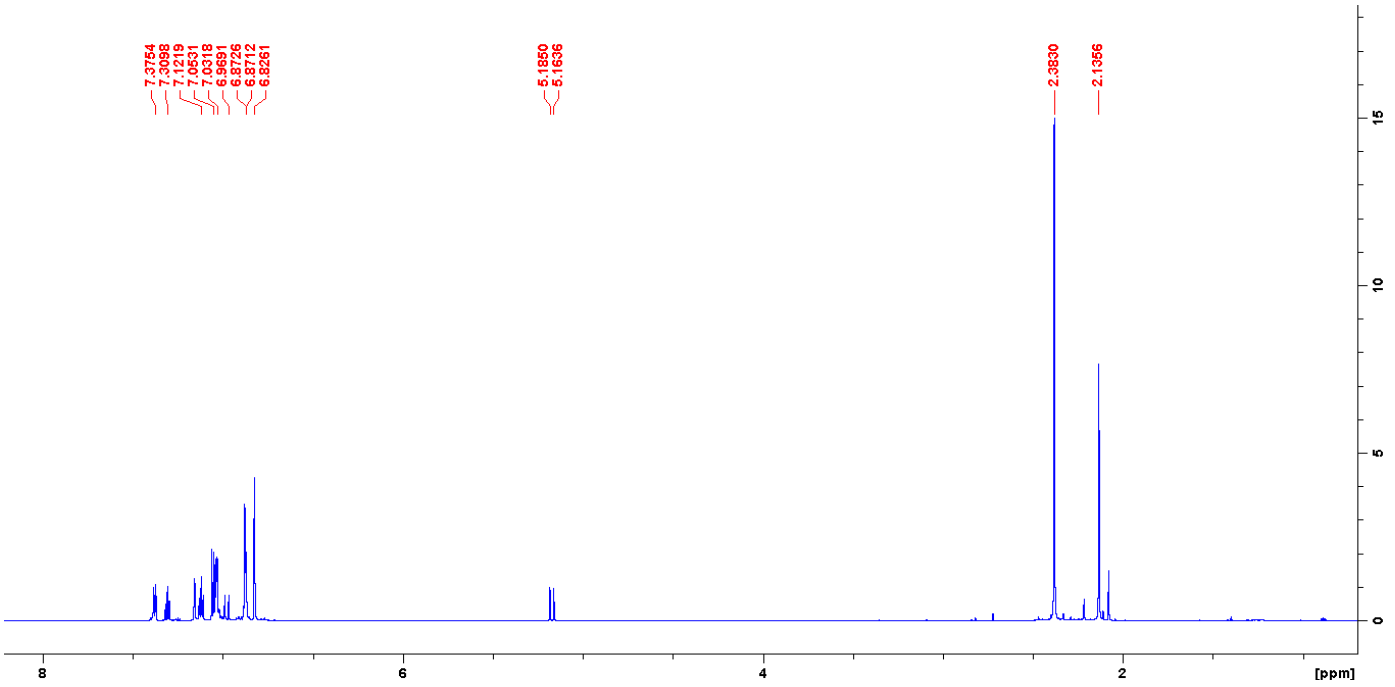


Figure S10. ^{1}H NMR of **2**. δ (700 MHz, 298 K, C_6D_6)

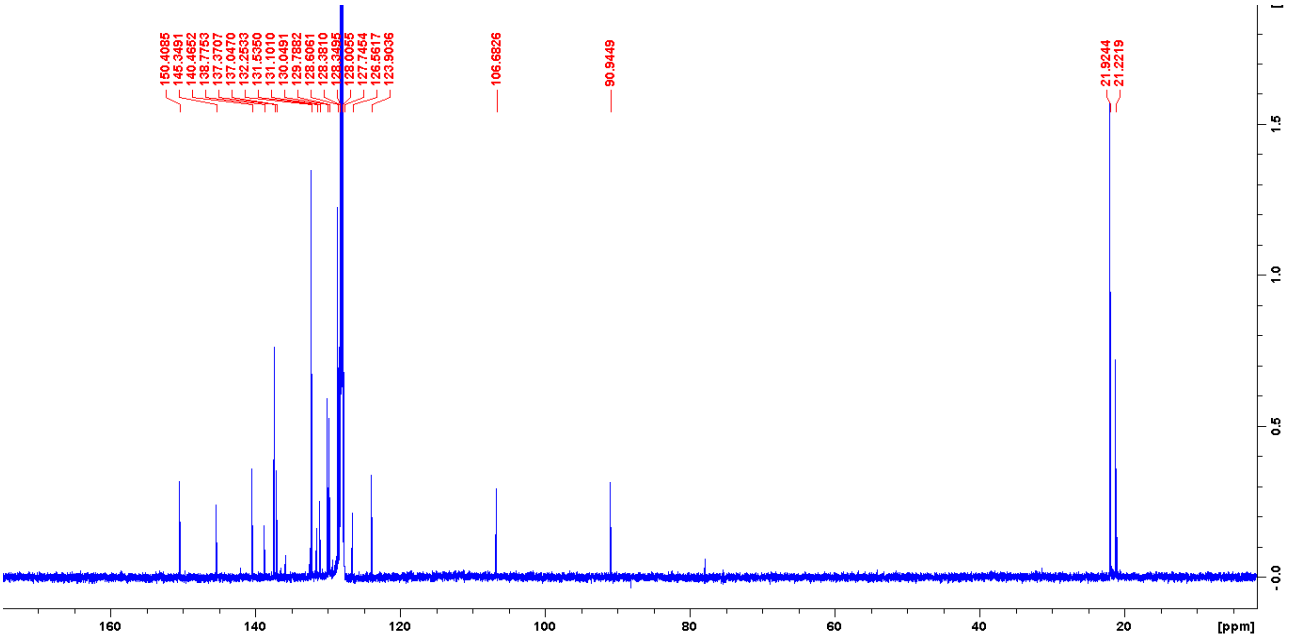


Figure S11. ^{13}C NMR of **2**. δ (700 MHz, 298 K, C_6D_6)

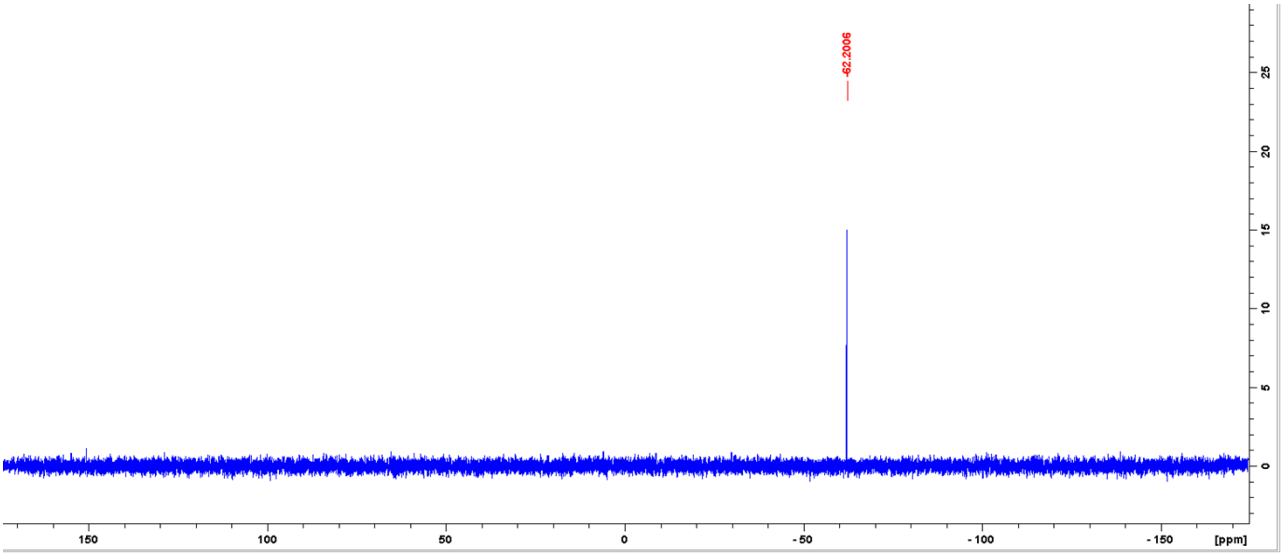


Figure S12. ^{29}Si NMR δ (500 MHz, 298 K, C_6D_6)

Mass Spectra

Compound 1a

ESI-HRMS (m/z) = [*m*-TerSi(NHC)$_2$]$^+$ = (M)$^+$ 589.37

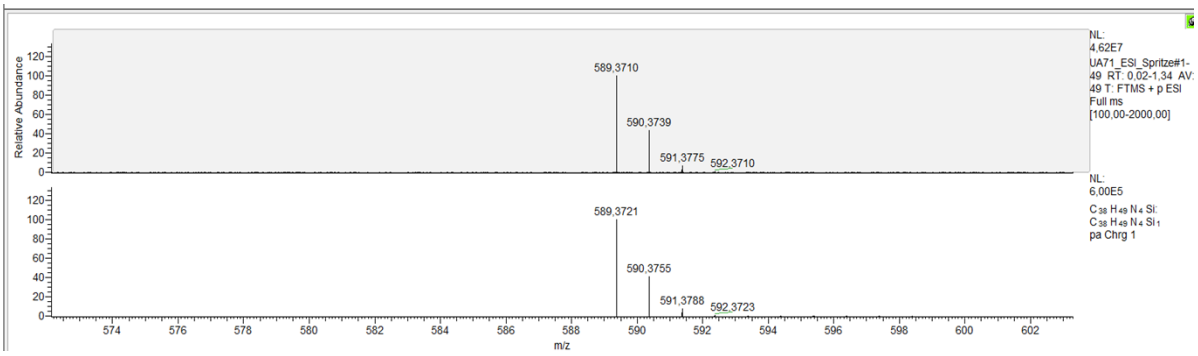


Figure S13. Mass Spectrometric data for **1a**.

Compound 1b

ESI-HRMS (m/z) = $[TippSi(NHC)_2]^+$ = $(M)^+$ 479.35

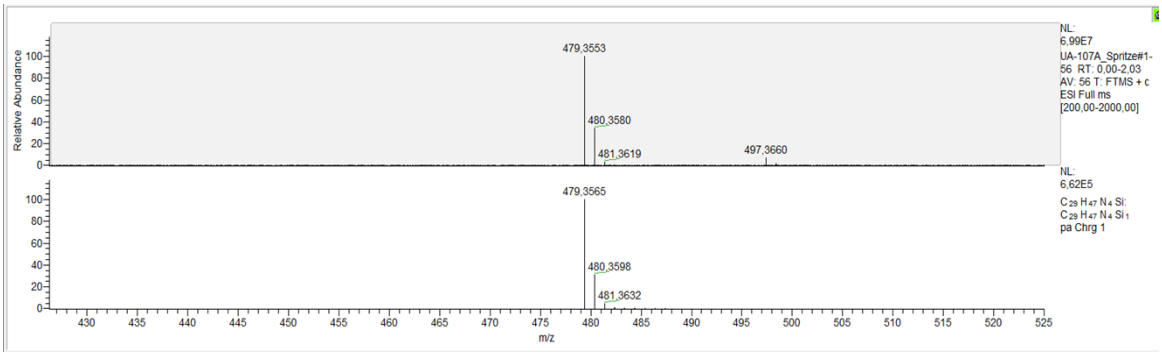


Figure S14. Mass Spectrometric data for **1b**.

Compound 2

APCI-HRMS (m/z) = [*m*-TerSi$(CCPh)_2$CHCHPh] $(M)^+$ 646.30

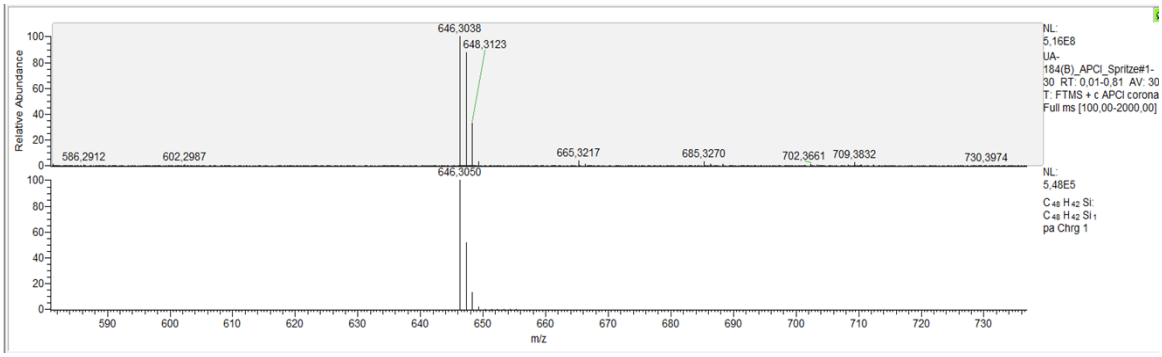


Figure S15. Mass Spectrometric data for **2**.

2. Crystallographic Data

General Considerations

Data for the single crystal structure determination of **1a** and **2** were collected on an Agilent SuperNova diffractometer, equipped with a CCD area Atlas detector and a mirror monochromator utilizing CuK_α radiation (**λ** = 1.5418 Å). The individual crystals were mounted on a glass capillary in per-fluorinated oil and measured in a cold N_2 flow.
The crystal structures were solved by Direct Methods and refined on $\mathbf{F}^2$ using full-matrix least squares with SHELXL-97 (G. M. Sheldrick, SHELXL-97, *Program for refinement of crystal structures*, University of Göttingen, Germany, **1997**). The positions of the H atoms of the carbon atoms were calculated by standard methods.

Compound **1a** [CCDC: 993048], Compound **2** [CCDC: 1000427]

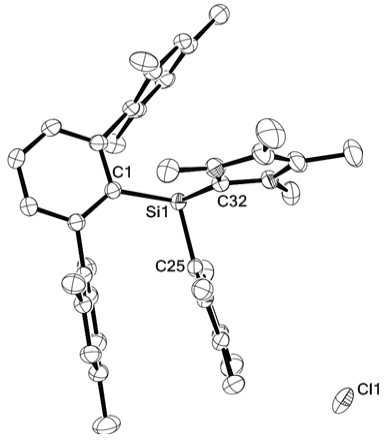


Figure S16. Molecular structure of compound **1a**. Thermal ellipsoids are drawn at 50% probability level. H atoms are omitted for clarity.

Table S 1. Crystal data and structure refinement for **1a**.

Empirical formula	C38 H49 Cl N4 Si	
Formula weight	625.35	
Temperature	150(2) K	
Wavelength	1.5418 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 15.3901(4) Å	α= 90°.
	b = 14.1529(3) Å	β= 110.025(3)°.
	c = 16.9834(5) Å	γ = 90°.
Volume	3475.59(16) $Å^3$	
Z	4	
Density (calculated)	1.195 Mg/m^3	
Absorption coefficient	1.536 mm^{-1}	
F(000)	1344	
Crystal size	0.41 x 0.31 x 0.17 mm^3	
Theta range for data collection	3.06 to 67.49°.	
Index ranges	-18<=h<=18, -15<=k<=16, -20<=l<=20	
Reflections collected	13880	
Independent reflections	6245 [R(int) = 0.0377]	
Completeness to theta = 67.49°	99.7 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.40050
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6245 / 0 / 411
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0496, wR2 = 0.1343
R indices (all data)	R1 = 0.0560, wR2 = 0.1415
Largest diff. peak and hole	0.505 and -0.416 e.Å^{-3}

Table S 2. Selected Bond lengths [Å] and angles [°] for **1a**.

Si(1)-C(1)	1.9355(19)	C(1)-Si(1)-C(32)	105.06(8)
Si(1)-C(32)	1.9481(19)	C(1)-Si(1)-C(25)	111.36(8)
Si(1)-C(25)	1.9665(19)	C(32)-Si(1)-C(25)	93.78(8)
N(1)-C(25)	1.355(2)	C(25)-N(1)-C(26)	111.22(17)
N(1)-C(26)	1.386(2)	C(25)-N(1)-C(28)	125.63(16)
N(1)-C(28)	1.459(3)	C(26)-N(1)-C(28)	123.11(17)
C(1)-C(2)	1.418(3)	C(2)-C(1)-C(6)	116.78(16)
C(1)-C(6)	1.426(2)	C(2)-C(1)-Si(1)	129.79(13)
N(2)-C(25)	1.363(2)	C(6)-C(1)-Si(1)	113.24(13)
N(2)-C(27)	1.390(3)	C(25)-N(2)-C(27)	111.19(17)
N(2)-C(31)	1.465(3)	C(25)-N(2)-C(31)	125.91(17)
C(2)-C(3)	1.394(3)	C(27)-N(2)-C(31)	122.88(17)
C(2)-C(7)	1.498(2)	C(3)-C(2)-C(1)	120.62(16)
N(3)-C(32)	1.358(2)	C(3)-C(2)-C(7)	116.71(16)
N(3)-C(34)	1.387(3)	C(1)-C(2)-C(7)	122.54(16)
N(3)-C(38)	1.463(3)	C(32)-N(3)-C(34)	110.86(17)
C(3)-C(4)	1.387(3)	C(32)-N(3)-C(38)	124.67(16)
N(4)-C(32)	1.354(2)	C(34)-N(3)-C(38)	124.44(17)
N(4)-C(33)	1.394(3)	C(4)-C(3)-C(2)	121.25(18)
N(4)-C(35)	1.462(3)	C(32)-N(4)-C(33)	110.57(17)
C(6)-C(16)	1.508(3)	C(32)-N(4)-C(35)	127.36(16)
		C(33)-N(4)-C(35)	121.43(17)

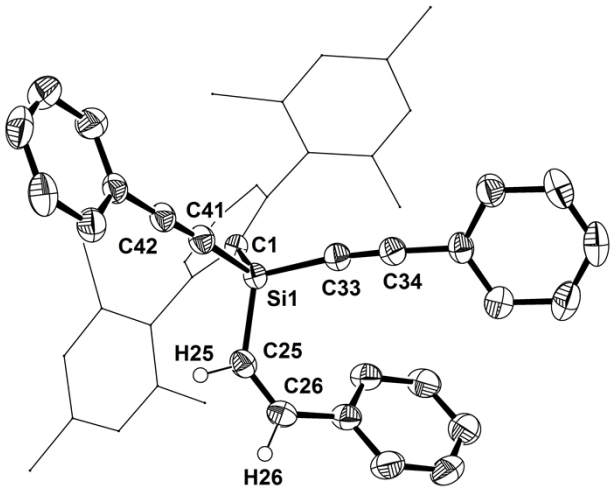


Figure S17. Molecular structure of compound **2**. Thermal ellipsoids are drawn at 50% probability level. H atoms (except for H25 and H26) are omitted for clarity.

Table S 3. Crystal data and structure refinement for **2**.

Empirical formula	C48 H42 Si	
Formula weight	646.91	
Temperature	150.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 26.3057(3) Å	α= 90°.
	b = 8.33770(10) Å	β= 99.1460(10)°.
	c = 34.2192(4) Å	γ = 90°.
Volume	7409.84(15) $Å^3$	
Z	8	
Density (calculated)	1.160 Mg/m^3	
Absorption coefficient	0.790 mm^{-1}	
F(000)	2752	
Crystal size	0.34 x 0.06 x 0.03 mm^3	
Theta range for data collection	2.62 to 67.50°.	

Index ranges	-29<=h<=31, -9<=k<=9, -40<=l<=40
Reflections collected	23693
Independent reflections	6679 [R(int) = 0.0372]
Completeness to theta = 67.50°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9782 and 0.7751
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6679 / 0 / 446
Goodness-of-fit on F^2	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0414, wR2 = 0.1147
R indices (all data)	R1 = 0.0470, wR2 = 0.1203
Largest diff. peak and hole	0.337 and -0.290 e.Å^{-3}

Table S 4. Selected Bond lengths [Å] and angles [°] for **2**.

		C(42)-C(43)	1.435(2)
Si(1)-C(33)	1.8281(15)	C(43)-C(48)	1.394(2)
Si(1)-C(41)	1.8320(16)	C(43)-C(44)	1.396(2)
Si(1)-C(25)	1.8713(15)		
Si(1)-C(1)	1.8913(15)	C(33)-Si(1)-C(41)	106.92(7)
C(1)-C(2)	1.415(2)	C(33)-Si(1)-C(25)	107.83(7)
C(1)-C(6)	1.4190(19)	C(41)-Si(1)-C(25)	103.26(7)
C(25)-C(26)	1.336(2)	C(33)-Si(1)-C(1)	112.34(6)
C(26)-C(27)	1.472(2)	C(41)-Si(1)-C(1)	110.80(7)
C(27)-C(32)	1.394(2)	C(25)-Si(1)-C(1)	115.03(7)
C(27)-C(28)	1.399(2)	C(26)-C(25)-Si(1)	133.36(12)
C(33)-C(34)	1.200(2)	C(25)-C(26)-C(27)	129.78(14)
C(34)-C(35)	1.439(2)	C(34)-C(33)-Si(1)	172.51(14)
C(35)-C(40)	1.391(2)	C(33)-C(34)-C(35)	176.21(17)
C(35)-C(36)	1.394(2)	C(42)-C(41)-Si(1)	176.72(14)
C(41)-C(42)	1.203(2)	C(41)-C(42)-C(43)	178.75(16)

3. DFT Calculations

Analysis of molecular orbitals of compound **1a** and **1b** were carried out at B3LYP/6-31G(d) level of theory. The NBO approach was used to calculate the orbital populations, Wiberg Bond Indices (WBI), and Natural Population Analysis (NPA). Mechanistic investigation were performed at the RI-B97-D/cc-pVTZ(SMD=acetonitrile)//RI-B97-D/6-31G* level of theory.[3] 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.[4]

Assessment of the electronic structure of **1a** and **1b**

Filippou et al investigated the electronic structure of $[SiI(NHC_1)(NHC_2)]I$, which shows structural similarities to **1a** and **1b** (see details in manuscript reference 11) and found, applying Bent's rule[5], that the electronic structure of compound $[SiI(NHC_1)(NHC_2)]I$ can be best described as anionic silicon species (right picture of scheme 2 in the manuscript). Bent's rule, originally stated for organic molecules, gives a good qualitative picture of the electronic structure claiming that the more electropositive the ligand the higher s character hybrid orbital belongs to it. Since Bent's rule certainly gives a good qualitative assumption in several cases we can assume that it may be applicable to silyliumylidenes as well. One can think that silyliumylidene has one p orbital that forms a covalent bond, lone pair with s character (because s is lower in energy than p orbitals), and two vacant p orbitals. If we assume that NHC forms donor-acceptor bond then the lone pair of carbene donates to the vacant p orbital therefore the sum of bond angles around the Si has to be 270 degree. If it is a zwitterionic compound with anionic silicon character, the shared electrons of Si towards the Si-C bonds have to come from hybridization that leads to planarization, in ideal case the degree of pyramidalization is 3 x 109.5° = 328.5° (of course the lone pair has higher s character that is why the degree of pyramidalization will be somewhat less than 328.5°) for silyl anion. For cationic silicon species with three covalent bonds the degree of pyramidalization is 3 x 120° = 360°. In our compound **1a**, the sum around the Si is 310.2°, the calculated DFT structure shows similar result 313.1°, indicating that our compound **1a** should be best described as an anionic silicon center similar to the work of Filippou et al (312°). However, Bent's rule was originally interpreted to molecules in which steric effects do not play an important role biasing the geometry. Therefore, we removed most of the bulky ligands, which has no direct electronic effect to the silicon center, (mesityl ligands and methyl groups of NHC) in the DFT calculation and found that the same analysis give different result as the sum of angles at Si is 291.1° which indicates a donor-acceptor structure for **1a**.

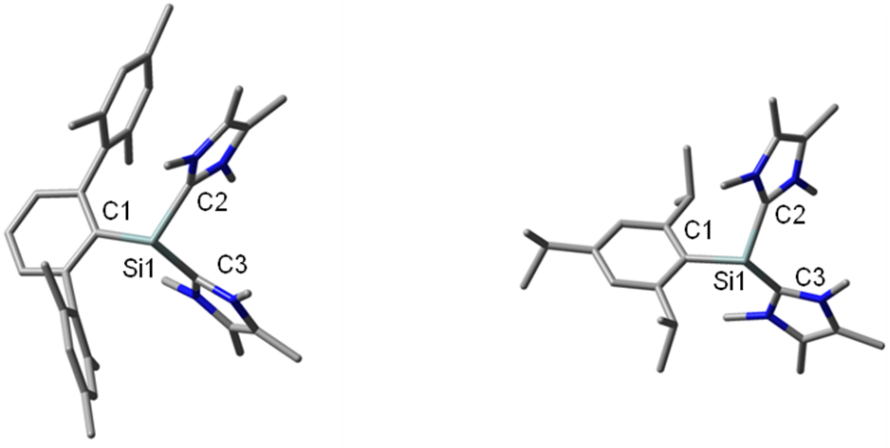
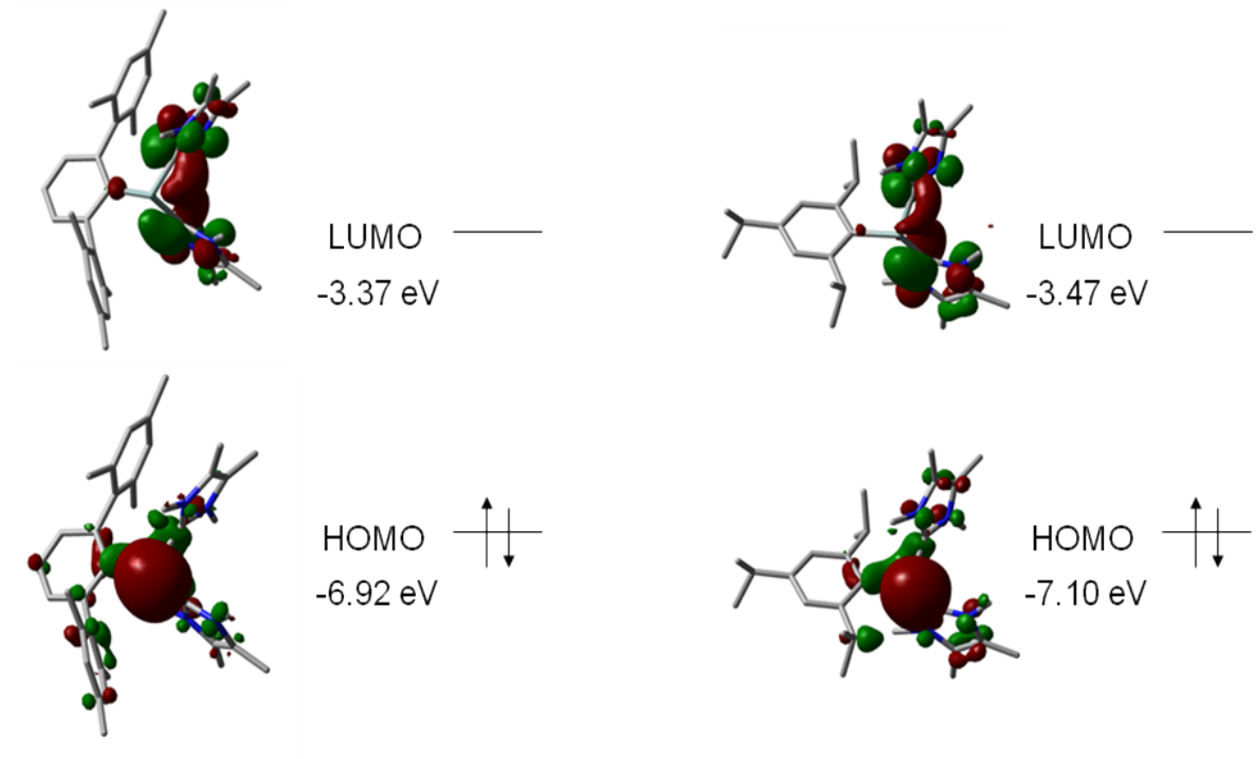


Figure S18. Optimized structure of compounds **1a** (left) and **1b** (right).



1a **1b**

Figure S19. Frontier molecular orbitals diagram of compound **1a** (left) and **1b** (right).

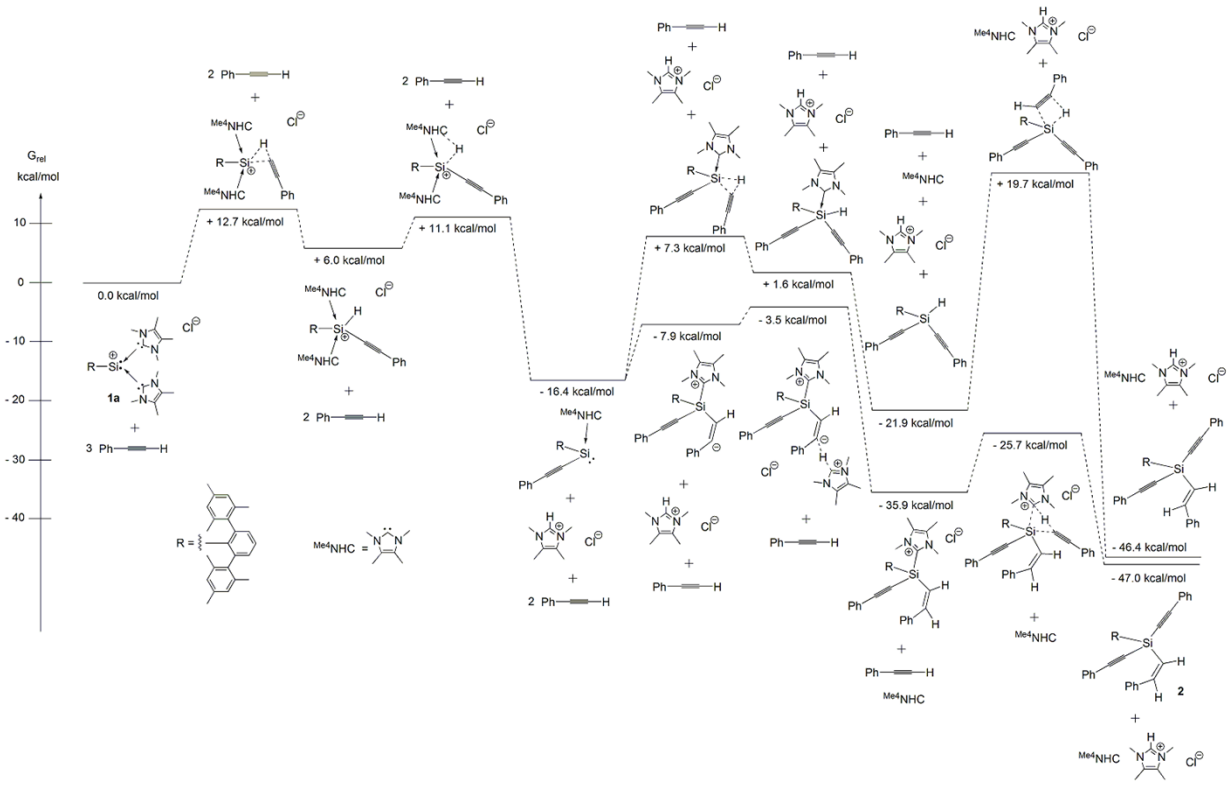


Figure S20. Potential energy surface for the reaction of donor-stabilized silyliumylidene cation **1a** with phenylacetylene for *E*-isomer and *Z*-isomer, **Possible Pathway 1.**

The calculated reaction profile is shown in Scheme 3. We propose the insertion of silicon center into the phenylacetylene terminal C-H bond as the initial step of the reaction giving a five coordinate transition state **TS1** (+ 12.7 kcal/mol). Subsequently, the release of one imidazolium chloride can result in the formation of the key intermediate, silylene **IT2** (-16.4 kcal/mol) through the intermediate **IT1** (+6.0 kcal/mol). The nucleophilic attack of silicon center in silylene **IT2** on second phenylacetylene can then lead to the zwitterionic structure **IT3** (-7.9 kcal/mol). The intermediate **IT3** would be rather unstable and might further lead to the **TS3** (-3.5 kcal/mol) via the proton transfer from $[NHC\text{-}H^+]Cl^-$ to the negative carbon with concomitant loss of the free NHC. This proton transfer process is associated with the attraction of opposite charges and the huge thermodynamic driving force resulting in the formation of a highly stable intermediate **IT4** (-35.9 kcal/mol). This step is proposed to determine the fate of the compound **2** as the *Z*-isomer since the steric hindrance of the bulky groups allows the protonation of **TS3** from only one side. The intermediate **IT4** can easily react with a third phenylacetylene via relatively low energy barrier, **TS4** (-25.7 kcal/mol). As a result, the elimination of $[NHC\text{-}H^+]Cl^-$ from **TS4** can finally lead to the formation of **2**, associated with large thermodynamic stability (-47.0 kcal/mol).

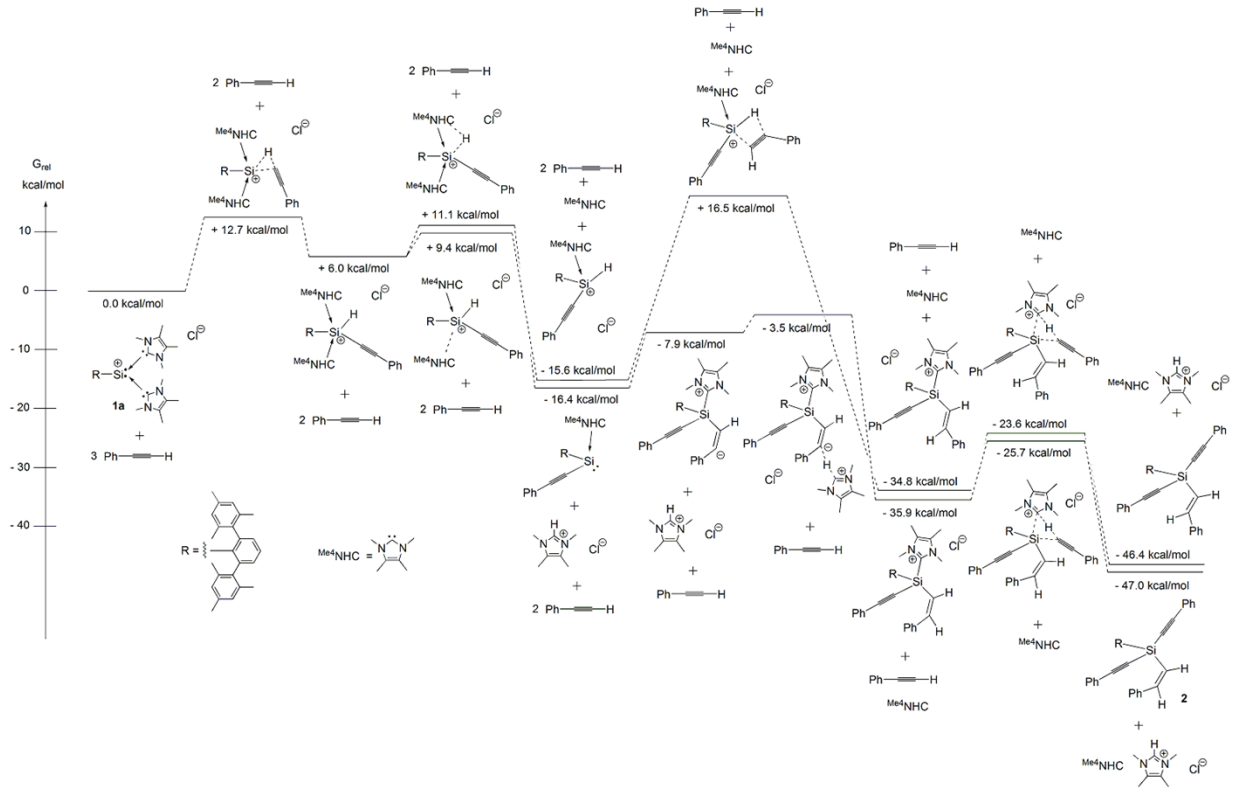


Figure S21. Potential energy surface for the reaction of donor-stabilized silyliumylidene cation **1a** with phenylacetylene for *E*-isomer and *Z*-isomer, ***Possible Pathway 2.***

Table S 5. Cartesian geometry of **2** at B97-D/6-31G* level in Angstrom [Å].

C	3.010980	-2.663717	0.843120
N	2.198899	-2.117545	-0.143555
C	1.304747	-1.216809	0.377454
N	1.578839	-1.219841	1.724333
C	2.615135	-2.100571	2.030926
C	2.389397	-2.435027	-1.564941
C	0.927053	-0.415674	2.759643
Si	0.226891	-0.071154	-0.815567
C	-1.517328	-0.987884	-0.735024
N	-2.168618	-1.717939	0.220671
C	-3.318640	-2.318878	-0.281097
C	-3.389265	-1.963874	-1.605412
N	-2.274808	-1.174737	-1.865951
C	-1.734482	-1.801051	1.609959
C	-2.037412	-0.579528	-3.183421
C	-4.268431	-3.106651	0.562698
C	-4.425575	-2.274073	-2.638298
C	3.116076	-2.317302	3.424056
C	4.100893	-3.643818	0.545107
C	0.205865	1.584209	0.193755
C	-0.910446	2.261022	0.770879

C	-0.736575	3.491772	1.436071
C	0.525606	4.087263	1.537173
C	1.626462	3.461778	0.935913
C	1.481780	2.236158	0.261100
C	-2.303011	1.727774	0.636508
C	-2.930269	1.787905	-0.639112
C	-4.208304	1.240581	-0.804795
C	-4.902115	0.643341	0.265272
C	-4.302600	0.662950	1.531277
C	-3.023379	1.217456	1.740920
C	2.690205	1.640447	-0.412554
C	3.723571	1.021964	0.335303
C	4.766151	0.361118	-0.340401
C	4.850809	0.352640	-1.741171
C	3.876771	1.064458	-2.464189
C	2.809575	1.718365	-1.829003
C	-2.248691	2.488672	-1.799812
C	-6.253210	-0.001819	0.041229
C	-2.478270	1.260965	3.160009
C	3.792113	1.107453	1.847671
C	5.995497	-0.343306	-2.452090
C	1.816406	2.504151	-2.659818
H	-1.611581	3.982813	1.868341
H	0.647032	5.039859	2.056502
H	2.612901	3.929150	0.973307
H	-4.685628	1.294757	-1.787930
H	-4.848241	0.250828	2.385806
H	-1.319207	1.983747	-2.105893
H	-1.960098	3.513725	-1.517708
H	-2.918636	2.544109	-2.671539
H	-6.741229	-0.256141	0.994661
H	-6.149367	-0.932056	-0.545683
H	-6.927196	0.663535	-0.523130
H	-1.401931	1.477500	3.184527
H	-2.665824	0.311971	3.689334
H	-2.980691	2.053248	3.740778
H	5.547911	-0.131200	0.246865
H	3.954874	1.120782	-3.553579
H	4.091535	0.143108	2.285637
H	2.841706	1.431299	2.286794
H	4.553241	1.847468	2.149223
H	6.870233	0.324115	-2.544044
H	5.708660	-0.648384	-3.470992
H	6.327821	-1.237786	-1.899640
H	2.230435	2.721602	-3.656043
H	1.551079	3.454736	-2.171531
H	0.880760	1.933380	-2.794016
H	-0.893646	-2.503420	1.710565
H	-2.575251	-2.131074	2.230086
H	-1.430810	-0.802065	1.922976

H	-5.072273	-3.518403	-0.062001
H	-4.731026	-2.462948	1.330313
H	-3.770783	-3.946693	1.073842
H	-5.222851	-2.886949	-2.197330
H	-4.003351	-2.830337	-3.491706
H	-4.881795	-1.351709	-3.034227
H	-2.714256	0.273031	-3.328819
H	-2.224273	-1.338203	-3.955251
H	-0.994114	-0.239925	-3.227265
H	0.361620	0.388466	2.283444
H	1.696792	0.017951	3.407940
H	0.263653	-1.047427	3.368163
H	3.882809	-3.103467	3.427154
H	2.305374	-2.628081	4.103803
H	3.566990	-1.401535	3.841579
H	4.573631	-3.977243	1.478624
H	4.880400	-3.189020	-0.088922
H	3.717484	-4.532243	0.017012
H	2.097400	-3.478090	-1.754982
H	3.447647	-2.287280	-1.817157
H	1.772883	-1.747668	-2.157866

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

C	-1.221075	-0.119564	0.000000
C	0.000000	0.599326	0.000000
C	1.221142	-0.119449	0.000000
C	1.215706	-1.519385	0.000000
C	0.000119	-2.223798	0.000000
C	-1.215556	-1.519505	0.000000
C	-0.000125	2.029262	0.000000
C	-0.000229	3.249098	0.000000
H	-0.000320	4.320677	0.000000
H	2.162396	0.432493	0.000000
H	2.163063	-2.062646	0.000000
H	0.000183	-3.315859	0.000000
H	-2.162842	-2.062880	0.000000
H	-2.162376	0.432306	0.000000

Table S 7. Cartesian geometry of Me^4NHC in Figure X at B97-D/6-31G* level in Angstrom [Å].

C	-0.685593	0.635422	-0.000332
C	0.685466	0.635477	-0.000210
N	1.062957	-0.716415	-0.001298
C	0.000108	-1.597607	-0.001183
N	-1.062873	-0.716510	-0.000331
C	1.664529	1.768839	0.000308
C	2.449660	-1.163893	0.000890
C	-2.449544	-1.164059	0.000936
C	-1.664700	1.768760	-0.000087
H	-2.438686	-2.261027	-0.002683

H	-2.981550	-0.795222	-0.892234
H	-2.978271	-0.801199	0.898549
H	-1.131931	2.731686	-0.000640
H	-2.320750	1.746122	0.888606
H	-2.321583	1.745680	-0.888137
H	1.131764	2.731763	0.003180
H	2.319523	1.747713	-0.889196
H	2.322486	1.744221	0.887536
H	2.979059	-0.796203	0.896100
H	2.980953	-0.799816	-0.894693
H	2.438853	-2.260868	0.003083

Table S 8. Cartesian geometry of $Me^4NHC\text{-}H^+$ in Figure X at B97-D/6-31G* level in Angstrom [Å].

C	0.690559	-0.665182	-0.000257
C	-0.690514	-0.665210	0.000027
N	-1.089613	0.673609	0.000071
C	-0.000044	1.459488	-0.000036
N	1.089566	0.673677	-0.000430
C	-1.673324	-1.792505	0.000402
C	-2.484061	1.145230	-0.000124
C	2.484020	1.145265	0.000528
C	1.673399	-1.792437	-0.000328
H	2.487650	2.241577	0.001860
H	2.993308	0.772367	-0.898233
H	2.992720	0.770174	0.898696
H	1.140505	-2.751878	-0.003603
H	2.319186	-1.763418	0.892651
H	2.323389	-1.759595	-0.890072
H	-1.140418	-2.751942	-0.001461
H	-2.322562	-1.760621	-0.889944
H	-2.319869	-1.762532	0.892781
H	-2.992582	0.773284	0.899470
H	-2.993547	0.769219	-0.897464
H	-2.487657	2.241536	-0.002672
H	0.000000	2.542938	-0.000765

Table S 9. Cartesian geometry of transition state (+ 12.7 kcal/mol) in Figure 3 at B97-D/6-31G* level in Angstrom [Å].

C	2.008436	-3.006223	1.407634
C	1.420178	-2.982226	0.122550
C	2.244973	-2.852504	-1.029002
C	3.614900	-2.618015	-0.865883
C	4.203130	-2.526934	0.411087
C	3.390389	-2.750493	1.529878
C	-0.053547	-3.144239	-0.092141
C	-0.891116	-2.032119	-0.400961
C	-2.270452	-2.271098	-0.690928
C	-2.775536	-3.583950	-0.660169
C	-1.948555	-4.666613	-0.337944
C	-0.594509	-4.443611	-0.058477

Si	-0.371974	-0.205437	-0.487110
C	-1.407115	0.684494	0.878294
N	-2.171011	1.802897	0.729766
C	-2.942337	2.022679	1.862313
C	-2.644693	1.017606	2.753498
N	-1.703843	0.210714	2.129480
C	-2.262321	2.698900	-0.438401
C	-3.911501	3.155655	1.964184
C	-3.172989	0.734505	4.123472
C	-1.145330	-0.977670	2.773420
C	-3.225703	-1.151451	-0.999051
C	-3.186572	-0.470970	-2.247963
C	-4.088946	0.580948	-2.479559
C	-5.043024	0.969365	-1.525559
C	-5.086118	0.267906	-0.309485
C	-4.209208	-0.794874	-0.036942
C	-2.226379	-0.833549	-3.366497
C	-5.994787	2.115186	-1.806884
C	-4.367297	-1.545192	1.273716
C	1.657330	-3.041319	-2.414892
C	5.675871	-2.208708	0.554104
C	1.229928	-3.372586	2.662068
C	1.499844	0.179925	-0.297972
N	2.347352	0.351265	-1.348176
C	3.600801	0.733084	-0.904512
C	3.538932	0.798193	0.467297
N	2.241188	0.453644	0.811469
C	2.068374	0.179957	-2.779805
C	1.736631	0.421273	2.180089
C	4.592650	1.148240	1.465877
C	4.730960	1.016727	-1.837901
C	0.749572	2.947316	-1.901311
C	-0.055655	2.394528	-2.697427
C	1.639193	3.498830	-0.935570
C	1.309672	3.483914	0.451279
C	2.194268	3.969229	1.420578
C	3.446396	4.488827	1.045503
C	3.789991	4.526074	-0.318029
C	2.904778	4.047902	-1.290443
H	0.066026	-5.280690	0.175344
H	-2.353379	-5.679998	-0.316579
H	-3.829341	-3.745937	-0.894391
H	4.246117	-2.520290	-1.753771
H	3.843186	-2.753896	2.525877
H	0.853885	-2.321734	-2.632879
H	1.205935	-4.042938	-2.505004
H	2.432267	-2.942138	-3.188855
H	6.022178	-2.354862	1.588550
H	5.875637	-1.159758	0.273610
H	6.288026	-2.842811	-0.107549

H	0.173586	-3.582720	2.449128
H	1.286022	-2.584322	3.433072
H	1.661047	-4.280023	3.115669
H	-5.834496	0.540611	0.440578
H	-4.037645	1.110994	-3.434362
H	-4.744135	-0.873525	2.060707
H	-3.425436	-1.998924	1.607014
H	-5.094275	-2.368933	1.171929
H	-6.660248	1.876513	-2.653330
H	-5.446211	3.032198	-2.083353
H	-6.627307	2.337677	-0.933535
H	-2.792375	-1.139938	-4.261800
H	-1.558808	-1.662311	-3.092400
H	-1.619022	0.047208	-3.640795
H	0.830049	1.033483	2.247539
H	2.495804	0.840924	2.847611
H	1.536150	-0.617835	2.464994
H	5.528160	1.387004	0.943571
H	4.788919	0.309616	2.154688
H	4.303476	2.036806	2.047931
H	5.625383	1.298380	-1.267727
H	4.478042	1.852108	-2.509516
H	4.974772	0.137967	-2.457325
H	2.695797	-0.640421	-3.153438
H	2.284101	1.126016	-3.286776
H	1.009960	-0.029592	-2.936938
H	-0.589664	-1.560119	2.038360
H	-1.965126	-1.590695	3.167991
H	-0.485122	-0.681035	3.600287
H	-3.872414	1.525750	4.423336
H	-2.364861	0.691193	4.872455
H	-3.711705	-0.227582	4.154674
H	-4.372514	3.170524	2.960599
H	-4.710186	3.050113	1.212032
H	-3.417463	4.125336	1.794215
H	-1.850555	3.677932	-0.155315
H	-3.321414	2.788388	-0.703669
H	-1.679805	2.318451	-1.287596
H	-0.681983	0.505021	-1.742639
H	3.169056	4.099672	-2.348594
H	4.751491	4.944993	-0.624573
H	4.132261	4.879441	1.799855
H	1.902035	3.958708	2.475022
H	0.336903	3.084978	0.749049

Table S 10. Cartesian geometry of intermediate (+ 6.0 kcal/mol) in Figure 3 at B97-D/6-31G* level in Angstrom [Å].

C	2.689593	4.186477	-1.701333
C	2.122562	3.598572	-0.542935
C	2.341118	4.206635	0.720422

C	3.106681	5.374576	0.815353
C	3.665785	5.950623	-0.337882
C	3.455314	5.353480	-1.592781
C	1.365602	2.395317	-0.632180
C	0.747902	1.332727	-0.683993
Si	-0.186504	-0.247675	-0.630197
C	1.530488	-1.387031	-1.275884
N	2.788019	-1.060249	-1.696103
C	3.382744	-2.102788	-2.414197
C	2.467862	-3.122868	-2.447938
N	1.351788	-2.660445	-1.747389
C	3.511000	0.176609	-1.377851
C	4.771787	-2.034316	-2.970939
C	2.564966	-4.498021	-3.030686
C	0.148505	-3.462383	-1.525604
C	-0.424589	-1.245878	1.020704
C	0.710050	-1.687472	1.784564
C	0.561818	-2.660056	2.795429
C	-0.678385	-3.229676	3.087791
C	-1.803411	-2.763150	2.407624
C	-1.703491	-1.770164	1.409446
C	2.108841	-1.140457	1.684183
C	2.385862	0.155723	2.196533
C	3.706317	0.629056	2.219033
C	4.781556	-0.159195	1.770968
C	4.499557	-1.456099	1.320070
C	3.189384	-1.969515	1.291832
C	1.283780	0.999019	2.801200
C	3.001039	-3.415851	0.871218
C	6.197302	0.380634	1.791232
C	-3.051891	-1.269572	0.962586
C	-3.583885	-0.125371	1.618134
C	-4.884285	0.300719	1.317752
C	-5.707971	-0.406212	0.422936
C	-5.190936	-1.569714	-0.164620
C	-3.884022	-2.022409	0.104884
C	-2.798746	0.581220	2.704319
C	-7.119959	0.067285	0.141315
C	-3.413235	-3.330688	-0.501537
C	-1.977924	0.944196	-0.713786
N	-2.989857	0.724622	-1.614544
C	-3.922165	1.764335	-1.612073
C	-3.479843	2.675557	-0.691053
N	-2.293802	2.159168	-0.168531
C	-3.129445	-0.418860	-2.525640
C	-5.149346	1.769634	-2.467469
C	-4.078359	3.967527	-0.234283
C	-1.508989	2.921678	0.800618
H	-2.794935	-3.141008	2.665813
H	-0.771710	-3.995757	3.859680

H	1.446857	-2.960570	3.358814
H	-5.279312	1.186660	1.823509
H	-5.825233	-2.158446	-0.834090
H	-1.747707	0.731783	2.423852
H	-2.788305	-0.028812	3.625617
H	-3.251322	1.554637	2.949042
H	-7.668899	-0.651717	-0.484651
H	-7.120803	1.040062	-0.376539
H	-7.684313	0.205150	1.076501
H	-2.408577	-3.240966	-0.936507
H	-4.105264	-3.671795	-1.287403
H	-3.353780	-4.123153	0.263385
H	5.323688	-2.098754	0.995659
H	3.901645	1.630416	2.611933
H	3.611986	-3.642487	-0.016145
H	1.953930	-3.650104	0.646615
H	3.325792	-4.097057	1.677026
H	6.527975	0.587363	2.823477
H	6.267682	1.330784	1.234029
H	6.906991	-0.334615	1.346245
H	1.690585	1.918544	3.247246
H	0.737309	0.441654	3.579995
H	0.551596	1.279278	2.034798
H	-2.630683	-0.204904	-3.482645
H	-4.195199	-0.600579	-2.692298
H	-2.700886	-1.312081	-2.073808
H	-5.727202	2.686057	-2.289896
H	-5.794672	0.909639	-2.231069
H	-4.904110	1.724074	-3.542062
H	-4.996436	4.175776	-0.800162
H	-3.387279	4.813892	-0.380873
H	-4.341923	3.935594	0.836983
H	-2.177009	3.300974	1.584016
H	-1.005210	3.759748	0.298283
H	-0.757083	2.276341	1.245574
H	-0.234842	-3.269520	-0.518586
H	0.402689	-4.525405	-1.614339
H	-0.623042	-3.209868	-2.269419
H	3.509285	-4.605490	-3.580022
H	1.739762	-4.708071	-3.730244
H	2.544170	-5.274001	-2.245538
H	4.988081	-2.943767	-3.548158
H	5.528065	-1.954448	-2.170476
H	4.901109	-1.167078	-3.639429
H	3.307637	0.947282	-2.134260
H	4.582104	-0.048098	-1.350737
H	3.199257	0.529579	-0.395946
H	-0.747178	-0.891109	-1.847738
H	1.911668	3.749340	1.612601
H	3.269924	5.836816	1.790982

H	4.263471	6.860823	-0.259061
H	3.888885	5.799185	-2.489676
H	2.519564	3.720874	-2.674086

Table S 11. Cartesian geometry of transition state (+ 11.1 kcal/mol) in Figure 3 at B97-D/6-31G* level in Angstrom [Å].

N	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.368663
N	1.334557	0.000000	1.688889
C	2.142082	-0.023212	0.549780
C	1.292765	-0.024899	-0.523957
Si	-1.563765	0.350782	2.806829
C	-2.374908	-1.407207	2.980300
C	-3.762044	-1.547086	3.329847
C	-4.274253	-2.790280	3.756289
C	-3.462186	-3.920762	3.859255
C	-2.130151	-3.823852	3.456454
C	-1.584990	-2.606123	2.995695
C	-4.815462	-0.478839	3.207058
C	-5.274846	-0.101888	1.916244
C	-6.339294	0.803443	1.791834
C	-6.992770	1.334920	2.918220
C	-6.564967	0.911288	4.184045
C	-5.507501	-0.002825	4.348693
C	-0.204732	-2.778706	2.418147
C	-0.096208	-3.004868	1.018494
C	1.156528	-3.290094	0.459816
C	2.310849	-3.416993	1.253760
C	2.174164	-3.255990	2.640007
C	0.932732	-2.957500	3.236111
C	-4.687595	-0.733856	0.672416
C	-8.130231	2.323132	2.757659
C	-5.180693	-0.466422	5.756725
C	-1.330048	-3.034771	0.139711
C	3.645807	-3.753399	0.619774
C	0.837599	-2.874013	4.747719
C	1.920548	0.049837	3.034721
C	3.636391	-0.067369	0.602646
C	1.577734	-0.077549	-1.990950
C	-1.163066	0.078764	-0.881859
C	-2.216239	1.611230	1.640970
C	-2.697320	2.390507	0.819615
C	-3.306572	3.281880	-0.109385
C	-3.068298	4.677338	-0.038917
C	-3.697618	5.543056	-0.941412
C	-4.566941	5.036425	-1.922866
C	-4.808099	3.654296	-1.999958
C	-4.186840	2.778556	-1.102015
C	-1.898289	1.575010	4.843827
N	-2.308119	2.844279	5.136660

C	-1.927663	3.228050	6.426705
C	-1.254172	2.163146	6.966243
N	-1.252348	1.172102	5.982345
C	-3.132327	3.705099	4.280229
C	-2.268003	4.557951	7.026389
C	-0.660681	1.975822	8.327400
C	-0.651549	-0.148791	6.167992
H	-1.491327	-4.709542	3.460192
H	-3.870596	-4.870182	4.210262
H	-5.335320	-2.856209	4.002857
H	1.227879	-3.454907	-0.619292
H	3.049565	-3.387960	3.282958
H	-2.015418	-2.205553	0.360345
H	-1.901867	-3.963623	0.316616
H	-1.056393	-3.004620	-0.926337
H	4.420239	-3.930389	1.380735
H	3.993669	-2.940235	-0.037664
H	3.569877	-4.656419	-0.005417
H	0.276535	-1.987527	5.073196
H	1.839415	-2.840633	5.203893
H	0.307655	-3.749029	5.160210
H	-7.078718	1.287503	5.073968
H	-6.677308	1.086759	0.791472
H	-5.174668	0.386811	6.452419
H	-4.209966	-0.972717	5.812511
H	-5.944803	-1.178000	6.115366
H	-8.987291	1.860224	2.239224
H	-7.818614	3.191923	2.152422
H	-8.484521	2.690786	3.733652
H	-5.232412	-0.412954	-0.227678
H	-4.721196	-1.834432	0.730824
H	-3.634259	-0.451277	0.559980
H	2.079557	1.094451	3.341146
H	2.875428	-0.483548	3.016473
H	1.266783	-0.451728	3.746537
H	4.048106	-0.082400	-0.414972
H	3.982799	-0.973573	1.122951
H	4.057226	0.806750	1.127794
H	2.662651	-0.069710	-2.162255
H	1.141407	0.782967	-2.524376
H	1.169985	-0.994570	-2.450198
H	-1.055024	-0.661091	-1.684834
H	-1.241302	1.088495	-1.309432
H	-2.063904	-0.131868	-0.312707
H	-1.279882	-0.903703	5.684730
H	-0.588909	-0.368490	7.240516
H	0.359154	-0.175006	5.731988
H	-0.733371	2.910295	8.898831
H	0.402628	1.690633	8.277361
H	-1.191008	1.192803	8.897197

H	-1.805148	4.649740	8.018562
H	-3.358163	4.682416	7.149416
H	-1.905641	5.391638	6.402397
H	-2.498006	4.310134	3.617647
H	-3.731792	4.357574	4.923200
H	-3.800854	3.083061	3.686891
H	-1.031264	1.155483	4.206436
H	-4.376480	1.705615	-1.150614
H	-5.483746	3.259284	-2.761295
H	-5.054768	5.716043	-2.624328
H	-3.509153	6.616243	-0.879685
H	-2.388952	5.065135	0.722691

Table S 12. Cartesian geometry of intermediate (- 16.4 kcal/mol) in Figure 3 at B97-D/6-31G* level in Angstrom [Å].

C	-2.566933	-2.694522	-0.861337
C	-2.168786	-2.076486	0.348025
C	-3.125240	-1.380935	1.129125
C	-4.455719	-1.317276	0.693160
C	-4.870276	-1.924826	-0.505000
C	-3.909901	-2.600202	-1.271669
C	-0.761334	-2.256087	0.840027
C	0.354890	-1.538074	0.312744
C	1.647719	-1.921031	0.793496
C	1.795534	-2.910396	1.785662
C	0.682452	-3.568854	2.319588
C	-0.587567	-3.243915	1.831548
Si	0.147099	-0.231609	-1.136737
C	1.358720	1.170105	-0.433649
N	1.329083	1.817371	0.767118
C	2.340199	2.772403	0.851378
C	3.019529	2.720742	-0.341259
N	2.388558	1.750737	-1.113463
C	0.319973	1.577312	1.801151
C	2.564307	3.630337	2.056294
C	4.229055	3.462362	-0.811206
C	2.790031	1.428853	-2.485177
C	2.924274	-1.339277	0.258709
C	3.416253	-1.756877	-1.008533
C	4.635187	-1.240674	-1.475878
C	5.385781	-0.313324	-0.730147
C	4.904576	0.058713	0.532966
C	3.702801	-0.459626	1.049217
C	2.665314	-2.777685	-1.840594
C	6.682253	0.253496	-1.277556
C	3.295231	-0.088996	2.462424
C	-2.718547	-0.638614	2.385525
C	-6.319622	-1.845257	-0.943850
C	-1.572630	-3.464131	-1.710588
C	-1.387615	0.729731	-0.690241

H	2.802287	-3.166215	2.126539
H	0.805103	-4.337386	3.086267
H	-1.472108	-3.763636	2.208929
H	5.008685	-1.573001	-2.449535
H	5.484870	0.758588	1.142046
H	1.751783	-2.338094	-2.276754
H	2.343329	-3.628470	-1.219665
H	3.297842	-3.153377	-2.660331
H	7.168697	0.917644	-0.545219
H	6.513488	0.834655	-2.202283
H	7.394938	-0.549088	-1.533673
H	2.205466	-0.091652	2.587778
H	3.690495	0.902378	2.734494
H	3.697127	-0.816458	3.189479
H	-5.183048	-0.761745	1.292094
H	-4.211825	-3.080249	-2.207452
H	-3.601980	-0.351078	2.976634
H	-2.180975	0.282957	2.106229
H	-2.045579	-1.236638	3.018919
H	-6.974166	-2.434884	-0.277206
H	-6.449625	-2.227041	-1.969023
H	-6.686042	-0.804224	-0.913786
H	-2.087230	-4.005488	-2.519821
H	-1.007642	-4.189926	-1.103121
H	-0.832326	-2.784033	-2.167056
H	-0.599963	2.125982	1.555638
H	0.723242	1.898498	2.769227
H	0.091285	0.506907	1.823104
H	3.414694	4.304094	1.880966
H	2.789418	3.023745	2.950088
H	1.680863	4.248904	2.288142
H	4.545162	4.189688	-0.050400
H	4.037148	4.010369	-1.749230
H	5.065976	2.767393	-0.992775
H	3.821666	1.057003	-2.484389
H	2.708828	2.333920	-3.106334
H	2.110916	0.652678	-2.861382
C	-2.393874	1.443595	-0.601416
C	-3.594481	2.194732	-0.464781
C	-4.835049	1.642145	-0.883364
C	-6.022358	2.366709	-0.733953
C	-6.006746	3.655296	-0.171713
C	-4.785162	4.217406	0.237076
C	-3.591614	3.499818	0.094356
H	-4.838502	0.642002	-1.313739
H	-6.966797	1.924992	-1.061904
H	-6.936239	4.217524	-0.056991
H	-4.763559	5.220469	0.670110
H	-2.642337	3.937935	0.410770

Table S 13. Cartesian geometry of intermediate (- 7.9 kcal/mol) in Figure 3 at B97-D/6-31G* level in Angstrom [Å].

C	-4.723672	1.262042	0.719875
C	-3.633783	0.661309	1.404389
C	-3.832775	0.190181	2.730585
C	-5.085966	0.301523	3.342978
C	-6.163518	0.882780	2.650974
C	-5.973467	1.362687	1.339896
C	-2.378725	0.485648	0.762015
C	-1.317080	0.241896	0.186080
Si	0.273388	-0.125711	-0.633372
C	1.488245	0.897583	0.477152
N	2.461392	1.792327	0.145244
C	3.079043	2.293377	1.287226
C	2.468684	1.695664	2.363528
N	1.499976	0.843240	1.843961
C	2.797814	2.198851	-1.225637
C	4.212927	3.267210	1.250196
C	2.711269	1.863781	3.830375
C	0.578451	0.050571	2.666554
C	0.733307	-1.965278	-0.288596
C	2.083033	-2.406942	-0.103030
C	2.376053	-3.770662	0.089581
C	1.363458	-4.738130	0.074254
C	0.043233	-4.332713	-0.158612
C	-0.281828	-2.976563	-0.342923
C	3.277358	-1.497650	-0.169642
C	3.980891	-1.126833	1.004295
C	5.147029	-0.349305	0.897904
C	5.669380	0.031258	-0.348955
C	4.987824	-0.386286	-1.504451
C	3.803981	-1.141302	-1.437800
C	3.538973	-1.605964	2.373579
C	3.137296	-1.605754	-2.718985
C	6.961106	0.821418	-0.448403
C	-1.721511	-2.663051	-0.624596
C	-2.140931	-2.369517	-1.943021
C	-3.491923	-2.052879	-2.176790
C	-4.440019	-2.052011	-1.143650
C	-4.011563	-2.391508	0.152023
C	-2.671882	-2.692789	0.426942
C	-1.176533	-2.439968	-3.112893
C	-5.887271	-1.681776	-1.397452
C	-2.238164	-2.953874	1.855353
C	0.226164	0.663222	-2.352642
C	-0.290954	1.877294	-2.355730
C	-1.009958	2.998735	-1.972466
C	-2.454939	2.933902	-1.903666
C	-3.216815	4.066623	-1.630529
C	-2.618416	5.324571	-1.401127

C	-1.213256	5.411063	-1.458907
C	-0.422400	4.296179	-1.738633
H	3.417702	-4.066753	0.238048
H	1.603520	-5.793924	0.218496
H	-0.760756	-5.071352	-0.204603
H	5.393701	-0.127540	-2.486902
H	5.673737	-0.059653	1.812729
H	2.177266	-1.095338	-2.887235
H	2.918330	-2.684487	-2.678329
H	3.783692	-1.407658	-3.588089
H	7.811063	0.246820	-0.040478
H	6.913153	1.764762	0.123257
H	7.194710	1.071431	-1.495165
H	2.465046	-1.827843	2.401011
H	3.777438	-0.858546	3.146743
H	4.062371	-2.538805	2.648217
H	-4.729868	-2.372561	0.976128
H	-3.807310	-1.801932	-3.193841
H	-3.103827	-2.942934	2.534759
H	-1.533619	-2.171586	2.185740
H	-1.715912	-3.918220	1.961260
H	-6.556439	-2.548317	-1.249323
H	-6.031477	-1.314078	-2.425605
H	-6.212965	-0.893847	-0.697188
H	-1.576839	-1.898279	-3.983175
H	-1.004616	-3.490040	-3.411628
H	-0.194509	-2.016431	-2.862858
H	-0.364918	0.596402	2.800180
H	1.057840	-0.145799	3.632774
H	0.372235	-0.899453	2.161985
H	3.530397	2.577582	3.992920
H	2.992183	0.910607	4.310335
H	1.816978	2.248231	4.350042
H	4.549504	3.485021	2.272971
H	3.923759	4.219233	0.775041
H	5.066749	2.851498	0.691460
H	3.766670	2.714187	-1.207608
H	2.014137	2.858751	-1.613028
H	2.866528	1.305915	-1.855656
H	-4.567379	1.635596	-0.294381
H	-6.806778	1.817828	0.798229
H	-7.141644	0.965026	3.129823
H	-5.224125	-0.068082	4.363152
H	-2.999908	-0.278232	3.259621
H	0.663138	4.414006	-1.802357
H	-0.722288	6.375152	-1.291915
H	-3.227380	6.207229	-1.193785
H	-4.307156	3.971682	-1.594685
H	-2.934696	1.969760	-2.082997
H	0.546533	0.124276	-3.261036

Table S 14. Cartesian geometry of transition state (- 3.5 kcal/mol) in Figure 3 at B97-D/6-31G* level in Angstrom [Å].

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.427611
C	1.268492	0.000000	2.100774
C	2.458601	-0.000147	1.367612
C	2.440410	-0.006228	-0.041322
C	1.201430	-0.012867	-0.713350
C	-1.198014	0.072997	2.163413
C	-1.821475	-0.558691	3.058287
Si	-1.701955	-2.341802	3.142786
C	-2.369562	-3.442670	4.615856
C	-3.712625	-3.929803	4.650913
C	-4.162519	-4.745639	5.710549
C	-3.316229	-5.079599	6.772916
C	-2.011216	-4.578538	6.782038
C	-1.534737	-3.771752	5.728931
C	-4.768545	-3.570597	3.640598
C	-5.206660	-4.515563	2.681615
C	-6.247481	-4.180914	1.799552
C	-6.908072	-2.945438	1.876466
C	-6.496177	-2.040683	2.866148
C	-5.445562	-2.330331	3.756256
C	-0.128586	-3.268410	5.868926
C	0.116082	-1.931356	6.262130
C	1.447909	-1.484400	6.355405
C	2.534492	-2.336087	6.111697
C	2.268488	-3.676578	5.778311
C	0.958408	-4.152772	5.650268
C	-4.610962	-5.912376	2.610366
C	-8.069990	-2.625881	0.954119
C	-5.097078	-1.344948	4.854003
C	-1.013692	-0.995419	6.648734
C	3.963087	-1.838106	6.193625
C	0.720215	-5.578693	5.192819
C	0.056083	-2.771888	2.868635
C	1.223633	-3.109065	2.668536
C	2.575704	-3.513334	2.504100
C	3.627896	-2.560596	2.541002
C	4.959207	-2.973885	2.419088
C	5.271723	-4.336267	2.256990
C	4.236735	-5.287066	2.214163
C	2.901866	-4.884893	2.334634
C	-2.592104	-2.992270	1.580950
N	-3.495176	-2.394090	0.748329
C	-3.815291	-3.239327	-0.310250
C	-3.106131	-4.399183	-0.127532
N	-2.371693	-4.235082	1.047203
C	-3.908432	-0.998187	0.864470

C	-4.788701	-2.866864	-1.381307
C	-3.058363	-5.647502	-0.948952
C	-1.449202	-5.231421	1.589846
H	-5.196762	-5.098809	5.699000
H	-3.677410	-5.704573	7.593818
H	-1.340591	-4.799134	7.616255
H	-7.019414	-1.087163	2.964593
H	-6.563294	-4.914522	1.051219
H	-4.119045	-0.868250	4.688208
H	-5.045230	-1.850377	5.830584
H	-5.856770	-0.551012	4.910482
H	-8.897428	-3.335041	1.106504
H	-7.785522	-2.700352	-0.110590
H	-8.457310	-1.613392	1.131138
H	-3.590004	-5.945146	3.008740
H	-4.603113	-6.278159	1.565496
H	-5.209529	-6.632851	3.208023
H	3.101682	-4.353045	5.567481
H	1.634333	-0.442393	6.632167
H	1.673277	-6.114589	5.072177
H	0.199777	-5.583882	4.220499
H	0.085658	-6.140848	5.895999
H	4.498223	-2.289581	7.039775
H	4.001916	-0.749991	6.317588
H	4.516825	-2.101559	5.284974
H	-0.679694	0.052409	6.626354
H	-1.363252	-1.222516	7.671553
H	-1.876085	-1.080822	5.978512
H	-0.425971	-5.027970	1.250947
H	-1.774548	-6.223384	1.260078
H	-1.474600	-5.190501	2.685480
H	-3.739452	-5.556366	-1.807305
H	-3.364238	-6.536530	-0.365570
H	-2.041664	-5.840365	-1.337329
H	-4.920465	-3.708588	-2.075373
H	-4.448566	-1.994005	-1.964057
H	-5.771554	-2.622056	-0.947129
H	-4.692245	-0.800274	0.125035
H	-3.019023	-0.363169	0.704215
H	-4.296274	-0.813385	1.871958
H	3.380816	-1.506579	2.679124
H	5.758620	-2.229073	2.451432
H	6.312657	-4.653753	2.165800
H	4.471486	-6.347638	2.091159
H	2.098524	-5.624061	2.319562
H	-0.957167	0.020732	-0.528727
H	1.172440	-0.010495	-1.811291
H	3.373150	-0.005921	-0.609242
H	3.413304	-0.004511	1.901151
H	1.285663	-0.010217	3.190944

H	-2.299627	-0.000120	3.876437
H	-1.254758	1.347506	2.413230
C	-1.193795	2.544646	2.469243
N	-1.768578	3.180165	3.448193
C	-1.547686	4.484333	3.267701
C	-0.752316	4.581072	2.036446
N	-0.587756	3.321896	1.620008
C	0.132194	2.911086	0.442507
C	-0.251705	5.787197	1.406247
C	-1.997453	5.576388	4.108907
C	-2.510588	2.593881	4.534145
H	-2.869744	3.381258	5.195178
H	-3.358895	2.038924	4.136250
H	-1.864270	1.918082	5.092257
H	-1.653877	6.521601	3.691238
H	-3.085448	5.574287	4.155626
H	-1.590823	5.453444	5.111633
H	0.302416	5.523541	0.506605
H	-1.088090	6.432368	1.141414
H	0.406535	6.311525	2.097422
H	0.528195	3.789102	-0.065617
H	0.953737	2.256318	0.729331
H	-0.540888	2.377161	-0.226676

Table S 15. Cartesian geometry of intermediate (- 35.9 kcal/mol) in Figure 3 at B97-D/6-31G* level in Angstrom [Å].

C	2.122455	2.853008	-1.408583
C	1.590107	2.705800	-0.105468
C	2.432388	2.296783	0.961401
C	3.757061	1.933577	0.683431
C	4.274175	1.973015	-0.624030
C	3.451338	2.462653	-1.649345
C	0.145061	3.009828	0.169332
C	-0.872039	2.007724	0.067645
C	-2.217307	2.384510	0.360374
C	-2.514074	3.713437	0.726171
C	-1.510506	4.681988	0.817093
C	-0.185685	4.324083	0.543374
Si	-0.277306	0.278604	-0.497266
C	-1.660750	-1.076711	-0.332686
N	-2.123276	-1.529642	0.863656
C	-3.002577	-2.590002	0.688733
C	-3.081879	-2.809066	-0.665588
N	-2.237881	-1.880485	-1.269748
C	-1.720190	-1.012181	2.175746
C	-3.717233	-3.246938	1.823403
C	-3.901802	-3.785386	-1.446568
C	-2.138177	-1.757050	-2.727619
C	-3.370195	1.429400	0.317139
C	-3.854162	0.945282	-0.925369

C	-4.910556	0.020863	-0.939104
C	-5.519456	-0.425084	0.246077
C	-5.076354	0.121130	1.460743
C	-4.023038	1.052110	1.517686
C	-3.277269	1.447636	-2.235438
C	-6.606401	-1.477724	0.210908
C	-3.628619	1.633731	2.864363
C	1.919845	2.252886	2.387101
C	5.671485	1.469512	-0.917725
C	1.319150	3.466348	-2.540135
C	0.976966	-0.420414	0.612586
H	-3.552218	3.977224	0.936141
H	-1.759358	5.707154	1.097912
H	0.613327	5.064669	0.611600
H	-5.285665	-0.341069	-1.901223
H	-5.572157	-0.172902	2.390676
H	-2.300426	0.994949	-2.466242
H	-3.118543	2.536246	-2.204605
H	-3.953775	1.215414	-3.072060
H	-7.249182	-1.424586	1.102896
H	-6.166762	-2.491213	0.178884
H	-7.242249	-1.369517	-0.681899
H	-2.546455	1.813153	2.940880
H	-3.938749	0.967084	3.683946
H	-4.118699	2.607368	3.031230
H	4.393803	1.588301	1.501185
H	3.853213	2.551735	-2.662956
H	2.622515	1.708645	3.035611
H	0.939081	1.757570	2.445038
H	1.794071	3.272064	2.792622
H	6.353691	1.660164	-0.074171
H	6.089965	1.943329	-1.820085
H	5.658793	0.377894	-1.091003
H	1.558957	2.984082	-3.500975
H	1.561448	4.538659	-2.643517
H	0.236087	3.396200	-2.368205
H	-0.852952	-1.576298	2.545561
H	-2.570805	-1.101612	2.859100
H	-1.455181	0.044550	2.080129
H	-4.297889	-4.103353	1.456735
H	-4.414364	-2.536406	2.298903
H	-3.018219	-3.610977	2.593055
H	-4.481025	-4.417286	-0.760910
H	-3.273385	-4.444889	-2.067691
H	-4.609782	-3.268366	-2.115136
H	-3.059416	-1.297718	-3.112839
H	-2.014054	-2.758465	-3.159256
H	-1.272815	-1.137823	-2.979915
C	1.900061	-0.870021	1.289533
C	3.052465	-1.322450	1.986281

C	3.024750	-1.591070	3.376698
C	4.192622	-1.994805	4.033738
C	5.394322	-2.135015	3.318101
C	5.427219	-1.871711	1.937474
C	4.267895	-1.467070	1.268520
H	2.090753	-1.471585	3.928981
H	4.168083	-2.197376	5.105901
H	6.302795	-2.447421	3.836145
H	6.360805	-1.978370	1.381761
H	4.278625	-1.259931	0.199769
C	0.308248	0.405015	-2.268367
C	1.371956	-0.167465	-2.892512
H	-0.146914	1.236923	-2.814991
H	1.683192	0.277827	-3.846104
C	2.213669	-1.286094	-2.453829
C	3.579625	-1.293310	-2.824290
C	4.426936	-2.331769	-2.419133
C	3.915837	-3.398551	-1.659475
C	2.555620	-3.418748	-1.309721
C	1.712375	-2.373306	-1.704343
H	3.973159	-0.463178	-3.415114
H	5.480416	-2.316682	-2.704856
H	4.571548	-4.214325	-1.350103
H	2.153244	-4.252116	-0.730904
H	0.651668	-2.407606	-1.451467

Table S 16. Cartesian geometry of transition state (- 25.7 kcal/mol) in Figure 3 at B97-D/6-31G* level in Angstrom [Å].

C	1.712375	-2.373306	-1.704343
C	2.213669	-1.286094	-2.453829
C	3.579625	-1.293310	-2.824290
C	4.426936	-2.331769	-2.419133
C	3.915837	-3.398551	-1.659475
C	2.555620	-3.418748	-1.309721
C	1.371956	-0.167465	-2.892512
C	0.308248	0.405015	-2.268367
Si	-0.277306	0.278604	-0.497266
C	0.976966	-0.420414	0.612586
C	1.900061	-0.870021	1.289533
C	3.052465	-1.322450	1.986281
C	3.024750	-1.591070	3.376698
C	4.192622	-1.994805	4.033738
C	5.394322	-2.135015	3.318101
C	5.427219	-1.871711	1.937474
C	4.267895	-1.467070	1.268520
C	-0.872039	2.007724	0.067645
C	0.145061	3.009828	0.169332
C	-0.185685	4.324083	0.543374
C	-1.510506	4.681988	0.817093
C	-2.514074	3.713437	0.726171

C	-2.217307	2.384510	0.360374
C	1.590107	2.705800	-0.105468
C	2.122455	2.853008	-1.408583
C	3.451338	2.462653	-1.649345
C	4.274175	1.973015	-0.624030
C	3.757061	1.933577	0.683431
C	2.432388	2.296783	0.961401
C	1.319150	3.466348	-2.540135
C	1.919845	2.252886	2.387101
C	5.671485	1.469512	-0.917725
C	-3.370195	1.429400	0.317140
C	-3.854162	0.945282	-0.925368
C	-4.910556	0.020863	-0.939103
C	-5.519456	-0.425084	0.246078
C	-5.076354	0.121130	1.460744
C	-4.023038	1.052110	1.517687
C	-3.277269	1.447636	-2.235437
C	-6.606401	-1.477723	0.210909
C	-3.628619	1.633731	2.864364
C	-1.843191	-1.255443	-0.310982
N	-2.305717	-1.708374	0.885360
C	-3.185018	-2.768734	0.710437
C	-3.264320	-2.987798	-0.643884
N	-2.420322	-2.059217	-1.248044
C	-1.902631	-1.190913	2.197450
C	-3.899674	-3.425670	1.845108
C	-4.084243	-3.964118	-1.424863
C	-2.320619	-1.935783	-2.705915
H	-3.552218	3.977224	0.936141
H	-1.759358	5.707154	1.097912
H	0.613327	5.064669	0.611600
H	-5.285665	-0.341069	-1.901222
H	-5.572157	-0.172901	2.390677
H	-2.300426	0.994949	-2.466242
H	-3.118543	2.536246	-2.204605
H	-3.953775	1.215414	-3.072059
H	-7.249182	-1.424585	1.102897
H	-6.166763	-2.491212	0.178885
H	-7.242249	-1.369516	-0.681898
H	-2.546455	1.813153	2.940881
H	-3.938749	0.967085	3.683947
H	-4.118698	2.607368	3.031231
H	4.393803	1.588301	1.501185
H	3.853213	2.551735	-2.662956
H	2.622515	1.708645	3.035611
H	0.939081	1.757570	2.445038
H	1.794071	3.272064	2.792622
H	6.353691	1.660164	-0.074171
H	6.089965	1.943329	-1.820085
H	5.658793	0.377894	-1.091003

H	1.558957	2.984082	-3.500975
H	1.561448	4.538659	-2.643517
H	0.236087	3.396200	-2.368205
H	-1.035393	-1.755030	2.567265
H	-2.753246	-1.280344	2.880804
H	-1.637622	-0.134182	2.101833
H	-4.480330	-4.282085	1.478440
H	-4.596805	-2.715138	2.320607
H	-3.200660	-3.789709	2.614760
H	-4.663466	-4.596018	-0.739205
H	-3.455826	-4.623622	-2.045986
H	-4.792223	-3.447099	-2.093431
H	-3.241858	-1.476451	-3.091135
H	-2.196495	-2.937198	-3.137552
H	-1.455257	-1.316556	-2.958211
H	2.090753	-1.471585	3.928981
H	4.168083	-2.197377	5.105901
H	6.302795	-2.447421	3.836145
H	6.360805	-1.978370	1.381761
H	4.278625	-1.259931	0.199769
H	-0.146914	1.236923	-2.814991
H	1.683192	0.277827	-3.846104
H	3.973159	-0.463178	-3.415114
H	5.480416	-2.316682	-2.704856
H	4.571548	-4.214325	-1.350103
H	2.153244	-4.252116	-0.730904
H	0.651668	-2.407606	-1.451467
H	-0.778469	-1.538549	-0.735574
C	-0.443708	-2.426972	0.152480
C	-0.129022	-3.503834	1.071088
C	0.244365	-4.494768	2.061609
C	0.668725	-5.765471	1.655124
C	1.029237	-6.722234	2.611490
C	0.965388	-6.408294	3.974341
C	0.541029	-5.137590	4.380827
C	0.180517	-4.180827	3.424461
H	0.718390	-6.009672	0.595020
H	1.359328	-7.710661	2.295302
H	1.245815	-7.152519	4.718257
H	0.491364	-4.893389	5.440931
H	-0.149574	-3.192401	3.740649

Table S 17. Cartesian geometry of the Z stereoisomer of the product (**2**) (- 47.0 kcal/mol) in Figure 3 at B97-D/6-31G* level in Angstrom [Å].

C	3.738871	3.175954	-2.901196
C	3.381994	2.923329	-1.552856
C	4.018111	3.660760	-0.521333
C	4.985020	4.622223	-0.836349
C	5.333185	4.865128	-2.176042

C	4.707131	4.140083	-3.204266
C	2.406519	1.936640	-1.225618
C	1.583627	1.083466	-0.896340
Si	0.415892	-0.228029	-0.350230
C	-1.280449	0.277506	-0.801473
C	-2.430139	0.526148	-1.157164
C	-3.786192	0.773999	-1.510131
C	-4.301727	2.094350	-1.514199
C	-5.644139	2.323033	-1.835920
C	-6.491032	1.246340	-2.152380
C	-5.985310	-0.064740	-2.152226
C	-4.642790	-0.307150	-1.837902
C	0.584132	-0.509579	1.538917
C	1.560155	-1.433225	2.021386
C	1.622541	-1.756545	3.389220
C	0.741576	-1.168273	4.304141
C	-0.177335	-0.213541	3.854898
C	-0.256849	0.136349	2.491113
C	2.598305	-2.023596	1.114720
C	3.687663	-1.222084	0.690942
C	4.618420	-1.761446	-0.216592
C	4.524899	-3.083257	-0.675532
C	3.474279	-3.882419	-0.189218
C	2.512407	-3.377557	0.697251
C	-1.184273	1.263102	2.140126
C	-0.646562	2.561591	1.959271
C	-1.514027	3.624287	1.649434
C	-2.900573	3.438991	1.544892
C	-3.416983	2.151245	1.765956
C	-2.583959	1.063256	2.064133
C	0.838013	2.830255	2.126235
C	-3.828045	4.595764	1.227274
C	-3.192310	-0.315997	2.197369
C	3.930204	0.166191	1.254251
C	5.538651	-3.648416	-1.651654
C	1.368429	-4.264398	1.143441
C	0.865764	-1.745351	-1.376918
C	0.096531	-2.768238	-1.825038
C	-1.292877	-3.114151	-1.477355
C	-1.857430	-2.856602	-0.206564
C	-3.167303	-3.254304	0.090398
C	-3.950157	-3.905385	-0.877427
C	-3.404531	-4.169805	-2.144728
C	-2.086506	-3.792272	-2.432152
H	2.383559	-2.463188	3.728085
H	0.792815	-1.427600	5.364190
H	-0.836990	0.294069	4.562325
H	-1.093460	4.623180	1.500834
H	-4.493844	1.983101	1.679083
H	-4.262241	-0.250529	2.450482

H	-2.682219	-0.923480	2.960351
H	-3.104697	-0.845998	1.236046
H	-4.340649	4.960402	2.135324
H	-4.611645	4.287688	0.515273
H	-3.275672	5.443982	0.792706
H	1.031905	3.913627	2.165975
H	1.418281	2.412248	1.289486
H	1.221523	2.369600	3.051081
H	5.444609	-1.132450	-0.560572
H	3.390911	-4.921497	-0.521859
H	1.566600	-5.315701	0.883080
H	0.430871	-3.965501	0.648439
H	1.197196	-4.197002	2.228663
H	6.234191	-2.868969	-1.999565
H	5.042241	-4.085047	-2.535110
H	6.134896	-4.452829	-1.186242
H	4.480764	0.093071	2.209852
H	2.996338	0.704184	1.454607
H	4.533022	0.769528	0.559643
H	1.896139	-1.736076	-1.749132
H	0.549522	-3.456579	-2.551035
H	-1.255651	-2.374662	0.564850
H	-3.575665	-3.060578	1.083507
H	-4.970823	-4.214125	-0.641559
H	-4.000895	-4.681255	-2.903683
H	-1.658774	-4.011037	-3.414012
H	-3.639076	2.918378	-1.251605
H	-6.032835	3.343916	-1.837818
H	-7.539256	1.429155	-2.398986
H	-6.640126	-0.903465	-2.399027
H	-4.244069	-1.322011	-1.834024
H	3.741274	3.468243	0.516185
H	5.468246	5.184603	-0.034536
H	6.088218	5.616178	-2.417772
H	4.974644	4.327211	-4.246478
H	3.248791	2.609664	-3.694616

Table S 18. Cartesian geometry of transition state (+ 7.3 kcal/mol) in Figure S 5 at B97-D/6-31G* level in Angstrom [Å].

C	-3.310643	-1.553588	2.051284
C	-2.664718	-0.337874	1.720224
C	-3.334085	0.602780	0.889891
C	-4.596028	0.280451	0.366170
C	-5.219587	-0.952442	0.631928
C	-4.562297	-1.852423	1.482475
C	-1.337636	0.013256	2.328163
C	-0.116456	0.024462	1.581303
C	1.048292	0.484102	2.268048
C	0.994487	0.842588	3.631025
C	-0.202027	0.779356	4.352877

C	-1.365679	0.374950	3.689578
Si	-0.086133	-0.383982	-0.337881
C	0.003696	1.480251	-1.502599
C	-0.249073	2.784062	-1.366918
C	-0.486025	4.214306	-1.339504
C	-0.231144	4.988026	-2.478097
C	-0.459926	6.368955	-2.451627
C	-0.943588	6.976161	-1.286567
C	-1.198469	6.202441	-0.147974
C	-0.969688	4.821515	-0.174443
C	2.377695	0.687015	1.599646
C	2.594110	1.848289	0.820127
C	3.869320	2.079926	0.271479
C	4.938389	1.199524	0.491070
C	4.704003	0.051440	1.267943
C	3.445264	-0.218316	1.822113
C	1.478351	2.848040	0.579839
C	6.314741	1.466878	-0.086598
C	3.229162	-1.511231	2.581488
C	-2.723795	1.959054	0.596037
C	-6.568401	-1.286121	0.022715
C	-2.705623	-2.531903	3.039965
C	-1.556237	-1.479693	-1.089795
N	-2.477992	-1.061227	-2.003643
C	-3.352552	-2.087977	-2.344605
C	-2.943686	-3.196909	-1.644866
N	-1.843132	-2.798403	-0.888880
C	-2.551375	0.282567	-2.582630
C	-1.050253	-3.687479	-0.036799
C	-3.500231	-4.585349	-1.620612
C	-4.509286	-1.886105	-3.269276
C	1.541200	-1.271587	-0.544828
C	2.637470	-1.743753	-0.869328
C	3.927155	-2.269673	-1.159940
C	4.230587	-3.641476	-0.955058
C	5.510341	-4.137845	-1.230149
C	6.516122	-3.283703	-1.714080
C	6.226482	-1.924679	-1.928497
C	4.950229	-1.419013	-1.659233
H	-2.320465	0.345799	4.221297
H	-0.232120	1.061635	5.407816
H	1.912828	1.183806	4.115961
H	-5.106067	1.013528	-0.266609
H	-5.040217	-2.806672	1.724431
H	-1.871060	1.867364	-0.098549
H	-2.335124	2.421403	1.517030
H	-3.469973	2.632759	0.145984
H	-6.937063	-2.261703	0.378192
H	-6.517863	-1.324566	-1.080607
H	-7.324235	-0.523970	0.278640

H	-1.609214	-2.499190	3.028817
H	-3.041313	-3.558986	2.826677
H	-3.016933	-2.289404	4.071280
H	5.516989	-0.662510	1.428169
H	4.030638	2.979571	-0.330112
H	4.190706	-1.975521	2.850580
H	2.675367	-2.220168	1.943522
H	2.638868	-1.358152	3.497907
H	7.043820	1.708093	0.707604
H	6.295315	2.310433	-0.794890
H	6.700970	0.579047	-0.617167
H	1.866589	3.756942	0.094139
H	0.989066	3.133826	1.525319
H	0.694927	2.418326	-0.068654
H	-0.161705	-4.030701	-0.584778
H	-1.676204	-4.534916	0.268148
H	-0.720801	-3.124891	0.842692
H	-4.361447	-4.653443	-2.299963
H	-3.840843	-4.868326	-0.609967
H	-2.753171	-5.331218	-1.940668
H	-5.049897	-2.832547	-3.409776
H	-4.185715	-1.526742	-4.260833
H	-5.213518	-1.144683	-2.856072
H	-3.516412	0.736414	-2.327150
H	-2.438201	0.211027	-3.675173
H	-1.732077	0.877280	-2.158080
H	4.718455	-0.367104	-1.818257
H	7.000350	-1.254932	-2.312165
H	7.514049	-3.674286	-1.925761
H	5.725630	-5.196503	-1.065801
H	3.448899	-4.306203	-0.580501
H	-1.167950	4.219674	0.711220
H	-1.574690	6.674762	0.758279
H	-1.121547	8.050324	-1.265977
H	-0.261665	6.970797	-3.337289
H	0.145077	4.515706	-3.384348
H	-0.028847	0.244443	-1.904743

Table S 19. Cartesian geometry of intermediate (+ 1.6 kcal/mol) in Figure S 5 at B97-D/6-31G* level in Angstrom [Å].

C	4.511742	-1.785351	0.646181
C	3.590980	-0.929817	1.302266
C	3.914279	-0.426588	2.588898
C	5.127801	-0.767849	3.196962
C	6.037719	-1.613984	2.537704
C	5.723242	-2.118100	1.264124
C	2.367165	-0.564736	0.673851
C	1.328616	-0.206459	0.119886
Si	-0.234705	0.332151	-0.658303
C	-1.480174	-0.950119	0.137538
N	-2.484071	-1.638268	-0.477988

C	-3.013866	-2.602231	0.371996
C	-2.321635	-2.511876	1.554197
N	-1.394370	-1.489389	1.388883
C	-2.934692	-1.483244	-1.866679
C	-4.140474	-3.501588	-0.020224
C	-2.465994	-3.283305	2.827950
C	-0.442898	-1.095234	2.431728
C	-0.705079	2.068939	0.000753
C	-2.027872	2.467542	0.370150
C	-2.299698	3.789150	0.774243
C	-1.291076	4.759484	0.806715
C	0.005503	4.399060	0.418672
C	0.308228	3.085651	0.021356
C	-3.220196	1.557795	0.314420
C	-3.686663	0.891474	1.472738
C	-4.845927	0.099367	1.394445
C	-5.587620	-0.006100	0.207096
C	-5.129872	0.690289	-0.924673
C	-3.958146	1.464687	-0.892420
C	-2.982755	1.047255	2.806480
C	-3.490620	2.190388	-2.139894
C	-6.870924	-0.814779	0.156046
C	1.725681	2.785707	-0.363489
C	2.090682	2.621663	-1.720281
C	3.402938	2.214801	-2.027793
C	4.366450	2.011651	-1.031494
C	4.006401	2.264688	0.304960
C	2.703447	2.637254	0.653972
C	1.127949	2.924899	-2.853515
C	5.751675	1.496228	-1.363766
C	2.327869	2.779341	2.115532
C	-0.270509	-0.035910	-2.512692
C	0.223267	-1.184434	-2.996676
C	0.932395	-2.263982	-2.395427
C	2.349912	-2.393028	-2.580757
C	3.049952	-3.497147	-2.102387
C	2.394277	-4.537872	-1.407863
C	1.004904	-4.439440	-1.218604
C	0.286550	-3.339798	-1.700941
H	-3.322978	4.049654	1.056619
H	-1.515452	5.782587	1.116912
H	0.807893	5.140680	0.417737
H	-5.694867	0.625693	-1.859712
H	-5.187316	-0.431616	2.288613
H	-2.514765	1.809796	-2.484785
H	-3.348953	3.265090	-1.942252
H	-4.216096	2.071925	-2.959800
H	-7.750343	-0.176910	0.355097
H	-6.870140	-1.618014	0.910546
H	-7.021879	-1.270236	-0.837012

H	-1.914500	1.266150	2.679744
H	-3.095072	0.137730	3.417795
H	-3.414473	1.885185	3.381423
H	4.744398	2.110328	1.096541
H	3.670309	2.046344	-3.075064
H	3.211635	2.649185	2.758983
H	1.580757	2.015559	2.393633
H	1.874348	3.758445	2.336725
H	6.536738	2.144529	-0.937000
H	5.906548	1.436238	-2.452724
H	5.898035	0.486972	-0.939329
H	1.322285	2.270577	-3.717211
H	1.246257	3.975116	-3.182518
H	0.079898	2.793209	-2.553109
H	0.451536	-1.730464	2.382976
H	-0.938516	-1.190004	3.406286
H	-0.143491	-0.057081	2.267452
H	-3.228264	-4.065492	2.707773
H	-2.775801	-2.632893	3.665246
H	-1.519223	-3.769930	3.115687
H	-4.376943	-4.183933	0.808202
H	-3.887269	-4.109786	-0.904641
H	-5.047179	-2.919783	-0.255283
H	-4.014943	-1.666828	-1.891736
H	-2.389703	-2.179645	-2.521727
H	-2.732776	-0.469183	-2.202450
H	4.250724	-2.177551	-0.335150
H	6.425360	-2.777544	0.749524
H	6.984431	-1.878340	3.014270
H	5.366740	-0.371181	4.187032
H	3.210180	0.241291	3.089184
H	-0.793608	-3.303094	-1.550893
H	0.468453	-5.235234	-0.688271
H	2.950101	-5.403287	-1.041987
H	4.130658	-3.554608	-2.270538
H	2.877350	-1.593118	-3.108032
H	-0.802718	0.680890	-3.160485

Table S 20. Cartesian geometry of intermediate (- 21.9 kcal/mol) in Figure S 5 at B97-D/6-31G* level in Angstrom [Å].

C	1.529232	4.751383	-1.823177
C	0.553543	4.007697	-1.061109
C	-0.417621	4.698135	-0.360255
C	-0.472962	6.090276	-0.389877
C	0.446067	6.825213	-1.124227
C	1.462313	6.159611	-1.847042
C	0.653963	2.589399	-1.002698
C	0.668970	1.358707	-0.913384
Si	0.614248	-0.451125	-0.688940
C	-1.055030	-1.058061	-1.185699
C	-2.143415	-1.415032	-1.535318

C	-3.480185	-1.842128	-1.879925
C	-4.578599	-1.013046	-1.542785
C	-5.880267	-1.413204	-1.867922
C	-6.108022	-2.630284	-2.526668
C	-5.025848	-3.456826	-2.867436
C	-3.708471	-3.071482	-2.547678
C	1.052236	-0.929746	1.104081
C	2.353492	-1.428740	1.395810
C	2.686099	-1.821256	2.707630
C	1.756802	-1.717216	3.745205
C	0.482617	-1.201483	3.477375
C	0.123446	-0.800448	2.177533
C	3.419446	-1.531852	0.342426
C	4.218743	-0.414554	0.044247
C	5.216767	-0.535630	-0.944004
C	5.435025	-1.739317	-1.627821
C	4.628739	-2.837969	-1.314196
C	3.629051	-2.753820	-0.332666
C	-1.236130	-0.201153	1.985256
C	-1.398147	1.205554	2.059830
C	-2.665378	1.754567	1.871497
C	-3.800481	0.954274	1.642344
C	-3.627479	-0.444200	1.631099
C	-2.369057	-1.032636	1.794376
C	-0.214378	2.095920	2.399863
C	-5.169093	1.564641	1.429270
C	-2.223723	-2.543640	1.747723
C	4.005050	0.918524	0.745083
C	6.510837	-1.847907	-2.692109
C	2.745920	-3.958839	-0.035038
H	1.602328	-1.088357	-1.599374
H	3.699176	-2.202931	2.902244
H	2.023837	-2.021476	4.758145
H	-0.252397	-1.091202	4.280953
H	-2.790200	2.844137	1.925379
H	-4.495851	-1.086376	1.470077
H	-3.206993	-3.028279	1.734599
H	-1.655999	-2.918114	2.602749
H	-1.683240	-2.843882	0.843253
H	-5.902989	1.167601	2.145894
H	-5.554626	1.336309	0.417394
H	-5.141509	2.659927	1.536458
H	-0.513752	3.154191	2.403846
H	0.606268	1.974969	1.678889
H	0.188416	1.848670	3.393399
H	5.841798	0.343181	-1.176063
H	4.777952	-3.782866	-1.835788
H	3.059827	-4.834785	-0.623522
H	1.689305	-3.741725	-0.270029
H	2.778357	-4.226794	1.039446

H	7.078947	-0.911184	-2.789505
H	6.076141	-2.079969	-3.677710
H	7.221963	-2.653221	-2.457173
H	3.928407	0.785691	1.838930
H	3.062079	1.394149	0.415194
H	4.825240	1.612871	0.530066
H	-4.389180	-0.075157	-1.024051
H	-6.723974	-0.765747	-1.601682
H	-7.126376	-2.936572	-2.778814
H	-5.194759	-4.402614	-3.382260
H	-2.869565	-3.704258	-2.807593
H	-1.167274	4.112401	0.219642
H	-1.283539	6.620001	0.180067
H	0.401482	7.912292	-1.143198
H	2.175390	6.714078	-2.417028
H	2.291402	4.230197	-2.365341

Table S 21. Cartesian geometry of transition state (+ 19.7 kcal/mol) in Figure S 5 at B97-D/6-31G* level in Angstrom [Å].

C	-2.650496	-1.311029	1.918336
C	-2.077470	-0.016884	1.968201
C	-2.861353	1.115238	1.647178
C	-4.174929	0.924473	1.177880
C	-4.741485	-0.354444	1.070987
C	-3.970248	-1.460525	1.470692
C	-0.667946	0.162295	2.452720
C	0.460391	0.174069	1.577973
C	1.737902	0.409332	2.158428
C	1.876730	0.595467	3.549984
C	0.763722	0.553061	4.394865
C	-0.502866	0.338202	3.840260
Si	0.287512	-0.121014	-0.348942
C	-0.972731	-1.384206	-0.762142
C	-1.870905	-2.172980	-1.049696
C	-2.958239	-3.058644	-1.291931
C	-4.129753	-2.590165	-1.939385
C	-5.218872	-3.446909	-2.134055
C	-5.162320	-4.779484	-1.689592
C	-4.004412	-5.253571	-1.050050
C	-2.908409	-4.405198	-0.852406
C	3.012753	0.505130	1.368545
C	3.372989	1.719127	0.732077
C	4.632888	1.819387	0.114030
C	5.558680	0.764360	0.143750
C	5.186968	-0.427218	0.785511
C	3.930496	-0.574396	1.392083
C	2.449068	2.922737	0.756379
C	6.933186	0.918643	-0.476542
C	3.556985	-1.881483	2.061852
C	-2.337733	2.520343	1.871788
C	-6.148733	-0.553816	0.544604

C	-1.845414	-2.526406	2.332418
C	-0.453146	1.544049	-0.778370
C	-0.984913	2.598249	-1.137048
C	-1.690500	3.786595	-1.478580
C	-1.011382	5.010279	-1.702273
C	-1.731100	6.167336	-2.023169
C	-3.131849	6.127549	-2.125325
C	-3.814177	4.918932	-1.902196
C	-3.105992	3.755426	-1.582493
H	1.543380	-1.117491	-0.271484
H	2.873322	0.781310	3.958436
H	0.880588	0.694940	5.471997
H	-1.389037	0.313422	4.479396
H	-4.772334	1.801162	0.908839
H	-4.396995	-2.464887	1.404020
H	-2.416779	-3.450564	2.155829
H	-1.573379	-2.480308	3.400641
H	-0.905119	-2.584465	1.763233
H	-6.806703	-0.996627	1.312912
H	-6.149009	-1.245889	-0.315036
H	-6.595989	0.400486	0.223796
H	-2.923745	3.255203	1.299961
H	-1.284315	2.612838	1.578101
H	-2.406615	2.787069	2.941777
H	4.905907	2.759521	-0.375315
H	5.881549	-1.270676	0.794147
H	4.321624	-2.650621	1.874164
H	2.586699	-2.247063	1.686619
H	3.442787	-1.757868	3.151537
H	6.889782	1.511326	-1.405177
H	7.372969	-0.062082	-0.713655
H	7.625081	1.439011	0.209775
H	2.090393	3.118201	1.780063
H	1.552952	2.770510	0.134735
H	2.972901	3.820103	0.390509
H	-4.171590	-1.550299	-2.265628
H	-6.116935	-3.073850	-2.631332
H	-6.015889	-5.443802	-1.840235
H	-3.956436	-6.287810	-0.702331
H	-2.009417	-4.764893	-0.349734
H	-3.625556	2.813883	-1.397727
H	-4.903320	4.884229	-1.976635
H	-3.688688	7.033260	-2.374686
H	-1.197281	7.105044	-2.192282
H	0.076272	5.037449	-1.616664
C	1.056182	-0.053733	-2.349715
C	2.037163	-0.717615	-1.886226
H	0.722047	0.402142	-3.272006
C	3.315450	-1.374518	-1.841478
C	4.397052	-0.764590	-2.518422

C	5.621239	-1.435243	-2.616197
C	5.786817	-2.693877	-2.015905
C	4.718887	-3.290747	-1.321901
C	3.485496	-2.639353	-1.238744
H	4.262541	0.223996	-2.957707
H	6.453273	-0.964385	-3.142152
H	6.747978	-3.207925	-2.083592
H	4.849361	-4.266936	-0.850913
H	2.646530	-3.081935	-0.701189

Table S 22. Cartesian geometry of product (- 46.4 kcal/mol) in Figure S 5 at B97-D/6-31G* level in Angstrom [Å].

C	2.681585	-4.430440	-0.987851
C	2.713007	-3.051783	-1.301099
C	3.881450	-2.529446	-1.906183
C	4.980199	-3.353862	-2.168581
C	4.944001	-4.718377	-1.824797
C	3.788853	-5.253748	-1.232878
C	1.556771	-2.211782	-0.953858
C	1.578181	-0.867605	-0.783147
Si	0.091470	0.093735	-0.165883
C	0.111482	0.390891	1.731779
C	1.354628	0.506667	2.421802
C	1.387438	0.753756	3.807404
C	0.202903	0.895310	4.538894
C	-1.024409	0.791791	3.876009
C	-1.085704	0.547822	2.488421
C	2.674107	0.366887	1.723354
C	3.273453	1.485816	1.100107
C	4.482444	1.307338	0.400884
C	5.123220	0.059517	0.338721
C	4.530538	-1.030021	1.002213
C	3.318087	-0.896631	1.693864
C	-2.460833	0.467293	1.892706
C	-3.070420	1.624992	1.355865
C	-4.372144	1.528128	0.828902
C	-5.091369	0.323290	0.854256
C	-4.475867	-0.808542	1.418970
C	-3.174461	-0.755720	1.937862
C	2.647483	2.864697	1.197858
C	6.421459	-0.123511	-0.422115
C	2.673544	-2.107003	2.335759
C	-2.355418	2.963542	1.375613
C	-6.501298	0.236851	0.303049
C	-2.519451	-2.012450	2.475324
C	0.085470	1.745946	-0.970513
C	0.151003	2.878530	-1.447801
C	0.243711	4.211983	-1.943222
C	0.364809	4.467130	-3.332609
C	0.461197	5.782790	-3.800125
C	0.439017	6.860336	-2.897362

C	0.319204	6.616829	-1.517835
C	0.221898	5.305682	-1.038974
C	-1.381918	-0.850874	-0.705738
C	-2.340247	-1.521843	-1.084366
C	-3.458177	-2.300602	-1.497380
C	-4.609298	-1.669502	-2.032933
C	-5.714334	-2.433872	-2.422712
C	-5.695820	-3.832553	-2.281144
C	-4.559915	-4.465785	-1.749109
C	-3.446401	-3.710968	-1.361097
H	2.357926	0.835238	4.302573
H	0.236144	1.087909	5.614308
H	-1.961149	0.902506	4.427309
H	-4.837239	2.422525	0.402633
H	-5.013743	-1.761019	1.432098
H	-3.235236	-2.848632	2.497221
H	-2.117638	-1.862315	3.490293
H	-1.669945	-2.303083	1.834326
H	-7.249433	0.212738	1.116105
H	-6.633924	-0.682480	-0.290760
H	-6.732902	1.103235	-0.337860
H	-2.974702	3.743993	0.904140
H	-1.396041	2.914058	0.839164
H	-2.132075	3.274073	2.411904
H	4.933847	2.167726	-0.102601
H	5.005149	-2.012986	0.950124
H	3.326928	-2.988333	2.254301
H	1.719593	-2.340774	1.834245
H	2.442205	-1.928380	3.398149
H	6.628578	0.739369	-1.075106
H	6.384263	-1.033865	-1.043609
H	7.277024	-0.237708	0.267214
H	2.785401	3.283727	2.210082
H	1.566488	2.831378	1.004349
H	3.105877	3.556004	0.474515
H	2.520108	-0.332086	-0.935743
H	0.623968	-2.758447	-0.763612
H	3.916930	-1.472082	-2.173569
H	5.867288	-2.933877	-2.649945
H	5.806332	-5.357996	-2.023157
H	3.748492	-6.313411	-0.967126
H	1.781591	-4.847761	-0.525709
H	-4.622125	-0.582919	-2.118813
H	-6.595559	-1.936491	-2.834125
H	-6.561947	-4.424954	-2.583411
H	-4.540969	-5.552032	-1.637256
H	-2.561128	-4.197053	-0.947073
H	0.128621	5.109113	0.030624
H	0.301467	7.451934	-0.813372
H	0.513967	7.885111	-3.266931

H	0.553984	5.968672	-4.872759
H	0.381044	3.625712	-4.027885

Table S 23. Cartesian geometry of transition state (+ 16.5 kcal/mol) in Figure S 6 at B97-D/6-31G* level in Angstrom [Å].

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.418058
C	1.233781	0.000000	2.119200
C	2.439183	-0.001058	1.409561
C	2.432043	-0.002185	0.003810
C	1.213177	-0.000876	-0.696618
C	-1.226121	0.023247	2.139624
C	-2.278594	0.078746	2.777407
Si	-3.767571	0.362558	3.762672
C	-4.665244	-1.313973	4.086331
N	-4.241700	-2.599585	3.974046
C	-5.271922	-3.482491	4.280504
C	-6.373697	-2.715621	4.584416
N	-5.975462	-1.388935	4.453902
C	-2.903182	-3.042404	3.556678
C	-5.090093	-4.965718	4.277814
C	-7.752375	-3.119001	5.002862
C	-6.873749	-0.239458	4.639958
C	-3.510407	1.236227	5.413156
C	-3.434737	2.657438	5.356935
C	-3.374957	3.405936	6.544687
C	-3.369119	2.761370	7.789047
C	-3.387165	1.361704	7.850692
C	-3.444268	0.585584	6.676681
C	-3.357051	3.345967	4.028508
C	-4.522185	3.897582	3.436679
C	-4.430905	4.482045	2.165185
C	-3.211028	4.542595	1.465633
C	-2.067149	4.005359	2.076138
C	-2.112533	3.417980	3.353093
C	-5.857572	3.826762	4.151017
C	-0.827007	2.927120	3.993128
C	-3.132191	5.193050	0.098983
C	-3.345560	-0.903478	6.818597
C	-4.429768	-1.661748	7.324773
C	-4.289072	-3.052473	7.470803
C	-3.083862	-3.708836	7.175048
C	-2.008930	-2.935260	6.704152
C	-2.115634	-1.546681	6.519412
C	-5.729965	-1.003265	7.745144
C	-2.926441	-5.199595	7.406292
C	-0.906584	-0.760243	6.042816
H	-3.333657	0.853161	8.815343
H	-3.322411	3.346482	8.709461
H	-3.314633	4.494143	6.482757
H	-5.135619	-3.633245	7.847973

H	-1.054012	-3.423055	6.489614
H	-5.926696	-0.083021	7.179596
H	-5.699220	-0.717755	8.810693
H	-6.578452	-1.695444	7.620674
H	-2.263777	-5.659305	6.653804
H	-3.899535	-5.715486	7.381666
H	-2.476825	-5.398486	8.395726
H	-1.016263	-0.421349	4.999472
H	0.001355	-1.378650	6.102503
H	-0.755692	0.143046	6.654368
H	-1.109313	4.046498	1.550268
H	-5.333191	4.895475	1.705978
H	-0.065309	2.723227	3.226523
H	-0.980242	2.013464	4.582714
H	-0.421203	3.691736	4.678377
H	-2.975373	6.282382	0.190838
H	-4.064168	5.043049	-0.469800
H	-2.293722	4.787467	-0.489390
H	-6.648307	4.316322	3.561458
H	-5.811573	4.307788	5.142480
H	-6.161258	2.778077	4.324854
H	-2.925239	-3.327525	2.494521
H	-2.614599	-3.896872	4.177172
H	-2.192040	-2.228326	3.705584
H	-6.043044	-5.461477	4.506857
H	-4.352999	-5.269547	5.037937
H	-4.741102	-5.330954	3.298134
H	-7.832023	-4.214030	5.011372
H	-8.519950	-2.726948	4.315915
H	-7.988949	-2.753859	6.016820
H	-7.610803	-0.494969	5.409164
H	-7.385473	-0.003441	3.694197
H	-6.294769	0.627535	4.980145
H	1.229623	0.006903	3.210335
H	3.386275	0.001212	1.952006
H	3.375391	-0.001571	-0.545057
H	1.209427	0.001377	-1.787890
H	-0.950781	0.006359	-0.535072
H	-4.901189	1.154335	2.862395
C	-4.007593	-0.259761	2.037097
H	-3.446270	-1.183247	1.902894
C	-4.859754	0.888330	1.795831
C	-5.706747	1.658621	0.906024
C	-6.887198	2.236045	1.388846
C	-7.704984	2.979774	0.529723
C	-7.342318	3.146080	-0.812222
C	-6.161867	2.568656	-1.295044
C	-5.344081	1.824926	-0.435921
H	-7.169300	2.106683	2.432687
H	-8.623206	3.428928	0.905289

H	-7.978439	3.724595	-1.480498
H	-5.879765	2.698018	-2.338885
H	-4.425859	1.375773	-0.811487

Table S 24. Cartesian geometry of intermediate (- 34.8 kcal/mol) in Figure S 6 at B97-D/6-31G* level in Angstrom [Å].

C	2.122455	2.853008	-1.408583
C	1.590107	2.705800	-0.105468
C	2.432388	2.296783	0.961401
C	3.757061	1.933577	0.683431
C	4.274175	1.973015	-0.624030
C	3.451338	2.462653	-1.649345
C	0.145061	3.009828	0.169332
C	-0.872039	2.007724	0.067645
C	-2.217307	2.384510	0.360374
C	-2.514074	3.713437	0.726171
C	-1.510506	4.681988	0.817093
C	-0.185685	4.324083	0.543374
Si	-0.277306	0.278604	-0.497266
C	-1.660750	-1.076711	-0.332686
N	-2.123276	-1.529642	0.863656
C	-3.002577	-2.590002	0.688733
C	-3.081879	-2.809066	-0.665588
N	-2.237881	-1.880485	-1.269748
C	-1.720190	-1.012181	2.175746
C	-3.717233	-3.246938	1.823403
C	-3.901802	-3.785386	-1.446568
C	-2.138177	-1.757050	-2.727619
C	-3.370195	1.429400	0.317139
C	-3.854162	0.945282	-0.925369
C	-4.910556	0.020863	-0.939104
C	-5.519456	-0.425084	0.246077
C	-5.076354	0.121130	1.460743
C	-4.023038	1.052110	1.517686
C	-3.277269	1.447636	-2.235438
C	-6.606401	-1.477724	0.210908
C	-3.628619	1.633731	2.864363
C	1.919845	2.252886	2.387101
C	5.671485	1.469512	-0.917725
C	1.319150	3.466348	-2.540135
C	0.976966	-0.420414	0.612586
H	-3.552218	3.977224	0.936141
H	-1.759358	5.707154	1.097912
H	0.613327	5.064669	0.611600
H	-5.285665	-0.341069	-1.901223
H	-5.572157	-0.172902	2.390676
H	-2.300426	0.994949	-2.466242
H	-3.118543	2.536246	-2.204605
H	-3.953775	1.215414	-3.072060
H	-7.249182	-1.424586	1.102896
H	-6.166762	-2.491213	0.178884

H	-7.242249	-1.369517	-0.681899
H	-2.546455	1.813153	2.940880
H	-3.938749	0.967084	3.683946
H	-4.118699	2.607368	3.031230
H	4.393803	1.588301	1.501185
H	3.853213	2.551735	-2.662956
H	2.622515	1.708645	3.035611
H	0.939081	1.757570	2.445038
H	1.794071	3.272064	2.792622
H	6.353691	1.660164	-0.074171
H	6.089965	1.943329	-1.820085
H	5.658793	0.377894	-1.091003
H	1.558957	2.984082	-3.500975
H	1.561448	4.538659	-2.643517
H	0.236087	3.396200	-2.368205
H	-0.852952	-1.576298	2.545561
H	-2.570805	-1.101612	2.859100
H	-1.455181	0.044550	2.080129
H	-4.297889	-4.103353	1.456735
H	-4.414364	-2.536406	2.298903
H	-3.018219	-3.610977	2.593055
H	-4.481025	-4.417286	-0.760910
H	-3.273385	-4.444889	-2.067691
H	-4.609782	-3.268366	-2.115136
H	-3.059416	-1.297718	-3.112839
H	-2.014054	-2.758465	-3.159256
H	-1.272815	-1.137823	-2.979915
C	1.900061	-0.870021	1.289533
C	3.052465	-1.322450	1.986281
C	3.024750	-1.591070	3.376698
C	4.192622	-1.994805	4.033738
C	5.394322	-2.135015	3.318101
C	5.427219	-1.871711	1.937474
C	4.267895	-1.467070	1.268520
H	2.090753	-1.471585	3.928981
H	4.168083	-2.197376	5.105901
H	6.302795	-2.447421	3.836145
H	6.360805	-1.978370	1.381761
H	4.278625	-1.259931	0.199769
C	0.308248	0.405015	-2.268367
C	1.371956	-0.167465	-2.892512
H	-0.146914	1.236923	-2.814991
H	1.683192	0.277827	-3.846104
C	2.213669	-1.286094	-2.453829
C	3.579625	-1.293310	-2.824290
C	4.426936	-2.331769	-2.419133
C	3.915837	-3.398551	-1.659475
C	2.555620	-3.418748	-1.309721
C	1.712375	-2.373306	-1.704343
H	3.973159	-0.463178	-3.415114

H	5.480416	-2.316682	-2.704856
H	4.571548	-4.214325	-1.350103
H	2.153244	-4.252116	-0.730904
H	0.651668	-2.407606	-1.451467

Table S 25. Cartesian geometry of transition state (- 23.6 kcal/mol) in Figure S 6 at B97-D/6-31G* level in Angstrom [Å].

C	0.180517	-4.180827	3.424461
C	0.244365	-4.494768	2.061609
C	0.668725	-5.765471	1.655124
C	1.029237	-6.722234	2.611490
C	0.965388	-6.408294	3.974341
C	0.541029	-5.137590	4.380827
C	-0.129022	-3.503834	1.071088
C	-0.443708	-2.426972	0.152480
C	-1.843191	-1.255443	-0.310982
N	-2.305717	-1.708374	0.885360
C	-3.185018	-2.768734	0.710437
C	-3.264320	-2.987798	-0.643884
N	-2.420322	-2.059217	-1.248044
Si	-0.277306	0.278604	-0.497266
C	-0.872039	2.007724	0.067645
C	0.145062	3.009828	0.169332
C	-0.185684	4.324083	0.543374
C	-1.510505	4.681988	0.817093
C	-2.514073	3.713437	0.726171
C	-2.217306	2.384510	0.360374
C	1.590107	2.705800	-0.105468
C	2.122455	2.853008	-1.408583
C	3.451338	2.462653	-1.649345
C	4.274175	1.973015	-0.624030
C	3.757061	1.933577	0.683431
C	2.432388	2.296783	0.961401
C	-3.370194	1.429401	0.317140
C	-3.854162	0.945282	-0.925368
C	-4.910556	0.020864	-0.939102
C	-5.519456	-0.425083	0.246079
C	-5.076354	0.121131	1.460745
C	-4.023037	1.052111	1.517688
C	1.319150	3.466348	-2.540135
C	5.671485	1.469511	-0.917726
C	1.919845	2.252886	2.387101
C	-3.277269	1.447636	-2.235437
C	-6.606401	-1.477722	0.210910
C	-3.628618	1.633732	2.864365
C	-1.902631	-1.190913	2.197450
C	-3.899674	-3.425670	1.845108
C	-4.084243	-3.964118	-1.424863
C	-2.320619	-1.935783	-2.705915
C	0.308248	0.405015	-2.268367
C	1.371956	-0.167465	-2.892512

H	2.003073	-1.006214	-2.563588
C	0.976966	-0.420414	0.612586
C	1.900061	-0.870021	1.289533
C	3.052465	-1.322450	1.986281
C	3.024751	-1.591070	3.376698
C	4.192623	-1.994805	4.033737
C	5.394323	-2.135015	3.318100
C	5.427219	-1.871711	1.937473
C	4.267896	-1.467070	1.268520
H	-3.552217	3.977224	0.936141
H	-1.759357	5.707154	1.097912
H	0.613328	5.064669	0.611600
H	-5.285665	-0.341068	-1.901221
H	-5.572156	-0.172900	2.390678
H	-2.300426	0.994949	-2.466242
H	-3.118543	2.536246	-2.204605
H	-3.953775	1.215414	-3.072059
H	-7.249182	-1.424584	1.102898
H	-6.166763	-2.491211	0.178886
H	-7.242249	-1.369515	-0.681897
H	-2.546454	1.813154	2.940881
H	-3.938748	0.967086	3.683948
H	-4.118697	2.607369	3.031232
H	4.393803	1.588301	1.501185
H	3.853213	2.551735	-2.662957
H	2.622515	1.708645	3.035611
H	0.939081	1.757570	2.445038
H	1.794071	3.272064	2.792622
H	6.353691	1.660163	-0.074172
H	6.089965	1.943328	-1.820086
H	5.658793	0.377893	-1.091004
H	1.558957	2.984082	-3.500975
H	1.561448	4.538659	-2.643517
H	0.236087	3.396200	-2.368205
H	-1.035393	-1.755030	2.567265
H	-2.753246	-1.280344	2.880804
H	-1.637622	-0.134182	2.101833
H	-4.480330	-4.282085	1.478440
H	-4.596805	-2.715138	2.320607
H	-3.200660	-3.789709	2.614760
H	-4.663466	-4.596018	-0.739205
H	-3.455826	-4.623622	-2.045986
H	-4.792223	-3.447099	-2.093431
H	-3.241858	-1.476451	-3.091135
H	-2.196495	-2.937198	-3.137552
H	-1.455257	-1.316556	-2.958211
H	2.090754	-1.471585	3.928981
H	4.168084	-2.197377	5.105900
H	6.302796	-2.447421	3.836144
H	6.360805	-1.978370	1.381760

H	4.278625	-1.259931	0.199769
H	-0.146914	1.236923	-2.814991
C	1.783159	0.420852	-4.152391
H	-0.778469	-1.538549	-0.735574
H	0.718391	-6.009672	0.595020
H	1.359328	-7.710661	2.295302
H	1.245815	-7.152519	4.718257
H	0.491364	-4.893389	5.440931
H	-0.149574	-3.192401	3.740649
C	3.144328	0.556748	-4.450304
C	3.541351	1.124778	-5.666739
C	2.577206	1.556912	-6.585262
C	1.216037	1.421016	-6.287349
C	0.819014	0.852986	-5.070914
H	3.894295	0.220610	-3.735824
H	4.600146	1.230486	-5.898472
H	2.886033	1.998758	-7.531474
H	0.466070	1.757154	-7.001829
H	-0.239781	0.747278	-4.839181

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