Supporting Information for:

Ring Expansion of a Ring Expanded Carbene

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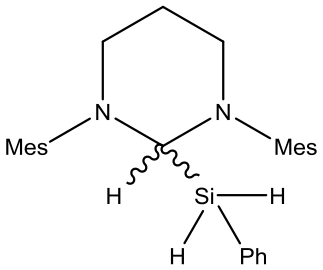
General Experimental Procedures

All manipulations were carried out using standard Schlenk line and glovebox techniques under an inert atmosphere of argon. NMR experiments were conducted in J. Young NMR tubes prepared and sealed in a Glovebox under argon. NMR spectra were collected at 298 K on a 500 MHz Agilent ProPulse NNR spectrometer ($^{13}C\{^1H\}$, 125.8 MHz; $^{29}Si\{^1H\}$, 99.4 MHz). The spectra were referenced relative to residual solvent resonances. Solvents for air- and moisture-sensitive reactions were provided by an Innovative Technology Solvent Purification System. C_6D_6 was purchased from Fluorochem Ltd. and dried over molten potassium prior to vacuum transfer into a sealed ampoule and storage in the glovebox under argon. Phenylsilane was purchased from Sigma-Aldrich Ltd. and used without further purification. 1,3-Bis(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene was synthesised by a literature procedure. [1]

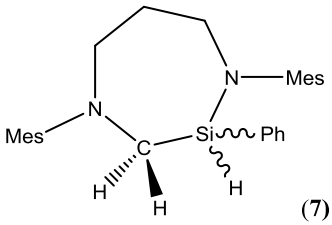
Synthesis of $[HC(SiH_2Ph)N(Mes)(CH_2)_3N(Mes)]$, 6



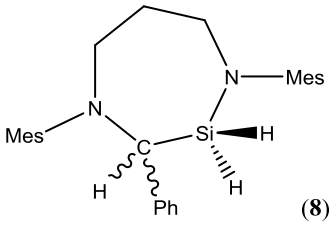
1,3-Bis(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene (100 mg, 0.312 mmol) was dissolved in toluene and treated with one equivalent of phenylsilane (57.9 µL, 0.312 mmol) in a sealed J. Young NMR tube. After stirring for 30 minutes at room temperature, the solvent was removed under vacuum to give a white solid. Single colourless crystals suitable for X-ray crystallography were grown by slow evaporation of a saturated pentane solution at room temperature (125 mg, 94%). ^1H NMR (300 MHz, C6D6, 298K): δ 7.07 – 7.00 (m, 1H, Ph CH), 6.95 – 6.88 (m, 2H, CH Ph), 6.86 – 6.80 (4H, CH Mes and Ph), 6.49 (2H, m-CH Mes), 5.30 (t, $^3J_{HH}$ = 2.5 Hz, 1H, SiCH), 4.01 (d, $^3J_{HH}$ = 2.5 Hz, 2H, SiH_2), 3.18 (dt, $^2J_{HH}$ = 12.1 Hz, $^3J_{HH}$ = 2.7 Hz, 2H, NCH_2), 2.89 (ddd, $^2J_{HH}$ = 12.1 Hz, $^3J_{HH}$ = 4.6, 2.2 Hz, 2H, NCH_2), 2.57 (s, 6H, CH_3), 2.18 (s, 6H, CH_3), 2.15 (m, 1H, NCH_2CH_2), 2.12 (s, 6H, CH_3), 1.29 (dq, $^2J_{HH}$ = 12.1 Hz, $^3J_{HH}$ = 2.5 Hz, 1H, NCH_2CH_2); $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 298K): δ 146.2 (s, N-C_{ipso} Mes), 139.5, 139.1 (s, *o*-*C* Mes), 136.0 (s, *o*-*C*H Ph), 135.6 (s, *p*-*C* Mes), 131.1 (s, *C*H Ph), 130.4 (s, C_{ipso} Ph), 129.4, 129.2 (s, *C*H Mes), 127.2 (s, *C*H Ph), 71.1 (s, Si*C*H), 53.1 (s, NCH_2), 28.7 (s, NCH_2CH_2), 21.0, 20.7, 20.3 ppm (s, CH_3); $^{29}Si\{^1H\}$ NMR (99.4 MHz, C_6D_6, 298K): δ –37.2 ppm. Elemental analysis (%). Found: C 78.10, H 8.49, N 6.63. Calculated for $C_{28}H_{36}SiN_2$: C 78.45, H 8.46, N 6.53.

Synthesis of [H_2CSiH(Ph)N(Mes)(CH_2)$_3$N(Mes)] (7) and [HC(Ph)SiH_2N(Mes)(CH_2)$_3$N(Mes)] (8)

[HC(SiH_2Ph)N(Mes)(CH_2)$_3$N(Mes)] (100 mg, 0.233 mmol) was dissolved in toluene and heated at 120 ºC in a sealed J. Young NMR tube for 4 days. Then the solvent was removed under vacuum to give a pale-yellow oil. Single colorless crystals suitable for X-ray crystallography were grown by slow evaporation of a saturated pentane solution at room temperature in a glovebox. Yield: 91 mg, 91% (7:8, 2:1). 7: ^{1}H NMR (500.1 MHz, C_6D_6, 298K): δ 7.46 – 7.42 (2H, Ph), 7.06 – 7.01 (3H, Ph), 6.83 (broad s, 1H, *m*-C*H* Mes), 6.79 – 6.76 (2H, *m*-C*H* Mes), 6.68 (broad s, 1H, *m*-C*H* Mes), 5.39 (d, $^1J_{SiH}$ = 204.4 Hz, $^3J_{HH}$ = 5.0 Hz, 1H, SiH), 3.30 – 3.03 (4H, NCH_2), 3.21 (1H, $SiCH_2$, identified by HSQC), 2.82 (d, $^2J_{HH}$ = 15.0 Hz, 1H, $SiCH_2$), 2.53, 2.48, 2.27, 2.17, 2.15, 2.06 (s, 3H, CH_3), 2.03, 1.94 (1H, NCH_2CH_2, identified by COSY and HSQC); ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 298K): δ 150.5, 144.5 (s, N-C_{ipso} Mes), 137.4 – 126.2 (s, C_{ipso} and *C*H of Ph and Mes), 56.9 (s, NCH_2), 53.3 (s, $SiNCH_2$), 44.5 (s, $SiCH_2$), 34.1 (s, NCH_2CH_2), 20.9, 20.9, 19.9, 19.7, 19.6, 19.2 ppm (s, CH_3); ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 298K): δ -17.4 ppm; 8: ^{1}H NMR (500.1 MHz, C_6D_6, 298K): δ 7.18 (d, $^3J_{HH}$ = 7.5 Hz, 2H, *o*-C*H* Ph), 7.06 – 7.02 (1H, *m*-C*H* Mes), 6.96 (t, $^3J_{HH}$ = 7.5 Hz, 2H, *m*-C*H* Ph), 6.86 (broad s, 1H, *m*-C*H* Mes), 6.80 – 6.74 (m, 2H, *m*-C*H* Mes and *p*-C*H* Ph), 6.42 (broad s, 1H, *m*-C*H* Mes), 5.06 (dd, $^2J_{HH}$ = 10.8 Hz, $^3J_{HH}$ = 5.2 Hz, 1H, SiH), 4.71 (d, $^3J_{HH}$ = 5.2 Hz, 1H, SiCH), 4.13 (d, $^2J_{HH}$ = 10.8 Hz, 1H, SiH), 3.46 (ddd, $^2J_{HH}$ = 14.3 Hz, $^3J_{HH}$ = 7.1, 1.6 Hz, 1H, NCH_2), 3.30 – 3.03 (3H, NCH_2), 2.31 (2H, NCH_2CH_2, identified by COSY and HSQC), 2.51, 2.50, 2.35, 2.25, 2.14, 1.95 ppm (s, 3H, CH_3); ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 298K): δ 147.0, 144.4 (s, N-C_{ipso} Mes), 138.7 (s, C_{ipso} Ph), 137.4 – 126.2 (s, C_{ipso} and *C*H of Ph and Mes), 61.2 (s, SiCH), 56.2 (s, NCH_2), 51.6 (s, $SiNCH_2$), 33.1 (s, NCH_2CH_2), 21.0, 20.7, 20.7, 20.2, 19.5, 18.5 ppm (s, CH_3); ^{29}Si{^{1}H} NMR (99.4 MHz, C_6D_6, 298K): δ –21.0 ppm. Elemental analysis (%). Found: C 78.01, H 8.55, N 6.72. Calculated for $C_{28}H_{36}SiN_2$: C 78.45, H 8.46, N 6.53.



(**7**)



(**8**)

NMR spectra

Figure S1: $^{29}Si\{^{1}H\}$ (top) and ^{1}H (bottom) NMR spectra (500.1 MHz, C_6D_6, 298K) of compound **6**, $[HC(SiH_2Ph)N(Mes)(CH_2)_3N(Mes)]$.

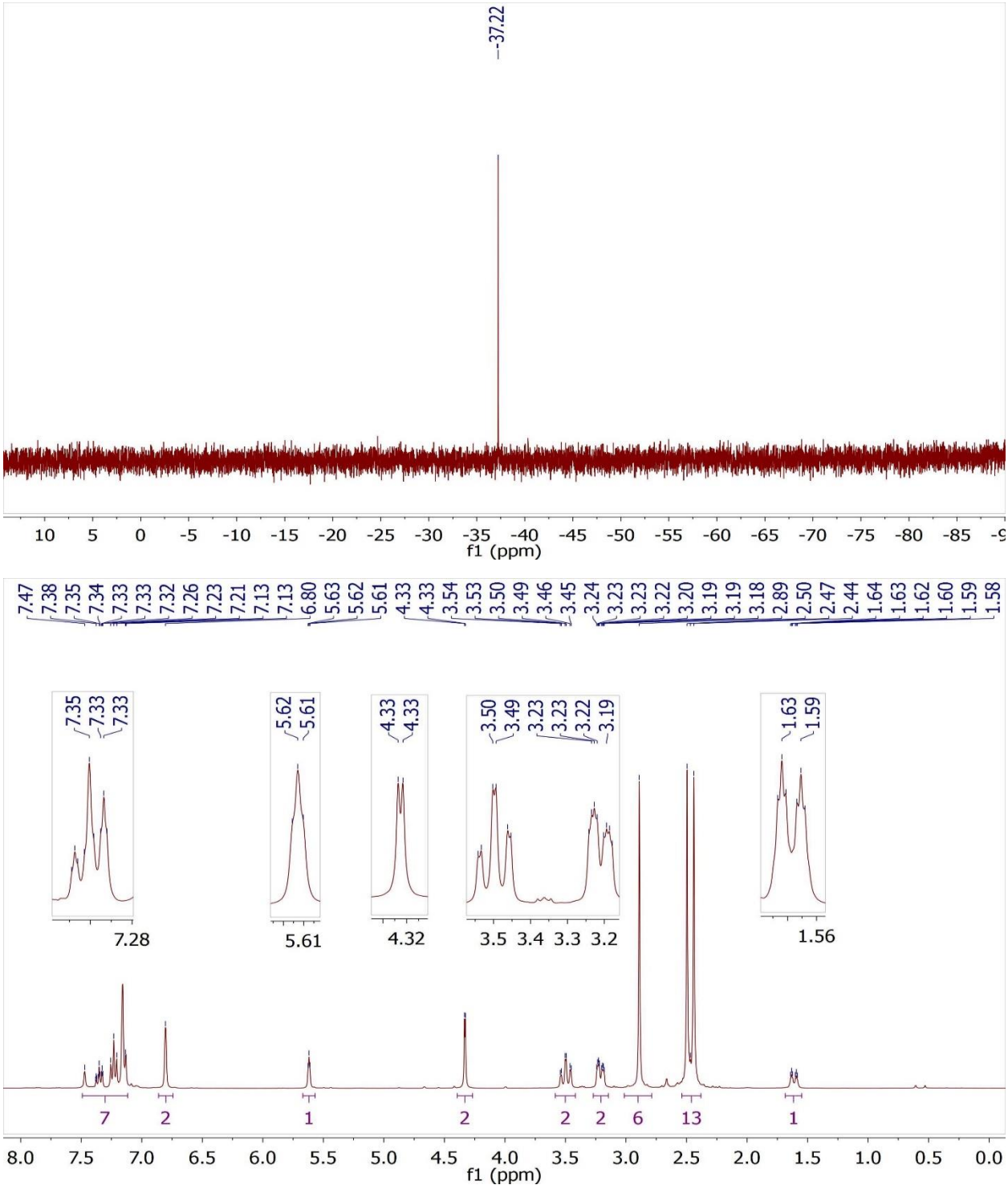


Figure S2: $^{13}C\{^{1}H\}$ NMR spectrum (500.1 MHz, C_6D_6, 298K) of compound **6**, [$HC(SiH_2Ph)N(Mes)(CH_2)_3N(Mes)$].

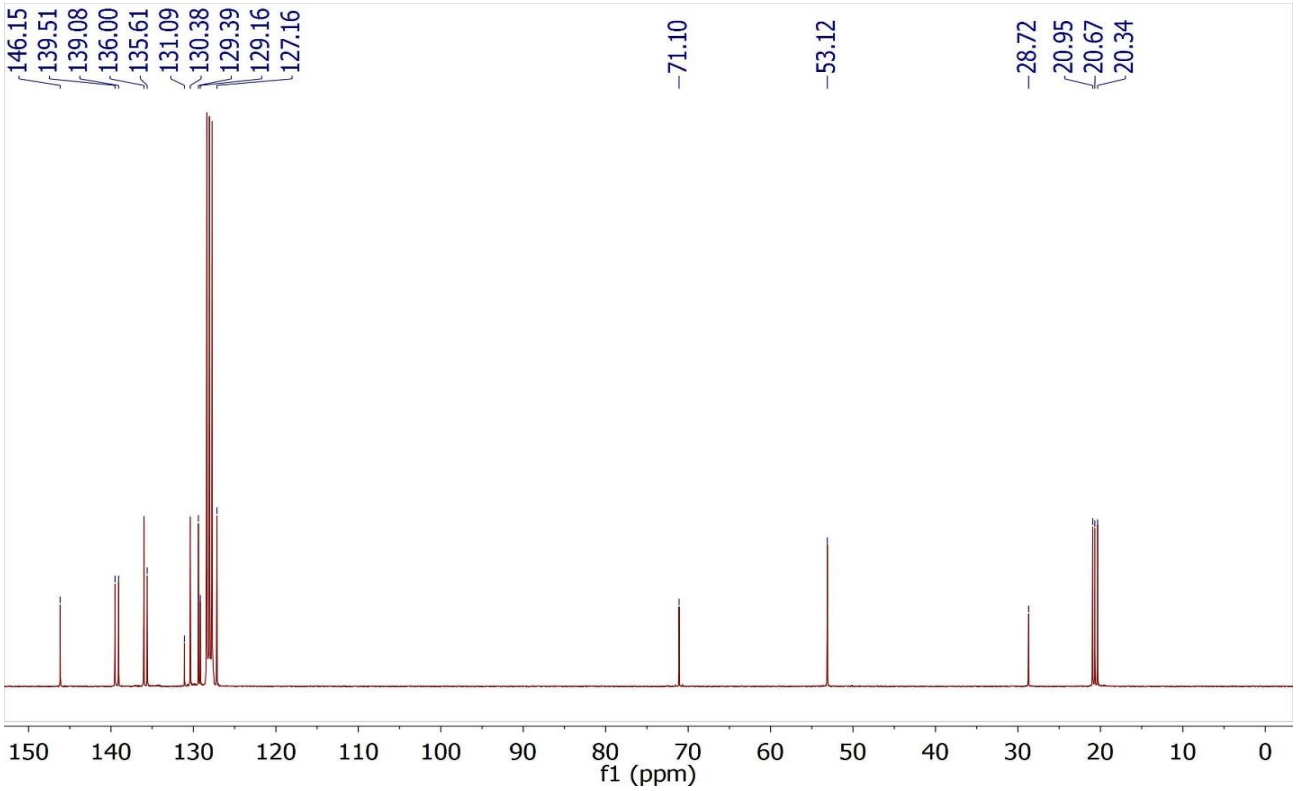


Figure S3: $^{29}Si\{^{1}H\}$ NMR spectrum (500.1 MHz, C_6D_6, 298K) of mixture (2:1) of the isomers **7** [$H_2CSiH(Ph)N(Mes)(CH_2)_3N(Mes)$] and **8** [$HC(Ph)SiH_2N(Mes)(CH_2)_3N(Mes)$].

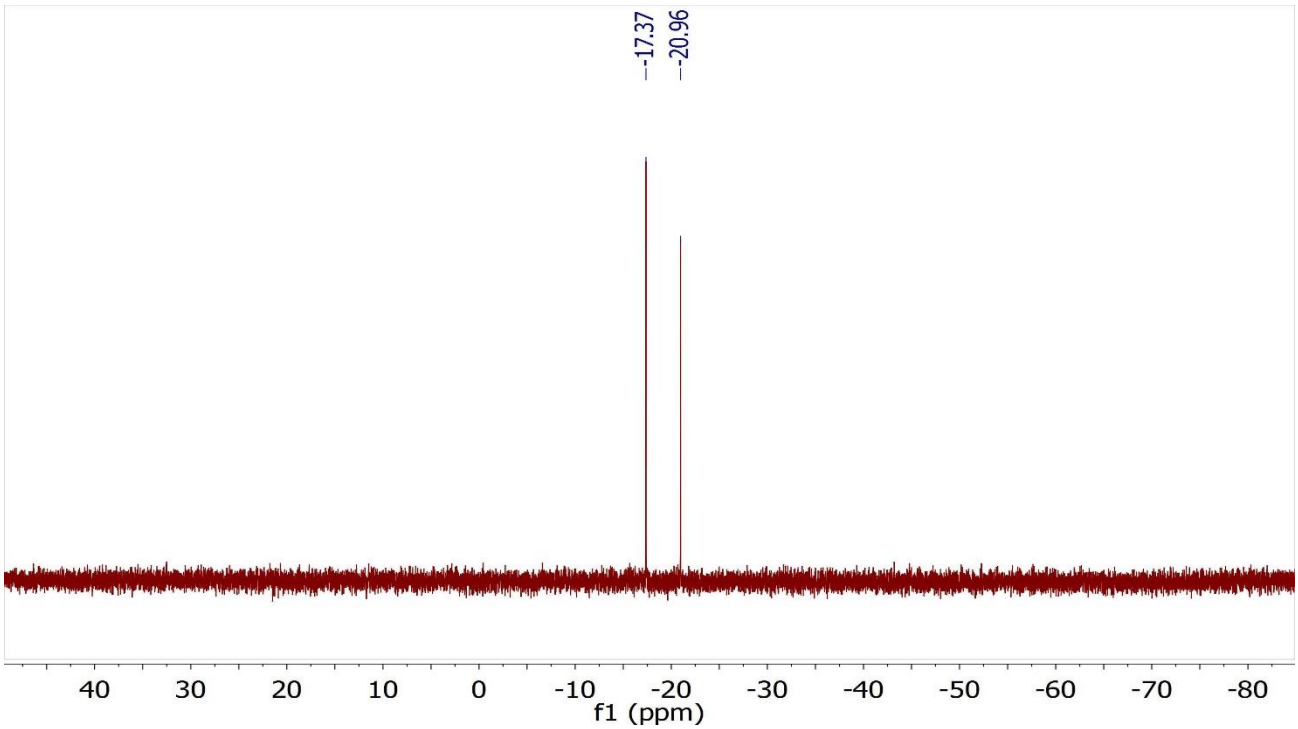


Figure S4: ^{1}H NMR spectrum (500.1 MHz, C_6D_6, 298K) of mixture (2:1) of the isomers **7** [$H_2CSiH(Ph)N(Mes)(CH_2)_3N(Mes)$] (top) and **8** [$HC(Ph)SiH_2N(Mes)(CH_2)_3N(Mes)$].) (bottom).

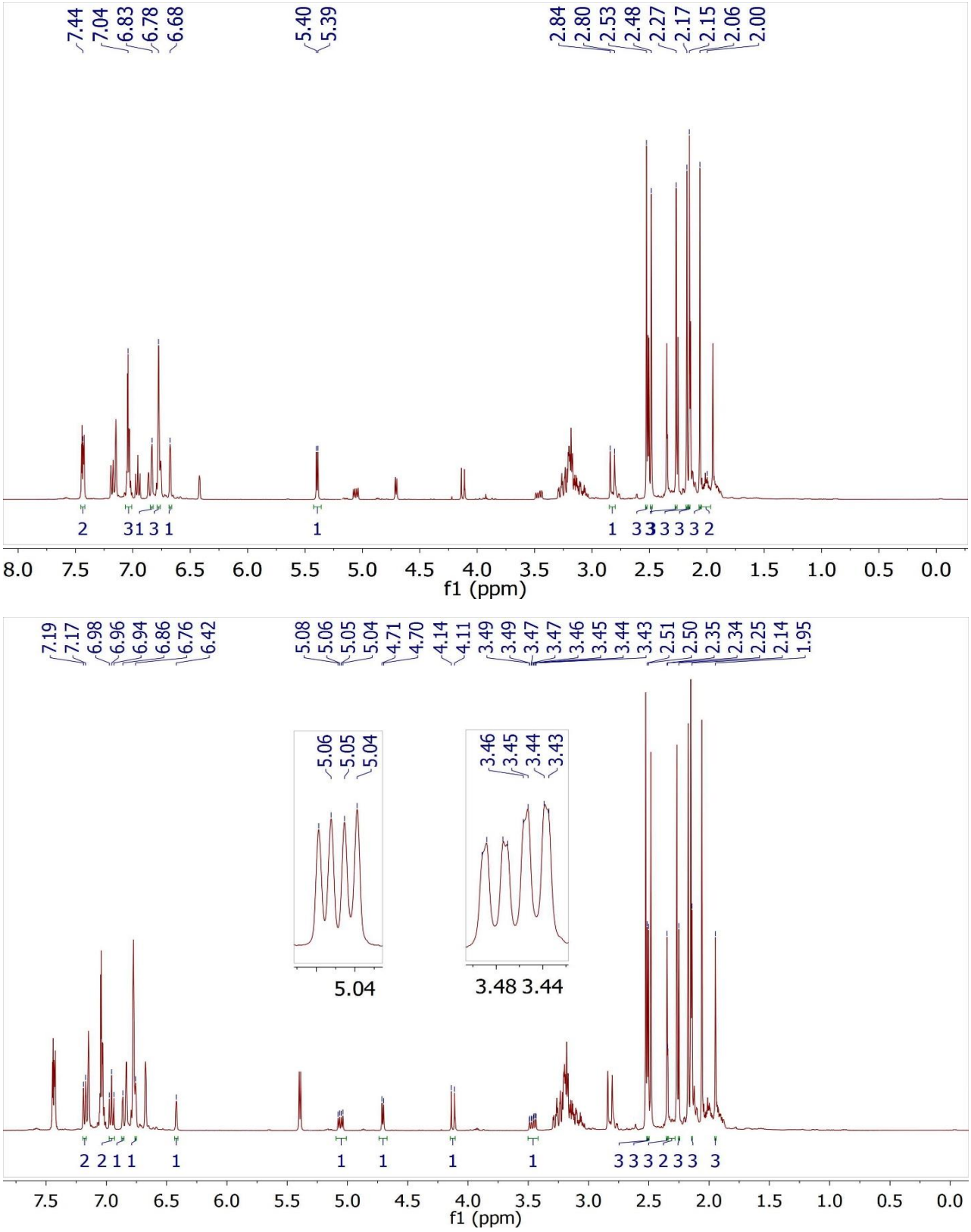
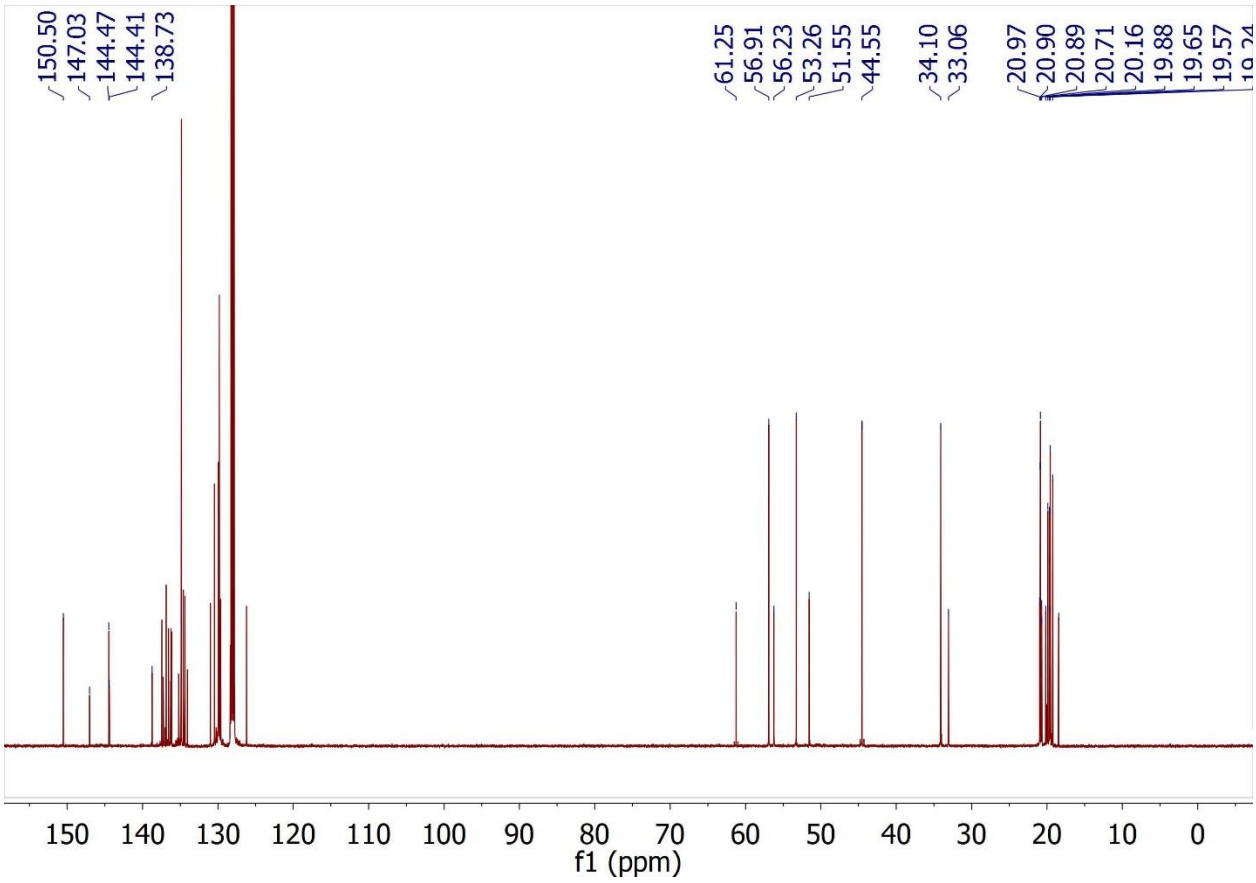


Figure S5: $^{13}C\{^{1}H\}$ NMR spectrum (500.1 MHz, C_6D_6, 298K) of mixture (2:1) of the isomers **7** [$H_2CSiH(Ph)N(Mes)(CH_2)_3N(Mes)$] and **8** [$HC(Ph)SiH_2N(Mes)(CH_2)_3N(Mes)$].



Computational Details

All theoretical calculations were performed within Gaussian 09 program[1]. Geometry optimizations without symmetry constraints were approved by using M06-2X density functional[2] and the def2-TZVP basis set[3] to determine both minima and transition state structures. Harmonic vibrational frequencies were computed at the same level of theory in order to characterize the stationary points as minima or TS on the potential energy surface. The vibrational frequencies were also utilized to evaluate the corresponding zero-point vibrational energies and thermochemical data within the harmonic limit, determined at 1 atm and 298 K. Transition state optimizations used the quadratic synchronous transit (QST) method.[4] All transition states were also confirmed using intrinsic reaction coordinate (IRC)[5] analysis to ensure that the connectivity between the local minima along the reaction pathway. Single point energy calculations were also performed to assess the M06-2X/def2-TZVP energetics, single-point calculations were employed by using the M06-2X/def2-TZVP optimized geometries with MP2, SCS-MP2[6] and SOS-MP2[7] with def2-TZVP and 6-311+G(d,p)[8] basis sets. Single-point energies were also calculated for all molecules with B3LYP[9,10] and B3LYP-D3(BJ).[11] In addition to computations in the gas phase calculation, the effect of solvent was investigated[12] with M06-2X, B3LYP, B3LYP-D3(BJ), MP2, SCS-MP2 and SOS-MP2 methods with both def2-TZVP and 6-311+G(d,p) basis sets with acetonitrile solvent (PCM with Truhlar's SMD model). All reported ΔG values are SCS-MP2 electronic energies inclusive of solvent effects with M06-2X/def2-TZVP thermochemical corrections, which combine the SCS-MP2/def2-TZVP electronic energy and M06-2X/def2-TZVP thermochemical correction, defined as SCS-MP2/def2-TZVP//M06-2X/def2-TZVP.

Table S1 of *ΔG* energies for the pathway reaction of H_3SiPh and $RENHC^{Me}$ (A_D) (T1-T3)(kJ mol−1).

Method/Basis set	A	TS1	B	TS2	C	TS3 (H)	D (H)	TS3 (Ph)	D (Ph)
M06-2X/def2-TZVP [a]	0.0	113.6	-55.7	87.6	38.1	52.7	-152.2	94.5	-118.0
MP2/def2-TZVP	0.0	98.9	-79.1	69.7	40.3	40.1	-168.2	75.7	-139.1
SOS-MP2/def2-TZVP	0.0	129.6	-48.0	102.8	50.7	70.0	-139.4	110.5	-105.4
SCS-MP2/def2-TZVP	0.0	119.4	-58.4	91.7	47.3	60.1	-149.0	98.9	-116.6
MP2/def2-TZVP/MeCN	0.0	97.4	-47.7	94.6	59.7	61.4	-129.4	92.4	-102.7
SOS-MP2/def2-TZVP/MeCN	0.0	127.1	-17.6	127.0	69.7	90.1	-101.3	125.8	-69.7
SCS-MP2/def2-TZVP/MeCN	0.0	117.2	-27.6	116.2	66.4	80.5	-110.7	114.7	-80.7
M06-2X/def2-TZVP/MeCN	0.0	112.6	-26.3	111.0	57.2	73.3	-115.6	110.1	-83.6
MP2/def2-TZVP/MeCN	0.0	107.1	-49.6	110.0	65.0	77.5	-118.4	106.5	-97.1
B3LYP-D3(BJ)/def2-TZVP	0.0	108.6	-41.3	90.3	46.9	54.2	-138.3	90.7	-101.9

[a] Calculated at M06-2X/def2-TZVP optimized geometry.

Table S2 of Δ*G* energies for the pathway reaction of H_3SiPh and $RENHC^{Ph}$ (A_D) (T1-T3)(kJ mol−1) with all calculations.

Method/Basis set	A	TS1	B	TS2	C	TS3 (H)	D (H)	TS3 (Ph)	D (Ph)
M06-2X/def2-TZVP [a]	0.0	115.5	-52.0	93.9	40.7	71.8	-175.4	75.0	-128.4
MP2/def2-TZVP	0.0	78.3	-91.9	58.0	37.9	56.2	-195.3	49.1	-157.9
SOS-MP2/def2-TZVP	0.0	135.1	-53.2	99.2	-27.4	85.2	-160.3	88.9	-120.7
SCS-MP2/def2-TZVP	0.0	116.2	-66.1	85.5	-32.5	75.5	-172.0	75.6	-133.1
MP2/def2-TZVP/MeCN	0.0	89.8	-64.2	65.0	55.3	60.1	-173.4	61.9	-60.0
SOS-MP2/def2-TZVP/MeCN	0.0	144.6	-26.4	104.6	67.8	87.9	-138.8	99.9	-25.5
SCS-MP2/def2-TZVP/MeCN	0.0	126.3	-39.0	91.4	63.6	78.6	-150.3	87.2	-37.0
M06-2X/def2-TZVP/MeCN	0.0	125.2	-25.3	100.7	57.3	75.6	-154.5	87.4	-105.8
MP2/def2-TZVP/MeCN	0.0	78.0	-77.4	68.2	54.9	71.1	-166.3	69.9	-136.8
B3LYP-D3(BJ)/def2-TZVP	0.0	83.7	-45.5	75.3	45.0	68.2	-166.3	66.3	-119.0
M06-2X/def2-TZVP [a]	0.0	93.8	-18.8	82.3	61.7	73.0	-146.0	78.2	-96.4

[a] Calculated at M06-2X/def2-TZVP optimized geometry.

RENHC^{Me} ring expansion pathway by silane (SiH_3Ph)

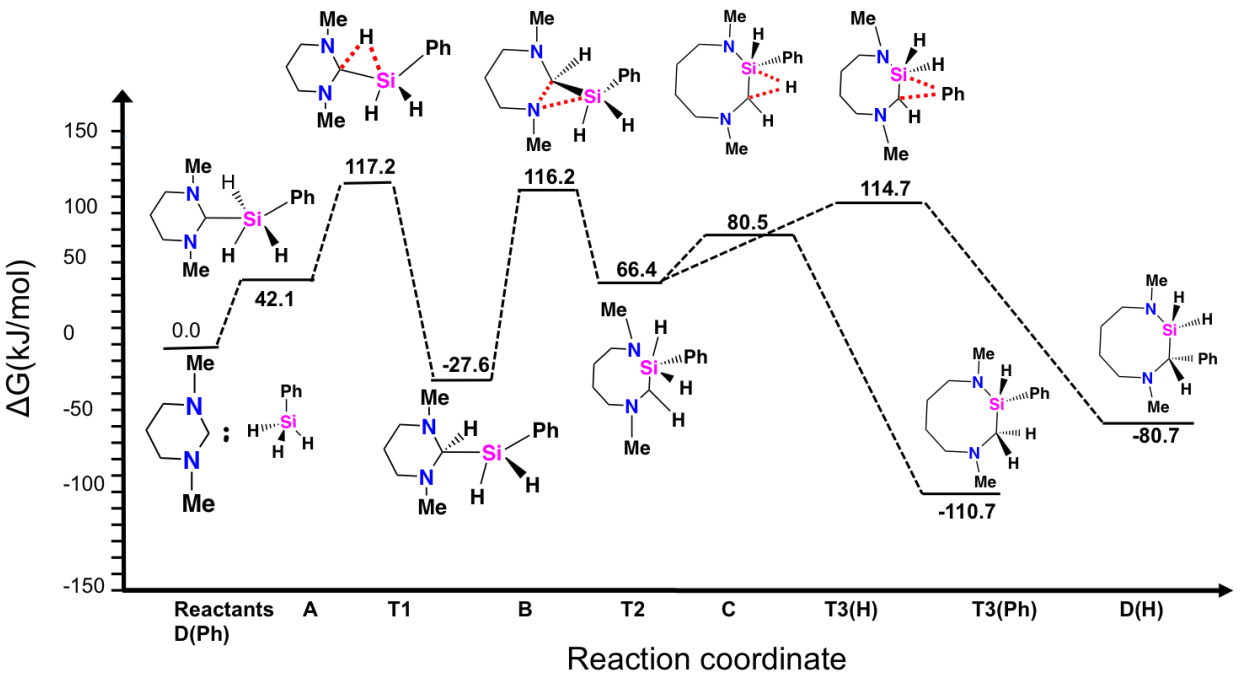
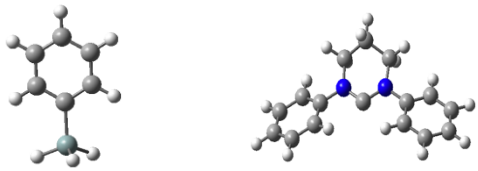
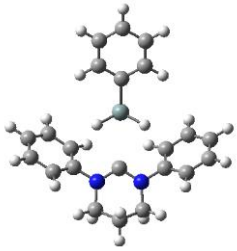
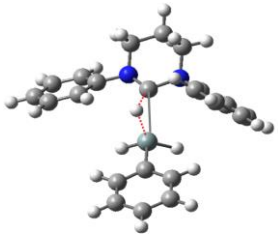
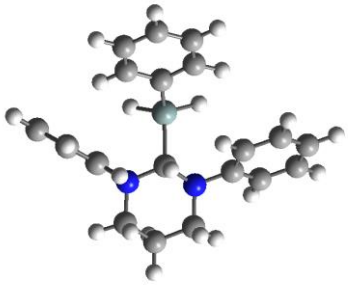
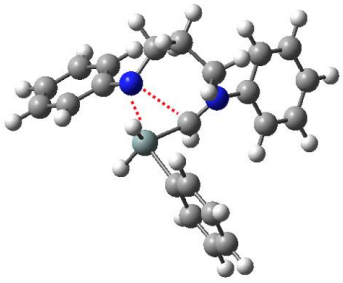
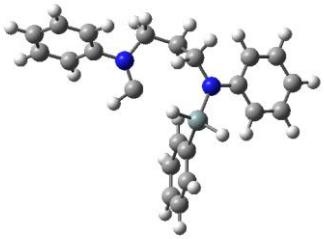
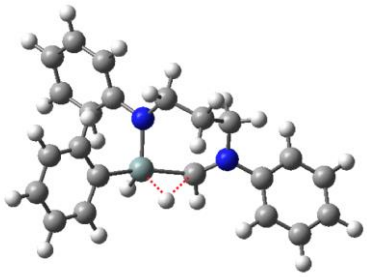
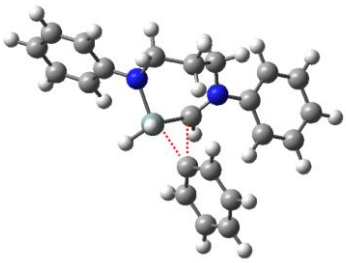
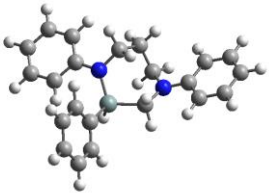
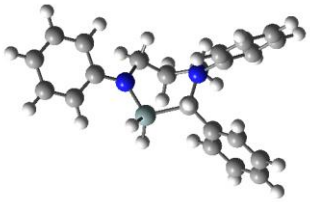


Table S2. M06-2X/def2-tzvp optimized geometries of ring insertion pathway for RENHC^{Ph} and SiH3Ph (A-D, T1-T3).

 Reactants	 A
 T1	 B
 T2	 C
 T3(H)	 T3(Ph)
 D(H)	 D(Ph)

Cartesian coordinates of optimized geometries

All geometries listed have been optimized at the **M06-2X/def2-tzvp** level of theory. Coordinates are enumerated in angstroms, SCF (E_0) energy and is expressed in Hartrees.

Cartesian coordinates for reactant

Cartesian coordinates for silane (SiH3Ph)

E_0 = -522.900461464

M06-2X/def2-TZVP optimized geometry (Å).

0 1

C	-2.96668300	1.53221600	-0.17086400
C	-3.14570900	0.16552300	-0.80140200
C	-3.45658900	-0.75431300	1.42487200
C	-1.67194100	1.69981200	0.63596400
H	-2.99368600	2.25635600	-0.99000500
H	-2.28172200	-0.07863500	-1.42735400
H	-1.80177400	1.20948400	1.59884300
N	-3.31652400	-0.95001600	0.14916000
N	-0.48377500	1.16368700	-0.00793900
C	-3.34883900	-2.24461700	-0.54219500
H	-2.40868900	-2.40410000	-1.07184500
H	-3.49730200	-3.03332800	0.18923300
H	-4.16436700	-2.25507500	-1.26781900
C	-0.11871000	1.82639400	-1.24372800
H	-0.04382500	2.90753800	-1.08362000
H	0.85191400	1.47279500	-1.59436600
H	-0.84624600	1.66311400	-2.04960000
H	-1.52202800	2.77028300	0.82255300
H	-3.81009500	1.74782800	0.48591700
H	-4.02217600	0.16713000	-1.45605800
Si	0.17345900	-0.36029900	0.42788400
H	-0.30589200	-1.51100700	-0.39421900
C	2.02860300	-0.32601700	0.19380900
C	2.71583300	-1.43076700	-0.31040900
C	2.76856300	0.80588300	0.54694800
C	4.09779000	-1.41378200	-0.45036300
H	2.16433600	-2.31797500	-0.60283800
C	4.14824600	0.83157700	0.40581500
H	2.25308500	1.68016400	0.93074600
C	4.81479600	-0.28137500	-0.09168900
H	4.61398800	-2.28064500	-0.84298800
H	4.70557000	1.71734900	0.68323900
H	5.89157500	-0.26357200	-0.20262700
H	-3.58535800	-1.75075400	1.88285500
H	-0.21580100	-0.61167000	1.83048300

Cartesian coordinates for RENHC^{Ph}

E_0 = -728.747615341

M06-2X/def2-TZVP optimized geometry (Å).

0 1

C	0.00008900	2.65443100	0.81073600
C	-1.23353100	2.10704800	0.12756100
C	-0.00001100	-0.06318300	0.05578400
C	1.23346500	2.10704400	0.12712700
H	0.00006400	3.74337800	0.77250200
H	-1.32798800	2.52069000	-0.88172000
H	2.13109200	2.37573800	0.68322900
N	-1.14340200	0.64369800	0.07135100
N	1.14337400	0.64368100	0.07128700
H	1.32740000	2.52046200	-0.88229500
H	0.00028800	2.35186600	1.85972700
H	-2.13091100	2.37556700	0.68415400
C	-2.37239500	-0.07219600	-0.02514000
C	-3.50662600	0.54301800	-0.54799300
C	-2.45581300	-1.39558100	0.40677900
C	-4.70475100	-0.15536900	-0.63734100
H	-3.46403600	1.56091500	-0.90919700
C	-3.65292400	-2.08165300	0.31207800
H	-1.56888400	-1.86591100	0.80342400
C	-4.78718600	-1.46863000	-0.20864100
H	-5.57394900	0.33784500	-1.05296000
H	-3.70224500	-3.10705100	0.65546300
H	-5.72088700	-2.01044700	-0.27751400
C	2.37237800	-0.07219700	-0.02514900
C	3.50641100	0.54284600	-0.54861700
C	2.45600300	-1.39531800	0.40750200
C	4.70457000	-0.15548000	-0.63789000
H	3.46358400	1.56055500	-0.91034500
C	3.65314800	-2.08135400	0.31285500
H	1.56922000	-1.86548700	0.80466800
C	4.78721200	-1.46851000	-0.20849800
H	5.57362800	0.33756800	-1.05399600
H	3.70265800	-3.10655600	0.65679700
H	5.72094400	-2.01028300	-0.27731400

Cartesian coordinates for optimized insertion pathway compounds H3SiPh-RENHCPh (A-D) &(T1-T3)

H3SiPh- RENHC^{Ph}, A

E_0 = -1251.65233776

M06-2X/def2-TZVP optimized geometry (Å).

0 1

C	3.99921900	0.00310600	-1.52224200
C	3.70164900	-1.23053800	-0.69528800
C	1.68685700	0.00118600	0.11334700
C	3.69941800	1.23647700	-0.69568900
H	5.04254900	0.00401500	-1.83644500
H	4.40985800	-1.31883300	0.13487800
H	3.79132200	2.13609500	-1.29883200
N	2.33836100	-1.14068600	-0.15814400
N	2.33645200	1.14414100	-0.15813700
H	4.40768500	1.32655200	0.13423100
H	3.37274100	0.00238400	-2.41665200
H	3.79554700	-2.13021800	-1.29801600
Si	-1.38532200	-0.00075400	-0.04823400
H	-0.87935600	-1.23274800	-0.68639000
H	-1.10972000	-0.00113000	1.40304600

C	-3.25630100	-0.00214300	-0.28531000
C	-3.97588600	1.19274900	-0.36275200
C	-3.97394600	-1.19814000	-0.36377500
C	-5.35701600	1.19678500	-0.50627800
H	-3.44769300	2.13966800	-0.31515200
C	-5.35507000	-1.20428700	-0.50730600
H	-3.44422700	-2.14424700	-0.31699400
C	-6.04955300	-0.00428300	-0.57803000
H	-5.89338100	2.13567000	-0.56617700
H	-5.88991200	-2.14399000	-0.56800600
H	-7.12618400	-0.00510100	-0.69274300
C	1.67718300	2.36298900	0.18811400
C	1.00612300	2.45838500	1.40280400
C	1.67079300	3.44597100	-0.68411400
C	0.32854500	3.62052200	1.73386800
H	1.00646400	1.60285800	2.06385900
C	0.99736900	4.61054800	-0.34339200
H	2.15786100	3.37496000	-1.64755700
C	0.32315100	4.70380400	0.86489000
H	-0.19491900	3.68038100	2.67931600
H	0.98969200	5.44235700	-1.03576400
H	-0.20404400	5.61156700	1.12653500
C	1.68120300	-2.36067000	0.18807100
C	1.67748300	-3.44396500	-0.68380100
C	1.00960900	-2.45703000	1.40239200
C	1.00627700	-4.60981200	-0.34305200
H	2.16495000	-3.37230500	-1.64699400
C	0.33426200	-3.62046000	1.73348400
H	1.00782900	-1.60129200	2.06316500
C	0.33160100	-4.70406300	0.86490000
H	1.00070200	-5.44186900	-1.03514600
H	-0.18960200	-3.68105900	2.67866400
H	-0.19383400	-5.61283600	1.12657700
H	-0.88133000	1.23267700	-0.68519300

H3SiPh- RENHC^{Ph}, T1

E_0 = -1251.62350671

M06-2X/def2-TZVP optimized geometry (Å).

0 1

C	0.01858100	1.40921500	2.20208600
C	1.07832300	0.35219500	2.41876700
C	-0.06669800	-0.93494600	0.69385900
C	-1.33395000	0.75645000	1.99622300
H	-0.03506600	2.08076500	3.05862900
H	0.86942200	-0.23615100	3.31872500
H	-2.00314600	1.48554500	1.54096200
N	1.07814000	-0.54496300	1.26683900
N	-1.23317700	-0.40511500	1.10049800
H	-1.77148100	0.43180200	2.94483800
H	0.27953200	1.99774100	1.32189200
H	2.06163300	0.79449100	2.53769500
Si	0.30580500	-0.23944700	-2.20165600
H	1.62794200	-0.32355100	-2.88902400
H	-0.73083900	-0.31977000	-3.27126500
C	0.20808000	1.52427500	-1.52846100
C	1.35500800	2.26578300	-1.21800600
C	-1.02991800	2.09660800	-1.20429100
C	1.27256200	3.52628800	-0.63756900
H	2.33113900	1.85516900	-1.45571400
C	-1.12074100	3.35521900	-0.62488500
H	-1.94312800	1.54983600	-1.42443500
C	0.03260800	4.07811400	-0.33997400
H	2.17685500	4.08433800	-0.42573200
H	-2.09317600	3.77970900	-0.40361300
H	-0.03518900	5.06332900	0.10355600
H	0.04743400	-1.15322900	-0.54278100
C	-2.42651800	-0.90672800	0.51864600
C	-2.38201800	-1.99037000	-0.36532700
C	-3.66389600	-0.33327100	0.81541100
C	-3.54505100	-2.45540900	-0.95479600
H	-1.44332600	-2.47758900	-0.58126900
C	-4.82222000	-0.81880700	0.22482800
H	-3.74739700	0.48491700	1.51365300
C	-4.77282800	-1.87477400	-0.66953800
H	-3.48530300	-3.28770100	-1.64384700
H	-5.76999500	-0.35939800	0.47368300
H	-5.67721700	-2.24674200	-1.13146800
C	2.28641900	-1.04883300	0.71579600
C	3.44121100	-0.26940000	0.69111200
C	2.29639200	-2.30584700	0.11511000
C	4.59372500	-0.75647700	0.09552000
H	3.43861000	0.73254200	1.09710700
C	3.45237300	-2.77996000	-0.48440600
H	1.39541500	-2.90491200	0.13450600
C	4.60771000	-2.01344900	-0.49262000
H	5.48208600	-0.13875500	0.07861400
H	3.44571300	-3.75791900	-0.94739300
H	5.50856200	-2.38693500	-0.96040200

H3SiPh- RENHC^{Ph},B

E_0 = -1251.69558224

M06-2X/def2-TZVP optimized geometry (Å).

0 1

C	-1.25583900	-3.66541800	-0.32576000
C	0.15732900	-3.21337500	-0.62212300
C	-0.45138000	-0.90525500	-0.03620900
C	-2.20192800	-2.52239200	-0.62217100
H	-1.51358500	-4.52732000	-0.94329200
H	0.25369200	-2.99642300	-1.69996900
H	-3.22859100	-2.79146700	-0.38094600
N	0.46809400	-2.03497200	0.18647200
N	-1.84010800	-1.33159900	0.15639700
H	-2.16692800	-2.28686500	-1.69975600
H	-1.33650200	-3.94966300	0.72471600
H	0.88597400	-3.98670700	-0.37529800
Si	-0.03967000	0.43641400	1.29917100
H	-1.29129200	0.90526300	1.92311100
H	0.80511100	-0.21139700	2.32026400
C	0.87308900	1.90411200	0.58209400
C	0.19002300	3.05178600	0.16971700
C	2.26388500	1.87959900	0.44478600
C	0.86971800	4.13306200	-0.37509700
H	-0.88763500	3.10569300	0.28598200
C	2.94744700	2.95726900	-0.10043400
H	2.82267600	1.00761100	0.76895600
C	2.25015900	4.08453400	-0.51415400
H	0.32409400	5.01516400	-0.68564900
H	4.02513100	2.91795200	-0.19906600
H	2.78220500	4.92697000	-0.93778000
H	-0.31531900	-0.52619700	-1.06937400
C	-2.81540000	-0.30921900	0.00004600
C	-2.57509100	0.88296700	-0.68121100
C	-4.07957100	-0.51120700	0.56073000
C	-3.56941700	1.85108400	-0.78174000
H	-1.61309800	1.07646300	-1.13682700
C	-5.06898000	0.44691300	0.44414900
H	-4.26168700	-1.42135500	1.11828900
C	-4.81934200	1.63996000	-0.22726800
H	-3.35646600	2.77370400	-1.30745100
H	-6.03696300	0.27174700	0.89605300
H	-5.59048300	2.39420600	-0.30845800
C	1.84612300	-1.66097800	0.01657100
C	2.73394500	-1.87966100	1.06477100
C	2.32501600	-1.12509300	-1.17760300
C	4.07798100	-1.56184100	0.92667800
H	2.34655000	-2.29514400	1.98591200
C	3.66836300	-0.80515200	-1.31519600
H	1.64656100	-0.95555900	-2.00450000
C	4.54806200	-1.02205800	-0.26366500
H	4.75811700	-1.73347600	1.75099800
H	4.02710900	-0.38262600	-2.24492100
H	5.59563300	-0.77219700	-0.37093500

H3SiPh- RENHC^{Ph}, T2

E_0 = -1251.63985237

M06-2X/def2-TZVP optimized geometry (Å).

0 1

6	1.457098	0.289103	2.599526
6	1.805831	1.565959	1.830070
6	0.513508	1.240572	-0.157200
6	-0.039869	-0.068084	2.566557

1	2.046604	-0.539390	2.202422
1	1.114163	2.370667	2.077260
1	-0.576764	0.705341	3.115375
7	1.705797	1.324506	0.377666
7	-0.626754	-0.166286	1.238378
1	-0.196791	-0.992124	3.129095
1	1.752228	0.431164	3.641703
1	2.814968	1.909083	2.048026
14	-1.225605	1.644079	0.534212
1	-1.222840	2.155141	1.921668
6	-2.892028	1.035927	-0.119925
6	-3.520664	1.734747	-1.151454
6	-3.579979	-0.039124	0.452457
6	-4.781172	1.369359	-1.610394
1	-3.017516	2.585378	-1.596738
6	-4.846926	-0.394994	0.016663
1	-3.105450	-0.610095	1.241424
6	-5.448306	0.305619	-1.022305
1	-5.243726	1.920148	-2.419903
1	-5.364280	-1.225551	0.480303
1	-6.433407	0.021408	-1.370683
1	0.533609	0.777599	-1.144744
1	-1.286495	2.988835	-0.194122
6	-0.451894	-1.367594	0.563300
6	0.258604	-2.462251	1.094946
6	-0.977721	-1.540425	-0.737214
6	0.409516	-3.645363	0.382950
1	0.706051	-2.405519	2.076109
6	-0.814850	-2.720571	-1.435084
1	-1.532953	-0.737017	-1.199611
6	-0.121938	-3.794843	-0.885729
1	0.960644	-4.459535	0.838106
1	-1.243147	-2.803043	-2.426604
1	0.000062	-4.717695	-1.435760
6	2.887044	0.927325	-0.331713
6	2.972993	1.188199	-1.696218
6	3.955531	0.323074	0.322805
6	4.098277	0.805320	-2.406507

H3SiPh- RENHC^{Ph}, C

E_0 = -1251.65337106

M06-2X/def2-TZVP optimized geometry (Å).

0 1

C	0.47230100	-1.96876500	-0.60670000
C	1.97635300	-1.79520300	-0.58527200
C	1.54123900	0.53623900	-0.03836300
C	-0.15927100	-1.86611700	0.79591100
H	0.02453300	-1.21418200	-1.25248800
H	2.43062900	-2.48106700	0.13489900
H	0.57012000	-1.43707100	1.48112200
N	2.40268800	-0.41998700	-0.23421900
N	-1.35277200	-1.03459000	0.85789800
H	-0.38835500	-2.86589800	1.17882000
H	0.27353100	-2.94293900	-1.05713500
H	2.41428600	-2.02424000	-1.55969400
Si	-1.27485500	0.51143900	1.66478200
H	-2.33320900	0.56673400	2.70575200
C	-1.61044000	1.98007300	0.55885900
C	-1.42535000	1.93528200	-0.82352400
C	-2.09883100	3.15970300	1.12297700
C	-1.71192600	3.03719000	-1.61610200
H	-1.04757500	1.02602800	-1.27517800
C	-2.37245300	4.27194600	0.33711500
H	-2.27542900	3.21354700	2.19271500
C	-2.17984400	4.20957600	-1.03551500
H	-1.57085600	2.98389300	-2.68833200
H	-2.74353200	5.18094200	0.79337200
H	-2.40037800	5.07074500	-1.65369100
H	2.11865800	1.44861300	0.18662300
H	0.02829700	0.57348300	2.35164800
C	-2.52425000	-1.51880700	0.27136500
C	-2.59666500	-2.79282800	-0.30963900
C	-3.69095100	-0.73511500	0.24978900
C	-3.77741600	-3.25639100	-0.87243100
H	-1.73222900	-3.43889300	-0.32550600
C	-4.86062000	-1.20899000	-0.31495300
H	-3.68864200	0.26110200	0.67189100
C	-4.92063600	-2.47510900	-0.88313200
H	-3.79392200	-4.24710700	-1.30957800
H	-5.73730600	-0.57362400	-0.31160600
H	-5.83719100	-2.84007800	-1.32580100
C	3.83647100	-0.25293400	-0.17113200
C	4.58213600	-0.95393600	0.76623500
C	4.45418300	0.63025000	-1.04490800
C	5.95378200	-0.75743500	0.83520300
H	4.08980700	-1.63007900	1.45351100
C	5.82622200	0.81878300	-0.97347200
H	3.85328900	1.16347000	-1.77062300
C	6.57821300	0.12570200	-0.03467000
H	6.53407600	-1.29192100	1.57576300
H	6.30817700	1.50698100	-1.65530100
H	7.64828900	0.27478100	0.02027500

H3SiPh- RENHC^{Ph}, T3(H)

E_0 = -1251.64462812

M06-2X/def2-TZVP optimized geometry (Å).

0 1

C	-0.93349400	-0.50986200	2.04778500
C	-2.10460800	-1.11091800	1.27487800
C	-1.58114400	0.19835600	-0.68505200
C	0.42469700	-1.08380100	1.66878900
H	-0.95270200	0.57926700	1.95824400
H	-2.98476100	-1.17379400	1.91064500
H	0.37793600	-2.16391100	1.84794200
N	-2.49023000	-0.29121200	0.10324200
N	0.81917800	-0.85497100	0.29106400
H	1.16902200	-0.68363400	2.37336300
H	-1.08219100	-0.72762900	3.10664700
H	-1.85922500	-2.11640900	0.92603700
Si	0.39417500	0.71185700	-0.50059800
H	-0.49734900	1.87385400	-0.00926100
H	-2.02793700	0.76092000	-1.51163500
H	0.43822000	0.76782800	-1.98166100
C	1.99785500	1.69736200	-0.07568700
C	2.12014900	2.96519300	-0.65212200
C	3.02183000	1.28769900	0.77918300
C	3.21079000	3.78480500	-0.40220800
H	1.33679600	3.32294700	-1.31630600
C	4.11648600	2.10310600	1.04799400
H	2.98389000	0.30670700	1.23869600
C	4.21521800	3.35318000	0.45583500
H	3.27990900	4.75878900	-0.87136600
H	4.89688300	1.75710900	1.71484200
H	5.06906500	3.98746300	0.65868300
C	-3.89629400	-0.05153300	-0.08856900
C	-4.79357000	-1.10877400	-0.01474700
C	-4.34048300	1.23674000	-0.34815800
C	-6.14413000	-0.87204100	-0.21948300
H	-4.43500700	-2.11081100	0.18295700
C	-5.69371700	1.46438900	-0.54954300
H	-3.62790600	2.05170900	-0.37652000
C	-6.59690000	0.41273100	-0.48774500
H	-6.84327500	-1.69645400	-0.17478200
H	-6.04193900	2.46970300	-0.74579800
H	-7.65168600	0.59368000	-0.64488300
C	1.92355700	-1.59041900	-0.14803700
C	2.66505900	-2.42639600	0.70255100
C	2.33281700	-1.52139100	-1.49093800
C	3.74605800	-3.15669700	0.22540300
H	2.42401100	-2.50166900	1.75232900
C	3.41568300	-2.24570200	-1.95048700
H	1.78677800	-0.89735600	-2.18425000
C	4.13564700	-3.07691800	-1.09999000
H	4.29268500	-3.78959600	0.91375200
H	3.69774000	-2.16184800	-2.99261400
H	4.98091100	-3.64424000	-1.46474000

H3SiPh- RENHC^{Ph}, T3(Ph)

E_0 = -1251.64462691
M06-2X/def2-TZVP optimized geometry (Å).
0 1

C	0.59929900	-0.94026300	2.26574800
C	-0.22018600	-1.82665800	1.33407700
C	-0.41357900	-0.10583600	-0.39923800
C	2.05021600	-0.67371600	1.84912300
H	0.05608300	-0.01078500	2.44646000
H	-0.98638100	-2.34209500	1.90990500
H	2.59563400	-1.62318600	1.88959000
N	-0.93546100	-1.12651500	0.24067100
N	2.17231200	-0.11170100	0.51767700
H	2.49054800	-0.02303700	2.62036500
H	0.63816900	-1.44765700	3.23193700
H	0.42590500	-2.58024200	0.87525200
Si	0.88282000	1.14036700	0.16727300
H	1.03446500	1.81161200	1.49153700
H	-0.90880800	0.10697100	-1.34198200
H	1.40033800	1.83858700	-1.02221100
C	-1.01541600	2.05233900	0.07534700
C	-1.51592800	2.61941100	-1.09746700
C	-1.75218400	2.23803600	1.24413200
C	-2.68702400	3.36709800	-1.10365800
H	-0.97581200	2.48240500	-2.03153500
C	-2.93324800	2.97078200	1.25253900
H	-1.39271900	1.81680900	2.17974100
C	-3.40372300	3.53770800	0.07481200
H	-3.04392000	3.81284500	-2.02422700
H	-3.48511600	3.10338400	2.17519400
H	-4.32149100	4.11180900	0.07555700
C	-2.19542800	-1.67391600	-0.16514600
C	-2.39301400	-3.05022700	-0.19132500
C	-3.22019000	-0.80790400	-0.53187100
C	-3.61633700	-3.55753400	-0.60126900
H	-1.59213600	-3.72266500	0.08507000
C	-4.43878900	-1.32831900	-0.94067900
H	-3.06786200	0.26403200	-0.47219800
C	-4.64116400	-2.70062300	-0.97814300
H	-3.76436700	-4.62889700	-0.63214800
H	-5.23635500	-0.65233200	-1.21913300
H	-5.59445500	-3.10145200	-1.29550500
C	3.43837300	-0.13706800	-0.05781800
C	4.60422400	-0.39095100	0.67972100
C	3.58419300	0.07221600	-1.44130200
C	5.84787800	-0.42813200	0.06173600
H	4.54862800	-0.54274300	1.74854600
C	4.82719900	0.04486900	-2.04279700
H	2.70026600	0.23369900	-2.04340600
C	5.97613800	-0.20677700	-1.29886300
H	6.72716600	-0.62498500	0.66298100
H	4.90003800	0.20728200	-3.11120200
H	6.94689300	-0.23418900	-1.77479700

H3SiPh- RENHC^{Ph}, D(H)
E_0 = -1251.7431247
M06-2X/def2-TZVP optimized geometry (Å).
0 1

C	0.55514400	0.08388000	2.46474100
C	1.99772900	-0.15753900	2.02942100
C	1.16568700	-1.27933600	0.04725600
C	-0.11315300	1.26384200	1.76361900
H	-0.05669900	-0.81575300	2.35300000
H	2.39690600	-1.03289600	2.56736200
H	0.64565200	2.03531900	1.58306700
N	2.11739600	-0.31542200	0.59738400
N	-0.80981300	0.92830000	0.52071300
H	-0.85375300	1.69687800	2.44173800
H	0.57933900	0.29341800	3.53557600
H	2.59036000	0.70962400	2.32579900
Si	-0.47796700	-0.48571000	-0.44226800
H	1.58798500	-1.74099100	-0.84619000
H	-0.39026300	-0.06645700	-1.85963200
C	3.37398700	-0.18649600	0.00235700
C	3.48154700	-0.16486900	-1.39613600
C	4.54540300	-0.03874600	0.75282600
C	4.70966300	-0.01110600	-2.01128600
H	2.58573900	-0.23211500	-2.00047100
C	5.77190500	0.12652300	0.12236500
H	4.51284800	-0.07274600	1.83214300
C	5.86923000	0.13781800	-1.25883000
H	4.75909300	0.00899900	-3.09267700
H	6.66248900	0.23483900	0.72869900
H	6.82766900	0.26362300	-1.74345500
C	-1.68091300	1.91188200	0.02207100
C	-1.62980000	3.23925900	0.46644900
C	-2.64712700	1.58725800	-0.94306400
C	-2.50118200	4.19301400	-0.04041700
H	-0.89734100	3.54432500	1.19845700
C	-3.50426100	2.54929800	-1.44704100
H	-2.75140200	0.56689200	-1.28949500
C	-3.44243500	3.86285900	-1.00136800
H	-2.43160000	5.21074800	0.32269500
H	-4.23828300	2.26119400	-2.18884500
H	-4.11797500	4.61085400	-1.39319500
H	1.01293200	-2.10310200	0.75711900
C	-1.82245800	-1.77580500	-0.26782300
C	-1.78548500	-2.94428800	-1.03409400
C	-2.85780500	-1.62552300	0.65625900
C	-2.74707600	-3.93248100	-0.88066500
H	-0.99762100	-3.08684500	-1.76770600
C	-3.82457600	-2.61044700	0.81348500
H	-2.91253200	-0.71907300	1.25071000
C	-3.76845800	-3.76522900	0.04591900
H	-2.70346300	-4.83062000	-1.48346500
H	-4.62330000	-2.47553900	1.53170800
H	-4.52172000	-4.53339700	0.16586400

H3SiPh- RENHC^{Ph}, D(Ph)
E_0 = -1251.72513679
M06-2X/def2-TZVP optimized geometry (Å).
0 1

C	-0.54370700	-0.44636600	2.31133700
C	0.75811300	0.24079500	1.90162800
C	0.65224800	-0.47460100	-0.47300900
C	-1.79881600	0.21149400	1.74177700
H	-0.53879400	-1.51054100	2.05891500
H	1.60724400	-0.40063400	2.17895800
H	-1.62201700	1.28991800	1.66438500
N	0.77649400	0.62918400	0.50336200
N	-2.19509900	-0.34906900	0.44695500
H	-2.63209800	0.06274100	2.43398200
H	-0.59146100	-0.41404400	3.40092200
H	0.85147200	1.16292200	2.47859800
Si	-1.07670200	-1.28025500	-0.50078400
H	-1.00389100	-2.69788900	-0.07471300
H	0.66896500	0.00894300	-1.45166300
H	-1.54307900	-1.25747400	-1.90005600
C	1.83907900	-1.41942100	-0.44154400
C	2.92558500	-1.18230100	-1.28458800
C	1.92119200	-2.48412600	0.45502300
C	4.05638500	-1.98401600	-1.23732400
H	2.88301600	-0.35102100	-1.97939000
C	3.05333300	-3.28559200	0.51007700
H	1.08868600	-2.70069500	1.11321000
C	4.12347800	-3.03890200	-0.33777300
H	4.88638100	-1.78350100	-1.90250800
H	3.09557000	-4.10841100	1.21213600
H	5.00392000	-3.66710000	-0.29957600
C	1.74651000	1.60251800	0.15013700
C	1.55870200	2.34985900	-1.01743400
C	2.87558000	1.85901500	0.92576900
C	2.47629100	3.31058700	-1.39977400
H	0.66720100	2.18502100	-1.61006500
C	3.78855900	2.83590500	0.54316400
H	3.05948100	1.28787000	1.82501900
C	3.60083600	3.56211300	-0.61984000
H	2.30445300	3.88118400	-2.30360100
H	4.65924900	3.01658700	1.16071500
H	4.31442400	4.31919400	-0.91594300
C	-3.50594700	-0.08204800	0.02440400
C	-4.19793900	1.04908000	0.47164300
C	-4.17426600	-0.95659500	-0.84295600
C	-5.49493200	1.30065100	0.04821900
H	-3.71747200	1.74851600	1.14065900
C	-5.46365600	-0.69016800	-1.26912500
H	-3.68898700	-1.86840700	-1.16685500
C	-6.13748900	0.44157900	-0.82922700
H	-6.00274300	2.18670000	0.40803400
H	-5.95224700	-1.38685300	-1.93850400
H	-7.14804800	0.64297300	-1.15740800

Single Crystal X-ray Diffraction Analysis

Single crystals of compounds **6** and **7/8** were grown from pentane solutions. Suitable crystals were selected and mounted on a SuperNova, Dual, Cu at zero, EosS2 diffractometer. The crystals were kept at 150.00(10) K during data collection. Using Olex2,[14] the structures were solved with the olex2.solve[15] structure solution program and refined with the ShelXL[16] refinement package. For **6** H1A and H1b were located and refined without restraints. Resolution of the electron density in **7/8** involved modelling the 66:34 disorder that pertained to atoms Si1, N1, N2, C1-C7 and C20-C28, over two proximate positions. To assist convergence, the disordered aromatic rings were treated as rigid hexagons and anisotropic displacement parameter restraints were included (on merit) for fractional occupancy atoms. Distance similarity restraints were also applied to chemically similar C-C, C-N, Si-N and Si-C metrics in the model. The hydrogen atoms attached to the silicon centres were located and refined freely.

Crystal Data for **6** (M =428.68 g mol^{-1}): monoclinic, space group $P2_1/c$ (no. 14), a = 15.8057(3) Å, b = 7.61260(10) Å, c = 20.7376(4) Å, β = 90.945(2)°, U = 2494.86(8) Å^3, Z = 4, T = 150.00(10) K, μ(MoKα) = 0.111 mm^{-1}, D_{calc} = 1.141 g/cm^3, 18688 reflections measured (5.94° ≤ 2θ ≤ 54.968°), 5619 unique (R_{int} = 0.0348) which were used in all calculations. The final R_1 was 0.0470 ($I > 2\sigma(I)$) and wR_2 was 0.1261 (all data).

Crystal Data for **7/8** (M =428.68 g mol^{-1}): monoclinic, space group $P2_1/n$ (no. 14), a = 13.2680(3) Å, b = 15.1828(3) Å, c = 13.2770(3) Å, β = 108.900(3)°, U = 2530.39(10) Å^3, Z = 4, T = 150.00(10) K, μ(CuKα) = 0.926 mm^{-1}, D_{calc} = 1.125 g/cm^3, 30974 reflections measured (8.188° ≤ 2θ ≤ 147.27°), 5081 unique (R_{int} = 0.0349) which were used in all calculations. The final R_1 was 0.0791 ($I > 2\sigma(I)$) and wR_2 was 0.2308 (all data).

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