Supplementary Material (ESI) for New Journal of Chemistry

Supplementary Information

Synthesis and Structure of Stable Base-Free Dialkylsilanimines

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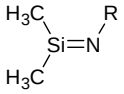
Contents

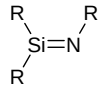
1. Details of Theoretical Study

All theoretical calculations were performed using a Gaussian 03[S1] program and reaction routes were searched by the GRRM method available in GRRM 1.2 program.[S2] Geometry optimization of **6a**-**6d** was carried out at the B3LYP/6-311+G(d,p) level. Optimized atomic coordinates of **6a**-**6d** are summarized in Tables S1-S4. Potential surface of **6a**-**6d** as a function of Si-N-R bent angle θ for model compounds were shown in Figure S1, which is the same as Figure 1 in the main text. Absorption band maxima and oscillator strength of **5a**-**5d** whose structural parameters were fixed to the experimental values determined by X-ray analysis were calculated at the TD-B3LYP/6-311+G(d,p) level. Excited states of **5a**-**5d** were summarized in Tables S5-S8 and Frontier Kohn-Sham orbitals and their energy levels of **5a**-**5d** were shown in Figures S2. For a reaction route search for formation of silanimines $H_2Si=NH$ (**7a**), betains **11a** and **15a** whose geometries were optimized at the B3LYP/6-311G(d) level were used as initial structures for GRRM methods.[S2] For exploration of low-barrier routes to **7a**, large-ADD (*l*ADD) method was applied.[S2d] Although automatic reaction route search using GRRM methods explored various reaction routes among H_3SiN isomers including **7a**, only the reaction routes to **7a** with the smallest activation barrier except for degenerate rearrangement such as a configuration inversion are shown in Scheme S1 in the main text, which is the same as Scheme 2 in the main text. For a reaction route search for formation of silanimines $Me_2Si=NMe$ (**7b**), equilibrium structures **11b**-**17b** and transition structures **TS12b**-**TS18b** were optimized at the B3LYP/6-31G(d) level. Optimized atomic coordinates and their energies of **7**-**TS18** are also summarized in Tables S9-S31. A plot of chemical shift of the unsaturated silicon atom (δSi_u) of (*N*-methyl)dimethylsilanimine **6b** as a function of Si-N-R bent angle calculated at the GIAO/B3LYP/6-311+G(2df,p)//B3LYP/6-311+G(d,p) level was shown in Figure S3.

Chart S1

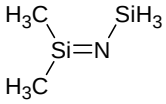


6a, R = SiH_3
6b, R = CH_3
6c, R = H
6d, R = SiH_3



7a, R = H
7b, R = CH_3

Table S1. Atomic Coordinates of **6a** Optimized at the B3LYP/6-311+G(d,p) Level

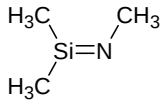


6a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	-0.856218	-0.012038	-0.000015
2	7	0	0.715678	-0.166731	-0.000021
3	14	0	2.404446	-0.011652	0.000007
4	6	0	-2.023519	-1.473347	-0.000007
5	6	0	-1.778438	1.618984	0.000022
6	1	0	2.995060	-0.662153	-1.204480
7	1	0	2.880600	1.405668	0.000197
8	1	0	2.995055	-0.662472	1.204325
9	1	0	-2.674028	-1.452070	0.880523
10	1	0	-1.461865	-2.407999	-0.001353
11	1	0	-2.676051	-1.450624	-0.878993
12	1	0	-2.424732	1.698968	-0.880343
13	1	0	-1.080930	2.457499	0.001003
14	1	0	-2.426315	1.698130	0.879292

(energy with zero point energy: -715.489464687 hartree)

Table S2. Atomic Coordinates of **6b** Optimized at the B3LYP/6-311+G(d,p) Level



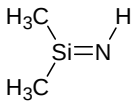
6b

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	0.373287	-0.035813	0.000000
2	7	0	-1.109152	-0.627997	0.000001
3	6	0	-2.442410	-0.087357	-0.000001
4	6	0	1.813344	-1.225258	-0.000000
5	6	0	0.903208	1.772004	-0.000000
6	1	0	-2.994473	-0.448349	0.877129
7	1	0	-2.510054	1.012596	-0.000024

8	1	0	-2.994486	-0.448386	-0.877107
9	1	0	2.446429	-1.080178	-0.880764
10	1	0	1.438165	-2.249284	-0.000017
11	1	0	2.446413	-1.080201	0.880778
12	1	0	1.512058	1.998994	0.881078
13	1	0	0.037115	2.436825	0.000019
14	1	0	1.512029	1.999005	-0.881095

(energy with zero point energy: -464.049964784 hartree)

Table S3. Atomic Coordinates of **6c** Optimized at the B3LYP/6-311+G(d,p) Level

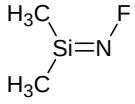


6c

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	0.012016	0.164821	-0.000001
2	7	0	0.383996	1.728239	0.000001
3	1	0	-0.328650	2.449525	-0.000001
4	6	0	1.415484	-1.065542	0.000000
5	6	0	-1.677632	-0.662233	0.000000
6	1	0	1.374067	-1.714032	0.880542
7	1	0	2.366569	-0.531495	0.000004
8	1	0	1.374072	-1.714027	-0.880546
9	1	0	-1.793908	-1.302196	-0.880784
10	1	0	-2.481552	0.075892	-0.000001
11	1	0	-1.793906	-1.302192	0.880788

(energy with zero point energy: -424.738357476 hartree)

Table S4. Atomic Coordinates of **6d** Optimized at the B3LYP/6-311+G(d,p) Level



6d

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	-0.348995	-0.000194	-0.000018
2	7	0	0.955441	-1.019359	0.000020
3	9	0	2.189572	-0.263366	-0.000005
4	6	0	-1.993686	-0.873849	0.000005
5	6	0	-0.288586	1.864413	0.000006
6	1	0	-2.581693	-0.609811	0.883343
7	1	0	-1.826523	-1.952531	-0.000061
8	1	0	-2.581738	-0.609708	-0.883273
9	1	0	-0.788372	2.272058	-0.883404
10	1	0	0.751980	2.193161	0.000003
11	1	0	-0.788328	2.271978	0.883479

(energy with zero point energy: -523.927546688 hartree)

Table S5. Transition energy, Wavelengths, and Oscillator Strengths of the Electronic Transitions of **5a** Calculated at the TD-B3LYP/6-311++G(d,p) Level (The 131th orbital is Highest Occupied n(N) Orbital Shown in Figure S2)

Excited State 1:	Singlet-A	4.1657 eV	297.63 nm	f=0.0002
130 ->132	0.17768			
131 ->132	0.66258			
Excited State 2:	Singlet-A	4.8980 eV	253.13 nm	f=0.0997
130 ->132	0.62492			
131 ->132	-0.17277			
Excited State 3:	Singlet-A	5.0637 eV	244.85 nm	f=0.0083
131 ->133	0.67832			
131 ->136	-0.12514			
Excited State 4:	Singlet-A	5.1796 eV	239.37 nm	f=0.0026
130 ->133	0.63177			
130 ->136	-0.14893			
131 ->137	-0.16655			
Excited State 5:	Singlet-A	5.1938 eV	238.72 nm	f=0.0114
128 ->138	0.11579			
129 ->132	0.14670			
130 ->133	0.22251			
131 ->135	0.25175			
131 ->136	-0.11234			
131 ->137	0.53253			
Excited State 6:	Singlet-A	5.2707 eV	235.24 nm	f=0.0144
128 ->138	0.16458			
129 ->132	0.40970			
129 ->137	0.19482			
130 ->137	-0.19050			
130 ->138	-0.10822			
131 ->134	-0.13226			
131 ->135	-0.18648			
131 ->136	-0.17625			
131 ->137	-0.19836			
131 ->138	0.19633			
Excited State 7:	Singlet-A	5.3384 eV	232.25 nm	f=0.0439
129 ->132	0.20972			
129 ->137	0.12442			
130 ->138	-0.13647			
131 ->133	0.11171			
131 ->134	0.44595			
131 ->136	0.40766			
Excited State 8:	Singlet-A	5.3561 eV	231.48 nm	f=0.0087
129 ->132	-0.32865			
130 ->135	-0.12748			
130 ->137	-0.17926			
131 ->134	0.21538			
131 ->135	-0.24039			
131 ->136	-0.11177			
131 ->137	0.18840			
131 ->138	0.39727			
Excited State 9:	Singlet-A	5.3655 eV	231.08 nm	f=0.0022
128 ->138	-0.13328			
129 ->132	0.21825			
129 ->137	-0.10656			
130 ->135	0.17611			
130 ->136	-0.14904			
130 ->137	0.42859			
130 ->138	0.16981			
131 ->134	0.13775			
131 ->135	-0.22480			
131 ->136	-0.10756			
131 ->138	0.22106			
Excited State 10:	Singlet-A	5.4136 eV	229.03 nm	f=0.0027
131 ->134	0.43616			
131 ->135	0.26977			
131 ->136	-0.37743			
131 ->137	-0.15940			
131 ->138	-0.10585			
Excited State 11:	Singlet-A	5.4344 eV	228.15 nm	f=0.0092
128 ->132	-0.10100			
130 ->133	0.15348			
130 ->134	0.40063			
130 ->135	0.16312			
130 ->136	0.40053			
130 ->137	0.17122			
130 ->138	-0.14758			
131 ->136	-0.14841			
Excited State 12:	Singlet-A	5.4589 eV	227.12 nm	f=0.0435
129 ->132	-0.17074			
129 ->137	0.17401			
130 ->134	-0.33526			
130 ->135	0.40663			
130 ->138	-0.30786			
131 ->136	-0.12025			
131 ->137	-0.10494			
Excited State 13:	Singlet-A	5.4620 eV	226.99 nm	f=0.0009
128 ->132	-0.10864			
130 ->138	0.10475			
131 ->135	0.44486			
131 ->136	0.15594			
131 ->137	-0.19680			
131 ->138	0.43136			
Excited State 14:	Singlet-A	5.5021 eV	225.34 nm	f=0.0021
128 ->132	0.62780			
129 ->132	-0.18372			
129 ->137	0.15896			
Excited State 15:	Singlet-A	5.5257 eV	224.38 nm	f=0.0007
130 ->134	-0.43880			
130 ->135	-0.19344			
130 ->136	0.44709			
130 ->137	0.15171			
Excited State 16:	Singlet-A	5.5747 eV	222.41 nm	f=0.0101
129 ->137	-0.18947			
130 ->135	0.41112			
130 ->136	0.21163			
130 ->137	-0.33639			
130 ->138	0.24530			
131 ->139	-0.10267			
Excited State 17:	Singlet-A	5.6598 eV	219.06 nm	f=0.0294
128 ->138	0.10250			
129 ->133	0.30684			
129 ->136	-0.19409			
130 ->135	0.12576			
130 ->138	0.22001			
130 ->139	-0.17299			
131 ->139	0.36633			
131 ->142	0.15134			
Excited State 18:	Singlet-A	5.7085 eV	217.19 nm	f=0.0212
129 ->133	0.46379			
129 ->136	-0.14702			
129 ->137	-0.12449			
130 ->139	-0.13272			
131 ->139	-0.26946			
131 ->141	-0.21305			
131 ->142	-0.17304			
Excited State 19:	Singlet-A	5.7519 eV	215.55 nm	f=0.0089
128 ->133	-0.12313			
128 ->136	0.14816			
129 ->133	0.32546			
130 ->139	0.41787			
130 ->142	0.12022			
131 ->140	-0.14221			
131 ->141	0.28861			
Excited State 20:	Singlet-A	5.7746 eV	214.71 nm	f=0.0090
128 ->138	-0.17200			
129 ->137	-0.12719			
130 ->138	-0.14618			
130 ->139	-0.24518			
131 ->140	-0.29100			
131 ->141	0.45730			
131 ->142	-0.11447			
Excited State 21:	Singlet-A	5.8039 eV	213.62 nm	f=0.0031
128 ->133	-0.29150			
128 ->136	0.13647			
128 ->138	-0.17716			
129 ->137	-0.16894			
130 ->138	-0.20868			
131 ->139	0.40413			
131 ->140	0.10621			
131 ->142	-0.16397			
Excited State 22:	Singlet-A	5.8129 eV	213.29 nm	f=0.0019
131 ->139	-0.14013			
131 ->140	0.58061			
131 ->141	0.27836			
131 ->142	0.14033			
Excited State 23:	Singlet-A	5.8267 eV	212.79 nm	f=0.0050
128 ->138	-0.17853			
129 ->137	-0.13194			
130 ->138	-0.16500			
131 ->140	-0.16694			
131 ->141	-0.19164			
131 ->142	0.51842			
Excited State 24:	Singlet-A	5.8358 eV	212.45 nm	f=0.0013
128 ->133	0.50844			
128 ->136	-0.14214			
128 ->138	-0.11261			
129 ->136	0.12716			
130 ->138	-0.12836			
130 ->139	0.23984			
130 ->141	0.17472			

131 ->139 0.14184

Table S6. Transition energy, Wavelengths, and Oscillator Strengths of the Electronic Transitions of **5b** Calculated at the TD-B3LYP/6-311++G(d,p) Level (The 127th orbital is Highest Occupied n(N) Orbital Shown in Figure S2)

Excited State 1:	Singlet-A	3.4286 eV	361.62 nm	f=0.0016
127 ->128	0.69528			
Excited State 2:	Singlet-A	4.3096 eV	287.70 nm	f=0.0012
127 ->129	0.68691			
127 ->132	0.13942			
Excited State 3:	Singlet-A	4.5862 eV	270.34 nm	f=0.0218
126 ->134	0.14169			
126 ->139	-0.10240			
127 ->130	0.11210			
127 ->132	-0.21693			
127 ->133	0.59192			
Excited State 4:	Singlet-A	4.5995 eV	269.56 nm	f=0.0067
127 ->129	-0.14135			
127 ->130	-0.28055			
127 ->131	-0.23873			
127 ->132	0.51917			
127 ->133	0.20776			
Excited State 5:	Singlet-A	4.6271 eV	267.95 nm	f=0.0017
127 ->130	-0.16763			
127 ->131	0.64462			
127 ->132	0.13031			
127 ->133	0.13527			
127 ->138	-0.10856			
Excited State 6:	Singlet-A	4.6467 eV	266.82 nm	f=0.0025
127 ->130	0.60511			
127 ->132	0.33283			
Excited State 7:	Singlet-A	4.7934 eV	258.66 nm	f=0.0682
127 ->134	0.59192			
127 ->135	0.25538			
127 ->137	-0.12088			
127 ->144	0.12346			
Excited State 8:	Singlet-A	4.9871 eV	248.61 nm	f=0.0315
126 ->128	0.50975			
127 ->136	-0.38569			
127 ->137	0.23513			
Excited State 9:	Singlet-A	5.0148 eV	247.24 nm	f=0.0272
126 ->128	-0.38572			
127 ->134	-0.10720			
127 ->135	0.43050			
127 ->136	-0.31488			
127 ->137	0.13655			
Excited State 10:	Singlet-A	5.0225 eV	246.86 nm	f=0.0185
126 ->128	0.27518			
127 ->134	-0.26205			
127 ->135	0.43105			
127 ->136	0.33057			
127 ->138	-0.17925			
Excited State 11:	Singlet-A	5.0703 eV	244.53 nm	f=0.0209
127 ->134	0.10843			
127 ->136	0.28027			
127 ->137	0.59996			
Excited State 12:	Singlet-A	5.0937 eV	243.41 nm	f=0.0124
127 ->135	0.17140			
127 ->136	0.11394			
127 ->138	0.64253			
Excited State 13:	Singlet-A	5.1929 eV	238.76 nm	f=0.2678
125 ->128	0.53722			
127 ->137	-0.10626			
127 ->140	-0.17745			
127 ->144	-0.21126			
127 ->145	-0.20407			
Excited State 14:	Singlet-A	5.2133 eV	237.82 nm	f=0.0921
125 ->128	-0.11669			
127 ->136	-0.13460			
127 ->139	0.64447			
127 ->140	-0.10995			
Excited State 15:	Singlet-A	5.4328 eV	228.21 nm	f=0.0087
125 ->128	0.14436			
127 ->139	0.12863			
127 ->140	0.55237			
127 ->141	0.16206			
127 ->142	0.22312			
127 ->143	0.14356			
Excited State 16:	Singlet-A	5.4874 eV	225.94 nm	f=0.0005
127 ->138	0.11505			
127 ->140	-0.19132			
127 ->141	0.56168			
127 ->143	0.29628			
127 ->145	-0.11737			
Excited State 17:	Singlet-A	5.5075 eV	225.12 nm	f=0.0025
124 ->128	0.15970			
125 ->128	0.23351			
126 ->133	0.11126			
127 ->141	0.13920			
127 ->142	-0.33135			
127 ->144	0.39732			
127 ->145	0.21643			
Excited State 18:	Singlet-A	5.5433 eV	223.66 nm	f=0.0005
124 ->128	-0.13447			
127 ->140	0.15545			
127 ->141	-0.20520			
127 ->142	-0.42275			
127 ->143	0.42020			
127 ->144	-0.15109			
Excited State 19:	Singlet-A	5.5591 eV	223.03 nm	f=0.0027
124 ->128	0.36044			
127 ->140	-0.14713			
127 ->141	-0.22882			
127 ->142	0.27564			
127 ->143	0.40329			
127 ->144	0.19866			
Excited State 20:	Singlet-A	5.5710 eV	222.55 nm	f=0.0004
124 ->128	0.49924			
127 ->141	0.11132			
127 ->142	-0.13097			
127 ->143	-0.11711			
127 ->144	-0.35572			
127 ->145	0.19552			
Excited State 21:	Singlet-A	5.5830 eV	222.07 nm	f=0.0020
124 ->128	-0.22065			
127 ->140	-0.19906			
127 ->142	0.20433			
127 ->144	-0.14355			
127 ->145	0.54834			
Excited State 22:	Singlet-A	5.5994 eV	221.43 nm	f=0.0007
126 ->129	0.65721			
126 ->132	0.19520			
Excited State 23:	Singlet-A	5.6742 eV	218.51 nm	f=0.0001
125 ->129	0.67595			
125 ->132	0.10802			
Excited State 24:	Singlet-A	5.7026 eV	217.42 nm	f=0.0008
127 ->141	-0.10890			
127 ->146	0.66816			

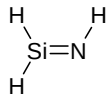
Table S7. Transition energy, Wavelengths, and Oscillator Strengths of the Electronic Transitions of **5c** Calculated at the TD-B3LYP/6-311++G(d,p) Level (The 144th orbital is Highest Occupied n(N) Orbital Shown in Figure S2)

```
Excited State  1:   Singlet-A     3.7845 eV  327.61 nm  f=0.0006
    144 -> 145       0.61075
    144 -> 146      -0.33072
Excited State  2:   Singlet-A     4.5645 eV  271.63 nm  f=0.0068
    144 -> 145       0.32870
    144 -> 146       0.60966
    144 -> 147      -0.11011

 Excited State  3:   Singlet-A     4.8073 eV  257.91 nm  f=0.0000
    144 -> 146       0.10208
    144 -> 147       0.66038
    144 -> 148       0.19403

 Excited State  4:   Singlet-A     4.8767 eV  254.24 nm  f=0.0004
    144 -> 147      -0.20698
    144 -> 148       0.61893
    144 -> 149       0.23538

 Excited State  5:   Singlet-A     4.8851 eV  253.80 nm  f=0.0001
    144 -> 148      -0.24108
    144 -> 149       0.65554

 Excited State  6:   Singlet-A     5.0819 eV  243.97 nm  f=0.0934
    143 -> 145       0.39239
    143 -> 146      -0.13707
    144 -> 150       0.47630
    144 -> 154       0.13227
    144 -> 155      -0.11601
    144 -> 162       0.15502

 Excited State  7:   Singlet-A     5.1242 eV  241.96 nm  f=0.1278
    143 -> 145       0.47412
    143 -> 146      -0.10261
    144 -> 150      -0.42666
    144 -> 152      -0.10680

 Excited State  8:   Singlet-A     5.2065 eV  238.13 nm  f=0.0122
    143 -> 145       0.20469
    143 -> 146       0.65260
    143 -> 147      -0.12966

 Excited State  9:   Singlet-A     5.2365 eV  236.77 nm  f=0.0107
    144 -> 151      -0.22968
    144 -> 152       0.64006

 Excited State 10:   Singlet-A     5.2612 eV  235.66 nm  f=0.0022
    144 -> 151       0.65842
    144 -> 152       0.23518

 Excited State 11:   Singlet-A     5.2843 eV  234.63 nm  f=0.0006
    144 -> 153       0.68772

 Excited State 12:   Singlet-A     5.2963 eV  234.09 nm  f=0.0030
    144 -> 150      -0.22461
    144 -> 154       0.61553
    144 -> 155      -0.16150
    144 -> 162       0.14695

 Excited State 13:   Singlet-A     5.4441 eV  227.74 nm  f=0.0014
    143 -> 146       0.11489
    143 -> 147       0.64305
    143 -> 148       0.16391
    144 -> 155       0.13456

 Excited State 14:   Singlet-A     5.4518 eV  227.42 nm  f=0.0120
    143 -> 147      -0.17506
    144 -> 150       0.12499
    144 -> 154       0.25476
    144 -> 155       0.50578
    144 -> 162      -0.30734

 Excited State 15:   Singlet-A     5.5163 eV  224.76 nm  f=0.0007
    143 -> 147      -0.16534
    143 -> 148       0.61329
    143 -> 149       0.29013

 Excited State 16:   Singlet-A     5.5239 eV  224.45 nm  f=0.0035
    143 -> 148      -0.28354
    143 -> 149       0.63109
```

Table S8. Transition energy, Wavelengths, and Oscillator Strengths of the Electronic Transitions of **5d** Calculated at the TD-B3LYP/6-311++G(d,p) Level (The 127th orbital is Highest Occupied n(N) Orbital Shown in Figure S2)

```
Excited State   1:   Singlet-A     3.9962 eV  310.26 nm  f=0.0006
    127 ->128         0.69501

Excited State   2:   Singlet-A     5.0185 eV  247.06 nm  f=0.0172
    127 ->129         0.69206
    127 ->132         0.11390

Excited State   3:   Singlet-A     5.1135 eV  242.47 nm  f=0.1934
    126 ->128         0.66062

Excited State   4:   Singlet-A     5.2907 eV  234.34 nm  f=0.0163
    127 ->129        -0.12145
    127 ->132         0.68424

Excited State   5:   Singlet-A     5.3535 eV  231.60 nm  f=0.0034
    127 ->130         0.68885
    127 ->131         0.11754

Excited State   6:   Singlet-A     5.3572 eV  231.44 nm  f=0.0001
    127 ->130        -0.11667
    127 ->131         0.69111

Excited State   7:   Singlet-A     5.5542 eV  223.23 nm  f=0.0037
    126 ->129         0.68464
    126 ->132         0.14651

Excited State   8:   Singlet-A     5.6460 eV  219.60 nm  f=0.0019
    127 ->134         0.34339
    127 ->135         0.50669
    127 ->136         0.15194
    127 ->138        -0.16058
    127 ->143         0.14924
    127 ->144         0.14431

Excited State   9:   Singlet-A     5.7369 eV  216.12 nm  f=0.0046
    125 ->128         0.66911
    127 ->133        -0.16209

Excited State  10:   Singlet-A     5.7400 eV  216.00 nm  f=0.0036
    125 ->128         0.15712
    127 ->133         0.68345

Excited State  11:   Singlet-A     5.7630 eV  215.14 nm  f=0.0016
    127 ->134         0.60262
    127 ->135        -0.30277
    127 ->138         0.13530

Excited State  12:   Singlet-A     5.7805 eV  214.49 nm  f=0.0044
    126 ->132        -0.12187
    127 ->135        -0.17309
    127 ->136         0.65511

Excited State  13:   Singlet-A     5.8261 eV  212.81 nm  f=0.0155
    124 ->128         0.19601
    126 ->129        -0.14734
    126 ->131         0.10277
    126 ->132         0.62077
    127 ->136         0.12542

Excited State  14:   Singlet-A     5.8435 eV  212.17 nm  f=0.0001
    127 ->137         0.68654

Excited State  15:   Singlet-A     5.8592 eV  211.61 nm  f=0.0249
    124 ->128         0.63713
    126 ->132        -0.19268
    127 ->135        -0.12125

Excited State  16:   Singlet-A     5.8838 eV  210.72 nm  f=0.0003
    126 ->130         0.68608
    126 ->131         0.12389
```

Table S9. Atomic Coordinates of **7a** Optimized at the B3LYP/6-311G(d) Level



7a

	Coordinates (Angstroms)		
	X	Y	Z
Si	-0.042797934190	-0.350355884680	-0.125908068535
N	-0.773560398445	1.041755741205	0.173530026814
H	1.376354613948	-0.632532298817	-0.480002492439
H	-0.860438397611	-1.574043956360	-0.052286765851
H	-0.306651103701	1.940866508651	0.150384170008

(ENERGY = -346.040785302272 hartree)

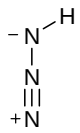
Table S10. Atomic Coordinates of **8a** Optimized at the B3LYP/6-311G(d) Level

8a

	Coordinates (Angstroms)		
	X	Y	Z
Si	-0.035785139916	-0.035785139899	-0.000000000000
H	1.491831862422	-0.056046722487	0.000000000000
H	-0.056046722507	1.491831862386	0.000000000000

(ENERGY = -290.636530345257 hartree)

Table S11. Atomic Coordinates of **9a** Optimized at the B3LYP/6-311G(d) Level



9a

	Coordinates (Angstroms)		
	X	Y	Z
H	-0.388004727514	-0.021300882647	0.875612889078
N	-0.171889079343	-0.303942649460	1.830779522341
N	0.346526377625	-1.427518502067	1.847882876144
N	0.826683429233	-2.435245965826	2.031912712438
ENERGY	=		

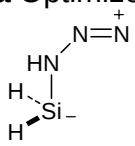
(ENERGY = -164.826629550428 hartree)

Table S12. Atomic Coordinates of N_2 (**10**) Optimized at the B3LYP/6-311G(d) Level

	Coordinates (Angstroms)		
	X	Y	Z
N	0.000000000000	0.000000000000	0.002251000000
N	0.000000000000	0.000000000000	1.107749000000

(ENERGY = -109.555929749 hartree)

Table S13. Atomic Coordinates of **11a** Optimized at the B3LYP/6-311G(d) Level

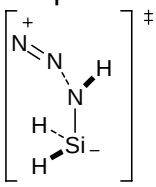


11a

	Coordinates (Angstroms)		
	X	Y	Z
N	0.522036032717	-0.075181802815	-0.141257147623
H	-0.009626208502	-0.331074507550	0.687210264871
N	2.698003392612	-0.986383748055	-0.309683700981
N	1.656784799889	-0.590153152642	-0.163682869322
Si	-0.226505869117	1.190675494656	-1.650160739611
H	-0.695089716058	2.119244350779	-0.530702882859
H	-1.510081530559	0.362889554918	-1.600689717304

(ENERGY = -455.491048419307 hartree)

Table S14. Atomic Coordinates of **12a** Optimized at the B3LYP/6-311G(d) Level

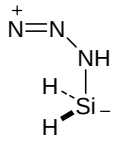


TS12a

	Coordinates (Angstroms)		
	X	Y	Z
N	0.474829206576	-0.192148674188	-0.241791975405
H	-0.154552079101	-0.665180844009	0.400319356809
N	2.739785382635	-0.880765821194	-0.231625852770
N	1.649344923497	-0.602242409964	-0.167363787614
Si	-0.272424802649	1.168446830791	-1.642072553926
H	0.701248529096	2.223731596817	-1.121016789724
H	-1.331420315320	1.482745009123	-0.586973533451

(ENERGY = -455.490310473375 hartree)

Table S15. Atomic Coordinates of **13a** Optimized at the B3LYP/6-311G(d) Level

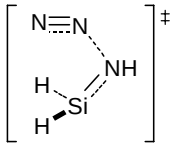


13a

	Coordinates (Angstroms)		
	X	Y	Z
N	0.433436238428	-0.504521478901	-0.817449663045
H	0.232824814931	-1.479467088655	-1.011610266526
N	2.373621432025	-0.034690288677	0.472109352084
N	1.475445113615	-0.343695763635	-0.130903358822
Si	-0.715866463480	1.049019754335	-1.467702214717
H	0.529185042309	1.787864291341	-1.945313955841
H	-0.685554507931	1.671338861785	-0.076364510249

(ENERGY = -455.494188338604 hartree)

Table S16. Atomic Coordinates of **TS14a** Optimized at the B3LYP/6-311G(d) Level

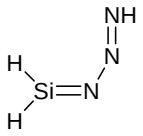


TS14a

	Coordinates (Angstroms)		
	X	Y	Z
N	0.363516043422	-0.447567246486	-0.893847672557
H	-0.087920589678	-1.347583873389	-0.797093707460
N	2.394150737857	0.055912328828	0.336585045890
N	1.432986343133	-0.436434676800	0.000829304575
Si	-0.630686571298	1.015961448234	-1.447493991828
H	0.461617427756	2.047314101238	-1.436225364874
H	-1.403129072169	1.435010287124	-0.216288636570

(ENERGY = -455.487665579201 hartree)

Table S17. Atomic Coordinates of **15a** Optimized at the B3LYP/6-311G(d) Level

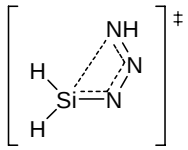


15a

	Coordinates (Angstroms)		
	X	Y	Z
N	0.410259493204	-0.844164643958	0.839219925981
H	0.745355055907	-1.019593841382	1.792702999402
N	1.279543300119	-0.115162673377	-1.051804513161
N	1.402762280825	-0.395746252280	0.218368271928
Si	0.533643037261	1.038167431862	-1.907392500047
H	-0.014329549808	2.287770932605	-1.333724839087
H	0.762510411237	1.028664250166	-3.358612670999

(ENERGY = -455.505307992230 hartree)

Table S18. Atomic Coordinates of **TS16a** Optimized at the B3LYP/6-311G(d) Level

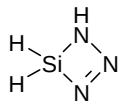


TS16a

	Coordinates (Angstroms)		
	X	Y	Z
N	0.230166335485	-0.434006306239	0.442336628459
H	0.148635854927	-0.521555650920	1.460274859806
N	1.678089926307	-0.169235927165	-1.148932852056
N	1.459915957346	-0.447247513130	0.109175066320
Si	0.432443559578	0.872784777603	-1.621610055376
H	0.131939446432	2.089549075229	-0.838562119833
H	0.204364092930	1.094653718586	-3.070604530708

(ENERGY = -455.499155638547 hartree)

Table S19. Atomic Coordinates of **17a** Optimized at the B3LYP/6-311G(d) Level

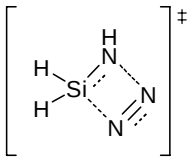


17a

	Coordinates (Angstroms)		
	X	Y	Z
N	0.139890530222	-0.158155213640	0.095781513615
H	-0.245595888497	-0.088454005681	1.027037753876
N	1.920256823010	-0.140849436174	-1.123763975166
N	1.493460022746	-0.541530444592	-0.001446008424
Si	0.366131302879	0.769190150300	-1.394683271175
H	0.507612880875	2.235514217856	-1.235818510511
H	-0.527230218934	0.467222175933	-2.539412759715

(ENERGY = -455.536384712226 hartree)

Table S20. Atomic Coordinates of **TS18a** Optimized at the B3LYP/6-311G(d) Level

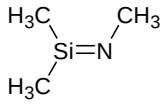


TS18a

	Coordinates (Angstroms)		
	X	Y	Z
N	-0.115327031817	-0.101361437772	0.067278185676
H	-0.665530115751	0.202264214083	0.863214374293
N	1.958857205006	-0.185843785457	-1.154967315519
N	1.766001436027	-0.529776796619	-0.056034951487
Si	0.335426964218	0.749288791694	-1.324022142429
H	0.862229591052	2.138875716955	-1.305530177289
H	-0.327251603826	0.528636457012	-2.637451740068

(ENERGY = -455.520667112055 hartree)

Table S21. Atomic Coordinates of **7b** Optimized at the B3LYP/6-31G(d) Level



7b

	Coordinates (Angstroms)		
	X	Y	Z
Si	-0.0212605373	-0.3692445563	-0.1467542177
N	-0.7258235765	1.0480015153	0.0725017821
C	1.8137953006	-0.7359065877	-0.4147548842
H	2.4039056381	0.1856389367	-0.4049746663
H	2.1978384433	-1.3994350151	0.3698042590
H	1.9750205710	-1.2382146862	-1.3765189319
C	-1.0908341142	-1.9095549397	-0.1504280513
H	-1.0125397723	-2.4458035244	-1.1037323184
H	-0.7881567759	-2.6057846617	0.6408554088
H	-2.1348101294	-1.6283346004	0.0095988219
C	-0.2875132874	2.4148938780	0.1410303899
H	-0.7971327634	3.0132514632	-0.6290174894
H	-0.5750386534	2.8549700419	1.1076639780
H	0.7969244368	2.5806444264	0.0174466193

(ENERGY = -463.968916443 hartree)

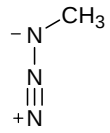
Table S22. Atomic Coordinates of **8b** Optimized at the B3LYP/6-31G(d) Level

8b

	Coordinates (Angstroms)		
	X	Y	Z
Si	0.4723781011	0.7041350426	1.7700330641
C	-1.4011276544	0.3204771072	1.5788554696
H	-1.9773460564	1.1696947157	1.1971673435
H	-1.6130314228	-0.5632738392	0.9617869911
H	-1.7903815180	0.0939647226	2.5866237916
C	1.0949247017	-1.1046430166	1.955723712
H	0.4405425953	-1.7391003293	2.5688592691
H	1.1003157804	-1.5511156136	0.9462391593
H	2.1183126431	-1.1700525694	2.3395008498

(ENERGY = -346.040785302272 hartree)

Table S23. Atomic Coordinates of **9b** Optimized at the B3LYP/6-31G(d) Level

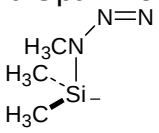


9b

	Coordinates (Angstroms)		
	X	Y	Z
C	-0.5061666341	0.1907039635	0.6467463797
H	0.3653432741	0.3132857966	-0.0084697805
H	-0.9395462694	1.1714291765	0.8442698583
H	-1.2529245026	-0.4311866567	0.1373642884
N	-0.1304081730	-0.3693233263	1.9574501299
N	0.3837141818	-1.4916277132	1.933315978
N	0.8677061232	-2.5204182403	2.0520921461

(ENERGY = -204.093314278 hartree)

Table S24. Atomic Coordinates of **11b** Optimized at the B3LYP/6-31G(d) Level

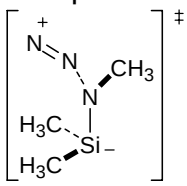


11b

	Coordinates (Angstroms)		
	X	Y	Z
Si	-1.058232158510	0.988717175541	-0.803210873774
N	-0.218379691534	-0.347656733979	0.721035518823
C	-2.699696601862	-0.043334681438	-0.908005996063
C	-1.620155757554	2.281013359485	0.532172564816
N	0.934174502814	-0.770967353922	0.503459613500
N	1.979754233423	-1.096636109108	0.205648273148
H	-2.553465207213	-1.007373544568	-1.410160891736
H	-3.222945782099	-0.221268174180	0.042526561251
H	-3.392742716541	0.532718291552	-1.540751646647
H	-0.772700952150	2.823914017660	0.968170972780
H	-2.228639215131	3.031570368265	0.004099028993
H	-2.245281273420	1.894104140747	1.349825234745
C	-0.834029925955	-0.806394859498	1.988817092302
H	-0.267859277726	-0.442138996090	2.851997186921
H	-1.835307782977	-0.379700535112	2.006536411054
H	-0.903119183567	-1.898431175349	2.018035939894

(ENERGY = -573.379412462817 hartree)

Table S25. Atomic Coordinates of **12b** Optimized at the B3LYP/6-31G(d) Level

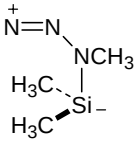


TS12b

	Coordinates (Angstroms)		
	X	Y	Z
N	0.400135965296	-0.336663277519	-0.333948827438
N	2.456708348529	-1.313630787137	-1.018323568715
N	1.478210163181	-0.891383794183	-0.621254404463
Si	-0.195257300504	1.340741046579	-1.660091524916
C	1.015203561973	2.583517910878	-0.788751923751
H	0.911749168402	2.651648106945	0.302429566355
H	2.066438573091	2.379445452106	-1.028114627030
H	0.799161188851	3.583259558406	-1.196388358031
C	-1.788422850572	1.726089970680	-0.621019059059
H	-2.192990761367	2.662146861580	-1.037292631218
H	-2.578291423606	0.975389449732	-0.750723434361
H	-1.637699075351	1.905459214557	0.452763648180
C	-0.312578277132	-0.896352635306	0.837058888481
H	0.214196771736	-0.651302627824	1.765171789633
H	-1.295556372127	-0.429731100636	0.846282710922
H	-0.423259500411	-1.981548788859	0.746310425405

(ENERGY = -573.378207488853 hartree)

Table S26. Atomic Coordinates of **13b** Optimized at the B3LYP/6-31G(d) Level

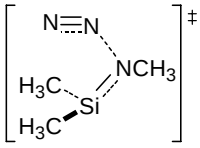


13b

	Coordinates (Angstroms)		
	X	Y	Z
Si	-0.284565918844	0.710114917585	-0.884405501241
N	0.472519728229	-0.538322341450	0.476165540491
C	-1.933693393074	-0.240999158839	-1.164110573279
C	-0.899884175245	2.066176695317	0.339888630225
C	1.864625498874	-1.006754995165	0.562729158957
N	-0.306664703724	-0.912678802541	1.412999223096
N	-1.237755226738	-1.068919598384	2.060260132595
H	-1.794556662066	-1.178896100670	-1.714271755704
H	-2.467452560683	-0.465312386970	-0.224650144164
H	-2.606097651247	0.387583874341	-1.764259142072
H	-0.076367396431	2.628093020091	0.795903878053
H	-1.512965815066	2.790210823241	-0.214711109963
H	-1.536081717329	1.665365541996	1.145416536242
H	1.914506916160	-2.100593696999	0.557076931326
H	2.352696225757	-0.611465052693	-0.329161358750
H	2.360950691405	-0.616053138859	1.457431924178

(ENERGY = -573.387950981540 hartree)

Table S27. Atomic Coordinates of **TS14b** Optimized at the B3LYP/6-31G(d) Level

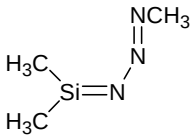


TS14b

	Coordinates (Angstroms)		
	X	Y	Z
Si	-1.201948728688	0.746994395062	-0.700637141444
N	-0.240435177406	-0.763898706853	-0.049208313298
C	-2.101897128900	1.368831322883	0.879366329752
C	0.258520394557	1.957177696077	-0.845558614496
C	-0.706003063015	-2.156761272811	-0.100626589446
N	0.730683117507	-0.566042323030	0.832161323385
N	1.507649099088	0.126354150168	1.326301202792
H	-2.596087952881	2.326559124104	0.669236284218
H	-2.876976013367	0.672632411180	1.219462938267
H	-1.400677953866	1.540305651022	1.710120789573
H	0.917507805460	1.729375606234	-1.690468497605
H	-0.095395768057	2.989199058091	-0.965062150125
H	0.873861771393	1.925985901795	0.078047428258
H	0.142927743426	-2.844138371437	-0.168123890576
H	-1.318591126587	-2.415432627632	0.770927268435
H	-1.314106168662	-2.237147494853	-1.002644017691

(ENERGY = -573.387684062413 hartree)

Table S28. Atomic Coordinates of **15b** Optimized at the B3LYP/6-31G(d) Level

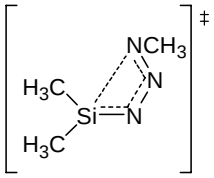


15b

	Coordinates (Angstroms)		
	X	Y	Z
Si	-0.204479675114	0.780811220403	-1.160446013600
N	-0.297996695665	-0.832794939928	1.562158114912
C	-0.208680653255	0.801374099531	-3.031084543563
C	-0.722064033825	2.368361468829	-0.300094955502
C	0.028471187629	-1.123740183644	2.959358145101
N	0.738303412795	-0.686566935631	0.864802951344
N	0.559515491351	-0.464010914960	-0.440687239188
H	-1.222082655180	0.948670325154	-3.421848137427
H	0.416261795519	1.613705388364	-3.420593347431
H	0.176547686773	-0.150102146130	-3.407418450394
H	-0.119157315158	3.218300154485	-0.641383211056
H	-1.773292025006	2.599085494749	-0.508918559400
H	-0.605542531575	2.258156428074	0.781511446891
H	-0.389949289523	-2.102692250490	3.223840300732
H	1.108694360281	-1.121516683141	3.147196260684
H	-0.463400960054	-0.377630685654	3.595543257891

(ENERGY = -573.417542207362 hartree)

Table S29. Atomic Coordinates of **TS16b** Optimized at the B3LYP/6-31G(d) Level

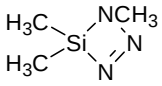


TS16b

	Coordinates (Angstroms)		
	X	Y	Z
Si	-0.467892025587	0.605672320485	-0.967893284647
N	-0.647178174805	-0.304023987465	1.352019804356
C	-1.093606576503	0.541328869385	-2.736750671671
C	-0.390408357571	2.359329562123	-0.297536908247
C	-0.709146906147	-0.244582491515	2.810791753064
N	0.474950136940	-0.689906722118	0.881632166950
N	0.547456535830	-0.633327242749	-0.441636971997
H	-2.188037049327	0.621972169906	-2.756981938502
H	-0.695034567446	1.361501396229	-3.345836437672
H	-0.818737858857	-0.413906958201	-3.193741802524
H	0.106981680254	3.021239981263	-1.017012970232
H	-1.399525369417	2.752956312120	-0.125726335816
H	0.151436861836	2.388450903104	0.650936925092
H	-1.567899478674	-0.827748757114	3.163683339530
H	0.210967139913	-0.627837037885	3.264155428580
H	-0.862512559509	0.795211804059	3.128199969775

(ENERGY = -573.412516910944 hartree)

Table S30. Atomic Coordinates of **17b** Optimized at the B3LYP/6-31G(d) Level

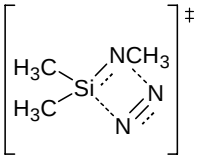


17b

	Coordinates (Angstroms)		
	X	Y	Z
Si	-0.403444058881	0.643914838652	-0.637415473726
N	-0.623900965951	-0.239253899375	0.898673606580
C	-1.593713134200	0.203362102362	-2.017431150858
C	-0.140486524827	2.492944073804	-0.460416492420
C	-1.242049272504	-0.285756167911	2.202726107111
N	0.662488581512	-0.760631125126	0.722037846696
N	1.093121170208	-0.367312402805	-0.416005096953
H	-2.583134496684	0.644226985420	-1.841763263275
H	-1.231336902240	0.577335412679	-2.982479044365
H	-1.710786045261	-0.882202146822	-2.092825388088
H	0.258042456398	2.921876980291	-1.387616669578
H	-1.082250956949	3.008819029943	-0.235161841758
H	0.570221819464	2.705356708008	0.344463782196
H	-2.319466486634	-0.462661344181	2.107898765721
H	-0.802159616155	-1.120538878201	2.757924737542
H	-1.090978667301	0.633993913277	2.787678955171

(ENERGY = -573.450276320618 hartree)

Table S31. Atomic Coordinates of **TS18b** Optimized at the B3LYP/6-31G(d) Level



TS18b

	Coordinates (Angstroms)		
	X	Y	Z
Si	-0.403352423416	0.604604841955	-0.536294234195
N	-0.844401969910	-0.153460332994	0.898998331613
C	-1.334139291562	0.291587805048	-2.141144658011
C	0.362607129313	2.325999551435	-0.583515403170
C	-1.790996410971	0.118031433115	1.946695547906
N	1.127741960151	-0.703262223114	0.706139099976
N	1.239254010678	-0.438333119881	-0.418580235391
H	-2.292337127271	0.829633461895	-2.119201358565
H	-0.779807511971	0.642615297686	-3.019269186378
H	-1.559036126626	-0.772320300553	-2.265522959915
H	0.932869765764	2.498473810963	-1.503834979121
H	-0.437443811438	3.077489692211	-0.543779223007
H	1.020884383990	2.496561698833	0.274189580026
H	-2.831370498380	0.092482380565	1.575946782227
H	-1.726909852022	-0.666166759558	2.714299431441
H	-1.654618116332	1.085766052403	2.458919694568

(ENERGY = -573.427154612577 hartree)

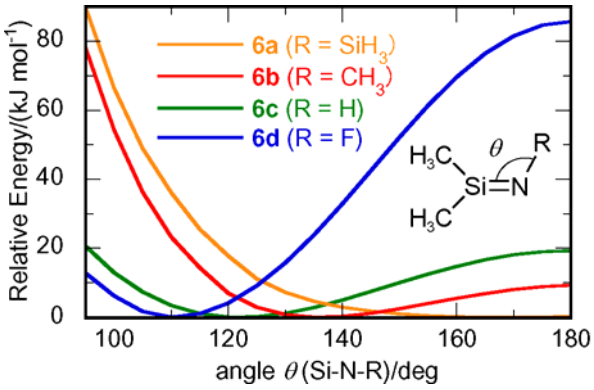


Figure S1. Relative energy of *N*-substituted dimethylsilanimines **6a**-**6d** as a function of Si-N-R bent angle calculated at the B3LYP/6-311+G(d,p) level.

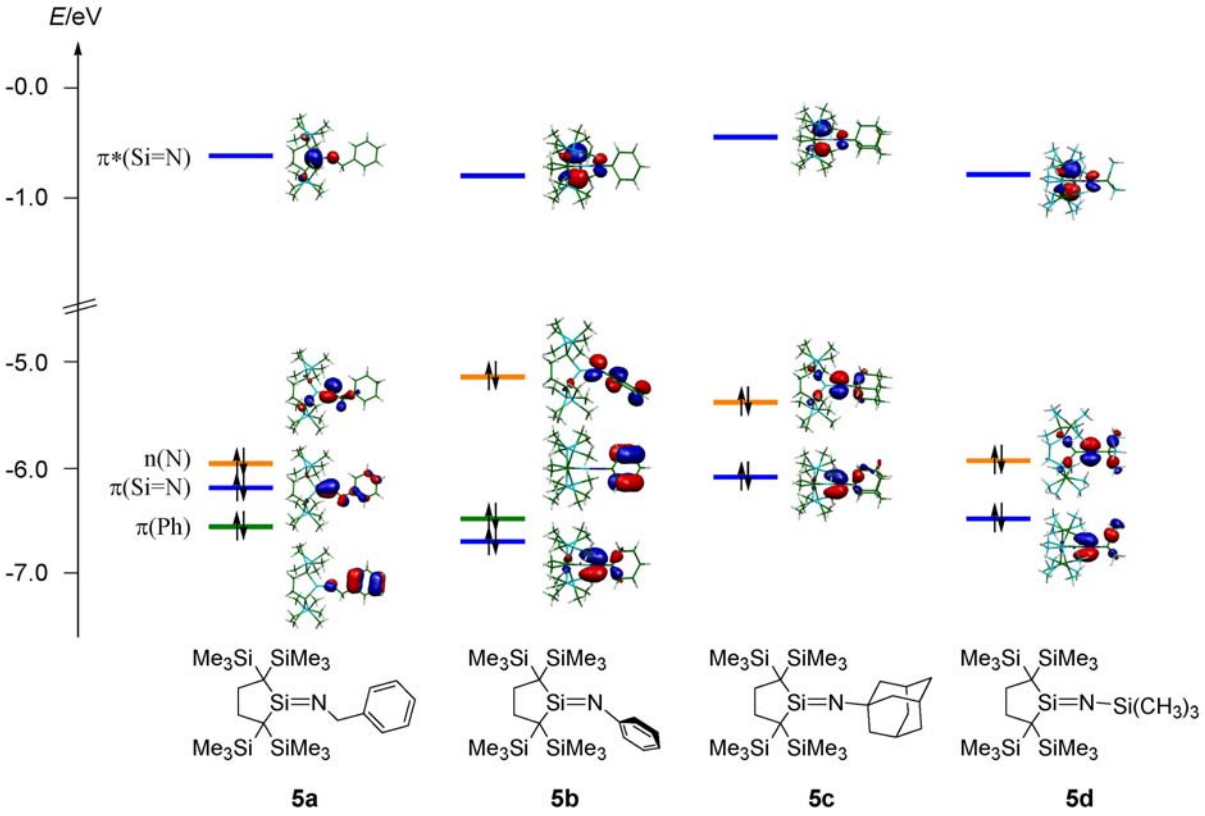
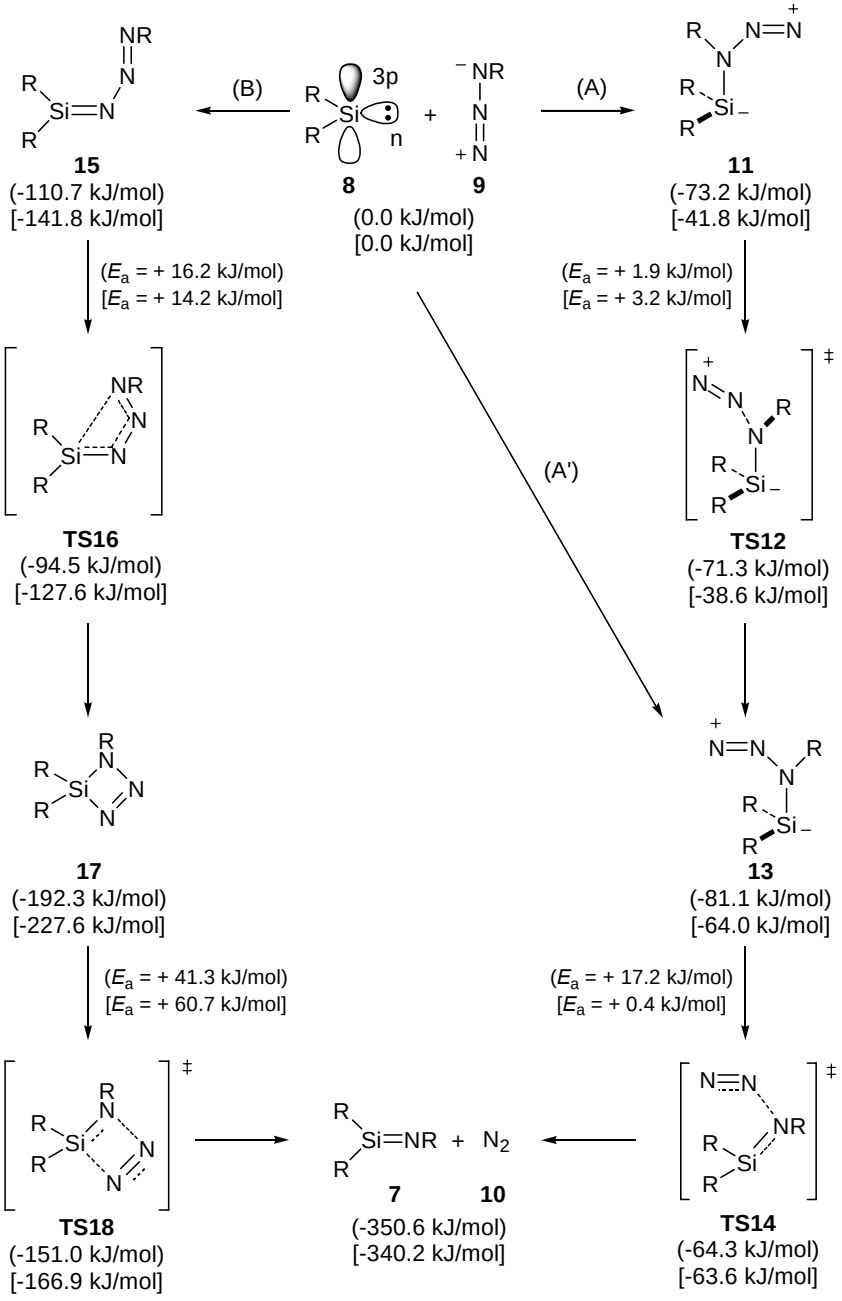


Figure S2. Frontier Kohn-Sham orbitals (B3LYP/6-311+G(d,p) level) of silanimines **5a**-**5d** whose structural parameters were fixed to the experimental values determined by X-ray analysis.



a, R = H; **b**, R = CH_3

Scheme S1. Possible reaction routes from silylene **8** and azide **9** to the corresponding silanimine **7** and nitrogen molecule (**10**) (**a**: R = H; **b**: R = CH_3). The values of relative energies in kJ mol^{-1} for R = H calculated at the B3LYP/6-311G(d) level are shown in parentheses and for R = CH_3 calculated at the B3LYP/6-31G(d) level in brackets, respectively.

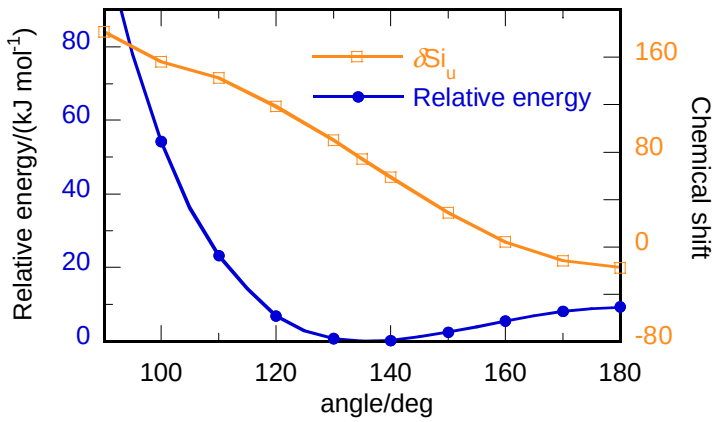


Figure S3. Plots of isotropic chemical shift of the unsaturated silicon atom (δSi_u relative to tetramethylsilane) of (*N*-methyl)dimethylsilanimine **6b** (orange line) and relative energy (blue line) as a function of Si-N-R bent angle calculated at the GIAO/B3LYP/6-311+G(2df,p)//B3LYP/6-311+G(d,p) level.

2. References

S1 Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

S2 (a) K. Ohno and S. Maeda, *Chem. Phys. Lett.*, 2004, **384**, 277. (b) S. Maeda and K. Ohno, *J. Phys. Chem. A*, 2005, **109**, 5742. (c) K. Ohno and S. Maeda, *J. Phys. Chem. A*, 2006, **110**, 8933. (d) S. Maeda and K. Ohno, *J. Phys. Chem. A* 2007, **111**, 4527.