# Supplementary Materials: Facile Access to Stable Silylium Ions Stabilized by *N*-Heterocyclic Imines

**Tatsumi Ochiai, Tibor Szilvási and Shigeyoshi Inoue**

## S1. Crystallographic Data for 7, 8, 9[OTf]

General Considerations: Data for the single crystal structure determinations of **7**, **8** and **9**[OTf] were collected on an Agilent SuperNova diffractometer, equipped with a CCDC area Atlas detector and a mirror monochromator utilizing Cu$K_\alpha$ radiation ($\lambda$ = 1.54184 Å). The crystal structures were solved by Direct Methods and refined on $F^2$ using full-matrix least squares with SHELXL-97 [1]. The positions of the H atoms at the carbon atoms were calculated by standard methods. CCDC deposition numbers: 1491068 for **7**, and 1491070 for **8**, 1491069 for **9**[OTf].

**Table S1.** Crystal data and structure refinement for **7**.

| | | |
|---|---|---|
| Empirical formula | $C_{29}H_{42}ClN_3Si$ | |
| Formula weight | 496.2 | |
| Temperature | 150(2) K | |
| Wavelength | 1.54184 Å | |
| Crystal system | Triclinic | |
| Space group | *P*-1 | |
| Unit cell dimensions | a = 9.5590(2) Å | $\alpha$ = 88.352(2)° |
| | b = 12.4732(4) Å | $\beta$ = 83.833(2)° |
| | c = 25.2203(7) Å | $\gamma$ = 78.766(2)° |
| Volume | 2932.27(14) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.124 Mg/m$^3$ | |
| Absorption coefficient | 1.687 mm$^{-1}$ | |
| F(000) | 1072 | |
| Crystal size | 0.402 × 0.096 × 0.038 mm$^3$ | |
| Theta range for data collection | 3.53 to 67.50° | |
| Index ranges | −11<=h<=9, −14<=k<=14, −30<=l<=29 | |
| Reflections collected | 20006 | |
| Independent reflections | 10553 [R(int) = 0.0262] | |
| Completeness to theta = 67.50° | 99.90% | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 1.00000 and 0.32135 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data/restraints/parameters | 10553/6/632 | |
| Goodness-of-fit on $F^2$ | 1.052 | |
| Final R indices [I > 2sigma(I)] | R1 = 0.0518, wR2 = 0.1454 | |
| R indices (all data) | R1 = 0.0607, wR2 = 0.1551 | |
| Largest diff. peak and hole | 1.008 and −0.761 e.Å$^{-3}$ | |

**Table S2.** Crystal data and structure refinement for **8**.

| | |
|---|---|
| Empirical formula | $C_{30}H_{42}F_3N_3O_3SSi$ |
| Formula weight | 609.82 |
| Temperature | 149.99(10) K |
| Wavelength | 1.54180 Å |
| Crystal system | Monoclinic |

**Table S2.** *Cont.*

| | | |
|---|---|---|
| Space group | $P2_1/c$ | |
| Unit cell dimensions | a = 10.93550(10) Å | $\alpha$ = 90° |
| | b = 17.13290(10) Å | $\beta$ = 99.0410(10)° |
| | c = 18.01170(10) Å | $\gamma$ = 90° |
| Volume | 3332.69(4) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.215 Mg/m$^3$ | |
| Absorption coefficient | 1.631 mm$^{-1}$ | |
| F(000) | 1296 | |
| Crystal size | 0.62 × 0.36 × 0.23 mm$^3$ | |
| Theta range for data collection | 3.58 to 67.50° | |
| Index ranges | −12<=h<=13, −20<=k<=20, −21<=l<=18 | |
| Reflections collected | 12722 | |
| Independent reflections | 5950 [R(int) = 0.0159] | |
| Completeness to theta = 67.50° | 99.10% | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 1.00000 and 0.4312 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data/restraints/parameters | 5951/0/380 | |
| Goodness-of-fit on F$^2$ | 1.031 | |
| Final R indices [I > 2sigma(I)] | R1 = 0.0539, wR2 = 0.1376 | |
| R indices (all data) | R1 = 0.0565, wR2 = 0.1396 | |
| Largest diff. peak and hole | 1.137 and −0.467 e.Å$^{-3}$ | |

**Table S3.** Crystal data and structure refinement for **9**[OTf].

| | | |
|---|---|---|
| Empirical formula | $C_{37}H_{52}F_3N_5O_3SSi$ | |
| Formula weight | 731.99 | |
| Temperature | 150.01(16) K | |
| Wavelength | 1.54184 Å | |
| Crystal system | Monoclinic | |
| Space group | $P2_1/c$ | |
| Unit cell dimensions | a = 10.3153(2) Å | $\alpha$ = 90° |
| | b = 17.1502(3) Å | $\beta$ = 100.2030(10)° |
| | c = 22.8540(3) Å | $\gamma$ = 90° |
| Volume | 3979.15(12) Å$^3$ | |
| Z | 4 | |
| Calculated density | 1.222 Mg/m$^3$ | |
| Absorption coefficient | 1.465 mm$^{-1}$ | |
| F(000) | 1560 | |
| Crystal size | 0.27 × 0.11 × 0.10 mm$^3$ | |
| Theta range for data collection | 3.24 to 67.49° | |
| Limiting indices | −11<=h<=12, −20<=k<=18, −19<=l<=27 | |
| Reflections collected/unique | 15496/7162 [R(int) = 0.0283] | |
| Completeness to theta = 67.49 | 99.90% | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 1.00000 and 0.40955 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data/restraints/parameters | 7162/0/463 | |
| Goodness-of-fit on F$^2$ | 1.023 | |
| Final R indices [I > 2sigma(I)] | R1 = 0.0479, wR2 = 0.1264 | |
| R indices (all data) | R1 = 0.0622, wR2 = 0.1393 | |
| Largest diff. peak and hole | 0.553 and −0.408 e.Å$^{-3}$ | |

*S1.1. Molecular Structure of* **7** *in the Solid State*

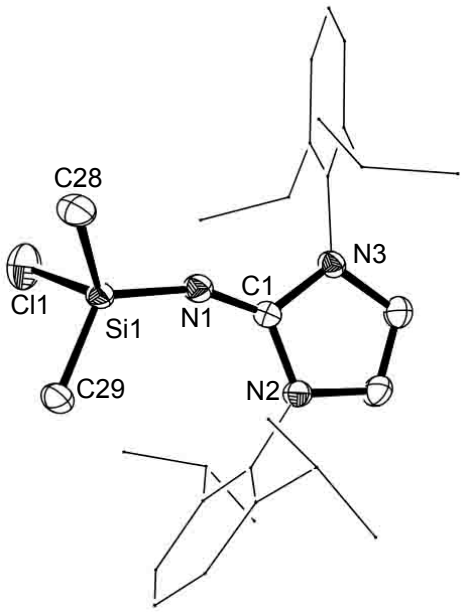



**Figure S1.** ORTEP representation of the molecular structure of one of the two independent molecules of **7** in the solid state. Thermal ellipsoids are at the 40% probability level. Hydrogen atoms are omitted for clarity. Dip groups are depicted as stick models. Selected bond lengths (Å) and bond angles (°); values for the not depicted molecules are given in square brackets: Si1–Cl1, 2.0975(9), [2.0766(9)]; Si1–N1, 1.6425(18), [1.6413(18)]; Si1–C29, 1.858(2), [1.857(3)]; Si1–C28, 1.861(2), [1.886(2)]; N1–C1, 1.273(3), [1.268(3)]; C1–N2, 1.383(3), [1.387(3)]; C1–N3, 1.387(3), [1.385(3)].

## S2. Details to the DFT Calculations

DFT calculations for electronic structure analysis were performed at the B3LYP/6-31G* level of theory while energy differences were calculated at B97-D/6-31G* level [2–7]. GIAO NMR chemical shifts were calculated at B3LYP/6-311G** level. Stationary points on the potential energy surface (PES) were characterized by harmonic vibrational frequency calculations. We calculated the electronic structure analysis at B97-D/6-31G* level as well and found generally negligible difference compared to B3LYP/6-31G* supporting that our results are independent from the chosen method. All calculations were carried out using GAUSSIAN 09 program [8,9].

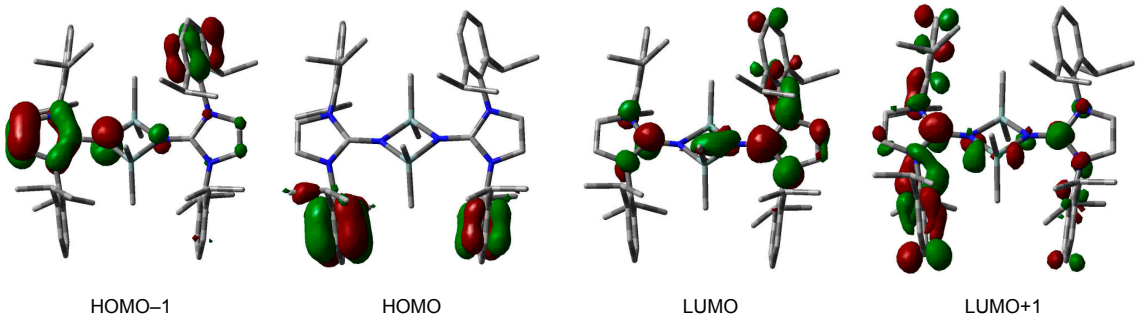



**Figure S2.** Kohn-Sham depictions of molecular orbitals (HOMO–1, HOMO, LUMO, LUMO+1) of **2**.

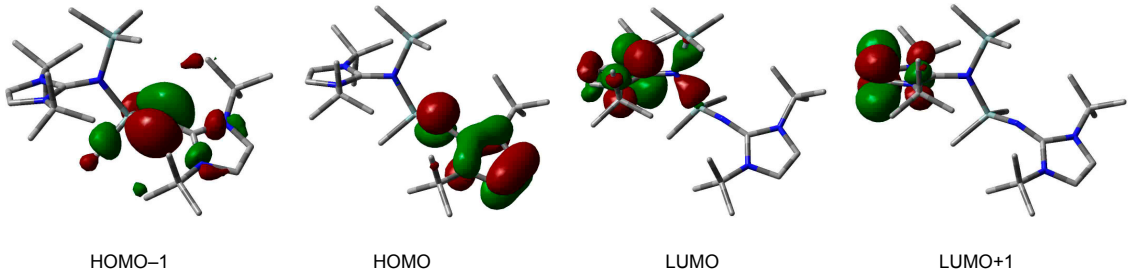



**Figure S3.** Kohn-Sham depictions of molecular orbitals (HOMO–1, HOMO, LUMO, LUMO+1) of **4**.

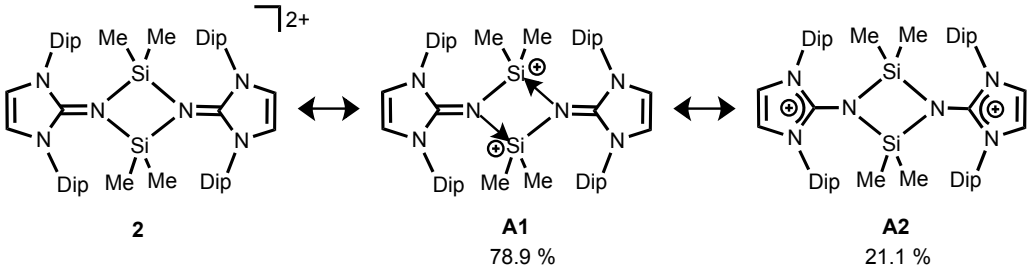



**Figure S4.** NRT-analysis of **2**.

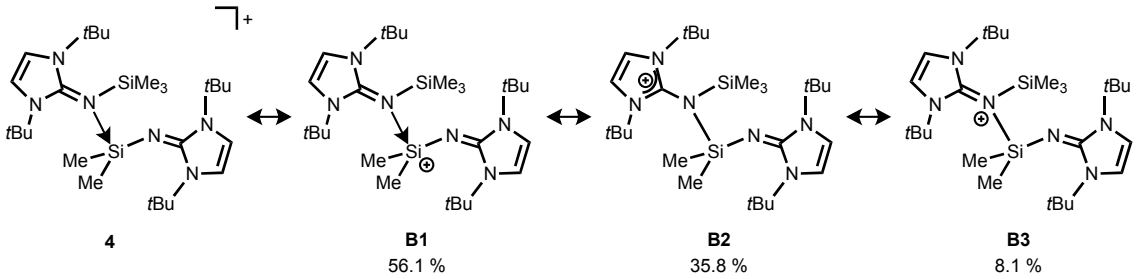



**Figure S5.** NRT-analysis of **4**.

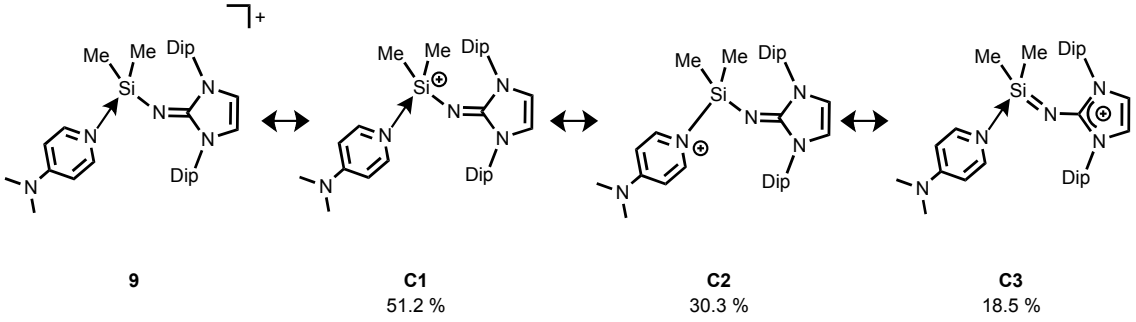
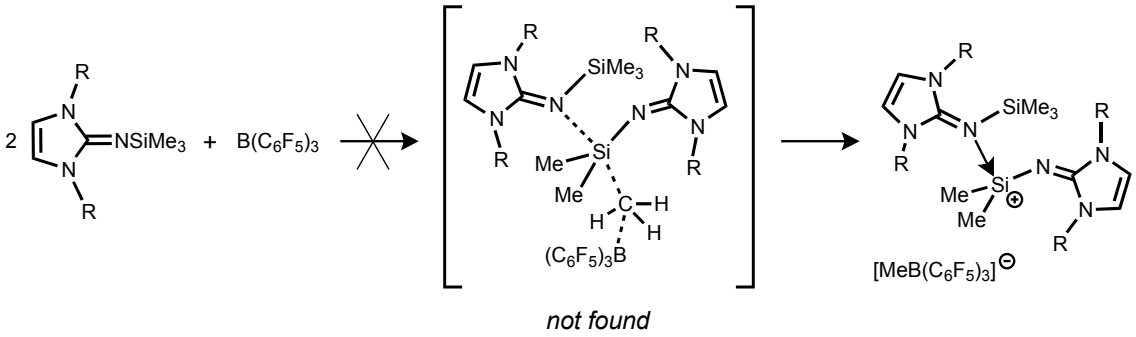



**Figure S6.** NRT-analysis of **9**.




**Scheme S1.** Reaction pathway involving a methyl abstraction supported by a precursor molecule.

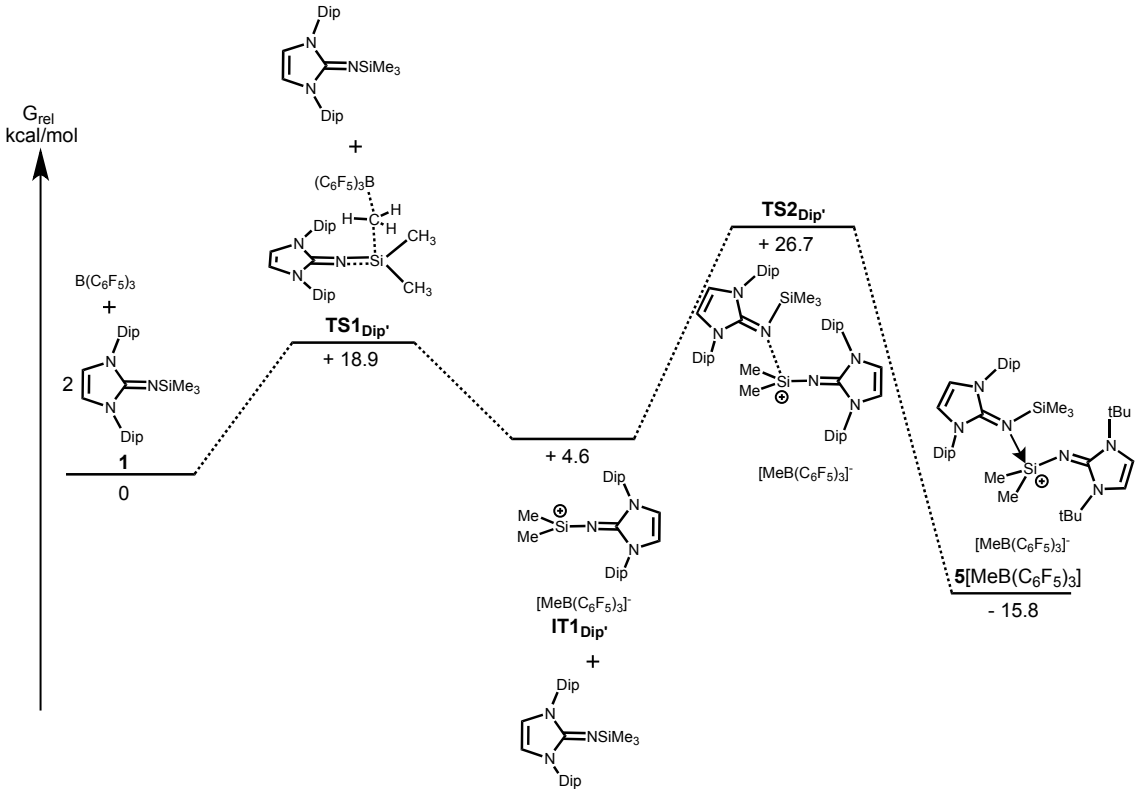



**Figure S7.** Reaction profile for the formation of the hypothetical silylium ion **5**[MeB($C_6F_5$)$_3$] (Dip = 2,6-diisopropylphenyl).

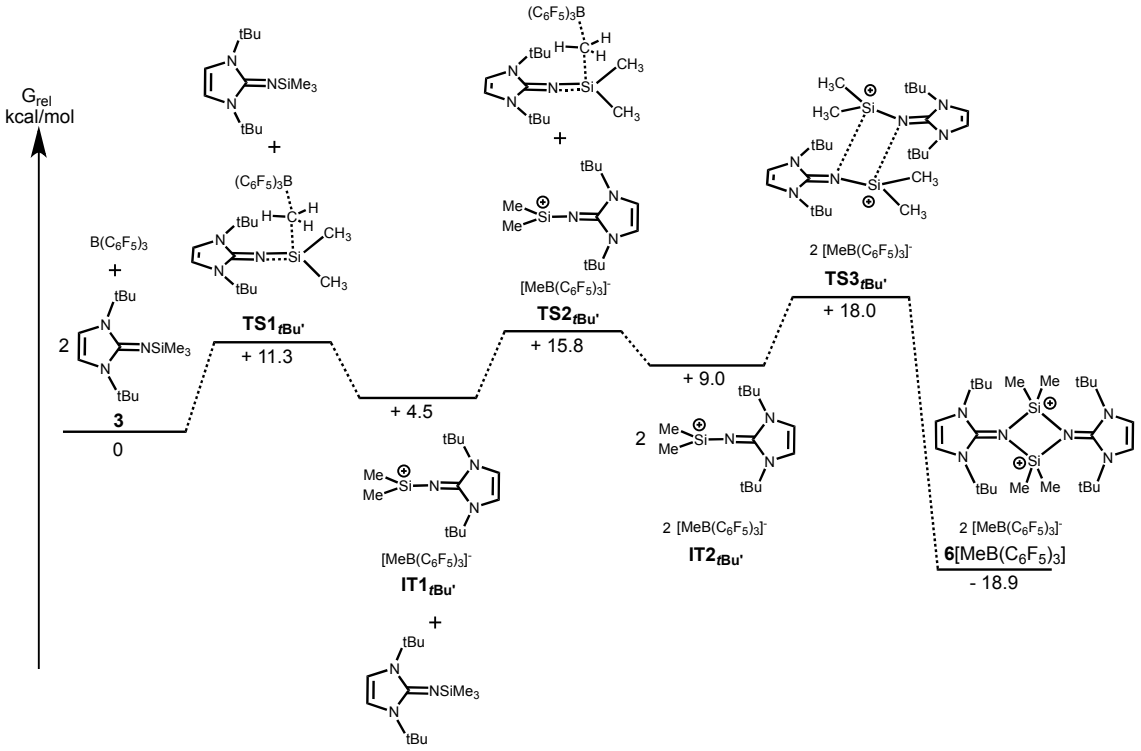



**Figure S8.** Potential energy profile for the formation of the hypothetical silylium ion **6**[MeB($C_6F_5$)$_3$]$_2$.

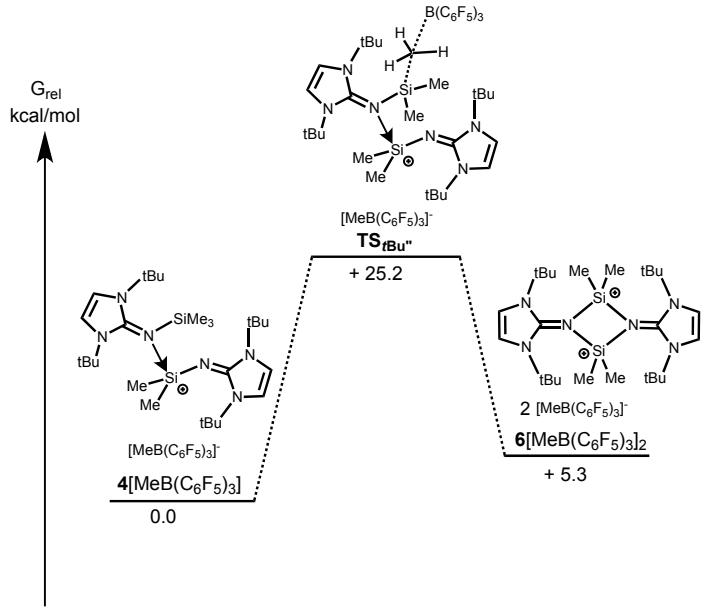



**Figure S9.** Potential energy profile for the formation of the hypothetical silylium ion **6**[MeB($C_6F_5$)$_3$]$_2$.

**Table S4.** Cartesian geometry of B($C_6F_5$)$_3$ in Angstrom [Å].

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| C | 2.34909 | −0.893652 | −0.717067 |
| C | 1.146691 | −1.077347 | −0.001193 |
| C | 1.04054 | −2.288618 | 0.715519 |
| C | 2.053799 | −3.253661 | 0.736068 |
| C | 3.227397 | −3.027831 | −0.000249 |
| C | 3.37774 | −1.842197 | −0.736519 |
| B | −0.000925 | −0.000292 | −0.000801 |
| C | −1.507107 | −0.455628 | −0.000361 |
| C | −2.503242 | 0.244135 | 0.714023 |
| C | −3.84602 | −0.149202 | 0.733626 |
| C | −4.237589 | −1.279743 | −0.000603 |
| C | −3.285817 | −2.004974 | −0.734589 |
| C | −1.949499 | −1.589948 | −0.714318 |
| F | −2.17636 | 1.328123 | 1.449191 |
| F | −4.758922 | 0.535965 | 1.441827 |
| F | −5.519081 | −1.66678 | −0.000109 |
| F | −3.667011 | −3.081034 | −1.442531 |
| F | −1.077058 | −2.31306 | −1.448069 |
| F | −0.060475 | −2.547354 | 1.452577 |
| F | 1.919396 | −4.385499 | 1.446972 |
| F | 4.20376 | −3.94371 | −0.000104 |
| F | 4.499361 | −1.634398 | −1.445827 |
| F | 2.536768 | 0.22201 | −1.453657 |
| C | 0.358413 | 1.531755 | 0.000089 |
| C | 1.463303 | 2.04392 | 0.713791 |
| C | 1.794293 | 3.403426 | 0.734132 |
| C | 1.010837 | 4.308261 | 0.000875 |
| C | −0.093351 | 3.847371 | −0.733138 |

**Table S4.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| C | −0.402358 | 2.482664 | −0.713646 |
| F | 2.239536 | 1.218632 | 1.447642 |
| F | −1.464452 | 2.089404 | −1.448309 |
| F | −0.83437 | 4.716291 | −1.440401 |
| F | 1.316923 | 5.611417 | 0.001409 |
| F | 2.844418 | 3.851003 | 1.442206 |

**Table S5.** Cartesian geometry of **1** in Angstrom [Å].

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| C | 2.778565 | −1.256836 | −0.50686 |
| C | 2.315422 | 0.047797 | −0.803515 |
| C | 3.168377 | 1.177172 | −0.82163 |
| C | 4.532483 | 0.967657 | −0.551562 |
| C | 5.020186 | −0.314469 | −0.271022 |
| C | 4.151603 | −1.412877 | −0.244322 |
| N | 0.935521 | 0.232175 | −1.13235 |
| C | −0.137591 | 0.177802 | −0.218634 |
| N | −1.268924 | 0.335306 | −1.044993 |
| C | −0.893731 | 0.465715 | −2.384001 |
| C | 0.462093 | 0.413012 | −2.439879 |
| C | −2.608563 | 0.100603 | −0.593924 |
| C | −3.427215 | 1.207056 | −0.271203 |
| C | −4.733618 | 0.942481 | 0.175913 |
| C | −5.199392 | −0.37401 | 0.300398 |
| C | −4.3666 | −1.45062 | −0.024876 |
| C | −3.054247 | −1.235117 | −0.48341 |
| N | −0.162479 | 0.017046 | 1.045137 |
| Si | 0.616553 | −0.084767 | 2.565702 |
| C | 0.409004 | −1.852449 | 3.259051 |
| C | −2.873105 | 2.628485 | −0.346083 |
| C | −2.159887 | 2.974454 | 0.983822 |
| C | −2.147377 | −2.41903 | −0.808304 |
| C | −1.753901 | −3.159044 | 0.489447 |
| C | 2.598612 | 2.574353 | −1.079245 |
| C | 3.6443 | 3.592322 | −1.575793 |
| C | 1.812916 | −2.443251 | −0.482735 |
| C | 2.317901 | −3.632927 | 0.357704 |
| C | −3.938382 | 3.690612 | −0.687206 |
| C | −2.79366 | −3.383699 | −1.826288 |
| C | 1.892797 | 3.111246 | 0.190268 |
| C | 1.480579 | −2.918392 | −1.917663 |
| C | 2.475498 | 0.344474 | 2.63424 |
| H | −1.63797 | 0.580268 | −3.163232 |
| H | 1.148982 | 0.484198 | −3.274728 |
| H | −5.392248 | 1.772705 | 0.433316 |
| H | −6.216479 | −0.559133 | 0.653682 |
| H | −4.733458 | −2.473859 | 0.077851 |
| H | −2.113237 | 2.651727 | −1.142967 |

**Table S5.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| H | −4.494948 | 3.428161 | −1.601385 |
| H | −3.449976 | 4.666135 | −0.840782 |
| H | −4.662846 | 3.810895 | 0.134825 |
| H | −2.891847 | 2.997588 | 1.808616 |
| H | −1.68262 | 3.966761 | 0.914449 |
| H | −1.398045 | 2.220268 | 1.224918 |
| H | −1.222164 | −2.03813 | −1.261501 |
| H | −3.708447 | −3.84222 | −1.416749 |
| H | −2.089077 | −4.195714 | −2.070403 |
| H | −3.060017 | −2.859488 | −2.758137 |
| H | −1.264171 | −2.464003 | 1.184092 |
| H | −1.060242 | −3.986106 | 0.261534 |
| H | −2.645072 | −3.583501 | 0.981501 |
| H | 5.220869 | 1.812968 | −0.557585 |
| H | 6.082989 | −0.457778 | −0.063796 |
| H | 4.546228 | −2.401572 | −0.009628 |
| H | 1.829615 | 2.487595 | −1.862604 |
| H | 1.407768 | 4.077498 | −0.027407 |
| H | 2.629921 | 3.267931 | 0.994684 |
| H | 1.13119 | 2.408755 | 0.554981 |
| H | 4.377231 | 3.829746 | −0.787307 |
| H | 3.140044 | 4.531279 | −1.853241 |
| H | 4.192207 | 3.215188 | −2.454175 |
| H | 0.879705 | −2.097833 | −0.016589 |
| H | 1.044141 | −2.10897 | −2.520391 |
| H | 0.75534 | −3.748186 | −1.879228 |
| H | 2.392766 | −3.279047 | −2.421737 |
| H | 3.176618 | −4.13219 | −0.121549 |
| H | 1.511703 | −4.37654 | 0.455787 |
| H | 2.621185 | −3.314013 | 1.36671 |
| H | 2.827328 | 0.277253 | 3.68023 |
| H | 3.093056 | −0.333305 | 2.025653 |
| H | 2.672455 | 1.36971 | 2.284326 |
| H | 0.844324 | −2.615227 | 2.593251 |
| H | −0.654913 | −2.104793 | 3.402419 |
| H | 0.909654 | −1.938367 | 4.239904 |
| C | −0.277111 | 1.113648 | 3.753208 |
| H | 0.10779 | 1.012766 | 4.783691 |
| H | −0.140011 | 2.165084 | 3.447225 |
| H | −1.361643 | 0.913541 | 3.771714 |

**Table S6.** Cartesian geometry of transition state (+18.9 kcal/mol) in Figure 3 in Angstrom [Å].

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| C | 4.352194 | −2.955952 | −0.732771 |
| C | 3.333584 | −2.625185 | 0.19029 |
| C | 2.366677 | −3.554531 | 0.635925 |
| C | 2.457015 | −4.868286 | 0.141942 |
| C | 3.45072 | −5.226261 | −0.778112 |
| C | 4.382555 | −4.276703 | −1.216214 |
| N | 3.297161 | −1.278814 | 0.69451 |

**Table S6.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| C | 2.865441 | −0.194838 | −0.053386 |
| N | 3.271545 | 0.92173 | 0.659097 |
| C | 3.932838 | 0.525874 | 1.820804 |
| C | 3.954829 | −0.835157 | 1.842429 |
| N | 2.28607 | −0.174115 | −1.217698 |
| Si | 1.280743 | −0.896456 | −2.293771 |
| C | 1.109124 | 0.066112 | −3.902007 |
| C | 3.03876 | 2.284553 | 0.245641 |
| C | 3.708671 | 2.756584 | −0.912117 |
| C | 3.431092 | 4.07051 | −1.324719 |
| C | 2.542504 | 4.883214 | −0.609168 |
| C | 1.933339 | 4.403901 | 0.55217 |
| C | 2.165018 | 3.093075 | 1.00916 |
| C | 4.756556 | 1.903617 | −1.632358 |
| C | 6.078883 | 1.896608 | −0.827039 |
| C | 1.535232 | 2.631269 | 2.321199 |
| C | 0.026341 | 2.94398 | 2.409424 |
| C | 1.268233 | −3.145977 | 1.610673 |
| C | 1.637339 | −3.553584 | 3.056583 |
| C | 5.397498 | −1.946319 | −1.203451 |
| C | 5.251212 | −1.655749 | −2.713766 |
| C | −1.196802 | −0.76399 | −1.492141 |
| B | −2.333705 | −0.075352 | −0.440723 |
| C | −2.037544 | −0.569955 | 1.128766 |
| C | −0.775271 | −0.360657 | 1.697053 |
| C | −0.422138 | −0.681634 | 3.011096 |
| C | −1.372082 | −1.279746 | 3.841947 |
| C | −2.665744 | −1.485706 | 3.347391 |
| C | −2.97464 | −1.112297 | 2.02739 |
| F | 0.225334 | 0.194628 | 0.944708 |
| F | 0.841491 | −0.482369 | 3.467327 |
| F | −1.037455 | −1.661204 | 5.091152 |
| F | −3.60347 | −2.025934 | 4.150414 |
| F | −4.262878 | −1.295315 | 1.667479 |
| C | −2.249305 | 1.57981 | −0.375884 |
| C | −3.095663 | 2.270045 | 0.510954 |
| C | −3.043522 | 3.651258 | 0.735036 |
| C | −2.106492 | 4.419873 | 0.031669 |
| C | −1.264993 | 3.793281 | −0.890985 |
| C | −1.349646 | 2.403076 | −1.06543 |
| F | −4.039007 | 1.582951 | 1.202005 |
| F | −0.481135 | 1.88825 | −1.984631 |
| F | −0.378524 | 4.529097 | −1.595739 |
| F | −2.007948 | 5.74685 | 0.25034 |
| F | −3.8699 | 4.247955 | 1.6182 |
| C | −3.742802 | −0.666573 | −1.072875 |
| C | −4.696089 | 0.087993 | −1.775371 |
| C | −5.837254 | −0.469087 | −2.377808 |
| C | −6.054514 | −1.84922 | −2.30313 |
| C | −5.124549 | −2.651495 | −1.627924 |
| C | −4.004526 | −2.048189 | −1.045617 |

**Table S6.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| F | −4.55567 | 1.429659 | −1.926453 |
| F | −6.720142 | 0.310629 | −3.036208 |
| F | −7.139255 | −2.402397 | −2.879023 |
| F | −5.317094 | −3.985781 | −1.554069 |
| F | −3.138821 | −2.890805 | −0.409957 |
| C | 1.120912 | −2.759256 | −2.50057 |
| C | 5.023213 | 2.334086 | −3.087962 |
| C | 2.27879 | 3.28154 | 3.513158 |
| C | −0.119581 | −3.706101 | 1.232762 |
| C | 6.827686 | −2.427937 | −0.870408 |
| H | 4.29639 | 1.259072 | 2.528729 |
| H | 4.366541 | −1.536575 | 2.557094 |
| H | 0.864477 | −3.2657 | −1.561572 |
| H | 0.353448 | −2.994397 | −3.255382 |
| H | 2.087741 | −3.171316 | −2.83714 |
| H | 0.139752 | 0.579189 | −3.969144 |
| H | 1.896624 | 0.834267 | −3.943061 |
| H | 1.20849 | −0.605712 | −4.770649 |
| H | −1.418155 | −0.474808 | −2.527603 |
| H | −1.206676 | −1.854813 | −1.390873 |
| H | −0.211717 | −0.345392 | −1.1628 |
| H | 3.913645 | 4.466378 | −2.217915 |
| H | 2.324846 | 5.893363 | −0.960246 |
| H | 1.247515 | 5.044628 | 1.107224 |
| H | 1.727307 | −5.609872 | 0.469074 |
| H | 3.496087 | −6.24878 | −1.158836 |
| H | 5.15362 | −4.560568 | −1.934995 |
| H | 1.64551 | 1.546486 | 2.40607 |
| H | −0.380357 | 2.519582 | 3.340938 |
| H | −0.161791 | 4.02888 | 2.42671 |
| H | −0.517837 | 2.511703 | 1.56248 |
| H | 1.867005 | 2.907418 | 4.4646 |
| H | 3.359576 | 3.063895 | 3.490657 |
| H | 2.158419 | 4.376899 | 3.489066 |
| H | 4.389239 | 0.872776 | −1.68189 |
| H | 5.683685 | 1.596499 | −3.57048 |
| H | 4.086442 | 2.395693 | −3.664267 |
| H | 5.525641 | 3.313876 | −3.137877 |
| H | 6.823214 | 1.252199 | −1.324677 |
| H | 6.493218 | 2.915691 | −0.758987 |
| H | 5.923252 | 1.517008 | 0.194503 |
| H | 1.206825 | −2.053611 | 1.585986 |
| H | 0.864455 | −3.20368 | 3.7574 |
| H | 1.717591 | −4.649929 | 3.139049 |
| H | 2.599721 | −3.112503 | 3.360006 |
| H | −0.87531 | −3.308111 | 1.924306 |
| H | −0.417164 | −3.415896 | 0.214944 |
| H | −0.14275 | −4.805403 | 1.301925 |
| H | 5.244556 | −0.997845 | −0.671546 |
| H | 6.014386 | −0.928013 | −3.033471 |
| H | 5.381726 | −2.575286 | −3.307079 |
| H | 4.259862 | −1.230266 | −2.930307 |
| H | 7.560865 | −1.664538 | −1.177048 |
| H | 6.941072 | −2.608456 | 0.210139 |
| H | 7.06538 | −3.363668 | −1.401399 |

**Table S7.** Cartesian geometry of intermediate (+4.6 kcal/mol) in Figure 3 in Angstrom [Å].

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| N | −0.115138 | −0.18523 | 1.053082 |
| N | 0.913488 | 0.04003 | −1.13394 |
| N | −1.272836 | 0.174323 | −1.001533 |
| C | −0.139604 | 0.025039 | −0.246152 |
| C | −0.931432 | 0.277516 | −2.346146 |
| C | 0.427001 | 0.173725 | −2.433363 |
| C | −2.610459 | 0.206661 | −0.456725 |
| C | −3.095617 | 1.431936 | 0.044977 |
| C | −4.39122 | 1.429329 | 0.593096 |
| C | −5.153643 | 0.256165 | 0.631584 |
| C | −4.636748 | −0.943891 | 0.123946 |
| C | −3.347427 | −0.999262 | −0.433419 |
| C | −2.264685 | 2.712969 | 0.035284 |
| C | −3.004915 | 3.871564 | −0.670278 |
| C | −1.871731 | 3.110543 | 1.477501 |
| C | −2.750203 | −2.318114 | −0.923804 |
| C | −3.773978 | −3.216645 | −1.650195 |
| C | −2.106648 | −3.075476 | 0.264833 |
| C | 2.288301 | −0.10358 | −0.735115 |
| C | 3.108019 | 1.051413 | −0.73741 |
| C | 4.437053 | 0.88923 | −0.306261 |
| C | 4.91278 | −0.360452 | 0.119079 |
| C | 4.072858 | −1.480015 | 0.109499 |
| C | 2.7371 | −1.38041 | −0.325577 |
| C | 2.551038 | 2.418431 | −1.143444 |
| C | 1.757847 | 3.048416 | 0.029314 |
| C | 3.62726 | 3.40304 | −1.643178 |
| C | 1.859832 | −2.628868 | −0.411701 |
| C | 2.290765 | −3.486443 | −1.626617 |
| C | 1.892525 | −3.470161 | 0.882169 |
| H | −1.692951 | 0.412968 | −3.10434 |
| H | 1.097233 | 0.182746 | −3.284123 |
| H | −4.802366 | 2.358413 | 0.990484 |
| H | −6.158038 | 0.275224 | 1.058468 |
| H | −5.241647 | −1.849929 | 0.161093 |
| H | −1.334406 | 2.529059 | −0.523453 |
| H | −3.273499 | 3.601495 | −1.70339 |
| H | −2.362228 | 4.765765 | −0.696606 |
| H | −3.929623 | 4.13552 | −0.134066 |
| H | −2.768767 | 3.332032 | 2.076919 |
| H | −1.234328 | 4.00915 | 1.465158 |
| H | −1.32411 | 2.291261 | 1.970092 |
| H | −1.948664 | −2.091595 | −1.644442 |
| H | −4.544138 | −3.590591 | −0.957704 |
| H | −3.258545 | −4.092138 | −2.07454 |
| H | −4.276699 | −2.675398 | −2.466486 |
| H | −1.353084 | −2.45086 | 0.767729 |
| H | −1.627254 | −4.002343 | −0.091147 |
| H | −2.878931 | −3.347869 | 1.00241 |
| H | 5.108711 | 1.746948 | −0.301525 |
| H | 5.947396 | −0.460403 | 0.451894 |
| H | 4.459974 | −2.450217 | 0.422906 |
| H | 1.840171 | 2.265047 | −1.970068 |
| H | 1.296614 | 3.994819 | −0.294206 |

**Table S7.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| H | 2.436002 | 3.267542 | 0.869573 |
| H | 0.960446 | 2.38219 | 0.390054 |
| H | 4.295981 | 3.715617 | −0.825369 |
| H | 3.139164 | 4.307821 | −2.035181 |
| H | 4.239633 | 2.9605 | −2.443617 |
| H | 0.816377 | −2.327287 | −0.575071 |
| H | 2.22194 | −2.909178 | −2.561825 |
| H | 1.641351 | −4.371918 | −1.712741 |
| H | 3.331121 | −3.828809 | −1.510374 |
| H | 2.898339 | −3.870008 | 1.08227 |
| H | 1.201304 | −4.32132 | 0.788458 |
| H | 1.579321 | −2.879147 | 1.760414 |
| Si | 0.785859 | −0.195086 | 2.401434 |
| C | 2.34113 | 0.793694 | 2.743029 |
| H | 2.755577 | 0.519806 | 3.726396 |
| H | 3.101169 | 0.62524 | 1.964484 |
| H | 2.110318 | 1.871452 | 2.749409 |
| C | 0.100569 | −1.191258 | 3.830026 |
| H | −0.796374 | −1.746037 | 3.519762 |
| H | −0.162783 | −0.526689 | 4.671705 |
| H | 0.85506 | −1.902103 | 4.207558 |

**Table S8.** Cartesian geometry of $[MeB(C_6F_5)_3]^-$ in Angstrom [Å].

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| C | −0.085722 | 2.169722 | 0.648489 |
| C | −0.55931 | 1.37916 | −0.413168 |
| C | −1.792109 | 1.813886 | −0.935125 |
| C | −2.472881 | 2.963955 | −0.507644 |
| C | −1.93008 | 3.736503 | 0.524443 |
| C | −0.726926 | 3.331193 | 1.110011 |
| B | 0.130953 | −0.040907 | −0.996766 |
| C | 0.260887 | −0.0072 | −2.649816 |
| F | −2.42865 | 1.094081 | −1.899717 |
| F | −3.653954 | 3.329334 | −1.066283 |
| F | −2.56533 | 4.852141 | 0.956464 |
| F | −0.204491 | 4.059693 | 2.127782 |
| F | 1.045234 | 1.841627 | 1.323388 |
| C | −0.90643 | −1.204383 | −0.39225 |
| C | −1.035707 | −1.36691 | 0.998178 |
| C | −1.935764 | −2.245505 | 1.612308 |
| C | −2.780836 | −3.022674 | 0.809889 |
| C | −2.696823 | −2.903752 | −0.580206 |
| C | −1.771863 | −2.008693 | −1.147717 |
| F | −0.238337 | −0.650691 | 1.834528 |
| F | −1.762569 | −1.97797 | −2.50592 |
| F | −3.510703 | −3.656574 | −1.362895 |
| F | −3.664489 | −3.87981 | 1.375008 |
| F | −2.003613 | −2.359794 | 2.961922 |
| C | 1.70902 | −0.267619 | −0.497571 |
| C | 2.254165 | −1.473811 | −0.030599 |
| C | 3.618443 | −1.662904 | 0.251659 |
| C | 4.517064 | −0.611783 | 0.050676 |
| C | 4.033036 | 0.608637 | −0.435558 |
| C | 2.665135 | 0.743663 | −0.703498 |
| F | 1.473902 | −2.572649 | 0.163467 |

**Table S8.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| F | 4.07849 | −2.8554 | 0.707034 |
| F | 5.83652 | −0.77264 | 0.313158 |
| F | 4.896286 | 1.634331 | −0.643621 |
| F | 2.281351 | 1.956317 | −1.189055 |
| H | 0.679588 | −0.958106 | −3.024926 |
| H | 0.957138 | 0.795331 | −2.947827 |
| H | −0.688098 | 0.160422 | −3.175773 |

**Table S9.** Cartesian geometry of transition state (+21.1 kcal/mol) in Figure 3 in Angstrom [Å].

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| C | 2.734114 | −3.530242 | 0.239799 |
| C | 3.036251 | −2.523765 | −0.702911 |
| C | 3.113383 | −2.746967 | −2.098919 |
| C | 2.879733 | −4.061703 | −2.542732 |
| C | 2.595863 | −5.089419 | −1.633623 |
| C | 2.511537 | −4.824989 | −0.261346 |
| N | 3.426732 | −1.217123 | −0.218716 |
| C | 2.624506 | −0.137891 | 0.019882 |
| N | 3.449998 | 0.884845 | 0.407251 |
| C | 4.76608 | 0.420911 | 0.451111 |
| C | 4.749723 | −0.881171 | 0.062085 |
| N | 1.27843 | −0.066048 | −0.064994 |
| Si | −0.033708 | −0.788033 | −1.08582 |
| C | 0.038243 | 0.035833 | −2.758806 |
| C | 3.082266 | 2.276468 | 0.580343 |
| C | 3.210295 | 2.855819 | 1.863095 |
| C | 2.891767 | 4.222349 | 1.984998 |
| C | 2.463935 | 4.964054 | 0.881513 |
| C | 2.370964 | 4.364691 | −0.383259 |
| C | 2.703535 | 3.013012 | −0.575 |
| C | 3.724399 | 2.092697 | 3.083892 |
| C | 2.874583 | 2.33837 | 4.352248 |
| C | 2.744664 | 2.402958 | −1.981388 |
| C | 4.211809 | 2.232196 | −2.455788 |
| C | 3.46096 | −1.630537 | −3.083005 |
| C | 2.726293 | −1.789857 | −4.435773 |
| C | 2.686955 | −3.251566 | 1.740817 |
| C | 4.025156 | −3.663889 | 2.40072 |
| C | −0.16982 | −2.642817 | −1.143679 |
| C | 5.194443 | 2.492398 | 3.368166 |
| C | 1.971878 | 3.209451 | −3.044769 |
| C | 4.987646 | −1.560373 | −3.334133 |
| C | 1.501667 | −3.950945 | 2.442189 |
| Si | 0.154592 | 0.523968 | 1.206844 |
| C | −0.082697 | 2.321237 | 1.567166 |
| C | 0.530309 | −0.433626 | 2.771257 |
| N | −1.155656 | −0.068354 | 0.099098 |
| C | −2.494649 | 0.134691 | 0.273145 |
| N | −3.199671 | 1.28735 | 0.00889 |

**Table S9.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| C | −4.504086 | 1.131771 | 0.466599 |
| C | −4.614687 | −0.121073 | 0.988206 |
| N | −3.377416 | −0.735341 | 0.859748 |
| C | −2.777988 | 2.437707 | −0.779851 |
| C | −2.657662 | 2.272041 | −2.188811 |
| C | −2.21565 | 3.391138 | −2.917843 |
| C | −1.946131 | 4.614957 | −2.290177 |
| C | −2.179938 | 4.767644 | −0.92203 |
| C | −2.634733 | 3.691836 | −0.135162 |
| C | −3.167621 | −2.165167 | 1.034444 |
| C | −2.755117 | −2.662128 | 2.291148 |
| C | −2.604676 | −4.058199 | 2.399064 |
| C | −2.870751 | −4.904113 | 1.314767 |
| C | −3.328172 | −4.378416 | 0.101626 |
| C | −3.506439 | −2.993402 | −0.066222 |
| C | −3.104768 | 0.997491 | −2.92365 |
| C | −2.705665 | 0.953947 | −4.417675 |
| C | −3.096918 | 3.968189 | 1.298605 |
| C | −4.521724 | 4.586263 | 1.252454 |
| C | −2.570556 | −1.751123 | 3.505067 |
| C | −1.648733 | −2.351244 | 4.587923 |
| C | −4.168404 | −2.443572 | −1.333138 |
| C | −5.708165 | −2.554223 | −1.180713 |
| C | −4.648077 | 0.83237 | −2.875552 |
| C | −2.181147 | 4.931579 | 2.091937 |
| C | −3.942272 | −1.427346 | 4.15362 |
| C | −3.749825 | −3.137985 | −2.648674 |
| H | −5.233815 | 1.919354 | 0.345399 |
| H | −5.4591 | −0.64875 | 1.410746 |
| H | 5.539259 | −1.612019 | −0.054335 |
| H | 5.577684 | 1.078223 | 0.731683 |
| H | 0.599745 | 2.661076 | 2.359638 |
| H | 0.029077 | 2.967726 | 0.686802 |
| H | −1.110108 | 2.436101 | 1.944327 |
| H | 0.346538 | −1.508075 | 2.650688 |
| H | 1.601792 | −0.293978 | 3.00247 |
| H | −0.03287 | −0.071659 | 3.642432 |
| H | −0.659449 | −0.419339 | −3.46783 |
| H | −0.188626 | 1.109692 | −2.698462 |
| H | 1.045233 | −0.074727 | −3.183881 |
| H | 0.20131 | −3.084095 | −0.209097 |
| H | −1.215963 | −2.950598 | −1.25395 |
| H | 0.420375 | −3.06646 | −1.969089 |
| H | −2.103748 | 3.317387 | −3.997911 |
| H | −1.6005 | 5.463047 | −2.88355 |
| H | −2.039124 | 5.742491 | −0.456198 |
| H | −2.291708 | −4.492327 | 3.347147 |
| H | −2.746688 | −5.982438 | 1.426681 |

**Table S9.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| H | −3.567485 | −5.051816 | −0.721163 |
| H | 2.98978 | 4.708978 | 2.955467 |
| H | 2.221339 | 6.021574 | 0.998995 |
| H | 2.070547 | 4.970068 | −1.237054 |
| H | 2.932327 | −4.287081 | −3.607402 |
| H | 2.435099 | −6.10461 | −2.000107 |
| H | 2.285838 | −5.636705 | 0.429946 |
| H | −2.65314 | 0.125732 | −2.420231 |
| H | −2.927988 | −0.045545 | −4.81906 |
| H | −3.30026 | 1.680654 | −4.991708 |
| H | −1.644655 | 1.175633 | −4.595356 |
| H | −4.928334 | −0.116438 | −3.358676 |
| H | −5.055981 | 0.824582 | −1.858898 |
| H | −5.12567 | 1.653157 | −3.43183 |
| H | −3.15989 | 3.015739 | 1.849668 |
| H | −2.517908 | 4.968309 | 3.138918 |
| H | −1.125863 | 4.627299 | 2.072112 |
| H | −2.253915 | 5.95437 | 1.692001 |
| H | −4.910208 | 4.713078 | 2.274677 |
| H | −4.481552 | 5.575995 | 0.77225 |
| H | −5.23467 | 3.975574 | 0.679354 |
| H | −3.919754 | −1.376464 | −1.431648 |
| H | −4.285766 | −2.663092 | −3.484635 |
| H | −2.670874 | −3.073686 | −2.855659 |
| H | −4.031743 | −4.201546 | −2.646708 |
| H | −6.206874 | −2.1028 | −2.052299 |
| H | −6.00522 | −3.612379 | −1.119148 |
| H | −6.06685 | −2.046491 | −0.27369 |
| H | −2.133962 | −0.802932 | 3.151857 |
| H | −3.793686 | −0.805694 | 5.050398 |
| H | −4.608508 | −0.883906 | 3.47024 |
| H | −4.443692 | −2.358399 | 4.459601 |
| H | −1.391518 | −1.576957 | 5.326022 |
| H | −2.165421 | −3.158952 | 5.128879 |
| H | −0.719892 | −2.764715 | 4.170425 |
| H | 3.154191 | −0.672221 | −2.631965 |
| H | 5.216147 | −0.737241 | −4.028995 |
| H | 5.549799 | −1.39078 | −2.405021 |
| H | 5.339181 | −2.501827 | −3.78374 |
| H | 2.828899 | −0.864443 | −5.023275 |
| H | 3.17523 | −2.601253 | −5.028343 |
| H | 1.653408 | −2.011078 | −4.305491 |
| H | 2.56116 | −2.169007 | 1.890295 |
| H | 1.460552 | −3.631385 | 3.495178 |
| H | 0.538153 | −3.711903 | 1.965049 |
| H | 1.619851 | −5.044964 | 2.435431 |
| H | 3.9982 | −3.449588 | 3.480721 |
| H | 4.202586 | −4.742072 | 2.265702 |
| H | 4.873501 | −3.117953 | 1.958834 |

**Table S9.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| H | 2.285173 | 1.406269 | −1.936788 |
| H | 4.224866 | 1.776879 | −3.459167 |
| H | 4.702934 | 3.215279 | −2.519953 |
| H | 4.80276 | 1.593833 | −1.785712 |
| H | 1.88977 | 2.608826 | −3.963065 |
| H | 0.959026 | 3.475951 | −2.711818 |
| H | 2.506539 | 4.136899 | −3.30274 |
| H | 3.697045 | 1.011565 | 2.871424 |
| H | 5.575152 | 1.938764 | 4.240289 |
| H | 5.855898 | 2.291096 | 2.511717 |
| H | 5.254287 | 3.569218 | 3.589234 |
| H | 3.225175 | 1.679731 | 5.161351 |
| H | 2.97197 | 3.376102 | 4.704407 |
| H | 1.810994 | 2.135836 | 4.174378 |

**Table S10.** Cartesian geometry of **2** in Angstrom [Å].

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| N | 1.226643 | −0.092927 | −0.101329 |
| N | 3.358153 | −1.257043 | −0.445762 |
| N | 3.474008 | 0.869552 | 0.045041 |
| C | 2.587928 | −0.159361 | −0.158561 |
| C | 4.777536 | 0.41539 | −0.144621 |
| C | 4.705469 | −0.906732 | −0.438365 |
| C | 3.230811 | 2.216818 | 0.514491 |
| C | 2.86205 | 2.397535 | 1.869944 |
| C | 2.698736 | 3.723989 | 2.306469 |
| C | 2.936881 | 4.806466 | 1.446303 |
| C | 3.35113 | 4.586899 | 0.12913 |
| C | 3.506942 | 3.280774 | −0.373095 |
| C | 2.751635 | 1.215381 | 2.836543 |
| C | 4.162134 | 0.753699 | 3.285395 |
| C | 1.892325 | 1.507194 | 4.082188 |
| C | 3.962078 | 3.071249 | −1.818806 |
| C | 5.439148 | 3.506435 | −1.980027 |
| C | 3.07319 | 3.828459 | −2.83357 |
| C | 2.975271 | −2.637266 | −0.64726 |
| C | 3.132603 | −3.516274 | 0.448062 |
| C | 2.915415 | −4.884201 | 0.199934 |
| C | 2.547289 | −5.334258 | −1.074424 |
| C | 2.383951 | −4.427528 | −2.130746 |
| C | 2.607296 | −3.052172 | −1.94477 |
| C | 3.490545 | −3.024031 | 1.850368 |
| C | 2.603988 | −3.677095 | 2.936942 |
| C | 4.984429 | −3.277574 | 2.165293 |
| C | 2.511593 | −2.056624 | −3.098277 |
| C | 3.887269 | −1.910143 | −3.795081 |
| C | 1.427964 | −2.427869 | −4.131911 |

**Table S10.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| N | −1.223137 | 0.047666 | −0.064947 |
| N | −3.284937 | 1.351643 | 0.197317 |
| N | −3.442627 | −0.812076 | 0.499749 |
| C | −2.554524 | 0.191415 | 0.18309 |
| C | −4.711437 | −0.266631 | 0.711066 |
| C | −4.613853 | 1.069406 | 0.5228 |
| C | −3.320144 | −2.238001 | 0.273084 |
| C | −3.359776 | −2.68975 | −1.066391 |
| C | −3.313641 | −4.079005 | −1.276355 |
| C | −3.279647 | −4.972017 | −0.199195 |
| C | −3.29995 | −4.490476 | 1.116117 |
| C | −3.32501 | −3.109857 | 1.387957 |
| C | −3.491306 | −1.754661 | −2.26597 |
| C | −4.818307 | −2.008383 | −3.018389 |
| C | −2.280313 | −1.895727 | −3.211531 |
| C | −3.396422 | −2.616653 | 2.831663 |
| C | −4.849225 | −2.708913 | 3.364198 |
| C | −2.457772 | −3.407719 | 3.775524 |
| C | −2.897639 | 2.725103 | −0.044569 |
| C | −3.056503 | 3.236447 | −1.35515 |
| C | −2.848082 | 4.617441 | −1.525731 |
| C | −2.506466 | 5.435488 | −0.440065 |
| C | −2.345727 | 4.889392 | 0.838935 |
| C | −2.540745 | 3.51642 | 1.069648 |
| C | −3.425943 | 2.339282 | −2.53853 |
| C | −2.829058 | 2.836697 | −3.875253 |
| C | −4.961301 | 2.198338 | −2.69101 |
| C | −2.390692 | 2.920321 | 2.468467 |
| C | −3.71668 | 3.045751 | 3.259929 |
| C | −1.24421 | 3.567685 | 3.276685 |
| H | 5.615412 | 1.091902 | −0.03922 |
| H | 5.466332 | −1.648387 | −0.642477 |
| H | 2.409892 | 3.917576 | 3.338793 |
| H | 2.81753 | 5.826349 | 1.815452 |
| H | 3.554356 | 5.435082 | −0.525365 |
| H | 2.278011 | 0.378606 | 2.303643 |
| H | 4.791821 | 0.456823 | 2.434835 |
| H | 4.072147 | −0.109181 | 3.964877 |
| H | 4.671995 | 1.564993 | 3.827346 |
| H | 2.38722 | 2.233017 | 4.745542 |
| H | 1.753973 | 0.578519 | 4.655508 |
| H | 0.903319 | 1.906307 | 3.814772 |
| H | 3.897261 | 1.999706 | −2.064106 |
| H | 5.548052 | 4.581622 | −1.770293 |
| H | 5.778108 | 3.320166 | −3.01062 |
| H | 6.102721 | 2.961261 | −1.290522 |
| H | 2.021895 | 3.504666 | −2.778809 |
| H | 3.439915 | 3.641321 | −3.854428 |
| H | 3.104696 | 4.914562 | −2.660188 |

**Table S10.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| H | 3.028527 | −5.599193 | 1.015119 |
| H | 2.385976 | −6.39962 | −1.246401 |
| H | 2.094757 | −4.794968 | −3.114938 |
| H | 3.321304 | −1.935081 | 1.892583 |
| H | 2.778337 | −3.181881 | 3.904841 |
| H | 2.850619 | −4.742028 | 3.062828 |
| H | 1.532976 | −3.605836 | 2.689991 |
| H | 5.204565 | −4.355614 | 2.12461 |
| H | 5.224841 | −2.913535 | 3.176289 |
| H | 5.642783 | −2.765113 | 1.448199 |
| H | 2.244484 | −1.07514 | −2.675914 |
| H | 4.664039 | −1.574992 | −3.091011 |
| H | 3.820263 | −1.175316 | −4.61285 |
| H | 4.202324 | −2.87477 | −4.222061 |
| H | 1.713735 | −3.32112 | −4.707978 |
| H | 1.303043 | −1.602097 | −4.848818 |
| H | 0.457383 | −2.626637 | −3.652215 |
| H | −5.551344 | −0.907444 | 0.942837 |
| H | −5.341139 | 1.867973 | 0.58401 |
| H | −3.331977 | −4.460029 | −2.298078 |
| H | −3.256666 | −6.047248 | −0.383418 |
| H | −3.299543 | −5.195184 | 1.94732 |
| H | −3.517101 | −0.713363 | −1.916405 |
| H | −5.683947 | −1.870638 | −2.352587 |
| H | −4.909833 | −1.306211 | −3.861975 |
| H | −4.853454 | −3.032464 | −3.420324 |
| H | −2.235302 | −2.905986 | −3.647079 |
| H | −2.352897 | −1.171945 | −4.038307 |
| H | −1.344653 | −1.713192 | −2.665104 |
| H | −3.099703 | −1.555161 | 2.851419 |
| H | −5.19593 | −3.753619 | 3.339099 |
| H | −4.891306 | −2.355466 | 4.40615 |
| H | −5.548199 | −2.104044 | 2.767929 |
| H | −1.441239 | −3.507059 | 3.364111 |
| H | −2.398124 | −2.900262 | 4.750234 |
| H | −2.846993 | −4.421032 | 3.955933 |
| H | −2.955747 | 5.056928 | −2.516682 |
| H | −2.359811 | 6.505623 | −0.594732 |
| H | −2.067944 | 5.538025 | 1.669072 |
| H | −3.014693 | 1.335233 | −2.338463 |
| H | −2.936121 | 2.053677 | −4.641118 |
| H | −3.366418 | 3.725914 | −4.238242 |
| H | −1.764475 | 3.101792 | −3.782746 |
| H | −5.415314 | 3.187239 | −2.85903 |
| H | −5.19265 | 1.561863 | −3.559613 |
| H | −5.42732 | 1.7475 | −1.804142 |
| H | −2.159019 | 1.847106 | 2.361006 |
| H | −4.544086 | 2.524035 | 2.757435 |
| H | −3.597816 | 2.614751 | 4.266488 |

**Table S10.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| H | −3.992789 | 4.106097 | 3.36918 |
| H | −1.482845 | 4.608397 | 3.543906 |
| H | −1.103774 | 3.01436 | 4.217541 |
| H | −0.292875 | 3.567374 | 2.722426 |
| Si | −0.042148 | −1.14751 | 0.646875 |
| Si | 0.053598 | 1.054528 | −0.884299 |
| C | 0.212714 | 2.846564 | −0.414124 |
| H | −0.568563 | 3.444875 | −0.897973 |
| H | 0.178471 | 3.021907 | 0.667137 |
| H | 1.173811 | 3.219401 | −0.784411 |
| C | 0.099658 | 0.831432 | −2.748569 |
| H | 0.183043 | −0.222853 | −3.042454 |
| H | −0.796577 | 1.250575 | −3.229001 |
| H | 0.970497 | 1.371683 | −3.159748 |
| C | −0.040518 | −0.992425 | 2.514037 |
| H | 0.830128 | −1.498438 | 2.959724 |
| H | −0.00538 | 0.066651 | 2.806774 |
| H | −0.939988 | −1.444626 | 2.953592 |
| C | −0.140923 | −2.882114 | −0.032169 |
| H | −0.082826 | −2.883815 | −1.128853 |
| H | 0.686615 | −3.494499 | 0.346149 |
| H | −1.070822 | −3.376387 | 0.266982 |

**Table S11.** Cartesian geometry of **3** in Angstrom [Å].

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| C | −0.001022 | −0.584754 | 0.026992 |
| N | 1.111584 | −1.452273 | −0.044649 |
| C | 0.674742 | −2.773582 | −0.150749 |
| C | −0.682626 | −2.771764 | −0.150863 |
| N | −1.115914 | −1.449287 | −0.04482 |
| C | 2.528832 | −1.000638 | 0.042638 |
| C | 3.469795 | −2.217125 | −0.042164 |
| C | −2.531935 | −0.993834 | 0.042654 |
| C | −3.476045 | −2.20784 | −0.042525 |
| N | 0.000362 | 0.684881 | 0.160725 |
| Si | 0.003788 | 2.360565 | −0.014021 |
| C | 0.002962 | 2.841442 | −1.866343 |
| C | −2.753519 | −0.286564 | 1.39721 |
| C | −2.837782 | −0.050849 | −1.141034 |
| C | 1.542737 | 3.160611 | 0.791672 |
| C | 2.837124 | −0.058947 | −1.141465 |
| C | 2.752245 | −0.29356 | 1.396995 |
| H | 1.359229 | −3.60656 | −0.228413 |
| H | −1.369407 | −3.602867 | −0.228644 |
| H | 2.170603 | 0.809177 | −1.128744 |
| H | 3.880563 | 0.287606 | −1.071768 |
| H | 2.706274 | −0.595965 | −2.094234 |
| H | 3.790176 | 0.071373 | 1.453573 |

**Table S11.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| H | 2.06685 | 0.553853 | 1.505409 |
| H | 2.581993 | −1.003108 | 2.222271 |
| H | 4.505728 | −1.853964 | 0.023184 |
| H | 3.297645 | −2.918923 | 0.788738 |
| H | 3.35161 | −2.752881 | −0.997041 |
| H | −2.06653 | 0.559589 | 1.50553 |
| H | −3.790752 | 0.080304 | 1.454169 |
| H | −2.584364 | −0.99656 | 2.222327 |
| H | −3.88037 | 0.298238 | −1.071235 |
| H | −2.169065 | 0.815602 | −1.127721 |
| H | −2.708177 | −0.587701 | −2.094065 |
| H | −4.511052 | −1.842053 | 0.022853 |
| H | −3.35918 | −2.743642 | −0.997537 |
| H | −3.305789 | −2.910334 | 0.788191 |
| H | 0.00554 | 3.938778 | −1.991405 |
| H | 0.890429 | 2.443913 | −2.38771 |
| H | −0.887978 | 2.448465 | −2.385241 |
| H | 1.514305 | 4.259547 | 0.685654 |
| H | 1.601496 | 2.933236 | 1.869974 |
| H | 2.47681 | 2.80232 | 0.327212 |
| C | −1.531405 | 3.165573 | 0.793857 |
| H | −1.499402 | 4.264511 | 0.689155 |
| H | −2.467095 | 2.810886 | 0.32985 |
| H | −1.589963 | 2.936994 | 1.871929 |

**Table S12.** Cartesian geometry of transition state (+11.3 kcal/mol) in Figure 4 in Angstrom [Å].

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| N | −3.812657 | −1.162689 | 0.228657 |
| C | −4.653869 | −0.490288 | 1.109699 |
| C | −4.868576 | 0.756462 | 0.618833 |
| N | −4.178404 | 0.869885 | −0.583893 |
| C | −3.514009 | −0.326076 | −0.847795 |
| C | −4.163396 | 2.087184 | −1.459982 |
| C | −2.73439 | 2.665474 | −1.51147 |
| N | −2.817506 | −0.640346 | −1.901912 |
| Si | −1.463165 | −0.638479 | −2.826215 |
| C | −0.906918 | −2.345753 | −3.435449 |
| C | −3.481682 | −2.628557 | 0.31566 |
| C | −4.226677 | −3.353154 | −0.825395 |
| C | −4.683373 | 1.703573 | −2.862118 |
| C | −5.09802 | 3.162735 | −0.869919 |
| C | −1.233807 | 0.705196 | −4.145157 |
| C | −1.96283 | −2.862613 | 0.207739 |
| C | −3.952001 | −3.17548 | 1.679076 |
| H | −4.982236 | −0.92247 | 2.04283 |
| H | −5.431649 | 1.573402 | 1.045875 |
| H | −3.90651 | −2.956548 | −1.798582 |
| H | −4.002103 | −4.43031 | −0.78268 |

**Table S12.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| H | −5.314168 | −3.214046 | −0.719926 |
| H | −1.581441 | −2.553529 | −0.767017 |
| H | −1.421703 | −2.330948 | 0.99762 |
| H | −1.770204 | −3.94067 | 0.320067 |
| H | −3.656773 | −4.232537 | 1.738434 |
| H | −3.476077 | −2.638099 | 2.513689 |
| H | −5.046211 | −3.122301 | 1.786815 |
| H | −2.023517 | 1.961906 | −1.945825 |
| H | −2.736825 | 3.573825 | −2.133543 |
| H | −2.386717 | 2.924976 | −0.506592 |
| H | −4.626645 | 2.58484 | −3.519751 |
| H | −4.087437 | 0.891879 | −3.293538 |
| H | −5.733545 | 1.377658 | −2.799729 |
| H | −5.091629 | 4.024383 | −1.552399 |
| H | −6.133048 | 2.797564 | −0.785312 |
| H | −4.749653 | 3.506218 | 0.116126 |
| H | −0.757313 | 1.604495 | −3.726607 |
| H | −0.59248 | 0.333907 | −4.961884 |
| H | −2.203397 | 1.001393 | −4.576703 |
| H | −1.788024 | −2.998835 | −3.550041 |
| H | −0.387397 | −2.290943 | −4.405997 |
| H | −0.234723 | −2.812285 | −2.698658 |
| C | 0.17831 | −0.07596 | −1.416633 |
| H | 0.790464 | 0.136565 | −2.298165 |
| H | −0.584433 | 0.658807 | −1.167464 |
| H | −0.032365 | −1.121954 | −1.197936 |
| B | 1.315759 | 0.132708 | −0.072807 |
| C | 2.58264 | −0.804676 | −0.556392 |
| C | 1.659531 | 1.72393 | 0.174966 |
| C | 0.525644 | −0.390574 | 1.291799 |
| C | 2.443188 | 2.056091 | 1.295318 |
| C | 2.739587 | 3.366761 | 1.685959 |
| C | 2.235307 | 4.433705 | 0.928391 |
| C | 1.457776 | 4.161046 | −0.202127 |
| C | 1.199191 | 2.827007 | −0.556103 |
| F | 2.971049 | 1.062764 | 2.053604 |
| F | 3.499462 | 3.616212 | 2.770614 |
| F | 2.498705 | 5.704972 | 1.283261 |
| F | 0.968491 | 5.178597 | −0.942456 |
| F | 0.443512 | 2.669799 | −1.688297 |
| C | 1.013975 | −1.354936 | 2.192476 |
| C | 0.293947 | −1.818141 | 3.306287 |
| C | −0.957868 | −1.264739 | 3.594951 |
| C | −1.456744 | −0.244988 | 2.777034 |
| C | −0.719411 | 0.155359 | 1.655009 |
| F | 2.238174 | −1.903237 | 2.030337 |
| F | 0.799116 | −2.776365 | 4.10699 |
| F | −1.684476 | −1.707827 | 4.640494 |

**Table S12.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| F | −2.648923 | 0.318334 | 3.072585 |
| F | −1.306347 | 1.130346 | 0.894047 |
| C | 3.860335 | −0.330756 | −0.900612 |
| C | 4.88593 | −1.152199 | −1.401999 |
| C | 4.651355 | −2.518195 | −1.591393 |
| C | 3.38972 | −3.041904 | −1.278289 |
| C | 2.407773 | −2.183154 | −0.775923 |
| F | 4.177041 | 0.981766 | −0.786509 |
| F | 6.091069 | −0.634187 | −1.711484 |
| F | 5.618318 | −3.318362 | −2.075983 |
| F | 3.139681 | −4.354496 | −1.463112 |
| F | 1.20062 | −2.772028 | −0.4975 |

**Table S13.** Cartesian geometry of intermediate (+4.5 kcal/mol) in Figure 4 in Angstrom [Å].

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| N | −1.107007 | −1.274014 | −0.002194 |
| C | −0.678692 | −2.587186 | −0.006976 |
| C | 0.688627 | −2.584751 | −0.006876 |
| N | 1.112422 | −1.269979 | −0.003268 |
| C | 0.001209 | −0.440502 | 0.001188 |
| C | 2.557843 | −0.816943 | −0.000676 |
| C | 2.817396 | 0.00351 | −1.280705 |
| N | −0.003682 | 0.872216 | 0.004833 |
| Si | −0.00417 | 2.473453 | −0.003373 |
| C | −1.594766 | 3.471766 | −0.014669 |
| C | −2.553224 | −0.825075 | 0.003207 |
| C | −2.811637 | −0.014449 | 1.289993 |
| C | 2.814743 | −0.003258 | 1.284419 |
| C | 3.481165 | −2.049821 | −0.002562 |
| C | 1.577291 | 3.486916 | 0.01108 |
| C | −2.816668 | −0.002251 | −1.274691 |
| C | −3.47281 | −2.060733 | −0.000422 |
| H | −1.364008 | −3.422971 | −0.008931 |
| H | 1.376857 | −3.417981 | −0.013145 |
| H | −2.154758 | 0.86049 | 1.356466 |
| H | −3.857517 | 0.326707 | 1.289086 |
| H | −2.652665 | −0.64601 | 2.177191 |
| H | −3.864252 | 0.333895 | −1.269051 |
| H | −2.163694 | 0.876347 | −1.332449 |
| H | −2.655811 | −0.623697 | −2.1687 |
| H | −4.511746 | −1.703974 | 0.00225 |
| H | −3.325541 | −2.673903 | −0.90218 |
| H | −3.323716 | −2.680426 | 0.896561 |
| H | 2.156292 | 0.8754 | −1.344495 |
| H | 3.861761 | 0.349802 | −1.273402 |
| H | 2.665105 | −0.622513 | −2.172941 |
| H | 3.859537 | 0.341546 | 1.281782 |

**Table S13.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| H | 2.155407 | 0.869738 | 1.351111 |
| H | 2.659016 | −0.634096 | 2.172678 |
| H | 4.518874 | −1.68935 | 0.000047 |
| H | 3.33359 | −2.669261 | 0.89479 |
| H | 3.337011 | −2.664174 | −0.904035 |
| H | 1.582983 | 4.199054 | −0.845665 |
| H | 1.62998 | 4.101946 | 0.939945 |
| H | 2.47482 | 2.843831 | −0.04347 |
| H | −1.63784 | 4.123088 | −0.905096 |
| H | −2.481011 | 2.822042 | −0.008161 |
| H | −1.635288 | 4.135215 | 0.86758 |

**Table S14.** Cartesian geometry of transition state (+12.6 kcal/mol) in Figure 4 in Angstrom [Å].

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| N | 3.553355 | −0.293631 | −0.7134 |
| C | 2.457163 | 0.32102 | −0.130363 |
| N | 2.774961 | 1.671575 | −0.061764 |
| C | 4.017428 | 1.873481 | −0.639792 |
| C | 4.489329 | 0.669651 | −1.049395 |
| N | 1.283887 | −0.281914 | 0.25103 |
| Si | 1.116582 | −0.866792 | 1.960753 |
| C | 0.757087 | −2.740291 | 2.068334 |
| C | 2.085831 | 2.800956 | 0.698696 |
| C | 0.570214 | 2.787803 | 0.468338 |
| C | 3.818798 | −1.75884 | −1.038669 |
| C | 3.05911 | −2.68676 | −0.079777 |
| Si | −0.441014 | −0.478514 | −1.355813 |
| C | 0.18831 | 0.644559 | −2.759413 |
| N | −1.938655 | −0.076991 | −0.747012 |
| C | −3.215909 | −0.040053 | −0.514267 |
| N | −4.036672 | 1.096825 | −0.550994 |
| C | −5.323954 | 0.773064 | −0.129571 |
| C | −5.357274 | −0.555329 | 0.130051 |
| N | −4.089811 | −1.077956 | −0.110668 |
| C | −3.638252 | 2.47996 | −0.964274 |
| C | −3.040218 | 3.17953 | 0.278038 |
| C | −3.824188 | −2.550266 | −0.212359 |
| C | −5.030105 | −3.352456 | 0.317005 |
| C | −0.416425 | −2.256079 | −2.054715 |
| C | −2.607377 | −2.884831 | 0.666248 |
| C | −3.626039 | −2.901458 | −1.704791 |
| C | −2.64179 | 2.414016 | −2.151569 |
| C | −4.88813 | 3.262545 | −1.434853 |
| C | −0.31269 | 0.049069 | 2.806981 |
| C | 2.795549 | −0.591893 | 2.838009 |
| C | 2.442284 | 2.679484 | 2.214644 |
| C | 2.608433 | 4.157091 | 0.160804 |
| C | 3.436894 | −1.992753 | −2.519196 |

**Table S14.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| C | 5.32861 | −2.0458 | −0.835806 |
| H | −6.104825 | 1.512118 | −0.023567 |
| H | −6.177366 | −1.161803 | 0.486765 |
| H | 5.4148 | 0.436863 | −1.554395 |
| H | 4.481541 | 2.844732 | −0.716677 |
| H | −5.934623 | −3.182741 | −0.285746 |
| H | −4.773528 | −4.419801 | 0.25019 |
| H | −5.242254 | −3.116463 | 1.371194 |
| H | −2.288121 | −3.923817 | 0.494955 |
| H | −1.778724 | −2.213956 | 0.437647 |
| H | −2.863947 | −2.769057 | 1.730645 |
| H | −2.911737 | −2.219601 | −2.173692 |
| H | −3.254795 | −3.931887 | −1.806942 |
| H | −4.588283 | −2.822157 | −2.234183 |
| H | −2.307739 | 2.524289 | 0.765097 |
| H | −2.54695 | 4.119155 | −0.011275 |
| H | −3.834323 | 3.413068 | 1.004511 |
| H | −1.617662 | 2.24616 | −1.81288 |
| H | −2.901634 | 1.591394 | −2.830883 |
| H | −2.681929 | 3.358013 | −2.71603 |
| H | −5.60682 | 3.436381 | −0.621071 |
| H | −4.553772 | 4.247782 | −1.790169 |
| H | −5.394559 | 2.743469 | −2.26263 |
| H | 3.26041 | −2.408092 | 0.9644 |
| H | 1.985188 | −2.675919 | −0.254931 |
| H | 3.431822 | −3.710094 | −0.233786 |
| H | 3.329135 | −3.07166 | −2.705695 |
| H | 2.488036 | −1.502797 | −2.76966 |
| H | 4.218298 | −1.604945 | −3.19087 |
| H | 5.48457 | −3.119819 | −1.010388 |
| H | 5.972854 | −1.513154 | −1.5482 |
| H | 5.644601 | −1.809786 | 0.191436 |
| H | 0.114349 | 1.813885 | 0.655996 |
| H | 0.125603 | 3.516371 | 1.159341 |
| H | 0.334298 | 3.112869 | −0.552329 |
| H | 1.573087 | 2.368123 | 2.808673 |
| H | 3.247193 | 1.955407 | 2.383906 |
| H | 2.785687 | 3.650517 | 2.602032 |
| H | 1.984737 | 4.943844 | 0.607746 |
| H | 3.647271 | 4.359076 | 0.460344 |
| H | 2.516973 | 4.219926 | −0.933874 |
| H | 1.640108 | −3.265081 | 2.466753 |
| H | −0.083598 | −2.930866 | 2.753463 |
| H | 0.500884 | −3.212719 | 1.111103 |
| H | −1.281096 | −0.300028 | 2.413031 |
| H | −0.294414 | −0.16328 | 3.890423 |
| H | −0.276317 | 1.140558 | 2.677177 |
| H | 3.200467 | −1.565508 | 3.158595 |

**Table S14.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| H | 3.564599 | −0.115267 | 2.210392 |
| H | 2.68035 | 0.026412 | 3.74293 |
| H | −0.832306 | −2.987925 | −1.349651 |
| H | −1.068497 | −2.27049 | −2.944252 |
| H | 0.564423 | −2.621983 | −2.386376 |
| H | 0.358169 | 1.6903 | −2.465951 |
| H | 1.135026 | 0.265821 | −3.180973 |
| H | −0.554261 | 0.647325 | −3.574491 |

**Table S15.** Cartesian geometry of **4** in Angstrom [Å].

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| N | −3.705636 | 1.084185 | −0.598193 |
| C | −2.849083 | 0.009582 | −0.282324 |
| N | −3.716042 | −1.093657 | −0.155667 |
| C | −5.015687 | −0.703982 | −0.487444 |
| C | −5.011276 | 0.62374 | −0.742378 |
| N | −1.547756 | 0.086813 | −0.125618 |
| Si | −0.12952 | −0.296337 | −0.952636 |
| C | −0.262698 | −1.957152 | −1.890605 |
| C | −3.47762 | −2.48537 | 0.365915 |
| C | −2.186863 | −2.571487 | 1.187526 |
| C | −3.350036 | 2.542332 | −0.523853 |
| C | −2.294757 | 2.869334 | −1.592918 |
| N | 1.286862 | −0.334011 | 0.245559 |
| Si | 1.312729 | −1.127485 | 1.887353 |
| C | 0.040653 | −0.29326 | 3.016189 |
| C | 2.433379 | 0.331045 | −0.117088 |
| N | 2.727126 | 1.665636 | 0.111393 |
| C | 3.973334 | 1.9476 | −0.427063 |
| C | 4.456304 | 0.811258 | −0.986707 |
| N | 3.523192 | −0.194223 | −0.788213 |
| C | 2.009245 | 2.732092 | 0.941645 |
| C | 2.555101 | 2.653732 | 2.381756 |
| C | 3.802627 | −1.578886 | −1.369697 |
| C | 3.543907 | −1.498046 | −2.887666 |
| C | 2.335585 | 4.122504 | 0.34116 |
| C | 0.486364 | 2.575308 | 0.929169 |
| C | 5.288847 | −1.924568 | −1.10047 |
| C | 2.952795 | −2.681657 | −0.729555 |
| C | 3.082143 | −0.935684 | 2.564773 |
| C | 0.947325 | −2.998613 | 1.803296 |
| C | 0.495627 | 0.914319 | −2.29414 |
| C | −3.443603 | −3.461079 | −0.828181 |
| C | −4.642603 | −2.871421 | 1.316288 |
| C | −4.595277 | 3.410617 | −0.794515 |
| C | −2.848156 | 2.834841 | 0.906413 |
| H | −5.827642 | 1.2702 | −1.030407 |

**Table S15.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| H | −5.83355 | −1.409048 | −0.528188 |
| H | 5.383982 | 0.647001 | −1.51488 |
| H | 4.425933 | 2.926345 | −0.374116 |
| H | −5.592258 | −3.021046 | 0.783829 |
| H | −4.389111 | −3.823558 | 1.805077 |
| H | −4.784399 | −2.10324 | 2.090977 |
| H | −2.106336 | −3.594683 | 1.582812 |
| H | −1.306518 | −2.363297 | 0.583175 |
| H | −2.206961 | −1.868047 | 2.030545 |
| H | −2.60673 | −3.232081 | −1.499728 |
| H | −3.330146 | −4.492591 | −0.459493 |
| H | −4.382185 | −3.399643 | −1.400105 |
| H | −2.033212 | 2.154016 | 1.17342 |
| H | −2.490538 | 3.874302 | 0.967647 |
| H | −3.673277 | 2.705674 | 1.624088 |
| H | −1.416179 | 2.240872 | −1.45368 |
| H | −2.702912 | 2.692798 | −2.600376 |
| H | −2.004809 | 3.928605 | −1.51249 |
| H | −5.381734 | 3.244053 | −0.043426 |
| H | −4.286419 | 4.464148 | −0.736398 |
| H | −5.005577 | 3.231058 | −1.80019 |
| H | 3.212731 | −2.818822 | 0.326857 |
| H | 1.885939 | −2.486593 | −0.812582 |
| H | 3.184712 | −3.61765 | −1.258637 |
| H | 3.832262 | −2.453843 | −3.35003 |
| H | 2.482578 | −1.314824 | −3.09979 |
| H | 4.14173 | −0.696475 | −3.347065 |
| H | 5.442377 | −2.980622 | −1.363478 |
| H | 5.985015 | −1.334095 | −1.712484 |
| H | 5.536903 | −1.789955 | −0.037246 |
| H | 0.142669 | 1.597276 | 1.262201 |
| H | 0.080106 | 3.337233 | 1.609676 |
| H | 0.075307 | 2.768358 | −0.066996 |
| H | 2.220538 | 1.740899 | 2.888738 |
| H | 3.655356 | 2.68872 | 2.388162 |
| H | 2.177564 | 3.518632 | 2.947994 |
| H | 1.664369 | 4.854236 | 0.811566 |
| H | 3.364911 | 4.448666 | 0.550491 |
| H | 2.159231 | 4.138102 | −0.744777 |
| H | 1.848 | −3.565603 | 2.090038 |
| H | 0.146735 | −3.264559 | 2.509999 |
| H | 0.641101 | −3.353395 | 0.810228 |
| H | −0.901106 | −0.141364 | 2.466382 |
| H | −0.163884 | −0.93592 | 3.889282 |
| H | 0.370974 | 0.686809 | 3.393245 |
| H | 3.787391 | −1.611586 | 2.055297 |
| H | 3.493302 | 0.081493 | 2.496507 |
| H | 3.078849 | −1.217085 | 3.63206 |

**Table S15.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| H | −0.35226 | −2.849023 | −1.252504 |
| H | −1.178006 | −1.906533 | −2.505561 |
| H | 0.578263 | −2.126057 | −2.581528 |
| H | 0.70659 | 1.933336 | −1.939766 |
| H | 1.419404 | 0.534594 | −2.760787 |
| H | −0.261665 | 0.991564 | −3.091606 |

**Table S16.** Cartesian geometry of **7** in Angstrom [Å].

| | | | |
|---|---|---|---|
| C | 2.580495 | −0.644357 | −0.310905 |
| N | 1.866245 | −1.793626 | −0.509466 |
| C | 2.558904 | −2.967458 | −0.598436 |
| C | 3.932135 | −3.041877 | −0.491114 |
| C | 4.700112 | −1.850764 | −0.276572 |
| C | 3.955212 | −0.632784 | −0.193175 |
| Si | −0.048535 | −1.763454 | −0.638905 |
| C | −0.358348 | −2.402119 | −2.385961 |
| N | 6.051767 | −1.877981 | −0.15851 |
| C | 6.779121 | −3.152823 | −0.246579 |
| N | −0.351345 | −0.153654 | −0.373647 |
| C | −1.133238 | 0.734611 | 0.145184 |
| N | −0.73616 | 1.996757 | 0.558955 |
| C | −1.83657 | 2.719227 | 1.029893 |
| C | −2.927221 | 1.913236 | 0.919377 |
| N | −2.500742 | 0.697048 | 0.3702 |
| C | 0.623208 | 2.439527 | 0.433636 |
| C | 1.079928 | 2.844162 | −0.840625 |
| C | 2.440643 | 3.183185 | −0.963445 |
| C | 3.299353 | 3.126644 | 0.140901 |
| C | 2.815811 | 2.722822 | 1.394484 |
| C | 1.466797 | 2.364458 | 1.567855 |
| C | 0.166956 | 2.891303 | −2.062827 |
| C | 0.584663 | 1.818124 | −3.095339 |
| C | 0.944316 | 1.83311 | 2.902437 |
| C | 1.649305 | 2.445413 | 4.129914 |
| C | −3.307994 | −0.453268 | 0.076388 |
| C | −3.74624 | −1.262975 | 1.148761 |
| C | −4.512744 | −2.400548 | 0.83047 |
| C | −4.802113 | −2.72291 | −0.499652 |
| C | −4.348931 | −1.903136 | −1.543945 |
| C | −3.599533 | −0.74243 | −1.28235 |
| C | −3.447437 | −0.911019 | 2.605495 |
| C | −3.024855 | −2.132595 | 3.452029 |
| C | −3.150596 | 0.201293 | −2.402578 |
| C | −4.015096 | 1.487782 | −2.406059 |
| C | −0.58448 | −3.014899 | 0.668684 |
| C | −4.682086 | −0.228725 | 3.244457 |
| C | −3.183422 | −0.429718 | −3.809234 |

**Table S16.** *Cont.*

| | | | |
|---|---|---|---|
| C | 1.055868 | 0.287538 | 2.927173 |
| C | 0.150724 | 4.298025 | −2.703208 |
| C | 6.795417 | −0.628311 | 0.058161 |
| H | 3.494048 | 2.688487 | 2.247394 |
| H | 2.114936 | −0.016583 | 2.880601 |
| H | 0.622083 | −0.110657 | 3.858993 |
| H | 0.532757 | −0.158097 | 2.068859 |
| H | 6.481154 | −0.146673 | 0.998967 |
| H | 7.865893 | −0.852665 | 0.117526 |
| H | 6.438938 | −3.850197 | 0.536558 |
| H | −0.277549 | −2.693672 | 1.676633 |
| H | −1.730342 | 3.735992 | 1.387943 |
| H | 4.34855 | 3.409906 | 0.029032 |
| H | 2.822559 | 3.500208 | −1.935092 |
| H | 1.629487 | 3.545822 | 4.098883 |
| H | 1.143134 | 2.111677 | 5.048676 |
| H | 2.700115 | 2.11984 | 4.195178 |
| H | 1.146582 | 4.572245 | −3.08641 |
| H | −0.553703 | 4.314383 | −3.550009 |
| H | −0.15934 | 5.063524 | −1.974872 |
| H | −3.96741 | 2.079472 | 1.167639 |
| H | −4.876274 | −3.041861 | 1.634129 |
| H | −5.388847 | −3.614961 | −0.727261 |
| H | −4.590851 | −2.166982 | −2.573102 |
| H | −2.615013 | −0.191082 | 2.624916 |
| H | −5.540448 | −0.919468 | 3.244232 |
| H | −4.464839 | 0.054688 | 4.286769 |
| H | −4.976036 | 0.676266 | 2.690835 |
| H | −2.168752 | −2.657604 | 3.003986 |
| H | −2.74286 | −1.797447 | 4.462557 |
| H | −3.851966 | −2.851345 | 3.561096 |
| H | −2.108623 | 0.490611 | −2.199117 |
| H | −4.217361 | −0.633497 | −4.13115 |
| H | −2.744272 | 0.275643 | −4.531234 |
| H | −2.614843 | −1.369821 | −3.855098 |
| H | −3.962539 | 2.021658 | −1.446989 |
| H | −3.666035 | 2.169433 | −3.198841 |
| H | −5.068311 | 1.235475 | −2.608746 |
| H | −0.124767 | 2.085466 | 2.975464 |
| H | −0.860034 | 2.662108 | −1.744015 |
| H | 0.556257 | 0.818823 | −2.63692 |
| H | −0.103154 | 1.835604 | −3.95641 |
| H | 1.603686 | 2.011575 | −3.468991 |
| H | 1.991645 | 0.267644 | −0.245037 |
| H | 4.438211 | 0.327195 | −0.033261 |
| H | 4.407457 | −4.015946 | −0.572804 |
| H | 1.962358 | −3.865197 | −0.758799 |
| H | 6.626618 | 0.074365 | −0.774431 |
| H | 6.627491 | −3.622083 | −1.23276 |

**Table S16.** *Cont.*

| | | | |
|---|---|---|---|
| H | −1.683418 | −3.098564 | 0.659729 |
| H | −0.170229 | −4.021264 | 0.487743 |
| H | −0.085252 | −1.650081 | −3.14286 |
| H | 0.203151 | −3.327373 | −2.599288 |
| H | −1.430715 | −2.626813 | −2.500938 |
| H | 7.849428 | −2.966105 | −0.10772 |

**Table S17.** Cartesian geometry of transition state (+26.7 kcal/mol) in Figure S7 in Angstrom [Å].

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| C | −2.637825 | −2.264143 | −2.786737 |
| C | −2.99308 | −2.248879 | −1.41646 |
| C | −3.138091 | −3.430475 | −0.647492 |
| C | −2.855922 | −4.652158 | −1.287536 |
| C | −2.475558 | −4.696928 | −2.631539 |
| C | −2.376539 | −3.513468 | −3.372589 |
| N | −3.351639 | −0.986392 | −0.795468 |
| C | −2.542748 | 0.055212 | −0.376329 |
| N | −3.416015 | 0.974858 | 0.19969 |
| C | −4.726173 | 0.518778 | 0.08407 |
| C | −4.685869 | −0.694397 | −0.519837 |
| N | −1.211135 | 0.20417 | −0.584055 |
| Si | 0.528893 | −1.376853 | 0.040691 |
| C | 0.735084 | −2.697197 | −1.301565 |
| C | −3.06832 | 2.090431 | 1.065197 |
| C | −3.38809 | 3.416458 | 0.685539 |
| C | −2.917837 | 4.451908 | 1.517251 |
| C | −2.223826 | 4.179465 | 2.698276 |
| C | −2.078567 | 2.854838 | 3.129784 |
| C | −2.527453 | 1.782434 | 2.341965 |
| C | −4.364934 | 3.766853 | −0.435533 |
| C | −3.952847 | 5.005249 | −1.261487 |
| C | −2.635061 | 0.376167 | 2.928984 |
| C | −4.086081 | 0.156771 | 3.434916 |
| C | −3.647021 | −3.453946 | 0.795361 |
| C | −2.834005 | −4.405979 | 1.706817 |
| C | −2.566705 | −0.976241 | −3.600339 |
| C | −3.98395 | −0.501208 | −4.003575 |
| Si | −0.622583 | 1.665306 | −1.556635 |
| C | −2.093996 | 2.32062 | −2.570922 |
| C | 0.589422 | 1.073377 | −2.881777 |
| C | 0.052623 | 2.952065 | −0.350825 |
| C | −0.057787 | −2.203641 | 1.626382 |
| N | 1.936797 | −0.447028 | 0.099778 |
| C | 3.169309 | −0.372868 | 0.468544 |
| N | 3.779225 | −0.820825 | 1.647168 |
| C | 5.13529 | −0.479242 | 1.669707 |
| C | 5.413704 | 0.147579 | 0.500952 |
| N | 4.228457 | 0.217282 | −0.240014 |

**Table S17.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| C | 3.098114 | −1.384475 | 2.772242 |
| C | 2.901123 | −2.785562 | 2.816983 |
| C | 2.284047 | −3.313157 | 3.963199 |
| C | 1.882024 | −2.476701 | 5.015246 |
| C | 2.093313 | −1.09503 | 4.942818 |
| C | 2.711101 | −0.517841 | 3.817253 |
| C | 4.227218 | 0.598093 | −1.626975 |
| C | 4.25651 | 1.971848 | −1.953881 |
| C | 4.364469 | 2.317601 | −3.314331 |
| C | 4.420221 | 1.332294 | −4.305369 |
| C | 4.366815 | −0.02285 | −3.954788 |
| C | 4.275081 | −0.421361 | −2.610042 |
| C | 4.193029 | 3.058804 | −0.882878 |
| C | 3.360057 | 4.280702 | −1.330686 |
| C | 4.257198 | −1.901296 | −2.22575 |
| C | 5.686736 | −2.39953 | −1.901051 |
| C | 3.37359 | −3.673027 | 1.662682 |
| C | 2.63351 | −5.022796 | 1.552658 |
| C | 2.985717 | 0.984776 | 3.768116 |
| C | 3.93173 | 1.40419 | 4.916653 |
| C | 5.613099 | 3.524497 | −0.478069 |
| C | 3.619194 | −2.804269 | −3.302238 |
| C | 4.895756 | −3.942541 | 1.771061 |
| C | 1.682634 | 1.810987 | 3.797796 |
| C | −5.762311 | 4.018229 | 0.193245 |
| C | −1.658774 | 0.085784 | 4.081722 |
| C | −5.136323 | −3.881441 | 0.834602 |
| C | −1.674948 | −1.078502 | −4.852622 |
| H | 5.754515 | −0.714139 | 2.526609 |
| H | 6.341446 | 0.532543 | 0.098575 |
| H | −5.469962 | −1.381182 | −0.806385 |
| H | −5.552536 | 1.107622 | 0.457639 |
| H | 1.158386 | 1.93226 | −3.276199 |
| H | 1.32324 | 0.353909 | −2.50935 |
| H | 0.034495 | 0.626981 | −3.72154 |
| H | 1.048465 | 2.652304 | 0.004951 |
| H | 0.135153 | 3.943096 | −0.825664 |
| H | −0.606451 | 3.053275 | 0.523125 |
| H | −2.072942 | 1.874456 | −3.577021 |
| H | −3.081484 | 2.117904 | −2.145181 |
| H | −2.001197 | 3.409615 | −2.69864 |
| H | 0.70193 | −2.259541 | −2.309917 |
| H | 1.725222 | −3.167549 | −1.181811 |
| H | −0.022451 | −3.491488 | −1.245994 |
| H | 0.14599 | −1.595411 | 2.513959 |
| H | −1.126583 | −2.446754 | 1.595453 |
| H | 0.48817 | −3.146792 | 1.752999 |

**Table S17.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| H | 4.396725 | 3.370188 | −3.59738 |
| H | 4.500987 | 1.619757 | −5.355607 |
| H | 4.401278 | −0.780501 | −4.737456 |
| H | 2.110203 | −4.387065 | 4.035149 |
| H | 1.405577 | −2.908243 | 5.897891 |
| H | 1.784938 | −0.45212 | 5.76909 |
| H | −3.122199 | 5.485629 | 1.238536 |
| H | −1.850417 | 4.999113 | 3.31483 |
| H | −1.631614 | 2.652185 | 4.101149 |
| H | −2.948434 | −5.578639 | −0.720533 |
| H | −2.262031 | −5.656327 | −3.106164 |
| H | −2.08617 | −3.56222 | −4.420908 |
| H | −4.465381 | 2.91105 | −1.114715 |
| H | −6.502928 | 4.214068 | −0.598523 |
| H | −6.108091 | 3.161775 | 0.793845 |
| H | −5.725607 | 4.89404 | 0.859741 |
| H | −4.599587 | 5.092227 | −2.147841 |
| H | −4.074594 | 5.927585 | −0.672354 |
| H | −2.907382 | 4.948298 | −1.591532 |
| H | −2.125148 | −0.211676 | −2.952586 |
| H | −3.91708 | 0.45062 | −4.553923 |
| H | −4.463219 | −1.246609 | −4.658097 |
| H | −4.628441 | −0.344438 | −3.126242 |
| H | −1.561851 | −0.079814 | −5.301509 |
| H | −0.674146 | −1.464621 | −4.60567 |
| H | −2.124527 | −1.73378 | −5.615474 |
| H | −3.578317 | −2.438919 | 1.215516 |
| H | −5.501192 | −3.875919 | 1.874038 |
| H | −5.780028 | −3.217055 | 0.239936 |
| H | −5.2466 | −4.901928 | 0.435112 |
| H | −3.134024 | −4.251654 | 2.754996 |
| H | −3.037403 | −5.458514 | 1.456158 |
| H | −1.752867 | −4.233226 | 1.622901 |
| H | −2.447848 | −0.353437 | 2.134723 |
| H | −1.712827 | −0.980278 | 4.346402 |
| H | −0.622112 | 0.318212 | 3.814049 |
| H | −1.924119 | 0.667437 | 4.979453 |
| H | −4.189955 | −0.865499 | 3.834287 |
| H | −4.315955 | 0.869435 | 4.242811 |
| H | −4.82742 | 0.290996 | 2.634872 |
| H | 3.711243 | 2.625533 | 0.00741 |
| H | 3.158065 | 4.930005 | −0.46471 |
| H | 3.904089 | 4.881295 | −2.077178 |
| H | 2.401379 | 3.972024 | −1.770836 |
| H | 5.549436 | 4.324939 | 0.277098 |
| H | 6.206745 | 2.701328 | −0.055582 |
| H | 6.146273 | 3.920124 | −1.357548 |
| H | 3.64957 | −2.005224 | −1.316081 |

**Table S17.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| H | 3.486928 | −3.819735 | −2.897595 |
| H | 2.635398 | −2.424165 | −3.616538 |
| H | 4.264218 | −2.883889 | −4.191648 |
| H | 5.65787 | −3.460228 | −1.601733 |
| H | 6.331808 | −2.308089 | −2.7899 |
| H | 6.137565 | −1.823386 | −1.080508 |
| H | 3.492002 | 1.218674 | 2.821452 |
| H | 4.154829 | 2.480937 | 4.84841 |
| H | 3.469551 | 1.210882 | 5.89808 |
| H | 4.880619 | 0.84677 | 4.87178 |
| H | 1.91748 | 2.886676 | 3.748888 |
| H | 1.036128 | 1.561068 | 2.944125 |
| H | 1.120086 | 1.627308 | 4.726973 |
| H | 3.199998 | −3.117333 | 0.72619 |
| H | 2.954456 | −5.537125 | 0.633725 |
| H | 2.878001 | −5.679898 | 2.402579 |
| H | 1.540064 | −4.906295 | 1.515211 |
| H | 5.22848 | −4.567552 | 0.926509 |
| H | 5.475105 | −3.009907 | 1.755183 |
| H | 5.118424 | −4.478941 | 2.70757 |

**Table S18.** Cartesian geometry of product (−15.8 kcal/mol) in Figure S7 in Angstrom [Å].

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| N | −3.435579 | 0.366254 | 0.935022 |
| C | −2.487463 | −0.480443 | 0.386674 |
| N | −3.205501 | −1.390384 | −0.375693 |
| C | −4.569261 | −1.147069 | −0.236019 |
| C | −4.710678 | −0.060962 | 0.565931 |
| N | −1.160157 | −0.527123 | 0.654617 |
| Si | −0.520094 | −2.046324 | 1.488546 |
| C | 0.727415 | −1.529152 | 2.80619 |
| C | −2.686074 | −2.189505 | −1.478605 |
| C | −3.239515 | 1.614748 | 1.657659 |
| Si | 0.050139 | 0.844332 | 0.388233 |
| C | −0.766265 | 1.977601 | −0.871464 |
| N | 1.496582 | 0.039169 | −0.024578 |
| C | 2.708193 | 0.493736 | −0.132101 |
| N | 3.17213 | 1.67862 | −0.729924 |
| C | 4.571236 | 1.741441 | −0.666202 |
| C | 4.999056 | 0.627245 | −0.023257 |
| N | 3.874027 | −0.141642 | 0.29587 |
| C | 2.407645 | 2.412402 | −1.699505 |
| C | 3.942012 | −1.38043 | 1.020889 |
| C | 0.331862 | 1.815837 | 1.994109 |
| C | 0.341684 | −3.148784 | 0.234596 |
| C | −1.974926 | −2.84636 | 2.437526 |
| H | 5.112309 | 2.573482 | −1.09967 |

**Table S18.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| H | 5.991384 | 0.293556 | 0.251379 |
| H | −5.589577 | 0.458622 | 0.920935 |
| H | −5.297598 | −1.76943 | −0.739243 |
| H | 1.175958 | −2.44089 | 3.237392 |
| H | 1.545431 | −0.941818 | 2.375894 |
| H | 0.258385 | −0.963712 | 3.625051 |
| H | 1.122696 | −2.530428 | −0.227905 |
| H | 0.837791 | −3.990626 | 0.74622 |
| H | −0.305044 | −3.544198 | −0.558383 |
| H | −1.829809 | −2.661757 | 3.514055 |
| H | −2.968428 | −2.452565 | 2.179177 |
| H | −1.998638 | −3.935667 | 2.291601 |
| H | 0.403082 | 1.157264 | 2.870578 |
| H | 1.288972 | 2.358019 | 1.910376 |
| H | −0.457545 | 2.556804 | 2.184213 |
| H | −0.447376 | 1.76832 | −1.897754 |
| H | −1.856589 | 1.911226 | −0.819284 |
| H | −0.494937 | 3.018274 | −0.653562 |
| C | 3.833529 | −2.596559 | 0.301799 |
| C | 3.944453 | −3.789844 | 1.035979 |
| C | 4.169634 | −3.77011 | 2.420315 |
| C | 4.283994 | −2.553464 | 3.100533 |
| C | 4.164626 | −1.3299 | 2.415568 |
| C | 3.637184 | −2.596599 | −1.216896 |
| H | 3.859407 | −4.747028 | 0.522 |
| H | 4.260787 | −4.710538 | 2.967818 |
| H | 4.462516 | −2.548016 | 4.176615 |
| C | 4.312172 | −0.005259 | 3.164948 |
| C | 1.962076 | 3.715979 | −1.388194 |
| C | 1.226137 | 4.404134 | −2.370521 |
| C | 0.933618 | 3.806573 | −3.602275 |
| C | 1.405577 | 2.518996 | −3.8913 |
| C | 2.17159 | 1.801924 | −2.955979 |
| C | 2.307646 | 4.382991 | −0.05942 |
| H | 0.87371 | 5.415653 | −2.163706 |
| H | 0.350495 | 4.352358 | −4.346963 |
| H | 1.200053 | 2.07085 | −4.864887 |
| C | 2.758638 | 0.440317 | −3.32905 |
| C | −2.680096 | −3.59882 | −1.390492 |
| C | −2.128465 | −4.312362 | −2.472586 |
| C | −1.631816 | −3.651589 | −3.599066 |
| C | −1.761277 | −2.261311 | −3.705942 |
| C | −2.32533 | −1.501105 | −2.667506 |
| C | −3.346177 | −4.364037 | −0.252942 |
| H | −2.096305 | −5.400902 | −2.42492 |
| H | −1.186606 | −4.222478 | −4.415919 |
| H | −1.44703 | −1.760073 | −4.620724 |
| C | −2.713073 | −0.043255 | −2.908338 |

**Table S18.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| C | −3.557657 | 2.826319 | 0.98788 |
| C | −3.384801 | 4.022088 | 1.710051 |
| C | −2.951454 | 4.015066 | 3.038784 |
| C | −2.697536 | 2.80067 | 3.686475 |
| C | −2.839868 | 1.574908 | 3.014558 |
| C | −4.165171 | 2.89847 | −0.41702 |
| H | −3.609575 | 4.970121 | 1.221265 |
| H | −2.825943 | 4.956622 | 3.576373 |
| H | −2.378968 | 2.804664 | 4.727755 |
| C | −2.62338 | 0.249406 | 3.73363 |
| H | −3.519359 | −3.673575 | 0.579405 |
| C | −4.729741 | −4.874451 | −0.730206 |
| C | −2.501454 | −5.546753 | 0.26884 |
| H | −5.244756 | −5.397348 | 0.091307 |
| H | −5.371248 | −4.046995 | −1.073921 |
| H | −4.611097 | −5.577391 | −1.569767 |
| H | −2.980118 | −5.976226 | 1.162707 |
| H | −2.429845 | −6.347627 | −0.483555 |
| H | −1.482429 | −5.229928 | 0.530791 |
| H | −2.119619 | −0.416229 | 3.027509 |
| C | −1.730681 | 0.348344 | 4.98537 |
| C | −3.983566 | −0.388466 | 4.106987 |
| H | −3.820945 | −1.366317 | 4.586565 |
| H | −4.525395 | 0.259637 | 4.814108 |
| H | −4.618813 | −0.541622 | 3.221765 |
| H | −1.503593 | −0.665093 | 5.35028 |
| H | −0.78336 | 0.86405 | 4.767414 |
| H | −2.239581 | 0.88643 | 5.800793 |
| H | −4.01123 | 1.935325 | −0.925806 |
| C | −5.693081 | 3.142671 | −0.314078 |
| C | −3.549547 | 4.003472 | −1.309112 |
| H | −6.14464 | 3.130321 | −1.318898 |
| H | −6.200137 | 2.387134 | 0.303883 |
| H | −5.886105 | 4.127398 | 0.139665 |
| H | −3.963023 | 3.914847 | −2.326167 |
| H | −3.812573 | 5.005243 | −0.935793 |
| H | −2.456238 | 3.92975 | −1.367719 |
| H | −2.693694 | 0.490755 | −1.952853 |
| C | −1.79343 | 0.709983 | −3.887955 |
| C | −4.169085 | 0.010109 | −3.442421 |
| H | −2.039706 | 1.782001 | −3.869793 |
| H | −0.735924 | 0.595637 | −3.62588 |
| H | −1.937339 | 0.350749 | −4.919736 |
| H | −4.474563 | 1.059612 | −3.58658 |
| H | −4.233021 | −0.506547 | −4.413075 |
| H | −4.880728 | −0.46414 | −2.751779 |
| H | 2.898571 | −1.815408 | −1.448757 |
| C | 4.956283 | −2.241912 | −1.948849 |

**Table S18.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| C | 3.100544 | −3.927651 | −1.782105 |
| H | 2.862248 | −3.796525 | −2.849186 |
| H | 3.858973 | −4.723803 | −1.70718 |
| H | 2.192171 | −4.258427 | −1.260641 |
| H | 4.788981 | −2.242382 | −3.038457 |
| H | 5.335946 | −1.251646 | −1.664254 |
| H | 5.730153 | −2.992434 | −1.720552 |
| H | 3.924656 | 0.800145 | 2.522617 |
| C | 3.518557 | 0.035568 | 4.489848 |
| C | 5.807731 | 0.28387 | 3.441707 |
| H | 3.614636 | 1.035223 | 4.942829 |
| H | 2.452825 | −0.176872 | 4.326824 |
| H | 3.91057 | −0.695235 | 5.214669 |
| H | 5.919448 | 1.248029 | 3.96364 |
| H | 6.236562 | −0.50658 | 4.078585 |
| H | 6.390569 | 0.323361 | 2.509097 |
| H | 3.400816 | 0.093709 | −2.510162 |
| C | 1.660986 | −0.625001 | −3.535305 |
| C | 3.657876 | 0.552599 | −4.581465 |
| H | 4.112126 | −0.426468 | −4.802972 |
| H | 3.076222 | 0.866462 | −5.462831 |
| H | 4.465635 | 1.284242 | −4.424433 |
| H | 2.124095 | −1.605933 | −3.727721 |
| H | 1.02588 | −0.710594 | −2.641198 |
| H | 1.032303 | −0.373582 | −4.403962 |
| H | 2.637103 | 3.597811 | 0.637572 |
| C | 3.492574 | 5.359767 | −0.257702 |
| C | 1.113632 | 5.118545 | 0.587773 |
| H | 1.423841 | 5.536129 | 1.558632 |
| H | 0.769875 | 5.956262 | −0.03939 |
| H | 0.264614 | 4.441942 | 0.762804 |
| H | 3.771109 | 5.823156 | 0.702504 |
| H | 4.374776 | 4.839517 | −0.662399 |
| H | 3.216475 | 6.160233 | −0.962877 |

**Table S19.** Cartesian geometry of transition state (+ 18.0 kcal/mol) in Figure S8 in Angstrom [Å].

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| N | 3.456641 | 0.987754 | −0.44128 |
| C | 2.611132 | −0.045507 | −0.087569 |
| N | 3.394437 | −1.184786 | 0.011827 |
| C | 4.695988 | −0.852613 | −0.321206 |
| C | 4.731674 | 0.473712 | −0.612459 |
| N | 1.232089 | 0.027424 | 0.004623 |
| Si | 0.000041 | −0.106157 | 1.336297 |
| C | 0.266511 | 1.253845 | 2.61645 |
| C | 3.074705 | −2.520849 | 0.682158 |
| C | 2.951502 | −2.225071 | 2.191129 |
| C | 3.204915 | 2.49957 | −0.552146 |

**Table S19.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| C | 2.226057 | 2.947773 | 0.54048 |
| N | −1.199252 | −0.040819 | −0.015398 |
| Si | 0.021704 | 0.022158 | −1.352509 |
| C | −0.467038 | 1.434394 | −2.502771 |
| C | −2.56915 | 0.079743 | −0.133993 |
| N | −3.445011 | −0.907264 | −0.540736 |
| C | −4.707538 | −0.348707 | −0.66864 |
| C | −4.627126 | 0.962892 | −0.328153 |
| N | −3.311057 | 1.241744 | 0.002747 |
| C | −3.314253 | −2.440539 | −0.567575 |
| C | −3.761476 | −2.930894 | 0.825001 |
| C | −2.960275 | 2.529633 | 0.752379 |
| C | −2.961366 | 2.154295 | 2.248252 |
| C | −0.34135 | −1.668206 | 2.342527 |
| C | −1.629938 | 3.125561 | 0.264965 |
| C | −4.05151 | 3.595091 | 0.503741 |
| C | −4.253212 | −2.997041 | −1.666077 |
| C | −1.895687 | −2.912684 | −0.884198 |
| C | 0.453603 | −1.375216 | −2.539994 |
| C | 1.822049 | −3.154462 | 0.061058 |
| C | 4.239513 | −3.513224 | 0.473182 |
| C | 4.542665 | 3.246518 | −0.340296 |
| C | 2.655582 | 2.812882 | −1.955251 |
| H | −5.568018 | −0.921726 | −0.981265 |
| H | −5.406433 | 1.710208 | −0.299585 |
| H | 5.570453 | 1.081683 | −0.916949 |
| H | 5.501353 | −1.571999 | −0.320878 |
| H | −0.254066 | −1.405717 | −3.384306 |
| H | 1.439086 | −1.11356 | −2.969247 |
| H | 0.534953 | −2.376184 | −2.108033 |
| H | −1.488667 | 1.16877 | −2.83788 |
| H | −0.528053 | 2.439978 | −2.073548 |
| H | 0.16717 | 1.458673 | −3.401695 |
| H | −1.405677 | −1.5978 | 2.632711 |
| H | −0.204575 | −2.626067 | 1.826795 |
| H | 0.236313 | −1.690464 | 3.278597 |
| H | 0.078386 | 2.279972 | 2.281213 |
| H | −0.335329 | 1.062214 | 3.518257 |
| H | 1.326565 | 1.194642 | 2.922263 |
| H | −1.346156 | 3.934205 | 0.95383 |
| H | −0.821252 | 2.395546 | 0.232561 |
| H | −1.75711 | 3.562142 | −0.735748 |
| H | −2.678417 | 3.030533 | 2.849433 |
| H | −3.968479 | 1.833109 | 2.552455 |
| H | −2.259604 | 1.341289 | 2.466226 |
| H | −3.693986 | 4.539871 | 0.93625 |
| H | −4.222805 | 3.755028 | −0.571039 |
| H | −5.000507 | 3.34859 | 1.00026 |

**Table S19.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| H | −1.15956 | −2.524347 | −0.177968 |
| H | −1.895493 | −4.010039 | −0.816106 |
| H | −1.617827 | −2.640888 | −1.908507 |
| H | −3.793981 | −4.030373 | 0.820848 |
| H | −3.056923 | −2.60649 | 1.604164 |
| H | −4.76542 | −2.555582 | 1.070682 |
| H | −4.012479 | −4.059447 | −1.81 |
| H | −5.314943 | −2.946022 | −1.386426 |
| H | −4.101041 | −2.47508 | −2.622515 |
| H | 2.090302 | 4.034964 | 0.448693 |
| H | 1.254599 | 2.46616 | 0.417958 |
| H | 2.619072 | 2.730444 | 1.544378 |
| H | 2.740832 | 3.895084 | −2.135577 |
| H | 3.224948 | 2.289008 | −2.736776 |
| H | 1.593363 | 2.557979 | −2.017514 |
| H | 4.306993 | 4.316439 | −0.260585 |
| H | 5.043437 | 2.933149 | 0.587188 |
| H | 5.229765 | 3.130826 | −1.190627 |
| H | 3.923798 | −4.478648 | 0.89249 |
| H | 4.460682 | −3.661866 | −0.594074 |
| H | 5.151356 | −3.208112 | 1.005638 |
| H | 1.551984 | −4.041064 | 0.652424 |
| H | 0.973361 | −2.471905 | 0.044247 |
| H | 2.036902 | −3.479998 | −0.966496 |
| H | 2.624495 | −3.13165 | 2.72049 |
| H | 3.928723 | −1.919027 | 2.592757 |
| H | 2.232689 | −1.424196 | 2.399063 |

**Table S20.** Cartesian geometry of product (−18.9 kcal/mol) in Figure S8 in Angstrom [Å].

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| C | 4.640825 | −0.824658 | 0.619754 |
| N | 3.357276 | −1.2169 | 0.281087 |
| C | 2.597076 | −0.083651 | 0.034334 |
| N | 3.447852 | 0.996954 | 0.173722 |
| C | 4.691575 | 0.531543 | 0.567257 |
| C | 3.050106 | −2.663935 | −0.113054 |
| C | 3.342747 | 2.474631 | −0.235756 |
| N | 1.21825 | −0.042391 | −0.080174 |
| Si | −0.082026 | −0.225551 | −1.314638 |
| C | −0.219293 | 1.035224 | −2.705395 |
| Si | 0.081797 | 0.225437 | 1.315023 |
| C | 0.324443 | 1.881465 | 2.181035 |
| N | −1.218414 | 0.043153 | 0.08044 |
| C | −2.597256 | 0.083595 | −0.033746 |
| N | −3.357681 | 1.215956 | −0.283755 |
| C | −4.64133 | 0.822469 | −0.620576 |
| C | −4.691923 | −0.533561 | −0.563652 |

**Table S20.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| N | −3.447951 | −0.997558 | −0.169357 |
| C | −3.050781 | 2.66451 | 0.105216 |
| C | −3.341763 | −2.474396 | 0.242857 |
| C | 0.224509 | −1.036611 | 2.704116 |
| C | −0.329911 | −1.881756 | −2.178865 |
| H | −5.518564 | −1.204635 | −0.750738 |
| H | −5.42272 | 1.526959 | −0.865385 |
| H | 5.518227 | 1.20198 | 0.756586 |
| H | 5.421967 | −1.530079 | 0.862682 |
| H | 0.320547 | −1.948051 | −3.065918 |
| H | −0.177737 | −2.786629 | −1.578416 |
| H | −1.363777 | −1.887103 | −2.563396 |
| H | −0.147671 | 2.085233 | −2.40983 |
| H | 0.549732 | 0.834386 | −3.470978 |
| H | −1.195357 | 0.88327 | −3.199863 |
| H | −0.542482 | −0.838271 | 3.472332 |
| H | 0.154112 | −2.0864 | 2.407426 |
| H | 1.201831 | −0.883279 | 3.195729 |
| H | 0.165796 | 2.786528 | 1.58253 |
| H | −0.324306 | 1.942529 | 3.069762 |
| H | 1.359148 | 1.891744 | 2.563075 |
| C | −4.192625 | 3.589416 | −0.363616 |
| C | −2.986972 | 2.684078 | 1.645086 |
| C | −1.753801 | 3.144423 | −0.556979 |
| H | −1.532379 | 4.157217 | −0.190394 |
| H | −0.913374 | 2.492123 | −0.320282 |
| H | −1.876862 | 3.191781 | −1.647885 |
| H | −2.722381 | 3.694053 | 1.990538 |
| H | −3.966661 | 2.41659 | 2.067852 |
| H | −2.237823 | 1.978533 | 2.022059 |
| H | −3.892525 | 4.621258 | −0.134742 |
| H | −4.357108 | 3.516386 | −1.449015 |
| H | −5.133515 | 3.394056 | 0.170324 |
| C | −4.472175 | −2.739365 | 1.269633 |
| C | −3.54182 | −3.351202 | −1.006786 |
| C | −2.012255 | −2.77196 | 0.931862 |
| H | −4.348041 | −3.761347 | 1.655308 |
| H | −4.407671 | −2.036163 | 2.113119 |
| H | −5.473138 | −2.673827 | 0.82287 |
| H | −3.582532 | −4.402807 | −0.687619 |
| H | −4.487567 | −3.12004 | −1.517945 |
| H | −2.715999 | −3.240251 | −1.720264 |
| H | −2.005056 | −3.839415 | 1.193636 |
| H | −1.155224 | −2.564762 | 0.289752 |
| H | −1.926081 | −2.192077 | 1.857485 |
| C | 4.472254 | 2.739961 | −1.263449 |
| C | 2.0127 | 2.774912 | −0.922598 |
| C | 3.545263 | 3.349193 | 1.015054 |

**Table S20.** *Cont.*

| Atomtype | X Coordinates | Y Coordinates | Z Coordinates |
|---|---|---|---|
| H | 2.006286 | 3.84289 | −1.182239 |
| H | 1.924954 | 2.196882 | −1.849183 |
| H | 1.156414 | 2.567325 | −0.279647 |
| H | 4.349623 | 3.763143 | −1.646427 |
| H | 5.473685 | 2.671176 | −0.818231 |
| H | 4.405121 | 2.038956 | −2.108563 |
| H | 3.585773 | 4.401303 | 0.69756 |
| H | 2.720559 | 3.237447 | 1.729718 |
| H | 4.491755 | 3.116949 | 1.524331 |
| C | 4.192572 | −3.590593 | 0.350713 |
| C | 1.753984 | −3.14623 | 0.549112 |
| C | 2.984489 | −2.67746 | −1.652923 |
| H | 3.892581 | −4.621479 | 0.117426 |
| H | 5.132989 | −3.392485 | −0.183049 |
| H | 4.357863 | −3.522436 | 1.436303 |
| H | 2.717904 | −3.68558 | −2.002211 |
| H | 2.235967 | −1.969224 | −2.02607 |
| H | 3.964024 | −2.409548 | −2.075758 |
| H | 1.531435 | −4.15732 | 0.178536 |
| H | 1.878712 | −3.198223 | 1.639633 |
| H | 0.9136 | −2.492418 | 0.31655 |

## References


1. Sheldrick, G.M. *SHELX–97 Program for Crystal Structure Determination*; Universität Göttingen: Göttingen, Germany, 1997.
2. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; et al. *Gaussian 09, Revision B.01*; Gaussian, Inc.: Wallingford, CT, USA, 2009.
3. Lee, C.; Yang, W.; Parr, R.G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **1988**, *37*, 785–789.
4. Becke, A.D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648.
5. Hay, P.J.; Wadt, W.R. Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. *J. Chem. Phys.* **1985**, *82*, 299–310.
6. Petersson, G.A.; Al-Laham, M.A. A complete basis set model chemistry. II. Open-shell systems and the total energies of the first-row atoms. *J. Chem. Phys.* **1991**, *94*, 6081–6090.
7. Blaudeau, J.-P.; McGrath, M.P.; Curtiss, L.A.; Radom, L. Extension of Gaussian-2 (G2) theory to molecules containing third-row atoms K and Ca. *J. Chem. Phys.* **1997**, *107*, 5016–5021.
8. Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
9. Weigend, F. Accurate Coulomb-fitting basis sets for H to Rn. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057–1065.