

## **Extremely narrow SiON angles in siloxy-substituted pyrrolidines and piperidines: a computational investigation**

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### **Supplementary information**

#### **Potential-energy scans for SiON angles**

##### *Pyrrole derivatives*

Calculations were performed on derivatives of pyrrole to provide a reference point from which any angle contractions in siloxy derivatives of saturated-rings could be measured. It was reassuring, therefore, to find that no acute angle contractions were detected for any of the derivatives studied; the SiON angles ranged from 109.6 to 115.6° (Table S1).

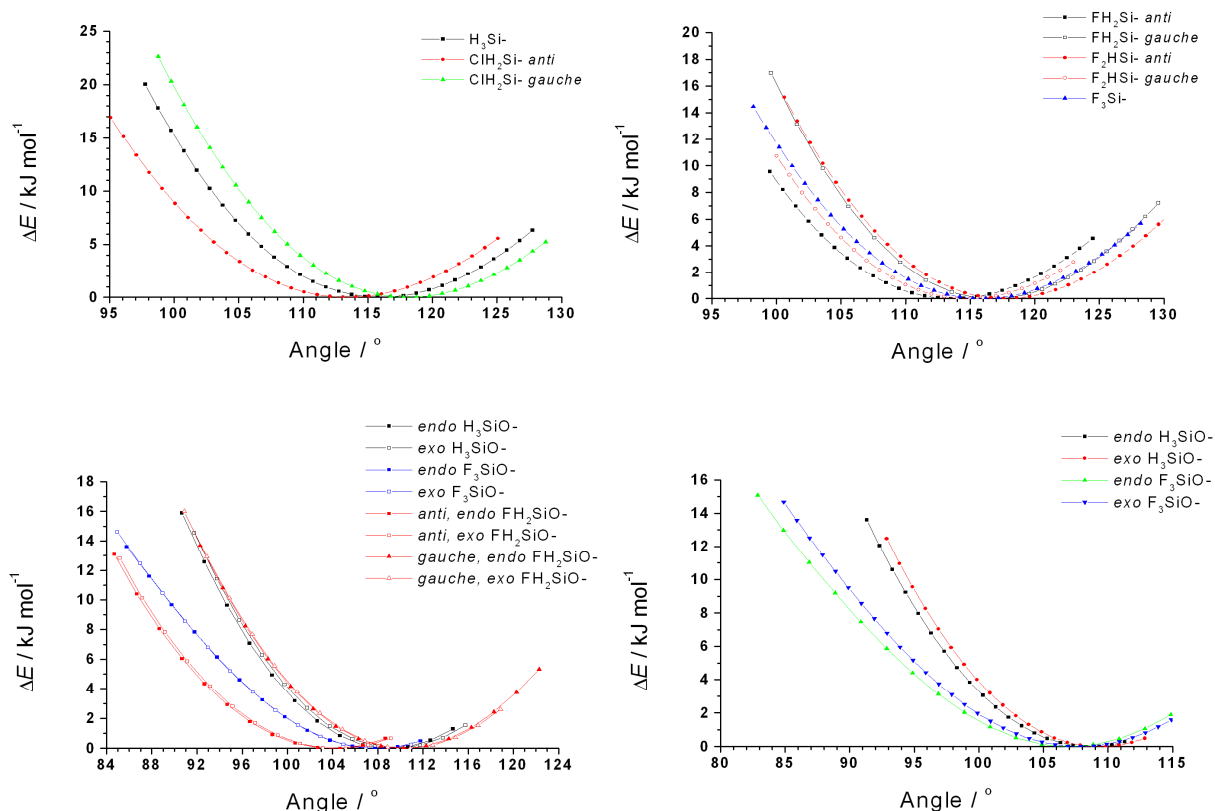
The potential-energy scans (RHF/6-31G\*) of the molecules studied revealed that the SiON unit is very flexible. At room temperature *anti*-H<sub>3</sub>SiO-pyrrole is expected to vibrate by ±6.5° about its minimum angle, according to a classical model of the vibration. This value is estimated by reference to Figure S1a, based on the maximum deviation from the minimum at 2.5 kJ mol<sup>-1</sup>, representing *kT* at ambient temperature. *Anti*-H<sub>3</sub>SiO-pyrrole displayed the lowest flexibility of any pyrrole derivative studied. The *anti*, *anti* and *gauche*, *anti* conformers of the ClH<sub>2</sub>SiO- derivative are expected to vibrate by about ±7.0° and ±6.5° about their minimum angle, respectively.

**Table S1** Calculated distances and angles (MP2/6-311++G\*\*) for siloxy derivatives of pyrrole, pyrrolidine and piperidine, and wavenumbers (B3PW91/6-311++G\*\*) associated with the SiON angle bends for those molecules.<sup>a</sup>

Molecule	Orientation <sup>b</sup>	SiO	ON	NC av.	SiON	ONC(4)	ONC(10)	C(4)NC(5)	SiONC(4)	SiONC(5)	Wavenumber
H <sub>3</sub> SiO-pyrrole	<i>anti, anti</i>	170.5	138.5	137.2	112.8	123.5	123.5	111.8	-96.7	96.7	101
F <sub>3</sub> SiO-pyrrole	<i>anti, anti</i>	165.3	139.5	137.2	113.2	122.9	122.9	112.2	-98.7	98.7	120
FH <sub>2</sub> SiO-pyrrole	<i>anti, anti</i>	169.1	139.0	137.2	109.6	123.3	123.3	111.8	-97.7	97.7	81
FH <sub>2</sub> SiO-pyrrole	<i>gauche, anti</i>	168.2	138.6	136.8	114.2	122.6	124.5	112.2	-79.7	111.1	98
F <sub>2</sub> HSiO-pyrrole	<i>anti, anti</i>	166.4	139.1	137.1	115.6	123.1	123.1	112.2	-97.9	97.9	70
F <sub>2</sub> HSiO-pyrrole	<i>gauche, anti</i>	167.0	139.1	137.1	111.5	124.1	122.6	112.2	-107.7	85.2	75
ClH <sub>2</sub> SiO-pyrrole	<i>anti, anti</i>	169.5	139.0	137.2	110.1	123.3	123.3	111.8	-98.0	98.0	73
ClH <sub>2</sub> SiO-pyrrole	<i>gauche, anti</i>	168.7	138.8	137.2	113.8	123.2	123.0	111.9	-102.1	95.0	98
H <sub>3</sub> SiO-pyrrolidine	<i>anti, anti, exo</i>	168.8	144.9	146.6	103.8	108.5	108.5	103.5	-124.1	124.1	101
H <sub>3</sub> SiO-pyrrolidine	<i>anti, anti, endo</i>	168.7	147.1	147.1	102.7	104.7	104.7	102.8	-126.1	126.1	110
F <sub>3</sub> SiO-pyrrolidine	<i>anti, anti, exo</i>	164.7	147.0	146.6	93.0	109.1	109.1	104.6	-123.2	123.2	33
F <sub>3</sub> SiO-pyrrolidine	<i>anti, anti, endo</i>	164.5	149.1	147.0	93.8	105.1	105.1	103.6	-125.5	125.5	45
FH <sub>2</sub> SiO-pyrrolidine	<i>anti, anti, exo</i>	168.3	145.6	146.6	91.2	109.4	109.4	104.3	-123.1	123.1	71
FH <sub>2</sub> SiO-pyrrolidine	<i>anti, anti, endo</i>	168.2	147.8	147.0	90.7	105.6	105.6	103.5	-125.4	125.4	79
FH <sub>2</sub> SiO-pyrrolidine	<i>gauche, anti, exo</i>	166.7	145.3	146.6	104.9	108.5	108.2	103.7	-120.1	128.0	125
FH <sub>2</sub> SiO-pyrrolidine	<i>gauche, anti, endo</i>	166.6	147.4	147.1	104.3	104.8	104.5	102.9	-122.3	129.9	181
H <sub>3</sub> SiO-piperidine	<i>anti, anti, equatorial</i>	168.8	146.0	146.3	102.9	105.9	105.9	110.6	-121.2	121.2	86
H <sub>3</sub> SiO-piperidine	<i>anti, anti, axial</i>	168.8	146.7	146.9	101.3	106.1	106.1	111.3	-120.7	120.7	93
F <sub>3</sub> SiO-piperidine	<i>anti, anti, equatorial</i>	165.4	148.6	146.4	85.9	107.3	107.3	112.0	-119.7	119.7	24
F <sub>3</sub> SiO-piperidine	<i>anti, anti, axial</i>	165.9	149.4	147.1	82.9	107.5	107.5	112.4	-119.3	119.3	61

<sup>a</sup> Bond lengths in pm, angles and torsion angles in degrees, and wavenumbers in cm<sup>-1</sup>. Coordinates for each of the calculations (MP2/6-311++G\*\*) are given in Tables S3–S22. <sup>b</sup> See text for definitions of orientations.

**Figure S1** Potential-energy scans (RHF/6-31G\*) of  $\angle$ SiON for (a) H<sub>3</sub>SiO-pyrrole and ClH<sub>2</sub>SiO-pyrrole, (b) FH<sub>2</sub>SiO-pyrrole, F<sub>2</sub>HSiO-pyrrole and F<sub>3</sub>SiO-pyrrole, (c) H<sub>3</sub>SiO-pyrrolidine, F<sub>3</sub>SiO-pyrrolidine and FH<sub>2</sub>SiO-pyrrolidine, and (d) H<sub>3</sub>SiO-piperidine and F<sub>3</sub>SiO-piperidine.



The fluorinated silyl derivatives, on the other hand, are calculated to vibrate, in a classical sense, by about  $\pm 7$  to  $\pm 7.5^\circ$  about their minimum angles (Figure S1b). Similar degrees of flexibility were reported for silylhydroxylamine derivatives.<sup>1-5</sup> For the pyrrole derivatives the wavenumbers (B3PW91/6-311++G\*\*) associated with the SiON angle bending are shown in Table S1. Where two conformations are possible, the lower values are always achieved for the *anti*, *anti* conformers.

#### *Pyrrolidine derivatives*

The nature of the saturated ring system of pyrrolidine allows the silyl compounds studied to adopt two different conformations that can facilitate angle contraction, ignoring possible conformations originating from the silyl moiety for the moment. Oxygen can be

in either an *endo* or an *exo* position relative to the ring. If different conformations have to be taken into account for the silyl moiety then, for example, a *gauche*, *anti*, *endo* conformation would describe first the position of the silyl substituent determining the conformation, *i.e.* the substituent determining the conformation of the silyl group is *gauche* to N(3), secondly the position of Si relative to the bisector of the C(4)NC(5) angle, which is *anti* for the molecules presented here, and thirdly the position of the oxygen atom relative to the ring, which can be either *endo* or *exo*.

The *anti*, *anti*, *exo* and *anti*, *anti*, *endo* conformers of the H<sub>3</sub>SiO- derivative show relatively narrow SiON angles of 103.8 and 102.7°, respectively. These values are significantly smaller than that reported for *anti*, *anti*-1-H<sub>3</sub>SiO-pyrrole, which has a calculated SiON angle of 112.8°. A similar observation was made for the SiON angle in 1-F<sub>3</sub>SiO-pyrrolidine, where the *anti*, *anti*, *exo* and *anti*, *anti*, *endo* conformers display SiON angles of 93.0 and 93.8°, respectively. The differences between the SiON angles of these two conformers and that of *anti*, *anti*-1-F<sub>3</sub>SiO-pyrrole are, at 19.4 and 20.0° for the *exo* and *endo* conformers, respectively, much more pronounced than for the *anti*, *anti*-H<sub>3</sub>SiO-derivative. For 1-FH<sub>2</sub>SiO-pyrrolidine it was noted that the difference between the SiON angle of the *anti*, *anti*, *endo* and *anti*, *anti*, *exo* conformers is similar to that between the *anti*, *anti*, *endo* and *anti*, *anti*, *exo* conformers of 1-F<sub>3</sub>SiO-pyrrolidine. The *gauche*, *anti*, *endo* and *gauche*, *anti*, *exo* conformers, on the other hand, show similar characteristics to the *anti*, *anti*-H<sub>3</sub>SiO- derivatives in terms of the differences between the SiON angles of the pyrrole and equivalent pyrrolidine derivatives. This shows that it is the substituent on Si that is in the *anti* position that has the most significant effect on the SiON angle. The values obtained from the theoretical methods for the pyrrolidine derivatives are very similar to the values obtained for the equivalent hydroxylamine derivatives. This suggests that the saturated ring system facilitates SiON angle contraction. It can also be concluded that *endo* and *exo* conformations have little effect on the SiON angle contraction and that, in terms of facilitating the Si⋯N interactions, the pyrrolidine moiety behaves similarly to the *N,N*-dimethylamino donor group.<sup>1-5</sup>

It is interesting to note that the SiO bond lengths appear to be relatively constant for each pyrrolidine derivative (Table S1). Also, with increasing electron-withdrawing capabilities of the silicon substituents, the SiO distance decreases. For *anti*, *anti*-1-F<sub>3</sub>SiO-pyrrolidine

*r*SiO was 4 pm shorter than for *anti*, *anti*-1-H<sub>3</sub>SiO-pyrrolidine. The ON distance, on the other hand, is noted to be longer by about 2 pm when the pyrrolidine group is *endo* to oxygen. The NC bond distance is relatively constant, although small differences of about 0.5 pm were noted between *endo* and *exo* conformations of the pyrrolidine moiety. Furthermore, the ONC and C(4)NC(5) angles for the pyrrolidine derivatives were wider by about 4 and 1°, respectively, for the *exo*-positioned pyrrolidine moiety compared with the *endo*-positioned one. Another notable difference was in  $\angle$ SiONC(4/5), where the absolute values for the conformers with *exo*-positioned oxygen atoms were about 2° smaller than those with *endo*-positioned atoms.

In all cases the *endo* conformation was lower in energy than the *exo* conformation (Table 2 in main section). However, the differences in energy are sufficiently low that the Boltzmann equation predicts that both would be present in significant amounts in a gas-phase sample at the temperature that would be required for a GED experiment.

The flexibility at room temperature of the SiON angles for each pyrrolidine derivative was estimated using potential-energy scans (RHF/6-31G\*). As shown in Figure S1c all the derivatives are expected to vibrate, in a classical sense, by between  $\pm 7$  and  $\pm 9.5^\circ$  about their minimum angles. Compared to silylhydroxylamine derivatives this is an increase of up to  $2.5^\circ$ .<sup>1-5</sup>

Derivatives with the pyrrolidine moiety *anti* to oxygen generally exhibit more flexibility, except in the case of 1-FH<sub>2</sub>SiO-pyrrolidine, whose *anti*, *anti*, *endo* and *anti*, *anti*, *exo* conformers are predicted to be equally flexible. 1-FH<sub>2</sub>SiO- and 1-F<sub>3</sub>SiO-pyrrolidine, with oxygen *exo* to their pyrrolidine group, display most SiON flexibility, at  $\pm 9.5^\circ$ . *Anti*, *anti*-1-H<sub>3</sub>SiO-pyrrolidine is expected to have the least flexible SiON bend in this series of compounds.

Analysis of calculated wavenumbers (B3PW91/6-311++G\*\*) showed some interesting trends with regard to the extent of the angle contraction in relation to the substituents on silicon (Table S1). The lowest wavenumber associated with the SiON angle bend was calculated for *anti*, *anti*, *exo*-1-F<sub>3</sub>SiO-pyrrolidine, at 33 cm<sup>-1</sup>, whereas the largest was seen for the *gauche*, *anti*, *endo* conformer of 1-FH<sub>2</sub>SiO-pyrrolidine, at 181 cm<sup>-1</sup>. Because both *anti*, *anti*, *endo/exo*-1-F<sub>3</sub>SiO-pyrrolidine and *anti*, *anti*, *endo/exo*-1-FH<sub>2</sub>SiO-pyrrolidine displayed acute contractions of their SiON angle, it was thought that the

wavenumber associated with the SiON bending would be fairly similar as their angles are relatively close. However, it appears that the wavenumbers are not linked to the SiON angles but rather to the number of electron-withdrawing silicon substituents and their electron-withdrawing strength. The wavenumbers associated with the SiON angle bend for *anti, anti, endo*- and *anti, anti, exo*-1-FH<sub>2</sub>SiO-pyrrolidine were calculated at 79 and 71 cm<sup>-1</sup>, respectively. In general, the wavenumbers were calculated to be slightly higher, by about 8 or 9 cm<sup>-1</sup>, for conformers with a pyrrolidine group in an *endo* position, with the exception of the *gauche, anti, endo* and *gauche, anti, exo* conformers, for which the difference was 56 cm<sup>-1</sup>. These conformers had the two largest SiON angles in the pyrrolidine series.

When the presence of a strong Si···N interaction leads to a highly acute angle there is a notable difference between the values for that angle calculated using the RHF and MP2 methods. RHF tends to predict SiON angles that are considerably wider than those calculated using MP2. Furthermore, as seen for (F<sub>3</sub>C)F<sub>2</sub>SiONMe<sub>2</sub>,<sup>6</sup> the difference in the SiON angle between RHF and MP2 can be in excess of 30°. From theory, 1-H<sub>3</sub>SiO-pyrrolidine, 1-F<sub>3</sub>SiO-pyrrolidine and 1-FH<sub>2</sub>SiO-pyrrolidine would be expected to exhibit narrow SiON angles and show marked differences between the values obtained from RHF and MP2 calculations. The largest difference between the RHF and MP2 methods was found for *anti,anti*-1-F<sub>3</sub>SiO-pyrrolidine, at 17.9°. *Anti, anti*-1-H<sub>3</sub>SiO-pyrrolidine showed the smallest difference (8.8°) for a compound expected to be influenced by the geminal donor-acceptor interactions. The differences are significant and support the hypothesis that the geminal donor-acceptor interactions will exert a strong influence on the molecular structures of 1-H<sub>3</sub>SiO-pyrrolidine, 1-F<sub>3</sub>SiO-pyrrolidine and 1-FH<sub>2</sub>SiO-pyrrolidine.

#### *Piperidine derivatives*

The boat conformations of the piperidine derivatives were ignored in this study because the energy differences between the lowest energy conformers (chair configuration) and the boat configurations were in excess of 30 kJ mol<sup>-1</sup>.

The nature of the saturated ring system of piperidine allows the silyl compounds to adopt two different chair conformations, ignoring possible conformations originating from the

silyl moiety. Oxygen can be in either an axial or an equatorial position relative to the ring. If different conformations of the silyl moiety are taken into account then, for example, the term *anti, anti, axial* would describe first the position of the silyl substituent, *i.e.* one substituent on the silyl group is *anti* to N(3), secondly the position of Si relative to the bisector of the C(4)NC(5) angle, which is *anti* for the molecules presented here, and thirdly the relative position of the oxygen atom relative to the ring, which can either be axial or equatorial. Both chair forms were studied in both their *anti, anti, axial* and *anti, anti, equatorial* conformations, and so these conformations are from now on referred to simply as axial or equatorial.

The SiON angles calculated for the *anti, anti*-1-H<sub>3</sub>SiO-derivatives of piperidine were similar to those obtained for the pyrrolidine analogues. Both axial and equatorial conformations display angles that are close to 100°. The SiON angle in the axial conformer is 101.3°, narrower than that in the equatorial conformer by 1.6°. The same observation was made for the 1-F<sub>3</sub>SiO-piperidine derivative, although the difference between the axial and equatorial conformers is, at 3°, almost twice the difference between the two *anti,anti*-1-H<sub>3</sub>SiO-piperidine conformers. The angles in both conformers of 1-F<sub>3</sub>SiO-piperidine are more acute, with SiON angles for the axial and equatorial conformers of 82.9 and 85.9°, respectively. In fact, these values lie within one standard deviation of the narrowest SiON angle determined by GED, that of the *anti* conformer of (F<sub>3</sub>C)F<sub>2</sub>SiONMe<sub>2</sub> [84.4(32)°].<sup>6</sup>

The bond distances in Table S1 show that the axial conformers of both piperidine derivatives have slightly longer bond distances than their corresponding equatorial conformers. The bond angles, apart from the SiON angle, of the axial conformers were marginally wider than those of the equatorial conformer. The torsion angles, though, were marginally wider for the equatorial conformers. The SiON angles were narrower for the axial conformer, and this becomes more pronounced on changing the substituents on silicon from hydrogen to fluorine. These observations are very different to those made for the pyrrolidine derivatives.

Unlike the pyrrolidine derivatives, the energy differences between the *anti, anti, equatorial* and *anti, anti, axial* conformers of 1-H<sub>3</sub>SiO- and 1-F<sub>3</sub>SiO-piperidine are substantial (Table 2 in main section). Furthermore, the equatorial conformations are

calculated to be more stable than the axial conformers. For 1-H<sub>3</sub>SiO-piperidine, a 6.6 kJ mol<sup>-1</sup> difference in energy would correspond to approximately 94% of the equatorial and 6% of the axial conformer in the gas phase (for an experiment performed at room temperature), if the equatorial and axial conformers reported here were the only conformations. For 1-F<sub>3</sub>SiO-piperidine, about 91% of the equatorial and 9% of the axial conformer would be expected in the gas phase, if only these two conformations are considered. If the mole fractions calculated from the theoretical data (MP2/6-311++G\*\*) were true experimentally, the axial conformers of both piperidine derivatives would contribute little towards the GED pattern. This could mean that structure refinements on the equatorial conformers alone might produce adequate structure determinations.

As explained in relation to the pyrrolidine derivatives earlier, molecules that exhibit a very acute angle contraction often show great differences in the SiON angle calculated by different methods. The most pronounced difference is seen between RHF and MP2 methods. This was observed for both piperidine derivatives (Table S2).

**Table S2** Values of the calculated SiON angle for the *anti*, *anti*, *endo* conformers of 1-H<sub>3</sub>SiO and 1-F<sub>3</sub>SiO-pyrrolidine, *anti*, *anti*, *exo*-1-FH<sub>2</sub>SiO-pyrrolidine, and the SiON angle for *anti*, *anti*, axial and *anti*, *anti*, equatorial conformations for the piperidine derivatives.<sup>a</sup>

Calculation	Pyrrolidines			Piperidines			
	H <sub>3</sub> SiO-	F <sub>3</sub> SiO-	FH <sub>2</sub> SiO-	H <sub>3</sub> SiO- equatorial	axial	F <sub>3</sub> SiO- equatorial	axial
RHF	111.9	111.7	107.4	112.3	111.5	111.7	111.1
MP2	102.7	93.8	90.7	102.9	101.3	85.9	82.9
B3PW91	105.3	97.8	90.2	105.6	104.0	88.1	83.3

<sup>a</sup> All angles in degrees. The 6-311++G\*\* basis set was used in all cases.

For 1-H<sub>3</sub>SiO-piperidine the differences between the RHF and MP2 values of the SiON angle were 9.4 and 10.2° for the *anti*, *anti*, equatorial and *anti*, *anti*, axial conformations, respectively. Compared to *anti*, *anti*-1-H<sub>3</sub>SiO-pyrrolidine, the difference between the RHF and MP2 methods is larger for the piperidine derivatives. This indicates that the geminal donor-acceptor interactions are stronger in the piperidine derivatives. The differences between the SiON angles obtained from RHF and MP2 for the *anti*, *anti*-F<sub>3</sub>SiO derivative are 25.8 and 28.2° for the equatorial and axial conformers, respectively.



Again the differences are more substantial for the *anti*, *anti*-1-F<sub>3</sub>SiO-piperidine conformers than for the equivalent pyrrolidine derivative, which showed a smaller difference (17.8°) in the SiON angles between RHF and MP2 methods.

From the potential-energy plots of the SiON angles of the piperidine derivatives it was observed that the shapes of the curves around the minimum-energy SiON angles were fairly wide [Figure S1(d)]. From the calculations (RHF/6-31G\*) the *anti*, *anti*, axial and *anti*, *anti*, equatorial conformers of 1-H<sub>3</sub>SiO-piperidine and 1-F<sub>3</sub>SiO-piperidine are expected to vibrate, in a classical sense, by  $\pm 7$  and  $\pm 8^\circ$  about their minimum angles. The SiON angles are expected to show very similar flexibilities to those of the silylhydroxylamines, which is supported by low wavenumbers associated with the SiON angle bend (Table S1). In fact, equatorial-1-F<sub>3</sub>SiO-piperidine has the lowest calculated wavenumber associated with the SiON angle deformation of all the molecules presented in this work.

The investigation of both 1-H<sub>3</sub>SiO-piperidine and 1-F<sub>3</sub>SiO-piperidine showed that the piperidine moiety is expected to accommodate angle contractions associated with the geminal donor-acceptor interactions. The theoretical data indicate that the piperidine group is a very facile donor for silyl compounds with the SiON motif. The calculated data suggest that the piperidine moiety is expected to yield even more acute angles than have previously been achieved with the *N,N*-dimethylamine donor group.<sup>1</sup>

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**Table S3** Calculated coordinates (MP2/6-311++G\*\*) for *anti, anti*-H<sub>3</sub>SiO-pyrrole.<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	-0.9589	-2.0786	0.0000
O(2)	0.5189	-1.2300	0.0000
N(3)	0.3467	0.1446	0.0000
C(4)	0.3860	0.9113	1.1350
H(5)	0.4068	0.4512	2.1118
C(6)	0.3860	2.2369	0.7104
H(7)	0.3795	3.1000	1.3619
C(8)	0.3860	2.2369	-0.7104
H(9)	0.3795	3.1000	-1.3619
C(10)	0.3860	0.9113	-1.1350
H(11)	0.4068	0.4512	-2.1118
H(12)	-0.5361	-3.4852	0.0000
H(13)	-1.7269	-1.7341	-1.2080
H(14)	-1.7269	-1.7341	1.2080

<sup>a</sup> Coordinates in Å.

**Table S4** Calculated coordinates (MP2/6-311++G\*\*) for *anti, anti*-F<sub>3</sub>SiO-pyrrole.<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	-0.2084	1.4829	0.0000
O(2)	-1.0374	0.0533	0.0000
N(3)	-0.2040	-1.0651	0.0000
C(4)	0.1005	-1.7672	1.1392
H(5)	-0.1231	-1.3642	2.1154
C(6)	0.7083	-2.9407	0.7112
H(7)	1.1189	-3.7002	1.3616
C(8)	0.7083	-2.9407	-0.7112
H(9)	1.1189	-3.7002	-1.3616
C(10)	0.1005	-1.7672	-1.1392
H(11)	-0.1231	-1.3642	-2.1154
H(12)	-1.3113	2.6155	0.0000
H(13)	0.7083	1.6306	-1.2839
H(14)	0.7083	1.6306	1.2839

<sup>a</sup> Coordinates in Å.

**Table S5** Calculated coordinates (MP2/6-311++G\*\*) for *anti, anti*-FH<sub>2</sub>SiO-pyrrole.<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	0.8966	1.6063	0.0000
O(2)	-0.6030	0.8244	0.0000
N(3)	-0.4096	-0.5523	0.0000
C(4)	-0.4554	-1.3203	1.1365
H(5)	-0.4804	-0.8603	2.1130
C(6)	-0.4554	-2.6438	0.7107
H(7)	-0.4483	-3.5071	1.3614
C(8)	-0.4554	-2.6438	-0.7107
H(9)	-0.4483	-3.5071	-1.3614
C(10)	-0.4554	-1.3203	-1.1365
H(11)	-0.4804	-0.8603	-2.1130
H(12)	0.5183	3.1680	0.0000
H(13)	1.6306	1.2876	-1.2265
H(14)	1.6306	1.2876	1.2265

<sup>a</sup> Coordinates in Å.

**Table S6** Calculated coordinates (MP2/6-311++G\*\*) for *gauche, anti*-FH<sub>2</sub>SiO-pyrrole.<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	-1.9419	-0.4095	0.2462
O(2)	-0.6392	-0.7069	-0.7755
N(3)	0.5787	-0.2599	-0.2880
C(4)	1.5724	-1.1129	0.1072
H(5)	1.3967	-2.1767	0.1589
C(6)	2.6835	-0.3164	0.3708
H(7)	3.6367	-0.6772	0.7311
C(8)	2.3289	1.0295	0.0909
H(9)	2.9551	1.9040	0.1988
C(10)	1.0060	1.0419	-0.3432
H(11)	0.3440	1.8302	-0.6689
H(12)	-3.0327	-1.1895	-0.3336
H(13)	-2.3364	1.1539	0.1895
H(14)	-1.5675	-0.7210	1.6262

<sup>a</sup> Coordinates in Å.

**Table S7** Calculated coordinates (MP2/6-311++G\*\*) for *anti, anti*-F<sub>2</sub>HSiO-pyrrole.<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	0.6771	-1.6941	0.0000
O(2)	1.2007	-0.1150	0.0000
N(3)	0.1995	0.8504	0.0000
C(4)	-0.2295	1.4836	1.1379
H(5)	0.0590	1.1242	2.1140
C(6)	-1.0363	2.5321	0.7108
H(7)	-1.5749	3.2066	1.3616
C(8)	-1.0363	2.5321	-0.7108
H(9)	-1.5749	3.2066	-1.3616
C(10)	-0.2295	1.4836	-1.1379
H(11)	0.0590	1.1242	-2.1140
H(12)	1.8717	-2.5180	0.0000
H(13)	-0.2295	-1.9804	-1.2830
H(14)	-0.2295	-1.9804	1.2830

<sup>a</sup> Coordinates in Å.

**Table S8** Calculated coordinates (MP2/6-311++G\*\*) for *gauche, anti*-F<sub>2</sub>HSiO-pyrrole.<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	1.5970	-0.0880	0.3331
O(2)	0.4076	-0.5544	-0.7426
N(3)	-0.8604	-0.2340	-0.2694
C(4)	-1.4603	0.9884	-0.4412
H(5)	-0.9062	1.8292	-0.8306
C(6)	-2.7742	0.8319	-0.0124
H(7)	-3.5141	1.6192	0.0204
C(8)	-2.9488	-0.5230	0.3779
H(9)	-3.8500	-0.9778	0.7645
C(10)	-1.7388	-1.1814	0.1862
H(11)	-1.4242	-2.2050	0.3224
H(12)	2.9324	-0.7379	-0.2425
H(13)	1.3155	-0.5196	1.6915
H(14)	1.7693	1.5005	0.3016

<sup>a</sup> Coordinates in Å.

**Table S9** Calculated coordinates (MP2/6-311++G\*\*) for *anti, anti*-ClH<sub>2</sub>SiO-pyrrole.<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	0.8618	1.1958	0.0000
O(2)	-0.6281	0.3879	0.0000
N(3)	-0.4261	-0.9875	0.0000
C(4)	-0.4738	-1.7551	1.1363
H(5)	-0.4989	-1.2948	2.1127
C(6)	-0.4738	-3.0788	0.7108
H(7)	-0.4655	-3.9421	1.3615
C(8)	-0.4738	-3.0788	-0.7108
H(9)	-0.4655	-3.9421	-1.3615
C(10)	-0.4738	-1.7551	-1.1363
H(11)	-0.4989	-1.2948	-2.1127
H(12)	0.3551	3.1650	0.0000
H(13)	1.6034	0.8720	-1.2218
H(14)	1.6034	0.8720	1.2218

<sup>a</sup> Coordinates in Å.

**Table S10** Calculated coordinates (MP2/6-311++G\*\*) for *gauche, anti*-ClH<sub>2</sub>SiO-pyrrole.<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	1.6032	-0.8790	-0.0741
O(2)	0.2201	-0.8957	0.8916
N(3)	-0.8825	-0.2947	0.3003
C(4)	-1.8382	-0.9951	-0.3908
H(5)	-1.6781	-2.0267	-0.6664
C(6)	-2.8946	-0.1135	-0.5927
H(7)	-3.7935	-0.3362	-1.1505
C(8)	-2.5618	1.1148	0.0405
H(9)	-3.1568	2.0170	0.0637
C(10)	-1.3086	0.9674	0.6245
H(11)	-0.6851	1.6270	1.2085
H(12)	2.5629	-1.6677	0.6973
H(13)	2.2972	1.0282	-0.2960
H(14)	1.2882	-1.3990	-1.4067

<sup>a</sup> Coordinates in Å.

**Table S11** Calculated coordinates (MP2/6-311++G\*\*) for *anti, anti, exo*-H<sub>3</sub>SiO-pyrrolidine.<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	1.2855	-2.0646	0.0000
O(2)	-0.2453	-1.3530	0.0000
N(3)	0.0355	0.0687	0.0000
C(4)	-0.6395	0.6747	1.1514
C(5)	-0.6395	0.6747	-1.1514
C(6)	-0.6395	2.1620	0.7787
C(7)	-0.6395	2.1620	-0.7787
H(8)	-0.1030	0.4443	2.0745
H(9)	-1.6637	0.2760	1.2189
H(10)	-0.1030	0.4443	-2.0745
H(11)	-1.6637	0.2760	-1.2189
H(12)	-1.5102	2.6727	1.1966
H(13)	0.2568	2.6546	1.1625
H(14)	-1.5102	2.6727	-1.1966
H(15)	0.2568	2.6546	-1.1625
H(16)	1.0161	-3.5150	0.0000
H(17)	2.0452	-1.6865	1.2065
H(18)	2.0452	-1.6865	-1.2065

<sup>a</sup> Coordinates in Å.

**Table S12** Calculated coordinates (MP2/6-311++G\*\*) for *anti, anti, endo*-H<sub>3</sub>SiO-pyrrolidine.<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	-1.7281	-1.5934	0.0000
O(2)	-0.9491	-0.0974	0.0000
N(3)	0.4737	-0.4735	0.0000
C(4)	1.0492	0.2401	1.1494
C(5)	1.0492	0.2401	-1.1494
C(6)	1.0492	1.7373	0.7754
C(7)	1.0492	1.7373	-0.7754
H(8)	0.4786	0.0031	2.0488
H(9)	2.0694	-0.1427	1.2659
H(10)	0.4786	0.0031	-2.0488
H(11)	2.0694	-0.1427	-1.2659
H(12)	0.1497	2.2226	1.1589
H(13)	1.9195	2.2503	1.1936
H(14)	0.1497	2.2226	-1.1589
H(15)	1.9195	2.2503	-1.1936
H(16)	-3.1647	-1.2548	0.0000
H(17)	-1.3902	-2.3701	1.2074
H(18)	-1.3902	-2.3701	-1.2074

<sup>a</sup> Coordinates in Å.

**Table S13** Calculated coordinates (MP2/6-311++G\*\*) for *anti, anti, exo*-F<sub>3</sub>SiO-pyrrolidine.<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	-0.1688	-1.5094	0.0000
O(2)	-1.1743	-0.2048	0.0000
N(3)	-0.0581	0.7515	0.0000
C(4)	-0.1883	1.6390	1.1601
C(5)	-0.1883	1.6390	-1.1601
C(6)	0.7484	2.7919	0.7790
C(7)	0.7484	2.7919	-0.7790
H(8)	0.0948	1.1134	2.0738
H(9)	-1.2336	1.9715	1.2358
H(10)	0.0948	1.1134	-2.0738
H(11)	-1.2336	1.9715	-1.2358
H(12)	0.3941	3.7366	1.1968
H(13)	1.7545	2.6090	1.1621
H(14)	0.3941	3.7366	-1.1968
H(15)	1.7545	2.6090	-1.1621
H(16)	-1.1163	-2.7926	0.0000
H(17)	0.7484	-1.6326	1.2971
H(18)	0.7484	-1.6326	-1.2971

<sup>a</sup> Coordinates in Å.

**Table S14** Calculated coordinates (MP2/6-311++G\*\*) for *anti, anti, endo*-F<sub>3</sub>SiO-pyrrolidine.<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	-1.0457	-1.0559	0.0000
O(2)	-0.5513	0.5131	0.0000
N(3)	0.8969	0.1588	0.0000
C(4)	1.4655	0.8686	1.1551
C(5)	1.4655	0.8686	-1.1551
C(6)	1.4655	2.3628	0.7759
C(7)	1.4655	2.3628	-0.7759
H(8)	0.8929	0.6275	2.0515
H(9)	2.4828	0.4794	1.2706
H(10)	0.8929	0.6275	-2.0515
H(11)	2.4828	0.4794	-1.2706
H(12)	0.5674	2.8500	1.1601
H(13)	2.3359	2.8747	1.1934
H(14)	0.5674	2.8500	-1.1601
H(15)	2.3359	2.8747	-1.1934
H(16)	-2.6405	-1.0087	0.0000
H(17)	-0.6218	-1.8775	1.2968
H(18)	-0.6218	-1.8775	-1.2968

<sup>a</sup> Coordinates in Å.

**Table S15** Calculated coordinates (MP2/6-311++G\*\*) for *anti, anti, exo*-FH<sub>2</sub>SiO-pyrrolidine.<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	-1.2094	1.4184	0.0000
O(2)	0.4399	1.0841	0.0000
N(3)	0.1803	-0.3492	0.0000
C(4)	0.8364	-0.9642	1.1582
C(5)	0.8364	-0.9642	-1.1582
C(6)	0.8364	-2.4500	0.7789
C(7)	0.8364	-2.4500	-0.7789
H(8)	0.2882	-0.7338	2.0741
H(9)	1.8579	-0.5646	1.2368
H(10)	0.2882	-0.7338	-2.0741
H(11)	1.8579	-0.5646	-1.2368
H(12)	1.7071	-2.9605	1.1963
H(13)	-0.0593	-2.9440	1.1620
H(14)	1.7071	-2.9605	-1.1963
H(15)	-0.0593	-2.9440	-1.1620
H(16)	-1.3097	3.0390	0.0000
H(17)	-1.8622	0.9691	1.2341
H(18)	-1.8622	0.9691	-1.2341

<sup>a</sup> Coordinates in Å.

**Table S16** Calculated coordinates (MP2/6-311++G\*\*) for *anti, anti, endo*-FH<sub>2</sub>SiO-pyrrolidine.<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	-1.1245	-1.5119	0.0000
O(2)	-0.7107	0.1185	0.0000
N(3)	0.7262	-0.2276	0.0000
C(4)	1.3028	0.4762	1.1547
C(5)	1.3028	0.4762	-1.1547
C(6)	1.3028	1.9709	0.7759
C(7)	1.3028	1.9709	-0.7759
H(8)	0.7271	0.2396	2.0506
H(9)	2.3212	0.0894	1.2718
H(10)	0.7271	0.2396	-2.0506
H(11)	2.3212	0.0894	-1.2718
H(12)	0.4030	2.4558	1.1586
H(13)	2.1726	2.4839	1.1940
H(14)	0.4030	2.4558	-1.1586
H(15)	2.1726	2.4839	-1.1940
H(16)	-2.7494	-1.5241	0.0000
H(17)	-0.7128	-2.1878	1.2341
H(18)	-0.7128	-2.1878	-1.2341

<sup>a</sup> Coordinates in Å.



**Table S17** Calculated coordinates (MP2/6-311++G\*\*) for *gauche, anti, exo*-FH<sub>2</sub>SiO-pyrrolidine.<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	2.1111	-0.4073	-0.1281
O(2)	0.7502	-0.5825	0.8190
N(3)	-0.3493	-0.1473	-0.0249
C(4)	-1.0157	0.9855	0.6267
C(5)	-1.3703	-1.1987	-0.0233
C(6)	-2.3565	1.0294	-0.1146
C(7)	-2.6041	-0.4483	-0.5401
H(8)	-0.4140	1.8905	0.5227
H(9)	-1.1533	0.7587	1.6951
H(10)	-1.0585	-2.0350	-0.6530
H(11)	-1.5173	-1.5566	1.0073
H(12)	-3.1495	1.4182	0.5281
H(13)	-2.2862	1.6746	-0.9930
H(14)	-3.5207	-0.8583	-0.1102
H(15)	-2.6765	-0.5283	-1.6270
H(16)	3.2158	-0.9071	0.6973
H(17)	2.3946	1.1573	-0.4362
H(18)	1.9761	-1.0876	-1.4186

<sup>a</sup> Coordinates in Å.

**Table S18** Calculated coordinates (MP2/6-311++G\*\*) for *gauche, anti, endo*-FH<sub>2</sub>SiO-pyrrolidine.<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	-1.9871	-0.4989	-0.2024
O(2)	-0.3773	-0.3784	-0.6146
N(3)	0.2989	-0.0456	0.6525
C(4)	0.9937	1.2236	0.3849
C(5)	1.4043	-1.0105	0.7445
C(6)	2.1508	0.8936	-0.5818
C(7)	2.4157	-0.6171	-0.3518
H(8)	0.2809	1.9558	0.0036
H(9)	1.3685	1.5688	1.3549
H(10)	1.0143	-2.0255	0.6533
H(11)	1.8304	-0.8843	1.7461
H(12)	1.8476	1.0778	-1.6142
H(13)	3.0296	1.5082	-0.3699
H(14)	2.2224	-1.1841	-1.2644
H(15)	3.4422	-0.8195	-0.0351
H(16)	-2.6631	-0.9026	-1.4407
H(17)	-2.5786	0.9460	0.2285
H(18)	-2.2070	-1.4154	0.9188

<sup>a</sup> Coordinates in Å.

**Table S19** Calculated coordinates (MP2/6-311++G\*\*) for *anti, anti*, equatorial-H<sub>3</sub>SiO-piperidine.<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	1.6495	-2.1245	0.0000
O(2)	0.0268	-1.6602	0.0000
N(3)	0.1060	-0.2027	0.0000
C(4)	-0.6006	0.2375	1.2027
C(5)	-0.6006	0.2375	-1.2027
C(6)	-0.6006	1.7645	1.2518
C(7)	-0.6006	1.7645	-1.2518
C(8)	-1.2658	2.3404	0.0000
H(9)	-0.0824	-0.1866	2.0674
H(10)	-1.6322	-0.1537	1.1917
H(11)	-0.0824	-0.1866	-2.0674
H(12)	-1.6322	-0.1537	-1.1917
H(13)	-1.1204	2.0913	2.1591
H(14)	0.4356	2.1171	1.3177
H(15)	-1.1204	2.0913	-2.1591
H(16)	0.4356	2.1171	-1.3177
H(17)	-1.2066	3.4343	0.0000
H(18)	-2.3306	2.0715	0.0000
H(19)	1.6133	-3.5997	0.0000
H(20)	2.3411	-1.6326	1.2070
H(21)	2.3411	-1.6326	-1.2070

<sup>a</sup> Coordinates in Å.

**Table S20** Calculated coordinates (MP2/6-311++G\*\*) for *anti, anti*, axial-H<sub>3</sub>SiO-piperidine.<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	-1.9539	-1.7129	0.0000
O(2)	-1.1337	-0.2376	0.0000
N(3)	0.2637	-0.6826	0.0000
C(4)	0.8714	-0.1196	1.2128
C(5)	0.8714	-0.1196	-1.2128
C(6)	0.8714	1.4091	1.2524
C(7)	0.8714	1.4091	-1.2524
C(8)	1.5478	1.9735	0.0000
H(9)	0.3385	-0.5418	2.0700
H(10)	1.8998	-0.5040	1.2331
H(11)	0.3385	-0.5418	-2.0700
H(12)	1.8998	-0.5040	-1.2331
H(13)	1.3845	1.7437	2.1616
H(14)	-0.1638	1.7628	1.3055
H(15)	1.3845	1.7437	-2.1616
H(16)	-0.1638	1.7628	-1.3055
H(17)	1.5073	3.0683	0.0000
H(18)	2.6101	1.6890	0.0000
H(19)	-3.3825	-1.3394	0.0000
H(20)	-1.6374	-2.4971	1.2087
H(21)	-1.6374	-2.4971	-1.2087

<sup>a</sup> Coordinates in Å.

**Table S21** Calculated coordinates (MP2/6-311++G\*\*) for *anti, anti*, equatorial-F<sub>3</sub>SiO-piperidine.<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	-0.7666	-1.5041	0.0000
O(2)	-1.4706	-0.0074	0.0000
N(3)	-0.0845	0.5274	0.0000
C(4)	0.0733	1.3311	1.2136
C(5)	0.0733	1.3311	-1.2136
C(6)	1.4998	1.8764	1.2526
C(7)	1.4998	1.8764	-1.2526
C(8)	1.7947	2.7040	0.0000
H(9)	-0.1287	0.6856	2.0711
H(10)	-0.6661	2.1467	1.2013
H(11)	-0.1287	0.6856	-2.0711
H(12)	-0.6661	2.1467	-1.2013
H(13)	1.6203	2.4768	2.1605
H(14)	2.1980	1.0337	1.3185
H(15)	1.6203	2.4768	-2.1605
H(16)	2.1980	1.0337	-1.3185
H(17)	2.8361	3.0421	0.0000
H(18)	1.1607	3.6007	0.0000
H(19)	-1.9910	-2.5343	0.0000
H(20)	0.0733	-1.8783	1.3068
H(21)	0.0733	-1.8783	-1.3068

<sup>a</sup> Coordinates in Å.

**Table S22** Calculated coordinates (MP2/6-311++G\*\*) for *anti, anti*, axial-F<sub>3</sub>SiO-piperidine.<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	-0.1715	-1.6477	0.0000
O(2)	-0.9276	-0.1712	0.0000
N(3)	0.4766	0.3376	0.0000
C(4)	0.6598	1.1347	1.2227
C(5)	0.6598	1.1347	-1.2227
C(6)	-0.2362	2.3703	1.2543
C(7)	-0.2362	2.3703	-1.2543
C(8)	-0.0232	3.2221	0.0000
H(9)	0.4799	0.4753	2.0747
H(10)	1.7205	1.4152	1.2289
H(11)	0.4799	0.4753	-2.0747
H(12)	1.7205	1.4152	-1.2289
H(13)	-0.0144	2.9422	2.1620
H(14)	-1.2814	2.0479	1.3142
H(15)	-0.0144	2.9422	-2.1620
H(16)	-1.2814	2.0479	-1.3142
H(17)	-0.7049	4.0789	0.0000
H(18)	1.0005	3.6224	0.0000
H(19)	-1.3820	-2.6993	0.0000
H(20)	0.6598	-2.0270	1.3130
H(21)	0.6598	-2.0270	-1.3130

<sup>a</sup> Coordinates in Å.

**Table S23** Calculated coordinates (MP2/6-311++G\*\*) for *anti, anti*-(F<sub>3</sub>C)F<sub>2</sub>SiO-aziridine.<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	-0.3910	0.4598	0.0000
O(2)	-0.0652	-1.1489	0.0000
N(3)	-1.3524	-1.8430	0.0000
C(4)	-1.1903	-3.1033	0.7446
C(5)	-1.1903	-3.1033	-0.7446
C(6)	1.3257	1.3066	0.0000
F(7)	-1.1903	0.9502	1.2872
F(8)	-1.1903	0.9502	-1.2872
F(9)	1.2171	2.6520	0.0000
F(10)	2.0487	0.9633	-1.0868
F(11)	2.0487	0.9633	1.0868
F(12)	-0.2329	-3.2239	-1.2380
F(13)	-2.0734	-3.4039	-1.2959
F(14)	-0.2329	-3.2239	1.2380
F(15)	-2.0734	-3.4039	1.2959

<sup>a</sup> Coordinates in Å.

**Table S24** Calculated coordinates (MP2/6-311++G\*\*) for *anti, anti, exo*-(F<sub>3</sub>C)F<sub>2</sub>SiO-azetidine.<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	-0.1927	0.5849	0.0000
O(2)	0.3971	-0.9527	0.0000
N(3)	-0.9103	-1.6151	0.0000
C(4)	-1.0374	-2.6517	1.0483
C(5)	-1.0374	-2.6517	-1.0483
H(6)	-1.5413	-2.3184	1.9569
H(7)	-0.0548	-3.0827	1.2734
H(8)	-1.5413	-2.3184	-1.9569
H(9)	-0.0548	-3.0827	-1.2734
C(10)	1.3495	1.7225	0.0000
F(11)	-1.0374	0.9674	1.2983
F(12)	-1.0374	0.9674	-1.2983
F(13)	1.0158	3.0311	0.0000
F(14)	2.1240	1.5096	-1.0869
F(15)	2.1240	1.5096	1.0869
C(16)	-1.7972	-3.4969	0.0000
H(17)	-1.6123	-4.5703	0.0000
H(18)	-2.8672	-3.2885	0.0000

<sup>a</sup> Coordinates in Å.

**Table S25** Calculated coordinates (MP2/6-311++G\*\*) for *anti, anti*, axial-(F<sub>3</sub>C)F<sub>2</sub>SiO-pyrrolidine.<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	0.0243	0.6030	0.0000
O(2)	0.8564	-0.8457	0.0000
N(3)	-0.5416	-1.3338	0.0000
C(4)	-0.7983	-2.1854	1.1696
C(5)	-0.7983	-2.1854	-1.1696
C(6)	-2.1104	-2.8771	0.7791
C(7)	-2.1104	-2.8771	-0.7791
H(8)	-0.8611	-1.5768	2.0723
H(9)	0.0334	-2.8960	1.2581
H(10)	-0.8611	-1.5768	-2.0723
H(11)	0.0334	-2.8960	-1.2581
H(12)	-2.1552	-3.8852	1.1959
H(13)	-2.9650	-2.3153	1.1614
H(14)	-2.1552	-3.8852	-1.1959
H(15)	-2.9650	-2.3153	-1.1614
F(16)	-0.7983	0.9933	1.3226
F(17)	-0.7983	0.9933	-1.3226
F(18)	1.4391	1.9022	0.0000
F(19)	2.2382	1.7719	-1.0868
F(20)	2.2382	1.7719	1.0868
F(21)	0.9829	3.1744	0.0000

<sup>a</sup> Coordinates in Å.

**Table S26** Calculated coordinates (MP2/6-311++G\*\*) for *anti, anti, exo*-(F<sub>3</sub>C)F<sub>2</sub>SiO-morpholine.<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	-0.1041	0.8220	0.0000
O(2)	1.1702	-0.2534	0.0000
N(3)	0.0409	-1.2221	0.0000
C(4)	0.1328	-2.0477	1.2049
C(5)	0.1328	-2.0477	-1.2049
C(6)	-1.0146	-3.0528	1.1600
C(7)	-1.0146	-3.0528	-1.1600
H(8)	0.0471	-1.4018	2.0815
H(9)	1.1020	-2.5624	1.2144
H(10)	0.0471	-1.4018	-2.0815
H(11)	1.1020	-2.5624	-1.2144
H(12)	-0.9526	-3.7206	2.0213
H(13)	-1.9758	-2.5190	1.1866
H(14)	-0.9526	-3.7206	-2.0213
H(14)	-1.9758	-2.5190	-1.1866
C(16)	0.7665	2.5329	0.0000
F(17)	-1.0146	0.8855	1.3200
F(18)	-1.0146	0.8855	-1.3200
F(19)	-0.1078	3.5630	0.0000
F(20)	1.5596	2.6891	-1.0870
F(21)	1.5596	2.6891	1.0870
O(22)	-0.9360	-3.8650	0.0000

<sup>a</sup> Coordinates in Å.



**Table S27** Calculated coordinates (MP2/6-311++G\*\*) for *anti, anti, exo*-(F<sub>3</sub>C)F<sub>2</sub>SiO-piperazine.<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	-0.0949	0.7938	0.0000
O(2)	1.2168	-0.2410	0.0000
N(3)	0.0879	-1.2134	0.0000
C(4)	0.1712	-2.0314	1.2137
C(5)	0.1712	-2.0314	-1.2137
C(6)	-1.0060	-3.0006	1.1991
C(7)	-1.0060	-3.0006	-1.1991
H(8)	0.1214	-1.3670	2.0782
H(9)	1.1244	-2.5743	1.2124
H(10)	0.1214	-1.3670	-2.0782
H(11)	1.1244	-2.5743	-1.2124
H(12)	-0.9475	-3.6361	2.0872
H(13)	-1.9423	-2.4192	1.2468
H(14)	-0.9475	-3.6361	-2.0872
H(15)	-1.9423	-2.4192	-1.2468
H(16)	-1.6540	-4.5252	0.0000
C(17)	0.7357	2.5259	0.0000
F(18)	-1.0060	0.8554	1.3221
F(19)	-1.0060	0.8554	-1.3221
F(20)	-0.1610	3.5375	0.0000
F(21)	1.5259	2.7021	-1.0870
F(22)	1.5259	2.7021	1.0870
N(23)	-0.9121	-3.8309	0.0000

<sup>a</sup> Coordinates in Å.

**Table S28** Calculated coordinates (MP2/6-311++G\*\*) for *anti, anti*, axial-(F<sub>3</sub>C)F<sub>2</sub>SiO-piperidine.<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	-0.0928	0.7866	0.0000
O(2)	1.2334	-0.2319	0.0000
N(3)	0.1050	-1.2083	0.0000
C(4)	0.1926	-2.0197	1.2188
C(5)	0.1926	-2.0197	-1.2188
C(6)	-1.0045	-2.9683	1.2536
C(7)	-1.0045	-2.9683	-1.2536
C(8)	-1.0359	-3.8452	0.0000
H(9)	0.1917	-1.3416	2.0740
H(10)	1.1444	-2.5697	1.2006
H(11)	0.1917	-1.3416	-2.0740
H(12)	1.1444	-2.5697	-1.2006
H(13)	-0.9386	-3.5773	2.1612
H(14)	-1.9234	-2.3741	1.3215
H(15)	-0.9386	-3.5773	-2.1612
H(16)	-1.9234	-2.3741	-1.3215
H(17)	-1.9277	-4.4800	0.0000
H(18)	-0.1621	-4.5103	0.0000
C(19)	0.7218	2.5269	0.0000
F(20)	-1.0045	0.8452	1.3226
F(21)	-1.0045	0.8452	-1.3226
F(22)	-0.1834	3.5309	0.0000
F(23)	1.5109	2.7106	-1.0869
F(24)	1.5109	2.7106	1.0869

<sup>a</sup> Coordinates in Å.

**Table S29** Calculated coordinates (MP2/6-311++G\*\*) for *anti, anti, exo*-(F<sub>3</sub>C)F<sub>2</sub>SiO-thiomorpholine.<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	0.2698	-1.0226	0.0000
O(2)	-1.2473	-0.3240	0.0000
N(3)	-0.3913	0.8953	0.0000
C(4)	-0.6798	1.6457	1.2267
C(5)	-0.6798	1.6457	-1.2267
C(6)	0.2930	2.8132	1.3440
C(7)	0.2930	2.8132	-1.3440
H(8)	-0.5478	0.9587	2.0659
H(9)	-1.7208	1.9917	1.1974
H(10)	-0.5478	0.9587	-2.0659
H(11)	-1.7208	1.9917	-1.1974
H(12)	0.0900	3.3474	2.2762
H(13)	1.3221	2.4417	1.3770
H(14)	0.0900	3.3474	-2.2762
H(15)	1.3221	2.4417	-1.3770
C(16)	-0.1252	-2.9015	0.0000
F(17)	1.1671	-0.8552	1.3213
F(18)	1.1671	-0.8552	-1.3213
F(19)	0.9862	-3.6697	0.0000
F(20)	-0.8508	-3.2586	-1.0870
F(21)	-0.8508	-3.2586	1.0870
S(22)	0.0923	4.0089	0.0000

<sup>a</sup> Coordinates in Å.

**Table S30** Calculated coordinates (MP2/6-311++G\*\*) for *anti, anti, exo, chair*-(F<sub>3</sub>C)F<sub>2</sub>SiO-1-aza-cyclohept-4-en-1-yl.<sup>a</sup>

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	0.2466	-0.9207	0.0000
O(2)	-1.2969	-0.2770	0.0000
C(3)	-0.0966	-2.8111	0.0000
F(4)	1.1433	-0.7464	1.3233
F(5)	1.1433	-0.7464	-1.3233
F(6)	1.0343	-3.5515	0.0000
F(7)	-0.8129	-3.1894	-1.0870
F(8)	-0.8129	-3.1894	1.0870
C(9)	-0.7359	1.6840	1.2439
C(10)	-0.7359	1.6840	-1.2439
C(11)	0.3187	2.7621	1.5158
C(12)	0.3187	2.7621	-1.5158
C(13)	0.1734	4.0032	0.6727
C(14)	0.1734	4.0032	-0.6727
N(15)	-0.4467	0.9576	0.0000
H(16)	-1.7457	2.1101	1.1813
H(17)	-0.7146	0.9407	2.0430
H(18)	-1.7457	2.1101	-1.1813
H(19)	-0.7146	0.9407	-2.0430
H(20)	0.2356	3.0287	2.5738
H(21)	1.3111	2.3104	1.3843
H(22)	0.2356	3.0287	-2.5738
H(23)	1.3111	2.3104	-1.3843
H(24)	0.0633	4.9533	1.1914
H(25)	0.0633	4.9533	-1.1914

<sup>a</sup> Coordinates in Å.