Stereoconvergent [1,2]- and [1,4]-Wittig Rearrangements of 2-Silyl-6-aryl-5,6-dihydropyrans. A Tale of Steric vs. Electronic Regiocontrol of Divergent Pathways.

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**Supporting Information**

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I. Optimization studies
Optimization studies were conducted following the General Procedure H in the manuscript at the temperature and reaction time specified in Table S1.

**Table S1.** Optimization of reaction conditions for the rearrangement of 1a and 2a.

| entry | substrate | solvent | Base (equiv) | Temp, °C (time) | [1,4]-dr (%)<sup>a</sup> | dr | [1,2]-dr (%)<sup>a</sup> | dr |
|-------|-----------|---------|--------------|----------------|--------------------------|----|--------------------------|----|
| 1<sup>b</sup> | 1a | THF | NaHMDS | 78 to 0 | nr | - | nr | - |
| 2<sup>b</sup> | 1a | THF | LiHMDS | 78 to rt | nr | - | nr | - |
| 3<sup>c</sup> | 1a | THF | KHMDS | 78 to rt | nr | - | nr | - |
| 4 | 1a | THF | MeLi | -15 (20 min) | 53 | 20:1 | 27 | >20:1 |
| 5 | 1a | THF | n-BuLi | -78 (5 min) | 58 | 15:1 | 24 | >20:1 |
| 6 | 1a | Hexanes | n-BuLi | -78 to 0 (3h) | 49 | 7:1 | 4 | >20:1 |
| 7 | 2a | THF | MeLi | 50 (1.5h) | 40 | 9:1 | 17 | 4:1 |
| 8 | 2a | THF | HexylLi | -35 (6h) | 6 | nd | 4 | nd |
| 9 | 2a | THF | n-BuLi | -30 (7h) | 60 | 20:1 | 30 | >20:1 |
| 10 | 2a | THF | sec-BuLi | -78 (3h) | 60 | 20:1 | 29 | >20:1 |
| 11 | 2a | THF | sec-BuLi | -78 to 0 (1h) | 49 | 13:1 | 24 | >20:1 |

nr = no rearrangement. nd = not detected. <sup>a</sup> isolated yields. <sup>b</sup> 1a was recovered. <sup>c</sup> partial desilylation of 1a and isomerization to cyclic enol ether took place.
II. HPLC traces of optically active compounds

(R)-S2-a ([α]D = −6.1°, c = 1, CHCl₃, 76% ee, Figure S1). Enantiomeric excess (ee) was determined by HPLC (CHIRALPAK OJ column, hexanes, 0.6 mL/min, 10 °C).

(+)-2a ([α]D = +66.2°, c = 0.72, CHCl₃, 76% ee, Figure S2) The enantiomeric excess of (+)-2a was determined by HPLC (CHIRALPAK OJ column, hexanes, 0.4 mL/min, 10 °C, tR(minor) = 14.9 min; tR(major) = 17.6 min). The enantiomeric excess of (−)-1a could not be obtained by HPLC but was inferred to be 76% ee based on that of (+)-2a.
Figure S2. HPLC trace of compound (+)-2a.

![HPLC trace of compound (+)-2a](image)

HPLC conditions for racemic (Figure S3) / enantioenriched 3a: CHIRALPAK OJ column, hexanes, 0.7 mL/min, 20 °C, $t_R(1S,2R) = 12.7$ min; $t_R(1R,2S) = 25.8$ min.

(−)-3a (dr = 20:1) in 62% ee ($[\alpha]_D = -25.6^\circ$, c = 0.83, CHCl₃, Figure S4)

(+)-3a (dr = 20:1) in 56% ee ($[\alpha]_D = +27^\circ$, c = 0.79, CHCl₃, Figure S5)

HPLC conditions for racemic (Figure S6) / enantioenriched 4a: CHIRALPAK OJ column, 0.5% iPrOH/hexanes, 0.4 mL/min, 20 °C, $t_R(1R,5R) = 20$ min; $t_R(1S,5S) = 25$ min.

(+)-4a (dr > 20:1) in 73% ee ($[\alpha]_D = +73.4^\circ$, c = 0.96, CHCl₃, Figure S7).

(−)-4a (dr > 20:1) in 74% ee ($[\alpha]_D = -52.7^\circ$, c = 0.48, CHCl₃, Figure S8).
Figure S3. HPLC trace of racemic compound 3a.

Figure S4. HPLC trace of compound (−)-3a.
Figure S5. HPLC trace of compound (+)-3a.

Figure S6. HPLC trace of racemic compound 4a.
Figure S7. HPLC trace of compound (+)-4a.

Figure S8. HPLC trace of compound (−)-4a.
III. $^1$H NMR spectra from Deuterium trapping experiments

Competitive ortho metallation vs allylic deprotonation of $2d$ – Preparation of compounds $\delta-2d$, $\delta^{-1}1d$, $\delta-3d$, $\delta^{-2}8$ and $\delta^{-2}9$

Scheme S1. Deuterium trapping experiment with compound $2d$.

Figure S9. $^1$H NMR spectra overlay of $\delta-2d$ and $2d$. 
Figure S10. $^1$H NMR spectra overlay of 2-d and 1-d.

Figure S11. $^1$H NMR spectra overlay of 3-d and 3-d.

Figure S12. $^1$H NMR spectra overlay of 8 and 8.
Figure S13. $^1$H NMR spectrum of δ-9.

Competitive ortho metallation vs allylic deprotonation of 2h – Preparation of compounds δ-2h, δ-1h, and δ-10

1. sec-BuLi (3 equiv) THF, -78 °C, 30 min

2. D$_2$O

δ-2h 43%

δ-1h 19%

δ-10 15%

Scheme S2. Deuterium trapping experiment with compound 2h.

Figure S14. $^1$H NMR spectra overlay of δ-2h and 2h.
Competitive thiophene metallation vs allylic deprotonation of 2aa – Observation of compounds δ-2aa, δ-3aa, and enolic 3aa

Scheme S3. Deuterium trapping experiment with compound 2aa.
Applying general procedure H to 2aa (16.8 mg, 0.07 mmol, 1 equiv) and sec-butyllithium (1.4 M in hexanes, 0.15 mL, 3 equiv) in THF (0.9 mL) at -78 °C for 3 hours, quenching with D₂O and following regular workup, afforded a mixture of δ-2aa (dr >20:1), δ-3aa (dr ~ 1.7:1), and enolic 3aa (dr not determined) in 0.36 : 2.7 : 2.3 ratio, as determined from the crude mixture by ¹H NMR (Figure S17 and Scheme S6).
Figure S17. $^1$H NMR spectra overlay of the crude reaction mixture vs. 2aa and 3aa.
Competitive ortho metellation vs allylic deprotonation of 2bb – Observation of compounds δ-2bb and δ-3bb.

Applying general procedure H to 2bb (9.8 mg, 0.044 mmol, 1 equiv) and sec-butyllithium (1.4 M in hexanes, 94 µL, 3 equiv) in THF (0.6 mL) at -78 °C for 1 hour, quenching with D₂O and following regular workup, afforded mostly δ-2bb (dr >20:1) and traces of δ-3aa (dr not determined), as determined from the crude mixture by ¹H NMR (Figure S18 and Scheme S7). Complete deuterium incorporation at the 5-position of the furyl group in δ-2bb is observed. Deuterium incorporation in δ-3aa was not determined due to overlap with other signals.

![Scheme S4. Deuterium trapping experiment with compound 2bb.](image)

Figure S18. ¹H NMR spectra overlay of the crude reaction mixture vs. 2bb and 3bb.
Trapping of intermediate allylic anion (species A in Scheme 13 in manuscript)

Applying general procedure H to 1a (73 mg, 0.314 mmol, 1 equiv) in THF (4 mL) was added n-butyllithium (1.4 M in hexanes, 0.78 mL, 3 equiv) quickly at -78 °C, and immediately (<1 second) D₂O was added quickly via syringe. After regular workup the crude reaction was analyzed by ¹H NMR (Figure S19). Compounds δ-1a, enolic 3aa, 4a and 11 were present in 1.0 : 0.33 : 0.17 : 0.11 ratio (Scheme S8).

Scheme S5. Deuterium trapping experiment with compound 1a.
Figure S19. $^1$H NMR spectra overlay of the reaction mixture vs 1a, 2a, 3a, 4a, and 11.
IV. Control experiments to discard [1,2]- / [1,4]- interconversion. Evidence for Keto-enol Equilibration of cyclopropyl Acylsilanes

In the early stage of this study, involving the rearrangement of diastereomers 1a and 2a, we were unable to obtain reproducible isolated yields of both [1,4]- (3a) and [1,2]- (4a) products. The ratios of 3a and 4a in the crude 1H NMR were varying in each experiment and the determination of diastereomeric ratio of 3a was complicated by the presence of additional signals in the cyclopropyl region (1.8–0.6 ppm). In addition, the integration of these signals correlated well with a doublet around 4.52 ppm (J = 7.5 Hz) and a singlet around 4.35 ppm. We later found that subjecting the reaction mixture to column chromatography immediately after workup (avoiding additional manipulation of the crude for 1H NMR analysis) provided compounds 3a and 4a reproducibly, however, we could not isolate the additional cyclopropyl compound. Additional spectral data (13C NMR, DEPT, COSY and IR) from the crude reaction mixture strongly suggests that this species is actually the enolic form of 3a.

Scheme S6. 1H NMR analysis of crude reaction mixture after rearrangement of 1a.

Following General Procedure H, to 1a (65 mg, 0.28 mmol, 1 equiv) in THF (3 mL) at -78 °C was added n-butyllithium (0.27 mL, 0.42 mmol, 1.5 equiv) dropwise. After 20 minutes the reaction was quenched with NH4Cl (sat) and worked up as previously described in section II. An aliquot of the crude reaction mixture was dissolved in CDCl3 and immediately analyzed by 1H NMR and IR. The IR spectra showed a large broad band at 3435 cm⁻¹ (OH from enolic 3a and 4a) and a small band at 1635 cm⁻¹ (C=O from keto 3a). The 1H NMR spectra (Figure S20) shows a mixture of keto 3a / enolic 3a / 4a present in 0.29 : 1.0 : 0.64 ratio (Scheme S9). Addition of D₂O led to disappearance of the singlet at 4.35 ppm, which has been assigned tentatively to the enol O-H proton of enolic 3a. The 13C NMR of the crude reaction mixture (Figure S21, different run, same conditions) shows peaks at 158 ppm and 104 ppm, attributable to the polarized enol C–C double bond. This assignment is consistent with the results of a DEPT experiment (Figure S22) and also with the COSY 2D spectra showing coupling of the enolic C–H bond with the cyclopropyl C–H methine (Figure S23).
Figure S20. $^1$H NMR spectra overlay of the crude reaction mixture after rearrangement of 1a showing both tautomeric forms of 3a and product 4a.

Figure S21. $^{13}$C NMR spectra overlay of the crude reaction mixture after rearrangement of 1a showing both tautomeric forms (keto/enol) of 3a and product 4a.
Figure S22. $^{13}$C NMR vs DEPT experiment of the crude reaction mixture after rearrangement of 1a showing both tautomeric forms (keto/enol) of 3a and product 4a.

Figure S23. COSY experiment of the crude reaction mixture after rearrangement of 1a showing both tautomeric forms (keto/enol) of 3a and product 4a.
Interestingly, after column chromatography the cyclopropyl acylsilanes were isolated as a single tautomer (keto form). In the case of 3a, the tautomeric mixture could be regenerated by enolization of keto 3a with LDA, followed by regular workup (Scheme S10 and Figure S24). Notice that in the $^1$H NMR of the crude reaction mixture there is not evidence of cyclopentenol 4a, ruling out isomerization of the lithium enolate ([1,4]-product) to the corresponding alkoxide ([1,2]-product). Similar results were obtained from 3i.

Scheme S10. Generation of keto/enol tautomers of 3a by LDA deprotonation/workup.

Figure S24. $^1$H NMR spectra of crude reaction mixture following enolization of 3a with LDA/workup procedure. The tautomeric forms (keto/enol) of 3a are present.

Analogously, deprotonation of the [1,2]-Wittig products 4a and 4i with n-butyllithium (1.1-1.5 equiv) at –78 °C for 3 hours followed by regular workup gave only 4a and 4i, without a trace of the corresponding cyclopropyl products.
V. X-ray Crystallographic Data

Compound 4s

Figure S25. ORTEP representation of compound 4s.

Experimental Section:

Single crystals of C21H28OSi (4s) were slowly crystallized from hexanes at -20 °C. A suitable crystal was selected and mounted on a nylon loop using Paratone Oil. The crystal was kept at 173.01 K during data collection. Data were collected using a Bruker APEX-II CCD (charge coupled device) based diffractometer equipped with an Oxford Cryostream low-temperature apparatus operating at 173 K. Data were measured using omega and phi scans of 0.5° per frame for 30 s. The total number of images was based on results from the program COSMO,1 where redundancy was expected to be 4.0 and completeness to 0.83 Å to 100%. Cell parameters were retrieved using APEX II software2 and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software3 which corrects for Lp. Scaling and absorption corrections were applied using SADABS4 multi-scan technique, supplied by George Sheldrick. Using Olex2,5 the structure was solved with the XS6 structure solution program using Direct Methods and refined with the XL6 refinement package using Least Squares minimisation.

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The structure was solved in the space group P2₁/c (no. 14). All non-hydrogen atoms are refined anisotropically. Hydrogens were calculated by geometrical methods and refined as a riding model. All drawings are done at 50% ellipsoids.

Table S2. Crystal data and structure refinement for compound 4s.

| Parameter                          | Value                        |
|------------------------------------|------------------------------|
| Identification code                | Compound 4s                  |
| Empirical formula                  | C₁₁₂₇H₂₂₃O₅Si                |
| Formula weight                     | 324.52                       |
| Temperature/K                      | 173.01                       |
| Crystal system                     | monoclinic                   |
| Space group                        | P2₁/c                        |
| a/Å                                | 9.95030 (10)                 |
| b/Å                                | 8.14580 (10)                 |
| c/Å                                | 22.6084 (3)                  |
| α/°                                | 90.00                        |
| β/°                                | 92.0430 (10)                 |
| γ/°                                | 90.00                        |
| Volume/Å³                          | 1831.32 (4)                  |
| Z                                  | 4                            |
| \(\rho_{\text{calc}}\) mg/mm³     | 1.177                        |
| m/mm⁻¹                             | 1.131                        |
| F(000)                             | 704.0                        |
| Crystal size/mm³                   | 0.428 × 0.316 × 0.191        |
| 2Θ range for data collection      | 7.82 to 136.62°              |
| Index ranges                       | -11 ≤ h ≤ 11, -9 ≤ k ≤ 9, -27 ≤ l ≤ 27 |
| Reflections collected             | 31801                        |
| exptl absorpt T max, min           | 0.7531, 0.6739               |
| Independent reflections           | 3328[R(int) = 0.0372]        |
| Data/restraints/parameters         | 3328/0/212                   |
| 2Θ 68.31 fraction collected       | 0.996                        |
| Goodness-of-fit on \(F^2\)        | 1.051                        |
| Final R indexes \([I>=2\sigma(I)]\) | \(R_1 = 0.0329, wR_2 = 0.0867\) |
| Final R indexes [all data]        | \(R_1 = 0.0354, wR_2 = 0.0887\) |
| Largest diff. peak/hole / e Å⁻³   | 0.38/-0.21                  |
Table S3. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\AA^2 \times 10^3$) for compound 4s. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{ij}$ tensor.

| Atom | $x$     | $y$      | $z$      | $U_{eq}$ |
|------|---------|----------|----------|----------|
| Si1  | 2474.5(3)| 8408.7(4)| 863.63(14)| 18.09(11) |
| O1   | 1957.2(10)| 6733.2(12)| 1850.2(4)  | 28.3(2)   |
| C1   | 2622.9(13)| 8269.2(16)| 1715.2(6)  | 21.4(3)   |
| C2   | 2076.4(13)| 9714.3(17)| 2093.0(6)  | 22.7(3)   |
| C3   | 3295.0(14)| 10855.7(18)| 2199.2(6)  | 28.8(3)   |
| C4   | 4448.3(14)| 9665(2)    | 2177.5(6)  | 31.1(3)   |
| C5   | 4087.1(14)| 8279.0(18)| 1916.0(6)  | 27.7(3)   |
| C6   | 753.3(13) | 10490.1(17)| 1895.7(5)  | 21.2(3)   |
| C7   | 618.5(13) | 12106.7(17)| 1740.7(6)  | 21.9(3)   |
| C8   | -642.7(13)| 12805.9(17)| 1570.0(5)  | 22.2(3)   |
| C9   | -772.0(14)| 14483.0(18)| 1417.3(6)  | 28.6(3)   |
| C10  | -1993.5(15)| 15127(2)   | 1246.8(7)  | 33.9(3)   |
| C11  | -3150.0(15)| 14122(2)   | 1226.7(7)  | 35.0(4)   |
| C12  | -3060.9(14)| 12503.7(19)| 1378.4(6)  | 29.9(3)   |
| C13  | -1809.7(13)| 11793.1(17)| 1553.5(6)  | 23.4(3)   |
| C14  | -1659.2(13)| 10123.0(17)| 1721.5(6)  | 25.2(3)   |
| C15  | -431.4(13)| 9499.4(17) | 1891.9(6)  | 24.3(3)   |
| C16  | 683.2(13) | 8129.0(17) | 594.8(6)   | 24.4(3)   |
| C17  | 486.4(15) | 7425(2)    | -28.7(8)   | 34.4(3)   |
| C18  | 3572.7(14)| 6761.7(17) | 555.1(7)   | 27.4(3)   |
| C19  | 3235.2(16)| 4980.1(19) | 712.2(8)   | 39.7(4)   |
| C20  | 3126.6(14)| 10454.7(16)| 621.7(6)   | 24.2(3)   |
| C21  | 3133.0(15)| 10684.7(19)| -52.0(6)   | 30.7(3)   |

Table S4. Anisotropic Displacement Parameters ($\AA^2 \times 10^3$) for compound 4s. The Anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^2U_{11} + ... + 2hka^bU_{12}]$

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| Si1  | 17.67(19)| 17.49(19)| 19.08(19)| 1.11(13) | 0.05(13) | 0.05(13) | -0.40(12) | -3.40(4) | -3.7(4)  | -0.6(5)  | -2.1(5)  | -3.0(6)  |
| O1   | 34.8(6)  | 24.5(5)  | 25.4(5)  | 7.8(4)   | -0.4(4)  | -0.4(4)  | -3.40(4) | -3.7(4)  | -0.6(5)  | -2.1(5)  | -3.0(6)  |
| C1   | 21.3(6)  | 21.9(6)  | 20.9(6)  | 4.3(5)   | -0.7(5)  | -0.7(5)  | -0.6(5)  | -2.1(5)  | -3.0(6)  |
| C2   | 21.9(6)  | 28.1(7)  | 18.1(6)  | 4.3(5)   | -0.7(5)  | -0.7(5)  | -2.1(5)  | -3.0(6)  |
| C3   | 23.0(7)  | 33.9(8)  | 29.1(7)  | -5.7(6)  | -4.2(5)  | -4.2(5)  | -3.0(6)  |
| C4   | 20.1(7)  | 44.1(9)  | 28.7(7)  | 0.6(6)   | -5.6(5)  | -5.6(5)  | -1.0(6)  |
| C5   | 22.9(7)  | 35.7(8)  | 24.1(7)  | 5.0(6)   | -3.9(5)  | -3.9(5)  | 5.3(6)   |
| C6   | 20.4(6)  | 27.6(7)  | 15.7(6)  | -2.8(5)  | 2.4(5)   | 2.4(5)   | -0.5(5)  |
| C7   | 19.6(6)  | 27.1(7)  | 19.2(6)  | -3.0(5)  | 2.7(5)   | 2.7(5)   | -3.9(5)  |
| C8 | 22.3(6) | 27.3(7) | 17.1(6) | -3.6(5) | 3.1(5) | -1.3(5) |
| C9 | 28.3(7) | 28.2(7) | 29.3(7) | -0.3(6) | 2.6(6) | -1.3(6) |
| C10 | 35.8(8) | 30.3(8) | 35.6(8) | 2.6(6) | 0.4(6) | 5.1(6) |
| C11 | 26.1(7) | 43.3(9) | 35.2(8) | -1.4(7) | -3.4(6) | 9.9(6) |
| C12 | 20.3(7) | 39.7(8) | 29.6(7) | -5.7(6) | 0.4(5) | -1.2(6) |
| C13 | 22.3(7) | 30.5(7) | 17.5(6) | -5.6(5) | 2.8(5) | -0.8(5) |
| C14 | 20.8(6) | 29.8(7) | 25.3(7) | -5.2(6) | 4.8(5) | -6.8(5) |
| C15 | 24.9(7) | 24.8(7) | 23.6(7) | -1.4(5) | 4.6(5) | -2.7(5) |
| C16 | 20.7(6) | 29.4(7) | 22.9(7) | -3.5(5) | -1.8(5) | -1.9(5) |
| C17 | 30.9(8) | 39.7(9) | 31.9(8) | -6.8(7) | -8.1(6) | -0.2(6) |
| C18 | 24.7(7) | 25.3(7) | 32.3(7) | -4.5(6) | 2.0(6) | 2.6(5) |
| C19 | 33.0(8) | 23.1(7) | 62.8(11) | -6.3(7) | -0.7(7) | 3.4(6) |
| C20 | 26.3(7) | 21.4(7) | 25.1(7) | 1.0(5) | 3.1(5) | -4.3(5) |
| C21 | 34.2(8) | 31.3(8) | 26.9(7) | 5.4(6) | 5.0(6) | -5.1(6) |

**Table S5. Bond Lengths for compound 4s.**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|------|------|----------|------|------|----------|
| Si1  | C1   | 1.9290(13)| C7   | C8   | 1.4191(19)|
| Si1  | C16  | 1.8765(13)| C8   | C9   | 1.414(2) |
| Si1  | C18  | 1.8802(14)| C8   | C13  | 1.4238(18)|
| Si1  | C20  | 1.8770(13)| C9   | C10  | 1.367(2) |
| O1   | C1   | 1.4532(15)| C10  | C11  | 1.412(2) |
| O1   | C2   | 1.5634(18)| C11  | C12  | 1.364(2) |
| C1   | C5   | 1.5105(18)| C12  | C13  | 1.4165(19)|
| C2   | C3   | 1.5400(18)| C13  | C14  | 1.419(2) |
| C2   | C6   | 1.5132(18)| C14  | C15  | 1.3653(19)|
| C3   | C4   | 1.505(2)  | C16  | C17  | 1.5281(19)|
| C4   | C5   | 1.319(2)  | C18  | C19  | 1.534(2) |
| C6   | C7   | 1.3680(19)| C20  | C21  | 1.5348(19)|
| C6   | C15  | 1.4283(18)|      |      |          |

**Table S6. Bond Angles for compounds 4s.**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Angle/° |
|------|------|------|---------|------|------|---------|
| C16  | Si1  | C1   | 110.74(6)| C7   | C6   | C15    | 117.95(12)|
| C16  | Si1  | C18  | 110.55(6)| C15  | C6   | C2     | 118.38(12)|
| C16  | Si1  | C20  | 110.34(6)| C6   | C7   | C8     | 122.26(12)|
| C18  | Si1  | C1   | 107.66(6)| C7   | C8   | C13    | 119.15(12)|
| C20  | Si1  | C1   | 109.16(6)| C9   | C8   | C7     | 121.74(12)|
\[
\begin{array}{cccccccc}
C20 & Si1 & C18 & 108.30(6) & C9 & C8 & C13 & 119.11(12) \\
O1 & C1 & Si1 & 103.96(8) & C10 & C9 & C8 & 120.79(13) \\
O1 & C1 & C2 & 111.31(10) & C9 & C10 & C11 & 120.16(14) \\
O1 & C1 & C5 & 112.55(11) & C12 & C11 & C10 & 120.44(14) \\
C2 & C1 & Si1 & 119.02(9) & C11 & C12 & C13 & 120.92(14) \\
C5 & C1 & Si1 & 109.78(9) & C12 & C13 & C8 & 118.58(13) \\
C5 & C1 & C2 & 100.50(10) & C12 & C13 & C14 & 123.36(13) \\
C3 & C2 & C1 & 104.62(10) & C14 & C13 & C8 & 118.05(12) \\
C6 & C2 & C1 & 117.99(10) & C15 & C14 & C13 & 121.11(12) \\
C6 & C2 & C3 & 117.76(12) & C14 & C15 & C6 & 121.45(13) \\
C4 & C3 & C2 & 101.72(12) & C17 & C16 & Si1 & 115.68(10) \\
C5 & C4 & C3 & 111.75(12) & C19 & C18 & Si1 & 117.01(10) \\
C4 & C5 & C1 & 112.58(12) & C21 & C20 & Si1 & 114.29(9) \\
C7 & C6 & C2 & 123.63(12) \\
\end{array}
\]

Table S7. Torsion Angles for compound 4s.

| A   | B   | C   | D   | Angle/° | A   | B   | C   | D   | Angle/° |
|-----|-----|-----|-----|---------|-----|-----|-----|-----|---------|
| Si1 | C1  | C2  | C3  | -91.98(11) | C8  | C9  | C10 | C11 | 0.6(2)  |
| Si1 | C1  | C2  | C6  | 41.15(15)  | C8  | C13 | C14 | C15 | -0.36(19) |
| Si1 | C1  | C5  | C4  | 108.59(12) | C9  | C8  | C13 | C12 | 0.58(18)  |
| O1  | C1  | C2  | C3  | 147.18(11) | C9  | C8  | C13 | C14 | -178.61(12) |
| O1  | C1  | C2  | C6  | -79.68(14) | C9  | C10 | C11 | C12 | 0.2(2)  |
| O1  | C1  | C5  | C4  | -136.14(13) | C10 | C11 | C12 | C13 | -0.6(2)  |
| C1  | Si1 | C16 | C17 | -152.54(10) | C11 | C12 | C13 | C8  | 0.2(2)  |
| C1  | Si1 | C18 | C19 | 60.73(13)  | C11 | C12 | C13 | C14 | 179.36(13) |
| C1  | Si1 | C20 | C21 | 176.91(10) | C12 | C13 | C14 | C15 | -179.51(13) |
| C1  | C2  | C3  | C4  | -28.21(13) | C13 | C8  | C9  | C10 | -1.0(2)  |
| C1  | C2  | C6  | C7  | -119.12(14) | C13 | C14 | C15 | C6  | -1.2(2)  |
| C1  | C2  | C6  | C15 | 63.27(15)  | C15 | C6  | C7  | C8  | -0.96(18) |
| C2  | C1  | C5  | C4  | -17.64(15) | C16 | Si1 | C1  | o1  | 52.16(10) |
| C2  | C3  | C4  | C5  | 18.46(16)  | C16 | Si1 | C1  | C2  | -72.33(11) |
| C2  | C6  | C7  | C8  | -178.57(12)| C16 | Si1 | C1  | C5  | 172.77(9) |
| C2  | C6  | C15 | C14 | 179.61(12)| C16 | Si1 | C18 | C19 | -60.36(13) |
| C3  | C2  | C6  | C7  | 7.95(18)  | C16 | Si1 | C20 | C21 | -61.17(12) |
| C3  | C2  | C6  | C15 | -169.66(11)| C18 | Si1 | C1  | O1  | -68.81(9) |
| C3  | C4  | C5  | C1  | -0.30(17) | C18 | Si1 | C1  | C2  | 166.71(10) |
| C5  | C1  | C2  | C3  | 27.78(13) | C18 | Si1 | C1  | C5  | 51.80(11) |
| C5  | C1  | C2  | C6  | 160.92(11)| C18 | Si1 | C16 | C17 | -33.30(13) |
| C6  | C2  | C3  | C4  | -161.47(11)| C18 | Si1 | C20 | C21 | 59.96(12) |
| C6  | C7  | C8  | C9  | 179.27(12)| C20 | Si1 | C1  | O1  | 173.84(8) |
Table S8. Hydrogen Atom Coordinates (Å\times 10^4) and Isotropic Displacement Parameters (Å^2\times 10^3) for compound 4s.

| Atom | x     | y     | z     | U(eq) |
|------|-------|-------|-------|-------|
| H1   | 2015  | 6564  | 2217  | 42    |
| H2   | 1908  | 9222  | 2489  | 27    |
| H3A  | 3345  | 11697 | 1885  | 35    |
| H3B  | 3268  | 11405 | 2589  | 35    |
| H4   | 5329  | 9885  | 2333  | 37    |
| H5   | 4682  | 7385  | 1860  | 33    |
| H7   | 1396  | 12784 | 1748  | 26    |
| H9   | 0     | 15171 | 1433  | 34    |
| H10  | -2065 | 16253 | 1142  | 41    |
| H11  | -3996 | 14575 | 1107  | 42    |
| H12  | -3849 | 11844 | 1366  | 36    |
| H14  | -2426 | 9427  | 1716  | 30    |
| H15  | -364  | 8382  | 2009  | 29    |
| H16A | 231   | 7394  | 874   | 29    |
| H16B | 226   | 9208  | 607   | 29    |
| H17A | 951   | 8121  | -310  | 52    |
| H17B | -476  | 7390  | -137  | 52    |
| H17C | 858   | 6311  | -39   | 52    |
| H18A | 3537  | 6863  | 118   | 33    |
| H18B | 4512  | 6981  | 692   | 33    |
| H19A | 3823  | 4235  | 500   | 60    |
| H19B | 2295  | 4751  | 597   | 60    |
| H19C | 3372  | 4816  | 1140  | 60    |
| H20A | 2567  | 11329 | 792   | 29    |
| H20B | 4056  | 10594 | 785   | 29    |
| H21A | 3693  | 9834  | -225  | 46    |
| H21B | 3498  | 11770 | -143  | 46    |
| H21C | 2212  | 10597 | -218  | 46    |
**Compound 7**

Experimental Section:

A colorless needle crystal with dimensions 0.36 x 0.09 x 0.03 mm was mounted on a Nylon loop using very small amount of paratone oil.

Data were collected using a Bruker CCD (charge coupled device) based diffractometer equipped with an Oxford Cryostream low-temperature apparatus operating at 173 K. Data were measured using omega and phi scans of 1.0° per frame for 30 s. The total number of images was based on results from the program COSMO where redundancy was expected to be 4.0 and completeness to 0.83 Å to 100%. Cell parameters were retrieved using APEX II software and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software which corrects for Lp. Scaling and absorption corrections were applied using SADABS multi-scan technique, supplied by George Sheldrick. The structures are solved by the direct method using the SHELXS-97 program and refined by least squares method on F^2, SHELXL-97, which are incorporated in SHELXTL-PC V 6.10.

The structure was solved in the space group P2_12_12_1 (# 19). All non-hydrogen atoms are refined anisotropically. Hydrogens were calculated by geometrical methods and refined as a riding model. The Flack parameter is used to determine chirality of the crystal studied, the value should be near zero, a value of one is the other enantiomer and a value of 0.5 is racemic. The Flack parameter was refined to -0.03 (19), confirming the absolute stereochemistry. Determination of absolute structure using Bayesian statistics on Bijvoet differences using the program within Platon also report that we have the correct enantiomer based on this comparison. All drawings are done at 50% ellipsoids.

**Acknowledgement.** The CCD based x-ray diffractometer at Michigan State University were upgraded and/or replaced by departmental funds.

The following are 50% thermal ellipsoidal drawings of the molecule in the asymmetric cell with various amount of labeling.
Figure S26. ORTEP representation of compound 7.

Note: The Model has Chirality at C1 (Verify)  S
Note: The Model has Chirality at C2 (Verify)  S
Figure S27. This is a drawing of the packing of compound 7 along the a-axis.
### Table S9. Crystal data and structure refinement for compound 7.

| Identification code       | rem312            |
|---------------------------|-------------------|
| Empirical formula         | C21 H24 N2 O6 Si  |
| Formula weight            | 428.51            |
| Temperature               | 173(2) K          |
| Wavelength                | 1.54178 Å         |
| Crystal system            | Orthorhombic      |
| Space group               | P 21 21 21        |
| Unit cell dimensions      | a = 6.6788(4) Å   |
|                          | b = 9.7813(6) Å   |
|                          | c = 33.0675(16) Å |
| Volume                    | 2160.2(2) Å³      |
| Z                         | 4                 |
| Density (calculated)      | 1.318 Mg/m³       |
| Absorption coefficient    | 1.304 mm⁻¹        |
| F(000)                    | 904               |
| Crystal size              | 0.36 x 0.09 x 0.03 mm³ |
| Theta range for data collection | 2.67 to 67.26°. |
| Index ranges              | -7≤h≤6, -11≤k≤11, -36≤l≤38 |
| Reflections collected     | 8614              |
| Independent reflections   | 3585 [R(int) = 0.0596] |
| Completeness to theta = 67.26° | 97.1 %         |
| Absorption correction     | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9644 and 0.6531 |
| Refinement method         | Full-matrix least-squares on F² |
| Data / restraints / parameters | 3585 / 0 / 274   |
| Goodness-of-fit on F²     | 1.088             |
| Final R indices [I>2sigma(I)] | R1 = 0.0834, wR2 = 0.2177 |
| R indices (all data)      | R1 = 0.1006, wR2 = 0.2276 |
| Absolute structure parameter | -0.03(9)         |
| Largest diff. peak and hole | 0.835 and -0.324 e.Å⁻³ |
Table S10. Atomic coordinates ($x \times 10^4$) and equivalent isotropic displacement parameters ($\overline{\text{Å}}^2 \times 10^3$) for compound 7. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

|       | x     | y     | z     | $U(\text{eq})$ |
|-------|-------|-------|-------|---------------|
| Si(1) | 1583(2)| 62(2) | 1972(1)| 35(1)        |
| O(1)  | 2080(6)| 1216(4)| 1184(1)| 36(1)        |
| O(2)  | -1217(7)| 1565(5)| 1296(2)| 50(1)        |
| O(3)  | 5487(7)| 3493(5)| 108(1) | 48(1)        |
| O(4)  | 3835(8)| 4826(7)| -282(2)| 67(2)        |
| O(5)  | -2145(9)| 6978(5)| 273(2) | 59(1)        |
| O(6)  | -3930(7)| 5826(5)| 696(2) | 49(1)        |
| N(1)  | 4014(7)| 4177(5)| 24(2)  | 37(1)        |
| N(2)  | -2407(9)| 6000(5)| 492(2) | 43(1)        |
| C(1)  | 2217(9)| -121(6)| 1402(2)| 34(1)        |
| C(2)  | 1213(10)| -1200(6)| 1118(2)| 34(1)        |
| C(3)  | 2652(10)| -1279(7)| 755(2) | 42(2)        |
| C(4)  | 4718(10)| -754(6)| 903(2) | 43(2)        |
| C(5)  | 4458(9)| -460(6)| 1349(2)| 37(1)        |
| C(6)  | 884(9)| -2563(6)| 1330(2)| 32(1)        |
| C(7)  | -1012(10)| -2850(7)| 1486(2)| 42(2)        |
| C(8)  | -1389(11)| -4057(7)| 1687(2)| 47(2)        |
| C(9)  | 124(11)| -4994(8)| 1736(2)| 50(2)        |
| C(10) | 2003(10)| -4719(6)| 1578(2)| 44(2)        |
| C(11) | 2391(11)| -3517(6)| 1373(2)| 40(2)        |
| C(12) | 350(10)| 1845(6)| 1133(2)| 34(1)        |
| C(13) | 560(9)| 2993(6)| 839(2) | 29(1)        |
| C(14) | -985(9)| 3937(6)| 802(2) | 31(1)        |
| C(15) | -806(9)| 4974(6)| 524(2) | 33(1)        |
| C(16) | 815(9)| 5111(6)| 267(2) | 36(1)        |
| C(17) | 2283(9)| 4140(6)| 306(2) | 34(1)        |
| C(18) | 2230(9)| 3102(6)| 590(2) | 30(1)        |
| C(19) | 2788(13)| 1680(8)| 2134(2)| 55(2)        |
| C(20) | -1128(10)| 118(9)| 2113(2)| 51(2)        |
| C(21) | 2819(12)| -1372(7)| 2255(2)| 46(2)        |
Table S11. Bond lengths [Å] and angles [°] for compound 7.

| Bond                  | Length      |
|-----------------------|-------------|
| Si(1)-C(19)           | 1.854(8)    |
| Si(1)-C(20)           | 1.870(7)    |
| Si(1)-C(21)           | 1.878(6)    |
| Si(1)-C(1)            | 1.943(6)    |
| O(1)-C(12)            | 1.320(7)    |
| O(1)-C(1)             | 1.496(7)    |
| O(2)-C(12)            | 1.209(8)    |
| O(3)-N(1)             | 1.222(7)    |
| O(4)-N(1)             | 1.201(7)    |
| O(5)-N(2)             | 1.213(7)    |
| O(6)-N(2)             | 1.232(7)    |
| N(1)-C(17)            | 1.485(8)    |
| N(2)-C(15)            | 1.470(8)    |
| C(1)-C(5)             | 1.543(8)    |
| C(1)-C(2)             | 1.562(9)    |
| C(2)-C(6)             | 1.521(8)    |
| C(2)-C(3)             | 1.541(9)    |
| C(2)-H(2)             | 1.0000      |
| C(3)-C(4)             | 1.552(9)    |
| C(3)-H(3A)            | 0.9900      |
| C(3)-H(3B)            | 0.9900      |
| C(4)-C(5)             | 1.511(10)   |
| C(4)-H(4A)            | 0.9900      |
| C(4)-H(4B)            | 0.9900      |
| C(5)-H(5A)            | 0.9900      |
| C(5)-H(5B)            | 0.9900      |
| C(6)-C(11)            | 1.380(9)    |
| C(6)-C(7)             | 1.396(9)    |
| C(7)-C(8)             | 1.378(10)   |
| C(7)-H(7)             | 0.9500      |
| C(8)-C(9)             | 1.373(10)   |
| C(8)-H(8)             | 0.9500      |
| C(9)-C(10)            | 1.386(10)   |
| C(9)-H(9)             | 0.9500      |
| Bond                        | Distance |
|-----------------------------|----------|
| C(10)-C(11)                 | 1.382(9) |
| C(10)-H(10)                 | 0.9500   |
| C(11)-H(11)                 | 0.9500   |
| C(12)-C(13)                 | 1.491(8) |
| C(13)-C(18)                 | 1.390(8) |
| C(13)-C(14)                 | 1.390(8) |
| C(14)-C(15)                 | 1.373(8) |
| C(14)-H(14)                 | 0.9500   |
| C(15)-C(16)                 | 1.383(8) |
| C(16)-C(17)                 | 1.372(9) |
| C(16)-H(16)                 | 0.9500   |
| C(17)-C(18)                 | 1.384(8) |
| C(18)-H(18)                 | 0.9500   |
| C(19)-H(19A)                | 0.9800   |
| C(19)-H(19B)                | 0.9800   |
| C(19)-H(19C)                | 0.9800   |
| C(20)-H(20A)                | 0.9800   |
| C(20)-H(20B)                | 0.9800   |
| C(20)-H(20C)                | 0.9800   |
| C(21)-H(21A)                | 0.9800   |
| C(21)-H(21B)                | 0.9800   |
| C(21)-H(21C)                | 0.9800   |
| C(19)-Si(1)-C(20)           | 108.9(4) |
| C(19)-Si(1)-C(21)           | 107.7(3) |
| C(20)-Si(1)-C(21)           | 108.9(4) |
| C(19)-Si(1)-C(1)            | 105.3(3) |
| C(20)-Si(1)-C(1)            | 117.1(3) |
| C(21)-Si(1)-C(1)            | 108.6(3) |
| C(12)-O(1)-C(1)             | 121.5(4) |
| O(4)-N(1)-O(3)              | 124.1(5) |
| O(4)-N(1)-C(17)             | 117.7(5) |
| O(3)-N(1)-C(17)             | 118.1(5) |
| O(5)-N(2)-O(6)              | 123.7(6) |
| O(5)-N(2)-C(15)             | 118.4(6) |
| O(6)-N(2)-C(15)             | 117.9(5) |
O(1)-C(1)-C(5)    101.1(5)
O(1)-C(1)-C(2)    106.0(4)
C(5)-C(1)-C(2)    101.7(5)
O(1)-C(1)-Si(1)   112.0(4)
C(5)-C(1)-Si(1)   109.9(4)
C(2)-C(1)-Si(1)   123.4(4)
C(6)-C(2)-C(3)    113.9(5)
C(6)-C(2)-C(1)    112.3(5)
C(3)-C(2)-C(1)    103.5(5)
C(6)-C(2)-H(2)    109.0
C(3)-C(2)-H(2)    109.0
C(1)-C(2)-H(2)    109.0
C(2)-C(3)-C(4)    106.9(5)
C(2)-C(3)-H(3A)   110.3
C(4)-C(3)-H(3A)   110.3
C(2)-C(3)-H(3B)   110.3
C(4)-C(3)-H(3B)   110.3
H(3A)-C(3)-H(3B)  108.6
C(5)-C(4)-C(3)    105.6(5)
C(5)-C(4)-H(4A)   110.6
C(3)-C(4)-H(4A)   110.6
C(5)-C(4)-H(4B)   110.6
C(3)-C(4)-H(4B)   110.6
H(4A)-C(4)-H(4B)  108.7
C(4)-C(5)-C(1)    105.2(5)
C(4)-C(5)-H(5A)   110.7
C(1)-C(5)-H(5A)   110.7
C(4)-C(5)-H(5B)   110.7
C(1)-C(5)-H(5B)   110.7
H(5A)-C(5)-H(5B)  108.8
C(11)-C(6)-C(7)   119.2(6)
C(11)-C(6)-C(2)   122.3(5)
C(7)-C(6)-C(2)    118.5(5)
C(8)-C(7)-C(6)    121.1(6)
C(8)-C(7)-H(7)    119.5
C(6)-C(7)-H(7)    119.5
C(9)-C(8)-C(7) 119.7(7)
C(9)-C(8)-H(8) 120.2
C(7)-C(8)-H(8) 120.2
C(8)-C(9)-C(10) 119.4(6)
C(8)-C(9)-H(9) 120.3
C(10)-C(9)-H(9) 120.3
C(11)-C(10)-C(9) 121.4(6)
C(11)-C(10)-H(10) 119.3
C(9)-C(10)-H(10) 119.3
C(6)-C(11)-C(10) 119.3(6)
C(6)-C(11)-H(11) 120.4
C(10)-C(11)-H(11) 120.4
O(2)-C(12)-O(1) 126.5(5)
O(2)-C(12)-C(13) 122.9(5)
O(1)-C(12)-C(13) 110.6(5)
C(18)-C(13)-C(14) 119.5(5)
C(18)-C(13)-C(12) 121.2(5)
C(14)-C(13)-C(12) 119.3(5)
C(15)-C(14)-C(13) 119.1(5)
C(15)-C(14)-H(14) 120.5
C(13)-C(14)-H(14) 120.5
C(14)-C(15)-C(16) 123.4(5)
C(14)-C(15)-N(2) 119.2(5)
C(16)-C(15)-N(2) 117.4(5)
C(17)-C(16)-C(15) 115.7(5)
C(17)-C(16)-H(16) 122.1
C(15)-C(16)-H(16) 122.1
C(16)-C(17)-C(18) 123.7(6)
C(16)-C(17)-N(1) 118.7(5)
C(18)-C(17)-N(1) 117.6(5)
C(17)-C(18)-C(13) 118.6(5)
C(17)-C(18)-H(18) 120.7
C(13)-C(18)-H(18) 120.7
Si(1)-C(19)-H(19A) 109.5
Si(1)-C(19)-H(19B) 109.5
H(19A)-C(19)-H(19B) 109.5
Si(1)-C(19)-H(19C)  109.5
H(19A)-C(19)-H(19C)  109.5
H(19B)-C(19)-H(19C)  109.5
Si(1)-C(20)-H(20A)  109.5
Si(1)-C(20)-H(20B)  109.5
H(20A)-C(20)-H(20B)  109.5
Si(1)-C(20)-H(20C)  109.5
H(20A)-C(20)-H(20C)  109.5
H(20B)-C(20)-H(20C)  109.5
Si(1)-C(21)-H(21A)  109.5
Si(1)-C(21)-H(21B)  109.5
H(21A)-C(21)-H(21B)  109.5
Si(1)-C(21)-H(21C)  109.5
H(21A)-C(21)-H(21C)  109.5
H(21B)-C(21)-H(21C)  109.5

Symmetry transformations used to generate equivalent atoms:
Table S12. Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for compound 7. The anisotropic displacement factor exponent takes the form: $-2p^2[ h^2 a^* a^* U_{11} + ... + 2h k a^* b^* U_{12} ]$

|       | $U_{11}$  | $U_{22}$  | $U_{33}$  | $U_{23}$  | $U_{13}$  | $U_{12}$  |
|-------|-----------|-----------|-----------|-----------|-----------|-----------|
| Si(1) | 31(1)     | 34(1)     | 39(1)     | 1(1)      | -2(1)     | 3(1)      |
| O(1)  | 27(2)     | 34(2)     | 46(2)     | 5(2)      | 0(2)      | 3(2)      |
| O(2)  | 34(3)     | 46(3)     | 69(3)     | 18(2)     | 13(2)     | 6(2)      |
| O(3)  | 35(3)     | 52(3)     | 58(3)     | -6(2)     | 9(2)      | 7(2)      |
| O(4)  | 48(3)     | 88(4)     | 65(3)     | 31(3)     | 20(2)     | 5(3)      |
| O(5)  | 60(4)     | 43(3)     | 75(3)     | 15(2)     | 6(3)      | 16(3)     |
| O(6)  | 35(3)     | 40(2)     | 72(3)     | -2(2)     | 5(2)      | 15(2)     |
| N(1)  | 24(3)     | 42(3)     | 46(3)     | 2(2)      | 7(2)      | -6(2)     |
| N(2)  | 45(3)     | 37(3)     | 47(3)     | -3(2)     | -3(3)     | 2(3)      |
| C(1)  | 25(3)     | 32(3)     | 45(3)     | 4(3)      | -2(2)     | 7(3)      |
| C(2)  | 30(3)     | 31(3)     | 41(3)     | -1(2)     | -1(3)     | 9(3)      |
| C(3)  | 40(4)     | 46(3)     | 40(3)     | 3(3)      | -3(3)     | 3(3)      |
| C(4)  | 34(3)     | 36(3)     | 60(4)     | 3(3)      | 6(3)      | 7(3)      |
| C(5)  | 16(3)     | 37(3)     | 57(4)     | 6(3)      | -4(3)     | 7(2)      |
| C(6)  | 29(3)     | 24(3)     | 42(3)     | -5(2)     | -3(3)     | -1(2)     |
| C(7)  | 29(3)     | 54(4)     | 43(3)     | -7(3)     | -2(3)     | 9(3)      |
| C(8)  | 43(4)     | 49(4)     | 47(4)     | -3(3)     | 9(3)      | -6(4)     |
| C(9)  | 62(5)     | 46(3)     | 42(4)     | 4(3)      | 3(3)      | -5(4)     |
| C(10) | 40(4)     | 32(3)     | 59(4)     | -2(3)     | -6(3)     | 9(3)      |
| C(11) | 41(4)     | 34(3)     | 46(4)     | -6(3)     | 1(3)      | -6(3)     |
| C(12) | 28(3)     | 25(3)     | 48(3)     | 2(2)      | 2(3)      | 3(3)      |
| C(13) | 26(3)     | 26(3)     | 36(3)     | -1(2)     | -1(2)     | 1(2)      |
| C(14) | 26(3)     | 28(3)     | 40(3)     | -3(2)     | -1(2)     | 1(2)      |
| C(15) | 33(3)     | 26(2)     | 40(3)     | -2(3)     | -2(2)     | 6(3)      |
| C(16) | 41(3)     | 30(3)     | 36(3)     | 1(2)      | -2(3)     | -5(3)     |
| C(17) | 29(3)     | 34(3)     | 39(3)     | -3(2)     | 4(3)      | 2(3)      |
| C(18) | 23(3)     | 26(3)     | 41(3)     | -4(2)     | 1(2)      | 6(2)      |
| C(19) | 58(5)     | 58(5)     | 50(4)     | -7(3)     | -7(4)     | -5(4)     |
| C(20) | 39(4)     | 69(5)     | 44(3)     | -1(3)     | 2(3)      | -7(4)     |
| C(21) | 54(5)     | 39(3)     | 43(4)     | 7(3)      | 1(3)      | 20(3)     |
Table S13. Hydrogen coordinates (x 10\(^4\)) and isotropic displacement parameters (Å\(^2\)x 10\(^3\)) for compound 7.

|      | x     | y     | z     | U(eq) |
|------|-------|-------|-------|-------|
| H(2) | -108  | -838  | 1024  | 41    |
| H(3A)| 2154  | -702  | 530   | 50    |
| H(3B)| 2764  | -2233 | 657   | 50    |
| H(4A)| 5764  | -1457 | 861   | 52    |
| H(4B)| 5107  | 86    | 756   | 52    |
| H(5A)| 5301  | 323   | 1432  | 44    |
| H(5B)| 4831  | -1268 | 1513  | 44    |
| H(7) | -2059 | -2201 | 1454  | 51    |
| H(8) | -2689 | -4242 | 1790  | 56    |
| H(9) | -116  | -5822 | 1878  | 60    |
| H(10)| 3045  | -5370 | 1611  | 52    |
| H(11)| 3681  | -3350 | 1262  | 48    |
| H(14)| -2149 | 3866  | 965   | 38    |
| H(16)| 905   | 5831  | 75    | 43    |
| H(18)| 3311  | 2476  | 615   | 36    |
| H(19A)| 2413 | 2415  | 1947  | 83    |
| H(19B)| 4246 | 1567  | 2133  | 83    |
| H(19C)| 2342 | 1913  | 2408  | 83    |
| H(20A)| -1261 | 397   | 2396  | 76    |
| H(20B)| -1719 | -791  | 2077  | 76    |
| H(20C)| -1824 | 777   | 1939  | 76    |
| H(21A)| 4242 | -1409 | 2183  | 68    |
| H(21B)| 2177 | -2239 | 2183  | 68    |
| H(21C)| 2685 | -1216 | 2547  | 68    |
Table S14. Torsion angles [°] for compound 7.

| Torsion Angle | Torsion Angle Value |
|---------------|---------------------|
| C(12)-O(1)-C(1)-C(5) | 175.7(5) |
| C(12)-O(1)-C(1)-C(2) | 69.9(6) |
| C(12)-O(1)-C(1)-Si(1) | -67.3(6) |
| C(19)-Si(1)-C(1)-O(1) | -40.6(5) |
| C(20)-Si(1)-C(1)-O(1) | 80.6(5) |
| C(19)-Si(1)-C(1)-C(5) | -155.7(4) |
| C(20)-Si(1)-C(1)-C(5) | -167.9(5) |
| C(21)-Si(1)-C(1)-C(5) | -169.1(5) |
| O(1)-C(1)-C(2)-C(6) | -169.3(4) |
| C(5)-C(1)-C(2)-C(6) | -38.3(7) |
| Si(1)-C(1)-C(2)-C(6) | 85.4(6) |
| O(1)-C(1)-C(2)-C(3) | 67.5(5) |
| C(5)-C(1)-C(2)-C(3) | -37.9(6) |
| Si(1)-C(1)-C(2)-C(3) | -161.6(4) |
| C(6)-C(2)-C(3)-C(4) | -100.2(6) |
| C(1)-C(2)-C(3)-C(4) | 22.0(6) |
| C(2)-C(3)-C(4)-C(5) | 2.9(7) |
| C(3)-C(4)-C(5)-C(1) | 27.2(7) |
| O(1)-C(1)-C(5)-C(4) | -68.5(6) |
| C(2)-C(1)-C(5)-C(4) | 40.6(6) |
| Si(1)-C(1)-C(5)-C(4) | 173.0(4) |
| C(3)-C(2)-C(6)-C(11) | 36.1(8) |
| C(1)-C(2)-C(6)-C(11) | -81.1(7) |
| C(3)-C(2)-C(6)-C(7) | -144.2(6) |
| C(1)-C(2)-C(6)-C(7) | 98.6(6) |
| C(11)-C(6)-C(7)-C(8) | 0.9(9) |
| C(2)-C(6)-C(7)-C(8) | -178.9(6) |
| C(6)-C(7)-C(8)-C(9) | 0.5(10) |
| C(7)-C(8)-C(9)-C(10) | -1.1(10) |
| C(8)-C(9)-C(10)-C(11) | 0.4(10) |
| Atom Bond & Angle | Value |
|------------------|-------|
| C(7)-C(6)-C(11)-C(10) | -1.5(9) |
| C(2)-C(6)-C(11)-C(10) | 178.2(6) |
| C(9)-C(10)-C(11)-C(6) | 0.9(10) |
| C(1)-O(1)-C(12)-O(2) | 11.6(9) |
| C(1)-O(1)-C(12)-C(13) | -168.7(5) |
| O(2)-C(12)-C(13)-C(18) | -165.3(6) |
| O(1)-C(12)-C(13)-C(18) | 14.9(8) |
| O(2)-C(12)-C(13)-C(14) | 11.7(9) |
| O(1)-C(12)-C(13)-C(14) | -168.0(5) |
| C(18)-C(13)-C(14)-C(15) | -1.3(8) |
| C(12)-C(13)-C(14)-C(15) | -178.4(5) |
| C(13)-C(14)-C(15)-C(16) | 2.2(9) |
| C(13)-C(14)-C(15)-N(2) | -178.0(5) |
| O(5)-N(2)-C(15)-C(14) | 173.2(6) |
| O(6)-N(2)-C(15)-C(14) | -5.6(8) |
| O(5)-N(2)-C(15)-C(16) | -7.0(8) |
| O(6)-N(2)-C(15)-C(16) | 174.2(5) |
| C(14)-C(15)-C(16)-C(17) | -0.5(8) |
| N(2)-C(15)-C(16)-C(17) | 179.6(5) |
| C(15)-C(16)-C(17)-C(18) | -2.1(9) |
| C(15)-C(16)-C(17)-N(1) | 176.6(5) |
| O(4)-N(1)-C(17)-C(16) | -17.6(8) |
| O(3)-N(1)-C(17)-C(16) | 165.9(6) |
| O(4)-N(1)-C(17)-C(18) | 161.1(6) |
| O(3)-N(1)-C(17)-C(18) | -15.4(8) |
| C(16)-C(17)-C(18)-C(13) | 2.9(9) |
| N(1)-C(17)-C(18)-C(13) | -175.8(5) |
| C(14)-C(13)-C(18)-C(17) | -1.1(8) |
| C(12)-C(13)-C(18)-C(17) | 176.0(5) |

Symmetry transformations used to generate equivalent atoms:
Space Group P2\(1\)2\(1\)2\(1\)
Wavelength 1.54178
Flack \(x\) .... -0.03
Flack (su) 0.09

Bijvoet Pairs 1395
Coverage ... 86.8
DiffCalcMax. 288.57
Outlier Crit 577.13
Sigma Crit. 0.25
Select Pairs 416
Number Plus 290
Number Minus 126
Aver. Ratio 0.986
RC ........ 0.955

Normal Prob. Plot
Sample Size. 1386
Corr. Coeff. 0.964
Intercept .. -0.032
Slope ...... 1.123

Bayesian Statistics
Type ....... Gaussian
Select Pairs 1386
P2(true).... 1.000
P3(true).... 1.000
P3(rac-twin) 0.6E-29
P3(false) .. 0.0E+00
G ............ 0.9415
G (su) ..... 0.0810
Hooft y .... 0.03
Hooft (su) . 0.04
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CDCl₃, 500 MHz

S1-b
$\text{CDCl}_3$, 500 MHz

$\text{S}1-\varepsilon$

$\text{Me}$

$\text{Me}$

$\text{Me}$

$\text{Me}$

$\text{Me}$

$\text{CDCl}_3$, 500 MHz
$^{13}C$-NMR (CDCl$_3$, 500 MHz)

![Chemical Structure]

$S1$
$\text{CDCl}_3$, 126 MHz
CDCl₃, 500 MHz

S53
\[ \text{CDCl}_3, 126 \text{ MHz} \]
$^{13}C$CDCl$_3$, 500 MHz

S1-aa

\[
\text{NH} \quad \text{CCl}_3 \quad \text{S}1\text{-aa} \quad \text{CDCl}_3
\]
$^1$H NMR (CDCl$_3$, 126 MHz): 

S1-cc
$^{1}J_{CH} = 3\, ppm$
CDCl₃, 500 MHz

OSiMe₃

SiMe₃

S₂-f
CDCl₃, 500 MHz

syn/anti 33-b

Me₃Si
CDCl₃, 500 MHz

.syn/ant S3-c

OMe
Me₃Si

CDCl₃, 126 MHz

syn/anti S₃-c

ppm
$\text{CDCl}_3$, 500 MHz

$\text{syn S3-D}$

$\text{Me}_3\text{Si}$

$\text{OMe}$

$\text{OMe}$
CDCl₃, 126 MHz

Syn 3-Si-D

Structure Image
anti $S_{3-d}$

CDCl$_3$, 126 MHz
$^{1}H$ NMR (CDCl$_3$, 500 MHz, syn/anti S$_3$-e)

![NMR Spectrum Diagram]

- 1.65 ppm (6H, s, Me$_3$Si)
- 4.22 ppm (2H, s, CH$_2$)
- 5.00 ppm (2H, s, CH$_2$)
- 7.83 ppm (2H, s, aromatic)

Chemical shifts in ppm.
$^1$H NMR (CDCl$_3$, 500 MHz)
anti S3-4

CDCl₃ 500 MHz

$\text{Me}_3\text{Si}$
CDCl$_3$, 600 MHz

$\text{dr} = 4:1$

$\text{syn/anti} = 3:1$

$\text{Me}_3\text{Si}$
CDCl₃, 151 MHz

dr = 4:1

syn/anti S₃⁻¹

CF₃
Me₃Si
O

S₁₀₁
CDCl₃ 600 MHz

syn S₃-K

Me₃Si

Ph
CDCl$_3$, 500 MHz

$\text{syn S3-1}$

![Chemical Structure](attachment:image.png)
CDCl₃, 126 MHz

syn S3-1

Me₃Si

18
anti S3-l

CDCl₃, 500 MHz
\[\text{CDCl}_3, 600 \text{ MHz}\]

anti S-3-m
CDCl$_3$, 500 MHz

Syn S3-n

Ph$_2$MeSi

\[
\text{Syn S3-n}
\]
$^{1}H$ NMR in CDCl$_3$, 126 MHz

syn S$_{3}$-n

\[ \text{Ph}^2\text{MeSi} \text{O} \]

\[ \text{CH}_2=\text{C} \text{Cl} \]
CDCl$_3$, 500 MHz

$\text{syn S30}$
$^1$H NMR (CDCl$_3$, 600 MHz) and $^13$C NMR

![NMR Spectrum]

**Chemical Structure**

![Chemical Structure Image]
$\text{CDCl}_3$, 126 MHz

anti-S3-o

$\text{Et}_3\text{Si}$

S121
CDCl₃, 151 MHz

anti S,3-p

PhMe₂S·OMe

S125
S126

C<sub>6</sub>D<sub>6</sub>, 600 MHz

<chem>PhMe<sub>2</sub>Si</chem>

<chem>Cl</chem>

<chem>Cl</chem>

<chem>syn S<sub>3</sub>-b</chem>
$\text{CDCl}_3$, 600 MHz

Syn $\text{S}3\text{R}$
CDCl$_3$ 600 MHz

$^{sy}$n S3-S

![Chemical Structure Image]
anti S3-s

Et3Si

CDCl3, 600 MHz
$^{1}J_{3}C\text{CDCl}_{3}$ 500 MHz

anti S-1

\[
\begin{array}{c}
\text{Me}^3Si \\
\text{Me} \\
\text{Me} \\
\end{array}
\]
CDCl₃ 600 MHz

syn/anti S₃-W
The image contains a graph with peaks at various ppm values and a chemical structure labeled as follows:

**Chemical Structure**

- 

**Spectroscopic Details**

- **Solvent:** CDCl₃
- **Frequency:** 500 MHz
- **Symmetry:** S₃ - x

The peaks are labeled with approximate ppm values indicating the chemical shifts.
$^3$CDC$_3$, 500 MHz
anti S$\text{S}_3$-x

![Chemical Structure](image_url)
$\text{CDCl}_3$ 500 MHz

$\text{syn S}^{-3}$-z

Me

Me

Me$_3$Si
CDCl$_3$ 500 MHz

anti S3-aa

Me$_3$Si
syn S3-bb
CDCl$_3$, 126 MHz
$^1$H NMR spectrum 

$^{13}$C NMR spectrum

$^1$H NMR (CDCl$_3$, 126 MHz):

S$^3$-bb
$^1$H NMR (CDCl$_3$, 151 MHz):

![NMR spectrum image]

Chemical shifts (ppm):
$^{1}$H NMR (CDCl$_3$, 600 MHz)
CDCl₃, 126 MHz
CDCl$_3$, 500 MHz
CDCl₃, 500 MHz

19

Me₃Si
S192

$\text{CDCl}_3$, 126 MHz

$^{19}$Me$_3$Si

Me

Me
CDCl₃ 500 MHz

$\text{Me}^3\text{Si}$
$^{29}S$
CDCl₃, 126 MHz

S198
CDCl₃, 500 MHz
CDCl₃ 500 MHz

\[
\begin{align*}
\text{CF}_3 & \quad \text{Me}_3\text{Si} \\
\end{align*}
\]
CDCl₃, 500 MHz
CDCl₃, 600 MHz
PhMeO

O

PhMe₂Si

CCl₃, 500 MHz

S215
$\text{S216}$

$\text{CDCl}_3 \: 126 \text{ MHz}$

$\text{PhMe}_2\text{Si}$
$^{1}H$ NMR (CDCl$_3$, 500 MHz)

Ph$_2$Mes$_1$...
$\text{CDCl}_3$ 500 MHz

\[ \text{H} \]

\[ \text{Ph}_2\text{Mes}! \]

S221
CDCl₃, 126 MHz

S222
$^{1}$H NMR (CDCl$_3$, 600 MHz)

**Chemical Shifts:**
- 3.3 ppm
- 2.12 ppm
- 1.0 ppm

**Structure:**
![Chemical Structure](image)
$	ext{CDCl}_3$, 151 MHz
CDCl$_3$ 151 MHz

$^{13}$C NMR
CDCl₃, 500 MHz

1H

Me₃Si
O

Me
$\text{CDCl}_3$, 500 MHz
CDCl₃ 600 MHz

O
Me₃Si

OMe

Me

Me

S249
CDCl₃, 500 MHz

$^\text{Me}$ O

$^\text{Me}^3\text{Si}$
CDCl₃, 500 MHz
Me₃Si

C₆D₆, 62.8 MHz

3a
CDCl₃, 300 MHz
Me₃Si
\[ \text{OMe} \] 

CDC\textsubscript{3}, 600 MHz

S279
$\text{Me}_3\text{Si}$

$\text{OMe}$

$\text{CDCl}_3$, 500 MHz

$3c$
$^{31}$C, $^{29}$Si, $^{1}$H NMR: CDCl$_3$, 126 MHz.

![Chemical Structure Image]

$\text{Me}$
S285

CDCl₃, 500 MHz

Me₃Si

OME

OH

4c
CDCl$_3$ 600 MHz
CDCl$_3$, 500 MHz

39

endo tautomer
CDCl₃, 151 MHz
$^1$H NMR (600 MHz, CDCl$_3$) ppm

4h

$\text{Me}_3\text{Si}$

$\text{OH}$

$\text{F}$

$\text{OC}$
CDCl₃, 500 MHz
CDCl₃, 600 MHz

Me₃Si, Cl
$^1$H NMR (600 MHz, CDCl$_3$) ppm
$\text{CDCl}_3$, 500 MHz

$3k$
$^{13}$C NMR (CDCl$_3$, 151 MHz)
$^{3}m$ CDCl$_{3}$ 600 MHz
OH
PhMe
2
Si
4m
O
H

CDCl₃ 126 MHz
1
0.3
4m
PhMe₂Si
HO
CDCl$_3$, 500 MHz

3n

Ph$_2$MeSi
CDCl$_3$, 600 MHz

3o
C<sub>6</sub>H<sub>12</sub>O<sub>3</sub>, CDCl<sub>3</sub>, 126 MHz

S<sub>341</sub>
31 Me3Si

CDCl3 500 MHz
Me₃Si

3.15

OH

Me

CDCl₃, 500 MHz

S346
CDCl₃, 500 MHz

4w
CDCl₃, 126 MHz
CDCl₃, 600 MHz
CDCl3, 126 MHz
dr = 1:0.6

Me₃Si
CDCl₃ 500 MHz

4aa

Me₃Si

S364
CDCl₃ 600 MHz
dr = 1:0.7
3bb

O
Me₃Si
3bb

CDCl₃, 151 MHz
dr = 1:0.7

S367
PhOH
Me3Si
(-)(1S,2S)-6
CDCl3 500 MHz
