B(C_6F_5)_3-promoted tandem silylation and intramolecular hydrosilylation: diastereoselective synthesis of oxasilinanes and oxasilepanes

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B(C₆F₅)₃-promoted tandem silylation and intramolecular hydrosilylation: diastereoselective synthesis of oxasilinanes and oxasilepanes

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Department of Chemistry, University of Nebraska–Lincoln, Lincoln, NE 68588-0304

Abstract

B(C₆F₅)₃ promotes regio- and stereoselective cyclizations of unsaturated alkoxy silanes to generate oxasilinanes and oxasilepanes. The same products are available directly from alkenols via tandem silylation and hydrosilylation.

Intramolecular hydrosilylation of alkenes is an important transformation in organic synthesis. Initially investigated for unsaturated silanes, the methodology is now often applied to unsaturated alkoxy- and aminosilanes, where stereospecific oxidative cleavage of the newly formed C-Si bond enables stereodefined synthesis of diols and aminoalcohols. The majority of examples involve metal-catalyzed 5-endo or 5-exo ring closures, although six-membered cyclizations have been reported. We now report regio- and stereoselective formation of oxasilinanes and oxasilepanes via formation and cyclization of unsaturated alkoxy silanes in the presence of a nonmetal catalyst.

In the course of investigations into the influence of Lewis acids on the ozonolysis of unsaturated silanes, we found that addition of B(C₆F₅)₃ to a solution of unsaturated alkoxy silane 1-Pr resulted in regioselective formation of oxasilinane 2-Pr with high 3,5-trans diastereoselectivity (Table 1). The cyclization proceeded efficiently at −78 °C or RT and in the presence of either stoichiometric or catalytic B(C₆F₅)₃. Cyclization was also observed for the dimethylsilyl ether (not shown), but the hydrolytic instability of this class of reactants led us to abandon this thread following the discovery of the tandem cyclizations discussed later.

Supporting Information Available. Details regarding preparation and characterization of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.
The cyclization, apparently the first intramolecular example of a known intermolecular hydroxysilylation,10 was investigated further using alkoxysilanes prepared as illustrated in Scheme 1. 6-endo cyclization onto an α-substituted styrene (3-Pr) proceeded slowly but in high yield and with high trans selectivity (Scheme 2). Cyclization onto a cyclobutene (5-Pr) proceeded much more slowly through a 6-endo pathway to furnish a modest yield of the cis-fused adducts (6-Pr) as a 5:1 mixture of sidechain epimers. A bishomoallyl substrate, 7-Pr, reacted very slowly through a 6-exo pathway to furnish a trans-3,6-disubstituted-2-oxa-1-silinane (8-Pr).

B(C₆F₅)₃ also catalyzes the reductive silylation of alcohols,11 and we became intrigued by the possibility of tandem silylation/hydrosilylation (Table 2). B(C₆F₅)₃-promoted reaction of alkenol 1 with stoichiometric Et₂SiH₂ or Ph₂SiH₂ generated oxasilinanes 2-Et or 2-Ph with very similar regio- and stereoselection as observed in the stepwise cyclizations. Although alcohols 3 and 5 decomposed under the tandem conditions, cyclohexenol 9 reacted to selectively furnish the 3,5-trans diastereomer of cis-fused octahydrobenzosilinanes 10-Et and 10-Ph; the lower yield for the Et₂SiH₂ reaction is likely related to undesired reductive deoxygenations (vida infra). Alkenol 11, which generates an intermediate siloxane capable of undergoing cyclization through electronically comparable 5-exo or 6-endo pathways, reacted only through the latter. Bishomoallyl alcohol 13 underwent selective reaction through a 7-endo pathway to furnish oxasilane 14-Et as a 62:38 cis/trans mixture.

Reactions employing Et₂SiH₂ often furnished a significant amount of byproducts appearing to result from alcohol deoxygenation.12 For example, reaction of benzylic alcohol 15 produced oxasilane 16-Et along with a byproduct identified as a disiloxane on the basis of mass spectrometry and oxidative desilalylation (Scheme 3).13-14 Application of the one-pot reaction through a 7-exo pathway to furnish a modest yield of the 3,6-trans-disubstituted 16-Pr formed C-Si bond with the carbocation,20 with the resulting conformation dictating approach of the hydride. Analogous stereoselectivity has been observed in formation of siloxanes through hydrogen atom deliver to carbon-centered radicals.21

Although 5-exo cyclizations are well-established for Pt- or Rh-catalyzed hydrosilylations,1-3 we observed selective 6-endo vs. 5-exo cyclization with a substrate where either mode would proceed via a secondary carbocation (Table 2, substrate 11). We also observed very different rates for 6-exo and 6-endo cyclizations involving electronically similar carbocation intermediates (7-Pr vs. 1-Pr). These results point to the importance of interactions between

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the alkene and the developing silylium-like species. The cis selectivity observed for six-membered ring annelations, which complements results from metal-catalyzed cyclizations, presumably reflects stereoelectronic requirements for trapping of the β-silyl cations. 23 The stereoselectivity of sidechain introduction results from cyclization through the low-energy conformer of a chair-like transition state (eq 1).

Several lines of evidence indicate that the tandem reactions and stepwise processes involve a common hydrosilylation step. Both processes proceed with nearly identical regio- and diastereoselectivity. Furthermore, dialkylsilyl ethers are observed (TLC) as intermediates in some of the slower reactions, and become the only product when cyclization is disfavored, as for allylic alcohol 17 (Scheme 3). Finally, a diene substrate reacts selectively across the homoallyl alcohol (eq 2).

The formation of deoxygenated byproducts is observed mainly in the tandem reactions. The chemoselective deoxygenation of unhindered alcohols by trialkylsilane and B(C₆F₅)₃ has been postulated to involve attack of a silylium ate complex on intermediate silyl ethers, suggesting the deoxygenations observed here result from intermolecular reductions directly competing with cyclization.

Overall, the transformation provides a new method for the regio- and stereoselective synthesis of cyclic siloxanes and derived diols. Given that B(C₆F₅)₃ has been reported to catalyze the hydrosilylation of ketones and aldehydes, it is likely the method could be extended to allow the synthesis of oxasilacycles from unsaturated aldehydes and ketones.

**Supplementary Material**

Refer to Web version on PubMed Central for supplementary material.

**Acknowledgments**

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References


8. Stereochemical assignments are based upon ^3J_H couplings, nOe correlations, and a literature correlation for diol 21.


21. Cai Y, Roberts BP. J Chem Soc, Perkin Trans 1. 1998;467. Ibid., 3653. In contrast to the results described in this work, we observed a single predominant conformation of oxasilinanes.


Scheme 1.
Preparation of alkoxysilanes

aInseparable 3:1 mixture with 1-chloro-1-alkylcyclobutane
Scheme 2.
Additional cyclizations
Scheme 3.
Byproduct formation

a 0.6 equivalents.
b 0.25 equivalents.
Scheme 4.
Oxidative desilylation
Scheme 5.
Proposed mechanism
### Table 1

Cyclization of 1-Pr<sup>a</sup>

<table>
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<tr>
<th>BAr&lt;sub&gt;3&lt;/sub&gt; (equiv)</th>
<th>temp (°C)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>t (h)</th>
<th>yield (%)</th>
<th>trans %</th>
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<td>82</td>
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<tr>
<td>0.4</td>
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<td>&lt; 0.1</td>
<td>88</td>
<td>nd</td>
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<tr>
<td>0.1</td>
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<td>&lt; 0.1</td>
<td>93</td>
<td>nd</td>
</tr>
<tr>
<td>0.07</td>
<td>rt</td>
<td>&lt; 0.1</td>
<td>84</td>
<td>94&lt;sup&gt;c&lt;/sup&gt;</td>
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</table>

<sup>a</sup>Prepared as illustrated in Scheme 1.

<sup>b</sup>Final temperature; reactants mixed at −78 °C.

<sup>c</sup>5% of the cis-diastereomer isolated.
Tandem silylation/hydrosilylation

<table>
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<tr>
<th>subs</th>
<th>n</th>
<th>R₁, R₂</th>
<th>X</th>
<th>t (h)</th>
<th>prod</th>
<th>yield (%)</th>
<th>trans %&lt;sup&gt;a&lt;/sup&gt;</th>
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<td>&gt;90</td>
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<tr>
<td>3</td>
<td>1</td>
<td>Ph, H</td>
<td>Ph</td>
<td>-</td>
<td>-</td>
<td>decomp</td>
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</tr>
<tr>
<td>5</td>
<td>1</td>
<td>(CH₂)₂</td>
<td>Ph</td>
<td>-</td>
<td>-</td>
<td>decomp</td>
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<tr>
<td>9</td>
<td>1</td>
<td>(CH₂)₄</td>
<td>Et</td>
<td>0.5</td>
<td>10-Et</td>
<td>39</td>
<td>90</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>(CH₂)₄</td>
<td>Ph</td>
<td>1</td>
<td>10-Ph</td>
<td>73</td>
<td>84</td>
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<tr>
<td>11&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>H, Me</td>
<td>Et</td>
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<tr>
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<td>1</td>
<td>12-Ph</td>
<td>24</td>
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<td>13</td>
<td>2</td>
<td>H, Me</td>
<td>Et</td>
<td>0.1</td>
<td>14-Et</td>
<td>73</td>
<td>38</td>
</tr>
</tbody>
</table>

<sup>a</sup>3,5 stereochemistry;

<sup>b</sup> cis ring fusion; see Scheme 3 for structure of 10-Ph.

<sup>c</sup>3.3:1 mixture of E/Z isomers.
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**OL 2010-018757**

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pdussault1@unl.edu

**Supporting Information - Experimental Procedures**

<table>
<thead>
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<th>General Experimental Procedures:</th>
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<tr>
<td>Alcohol precursors</td>
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<tr>
<td>2-Methyldec-1-en-4-ol (1):</td>
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<tr>
<td>2-Phenyldec-1-en-4-ol (3):</td>
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<td>1-Cyclobutenyloctan-2-ol (5):</td>
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<tr>
<td>2-Methyl-2-dodecen-6-ol (7):</td>
<td>3</td>
</tr>
<tr>
<td>1-Cyclohexenyloctan-2-ol (9):</td>
<td>3</td>
</tr>
<tr>
<td>Undec-2-en-5-ol (11):</td>
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<td>2-Methylundec-1-en-5-ol (13):</td>
<td>4</td>
</tr>
<tr>
<td>3-Methyl-1-phenylbut-3-en-1-ol (15):</td>
<td>4</td>
</tr>
<tr>
<td>2-Methylnon-1-en-3-ol (17):</td>
<td>4</td>
</tr>
</tbody>
</table>

| Diisopropylsilyl ethers         |   |
| Diisopropyl-(2-methyldec-1-en-4-oxy)silane (1-Pr): | 4 |
| Diisopropyl-(2-phenyldec-1-en-4-oxy) silane (3-Pr): | 4 |
| Diisopropyl-(1-cyclobutenyloctyl-2-oxy)silane (5-Pr): | 5 |
| Diisopropyl-(2-methyl-2-dodecen-6-oxy)silane (7-Pr): | 5 |

| B(C₆F₅)₃-catalyzed cyclizations of diisopropylsilyl ethers (illustrated for 1-Pr) |   |
| (trans)-1,1-Diisopropyl-3-hexyl-5-methyl-2,1-oxasilinane (trans-2-Pr) and cis-2-Pr | 6 |
| (trans)- 1,1-Diisopropyl-3-hexyl-5-phenyl-2,1-oxasilinane (trans-4-Pr): | 7 |
| (3α,5α,6α), (3β,5α,6α)-1,1-Diisopropyl-3-hexyl-2-oxa-1-sila[4.2.0] bicyclooctane (6-Pr): | 7 |
| (trans)-1,1-Diisopropyl-3-hexyl-6-isopropyl-2,1-oxasilinane (8-Pr): | 8 |

| B(C₆F₅)₃-catalyzed tandem silylation/hydrosilylation (general procedure) |   |
| 1,1-Diethyl-3-hexyl-5-methyl-2,1-oxasilinane (2-Et): | 9 |
| 1,1-Diphenyl-3-hexyl-5-methyl-2,1-oxasilinane (2-Ph): | 9 |
| (3β,5α,6α) and (3α,5α,6α)-2,1-Benzoxasilin, octahydro-1,1-diethyl-3-hexyl (10-Et) | 9 |
| (3β,5α,6α)−2,1-Benzoxasilin, octahydro, 1,1-diphenyl-3-hexyl ((3β,5α,6α)−10-Ph) and (3α, 5α,6α)-2,1-Benzoxasilin, octahydro, 1,1-diphenyl-3-hexyl ((3α, 5α,6α)-10-Ph) | 10 |
| (3,6-trans) and (3,6-cis)-1,1-Diethyl-3-hexyl-6-methyl-2,1-oxasilinane (trans-12-Et and (cis)-12-Et) | 11 |
| (3,6-trans) and (3,6-cis)-1,1-Diphenyl-3-hexyl-6-methyl-2,1-oxasilinane (trans-12-Ph and (cis)-12-Ph): | 12 |

2,1-Benzoxasilin, octahydro, 1,1-diethyl-3-hexyl (10-Et) and (3β,5α,6α)-2,1-Benzoxasilin, octahydro, 1,1-diphenyl-3-hexyl ((3β,5α,6α)-10-Ph) and (3α, 5α,6α)-2,1-Benzoxasilin, octahydro, 1,1-diphenyl-3-hexyl ((3α, 5α,6α)-10-Ph)
\( (trans- \text{ and } cis-14-Et) \).

\( (3,5-trans)-1,1\text{-Diethyl-5-methyl-3-phenyl-2,1-oxasilinane (16-Et)}: \)

Diethyl (2-methylnon-1-en-3-oxy)silane (18-Et):

Oxidative Desilylation:

- (Tamao oxidation) 2-Methylundecane-1,5-diol (19):
- (Woerpel oxidation) 2-(2-Hydroxyoctyl)-cyclohexanol (20):
- 3-Methyl-1-phenyl-1,4-butanediol (21)

References

General Experimental Procedures:

Tetrahydrofuran (THF) was distilled from Na/Ph₂CO under N₂. Dichloromethane (CH₂Cl₂) was distilled from CaH₂. Stock solutions of B(C₆H₅)₃ were prepared either by: A) Transferring a freshly opened commercial sample (typically 1.0 g) into a oven-dried flask under N₂ followed by dissolution (0.2 M) in freshly distilled (Na/Ph₂CO) toluene; or B) Working inside a glove box under inert atmosphere, dividing a 1.0 g commercial sample of B(C₆F₅)₃ into individual vials (ca. 200 mg/vial). The vials were removed from the glove box to prepare stock solutions in toluene (0.2 M) that were used immediately and then discarded.¹ B(C₆H₅)₃ dissolves completely in toluene at 0.2M; the solubility of the hydrate is significantly lower. All other reagents and solvents were used as purchased unless otherwise noted. Thin layer chromatography (TLC) was performed on 0.25 mm hard-layer silica G plates; developed plates were visualized with a hand-held UV lamp and/or by staining with one of the following: 1% ceric sulfate and 10% ammonium molybdate in 10% H₂SO₄ (general stain, after charring) or 1% aq. KMnO₄ (for alkenes). Analytical and preparative HPLC were performed on a 4.6 mm x 25 cm Si column (5 µm) or 21.4 mm x 25 cm Si column (8 µm); both employed RI detection. NMR spectra were recorded at 400 MHz \(^1\text{H}\) or 100 MHz \(^1\text{C}\) in CDCl₃ unless otherwise indicated. \(^1\text{H}\) NMR signals are reported as: [chemical shift (multiplicity, integration, J couplings in Hz, other information). Infrared spectra were recorded as neat films (ZnSe crystal or NaCl plates) with selected absorbances reported in wave numbers (cm⁻¹). High resolution mass spectrometry was conducted at the Nebraska Center for Mass Spectrometry.

Preparation of Alcohols:

\textbf{2-Methyldec-1-en-4-ol (1)}: Into a 0 °C solution of heptanal (3.5 mL, 25 mmol) in THF (10 mL) was added dropwise a solution of 2-methylallyl magnesium chloride in THF (50 mL, nominally 0.5 \(M\)). After 20 min, the reaction was quenched with water (20 mL), acidified with conc. HCl (~
3 mL) and extracted with 10% EA/Hex (250 mL x 2). The combined extracts were sequentially washed with 10% aq. HCl and water. A standard workup and purification (5% EA/Hex) furnished 3.53 g (82%) of a compound with spectral properties matching literature reports.ii

2-Phenyldec-1-en-4-ol (3)iii was prepared by ene reaction of heptanal with α-methylstryrene by the procedure of Snider:iv  

\[
{^1}H \delta 7.44-7.41 (2H); 7.38-7.33 (2H); 7.32-7.27 (2H); 5.43 (d, 1H, 1.6); 5.18 (bs, 1H); 3.66 (m, 1H), 2.84 (ddd, 1H, 14, 4, 1; AB with 2.67), 2.67 (dd, 1H, 14, 9); 1.69 (d, 1H, 3); 1.4-1.5 (3H), 1.2-1.3 (6 H), 0.88 (t, 3H, 6.5); 13C δ 145.5, 140.5, 128.4, 127.7, 126.2, 115.2, 69.4, 43.8, 37.0, 31.8, 29.3, 25.6, 22.6, 14.1; IR 3368 (s, b); 2927, 2856, 1626, 1444, 898, 705 cm\textsuperscript{-1}; HRFAB MS calc. For C_{16}H_{24}OLi (M+Li): 239.1984; found 239.1984.

1-Cyclobutenyloctan-2-ol (5) was prepared from methylenecyclobutane (1.0 g, 15 mmol) and heptanal (2.7 mL, 1.3 equiv) by a similar procedure as for 3 to afford 0.99 g of alcohol 5 as an inseparable 3:1 mixture with 1-chlorocyclobutyl-2-octanol. The spectra of the product (R_f = 0.3, 10% EA) matched a literature report. v

2-Methyl-2-dodecen-6-ol (7) was prepared (1.39 g, 71%) by reaction of the Grignard reagent derived from 5-bromo-2-methyl-2-pentene (2.0 mL, 15 mmmol) with a slight excess of heptanal: R_f=0.4 (5% EA/hex); \(^1\)H δ 5.14 (bt, 1H, 6); 3.60 (m, 1H); 2.09 (m, 2H); 1.69 (bs, 3H); 1.63 (bs, 3H); 1.55-1.38 (6H); 1.35-1.23 (6H); 0.89 (t, 3H, 7); \(^{13}\)C δ 132.0; 124.2; 71.8; 37.5, 37.3, 31.8, 29.4, 25.7, 25.6, 24.4, 22.6, 17.6, 14.1; IR: 3377 (b, s, OH); 3328, 2924, 2855, 1454, 1377 cm\textsuperscript{-1}; 2928, 2864, 2092, 1463, 1379, 1056, 1001, 837 cm\textsuperscript{-1}; HRFAB calculated for C_{13}H_{25}O (M-H): 197.1905; found 197.1912 (-5.4 ppm); M+ also observed at 196.1813.

1-Cyclohexenyloctan-2-ol (9) was prepared from the reaction of heptanal (1.12 mL, 8.0 mmol), methylenecyclohexane (1.12 mL, 10 mol) and Me_2AlCl (12 mL, nominally 1 M solution in hexanes) by a similar procedure as for 3. The product (1.23 g, 73%) displayed spectra consistent with literature reports. vi R_f=0.4 (10% EA/Hex)

(E,Z)-Undec-2-en-5-ol (11) was prepared (1.17 g, 86%) from prop-1-enylmagnesium bromide (24 mL, nominally 0.5M in THF), epoxyoctane (1.2 mL, 8 mmol) and CuI(0.152g, 0.8 mmol).
The product was a 3.3:1 mixture of E- and Z-isomers based upon integration of the \(^1\)H signals at \(\delta 1.64\) and \(1.69\) ppm. Spectral properties matched literature reports.\(^{\text{vii}}\) \(R_f=0.4\) (10\% EA/Hex).

**2-Methylundec-1-en-5-ol (13)\(^{\text{viii}}\)** was prepared (1.45 g, 98\%) from 2-methylallyl magnesium chloride (24 mL, nominally 0.5M in THF), 2-hexyloxirane (1.2 mL, 8 mmol) and CuI(0.152g, 0.8 mmol) by a similar manner as 15. \(R_f=0.3\) (10\% EA/Hex).

**3-Methyl-1-phenylbut-3-en-1-ol (15)\(^{\text{ix}}\)** was prepared (1.30 g, quant.) from reaction of benzaldehyde (0.85 mL, 8.0 mmol) and 2-methylallyl magnesium chloride (20.8 mL, nominally 0.5M in THF) by a procedure similar to that applied for 1. Spectral properties matched a literature report.\(^{\text{ix}}\) \(R_f=0.3\) (10\% EA/Hex)

**2-Methylnon-1-en-3-ol (17)\(^x\)** was prepared (1.05 g, 84\%) from heptanal (1.12 mL, 8.00 mmol) and allylmagnesium chloride (20.8 mL, nominally 0.5M solution in THF) by a similar procedure as used for 1. \(R_f=0.2\) (10\% EA/Hex). Spectral properties matched a literature report.

**Alkoxyisilanes:**

**Diisopropyl(2-methyldec-1-en-4-oxy)silane (1-Pr)**

Into a THF (15 mL) solution of 2-methyldec-1-en-4-ol (0.724 g, 4.30 mmol) was added sodium bis(trimethylsilyl)amide (4.3 mL, nominally 2\(M\)) followed by SiCl\((i-\text{Pr})_2\) (1.1 mL) . After 4 h the reaction was quenched with brine and extracted with hexane (2 x 200 mL). The combined organic extracts were concentrated *in vacuo* and the residue was purified by flash chromatography in hexane to afford 1.09 g (89\%) of the silyl ether: \(R_f=0.4\) (hexane); \(^1\)H (600 MHz) \(\delta 4.78\) (app. s, 1H), 4.78(app. s, 1H), 4.21(s, 1H), 3.85(p, 1H, 5.7), 2.27(dd, 6 and 13.2), 2.17(dd, 1H, 7.2 and 13.2), 1.75(s, 3H), 1.43 (m, 10H), 1.05(m, 12H), 0.95(m, 2H), 0.90(t, 3H, 6.0); \(^{13}\)C (150 MHz) \(\delta 142.9, 112.8, 73.0, 45.7, 36.7, 31.9, 29.4, 25.2, 22.9, 22.6, 17.60, 17.57, 17.46, 14.1, 12.73, 12.71\); IR 2927, 2862, 2097, 1642, 1463, 1377 cm\(^{-1}\). HRMS (Cl) calc. for C\(_{17}\)H\(_{35}\)OSi (M-H)\(^+\): 283.2457; found 283.2469 (4.2 ppm); M\(^+\) (284.2543) observed in lower abundance.
Diisopropyl-(2-phenyldec-1-en-4-oxy)silane (3-Pr) was prepared (0.435 g, 70%) from alcohol 3 (0.428 g, 1.8 mmol) by a procedure similar to that applied to the synthesis of 1-Pr: R_f = 0.9 (5% EA/hex); ^1H δ 7.42 (bd, 2H, 8), 7.34 (bt, 2H, 8), 7.72 (app tt, 1H, 8, 1); 5.32 (d, 1H, 1.6), 5.13 (bs, 1H); 4.18 (bt, 1H, 1.6), 3.76 (m, 1H), 2.81 (ddd, 1H, 14, 5.8, 1); 2.64 (ddd, 1H, 14, 6.4, 1); 1.55-1.36 (3H), 1.33-1.18 (7H); 1.04-0.98 (12H, overlapping Me doublets); 0.98 -0.91 (m, 2H); 0.88 (t, 3H, 6.4); ^13C δ 145.7, 141.2, 128.2, 127.3, 126.3, 114.9, 72.9, 43.2, 36.5, 31.8, 29.4, 24.9, 22.6, 17.54, 17.48, 14.41, 14.07, 12.64, 12.61; IR: 3031, 2954, 2865, 3095, 1462, 1254 cm^{-1}; HRFAB Calc. For C_{22}H_{37}OSi (M-H)^+: 345.2613; found 345.2605 (2.5 ppm).

Diisopropyl(1-cyclobutenyloctyl-2-oxy)silane (5-Pr) was prepared in 55% yield (485 mg) from 5 (546 mg, estimated 2.25 mmol based upon purity) by a similar procedure as for 1-Pr: R_f = 0.3 (hexane); ^1H δ 5.72 (s, 1H); 4.20 (s, 1H); 3.81 (apparent pentet, 1H, 5-6); 2.45 (m, 2H), 2.35 (bs, 2H); 2.22 (m, 2H); 1.5-1.23 (10H); 1.07-1.02 (12H, isopropyl groups); 0.895 (t, 3H, 6.5); ^13C δ 147.3, 129.3, 73.1, 38.8, 36.9, 32.0, 31.9, 29.4, 27.0, 25.3, 22.6, 17.6, 17.5, 17.4, 14.1, 12.7; IR 2926, 2864, 2089, 1462, 1055, 837 cm^{-1}; HRFAB Calc. For C_{18}H_{35}OSi (M-H)^+: 295.2457; found 295.2452 (1.7 ppm).

Diisopropyl-(2-methyl-2-dodecen-6-oxy)silane (7-Pr) was prepared (0.707g, 73%) from alcohol 7 (617 mg, 3.1 mmol) by a similar procedure as for 1-Pr: R_f = 0.3 (hexane); ^1H δ 5.12 (bt, 1H, 6-7), 4.21 (s, 1H), 3.69 (pentet, 1H, 6.4); 2.08 & 1.98 (ABXY, 2H), 1.69 (s, 3H); 1.62 (s, 3H); 1.53-1.45 (4H), 1.35-1.25 (8H), 1.08-1.02 (12H, isopropyl), 0.90 (t, 3H, 6); ^13C δ 131.4, 124.5, 74.3, 36.9, 36.8, 31.9, 29.5, 25.7, 25.3, 24.0, 22.6, 17.64, 17.59, 17.5, 14.1, 12.7; IR 2929, 2864, 2088, 1463, 1377, 1063, 1002, 841, 800 cm^{-1}; HRFAB Calc. For C_{19}H_{39}OSi (M-H)^+: 311.2770; found 311.2773 (1.0 ppm).

General Procedure for intramolecular hydrosilylation (illustrated for 1-Pr). To an anhydrous toluene solution (6 mL) of 1-Pr (0.285g, 1.00 mmol), either at -78, 0 °C, or rt, was added B(C_{6}F_{5})_{3}. The amount of catalyst ranged from 0.1 to 1.0 eq, as a 0.2M solution in toluene. After the reaction was complete (TLC), the reaction was quenched with sat. aq. NaHCO_{3} (5 mL) and the resulting mixture extracted with hexane (2 X 100 mL). The combined organic layers were concentrated in vacuo and the residue was purified by flash chromatography (hexane) to afford
trans-2-Pr (236 mg, 83%) followed by a small amount of cis-2-Pr (18 mg, 6%). Analysis of the crude reaction mixtures by GC/MS generally found 91-95% of the trans isomer; the minor (syn) byproduct eluted first on GC. Both diasteromers displayed a predominant fragment at m/z 241, [M-iPr]. The stereochemistry was assigned based upon the relative strength of nOe transfer in the trans and cis isomers (see Scheme below), and by the magnitude of the axial/axial and axial/equatorial couplings for $^3J_{5,6}$ couplings. The stereochemical assignment was supported by a correlation of the $^3J_H$ of the minor (cis) byproduct with a literature report for similar molecules.\textsuperscript{xii}

(3,5-trans)-1,1-Diisopropyl-3-hexyl-5-methyl-2,1-oxasilinane (trans-2-Pr)

R$_f$ = 0.2 (hexane); $^1$H $\delta$ 3.99(m, 1H), 1.96(m, 1H), 1.57(m, 1H), 1.38(m 11H), 0.99(m, 12H), 0.95(m, 4H), 0.88[m, 4H, includes 0.89(t, 3H, 6.8), and peak at 0.90], 0.80(ddd, 1H, J$_1$=1.6, J$_2$=4.8, J$_3$=14.8), 0.28(dd, 1H, 10.4 and 14.8); $^{13}$C $\delta$ 72.0, 41.3, 37.5, 31.9, 29.4, 26.3, 26.1, 23.8, 22.6, 17.28, 17.27; 17.19, 17.16, 15.1, 14.1, 13.7, 13.1; IR (2942, 2931, 2864, 1464 cm$^{-1}$); HRFABMS (3-NBA) calc. for C$_{14}$H$_{29}$OSi [M-(i-Pr)$^+$]: 241.1988; found 241.1992 (1.7 ppm). Diaxial couplings and nOe excitations are summarized in the accompanying graphic.

(3,5-cis)-1,1-Diisopropyl-3-hexyl-5-methyl-2,1-oxasilinane (cis-2-Pr): 

R$_f$ = 0.4 (hexane); $^1$H $\delta$ 3.76(m, 1H), 1.77(m, 1H), 1.51(d of q., 1H, 2 and 13.6), 1.38(m 11H), 1.04-0.94 [m, 15H, peak at 1.00 (d, 6.5) visible nOe upon irradiation at 0.21], 0.89[m, 5H,
includes 0.89(t, 3H, 6.8), and other peaks], 0.72(ddd, 1H, J₁=2.4, J₂=4.0, J₃=14.4), 0.21(dd, 1H, 12.8 and 14.4); ¹³C δ 74.6, 44.3, 39.1, 31.9, 29.7, 29.4, 27.5, 25.3, 22.7, 17.71, 17.68, 17.14, 17.10, 15.7, 14.1, 13.1, 12.3; IR identical to anti-2-Pr. Diagonal couplings and nOe excitations are summarized in the accompanying graphic.

The ¹H NMR spectra of cis-3,5-disubstituted 2,1-oxasilacyclohexanes display H₃ (axial) as a ddd between 3.45 and 3.7 ppm and with individual coupling constants of up to 11 Hz.¹¹ The same work found the ²J coupling for H₆/H₆' to be 14 Hz, and the axial/axial and equatorial/axial ³J₅⁻₆ couplings to be 13.3 and 3.5 Hz, respectively. These values agree closely with our observations for cis-2-Pr.

(3,5-trans)- 1,1-Diisopropyl-3-hexyl-5-phenyl-2,1-oxasilinane (trans-4-Pr):

By a procedure similar to that described for 1-Pr, cyclization of silane 3-Pr (0.299 g, 0.862 mmol) furnished 0.257 g (86% yield) of 4-Pr: R₉ = 0.3 (5% EA/hex); ¹H δ 7.34 (t, 2H, 7.5); 7.27 (bd, 2H, 7.5); 7.22 (bd, 1H, 7.5); 4.16 (m, 1H); 3.05 (bt, 1H, 12.5), 1.96 (near dt, 12, 6; on same CH₂ as 1.75); 1.77 (m, 1H, on same CH₂ as 1.55); 1.75 (m, 1H, on same CH₂ as 1.96); 1.55 (m, 1H, on same CH₂ as 1.78), 1.5 (m, 1H, on same CH₂ as peak buried at 1.32), 1.4-1.26 (7H, includes portion of CH₂ shared with 1.5 as well as three CH₂-related spin systems), 1.12 (d, 3H, 7), 1.10 (3H, obscured), 1.09 (d, 3H, 7), 1.02 (6H, broad s), 0.98 (m, 1H, part of CH₂ with 0.90); 0.92 (t, 3H, 7), 0.90 (partially obscured dd, 20, 14). Through-space (nOe) correlations: Excitation of 4.16: collapses 1.96 to dt (6,14) as H₄ equatorial); enhances 1.77, 1.75, 1.5, 1.32; Excitation of 3.05 enhances 7.27, 1.77, 1.5, (shows evidence of direct coupling to 1.96); enhances d at 1.11, 1.09, and m/b at 1.00 and 0.08; enhances methyl at 0.89?¹³C 149.8, 128.5, 126.4, 125.9, 73.0, 40.7, 37.0, 34.4, 31.9, 29.4, 26.5, 22.7, 17.34, 17.27, 17.21, 17.16, 15.7, 14.1, 13.9, 13.0; HR-FAB calcd. C₂₂H₃₈OSi (M-H): 345.2613; found: 345.2605 (2.5 ppm)

1,1-Diisopropyl-3-hexyl-2-oxa-1-sila[4.2.0] bicyclooctane (6-Pr) was prepared (65 mg, 32%) as a separable mixture of diastereomers by cyclization of 5-Pr (200 mg, 0.67 mmol).

Diastereomer 1 (3α,5α,6α); 54 mg; R₉ = 0.3 (hexane); ¹H δ 3.58 (m, 1H, methine, cross speaks to spin system centered on 1.5 ppm); 2.51 (m, 1H, methine, coupled to 2.38, 1.95, 1.57); 2.38 (apparent pentet, 1H, part of methylene, coupled to 2.51, 1.99, 1.95, 1.68, 1.57); 1.99 (m, 1H, methine); 1.95 (m, 1H, part of methylene); 1.68 (dd, 1H, 13, 6); 1.57 (m, 1H); 1.55-1.25 (11H)

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1.04-9.97 (12H, 4 Me in isopropyl); 0.898 (t, 3H, 6.4), 0.88 (m, 1H), no E from 3.58 reveals as apparent pentet; $^{13}$C δ 73.18, 29.17, 38.61, 36.28, 21.97, 30.92, 29.41, 25.32, 26.69, 21.96, 18.57, 17.64, 17.53, 17.47, 17.07, 14.12, 13.44, 12.99; IR 2926, 2802, 1463, 1131, 1040, 882 cm$^{-1}$.

_Diastereomer 2 (3β,5α,6α):_ 11.6 mg; $R_f = 0.2$ (hexane); $^1$H δ 4.11 (m or apparent heptet, 1H); 2.825 (m, 1H; coupled into 2.2, 1.92, 1.47; correlates with methine C at 32.6 ppm); 2.24 (m, 1H; correlates with methylene C at 26 ppm), 2.13 (m, 1H, correlates with methylene at 26 ppm), 2.06 (m, 1H, correlates with methylene at 20 ppm), 1.92 (m, 2H correlates with methylene at 26 and methine at 17); 1.47 (m, 4H), 1.4-1.25 (9H), 1.15-1.05 (1H); 1.07 (m, 3H, 1.03 (app d, 3H, 6.4), 0.997 (d, 3H, 6.7); 0.94 (d, 3H, 6.7); 0.83 (m, 1H); $^{13}$C δ 69.55, 38.79, 37.78, 32.64, 31.97, 29.44, 26.28, 25.71, 22.68, 20.07, 17.53, 17.43, 17.33, 17.13, 16.24, 14.10, 13.18, 13.12; IR 2927, 2803, 1464, 1092, 993, 882 cm$^{-1}$; HRMS calcd. for $C_{18}H_{35}OSi$ (M-H)$^+$: 295.2457; found: 295.2456 (6.4 ppm).

_(trans) 1,1-Diisopropyl-3-hexyl-6-isopropyl-2,1-oxasilinane (8-Pr) was prepared (87 mg, 20% yield) from 7-Pr (419 mg, 1.34 mmol) by a similar procedure (0.2 equiv B(C$_6$F$_5$)$_3$) as for 2-Pr, except that the reaction was warmed to 0° C and held at that temperature for 16 h. Following a careful flash chromatography to remove a large amount of byproduct, the product was isolated as a single product by NMR and GC/MS: $R_f = 0.5$ (hexane); $^1$H δ 3.68 (m, 1H; C3-axial), 2.05 (dtd, 1H, 12.8, 5, 2.4; H5-eq, HMQC shows relationships to 1.35; COSY shows couplings to H5-axial, H4-axial, H6); 1.69 (m, 2H; 1H includes H4-axial; linked by COSY to H4-eq at 1.15); 1H is CH of C6 sidechain, with correlations to C6 and sidechain methylenes); 1.5-1.25 (9H, includes: 1.35 m for H5-axial; multiple spin systems from sidechain CH$_2$ groups); 1.15 (m, 1H, C4-eq); 1.11 (d, 3H, 6-7, iPrSi); 1.09 (d, 3H, 6-7, iPrSi); 1.10 (m, 1H, CH), 1.05 (d, 3H, ~7, iPrSi); 1.00 (d, 3H, ~7, iPrSi); 0.96 and 0.93 (each d, 3H, J ~6.5, Me$_2$CHC$_6$); 0.89 (t, 3H, 4-5, Me); 0.63 (ddd, 13, 9, 5, H6, COSY to iPrCH at 1.7); GC-MS: single major peak at 28.17 min (269, [M-iPr]); $^{13}$C δ 74.6, 39.2, 36.4, 32.2, 31.6, 29.6, 28.8, 27.6, 25.7, 24.8, 22.9, 22.0. 19.8, 18.6, 18.1, 17.8, 14.4, 13.8, 13.1; IR 2927, 2865 (s); 1464, 1382, 1068 cm$^{-1}$; HRFAB calc for $C_{19}H_{39}OSi$ (M-H)$^+$: 311.2770; found 311.2783 (3.9 ppm); (M+H)$^+$ at 312.2818 also observed.
General procedure for tandem silylation/hydrosilylation: Into a solution of unsaturated alcohol (typically 1 mmol) in 6 mL anhydrous toluene was added diethylsilane or diphenylsilane (1.2 mmol). The solution was cooled to 0 °C and B(C₆F₅)₃ was added (typically 0.1-0.5 equiv) from a 0.2-0.3 M stock solution in anhydrous toluene, resulting in vigorous bubbling. Once the alkene had largely disappeared (TLC), the reaction was quenched with 10% aq. NaHCO₃ (30 mL). The resulting mixture was extracted with hexane (2 x 50 mL) and the crude products were purified by flash or column chromatography.

(3,5-trans)-1,1-Diethyl-3-hexyl-5-methyl-1-oxa-2-silinane (2-Et)
Using the tandem procedure described above, alcohol 1 (0.34 g, 2.0 mmol) was reacted with diethylsilane(0.33 mL, 2.6 mmol). TLC indicated that the reaction was completed within 5 minutes. Column chromatography using 0-5% EA/hex as the eluting solvent afforded 0.24g (47%) of the silacyclohexane. A small portion of the product was purified by semi-preparative HPLC (21 x 250mm, 5 mL/minute of 1% EA/hex): R_f =0.58 (5% EA/hex ); ¹H δ 3.93-3.99(1H), 1.98-2.06(1H), 1.55-1.59(1H), 1.36-1.50(4H), 1.27(7H, m), 1.01(3H, d, 6.7), 0.94(3H, t, 6.4), 0.94(3H, t, 7.9), 0.88(3H, t, 6.8), 0.72(1H, ddd, 1.4, 4.6, 14.5), 0.57(4H, q, 7.5), 0.33(1H, dd, 10, 14.5); ¹³C δ 72.0, 41.4, 37.3, 31.9, 29.4, 26.3, 25.7, 24.1, 22.6, 17.7, 14.1, 7.6, 6.9, 6.7, 6.5; IR: 2953, 2925, 2874, 1458, 1413, 1156, 1047, 1003, 762 cm⁻¹. HR-FABMS calcd. for C₁₅H₃₂O[M+H]^+: 257.2301; Found: 257.2300

(3,5-trans)-1,1-Diphenyl-3-hexyl-5-methyl-1-oxa-2-silinane (2-Ph) was prepared (0.59 g, 84%) from alcohol 1 (0.34 g, 2.0 mmol) and diphenylsilane (0.41 mL, 2.2 mmol) using the tandem procedure described above. The reaction was conducted for 10 min and the crude product was purified by gradient flash chromatography (0-5% EA/hex). A small portion of the product was purified by semi-preparative HPLC (21x250 mm, 5 mL/min of 1% EA/hex). The major product was assigned by comparison with 1-Pr: R_f = 0.23 (2% EA/hex ); ¹H δ 7.51-7.61(5H), 7.30-7.42(5H), 4.16-4.21(1H), 1.24-1.28(1H), 1.27-1.63(15H), 1.03(3H, d, 6.8), 0.87(3H, t, 6.8), 0.79-0.95(2H); ¹³C δ 137.26, 137.24, 134.2, 134.1, 129.63, 129.57, 127.78, 127.73, 72.2, 41.6, 37.5, 31.8, 29.2, 26.1, 25.0, 24.8, 22.6, 19.0, 14.1; IR: 3068, 3049, 3000, 2954, 2925, 2856, 1454, 1428, 1151, 1116, 1041, 997, 821, 756, 731, 699 cm⁻¹; HR FABMS calcd. for C₂₃H₃₃OSi [MH]^+: 353.2307; found: 353.2300 (1.7 ppm).
(3β,5α,6α) and (3α,5α,6α)  **2,1-Benzoxasilin, octahydro-1,1-diethyl-3-hexyl (10-Et)**: Using the tandem procedure described above, alcohol 9 (0.21 g, 1.00 mmol) was reacted with diethylsilane (0.17 mL, 1.3 mmol) for 30 min, to furnish, after standard workup and chromatography, 0.11 g (39%) of the oxasilane. A small portion of the product was purified by semi-preparative HPLC (21x250 mm, 5 mL/min of 1% EA/hex) to furnish a 5:1 mixture of C₃ epimers. Traces of several minor components were visible (RI detection) just before elution of the major product: $R_f$ = 0.34 (2% EA/hex); $^1$H δ 3.87(1H, m), 1.95-1.99(1H), 1.61-1.78(3H), 1.27-1.52(17H), 1.13(1H, q, 5.2 ), 0.97(3H, t, 8.0), 0.95(3H, t, 8.0), 0.88(3H, t, 6.8), 0.69-0.78(1H), 0.55-0.66(3H). $^{13}$C δ 70.0, 38.6, 38.1, 33.5, 31.9, 31.5, 29.4, 26.0, 25.4, 25.0, 24.7, 24.5, 22.7, 14.1, 6.8, 6.7, 6.2; IR: 2852, 1459, 1413, 1377, 1237, 1187, 1127, 1097, 1059, 1004, 972, 934, 802, 724 cm$^{-1}$; MS: HR-FAB: calcd. for C₁₈H₃₆O[M-H]$^+$: 295.2456; found: 295.2448. The stereochemistry of the major product was assigned in analogy with 10-Ph (below) and by the chemical shifts for the axial H₃-axial (3.7 ppm) in the trans/cis isomer (major) vs. the equatorial H₃ (3.9 ppm) in the cis/cis isomer (minor).

(3β,5α,6α) and (3α,5α,6α)-**2,1-Benzoxasilin, octahydro, 1,1-diphenyl-3-hexyl (10-Ph)**

Using the tandem procedure described above, alkenol 9 (0.22 g, 1.1 mmol) was reacted with in diphenylsilane (0.21 mL, 1.1 mmol) for 1 h, to furnish, after standard workup and a gradient flash chromatography (0-5% EA/hex), 0.30 g (73%) of the cyclic oxasilane as a 1:5 mixture (NMR) of the cis/cis and trans/cis isomers, differing in the stereochemistry at C₃. R$_t$ = 0.50 (2% EA/hex); HR FABMS calc. for C$_{26}$H$_{37}$OSi [MH]$^+$: 393.2613; found: 393.2629 (3.8 ppm). A small portion of the product was further purified by semi-preparative HPLC (21 x 250mm, 5 mL/min of 1% EA/hex); the minor product eluted first.

**cis/cis** (3α,5α,6α)- (minor) $^1$H δ 7.65-7.69(2H), 7.49-7.51(2H), 7.28-7.45(6H), 3.84-3.89(1H; COSY correlation with spin systems at δ 2.1, 1.96; weak correlation with δ 1.5; nOe observed to 2.1 and 1.2); 2.05-2.10(1H, correlates only with δ 1.96), 1.93-1.99(1H, correlates with δ 3.9, 2.05, 1.2), 1.42-1.71(12H), 1.19-1.39(10H), 1.2 (1H, obscured t or dd, correlates with 1.97, 1.7); 0.90(3H, t, 6.8); $^{13}$C δ 135.6, 134.5, 134.3, 129.6, 129.5, 127.9, 127.5, 74.7, 38.8, 35.3, 34.5, 33.5, 32.0, 29.4, 27.9, 25.4, 22.9, 22.7, 22.3, 21.2, 14.2; IR 3068, 3048, 3000, 2925, 2855,
trans,cis (3β,5α,6α) (major) $^1$H δ 7.65 (m, 2H; nOe to 1.7), 7.55 (2H; modest nOe to 4.3), 7.31-7.41 (6H), 4.31 (1H, m, H$_3$; correlates with 1.6, 1.5; significant nOe to d 7.7, 2.1; this proton appears to be significantly deshielded by the edge of the neighboring arene; this assumption is supported by the observation of mutual nOes involving the arene as well as by MM2 calculations; 2.20 (m, 1H; COSY crosspeaks with 2.1, 1.5-1.6; nOe to 1.73, 1.5, 1.4), 2.07 (ddd, 1H, J values estimated as 13-14, 8, 3-4; COSY with 2.2, 1.5; nOe to peaks at d 4.3, 1.4), 1.83 (m, 1H; correlates to 1.45; nOe with d 1.5, 1.3), 1.73 (dt, 1H; weak COSY with 1.83; nOe to 2.2, 1.5), 1.17-1.48 (20H), 0.87 (3H, t, 6.8); $^{13}$C δ 137.8, 136.7, 134.6, 134.3, 134.2, 129.5, 129.3, 127.8, 127.7, 127.6, 72.4, 37.7, 37.6, 32.6, 31.8, 29.5, 29.3, 26.1, 25.3, 24.8, 24.5, 24.0, 22.6, 14.1; IR 3068, 3048, 3022, 2999, 2920, 2851, 1590, 1486, 1447, 1428, 1376, 1187, 1114, 1057, 997, 938, 916, 821, 801, 772, 699 cm$^{-1}$.

Using the tandem procedure described above, alkenol 11 (0.34 g, 2.0 mmol) was reacted with Et$_2$SiH$_2$ (0.33 mL, 2.6 mmol) for 5 minutes to furnish, following standard workup and chromatography (0-5% EA/hex), a 2.7: 1 mixture of trans- and cis-12-Et (81.9 mg, 16%): $R_f$ = 0.41 (2% EA/hex); HREIMS calc. for C$_{15}$H$_{31}$OSi (M-H)$^+$: 255.2244; found 255.2142 (0.9 ppm). A small portion of the product was purified by semi-preparative HPLC (21 x 250 mm, 5 mL/min 1% EA/hex); the major (trans) and minor (cis) isomers elute at 16 and 17 min, respectively.

The assignment of cis- and trans oxasilanes was based upon the upfield $^1$H chemical shift for the axial H$_3$.

trans-12: $^1$H δ 3.60-3.65 (1H), 1.83-1.89 (1H), 1.61-1.66 (1H), 1.20-1.47 (12H), 0.99 (3H, t, 7.9), 0.98 (3H, t, 7.9), 0.91 (3H, t, 6.8), 0.88 (3H, t, J=6.8), 0.49-0.84 (4H); $^{13}$C δ 74.5, 38.7, 35.8, 32.7, 31.9, 29.4, 25.5, 22.7, 17.5, 15.7, 14.1, 6.7, 5.0, 1.7; IR 2954, 2927, 2876, 2858, 1461, 1377, 1236, 1087, 1042, 1014, 836, 724 cm$^{-1}$.

cis-12: $^1$H δ 3.70-3.76 (1H), 1.82-1.90 (1H), 1.62-1.69 (1H), 1.24-1.56 (14H), 1.02 (3H, d, 7.6), 0.97 (3H, t, 7.9), 0.96 (3H, t, 7.9), 0.88 (3H, t, 6.8), 0.51-0.74 (4H); $^{13}$C δ 74.2, 38.1, 31.9, 30.8, 29.8, 29.3, 25.8, 22.7, 15.0, 14.4, 14.1, 6.8, 6.3, 4.2, 4.1; IR 2953, 2927, 2874, 1460, 1413, 1377, 1235, 1161, 1138, 1088, 1044, 1005 cm$^{-1}$.
(trans) and (cis)-1,1-Diphenyl-3-hexyl-6-methyl-1-oxa-2-silacyclohexane (trans- and cis-12-Ph). Using the tandem procedure described above, alcohol 11 (0.34 g, 2.0 mmol) was reacted with Ph₂SiH₂ (0.41 mL, 2.2 mmol) for 1 h. The crude products were subjected to column chromatography using 0-5% EA/hex as the eluting solvent to afford 0.17 g (24%) of the oxasilacyclohexane. A small portion of the product was further purified by semi-preparative HPLC (21x250mm, 1% EA/hexane, 5 mL/min), which partially resolved the major and minor isomers. The predominant isomer was assigned as trans on the basis of the 3.85 ppm chemical shift for the axial H₃: Rᵣ = 0.32 (2% EA/hex); ¹H (mixture of diastereomers) δ 7.65-7.68(m), 7.53-7.55(m), 7.30-7.44(m) 4.02-4.07(m), 3.85-3.90(m), 1.94-2.04(m), 1.78-1.86(m), 1.39-1.74(m), 1.13(d, 3H, 7.2), 1.07(d, 3H, 8), 0.87-0.92(m); ¹³C (mixture of two diastereomers) δ 136.0, 135.1, 134.5, 134.4, 134.3, 129.8, 129.6, 129.5, 127.9, 127.8, 127.7, 127.6, 75.8, 74.8, 38.8, 38.6, 35.9, 32.3, 31.9, 30.2, 30.1, 29.39, 29.36, 25.5, 25.4, 22.7, 19.4, 16.3, 15.3, 14.1, 13.9; IR: 3069, 3048, 2927, 2857, 1457, 1428, 1117, 1042, 987, 933, 736, 700 cm⁻¹; HRFAB calc. for C₂₃H₂₃OSi (M+H)⁺: 353.2300; found: 353.2293 (2.1 ppm).

(3,6-trans) and (3,6-cis)-1,1-Diethyl-3-hexyl-6-methyl-2-oxa-1-silepane (trans- and cis-14-Et). Using the tandem procedure described above, alcohol 13 (0.360 g, 1.95 mmol) was reacted with diethylsilane (0.28 mL, 2.2 mmol) for 5 min, to furnish, following standard workup and chromatography, 0.29 g (55%) of a 38:62 mixture of 3,6-trans- and 3,6-cis-oxasilacycloheptanes accompanied by 0.16 g of an unknown side product. A small portion of the product was further purified by semi-preparative HPLC (21 x 250mm, 5 mL/min 1% EA/hex); the major and minor diastereomers eluting at 17.0 and 18.0 min, respectively: Rᵣ = 0.2 (hexane); IR: 2982, 2953, 2925, 2874, 1461, 1377, 1237, 1090, 1007, 850, 757 cm⁻¹; HREIMS calcd. for C₁₆H₃₄OSi[M-C₂H₅]⁺: 241.1764; found: 241.1986.

Diastereomer 1((trans, minor): ¹H δ 3.59 (td, 1H, 8.6, 4), 1.73(m, 3H), 1.26-1.48(11H), 1.08 (m, 1H), 0.99(3H, d, 6.6), 0.95(3H, t, 7.9), 0.94(3H, t, 7.9), 0.88(3H, t, 6.8), 0.69 (dt, 1H, 15, 2) 1H), 0.48-0.63(5H). ¹³C δ 75.0, 39.9, 39.3, 38.4, 32.0, 31.0, 29.3, 28.8, 26.1, 23.3,22.7, 14.1, 7.00, 6.8, 6.1, 5.9


Diasteromer 2 ((cis, major): $^1$H $\delta$ 3.76 (m, 1H), 1.96 (m, 1H), 1.34-1.73(17H), 1.01(3H, d, 6.7), 0.94(6H, t, 7.9), 0.88(3H, t, 6.8), 0.73 (m,1H), 0.51-0.63(5H). $^{13}$C $\delta$ 73.8, 38.4, 35.2, 34.6, 31.9, 29.44, 29.37, 26.2, 25.6, 22.7, 22.1, 14.1, 7.3, 6.9, 6.8, 6.3

(trans)-1,1-Diethyl-5-methyl-3-phenyl-2-oxa-1-silinane (trans-16-Et) was prepared as a single diastereomer from 15 (0.32g, 2.0 mmol) and Et$_2$SiH$_2$ (0.33 mL, 2.6 mmol ) using procedure “B” described above except that the reaction temperature was held between 5 and 10 °C. The product was assigned as the trans-isomer in analogy with 2-Pr; this was confirmed by a correlation via diol 21 (vida infra). The crude product was purified by column chromatography (0-5% EA/Hex) to furnish 0.25 g of a diethylsiloxysiloxane byproduct followed by 0.25 g (51%) 16-Et, predominantly as the trans diastereomer. A small portion of the product was further purified by semi-preparative HPLC (21 x 250mm, 5 mL/min of 1% EA/hex).

16-Et: R$_f$ = 0.2 (hexane) or 0.4 in 5% EA/hex); $^1$H $\delta$ 7.24-7.28(1H), 7.34-7.40(4H), 5.19(1H, dd, 3.9, 7.5), 2.19 (m, 1H), 1.85(1H, ddd, 14.1, 7.5, 3), 1.73(1H, ddd, 14.1, 7.1, 4), 1.17(3H, d, 6.9), 1.05(3H, t, 7.9), 1.05(3H, t, 7.9), 0.94(1H, dd, 5.7, 12.2), 0.74(2H, q, 7.9), 0.69(2H, q, 7.9), 0.55(1H, ddd, 7.0, 14.7); $^{13}$C $\delta$ 145.7, 128.1, 126.6, 125.4, 71.9, 43.7, 25.0, 23.5, 16.5, 8.0, 7.3, 6.7, 6.6; IR: 3087, 3063, 3028, 2953, 2874, 1494, 1453, 1412, 1377, 1354, 1236, 1207, 1137, 1088, 1066, 1005, 907, 853, 809, 737, 699 cm$^{-1}$; HR-FABMS calcd. for C$_{15}$H$_{24}$OSi:[M+H]$^+$: 247.1517; found: 247.1527.

Byproduct: R$_f$ = 0.8 in 5% EA/hex. The byproduct displayed major ions at 343 (M-H)$^+$ and 189 (M-Si(Et)$_2$Osi(Et)$_2$H)$^+$ in the GC/MS spectra, and was tentatively assigned as 1,1-diethyl-1-(diethylsiloxy)-2-methyl-4-phenylbutyl silane. This assignment was supported by the lack of a carbinol HC and the presence of silane (4.5 ppm, narrow pentet) and multiple Et$_2$Si spin systems (1.1-0.87 for methyl groups; 0.7-0.45 for ethyl) in a complicated $^1$H NMR spectrum. $^{13}$C: 143.1, 128.4, 128.3, 125.5, 42.7, 33.7, 28.6, 22.9, 22.8, 7.4, 7.3, 7.1, 6.8, 6.6. Oxidative cleavage (Tamao oxidation, below) furnished 2-methyl-4-phenyl-1-butanol:xii R$_f$ = 0.3 (20% EA/hex); $^1$H $\delta$ 7.30 (app t, 2H, 7); 7.22-7.18 (3H); 3.54 (dd, 1H, ABX, 10.8, 6); 3.48 (dd, 1H, ABX, 10.8 6.4); 2.73 (ddd, ABXY, 1H, 13.6, 10, 5.6); 2.62 (ddd, ABXY, 13.6, 10, 6); 1.79 (m, 1H); 1.68 (apparent hextet, 1H, 6-7); 1.58 (1H, bs, OH); 1.46 (m, 1H); 1.008 (d, 3H, 7.2). IR (ATR crystal) 3346 (s, broad), 2926, 2873, 1454, 1037 cm$^{-1}$; HREI: calcd. for C$_{11}$H$_{16}$O.$[M]^+164.1204$; Found: 164.1204 (1.6 ppm).
Diethyl (2-methylnon-1-en-3-oxy) silane (18-Et): Attempted one-pot reaction of 2-methyl non-1-en-3-ol (17, 0.22 g, 1.4 mmol) with diethyilsilane (0.20 mL, 1.1 equiv) and B(C$_6$F$_5$)$_3$ (0.2 g, n toluene, ~0.4 mmol) as described for the synthesis of 2-Et furnished the corresponding diethylsilyl ether, 18-Et as an inseparable mixture with small amounts of one or more siloxanes: R$_f$ = 0.8 (hexane); $^1$H: δ 4.85 (bs, 1H); 4.75 (bs, 1H); 4.51 (app pentet, 2.4, residual diethyilsilane); 4.16 (t, 1H, 6.4); 1.68 (s, 3H); 1.45 (s, 0.7H, residual Si-H); 1.5 (m, 2H), 1.33-1.18 (8H); 1.0 - 0.92 (19 H, including some silane); 0.88 (t, 3H); 0.62 (dq, 4H, 7, 2); 0.53 (m, 8H, residual silane and siloxane); $^{13}$C: δ 147.4; 110.49; 76.71, 36.02, 31.9, 29.4, 25.5, 22.7, 17.1, 14.1, 7.47, 7.24, 6.97, 6.64, 6.61, 6.55; IR 2954, 2116, 1450 cm$^{-1}$. HRMS was attempted but gave no recognizable fragments.

Oxidation to diols

Tamao oxidation$^{xiii}$ (illustrated for (2R*,5S*)-2-methylundecane-1,5-diol (19): 135 mg (0.50 mmol) of 14-Et wa reacted with KF (0.058 g, 2 eq), KHCO$_3$ (0.100 g, 2 eq), 30% H$_2$O$_2$ (1 mL, 20 eq, ca. 9M in H$_2$O) in MeOH/THF for 48 h to afford 0.030 g (30%) of diol 19 as an inseparable mixture of diasteromers. R$_f$ = 0.2 (30% EA/hex); $^1$H δ 3.58 (m, 1H); 3.47 (t, 2H, 6; or bd, 1H, ~6, depending upon sample concentration), 2.3 (broad, 2H, varies with concentration); 0.89 (app t, 3H, 8); 0.857 (appt t, 3H, 8); 1.8-1.2 (15H); 0.85-0.92 (6H); $^{13}$C δ 72.4, 72.0, 67.8, 67.6, 37.53, 37.49, 35.8, 35.3, 34.3, 34.0, 31.8, 29.3, 28.9, 28.6, 25.7, 25.6, 22.6. 20.8, 16.8, 16.4, 14.1; The major diasteromer was assigned as 2R*,5S* based upon comparision with $^{13}$C data reported for a similar diol (major: 71.8, 67.8 ppm; minor 72.3, 67.6 ppm.$^{xiv}$ IR 3330 (b, OH), 2926, 2856, 1458, 1030 cm$^{-1}$; HRFAB calc. For C$_{12}$H$_{27}$O$_2$ [MH]$^+$: 203.2011; found: 203.2014 (1.3 ppm).

Oxidation of 88 mg (0.33 mmol) of the major (2$^{nd}$ eluting isomer) of 14-Et using the Woerpel procedure described below afforded 36.8 mg (56%) of 19. Spectral details were identical to those reported above.

Woerpel oxidation:$^{xv}$ 2-(2-Hydroxyoctyl)-cyclohexanol (20): To a solution of tert-butyl hydroperoxide (0.73 mL, 5-6M in decane) in 3 mL DMF at 0 $^\circ$C was added cesium hydroxide
(0.52 g, 3.1 mmol). The reaction mixture was allowed to warm to 25 °C, whereupon a solution of oxasilane 10-Ph (0.10 g, 0.26 mmol) in 2 mL DMF was added dropwise. After 10 minutes, tetrabutylammonium fluoride (1.3 mL, 1 M in THF) was added. The reaction solution was stirred at RT for 2 h and then quenched with 10 mL of 10% aq. sodium bisulfite. The mixture was extracted with ether (2 x 20 mL) and the combined organic layers were dried and concentrated. The residue was subject to column chromatography using 40% EA/hex as eluting solvent to afford 22.8 mg (38%) of diol 20: Rf = 0.50 (50% EA/hex); IR (same except where noted): 3329-32, 2927-8, 2856, 1450, 1071 (diast 2), 1039 (diast 1), 976 cm⁻¹; HRMS calc. for C₁₄H₂₉O₂ (MH)⁺: 229.2168; found: 229.2159 (3.5 ppm).

Diastereomer 1: ¹H δ 3.95 (1H, m), 3.73-3.78 (1H), 2.19 (2H, s), 1.65-1.72 (4H), 1.48-1.61 (3H), 1.29-1.47 (14H), 0.88 (3H, t, 6.6) ¹³C δ 69.2, 69.1, 40.0, 38.1, 38.0, 33.1, 31.8, 29.3, 27.1, 25.8, 25.4, 22.6, 20.5, 14.1

Diastereomer 2: ¹H δ 3.90-3.93 (1H), 3.65-3.70 (1H), 1.72-1.75 (1H), 1.25-1.61 (18H), 0.88 (3H, t, 6.6); ¹³C δ 70.9, 70.0, 39.4, 39.1, 38.7, 32.4, 31.8, 29.3, 28.2, 25.6, 24.3, 22.6, 21.4, 14.1 MS:

(1R*,3S*) 3-Methyl-1-phenyl-1,4-butanediol (21) was prepared in 69% by oxidation of oxasilane 16-Et using the Woerpel procedure described above: Rf = 0.2 (40% EA/hex); The product was assigned by comparison with literature reports. Rf = 0.2 (40% EA/hex); ¹H δ 4.89 (dd, 1H, 7.6, 4.7); 3.57 (dd, ABX, 1H, 10.4, 4.4); 3.52 (dd, ABX, 1H, 10.4, 6.4); 1.9-1.7 (3-4H, includes both ABX and a multiplet); 0.97 (d, 3H, 6.8); ¹³C δ 144.7, 128.4, 127.4, 125.8, 71.8, 67.9, 43.5, 32.2, 17.2.

References:


Denmark, S. E.; Yang, S. *Tetrahedron*, **2004**, *60*, 9695-9708.


B(C₆F₅)₃-promoted tandem silylation and intramolecular hydrosilylation: diastereoselective synthesis of oxasilinanes and oxasilepanes

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pdussault1@unl.edu

Supporting Information: ¹H and ¹³C NMR spectra

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Diols

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width: 8278.15 Hz = 20.6885 Hz/pt
number of scans: 16

freq. of 0 ppm: 400.130000 MHz
processed size: 32768 complex points
LB: 0.300  GF: 0.0000
Hz/cm: 128.818  ppm/cm: 0.32194

SI_NMR 11
SpinWorks 2.5: 13C NMR

file: D:\CX_RVS_paper\More spectra\cx-6-23\2\fid   expt: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 22075.06 Hz = 219.384162 ppm = 0.336839 Hz/pt
number of scans: 43
freq. of 0 ppm: 100.612769 MHz
processed size: 65536 complex points
LB: 1.000   GB: 0.0000
Hz/cm: 747.188   ppm/cm: 7.42563

SI_NMR 12
SpinWorks 2.5: 13C NMR

file: D:\Roman's\rvs-4-312\fid  expt: <zgpg3
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 22075.06 Hz = 219.384162 ppm = 0.336839 Hz/pt
number of scans: 398

freq. of 0 ppm: 100.612769 MHz
processed size: 65536 complex points
LB:  1.000  GB:  0.0000
Hz/cm:  562.193  ppm/cm:  5.58714

SI_NMR 14
SpinWorks 2.5: 1D Proton NMR

[Chemical structure image]

file: D:\CX_RVS_paper\More spectra\cx-6-19-sm\1\fid
expt: <zg30>
transmitter freq.: 400.132471 MHz
time domain size: 65536 points
width: 8278.15 Hz = 20.688513 ppm = 0.126314 Hz/pt
number of scans: 16

freq. of 0 ppm: 400.130010 MHz
processed size: 32768 complex points
LB: 0.300  GB: 0.0000
Hz/cm: 123.360  ppm/cm: 0.30830

SI_NMR 15
SpinWorks 2.5: 13C NMR

file: D:\CX_RVS_paper\More spectra\cx-6-19-sm2\fid  expt: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 22075.06 Hz = 219.384162 ppm = 0.336839 Hz/pt
number of scans: 38
freq. of 0 ppm: 100.612774 MHz
processed size: 65536 complex points
LB: 0.300  GB: 0.0000
Hz/cm: 882.914  ppm/cm: 8.77449

SI_NMR 16
SpinWorks 2.5: 1D P

file: D:\Roman's\rvs-4-30\1\fid   expt: <zg30>
transmitter freq.: 400.132471 MHz
time domain size: 32768 points
width: 8278.15 Hz = 20.688513 ppm = 0.252629 Hz/pt
number of scans: 16
freq. of 0 ppm: 400.130000 MHz
processed size: 32768 complex points
LB: 0.300  GB: 0.0000
Hz/cm: 138.813  ppm/cm: 0.34692

file: D:\Roman's\rvs-4-30\1\fid   expt: <zg30>
transmitter freq.: 400.132471 MHz
time domain size: 32768 points
width: 8278.15 Hz = 20.688513 ppm = 0.252629 Hz/pt
number of scans: 16
freq. of 0 ppm: 400.130000 MHz
processed size: 32768 complex points
LB: 0.300  GB: 0.0000
Hz/cm: 138.813  ppm/cm: 0.34692

SI_NMR 17
SpinWorks 2.5: 13C NMR

file: D:\Roman's\rvs-4-30\2\fid
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 22075.06 Hz = 219.384162 ppm = 0.336839 Hz/pt
number of scans: 77

freq. of 0 ppm: 100.612769 MHz
processed size: 65536 complex points
LB: 1.000   GB: 0.0000
Hz/cm:  621.862    ppm/cm:   6.18013

SI_NMR 18
SpinWorks 2.5: 1D Proton NMR

file: D:\CX_RVS_paper\More spectra\cx-6-20-sm1\fid  expt: <zg30>
transmitter freq.: 400.132471 MHz
time domain size: 65536 points
width: 8278.15 Hz = 20.688513 ppm = 0.126314 Hz/pt
number of scans: 16

freq. of 0 ppm: 400.130000 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000
Hz/cm: 126.996 ppm/cm: 0.31738

SI_NMR 19
SpinWorks:

![Compound Diagram](image)

**Details:**
- **File Path:** D:\CX_RVS_paper\More spectra\cx-6-20-crude\2\fid
- **Expt:** zgpg30
- **Transmitter freq.:** 100.622830 MHz
- **Time domain size:** 65536 points
- **Width:** 22075.06 Hz = 219.384162 ppm = 0.336839 Hz/pt
- **Number of scans:** 67
- **Freq. of 0 ppm:** 100.612769 MHz
- **Processed size:** 65536 complex points
- **LB:** 1.000, **GB:** 0.0000
- **Hz/cm:** 662.012, **ppm/cm:** 6.57915

SI_NMR 20
SpinWorks 2.5:

<table>
<thead>
<tr>
<th>PPM</th>
<th>8.0</th>
<th>7.6</th>
<th>7.2</th>
<th>6.8</th>
<th>6.4</th>
<th>6.0</th>
<th>5.6</th>
<th>5.2</th>
<th>4.8</th>
<th>4.4</th>
<th>4.0</th>
<th>3.6</th>
<th>3.2</th>
<th>2.8</th>
<th>2.4</th>
<th>2.0</th>
<th>1.6</th>
<th>1.2</th>
<th>0.8</th>
<th>0.4</th>
<th>0.0</th>
</tr>
</thead>
</table>

file: D:\CX_RVS_paper\Lost RVS-CX Spectra\rvs-4-4-h1\fid  
transmitter freq.: 400.132471 MHz  
time domain size: 32768 points  
width: 8278.15 Hz = 20.688513 ppm = 0.252629 Hz/pt  
number of scans: 16  

freq. of 0 ppm: 400.130009 MHz  
processed size: 32768 complex points  
LB: 0.300  GB: 0.0000  
Hz/cm: 141.280 ppm/cm: 0.35308
SpinWorks 2.5: 13C NMR

file: D:\CX_RVS_paper\Lost RVS-CX Spectra\rvs-4-4-c13\fid
expt: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 22075.06 Hz = 219.384162 ppm = 0.336839 Hz/pt
number of scans: 162

freq. of 0 ppm: 100.612770 MHz
processed size: 65536 complex points
LB: 1.000  GB: 0.0000
Hz/cm: 618.133  ppm/cm: 6.14307

SI_NMR 22
SpinWorks 2.5: 1D Proton NMR

file: D:\CX_RVS_paper\Lost RVS-CX Spectra\rvs-4-74\3\fid
expt: <zg30>
transmitter freq.: 400.132471 MHz
time domain size: 65536 points
width: 8278.15 Hz = 20.688513 ppm = 0.126314 Hz/pt
number of scans: 16

freq. of 0 ppm: 400.130006 MHz
processed size: 32768 complex points
LB: 0.300
GB: 0.0000
Hz/cm: 140.241 ppm/cm: 0.35049

SI_NMR 23
SpinWorks 2.5: 13C NMR

file: D:\CX_RVS_paper\Lost RVS-CX Spectra\rvs-4-74\2\fid  expt: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 32768 points
width: 22075.06 Hz = 219.384162 ppm = 0.673677 Hz/pt
number of scans: 323

freq. of 0 ppm: 100.612771 MHz
processed size: 16384 complex points
LB:  1.000  GB: 0.0000
Hz/cm: 612.154  ppm/cm: 6.08365

3-Pr
SpinWorks 2.5: 1D Proton NMR

file: D:\CX_RVS_paper\Lost RVS-CX Spectra\rvs-4-67\1\fid
expt: <zg30>
transmitter freq.: 400.132471 MHz
time domain size: 65536 points
width: 8278.15 Hz = 20.688513 ppm = 0.126314 Hz/pt
number of scans: 16

freq. of 0 ppm: 400.130006 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000
Hz/cm: 130.632 ppm/cm: 0.32647

SI_NMR 25
SpinWorks 2.5: 13C NMR

file: D:\CX_RVS_paper\Lost RVS-CX Spectra\rvs-4-67\2\fid
expt: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 32768 points
width: 22075.06 Hz = 219.384162 ppm = 0.673677 Hz/pt
number of scans: 645

freq. of 0 ppm: 100.612769 MHz
processed size: 16384 complex points
LB: 1.000  GB: 0.0000
Hz/cm: 611.461  ppm/cm: 6.07676

SI_NMR 26
SpinWorks 2.5: 1D Proton NMR

![NMR spectrum graph]

file: D:\CX_RVS_paper\Lost RVS-CX Spectra\cx-6-20-f3\fid  expt: <zg30>
transmitter freq.: 400.132471 MHz
time domain size: 65536 points
width: 8278.15 Hz = 20.688513 ppm = 0.126314 Hz/pt
number of scans: 16
freq. of 0 ppm: 400.130010 MHz
processed size: 32768 complex points
LB: 0.300  GB: 0.0000
Hz/cm: 148.032  ppm/cm: 0.36996

SI_NMR 27
SpinWorks 2.5: 13C NMR

file: D:\CX_RVS_paper\Lost RVS-CX Spectra\cx-6-20-f3\f3\fid expt: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 22075.06 Hz = 219.384162 ppm = 0.336839 Hz/pt
number of scans: 105

freq. of 0 ppm: 100.612769 MHz
processed size: 65536 complex points
LB: 1.000  GB: 0.0000
Hz/cm: 619.078  ppm/cm: 6.15247

SI_NMR 28
SiO<sub>hexyl</sub>Ph<sub>2</sub>-Ph

SI_NMR 31
SpinWorks 2.5:

file: D:\CX_RVS_paper\rvs-4-21\1\fid  expt: <zg30>
transmitter freq.: 400.132471 MHz
time domain size: 32768 points
width: 8278.15 Hz = 20.688513 ppm = 0.252629 Hz/pt
number of scans: 16

freq. of 0 ppm: 400.130006 MHz
processed size: 32768 complex points
LB: 0.300  GB: 0.0000
Hz/cm: 74.120  ppm/cm: 0.18524

SI_NMR 33
SpinWorks 2.5: 13C NMR

file: D:\Roman's\rvs-4-26-12\1\fid
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 22075.06 Hz = 219.384162 ppm = 0.336839 Hz/pt
number of scans: 316

freq. of 0 ppm: 100.612770 MHz
processed size: 65536 complex points
LB: 1.000 GB: 0.0000
Hz/cm: 345.548 ppm/cm: 3.43409

SI_NMR 34
file: D:\CX_RVS_paper\rvs-4-78\1\> 
transmitter freq.: 500.132001 MHz 
time domain size: 65536 points 
width: 5000.00 Hz = 9.997361 ppm = 0.076294 Hz/pt 
number of scans: 8

freq. of 0 ppm: 500.130005 MHz 
processed size: 32768 complex points 
LB: 0.300  GB: 0.0000
Hz/cm: 157.019  ppm/cm: 0.31396

SI_NMR 35
SpinWorks 2

file: D:\CX_RVS_paper\rvs-4-78\2\fid  
transmitter freq.: 125.770364 MHz
time domain size: 32768 points
width: 30030.03 Hz = 238.768729 ppm = 0.916444 Hz/pt
number of scans: 168

freq. of 0 ppm: 125.757789 MHz
processed size: 32768 complex points
LB:  1.000  GB:  0.0000
Hz/cm:  816.735  ppm/cm:  6.49386

4-Pr
SpinWorks 2.5: 1D Proton NMR

6-Pr diast 1

file: D:\CX_RVS_paper\Lost RVS-CX Spectra\rvs-4-69-2\1\fid
expt: <zg30>
transmitter freq.: 400.132471 MHz
time domain size: 65536 points
width: 8278.15 Hz = 20.688513 ppm = 0.126314 Hz/pt
number of scans: 16

freq. of 0 ppm: 400.130005 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000
Hz/cm: 128.814 ppm/cm: 0.32193

SI_NMR 37
SpinWorks 2.5: $^{13}$C NMR

6-Pr diast 1

file: D:\CX_RVS_paper\Lost RVS-CX Spectra\rvs-4-69-2\fid  
file: <zgpg30>

transmitter freq.: 100.622830 MHz

time domain size: 32768 points

width: 22075.06 Hz = 219.384162 ppm = 0.673677 Hz/pt

number of scans: 409

freq. of 0 ppm: 100.612769 MHz

processed size: 16384 complex points

LB: 1.000  GB: 0.0000

Hz/cm: 366.323  ppm/cm: 3.64055

SI_NMR 38
file: D:\CX_RVS_paper\Lost RVS-CX Spectra\rvs-4-69-1\1\fid
expt: <zg30>
transmitter freq.: 400.132471 MHz
time domain size: 65536 points
width: 8278.15 Hz = 20.688513 ppm = 0.126314 Hz/pt
number of scans: 16

freq. of 0 ppm: 400.130005 MHz
processed size: 32768 complex points
LB: 0.300  GB: 0.0000
Hz/cm: 141.279  ppm/cm: 0.35308

SI_NMR 39
SpinWorks 2.5: $^{13}$C NMR

$iPr$, $iPr$

O

hex

6-Pr diast 2

file: D:\CX_RVS_paper\Lost RVS-CX Spectra\rvs-4-69-12\fid
transmitter freq.: 100.622830 MHz
time domain size: 32768 points
width: 22075.06 Hz = 219.384162 ppm = 0.673677 Hz/pt
number of scans: 263

freq. of 0 ppm: 100.612769 MHz
processed size: 16384 complex points
LB: 1.000  GB: 0.0000
Hz/cm: 596.919  ppm/cm: 5.93224

SI_NMR 40
SpinWorks 2.5:

file: D:\CX_RVS_paper\rvs-4-76-1\1\fid
expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10330.58 Hz = 20.655659 ppm = 0.157632 Hz/pt
number of scans: 16

freq. of 0 ppm: 500.130008 MHz
processed size: 32768 complex points
LB: 0.300  GB: 0.0000
Hz/cm: 80.537  ppm/cm: 0.16103

SI_NMR 41
SpinWorks 2.5:

file: D:\CX_RVS_paper\rvs-4-76-1\fid
expt: <zgpg30>
transmitter freq.: 125.770364 MHz
time domain size: 16384 points
width: 30030.03 Hz = 238.768729 ppm = 1.832888 Hz/pt
number of scans: 256

freq. of 0 ppm: 125.757762 MHz
processed size: 32768 complex points
LB: 1.000 GB: 0.0000
Hz/cm: 436.295 ppm/cm: 3.46898
10-Et (5:1 mixture)
10-Ph diast 1 (minor)
10-Ph diast 1 (minor)
10-Ph diast 2 (major)
10-Ph diast 2 (major)
14-Et (minor)
14-Et
(major)
SpinWorks 2.5: 13C NMR

14-Et mixture

file: D:\CX_RVS_paper\cx-6-31-f2\2\fid
expt: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 22075.06 Hz = 219.384162 ppm = 0.336839 Hz/pt
number of scans: 214
freq. of 0 ppm: 100.612771 MHz
processed size: 65536 complex points
LB: 0.000 GB: 0.000
Hz/cm: 365.630 ppm/cm: 3.63367

SI_NMR 55
file: D:\CX_RVS_paper\cx-6-42\1\fid  
expt: <zg30>
transmitter freq.: 400.132471 MHz

time domain size: 65536 points
width: 8278.15 Hz = 20.688513 ppm = 0.126314 Hz/pt
number of scans: 16

freq. of 0 ppm: 400.130010 MHz
processed size: 32768 complex points
LB: 0.300  GB: 0.0000
Hz/cm: 135.826  ppm/cm: 0.33945
SpinWorks 2.5: 13C NMR

file: D:\CX_RVS_paper\cx-6-42\2\fid  exp: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 22075.06 Hz = 219.384162 ppm = 0.336839 Hz/pt
number of scans: 67

freq. of 0 ppm: 100.612775 MHz
processed size: 65536 complex points
LB: 1.000  GB: 0.0000
Hz/cm: 385.712  ppm/cm: 3.83325

SI_NMR 59
hexyl
20-diastereomer 1

SI_NMR 60
26 diastereomer 2
SpinWorks 2.5: 1D Γ

file: D:\CX_RVS_paper\More spectra\cx-6-25\1\fid  expt: <zg30>
transmitter freq.: 400.132471 MHz
time domain size: 65536 points
width: 8278.15 Hz = 20.688513 ppm = 0.126314 Hz/pt
number of scans: 16
freq. of 0 ppm: 400.130000 MHz
processed size: 32768 complex points
LB: 0.300  GB: 0.0000
Hz/cm: 142.318  ppm/cm: 0.35568

SI_NMR 64
SpinWorks

[Chemical structure image]

file: D:\CX_RVS_paper\More spectra\cx-6-25\2\fid
expt: <zgpg30>
transmitter freq.: 100.622830 MHz

freq. of 0 ppm: 100.612774 MHz
processed size: 65536 complex points

LB: 0.300  GB: 0.0000
Hz/cm: 608.691  ppm/cm: 6.04924

number of scans: 75

SI_NMR 65