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REGIODIVERGENT MEDIUM-RING OXASILACYCLE SYNTHESIS FROM DIALLYLSILANES

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Abstract – Medium-ring (7-9 membered) oxasilacycles were synthesized by sequential electrophile-promoted rearrangement of diallylsilanes, etherification with an alkene-containing alcohol, and ring-closing metathesis (RCM). Depending on the choice of catalyst for the RCM, different oxasilacycle products could be obtained. The Grubbs first-generation catalyst cleanly afforded allyl ether oxasilacycles whereas the second-generation Grubbs catalyst selected for the regioisomeric cyclic enol ether, resulting from RCM followed by isomerization. Isomerization during RCM was suppressed by substitution at the allyl ether position. The use of homoallyl ether- or non-ether substrates, and/or the addition of benzoquinone also prevented isomerization during RCM, suggestive of a ruthenium hydride-based double bond migration mechanism. Both product subclasses represent useful synthetic intermediates. As an initial demonstration, this sequence was used to prepare the side-chain of the natural product psymberin, as well as a ulosonic acid analogue.

INTRODUCTION

Recently, our group reported the discovery of an iodine-promoted rearrangement of diallylsilanes.[1] The reaction is proposed to proceed through intramolecular allylation of an intermediate cation giving iodosilane **1** as the initially formed product (Figure 1A). Subsequent addition of an alcohol such as isopropanol (*i*PrOH) generated stable silyl ether products **2**.[2] Rather than using isopropanol, we recognized that trapping the iodosilane intermediate **1** with an alkene-containing alcohol would set the stage for

oxasilacycle formation through ring-closing metathesis (RCM, Figure 1B).[3] Previous examples of methods using RCM to generate synthetically valuable oxasilacycles motivated us to investigate the synthesis of and subsequent RCM reactions of dienyl silyl ethers **3**.[4]

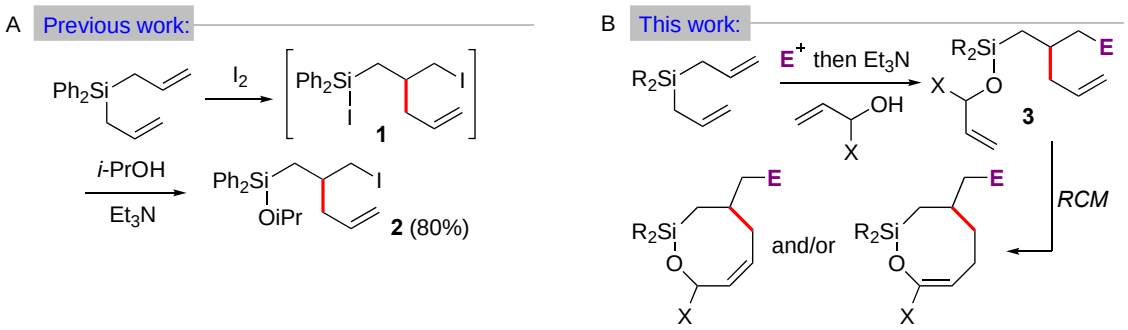
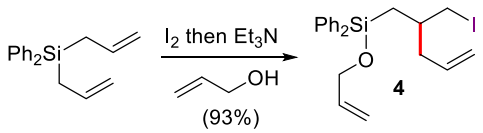


Figure 1. Previously described iodine-promoted diallylsilane rearrangement (left) and this work wherein an alkene-containing alcohol is used allowing for oxasilacycle formation by RCM with or without concomitant isomerization.

RESULTS AND DISCUSSION

Previously, we discovered diallyldiphenylsilane was optimal for our iodine-promoted rearrangements.[1,2] Our RCM investigations, therefore, began with the preparation of dienyl diphenylsilyl ether **4** by initial treatment of diallyldiphenylsilane with iodine at room temperature (rt) for 3 h (Scheme 1). To the same flask was then added triethylamine followed by allyl alcohol, providing compound **4** in 93% yield.



Scheme 1. Synthesis of RCM precursor **4**

With compound **4** in hand, our RCM investigations commenced using the Grubbs first-generation- (**Ru-I**)[5] or second-generation catalyst (**Ru-II**)[6] in dichloromethane (DCM) as solvent at rt. Both catalysts promoted the RCM, however different products were obtained depending on the choice of catalyst (Figure 2). The NMR spectrum of the crude product mixture from the reaction using **Ru-I** gave prominent signals matching what was expected for the 8-membered ring ether **5**, with alkene signals at 5.79 and 5.60 ppm (top, blue trace, H_A and H_B). The NMR spectrum obtained from the reaction with **Ru-II** (bottom, red trace) did not contain these alkene signals, instead showing prominent signals at 6.49 and 4.84 ppm that were coupled to one another according to COSY NMR. Together, these NMR signals were interpreted as belonging to an enol ether, suggesting isomerization had occurred during the **Ru-II** reaction.

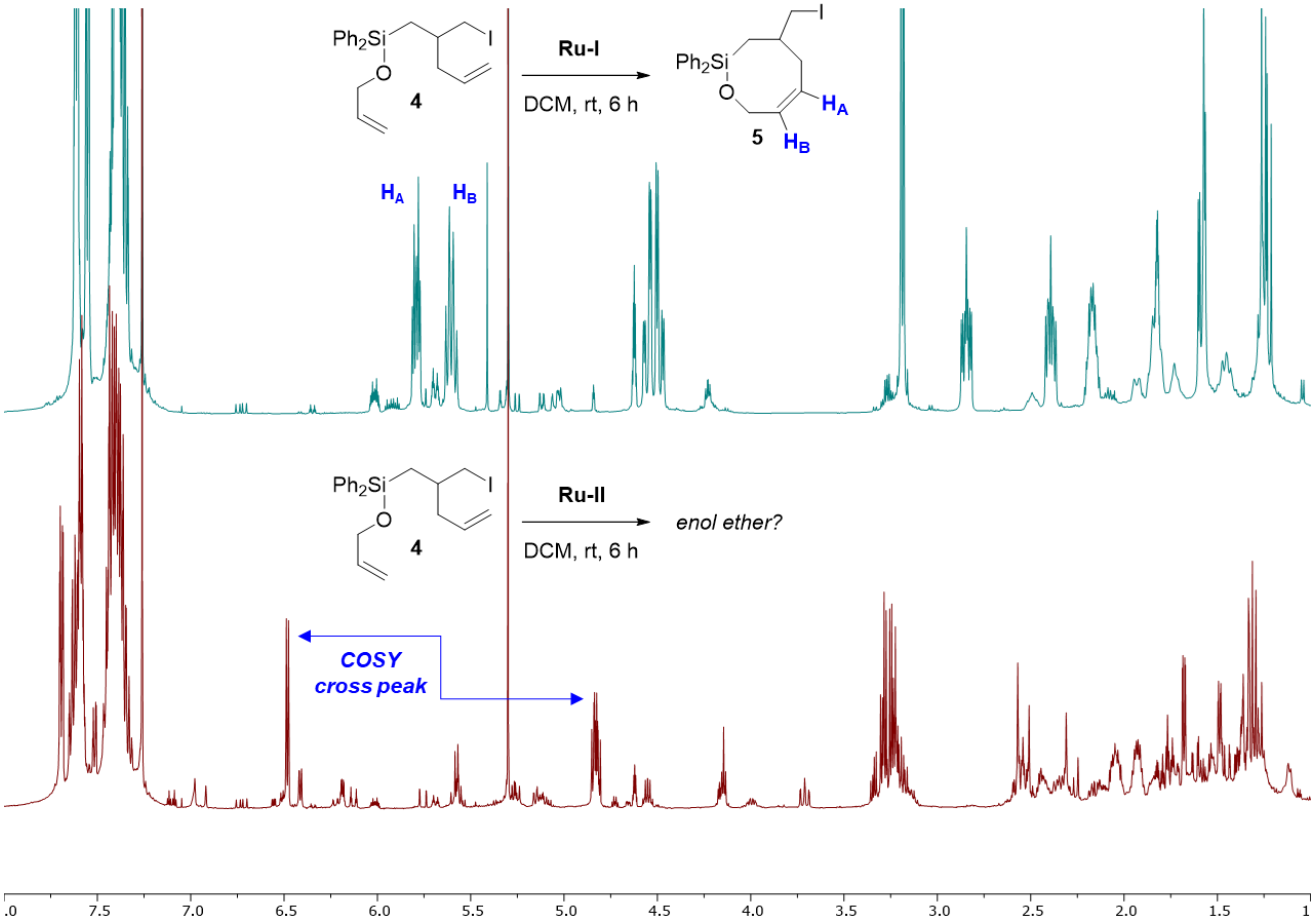
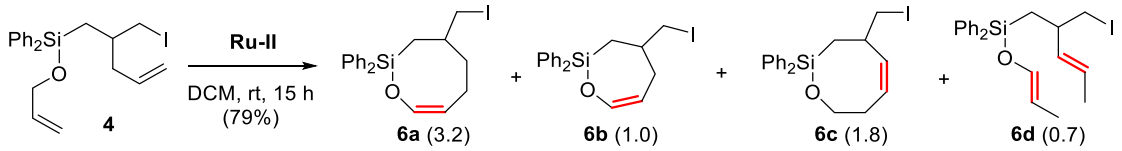


Figure 2. Comparison of ^{1}H NMR spectra of the crude product mixtures obtained from the reaction of **4** with **Ru-I** (top) and **Ru-II** (bottom)

The formation of enol ethers as a result of isomerization during RCM has been described by other groups.[7] For our system, two different cyclic silyl enol ether RCM/isomerization products can be envisioned. If RCM occurred first (i.e. producing **5**) followed by isomerization, we would expect the 8-membered enol ether **6a** (Scheme 2). RCM post-isomerization, by contrast, would generate the 7-membered ring compound **6b**. Ultimately, detailed NMR analysis combined with high-resolution mass spectrometry confirmed that it was the 8-membered ring isomerized product **6a** that was obtained as the major product from the **Ru-II** catalyzed reaction. Moreover, the isomerization was not 100% selective. Careful purification of the crude product mixture by flash chromatography on silica gel allowed for the separation and characterization of several additional minor products. Among them was the regioisomeric RCM/isomerization product **6c**, where isomerization occurred in a different direction compared to the enol ether **6a**, along with the bis-isomerized non-RCM product **7**. Although not isolated in pure form, we assigned minor peaks observed in the NMR spectrum of purified **6a** to the 7-membered ring enol ether **6b**, which was later confirmed by mass spectrometry.[8] Based on ^{1}H NMR integrations of the crude product mixture, the ratio between the different ring sized enol ether products **6a** and **6b** obtained was 3.2:1 respectively.



Scheme 2. RCM of **4** with **Ru-II**. The relative distribution of the different products **6a-6d** is given in parentheses based on ^{1}H NMR analysis of the crude product mixture.

To probe the mechanism of product formation in the **Ru-II** RCM/isomerization, a time course study was conducted in CD_2Cl_2 at rt in which NMR spectra were recorded at 15 min, 1, 2.5, 4.5, and 24 h (Figure 3). RCM to non-isomerized product **5** and bis-isomerized **6d** was rapid; 15 min was enough to convert nearly 50% of the starting material **4**. After 1 h, **5** was the major component with trace amounts of isomerized products **6a** and **6b** appearing. After 4.5 h, **5** was consumed and had undergone isomerization to primarily **6a**. Note that the sample becomes increasingly enriched in the 8-membered ring enol ether **6a** relative to the 7-membered ring enol ether **6b** over the course of the reaction. This is consistent with **6a** resulting from isomerization of RCM product **5** which constitutes the major component in the mixture at 1 h, whereas **6b** arises from isomerization of the starting diene **4** followed by RCM.[8]

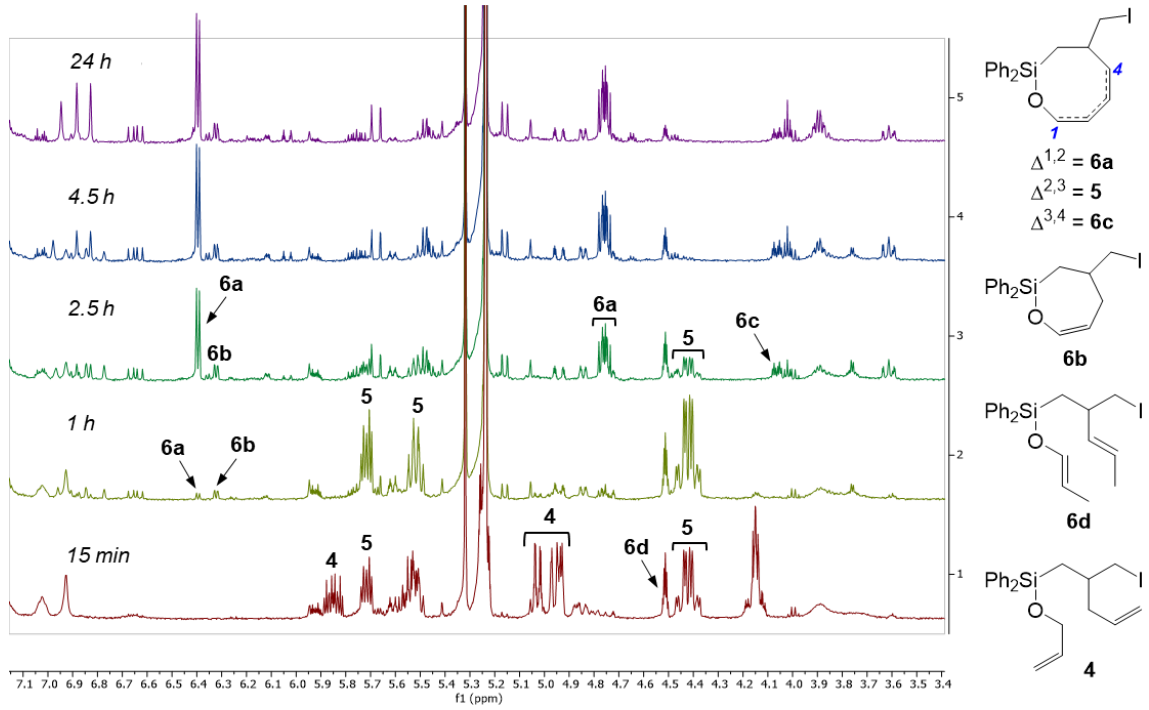
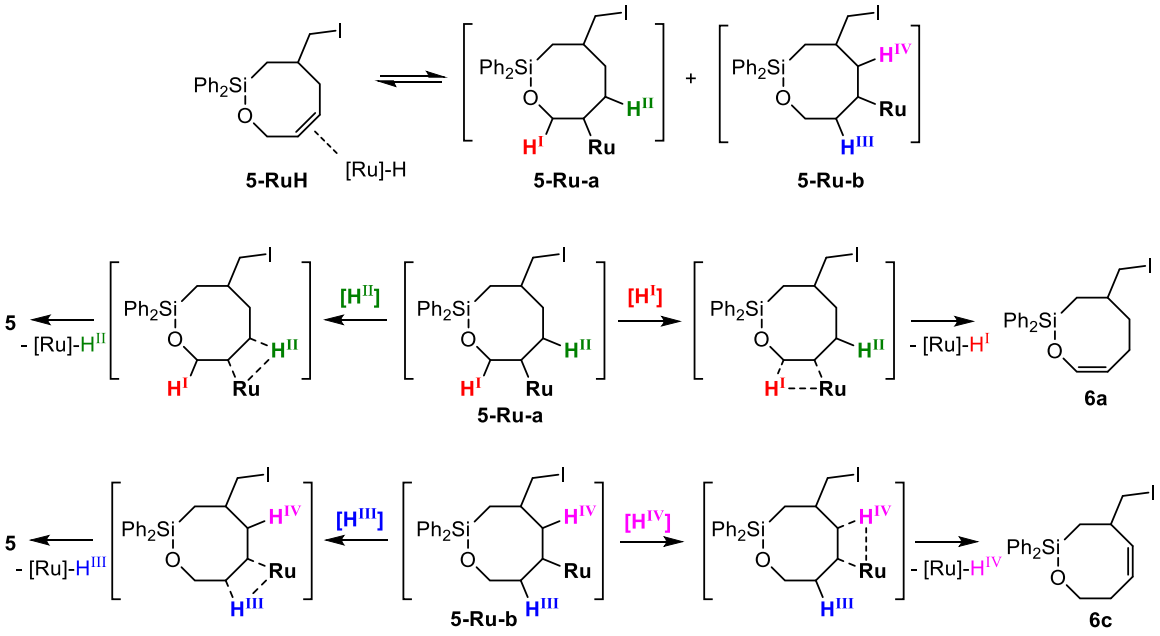


Figure 3. NMR time course study of **4** subjected to RCM in CD_2Cl_2 using catalyst **Ru-II**. Select signals have been identified that correspond to the different numbered compounds. The results indicate RCM product **5** is formed first (~50% conversion within 15 min) followed by its isomerization to **6a** within 4.5 h (blue trace).

Other groups have reported catalyst-dependent isomerization in metathesis reactions,[9] with **Ru-II** more prone to promoting isomerization.[10] Different mechanisms have been proposed to explain these observations, but generally converge on the formation of a ruthenium hydride species (Ru-H) that is responsible for isomerization.[11-17] Assuming an Ru-H is formed in our reactions, addition to the alkene in **5** can give rise to intermediates **5-Ru-a** and **5-Ru-b** (Scheme 3). Depending on which neighboring proton is subsequently eliminated, different products will be obtained. For example, intermediate **5-Ru-a** has two neighboring protons available for elimination (H^I and H^{II}). Elimination of H^{II} would regenerate the initial RCM product **5** whereas loss of H^I gives enol ether **6a**. The same rationale can be applied to explain the formation of **6b**. Elimination of H^{III} from intermediate **5-Ru-b** would regenerate the starting ring-closed product **5** while elimination of H^{IV} will lead to isomerized product **6b**. Surprisingly, despite the possible routes to regenerate product **5** even in the presence of Ru-H species, this compound was not observed when the reaction was run to completion using **Ru-II**, while **6a** and **6c** were isolated at 55% and 12% yield respectively.



Scheme 3. Ru-H based mechanism for formation of RCM/isomerization products **6a** and **6c**

To better understand the product distribution from these RCM reactions, DFT calculations were performed to calculate the relative energies of the different products (Figure 4). Among the possible 8-membered ring products, compound **5** was calculated to be highest energy, which would explain why it was not observed under conditions with presumed thermodynamic control. The enol ether **6a** was more stable than both **5** and the regioisomeric isomerized RCM product **6c**, consistent with **6a** being the major product obtained in our reactions along with other comparative studies on the relative energies of allyl- versus vinyl ether isomers.[18] The most stable isomer **6e** containing a tri-substituted alkene was not observed in our reactions,

which we attribute to steric inhibition of either Ru-H addition to **6c** or the subsequent beta-hydride elimination step required to form this isomer (ref. Scheme 3). A similar steric argument was proposed by Seo and Rhee to explain the lack of trisubstituted alkene formation in their recent ruthenium-catalyzed olefin migration study.[19]

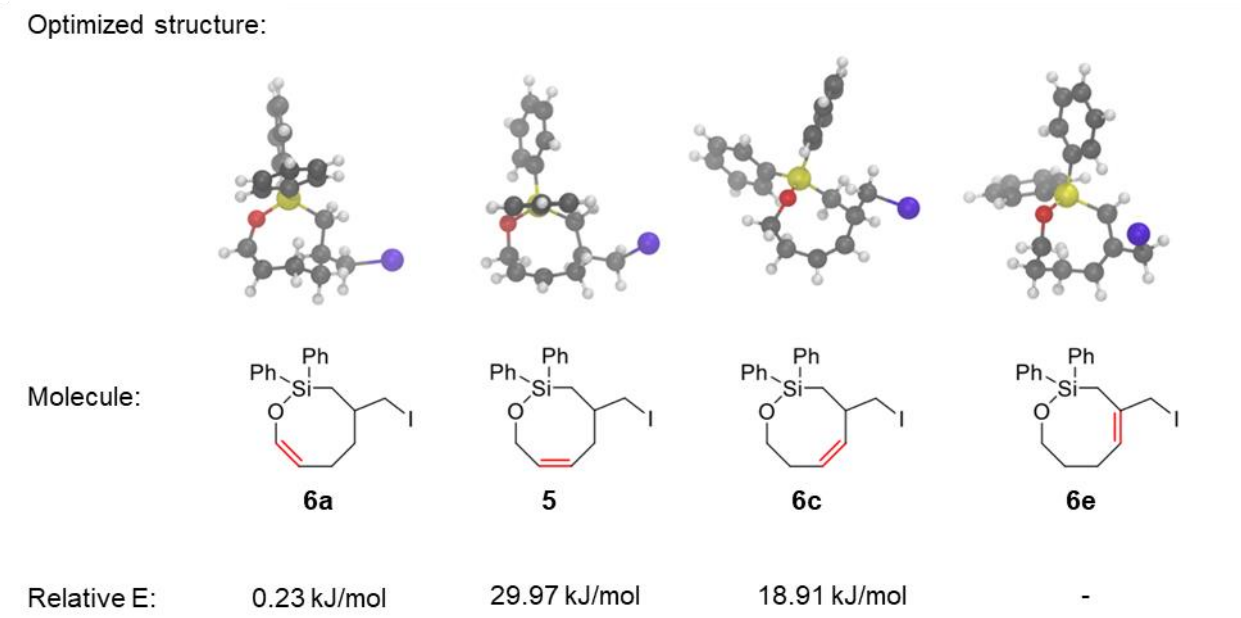
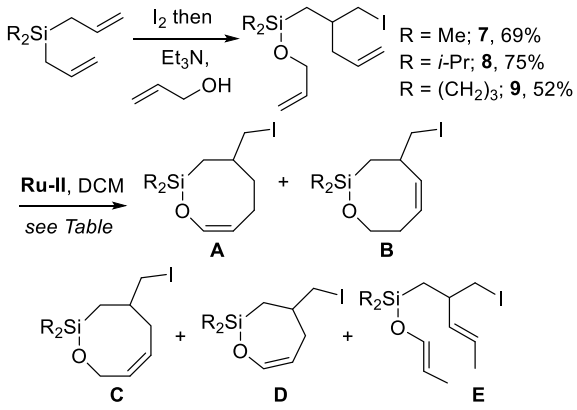


Figure 4. Results from DFT relative energy calculations of the different possible 8-membered ring RCM products. Consistent with these calculations, compound **6a** being more stable than **5** or **6c** was obtained as the major product.

To further examine potential steric effects on the RCM/isomerization process, we prepared several additional RCM precursors (**7**-**9**) containing different substituents on silicon by iodine rearrangement of the corresponding diallylsilanes and allyl alcohol etherification (Scheme 4). Treatment of these compounds with **Ru-II** in DCM at rt for 15 h gave a mixture of RCM and isomerized products as summarized in the accompanying table. All four of these silanes were able to undergo RCM in high yield with the exception of the dimethylsilane. We hypothesize that larger groups on silicon aid the RCM through a Thorpe-Ingold type effect.[20] No starting material was recovered from the dimethylsilane RCM, with the mass balance presumed to be oligomeric material. Additionally, the dimethylsilane RCM product (**10**) was found to be less stable to purification by chromatography on silica, which could also have contributed to the lower isolated yields. The 8-membered ring enol ethers (**A**) were the major products in all cases and none of the non-isomerized RCM product (**C**) was observed. Additionally, the ratio of isomerized 8-membered ring RCM products **A** and **B** were generally comparable among the different silanes suggesting the selectivity for isomerization directionality is not influenced to a large extent by the groups on silicon.



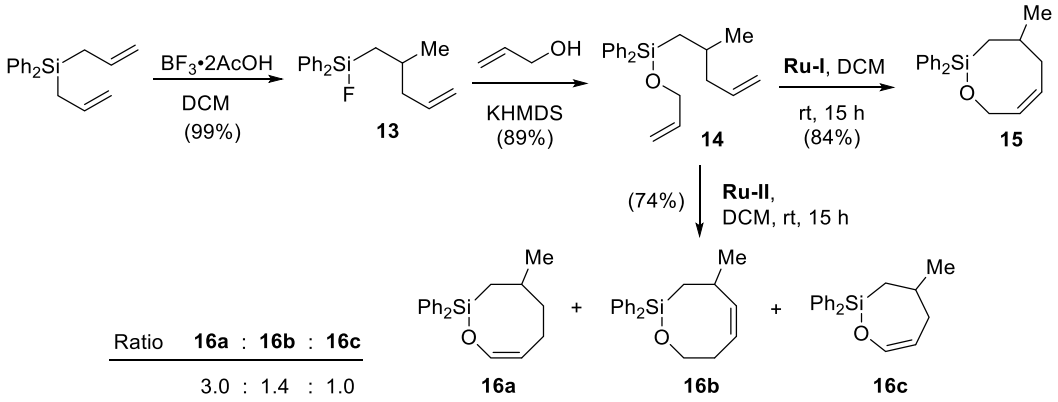
Scheme 4. Synthesis and RCM of differentially silicon-substituted dienes

Table. Yields and ratios of products **A**-**E** from RCM reactions of compounds **5**, **7**-**9** (see Scheme 4)

R	Yield*	A	B	C	D	E
Ph (**6**)	69	3.2	1.8	-	1.0	0.7
Me (**10**)	28	2.6	1.4	-	1.0	0**
i-Pr (**11**)	65	3.2	0**	-	1.0	0**
$(CH_2)_3$ (**12**)	77	3.3	1.3	-	0**	0**

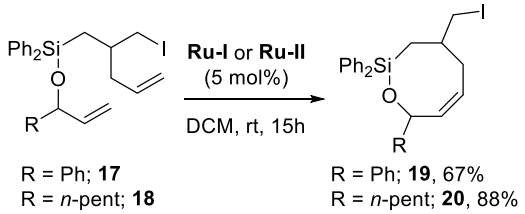
Notes for Table: All reactions were performed with 5 mol% **Ru-II** in DCM for 15 h. Ratios were determined by NMR integrations. *Combined yield of enol ethers **A** and **D**. **Peaks corresponding to this compound were not observed in NMR spectra, however overlapping signals could have prevented the detection of very small amounts.

We also questioned whether the pendant iodomethyl group in **4** might affect the RCM results. To test this, we adopted the acid-promoted rearrangement conditions described by Suslova et al. for the preparation of compound **13** containing a methyl group at this position (Scheme 5).[21,22] Etherification of **13** in preparation for RCM by fluorine substitution was more challenging than for the iodosilanes that we obtained from the iodine-promoted rearrangement. For instance, using our standard etherification conditions, (allyl alcohol, triethylamine, DCM, rt), no reaction was observed. A stronger nucleophile was therefore created by deprotonation of allyl alcohol with KHMDS. The resulting potassium alkoxide was then able to substitute the fluorine atom, giving ether **14** in 89% yield. Compound **14** was treated with catalyst **Ru-II** in DCM at rt. Exchanging the iodomethyl group in **4** with the methyl group in **14** had little to no effect on RCM/isomerization. For instance, the ratio of isomerized RCM products **16a**:**16b**:**16c** obtained from the reaction with **Ru-II** for the methyl-substituted series was 3:1.4:1, while the iodomethyl gave comparable ratios of 3.2:1.8:1 (**6a**:**6c**:**6b**). Additionally, like with the iodomethyl compound **4**, the use of **Ru-I** with **14** resulted only in RCM, giving oxasilacycle **15** in 84% yield.



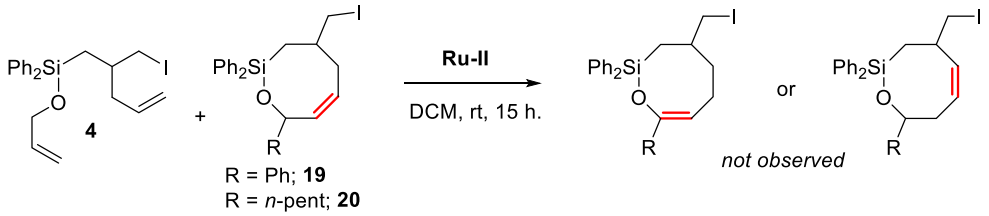
Scheme 5. Synthesis and RCM reactions of methyl-substituted dienylsilane **14**

To further examine the role of substrate structure on the RCM/isomerization, we prepared phenyl- and hexyl-substituted dienes **17** and **18** by iodine rearrangement followed by etherification with the appropriately substituted allylic alcohol (Scheme 6). Interestingly, RCM reactions of **17** and **18** using either the **Ru-I** or **Ru-II** catalyst gave only non-isomerized RCM products **19** and **20** respectively as 1:1 mixtures of diastereomers. The lack of isomerization in these RCM reactions, even when using the **Ru-II** catalyst, demonstrates that the phenyl and hexyl groups were able to effectively hinder the isomerization. It is possible that the alkene in RCM products **19** and **20** is unable to coordinate to the catalyst preventing formation of a Ru-H species responsible for isomerization.[23] Alternatively, the isomerizing Ru-H species generated otherwise cannot effectively bind to the alkene in these RCM products. Hydrometallation could also occur, but the subsequent beta-hydride elimination to form the corresponding trisubstituted alkene enol ether is hindered in these systems thereby regenerating **19** and **20**. This latter explanation, however, would fail to explain why isomerization in the other direction (e.g. compound **6c** from **4**) was not observed in these reactions if indeed a Ru-H species was present and responsible for the isomerization.



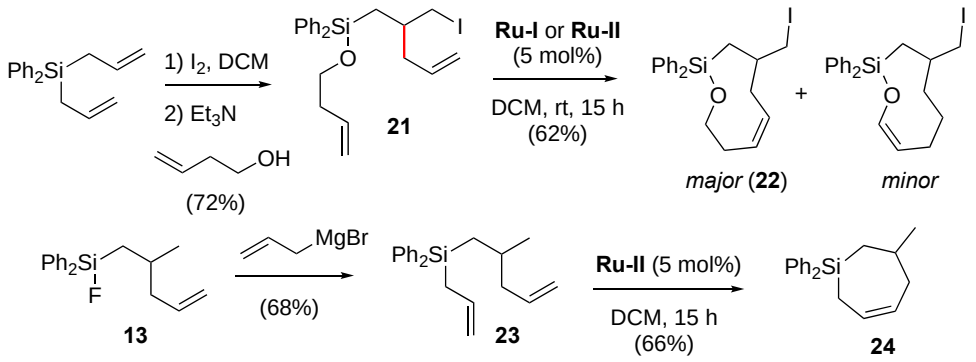
Scheme 6. Synthesis of phenyl and *n*-pentyl substituted oxasilacycles **19** and **20** by RCM

To distinguish between these possibilities, the RCM of **4** using **Ru-II** was performed in the presence of **19** or **20** (Scheme 7). In both of these reactions, compounds **19** and **20** were recovered without any evidence for isomerization according to ^{1}H NMR analysis. Therefore, even under conditions that generate a **Ru-II** derived species capable of isomerization, compounds **19** and **20** resist double bond migration, presumably by preventing the hydrometallation step of an Ru-H mediated isomerization process.



Scheme 7. RCM of **4** in the presence of **19** and **20**

To determine how ring size and heteroatom placement might affect the RCM/isomerization, a 9-membered ring oxasilacycle synthesis was also explored. The RCM precursor was synthesized by a one-pot sequence of iodine rearrangement and etherification using 3-buten-1-ol (Scheme 8). In this way, diene **21** was obtained in 72% yield from diallyldiphenylsilane. Subjecting **21** to RCM with **Ru-I** in DCM at rt for 15 h gave mostly starting material and only trace amounts of the RCM product **22**. Switching to the **Ru-II** catalyst resulted in the formation of mostly **22**, while isomerization to an enol ether did not occur to a large extent (<10%, See Supporting Information). One possible explanation for the decreased isomerization in the RCM of **21** is the lack of an allylic ether in the initially formed RCM product **22**, which are known to be particularly susceptible to isomerization during metathesis processes.[7,24-31] Consistent with this observation, the RCM of non-ether **23** also proceeded without isomerization, giving exclusively **24** as the only RCM product obtained even when using **Ru-II**.



Scheme 8. RCM reactions of homoallyl ether **21** and non-ether **23**

Based on the mechanism proposed by Bourgeois et al.,[23] we can explain our results by considering RCM products such as **5** and **15** to be more activated toward formation of a Ru-H isomerizing species. More specifically, in RCM product **22**, the carbons immediately adjacent to the alkene do not contain an oxygen atom that increases the acidity of those hydrogens (Figure 5). Whereas the allylic position in RCM product **5** is more easily deprotonated leading ultimately to the formation of a Ru-H and isomerization.

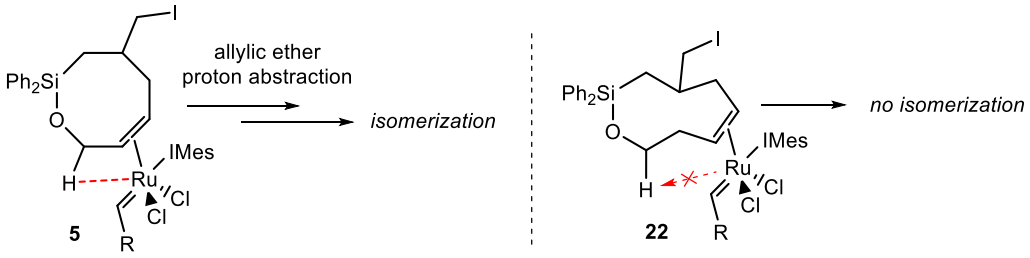
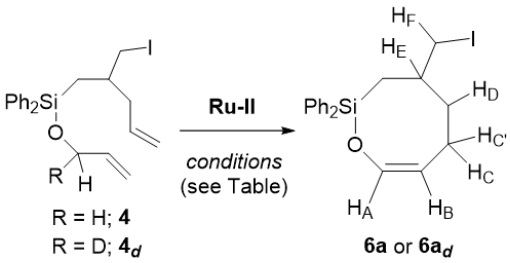


Figure 5. Possible proton abstraction mechanism to explain the different isomerization reactivity for 9-membered ring **22** versus 8-membered ring oxasilacycle **5**. The increased acidity of the allylic proton in **5** could contribute to the formation of Ru-H species responsible for the observed isomerization in these systems.

Substitution with deuterium at the allylic position of allyl ethers has been used to study the mechanism of isomerization of these compounds by **Ru-II**.[7a,12,32] For the same purpose, we prepared and examined RCM of a deuterated analogue $\mathbf{4}_{\boldsymbol{d}}$ (Scheme 9). Treatment of $\mathbf{4}_{\boldsymbol{d}}$ with **Ru-II** in DCM at rt gave, as expected, primarily the RCM/isomerization enol ether $\mathbf{6a}_{\boldsymbol{d}}$. Quantitative recovery of the deuterium was, however, not obtained according to ^{1}H NMR analysis (see accompanying Table). This was also true for a reaction employing sequential treatment of $\mathbf{4}_{\boldsymbol{d}}$ with **Ru-I** (forming $\mathbf{5}_{\boldsymbol{d}}$) followed by **Ru-II**, with deuterium detected only at the original position from the starting material (H_A) and not at the allylic position (H_C/$H_{C'}$) as would be expected following isomerization via an Ru-D species. Repeating the labeling study in CD_2Cl_2 gave identical deuterium recovery indicating that H/D exchange with the solvent is not occurring. H/D exchange between a Ru-D (or Ru-H) and the NHC ligand has been reported for complexes of this type,[12] which could explain the loss of deuterium from substrate $\mathbf{4}_{\boldsymbol{d}}$ that we observed. At this stage, however, a process involving H/D exchange of a Ru-D intermediate with adventitious water cannot be excluded.

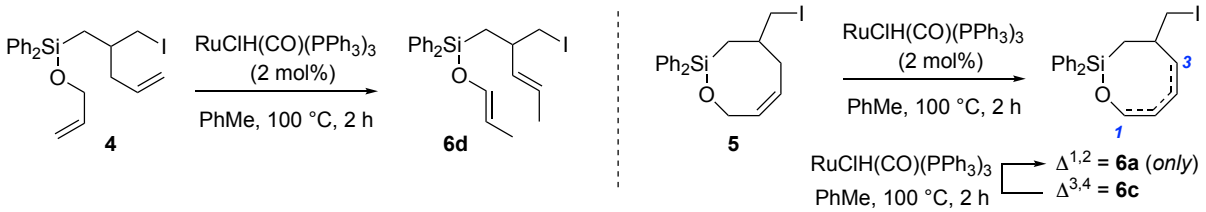


Signal	**4** / **Ru-II**	**4**$_d$ / **Ru-II**	**4**$_d$ / **Ru-I** then **Ru-II**	**4**$_d$ / **Ru-II**, CD_2Cl_2
H_A	0.97	0.39	0.41	0.37
H_B	1.18*	1.17*	0.89	1.04
H_C	1.06	1.00	0.95	1.04
$H_{C'}$	1.13*	1.04*	0.97	1.10
H_D	1.07*	1.02	1.02	1.10
H_E	1.10	1.01*	0.98	1.07
H_F	1.00	1.00	1.00	1.00

Notes for Table: All reactions were performed using compound **4** or **4**$_d$, catalyst **Ru-I** and/or **Ru-II** (5 mol%) in DCM at rt for 15 h unless indicated otherwise. Integrations for H_F were normalized to 1.00 (red text). *Overlapping signals could have resulted in a higher than actual integration value.

Scheme 9. RCM reactions and NMR analysis of deuterated substrate $\mathbf{4}_{\boldsymbol{d}}$

Nonetheless, we still suspected a ruthenium hydride was responsible for isomerization in our reactions, and set out to compare how a preformed Ru-H ($RuClH(CO)(PPh_3)_3$ might promote isomerization of the dialkene RCM precursor **4**, along with the associated RCM products **5** and **6**.[33] When diene **4** was subjected to the isomerization conditions described by Morgans et al. using $RuClH(CO)(PPh_3)_3$,[34] the results showed 100% conversion of the starting material (Scheme 10). The major product was **6d** wherein both alkenes have isomerized, which we also obtained in small amounts from **Ru-II** catalyzed reactions (ref. Scheme 2). Treatment of RCM product **5** with $RuClH(CO)(PPh_3)_3$ yielded 100% conversion to enol ether **6a** (Figure 7). None of the isomeric **6c** was detected by NMR analysis from this reaction. Furthermore, when **6c** was subjected to the same conditions, isomerization to **6a** was also observed in 100% conversion (Figure 7). This further corroborates conversion between isomerization products is possible, and that **6a** is favored in line with our relative energy calculations.

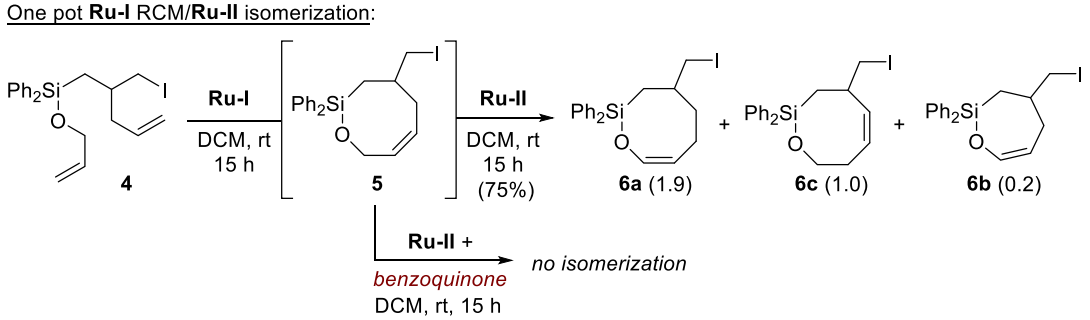


Scheme 10. Reactions of **4**, **5**, and **6c** with $RuClH(CO)(PPh_3)_3$

The results we obtained from experiments with $RuClH(CO)(PPh_3)_3$ provide support for a Ru-H based isomerization in our RCM reactions. However, there are some notable differences. For instance, $RuClH(CO)(PPh_3)_3$ isomerization of RCM product **5** was completely regioselective, giving exclusively enol ether **6a**. RCM reactions with **Ru-II**, in contrast, gave a mixture of **6a** and its regioisomer **6c** as an approximately 2:1 mixture. One explanation for these differences is that the nature of the Ru-H species formed during the RCM reactions is not identical to $RuClH(CO)(PPh_3)_3$, and this **Ru-II**-derived Ru-H is a less selective isomerization catalyst. It is also possible that other double bond migration processes might occur during the **Ru-II** reaction, for example involving ruthenium nanoparticles,[35] and could contribute to the differing selectivity observed.

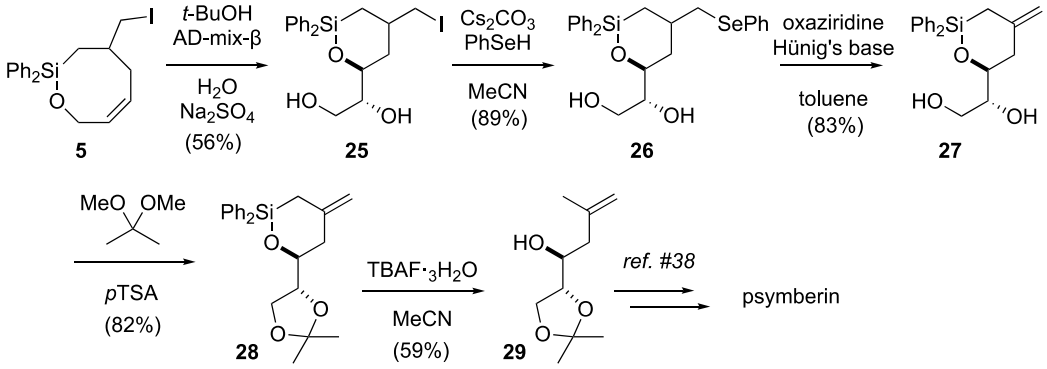
Certain additives such as benzoquinone are known to prevent isomerization.[36] To assess the ability of benzoquinone to suppress isomerization in our RCM reactions, we performed two experiments. In one, compound **4** was first treated with **Ru-I**. Once **4** was completely consumed and converted to **5** according to ^1H NMR analysis, **Ru-II** was then added to the same flask and allowed to react for 15 h (Scheme 11). This sequential **Ru-I**/**Ru-II** addition protocol gave isomerization products **6a** and **6c** in comparable ratios

to that obtained when just using **Ru-II** (1.8:1 vs. 1.9:1 **6a**:**6c**). Significantly less of the 7-membered enol ether **6b** was formed from this sequential catalyst addition (4.6:1 using **Ru-II** vs. 9.5:1 using **Ru-I**/**Ru-II**). Yet it is interesting that **6b** is nonetheless produced, indicating ring opening of **5** (or **6a**/**6c**) is possible, followed by isomerization and RCM thereby generating the ring-contracted product **6b**. The only isomerized product not detected in the one-pot sequential **Ru-I**/**Ru-II** catalyzed reaction was **6d**, wherein both double bonds have isomerized and RCM has not occurred. This is expected since the precursor **4** was consumed upon treatment with **Ru-I** and converted to **5**. For the second experiment, sequential treatment with **Ru-I** and **Ru-II** was again performed. However, prior to the **Ru-II** addition, benzoquinone (3 equiv.) was also added. In this case, only **5** was obtained, demonstrating the effectiveness of benzoquinone for preventing this isomerization process.



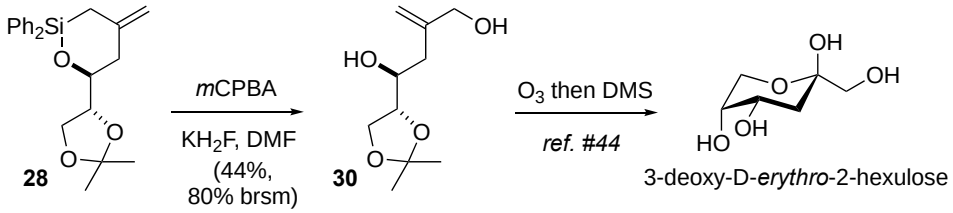
Scheme 11. Results from sequential treatment of **4** with **Ru-I** then **Ru-II** or **Ru-II** and benzoquinone. The relative distribution of the different products **6a**-**6c** is given in parentheses based on ^{1}H NMR analysis of the crude product mixture.

With efficient and selective access to these various oxasilacycles, studies are underway to explore their potential as synthetic intermediates. As an initial demonstration, dihydroxylation of **5** using Sharpless' conditions[37] (SADH) occurred with concomitant ring-contraction, resulting in isolation of the six-membered oxasilacycle diol **25** (Scheme 12). Elimination of the iodide to generate exomethylene-containing **27** was performed using a previously optimized two-step procedure via selenoether **26**.[2] Protection of the diol in **27** as its cyclic acetal followed by desilylation with TBAF gave **29** and bisected the synthetic route to the natural product psymberin described by Jiang et al.[38] A comparison of the optical rotation measured for **29** to that previously reported[38] ($[\alpha]_D$ +0.68 ($CHCl_3$, *c* 0.50) vs. $[\alpha]_D$ +16.8 ($CHCl_3$, *c* 1.0) indicated the SADH of **5** occurred with little to no enantioselectivity. SADH of *cis*-disubstituted alkenes is known to be challenging, generally occurring with lower yield and enantioselectivity.[39,40] Nonetheless, with optimization of the dihydroxylation (or a similar reaction),[41] we believe the sequence represents an efficient method for synthesizing the psymberin side chain.



Scheme 12. Synthesis of compound **29**, a known synthetic precursor to the natural product psymberin,[38] from oxasilacycle **5**

Alternatively, oxidative desilylation of **28** produced diol **30** (Scheme 13). Among the different conditions screened to promote this oxidative cleavage (e.g. fluoride source, solvent),[42] we found the original Tamao conditions to be most effective,[43] providing the diol in 44% yield along with unreacted starting material that were easily separable by chromatography on silica. Ozonolysis of **30** gives 3-deoxy-D-*erythro*-2-hexulose, a C-1 reduced analogue of a natural and essential ulosonic acid of biological interest.[44]



Scheme 13. Synthesis of 3-deoxy-D-*erythro*-2-hexulose from **28** according to the method of Gintner et al.[44]

CONCLUSION

In summary, we have developed an efficient synthesis of medium-ring oxasilacycles starting from diallylsilanes using a sequence of electrophile-promoted rearrangement, etherification, and RCM. Moreover, conditions and substrates have been identified that allow for the selective formation of either the direct RCM cyclic allyl ether product, or the corresponding enol ether resulting from isomerization post RCM. Selectivity for these different products was catalyst dependent, with RCM reactions employing **Ru-II** producing primarily the 8-membered ring silyl enol ether, whereas catalyst **Ru-I** cleanly gives the non-isomerized cyclic allyl ether oxasilacycle. Benzoquinone was effective for preventing isomerization during RCM with **Ru-II**, providing evidence for an Ru-H based isomerization mechanism which was supported by experiments using a preformed Ru-H. Substitution at the allylic ether position also prevented isomerization, suggesting certain steric factors associated with the observed isomerization process. Additionally, the presence of an allyl ether was key to the isomerization occurring, with both homoallyl- and non-ether substrates resisting isomerization during RCM. The ratio of isomerized products obtained

generally follows relative stability trends, yet the absence of the most stable tri-substituted alkene product was interpreted as further evidence for the influential role of sterics in these reactions. Both the non-isomerized allyl ether medium-ring oxasilacyles generated and the corresponding isomerized enol ether regioisomers represent potentially useful synthetic intermediates. With the ability to selectively access each of these compound classes in two steps and high yield from readily available starting materials, we anticipate this methodology will find applications in target-oriented synthesis campaigns. As an initial demonstration, the sequence was used to prepare the psymberic side-chain and a ulosonic acid analogue

EXPERIMENTAL

All reactions were carried out under N_2 in flame-dried glassware. The solvents used were dried by passing the solvent through a column of activated alumina under nitrogen immediately prior to use. All reagents were purchased and used as received unless otherwise mentioned. All TLC analysis used 0.25 mm silica layer fluorescence UV_{254} plates. Flash chromatography: SilaCycle silica gel P60 (230-400 mesh). IR: Thermo iS10 FT-IR with single-bounce diamond ATR. Optical Rotation: Rudolph Research Analytical Autopol IV polarimeter. NMR: Spectra were recorded on a Varian Mercury 300, or Inova 500 spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm, coupling constants (*J*) in Hz. The solvent signals were used as references (residual $CHCl_3$ in $CDCl_3$: $\delta_H \equiv 7.26$ ppm, $CDCl_3$: $\delta_C \equiv 77.0$ ppm; residual CH_2Cl_2 in CD_2Cl_2: $\delta_H \equiv 5.32$ ppm, CD_2Cl_2: $\delta_C \equiv 54.0$ ppm; residual C_6H_6 in C_6D_6: $\delta_H \equiv 7.15$ ppm, C_6D_6: $\delta_C \equiv 128.0$ ppm).

General procedure A: iodine-mediated rearrangement/etherification of diallylsilanes. To a 0.1 M solution of the diallylsilane in DCM at rt was added I_2 (1 equiv.) and the mixture was stirred for 3 h. The reaction was cooled to 0 ºC and then triethylamine (3 equiv.) followed by the alcohol (1.5 equiv.) were added. The solution was allowed to slowly warm to rt over 3 h and stirred at this temperature for another 1-2 h (until the reaction was complete by TLC). The reaction was quenched with water and extracted with DCM. The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by chromatography on silica (10:1 hexanes:EtOAc) gave the corresponding silyl ether as a colorless oil.

General procedure B: oxasilacycle formation by ring-closing metathesis. To a 0.05 M solution of the dienylsilyl ether in degassed DCM at rt was added **Ru-I** or **Ru-II** (0.05 equiv.). The mixture was stirred for 15 h before concentrating *in vacuo* and purifying by flash chromatography on silica (2:1 hexanes:DCM).

(Allyloxy)(2-(iodomethyl)pent-4-en-1-yl)diphenylsilane (4). Following general procedure A, compound **4** was obtained by reacting diallyldiphenylsilane (5 mL, 18.9 mmol) with I_2 (4.8 g, 18.9 mmol) in DCM (190 mL), followed by triethylamine (7.9 mL, 56.7 mmol) and allyl alcohol (26 mL, 37.8 mmol). The crude product was purified by chromatography on silica (10:1 hexanes:EtOAc, $R_f = 0.5$) to yield **4** (7.84 g, 93%);

colorless oil; IR 3069, 2970, 2911, 1639, 1589, 1428, 1381, 1368, 1219, 1109, 1021, 997, 914, 877, 732 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.55 (m, 4H), 7.50 – 7.34 (m, 6H), 5.92 (ddt, *J* = 17.1, 10.4, 4.6 Hz, 1H), 5.60 (ddt, *J* = 17.2, 10.1, 7.2 Hz, 1H), 5.32 (dq, *J* = 17.1, 1.9 Hz, 1H), 5.11 (dq, *J* = 10.4, 1.7 Hz, 1H), 5.08 – 4.99 (m, 2H), 4.25 – 4.21 (m, 2H), 3.28 (dd, *J* = 9.6, 4.3 Hz, 1H), 3.25 (dd, *J* = 9.7, 4.9 Hz, 1H), 2.22 – 2.11 (m, 1H), 2.07 (dt, *J* = 14.0, 7.5 Hz, 1H), 1.57 – 1.47 (m, 1H), 1.29 (dd, *J* = 15.0, 6.2 Hz, 1H), 1.24 (dd, *J* = 15.0, 6.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.6, 135.5, 134.74, 134.67, 134.65, 130.11, 130.08, 128.0, 127.8, 117.4, 114.6, 64.5, 41.3, 34.4, 19.64, 19.61; HRMS-TOF (ESI+) Calcd for $C_{21}H_{26}IOSi$ (M + H): 449.0798. Found 449.0797.

((Allyl-1-*d*)oxy)(2-(iodomethyl)pent-4-en-1-yl)diphenylsilane (4*d*). Following general procedure A, compound **4*d*** was obtained by reacting diallyldiphenylsilane (0.26 mL, 1.0 mmol) with I_2 (0.25 g, 1.0 mmol) in DCM (19 mL), followed by triethylamine (0.35 mL, 2.5 mmol) and prop-2-en-1-*d*-1-ol (0.1 mL, 1.5 mmol). The crude product was purified by chromatography on silica (10:1 hexanes:EtOAc, R_f = 0.5) to yield **4*d*** (0.35 g, 78%); colorless oil; IR 3069, 2970, 1638, 1589, 1428, 1380, 1219, 1109, 1021, 997, 915, 880 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 4H), 7.48 – 7.38 (m, 6H), 5.94 (ddd, *J* = 17.1, 10.4, 4.6 Hz, 1H), 5.63 (ddt, *J* = 17.2, 10.2, 7.2 Hz, 1H), 5.35 (d, *J* = 17.1 Hz, 1H), 5.15 (dt, *J* = 10.4, 1.7 Hz, 1H), 5.10 – 5.03 (m, 2H), 4.24 (dt, *J* = 15.4, 2.3 Hz, 1H), 3.31 (dd, *J* = 9.7, 4.3 Hz, 1H), 3.28 (dd, *J* = 9.6, 4.9 Hz, 1H), 2.24 – 2.15 (m, 1H), 2.10 (dt, *J* = 14.3, 7.5 Hz, 1H), 1.63 – 1.51 (m, 1H), 1.38 – 1.22 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.50, 135.48, 134.71, 134.65, 134.62, 130.09, 130.06, 129.97, 127.96, 127.81, 117.36, 114.64, 64.17 (t, *J* = 21.7 Hz, 1C), 41.23, 34.38, 19.63, 19.59; HRMS-TOF (ESI+) Calcd for $C_{21}H_{25}DIOSi$ (M + H): 450.0860. Found 450.0862.

(*Z*)-4-(Iodomethyl)-2,2-diphenyl-3,4,5,6-tetrahydro-1,2-oxasilocine (5). Following general procedure B, diene **4** (3.0 g, 6.7 mmol) was reacted with **Ru-I** (0.275 g, 0.33 mmol) in DCM (134 mL). Purification of the crude product mixture by flash chromatography on silica gel (2:1 hexanes:DCM, R_f = 0.3) gave **5** (2.1 g, 74%); colorless oil; IR 2955, 2928, 2865, 1450, 1370, 1310, 1235, 1121, 1065, 978, 884, 755, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 2H), 7.56 – 7.53 (m, 2H), 7.43 – 7.38 (m, 6H), 5.79 (dt, *J* = 11.2, 4.7 Hz, 1H), 5.60 (dddt, *J* = 11.3, 9.8, 8.2, 1.6 Hz, 1H), 4.55 (dd, *J* = 15.5, 4.5 Hz, 1H), 4.48 (dd, *J* = 15.6, 5.2 Hz, 1H), 3.18 (d, *J* = 7.7 Hz, 2H), 2.84 (ddd, *J* = 13.7, 9.6, 4.3 Hz, 1H), 2.39 (ddd, *J* = 13.5, 8.3, 5.5 Hz, 1H), 2.17 (ddtd, *J* = 11.3, 9.7, 7.1, 4.3 Hz, 1H), 1.58 (ddd, *J* = 14.9, 4.3, 1.0 Hz, 1H), 1.23 (dd, *J* = 14.9, 10.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.6, 134.8, 134.11, 134.06, 131.8, 129.93, 129.87, 127.97, 127.95, 127.3, 62.2, 37.4, 31.8, 19.4, 16.9; HRMS-TOF (ESI+) Calcd for $C_{19}H_{21}INaOSi$ (M + Na): 443.0304. Found 443.0300.

(*Z*)-4-(Iodomethyl)-2,2-diphenyl-3,4,5,6-tetrahydro-1,2-oxasilocine (6a). Following general procedure B, diene **4** (2.0 g, 4.5 mmol) was reacted with **Ru-II** (0.19 g, 0.22 mmol) in DCM (90 mL). Purification of the crude product mixture by flash chromatography on silica gel (2:1 hexanes:DCM, R_f = 0.5) gave **6a**

(0.51 g, 27%) along with a fraction containing ~1:1 **6a** and **6b** (0.53 g, 28%); IR 3056, 2973, 1640, 1565, 1350, 1194, 1067, 910, 730 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.62 – 7.57 (m, 2H), 7.47 – 7.34 (m, 6H), 6.49 (d, *J* = 5.8 Hz, 1H), 4.84 (ddd, *J* = 9.8, 7.3, 5.8 Hz, 1H), 3.30 (dd, *J* = 9.5, 5.6 Hz, 1H), 3.25 (dd, *J* = 9.5, 5.3 Hz, 1H), 2.56 (tdd, *J* = 13.3, 9.8, 3.7 Hz, 1H), 2.10 – 2.01 (m, 1H), 1.97 – 1.90 (m, 1H), 1.77 (tt, *J* = 12.9, 3.7 Hz, 1H), 1.42 – 1.26 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.3, 134.4, 133.8, 130.2, 130.1, 128.1, 127.8, 112.8, 36.0, 33.6, 21.4, 21.2, 20.9; HRMS-TOF (ESI+) Calcd for $C_{19}H_{22}IOSi$ (M + H): 421.0485. Found 421.0479.

(*Z*)-4-(Iodomethyl)-2,2-diphenyl-3,4,7,8-tetrahydro-1,2-oxasilocine (6c). Following general procedure B, diene **4** (2.0 g, 4.5 mmol) was reacted with **Ru-II** (0.19 g, 0.22 mmol) in DCM (90 mL). Purification by chromatography on silica (2:1 hexanes:DCM, R_f = 0.3) gave **6c** (0.22 g, 12%); colorless oil; IR 3062, 2983, 1736, 1614, 1415, 1274, 1267, 1129, 1078, 930 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.58 (m, 2H), 7.53 – 7.49 (m, 2H), 7.42 – 7.30 (m, 6H), 5.57 (m, 2H), 4.15 (dt, *J* = 11.0, 3.4 Hz, 1H), 3.71 (ddd, *J* = 12.6, 11.1, 1.8 Hz, 1H), 3.34 (dd, *J* = 9.5, 5.3 Hz, 1H), 3.28 (dd, *J* = 9.5, 7.6 Hz, 1H), 3.18 – 3.12 (m, 1H), 2.57 – 2.46 (m, 1H), 2.06 – 1.97 (m, 1H), 1.61 (dd, *J* = 14.7, 2.6 Hz, 1H), 1.43 (dd, *J* = 14.7, 12.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.2, 134.8, 134.0, 129.8, 129.7, 128.0, 127.7, 127.4, 64.7, 35.9, 31.5, 25.5, 16.7; HRMS-TOF (ESI+) Calcd for $C_{19}H_{22}IOSi$ (M + H): 421.0485. Found 421.0484.

((*E*)-2-(Iodomethyl)pent-3-en-1-yl)diphenyl((*E*)-prop-1-en-1-yl)oxy)silane (6d). Following general procedure B, diene **4** (2.0 g, 4.5 mmol) was reacted with **Ru-II** (0.19 g, 0.22 mmol) in DCM (90 mL). Purification by chromatography on silica (2:1 hexanes:DCM, R_f = 0.6) gave **6d** (0.21 g, 11%); colorless oil; IR 2955, 2910, 2875, 1607, 1459, 1414, 1384, 1364, 1238, 1182, 1162, 1118, 1103, 1071, 1004, 948, 828, 723 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 4H), 7.44 – 7.35 (m, 6H), 6.20 – 6.17 (m, 1H), 5.29 (dd, *J* = 15.0, 6.3 Hz, 1H), 5.13 (ddd, *J* = 15.0, 8.4, 1.4 Hz, 1H), 4.55 (tt, *J* = 9.2, 5.4 Hz, 1H), 3.22 (dd, *J* = 9.4, 5.7 Hz, 1H), 3.17 (dd, *J* = 9.5, 6.2 Hz, 1H), 2.42 (q, *J* = 8.6 Hz, 1H), 1.68 (dd, *J* = 6.7, 1.8 Hz, 3H), 1.55 (dd, *J* = 15.0, 5.0 Hz, 1H), 1.49 (d, *J* = 6.4 Hz, 3H), 1.30 (dd, *J* = 15.0, 9.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.2, 134.8, 134.0, 129.8, 129.7, 128.0, 127.7, 127.4, 64.7, 35.9, 31.5, 25.5, 16.6; HRMS-TOF (ESI+) Calcd for $C_{21}H_{25}INaOSi$ (M + Na): 471.0617. Found 471.0614.

(Allyloxy)-(2-(iodomethyl)pent-4-en-1-yl)dimethylsilane (7). Following general procedure A, diallylmethylsilane (0.28 mL, 1.54 mmol) was treated with I_2 (0.39 g, 1.54 mmol) in DCM (15.4 mL), followed by triethylamine (0.65 mL, 4.63 mmol) and allyl alcohol (0.21 mL, 3.08 mmol). The crude product was purified by chromatography on silica (10:1 hexanes:EtOAc, R_f = 0.5) to give **7** (0.35 g, 69%); colorless oil; IR 3068, 2972, 2951, 1610, 1569, 1418, 1410, 1353, 1311, 1201, 1109, 1021, 997, 914, 877, 732 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.92 (ddt, *J* = 17.1, 10.5, 4.8 Hz, 1H), 5.70 (ddt, *J* = 17.2, 10.1, 7.2 Hz, 1H), 5.26 (dd, *J* = 17.1, 1.8 Hz, 1H), 5.17 – 5.04 (m, 3H), 4.15 (dq, *J* = 4.7, 1.6 Hz, 2H), 3.33 (dd, *J* = 9.6, 4.4 Hz, 1H), 3.28 (dd, *J* = 9.6, 5.2 Hz, 1H), 2.20 (dddt, *J* = 13.7, 6.9, 5.5, 1.4 Hz, 1H), 2.14 – 2.06 (m, 2H),

0.72 (dd, *J* = 6.8, 1.0 Hz, 2H), 0.16 (s, 3H), 0.16 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.0, 135.5, 117.4, 114.6, 63.8, 41.1, 34.9, 22.3, 19.2, -1.2, -1.3; HRMS-TOF (ESI+) Calcd for $C_{11}H_{22}IOSi$ (M + H): 325.0485. Found 325.0482.

(Allyloxy)-(2-(iodomethyl)pent-4-en-1-yl)diisopropylsilane (8). Following general procedure A, diallyldiisopropylsilane (1.04 g, 5.34 mmol) was treated with I_2 (1.36 g, 5.34 mmol) in DCM (53.4 mL), followed by triethylamine (2.25 mL, 16.03 mmol) and allyl alcohol (0.73 mL, 10.68 mmol). The crude product was purified by chromatography on silica (10:1 hexanes:EtOAc, R_f = 0.45) to give **8** (1.5 g, 75%); colorless oil; IR 3042, 2972, 2911, 1614, 1562, 1435, 1410, 1364, 1207, 1151, 1009, 998, 901, 876, 731 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.00 – 5.88 (m, 2H), 5.34 – 5.25 (m, 2H), 5.18 – 5.08 (m, 2H), 4.26 – 4.24 (m, 2H), 4.02 (ddt, *J* = 12.5, 5.6, 1.5 Hz, 1H), 3.94 (ddt, *J* = 12.5, 5.6, 1.5 Hz, 1H), 2.22 (dddd, *J* = 14.3, 7.5, 5.2, 3.7 Hz, 1H), 2.19 – 2.09 (m, 1H), 1.27 (d, *J* = 6.0 Hz, 3H), 1.19 (dd, *J* = 14.7, 5.7 Hz, 1H), 1.08 – 1.03 (m, 12H), 0.95 (dd, *J* = 14.7, 7.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.0, 130.0, 129.8, 129.5, 64.6, 41.6, 28.3, 26.8, 22.3, 19.2; HRMS-TOF (ESI+) Calcd for $C_{15}H_{30}IOSi$ (M + H): 381.1111. Found 381.1110.

1-(Allyloxy)-1-(2-(iodomethyl)pent-4-en-1-yl)siletane (9). Following general procedure A, diallylsilacyclobutane (0.47 g, 3.06 mmol) was treated with I_2 (0.77 g, 3.06 mmol) in DCM (30.6 mL), followed by triethylamine (1.29 mL, 9.17 mmol) and allyl alcohol (0.42 mL, 6.11 mmol). The crude product was purified by chromatography on silica (10:1 hexanes:EtOAc, R_f = 0.5) to give **9** (0.54 g, 52%); colorless oil; IR 3078, 2954, 2940, 1604, 1573, 1452, 1427, 1365, 1314, 1207, 1178, 1042, 998, 901, 864, 738 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.92 – 5.78 (m, 1H), 5.77 – 5.67 (m, 1H), 5.19 – 5.07 (m, 2H), 5.01 – 4.90 (m, 2H), 3.33 (ddd, *J* = 9.6, 4.6, 1.7 Hz, 2H), 3.31 – 3.27 (m, 2H), 2.27 – 2.18 (m, 1H), 2.18 – 2.10 (m, 1H), 2.08 – 1.94 (m, 1H), 1.29 – 1.20 (m, 6H) 0.88 (dd, *J* = 7.0, 3.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.3, 132.7, 117.6, 114.3, 41.0, 35.0, 24.8, 22.9, 20.0, 19.3, 18.6, 13.9; HRMS-TOF (ESI+) Calcd for $C_{12}H_{22}IOSi$ (M + H): 337.0485. Found 337.0486.

(*Z*)-4-(Iodomethyl)-2,2-dimethyl-3,4,5,6-tetrahydro-1,2-oxasilocine (10). Following general procedure B, **7** (0.073 g, 0.22 mmol) was added to DCM (4.4 mL), the solution was degassed, **Ru-II** (0.009 g, 0.011 mmol) was added, and the mixture was stirred for 15 h. Purification of the crude product by flash chromatography on silica gel (2:1 hexanes:DCM, R_f = 0.6) gave **10** (0.021 g, 28%); colorless oil; IR 3069, 2978, 2954, 2857, 1631, 1554, 1417, 1410, 1352, 1205, 1117, 1030, 992, 906, 865, 732 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.29 (dd, *J* = 5.7, 1.0 Hz, 1H), 4.82 – 4.74 (m, 1H), 3.26 (dd, *J* = 9.6, 5.7 Hz, 1H), 3.13 (dd, *J* = 8.9, 6.5 Hz, 1H), 2.63 – 2.45 (m, 1H), 1.96 (ddt, *J* = 15.2, 7.8, 3.8 Hz, 1H), 1.76 (tt, *J* = 13.1, 4.0 Hz, 1H), 1.33 – 1.21 (m, 2H), 0.86 (dd, *J* = 15.2, 10.1 Hz, 1H), 0.61 (dd, *J* = 15.1, 1.1 Hz, 1H), 0.23 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.07, 114.61, 41.08, 34.94, 22.31, 19.26, -1.21, -1.25; HRMS-TOF (ESI+) Calcd for $C_9H_{18}IOSi$ (M + H): 297.0172. Found 297.0171.

(*Z*)-4-(Iodomethyl)-2,2-diisopropyl-3,4,5,6-tetrahydro-1,2-oxasilocine (11). Following general procedure B, **8** (0.059 g, 0.16 mmol) was added to DCM (3.2 mL), the solution was degassed, **Ru-II** (0.007 g, 0.08 mmol) was added, and the mixture was stirred for 15 h. Purification of the crude product by flash chromatography on silica gel using 2:1 hexanes:DCM (R_f = 0.5) gave **11** (0.034 g, 65%); colorless oil; IR(ATR): 3072, 2981, 2953, 1632, 1549, 1428, 1417, 1342, 1310, 1211, 1110, 1063, 998, 867, 745 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.36 (d, *J* = 5.7 Hz, 1H), 4.68 (ddd, *J* = 10.1, 6.8, 5.7 Hz, 1H), 3.24 (dd, *J* = 9.5, 5.7 Hz, 1H), 3.18 (dd, *J* = 9.4, 5.9 Hz, 1H), 2.51 – 2.41 (m, 1H), 1.95 – 1.88 (m, 2H), 1.72 (dddd, *J* = 17.2, 9.2, 4.0, 0.9 Hz, 1H), 1.68 – 1.61 (m, 1H), 1.23 (ddt, *J* = 13.2, 11.3, 4.1 Hz, 1H), 1.19 – 1.13 (m, 1H), 1.09 (d, *J* = 6.5 Hz, 6H), 1.07 (d, *J* = 6.5 Hz, 3H), 0.84 – 0.66 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.9, 127.5, 37.9, 31.8, 18.0, 17.9, 17.8, 17.4, 17.2, 14.3, 14.2, 13.2, 13.0; HRMS-TOF (ESI+) Calcd for $C_{13}H_{26}IOSi$ (M + H): 353.0798. Found 353.0796.

(*Z*)-10-(Iodomethyl)-5-oxa-4-silaspiro[3.7]undec-6-ene (12). Following general procedure B, **9** (0.056 g, 0.17 mmol) was added to DCM (3.4 mL), the solution was degassed, **Ru-II** (0.008 g, 0.09 mmol) was added, and the mixture was stirred for 15 h. Purification of the crude product by flash chromatography on silica gel using 2:1 hexanes:DCM (R_f = 0.5) gave **12** (0.033 g, 77%); colorless oil; IR(ATR): 3069, 2970, 2911, 1639, 1589, 1428, 1428, 1381, 1368, 1219, 1109, 1021, 997, 914, 877, 732 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 6.36 (d, *J* = 5.8 Hz, 1H), 4.68 (ddd, *J* = 10.2, 6.8, 5.7 Hz, 1H), 3.24 (dd, *J* = 9.5, 5.8 Hz, 1H), 3.18 (dd, *J* = 9.4, 5.9 Hz, 1H), 2.52 – 2.40 (m, 1H), 1.99 – 1.86 (m, 2H), 1.77 – 1.63 (m, 1H), 1.38 – 1.12 (m, 3H), 1.11 – 1.00 (m, 4H), 0.77 (dd, *J* = 15.1, 9.9 Hz, 1H), 0.69 (dt, *J* = 15.2, 1.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.9, 111.6, 36.4, 33.5, 21.4, 20.9, 17.9, 17.6, 17.5, 17.4, 17.4, 13.0, 12.6. HRMS-TOF (ESI+) Calcd for $C_{10}H_{18}IOSi$ (M + H): 309.0172. Found 309.0171.

Fluoro(2-methylpent-4-en-1-yl)diphenylsilane (13). Into a flame dried flask under nitrogen was added diallyldiphenylsilane (0.21 g, 0.78 mmol) and DCM (0.50 mL). Into a separate flask, BF_3·2AcOH (0.15 g, 0.78 mmol) and DCM (0.76 mL) were added to make a diluted solution, which was then added slowly over the course of 10 min. to the flask containing the diallylsilane. After addition, the resulting mixture was stirred at room temperature for 4.5 h. The reaction was quenched using DI water (10 mL) and extracted with DCM (3 x 10 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The resulting product **13** (0.22 g, 99%) was used directly; IR(ATR): 2955, 2930, 2875, 1460, 1352, 1344, 1254, 1143, 1103, 1004, 969, 835, 774, 741, 724, 666 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.70 (m, 1H), 7.63 – 7.58 (m, 3H), 7.48 – 7.43 (m, 3H), 7.43 – 7.37 (m, 3H), 5.73 (ddtd, *J* = 17.2, 10.4, 7.0, 2.6 Hz, 1H), 5.02 – 4.92 (m, 2H), 2.12 – 2.05 (m, 1H), 2.05 – 1.97 (m, 1H), 1.89 (dttd, *J* = 18.2, 9.0, 5.0, 4.0, 2.1 Hz, 1H), 1.37 (dddd, *J* = 18.5, 11.0, 5.6, 3.1 Hz, 1H), 1.11 (dddd, *J* = 15.6, 9.1, 6.6, 2.9 Hz, 1H), 0.96 (dd, *J* = 6.8, 2.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.1, 134.5, 134.0, 132.1,

130.5, 128.3, 128.0, 116.2, 44.5, 28.5, 22.5, 21.9, 21.8; HRMS-TOF (ESI+) Calcd for $C_{18}H_{21}FNaSi$ (M + Na): 307.1294. Found 307.1289.

(Allyloxy)(2-methylpent-4-en-1-yl)diphenylsilane (14). Allyl alcohol (0.02 mL, 0.25 mmol) was dissolved in THF (0.88 mL) and cooled to 0 °C. A solution of potassium bis(trimethylsilyl)amide (KHMDS, 0.50 mL, 0.5 M solution in toluene) was added and the mixture was stirred at 0 °C for 30 min. Fluorosilane **8** (0.22 g, 0.17 mmol) was then added and the solution was allowed to warm to room temperature for 15 h. The reaction was quenched with water (15 mL) and extracted with methyl *tert*-butyl ether (3 x 15 mL). The combined organic extracts were dried over $MgSO_4$, and concentrated by rotary evaporation. The crude mixture was purified by column chromatography on silica (10:1 hexanes:EtOAc, R_f = 0.3) to yield **14** (0.056 g, 89%); colorless oil; IR 3068, 2920, 1589, 1427, 1400, 1203, 1110, 1059, 943, 909, 729 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 4H), 7.42 – 7.34 (m, 6H), 5.94 (ddt, *J* = 17.1, 10.4, 4.6 Hz, 1H), 5.73 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.35 (dq, *J* = 17.0, 1.9 Hz, 1H), 5.13 (dq, *J* = 10.4, 1.7 Hz, 1H), 4.97 – 4.89 (m, 2H), 4.23 (dt, *J* = 4.6, 1.7 Hz, 2H), 2.09 – 2.03 (m, 1H), 1.97 (dtt, *J* = 13.6, 6.9, 1.1 Hz, 1H), 1.85 – 1.75 (m, 1H), 1.34 (dd, *J* = 15.2, 5.0 Hz, 1H), 1.08 (dd, *J* = 15.2, 8.7 Hz, 1H), 0.93 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.5, 136.8, 135.4, 135.3, 134.7, 129.8, 127.8, 115.9, 114.4, 64.3, 44.7, 28.7, 22.6, 21.5; HRMS-TOF (ESI+) Calcd for $C_{21}H_{27}OSi$ (M + H): 323.1831. Found 323.1831.

(*Z*)-4-Methyl-2,2-diphenyl-3,4,5,8-tetrahydro-1,2-oxasilocine (15). Following general procedure B, diene **14** (0.0524 g, 0.1625 mmol) was reacted with **Ru-I** (0.009 g, 0.0112 mmol) in DCM (4.0 mL). Purification by column chromatography on silica (10:1 hexanes:EtOAc, R_f = 0.5) gave **15** (0.040 g, 84%); colorless oil; IR 3078, 2917, 1591, 1420, 1389, 1211, 1109, 972, 910, 729 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 7.4, 1.8 Hz, 2H), 7.57 (dd, *J* = 7.6, 1.5 Hz, 2H), 7.39 (dddd, *J* = 18.6, 9.4, 4.4, 2.8 Hz, 6H), 5.79 (dt, *J* = 10.7, 5.2 Hz, 1H), 5.71 (dt, *J* = 11.1, 8.6 Hz, 1H), 4.52 (qd, *J* = 14.8, 5.1 Hz, 2H), 2.68 – 2.61 (m, 1H), 2.14 – 2.07 (m, 2H), 1.41 (dd, *J* = 15.2, 4.0 Hz, 1H), 1.20 (dd, *J* = 15.2, 10.1 Hz, 1H), 1.07 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.4, 134.2, 134.0, 130.6, 130.5, 130.0, 129.6, 129.6, 128.1, 128.1, 127.9, 127.8, 116.3, 61.6, 34.6, 29.5, 25.2, 21.6; HRMS-TOF (ESI+) Calcd for $C_{19}H_{23}OSi$ (M + H): 295.1518. Found 295.1518.

(*Z*)-4-Methyl-2,2-diphenyl-3,4,5,6-tetrahydro-1,2-oxasilocine (16a). Following general procedure B, diallylsilane **14** (0.072 g, 0.223 mmol) was reacted with **Ru-II** (0.010 g, 0.012 mmol) in DCM (10.9 mL). Purification by column chromatography on silica (2:1 hexanes:DCM, R_f = 0.4) gave **16a** (0.036 g, 55%) as an inseparable 4:1 mixture with **16c**; IR 3067, 2918, 1589, 1477, 1427, 1400, 1262, 1110, 1071, 1022, 997, 907, 730 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.67 – 7.64 (m, 2H), 7.57 (dt, *J* = 6.5, 1.6 Hz, 2H), 7.44 – 7.31 (m, 6H), 6.44 (d, *J* = 5.8 Hz, 1H), 4.78 (ddd, *J* = 9.9, 7.2, 5.8 Hz, 1H), 2.55 (tdd, *J* = 13.2, 9.5, 3.6 Hz, 1H), 2.05 – 2.00 (m, 1H), 1.97 (ddq, *J* = 14.3, 7.7, 4.2, 3.5 Hz, 1H), 1.60 (tt, *J* = 13.0, 3.9 Hz, 1H), 1.30 – 1.15 (m, 3H), 1.06 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.1, 134.5, 133.9, 129.9, 128.1,

127.9, 113.2, 38.1, 27.1, 26.6, 21.9, 21.7; HRMS-TOF (ESI+) Calcd for $C_{19}H_{22}NaOSi$ (M + Na): 317.1338. Found 317.1335.

(*Z*)-4-Methyl-2,2-diphenyl-3,4,5,8-tetrahydro-1,2-oxasilocine (16b). Following general procedure B, diallylsilane **14** (0.072 g, 0.223 mmol) was reacted with **Ru-II** (0.010 g, 0.012 mmol) in DCM (10.9 mL). Purification by column chromatography on silica (2:1 hexanes:DCM, R_f = 0.3) gave **16b** (0.012 g, 19%); colorless oil; IR 3073, 2921, 1617, 1523, 1459, 1362, 1154, 1069, 998, 924, 750 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 2H), 7.56 – 7.52 (m, 2H), 7.41 – 7.30 (m, 6H), 5.77 (dt, *J* = 10.7, 5.2 Hz, 1H), 5.72 – 5.65 (m, 1H), 4.52 (dd, *J* = 14.9, 4.8 Hz, 1H), 4.47 (dd, *J* = 14.8, 5.6 Hz, 1H), 2.70 – 2.60 (m, 1H), 2.15 – 2.07 (m, 2H), 1.38 (dd, *J* = 15.3, 4.3 Hz, 1H), 1.17 (dd, *J* = 15.1, 10.1 Hz, 1H), 1.05 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.1, 134.4, 133.9, 129.91, 129.86, 128.0, 127.87, 127.85, 113.1, 38.1, 27.1, 26.6, 21.9, 21.7; HRMS-TOF (ESI+) Calcd for $C_{19}H_{23}OSi$ (M + H): 295.1518. Found 295.1513.

(2-(Iodomethyl)pent-4-en-1-yl)diphenyl((1-phenylallyl)oxy)silane (17). Following general procedure A, **17** was obtained by reacting diallyldiphenylsilane (0.25 g, 0.94 mmol) with I_2 (0.24 g, 0.95 mmol) in DCM (9.5 mL), followed by triethylamine (0.39 mL, 2.84 mmol) and 1-phenylprop-2-en-1-ol[45] (0.20 g, 1.48 mmol). The crude product was purified by chromatography on silica (10:1 hexanes:EtOAc, R_f = 0.6) to yield **17** (0.35 g, 70%) as a 1:1 mixture of diastereomers; *Spectral data for the mixture of diastereomers:* IR 3054, 2917, 1636, 1589, 1447, 1428, 1328, 1155, 1111, 951, 781, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 8H), 7.51 – 7.47 (m, 8H), 7.44 – 7.22 (m, 14H), 5.97 – 5.87 (m, 2H), 5.62 – 5.40 (m, 2H), 5.22 – 5.12 (m, 4H), 5.05 (d, *J* = 10.7 Hz, 2H), 4.96 (d, *J* = 9.4 Hz, 2H), 3.24 – 3.12 (m, 2H), 3.06 – 3.01 (m, 2H), 2.15 – 1.87 (m, 6H), 1.30 – 1.10 (m, 4H), 0.85 – 0.75 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.6, 135.5, 134.8, 130.0, 128.3, 127.9, 127.9, 127.8, 127.4, 126.4, 126.4, 117.3, 117.2, 114.2, 114.2, 41.3, 41.0, 34.3, 34.2, 20.2, 20.1, 19.9 19.8; HRMS-TOF (ESI+) Calcd for $C_{27}H_{29}INaOSi$ (M + Na): 547.0930. Found 547.0928.

(2-(Iodomethyl)pent-4-en-1-yl)(non-1-en-3-yloxy)diphenylsilane (18). Following general procedure A, **18** was obtained by reacting diallyldiphenylsilane (0.25 g, 0.95 mmol) with I_2 (0.24 g, 0.95 mmol) in DCM (9.5 mL), followed by triethylamine (0.39 mL, 2.84 mmol) and 1-octen-3-ol[46] (0.2426 g, 1.8921 mmol). The crude product was purified by chromatography on silica (10:1 hexanes:EtOAc, R_f = 0.5) to yield **18** (0.38 g, 76%) as a 1:1 mixture of diastereomers; *Spectral data for the mixture of diastereomers:* IR 3069, 2918, 1636, 1590, 1427, 1401, 1389, 1155, 1110, 977, 832, 729 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.54 (m, 8H), 7.43 – 7.34 (m, 12H), 5.82 (dddd, *J* = 17.2, 10.4, 6.8, 3.6 Hz, 2H), 5.61 (ddt, *J* = 17.2, 10.2, 7.2 Hz, 2H), 5.05 – 4.97 (m, 8H), 4.14 – 4.09 (m, 2H), 3.28 (ddd, *J* = 9.5, 7.0, 4.1 Hz, 2H), 3.20 (dt, *J* = 9.5, 5.5 Hz, 2H), 2.15 – 2.07 (m, 2H), 2.06 – 1.99 (m, 2H), 1.57 – 1.47 (m, 6H), 1.46 – 1.38 (m, 2H), 1.28 – 1.10 (m, 14H), 0.85 (td, *J* = 7.3, 1.5 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.9, 140.9, 135.7, 135.6, 135.2, 135.0, 134.9, 134.5, 129.9, 128.0, 127.8, 127.8, 127.6, 117.3, 114.7, 75.1, 41.4, 41.1, 37.7, 34.4,

31.7, 24.5, 22.6, 20.1, 19.9, 14.0; HRMS-TOF (ESI+) Calcd for $C_{26}H_{35}INaOSi$ (M + Na): 541.1400. Found 541.1401.

(*Z*)-4-(Iodomethyl)-2,2,8-triphenyl-3,4,5,8-tetrahydro-1,2-oxasilocine (19). Following general procedure B, diene **17** (0.0801 g, 0.15 mmol) was reacted with **Ru-II** (0.07 g, 0.007 mmol) in DCM (3.0 mL). Purification by column chromatography on silica (2:1 hexanes:DCM, R_f = 0.5) gave **19** (0.05 g, 67%) as a 1:1 mixture of diastereomers; *Spectral data for the mixture of diastereomers:* IR 2954, 1731, 1697, 1602, 1436, 1213, 1053, 974, 812, 701 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.56 (m, 8H), 7.52 – 7.46 (m, 4H), 7.45 – 7.28 (m, 18H), 6.00 (dd, *J* = 10.8, 6.8 Hz, 1H), 5.81 – 5.70 (m, 4H), 5.56 (ddd, *J* = 11.2, 9.6, 8.3 Hz, 1H), 3.32 (dd, *J* = 9.6, 6.1 Hz, 1H), 3.29 (dd, *J* = 9.6, 7.2 Hz, 1H), 3.20 – 3.14 (m, 2H), 2.91 (ddd, *J* = 12.8, 9.0, 3.4 Hz, 1H), 2.67 (dt, *J* = 13.3, 6.4 Hz, 1H), 2.62 – 2.56 (m, 1H), 2.55 – 2.48 (m, 1H), 2.40 (ddd, *J* = 13.2, 9.0, 6.8 Hz, 1H), 2.07 (dtp, *J* = 16.5, 6.7, 3.8, 3.4 Hz, 1H), 1.74 (dd, *J* = 15.1, 5.3 Hz, 1H), 1.65 (dd, *J* = 15.1, 3.4 Hz, 1H), 0.90 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.8, 143.3, 136.5, 135.7, 134.7, 134.2, 134.1, 134.0, 133.9, 130.2, 129.9, 129.8, 129.7, 128.8, 128.4, 128.0, 127.9, 127.9, 127.2, 127.1, 125.9, 125.8, 72.6, 70.6, 38.5, 37.1, 32.9, 32.2, 20.9, 19.9, 18.5, 15.4; HRMS-TOF (ESI+) Calcd for $C_{25}H_{26}IOSi$ (M + H): 497.0798. Found 497.0795.

(*Z*)-8-Hexyl-4-(iodomethyl)-2,2-diphenyl-3,4,5,8-tetrahydro-1,2-oxasilocine (20). Following general procedure B, diene **18** (0.1401 g, 0.2631 mmol) was reacted with **Ru-II** (0.011 g, 0.013 mmol) in DCM (7.0 mL). Purification by column chromatography on silica (2:1 hexanes:DCM, R_f = 0.5) gave **18** (0.124 g, 88%) as a 1:1 mixture of diastereomers; *Spectral data for the mixture of diastereomers:* IR 2955, 1732, 1699, 1606, 1436, 1265, 1170, 830, 734 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 (tt, *J* = 7.9, 1.9 Hz, 6H), 7.44 – 7.30 (m, 14H), 5.78 (dd, *J* = 11.0, 6.2 Hz, 1H), 5.66 – 5.56 (m, 2H), 5.45 (dt, *J* = 11.2, 8.9 Hz, 1H), 4.57 (dq, *J* = 12.8, 6.2 Hz, 2H), 3.26 (dd, *J* = 9.6, 6.0 Hz, 1H), 3.22 (dd, *J* = 9.6, 7.4 Hz, 1H), 3.12 (dd, *J* = 8.2, 6.3 Hz, 1H), 3.09 (dd, *J* = 8.2, 5.4 Hz, 1H), 2.79 (ddd, *J* = 12.8, 8.9, 3.5 Hz, 1H), 2.54 (dt, *J* = 13.1, 6.6 Hz, 1H), 2.49 – 2.45 (m, 1H), 2.44 – 2.38 (m, 1H), 2.24 (ddd, *J* = 13.2, 8.8, 6.4 Hz, 1H), 2.02 – 1.95 (m, 1H), 1.78 – 1.71 (m, 2H), 1.66 – 1.59 (m, 3H), 1.56 – 1.50 (m, 1H), 1.44 – 1.39 (m, 1H), 1.36 – 1.16 (m, 13H), 0.89 (td, *J* = 7.0, 2.9 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.7, 136.3, 134.2, 134.0, 133.9, 129.9, 129.7, 129.6, 129.5, 128.2, 127.8, 127.8, 127.6, 71.2, 69.5, 38.4, 38.0, 37.7, 37.1, 32.6, 32.3, 31.8, 25.3, 25.2, 22.7, 20.6, 19.5, 18.5, 15.6, 14.1; HRMS-TOF (ESI+) Calcd for $C_{24}H_{32}IOSi$ (M + H): 491.1267. Found 491.1263.

(But-3-en-1-yloxy)(2-(iodomethyl)pent-4-en-1-yl)diphenylsilane (21). Following general procedure A, the diallyl product was obtained by reacting diallyldiphenylsilane (0.5 mL, 1.89 mmol) with I_2 (0.48 g, 1.89 mmol) in DCM (19 mL), followed by triethylamine (0.80 mL, 5.67 mmol) and 3-buten-1-ol (0.27 g, 3.78 mmol). The crude product was purified by chromatography on silica (20:1 hexanes:EtOAc, R_f = 0.7) to yield **21** (0.63 g, 72%); colorless oil; IR 2930, 1697, 1645, 1632, 1231, 987, 972 cm^{-1}; ^1H NMR (500 MHz,

$CDCl_3$) δ 7.60 – 7.56 (m, 4H), 7.44 – 7.36 (m, 6H), 5.80 (ddt, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.60 (ddt, *J* = 17.2, 10.2, 7.2 Hz, 1H), 5.10 – 4.98 (m, 4H), 3.77 – 3.67 (m, 2H), 3.31 – 3.23 (m, 2H), 2.31 (qt, *J* = 6.7, 1.4 Hz, 2H), 2.20 – 2.11 (m, 1H), 2.10 – 2.03 (m, 1H), 1.55 – 1.48 (m, 1H), 1.25 (dd, *J* = 15.5, 6.9 Hz, 1H), 1.21 (dd, *J* = 15.2, 6.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.6, 135.2, 134.7, 134.7, 134.7, 134.7, 130.0, 130.0, 127.9, 127.8, 117.3, 116.6, 63.2, 41.3, 37.1, 34.5, 19.7, 19.5; HRMS-TOF (ESI+) Calcd for $C_{22}H_{28}IOSi$ (M + H): 463.0954. Found 463.0954.

(*Z*)-4-(Iodomethyl)-2,2-diphenyl-2,3,4,5,8,9-hexahydro-1,2-oxasilonine (22). Following general procedure B, diallylsilane **21** (60 mg, 0.13 mmol) was reacted with the **Ru-II** (11 mg, 0.013 mmol) in DCM (5 mL). The crude product was purified by chromatography on silica (20:1 hexanes:EtOAc, R_f = 0.6) to give **22** (35 mg, 62%); colorless oil; IR 2954, 2927, 1630, 1614, 1401, 1323, 1108, 1040, 948 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (td, *J* = 7.5, 1.6 Hz, 4H), 7.42 – 7.33 (m, 6H), 5.79 – 5.71 (m, 1H), 5.55 (td, *J* = 10.6, 6.2 Hz, 1H), 3.89 (ddd, *J* = 10.9, 6.6, 2.0 Hz, 1H), 3.68 (ddd, *J* = 10.7, 8.8, 1.5 Hz, 1H), 3.22 (dd, *J* = 9.2, 8.2 Hz, 1H), 3.17 (dd, *J* = 9.2, 6.7 Hz, 1H), 2.79 (ddd, *J* = 14.3, 10.3, 4.8 Hz, 1H), 2.48 (dt, *J* = 15.9, 8.4 Hz, 1H), 2.39 (dt, *J* = 12.6, 5.6 Hz, 1H), 2.25 (dt, *J* = 14.7, 7.5 Hz, 1H), 2.21 – 2.15 (m, 1H), 1.44 (ddd, *J* = 14.7, 3.2, 1.1 Hz, 1H), 1.22 (dd, *J* = 14.7, 10.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.4, 129.9, 129.8, 129.2, 127.9, 127.9, 64.2, 36.8, 32.2, 30.1, 19.2, 17.2; HRMS-TOF (ESI+) Calcd for $C_{20}H_{23}INaOSi$ (M + Na): 457.0461. Found 457.0460.

Allyl(2-methylpent-4-en-1-yl)diphenylsilane (23). Into a flame dried flask under nitrogen, fluorosilane **13** (0.055 g, 0.19 mmol) and pentane (0.35 mL) were added and cooled to -78 °C. A solution of allylmagnesium bromide (0.21 mL, 1.0 M solution in ether) was added dropwise and the resulting mixture was then stirred at 0 °C for 2 h before warming to room temperature for 8 h. The reaction mixture was diluted with hexanes (10 mL) and then quenched with aq. NH_4Cl (15 mL) and extracted with hexanes (3 x 10 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude product mixture was purified by column chromatography on silica gel (10:1 hexanes:methyl *tert*-butyl ether, R_f = 0.5) to yield **23** (0.041 g, 68%); colorless oil; IR 3062, 2971, 2911, 1601, 1554, 1428, 1376, 1219, 1109, 1021, 997, 914, 877, 732 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 4H), 7.43 – 7.34 (m, 6H), 5.87 – 5.67 (m, 2H), 5.00 – 4.86 (m, 4H), 2.16 (ddd, *J* = 6.7, 3.0, 1.5 Hz, 2H), 2.03 (dddt, *J* = 12.9, 7.1, 5.7, 1.3 Hz, 1H), 1.96 – 1.89 (m, 1H), 1.78 (dddd, *J* = 13.9, 12.3, 7.1, 4.3 Hz, 1H), 1.30 (dd, *J* = 15.0, 5.0 Hz, 1H), 1.05 – 0.97 (m, 1H), 0.85 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.4, 135.0, 134.1, 133.7, 129.5, 129.2, 127.7, 115.9, 114.7, 114.5, 44.9, 29.1, 22.8, 21.3, 20.0, 19.9; HRMS-TOF (ESI+) Calcd for $C_{21}H_{27}Si$ (M + H): 307.1882. Found 307.1882.

(*Z*)-3-Methyl-1,1-diphenyl-2,3,4,7-tetrahydrosilepine (24). Following general procedure B, diene **23** (0.066 g, 0.21 mmol) was reacted with **Ru-II** (0.0179 g, 0.0211 mmol) in DCM (9.4 mL). Purification by column chromatography on silica (4:1 hexanes:DCM, R_f = 0.2) gave **24** (0.04 g, 66%); colorless oil; IR

3054, 2968, 2921, 1641, 1589, 1434, 1167, 1123, 1010, 996, 911, 878, 732 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.45 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.41 – 7.29 (m, 6H), 5.82 – 5.75 (m, 1H), 5.63 (dtd, *J* = 10.2, 7.8, 1.9 Hz, 1H), 2.23 (ddd, *J* = 14.5, 6.7, 2.0 Hz, 1H), 2.16 (tdd, *J* = 9.1, 7.7, 3.9 Hz, 1H), 2.09 (ddd, *J* = 7.9, 4.0, 2.1 Hz, 1H), 2.03 (ddd, *J* = 14.5, 8.1, 1.5 Hz, 1H), 1.99 – 1.93 (m, 1H), 1.58 (ddt, *J* = 14.7, 3.3, 1.5 Hz, 1H), 1.11 (dd, *J* = 14.8, 11.2 Hz, 1H), 1.05 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.8, 134.2, 129.2, 129.1, 128.7, 127.8, 127.8, 127.1, 36.7, 29.6, 27.8, 25.4, 13.7; HRMS-TOF (ESI+) Calcd for $C_{19}H_{23}Si$ (M + H): 279.1569. Found 279.1563.

4-(Iodomethyl)-2,2-diphenyl-1,2-oxasilinan-6-yl)ethane-1,2-diol (25). To a stirring solution of *tert*-butyl alcohol (4.47 mL) and deionized water (4.47 mL), AD-mix-β (1.2539 g, 1.609 mmol) was added and stirred at room temperature until the solution became transparent. After cooling to 0 °C, compound **5** (0.3757 g, 0.8937 mmol) was added and the solution was allowed to warm to slowly warm to room temperature and stirred for 70 h. The solution was cooled to 0 °C and Na_2SO_4 (1 g) was added and the mixture was stirred for 4 h. After filtering through celite, the solution was extracted with DCM (3 x 15 mL), and the combined organic extracts were dried over $MgSO_4$ and concentrated by rotary evaporation. Purification by column chromatography on silica (1:2 hexanes:EtOAc, R_f = 0.4) gave **25** (0.227 g, 56%) as a 1:1 mixture of diastereomers; *Spectral data for the mixture of diastereomers:* IR 3382, 3068, 2920, 1589, 1427, 1400, 1203, 1110, 1059, 943, 909, 729 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.60 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.54 – 7.52 (m, 2H), 7.51 – 7.47 (m, 2H), 7.47 – 7.33 (m, 12H), 4.15 (ddd, *J* = 10.7, 6.9, 4.1 Hz, 1H), 4.12 (dd, *J* = 14.2, 7.1 Hz, 1H), 4.03 (ddd, *J* = 11.3, 5.2, 1.8 Hz, 1H) 3.89 – 3.74 (m, 4H), 3.70 – 3.59 (m, 2H), 3.28 (dd, *J* = 9.7, 5.5 Hz, 1H), 3.24 – 3.16 (m, 2H), 2.64 (bs, 1H), 2.48 (bs, 1H), 2.44 – 2.36 (m, 1H), 2.28 (bs, 1H), 2.12 (dddd, *J* = 14.3, 7.2, 3.5, 1.2 Hz, 1H), 2.09 – 2.07 (m, 1H), 1.94 – 1.86 (m, 1H), 1.80 (ddd, *J* = 14.3, 7.9, 4.0 Hz, 1H), 1.57 – 1.50 (m, 2H), 1.34 – 1.24 (m, 2H), 1.18 (dd, *J* = 15.0, 8.5 Hz, 1H), 0.86 (dd, *J* = 14.4, 13.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.3, 135.2, 134.3, 134.24, 134.22, 134.18, 134.1, 134.0, 133.2, 130.6, 130.5, 130.44, 130.36, 128.4, 128.23, 128.20, 128.18, 128.1, 76.1, 74.5, 73.6, 72.2, 63.8, 63.5, 37.8, 36.6, 35.2, 33.5, 18.9, 18.5, 17.1, 16.1; HRMS-TOF (ESI+) Calcd for $C_{19}H_{24}IO_3Si$ (M + H): 455.0539. Found 455.0541.

(2,2-Diphenyl-4-((phenylselanyl)methyl)-1,2-oxasilinan-6-yl)ethane-1,2-diol (26). Compound **25** (0.8479 g, 1.8661 mmol) was dissolved in MeCN (9.33 mL) and cesium carbonate (0.9149 g, 2.808 mmol) was then added followed by the dropwise addition of benzeneselenol (0.28 mL, 2.6125 mmol). After stirring at room temperature for 1 h, the reaction was quenched with aq. NH_4Cl (25 mL), extracted with methyl *tert*-butyl ether (3 x 20 mL). The combined organic extracts were washed with 15% aq. NaOH (25 mL), dried over $MgSO_4$, and concentrated rotary evaporation. Purification by column chromarography on silica (1:2 hexanes:EtOAc, R_f = 0.3) gave **26** (0.802 g, 89%) as a 1:1 mixture of diastereomers; *Spectral data for the mixture of diastereomers:* IR 3067, 2918, 1589, 1477, 1427, 1400, 1262, 1110, 1071, 1022,

997, 907, 730 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.57 (dd, *J* = 7.6, 1.5 Hz, 2H), 7.50 – 7.46 (m, 6H), 7.45 – 7.37 (m, 12H), 7.36 – 7.32 (m, 4H), 7.25 – 7.21 (m, 4H), 4.17 – 4.15 (m, 1H), 4.12 (dd, *J* = 14.1, 7.2 Hz, 1H), 3.97 (ddd, *J* = 11.4, 5.1, 1.7 Hz, 1H), 3.84 – 3.74 (m, 4H), 3.63 (q, *J* = 5.4 Hz, 1H), 3.55 (p, *J* = 5.8 Hz, 1H), 3.00 (dd, *J* = 12.2, 6.5 Hz, 1H), 2.93 (dd, *J* = 12.0, 6.5 Hz, 1H), 2.90 (dd, *J* = 7.5, 5.2 Hz, 1H), 2.52 (d, *J* = 7.0 Hz, 1H), 2.43 (m, 1H), 2.35 (d, *J* = 6.6 Hz, 1H), 2.20 (dd, *J* = 7.7, 4.2 Hz, 1H), 2.08 – 1.96 (m, 2H), 1.81 (ddd, *J* = 14.3, 6.9, 3.4 Hz, 1H), 1.63 (dt, *J* = 14.3, 2.7 Hz, 1H), 1.50 (dd, *J* = 15.0, 5.3 Hz, 1H), 1.37 – 1.23 (m, 3H), 0.90 – 0.78 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.3, 134.2, 134.1, 133.9, 132.9, 132.8, 130.5, 130.31, 130.27, 130.2, 129.11, 128.3, 128.2, 128.1, 128.0, 126.99, 126.96, 76.4, 74.5, 73.8, 72.3, 63.7, 63.5, 60.4, 39.4, 37.7, 35.62, 34.9, 31.3, 21.1, 18.1, 16.5, 14.2; HRMS-TOF (ESI+) Calcd for $C_{25}H_{29}IO_3SeSi$ (M + H): 485.1051. Found 485.1056.

(2,2-Diphenyl-4-((phenylselanyl)methyl)-1,2-oxasilinan-6-yl)ethane-1,2-diol (27). Selenoether **26** (0.8021 g, 1.6588 mmol) was dissolved in toluene (5.92 mL) and then diisopropylethylamine (1.44 mL, 8.2939 mmol) was added. 3-Phenyl-2-(phenylsulfonyl)-1,2-oxaziridine (0.4773 g, 1.8266 mmol) was then added in three equal portions every 10 min. After the last addition, the solution was stirred at room temperature for an additional 10 min. before heating to 100 °C for 5 h. After cooling to room temperature, the reaction was quenched with aq. $NaHCO_3$ (15 mL) and extracted with methyl *tert*-butyl ether (3 x 15 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated by rotary evaporation. Purification by column chromatography on silica (1:1 hexanes:EtOAc, R_f = 0.3) gave **27** (0.449 g, 83%); yellow oil; IR 3068, 2917, 1636, 1589, 1447, 1428, 1328, 1155, 1111, 951, 781, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 2H), 7.55 – 7.52 (m, 2H), 7.47 – 7.35 (m, 6H), 4.83 (dt, *J* = 5.5, 1.8 Hz, 2H), 4.02 (ddd, *J* = 11.0, 5.3, 2.4 Hz, 1H), 3.84 (m, 2H), 3.71 (m, 1H), 2.50 (dt, *J* = 13.0, 2.2 Hz, 2H), 2.34 (dd, *J* = 14.0, 1.8 Hz, 1H), 2.29 (d, *J* = 12.2 Hz, 1H), 2.09 (dt, *J* = 13.8, 2.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.8, 134.4, 134.2, 133.3, 130.5, 130.3, 128.1, 111.2, 77.5, 74.4, 63.5, 60.4, 40.6, 24.2, 21.1, 14.2; HRMS-TOF (ESI+) Calcd for $C_{19}H_{23}O_3Si$ (M + H): 327.1416. Found 327.1417.

(2,2-Dimethyl-1,3-dioxolan-4-yl)-4-methylene-2,2-diphenyl-1,2-oxasilinane (28). Compound **27** (0.0487 g, 0.1492 mmol) was dissolved in acetone (0.77 mL) before adding 2,2-dimethoxypropane (0.08 mL, 0.6126 mmol) and *p*-toluenesulfonic acid (0.0030 g, 0.0174 mmol). After stirring for 1 h at room temperature, triethylamine (0.05 mL) was added and the solution was concentrated by rotary evaporation. Purification by column chromatography on silica (4:1 hexanes:EtOAc, R_f = 0.6) gave **28** (0.0446 g, 83%); yellow oil; IR 3069, 2918, 1636, 1590, 1427, 1401, 1389, 1155, 1110, 977, 832, 729 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 2H), 7.55 – 7.52 (m, 2H), 7.44 – 7.34 (m, 6H), 4.83 (d, *J* = 1.8 Hz, 2H), 4.13 (m, 1H), 4.03 (m, 2H), 3.82 (ddd, *J* = 10.3, 7.8, 2.7 Hz, 1H), 2.67 (ddd, *J* = 13.2, 2.7, 1.6 Hz, 1H), 2.32 (dd, *J* = 13.9, 1.7 Hz, 1H), 2.20 (dd, *J* = 13.1, 10.0 Hz, 1H), 2.10 (dt, *J* = 13.8, 2.0 Hz, 1H), 1.41 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.7, 135.0, 134.4, 134.0, 130.3, 128.0, 110.9, 109.5,

79.1, 67.7, 41.8, 26.8, 25.4, 24.3; HRMS-TOF (ESI+) Calcd for $C_{22}H_{27}O_3Si$ (M + H): 367.1729. Found 367.1729.

(2,2-Dimethyl-1,3-dioxolan-4-yl)-3-methylbut-3-en-1-ol (29). To a solution of acetal **28** (0.0446 g, 0.1217 mmol) in MeCN (1.22 mL) was added tetrabutylammonium fluoride trihydrate (0.2315 g, 0.7337 mmol) and the mixture was heated to 65 °C for 1 h. The reaction was quenched with saturated aq. NH_4Cl (15 mL), extracted with EtOAc (3 x 15 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated by rotary evaporation. Purification by column chromatography on silica (2:1 hexanes:EtOAc, R_f = 0.3) gave **29** (0.0133 g, 59%); colorless oil; $[\alpha]_D$ 0.68 ($CHCl_3$, *c* = 0.50); *NMR data matched that previously reported:*[38] ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.89 (p, *J* = 1.6 Hz, 1H), 4.81 (dq, *J* = 2.1, 0.9 Hz, 1H), 4.00 (m, 3H), 3.85 (dtd, *J* = 9.1, 4.4, 2.1 Hz, 1H), 2.30 (ddd, *J* = 14.0, 4.0, 1.3 Hz, 1H), 2.11 (ddd, *J* = 14.0, 9.4, 0.9 Hz, 1H), 1.99 (d, *J* = 2.4 Hz, 1H), 1.78 (t, *J* = 1.1 Hz, 3H), 1.43 (s, 3H), 1.36 (s, 3H).

(2,2-Dimethyl-1,3-dioxolan-4-yl)but-3-ene-1,3-diol (30). To a solution of **29** (0.1068 g, 0.2914 mmol) in DMF (1.46 mL) was added potassium bifluoride (0.0458 g, 0.0586 mmol) followed by *m*CPBA (0.1260 g, 0.7301 mmol). After stirring at room temperature for 3 h, the reaction was quenched with saturated aq. $NaHCO_3$ (15 mL) and extracted with EtOAc (3 x 15 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated by rotary evaporation. Purification by column chromatography on silica (4:1 hexanes:EtOAc, R_f = 0.1) gave **30** (0.0260 g, 44%) and **29** (0.038 g, 36%) as separable oils; *NMR data matched that previously reported:*[44] ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.12 (s, 1H), 4.99 (s, 1H), 4.08 (m, 2H), 4.00 (m, 2H), 3.91 (m, 1H), 3.78 (ddd, *J* = 9.3, 5.2, 3.1 Hz, 1H), 2.43 (ddd, *J* = 14.3, 3.1, 1.1 Hz, 1H), 2.14 (ddd, *J* = 14.3, 9.3, 1.0 Hz, 1H), 1.40 (s, 3H), 1.33 (s, 3H).

Relative Energy Calculations Parameters. DFT calculations were performed to calculate the relative energies of RCM products **5** and **6a-c** as shown in Figure 4. Calculations were performed using the ORCA software package using the def2-TZVP basis set (valence triple-zeta polarization) with an effective core potential (ECP) for the Iodine atom. DFT Geometry optimization was first performed at using DFT using the BP86 functional followed by a geometry optimization using the B3LYP functional. Both calculations used Grimme's DFT-D3 dispersion correction with Becke-Johnson damping (D3BJ). The structure obtained using the B3LYP functional was further optimized using second order Moller-Plesset perturbation theory (MP2). Geometry optimization at the MP2 level used the resolution identity approximation (RI) that speeds up the MP2 calculation with minimal loss in accuracy. Structures shown are the final geometry optimized structure at the RI-MP2 level. For comparison of the relative energies, a single point MP2 energy calculation was performed on each of the optimized structures without the RI approximation. All calculations were run on the SDSC Expanse supercomputer. The DFT calculations were performed on 32 cpu cores and the MP2 calculation was performed on 128 cpu cores.

SUPPORTING INFORMATION

Supplementary (synthesis of the starting azides, HPLC chromatograms, IR, ^{1}H and ^{13}C NMR, MS spectra, etc.) data associated with this article can be found, in the online version, at URL: https://www.heterocycles.jp/newlibrary/downloads/PDFsi/27751/104/11

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