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Anodic cyclization reactions: probing the chemistry of *N*,*O*-ketene acetal derived radical cations

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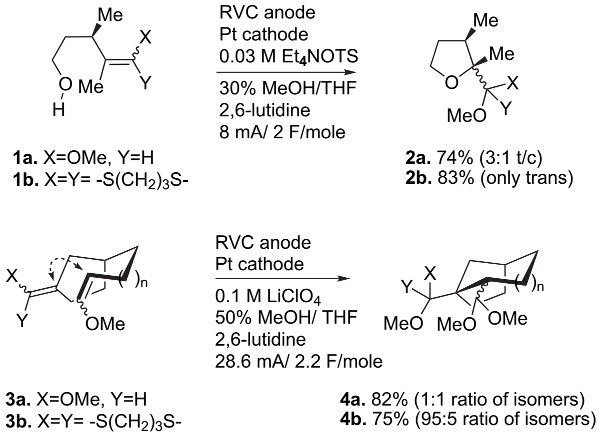
Abstract—The chemical reactivity of radical cations derived from *N*,*O*-ketene acetals has been examined and compared with the reactivity of radical cations derived from both ketene dithioacetals and enol ethers. Synthetically, the *N*,*O*-ketene acetal radical cations lead to more efficient cyclization reactions than either the ketene dithioacetal or enol ether derived radical cations. Cyclic voltammetry experiments using allylsilane trapping groups show that the efficiency of these cyclizations is not due to the *N*,*O*-ketene acetal radical cations being more reactive but rather more stable to decomposition. Finally, cyclizations using chiral oxizolidinones were examined.

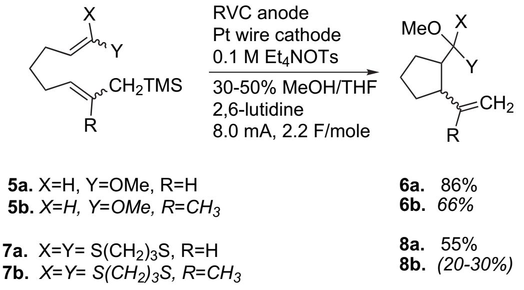
1. Introduction

Intramolecular anodic olefin coupling reactions using ketene dithioacetal initiating groups often afford high levels of stereoselectivity.[1–4] Consider the reactions illustrated in Scheme 1. In both examples, the reaction originating from oxidation of the ketene dithioacetal was far more selective than the analogous reaction originating from oxidation of the enol ether. While the stereochemistry of reactions originating from enol ether oxidation can often be rationalized by kinetic considerations,[5] the same cannot be said for reactions originating from ketene dithioacetal oxidation. For example, the difference in stereoselectivity obtained for the oxidation of **3a** and **3b** is most consistent with the oxidation of **3b** leading to a reaction controlled by thermodynamics. This hint that the enol ether and ketene dithioacetal reactions might be governed by different mechanistic concerns suggests that while the reactions look very similar, the radical cation intermediates might be quite different.



Scheme 1.

It did not take long to identify other significant differences between enol ether and ketene dithioacetal derived cyclizations. Enol ethers undergo efficient oxidative cyclizations with less reactive allylsilane trapping groups while ketene dithioacetals do not (Scheme 2).[6] This is especially true for cyclizations utilizing trisubstituted allylsilane trapping groups. The oxidation of **7b** led to a product that was so messy that the cyclic product (**8b**) could not be isolated in pure form. These observations led to a working model for the cyclizations that treated the radical cation derived from oxidation of a ketene dithioacetal as being less reactive than the radical cation derived from oxidation of an enol ether.



Scheme 2.

Keywords: Anodic electrochemistry; Oxidative cyclizations; Radical cations; Ketene acetals.

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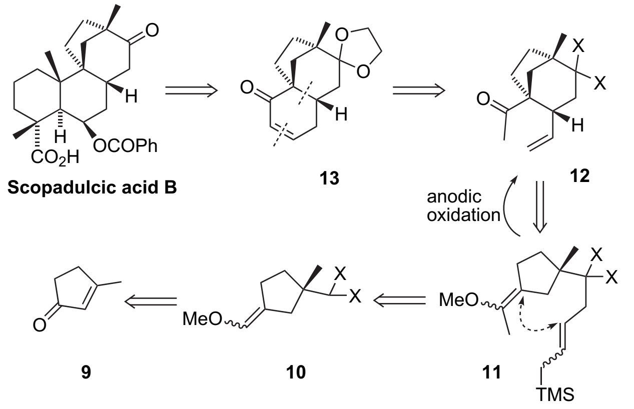
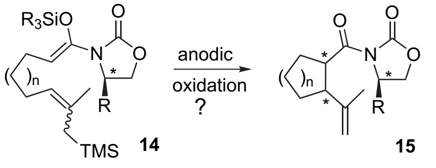
The suggestion that the reactivity of a radical cation can be altered by varying the substituents bound to it is very intriguing. If a change from a methoxy substituent to two thioether groups caused the radical cation to be less reactive, then possibly other changes would lead to a more reactive radical cation. Such a discovery would be extremely useful. Consider the retrosynthetic analysis of scopadulcic acid B illustrated in Scheme 3.[7] The key step in this proposed synthesis would involve an anodic cyclization of **11** to form the bridged bicyclic intermediate **12**. A hydroboration/oxidation sequence would then convert the olefin to an aldehyde for use in an intramolecular aldol condensation. The strength of the route is that the oxidative cyclization reaction would lead to a product having all of the carbons needed for completing the third ring. However, the proposal is badly flawed in that oxidative cyclization reactions using less reactive allylsilane trapping groups are normally not compatible with the simultaneous formation of six-membered rings and quaternary centers.[6b,8] But is this always the case? Are there more reactive radical cations that would allow for this transformation? With these questions in mind, we began to expand our exploration of oxidative cyclization reactions by diversifying the nature of the radical cation intermediate.



Scheme 3.

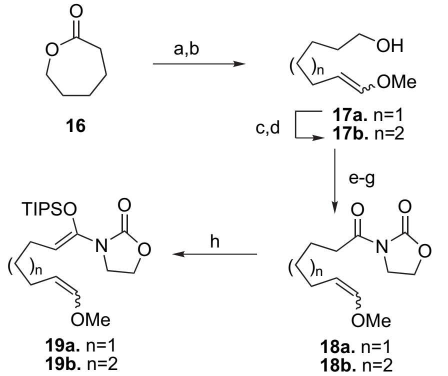
2. *N*,*O*-Ketene acetal substrates—an initial look

The first question that needed to be addressed was whether the lower efficiency of the dithioketene acetal derived cyclizations with allylsilane trapping groups was representative of all ketene acetal groups or specifically a result of the dithiane moiety. For this reason, we decided to build an oxazolidone based ketene acetal substrate (Scheme 4). Oxazolidinone ketene acetals were selected for this effort because they are stable and can be isolated by chromatography. This enabled the use of clean substrates for the electrolysis reactions. In addition, oxazolidinone ketene acetals possessing a stereogenic atom have been utilized in asymmetric alkylation and aldol reactions. Their availability suggested the possibility of studying asymmetric oxidative cyclization reactions (Scheme 4).



Scheme 4.

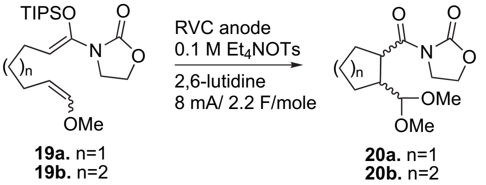
Initially, the very reactive enol ether trapping group was selected for the cyclizations.[9] This was done in order to probe the compatibility of the *N*,*O*-ketene acetal groups with the anodic oxidations using substrates that had the best possible chance for cyclization. The substrates were synthesized as outlined in Scheme 5. Both five- and six-membered ring precursors were made by nearly identical routes. The only difference was that the six-membered ring precursor required a one carbon chain extension. The yields in the scheme for steps e–h are given for the synthesis of the five-membered ring substrate. Yields for the six-membered ring substrate are included in Section 7.



Scheme 5. Reagents: (a) Dibal-H, THF/CH_2Cl_2 (1:1), −78 °C–0 °C, 15 min; (b) Ph_3PCH_2OMeCl, *s*-BuLi, THF, −78 °C–rt, 12 h, 90% (two steps); (c) 4 N HCl/acetone (1:1), 0 °C–rt, 1 h; (d) Ph_3PCH_2OMeCl, *s*-BuLi, THF, −78 °C–rt, 3 h, 70% (two steps); (e) PDC, DMF, 0 °C–rt, 12 h, 44%; (f) Et_3N, Pivaloyl chloride, THF, −20 °C, 2 h; (g) LiCl, 2-Oxazolidinone, −20 °C–rt, 6 h, 62% (two steps) and (h) i. LDA, THF, −78 °C, 1 h, ii. TIPSOTf, −78 °C–rt, 5 h, 87%.

The electrolyses of **19a** and **19b** were conducted in an undivided cell using constant current conditions (8 mA/ 2.2 F/mol), a reticulated vitreous carbon (RVC) anode and cathode, 2,6-lutidine as a proton scavenger, and a 0.1 M tetraethylammonium tosylate electrolyte solution.[10] The solvent for the reaction was either methanol or a mixture of methanol and THF as indicated in Table 1. The overall process was neutral since acid is generated at the anode and base (from the reduction of methanol) is generated at the cathode. Hence the added proton scavenger played no

Table 1



Substrate	Solvent	Product	Yield (%)	Isomer ratio
19a	MeOH	**20a**	74	2:1
19a	4:1 MeOH/THF	**20a**	87	3:2
19b	MeOH	**20b**	63[a]	1:2
19b	4:1 MeOH/THF	**20b**	65	1:2

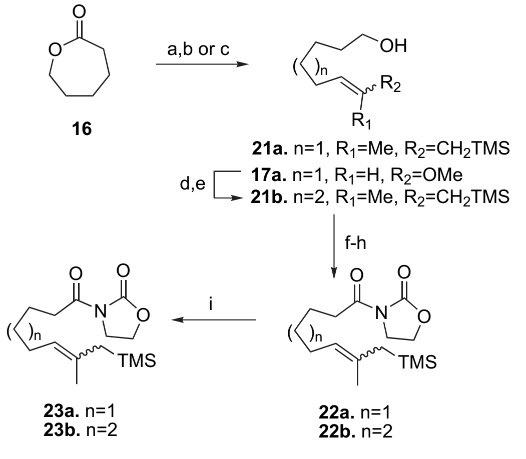
[a] 7% recovered starting material.

net role in the reaction. However, due to the acid sensitivity of ketene acetal, the presence of 2,6-lutidine was important for maintaining the neutrality of the reaction in the region immediately surrounding the anode. Using these conditions, both reactions led to good yields of cyclized product. For the oxidation of **19a**, a 74% isolated yield of **20a** was obtained when methanol was used as solvent. The reaction benefited from the use of THF as a cosolvent. An 87% isolated yield of cyclized product was obtained with the addition of 20% THF as a cosolvent. Like previous enol ether–enol ether coupling reactions,[9] the cyclization did not lead to the formation of products in stereoselective fashion. In this case, the ratio of stereoisomers of the newly formed C–C bond ranged from 2:1 to 3:2. The major isomer was not assigned since the isomers could not be separated and the NMR signals for the methine protons overlap.

The oxidation of **19b** in methanol solvent led to a 63% isolated yield of **20b** in a 1:2 ratio of cis/trans isomers. With the use of the THF cosolvent, a 65% unoptimized yield of product was obtained having the same 1:2 ratio of cis/trans isomers. The poor diastereoselectivity obtained for the cyclization of **20b** was consistent with the stereochemical outcome of earlier anodic cyclizations using enol ether derived radical cations and enol ether trapping groups.[9]

3. *N*,*O*-Ketene acetal radical cations and allylsilane trapping groups

With the oxidations of **19a** and **19b** leading to good yields of cyclic product, it was time to determine if a radical cation derived from an *N*,*O*-ketene acetal would be reactive enough to cyclize with a less efficient allylsilane trapping group. To this end, cyclization substrates **23a** and **23b** were synthesized as outlined in Scheme 6. These syntheses paralleled the syntheses of **19a** and **19b**. The ylide used for generating the trisubstituted allylsilane was prepared in situ from ethyltriphenylphosphonium bromide according to the known literature procedure.[11] As in the earlier synthesis of **19b**, the six-membered ring substrate was made by doing a one carbon chain extension of the aldehyde generated from Dibal-H reduction of the ε-caprolactone. The yields given in Scheme 6 for steps f–i are for the five-membered ring substrate. Yields for the six-membered ring case are again given in the Section 7.

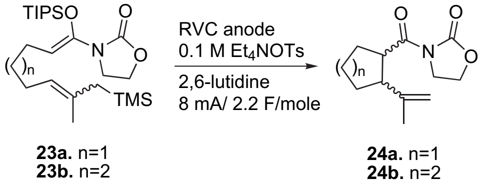


Scheme 6. Reagents: (a) Dibal-H, THF/CH_2Cl_2 (1:1), −78 °C–0 °C, 15 min; (b) $Ph_3PC(CH_3)CH_2TMS$, *s*-BuLi, THF, −78 °C–rt, 65% (two steps); (c) Ph_3PCH_2OMeCl, *s*-BuLi, THF, −78 °C–rt, 12 h, 90% (two steps); (d) 4 N HCl/acetone (1:1), 0 °C–rt, 1 h; (e) $Ph_3PC(CH_3)CH_2TMS$, *s*-BuLi, THF, −78 °C–rt, 12 h, 58% (two steps); (f) PDC, DMF, 0 °C–rt, 12 h. 49%; (g) Et_3N, Pivaloyl chloride, THF, −20 °C, 2 h; (h) LiCl, 2-Oxazolidinone, −20 °C–rt, 6 h, 91% (two steps) and (i) i. LDA, THF, −78 °C, 1 h, ii. TIPSOTf, −78 °C–rt, 5 h, 83%.

Once synthesized, the allylsilane substrates were electrolyzed using the same conditions described above (Table 2). From the start, it was obvious that cyclization reactions originating from the oxidation of *N*,*O*-ketene acetals proceed far better than do cyclizations originating from the oxidation of a ketene dithioacetal. Electrolysis of **23a** in 4:1 MeOH/THF led to a 70% isolated yield of cyclized product **24a**. The use of dichloromethane as the cosolvent led to a 74% yield of cyclized product along with 7% recovered starting material. Surprisingly, cyclized product was formed even in the absence of a cosolvent. This was a surprise because enol ether–allylsilane coupling reactions require a cosolvent.[6a] Without it, they predominately form products derived from methanol trapping of the radical cation prior to cyclization. The fact that the *N*,*O*-ketene acetal reactions do not require a cosolvent suggests that *N*,*O*-ketene acetal derived radical cations undergo the cyclizations more efficiently than not only ketene dithioacetal radical cations but also the more reactive enol ether radical cations. While it was not clear that the differences observed were really due to changes in radical cation reactivity (vide infra), it was clear that the conclusions made with respect to ketene dithioacetal radical cations cannot be universally applied to all ketene acetal substrates.

While the oxidation of **23a** led nicely to cyclized products, it was not stereoselective. In each case, a 3:2 ratio of cis and trans-products was obtained. This ratio was consistent with the mixtures observed for enol ether–allylsilane coupling reactions leading to five-membered rings (substrates **5a** and **5b** in Scheme 2).[6a] In both cases, one would expect a reaction controlled by thermodynamics to place the groups on the ring trans to each other. Hence, the formation of a stereochemical mixture was most consistent with the reactions being controlled by kinetics and the result of five-membered ring transition states not having well defined

Table 2



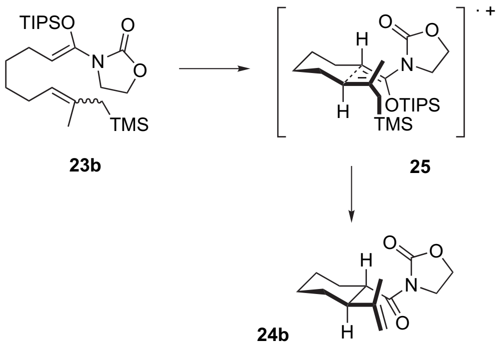
Substrate	Solvent	Product	Yield (%)	Isomer ratio
23a	MeOH	**24a**	51	3:2
23a	4:1 MeOH/THF	**24a**	70	3:2
23a	1:4 MeOH/CH_2Cl_2	**24a**	74[a]	3:2
23b	MeOH	**24b**	54	trans
23b	4:1 MeOH/THF	**24b**	71	trans
23b	1:4 MeOH/CH_2Cl_2	**24b**	54[b]	trans
23c[c]	4:1 MeOH/THF	**24b**	60	trans

[a] 7% recovered starting material.

[b] 10 F/mol.

[c] TBS enol ether.

pseudoequatorial and pseudoaxial positions. The oxidation of **23b** supported the suggestion that cyclizations originating from the radical cation of an *N*,*O*-ketene acetal was under kinetic control. Cyclizations leading to six-membered rings have well defined pseudoaxial and pseudoequatorial positions in their transition states. Since both allylsilane[5] and ketene acetal[4a] groups are known to prefer pseudoequatorial positions in anodic cyclizations, a kinetically controlled reaction resulting from the oxidation of **23b** was expected to afford predominately trans-product (Scheme 7). This was the case. Electrolysis of **23b** using 4:1 MeOH/THF as solvent led to a 71% isolated yield of the trans six-membered ring product (Table 2). Only a small amount (<5%) of a second cyclized product (assumed to be the cis-isomer) was observed in the ^{1}H NMR spectrum of the crude reaction material. The stereochemistry of the major product was assigned using the coupling patterns observed in the ^{1}H NMR spectrum for the ring methine protons. Both protons show the triplet of doublets pattern consistent with the protons being axial and trans to each other.



Scheme 7.

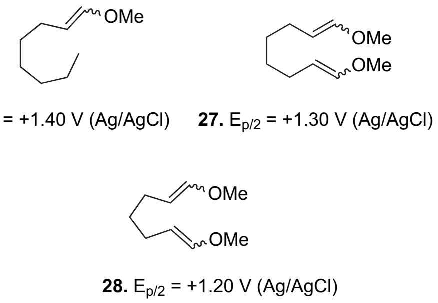
The oxidation of **23b** using dichloromethane as the cosolvent led to a much less efficient cyclization (10 F/mol of charge was needed to obtain 54% of the cyclized product). However, the cyclization still proceeded without the use of a cosolvent in spite of the slower six-membered ring formation. With methanol as solvent, the oxidation led to a 57% isolated yield of the trans-product.

Finally, the compatibility of the anodic oxidation with the less stable TBS enol ether was examined. The oxidation of **23c** in 4:1 MeOH/THF (all other conditions the same) led to a 60% isolated yield of the trans material. In this reaction, a significant amount of imide byproduct from methanolysis of the ketene acetal was observed.

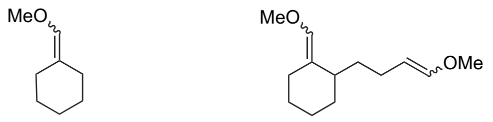
At this point it was clear that radical cations derived from the *N*,*O*-ketene acetals lead to more efficient cyclizations than either radical cations derived from enol ethers or radical cations derived from ketene dithioacetals. Our working model suggested that this results from the *N*,*O*-ketene acetals being more reactive than their ketene dithioacetal and enol ether counterparts. But was this really true?

4. Cyclic voltammetry—measuring relative rates

A number of years ago,[9] we observed that the potential measured by cyclic voltammetry for a bis enol ether substrate was dependent upon the length of the tether connecting the olefins. Substrates expected to give rise to faster cyclizations afforded lower potentials.[12] For example, a bis methoxyenol ether substrate leading to six-membered ring formation (**27**) had an oxidation potential 100 mV lower than that of a mono methoxyenol ether (**26**) whereas an analogous bis methoxyenol ether substrate leading to five-membered ring formation (**28**) had an oxidation potential 200 mV lower than that of a mono methoxyenol ether (Scheme 8). A five-membered ring precursor (**30**) showed a drop in potential of about 150 mV relative to its corresponding mono enol ether (**29**) even when the reaction required the formation of a quaternary carbon (Scheme 9). These observations are consistent with an oxidation reaction that is followed by a cyclization fast enough to influence the concentration of the radical cation at the electrode surface (Scheme 9). In this scenario, the oxidation reaction (k_1) leads to a radical cation that undergoes either the transfer of an electron back to the electrode (k_{-1}) or cyclization (k_2). If one assumes a steady state concentration of the radical cation, then solving for this concentration and plugging the resulting expression into the Nernst equation affords an equation relating the observed potential to the rate of cyclization. Since E^0 in this equation is positive and everything following the minus sign is positive, a faster cyclization will lead to a lower value for E_{obs}. Hence, the value measured for E_{obs} provides a method for measuring the relative rates of various cyclizations.



Scheme 8.



29. $E_{p/2}$=+1.16V (Ag/AgCl) **30.** $E_{p/2}$=+1.01V (Ag/AgCl)

A shift in potential?

$$\text{SM} \xrightleftharpoons[k_{-1}]{k_1} [\text{radical cation}] \xrightarrow{k_2} \text{Product}$$

Using steady state kinetics,...

$$[\text{radical cation}] = \frac{k_1[\text{SM}]}{(k_{-1}+k_2)}$$

...and then the Nernst equation

$$E_{obs} = E^o - RT/nF \ln \frac{[\text{SM}]}{[\text{radical cation}]} = E^o - RT/nF \ln \frac{(k_{-1}+k_2)}{k_1}$$

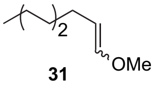
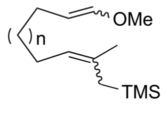
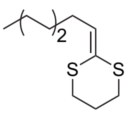
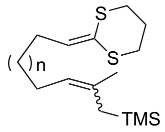
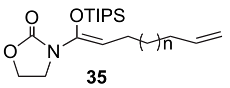
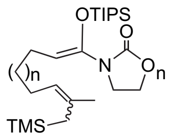
Scheme 9.

An alternative explanation for the drop in potentials that invokes an associative electron transfer where oxidation and cyclization occur in a concerted fashion can be viewed as a limiting example of this general scheme. In this case, the more the overlap between the olefins during the electron-transfer step, the lower is the oxidation potential observed. Of course, the extent of overlap between the olefins during the electron-transfer step is directly related to the rate of cyclization. Therefore, the value of E_{obs} would again provide a method for measuring the relative rates of various cyclizations.

With this in mind, we undertook a CV study of the ketene acetal based substrates in order to determine the relative reactivity of the radical cation intermediates towards allylsilane trapping groups. In order to establish a baseline for these studies, the shifts in potential associated with the coupling of an enol ether to an allylsilane trapping group were examined (Table 3). The parent enol ether **31** was measured to have a potential ($E_{p/2}$) of +1.44 V versus Ag/AgCl[13] using a Pt anode, a sweep rate of 25 mV/s, and a 0.1 M $LiClO_4$ in acetonitrile electrolyte solution. A substrate concentration of 0.025 M was used. All of the potentials listed in Table 3 were obtained using identical conditions. For the six-membered ring enol ether/allylsilane precursor (**32b**), a drop in potential of 100 mV relative to the parent enol ether **31** was observed. For the five-membered ring precursor (**32a**) an additional 80 mV drop in potential (a 180 mV drop for the substrate relative to the parent enol ether **31**) was observed. The smaller drop in potential for the six-membered ring precursor **32b** confirmed that the cyclization derived from this substrate proceeds more slowly than the cyclization originating from the five-membered ring precursor **32a**.

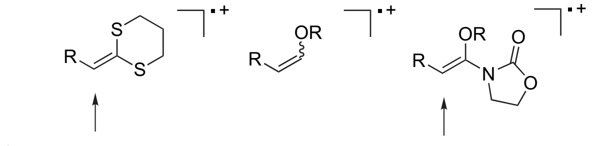
Next, attention was turned towards the cyclizations originating from oxidation of a ketene dithioacetal. In this case, the potential measured for the six-membered ring cyclization substrate (**34b**) was only 30 mV lower than the potential measured for the parent ketene dithioacetal **33**. The five-membered ring substrate (**34a**) had a potential only 50 mV lower than the parent ketene dithioacetal **33**. Clearly, these cyclizations were slower than the cyclizations resulting from oxidation of enol ethers **32a** and **32b**, an observation that was consistent with our working model for the reactions. Following these measurements, attention was turned to the *N*,*O*-ketene acetal derived cyclizations. Surprisingly, the drop in potential measured for substrates **23a** and **23b** was not significantly different than the drop in potential measured for the ketene dithioacetal substrates **34a** and **34b**. For **23b**, a 40 mV drop in potential was measured relative to **35**, while for **23a** an 80 mV drop in potential relative to **35** was observed. In neither case was the drop in potential close to what was observed for the enol ether derived radical cations. This result indicated that the most efficient (*N*,*O*-ketene acetal) and least efficient (ketene dithioacetal) cyclization reactions from a yield perspective proceeded roughly at the same rate, whereas, the cyclization with an intermediate efficiency (enol ether) proceeded much faster than either of the others. Clearly, our working model for the cyclizations was not correct. The yield of the electrolyses did not depend solely on the rate of the cyclization reaction.

Table 3

Ag/AgCl reference electrode Pt anode, 25 mV/s 0.1 M $LiClO_4$ in CH_3CN 0.025 M [substrate]	Potential V ($E_{p/2}$)		Potential V ($E_{p/2}$)
 **31**	+1.44		**32a** n=1 +1.26 **32b** n=2 +1.34
 **33**	+1.15		**34a** n=1 +1.10 **34b** n=2 +1.12
 **35**	+1.15		**23a** n=1 +1.07 **23b** n=2 +1.11

So what does control the yield of an anodic olefin coupling reaction? Typically, when the reactions give a low yield of the desired cyclic product they form products that are derived from either trapping of the initially formed radical cation with solvent, proton elimination from the uncyclized radical cation, or polymerization. Hence, the yield of cyclic product obtained depends on a partitioning between intramolecular trapping of the initially formed radical cation versus solvent trapping, elimination, and polymerization. If higher yielding cyclizations are not faster with respect to the intramolecular reaction, then the radical cation intermediates involved must be more stable with respect to the decomposition reactions. In other words, switching from the ketene dithioacetal to the *N*,*O*-ketene acetal did not lead to a more reactive radical cation, but rather a more stable one.

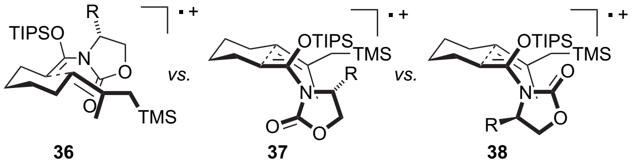
It is tempting to speculate that the differences in cyclization efficiency observed for the reactions above result from the ability of the substituents on the radical cation to stabilize a cation (Scheme 10). It is known that enol ether radical cations react with allyl- and vinylsilanes in a ‘radical-like’ fashion meaning that the reaction leads to a radical at the terminating end of the cyclization.[14] At the same time, two of the three decomposition pathways (methanol trapping and elimination) are clearly ‘cation-like’ processes and the third leads to a polymethoxylated polymer that may also be ‘cation-like’ in origin. Do substituents on the radical cation that stabilize a cation reduce the rate of decomposition and afford more time for the ‘radical-type’ cyclization that leads to the desired product? Efforts are underway to begin addressing this question with more electron-rich ketene acetal derivatives.



Scheme 10.

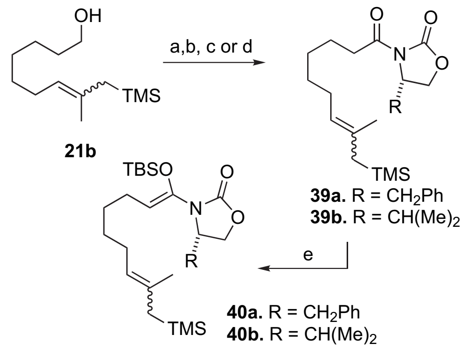
5. Chiral auxiliaries

The degree of stereoselectivity obtained for the cyclization originating from **23b** provided an excellent opportunity to probe the potential for asymmetric anodic olefin coupling reactions. Two key, contradictory literature precedents formed the backdrop for this effort. First, Evans and co-workers demonstrated that chiral oxazolidinones are very useful auxiliaries for inducing asymmetry into both aldol and alkylation reactions using silyl based *N*,*O*-ketene acetal derivatives directly analogous to substrates **23a** and **23b**.[15,16] In these reactions, the chiral auxiliaries adopt a conformation that minimizes the dipole of the substrate in the transition state leading to product. Second, Sibi and co-workers have shown that chiral oxazolidinone groups are not useful auxiliaries for inducing asymmetry into radical reactions that originate from a radical on the carbon alpha to the imide carbonyl.[17,18] In these cases, rotation around the bond connecting the nitrogen of the chiral oxazolidinone to the carbonyl of the substrate interferes with the auxiliaries ability to place the sterically bulky directing group on a single face of the substrate. For a radical cation initiated cyclization, the problem can be summarized using the transition state structures as illustrated in Scheme 11. Transition state **36** represents the preferred transition state (relative to **37**) if the radical cation cyclization behaves in a fashion analogous to the aldol and alkylation reactions studied by Evans. In this picture, the large allylsilane group would approach the face of the radical cation opposite to the sterically bulky substituent on the oxazolidinone. Transition states **36** and **38** represent the two preferred transition states if the radical cation cyclization behaves in a fashion analogous to the radical reactions studied by Sibi. In this case, rotation around the bond connecting the nitrogen of the oxazolidinone and C1 of the substrate leads to two conformations that place the bulky R group of the chiral oxazolidinone on opposite faces of the radical cation. Approach of the allylsilane moiety away from the R group would then lead to a mixture of diastereomers.



Scheme 11.

To test which of these two scenarios best describes the radical cation cyclizations, electrolysis substrates **40a** and **40b** were prepared (Scheme 12). The syntheses began with the formation of imides **39a** and **39b** in a fashion identical to that used in Scheme 7. However, formation of the ketene acetal moiety needed for the oxidation proved to be more challenging. With the extra steric bulk of the chiral auxiliary, efforts to synthesize the triisopropylsilyl ketene acetal were not successful. In each case, the starting imide was recovered without silylation. Fortunately, using the same reaction conditions, the less hindered *tert*-butyldimethylsilyl ketene acetal could be made in a 57% isolated yield (along with 39% of the recovered starting material) when the benzyl substituted oxazolidinone was used (**40a**) and an 88% isolated yield when the isopropyl substituted oxazolidinone was used (**40b**). The TBS based ketene acetals were significantly less stable to the electrolysis conditions than ones possessing the TIPS group. However, they did allow us to assess the utility of the chiral auxiliaries for effecting asymmetric anodic olefin coupling reactions.

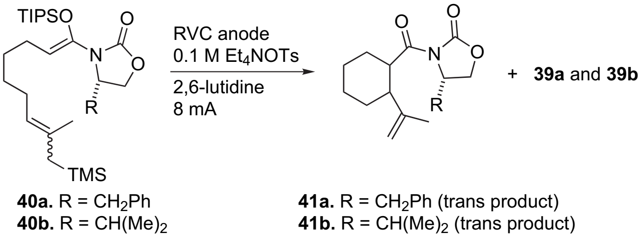


Scheme 12. Reagents: (a) PDC, DMF, 0 °C, 12 h, 65%; (b) Et_3N, Pivaloyl chloride, THF, −20 °C, 2 h; (c) LiCl, (4*S*,5*R*)-(−)-4-Methyl-5-phenyl-2-oxazolidinone, −20 °C–rt, 6 h, 94%; (d) LiCl, (*S*)-(−)-4-Isopropyl-2-oxazolidinone, −20 °C–rt, 6 h, 85% and (e) i. LDA, THF, −78 °C, 30–90 min. ii. TBSOTf, −78 °C–rt, 6–8 h, 57% (with 39% **39a**) for **40a**, 88% for **40b**.

The oxidation of **40a** was conducted using the same constant current electrolysis conditions as described earlier (Table 4). Unfortunately, only poor yields of the cyclized product could be obtained. In the best case, a 20% yield of product **41a** was obtained. For this product, only the two trans-diastereomers were observed. These diastereomers were separated, characterized, and then their experimental ratio (2:1) determined by integration of the proton NMR spectrum taken for the crude reaction product. Efforts to optimize the yield for the reaction were halted when it became clear that the chiral auxiliary was not effective for inducing asymmetry into the oxidative cyclization.

The oxidation of **40a** suggested that the chiral auxiliary rotated and that the radical cation behaved in a fashion analogous to the radical chemistry of Sibi and co-workers rather

Table 4



Substrate	Solvent	# (F/mol)	Recovered **40** (%)	**41**	**39**	Diast. ratio
40a	4:1 MeOH/THF	2.2	0	20	45	2:1
40a	MeOH	2.2	0	15	53	2:1
40a	1:4 MeOH/CH_2Cl_2	2.2	37	6	10	2:1
40b	4:1 MeOH/THF	2.2	10	20	20	1:1.5
40b	4:1 MeOH/CH_3CN	2.2	27	20	13	2:1
40b	1:1 MeOH/CH_3CN	2.2	11	26	8	2:1
40b	1:4 MeOH/CH_2Cl_2	2.2	26	25	8	1:1.5
40b	1:4 MeOH/CH_2Cl_2	4.7	<8	42	6	1:1.5
40b	1:1 MeOH/CH_2Cl_2	3.0	<5	40	7	2:1

than the alkylation chemistry of Evans and co-workers. But what if the poor selectivity obtained from **40a** was simply a result of the benzyl group being too small to be effective? The use of the larger isopropyl group in **40b** was studied in order to address this issue. If the poor diastereoselectivity obtained from the oxidation of **40a** was due to the benzyl group being too small, then the use of the larger isopropyl group in **40b** should improve the diastereoselectivity. However, if the poor diastereoselectivity obtained from the oxidation of **40a** was due to rotation of the chiral auxiliary, then the use of the larger inducing group would not help. The electrolyses of **40b** is summarized in Table 4. While alterations in the solvent used and amount of current employed helped to improve the yield of the cyclizations, the diastereoselectivity of the reaction remained poor in all cases.

In the end, neither the benzyl nor the isopropyl directing group induces a significant degree of asymmetry into the process, a result consistent with rotation of the chiral auxiliary and the radical cation cyclizations being analogous to the corresponding radical reactions.

6. Conclusions

Our work with *N*,*O*-ketene acetal derived radical cations has led to two major findings. First, the use of an *N*,*O*-ketene acetal initiating group for anodic olefin coupling reactions leads to more efficient carbon–carbon bond formation than the use of either an enol ether or a ketene dithioacetal initiating group. The higher yield of cyclic product in these reactions is not due to the cyclizations being faster but rather the radical cation intermediates being more stable to decomposition. Knowing that a change in the substituents on a radical cation can dramatically improve the yield of subsequent cyclization, current efforts are aimed at identifying ketene acetal groups that will allow for the simultaneous formation of both quaternary carbons and six-membered rings.[19]

Second, the experiment using chiral oxazolidinones demonstrated that the radical cation cyclizations are analogous to asymmetric radical reactions in that rotation of the chiral auxiliary precludes useful levels of induction. This observation will be critical for designing future asymmetric anodic olefin coupling reactions that would appear to require the use of either a Lewis acid to stop rotation of the auxiliary[18] or a C_2-symmetric chiral auxiliary.

7. Experimental

7.1. 7-Methoxy-hept-6-en-1-ol (17a)

To a flame-dried 500-mL round-bottom flask under an argon atmosphere were added ε-caprolactone (5.597 g, 48.5 mmol) and 300 mL of anhydrous solvent (CH_2Cl_2/THF=1:1). The reaction was cooled to −78 °C and 1 M DIBAL solution in toluene (50 mL, 50 mmol) was added dropwise. The reaction was stirred at −78 °C for 15 min. The reaction was then allowed to warm to room temperature, quenched with 200 mL of ether and 60 mL of H_2O, and stirred until it became a translucent white gel. The solution was further diluted with 200 mL of ether, Celite 545 added, and then stirred until the solution became clear. The resulting mixture was filtered and concentrated in vacuo. The crude product was diluted with 200 mL of ether and dried using anhydrous $MgSO_4$. It was then filtered and concentrated in vacuo the second time. The crude product was then taken up in 60 mL of anhydrous THF and used directly in the following steps. (The hemiacetal should not be left concentrated in order to avoid polymerization).

A flame-dried 500-mL round-bottom flask under an argon atmosphere was charged with a stirred suspension of (methoxymethyl)triphenylphosphonium chloride (34.985 g, 100 mmol) in 220 mL of anhydrous THF. The reaction was cooled to −78 °C, a 1.4 M *sec*-butyllithium solution in cyclohexane (110 mL, 154 mmol) was added dropwise, and the resulting dark brown mixture allowed to warm from −78 °C to room temperature over 3 h. When complete, the reaction was recooled to −78 °C and the crude hemiacetal synthesized above in 60 mL of anhydrous THF added via cannula. The mixture was allowed to warm to room temperature and stirred overnight. In the morning, the reaction was quenched with 300 mL of satd $NaHCO_3$. The aqueous phase was then extracted with ether (6×300 mL) and the combined organic layers dried over $MgSO_4$, filtered and concentrated in vacuo. At this point 150 mL of 1:3 ether/hexane was added to the crude product and the mixture stirred for 4 h. (This will precipitate most of triphenylphosphine and triphenylphosphine oxide.) The mixture was filtered and concentrated in vacuo for the second time. The crude product was chromatographed through a silica gel column (crude/gel=1/15~20) with 2–3% Et_3N in 1:6 EtOAc/hexane to afford the desired product **17a** (6.488 g, 45 mmol, 93%, over 2 steps) as a yellow oily liquid. The spectral data were as follows: ^1H NMR ($CDCl_3$/300 MHz) δ 6.28 (dt, J=12.6, 1.2 Hz, trans H8, 0.56H), 5.87 (dt, J=6.3, 1.4 Hz, cis H8, 0.44H), 4.72 (dt, J=12.6, 7.4 Hz, trans H7, 0.61H), 4.34 (td, J=7.4, 6 Hz, cis H7, 0.39H), 3.63 and 3.63 (t and t, J=6.6 and 6.8 Hz, H2, 2H), 3.58 (s, cis H9, 1.29H), 3.50 (s, trans H9, 1.71H), 2.13–2.02 (m, cis H6, 0.88H), 1.98–1.88 (m, trans H6, 1.12H), 1.70 (br s, H1, 1H), 1.63–1.51(m, H3, 2H), 1.44–1.30 (m, H4 and H5, 4H); ^{13}C NMR ($CDCl_3$/300 MHz) δ 147.2, 146.3, 106.9, 103.1, 63.1, 63.1, 59.6, 56.0, 32.8, 30.7, 29.7, 27.8, 25.4, 25.3, 23.9; IR (neat/NaCl) 3342, 3033, 2998, 2931, 2856, 1656, 1462, 1391, 1208, 1110, 1054, 933, 736 cm^{-1}; LRMS (EI) 144 ([M]$^+$, 4), 97 (10), 72 (100); HRMS (EI) *m*/*z* calculated for $C_8H_{16}O_2$ [M]$^+$ 144.1150, found 144.1155.

7.2. 3-(7-Methoxy-hept-6-enoyl)-oxazolidin-2-one (18a)

To a flamed-dried 100-mL round-bottom flask under an argon atmosphere were added **17a** (1.503 g, 10.4 mmol) and 60 mL of anhydrous DMF. The reaction was cooled to 0 °C and the solution was treated with pyridinium dichromate (PDC) (15.806 g, 42.0 mmol). The temperature of mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched with 600 mL of water, the aqueous layer extracted with ether (10×150 mL), and the combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. The crude product was eluted with 1:4 ether/hexane through a silica gel column (crude/gel=1:25) to afford the acid product (0.722 g, 4.6 mmol, 44%) as a colorless oily liquid.

A solution of the acid synthesized above (0.47 g, 3.0 mmol) and 20 mL of anhydrous THF was placed in a 100-mL round-bottom flask under an argon atmosphere. After cooling the reaction to −20 °C, anhydrous Et_3N (2.0 mL, 14.3 mmol) was added dropwise followed by trimethylacetyl chloride (0.44 mL, 3.5 mmol). The resulting white suspension solution was stirred at −20 °C. After 2 h, oven-dried lithium chloride (0.155 g, 3.6 mmol) and 2-oxazolidone (0.325 g, 3.7 mmol) were added, the reaction allowed to warm slowly to room temperature, and the room temperature solution stirred for 8 h. After this point, the reaction was concentrated to about 10% of its initial volume. The residue was filtered through a pad of silica gel with 3% Et_3N in ether as eluant. After concentration in vacuo, the crude product was chromatographed through a silica gel column (crude/gel=1:30) with 2–3% Et_3N in 1:4 EtOAc/hexane as eluant in order to afford the desired imide **18a** (0.416 g, 1.8 mmol, 62%) as a colorless oily liquid. The spectral data were as follows: ^{1}H NMR ($CDCl_3$/300 MHz) δ 6.29 (d with fine coupling, J=12.6 Hz, trans H8, 0.81H), 5.88 (dt, J=6.0, 1.4 Hz, cis H8, 0.19H), 4.71 (dt, J=12.6, 7.4 Hz, trans H7, 0.79H), 4.42 (t, J=8.1 Hz, H1, 2H), 4.32 (apparent td, J=7.2, 6.0 Hz, cis H7, 0.21H), 4.02 (t, J=8.1 Hz, H2, 2H), 3.57 (s, cis H9, 0.57H), 3.49 (s, trans H9, 2.43H), 2.91 (t, J=7.5 Hz, H3, 2H), 2.13–2.03 (m, cis H6, 0.42H), 2.01–1.91 (m, trans H6, 1.58H), 1.73–1.60 (m, H4, 2H), 1.47–1.36 (m, H5, 2H); ^{13}C NMR ($CDCl_3$/300 MHz) δ 173.5, 173.4, 153.6, 147.3, 146.4, 106.3, 102.5, 62.1, 59.5, 55.9, 42.5, 34.9, 30.1, 29.2, 27.4, 23.8, 23.6, 23.5; IR (neat/NaCl) 3540, 3380, 2930, 2855, 1773, 1698, 1457, 1389, 1209, 1039, 937, 760 cm^{-1}; LRMS (EI) 209 (13), 140 (100); HRMS (EI) m/z calculated for $C_{11}H_{17}NO_4$ $[M]^+$ 227.1158, found 227.1157.

7.3. 3-(7-Methoxy-1-triisopropylsilanyloxy-hepta-1,6-dienyl)-oxazolidin-2-one (19a)

Into a flamed-dried 50-mL round-bottom flask under an argon atmosphere were placed freshly distilled diisopropyl amine (0.23 mL, 1.6 mmol) and 5 mL of anhydrous THF. The reaction was cooled to −0 °C, 1.6 M *n*-butyllithium (1 mL, 1.6 mmol) was added dropwise, and then the mixture stirred for 30 min. The reaction was then cooled to −78 °C, a solution of imide **18a** (0.299 g, 1.3 mmol) in 5 mL of anhydrous THF was added via a cannula, and the resulting solution stirred for 20 min. While the reaction was still at −78 °C, triisopropylsilyl trifluoromethanesulfonate (0.42 mL, 1.6 mmol) was added. This mixture was allowed to slowly warm to room temperature and stirred for 5 h. The reaction mixture was concentrated to 10% of its original volume and the residue was filtered through a pad of silica gel with 3% Et_3N in ether as eluant. After concentration in vacuo, the crude product was chromatographed through a silica gel column (crude/gel=1:25) using 2–3% Et_3N in 2:3 ether/hexane as eluant in order to afford the desired ketene acetal **19a** (0.438 g, 1.1 mmol, 87%) as a colorless oily liquid. The spectral data were as follows: ^{1}H NMR ($CDCl_3$/300 MHz) δ 6.27 (d with fine coupling, J=12.6 Hz, trans H8, 0.78H), 5.86 (dt, J=6.0, 1.5 Hz, cis H8, 0.22H), 4.69 (dt, J=13.5, 7.2 Hz, trans H7, 0.78H), 4.66 (t, J=7.2 Hz, H3, 0.22H), 4.65 (t, H3, J=7.2 Hz, 0.78H), 4.31 (dd of H1 with cis H7 buried, J=8.8, 7.1 Hz, 2.22H), 3.77 (dd, J=8.8, 7.1 Hz, H2, 2H), 3.56 (s, cis H9, 0.66H), 3.49 (s, trans H9, 2.34H), 2.16–2.02 (m of H4 with cis H6 buried, 2.44H), 1.94 (dtd, J=7.4, 7.2, 1.1 Hz, trans H6, 1.56H), 1.41 (p, J=7.4 Hz, H5, 2H), 1.25–1.07 (m of H11 with d of H10 at 1.11, J=5.4 Hz, 21H); ^{13}C NMR ($CDCl_3$/300 MHz) δ 156.0, 147.4, 146.5, 140.1, 106.6, 105.0, 104.8, 102.7, 61.8, 59.6, 56.0, 46.6, 30.6, 29.7, 27.6, 25.3, 25.0, 23.8, 18.0, 13.2; IR (neat/NaCl) 3518, 3055, 2944, 2868, 1770, 1681, 1463, 1398, 1268, 1210, 1109, 1040, 933, 883, 685 cm^{-1}; LRMS (EI) 383 (M^+, 2), 368 ($[M-CH_3]^+$, 10), 340 ($[M-C(CH_3)_2]^+$, 100), 244 (92), 200 (40); HRMS (EI) m/z calculated for $C_{20}H_{37}NO_4Si$ $[M]^+$ 383.2492, found 383.2489.

7.4. 3-(2-Dimethoxymethyl-cyclopentanecarbonyl)-oxazolidin-2-one (20a)

Under an argon atmosphere, a solution of oven-dried tetraethylammonium tosylate (0.453 g, 1.5 mmol), ketene acetal **19a** (0.094 g, 0.25 mmol), and 2,6-lutidine (0.22 mL, 1.5 mmol) in 15 mL of anhydrous solution (THF/MeOH=1:4) was placed in a flame-dried 25-mL three-necked round-bottom flask equipped with a reticulated vitreous carbon (RVC) anode and a RVC cathode. The reaction was electrolyzed at a constant current of 8 mÅ until 2.2 F/mol of charge was passed. The solution was concentrated to 10% of its original volume and then diluted with 80 mL of pure ether to precipitate tetraethylammonium tosylate. The reaction was then dried over sodium sulfate for 2–3 h, filtered and concentrated in vacuo. The crude product was chromatographed through a silica gel column (crude/gel=1:30) using 2–3% Et_3N in 3:1 ether/hexane as eluant in order to afford the desired product **20a** (0.055 g, 0.21 mmol, 87%) as a colorless oily liquid. The spectral data were as follows: ^{1}H NMR ($CDCl_3$/300 MHz) δ 4.34 (t, J=7.8 Hz, H1, 0.7H), 4.33 (t, J=7.8 Hz, H1, 1.3H), 4.21 (d, J=9.3 Hz, H8, 0.65H), 4.15 (d, J=7.8 Hz, H8, 0.35H), 4.05–3.81 (m of H2 with H3 buried, 3H), 3.23 (s, H9, 1.05H), 3.21 (s, H9, 1.05H), 3.19 (s, H9, 1.95H), 3.14 (s, H9, 1.95H), 2.79–2.61 (m, H7, 1H), 2.12–1.40 (m, H4, H5 and H6, 6H); ^{13}C NMR ($CDCl_3$/300 MHz) δ 176.5, 175.0, 153.5, 153.5, 107.4, 104.3, 61.9, 61.8, 54.3, 53.4, 52.2, 51.5, 46.1, 44.6, 44.3, 43.7, 43.0, 42.9, 31.9, 29.3, 28.2, 28.0, 25.3, 24.4; IR (neat/NaCl) 3535, 3372, 2956, 2831, 1770, 1694, 1524, 1480, 1454, 1385, 1223, 1045, 973, 926, 761, 706 cm^{-1}; LRMS (EI) 226 (43), 166 (63), 138 (100); HRMS (FAB) m/z calculated for $C_{12}H_{19}NO_5$ $[M+Li]^+$ 264.1423, found 264.1424.

7.5. 8-Methoxy-oct-7-en-1-ol (17b)

At 0 °C, 240 mL of 1 N HCl/acetone (1:1) was added to a 500-mL round-bottom flask containing enol ether **17a** (8.694 g, 60.3 mmol). The reaction was allowed to warm to room temperature and stirred for 1 h (TLC). The reaction was recooled to 0 °C and the pH of the reaction was adjusted to 6∼8 using 10% NaOH and satd $NaHCO_3$. After excess NaCl was added, the reaction was extracted with ether (6×200 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. The crude aldehyde was used directly in the following step without purification. This crude aldehyde should be diluted with solvent (CH_2Cl_2 or ether) or it will polymerize during storage.

To a flamed-dried 1000-mL round-bottom flask under an argon atmosphere was added a stirred suspension of (methoxymethyl)triphenylphosphonium chloride (42.667 g, 120.7 mmol) in 400 mL of anhydrous THF. The mixture was cooled to −78 °C, 1.4 M *sec*-butyllithium solution in cyclohexane (115 mL, 161 mmol) was added dropwise, and the resulting dark brown mixture allowed to warm from −78 °C to room temperature over 3 h. The reaction was recooled to −78 °C and the crude aldehyde synthesized above in 60 mL of anhydrous THF added via a cannula. The mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched with 450 mL of satd $NaHCO_3$. The aqueous phase was extracted with ether (6×300 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. At this point the crude reaction mixture was taken up in 150 mL of 1:3 ether/hexane and allowed to stand for 4 h. This procedure precipitates most of the Ph_3PO. The mixture was filtered and concentrated in vacuo for the second time. The crude product was chromatographed through a silica gel column (crude/gel=1:15∼20) with 2–3% Et_3N in 1:8 EtOAc/hexane as eluant in order to afford the desired product **17b** (6.658 g, 42.1 mmol, 70%, over 2 steps) as a yellow oily liquid. The spectral data were as follows: ^1H NMR ($CDCl_3$/300 MHz) δ 6.28 (dt, J=12.6, 1.5 Hz, trans H9, 0.56H), 5.87 (dt, J=6.3, 1.4 Hz, cis H9, 0.44H), 4.72 (dt, J=12.6, 7.4 Hz, trans H8, 0.58H), 4.34 (td, J=7.4, 1.4 Hz, cis H7, 0.43H), 3.63 and 3.63 (t and t, J=6.6 and 6.8 Hz, H2, 2H), 3.58 (s, cis H10, 0.43H), 3.50 (s, trans H9, 0.57H), 2.15–2.02 (br s, H1, 1H), 2.12–2.0 (m, cis H7, H), 1.97–1.87 (m, trans H7, 0.9H), 1.63–1.51(m, H3, 1.1H), 1.63–1.49 (m, H3, 2H), 1.41–1.28 (m, H4, H5 and H6, 6H); ^{13}C NMR ($CDCl_3$/300 MHz) δ 147.0, 146.1, 107.1, 103.2, 63.0, 63.0, 59.6, 56.0, 32.8, 30.8, 29.8, 29.1, 28.9, 27.7, 25.7, 25.7, 23.8; IR (neat/NaCl) 3343, 3033, 2997, 2929, 2855, 1656, 1463, 1390, 1208, 1108, 1056, 934, 737 cm^{-1}; LRMS (EI) 158 ($[M]^+$, 20), 143 (100), 125 (80); HRMS (EI) *m*/*z* calculated for $C_9H_{18}NO_2$ $[M]^+$ 158.1307, found 158.1318.

7.6. 3-(8-Methoxy-oct-7-enoyl)-oxazolidin-2-one (18b)

The acid substrate was prepared using the same method for the synthesis of imide **18a** as described above using **17b** (3.083 g, 19.5 mmol), 200 mL of anhydrous DMF, and PDC (29.932 g, 78.0 mmol). The crude product was chromatographed through a silica gel column (crude/gel=1:25) using 1:2 ether/hexane as eluant in order to afford the acid product (1.47 g, 8.5 mmol, 44%) as a colorless oily liquid.

The coupling reaction was accomplished using the same method as described above for the synthesis of imide **18a**. In this experiment was used the acid made above (1.11 g, 6.4 mmol) in 65 mL of anhydrous THF, anhydrous Et_3N (3.6 mL, 25.8 mmol), trimethylacetyl chloride (0.8 mL, 6.4 mmol), oven-dried lithium chloride (0.2649 g, 6.4 mmol) and 2-oxazolidone (0.574 g, 6.5 mmol). The crude product was chromatographed through a silica gel column (crude/gel=1:30) using 2–3% Et_3N in 3:4 ether/hexane as eluant in order to afford the desired imide **18b** (1.003 g, 4.2 mmol, 65%) as a colorless oily liquid. The spectral data were as follows: ^1H NMR ($CDCl_3$/300 MHz) δ 6.27 (d with fine coupling, J=12.6 Hz, trans H9, 0.80H), 5.87 (dt, J=6.3, 1.2 Hz, cis H9, 0.20H), 4.71 (dt, J=12.6, 7.2 Hz, trans H8, 0.75H), 4.41 (t, J=8.1 Hz, H1, 2H), 4.32 (apparent td, J=7.5, 6.3 Hz, cis H8, 0.25H), 4.02 (t, J=8.1 Hz, H2, 2H), 3.57 (s, cis H10, 0.58H), 3.50 (s, trans H10, 2.42H), 2.91 (t, J=7.5 Hz, H3, 2H), 2.11–2.01 (m, cis H7, 0.4H), 1.98–1.87 (m, trans H7, 1.60H), 1.73–1.59(m, H4, 2H), 1.44–1.32 (m, H5 and H6, 4H); ^{13}C NMR ($CDCl_3$/300 MHz) δ 173.7, 173.7, 153.7, 147.2, 146.3, 106.8, 103.0, 62.2, 59.6, 56.0, 42.7, 35.2, 30.6, 29.6, 28.8, 28.6, 27.6, 24.2, 24.2, 23.8; IR (neat/NaCl) 3538, 2993, 2930, 2855, 1781, 1700, 1655, 1388, 1208, 1115, 1040, 935, 761 cm^{-1}; LRMS (EI) 242 ($[M+H]^+$ (22), 209 (17), 176 (19), 154 (96), 142 (37), 129 (61), 112 (100); HRMS (EI) *m*/*z* calculated for $C_{12}H_{19}NO_4$ $[M+H]^+$ 242.1392, found 242.1401.

7.7. 3-(8-Methoxy-1-triisopropylsilanyloxy-octa-1,7-dienyl)-oxazolidin-2-one (19b)

The triisopropylsilyl enol ether was prepared using the method described as above for the synthesis of ketene acetal **19a**. In this case, the reaction utilized freshly distilled diisopropyl amine (0.82 mL, 5.9 mmol) and 40 mL anhydrous THF in 100-mL round-bottom flask along with 2.5 M *n*-butyllithium (2.1 mL, 5.3 mmol), a solution of imide **18b** (1.003 g, 4.2 mmol) in 20 mL of anhydrous THF, and triisopropylsilyl trifluoromethanesulfonate (1.4 mL, 5.1 mmol). The crude product was chromatographed through a silica gel column (crude/gel=1:25) using 2–3% Et_3N in 4:5 ether/hexane as eluant in order to afford the desired ketene acetal **19b** (1.314 g, 3.3 mmol, 80%) as a colorless oily liquid. The spectral data were as follows: ^1H NMR ($CDCl_3$/300 MHz) δ 6.26 (d, J=12.6 Hz, trans H9, 0.82H), 5.85 (apparent d, J=6.3 Hz, cis H9, 0.18H), 4.70 (dt, J=12.6, 7.4 Hz, trans H8, 0.82H), 4.64 (t, J=7.4 Hz, H3, 1H), 4.30 (dd of H1 with cis H8 buried, J=8.5, 7.6 Hz, 2.18H), 3.77 (dd, J=8.5, 7.6 Hz, H2, 2H), 3.56 (s, cis H10, 0.54H), 3.48 (s, trans H10, 2.46H), 2.16–1.99 (m of H4 with cis H7 buried, 2.36H), 1.96–1.84 (m, trans H7, 1.64H), 1.50–1.28 (m, H5 and H6, 4H), 1.25–1.07 (m of H12 with d of H11 at 1.10, J=6.0 Hz, 21H); ^{13}C NMR ($CDCl_3$/300 MHz) δ 156.0, 147.2, 146.2, 140.0, 107.0, 105.1, 105.0, 103.1, 61.8, 59.6, 56.0, 46.6, 30.7, 29.7, 29.2, 28.9, 27.7, 25.5, 25.5, 23.8, 18.0, 13.2; IR (neat/NaCl) 3517, 3055, 2944, 2867, 1767, 1678, 1655, 1464, 1399, 1277, 1209, 1131, 1040, 883, 686 cm^{-1}; LRMS (EI) 397 (M^+, 2), 382 ($[M-CH_3]^+$, 12), 354 ($[M-C(CH_3)_2]^+$, 100), 244 (97), 200 (89), 128 (68); HRMS (EI) *m*/*z* calculated for $C_{21}H_{39}NO_4Si$ $[M]^+$ 397.2648, found 397.2765 for $[M]^+$ and 382.2424 for $[M-CH_3]^+$.

7.8. 3-(2-Dimethoxymethyl-cyclohexanecarbonyl)-oxazolidin-2-one (20b)

The cyclization was conducted using the same procedure described above for the synthesis of **20a**. This experiment utilized oven-dried tetraethylammonium tosylate (0.607 g, 2.0 mmol), ketene acetal **19b** (0.096 g, 0.02 mmol), 20 mL 1:4 THF/MeOH, 2,6-lutidine (0.22 mL, mmol), an RVC anode and cathode, a constant current of 8 mÅ, and 2.2 F/mol of charge. The crude product was chromatographed through a silica gel column (crude/gel=1:30) using 2–3% Et_3N in 3:5 EtOAc/hexane as eluant in order to afford the desired product **20b** (0.041 g, 0.015 mmol, 63%) as a colorless oily liquid. The spectral data were as follows: ^{1}H NMR ($CDCl_3$/300 MHz) δ 4.51–4.33 (m of H1 with cis H9 buried, 2.27H), 4.13 (d, J=7.2 Hz, trans H9, 0.73H), 4.09–4.89 (m, H2, 2H), 3.85–3.61 (m, cis and trans H3, 1H), 3.29 (s, cis H10, 0.81H), 3.24 (s, trans H10, 2.19H), 3.23 (s, cis H10, 0.81H), 3.20 (s, trans H10, 2.19H), 2.26–2.04 (m, H8, 1H), 1.98–0.94 (m, H4, H5, H6 and H7, 8H); ^{13}C NMR ($CDCl_3$/300 MHz) δ 177.1, 175.3, 153.8, 153.3, 107.5, 104.4, 61.9, 54.2, 53.9, 53.0, 52.6, 51.8, 43.2, 43.0, 41.8, 41.7, 40.3, 39.9, 30.3, 29.8, 27.1, 26.1, 25.6, 25.4, 25.3, 25.0, 23.7, 23.5; IR (neat/NaCl) 3585, 3534, 3373, 2930, 2857, 1789, 1770, 1728, 1694,1480, 1454, 1385, 1325, 1262, 1223, 1046, 985, 943, 761, 705 cm^{-1}; LRMS (EI) 240 ([M−OCH_3]$^+$, 19), 208 (9), 185 (23), 180 (40), 152 (59), 125 (59), 93 (53), 81 (44), 75 (100); HRMS (EI) *m*/*z* calculated for $C_{13}H_{21}NO_5$ [M$^+$] 271.1420, found 240.1231 for [M−OCH_3]$^+$.

7.9. 7-Methyl-8-trimethylsilanyl-oct-6-en-1-ol (21a)

The hemiacetal from the reduction of ε-caprolactone was prepared using the same method as for the synthesis of enol ether (**17a**) as described above.

A flamed-dried 500-mL round-bottom flask under an argon atmosphere was charged with a suspension of (ethyl)triphenylphosphonium bromide (18.567 g, 49.5 mmol) in 150 mL of anhydrous THF. The mixture was cooled to −78 °C, a 1.4 M *sec*-butyllithium solution in cyclohexane (37 mL, 51.8 mmol) was added dropwise, and the resulting dark brown mixture allowed to warm from −78 °C to room temperature over a period of 3 h. The reaction was recooled to −78 °C, iodomethyl-trimethylsilane (7.2 mL, 50.2 mmol) was added dropwise, and the mixture was allowed to warm to room temperature. After 3 h, the mixture became a cloudy red-brown solution. To this mixture was added a 1.6 M *n*-butyllithium in hexane (32 mL, 51.2 mmol) in a dropwise fashion. The resulting dark brown mixture was allowed to warm from −78 °C to room temperature over a period of 3 h. The reaction was recooled to −78 °C and then the crude hemiacetal (2.4 g, 20.7 mmol) in 40 mL of anhydrous THF added via a cannula. The mixture was allowed to warm to room temperature and stirred overnight. The reaction was then quenched with 300 mL of satd $NaHCO_3$. The layers were separated and the aqueous phase was extracted with ether (6×300 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. The crude product was then taken up in 150 mL of 1:3 ether/hexane and allowed to stand for 4 h in order to precipitate most of the triphenylphosphine and triphenylphosphine oxide present in the crude. This mixture was filtered and concentrated in vacuo for the second time. The crude product was chromatographed through a silica gel column (crude/gel=1:25) using 2–3% Et_3N in 1:2 ether/hexane in order to afford the desired product **21a** (2.793 g, 13.0 mmol, 63%) as a colorless oily liquid. The spectral data were as follows: ^{1}H NMR ($CDCl_3$/300 MHz) δ 5.03–4.89 (m, H7, 1H), 3.63 and 3.62 (t and t, J=6.3 and 6.3 Hz, H2, 2H), 2.03–1.85 (m, H6, 2H), 1.68–1.64 (m, allylic coupling, H8, 1.65H), 1.59–1.56 (m, allylic coupling, H8, 1.35H), 1.65–1.51 (m, H1 and H3, 3H), 1.49 (s, H9, 1.26H), 1.45 (s, H9, 0.74H), 1.41–1.38 (m, H4 and H5, 4H), 0.02 (s, H10, 5.35H), −0.01 (s, H10, 3.65H); ^{13}C NMR ($CDCl_3$/300 MHz) δ 133.2, 132.9, 122.7, 122.3, 63.2, 63.2, 33.0, 33.0, 30.1, 30.0, 30.0, 28.7, 28.3, 26.4, 25.8, 25.5, 23.4, 18.8, −0.5, −1.1; IR (neat/NaCl) 3337, 2931, 2857, 1659, 1436, 1416, 1376, 1248, 1162, 1055, 840, 755, 693 cm^{-1}; LRMS (EI) 214 ([M]$^+$, 100), 199 (8), 143 (47), 129 (88); HRMS (EI) *m*/*z* calculated for $C_{12}H_{26}OSi$ [M]$^+$ 214.1753, found 214.1747.

7.10. 3-(7-Methyl-8-trimethylsilanyl-oct-6-enoyl)-oxazolidin-2-one (22a)

The acid substrate was prepared using the same method as described above during the synthesis of imide **18a**. In this case, the experiment used **21a** (3.236 g, 15.1 mmol), 100 mL of anhydrous DMF in a 250 mL flame-dried round-bottom flask, and PDC (22.32 g, 59.3 mmol). The crude product was chromatographed through a silica gel column (crude/gel=1:25) using 1:2 ether/hexane as eluant in order to afford the acid product (1.6805 g, 7.4 mmol, 49%) as a colorless oily liquid.

The coupling reaction was also performed using the same method as described earlier for the synthesis of imide **18a**. In this experiment, the acid made in the preceding paragraph (1.384 g, 6.1 mmol), 65 mL of anhydrous THF in flamed-dried 100-mL round-bottom flask, Et_3N (3.4 mL, 24.3 mmol), trimethylacetyl chloride (0.75 mL, 6.1 mmol), oven-dried lithium chloride (0.258 g, 6.2 mmol), and 2-oxazolidone (0.548 g, 6.2 mmol) were used. The crude product was chromatographed through a silica gel column (crude/gel=1:30) with 2–3% Et_3N in 1:1 ether/hexane as eluant in order to afford the desired imide **22a** (1.634 g, 5.5 mmol, 91%) as a colorless oily liquid. The spectral data were as follows: ^{1}H NMR ($CDCl_3$/300 MHz) δ 5.01–4.88 (m, H7, 1H), 4.94 (t, J=8.0 Hz, H1, 2H), 4.00 (t, J=8.0 Hz, H2, 2H), 2.90 (t, J=7.8 Hz, H3, 2H), 2.04–1.87 (m, H6, 2H), 1.71–1.59 (m, H4, 2H), 1.67–1.62 (m, allylic coupling, H8, 2.18H), 1.53–1.55 (m, allylic coupling, H8, 0.82H), 1.48 (s, H9, 1.38H), 1.44 (s, H9, 0.62H), 1.45–1.31 (m, H5, 2H), 0.01 (s, H10, 5.78H), −0.02 (s, H10, 3.22H); ^{13}C NMR ($CDCl_3$/300 MHz) δ 173.7, 153.7, 133.4, 133.1, 122.2, 121.9, 62.2, 42.7, 35.2, 35.2, 30.0, 29.8, 29.6, 28.4, 28.1, 26.4, 24.2, 24.1, 23.4, 18.8, −0.5, −1.1; IR (neat/NaCl) 3546, 3384, 2951, 1782, 1700, 1478, 1387, 1246, 1110, 1040, 953, 851, 760, 695 cm^{-1}; LRMS (EI) 297 ([M]$^+$, 2), 195 (8), 160 (100); HRMS (EI) *m*/*z* calculated for $C_{15}H_{27}NO_3Si$ [M]$^+$ 297.1760, found 297.1765.

7.11. 3-(7-Methyl-1-triisopropylsilanyloxy-8-trimethylsilanyl-octa-1,6-dienyl)-oxazolidin-2-one (23a)

The TIPS silyl enol ether was prepared using the same method as described earlier for the synthesis of ketene acetal **19a**. This experiment used freshly distilled diisopropyl amine (0.65 mL, 4.6 mmol) and 20 mL of anhydrous THF in a 100-mL round-bottom flask, a 1.6 M *n*-butyllithium in hexane solution (2.9 mL, 4.6 mmol), imide **22a** (1.234 g, 4.2 mmol), 16 mL of anhydrous THF, and triisopropylsilyl trifluoromethanesulfonate (1.3 mL, 4.7 mmol) in a 50-mL pear-bottom flask. The crude product was chromatographed through a silica gel column (crude/gel=1:25) with 2–3% Et_3N in 1:2 ether/hexane as eluant in order to afford the desired ketene acetal **23a** (1.567 g, 3.5 mmol, 83%) as a colorless oily liquid. The spectral data were as follows: ^{1}H NMR ($CDCl_3$/300 MHz) δ 5.00–4.88 (m, H7, 1H), 4.65 and 4.64 (t and t, J=7.2 and 7.2 Hz, H3, 1H), 4.29 (dd, J=8.7, 7.2 Hz, H1, 2H), 3.75 (dd, J=8.7, 7.2 Hz, H2, 2H), 2.09 (dt, J=7.5, 7.5 Hz, H4, 2H), 2.02–1.84 (m, H6, 2H), 1.64 (m, allylic coupling, H8, 2.04H), 1.56 (s, H8, 0.96H), 1.48 (s, H9, 1.36H), 1.43 (s, H9, 0.64H), 1.37 (p, J=7.5 Hz, H5, 2H), 1.10 (m of H12 with d of H11 at 1.06, J=5.7 Hz, 21H), 0.00 (s, H10, 6.12H), −0.03 (s, H10, 2.88H); ^{13}C NMR ($CDCl_3$/300 MHz) δ 155.9, 140.0, 133.3, 133.0, 122.4, 122.1, 105.0, 61.8, 46.6, 30.1, 30.0, 29.8, 28.4, 28.2, 26.4, 25.4, 25.4, 23.3, 18.0, 13.2, −0.6, −1.1; IR (neat/NaCl) 3519, 2946, 2867, 1770, 1681, 1464, 1398, 1248, 1054, 883, 856, 687 cm^{-1}; LRMS (EI) 453 (M$^+$, 5), 410 ([M−CH(CH$_3$)$_2$]$^+$, 67), 366 (14), 244 (100), 210 (36), 200 (51), 128 (59); HRMS (EI) *m*/*z* calculated for $C_{24}H_{47}NO_3Si_2$ [M$^+$] 453.3095, found 453.3097.

7.12. 3-(2-Isopropenyl-cyclopentanecarbonyl)-oxazolidin-2-one (24a)

The anodic cyclization was conducted using the same procedure as described above for the synthesis of **20a**. The experiment used oven-dried tetraethylammonium tosylate (0.517 g, 1.7 mmol), ketene acetal **23a** (0.225 g, 0.05 mmol), 17 mL 1:4 THF/MeOH, 2,6-lutidine (0.36 mL, 3.1 mmol), an RVC anode and cathode, a constant current of 8 mÅ, and 2.2 F/mol of charge. The crude product was chromatographed through a silica gel column (crude/gel=1:35) with 2–3% Et_3N in 1:1 ether/hexane as eluant in order to afford the desired product **24a** (0.083 g, 0.037 mmol, 75%) as white solid, and 0.016 g of starting material **23a** was recovered (0.03 mmol, 7%). The spectral data were as follows: *Isomer 1*: ^{1}H NMR ($CDCl_3$/300 MHz) δ 4.72 and 4.70 (s and s, H9, 2H), 4.41–4.16 (m, H1 and H3, 3H), 4.05–3.81 (m, H2, 2H), 3.01 (dt, approx. J=8.3, 8.3 Hz, H7, 1H), 2.13–1.97, 1.95–1.76 and 1.64–1.52 (m, H4, H5 and H6, 6H), 1.67 (s, H8, 3H); ^{13}C NMR ($CDCl_3$/300 MHz) δ 175.0, 153.5, 146.2, 111.7, 62.0, 50.0, 46.8, 43.0, 30.4, 29.1, 24.7, 22.1; IR (neat/NaCl) 3508, 3363, 3083, 2957, 2868, 1778, 1690, 1644, 1477, 1388, 1362, 1249, 1226, 1107, 1038, 914, 894, 699 cm^{-1}; LRMS (EI) 223 (M$^+$, 9), 182 (69), 136 (100), 121 (49), 108 (53), 93 (69), 88 (69); HRMS (EI) *m*/*z* calculated for $C_{12}H_{17}NO_3$ [M$^+$] 223.1208, found 223.1199. *Isomer 2*: ^{1}H NMR ($CDCl_3$/300 MHz) δ 4.71 and 4.68 (s and s, H9, 2H), 4.38 (t, J=8.3 Hz, H1, 2H), 4.00 (t of H2 with H3 buried, J=8.3 Hz, 3H), 3.00 (dt, J=9.8, 8.9 Hz, H7, 1H), 2.28–2.10, 2.01–1.87 and 1.83–1.46 (m of H4, H5 and H6 with s of H8 at 1.70, 9H); ^{13}C NMR ($CDCl_3$/300 MHz) δ 176.4, 153.4, 146.7, 110.3, 62.0, 50.8, 46.5, 43.0, 31.7, 31.2, 24.9, 20.6; IR (neat/NaCl) 3538, 3075, 2979, 2953, 2871, 1795, 1772, 1682, 1645, 1485, 1386, 1362, 1223, 1041, 899, 757 cm^{-1}; LRMS (EI) 223 (M$^+$, 16), 136 (100), 121 (100), 109 (80), 108 (73), 93 (100), 88 (66); HRMS (EI) *m*/*z* calculated for $C_{12}H_{17}NO_3$ [M$^+$] 223.1208, found 223.1212.

7.13. 8-Methyl-9-trimethylsilanyl-non-7-en-1-ol (21b)

The aldehyde from the hydrolysis of enol ether **17a** was prepared using the same method for the synthesis of **17b** as described above. This experiment used enol ether **17a** (3.671 g, 25.5 mmol) and 300 mL of 4 N HCl/acetone (1:1) in a 500-mL round-bottom flask. The crude aldehyde was used directly in the following step without purification. The aldehyde was diluted with solvent (CH_2Cl_2 or ether) in order to avoid polymerization.

The allylsilane alcohol **21b** was prepared using the same method as described earlier for the synthesis of **21a** using ethyltriphenylphosphonium bromide (23.538 g, 62.8 mmol) and 250 mL of anhydrous THF in a 500 mL flame-dried round-bottom flask, a 1.4 M *sec*-butyllithium solution in cyclohexane (48 mL, 67.2 mmol), iodomethyl-trimethylsilane (9.4 mL, 62.7 mmol), a 1.6 M *n*-butyllithium solution in hexane (41 mL, 65.6 mmol), and the crude aldehyde synthesized above in 40 mL of anhydrous THF. The crude product was chromatographed through a silica gel column (crude/gel=1:25) using 2–3% Et_3N in 1:1.5 ether/hexane as eluant in order to afford the desired product **21b** (3.433 g, 15 mmol, 59%, over 2 steps) as an almost colorless oily liquid. The spectral data were as follows: ^{1}H NMR ($CDCl_3$/300 MHz) δ 5.02–4.89 (m, H8, 1H), 3.63 and 3.61 (apparent overlap of t and t, J=6.3 and 6.6 Hz, H2, 2H), 2.02–1.83 (m, H7, 2H), 1.68–1.64 (m, allylic coupling, H9, 1.34H), 1.66–1.52 (m, H1 and H3, 3H), 1.59–1.56 (m, allylic coupling, H9, 1.63H), 1.49 (s, H10, 0.46H), 1.45 (s, H10, 0.54H), 1.40–1.25 (m, H4, H5 and H6, 6H), 0.02 (s, H11, 4.15H), −0.01 (s, H11, 4.85H); ^{13}C NMR ($CDCl_3$/300 MHz) δ 133.0, 132.7, 122.8, 122.5, 63.1, 33.0, 32.9, 30.3, 30.1, 30.0, 29.5, 29.2, 28.7, 28.2, 26.4, 25.9, 25.9, 23.3, 18.8, −0.5, −1.1; IR (neat/NaCl) 3326, 2929, 2855, 1658, 1437, 1416, 1376, 1248, 1162, 1056, 856, 756, 694 cm^{-1}; LRMS (EI) 228 ([M]$^+$, 84), 143 (100), 129 (73); HRMS (EI) *m*/*z* calculated for $C_{13}H_{28}OSi$ [M]$^+$ 228.1909, found 228.1922.

7.14. 3-(8-Methyl-9-trimethylsilanyl-non-7-enoyl)-oxazolidin-2-one (22b)

The acid intermediate was prepared using the same method as described for the synthesis of acid **18a**. This experiment used **21b** (2.175 g, 9.5 mmol), 50 mL of anhydrous DMF, and PDC (12.434 g, 33 mmol). The reaction was quenched with 500 mL of water, the layers separated, and the aqueous layer extracted with ether (12×150 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. The crude product was chromatographed through a silica gel column (crude/gel=1:25) using 1:6 EtOAc/hexane as eluant to afford the acid product (1.484 g, 6.1 mmol, 64%) as an almost colorless oily liquid.

The imide intermediate was prepared using the procedure as described earlier for the synthesis of imide **18a**. This experiment used 0.146 g (6.0 mmol) of the acid synthesized in the preceding paragraph in 20 mL of anhydrous THF, anhydrous Et_3N (0.4 mL, 2.9 mmol), trimethylacetyl chloride (0.08 mL, 6.4 mmol), oven-dried lithium chloride (0.03 g, 7.2 mmol), and 2-oxazolidone (0.06 g, 6.7 mmol). The crude product was chromatographed through a silica gel column (crude/gel=1:30) using 2–3% Et_3N in 3:4 ether/hexane as eluant in order to afford the desired imide **22b** (0.171 g, 5.8 mmol, 96%) as a colorless oily liquid. The spectral data were as follows: ^{1}H NMR ($CDCl_3$/300 MHz) δ 5.01–4.87 (m, H8, 1H), 4.40 (t, J=8.1 Hz, H1, 2H), 4.00 (t, J=8.0 Hz, H2, 2H), 2.90 (apparent t, J=7.5 Hz, H3, 2H), 2.02–1.82 (m, H7, 2H), 1.72–1.58 (m, H4, 2H), 1.67–1.62 (m, allylic coupling, H9, 1.50H), 1.58–1.55 (m, allylic coupling, H9, 1.50H), 1.48 (s, H10, 1H), 1.44 (s, H10, 1H), 1.42–1.29 (m, H5 and H6, 4H), 0.01 (s, H11, 4.50H), −0.02 (s, H11, 4.50H); ^{13}C NMR (CDCl$_3$/300 MHz) δ 173.7, 153.7, 133.1, 132.8, 122.6, 122.3, 62.2, 42.7, 35.3, 35.3, 30.0, 30.0, 29.9, 29.1, 28.9, 28.5, 28.1, 26.4, 24.4, 24.4, 23.3, 18.8, −0.5, −1.1; IR (neat/NaCl) 3545, 3385m, 2952, 2929, 2855, 1782, 1700, 1479, 1387, 1247, 1224, 1040, 857, 760, 696 cm^{-1}; LRMS (EI) 311 ([M]$^+$, 5), 160 (100), 144 (11); HRMS (EI) *m/z* calculated for $C_{16}H_{29}NO_3Si$ [M]$^+$ 311.1917, found 311.1929.

7.15. 3-(8-Methyl-1-triisopropylsilanyloxy-9-trimethylsilanyl-nona-1,7-dienyl)-oxazolidin-2-one (23b)

The triisopropylsilyl enol ether was prepared using the same method as described earlier for the synthesis of ketene acetal **19a**. This experiment used freshly distilled diisopropyl amine (0.33 mL, 2.4 mmol) in 15 mL of anhydrous THF, a 1.6 M *n*-butyllithium (1.5 mL, 2.4 mmol) in hexane solution, imide **22b** (0.669 g, 2.1 mmol) in 10 mL anhydrous THF, and triisopropylsilyl trifluoromethanesulfonate (1.3 mL, 4.7 mmol). The crude product was chromatographed through a silica gel column (crude/gel=1:25) using 2–3% Et$_3$N in 1:2 ether/hexane as eluant in order to afford the desired ketene acetal **23b** (0.814 g, 1.7 mmol, 81%) as an almost colorless oily liquid. The spectral data were as follows: ^{1}H NMR (CDCl$_3$/300 MHz) δ 4.99–4.87 (m, H8, 1H), 4.63 (t, *J*=7.2 Hz, H3, 1H), 4.29 (dd, *J*=8.4, 7.1 Hz, H1, 2H), 3.75 (dd, *J*=8.4, 7.1 Hz, H2, 2H), 2.08 (dt, *J*=7.2, 7.0 Hz, H4, 2H), 1.99–1.83 (m, H7, 2H), 1.64 (m, allylic coupling, H9, 1.5H), 1.55 (s, H9, 1.5H), 1.47 (s, H10, 1H), 1.43 (s, H10, 1H), 1.40–1.26 (m, H5 and H6, 4H), 1.23–1.06 (m of H13 with d of H12 at 1.09, *J*=6 Hz, 21H), 0.00 (s, H11, 4.5H), −0.03 (s, H11, 4.5H); ^{13}C NMR (CDCl$_3$/300 MHz) δ 155.9, 139.9, 132.9, 132.6, 122.7, 122.4, 105.1, 105.1, 61.8, 46.6, 30.0, 29.9, 29.4, 29.1, 28.5, 28.1, 26.4, 25.6, 25.5, 23.3, 17.9, 13.1, −0.6, −1.1; IR (neat/NaCl) 2946, 2868, 1769, 1680, 1464, 1399, 1368, 1279, 1248, 1061, 1040, 883, 856, 687 cm^{-1}; LRMS (EI) 467 (M$^+$, 11), 452 ([M−CH$_3$]$^+$, 5), 424 ([M−CH(CH$_3$)$_2$]$^+$, 52), 244 (100), 200 (56), 128.1 (37); HRMS (EI) *m/z* calculated for $C_{25}H_{49}NO_3Si_2$ [M]$^+$ 467.3251, found 467.3256.

7.16. 3-(2-Isopropenyl-cyclohexanecarbonyl)-oxazolidin-2-one (24b)

The anodic cyclization was conducted using the same procedure as described for the synthesis of **20a**. This experiment used oven-dried tetraethylammonium tosylate (0.459 g, 1.5 mmol), ketene acetal **23b** (0.091 g, 0.19 mmol), 15 mL of 1:4 THF/MeOH, 2,6-lutidine (0.16 mL, 1.4 mmol), an RVC anode and cathode, a constant current of 8 mÅ, and 2.2 F/mol of charge. The crude product was chromatographed through a silica gel column (crude/gel=1:35) using 2–3% Et$_3$N in 1:1 ether/hexane as eluant in order to afford the desired product **24b** (0.033 g, 0.14 mmol, 71%) as white solid. The spectral data were as follows: ^{1}H NMR (CDCl$_3$/300 MHz) δ 4.66 and 4.66 (s and s, H10, 2H), 4.40–4.32 (apparent t, *J*=8.1 Hz, H1, 2H), 3.96 (t, *J*=8.1 Hz, H2, 2H), 3.88 (td, *J*=11.2, 3.6 Hz, H3, 1H), 2.38 (td, *J*=11.2, 3.2 Hz, H8, 1H), 2.02–1.94 and 1.86–1.73 (m, H4 and H7, 4H), 1.71 (s, H9, 3H), 1.46–1.13 (m, H5 and H6, 4H); ^{13}C NMR (CDCl$_3$/300 MHz) δ 176.3, 153.5, 149.3, 109.8, 61.9, 47.0, 45.1, 42.8, 31.9, 30.5, 26.2, 25.7, 21.5; IR (neat/NaCl) 3080, 2938, 2912, 2850, 1788, 1766, 1689, 1648, 1475, 1437, 1384, 1360, 1270, 1193, 1038, 942, 909, 759 cm^{-1}; LRMS (EI) 237 (2), 150 (100), 135 (28); HRMS (EI) *m/z* calculated for $C_{13}H_{19}NO_3$ [M]$^+$ 237.1365, found 237.1362.

7.17. 3-[1-(*tert*-Butyl-dimethyl-silanyloxy)-8-methyl-9-trimethylsilanyl-ona-1,7-dienyl]-oxazolidin-2-one (23c)

The *tert*-butyldimethylsilyl enol ether was prepared using the same method as described above for the synthesis of ketene acetal **19a**. In this experiment, freshly distilled diisopropyl amine (0.22 mL, 1.6 mmol) in 20 mL anhydrous THF was used along with a 2.5 M solution of *n*-butyllithium in hexane (0.63 mL, 1.6 mmol), imide **22b** (0.457 g, 1.5 mmol) in 10 mL of anhydrous THF, and *tert*-butyldimethylsilyl trifluoromethanesulfonate (0.38 mL, 1.6 mmol). The crude product was chromatographed through a silica gel column (crude/gel=1:25) using 2–3% Et$_3$N in 1:2 ether/hexane as eluant in order to afford the desired product **23c** (0.347 g, 0.8 mmol, 56%) as an almost colorless oily liquid. The spectral data were as follows: ^{1}H NMR (CDCl$_3$/300 MHz) δ 5.02–4.89 (m, H8, 1H), 4.75 (t, *J*=7.2 Hz, H3, 0.35H), 4.75 (t, *J*=7.2 Hz, H3, 0.65H), 4.32 (dd, *J*=8.7, 7.4 Hz, H1, 2H), 3.74 (dd, *J*=8.7, 7.4 Hz, H2, 2H), 2.07 (dt, *J*=7.2, 7.2, H4, 2H), 2.02–1.84 (m, H7, 2H), 1.67 (m, allylic coupling, H9, 1.05H), 1.58 (m, allylic coupling, H9, 1.95H), 1.50 (s, H10, 0.7H), 1.46 (s, H10, 1.3H), 1.43–1.23 (m, H5 and H6, 4H), 0.97 (s, H13, 9H), 0.18 (s, H12, 6H), 0.023 (s, H11, 3.15H), 0.002 (s, H11, 5.85H); ^{13}C NMR (CDCl$_3$/300 MHz) δ 155.9, 139.1, 133.1, 132.8, 122.8, 122.5, 106.7, 106.7, 61.9, 45.6, 30.1, 30.0, 23.0, 29.5, 29.2, 28.6, 28.2, 26.5, 25.8, 25.6, 25.5, 23.4, 18.8, 18.2, 14.3, −0.5, −1.0, −4.5; IR (neat/NaCl) 2954, 2930, 2857, 1766, 1683, 1472, 1402, 1249, 1041, 841, 783 cm^{-1}; LRMS (EI) 425 ([M]$^+$, 1), 410 ([M−CH$_3$]$^+$, 12), 368 ([M−C(CH$_3$)$_2$]$^+$, 42), 202 (100), 160 (90); HRMS (EI) *m/z* calculated for $C_{22}H_{43}NO_3Si_2$ [M]$^+$ 425.2782, found 425.2773.

7.18. (*S*)-(−)-4-Benzyl-3-(8-methyl-9-trimethylsilanyl-non-7-enoyl)-oxazolidin-2-one (39a)

The imide intermediate **39a** was prepared using the procedure as described earlier for the synthesis of imides **18a** and **22b**. This experiment used the acid derived from **21b** (see above) in 90 mL of anhydrous THF, anhydrous Et$_3$N (5.0 mL, 35.9 mmol), trimethylacetyl chloride (1.1 mL, 8.8 mmol), oven-dried lithium chloride (0.345 g, 8.4 mmol), and (*S*)-(−)-4-benzyl-2-oxazolidinone (1.491 g, 8.3 mmol). The crude product was chromatographed through a silica gel column (crude/gel=1:30) with 2–3% Et$_3$N in 1:4 ether/hexane as eluant in order to afford the desired imide **39a** (2.729 g, 6.8 mmol, 82%) as a colorless oily liquid. The spectral data were as follows: ^{1}H NMR (CDCl$_3$/300 MHz) δ 7.35–7.15 (m, H4, H4′, H5, H5′, H6, 5H), 5.01–4.88 (m, H12, 1H), 4.69–4.59 (m, H2, 1H), 4.21–4.10 (m, H1 and H1′, 2H), 3.27 (dd, *J*=13.2, 3.2 Hz, H3, 1H), 3.02–2.80 (m, H7, 2H), 2.74 (dd, *J*=13.2, 9.6 Hz, H3′, 1H), 2.03–1.83 (m, H11, 2H), 1.72–1.60 (m, H8, 2H), 1.68–1.61 and 1.58–1.54 (m and m, allylic coupling, H13, 3H), 1.48 and 1.43 (s and s, H14, 2H), 1.42–1.26 (m, H9 and H10, 4H), 0.00 and

0.03 (s and s, H15, 9H); ^{13}C NMR ($CDCl_3$/300 MHz) δ 173.4, 153.5, 135.5, 133.0, 132.8, 129.5, 129.0, 127.4, 122.6, 122.3, 66.2, 55.2, 38.0, 35.6, 30.0, 29.9, 29.8, 29.0, 28.9, 28.5, 28.1, 26.4, 24.4, 24.3, 23.3, 18.7, −0.6, −1.1; IR (neat/NaCl) 3550, 3385, 2930, 2856, 1790, 1770, 1704, 1704, 1698, 1604, 1454, 1385, 1246, 1210, 1107, 1029, 875, 701 cm^{-1}; LRMS (EI) 401 ([M]$^+$, 10), 250 (100), 73 (59); HRMS (EI) *m/z* calculated for $C_{23}H_{35}NO_3Si$ [M]$^+$ 401.2386, found 401.2381.

7.19. (*S*)-(−)-4-Benzyl-3-[1-(*tert*-butyl-dimethyl-silanyl-oxy)-8-methyl-9-trimethylsilanyl-nona-1,7-dienyl]-oxazolidin-2-one (40a)

The *tert*-butyldimethylsilyl enol ether **40a** was prepared using the same method initially as described above for the synthesis of ketene acetal **19a** above. In this experiment, freshly distilled diisopropyl amine (0.18 mL, 1.3 mmol) in 20 mL anhydrous THF was used along with a 1.6 M *n*-butyllithium (0.86 mL, 1.4 mmol), imide **39a** (0.461 g, 1.2 mmol) in 20 mL of anhydrous THF, and *tert*-butyldimethylsilyl trifluoromethanesulfonate (0.35 mL, 1.5 mmol). The crude product was chromatographed through a silica gel column (crude/gel=1:25) using 2–3% Et_3N in 1:4 ether/hexane as eluant in order to afford the desired ketene acetal **40a** (0.335 g, 0.65 mmol, 57%) as a colorless oily liquid and starting material **40a** (∼0.18 g, 0.45 mmol, 39%). The spectral data were as follows: ^{1}H NMR ($CDCl_3$/300 MHz) δ 7.36–7.12 (m, H4, H4′, H5, H5′, H6, 5H), 5.04–4.90 (m, H12, 1H), 4.86 (dd, *J*=6.3, 6.3 Hz, H7, 1H), 4.24–4.10 (m, H1 and H1′, 2H), 4.08–3.97 (m, H2, 1H), 3.2 (dd, *J*=13.5, 3.3 Hz, H3, 1H), 2.61 (dd, *J*=13.5, 9.6 Hz, H3′, 1H), 2.32–1.85 (m, H8 and H11, 4H), 1.69–1.63 (m, allylic coupling, H13, 1.59H), 1.61–1.56 (m, allylic coupling, H13, 1.41H), 1.48 and 1.43 (s and s, H14, 2H), 1.48–1.30 (m, H9 and H10, 4H), 1.00 (s, H17, 9H), 0.23 and 0.17 (s and s, H16 and H16′, 6H), 0.0 and −0.02 (s and s, H15, 9H); ^{13}C NMR ($CDCl_3$/300 MHz) δ 155.5, 137.2, 135.8, 132.9, 132.7, 129.5, 129.0, 127.2, 122.6, 122.3, 109.9, 66.7, 56.3, 38.3, 38.2, 30.0, 29.9, 29.8, 29.3, 29.1, 28.4, 28.0, 26.3, 25.7, 25.6, 25.5, 23.3, 18.7, 18.1, −0.6, −1.1, −4.4, −4.7; IR (neat/NaCl) 3520, 3087, 3063, 3068, 2928, 2857, 1770, 1682, 1644, 1585, 1497, 1454, 1393, 1248, 1122, 1090, 1043, 838, 699 cm^{-1}; LRMS (EI) 401 ([M]$^+$, 10), 250 (100), 73 (59); HRMS (EI) *m/z* calculated for $C_{23}H_{35}NO_3Si$ [M]$^+$ 401.2386, found 401.2381.

7.20. (*S*)-(−)-4-Benzyl-3-(2-isopropenyl-cyclohexane-carbonyl)-oxazolidin-2-one (41a)

The anodic cyclization was conducted using the same procedure as described for the synthesis of **20a**. This experiment used oven-dried tetraethylammonium tosylate (0.458 g, 1.5 mmol), ketene acetal **40a** (0.0959 g, 0.19 mmol), 15 mL MeOH, 2,6-lutidine (0.14 mL, 1.2 mmol), an RVC anode and cathode, a constant current of 8 mÅ, and 2.2 F/mol of charge. The crude product was chromatographed (crude/gel=1:30) through a silica gel column using 2–3% Et_3N in 1:4 ether/hexane as eluant in order to afford the desired product **41a** (0.008 g, 0.0023 mmol, 13%) as a colorless oil and imide **39a** (0.039 g, 0.1 mmol, 53%). A second chromatography (crude/gel=1:60) was performed to further separate two isomers using 2–3% Et_3N in 1:4 ether/hexane as eluant. The spectral data were as follows: *Isomer 1* (*trans*): ^{1}H NMR ($CDCl_3$/600 MHz) δ 7.35–7.18 (m, H4, H4′, H5, H5′ and H6, 5H), 4.70–4.67 (m, allylic coupling, H14 and H14, 2H), 4.67–4.61 (m, H2, 1H), 4.17–4.12 (m, H1 and H1′, 2H), 3.84 (dt, *J*=3.3, 11.0 Hz, H7, 1H), 3.22 (dd, *J*=2.7, 13.5 Hz, H3, 1H), 2.74 (dd, *J*=9.6, 13.2 Hz, H3′, 1H), 2.41 (dt, *J*=3.3, 11.0 Hz, H12, 1H), 2.11–2.05 (m, H9, 1H), 1.88–1.77 (m, H8, H10, and H11, 3H), 1.73 (s, H13, 3H), 1.46–1.30 (m, H8′, H9′, and H10′, 3H), 1.28–1.19 (m, H11′, 1H); ^{13}C NMR ($CDCl_3$/600 MHz) δ 176.1, 153.4, 149.5, 135.5, 129.7, 129.1, 127.5, 109.8, 66.2, 55.3, 46.8, 45.4, 38.1, 32.0, 30.6, 26.6, 26.3, 25.8, 21.7. *Isomer 2* (*trans*): ^{1}H NMR ($CDCl_3$/600 MHz) δ 7.34–7.19 (m, H4, H4′, H5, H5′, and H6, 5H), 4.79–4.77 and 4.75–4.72 (m, allylic coupling, H14 and H14′, 2H), 4.68–4.63 (m, H2, 1H), 4.16–4.09 (m, H1 and H1′, 2H), 3.96 (dt, *J*=3.2, 11.0 Hz, H7, 1H), 3.23 (dd, *J*=3.3, 13.5 Hz, H3, 1H), 2.62 (dd, *J*=9.9, 13.5 Hz, H3′, 1H), 2.46 (dt, *J*=3.2, 11.0 Hz, H12, 1H), 2.00–1.95 (m, H8, 1H), 1.87–1.82 (m, H11, 1H), 1.82–1.78 (m, H9 and H10, 2H), 1.77–1.75 (m, allylic coupling, H13, 3H), 1.47–1.23 (m, H8′, H9′, H10′, H11′, 4H); ^{13}C NMR ($CDCl_3$/600 MHz) δ 176.3, 153.5, 149.0, 135.7, 129.7, 129.1, 127.4, 110.5, 65.9, 44.4, 47.5, 45.0, 38.1, 31.9, 30.6, 26.2, 25.7, 21.5.

7.21. (*S*)-(−)-4-Isopropyl-3-(8-methyl-9-trimethyl-silanyl-non-7-enoyl)-oxazolidin-2-one (39b)

The imide intermediate **39b** was prepared using the procedure as described earlier for the synthesis of imide **18a** and **22b**. This experiment used the acid derived from alcohol **21b** (0.481 g, 2.0 mmol) in 30 mL of anhydrous THF, anhydrous Et_3N (1.2 mL, 8.6 mmol), trimethylacetyl chloride (0.26 mL, 2.1 mmol), oven-dried lithium chloride (0.095 g, 2.3 mmol), and (*S*)-(−)-4-benzyl-2-oxazolidinone (0.276 g, 2.1 mmol). The crude product was chromatographed through a silica gel column (crude/gel=1:30) with 2–3% Et_3N in 1:5 ether/hexane as eluent in order to afford the desired imide **39b** (0.599 g, 1.7 mmol, 85%) as a colorless oily liquid. The spectral data were as follows: ^{1}H NMR ($CDCl_3$/300 MHz) δ 5.02–4.88 (m, H10, 1H), 4.47–4.39 (m, H2, 1H), 4.26 (apparent t, *J*=9.0 Hz, H1, 1H), 4.19 (dd, *J*=9.0, 3.3 Hz, H1′, 1H), 3.05–2.78 (m, H5, 2H), 2.37 (m, H3, 1H), 2.03–1.82 (m, H9, 2H), 1.72–1.59 (m, H6, 2H), 1.68–1.63 (m, allylic coupling, H11, 1.61H), 1.59–1.56 (m, allylic coupling, H11, 1.39H), 1.49 (s, H12, 1.04H), 1.45 (s, H12, 0.96H), 1.42–1.29 (m, H7 and H8, 4H), 0.91 and 0.87 (d and d, *J*=7.2, 6.9 Hz, H4 and H4′, 6H), 0.01 and −0.01 (s and s, H13, 9H); ^{13}C NMR ($CDCl_3$/300 MHz) δ 173.2, 154.0, 132.8, 132.5, 122.5, 122.2, 63.3, 58.3, 35.4, 29.8, 29.8, 29.7, 28.9, 28.7, 28.4, 28.3, 28.0, 26.2, 24.5, 24.4, 18.6, 17.9, 14.7, −0.7, −1.3; IR (neat/NaCl) 2957, 2876, 2856, 1785, 1703, 1386, 1247, 1206, 858 cm^{-1}; LRMS (EI) 353 ([M]$^+$, 6), 202 (100), 158 (9); HRMS (EI) *m/z* calculated for $C_{19}H_{35}NO_3Si$ [M]$^+$ 353.2386, found 353.2384.

7.22. 3-[1-(*tert*-Butyl-dimethyl-silanyloxy)-8-methyl-9-trimethyl-silanyl-nona-1,7-dienyl]-(*S*)-(−)-4-isopropyl-oxazolidin-2-one (40b)

The *tert*-butyldimethylsilyl enol ether **40b** was prepared using the same method as described earlier for the synthesis of ketene acetal **19a**. In this experiment, freshly distilled diisopropyl amine (0.2 mL, 1.4 mmol) in 30 mL of anhydrous THF was used along with 1.6 M *n*-butyllithium (0.87 mL, 1.4 mmol), imide **39b** (0.363 g, 1.0 mmol) in 20 mL of anhydrous THF, and *tert*-butyldimethylsilyl trifluoromethanesulfonate (0.34 mL, 1.5 mmol). The crude product was chromatographed through a silica gel column (crude/gel=1:25) using 2–3% Et_3N in 1:4 ether/hexane as eluant in order to afford the desired ketene acetal **40b** (0.423 g, 0.9 mmol, 88%) as a colorless oily liquid. The spectral data were as follows: ^{1}H NMR ($CDCl_3$/300 MHz) δ 5.02–4.88 (m, H10, 1H), 4.83–4.75 (m, H5, 1H), 4.23 (apparent t, J=9.0 Hz, H1, 1H), 4.07 (dd, J=9.3, 8.7 Hz, H1′, 1H), 3.98–3.90 (m, H2, 1H), 2.22–1.84 (m, H3, H6 and H5, 5H), 1.68–1.63 and 1.59–1.55 (m and m, allylic coupling, H11, 3H), 1.49 and 1.45 (s and s, H12, 2H), 1.43–1.24 (m, H7 and H8, 4H), 0.96 (s, H15, 9H), 0.92 and 0.90 (d and d, J=3.3, 3.0 Hz, H4 and H4′, 6H), 0.2 and 0.15 (s and s, H14 and H14′, 6H), 0.02 and −0.01 (s and s, H13, 9H); ^{13}C NMR ($CDCl_3$/300 MHz) δ 156.1, 137.7, 133.1, 132.8, 122.8, 122.5, 109.6, 63.3, 59.1, 30.0, 29.9, 29.4, 29.2, 28.9, 28.5, 28.1, 26.5, 25.8, 25.6, 25.5, 23.4, 18.8, 18.2, 17.8, 15.2, −0.5, −1.0, −4.3, −4.6; IR (neat/NaCl) 2956, 2930, 2857, 1768, 1683, 1472, 1463, 1401, 1248, 1053, 841, 784 cm^{-1}; LRMS (EI) 467 (M$^+$, 11), 452 ($[M-CH_3]^+$, 25), 410 (100), 244 (75), 202 (75); HRMS (EI) *m/z* calculated for $C_{25}H_{49}NO_3Si_2$ [M$^+$] 467.3251, found 467.3248.

7.23. 3-(2-Isopropenyl-cyclohexanecarbonyl)-(*S*)-(−)-4-isopropyl-oxazolidin-2-one (41b)

The anodic cyclization was conducted using the same procedure as described for the synthesis of **20a**. This experiment used oven-dried tetraethylammonium tosylate (0.6240 g, 2.1 mmol), ketene acetal **40b** (0.1052 g, 0.23 mmol), 20 mL of a 1:1 CH_2Cl_2/MeOH mixture, 2,6-lutidine (0.2 mL, 1.33 mmol), an RVC anode and cathode, a constant current of 8 mÅ, and 2.2 F/mol of charge. The crude product was chromatographed through a silica gel column (crude/gel=1:40) using 2–3% Et_3N in 1:6 ether/hexane as eluant in order to afford the desired product **41b** (0.0105 g of *Isomer 1*, 0.038 mmol, 17%, and 0.0159 g of *Isomer 2*, 0.057 mmol, 25%) as colorless oil. The spectral data were as follows: *Isomer 1* (*trans*): ^{1}H NMR ($CDCl_3$/300 MHz) δ 4.70–4.65 (m, allylic coupling, H12, 2H), 4.46–4.39 (m, H2, 1H), 4.27–4.15 (m, H1 and H1′, 2H), 3.90 (dt, J=3.6, 11.1 Hz, H5, 1H), 2.38 (dt, J=3.0, 13 Hz, H10, 1H), 2.32 (dqq, J=1.2, 7.1, 7.1 Hz, H3, 1H), 2.11–2.02 and 1.88–1.76 (m, H6 and H9, 4H), 1.74–1.71 (m, allylic coupling, H11, 3H), 1.52–1.15 (m, H7 and H8, 4H), 0.90 and 0.86 (d and d, J=7.2, 6.9 Hz, H4 and H4′, 6H); ^{13}C NMR ($CDCl_3$/300 MHz) δ 176.0, 154.0, 149.6, 109.6, 63.5, 58.2, 46.6, 45.6, 32.1, 31.0, 29.9, 28.8, 26.3, 25.9, 21.7, 18.1; IR (neat/NaCl) 3537, 3384, 3076, 2929, 1779, 1698, 1644, 1487, 1447, 1384, 1300, 1203, 1090, 944, 892, 708 cm^{-1}; LRMS (EI) 279 (M$^+$, 7), 242 (10), 150 (100); HRMS (EI) *m/z* calculated for $C_{16}H_{25}NO_3$ [M$^+$] 279.1834, found 279.1825. *Isomer 2* (*trans*): ^{1}H NMR ($CDCl_3$/300 MHz) δ 4.77–4.73 and 4.70–4.66 (m, allylic coupling, H12, 2H), 4.47–4.40 (m, H2, 1H), 4.26–4.13 (m, H1 and H1′, 2H), 3.99 (dt, J=3.6, 11.1 Hz, H5, 1H), 2.41 (dt, J=3.2, 11.4 Hz, H10, 1H), 2.27 (m, H3, 1H), 2.00–1.90 and 1.86–1.76 (m, H6 and H9, 4H), 1.75–1.72 (m, allylic coupling, H11, 3H), 1.48–1.18 (m, H7 and H8, 4H), 0.88 and 0.82 (d and d, J=6.9, 6.8 Hz, H4 and H4′, 6H); ^{13}C NMR ($CDCl_3$/300 MHz) δ 176.1, 154.0, 148.9, 110.3, 63.0, 58.6, 31.9, 30.5, 28.5, 27.1, 26.2, 25.6, 21.3, 18.1; IR (neat/NaCl) 3536, 3380, 3074, 2929, 1772, 1700, 1645, 1487, 1448, 1385, 1300, 1259, 1204, 1060, 894, 777, 711 cm^{-1}; LRMS (EI) 279 (M$^+$, 4), 200 (12), 186 (100), 150 (71), 100 (32), 73 (57); HRMS (EI) *m/z* calculated for $C_{16}H_{25}NO_3$ [M$^+$] 279.1834, found 279.1839.

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